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Supporting Information

Gold-Catalyzed Synthesis of Chromanes, Dihydrobenzofurans, Dihydroindoles and Tetrahydroquinolines

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[+] Crystallographic investigation

Experimental Section

General methods: Chemicals (Aldrich, Fluka, Lancaster, and Merck) were used without further purification. Diethyl ether and tetrahydrofuran were dried over sodium. Complex **21**[1] was prepared according to published procedures. NMR spectra were recorded on Bruker AVANCE 500, AVANCE 300 and AVANCE 250 spectrometers. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ^{13}C assignment was achieved via DEPT 90 and DEPT 135 spectra. MS spectra were recorded on a Finnigan MAT 90 a Varian 711 or a micrOTOF-Q spektometer. IR spectra were recorded on a Bruker Vector 22.

General procedure 1 (GP 1): Trichloroethylen addition to alcohols:[2]

1.5 Equivalents NaH were dissolved in THF. Over a period of 20 minutes 1 equivalent of alcohol in THF was added drop by drop. After 30 minutes the solution was cooled to –78 °C and 1.2 equivalents of trichloroethylene were added. After removal of the cooling bath the mixture was stirred for 16 h. The reaction was quenched with water, extracted with DCM or pentane and washed with brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure 2 (GP 2): Preparation of trimethylsilyl-protected ynamides:[3]

1 Equivalent of tosylamide was dissolved in toluene. 1.05 equivalents of *n*-BuLi were added at 0 °C and the solution was stirred for 1 h. After 1.3 equivalents of trimethylsilylethynylphenyliodonium triflate[4] were added the mixture was stirred for 1-3 d at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure 3 (GP 3): Deprotection of trimethylsilyl-protected ynamides:[3]

1 Equivalent of silyl protected ynamide was dissolved in THF. After the addition of 2.5 equivalents of TBAF at 0 °C the reaction was stirred for 5 min and quenched with a saturated NH_4Cl solution. The aqueous layer was extracted with ethyl acetate and the combined organic phases were dried over $MgSO_4$. After filtration and removal of the solvent the products were gained as pure compounds.

General procedure 4 (GP 4): Preparation of dichlorovinylamides:[5]

1 Equivalent alcohol, 1.2 equivalents of *N*-formyl-toluenesulfonamide and 1.3-1.5 equivalents of PPH_3 were dissolved in THF and 1.3-1.5 equivalents of DIAD were added at 0 °C. The mixture was stirred for 16 h at room temperature. After removal of the solvent the mixture was purified by a short flash column chromatography (petroleum ether/ethyl acetate) to obtain a mixture of *N*- and *O*-alkylated products. These were dissolved in THF and 2-3 equivalents of PPh_3 were added. After the temperature was allowed to raise to 60 °C, 10 equivalents of CCl_4 were added over a period of 3-6 h and the mixture was stirred for 16-48 h. After cooling to 20 °C saturated $NaHCO_3$-solution was added and and the mixture was extracted three times with diethyl ether. The combined organic phases were dried over $MgSO_4$, filtered, the solvent removed in vacuo and the residue was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure 5 (GP 5): Preparation of ynamides by chloride elimination of dichlorovinylamides:[5]

1 Equivalent of dichlorovinylamide was dissolved in THF and cooled to –78 °C. After the addition of 2.3 equivalents of *n*-BuLi (1.6 M in hexane) the solution was stirred for 5-30 min. The reaction was monitored by TLC. After complete conversion MeOH was added. After addition of brine, the mixture was extracted with diethyl ether dried over $MgSO_4$, filtered and purified by column chromatography

(petroleum ether/ethyl acetate/ triethylamine) after removal of the solvent.

General procedure 6 (GP 6): Gold catalysis:
In a NMR tube 1 equivalent of starting material was dissolved in 600 µL of the corresponding deuterated solvent. Then 3-5 mol% of the catalyst precursor was added and the reaction was monitored by ^{1}H NMR. After completion the solvent was removed under reduced pressure and the product was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure 7 (GP 7): Preparation of alkynylethers and subsequent gold catalyzed reaction (method A):
1 Equivalent of dichlorovinylether was dissolved in diethyl ether and cooled to –78 °C. After the addition of 2 equivalents of *t*-BuLi (1.7 M in pentane) the solution was stirred for 10 min and then quenched with MeOH. After warming to rt, water was added and the mixture was extracted three times with diethyl ether and the aqueous phase was dried over $MgSO_4$. After filtration and evaporation of the solvent the alkynylether was directly used for gold catalysis. Therefor it was redissolved in $CDCl_3$ and 3 mol% of $AuCl_3$ were added. After complete conversion the solvent was removed and the product was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure 8 (GP 8): Preparation of alkynylethers[5] and subsequent gold catalyzed reaction (method B):
1 Equivalent of dichlorovinylether and 2 equivalents of TMEDA were dissolved in diethyl ether and cooled to –78 °C. After the addition of 2 equivalents *n*-BuLi (1.6 M in hexane) the mixture was stirred for 30 min at –78 °C and for another 30 min at –40 °C. After the addition of ethanol at –78 °C and water at rt, the mixture was extracted three times with diethyl ether and dried over $MgSO_4$. After filtration and evaporation of the solvent the alkynylether was directly used for gold catalysis. Therefore it was redissolved in CD_3CN and 5 mol% of $AuCl_3$ were added. After

complete conversion the solvent was removed and the product was purified by column chromatography (petroleum ether/ethyl acetate).

3-(5-Methylfuran-2-yl)-propan-1-ol (18c):

3.00 g (36.5 mmol) 2-methylfuran were dissolved in 30 ml THF. After the addition of 15.3 ml (24.4 mmol, 1.6 M in *n*-hexane) *n*-BuLi at 0 °C, the mixture was stirred for 2 h at room temperature. After cooling to –78 °C, 1.60 ml (24.4 mmol) oxetan were added. After 5 min 3.1 ml (24.4 mmol) boron trifluoride etherate were slowly added and the mixture was warmed to room temperature within 30 min 10 ml $NaHCO_3$ solution were added and the mixture was neutralized with 2N HCl. The solution was extracted with Et_2O and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. Column chromatography on silica gel (pentane/ ethyl acetate, 10:1) afforded 2.20 g (15.6 mmol, 64%) of **18c** as a yellow oil.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.33 (s, 1 H), 1.89 (tt, *J* = 7.4 Hz, 6.3 Hz, 2 H), 2.25 (dd, *J* = 1.0 Hz, 0.4 Hz, 3 H), 2.68 (t, *J* = 7.4 Hz, 2 H), 3.70 (t, *J* = 6.3 Hz, 2 H), 5.84 (m, 1 H), 5.88 (m, 1 H). Spectroscopic data confirmed by ref. [7].

2-(2-[(1,2-Dichloroethenyl)oxy]hexyl)furan (23a):

As described in **GP 1**, 32.8 mg (1.43 mmol) NaH, 160 mg (0.95 mmol) 1-furan-2-ylhexan-2-ol **16a**[8] and 180 µl (1.14 mmol) trichloroethylen in 10 ml THF furnished 198 mg (752 µmol, 79%) **23a**, after purification by column chromatography (petroleum ether) as a colorless oil.

R_f (PE) = 0.34 IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2933, 2359, 2340, 1630, 1278, 1091, 827. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.90 (t, *J* = 7.3 Hz, 3 H), 1.25-1.51 (m, 4 H), 1.58-1.71 (m, 2 H), 2.91 (dd, *J* = 15.3 Hz, 6.8 Hz, 1 H), 3.04 (dd, *J* = 15.3 Hz, 5.9 Hz, 1 H), 4.55-4.60 (m, 1 H), 5.49 (s, 1 H), 6.14 (dd, *J* = 3.4 Hz, 0.8 Hz, 1 H), 6.30 (dd, *J* = 3.4 Hz, 1.8 Hz, 1 H), 7.33 (dd, *J* = 1.8 Hz, 0.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.12 (q), 22.73 (t), 27.11 (t), 32.73 (t), 33.16 (t), 80.76 (d), 98.15 (d), 107.58 (d), 110.57 (d), 141.68

(d), 142.93 (s), 151.44 (s). MS (EI(+)): *m/z (%):* 262 $[M]^+$, 151 (39), 107 (8), 81 (100), 41 (10). HRMS (EI(+)): $C_{12}H_{16}Cl_2O_2$: calcd 262.0527; found, 262.0527.

2-(2-[(1,2-Dichloroethenyl)oxy]ethyl)-5-methylfuran (23b):
As described in **GP 1**, 475 mg (11.9 mmol) NaH, 1.00 g (7.93 mmol) 2-(5-methylfuran-2-yl)ethanol[8] **16b**, 854 µl (9.52 mmol) trichloroethylen in 20 ml THF furnished 1.40 g (6.33 mmol, 80%) **23b**, after purification by column chromatography (petroleum ether/ethyl acetate, 100:1) as a yellow oil.
R_f (PE:EE, 10:1) = 0.66. IR (film): $\tilde{\nu}$ = 3107 cm^{-1}, 2954, 2922, 1628, 1571, 1276, 1217, 1095, 1020, 893, 826, 782, 631. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 3.01 (t, *J* = 7.2 Hz, 2 H), 4.23 (t, *J* = 7.2 Hz, 2 H), 5.52 (s, 1 H), 5.87 (d, *J* = 2.9 Hz, 1 H), 6.02 (d, *J* = 2.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.51 (q), 28.13 (t), 69.75 (t), 98.19 (d), 106.12 (d), 107.49 (d), 143.41 (s), 149.06 (s), 151.13 (s). $C_9H_{10}Cl_2O_2$ (220.01): calcd C 48.89, H 4.60; found C 48.79 H 4.56. MS (FAB(+)): *m/z (%):* 220 (5) $[M]^+$, 109 (100), 95 (15), 43 (26).

2-(2-[(1,2-Dichloroethenyl)oxypropyl)-5-methylfuran (23c):
As described in **GP 1**, 145 mg (6.30 mmol) NaH, 593 mg (4.20 mmol) **16c**, 452 µl (5.00 mmol) trichloroethylen in 20 ml THF furnished 655 mg (2.77 mmol, 66%) **23c**, after purification by column chromatography (petroleum ether/ethyl acetate, 100:1) as a yellow oil.
R_f (PE:EE, 10:1) = 0.60. IR (film): $\tilde{\nu}$ = 1740 cm^{-1}, 1627, 1570, 1437, 1274, 1218, 1095, 1019, 829, 720. ^1H-NMR ($CDCl_3$, 500 MHz): δ = 2.02 (tt, *J* = 7.8 Hz, 6.2 Hz, 2 H), 2.25 (s, 3 H), 2.76 (t, *J* = 7.8 Hz, 2 H), 4.05 (t, *J* = 6.2 Hz, 2 H), 5.51 (s, 1 H), 5.85 (d, *J* = 2.9 Hz, 1 H), 5.91(d, *J* = 2.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.52 (q), 24.33 (t), 27.53 (t), 70.98 (t), 97.82 (d), 105.86 (d), 106.14 (d), 143.71 (s), 150.64 (s), 152.78 (s). MS (FAB(+)): *m/z (%):* 234 (18) $[M-H]^+$, 199 (7), 151 (16), 123 (36), 95 (100), 43

(37). $C_{10}H_{12}Cl_2O_2$ (235.11): calcd C 51.09, H 5.14; found C 51.18, H 5.25.

2-[3-(1,2-Dichloroethenyloxy)butyl]furan (23d):

As described in **GP 1**, 257 mg (10.7 mmol) NaH, 1.00 g (7.13 mmol) 4-furan-2-yl-butan-2-ol[11] **16d**, 770 µl (8.56 mmol) trichloroethylen in 30 ml THF furnished 1.26 g (5.35 mmol, 75%) **23d**, after purification by column chromatography (petroleum ether) as a clear liquid.

R_f (PE) = 0.25. IR (neat): $\tilde{\nu}$ = 3107 cm^{-1}, 2977, 2853, 1654, 1625, 1598, 1507, 1448, 1381, 1337, 1274, 1145, 1088, 1077, 1050, 1007, 922, 825, 728, 642, 621. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.31 (d, *J* = 6.3 Hz, 3 H), 1.88-1.99 (m, 1 H), 2.02-2.11 (m, 1 H), 2.76-2.92 (m, 2 H), 4.37-4.48 (m, 1 H), 5.55 (s, 1 H), 6.02 (dd, *J* = 3.1 Hz, 0.8 Hz, 1 H), 6.28 (dd, *J* = 3.1 Hz, 1.9 Hz, 1 H), 7.31 (dd, *J* = 1.9 Hz, 0.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 19.31 (q), 23.78 (t), 34.13 (t), 77.82 (d), 98.61 (d), 105.23 (d), 110.15 (d), 141.07 (d), 142.70 (s), 155.03 (s). MS (EI(+)): *m/z (%):* 411 (100) $[M]^+$, 234 (0.1), 123 (15), 81 (100), 53 (10). $C_{10}H_{12}Cl_2O_2$ (235.11): calcd C 51.09, H 5.14; found C 50.96, H 5.27.

1,2-Dichlor-1-decyloxyethen (23e):

As described in **GP 1**, 219 mg (9.50 mmol) NaH, 1.00 g (6.32 mmol) decanol, 680 µl (7.58 mmol) trichloroethylen in 20 ml THF furnished 1.12 g (4.42 mmol, 70%) **23e**, after purification by column chromatography (petroleum ether) as a clear liquid.

R_f (PE) = 0.46. IR (film): $\tilde{\nu}$ = 2923 cm^{-1}, 2853, 1627, 1466, 1273, 1084, 826. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.22-1.36 (m, 12 H), 1.38-1.47 (m, 2 H), 1.66-1.72 (m, 2 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 5.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.34 (q), 22.91 (t), 25.89 (t), 29.08 (t), 29.42 (t), 29.52 (t), 29.71 (t), 29.73 (t), 32.11 (t), 72.34 (t), 97.72 (d), 144.04 (s). MS (EI(+)): *m/z (%):* 254 $[M+H]^+$, 141 (10), 85 (51), 71 (51), 57 (100), 43 (77), 41 (22), 29 (10). $C_{12}H_{22}Cl_2O$ (253.21): calcd C 56.92, H 8.76; found C 56.82, H 8.96.

***tert*-Butyl[3-(5-methylfuran-2-yl)propyl][(4-methylphenyl)sulfonyl]carbamate (28a):**

1.49 g (5.49 mmol) *N*-*t*-butoxycarbonyl-*p*-toluenesulfonamide[10], 700 mg (4.99 mmol) **18c** and 1.70 g (6.50 mmol) PPh_3 were dissolved in 30 ml THF. After the addition of 1.28 ml (6.50 mmol) DIAD at 0 °C, the mixture was stirred for 16 h at room temperature. Purification by column chromatography (petroleum ether/ ethyl acetate, 20:1) furnished 1.71 g (4.35 mmol, 87%) **28a** as a yellow solid.

Mp.: 75 °C. R_f (PE:EE, 10:1) = 0.23. IR (film): $\tilde{\nu}$ = 2978 cm^{-1}, 1724, 1597, 1570, 1454, 1351, 1284, 1215, 1151, 1106, 1084, 1038, 1006, 968, 956, 842, 813, 802, 768, 745, 715, 703, 596. ^1H NMR ($CDCl_3$, 250 MHz): d = 1.33 (s, 9 H), 2.03-2.15 (m, 2 H), 2.26 (s, 3 H), 2.44 (s, 3 H), 2.65 (t, *J* = 7.6 Hz, 2 H), 3.85-3.89 (m, 2 H), 5.85 (d, *J* = 2.9 Hz, 1 H), 5.93 (d, *J* = 2.9 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 7.80 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 63 MHz): d = 13.55 (q), 21.63 (q), 25.38 (t), 27.89 (q, 3 C), 28.55 (t), 46.71 (t), 84.14 (s), 105.71 (d), 105.88 (d), 127.85 (d, 2 C), 129.26 (d, 2 C), 137.45 (s), 144.07 (s), 150.44 (s), 150.96 (s), 153.05 (s). MS (EI (+)): *m/z* (%): 393 (100) $[M]^+$, 338 (86), 337 (86), 320 (81), 293 (75), 250 (64), 227 (58), 210 (53), 184 (47), 182 (46), 155 (39), 138 (35), 121 (31), 109 (28), 91 (23), 79 (20), 65 (17), 57 (15), 41 (10). HRMS (EI (+)): $C_{20}H_{27}NO_5S$: calcd 393.1610, found 393.1607.

***tert*-Butyl-(3-furan-2-yl)-1-methylpropyl][(4-methylphenyl)sulfonyl]carbamate (28b):**

1.49 g (5.49 mmol) *N*-*t*-butoxycarbonyl-*p*-toluenesulfonamide[10], 700 mg (4.99 mmol) 4-furan-2-yl-butan-2-ol[11] **18d** and 1.70 g (6.50 mmol) PPh_3 were dissolved in 30 ml THF. After the addition of 1.28 ml (6.50 mmol) DIAD at 0 °C, the mixture was stirred for 16 h at room temperature. Purification by column chromatography (petroleum ether/ ethyl acetate, 20:1) furnished 1.66 g (4.22 mmol, 85%) **28b** as a yellow solid.

Mp.: 72 °C. R_f (PE:EE, 10:1) = 0.23. IR (film): $\tilde{\nu}$ = 2982 cm^{-1}, 1725, 1598, 1449, 1348, 1273, 1145, 1087, 1037, 989, 941, 842,

814, 750, 666, 593. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.37 (s, 9 H), 1.47 (t, *J* = 6.9 Hz, 3 H), 2.01-2.08 (m, 1 H), 2.27-2.35 (m, 1 H), 2.43 (s, 3 H), 2.61-2.71 (m, 2 H), 4.58-4.65 (m, 1 H), 6.03 (dd, *J* = 3.2, 0.8 Hz, 1 H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 7.31 (dd, *J* = 1.9, 0.8 Hz, 1 H), 7.77 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 19.73 (q), 21.62 (q), 25.60 (t), 27.99 (q, 3C), 33.28 (t), 54.86 (d), 84.11 (s), 105.14 (d), 110.19 (d), 127.85 (d, 2C), 129.25 (d, 2 C), 137.84 (s), 140.96 (d), 143.88 (s), 150.80 (s), 155.13 (s). MS (ESI (+)): *m/z (%):* 416 (100) $[M+Na]^+$, 809 $[2M+Na]^+$ (8). HRMS (ESI (+)): $C_{20}H_{27}NNaO_5S$: calcd 416.1502; found 416.1493.

4-Methyl-*N*-[3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (24e):[12]

1.71 g (11.7 mmol) NaI were dissolved in 30 ml acetonitrile. After the addition of 1.46 ml (11.4 mmol) TMSCl at 0 °C the mixture was stirred for 45 min. 1.50 g (3.81 mmol) **28a** were added and the reaction was stirred for 1.5 h at room temperature. 5 ml MeOH and 20 ml H_2O were added and the mixture was extracted with DCM, dried over $MgSO_4$, filtered and purified by column chromatography (petroleum ether/ ethyl acetate, 7:1) to furnish 826 mg (2.82 mmol, 74%) **24e** as a yellow solid.

Mp.: 52 °C. R_f (PE:EE, 10:1) = 0.07. IR (film): $\tilde{\nu}$ = 3265 cm^{-1}, 2921, 1597, 1569, 1426, 1311, 1237, 1217, 1190, 1147, 1084, 1016, 974, 942, 887, 815, 775, 705, 669, 609, 576. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.77 (m, 2 H), 2.21 (s, 3 H), 2.43 (s, 3 H), 2.56 (t, *J* = 7.0 Hz, 2 H), 2.95-2.99 (m, 2 H), 4.58 (t, *J* = 6.2 Hz, 1 H), 5.80 (m, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.5 (q), 21.54 (q), 25.02 (t), 28.21 (t), 42.55 (t), 105.90 (d), 106.12 (d), 127.11 (d, 2 C), 129.72 (d, 2 C), 136.97 (s), 143.40 (s), 150.62 (s), 152.62 (s). MS (EI (+)): *m/z (%):* 293 (77) $[M]^+$, 155 (13), 138 (50), 122 (35), 109 (100), 95 (49), 91 (39), 65 (8). HRMS (EI (+)):$C_{15}H_{19}NO_3S$: calcd 293.1086; found 293.1087.

***N*-(3-Furan-2-yl-1-methyl-1-propyl)-4-methylbenzenesulfonamide (24g):**[12]

1.71 g (11.7 mmol) NaI were dissolved in 30 ml acetonitrile. After the addition of 1.46 ml (11.4 mmol) TMSCl at 0 °C the mixture was stirred for 45 min. 1.50 g (3.81 mmol) **28b** were added and the reaction was stirred for 2 h at room temperature. 5 ml MeOH and 20 ml H_2O were added and the mixture was extracted with DCM, dried over $MgSO_4$, filtered and purified by column chromatography (petroleum ether/ ethyl acetate, 7:1) to furnish 300 mg (1.07 mmol, 28%) **24g** as a yellow solid.

Mp.: 106 °C. R_f (PE:EE, 7:1) = 0.07. IR (film): $\tilde{\nu}$ = 3267 cm^{-1}, 1595, 1429, 1305, 1154, 1086, 1039, 995, 937, 813, 756, 661, 582. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.03 (d, *J* = 6.6 Hz, 3 H), 1.65-1.75 (m, 2 H), 2.42 (s, 3 H), 2.52-2.66 (m, 2 H), 3.30-3.37 (m, 1 H), 4.62 (d, *J* = 8.4 Hz, 1 H), 5.89 (dd, *J* = 3.2 Hz, 0.8 Hz, 1 H), 6.24 (dd, *J* = 3.2 Hz, 1.9 Hz, 1 H), 7.25 (dd, *J* = 1.9 Hz, 0.8 Hz, 1 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.65 (q), 21.74 (q), 24.34 (t), 36.76 (t), 49.62 (d), 105.24 (d), 110.25 (d), 127.16 (d, 2 C),129.79 (d, 2 C), 138.21 (s), 141.03 (d), 143.38 (s), 155.04 (s). MS (ESI (+)): *m/z (%):* 316 (100) $[M+Na]^+$, 294 $[M+H]^+$ (5). $C_{15}H_{19}NO_3S$ (293.38): calcd C 61.41, H 6.53, N 4.77; found C 61.25, H 6.58, N 4.69.

4-Methyl-*N*-[1-methyl-3-(5-methylfuran-2-yl)propyl)benzenesulfonamide (24f):

2.00 g (13.1 mmol) 4-(5-methylfuran-2-yl)butan-2-one[13], 2.25 g (13.1 mmol) tosylamide and 5 ml (35.2 mmol) NEt_3 were dissolved in 100 ml DCM. After cooling to 0 °C, 0.62 ml (5.60 mmol) $TiCl_4$ dissolved in 10 ml DCM were added and the mixture was stirred for 16 h at room temperature. Water was added, the solution was extracted with DCM and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure, the residue was redissolved in 20 ml MeOH and 496 mg (13.1 mmol) $NaBH_4$ were added at 0 °C. The mixture was stirred for 2 h at room temperature. After the addition of 20 ml H_2O, the solution was extracted with

DCM, dried over $MgSO_4$, filtered and and purified by column chromatography (petroleum ether/ ethyl acetate, 20:1) to furnish 945 mg (2.76 mmol, 21% over 2 steps) **24f** as a white solid.

Mp.: 95 °C. R_f (PE:EE, 10:1) = 0.08. IR (film): $\tilde{\nu}$ = 3255 cm^{-1}, 2967, 1567, 1568, 1429, 1312, 1216, 1152, 1135, 1081, 1041, 1024, 982, 944, 849, 824,799, 575. ^1H NMR ($CDCl_3$ 500 MHz): δ = 1.05 (d, *J* = 6.8 Hz, 3 H), 1.62-1.74 (m, 2 H), 2.23 (s, 3 H), 2.42 (s, 3 H), 2.45-2.59 (m, 2 H), 3.32-3.41 (m, 1 H), 4.26 (d, *J* = 8.2 Hz, 1 H), 5.76 (d, *J* = 3.0 Hz, 1 H), 5.80 (d, *J* = 3.0 Hz, 1 H), 7.29 (d, *J* = 8.3 Hz, 2 H) 7.74 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.63 (q), 21.68 (q), 21.98 (q), 24.44 (t), 35.98 (t), 49.73 (d), 105.79 (d), 105.86 (d), 127.06 (d, 2 C), 129.68 (d, 2 C), 138.27 (s), 143.39 (s), 150.59 (s), 153.12 (s). MS (ESI (+)): *m/z (%):* 330 (100) $[M+Na]^+$. $C_{16}H_{21}NO_3S$ (307.41): calcd C 62.76, H 6.96, N 4.11; found C 62.51, H 6.89, N 4.56.

4-Methyl-*N*-[(5-methylfuran-2-yl)ethyl][(trimethylsilyl) ethynyl]benzenesulfonamide (26a):

As described in **GP 2**, 500 mg (1.79 mmol) 4-methyl-*N*-[2-(5-methylfuran-2-yl)ethyl]benzenesulfonamide[14] **16a**, 1.20 ml (1.6 M in hexane, 1.87 mmol) *n*-BuLi and 1.05 g (2.33 mmol) trimethylsilylethynylphenyliodoniumtriflate in 20 ml toluene were reacted for 3 d. Purification by column chromatography (petroleum ether/ ethyl acetate, 40:1) afforded 437 mg (1.16 mmol, 65%) **26a** as a yellow liquid.

R_f (PE:EE, 3:1): 0.36. IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2167, 1597, 1367, 1249, 1170, 1091, 844, 760, 712, 663, 638. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.01 (s, 9 H), 2.06 (s, 3 H), 2.29 (s, 3 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 3.40 (t, *J* = 7.6 Hz, 2 H), 5.66 (m, 1 H), 5.74 (d, *J* = 3.0 Hz, 1 H), 7.14-7.17 (m, 2 H), 7.59-7.61 (m, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 0.03 (q, 3 C), 13.45 (q), 21.57 (q), 26.91 (t), 49.69 (t),73.53 (s), 94.45 (s), 105.98 (d), 107.42 (d), 127.66 (d, 2C), 129.51 (d, 2 C), 134.40 (s), 144.49 (s), 149.33 (s), 150.98 (s). MS (EI (+)): m/z (%): 376 (8) $[MH]^+$, 360 (11), 332 (13), 311 (12), 280 (19), 220 (51), 155 (23), 147 (100), 108 (48),

95 (87), 73 (53), 43 (23). $C_{19}H_{25}NO_3SSi$ (375.13): calcd C 60.76, H 6.71, N 3.73; found C 60.83, H 6.69, N 3.78.

***N*-(2-Furan-2-ylethyl)-4-methyl-*N*-[(trimethylsilyl)ethynyl]benzenesulfonamide (26b):**

As described in **GP 2**, 1.40 g (5.28 mmol) *N*-(2-furan-2-ylethyl)-4-methylbenzenesulfonamide **24b**, 3.30 ml (1.6 M in hexane, 5.28 mmol) *n*-BuLi and 3.09 g (6.86 mmol) trimethylsilylethynylphenyliodoniumtriflate in 30 ml toluene were reacted for 16h. Purification by column chromatography (petroleum ether/ ethyl acetate, 30:1) afforded 1.24 g (3.42 mmol, 65%) **26b** as a yellow liquid.

R_f (PE:EE, 20:1) = 0.23. IR (oil): $\tilde{\nu}$ = 2960 cm^{-1}, 2163, 1597, 1397, 1248, 1169, 1090, 1010, 977, 842, 813, 732, 708, 661, 632. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.16 (s, 9 H), 2.45 (s, 3 H), 2.96 (t, *J* = 7.6 Hz, 2 H), 3.59 (t, *J* = 7.6 Hz, 2 H), 6.04 (dd, *J* = 3.3, 0.7 Hz, 1 H), 6.26 (dd, *J* = 3.3 H, 1.8 Hz, 1 H), 7.29 (dd, *J* = 3.3, 0.7 Hz, 1 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 0.26 (q, 3 C), 21.79 (q), 27.10 (t), 49.84 (t), 73.80 (s), 94.64 (s), 107.00 (d), 110.46 (d), 127.90 (d, 2C), 129.77 (d, 2 C), 134.63 (s), 141.69 (d), 144.79 (s), 151.40 (s). MS (ESI (+)): *m/z (%):* 384 (84) $[M+Na]^+$. HRMS (ESI (+)): $C_{18}H_{23}NNaO_3SSi$: calcd 384.1060; found 384.1051.

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl][(trimethylsilyl)ethynyl]benzenesulfonamide (26c):

As described in **GP 2**, 800 mg (3.02 mmol) 4-methyl-*N*-(5-methylfuran-2-ylmethyl)benzenesulfonamide[15] **24c**, 2.00 ml (1.6 M in hexanes, 3.20 mmol) *n*-BuLi and 1.77 g (3.93 mmol) trimethylsilylethynylphenyliodoniumtriflate in 30 ml toluene were reacted for 16h. Purification by column chromatography (petroleum ether/ ethyl acetate, 30:1) afforded 473 mg (1.31 mmol, 43%) **26c** as a yellow solid.

Mp.: 29 °C. R_f (PE:EE, 20:1) = 0.19. IR (neat): $\tilde{\nu}$ = 2962 cm^{-1}, 2169, 1597, 1567, 1359, 1310, 1286, 1247, 1163, 1088, 968, 947, 917,

840, 814, 796, 763, 712, 655, 577. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.11 (s, 9 H), 2.14 (s, 3 H), 2.44 (s, 3 H), 4.48 (s, 2 H), 5.81 (d, *J* = 3.3 Hz, 1 H), 6.11 (d, *J* = 3.3 Hz, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 0.17 (q, 3 C), 13.58 (q), 21.78 (q), 48.36 (t), 74.01 (s), 95.02 (s), 106.44 (d), 111.69 (d), 128.13 (d, 2 C), 129.45 (d, 2 C), 134.80 (s), 144.54 (s), 145.96 (s), 152.85 (s). MS (CI(+)): *m/z* (%): 360 (8) $[M-H]^+$, 325 (14), 308 (17), 189 (24), 152 (58), 110 (41), 95 (100). $C_{18}H_{23}NO_3SSi$ (361.53): calcd C 59.80, H 6.41, N 3.87; found C 59.80, H 6.40, N 3.79.

4-Methyl-*N*-nonylbenzenesulfonamide (24d):

500 mg (3.49 mmol) nonylamine, 740 µl (5.24 mmol) triethylamine and 4.26 mg (34.9 µmol) DMAP were dissolved in 30 ml DCM. After the addition of 732 mg (3.84 mmol) tosylchloride the solution was stirred for 4 h at room temperature. After the addition of water, the solution was twice extracted with DCM. The combined organic phases were dried over $MgSO_4$. After filtration, purification by column chromatography (petroleum ether/ ethyl acetate, 10:1) afforded 972 mg (3.27 mmol, 94%) 4-methyl-*N*-nonylbenzenesulfonamide **24d** as a white solid.

Mp.: 34 °C. *Rf* (PE:EE, 6:1) = 0.19. IR (film): $\tilde{\nu}$ = 3232 cm^{-1}, 2923, 2851, 1597, 1436, 1329, 1304, 1289, 1161, 1095, 1082, 1067, 903, 817, 667, 581. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.17-1.29 (m, 12 H), 1.41-1.46 (m, 2 H), 2.43 (s, 3 H), 2.92 (m, 2 H), 4.44 (t, *J* = 6.2 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 12.29 (q), 21.70 (q), 22.83 (t), 26.89 (t), 29.24 (t), 29.37 (t), 29.57 (t), 29.74 (t), 32.02 (t), 43.42 (t), 127.28 (d, 2 C), 129.87 (d, 2 C), 137.16 (s), 143.50 (s). MS (EI(+)): m/z (%): 297 $[M]^+$ (9), 184 (100), 172 (30), 155 (83), 142 (40), 91 (40). $C_{16}H_{27}NO_2S$ (297.46): calcd C 64.61, H 9.15, N 4.71; found C 64.64, H 9.05, N 4.71.

4-Methyl-*N*-nonyl-*N*-[(trimethylsilyl)ethynyl]benzenesulfonamide (26d):

As described in **GP 2**, 700 mg (2.35 mmol) 4-methyl-*N*-nonylbenzenesulfonamide **24d**, 1.54 ml (1.6 M in hexane, 2.47 mmol) *n*-BuLi and 1.38 g (3.06 mmol) trimethylsilylethynylphenyliodoniumtriflate in 15 ml toluene were reacted for 16 h. Purification by column chromatography (petroleum ether/ ethyl acetate, 50:1) afforded 443 mg (1.13 mmol, 48%) **26d** as a yellow solid.

Mp.: 20 °C. R_f (PE:EE, 20:1) = 0.25. IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2919, 2852, 2160, 1596, 1466, 1383, 1355, 1248, 1169, 1091, 1034, 1005, 993, 838, 813, 759, 730, 640, 568. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.15 (s, 9 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 1.21-1.30 (m, 12 H), 1.57-1.63 (m, 2 H), 2.45 (s, 3 H), 3.27 (t, *J* = 7.1 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 0.34 (q, 3 C), 14.32 (q), 21.86 (q), 22.86 (t), 26.40 (t), 27.90 (t), 29.27 (t), 29.40 (t), 29.61 (t), 32.07 (t), 51.47 (t), 73.26 (s), 95.33 (s), 127.96 (d, 2 C), 129.77 (d, 2 C), 134.76 (s), 144.69 (s). MS (EI(+)): *m/z (%):* 393 $[M]^+$, 378 (79), 314 (23), 286 (24), 273 (41), 252 (70), 238 (100), 224 (32), 200 (59), 186 (41), 168 (51), 155 (75), 149 (27), 112 (59), 91 (43), 73 (66), 43 (27). $C_{21}H_{35}NO_2SSi$ (393.66): calcd C 64.07, H 8.96, N 3.56; found C 64.17, H 8.98, N 3.50.

_N_-Ethynyl-4-methyl-_N_-[(5-methylfuran-2-yl)ethyl]benzolsulfonamid (27a):

As described in **GP 3**, 267 mg (711 µmol) protected ynamide **26a** and 557 mg (1.77 mmol) TBAF in 15 ml THF afforded 215 mg (709 mmol, 100%) of **27a** as an yellow oil.

R_f (PE:EE, 3:1): 0.43. IR (film): $\tilde{\nu}$ = 3287 cm^{-1}, 2921, 2134, 1596, 1570, 1452, 1364, 1214, 1168, 1091, 1020, 965, 785, 708, 686, 662, 642. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.04 (s, 3 H), 2.26 (s, 3 H), 2.58 (s, 1 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 3.39 (t, *J* = 7.6 Hz, 2 H), 5.64 (m, 1 H), 5.73 (d, *J* = 2.9 Hz, 1 H), 7.14-7.16 (m, 2 H), 7.59-7.61 (m, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.68 (q), 21.68 (q), 26.96 (t), 49.91 (t), 59.45 (d), 75.66 (s), 106.10 (d), 107.62 (d), 127.68 (d, 2 C), 129.84 (d,2 C), 134.64 (s), 144.78

(s), 149.26 (s), 151.25 (s). MS (EI (+)): m/z (%): 303 (11), 288 (12), 260 (10), 196 (16), 155 (16), 122 (31), 108 (20), 95 (100), 91 (36). $C_{16}H_{17}NO_3S$ (303.38): calcd C 63.34, H 5.65, N 4.62; found C 63.43, H 5.92, N 4.62.

***N*-Ethynyl-*N*-[(furan-2-yl)ethyl]-4-methylbenzenesulfonamide (27b):**

As described in **GP 3**, 900 mg (2.48 mmol) protected ynamide **26b** and 1.96 g (6.22 mmol) TBAF in 20 ml THF afforded 715 mg (2.47 mmol, 100%) of **27b** as an yellow solid.

Mp.: 32 °C. R_f (PE:EE, 20:1) = 0.12. IR (film): $\tilde{\nu}$ = 3283 cm^{-1}, 2131, 1595, 1505, 1451, 1431, 1356, 1310, 1295, 1261, 1188, 1067, 1091, 1010, 952, 881, 849, 809, 746, 699, 680, 640, 602. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.45 (s, 3 H), 2.76 (s, 1 H), 2.98 (t, *J* = 7.6 Hz, 2 H), 3.60 (t, *J* = 7.6 Hz, 2 H), 6.06 (dd, *J* = 3.2 Hz, 0.7 Hz, 1 H), 6.26 (dd, *J* = 3.2 Hz, 1.8 Hz, 1 H), 7.29 (dd, *J* = 1.8 Hz, 0.7 Hz, 1 H), 7.34 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.80 (q), 27.00 (t), 49.78 (t), 59.64 (d), 75.70 (s), 107.10 (d), 110.45 (d), 127.77 (d, 2 C), 129.98 (d, 2 C), 134.67 (s), 141.76 (d), 144.95 (s), 151.19 (s). MS (EI (+)): *m/z* (%): 289 (16) $[M]^+$, 274 (28), 261 (16), 196 (17), 155 (67), 132 (30), 108 (36), 91 (100), 81 (74), 65 (18). $C_{15}H_{15}NO_3S$ (289.35): calcd C 62.26, H 5.23, N 4.84; found C 62.11, H 5.38, N 4.71.

***N*-Ethynyl-4-methyl-*N*-[(5-methylfuran-2-yl)methyl]benzenesulfonamide (27c):**

As described in **GP 3**, 150 mg (415 µmol) protected ynamide **26c** and 328 mg (1.04 mmol) TBAF in 10 ml THF afforded 125 mg (411 µmol, 99%) of **27c** as an yellow solid.

Mp.: 64 °C. R_f (PE:EE, 10:1) = 0.16. IR (film): $\tilde{\nu}$ = 3297 cm^{-1}, 2922, 2357, 2135, 1597, 1561, 1365, 1170, 1090, 1020, 966, 944, 666, 632. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.13 (s, 3 H), 2.43 (s, 3 H), 2.71 (s, 1 H), 4.50 (s, 2 H), 5.82 (d, *J* = 3.1 Hz, 1 H), 6.14 (d, *J* = 3.1 Hz, 1 H), 7.30 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H).^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.59 (q), 21.77 (q), 48.20 (t), 59.82 (d), 75.95 (s), 106.49 (d), 111.74 (d), 128.02 (d, 2 C),

129.66 (d, 2 C), 134.93 (s), 144.71 (s), 145.82 (s), 153.08 (s). MS (ESI (+)): *m/z (%):* 312 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{15}H_{15}NNaO_3S$: calcd 312.0665; found 312.0658.

***N*-Ethynyl-4-methyl-*N*-nonylbenzenesulfonamide (27d):**

As described in **GP 3**, 370 mg (939 µmol) protected ynamide **26d** and 741 mg (2.35 mmol) TBAF in 15 ml THF afforded 299 mg (930 µmol, 99%) of **27d** as a yellow solid.

Mp.: 52 °C. R_f (PE:EE, 20:1) = 0.16. IR (film): $\tilde{\nu}$ = 2917 cm^{-1}, 2852, 2133, 1597, 1470, 1358, 1167, 1124, 1091, 1033, 978, 943, 909, 879, 807, 731, 713, 655, 616, 585. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, *J* = 7.1 Hz, 3 H), 1.22-1.31 (m, 12 H), 1.63 (p, *J* = 7.1 Hz, 2 H), 2.45 (s, 3 H), 2.72 (s, 1 H), 3.29 (t, *J* = 7.2 Hz, 2 H), 7.35 (d, *J* = 7.3 Hz, 2 H), 7.80 (d, *J* = 7.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.25 (q), 21.80 (q), 22.80 (t), 26.32 (t), 27.78 (t), 29.20 (t), 29.32 (t), 29.54 (t), 31.99 (t), 51.35 (t), 59.14 (d), 76.23 (s), 127.79 (d, 2 C), 129.91 (d, 2 C), 134.83 (s), 144.78 (s). MS (ESI (+)): *m/z (%):* 344 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{18}H_{27}NNaO_2S$: calcd 344.1655; found, 344.1649.

***N*-(2,2-Dichlorovinyl)-*N*-(3-furan-2-yl-1-methylpropyl)-4-methylbezenesulfonamide (32a):**

As described in **GP 4**, 1.00 g (7.13 mmol) 4-furan-2-yl-butan-2-ol[11] **21d**, 1.72 g (8.56 mmol) *N*-formyl-toluenesulfonamide, 3.04 g (11.5 mmol) PPH_3 and 2.28 ml (11.5 mmol) DIAD were converted in 50 ml THF. After a short column chromatography (petroleum ether/ ethyl acetate, 30:1), the residue was dissolved in 75 ml THF and 4.52 g (17.2 mmol) PPh_3 and 5.67 ml (58.7 mmol) CCl_4 furnished 530 mg (1.52 mmol, 21% over 2 steps) **32a** (16h reaction time) as a yellow solid, after purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 30:1).

Mp.: 52 °C. R_f (PE:EE, 10:1) = 0.12. IR (solid): $\tilde{\nu}$ = 3027 cm^{-1}, 2976, 2922, 1621, 1598, 1573, 1467, 1351, 1323, 1262, 1220,1090, 1021, 1011, 852, 802, 770, 653, 570. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.93 (d, *J* = 6.8 Hz, 3 H), 1.58-1.75 (m, 2 H), 2.43 (s, 3 H),

2.62-2.81 (m, 2 H), 3.99–4.07 (m, 1 H), 5.99 (dd, *J* = 3.2, 0.8 Hz, 1 H), 6.28 (dd, *J* = 3.2, 1.8 Hz, 1 H), 6.57 (s, 1 H), 7,27 (dd, *J* = 1.8, 0.8 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 17.63 (q), 21.74 (q), 25.25 (t), 33.84 (t), 56.26 (d), 105.38 (d), 110.29 (d), 121.22 (d), 127.58 (d, 2 C), 130.01 (d, 2 C), 132.92 (s), 136.68 (s), 141.13 (d), 144.15 (s), 155.09 (s). MS (ESI (+)): *m/z (%):* 410 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{17}H_{19}Cl_2NNaO_3S$: calcd 410.0355; found 410.0342.

4-(5-Methylfuran-2-yl)butan-2-ol (21b):

10.0g (65.7 mmol) 4-(5-methylfuran-2-yl)butan-2-one[13] were dissolved in 150 ml MeOH and 3.00 g (78.8 mmol) $NaBH_4$ were added at 0 °C. After stirring at 20 °C for 16 mh the solution was quenched with 50 ml H_2O and extracted three times with 20 ml DCM. The combined organic phases were dried over $MgSO_4$. filtered and purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 4:1) yielded 9.61 g (63 mmol, 95%) **21b** as a yellow oil.

R_f (PE:EE, 10:1) = 0.04. IR (film): $\tilde{\nu}$ = 3338 cm^{-1}, 2965, 2922, 1618, 1570, 1453, 1374, 1219, 1126, 1071, 1020, 954, 780, 653, 617. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19-1.25 (d, *J* = 6.3 Hz, 3 H), 1.44 (bs, 1 H), 1.59 (s, 1 H), 1.71-1.82 (m, 2 H), 2.25 (s, 3 H), 2.59–2.78 (m, 2 H) 5.81-5.89 (m, 2 H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ = 13.61 (q), 23.57 (q), 24.55 (t), 37.62 (t), 67.49 (d), 105.59 (d), 105.93 (s), 150.47 (s) 154.02 (s). MS (ESI (+)): *m/z (%):* 177 $[M+Na]^+$. HRMS (ESI (+)): $C_9H_{14}NaO_2$: calcd 177.0886; found, 177.0888.

***N*-(2,2-Dichlorovinyl)-4-methyl-*N*-[1-methyl-3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (32b):**

As described in **GP 4**, 2.00 g (13.0 mmol) **21b** , 3.10 g (15.6 mmol) *N*-formyl-toluenesulfonamide, 5.61 g (21.4 mmol) PPH_3 and 4.20 ml (21.4 mmol) DIAD were converted in 80 ml THF. After a short column chromatography (petroleum ether/ ethyl acetate, 30:1), the residue was dissolved in 150 ml THF and 10.6 g (38.3 mmol) PPh_3 and 12.5 ml

(130 mmol) CCl_4 furnished 1.05 g (2.62 mmol, 20% over 2 steps) **32b** (16 h reaction time) as a yellow solid, after purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 50:1).

Mp.: 61 °C. R_f (PE:EE, 10:1) = 0.04. IR (solid): $\tilde{\nu}$ = 3034 cm^{-1}, 2979, 2911, 1620, 1598, 1574, 1494, 1453, 1305, 1215, 1162, 1089, 1022, 981, 922, 857, 811, 875, 727, 663, 572. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.94 (d, *J* = 6.8 Hz, 3 H), 1.56-1.73 (m, 2 H), 2.24 (s, 3 H), 2.44 (s, 3 H), 2.55-2.73 (m, 2 H), 3.99–4.08 (m, 1 H), 5.81–5.86 (m, 2 H), 6.06 (s, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H). 7.70 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.65 (q), 17.67 (q), 21.72 (q), 25.03 (t), 33.95 (t), 56.33 (d), 105.95 (d), 105.98 (d), 121.30 (d), 127.56 (d, 2 C), 129.94 (d, 2 C), 132.79 (s), 136.75 (s), 144.09 (s), 150.55 (s), 153.20 (s). MS (ESI (+): *m/z (%):* 424 (100) $[M+Na]^+$. $C_{18}H_{21}Cl_2NO_3S$ (402.34): calcd C 53.60, H 5.26, N 3,44; found C 53.73, H 5.26, N 3.48.

_N_-(2,2-Dichlorovinyl)-4-methyl-_N_-[3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (32c):

As described in **GP 4**, 700 g (5.00 mmol) 3-(5-methylfuran-2-yl)propan-2-ol **18c**, 1.21 g (6.00 mmol) *N*-formyl-toluenesulfonamide, 1.71 g (6.50 mmol) PPH_3 and 1.30 ml (6.50 mmol) DIAD were converted in 50 ml THF. After a short column chromatography (petroleum ether/ ethyl acetate, 10:1), the residue was dissolved in 50 ml THF and 3.93 g (15 mmol) PPh_3 and 4.66 ml (50 mmol) CCl_4 furnished 1.11 g (2.86 mmol, 57% over 2 steps) **32c** (48 h reaction time) as a yellow solid, after purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 30:1).

Mp.: 79 °C, R_f (PE:EE, 10:1) = 0.36. IR (solid): $\tilde{\nu}$ = 2978 cm^{-1}, 1621, 1598, 1573, 1467, 1393, 1351, 1323, 1262, 1162, 1011, 930, 852, 802, 770, 718, 653, 570. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.84 (p, *J* = 8.1 Hz, 2 H), 2.24 (s, 3 H), 2.44 (s, 3 H), 2.61 (t, *J* = 8.1 Hz, 2 H), 3.36 (t, *J* = 8.1 Hz, 2 H), 5.83 (d, *J* = 3.1 Hz, 1 H), 5.87 (d, *J* = 3.1 Hz, 1 H), 6.27 (s, 1 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.68 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): 13.65 (q),

21.74 (q), 25.23 (t), 27.23 (t), 48.70 (t), 106.03 (d), 106.23 (d), 124.80 (s), 125.04 (d), 127.46 (d, 2 C), 130.02 (d, 2 C), 135.57 (s), 144.31 (s), 150.72 (s), 152.78 (s). MS (ESI (+)): *m/z (%):* 410 (100) $[M+Na]^+$. $C_{17}H_{19}Cl_2NO_3S$ (388.31): calcd C 52.64, H 4.97, N 3.49; found C 52.58, H 4.93, N 3.61.

_N_-Ethynyl-_N_-(3-furan-2-yl-1-methylpropyl)-4-methylbenzenesulfonamide (33a):

As described in **GP 5**, 400 mg (1.03 mmol) **32a**, and 1.48 ml (2.37 mmol) *n*-BuLi (1.6 M in hexane) in 10 ml THF were converted within 5 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate/ triethylamine, 40:2:1) afforded 269 mg (848 µmol, 82%) **33a** as a yellow solid.

Mp.: 69 °C. R_f (PE:EE:Et_3N, 40:2:1) = 0.09. IR (solid): $\tilde{\nu}$ = 3276 cm^{-1}, 2132, 1596, 1493, 1446, 1355, 1321, 1306, 1164, 1010, 966, 936, 922, 904, 884, 813, 731, 706, 681, 581. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (d, *J* = 6.6 Hz, 3 H), 1.70-1.81 (m, 1 H), 1.84-1.94 (m, 1 H), 2.44 (s, 3 H), 2.48-2.68 (m, 2 H), 2.80 (s, 1 H), 3.92-4.04 (m, 1 H), 5.99 (dd, *J* = 3.1, 0.9 Hz, 1 H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1 H), 7.29 (dd, *J* = 1.9, 0.9 Hz, 1 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.80 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 18.68 (q), 21.81 (q), 24.77 (t), 33.05 (t), 55.83 (d), 61.34 (d), 72.94 (s), 105.43 (d), 110.30 (d), 127.65 (d, 2 C), 129.93 (d, 2 C), 135.97 (s), 141.15 (d), 144.77 (s), 154.87 (s). MS (ESI (+)): *m/z (%):* 340 (100) $[M+Na]^+$. $C_{17}H_{19}NO_3S$ (317.40): calcd C 64.33, H 6.03, N 4.41; found C 63.99, H 6.05, N 4.39.

_N_-Ethynyl-4-methyl-_N_-[1-methyl-3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (33b):

As described in **GP 5**, 15.0 mg (37.3 µmol) **32b**, and 54.0 µl (85.7 µmol) *n*-BuLi (1.6 M in hexane) in 5 ml THF were converted within 5 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate/ triethylamine, 40:2:1) afforded 11.1 mg (33.5 µmol, 90%) **33b** as a yellow oil.

R_f (PE:EE, 10:1) = 0.33. IR (film): $\tilde{\nu}$ = 3290 cm^{-1}, 2926, 2360, 2128, 1734, 1596, 1570, 1450, 1359, 1165, 1090, 1020, 971, 814, 786,

680, 632. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (d, *J* = 6.6 Hz, 3 H), 1.67-1.94 (m, 2 H), 2.24 (s, 3 H), 2.44 (s, 3 H), 2.47-2.57 (m, 2 H), 2.79 (s, 1 H), 3.93–4.04 (m, 1 H), 5.83–5.85 (m, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.80 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.64 (q), 18.66 (q), 21.77 (q), 24.82 (t), 33,19 (t), 55.86 (d), 61.34 (d), 72.99 (s), 105.94 (d), 105.99 (d), 127.59 (d, 2 C), 129.93 (d, 2 C), 135.99 (s), 144.71 (s), 150.58 (s), 152.99 (s). MS (ESI (+)): *m/z (%):* 332 (10) $[M+H]^+$, 354 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{18}H_{21}NNaO_3S$: calcd 354.1134; found 354.1139.

_N_-Ethynyl-4-methyl-_N_-[3-(5-methylfuran-2-yl)propyl]benzenesulfonamide (33c):

As described in **GP 5** 400 mg (1.03 mmol) **32c**, and 1.48 ml (2.37 mmol) *n*-BuLi (1.6 M in hexane) in 10 ml THF were converted within 30 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate/ triethylamine, 40:2:1)afforded 322 mg (1.01 mmol, 99%) **33c** as a yellow solid.

Mp.: 41 °C. R_f (PE:EE, 10:1) = 0.15. IR (solid): $\tilde{\nu}$ = 3266 cm^{-1}, 2952, 2926, 2134, 1618, 1598, 1571, 1494, 1464, 1448, 1356, 1310, 1216, 1167, 1096, 1024, 969, 809, 777, 755, 722, 710, 697, 655. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.97 (p, *J* = 7.2 Hz, 2 H), 2.24 (s, 3 H), 2.45 (s, 3 H), 2.61 (t, *J* = 7.2 Hz, 2 H), 2.74 (s, 1 H), 3.35 (t, *J* = 7.2 Hz, 2 H), 5.83 (d, *J* = 2.9 Hz,1 H), 5.87 (d, *J* = 2.9 Hz, 1 H) 7.35 (d, *J* = 8.4 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.64 (q), 21.80 (q), 24.88 (t), 26.42 (t), 50.65 (t), 59.34 (d), 76.06 (s), 106.00 (d), 106.25 (d), 127.79 (d, 2 C), 129.94 (d, 2 C), 134.63 (s), 144.88 (s), 150.73 (s), 152.61 (s). MS (ESI (+)): *m/z (%):* 340 (100) $[M+Na]^+$. $C_{17}H_{19}NO_3S$ (317.40): calcd C 64.33, H 6.03, N 4.41; found C 64.33, H 6.04, N 4.32.

2-Butyl-2,3-dihydrobenzofuran-7-ol (35a):

As described in **GP 7**, 110 mg (418 µmol) **23a** and 0.49 ml (1.7 M in pentane, 840 µmol) *t*-BuLi were reacted in 10 ml Et_2O for 10 min.

The alkynylether **34a** was dissolved in $CDCl_3$ and 3.80 mg (12.5 µmol) $AuCl_3$ were added. After 30 min purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 40:1) afforded 35.3 mg (184 µmol, 44% over 2 steps) **35a** as a yellow oil.

34a: IR (film): $\tilde{\nu}$ = 3318 cm^{-1}, 2957, 2364, 2338, 2219, 2178, 2147, 1505, 1100, 740. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.91 (t, *J* = 7.2 Hz, 3 H), 1.30-1.40 (m, 3 H), 1.42-1.51 (m, 1 H), 1.58 (s, 1 H), 1.59-1.65 (m, 1 H), 1.72-1.79 (m, 1 H), 2.96 (dd, *J* = 15.3 Hz, 6.2 Hz, 1 H), 3.13 (dd, *J* = 15.3, 6.4 Hz, 1 H), 4.24-4.30 (m, 1 H), 6.15 (dd, *J* = 3.4, 0.8 Hz, 1 H), 6.31 (dd, *J* = 3.4, 1.9 Hz, 1 H), 7.34 (dd, *J* = 1.9, 0.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.01 (q), 22.51 (t), 27.22 (t), 28.20 (d), 32.09 (t), 32.58 (t), 87.35 (d), 89.32 (s), 107.72 (d), 110.61 (d), 141.80 (d), 151.01 (s).

35a: R_f (PE:EE, 40:1) = 0.08. IR (film): $\tilde{\nu}$ = 3386 cm^{-1}, 2931, 2859, 1620, 1476, 1299, 1220, 1176, 1028, 764, 720. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.35-1.44 (m, 3 H), 1.45-1.52 (m, 1 H), 1.66-1.73 (m, 1 H), 1.82-1.89 (m, 1 H), 2.90 (dd, *J* = 15.3, 7.9 Hz, 1 H), 3.13 (dd, *J* = 15.3, 8.9 Hz, 1 H), 4.79-4.85 (m, 1 H), 4.92 (s, 1 H), 6.72 (s, 3 H; in C_6D_6: 6.61 (d, *J* = 7.7 Hz, 1 H), 6.70 (t, *J* = 7.7 Hz, 1 H), 6.83 (d, *J* = 7.7 Hz, 1 H)). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.23 (q), 22.82 (t), 27.81 (t), 35.93 (t), 36.42 (t), 84.81 (d), 114.83 (d), 117.17 (d), 128.02 (s), 140.39 (s), 146.63 (s). MS (EI(+)): *m/z (%):* 192 (68) $[M]^+$, 149 (17), 136 (29), 123 (100), 107 (10), 77 (63). HRMS (EI (+)): $C_{12}H_{16}O_2$: calcd 192.1150; found 192.1146.

2,3-Dihydro-6-methyl-1-benzofuran-7-ol (35b):

Method A: As described in **GP 7**, 300 mg (1.36 mmol) **23b** and 1.60 ml (1.7 M in pentane, 2.72 mmol) *t*-BuLi were reacted in 10 ml Et_2O for 1h. The alkynylether **34b** was dissolved in $CDCl_3$ and 12.4 mg (41.0 µmol) $AuCl_3$ were added. After 30 min purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 105 mg (702 µmol, 52% over 2 steps) **35b** as a colorless solid.

Method B: As described in **GP 8**, 75 mg (340 µmol) **23b,** 103 µl (680 µmol) TMEDA and 400 µl (1.6 M in hexane, 680 µmol) *n*-BuLi were reacted in 5 ml Et_2O. The alkynylether **34b** was dissolved in CD_3CN and 5.05 mg (17.0 µmol) $AuCl_3$ were added. After 30 min purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 15.0 mg (99.8 µmol, 29% over 2 steps) **35b** as a colorless solid and 3.00 mg (20.2 µmol, 6%) **36**.

34b: IR (film): $\tilde{\nu}$ = 3311 cm^{-1}, 2922, 2359, 2341, 2150, 1618, 1570, 1463, 1383, 1216, 1183, 1121, 1091, 1020, 937, 782, 645, 613, 560. ^1H NMR (CD_3CN, 500 MHz): d = 1.76 (s, 1 H), 2.22 (s, 3 H), 3.01 (t, *J* = 6.5 Hz, 2 H), 4.25 (t, *J* = 6.5 Hz, 2 H), 5.91 (d, *J* = 2.9 Hz, 1 H), 6.03 (d, *J* = 2.9 Hz, 1 H). ^{13}C NMR (CD_3CN, 126 MHz): d = 12.22 (q), 26.56 (t), 27.01 (d), 76.25 (t), 90.04 (s), 105.99 (d), 107.33 (d), 148.85 (s), 150.85 (s).

35b: Mp.: 82 °C. R_f (PE:EE, 10:1) = 0.20. IR (solid): $\tilde{\nu}$ = 3051 cm^{-1}, 2923, 2861, 1843, 1626, 1599, 1508, 1481, 1444, 1386, 1360, 1306, 1279, 1241, 1219, 1184, 1149, 1016, 967, 951, 894, 842, 788, 759, 737, 721, 649, 606. ^1H NMR (CD_3CN, 500 MHz): d = 2.16 (s, 3 H), 3.14 (t, *J* = 8.7 Hz, 2 H), 4.53 (t, *J* = 8.7 Hz, 2 H), 4.81 (s, 1 H), 6.55 (d, *J* = 7.5 Hz, 1 H), 6.59 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR (CD_3CN, 126 MHz): d = 15.17 (q), 30.47 (t), 72.30 (t), 115.84 (d), 122.71 (d), 123.84 (s), 125.04 (s), 138.62 (s), 146.73 (s). MS (FAB(+)): *m/z* (%): 150 (100) $[M]^+$, 131 (7), 121 (7), 107 (8), 91 (7), 77 (8). HRMS (EI (+)): $C_9H_{10}O_2$: calcd 150.0681; found 150.0681.

36: R_f (PE:EE, 10:1) = 0.33. IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2923, 1740, 1712, 1628, 1569, 1233, 1167, 1132, 1037, 1019, 830, 779. ^1H-NMR ($CDCl_3$, 500 MHz): d = 2.05 (s, 3 H), 2.25 (s, 3 H), 2.91 (t, *J* = 6.8 Hz, 2 H), 4.28 (t, *J* = 6.8 Hz, 2 H), 5.86 (m, 1 H), 5.94 (d, *J* = 2.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 500 MHz): d = 13.62 (q), 21.09 (q), 27.91 (t), 62.65 (t), 106.15 (d), 107.10 (d), 150.03 (s), 151.13 (s), 171.14 (s). HRMS (EI (+)): $C_9H_{10}O_2$: calcd 168.0786; found 168.0807.

7-Methyl-chroman-8-ol (35c):

As described in **GP 8**, 197 mg (840 µmol) **23c,** 255 µl TMEDA (1.68 mmol) and 1.05 ml (1.6 M in hexane, 1.68 mmol) *n*-BuLi were reacted in 5 ml Et_2O. The alkynylether **34c** was dissolved in 3 ml CD_3CN and 11.3 mg (42.0 µmol) $AuCl_3$ were added. After 30 min purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 62.3 mg (390 µmol, 46% over 2 steps) **35c** as a colorless solid.

34c: IR (film): $\tilde{\nu}$ = 3313 cm^{-1}, 2924, 2360, 2340, 2151, 1570, 1456, 1219, 1121, 1020, 939, 669, 632, 607, 583. ^1H NMR ($CDCl_3$, 300 MHz): d = 1.55 (s, 1 H), 1.92 (tt, *J* = 7.4, 6.4 Hz, 2 H), 2.02 (s, 3 H), 2.47 (t, *J* = 7.4 Hz, 2 H), 3.91 (t, *J* = 6.4 Hz, 2 H), 5.69 (d, *J* = 3.0, 1 H), 5.74 (d, *J* = 3.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): d = 14.09 (q), 24.94 (t), 27.96 (d), 28.59 (t), 79.55 (t), 92.22 (s), 107.53 (d), 118.71 (s), 152.04 (s), 154.23 (s).

35c: Mp.: 84 °C. R_f (PE:EE, 10:1) = 0.25. IR (solid): $\tilde{\nu}$ = 3443 cm^{-1}, 3050, 2992, 2941, 2917, 2849, 1854, 1715, 1630, 1586, 1509, 1472, 1350, 1332, 1269, 1249, 1160, 1090, 1062, 981, 786, 667, 570. ^1H NMR ($CDCl_3$, 500 MHz): d = 2.04 (m, 2 H), 2.25 (s, 3 H), 2.78 (t, *J* = 6.4 Hz, 2 H), 4.27 (t, *J* = 5.1 Hz, 2 H), 5.55 (s, 1 H), 6.53 (d, *J* = 7.9 Hz, 1 H), 6.64 (d, *J* = 7.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 500 MHz): d = 15.17 (q), 22.55 (t), 24.12 (t), 66.90 (t), 119.62 (d), 119.67 (d), 121.33 (s), 121.78 (s), 141.51 (s), 142.79 (s). MS (FAB(+)): *m/z (%):* 164 (100) $[M]^+$, 149 (10), 136 (40). HRMS (EI (+)): $C_{10}H_{12}O_2$: calcd 164.0837; found 164.0837.

2-Methylchroman-8-ol (35d):

Method A: As described in **GP 7**, 400 mg (1.70 mmol) **23d** and 2.27 ml (1.5 M in pentane, 3.40 mmol) *t*-BuLi were reacted in 10 ml Et_2O for 30 min. The alkynylether **34d** was dissolved in 10 ml $CDCl_3$ and 15.5 mg (51.0 µmol) $AuCl_3$ were added. After 10 min purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 167 mg (1.02 µmol, 60% over 2 steps) **35d** as a colorless solid.

34d: IR (film): $\tilde{\nu}$ = 3315 cm^{-1}, 2937, 2360, 2146, 1507, 1447, 1381, 1111, 1008, 733. ^1H NMR ($CDCl_3$, 300 MHz): d = 1.41 (d, *J* = 6.3 Hz,

3 H), 1.56 (s, 1 H), 1.84-1.96 (m, 1 H), 2.01-2.14 (m, 1 H), 2.68-2.85 (m, 2 H), 4.14-4.25 (m, 1 H), 6.03 (dd, *J* = 3.3, 0.8 Hz, 1 H), 6.28 (dd, *J* = 3.3, 1.9 Hz, 1 H), 7.31 (dd, *J* = 1.9, 0.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 63 MHz): d = 19.12 (q), 23.92 (t), 27.91 (d), 33.78 (t), 84.52 (d), 89.48 (s), 105.54 (d), 110.32 (d), 141.29 (d), 154.76 (s).

35d: Mp.: 58 °C R_f (PE:EE, 40:1) = 0.19. IR (solid): $\tilde{\nu}$ = 3445 cm^{-1}, 2975, 2937, 1595, 1472, 1386, 1366, 1336, 1253, 1235, 1206, 1176, 1142, 1107, 1075, 1049, 1032, 992, 931, 958, 842, 763, 725, 688. ^{1}H NMR (CD_2Cl_2, 500 MHz): d = 1.42 (d, *J* = 6.2 Hz, 3 H), 1.73 (dddd, *J* = 13.7, 11.6, 10.3, 5.6 Hz, 1 H), 2.01 (dddd, *J* = 13.7, 6.10, 2.9, 2.1 Hz, 1 H), 2.73 (ddd, *J* = 16.7, 5.6, 3.0 Hz, 1 H), 2.84 (ddd, *J* = 16.7, 11.6, 6.1 Hz, 1 H), 4.19 (dqd, *J* = 10.3, 6.2, 2.1 Hz, 1 H), 5.57 (s, 1 H), 6.56-6.60 (m, 1 H), 6.67-6.71 (m, 2 H; in C_6D_6: 6.49 (d, *J* = 7.7 Hz, 1 H), 6.71 (t, *J* = 7.7 Hz, 1 H), 6.96 (d, *J* = 7.7 Hz, 1 H). ^{13}C NMR (CD_2Cl_2, 126 MHz): d = 22.94 (q), 26.24 (t), 31.29 (t), 75.05 (d), 113.67 (d), 121.78 (d), 122.22 (d), 124.22 (s), 144.06 (s), 146.67 (s). MS (EI(+)): *m/z (%):* 164 [M]$^+$ (100), 149 (13), 122 (100), 94(14), 77 (10), 66 (18), 39 (17). $C_{10}H_{12}O_2$ (164.20): calcd C 73.15, H 7.37; found C 72.81, H 7.39.

***N*-Nonylpyridin-2-carboxamid:**

1.23 g (10.0 mmol) *N*-nonylpyridin-2-carboxamid were dissolved in 20 ml THF. 1.78 g (11.0 mmol) DCI were added and the suspension became a clear solution. 1.43 g (10.0 mmol) of nonylamine dissolved in 10 ml THF were added and the reaction was stirred for 24h at rt. 20 ml of water were added and the mixture was extracted three times with ethyl acetate, dried over $MgSO_4$, filtered and purified by column chromatography on silica gel (petroleum ether /ethyl acetate, 5:1). 2.03 g (8.18 mmol, 82%) product were gained as colorless oil.

R_f (PE:EE, 2:1) = 0.39. IR (oil): $\tilde{\nu}$ = 2925 cm^{-1}, 2854, 1676, 1590, 1569, 1527, 1465, 1433. ^{1}H NMR ($CDCl_3$, 500 MHz): d = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.24-1.42 (m, 12 H), 1.60-1.66 (m, 2 H), 3.44-3.48 (m, 2 H), 7.41 (dd, *J* = 7.5, 4.8 Hz, 1 H), 7.83 (t, *J* = 7.8 Hz, 1

H), 8.04 (bs, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 8.54 (d, *J* = 4.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): d = 14.24 (q), 22.80 (t), 27.16 (t), 29.40 (t), 29.48 (t), 29.64 (t), 29.82 (t), 32.00 (t), 39.62 (t), 122.32 (d), 126.13 (d), 137.45 (d), 148.13 (d), 150.30 (s), 164.33 (s). MS (CI(+)): *m/z (%):* 249 $[M]^+$ (100), 231 (19), 142 (19), 135 (20), 106 (10), 78 (12). $C_{15}H_{24}N_2O$ (248.36): calcd C 72.54, H 9.74, N 11.28; found C 72.14, H 9.53, N 11.04.

Gold catalyst 41:

236 mg (590 µmol) $NaAuCl_4 \cdot 2H_2O$ were dissolved in 20 ml EtOH and 147 mg (590 µmol) pyridine-2-carboxylic-acid-nonylamide dissolved in 10 ml EtOH were added and the mixture was heated under reflux for 2h. The mixture was purified by column chromatography on silica gel (petroleum ether /ethyl acetate, 1:1). 116 mg (38.0 µmol, 38%) **41** were gained as orange solid.

Mp.: 76 °C. R_f (PE:EE, 2:1) = 0.13. IR (solid): $\tilde{\nu}$ = 2915 cm^{-1}, 2847, 1645, 1610, 1431, 1378, 1297, 1277, 1153, 1105, 1056, 793, 755, 720, 691, 666. ^{1}H NMR ($CDCl_3$, 500 MHz): d = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.22-1.39 (m, 12 H), 1.64-1.70 (m, 2 H), 3.60-3.63 (m, 2 H), 7.83 (ddd, *J* = 7.7, 5.8, 1.8 Hz, 1 H), 8.14 (dd, *J* = 7.7, 1.8 Hz, 1 H), 8.34 (td, *J* = 7.7, 1.4 Hz, 1 H), 9.50 (dd, *J* = 5.8, 1.4 Hz , 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): d = 14.27 (q), 22.82 (t), 26.94 (t), 29.43 (t), 29.60 (t), 29.69 (t), 30.45 (t), 32.03 (t), 48.23 (t), 128.86 (d), 128.88 (d), 144.25 (d), 144.94 (d), 150.91 (s), 170.22 (s). MS (CI(+)): *m/z (%):* 515 $[MH]^+$, 249 (100), 231 (10), 191 (10), 142 (41), 135 (26), 106 (20), 78 (22). HRMS (CI (+)): $C_{15}H_{23}AuCl_2N_2O$: calcd 514.0853; found 514.0836.

6-Methyl-1-[(4-methylphenyl)sulfonyl]indolin-7-ol (39a):

According to **GP 6**, 76.0 mg (251 µmol) **27a** and 3.82 mg (12.6 µmol) $AuCl_3$ were reacted in CD_3CN for 5 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 47.0 mg (155 µmol, 62%) **39a** as a white solid.

Mp: 114 °C. R_f (PE:EE, 3:1)= 0.40. IR (solid): $\tilde{\nu}$ = 3568 cm^{-1}, 3547, 3484, 2934, 2183, 2168, 2018, 1992, 1597, 1497, 1454, 1350, 1329, 1308, 1261, 1218, 1204, 1156, 1089, 1030, 978, 961, 942, 844, 795,

784, 751, 722. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.23 (s, 3 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 2.32 (s, 3 H), 3.92 (t, *J* = 7.5 Hz, 2 H), 6.43 (d, *J* = 7.5 Hz, 1 H), 6.81 (d, *J* = 7.5 Hz, 1 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 16.19 (q), 21.74 (q), 28.92 (t), 53.05 (t), 115.84 (d), 126.15 (s), 127.44 (d, 2 C), 128.12 (s), 129.13 (d, 2 C), 129.74 (d), 133.35 (s), 135.12 (s), 144.68 (s), 146.88 (s). MS (EI (+)): m/z (%): 303 (40) $[M]^+$, 148 (100), 133 (8), 91 (6). $C_{16}H_{17}NO_3S$ (303.38): calcd C 63.34, H 5.65, N 4.62; found C 63.33, H 5.72, N 4.56.

1-[(4-methylphenyl)sulfonyl]indolin-7-ol (39b):

According to **GP 6**, 100 mg (346 µmol) **27b** and 4.20 mg (10.4 µmol) complex **40** were reacted in CD_3CN for 5 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 10:1) afforded 13.0 mg (44.9 µmol, 13%) **39b** as a white solid. Using the same procedure with 5.36 mg (10.4 µmol) catalyst **41** yielded 9.20 mg (32.0 µmol, 9%) **39b** after 1 h reaction time.

MP.: 87 °C. R_f (PE:EE, 5:1) = 0.18. IR (solid): $\tilde{\nu}$ = 3390 cm^{-1}, 1599, 1486, 1461, 1321, 1239, 1208, 1149, 1085, 932, 843, 818, 746, 720,678, 618. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.37 (t, *J* = 7.7 Hz, 2 H), 2.38 (s, 3 H), 4.00 (t, *J* = 7.7 Hz, 2 H), 6.62 (d, *J* = 7.6 Hz, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.67 (q), 29.20 (t), 52.72 (t), 116.81 (d), 117.38 (d), 127.53 (d, 2 C), 128.03 (d), 128.33 (s), 129.95 (d, 2 C), 133.28 (s), 137.73 (s), 144.89 (s), 148.61 (s). MS (ESI (+)): *m/z (%):* 312 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{15}H_{15}NNaO_3S$: calcd 312.0665; found, 312.0660.

2-Methyl-1-[(4-methylphenyl)sulfonyl]-1,2,3,4-tetrahydroquinolin-8-ol (42a):

According to **GP 6**, 100 mg (320 µmol) **33a** and 2.91 mg (9.60 µmol) $AuCl_3$ were reacted in $CDCl_3$ at 0 °C for 5 min. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 80:1) afforded 17.0 mg (54.0 µmol, 17%) **42a** as a white

solid. Using the same procedure with 30.0 mg (94.5 mmol) **33a** and 1.92 mg (4.73 µmol) catalyst **40** yielded 7.70 mg (24.3 µmol, 26%) **42a** after 1 h reaction time at rt in CD_3CN. With 2.44 mg (4.73 µmol) catalyst **41**, the same scale delivered 11.1 mg (35.0 µmol, 37%) of **42a** at rt in CD_3CN after 16 h.

Mp: 132 °C. R_f (PE:EE, 20:1): 0.21. IR (solid): $\tilde{\nu}$ = 3489 cm^{-1}, 2960, 1697, 1595, 1471, 1345, 1304, 1237, 1214, 1156, 1091, 1023, 944, 924, 818, 792, 756, 707, 670. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.03-1.19 (m, 2 H), 1.27 (d, *J* = 6.5 Hz, 3 H), 2.05-2.13 (m, 2 H), 2.40 (s, 3 H), 4.29-4.37 (m, 1 H), 6.53 (d, *J* = 7.5 Hz, 1 H), 6.97 (ddd, *J* = 8.3, 1.4, 0.7 Hz, 1 H), 7.08 (*visible* t, *J* = 7.9 Hz, 1 H), 7.19 (d, *J* = 8.3 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.58 (s, 1 H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 21.76 (q), 23.91 (q), 26.26 (t), 33.25 (t), 54.39 (d), 117.18 (d), 119.60 (d), 123.00 (s), 127.44 (d, 2 C), 128.45 (d), 129.72 (d, 2 C), 134.55 (s), 139.73 (s), 144.34 (s), 153.93 (s). MS (ESI (+)): *m/z (%):* 340 (100) $[M+Na]^+$. HRMS (ESI (+)): $C_{17}H_{19}NNaO_3S$: calcd 340.0978; found, 340.0966.

2,7-Dimethyl-1-[(4-methylphenyl)sulfonyl]-1,2,3,4-tetrahydroquinolin-8-ol (42b):

According to **GP 6**, 75.0 mg (226 µmol) **33b** and 2.10 mg (6.78 µmol) $AuCl_3$ were reacted in $CDCl_3$ for 5 min at 0 °C. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 65.8 mg (199 µmol, 88%) **42b** as a white solid.

Mp: 122 °C. R_f (PE:EE, 10:1): 0.31. IR (solid): $\tilde{\nu}$ = 3474 cm^{-1}, 2930, 2866, 1595, 1497, 1457, 1345, 1210, 1193, 1159, 1096, 1037, 1010, 938, 819, 802, 756, 669, 580. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.95-1.15 (m, 2 H), 1.26 (d, *J* = 6.4 Hz, 3 H), 1.98-2.13 (m, 2 H), 2.31 (s, 3 H), 2.40 (s, 3 H), 4.26-4.38 (m, 1), 6.42 (d, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 8.3 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.55 (s, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 16.59 (q), 21.76 (q), 23.95 (q), 26.05 (t), 33.31 (t), 54.35 (d), 118.60 (d), 122.53 (s), 125.90 (s), 127.49 (d, 2 C), 129.62 (d), 129.66 (d, 2 C), 134.64 (s), 137.00 (s), 144.24 (s), 152.14 (s). MS (ESI

(+)): *m/z (%):* 354 $[M+Na]^+$. $C_{18}H_{21}NO_3S$ (331.43): calcd C 65.23, H 6.39, N 4.23; found C 65.25, H 6.52, N 4.11.

7-Methyl-1-[(4-methylphenyl)sulfonyl]-1,2,3,4-tetrahydroquinolin-8-ol (42c):

According to **GP 6**, 70.0 mg (221 µmol) **33c** and 2.01 mg (6.63 µmol) $AuCl_3$ were reacted in $CDCl_3$ for 5 min at 0 °C. Purification by column chromatography on silica gel (petroleum ether /ethyl acetate, 20:1) afforded 46.9 mg (148 µmol, 67%) **42c** as a white solid.

Mp: 91 °C. R_f (PE:EE, 20:1): 0.11. IR (solid): $\tilde{\nu}$ = 3475 cm^{-1}, 2952, 2919, 1598, 1456, 1437, 1338, 1248, 1223, 1155, 1094, 1007, 940, 873, 810, 787, 705, 672, 610. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.71-1.75 (m, 4 H), 2.30 (s, 3 H), 2.40 (s, 3 H), 3.72-3.75 (m, 2 H), 6.44 (d, *J* = 7.5 Hz, 1 H), 6.96 (d, *J* = 7.5 Hz, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.72 (s, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 16.51 (q), 21.77 (q), 23.08 (t), 24.85 (t), 46.88 (t), 119.54 (d), 124.82 (s), 125.54 (s), 127.63 (d, 2 C), 129.69 (d), 129.75 (d, 2 C), 134.75 (s), 135.14 (s), 144.40 (s), 150.98 (s). MS (ESI (+)): *m/z (%):* 340 (100) $[M+Na]^+$. $C_{17}H_{19}NO_3S$ (317.40): calcd C 64.33, H 6.03, N 4.41; found C 64.51, H 6.03, N 4.30.

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