Gold-catalyzed domino processes constitute a useful alternative to C-H functionalization for the synthesis of functionalized (hetero)arenes. Herein, we report computational studies on the gold-catalyzed cyclization alkylation of keto-allenes with ethynylenbenziodoxole (EBX) reagents, which identified a gold(I) picolinate complex as the active catalyst, giving first mechanistic insights into this transformation.

Alkynyl substituted heterocycles are interesting building blocks for synthetic chemistry, due to the preponderance of heterocycles in drugs, agrochemicals and organic materials, as well as the multiple transformations available for the functionalization of the alkyne group. These compounds are usually accessed using the Sonogashira cross coupling reaction, but this transformation is based on the availability of the corresponding aryl halides. In order to develop more efficient synthetic methods, direct C-H alkylation reactions have been introduced in the last decades. Nevertheless, these approaches are usually based on the use of directing groups, or are limited to the most reactive position of heterocycles. In order to increase the flexibility and efficiency for the synthesis of alkynylated heterocycles, Waser and co-workers turned to the use of domino cyclization-alkynylation reactions. This approach gave access to alkynylated heterocycles, which could not be synthesized via C-H functionalization. In particular, the gold(III)-catalyzed cyclization-alkynylation of keto allenes using EthynylBenziodoXole (EBX) reagent 1b gave access to C3-alkynylated poly-substituted furans, whereas C2-alkynylated furans were obtained via C-H alkylation with TIPS-EBX (1a) and a gold (I) catalyst (Scheme 1). The use of gold(III) dichloride picolinate catalyst 2 was crucial for success, as well as the use of bistrifluoromethyl benziodoxole 1b. As the reaction mechanism was not known, it was very difficult to rationalize the differences between the two catalytic processes.

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** C-H vs domino cyclization-alkynylation: two different active catalysts?

Herein, we report computational studies on the domino cyclization-alkynylation reaction, which indicated that an in situ formed gold(I) complex is in fact the active catalyst. The picolinate ligand was found to significantly diminish the activation energy for the oxidative addition of EBX reagents on a gold(I) intermediate. These first insights into the reaction mechanism will be useful for the development of domino processes using gold catalysts and EBX reagents.

As no gold complex relevant to the catalytic cycle could be isolated, proposing a mechanism for the domino alkylation process was especially challenging. Based on the work of Hashmi and co-workers on the gold-catalyzed cyclization of...
allenes, activation of the \( \pi \) system of allene 3 by the gold catalyst (I) followed by cyclization to give aurated furan II can be reasonably expected (Scheme 2). At this point, alkynylation with EBX 1c would close the catalytic cycle. The alkynylation step was particularly intriguing, as the superiority of Au(III) catalyst 2 seemed to exclude a redox mediated process. We initially hypothesized an activation of the triple bond of 1c by the gold catalyst, followed by insertion, \( \alpha \)-elimination and 1,2-silyl shift to give the observed product. Ariafard showed later by computation that an iodine to gold alkyne exchange was possible on gold(I) complexes. If this transformation can also be achieved for gold(III) intermediates, other mechanisms would need to be considered for the alkynylation step.

In order to investigate this possibility, we setup to perform computation using B3LYP-D3-PCM/def2-QZVP:6-311+G(2d,p)//B3LYP-PCM/LANL2DZ:6-31G(d) calculations in iPrOH. An energetically accessible cyclization pathway was identified for the reaction of complex 2 with allene 3 in presence of sodium bicarbonate to give organogold intermediate 9 (Fig. 1). This process involved ligand exchange to give allene complex 6, cyclization via transition state TS6-7 and deprotonation. The energy barriers for ligand exchange and cyclization were higher (27.6 and 27.0 kcal/mol respectively) than for deprotonation. The more challenging alkynylation step was investigated next (Fig. 2). Ligand exchange between chloride and EBX reagent 1c via associative transition state TS9-10 required only 17.4 kcal/mol and gave \( \pi \) bond alkyne complex 10. As observed previously on gold(I) intermediates, alkyne shift from iodine to gold was easy, with a barrier of only 2.8 kcal/mol, and led to the formation of the more stable gold alkynyl complex 11. However, in contrast to related gold(I) and palladium(II) complexes, the favoured reaction pathway for 11 was not 1,2-aryl shift, but reductive elimination on gold via low lying three-atom transition state TS11-12 to give gold(I) complex 12 and iodonium bound alkyne 13. This result was unexpected, and did not allow to close the catalytic cycle, as a stoichiometric amount of gold(III) complex would be needed.

**Scheme 2** Working model for the reaction mechanism with methyl allene 3 and reagent 1c.

**Fig. 1** Gibbs energy profile for the cyclization of allene 3 mediated by gold(III) complex 2.
We wondered if complex 12 could also be a competent catalyst. In fact, 12 was efficient to promote the cyclization of allene 3 to organogold(I) furan complex 18 (Gibbs energy barriers for ligand exchange, cyclization and deprotonation of 5.9, 17.0 and 1.9 kcal/mol respectively, Fig. 3). The reaction of 18 with reagent 1c was then examined (Fig. 4). After a reorientation of the picolinic acid ligand to give complex 19, an oxidative addition transition state TS$_{19-20}$ was observed, with an energy of only 21.7 kcal/mol. The formed gold(III) complex 20 can then undergo reductive elimination via three-atom transition state TS$_{20-22}$ (15.8 kcal/mol) to give the gold $\pi$-complex 22 of the product 4, which is in equilibrium with linear complex 23. Importantly, complex 18 needs to rearrange to 19 for accessing transition state TS$_{19-20}$ in which the nitrogen atom of the picolinate ligand is capable of interacting with the gold centre. When the nitrogen atom was not involved in the transition state, the energy was found to be 6.9 kcal/mol higher (Fig. 5, TS''$_{19-20}$).
The transition states $\text{TS}^{\text{III}}_{11-12}$ bearing a carbonate ligand or $\text{TS}^{\text{IV}}_{11-12}$ with no extra ligand were also higher in energy. This result is in accordance with the importance of the picolinic acid ligand observed experimentally.

In retrospect, it appears surprising that gold(I) catalysts had been found inactive in our original work.\textsuperscript{46} However, preliminary catalyst screening experiments were performed with another hypervalent iodine reagent (TIPS-EBX (1a)), which was less efficient in this process. We decided therefore to re-investigated the reaction of phenyl-allene ketone 24 in presence of a gold(I) catalyst, but with EBX reagent 1b. When Au(I)Cl was used as catalyst with picolinic acid (25) as additive, the cyclization alkylation product 26 was obtained in yield and reaction time comparable to those with gold(III) complex 2 (Scheme 3). When 25 was omitted, 26 could be obtained only in moderate yield.

Based on the computational results and this experimental confirmation, a refined mechanism can be proposed (Scheme 4). In an initiation step, allene 3 and EBX 1c react with gold complex 2 to give gold(I) complex 12 and iodonium 13. The former then reacts with allene 3 to initiate a gold (I/III) catalytic cycle via complex 15. Cyclization followed by deprotonation gives then organogold intermediate 18. Oxidative addition proceeds via key transition state $\text{TS}^{19-20}$, for which the picolinic acid ligand plays an essential role in lowering the energy. The resulting gold(III) complex 20 then undergoes reductive elimination to give $\pi$-complex 23. Ligand exchange with allene 3 via a three coordinate intermediate (27) lying 9.6 kcal/mol above 23 closes the catalytic cycle.
In summary, we have performed computational studies of the gold-catalyzed cyclization-alkynylation domino process of ketoallenes. Our results showed that the used gold(III) complex was a precursor of an active gold(I) catalyst, and that the picolinic acid ligand was essential for lowering the energy of the key oxidative addition transition state. These mechanism insights will be highly useful for developing new transformations based on gold catalysis and hypervalent iodine reagents.

Computational Details

Gaussian 09 was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory (DFT) in iPrOH using the CPCM solvation model. The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Au and I. The 6-31G(d) basis set was used for other atoms. Polarization functions were also added for Au ($\xi_f = 1.050$) and I ($\xi_f = 0.289$). This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single-point energy calculations by employing the D3 empirical dispersion correction for all of the structures with a larger basis set (BS2) in iPrOH using the CPCM solvation model. BS2 utilizes the quadruple-ξ valence def2-QZVP basis set on Au and I and 6-311+G(2d,p) basis set for other atoms. The relative Gibbs free energies obtained from the B3LYP-D3-PCM/def2-QZVP:6-311+G(2d,p)//B3LYP-PCM/LANL2DZ:6-31(G) calculations are adjusted by the method proposed by Okuno and finally used for interpretation.

Acknowledgments

We thank the Swiss National Science Foundation (Grant No. 200021_159920) for financial support.

Notes and references

5. Selected examples of domino cyclization-alkynylation reactions for the synthesis of alkynylated heterocycles: (a) A. Arcadi, S. Cacchi, G. Fabrizi, F. Marinelli and L. M. Parisi,
Journal Name

8 To simplify computations, the mechanism was studied with smaller allene ketone 3 and trimethylsilyl EBX reagent 1c.
9 (a) A. Ariafard, ACS Catalysis, 2014, 4, 2896. (b) A. Ariafard Organometallics 2014, 33, 7318.
10 See computational details. For Cartesian coordinates see table S1 in the ESI.
**Graphical Abstract:**

New insights into the mechanism of gold-catalyzed domino reactions with hypervalent iodine reagents revealed by computation and confirmed by experiments.
# Supporting Information

## Table of content

1. Cartesian coordinates (Table S1)  
2. General synthetic methods  
3. Domino cyclization-alkynylation reaction

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<td>3. Domino cyclization-alkynylation reaction</td>
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1. Cartesian coordinates (Table S1)

Table S1. Cartesian coordinates and energies for all of the calculated structures.

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E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.151007 au

E (B3LYP/BS1) = -2350.085874 au
H (B3LYP/BS1) = -2349.845699 au
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G (B3LYP/BS1) = -2349.941575 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2350.873543 au

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G (B3LYP/BS1) = -2816.676625 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.563024 au

1  -1.98041900 -0.18309800 -1.07952000
C  -2.76135100 -0.13988300 0.90892900
O  -3.82219100 0.84227600 -1.39330700
C  -4.67830100 0.94054700 -0.31062600
C  -4.02666500 0.43089800 0.98411600
C  -4.62771800 0.48822100 2.24996300
C  -2.06930700 -0.64018700 2.00011600
C  -3.96006000 -0.00425900 3.37153800
H  -5.61421100 0.92002100 2.35868600
C  -2.68739400 -0.56378100 3.25125100
H  -1.07947300  -1.06840200  1.89918800
H  -4.43965900  0.05153100  4.34354200
H  -2.16559300  -0.94310300  4.12414400
C  -0.21297600  -1.29316400  0.02061500
C  0.61743900  -2.22859400  -0.50149400
Si  1.59341500  -3.85099900  -0.73196100
C  3.21414200  -3.71679900  -0.20894300
C  3.79847900  -2.84870900  -0.11437200
C  0.45216700  -5.17992700  -0.04090100
H  -0.50938700  -5.19543200  -0.56520300
H  0.92303500  -6.16232000  -0.16896500
C  0.26171000  -5.03283700  1.02759900
C  1.85420600  -4.00956100  -2.58735900
H  2.39861800  -3.14673200  -2.98458900
H  2.43779500  -4.91392800  -2.79865600
H  0.89995500  -4.08853300  -3.11931500
Au  1.76342100  -0.18388800  -0.37941900
Cl  1.66935200  0.00142000  -2.85364000
C  1.83293800  -0.22888500  1.64054200
C  2.20611500  0.83955700  2.39899900
C  1.71131900  -0.78840700  3.81105000
C  2.54096400  1.83715500  2.16870100
O  2.13156500  0.51400500  3.72421000
C  1.57013800  -1.36021900  5.17846700
C  2.52532600  -1.34551500  5.71737200
C  0.84462200  -0.79481000  5.77575000
C  1.22893200  -2.39658000  5.11390000
C  1.51137900  -1.29023400  2.55715200
H  1.17653000  -2.29027300  2.32771000
C  -5.04296000  2.44662200  -0.17625300
C  -5.93831400  0.08903200  -0.63756400
F  -6.51962800  0.49140900  -1.77945100
F  -5.49737200  2.94362700  -1.33709600
F  -5.99304400  2.67224500  0.75850700
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N  6.71399900  1.59169900  -0.34927300
H  5.76439400  5.35606200  -0.13009800
H  3.99023700  3.58439700  -0.18274000
H  8.17329200  4.63653000  -0.22320800
H  8.68423100  2.20024700  -0.36276100
O  3.16520500  1.31283500  -0.31752900

S12
C  4.40579700  0.86443800  -0.33044600
O  4.72285200  -0.31876800  -0.36784000

TS_{10-11}
E (B3LYP/BS1) = -2817.013651 au
H (B3LYP/BS1) = -2816.544655 au
G (B3LYP/BS1) = -2816.675679 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.558952 au

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O  -3.60982000  -0.67736600  1.14013300
C  -4.22954100  -1.12165880  0.02115500
C  -3.52929200  -0.80928600  -1.28124200
C  -3.96895200  -1.17438800  -2.56119800
C  -1.64883500  0.38910200  -2.30370600
C  -3.26390200  -0.76455000  -3.69315100
H  -4.86056600  -1.77799800  -2.67153200
C  -2.11085200  0.01054700  -3.56807500
H  -0.74678800  0.98147800  -2.20435600
H  -3.61950800  -1.05634000  -4.67613900
H  -1.56002600  0.32664000  -4.44831500
C  -0.01374700  1.58402000  0.13439500
C  0.18245800  2.82211000  0.06842200
Si  0.51114000  4.68230000  -0.05741400
C  0.10064000  5.20312600  -1.81533800
H  -0.95472200  5.02349500  -2.04738300
H  0.29719200  6.27489500  -1.93963900
H  0.71195500  4.65820700  -2.54230400
C  -0.62666100  5.45981500  1.22653700
H  -0.39215400  5.10577000  2.23573300
H  -0.49310400  6.54836600  1.20641000
H  -1.67980100  5.24513800  1.01726000
C  2.33581100  4.87344700  0.36778800
H  2.97075100  4.33689100  -0.34484600
H  2.60172700  5.93682500  0.32937200
H  2.55194100  4.50270000  1.37519600
Au  1.82833300  0.61543900  -0.12395000
Cl  2.00639900  1.25791500  -2.51561700
C  1.75293400  0.11615900  1.82960700
C  1.60236700  0.97087400  2.87956000
C  1.80546800  -1.05749900  3.73844400
H  1.47125400  2.03739700  2.96729500
O  1.63719900  0.26856400  4.05305100
C  1.86608400  -2.01354200  4.87845900
H  2.70199900  -1.78288900  5.55015500
H  0.94556800  -1.98573700  5.47432400
H  1.99979100  -3.03082200  4.50168900
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**III**

\[ E \text{(B3LYP/BS1)} = -2817.027374 \, \text{au} \]

\[ H \text{(B3LYP/BS1)} = -2816.556838 \, \text{au} \]

\[ G \text{(B3LYP/BS1)} = -2816.687601 \, \text{au} \]

\[ E \text{(B3LYP-D3/BS2// B3LYP/BS1)} = -3104.573796 \, \text{au} \]
TS11-12
E (B3LYP/BS1) = -2817.016007 au
H (B3LYP/BS1) = -2816.547017 au
G (B3LYP/BS1) = -2816.677551 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.562761 au
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12

E (B3LYP/BS1) = -1032.137413 au
H (B3LYP/BS1) = -1032.032244 au
G (B3LYP/BS1) = -1032.084622 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1032.658932 au

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13

E (B3LYP/BS1) = -1784.940995 au
H (B3LYP/BS1) = -1784.576486 au
G (B3LYP/BS1) = -1784.675262 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2071.940733 au

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G (B3LYP/BS1) = -840.924859 au
E (B3LYP-D3/BS2//B3LYP/BS1) = -841.646072 au
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E (B3LYP-D3/BS2//B3LYP/BS1) = -841.633567 au

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G (B3LYP/BS1) = -840.952952 au
E (B3LYP-D3/BS2//B3LYP/BS1) = -841.666961 au

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\[
G_{\text{B3LYP/BS1}} = -1429.548175 \text{ au}
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\[
E_{\text{B3LYP-D3/BS2// B3LYP/BS1}} = -1430.389768 \text{ au}
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H  7.97907000  0.55822300  0.13031200
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H (B3LYP/BS1) = -1429.461047 au
G (B3LYP/BS1) = -1429.544651 au
E (B3LYP-D3/BS2//B3LYP/BS1) = -1430.385191 au

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C  -2.73134500  -2.20926800  0.48908100
C  -2.74518700  -0.36795500  -0.82782200
C  -4.04357200  -1.85748300  0.19846700
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H  -2.61218700  0.74248500  -0.17336400
H  -2.60610800  -0.05648700  -1.86315800
H  -2.44556100  -3.02730500  1.13635900
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H  -5.84684600  -1.70868500  1.32909200
H  -6.00007600  -2.62837500  -0.17370100
O  -2.45380500  1.90487600  0.48146300
C  -2.55941100  2.96505700  -0.39206800
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O  -3.72843700  3.39251400  -0.63985100
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Na  -4.71357000  2.22494300  1.02046100
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C  4.94655700  -0.84443700  -0.06464500
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C  6.93121300  0.48682200  0.14024500
C  6.09800300  1.59187400  0.33707100
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O  2.02644100  1.31335200  0.33242300

18
E (B3LYP/BS1) = -840.638155 au
H (B3LYP/BS1) = -840.441873 au
G (B3LYP/BS1) = -840.507465 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.214661 au

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G (B3LYP/BS1) = -840.496513 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.207920 au

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TS^{II}_{19-20}

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H (B3LYP/BS1) = -2356.479282 au
G (B3LYP/BS1) = -2356.610527 au
E (B3LYP-D3/BS2//B3LYP/BS1) = -2644.450105 au

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\end{align*}
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\text{TS}^{\text{III}}_{19-20}
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\text{E (B3LYP/BS1)} & = -2969.505893 \text{ au} \\
\text{H (B3LYP/BS1)} & = -2969.11398 \text{ au} \\
\text{G (B3LYP/BS1)} & = -2969.248058 \text{ au} \\
\text{E (B3LYP-D3/BS2// B3LYP/BS1)} & = -3257.024144 \text{ au} \\
\end{align*}

\begin{align*}
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**TS^IV_{19-20}**

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E (B3LYP-D3/BS2//B3LYP/BS1) = -2668.299476 au
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20

E (B3LYP/BS1) = -1325.899941 au
H (B3LYP/BS1) = -1325.569479 au
G (B3LYP/BS1) = -1325.65583 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.591313 au

C      -1.55800000  -0.46366500   0.00589100
C       -2.77421300  -0.60801600  -0.00636800
Si     -4.60455000  -0.85025000  -0.02542400
C      -5.37788600   0.30909400  1.25207300
H      -5.15622000   1.35843900  1.02549900
H      -6.46864800   0.19124500  1.26479500
H      -5.00577900   0.09541200  2.26083000
C      -5.24467400  -0.44148200 -1.75673700
H      -4.79731800  -1.09737900 -2.51256800
H      -6.33371100   0.56961000 -1.80286200
H      -5.01688900   0.59499700 -2.03139400
C     -4.98531700  -2.64939900  0.41028600
H     -4.61082800  -2.90477300  1.40842300
H      -6.06842300  -2.82408500  0.40318800
H     -4.52891700  -3.33987000 -0.30838900
Au     0.39013100  -0.28718100  0.02371000
C      3.04787200  -1.49945500 -0.05200100
C      4.42538400  -1.68273800 -0.05046500
C      5.25801200  -0.56747200  0.04265800
C      4.68554100   0.70160600  0.13169100
C      3.29865600   0.81901400  0.12657900
N      2.50814200  -0.26301500  0.03603000
H      6.33672400  -0.68607500  0.04562700
H      4.81136600  -2.69244700 -0.12212500
H      5.29644300   1.59407400  0.20486300
H      2.79825100   1.77756000  0.19177700
O      0.81848300  -2.36835700 -0.14457200
C      2.08618600  -2.67134500 -0.15223700
O      2.53502900  -3.81089000 -0.23391600
C      0.11114300  1.69348400  0.16814300
C      0.23346600  2.65256700 -0.89876300
C     -0.14660500  2.40660700  1.29842800
C      0.05588400  3.88344000 -0.33543400
O     -0.17582100  3.74494300  1.00906400
H      0.43311900  2.45078500 -1.94173800
C      0.06667100  5.27062500 -0.87711700
H      0.25646600  5.24593300 -1.95338100
H     -0.89342400  5.77390100 -0.70927700
H      0.84623800  5.88068000 -0.40462100
H     -0.32669500  2.14038900  2.32801400

21
E (B3LYP/BS1) = -1031.105014 au
H (B3LYP/BS1) = -1030.970813 au
G (B3LYP/BS1) = -1031.0317 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1317.923469 au
TS20-22
E (B3LYP/BS1) = -1325.877352 au
H (B3LYP/BS1) = -1325.548889 au
G (B3LYP/BS1) = -1325.633937 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.565396 au
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E (B3LYP/BS1) = -1325.952084 au
H (B3LYP/BS1) = -1325.621282 au
G (B3LYP/BS1) = 1325.706654 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.641128 au
H   1.13820900  2.96658100  -0.17810100
O   2.28706200 -1.52683300   0.01986600
C   3.42748100 -0.93909900   0.06962700
O   4.53369000 -1.49074500   0.13099200
H   2.48450300  1.26751500   0.06962700
C   -3.90708700  1.32158700  -0.19176900
C   -2.11356000  2.55301300   0.36425900
C   -4.28399100  2.61915900  -0.03874200
O   -3.18627300  3.37839100   0.30474900
H   -5.58102300  3.33770000   0.36425900
H   -6.36841700  2.63158400  -0.43983000
H   -5.86391200  3.81959100   0.77897400
H   -5.53255200  4.11774100   0.93378800
H   -1.17236900  3.00231900  -0.64033800
TS22-23
E (B3LYP/BS1) = -1325.933638 au
H (B3LYP/BS1) = -1325.604537 au
G (B3LYP/BS1) = -1325.691702 au
E (B3LYP-D3/BS2//B3LYP/BS1) = -1326.619813 au
C   2.09919000  0.53028400   0.25296600
C   1.19562400  1.38964000   0.12970800
Si  0.48796800  3.13977800   0.15967200
C   -1.07895800  3.10115600  1.20453200
H   -0.86422100  2.78294200  2.23108700
H   -1.52720100  4.10128300  1.24904200
H   -1.82245700  2.41458800   0.78389600
C   1.81147400  4.24279300   0.92606300
H   2.73434400  4.22632000   0.33556300
H   1.45754100  5.28012800   0.97085700
H   2.05281500  3.92474200  1.94649800
C   0.12816700  3.61497200  -1.62786100
H   -0.60348600  2.93651100  -2.08092200
H   -0.28007600  4.63205100  -1.67221000
H   1.03889300  3.59018800  -2.23686100
Au  0.00577200 -0.28935900  -0.42815800
C   -3.51868300 -1.35337800   0.07863200
C   -3.82703300 -0.22571600  -0.69265400
C   -4.98844800  0.49158400  -0.40497100
C   -5.79459800  0.06403000   0.64837200
C   -5.40210900 -1.07241000  1.36194900
N   -4.29851300 -1.77660600  1.08961100
H   -5.25652000  1.36561200  -0.99170300
H   -3.16785300  0.06742400  -1.50063800
H   -6.70569900  0.59076900   0.91443000
H   -6.00860700 -1.43295700  2.19143100
O   -2.13350400 -3.29430100   0.27867100
C   -2.27214400 -2.17915700  -0.20946700
O       -1.42109100  -1.63019000  -1.05918900
C        3.22632000  -0.30487200  0.42733300
C        4.15259300  -0.77850300  -0.57947600
C        3.67576000  -0.81589300  1.62259500
C        5.08183200  -1.52562600  0.07160900
O        4.78869600  -1.54601500  1.42316200
H        4.11034400  -0.57261800  -1.63907900
C        6.28691600  -2.28339700  -0.35870400
H        6.41136300  -2.19304000  -1.44046400
H        7.19217200  -1.90099300  0.12733500
H        6.19810700  -3.34694400  -0.10785800
H        3.31435000  -0.73616700  2.63652300

23
E (B3LYP/BS1) = -1325.943912 au
H (B3LYP/BS1) = -1325.613654 au
G (B3LYP/BS1) = -1325.705712 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.626461 au

C       -2.38017000  0.17252900  0.11710400
C       -2.00104500 -1.01800000  0.04004100
Si      -2.36443400 -2.87319000  0.02899000
C       -1.35157300 -3.64944100  1.41465900
H       -1.62596100 -3.23178400  2.39003100
H       -1.52580600 -4.73177400  1.45029100
H       -0.27912500 -3.48266700  1.26266600
C       -4.21635500 -3.07228300  0.32359200
H       -4.79969800 -2.58136700 -0.46345800
H       -4.48446000 -4.13603600  0.32901900
H       -4.51469900 -2.64479600  1.28743800
C       -1.85441300 -3.52735200 -1.66299800
H       -0.78849300 -3.35482100 -1.85029300
H       -2.03915000 -4.60695200  1.72221200
H       -2.42394600 -3.04367500 -2.46476500
Au      -0.00610200 -0.31095700 -0.17852800
C       4.22017100  0.46180900  0.19689000
C       4.66640700  0.41857600 -1.12987600
C       6.02142300  0.62063300 -1.39156900
C       6.88158800  0.85792500 -0.32099300
C       6.34103600  0.88142400  0.96796400
N       5.04491100  0.68980800  1.23396200
H       6.39586300  0.59282400 -2.41085700
H       3.95905600  0.23003900 -1.92794700
H       7.94396900  1.02108200 -0.47291400
H       6.98485900  1.06360200  1.82712700
O       2.35898200  0.28607400  1.70304100
C       2.75278800  0.24824900  0.53782000
O       2.00792100  0.03231700 -0.51566000
C      -2.90121000  1.47829500  0.20194000
C      -3.31392400  2.35396000 -0.87589500
C  -3.14857500  2.17287600  1.36533900
C  -3.77420600  3.49162400 -0.29484000
O  -3.67252400  3.37679800  1.08168900
H  -3.26501500  2.13809000 -1.93317000
C  -4.33686000  4.76648800 -0.81360900
H  -4.36130600  4.74034400 -1.90563500
H  -5.35753900  4.92862900 -0.44775200
H  -3.73041900  5.62451100 -0.50079800
H  -3.00392000  1.93097900  2.40740700

27
E (B3LYP/BS1) = -1595.241941 au
H (B3LYP/BS1) = -1594.808855 au
G (B3LYP/BS1) = -1594.914555 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1596.036855 au

C  1.20295700  1.72438100 -0.18790800
C  2.22678900  1.14363300  0.21970000
Si  3.92818000  0.82175100  0.93219400
C  4.99035900  0.05197100 -0.35678500
H  5.06024800  0.53961600 -1.27660900
H  6.00633800 -0.18795700  0.03390500
H  4.59836700 -1.04033400 -0.61724200
C  4.61994600  2.53767400  1.31319700
H  3.98731000  3.07356900  2.02933900
H  5.62317100  2.44985900  1.74843300
H  4.69856900  3.14541400  0.40476200
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H  3.12046300  0.32662200  3.24176100
Au  0.70912500 -0.63359400 -0.23195800
C  0.31431300  2.75891000 -0.59997200
C  0.65330400  4.16854300 -0.62244000
C  0.97637000  2.67630200 -1.05760200
C  0.44333800  4.82456100 -1.08445100
H  1.64895600  1.84326800 -1.19180700
O  1.44210900  3.91356300 -1.35145300
H  1.59655600  4.60650200 -0.32917800
C  0.75682400  6.25605400 -1.34351200
H  1.01123900  6.42479200 -2.39678700
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H  0.10894800  6.87502500 -1.09537500
C  3.54470300  0.55523600  0.79535400
C  4.23031700  0.08040600  2.00879700
C  5.60133400  0.16713500  2.04045600
C  6.23869900  0.54938800  0.86037800
C  5.46861200  0.66456700 -0.29969200
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**Cl**

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\[ E (B3LYP-D3/BS2// B3LYP/BS1) = -460.410349 \text{ au} \]

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\[ E (B3LYP-D3/BS2// B3LYP/BS1) = -588.700665 \text{ au} \]

**HNa\textsubscript{2}CO\textsubscript{3}**

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2. General method

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 10 ppm, Karl-Fischer titration). NEt₃ and pyridine were distilled under nitrogen from KOH. Gold chloride was purchased from Aldrich and kept in desiccator under anhydrous condition (decrease of reactivity has been observed for catalyst if prolonged exposition to air (ca 1 month). All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ¹H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation). ¹³C-NMR spectra were recorded with ¹H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, br = broad). Gas chromatographic and low resolution mass spectrometric measurements were performed on a Perkin-Elmer Clarus 600 gas chromatographer and mass spectrometer using a Perkin-Elemer Elite fused silica column (length: 30 m, diameter: 0.32 mm) and Helium as carrier gas. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. HPLC measurement were done on a JASCO HPLC system with an AS2055 Autosampler, a PU 2089 Pump, a UV 2075 detector and a SEDEX 85 (SEDERE) detector using a CHIRALPAK IC column from DAICEL Chemical Industries Ltd. HPLC grade solvents from Sigma-Aldrich were used.
3. Domino cyclization-alkynylation reaction

The synthesis of reagents and starting materials has been reported in our previous publication\(^1\) and is re-copied here for easier reproduction of the results.

**Triisopropylsilyl trimethylsilylacetylene (29)**

Following a reported procedure,\(^2\) \(n\)-butyllithium (2.5 M in hexanes, 12.0 mL, 29.9 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (28) (3.0 g, 30 mmol, 1.0 equiv) in THF (48 mL) at \(-78^\circ\text{C}\). The mixture was then warmed to 0 °C and stirred for 5 min. The mixture was then cooled back to \(-78^\circ\text{C}\) and chlorotriisopropylsilane (6.4 mL, 30 mmol, 1.0 equiv) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (40 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 60 mL). The organic layer was washed with water and brine, then dried over MgSO\(_4\), filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by Kugelrohr distillation (56-57°C/0.25 mmHg) to yield 29 (7.16 g, 28.0 mmol, 92% yield) as a colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 1.08\) (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR \(\nu 2959\) (m), 2944 (m), 2896 (w), 2867 (m), 1464 (m), 1385 (w), 1250 (m), 996 (w), 842 (s), 764 (s), 675 (m), 660 (m). Characterization data of 21 corresponded to the literature values.\(^\text{S112}\)

**1-Hydroxy-1,2-benziodoxol-3-(1\(H\))-one (31)**

Following the reported procedure,\(^3\) NaIO\(_4\) (7.24 g, 33.8 mmol, 1.05 equiv) and 2-iodobenzoic acid (30) (8.00 g, 32.2 mmol, 1.00 equiv) were suspended in 30% (v:v) aq. AcOH (48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product 31 (8.3 g, 31 mmol, 98%) as a colorless solid.

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\(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 8.02 (dd, 1 H, \(J = 7.7, 1.4\) Hz, Ar\(H\)), 7.97 (m, 1 H, Ar\(H\)), 7.85 (dd, 1 H, \(J = 8.2, 0.7\) Hz, Ar\(H\)), 7.71 (td, 1 H, \(J = 7.6, 1.2\) Hz, Ar\(H\)); \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4; IR \(\nu\) 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m); the reported values correspond to the ones in literature.\(^{13}\)

1-[(Tri\textit{iso}-propylsilyl)-ethynyl]-1,2-benziodoxol-3(1H)-one (TIPS-EBX, 1a)

Following a reported procedure,\(^4\) 2-iodosylbenzoic acid (31) (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirrer. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 0 °C. Trimethylsilyl triflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(tri\textit{iso}-propylsilyl)acetylene (29) (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in DCM (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (200 mL) and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (200 mL). The organic layers were combined, washed with a saturated solution of NaHCO\(_3\) (2 x 200 mL), dried over MgSO\(_4\), filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (ca 120 mL) afforded 1a (30.1 g, 70.2 mmol, 86%) as colorless crystals.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.44 (m, 1 H, Ar\(H\)), 8.29 (m, 1 H, Ar\(H\)), 7.77 (m, 2 H, Ar\(H\)), 1.16 (m, 21 H, TIPS). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.4, 134.6, 132.3, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1. IR \(\nu\) 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1584 (m), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 883 (m), 833 (m), 742 (m), 702 (s), 636 (m); Melting point (Dec.) 170-176°C; Characterization data of 6 corresponded to the literature values.\(^4\)

1-Chloro-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (34)

Following a reported procedure, \(^5\) TMEDA (distilled over KOH) (1.26 mL, 8.20 mmol, 0.2 equiv) was added to a solution of \(^{n}\)BuLi (2.5 M in hexanes, 36.6 mL, 91.6 mmol, 2.2 equiv). After 15 min, the cloudy solution was cooled to 0 °C and 32 (7.0 mL, 42 mmol, 1 equiv) in THF (6 mL) was added dropwise. The reaction was stirred 30 min at 0 °C and then at RT overnight. I\(_2\) (11.2 g, 44.0 mmol, 1.06 equiv) was then added portions wise at 0 °C and the mixture stirred at 0 °C for 30 min and 4 h at RT. The reaction was quenched with saturated NH\(_4\)Cl. Et\(_2\)O (100 mL) was added and the layers were separated. The aqueous layer was then extracted twice with Et\(_2\)O (3 x 50 mL). The organic layers were combined, washed twice with saturated NaS\(_2\)O\(_3\) (2 x 50 mL), dried over MgSO\(_4\), filtered and concentrated under reduced pressure to afford 15.6 g of crude 33 as an brown oil which was used without further purification.

The crude oil was dissolved in wet CH\(_2\)Cl\(_2\) (40 mL) in the dark under air. \(^{t}\)BuOCl (5.2 mL, 44 mmol, 1.05 equiv) was then added dropwise at 0 °C. After 30 min, the resulting suspension was filtered to afford 33 (7.30 g, 18.1 mmol, 43%) as a yellow solid. The mother liquors were carefully reduced to one third and filtered to afford more 34 (3.51 g, 8.71 mmol, 21%) as a yellow solid. Combined yield: 64%. Mp 167 – 169 °C, Lit: 166-168 °C.\(^{[5]}\)\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.09 (d, 1 H, \(J = 8.4\) Hz, ArH), 7.85 (m, 1 H, ArH), 7.73 (m, 2 H, ArH).\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 133.8, 132.1, 131.6, 129.7, 128.5, 122.8 (q, 290 Hz), 113.4, 84.8. The melting point and the \(^1\)H NMR correspond to the reported values. \(^5\)

1-Hydroxy-3,3-bis(trifluoromethyl)-3-(\(IH\))-1,2-benziodoxole (35)

Following a preported procedure, \(^6\) Et\(_3\)BnNCl (83 mg, 0.36 mmol, 0.05 equiv) was added to a stirring solution of 34 (10.7 g, 26.5 mmol, 1 equiv) in CH\(_2\)Cl\(_2\) (150 mL) and KOH (1.48 g, 26.5 mmol, 1 equiv) in water (28 mL). The reaction was stirred overnight under air. The organic layer was separated and dried over MgSO\(_4\). The resulting solid was purified over a silica plug eluting with EtOAc, then recristallized in EtOAC (about 50 mL) and washed with pentane to afford 35 (7.42 g, 19.2 mmol, 73%) as a white solid. \(^1\)H NMR (400 MHz, DMSO) δ 7.96 (m, 2 H, ArH), 7.73 (m, 2 H, ArH).\(^{13}\)C NMR (101 MHz, DMSO) δ 133.3, 131.0, 130.8, 128.9, 127.9, 123.4 (q, \(J = 290\) Hz), 117.2, 83.7 (m). IR 1464 (w), 1435 (w), 1290 (w), 1263 (m), 1185 (s), 1139 (s), 1103 (m), 1041 (w), 1021 (w), 952 (s), 760 (m), 692 (m).

1-[(Triisopropylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(\(IH\))-1,2-benziodoxole (1b)


TMSOTf (3.80 g, 17.1 mmol, 1.1 equiv) was added to 35 (6.00 g, 15.5 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (200 mL) at RT. After 20 min, the solution was concentrated under reduced pressure at 0 °C and the reaction flask was refilled with Ar. Then the resulting yellow solid was dissolved in dry CH$_3$CN (200 mL). (Trimethylsilyl)(triisopropylsilyl)acetylene (29) (5.14 g, 20.2 mmol, 1.3 equiv) was added and after 20 min a few drops of pyridine were added. The reaction was then concentrated under vacuum, the residues were dissolved in Et$_2$O and the solutions filtered through a silica plug (eluant Et$_2$O). The resulting solid was recrystallized in pentane to afford 1b (5.43 g, 9.87 mmol, 64%) as a white crystalline solid. Ref (PET/Et$_2$O 95/5): 0.4. Mp 131 – 132 °C. 1H NMR (400 MHz, CDCl$_3$) (ca 0.10 mmol/mL) δ 8.36 (dd, 1 H, J = 7.9, 1.7 Hz, ArH), 7.84 (d, 1 H, J = 6.7 Hz, ArH), 7.68 (m, 2H, ArH), 1.15 (m, 21 H, TIPS). 13C NMR (101 MHz, CDCl$_3$) δ 132.7, 131.1, 129.9, 129.9 (m), 128.2, 123.6 (q, 288 Hz), 112.1, 110.8, 81.4 (m), 69.7, 18.5, 11.2. IR 2947 (m), 2868 (m), 2249 (w), 1566 (w), 1465 (m), 1438 (w), 1387 (w), 1264 (s), 1218 (m), 1184 (s), 1149 (s), 1071 (w), 994 (w), 951 (s), 910 (m), 873 (w), 732 (s), 696 (s), 655 (s), 655 (s). HRMS(ESI) calcd for C$_{20}$H$_{26}$OF$_6$Si$^+$ (M+H) 551.0702, found 551.0723.

**General procedure for the preparation of propargylic alcohols:**

A 50 mL two-necked flask was charged with Mg (321 mg, 13.2 mmol, 1.32 equiv), HgCl$_2$ (2.7 mg, 0.10 mmol, 0.01 equiv) and dry diethyl ether (30 mL), then propargyl bromide was added dropwise (2.86 g, 12.0 mmol, 1.20 equiv). When the solution became homogeneous, the aldehyde (10.0 mmol, 1.00 equiv) was added dropwise. The reaction was quenched with a sat NH$_4$Cl solution (30 mL) when TLC (Pentane/EtOAc: 5/1) indicated that the benzaldehyde was completely consumed. The aqueous and organic layers were separated, the aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic layers were dried over MgSO$_4$, concentrated under vaccum and purified by column chromatography (Pentane/EtOAc: 5/1).

Phenylbut-3-yn-1-ol (36) was obtained as a transparent oil (1.09 g, 7.46 mmol, 75%). 1H NMR (400 MHz, CDCl$_3$) δ 7.42-7.30 (m, 5 H, ArH), 4.82 (m, 1 H, CHPh), 3.23 (d, 1 H, J = 3.8 Hz, OH), 2.62 (m, 2 H, CH$_2$), 2.09 (t, 1 H, J = 2.6 Hz, alkyne CH). 13C NMR (101 MHz, CDCl$_3$) δ 142.3, 128.1, 127.6, 125.6, 80.6, 72.0, 70.7, 28.9. The 1H NMR data corresponds to the literature.

**Typical procedure to prepare ketone allene:**

Following a reported procedure, a solution of 36 (1.31 g, 9.00 mmol, 1 equiv) and CH$_3$CN (40 mL) was added into a solution of H$_5$IO$_6$ (2.15 g, 9.45 mmol, 1.05 equiv) and CH$_3$CN (40 mL) by an addition funnel at 0 °C. Then, pyridiniumchlorochromat (PDC) (38 mg, 0.18 mmol, 0.02 equiv) was added into the mixture in three portions. The ice bath was removed and the

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reaction was diluted with EtOAc (100 mL) when TLC (Pentane/EtOAc: 10/1) showed that all starting material was consumed. The organic layer was washed with a mixture of brine and water (25 mL / 25 mL), sat Na₂S₂O₃ (50 mL), brine (50 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (Pentane/EtOAc: 10/1).

**1-Phenylbuta-2,3-dien-1-one (24)** was obtained following as a brown solid (0.73 g, 5.5 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (m, 2 H, ArH), 7.54 (m, 1 H, ArH), 7.44 (m, 2 H, ArH), 6.43 (t, 1 H, J = 6.5 Hz, CH), 5.25 (d, 2 H, J = 6.5 Hz, CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 217.0, 190.9, 137.4, 132.7, 128.6, 128.3, 93.2, 79.2. The NMR data corresponds to the literature.⁹

**Domino cyclization-alkynylation reaction:**

The optimization data from our previous publication is copied again here for information. New experiments are given in bold (entry 16 and 17 in table S3).

**Optimization of the reaction with TIPS-EBX (1a):**

TIPS-EBX (1a) (51 mg, 0.12 mmol, 1.2 equiv), base (0.12 mmol, 1.2 equiv) and catalyst (0.005 mmol, 0.050 equiv) were added into a solution of 1-phenylbuta-2,3-dien-1-one (24) (15 mg, 0.10 mmol, 1.0 equiv) and CH₃CN (5 mL). The reaction was stopped after 72 h. Isolated yields after column chromatography (SiO₂, pentane) are given.

The complete list of experiments for the optimization of the domino alkynylation with TIPS-EBX (1a) reagent is shown in Table S2.

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Table S2: Optimization with TIPS-EBX (1a) reagent:

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[a] Only cyclization product without alkynylation was obtained

Optimization of the reaction with 1b:

General procedure: 1-[(triisopropylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(1H)-1,2-benziodoxole (1b) (110 mg, 0.200 mmol, 2.00 equiv), Na₂CO₃ (21 mg, 0.20 mmol, 2.0 equiv) and catalyst (0.005 mmol, 0.050 equiv) were added into a solution of 1-phenylbuta-2,3-dien-1-one (24) (15 mg, 0.10 mmol, 1.0 equiv) and iso-propanol (5 mL). The reaction was stopped after 72 h. 1 mL of mixture was mixed with 0.16 mL n-decane solution (0.125 M in CH₃CN) and injected into the GC-MS chromatographer. The following oven program was used: Initial temperature: 50 °C, Ramp: 10.0 °C/min to 250 °C, hold 25 min at 250 °C). Yields were determined by GC-MS, based on the following calibration.

A 0.125 M standard solution was prepared by dissolving n-decane (0.242 mL, 1.25 mmol) in CH₃CN (10 mL).

1-Phenylbuta-2,3-dien-1-one (24) (7.2 mg, 0.054 mmol) was dissolved in CH₂Cl₂ (1.0 mL) (solution O).

- 25 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution A;
- 50 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution B;
- 75 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution C;
100 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution D;

GC-MS chromatograms were acquired for solutions A, B, C and D and in each of them the ratio between the integrals of the signals corresponding to compound 24 (retention time: 13.8 min) and to the internal standard (retention time: 15.9 min) was calculated. These observed ratios by integration of the chromatogram peaks and the ratios (mmol 24/mmol n-decane) were used as the axis of the calibration graph.

Triisopropyl((5-phenylfuran-3-yl)ethynyl)silane (26) (16.2 mg, 0.0500 mmol) was dissolved in CH₂Cl₂ (1.0 mL) (solution P).

- 25 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution E;
- 50 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution F;
- 75 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution G;
- 100 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH₂Cl₂ (600 µL) to obtain solution H;

GC-MS chromatograms were acquired for solutions E, F, G and H and in each of them the ratio between the integrals of the signals corresponding to compound 26 (retention time: 30.7 min) and to the internal standard (retention time: 15.9 min) was calculated. These observed ratios by integration of the chromatogram peaks and the ratios (mmol 26/mmol n-decane) were used as the axis of the calibration graph.
The complete list of experiments for the optimization of the domino alkynylation with benziodoxole reagent 1b is shown in Table S3:

**Table S3**: Optimization with bistrifluoromethyl benziodoxole reagent 1b:

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>-</td>
<td>CH₃CN</td>
<td>50[^a]</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>-</td>
<td>CH₃CN</td>
<td>&lt;5</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-</td>
<td>CH₃CN</td>
<td>&lt;5</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Na₂CO₃</td>
<td>CH₃CN</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>Na₂CO₃</td>
<td>CH₃CN</td>
<td>73</td>
</tr>
<tr>
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<td>2</td>
<td>Na₂CO₃</td>
<td>CH₂Cl₂</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>Na₂CO₃</td>
<td>THF</td>
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<td>8</td>
<td>2</td>
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<td>23</td>
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<tr>
<td>9</td>
<td>2</td>
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<td>'PrOH</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>AuCl₃</td>
<td>Na₂CO₃</td>
<td>'PrOH</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>AuCl₃+Pyridine</td>
<td>Na₂CO₃</td>
<td>'PrOH</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
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<td>Na₂CO₃</td>
<td>'PrOH</td>
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<tr>
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<td>Na₂CO₃</td>
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<tr>
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<td>'PrOH</td>
<td>0</td>
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<tr>
<td>15</td>
<td>AuCl₃+picolinic acid (25)</td>
<td>Na₂CO₃</td>
<td>'PrOH</td>
<td>81</td>
</tr>
<tr>
<td>16</td>
<td>AuCl + picolinic acid (25)</td>
<td>Na₂CO₃</td>
<td>'PrOH</td>
<td>73[^b]</td>
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<tr>
<td>17</td>
<td>AuCl</td>
<td>Na₂CO₃</td>
<td>'PrOH</td>
<td>35[^b]</td>
</tr>
</tbody>
</table>

[^a] 14% cyclization product without alkynylation was obtained. [^b] Isolated yield after column chromatography.
Triisopropyl((5-phenylfuran-3-yl)ethynyl)silane (26)

R_f (Pentane): 0.7.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (app d, 3 H, $J = 8.1$ Hz, ArH + FuranH), 7.39 (t, 2 H, $J = 7.5$ Hz, ArH), 7.29 (d, 1 H, $J = 7.5$ Hz, ArH), 6.69 (s, 1 H, FuranH), 1.12 (m, 21 H, TIPS). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.9, 145.6, 130.1, 128.7, 127.9, 123.9, 109.8, 107.8, 97.7, 92.9, 18.6, 11.3. IR 2943 (s), 2923 (m), 2865 (s), 2157 (m), 1746 (w), 1463 (m), 1384 (w), 1253 (w), 1228 (w), 1191 (w), 1144 (m), 1072 (w), 1016 (m), 992 (s), 883 (s), 808 (m). HRMS (ESI) calcd for C$_{21}$H$_{29}$OSi$^+$ [M+H]$^+$ 325.1982; found 325.1987.