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Supporting Information

Gold Catalysis: The Phenol Synthesis in the Presence of Functional Groups

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Supplementary Material

1. General Procedure for the condensation of aldehydes and amines

A solution of aldehyde and 3.00 g $MgSO_4$ in about 30 mL dichloromethane is treated with propargyl amine. The reaction mixture is stirred for 20 hours at ambient temperature, the solution filtered and the solvent evaporated. The crude product used without further purification.

2. General Procedure for the reduction of imines

To a solution of imine in about 20 ml dry methanol is added $NaBH_4$ at + 10 °C and the reaction mixture is stirred at ambient temperature for two hours. After additon of 100 ml of water, the water/methanol phase is extracted three times with dichloromethane and the combined organic layers are dried over $MgSO_4$. The crude product used without further purification.

3. General Procedure for the tosylation of amines

A solution of amine in dichloromethane is treated with one equivalent triethylamine and 1 mol-% 4-*N*,*N*-dimethylaminopyridine. One equivalent toluene-4-sulfonic acid chloride is added at 0 °C and the reaction mixture is stirred for further 30 min at 0 °C and additional 18 hours at ambient temperature. After hydrolysis and extraction of the aequous phase with dichloromethane, the combined organic layers are dried over $MgSO_4$. The crude product is purifed by either column chromatography on silica or recrystallisation.

1k: According to general procedures 1, 2, 3, 3.00 g (17.1 mmol) 2-Bromfurfural, 1.13 g (20.5 mmol) propargyl amine, 629 mg (17.1 mmol) $NaBH_4$, 1.01 g (10.0 mmol) triethylamine and 1.90 g (10.0 mmol) toluene-4-sulfonic acid chloride are used.

(*E*)-*N*-((5-bromofuran-2-yl)methylene)prop-2-yn-1-amine: ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.54 (t, *J* = 2.4 Hz, 1 H), 4.50 (t, *J* = 2.2 Hz, 2 H), 6.40 (d, *J* = 3.5 Hz, 1 H), 6.73 (d, *J* = 3.5 Hz, 1 H), 8.31 (t, *J* = 2.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 46.5 (t), 76.6 (d), 77.8 (s), 113.5 (d), 116.5 (d), 126.1 (s), 149.3 (d), 153.2 (s).

N-((5-bromofuran-2-yl)methyl)prop-2-yn-1-amine: IR (NaCl): $\tilde{n}$ = 3300, 2978, 2935, 2838, 1501, 1443, 1376, 1330, 1201, 1124, 1099, 1048, 1014, 949. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.53 – 1.85 (bs, 1 H), 2.24 (t, J = 2.3 Hz, 1 H), 3.42 (d, J = 2.4 Hz, 2 H), 3.84 (s, 2 H), 6.21 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 36.9 (d), 44.3 (d), 71.7 (d), 81.2 (s), 110.2 (d), 111.6 (d), 120.8 (s), 154.8 (s). HRMS (70 eV): $^{12}C_8{}^{1}H_7{}^{79}Br{}^{14}N{}^{16}O$: calcd. 211.9710, found 211.971099; $^{12}C_8{}^{1}H_8{}^{79}Br{}^{14}N{}^{16}O$: calcd. 212.9790, found 212.978925.

The crude **1k** is purified via column chromatography on silica (petrol ether/ethyl acetate, 5:2) to yield 883 mg (10 %) **1k** as colorless solid. IR (NaCl): $\tilde{n}$ = 3294, 1597, 1498, 1438, 1350, 1329, 1162, 1092. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.10 (t, *J* = 2.5 Hz, 1 H), 2.43 (s, 3 H), 4.04 (d, *J* = 2.5 Hz, 2 H), 6.20 (d, *J* = 3.2 Hz, 1 H), 6.27 (d, *J* = 3.2 Hz, 1 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.4 (q), 36.2 (t), 42.6 (t), 74.0 (t), 76.2 (s), 112.0 (d), 112.5 (d), 121.9 (s), 127.5 (d), 129.4 (d), 135.7 (s), 143.6 (s), 150.6 (s). MS (70 ev): *m/z* (%): 369 (10) [M^+], 132 (100), 288 (22), 212 (95), 159 (31), 104 (32), 91 (72). $C_{15}H_{14}BrNO_3S$ (368.25): calcd. C 48.92, H 3.83, N 3.80, found C 48.98, H 3.97, N 3.93.

1l: According to general procedures 1, 2, 3, 1.00 g (5.29 mmol) 4-Brom-5-methylfurfural, 870 mg (15.9 mmol) propargyl amine, 200 mg (5.29 mmol) $NaBH_4$, 535 mg (5.29 mmol) triethylamine and 1.01 g (5.29 mmol) toluene-4-sulfonic acid chloride are used. The crude product is recrystallised from diethyl ether/hexane/dichloromethane to yield 1.28 g (63 %, 3 steps) **1l** as colorless solid. M.p. 121-122 °C. IR (NaCl): $\tilde{n}$ = 3277 cm^{-1}, 3127, 2981, 2918,

2117, 1916, 1644, 1602, 1568, 1496, 1453, 1436, 1414, 1353, 1296, 1258, 1222, 1159, 1114, 1036, 993, 962, 918, 815, 773, 740, 709. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.08 (t, *J* = 2.5 Hz, 1H), 2.18 (s, 3H), 2.42 (s, 3H), 4.03 (d, *J* = 2.5 Hz, 2H), 4.35 (s, 2H), 6.23 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 11.74 (q), 21.50 (q), 36.20 (t), 42.67 (t), 74.12 (d), 76.23 (s), 96.41 (s), 113.67 (d), 127.68 (d, 2C), 129.45 (d, 2C), 135.84 (s), 143.68 (s), 146.78 (s), 149.93 (s). MS (70 ev): *m/z* (%): 383 (15)[M^+, ^{81}Br], 381 (14)[M^+, ^{79}Br], 228 (85)[^{81}Br], 226 (100)[^{79}Br], 200 (54)[^{81}Br], 188 (51)[^{79}Br], 175 (48)[^{81}Br], 173 (46)[^{79}Br], 91 (53). $C_{16}H_{16}NO_3Br$ (382.28.): calcd. C 50.27, H 4.22, N 3.66; found C 50.51, H 4.32, N 3.70.

1m: 570 mg (4.10 mmol) *N,N*-dimethylfurfurylamine in about 5 ml diethyl ether are treated with 800 µL (8.53 mmol) propargylbromide in about 2 ml diethyl ether and the mixture is stirred two hours at ambient temperature. After filtration, the crude product is washed with small amounts of diethyl ether and dried in vacuo. Yield: 41 % (pale yellow solid). M.p.: 104-106 °C, IR (film, NaCl): $\tilde{n}$ = 3854 cm^{-1}, 3424, 3298, 3181, 3010, 2925, 2344, 2198, 2122, 1654, 1610, 1555, 1475, 1458, 1414, 1386, 1225, 1141, 1022, 982, 967, 954, 926, 865, 800, 730, 642. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.97 (t, *J* = 2.4 Hz, 1 H), 3.44 (s, 6 H), 4.82 (d, *J* = 2.5 Hz, 2 H), 5.09 (s, 2 H), 6.05 (d, *J* = 3.1 Hz, 1 H), 6.82 (d, *J* = 3.2 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.8 (q), 49.9 (q, 2 C), 54.0 (t), 59.9 (t), 71.7 (d), 85.4 (s), 107.7 (d), 118.9 (d), 140.2 (s), 156.0 (s). FAB-MS (positive-ion, matrix: NBA, *m/z* (%)): 178 (100) [cation], 154 (96), 137 (58), 95 (25). $C_{11}H_{16}BrNO$ (258.0) calcd.: C 51.21, H 6.20, N 5.43 found: C 51.21, H 6.39, N 5.55.

1n: obtained in quanititative yield as a pale yellow solid via passing **1m** through an ion exchange resin (DOWEX, 2X8, 50-100 mesh). M.p.: 112-113 °C. IR (Film, NaCl): $\tilde{n}$ = 3854 cm^{-1}, 3751, 3676, 3288, 2369, 2344, 1718, 1654, 1560, 1477, 1458, 1030, 838. ^{1}H NMR (250

MHz, CD_3CN): δ = 2.34 (s, 3 H), 3.07 (s, 6H), 3.24 (t, *J* = 2.5 Hz, 1 H), 4.08 (d, *J* = 2.5 Hz, 2 H), 4.48 (s, 2 H), 6.19 (d, *J* = 3.2 Hz, 1 H), 6.72 (d, *J* = 3.2 Hz, 1 H). ^{13}C NMR (62.9 MHz, CD_3CN): δ = 12.7 (q), 49.9 (q, 2 C), 53.6 (t), 59.9 (t), 70.9 (d), 81.8 (s), 107.6 (d), 118.4 (d), 139.9 (s), 156.5 (s). FAB-MS (positiv-Ion, Matrix: Glycerin, *m/z* (%)): 270 (6), 234 (5), 178 (100) [Kation], 95 (28), 84 (7), 58 (7). FAB-MS (negativ-Ion, Matrix: Glycerin, *m/z* (%)): 237 (10), 193 (7), 145 (100) [Anion], 101 (8), 59 (12). $C_{11}H_{16}F_6NOP$ (323.0) calcd.: C 40.90, H 4.95, N 4.33, found: C 41.13, H 5.05, N 4.27.

1o: 68.5 mg (1.7 %) **1o** as dark yellow solid are obtained as side product in the preparation of **1t**. R_f (PE/EE; 8:2) = 0.36. M.p.: 81-82 °C. IR (KBr): $\tilde{n}$ = 3250 cm^{-1}, 2895, 2080, 1590, 1555, 1482, 1430, 1419, 1338, 1319, 1260, 1249, 1202, 1173, 1149, 999, 960, 908, 872, 782, 748, 722, 690, 663, 641, 564, 528, 512. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.08 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 4.01 (d, *J* = 2.4 Hz, 2H), 4.42 (s, 2H), 4.46 (s, 2H), 6.23 (d, *J* = 3.3 Hz, 1H), 6.26 (d, *J* = 3.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.45 (q), 36.26 (t), 37.21 (t), 42.75 (t), 74.03 (d), 76.22 (s), 110.48 (d), 111.01 (d), 127.60 (d, 2C), 129.45 (d, 2C), 135.71 (s), 143.67 (s), 149.59 (s), 150.40 (s). MS (70 eV): *m/z* (%) = 339 (4) [^{37}Cl, M$^+$], 337 (9) [^{35}Cl, M$^+$], 184 (33), 182 (100), 154 (20), 146 (26), 129 (23), 91 (28), 39 (7). HRMS ($^{12}C_{16}{}^1H_{16}{}^{14}N^{16}O_3{}^{35}Cl^{32}S$): calcd. 337.0539 found 337.0539.

1p: According to general procedures 1, 2, 3, 1.00 g (7.93 mmol) 5-hydroxymethylfurfural, 560 µl (446 mg, 8.70 mmol) propargyl amine, 320 mg (8.50 mmol) $NaBH_4$, 535 mg (5.29 mmol) triethylamine and 1.35 g (6.88 mmol) toluene-4-sulfonic acid chloride are used. The crude product is dried in vacuo and purified via column chromatography on silica (petrol ether/ethyl acetate, 1:3) to yield 103 mg (79 %, 2 steps) (5-((prop-2-ynylamino)methyl)furan-2-yl)methanol as brown viscous oil. R_f(PE/EE, 1:3) = 0.16. IR (Film, NaCl): $\tilde{n}$ = 3392 cm^{-1}, 2900, 2803, 1435, 1341, 1322, 1172, 998, 776. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.81 (bs,

2H), 2.18 (t, *J* = 2.3 Hz, 1H), 3.36 (d, *J* = 2.5 Hz, 2H), 3.80 (s, 2H), 4.50 (s, 2H), 6.10 (d, *J* = 3.1 Hz, 1H), 6.14 (d, *J* = 3.1 Hz, 1H). ^{13}C NMR (CD_3CN, 126 MHz): δ = 37.55 (t), 45.08 (t), 57.86 (t), 72.24 (d), 81.87 (s), 108.75 (d), 108.81 (d), 154.27 (s), 154.15 (s). MS (70 eV): *m/z* (%) = 165 (10)[M^+], 164 (32)[M^+- H], 136 (100), 134 (44), 111 (29), 39 (22). HRMS ($^{12}C_9{}^1H_{11}{}^{14}N_1{}^{16}O_2$): calcd. 165.0790; found 165.0778.

The crude **1p** is purified via column chromatography on silica (petrol ether/ethyl acetate/dichloromethane, 2.2:1:2) to yield 1.22 g (54 %, 3 steps) **1p** as colorless solid. R_f(PE/EE/CH_2Cl_2, 2:1:2) = 0.26. IR (Film, NaCl): $\tilde{n}$ = 3595 cm^{-1}, 3296, 2220, 1580, 1338, 1148, 1073, 999, 780. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.83 (bs, 1H), 2.00 (t, *J* = 2.4 Hz, 1H), 2.36 (s, 3H), 3.96 (d, *J* = 2.4 Hz, 2H), 4.35 (s, 2H), 4.43 (d, *J* = 4.3 Hz, 2H), 6.12 (d, *J* = 3.1 Hz, 1H), 6.17 (d, *J* = 3.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.52 (q), 36.22 (t), 42.88 (t), 57.35 (t), 73.95 (d), 76.40 (s), 108.45 (d), 110.81 (d), 127.77 (d, 2C), 129.46 (d, 2C), 135.97 (s), 143.68 (s), 148.50 (s), 154.60 (s). MS (70 eV): *m/z* (%) = 319 (10)[M^+], 164 (100), 146 (70), 111 (33), 91 (42), 39 (17). $C_{16}H_{17}NO_4S$ (319.4): calcd. C 60.17, H 5.37, N 4.39; found C 60.37, H 5.59, N 4.20.

1q: To a solution of 1.50 g (11.9 mmol) 5-hydroxymethylfurfural, which was treated with 810 mg (14.4 mmol) potassium hydroxide (solution in water, 6 ml) were added 3.54 g (23.8 mmol) propargyl bromide (80%, w/w in toluene) and the reaction mixture was refluxed for three hours. After cooling to ambient temperature, the mixture was extracted with diethyl ether, the combined organic layers dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography on silica (petrol ether/ethyl acetate/dichloromethane, 10:1:3) of the crude product yielded 1.03 g (68 %) **1q** as a yellow oil (solid at -25 °C). R_f(PE/EE/CH_2Cl_2, 10:1:3) = 0.24. IR (Film, NaCl): $\tilde{n}$ = 3260 cm^{-1}, 3100, 3825, 2100, 1674, 1575, 1513, 1431, 1390, 1333, 1264, 1178, 1068, 1004, 922, 790, 762, 746, 732. ^{1}H NMR ($CDCl_3$, 300 MHz): δ

= 2.50 (t, *J* = 2.4 Hz, 1H), 4.22 (d, *J* = 2.4 Hz, 2H), 4.64 (s, 2H), 6.56 (d, *J* = 3.6 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 9.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 58.12 (t), 63.67 (t), 75.86 (d), 78.98 (s), 112.14 (d), 126.21 (d), 153.12 (s), 157.69 (s), 178.13 (d). MS (70 eV): *m/z* (%) = 164 (57)[M^+], 135 (40), 134 (88), 125 (65), 109 (65), 81 (36), 53 (50), 39 (100), 29 (23). $C_9H_8O_3$ (164.2): calcd. C 65.85, H 4.91; found C 65.58, H 4.95.

1s: To a solution of 250 mg (1.52 mmol) **1q** and 295 mg (3.04 mmol) sulfaminic acid in 10.0 ml water are added 5.0 ml of an aequous solution of 138 mg (1.53 mmol) sodium chlorite and 153 mg (1.13 mmol) sodium hydrogenphosphate, dropwise over a period of five minutes. The solvent was removed in vacuo, the residue redissolved in methanol/ethanol and filtered. Column chromatography (methanol/chloroform, 1:3) yielded 217 mg (79 %) of **1s**. M.p. 117 °C. R_f (methanol/chloroform; 1:3) = 0.17. IR (KBr): $\tilde{n}$ = 3275 cm^{-1}, 3260, 3110, 2850, 2532, 1681, 1588, 1538, 1518, 1450, 1418, 1392, 1336, 1297, 1206, 1145, 1053, 1009, 978, 924, 802, 735, 728, 671, 644, 532. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.49 (t, *J* = 2.4 Hz, H), 4.22 (d, *J* = 2.4 Hz, 2H), 4.64 (s, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 7.29 (d, *J* = 3.5 Hz, 1H), 10.10 (br s, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 57.62 (t), 63.26 (t), 75.40 (d), 78.75 (s), 111.65 (d), 120.84 (d), 143.65 (s), 156.54 (s), 163.16 (s). MS (70 eV): *m/z* (%): 180 (60)[M^+], 150 (100), 141 (68), 135 (46), 125 (92), 105 (26), 79 (33), 39 (48). $C_9H_8O_4$: calcd. C 60.00, H 4.48.; found C 59.55, H 4.68.

1t: According to general procedures 1, 2, 3, 2.00 g (11.9 mmol) 5-acetoxy-2-furfural, 656 mg (11.9 mmol) propargyl amine, 450 mg (12.2 mmol) $NaBH_4$, 1.20 g (11.9 mmol) triethylamine and 2.27 g (11.9 mmol) toluene-4-sulfonyl acid chloride are used. The crude products are purified via column chromatography on silica (petrol ether/ethyl acetate, 85:15-70:30) to yield 68.5 mg (1.7%) **1o** as dark yellow solid, 291 mg (6.8%) **1r** as colorless crystals and 1.12 g (29.5%) **1p** as brown viscous oil. **1p:** R_f (PE/EE; 8:2) = 0.22. M.p.: 75-76 °C. IR (KBr): $\tilde{n}$ =

3263 cm^{-1}, 1712, 1588, 1334, 1322, 1238, 1146, 1111, 1076, 1000, 967, 941, 896, 873, 772, 742, 725, 684, 638. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.05 (s, 3H), 2.08 (t, *J* = 2.5 Hz, 1H), 2.41 (s, 3 H), 4.02 (d, *J* = 2.5 Hz, 2H), 4.41 (s, 2H), 4.92 (s, 2H), 6.25 (d, *J* = 3.2 Hz, 1H), 6.30 (d, *J* = 3.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.28 (q), 21.94 (q), 36.72 (t), 43.27 (t), 58.37 (t), 74.55 (d), 76.69 (s), 111.32 (d), 111.68 (d), 128.15 (d, 2C), 129.92 (d, 2C), 136.19 (s), 144.13 (s), 149.97 (s), 150.28 (s), 171.00 (s). MS (70 eV): *m/z* (%) = 361 (11) [M^+], 301 (31), 222 (11), 206 (20), 178 (26), 163 (31), 146 (100), 91 (27), 39 (6). $C_{18}H_{19}NO_5S$ (361.4) calcd. C 59.82, H 5.30, N 3.88; found C 59.77, H 5.36, N 5.87.

1u: According to general procedures 1, 2, 3, 750 mg (5.95 mmol) 5-hydroxymethylfurfural, 610 mg (11.9 mmol) propargyl amine, 220 mg (5.95 mmol) $NaBH_4$, 601 mg (5.95 mmol) triethylamine and 1.32 g (5.95 mmol) nitrophenyl-4-sulfonyl acid chloride are used. The crude product is purified via column chromatography on silica (petrol ether/ethyl acetate, 2:1) to yield 910 mg (44 %, 3 steps) *N*-(5-hydroxymethylfuran-2-ylmethyl)-4-nitro-*N*-prop-2-ynylbenzensulfonamide as yellow solid. M.p. 130-132 °C. R_f (PE:EE, 2:1) = 0.16. IR (film): $\tilde{n}$ = 3569 cm^{-1}, 3472, 3267, 3100, 1605, 1527, 1437, 1403, 1347, 1161, 1095, 1058, 1006, 922, 878, 808, 765, 704, 660, 610. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.91 (bs, 1H), 2.11 (t, *J* = 2.4 Hz, 1H), 4.08 (d, *J* = 2.4 Hz, 2H), 4.47 (s, 2H), 4.50 (s, 2H), 6.20 (d, *J* = 3.1 Hz, 1H), 6.28 (d, *J* = 3.1 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 8.34 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 36.53 (t), 43.23 (t), 57.34 (t), 74.58 (d), 75.89 (s), 108.66 (d), 111.40 (d), 124.17 (d, 2C), 128.99 (d, 2C), 144.91 (s), 147.76 (s), 150.26 (s), 155.00 (s). MS (70 eV): *m/z* (%): 350 (9)[M^+], 332 (7), 164 (28), 146 (100), 111 (43). $C_{15}H_{14}N_2O_6S$ (350.35): calcd. C 51.42, H 4.03, N 8.00; found C 51.15, H 4.03, N 8.00.

To a solution of 750 mg (2.14 mmol) *N*-(5-hydroxymethylfuran-2-ylmethyl)-4-nitro-*N*-prop-2-ynylbenzensulfonamide, 239 mg (2.36 mmol) triethylamine and 13.1 mg (107 µmol, 5 mol-%) *N*,*N*-dimethylaminopyridine in 30.0 ml dichloromethane are added 284 mg (2.36 mmol) trimethylacetylchloride and the reaction mixture is stirred for 48 hours at ambient temperature. After hydrolysis, extraction of the aequous phase with dichloromethane and drying of the combined organic layers over $MgSO_4$, the crude product is purified via column chromatography on silica (petrol ether/ethyl acetate, 10:2) yielding 681 mg (73 %) **1u** as colorless solid. M.p. 89-91 °C. R_f (PE:EE, 10:2) = 0.16. IR (film): $\tilde{n}$ = 3274 cm^{-1}, 3110, 2978, 1730, 1606, 1528, 1480, 1401, 1350, 1305, 1278, 1196, 1165, 1148, 1108, 1024, 979, 947, 925, 894, 855, 831, 813, 774, 757, 736, 703, 680, 614. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.19 (s, 9H), 2.09 (t, *J* = 2.4 Hz, 1H), 4.08 (d, *J* = 2.4 Hz, 2H), 4.47 (s, 2H), 4.94 (s, 2H), 6.29 (d, *J* = 3.3 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 8.36 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.10 (q, 3C), 36.45 (t), 38.79 (s), 43.16 (t), 57.90 (t), 74.58 (d), 75.74 (s), 110.87 (d), 111.43 (d), 124.16 (d, 2C), 128.99 (d, 2C), 144.88 (s), 148.24 (s), 150.22 (s), 150.88 (s), 178.00 (s). MS (70 eV): *m/z* (%): 434 (3)[M^+], 332 (22), 162 (61), 146 (89), 110 (12), 94 (25), 57 (100). $C_{20}H_{22}N_2O_7S$ (434.47): calcd. C 55.29, H 5.10, N 6.45; found C 54.47, H 5.09, N 6.23.

7: To a solution of 1.50 ml (38.0 mmol) propargyl alcohol, 8.00 ml (57.0 mmol) triethylamine and 187 mg (4 Mol-%) 4-*N*,*N*-dimethylaminopyridine in about 20 ml dichloromethane are added 3.78 ml (38.0 mmol) furan-2-carbonic acid chloride at 0 °C. The reaction mixture is stirred for further 30 min at 0 °C and 18 hours at ambient temperature. After hydrolysis and extraction of the aequous phase with dichloromethane, the combined organic layers are dried over $MgSO_4$. After column cromatography (hexane/ethyl acatate, 2:1), 3.79 g of **7** (67 %) are obtained as pale yellow liquid. IR (Film, NaCl): $\tilde{n}$ = 3295 cm^{-1}, 3143, 2950, 2402, 2345, 2130, 1729, 1580, 1570, 1508, 1474, 1437, 1398, 1370, 1296, 1232, 1179, 1113, 1076, 1020,

984, 956, 935, 902, 885, 841, 809, 762, 615, 595. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.51 (t, *J* = 2.5 Hz, 1 H), 4.90 (d, *J* = 2.5 Hz, 2 H), 6.53 (dd, *J* = 1.8 Hz, 3.6 Hz, 1 H), 7.25 (d, *J* = 3.6 Hz), 7.60 (d, *J* = 1.8 Hz, 1 H). substance characterized according to [60].

8: According to general procedures 1, 2, 3, 3.07 g (32.3 mmol) pyrrol-2-carboxaldehyde, 2.2 ml (32.1 mmol) propargyl amine, 1.43 g (37.9 mmol) $NaBH_4$, 8.80 ml (63.2 mmol) triethylamine and 12.0 g (63.2 mmol) toluene-4-sulfonic acid chloride are used. After column cromatography (hexane/aceton, 3:1), 3.48 g **8** are obatained as colorless solid (38% 3 steps, JW-16). M.p.: 113-114 °C. R_f (H/A, 3:1) = 0.29. IR (Film, NaCl): $\tilde{n}$ = 3404 cm^{-1}, 3288, 3103, 2922, 2374, 2345, 2119, 1701, 1598, 1543, 1493, 1429, 1410, 1346, 1328, 1307, 1245, 1186, 1161, 1118, 1096, 1066, 1028, 964, 923, 893, 814, 762, 731, 662. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08 (t, *J* = 2.4 Hz, 1 H), 2.45 (s, 3 H), 4.01 (d, *J* = 2.4 Hz, 2 H), 4.31 (s, 2 H), 6.08-6.16 (m, 2 H), 6.78-6.84 (m, 1 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 8.69 (br s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4 (q), 35.6 (t), 42.8 (t), 73.5 (d), 76.7 (s), 107.9 (d), 109.3 (d), 119.09 (d), 124.5 (s), 127.5 (d), 129.5 (d), 136.0 (s, 2 C), 143.6 (s, 2 C). MS (70 eV, *m/z* (%)): 288 (26) [M^+], 133 (43), 132 (47), 105 (50), 91 (21), 80 (100). $C_{15}H_{16}N_2O_2S$ (288.2) calcd.: C 62.51, H 5.55, N 9.72 found: C 62.64, H 5.61, N 9.48.

9: To a solution of 4.30 g (37.9 mmol) potassium-*tert*-butoxide in about 30 ml *N*,*N*-dimethylformamide are added 3.00 g (31.6 mmol) pyrrol-2-carboxaldehyde at 0 °C with heavy stirring wich is then continued for additional 1.5 hours at ambient temperature. After repeated cooling to 10 °C, 8.40 g (44.2 mmol) toluene-4-sulfenic acid chloride in about 30 ml *N*,*N*-dimethylformamide are added and the reaction mixture is stirred for 18 hours at ambient temperature. The black recation mixture is hydrolysed with 800 ml of brine, extracted with ethyl acetate and the organic layer dried over $MgSO_4$. After removal of the solvent, the crude product is recrystallised from diethyl ether. 2.17 g (28 %) 1-(toluene-4-sulfonyl)-1*H*-pyrrol-2-

carboxaldehyde are obtained as colorless crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 6.40 (t, *J* = 3.4 Hz, 1 H), 7.15 (dd, *J* = 1.7, 3.7 Hz, 1 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.62 (dd, *J* = 1.7, 3.0 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 9.97 (s, 1 H).

According to general procedures 1, 2, 3, 2.17 g (8.70 mmol) toluene-4-sulfonyl-pyrrol-2-carboxaldehyde, 720 µl (10.5 mmol) propargyl amine, 460 mg (12.2 mmol) $NaBH_4$, 1.45 mL (10.4 mmol) triethylamine and 1.66 g (8.70 mmol) toluene-4-sulfonic acid chloride are used. After column cromatography (hexane/ethyl acetate, 5:1), 560 mg **9** are obatained as colorless solid (15% 4 steps). M.p.: 107-117 °C. R_f (H/EE, 5:1) = 0.08. IR (Film, NaCl): $\tilde{n}$ = 3309 cm^{-1}, 2374, 2344, 2254, 1708, 1654, 1560, 1543, 1352, 1163, 1093, 908, 733, 650. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (t, *J* = 2.4 Hz, 1 H), 2.42 (s, 3 H), 2.44 (s, 3 H), 3.73 (d, *J* = 2.4 Hz, 2 H), 4.56 (s, 2 H), 6.22 (t, *J* = 3.4 Hz, 2 H), 6.31 (m, 1 H), 7.31 (m, 4 H), 7.72 (d, *J* = 7.0 Hz, 2 H), 7.76 (d, *J* = 7.3 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4 (q), 21.5 (q), 36.0 (t), 42.9 (t), 74.0 (d), 76.1 (s), 111.4 (d), 116.1 (d), 123.8 (d), 127.0 (d, 2 C), 127.8 (s), 127.9 (d, 2 C), 129.3 (d, 2 C), 129.8 (d, 2 C), 135.3 (s), 135.7 (s), 143.6 (s), 144.9 (s). MS (70 eV, *m/z* (%)): 442 (5) [M^+], 287 (67), 222 (20), 155 (33), 91 (100). $C_{22}H_{22}N_2O_4S_2$ (443.3) calcd.: C 59.74, H 4.97, N 6.33 found: C 59.65, H 5.07, N 6.43.

11: According to general procedures 1, 2, 3, 2.56 g (23.8 mmol) 5-methylthiophene-2-carboxaldehyde, 1.63 ml (23.8 mmol) propargyl amine, 1.00 g (26.5 mmol) $NaBH_4$, 3.67 ml (26.4 mmol) triethylamine and 5.03 g (26.4 mmol) toluene-4-sulfonic acid chloride are used. After column cromatography (hexane/ethyl acetate, 5:1), 2.41 mg **11** are obatained as colorless solid (32% 3 steps). M.p.: 81-82 °C. R_f (H/EE, 5:1) = 0.24. IR (Film, NaCl): $\tilde{n}$ = 3281 cm^{-1}, 2921, 2370, 2344, 1734, 1654, 1597, 1560, 1543, 1492, 1438, 1348, 1328, 1260, 1222, 1161, 1118, 1092, 1040, 896, 803. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04 (t, *J* = 2.4 Hz, 1 H), 2.43 (s, 6 H), 4.03 (d, *J* = 2.4 Hz, 2 H), 4.43 (s, 2 H), 6.57 (d, *J* = 3.4 Hz, 1 H), 6.78 (d, *J*

= 3.4 Hz, 1 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.76 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.3 (q), 21.4 (q), 35.1 (t), 44.6 (t), 73.9 (d), 76.2 (s), 124.6 (d), 127.6 (d, 2 C), 127.9 (d, 2 C), 129.4 (d), 134.7 (s), 135.8 (s), 141.1 (s), 143.5 (s). MS (70 eV, *m/z* (%)): 319 (32) [M^+], 164 (100), 163 (52), 136 (68), 111 (76). $C_{16}H_{17}NO_2S_2$ (319.3) calcd.: C 60.19, H 5.32, N 4.38, found: C 60.38, H 5.26, N 4.26.

12: A suspension of 2.00 g (11.7 mmol) 1-phenylethane-1-on-2-ammoniumhydrochloride in about 10 ml dichloromethane is treated with 3.25 ml (2.36 g, 23.3 mmol) triethylamine and 31.2 mg (256 μmol) *N*,*N*-dimethylaminopyridine. At 0 °C, 1.07 ml (2.02 g, 12.8 mmol) bromoacetylchloride are added and the reaction mixture is stirred for one hour at ambient temperature. After hydrolysis, extraction of the aequous phase with dichloromethane and drying over $MgSO_4$, 1.50 g (5.60 mmol) of the crude product are refluxed for one hour with 7.00 ml (excess) $POCl_3$. The reaction mixture is poured on ice, neutralized to pH 7 by adding $NaHCO_3$ and extracted with dichloromethane. After drying over $MgSO_4$, 1.14 g (86 %) of the crude product are added to a solution of 1.17g (5.60 mmol) *N*-(4-toluene-sulfonyl)-propargylamine and 2.37 g (16.8 mmol) K_2CO_3 in about 10 ml of aceton. After 18 hours, the solvent is removed in vacuo, the residue redissolved in water/dichloromethane and the aequous phase extracted with dichloromethane. The crude product is washed with diethyl ether. 948 mg (20 %, 3 steps) **12** are obtained as pale yellow solid. M.p.: 100-103 °C. R_f (PE:EE, 3:1) = 0.21. IR (neat): $\tilde{n}$ = 3285 cm^{-1}, 3029, 2355, 1734, 1598, 1554, 1491, 1450, 1350, 1161, 1121, 1091, 1065, 1032, 1010, 900. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.18 (t, *J* = 2.5 Hz, 1 H), 2.40 (s, 3 H), 4.30 (d, *J* = 2.5 Hz, 2 H), 4.72 (s, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.36 – 7.40 (m, 1 H), 7.42 – 7.47 (m, 2 H), 7.54 – 7.59 (m, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.5 (q), 37.3 (t), 43.1 (t), 74.3 (d), 76.2 (s), 121.9 (d), 124.3 (d), 127.4 (s), 127.6 (d), 128.7 (d), 128.8 (d), 129.6 (d), 135.8 (s), 143.9 (s), 152.2 (s),

157.9 (s). MS (CI, positive-ion, reaktand gas: CH_4): *m/z* (%): 367 (95) [MH^+], 211 (100), 158 (76). $C_{20}H_{18}N_2O_3S$ (366.43): calcd. C 65.55, H 4.95, N 7.64; found C 65.30, H 4.99, N 7.76.

13: 2.66 g (45.0 mmol) acetic amide, 1.77 ml (2.0 g, 15.0 mmol) 3-chloroacetylaceton and ca. 5.0 ml concentrated acetic acid are heated to 145 °C for five hours wtih reflux. After cooling to room temperature, the reaction mixture is poured on ice, made alkaline with sodium hydroxide and extracted with dirchloromethane. After drying over $MgSO_4$ and removal of the solvent, 1.78 (79 %) of crude 2,4-dimethyl-5-acetyloxazole are obtained as pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 2.45 (s, 3 H), 2.49 (s, 3 H).

To a solution of 1.78 g (11.0 mmol) 2,4-Dimethyl-5-acetyloxazol in 10 ml dry methanol are added 545 mg (14.0 mmol) sodium borohydride. The reacion mixture is stirred for two hours at ambient temperature and hydrolysed with NH_4Cl solution. The aequous layer is extracted with dichloromethane. After drying over $MgSO_4$ and removal of the solvent, 1.37 g (89 %) 1-(2,4-Dimethyloxazol-5-yl)-ethanol are obtained as dark yellow oil. R_f (PE:EE, 1:1) = 0.08. IR (neat): $\tilde{n}$ = 3266 cm^{-1}, 2979, 2929, 2870, 1580, 1443, 1407, 1336, 1269, 1216, 1086, 1009, 957, 894. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (d, *J* = 6.5 Hz, 3 H), 1.71 (s, 3 H), 2.01 (s, 3 H), 4.56 (q, *J* = 6.5 Hz, 1 H), 5.10 – 5.54 (bs, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.3 (q), 13.3 (q), 21.1 (q), 59.8 (d), 130.0 (s), 148.3 (s), 159.2 (s). MS (EI, 70 eV): *m/z* (%): 141 (28) [M^+], 126 (100), 68 (12), 42 (18). HRMS (70 eV): $C_7H_{11}NO_2$: calcd. 171.0790; found 141.0798.

360 mg (2.60 mmol) 1-(2,4-Dimethyloxazol-5-yl)-ethanol are dissolved in about 10 ml dry *N*,*N*-dimethylformamide and treated with 62.4 mg (2.60 mmol) sodium hydride. 430 µl (345 mg, 3.90 mmol) propargyl bromide (solution in toluene, 80 % w/w) are added and the reaction mixture is stirred for 18 hours at ambient temperature. After hydrolysis with 100 ml

brine, the aequous phase is extracted with dichloromethane and dried over Na_2SO_4. The crude product is washed with petrol ether and 163 mg (36 %) **13** are obtained as yellow oil. R_f (PE:EE, 1:1) = 0.44. IR (neat): $\tilde{n}$ = 3293 cm^{-1}, 2983, 2929, 2359, 2339, 1582, 1441, 1384, 1334, 1262, 1082. ^1H NMR (CD_3CN, 250 MHz): δ = 1.42 (d, *J* = 7.0 Hz, 3 H), 2.07 (s, 3 H), 2.32 (s, 3 H), 2.66 (t, *J* = 2.6 Hz, 1 H), 3.89 (dd, *J* = 2.6 Hz, 16.0 Hz, 1 H), 4.01 (dd, *J* = 2.6 Hz, 16.0 Hz, 1 H), 4.71 (q, *J* = 7.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 11.2 (q), 14.0 (q), 19.4 (q), 55.1 (t), 66.0 (d), 74.4 (d), 79.6 (s), 134.2 (s), 144.3 (s), 160.7 (s). MS (CI, positive-ion, reactand gas: CH_4): *m/z* (%): 180 (100) [M^+], 124 (24). HRMS (CI, postive-ion): $C_{10}H_{13}NO_2$: calcd. 180.1025; found 180.1021 ([MH]$^+$).

15: 5.44 g (45.0 mmol) acetic amide, 1.77 ml (2.0 g, 15.0 mmol) 3-chloroacetylaceton and ca. 5.0 ml concentrated acetic acid are heated to 145 °C for six hours wtih reflux. After cooling to room temperature, the reaction mixture is poured on ice, made alkaline with sodium hydroxide and extracted with dirchloromethane. After drying over $MgSO_4$ and removal of the solvent, 2.39 (79 %) of crude 2-phenyl-4-methyl-5-acetyloxazole are obtained as pale yellow solid (CK-07). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 2.57 (s, 3 H), 7.41 – 7.59 (m, 3 H), 8.07 – 8.16 (m, 2 H).

To a solution of 1.00 g (4.90 mmol) 2-phenyl-4-methyl-5-acetyloxazole in 10 ml dry methanol are added 226 mg (5.90 mmol) sodium borohydride. The reacion mixture is stirred for two hours at ambient temperature and hydrolysed with NH_4Cl solution. The aequous layer is extracted with dichloromethane. After drying over $MgSO_4$ and removal of the solvent, 953 g (95 %) 1-(4-Methy-2-phenyloxazol-5-yl)ethanol are obtained as pale yellow solid. M.p.: 68 – 69 °C. R_f (PE:EE, 1:1) = 0.11. IR (neat): $\tilde{n}$ = 3292 cm^{-1}, 3065, 2986, 2927, 2359, 1717, 1673, 1449, 1371, 1353, 1273, 1245, 1093, 1072. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.62 (d, *J* = 6.6 Hz, 3 H), 2.23 (s, 3 H), 5.00 (q, *J* = 6.6 Hz, 1 H),7.39 – 7.49 (m, 3 H), 7.96 – 8.08 (m, 2

H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 11.5 (q), 21.7 (q), 61.3 (d), 126.3 (d), 127.2 (s), 128.8 (d), 130.3 (d), 132.8 (s), 148.1 (s), 159.9 (s). MS (CI postitive-ion, reactand gas: CH_4): *m/z* (%): 204 (100) [M^+ + H], 203 (64), 188 (20), 186 (48). $C_{12}H_{13}NO_2$ (203.10): calcd. C 70.92, H 6.45, N 6.89; found C 70.69, H 6.45, N 6.76.

953 mg (4.70 mmol) 1-(4-Methy-2-phenyloxazol-5-yl)ethanol are dissolved in about 10 ml dry *N*,*N*-dimethylformamide and treated with 118 mg (4.90 mmol) sodium hydride. 813 µl (868 mg, 7.40 mmol) propargyl bromide (solution in toluene, 80 % w/w) are added and the reaction mixture is stirred for 18 hours at ambient temperature. After hydrolysis with 100 ml brine, the aequous phase is extracted with dichloromethane and dried over Na_2SO_4. The crude product is washed with petrol ether and 321 mg (27 %) **15** are obtained as yellow oil. M.p.: 23 – 25 °C. R_f (PE:EE, 5:1) = 0.26. IR (neat): $\tilde{n}$ = 3283 cm^{-1}, 2985, 2926, 1717, 1695, 1485, 1449, 1374, 1351, 1263, 1080. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.62 (d, *J* = 6.8 Hz, 3 H), 2.29 (s, 3 H), 2.43 (t, *J* = 2.5 Hz, 1 H), 3.97 (dd, *J* = 2.5 Hz, 15.7 Hz, 1 H), 4.15 (dd, *J* = 2.5 Hz, 15.7 Hz, 1 H), 4.88 (q, *J* = 6.8 Hz, 1 H), 7.47 – 7.57 (m, 3 H), 8.01 – 8.07 (m, 2 H). ^{13}C NMR ($CDCl_3$, 127 MHz): δ = 13.4 (q), 21.5 (q), 57.07 (t), 68.1 (d), 76.4 (d), 81.4 (s), 128.3 (d), 129.2 (s), 130.6 (d), 132.3 (d), 137.7 (s), 146.6 (s), 162.6 (s). MS (EI, 70 eV): *m/z* (%): 241 (21) [M^+], 186 (100), 197 (72), 105 (88), 77 (50). HRMS (70 eV): $C_{15}H_{15}NO_2$: calcd. 241.1103; found 241.1102.

17: According to general procedure 3, 1.60 g (9.57 mmol) 2,4-dimethoxybenzylamine, 970 mg (9.57 mmol) triethylamine and 1.82 g (9.57 mmol) toluene-4-sulfonic acid chloride are used. The crude product is recrystallised from dichloromethane/diethyl ether to yield 2.09 g (68 %) (2,4-Dimethoxybenzyl)prop-2-ynylamine as colorless crystals. M.p.: 96-97 °C. IR (KBR): $\tilde{n}$ = 3222 cm^{-1}, 2869, 1602, 1452, 1330, 1304, 1289, 1191, 1153, 1102, 1075, 1017, 928, 802, 660. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3H), 3.69 (s, 3H), 3.75 (s, 3H), 4.06

(d, *J* = 6.2 Hz, 2H), 5.00 (t, *J* = 6.2 Hz, 1H), 6.31 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.44 (q), 43.21 (t), 55.16 (q), 55.35 (q), 98.34 (d), 103.80 (d), 116.83 (s), 127.01 (d, 2C), 129.32 (d, 2C), 130.45 (d), 137.27 (s), 142.91 (s), 158.19 (s), 160.80 (s). MS (70 eV): *m/z* (%) = 321 (61) (M^+), 166 (100), 152 (63), 121 (30), 91 (32). $C_{16}H_{19}NO_4S$ (321.4): calcd. C 59.79, H 5.96, N 4.36; found C 59.70, H 5.96, N 4.33.

A solution of 1.88 g (5.84 mmol) (2,4-dimethoxybenzyl)prop-2-ynylamine and 2.00 g K_2CO_3 (excess) is treated with 3.85 g (25.8 mmol) propargyl bromide (80% w/w in toluene) and the reaction mixture is stirred for 24 hours at ambient temperature. The solvent is evaporated, the residue redissolved in water/dichloromethane, the aequous phase extracted with dichloromethane, the combined organic layers dried over $MgSO_4$. Recrystallization from diethyl ether/dichloromethane yielded 1.43 g (46 %) **15** as colorless crystals. M.p.: 110 °C. IR (KBr): $\tilde{n}$ = 3228 cm^{-1}, 2992, 2980, 2883, 2809, 2100, 1600, 1500, 1459, 1450, 1430, 1331, 1318, 1281, 1200, 1148, 1102, 1180, 1147, 1118, 1003, 938, 920, 870, 819, 798, 739, 700, 681, 671, 639. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 3.98 (d, *J* = 2.4 Hz, 2H), 4.35 (s, 2H), 6.40-6.47 (m, 2H), 7.28-7.31 (m, 3H), 7.78 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.50 (q), 35.90 (t), 44.24 (t), 55.28 (q), 55.33 (q), 73.36 (d), 76.75 (s), 98.43 (d), 104.19 (d), 115.56 (s), 127.82 (d, 2C), 129.30 (d, 2C), 131.00 (d), 136.37 (s), 143.23 (s), 158.81 (s), 160.77 (s). MS (70 eV): *m/z* (%) = 359 (23) (M^+), 204 (61), 176 (47), 164 (31), 151 (100), 121 (30), 91 (25), 39 (8). $C_{19}H_{21}NO_4S$ (359.4): calcd. C 63.49, H 5.89, N 3.90; found C 63.42, H 5.88, N 3.87.

18: According to general procedures 1, 2, 3, 2.00 g (20.8 mmol) 3-furfural **69**, 1.15 g (20.8 mmol) propargyl amine, 787 mg (20.8 mmol) $NaBH_4$, 2.53 g (18.7 mmol) triethylamine and 3.57 g (18.7 mmol) toluene-4-sulfonic acid chloride are used. The crude product is dried in

vacuo and purified via column chromatography on silica (petrol ether/ethyl acetate, 7:3) to yield 2.1 g (74 %, 2 steps) furan-3-ylmethylprop-2-ynylamine as colorless liquid. R_f (PE/EE, 6:4) = 0.27. IR (Film, NaCl): $\tilde{n}$ = 3278 cm^{-1}, 2889, 2815, 1590, 1491, 1440, 1378, 1320, 1145, 1091, 1050, 1003, 876, 855, 768, 712. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.58 (bs, 1H), 2.24 (t, *J* = 2.4 Hz, 1H), 3.43 (d, *J* = 2.4 Hz, 2H), 3.75 (s, 2H), 6.39-6.40 (m, 1H), 7.38-7.39 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 37.19 (t), 42.59 (t), 71.61 (d), 81.82 (s), 110.49 (d), 123.05 (s), 140.18 (d), 143.18 (d). MS (70 eV): *m/z* (%) = 135 (20)[M^+], 134 (49)[M^+- H], 107 (13), 106 (76), 82 (100), 81 (88), 54 (28), 53 (32), 39 (40). HRMS ($^{12}C_8{}^1H_9{}^{14}N_1{}^{16}O_1$): calcd.: 135.0684; found: 135.0676

Recrystallization from from diethyl ether/dichloromethane yields 2.49 g **18** as colorless solid (49 %, 3 steps). M.p.: 91-92°C. IR (KBr): $\tilde{n}$ = 3278 cm^{-1}, 3117, 2955, 2884, 2840, 2090, 1927, 1558, 1497, 1445, 1422, 1378, 1361, 1332, 1316, 1298, 1246, 1218, 1146, 1109, 1075, 1047, 998, 960, 912, 878, 850, 798, 780, 740, 727, 693, 674, 640, 602, 575, 553, 530, 516. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.03 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.99 (d, *J* = 2.4 Hz, 2H), 4.23 (s, 2H), 6.38 (m, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.36 (m, 1H), 7.37 (m, 1H), 7.75 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 21.44 (q), 35.30 (t), 40.57 (t), 73.97 (d), 76.20 (s), 110.56 (d), 118.99 (s), 127.66 (d, 2C), 129.42 (d, 2C), 135.73 (s), 141.57 (d), 143.58 (d), 143.58 (s). MS (70 eV): *m/z* (%) = 288 (0.5)[M^+], 224 (1.4), 208 (1), 155 (8), 134 (100), 107 (28), 107 (32), 91 (48), 65 (16), 53 (18), 39 (39 (17). $C_{15}H_{15}NO_3S$ (289.4): calcd. C 62.27, H 5.22, N 4.84; found C 62.30, H 5.22, N 4.84.