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Supporting Information

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Preparation of Polyfunctional Arynes via 2-Magnesiated Aryl Arylsulfonates

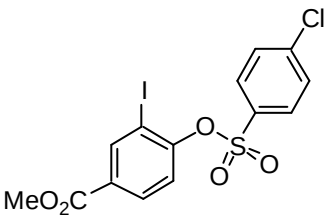
Ioannis Sapountzis, Wenwei Lin, Markus Fischer and Paul Knochel*
Ludwig-Maximilians-Universität München, Department Chemie
Butenandtstrasse 5-13, Haus F, 81377 München (Germany)
Fax: (+49) 089 21 80 776 80
e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under a nitrogen 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 (110 mmol) were placed in an Ar-flushed flask and THF (50 mL) was added. A solution of *i*PrCl (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 formation of aryl-sulfonates from the corresponding phenols (TP 1)
A 100 mL round–bottom flask, equipped with a magnetic stirring bar, was charged with the corresponding phenol (20 mmol) and dry pyridine (20 mL) was added. To the solution was added 4-chloro-benzenesulfonyl chloride (5.07 g, 24.0 mmol) portionwise. After addition was completed, the reaction mixture was stirred at room temperature overnight. Then the solvent was evaporated *in vacuo*. 50 mL of water was added to the mixture residue. This mixture was diluted with 100 mL CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 (100 mL) and brine (100 mL), and then dried over Na_2SO_4. After filtration, solvent was evaporated *in vacuo*. Recrystallization from CH_2Cl_2 and ethanol yielded the product.

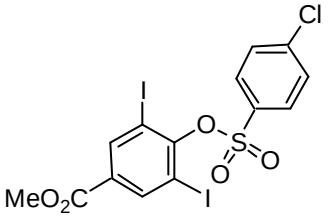
Synthesis of methyl 4-{[(4-chlorophenyl)sulfonyl]oxy}-3-iodobenzoate (2g):



Prepared according to **TP 1** from methyl 4-hydroxy-3-iodobenzoate (3.05 g, 11 mmol), 4-chlorobenzenesulfonyl chloride (2.79 g, 13 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **2g** as a colourless solid (4.92 g, 99 %).
mp.: 79.5-80.5 °C.

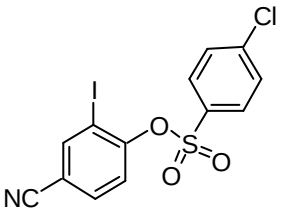
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.40 (d, ^4J(H,H) = 2 Hz, 1H), 8.00 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H), 7.86 (d, ^3J(H,H) = 9 Hz, 2H), 7.50 (d, ^3J(H,H) = 9 Hz, 2H), 7.42 (d, ^3J(H,H) = 8 Hz, 1H), 3.84 (s, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 164.5, 152.9, 141.7, 141.4, 133.9, 130.9, 130.2, 129.7, 122.5, 112.5, 89.6, 52.5.
MS (70 eV, EI): m/z (%): 451 (72) [M^+], 420 (7), 276 (15), 245 (19), 175 (100), 150 (13), 119 (18), 111 (46), 63 (11).
IR (KBr): $\tilde{n}$ = 3093 (m), 1726 (vs), 1588 (m), 1568 (w), 1474 (m), 1436 (m), 1390 (vs), 1282 (vs), 1248 (s), 1209 (s), 1180 (vs), 1114 (m), 1093 (s), 1036 (s), 910 (w), 884 (m), 869 (s), 829 (s), 734 (s), 660 (s), 608 (m), 577 (s), 482 (m).
HRMS for **$C_{14}H_{10}ClIO_5S$** (451.8982): found 451.8965.
$C_{14}H_{10}ClIO_5S$: calc.: C: 37.15; H: 2.23; S: 7.08; found: C: 36.95; H: 2.26; S: 7.32.

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



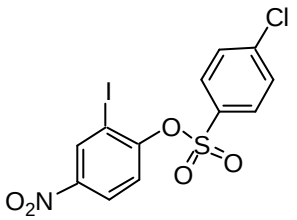
Prepared according to **TP 1** from methyl 4-hydroxy-3,5-diiodobenzoate (1.62 g, 4.0 mmol), 4-chlorobenzenesulfonyl chloride (1.16 g, 4.8 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **2h** as a colourless solid (2.21 g, 95 %).
mp.: 140-141 °C.
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d= 8.39 (s, 2H), 7.90 (d, ^3J(H,H) = 9 Hz, 2H), 7.52 (d, ^3J(H,H) = 9 Hz, 2H), 3.85 (s, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 163.3, 154.7, 141.9, 141.7, 136.4, 131.1, 130.5, 129.9, 89.2, 52.9.
MS (70 eV, EI): m/z (%): 578 (43) [M^+], 402 (27), 372 (20), 276 (21), 245 (29), 175 (100), 158 (12), 111 (33), 63 (9).
IR (KBr): $\tilde{n}$ = 3435 (m), 1716 (vs), 1584 (m), 1543 (m), 1478 (m), 1441 (m), 1397 (s), 1371 (vs), 1279 (vs), 1208 (vs), 1184 (vs), 1174 (vs), 1126 (m), 1095 (s), 1047 (m), 965 (w), 873 (s), 873 (s), 764 (s), 743 (s), 718 (s), 645 (m), 616 (s), 557 (m), 478 (m).
HRMS for **$C_{14}H_9ClI_2O_5S$** (577.7949): found 577.7953.
$C_{14}H_9ClI_2O_5S$: calc.: C: 29.06; H: 1.57; found: C: 29.29; H: 1.60.

Synthesis of 4-cyano-2-iodophenyl 4-chlorobenzenesulfonate (2i):



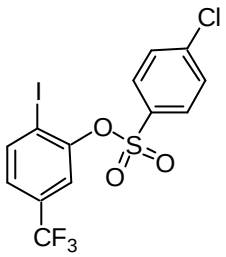
Prepared according to **TP 1** from 4-cyano-2-iodophenol (1.22 g, 5.0 mmol), 4-chlorobenzenesulfonyl chloride (1.27 g, 6.0 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **2i** as a colourless solid (1.60 g, 77 %).
mp.: 149-150 °C.
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.05 (d, ^{4}J(H,H) = 2 Hz, 1H), 7.86 (d, ^{3}J(H,H) = 9 Hz, 2H), 7.67 (dd, ^{3}J(H,H) = 8 Hz, ^{4}J(H,H) = 2 Hz, 1H), 7.53 (d, ^{3}J(H,H) = 9 Hz, 2H), 7.49 (d, ^{3}J(H,H) = 8 Hz, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 153.4, 144.0, 142.5, 134.2, 133.9, 130.6, 130.3, 123.8, 116.5, 113.1, 90.9.
MS (70 eV, EI): m/z (%): 418 (13) [M^+], 175 (100), 111 (79), 89 (6), 75 (28), 62 (11).
IR (KBr): $\tilde{n}$ = 3066 (m), 2229 (vs), 1587 (s), 1570 (s), 1477 (vs), 1399 (m), 1361 (vs), 1283 (m), 1214 (vs), 1181 (s), 1174 (s), 1155 (s), 1087 (vs), 1016 (m), 918 (m), 875 (vs), 833 (s), 825 (vs), 809 (vs), 759 (s), 704 (m), 665 (m), 640 (vs), 588 (m), 542 (s), 490 (m).
HRMS for **$C_{13}H_7ClINO_3S$** (418.8880): found 418.8871.
$C_{13}H_7ClINO_3S$: calc.: C: 37.21; H: 1.68; N: 3.34; found: C: 37.24; H: 1.68; N: 3.34.

Synthesis of 4-nitro-2-iodophenyl 4-chlorobenzenesulfonate (2j):



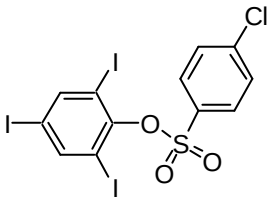
Prepared according to **TP 1** from 4-nitro-2-iodophenol (2.65 g, 10 mmol), 4-chlorobenzenesulfonyl chloride (2.54 g, 12 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **2j** as a pale yellow solid (3.99 g, 91 %).
mp.: 149-150 °C.
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.05 (d, ^{4}J(H,H) = 2 Hz, 1H), 7.86 (d, ^{3}J(H,H) = 9 Hz, 2H), 7.67 (dd, ^{3}J(H,H) = 8 Hz, ^{4}J(H,H) = 2 Hz, 1H), 7.53 (d, ^{3}J(H,H) = 9 Hz, 2H), 7.49 (d, ^{3}J(H,H) = 8 Hz, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 153.4, 144.0, 142.5, 134.2, 133.9, 130.6, 130.3, 123.8, 116.5, 113.1, 90.9.
MS (70 eV, EI): m/z (%): 439 (24) [M^+], 175 (100), 159 (4), 139 (6), 111 (79), 91 (2), 75 (22), 63 (19).
IR (KBr): $\tilde{n}$ = 3096 (m), 1584 (m), 1572 (m), 1523 (vs), 1476 (s), 1460 (s), 1398 (s), 1361 (vs), 1347 (vs), 1292 (m), 1250 (m), 1209 (vs), 1183 (s), 1173 (s), 1113 (m), 1087 (s), 1035 (m), 902 (m), 884 (vs), 845 (vs), 828 (s), 766 (vs), 754 (s), 737 (s), 710 (s), 652 (s), 615 (s), 548 (m), 483 (m).
HRMS for **$C_{13}H_7ClINO_3S$** (438.8778): found 438.8774.
$C_{13}H_7ClINO_3S$: calc.: C: 37.21; H: 1.68; N: 3.34; found: C: 37.24; H: 1.68; N: 3.34.

Synthesis of 2-iodo-5-(trifluoromethyl)phenyl 4-chlorobenzenesulfonate (2k):



Prepared according to **TP 1** from 2-iodo-5-(trifluormethyl)phenol (1.44 g, 5 mmol), 4-chlorobenzenesulfonyl chloride (1.27 g, 6 mmol). Reaction time: 12 h. Recrystallization from ethanol yielded **2k** as a colourless solid (2.10 g, 91 %).
mp.: 64.5-65.5 °C.
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.92 (d, ^{3}J(H,H) = 8 Hz, 1H), 7.88 (d, ^{3}J(H,H) = 8 Hz, 2H), 7.58-7.53 (m, 3H), 7.26-7.22 (m, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 150.0, 141.9, 140.9, 133.8, 133.1 (q, ^{3}J(C,F) = 33 Hz), 130.2, 129.8, 127,2 (q, ^{2}J(C,F) = 273 Hz), 126,4 (q, ^{4}J(C,F) = 4 Hz), 120.6 (q, ^{4}J(C,F) = 4 Hz), 94.8.
MS (70 eV, EI): m/z (%): 461 (17) [M^+], 297 (9), 175 (100), 160 (11), 132 (14), 111 (70), 75 (19), 63 (12).
IR (KBr): $\tilde{n}$ = 3098 (m), 1924 (w), 1605 (m), 1582 (w), 1477 (m), 1391 (vs), 1325 (vs), 1259 (m), 1199 (vs), 1174 (vs), 1123 (vs), 1024 (m), 916 (vs), 906 (s), 830 (m), 823 (m), 779 (vs), 757 (s), 714 (s), 656 (m), 619 (s), 555 (m), 485 (w), 475 (m).
HRMS for **$C_{13}H_7ClF_3IO_3S$** (461.8805): found 461.8800.
$C_{13}H_7ClF_3IO_3S$: calc.: C: 33.75; H: 1.53; I: 27.43; found: C: 33.78; H: 1.64; I: 27.27.

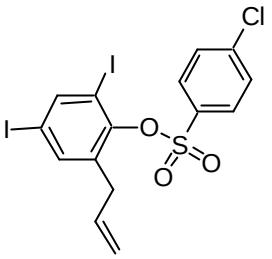
Synthesis of 4-chloro-benzenesulfonic acid 2,4,6-triiodophenyl ester:



Preparation according to **TP 1** from 2,4,6-triiodophenol (9.436 g, 20.0 mmol) yielded 4-chloro-benzenesulfonic acid 2,4,6-triiodophenyl ester (11.64 g, 90 %) as white solid (mp.: 123.8 – 124.7 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.10 (s, 2 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 151.59, 148.26, 141.54, 136.27, 130.38, 129.67, 93.13, 91.65.
IR (KBr): ?/cm^{-1} = 3085 (w), 3042 (w), 1916 (w), 1734 (w), 1636 (w), 1585 (m), 1533 (m), 1477 (m), 1409 (s), 1400 (s), 1383 (s), 1282 (w), 1210 (s), 1176 (s), 1092 (m), 1042 (m), 1016 (m), 967 (w), 855 (s), 830 (m), 761 (s), 739 (s), 714 (s), 700 (m), 632 (m), 618 (s), 565 (s), 516 (w), 481 (m), 471 (m).

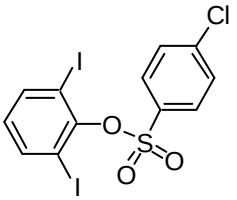
MS (EI, 70 eV): m/z (%) = 648 (12), 646 (M^+, 34), 472 (10), 471 (100), 344 (22), 189 (17), 177 (10), 175 (28), 111 (15), 62 (14).
HR-MS: ($C_{12}H_6ClI_3O_3S$) calculated 645.6860 found: 645.6842

Synthesis of 4-chloro-benzenesulfonic acid 2-allyl-4,6-diiodo-phenyl ester (2l):



A dry and argon-flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 2,4,6-triiodo-phenyl ester (5.17 g, 8.0 mmol) in dry THF (15.0 mL). *i*PrMgCl (1.07 M/THF, 8.2 mL, 1.1 equiv.) was then added dropwise at –78 °C. After 30 minutes, CuCN·2LiCl (1.0 M/THF, 8.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 min. Then allyl bromide (1.36 mL, 16.0 mmol, 2.0 equiv.) was added at –78°C, and the resulting mixture was warmed to room temperature and stirred for 1 hour. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 250: 1) yielded **2l** (3.770 g, 84 %) as colorless oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.00-7.94 (m, 3 H), 7.60-7.54 (m, 3 H), 5.92-5.76 (m, 1 H), 5.21-5.10 (m, 2 H), 3.54-3.47 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 148.80, 145.94, 141.35, 139.96, 138.32, 135.56, 134.40, 130.14, 129.56, 118.13, 92.90, 92.11, 35.44.
IR (film): ?/cm^{-1} = 3089 (m), 2978 (w), 2920 (w), 2563 (w), 1913 (w), 1731 (w), 1639 (m), 1589 (m), 1569 (m), 1540 (m), 1477 (m), 1425 (s), 1383 (s), 1282 (m), 1246 (w), 1204 (s), 1184 (s), 1127 (s), 1084 (s), 1014 (m), 995 (m), 923 (m), 862 (s), 835 (s), 765 (s), 723 (s), 675 (w), 645 (m), 625 (s), 568 (s), 522 (w), 481 (m).
MS (EI, 70 eV): m/z (%) = 562 (6), 560 (M^+, 17), 386 (18), 385 (94), 258 (100), 257 (37), 175 (12), 159 (12), 131 (32), 111 (20), 77 (23), 76 (10), 75 (17).
HR-MS: ($C_{15}H_{11}ClI_2O_3S$) calculated 559.8207 found: 559.8246

Synthesis of 4-chloro-benzenesulfonic acid 2,6-diiodo-phenyl ester (2m):



Preparation according to **TP 1** from 2,6-diiodophenol (2.422 g, 7.0 mmol) [3], pyridine (5 mL), 4-chloro-benzenesulfonyl chloride (1.773 g, 8.4 mmol) yielded 4-chloro-benzenesulfonic acid 2,6-diiodo-phenyl ester (3.352 g, 92 %) as white solid (mp.: 127.4 – 127.8 °C).

^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.00-7.94 (m, 2 H), 7.16 (d, *J* = 7.96 Hz, 2 H), 7.60-7.54 (m, 2 H), 6.67 (t, *J* = 7.96 Hz, 1 H).

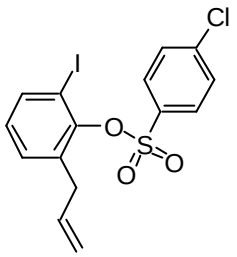
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 151.32, 141.34, 140.82, 136.53, 130.41, 129.75, 129.60, 90.60.

IR (KBr): ?/cm^{-1} = 3088 (w), 1929 (w), 1638 (w), 1586 (w), 1572 (w), 1556 (w), 1476 (w), 1431 (w), 1408 (m), 1388 (s), 1282 (w), 1210 (m), 1179 (s), 1092 (m), 1066 (w), 1037 (w), 1014 (w), 855 (s), 833 (w), 828 (w), 775 (m), 763 (s), 741 (m), 706 (m), 690 (m), 623 (m), 610 (m), 561 (m), 480 (w), 459 (w).

MS (EI, 70 eV): m/z (%) = 522 (20), 520 (M^+, 55), 345 (48), 317 (12), 218 (60), 190 (10), 177 (38), 175 (100), 159 (16), 113 (17), 111 (54), 75 (27), 63 (56), 62 (15).

HR-MS: ($C_{12}H_7ClI_2O_3S$) calculated 519.7894 found: 519.7848

Synthesis of 4-chloro-benzenesulfonic acid 2-allyl-6-iodo-phenyl ester (2m):



A dry and argon-flushed 10 mL Schlenk tube, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 2,6-diiodo-phenyl ester (520 mg, 1.0 mmol) in dry THF (5 mL). *i*PrMgCl (0.92 M/THF, 1.2 mL, 1.1 equiv.) was added dropwise at –78 °C. After 30 min, CuCN·2LiCl (1.0 M/THF, 1.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 min. Then, allyl bromide (0.17 mL, 2.0 mmol, 2.0 equiv.) was added at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 h. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 200 : 1) yielded **2m** (406 mg, 93 %) as colorless oil.

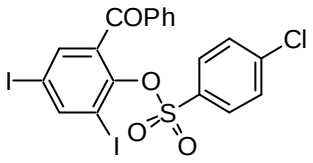
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.00-7.93 (m, 2 H), 7.63 (dd, *J* = 7.96, 1.77 Hz, 1 H), 7.57-7.51 (m, 2 H), 7.25 (d, *J* = 7.96 Hz, 1 H), 6.92 (t, *J* = 7.96 Hz, 1 H), 5.93-5.78 (m, 1 H), 5.15-5.06 (m, 2 H), 3.57-3.52 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): d = 148.62, 141.11, 138.48, 136.43, 135.84, 135.20, 131.12, 130.15, 129.46, 128.63, 117.32, 90.75, 35.75.

IR (film): ?/cm^{-1} = 3090 (w), 2979 (w), 2918 (w), 1639 (w), 1586 (m), 1478 (m), 1452 (w), 1427 (s), 1398 (m), 1380 (s), 1281 (w), 1202 (s), 1186 (s), 1163 (m), 1112 (w), 1091 (s), 1070 (m), 1015 (m), 995 (w), 921 (m), 865 (s), 829 (s), 765 (s), 713 (s), 698 (m), 648 (s), 624 (m), 562 (s), 482 (m).

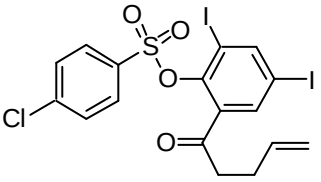
MS (EI, 70 eV): m/z (%) = 436 (4), 434 (M^+, 11), 259 (35), 258 (13), 257 (14), 175 (15), 133 (10), 132 (100), 131 (50), 111 (19), 104 (23), 103 (17), 78 (11), 77 (15).
HR-MS: ($C_{15}H_{12}ClIO_3S$) calculated 433.9240 found: 433.9205

Synthesis of 4-chloro-benzenesulfonic acid 2-benzoyl-4,6-diiodo-phenyl ester (2n):



A dry and argon-flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 2,4,6-triiodo-phenyl ester (5.171 g, 8.0 mmol) in dry THF (15.0 mL). *i*PrMgCl (1.07 M/THF, 8.2 mL, 1.1 equiv.) was then added dropwise at –78 °C. After 30 min, CuCN·2LiCl (1.0 M/THF, 8.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 min. Then benzoyl chloride (1.86 mL, 16.0 mmol, 2.0 equiv.) was added at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 h. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 80 : 1) yielded **2n** (2.646 g, 53 %) as white solid (mp.: 184.2 – 185.1 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.33 (d, *J* = 2.21 Hz, 1 H), 7.77 (d, *J* = 2.21 Hz, 1 H), 7.72-7.67 (m, 2 H), 7.64-7.57 (m, 3 H), 7.49-7.41 (m, 2 H), 7.40-7.34 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): 190.78, 150.24, 146.81, 141.49, 139.42, 136.10, 135.48, 133.97, 133.69, 130.21, 129.95, 129.47, 128.40, 94.42, 92.46.
IR (KBr): ?/cm^{-1} = 3088 (w), 3064 (w), 1908 (w), 1668 (s), 1593 (m), 1536 (m), 1477 (m), 1448 (m), 1420 (m), 1399 (m), 1384 (s), 1315 (w), 1274 (s), 1245 (m), 1211 (s), 1184 (s), 1121 (m), 1084 (s), 1014 (w), 950 (m), 898 (w), 858 (s), 826 (m), 804 (w), 778 (s), 760 (m), 729 (m), 707 (s), 652 (s), 618 (s), 565 (s), 521 (w), 510 (w), 482 (m), 472 (w).
MS (EI, 70 eV): m/z (%) = 624 (M^+, 2), 450 (29), 449 (100), 448 (31), 323 (9), 322 (38), 195 (11), 175 (12), 139 (15), 111 (14), 105 (18), 77 (27).
HR-MS: ($C_{19}H_{11}ClI_2O_4S$) calculated 623.8156 found: 623.8199

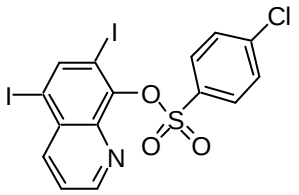
Synthesis of 4-chloro-benzenesulfonic acid 2-(pent-4-enoyl)-4,6-diiodo-phenyl ester (2o):



A dry and argon-flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 2,4,6-triiodo-phenyl ester (1.939 g, 3.0 mmol) in dry THF (10 mL). *i*PrMgCl (0.92 M/THF, 3.6 mL, 3.3 equiv.)

was then added dropwise at –78 °C. After 30 min, CuCN·2LiCl (1.0 M/THF, 3.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 min. Then pent-4-enoyl chloride [3] (6.0 mmol, 2.0 equiv.) in THF was added at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 h. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 50 : 1) yielded **2o** (1.139 g, 63 %) as yellow solid (mp.: 151.5 – 152.4 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.22-8.16 (m, 1 H), 7.86-7.76 (m, 3 H), 7.59-7.49 (m, 2 H), 5.91-5.75 (m, 1 H), 5.10-4.95 (m, 2 H), 3.04-2.94 (m, 2 H), 2.48-2.37 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 198.30, 150.13, 146.09, 142.03, 138.38, 137.77, 136.64, 133.73, 130.40, 129.82, 115.59, 93.68, 92.85, 40.90, 27.94.
IR (KBr): ?/cm^{-1} = 3087 (w), 3062 (w), 3044 (w), 1918 (w), 1856 (w), 1774 (w), 1703 (s), 1640 (m), 1585 (m), 1567 (m), 1537 (m), 1478 (m), 1449 (w), 1416 (s), 1400 (m), 1381 (m), 1352 (s), 1286 (m), 1270 (m), 1202 (s), 1178 (s), 1145 (s), 1085 (s), 1055 (w), 1014 (m), 1000 (m), 929 (m), 879 (m), 855 (s), 836 (m), 822 (m), 811 (m), 783 (m), 768 (s), 753 (s), 723 (s), 692 (w), 650 (m), 608 (m), 595 (m), 558 (s), 509 (m), 480 (m).
MS (EI, 70 eV): m/z (%) = 602 (M^+, 3), 549 (11), 547 (23), 427 (64), 426 (14), 410 (75), 374 (10), 373 (100), 372 (22), 300 (14), 218 (12), 189 (10), 177 (15), 175 (47), 113 (12), 111 (35), 55 (17).
HR-MS: ($C_{17}H_{13}ClI_2O_4S$) calculated 601.8313 found: 601.8302

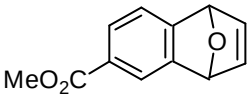
Synthesis of 4-chloro-benzenesulfonic acid 5,7-diiodo-quinolin-8-yl ester (2p):



Preparation according to **TP 1** from 5,7-diiodo-quinolin-8-ol (7.939 g, 20 mmol) yielded **2p** (9.488 g, 83 %) as pale green solid (mp.: 140.8 – 141.6 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.70-8.64 (m, 1 H), 8.49 (s, 1 H), 8.33-8.26 (m, 1 H), 8.06-7.97 (m, 2 H), 7.58-7.44 (m, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 151.26, 149.41, 145.46, 141.96, 140.70, 140.44, 136.63, 131.07, 130.31, 129.08, 123.79, 97.05, 92.87.
IR (KBr): ?/cm^{-1} = 3087 (w), 1917 (w), 1586 (m), 1569 (m), 1546 (m), 1470 (m), 1443 (m), 1397 (m), 1378 (s), 1341 (m), 1282 (w), 1233 (w), 1208 (m), 1188 (s), 1173 (s), 1131 (w), 1090 (m), 1059 (s), 1040 (m), 1015 (m), 914 (w), 867 (w), 851 (w), 836 (m), 826 (m), 795 (s), 786 (s), 754 (m), 706 (m), 693 (m), 673 (m), 632 (m), 621 (m), 596 (w), 585 (m), 545 (w), 521 (m), 481 (m).
Anal. Calcd for $C_{15}H_8ClI_2NO_3S$: C, 31.52; H, 1.41; N, 2.45; S, 5.61. **Found:** C, 31.71; H, 1.39; N, 2.45; S, 5.87.

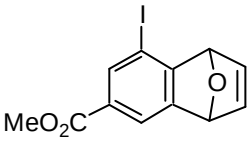
Typical procedure of generation and trapping of functionalized arynes (TP 2):
A dry and argon-flushed 10 mL Schlenk tube, equipped with a magnetic stirrer and a septum, was charged with a solution of the corresponding arylsulfonates (0.5 mmol) in dry THF (3 mL). *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) was then added dropwise at –78 °C. After 30 minutes, furan (0.18 mL, 5 equiv.) was added slowly at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 hour. Saturated aqueous NH_4Cl solution was then added, and then the resulting mixture was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography furnished the products.

Synthesis of 1,4-dihydro-7-methoxycarbonyl-1,4-epoxynaphthalin (4a):



Prepared according to **TP 2** from methyl 4-{[(4-chlorophenyl)sulfonyl]oxy}-3-iodobenzoate (452 mg, 1 mmol), *i*PrMgCl (1.2 mL, 1.1 mmol, 0.9 M in THF) and furan (304 mg, 5 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded **4a** as a colourless solid (188 mg, 93%).
mp.: 99.5-101 °C.
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.85 (d, ^4J(H,H) = 1 Hz, 1H), 7.75 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 1 Hz, 1H), 7.29 (d, ^4J(H,H) = 1 Hz, 1H), 7.05-6.98 (m, 2H), 5.74-5.72 (m, 2H), 3.80 (s, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 167.9, 154.8, 149.5, 143.3, 141.4, 128.1, 127.3, 120.7, 119.9, 82.6, 82.5, 52.0.
MS (70 eV, EI): m/z (%): 202 (11) [M^+], 176 (33), 174 (40), 171 (28), 146 (27), 143 (36), 129 (20), 115 (100), 89 (9), 75 (3), 63 (7).
IR (KBr): $\tilde{n}$ = 3014 (m), 1727 (vs), 1569 (m), 1453 (m), 1429 (m), 1275 (vs), 1244 (s), 1216 (m), 1191 (m), 1132 (s), 1072 (m), 994 (m), 976 (m), 901 (m), 876 (m), 854 (s), 829 (s), 791 (m), 769 (s), 725 (s), 675 (m), 645 (m).
HRMS for **$C_{12}H_{10}O_3$** (202,0630): found 202,0629.
$C_{11}H_7NO$: calc.: C: 71.28; H: 4.98; found: C: 71.23; H: 4.98.

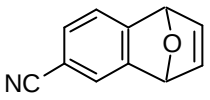
Synthesis of 1,4-dihydro-7-methoxycarbonyl-5-iodo-1,4-epoxynaphthalin (4b)



Prepared according to **TP 2** from methyl 4-{[(4-chlorophenyl)sulfonyl]oxy}-3,5-diiodobenzoate (578 mg, 1 mmol), *i*PrMgCl (1.2 mL, 1.1 mmol, 0.9 M in THF) and furan (304 mg, 5 mmol). Reaction time: 5h. Purification by flash chromatography (pentane/diethyl ether = 3:1) yielded **4b** as a colourless solid (231 mg, 71 %).
mp.: 121.0-122.0 °C.
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.02 (d, ^4J(H,H) = 1 Hz, 1H), 7.77 (m, 1H), 7.08-7.06 (m, 2H), 5.87 (m, 1H), 5.65 (m, 1H), 3.87 (s, 3H).

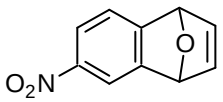
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 165.5, 159.8, 151.3, 143.8, 141.9, 136.5, 129.3, 120.1, 86.0, 85.5, 82.4, 52.4.
MS (70 eV, EI): m/z (%): 327 (15) [M^+], 301 (29), 270 (17), 240 (35), 173 (100), 142 (25), 129 (17), 114 (40), 102 (5),87 (11), 74 (7), 63 (13).
IR (KBr): $\tilde{n}$ = 3010 (m), 1724 (vs), 1571 (m), 1454 (m), 1431 (m), 1375 (m), 1274 (vs), 1234 (m), 1218 (m), 1193 (m), 1175 (m), 1163 (m), 1131 (s), 1073 (m), 993 (m), 976 (m), 898 (m), 872 (m), 855 (s), 794 (m), 766 (s), 715 (s), 672 (m), 645 (m).
HRMS for **$C_{12}H_9IO_3$** (327.9596): found: 327.9605.

Synthesis of 1,4-dihydro-7-cyano-1,4-epoxynaphthalin (4c):



Prepared according to **TP 2** from 4-cyano-2-iodophenyl 4-chlorobenzenesulfonate (419 mg, 1 mmol), *i*PrMgCl (1.2 mL, 1.1 mmol, 0.9 M in THF) and furan (304 mg, 5 mmol). Reaction time: 8 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded product **4c** as a colourless solid (132 mg, 78 %).
mp.: 97.0-98.5 °C.
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): d = 7.45 (s, 1H), 7.35-7.33 (m, 2H), 7.05-7.01 (m, 2H), 5.76-5.72 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): d= 154.6, 150.5, 143.1, 142.5, 130.9, 122.8, 120.6, 119.1, 108.8, 82.1, 81.9.
MS (70 eV, EI): m/z (%): 169 (20) [M^+], 141 (100), 114 (47), 88 (10), 75 (7), 63 (16).
IR (KBr): $\tilde{n}$ = 2225 (vs), 1455 (m), 1418 (m), 1277 (s), 1200 (w), 1072 (w), 992 (s), 863 (vs), 852 (s), 842 (vs), 746 (m), 705 (s), 645 (m), 614 (s), 577 (w).
HRMS for **$C_{11}H_7NO$** (169,0528): found 169.0515.
$C_{11}H_7NO$: calc.: C: 78.09; H: 4.17; N: 8.28; found: C: 77.89; H: 4.07; N: 8.32.

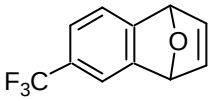
Synthesis of 1,4-dihydro-7-nitro-1,4-epoxynaphthalin (4d):



Prepared according to **TP 2** from 2-iodo-4-nitrophenyl 4-chlorobenzenesulfonate (439 mg, 1 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF) and furan (304 mg, 5 mmol). Reaction time: 12 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded product **4d** as a pale yellow solid (147 mg, 78 %).
mp.: 104.0-105.5 °C.
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.03 (d, ^4J(H,H) = 2 Hz, 1H), 7.95 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H), 7.35 (d, ^4J(H,H) = 8 Hz, 1H), 7.10-7.02 (m, 2H), 5.80-5.78 (m, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 156.8, 151.7, 146.2, 143.8, 143.5, 142.7, 122.7, 120.5, 115.6, 82.4.
MS (70 eV, EI): m/z (%): 189 (7) [M^+], 163 (18), 144 (16), 115 (100), 89 (18), 77 (4), 64 (11), 51 (3).

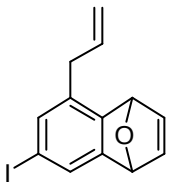
IR (KBr): $\tilde{n}$ = 3434 (w), 1614 (w), 1603 (m), 1543 (m), 1518 (vs), 1445 (m), 1380 (w), 1363 (m), 1340 (vs), 1317 (s), 1301 (m), 1277 (s), 1198 (m), 1172 (m), 1140 (s), 1056 (s), 988 (s), 869 (s), 849 (vs), 749 (s), 753 (s), 734 (m), 700 (vs), 673 (m), 642 (s), 568 (m), 543 (m).
HRMS for **$C_{10}H_7NO_3$** (189.0426): found: 189.0430
$C_{10}H_7NO_3$: calc.: C: 63.49; H: 3.73; N: 7.40; found: C: XX; H: 3.73; N: 7.40;

Synthesis of 1,4-dihydro-7-trifluoromethyl-1,4-epoxynaphthalin (4e):



Prepared according to **TP 2** from 2-iodo-5-(trifluoromethyl)phenyl 4-chlorobenzenesulfonate (463 mg, 1 mmol), *i*PrMgCl (1.6 mL, 1.1 mmol, 0.7 M in THF) and furan (304 mg, 5 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded **4e** as a colourless oil (159 mg, 75 %).
^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): d = 7.45 (s, 1H), 7.32-7.27 (m, 2H), 7.06-7.02 (m, 2H), 5.75-5.72 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): d = 153.3, 150.3, 143.1, 142.7, 127.6 (q, ^3J(C,F) = 30 Hz), 123.2 (q, ^2J(C,F) = 272 Hz), 122.9 (q, ^4J(C,F) = 4 Hz), 119.9, 116.9 (q, ^4J(C,F) = 4 Hz), 82.1, 77.5.
MS (70 eV, EI): m/z (%): 212 (10) [M^+], 199 (38), 184 (100), 164 (22), 151 (13), 13 (23), 115 (72), 107 (4), 88 (5), 75 (4), 63 (6).
IR (KBr): $\tilde{n}$ = 1427 (w), 1355 (m), 1321 (vs), 1275 (s), 1164 (s), 1121 (vs), 1049 (s), 994 (m), 871 (m), 851 (s), 837 (s), 750 (w), 698 (m), 636 /m), 543 (w).
HRMS for **$C_{11}H_7F_3O$** (212.0449): found 212.0461.

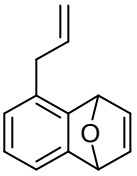
Synthesis of 5-allyl-1,4-dihydro-1,4-epoxy-7-iodonaphthalene (4f):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 2-allyl-4,6-diiodo-phenyl ester **2l** (280 mg, 0.5 mmol), *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) and furan (0.18 mL, 5 equiv.). Purification by flash chromatography (*n*-pentane : CH_2Cl_2 : ether = 200 : 50 : 1) yielded **4f** (137 mg, 88 %) as colorless oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 7.46 (s, 1 H), 7.16 (d, *J* = 1.3 Hz, 1 H), 6.98 (m, 2 H), 5.95-5.81 (m, 1 H), 5.78-5.76 (m, 1 H), 5.67-5.65 (m, 1 H), 5.14-4.96 (m, 2 H), 3.44-3.24 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 151.56, 148.05, 142.64, 142.61, 136.08, 134.69, 134.08, 127.47, 116.59, 90.21, 81.82, 80.72, 36.92.
IR (film): ?/cm^{-1} = 3074 (w), 3016 (w), 2974 (w), 2910 (w), 1839 (w), 1723 (w), 1634 (m), 1607 (w), 1589 (m), 1560 (w), 1435 (m), 1406 (w), 1392 (w), 1331 (w), 1278 (m), 1220 (w), 1174 (w), 1134 (w), 1074 (w), 1012 (m), 962 (w), 942 (w), 919 (m), 890 (w),

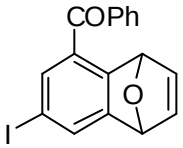
855 (s), 830 (s), 801 (m), 726 (m), 690 (w), 654 (w), 641 (m), 591 (w), 579 (m), 554 (w).
MS (EI, 70 eV): m/z (%) = 310 (M^+, 77), 282 (10), 281 (10), 241 (19), 165 (12), 156 (13), 155 (100), 154 (24), 153 (41), 152 (18), 129 (19), 128 (19), 127 (12).
HR-MS: ($C_{13}H_{11}OI$) calculated 309.9855 found: 309.9843

Synthesis of 5-allyl-1,4-dihydro-1,4-epoxynaphthalene (4g):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 2-allyl-6-iodo-phenyl ester **2m** (217 mg, 0.5 mmol), *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) and furan (0.18 mL, 5 equiv.). Purification by flash chromatography (*n*-pentane : CH_2Cl_2 : ether = 200 : 50 : 1) yielded **4g** (78 mg, 83 %) as colorless oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 7.17-7.10 (m, 1 H), 7.05-6.98 (m, 2 H), 6.96-6.90 (m, 1 H), 6.82-6.76 (m, 1 H), 6.02-5.86 (m, 1 H), 5.83 (bs, 1 H), 5.71 (bs, 1 H), 5.12-4.96 (m, 2 H), 3.52-3.32 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 148.80, 147.77, 143.03, 142.57, 136.96, 132.00, 126.02, 125.16, 118.34, 115.93, 82.28, 80.85, 37.34.
IR (film): ?/cm^{-1} = 3078 (m), 3055 (m), 3010 (m), 2977 (w), 1638 (m), 1610 (w), 1486 (w), 1470 (m), 1435 (m), 1420 (m), 1376 (m), 1280 (s), 1192 (m), 1180 (m), 1159 (w), 1081 (w), 1018 (m), 995 (m), 965 (w), 917 (m), 872 (s), 857 (s), 831 (s), 778 (s), 751 (s), 724 (s), 693 (m), 646 (m), 620 (w), 590 (w), 567 (m), 556 (m).
MS (EI, 70 eV): m/z (%) = 184 (M^+, 20), 165 (9), 156 (36), 155 (51), 154 (9), 153 (22), 152 (12), 141 (43), 129 (38), 128 (42), 127 (16), 116 (10), 115 (100), 77 (8).
HR-MS: ($C_{13}H_{12}O$) calculated 184.0888 found: 184.0910

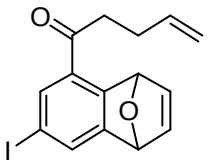
Synthesis of 5-benzoyl-1,4-dihydro-1,4-epoxy-7-iodonaphthalene (4h):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 2-benzoyl-4,6-diiodo-phenyl ester **2n** (312 mg, 0.5 mmol), *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) and furan (0.18 mL, 5 equiv.). Purification by flash chromatography (*n*-pentane : ether = 40 : 1) yielded **4h** (128 mg, 68 %) as pale yellow oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 7.80-7.71 (m, 3 H), 7.67-7.47 (m, 4 H), 7.14-7.08 (m, 1 H), 7.05-7.00 (m, 1 H), 5.83-5.80 (m, 1 H), 5.74-5.70 (m, 1 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 194.32, 152.92, 151.84, 143.05, 142.79, 136.93, 134.08, 133.16, 132.78, 131.98, 129.83, 128.61, 89.33, 82.25, 81.37.
IR (film): ?/cm^{-1} = 3060 (w), 2966 (w), 1657 (s), 1597 (m), 1448 (m), 1425 (w), 1381 (w), 1327 (m), 1271 (s), 1240 (w), 1198 (w), 1173 (m), 1088 (w), 1040 (m), 1023 (m),

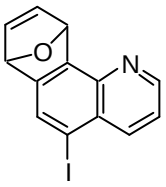
866 (s), 853 (s), 811 (w), 754 (w), 725 (m), 716 (m), 695 (w), 676 (w), 641 (w), 662 (w), 625 (w), 579 (w), 549 (w).
MS (EI, 70 eV): m/z (%) = 374 (M^+, 13), 361 (12), 348 (23), 347 (11), 346 (53), 345 (69), 323 (8), 320 (9), 269 (12), 241 (12), 220 (19), 219 (100), 218 (57), 217 (8), 202 (18), 201 (9), 193 (21), 191 (29), 190 (32), 189 (86), 165 (44), 164 (12), 163 (15), 155 (92), 147 (20), 114 (25), 113 (22), 105 (90), 77 (59), 51 (12).
HR-MS: ($C_{17}H_{11}IO_2$) calculated 373.9804 found: 373.9825

Synthesis of 5-(pent-4-enoyl)-1,4-dihydro-1,4-epoxy-7-iodonaphthalene (4i):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 2-(pent-4-enoyl)-6-iodo-phenyl ester **2o** (301 mg, 0.5 mmol), *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) and furan (0.18 mL, 5 equiv.). Purification by flash chromatography (*n*-pentane : ether = 20 : 1) yielded **4i** (125 mg, 71 %) as yellow oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 7.73 (s, 1 H), 7.68 (s, 1 H), 7.12-7.06 (m, 1 H), 7.01-6.95 (m, 1 H), 6.30 (bs, 1 H), 5.95-5.79 (m, 1 H), 5.66 (bs, 1 H), 5.13-4.97 (m, 2 H), 3.03-2.93 (m, 2 H), 2.52-2.40 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 198.36, 153.23, 151.40, 143.03, 142.84, 136.73, 132.59, 132.43, 132.40, 115.56, 89.79, 82.55, 80.85, 38.25, 27.58.
IR (film): ?/cm^{-1} = 3076 (w), 3010 (w), 2977 (w), 2918 (w), 1685 (s), 1641 (w), 1588 (m), 1435 (w), 1410 (w), 1385 (w), 1322 (w), 1277 (m), 1243 (w), 1212 (m), 1175 (w), 1145 (w), 1097 (m), 1064 (m), 997 (w), 915 (m), 856 (s), 804 (w), 736 (w), 702 (w), 644 (m), 587 (w), 568 (w).
MS (EI, 70 eV): m/z (%) = 352 (M^+, 9), 324 (11), 297 (23), 296 (9), 285 (31), 271 (14), 270 (16), 269 (100), 268 (50), 241 (36), 181 (9), 155 (11), 153 (10), 142 (11), 128 (17), 116 (15), 115 (30), 114 (40), 113 (23), 88 (11), 63 (13), 59 (12), 55 (19).
HR-MS: ($C_{15}H_{13}IO_2$) calculated 351.9960 found: 351.9927

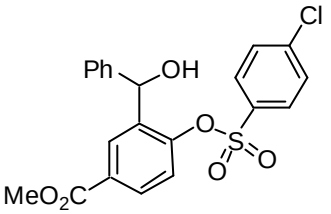
Synthesis of 5-iodo-7,10-dihydro-7,10-epoxy-benzo[h]quinoline (4j):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 5,7-diiodo-quinolin-8-yl ester **2p** (571 mg, 1.0 mmol), *i*PrMgCl (0.47 mL, 1.01 equiv., 1.07 M in THF) and furan (0.18 mL, 5 equiv.). Purification by flash chromatography (*n*-pentane : ether = 4 : 1) yielded **4j** (248 mg, 77 %) as yellow solid (mp.: 138.0 – 139.0 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.82-8.77 (m, 1 H), 8.33-8.27 (m, 1 H), 8.13 (s, 1 H), 7.35-7.25 (m, 2 H), 7.17-7.13 (m, 1 H), 6.52-6.48 (m, 1 H), 5.91-5.88 (m, 1 H).

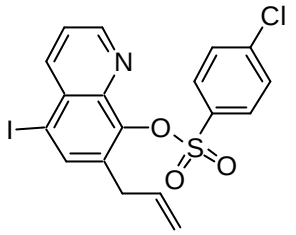
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 154.34, 151.46, 150.56, 144.08, 144.05, 142.19, 140.62, 130.98, 127.88, 122.16, 94.91, 82.76, 81.20.
IR (KBr): ?/cm^{-1} = 3068 (w), 3016 (w), 2926 (w), 1635 (w), 1602 (m), 1558 (w), 1502 (m), 1440 (w), 1385 (w), 1327 (w), 1278 (w), 1240 (w), 1185 (w), 1139 (w), 1089 (w), 1052 (w), 1013 (m), 964 (w), 932 (w), 896 (m), 865 (s), 835 (m), 803 (w), 778 (m), 727 (m), 696 (w), 677 (w), 638 (w), 627 (m), 544 (w).
MS (EI, 70 eV): m/z (%) = 321 (M^+, 27), 295 (55), 294 (12), 293 (95), 281 (10), 207 (22), 183 (11), 168 (11), 167 (22), 166 (100), 165 (28), 164 (26), 140 (40), 139 (26), 138 (14), 116 (10), 113 (10), 75 (10), 73 (13), 63 (14), 59 (13), 55 (15), 41 (13).
HR-MS: ($C_{13}H_8INO$) calculated 320.9651 found: 320.9621

Synthesis of methyl 4-{[(4-chlorophenyl)sulfonyl]oxy}-3-[hydroxy(phenyl)methyl]benzoate (5)



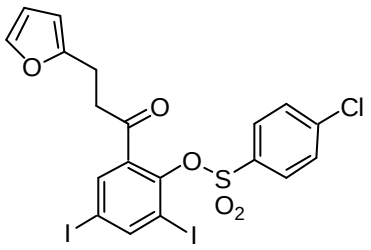
A dry and argon-flushed 25 mL Schlenk tube, equipped with a magnetic stirrer and a septum, was charged with methyl 4-{[(4-chlorophenyl)sulfonyl]oxy}-3-iodobenzoate **2g** (452 mg, 1 mmol) and dry THF was added. The solution was cooled to –78 °C and *i*PrMgCl (1.2 mL, 1.1 mmol, 0.9 M in THF) was added dropwise. After 30 min benzaldehyde (212 mg, 2 mmol) was added at –78 °C, and the resulting mixture was stirred at this temperature for 1 h. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded **5** as a colourless solid (410 mg, 95 %).
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.26 (d, ^4J(H,H) = 2 Hz, 1H), 7.92 (dd, ^3J(H,H) = 8 Hz, ^4J(H,H) = 2 Hz, 1H), 7.77 (d, ^3J(H,H) = 9 Hz, 2H), 7.51 (d, ^3J(H,H) = 9 Hz, 2H), 7.34-7.28 (m, 5H), 7.12 (d, ^3J(H,H) = 8 Hz, 1H), 5.98 (s, 1H), 3.90 (s, 3H), 2.5 (s_br, 1OH).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 166.2, 150.2, 142.2, 142.0, 137.7, 134.1, 130.8, 130.7, 130.2, 129.8, 128.9, 128.2, 126.9, 121.8, 112.9, 70.3, 52.7.
MS (70 eV, EI): m/z (%): 432 (1) [M^+], 401 (3), 257 (100), 239 (27), 209 (3), 179 (25), 159 (4), 111 (7), 77 (5), 51 (3).
IR (KBr): $\tilde{n}$ = 3470 (s), 1708 (vs), 1606 (m), 1587 (m), 1478 (w), 1458 (m), 1439 (s), 1398 (m), 1378 (vs), 1290 (vs), 1258 (s), 1195 (s), 1186 (vs), 1171 (s), 1125 (m), 1086 (s), 1043 (m), 1027 (w), 1015 (m), 907 (m), 856 (vs), 839 (s), 781 (vs), 764 (s), 741 (m), 712 (m), 702 (s), 650 (m), 616 (s), 600 (m), 590 (m), 556 (m), 486 (w).
HRMS for **$C_{21}H_{17}ClO_6S$** (432.0431): found 432.0418.
$C_{21}H_{17}ClO_6S$: calc.: C: 58.27; H: 3.96; S: 7.41; found: C: 58.62; H: 4.24; S: 7.60.

Synthesis of 4-chloro-benzenesulfonic acid 7-allyl-5-iodo-quinolin-8-yl ester (6):



A dry and argon-flushed 10 mL Schlenk tube, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 5,7-diiodo-quinolin-8-yl ester **2p** (571 mg, 1.0 mmol) in dry THF (5 mL). *i*PrMgCl (0.92 M/THF, 1.20 mL, 1.1 equiv.) was then added dropwise at –78 °C. After 30 min, CuCN·2LiCl (1.0 M/THF, 1.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 min. Then allyl bromide (0.17 mL, 2.0 mmol, 2.0 equiv.) was added at -78°C, and the resulting mixture was warmed to room temperature and stirred for 1 h. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 200 : 1) yielded **6** (394 mg, 81%) as white solid (mp.: 118.6 – 119.6 °C).
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.59-8.53 (m, 1 H), 8.29-8.21 (m, 1 H), 8.09-8.00 (m, 3 H), 7.56-7.46 (m, 2 H), 7.42-7.34 (m, 1 H), 6.06-5.89 (m, 1 H), 5.26-5.15 (m, 2 H), 3.76-3.67 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 150.66, 144.36, 142.10, 140.45, 140.02, 139.12, 136.23, 135.69, 134.49, 130.24, 129.84, 128.88, 122.81, 117.97, 96.43, 34.47.
IR (KBr): ?/cm^{-1} = 3088 (w), 2977 (w), 1638 (w), 1609 (w), 1590 (m), 1575 (w), 1552 (w), 1477 (m), 1456 (w), 1379 (s), 1350 (m), 1298 (w), 1285 (m), 1236 (w), 1225 (m), 1202 (m), 1187 (s), 1179 (s), 1142 (m), 1089 (s), 1069 (s), 1044 (w), 1014 (m), 992 (m), 927 (m), 895 (w), 883 (w), 835 (m), 812 (m), 793 (s), 754 (m), 712 (m), 700 (w), 671 (w), 659 (m), 623 (s), 603 (m), 584 (m), 530 (m), 480 (m).
Anal. Calcd for $C_{18}H_{13}ClINO_3S$: C, 44.51; H, 2.70; N, 2.88; S, 6.60. **Found:** C, 44.66; H, 2.73; N, 2.84; S, 6.50.

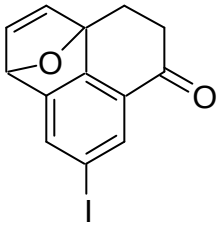
Synthesis of 4-chloro-benzenesulfonic acid 2-(3-furan-2-yl-propionyl)-4,6-diiodo-phenyl ester (2q):



A dry and argon-flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with a solution of 4-chloro-benzenesulfonic acid 2,4,6-triiodo-phenyl ester (1.939 g, 3.0 mmol) in dry THF (10 mL). *i*-PrMgCl (0.92 M/THF, 3.6 mL, 3.3 equiv.)

was then added dropwise at –78 °C. After 30 minutes, CuCN·2LiCl (1.0 M/THF, 3.0 mL, 1.0 equiv.) was added slowly at –78 °C, and the resulting mixture was stirred at this temperature for 10 minutes. Then 3-furan-2-yl-propionyl chloride [4] (6.0 mmol, 2.0 equiv.) in THF was added at –78 °C, and the resulting mixture was warmed to room temperature and stirred for 1 hour. Thereafter, the reaction was quenched with saturated aqueous NH_4Cl solution; the mixture was then poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 40 mL). The organic fractions were dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (*n*-pentane : ether = 200 : 1) yielded **2q** (1.287 g, 65 %) as yellow oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 8.20 (d, *J* = 2.21 Hz, 1 H), 7.84 (t, *J* = 2.21 Hz, 1 H), 7.81 (t, *J* = 2.21 Hz, 1 H), 7.79 (d, *J* = 2.21 Hz, 1 H), 7.57 (t, *J* = 2.21 Hz, 1 H), 7.54 (t, *J* = 2.21 Hz, 1 H), 7.29 (dd, *J* = 2.21 Hz, 0.89 Hz, 1 H), 6.27 (dd, *J* = 3.10 Hz, 2.21 Hz, 1 H), 6.03 (dd, *J* = 3.10 Hz, 0.89 Hz, 1 H), 3.28-3.21 (m, 2 H), 3.08-3.01 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 197.8, 154.0, 150.3, 146.1, 142.1, 141.2, 138.4, 137.5, 133.7, 130.5, 129.9, 110.3, 105.6, 93.8, 92.8, 40.1, 22.6.
IR (KBr): ?/cm^{-1} = 2924 (w), 1700 (m), 1633 (m), 1416 (w), 1386 (m), 1206 (m), 1176 (m), 1148 (m), 1087 (m), 1013 (w), 860 (w), 830 (w), 767 (m), 722 (m), 623 (w), 566 (w).
MS (EI, 70 eV): m/z (%) = 642 (M^+, 2), 516 (2), 468 (41), 467 (21), 450 (60), 374 (10), 373 (100), 342 (11), 341 (10), 324 (10), 247 (33), 218 (12), 114 (10), 112 (34), 111 (10), 95 (51), 94 (21).
HR-MS: ($C_{19}H_{13}ClI_2O_5S$) calculated 641.8262 found: 641.8279

Synthesis of 8-iodo-2,3,3a,6-tetrahydro-3a,6-epoxy-1*H*-phenalen-1-one (7):



Preparation according to **TP 2** from 4-chloro-benzenesulfonic acid 2-(3-furan-2-yl-propionyl)-4,6-diiodo-phenyl ester **2q** (400 mg, 0.62 mmol) and *i*-PrMgCl (0.79 mL, 1.01 equiv., 0.79 M in THF). Purification by flash chromatography (*n*-pentane : ether = 50 : 1) yielded **7** (98 mg, 48 %) as brown oil.
^{1}H-NMR ($CDCl_3$, 300 MHz): d = 7.75 (d, *J* = 0.89 Hz, 1 H), 7.71 (d, *J* = 0.89 Hz, 1 H), 7.16-7.08 (m, 2 H), 5.74 (d, *J* = 1.77 Hz, 1 H), 2.95-2.52 (m, 4 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 194.2, 156.0, 151.8, 144.6, 141.5, 133.6, 129.0, 128.4, 91.1, 86.1, 82.2, 36.1, 26.3.
IR (film): ?/cm^{-1} = 3073 (w), 2957 (m), 2873 (w), 2249 (w), 1689 (s), 1588 (m), 1570 (w), 1453 (w), 1416 (m), 1337 (s), 1302 (m), 1277 (w), 1252 (s), 1217 (m), 1179 (m), 1088 (s), 1058 (w), 998 (m), 963 (m), 946 (m), 902 (m), 868 (s), 834 (w), 808 (m), 762 (w), 728 (s), 705 (m), 677 (m), 646 (m), 598 (m), 554 (m).
MS (EI, 70 eV): m/z (%) = 325 (11), 324 (M^+, 100), 323 (12), 168 (11), 141 (10), 139 (14).
HR-MS: ($C_{13}H_9IO_2$) calculated 323.9647 found: 323.9645

References and Notes:

[1] H.-S. Lin, L. A. Paquette, *Synth. Commun.* **1994**, *24*, 2503.
[2] R. C. Cambie, P. S. Rutledge, T. Smith-Palmer, P. D. Woodgate, *J. C. S., Perkin Trans 1* **1976,** *11*, 1161.
[3] A solution containing 0.6 mL (6.0 mmol) of 4-pentenoic acid in 20 mL of CH_2Cl_2 was treated dropwise with oxalyl chloride (1.0 mL, 12.0 mmol). The mixture was stirred at room temperature for 12 h, and the solvent and the excess amount of oxalyl chloride was removed under reduced pressure. The resulting 4-pentenoyl chloride was dissolve in a 5 mL of THF and was used without further purification.
[4] Padwa, A.; Wisnieff, T. J.; Walsh E. J.*J. Org. Chem.* **1989,** *54*, 299-308.