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Supporting Information

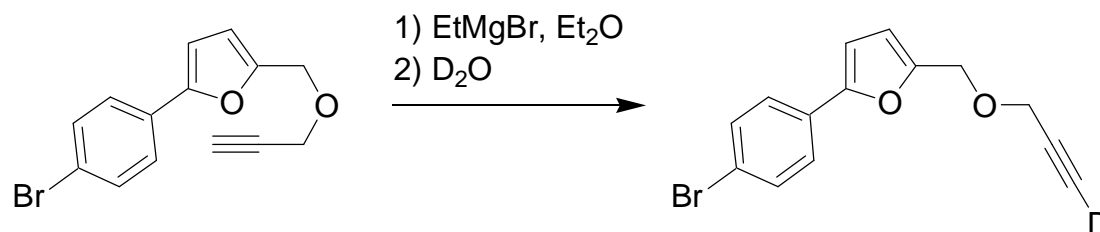
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Gold Catalysis: Deuterated Substrates as the Key for an Experimental Insight into the Mechanism and the Selectivity of the Phenol Synthesis

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and Wolfgang Frey

Supporting Information

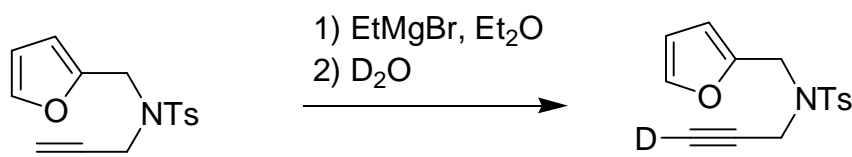
2-(4-Bromophenyl)-5-[[^{3-²H}prop-2-yn-1-yloxy]methyl]furan (**3**):



The undeuterated substrate (200 mg, 687 μmol) was dissolved in 20 ml of absolute Et_2O . The solution was cooled to -40°C and the EtMgBr (2.07 ml (1 M in Et_2O), 2.07 mmol) was added. After warming to room temperature over 1 hour the reaction was quenched with D_2O (126 μl , 6.90 mmol). After column chromatography on silica, using hexanes/ethyl acetate (3:1) as eluent, product **3** (190 mg, 94 %) was isolated as a colourless solid

Mp.: 58°C . R_f (PE:EE, 3:1) = 0.24. IR (solid): $\nu(\text{tilde}) = 3227\text{ cm}^{-1}$, 2909, 2554, 1952, 1476, 1405, 1382, 1352, 1263, 1199, 1179, 1065, 1025, 1005, 957, 930, 920, 825. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 2.49$ (t, $J = 2.3$ Hz, 8.2% H), 4.21 (s, 2 H), 4.61 (s, 2 H), 6.61 (d, $J = 3.3$ Hz, 1 H), 6.65 (d, $J = 3.3$ Hz, 1 H), 7.49 (d, $J = 8.6$ Hz, 2 H), 7.54 (d, $J = 8.6$ Hz, 2 H). $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 56.93$ (t), 63.30 (t), 75.12 (t, $J = 38.3$ Hz), 78.93 (t, $J = 7.4$ Hz), 106.36 (d), 112.56 (d), 121.46 (s), 125.54 (d, 2 C), 129.65 (s), 131.93 (d, 2 C), 150.84 (s), 153.59 (s). MS (EI (+)): m/z (%): 291 [$\text{M}]^+$ (59), 250 (30), 235 (100), 205 (13), 183 (10), 155 (14), 128 (44), 115 (16), 57 (11). $\text{C}_{14}\text{H}_{10}\text{DBrO}_2$ (292.15): calcd C 57.56, H+D 3.79; found C 57.88, H+D 3.96.

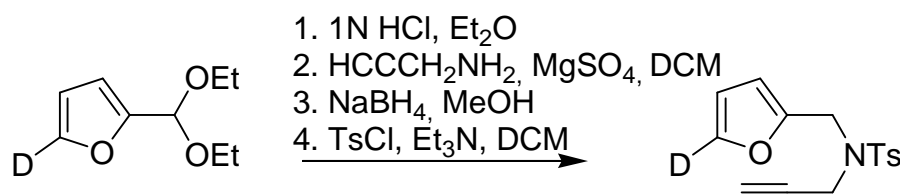
N-(Furan-2-ylmethyl)-4-methyl-*N*-(^{3-²H}prop-2-yn-1-yl)benzenesulfonamide (**6**)



The undeuterated substrate (1.00 g, 3.46 mmol) was dissolved in 40 ml of absolute Et_2O . The solution was cooled to -40°C and the EtMgBr (10.4 ml (1 M in Et_2O), 10.4 mmol) was added. After warming up to -20°C over 1 hour the reaction was quenched with D_2O (34.6 mmol, 625 μl). After column chromatography on silica, using hexanes/ethyl acetate (3:1) as eluent, product **6** (994 mg, 99 %) was isolated as a colourless solid.

Mp.: 61 °C. R_f (PE:EE, 5:1) = 0.21. IR (solid): $\nu(\text{tilde}) = 3145 \text{ cm}^{-1}$, 3128, 2984, 2913, 2583, 1978, 1597, 1503, 1435, 1348, 1324, 1158, 1147, 1114, 1091, 1053, 953, 910, 884, 813, 753, 727, 662. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.07$ (t, $J = 2.4$ Hz, 0.3 % H), 2.43 (s, 3 H), 4.02 (s, 2 H), 4.43 (s, 2 H), 6.29-6.31 (m, 2 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 7.35 (dd, $J = 1.7, 0.9$ Hz, 1 H), 7.73 (d, $J = 8.2$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 21.58$ (q), 36.13 (t), 42.72 (t), 73.71 (t, $J = 38.3$ Hz), 76.13 (t, $J = 7.4$ Hz), 110.14 (d), 110.55 (d), 127.90 (d, 2 C), 129.64 (d, 2 C), 136.10 (s), 143.12 (s), 143.77 (s), 148.75 (s). MS (EI(+)): m/z (%): 290 (4) $[\text{M}]^+$, 135 (100), 107 (34), 91 (31), 81 (45), 65 (8), 53 (15). $\text{C}_{15}\text{H}_{14}\text{DNO}_3\text{S}$ (290.36): calcd C 62.05, H+D 5.21, N 4.82; found C 62.13, H+D 5.28, N 4.81.

***N*-[(5- ^2H)Furan-2-ylmethyl]-4-methyl-*N*-prop-2-yn-1-ylbenzenesulfonamide (**8**):**

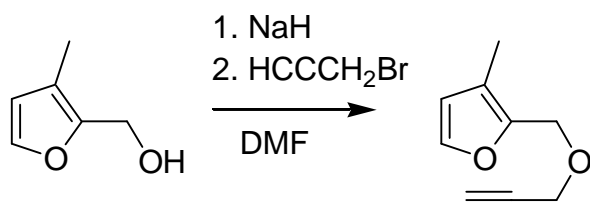


Diethylacetal-protected 2-*d*-furfural (1.5 g, 8.8 mmol) was dissolved in 30 ml Et_2O . After adding 15 ml of 1 N HCl, the mixture was stirred for 2 hours at room temperature. The solution was extracted with 3×20 ml DCM and 2×20 ml NaHCO_3 -solution. The combined organic phases were collected and MgSO_4 (5.00 g, 41.5 mmol) and propargylamine (665 μl , 9.70 mmol) was added. After 16 hours at room temperature the MgSO_4 was filtered off, the filtrate was concentrated in vacuo and redissolved in MeOH. 330 mg (8.80 mmol) of NaBH_4 were added and the reaction mixture was stirred for 3 hours at room temperature. 10 ml H_2O were added and the aqueous phase was extracted with 3×20 ml DCM. The combined organic layers were dried with NaSO_4 and the solvent was removed in vacuo. The residue was dissolved in 20 ml DCM and TsCl (1.68 g, 8.80 mmol) and Et_3N (1.22 ml, 8.80 mmol) were added. After 16 hours 20 ml H_2O were added, the solution was extracted with 3×20 ml DCM, dried with MgSO_4 and the solvent was removed. Column chromatography on silica, using hexanes/ethyl acetate (5:1) as eluent, provided product **8** (1.18 g, 46 %) as a colourless solid

Mp.: 61 °C. R_f (PE:EE, 5:1) = 0.22. IR (solid): $\nu(\text{tilde}) = 3281 \text{ cm}^{-1}$, 2983, 2914, 2359, 1597, 1467, 1434, 1347, 1324, 1157, 1114, 1090, 1053, 1017, 888, 814, 764, 727, 662; ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.07$ (t, $J = 2.3$ Hz, 1 H), 2.43 (s, 2 H), 4.02 (d, $J = 2.3$ Hz, 2 H), 4.43 (s, 2 H), 6.29-6.31 (m, 2 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 7.35 (d, $J = 8.2$ Hz, 2 H). ^{13}C NMR

(CDCl₃, 126 MHz): δ = 21.69 (q), 36.26 (t), 42.83 (t), 74.07 (d), 76.59 (s), 110.14 (d), 110.34 (d), 127.90 (d, 2 C), 129.64 (d, 2 C), 136.11 (s), 142.89 (t, J = 30.9 Hz), 143.77 (s), 148.67 (s). MS (EI(+)): m/z (%): 290 (3) [M]⁺, 135 (100), 107 (27), 91 (31), 82 (43), 66 (6), 54 (13). C₁₅H₁₄DNO₃S (290.36): calcd C 62.05, H+D 5.23, N 4.82; found C 61.82, H+D 5.17, N 4.79.

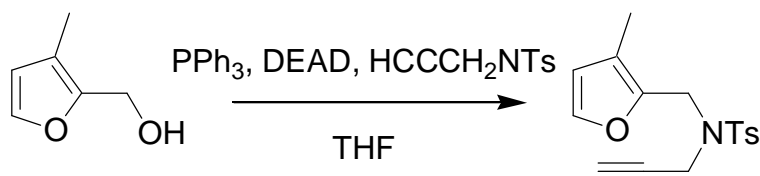
3-Methyl-2-[(prop-2-yn-1-yloxy)methyl]furan (10a):



3-Methylfurfuryl alcohol (500 mg, 4.46 mmol) was dissolved in 10 ml of DMF and NaH (128 mg, 5.35 mmol) were added at 0°C. The solution was stirred for 30 minutes and propargylbromid (636 mg, 5.35 mmol, 80% in toluene) was added. After 16 hours the reaction was quenched with 20 ml H₂O and extracted with 3 × 20 ml Et₂O. After drying with MgSO₄ and evaporation, column chromatography on silica, using hexanes/ethyl acetate (10:1) provided product **10a** (652 mg, 97 %) as a yellow oil.

R_f (PE:EE, 10:1) = 0.21. IR (solid): $\nu(\text{tilde})$ = 3289 cm⁻¹, 2860, 1507, 1442, 1350, 1156, 1122, 1071, 937, 891, 747. ¹H NMR (CDCl₃, 500 MHz): δ = 2.08 (s, 3 H), 2.46 (t, J = 2.4 Hz, 1 H), 4.13 (d, J = 2.4 Hz, 2 H), 4.54 (s, 2 H), 6.22 (d, J = 1.8 Hz, 1 H), 7.32 (d, J = 1.8 Hz, 1 H). ¹³C NMR (CDCl₃, 126 MHz): δ = 10.13 (q), 56.81 (t), 61.29 (t), 74.89 (d), 79.92 (s), 113.26 (d), 120.23 (s), 142.47 (d), 146.65 (s). MS (EI(+)): m/z (%): 150 (44) [M]⁺, 120 (27), 95 (100), 65 (10), 53 (8), 41 (23), 39 (30). C₉H₁₀O₂ (150.17): calcd C 71.98, H 6.71; found C 71.68, H 6.86.

4-Methyl-N-[(3-methylfuran-2-yl)methyl]-N-prop-2-yn-1-ylbenzolsulfonamid (10b):

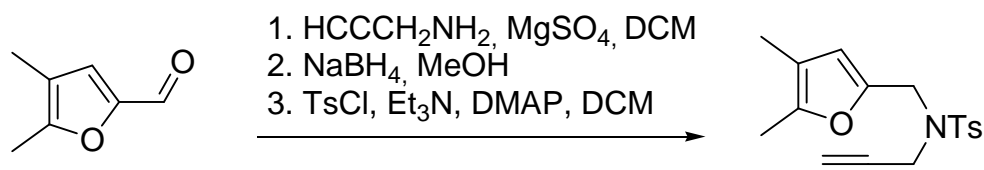


3-Methylfurfuryl alcohol (250 mg, 2.23 mmol), and tosylated propargylamine (561 mg, 2.68 mmol) were dissolved in 15 ml of THF. After addition of PPh₃ (790 mg, 3.01 mmol) and DEAD (480 μ l, 3.01 mmol) at 0°C, the reaction mixture was stirred for 16 hours at room

temperature, then the solvent was removed, column chromatography on silica using hexanes/ethyl acetate (20:1) as eluent, provided product **10b** (544 mg, 80 %) as a colourless solid.

Mp.: 68 °C. R_f (PE:EE, 10:1) = 0.17. IR (solid): $\nu(\text{tilde}) = 3275 \text{ cm}^{-1}$, 2923, 1598, 1346, 1154, 1106, 1090, 1034, 921, 885, 816, 777, 735, 664, 585. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 2.03$ (s, 3 H), 2.05 (t, $J = 2.4$ Hz, 1 H), 2.43 (s, 3 H), 3.98 (d, $J = 2.4$ Hz, 2 H), 4.39 (s, 2 H), 6.17 (d, $J = 2.0$ Hz, 1 H), 7.26 (m, 1 H), 7.29 (d, $J = 8.4$ Hz, 2 H), 7.74 (d, $J = 8.4$ Hz, 2 H). $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 9.86$ (q), 21.71 (q), 36.13 (t), 40.92 (t), 73.85 (d), 76.91 (s), 113.15 (d), 119.92 (s), 127.94 (d, 2 C), 129.60 (d, 2 C), 136.20 (s), 142.24 (d), 143.68 (s), 143.95 (s). MS (EI(+)): m/z (%): 303 (3) $[\text{M}]^+$, 148 (100), 120 (37), 95 (58), 65 (11), 41 (11). $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$ (303.38): calcd C 63.34, H 5.65, N 4.62; found C 62.96, H 5.60, N 4.57.

***N*-[(4,5-Dimethylfuran-2-yl)methyl]-4-methyl-*N*-prop-2-yn-1-ylbenzenesulfonamide (12):**

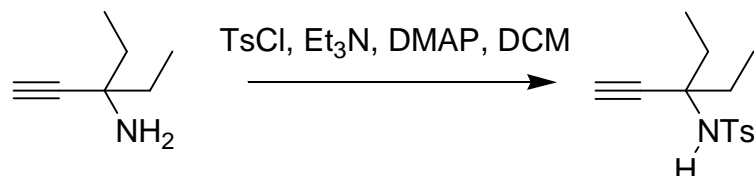


4,5-Dimethylfurfural (1.00 g, 8.06 mmol) was dissolved in 30 ml of DCM. MgSO_4 (5.00 g, 41.5 mmol) and propargylamine (1.22 ml, 16.1 mmol) were added. After stirring for 16 hours at room temperature, the MgSO_4 was filtered off and the filtrate was evaporated. After the residue was dissolved in MeOH, NaBH_4 (335 mg, 8.87 mmol) was added in small portions over 30 minutes. After 2 hours, water was added and the mixture was extracted with 3×30 ml DCM. The combined organic layers were dried with MgSO_4 and the solvent was removed in vacuo. The residue was dissolved in 40 ml DCM and TsCl (1.52 g, 8.06 mmol), Et_3N (1.12 ml, 8.06 mmol) and DMAP (9.84 mg, 80.6 μmol) were added. After 16 hours 30 ml H_2O were added, the solution was extracted with 3×30 ml DCM, dried with MgSO_4 and the solvent was removed. Column chromatography on silica, using hexanes/ethyl acetate (20:1) as eluent, provided product 12 (1.49 g, 58%) as a colourless solid.

Mp.: 109 °C. R_f (PE:EE, 10:1) = 0.18. IR (solid): $\nu(\text{tilde}) = 3281 \text{ cm}^{-1}$, 2921, 1598, 1371, 1346, 1326, 1220, 1158, 1093, 1064, 1000, 967, 917, 890, 817, 801, 751, 713, 680, 659, 609, 585. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.87$ (s, 3 H), 2.05 (t, $J = 2.4$ Hz, 1 H), 2.11 (s, 3 H), 2.42 (s, 3 H), 4.02 (d, $J = 2.4$ Hz, 2 H), 4.33 (s, 2 H), 6.05 (s, 1 H), 7.28 (d, $J = 8.2$ Hz, 2 H), 7.73 (d, $J = 8.2$ Hz, 2 H). $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 9.78$ (q), 11.35 (q), 21.57 (q),

35.99 (t), 42.85 (t), 73.79 (d), 76.67 (s), 113.42 (d), 114.64 (d), 127.83 (d, 2 C), 129.61 (d, 2 C), 136.14 (s), 143.60 (s), 145.26 (s), 148.15 (s). MS (EI(+)): m/z (%): 317 (23) $[M]^+$, 162 (81), 134 (67), 109 (100), 91 (32), 65 (13), 43 (32). $C_{17}H_{19}NO_3S$ (317.40): calcd C 64.33, H 6.03, N 4.41; found C 64.14, H 6.09, N 4.41.

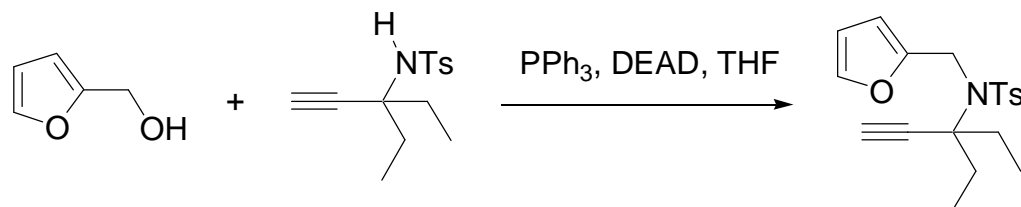
***N*-(1,1-Diethylprop-2-yn-1-yl)-4-methylbenzenesulphonamide:**



The amin (1.00 g, 8.99 mmol) was dissolved in 30 ml DCM, and Et_3N (2.10 ml, 15.0 mmol), DMAP (11.0 mg, 90.0 μmol) and TsCl (1.99 g, 10.0 mmol) were added. After 16 hours the solution was quenched with 30 ml H_2O and extracted with 3×30 ml DCM. After the combined organic phases were dried with $MgSO_4$, the solvent was removed in vacuum, and the residue was dissolved in Et_2O and crystallization yielded the product (1.80 g, 75%) as colourless crystals.

Mp.: 72 °C. R_f (PE:EE, 4:1) = 0.23. IR (solid): $\nu(\text{tilde}) = 3279\text{ cm}^{-1}$, 2976, 1596, 1460, 1406, 1315, 1163, 1143, 1092, 1035, 986, 965, 881, 657. 1H NMR ($CDCl_3$, 500 MHz): $\delta = 0.93$ (t, $J = 7.4$ Hz, 6 H), 1.78 (q, $J = 7.4$ Hz, 4 H), 2.15 (s, 1 H), 2.42 (s, 3 H), 4.79 (bs), 7.26 (d, $J = 8.3$ Hz, 2 H), 7.79 (d, $J = 8.3$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 8.32$ (q, 2 C), 21.48 (t, q), 32.33 (t, 2 C), 58.55 (s), 73.72 (d), 83.04 (s), 127.52 (d, 2 C), 129.15 (d, 2 C), 139.26 (s), 143.00 (s). MS (EI(+)): m/z (%): 265 $[M]^+$, 236 (100), 155 (61), 91 (72), 65 (12). HRMS (CI (+)): $C_{14}H_{19}NO_2S$: calcd 265.1132; found. 265.1129.

***N*-(1,1-Diethyl-prop-2-yn-1-yl)-*N*-furan-2-ylmethyl-4-methyl-benzenesulfonamide(16):**



Furfuryl alcohol (149 mg, 1.52 mmol), and *N*-(1,1-diethylprop-2-yn-1-yl)-4-methylbenzenesulphonamide (200 mg, 0.76 mmol) were dissolved in 20 ml of THF. After the addition of PPh_3 (472 mg, 1.80 mmol) and DEAD (283 μl , 1.80 mmol) at 0°C, the reaction mixture was stirred for 16 hours at room temperature. After the solvent was removed column

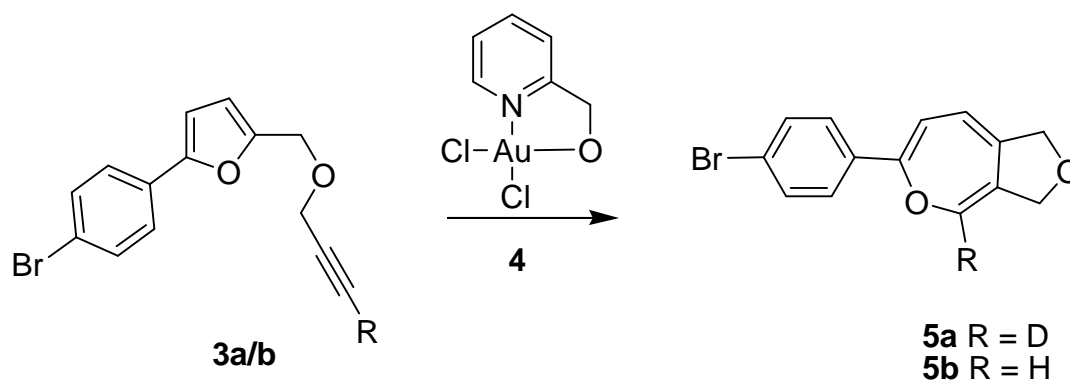
chromatography on silica, using hexanes/ethyl acetate (20:1) as eluent, provided product **16** (119 mg, 45 %) as a yellow oil.

Mp.: 186 °C. R_f (PE:EE, 20:1) = 0.24. IR (solid): $\nu(\text{tilde}) = 3270 \text{ cm}^{-1}$, 2973, 2880, 1598, 1461, 1329, 1158, 1090, 1006, 933, 892, 833, 632. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.89$ (t, $J = 7.5$ Hz, 6 H), 1.84-1.91 (m, 2 H), 2.21-2.19 (m, 2 H), 2.39 (s, 3 H), 2.44 (s, 1 H), 4.75 (s, 2 H), 6.29 (m, 2 H), 7.19 (d, $J = 8.3$ Hz, 2 H), 7.29 (m, 1 H), 7.60 (d, $J = 8.3$ Hz, 2 H). $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 9.50$ (q, 2 C), 21.62 (q), 32.78 (t, 2 C), 44.64 (t), 67.39 (s), 75.95 (d), 83.57 (s), 109.34 (d), 110.70 (d), 127.62 (d, 2 C), 129.23 (d, 2 C), 139.91 (s), 141.43 (d), 142.89 (s), 152.36 (s). MS (ESI(+)): m/z (%): 368 $[\text{M}+\text{Na}]^+$. HRMS (ESI (+)): $\text{C}_{19}\text{H}_{23}\text{N}_1\text{NaO}_3\text{S}$: calcd 368.1291; found 368.1290.

General procedure for gold catalysis

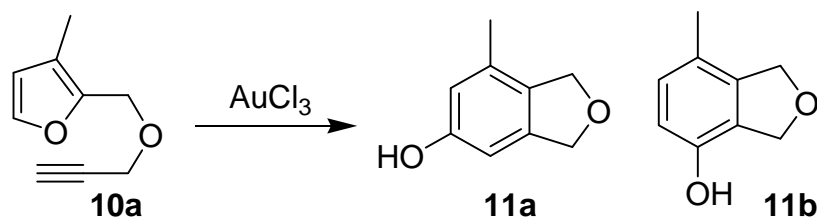
1 Equivalent of starting material was dissolved in 600 μl of the corresponding deuterated solvent in a NMR tube or for larger scale reactions in undeuterated solvents in normal flasks. Then 3-5 mol% of the catalyst precursor were added and the reaction was monitored by $^1\text{H NMR}$ or in undeuterated solvents by TLC. After completion the solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel (hexanes/ethyl acetate).

Preparation of 5a/b



According to the general procedure, **3a** (20.0 mg, 68.5 μmol) and catalyst **4** (1.28 mg, 3.40 μmol) were monitored by $^1\text{H NMR}$ in CDCl_3 . After 30 minutes intermediate **5** had formed and could be analyzed by $^1\text{H NMR}$.^[1] $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 4.64$ (m, 4 H), 5.32 (s, 1 H (**5b**); 9% H (**5a**)), 6.24 (d, $J = 7.7$ Hz, 1 H), 6.34 (d, $J = 7.7$ Hz, 1 H), 7.46 (d, $J = 8.8$ Hz, 2 H), 7.51 (d, $J = 8.8$ Hz, 2 H).

7-Methyl-1,3-dihydro-2-benzofuran-5-ol (11a) and 7-methyl-1,3-dihydro-2-benzofuran-4-ol (11b):

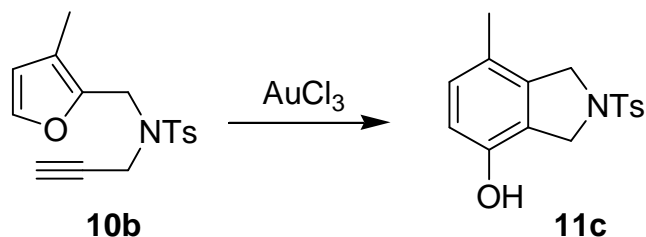


According to the general procedure **10a** (190 mg, 0.98 mmol) and AuCl_3 (19 mg, 63 μmol) in 10 ml CH_3CN furnished after 2 hours **11b** (170 mg, 90%) as colourless crystals and **11a** (7.8 mg, 4.1%) as a colourless solid (column chromatography using hexanes/ethyl acetate (20:1) as eluent).

11a: Mp.: 97 °C. R_f (PE:EE, 5:1) = 0.16. IR (solid): $\nu(\text{tilde}) = 3226 \text{ cm}^{-1}$, 2850, 1606, 1460, 1370, 1319, 1256, 1137, 1052, 1025, 989, 891, 843, 799, 735, 657. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.18$ (s, 3 H), 5.02-5.03 (m, 2 H), 5.06-5.08 (m, 2 H), 5.16 (t, $J = 2.3$ Hz, 1 H), 6.52-6.53 (m, 1 H), 6.53-6.55 (m, 1 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 18.99$ (q), 72.89 (t), 73.99 (t), 105.28 (d), 115.45 (d), 130.20 (s), 132.73 (s), 140.48 (s), 155.82 (s). MS (EI(+)): m/z (%): 150 [M] $^+$, 122 (48), 121 (100), 107 (39), 91 (40), 77 (42). HRMS (EI (+)): $\text{C}_9\text{H}_{10}\text{O}_2$: calcd 150.0681; found 150.0671.

11b: Mp.: 121 °C. R_f (PE:EE, 5:1) = 0.18. IR (solid): $\nu(\text{tilde}) = 3186 \text{ cm}^{-1}$, 2843, 1606, 1508, 1469, 1446, 1363, 1318, 1283, 1155, 1058, 1037, 991, 946, 888, 797, 688, 604. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.16$ (s, 3 H), 5.04 (s, 1 H), 5.08 (s, 2 H), 5.17 (s, 2 H), 6.58 (d, $J = 8.0$ Hz, 1 H), 6.91 (d, $J = 8.0$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 18.04$ (q), 72.40 (t), 73.79 (t), 114.20 (d), 123.43 (s), 124.84 (s), 129.77 (d), 140.22 (s), 148.15 (s). MS (EI(+)): m/z (%): 150 (100) [M] $^+$, 122 (34), 121 (82), 107 (27), 91 (20), 77 (23). $\text{C}_9\text{H}_{10}\text{O}_2$ (150.17): calcd C 71.98, H 6.71; found C 71.66, H 6.76.

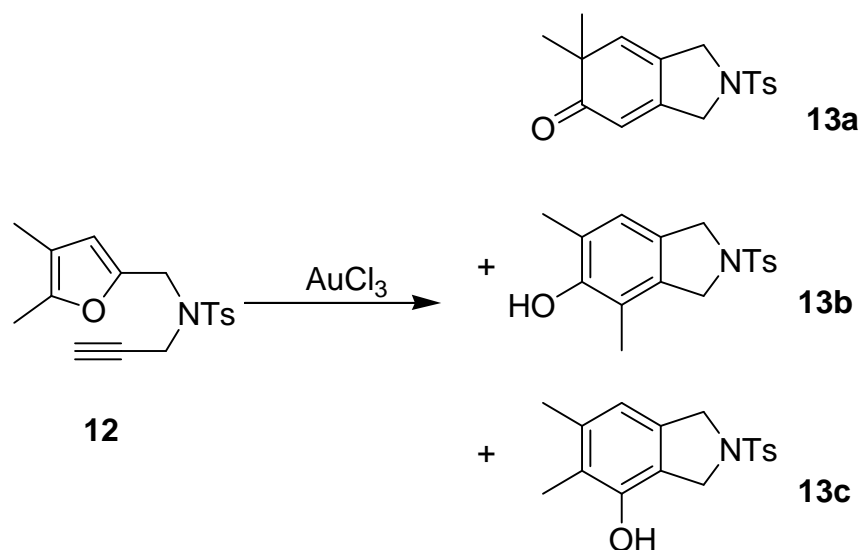
7-Methyl-2-[(4-methylphenyl)sulfonyl]-2,3-dihydro-1-isoindol-4-ol (11c):



According to the general procedure **10b** (750 mg, 0.25 mmol) and 3.80 mg (12.5 μmol) AuCl_3 in CDCl_3 furnished after 1 hour 66.0 mg (88%) of **11c** as a colourless solid (column chromatography using hexanes/ethyl acetate (10:1) as eluent).

Mp.: 214°C. R_f (PE:EE, 3:1) = 0.18. IR (solid): $\nu(\text{tilde}) = 3384 \text{ cm}^{-1}$, 2965, 2920, 2848, 1595, 1454, 1304, 1285, 1262, 1149, 1101, 813, 713, 694, 658, 585, 569. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.07$ (s, 3 H), 2.38 (s, 3 H), 4.49 (s, 2 H), 4.56 (s, 2 H), 5.43 (bs, 1 H), 6.55 (d, $J = 8.0$ Hz, 1 H), 6.82 (d, $J = 8.0$ Hz, 1 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 7.74 (d, $J = 8.2$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 17.73$ (q), 21.50 (q), 52.08 (t), 53.59 (t), 114.39 (d), 122.24 (s), 123.83 (s), 127.57 (d, 2 C), 129.79 (d), 129.88 (d, 2 C), 133.69 (s), 136.65 (s), 143.73 (s), 149.28 (s). MS (EI(+)): m/z (%): 303 [$\text{M}]^+$, 147 (100), 146 (18), 139 (10), 91 (36). HRMS (EI (+)): $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$: *cacd* 303.0929; found 303.0920.

6,6-Dimethyl-2-[(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydro-5H-isoindol-5-one (13a), 4,6-Dimethyl-2-[(4-methylphenyl)sulfonyl]-2,3-dihydro-1H-isoindol-5-ol (13b) and 5,6-Dimethyl-2-[(4-methylphenyl)sulfonyl]-2,3-dihydro-1H-isoindol-4-ol (13c):



According to the general procedure **12** (500 mg, 1.58 mmol) and AuCl_3 (24.0 mg, 79.0 μmol) in 10 ml CH_3CN furnished after 1 hour **13c** (257 mg, 51%) as colourless solid, **13b** (51 mg, 10%) as a colourless solid and **13a** (50 mg, 10%) as a yellow solid (column chromatography using hexanes/ethyl acetate/dichloromethane (10:2:1) as eluent).

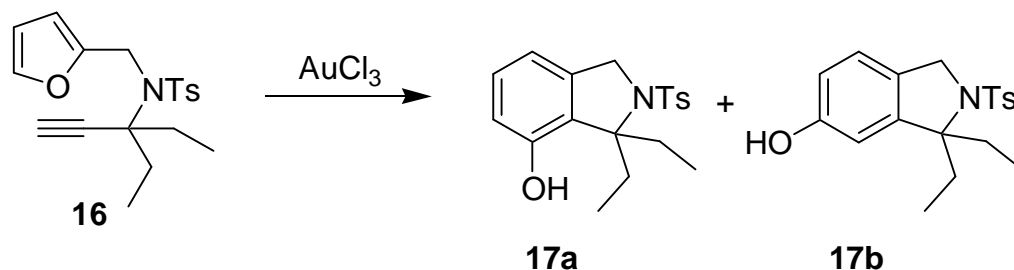
13a: Mp.: 68 °C. R_f (PE:EE:DCM, 10:2:1) = 0.21. IR (solid): $\nu(\text{tilde}) = 3145 \text{ cm}^{-1}$, 2965, 1716, 1595, 1361, 1298, 1246, 1163, 1090, 1051, 806, 772, 673, 657, 581. ^1H NMR (acetone- d_6 , 500 MHz): $\delta = 1.01$ (s, 6 H), 2.41 (s, 3 H), 2.68 (d, $J = 1.1$ Hz, 2 H), 3.42 (d, $J = 1.1$ Hz, 2 H), 7.05-7.06 (m, 2 H), 7.43 (d, $J = 8.3$ Hz, 2 H), 7.82 (d, $J = 8.3$ Hz, 2 H). ^{13}C NMR (acetone-

d^6 , 126 MHz): $\delta = 21.47$ (q), 24.77 (q, 2 C), 35.48 (t), 35.86 (t), 44.39 (s), 117.37 (d), 117.45 (d), 123.79 (s), 124.73 (s), 127.69 (d, 2 C), 130.96 (d, 2 C), 137.29 (s), 146.13 (s), 211.96 (s). MS (EI(+)): m/z (%): 317 $[M]^+$, 289 (30), 134 (100), 92 (38), 91 (42), 65 (15). HRMS (EI (+)): $C_{17}H_{19}NO_3S$: calcd 317.1086; found 317.1082.

13b: Mp.: 144 °C. R_f (PE:EE, 2:1) = 0.24. IR (solid): $\nu(\text{tilde}) = 2919\text{ cm}^{-1}$, 1595, 1470, 1334, 1226, 1189, 1158, 1095, 1066, 821, 668. $^1\text{H NMR}$ (acetone- d^6 , 500 MHz): $\delta = 2.09$ (s, 3 H), 2.17 (s, 3 H), 2.38 (s, 3 H), 4.486 (s, 2 H), 4.492 (s, 2 H), 6.80 (s, 1 H), 7.29 (s, 1 H), 7.41 (d, $J = 8.3$ Hz, 2 H), 7.79 (d, $J = 8.3$ Hz, 2 H). $^{13}\text{C NMR}$ (acetone- d^6 , 126 MHz): $\delta = 12.59$ (q), 16.89 (q), 21.38 (q), 54.00 (t), 54.56 (t), 119.38 (s), 122.42 (d), 125.07 (s), 127.36 (s), 128.52 (d, 2 C), 130.65 (d, 2 C), 134.91 (s), 134.93 (s), 144.45 (s), 153.47 (s). MS (EI(+)): m/z (%): 317 $[M]^+$, 162 (44), 161 (100), 91 (27), 65 (8). HRMS (EI (+)): $C_{17}H_{19}NO_3S$: calcd 317.1086; found 317.1079.

13c: Mp.: 237 °C. R_f (PE:EE, 2:1) = 0.30. IR (solid): $\nu(\text{tilde}) = 3421\text{ cm}^{-1}$, 1591, 1455, 1337, 1302, 1251, 1151, 1111, 1084, 1048, 833, 813, 706, 672. $^1\text{H NMR}$ (DMSO- d^6 , 500 MHz): $\delta = 1.98$ (s, 3 H), 2.11 (s, 3 H), 2.386 (s, 3 H), 4.42 (s, 2 H), 4.45 (s, 2 H), 6.51 (s, 1 H), 7.42 (d, $J = 8.3$ Hz, 2 H), 7.72 (d, $J = 8.3$ Hz, 2 H), 8.82 (s, 1 H). $^{13}\text{C NMR}$ (acetone- d^6 , 126 MHz): $\delta = 11.52$ (q), 20.07 (q), 20.99 (q), 52.07 (t), 53.79 (t), 114.80 (d), 119.78 (s), 122.11 (s), 127.38 (d, 2 C), 130.03 (d, 2 C), 133.65 (s, 2 C), 137.46 (s), 143.70 (s), 149.35 (s). MS (EI(+)): m/z (%): 317 (14) $[M]^+$, 162 (67), 161 (100), 91 (33), 65 (6). HRMS (EI (+)): $C_{17}H_{19}NO_3S$: calcd 317.1086; found. 317.1079.

3,3-Diethyl-2-[(4-methylphenyl)sulfonyl]-2,3-dihydro-1H-isoindol-4-ol (17a) and 3,3-Diethyl-2-[(4-methylphenyl)sulfonyl]-2,3-dihydro-1H-isoindol-5-ol (17b):



According to the general procedure **16** (100 mg, 290 μmol) and 4.40 mg (14.5 μmol) AuCl_3 in CDCl_3 furnished after 4 hours 14.9 mg of **17a** (15%) and 73.3 mg (73%) of **17b** as colourless solids (column chromatography using hexanes/ethyl acetate (10:1) as eluent).

17a: Mp.: 186 °C. R_f (PE:EE, 4:1) = 0.22. IR (solid): $\nu(\tilde{)} = 3381 \text{ cm}^{-1}$, 2969, 1602, 1472, 1458, 1306, 1285, 1131, 1093, 1060, 1041, 819, 775, 700, 662, 576, 559. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 0.46$ (t, $J = 7.4$ Hz, 6 H), 2.18-2.25 (m, 2 H), 2.40 (s, 3 H), 2.42-2.49 (m, 2 H), 4.60 (s, 2 H), 5.00 (bs, 1 H), 6.57 (d, $J = 7.7$ Hz, 1 H), 6.71 (d, $J = 7.7$ Hz, 1 H), 7.09 (t, $J = 7.7$ Hz, 1 H), 7.29 (d, $J = 8.3$ Hz, 2 H), 7.82 (d, $J = 8.3$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 9.01$ (q, 2 C), 21.49 (q), 30.84 (t, 2 C), 55.04 (t), 81.63 (s), 114.44 (d), 114.46 (d), 126.99 (s), 127.06 (d, 2 C), 128.89 (d), 129.36 (d, 2 C), 137.71 (s), 138.09 (s), 142.80 (s), 150.06 (s). MS (CI(+)): m/z (%): 346 $[\text{MH}]^+$ (61), 316 (100), 175 (32). HRMS (CI(+)): $\text{C}_{19}\text{H}_{24}\text{NO}_3\text{S}$ $[\text{MH}]^+$: calcd 346.1477; found 346.1484.

17b: Mp.: 68 °C. R_f (PE:EE, 4:1) = 0.13. IR (solid): $\nu(\tilde{)} = 3350 \text{ cm}^{-1}$, 2968, 1600, 1458, 13114, 1143, 1092, 1042, 814, 708, 681, 655, 599, 567. ^1H NMR (CDCl_3 , 500 MHz): $\delta = 0.45$ (t, $J = 7.3$ Hz, 6 H), 1.68-1.75 (m, 2 H), 2.41 (s, 3 H), 2.47-2.54 (m, 2 H), 4.53 (s, 2 H), 4.82 (bs, 1 H), 6.42 (d, $J = 2.4$ Hz, 1 H), 6.71 (dd, $J = 8.3$ Hz, $J = 2.4$ Hz, 1 H), 7.00 (d, $J = 8.3$ Hz, 1 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 7.82 (d, $J = 8.2$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 8.52$ (q, 2 C), 21.49 (q), 33.76 (t, 2 C), 54.13 (t), 80.35 (s), 108.00(d), 115.07 (d), 122.93 (d), 127.11 (d, 2 C), 127.80 (s), 129.38 (d, 2 C), 137.92 (s), 142.88 (s), 144.19 (s), 155.67 (s). MS (EI(+)): m/z (%): 345 $[\text{M}]^+$, 316 (100), 155 (15), 91 (36), 65 (6). HRMS (CI(+)): $\text{C}_{19}\text{H}_{24}\text{NO}_3\text{S}$ $[\text{MH}]^+$: calcd 346.1477; found 346.1484.

Computational details

Full and partial geometry optimizations were performed at the HF/6-31G* level for the products and the intermediates ($\text{Y} = \text{H}, \text{CH}_3$) respectively (Figure 5). In the partial optimization, two bond angles, C2-C1-H and C6-C1-H, are fixed to 90° to keep the zwitterionic forms. Frequency analyses were performed to confirm minimum structures. Due to the partial geometry optimization, the intermediates have one imaginary frequency of about 300 cm^{-1} which is the mode which moves the fixed H atom to neighboring carbon atoms. PCM calculations were also performed to consider polar solvent effects (water, $\epsilon = 78.6$). The UFF definition of the atomic radii for the solute was used. The Gaussian 03 program suite^[2] was used for the quantum chemical calculations.

References

[1] A. S. K. Hashmi, E. Kurpejovic, M. Wölfle, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2007**, 1743-1750.

[2] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.