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Regioselective transformation of alkynes into cyclic acetals and thioacetals with a gold(I) catalyst: comparison with Brønsted acid catalysts

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ABSTRACT

Au(I) catalyzes the transformation of alkynes into cyclic acetals and thioacetals at much higher rate than Brønsted acids. The reaction appears to be general for a range of alkynes and diols or dithiols, which are efficiently transformed with high selectivities. One of the salient features of this reaction process is the high reactivity of the enol ether or enol thioether intermediates, which undergo a rapid isomerization reaction to afford the cyclic acetals or thioacetals, so that isolation or subsequent activation processes are not required. This type of reactions allows us to synthesize a series of fragrances.

1. Introduction

Cyclic acetals and thioacetals are important molecules for protecting carbonyl groups in organic synthesis[1] and for the generation of chiral auxiliaries for asymmetric induction.[2] They also have interest for the production of polymers, pharmaceuticals and fragrances.[3–5] Classical methods to obtain cyclic acetals involve the reaction of an aldehyde or ketone with an alcohol with azeotropic removal of water or transacetalization reactions. When the ketone is not stable, this procedure involves large excess of reactant and tedious work-up procedures.[1,6] Recently, the direct transformation of unactivated alkynes into ketones or acetals upon water or alcohol addition, respectively, has become one of the most useful functionalizations of simple alkynes, and a variety of catalysts have been extensively studied.[7–9] For instance, transition metals salts including mercury(II),[7] palladium(II)[8] as well as a Zeise-type platinum compound[9] catalyze the hydration of many alkynes to afford ketones; whereas formation of cyclic acetals has been described to occur with the assistance of a cationic iridium complex.[10] In the case of gold, it has been recently reported that this metal working either in homogeneous or heterogeneous phase can efficiently catalyze reactions involving alkynes.[11] Indeed, it has been described that the use of cationic gold(I) complexes for the direct formation of dimethyl acetals from alkynes by addition of methanol, and protons as cocatalyst,[12] whereas gold(III) efficiently catalyzes the addition of water and methanol to nonactivated alkynes forming ketones and acetals.[13] It should be remarked that despite the fact that dimethyl acetals were successfully obtained with this Au(III) catalyst, direct conversion of alkynes into cyclic acetals was not possible. AuCl or $AuCl_3$ can also be used as catalysts in the formation of interesting bicyclic ketals by using two intramolecular hydroxyl groups as nucleophiles.[14] Similarly, a combination of intramolecular and intermolecular additions in the case of a homopropargylic alcohol can be catalyzed by $AuPPh_3Cl/AgBF_4$, in the presence of 10% acid.[15]

In this work we present that gold(I)/$AgBF_4$ can catalyze very efficiently the formation of cyclic acetals and thioacetals with five to eight membered ring from alkynes and diols and thiols, without adding acid. To the best of our knowledge there is no precedent for forming this last type of compounds from alkynes using gold catalysts. We can oversee interesting applications of this reaction and, as one example, the synthesis of a molecule with blossom orange scent is presented. We will show that with this catalyst the formation of cyclic acetals and thioacetals takes place in a direct way through a two step transformation starting from alkynes and diols or thiols to afford enol ethers(thioethers) intermediates. In our reaction system, the intermediate reaction product undergoes a rapid isomerization to the corresponding cyclic acetal and thioacetal so that isolation of the enol ether/thioether is not required. One of the main advantages of this experimental procedure is that most of the inconveniences associated with classical acetalization reactions, such as the use of an excess of reagent or tedious work-up procedures can be overcome.

2. Results and discussion

2.1. Synthesis of acetals and thioacetals with Au(I)/Ag(I) system

The reaction of 1,2-ethanediol with a series of alkynes such as phenylacetylene, benzylacetylene and 1-hexyne was carried out at

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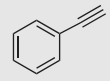
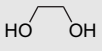
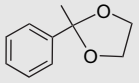
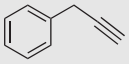
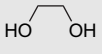
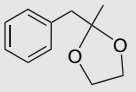
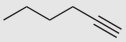
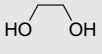
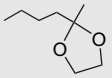
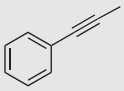
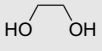
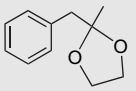
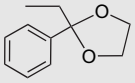
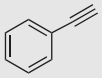
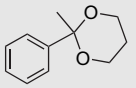
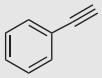
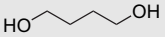
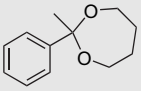
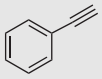
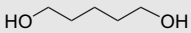
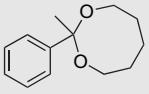
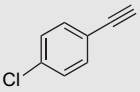
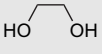
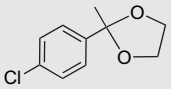
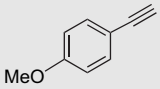
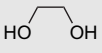
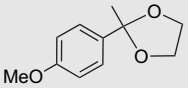
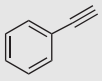
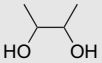
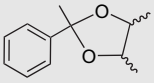
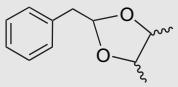
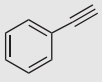
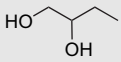
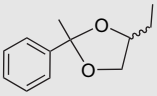
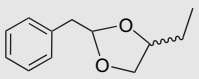
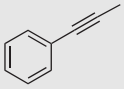
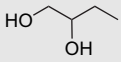
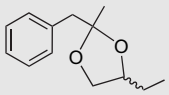
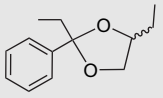
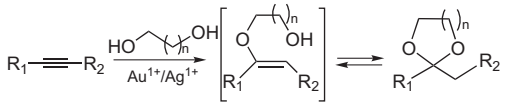
Table 1
Au(I)/$AgBF_4$ catalyzed the direct formation of cyclic acetals from alkynes and diols[a]

Entry	Alkyne	Diol	Products	Time (h)	Alkyne conversion[b] (%)	$S^{b,c}$ (%)	Yield[h] (%)
1			 **1**	4	100	75 (93)[d]	87
2			 **2**	0.33	100	82 (87)[d]	76
3			 **3**	0.2	100	77 (89)[d]	79
4			 **2** (68%)  **4** (32%)	3	15	90	—
5			 **5**	4	100	96	82
6			 **6**	0.5	100	60 (83)[d]	76
7			 **7**	4[e]	100	76	68
8			 **8**	6[f]	51	88	41
9			 **9**	0.75	80	96	65
10			 **10**[i] (97%)  **11**[i] (3%)	1	100	90	78
11			 **12**[i] (94%)  **13**[i] (6%)	0.5 (48)[g]	100	91 (94)[d]	85
12			 **14**[i] (66%)  **15**[i] (34%)	3	60	91 (94)[d]	35
13			**16**[i]	1.5	100	94	83
14			**17**	6	80	98	60
15			**18**	4	100	94	84

[a] Reaction conditions: alkyne (1.1 mmol), diol (1 mmol), $AuPPh_3Cl$ (0.02 mmol), $AgBF_4$ (0.02 mmol), toluene (1 mL), 100 °C, N_2.
[b] Calculated by CG using *n*-dodecane as internal standard.
[c] Selectivity (%).
[d] Results in parentheses refer to reactions with starting reagents dried on activated molecular sieves (4 Å).
[e] Reaction was carried out at 60 °C.
[f] Reaction was carried out at 120 °C.
[g] Reaction was carried out at 25 °C.
[h] Isolated yield of main product.
[i] Mixture of diastereoisomers.

100 °C, in the presence of $AuPPh_3Cl/AgBF_4$. In all cases, the main reaction product was the corresponding cyclic acetal, together with minor amounts of ketones (entries 1–3, Table 1). The addition of the diol takes place almost exclusively at the most substituted carbon atom of the alkyne to produce the expected cyclic acetal. This transformation should involve the initial regioselective formation of an enol ether intermediate, which would undergo a rapid thermal isomerization to the more stable cyclic acetal (Scheme 1).



Scheme 1. Gold(I) catalyzes the transformation of alkynes into cyclic acetals.

Control experiments showed that the formation of cyclic acetals did not occur with $AgBF_4$ or $AuPPh_3Cl$ alone. This indicates that $AgBF_4$ is necessary to generate a cationic gold(I) in solution that, otherwise, may not exist in a free form but coordinated with whatever donor molecules (alkynes, diols) are present in solution.[12]

Additional experiments were carried out with catalytic amounts of a Brønsted acid (*p*-TsOH) to compare its effect on reactivity (see Section 2.2).

The formation of minor amounts of ketones can be explained by the hydrolysis of the acetals and/or by hydration of the alkyne. To check this, we carried out the reaction under anhydrous conditions by drying the reactants with molecular sieves (4 Å). The results obtained show that a decrease in the yield to the ketone is observed (entries 1–3 and 6, Table 1). Moreover, control experiments with phenylacetylene, water (in the absence of the diol) and the Au^{+1}/Ag^{+1} catalyst were carried out and in this case the aromatic ketone was detected only at the level of traces. Similar results were also found when using iridium complexes as catalysts.[10] We can then conclude that gold in the $AuPPh_3Cl/AgBF_4$ system can efficiently catalyze the formation of a five membered ring cyclic acetal by reacting 1,2-ethanediol with a series of alkynes and the ketone obtained as subproduct is formed by the hydrolysis of the acetal if water is present in the reaction media.

It appears that the process presented here could be used to synthesize cyclic acetals with six or more membered rings by properly selecting the diol. Results from Table 1 (entries 1–7) show that cyclic acetals with five and six membered rings can be efficiently formed and they are perfectly stable, provided that there is not water and acid present. In the case of seven and eight membered ring cyclic acetals, the results from Table 1 (entries 6 and 7) indicate that they can also be formed. The lower yield (~80%) obtained in this case can be due to the typical ring strains of larger cyclic molecules, which make cyclic acetals with larger ring less stable and very prone to undergo undesired ring opening reactions. Nevertheless, we have seen that gold can catalyze the formation of cyclic acetals with, at least, five to eight membered rings. From the point of view of the alkyne reactivity, it is interesting to notice that the rate of addition of 1,2-ethanediol to the aliphatic alkyne (1-hexyne) was much faster than to the aromatic one (1-phenylacetylene) (entries 1 and 3 in Table 1). This could be explained not only taking into account the relative electrophilicity of the sp hybridization towards the hydroxyl group of the diol but, presumably, also because of steric effects. These steric effects might contribute to slow down the addition to the alkyne, especially when bulky substituents such as a phenyl group, are directly bound to the triple bond.

In order to explore the scope of the catalytic process presented here, we have studied a series of reactions involving different combinations of alkynes and diols. Various *p*-aryl substituted acetylenic compounds (Cl, OCH_3) with different electrodonor or electron withdrawing properties were reacted with 1,2-ethanediol and the results are given in Table 1 (entries 8 and 9). The electrodonor or withdrawing ability of the substituent at the aromatic position did not influence the very high regioselectivity to the Markovnikov substitution. Nonetheless, the conversion towards the cyclic acetal improved significantly with the *p*-methoxyaryl acetylene with respect to the *p*-halogenaryl substituted derivative, owing to the higher electron density in the acetylenic group in the former case.[12]

The reactivity of aliphatic and aromatic alkynes is compared in Figure 1 and Table 1 (entries 3 and 9). The experimental results show that aliphatics react faster than aromatic alkynes, while in both cases selectivity towards the cyclic acetal formation remains constant during the experiments, confirming the stability of both products in the reaction media.

The gold catalytic system also catalyzes efficiently the addition of secondary alcohols such as 2,3-butanediol to terminal acetylenic groups (entry 10 in Table 1), being the secondary alcohols more reactive than primary, in contrast what it occurs during the formation of acyclic acetals.[12] Furthermore, the addition of 1,2-butanediol to internal and terminal alkynes, i.e., 1-methyl-2-phenylacetylene and 1-phenylacetylene, leads to formation of interesting mixed or asymmetric cyclic acetals with high conversions and selectivities (entries 11 and 12 in Table 1), and turnover frequencies in the order of 250 mmol alkyne per mmol of catalyst per hour (Table 2). As can

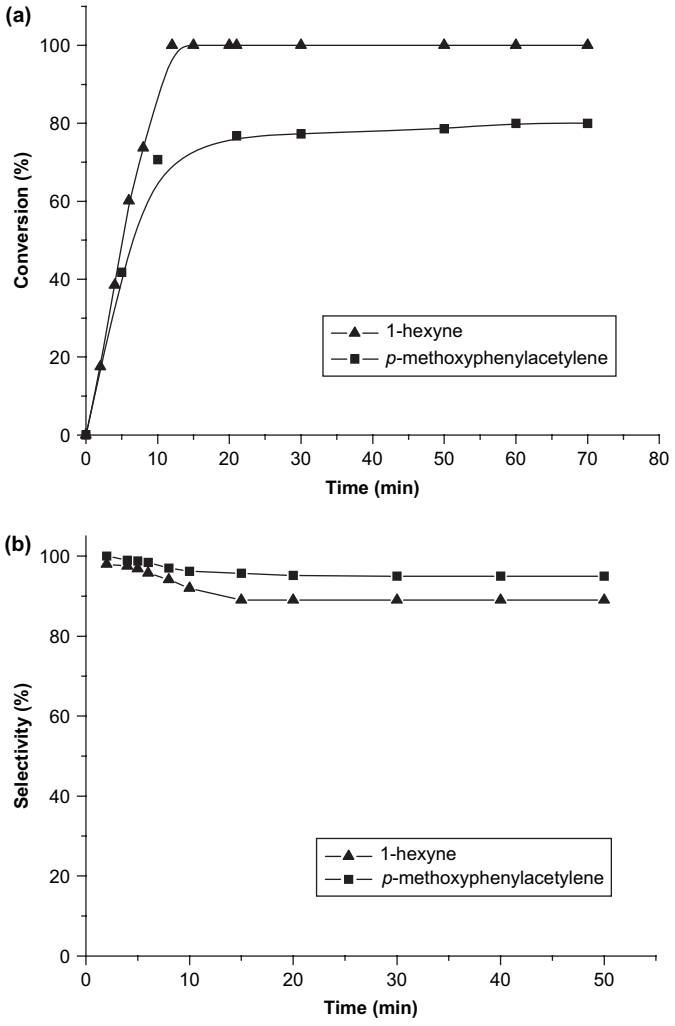
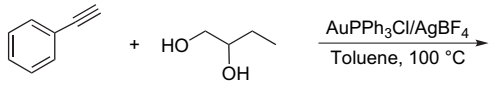


Figure 1. Evolution of conversion/selectivity with time for the acetalization reaction of 1-hexyne and *p*-methoxyphenylacetylene with 1,2-ethanediol catalyzed by $AuPPh_3Cl/AgBF_4$.

Table 2
TON and TOF (h^{-1}) values calculated for the acetalization reaction of 1-phenylacetylene and 1,2-butanediol with 0.02 mmol of catalyst $AuPPh_3Cl/AgBF_4$



Substrates (mmol)	Time (h)	Conversion (%)	TOF[a] (h^{-1})	TON[b]
1	0.5	100	117	50
2	0.75	100	172	100
4	5	80	265	164

[a] Calculated as mmol of alkyne transformed/mmol of catalyst/h.
[b] Calculated as mmol of alkyne transformed/mmol of catalyst.

be seen in Table 1, when reacting 2,3-butanediol and 1,2-butanediol with 1-phenylacetylene, minor amounts of anti-Markovnikov products are formed (entries 10 and 11).

The scope of the reaction has been extended to different alkynes with steric hindrance. The reaction of 3,3-dimethyl-1-butyne and 2-ethynyltoluene with 1,2-ethanediol occurred to high conversion at 100 °C over 4–6 h in toluene to form the corresponding cyclic acetals (entries 14 and 15, Table 1). High selectivities were observed in both cases (98% and 94%, respectively).

The catalytic properties of other gold salts have been studied by reacting phenylacetylene and 1,2-ethanediol in the presence of AuCl, $AuCl_3$ and $NaAuCl_4$. In these conditions the reaction does not proceed even in the presence of $AgBF_4$ or $CuCl_2$,[16] which has been shown to stabilize the Au(III) ($AuCl_3$) during the addition of alcohols to alkenes.

The catalytic process described here could be applied to the synthesis of fructone (ethyl 2-methyl-1,3-dioxolane-2-acetate)[5b] and blossom orange fragrances.[5a] We show this possibility by synthesizing 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane, which is a fragrance with blossom orange scent. The commercial synthesis of this compound is carried out by acetalization reaction between methyl naphthyl ketone and propylene glycol using liquid[5c] or solid acids.[5a] We have successfully performed the synthesis of this compound by reacting naphthylene-2-acetylene and propylene glycol in the presence of $Au(I)/AgBF_4$ under similar reaction conditions than for other cyclic acetals (entry 13 in Table 1). Total conversion is obtained after 1.5 h at 100 °C with high selectivity.

After the successful synthesis of cyclic acetals from alkynes and diols catalyzed by $Au(I)/AgBF_4$ we have explored the possibility to synthesize cyclic thioacetals using the same catalyst. Protection of carbonyl compounds as dithioacetals is an important transformation due to the higher stability of these sulfur compounds with respect to cyclic acetals under both acidic and basic conditions. In addition, they also very often serve as masked acyl anion equivalents or masked methylene functions in carbon–carbon bond forming reactions. Moreover, various 1,3-dithiane derivatives play an important role as valuable building blocks in natural product synthesis.[17]

The results in Table 3 indicate that phenylacetylene can be easily and regioselectively converted into cyclic thioacetals by reacting the alkyne with the corresponding dithiol in the presence of $AuPPh_3Cl/AgBF_4$ under similar reaction conditions than the diols. Nonetheless, it is necessary to remark that higher amounts of catalyst and longer reaction times were required for the synthesis of cyclic thioacetals. Moreover, anti-Markovnikov products are formed in ratio 10–20% (entries 1, 3 and 4, Table 3). This ratio is much higher than that in the case of diols. On the other hand, the stability of six and seven membered ring thioacetals is higher than the corresponding cyclic acetals, but selectivities are lower than for cyclic acetals because of the slower reaction rate for the synthesis of cyclic thioacetals that gives further possibilities to polymerization of alkynes to proceed.

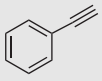
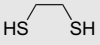
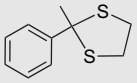
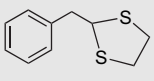
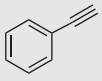
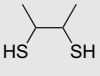
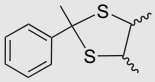
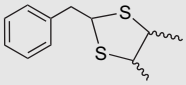
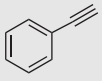
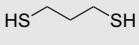
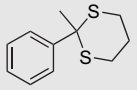
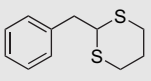
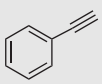
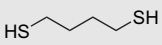
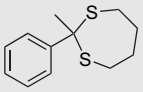
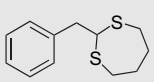
2.2. Catalysis by Au(I)/Ag(I) system versus catalysis by *p*-TsOH

There are a few gold-catalyzed reactions in the literature that can be alternatively catalyzed by Brønsted acids.[18,19] However, there are many more examples in which Brønsted acids act as gold cocatalysts.[12,15,18]

In order to explore how a Brønsted acid affects the acetalization/thioacetalization reaction, we have described few examples carried out in the presence of $Au(I)/AgBF_4$ and a catalytic amount of *p*-TsOH as cocatalyst, as well as only with the Brønsted acid (Tables 4 and 5).

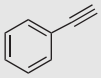
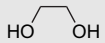
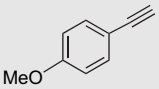
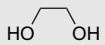
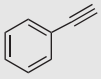
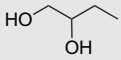
The results obtained when reacting diols are shown in Table 4. According to the literature, an increase of the reaction rate was observed when *p*-TsOH was added together with the gold catalyst.[12,15,18] For example, the rate of reaction for 1-phenylacetylene with 1,2-ethanediol increases by ~1 order of magnitude when adding *p*-TsOH to the reaction in the presence of gold. Similarly, when *p*-methoxyphenylacetylene was used as substrate, the reaction was completed in 0.33 h (0.75 h without Brønsted acid) with total conversion of the alkyne (entry 9, Table 1 and entry 2, Table 4).

Table 3
$Au(I)/AgBF_4$ catalyzed the direct formation of dithiolanes from alkynes and dithiols[a]

Entry	Alkyne	Dithiol	Products				Time (h)	Alkyne conversion[b] (%)	$S^{b,c}$ (%)	Yield[d] (%)
1				**19** (92%)		**20** (8%)	20	100	70	45
2				**21**[e] (97%)		**22**[e] (3%)	24	95	60	51
3				**23** (80%)		**24** (20%)	30	90	55	35
4				**25** (91%)		**26** (9%)	10	98	40	26

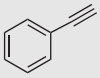
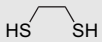
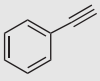
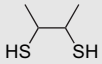
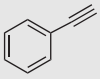
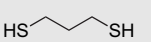
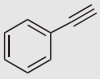
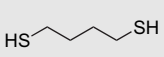
[a] Reaction conditions: alkyne (1.1 mmol), dithiol (1 mmol), $AuPPh_3Cl$ (0.05 mmol), $AgBF_4$ (0.05 mmol), toluene (1 mL), 100 °C, N_2.
[b] Calculated by CG using *n*-dodecane as internal standard.
[c] Selectivity (%).
[d] Isolated yield of main product.
[e] Mixture of diastereoisomers.

Table 4
Influence of *p*-TsOH for acetalization reactions

Entry	Alkyne	Diol	Au(I)/$AgBF_4$/*p*-TsOH[a]				*p*-TsOH[b]			
			Products	Time (h)	Alkyne conversion[c] (%)	$S^{c,d}$ (%)	Products	Time (h)	Alkyne conversion[c] (%)	$S^{c,d}$ (%)
1			**1**	0.5	100	85	**1**	24	4	—
2			**9**	0.33	100	87	**9**	28	25	84
3			**12**[h] (94%)/**13**[h] (6%)	21[e]	100	82	**12**[h] (94%)/**13**[h] (6%)	24	0(10)[f](18)[g]	—

[a] Reaction conditions: alkyne (1.1 mmol), diol (1 mmol), $AuPPh_3Cl$ (0.02 mmol), $AgBF_4$ (0.02 mmol), *p*-TsOH (0.02 mmol), toluene (1 mL), 100 °C, N_2.
[b] Reaction conditions: alkyne (1.1 mmol), diol (1 mmol), *p*-TsOH (0.02 mmol), toluene (1 mL), 100 °C, N_2.
[c] Calculated by CG using *n*-dodecane as internal standard.
[d] Selectivity (%).
[e] Reaction was carried out at 25 °C.
[f] Results refer to reaction at 100 °C.
[g] Results refer to reaction with *p*-TsOH (0.05 mmol).
[h] Mixture of diastereoisomers.

Table 5
Influence of *p*-TsOH for thioacetalization reactions

Entry	Alkyne	Diol	Au(I)/$AgBF_4$/*p*-TsOH[a]				*p*-TsOH[b]			
			Products	Time (h)	Alkyne conversion[c] (%)	$S^{c,d}$ (%)	Time (h)	Products	Alkyne conversion[c] (%)	$S^{c,d}$ (%)
1			**19** (96%)/**20** (4%)	3	100	70	14	**19** (80%)/**20** (20%)	99	80
2			**21**[e] (92%)/**22**[e] (8%)	10	95	75	50	**21**[e] (49%)/**22**[e] (51%)	75	60
3			**23** (85%)/**24** (15%)	9	100	75	15	**23** (80%)/**24** (20%)	98	75
4			**25** (88%)/**26** (12%)	2.5	100	40	40	**25** (20%)/**26** (80%)	100	40

[a] Reaction conditions: alkyne (1.1 mmol), dithiol (1 mmol), $AuPPh_3Cl$ (0.05 mmol), $AgBF_4$ (0.05 mmol), *p*-TsOH (0.05 mmol), toluene (1 mL), 100 °C, N_2.
[b] Reaction conditions: alkyne (1.1 mmol), dithiol (1 mmol), *p*-TsOH (0.05 mmol), toluene (1 mL), 100 °C, N_2.
[c] Calculated by CG using *n*-dodecane as internal standard.
[d] Selectivity (%).
[e] Mixture of diastereoisomers.

The reaction described in entry 3 (Table 4) was carried out at 25 °C over 21 h whereas without acid 48 h was required (entry 11, Table 1). In all cases, the selectivity decreases with respect to the reactions without acid. When the reactions were performed with *p*-TsOH alone (2 mol %), the conversions were significantly lower than with gold or even no reaction occurs (entries 1–3 in Table 4). An increase of the *p*-TsOH from 2 to 5 mol % and working at 100 °C gave only 20% conversion (entry 3).

The comparative studies of thioacetals formation with addition of *p*-TsOH are illustrated in Table 5. The reaction of 1-phenylacetylene and different thiols with 5 mol % of $AuPPh_3Cl/AgBF_4$ and 5 mol % of *p*-TsOH gives high conversion at 100 °C in 3–10 h, demonstrating that the presence of Brønsted acid accelerates these reactions. Furthermore, the selectivities were similar (entries 1 and 4, Table 5) or higher than the reaction without acid (entries 2 and 3, Table 5). We have also performed these reactions with *p*-TsOH alone (5 mol %), observing in this case that it is possible to obtain high conversions, in contrast to what was observed with diols. It is noteworthy that when the catalyst is a Brønsted acid longer reaction times are required (14–50 h) and led to a different ratio of thioacetal products than when using gold catalyst. When using only a Brønsted acid as catalyst, anti-Markovnikov products were formed in higher ratio being the reactions less regioselective. For example, the reaction of 1-phenylacetylene with 2,3-buthanedithiol gave a ~1:1 ratio of Markovnikov and anti-Markovnikov products, **21** and **22**, respectively (entry 2), whereas with 1,4-butanedithiol, the main product was anti-Markovnikov compound **26** (80%) (entry 4).

In summary, these experiments have proven that addition of a catalytic amount of *p*-toluenesulphonic acid to Au(I)/Ag(I) system accelerates the acetalization and thioacetalization reactions serving the Brønsted acid as cocatalyst. However, the use of *p*-TsOH alone (2–5 mol %) to acetals formation yields very low conversions. Finally, *p*-toluenesulphonic acid catalyzes the thioacetalization reactions but in almost all cases, it is less regioselective than gold giving more of the anti-Markovnikov products.

3. Conclusion

In conclusion, Au(I) as $AuPPh_3Cl$ in combination with $AgBF_4$ efficiently catalyzes the direct and regioselective formation of cyclic acetals and thioacetals with five to eight membered rings from alkynes and diols or dithiols. *p*-Toluenesulphonic acid can be used as an effective cocatalyst. The results obtained clearly indicate the generality of the reaction with respect to both the alkyne and the diol or dithiol. There are not severe limitations on the use of different substrates since highly reactive electrophilic bonds are not necessary in the current reaction system and severe reaction conditions are not required. The addition of the diol or dithiol takes place almost exclusively at the most substituted carbon atom of the alkyne to produce the cycle. This procedure represents an efficient alternative to other processes involving ketones, specially when cyclic acetals and thioacetals with more than six membered ring atoms have to be obtained.

4. Experimental

4.1. General

Commercially available reagents including $AuPPh_3Cl$ and $AgBF_4$ were purchased from Sigma–Aldrich. 1,2-Ethanediol, 1,4-butanediol and 1,2-butanediol were dried on activated molecular sieves (4 Å). GC/MS analyses were performed on an Agilent 5973N spectrometer equipped with the same column and in the same conditions as GC. ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ with TMS as an internal standard at 25 °C on a Bruker Avance 300.

4.2. General procedure for acetalization reactions

Catalytic reactions were carried out under N_2 atmosphere in a closed glass reactor (2.5 mL) equipped with a micro-syringe trough, which can take a sample to analysis. To a catalytic amount of $AuPPh_3Cl$ (0.02 mmol, 0.0099 g)/$AgBF_4$ (0.02 mmol, 0.0039 g), a mixture of the appropriate alkyne (1.1 mmol) and the diol (1 mmol) in 1 mL of toluene was added. The reaction mixture was stirred at 100 °C and monitored by gas chromatography. When the reaction was completed, the solvent was evaporated under vacuo. The crude product was purified by PLC chromatography on silica gel, using a 99:1 mixture of hexane/Et_2O as eluent.

4.2.1. 2-Methyl-2-phenyl-1,3-dioxolane (**1**)

Isolated yield 87%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41, 7.26 (m, m, 2:3, $5CH_{ar}$), 3.96, 3.70 (m, m, 2H each, O–CH_2), 1.58 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.7 (C_{qar}), 128.6, 128.2, 125.6 (CH_{ar}), 109.2 (C_q–CH_3), 64.8 (O–CH_2), 28.0 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=164 (10) [M^+], 105 (100), 163 (90), 101 (50), 77 (32), 51 (11), 73 (10), 106 (8), 78 (4), 91 (4).

4.2.2. 2-Benzyl-2-methyl-1,3-dioxolane (**2**)

Isolated yield 76%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 (m, 5H, $5CH_{ar}$), 3.81, 3.67 (m, m, 2H each, O–CH_2CH_2–O), 2.84 (s, 2H, Ph–CH_2), 1.22 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3 (C_{qar}), 130.9, 128.3, 126.7 (CH_{ar}), 110.1 (C_q–CH_3), 65.2 (O–CH_2CH_2–O), 45.7 (Ph–CH_2), 24.7 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=179 [M^+], 87 (100), 91 (38), 65 (12), 88 (9), 105 (6).

4.2.3. 2-n-Butyl-2-methyl-1,3-dioxolane (**3**)

Isolated yield 79%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.86 (m, 4H, O–CH_2CH_2–O), 1.54, 1.27 (m, m, 2:4, –$CH_2CH_2CH_2CH_3$), 1.24 (s, 3H, C_q–CH_3), 0.83 (s, 3H, –$CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 110.6 (C_q–CH_3), 64.9 (O–CH_2CH_2–O), 39.3, 26.6, 23.3 (–$CH_2CH_2CH_2CH_3$), 24.1 (C_q–CH_3), 14.4 (–$CH_2CH_2CH_2CH_3$). MS (80 eV): *m*/*z* (%)=144 [M^+], 87 (100), 129 (49), 85 (22), 57 (20), 55 (11), 88 (10), 71 (6), 72 (5), 130 (4).

4.2.4. 2-Methyl-2-phenyl-1,3-dioxane (**5**)

Isolated yield 82%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.34 (m, 5H, $5CH_{ar}$), 3.75 (m, 4H, O–CH_2CH_2), 2.02, 1.12 (m, m, 1H each, O–CH_2CH_2), 1.43 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.6 (C_{qar}), 129.1, 128.0, 127.2 (CH_{ar}), 100.9 (C_q–CH_3), 61.6 (O–CH_2CH_2), 32.8 (C_q–CH_3), 25.9 (O–CH_2CH_2). MS (80 eV): *m*/*z* (%)=177 [M^+], 163 (100), 105 (88), 101 (42), 77 (25), 164 (10).

4.2.5. 2-Methyl-2-phenyl-1,3-dioxepane (**6**)

Isolated yield 76%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52, 7.30 (m, m, 2:3, $5CH_{ar}$), 3.80, 3.60 (m, m, 2H each, O–CH_2CH_2), 1.65, 1.59 (m, m, 2H each, O–CH_2CH_2), 1.50 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.2 (C_{qar}), 128.3, 127.7, 126.2 (CH_{ar}), 103.0 (C_q–CH_3), 63.5 (O–CH_2CH_2), 29.9 (C_q–CH_3), 27.8 (O–CH_2CH_2). MS (80 eV): *m*/*z* (%)=192 [M^+], 136 (100), 121 (90), 87 (42), 103 (25), 137 (20), 77 (19), 59 (17). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.19; H, 8.11.

4.2.6. 2-Methyl-2-phenyl-1,3-dioxocane (**7**)

Isolated yield 68%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.42, 7.12 (m, m, 2:3, $5CH_{ar}$), 3.50, 3.55 (m, m, 2H each, O–CH_2CH_2), 1.54, 1.46, 1.45 (m, m, m, 2H each, O–$CH_2CH_2CH_2$), 1.50 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.8 (C_{qar}), 129.4, 128.4, 126.6 (CH_{ar}), 101.4 (C_q–CH_3), 61.5 (O–CH_2CH_2), 30.3, 30.2, 29.9 (O–$CH_2CH_2CH_2$), 27.5 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=206 [M^+], 161 (100), 105 (100), 121 (49), 191 (40), 77 (36), 169 (22), 162 (15), 120 (10). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.25; H, 8.36.

4.2.7. 2-(4-Chlorophenyl)-2-methyl-1,3-dioxolane (**8**)

Isolated yield 41%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.34, 7.22 (d, d, $^3J_{HH}$=7.5 Hz, 2H each, $4CH_{ar}$), 3.96, 3.68 (m, m, 2H each, O–CH_2CH_2–O), 1.56 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.3 (C_{qar}), 134.1 (C_{qar}–Cl), 128.7, 127.2 (CH_{ar}), 108.8 (C_q–CH_3), 64.9 (O–CH_2CH_2–O), 27.9 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=198 [M^+], 183 (100), 139 (100), 185 (74), 141 (41), 87 (34), 111 (33), 75 (23), 184 (22), 103 (19), 167 (15).

4.2.8. 2-(4-Methoxyphenyl)-2-methyl-1,3-dioxolane (**9**)

Isolated yield 65%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32, 6.79 (d, d, $^3J_{HH}$=7.3 Hz, 2H each, $4CH_{ar}$), 3.94, 3.70 (m, m, 2H each, O–CH_2CH_2–O), 3.72 (s, 3H, Ar–OCH_3), 1.57 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6 (C_{qar}–OCH_3), 135.9 (C_{qar}), 126.9, 113.9 (CH_{ar}), 109.2 (C_q–CH_3), 64.8 (O–CH_2CH_2–O), 55.6 (–OCH_3), 28.0 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=194 (4) [M^+], 179 (100), 135 (56), 180 (11), 77 (10), 87 (8), 92 (7), 163 (6), 136 (5), 91 (5), 107 (5). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found: C, 67.93; H, 7.11.

4.2.9. 2-Methyl-2-phenyl-4,5-dimethyl-1,3-dioxolane (**10**)

Isolated yield 78%, >95% pure by GC. Mixture of diastereoisomers. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.23 (m, m, 2:3, $5CH_{ar}$), 3.71, 3.42 (dq, dq, 1H each, $^3J_{HH}$=6.0, 8.3 Hz, O–C*H*(Me)C*H*(Me)–O), 1.57 (s, 3H, C_q–CH_3), 1.22, 1.11 (d, d, 3H each, $^3J_{HH}$=6.0 Hz, O-CH(C*H*$_3$)CH(C*H*$_3$)–O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.6 (C_{qar}), 128.4, 127.9, 125.5 (CH_{ar}), 108.2 (C_q–CH_3), 79.3, 78.6 (–O–CH(Me)CH(Me)–O), 29.4 (C_q–CH_3), 17.5, 16.9 (–O–CH(C*H*$_3$)CH(C*H*$_3$)–O). MS (80 eV): *m*/*z* (%)=192 [M^+], 177 (100), 105 (81), 147 (25), 104 (22), 77 (20). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.20; H, 7.86.

4.2.10. 2-Methyl-2-phenyl-4-ethyl-1,3-dioxolane (**12**)

Isolated yield 85%, >95% pure by GC. Mixture of diastereoisomers (ratio **12a**/**12b**=1.8:1). Compound **12a**: ^1H NMR

($CDCl_3$, 300 MHz): δ 7.44, 7.25 (m, m, 2:3, $5CH_{ar}$), 4.09, 3.30 (m, m, 1H each, O–CH_2), 4.07 (m, 1H, O–CH), 1.56 (s, 3H, C_q–CH_3), 1.48, 1.30 (m, m, 1H each, –CH_2CH_3), 0.85 (t, 3H, $^3J_{HH}$=7.5 Hz, –CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.1 (C_{qar}), 128.4, 128.0, 125.5 (CH_{ar}), 109.3 (C_q–CH_3), 79.0 (O–CH), 70.1 (O–CH_2), 28.6 (C_q–CH_3), 26.9 (–CH_2CH_3), 10.5 (–CH_2–CH_3). MS (80 eV): *m*/*z* (%)=192 [M^+], 177 (100), 105 (78), 55 (48), 43 (35), 123 (34), 77 (32). Compound **12b**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41, 7.31 (m, m, 2:3, $5CH_{ar}$), 3.80, 3.53 (m, m, 1H each, O–CH_2), 3.77 (m, 1H, O–CH), 1.62, 1.54 (m, m, 1H each, –CH_2CH_3), 1.58 (s, 3H, C_q–CH_3), 0.88 (t, 3H, $^3J_{HH}$=7.5 Hz, –CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.3 (C_{qar}), 128.5, 128.0, 125.6 (CH_{ar}), 109.3 (C_q–CH_3), 77.4 (O–CH), 69.4 (O–CH_2), 28.7 (C_q–CH_3), 27.0 (–CH_2CH_3), 10.1 (–CH_2CH_3). MS (80 eV): *m*/*z* (%)=192 [M^+], 177 (100), 105 (94), 55 (47), 123 (41), 77 (36), 43 (30). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.22; H, 8.10.

4.2.11. 2-Benzyl-2-methyl-4-ethyl-1,3-dioxolane (**14**)

Isolated yield 35%, >95% pure by GC. Mixture of diastereoisomers (ratio **14a**/**14b**=1.25:1). Compound **14a**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.19 (m, 5H, CH_{ar}), 3.86, 3.42 (dd, dd, 1H each, $^2J_{HH}$=7.3 Hz, $^3J_{HH}$=5.8, 6.2 Hz resp., O–CH_2), 3.72 (q, 1H, O–$CHCH_2CH_3$), 2.83 (s, 2H, Ph–CH_2), 1.56, 1.43 (m, m, 1H each, –O–$CHCH_2CH_3$), 1.26 (s, 3H, C_q–CH_3), 0.83 (t, 3H, $^3J_{HH}$=7.5 Hz, –O–$CHCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.5 (C_{qar}), 130.8, 128.3, 126.7 (CH_{ar}), 110.4 (C_q–CH_3), 78.2 (O–$CHCH_2CH_3$), 69.8 (O–CH_2), 45.8 (Ph–CH_2), 26.8 (–O–$CHCH_2CH_3$), 25.8 (C_q–CH_3), 10.2 (–O–$CHCH_2CH_3$). MS (80 eV): *m*/*z* (%)=206 [M^+], 115 (100), 55 (66), 43 (63), 91 (32), 61 (11), 65 (8), 105 (8), 116 (7), 39 (5), 117 (5). Compound **14b**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.19 (m, 5H, CH_{ar}), 3.92, 3.09 (dd, dd, 1H each, O–CH_2), 3.86 (m, 1H, –O–$CHCH_2CH_3$), 2.86 (s, 2H, Ph–CH_2), 1.56, 1.44 (m, m, 1H each, –O–$CHCH_2CH_3$), 1.23 (s, 3H, C_q–CH_3), 0.80 (t, 3H, –O–$CHCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.3 (C_{qar}), 128.8, 126.2, 124.7 (CH_{ar}), 108.2 (C_q–CH_3), 75.8 (O–$CHCH_2CH_3$), 68.0 (O–CH_2), 44.7 (Ph–CH_2), 24.3 (–O–$CHCH_2CH_3$), 23.0 (C_q–CH_3), 8.3 (–O–$CHCH_2CH_3$). MS (80 eV): *m*/*z* (%)=206 [M^+], 115 (100), 55 (63), 43 (56), 91 (37), 61 (10), 65 (8), 105 (8), 116 (7), 117 (5), 39 (5). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.31; H, 8.96.

4.2.12. 2-Ethyl-2-phenyl-4-ethyl-1,3-dioxolane (**15**)

Mixture of diastereoisomers (ratio **15a**/**15b**=3:1). Compound **15a**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.38, 7.23 (m, m, 2:3, $5CH_{ar}$), 3.78, 3.51 (m, m, 1H each, O–CH_2), 3.77 (m, 1H, O–CH), 1.83 (c, 2H, $^3J_{HH}$=7.5 Hz, C_q–CH_2CH_3), 1.65, 1.52 (m, m, 1H each, O–CH–CH_2CH_3), 0.88 (t, 3H, $^3J_{HH}$=7.3 Hz, O–CH–CH_2CH_3), 0.82 (t, 3H, C_q–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.2 (C_{qar}), 125.9, 125.8, 123.8 (CH_{ar}), 108.7 (C_q–CH_2CH_3), 74.8 (O–CH), 67.2 (O–CH_2), 31.8 (C_q–CH_2CH_3), 24.4 (O–CH–CH_2CH_3), 7.7 (O–CH–CH_2CH_3), 5.8 (C_q–CH_2CH_3). MS (80 eV): *m*/*z* (%)=206 [M^+], 177 (100), 105 (78), 123 (42), 55 (36), 77 (29), 147 (17), 117 (13), 178 (12), 57 (10), 129 (8). Compound **15b**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41, 7.27 (m, m, 2:3, $5CH_{ar}$), 4.07, 3.27 (m, m, 1H each, O–CH_2), 4.03 (m, 1H, O–CH), 1.79 (c, 2H, C_q–CH_2CH_3), 1.30, 1.18 (m, m, 1H each, O–CH–CH_2CH_3), 0.85 (t, 3H, O–CH–CH_2CH_3), 0.79 (t, 3H, C_q–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.0 (C_{qar}), 125.5, 125.4, 123.7, (CH_{ar}), 108.8 (C_q–CH_2CH_3), 75.2 (O–CH), 67.7 (O–CH_2), 32.1 (C_q–CH_2CH_3), 24.6 (O–CH–CH_2CH_3), 8.1 (O–CH–CH_2CH_3), 5.9 (C_q–CH_2CH_3).

4.2.13. 2-Methyl-2-naphthyl-4-methyl-1,3-dioxolane (**16**)

Isolated yield 83%, >95% pure by GC. Mixture of diastereoisomers (ratio **16a**/**16b**=2:1). Compound **16a**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.85, 7.69, 7.47, 7.33 (m, m, m, m, 1:3:1:2, $7CH_{ar}$), 3.94 (m, 1H, O–CH–CH_3), 3.79, 3.45 (dd, dd, 1H each, $^3J_{HH}$=6.8 Hz, $^2J_{HH}$=7.5 Hz, O–CH_2), 1.64 (s, 3H, C_q–CH_3), 1.21 (d, 3H, $^3J_{HH}$=6.03 Hz, O–CH–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.6, 133.4, 133.3 (C_{qar}), 128.6, 128.4, 128.0, 126.5, 126.4, 124.2, 124.1 (CH_{ar}), 109.5 (C_q–CH_3), 72.3 (O–CH), 71.3 (O–CH_2), 28.8 (C_q–CH_3), 19.4 (O–CH–CH_3). MS (80 eV): *m*/*z* (%)=228 (15) [M^+], 213 (100), 155 (86), 127 (37), 101 (17), 214 (15), 156 (10). Compound **16b**: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.89, 7.73, 7.50, 7.35 (m, m, m, m, 1:3:1:2, $7CH_{ar}$), 4.28 (m, 1H, O–CH–CH_3), 4.04, 3.21 (dd, dd, 1H each, $^3J_{HH}$=5.8 Hz, $^2J_{HH}$=8.1 Hz, O–CH_2), 1.60 (s, 3H, C_q–CH_3), 1.07 (d, 3H, $^3J_{HH}$=6.0 Hz, O–CH–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.5, 133.3, 133.3 (C_{qar}), 128.7, 128.3, 128.0, 126.4, 126.3, 124.2, 124.1 (CH_{ar}), 109.5 (C_q–CH_3), 723.6 (O–CH), 71.5 (O–CH_2), 28.7 (C_q–CH_3), 18.7 (O–CH–CH_3). MS (80 eV): *m*/*z* (%)=228 (13) [M^+], 213 (100), 155 (90), 127 (39), 214 (16), 101 (11), 156 (11). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.41; H, 7.01.

4.2.14. 2-Methyl-2-tert-butyl-1,3-dioxolane (**17**)

Isolated yield 60%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.87, 3.82 (m, m, 2H each, O–CH_2CH_2–O), 1.17 (s, 3H, O–C_q–CH_3), 0.90 (s, 9H, C_q–$(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 112.95 (O–C_q–CH_3), 64.9 (O–CH_2CH_2–O), 37.9 (C_q–$(CH_3)_3$), 24.2 (C_q–$(CH_3)_3$), 18.2 (C_q–O–CH_3). MS (80 eV): *m*/*z* (%)=144 [M^+], 87 (100), 43 (46), 129 (17), 57 (15), 41 (14), 29 (7), 39 (7), 99 (7), 69 (5), 27 (5).

4.2.15. 2-Methyl-2-(2-methylphenyl)-1,3-dioxolane (**18**)

Isolated yield 84%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47 (m, 1H, CH_{ar}), 7.09 (m, 3H, CH_{ar}), 3.95, 3.65 (m, m, 2H each, O–CH_2), 2.42 (s, 3H, C_{qar}–CH_3), 1.61 (s, 3H, Ar–C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.5, 134.6 (C_{qar}), 130.9, 126.9, 125.0, 124.6 (CH_{ar}), 108.4 (C_q–CH_3), 63.1 (O–CH_2), 25.2 (Ar–C_q–CH_3), 19.8 (C_{qar}–CH_3). MS (80 eV): *m*/*z* (%)=178 [M^+], 163 (100), 119 (45), 91 (25), 164 (12), 65 (8), 39 (5), 105 (5), 115 (5), 120 (4), 77 (3). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 73.97; H, 7.91.

4.3. General procedure for thioacetalization reactions

These catalytic reactions were carried out under analogous conditions to acetalization reactions. To a catalytic amount of $AuPPh_3Cl$ (0.05 mmol, 0.025 g)/$AgBF_4$ (0.05 mmol, 0.010 g), a mixture of the appropriate alkyne (1.1 mmol) and the dithiol (1 mmol) in 1 mL of toluene was added. The reaction mixture was stirred at 100 °C and monitored by gas chromatography. When the reaction was completed, the solvent was evaporated under vacuo. The crude product was purified by PLC chromatography on silica gel, using a 99:1 mixture of hexane/Et_2O as eluent.

4.3.1. 2-Methyl-2-phenyl-1,3-dithiolane (**19**)

Isolated yield 45%, >95% pure by GC. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66, 7.19 (d, m, 2:3, $^3J_{HH}$=7.2 Hz, $5CH_{ar}$), 3.35, 3.26 (m, m, 2H each, S–CH_2CH_2), 2.06 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.4 (C_{qar}), 128.5, 127.5, 127.3 (CH_{ar}), 69.1 (C_q–CH_3), 40.8 (S–CH_2CH_2), 34.4 (C_q–CH_3). MS (80 eV): *m*/*z* (%)=196 (62) [M^+], 181 (100), 121 (93), 167 (86), 196 (62), 103 (60), 168 (46), 77 (34), 136 (28), 59 (17), 51 (12). Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.22; H, 6.12. Found: C, 61.31; H, 6.32.

4.3.2. 2-Methyl-2-phenyl-4,5-dimethyl-1,3-dioxolane (**21**)

Isolated yield 51%, >95% pure by GC. Mixture of diastereoisomers. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.67, 7.19 (m, m, 2:3, $5CH_{ar}$), 3.54, 3.41 (m, m, 1H each, S–CH(Me)CH(Me)–S), 2.07 (s, 3H, C_q–CH_3), 1.31, 1.29 (d, d, 3H each, S–CH(*Me*)CH(*Me*)–S). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.0 (C_{qar}), 128.4, 127.3, 127.0 (CH_{ar}), 67.0 (C_q–CH_3), 37.0 (S–$CH(CH_3)CH(CH_3)$–S), 36.1 (C_q–CH_3), 17.2 (S–CH(*Me*)CH(*Me*)–S). MS (80 eV): *m*/*z* (%)=224 (25) [M^+], 167 (100), 168 (94), 121 (50), 103 (40), 169 (18), 77 (17), 59 (16), 209 (15), 136 (10). Anal. Calcd for $C_{12}H_{16}S_2$: C, 64.28; H, 7.14. Found: C, 64.67; H, 7.31.

*4.3.3. 2-Methyl-2-phenyl-1,3-dithiane (**23**)*

Isolated yield 35%, >95% pure by GC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.86, 7.30, 7.18 (d, t, t, 2:2:1, $^3J_{HH}$=7.5 Hz, $5CH_{ar}$), 2.65 (m, 4H, S–CH_2CH_2), 1.87 (q, 2H, $^3J_{HH}$=5.0 Hz, S–CH_2CH_2), 1.72 (s, 3H, C_q-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.2 (C_{qar}), 129.0, 128.2, 127.5 (CH_{ar}), 54.4 (C_q–CH_3), 33.2 (C_q–CH_3), 28.5 (S–CH_2CH_2), 25.1 (S–CH_2CH_2). MS (80 eV): *m*/*z* (%)=210 (58) [M^+], 136 (100), 121 (80), 103 (30), 77 (22), 59 (13), 149 (9). Anal. Calcd for $C_{11}H_{14}S_2$: C, 62.86; H, 6.67. Found: C, 62.67; H, 6.72.

*4.3.4. 2-Methyl-2-phenyl-1,3-dithiepane (**25**)*

Isolated yield 26%, >95% pure by GC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72, 7.26, 7.15 (d, t, t, 2:2:1, $^3J_{HH}$=7.5 Hz, $5CH_{ar}$), 2.84, 2.70 (m, m, 2H each, S–CH_2CH_2), 1.92 (m, 4H, S–CH_2CH_2), 1.88 (s, 3H, C_q–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.6 (C_{qar}), 130.1, 128.9, 128.6 (CH_{ar}), 50.4 (C_q–CH_3), 35.3 (C_q–CH_3), 31.9 (S–CH_2CH_2), 25.9 (S–CH_2CH_2). MS (80 eV): *m*/*z* (%)=224 (22) [M^+], 136 (100), 121 (95), 87 (50), 103 (28), 77 (24), 59 (23), 224 (22), 137 (19), 119 (14), 88 (14). Anal. Calcd for $C_{12}H_{16}S_2$: C, 64.28; H, 7.14. Found: C, 64.16; H, 6.97.

*4.3.5. 2-Benzyl-1,3-dithiepane (**26**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (m, 5H, CH_{ar}), 4.4 (t, 1H, S–CH), 3.14 (d, 2H, C_{qar}–CH_2), 2.85, 2.75 (m, m, 2H each, S–CH_2CH_2), 2.00 (m, 4H, S–CH_2CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.9 (C_{qar}), 129.8, 128.8, 128.7, 127.2, 125.9 (CH_{ar}), 54.4 (S–CH), 43.8 (C_{qar}–CH_2), 32.1 (S–CH_2CH_2), 31.5 (S–CH_2CH_2). MS (80 eV): *m*/*z* (%)=224 (7) [M^+], 133 (100), 91 (27), 135 (24), 55 (14), 87 (12), 134 (10), 65 (7), 77 (5), 104 (5).

4.4. General procedure for acetalization and thioacetalization reactions with *p*-toluenesulphonic acid

These catalytic reactions were carried out under similar conditions to acetalization/thioacetalization reactions with the addition of the corresponding amount of *p*-TsOH.

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