

Heterogeneous Gold-Catalysed Synthesis of Phenols

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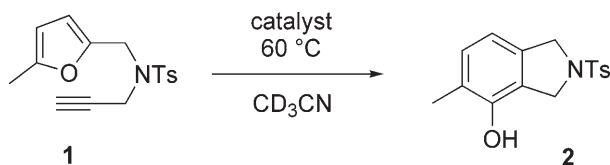
Abstract: Nanoparticles of gold supported on nanocrystalline CeO₂ catalyse the isomerisation of ω -alkynylfurans to phenols. Initial leaching of gold was observed, which could be minimised by calcining. Subsequent runs showed that once all soluble species had leached, the surface-bound, cationic gold species is still active and can reach turnover numbers of up

to 391. This is the first time that a heterogeneous gold catalyst showed activity in the gold-catalysed phenol synthesis.

Keywords: alkynes; arenes; furans; gold; homogeneous catalysis

Introduction

Since Haruta and co-workers showed the high activity of gold catalysts for the selective oxidation of CO,^[1] much work has been carried out in the field of gold catalysis.^[2] In spite of the many reactions studied with gold catalysts, there are few examples of gold-catalysed carbon-carbon bond formations, and the vast majority of these are carried out using homogeneous catalysts.^[3] Only a couple of examples deal with the possible use of heterogeneous gold catalysts for carbon-carbon bond formation.^[4,5] The isomerisation of ω -alkynylfurans to phenols,^[6] a new reaction first discovered with gold catalysts, is catalysed by AuCl₃ and related homogeneous Au(III) complexes. In the present work we show for the first time that a heterogeneous gold on cerium oxide catalyst, possessing cationic gold species, is active and selective for this synthesis of phenols (Scheme 1). The reaction is carried out under mild conditions leading to almost 100% conversion and selectivity.



Scheme 1. Reaction Scheme of Au/CeO₂-catalysed phenol synthesis.

The gold on cerium oxide catalyst was chosen due to the high percentage of cationic gold present in this system. As previously described, nanocrystalline cerium oxide is able to stabilise cationic species of gold.^[4,7] Therefore it appeared as a good candidate to be employed for the study of C–C bond formation. Previous efforts using a variety of heterogeneous gold catalysts like gold on carbon, gold on Fe₂O₃, gold on SiO₂, gold on TiO₂ and stabilised gold nanoparticles had failed.^[8] In this work we will show a comparison between homogeneous Au(III) complexes and the heterogeneous Au/CeO₂ catalyst, using the cyclisation of alkyne **1** to phenol **2** as a test reaction (Scheme 1).

Results and Discussion

Initial experiments were carried out using CDCl₃ as solvent and the reactions were monitored by ¹H NMR; the Au/CeO₂ catalyst showed high activity and yield of the wanted product **2** achieving almost 100% conversion after 20 h of reaction. However, tests carried out to verify that the catalysis was occurring heterogeneously, gave a negative result. Analysis by atomic absorption spectroscopy (AAS)^[9] showed the presence of gold in the reaction mixture and the filtrate solution possessed high catalytic activity (85% conversion of **1** after 24 h). The CDCl₃ solvent could be responsible for the gold leaching, since the presence of gold hydroxide and oxy-hydroxide on the catalyst surface^[4] may determine an interaction with the

halogenated solvent forming soluble gold complexes. We therefore decided to use a non-halogenated solvent, such as CD_3CN , to investigate if the leaching problem could be avoided. The use of CD_3CN resulted in complete conversion of the substrate **1** to the desired product **2** after 24 h. Atomic absorption analysis on the reaction solution revealed the presence of 25 ppm of gold in solution (in 3 mL of acetonitrile this corresponds to 59 μg of gold, which is less than 6% of the total amount of gold on the catalyst) and activity tests on the filtrate solution showed a conversion of the 22% of substrate **1** after 24 h reaction [which corresponds to a turnover number (TON) of 327 for the gold present in the filtrate]. A TON of 19.2 (calculated as moles of substrate converted per mole of gold present on the catalyst) show that the reaction process is catalytic and the results are very similar to those obtained with AuCl_3 by Hashmi et al.,^[6] where the TON reaches 50. Since not all the gold atoms present on the heterogeneous catalysts are catalytically active (particle size in the range of 3–4 nm), it can be stated that the real TON of the active sites of the supported gold catalyst should be much higher than 19, probably even superior to the activity reported for the best homogeneous catalysts so far, *N,O*-complexes of gold(III).^[10] Further catalyst reuses show that leaching strongly decreases and has practically disappeared after the third reuse (Figure 1). In this case the conversion was 35% after 24 hours compared to 100% of the original catalyst (first use) at the same reaction time. The leaching test, after the third catalyst reuse, gave a conversion of 1.3% after 40 hours of reaction for the leached gold in homogeneous phase. Despite the fact that the solid catalyst has lost activity in the second and third reuse, it can still achieve 100% conversion of the substrate **1** with a longer reaction time (40 hours for the second and 55 hours for the third one). In this case, it looks like that an autocatalytic behaviour may occur suggesting that for example the decrease of pH by producing the acidic phenol slightly influences the reaction rate. This effect is under investigation.

In order to investigate the possibility of reducing or even eliminating gold leaching, the fresh catalyst was treated at high temperature (300 °C) in both oxidising

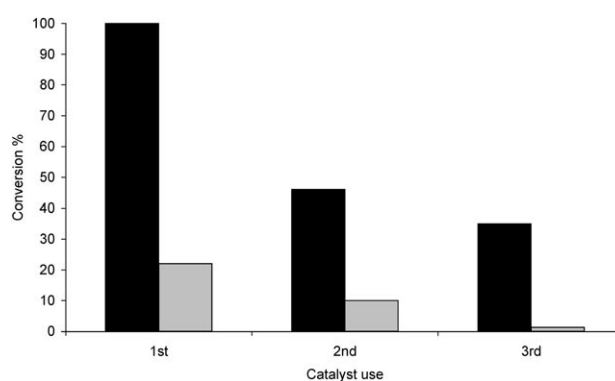


Figure 1. 1.8% Au/CeO_2 catalysts for phenol synthesis after different uses (24 h reaction time, black columns). Reaction tests of the corresponding liquid phases for catalytic activity (40 h reaction time, grey columns).

(air) and reducing (H_2) atmospheres in order to increase the interaction of the gold particles with the support and at the same time to discuss the active gold species (Au^{3+} or Au^0) on the heterogeneous catalyst. The sample treated with hydrogen showed poor catalytic activity leading to only 13% conversion of substrate **1** even after 6 days of reaction. The reduced amount of cationic gold species, after H_2 treatment, could account for the lower activity of this catalyst compared to the untreated sample (Table 1).

The catalyst sample treated with air did not differ in its catalytic activity compared to the untreated one, thus the reaction in CDCl_3 showed significant gold leaching and the filtrate solution presented high catalytic activity. As in the case of the untreated catalyst sample, the reaction was studied using CD_3CN as solvent, and high catalytic activity was found. Gold leaching was also investigated in this case by carrying out the reaction using the filtrate solution and by AAS analysis of the reaction mixture. After 24 h the conversion of **1** was 17%, and AAS showed the presence of 6.4 ppm of Au in solution (corresponding to a very small part, 1.5%, of the gold initially present). These values are much lower than those obtained with the uncalcined sample. After one recycle of the calcined sample, leaching is reduced and the homogeneous reaction as well, while the heterogeneous reac-

Table 1. Relative amount of the different gold species determined by FT-IR using CO as probe molecule.

Entry	Catalyst	$\text{Au}^{3+}/\text{Au}_\text{T}$	$\text{Au}^+/\text{Au}_\text{T}$	$\text{Au}^0/\text{Au}^\text{T}$	$(\text{Au}^+ + \text{Au}^{3+})/\text{Au}^0$
1	Au/CeO_2	0.29	0.37	0.25	2.67
2	Au/CeO_2	0.27	0.34	0.38	1.6
3	Au/CeO_2	0.22	0.32	0.32	1.67
4	Au/CeO_2	0.03	0.36	0.55	0.71
5	Au/CeO_2	0	0.37	0.52	0.7

Entry 1: untreated; entry 2: air treatment at 300 °C; entry 3: H_2 treatment at 100 °C; entry 4: sample dried at 100 °C for 48 h; entry 5: H_2 treatment at 300 °C. Au_T : total amount of gold; Au^0 : IR band at 2100 cm^{-1} ; Au^+ : IR band at 2154 cm^{-1} ; Au^{3+} : IR band at 2138 cm^{-1} .

tion decreases from 100% to 85%. It appears that, by calcinations of the catalyst in an air stream, the interaction of the gold with the support becomes stronger, further stabilising the active gold species and limiting the leaching.

FT-IR studies, carried out using CO as probe molecule, showed the presence of different gold species on the catalyst surface. In particular, untreated catalysts dried for a short time in an oven and not treated at high temperature in reducing atmospheres present a higher fraction of cationic gold and more specifically Au^{3+} .

In the case of the homogeneous catalyst, it was evidenced that Au(III) was the active species. Also in our case when the fraction of cationic gold (Au^{3+}), determined by CO adsorption, decreases with respect to the total gold (Au^{tot}) the activity decrease (see Figure 2) and, despite the lack of catalyst samples

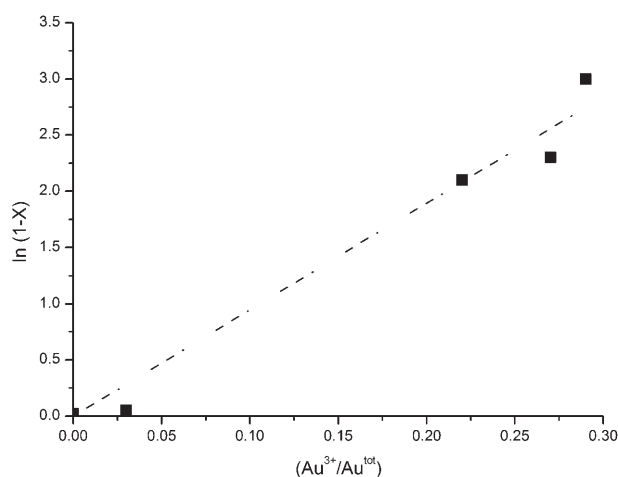


Figure 2. Correlation between the first order apparent rate constant and the amount of cationic gold for phenol synthesis. Reaction conditions: 100 μmol of **1**, 3 mL of CD_3CN , 60 °C, Au/CeO_2 (5 mol% of Au with respect to **1**).

with $\text{Au}^{3+}/\text{Au}^{\text{tot}}$ between 0.1 and 0.2, we can see a direct correlation between the fraction of cationic gold and the first order apparent rate constant. These results will support the existence of a parallelism between homogeneous and heterogeneous gold catalysts in this case, as has been found for homocoupling and heterocoupling Suzuki reaction^[4,11,12] and in general for cationic gold as a Lewis acid catalyst.^[13]

In a first approximation, if we consider the cationic gold(III) detected by CO adsorption as the active sites for phenol synthesis; then it is possible to calculate a TON by dividing the number of molecules of product obtained by the active sites corresponding to cationic Au. A theoretical estimation of the amount of Au^{3+} active sites was realised considering the total gold present as clusters of 3.5 nm and calculating the

number of surface exposed gold atoms. Once estimated, the number of 3.5 nm clusters present and the number of the total gold atoms exposed together with the ratio $\text{Au}^{3+}/\text{Au}^{\text{tot}}$, determined by FT-IR, we could calculate the number of surface exposed Au^{3+} . From the results presented in Table 2, two conclusions can be drawn. The first one is that the TON values are very similar for all catalysts supporting the hypothesis that the surface Au^{3+} species are the active sites for the isomerisation of ω -alkynylfurans to phenols on solid gold catalysts. Secondly, the TON obtained on the basis of cationic gold detected by CO adsorption is even superior to the one obtained for homogeneous gold catalysts^[6], something which can be explained on the basis of a surface concentration effect on high surface area porous catalysts.^[14]

Table 2. TON calculated as number of molecules of product obtained per active site after 24 h reaction.

Entry	Catalysts	Conversion of 1 [%]	TON
1	Au/CeO_2	100	338
2	Au/CeO_2	90	326
3	Au/CeO_2	88	391
4	Au/CeO_2	5	163
5	Au/CeO_2	0	0

Entry 1: as prepared catalyst; entry 2: air treatment at 300 °C; entry 3: H_2 treatment at 100 °C; entry 4: sample dried at 100 °C for 48 h; entry 5: H_2 treatment at 300 °C.

Conclusions

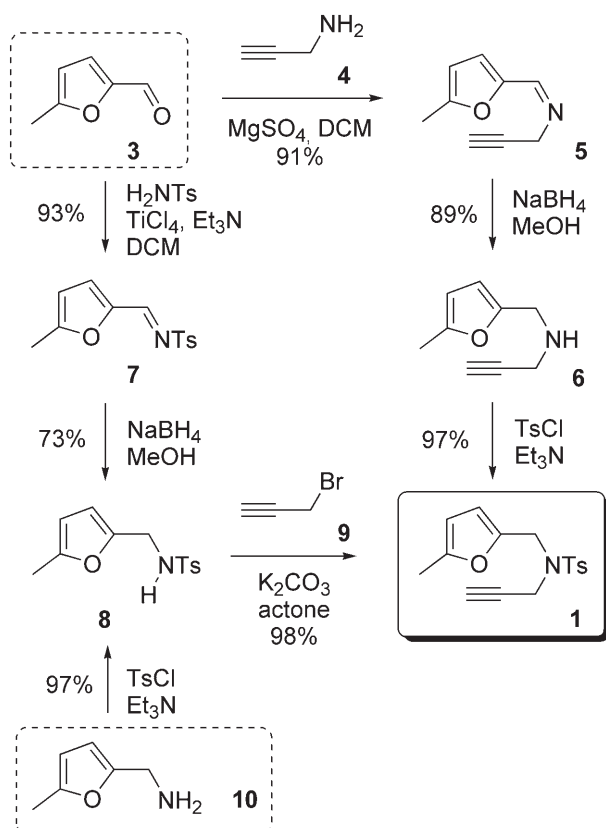
We have shown that nanoparticles of gold supported on nanocrystalline CeO_2 are able to catalyse the synthesis of phenols by isomerisation of ω -alkynylfurans. Cationic gold is the active site for the reaction and these species are very well stabilised on gold supported on nanocrystalline CeO_2 .

Caution should be taken about leaching of gold from the catalyst, because the leached species give very high turnover numbers (TON). By calcining the catalyst before use and using acetonitrile as solvent, leaching was minimised. The cationic gold species measured on the catalyst by IR-CO adsorption give a TON similar to the one reported previously for some of the homogeneous catalysts.

Experimental Section

The Au on cerium oxide catalyst was prepared using HAuCl_4 as precursor and nanocrystalline CeO_2 as support following a procedure previously reported^[15]

Different routes to the standard test substrate **1** for this type of chemistry were investigated (Scheme 2). The two commercially available starting materials are 5-methylfufu-



Scheme 2. Tested routes to **1**.

ral (**3**) and 5-methylfurfurylamine (**10**). Compound **3** is the cheaper starting material, but here in both possible routes (via **5/6** or via **7/8**), three steps are needed. Propargylamine (**4**) is relatively expensive, making the route via **5/6** less favourable. The approach via **10** uses the significantly more expensive starting material, but only two steps are needed. Our experiments proved that, if one also takes into account the yields obtained, the approach via **3/7/8** is economically the best one while the approach via **10/8** is the fastest one.

Synthesis of (5-Methylfuran-2-ylmethylene)prop-2-ynylamine (**5**)

To **3** (5.00 g, 45.4 mmol) in dichloromethane (40 mL), MgSO_4 (6.00 g, 49.8 mmol) and **4** (2.50 g, 45.4 mmol) were added. The reaction mixture was stirred at room temperature for one day. After filtration, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 3:1) to afford **5** as a yellow oil; yield: 6.08 g (91%); R_f (hexanes/ethyl acetate, 3:1)=0.31; IR (film): $\nu=3295, 2925, 2898, 1646, 1589, 1532, 1386, 1369, 1353, 1304, 1200, 1023, 996, 946, 913 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta=2.33$ (s, 3H), 2.50 (t, $J=2.4 \text{ Hz}$, 1H), 4.47–4.49 (m, 2H), 6.05–6.08 (m, 1H), 6.65 (d, $J=3.2 \text{ Hz}$, 1H), 8.30 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 64.9 MHz): $\delta=13.7$ (q), 46.4 (t), 76.1 (d), 78.4 (s), 108.0 (d), 116.7 (d), 150.0 (d), 155.7 (s) (1 s is hidden); MS

(80 eV): m/z (%): 147 (100) [M^+], 120 (69); anal. calcd. for $\text{C}_9\text{H}_9\text{NO}$ (147.2): C 73.45, H 6.16, N 9.52; found: C 73.34, H 6.42, N 9.43.

Synthesis of (5-Methylfuran-2-ylmethyl)prop-2-ynylamine (**6**)

Compound **5** (5.00 g, 34.0 mmol) was dissolved in MeOH (30 mL) and sodium borohydride (1.29 g, 34.1 mmol) was added at room temperature in small portions. Most of the solvent was removed under vacuum and the residue was purified by column chromatography (hexanes/ethyl acetate, 3:1). Thus **6** was obtained as a yellow oil; yield: 4.50 g (89%); R_f (hexanes/ethyl acetate, 4:1)=0.13; IR (film): $\nu=3293, 2922, 2834, 1569, 1450, 1354, 1330, 1218, 1101, 1020, 929, 785 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta=1.54$ (br s, 1H), 2.23 (t, $J=2.4 \text{ Hz}$, 1H), 2.26 (s, 3H), 3.42 (d, $J=2.4 \text{ Hz}$, 2H), 3.81 (s, 2H), 5.86–5.87 (m, 1H), 6.08 (d, $J=2.9 \text{ Hz}$, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 64.9 MHz): $\delta=13.4$ (q), 36.9 (t), 44.5 (t), 71.4 (d), 81.6 (s), 105.8 (d), 108.2 (d), 150.8 (s), 151.6 (s); MS (80 eV): m/z (%)=149 (18) [M^+], 148 (27), 120 (48), 95 (100); $\text{C}_9\text{H}_{11}\text{NO}$ (149.2); HR-MS: calcd. 149.0840; found: 149.0839.

Synthesis of **1** from **6**

To **6** (4.00 g, 26.8 mmol) and triethylamine (2.71 g, 26.8 mmol) in dichloromethane (30 mL) at room temperature TsCl (5.11, 26.8 mmol) was added in small portions and then stirred overnight. After the slow addition of water (50 mL), separation of the organic layer, two extractions of the aqueous layer with dichloromethane (2×20 mL), the combined organic layers were dried over MgSO_4 and then filtered. Then the solvent was removed under vacuum and the residue was recrystallised from diethyl ether. Most of **8** crystallised,^[16] more **8** was isolated from the mother liquor by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane, 8:1:1), to provide a combined crop of **8**; yield: 7.88 g, (26.0 mmol, 97%); R_f (hexanes/ethyl acetate, 2:1)=0.44; mp 68–71 °C; IR (film): $\nu=3286, 2923, 1712, 1598, 1564, 1336, 1349, 1332, 1221, 1162, 1093, 1021, 973, 919, 891, 799, 765, 737, 665, 579 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta=2.06$ (t, $J=2.5 \text{ Hz}$, 1H), 2.19 (s, 3H), 2.42 (s, 3H), 4.01 (d, $J=2.5 \text{ Hz}$, 2H), 4.37 (2, 2H), 5.86 (d, $J=3.1 \text{ Hz}$, 1H), 6.15 (d, $J=3.1 \text{ Hz}$, 1H), 7.28 (d, $J=8.4 \text{ Hz}$, 2H), 7.73 (d, $J=8.4 \text{ Hz}$, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 62.9 MHz): $\delta=13.35$ (q), 21.45 (q), 35.84 (t), 42.70 (t), 73.64 (d), 76.43 (s), 106.08 (d), 111.86 (d), 127.62 (d, 2 C), 129.25 (d, 2 C), 135.95 (s), 143.33 (s), 146.31 (s), 152.62 (s); anal. calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$ (303.4): C 63.34, H 5.65, N 4.61; found: C 63.09, H 5.51, N 4.66.

Synthesis of 4-Methyl-N-(5-methylfuran-2-yl-methylene)benzenesulfonamide (**7**)

This reaction was conducted in analogy to the literature.^[17] Compound **3** (5.00 g, 45.4 mmol), tosylamide (11.6 g,

90.8 mmol) and triethylamine (23.0 g, 227 mmol) were dissolved in dichloromethane (150 mL) and cooled to 0 °C. TiCl_4 (4.31 g, 22.7 mmol) in dichloromethane (15 mL) was added at that temperature, then the ice-bath was removed and stirring was continued for 30 min (monitoring by TLC). The mixture was hydrolysed with saturated NaHCO_3 solution, the phases were separated and the aqueous phase was extracted with dichloromethane (2×70 mL) and the combined organic layers were washed with water (50 mL). After drying over MgSO_4 and filtration, the crude product (93 %) can be used in the next step directly. By recrystallisation of a portion of the crude material, analytically pure **7** was obtained in the form of colourless crystals: R_f (petrol ether/ethyl acetate, 1:1)=0.37; mp 118–119 °C; IR (film): ν =3087, 1600, 1548, 1507, 1284, 1148, 1088, 1034, 830, 800, 670 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ =2.42 (s, 6H), 6.29 (d, J =3.6 Hz, 1H), 7.25 (d, J =3.6 Hz, 1H), 7.28–7.33 (m, 2H), 7.82–7.89 (m, 2H), 8.68 (s, 1H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ =14.4 (q), 21.6 (q), 111.0 (d, 2 C), 128.0 (d, 2 C), 129.7 (d, 2 C), 135.7 (s), 144.3 (s), 147.7 (s), 154.8 (s), 162.1 (d); MS (70 eV): m/z (%)=263 (48) [M^+], 172 (21), 155 (22), 108 (34), 91 (100), 65 (17); anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$ (263.1): C 59.30, H 4.98, N 5.32; found: C 59.24, H 5.00, N 5.22.

Synthesis of 4-Methyl-N-(5-methylfuran-2-yl-methyl)benzenesulfonamide (**8**) from **7**

To **7** (4.00 g, 15.2 mmol) in MeOH (30 mL) NaBH_4 (575 mg, 15.2 mmol) was added in small portions at room temperature, then the solution was stirred over night. After hydrolysis (30 mL H_2O), phase separation, drying of the organic phase and the usual work-up by crystallisation and chromatography of the mother liquor **8** was obtained; yield: 73 % (68 % over two steps).

Synthesis of **1** from **8**

Compound **8** (4.00 g, 15.1 mmol) was dissolved in acetone (30 mL), K_2CO_3 (4.00 g, 28.9 mmol) and **9** (2.38 g, 20.0 mmol) were added and the mixture was stirred at room temperature for 24 h. Then the solvent was removed under vacuum, the residue was taken up in water (30 mL) and dichloromethane (20 mL) and the product was extracted with two additional portions of dichloromethane (20 mL). After removal of the solvent, the residue was recrystallised from diethyl ether and the mother liquor was purified by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane, 8:1:1) to afford **1**; yield: 4.48 g (14.8 mmol, 98 %).

Synthesis of **8** from **10**

To **10** (5.00 g, 45.0 mmol) and triethylamine (4.55 g, 45.0 mmol) in dichloromethane (60 mL) at room temperature TsCl (8.58 g, 45.0 mmol) was added in small portions and then stirred overnight. After the slow addition of water

(60 mL), separation of the organic layer, two extractions of the aqueous layer with dichloromethane (2×20 mL), the combined organic layers were dried over MgSO_4 and then filtered. Then the solvent was removed under vacuum and the residue was recrystallised from diethyl ether. Most of **8** crystallised,^[16] more **8** was isolated from the mother liquor by column chromatography on silica gel (hexanes/ethyl acetate 2:1), to afford **8**; combined yield: 11.6 g (43.7 mmol, 97 %); R_f (hexanes/ethyl acetate, 1:1)=0.41; mp 82–83 °C; IR (film): ν =3256, 2923, 1598, 1570, 1436, 1350, 1321, 1220, 1186, 1093, 1040, 1018, 930, 815, 790 cm^{-1} ; ^1H NMR (CDCl_3 , 250 MHz): δ =2.11 (s, 3H), 2.41 (s, 3H), 4.09 (d, J =5.7 Hz, 2H), 4.95 (t, J =5.7 Hz, 1H), 5.76 (m, 1H), 5.95 (d, J =3.1 Hz, 1H), 7.24–7.27 (m, 2H), 7.65–7.73 (m, 2H); ^{13}C NMR (CDCl_3 , 64.9 MHz): δ =13.1 (q), 21.3 (q), 40.1 (t), 106.0 (d), 108.9 (d), 127.0 (d, 2 C), 129.4 (d, 2 C), 136.8 (s), 143.1 (s), 147.4 (s), 152.0 (s); MS (80 eV): m/z (%)=265 (9) [M^+], 110 (100), 109 (97), 95 (24); anal. calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$ (265.3): C 59.04, H 5.86, N 5.09; found: C 58.85, H 5.70, N 5.28.

Gold Catalysis Reactions

The substrate **1** was taken up in the solvent and the catalyst was added. The reaction could be monitored by TLC or NMR, when complete the catalyst was removed by filtration and column chromatography on silica gel (hexanes/ethyl acetate, 7:1) furnished **2**; R_f (hexanes/ethyl acetate, 5:1)=0.27.^[6a]

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