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Supporting Information

Gold Catalysis: No Steric Limitations in the Phenol Synthesis

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Supporting Information

Experimental Section

General methods: Chemicals (Aldrich, Fluka, Lancaster, and Merck) were used without further purification. Diethyl ether and tetrahydrofuran were dried over sodium. $[\mu\text{-Cl}(AuPPh_3)_2]BF_4$[1] and complex **30**[2] were prepared according to published procedures. NMR spectra were recorded on Bruker ARX500, ARX300 and AMX250 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 DEPT90 and DEPT135 spectra. MS spectra were recorded on a Finnigan MAT 90 or Varian 711. IR spectra were recorded on a Bruker Vector 22.

General procedure 1 (GP 1) – Grignard reaction of aromatic aldehyds: The aldehyde was dissolved in diethyl ether under nitrogen at -40°C, then 2 equivalents propargylmagnesium bromide were added drop wise and stirred for 1 h at 10°C. The mixture was cooled down to 0°C and ammonium chloride was added. The layers were separated and the aqueous layer was extracted with diethyl ether twice, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 2 (GP 2) – Dess-Martin oxidation of homopropargylic alcohols: 1 equivalent of homopropargylic alcohol was dissolved in dichloromethane at room temperature and 1.1 equivalents of Dess-Martin periodinane was added and stirred for 12 h. After completion (monitored by TLC) the crude product was obtained and purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 3 (GP 3) – Silver catalyzed cyclization of allenyl ketones: 1 equivalent of allenyl ketone was dissolved in

acetone at room temperature and 0.22 equivalents of silver nitrate was added and stirred for 12 h in the absence of light. After completion (monitored by TLC) the crude product was obtained and purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 4 (GP 4) – Vilsmeier formylation of substituted furans: At 0°C 2 equivalents phosphorus oxychloride were added to *N,N*-dimethylformamide under nitrogen. Then a solution of 1 equivalent furan in *N,N*-dimethylformamide was added and the reaction mixture was allowed to warm to room temperature and stirred for 30 min before the mixture was heated at 40°C for 12 h. After the reaction mixture was cooled to 0°C, water was added and pH 6 was set. The mixture was extracted with diethyl ether twice, the organic layer was washed with sodium hydrogensulfate, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 5 (GP 5) – Synthesis of substituted sulfonamides: 1 equivalent substituted furfural was dissolved in dichloromethane and 1 equivalent propargyl amine and magnesium sulfate (excess) were added and the mixture stirred at room temperature for 24 h. Dichloromethane was removed under reduced pressure. Methanol was added and the imine was reduced by 1 equivalent of sodium borohydride for 3 h. After water was added the mixture was extracted with dichloromethane twice, dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane 1 equivalent tosyl chloride and 1 equivalent triethyl amine were added and stirred for 12 h at room temperature. After water was added the mixture was extracted with dichloromethane twice, dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 6 (GP 6) – Nitroaldol condensation of substituted furfurals: 2 equivalents of potassium hydroxide were dissolved in 2 equivalents nitromethane and methanol and stirred for 15 min at room temperature. Then a solution of 1 equivalent furfural in methanol was added at 0°C and stirred an additional time of 45 min at room temperature. The reaction mixture was hydrolysed with 50 wt-% hydrochloric acid and the precipitate was washed with water and subsequently dissolved in dichloromethane, the solution was dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 7 (GP 7) – Nitro olefine reduction with lithium aluminium hydride and subsequent tosylation: A solution of 1 equivalent nitro olefine in diethyl ether was added to a suspension of 2 equivalents lithium aluminium hydride in diethyl ether at 0°C under nitrogen. After the addition was complete, the mixture was stirred at reflux for 16h. After cooling to room temperature, 15% aq. NaOH and subsequently water were added. The solid was removed by filtration. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate before the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and 1 equivalent tosyl chloride and 1 equivalent triethyl amine were added. The reaction mixture was stirred for 12 h at room temperature, then water was added. The mixture was extracted with dichloromethane twice, dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 8 (GP 8) – Propargylation of sulfonamides: 1 equivalent of sulfonamide was dissolved in acetone at room temperature and 3 equivalents of caesium carbonate and 3

equivalents of propargyl bromide (80 wt% solution in toluene) were added and stirred over night. The solvent was removed under reduced pressure, the residue was dissolved in water, extracted with dichloromethane, dried over anhydrous sodium sulfate and the solvent was removed in vacuo. Column chromatography on silica gel (hexanes/EtOAc) furnished the propargylated sulfonamides.

General procedure 9 (GP 9) – Gold catalysis: In a NMR tube 1 equivalent of starting material was dissolved in 600 µL of the corresponding deuterated solvent. Then 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 on silica gel (hexanes/EtOAc).

Synthesis of propargylmagnesium bromide[3]: 1.5 g (62.0 mmol) Mg and dry Et_2O was placed into a flask. 60.0 mg $HgCl_2$ were added and the mixture was stirred for 30 min at 20°C, then the mixture was cooled to 0°C and 400 µl propargylbromide was added in one portion to start the reaction within 20 min. The remaining propargylbromide was added dropwise over 30 min and a temperature below 10°C. After an additional 45 min below 10°C the solution was decanted from the excess of Mg.

Synthesis of Adamantane-1-carboxylic acid methylester(34): 4.34 g (24.0 mmol) adamantane carboxylic acid, 2.4 g (72.0 mmol) methanol and 120 mg (630 µmol) *p*-toluenesulfonic acid in 20 ml tetrachloromethane was stirred for 15 h under reflux. Then sodium carbonate solution was added and the reaction mixture was extracted with dichloromethane twice. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.68-1.74 (m, 6H), 1.88-1.89 (m, 6H), 2.01 (m, 3H), 3.65 (s, 3H).
According to lit. [4].

1-Adamantanemethanol(35): 1g (5.15 mmol) **34** was dissolved in 30 ml abs. dichloromethane at -78°C then 11.3 ml of a 1M solution of diisobutylaluminium hydride in n-hexane were added dropwise. After 4.5 h at -78°C methanol was added and the organic layer was washed with water, dried over anhydrous sodium sulfate before the solvent was removed under reduced pressure. 628 mg (74%) **35** was furnished after purification by column chromatography on silica gel. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.53-1.92 (m, 17H), 3.23 (s, 1H).
According to lit. [5].

Adamantane-1-carbaldehyde(21e): 6.20 g (80.0 mmol) dimethylsulfoxide was dissolved in 100 ml abs. dichloromethane at -60°C, 12.60 g (60 mmol) trifluoroacetic anhydride in 40 ml dichloromethane was added drop by drop. After 10 min 6.60 g (40.0 mmol) 1-adamantanemethanol in 80 ml dichloromethane were added and the mixture was stirred for 10 min. Triethyl amine subsequently 6 N hydrochloric acid and finally water were added. The organic layer was extracted, dried over anhydrous sodium sulfate before the solvent was removed under reduced pressure. The residue was destilled under reduced pressure. 4.73 g (72%) **21e** were isolated. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.53-2.07(m, 15H), 9.31 (s, 1H).
According to lit. [5].

1-(2,4,6-Trimethylphenyl)but-3-yn-1-ol(22a): As described in GP 1, 7.00 g (47.0 mmol) **21a**, 67.8 ml (94.5 mmol) propargylmagnesium bromide in 40 ml ethyl ether furnished 8.10 g (94%) **22a**, after purification by column chromatography (hexanes/ethyl acetate, 20:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.07 (t, *J* = 2.6 Hz, 1H), 2.24 (s, 3H), 2.42 (s, 6H), 2.50 (ddd, *J* = 16.9, 5.0, 2.6 Hz, 1H), 2.83 (ddd, *J* = 16.9, 9.4, 2.6 Hz, 1H), 5.35 (dd, *J* = 9.4, 5.0 Hz, 1H), 6.83 (s, 2H).
According to lit.[7].

1-(4-Methoxy-2,6-dimethylphenyl)but-3-yn-1-ol(22b): As described in GP 1, 2.47 g (15.0 mmol) **21b**, 21.5 ml (30.0 mmol)

propargylmagnesium bromide in 20 ml ethyl ether furnished 2.06 g (67%) **22b**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 10:2:1). Mp.: 48-51°C. R_f (hexanes/dichloromethane/ethyl acetate, 10:2:1) = 0.18. IR (neat): $\tilde{\nu}$ = 3486 cm^{-1}, 3261, 2944, 1596, 1454, 1299, 1185, 1140, 1034, 1001, 858, 669, 579. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.07 (t, *J* = 2.6 Hz, 1H), 2.20 (d, *J* = 2.2 Hz, 1H), 2.44 (s, 6H), 2.57 (ddd, *J* = 16.9, 5.3, 2.6 Hz, 1H), 2.87 (ddd, *J* = 16.9, 9.3, 2.6 Hz, 1H), 3.76 (s, 3H), 5.31 (ddd, *J* = 9.3, 5.3, 2.2 Hz, 1H), 6.55 (s, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 21.08 (q, 2C), 26.19 (t), 55.06 (q), 69.96 (d), 70.68 (d), 81.46 (s), 114.62 (d, 2C), 129.98 (s), 137.94 (s, 2C), 158.35 (s). $C_{13}H_{16}O_2$ (204.26): calcd. C 76.44, H 7.90; found C 76.56, H 7.83. MS (EI, 70 eV): *m/z* (%) = 204 (11)[M^+], 165 (100), 137 (11), 122 (13).

1-(2-Methoxy-4,6-dimethylphenyl)but-3-yn-1-ol(22c): As described in GP 1, 1.04 g (6.70 mmol) **21c**, 9.60 ml (13.4 mmol) propargylmagnesium bromide in 15 ml ethyl ether furnished 1.14 g (83%) **22c**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 10:2:1). Mp.: 59-61°C. R_f (hexanes/dichloromethane/ethyl acetate, 10:2:1) = 0.18. IR (neat): $\tilde{\nu}$ = 3249 cm^{-1}, 2917, 1611, 1577, 1458, 1418, 1307, 1227, 1147, 1087, 1007, 843, 696. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.19 (t, *J* = 2.7 Hz, 1H), 2.51 (s, 3H), 2.56 (s, 3H), 2.69 (ddd, *J* = 16.6, 6.7, 2.7 Hz, 1H), 2.85 (ddd, *J* = 16.6, 7.6, 2.7 Hz, 1H), 3.86 (s, 3H), 4.02 (d, *J* = 11.2 Hz, 1H), 5.06 (ddd, *J* = 11.2, 7.6, 6.7 Hz, 1H), 6.60 (s, 1H), 6.62 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.38 (q), 21.78 (q), 27.42 (t), 55.65 (q), 69.77 (d), 69.88 (d), 82.13 (s), 110.35 (d), 124.74 (d), 125.64 (s), 136.96 (s), 138.59 (s), 157.87 (s). $C_{13}H_{16}O_2$ (204.26): calcd. C 76.44, H 7.90; found C 76.31, H 7.84. MS (EI, 70 eV): *m/z* (%) = 204 (6)[M^+], 165 (100), 135 (23).

1-(2,6-Dichlorophenyl)but-3-yn-1-ol(22d): As described in GP 1, 6.00 g (34.0 mmol) **21d**, 50 ml (51.4 mmol) propargylmagnesium

bromide in 40 ml ethyl ether furnished 5.21 g (71%) **22d** as a yellow oil, after purification by column chromatography (hexanes/ethyl acetate, 20:1). R_f (hexanes/ethyl acetate 20:1) = 0.12. IR (neat): $\tilde{\nu}$ = 3299 cm^{-1}, 1581, 1561, 1437, 1182, 1087, 1046, 616. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.03 (t, *J* = 2.7 Hz, 1H), 2.85 (ddd, *J* = 16.8, 6.5, 2.7 Hz, 1H), 3.03 (ddd, *J* = 16.8, 8.4, 2.7 Hz, 1H), 3.08 (d, *J* = 9.2 Hz, 1H), 5.66 (ddd, *J* = 9.2, 8.4, 6.5 Hz, 1H), 7.15-7.18 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 25.38 (t), 70.28 (d), 70.63 (d), 79.81 (s), 129.40 (d, 2C), 129.43 (d), 134.50 (s, 2C), 135.94 (s). $C_{10}H_8Cl_2O$ (215.1): calcd. C 55.84, H 3.75; found C 55.66, H 3.82. MS (EI, 70 eV): *m/z* (%) = 214 (1) [M^+], 175 (100), 139 (10), 111 (30), 75 (27).

1-(2,4,6-Trimethylphenyl)buta-2,3-dien-1-one(23a): As described in GP 2, 3.57 g (19.0 mmol) homo-propargylalcohol **22a**, 8.92 g (21.0 mmol) DMP in 10 ml dichloromethane furnished 2.98 g (84%) **23a**, after purification by column chromatography on silica gel. R_f (PE/EE; 30:1) = 0.30. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.19 (s, 6H), 2.27 (s, 3H), 5.00 (d, *J* = 6.4 Hz, 2H), 6.08 (t, *J* = 6.4 Hz, 1H), 6.80 (s, 2H).
According to lit. [7].

1-(4-Methoxy-2,6-dimethylphenyl)buta-2,3-dien-1-one(23b): As described in GP 2, 1.24 g (6.08 mmol) homo-propargylalcohol **22b**, 2.84 g (6.69 mmol) DMP in 15 ml dichloromethane furnished 1.01 g (83%) **23b**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 40:5:1). R_f (hexanes/dichloromethane/ethyl acetate, 40:5:1) = 0.19. Mp.: 59-60°C. IR (neat): $\tilde{\nu}$ = 3245 cm^{-1}, 2981, 1927, 1637, 1600, 1467, 1448, 1318, 1267, 1094, 1034, 851, 831. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.22 (s, 6H), 3.78 (s, 3H), 5.01 (d, *J* = 6.3 Hz, 2H), 6.09 (t, *J* = 6.3 Hz, 1H), 6.52 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 19.89 (q, 2C), 55.40 (q), 79.03 (t), 98.78 (d), 112.97 (d, 2C), 133.44 (s), 135.94 (s, 2C), 159.69 (s), 200.35 (s), 218.48 (s). MS (EI, 70

eV): *m/z* (%) = 202 (32)[M^+], 163 (100), 135 (15), 91 (12). HRMS (EI, 70 eV): $C_{13}H_{14}O_2$: calcd. 202.0994; found 202.0993.

Acetic acid-3(4-methoxy-2,6-dimethylphenyl)1-methyl-3-oxopropenylester(27): R_f (hexanes/ethyl acetate, 10:1) = 0.30 IR (neat): $\tilde{\nu}$ = 2959 cm^{-1}, 1763, 1605, 1317, 1195, 1160, 1136, 1025, 543. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.18 (s, 3H), 2.25 (s, 6H), 2.26 (d, *J* = 0.9 Hz, 3H), 3.78 (s, 3H), 6.18 (q, *J* = 0.9 Hz, 1H), 6.55 (s, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 18.20 (q), 19.67 (q, 2C), 20.73 (q), 54.69 (q), 112.91 (d, 2C), 118.96 (d), 134.69 (s), 135.26 (s, 2C), 159.41 (s), 162.75 (s), 167.67 (s), 197.72 (s). MS (EI, 70 eV): *m/z* (%) = 262 (29)[M^+], 231 (13), 219 (22), 205 (100), 163 (84), 136 (17), 91 (17), 43 (68). HRMS(EI, 70 eV): $C_{15}H_{18}O_4$: calcd. 262.1205; found 262.1204.

1-(2-Methoxy-4,6-dimethylphenyl)buta-2,3-dien-1-one(23c): As described in GP 2, 1.52 g (7.52 mmol) homo-propargylalcohol **22c** 3.51 g (8.27 mmol) DMP in 18 ml dichloromethane furnished 1.24 g (82%) **23c**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 40:5:1). R_f (hexanes/dichloromethane/ethyl acetate, 40:5:1) = 0.19. Mp.: 48-49°C. IR (neat): $\tilde{\nu}$ = 2989 cm^{-1}, 1957, 1648, 1609, 1577, 1456, 1315, 1265, 1236, 1165, 1095, 1033, 858, 826. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.19 (s, 3H), 2.31 (s, 3H), 3.77 (s, 3H), 5.03 (d, *J* = 6.4 Hz, 2H), 6.10 (t, *J* = 6.4 Hz, 1H), 6.54 (s, 1H), 6.60 (s, 1H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 18.71 (q), 21.51 (q), 55.51 (q), 78.64 (t), 98.02 (d), 109.67 (d), 123.12 (d), 126.63 (s), 131.34 (s), 135.64 (s), 139.89 (s), 156.37 (s), 197.10 (s). $C_{13}H_{14}O_2$ (202.3): calcd. C 77.20, H 6.98; found C 77.08, H 6.99. MS (EI, 70 eV): *m/z* (%) = 202 (31)[M^+], 163 (100).

1-(2,6-Dichlorophenyl)buta-2,3-dien-1-one(23d): As described in GP 2, 2.48 g (11.5 mmol) homo-propargylalcohol **22d** 5.38 g (12.7 mmol) DMP in 20 ml dichloromethane furnished 2.08 g (85%) **23d**, after purification by column chromatography on silica gel (hexanes/

ethyl acetate, 30:1). R_f (hexanes/ethyl acetate 10:1) = 0.22. M.p.: 48°C. IR(neat): $\tilde{\nu}$ = 3309 cm^{-1}, 3062, 2988, 1951, 1909, 1656, 1428, 1294, 877. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 5.12 (d, *J* = 6.3 Hz, 2H), 6.13 (t, *J* = 6.3 Hz, 1H), 7.23-7.32 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 79.86 (t), 97.19 (d), 127.73 (d, 2C), 130.40 (d), 131.41 (s, 2C), 137.87 (s), 192.11 (s), 219.01 (s). $C_{10}H_6Cl_2O$ (213.1): calcd. C 56.37, H 2.84; found C 56.24, H 2.92. MS (EI, 70 eV): *m/z* (%) = 214 (6) [^{36}Cl, M^+], 212 (10) [^{35}Cl, M^+], 173 (100), 145 (17), 109 (13).

1-Adamantan-1-ylbuta-2,3-dien-1-one(23e): As described in GP 2, 1.00 g (4.92 mmol) homo-propargylalcohol **22e** 2.50 g (5.90 mmol) DMP in 40 ml dichloromethane furnished 845 mg (85%) **23e**, after purification by column chromatography on silica gel (hexanes/ ethyl acetate, 30:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.71-2.06 (m, 15H), 5.18 (d, *J* = 6.5 Hz, 2H), 6.20 (t, *J* = 6.5 Hz, 1H).
According to lit. [4]

2-(2,4,6-Trimethylphenyl)furan(24a): As described in GP 3, 1.00 g (5.37 mmol) **23a**, 197 mg (1.92 mmol) silver nitrate in 6 ml acetone furnished 890 mg (89%) **24a**, after purification by column chromatography on silica gel (hexanes/ ethyl acetate, 30:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.54 (s, 6H), 2.16 (s, 3H), 6.25 (m, 1H), 6.48 (m, 1H), 6.92 (s, 2H), 7.49 (m, 1H).
According to lit. [6]

2-(4-Methoxy-2,6-dimethylphenyl)furan(24b): As described in GP 3, 1.13 g (5.56 mmol) **23b**, 210 mg (1.24 mmol) silver nitrate in 15 ml acetone furnished 880 mg (78%) **24b**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 100:5:1). R_f (hexanes/dichloromethane/ethyl acetate, 100:5:1) = 0.21. Mp.: 29-30°C. IR (neat): $\tilde{\nu}$ = 2965 cm^{-1}, 1607, 1463, 1313, 1191, 1154, 1071, 1024, 998, 875, 731, 598. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.17 (s, 6H), 3.81 (s, 3H), 6.23 (m, 1H), 6.47 (m, 1H), 6.64 (s, 2H), 7.49 (m, 1H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ =

20.93 (q, 2C), 55.02 (q), 109.05 (d), 110.28 (d), 112.77 (d, 2C), 123.68 (s), 140.08 (s, 2C), 141.41 (d), 152.25 (s), 159.46 (s). MS (EI, 70 eV): *m/z* (%) = 202 (100)[M^+], 187 (17), 173 (17), 159 (16). HRMS (EI, 70 eV): $C_{13}H_{14}O_2$: calcd. 202.0994; found 202.0994.

2-(2-Methoxy-4,6-dimethylphenyl)furan(24c): As described in GP 3, 299 mg (1.48 mmol) **23c**, 55.0 mg (325 µmol) silver nitrate in 6 ml acetone furnished 228 mg (76%) **24c**, after purification by column chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 100:5:1) R_f (hexanes/dichloromethane/ethyl acetate, 100:5:1) = 0.24. Mp.: 51-52°C. IR (neat): $\tilde{\nu}$ = 3139 cm^{-1}, 2939, 1714, 1613, 1559, 1460, 1373, 1312, 1244, 1171, 1147, 1097, 1005, 897, 842, 738, 598. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.30 (s, 3H), 2.40 (s, 3H), 3.81 (s, 3H), 6.46 (m, 1H), 6.54 (m, 1H), 6.55 (s, 1H), 6.75 (s, 1H), 7.56 (m, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 21.10 (q), 22.05 (q), 56.21 (q), 109.87 (d), 110.46 (d), 110.92 (d), 117.87 (s), 124.03 (d), 139.68 (s), 139.79 (s), 141.87 (d), 150.29 (s), 158.30 (s). $C_{13}H_{14}O_2$ (202.3): calcd. C 77.20, H 6.98; found C 76.88, H 6.96. MS (EI, 70 eV): *m/z* (%) = 202 (100)[M^+], 187 (10), 173 (19), 159 (29).

2-(2,6-Dichlorophenyl)furan(24d): As described in GP 3, 451 mg (2.12 mmol) **23d**, 79.2 mg (466 µmol) silver nitrate in 5 ml acetone furnished 319 mg (71%) **24d**, after purification by column chromatography on silica gel (hexanes/ ethyl acetate, 30:1). R_f (hexanes/ethyl acetate 10:1) = 0.44. M.p.: 29°C. IR (neat): $\tilde{\nu}$ = 3154 cm^{-1}, 3123, 3060, 1425, 1373, 1153, 998, 803. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 6.54-6.57 (m, 2H), 7.23-7.27 (m, 1H), 7.37-7.41 (m, 2H), 7.57-7.60 (m, 1H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 110.51 (d), 111.52 (d), 128.20 (d, 2C), 129.90 (s), 130.27 (d), 136.40 (s), 142.72 (d), 147.59 (s, 2C). $C_{10}H_6Cl_2O$ (213.1): calcd. C 56.37, H 2.84; found C 56.51, H 2.95. MS (EI, 70 eV): *m/z* (%) = 214 (66) [M^+], 212 (100), 183 (32), 149 (82), 113 (23), 74 (14).

2-Adamantan-1-ylfuran(24e): As described in GP 3, 845 mg (4.17 mmol) **23e**, 156 mg (919 µmol) silver nitrate in 5 ml acetone furnished 734 mg (87%) **24e**, after purification by column chromatography on silica gel (hexanes/ ethyl acetate, 50:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.71-2.06 (m, 15H), 5.89 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.25 (dd, *J* = 3.2, 1.8 Hz, 1H), 7.28 (dd, *J* = 1.8, 0.8 Hz, 1H).
According to lit. [7].
5-(2,4,6-Trimethylphenyl)furan-2-carbaldehyde(25a): As h in GP 4, 500 mg (2.68 mmol) furan **24a**, 830 mg (5.37 mmol) phosphorus oxychloride in 3 ml *N,N*-dimethylformamide furnished 490 mg (87%) **25a** as a colourless solid after purification by column chromatography on silica gel (hexanes/ethyl acetate, 30:1). R_f (hexanes/ethyl acetate 30:1) = 0.20. Mp.: 84-86°C. IR (neat): $\tilde{\nu}$ = 2921 cm^{-1}, 2849, 1662, 1525, 1467, 1384, 1349, 1279, 1233, 1188, 1020, 969, 855, 818, 768. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.17 (s, 6H), 2.31 (s, 3H), 6.48 (m, 1H), 7.25 (s, 2H), 7.34 (m, 1H), 9.87 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.82 (q, 2C), 21.57 (q), 112.95 (d), 122.46 (d), 126.79 (s), 128.95 (d, 2C), 138.51 (s, 2C), 140.05 (s), 152.66 (s), 159.66 (s), 178.00 (d). MS (EI, 70 eV): *m/z* (%) = 214 (100)[M$^+$], 157 (28), 142 (13). HRMS (EI, 70 eV): $C_{14}H_{14}O_2$: calcd. 214.0994; found 214.0994.

2-(4-Methoxy-2,6-dimethylphenyl)furan-2-carbaldehyde(25b): As h in GP 4, 140 mg (690 µmol) furan **24b**, 310 mg (2.03 mmol) phosphorus oxychloride in 3 ml *N,N*-dimethylformamide furnished 153 mg (96%) **25b** as a yellow solid after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 10:1) = 0.16. Mp.: 45-47°C. IR: $\tilde{\nu}$ = 3106 cm^{-1}, 2935, 2832, 1654, 1599, 1521, 1469, 1380, 1313, 1236, 1194, 1155, 1074, 1029, 967, 828, 768. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.20 (s, 6H), 3.82 (s, 3H), 6.48 (d, *J* = 3.5 Hz, 1H), 7.27 (s, 2H), 7.35 (d, *J* = 3.5 Hz, 1H), 9.65 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.84 (q, 2C), 55.22 (q), 112.67 (d), 113.18 (d, 2C), 121.89 (s), 122.2 (d), 140.04 (s, 2C), 152.26 (s), 159.24 (s), 160.31 (s), 177.57 (d).

$C_{14}H_{14}O_3$ (230.3): calcd. C 73.03, H 6.13; found C 72.93, H 6.15. MS (EI, 70 eV): *m/z* (%) = 230 (100)[M^+], 173 (39), 115 (13).

2-(2-Methoxy-4,6-dimethylphenyl)furan-2-carbaldehyde(25c): As described in GP 4, 357 mg (1.77 mmol) furan **24c**, 812 mg (5.30 mmol) phosphorus oxychloride in 10 ml *N,N*-dimethylformamide furnished 340 mg (83%) **25c** as a colourless solid after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 10:1) = 0.16. M.p.: 46-48°C. IR: $\tilde{\nu}$ = 2921 cm $^{-1}$, 2837, 1739, 1667, 1609, 1576, 1510, 1462, 1308, 1240, 1167, 1093, 1022, 802, 768. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.33 (s, 3H), 2.35 (s, 3H), 3.79 (s, 3H), 6.63 (s, 1H), 6.70 (d, *J* = 3.7 Hz, 1H), 6.71 (s, 1H), 7.34 (d, *J* = 3.7 Hz, 1H), 9.63 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 21.37 (q), 22.10 (q), 56.09 (q), 109.88 (d), 114.01 (d), 115.97 (s), 122.76 (d), 124.45 (d), 139.68 (s), 141.32 (s), 152.25 (s), 157.29 (s), 158.45 (s), 177.69 (d). MS (EI, 70 eV): *m/z* (%) = 230 (100)[M^+], 173 (14), 159 (10), 115 (10), 55 (13). HRMS (EI, 70 eV): $C_{14}H_{14}O_3$: calcd.230.0943; found 230.0943.

5-(2,6-Dichlorophenyl)furan-2-carbaldehyde(25d): As h in GP 4, 1.28 g (6.01 mmol) furan **24d**, 1.85 g (12.03 mmol) phosphorus oxychloride in 10 ml *N,N*-dimethylformamide furnished 753 mg (52%) **25d** as a colourless solid, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 20:1). R_f (hexanes/ethyl acetate 10:1) = 0.19. M.p.: 59°C. IR (neat): $\tilde{\nu}$ = 3119 cm^{-1}, 3055, 2846, 1667, 1521, 1433, 1417, 1186, 1024, 788. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 6.72 (d, *J* = 3.6 Hz, 1H), 7.24-7.41 (m, 3H), 7.35 (d, *J* = 3.6 Hz, 1H), 9.70 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 114.49 (d), 121.31 (d), 128.35 (d, 2C), 128.42 (s), 129.61 (s), 131.46 (d), 136.31 (s), 152.81 (s), 153.22 (s), 177.96 (d). $C_{11}H_6Cl_2O_2$ (241.1): calcd. C 54.80, H 2.51; found C 54.75, H 2.66. MS (EI, 70 eV): *m/z* (%) = 240 (100) [M^+], 212 (6), 183 (57), 149 (23).

5-Adamantan-1-ylfuran-2-cabaldehyde(25e): As h in GP 4, 734 mg (3.62 mmol) furan **24e**, 1.11 g (7.26 mmol) phosphorus oxychloride in 10 ml *N,N*-dimethylformamide furnished 421 mg (51%) **25e** as a colourless solid, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 20:1). R_f (hexanes/ethyl acetate 20:1) = 0.18. M.p.: 78°C. IR (neat): $\tilde{\nu}$ = 2902 cm^{-1}, 2847, 1667, 1518, 1355, 1189, 1016, 757. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.74-2.08 (m, 15H), 6.18 (d, *J* = 3.4 Hz, 1H), 7.16 (d, *J* = 3.4 Hz, 1H), 9.52 (s, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 28.02 (d, 3C), 35.30 (s), 36.51 (t, 3C), 40.68 (t, 3C), 105.50 (d, 2C), 151.47 (s), 171.47 (s), 177.16 (s). $C_{15}H_{18}O_2$ (230.3): calcd. C 78.23, H 7.88; found C 77.98, H 7.84. MS (EI, 70 eV): *m/z* (%) = 230 (100) [M^+], 201 (2), 187 (6), 173 (34), 137 (12), 117 (6), 94 (11).

4-Methyl-*N*-prop-2-ynyl-*N*-[5-(2,4,6-trimethylphenyl)furan-2-ylmethyl]benzenesulfonamide(26a): As described in GP 5, 490 mg (2.29 mmol) **25a**, 228 µl (3.44 mmol) propargyl amine in 10 ml dichloromethane, subsequently 87.0 mg (2.29 mmol) sodium borohydrid in 10 ml methanol and finally 230 mg (2.29 mmol) triethyl amine and 440 mg (2.29 mmol) tosyl chloride in 5 ml dichloromethane furnished 690 mg (74%) **26a** after purification by column chromatography on silica gel (hexanes/ethyl acetate, 30:1). R_f (hexanes/ethyl acetate 30:1) = 0.12. M.p.: 95°C. IR (neat): $\tilde{\nu}$ = 3263 cm^{-1}, 2916, 2196, 1969, 1349, 1161, 1116, 1088, 1013, 887, 798, 663. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.10 (s, 7H), 2.31 (s, 3H), 2.37 (s, 3H), 4.05 (d, *J* = 2.4 Hz, 2H), 4.50 (s, 2H), 6.16 (d, *J* = 3.2 Hz, 1H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.90 (m, 2H), 7.73 (m, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.86 (q, 2C), 21.49 (q), 21.88 (q), 36.47 (t), 43.29 (t), 74.29 (d), 77.61 (s), 77.66 (s), 110.37 (d), 111.39 (d), 128.18 (d, 2C), 128.66 (d, 2C), 129.80 (d, 2C), 136.48 (s), 138.51 (s, 2C), 138.87 (s), 143.93 (s), 147.93 (s), 153.24 (s). $C_{24}H_{25}NO_3S$ (407.5): calcd. C 70.73, H 6.18, N 3.44, S 7.87; found C 70.70, H 6.23, N 3.38, S 7.89. MS (EI, 70 eV): *m/z* (%) = 407 (100)[M^+], 251 (72), 224 (29), 199 (54), 91 (21).

4-Methyl-*N*-prop-2-ynyl-*N*-[5-(4-methoxy-2,6-dimethylphenyl)furan-2-ylmethyl]benzenesulfonamide(26b): As described in GP 5, 695 mg (3.05 mmol) **25b**, 240 µl (3.44 mmol) propargyl amine in 10 ml dichloromethane, subsequently 115 mg (3.05 mmol) sodium borohydrid in 10 ml methanol and finally 310 mg (3.05 mmol) triethyl amine and 580 mg (3.05 mmol) tosyl chloride in 5 ml dichloromethane furnished 920 mg (71%) **26b** as a colorless solid after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 10:1) = 0.10. Mp.: 105-107°C. IR (neat): $\tilde{\nu}$ = 3256 cm^{-1}, 2920, 2117, 1600, 1452, 1346, 1318, 1304, 1192, 1161, 1116, 1092, 1009, 891, 843. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.10 (t, *J* = 2.5 Hz, 1H), 2.11 (s, 6H), 2.38 (s, 3H), 3.81 (s, 3H), 4.05 (d, *J* = 2.5 Hz, 2H), 4.50 (s, 2H), 6.14 (d, *J* = 3.1 Hz, 1H), 6.39 (d, *J* = 3.1 Hz, 1H), 6.62 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.82 (q, 2C), 21.53 (q), 36.09 (t), 42.96 (t), 55.18 (q), 73.93 (d), 76.68 (s), 110.05 (d), 111.02 (d), 112.84 (d, 2C), 123.38 (s), 127.79 (d, 2C), 129.42 (d, 2C), 136.14 (s), 139.96 (s, 2C), 143.56 (s), 147.52 (s), 152.79 (s), 159.58 (s). $C_{24}H_{25}NO_4S$ (423.5): calcd. C 68.06, H 5.95, N 3.31, S 7.57; found C 67.80, H 5.96, N 3.28, S 7.60. MS (EI, 70 eV): *m/z* (%) = 423 (100)[M^+], 267 (78), 215 (88), 91 (46), 60 (58).

4-Methyl-*N*-prop-2-ynyl-*N*-[5-(2-methoxy-4,6-dimethylphenyl)furan-2-ylmethyl]benzenesulfonamide(26c): As described in GP 5, 106 mg (464 µmol) **25c**, 47.0 µl (696 µmol) propargyl amine in 10 ml dichloromethane, subsequently 87.0 mg (2.29 mmol) sodium borohydrid in 10 ml methanol and finally 47.0 mg (464 µmol) triethyl amine and 88.0 mg (464 µmol) tosyl chloride in 5 ml dichloromethane furnished 106 mg (65%) **26c** as yellow oil after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 10:1) = 0.09. IR (neat): $\tilde{\nu}$ = 3276 cm^{-1}, 2921, 1611, 1599, 1574, 1463, 1348, 1312, 1119, 1092, 1017, 891, 661, 679. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.06 (t, *J* = 2.4 Hz, 1H), 2.17 (s, 3H), 2.32 (s, 3H), 2.34 (s, 3H), 3.73 (s,

3H), 4.05 (d, *J* = 2.4 Hz, 2H), 4.47 (s, 2H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.37 (d, *J* = 3.2 Hz, 1H), 6.59 (s, 1H), 6.66 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.90 (q), 21.57 (q), 21.70 (q), 36.31 (t), 43.23 (t), 55.82 (q), 73.96 (d), 77.01 (s), 109.59 (d), 111.12 (d), 111.21 (d), 117.18 (s), 123.78 (d), 127.85 (d, 2C), 129.53 (d, 2C), 136.33 (s), 139.04 (s), 139.50 (s), 143.59 (s), 147.44 (s), 150.47 (s), 157.81 (s). MS (EI, 70 eV): *m/z* (%) = 423 (100)[M^+], 267 (72), 215 (91), 91 (30). HRMS (EI, 70 eV): $C_{24}H_{25}NO_4S$ calcd. 423.1504; found 423.1506.

***N*[5(2,6-Dichlorophenyl)furan-2-ylmethyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide(26d):** 320 mg (1.32 mmol) **25d**, was reduced by 50.2 mg (1.32 mmol) sodium borohydride in 40 ml methanol for 3 h. After water was added, the mixture was extracted with dichloromethane twice, dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure. The residue was dissolved in tetrahydrofuran, 360 mg (1.72 mmol) 4-Methyl-*N*-prop-2-ynyl-benzenesulfonamide and 451 mg (1.72 mmol) triphenylphosphin were added, the mixture was cooled at 0°C then 299 mg (1.72 mmol) diethylazodicarboxylate were added. The reaction mixture was stirred for 12 h at room temperature. Then the solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate, brine was added and the mixture was extracted with ethyl acetate twice, dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure. After the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 10:1) 468 mg (82%) **26d** was obtained as a yellow oil. R_f (hexanes/ethyl acetate 5:1) = 0.20. IR (neat): $\tilde{\nu}$ = 3293 cm^{-1}, 2921, 1557, 1428, 1347, 1187, 1117, 891. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.11 (t, *J* = 2.4 Hz, 1H), 2.36 (s, 3H), 4.08 (d, *J* = 2.4 Hz, 2H), 4.54 (s, 2H), 6.43-6.47 (m, 2H), 7.21-7.39 (m, 5H), 7.71-7.75 (m, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 21.57 (q), 36.18 (t), 42.81 (t), 73.98 (d), 76.66 (s), 111.14 (d), 112.64 (d), 127.80 (d, 2C), 128.23 (d, 2C), 129.46 (d, 2C), 129.53 (s), 130.39 (d), 136.07

(s), 136.26 (s), 143.58 (s), 147.81 (s), 149.08 (s, 2C). $C_{21}H_{17}Cl_2NO_3S$ (434.3): calcd. C 58.07, H 3.95, N 3.22; found C 58.05, H 4.05, N 3.29. MS (EI, 70 eV): *m/z* (%) = 433 (18) [M^+], 278 (100), 250 (69), 225 (19), 173 (11).

***N*(5-Adamantan-1-ylfuran-2-ylmethyl)-4-methyl-*N*-prop-2-ynylbenzenesulfonamide(26e):** As described in GP 5, 390 mg (1.69 mmol) **25e**, 93.3 mg (1.69 mmol) propargyl amine in 10 ml dichloromethane, subsequently 63.9 mg (1.69 mmol) sodium borohydrid in 10 ml methanol and finally 171 mg (1.69 mol) triethyl amine and 322 mg (1.69 mol) tosyl chloride in 5 ml dichloromethane furnished 296 mg (41%) **26e** as yellow oil after purification by column chromatography on silica gel (hexanes/ethyl acetate, 20:1). R_f (hexanes/ethyl acetate 10:1) = 0.20. IR (neat): $\tilde{\nu}$ = 3279 cm^{-1}, 2902, 2849, 1493, 1348, 1158, 1092, 922. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.70-2.02 (m, 15H), 2.07 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.99 (d, *J* = 2.4 Hz, 2H), 4.41 (s, 2H), 5.80 (d, *J* = 3.1 Hz, 1H), 6.16 (d, *J* = 3.1 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 21.51 (q), 28.18 (d, 3C), 34.45 (s), 36.07 (t), 36.67 (t, 3C), 41.02 (t, 3C), 43.01 (t), 73.56 (d), 76.80 (s), 102.10 (d), 110.44 (d), 127.73 (d, 2C), 129.45 (d, 2C), 136.28 (s), 143.38 (s), 146.04 (s), 165.29 (s). $C_{25}H_{29}NO_3S$ (423.2). MS (CI (+)): *m/z* (%) = 423 (41) [M^+], 268 (100), 240 (65), 222(74), 215 (67), 183 (4), 135 (24). HRMS (CI (+)): calcd. 423.1868; found 423.1874.

2-(2-Nitrovinyl)-5-(2,4,6-trimethylphenyl)-furan(36a): As described in GP 6, 156 mg (728 µmol) furfural **25a**, 89.0 mg (1.46 mmol) nitro methane and 82 mg (1.45 mmol) potassium hydroxyd in 8 ml methanol furnished 90 mg (48%) **36a**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 30:1). R_f (hexanes/ethyl acetate 30:1) = 0.25. M.p.: 161°C. IR (neat): $\tilde{\nu}$ = 2920 cm^{-1}, 1670, 1609, 1558, 1317, 1023. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.21 (s, 6H), 2.33 (s, 3H), 6.47 (d, *J* = 3,4 Hz, 1H), 6.96 (s, 2H), 7.00 (d, *J* = 3.4 Hz, 1H), 7.51 (d, *J* = 13.1 Hz, 1H), 7.80 (d,

J = 13.1 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.55 (q, 2C), 21.14 (q), 113.43 (d), 121.49 (d), 125.51 (d), 126.42 (s), 128.70 (d, 2C), 133.96 (d), 137.99 (s, 2C), 139.65 (s), 145.76 (s), 157.89 (s). MS (EI, 70 eV): *m/z* (%) = 257 (77) [M^+], 214 (100), 157 (28). HRMS (EI, 70 eV): $C_{15}H_{15}NO_3$ calcd. 257.1052; found 257.1051.

2-(2-Nitrovinyl)-5-(4-methoxy-2,6-dimethylphenyl)-furan(36b): As described in GP 6, 296 mg (1.28 mmol) furfural **25b**, 157 mg (2.57 mmol) nitro methane and 144 mg (2.57 mmol) potassium hydroxyd in 8 ml methanol furnished 207 mg (59%) **36b**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 25:1). R_f (hexanes/ethyl acetate 5:1) = 0.44. M.p.: 72°C. IR (neat): $\tilde{\nu}$ = 3111 cm^{-1}, 2960, 1629, 1598, 1487, 1312, 1213, 1029, 945. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.22 (s, 6H), 3.83 (s, 3H), 6.45 (d, *J* = 3.4 Hz, 1H), 6.67 (s, 2H), 6.99 (d, *J* = 3.4 Hz, 1H), 7.51 (d, *J* = 13.2 Hz, 1H), 7.79 (d, *J* = 13.2 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.97 (q, 2C), 55.22 (q), 113.30 (d, 2C), 113.52 (d), 121.62 (d), 121.88 (s), 125.55 (d), 133.90 (d), 139.91 (s), 145.71 (s, 2C), 157.85 (s), 160.21 (s). $C_{15}H_{15}NO_4$ (273.3): calcd. C 65.92, H 5.53, N 5.13; found C 65.75, H 5.58, N 5.06. MS (EI, 70 eV): *m/z* (%) = 273 (96) [M^+], 230 (100), 173 (31), 151 (19), 115 (12).

2-(2-Nitrovinyl)-5-(2-methoxy-4,6-dimethylphenyl)-furan(36c): As described in GP 6, 534 mg (2.32 mmol) furfural **25c**, 284 mg (4.65 mmol) nitro methane and 261 mg (4.65 mmol) potassium hydroxyd in 8 ml methanol furnished 324 mg (50%) **36c**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 25:1). R_f (hexanes/ethyl acetate 5:1) = 0.44. M.p.: 86°C. IR (neat): $\tilde{\nu}$ = 3186 cm^{-1}, 3132, 3050, 2938, 1610, 1500, 1483, 1302, 1033, 804. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.36 (s, 6H), 3.82 (s, 3H), 6.65 (s, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 6.74 (s, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 7.51 (d, *J* = 13.1 Hz, 1H), 7.80 (d, *J* = 13.1 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 21.38 (q), 21.74 (q), 55.72 (q), 109.55 (d), 114.71 (d), 122.14 (d), 124.29 (d), 125.62 (d), 129.73 (s), 133.44 (d), 138.86 (s), 140.81 (s), 145.29 (s), 155.75 (s), 157.85 (s).

$C_{15}H_{15}NO_4$ (273.3): calcd. C 65.92, H 5.53, N 5.13; found C 65.64, H 5.56, N 5.00. MS (EI, 70 eV): *m/z* (%) = 273 (100) [M^+], 230 (97), 173 (19), 141 (9), 115 (10).

4-Methyl-*N*-{2-[5-(2,4,6-trimethylphenyl)furan-2-yl]ethyl}benzenesulfonamide(37a): As described in GP 7, 154 mg (600 µmol) nitro olefine **36a**, 68.3 mg (1.80 mmol) lithium aluminium hydride in 10 ml diethyl ether and finally 114 mg (600 µmol) tosyl chloride, 60.7 mg (600 µmol) triethyl amine in 8 ml dichloromethane furnished 90 mg (39%) **37a,** after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 10:1) = 0.10. M.p.: 91°C. IR (neat): $\tilde{\nu}$ = 3258 cm^{-1}, 2920, 1439, 1324, 1151, 1070, 1053. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.12 (s, 6H), 2.30 (s, 3H), 2.42 (s, 3H), 2.82 (t, *J* =6.4 Hz, 2H), 3.25 (“q”, *J* = 6.4 Hz, 2H), 4.48 (t, *J* = 6.1 Hz, 1H), 6.11 (d, *J* = 3.1 Hz, 1H) 6.13 (d, *J* = 3.1 Hz, 1H), 6.91 (s, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.53 (q, 2C), 21.08 (q), 21.50 (q), 28.41 (t), 41.86 (t), 107.92 (d), 109.85 (d), 127.07 (d, 2C), 127.93 (s), 128.34 (d, 2C), 129.73 (d, 2C), 136.95 (s), 138.06 (s, 2C), 138.41 (s) 143.47 (s), 150.56 (s), 151.45 (s). $C_{22}H_{25}NO_3S$ (383.5): calcd. C 68.90, H 6.57, N 3.65; found C 69.07, H 6.58, N 3.57. MS (EI, 70 eV): *m/z* (%) = 383 (48) [M^+], 212 (51), 199 (100), 155 (21).

***N*-{2[5(4-Methoxy-2,6-dimethylphenyl)furan-2-yl]ethyl}4-methylbenzenesulfonamide(37b):** As described in GP 7, 116 mg (424 µmol) nitro olefine **36b**, 48.3 mg (1.27 mmol) lithium aluminium hydride in 7 ml diethyl ether and finally 80.8 mg (424 µmol) tosyl chloride, 42.9 mg (424 µmol) triethyl amine in 8 ml dichloromethane furnished 50 mg (42%) **37b,** after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.15. M.p.: 38°C. IR (neat): $\tilde{\nu}$ = 3250 cm^{-1}, 2919, 2838, 1598, 1469, 1316, 1150, 1073, 810. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.12 (s, 6H), 2.42 (s, 3H), 2.82 (t, *J* =6.4 Hz, 2H), 3.27 (“q”, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 4.48 (t, *J* =

6.2 Hz, 1H), 6.10-6.11 (m, 2H), 6.63 (s, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.87 (q, 2C), 21.53 (q), 28.37 (t), 41.83 (t), 55.17 (q), 107.92 (d), 109.86 (d), 112.86 (d, 2C), 123.44 (s) 127.05 (d, 2C), 129.73 (d, 2C), 136.84 (s), 139.88 (s, 2C) 143.49 (s), 150.48 (s), 151.61 (s), 159.45 (s). $C_{22}H_{25}NO_4S$ (399.50): calcd. C 66.14, H 6.31, N 3.51; found C 66.55, H 6.52, N 3.54. MS (EI, 70 eV): *m/z* (%) = 399 (41) [M^+], 215 (100), 155 (10), 91 (17).

***N*-{2[5(2-Methoxy-4,6-dimethylphenyl)furan-2-yl]ethyl}4-methylbenzenesulfonamide(37c):** As described in GP 7, 143 mg (523 µmol) nitro olefine **36c**, 59.6 mg (1.57 mmol) lithium aluminium hydride in 7 ml diethyl ether and finally 99.7 mg (523 µmol) tosyl chloride, 52.9 mg (523 µmol) triethyl amine in 8 ml dichloromethane furnished 130 mg (62%) **37c,** after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.15. M.p.: 85°C. IR (neat): $\tilde{\nu}$ = 3278 cm^{-1}, 2922, 2856, 1611, 1598, 1494, 1310, 1154, 1091, 831. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.20 (s, 3H), 2.35 (s, 3H), 2.40 (s, 3H), 2.79 (t, *J* =6.3 Hz, 2H), 3.27 (“q”, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 4.81 (t, *J* = 6.2 Hz, 1H), 6.09 (d, *J* = 3.1 Hz, 1H) 6.29 (d, *J* = 3.1 Hz, 1H), 6.63 (s, 1H), 6.69 (s, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 20.79 (q), 21.48 (q), 21.62 (q), 28.13 (t), 41.92 (t), 55.79 (q), 107.96 (d), 109.04 (d), 110.83 (d), 117.05 (s), 123.60(d) 127.06 (d, 2C), 129.66 (d, 2C), 137.07 (s), 138.58 (s), 139.33 (s) 143.32 (s), 149.07 (s), 150.60 (s), 157.68 (s). $C_{22}H_{25}NO_4S$ (399.5): calcd. C 66.14, H 6.31, N 3.51; found C 65.94, H 6.36, N 3.59. MS (EI, 70 eV): *m/z* (%) = 399 (36) [M^+], 228 (28), 215 (100), 91 (10).

4-Methyl-*N*-prop-2-ynyl-*N*-{2-[5-(2,4,6-trimethylphenyl)furan-2-yl]-ethyl}-benzenesulfonamide(38a): As described in GP 8, 70 mg (205 µmol) sulfonamide **37a**, 87.7 mg (614 µmol) propargyl bromide (80 wt% solution in toluene) and 577 mg (1.77 mmol) caesium carbonate in 5 ml acetone furnished 33.4 mg (39%) **38a**, after purification by

column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 5:1) = 0.20. M.p.: 100°C. IR (neat): $\tilde{\nu}$ = 3253 cm^{-1}, 2949, 2918, 1373, 1307, 1120, 1070, 795. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.03 (t, *J* = 2.5 Hz, 1H), 2.18 (s, 6H), 2.31 (s, 3H), 2.42 (s, 3H), 2.95-3.01 (m, 2H), 3.47-3.53 (m, 2H), 4.11 (d, *J* = 2.5 Hz, 2H), 6.15 (d, *J* = 3.1 Hz, 1H), 6.19 (d, *J* = 3.1 Hz, 1H), 6.92 (s, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 20.57 (q, 2C), 21.08 (q), 21.52 (q), 27.65 (t), 37.00 (t), 45.44 (t), 73.76 (d), 76.69 (s), 107.45 (d), 109.90 (d), 127.68 (d, 2C), 128.20 (s), 128.28 (d, 2C), 129.48 (d, 2C), 135.94 (s), 138.21 (s), 138.26 (s), 143.52 (s), 151.00 (s, 2C), 151.28 (s). MS (CI,positiv-Ion): *m/z* (%) = 421 (100) [M^+], 222 (66), 199 (36), 155 (17), 91 (9). HRMS (EI, 70 eV): $C_{25}H_{27}NO_3S$ (421.6) calcd. 421.1712; found 421.1714.

4-Methyl-*N*-prop-2-ynyl-*N*-{2-[5-(4-methoxy-2,6-dimethylphenyl)furan-2-yl]-ethyl}-benzenesulfonamide(38b): As described in GP 8, 130 mg (324 µmol) sulfonamide **37b**, 145 mg (974 µmol) propargyl bromide (80 wt% solution in toluene) and 317 mg (974 µmol) caesium carbonate in 5 ml acetone furnished 114 mg (80%) **38b**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.26. M.p.: 72°C. IR (neat): $\tilde{\nu}$ = 3253 cm^{-1}, 2963, 2918, 2834, 1598, 1437, 1258, 1119, 1015. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.03 (t, J = 2.4 Hz, 1H), 2.18 (s, 6H), 2.42 (s, 3H), 2.98 (t, *J* = 7.3 Hz, 2H), 3.49 (m, 2H), 3.80 (s, 3H), 4.10 (d, *J* = 2.4 Hz, 2H), 6.13 (d, *J* = 3.1 Hz, 1H), 6.18 (d, *J* = 3.1 Hz, 1H), 6.63 (s, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.90 (q, 2C), 21.54 (q), 27.65 (t), 36.98 (t), 45.41 (t), 55.16 (q), 73.77 (d), 76.67 (s), 107.45 (d), 109.92 (d), 112.81 (d, 2C), 123.75 (s), 127.68 (d, 2C), 129.48 (d, 2C), 129.60 (s), 135.92 (s), 140.04 (s, 2C), 143.52 (s), 150.95 (s), 159.38 (s). MS (EI, 70 eV): *m/z* (%) = 437 (39) [M^+], 222 (77), 215 (100), 155 (61), 91 (34). HRMS (EI, 70 eV): $C_{25}H_{27}NO_4S$ (437.6) calcd. 437.1661; found 437.1661.

***N*-{2-[5-(2-Methoxy-4,6-dimethylphenyl)furan-2-yl]-ethyl}-4-methyl-*N*-prop-2-ynylbenzenesulfonamide(38c):** As described in GP 8, 49.5 mg (124 µmol) sulfonamide **37c**, 55.3 mg (372 µmol) propargyl bromide (80 wt% solution in toluene) and 121 mg (372 µmol) caesium carbonate in 5 ml acetone furnished 35.3 mg (65%) **38c**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.26. M.p.: 89°C. IR (neat): $\tilde{\nu}$ = 3249 cm^{-1}, 2922, 1574, 1463, 1313, 1156, 1035, 1015, 968, 810. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.03 (t, *J* = 2.4 Hz, 1H), 2.25 (s, 3H), 2.34 (s, 3H), 2.41 (s, 3H), 2.97-3.00 (m, 2H), 3.49-3.52 (m, 2H), 3.77 (s, 3H), 4.10 (d, *J* = 2.4 Hz, 2H), 6.19 (d, *J* = 3.1 Hz, 1H), 6.33 (d, *J* = 3.1 Hz, 1H), 6.61 (s, 1H), 6.69 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.86 (q), 21.53 (q), 21.62 (q), 27.75 (t), 37.00 (t), 45.40 (t), 55.73 (q), 73.66 (s), 76.84 (d), 107.73 (d), 109.32 (d), 110.88 (d), 117.33 (s), 123.58 (d) 127.70 (d, 2C), 129.46 (d, 2C), 135.92 (s), 138.99 (s), 139.17 (s), 143.48 (s), 148.72 (s), 150.86 (s), 157.64 (s). $C_{25}H_{27}NO_4S$ (437.6): calcd. C 68.62, H 6.22, N 3.20; found C 68.21, H 6.24, N 3.16. MS (EI, 70 eV): *m/z* (%) = 437 (34) [M^+], 222 (30), 215 (100), 155 (31), 91 (19).

2-(Toluene-4-sulfonyl)-5-(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-isoindol-4-ol(28a): As described in GP 9, 50 mg (123 µmol) **26a** and 2.50 mg (6.13 µmol) catalyst **30** in chloroform furnished in 20 h 43.5 mg (87%) **28a**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 5:1). R_f (hexanes/ethyl acetate 5:1) = 0.19. M.p.: 163-166°C. IR (neat): $\tilde{\nu}$ = 3383 cm^{-1}, 2917, 1590, 1458, 1343, 1294, 1211, 1154, 1097, 1062, 803, 662. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.95 (s, 6H), 2.32 (s, 3H), 2.42 (s, 3H), 4.64 (d, *J* = 1.1 Hz, 2H), 4.66 (d, *J* = 1.1 Hz, 2H), 4.68 (s, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 2H), 7.33 (m, 2H), 7.81 (m, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.55 (q, 2C), 21.43 (q), 21.89 (q), 52.04 (t), 54.46 (t), 114.97 (d), 122.89

(s), 125.80 (s), 128.09 (d, 2C), 129.29 (d, 2C), 130.16 (d, 2C), 130.37 (d), 130.84 (s), 134.53 (s), 137.92 (s, 2C), 138.23 (s), 138.80 (s), 143.89 (s), 147.95 (s). MS (EI, 70 eV): *m/z* (%) = 407 (26)[M^+], 251 (100), 132 (12), 91 (26). HRMS (EI, 70 eV): $C_{24}H_{25}NO_3S$: calcd. 407.1555; found 407.1553.

2-(Toluene-4-sulfonyl)-5-(4-methoxy,2,6-dimethylphenyl)-2,3-dihydro-1*H*-isoindol-4-ol(28b): As described in GP 9, 58.0 mg (137 µmol) **26b** and 41.5 mg (6.84 µmol) gold(III)-chloride (5 wt% solution in acetonitrile) in acetonitrile furnished in 10 h 51.0 mg (88%) **28b**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 5:1). R_f (hexanes/ethyl acetate 5:1) = 0.15. M.p.: 150-153°C. IR (neat): $\tilde{\nu}$ = 3452 cm^{-1}, 2920, 2842, 1589, 1457, 1340, 1319, 1300, 1234, 1157, 1099, 998, 660, 591. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.96 (s, 6H), 2.42 (s, 3H), 3.82 (s, 3H), 4.65 (m, 5H), 6.71 (s, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 20.60 (q, 2C), 21.55 (q), 51.66 (t), 54.08 (t), 55.20 (q), 113.51 (d, 2C), 114.58 (d), 122.42 (s), 125.16 (s), 125.57 (s), 127.73 (d, 2C), 129.81 (d, 2C), 130.34 (d), 134.04 (s), 137.57 (s), 139.57 (s, 2C), 143.54 (s), 147.82 (s), 159.59 (s). $C_{24}H_{25}NO_4S$ (423.5): calcd. C 68.06, H 5.95, N 3.31; found C 68.03, H 6.26, N 3.06. MS (EI, 70 eV): *m/z* (%) = 423 (48)[M^+], 267 (100), 91 (17).

2-(Toluene-4-sulfonyl)-5-(2-methoxy,4,6-dimethylphenyl)-2,3-dihydro-1*H*-isoindol-4-ol(28c): As described in GP 9, 21.0 mg (49.6 µmol) **26c** and 15.0 mg (2.46 µmol) gold(III)-chloride (5 wt% solution in acetonitrile) in acetonitrile furnished in 50 min 18.5 mg (88%) **28c**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 5:1). R_f (hexanes/ethyl acetate 5:1) = 0.13. M.p.: 65-66°C. IR (neat): $\tilde{\nu}$ = 3422 cm^{-1}, 2921, 2858, 1595, 1570, 1456, 1302, 1157, 1093, 812. ^{1}H-NMR (CD_3CN, 300 MHz): δ = 1.89 (s, 3H), 2.35 (s, 3H), 2.41 (s, 3H), 3.63 (s, 3H), 4.56 (d, *J* = 1.4 Hz, 2H), 4.63 (d, *J* = 1.4 Hz, 2H), 6.14 (s, 1H), 6.74 (s,

1H), 6.76 (s, 1H), 6.83 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ = 20.40 (q), 21.86 (q), 21.97 (q), 52.15 (t), 54.49 (t), 56.13 (q), 109.86 (d), 114.66 (d), 120.26 (s), 122.97 (s), 123.19 (s), 124.35 (d), 128.04 (d, 2C), 130.12 (d, 2C), 131.50 (d), 134.22 (s), 137.74 (s), 139.60 (s), 140.05 (s), 143.88 (s), 148.56 (s), 157.62 (s). MS (EI, 70 eV): *m/z* (%) = 423(37)[M^+], 267 (100). HRMS (EI, 70 eV): $C_{24}H_{25}NO_4S$: calcd. 423.1504; found 423.1505.

5(2,6-Dichlorophenyl)-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-isoindol-4-ol(28d): As described in GP 9, 30.8 mg (70.9 µmol) **26d** and 1.45 mg (3.45 µmol) complex **30** in chloroform furnished in 3 days 19.5 mg (63%) **28d**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 2:1) = 0.40. M.p.: 172°C. IR (neat): $\tilde{\nu}$ = 3365 cm^{-1}, 2923, 2854, 1592, 1556, 1427, 1340, 1305, 1154, 1096, 780. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.41 (s, 3H), 4.66 (s, 4H), 4.83 (s, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 7.25-7.45 (m, 5H), 7.78 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 21.55 (q), 51.70 (t), 54.17 (t), 114.84 (d), 122.53 (s), 123.51 (s), 127.69 (d, 2C), 128.59 (d, 2C), 129.88 (d, 2C), 130.52 (d), 130.62 (d), 133.43 (s), 133.85 (s), 136.36 (s, 2C), 139.03 (s), 143.71 (s), 147.73 (s). MS (EI, 70 eV): *m/z* (%) = 433 (12) [M^+], 278 (100), 207 (58), 155 (22). HRMS (EI, 70 eV): $C_{21}H_{17}Cl_2NO_3S$: calcd. 433.0306; found 433.0300.

2-(2,6-Dichlorophenyl)-4-methylene-6-(toluene-4-sulfonyl)-4,5,6,7-tetrahydrofuro[2,3-*c*]pyridine(31): As described in GP 9, 39.8 mg (91.6 µmol) **26d** and 4.77 mg (4.58 µmol) complex **32** in chloroform furnished in 2 days 15.5 mg (39%) **28d** and 17.0 mg (43%) **31**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 5:1) = 0.49. M.p.: 53°C. IR (neat): $\tilde{\nu}$ = 2924 cm^{-1}, 2850, 1694, 1655, 1494, 1344, 1190, 1089, 814. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.37 (s, 3H), 4.12 (t, *J* = 1.3 Hz, 2H), 4.51 (s, 2H), 4.98 (m, 1H), 5.07 (m, 1H), 6.45 (s, 1H),

7.20-7.40 (m,, 5H), 7.66 (d, *J* = 8.3 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 21.51 (q), 43.75 (t), 49.50 (t), 77.20 (s), 107.64 (t), 107.87 (d), 119.27 (s), 127.60 (d, 2C), 128,24 (d, 2C), 129.50 (d, 2C), 130.64 (d), 132.32 (s), 134.22 (s), 136.28 (s, 2C), 143.60 (s), 147.26 (s), 147.38 (s). MS (EI, 70 eV): *m/z* (%) = 433 (14) [M^+], 277 (100), 214 (16), 173 (31), 91 (53). HRMS (EI, 70 eV): $C_{21}H_{17}Cl_2NO_3S$: calcd. 433. 0306; found 433. 0299.

5-Adamantan-1-yl-2(toluene-4-sulfonyl)-2,3-dihydro-1*H*-isoindol-4-ol(28e): As described in GP 9, 27.0 mg (63.7 µmol) **26e** and 1.3 mg (3.19 µmol) complex **30** in chloroform furnished in 10 min 17.9 mg (67%) **28e**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 5:1) = 0.20. M.p.: 230°C. IR (neat): $\tilde{\nu}$ = 3447 cm^{-1}, 2903, 2844, 1737, 1492, 1311, 1251, 1157, 799. ^{1}H-NMR (CD_2Cl_2, 500 MHz): δ = 1.75-2.04 (m, 15H), 2.38 (s, 3H), 4.53-4.54 (m, 4H), 4.71 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR (CD_2Cl_2, 126 MHz): δ = 21.61 (q), 29.46 (d, 3C), 36.90 (s), 37.20 (t, 3C), 41.40 (t, 3C), 51.82 (t), 54.38 (t), 114.99 (d), 124.34 (s), 127.47 (d), 127.95 (d, 2C), 130.24 (d, 2C), 133.96 (s), 135.75 (s), 135.86 (s), 144.36 (s), 150.04 (s). MS (EI, 70 eV): *m/z* (%) = 423 (10)[M^+], 268 (100), 210 (13), 135 (21), 91 (47). HRMS: $C_{25}H_{29}NO_3S$ (423.2): calcd. 423.1868; found 423.1867.

2-(Toluene-4-sulfonyl)-7-(2,4,6-trimethylphenyl)-1,2,3,4-tetrahydro-isoquinolin-8-ol(39a): As described in GP 9, 13.6 mg (32.2 µmol) **38a** and 661 µg (1.61 µmol) complex **30** in chloroform furnished in 3 days 5.6 mg (40%) **39a**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 10:1). R_f (hexanes/ethyl acetate 5:1) = 0.16. M.p.: 73°C. IR (neat): $\tilde{\nu}$ = 3516 cm^{-1}, 2920, 1440, 1375, 1159, 1018. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.95 (s, 6H), 2.33 (s, 3H), 2.42 (s, 3H), 2.97 (t, *J* = 5.8 Hz, 2H), 3.38 (t, *J* = 5.8 Hz, 2H), 4.23 (s, 2H), 4.66 (s, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.98 (s, 2H), 7.33

(d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 20.18 (q, 2C), 21.07 (q), 21.51 (q), 28.95 (t), 43.48 (t), 43.62 (t), 118.69 (d), 120.59 (d), 123.47 (s), 127.79 (s), 127.81 (d, 2C), 128.84 (d, 2C), 129.66 (d, 2C), 130.87 (s), 133.33 (s), 133.79 (s), 137.97 (s, 2C), 138.26 (s), 143.48 (s), 148.64 (s). MS (EI 70 eV): *m/z* (%) = 421 (26) [M^+], 265 (100), 238 (36), 147 (6), 119 (3), 91 (18). HRMS (EI, 70 eV): $C_{25}H_{27}NO_3S$ (421.55) calcd. 421.1712; found 421.1715.

7-(4-Methoxy-2,6-dimethylphenyl)-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-isoquinolin-8-ol(39b): As described in GP 9, 35.0 mg (80.0 µmol) **38b** and 1.64 mg (4.00 µmol) complex **30** in chloroform furnished in 5 days 21.6 mg (62%) **39b**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.11. M.p.: 166°C. IR (neat): $\tilde{\nu}$ = 2923 cm^{-1}, 2832, 1600, 1577, 1465, 1439, 1368, 1335, 1161, 1151, 991. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.97 (s, 6H), 2.42 (s, 3H), 2.97 (t, *J* = 5.8 Hz, 2H), 3.38 (t, *J* = 5.8 Hz, 2H), 3.82 (s, 3H), 4.23 (s, 2H), 4.68 (s, 1H), 6.71 (s, 2H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.58 (q, 2C), 21.52 (q), 28.96 (t), 43.48 (t), 43.62 (t), 55.17 (q), 113.41 (d, 2C), 118.62 (s), 120.55 (d), 123.21 (s), 126.00 (s), 127.80 (d, 2C), 128.11 (d), 129.66 (d, 2C), 133.31 (s), 133.82 (s), 139.64 (s, 2C) 143.47 (s), 148.89 (s), 159.45 (s). $C_{25}H_{27}NO_4S$ (437.6): calcd. C 68.62, H 6.22, N 3.20; found C 68.27, H 6.33, N 3.17. MS (EI, 70 eV): *m/z* (%) = 437 (30) [M^+], 281 (100), 254 (28), 91 (9).

7-(2-Methoxy-4,6-dimethylphenyl)-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-isoquinolin-8-ol(39c): As described in GP 9, 25.5 mg (58.4 µmol) **38c** and 1.20 mg (2.92 µmol) complex **30** in chloroform furnished in 2 h 13.5 mg (53%) **39c**, after purification by column chromatography on silica gel (hexanes/ethyl acetate, 8:1). R_f (hexanes/ethyl acetate 5:1) = 0.11. M.p.: 215°C. IR (neat): $\tilde{\nu}$ =3498 cm^{-1}, 2920, 2831, 1604, 1571, 1440, 1333, 1154, 1094, 991.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.00 (s, 3H), 2.37 (s, 3H), 2.42 (s, 3H), 2.95-2.99 (m, 2H), 3.30-3.43 (m, 2H), 3.71 (s, 3H), 4.21 (d, *J* = 15.8 Hz, 1H), 4.28 (d, *J* = 15.8 Hz, 1H), 4.92 (s, 1H), 6.66 (s, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.78 (s, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 20.08 (q), 21.52 (q), 21.63 (q), 29.04 (t), 43.43 (t), 43.73 (t), 55.78 (q), 109.52 (d), 119.07 (s), 120.34 (d), 120.78 (s), 123.96 (d), 127.80 (d, 2C), 128.89 (d), 129.72 (d, 2C), 129.74 (s), 133.35 (s), 133.80 (s), 139.34 (s), 139.50 (s), 143.42 (s), 149.34 (s), 157.32 (s). MS (EI, 70 eV): *m/z* (%) = 466 (12) [$M(C_2H_5)^+$], 438 (100) [MH^+], 282 (59), 254 (13), 157 (6). HRMS (CI, (+)): $C_{25}H_{27}NO_4S$ (437.6): calcd. 437.1661; found 437.1638.

[1] R. Uson, A. Laguna, M. V. Castrillo, *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 317-324.

[2] A. Dar, K. Moss, S. M. Cottrill, R. V. Parish, C. A. McAuliffe, R. G. Pritchard, B. Beagley, J. Sandbank, *J. Chem. Soc. Dalton Trans.* **1992**, *1*, 1907-1913.

[3] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1971**, 34-37, 94-97, 103.

[4] C. H. Ridyard, R. A. Whittaker, S. D. Higgins, S. M. Roberts, A. J. Willets, *J. Chem. Soc*. Perkin Trans. **1996,** *2*, 1811-1820.

[5] A. K. Kar, D. A. Lightner, *J. Heterocycl. Chem*. **1998**, *35*, 795-804.

[6] N. Platzer, N. Ronzani, C. Lang, C. Lange, *Org. Magn. Res.* **1982**, *18*, 14-18.

[7] A. S. K. Hashmi, T. L. Rupert, T. Knöfel, J. W. Bats, *J. Org. Chem.* **1997**, *62*, 7295-7304.