Silver-catalyzed Carboxylative Cyclization of Primary Propargyl Alcohols with CO$_2$

Saumya Dabral$^{[a]}$, Bilguun Bayarmagnai$^{[a]}$, Marko Hermsen$^{[b]}$, Jasmin Schießl$^{[c]}$, Verena Mormul$^{[b]}$, A. Stephen K. Hashmi$^{[a,c]}$ and Thomas Schaub$^{*[a,b]}

[a] Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 584, 69120 Heidelberg (Germany)
[b] BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen (Germany)
[c] Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

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1. General Information

1.1. Materials and Methods

AgOAc (99.99% purity) and DavePhos (97% purity) were purchased from Sigma-Aldrich. Thin-layer chromatography (TLC) analysis was performed on Macherey-Nagel Polygram SIL G/UV254 plates. The reactions were performed in either a 90 mL Fisher-Porter tube containing a Teflon-coated stirrer bar or in a 40 mL steel autoclave equipped with a magnetic overhead stirrer purchased from Premex.

1.2. Instruments

NMR spectra were recorded on either Bruker 200 (\(^1\)H NMR: 200 MHz, \(^{13}\)C NMR: 50 MHz) at CaRLa or on a Bruker AVANCE III 400 (\(^1\)H NMR: 400 MHz, \(^{13}\)C NMR: 101 MHz) spectrometer at the Institute of Organic Chemistry/Heidelberg University. Chemical shifts (\(\delta\)) are given in ppm relative to the residual solvent peak (CD\(_3\)CN: \(\delta = 1.94\) ppm, CDCl\(_3\): \(\delta = 7.26\) ppm). Spin-spin coupling constants (\(J\)) are given in Hz. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br.s (broad singlet). Mass spectra were recorded on a Vacuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. IR spectra (in cm\(^{-1}\)) were recorded on a Varian 2000, Scimitar Series, FTS2000, as KBr pellets at room temperature. \textit{In situ} (room temperature measurements) IR spectra were recorded using a Mettler Toledo React IR 10. Crystal structure analyses were accomplished on Bruker Smart CCD or Bruker APEX diffractometers. Elemental Analysis measurements were performed by the Mikroanalytisches Laboratorium der Chemischen Institut der Universität Heidelberg. Melting points were measured with a Büchi Melting Point B-540 apparatus.

2.0. Reaction optimization for the carboxylative cyclization of 1

2.1. Protocols for carboxylation reactions

Standard procedure A

Screening reactions with propargyl alcohol 1 were performed in a ChemSpeed Accelerator SLT 106 high-throughput robot system. Alcohol 1 (1.00 mmol), [M]-catalyst (5 mol\%) and ligand (5 mol\%) in organic solvent (2 mL) were pressurized with CO\(_2\) (20 bar) and stirred at room temperature for 12 h. After releasing the CO\(_2\) overpressure, anisole (1.00 mmol) and CDCl\(_3\) (1 mL) were added to the reaction mixture and stirred for 5 min. The resulting mixture was analysed by \(^1\)H NMR to determine the yield.

Standard procedure B

A Fisher-Porter tube with Teflon-coated stirrer-bar was charged with 1 (5.00 mmol), [M]-catalyst (5 mol\%), and ligand (5 mol\%) and solvent (5 mL). The reaction mixture was pressurized with CO\(_2\) (8 bar) and stirred at room temperature for 16 h. Then CO\(_2\) overpressure was carefully released and solvent evaporated. For recyclability test, the resulting crude mixture was distilled by a Kugelrohr (0.5 mbar, 100 °C). The corresponding cyclic carbonate product was obtained pure. A fresh batch of propargyl alcohol 1 in DCM was then added to the remaining silver-DavePhos crude under CO\(_2\) pressure and the process was repeated.
2.2. Table S1. Screening of various ligands for the carboxylative cyclization of 1 to 2.[a]

| Ligand | Yield (1) | Yield (2) | Yield (3) |
|--------|-----------|-----------|-----------|
| L1     | 185%      | 20%       | 30%       |
| L2     | 151%      | 20%       | 30%       |
| L3     | 138%      | 20%       | 30%       |
| L4     | 195%      | 34%       | 30%       |
| L5     | 133%      | 30%       | 30%       |
| L6     | 211%      | 241%      | 315%      |
| L7     | 10%       | 241%      | 315%      |
| L8     | 10%       | 280%      | 320%      |
| L9     | 10%       | 251%      | 327%      |
| L10    | 10%       | 274%      | 327%      |
| L11    | 10%       | 243%      | 35%       |
| L12    | 10%       | 254%      | 315%      |
| L13    | 10%       | 247%      | 320%      |
| L14    | 10%       | 262%      | 318%      |
| L15    | 10%       | 262%      | 33%       |
| L16    | 10%       | 232%      | 34%       |
| L17    | 10%       | 234%      | 36%       |
| L18    | 10%       | 21%       | 30%       |
| L19    | 10%       | 195%      | 30%       |
| L20    | 10%       | 210%      | 310%      |
| L21    | 10%       | 239%      | 32%       |
| L22    | 10%       | 238%      | 32%       |
| L23    | 10%       | 129%      | 32%       |
| L24    | 10%       | 130%      | 32%       |
| L25    | 10%       | 241%      | 32%       |
| L26    | 10%       | 257%      | 32%       |
| L27    | 10%       | 277%      | 32%       |
| L28    | 10%       | 128%      | 32%       |
| L29    | 10%       | 130%      | 32%       |
| L30    | 10%       | 178%      | 32%       |
| L31    | 10%       | 195%      | 32%       |
| L32    | 10%       | 172%      | 35%       |

[a]Yields were determined by $^1$H NMR spectroscopy using anisole as an internal standard
### 2.3. Table S2. Screening of various metal salts for the carboxylative cyclization of 1 to 2

![Diagram](image)

| Entry | [M] | Ligand | 2 [%][a] |
|-------|-----|--------|----------|
| 1     | AgOAc | DavePhos | 98       |
| 2     | -    | DavePhos | 0        |
| 3     | AgOAc | -      | 0        |
| 4     | Cs₂CO₃ | DavePhos | 0        |
| 5     | NaOAc | DavePhos | 0        |
| 6     | AgBF₄[b] | DavePhos | 0        |
| 7     | PdCl₂ | DavePhos | 0        |
| 8     | XPhos AuNTf₂ | - | 0        |
| 9     | AuCl | DavePhos | 0        |
| 10    | [Au][c] | - | 0        |
| 11    | PPh₃AuCl | DavePhos | 0        |
| 12    | RuCl₃ | DavePhos | 0        |
| 13    | Ru₃CO₁₂ | DavePhos | 0        |
| 14    | Ru₃CO₁₂ | DMAP | 0        |
| 15    | Ru₃CO₁₂ | NEt₃ | 0        |
| 16    | Ru₃CO₁₂ | 2,2'-bipyridine | 0        |
| 17    | ZnI₂ | DavePhos | 0        |
| 18    | ZnI₂ | DMAP | 0        |
| 19    | ZnI₂ | 1,10-phenanthroline | 0        |
| 20    | ZnI₂ | 2,2'-bipyridine | 0        |
| 21    | ZnI₂ | DBU | 0        |
| 22    | ZnI₂ | NEt₃ | 0        |
| 23    | CuI | DavePhos | 0        |
| 24    | CuI | DMAP | 0        |
| 25    | CuI | 1,10-phenanthroline | 0        |
| 26    | CuI | 2,2'-bipyridine | 0        |
| 27    | CuI | DBU | 0        |
| 28    | CuOAc | DavePhos | traces |
| 29    | CuOAc | DMAP | 0        |
| 30    | CuOAc | 1,10-phenanthroline | 0        |
| 31    | CuOAc | 2,2'-bipyridine | 0        |
| 32    | CuOAc | DBU | 0        |
| 33    | CuOAc | NEt₃ | 0        |

Reaction conditions: Propargyl alcohol 1 (1 mmol), [M]-catalyst (5 mol%) and ligand (5 mol%) in anhydrous DCM (2 mL) were pressurized with CO₂ (20 bar) and stirred for 12 h. [a] Yields were determined by ¹H NMR spectroscopy using anisole as an internal standard. [b] 5 mol% NaOAc. [c] 5 mol% [Bis(trifluoromethanesulfonyl)imide](PPh₃)gold(I).
2.4. Table S3. Screening of solvents for the carboxylative cyclization of 1 to 2

![Chemical structure of 1 to 2]

| Entry | solvent  | Yield 2 [%][a] |
|-------|----------|---------------|
| 1     | DCM      | 98            |
| 2     | acetone  | 96            |
| 3     | DMF      | 84            |
| 4     | MeCN     | 85            |
| 5     | 1,4-dioxane | 0         |
| 6     | toluene  | 0             |

Reaction conditions: Propargyl alcohol 1 (5 mmol), AgOAc (5 mol%) and DavePhos (5 mol%) in solvent (5 mL) were pressurized with CO$_2$ (8 bar) and stirred for 16 h. [a] Yields were determined by $^1$H NMR spectroscopy using anisole as an internal standard.

2.5. Table S4. Recycling the Ag-Davephos catalytic system.

![Chemical structure of 1 to 2]

| Cycle (Recycling the catalyst system) | Yield 2 [%][b] |
|--------------------------------------|---------------|
| 1                                    | 98            |
| 2                                    | 84            |
| 3                                    | 70            |
| 4                                    | 70            |

[a] Propargyl alcohol 1 (5 mmol), Ag salt (5 mol%) and additive (5 mol%) in anhydrous DCM (2 mL) were pressurized with CO$_2$ (8 bar) and stirred for 16 h. After a Kugelrohr-Distillation (100 °C, 0.5 mbar) product 2 was isolated and the residual crude used for further reaction. [b] Isolated yields.

The recyclability of this catalytic system was shown by simply distilling out product 2 from the reaction mixture and adding a fresh batch of propargyl alcohol 1 in DCM to the remaining silver-DavePhos crude (Table S4). Under CO$_2$ pressure, this step could be repeated up to four times thus demonstrates the utility and robustness of the new system in first attempts No silver-mirror or silver black formation was observed in the recycling.
3.0. Synthesis of but-2-ynol derivatives as starting materials

4-hydroxybut-2-yn-1-yl acetate\([\text{I}]\) (5a)

\[
\text{HO-CH} &=& \text{OH} \\
(1.0 \text{ eq.}) \\
\text{Et}_3\text{N} \quad \text{(1.4 eq.)} \\
\text{DCM/THF (3:1)} \\
\text{45\%} \\
\text{Colorless liquid}
\]

Distilled Et\(_3\)N (11.3 mL, 81.3 mmol, 1.4 eq.) was added to a solution of but-2-yn-1,4-diol (5.0 g, 58.0 mmol, 1.0 eq.) in dry DCM/THF (24 mL/8 mL), and the resulting suspension was stirred at room temperature until dissolution was complete. Acetic acid anhydride (6.0 mL, 63.7 mmol, 1.1 eq.) was then added dropwise to the reaction mixture at 0 °C over 30 min. The reaction mixture was then warmed to room temperature and stirred overnight. Water was added and the reaction mixture was extracted with DCM (4 × 30 mL). The collected organic layers were dried over anhydrous Na\(_2\)SO\(_4\) and the solvents were evaporated under vacuum. Flash chromatography of the crude products (silica gel, EtOAc/PE 2:3) gave the pure product (\(R_f = 0.33\)) as a colourless oil (3.34 g, 45%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 4.63\) (t, \(J = 1.8\) Hz, 2 H), 4.22 (t, \(J = 1.8\) Hz, 2 H), 3.17 (br.s, 1 H), 2.03 (s, 3 H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 170.7, 85.2, 79.2, 52.4, 50.5, 20.7\).

IR (film): \(\nu = 3433, 3019, 2944, 2404, 1743\) (C=O) cm\(^{-1}\).

HRMS (EI): \(m/z\) calcd. for C\(_6\)H\(_8\)O\(_3\) : 128.0468 [M\(^+\)]; found: 128.0461.

4-hydroxybut-2-yn-1-yl methyl carbonate\([\text{II}]\) (6a)

But-2-yn-1,4-diol (15 g, 174 mmol, 3.0 eq.) dissolved in anhydrous DCM (350 mL) was cooled to 0 °C. \(N,N\)-diisopropylethylamine (DIPEA, 32.5 mL, 191.7 mmol, 3.3 eq.) and \(N,N\)-dimethylpyridin-4-amine (DMAP, 708 mg, 5.8 mmol, 0.1 eq.) were then added to the above solution followed by the dropwise addition of methyl chloroformate (4.49 mL, 58.1 mmol, 1.0 eq.) via a syringe. The reaction mixture was stirred at 0 °C for 2 h followed by stirring overnight at room temperature. The reaction mixture was concentrated to half of its original volume followed by the addition of Et\(_2\)O (60 mL) and sat. NaHCO\(_3\) (60 mL). The phases were separated and the organic phase was washed three times with sat. NaHCO\(_3\) before drying it over MgSO\(_4\). The solvent was removed under reduced pressure and the crude was purified by column chromatography (silica gel, EtOAc/PE 2:3) yielding the product (\(R_f = 0.32\)) as a colourless oil (7.3 g, 87%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.76\) (t, \(J = 1.8\) Hz, 2 H), 4.30 (t, \(J = 1.8\) Hz, 2 H), 3.81 (s, 3 H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 155.3, 85.9, 79.1, 55.6, 55.2, 50.9\).

IR (film): \(\nu = 3418, 3013, 2961, 2865, 1742\) (C=O), 1587, 1449, 1378, 1284, 1141, 1022, 949, 903, 791, 607, 565, 534.

HRMS (EI): \(m/z\) calcd. for C\(_6\)H\(_8\)O\(_4\): 144.0417 [M\(^+\)]; found: 144.0408.
4-(benzyloxy)but-2-yn-1-ol[2] (7a)

But-2-yne-1,4-diol (3.9 g, 45.3 mmol, 2.0 eq.) was added into a solution of KOH (2.5 g, 45.3 mmol, 2.0 eq.) in water (40 mL). The mixture was stirred for 10 min at room temperature. Benzyl bromide (3.9 g, 22.6 mmol, 1.0 eq.) was then added dropwise into the above solution and the mixture was stirred for 2 days at room temperature. The reaction mixture was extracted with DCM, the combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The organic layer was concentrated under vacuum. Flash chromatography on silica gel (EtOAc/PE 3:7) yielded the desired mono-benzylated alcohol (Rf = 0.31) as colourless oil (3.0 g, 75%).

1H NMR (400 MHz, CDCl₃): δ = 7.25–7.15 (m, 5 H), 4.48 (s, 2 H), 4.17 (t, J = 1.8 Hz, 2 H), 4.10 (t, J = 1.8 Hz, 2 H), 2.81 (s, 1 H). 13C NMR (101 MHz, CDCl₃): δ = 137.2, 128.4 (2 C), 128.1, 127.9 (2 C), 85.1, 81.3, 71.7, 57.4, 50.7. IR (film): ν = 3386, 2922, 2866, 1716 (C=O), 1497, 1454, 1385, 1354, 1265, 1209, 1126, 1071, 1027, 938, 805, 748, 699, 606. HRMS (EI): m/z calcd. for C₁₁H₁₂O₂: 176.0832 [M+]; found: 176.0827.

4-hydroxybut-2-yn-1-yl methacrylate (8a)

Distilled Et₃N (5.6 mL, 40.6 mmol, 1.4 eq.) was added to a solution of but-2-yne-1,4-diol (2.5 g, 29.0 mmol, 1.0 eq.) in dry DCM/THF (12 mL/4 mL), and the resulting suspension was stirred at room temperature until dissolution was complete. Methacrylic anhydride (4.75 mL, 31.9 mmol, 1.1 eq.) was then added dropwise to the reaction mixture at 0 °C over 30 min. The reaction mixture was then warmed to room temperature and stirred overnight. Water was added and the reaction mixture was extracted with DCM (2 × 30 mL). The collected organic layers were dried over anhydrous Na₂SO₄ and the solvents were evaporated under vacuum. Flash chromatography of the crude products (silica gel, EtOAc/PE 3:7) gave the pure product (Rf = 0.24) as a colourless oil (2.3 g, 52%).

1H NMR (400 MHz, CDCl₃): δ = 6.12–6.13 (m, 1 H), 5.60–5.58 (s, 1 H), 4.76 (t, J = 1.8 Hz, 2 H), 4.27 (t, J = 1.8 Hz, 2 H), 2.61 (br.s, 1 H), 1.93–1.92 (m, 3 H). 13C NMR (101 MHz, CDCl₃): δ = 166.9, 135.7, 126.7, 85.2, 79.7, 52.6, 50.9, 18.3. IR (film): ν = 3428, 2930, 2868, 1723 (C=O), 1637, 1438, 1405, 1317, 1295, 1153, 1013, 972, 946, 815, 653, 569, 526. HRMS (EI): m/z calcd. for C₈H₁₀O₃: 154.0625 [M⁺]; found: 154.0618.
2-(((4-hydroxybut-2-yn-1-yl)oxy)carbonyl)amino)ethyl methacrylate (9a)

Distilled Et₃N (8.9 mL, 63.8 mmol, 1.1 eq.) was added to a solution of but-2-yne-1,4-diol (5.0 g, 58.0 mmol, 1.0 eq.) in dry DCM/THF (24 mL/8 mL), and the resulting suspension was stirred at room temperature until dissolution was complete. 2-isocyanatoethyl methacrylate (8.2 mL, 58.0 mmol, 1.0 eq.) was then added dropwise to the reaction mixture at 0 °C over 30 min. The reaction mixture was then warmed to room temperature and stirred overnight. Water was added and the reaction mixture was extracted with DCM (4 × 30 mL). The collected organic layers were dried over anhydrous Na₂SO₄ and the solvents were evaporated under vacuum. Flash chromatography of the crude (silica gel, EtOAc/PE 7:3) gave the pure product (Rᵣ = 0.35) as a colourless oil (8.4 g, 60%).

¹H NMR (400 MHz, CDCl₃): δ = 6.13–6.12 (m, 1 H), 5.61–5.60 (s, 1 H), 5.06 (br.s, 1 H), 4.73 (s, 2 H), 4.31–4.30 (m, 2 H), 4.26–4.23 (m, 2 H), 3.54–3.50 (m, 2 H), 1.95 (s, 3 H), 1.73 (br.s, 1 H). ¹³C NMR (101 MHz, CDCl₃): δ = 167.2, 155.5, 135.9, 126.1, 84.9, 80.2, 63.6, 52.9, 51.1, 14.0, 18.3. IR (film): ν = 3362, 2956, 1704 (C=O), 1636, 1535, 1453, 1321, 1298, 1151, 1019, 951, 816, 774, 653. HRMS (ESI): m/z calcd. for C₁₁H₁₅NO₅: 264.0842 [M+Na⁺]; found: 264.0842.

4,4'-(1,4-phenylenebis(methylene))bis(oxy))bis(but-2-yn-1-ol) (14a)

But-2-yne-1,4-diol (2.6 g, 30.2 mmol, 4.0 eq.) dissolved in anhydrous THF (10 mL) was added dropwise into a 100 mL argon flushed three-neck round bottom flask containing a solution of NaH (0.37 g, 15.2 mmol, 2.0 eq.) in anhydrous THF (12 mL). After stirring for 30 min, 1,4-bis(bromomethyl) benzene (1.97 g, 7.55 mmol, 1.0 eq.) was added and the mixture was refluxed overnight. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, EtOAc/PE 7:3) to afford the desired product (Rᵣ = 0.44) as white solid (1.62 g, 78%).

¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.27 (m, 4 H), 4.60 (s, 4 H), 4.33 (m, 4 H), 4.21 (t, J = 1.8 Hz, 4 H), 1.59 (br.s, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ = 137.2 (2 C), 128.4 (4 C), 84.9 (2 C), 81.9 (2 C), 71.6 (2 C), 57.6 (2 C), 51.3 (2 C). IR (KBr): ν = 3279, 3201, 2914, 1402, 1368, 1342, 1236, 1138, 1069, 1007, 989, 839, 759, 585, 537 cm⁻¹. HRMS (EI): m/z calcd. for C₁₆H₁₈O₄: 274.1176 [M⁺]; found: 274.1199.
bis(4-hydroxybut-2-yn-1-yl) (4-methyl-1,3-phenylene)dicarbamate (15a)

\[
\begin{align*}
\text{C}_{5}\text{H}_{5}N\text{CO} + \text{HO} \equiv \text{C} \equiv \text{OH} & \quad 120{}^\circ C \quad 1 \text{h} \quad \text{Ar} \\
\text{Colorless solid mp: 99.6–100.2} \ {}^\circ C
\end{align*}
\]

2,4-diisocyanato-1-methylbenzene (1.0 g, 5.8 mmol, 1.0 eq.) dissolved in anhydrous DMF (5.0 mL) was added dropwise (2 drop/sec) into an argon purged 100 mL three-neck round bottom flask containing but-2-yne-1,4-diol (1.5 g, 17.4 mmol, 3.0 eq.) at 120 °C. After the addition was complete, the reaction mixture was further stirred for 1 h at 120 °C after which it was brought down to room temperature. Distilled water (90 mL) was then added to the above reaction mixture and the product was let to crystallize in the freezer overnight. The crystals were filtered and recollected in a 250 mL round bottom flask containing 150 mL water. The mixture was then refluxed at 110 °C, followed by hot filtration. The oligomers were separated by filtration while the filtrate at the bottom was cooled down to obtain the product as a white solid (1.2 g, 60%).

\(^1\text{H NMR (400 MHz, CD}_3\text{CN):} \delta = 7.79 (\text{br.s, 1 H}), 7.73 (\text{br.s, 1 H}), 7.21 (\text{s, 1 H}), 7.18–7.15 (\text{m, 1 H}), 7.13–7.11 (\text{m, 1 H}), 4.78 (\text{t, J = 1.8 Hz, 2 H}), 4.76 (\text{t, J = 1.8 Hz, 2 H}), 4.21–4.18 (\text{m, 4 H}), 3.18–3.14 (\text{m, 2 H}), 2.18 (\text{s, 3 H}). \ ^{13}\text{C NMR (101 MHz, CD}_3\text{CN):} \delta = 154.4, 153.9, 137.8, 137.2, 131.6, 126.0, 116.2, 114.4, 86.5 (2 \text{ C}), 80.0 (2 \text{ C}), 53.6 (2 \text{ C}), 53.4, 50.6, 17.3. \text{IR (KBr):} \nu = 3292, 1704 (\text{C=O}), 1605 (\text{C=O}), 1539, 1498, 1451, 1429, 1318, 1283, 1235, 1185, 1144, 1060, 1015, 882, 817, 762 \text{ cm}^{-1}. \text{HRMS (ESI):} m/z \text{ calcd. for } \text{C}_{17}\text{H}_{18}\text{N}_{2}\text{O}_{6}: 369.106 [\text{M+Na}^+] \text{; found: 369.106.}

1,8-Bis(4-hydroxy-2-butyn-1-oxy)-3,6-dioxaoctane\[^4\] (16a)

The diol was synthesized in two steps.

**Step 1:** Synthesis of 4,7,10,13-tetraoxahexadeca-1,15-diyne

In an argon flushed 100 mL three-neck round bottom flask was charged a solution of 2,2’-(ethane-1,2-diylbis(oxy))bis(ethan-1-ol) (2.13 g, 14.2 mmol, 1.0 eq.) in THF (5 mL) to a cooled (0 °C) suspension of t-BuOK (3.67 g, 32.6 mmol, 2.3 eq.) in 30 mL of THF.
The resulting reaction mixture was allowed to warm to room temperature and was then added dropwise to an ice cooled solution (0 °C) of propargyl bromide (6.3 mL, 80% w/w, 56.5 mmol, 4.0 eq.) in 120 mL of THF, under argon atmosphere. The reaction mixture was stirred for an additional 18 h and the reaction let to warm to room temperature. A 3:1 brine/water (75 mL) solution was then added to the above mixture and the aqueous layer was extracted with EtOAc (3 × 50 mL) followed by drying in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/PE 1:1) to afford bis(propargyl ether) (2.24 g, 70%) as yellow oil.

**Step 2:** Synthesis of 1,8-Bis(4-hydroxy-2-butyn-1-oxy)-3,6-dioxaoctane

In an argon-flushed 250 mL three-neck round bottom flask was added a solution of bis(propargyl) ether (2.5 g, 11.0 mmol, 1 eq.) in 91 mL of THF and TMEDA (16.7 mL, 110 mmol, 10 eq.). The mixture was then cooled to -78 °C, followed by the drop-wise addition of n-BuLi (16.5 mL, 1.6 M solution, 26.6 mmol, 2.4 eq.). After an additional 5 min stirring, a suspension of paraformaldehyde (7.2 g, 240 mmol) in 7 mL of THF under argon was added via syringe. The reaction mixture was slowly allowed to warm to room temperature and stirred for an additional 1 h before diluting with 150 mL of saturated aqueous NaH$_2$PO$_4$. The aqueous layer was extracted with EtOAc (3 × 60 mL), and the combined organic layers were washed with 120 mL of saturated NaHCO$_3$ and 120 mL of brine. The residue upon drying and concentration was purified by flash chromatography on silica gel (EtOAc/Methanol 98:2) to afford the diol ($R_f$ 0.35) as a pale yellow solid (1.3 g, 42%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 4.25 (t, $J = 1.8$ Hz, 4 H), 4.20 (t, $J = 1.8$ Hz, 4 H), 3.67–3.63 (m, 12 H), 3.05 (br.s, 2 H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 85.2 (2 C), 81.3 (2 C), 70.6 (2 C), 70.5 (2 C), 69.1 (2 C), 58.7 (2 C), 50.7 (2 C). IR (film): $\nu =$ 3383, 2912, 2873, 2240, 1715, 1457, 1349, 1252, 1119, 1093, 943, 843, 616. HRMS (ESI): m/z calcd. for C$_{14}$H$_{22}$O$_6$: 309.131 [M+Na$^+$]; found: 309.131.

### 4.0. General procedure for the carboxylative cyclization of but-2-ynol derivatives

The corresponding alkylnols used for the synthesis of the exo-vinylencarbonates 2, 5, 6, 7, 8, 9, 14, 15 and 16 were prepared according to the procedures give above. The corresponding alkylnols for the synthesis of the exo-vinylencarbonates 2, 4, 10, 11, 12 and 13 where purchased by Aldrich and used as received.

A steel autoclave was charged with the corresponding Alkylnol (5.0 mmol), AgOAc (1 or 2 mol%), Davephos-Ligand (1 or 2 mol%) and solvent (10 mL) under atmospheric conditions. The reaction mixture was pressurized with CO$_2$ (20 bar) and stirred at room temperature for 18 h. Then CO$_2$ overpressure was carefully released and solvent evaporated. The resulting crude mixture was purified by flash column chromatograph on silica gel (the solvents used for the flash chromatography are given for each compound in brackets after the $R_f$).
5.0. Characterization of the isolated exo-vinylene carbonate products

4-methylokene-1,3-dioxolan-2-one\(^{[6]}\) (2)

White solid, 450 mg (90%), mp: 28.3–29.0 °C. \(R_f\) (EtOAc/PE 3:7) = 0.38. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 4.98–4.96\) (m, 2 H), 4.84–4.80 (m, 1 H), 4.42–4.37 (m, 1 H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 152.8, 148.8, 87.1, 67.6\). IR (KBr): \(\nu = 2974, 1836\) (C=O), 1695, 1394, 1464, 1359, 1287, 1128, 1062, 974, 853, 767, 727 cm\(^{-1}\). HRMS (EI): \(m/z\) calcd. for C\(_4\)H\(_4\)O\(_3\): 100.0155 [M\(^{+}\)]; found: 100.0154.

(Z)-4-(2-hydroxyethylidene)-1,3-dioxolan-2-one (4)

Colorless oil, 423 mg (65%). \(R_f\) (EtOAc/PE 1:1) = 0.62. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 4.97–4.88\) (m, 3 H), 4.18–4.15 (m, 2 H), 3.33 (s, 1 H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 152.9, 143.2, 102.4, 67.6, 55.7\). IR (KBr): \(\nu = 3649, 3565, 3134, 3026, 2974, 2416, 2261, 1856\) (C=O), 1812, 1694, 1465, 1395, 1359, 1287, 1129, 1062, 974, 853, 767, 727, 548 cm\(^{-1}\). HRMS (EI): \(m/z\) calcd. for C\(_5\)H\(_6\)O\(_4\): 130.0260 [M\(^{+}\)]; found: 130.0259.

(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl acetate (5)

Colorless oil, 688 mg (80%). \(R_f\) (EtOAc/PE 3:7) = 0.35. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.01–4.92\) (m, 3 H), 4.71–4.67 (m, 2 H), 2.05 (m, 3 H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 170.8, 152.0, 145.4, 97.9, 67.4, 57.7, 20.9\). IR (KBr): \(\nu = 2971, 2257, 1830\) (C=O), 1727 (C=O), 1462, 1374, 1435, 1132, 1231, 1096, 1028, 965, 765, 733 cm\(^{-1}\). HRMS (EI): \(m/z\) calcd. for C\(_7\)H\(_8\)O\(_5\): 172.0366 [M\(^{+}\)]; found: 172.0391. Anal. Calcd. for C\(_7\)H\(_8\)O\(_5\): C 48.84%, H 4.68%, Found: C 49.23%, H 5.00%.

(Z)-methyl (2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) carbonate (6)

Colorless oil, 611 mg (65%). \(R_f\) (EtOAc/PE 3:7) = 0.24. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.02–4.97\) (m, 3 H), 4.81–4.77 (m, 2 H), 3.80 (s, 3 H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 155.8, 152.0, 146.1, 97.5, 67.5, 61.1, 55.3\). IR (KBr): \(\nu = 3017, 2967, 2351, 2214, 1834\) (C=O), 1749 (C=O), 1681, 1448, 1371, 1262, 1130, 1050, 943, 766, 567 cm\(^{-1}\). HRMS (EI): \(m/z\) calcd. for C\(_7\)H\(_8\)O\(_6\): 188.0315 [M\(^{+}\)]; found: 188.0303. Anal. Calcd. for C\(_7\)H\(_8\)O\(_6\): C 44.69, H 4.29%, Found: C 44.41%, H 5.13%.

(Z)-4-(2-(benzyloxy)ethylidene)-1,3-dioxolan-2-one (7)

Colorless oil, 770 mg (70%). \(R_f\) (EtOAc/PE 3:7) = 0.44. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.37–7.29\) (m, 5 H), 4.99–4.92 (m, 3 H), 4.53 (s, 2 H), 4.23–4.18 (m, 2 H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 152.4, 144.0, 137.9, 128.5\) (2 C), 127.9 (3 C), 100.3, 72.8, 67.4, 63.4. IR (KBr): \(\nu = 3065, 3038, 3032, 2867, 1839\) (C=O), 1723, 1455, 1381, 1274, 1210, 1108, 1045, 912, 734, 700 cm\(^{-1}\). HRMS (EI): \(m/z\) calcd.
for C\textsubscript{12}H\textsubscript{12}O\textsubscript{4}: 220.0730 [M\textsuperscript{+}]; found: 220.0735. Anal. Calcd. for C\textsubscript{12}H\textsubscript{12}O\textsubscript{4}: C 65.45%, H 5.49%, Found: C 65.40%, H 5.53%.

\textbf{(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl methacrylate (8)}

White solid, 812 mg (82%). mp: 36.1–36.3 °C. \textit{R\textsubscript{f}} (EtOAc/PE 3:7) = 0.52. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 6.12–6.11 (m, 1 H), 5.59–5.58 (m, 1 H), 5.02–4.99 (m, 3 H), 4.80–4.78 (m, 2 H), 1.94 (s, 3 H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 167.2, 152.1, 145.4, 136.1, 126.2, 98.1, 67.4, 58.0, 18.4. IR (KBr): \textbf{\nu} = 3402, 2933, 2356, 216.9, 1818 (C=O), 1707 (C=O), 1632, 1534, 1455, 1400, 1383, 1326, 1288, 1229, 1156, 1133, 1088, 1045, 1011, 971, 920, 868, 841, 817, 766, 732, 645, 617, 571 cm\textsuperscript{-1}. HRMS (EI): \textit{m/z} calcd. for C\textsubscript{9}H\textsubscript{10}O\textsubscript{5}: 198.0523 [M\textsuperscript{+}]; found: 198.0519. Anal. Calcd. for C\textsubscript{9}H\textsubscript{10}O\textsubscript{5}: C 54.55%, H 5.09%, Found: C 54.77%, H 5.13%.

\textbf{(Z)-2-(((2-(2-oxo-1,3-dioxolan-4-ylidene)ethoxy)carbonyl)amino)ethyl methacrylate (9)}

White solid, 1.34 g (94%). mp: 86.5–86.7 °C. \textit{R\textsubscript{f}} (EtOAc/PE 1:1) = 0.24. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 6.12–6.11 (m, 1 H), 5.59–5.57 (m, 1 H), 5.00–4.97 (m, 3 H), 4.71–4.69 (m, 2 H), 4.24–4.21 (m, 2 H), 3.51–3.47 (m, 2 H), 1.94 (s, 3 H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 167.4, 156.2, 152.1, 145.2, 136.1, 126.2, 98.6, 67.4, 63.7, 58.3, 40.4, 18.4. IR (KBr): \textbf{\nu} = 3360, 3060, 1826 (C=O), 1726 (C=O), 1690 (C=O), 1632, 1539, 1471, 1437, 1385, 1327, 1306, 1253, 1217, 1139, 1046, 1012, 967, 936, 873, 805, 760, 736, 621, 557 cm\textsuperscript{-1}. HRMS (ESI): \textit{m/z} calcd. for C\textsubscript{12}H\textsubscript{15}NO\textsubscript{7}: 308.074 [M+Na\textsuperscript{+}]; found: 308.074. Anal. Calcd. for C\textsubscript{12}H\textsubscript{15}NO\textsubscript{7}: C 50.53%, H 5.30%, N 4.91%, Found: C 50.24%, H 5.06%, N 5.06%.

\textbf{4-methyl-5-methylene-1,3-dioxolan-2-one[6]} (10)

Light yellow oil, 524 mg (92%). \textit{R\textsubscript{f}} (EtOAc/PE 3:7) = 0.57. \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 5.31–5.20 (m, 1 H), 4.82 (dd, \textit{J} = 4.0 Hz, 2.5 Hz, 1 H), 4.35 (dd, \textit{J} = 4.0 Hz, 2.0 Hz m, 1 H), 1.56 (d, \textit{J} = 6.5 Hz, 3 H). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}): \textbf{\textdelta} = 154.7, 152.0, 86.7, 76.3, 20.5. IR (KBr): \textbf{\nu} = 2991, 1837 (C=O), 1752, 1686, 1458, 1379, 1351, 1324, 1156, 1112, 1080, 1044, 1007, 856, 769, 710, 640, 587, 556 cm\textsuperscript{-1}. HRMS (EI): \textit{m/z} calcd. for C\textsubscript{5}H\textsubscript{6}O\textsubscript{3}: 114.0311 [M\textsuperscript{+}]; found: 114.0326.
4,4-dimethyl-5-methylene-1,3-dioxolan-2-one\textsuperscript{[6]} (11)

Viscous oil, 557 mg (87\%). $R_f$ (EtOAc/PE 3:7) = 0.65. $^1$H NMR (200 MHz, CDCl$_3$): $\delta =$ 4.74 (d, $J =$ 3.9 Hz, 1 H), 4.31 (d, $J =$ 3.9 Hz, 1 H), 1.58 (s, 6 H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta =$ 158.8, 151.3, 85.4, 84.7, 27.6 (2 C). HRMS (EI): m/z calcd. for C$_6$H$_8$O$_3$: 128.0468 [M$^+$]; found: 128.0469.

(Z)-5-(2-hydroxy-2-methylpropylidene)-4,4-dimethyl-1,3-dioxolan-2-one\textsuperscript{[7]} (12)

Colorless oil, 837 mg (90\%). $R_f$ (EtOAc/PE 3:7) = 0.26. $^1$H NMR (200 MHz, CDCl$_3$): δ = 4.70 (s, 1 H), 2.91 (s, 1 H), 1.42 (s, 6 H), 1.27 (s, 6 H). $^{13}$C NMR (50 MHz, CDCl$_3$): δ = 151.1, 149.0, 109.6, 84.9, 69.4, 29.8 (2 C), 27.4 (2 C). IR (KBr): $\nu =$ 3461, 2982, 2937, 1818 (C=O), 1712, 1548, 1563, 1373, 1286, 1250, 1168, 1055, 1023, 980, 924, 770 cm$^{-1}$. HRMS (ESI): m/z calcd. for C$_9$H$_{14}$O$_4$: 187.0965 [M$^+$+H$^+$]; found: 187.0968.

4-methyl-5-methylene-4-(4-methylpent-3-en-1-yl)-1,3-dioxolan-2-one (13)

Colorless oil, 922 mg (94\%). $R_f$ (EtOAc/PE 3:7) = 0.81. $^1$H NMR (300 MHz, CDCl$_3$): δ = 5.07–5.01 (m, 1 H), 4.80 (d, $J =$ 3.9 Hz, 1 H), 4.27 (d, $J =$ 3.9 Hz, 1 H), 2.15–1.97 (m, 2 H) 1.94–1.84 (m, 1 H), 1.76–1.68 (m, 1 H), 1.66 (s, 3 H), 1.57 (s, 6 H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 157.7, 151.5, 133.3, 122.0, 87.2, 85.6, 40.3, 26.6, 25.7, 22.0, 17.7. IR (KBr): $\nu =$ 2981, 1829 (C=O), 1685, 1451, 1379, 1303, 1260, 1221, 1183, 1154, 1121, 1102, 1069, 1033, 767 cm$^{-1}$. HRMS (EI): m/z calcd. for C$_{11}$H$_{16}$O$_3$: 196.1094 [M$^+$]; found: 196.1113. Anal. Calcd. for C$_{11}$H$_{16}$O$_3$: C 67.32%, H 8.22%, Found: C 66.94%, H 8.34%.

(4Z,4′Z)-4,4′-(((1,4-phenylenebis(methylene))bis(oxy))bis(ethan-2-yl-1-ylidene))bis(1,3-dioxolan-2-one) (14)

White solid, 1.56 g (86\%), mp: 108.6–109.0 °C. $R_f$ (EtOAc/PE 9:1) = 0.71. $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.33–7.26 (m, 4 H), 5.00–4.93 (m, 6 H), 4.52 (m, 4 H), 4.21–4.16 (m, 4 H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 152.2 (2 C), 144.0 (2 C), 137.4 (2 C), 128.0 (4 C), 100.3 (2 C), 72.5 (2 C), 67.3 (2 C), 63.3 (2 C). IR (KBr): $\nu =$ 2855, 1833 (C=O), 1702, 1461, 1385, 1295, 1212, 1134, 1085, 1055, 1035, 976, 905, 835, 821, 763 cm$^{-1}$. HRMS (ESI): m/z calcd. for C$_{18}$H$_{18}$O$_8$: 363.107 [M$^+$+H$^+$]; found: 363.107. Anal. Calcd. for C$_{18}$H$_{18}$O$_8$: C 59.67%, H 5.01%, Found: C 59.54%, H 4.76%.
bis((Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) (4-methyl-1,3-phenylene) dicarbamate (15)

White solid, 2.02 g (93%), mp: 175.5–176.1 °C. $R_t$ (EtOAc/PE 1:1) = 0.15. $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ = 7.75–7.70 (m, 2 H), 7.12–7.11 (m, 3 H), 5.05–5.00 (m, 6 H), 4.76–4.69 (m, 4 H), 2.17 (s, 3 H). $^{13}$C NMR (101 MHz, CD$_3$CN): $\delta$ = 154.9, 154.4, 153.7, 147.3 (2C), 138.1, 137.4, 131.6 (2 C), 125.7, 116.1, 114.4, 98.2 (2 C), 68.9 (2 C), 59.2, 59.0, 17.3. IR (KBr): $\nu$ = 3360, 1830 (C=O), 1723, 1606, 1542, 1457, 1387, 1284, 1224, 1179, 1130, 1098, 1042, 874, 815, 764, 730, 666 cm$^{-1}$. HRMS (ESI): m/z calcd. for C$_{19}$H$_{18}$N$_2$O$_{10}$: 457.086 [M+Na$^+$]; found: 457.085. Anal. Calcd. for C$_{19}$H$_{18}$N$_2$O$_{10}$: C 52.54%, H 4.18%, N 6.45%, Found: C 52.62%, H 4.22%, N 6.55%.

(4Z,4″Z)-4,4″-((3,6,9,12-tetraoxatetradecane-1,14-diylidene)bis(1,3-dioxolan-2-one) (16)

Colorless oil, 1.78 g (95%). $R_t$ (EtOAc /MeOH 98:2) = 0.38. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.00–4.90 (m, 6 H), 4.20–4.15 (m, 4 H), 3.65–3.58 (m, 12 H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 152.4 (2 C), 144.1 (2 C), 100.4 (2 C), 70.8 (2 C), 70.7 (2 C), 69.9 (2 C), 67.5 (2 C), 64.3 (2 C). IR (KBr): $\nu$ = 2872, 1833 (C=O), 1723, 1464, 1381, 1297, 1214, 1131, 1106, 1046, 949, 870, 765, 733 cm$^{-1}$. HRMS (ESI): m/z calcd. for C$_{16}$H$_{22}$O$_{10}$: 397.110 [M+Na$^+$]; found: 397.110. Anal. Calcd. for C$_{16}$H$_{22}$O$_{10}$: C 51.34%, H 5.92%, Found: C 51.48%, H 6.00%.

6.0. Synthesis of the [(DavePhos)Ag(OAc)] complex

The complex was synthesized following a literature procedure published for [(XPhos)Ag(OAc)]. [5]

DavePhos (200 mg, 0.51 mmol) was dissolved in toluene (3 mL). This mixture was then added dropwise to silver (I) acetate (80 mg, 0.51 mmol). The colourless solution was stirred for another 12 h and filtered to remove the insoluble material. The solvent of the filtrate was then removed by rotary evaporation. The residue was triturated with Hexane to obtain colorless solid. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 7.61–7.33 (m, 5 H), 7.15–6.98 (m, 3 H), 2.50 (s, 6 H), 2.00 (s, 3 H), 1.93–1.00 (m, 22 H). $^{31}$P ($^1$H) NMR (50 MHz, CDCl$_3$): $\delta$ = 25.0 (d, $J$ = 25.0 Hz), 16.0 (d, $J$ = 15.8 Hz). IR (KBr): $\nu$ = 3053, 2925, 2848, 2889, 1571 (C=O), 1493, 1394, 1327, 1052, 946, 919, 818, 745, 616, 498, 459 cm$^{-1}$. HRMS (ESI): m/z calcd. for C$_{26}$H$_{36}$AgNP: 500.1631 [M-OAc]$^+$; found: 500.1645. Anal. Calcd. for C$_{26}$H$_{39}$AgNO$_2$P: C 60.00%, H 7.01%, N 2.50% Found: C 60.21%, H 7.06%, N 2.39%.
$^{1}$H NMR of [(DavePhos)Ag(OAc)] complex

$^{31}$P{$^{1}$H} NMR of [(DavePhos)Ag(OAc)] complex
7.0. Following the reaction progress for the carboxylative cyclization of propargyl alcohol 1 by Infrared spectroscopy

![Chemical Reaction Diagram](image)

**Figure S1.** Carboxylative cyclization of propargyl alcohol 1 to 2 followed by Infrared Spectroscopy.
8.0 Reactions conducted with, 3-phenylprop-2-yn-1-ol, 2-butin-1-ol and 3-pentin-1-ol.
9.0. Nucleophilic ring opening reaction of EVC 7

9.1. General reaction procedure

A 25 mL round bottom flask containing 7 (50 mg, 0.23 mmol, 1.0 eq.) was charged with either EtOH (1.1 eq.) with catalytic amounts of DBU (0.01 eq.) or pyrrolidine (1.1 eq.) in the presence of MeCN (2 mL). The reaction mixture was stirred overnight at room temperature. The products 17 and 18 were isolated by column chromatography on silica using EtOAc.

9.2. Product characterization

4-(benzyloxy)-2-oxobutyl ethyl carbonate (20)

Colorless oil (95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.27–7.20 (m, 5 H), 4.64 (s, 2 H), 4.43 (s, 2 H), 4.15 (q, $J = 7.14$ Hz, 2 H), 3.69 (t, $J = 6.15$ Hz, 2 H), 2.63 (t, $J = 6.15$ Hz, 2 H), 1.25 (t, $J = 7.14$ Hz, 3 H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta =$ 202.3, 154.8, 138.0, 128.6 (2 C), 127.9 (3 C), 73.5, 71.1, 64.9, 64.8, 39.5, 14.3. IR (film): $\nu =$ 3031, 2870, 1809 ($C=O$), 1733 ($C=O$), 1496, 1455, 1421, 1373, 1252, 1162, 1094, 101, 962, 878, 787, 739, 699 cm$^{-1}$. HRMS (ESI): $m/z$ calcd. for C$_{14}$H$_{18}$O$_5$: 289.1045 [M+Na$^+$]; found: 289.1046.

4-(benzyloxy)-2-oxobutyl pyrrolidine-1-carboxylate (21)

Colorless oil (89%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta =$ 7.38–7.27 (m, 5 H), 4.63 (s, 2 H), 4.48 (s, 2 H), 3.71 (t, $J = 6.15$ Hz, 2 H), 3.40–3.28 (m, 4 H), 2.68 (t, $J = 6.15$ Hz, 2 H), 1.90–1.82 (m, 4 H). $^{13}$C NMR (101 MHz, CD$_3$CN): $\delta =$ 204.7, 154.5, 139.2, 128.9 (2 C), 128.2 (2 C), 128.1, 73.1, 69.2, 65.3, 46.7, 46.3, 39.5, 26.0, 25.1. IR (film): $\nu =$ 3063, 3030, 2974, 2954, 2875, 1801($C=O$), 1714 ($C=O$), 1531, 1434, 1364, 1253, 1226, 1179, 1104, 1026, 983, 961, 912, 859, 804, 765, 740, 699 cm$^{-1}$. HRMS (ESI): $m/z$ calcd. for C$_{16}$H$_{21}$NO$_4$: 314.1362 [M+Na$^+$]; found: 314.1363.
10.0 $^1$H and $^{13}$C NMR spectra of the starting materials and isolated products

$^1$H NMR of 4-hydroxybut-2-yn-1-yl acetate (5a)

$^1$C($^1$H) NMR of 5a
$^1$H NMR of 4-hydroxybut-2-yn-1-yl methyl carbonate (6a)

$^1$C$^1$H NMR of 6a
$^1H$ NMR of 4-(benzyloxy)but-2-yn-1-ol (7a)

$^1C(^1H)$ NMR of 7a
$^1$H NMR of 4-hydroxybut-2-yn-1-yl methacrylate (8a)

$^1$C$^1$H NMR of 8a
$^1$H NMR of 2-(((4-hydroxybut-2-yn-1-yl)oxy)carbonyl)amino)ethyl methacrylate (9a)

$^1$C($^1$H) NMR of 9a
'H NMR of 4,4'-((1,4-phenylenebis(methylene))bis(oxy))bis(but-2-yn-1-ol) (14a)

\[\text{\H NMR of } 4,4'-(1,4-phenylenebis(methylene))bis(oxy))bis(but-2-yn-1-ol) (14a)\]

\[\text{\C{\H} NMR of } 14a\]

\[\begin{align*}
109.2 & \quad 150.3 & \quad 129.1 & \quad 129.9 & \quad 126.1 & \quad 155.5 & \quad 167.2
\end{align*}\]
$^1$H NMR of bis(4-hydroxybut-2-yn-1-yl) (4-methyl-1,3-phenylene)dicarbamate (15a)

$^1$C{$^1$H} NMR of 15a
$^1$H NMR of 1,8-Bis(4-hydroxy-2-butyn-1-oxy)-3,6-dioxaoctane (16a)

$^1$C($^1$H) NMR of 16a
\(^1\)H NMR of 4-methylene-1,3-dioxolan-2-one (2)

\(^1\)C\(^{\text{\(\Delta\)}}\) NMR of 2
$^1$H NMR of (Z)-4-(2-hydroxyethylidene)-1,3-dioxolan-2-one (4)

$^1$C($^1$H) NMR of 4
$^1$H NMR of (Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl acetate (5)

$^1$C$^1$H NMR of 5
$^1$H NMR of (Z)-methyl (2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) carbonate (6)

$^1$C{$^1$H} NMR of 6
$^1$H NMR of (Z)-4-(2-(benzyloxy)ethylidene)-1,3-dioxolan-2-one (7)

$^1$C($^1$H) NMR of 7
\(^1\text{H NMR of (Z)-2-(2-oxo-1,3-dioxolan-4-yldene)ethyl methacrylate (8)}\)

\[^1\text{C}\{^1\text{H}\} \text{ NMR of 8}\]
$^1$H NMR of (Z)-2-(3-(2-oxo-1,3-dioxolan-4-ylidene)propanamido)ethyl methacrylate (9)

$^1$C($^1$H) NMR of 9
$^1$H NMR of 4-methyl-5-methylene-1,3-dioxolan-2-one (10)

$^1$C($^1$H) NMR of 10
$^1$H NMR of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (11)

$^1$C$^1$H NMR of 11
$^1$H NMR of (Z)-5-(2-hydroxy-2-methylpropylidene)-4,4-dimethyl-1,3-dioxolan-2-one (12)

$^1$C($^1$H) NMR of 12
$^1$H NMR of 4-methyl-5-methylene-4-(4-methylpent-3-en-1-yl)-1,3-dioxolan-2-one (13)

$^1$C{$^1$H} NMR of 13
$^1$H NMR of $(4Z,4'Z)-4,4'(((1,4$-phenylenebis(methylene))bis(oxy))bis(ethan-2-yl-1-ylidene))bis(1,3-dioxolan-2-one)$ (14)

$^1$C$^1$H NMR of 14
^1H NMR of bis((Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl)(4-methyl-1,3-phenylene)di carbamate (15)

^1C(^1H) NMR of 15
$^1$H NMR of (4Z,4'$Z$)-4,4'$-(3,6,9,12-tetraoxatetradecane-1,14-diylidene)bis(1,3-dioxolan-2-one) (16)

$^1$C {$^1$H} NMR of 16
$^1$H NMR of 4-(benzyloxy)-2-oxobutyl ethyl carbonate (20)

$^1$C($^1$H) NMR of 20
$^1$H NMR of 4-(benzyloxy)-2-oxobutyl pyrrolidine-1-carboxylate (21)

$^1$C($^1$H) NMR of 21
11.0 Computational studies

Methodology

All geometries were optimized at the BP86/def2-SV(P) level\cite{8, 9, 10} with the COSMO solvation model\cite{11} using the relative permittivity of acetonitrile ($\varepsilon = 36.64$). Final electronic energies were calculated at the PBE0-D3(BJ)/def2-QZVPP level\cite{12} employing dispersion correction with Becke-Johnson damping.\cite{13, 14} Calculations were carried out with the TURBOMOLE program [TURBOMOLE V 7.0; TURBOMOLE GmbH: Karlsruhe, Germany, 2015. http://www.turbomole.com.] using the resolution-of-identity approximation and the corresponding auxiliary basis sets.\cite{15, 16, 17}

Thermal corrections and zero-point vibrational energies were calculated at $T = 298.15$ K and $p = 1$ bar. The thermodynamic reference for all species except CO$_2$ was set to $\chi = 0.01$, for CO$_2$, $\chi = 0.32$ was used as reference, corresponding to the mole fraction of CO$_2$ in acetonitrile at 298.15 K and 20 bar from interpolation of experimentally available data.\cite{18} Free enthalpies of solvation in acetonitrile as corrections for the gas phase geometries were computed with the conductor-like screening model for real solvents\cite{19} (COSMO-RS) using the COSMO therm program (Version C 3.0, Release, revision 1744). [COSMO therm, Version C3.0, Release 1501; COSMO logic GmbH & Co KG: Leverkusen, Germany, 2014. http://www.cosmologic.de.] In cases where we employed the approach of correcting gas phase energies with free enthalpies of solvation from COSMO-RS, the thermodynamic reference for CO$_2$ was set to $p = 20$ bar. All discussed energies are free enthalpies with solvent correction in MeCN (either through COSMO or COSMO-RS as indicated).
Solvent Modeling and Stereoselectivity

To obtain the correct preference of $Z$ over $E$ isomer, as presented in the paper, it was necessary to optimize geometries and calculate single point energies with COSMO solvation using the relative permittivity of acetonitrile ($\varepsilon = 36.64$).

In comparison, a different energetic order is obtained for both transition states leading to $E$ and $Z$ when structure optimization and final energy calculations are carried out in the gas phase, even when free enthalpy of solvation is calculated within the COSMO-RS framework.

Figure S2. Free energy profile for the reaction with gas phase geometries and addition of solvation effects with COSMO-RS. The preference of $Z$ over $E$ isomer is inverted when compared to the structures optimized with COSMO using acetonitrile as solvent.

Here, a preference of $E$ ($\text{TS-D'}$) over $Z$ ($\text{TS-E'}$) of 14.8 kJ/mol is predicted. This is likely due to the disfavoring of charge separation in the gas phase which occurs for the $\text{TS-E'}$ leading to the $Z$ isomer (basically an anti addition of silver and carbonate oxygen onto the double bond), since the carbonate anion and silver cation are separated during the transition state. In the other transition state, $\text{TS-D'}$, the carbonate anion and silver cation are very close, making this more favorable in the gas phase. The general shape of the reaction path is otherwise similar, both barriers and overall reaction enthalpies are predicted to be larger with the gas phase geometries, and the hydrogen carbonate/carbon dioxide and propargylic alcohol equilibrium is predicted to be less endergonic with respect to the hydrogen carbonate.
Thorpe-Ingold Effect

Since we firstly report the cyclization of unsubstituted exo-vinylene carbonates, we were interested whether there was a similar trend as compared to the Thorpe-Ingold effect. We therefore calculated the O-C-C angles at the unsubstituted carbon atom for the propargylic hydrogen carbonate and similarly looked at the methyl- and dimethyl-substituted carbonates. Additionally, we computed the corresponding free enthalpies of cyclization. For this comparison, we looked at the linear conformers of the hydrogen carbonates and used our regular approach of correcting gas phase energies and geometries with COSMO-RS. As we expected, with larger substituents, the O-C-C angle in the substrate shrinks:

| R¹  | R²  | O-C-C Angle [°] | ΔG<sub>cyclization</sub> [kJ/mol] |
|-----|-----|----------------|---------------------------------|
| H   | H   | 109.1          | -117.3                          |
| H   | Me  | 107.2          | -124.9                          |
| Me  | Me  | 103.2          | -144.0                          |

Scheme S1. O-C-C angles and free enthalpies of cyclization for differently substituted propargylic hydrogen carbonates.

Likewise, a similar trend is obtained for the free enthalpy of cyclization, which is more exergonic for the higher substituted hydrogen carbonates which exhibit a lower O-C-C angle.

Difference between E and Z isomers

We calculated the difference between the E and Z isomers of the exovinylene carbonates from 1,4-butyndiol and the related acetate, 4-hydroxybut-2-yn-1-yl acetate (products 4 and 5 in the substrate scope). At the level of our calculations for the mechanism in the paper including COSMO solvation in acetonitrile, we find only a very small difference: a preference of the Z isomer of 0.1 kJ/mol for 4 and 0.6 kJ/mol for 5. This also suggests that the formation of the Z isomer, which is exclusively obtained in experiment, is kinetically favored, which is supported by our calculations.
## Energies

Table S5. COSMO calculations with correct prediction of *E/Z* preference. Total free enthalpies, electronic energies at the level of optimization (BP86/def2-SV(P)) and final electronic energies (PBE0-D3(BJ)/def2-QZVPP), both including solvation energies from the COSMO solvation model in acetonitrile as well as thermodynamic corrections and zero-point vibrational energies.

| Structure                         | Total G [kJ/mol] | BP86/def2-SV(P) [Eh] | PBE0-D3(BJ)/def2-QZVPP [Eh] | ΔG<sub>gas</sub> [kJ/mol] | ZPVE [kJ/mol] |
|-----------------------------------|------------------|----------------------|-----------------------------|---------------------------|--------------|
| **CO**                            | -494880.25       | -188.467116          | -188.478829                 | -26.33                    | 29.90        |
| Propargylic Alcohol               | -503332.86       | -191.719334          | -191.737928                 | 86.42                     | 156.10       |
| AcOH                              | -601057.18       | -228.928679          | -228.959071                 | 86.19                     | 157.10       |
| Propynyl Hydrogen Carbonate       | -998159.55       | -380.185287          | -380.217616                 | 113.07                    | 195.70       |
| Exovinylene Carbonate             | -998279.17       | -380.242470          | -380.267019                 | 123.16                    | 201.60       |
| A                                 | -4680197.40      | -1783.182540         | -1783.120518                | 1396.26                   | 1578.00      |
| B                                 | -5077322.66      | -1934.445369         | -1934.386707                | 1422.69                   | 1616.00      |
| C                                 | -5077317.37      | -1934.435996         | -1934.386905                | 1426.13                   | 1615.00      |
| TS-D                              | -5077258.05      | -1934.418638         | -1934.362509                | 1421.40                   | 1612.00      |
| TS-E                              | -5077289.25      | -1934.421102         | -1934.372961                | 1417.64                   | 1612.00      |
| F                                 | -5077348.43      | -1934.461329         | -1934.401117                | 1432.38                   | 1622.00      |
| G                                 | -5077351.27      | -1934.460540         | -1934.401359                | 1430.18                   | 1622.00      |
| 4 (Hydroxy Vinylene Carbonate) E  | -1298737.76      | -494.684279          | -494.734030                 | 197.66                    | 310.45       |
| 4 (Hydroxy Vinylene Carbonate) Z  | -1298737.91      | -494.684787          | -494.733932                 | 197.26                    | 310.59       |
| 5 (Acetyl Vinylene Carbonate) E   | -1699218.46      | -647.254031          | -647.299890                 | 278.58                    | 416.13       |
| 5 (Acetyl Vinylene Carbonate) Z   | -1699219.05      | -647.254784          | -647.299889                 | 278.24                    | 416.14       |

Table S6. Gas phase calculations with COSMO-RS corrections that predict the wrong *E/Z* preference. Total free enthalpies, electronic energies at the level of optimization (BP86/def2-SV(P)) and final electronic energies (PBE0-D3(BJ)/def2-QZVPP), as well as thermodynamic corrections and zero-point vibrational energies and solvation contributions in acetonitrile to free enthalpy from COSMO-RS using COSMO therm.

| Structure                         | Total G [kJ/mol] | BP86/def2-SV(P) [Eh] | PBE0-D3(BJ)/def2-QZVPP [Eh] | ΔG<sub>gas</sub> [kJ/mol] | ZPVE [kJ/mol] | ΔG<sub>solv</sub> [kJ/mol] |
|-----------------------------------|------------------|----------------------|-----------------------------|---------------------------|--------------|--------------------------|
| **CO**                            | -494861.43       | -188.464016          | -188.475550                 | -26.38                    | 29.87        | 11.1                     |
| Propargylic Alcohol               | -503317.13       | -191.708767          | -191.726737                 | 84.51                     | 154.60       | -11.8                    |
| AcOH                              | -601038.81       | -228.918379          | -228.947202                 | 84.48                     | 156.50       | -11.1                    |
| Propynyl Hydrogen Carbonate       | -998146.79       | -380.167841          | -380.198944                 | 109.60                    | 193.80       | -32.8                    |
| Exovinylene Carbonate             | -998264.09       | -380.230609          | -380.253550                 | 121.42                    | 200.40       | -18.5                    |
| A'                                | -4680213.69      | -1783.162310         | -1783.097196                | 1390.84                   | 1577.00      | -72.1                    |
| B'                                | -5077343.98      | -1934.421706         | -1934.361023                | 1418.03                   | 1615.00      | -86.5                    |
| C'                                | -5077320.75      | -1934.406835         | -1934.352321                | 1419.84                   | 1612.00      | -87.9                    |
| TS-D'                             | -5077265.74      | -1934.394796         | -1934.333754                | 1418.49                   | 1611.00      | -80.3                    |
| TS-E'                             | -5077250.90      | -1934.382339         | -1934.324998                | 1423.10                   | 1621.00      | -93.0                    |
| F'                                | -5077376.24      | -1934.439724         | -1934.378001                | 1424.15                   | 1621.00      | -80.3                    |
| G'                                | -5077373.56      | -1934.436904         | -1934.374196                | 1423.38                   | 1621.00      | -86.8                    |
Table S7. Different substituted and unsubstituted hydrogen carbonates and the corresponding exo-vinylene carbonates. Total free enthalpies, electronic energies at the level of optimization (BP86/def2-SV(P)) and final electronic energies (PBE0-D3(BJ)/def2-QZVPP), as well as thermodynamic corrections and zero-point vibrational energies and solvation contributions in acetonitrile to free enthalpy from COSMO-RS using COSMOtherm.

| Structure                        | Total G [kJ/mol] | BP86/def2-SV(P) [E\text{h}] | PBE0-D3(BJ)/def2-QZVPP [E\text{h}] | \(\Delta G_{\text{gas}}\) [kJ/mol] | ZPVE [kJ/mol] | \(\Delta G_{\text{solv}}\) [kJ/mol] |
|----------------------------------|------------------|------------------------------|------------------------------------|----------------------------------|---------------|----------------------------------|
| Hydrogen Carbonate (H,H)         | -998146.79       | -380.167841                  | -380.198944                        | 109.60                           | 193.80        | -32.8                            |
| Hydrogen Carbonate (H,Me)        | -1101228.65      | -419.453190                  | -419.486422                        | 176.66                           | 265.30        | -32.4                            |
| Hydrogen Carbonate (Me,Me)       | -1204297.14      | -458.731851                  | -458.768462                        | 243.40                           | 334.80        | -32.7                            |
| Exovinylene Carbonate (H,H)      | -998264.09       | -380.230609                  | -380.253550                        | 121.42                           | 200.40        | -18.5                            |
| Exovinylene Carbonate (H,Me)     | -1101353.57      | -419.518381                  | -419.543670                        | 187.60                           | 271.50        | -18.0                            |
| Exovinylene Carbonate (Me,Me)    | -1204441.11      | -458.803798                  | -458.832777                        | 253.41                           | 341.30        | -17.8                            |
## Structures

Cartesian coordinates of structures optimized with COSMO in acetonitrile, distances in atomic units (\(a_0\)).

### CO2

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| C   | -0.0000915 | -0.0000901 | 0.9090903 |
| O   | -0.0000992 | -0.0000923 | -1.1743165 |
| O   | 0.00009108 | 0.0000028  |   1.1743388 |

### Propargylic Alcohol

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| C   | 0.4992803   | 0.431557 | -0.3184449 |
| C   | 1.6185757   | 0.8326786 | -0.6202812 |
| C   | -0.8297873  | -0.0521655 | 0.9253490 |
| H   | -1.5539266  | 0.1176253  | -0.7347190 |
| O   | -0.8571390  | -1.4519581  | 0.3025926 |
| H   | -1.1942179  | 0.5466552  | 0.9639694 |
| H   | -0.2896703  | -1.6146361  | 1.149691 |
| H   | 2.6089662  | 1.1792529  | -0.9026278 |

### Propynyl Hydrogen Carbonate

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| C   | -0.1798813  | -2.4156689 | 0.6589381 |
| C   | -0.5625674  | -1.3629994  | 0.1763699 |
| C   | -1.6503666  | -0.1165974  | -0.4635117 |
| O   | -0.8575886  | 1.0556591  | 0.3742138 |
| H   | -0.7069851  | 0.9056049  | -1.4536526 |
| H   | -2.1596179  | -0.0821353  | -0.3914536 |
| C   | 0.1799859  | -3.3499293  | 1.0870511 |
| O   | 0.5914105   | 1.5535486  | 0.2736145 |
| H   | 1.3504994   | 0.8864662  | -0.6167817 |
| O   | 0.9457829  | 2.5116817  | 0.9341664 |
| H   | 2.2422680  | 1.3165189  | -0.6389533 |

### AcOH

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| C   | 0.5223247  | 0.2652928  | -0.0627958 |
| C   | -0.9687373  | 0.6339088  | -0.0646298 |
| O   | 1.8739992  | 1.3353991  | -0.2671281 |
| H   | -1.2673771  | -0.8122971  | -0.6657476 |
| H   | -1.2624252  | -0.2448770  | 1.0319278 |
| H   | -1.5051404  | 0.9548398  | -0.3428094 |
| O   | 1.2166160  | -0.8796617  | 0.1546539 |
| H   | 2.1806561  | -0.6548648  | 0.1179999 |

### Exovinyline Carbonate

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| C   | -1.3777470  | -1.1522010  | -0.5291611 |
| C   | -0.4378638  | -0.3147687  | -0.064617 |
| C   | 0.8549766  | 0.1728395  | -0.6956299 |
| O   | -0.5216824  | 0.2923622  | 1.1880076 |
| H   | -2.2659790  | -1.3951989  | 0.0751905 |
| H   | -1.2639180  | -1.6061360  | -0.5270819 |
| C   | 0.5747914  | 1.0958643  | 1.3843844 |
| O   | 0.7568111  | 1.7419661  | 2.3849735 |
| O   | 1.3963514  | 1.9542288  | 0.3150794 |
| O   | 0.6982932  | 0.7555838  | -1.6280158 |
| H   | 1.5836487  | -0.6417940  | -0.8885229 |

### A

|     | \(x\)  | \(y\)  | \(z\)  |
|-----|--------|--------|--------|
| Ag  | -1.3028173  | 0.2879296  | -1.2428994 |
| C   | -3.4434165  | 1.7381348  | -2.3364915 |
| O   | -3.3485963  | 2.1735994  | -1.1649864 |
| O   | -2.7042945  | 0.7878351  | -2.8171555 |
| C   | -4.8424998  | 2.3325321  | -3.3066528 |
| H   | -5.8673946  | 1.5288881  | -3.7810415 |
| H   | -3.9326826  | 2.8647997  | -4.1293931 |
| H   | -5.1306110  | 3.0478477  | -2.7921606 |
| P   | 0.1383459  | -0.7612885  | 0.3912177 |
| C   | -0.8088543  | -0.7035069  | 2.0762824 |
| H   | -0.1656666  | -1.6467344  | 2.5662934 |
| C   | 0.0391830  | 0.4994278  | 2.8778903 |
| H   | -0.4236864  | 1.4379162  | 2.3410689 |
| H   | 1.1487558  | 0.4716165  | 2.9181397 |
| C   | -0.5292705  | 0.5267637  | 4.3106314 |
| H   | -0.1577227  | -0.3645224  | 4.8669858 |
| H   | -0.1349242  | 1.4241674  | 4.8458686 |
| C   | -2.0669649  | 0.5365672  | 4.3241417 |
| H   | -2.4464671  | 0.4981229  | 5.3678535 |
| Atom | Coordinates | Atomic Number |
|------|-------------|---------------|
| H    | -2.4366714  | 1             | 3.877524   |
| C    | -2.6241082  | 6             | 3.511930   |
| H    | -3.7578998  | 1              | 3.468444   |
| H    | -2.3648260  | 1              | 4.024116   |
| C    | -2.9573788  | 6              | 2.878435   |
| H    | -2.3911010  | 1              | 1.535082   |
| H    | -2.4769437  | 1              | 1.521074   |
| C    | 0.3143399   | 6              | -0.126047  |
| H    | 1.0266348   | 1              | 0.619417   |
| C    | -1.8166992  | 6              | -0.824438  |
| H    | -1.7774618  | 1              | -0.686517  |
| H    | -1.4120893  | 1              | 1.013657   |
| C    | -0.8462663  | 6              | -0.445441  |
| H    | -0.1848068  | 1              | 0.292061   |
| C    | -1.8334609  | 6              | -0.396429  |
| H    | -0.2372149  | 1              | -1.856614  |
| H    | -0.0882846  | 1              | -2.176674  |
| H    | -0.9519473  | 1              | -2.662839  |
| C    | 1.0938960   | 6              | -1.945089  |
| H    | 1.5047987   | 1              | -2.978522  |
| H    | 1.8456312   | 1              | -1.277629  |
| C    | 0.9268355   | 6              | -1.537248  |
| H    | 0.9113752   | 1              | -1.584658  |
| H    | 0.2612581   | 1              | -2.271355  |
| C    | 1.9216543   | 6              | -0.397523  |
| H    | 2.7425821   | 1              | 1.318019   |
| H    | 2.2982920   | 1              | 1.994221   |
| C    | 4.1251135   | 6              | 1.389206   |
| H    | 4.7368517   | 1              | 2.117793   |
| C    | 4.7187756   | 6              | 0.517278   |
| H    | 5.8048495   | 1              | 0.546543   |
| C    | 3.9144552   | 6              | -0.392948  |
| H    | 3.3765498   | 1              | 1.062612   |
| C    | 2.5119558   | 6              | -0.464978  |
| H    | 1.7555676   | 1              | -1.586427  |
| C    | 0.8312159   | 6              | -1.903121  |
| H    | 0.1447871   | 1              | -2.289638  |
| H    | -0.5759231  | 1              | -2.896137  |
| H    | 0.3729474   | 1              | -3.619271  |
| H    | -0.1818186  | 1              | -4.428945  |
| C    | 1.3123696   | 6              | -3.916919  |
| H    | 1.5088781   | 1              | -4.957269  |
| C    | 1.9913089   | 6              | 1.141140   |
| H    | 2.7127374   | 6              | -0.307296  |
| C    | 6.5937998   | 1              | 0.128862   |
| H    | 1.7154669   | 1              | 0.916682   |
| H    | 1.4567436   | 1              | 1.997373   |
| H    | 1.9789106   | 1              | 0.649109   |
| H    | 2.6135023   | 1              | 0.764306   |
| H    | -0.6310336  | 6              | 0.362558   |
| H    | -0.8216435  | 1              | 1.478426   |
| H    | -1.5092588  | 1              | -0.129735  |
| H    | -0.5535111  | 1              | 0.651426   |

| Ag    | -0.8408333 -0.4467839 0.0951235 |
| C     | -3.5836659 -0.2439256 0.7913942 |
| O     | -3.1003657 0.2387078 1.8280257 |
| Ag    | 0.2862308 -0.7268852 -0.2289299 |
| C     | 0.9678592 0.2686174 0.7228176 |
| P     | 1.5937006 -0.6069756 0.1863363 |
| C     | 2.1632651 -0.8687077 1.8623176 |
| H     | 3.0739515 -1.5976776 1.7589779 |
| C     | 2.5591469 0.4565052 2.5619393 |
| H     | 1.6893843 1.1299918 2.5904939 |
| C     | 3.3373370 0.9681256 1.9778795 |
| H     | 3.0705173 0.1974132 3.9931032 |
| H     | 4.0224921 -0.3856623 3.9466169 |
| C     | 3.1993221 1.1673345 4.4746408 |
| C     | 2.0492135 -0.5864638 4.8414303 |
| H     | 2.4859661 -0.7952875 5.8566794 |
| C     | 1.4509661 0.9545610 5.0002796 |
| H     | 1.6298966 -1.8859942 4.1451243 |
| C     | 0.8448067 -2.4089505 4.7323878 |
| H     | 2.5069259 -2.5765254 4.0987702 |
| C     | 1.1166630 -1.6254747 2.7111448 |
| H     | 0.1876614 -1.9072876 2.7657366 |
|   |   |   |   |
|---|---|---|---|
| H | -1.7826453 | -2.7234968 | -0.8260598 |
| H | -1.5464002 | -3.1959695 | 0.8834609 |
| C | -0.9905874 | -4.7460233 | -0.5456712 |
| H | -0.4083394 | -5.2952507 | 0.2276745 |
| C | -2.0892227 | -5.1954807 | -0.5585637 |
| H | -3.0732732 | -4.9062801 | -1.9121494 |
| H | -0.2105910 | -5.9826586 | -2.165622 |
| C | -0.9482893 | -4.4526086 | -2.7643195 |
| C | 1.0724668 | -4.2299139 | -1.9221364 |
| C | 1.5429969 | -4.3113321 | -2.9284824 |
| H | 1.7599770 | -4.7692744 | -1.2114541 |
| C | 0.9794571 | -2.7462172 | -1.5185419 |
| H | 1.9937916 | -2.2924334 | -1.5010394 |
| C | 3.9964053 | -2.1967696 | -2.2919104 |
| C | 1.9538363 | -0.2858609 | 0.3618241 |
| C | 2.8163816 | -1.9618012 | 1.2949398 |
| H | 2.3729983 | -1.8318144 | 1.8584418 |
| C | 4.2087921 | -0.8917980 | 1.2243524 |
| H | 4.8292353 | -1.5167705 | 1.8931499 |
| C | 4.7966403 | 0.9592440 | 0.3748082 |
| H | 5.8939675 | 0.1945762 | 0.3699824 |
| C | 3.9057548 | 0.8456271 | -0.4548414 |
| H | 4.4468596 | 1.6633671 | -1.1955385 |
| C | 2.5743356 | 0.7087876 | -0.4685599 |
| C | 1.8017685 | 1.5621486 | -1.4125539 |
| C | 0.9308191 | 2.6413242 | -0.9822485 |
| C | 0.2109967 | 3.3515999 | -1.9827080 |
| H | -0.4719548 | 4.1609189 | -1.6859084 |
| C | 0.3759669 | 3.9757166 | -3.3495975 |
| C | 1.2724888 | 2.0816422 | -3.7685445 |
| H | 1.4176899 | 1.8640414 | -4.8393876 |
| C | 1.9714514 | 1.3491509 | -2.7948630 |
| H | 2.6551184 | 0.5413866 | -3.1061916 |
| N | 0.7806416 | 2.9625627 | 0.364791 |
| C | 1.9808262 | 3.3591672 | 1.1254588 |
| C | 1.7928329 | 3.2695580 | 2.2177866 |
| C | 2.7615690 | 4.4215023 | 0.9087795 |
| H | 2.8412182 | 2.7106048 | 0.8744159 |
| C | -0.3794605 | 3.7616422 | 0.7692042 |
| C | -0.4758881 | 3.7327153 | 1.8767971 |
| H | -1.3063781 | 3.3348533 | 0.3323724 |
| C | -0.2893694 | 4.6395820 | 0.7472256 |
| C | -1.7447168 | -0.1722217 | -3.5020550 |
| C | -2.5675586 | 0.7241440 | -3.2743083 |
| H | -1.1184168 | -0.9656717 | -3.8998808 |
| C | -3.5898961 | 1.7777057 | -3.1247683 |
| H | -4.1447979 | 1.8637227 | -4.6561339 |
| O | -4.5643845 | 1.4897635 | -2.1275120 |
| H | -3.0887685 | 2.7514664 | -2.9243955 |
| C | -4.1746472 | 1.6791463 | -0.7639858 |
| O | -5.1085191 | 1.5858640 | 0.6371439 |
| O | -2.9398663 | 1.9255759 | -0.5699254 |
| H | -9.1955996 | 3.6610340 | -4.9991515 |

TS - D

|   |   |   |   |
|---|---|---|---|
| Ag | -0.8577183 | 0.1440791 | -0.8978289 |
| P | 1.0784531 | -0.8581947 | -0.9149199 |
| C | 0.7006605 | -1.9181021 | 1.5261994 |
| H | 1.5521614 | -2.7393406 | 1.9415181 |
| C | 0.9912012 | -1.1189311 | 2.8295994 |
| H | 0.3131906 | -0.2268648 | 2.8666779 |
| C | 0.2025945 | -0.7126156 | 2.8907504 |
| C | 0.6899816 | -1.9659387 | 4.7660283 |
| H | 1.4488660 | -2.7814666 | 4.1512748 |
| H | 0.8093484 | -1.3392887 | 4.9892227 |
| C | -0.7166720 | -2.5857851 | 4.0255199 |
| H | -0.8877597 | -3.2282829 | 4.9191882 |
| C | -1.4833117 | -1.7769528 | 4.9558986 |
| C | -0.9129324 | -3.3937857 | 2.7335881 |
| H | -1.9559334 | -3.7776235 | 2.6723279 |
| H | -0.2375410 | -4.2836716 | 2.7392739 |
| C | -0.6253298 | -2.5318582 | 1.4900941 |
| C | -1.3732318 | -1.7069901 | 1.4485137 |
| C | -0.7739915 | -3.1393557 | 0.5712935 |
| C | 1.7851637 | -2.9128955 | -1.3356472 |
| H | 2.7278626 | -2.4253947 | -0.9664361 |
| C | 0.8519027 | -3.1915480 | -1.6613671 |
|   |   |   |   |   |
|---|---|---|---|---|
| H | -0.1574717 | -2.8358456 | -1.4706099 |
| C | 0.4978935 | -3.7736190 | -0.0928023 |
| H | 1.4006419 | -4.2765118 | -2.0685527 |
| H | 2.2644601 | -4.7721372 | -1.5106986 |
| C | 0.8553356 | -5.9679733 | -2.2288719 |
| C | 1.8814762 | -3.6965712 | -3.3083687 |
| H | 2.3601500 | -4.3596255 | -3.9736924 |
| C | 1.0019223 | -3.2934618 | -3.8645724 |
| C | 2.6596410 | -2.4575451 | -3.0686171 |
| H | 3.1633895 | -1.9461299 | -3.9494277 |
| H | 3.7912284 | -2.8734583 | -2.5573978 |
| C | 2.2432634 | -1.4293018 | -2.0411604 |
| H | 2.9820243 | -0.6277722 | -1.8172470 |
| H | 1.3737286 | -0.9322329 | -2.5359831 |
| C | 2.5377913 | 0.2231278 | 0.7883503 |
| C | 3.6309114 | -0.4627567 | 1.3741494 |
| H | 3.5249934 | -1.5238457 | 1.6562409 |
| C | 4.8621861 | 0.1677391 | 1.5988649 |
| H | 5.8924489 | -0.3938880 | 2.0589101 |
| C | 5.8286671 | 1.5165233 | 1.2198182 |
| H | 5.9944831 | 2.0268714 | 1.3727329 |
| C | 3.9535672 | 2.2659860 | 0.6466898 |
| H | 4.6791391 | 3.2624436 | 0.3660337 |
| C | 2.6918670 | 1.5926554 | 0.4339903 |
| C | 1.6275885 | 2.4266442 | -0.2170868 |
| C | 0.4539964 | 2.9822023 | 0.4637129 |
| C | -0.4728811 | 3.6776935 | -0.2714839 |
| H | -1.3776382 | 4.0544226 | 0.2270236 |
| C | -0.2586952 | 4.9119384 | -1.6176199 |
| H | 0.9036953 | 3.5776931 | -2.2744925 |
| C | 1.0894542 | 3.8356737 | -3.3299087 |
| C | 1.8317199 | 2.7973298 | -1.5640699 |
| H | 2.7425193 | 2.4371860 | -2.0716955 |
| N | 6.2118616 | 2.5622597 | 1.8236549 |
| C | 1.1783362 | 3.0353419 | 2.1825616 |
| H | 1.0492527 | 2.4873087 | 3.7599596 |
| H | 1.0414449 | 4.1251822 | 3.0939801 |
| H | -2.2172318 | 2.8824230 | 2.4618445 |
| C | -1.1593681 | 2.6769204 | 2.3966684 |
| H | -1.2418565 | 2.1496864 | 3.2757647 |
| C | -1.8571883 | 2.1921648 | 1.5841614 |
| C | -1.4906224 | 3.7362408 | 2.4647336 |
| C | -2.6191530 | 0.8044345 | -1.7256124 |
| C | -3.7284821 | 0.1031978 | -1.9972594 |
| H | -2.6758521 | 1.8465998 | -2.1941719 |
| C | -5.9252196 | 0.4588128 | -2.7686759 |
| H | -4.6775401 | 0.7658594 | -3.7564312 |
| O | -5.7876202 | -0.7716443 | -2.6904967 |
| H | -5.6137550 | 1.2429909 | -2.1843243 |
| C | -5.0390997 | -1.7397203 | -2.0340325 |
| O | -5.4899250 | -2.8599138 | -1.8513035 |
| O | -3.8927614 | -1.2598677 | -1.6184438 |
| H | -1.0832921 | 4.6277544 | -2.1486057 |

| G |   |   |   |
|---|---|---|---|
| Ag | -0.4529070 | -0.9232808 | -0.2387024 |
| P | 1.0482270 | 0.9595633 | 0.0633804 |
| C | 1.9736636 | 0.9772095 | 1.6578327 |
| H | 3.0046094 | 1.3433732 | 1.4362863 |
| C | 1.3312676 | 1.9128692 | 2.7685628 |
| H | 0.2745231 | 1.5975729 | 2.8659892 |
| C | 1.2924686 | 2.9574643 | 2.3369585 |
| H | 2.8981181 | 1.8734408 | 4.9418723 |
| C | 3.1219645 | 2.2935748 | 3.8864741 |
| H | 1.5925617 | 2.5384171 | 4.7782140 |
| C | 2.2171449 | 0.4455514 | 4.5896689 |
| C | 2.8197626 | 0.4446522 | 5.5355928 |
| C | 1.2019217 | 0.9719416 | 4.8732918 |
| C | 2.8401143 | -0.4996792 | 3.5587849 |
| H | 2.8637919 | -1.5441061 | 3.9426973 |
| H | 3.9099528 | -0.2038580 | 3.3735249 |
| C | 2.0867525 | -0.4661128 | 2.2268987 |
| C | 1.0298816 | -0.8407807 | 2.3906311 |
| H | 2.5397060 | -1.1505686 | 1.4953325 |
| C | 2.3957267 | 0.7623198 | -1.3148766 |
| H | 3.0899548 | 1.6438439 | -1.1768419 |
| C | 2.2054193 | -0.5242301 | -1.1692951 |
|     |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|
| H   | 2.502786 | -1.3926232 | -1.1795533 |
| H   | 3.7347227 | -0.5478832 | -0.1919572 |
| C   | 4.2357097 | -0.6872553 | -2.3948814 |
| H   | 5.0694171 | 0.1115707 | -2.2116227 |
| C   | 4.7674331 | -1.0588003 | -2.182136 |
| C   | 3.5803573 | -0.5986438 | -3.6924151 |
| H   | 4.3525615 | -0.6807546 | -4.4906149 |
| H   | 2.8868887 | -1.4626442 | -3.8297717 |
| C   | 2.7936885 | 0.7137294 | -3.8417443 |
| C   | 2.2828108 | 0.7536722 | -4.8368797 |
| C   | 3.5049451 | 1.5741284 | -3.815692 |
| C   | 1.7535263 | 0.8815101 | -2.7180681 |
| C   | 1.2247924 | 1.8540276 | -2.8310273 |
| H   | 0.9786650 | 0.0842707 | -2.8147412 |
| C   | 0.5209750 | 2.7156624 | -0.2966810 |
| C   | 1.5158664 | 3.7209470 | -0.2956364 |
| H   | 2.5407322 | 3.4539613 | 0.1628699 |
| C   | 1.2399533 | 5.0596655 | -0.5210194 |
| H   | 2.0357571 | 5.8179147 | -0.4411749 |
| C   | -0.0504364 | 5.4143677 | -0.9495921 |
| H   | 0.2818665 | 6.4579929 | -1.2199459 |
| C   | -1.0477283 | 4.4315268 | -1.0368384 |
| H   | -2.0635174 | 4.7114482 | -1.3561852 |
| C   | -0.7955964 | 3.0778203 | -0.6913494 |
| C   | -1.9284344 | 2.1048697 | -0.8470932 |
| C   | -2.5790395 | 1.4658293 | -0.258876 |
| C   | -3.6261523 | 0.5499277 | -0.0259537 |
| H   | -4.1485573 | 0.0498659 | 0.8024029 |
| C   | -4.0393414 | 0.2838606 | -1.3468979 |
| C   | -3.4227655 | 0.9362633 | -2.4195181 |
| H   | -3.7418189 | 0.7413348 | -3.4565312 |
| C   | -2.3785711 | 1.8398946 | -2.1578828 |
| H   | -1.8711485 | 2.3449853 | -2.9973476 |
| N   | -2.1798953 | 1.7245025 | 1.5938462 |
| C   | -3.3203559 | 3.0973228 | 2.0828263 |
| H   | -1.7070808 | 3.2317685 | 3.0085471 |
| C   | -3.8596322 | 3.3415839 | 2.3374238 |
| H   | -1.9682987 | 3.8265453 | 1.3274994 |
| C   | -2.5565595 | 0.7454815 | 2.6653297 |
| H   | -1.968763 | 0.9467135 | 3.5292799 |
| C   | -2.3185289 | -0.2866558 | 2.2529512 |
| C   | -3.8417978 | 0.7849004 | 2.8866369 |
| C   | -1.4684284 | -2.7261008 | -0.5177620 |
| C   | -1.6357476 | -3.9376366 | -0.1421075 |
| H   | -2.4569161 | -2.7259134 | -1.0223352 |
| C   | 0.3251835 | -4.3667595 | 0.5776754 |
| H   | 0.2876172 | -4.0093956 | 1.6210692 |
| O   | 0.1187930 | -5.8233336 | 0.6234661 |
| H   | 1.1580877 | -4.1115511 | 0.0377712 |
| C   | -1.0536664 | -6.2162105 | 0.6719437 |
| O   | -1.4167486 | -7.3688993 | -0.6139185 |
| O   | -1.7841851 | -5.1498906 | -0.3720794 |
| H   | -4.8625537 | -0.4293989 | -1.5160343 |

4 (Hydroxy Vinyldene Carbonate) E

|     |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|
| C   | -0.8631933 | -0.0165637 | 0.6196887 |
| O   | -2.0418408 | -0.1982774 | 0.6826745 |
| C   | -2.5747032 | -0.1731637 | -1.833774 |
| O   | -1.6069718 | 0.0521688 | -2.0961721 |
| C   | -0.3368238 | 0.2232624 | -1.4468748 |
| O   | 0.1104579 | -0.0451666 | 1.1166630 |
| O   | -3.7448992 | -0.3336837 | -1.4254354 |
| H   | 0.9372672 | 1.2455574 | -1.6546912 |
| H   | 0.3861393 | -0.5175211 | -1.8548771 |
| H   | -0.3653234 | -0.2368975 | 2.0944243 |
| C   | 1.5949897 | 0.1790637 | 1.9947558 |
| O   | 2.2369531 | -0.9434390 | 1.7026998 |
| H   | 1.9547413 | 0.3376961 | 0.9459726 |
| H   | 1.8296887 | 1.1187084 | 1.6579471 |
| H   | 3.1792981 | -0.7017645 | 1.8395147 |

4 (Hydroxy Vinyldene Carbonate) Z

|     |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|
| C   | 0.0169189 | -0.0269891 | -0.5185861 |
| O   | -1.3862511 | 0.0715395 | -0.2799698 |
| C   | -2.0559069 | 0.2649787 | -1.4634255 |
| O   | -1.1873813 | 0.2815299 | -2.4957989 |
| O   | 0.1621200 | 0.8761297 | -2.0195876 |
Cartesian coordinates of structures optimized in the gas phase, distances in atomic units (a_0).

**CO2**

| C  | O  | H  |
|----|----|----|
| 0.8891362 | -0.1991380 | 0.4594418 |
| -3.2498784 | 0.3985308 | -1.5472546 |
| 0.7840494 | 0.9440169 | -2.3360229 |
| 0.5649616 | -0.8463204 | -2.4817611 |
| 1.9439355 | -0.2572539 | 0.1585233 |
| 0.8501718 | -0.3074527 | 1.9243733 |
| 0.1382355 | 0.6392654 | 2.6357497 |
| -0.5096574 | -0.1427412 | 2.1635814 |
| 0.6136574 | -1.3566972 | 2.2585133 |
| 1.2796338 | 0.4456618 | 3.5032237 |

**AcOH**

| C  | O  | H  |
|----|----|----|
| 0.5248971 | 0.2671994 | -0.9626827 |
|   |   |   |   |
|---|---|---|---|
| C  | -0.9688101 | 0.0329165 | -0.0943979 |
| O  | 1.0782217 | 1.3309877 | -0.2612594 |
| H  | -1.2583993 | -0.8143683 | -0.6622139 |
| H  | -1.2654997 | -0.2424334 | 1.0319324 |
| H  | -1.5008660 | 0.9549834 | -0.3077560 |
| O  | 1.2179374 | -0.8890193 | 0.1537969 |
| H  | 2.1733589 | -0.6462661 | 0.1124893 |

**Propynol Hydrogen Carbonate**

| C  | -0.1795665 | -2.4219930 | 0.6636068 |
| C  | -0.5625281 | -1.3664351 | 0.1821455 |
| C  | -1.0409063 | -0.1118496 | -0.4901237 |
| O  | -0.6695705 | 1.0543671 | 0.3768159 |
| H  | -0.6888460 | -0.0045461 | -1.4489572 |
| H  | -2.1514899 | -0.0644603 | -0.3976287 |
| H  | 0.1633846 | -3.3538797 | 1.9943926 |
| O  | 0.5878146 | 1.5557125 | 0.2793859 |
| O  | 1.3419821 | 0.9927012 | -0.6566233 |
| H  | 0.9668532 | 2.4967138 | 0.9452118 |
| H  | 2.2242324 | 1.3385992 | -0.6382237 |

**Exovinyl Carbonate**

| C  | -1.3749869 | -1.1518116 | -0.5325254 |
| C  | -0.4414199 | -0.3122169 | -0.0608929 |
| C  | 0.8526877 | 0.1757773 | -0.6886596 |
| O  | -0.5252977 | 0.2894017 | 1.1789196 |
| H  | -2.2653975 | -1.3995779 | 0.0662074 |
| H  | -1.2571395 | -1.6093485 | -1.5360468 |
| C  | 0.5784828 | 1.1028282 | 1.3936919 |
| O  | 0.7648820 | 1.7456093 | 2.3813979 |
| O  | 1.3992986 | 1.9455084 | 0.3071424 |
| H  | 0.6926865 | 0.7496214 | -1.6284305 |
| H  | 1.5767338 | -0.6459431 | -0.8898436 |

**A’**

| Ag | -1.3005578 | 0.2813612 | -1.2761247 |
| C  | -3.4409869 | 1.7354537 | -2.1749088 |
| O  | -3.1809511 | 2.1580373 | -1.0215809 |
| O  | -2.7682163 | 0.7949497 | -2.7675661 |
| C  | -4.5977778 | 2.3434750 | -2.9667766 |
| H  | -5.2589421 | 1.5413462 | -3.6659828 |
| H  | -4.1839589 | 2.8775320 | -3.8683721 |
| H  | -5.1740843 | 3.0548162 | -2.3621206 |
| P  | 0.1436298 | -0.7641360 | 0.2601966 |
| C  | -0.5332291 | -0.6973562 | 2.0260844 |
| H  | -0.2909521 | -1.6356562 | 2.5369427 |
| C  | 0.0835459 | 0.5161604 | 2.8214393 |
| H  | -0.2569074 | 1.4456137 | 2.2580153 |
| H  | 1.1059137 | 0.4877795 | 2.8892474 |
| C  | -0.6079667 | 0.5866475 | 4.2377008 |
| H  | -0.2531114 | -0.2993333 | 4.8259384 |
| H  | -0.2221998 | 1.4531652 | 4.7656031 |
| C  | -2.1449305 | 0.5806785 | 4.2197168 |
| H  | -2.5515999 | 0.5822630 | 5.2474485 |
| H  | -2.5015916 | 1.5299653 | 3.7330494 |
| C  | -2.6389302 | -0.6415354 | 3.4167429 |
| H  | -3.7931560 | -0.5767170 | 3.3466699 |
| H  | -2.4381771 | -1.5591838 | 3.9599344 |
| C  | -0.8418950 | -0.6677783 | 1.9983614 |
| H  | -2.4107894 | 0.2361547 | 1.4216442 |
| H  | -2.4986389 | -1.5453748 | 1.4564199 |
| C  | 0.3349635 | -2.6037715 | -0.1466271 |
| H  | 1.0253235 | -3.9281927 | 0.6264242 |
| C  | -1.0005833 | -3.3753679 | -0.9774727 |
| H  | -1.7385561 | -2.8814269 | -0.7546679 |
| H  | -1.4282048 | -3.3225256 | 0.9480518 |
| C  | -0.8271761 | -4.8568814 | -0.4919091 |
| H  | -0.1908909 | -5.3763867 | 0.2642082 |
| H  | -1.8175233 | -5.3591228 | -0.4767739 |
| C  | -0.1799271 | -4.9868153 | -1.8788356 |
| H  | -0.0308969 | -6.9687768 | -2.1329584 |
| H  | -0.9394778 | -4.5711811 | -2.6506380 |
| C  | 1.1582487 | -4.2308417 | 1.9348989 |
| H  | 1.5989732 | -4.2906534 | -2.9554504 |
| H  | 1.8894121 | -4.7206887 | -1.2473197 |
| C  | 0.9992134 | -2.7535388 | -1.5336469 |
| H  | 1.9766839 | -2.2396088 | -1.5561268 |
| H  | 0.3484375 | -2.2356233 | -2.2853297 |
| C  | 1.9287354 | -0.2647927 | 0.4016247 |
| C  | 2.7343866 | -0.9589659 | 1.3364541 |
| H  | 2.2741113 | -1.7069753 | 2.0964652 |
| C  | 4.1156333 | -0.7350918 | 1.4394971 |
| H  | 4.7149123 | -1.2918461 | 2.1767519 |
| C  | 4.7229452 | 0.1894292 | 0.5665769 |
| H  | 5.8108138 | 0.3657339 | 0.6169312 |
| C  | 3.9364714 | 0.8292920 | -0.3561744 |
| C  | 4.4077364 | 1.5286324 | -1.8284485 |
| C  | 2.5347857 | 0.7915143 | -0.4597415 |
| C  | 1.7946564 | 1.4767179 | -1.5946501 |
| C  | 6.8639929 | 2.5241194 | -1.2154898 |
| C  | 0.1758974 | 3.1148625 | -2.3062589 |
| H  | -0.5596551 | 3.9082486 | -2.1176783 |
| C  | 0.4196687 | 2.7157638 | -3.6319158 |
| H  | -0.1546261 | 3.1963978 | -4.4476629 |
| C  | 1.3618120 | 1.7253991 | -3.9152485 |
| H  | 1.5596466 | 1.4163809 | -4.9524542 |
| C  | 2.0422557 | 1.1187492 | -2.8483778 |
| H  | 2.7881716 | 0.3122944 | -3.9497624 |
| N  | 0.6161372 | 2.9464413 | 0.1137149 |
| C  | 1.7506538 | 3.4577554 | 0.8864834 |
| H  | 1.4975149 | 3.4564955 | 1.9642907 |
| C  | 2.0199561 | 4.5097233 | 0.5824238 |
| C  | 2.6496683 | 2.9267871 | 0.7413216 |
| C  | -0.597020 | 3.7207147 | 0.3566353 |
| H  | -0.7879388 | 3.7427034 | 1.4528497 |
| H  | -1.4741673 | 3.2466637 | -0.1376727 |
| H  | -0.5106310 | 4.7876685 | 0.9156464 |

B'  

| Ag | -0.9862815 | -0.2358127 | -1.2826216 |
| C  | -3.3802223 | 1.1198887 | -2.5876328 |
| O  | -2.2875808 | 0.1369485 | -2.9341293 |
| O  | -3.9812271 | 1.7035718 | -1.4875325 |
| O  | -3.8675913 | 1.5124696 | -3.6204216 |
| P  | 0.3491907 | -0.9988104 | 0.4916351 |
| C  | -6.4969494 | -0.8232703 | 2.1681749 |
| H  | -0.1539664 | -1.6956356 | 2.7926115 |
| C  | -0.6975819 | 0.4791832 | 2.9127143 |
| H  | -0.3488279 | 1.3439113 | 2.2557599 |
| H  | 1.0003794 | 0.5202238 | 3.0774931 |
| C  | -0.6295584 | 0.6192287 | 4.2624943 |
| C  | -0.4819733 | -0.1958178 | 4.9478623 |
| C  | -0.6448897 | 1.5727941 | 4.7459828 |
| C  | -2.3559394 | 0.5192918 | 4.1945579 |
| C  | -2.8526746 | 0.5878186 | 5.0998692 |
| H  | -2.7197553 | 1.4063176 | 3.5245144 |
| C  | -2.7552933 | -0.7685717 | 3.3671264 |
| H  | -3.8554467 | -0.7981457 | 3.2966787 |
| C  | -2.9088641 | -1.6528420 | 4.9892924 |
| C  | -2.0295682 | -0.8916687 | 2.0138944 |
| H  | -2.3507566 | -0.0601431 | 3.1424663 |
| C  | -2.3559825 | -1.8307602 | 1.5840426 |
| C  | 0.7071679 | -2.8445076 | 0.2939869 |
| H  | 1.3514586 | -3.1376375 | 1.1561562 |
| C  | -0.5722775 | -3.7076651 | 0.3243406 |
| H  | -1.2758726 | -3.3437940 | -0.4626385 |
| H  | -1.8987044 | -3.9591737 | 1.2988731 |
| C  | -2.5816144 | -5.1985721 | 0.8866877 |
| C  | 0.3395227 | -5.8789322 | 0.9449987 |
| H  | -1.2081496 | -5.7791899 | 0.8765799 |
| C  | 0.5242566 | -5.4264894 | -1.2180252 |
| H  | 0.7711807 | -6.4990777 | -1.3421662 |
| H  | -0.1192227 | -5.1414125 | -2.0859242 |
| C  | 1.8043641 | -4.5688485 | -1.2415086 |
| H  | 2.3401614 | -4.6958976 | -2.2096644 |
| C  | 2.5019708 | -4.9276556 | -0.4464924 |
| C  | 1.4968364 | -3.9777576 | -1.9492921 |
| C  | 2.4418988 | -2.4967069 | -1.9036629 |
| C  | 0.897545 | -2.8899623 | -1.8703316 |
| C  | 2.0675324 | -0.3305174 | 0.7191333 |
| C  | 2.8566030 | -0.8773306 | 1.7510566 |
| C  | 4.2129738 | -1.6689911 | 2.4476082 |
| C  | 4.2034322 | -0.5261332 | 1.9181122 |
| H  | 4.7914258 | -0.9674613 | 2.7392557 |
| C     | 4.7929283 | 0.3815544 | 1.0221214 |
| H     | 5.856409  | 0.6574242 | 1.1248051 |
| C     | 4.0201226 | 0.9414978 | -0.0044454 |
| H     | 4.4758558 | 1.6633814 | -0.7924378 |
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| C     | 1.9257516 | 1.2437628 | -1.3318968 |
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| C     | 6.2477260 | 2.6877414 | -2.3672342 |
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| H     | 0.0521899 | 2.5731295 | -4.5197394 |
| C     | 1.6419380 | 1.2789599 | -3.7784131 |
| H     | 1.9322779 | 0.9017552 | -4.7721027 |
| C     | 2.2978142 | 0.8127759 | -2.6252720 |
| H     | 3.0914676 | 0.0569080 | -2.7154413 |
| N     | 0.6251927 | 2.7331231 | 0.9853956 |
| C     | 1.5597607 | 3.3935404 | 0.8786025 |
| H     | 1.2284809 | 3.4621437 | 1.9387394 |
| H     | 1.7639566 | 4.4351703 | 0.5135363 |
| C     | 2.5103371 | 2.8265836 | 0.8568979 |
| C     | 0.7553566 | 3.4298681 | 0.1810442 |
| H     | -1.0359464 | 3.5078399 | 1.2550151 |
| H     | -1.5523476 | 2.8605122 | -0.3566759 |
| H     | -0.7132760 | 4.4745973 | -0.2267205 |
| C     | -4.677935 | 2.6634142 | -3.3616483 |
| H     | -5.8186585 | 2.5192719 | -3.9494360 |
| H     | -4.9191585 | 2.7101507 | -2.2761638 |
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| Ag  | -1.2652971 | 0.4767736 | -1.2432525 |
| P   | 0.2099736 | -0.7086321 | 0.2469998 |
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| H   | -0.2171115 | -1.6785208 | 2.4660739 |
| C   | 0.1422925 | 0.4257666 | 2.8966258 |
| H   | -0.0273827 | 1.4049673 | 2.3876248 |
| H   | 1.2445333 | 0.3963597 | 2.9765891 |
| C   | -0.4823845 | 0.4458274 | 4.2995551 |
| H   | -0.2142221 | -0.4994067 | 4.8399180 |
| H   | -0.0313336 | 1.2748619 | 4.8916467 |
| C   | -2.0128345 | 0.5854458 | 4.2507097 |
| H   | -2.4365513 | 0.5556979 | 5.2862504 |
| H   | -2.2813917 | 1.5662794 | 3.8244927 |
| C   | -2.5394861 | -0.5123309 | 3.7733474 |
| H   | -3.7311161 | -0.3479544 | 3.2733259 |
| H   | -2.5049299 | -1.5906577 | 3.8677004 |
| C   | -2.0147771 | -0.5291293 | 1.9707349 |
| H   | -2.2676089 | 0.4283762 | 1.4661057 |
| H   | -2.4844876 | -1.3338843 | 1.3628248 |
| C   | 6.3227731 | -2.5468809 | -0.1951099 |
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| H   | -1.7377666 | -2.7996181 | -0.8862918 |
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| C   | 1.1253673 | -4.2900447 | -2.9579303 |
| H   | 1.6005837 | -4.2706271 | -2.9820520 |
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| H   | 2.0391431 | -2.2825487 | -1.5351864 |
| C   | 0.4454447 | -2.1579660 | -2.3322897 |
| C   | 0.1525930 | -0.2865239 | 0.3824729 |
| C   | 2.8131584 | -1.9699993 | 1.2588689 |
| H   | 2.3372833 | -1.8155875 | 1.9860763 |
| C   | 4.2081448 | -0.9093405 | 1.3178257 |
| H   | 4.7998113 | -1.5267999 | 2.0129164 |
| C   | 4.8329520 | 0.0222870 | 0.4741573 |
| H   | 5.9289625 | 0.1423183 | 0.4991523 |
| C   | 4.9552603 | 0.8196447 | -0.3657186 |
| H   | 4.5417850 | 1.5563386 | -1.9356283 |
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H -0.1082916 3.5856162 -4.1268076

TS - D'
Ag -1.2226132 0.2154393 -1.3923765
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| C | 1.0772715 | 2.5744623 | -0.6614944 |
| C | -0.1957670 | 2.9825616 | -0.1334289 |
| C | -1.1287791 | 3.5544531 | -1.0467845 |
| H | -2.1207553 | 3.8573798 | -0.6762272 |
| C | -0.8118616 | 3.7719353 | -2.3899092 |
| C | 0.4587269 | 3.4388617 | -2.8846048 |
| H | 0.7239956 | 3.6295815 | -3.9382264 |
| C | 1.3638949 | 2.8424290 | -2.0127237 |
| H | 2.3739946 | 2.5346889 | -2.3967557 |
| N | -0.8255648 | 2.8911825 | 1.2277255 |
| C | 0.3596641 | 3.3952613 | 2.2354793 |
| H | 0.6859672 | 2.8921657 | 3.2142184 |
| H | 0.1421930 | 4.4897619 | 2.3703648 |
| H | 1.4198272 | 3.2762740 | 1.9696331 |
| C | -1.9318464 | 2.9909614 | 1.6986714 |
| H | -2.0466538 | 2.5965606 | 2.6375679 |
| H | -2.5656019 | 2.2848881 | 0.9337764 |
| H | -2.3059772 | 3.9596011 | 1.6168072 |
| C | -2.6113219 | 0.2768176 | -3.0675468 |
| C | -3.7243961 | 0.3879709 | -2.4865117 |
| H | -2.1635881 | 0.0792499 | -4.0453444 |
| C | -5.1464193 | 0.4141487 | -2.0862539 |
| H | -5.7513112 | -0.9726665 | -2.8873688 |
| O | -5.3815793 | 0.3682201 | -0.8931897 |
| H | -5.4868974 | 1.4745895 | -1.9980364 |
| C | -4.3811067 | 0.0366249 | 0.0736858 |
| O | -4.4965396 | 0.3634599 | 1.1660314 |
| O | -3.4666951 | 0.7349319 | -0.3512199 |
| H | -1.5875222 | 4.2236811 | -3.0534095 |

**TS - E**

|   |   |   |   |
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| Ag | 1.4498620 | -0.8325650 | -1.0037789 |
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| C | -0.6755871 | 0.6391103 | 1.9834341 |
| H | 0.1685970 | 1.6208515 | 2.4657990 |
| C | -1.5379749 | 0.2662644 | 2.3076274 |
| H | -1.8096577 | -0.6445564 | 1.7262518 |
| H | -2.2269187 | 1.9697293 | 1.9676432 |
| C | -1.7333668 | 0.9169279 | 3.8161345 |
| H | -1.5796795 | 0.9776112 | 4.3693070 |
| H | -2.7879647 | -0.2636210 | 4.0966726 |
| C | -0.7621873 | -1.0420303 | 4.3583575 |
| H | -0.9005858 | -1.1689313 | 5.4557195 |
| H | -0.9941968 | -2.8267823 | 3.8926462 |
| C | 0.9381555 | -0.6647511 | 4.9426941 |
| H | 1.3879444 | -1.4629685 | 4.3815152 |
| C | 0.9689566 | 0.2609651 | 4.6042281 |
| C | 0.8998473 | -0.4395252 | 2.5340637 |
| H | 0.7420996 | -1.3912573 | 1.9864752 |
| C | 1.9554447 | -0.1346891 | 2.3376377 |
| C | 1.3082142 | 2.4515731 | 0.9385894 |
| C | 0.7495808 | 3.2667137 | 0.5562069 |
| C | 2.6576289 | 2.2566522 | 0.7653573 |
| H | 3.1829450 | 1.3747974 | 0.3244996 |
| H | 4.2955997 | 2.0524100 | 1.8414292 |
| C | 3.5668492 | 3.5935071 | 0.6393418 |
| C | 3.0829682 | 4.3531511 | 1.1853432 |
| C | 4.5301163 | 3.3107477 | 1.1418759 |
| C | 3.7761763 | 3.9933347 | -0.8296104 |
| H | 4.3919812 | 4.0285307 | -0.8962959 |
| H | 4.3573534 | 3.1028792 | -1.3462891 |
| C | 2.4344884 | 4.1946505 | -1.5536137 |
| C | 2.6096764 | 4.3414631 | -2.6279214 |
| H | 1.9096346 | 4.9842309 | -1.155441 |
| C | 1.5325175 | 2.8604914 | -1.4346617 |
| C | 0.5571130 | 3.0469263 | -1.9364224 |
| H | 2.6105794 | 2.9962229 | -1.9732522 |
| C | -1.3567673 | 1.4752126 | -0.6292992 |
| C | -1.8871937 | 2.7232323 | -0.2269668 |
| H | -1.4162668 | 3.2746888 | 0.6161832 |
| C | -2.9953362 | 3.2944289 | -0.8620829 |
| H | -3.3879965 | 4.2674475 | -0.5228748 |
| C | -3.5834996 | 2.6238483 | -1.9477164 |
| H | -4.4383222 | 3.9703110 | -2.4815139 |
| C | -3.8653717 | 1.3756036 | -2.3437989 |
| H | -3.5801145 | 0.8344458 | -3.1791987 |
|   |   |   |   |   |
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| C | -1.5226229 | -0.5772366 | -2.1425361 |
| C | -1.7299309 | -1.8171523 | -1.4826395 |
| C | -1.1229088 | -2.9849140 | -2.6217202 |
| H | -1.1881558 | -3.9415191 | -1.4824390 |
| C | -0.4039949 | -2.9576898 | -3.2243798 |
| C | -0.2755994 | -1.7625184 | -3.9568295 |
| H | 0.2651462 | -1.7346603 | -4.9110991 |
| C | -0.8304194 | -0.5876677 | -3.4159909 |
| H | -0.7075739 | 0.3765404 | -3.9465109 |
| N | -2.4724262 | -1.8867088 | -2.2895353 |
| C | -3.8309495 | -1.3456258 | -0.2757738 |
| H | -4.1657330 | -1.1968594 | 0.7752301 |
| H | -4.5551099 | -2.9437884 | -0.7712327 |
| H | -3.8869188 | -0.3668918 | -0.7874241 |
| C | -2.4887909 | -3.1391142 | 0.4993447 |
| C | -2.8015876 | -2.9285435 | 1.5118595 |
| H | -1.3743147 | -3.5257787 | 0.5755921 |
| H | -3.0405584 | -3.9938868 | 0.0415389 |
| C | 3.0053954 | -1.9711271 | -2.1368279 |
| C | 2.9486395 | -2.7666370 | -1.1593245 |
| H | 2.9658580 | -1.8641244 | -3.2241083 |
| C | 3.1302969 | -3.3314976 | 0.1958295 |
| H | 3.5373916 | -2.5525107 | 0.8622859 |
| O | 1.9159931 | -3.7683063 | 0.7346686 |
| H | 3.8925692 | -4.1471203 | 0.1114003 |
| C | 1.1890101 | -4.6292597 | -0.2312043 |
| O | 0.1207766 | -5.0662335 | 0.1964976 |
| O | 1.7749743 | -4.7198756 | -1.3454803 |
| H | 0.6632990 | -3.8905131 | -3.5761198 |

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| C   | 2.0716371 | 1.8874057 | 0.9832507 |
| C   | 0.9567338 | 2.5306281 | -0.6853455 |
| C   | -0.3239324 | 2.8397974 | -0.1188542 |
| C   | -1.2867434 | 3.4249824 | -0.9658966 |
| H   | -2.2922861 | 3.6637278 | -0.5821319 |
| C   | -1.0826423 | 3.7261315 | -2.3097357 |
| C   | 0.2363811 | 3.4535773 | -2.8526851 |
| H   | 0.4618279 | 3.6871363 | -3.9952328 |
| C   | 1.2178500 | 2.8666708 | -2.9322079 |
| H   | 2.2053354 | 3.6291359 | -2.4485994 |
| N   | -0.8139385 | 3.5252980 | 1.2494188 |
| C   | 0.2087770 | 3.2282970 | 2.1499965 |
| H   | 0.5002589 | 3.7151537 | 3.2297964 |
| H   | -0.6123625 | 4.3099532 | 2.3621012 |
| H   | 1.2752870 | 3.2921866 | 1.9833737 |
| C   | -2.0192661 | 2.5096516 | 1.6287225 |
| H   | -2.9036617 | 2.0194895 | 2.6242132 |
| H   | -2.6084118 | 1.9663232 | 0.9623384 |
| H   | -2.4896602 | 3.5206336 | 1.7155038 |
| C   | -2.9736797 | 0.0281505 | -2.3866191 |
| C   | -4.1545691 | 0.5996166 | -1.9866031 |
| H   | -2.9829419 | -0.3341831 | -3.4368287 |
| C   | -5.4998128 | 0.6494195 | -2.6886375 |
| H   | -5.9422648 | -0.3295767 | -2.9685499 |
| O   | -6.3529560 | 1.2698480 | -1.7114847 |
| H   | -5.4583309 | 1.2995988 | -3.5916322 |
| C   | -5.6622384 | 1.4743359 | -0.5535634 |
| O   | -6.1155583 | 1.9767935 | 0.4465857 |
| O   | -4.3759619 | 1.0297234 | -0.6864167 |
| H   | -1.8199063 | 4.1724669 | -2.9314571 |

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Ag  | 1.0199039 | -1.2458676 | -0.6760519 |
P   | 0.1977443 | 0.8764836 | 0.1644473 |
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H   | 0.2825240 | 1.9859220 | 2.3568880 |
C   | -1.3856909 | 0.6023149 | 2.5544041 |
H   | -1.6606997 | -0.4157432 | 2.1935669 |
C   | -2.1315221 | 1.2996432 | 2.1160319 |
C   | -1.4678324 | 0.6548367 | 4.0926372 |
H   | -1.2997282 | 1.7957358 | 0.4363997 |
C   | -2.4972866 | 0.3389259 | 4.4199049 |
C   | -0.4316401 | -0.2637707 | 4.7606321 |
H   | -0.4788776 | -0.1615382 | 5.8683797 |
H   | -0.6897411 | -1.3271966 | 4.5313737 |
C   | 0.9858669 | 0.9419355 | 4.2515938 |
C   | 1.7297312 | -0.6797816 | 4.6592714 |
H   | 1.2931913 | 1.0599997 | 4.5943363 |
C   | 1.0596365 | -0.0264276 | 2.7140291 |
H   | 0.8392366 | -1.0954300 | 2.3713675 |
H   | 2.0944194 | 0.1976446 | 2.3741687 |
C   | 1.4535642 | 0.2251864 | -0.2613029 |
H   | 1.6359111 | 3.1807644 | 0.1356944 |
C   | 2.8398059 | 1.9981221 | 0.3795887 |
H   | 3.2179838 | 0.9918364 | 0.8631897 |
H   | 2.7028286 | 1.9917151 | 1.4887343 |
C   | 3.8496464 | 3.0815809 | -0.8526721 |
H   | 3.5287576 | 4.0659642 | 0.3643082 |
C   | 4.8439777 | 2.8598354 | 0.3968576 |
C   | 3.9693212 | 3.1911187 | -1.5815204 |
C   | 4.6634244 | 4.0862770 | -1.8663093 |
C   | 3.9444496 | 2.2473880 | -1.9886093 |
C   | 2.8502963 | 3.4289772 | -2.2499556 |
C   | 2.6592327 | 3.4585647 | -3.3251741 |
C   | 2.1944573 | 4.4282429 | -1.9001635 |
C   | 1.5728233 | 2.3499218 | -1.7985145 |
H   | 0.5787148 | 2.5526772 | -2.2468177 |
H   | 1.9019218 | 1.3595734 | -2.2971252 |
C   | -1.3558367 | 1.6778688 | -0.4674207 |
C   | -1.7134879 | 2.9336660 | 0.0861244 |
H   | -1.1207982 | 3.3568078 | 0.9687412 |
H   | -2.0802050 | 3.6725133 | -0.4093951 |
H   | -3.0544251 | 4.6446740 | 0.0442141 |
C   | -3.5455665 | 3.1672928 | -1.4868385 |
C   | -4.3932761 | 3.7396607 | -1.8980992 |
C   | -3.2975854 | 1.9236631 | -2.6362978 |
C   | -3.7954418 | 1.5172839 | -2.8765155 |
Cartesian coordinates of hydrogen carbonates and corresponding cyclic exo-vinylene carboxantes, distances in atomic units (\(a_0\)).

| Hydrogen Carbonate (H, H) |  |  |  |
|---|---|---|---|
| C | -2.7273166 | -1.1638976 | -0.6859774 |
| C | -1.5699244 | -0.7994881 | -0.5574274 |
| C | -0.1739387 | -0.3912043 | -0.4335084 |
| O | 2.1439309 | 0.5764045 | 0.1582946 |
| C | 1.1579194 | 1.0870738 | 0.8592933 |
| O | 3.3359081 | 1.8674916 | 1.8455366 |
| O | -0.0539352 | 0.5714505 | 0.6445334 |
| H | 3.7573610 | -1.4861912 | -0.7926116 |
| H | 0.1855228 | 0.6584242 | -1.3823349 |
| H | 0.4782414 | -1.2796023 | -0.2299192 |
| H | 2.9083232 | 0.9758848 | 0.4656410 |

| Hydrogen Carbonate (H, Me) |  |  |  |
|---|---|---|---|
| C | -2.7113135 | -1.3593192 | -0.9395325 |
| C | -1.5852210 | -0.8882414 | -0.9656879 |
| C | -0.2242679 | -0.3456147 | -0.1480976 |
| O | 2.0665098 | 0.1610922 | 1.0512857 |
| C | 1.0528989 | 0.9799279 | 1.4724958 |
| O | 1.1846498 | 1.8591031 | 2.2917972 |
| O | -0.1199812 | 0.7942591 | 0.8759150 |
| C | 3.7119723 | -1.7719774 | -0.9555331 |
| C | 0.1085340 | 0.2359248 | -1.5211741 |
| H | 3.5029564 | -1.1476607 | 0.1139256 |
| H | 2.8608691 | 0.4463200 | 1.5626406 |
| H | 1.1564605 | 0.5928222 | 1.5365109 |
| H | 0.0745633 | 0.9784663 | -1.7573904 |
| H | -0.1083360 | -0.5459633 | -2.3921142 |

| Hydrogen Carbonate (Me, Me) |  |  |  |
|---|---|---|---|
| C | -2.9731648 | -0.8941441 | -0.2254217 |
| C | -1.7922312 | -0.5996511 | -0.1568712 |
| C | -0.3533814 | -0.1756525 | -0.1273854 |
| O | 1.9066312 | 0.0346436 | 0.7192468 |
| C | 0.8784660 | 1.3759318 | 1.4311334 |
| O | 0.8935027 | 2.1371871 | 2.3713664 |
| O | -0.2478447 | 0.7952024 | 0.9513712 |
| H | -0.4233427 | -1.0622601 | -0.2718254 |
| C | 0.0518804 | 0.4877445 | -1.4586499 |
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