Preparation and Utility of Cyclic Enol Carbonates

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This article is dedicated to Professor Mukaiyama on the occasion of his 77th birthday.

Abstract: Treatment of iodo carbonates with LiHMDS at low temperature readily affords cyclic enol carbonates with either five- or six-membered rings. Reaction with potassium tert-butoxide results in the in situ formation of an enolate which after transmetallation participates in aldol or Mannich reactions. Alternatively, the potassium enolates can be trapped with silylating or trifluorinating agents. The regio- and stereoselective generation of silyl enol ethers with up to four substituents can be achieved.

Key words: enols, aldol reactions, tandem reactions, stereoselectivity, regioselectivity

Iodocarbonate cyclization on an allylic,\(^1\) or particularly a homoallylic r-system,\(^1,2\) is a well established and valuable synthetic operation. First described by Cardillo in 1981, a number of conditions\(^1,2\) now exist to effect this transformation with various levels of diastereoselectivity. Smith’s IBr protocol\(^2b\) generally provides the highest ratio of syn to anti products 1. The resulting iodo carbonates 1 are versatile intermediates providing facile access to a wide variety of structural motifs,\(^1,2\) including epoxy alcohols, diols, triols, and cyclic carbonates. One area of investigation that has received scant attention is a base-induced dehydrohalogenation to form various cyclic enol carbonates 2 (Scheme 1).

Scheme 1 Strategy for the preparation of cyclic enol carbonates and use as an enolate equivalent

Alkylidene products are known when the ring size is five and are typically prepared by condensation of a propargylic alcohol with carbon dioxide in the presence of a catalyst.\(^3\) Subsequent work has demonstrated that these compounds are useful synthetic intermediates for the preparation a wide variety of compounds such as oxazolidinones, \(\beta\)-oxopropyl carbonates and carboxamides, furanone derivatives and other heterocycles, cyclopropanes, optically active bicyclic carbonates and 1,2-diols.\(^4,7\)

There have been two previous reports of routes that afford products of type 2. The first by Marshall\(^8\) utilizes an iodolactonization reaction of homopropargylic alcohols followed by reduction with tributyl tin hydride. Heathcock’s\(^9\) approach employs a conjugate reduction of a \(\beta\)-phenyl carbonate enone using Stryker’s reagent.\(^10\) In both cases the substrate scope is not well established and the reagents involved are toxic or expensive. It is known that the six-membered cyclic enol carbonates 2 are precursors to \(\beta\)-hydroxy ketones, \(\beta\)-keto carbonates, and \(\alpha,\beta\)-hydroxy ketones.\(^8,9\)

Addition of an appropriately chosen metal nucleophile to 2 might allow for the in situ generation of an enolate (Scheme 1) that then could be trapped or participate in aldol or Michael reactions. If the cyclic enol carbonates 2 contained geometrically defined substituents on the alkylidene terminus, it should be possible to generate enolates in a regio- and stereoselective fashion. This report summarizes our efforts to achieve these objectives.

The study was initiated on the iodo carbonate derived from benzaldehyde 4. In general, all additional substrates were prepared following the sequence shown in Scheme 2,\(^11\) wherein an aldehyde was allylated and then protected in situ when possible\(^12\) as the tert-butyli carbonate with Boc\(_2\)O. Most often, the iodine-induced electrophilic cyclization was performed utilizing Smith’s conditions\(^2b\) to simplify isolation and characterization. However, since IBr is incompatible with polyolefinic substrates,\(^2b\) the milder I\(_2\)-MeCN system of Bartlett\(^2b\) was used in some cases.

Scheme 2 General approach to the synthesis of iodo carbonate starting materials

With multi-gram quantities of 4 readily available we began optimization of the desired elimination reaction (Table 1). A number of amine bases (Et\(_3\)N, DBU, and Hunig’s Base) and inorganic bases (NaH, KH, CsCO\(_3\), and K\(_2\)CO\(_3\)) were either ineffective or did not provide the desired product 5 in good yield. For example DBU slowly converted the starting material to product 5 (Table 1, entries 1 and 2) but upon prolonged stirring only the unde-
sired double elimination product 6 was observed. In contrast LiHMDS (Table 1, entry 4) afforded the desired cyclic enol carbonate 5 in very high yield with little or no elimination products. Changing to the corresponding sodium or potassium bis(trimethylsilyl) amides (Table 1, entries 5 and 6), and other strong bases such as LDA or potassium tert-butoxide was less effective. Further optimization of the reaction indicated that THF was the solvent of choice. As the temperature was raised, or the amount of base increased, the amount of product was markedly reduced. It appears that LiHMDS at this temperature combines the necessary basicity with low nucleophilicity to avoid undesired side reactions.

A series of iodo carbonates was then prepared to test the generality of this approach to various cyclic enol carbonates. These results are collected in Table 2. The previously optimized conditions performed well for nearly all types of substrates tested, be they aromatic (Table 2, entries 1 to 5), conjugated (Table 2, entry 6), or aliphatic (Table 2, entries 7 to 11). One exception relates to a substrate derived from a syn crotylation of benzaldehyde (Table 2, entry 3). The exceptionally slow rate and low yield of this reaction is consistent with an expected E2 dehydrohalogenation creating 1,3-allylic strain in the transition state to products. Both syn and anti iodo carbonates behaved similarly, affording the same product in similar yield and reaction time (Table 2, entries 1 and 6). Thus the selectivity in the iodo carbonate cyclization protocols is not of significant concern. Finally we tested the approach developed for the synthesis of the six-membered family of enol carbonates on a five-membered analogue (Table 2, entry 11).

### Table 1 Effect of the Base

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield of 5 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>DBU</td>
<td>20</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>DBU</td>
<td>20</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>LDA</td>
<td>–78</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>LiHMDS</td>
<td>–78</td>
<td>1</td>
<td>94 (91&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>5</td>
<td>NaHMDS</td>
<td>–78</td>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>KHMDS</td>
<td>–78</td>
<td>1</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>KO-t-Bu</td>
<td>–78</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> All reactions performed on a 0.46 mmol scale.<br><sup>b</sup> HPLC yield.<br><sup>c</sup> Isolated yield.

### Table 2 Substrate Scope for Preparation of Cyclic Enol Carbonates<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>No.</th>
<th>Product, yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>5</td>
<td>91 (89&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>2</td>
<td>71</td>
<td>7</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>81</td>
<td>8</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>91</td>
<td>9</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>10</td>
<td>92 (87&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>11</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>12</td>
<td>12</td>
<td>56 (69&lt;sup&gt;c&lt;/sup&gt;)</td>
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<tr>
<td>8</td>
<td>13</td>
<td>13</td>
<td>91</td>
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<td>9</td>
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<td>14</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>15</td>
<td>99</td>
</tr>
<tr>
<td>11</td>
<td>16&lt;sup&gt;f&lt;/sup&gt;</td>
<td>16</td>
<td>82</td>
</tr>
</tbody>
</table>

<sup>a</sup> All reactions performed on 0.1 to 1.0 mmol scale.<br><sup>b</sup> Isolated yields.<br><sup>c</sup> Anti analogue of substrate.<br><sup>d</sup> Determined by <sup>1</sup>H NMR.<br><sup>e</sup> 30 mmol scale.<br><sup>f</sup> Syn to anti 2.2:1.0.

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**Scheme 3** Formation of β-keto carbonates

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entry 11b) and were pleased to see that the reaction conditions worked equally well. This approach affords another route to this useful class of molecules.

Attention was then focused on finding a suitable nucleophile for the in situ preparation of the enolates. Extensive screening and optimization resulted in the two sets of conditions shown in Scheme 3.

Initially potassium tert-butoxide did not appear to be a good candidate to effect this transformation; however this was in large part due to the rate of addition of the base which is quite important as the reaction is extremely rapid (Scheme 3, protocol A). With very short reaction times, 27 was formed in excellent yields (Scheme 3, protocol A). Quenching studies at increasing reaction times indicated that the stability of the enolate was low as widely differing amounts of 27 were observed. The addition of ZnCl₂ prior to the base improved the consistency of the reaction, presumably by mitigating the enolate basicity and the rate of addition was no longer an issue (Scheme 3, protocol B). In this case more t-BuOK must be added as some of this reagent is consumed by reacting with ZnCl₂. For most purposes the simple protocol that lacks this latter reagent is preferred, provided quenching or further reaction is rapid.

The lithium and sodium analogues were far less effective as were any other solvents except THF. Finally increases in temperature resulted in a serious decrease in the yield.

Quenching the reaction of 4-methylene-6-phenyl[1,3]dioxan-2-one (5) and t-BuOK shortly after the addition of the base resulted in nearly full deuterium incorporation. Attempts to trap the potassium enolate–alkoxide with various aldehydes in an aldol reaction failed to yield any of the expected addition product. However we did observe some aldol product that had eliminated the Boc-protected carbinol, suggesting that the potassium enolate–alkoxide was too basic a species. Consequently we investigated the reactivity of several metal enolates prepared by the addition of various metal salts (Table 3, entries 1 to 8).

The most useful additive we have identified to date is zinc chloride (Table 3, entry 2) which gave very high yields (80 to 95%) for all classes of aldehydes (aromatic, conjugated, and aliphatic) and imines tested, although it exhibited relatively poor diastereoselectivity (1:1 to 3:1).13 In

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Yield (%)a</th>
<th>drb</th>
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<tr>
<td>1</td>
<td>–</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>ZnCl₂</td>
<td>83 (81)c</td>
<td>2.2:1</td>
</tr>
<tr>
<td>3</td>
<td>MgBr₂·OBt₂</td>
<td>20</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>TiCl₄</td>
<td>29</td>
<td>1:1.2</td>
</tr>
<tr>
<td>5</td>
<td>Bu₃BOTf</td>
<td>83d</td>
<td>6.7:1</td>
</tr>
<tr>
<td>6</td>
<td>Cy₂BCl</td>
<td>69d</td>
<td>3.2:1</td>
</tr>
<tr>
<td>7</td>
<td>9-BBNOTf</td>
<td>72d</td>
<td>1.5:1</td>
</tr>
<tr>
<td>8</td>
<td>Cp₂ZrCl₂</td>
<td>48</td>
<td>1.2:1</td>
</tr>
</tbody>
</table>

a Reactions performed on a 0.46 mmol scale.
b Determined by 1H NMR.
c Isolated yield.
d Oxidative work up [30% H₂O₂– NaOH (1 M)–Et₂O).

The most useful additive we have identified to date is zinc chloride (Table 3, entry 2) which gave very high yields (80 to 95%) for all classes of aldehydes (aromatic, conjugated, and aliphatic) and imines tested, although it exhibited relatively poor diastereoselectivity (1:1 to 3:1).13 In

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>No.</th>
<th>Product, yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>29, 99</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>30, 97</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17</td>
<td>31, 82</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>26</td>
<td>32, 94</td>
<td></td>
</tr>
</tbody>
</table>

a All reactions performed on a 0.50 mmol scale.
b Isolated yields.
some cases the diastereoselectivity can be improved by use of Bu₂BOTf (Table 3, entry 5); however this is not a general effect.\textsuperscript{15}

Upon addition of a solution of \textit{N}-phenyltrifluoromethane sulfonamide\textsuperscript{14} to the potassium enolate, vinyl triflates were isolated in excellent yields (Table 4, entries 1 to 4). Alternatively the addition of TBSOTf yielded silyl enol ethers that were easily purified using conventional techniques.\textsuperscript{15} These results are collected in Table 5.

In general this transformation was very efficient (Table 5, entries 1 to 9) for all substrates tested. Of particular interest was whether the stereochemical information in configurationally defined cyclic enol carbonates would be maintained on conversion to the silyl enol ether.\textsuperscript{16} To this end we prepared a number of such compounds (19, 20, 33–35) using methodology discussed above or via other literature protocols (33, 34 and 35\textsuperscript{15}).

Subjecting the cyclic enol carbonates 19, 20, 33–35 (Table 5, entries 6 to 9) to the stated reaction conditions in most cases yielded products 41–44 in which the stereochemical information present in the starting materials was maintained. The same was not true for the E(O)-cyclic enol enolate 19, where a mixture of isomers was observed (40). It seems plausible that the metal–oxygen ion pair under these conditions is not sufficiently tight to prevent enolate isomerization. The products 43 and 44, based upon tetrasubstituted cyclic enol carbonates 34 and 35 are the equivalent of the regio- and stereoselective synthesis of a silyl enol ether of an \(\alpha,\alpha’\)-disubstituted ketone. To our knowledge, very few methods\textsuperscript{19–21} exist to prepare such compounds especially in an acyclic system.

In summary, treatment of iodo carbonates with LiHMDS at low temperature affords cyclic enol carbonates with either five- or six-membered-ring sizes in good to excellent yields. Reagents involved in their preparation are inexpensive, and the reactions are easy to perform while the products are stable and often solids. Ready access to such compounds will allow for the development of some useful chemistry to prepare a variety of other structural motifs, as has already been demonstrated in the five-membered-ring series. For example, we have demonstrated that reaction with potassium \textit{tert}-butoxide results in the in situ formation of enolates which after transmetallation participate in aldol or Mannich reactions. Alternatively, the potassium enolates may be trapped with silylating or triflating agents. In most cases this allows the regio- and stereoselective generation of silyl enol ethers with up to four substituents which is difficult to accomplish by other means.

The following includes representative experimental procedures and details for isolation of compounds. All reported preparations of substrates are unoptimized. Full characterisation of all novel, and partial characterisation of known, compounds presented in the report are described.

\textsuperscript{1}H NMR were recorded using Varian instruments at 300, 400 or 500 MHz. \textsuperscript{13}C NMR were recorded using Varian instruments at 75, 100, or 125 MHz. \textsuperscript{19}F NMR were recorded using Varian instruments at 282, or 376 MHz. NMR shifts are reported relative to a TMS internal standard or relative to BF\textsubscript{3}·OEt\textsubscript{2} for \textsuperscript{19}F. IR spectra were obtained using a Perkin–Elmer FT-IR spectrometer (spectrum 1000).

### Table 5 Substrate Scope for Conversion to Silyl Enol Ethers\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate No.</th>
<th>Product, yield (%)\textsuperscript{b}</th>
<th>Entry</th>
<th>Substrate No.</th>
<th>Product, yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19</td>
<td>36, 81</td>
<td>20</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>37, 80</td>
<td>21</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>38, 93</td>
<td>33</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>26</td>
<td>39, 96</td>
<td>34</td>
<td>E(O):Z(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>E(O):Z(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>39, 96</td>
<td>35</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Z(O):E(O) 30:1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All reactions performed on a 0.1 to 1.0 mmol scale.

\textsuperscript{b} Isolated yields.

\textsuperscript{c} Determined by \textsuperscript{1}H NMR.
HRMS were obtained on a VG 70-250S (double focusing) mass spectrometer at 70 eV or an ABI/Sciox Qstar mass spectrometer with an ESI source. MS/MS and accurate mass capabilities. HPLC analysis was performed using a Hewlett Packard Series 1100 HPLC with a UV detector. Ms were determined using a Fisher-Johns mp apparatus and are uncorrected.

THF, dioxane, and Et2O were distilled from sodium–benzophenone. Pentane, toluene, CH2Cl2, and MeCN were distilled from calcium hydride or used as ACS reagents if noted. LiHMDS (1 M, THF), t-BuOK (1 M, THF), ZnCl2 (1 M, Et2O), and Bu2BOTf (1 M, CH2Cl2) were purchased from Aldrich as solutions and used as received. AllylMgBr was purchased from Aldrich as a solution (1.0 M) in Et2O, and was titrated periodically. IBr, I2, and various other organics were dried (MgSO4), filtered, and concentrated in vacuo. Attempts were made to purify the product by flash chromatography; however, separation of the product from the remaining starting material was not possible. Freshly distilled THF was added to the crude reaction mixture, the resulting solution recooled to ~78 °C, and KHMTDS (0.75 equiv) was added via syringe. This resulted in consumption of the starting material although it did not seem to afford additional product. The reaction was quenched and worked up as noted above and the resulting crude mixture was purified by flash chromatography (10 to 17% EtOAc–hexanes) to afford the product.

Yield: 33%; viscous light yellow oil; Rf = 0.23 (17% EtOAc–hexanes).

IR (neat): 2980, 1767, 1670, 1455, 1279, 1202, 1076, 699 cm–1.

1HNMR (400 MHz, CDCl3): δ = 7.43–7.35 (m, 3 H), 7.29–7.26 (m, 2 H), 5.54 (dd, J = 3.6, 1 H), 4.86–4.84 (m, 1 H), 4.40–4.38 (m, 1 H), 3.08–3.01 (m, 1 H), 0.97 (d, J = 7.2 Hz, 3 H).

13CNMR (100 MHz, CDCl3): δ = 155.5, 146.2, 134.7, 128.7, 128.7, 125.9, 93.8, 81.6, 35.2, 11.7.

HRMS: m/z calcd for C12H13O3Na: 213.0865; found: 213.0863.

(5S,6S)-5-Methyl-4-methylene-6-phenyl[1,3]dioxan-2-one (17)
Prepared according to the general protocol outlined for the preparation of compound 5 with 7 (1.85 g, 5.8 mmol). The product was purified by flash chromatography (17% EtOAc–hexanes) and was recovered as an oil.

Yield: 96%; colorless oil; Rf = 0.18 (17% EtOAc–hexanes).

IR (thin film, CH2Cl2): 3037, 2925, 1769, 1697, 1455, 1232, 1067, 759 cm–1.

1HNMR (400 MHz, CDCl3): δ = 7.46–7.34 (m, 5 H), 5.44 (dd, J = 10.8, 3.6 Hz, 1 H), 4.87–4.85 (m, 1 H), 4.43–4.42 (m, 1 H), 2.94 (dd, J = 15.2, 3.2 Hz, 1 H), 2.80 (dd, J = 15.2, 10.8, 1.6 Hz, 1 H).

13CNMR (100 MHz, CDCl3): δ = 150.5, 146.4, 136.5, 129.3, 129.0, 125.7, 94.8, 78.8, 33.3.

HRMS (electrospray): m/z calcd for C12H13O3Na: 213.0527; found: 213.0521.

(5S,6S)-5-Methyl-4-methylene-6-phenyl[1,3]dioxan-2-one (18)
A 25 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. To this was added 8 (750 mg, 2.26 mmol) and freshly distilled THF (10 mL). The mixture was cooled to ~78 °C and LiHMDS (2.71 mL, 2.71 mmol) was added dropwise. After the typical reaction time of 1 h, very poor conversion was noted. After an approximately equal volume of aq NH4Cl was added via syringe and the mixture allowed to warm to r.t. where it was then transferred to a separating funnel with Et2O and additional aq NH4Cl. The organic layer was isolated and the aq phase extracted a second time with Et2O. The combined organics were dried (MgSO4), filtered, and concentrated in vacuo. Attempts were made to purify the product by flash chromatography; however, separation of the product from the remaining starting material was not possible. Freshly distilled THF was added to the crude reaction mixture, the resulting solution recooled to ~78 °C, and KHMTDS (0.75 equiv) was added via syringe. This resulted in consumption of the starting material although it did not seem to afford additional product. The reaction was quenched and worked up as noted above and the resulting crude mixture was purified by flash chromatography (10 to 17% EtOAc–hexanes) to afford the product.

Yield: 33%; viscous light yellow oil; Rf = 0.23 (17% EtOAc–hexanes).

IR (neat): 2980, 1767, 1670, 1455, 1279, 1202, 1076, 699 cm–1.

1HNMR (400 MHz, CDCl3): δ = 7.43–7.35 (m, 3 H), 7.29–7.26 (m, 2 H), 5.54 (dd, J = 3.6 Hz, 1 H), 4.86–4.84 (m, 1 H), 4.40–4.38 (m, 1 H), 3.08–3.01 (m, 1 H), 0.97 (d, J = 7.2 Hz, 3 H).

13CNMR (100 MHz, CDCl3): δ = 155.5, 146.2, 134.7, 128.7, 128.7, 125.9, 93.8, 81.6, 35.2, 11.7.

HRMS: m/z calcd for C12H13O3Na: 213.0865; found: 213.0863.

(5S,6S)-5-Methyl-4-methylene-6-phenyl[1,3]dioxan-2-one (18)
Prepared according to the general protocol outlined for the preparation of compound 5 with 7 (230 mg, 1.0 mmol). The product was purified by flash chromatography (17% EtOAc–hexanes) and was recovered as an oil.

Yield: 87% (single olefin isomer to the detection levels of 1H NMR); colorless oil; Rf = 0.40 (25% EtOAc–hexanes).

IR (neat): 2933, 2925, 1769, 1697, 1455, 1232, 1067, 759 cm–1.

1HNMR (400 MHz, CDCl3): δ = 7.45–7.36 (m, 5 H), 5.42–5.36 (m, 2 H), 3.05 (dd, J = 15.6, 3.2 Hz, 1 H), 2.73–2.64 (m, 1 H), 1.61 (dd, J = 7.2, 1.6 Hz, 3 H).

13CNMR (100 MHz, CDCl3): δ = 147.0, 144.2, 136.9, 129.2, 128.9, 125.8, 105.1, 78.4, 29.2, 10.6.

HRMS (electrospray): m/z calcd for C12H13O3Na: 227.0678; found: 227.0682.
\(J = 15.2, 3.6 \text{ Hz, 1 H), 2.78–2.73 (m, 1 H), 1.72 (dd, J = 7.2, 1.6 \text{ Hz, 3 H).}
\)

\(^{13} \text{C NMR (100 MHz, CDCl}_3\): } \delta = 146.9, 143.5, 136.9, 129.2, 128.9, 125.7, 79.4, 33.7, 9.5.

HRMS (electrospray): \(m/z\) calcd for \(\text{C}\_\text{H}_\text{O}_\text{Na}: 227.0678; \text{found: 227.0681.}
\)

\((-\)
\(+\)\text{-}4\text{-Methylene}-\text{-}(6\text{-F})\text{-styryl}[1,3\text{-}]dioxan-2\text{-one (21)}
\)
Prepared according to the general protocol outlined for the preparation of compound 5 with 11 (360 mg, 1.05 mmol). The product was purified by flash chromatography (17% to 25% EtOAc–hexanes) and was recovered as a solid.

Yield: 80%; white solid; \(R_f = 0.37 (25\% \text{ EtOAc–hexanes).}

Yield: 80%; white solid; \(R_f = 0.37 (25\% \text{ EtOAc–hexanes).}

\(-\)
\(+\text{-}4\text{-Cyclohexyl-5-methyl-6-methylene}[1,3\text{-}]dioxan-2\text{-one (22)}
\)
Prepared according to the general protocol outlined for the preparation of compound 5 with 12 (110 mg, 0.43 mmol). The product was purified by flash chromatography (50% pentane–Et\(_2\text{O})).\)

Yield: 56%; colorless oil; \(R_f = 0.34 (50\% \text{ pentane–Et}_{2}\text{O).}

IR (neat): 2927, 1769, 1674, 1354, 1284, 1227, 1136, 1070 cm\(^{-1}\).

\(-\)4-Methyl-6-methylene[1,3]-dioxan-2-one (23)\#\nPrepared according to the general protocol outlined for the preparation of compound 5 with 13 (137 mg, 0.41 mmol). The product was purified by flash chromatography (10% EtOAc–hexanes) and was recovered as an oil.

Yield: 91%; colorless oil; \(R_f = 0.38 (17\% \text{ EtOAc–hexanes).}

\(-\)
\(+\text{-4-Methylene-6-}\text{-}(3\text{-phenylpropyl)}[1,3\text{-}]dioxan-2\text{-one (24)}
\)
Prepared according to the general protocol outlined for the preparation of compound 5 with 14 (750 mg, 2.1 mmol). The product was purified by flash chromatography (17 to 25% EtOAc–hexanes) and was recovered as an oil.

Yield: 93%; colorless oil; \(R_f = 0.41 (33\% \text{ EtOAc–hexanes).}

IR (neat): 2927, 1773, 1673, 1365, 1282, 1172, 1073 cm\(^{-1}\).

\(-\)4-HNR (400 MHz, CDCl\(_3\): \(\delta = 7.41–7.29 (m, 5 \text{ H}), 6.76 (d, J = 16.0 \text{ Hz, 1 H}), 6.17 (dd, J = 16.0, 6.8 \text{ Hz, 1 H}), 5.11–5.05 (m, 1 \text{ H}), 4.86 (s, 1 \text{ H}), 4.43 (s, 1 \text{ H}), 2.88 (dd, J = 15.0, 3.2 Hz, 1 \text{ H}), 2.08 (dd, J = 15.0, 8.8 Hz, 1 \text{ H}).

\(-\)4-Cyclohexyl-5-methyl-6-methylene[1,3]-dioxan-2-one (25)\#\nPrepared according to the general protocol outlined for the preparation of compound 5 with 15 (2.67 g, 5.1 mmol). The product was purified by flash chromatography (10% EtOAc–hexanes) and was recovered as an oil.

Yield: 99%; colorless oil; \(R_f < 0.17 (17\% \text{ EtOAc–hexanes).}

IR (neat): 2930, 1776, 1673, 1117, 1109, 703 cm\(^{-1}\).

\(-\)4-Methyl-5-methylene-4-(4-methylpent-3-enyl)[1,3]-dioxolan-2-one (26)\#\nPrepared according to the general protocol outlined for the preparation of compound 5 with 16 (324 mg, 1.0 mmol) and an extended reaction time of 2 h. The product was purified by flash chromatography (5% EtOAc–hexanes) and was recovered as an oil.

Yield: 82%; colorless oil; \(R_f = 0.46 (17\% \text{ EtOAc–hexanes).}

\(-\)4Z)-4-Benzylidene-6-phenyl[1,3]-dioxan-2-one (33)\#\nA 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. To this was added 5 (190.2 mg, 1.0 mmol), dioxane (3 mL), PPh\(_3\) (26 mg, 0.1 mmol), CF\(_2\)CO\(_2\)Ag (243 mg, 1.1 mmol), iodobenzene (123 \text{ mL, 1.1 mmol}) and finally Pd(OAc)\(_2\) (22 mg, 0.1 mmol). The reaction mixture was heated to 100 \^\circ\text{C} and left for 20 h and then the flask was allowed to cool to r.t. Approximately an equal volume of aq NH\(_4\)Cl was added and the contents transferred to a separating funnel with CH\(_2\)Cl\(_2\). The organic layer was isolated, the aq layer back extracted with CH\(_2\)Cl\(_2\) and the combined organic layers were dried (MgSO\(_4\)), filtered and concentrated in vacuo. The crude residue was analyzed by \(\text{H NMR (300 MHz, CDCl}_3\): } \delta = 7.66–7.52 (m, 4 \text{ H}, 7.46–7.36 (m, 6 \text{ H}), 4.80–4.72 (m, 1 \text{ H}), 4.72–4.63 (m, 1 \text{ H}), 4.35–4.33 (m, 1 \text{ H}), 3.88 (dd, J = 10.8, 8.4, 4.5 Hz, 1 \text{ H}), 3.76 (dd, J = 10.8, 5.4, 5.4 Hz, 1 \text{ H}), 2.73 (dd, J = 15.3, 3.3 Hz, 1 \text{ H}), 2.52–2.42 (m, 1 \text{ H}), 2.05–1.92 (m, 1 \text{ H}), 1.90–1.78 (m, 1 \text{ H}), 1.05 (s, 9 \text{ H}).

\(-\)\text{IR (thin film, CHCl}_3\): } 3051, 2915, 1768, 1681, 1242, 1203, 1163, 872, 752 cm\(^{-1}\).

1. C NMR (CDCl\(_3\)): \(\delta = 146.9, 143.5, 136.9, 129.2, 128.9, 125.7, 79.4, 33.7, 9.5.

HRMS (electrospray): \(m/z\) calcd for \(\text{C}\_\text{H}_\text{O}_\text{Na}: 232.1100; \text{found: 232.1085.}

\(-\)4-\text{-}(\text{[\text{Butyl(diphenyl)silyl}oxy]ethyl})-6-methylene[1,3]-dioxan-2-one (34)\#\nPrepared according to the general protocol outlined for the preparation of compound 5 with 17 (2.67 g, 5.1 mmol) and an extended reaction time of 2 h. The product was purified by flash chromatography (10% EtOAc–hexanes) and was recovered as an oil.

Yield: 99%; colorless oil; \(R_f < 0.17 (17\% \text{ EtOAc–hexanes).}

HRMS (electrospray): \(m/z\) calcd for \(\text{C}\_\text{H}_\text{O}_\text{Na}: 232.1100; \text{found: 232.1085.}

(4Z)-4-(\text{1-Phenylbut-3-enylidene)}[1,3]-dioxolan-2-one (35)\#\nA 250 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. To this was added 22-butyn-1-ol

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Compound \( (4Z)-4-(1\text{-Phenylbut-3-enylidene})[1,3]dioxolan-2-one \) (35)

Prepared according to the protocol outlined for the preparation of compound 34 with 3-phenyl-2-propyn-1-ol and tert-butyl imidate. The crude product was absorbed on silica, partially purified by flash chromatography (5% EtOAc–hexanes) and was recovered as a solid.

Yield: 26%; white granular solid; \( R_f = 0.28 \) (17% EtOAc–hexanes); mp 59 °C.

IR (thin film, CHCl3): 3065, 2921, 1816, 1698, 1374, 1242, 1123, 764 cm\(^{-1}\).

HRMS (electrospray): \( m/z \) calcd for \( C_{13}H_{12}O_3Na \): 239.0678; found: 239.0679.

IR (neat): 3081, 2920, 1825, 1732, 1372, 1242, 1185, 1131, 1050, 767 cm\(^{-1}\).

HRMS (electrospray): \( m/z \) calcd for \( C_{13}H_{12}O_3Na \): 239.0678; found: 239.0679.

IR (thin film, CH2Cl2): 3065, 2920, 1816, 1698, 1374, 1242, 1123, 764 cm\(^{-1}\).

HRMS (electrospray): \( m/z \) calcd for \( C_{13}H_{12}O_3Na \): 239.0678; found: 239.0679.

Formation of \( \beta \)-Keto Carbonates; (2)-Carboxylic Acid tert-Butyl Ester 3-Oxo-1-phenylbutyl Ester (27)

Protocol A

A 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. It was then charged with 5 (95 mg, 0.5 mmol) and THF (2.5 mL). The resulting solution was cooled to \(-78^\circ\text{C} \) and tert-ButOK (0.6 mL, 0.6 mmol) was added over 10 s, the reaction was left for 10 s, then aq NH4Cl (2.0 mL) was added and the mixture warmed to r.t. The reaction contents were transferred to a separating funnel with additional aq NH4Cl and Et2O and the organic layer isolated. The aq phase was extracted once with Et2O and the combined organics were dried (MgSO4), filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (17% EtOAc–hexanes) to afford the desired product as a white solid (yield 97%).

Yield: 97%; white solid; \( R_f = 0.48 \) (25% EtOAc–hexanes); mp 65 °C.

IR (thin film, CH2Cl2): 3035, 2980, 2933, 1745, 1456, 1369, 1276, 1158, 1100, 1042, 860, 700 cm\(^{-1}\).

HRMS (electrospray): \( m/z \) calcd for \( C_{13}H_{12}O_3Na \): 287.1264; found: 287.1265.

In situ Enolate Formation and Aldol or Mannich Reaction; Mixture of tert-Butyl-(1S*,5S*)-3-hydroxy-3-oxo-1,5-diphenylpentyl Carbonate and tert-Butyl-(1S*,5R*)-3-hydroxy-3-oxo-1,5-diphenylpentyl Carbonate (28)

Representative Procedure (ZnCl2)

A 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. It was then charged with 5 (95 mg, 0.5 mmol) and THF (2.5 mL). The resulting solution was cooled to \(-78^\circ\text{C} \) and tert-ButOK (0.6 mL, 0.6 mmol) was added over 10 s, left for 10 s, then ZnCl2 (0.6 mL, 0.6 mmol) was added over 10 s, and the reaction mixture stirred an additional 5 min. Benzaldehyde (102 mL, 1.0 mmol) was then added dropwise and the temperature maintained for an additional 4 h. An approximately equal volume of aq NH4Cl was added and the reaction vessel warmed to r.t. The contents were then transferred to a separating funnel with Et2O and additional aq NH4Cl, and the organic layer isolated. The aq layer was back extracted with Et2O and the combined organics dried (MgSO4), filtered, and concentrated in vacuo. The crude residue was then purified by flash chromatography (17% EtOAc–hexanes) to afford the product as an inseparable mixture of diastereomers.

Yield: 92%; colorless oil.

Representative Procedure (Bu2BOTf)

A 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. It was then charged with 5 (95 mg, 0.5 mmol) and THF (2.5 mL). The resulting solution was cooled to \(-78^\circ\text{C} \) and tert-ButOK (0.6 mL, 0.6 mmol) was added over 10 s, left for 10 s, then Bu2BOTf (0.6 mL, 0.6 mmol) was added over 10 s and the reaction mixture stirred an additional 5 min. Benzaldehyde (102 mL, 1.0 mmol) was then added dropwise and the temperature maintained for an additional 4 h. An approximately equal volume of aq NH4Cl was added and the reaction vessel warmed to r.t. The contents were then transferred to a separating funnel with Et2O and additional aq NH4Cl, and the organic layer isolated. The aq layer was back extracted with Et2O and the combined organics dried...
(MgSO₄), filtered, and concentrated in vacuo. The crude residue was diluted with Et₂O (5 mL), NaOH (3 M: 1 mL) was added followed byaq H₂O₂ (30%; 1 mL) and stirred slowly for 8 h (note typical phosphate buffered oxidation in MeOH causes destruction of product). To this was then addedaq NH₄Cl andEt₂O, the reaction contents were transferred to a separating funnel and the organic layer was isolated. The aq layer was extracted withEt₂O, the combined organics were dried (MgSO₄), filtered, and concentrated in vacuo. The crude reaction mixture was dried under high vacuum and the diastereomeric ratio determined by ¹H NMR (dr 6:7:1, diagnostic signals: major δ = –5.18 (dd, J = 7.5, 4.3 Hz, 1 H); minor δ = 5.12 (dd, J = 9.8, 2.5 Hz, 1 H)). The crude residue was then purified by flash chromatography (10 to 17% EtOAc–hexanes) to afford the product as an inseparable mixture of diastereomers.

Yield: 83%; colorless oil; Rf = 0.14 (17% EtOAc–hexanes).

Formation of Vinyl Triflates; (±)-1-{[(tert-Butoxycarbonyloxy)oxy]-2,6-dimethyl-1-methylenevinyl Trifluoromethanesulfonate (29); General Procedure

A 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. To this was added 5 (95 mg, 0.5 mmol) andTHF (2.5 mL). The resulting solution was cooled to –78 °C and thenBuOK (0.6 mL, 0.6 mmol) was added over 10 s, left for 10 s, then (CF₃SO₂)₂NPh (250 mg, 0.7 mmol) was added over 10 s as a solution in THF (0.6 mL). The resulting mixture was stirred for 90 min, an approximately equal volume of H₂O was added, and the cold flask warmed to r.t. The reaction contents were transferred to a separating funnel with additional H₂O and Et₂O, and the organic layer was isolated. The aq layer was extracted with Et₂O, and the combined organics were dried (MgSO₄), filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (0 to 5% EtOAc–hexanes) to afford the product as an inseparable mixture of diastereomers.

Yield: 99%; colorless oil; Rf = 0.26 (5% EtOAc–hexanes).

IR (neat): 3414, 3068, 1671, 1672, 1445, 1419, 1214, 1130 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.41–7.30 (m, 10 H), 6.09–6.04 (m, 1 H), 5.23–5.11 (m, 1 H), 3.25–3.16 (m, 2 H), 2.95–2.75 (m, 3 H), 1.48 (m, 9 H).

¹³C NMR (100 MHz, CDCl₃): δ = 140.6, 139.4, 139.4, 128.7, 128.6, 128.4, 127.7, 126.3, 126.3, 125.6, 125.6, 125.6, 123.9, 123.9, 122.6, 118.3, 44.4, 31.9, 27.7.

HRMS (electrospray): m/z calcd for C₁₂H₁₇F₃O₆Na⁺: 357.0590; found: 357.0590.

1-[(1R*,2S*)-2-{[(tert-butoxycarbonyloxy)oxy]-1-methyl-2-phenyl-ethyl}vinyl Trifluoromethanesulfonate (31)

Prepared according to the protocol outlined for the preparation of compound 29 with (17 (102 mg, 0.50 mmol). The crude product was purified by flash chromatography (0 to 5% EtOAc–pentane) and was recovered as an oil.

Yield: 92%; colorless oil; Rf = 0.41 (10% EtOAc–pentane).

IR (neat): 2984, 1745, 1665, 1415, 1278, 938, 700 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.39–7.31 (m, 5 H), 5.49 (dd, J = 8.8 Hz, 1 H), 5.23 (d, J = 4.0 Hz, 1 H), 5.03 (d, J = 4.0 Hz, 1 H), 2.94 (qd, J = 8.8, 7.2 Hz, 1 H), 1.42 (s, 9 H), 0.97 (d, J = 7.2 Hz, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 156.4, 152.4, 137.3, 128.6, 128.5, 127.2, 118.5 (q, J = 319), 82.6, 78.8, 44.4, 27.7, 14.5.

¹⁹F NMR (376 MHz, CDCl₃): δ = –74.2.

HRMS (electrospray): m/z calcd for C₁₁H₁₇F₃O₆Na⁺: 433.0903; found: 433.0909.

(±)-2-{[(tert-Butoxycarbonyloxy)oxy]-2,6-dimethyl-1-methylene-5-ethyl Trifluoromethanesulfonate (32)

Prepared according to the protocol outlined for the preparation of compound 29 with 26 (98 mg, 0.50 mmol). The crude product was purified by flash chromatography (0 to 5% EtOAc–pentane) and was recovered as an oil.

Yield: 94%; colorless oil; Rf = 0.36 (10% EtOAc–pentane).

IR (neat): 2981, 2934, 1748, 1445, 1423, 1286, 1216, 1147, 944 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.41 (d, J = 4.5 Hz, 1 H), 5.32 (d, J = 4.5 Hz, 1 H), 5.16–5.10 (m, 1 H), 2.91 (d, J = 3.6 Hz, 1 H), 1.44 (s, 9 H).

¹³C NMR (75 MHz, CDCl₃): δ = 155.1, 151.2, 132.8, 122.6, 118.3 (q, J = 315 Hz), 103.9, 82.6, 81.2, 37.1, 27.8, 25.8, 22.1, 22.0, 17.6.

¹⁹F NMR (282 MHz, CDCl₃): δ = –74.6.

HRMS (electrospray): m/z calcd for C₁₉H₂₆F₃O₆Na⁺: 425.1226; found: 425.1225.

Formation of Silyl Enol Ethers; (±)-tert-Butyl 3-{[(tert-Butyl(dimethyl)silyloxy)oxy]-1-phenylbut-3-enyl Carbonate (36); General Procedure

A 10 mL round-bottom flask was flame dried under a stream of nitrogen and allowed to cool to r.t. To this was added 5 (95 mg, 0.5 mmol) andTHF (2.5 mL). The resulting solution was cooled to –78 °C and thenBuOK (0.6 mL, 0.6 mmol) was added over 10 s, left for 10 s, then (CF₃SO₂)₂NPh (250 mg, 0.7 mmol) was added over 10 s as a solution in THF (0.6 mL). The resulting mixture was stirred for 90 min, an approximately equal volume of H₂O was added, and the cold flask warmed to r.t. The reaction contents were transferred to a separating funnel with additional H₂O and Et₂O, and the organic layer was isolated. The aq layer was extracted with Et₂O, and the combined organics were dried (MgSO₄), filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (0 to 5% EtOAc–pentane) and was recovered as an oil.

Yield: 97%; colorless oil; Rf = 0.43 (10% Et₂O–pentane).

IR (neat): 2985, 1742, 1445, 1215, 1130, 942, 885 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.21 (d, J = 3.6 Hz, 1 H), 5.06 (d, J = 3.6 Hz, 1 H), 4.99–4.88 (m, 1 H), 2.67 (dd, J = 15.3, 7.2 Hz, 1 H), 2.54 (dd, J = 15.3, 5.4 Hz, 1 H), 1.48 (s, 9 H), 1.34 (d, J = 6.3 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 152.7, 152.5, 118.5 (q, J = 319 Hz), 107.1, 82.4, 69.9, 40.5, 27.7, 19.7.

¹⁹F NMR (282 MHz, CDCl₃): δ = –73.8.

HRMS (electrospray): m/z calcd for C₁₁H₁₇F₃O₆Na⁺: 357.0590; found: 357.0602.

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Prepared according to the protocol outlined for the preparation of vinyl\[but-3-enyl Carbonate (37)

\[ \begin{align*}
\text{J} & = 1 \text{ H}, \\
\text{J} & = 2.44 (\text{dd}, \\
\text{J} & = 8.4, 6.0 \text{ H}, 1 \text{ H}), 2.65 (\text{dd}, J = 14.0, 8.8 \text{ H}, 1 \text{ H}), 2.43 (\text{dd}, J = 14.0, 5.6 \text{ H}, 1 \text{ H}), 1.43 (s, 9 \text{ H}), 0.95 (s, 9 \text{ H}), 0.17 (s, 3 \text{ H}), 0.16 (s, 3 \text{ H}).
\end{align*} \]

\[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{17}H_{27}O_{5}NaSi: 407.2598; \\
& \text{found: 407.2591.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl} 3-\{(\text{tert-butyl}(dimethyl)silyl)oxy\}-1-\{(E\)-2-phenylvinyl\}but-3-enyl Carbonate (37)

Prepared according to the protocol outlined for the preparation of compound 36 with 21 (42 mg, 0.19 mmol). The crude product was purified by flash chromatography (2.5% Et\text{3}N–pentane) and was recovered as an oil.

Yield: 80%; colorless oil; \(R_f \approx 0.73 \text{ (2.5\% Et}_{3}\text{N–pentane).} \)

IR (neat): 2931, 2859, 1741, 1633, 1369, 1279, 1165, 1017, 840 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{34}H_{54}O_{9}NaSi: 591.3557; \\
& \text{found: 591.3556.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl}-(3\{\text{tert-butyl(dimethyl)silyl)oxy}\}-1\{-[(E)-2-phenylvinyl\}but-3-enyl Carbonate (38)

Prepared according to the protocol outlined for the preparation of compound 36 with 22 (68 mg, 0.50 mmol). The crude product was purified by flash chromatography (2\% Et\text{3}N–pentane) and was recovered as an oil.

Yield: 93%; colorless oil; \(R_f \approx 0.37 \text{ (2\% Et}_{3}\text{N–pentane).} \)

IR (neat): 2932, 2859, 1739, 1633, 1368, 1284, 1172, 1016, 839 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{35}H_{56}O_{9}NaSi: 591.3557; \\
& \text{found: 591.3556.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl} 1-(\{\text{tert-butyl(dimethyl)silyl)oxy\}vinyl)-1,5-dimethylhex-4-\text{enyl Carbonate (39)}

Prepared according to the protocol outlined for the preparation of compound 36 with 26 (98 mg, 0.50 mmol). The crude product was purified by flash chromatography (0 to 5\% Et\text{3}O in 5\% Et\text{3}N–pentane) and was recovered as an oil.

Yield: 96%; colorless oil; \(R_f \approx 0.86 \text{ (5\% Et}_{3}\text{O, 5\% Et}_{3}\text{N, 90\% pentane).} \)

IR (neat): 2932, 2859, 1745, 1632, 1464, 1369, 1285, 1109, 1070 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{36}H_{58}O_{9}NaSi: 631.3780; \\
& \text{found: 631.3779.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl}-(3\{\text{tert-butyl(dimethyl)silyl)oxy}\}-1\{-[(E)-2-phenylvinyl\}but-3-enyl Carbonate (40)

Prepared according to the protocol outlined for the preparation of compound 36 with 19 (115 mg, 0.56 mmol). Analysis of the crude reaction mixture by 1H NMR indicated a ratio of \(E\):(Z) 0.9 silyl enol ethers of ca. 4:2.1. The crude product was purified by flash chromatography (0 to 4\% Et\text{3}O in 0.5\% Et\text{3}N–pentane) and was recovered as an inseparable mixture of olefin isomers. Spectral data are reported only for the major component \(E\) silyl enol ether.

Yield: 93%; colorless oil; \(R_f \approx 0.62 \text{ (5\% Et}_{3}\text{O, 0.5\% Et}_{3}\text{N, 94.5\% pentane).} \)

IR (neat): 2931, 2859, 1743, 1672, 1472, 1368, 1279, 1165 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{19}H_{31}O_{3}Si: 275.1825; \\
& \text{found: 275.1820.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl} (3\{\text{tert-butyl(dimethyl)silyl)oxy\}-1\{-[(E)-2-phenylvinyl\}but-3-enyl Carbonate (41)

Prepared according to the protocol outlined for the preparation of compound 36 with 26 (66 mg, 0.32 mmol). Analysis of the crude reaction mixture by 1H NMR indicated a ratio of \(Z\):(E) 0.9 silyl enol ethers of >30:1. The crude product was purified by flash chromatography (0 to 4\% Et\text{3}O in 0.5\% Et\text{3}N–pentane) and was recovered as an oil. The assigned geometry of the silyl enol ether was consistent with results of NOE experiments.

Yield: 74%; colorless oil; \(R_f \approx 0.62 \text{ (5\% Et}_{3}\text{O, 0.5\% Et}_{3}\text{N, 94.5\% pentane).} \)

IR: 2931, 2859, 1743, 1679, 1471, 1368, 1278, 1163, 1094 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{19}H_{31}O_{3}Si: 275.1825; \\
& \text{found: 275.1820.}
\end{align*} \]

(\(\pm\))-\text{tert-Butyl}-(3\{\text{tert-butyl(dimethyl)silyl)oxy\}-1\{-[(E)-2-phenylvinyl\}but-3-enyl Carbonate (42)

Prepared according to the protocol outlined for the preparation of compound 36 with 33 (27 mg, 0.10 mmol). Analysis of the crude reaction mixture by 1H NMR indicated a single silyl enol ether. The crude product was purified by flash chromatography (3\% Et\text{3}N–pentane) and was recovered as an oil.

Yield: 93%; colorless oil; \(R_f \approx 0.59 \text{ (3\% Et}_{3}\text{N–pentane).} \)

IR: 2930, 2857, 1747, 1651, 1471, 1368, 1278, 1163, 986 cm\(^{-1}\). \[ \begin{align*}
\text{HRMS (electrospray): } m/z & \text{ calcld for } C_{19}H_{31}O_{3}Si: 275.1825; \\
& \text{found: 275.1820.}
\end{align*} \]
 tert-Butyl-(2E)-2-[[tert-butyl(dimethyl)silyloxy]-3-methyl-hexa-2,5-dienyl Carbonate (43)
Prepared according to the protocol outlined for the preparation of compound 36 with 34 (77 mg, 0.50 mmol). Analysis of the crude reaction mixture by $^1$H NMR indicated a single silyl enol ether. The crude product was purified by flash chromatography (0 to 5% Et$_2$O in 0.5% Et$_3$N–pentane) and was recovered as an oil.

Yield: 99%; colorless oil; R$_f$ = 0.56 (5% Et$_2$O, 0.5% Et$_3$N, 94.5% hexane), 0.74 (0.5% Et$_3$N–pentane)

IR (neat): 2932, 2859, 1744, 1472, 1370, 1284, 1164, 997, 837 cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.29–7.23 (m, 4 H), 7.21–7.15 (m, 1 H), 5.83–5.70 (m, 1 H), 5.07–4.94 (m, 2 H), 4.67 (s, 2 H), 3.15 (d, $J = 5.7$ Hz, 2 H), 1.50 (s, 9 H), 0.71 (s, 9 H), $-0.21$ (s, 6 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 153.8, 142.3, 140.3, 136.3, 129.6, 128.0, 126.6, 123.3, 115.5, 82.3, 65.7, 37.4, 28.0, 25.7, 18.3, $-4.5$.

HRMS (electrospray): m/z calcd for C$_{22}$H$_{29}$OSi $[M – OC(O)OBoc]$: 599.1982; found: 599.1980.

hexa-2,5-dienyl Carbonate (43)

IR (neat): 2932, 2859, 1744, 1472, 1370, 1284, 1164, 997, 837 cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.29–7.23 (m, 4 H), 7.21–7.15 (m, 1 H), 5.83–5.70 (m, 1 H), 5.07–4.94 (m, 2 H), 4.67 (s, 2 H), 3.15 (d, $J = 5.7$ Hz, 2 H), 1.50 (s, 9 H), 0.71 (s, 9 H), $-0.21$ (s, 6 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 153.8, 142.3, 140.3, 136.3, 129.6, 128.0, 126.6, 123.3, 115.5, 82.3, 65.7, 37.4, 28.0, 25.7, 18.3, $-4.5$.

HRMS (electrospray): m/z calcd for C$_{22}$H$_{29}$OSi $[M – OC(O)OBoc]$: 599.1982; found: 599.1980.

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References


(15) Purified by flash chromatography utilizing an eluent that contained 0.5% Et$_3$N. Trimethylsilyl and triethylsilyl triflates gave products of low stability.

(16) To the best of our knowledge neither vinyl triflates nor silyl enol ethers containing a $\beta$-tert-butyl carbonate moiety have previously been prepared. Nor have the parent ketene compounds ever been used directly in an aldol or Michael reaction. This is perhaps a reflection of their base sensitivity.