Cascade Transformation of Carbon Dioxide and Alkyne-1,*n*-diols into Densely Substituted Cyclic Carbonates

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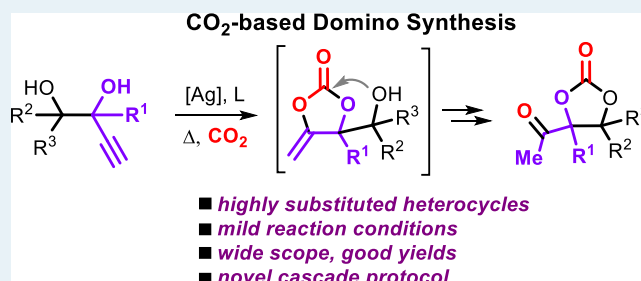
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ABSTRACT: A silver-catalyzed cascade conversion of modular alkyne-1,*n*-diols and carbon dioxide has been developed allowing for the selective formation of keto-functionalized cyclic carbonates. The protocol is characterized by its operational simplicity, excellent scope of carbonate-based heterocycles, and mild reaction conditions. *In situ* IR studies, control experiments, and detailed computational analysis of these manifolds reveal the intermediacy of an α-alkylidene carbonate that is intercepted by an intramolecular alcohol nucleophile. The synthetic potential of this conceptually attractive CO_2 transformation is demonstrated in the preparation of larger ring carbonates and their thermal rearrangement to sterically crowded, five-membered fused carbonate products.

CO_2-based Domino Synthesis

- highly substituted heterocycles
- mild reaction conditions
- wide scope, good yields
- novel cascade protocol

The reutilization of carbon-containing waste into value-added products through catalysis provides an attractive route in the context of circular chemistry.[1] The implication of circular principles will realize an improved usage of our natural resources, thereby embracing a sustainable future and a more efficient carbon management.[2] Carbon dioxide (CO_2) represents the most simple carbon-based reagent available for the fabrication of various products including pharmaceuticals,[3] polymerizable monomers,[4] synthetic intermediates,[5] and bulk chemicals.[6] Despite the difficulties encountered in the catalytic transformation of CO_2, much progress has been noted in the last 10 years with outstanding advances in both reductive[7] and nonreductive conversions.[8] A prominent, nonreductive conversion process is the [3 + 2] cycloaddition of CO_2 to epoxides providing cyclic carbonates as products. These compounds have gained a great deal of synthetic importance over the last few years as suitable starting points for decarboxylative formation of compounds with elusive stereocenters[9] and the creation of more sustainable CO_2-based polymers and materials.[10]

The [3 + 2] cycloaddition strategy for the generation of cyclic carbonates generally works well for mono- and disubstituted epoxides but shows important limitations for even more sterically demanding oxiranes. To overcome this challenge, new conceptual designs have emerged that capitalize on alternative reactivity patterns.

For instance, the use of substrate-controlled manifolds such as the one presented in Scheme 1a allows for the design of highly 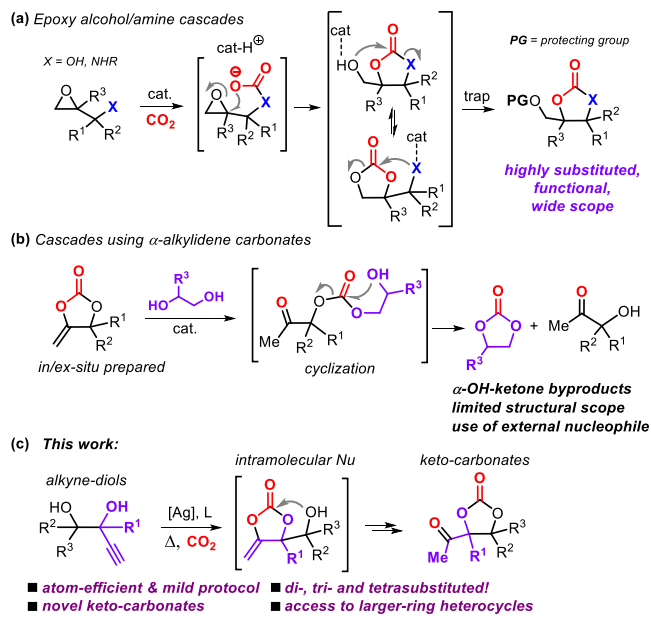elusive and complex carbonate structures through unique cascade processes, provided that a suitable trapping mechanism is available.[11]

Similar though different in its design is the interception of reactive *in* or *ex situ* prepared α-alkylidene carbonates by diol reagents in a formal domino transesterification process (Scheme 1b) giving a 1:1 mixture of a new cyclic carbonate and an α-hydroxy ketone.[12] Whereas these cascade designs are able to provide some though a rather limited degree of structural diversity, the coformation of a ketone byproduct renders them atom-inefficient. To expedite new types of cascade processes providing new types of carbonate structures, we sought to merge the presence of an intramolecular alcohol (pro)nucleophile and a reactive exocyclic double bond to promote a new rearrangement process that would give access to keto-functionalized cyclic carbonates while enabling an ample scope in substitution and functionality (Scheme 1c). The key to this new approach is the use of an alkyne-1,2-diol that under appropriate reaction conditions induces a skeletal rearrangement of an initially formed α-alkylidene carbonate with the formation of the keto group as a thermodynamic driving force. Here, we describe the development and mechanistic rationale for this conceptual novel catalytic domino process, thus expanding the current portfolio of highly substituted (saturated) cyclic carbonates.

Scheme 1. (a) Substrate-Controlled Cascade Leading to Highly Substituted Cyclic Carbonates, (b) Domino Transesterification Process Involving External Diols, and (c) This Work: A Novel Cascade Process


(a) *Epoxy alcohol/amine cascades*

(b) *Cascades using α-alkylidene carbonates*

(c) *This work:*

Scheme 2. Scope of Disubstituted Keto-Based Cyclic Carbonates (2a–2s) Derived from Alkyne-1,2-diols 1a–1s

2a: X = H, 88%
2b: X = Me, 88%
2c: X = OMe, 91%
2d: X = tBu, 71%
2e: X = F, 87%
2f: X = Cl, 86%
2g: X = Br, 83%
2h: X = I, 80%
2i: X = CF₃, 59%
2j: X = CO₂Me, 84%

X-ray of 2a
CCDC-2088491

2k: 95%
2l: 57% [a]
2m: 90%
2n: X = S, 81%
2o: X = O, 77%
2p: 78%
2q: 86%
2r: 57%
2s: 95%

[a]The reaction was performed at 60 °C.

At the onset of our studies, we selected an alkyne-1,2-diol reagent **1a** as a model substrate (Tables 1 and S1)[13] and AgOAc/DavePhos (*rac*-**L1**) as catalyst precursors using CH₃CN as a solvent.[14] Both the Ag salt and phosphine ligand alone are not effective (Table S1), but their combination (Table 1, entry 1: 10 mol % each) provides a high level of substrate conversion at 35 °C with a moderate yield of **2a** (56%). Since the NMR and IR analyses ($\nu = 1803$ and $1729\ cm^{-1}$) of the isolated sample of **2a** were not conclusive and indicated the formation of a product different from an α-alkylidene carbonate, X-ray analysis was performed, which unambiguously confirmed the formation of a keto-substituted cyclic carbonate (*vide infra*, Scheme 2).[15] The transformation of **1a** into **2a** can also be performed at 25 °C (entry 2) but requires a longer reaction time (48 h) to afford a similar yield of **2a**. The nature of the phosphine ligand is crucial as simple ligands such as PPh₃, dppe (entries 3 and 4, Table 1), and DPEPhos (entry 14, Table S1) proved to be unproductive. Then, we decided to examine other bulky monophosphine ligands (**L2–L6**, entries 5–9), with BrettPhos **L6** providing the best performance with **2a** produced in excellent yield (91% by NMR, 85% isolated; entry 9, Table 1).

To make the protocol more attractive, we investigated the use of lower loadings of both the Ag precursor and **L6** (entries 10–13, 5.0 mol %). By slightly increasing the reaction temperature to 40 °C, the full conversion of **1a** could be realized within 6 h while using AgF as a precursor (entry 13), giving **2a** in high isolated yield (88%). Lower loadings of AgF/**L6** or changing the solvent (entries 14–16, Table 1, and Table S1) did not further improve the process outcome.[16]

The scope of this transformation (Scheme 2) was then further explored using the optimized conditions (Table 1, entry 13). In general, good-to-excellent isolated yields of the keto-carbonates were achieved under mild temperature (40 °C) and pressure (1 bar) conditions. A wide range of 3-aryl-3-keto-carbonates could be produced (**2a–2k**) with electronically diverse *para-* and *meta*-substituents. The presence of other
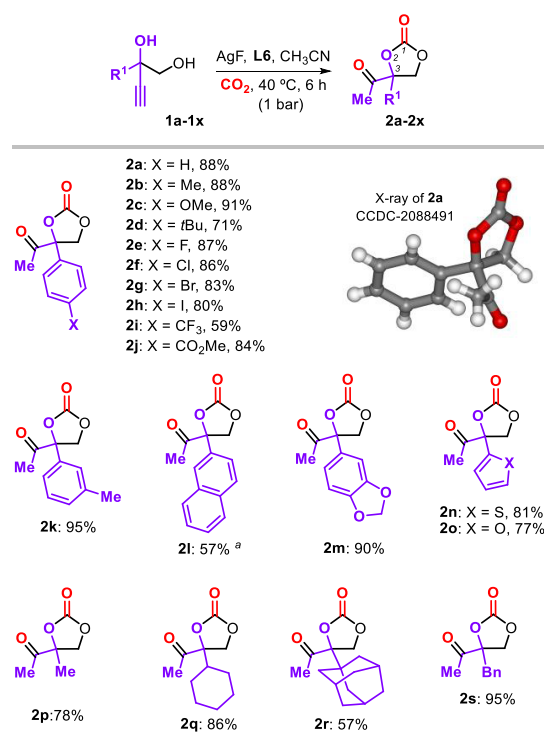
(hetero)aryl groups (**2l–2o**) in the keto-carbonate product is also tolerated, though for naphthyl-substituted **2l**, a reaction temperature of 60 °C was required to allow for an appreciable product yield, most likely as a result of increased steric congestion in the intermediate of Scheme 1c. Apart from aryl groups, various primary, secondary, and tertiary alkyl groups can also be introduced as illustrated by the successful preparation of **2p–2s**, with the adamantyl-based **2r** (57%) being particularly noteworthy.

Next, we decided to challenge the developed protocol further using substituted (cf., R²) alkynyl-1,2-diols **3a–3m**. Trisubstituted, aryl-functionalized keto-carbonates **4a–4d** were obtained in good isolated yields (76–90%) and under high diastereocontrol (*dr* > 95:5), whereas methyl-substituted products **4e–4g** (62–77%) were produced with lower *dr* values, which is ascribed to an apparent lower degree of diastereocontrol in the intramolecular attack of the secondary alcohol on the α-alkylidene carbonate intermediate (Scheme 1c). Encouraged by the low-temperature formation of typically challenging trisubstituted keto-carbonates,[5e] we then considered alkyne-1,2-diols with three substitutions (R¹–R³, Scheme 3, top) to forge sterically more demanding keto-carbonates. Under relatively mild conditions (40 °C, 1 bar), the formation of tetrasubstituted carbonate heterocycles **4h–4m** could be accommodated in typical good isolated yields of up to 91%. Both spirofused cycloalkyl rings (**4h** and **4i**) and different combinations of aryl/alkyl substituents (**4j–4m**) are tolerated in the product skeletons, further highlighting the excellent scope of this transformation. It should be noted that the formation of highly substituted cyclic carbonates such as those in Scheme 3 represents a huge challenge, and the results described so far thus demonstrate a substantial advance in this area.

Table 1. Screening and Optimization of the Ag-Catalyzed Conversion of Alkyne-1,2-diol 1a and CO_2 into Keto-Substituted Cyclic Carbonate 2a[a]
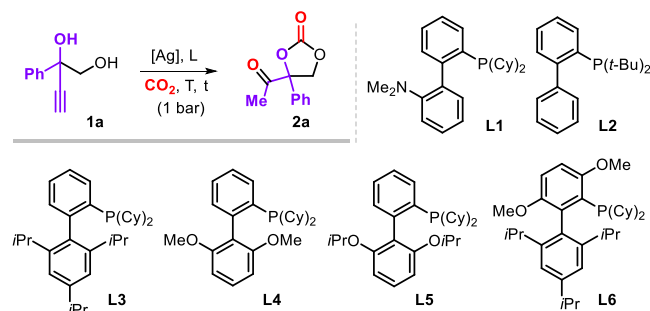
entry	t, T[b]	[Ag][b]	[L][b]	C[b,c]	Yield[b,c]
1	24, 35	AgOAc, 10	L1, 10	96	56
2	48, 25	AgOAc, 10	L1, 10	83	62
3	24, 25	AgOAc, 10	PPh₃, 10	<10	<10
4	24, 25	AgOAc, 10	dppe, 10	0	0
5[d]	24, 25	AgOAc, 10	L2, 10	77	66 (63)
6[d]	24, 25	AgOAc, 10	L3, 10	82	74 (66)
7[d]	24, 25	AgOAc, 10	L4, 10	84	73 (68)
8	24, 25	AgOAc, 10	L5, 10	85	63
9[d]	24, 25	AgOAc, 10	L6, 10	>99	91 (85)
10	24, 25	AgOAc, 5	L6, 5.0	73	69
11	24, 40	AgOAc, 5	L6, 5.0	93	85
12	24, 40	AgF, 5	L6, 5.0	>99	90
13[d]	6, 40	AgF, 5	L6, 5.0	>99	91 (88)
14	6, 40	AgF, 2.5	L6, 2.5	12	<5
15[e]	6, 40	AgF, 5	L6, 5.0	>99	18
16[f]	6, 40	AgF, 5	L6, 5.0	>99	17

[a]General conditions: 1a (0.30 mmol), CH_3CN (0.60 mL), [Ag]/[L], and T/t as indicated. [b]Time in h, temperature in °C, [Ag] and [L] in mol %, and conversion (C) of 1a and the yield of 2a in %. [c]Conversion and yield based on ¹H NMR ($CDCl_3$) analysis, using mesitylene as the internal standard. [d]In brackets, the isolated yield of 2a. [e]THF as a solvent. [f]MeOH as a solvent.

To shed light on the formation mechanism of these keto-carbonates, DFT analysis[17] of the benchmark reaction involving 1a and CO_2 was performed using a Ag catalyst derived from L1 (Figure 1).[18−21] The reason for this catalyst choice was to be able to directly compare the first part of the manifold with that computed previously[14] in the conversion of a more simple propargylic alcohol precursor by the Ag(L1)OAc catalyst. In our calculations, we used therefore the same complex as a starting point together with substrate 1a and CO_2 as a zero reference (Figure 1, denoted as Reactants). The phosphine substituents are not symmetric and can rotate at room temperature. All structures were therefore calculated with the same fixed phosphine chiral conformation. Note that substrate 1a has a chiral center giving rise to diastereoisomeric intermediates and transition states for the chosen conformation of the Ag complex derived from L1. For simplicity, we provide in Figure 1 only the lowest energetic pathway based on (R)-1a (see the Supporting Information for full details and comments).
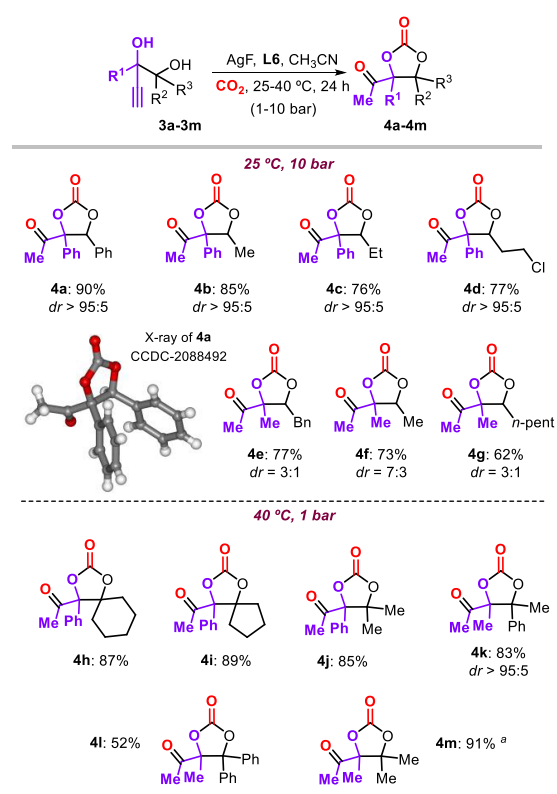
The overall mechanistic pathway for the conversion of (R)-1a includes different key stages: initial CO_2 activation by propargylic diol followed by an attack on the triple bond, a carbonate isomerization step involving a pendant alcohol, and a tautomerization step. Notably, all of these steps are facilitated by several proton transfer/H-abstraction sequences that advance the reaction manifold. First, the tertiary alcohol in substrate (R)-1a is deprotonated by the acetate anion bound to Ag(L1), thereby obtaining an alkoxide species while activating CO_2 via a

concerted TS-1 (19.7 kJ·mol⁻¹) producing the first intermediate A located at 15.6 kJ·mol⁻¹ together with a molecule of acetic acid.[21] The latter is not involved during the formation of the subsequent intermediates B, C, and D. In intermediate B (at −0.2 kJ·mol⁻¹), the initial alkyne coordination is replaced by an O-coordination of the formed linear carbonate after CO_2 activation. Then, the alkyne coordination is restored in intermediate C (−4.1 kJ·mol⁻¹), giving rise to a bidentate coordination mode. Through intermediate C, the system is set up toward the formation of an alkylidene cyclic carbonate going through TS-2: in this transition state, the cyclic carbonate ring that is formed can have two mutual orientations with respect to the fixed conformation of the Ag(L1) complex, thus producing two different diastereoisomers.[22]

In TS-2 (at 63.0 and 55.1 kJ·mol⁻¹), both TS-2A and TS-2B differ in the double-bond configuration being Z and E, respectively. The resultant isomers D-A (at -5.0 kJ·mol⁻¹) and D-B (at −19.6 kJ·mol⁻¹) mimic the structures reported by Schaub, Hashmi, and co-workers before final protodemetalation affording alkylidene carbonates. Our pathway aligns well with the possibility of having Z- and E-configured TSs, and the energetic spans related to this first part of the mechanism for the conversion of (R)-1a are 67.1 and 59.2 kJ·mol⁻¹, with the (E) isomer being most favored.[23]

For the other intermediate E, located between TS-2 and TS-3, also the Z and E isomers (designated A and B) were calculated. For intermediates E (at 27.2 and 12.1 kJ·mol⁻¹) also the Z

Scheme 3. Scope of Tri- and Tetrasubstituted Keto-Based Cyclic Carbonates (4a–4m) Derived from Substituted Alkyne-1,2-diols 3a–3m

4a: 90%
dr > 95:5

4b: 85%
dr > 95:5

4c: 76%
dr > 95:5

4d: 77%
dr > 95:5

X-ray of **4a**
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4e: 77%
dr = 3:1

4f: 73%
dr = 7:3

4g: 62%
dr = 3:1

4h: 87%

4i: 89%

4j: 85%

4k: 83%
dr > 95:5

4l: 52%

4m: 91% [a]

[a]The reaction time was 48 h.

isomer is energetically less favored. The only difference compared to intermediates **D** is the presence of a molecule of acetic acid, which enables a protodemetalation through **TS-3A** and **TS-3B** (at 39.3 and 19.2 kJ·mol^{-1}, respectively). The following intermediate **F** located at −61.6 kJ·mol^{-1} has an OAc ligand coordinating to the metal center, and the stereogenic information around the double bond is erased from this stage on. In **F**, the pendant alcohol of the cyclic carbonate is prepared for deprotonation by the OAc ligand, providing intermediate **G** (at −5.0 kJ·mol^{-1}). It was not possible to determine a transition state structure for this uphill process.

Subsequent decoordination of the carbonate-*O* through intermediate **H** (at −38.8 kJ·mol^{-1}) and rotation and re-coordination of the carbonate via the *O*-atom next to the olefin unit give intermediate **I** (at -20.6 kJ·mol^{-1}). An isomerization process occurs via tetrahedral **TS-4** (at −8.2 kJ·mol^{-1}), and a new five-membered cyclic carbonate is produced with an enol substituent coordinated to the metal via the *O*-center (i.e., intermediate **J** at −93.3 kJ·mol^{-1}). A more stable intermediate **K** (at −103.8 kJ·mol^{-1}) is obtained via an *O*-to-*C* rearrangement that involves the coordinated enolate.

To form the final product, first, a molecule of HOAc approaches the Ag complex in intermediate **L** (−83.1 kJ·mol^{-1}) and a proton transfer from HOAc to the C atom of the initial enolate fragment through **TS-5** (at −21.6 kJ·mol^{-1}) releases the ensemble based on the keto-carbonate **2a** and the catalyst Ag(**L1**)OAc (at −140.5 kJ·mol^{-1}). From Figure 1, the determining transition state (TDTS) is **TS-2**, with a maximum energetic span of 67.1 kJ·mol^{-1} (16.0 kcal·mol^{-1}). This data corroborates well with the experimental finding that substrate (*R*)-**1a** can be converted into keto-carbonate **2a** under ambient

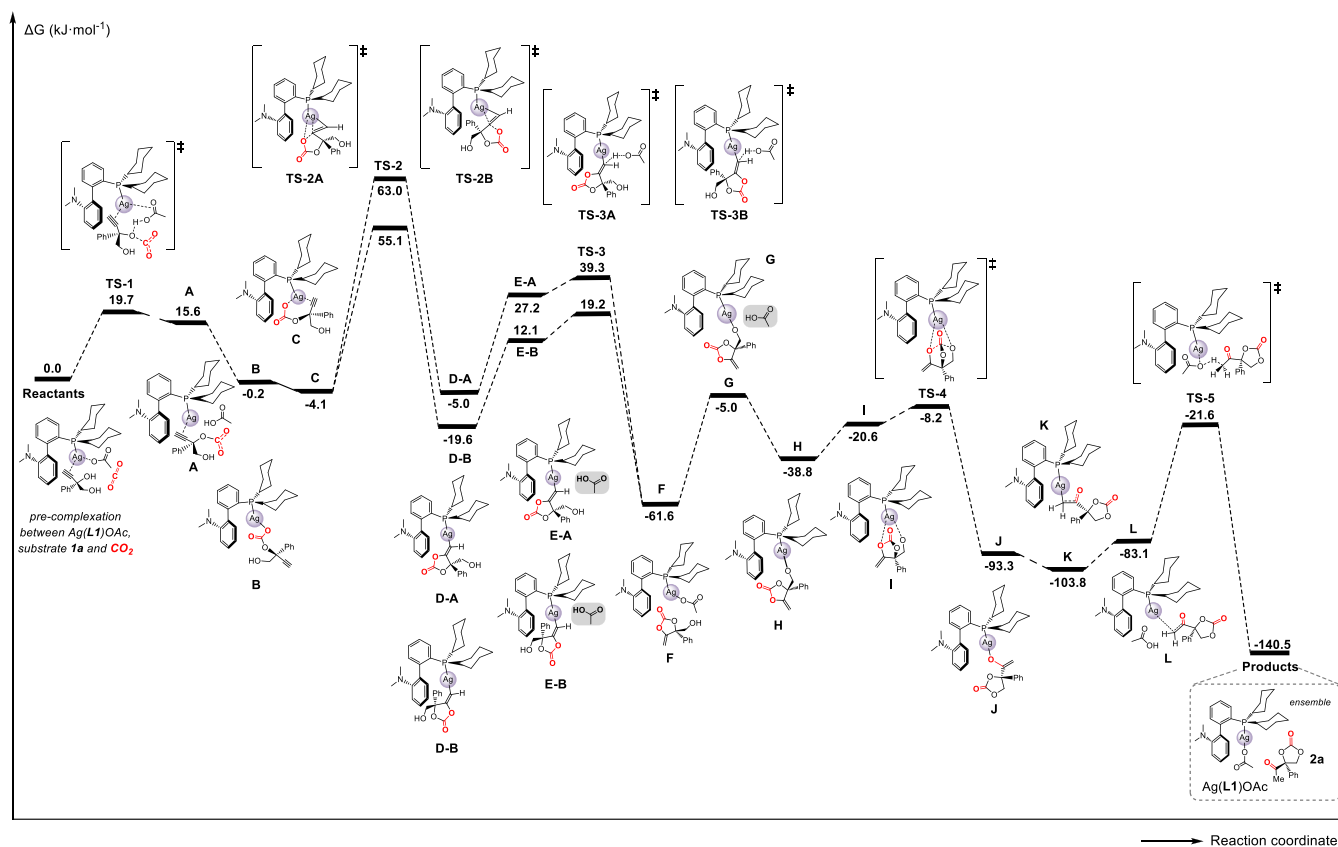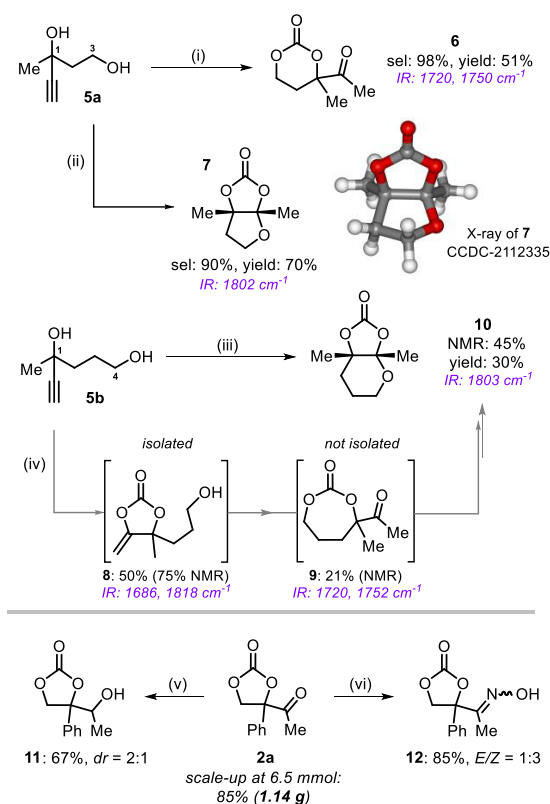**Figure 1.** DFT-calculated pathway for the conversion of (*R*)-**1a** into keto-carbonate **2a** by catalyst Ag(**L1**)OAc in the presence of carbon dioxide.

Scheme 4. Conversion of Alkyne-1,3- and Alkyne-1,4-diols 5a and 5b into Derivatives 6−10 with Their Diagnostic IR Data[a]

[a]Reaction conditions: (i) AgI/TBAOPh (5 mol %), DMSO (2.2 M), 25 °C, 24 h, 15 bar CO_2; (ii) AgI/TBAOPh (5 mol %), ACN (4.4 M), 80 °C, 24 h, 15 bar CO_2; (iii) AgI/DBU (5 mol %), ACN, 80 °C, 24 h, 15 bar CO_2; (iv) AgI/TBAOPh (5 mol %), DMSO (2.2 M), 25 °C, 24 h, 15 bar CO_2; (v) NaBH$_4$ (1.1 equiv), THF/MeOH (4:1), 0 °C, 1 h; and (vi) H$_2$NOH·HCl (2 equiv), pyr (2 equiv), EtOH, r.t., 16 h.

conditions, while the same profile holds for (*S*)-**1a** using the other catalyst enantiomer.

Finally, we examined whether the use of higher homologues of the alkyne-1,2-diols would serve as suitable reagents toward larger ring carbonates (Scheme 4) and their synthetic utility. The treatment of alkyne-1,3-diol **5a** with CO_2 (15 bar) at 25 °C in the presence of the catalyst AgI/TBAOPh in DMSO (2.2 M) gave the six-membered keto-carbonate **6** with high chemoselectivity (98%) and appreciable isolated yield (51%, see the Supporting Information for further details; entry 1, Table S5).[24] Interestingly, we found that under similar conditions while raising the reaction temperature and changing the solvent to ACN (4.4 M), the chemoselectivity changed toward a unique, bicyclic tetrasubstituted five-membered cyclic carbonate **7** (70%; entry 14, Table S5), which was unambiguously identified by X-ray crystallography.[15] Although its formation mechanism is yet unclear, we believe that **6** is a viable precursor for **7** and ring opening of **6** by the phenolate salt is likely involved, followed by rearrangement into the thermodynamically more stable product **7**. To further examine the utility of our cascade protocol, we also subjected alkyne-1,4-diol **5b** to a similar carboxylation process. After some optimization (see the Supporting Information, Table S6), we found that a bicyclic, tetrasubstituted carbonate **10** could be produced in 45% NMR yield (33% isolated) in the presence of AgI/DBU as the catalyst (entry 11, Table S6).

Analogous to the formation of **6**, product **10** needs a seven-membered keto-carbonate **9** with the alkylidene carbonate **8** being the precursor for **9**. Both could indeed be observed and identified by both ^{1}H NMR and operando IR spectroscopy (see the Supporting Information for details). These combined findings indeed suggest further potential of our cascade protocol to access otherwise elusive cyclic carbonate scaffolds.

We then finally probed whether the keto-based carbonate **2a** could be transformed while maintaining the carbonate ring intact (Scheme 4, lower part). The scale-up of **2a** was easily performed to gram quantities allowing for postsynthetic transformations to be examined. The ketone group could be reduced in the presence of NaBH$_4$ to afford the corresponding alcohol **11** in 67% yield, where the ketone could also be converted into an imine (**12**: 85% yield). These results suggest that the carbonate rings in the five-membered keto-carbonates are rather stable.

In summary, we have developed an efficient and new cascade process promoted by a Ag catalyst that involves the use of alkyne-1,2-diols as modular substrates providing access to a wide range of keto-substituted five-membered carbonates with different and unique degrees of substitutional complexity. Detailed computational analysis has shown the key rationale for the formation of these keto-carbonates, with the five-membered carbonates being the most thermodynamically stable products. Preliminary investigations focusing on applying the cascade protocol for the creation of larger ring carbonates demonstrate that these less stable analogues of their five-membered congeners can be used as intermediates of otherwise elusive tetrasubstituted carbonate scaffolds and therefore expand the synthetic importance of cascade approaches in the valorization of carbon dioxide.

■ ASSOCIATED CONTENT

Ⓢi Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c05773.

Experimental details, NMR and IR spectra, and computational details (PDF)

X-ray crystallographic analysis data (CIF)

X-ray crystallographic analysis data (CIF)

X-ray crystallographic analysis data (CIF)

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Notes

The authors declare no competing financial interest.

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(16) In the last two reactions of Table 1, a much lower chemoselectivity towards the keto-carbonate 2a was observed, with various unidentified products in the crude mixture.

(17) The Gaussian 16 program was used with implemented functional and basis set PBE0-D3(BJ)/SDD/def2tzv being chosen[14,18,19] using dispersion correction with Becke−Johnson damping.[20,21] All calculations were carried out at 298 K using an acetonitrile solvent model SMD. Full access to the computational data is provided through: http://dx.doi.org/10.19061/iochem-bd-1-214.

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(23) The (*E*)-isomer in **TS-2** and the subsequent intermediate **D** has the carbonate substituents pointing away from the biaryl section of the ligand **L1**, and the Ag and carbonate-O atom reside on the same side of the C═C bond.

(24) The choice for AgI/TBAOPh as catalyst came from a screening study, that showed better performance of this system compared to AgF/**L6** that was utilized for the product scope phase. Further to this, carbonate **6** proved to be less stable than the five-membered keto-carbonates under the chromatographic conditions and some loss of product was thus noticed upon work up. See the Supporting Information for more details. For the previous use of this catalyst see Ngassam Tounzoua, C.; Grignard, B.; Brege, A.; Jérôme, C.; Tassaing, T.; Mereau, R.; Detrembleur, C. A Catalytic Domino Approach toward Oxo-Alkyl Carbonates and Polycarbonates from CO_2, Propargylic Alcohols, and (Mono- and Di-)Alcohols. *ACS Sustainable Chem. Eng.* **2020**, *8*, 9698−9710.