Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Preparation of Functionalized Arylmagnesium Reagents by the Addition of Magnesium Aryl Thiolates and Amides to Arynes

Wenwei Lin, Ioannis Sapountzis and Paul Knochel*

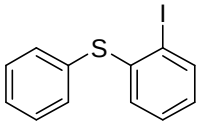
Ludwig-Maximilians-Universität München, Department Chemie und Biochemie
Butenandtstrasse 5-13, Haus F, 81377 München (Germany)
Fax: (+49) 089 21 80 776 80
e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under an argon atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continuously refluxed and freshly 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 and capillary GC.

Preparation of the reagent *i*PrMgCl:
Magnesium turnings (2.67 g, 110 mmol) were placed in an Ar-flushed flask and THF (50 mL) was added. A solution of *i*PrCl (7.85 g, 100 mmol) in THF (50 mL) was slowly added at room temperature. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at room temperature. The grey solution of *i*PrMgCl was cannulated to another flask under Argon and removed in this way from excess of magnesium. A yield of ca. 95–98 % of *i*PrMgCl is obtained and the *i*PrMgCl-solution is titrated prior to use by the method of Paquette.[1]

Typical procedure for the generation of aryl thioethers (6a-d) by addition reaction to benzyne followed by quenching with iodine (TP 1):
A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding arylthiol (1.0 mmol) in dry THF (3 mL). After cooling to –78 °C, *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF) was added dropwise and stirred for 10 min. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The resulting mixture was then added to a solution of iodine (508 mg, 2.0 equiv.) in dry THF (2 mL) at –78 °C. After the addition, the mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**6a-d**).

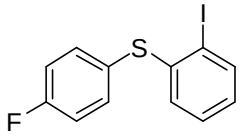
Synthesis of 2-iodophenyl phenyl sulfide (6a):



Prepared according to **TP 1** from thiophenol (111 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and iodine (508 mg, 2.0 mmol). Purification by flash chromatography (*n*-pentane) yielded **6a** as a white solid (260 mg, 83 %).
mp.: 55.6-56.6 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.86 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.48-7.35 (m, 5H), 7.21 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz,

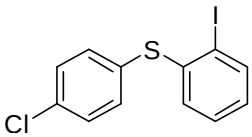
1H), 6.99 (dd, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H), 6.88 (td, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 142.16, 139.58, 133.90, 132.95, 129.55, 129.45, 128.66, 128.20, 127.41, 99.42. **MS** (70 eV, EI): *m/z* (%): 312 (100) [M^+], 199 (11), 186 (16), 185 (32), 184 (84), 152 (11), 151 (9), 139 (8). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3436 (bs), 1552 (m), 1564 (w), 1474 (m), 1440 (s), 1421 (m), 1254 (m), 1009 (m), 999 (w), 743 (vs), 706 (m), 689 (m), 641 (w), 516 (w). **HRMS** for **$C_{12}H_9IS$** (311.9470): found: 311.9463.
Spectral data match those reported in the literature.[2]

Synthesis of 4-fluorophenyl 2-iodophenyl sulfide (6b):



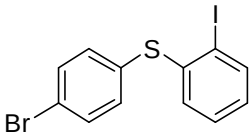
Prepared according to **TP 1** from 4-fluorothiophenol (128 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and iodine (508 mg, 2.0 mmol). Purification by flash chromatography (*n*-pentane) yielded **6b** as a white solid (297 mg, 90 %).
mp.: 93.7-94.7 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25 °C): d = 7.82 (dd, ^{3}J(H,H) = 7.94 Hz, ^{4}J(H,H) = 1.22 Hz, 1H), 7.49-7.42 (m, 2H), 7.19 (td, ^{3}J(H,H) = 7.94 Hz, ^{4}J(H,H) = 1.22 Hz, 1H), 7.13-7.06 (m, 2H), 6.89-6.82 (m, 2H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 163.01 (d, ^{1}J(F,C) = 249 Hz), 142.61, 139.66, 135.80 (d, ^{3}J(F,C) = 8 Hz), 128.86, 128.72, 128.64, 127.30, 116.89 (d, ^{2}J(F,C) = 22 Hz), 98.36. **MS** (70 eV, EI): *m/z* (%): 331 (13), 330 (93) [M^+], 204 (10), 203 (58), 202 (100), 183 (17), 170 (14), 157 (9), 101 (9), 83 (8). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 1589 (s), 1563 (w), 1490 (vs), 1466 (w), 1440 (s), 1422 (m), 1396 (w), 1256 (w), 1224 (s), 1154 (m), 1090 (w), 1036 (w), 1009 (s), 834 (s), 817 (w), 750 (vs), 704 (w), 644 (w), 634 (w), 527 (m). **HRMS** for **$C_{12}H_8FIS$** (329.9375): found: 329.9370.

Synthesis of 4-chlorophenyl 2-iodophenyl sulfide (6c):



Prepared according to **TP 1** from 4-chlorothiophenol (145 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and iodine (508 mg, 2.0 mmol). Purification by flash chromatography (*n*-pentane) yielded **6c** as a white solid (291 mg, 84 %).
mp.: 89.0-90.0 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.83 (dd, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H), 7.32-7.28 (m, 4H), 7.20 (td, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H), 6.99 (dd, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H), 6.88 (td, ^{3}J(H,H) = 7.96 Hz, ^{4}J(H,H) = 1.33 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 141.32, 139.81, 134.25, 133.76, 132.80, 130.03, 129.74, 128.83, 127.93, 100.17. **MS** (70 eV, EI): *m/z* (%): 348 (28), 346 (73) [M^+], 185 (14), 184 (100), 183 (18), 139 (15), 108 (11), 92 (15). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3085 (w), 1902 (w), 1639 (w), 1572 (w), 1562 (w), 1474 (s), 1440 (s), 1422 (s), 1386 (m), 1256 (m), 1172 (w), 1092 (s), 1036 (w), 1008 (s), 856 (w), 828 (m), 820 (s), 747 (vs), 702 (w), 642 (w), 510 (m). **HRMS** for **$C_{12}H_8ClIS$** (345.9080): found: 345.9086.

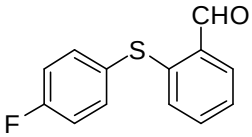
Synthesis of 4-bromophenyl 2-iodophenyl sulfide (6d):



Prepared according to **TP 1** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and iodine (508 mg, 2.0 mmol). Purification by flash chromatography (*n*-pentane) yielded **6d** as a white solid (321 mg, 82 %).
mp.: 88.1-88.8 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.85 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.51-7.45 (m, 2H), 7.26-7.20 (m, 3H), 7.04 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 6.91 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 141.07, 139.87, 133.80, 133.62, 132.68, 130.34, 128.89, 128.09, 122.24, 100.52. **MS** (70 eV, EI): *m/z* (%): 392 (17), 390 (16) [M^+], 185 (13), 184 (100), 139 (10), 92 (15). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3080 (w), 3053 (w), 1910 (w), 1654 (w), 1644 (w), 1564 (m), 1468 (s), 1439 (s), 1423 (s), 1386 (m), 1251 (w), 1174 (w), 1088 (w), 1071 (m), 1035 (w), 1007 (s), 950 (w), 834 (m), 821 (s), 748 (vs), 730 (m), 707 (m), 700 (m), 642 (w), 532 (w), 492 (m). **HRMS** for **$C_{12}H_8BrIS$** (389.8575): found: 389.8561.

Typical procedure for the generation of aryl thioethers (6e-g, 6k, 6l) by addition reaction to benzyne followed by quenching with DMF (TP 2):
A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding arylthiol (1.0 mmol) in dry THF (3 mL). After cooling to –78 °C, *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF) was added dropwise and stirred for 10 min. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. Then the reaction mixture was cooled to –40 °C and DMF (0.20 mL, 2.5 equiv.) was added. The mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**6e-g**, **6k**, **6l**).

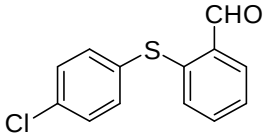
Synthesis of 2-[(4-fluorophenyl)sulfanyl]benzaldehyde (6e):



Prepared according to **TP 2** from 4-fluorothiophenol (128 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by washing with *n*-pentane yielded **6e** as a yellow solid (181 mg, 78 %).
mp.: 98.4-99.4 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25 °C): d = 10.32 (s, 1H), 7.84 (dd, ^3J(H,H) = 7.63 Hz, ^4J(H,H) = 1.53 Hz, 1H), 7.48-7.42 (m, 2H), 7.37 (td, ^3J(H,H) = 7.63 Hz, ^4J(H,H) = 1.53 Hz, 1H), 7.29 (td, ^3J(H,H) = 7.63 Hz, ^4J(H,H) = 1.22 Hz, 1H), 7.13-7.06 (m, 2H), 6.96 (dd, ^3J(H,H) = 7.94 Hz, ^4J(H,H) = 0.61 Hz, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 191.25, 163.08 (d, ^1J(F,C) = 249 Hz), 142.13, 136.07 (d, ^3J(F,C) = 8 Hz), 133.93, 133.12, 132.50, 128.99, 127.73, 125.82, 116.94 (d, ^2J(F,C) = 22 Hz). **MS** (70 eV, EI): *m/z* (%): 233 (16), 232 (100) [M^+], 231 (33), 204 (14), 203 (87), 202 (38), 183 (10), 170 (11), 136

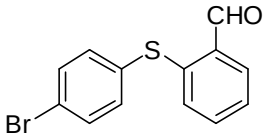
(35), 104 (11). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3090 (w), 3065 (w), 3048 (w), 2855 (w), 2762 (w), 1696 (m), 1672 (vs), 1587 (m), 1554 (m), 1491 (s), 1457 (s), 1440 (m), 1399 (m), 1302 (m), 1258 (m), 1221 (s), 1191 (s), 1155 (m), 1126 (w), 1090 (w), 1066 (w), 1043 (w), 1014 (w), 846 (m), 832 (s), 814 (w), 766 (s), 674 (w), 658 (m), 635 (w), 527 (m), 499 (w). **HRMS** for **$C_{13}H_9FOS$** (232.0358): found: 232.0370.

Synthesis of 2-[(4-chlorophenyl)sulfanyl]benzaldehyde (6f):



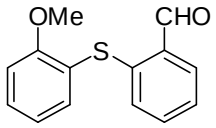
Prepared according to **TP 2** from 4-chlorothiophenol (145 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 20/1) yielded **6f** as a yellow solid (182 mg, 73 %).
mp.: 72.6-73.5 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 10.36 (s, 1H), 7.88 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.46-7.31 (m, 6H), 7.08 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.33 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 191.33, 140.89, 134.73, 134.39, 134.11, 133.72, 132.20, 131.79, 130.16, 129.89, 126.49. **MS** (70 eV, EI): *m/z* (%): 250 (40), 249 (22), 248 (100) [M^+], 247 (22), 221 (10), 219 (28), 213 (31), 185 (33), 184 (70), 152 (10), 139 (14), 109 (14), 108 (15), 104 (22), 76 (12). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3079 (w), 2850 (w), 2755 (w), 1907 (w), 1693 (s), 1674 (vs), 1586 (m), 1572 (m), 1553 (m), 1476 (m), 1458 (s), 1438 (m), 1393 (m), 1300 (w), 1258 (w), 1199 (s), 1174 (w), 1126 (w), 1094 (m), 1083 (m), 1068 (w), 1042 (w), 1015 (m), 844 (m), 831 (m), 822 (s), 762 (s), 746 (m), 676 (m), 656 (m), 514 (w), 490 (w). **HRMS** for **$C_{13}H_9ClOS$** (248.0063): found: 248.0043.

Synthesis of 2-[(4-bromophenyl)sulfanyl]benzaldehyde (6g):



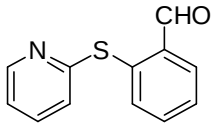
Prepared according to **TP 2** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 20/1) yielded **6g** as a yellow solid (220 mg, 75 %).
mp.: 78.0-78.7 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 10.35 (s, 1H), 7.87 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.51-7.46 (m, 2H), 7.42 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.34 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.29-7.24 (m, 2H), 7.09 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.33 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 191.28, 140.54, 134.43, 134.11, 133.77, 132.78, 132.54, 132.09, 130.34, 126.58, 122.71. **MS** (70 eV, EI): *m/z* (%): 294 (76), 293 (26), 292 (78) [M^+], 291 (14), 213 (43), 185 (33), 184 (100), 152 (16), 139 (14), 136 (64), 109 (14), 108 (16), 104 (13), 76 (14). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3079 (w), 2852 (w), 2829 (w), 2754 (m), 1976 (w), 1911 (w), 1674 (vs), 1587 (m), 1562 (m), 1464 (m), 1443 (w), 1404 (m), 1386 (m), 1301 (w), 1266 (w), 1204 (m), 1166 (w), 1130 (w), 1090 (w), 1069 (m), 1008 (m), 848 (m), 830 (m), 814 (m), 760 (s), 732 (w), 676 (m), 657 (w), 532 (w), 478 (w). **HRMS** for **$C_{13}H_9BrOS$** (291.9557): found: 291.9568.

Synthesis of 2-[(2-methoxyphenyl)sulfanyl]benzaldehyde (6k):



Prepared according to **TP 2** from 2-methoxythiophenol (140 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by washing with *n*-pentane yielded **6k** as a yellow solid (196 mg, 80 %).
mp.: 103.2-104.2 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25 °C): d = 10.43 (s, 1H), 7.87 (dd, ^{3}J(H,H) = 7.74 Hz, ^{4}J(H,H) = 1.29 Hz, 1H), 7.40-7.25 (m, 4H), 7.08 (d, ^{3}J(H,H) = 7.31 Hz, 1H), 6.96-6.92 (m, 2H), 3.81 (s, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$, 25 °C): d = 191.64, 158.65, 140.58, 134.43, 134.07, 133.83, 131.37, 130.47, 130.19, 126.19, 121.47, 121.13, 111.26, 55.79. **MS** (70 eV, EI): *m/z* (%): 245 (14), 244 (100) [M^+], 213 (13), 201 (11), 200 (12), 184 (17), 171 (11), 108 (27), 105 (11). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3010 (w), 2932 (w), 2848 (w), 2830 (w), 2754 (w), 1694 (m), 1676 (vs), 1585 (s), 1557 (s), 1476 (vs), 1461 (vs), 1442 (m), 1428 (m), 1399 (s), 1296 (m), 1274 (s), 1262 (m), 1250 (s), 1196 (s), 1162 (m), 1131 (m), 1068 (m), 1022 (s), 852 (m), 843 (m), 799 (m), 760 (vs), 686 (w), 676 (m), 656 (m). **HRMS** for **$C_{14}H_{12}O_2S$** (244.0558): found: 244.0551.

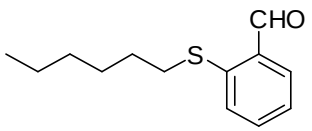
Synthesis of 2-(2-pyridinylsulfanyl)benzaldehyde (6l):



Prepared according to **TP 2** from pyridine-2-thiol (111 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether/methylene chloride = 10/1/2) yielded **6l** as a yellow oil (176 mg, 82 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): d = 10.37 (s, 1H), 8.36 (d, ^{3}J(H,H) = 4.57 Hz, 1H), 8.01 (ddd, ^{3}J(H,H) = 7.63 Hz, ^{4}J(H,H) = 1.53 Hz, ^{5}J(H,H) = 0.92 Hz 1H), 7.61-7.47 (m, 4H), 7.07-7.00 (m, 2H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 191.57, 158.44, 149.72, 137.08, 136.90, 135.87, 134.42, 134.22, 129.45, 129.09, 122.28, 120.73. **MS** (70 eV, EI): *m/z* (%): 215 (8) [M^+], 214 (10), 187 (18), 186 (100), 182 (12), 109 (11), 78 (10). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3061 (w), 2858 (w), 1695 (vs), 1651 (w), 1586 (m), 1574 (s), 1560 (m), 1450 (s), 1417 (s), 1383 (w), 1282 (w), 1262 (m), 1198 (s), 1114 (m), 1087 (w), 1059 (m), 1044 (w), 986 (w), 825 (m), 759 (s), 722 (m), 634 (w). **HRMS** for **$C_{12}H_9NOS$** (215.0405): found: 215.0421.

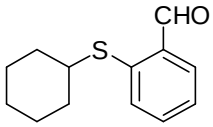
Synthesis of 2-(hexylsulfanyl)benzaldehyde (6m):



Prepared according to **TP 2** from hexane-1-thiol (236 mg, 2.0 mmol), *i*PrMgCl (2.81 mL, 3.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.40 mL, 5.0 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 50/1) yielded **6m** as a yellow oil (149 mg, 67 %).

^{1}H-NMR (600 MHz, $CDCl_3$, 25 °C): d = 10.39 (s, 1H), 7.82 (d, ^3J(H,H) = 7.74 Hz, 1H), 7.50 (t, ^3J(H,H) = 7.74 Hz, 1H), 7.41 (d, ^3J(H,H) = 7.74 Hz, 1H), 7.28 (t, ^3J(H,H) = 7.74 Hz, 1H), 2.94 (t, ^3J(H,H) = 7.74 Hz, 2H), 1.72-1.65 (m, 2H), 1.48-1.42 (m, 2H), 1.33-1.26 (m, 4H), 0.88 (t, ^3J(H,H) = 7.31 Hz, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$, 25 °C): d = 191.40, 142.26, 134.03, 133.82, 131.79, 128.22, 125.20, 33.36, 31.30, 28.59, 28.52, 22.46, 13.95. **MS** (70 eV, EI): *m/z* (%): 222 (55) [M^+], 161 (11), 151 (70), 148 (10), 147 (20), 139 (16), 138 (73), 137 (100), 135 (12), 134 (11), 123 (14), 110 (70), 109 (43), 104 (31), 77 (13), 65 (18), 55 (11), 45 (14), 43 (27), 41 (30). **IR** (film): $\tilde{n}$ (cm^{-1}) = 2956 (m), 2928 (s), 2856 (m), 2733 (w), 1694 (vs), 1588 (m), 1560 (w), 1460 (m), 1440 (w), 1397 (w), 1261 (w), 1195 (m), 1128 (w), 845 (w), 825 (w), 751 (m), 680 (w), 657 (w), 636 (w). **HRMS** for **$C_{13}H_{18}OS$** (222.1078): found: 222.1081.

Synthesis of 2-(cyclohexylsulfanyl)benzaldehyde (6n):



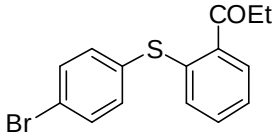
Prepared according to **TP 2** from cyclohexanethiol (232 mg, 2.0 mmol), *i*PrMgCl (2.81 mL, 3.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.40 mL, 5.0 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 100/1) yielded **6n** as a yellow oil (161 mg, 73 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): d = 10.55 (s, 1H), 7.87-7.83 (m, 1H), 7.52-7.46 (m, 2H), 7.34-7.29 (m, 1H), 3.15-3.07 (m, 1H), 2.00-1.92 (m, 2H), 1.80-1.72 (m, 2H), 1.63-1.56 (m, 1H), 1.45-1.17 (m, 5H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 191.95, 139.87, 135.98, 133.71, 132.71, 129.83, 126.72, 47.26, 33.05, 25.88, 25.54. **MS** (70 eV, EI): *m/z* (%): 220 (59) [M^+], 173 (20), 139 (18), 138 (100), 137 (40), 110 (14), 109 (18), 104 (25), 83 (11), 55 (21). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3368 (w), 3061 (w), 2930 (s), 2853 (m), 2734 (w), 1693 (vs), 1649 (w), 1587 (m), 1559 (w), 1458 (m), 1449 (m), 1397 (w), 1377 (w), 1340 (w), 1288 (w), 1260 (m), 1193 (m), 1061 (w), 997 (w), 844 (w), 824 (m), 758 (m), 714 (w), 635 (w). **HRMS** for **$C_{13}H_{16}OS$** (220.0922): found: 220.0906.

Typical procedure for the generation of aryl thioethers (6h, 6i, and 6o) by addition reaction to benzyne followed by quenching with acid chloride or allyl bromide in the presence of CuCN·2LiCl (TP 3):

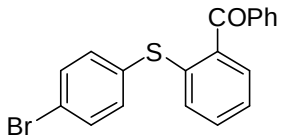
A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding arylthiol (1.0 mmol) in dry THF (3 mL). After cooling to –78 °C, *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF) was added dropwise and stirred for 10 min. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The reaction mixture was cooled to –78 °C, and then CuCN·2LiCl (1.0 M/THF, 1.0 mL, 1.0 equiv.) was added and stirred for 20 min. After acid chloride (2.5 equiv.) was added at –78 °C, the solution was allowed to warm to RT and stirred for an additional 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the products (**6h**, **6i**, and **6o**).

Synthesis of 1-{2-[(4-bromophenyl)sulfanyl]phenyl}-1-propanone (6h):



Prepared according to **TP 3** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (1.0 mL, 1.0 equiv., 1.0 M in THF) and propionyl chloride (0.22 mL, 2.5 mmol). Purification by washing with *n*-pentane yielded **6h** as a yellow solid (288 mg, 90 %).
mp.: 121.2-122.0 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$, 25 °C): d = 7.80 (dd, ^{3}J(H,H) = 7.63 Hz, ^{4}J(H,H) = 1.53 Hz, 1H), 7.53-7.49 (m, 2H), 7.37-7.33 (m, 2H), 7.26 (td, ^{3}J(H,H) = 7.63 Hz, ^{4}J(H,H) = 1.53 Hz, 1H), 7.19 (td, ^{3}J(H,H) = 7.63 Hz, ^{4}J(H,H) = 1.53 Hz, 1H), 6.93 (dd, ^{3}J(H,H) = 7.63 Hz, ^{4}J(H,H) = 1.53 Hz, 1H), 3.00 (q, ^{3}J(H,H) = 7.32 Hz, 2H), 1.24 (t, ^{3}J(H,H) = 7.32 Hz, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, 25 °C): d = 202.14, 140.09, 135.95, 135.50, 132.97, 132.71, 131.79, 129.50, 128.79, 124.97, 123.04, 33.43, 8.25. **MS** (70 eV, EI): *m/z* (%): 322 (28), 320 (27) [M^+], 293 (23), 291 (21), 213 (16), 212 (100), 184 (33), 139 (12), 137 (27). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3082 (w), 2984 (w), 2938 (w), 2901 (w), 1674 (vs), 1585 (m), 1564 (w), 1461 (m), 1431 (m), 1409 (w), 1388 (w), 1375 (w), 1349 (m), 1273 (w), 1216 (s), 1140 (w), 1098 (w), 1090 (w), 1065 (m), 1008 (s), 954 (m), 942 (m), 842 (m), 822 (m), 750 (s), 730 (m), 686 (w), 643 (w), 538 (w), 488 (w), 474 (w). **HRMS** for **$C_{15}H_{13}BrOS$** (319.9870): found: 319.9881.

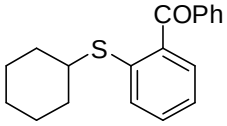
Synthesis of {2-[(4-bromophenyl)sulfanyl]phenyl}(phenyl)methanone (6i):



Prepared according to **TP 3** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (1.0 mL, 1.0 equiv., 1.0 M in THF), and benzoyl chloride (0.17 mL, 1.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 100/1) yielded **6i** as a yellow oil (324 mg, 88 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.78-7.73 (m, 2H), 7.59-7.52 (m, 1H), 7.45-7.30 (m, 6H), 7.29-7.23 (m, 2H), 7.19-7.13 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 196.19, 139.81, 137.15, 135.90, 134.20, 133.73, 133.16, 132.31, 131.91, 130.97, 130.02, 129.59, 128.39, 126.46, 121.87. **MS** (70 eV, EI): *m/z* (%): 370 (62), 369 (16), 368 (100) [M^+], 213 (29), 212 (35), 207 (37), 197 (34), 185 (13), 184 (43), 152 (14), 139 (13), 105 (46), 97 (18), 77 (46), 57 (16), 55 (10), 41 (20). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3060 (m), 2970 (w), 2928 (w), 1905 (w), 1715 (w), 1668 (vs), 1596 (m), 1581 (m), 1472 (s), 1448 (s), 1433 (m), 1386 (m), 1315 (s), 1286 (s), 1268 (s), 1202 (m), 1176 (m), 1153 (m), 1089 (m), 1069 (m), 1009 (s), 927 (m), 899 (m), 815 (m), 764 (m), 743 (m), 729 (m), 701 (s), 686 (m), 637 (m), 530 (w), 476 (m). **HRMS** for **$C_{19}H_{13}BrOS$** (367.9870): found: 367.9885.

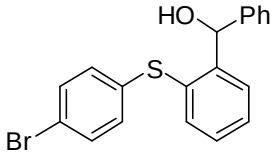
Synthesis of [2-(cyclohexylsulfanyl)phenyl](phenyl)methanone (6o):



Prepared according to **TP 3** from cyclohexanethiol (232 mg, 2.0 mmol), *i*PrMgCl (2.81 mL, 3.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (1.0 mL, 1.0 equiv., 1.0 M in THF), and benzoyl chloride (0.35 mL, 3.0 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 100/1) yielded **6o** as a yellow oil (246 mg, 83 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.80-7.75 (m, 2H), 7.59-7.51 (m, 2H), 7.46-7.38 (m, 3H), 7.34-7.29 (m, 2H), 3.11-3.00 (m, 1H), 1.92-1.16 (m, 10H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 197.03, 142.51, 137.43, 133.68, 133.06, 132.92, 129.95, 129.92, 128.31, 128.20, 126.33, 47.32, 33.04, 25.85, 25.59. **MS** (70 eV, EI): *m/z* (%): 296 (12) [M^+], 214 (33), 213 (100), 197 (10), 184 (14), 105 (10), 77 (10). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3325 (w), 3059 (w), 2930 (s), 2852 (m), 1720 (m), 1669 (vs), 1596 (m), 1582 (m), 1448 (s), 1433 (m), 1315 (m), 1285 (s), 1247 (m), 1178 (w), 1152 (w), 1065 (w), 1026 (w), 998 (w), 928 (m), 765 (m), 750 (m), 704 (s), 688 (m), 636 (m). **HRMS** for **$C_{19}H_{20}OS$** (296.1235): found: 296.1250.

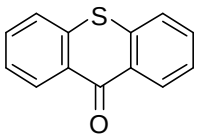
Synthesis of {2-[(4-bromophenyl)sulfanyl]phenyl}(phenyl)methanol (6j):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 4-bromothiophenol (190 mg, 1.0 mmol) in dry THF (3 mL). After cooling to –78 °C, *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF) was added dropwise and stirred for 10 min. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The reaction mixture was cooled to –78 °C, then benzaldehyde (0.15 mL, 1.5 mmol) was added and the resulting mixture was stirred for 3 h at the this temperature. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 20/1) yielded **6j** as a yellow oil (315 mg, 85 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.62 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.39-7.18 (m, 10H), 6.98-6.92 (m, 2H), 6.31 (s, 1H), 2.42 (s, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 145.34, 142.68, 135.86, 134.36, 132.08, 131.72, 130.84, 128.80, 128.52, 128.38, 127.80, 127.53, 126.94, 120.31, 73.28. **MS** (70 eV, EI): *m/z* (%): 372 (42), 370 (49) [M^+], 354 (11), 353 (22), 351 (19), 277 (19), 275 (17), 274 (11), 273 (39), 271 (14), 215 (16), 214 (70), 213 (100), 212 (23), 197 (65), 185 (10), 184 (39), 182 (28), 181 (81), 165 (36), 153 (14), 152 (30), 139 (12), 137 (21), 132 (14), 109 (19), 108 (10), 105 (52), 91 (10), 77 (51), 51 (14). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3392 (brm), 3060 (w), 3029 (w), 2921 (w), 1726 (w), 1588 (w), 1568 (w), 1494 (w), 1471 (vs), 1453 (m), 1439 (m), 1386 (m), 1180 (w), 1087 (m), 1069 (w), 1007 (vs), 811 (m), 758 (s), 699 (s), 648 (w), 601 (w), 478 (w). **HRMS** for **$C_{19}H_{15}BrOS$** (370.0027): found: 370.0027.

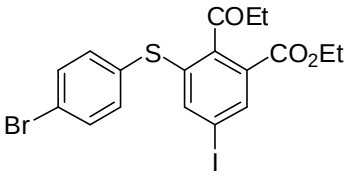
Synthesis of thioxanthon (10):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-mercapto-benzoic acid (154 mg, 1.0 mmol) in dry THF (3 mL). After cooling to –78 °C, *i*PrMgCl (2.81 mL, 3.0 equiv., 1.07 M in THF) was then added dropwise and stirred for 10 min. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was warmed to RT and stirred for 30 min. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 150/1) yielded **10** as a yellow solid (182 mg, 86 %).
mp.: 211.1-212.1 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.63-8.57 (m, 2H), 7.62-7.51 (m, 4H), 7.46 (ddd, ^3J(H,H) = 7.96 Hz, ^3J(H,H) = 6.63 Hz, ^4J(H,H) = 1.77 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 179.84, 137.20, 132.17, 129.78, 129.18, 126.21, 125.90. **MS** (70 eV, EI): *m/z* (%): 212 (100) [M^+], 184 (45), 152 (9), 139 (12), 59 (9). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3061 (w), 1646 (s), 1592 (vs), 1568 (w), 1460 (w), 1436 (s), 1321 (vs), 1258 (w), 1170 (w), 1162 (m), 1124 (w), 1084 (w), 1074 (w), 1033 (w), 928 (w), 805 (w), 744 (m), 732 (vs), 666 (m), 626 (m), 482 (m). **HRMS** for **$C_{13}H_8OS$** (212.0296): found: 212.0282.

Typical procedure for the generation of polyfunctional aryl thioethers (13a and 13b) by addition reaction to functional aryne followed by quenching with acid chloride or allyl bromide in the presence of CuCN·2LiCl (TP 4):
A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 4-bromothiophenol (190 mg, 1.0 mmol) in dry THF (2 mL). After cooling to –78 °C, *i*PrMgCl (1.41 mL, 3.0 equiv., 1.07 M in THF) was added dropwise and stirred for 10 min. Ethyl 2-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (**11**) (296 mg, 0.5 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was warmed to RT and stirred for 2 h. The reaction mixture was cooled to –78 °C, and then CuCN·2LiCl (1.0 M/THF; 0.5 mL, 1.0 equiv. for **13a**; 0.25 mL, 0.5 equiv. for **13b**) was added and stirred for 20 min. Propionyl chloride or allyl bromide (4.0 equiv.) was added at –78 °C, and the solution was allowed to warm to RT and kept stirring for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**13a** and **13b**).

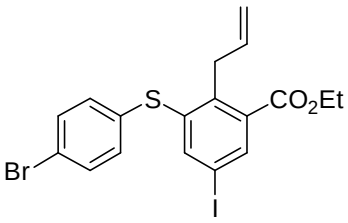
Synthesis of ethyl 3-[(4-bromophenyl)sulfanyl]-5-iodo-2-propionylbenzoate (13a):



Prepared according to **TP 4** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.41 mL, 3.0 equiv., 1.07 M in THF), ethyl 2-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (**11**) (296 mg, 0.5 mmol), CuCN·2LiCl (0.5 mL, 1.0 equiv., 1.0 M in THF) and propionyl chloride

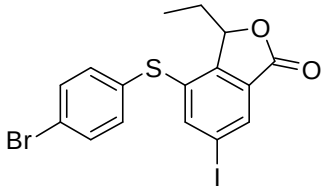
(0.17 mL, 2.0 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **13a** as a yellow solid (176 mg, 68 %).
mp.: 134.4-135.7 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.26 (d, ^4J(H,H) = 1.77 Hz, 1H), 7.76 (d, ^4J(H,H) = 1.77 Hz, 1H), 7.46-7.40 (m, 2H), 7.17-7.11 (m, 2H), 4.33 (q, ^3J(H,H) = 7.08 Hz, 2H), 2.84 (q, ^3J(H,H) = 7.08 Hz, 2H), 1.35 (t, ^3J(H,H) = 7.08 Hz, 2H), 1.23 (t, ^3J(H,H) = 7.08 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 205.29, 163.76, 145.97, 145.27, 138.60, 133.52, 133.49, 132.61, 132.35, 129.55, 122.11, 94.02, 62.17, 37.32, 14.04, 7.50. **MS** (70 eV, EI): *m/z* (%): 520 (46), 518 (43) [M^+], 492 (19), 491 (100), 490 (18), 489 (95), 474 (13), 463 (61), 462 (16), 461 (59), 446 (14), 445 (69), 444 (13), 443 (66), 382 (18), 365 (12), 338 (43), 335 (11), 318 (16), 317 (14), 316 (13), 183 (20), 182 (32), 139 (11), 57 (26). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 2982 (w), 1716 (vs), 1698 (vs), 1558 (m), 1469 (m), 1283 (vs), 1257 (s), 1210 (m), 1129 (w), 1105 (w), 1069 (w), 1022 (w), 1010 (m), 948 (m), 820 (m), 792 (w), 772 (w). **HRMS** for **$C_{18}H_{16}BrIO_3S$** (517.9048): found: 517.9089.

Synthesis of ethyl 2-allyl-3-[(4-bromophenyl)sulfanyl]-5-iodobenzoate (13b):



Prepared according to **TP 4** from 4-bromothiophenol (190 mg, 1.0 mmol), *i*PrMgCl (1.41 mL, 3.0 equiv., 1.07 M in THF), ethyl 2-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (**11**) (296 mg, 0.5 mmol), CuCN·2LiCl (0.25 mL, 0.5 equiv., 1.0 M in THF) and allyl bromide (0.17 mL, 2.0 mmol). Purification by flash chromatography (*n*-pentane) yielded **13b** as a yellow solid (181 mg, 72 %).
mp.: 54.1-55.2 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 8.00 (d, ^4J(H,H) = 1.77 Hz, 1H), 7.63 (d, ^4J(H,H) = 1.77 Hz, 1H), 7.47-7.41 (m, 2H), 7.15-7.09 (m, 2H), 5.96-5.82 (m, 1H), 5.05-4.89 (m, 2H), 4.35 (q, ^3J(H,H) = 7.08 Hz, 2H), 3.90-3.86 (m, 2H), 1.38 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 166.15, 143.30, 140.42, 138.99, 138.03, 135.37, 134.19, 134.09, 132.60, 132.46, 121.68, 116.21, 91.27, 61.62, 34.59, 14.18. **MS** (70 eV, EI): *m/z* (%): 504 (100), 502 (99) [M^+], 489 (51), 487 (49), 461 (31), 459 (29), 457 (27), 443 (87), 441 (82), 378 (59), 377 (32), 376 (50), 301 (72), 222 (41), 221 (61), 192 (65), 115 (62). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3078 (w), 2979 (w), 2933 (w), 1724 (vs), 1635 (w), 1556 (w), 1472 (m), 1433 (w), 1385 (w), 1365 (w), 1254 (s), 1185 (w), 1123 (w), 1096 (m), 1069 (w), 1009 (m), 915 (w), 817 (m), 784 (w). **HRMS** for **$C_{18}H_{16}BrIO_2S$** (501.9099): found: 501.9115.

Synthesis of 4-[(4-bromophenyl)sulfanyl]-3-ethyl-6-iodo-2-benzofuran-1(3*H*)-one (13c):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 4-bromothiophenol (190 mg, 1.0 mmol) in dry THF (2 mL). After cooling to –78 °C, *i*PrMgCl (1.41 mL, 3.0 equiv., 1.07 M in THF) was added

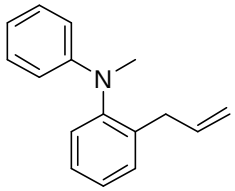
dropwise and stirred for 10 min. Ethyl 2-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (**11**) (296 mg, 0.5 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was warmed to RT and stirred for 2 h. Then, the reaction mixture was cooled to –78 °C. Propionaldehyde (0.15 mL, 4.0 equiv.) was added at –78 °C, and then the solution was allowed to warm to RT and kept stirring for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **13c** as a yellow oil (152 mg, 64 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.08 (d, ^4J(H,H) = 1.33 Hz, 1H), 7.67 (d, ^4J(H,H) = 1.33 Hz, 1H), 7.54-7.49 (m, 2H), 7.25-7.19 (m, 2H), 5.26 (dd, ^3J(H,H) = 7.08 Hz, ^3J(H,H) = 3.10 Hz, 1H), 2.44-2.30 (m, 1H), 1.96-1.80 (m, 1H), 0.87 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 168.14, 147.93, 143.31, 133.46, 133.20, 133.17, 133.10, 130.79, 129.53, 123.13, 94.66, 82.18, 25.35, 8.48. **MS** (70 eV, EI): *m/z* (%): 476 (69), 474 (67) [M^+], 447 (21), 445 (21), 419 (17), 417 (19), 367 (18), 366 (100), 365 (36), 338 (18), 183 (24), 182 (20), 139 (17). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3065 (w), 2969 (m), 2934 (m), 2877 (w), 1770 (vs), 1588 (m), 1568 (m), 1472 (s), 1442 (m), 1385 (m), 1333 (m), 1276 (m), 1232 (m), 1173 (m), 1110 (m), 1087 (m), 1068 (s), 1008 (m), 969 (m), 868 (m), 817 (m), 779 (m), 729 (w), 481 (m). **HRMS** for **$C_{16}H_{12}BrIO_2S$** (473.8786): found: 473.8790.

Typical procedure for the generation of tertiary amides (7a-b and 7f-g) by addition reaction to benzyne followed by quenched with acid chloride or allyl bromide in the presence of CuCN·2LiCl (TP 5):

A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding secondary amine (1.0 mmol) in dry THF (3 mL). After cooling to –20 °C, *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –78 °C and *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The reaction mixture was cooled to –78 °C, and then CuCN·2LiCl (1.0 M/THF; 0.5 mL, 0.5 equiv. for **7a** and **7f**; 1.0 mL, 1.0 equiv. for **7b** and **7g**) was added and stirred for 20 min. Acid chloride or allyl bromide (2.5 equiv.) was added at –78 °C, and the solution was allowed to warm to RT and kept stirring for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**7a-b** and **7f-g**).

Synthesis of 2-allyl-*N*-methyl-*N*-phenylaniline (7a):

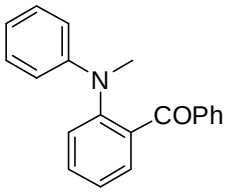


Prepared according to **TP 5** from *N*-methylaniline (107 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (0.5 mL, 0.5 equiv., 1.0 M in THF), and allyl bromide (0.21 mL, 2.5 mmol).

Purification by flash chromatography (*n*-pentane) yielded **7a** as a colourless oil (185 mg, 83 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.34-7.10 (m, 6H), 6.73-6.66 (m, 1H), 6.54-6.49 (m, 2H), 5.95-5.80 (m, 1H), 5.04-4.94 (m, 2H), 3.29-3.24 (m, 2H), 3.19 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 149.39, 146.64, 138.97, 136.98, 130.51, 128.90, 128.62, 128.04, 126.66, 116.86, 115.89, 112.93, 39.64, 35.48. **MS** (70 eV, EI): *m/z* (%): 223 (100) [M^+], 222 (39), 221 (15), 208 (37), 207 (15), 194 (91), 193 (38), 180 (23), 167 (20), 165 (14), 155 (48), 147 (19), 120 (15), 115 (36), 111 (15), 107 (15), 106 (16), 97 (33), 95 (22), 91 (59), 85 (15), 83 (31), 82 (19), 81 (18), 77 (27), 74 (17), 73 (22), 71 (23), 70 (16), 69 (43), 67 (18), 59 (39), 57 (49), 56 (15), 55 (39), 45 (27), 43 (35), 42 (17), 41 (43). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3061 (w), 3024 (w), 2893 (w), 2810 (w), 1638 (w), 1603 (s), 1594 (s), 1576 (m), 1500 (vs), 1449 (m), 1430 (w), 1344 (m), 1300 (w), 1256 (m), 1187 (w), 1137 (w), 1114 (w), 991 (w), 915 (w), 870 (w), 774 (w), 748 (s), 692 (m). **HRMS** for **$C_{16}H_{17}N$** (223.1361): found: 223.1376.

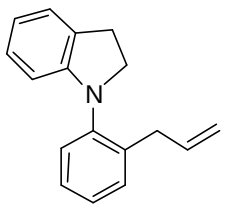
Synthesis of [2-(methylanilino)phenyl](phenyl)methanone (7b):



Prepared according to **TP 5** from *N*-methylaniline (107 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (1.0 mL, 1.0 equiv., 1.0 M in THF), and benzoyl chloride (0.17 mL, 1.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **7b** as a yellow oil (244 mg, 85 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.55-7.47 (m, 4H), 7.45-7.38 (m, 1H), 7.30-7.22 (m, 4H), 7.05-6.98 (m, 2H), 6.70-6.63 (m, 1H), 6.48-6.43 (m, 2H), 3.02 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 197.35, 148.40, 147.30, 137.71, 136.54, 132.51, 132.08, 130.33, 129.08, 128.62, 127.78, 126.83, 124.77, 118.65, 115.38, 40.52. **MS** (70 eV, EI): *m/z* (%): 287 (75) [M^+], 271 (23), 270 (100), 210 (17), 167 (17), 105 (11), 91 (12), 77 (20). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3060 (w), 3027 (w), 2932 (w), 2887 (w), 2814 (w), 1730 (w), 1662 (s), 1593 (vs), 1579 (m), 1499 (vs), 1487 (vs), 1450 (s), 1426 (w), 1348 (s), 1316 (s), 1287 (s), 1258 (s), 1187 (w), 1153 (m), 1136 (m), 1113 (m), 1097 (m), 1070 (w), 1026 (w), 936 (m), 866 (w), 749 (s), 708 (s), 693 (s), 639 (s), 569 (w), 515 (w). **HRMS** for **$C_{20}H_{17}NO$** (287.1310): found: 287.1300.

Synthesis of 1-(2-allylphenyl)indoline (7f):

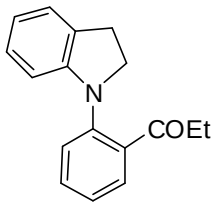


Prepared according to **TP 5** from 2,3-dihydro-1H-indole (119 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (0.5 mL, 0.5 equiv., 1.0 M in THF), and allyl bromide (0.21 mL,

2.5 mmol). Purification by flash chromatography (*n*-pentane) yielded **7f** as a colourless oil (155 mg, 66 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.32-7.11 (m, 5H), 6.99-6.92 (m, 1H), 6.66 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.33 Hz, 1H), 6.18 (d, ^3J(H,H) = 7.52 Hz, 1H), 6.02-5.87 (m, 1H), 5.07-4.98 (m, 2H), 3.82-3.67 (m, 2H), 3.46-3.40 (m, 2H), 3.15-3.07 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 151.35, 143.77, 138.41, 137.42, 130.34, 129.98, 127.64, 127.12, 126.13, 125.16, 124.52, 117.79, 115.72, 108.09, 55.43, 35.56, 28.91. **MS** (70 eV, EI): *m/z* (%): 235 (84) [M^+], 234 (53), 233 (22), 232 (22), 220 (51), 218 (77), 217 (36), 206 (100), 205 (65), 204 (87), 115 (22). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3073 (w), 3025 (w), 2976 (w), 2923 (w), 2847 (w), 1638 (w), 1608 (m), 1597 (m), 1580 (w), 1487 (vs), 1460 (m), 1373 (m), 1328 (w), 1290 (m), 1262 (m), 1224 (m), 1057 (w), 915 (m), 764 (m), 746 (s). **HRMS** for **$C_{17}H_{17}N$** (235.1361): found: 235.1351.

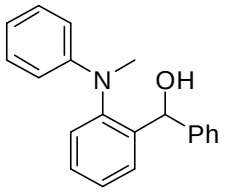
Synthesis of 1-[2-(2,3-dihydro-1*H*-indol-1-yl)phenyl]-1-propanone (7g):



Prepared according to **TP 5** from 2,3-dihydro-1H-indole (119 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), CuCN·2LiCl (1.0 mL, 1.0 equiv., 1.0 M in THF), and propionyl chloride (0.22 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **7g** as a yellow oil (156 mg, 62 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.42 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.35 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.27 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.12 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.09-7.04 (m, 1H), 6.90 (t, ^3J(H,H) = 7.52 Hz, 1H), 6.64 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 0.89 Hz, 1H), 6.41 (d, ^3J(H,H) = 7.52 Hz, 1H), 3.70 (t, ^3J(H,H) = 8.40 Hz, 2H), 3.03 (t, ^3J(H,H) = 8.40 Hz, 2H), 2.77 (q, ^3J(H,H) = 7.08 Hz, 2H), 0.94 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 206.52, 149.40, 143.17, 137.26, 131.97, 130.47, 129.04, 127.18, 124.84, 124.74, 122.95, 119.11, 108.54, 55.44, 34.93, 28.78, 8.59. **MS** (70 eV, EI): *m/z* (%): 251 (100) [M^+], 222 (60), 220 (15), 218 (23), 205 (13), 204 (57), 194 (20), 193 (13), 111 (14). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3066 (w), 3027 (w), 2974 (w), 2936 (w), 2876 (w), 2849 (w), 1688 (s), 1606 (m), 1594 (m), 1572 (w), 1486 (vs), 1460 (s), 1447 (m), 1376 (m), 1334 (w), 1262 (m), 1209 (m), 947 (w), 744 (s). **HRMS** for **$C_{17}H_{17}NO$** (251.1310): found: 251.1286.

Synthesis of [2-(methylanilino)phenyl](phenyl)methanol (7c):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of *N*-methylaniline (107 mg, 1.0 mmol) in dry THF (3 mL). After cooling to –20 °C, *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added

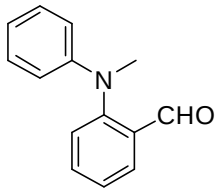
dropwise and stirred for 30 min. The reaction mixture was cooled to –78 °C and *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The reaction mixture was cooled to –78 °C, and benzaldehyde (0.12 mL, 1.2 mmol) was added and stirred for 3 h at the same temperature. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 20/1) yielded **7c** as a yellow oil (232 mg, 80%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.61-7.56 (m, 1H), 7.33-7.02 (m, 10H), 6.75-6.68 (m, 1H), 6.53-6.47 (m, 2H), 5.86 (s, 1H), 2.85 (s, 3H), 2.62 (s, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 149.40, 146.06, 143.58, 142.36, 129.39, 128.97, 128.52, 128.21, 127.93, 127.27, 127.04, 126.68, 117.57, 113.44, 72.21, 39.66. **MS** (70 eV, EI): *m/z* (%): 287 (75) [M^+], 271 (23), 270 (100), 210 (17), 167 (17), 105 (11), 91 (12), 77 (20). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3537 (m), 3392 (brm), 3061 (m), 3029 (m), 2883 (m), 2812 (w), 1602 (s), 1575 (m), 1499 (vs), 1451 (s), 1344 (s), 1299 (m), 1257 (m), 1182 (m), 1157 (w), 1137 (w), 1110 (w), 1088 (w), 1066 (w), 1032 (m), 1017 (m), 917 (w), 871 (w), 846 (w), 749 (s), 718 (m), 696 (s), 649 (w), 598 (w), 579 (w), 491 (w). **HRMS** for **$C_{20}H_{19}NO$** (289.1467): found: 289.1450.

Typical procedure for the generation of tertiary amides (7d and 7h) by addition reaction to benzyne followed by trapping with DMF (TP 6):

A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding secondary amine (1.0 mmol) in dry THF (3 mL). After cooling to –20 °C, *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –78 °C and *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. Then, the reaction mixture was cooled to –40 °C and DMF (0.19 mg, 2.5 equiv.) was added. Thereafter, the mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**7d** and **7h**).

Synthesis of 2-(methylanilino)benzaldehyde (7d):

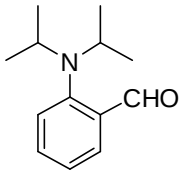


Prepared according to **TP 6** from *N*-methylaniline (107 mg, 1.0 mmol), *i*PrMgCl (1.88 mL, 2.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 250/1) yielded **7d** as a yellow oil (156 mg, 74 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 10.13 (s, 1H), 7.93 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.61 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.35-7.28 (m, 1H), 7.26-7.15 (m, 3H), 6.83-6.77 (m, 1H), 6.74-6.69 (m, 2H), 3.35 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 191.16, 151.91, 150.01, 135.72, 132.69, 129.19, 128.86, 127.64,

125.93, 119.08, 115.12, 41.44. **MS** (70 eV, EI): *m/z* (%): 211 (100) [M^+], 210 (14), 194 (32), 182 (36), 168 (38), 167 (37). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3064 (m), 3036 (w), 2925 (w), 2852 (w), 1693 (vs), 1593 (vs), 1498 (vs), 1485 (vs), 1454 (m), 1385 (m), 1343 (m), 1291 (m), 1268 (m), 1249 (m), 1190 (m), 1158 (w), 1132 (m), 1111 (w), 1065 (w), 1031 (w), 869 (w), 821 (m), 775 (m), 751 (s), 694 (m), 639 (w). **HRMS** for **$C_{14}H_{13}NO$** (211.0997): found: 211.0989.

Synthesis of 2-(diisopropylamino)benzaldehyde (7h):



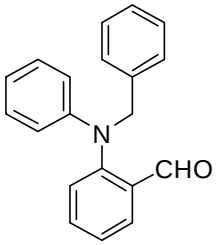
Prepared according to **TP 6** from diisopropylamine (304 mg, 3.0 mmol), *i*PrMgCl (3.74 mL, 4.0 equiv., 1.07 M in THF), 2-iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **7h** as a yellow oil (51 mg, 25 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 10.66 (s, 1H), 7.86 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.57-7.50 (m, 1H), 7.38-7.33 (m, 1H), 7.30-7.23 (m, 1H), 3.69-3.55 (m, 2H), 0.97 (d, ^3J(H,H) = 6.19 Hz, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 193.88, 151.08, 137.03, 133.61, 129.71, 127.04, 125.41, 49.52, 21.23. **MS** (70 eV, EI): *m/z* (%): 205 (16) [M^+], 190 (56), 155 (17), 154 (12), 148 (40), 144 (24), 132 (15), 130 (68), 120 (38), 118 (13), 97 (17), 95 (10), 92 (13), 91 (77), 85 (13), 83 (17), 81 (13), 78 (11), 77 (39), 71 (16), 69 (18), 65 (15), 57 (45), 56 (10), 55 (25), 51 (16), 43 (100), 42 (53), 41 (61). **IR** (film): $\tilde{n}$ (cm^{-1}) = 2971 (m), 2930 (m), 2855 (w), 1690 (vs), 1651 (w), 1593 (m), 1480 (w), 1450 (w), 1382 (w), 1364 (w), 1270 (w), 1234 (w), 1179 (w), 824 (w), 770 (w), 747 (w). **HRMS** for **$C_{13}H_{19}NO$** (205.1467): found: 205.1501.

Typical procedure for the generation of tertiary amides (7e and 7i) by addition reaction to benzyne followed by trapping with DMF (TP 7):

A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the corresponding secondary amine (1.0 mmol) in dry DME (4 mL). After cooling to –20 °C, *i*PrMgCl (0.98 mL, 1.05 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –70 °C and *i*PrMgCl (1.60 mL, 1.70 equiv., 1.07 M in THF) was added. Toluene-4-sulfonic acid 2-iodo-phenyl ester (636 mg, 1.7 mmol) dissolved in dry DME (2 mL) was added and stirred vigorously for 2 h at the same temperature. Thereafter, the resulting mixture was warmed slowly to 0 °C during 2h, and then stirred at the same temperature for 1 h. Then, the reaction mixture was cooled to –40 °C and DMF (0.19 mg, 2.5 equiv.) was added. Thereafter, the mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography furnished the desired products (**7e** and **7i**).

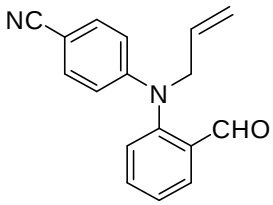
Synthesis of 2-(benzylanilino)benzaldehyde (7e):



Prepared according to **TP 7** from benzyl-phenyl-amine (183 mg, 1.0 mmol), *i*PrMgCl (2.58 mL, 2.75 equiv., 1.07 M in THF), toluene-4-sulfonic acid 2-iodo-phenyl ester (636 mg, 1.7 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 200/1) yielded **7e** as a yellow oil (204 mg, 71%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 10.11 (s, 1H), 7.89 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.57 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.34-7.08 (m, 9H), 6.80-6.69 (m, 3H), 4.96 (s, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 190.84, 150.48, 149.93, 138.00, 135.69, 132.86, 129.30, 129.21, 128.62, 128.34, 127.20, 127.11, 126.10, 119.37, 115.65, 57.58. **MS** (70 eV, EI): *m/z* (%): 287 (100) [M^+], 286 (16), 270 (37), 210 (16), 209 (28), 196 (40), 195 (12), 182 (12), 180 (17), 168 (17), 167 (41), 166 (11), 106 (13), 91 (95), 77 (15), 65 (10). **IR** (film): $\tilde{n}$ (cm^{-1}) = 2871 (w), 2841 (w), 2748 (w), 1694 (vs), 1591 (s), 1574 (w), 1496 (vs), 1480 (m), 1452 (m), 1392 (m), 1375 (w), 1350 (m), 1291 (w), 1270 (m), 1253 (m), 1229 (w), 1186 (w), 820 (w), 782 (m), 750 (s), 736 (m), 694 (m), 591 (w). **HRMS** for **$C_{20}H_{17}NO$** (287.1310): found: 287.1306.

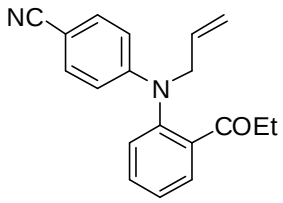
Synthesis of 4-(allyl-2-formylanilino)benzonitrile (7i):



Prepared according to **TP 7** from 4-allylamino-benzonitrile (158 mg, 1.0 mmol), *i*PrMgCl (2.58 mL, 2.75 equiv., 1.07 M in THF), toluene-4-sulfonic acid 2-iodo-phenyl ester (636 mg, 1.7 mmol), and DMF (0.20 mL, 2.5 mmol). Purification by flash chromatography (*n*-pentane/diethyl ether = 5/1) yielded **7i** as a yellow oil (191 mg, 73%).

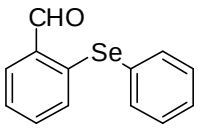
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 10.00 (s, 1H), 7.98 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.72 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.49 (td, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.41-7.35 (m, 2H), 7.30 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 1.77 Hz, 1H), 6.62-6.56 (m, 2H), 6.00-5.86 (m, 1H), 5.30-5.21 (m, 2H), 4.37-4.32 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d= 190.00, 151.70, 147.53, 136.18, 133.38, 133.12, 131.67, 130.09, 129.76, 128.03, 119.72, 118.59, 113.49, 100.13, 55.75. **MS** (70 eV, EI): *m/z* (%): 263 (18), 262 (100) [M^+], 261 (26), 245 (31), 235 (16), 234 (20), 233 (68), 221 (27), 220 (19), 219 (25), 218 (25), 205 (21), 193 (21), 192 (64), 191 (14), 132 (19), 117 (12), 102 (13), 77 (11). **IR** (film): $\tilde{n}$ (cm^{-1}) = 2853 (w), 2217 (s), 1694 (s), 1606 (vs), 1594 (vs), 1511 (vs), 1482 (m), 1456 (m), 1379 (m), 1269 (w), 1256 (m), 1224 (w), 1178 (m), 823 (m), 775 (m), 741 (m), 546 (m). **HRMS** for **$C_{17}H_{14}N_2O$** (262.1106): found: 262.1085.

Synthesis of 4-(allyl-2-propionylanilino)benzonitrile (7j):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 4-allylamino-benzonitrile (158 mg, 1.0 mmol) in dry DME (4 mL). After cooling to –20 °C, *i*PrMgCl (0.98 mL, 1.05 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –70 °C and *i*PrMgCl (1.60 mL, 1.70 equiv., 1.07 M in THF) was added. Toluene-4-sulfonic acid 2-iodo-phenyl ester (636 mg, 1.7 mmol) dissolved in dry DME (2 mL) was added and stirred vigorously for 2 h at the same temperature. Thereafter, the resulting mixture was warmed slowly to 0 °C during 2h and then stirred at the same temperature for 1 h. The reaction mixture was cooled to –78 °C, and then CuCN·2LiCl (1.0 M/THF, 1.0 mL, 1.0 equiv.) was added and stirred for 20 min. Thereafter, propionyl chloride (0.44 mL, 5.0 mmol) was added at –78 °C, and the reaction mixture was allowed to warm to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 5/1) yielded **7j** as a yellow solid (220 mg, 76%).
mp.: 83.1-84.6 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.63 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.54 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.44-7.34 (m, 3H), 7.27-7.23 (m, 1H), 6.56-6.51 (m, 2H), 5.96-5.83 (m, 1H), 5.28-5.19 (m, 2H), 4.25-4.20 (m, 2H), 2.70 (q, ^3J(H,H) = 7.08 Hz, 2H), 0.98 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 203.73, 151.08, 143.00, 138.66, 133.20, 132.71, 132.33, 130.16, 129.50, 127.61, 120.04, 117.80, 113.44, 99.39, 55.50, 34.79, 8.03. **MS** (70 eV, EI): *m/z* (%): 290 (44) [M^+], 262 (18), 261 (18), 234 (18), 233 (67), 220 (14), 218 (10), 205 (12), 192 (15), 102 (11), 57 (14). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 2215 (s), 1683 (s), 1606 (vs), 1593 (m), 1510 (vs), 1483 (m), 1448 (m), 1376 (s), 1342 (m), 1253 (m), 1180 (m), 946 (w), 937 (m), 861 (w), 823 (m), 776 (m), 741 (m), 544 (m), 490 (m). **HRMS** for **$C_{19}H_{18}N_2O$** (290.1419): found: 290.1390.

Synthesis of 2-(phenylselanyl)benzaldehyde (15a):



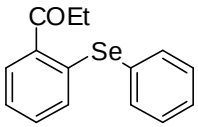
A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of phenylselenol (157 mg, 1.0 mmol) in dry THF (3 mL). After cooling to –20 °C, *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –78 °C and *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. Then, the reaction mixture was cooled to –40 °C and DMF (0.20 mL, 2.5 equiv.) was added. Thereafter, the mixture was warmed to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over

anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 50/1) yielded **15a** as a yellow solid (223 mg, 85 %).

mp.: 54.8-56.4 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 10.15 (s, 1H), 7.82-7.78 (m, 1H), 7.64-7.60 (m, 2H), 7.45-7.22 (m, 5H), 7.03-6.99 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 192.40, 139.43, 136.63, 134.87, 133.72, 133.63, 129.88, 129.73, 128.99, 128.06, 125.40.

MS (70 eV, EI): *m/z* (%): 262 (100) [M^+], 261 (26), 260 (45), 259 (23), 258 (18), 232 (17), 184 (28), 154 (43), 152 (18), 77 (14). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 3064 (w), 2863 (w), 2742 (w), 1689 (m), 1666 (vs), 1581 (m), 1552 (m), 1477 (w), 1453 (s), 1439 (m), 1391 (m), 1301 (m), 1254 (w), 1200 (s), 1120 (w), 1034 (m), 1022 (w), 1000 (w), 842 (m), 759 (s), 736 (m), 688 (m), 660 (m), 650 (w), 479 (w). **HRMS** for **$C_{13}H_{10}OSe$** (261.9897): found: 261.9894.

Synthesis of 1-[2-(phenylselanyl)phenyl]-1-propanone (15b):



A dry and argon-flushed 25 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of phenylselenol (157 mg, 1.0 mmol) in dry THF (3 mL). After cooling to –20 °C, *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added dropwise and stirred for 30 min. The reaction mixture was cooled to –78 °C and *i*PrMgCl (0.94 mL, 1.0 equiv., 1.07 M in THF) was added. 2-Iodophenyl 4-chlorobenzenesulfonate (**1a**) (394 mg, 1.0 mmol) dissolved in dry THF (2 mL) was added and stirred vigorously for 30 min at the same temperature. Thereafter, the resulting mixture was immediately warmed to 0 °C and stirred for 10 min. The reaction mixture was cooled to –78 °C, and then CuCN·2LiCl (1.0 M/THF, 1.0 mL, 1.0 equiv.) was added and stirred for 20 min. Thereafter, propionyl chloride (0.22 mL, 2.5 mmol) was added at –78 °C, and the reaction mixture was allowed to warm to RT and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 (3 x 40 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash chromatography (*n*-pentane/diethyl ether = 100/1) yielded **15b** as a yellow oil (253 mg, 87 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.96-7.91 (m, 1H), 7.69-7.64 (m, 2H), 7.44-7.34 (m, 3H), 7.21-7.12 (m, 2H), 7.01-6.94 (m, 1H), 3.03 (q, ^3J(H,H) = 7.52 Hz, 2H), 1.26 (t, ^3J(H,H) = 7.52 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 201.26, 140.08, 137.21, 133.62, 132.16, 130.54, 129.64, 129.54, 129.50, 128.87, 124.53, 32.06, 8.22. **MS** (70 eV, EI): *m/z* (%): 290 (73) [M^+], 288 (35), 287 (12), 286 (14), 263 (18), 262 (14), 261 (100), 259 (48), 258 (16), 257 (18), 232 (39), 230 (20), 213 (15), 185 (13), 153 (13), 152 (35), 77 (19). **IR** (film): $\tilde{n}$ (cm^{-1}) = 3056 (w), 2977 (w), 2937 (w), 1667 (vs), 1585 (m), 1557 (w), 1460 (m), 1434 (m), 1378 (w), 1351 (w), 1268 (w), 1219 (s), 1139 (w), 1034 (w), 1021 (w), 1012 (w), 954 (m), 743 (s), 695 (m). **HRMS** for **$C_{15}H_{14}OSe$** (290.0210): found: 290.0215.

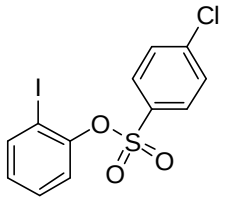
Preparation of the starting materials:

Typical procedure for the formation of aryl-sulfonates from the corresponding phenols (TP 8)

A 100 mL round–bottom flask, equipped with a magnetic stirring bar, was charged with the corresponding phenol (20 mmol) dissolved in dry pyridine (20 mL). Then, the corresponding benzenesulfonyl chloride (24 mmol) was added portionwise and the reaction mixture was stirred at RT overnight. Thereafter, pyridine was evaporated *in vacuo*. Water (50 mL) was added to the mixture residue, and this mixture was diluted with 100 mL CH_2Cl_2. The organic

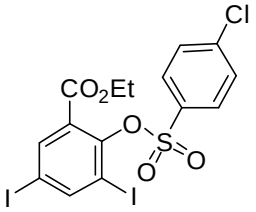
phase was washed with sat. aq. Na_2CO_3 (100 mL) and brine (100 mL), and then dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 and ethanol yielded the desired products.

Synthesis of 2-iodophenyl 4-chlorobenzenesulfonate (1a):



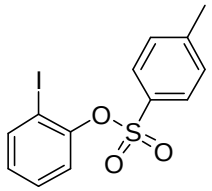
Prepared according to **TP 8** from 2-iodophenol (4.40 g, 20 mmol), 4-chlorobenzenesulfonyl chloride (5.07 g, 24 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **6a** as a colourless solid (7.50 g, 95 %).
mp.: 89-90°C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.85 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.78-7.74 (m, 1H), 7.51 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.37-7.33 (m, 2H), 7.03-6.95 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 149.8, 141.4, 140.2, 134.3, 130.3, 129.5, 128.6, 123.1, 112.6, 90.0. **MS** (70 eV, EI): *m/z* (%): 394 (62) [M^+], 298 (4), 218 (20), 190 (17), 175 (100), 139 (4), 111 (66), 92 (42), 75 (27), 64 (32). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 1584 (m), 1572 (m), 1462 (s), 1380 (vs), 1283 (m), 1199 (vs), 1174 (vs), 1085 (s), 866 (vs), 854 (vs), 774 (vs), 727 (vs), 619 (vs), 606 (vs), 557 (vs), 483 (m). **HRMS** for **$C_{12}H_8ClIO_3S$** (393.8927): found: 393.8937.
Anal. Calcd for $C_{12}H_8ClIO_3S$: C, 36.52; H, 2.04. **Found:** C, 36.89; H, 2.08.

Synthesis of ethyl 2-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (11):



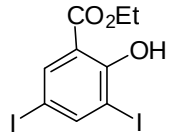
Prepared according to **TP 8** from ethyl 2-hydroxy-3,5-diiodobenzoate (4.18 g, 10 mmol), 4-chlorobenzenesulfonyl chloride (2.54 g, 12 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **16** as a colourless solid (5.50 g, 93 %).
mp.: 96.8-97.5°C. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25 °C): d = 8.19 (d, ^4J(H,H) = 1.72 Hz, 1H), 8.15 (d, ^4J(H,H) = 1.72 Hz, 1H), 7.80 (d, ^3J(H,H) = 8.60 Hz, 2H), 7.53 (d, ^3J(H,H) = 8.60 Hz, 2H), 4.37 (q, ^3J(H,H) = 7.31 Hz, 2H), 1.42 (t, ^3J(H,H) = 7.31 Hz, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$, 25 °C): d = 163.40, 150.77, 147.70, 141.66, 140.49, 134.78, 130.31, 129.80, 129.78, 92.94, 92.05, 62.46, 13.92. **MS** (70 eV, EI): *m/z* (%): 592 (10) [M^+], 417 (35), 373 (28), 372 (100), 262 (14), 245 (10), 189 (10), 177 (10), 175 (26), 111 (26). **IR** (KBr): 3088 (w), 2983 (w), 1721 (vs), 1587 (w), 1570 (m), 1537 (w), 1478 (m), 1464 (w), 1446 (w), 1419 (s), 1385 (vs), 1300 (s), 1274 (vs), 1252 (s), 1212 (vs), 1202 (vs), 1180 (vs), 1106 (m), 1093 (s), 1082 (s), 1009 (s), 890 (w), 865 (s), 849 (s), 836 (m), 787 (s), 763 (vs), 736 (s), 711 (s), 652 (w), 624 (s), 567 (s), 485 (m). **HRMS** for **$C_{15}H_{11}ClI_2O_5S$** (591.8105): found: 591.8127.

Synthesis of toluene-4-sulfonic acid 2-iodo-phenyl ester:



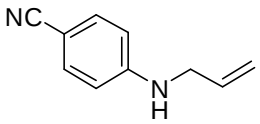
Prepared according to **TP 8** from 2-iodophenol (4.40 g, 20 mmol), 4-methyl-benzenesulfonyl chloride (4.58 g, 24 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded the final product as a colourless solid (6.73 g, 90 %).
mp.: 85-86°C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 7.79 (m, 3H), 7.33 (m, 4H), 6.97 (m, 1H), 2.46 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 150.0, 145.7, 140.1, 132.9, 129.8, 129.5, 128.8, 128.3, 123.0, 88.8, 21.7. **MS** (70 eV, EI): *m/z* (%): 374 (83) [M^+], 155 (100), 91 (54). **IR** (KBr): $\tilde{n}$ (cm^{-1}) = 1462 (s), 1377 (vs), 1199 (s), 1185 (s), 1170 (vs), 1090 (m), 943 (w), 868 (s), 858 (s), 812 (m), 766 (vs), 734 (s), 708 (s), 665 (s), 561 (vs), 549 (s). **HRMS** for **$C_{13}H_{11}IO_3S$** (373.9474): found: 373.9507. **Anal. Calcd for $C_{12}H_8ClIO_3S$:** C, 41.73; H, 2.96; S, 8.57. **Found:** C, 41.38; H, 2.96; S, 8.31.

Synthesis of ethyl 2-hydroxy-3,5-diiodobenzoate:



A 250 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with iodine (10.16 g, 40.0 mmol) and silver sulfate (12.46 g, 40.0 mmol) in ethanol (100 mL). 2-Hydroxy-benzoic acid ethyl ester (3.32g, 20 mmol) was then added and the mixture was stirred vigorously at RT until tlc analysis indicated the end of the reaction. The reaction mixture was filtered through a glass sinter. The solids on the sinter were washed with ethyl acetate (2 x 100 mL) and the filtrate was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (100 mL), and the resulting mixture was washed with water (100 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Recrystallization from ethanol yielded the final product as a pale yellow solid (6.52 g, 78 %).
mp.: 126.8-127.9°C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): d = 11.67 (s, 1H), 8.17 (d, ^{4}J(H,H) = 2.20 Hz, 1H), 8.10 (d, ^{4}J(H,H) = 2.20 Hz, 1H), 4.42 (q, ^{3}J(H,H) = 7.15 Hz, 2H), 1.42 (t, ^{3}J(H,H) = 7.15 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 168.42, 160.15, 151.87, 138.38, 114.40, 86.77, 80.60, 62.49, 14.10. **MS** (70 eV, EI): *m/z* (%): 418 (71) [M^+], 373 (10), 372 (100), 246 (18), 245 (10), 91 (12), 72 (16), 63 (11), 62 (12), 59 (31), 55 (13), 45 (11), 43 (12), 41 (15). **IR** (KBr): 1722 (w), 1665 (vs), 1589 (m), 1581 (m), 1472 (w), 1433 (m), 1416 (m), 1399 (s), 1371 (m), 1307 (vs), 1277 (m), 1234 (vs), 1183 (vs), 1103 (w), 1014 (s), 898 (w), 880 (m), 864 (w), 792 (s), 730 (m), 716 (m), 704 (w), 654 (m), 575 (w), 546 (w), 408 (w). **HRMS** for **$C_9H_8I_2O_3$** (417.8563): found: 417.8599.

Synthesis of 4-(allylamino)benzonitrile:



Prepared according to the procedure reported by S.-C. Yang.[3]

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.44-7.38 (m, 2H), 6.60-6.54 (m, 2H), 5.96-5.83 (m, 1H), 5.31-5.18 (m, 2H), 4.39 (s, 1H), 3.84-3.78 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): d = 151.10, 133.76, 133.62, 120.37, 116.97, 112.36, 98.88, 45.59. **MS** (70 eV, EI): *m/z* (%): 158 (93) [M^+], 157 (68), 155 (14), 142 (16), 132 (12), 131 (100), 130 (17), 129 (26), 102 (25). **IR** (film): 3376 (m), 2213 (s), 1607 (vs), 1527 (s), 1337 (m), 1280 (w), 1174 (m), 994 (w), 922 (w), 824 (m), 544 (m). **HRMS** for **$C_{10}H_{10}N_2$** (158.0844): found: 158.0853.
Spectral data match those reported in the literature.[4]

References and Notes:

[1] H.-S. Lin, L. A. Paquette, *Synth. Commun.* **1994**, *24*, 2503.
[2] H. Yoshida, T. Terayama, J. Ohshita, A. Kunai, *J. Chem. Soc. Chem. Commun.* **2004**, 1980.
[3] S.-C. Yang, C.-W. Hung, *Synthesis* **1999**, 1747.