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Copper-Promoted Coupling of Carbon Dioxide and Propargylic Alcohols: Expansion of Substrate Scope and Trapping of Vinyl Copper Intermediate

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Abstract: We have successfully demonstrated that in the presence of *N*,*N*-diisopropylethylamine, copper iodide could efficiently catalyze the coupling of internal propargylic alcohols with carbon dioxide to afford the corresponding α-alkylidene cyclic carbonates in moderate to excellent yields. Moreover, we have developed a new and versatile protocol for the chemo- and stereoselective synthesis of a wide range of (*E*)-α-iodoalkylidene cyclic carbonates from carbon dioxide, propargylic alcohols and potassium iodide using copper salt as the promoter. The process is proposed to proceed through the trapping of the vinyl copper intermediate by in situ generated triiodide ion as electrophile.

Keywords: carbon dioxide fixation; copper; cyclic carbonate; propargylic alcohols; vinyl copper intermediate

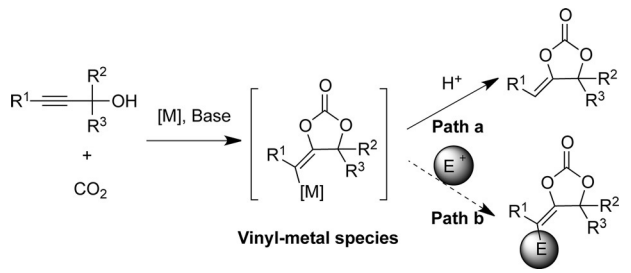
Introduction

Carbon dioxide (CO_2), one of the major anthropogenic greenhouse gases, has recently attracted much attention from both academic and industrial fields since the increasing concentration of carbon dioxide in the atmosphere contributes to the presently observed climate change phenomenon. On the other hand, carbon dioxide has been regarded as a nontoxic, abundant and renewable C1 feedstock for the synthesis of a variety of valuable chemicals. Thus, the development of novel and efficient methodologies for the chemical fixation of CO_2 has become one of the most important research topic for chemists.[1]

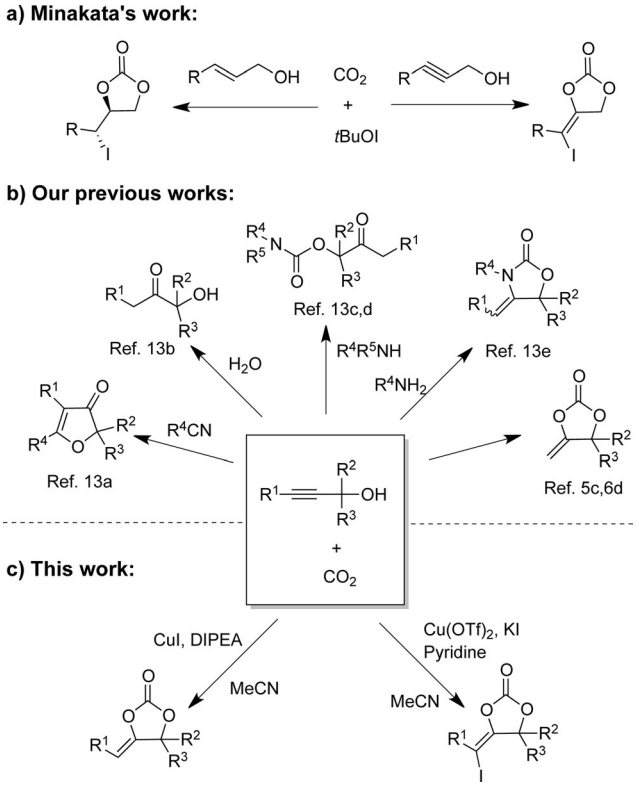
The synthesis of α-alkylidene cyclic carbonates through the coupling reaction between propargylic alcohols and CO_2 is regarded as one of the most important methods for the utilization of CO_2, because α-alkylidene cyclic carbonates are versatile building blocks used for different synthetic purposes.[2] After the pioneering works by Laas,[3a] Sasaki[3b] and Inoue,[3c] many efficient transition metal catalysts and organocatalysts, such as palladium,[4] copper,[5] silver,[6] tri-*n*-butylphosphine,[7] N-heterocyclic carbenes,[8] *tert*-butyl hypoiodite,[9] guanidines,[10] functionalized imidazolium betaines,[11] and N-heterocyclic olefins,[12] have been employed for this reaction.

Among above-mentioned transition-metal catalysts, copper catalysts attracted our special attention[3a,5] because of the easy availability and cost-effectiveness in comparison with other reported transition-metal catalysts. However, all of the existing copper-based protocols were not applicable to internal propargylic alcohols. Therefore, it still remains a challenge to expand the substrate scope of copper-promoted coupling of CO_2 and propargylic alcohols for economic and versatile synthesis of α-alkylidene cyclic carbonates.

Moreover, it is commonly proposed that the reaction between CO_2 and propargylic alcohols catalyzed by transition metals such as silver salts proceeds through a vinyl metal species, and the subsequent protodemetallation will occur to yield the cyclic carbonate (Scheme 1, path a).[6a,c] Although the putative vinyl metal intermediate has never been isolated, it is reasonable to envisage that functionalized alkylidene cyclic carbonates could be obtained if the intermediate can be trapped with an electrophile E^+ (Scheme 1, path b). However, to the best of our knowledge, such a process has not been reported yet. We focused on the synthesis of (*E*)-α-iodoalkylidene cyclic carbonates by trapping the above-described vinyl metal in-



Scheme 1. Proposed mechanism for the coupling of CO_2 with propargylic alcohols.



Scheme 2. The reactions involving CO_2 and propargylic alcohols.

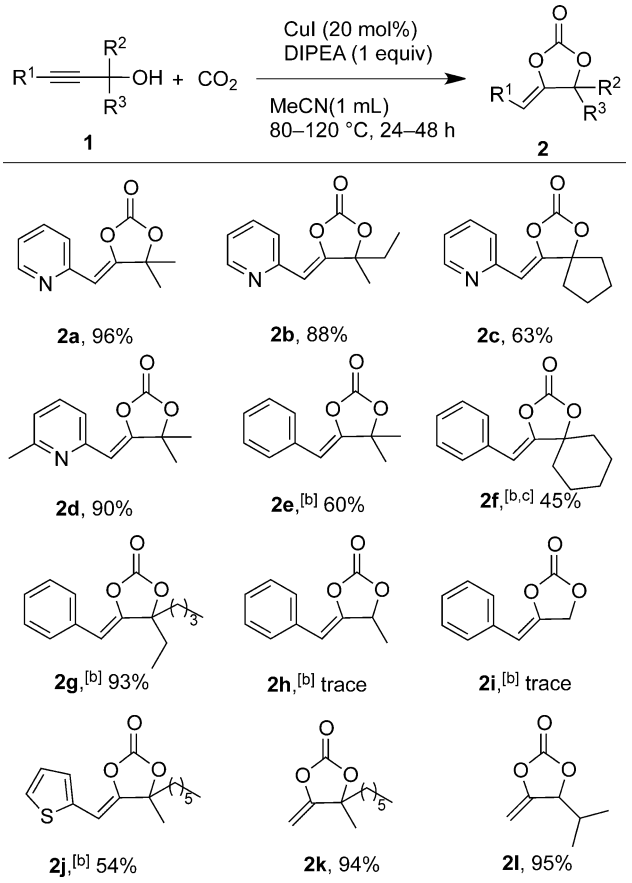
termediate with a source of electrophilic iodine, since only one elegant method has been developed by Minakata and co-workers for the synthesis of this important class of heterocycles directly from CO_2 under very mild reaction conditions (−20 °C and 1atm) using *t*BuOI generated in situ from the NaI-*t*BuOCl combination (Scheme 2 a).[9]

As part of our continuing interest in the development of efficient methods for the conversion of CO_2 into useful chemicals using propargylic alcohols as the coupling partners (Scheme 2 b),[5c,6d,13] Herein, we wish to report that, in conjunction with *N*,*N*-diisopropylethylamine (DIPEA), copper iodide could efficiently catalyze the coupling of internal propargylic alcohols with CO_2 to give the corresponding α-alkylidene cyclic carbonates in moderate to excellent yields. More importantly, we hope to present a new method for the chemo- and stereoselective synthesis of a series of (*E*)-α-iodoalkylidene cyclic carbonates from CO_2, propargylic alcohols and potassium iodide (Scheme 2 c). In comparison with Minakata's method mentioned above, relatively stable and easy-to-handle copper salts were used as the promoter in our present method, thus avoiding the use of light- and heat-sensitive *tert*-butyl hypochlorite (*t*BuOCl). Moreover, although high temperature (110 °C) and CO_2 pressure (4 MPa) were required and a significant solvent effect was observed in our process, our reaction has broad scope and high functional group tolerance.

Results and Discussion

In our previous work, it was found that (*Z*)-4,4-dimethyl-5-((pyridin-2-yl)methylene)-1,3-dioxolan-2-one (**2a**) could be obtained as the major product in 59% yield when treating 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol (**1a**) with 20 mol% of CuI in wet acetonitrile under CO_2 atmosphere (2 MPa) at 70 °C in the presence of pyridine.[13a] This result indicated that by careful optimization of reaction conditions, copper iodide might efficiently catalyze the coupling of internal propargylic alcohol with CO_2 to give the corresponding α-alkylidene cyclic carbonates. After extensive screening of the reaction conditions, we were pleased to find that by using 20 mol% of CuI as catalyst in conjunction with 1 equiv of *N*,*N*-diisopropylethylamine (DIPEA) as the base, the coupling reaction of CO_2 and 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol (**1a**) furnished the desired product **2a** in 96% yield under 4 MPa of CO_2 after 24 h in MeCN (Table 1). Other internal propargylic alcohols with different R^2 and R^3 substituents were further examined under the same reaction conditions and all gave the corresponding products (**2a**–**2c**) in moderate to excellent yields. The substrate with a Me group at position 6 of the pyridyl ring could also undergo the reaction to afford the desired product **2d** in high yield. Tertiary propargylic alcohols bearing a phenyl group at the acetylenic terminus showed lower reactivity, but they could be successfully converted into the desired products in moderate to good yields when the reaction temperature was increased to 120 °C. For example, products **2e**, **2f**, and **2g** could be obtained in 60%, 45%, and 93% yields, respectively. However, only trace of product **2h** or **2i** was detected by GC-MS analysis when the corresponding secondary or primary internal propargylic alcohols were employed for the reaction. Pleasingly, product **2j** with a 2-thiophenyl group could be obtained in a moderate yield (54%). As expected, the catalytic system is found to be very efficient for tertiary or secondary terminal propargylic al-

Table 1. Synthesis of various α-alkylidene cyclic carbonates with CuI as catalyst.[a]



[a] Reaction conditions: propargylic alcohol (0.25 mmol), CuI (0.05 mmol), DIPEA (0.25 mmol), MeCN (1 mL), CO_2 (4 MPa), 80 °C, 24 h. Yields of isolated products are given.
[b] The reaction was carried out at 120 °C.
[c] 48 h.

cohol, affording the corresponding products **2k** and **2l** in excellent yields. But terminal primary alcohols could not be transformed into the desired product and the starting material was recovered. The *Z*-configuration of the product **2f** was confirmed unambiguously by an X-ray crystallographic analysis (Figure 1).[14] The configurations of other α-alkylidene cyclic carbonates (**2a**–**2e**, **2g** and **2j**) were also determined to be (*Z*) by NOE experiments.[15] The selective formation of (*Z*)-5-alkylidene-1,3-dioxolan-2-one indicates that the reaction mechanism may involve a copper-assisted nucleophilic *trans* addition of carbonate anions to the C–C triple bond, similar to that of silver-catalyzed coupling of CO_2 and propargylic alcohols.[6a,c]

Next, we turned our attention to the synthesis of (*E*)-α-iodoalkylidene cyclic carbonates by trapping the putative vinyl copper intermediate. We initially investigated the synthesis of (*E*)-5-(iodo(pyridin-2-yl)-

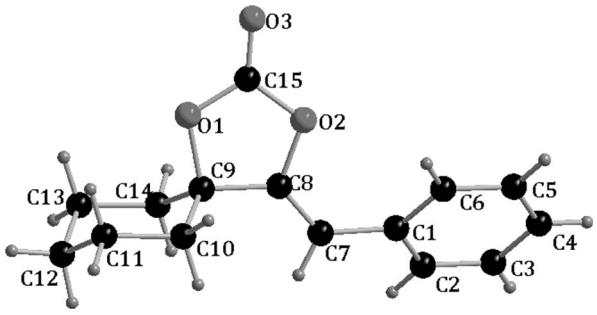


Figure 1. X-ray structure of compound **2f**.

methylene)-4,4-dimethyl-1,3-dioxolan-2-one (**3a**) from **1a**, and the preliminary results are outlined in Table 2.

An initial attempt using I_2 as electrophile provided complete conversion of propargylic alcohol **1a**, but only a complicated mixture was obtained without the formation of desired product (Table 2, entry 1). Replacing the I_2 with NIS or increasing the amount of CuI to 1 equiv did not give even a trace of the desired product (entries 2 and 3). However, we were pleased to observe that the use of 1 equiv of $CuCl_2$ in conjunction with 2 equiv of NaI in the presence of 1 equiv of pyridine generated the desired product **3a**, although in a relatively low yield (18%). Note that in this case cyclic carbonate **2a** was not observed (entry 4). As it is well-known that copper(II) ions can oxidize iodide ions to iodine (eq 1), and iodine can further react with surplus I^- to reach an equilibrium with triiodide (I_3^-) (eq 2),[16] we suggest that in this transformation triiodide ion, generated in situ from $CuCl_2$ and NaI, might act as an electrophile for the formation of **3a**.

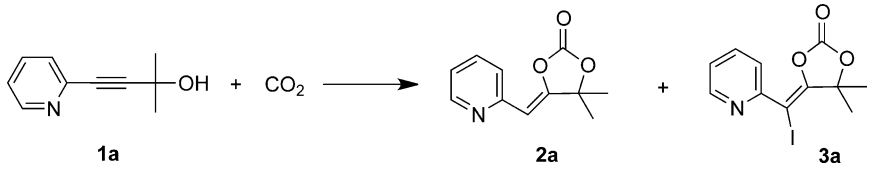
$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2 \quad (1)$$

$$I_2 + I^- \rightleftharpoons I_3^- \quad (2)$$

Interestingly, replacing NaI with KI as iodine source dramatically increased the yield of product **3a** to 53% (entry 5). Increasing the amount of $CuCl_2$ to 2 equiv alone did not increase the yield of **3a** but led to the formation of (*E*)-3,4-dichloro-2-methyl-4-(pyridin-2-yl)but-3-en-2-ol as a major side product in 46% yield (entry 6). Subsequently, we found that the use of 2 equiv of $CuCl_2$ combined with 4 equiv of KI and 1 equiv of pyridine furnished the expected product **3a** as the sole product in 93% yield (entry 7).

With these good results at hand, we then examined the effect of copper source, base, and solvent on the reaction of **1a**. Table 3 shows that the use of $Cu(OTf)_2$ instead of $CuCl_2$ could further improve the yield of **3a** while other copper(II) salts tested such as $CuBr_2$, $Cu(OAc)_2$, $CuSO_4$ and $Cu(NO_3)_2$ gave inferior results (Table 3, entries 1–6). To our surprise, cuprous

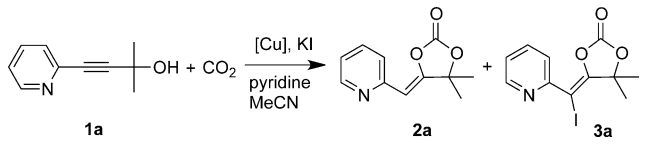
Table 2. One-pot synthesis of of (*E*)-5-(iodo(pyridin-2-yl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (**3a**) under different conditions.[a]



Entry	Catalyst system	Temperature [°C]	Conversion of **1a** [%][b]	**3a**/**2a**[b]	Yield of **3a** [%][c]
1	CuI (0.2 equiv), DIPEA (1 equiv), I_2 (2 equiv)	90	>99	–	–
2	CuI (0.2 equiv), DIPEA (1 equiv), NIS (2 equiv)	90	>99	–	–
3	CuI (1 equiv), DIPEA (1 equiv), I_2 (2 equiv)	90	>99	–	–
4	$CuCl_2$ (1 equiv), pyridine (1 equiv), NaI (2 equiv)	110	23	1:0	18
5	$CuCl_2$ (1 equiv), pyridine (1 equiv), KI (2 equiv)	110	70	11:1	53
6	$CuCl_2$ (2 equiv), pyridine (1 equiv), KI (2 equiv)	110	94	1:0	41[d]
7	$CuCl_2$ (2 equiv), pyridine (1 equiv), KI (4 equiv)	110	93	1:0	93

[a] Reaction conditions: **1a** (0.25 mmol), CO_2 (4 MPa), MeCN (3 mL), 24 h.
[b] Determined by GC.
[c] GC yield of **3a**.
[d] (*E*)-3,4-dichloro-2-methyl-4-(pyridin-2-yl)but-3-en-2-ol as a by-product was also isolated in 46% yield.

Table 3. Influence of copper salt on the formation of **3a**.[a]



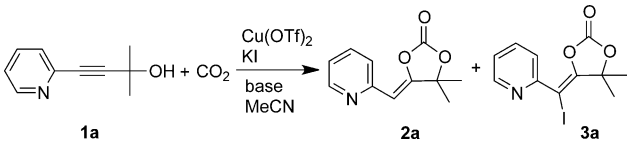
Entry	Cu salt	Conversion of **1a** [%][b]	**3a**/**2a**[b]	Yield of **3a** [%][c]
1	$CuCl_2$	93	1:0	93
2	$CuBr_2$	64	20:1	39
3	$Cu(OAc)_2$	50	25:1	47
4	$CuSO_4$	>99	3:1	67
5	$Cu(NO_3)_2$	30	1:0	18
6	$Cu(OTf)_2$	>99	1:0	99(96)
7	CuCl	>99	9:1	90
8[d]	CuCl	67	1:3.5	15

[a] Reaction conditions: **1a** (0.25 mmol), copper salt (0.5 mmol), pyridine (0.25 mmol), KI (1 mmol), CO_2 (4 MPa), MeCN (3 mL), 110 °C, 24 h.
[b] Determined by GC analysis.
[c] GC yield. Number in parenthesis is isolated yield.
[d] The reaction was carried out with strict exclusion of air.

chloride could also afford the desired product **3a** in 90% yield with a 9:1 ratio of **3a**/**2a** (entry 7). This might contribute to the fact that cuprous chloride could be rapidly oxidized by molecular oxygen to copper(II),[17] since the reaction was carried out with no effort to exclude oxygen. A control experiment showed that when the reaction was performed with strict exclusion of air, only 15% yield of product **3a** was obtained along with **2a** as the major product (entry 8).

Then, the influence of organic base on the formation of **3a** was investigated with $Cu(OTf)_2$ as the promoter. As shown in Table 4, the nature of organic base has a dramatic impact on the reaction. Pyridine was proven to be the most effective one for the transformation (entry 1). (*N*,*N*-dimethylamino)pyridine (DMAP) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) could give the desired product **3a** in 85% and 87% yields, respectively (entries 3 and 6). However, replacing pyridine with 1,4-diazabicyclo[2.2.2]octane (DABCO), DIPEA or triethylamine (TEA) made the reaction quite sluggish with poor selectivity to yield

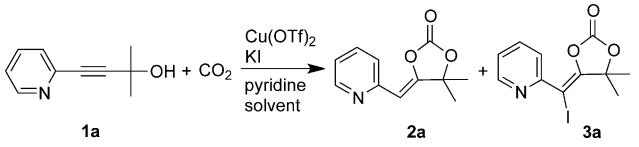
Table 4. Influence of organic base on the formation of **3a**.[a]



Entry	Base	Conversion of **1a** [%][b]	**3a**/**2a**[b]	Yield of **3a** [%][c]
1	Pyridine	>99	1:0	99
2	DABCO	29	10:1	20
3	DMAP	90	1:0	85
4	DIPEA	21	1:3	4
5	TEA	29	1:1	13
6	DBU	98	11:1	87

[a] Reaction conditions: **1a** (0.25 mmol), $Cu(OTf)_2$ (0.5 mmol), base (0.25 mmol), KI (1 mmol), CO_2 (4 MPa), MeCN (3 mL), 110 °C, 24 h.
[b] Determined by GC analysis.
[c] GC yield.

Table 5. Influence of solvent on the formation of **3a**.[a]



Entry	Base	Conversion of **1a** [%][b]	**3a**/**2a**[b]	Yield of **3a** [%][c]
1	MeCN	>99	1:0	99
2	THF	24	–	–
3	1,4-dioxane	81	1:0	7
4	DMF	90	20:1	79
5	CH_2Cl_2	10	1:2	3

[a] Reaction conditions: **1a** (0.25 mmol), $Cu(OTf)_2$ (0.5 mmol), pyridine (0.25 mmol), KI (1 mmol), CO_2 (4 MPa), solvent (3 mL), 110 °C, 24 h.
[b] Determined by GC analysis.
[c] GC yield.

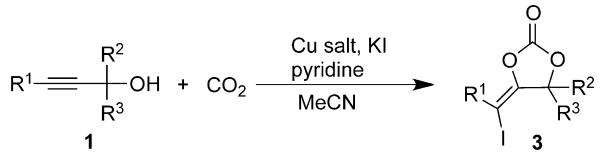
3a, and large amount of starting material was recovered (entries 2, 4 and 5).

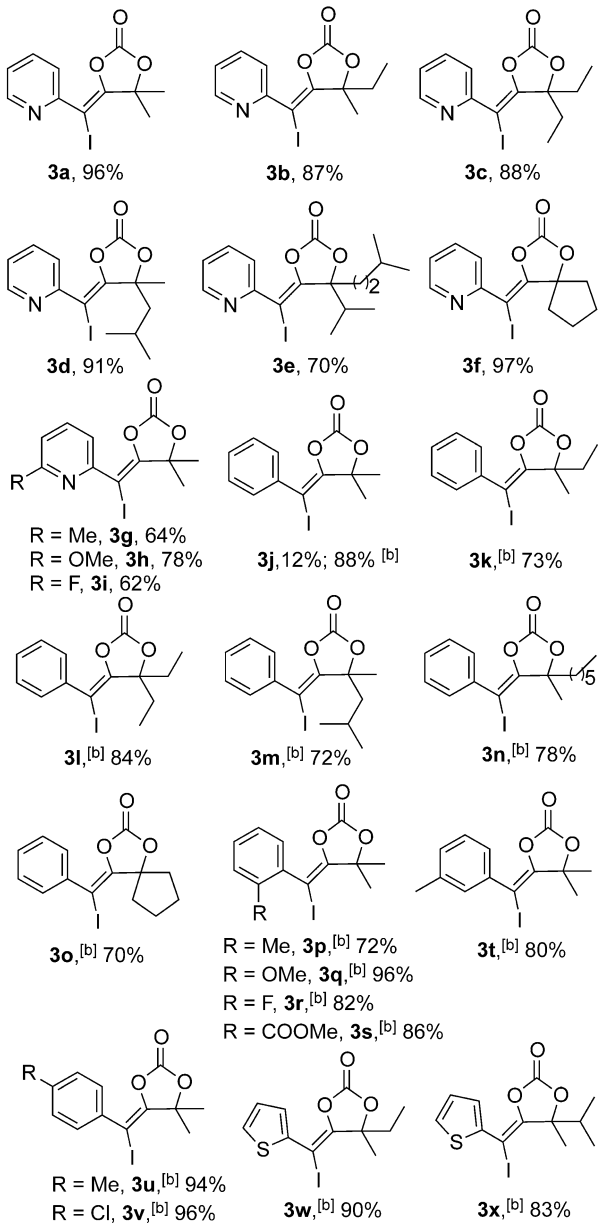
Finally, the effect of solvent on the yield of **3a** is shown in Table 5. It is easy to conclude that the yield of **3a** is strongly dependent on the reaction media since none or only a little amount of **3a** was observed when the reaction was performed in 1,4-dioxane, THF or CH_2Cl_2 (entries 2, 3 and 5). The reaction in DMF gave **3a** in 79% yield with a 20:1 ratio of **3a**/**2a**. Thus, MeCN was identified as the most suitable medium for the formation of **3a**.

With the optimized reaction conditions in hand, we then explored the scope and limitations of our protocol (Table 6). Gratifyingly, a range of internal tertiary propargylic alcohols with a pyridyl ring at the acetylenic terminus underwent smooth transformation to generate the corresponding products in good to excellent yields (products **3a**–**3i**). The lower yield (70%) of product **3e** might be due to steric hindrance effect. But the substrate with a cyclopentyl at the propargylic position gave the spirocyclic product **3f** with an excellent yield. Notably, the presence of a substituent at the 6-position of 2-pyridyl ring, such as Me, OMe and F groups, would decrease the reactivity of the substrates, affording the corresponding products in lower yields (products **3g**–**3i**)

To our surprise, when the above reaction condition was applied to 2-methyl-4-phenylbut-3-yn-2-ol, the product **3j** was isolated only in 12% yield together with large amount of unidentified products. Pleasingly, when the copper source was switched to CuCl, an improved yield (88%) was obtained. These results indicate that the nature of R^1 substituent attached at the alkyne terminus of the propargylic alcohols has profound influence on the formation of iodoalkylidene cyclic carbonate. Thus, with the CuCl reaction system, a variety of iodoalkylidene cyclic carbonate bearing a phenyl ring could be obtained in high to excellent yields (products **3j**–**3v**). Notably, a variety of electron-donating or electron-withdrawing groups on

Table 6. Synthesis of various (*E*)-iodoalkylidene cyclic carbonates.[a]





[a] Reaction conditions: propargylic alcohol (0.25 mmol), $Cu(OTf)_2$ (0.5 mmol), KI (1 mmol), pyridine (0.25 mmol), MeCN (3 mL), CO_2 (4 MPa), 110 °C, 24 h. Yields of isolated products are given.
[b] The reaction was performed with CuCl (0.5 mmol) as copper source.

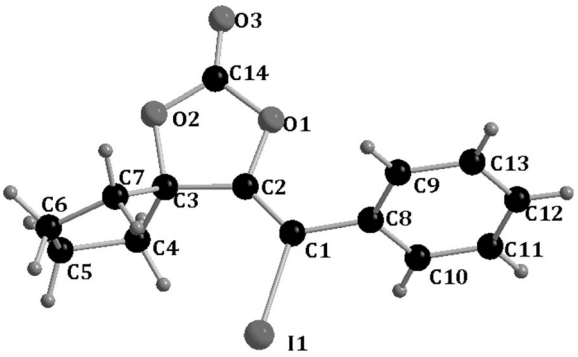
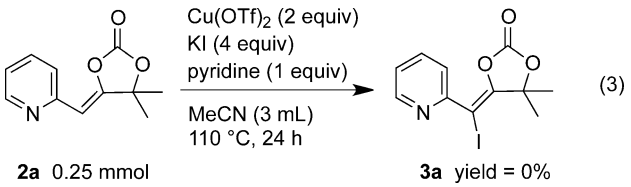


Figure 2. X-ray structure of compound **3o**.

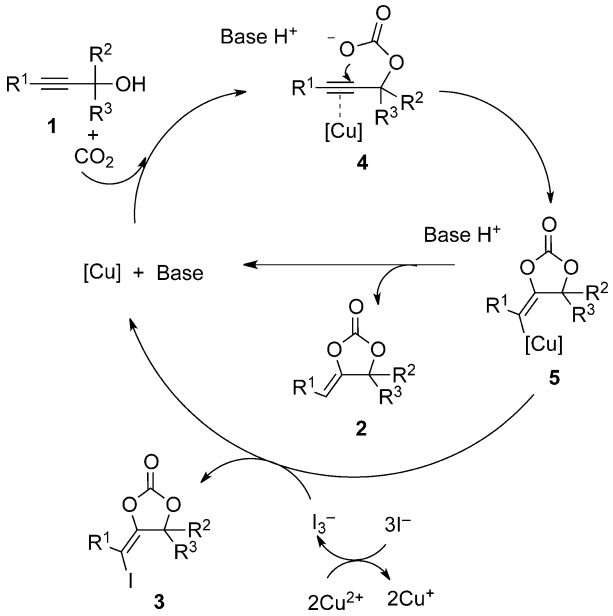
the benzene ring of the propargylic alcohols, including Me, OMe, COOMe, F and Cl substituents, were well tolerated in this reaction (products **3p**–**3v**). Moreover, thiophen-2-yl substituted propargylic alcohols also reacted well to give rise to the desired products in high yields (products **3w** and **3x**). However, the reaction with terminal propargylic alcohols led to a complex mixture, and the expected product was not observed, which might be ascribed to the relative instability of the vinyl copper species in the absence of a stabilizing group. The *E* configuration of the product **3o** was confirmed by X-ray crystallographic analysis, as shown in Figure 2.[18]

In order to gain more insight into the formation of (*E*)-α-iodoalkylidene cyclic carbonate, **2a** was subjected to the standard reaction conditions as described in Table 6. However, none of **3a** was detected, and the starting material was recovered (eq 3). This result indicates that **2a** is not the intermediate for the formation of **3a**.



(3)

On the basis of the above-described observations and previous reports,[6a,c,13,16] a plausible mechanism for the reaction is proposed in Scheme 3. Initially, propargylic alcohol **1** enters into coupling with CO_2 in the presence of copper salt and base to generate a vinyl copper intermediate **5** via a carbonate anion **4**. Then, protonolysis of **5** will take place to give the α-alkylidene cyclic carbonate **2**. Alternatively, in the presence of electrophilic triiodide ion (I_3^-), which is generated in situ from the interaction of Cu^{2+} and I^- ions, iododemetallation of **5** will occur prior to protonation, affording the corresponding iodoalkylidene cyclic carbonate **3**.



Scheme 3. Plausible mechanism for the reaction.

Conclusions

In conclusion, we have demonstrated that copper iodide could effectively catalyze the coupling reaction of internal propargylic alcohols with CO_2 in the presence of *N*,*N*-diisopropylethylamine, affording the corresponding α-alkylidene cyclic carbonates in moderate to excellent yields. More importantly, we have successfully developed a protocol for chemo- and stereoselective synthesis of a variety of (*E*)-α-iodoalkylidene cyclic carbonates. The process is proposed to proceed through the trapping of the vinyl copper intermediate by in situ generated triiodide ion as the electrophile. The advantages of the presented method include the use of readily available and easy-to-handle copper salt as the promoter as well as the wide substrate scope. Further investigation on the mechanism as well as the application of this protocol to construct more complex molecules are underway in our lab.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm,

length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were recorded in KBr disks with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. Internal propargylic alcohols were synthesized according to the literature procedure.[19] Other compounds were commercially purchased and used without further purification.

General procedure for preparation of (*Z*)-α-alkylidene cyclic carbonates 2

To a 25 mL polytetrafluoroethylene (PTFE) reaction vessel, propargylic alcohol **1** (0.25 mmol), CuI (0.05 mmol), *N,N*-diisopropylethylamine (0.25 mmol) and MeCN (1.0 mL) were added successively. The vessel was fixed into a stainless steel autoclave. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 24 h and the pressure was kept constant during the reaction. When the reaction was complete, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. After removing the volatile compounds under vacuum, the crude product was purified by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to give the desired product.

(*Z*)-4,4-Dimethyl-5-((pyridin-2-yl)methylene)-1,3-dioxolan-2-one (2a):[7e] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 4.8 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.18–7.14 (m, 1H), 5.82 (s, 1H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 152.0, 150.8, 149.3, 136.7, 123.5, 122.1, 102.8, 85.8, 27.6; NOE: 2.3%.

(*Z*)-4-Ethyl-4-methyl-5-(pyridin-2-ylmethylene)-1,3-dioxolan-2-one (2b): yellow oil; IR (KBr): 2943, 1832, 1032, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 5.6 Hz, 1H), 5.79 (s, 1H), 2.07–1.98 (m, 1H), 1.93–1.84 (m, 1H), 1.69 (s, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 152.1, 151.1, 149.3, 136.6, 123.4, 122.1, 103.2, 88.8, 33.6, 26.0, 7.5; MS (EI, 70 eV): *m/z* (%) = 219 M$^+$], 160, 146, 119 (100), 91, 64; HRMS-ESI (*m/z*): calcd for $C_{12}H_{14}NO_3$ $(M+H)^+$: 220.0968; found: 220.0971; NOE: 3.0%.

(*Z*)-4-(Pyridin-2-ylmethylene)-1,3-dioxaspiro[4.4]nonan-2-one (2c): yellow oil; IR (KBr): 2958, 1710, 1015, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 7.88 (s, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.15 (s, 1H), 5.84 (s, 1H), 2.34–2.27 (m, 2H), 2.07–1.99 (m, 2H), 1.93–1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 152.2, 151.0, 149.3, 136.6, 123.6, 122.0, 103.0, 95.5, 40.9, 24.5; MS (EI, 70 eV): *m/z* (%): 231 M$^+$], 158, 146, 119 (100), 91, 64; HRMS-ESI (*m/z*): calcd for C_{13} $H_{12}NO_3$ $(M\text{-}H)^-$: 230.0823; found: 230.0804; NOE: 2.9%.

(*Z*)-4,4-Dimethyl-5-((6-methylpyridin-2-yl)methylene)-1,3-dioxolan-2-one (2d): yellow solid; mp: 54–56 °C; IR (KBr): 2987, 1748, 1052, 791 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 5.78 (s, 1H), 2.52 (s, 3H), 1.69 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 153.3, 151.3, 150.9, 136.9, 121.7, 120.6, 103.1, 85.8, 27.6, 24.4; MS (EI, 70 eV): *m/z* (%) = 219 M$^+$], 160, 146 (100), 132, 91, 77; HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}O_3N$ (M^+): 219.0890; found: 219.0889; NOE: 9.5%.

(*Z*)-5-Benzylidene-4,4-dimethyl-1,3-dioxolan-2-one (2e):[7e] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 1H), 5.53 (s, 1H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 150.7, 132.4, 128.6, 128.4, 127.6, 101.5, 85.50, 27.7; NOE: 11.3%.

(*Z*)-4-Benzylidene-1,3-dioxaspiro[4.5]decan-2-one (2f):[6a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.30–7.28 (m, 1H), 5.51 (s, 1H), 2.09 (d, J = 9.6 Hz, 2H), 1.87–1.69 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 150.9, 132.5, 128.6, 128.4, 127.5, 101.7, 87.3, 36.6, 24.4, 21.7.

(*Z*)-5-Benzylidene-4-butyl-4-ethyl-1,3-dioxolan-2-one (2g): yellow oil; IR (KBr): 2961, 1830, 1066, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.27–7.23 (m, 1H), 5.43 (s, 1H), 2.05–1.93 (m, 2H), 1.84–1.70 (m, 2H), 1.46–1.29 (m, 4H), 1.00 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 148.3, 132.5, 128.6, 128.4, 127.4, 101.9, 91.3, 39.0, 32.4, 24.9, 22.4, 13.8, 7.1; MS (EI, 70 eV): *m/z* (%) = 260 M$^+$], 216, 145, 118 (100), 90; HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}O_3Na$ $(M+Na)^+$: 283.1305; found: 283.1299; NOE: 11.0%.

(*Z*)-4-Hexyl-4-methyl-5-(thiophen-2-ylmethylene)-1,3-dioxolan-2-one (2j): IR (KBr): 2930, 1828, 1038, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 3.2 Hz, 1H), 7.02 (dd, J = 5.2, 4.0 Hz, 1H), 5.76 (s, 1H), 1.95–1.89 (m, 1H), 1.81–1.73 (m, 1H), 1.64 (s, 3H), 1.35–1.23 (m, 8H), 0.87 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 148.3, 134.9, 127.1, 126.9, 126.0, 95.9, 87.7, 40.6, 31.4, 28.9, 26.2, 22.9, 22.4, 13.9; MS (EI, 70 eV): *m/z* (%) = 280 M$^+$], 153, 137, 124 (100), 96, 69; HRMS-ESI (*m/z*): calcd for $C_{15}H_{20}O_3S(M^+)$: 280.1128; found: 280.1127; NOE: 1.0%.

4-Hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2k):[6d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.77 (d, J = 3.2 Hz, 1H), 4.47–3.94 (m, 1H), 1.87–1.81 (m, 1H), 1.71–1.64 (m, 1H), 1.56 (s, 3H), 1.39–1.22 (m, 8H), 0.86–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 151.5, 87.2, 85.4, 40.4, 31.4, 28.8, 26.2, 22.8, 22.4, 13.9.

4-Isopropyl-5-methylene-1,3-dioxolan-2-one (2l):[6d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.01 (s, 1H), 4.89 (s, 1H), 4.35 (d, J = 1.6 Hz, 1H), 1.08 (d, J = 7.2 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 87.4, 84.1, 32.7, 17.5, 14.9.

General procedure for preparation of (*E*)-α-iodoalkylidene cyclic carbonates 3

To a 25 mL polytetrafluoroethylene (PTFE) reaction vessel, propargylic alcohol **1** (0.25 mmol), $Cu(OTf)_2$ (0.5 mmol), KI (1 mmol), pyridine (0.25 mmol) and MeCN (3.0 mL) were added successively. The vessel was fixed into a stainless steel autoclave. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature under magnetic stirring for 24 h and the pressure was kept constant during the reaction. When the reaction was complete, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The residual material was diluted with di-

ethyl ether (30 mL) and then filtered. The volatile compounds were removed under vacuum and the crude product was purified by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to give the desired product.

(*E*)-5-(Iodo(pyridin-2-yl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3a): pale yellow solid; mp: 113–115 °C; IR (KBr): 2924, 1813, 1660, 1277, 1028, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.65$ (s, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 6.4$ Hz, 1H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$, 150.8, 149.4, 149.3, 136.4, 123.6, 123.3, 87.5, 72.7, 25.1; MS (EI, 70 eV): *m/z* (%) = 331 [M^+], 287 (100), 258, 217, 160, 117, 90, 63; HRMS-ESI (*m/z*): calcd for $C_{11}H_{11}INO_3$ $(M+H)^+$: 331.9778; found: 331.9781.

(*E*)-4-Ethyl-5-(iodo(pyridin-2-yl)methylene)-4-methyl-1,3-dioxolan-2-one (3b): yellow solid; mp: 107–108 °C; IR (KBr): 2977, 1824 1649, 1269, 1045, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.65$ (s, 1H), 7.66 (td, $J = 7.6$, 1.6 Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.18 (dd, $J = 6.4$, 5.2 Hz, 1H), 2.63–2.53 (m, 1H), 2.09–1.99 (m, 1H), 1.95 (s, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$, 149.6, 149.5, 149.4, 136.4, 123.6, 123.3, 90.6, 73.3, 30.2, 23.9, 7.4; MS (EI, 70 eV): *m/z* (%) = 345 [M^+], 273 (100), 245, 146, 90; HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}INO_3$ $(M+H)^+$: 345.9935; found: 345.9940.

(*E*)-4,4-Diethyl-5-(iodo(pyridin-2-yl)methylene)-1,3-dioxolan-2-one (3c): yellow solid; mp: 137–138 °C; IR (KBr): 2973, 1815, 1651, 1264, 1056, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.66$ (d, $J = 4.0$ Hz, 1H), 7.65 (td, $J = 7.7$, 1.7 Hz, 1H), 7.58 (d, $J = 7.9$ Hz, 1H), 7.18 (dd, $J = 6.5$, 5.0 Hz, 1H), 2.62–2.53 (m, 2H), 2.05–1.94 (m, 2H), 1.05 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.2$, 149.8, 149.4, 148.1, 136.4, 123.5, 123.2, 94.1, 74.3, 29.1, 7.2; MS (EI, 70 eV): *m/z* (%) = 359 [M^+], 315, 287, 245 (100), 90; HRMS-ESI (*m/z*): calcd for $C_{13}H_{15}INO_3$ $(M+H)^+$: 360.0091; found: 360.0090.

(*E*)-5-(Iodo(pyridin-2-yl)methylene)-4-isobutyl-4-methyl-1,3-dioxolan-2-one (3d): pale yellow oil; IR (KBr): 2920, 1815, 1647, 1211, 1065, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40$–7.32 (m, 4H), 2.47 (d, $J = 9.6$ Hz, 1H), 1.96–1.87 (m, 5H), 1.08 (d, $J = 6.0$ Hz, 3H), 1.02 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.7$, 148.0, 138.5, 129.2, 128.7, 128.3, 89.7, 71.0, 44.89, 25.3, 24.7, 23.6; MS (EI, 70 eV): *m/z* (%) = 373 [M^+], 273, 245 (100), 217, 90; HRMS-ESI (*m/z*): calcd for $C_{14}H_{17}INO_3$ $(M+H)^+$: 374.0248; found: 374.0250.

(*E*)-5-(Iodo(pyridin-2-yl)methylene)-4-isopentyl-4-isopropyl-1,3-dioxolan-2-one (3e): pale yellow oil; IR (KBr): 2971, 1825, 1650, 1274, 1057, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.68$ (d, $J = 4.4$ Hz, 1H), 7.74–7.62 (m, 1H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.19 (m, 1H), 2.51 (d, $J = 4.0$ Hz, 1H), 2.48 (d, $J = 4.0$ Hz, 1H), 2.00–1.82 (m, 4H), 1.04 (d, $J = 6.4$ Hz, 6H), 0.99 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$, 149.7, 149.6, 149.2, 136.4, 123.6, 123.3, 93.3, 75.2, 44.9, 24.4, 23.9, 23.6; MS (EI, 70 eV): *m/z* (%) = 415 [M^+], 315, 272, 245 (100), 188, 146, 130, 90, 78; HRMS-ESI (*m/z*): calcd for $C_{17}H_{22}INO_3Na$ $(M+Na)^+$: 438.0537; found: 438.0531.

(*E*)-4-(Iodo(pyridin-2-yl)methylene)-1,3-dioxaspiro[4.4]-nonan-2-one (3f): yellow solid; mp: 103–105 °C; IR (KBr): 2955, 1816, 1622, 1283, 1028, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.63$ (d, $J = 3.1$ Hz, 1H), 7.67–7.58 (m, 2H), 7.17 (t, $J = 5.9$ Hz, 1H), 2.86–2.81 (m, 2H), 2.18–2.14 (m, 2H), 2.05–1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 154.3$, 149.6, 149.2, 148.8, 136.5, 123.7, 123.2, 97.0, 72.8, 37.5, 25.2; MS (EI, 70 eV): *m/z* (%) = 357 [M^+], 313, 272 (100), 244, 216, 158, 90, 63; HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INO_3$ $(M+H)^+$: 357.9935; found: 357.9947.

(*E*)-5-(Iodo(6-methylpyridin-2-yl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3g): yellow solid; mp: 107–108 °C; IR (KBr): 2961, 1823, 1650, 1279, 1074, 788 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.54$ (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 2.57 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 158.3$, 153.7, 150.3, 149.3, 136.5, 122.9, 120.5, 87.3, 72.7, 25.1, 24.5; MS (EI, 70 eV): *m/z* (%) = 345 [M^+], 301, 272, 260, 174, 146, 131(100), 104, 77; HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}INO_3$ $(M+H)^+$: 345.9948; found: 345.9935.

(*E*)-5-(Iodo(6-methoxypyridin-2-yl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3h): yellow solid; mp: 98–99 °C; IR (KBr): 2982, 2920, 1822, 1647, 1581, 1464, 1260, 1148, 1074, 1026, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (t, $J = 8.0$ Hz, 1H), 7.28 (s, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 3.98 (s, 3H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 163.2, 150.7, 150.3, 149.5, 138.9, 116.3, 110.6, 87.73, 75.2, 53.6, 25.2; MS (EI, 70 eV): *m/z* (%) = 361 [M^+], 317, 162, 147 (100), 77; HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}INO_4$ $(M+H)^+$: 361.9883; found: 361.9884.

(*E*)-5-((6-Fluoropyridin-2-yl)iodomethylene)-4,4-dimethyl-1,3-dioxolan-2-one (3i): yellow solid; mp: 130–132 °C; IR (KBr): 2989, 2919, 1822, 1661, 1271, 1152, 1074, 796 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (q, $J = 8.0$ Hz, 1H), 7.60 (dd, $J = 7.6$, 1.6 Hz, 1H), 6.84 (dd, $J = 8.4$, 2.8 Hz, 1H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 162.5$, 152.7, 151.7, 149.0, 141.6, 121.0, 109.5, 87.6, 70.5, 25.0; MS (EI, 70 eV): *m/z* (%) = 349 [M^+], 304, 178, 135 (100), 108; HRMS-ESI (*m/z*): calcd for $C_{11}H_{10}FINO_3$ $(M+H)^+$: 349.9684; found: 349.9684.

(*E*)-5-(Iodo(phenyl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3j): yellow solid; mp: 105–106 °C; IR (KBr): 3051, 2922, 1803, 1669, 1269, 1140, 1072, 1027, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–7.24 (m, 5H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.5$, 148.7, 138.3, 129.2, 128.7, 128.2, 87.0, 70.0, 25.2; MS (EI, 70 eV): *m/z* (%): 330 [M^+], 286, 131(100), 115, 91; HRMS-ESI (*m/z*): calcd for $C_{12}H_{11}INaO_3$ $(M+Na)^+$: 352.9645; found: 352.9645.

(*E*)-4-Ethyl-5-(iodo(phenyl)methylene)-4-methyl-1,3-dioxolan-2-one (3k): pale yellow solid; mp: 64–65 °C; IR (KBr): 2960, 1821, 1651, 1283, 1082, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–7.24 (m, 5H), 2.58–2.49 (m, 1H), 2.05–1.92 (m, 1H), 1.92 (s, 3H), 1.05 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.8$, 147.4, 138.5, 129.2, 128.7, 128.3, 90.1, 70.6, 30.2, 24.1, 7.5; MS (EI, 70 eV): *m/z* (%) = 344 [M^+], 244, 216, 145, 89 (100); HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INaO_3$ $(M+Na)^+$: 366.9802; found: 366.9810.

(*E*)-4,4-Diethyl-5-(iodo(phenyl)methylene)-1,3-dioxolan-2-one (3l): yellow solid; mp: 103–104 °C; IR (KBr): 2960, 1813, 1650, 1265, 1084, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40$–7.24 (m, 5H), 2.57–2.47 (m, 2H), 2.03–1.92 (m, 2H), 1.06 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.1$, 145.9, 138.5, 129.2, 128.7, 128.3, 93.6, 71.3, 29.2, 7.3; MS (EI, 70 eV): *m/z* (%) = 358 [M^+], 286, 244, 216,

89 (100); HRMS-ESI (*m/z*): calcd for $C_{14}H_{15}INaO_3$ $(M+Na)^+$: 380.9958; found: 380.9958.

(*E*)-5-(Iodo(phenyl)methylene)-4-isobutyl-4-methyl-1,3-dioxolan-2-one (3m): pale yellow oil; IR (KBr): 2959, 1818, 1663, 1286, 1065,757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.40–7.24 (m, 5H), 2.50–2.43 (m, 1H), 1.95–1.86 (m, 5H), 1.07 (d, $J=6.4$ Hz, 3H), 1.02 (d, $J=6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.7$, 148.0, 138.5, 129.2, 128.7, 128.3, 89.7, 71.0, 44.9, 25.3, 24.7, 23.6, 23.6; MS (EI, 70 eV): *m/z* (%) = 372 M^+], 272, 244(100), 145, 89; HRMS-ESI (*m/z*): calcd for $C_{15}H_{17}INaO_3$ $(M+Na)^+$: 395.0115; found: 395.0104.

(*E*)-4-Hexyl-5-(iodo(phenyl)methylene)-4-methyl-1,3-dioxolan-2-one (3n): yellow oil; IR (KBr): 2928, 1820, 1664, 1274, 1077, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.41$–7.24 (m, 5H), 2.54–2.46 (m, 1H), 1.98–1.91 (m, 4H), 1.46–1.33 (m, 8H), 0.91 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.8$, 147.7, 138.4, 129.2, 128.7, 128.3, 89.8, 70.6, 36.9, 31.4, 28.8, 24.4, 23.0, 22.5, 14.0; MS (EI, 70 eV): *m/z* (%) = 400 M^+], 272, 244 (100), 216, 89; HRMS-ESI (*m/z*): calcd for $C_{17}H_{21}INaO_3$ $(M+Na)^+$: 423.0428; found: 423.0420.

(*E*)-4-(Iodo(phenyl)methylene)-1,3-dioxaspiro[4.4]nonan-2-one (3o): yellow solid; mp: 126–127 °C; IR (KBr): 2960, 1826, 1650, 1275, 1054, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.43$–7.24 (m, 5H), 2.85–2.78 (m, 2H), 2.19–2.14 (m, 2H), 2.04–1.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=150.0$, 146.5, 138.4, 129.3, 128.7, 128.2, 96.6, 70.6, 37.6, 25.2; MS (EI, 70 eV): *m/z* (%) = 356 M^+], 271, 244(100), 129, 89; HRMS-ESI (*m/z*): calcd for $C_{14}H_{13}INaO_3$ $(M+Na)^+$: 378.9802; found: 378.9802.

(*E*)-5-(Iodo(o-tolyl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3p): pale yellow solid; mp: 108–109 °C; IR (KBr): 2990, 2922, 2360, 1821, 1764, 1657, 1374, 1244, 1063, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.18$ (d, $J=$ 8.3 Hz, 4H), 2.25 (s, 3H), 1.96 (d, $J=10.5$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.4$, 148.8, 137.8, 135.2, 130.4, 129.0, 128.8, 126.2, 86.6, 67.7, 25.3, 25.1, 19.2; MS (EI, 70 eV): *m/z* (%) = 344 M^+], 300, 257, 173, 130 (100); HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INaO_3$ $(M+Na)^+$: 366.9802; found: 366.9797.

(*E*)-5-(Iodo(2-methoxyphenyl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3q): yellow oil; IR (KBr): 2980, 2920, 1834, 1647, 1261, 1026, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.37$ (t, $J=8.0$ Hz, 1H), 7.17 (d, $J=7.6$ Hz, 1H), 6.94 (t, $J=7.6$ Hz, 1H), 6.87 (d, $J=8.4$ Hz, 1H), 3.85 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=155.8$, 149.8, 149.2, 130.4, 130.2, 127.1, 120.5, 111.4, 86.7, 64.2, 55.6, 25.2; MS (EI, 70 eV): *m/z* (%) = 356 M^+], 316, 161(100), 146, 91; HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INaO_4$ $(M+Na)^+$: 382.9751; found: 382.9753.

(*E*)-5-((2-Fluorophenyl)iodomethylene)-4,4-dimethyl-1,3-dioxolan-2-one (3r): yellow solid; mp: 98–100 °C; IR (KBr): 2920, 1823, 1644, 1451, 1233, 1150, 1070, 1026, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.32$–7.25 (m, 2H), 7.15 (t, $J=7.6$ Hz, 1H), 7.05 (t, $J=8.8$ Hz, 1H), 1.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.5$, 150.7, 149.3, 131.0, 130.8, 126.3, 124.2, 116.1, 86.7, 59.4, 25.1; MS (EI, 70 eV): *m/z* (%) = 348 M^+], 304, 234, 149(100), 109; HRMS-ESI (*m/z*): calcd for $C_{12}H_{10}FINaO_3$ $(M+Na)^+$: 370.9551; found: 370.9549.

(*E*)-Methyl 2-((5,5-dimethyl-2-oxo-1,3-dioxolan-4-ylidene)iodomethyl)benzoate (3s): yellow solid; mp: 57–58 °C; IR (KBr): 2989, 2920, 1819, 1724, 1681, 1433, 1259, 1150, 1067, 1026, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.00$ (d, $J=8.0$ Hz, 1H), 7.55 (t, $J=7.6$ Hz, 1H), 7.39 (t, $J=$ 7.6 Hz, 1H), 7.30 (d, $J=8.0$ Hz, 1H), 3.91 (s, 3H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.0$, 149.5, 148.1, 139.7, 132.5, 131.0, 130.4, 128.8, 128.2, 86.7, 66.7, 52.1, 25.1, 24.6; MS (EI, 70 eV): *m/z* (%) = 387 M^+], 274, 261, 189(100); HRMS-ESI (*m/z*): calcd for $C_{14}H_{13}INaO_5$ $(M+Na)^+$: 410.9700; found: 410.9703.

(*E*)-5-(Iodo(m-tolyl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3t): yellow solid; mp: 111–112 °C; IR (KBr): 2984, 2920, 1815, 1670, 1273, 1275, 1147, 1072, 1027, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.25$–7.17 (m, 3H), 7.07 (d, $J=7.2$ Hz, 1H), 2.34 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.5$, 148.5, 138.3, 138.0, 129.7, 129.5, 128.1, 126.3, 87.0, 70.2, 25.2, 21.3; MS (EI, 70 eV): *m/z* (%) = 344 M^+], 300, 285, 145(100), 130; HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INaO_3$ $(M+Na)^+$: 366.9802; found: 366.9806.

(*E*)-5-(Iodo(p-tolyl)methylene)-4,4-dimethyl-1,3-dioxolan-2-one (3u): yellow solid; mp: 57–59 °C; IR (KBr): 2986, 2920, 1819, 1677, 1461, 1271, 1148, 1070, 1025, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.30$ (d, $J=8.0$ Hz, 2H), 7.15 (d, $J=8.0$ Hz, 2H), 2.36 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.6$, 148.4, 138.8, 135.5, 129.1, 128.9, 87.0, 70.5, 25.3, 21.2; MS (EI, 70 eV): *m/z* (%) = 344 M^+], 300, 145 (100), 130, 77; HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}INaO_3$ $(M+Na)^+$: 366.9802; found: 366.9804.

(*E*)-5-((4-Chlorophenyl)iodomethylene)-4,4-dimethyl-1,3-dioxolan-2-one (3v): yellow solid; mp: 123–124 °C; IR (KBr): 2990, 2923, 1814, 1661, 1392, 1268, 1148, 1096, 1025, 801, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.33$ (q, $J=$ 8.8 Hz, 4H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 149.2, 149.2, 136.8, 134.5, 130.6, 128.4, 87.1, 68.2, 25.1; MS (EI, 70 eV): *m/z* (%) = 364 M^+], 285, 165, 130 (100); HRMS-ESI (*m/z*): calcd for $C_{12}H_{10}ClINaO_3$ $(M+Na)^+$: 386.9255; found: 386.9248.

(*E*)-4-Ethyl-5-(iodo(thiophen-2-yl)methylene)-4-methyl-1,3-dioxolan-2-one (3w): brown oil; IR (KBr): 2960, 1826, 1649, 1284, 1080, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.46–7.44 (m, 2H), 7.08 (t, $J=4.0$ Hz, 1H), 2.57–2.48 (m, 1H), 2.06–1.97 (m, 1H), 1.91 (s, 3H), 1.00 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.3$, 146.3, 139.5, 130.8, 127.7, 126.7, 90.9, 64.1, 30.6, 24.3, 7.4; MS (EI, 70 eV): *m/z* (%) = 350 M^+], 306, 250 (100), 123, 95; HRMS-ESI (*m/z*): calcd for $C_{11}H_{11}INaO_3S$ $(M+Na)^+$: 372.9366; found: 372.9366.

(*E*)-5-(Iodo(thiophen-2-yl)methylene)-4-isopropyl-4-methyl-1,3-dioxolan-2-one (3x): brown oil; IR (KBr): 2964, 2924, 1824, 1633, 1384, 1226, 1131, 1054, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.44$ (t, $J=4.4$ Hz, 2H), 7.09–7.06 (m, 1H), 2.89–2.82 (m, 1H), 1.92 (s, 3H), 1.14 (d, $J=6.8$ Hz, 3H), 1.00 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.6$, 147.8, 139.7, 130.7, 127.7, 126.8, 92.6, 63.7, 33.8, 22.7, 16.6, 15.6; MS (EI, 70 eV): *m/z* (%) = 364 M^+], 250 (100), 222, 123, 95; HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}INaO_3S$ $(M+Na)^+$: 386.9522; found: 386.9511.

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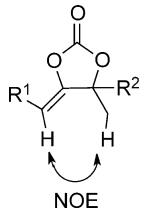
[14] CCDC-1040316 contains the supplementary crystallographic data for compound **2f**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[15] In NOE experiments, a correlation between the olefinic proton and the methyl or methylene protons bound to the C-4 carbon on the 1,3-dioxolan-2-one ring of the products (**2a**–**2e**, **2g** and **2j**) was detected, indicating the formation of (*E*)-α-iodoalkylidene cyclic carbonates.



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[18] CCDC-914524 contains the supplementary crystallographic data for compound **3o**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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