CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501268

Gold Catalysis: Phenol Synthesis in the Presence of Functional Groups

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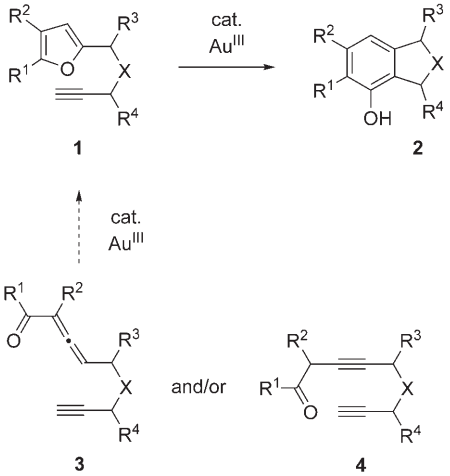
Abstract: The effect of different substituents, such as bromo, chloromethyl, hydroxymethyl, formyl, acetyl, carboxy, and acylated hydroxymethyl and ammonium groups, on the furan ring of substrates in gold-catalyzed phenol synthesis has been investigated. The furan ring was also replaced by different heterocycles, such as pyrroles, thiophenes, oxazoles, and a 2,4-dimethoxyphenyl group; gold catalysis then delivered no phenols, but occasionally other products were obtained. $[Ru_3(CO)_{12}]$ also catalyzed the conversion of **1** at a low rate, $[Os_3(CO)_{12}]$ failed as a catalyst, and with $[Co_2(CO)_8]$ the alkyne complex **19** can be obtained, it does not lead to any phenol but reacts with norbornene to give the product of a Pauson–Khand reaction. Efforts to prepare vinylidene complexes of **1** provided the only evidence for these species; in the presence of a phosphane ligand with ruthenium an interesting deoxygenation to **22** was observed. The phenol **2c** was converted to the allyl ether, a building block for *para*-Claisen rearrangements, and to the aryl triflate, a building block for cross-coupling reactions.

Keywords: arenes · gold · homogeneous catalysis · Pauson–Khand reaction · ruthenium

Introduction

The gold-catalyzed[1] synthesis of phenols **2** from furans **1** (Scheme 1) has attracted considerable attention. It is a highly selective and very robust reaction, neither water nor oxygen need to be excluded, and due to the absence of paramagnetic species it can conveniently be monitored by NMR spectroscopy.[2]

After our initial publication[2] in which we also described that the furans **1** could potentially be generated in situ from allenyl ketones **3** or propargyl ketones **4**, Echavarren and co-workers[3] discovered that platinum(II) can also catalyze the reaction of **1** to **2**. They were able to reveal significant mechanistic details of this reaction by the observation of side products and theoretical calculations; these mechanistic insights subsequently led to spectacular developments in the field of enyne cyclization reactions[4] (a 1,6-enyne is a substructure of **1**). Our group, at the same time as Echavarren's group, observed that platinum(II) catalyzes these reactions; in addition we found that other d^8 complexes, such as palladium(II), iridium(I), and rhodium(I), are also active.[5] Never-



Scheme 1. Gold-catalyzed phenol synthesis.

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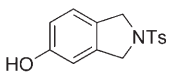
Supporting information for this article (experimental procedures and data for **1k**–**1q**, **1s**–**1u**, **7**–**9**, **11**–**13**, **15**, **17**, and **18**) is available on the WWW under http://www.chemeurj.org/ or from the author.

theless, the gold catalysts are by far the most active and with gold, unlike in the platinum-catalyzed reactions, no significant amounts of side products were observed.[6] Recently, we proved experimentally that arene oxides are intermediates of the reaction.[7] In addition we investigated reactions involving gold complexes with *N*- and *N*,*O*-ligands which allowed the amount of catalyst used to be reduced to 0.07 mol% (1180 turnovers) and which also made possible an efficient synthesis of benzo-anellated six-membered heterocycles[6] (in all but one of the then known examples a tether of three atoms had been used; for a satisfactory conversion of substrates with a tether of four atoms about 6 mol%[2] of $AuCl_3$ instead of the usual 2 mol% were needed). After investigating the applications of the synthesis of furfuryl-substituted arenes and biaryl compounds,[8] a further study of the methodology revealed that in principle a gold-catalyzed tandem hydroarylation/cycloisomerization process leading to the formation of five new bonds is possible, while the reaction of **1** to **2** leads to only four new bonds.[9] The only example in natural product synthesis so far is the total synthesis of the sesquiterpene Jungianol in six steps without using a single protecting group.[10]

In most of the known examples apart from an *N*-sulfonyl group, an oxygen atom, or a propargylic carbonyl group in the tether no functional groups other than the reacting alkyne and furan subunits were present (Table 1, entries 1–9). The only exception is with substrate **1j** (Table 1, entry 10), for which the initially formed *o*-alkynylphenol isomerizes to the benzofuran **6** in a second gold-catalyzed step.[5] The formation of the constitutional isomer **5** in addition to **2i** (Table 1, entry 9) on the other hand shows that the absence of a substituent R^1 is also problematic.

For further synthetic applications it was important to study the tolerance of this catalytic reaction to the presence



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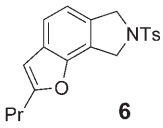

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Table 1. Different substrates already tested in the cycloisomerization of *ω*-alkynylfurans **1** (R^2=H).

Entry	Substrate	R^1	R^3	R^4	X	Product (Yield [%])
1	**1a**	CH_3	H	H	CH_2	**2a** (65)
2	**1b**	CH_3	H	H	O	**2b** (69)
3	**1c**	CH_3	H	H	NTs	**2c** (97)
4	**1d**	CH_3	CH_3	H	NTs	**2d** (94)
5	**1e**	CH_3	H	CH_3	NTs	**2e** (93)
6	**1f**	CH_3	H	H	NNs	**2f** (96)
7	**1g**	CH_3	H	H	$C(CO_2Me)_2$	**2g** (88)
8	**1h**	CH_3	H	H	$N(Ts)CH_2$	**2h** (81)[a]
9	**1i**	H	H	H	NTs	**2i** (31) + **5** (51)
10	**1j**	C=CPr	H	H	NTs	**2j** (23) + **6** (48)

[a] 6.0 mol% $AuCl_3$.

of different functional groups at different positions. Herein we present the results of our investigation.

Results and Discussion

Catalysis reactions: We started with the 2-bromofuran derivative **1k** (Table 2) that is readily available from 5-bromofurfural. No conversion was observed. This is in accord with related results of Echavarren and co-workers[11] who also did not observe a phenol with the analogous 5-bromofuryl propargyl ether and $PtCl_2$ as catalyst, but could optimize the reaction conditions to obtain a side product.[12] Placing the bromo substituent at a different position on the furan ring (**1l**, Table 2, entry 2) delivered **2l**, which immediately precipitated from the acetonitrile solution. Compound **2l** is only soluble in DMSO; purification by precipitation from DMSO with H_2O led to heavy losses of the product but delivered analytically pure material. Substrate **1m** has a dimethylammonium group in the tether; with bromide as the counteranion no conversion was observed (Table 2, entry 3). We assumed that 20 equivalents of Br^- with respect to the catalyst simply blocked the coordination sites for the substrate by competitive coordination. Use of the hexafluorophosphate **1n** proved this hypothesis (Table 2, entry 4); a 48% yield of the product **2n** was obtained. Then **1o** bearing a chloromethyl substituent was tested. An 80% yield of **2o** was observed by NMR spectroscopy, but we did not succeed in isolating the neat product; a reaction of the benzylic chloride with nucleophilic groups (for example, the phenolic hydroxy group) during the work up is probably responsible for this. Most unfortunately the corresponding alcohol (**1p**, Table 2, entry 6), aldehyde (**1q**, Table 2, entry 7), ketone (**1r**, Table 2, entry 8), and carboxylate (**1s**, Table 2, entry 9) did not react. In the case of **1p** and **1q** a gold mirror was observed after a short time.[13] The reason for performing these experiments was the low selectivity observed with substrates with R^1=H (see **1i**, Table 1, entry 9). If the conversion of **1q** or **1s** had been successful, a subsequent decarbonylation[14] or retro-Kolbe–Schmitt reaction[15] would have delivered **2i** without **5** being produced as a side product. In the case of a successful conversion of **1p**, **2p** could have been oxidized to either **1q** or **1s**. Ketone **1r** was tested in order to see whether the reducing aldehyde group in **1q** was responsible for the failure of the catalysis or whether the presence of an acceptor in general is a problem, which indeed seems to be the case. Switching from the alcohol **1p** to the acetate **1t** gave a satisfactory conversion, but as with the chloride **1o**, isolation of the product was a significant problem. Finally, the pivaloyl-protected **1u** allowed isolation of **2u** in a satisfactory yield (Table 2, entry 11).

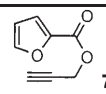
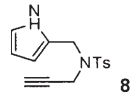
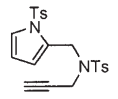
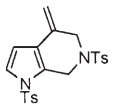
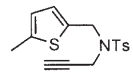
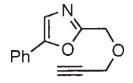
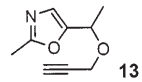
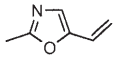
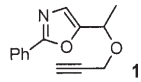
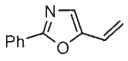
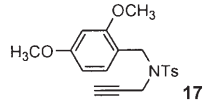
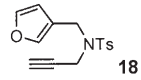
Next we discuss the effect of location of the carbonyl substituent on the furan ring and the variation of the heterocycle in the starting material (Table 3). Instead of the furan ring in **1** several other synthetically relevant heterocycles were investigated.

Table 2. Different functionalized substrates **1** in gold-catalyzed phenol synthesis ($R^3 = R^4 = H$).

Entry	Substrate	R^1	R^2	X	T [°C]	t [h]	Product	Yield [%][a]
1	**1k**	Br	H	NTs	50	24	–	–
2	**1l**	CH_3	Br	NTs	RT	24	**2l**	93 (36)
3	**1m**	CH_3	H	NMe_2^+ Br^-	50	24	–	–
4	**1n**	CH_3	H	NMe_2^+ PF_6^-	50	26	**2n**	48
5	**1o**	CH_2Cl	H	NTs	RT	72	**2o**	80 (–)
6	**1p**	CH_2OH	H	NTs	RT	24	–	–
7	**1q**	CHO	H	O	RT	24	–	–
8	**1r**	Ac	H	NTs	60	24	–	–
9	**1s**	CO_2H	H	O	80	24	–	–
10	**1t**	CH_2OAc	H	NTs	RT	24	**2t**	90 (6)
11	**1u**	CH_2OPiv	H	NNs	RT	72	**2u**	90 (62)

[a] Determined by NMR spectroscopy; yields of isolated products are given in parentheses.

Table 3. Gold-catalyzed reactions of other heterocycles with alkynyl groups in the side chain.

Entry	Substrate	Catalyst	T [°C]	t [h]	Product	Yield [%][a]
1	 **7**	$AuCl_3$	50	24	–	–
2	 **8**	$AuCl_3$	RT	1	–	–[b]
3	 **9**	$AuCl_3$[c]	RT	0.5	 **10**	(77)
4	 **11**	$AuCl_3$	50	24	–	–
5	 **12**	$AuCl_3$	50	15	–	–
6	 **13**	$Na[AuCl_4]\cdot 2H_2O$	50	15	 **14**	51
7	 **15**	$Na[AuCl_4]\cdot 2H_2O$	50	15	 **16**	67
8	 **17**	$AuCl_3$	RT	24	–	–
9	 **18**	$AuCl_3$	RT	168	–	–

[a] Determined by NMR spectroscopy; yields of isolated products are given in parentheses. [b] Rapid catalyst deactivation occurred. [c] 10 mol% $AuCl_3$.

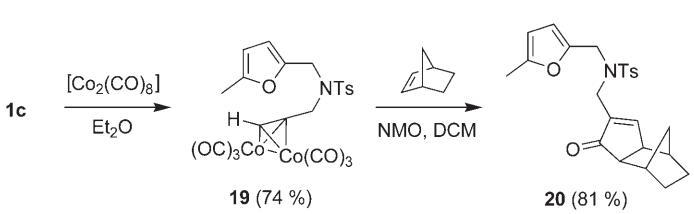
Table 4. Reaction of **1c** in the presence of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ as catalysts under different conditions.

Entry	Catalyst	Mol%	Solvent	Additive	T [°C]	t [h]	Yield of **2c** [%]
1	$[Ru_3(CO)_{12}]$	6.1	CD_3CN	–	50	21	–
2	$[Ru_3(CO)_{12}]$	5.0	$CDCl_3$	–	50	11	64
3	$[Ru_3(CO)_{12}]$	4.3	C_6D_6	–	50	11	66
4	$[Ru_3(CO)_{12}]$	2.7	[D$_6$]acetone	–	50	10	–
5	$[Os_3(CO)_{12}]$	4.4	CD_3CN	Me_3NO	50	5	–
6	$[Os_3(CO)_{12}]$	4.9	$CDCl_3$	Me_3NO	50	10	–
7	$[Os_3(CO)_{12}]$	4.8	C_6D_6	Me_3NO	50	10	–
8	$[Os_3(CO)_{12}]$	5.0	CD_2Cl_2	Me_3NO/CD_3CN	35	21	–
9	$[Os_3(CO)_{12}]$	5.0	[D$_6$]DMSO	–	120	5	traces

The ester **7** as well as the pyrrole **8** gave no conversion (Table 3, entries 1 and 2). Switching to the *N*-tosyl-pyrrole **9** gave instead of the desired aniline the anellated pyrrole **10** in good yield (Table 3, entry 3). With furans and Pt^{II} catalysts Echavarren and co-workers observed similar reactions.[16] The thiophene **11** (Table 3, entry 4) was completely inactive, which again is in accord with the observations of Echavarren and co-workers[11] with Pt^{II} catalysts. The oxazoles **12**, **13**, and **15** (Table 3, entries 5–7) would have provided a nice route to 3-hydroxy- or 4-hydroxypyridines, but either no conversion occurred or propargyl alcohol was eliminated to give the vinyloxazoles **14** and **16**. The dimethoxybenzyl derivative **17** underwent a 50% conversion, but no clean compound could be isolated from the complex product mixture. Compound **18** with the side-chain attached to the 3-position of the furan ring did not react at all.

We also studied the effect of catalyst on the reaction. First, we used $[Ru_3(CO)_{12}]$ as another d^8 system. For the conversion of **1c** to **2c** a yield of up to 66% could be obtained (Table 4, entries 1–4), but use of a noncoordinating solvent such as chloroform or benzene was essential. However, the reactions were slower than with the gold catalysts and the selectivity was also lower. On the other hand, $[Os_3(CO)_{12}]$ did not provide **2c** in significant amounts under any of the tested conditions (Table 4, entries 5–9). Since the creation of a free coordination site in $[Os_3(CO)_{12}]$ is much more difficult than in $[Ru_3(CO)_{12}]$, either Me_3NO had to be added (Table 4, entries 5–8)[17] or the reaction had to be conducted at 120°C (Table 4, entry 9).[18]

We then switched to another carbonyl complex, $[Co_2(CO)_8]$. In stoichiometric reactions with **1c** the (alkyne)hexacarbonyldicobalt complex **19** was isolated, which was characterized by crystal-structure analysis (Scheme 2, Figure 1).[19] In the solid-state structure both the furan and phenyl groups are approximately planar. Atom C11 deviates 0.100 Å from the furan plane, while the sulfur atom deviates



Scheme 2. Reaction of **1c** with $[Co_2(CO)_8]$ and subsequent Pauson–Khand reaction with norbornene.

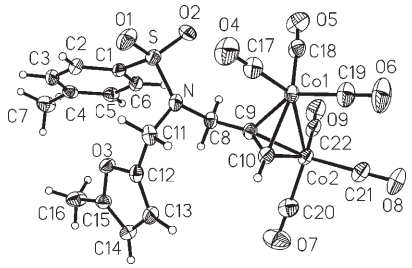
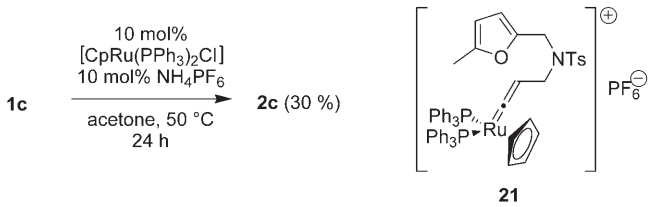


Figure 1. Solid-state structure of **19**.

0.086 Å from the phenyl plane. The alkyne group is coordinated to two $Co(CO)_3$ groups. The C9–C10 bond has a length of 1.333(2) Å which corresponds to a C=C double bond and therefore has been considerably lengthened by coordination. This is also reflected in the ^{1}H NMR spectrum; the signal of the terminal alkyne position shifts from $\delta =$ 2.06 ppm (t, $J = 2.4$ Hz, 1H) in **1c** to $\delta = 5.96$ ppm (s, 1H) in **19**. The C8-C9-C10 and C9-C10-H10 angles are 145.0(1) and 142°, respectively. Very similar dimensions have been found in the crystal structures of other propynyl-bis(tricarbonylcobalt) compounds listed in the Cambridge Structural Database. The nitrogen atom shows only a small deviation from planarity: the sum of the three valence angles about the nitrogen atom is 355.2°. The shortest intramolecular contacts are H2···O1 2.50 Å, H8A···O2 2.37 Å, and H11A···O1 2.46 Å. The crystal packing shows four intermolecular C–H···O interactions with H···O distances between 2.46 and 2.60 Å.

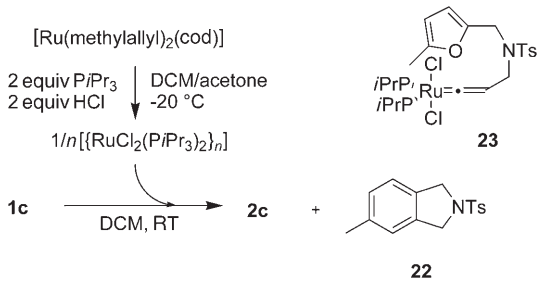
While no intramolecular reaction with the furan ring could be induced by the cobalt carbonyl fragment, π-coordination of the alkyne and a subsequent intermolecular Pauson–Khand reaction with norbornene proceeded readily to give **20**. This example shows that the preparation of π complexes of the alkyne unit in **1c** is possible. On the other hand, alkynyl or vinylidene complexes were not formed. In efforts to obtain stoichiometric [Ph_3PAu^I-alkynyl] complexes[20] of **1c** or vinylidene complexes **21** the known compound **2c** was isolated (Scheme 3). However a small amount



Scheme 3. Reaction of **1c** with $[CpRu(PPh_3)_2Cl]$.

of a material which could, according to ^{31}P NMR and FAB mass spectra, be **21** was also separated. This shows that not only the d^8 Ru^0 system but also the d^6 Ru^{II} are suitable precatalysts.

When starting with $[Ru(methylallyl)_2(cod)]$ instead of $[CpRu(PPh_3)_2Cl]$, the ^{1}H and ^{31}P NMR spectra again provided evidence for a vinylidene species, in this case **23**. A small amount of a by-product was isolated and identified by crystal-structure analysis as the deoxygenated arene **22** (Scheme 4, Figure 2).[19]



Scheme 4. Reaction of **1c** with $[Ru(methylallyl)_2(cod)]$.

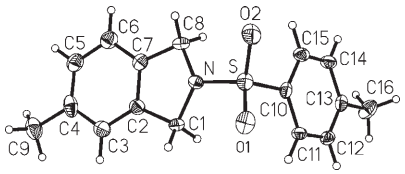


Figure 2. Solid-state structure of **22**.

We assume that the oxygen atom ends up at the phosphane moiety, probably transferred from the intermediate arene oxide.[6] Examples of the deoxygenation of arene oxides by phosphanes exist in the literature.[21]

Finally, we looked at possible further derivatizations of **2**. After allylation to **24** (the crystal structure is shown in Figure 3)[19] a thermal *para*-Claisen rearrangement to **25** was possible (Scheme 5), providing a convenient route to further substitution in the *para*-position of the pentasubstituted benzene ring. The olefin group can be utilized in further steps. The triflate **26** can also be formed (the solid-state structure

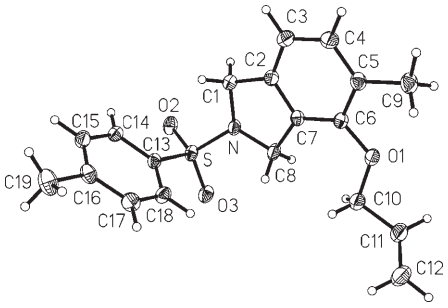
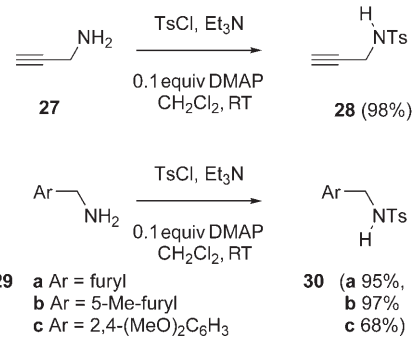
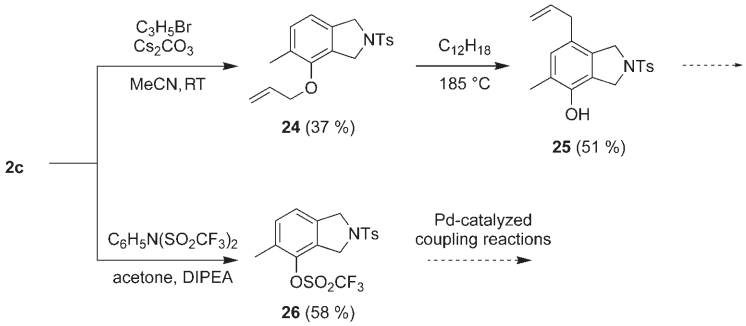


Figure 3. Solid-state structure of **24**.



Scheme 6. Crystalline intermediates of the syntheses of substrates **1**.



Scheme 5. Further derivatization of **2c**.

is shown in Figure 4)[19] and is also a useful group for further cross-coupling or reduction reactions.

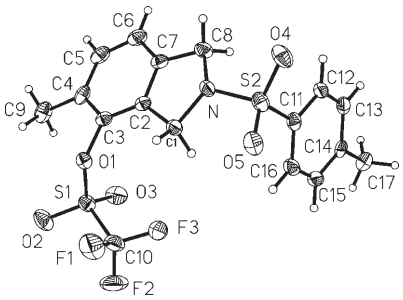


Figure 4. Solid-state structure of **26**.

Structural studies and implications for reactivity: Several of the substrates **1** and products **2** crystallized and crystal structures could be obtained.[19]

In addition crystal structures could also be obtained of the compounds formed during the synthesis of the substrates **1** (see the Supporting Information). Tosylation of propargylamine **27** delivered the *N*-propargyltosylamide **28**, tosylation of the fururylamines **29a** and **29b** gave the synthetic intermediates **30a** and **30b**, and from the benzylamine **29c** the tosylamide **30c** was obtained (Scheme 6).[19]

The crystal structures of the substrates **1c**, **1e**, **1f**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1t**, **8**, **9**, **11**, and **18** were analyzed with respect to the relative orientation of the reactive subunits, the alkyne and heterocycle. A comparison of these structures shows that there are two major families of conformers in the solid state; only **1k** has a significantly different conformation in the crystal.

In the first family, **1c**, **1e**, **1f**, **1i**, **1j**, **1l**, **1t**, **8**, **9**, **11**, and **18**, the relative orientations differ only slightly (Figure 5). This is remarkable, especially since the side chains of these substrates are quite different, which strongly suggests that this conformation is an absolute minimum for these sulfonamide-tethered ω-alkynylfurans.

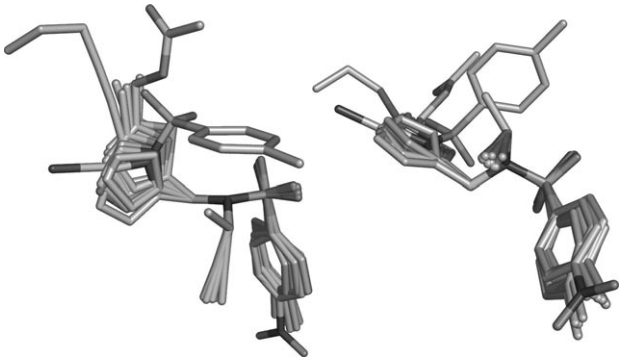


Figure 5. Superimposition of the amino moieties of compounds **1c**, **1e**, **1f**, **1i**, **1j**, **1l**, **1t**, **8**, **9**, **11**, **18**; two different views are shown.

In the second family, **1m**, **1n**, and **1s**, there are also pronounced similarities, even though they again possess different side chains (Figure 6). Once more this suggests that this conformation is an absolute minimum for the ω-alkynylfurans with an ether or ether-like dimethylammonium tether.

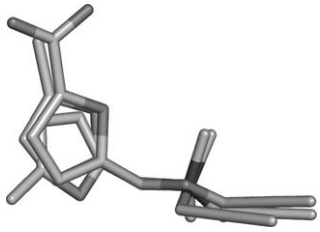


Figure 6. Superimposition of **1m**, **1n**, and **1s**.

In **1k** the alkynyl group and the furan ring are very close; they occupy a conformation which is ready for cyclization. That the conformation of this sulfonamide differs from the conformations of all the other sulfonamides shown in Figure 5 might be due to packing effects.

Since these conformations were observed in the crystalline state, we investigated whether high steric barriers for the interconversion of different conformers exist. We started with **1s**, the simplest starting material with only an oxygen atom in the tether which has only a few unknown parameters and for which also a crystal structure was available (Figure 7), as the first model system. We used the MM3

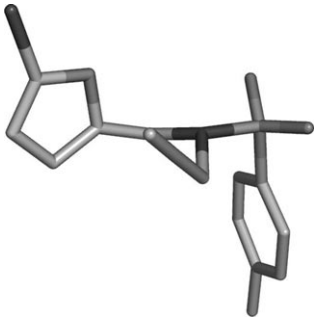


Figure 7. Conformation of **1k** in the crystal state.

force field[22] and the TINKER program [23] and initially optimized the geometry of the crystal structure, which was reproduced well. Then the dynamic behavior was investigated in a molecular dynamics simulation ($T=400$ K; $\Delta t=0.5$ fs; $t=25$ ps); this calculation showed that there are no torsional barriers which cannot be passed under these conditions (an mpg movie is included in the Supporting Information). We then turned to **1k**; we were faced with the problem that no force-field parameters have been published for the sulfonamide moiety, so these parameters were generated by comparison with similar groups. A test of these new parameters nicely reproduced the geometry obtained in the crystal structure analysis. The subsequent molecular dynamics simulation performed under the same conditions as mentioned above for **1s** also provided no evidence for barriers that cannot be passed (another mpg movie is included in the Supporting Information). The conformational changes are dominated by rotations around N–C and C–C single bonds in combination with inversion vibrations at the nitrogen atom of the sulfonamide (compare below). Thus the failure of these substrates to react with the gold catalysts to give phenols is clearly not due to steric effects of the substituents, which would not allow the proper conformation to be occupied for cyclization; the electronic effects of these substituents must be the cause of the lack of reactivity.

Hence the results can be interpreted as follows: The failure of **1p** to react can be assigned to the reduction of the catalyst by the furyl alcohol as discussed above; the failure of all three acceptor-substituted derivatives **1q**–**1s** shows that the acceptor inhibits the reaction. If the gold-catalyzed reaction follows the path suggested by Echavarren and coworkers[3] on the basis of the side-products and calculations for the platinum-catalyzed case, it can be assumed that the initial cyclopropanation (see also species **C** in reference [7]) of the enol-ether substructure of the furan is not electronically compatible with an acceptor substituent on the furan ring. The failure of **1k** to react can be explained similarly since the bromo substituent also deactivates the π system.

Regarding the catalysis products, superposition of **2b**, **2c**, **2j**, **22**, **24**, and **26** shows a high conformational similarity (Figure 8). With the exception of **2c** even the tosyl groups have the same orientation with respect to the anellated phenol.

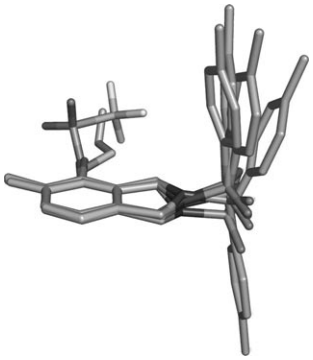


Figure 8. Superimposition of the products **2b**, **2c**, **2j**, **22**, **24**, and **26**.

In all the sulfonamides the nitrogen atom has a pyramidal conformation, even in derivatives with only one carbon substituent and one hydrogen atom on the nitrogen. Typical deviations of the bond angles at the nitrogen atom from 360° are 15.2° for **28**, 17.2° for **30a**, 15.2° for **30b**, and 21.6° for the benzyl derivative **30c**. Looking along the N–S bond, owing to this pyramidalization, a pseudostaggered conformation is observed, the phenyl ring attached to the sulfur atom is always arranged between the two substituents on the nitrogen atom, as exemplified in Figure 9 for **28**. As mentioned above, inversions at this nitrogen atom are strongly involved in the conformational changes of the substrates.

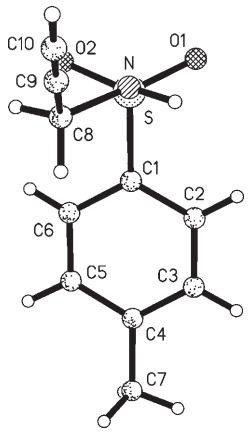


Figure 9. The view along the N–S bond of **28** shows a conformation typical of all the sulfonamides investigated.

Conclusion

The observation that certain substituents are tolerated in gold-catalyzed phenol synthesis and others are not, that a bromo substituent is tolerated at a certain position and not at

another, and that other five-membered heterocycles do not undergo similar reactions, is one part of the mechanistic puzzle for this reaction; the final mechanistic picture must also explain these facts. For the substituted furans it has been shown that substituents that deactivate the π system of the furan are not tolerated; molecular modeling confirmed that there are no steric factors preventing these substrates from occupying a reactive conformation.

The catalytic activity of $[Ru_3(CO)_{12}]$ shows how general the cycloisomerization reaction is for a d^8-configurated complex. The deoxygenation in the presence of a phosphane ligand and a ruthenium complex demands further investigation and the *para*-Claisen rearrangements of the allyl ether **2c** and the triflate of **2c** show how the products might serve as building blocks and be further converted in subsequent syntheses.

Experimental Section

General methods: Melting points were taken by using a Fischer–Johns Melting Apparatus and are uncorrected. IR spectra were recorded on a Bruker IFS 28 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Bruker AC 250, Bruker ARX 300 or Bruker ARX 500. NMR spectra were recorded in $CDCl_3$, except when otherwise stated. Chemical shifts are given in ppm relative to $CDCl_3$ (^{1}H, δ = 7.26 ppm; ^{13}C, δ = 77.16 ppm). LRMS and HRMS were taken on a Finnigan MAT 95 or a Varian MAT 711 spectrometer. All commercially available compounds were used without further purification.

General procedure for gold-catalyzed reactions: The test substrate was dissolved in acetonitrile and a solution of the gold catalyst in acetonitrile (10% w/w) was added. The reaction was monitored by either thin-layer chromatography or by ^{1}H NMR spectroscopy.

2l: According to the general procedure, **1l** (700 mg, 1.83 mmol) and $AuCl_3$ (27.7 mg, 91 μmol, 5.0 mol%) in acetonitrile (15 mL) were used. After 24 h, a colorless precipitate was filtered, washed with water, methanol, and diethyl ether and dried in vacuo to yield 255 mg (36%) of **2l**. M.p. 235–245 °C; IR (KBr): $\tilde{\nu}$ = 3498, 1578, 1425, 1323, 1230, 1138, 1098, 1051, 809, 795, 763, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.13 (s, 3H), 2.41 (s, 3H), 4.49 (s, 2H), 4.54 (s, 2H), 5.54 (s, 1H), 7.09 (s, 1H), (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.03 (q), 21.50 (q), 52.96 (t), 53.23 (t), 109.57 (s), 120.28 (s), 122.73 (d), 127.53 (d, 2C), 128.42 (s), 129.86 (d. 2C), 133.60 (s), 136.64 (s), 143.77 (s), 149.67 (s) ppm. MS (70 eV): m/z (%): 383 (16) [^{81}Br−M^+], 381 (17) [^{79}Br−M^+], 269 (11), 267 (10), 228 (90), 226 (100), 157 (13), 155 (21), 91 (78); elemental analysis calcd (%) for $C_{16}H_{16}BrNO_3S$ (382.28): C 50.27, H 4.22, N 3.66; found: C 50.25, H 4.33, N 3.93.

2n: According to the general procedure, **1n** (8.00 mg, 24.8 μmol) and $AuCl_3$ (380 μg, 1.2 μmol, 5.0 mol%) in acetonitrile (500 μL) were used. After 26 h, the product **2n** was characterized by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_3CN, 250 MHz): δ = 3.07 (s, 6H), 3.27 (s, 3H), 4.72 (d, J = 5.4 Hz, 4H), 6.85 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (CD_3CN, 62.9 MHz): δ = 15.2 (q), 52.9 (q, 2C), 68.9 (t), 70.9 (t), 115.0 (d), 119.2 (s), 125.6 (s), 132.2 (s), 132.3 (d), 150.3 (s) ppm.

2o: According to the general procedure, **1o** (20.7 mg, 61.3 μmol) and $AuCl_3$ (9.27 mg, 3.06 μmol, 5.0 mol%) in acetonitrile (500 μL) were used. The reaction was monitored by ^{1}H NMR spectroscopy. After 80 h, 80% of the starting material had been converted, according to characteristic signals of phenolic protons at δ = 6.77 (d, J = 8.3 Hz, 1H) and 7.24 ppm (d, J = 8.3 Hz, 1H).

2t: According to the general procedure, **1t** (193 mg, 531 μmol) and $AuCl_3$ (8.05 mg, 26.5 μmol, 5.0 mol%) in acetonitrile (3.0 mL) were used. The reaction was monitored by ^{1}H NMR spectroscopy. After 24 h, the crude product was purified by column chromatography on silica (petrol ether (PE)/ethyl acetate (EA)/dichloromethane (DCM), 5:1:5) to yield 11.0 mg (6%) of **2t** as a colorless solid. R_f (PE/EA/DCM, 5:1:5) = 0.24. M.p. 122–124 °C; IR (neat): 3395, 2951, 2859, 1744, 1731, 1625, 1598, 1495, 1453, 1379, 1361, 1315, 1260, 1216, 1149, 1107, 1079, 1045, 1017, 943, 917, 836, 812, 785, 712, 699, 666, 589, 568, 537 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.08 (s, 3H), 2.40 (s, 3H), 4.59 (s, 2H), 4.60 (s, 2H), 5.04 (s, 2H), 6.70 (d, J = 7.7 Hz, 1H), 7.14 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 8.38 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.86 (q), 21.48 (q), 51.81 (t), 54.12 (t), 62.67 (t), 114.32 (d), 120.53 (s), 125.20 (s), 127.61 (d, 2C), 129.78 (d, 2C), 132.66 (d), 133.63 (s), 139.82 (s), 143.61 (s), 151.08 (s), 174.33 (s) ppm. MS (FAB positive-ion, matrix: *p*-nitrobenzyl alcohol): m/z (%): 723 (1) [$2M$+H$^+$], 494 (3) [M+Cs$^+$], 384 (5) [M+Na$^+$], 362 (66) [M^+], 302 (32), 206 (16), 155 (15), 146 (100), 133 (38) [Cs$^+$], 91 (51), 55 (44), 43 (33). HRMS (FAB positive-ion, matrix: *p*-nitrobenzyl alcohol): calcd for $^{12}C_{18}{}^1H_{20}{}^{14}N_1{}^{16}O_5{}^{32}S_1$: 362.1062; found: 362.1070.

2u: According to the general procedure, **1u** (55.0 mg, 127 μmol) and $AuCl_3$ (1.92 mg, 6.33 μmol, 5.0 mol%) in acetonitrile (500 μL) were used. The reaction was monitored by ^{1}H NMR spectroscopy. After three days, the crude product was purified by column chromatography on silica (petrol ether/ethyl acetate 4:1) to yield 34.0 mg (62%) of **2u** as a pale yellow solid. M.p. 172–173 °C. R_f (PE:EA, 4:1) = 0.20. IR (film): $\tilde{\nu}$ = 3256, 3108, 2975, 2875, 1697, 1625, 1597, 1527, 1471, 1340, 1285, 1157, 1042, 949, 854, 813, 736, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.16 (s, 9H), 4.64 (s, 2H), 4.66 (s, 2H), 5.03 (s, 2H), 6.71 (d, J = 7.7 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 9.0 Hz, 2H), 8.36 (d, J = 9.0 Hz, 1H), 8.64 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 27.41 (q, 3C), 39.03 (s), 52.12 (t), 54.37 (t), 63.04 (t), 114.35 (d), 121.07 (s), 124.57 (d, 2C), 124.60 (s), 128.72 (d, 2C), 133.11 (d), 139.01 (s), 143.00 (s), 150.25 (s), 151.40 (s), 182.05 (s) ppm; MS (DCI negative-ion, reactand gas: CH_4): m/z (%): 434 (19) [M^+], 332 (100), 258 (3), 186 (5). HRMS (DCI negative-ion, reactand gas: CH_4): calcd for $C_{20}H_{22}N_2O_7S$: 434.1148; found: 434.1157; elemental analysis calcd (%) for $C_{20}H_{22}N_2O_7S$ (434.46): C 55.29, H 5.10, N 6.45; found: C 53.11, H 4.81, N 5.48.

10: According to the general procedure, **9** (420 mg, 949 μmol) and $AuCl_3$ (28.8 mg, 94.9 μmol, 10 mol%) in acetonitrile (3.0 mL) were used. After 15 minutes, the reaction was stopped by cooling, the solvent removed in vacuo, and the crude product purified by column chromatography on silica (hexane/ethyl acetate, 1:1) to yield 341 mg (77%) of **10** as a dark yellow solid. R_f (H/EA, 1:1) = 0.6. IR (film, NaCl): $\tilde{\nu}$ = 3482, 3288, 3146, 3065, 2957, 2924, 2874, 2588, 2257, 1919, 1686, 1647, 1597, 1494, 1451, 1374, 1344, 1162, 1121, 1090, 1038, 1018, 912, 814, 734, 703, 673 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.33 (s, 3H), 2.42 (s, 3H), 3.96 (s, 2H), 4.59 (s, 2H), 4.86 (s, 1H), 5.00 (s, 1H), 6.20 (d, J = 3.8 Hz, 1H), 7.06 (d, J = 3.3 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.5 (q), 21.7 (q), 43.8 (t), 49.1 (t), 107.7 (t), 107.8 (d), 121.9 (d), 122.8 (s), 125.3 (s), 127.1 (d, 2C), 127.5 (d, 2C), 129.3 (d, 2C), 130.4 (d, 2C), 132.7 (s), 134.5 (s), 135.5 (s), 143.5 (s), 145.8 (s) ppm; MS (70 eV): m/z (%): 442 (5) [M^+], 286 (19), 199 (22), 155 (37), 91 (100), 65 (16), 44 (21), 18 (60).

14: According to the general procedure, **13** (37.0 mg, 207 μmol) and Na[$AuCl_4$]·2H_2O (4.10 mg, 10.3 μmol, 5.0 mol%) in acetonitrile (500 μL) were used. After 15 h at 50 °C, the product was characterized by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_3CN, 300 MHz): δ = 2.01 (s, 3H), 2.29 (s, 3H), 5.06 (d, J = 11.1 Hz, 1H), 5.42 (d, J = 17.5 Hz, 1H), 6.48 (dd, J = 11.1, 17.5 Hz, 1H) ppm.

16: According to general procedure, **15** (30.0 mg, 124 μmol) and Na[$AuCl_4$]·2H_2O (2.50 mg, 6.2 μmol, 5.0 mol%) in acetonitrile (500 μL) were used. After 15 h at 50 °C, the crude product was purified by column chromatography on silica (petrol ether/ethyl acetate, 5:1) to yield 9.7 mg (30%) of **16** as a colorless oil. R_f (PE:EA, 5:1) = 0.38. IR (neat): $\tilde{\nu}$ = 2922, 2360, 1682, 1646, 1573, 1546, 1486, 1449, 1421, 1125, 977, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.26 (s, 3H), 5.26 (d, J = 11.1 Hz, 1H), 5.71 (d, J = 17.5 Hz, 1H), 6.57 (dd, J = 11.1, 17.5 Hz, 1H), 7.41–7.48 (m, 3H), 8.01–8.08 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 11.9 (q), 113.1 (t), 121.3 (d), 126.3 (d), 127.4 (s), 128.7 (d), 130.3 (d), 135.1 (s),

145.2 (s), 159.8 (s) ppm; MS (EI, 70 eV): *m/z* (%): 185 (100) [M^+], 116 (28), 104 (19), 86 (20), 84 (30); HRMS (EI, 70 eV): calcd for $C_{12}H_{11}NO$: 185.0841; found 185.0840.

19: A solution of octacarbonyldicobalt (260 mg, 760 μmol) in diethyl ether (ca. 20 mL) was treated with a solution of 4-methyl-*N*-(5-methylfuran-2-ylmethyl)-*N*-prop-2-ynylbenzenesulfonamide (230 mg, 759 μmol) in diethyl ether (ca. 5.0 mL) under argon. After stirring the reaction mixture for 72 h, the crude product was purified by column chromatography on silica (hexane(H)/ethyl acetate, 5:1) to give 330 mg (74%) of **61** as dark crystals. M.p.: 128°C. R_f (H/EA, 5:1) = 0.34. IR (neat): $\tilde{\nu}$ = 2370, 2344, 2094, 2057, 2019, 1654, 1560, 1432, 1347, 1327, 1220, 1156, 1092, 1068, 1021, 972, 915, 886, 814, 790, 762, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.11 (s, 3H), 2.44 (s, 3H), 4.48 (s, 2H), 4.52 (s, 2H), 5.84 (d, J = 2.2 Hz, 1H), 5.96 (s, 1H), 6.02 (d, J = 3.0 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.3 (q), 21.5 (q), 29.7 (t), 30.9 (t), 73.3 (d), 89.7 (s), 106.3 (d), 111.0 (d), 127.4 (d, 2C), 129.5 (d, 2C), 137.2 (s), 143.2 (s), 147.0 (s), 152.6 (s), 199.2 (CO) ppm; MS (70 eV): *m/z* (%): 561 (5), 533 (13), 505 (18), 477 (4), 449 (8), 421 (65), 28 (100); elemental analysis calcd (%) for $C_{22}H_{17}Co_2NO_9S$ (589.1): C 44.85, H 2.89, N 2.38; found: C 45.01, H 2.97, N 2.54.

20: *N*-Methylmorpholine *N*-oxide (310 mg, 2.65 mmol) was added to a solution of **19** (260 mg, 441 μmol) and norbornene (49.9 mg, 530 μmol) in dichloromethane (ca. 5 mL) and the reaction mixture was stirred for 16 h at ambient temperature. After filtration and removal of the solvent in vacuo, the crude product was purified by column chromatography on silica (hexane/ethyl acetate, 1:1) to give 153 mg (81%) of **20** as a yellow oil. R_f (H/EA, 1:1) = 0.54. IR (film): $\tilde{\nu}$ = 3278, 3032, 2957, 2874, 2254, 1918, 1694, 1630, 1598, 1560, 1522, 1494, 1449, 1340, 1221, 1160, 1093, 1020, 912, 815, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (s, 2H) 1.21 (s, 1H), 1.24 (s, 2H), 1.27 (s, 1H), 1.57 (m, 3H), 2.09 (s, 3H), 2.31 (br s, 1H), 2.40 (s, 3H), 2.52 (br s, 1H), 3.86 (s, 2H), 4.28 (s, 2H), 5.75 (br s, 1H), 5.97 (d, J = 3.1 Hz, 1 Hz), 7.25 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.4 (q), 21.4 (q), 28.3 (t), 29.0 (t), 31.1 (t), 37.9 (d), 38.9 (d), 42.7 (t), 45.0 (t), 48.4 (d), 54.4 (d), 106.3 (d), 110.9 (d), 127.5 (d, 2C), 129.5 (d, 2C), 136.0 (s), 137.4 (s), 143.7 (s), 143.9 (s), 152.3 (s), 161.7 (d), 209.7 (C=O) ppm; MS (70 eV): *m/z* (%): 425 (1) [M^+], 270 (78), 176 (61), 18 (100).

21: Compound **1c** (75.1 mg, 248 μmol) was added to a solution of [CpRu(PPh$_3$)$_2$Cl] (60.0 mg, 82.6 μmol) and NH_4PF_6 (16.2 mg, 99.1 μmol) in methanol (ca. 50 mL) and the reaction mixture was stirred for 4 h at ambient temperature. After removal of the solvent in vacuo, the residue was redissolved in dichloromethane and the insoluble white precipitate filtered off. The crude product was obtained by precipitation with diethyl ether and then dried in vacuo. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = −143.0 (sept., J = 4.4 Hz, PF_6^-), 40.8 (d, J = 26.8 Hz), 41.3 (d, J = 26.8 Hz) ppm; FAB-MS (positive-ion): *m/z* (%): 994 (12) [cation], 719 (19), 429 (48), 352 (12), 279 (100), 183 (18), 133 (32), 107 (38), 91 (53), 69 (65), 55 (81).

23: P*i*Pr$_3$ (201 mg, 1.3 mmol) was added to a solution of [Ru(methylallyl)$_2$(cod)] (200 mg, 627 μmol) in dichloromethane (ca. 25 mL) and acetone (16 mL) and the mixture was cooled to −20°C. After addition of HCl in methanol (1.25 M, 1.3 mmol, 1.0 mL, Fluka) and stirring for 30 min at −20°C, **1c** (950 mg, 3.1 mmol) was added and the reaction mixture stirred for another 20 h at ambient temperature. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (dd, J = 7.0, 13.9 Hz, 36H), 2.14 (m, 6H), 2.21 (s, 3H), 2.43 (s, 3H), 4.03 (d, J = 2.5 Hz, 2H), 4.38 (s, 2H), 4.58 (s, 1H), 5.87 (d, J = 2.8 Hz, 1H), 6.16 (d, J = 2.8 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 59.7 (s) ppm.

24: Allylic bromide (500 μL, 6.0 mmol) was slowly added to a solution of **2c** (240 mg, 792 μmol) and Cs_2CO_3 (535 mg, 1.64 mmol) in acetonitrile (ca. 30 mL) and the reaction mixture was stirred for 20 h at ambient temperature. After removal of the solvent in vacuo, the crude product was purified by column chromatography on silica (hexane/ethyl acetate/dichloromethane, 8:1:1) to give 100 mg (37%) of **24** as a colorless solid. M.p. 91–96°C. R_f (H/EA/DCM, 8:1:1) = 0.22. IR (film, NaCl): $\tilde{\nu}$ = 2923, 2366, 2344, 1596, 1458, 1348, 1315, 1215, 1164, 1098, 1054, 998, 930, 813, 712, 665 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.23 (s, 3H), 2.40 (s, 3H), 4.36 (br d, J = 5.5 Hz, 2H), 4.58 (s, 2H), 4.65 (s, 2H), 5.26 (dd, J = 1.2, 10.4 Hz, 1H), 5.37 (dd, J = 1.5, 17.1 Hz, 1H), 6.03 (ddt, J = 10.4, 17.1, 22.9 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz,): δ = 15.8 (q), 21.3 (q), 51.9 (t), 53.5 (t), 73.0 (t), 117.5 (d), 117.8 (t), 127.4 (d, 2C), 128.1 (s), 129.7 (d, 2C), 131.1 (d), 133.3 (d), 133.5 (s), 135.6 (s), 143.5 (s), 152.2 (s) ppm; one s not detected; MS (70 eV): *m/z* (%): 342 (11) [M^+], 313 (11), 302 (18), 301 (100), 187 (23), 158 (20), 155 (34), 146 (80), 118 (26), 91 (92), 41 (31); elemental analysis calcd (%) for $C_{19}H_{21}NO_3S$ (343.2): C 66.48, H 6.12, N 4.08; found: C 66.45, H 5.85, N 4.18.

25: A solution of **24** (60.0 mg, 175 μmol) in triethylbenzene (ca. 2.0 mL) was heated for 3 h at 185°C under argon. The crude product was purified by column chromatography on silica (hexane/ethyl acetate/dichloromethane, 6:1:2) to yield 30.8 mg (51%) of **25** as a colorless solid. M.p. 169–174°C. R_f (H/EA/DCM, 6:1:2) = 0.16; IR (film): $\tilde{\nu}$ = 3448, 2922, 2371, 2345, 1701, 1637, 1598, 1496, 1458, 1341, 1219, 1160, 1098, 1017, 916, 814, 720, 708, 665 cm^{-1}; ^1H NMR ([D$_6$]acetone, 250 MHz): δ = 2.14 (s, 3H), 2.37 (s, 3H), 3.17 (d, J = 6.5 Hz, 2H), 4.53 (s, 4H), 4.93 (d, J = 4.0 Hz, 1H), 4.96, (d, J = 2.4 Hz, 1H), 5.83 (ddt, J = 2.4, 4.0, 6.5 Hz, 1H), 6.79 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR ([D$_6$]acetone, 62.9 MHz): δ = 15.8 (q), 21.3 (q), 37.2 (t), 52.7 (t), 53.6 (t), 115.6 (t), 123.4 (s), 124.7 (s), 126.0 (s), 128.4 (d, 2C), 130.6 (d, 2C), 131.8 (d), 134.7 (s), 137.4 (d), 144.7 (s), 149.1 (s) ppm; one s not detected; MS (70 eV): *m/z* (%): 343 (39) [M^+], 188 (100), 160 (13), 91 (26); elemental analysis calcd (%) for $C_{19}H_{21}NO_3S$ (343.2): C 66.48, H 6.12, N 4.08; found: C 66.24, H 5.94, N 4.19.

26: According to the general procedure, **1c** (800 mg, 2.64 mmol) was treated with a solution of $AuCl_3$ (400 mg, 132 μmol, 5 mol%) in CD_3CN (10% w/w). After removal of the solvent in vacuo, the residue was redissolved in acetone and diisopropylethylamine (DIPEA) (900 μL, 5.28 mmol) and *N,N*-bis(trifluormethanesulfonyl)aniline (1.89 g, 5.28 mmol) were added. The reaction mixture was stirred for 18 h at ambient temperature, the solvent evaporated, and the residue redissolved in dichloromethane and extracted with saturated $NaHCO_3$ solution. The crude product was purified by column chromatography on silica (hexane (H)/acetone (A), 2:1) to give 642 mg (58%) of **26** as a pale-yellow solid. M.p. 110–111°C. R_f (H/A, 2:1) = 0.46. IR (film): $\tilde{\nu}$ = 2369, 2344, 1654, 1560, 1458, 1406, 1352, 1215, 1166, 1137, 1097, 1034, 970, 926, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.36 (s, 3H), 2.43 (s, 3H), 4.63 (s, 2H), 4.73 (s, 2H), 7.08 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.3 (q), 21.5 (q), 51.8 (t), 53.7 (t), 121.0 (s), 122.5 (d), 127.6 (d, 2C), 129.9 (d, 2C), 130.0 (s), 130.9 (s), 132.2 (d), 133.4 (s), 137.4 (s), 141.9 (s), 144.0 (s) ppm; ^{19}F NMR ($CDCl_3$, 235.3 MHz): δ = −74.9 (s) ppm. MS (70 eV): *m/z* (%): 435 (25) [M^+], 281 (13), 280 (100), 147 (57), 91 (49); elemental analysis calcd (%) for $C_{17}H_{16}F_3NO_5S_2$ (435.3): C 46.91, H 3.68, N 3.22; found: C 47.11, H 3.71, N 3.22.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (Ha 1932/6-2), the Fonds der Chemischen Industrie (Chemiefonds fellowship for J.P.W.), and the Karl-Ziegler-Stiftung for their generous support. Gold salts were donated by Umicore.

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Received: October 12, 2005
Revised: February 9, 2006
Published online: May 23, 2006

