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Gold catalysis contra platinum catalysis in hydroarylation contra phenol synthesis

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Abstract—Three silylated γ-alkynylfurans were prepared and subjected to both gold and platinum catalysts. The TMS- and the TBDMS-substituted furans reacted. With $AuCl_3$ and the binuclear $[(Ph_3PAu)_2Cl][BF_4]$ catalyst a hydroarylation of the alkyne was observed. $Na[AuCl_4]$ gave phenols as the product, but these were formed only after in situ desilylation of the starting material by the gold catalyst and thus the wrong isomer dominated. Only with $PtCl_2(MeCN)_2$ phenols with a silyl group were formed. The TBDPS-substituted furan failed to react. Two alkynylsilanes were synthesized, but they also failed to react.

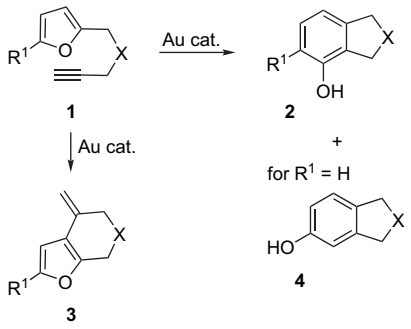
1. Introduction

Gold catalysts have recently attracted significant attention.[1,2] Among the new achievements in homogeneous gold-catalyzed reactions[2] the gold-catalyzed phenol synthesis[3] is one of the few examples of a previously unknown reaction made possible by gold catalysts. It added a new pathway to the family of the enyne cycloisomerization reactions. But in competition with the cycloisomerization to the phenols **2**, the γ-alkynylfurans **1** can also undergo a hydroarylation[4] reaction, leading to anellated furans **3** (Scheme 1).[3j,k] One additional synthetic challenge was the synthesis of phenols of type **2** without substituent in *ortho*-position to the hydroxyl group (R^1=H), because the corresponding furans, not possessing a substituent in 5-position of the furan ring, usually deliver a mixture of the positional isomers **2** and **4**, with **4** being the major component.

One concept was to block that position with a silyl group ($R^1=SiR^2_3$) as an auxiliary substituent, which on the other hand might also serve as point for further functionalization. Here we report our observations in the course of this investigation.

2. Results and discussion

The substrates were easily available from furan (**5**). In the first step it was lithiated with *n*-BuLi at room temperature and then a chlorosilane was added (Scheme 2). Subsequently, another lithiation of the 2-silylfurans **6** with *n*-BuLi and formylation with DMF[5] delivered the 5-silylfurfurals **7**. Crucial for the metallation was a temperature not below 0 °C and a reaction time not under 3 h, other experiments were unsuccessful in our hands.



Scheme 1. Possible isomers from the phenol synthesis and competing hydroarylation (X=O, NR^2, CR^2_2).

The first experiment was done with the TMS-protected **8a**. With $AuCl_3$ as catalyst not the typical phenol but the anellated furan **9a** with an exocyclic double bond, the product of an intramolecular hydroarylation,[4] was formed (Scheme 3).

After 35–40 min, in situ NMR spectroscopy showed 65% conversion, then the polymerization started. Therefore, it was worked up before a complete conversion was reached (a second sample after 24 h did not show signals of **9a** any more). Due to the sensitivity of the material and a quite similar R_f value of **8a** and **9a**, a complete separation of **9a** from

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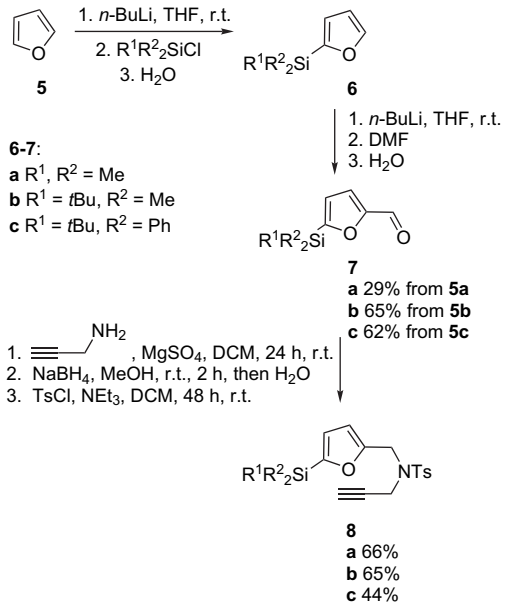
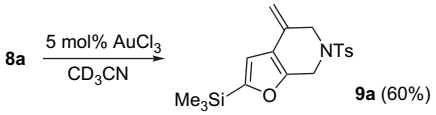
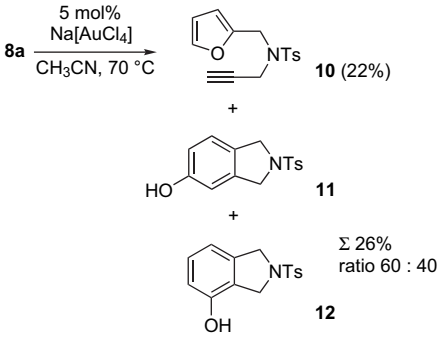


Scheme 2. Preparation of the substrates **8a–c**.



Scheme 3. Reaction of the TMS-substituted furan **8a** with $AuCl_3$.

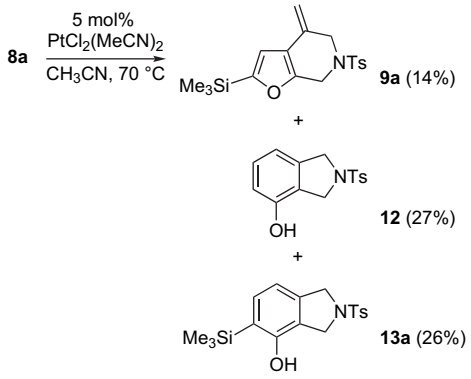
remaining substrate was not possible. Still the ^{1}H NMR data correlated well with the data of closely related substrates.[3j] $Na[AuCl_4]$ also catalyzes the phenol synthesis, but is less active and possesses a higher thermal stability. Indeed, with $Na[AuCl_4]$ a different product distribution was observed; the known[3a] phenols **11** and **12** were obtained in a ratio of 3:2, in addition significant amounts of the furan **10** were isolated (Scheme 4).



Scheme 4. Conversion of **8a** with $Na[AuCl_4]$.

The absence of silylated phenol indicated that the phenol synthesis proceeded only after desilylation of the furan, the ratio of **11**:**12** also corresponded to the value obtained from the substrate not bearing a silyl group.[3a]

After testing a number of gold catalysts without much success, with $PtCl_2(CH_3CN)_2$ as catalyst for the phenol synthesis,[2b,c] indeed the desired **13a** was obtained (26% yield), along with desilylated **12** in 27% yield. Since the silyl group was used in the sense of an auxiliary group anyway, this adds to 53% of the products with the hydroxy group at the desired position of the arene. Again **9a** was observed as side-product (Scheme 5).



Scheme 5. Conversion of **8a** with $PtCl_2(CH_3CN)_2$ as catalyst.

The structure of **13** could be confirmed by X-ray structure analysis (Fig. 1).[6] The aromatic ring is not perfectly planar. The dihedral angle C2–C3–C4–C5 of 4.2 ° results from the steric repulsion of the OH– and the silyl group. Thus the atoms Si1 and O1 deviate by 0.107 Å (Si) and 0.070 Å (O) from the ideal plane of the aromatic core in opposite directions.

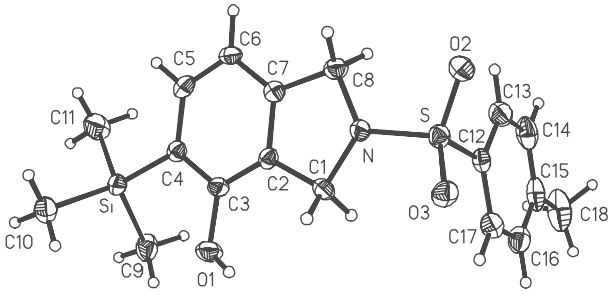
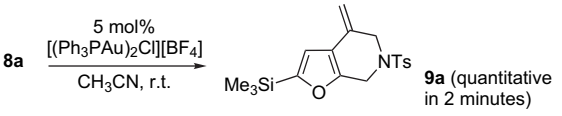


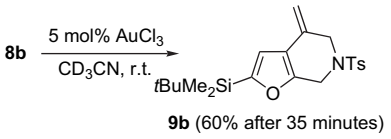
Figure 1. Solid state structure of silylphenol **13a**.

The last catalyst tested with **8a** was the gold(I) complex $[(Ph_3PAu)_2Cl][BF_4]$.[3j] The catalyst was very active, after 2 min the conversion was complete. The only product was again the hydroarylation product **9a** (Scheme 6). Pure **9a** is highly reactive, even in solution after two days at room temperature an almost complete decomposition was observed.



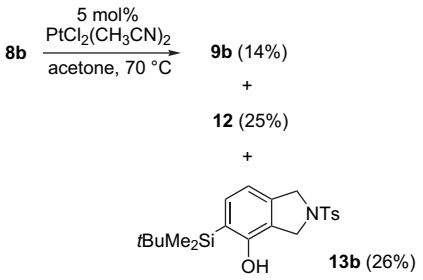
Scheme 6. Conversion of **8a** with gold(I) catalyst $[(Ph_3PAu)_2Cl][BF_4]$.

Changing to **8b** with the more stable *tert*-butyldimethylsilyl group on the furan ring delivered a similar result with $AuCl_3$. Compound **9b** with the exocyclic double bond (characteristic ^{13}C NMR signal of a vinylic methylene group at 112 ppm) was formed. Again, after about 60% conversion a polymerization of the product became relevant (Scheme 7).



Scheme 7. Reaction of **8b** with $AuCl_3$ as the catalyst.

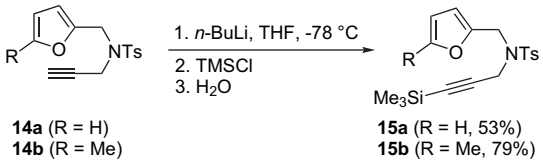
The reaction of **8b** with $PtCl_2(CH_3CN)_2$ also paralleled the observations made with **8a** and this catalyst. An almost identical yield of **12** and **13b** (51% together) was obtained. In addition **9b** was formed (Scheme 8).



Scheme 8. Reaction of **8b** with $PtCl_2(CH_3CN)_2$ as the catalyst.

Compound **8c** failed to undergo catalysis with either gold or platinum catalysts. Since the large *tert*-butyldiphenylsilyl group is too far from the reaction centre to shield it sterically, the relative electron withdrawing nature of this group diminishes the nucleophilic reactivity of the furan ring and the catalyst decomposes as the reaction is too slow.

In order to further explore the behaviour of silyl groups in these catalysis reactions, the alkynylsilanes **15a** and **15b** were prepared as shown in Scheme 9.



Scheme 9. Preparation of the alkynylsilanes **15a** and **15b**.

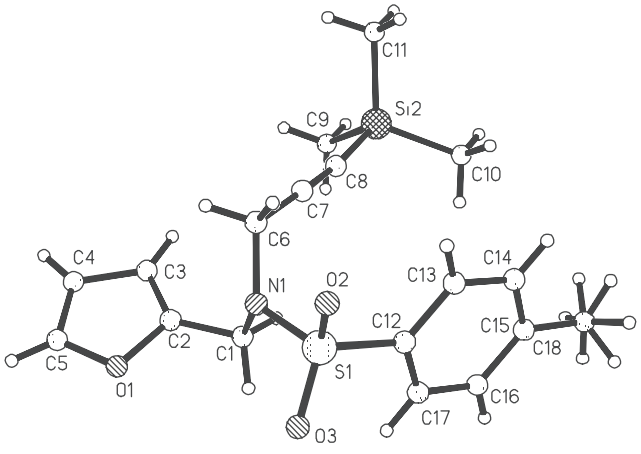
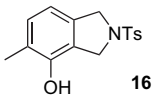


Figure 2. Solid state structure of **15a**.

Compound **15a** could be characterized by a crystal structure analysis (Fig. 2).[6] Compounds **15a** and **15b** prove to be unreactive under the various conditions described above. Only with 5 mol % $Na[AuCl_4]$ a partial desilylation and a subsequent formation of **11** and **12** from **15a** in the same ratio as shown in Scheme 4 was observed, **15b** led to the known phenol **16** (Scheme 10).



Scheme 10. Compound **16** is formed from **15b** by desilylation/isomerization.

3. Conclusion

Gold(I) catalysts efficiently serves as a hydroarylation catalyst for the silylated γ-alkynylfurans, while the platinum(II) catalyst shows a high selectivity towards the phenolic products. Gold(III) catalysts shows a significant potential to serve as a desilylation catalyst, which ultimately leads to a mixture of hydroarylation and desilylated phenolic products.

4. Experimental

4.1. (5-Trimethylsilanyl)furan-2-carbaldehyde 7a

Furan (5.00 g, 73.4 mmol) in THF (50 ml) was stirred with *n*-butyllithium (45.9 ml of a 1.6 M solution in hexane, 73.4 mmol) for 4 h at room temperature. Then trimethylchlorosilane (10 ml, 11.6 g, 107 mmol) was added and stirring was continued for 4 h at room temperature. After hydrolysis it is extracted with diethyl ether (3×150 ml), the combined extracts were dried over magnesium sulfate, filtered and the solvent removed in vacuo. The residue was taken up in THF (50 ml) and at room temperature *n*-butyllithium (45.9 ml of a 1.6 M solution in hexane) was added. After 4 h DMF (8.00 ml, 8.51 g, 116 mmol) was added. After 1 h water (50 ml) was added. After extraction with diethyl ether (3×150 ml) the extracts were dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue (3.58 g, 29%) was pure enough for the next steps. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.32 (s, 9H), 6.74 (d, J=3.5 Hz, 1H), 7.21 (d, J=3.5 Hz, 1H), 9.68 (s, 1H).

4.2. 5-(*tert*-Butyldimethylsilanyl)-furan-2-carbaldehyde 7b

Furan (2.50 g, 36.7 mmol) in THF (50 ml) was stirred with *n*-butyllithium (23.0 ml of a 1.6 M solution in hexane, 36.7 mmol) for 4 h at room temperature. Then *tert*-butyldimethylchlorosilane (8.30 g, 55.1 mmol, 1.5 equiv) was added and stirring was continued for 4 h at room temperature. Water was added, after extractions with diethyl ether (3× 150 ml) the combined organic extracts were dried over magnesium sulfate, filtered and the solvent removed in vacuo. The residue was taken up in THF (50 ml) and *n*-butyllithium (23.0 ml of a 1.6 M solution in hexane) was added. After 4 h DMF (4.00 ml, 4.26 g, 58.3 mmol) was added and stirring was continued for 1 h. Water (50 ml) was added, after

extractions with diethyl ether (2×150 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The brown residue (5.02 g, 65%) was pure enough for the next steps. For analytical purposes a small sample was purified by column chromatography to deliver **7b** as a yellow oil. R_f (petrol ether/ethyl acetate, 20:1)=0.14. IR (film): $\tilde{\nu}$=2936 cm^{-1}, 2857, 2812, 2359, 1734, 1683, 1559, 1463, 1369, 1258, 1215, 1109, 967, 928, 811, 774, 679. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.26 (s, 6H), 0.91 (s, 9H), 6.75 (d, J=3.5 Hz, 1H), 7.20 (d, J=3.5 Hz, 1H), 9.67 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=−6.41 (q, 2C), 16.79 (s), 26.28 (q, 3C), 120.44 (d), 122.68 (d), 156.90 (s), 167.40 (s), 178.09 (d). MS (70 eV): *m/z* (%): 210 (8) [M^+], 182 (6), 153 (56), 125 (69), 75 (100). $C_{11}H_{18}O_2Si$ (210.35): calcd C 62.81, H 8.63; found C 62.81, H 8.71.

4.3. (5-*tert*-Butyldiphenylsilanyl)furan-2-carbaldehyde 7c

Furan (600 mg, 8.81 mmol) in THF (20 ml) was stirred with *n*-butyllithium (5.51 ml of a 1.6 M solution in hexane, 8.81 mmol) for 4 h at room temperature. Then *tert*-butyldiphenylchlorosilane (2.91 g, 10.6 mmol, 1.2 equiv) was added and stirring was continued for another 4 h at room temperature. Water was added and after extractions with diethyl ether (3×100 ml) the combined organic extracts were dried over magnesium sulfate, filtered and the solvent removed in vacuo. The residue was taken up in THF (50 ml) and *n*-butyllithium (5.51 ml of a 1.6 M solution in hexane) was added at room temperature. After 4 h DMF (2.00 ml, 2.13 g, 29.1 mmol) was added and stirring was continued for 1 h. Water was added and after extractions with diethyl ether (3×150 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The brown residue was filtered over a short silica gel column and eluted with ethyl acetate. After removal of the solvent this provided **7c** as a yellow solid, which could be used in the next step without further purification. Mp 83–85 °C. R_f (petrol ether/ethyl acetate, 25:1)=0.13. IR (film): $\tilde{\nu}$=3066 cm^{-1}, 2932, 2857, 2361, 1672, 1153, 1462, 1386, 1265, 1182, 1103, 1012, 962, 924, 818, 752, 697. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.19 (s, 9H), 6.71 (d, J=3.5 Hz, 1H), 7.25 (d, J=3.5 Hz, 1H), 7.34–7.48 (m, 6H), 7.59–7.65 (m, 4H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ=18.86 (s), 27.76 (q, 3C), 126.22 (d), 127.85 (d), 128.04 (d, 4C), 130.04 (d, 2C), 132.25 (s, 2C), 136.25 (d, 4C), 157.53 (s), 164.71 (s), 178.38 (d). MS (70 eV): *m/z* (%): 334 (3) [M^+], 277 (68), 239 (36), 199 (75), 183 (100). HRMS (70 eV): $C_{21}H_{22}O_2Si$: calcd 334.1389; found 334.1388.

4.4. 4-Methyl-*N*-prop-2-ynyl-*N*-(5-trimethylsilanyl-furan-2-ylmethyl)benzenesulfonamide 8a

Compound **7a** (1.50 g, 8.91 mmol) in DCM (30 ml) was stirred with propargyl amine (1.47 g, 26.7 mmol, 3.00 equiv) and $MgSO_4$ (4.00 g) overnight at room temperature. After filtration the solvent was removed in vacuo, the residue taken up in methanol (30 ml) and sodium borohydride (337 mg, 8.91 mmol, 1.00 equiv) was added at room temperature. After 2 h water was added (50 ml), after extractions with DCM (3×100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was taken up in DCM (30 ml) and stirred with triethylamine (902 mg, 8.91 mmol, 1.00 equiv) and tosyl chloride (1.70 g, 8.91 mmol, 1.00 equiv) overnight. Water (50 ml) was added, after extractions with DCM (3×100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. Column chromatography delivered **8a** (2.12 g, 66%) as a yellow oil. R_f (petrol ether/ethyl acetate, 20:1)=0.13. IR (film): $\tilde{\nu}$=3279 cm^{-1}, 2945, 2230, 1679, 1590, 1481, 1420, 1340, 1320, 1293, 1240, 1172, 1151, 1078, 1045, 998, 925, 828, 792, 780, 637, 609. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.20 (s, 9H), 2.07 (t, J=2.5 Hz, 1H), 2.42 (s, 3H), 4.01 (d, J=2.5 Hz, 2H), 4.48 (s, 2H), 6.25 (d, J=3.1 Hz, 1H), 6.50 (d, J=3.1 Hz, 1H), 7.27 (d, J=8.3 Hz, 2H), 7.73 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ=−1.62 (q, 3C), 21.62 (q), 36.35 (t), 43.01 (t), 73.78 (d), 76.73 (s), 109.94 (d), 120.35 (d), 127.82 (d, 2C), 129.57 (d, 2C), 136.18 (s), 143.59 (s), 152.86 (s), 161.24 (s). MS (70 eV): *m/z* (%): 361 (11) [M^+], 206 (100), 178 (42), 147 (14), 134 (29), 106 (8), 91 (35). $C_{18}H_{23}NO_3SSi$ (361.54): calcd C 59.80, H 6.41, N 3.87; found C 59.65, H 6.30, N 3.90.

4.5. *N*-[5-(*tert*-Butyldimethylsilanyl)furan-2-ylmethyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide 8b

Compound **7b** (1.00 g, 4.75 mmol) in DCM (30 ml) was stirred with propargyl amine (790 mg, 14.3 mmol, 3.00 equiv) and $MgSO_4$ (4.00 g) overnight at room temperature. After filtration the solvent was removed in vacuo, methanol (30 ml) was added and sodium borohydride (180 mg, 4.75 mmol, 1.00 equiv) was added at room temperature. After 2 h water (50 ml) was added, after extractions with DCM (3×100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was taken up in DCM (30 ml), triethylamine (481 mg, 4.75 mmol, 1.00 equiv) and tosyl chloride (906 mg, 4.75 mmol, 1.00 equiv) were added and stirred overnight. Water (50 ml) was added, after extractions with DCM (3× 100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. Column chromatography on silica gel delivered **8b** (1.12 g, 65%) as a yellow oil, which solidified at −25 °C in the freezer to a caramel-like solid with a melting point of 49 °C. Mp 49–50 °C. R_f (petrol ether/ethyl acetate, 10:1)=0.30. IR (film): $\tilde{\nu}$=3301 cm^{-1}, 2927, 2855, 1769, 1596, 1465, 1347, 1297, 1252, 1214, 1186, 1157, 1092, 1065, 1017, 943, 897, 803, 770, 731, 659, 617, 575. ^1H NMR ($CDCl_3$, 500 MHz): δ=0.17 (s, 6H), 0.87 (s, 9H), 2.08 (t, J=2.5 Hz, 1H), 2.41 (s, 3H), 4.01 (d, J=2.5 Hz, 2H), 4.47 (s, 2H), 6.27 (d, J=3.2 Hz, 1H), 6.53 (d, J=3.2 Hz, 1H), 7.27 (d, J=8.4 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=−6.24 (q, 2C), 16.83 (s), 21.68 (q), 26.41 (q, 3C), 36.36 (t), 42.99 (t), 73.92 (d), 76.75 (s), 109.91 (d), 121.68 (d), 128.87 (d, 2C), 129.64 (d, 2C), 136.18 (s), 143.67 (s), 153.07 (s), 159.77 (s). MS (70 eV): *m/z* (%): 403 (32) [M^+], 346 (100), 248 (91), 190 (39), 149 (90), 91 (50). $C_{21}H_{29}NO_3SSi$ (403.62): calcd C 62.42, H 7.24, N 3.47; found C 62.46, H 7.32, N 3.38.

4.6. *N*-[5-(*tert*-Butyldiphenylsilanyl)-furan-2-ylmethyl]-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide 8c

Compound **7c** (1.00 g, 2.99 mmol) in DCM (30 ml) was stirred with propargyl amine (500 mg, 9.99 mmol) and

$MgSO_4$ (4.00 g) at room temperature overnight. After filtration the solvent was removed in vacuo, the residue taken up in methanol (30 ml) and sodium borohydride (113 mg, 2.99 mmol, 1.00 equiv) was added and stirred at room temperature for 2 h. Water (50 ml) was added, after extractions with DCM (100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was taken up in DCM (30 ml) and stirred with triethylamine (303 mg, 2.99 mmol, 1.00 equiv) and tosyl chloride (570 mg, 2.99 mmol, 1.00 equiv) overnight. Water (50 ml) was added, after extractions with DCM (3× 100 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. Column chromatography on silica gel delivered **8c** (694 mg, 44%) as a yellow oil. R_f (petrol ether/ethyl acetate, 10:1)=0.20. IR (film): $\tilde{\nu}$=3273 cm^{-1}, 2933, 2857, 1767, 1593, 1466, 1427, 1345, 1257, 1155, 1096, 1065, 1011, 893, 809, 738, 698, 657, 612, 577. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.11 (s, 9H), 2.08 (t, J=2.4 Hz, 1H), 2.38 (s, 3H), 4.04 (d, J=2.4 Hz, 2H), 4.54 (s, 2H), 6.33 (d, J=3.2 Hz, 1H), 6.53 (d, J=3.2 Hz, 1H), 7.22 (d, J=8.2 Hz, 2H), 7.30–7.44 (m, 6H), 7.55–7.60 (m, 4H), 7.72 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ=18.70 (s), 21.64 (q), 27.83 (q, 3C), 36.38 (t), 43.02 (t), 74.11 (d), 76.67 (s), 110.05 (d), 125.57 (d), 127.79 (d, 4C), 127.82 (d, 2C), 129.63 (d, 2C), 129.66 (d, 2C), 133.51 (s, 2C), 136.11 (s), 136.24 (d, 4C), 143.71 (s), 154.16 (s), 156.97 (s). MS (FAB positive-ion, matrix: 3-nitrobenzylalcohol): m/z (%): 528 (16) [M^++H], 527 (5) [M^+], 470 (64), 319 (100), 259 (27), 222 (75), 199 (46), 135 (38), 91 (17). HRMS (FAB positive-ion, matrix: 3-nitrobenzylalcohol): [M+Na]$^+$: calcd 550.1848; found 550.1830. $C_{31}H_{33}NO_3SSi$ (527.76): calcd C 70.55, H 6.30, N 2.65; found C 71.63, H 6.77, N 2.65.

4.7. 4-Methylene-6-(toluene-4-sulfonyl)-2-trimethylsilanyl-4,5,6,7-tetrahydrofuro[2,3-*c*]pyridine 9a

To **8a** (100 mg, 277 μmol) and CD_3CN (0.5 ml) in an NMR tube a stock-solution of $AuCl_3$ in CD_3CN (42.0 mg containing 10 wt % $AuCl_3$, 4.20 mg, 13.8 μmol, 5 mol % $AuCl_3$) was added at room temperature. The reaction was monitored by ^1H NMR spectroscopy. After 30 min 65% of the starting material was consumed, the reaction was worked up because the product started to polymerize (a second sample was not worked up, after 24 h no more product **9a** was detectable in the NMR, only very broad, unspecific peaks were visible). The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel. Thus **9a** (59.6 mg, 60%) was obtained. R_f (petrol ether/ethyl acetate, 20:1)=0.12. IR (film): $\tilde{\nu}$=2958 cm^{-1}, 2362, 1654, 1349, 1251, 1163, 1093, 1045, 924, 841, 758. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.22 (s, 9H), 2.37 (s, 3H), 3.98 (t, J=1.3 Hz, 2H), 4.39 (s, 2H), 4.89 (m_c, 1H), 5.00 (m_c, 1H), 6.50 (s, 1H), 7.20 (d, J=8.4 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=−1.58 (q, 3C), 21.58 (q), 44.35 (t), 49.76 (t), 106.85 (t), 115.53 (d), 118.39 (s), 127.69 (d, 2C), 129.50 (d, 2C), 132.84 (s), 134.05 (s), 151.14 (s), 160.87 (s), one C (s) not detected.

4.8. Reaction of 8a with $PtCl_2(CH_3CN)_2$

Compound **8a** (500 mg, 1.38 mmol) in acetone (5 ml) and $PtCl_2(CH_3CN)_2$ (24 mg, 69 μmol, 5 mol %) were stirred overnight at 70 °C. The solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel. Thus starting material **8a** (69 mg, 14%), **12** (108 mg, 27%)[3a] and **13** (131 mg, 26%) were obtained. Crystals for the X-ray single crystal structure analysis were obtained from ether/DCM. Compound **12**: ^1H NMR (CD_3CN, 300 MHz): δ=2.40 (s, 3H), 4.51–4.53 (m, 2H), 4.57–4.59 (m, 2H), 6.66 (d, J=8.0 Hz, 1H), 6.71 (d, J=7.6 Hz, 1H), 7.09 (dd, J=8.0 Hz, 7.6 Hz, 1H), 7.21 (s, 1H), 7.39 (d, J=8.2 Hz, 2H), 7.77 (d, J=8.2 Hz, 2H). 2-(Toluene-4-sulfonyl)-5-trimethylsilanyl-2,3-dihydro-1*H*-isoindol-4-ol **13a**: mp 166–168 °C. R_f (petrol ether/ethyl acetate, 10:1)=0.08. IR ($CDCl_3$): $\tilde{\nu}$=3451 cm^{-1}, 2955, 1586, 1423, 1315, 1247, 1214, 1158, 1099, 1015, 885, 836, 763, 724, 659. ^1H NMR ($CDCl_3$, 500 MHz): δ=0.28 (s, 9H), 2.40 (s, 3H), 4.61 (m, 2H), 4.63 (m, 2H), 5.12 (s, 1H), 6.75 (d, J=7.5 Hz, 1H), 7.23 (d, J=7.5 Hz, 1H), 7.31 (d, J=8.3 Hz, 2H), 7.76 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=−0.40 (q, 3C), 21.85 (q), 51.67 (t), 54.51 (t), 115.12 (d), 122.21 (s), 124.94 (s), 127.92 (d, 2C), 130.23 (d, 2C), 133.90 (s), 135.58 (d), 139.93 (s), 144.17 (s), 155.80 (s). MS (70 eV): m/z (%): 361 (29) [M^+], 277 (6), 206 (100), 163 (28), 91 (91). $C_{18}H_{23}NO_3SSi$ (361.54): calcd: C 59.80, H 6.41, N 3.87; found: C 59.68, H 6.39, N 3.79.

4.9. 2-*tert*-Butylmethylsilanyl-4-methylene-6-(toluene-4-sulfonyl)-4,5,6,7-tetrahydrofuro[2,3-*c*]pyridine 9b

The reaction of **8b** (50.2 mg, 124 μmol) in CD_3CN (0.5 ml) with a stock-solution of $AuCl_3$ in CD_3CN (18.8 mg of a 10 wt % solution, 1.88 mg, 6.20 μmol, 5 mol % $AuCl_3$) at room temperature was monitored by ^1H NMR spectroscopy. After 80 min the ratio of starting material to product is 62:38. The reaction is very clean, but a complete conversion is not even reached after 24 h. Instead, **9b** starts to decompose, then the ratio is 58:42. A DEPT 135 spectrum shows the characteristic olefinic methylene group at 122 ppm. ^1H NMR (CD_3CN, 300 MHz): δ=0.20 (s, 6H), 0.91 (s, 9H), 2.34 (s, 3H), 4.06 (t, J=1.4 Hz, 2H), 4.44 (s, 2H), 4.94–4.97 (m, 1H), 5.02–5.05 (m, 1H), 6.66 (s, 1H), 7.23 (d, J=8.2 Hz, 2H), 7.61 (d, J=8.2 Hz, 2H).

4.10. Reaction of 8b with $PtCl_2(CH_3CN)_2$

Compound **8b** (95.0 mg, 235 μmol) in acetone-d_6 and $PtCl_2(CH_3CN)_2$ (4.11 mg, 11.8 μmol, 5 mol %) were heated to 60 °C overnight. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel. Thus **9b** (12 mg, 13%), **12** (17 mg, 25%) and **13b** (25 mg, 26%) were obtained. 5-(*tert*-Butyldimethylsilanyl)-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-isoindol-4-ol **13b**: R_f (petrol ether/ethyl acetate, 10:1)=0.10. IR (film): $\tilde{\nu}$=3266 cm^{-1}, 2929, 2856, 2362, 1713, 1600, 1468, 1291, 1256, 1156, 1092, 1007, 815, 666. ^1H NMR ($CDCl_3$, 500 MHz): δ=0.31 (s, 6H), 0.87 (s, 9H), 2.40 (s, 3H), 4.61 (s, 4H), 5.18 (br s, 1H), 6.75 (d, J=7.5 Hz, 1H), 7.21 (d, J=7.5 Hz, 1H), 7.31 (d, J=8.3 Hz, 2H), 7.77 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=−4.50 (q, 2C), 17.70 (s), 21.63 (q), 26.70 (q, 3C), 51.60 (t), 54.30 (t), 114.60 (d), 121.57 (s), 122.49 (s), 127.74 (d, 2C), 129.97 (d, 2C), 133.79 (s), 136.71 (d), 139.78 (s), 143.84 (s), 155.88 (s). MS (70 eV): m/z (%): 403 (6) [M^+], 346 (100),

229 (16), 190 (32), 163 (50), 91 (49). HRMS (70 eV): $C_{21}H_{29}NO_3S$: calcd 403.1637; found: 403.1632. $C_{21}H_{29}NO_3S$ (403.62): calcd: C 62.49, H 7.24, N 3.47; found: C 60.32, H 7.23, N 2.94.

4.11. *N*-Furan-2-ylmethyl-4-methyl-*N*-(3-trimethylsilanyl-prop-2-ynyl)-benzenesulfonamide 15a

To **14a**[3a] (920 mg, 3.17 mmol) in THF (15 ml) at −78 °C *n*-butyllithium (2.00 ml of a 1.6 M solution in hexane, 3.20 mmol) was added. After stirring at that temperature for 30 min, the reaction mixture was warmed to 0 °C and trimethylsilylchloride (1.2 ml, 1.03 g, 9.50 mmol) was added. Water was added (10 ml), after extractions with DCM (3×15 ml), the combined organic extracts were dried over magnesium sulfate, filtered and the solvent was removed in vacuo. Column chromatography delivered **15a** (610 mg, 53%) as a colourless solid. By evaporation of a solution in petrol ether/DCM single crystals for a crystal structure analysis were obtained. Mp 83 °C. R_f (petrol ether/ethyl acetate/DCM, 18:1:1)=0.18. IR (KBr): $\tilde{\nu}$=3030 cm^{-1}, 2930, 2900, 1491, 2145, 1590, 1339, 1320, 1236, 1155, 997, 983, 876, 832, 749, 730, 646. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=0.00 (s, 9H), 2.41 (s, 3H), 4.02 (s, 2H), 4.40 (s, 2H), 6.27 (m, 2H), 7.27 (d, J=8.2 Hz, 2H), 7.34 (d, J=0.9 Hz, 1H), 7.72 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=−0.37 (q, 3C), 21.56 (q), 37.18 (t), 42.78 (t), 91.26 (s), 97.69 (s), 109.94 (d), 110.40 (d), 127.81 (d, 2C), 129.55 (d, 2C), 135.98 (s), 142.98 (d), 143.49 (s), 148.67 (s). MS (70 eV): m/z (%)=361 (1) [M$^+$], 346 (3), 322 (2), 288 (3), 250 (4), 206 (100), 177 (7), 155 (6), 133 (16), 111 (3), 91 (14), 81 (48), 73 (34), 53 (8). $C_{18}H_{23}NO_3SSi$ (361.5): calcd C 59.80, H 6.41, N 3.87; found C 59.91, H 6.38, N 3.84.

4.12. 4-Methyl-*N*-(5-methylfuran-2-ylmethyl)-*N*-(3-trimethylsilanylprop-2-ynyl)benzenesulfonamide 15b

To **14b**[3a] (1.00 g, 3.30 mmol) in THF (30 ml) at −78 °C *n*-butyllithium (2.06 ml of a 1.6 M solution in hexane, 3.30 mmol) was added. After stirring for 30 min an excess of trimethylsilylchloride was added and the reaction mixture slowly warmed to room temperature. Water (50 ml) was added, after extraction with DCM (3×60 ml), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed in vacuo. Column chromatography delivered **15b** (978 mg, 79%) as a colourless solid. Mp 81–82 °C. R_f (petrol ether/ethyl acetate/DCM; 10:1:1)=0.42. IR (KBr): $\tilde{\nu}$=2930 cm^{-1}, 2895, 2865, 2143, 1914, 1668, 1589, 1542, 1431, 1340, 1322, 1238, 1152, 1100, 1078, 1046, 1003, 985, 956, 875, 930, 793, 762, 746, 717, 643. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=0.01 (s, 9H), 2.22 (d, J=1.1 Hz, 3H), 2.42 (s, 3H), 4.02 (s, 2H), 4.35 (s, 2H), 5.86 (qd, J=3.1 Hz, 1.1 Hz, 1H), 6.14 (d, J=3.1 Hz, 1H), 7.28 (d, J=8.2 Hz, 2H), 7.74 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): −0.41 (q, 3C), 13.55 (q), 21.50 (q), 36.99 (t), 42.86 (t), 91.07 (s), 97.78 (s), 106.20 (d), 110.95 (d), 127.79 (d, 2C), 129.44 (d, 2C), 136.00 (s), 143.34 (s), 146.43 (s), 152.77 (s). MS (70 eV): m/z (%): 375 (10) [M$^+$], 302 (4), 266 (6), 220 (100), 191 (30), 147 (13), 95 (48), 91 (10), 73 (21). $C_{19}H_{25}NO_3SSi$ (375.57): calcd C 60.76, H 6.71, N 3.73; found C 60.57, H 6.61, N 3.70.

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References and notes

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6. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 633391, 633692. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).