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Gold-catalyzed rearrangement of propargylic *tert*-butyl carbonates

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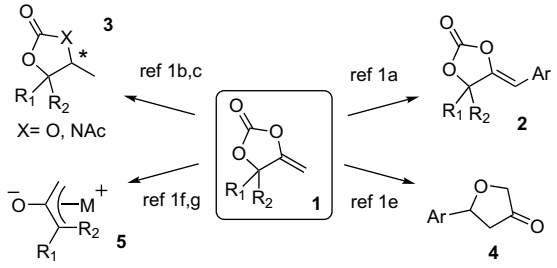
ABSTRACT

Diversely substituted 4-alkylidene-1,3-dioxolan-2-ones are efficiently synthesized by a gold(I)-catalyzed rearrangement of propargylic *tert*-butyl carbonates. The substrates are readily accessible and the transformation, which is performed under mild reaction conditions using a low loading of catalyst, allows the synthesis of cyclic carbonates, which would be less efficiently obtained using traditional methods. This procedure has also been applied to the stereoselective synthesis of (*E*)- or (*Z*)-4-halomethylene-1,3-dioxolan-2-ones, which proved to be suitable substrates for palladium-catalyzed cross-coupling reactions.

1. Introduction

4-Alkylidene-1,3-dioxolan-2-ones **1** and their derivatives are structurally interesting building blocks for organic synthesis. They indeed represent a masked form of 1,2-hydroxyketones that can be used as substrates in a range of transformations (Scheme 1).[1]

Dixneuf and co-workers have shown for instance that compounds **1** were suitable substrates for the Heck reaction, thus allowing the selective formation (*Z*)-4-phenylmethylene-1,3-dioxolan-2-ones **2**.[1a] The same authors also reported that cyclic carbonates **1** or carbamates could be enantioselectively hydrogenated using chiral ruthenium(II) complexes to ultimately furnish optically active 1,2-diols carbonates and *N*-acyloxazolidinones **3**.[1b,c] A similar procedure has been recently reported by Shin and co-workers for the selective hydrogenation or hydroboration of 4-substituted-5-methylene-oxazolidon-2-ones.[1d] Inoue and co-workers also reported the formation of substituted dihydrofuranones **4** by a palladium-catalyzed reaction of cyclic carbonate **1** with an aromatic aldehyde,[1e] and the group of Murai described the use of carbonate **1** for the synthesis of oxatrimethylenemethane–palladium or platinum complexes **5**.[1f,g] However, despite the synthetic potential of 4-alkylidene-1,3-dioxolan-2-ones, the number of their synthetic applications remains limited. This is mainly due to a lack of general and efficient synthetic procedures to access such structural units.



Scheme 1. Reported transformations of 4-alkylidene-1,3-dioxolan-2-ones **1**.

4-Alkylidene-1,3-dioxolan-2-ones are indeed typically prepared by the reaction of propargylic alcohols with carbon dioxide.[2] This transformation also requires the use of a catalyst, which can be a metallic species (ruthenium,[2a] cobalt,[2b] copper,[2c–f] palladium[2g–i] or silver[2j,k]), a phosphine[2l–o] or even an inorganic base.[2h] However, the scope remains limited, as these transformations are generally restricted to the use of tertiary alcohol, due to a reduced reactivity or even a lack of reactivity in the cases of mono- and disubstituted propargylic alcohols. Moreover, some of these procedures require a high carbon dioxide pressure (10 MPa) and/or a high temperature of reaction (100 °C) to efficiently afford the cyclic carbonates. Given the restrictions of these procedures, we thought that a new access to 4-alkylidene-1,3-dioxolan-2-ones would be desirable and decided to design a new route, which would allow the easy and efficient synthesis of a wide range of such compounds.

There has been an ongoing interest for gold catalysis in organic synthesis during the last ten years, which has been recently highlighted by the appearance of numerous reviews in the literature.[3] Gold complexes have indeed proved to be efficient and mild catalysts that can selectively activate alkynes, alkenes, and allenes toward the addition of a wide range of nucleophiles. Several gold-catalyzed methodologies leading to various oxygen-containing heterocycles have thus been developed.[4] Following our ongoing

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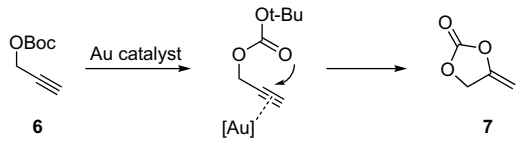
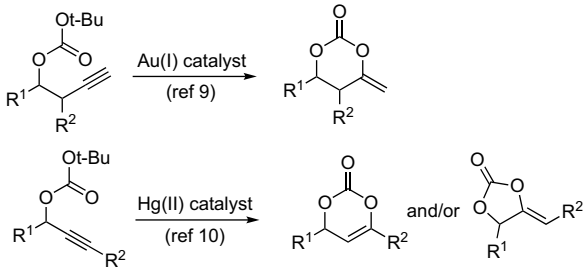


Scheme 2. Synthetic approach to 4-methylene-1,3-dioxolan-2-ones from propargylic carbonates.

efforts to develop new gold-catalyzed methodologies,[5] we conjectured that a cationic gold complex could be used to promote the rearrangement of a propargylic *tert*-butyl carbonate precursor **6** into the desired 4-alkylidene-1,3-dioxolan-2-one **7** (Scheme 2).[6]

This approach would be similar to the well-documented iodine-mediated cyclization of allylic and homoallylic *tert*-butyl carbonates[7] and would formally correspond to the internal deprotection of a Boc group using a gold–alkyne complex as the acidic species. It would also differ from the majority of the previously reported methodologies,[2] since the carbonate functionality of the final product would already be present in the structure of the substrate under a latent form. Notably, the *tert*-butyloxycarbonyl group has already proved to be a valuable nucleophilic partner for the gold-catalyzed synthesis of oxygenated heterocycles such as butenolides,[8a] dioxolanones,[8b] oxazolidinones,[1d,8c,d] and oxazolones.[8e,f] Of special interest are the procedures reported by the groups of Shin[9] and Nishizawa[10] for the respective gold- and mercury-catalyzed synthesis of dioxanones and dioxonones (Scheme 3).

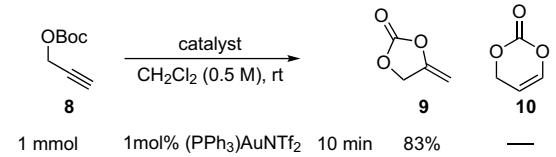


Scheme 3. Synthesis of dioxanones by Shin and dioxinones by Nishizawa.

2. Results and discussion

2.1. Synthesis of 4-alkylidene-1,3-dioxolan-2-ones

In order to validate our synthetic approach, the simple propargylic *tert*-butyloxycarbonate **8** was first chosen as a model substrate (Scheme 4). A rapid and clean conversion of **8** was observed when the reaction was performed in dichloromethane, on a 1 mmol scale, with 1 mol% of the bench stable $(PPh_3)AuNTf_2$.[11] Cyclic carbonate **9** was isolated in 83% yield under these conditions.



Scheme 4. Rearrangement of propargylic *tert*-butyloxycarbonate **8**.

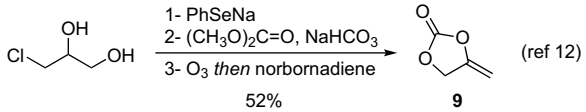
Notably, the reaction was regiospecific since no trace of carbonate **10**, resulting from a possible 6-*endo* cyclization could be observed.[10]

Control experiments also led to the conclusion that $HNTf_2$ and $AgNTf_2$ were not suitable catalysts for this transformation. Interestingly, the loading of the catalyst could be reduced to 0.1 mol%, when the reaction was performed on a 12 mmol and no noticeable loss of efficiency was observed. This result contrasts with that previously reported by Trost and co-workers who described the synthesis of **9**, in a three-step sequence, with an overall yield of 52% (Scheme 5).[12]

This new rearrangement appears to be quite general since a large variety of diversely substituted terminal alkynes **11a–m** reacted under the same reaction conditions (1 mol% of stable $(PPh_3)AuNTf_2$ in dichloromethane) to furnish cyclic carbonates **12a–m** in moderate to excellent yields (40–100%) (Table 1).

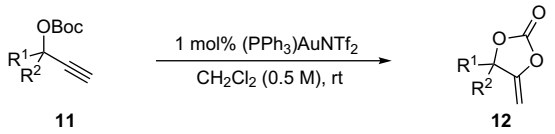
The reaction was rapid and a complete conversion of the substrate was generally observed after 1 h, with the exception of secondary and tertiary *tert*-butyloxycarbonates **11f** (entry 6), **11g** (entry 7), **11l** (entry 12), and **11m** (entry 13), which were less reactive. In these cases, the presence of a carbocation stabilizing group at the propargylic position of **11** (phenyl, vinyl, cyclopropyl groups) led to the competitive formation of various side-products. While the reaction conditions are relatively mild, the gold catalyst seems to be acidic enough to induce a competitive fragmentation of the C–O propargylic bond leading to undesired products. A higher loading of $(PPh_3)AuNTf_2$ (3 mol%) or the use of the more electrophilic gold complex $[Ph_3PAu(NC–CH_3)]SbF_6$ (1 mol%) was required in the case of cyclopropyl derivative **11g** to reach completion (entry 7). Interestingly, these side-products were not observed in the case of tertiary *tert*-butyloxycarbonates bearing simple alkyl groups at the propargylic position (entries 8–11). The transformation proved however to be compatible with various functionalities such as a phenyl group (entries 2, 6, and 12), an alkene (entries 3, 11, and 13), a silyl ether (entry 4) or an ester (entry 11). Notably, the rearrangement of alkyne **11e** was regioselective and exclusively furnished **12e**. The 5-*exo* cyclization proved to be a more favored process than the 6-*exo* cyclization that would furnish a six-membered cyclic carbonate, as previously reported by Shin and co-workers.[9] The androstene case was particularly interesting, since the corresponding cyclized product precipitates from the reaction medium under the reaction conditions used (entry 11). A simple filtration of the crude mixture furnished pure cyclic carbonate **12k** in 90% yield. The possibility of cyclizing secondary *tert*-butyloxycarbonates (entries 1–7) emphasizes the potential of this transformation since the corresponding cyclic carbonates would be less conveniently obtained using the previously reported methods.[2]

We next focused our attention onto a possible extension of this transformation to the rearrangement of internal alkynes. The results of this study are presented in Table 2. Substrates **13a–g** proved to be reactive as well, while the reaction times were generally longer and the yields lower (60–87%) than for the rearrangement of terminal alkynes. Substrates **13a–c** exclusively produced the (*Z*)-isomers of desired cyclic carbonates **14a–c** (entries 1–3). Substrate **13a**, bearing an ester group at the alkyne terminus furnished compound **14a** as the result of a gold-catalyzed Michael type addition of the Boc group onto the activated alkyne. Once again, $(PPh_3)AuNTf_2$ proved to be a relatively mild catalyst as attested by the rearrangement of internal alkynes **13b** and **13c** for which the second Boc group remains intact under the reaction conditions

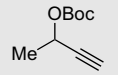
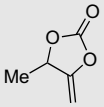
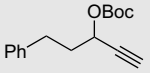
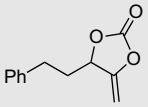
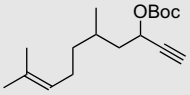
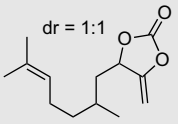
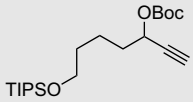
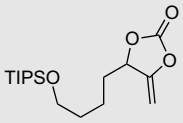
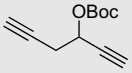
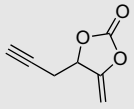
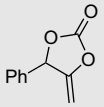
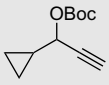
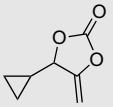
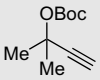
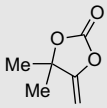
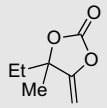
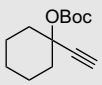
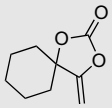
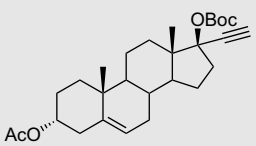
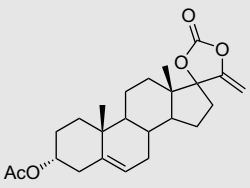
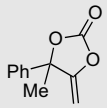


Scheme 5. Synthesis of **9** by Trost and co-workers.

Table 1
Reaction scope for the transformation of terminal alkynes **11a–m**

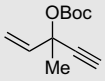
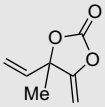


11 **12**

Entry	Substrate **11**		Product **12**		Time	Yield[a]
1		**11a**		**12a**	15 min	94
2		**11b**		**12b**	5 min	100
3		**11c**		**12c**	10 min	91 dr=1:1
4		**11d**		**12d**	5 min	96
5		**11e**		**12e**	5 min	95
6		**11f**		**12f**	10 h	74
7		**11g**		**12g**	5 h 1 h	49[b] 49[c]
8		**11h**		**12h**	5 min	85
9		**11i**		**12i**	5 min	98
10		**11j**		**12j**	30 min	96
11		**11k**		**12k**	10 min	90
12		**11l**		**12l**	17 h	76

(*continued on next page*)

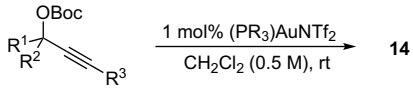
Table 1 (*continued*)

Entry	Substrate **11**		Product **12**		Time	Yield[a]
13		**11m**		**12m**	18 h	40

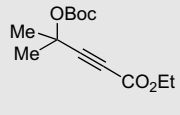
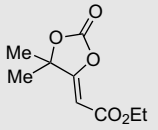
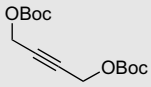
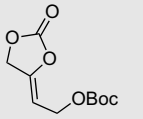
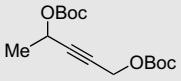
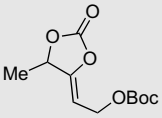
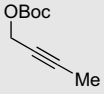
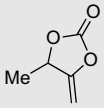
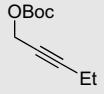
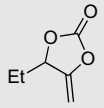
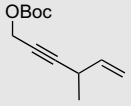
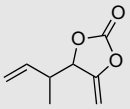
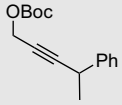
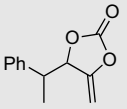
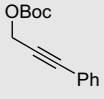
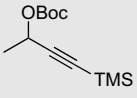
[a] Isolated yield.
[b] With 3 mol % of $(PPh_3)AuNTf_2$.
[c] With 1 mol % of $[Ph_3PAu(NC–CH_3)]SbF_6$.

(entries 2 and 3). Thus, remarkably, unsymmetrical substrate **13b**, stereoselectively produces **14b** as the result of a Thorpe–Ingold effect favoring a faster cyclization of the more substituted *tert*-butyloxycarbonate. Curiously, *tert*-butyloxycarbonates **13d–g** did not react under the same reaction conditions (entries 4–7). The rearrangement was however effective when the more electrophilic gold complex $[(p\text{-}CF_3Ph)_3P]AuNTf_2$ was used as the catalyst. Under these new conditions, *exo*-methylene compounds **12a** and **14e–g** were obtained in moderate yields (60–68%) following an unexpected reaction pathway. The cyclic carbonate motif in compounds **12a** and **14e–g** was indeed shifted from one carbon in comparison with the structures of the compounds obtained in the cases studied previously. The reactions of substrates **13f** and **13g**, possessing an asymmetric center at the propargylic position, produced diastereoisomeric mixtures of cyclic carbonates. Even if the selectivity was modest, it notably increased as a function of the steric hindrance induced by the group located at the propargylic position (compare entry 6 with entry 7).

Table 2
Reaction scope for the transformation of internal alkynes **13a–i**



13

Entry	Substrate **13**		Product **14**		Time	Yield[a]
1[b]		**13a**		**14a**	2 h	87
2[b]		**13b**		**14b**	50 min	62
3[b]		**13c**		**14c**	30 min	77
4[c]		**13d**		**12a**	24 h	62
5[c]		**13e**		**14e**	24 h	60
6[c]		**13f**		**14f**	20 h	68 dr=1:1.6
7[c]		**13g**		**14g**	20 h	66 dr=1:3.9
8[b,c]		**13h**	—		20 h	—
9[b,c]		**13i**	—		3 h	—

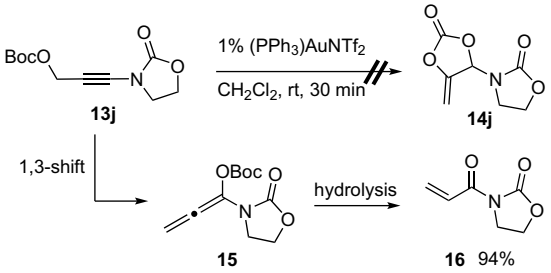
[a] Isolated yield.
[b] With $(PPh_3)AuNTf_2$.
[c] With $[(p\text{-}CF_3Ph)_3P]AuNTf_2$.

Disappointing results were obtained in the case of internal alkynes **13h** and **13i** (entries 8 and 9), whatever the catalyst used. In the first case, the substrate was unreactive, while numerous products derived from the degradation of the Boc group were formed when TMS derivative **13i** was used as the substrate. While alkyne **13j** was described in our preliminary communication[6] as leading to cyclic carbonate **14j**, reexamination of NMR spectra led to the conclusion that the structure of the product had been initially misassigned (Scheme 6). Rearrangement of **13j**, in the presence of 1 mol % of $(PPh_3)AuNTf_2$ actually furnished compound **16** as the result of a 1,3-*tert*-butoxycarbonyl migration followed by the hydrolysis of the resulting *tert*-butoxycarbonyloxyallene **15** by traces of water.[13]

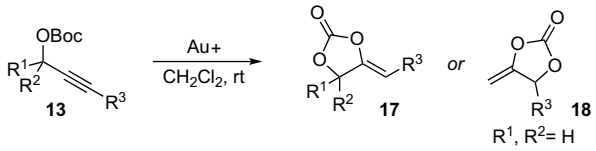
2.2. Mechanistic proposal

The results obtained during the scope of the transformation led to the conclusion that the structure of the cyclic carbonates (**17** or **18**) furnished by the gold-catalyzed rearrangement of propargylic *tert*-butyloxycarbonates **13** was significantly dependant on the nature of the substituent attached at the alkyne terminus (Scheme 7).[14]

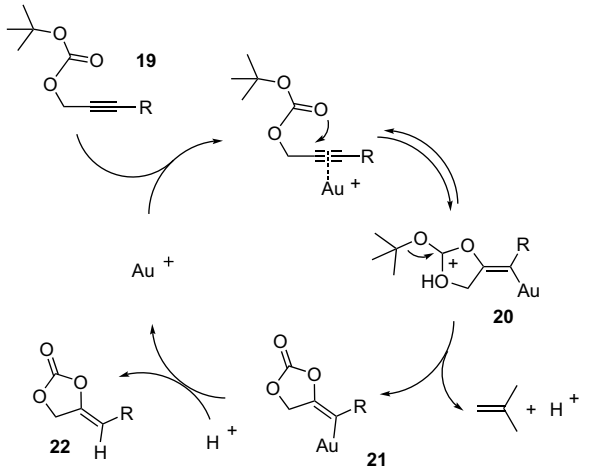
A mechanistic proposal that accounts for the formation of cyclic carbonates of type **17** is given in Scheme 8. Gold(I)-activation of the alkyne moiety in substrate **19** promotes the nucleophilic addition of



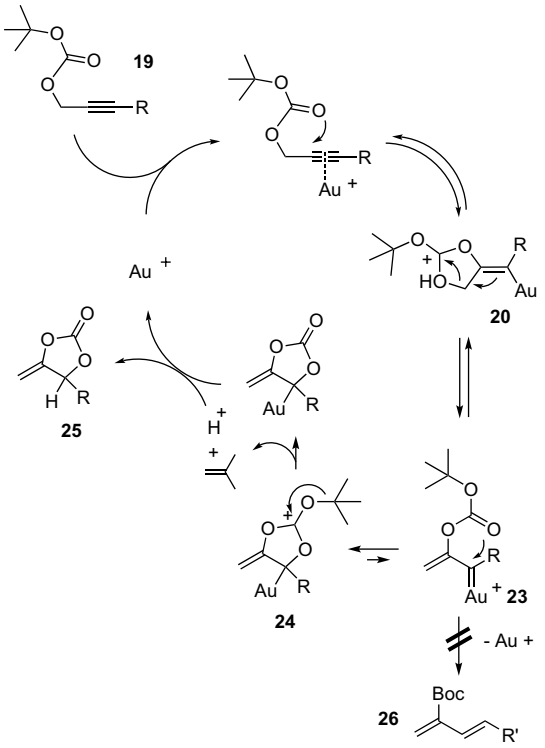
Scheme 6. Rearrangement of propargylic *tert*-butyloxycarbonate **13j**.



Scheme 7. Divergence in the rearrangement of propargylic *tert*-butyloxycarbonates.



Scheme 8. Mechanistic proposal for the formation of cyclic carbonate of type **17**.



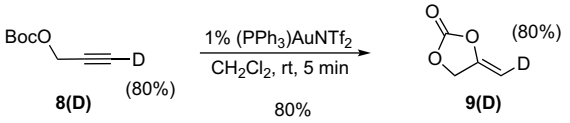
Scheme 10. Mechanistic proposal for the formation of cyclic carbonate of type **18**.

the *tert*-butyloxycarbonyl group that leads to the formation of the intermediate cationic species **20**. A selective fragmentation of the C–O bond of the *tert*-butyloxy group subsequently furnishes the neutral vinyl–gold species **21** with release of isobutene. A final protodemetallation step finally gives cyclic carbonate **22**. This mechanism seems to be favored in the case of terminal alkynes (see Table 1) or alkynes possessing electron-withdrawing groups (see Table 2, entry 1). Substrates possessing a second propargylic BocO group are also rearranged following this reaction pathway (see Table 2, entries 2 and 3).

The *anti* addition of the *tert*-butyloxycarbonyl group onto the activated alkyne combined with the stereoselective protodemetallation step are in agreement with the stereospecific formation of compounds **14a–c** (see Table 2, entries 1–3). The exclusive formation of compound **8(D)** during the rearrangement of 80% deuterated alkyne **9(D)** is also in agreement with this mechanistic proposal (Scheme 9).

A plausible reaction pathway that may explain the formation of cyclic carbonates of type **18** is presented in Scheme 10. After an identical nucleophilic addition of the *tert*-butyloxycarbonyl group onto the activated alkyne, the fragmentation of the internal C–O bond in intermediate **20** could alternatively occur to give the stabilized gold carbene **23** (Scheme 10). A subsequent cyclization of the Boc group, followed by a sequence of fragmentation and protodemetallation would finally furnish cyclic carbonate **25**.

This mechanism can account for the selectivity observed in the case of substrates **13f** and **13g** (see Table 2). Interestingly, the formation of intermediate **23** might be followed by a 1,2-hydride shift leading to the formation of a 1,3-diene **26**, as recently reported by Zhang and co-workers.[15] The formation of such dienes was not observed during the rearrangement of substrates **13f** and **13g**, for which this 1,2-hydride shift would be especially favored. This selectivity may result from a greater stability of intermediate **24** compared to **23**.[14]

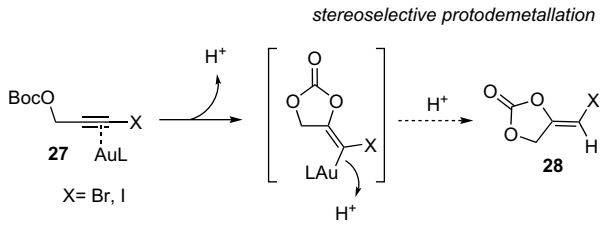


Scheme 9. Rearrangement of propargylic *tert*-butyloxycarbonate **8(D)**.

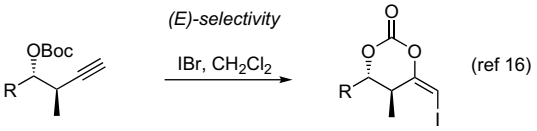
2.3. Synthesis of 4-(*Z*-halomethylene)-1,3-dioxolan-2-ones

Vinyl bromides and iodides are synthetically useful building blocks that can be used in a range of transformations, among which transition metal-catalyzed cross-coupling reactions occupy a predominant place. We were particularly intrigued to see if the protocol used for the rearrangement of terminal propargylic *tert*-butyl carbonates could also be applied to the formation of haloalkenes **28** using as substrates haloalkynes **27** (Scheme 11).

This approach would be particularly interesting for two main reasons. Following the same mechanistic proposal than that proposed for the rearrangement of terminal alkynes (see Scheme 8), this procedure would allow the *stereoselective* formation of (*Z*)-haloalkenes. Secondly, it is noteworthy that these isomers could not be obtained following the methods previously developed for the direct iodocyclization of similar homopropargylic *tert*-butyl carbonates[16] since the use of a source of electrophilic iodine exclusively furnishes the opposite (*E*)-isomers (Scheme 12). It is also



Scheme 11. Synthetic approach to 4-(*Z*-halomethylene)-1,3-dioxolan-2-ones.



Scheme 12. Literature precedent for the iodocyclization of homopropargylic *tert*-butyl carbonates.

important to note that these haloalkenes could not be obtained using the mercury-catalyzed reaction developed by Nishizawa.[10]

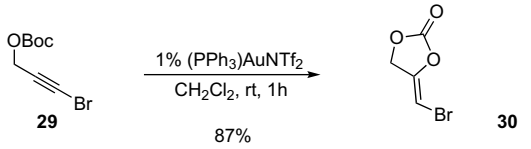
We chose simple bromoalkyne **29** as a model substrate to study the feasibility of the transformation (Scheme 13). To our delight, the desired reaction did happen with 1 mol % of $(PPh_3)AuNTf_2$ using dichloromethane as the solvent and bromoalkyne **30** was formed in 87% yield with a complete (*Z*) selectivity.

This procedure was applied to a series of diversely substituted haloalkynes, and the results are presented in Table 3. The reaction proved to be rapid in all the cases. The presence of a halogen atom at the alkyne terminus did not induce a change in the kinetics of the cyclization (compare results of Table 3 with those of Table 1).

Bromoalkyne **31a**, possessing an extra methyl substituent at the propargylic position, cyclized more rapidly and (*Z*)-bromoalkyne **32a** was isolated in an excellent 95% yield. Since iodoalkenes are generally more desirable than their bromo analogs for transition metal-catalyzed cross-coupling reactions, we focused more particularly our attention on the transformation of iodoalkynes. Results presented in entries 2–7 demonstrate that a range of secondary and tertiary iodoalkynes bearing a variety of substituents could be selectively rearranged to the corresponding (*Z*)-iodoalkenes **32b**–**g** in generally good yields. A phenyl group (entry 3), an alkene (entry 4) or a silyl ether (entry 5) was compatible functionalities. A disappointing result was however obtained in the case of alkyne **31f** possessing a cyclopropyl group at the propargylic position. Only traces of the corresponding iodoalkene **32f** were obtained when $(PPh_3)AuNTf_2$ was used as the catalyst. The more electrophilic $[Ph_3PAu(NC–CH_3)]SbF_6$ complex was required to improve the formation of **32f**, which could be isolated in a modest 32% yield. As previously suggested, $(PPh_3)AuNTf_2$ might be acidic enough to activate the OBoc group and cause the degradation of the substrate by formation of a positive charge at the propargylic position. This process would be especially favored in this case due to the presence of the cyclopropyl ring.

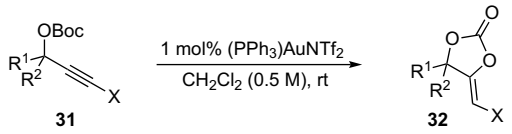
2.4. Synthesis of 4-(*E*-iodomethylene)-1,3-dioxolan-2-ones

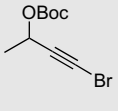
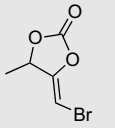
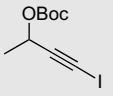
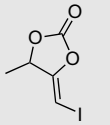
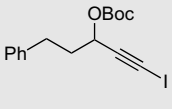
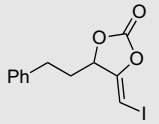
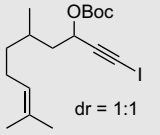
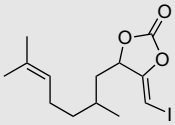
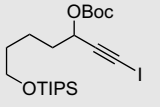
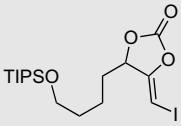
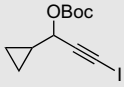
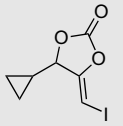
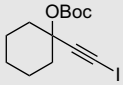
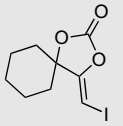
We next envisaged to synthesize the (*E*)-isomers of 4-iodomethylene-1,3-dioxolan-2-ones, which one could not be obtained by the rearrangement of iodoalkynes derivatives, due to the stereospecificity of the transformation. The development of another gold-catalyzed reaction allowing the stereoselective formation of the (*E*) isomers would however be synthetically useful since either one or the other isomer could be selectively obtained from the same propargylic *tert*-butyl carbonate precursor. Our synthetic approach is depicted in Scheme 14. Since a stereoselective protodemetallation was proposed as the last step in the rearrangement of propargylic *tert*-butyl carbonates into 4-methylene-1,3-dioxolan-2-ones (Scheme 8), we envisaged to trap the intermediate



Scheme 13. Formation of (*Z*)-bromoalkene **30**.

Table 3
Reaction scope for the formation of 4-(*Z*-halogenomethylene)-1,3-dioxolan-2-ones **32a–g**

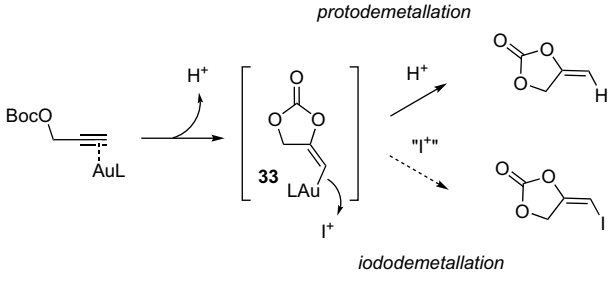


Entry	Substrate **31**		Product **32**		Time	Yield[a]
1		**31a**		**32a**	20 min	87
2		**31b**		**32b**	10 min	95
3		**31c**		**32c**	5 min	99
4		**31d**		**32d**	5 min	97 dr=1:1
5		**31e**		**32e**	5 min	69
6[b]		**31f**		**32f**	1 h	32
7		**31g**		**32g**	5 min	83

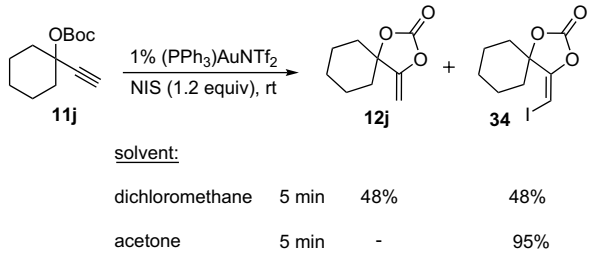
[a] Isolated yield.
[b] With 1 mol % of $[Ph_3PAu(NC–CH_3)]SbF_6$.

vinyl–gold species **33** by a source of an electrophilic iodine before the protonation occurs.[17]

NIS was chosen as the electrophile[17] and the reaction attempted using alkyne **11j** as the substrate (Scheme 15). Using the conditions previously developed for the simple rearrangement of propargylic



Scheme 14. Synthetic approach to 4-(*E*-iodomethylene)-1,3-dioxolan-2-ones.



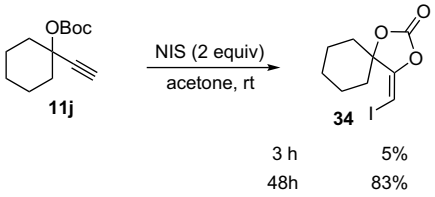
Scheme 15. Formation of (*E*)-iodoalkene **34**.

tert-butyl carbonates (1 mol % of $(PPh_3)AuNTf_2$, dichloromethane as the solvent) with a slight excess of NIS (1.2 equiv), the reaction was very rapid and a 1:1 mixture of the desired (*E*)-iodinated product **34** and the protodemetallated product **12j** was formed. In order to improve the formation of **34**, the reaction was attempted using a more polar solvent. We indeed hypothesized that the protonation should be slowed down in a polar solvent thus favoring the trapping of the vinyl–gold intermediate by NIS. Gratifyingly, the use of acetone as the solvent had a dramatic effect on the selectivity while the rate of the reaction remains the same. Compound **34** was exclusively and stereoselectively formed under these conditions and isolated in 95% yield.

While the iodine-mediated cyclization of allylic and homoallylic *tert*-butyl carbonates is well documented,[7] no example of the same transformation applied to propargylic derivatives has been reported. Mathew and co-workers have however described the direct iodocyclization of a series of homopropargylic *tert*-butyl carbonates using IBr as the source of electrophilic iodine (Scheme 12).[16] In order to evaluate the role of the gold catalyst during this reaction, a control experiment was performed (Scheme 16). Under the same reaction conditions with a twofold excess of NIS and without $(PPh_3)AuNTf_2$, the formation of iodoalkene **34** was slow. This compound could however be isolated in 82% yield after 48 h.

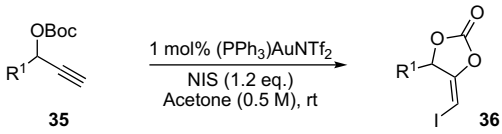
Even if this control experiment does not prove that iodoalkene **34** is formed after an iododemetallation step when the gold complex is used, the difference observed in the kinetics reflects the major role played by this complex in the transformation. Incidentally, such an iododemetallation step has been invoked in a series of other gold mediated transformations.[17]

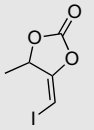
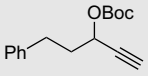
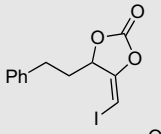
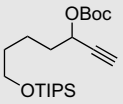
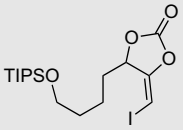
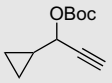
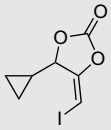
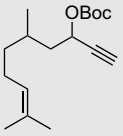
A rapid exploration of the scope of the reaction was next performed using diversely substituted secondary propargylic alcohol derivatives **35a–f** (Table 4). While the yield was excellent when tertiary propargylic alcohol derivative **11j** was used as the substrate (Scheme 15), iodoalkenes **36a–d** were only obtained in low to moderate yields (35–76%), but with a complete stereoselectivity. It is interesting to note that in most cases, the iodocyclization was a slower process than the simple cyclization (compare the results in Table 1 with those in Table 4), perhaps the consequence of a lower activity of the gold complex in acetone than in dichloromethane. Even if the reaction was rapid in the case of monomethyl substituted substrate **35a**, it was however surprisingly inefficient, and compound **36a** was isolated in a low 35% yield (entry 1). With a longer side chain such as in the case of alkynes **35b** and **35c**, the



Scheme 16. Control experiment for the formation of (*E*)-iodoalkene **34**.

Table 4
Reaction scope for the formation of 4-(*E*-iodomethylene)-1,3-dioxolan-2-ones **35**



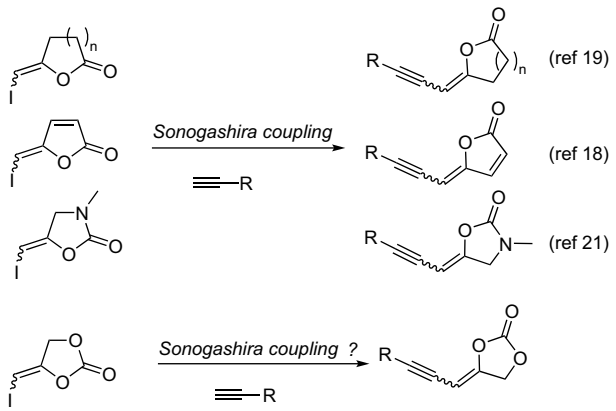
Entry	Substrate **35**		Product **36**		Time	Yield[a]
1		**35a**		**36a**	5 min	35
2		**35b**		**36b**	45 min	66
3		**35c**		**36c**	15 min	64
4[b]		**35d**		**36d**	1 h	76
5		**35e**	—		5 min	—
6		**35f**	—		15 min	—

[a] Isolated yield.
[b] With 1 mol % of $[Ph_3PAu(NC–CH_3)]SbF_6$.

yields were improved to 66% and 64%, while the reaction times were increased (entries 2 and 3). It is particularly noteworthy that only limited desilylation occurred in the case of substrate **35c** due to the mildness of the reaction conditions used. Cyclopropyl derivative **35d** also furnished the desired iodoalkene **36d** in a good 76% yield (entry 4). As in the case of the simple rearrangement (Table 1, entry 7), the use of the more electrophilic $[Ph_3PAu(NC–CH_3)]SbF_6$ gold complex was however required to obtain a complete conversion of **35d**. This transformation is however not a general process as indicated by the results obtained when the transformation was attempted using substrates **35e** and **35f** (entries 5 and 6). In these cases, the corresponding iodoalkenes could not be isolated and only degradation products were obtained. This contrasting reactivity remains unclear even if the occurrence of competitive side reactions initiated by the interaction of NIS with the alkene might be invoked for substrate **35e**.

2.5. Palladium cross-coupling reactions

Having in hand a series of 4-halogenomethylene-1,3-dioxolan-2-ones, we attempted to use these compounds as substrates in palladium cross-coupling reactions. We first focused our attention on the Sonogashira coupling. This transformation has already been successfully applied to the coupling of various alkynes with cyclic

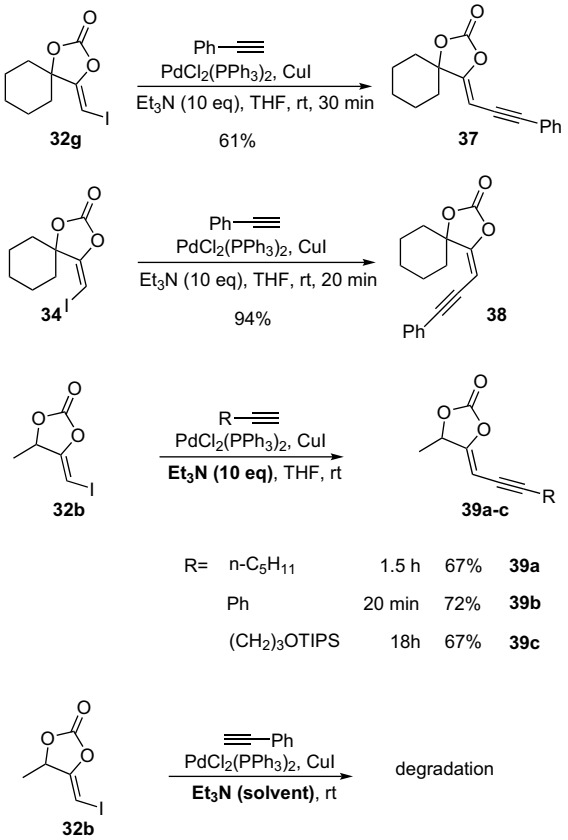


Scheme 17. Literature precedents for the Sonogashira cross-coupling reaction of substrates structurally closed to dioxolanones.

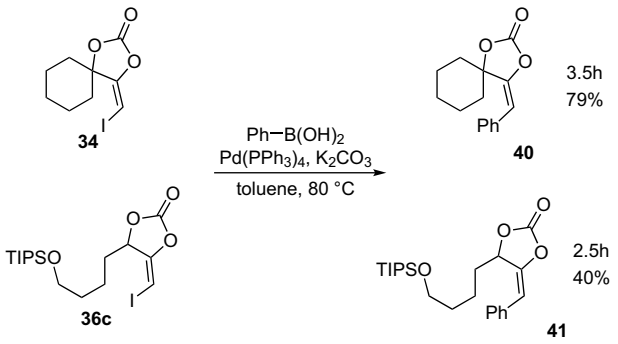
derivatives furanones,[18] dihydrofuranones,[19] tetrahydropyranones[19,20] or oxazolidinones[21] and could therefore be envisaged in the case of dioxolanones (Scheme 17).

The results of this study are summarized in Scheme 18. To our delight, the reaction of (*Z*)-iodoalkene **32g** with phenylacetylene under classical Sonogashira reaction conditions led to the formation of enyne **37**, which was isolated in a moderate 61% yield. Surprisingly, the reaction of the isomeric (*E*)-iodoalkene **34** was more efficient and furnished the corresponding enyne **38** in an excellent 94% yield. Various alkynes could be used as partners in the Sonogashira coupling as attested by the transformation of iodoalkene **32b** into enynes **39a–c** (67–72% yield).[22]

Interestingly, the quantity of triethylamine used for the Sonogashira cross-coupling proved to be highly important. Indeed, the



Scheme 18. Attempts of Sonogashira cross-coupling reaction with 4-(iodomethylene)-1,3-dioxolan-2-ones.



Scheme 19. Examples of Suzuki cross-coupling reaction with 4-(iodomethylene)-1,3-dioxolan-2-ones.

reaction between (*Z*)-iodoalkene **32a** and phenylacetylene, which was relatively efficient when only 10 equiv of triethylamine were used, only furnished degradation products when the base was used as the solvent. We were also surprised by the reactivity of (*E*)-iodoalkene **36a**. While (*Z*) isomer **32b** reacted with triisopropyl-pent-4-ynyloxy-silane to give enyne **39c** in 67% yield, the reaction with (*E*) isomer **36a** only led to degradation products under the same reaction conditions.

Attempts to perform Suzuki cross-coupling reactions with dioxolanones derivatives were also successful (Scheme 19).[22] Enynes **34** and **36c** reacted for instance with phenylboronic acid in the presence of tetrakis(triphenylphosphine)palladium(0) and potassium carbonate in toluene at 80 °C to give dioxolanones **40** and **41** in, respectively, 79% and 40% yield. However, the reaction proved to be more sluggish for this coupling probably due to the higher temperature used and the instability of the vinylcarbonate functionality under the basic conditions used.

In summary, we have shown that gold(I) complexes efficiently catalyze the formation of a variety of 4-(alkylidene)-1,3-dioxolan-2-ones from readily available propargylic *tert*-butyl carbonates. The loading of the catalyst is low (1 mol%) and the reaction conditions mild enough to insure a compatibility with diversely substituted substrates. The structure of the cyclic carbonates obtained also appears to be dependant on the nature of the substituent attached at the terminus of the alkyne. An extension of the procedure to the stereoselective formation of (*E*)- or (*Z*)-4-(halomethylene)-1,3-dioxolan-2-ones has also been developed, using, respectively, haloalkynes or terminal alkynes as the substrates. These transformations furnished valuable haloalkenes, which proved to be suitable substrates for Sonogashira and Suzuki cross-coupling reactions.

3. Experimental

3.1. General information

Commercially available reagents were used as received without further purification. Dry Et_2O and THF were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 from CaH_2. Flash column chromatography was performed over silica gel 60 by Merck (40–63 μm). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with a Perkin–Elmer FT-1600 spectrometer. Mass spectra were recorded with a Hewlett–Packard HP-5890 B spectrometer using electron ionization (EI^+) or chemical ionization with ammonia (CI^+, NH_3) methods. High resolution mass spectra were recorded with a Jeol GCmate II spectrometer using the electron ionization (EI^+) method. R_3P-Au-NTf_2 catalysts were synthesized as previously described.[11]

3.2. Au(I)-catalyzed formation of 4-alkylidene-1,3-dioxolan-2-ones

General procedure: To a solution of propargylic *tert*-butyl carbonate (1 equiv) in dichloromethane (0.5 M) at room temperature was added the gold catalyst (0.01 equiv). The mixture was stirred at room temperature and monitored periodically by TLC. Upon completion, the mixture was either directly filtered through a silica pad pre-impregnated with dichloromethane or evaporated and then chromatographed with a petroleum ether/diethyl ether mixture to give the expected product.

*3.2.1. 4-Methylene-1,3-dioxolan-2-one (**9**)*

Yield: 83%. Solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01 (t, J=2.3 Hz, 2H), 4.93–4.90 (m, 1H), 4.45–4.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 148.9, 87.4, 67.6. IR (CCl_4): cm^{-1} 2925, 1855, 1708, 1681, 1283, 1119, 1067. Mp (°C): 28–29. MS (CI^+, NH_3) m/z 118 (MNH_4^+). HRMS (EI^+) m/z calculated for $C_4H_4O_3$: 100.0160, found: 100.0159.

*3.2.2. 4-Methyl-5-methylene-1,3-dioxolan-2-one (**12a**)*

Yield: 94%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.28–5.19 (m, 1H), 4.85–4.78 (m, 1H), 4.37–4.33 (m, 1H), 1.59–1.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 151.8, 86.5, 76.2, 20.3. IR (CCl_4): cm^{-1} 2989, 2934, 1844, 1707, 1682, 1317, 1279, 1145, 1085, 1003. MS (CI^+, NH_3): m/z 132 (MNH_4^+), 102, 85. HRMS (EI^+): m/z calculated for $C_5H_6O_3$: 114.0317, found: 114.0313.

*3.2.3. 4-Methylene-5-phenethyl-1,3-dioxolan-2-one (**12b**)*

Yield: quant. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.27–7.21 (m, 3H), 5.17–5.14 (m, 1H), 4.89 (dd, J=2.4, 4.0 Hz, 1H), 4.37 (dd, J=2.0, 4.0 Hz, 1H), 2.93–2.75 (m, 2H), 2.20–2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 151.9, 139.5, 128.6, 128.3, 126.4, 86.8, 78.6, 36.5, 30.2. IR (CCl_4): cm^{-1} 3065, 3028, 2950, 2930, 2862, 1842, 1705, 1681, 1497, 1452, 1341, 1282, 1131, 1085, 1045, 1004. MS (EI^+): m/z 204 (M^+), 160, 145, 117, 105. HRMS (EI^+): m/z calculated for $C_{12}H_{12}O_3$: 204.0787, found: 204.0781.

*3.2.4. 4-(2,6-Dimethyl-hept-5-enyl)-5-methylene-1,3-dioxolan-2-one (**12c**)*

Yield: 91%. Yellow oil (isolated as a 1:1 mixture of diastereoisomers). ^{1}H NMR (400 MHz, $CDCl_3$) for the mixture of diastereoisomers: δ 5.23–5.16 (m, 1H), 5.11–5.06 (m, 1H), 4.85–4.83 (m, 1H), 4.33–4.31 (m, 1H), 2.09–1.93 (m, 2H), 1.94–1.13 (m, 5H), 1.69 (s, 3H), 1.61 (s, 3H), 1.00 (d, J=6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) for the mixture of diastereoisomers: δ 154.0, 154.0, 152.0, 131.8, 131.8, 123.9, 123.9, 86.6, 86.5, 78.6, 78.1, 42.5, 42.5, 37.2, 36.1, 29.2, 28.6, 25.6, 25.2, 25.1, 19.8, 18.7, 17.6, 17.6. IR (CCl_4): cm^{-1} 2965, 2925, 2859, 1834, 1703, 1680, 1452, 1378, 1340, 1282, 1135, 1077, 1017. MS (EI^+): m/z 224 (M^+). HRMS (EI^+): m/z calculated for $C_{13}H_{20}O_3$: 224.1413, found: 224.1420.

*3.2.5. 4-Methylene-5-(4-triisopropylsilanyloxy-butyl)-1,3-dioxolan-2-one (**12d**)*

Yield: 96%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19–5.16 (m, 1H), 4.86 (dd, J=2.4, 3.9 Hz, 1H), 4.35 (dd, J=1.9, 3.9 Hz, 1H), 3.71 (t, J=5.8 Hz, 2H), 1.97–1.77 (m, 2H), 1.68–1.50 (m, 4H), 1.13–1.01 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 152.0, 86.7, 79.8, 62.8, 34.6, 32.1, 20.6, 17.9, 11.9. IR (CCl_4): cm^{-1} 2945, 2865, 2727, 2251, 1842, 1746, 1704, 1681, 1462, 1383, 1338, 1280, 1105, 1011. MS (EI^+): m/z 328 (M^+), 286, 242, 223, 211, 199. HRMS (EI^+): m/z calculated for $C_{17}H_{32}O_4Si$: 328.2070, found: 328.2083.

*3.2.6. 4-Methylene-5-prop-2-ynyl-1,3-dioxolan-2-one (**12e**)*

Yield: 95%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31–5.27 (m, 1H), 5.00 (dd, J=2.3, 4.1 Hz, 1H), 4.62 (dd, J=1.9, 4.1 Hz, 1H), 2.88 (ddd, J=2.7, 6.0, 17.2 Hz, 1H), 2.77 (ddd, J=2.7, 4.5, 17.2 Hz, 1H), 2.18 (t, J=2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 151.6, 88.2, 76.7, 76.0, 72.6, 25.3. IR (CCl_4): cm^{-1} 3310, 1850, 1685, 1328, 1288, 1129, 1075. MS (CI^+, NH_3): m/z 156 (MNH_4^+). HRMS (EI^+): m/z calculated for $C_7H_6O_3$: 138.0317, found: 138.0320.

*3.2.7. 5-Methylene-4-phenyl-1,3-dioxolan-2-one (**12f**)*

Yield: 74%. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.48 (m, 3H), 7.47–7.44 (m, 2H), 6.13 (dd, J=2.1, 2.5 Hz, 1H), 5.03 (dd, J=2.5, 4.0 Hz, 1H), 4.35 (dd, J=2.1, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 151.9, 134.9, 130.3, 129.3, 127.4, 89.3, 81.4. IR (CCl_4): cm^{-1} 1845, 1711, 1684, 1301, 1261, 1127, 1040. MS (CI^+, NH_3): m/z 194 (MNH_4^+). HRMS (EI^+): m/z calculated for $C_{10}H_8O_3$: 176.0473, found: 176.0480.

*3.2.8. 4-Cyclopropyl-5-methylene-1,3-dioxolan-2-one (**12g**)*

Yield: 49%. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88 (dd, J=2.5, 3.6 Hz, 1H), 4.57 (dd, J=2.1, 8.4 Hz, 1H), 4.50 (dd, J=2.0, 3.7 Hz, 1H), 1.35–1.19 (m, 1H), 0.81–0.71 (m, 2H), 0.64–0.53 (m, 1H), 0.55–0.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 151.9, 87.4, 84.0, 14.3, 2.6, 2.2. IR (CCl_4): cm^{-1} 3088, 3013, 2966, 2927, 2860, 1843, 1681, 1378, 1320, 1277, 1181, 1130, 1045. MS (EI^+): m/z 140 (M^+). HRMS (EI^+): m/z calculated for $C_7H_8O_3$: 140.0474, found: 140.0478.

*3.2.9. 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (**12h**)*

Yield: 85%. Solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (d, J=3.9 Hz, 1H), 4.31 (d, J=3.9 Hz, 1H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 151.2, 85.2, 84.6, 27.4. IR (CCl_4): cm^{-1} 2988, 1906, 1838, 1708, 1678, 1258, 1173, 1080, 1025. Mp (°C): 28–29. MS (CI^+, NH_3): m/z 146 (MNH_4^+). HRMS (EI^+): m/z calculated for $C_6H_8O_3$: 128.0473, found: 128.0475.

*3.2.10. 4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (**12i**)*

Yield: 98%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.82 (d, J=3.9 Hz, 1H), 4.27 (d, J=3.9 Hz, 1H), 1.92 (dd, J=7.4, 14.7 Hz, 1H), 1.76 (dd, J=7.4, 14.7 Hz, 1H), 1.59 (s, 3H), 0.99 (t, J=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 151.4, 87.5, 85.5, 33.2, 25.8, 7.1. IR (CCl_4): cm^{-1} 2980, 2935, 2839, 1703, 1677, 1291, 1229, 1151, 1090, 1040. MS (CI^+, NH_3) m/z 160 (MNH_4^+), 139, 117, 102, 85. HRMS (EI^+): m/z calculated for $C_7H_{10}O_3$: 142.0630, found: 142.0624.

*3.2.11. 4-Methylene-1,3-dioxa-spiro[4.5]decan-2-one (**12j**)*

Yield: 96%. Heavy oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81 (d, J=3.8 Hz, 1H), 4.33 (d, J=3.8 Hz, 1H), 2.07–2.03 (m, 2H), 1.84–1.58 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 151.2, 86.2, 85.3, 36.3, 24.1, 21.4. IR (CCl_4): cm^{-1} 2942, 2862, 1842, 1703, 1676, 1264, 1196, 1128, 1059, 1022. MS (CI^+, NH_3) m/z 186 (MNH_4^+). HRMS (EI^+): m/z calculated for $C_9H_{12}O_3$: 168.0786, found: 168.0791.

*3.2.12. Androstene derivative (**12k**)*

Yield: 90%. Crystalline. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.28 (d, J=4.8 Hz, 1H), 4.83 (d, J=3.8 Hz, 1H), 4.55–4.42 (m, 1H), 4.31 (d, J=3.8 Hz, 1H), 2.43–2.14 (m, 3H), 2.10–1.94 (m, 2H), 1.94 (s, 3H), 1.93 (br d, J=10.5 Hz, 2H), 1.71–1.60 (m, 1H), 1.54–1.26 (m, 8H), 1.29–1.17 (m, 1H), 1.07–1.01 (m, 1H), 0.95 (s, 3H), 0.90 (s, 3H), 1.00–0.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 157.6, 151.3, 139.6, 121.6, 96.8, 88.8, 73.4, 49.2, 49.0, 47.1, 37.9, 36.7, 36.4, 34.1, 31.8, 31.2, 30.9, 27.5, 22.9, 21.2, 20.0, 19.1, 14.0. IR (CCl_4): cm^{-1} 2949, 2907, 1835, 1735, 1674, 1369, 1245, 1137, 1080, 1030. Mp (°C): 195–200. MS (CI^+, NH_3) m/z 419 (MNH_4^+), 355, 339. HRMS (EI^+): m/z calculated for $C_{24}H_{32}O_5$: 400.2250, found: 400.2257.

*3.2.13. 4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one (**12l**)*

Yield: 76%. Heavy yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.27 (m, 5H), 4.86 (d, J=4.0 Hz, 1H), 4.38 (d, J=4.0 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 151.2, 139.3, 129.2, 128.9, 124.8, 88.2, 87.2, 27.6. IR (CCl_4): cm^{-1} 3660, 3065, 2991, 2935, 1843, 1680,

1294, 1222, 1071. MS (CI^+, NH_3): *m/z* 208 (MNH_4^+), 157, 140. HRMS (EI^+): *m/z* calculated for $C_{11}H_{10}O_3$: 190.0630, found: 190.0622.

*3.2.14. 4-Methyl-5-methylene-4-vinyl-1,3-dioxolan-2-one (**12m**)*

Yield: 40%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.94 (d, *J*=10.6, 17.1 Hz, 1H), 5.49 (d, *J*=17.1 Hz, 1H), 5.33 (d, *J*=10.6 Hz, 1H), 4.88 (d, *J*=3.9 Hz, 1H), 4.34 (d, *J*=3.9 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 151.0, 136.1, 116.6, 87.2, 85.7, 25.5. IR (CCl_4): cm^{-1} 3671, 3097, 2988, 2931, 2864, 1843, 1754, 1679, 1291, 1227, 1125, 1023. MS (CI^+, NH_3) *m/z* 158 (MNH_4^+). HRMS (EI^+) *m/z* calculated for $C_7H_8O_3$: 140.0473, found: 140.0476.

*3.2.15. [5,5-Dimethyl-2-oxo-1,3-dioxolan-(4E)-ylidene]-acetic acid ethyl ester (**14a**)*

Yield: 87%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 5.17 (br s, 1H), 4.26 (d, *J*=6.8 Hz, 2H), 1.69 (s, 6H), 1.35 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 163.1, 149.9, 93.4, 85.5, 60.9, 27.3, 14.2. IR (CCl_4): cm^{-1} 3050, 2984, 1854, 1719, 1694, 1262. Mp (°C): 77–78. MS (CI^+, NH_3): *m/z* 218 (MNH_4^+), 201 (MH^+). HRMS (EI^+): *m/z* calculated for $C_9H_{12}O_5$: 200.0685, found: 200.0688.

*3.2.16. tert-Butyl (E)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl carbonate (**14b**)*

Yield: 62%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.9 (dd, *J*=1.4, 3.4 Hz, 2H), 4.96–4.91 (m, 1H), 4.63 (dd, *J*=1.4, 7.2 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 151.9, 145.6, 97.4, 82.51, 67.4, 59.9, 27.7. IR (CCl_4): cm^{-1} 2980, 1855, 1724, 1391, 1366, 1269, 1167, 1094, 1052. MS (CI^+, NH_3): *m/z* 248 (MNH_4^+), 192. HRMS (EI^+): *m/z* calculated for $C_{10}H_{14}O_6$: 230.0790, found: 230.0795.

*3.2.17. tert-Butyl (E)-2-(5-methyl-2-oxo-1,3-dioxolan-4-ylidene)ethyl carbonate (**14c**)*

Yield: 77%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.26–5.21 (m, 1H), 4.87 (td, *J*=1.9, 7.3 Hz, 1H), 4.63 (dd, *J*=1.2, 7.3 Hz, 2H), 1.53 (d, *J*=6.5 Hz, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 151.2, 151.1, 96.8, 82.5, 76.1, 59.9, 27.6, 20.2. IR (CCl_4): cm^{-1} 3683, 2981, 2933, 1847, 1742, 1271, 1144, 1099, 1029. MS (CI^+, NH_3): *m/z* 262 (MNH_4^+), 218, 206. HRMS (EI^+): *m/z* calculated for $C_{11}H_{14}O_6$: 244.0947, found: 244.0944.

*3.2.18. 4-Methyl-5-methylene-1,3-dioxolan-2-one (**14e**)*

Yield: 60%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.17–5.13 (m, 1H), 4.86 (dd, *J*=2.4, 3.9 Hz, 1H), 4.35 (dd, *J*=2.4, 3.9 Hz, 1H), 2.00–1.74 (m, 2H), 1.04 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 152.1, 86.7, 80.6, 27.7, 7.8. IR (CCl_4): cm^{-1} 2976, 2937, 1843, 1705, 1681, 1334, 1282, 1139, 1091. MS (CI^+, NH_3): *m/z* 146 (MNH_4^+), 139, 117, 102. HRMS (EI^+): *m/z* calculated for $C_6H_8O_3$: 128.0473, found: 128.0478.

*3.2.19. 4-(1-Methyl-allyl)-5-methylene-1,3-dioxolan-2-one (**14f**)*

Yield: 68% (isolated as a mixture of *syn* and *anti* isomers, dr=1:1.6). ^1H NMR (400 MHz, $CDCl_3$) for the mixture of isomers: δ 5.81–5.72 (m, $1H_{minor}$+$1H_{major}$), 5.29–5.10 (m, $3H_{minor}$+$3H_{major}$), 4.95–4.91 (m, $1H_{minor}$+$1H_{major}$), 4.45 (dd, *J*=1.8, 3.9 Hz, $1H_{minor}$), 4.42 (dd, *J*=1.8, 3.9 Hz, $1H_{major}$), 2.72–2.56 (m, $1H_{minor}$+$1H_{major}$), 1.23 (d, *J*=6.9 Hz, $3H_{major}$), 1.15 (d, *J*=7.0 Hz, $3H_{minor}$). ^{13}C NMR (100 MHz, $CDCl_3$) for the *major isomer*: δ 152.1, 151.3, 134.4, 119.1, 87.9, 82.7, 41.4, 14.2; for the *minor isomer*: δ 152.1, 151.4, 136.4, 118.3, 88.0, 82.4, 42.1, 13.5. IR (CCl_4): cm^{-1} 2977, 1845, 1705, 1680, 1332, 1288, 1132, 1055. MS (CI^+, NH_3): *m/z* 172 (MNH_4^+). HRMS (EI^+): *m/z* calculated for $C_8H_{10}O_3$: 154.0630, found: 154.0627.

*3.2.20. 4-Methylene-5-(1-phenyl-ethyl)-1,3-dioxolan-2-one (**14g**)*

Yield: 66% (separable mixture of *syn* and *anti* isomers, dr=1:3.9).

Major isomer: ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 5H), 5.35 (ddd, *J*=2.0, 2.0, 3.8 Hz, 1H), 4.83 (dd, *J*=2.0, 3.8 Hz, 1H), 4.20 (dd, *J*=2.0, 3.8 Hz, 1H), 3.7 (qd, *J*=3.8, 7.2 Hz, 1H), 1.53 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.1, 137.6, 128.7, 128.6, 127.9, 88.4, 83.4, 43.5, 15.4. IR (CCl_4): cm^{-1} 2976, 1844, 1681, 1133, 1047. MS (CI^+, NH_3): *m/z* 222 (MNH_4^+). HRMS (EI^+): *m/z* calculated for $C_{12}H_{12}O_3$: 204.0786, found: 204.0788.

Minor isomer: ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.30 (m, 5H), 5.29 (ddd, *J*=2.1, 2.1, 5.6 Hz, 1H), 4.86 (dd, *J*=2.1, 3.9 Hz, 1H), 4.05 (dd, *J*=2.1, 3.9 Hz, 1H), 3.13 (qd, *J*=5.6, 7.1 Hz, 1H), 1.47 (d, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.8, 139.9, 129.0, 128.9, 127.8, 88.4, 83.4, 44.6, 15.6. IR (CCl_4): cm^{-1} 2978, 1843, 1681, 1131, 1050. MS (CI^+, NH_3): *m/z* 222 (MNH_4^+). HRMS (EI^+): *m/z* calculated for $C_{12}H_{12}O_3$: 204.0786, found: 204.0787.

*3.2.21. 3-Acryloyl-oxazolidin-2-one (**16**)*

Yield: 94%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J*=10.5, 17.0 Hz, 1H), 6.60 (dd, *J*=1.8, 17.0 Hz, 1H), 5.95 (dd, *J*=1.8, 17.0 Hz, 1H), 4.49 (t, *J*=8.0 Hz, 2H), 4.13 (t, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.07 (2C), 153.4, 131.8, 127.0, 62.2, 42.6. IR (CCl_4): cm^{-1} 1791, 1693, 1408, 1382, 1324, 1257, 1220. Mp (°C): 73–74. MS (CI^+, NH_3): *m/z* 159, 142. HRMS (EI^+): *m/z* calculated for $C_7H_7NO_5$: 185.0324, found: 185.0321.

*3.2.22. 4-[1-Bromo-meth-(Z)-ylidene]-1,3-dioxolan-2-one (**30**)*

Yield: 87%. Colorless crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 5.5 (t, *J*=2.1 Hz, 1H), 5.02 (d, *J*=2.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 145.0, 78.9, 67.5. Mp (°C): 100–103. MS (CI^+, NH_3): *m/z* 196 (MNH_4^+), 192, 188, 178, 169, 156. HRMS (EI^+): *m/z* calculated for $C_4H_3BrO_3$: 177.9266, found: 177.9262.

*3.2.23. 4-[1-Bromo-meth-(Z)-ylidene]-5-methyl-1,3-dioxolan-2-one (**32a**)*

Yield: 87%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 5.44 (d, *J*=2.0 Hz, 1H), 5.28 (qd, *J*=2.0, 6.5 Hz, 1H), 1.62 (d, *J*=6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 150.4, 79.0, 76.4, 20.3. IR (CCl_4): cm^{-1} 3098, 2989, 2933, 1857, 1689, 1379, 1325, 1288, 1164, 1140, 1103, 1078, 1035. MS (EI^+): *m/z* 194, 192 (M^+), 150, 148, 120, 122. HRMS (EI^+): *m/z* calculated for $C_5H_5O_3Br$: 191.9422, found: 191.9419.

*3.2.24. 4-[1-Iodo-meth-(Z)-ylidene]-5-methyl-1,3-dioxolan-2-one (**32b**)*

Yield: 95%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 5.38 (d, *J*=1.9 Hz, 1H), 5.29 (qd, *J*=1.9, 6.5 Hz, 1H), 1.61 (d, *J*=6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 150.2, 76.8, 45.8, 20.2. IR (CCl_4): cm^{-1} 3086, 2988, 2933, 2867, 1844, 1675, 1447, 1379, 1324, 1276, 1140, 1103, 1076, 1033. MS (EI^+): *m/z* 240 (M^+). HRMS (EI^+): *m/z* calculated for $C_5H_5O_3I$: 239.9248, found: 239.9280.

*3.2.25. 4-[1-Iodo-meth-(Z)-ylidene]-5-phenethyl-1,3-dioxolan-2-one (**32c**)*

Yield: 99%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J*=7.0 Hz, 2H), 7.25 (t, *J*=7.4 Hz, 1H), 7.20 (d, *J*=6.9 Hz, 2H), 5.35 (d, *J*=1.9 Hz, 1H), 5.15 (td, *J*=1.8, 5.9 Hz, 1H), 2.94–2.78 (m, 2H), 2.22–2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 150.3, 139.1, 128.7, 128.3, 126.6, 79.3, 45.9, 36.3, 30.1. IR (CCl_4): cm^{-1} 3085, 3028, 2973, 2930, 2863, 1849, 1674, 1601, 1497, 1451, 1341, 1279, 1145, 1110, 1081, 1034. MS (EI^+): *m/z* 330 (M^+), 285, 267, 203. HRMS (EI^+): *m/z* calculated for $C_{12}H_{11}O_3I$: 329.9753, found: 329.9748.

*3.2.26. 4-(2,6-Dimethyl-hept-5-enyl)-5-methylene-1,3-dioxolan-2-one (**32d**)*

Yield: 97%. Pink oil (isolated as a 1:1 mixture of diastereoisomers). ^1H NMR (400 MHz, $CDCl_3$) for the mixture of diastereoisomers: δ 5.38 (d, *J*=1.9 Hz, 1H), 5.28–5.23 (m, 1H), 5.13–5.09 (m, 1H), 2.13–1.92 (m, 3H), 1.85–1.17 (m, 4H), 1.74 (s, 3H), 1.65 (s, 3H), 1.06–1.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) for the

mixture of diastereoisomers: δ 154.4, 154.3, 150.3, 131.9, 123.8, 123.8, 79.2, 78.8, 45.7, 45.5, 42.2, 37.0, 36.1, 29.0, 28.5, 25.6, 25.1, 25.0, 19.7, 18.7, 17.6, 17.6. IR (CCl_4): cm^{-1} 3086, 2961, 2925, 2856, 1853, 1674, 1455, 1377, 1338, 1279, 1143, 1079. MS (EI^+): *m*/*z* 350 (M^+), 319, 264, 237, 223. HRMS (EI^+): *m*/*z* calculated for $C_{13}H_{19}O_3I$: 350.0379, found: 350.0388.

*3.2.27. 4-[1-Iodo-meth-(Z)-ylidene]-5-(4-triisopropyl silanyloxy-butyl)-1,3-dioxolan-2-one (**32e**)*

Yield: 69%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (d, *J*=1.8 Hz, 1H), 5.21–5.17 (m, 1H), 3.71 (t, *J*=5.5 Hz, 2H), 1.97–1.81 (m, 2H), 1.67–1.48 (m, 4H), 1.15–0.94 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 150.4, 80.4, 62.6, 45.6, 34.4, 32.0, 20.5, 17.9, 11.9. IR (CCl_4): cm^{-1} 3086, 2945, 2894, 2865, 1853, 1674, 1463, 1383, 1339, 1280, 1141, 1110, 1068, 1014. MS (EI^+): *m*/*z* 454 (M^+), 411, 368, 337. HRMS (EI^+): *m*/*z* calculated for $C_{17}H_{31}O_4SiI$: 454.1037, found: 454.1041.

*3.2.28. 4-Cyclopropyl-5-[1-iodo-meth-(Z)-ylidene]-1,3-dioxolan-2-one (**32f**)*

Yield: 32%. Orange oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (d, *J*=1.8 Hz, 1H), 4.53 (dd, *J*=1.7, 8.7 Hz, 1H), 1.28–1.21 (m, 1H), 0.84–0.76 (m, 2H), 0.64–0.55 (m, 1H), 0.55–0.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 150.2, 84.8, 46.7, 14.2, 3.0, 2.5. IR (CCl_4): cm^{-1} 3089, 3012, 2926, 2855, 1855, 1674, 1320, 1274, 1142, 1107, 1037. MS (EI^+): *m*/*z* 266 (M^+), 222, 205, 192, 180. HRMS (EI^+): *m*/*z* calculated for $C_7H_7O_3I$: 265.9440, found: 265.9447.

*3.2.29. 4-[1-Iodo-meth-(Z)-ylidene]-1,3-dioxa-spiro[4.5]decan-2-one (**32g**)*

Yield: 83%. White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 5.34 (s, 1H), 2.06 (br d, *J*=9.2 Hz, 2H), 1.82–1.64 (m, 7H), 1.41–1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 149.8, 87.5, 45.3, 36.5, 24.2, 21.6. IR (CCl_4): cm^{-1} 2943, 1846, 1668, 1192, 1048. Mp (°C): 133–134. MS (CI^+, NH_3): *m*/*z* 312 (MNH_4^+). HRMS (EI+): *m*/*z* calculated for $C_9H_{11}IO_3$: 293.9753, found: 293.9751.

3.3. Au(I)-catalyzed formation of (*E*)-iodo-alkylidene-1,3-dioxolan-2-ones

General procedure: To a solution of propargylic *tert*-butyl carbonate (1 equiv) in acetone (0.5 M) at room temperature were added *N*-iodosuccinimide (1.2 equiv) and the gold catalyst (0.01 equiv). The mixture was stirred at room temperature and monitored periodically by TLC. Upon completion, the mixture was evaporated and then chromatographed with the appropriate mixture of petroleum ether and diethyl ether to give the expected product.

*3.3.1. 4-[1-Iodo-meth-(E)-ylidene]-1,3-dioxa-spiro[4.5]decan-2-one (**34**)*

Yield: 95%. ^1H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 1H), 2.49 (td, *J*=4.6, 13.9 Hz, 2H), 1.95 (br d, *J*=13.9 Hz, 2H), 1.83–1.66 (m, 5H), 1.44–1.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 150.1, 88.2, 47.6, 32.6, 24.2, 21.4. IR (CCl_4): cm^{-1} 2944, 2864, 1841, 1658, 1264, 1204, 1128, 1057. Mp (°C): 135–136. MS (CI^+, NH_3): *m*/*z* 312 (MNH_4^+). HRMS (EI^+): *m*/*z* calculated for $C_9H_{11}IO_3$: 293.9753, found: 293.9753.

*3.3.2. 4-[1-Iodo-meth-(E)-ylidene]-5-methyl-1,3-dioxolan-2-one (**36a**)*

Yield: 35%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.91 (d, *J*=2.2 Hz, 1H), 5.26 (qd, *J*=2.2, 6.5 Hz, 1H), 1.73 (d, *J*=6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 151.1, 78.0, 50.1, 18.4. IR (CCl_4): cm^{-1} 3085, 2988, 2933, 2866, 1841, 1673, 1450, 1376, 1318, 1279, 1139, 1119, 1073, 1035. MS (EI^+): *m*/*z* 240 (M^+), 196. HRMS (EI^+): *m*/*z* calculated for $C_5H_5O_3I$: 239.9248, found: 239.9272.

*3.3.3. 4-[1-Iodo-meth-(E)-ylidene]-5-phenethyl-1,3-dioxolan-2-one (**36b**)*

Yield: 66%. Pink oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.27–7.24 (m, 3H), 5.93 (d, *J*=2.2 Hz, 1H), 5.16 (dt, *J*=2.3, 8.3 Hz, 1H), 2.91–2.84 (m, 1H), 2.80–2.73 (m, 1H), 2.57–2.49 (m, 1H), 2.30–2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 150.0, 139.2, 128.6, 128.4, 126.5, 80.5, 50.6, 33.2, 29.9. IR (CCl_4): cm^{-1} 3085, 3029, 2954, 2927, 2859, 1843, 1670, 1498, 1453, 1332, 1281, 1144, 1103, 1077, 1035, 1004. MS (EI^+): *m*/*z* 330 (M^+), 285, 220, 205. HRMS (EI^+): *m*/*z* calculated for $C_{12}H_{11}O_3I$: 329.9753, found: 329.9753.

*3.3.4. 4-[1-Iodo-meth-(E)-ylidene]-5-(4-triisopropyl silanyloxy-butyl)-1,3-dioxolan-2-one (**36c**)*

Yield: 64%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.91 (d, *J*=2.2 Hz, 1H), 5.20 (dt, *J*=2.5, 7.5 Hz, 1H), 3.71 (t, *J*=5.9 Hz, 2H), 2.23–2.14 (m, 1H), 2.04–1.94 (m, 1H), 1.67–1.52 (m, 4H), 1.12–1.02 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 150.4, 81.5, 62.6, 50.3, 32.1, 31.5, 20.1, 18.0, 11.9. IR (CCl_4): cm^{-1} 3311, 3085, 2961, 2865, 2727, 2238, 1858, 1744, 1670, 1462, 1383, 1333, 1277, 1254, 1118, 1017. MS (EI^+): *m*/*z* 454 (M^+), 411, 368, 337, 325. HRMS (EI^+): *m*/*z* calculated for $C_{17}H_{31}O_4SiI$: 454.1037, found: 454.1036.

*3.3.5. 4-Cyclopropyl-5-[1-iodo-meth-(E)-ylidene]-1,3-dioxolan-2-one (**36d**)*

Yield: 76%. Pink oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, *J*=2.1 Hz, 1H), 4.83 (dd, *J*=2.0, 7.1 Hz, 1H), 1.41–1.29 (m, 1H), 0.91–0.78 (m, 2H), 0.76–0.68 (m, 1H), 0.61–0.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 150.9, 83.8, 51.1, 13.1, 5.7, 2.4. IR (CCl_4): cm^{-1} 3085, 3015, 2927, 2856, 1839, 1670, 1311, 1270, 1139, 1103, 1031, 1020. MS (EI^+): *m*/*z* 266 (M^+), 222, 207, 192. HRMS (EI^+): *m*/*z* calculated for $C_7H_7O_3I$: 265.9440, found: 265.9434.

3.4. Pd-catalyzed transformations of iodo-alkylidene-1,3-dioxolan-2-ones

General procedure for the Sonogashira coupling: To a solution of halogenated derivative (1 equiv) in THF (0.25 M) were added the corresponding terminal alkyne (2 equiv), $PdCl_2(PPh_3)_2$ (0.2 equiv), CuI (0.04 equiv), and NEt_3 (10 equiv). The mixture was stirred at room temperature and monitored periodically by TLC. Upon completion, it was quenched with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The crude mixture was then loaded onto a silica gel column and chromatographed with the appropriate mixture of petroleum ether and diethyl ether to give the expected product.

*3.4.1. 4-[3-Phenyl-prop-2-yn-(Z)-ylidene]-1,3-dioxa-spiro[4.5]decan-2-one (**37**)*

Yield: 61%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.44 (m, 2H), 7.35–7.32 (m, 3H), 5.01 (s, 1H), 2.06 (d, *J*=12.3 Hz, 2H), 1.80–1.58 (m, 7H), 1.38–1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 150.5, 131.4, 128.5, 128.3, 122.7, 95.5, 86.9, 83.0, 80.5, 36.4, 24.2, 21.5. IR (CCl_4): cm^{-1} 3056, 2943, 2863, 1844, 1679, 1492, 1447, 1346, 1260, 1191, 1126, 1052, 1007. MS (EI^+): *m*/*z* 268 (M^+), 196, 167, 149. HRMS (EI^+): *m*/*z* calculated for $C_{17}H_{16}O_3$: 268.1100, found: 268.1097.

*3.4.2. 4-[3-Phenyl-prop-2-yn-(E)-ylidene]-1,3-dioxa-spiro[4.5]decan-2-one (**38**)*

Yield: 94%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.37 (m, 2H), 7.41–7.36 (m, 3H), 5.86 (s, 1H), 2.42 (td, *J*=3.5, 14.1 Hz, 2H), 2.01 (d, *J*=13.9 Hz, 2H), 1.86–1.65 (m, 5H), 1.38–1.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 150.4, 130.8, 128.5, 128.4, 122.6, 95.6, 88.0, 84.5, 81.3, 33.3, 24.5, 21.4. IR (CCl_4): cm^{-1} 3060, 2942,

2860, 1842, 1670, 1492, 1446, 1352, 1264, 1213, 1177, 1126, 1072, 995. MS (EI^+): *m*/*z* 268 (M^+), 224, 196, 167. HRMS (EI^+): *m*/*z* calculated for $C_{17}H_{16}O_3$: 268.1100, found: 268.1112.

*3.4.3. 4-Methyl-5-oct-2-yn-(Z)-ylidene-1,3-dioxolan-2-one (**39a**)*

Yield: 67%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.30 (q, *J*=6.5 Hz, 1H), 4.82 (q, *J*=2.2 Hz, 1H), 2.35 (td, *J*=2.2, 7.1 Hz, 2H), 1.58 (d, *J*=6.5 Hz, 3H), 1.58–1.51 (m, 2H), 1.41–1.26 (m, 4H), 0.91 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 151.2, 97.4, 84.5, 76.3, 71.2, 31.0, 28.1, 22.1, 20.4, 19.5, 13.9. IR (CCl_4): cm^{-1} 2932, 2863, 2222, 1853, 1690, 1457, 1375, 1355, 1330, 1307, 1214, 1140, 1103, 1078, 1031. MS (EI^+): *m*/*z* 208 (M^+), 161, 149, 121, 117, 107. HRMS (EI^+): *m*/*z* calculated for $C_{12}H_{16}O_3$: 208.1100, found: 208.1104.

*3.4.4. 4-Methyl-5-[3-phenyl-prop-2-yn-(Z)-ylidene]-1,3-dioxolan-2-one (**39b**)*

Yield: 72%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.35–7.30 (m, 3H), 5.37 (qd, *J*=2.0, 6.5 Hz, 1H), 5.07 (d, *J*=2.0 Hz, 1H), 1.63 (d, *J*=6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 151.0, 131.5, 128.3, 122.6, 95.6, 84.1, 80.1, 76.5, 20.3. IR (CCl_4): cm^{-1} 3059, 2983, 2959, 2928, 2865, 1851, 1687, 1306, 1206, 1138, 1102, 1081, 1041. MS (EI^+): *m*/*z* 214 (M^+), 142, 141, 115. HRMS (EI^+): *m*/*z* calculated for $C_{13}H_{10}O_3$: 214.0630, found: 214.0623.

*3.4.5. 4-Methyl-5-[6-triisopropylsilanyloxy-hex-2-yn-(Z)-ylidene]-1,3-dioxolan-2-one (**39c**)*

Yield: 67%. Brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.30 (q, *J*=6.4 Hz, 1H), 4.81 (q, *J*=2.1 Hz, 1H), 3.78 (t, *J*=6.0 Hz, 2H), 2.48 (td, *J*=1.9, 7.0 Hz, 2H), 1.80–1.74 (m, 2H), 1.57 (d, *J*=6.5 Hz, 3H), 1.12–1.00 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 151.1, 97.0, 84.4, 76.3, 71.3, 61.7, 31.7, 20.4, 17.9, 17.6, 16.0, 12.2, 11.9. IR (CCl_4): cm^{-1} 2944, 2894, 2865, 1847, 1691, 1463, 1307, 1213, 1138, 1105, 1078, 1031. MS (EI^+): *m*/*z* 352 (M^+), 309, 265, 237, 223. HRMS (EI^+): *m*/*z* calculated for $C_{19}H_{32}O_4Si$: 352.2070, found: 352.2071.

General procedure for the Suzuki coupling: To a solution of halogenated derivative (1 equiv) in toluene (0.5 M) was added K_2CO_3 powder (2.5 equiv), phenylboronic acid (1.1 equiv), and tetrakis(triphenylphosphine)palladium(0) (0.05 equiv). The mixture was stirred at 80 °C and monitored periodically by TLC. Upon completion, it was quenched with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The crude mixture was then loaded onto a silica gel column and chromatographed with the appropriate mixture of petroleum ether and diethyl ether to give the expected product.

*3.4.6. 4-[1-Phenyl-meth-(E)-ylidene]-1,3-dioxa-spiro[4.5]decan-2-one (**40**)*

Yield: 79%. Yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 3H), 7.22 (d, *J*=7.2 Hz, 2H), 6.45 (s, 1H), 1.98–1.93 (m, 2H), 1.80–1.59 (m, 7H), 1.05–0.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.3, 132.0, 129.3, 128.3, 127.7, 105.4, 87.2, 35.2, 24.2, 21.3. IR (CCl_4): cm^{-1} 3060, 3027, 2941, 2861, 1826, 1694, 1448, 1350, 1267, 1214, 1157, 1130, 1056, 1002. MS (EI^+): *m*/*z* 244 (M^+), 200, 185. HRMS (EI^+): *m*/*z* calculated for $C_{15}H_{16}O_3$: 244.1100, found: 244.1096.

*3.4.7. 4-[1-Phenyl-meth-(E)-ylidene]-5-(4-triisopropylsilanyloxy-butyl)-1,3-dioxolan-2-one (**41**)*

Yield: 40%. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J*=7.7 Hz, 2H), 7.27 (t, *J*=8.0 Hz, 1H), 7.15 (d, *J*=7.3 Hz, 2H), 6.37 (d, *J*=2.2 Hz, 1H), 5.70 (dt, *J*=2.6, 7.6 Hz, 1H), 3.61 (t, *J*=5.7 Hz, 2H), 1.91–1.83 (m, 1H), 1.72–1.62 (m, 1H), 1.57–1.43 (m, 4H), 1.11–0.99 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 147.6, 132.2, 128.9, 127.8, 127.5, 105.6, 79.8, 62.6, 32.0, 31.6, 20.4, 17.9, 11.9. IR (CCl_4): cm^{-1} 3062, 3028, 2945, 2893, 2865, 1838, 1691, 1462, 1381, 1344, 1225, 1179, 1123, 1070, 1018. MS (EI^+): *m*/*z* 404 (M^+), 359, 331. HRMS (EI^+): *m*/*z* calculated for $C_{23}H_{36}O_4Si$: 404.2383, found: 404.2365.

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