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Phosphine-catalyzed fixation of CO_2 with γ-hydroxyl alkynone under ambient temperature and pressure: kinetic resolution and further conversion†

Yao-Liang Sun,[a,b] Yin Wei *[a] and Min Shi *[a,b,c]

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Multiple skeleton derived γ-hydroxyl alkynones could be activated by phosphine, which then underwent cycloaddition with CO_2 to afford functionalized carbonate products under ambient temperature and pressure. These functionalized carbonate products could easily release CO_2 under heating conditions, giving a diversity of furanones in excellent yields. The optically active functionalized cyclic carbonates could be afforded through the kinetic resolution of propargyl alcohols *via* carbon dioxide fixation catalyzed by a new series of sterically hindered and highly nucleophilic bifunctional amino acid-derived phosphine catalysts with moderate to excellent selectivities. Plausible mechanisms were proposed and supported by isotope-labeling experiments and DFT calculations.

Introduction

Due to global warming associated with greenhouse gas emissions, effectively reducing carbon dioxide (CO_2) in the atmosphere has attracted a lot of attention from the scientific community; direct conversion of CO_2 to useful chemical products not only reflects the exploration of environmental protection issues, but also has many advantages such as low-cost, easy availability, abundance, nontoxicity, and inherent renewability.[1] Among the carbon dioxide fixation products, cyclic carbonates[2] are quite important in industrial materials, which are frequently used as predominant monomers for polycarbonates or electrolytes in lithium-ion-battery half-cells.[3] Furthermore, cyclic carbonates have great potential in synthetic transformations; their synthetic value and relevant mechanistic studies have been continuously improved in these years.[4] Meanwhile, along with the increasing requirement of CO_2 as a useful renewable carbon resource participating in the stereo-controlled preparation of value-added commodities,[5] a cobalt complex was firstly and widely used in catalytic enantioselective reactions for the synthesis of chiral carbonates and polycarbonates through kinetic resolution of racemic epoxides *via* CO_2 fixation.[6] Transition metals (Ni,[7] Pd,[8] Rh,[9] Ir,[10] Cu,[11] and Ag[12]) were also frequently used in catalytic asymmetric CO_2 fixation, affording different useful compounds like chiral alcohols, acids, esters, carbonates and carbamates.

α-Alkylidene cyclic carbonates are a class of carbonates with special properties, which could be produced by the reaction of CO_2 with propargylic alcohols under metal[13] or metal-free[14,15] catalysis. Recently, many efforts have been devoted to increase the efficiency of this green route to fix CO_2, which means to look for mild reaction conditions and to achieve a wide range of substrate scopes. Yamada and co-workers first developed silver catalytic systems to combine CO_2 with different propargyl alcohols to afford α-alkylidene cyclic carbonates and carbonyl compounds under 1.0 MPa of CO_2.[16] Ikariya[17] and Lu[18] independently reported *N*-heterocyclic carbenes (NHCs) and NHC–CO_2 adducts served as potent organocatalysts to promote carbon dioxide fixation reaction under pressurized and heating conditions. Further transformations of α-alkylidene cyclic carbonates have also been studied. Using metal catalysts such as Pd,[19] Pt,[20] Rh,[21] and Ni[22] could easily transform α-alkylidene cyclic carbonates to oxygen heterocycles or carboxylic acid compounds.

In recent years, the nucleophilic phosphine-catalyzed reactions[23] have been recognized as reliable methods which could combine olefins,[24] allenes,[25] alkynes,[26] or Morita–Baylis–Hillman adducts (MBHADs)[27] with other electrophilic or nucleophilic reagents to afford highly functionalized products.

[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: weiyin@sioc.ac.cn, mshi@mail.sioc.ac.cn*
[b]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*
[c]*State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China*

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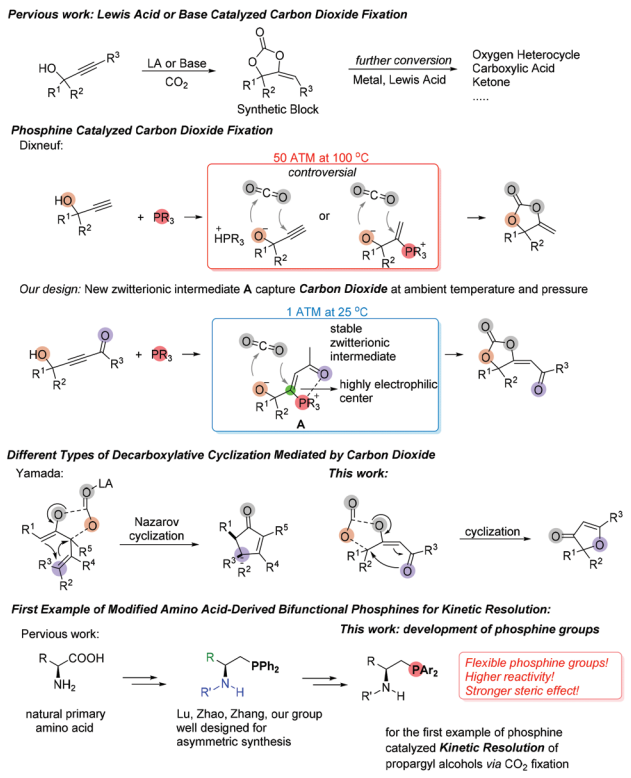
As early as 1989, Dixneuf *et al*. synthesized α-alkylidene cyclic carbonates by using tributylphosphine as a catalyst under harsh reaction conditions with 5.0 MPa pressure of CO_2 at 100 °C for 8 h (Scheme 1).[15] They proposed that tertiary phosphine either acted as a Brønsted base catalyst to undergo proton abstraction from the alcohol or as a nucleophilic catalyst to generate a zwitterionic intermediate before incorporating CO_2. Based on the commonly accepted mechanisms of nucleophilic phosphine-catalyzed reactions in recent years, we hypothesized that introducing an electron deficient group on the alkyne's terminal position of substrate might lead to the very stable zwitterionic intermediate **A**, which could facilitate the following process of CO_2 fixation since the oxygen nucleophilic site of intermediate **A** would directly attack carbon dioxide and the subsequent cyclization step would be easier to proceed due to the presence of a highly electrophilic center (Scheme 1). Recently, Yamada disclosed a Lewis-acid catalyzed decarboxylative[28] Nazarov cyclization of cyclic carbonate derivatives, which underwent a cationic intermediate directed 4π-ring-closure process to afford 2-cyclopentenones.[29] We anticipate that the α,β-unsaturated 4π system with a carbonyl group of functionalized cyclic carbonates could also participate in a decarboxylative ring-closure process to provide a range of novel furanone derivatives (Scheme 1).

In the past decade, Lu established a family of bifunctional amino acid-derived phosphine catalysts that were efficient catalysts in asymmetric reactions for the enantioselective construction of all-carbon quaternary stereogenic centers.[30,31] Zhao,[31] Zhang[32] and our group[33] also made the corresponding contributions in this area. The amino acid-derived phosphine catalysts have modular, tunable, dipeptide scaffolds and abundant derived amino groups as H-bond donors to adapt a variety of catalytic requirements. Although many highly efficient chiral phosphine catalysts have been frequently applied in asymmetric reactions, the use of chiral phosphine catalysts for kinetic resolution of racemic compounds was still a challenge. Vedejs and co-workers first developed kinetic resolution of secondary alcohols *via* chiral phosphine-catalyzed acylation.[34] However, there is no report on the kinetic resolution of propargyl alcohols *via* CO_2 fixation in the catalysis of chiral phosphines. In order to obtain optically active functionalized cyclic carbonates, we investigated a series of chiral phosphine catalysts to realize the kinetic resolution of propargyl alcohols *via* CO_2 fixation and found that substituents on the phosphine center had a significant effect on the stereoselectivity of the reaction. Thus, we studied the performance of a new series of sterically hindered and highly nucleophilic bifunctional amino acid-derived phosphine catalysts in this reaction. Herein, we wish to report the first example of chiral phosphine catalyzed kinetic resolution of propargyl alcohols *via* carbon dioxide fixation in good yields with moderate to good selectivities (Scheme 1). We also conducted the mechanistic studies to reveal the detailed mechanisms through isotope-labeling experiments and DFT calculations.



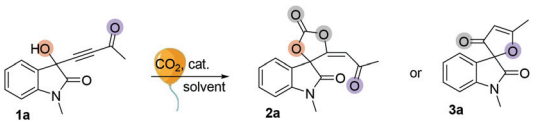
Scheme 1 Newly designed phosphine-catalyzed reactions of alkynones with other substrates.

Results and discussion

Experimental investigations

We initially tested the reaction outcomes employing 3-hydroxy-1-methyl-3-(3-oxobut-1-yn-1-yl)indolin-2-one **1a** and carbon dioxide (balloon, 1 atm) as substrates in the presence of phosphine, and subsequently optimized the reaction conditions. The results are shown in Table 1. It was found that isatin-derived spirocarbonate **2a** was obtained in 81% yield with 0.2 equiv. of PBu_3 in THF at room temperature for 3 h (entry 1). The solvent effect was first investigated, and it was identified that THF was better than other solvents such as DCM, ether, MTBE and ethyl acetate (entries 2–6). It is interesting to note that when MeOH was used as a solvent, only isatin-derived furanone **3a** was obtained in 49% yield (entry 3). Decreasing the concentration of the reaction mixture retarded the reaction, and **1a** was recovered in 56% yield (entry 7). Employing other phosphine catalysts did not significantly improve the yield of **2a**, giving **2a** in yields ranging from trace to 66% (entries 8–12). Using other Lewis base catalysts such as DMAP and DABCO only gave **2a** in yields of 20% and 31%, respectively (entries 13 and 14). The reaction could not take place in the presence of K_2CO_3, suggesting that the reaction could not be initiated by the deprotonation process with a Brønsted base catalyst (entry 15). The structures of **2a** and **3a** have been assigned by X-ray diffraction. Their ORTEP drawings are shown in Tables 2 and 3 and the CIF data are also summarized in the ESI.†

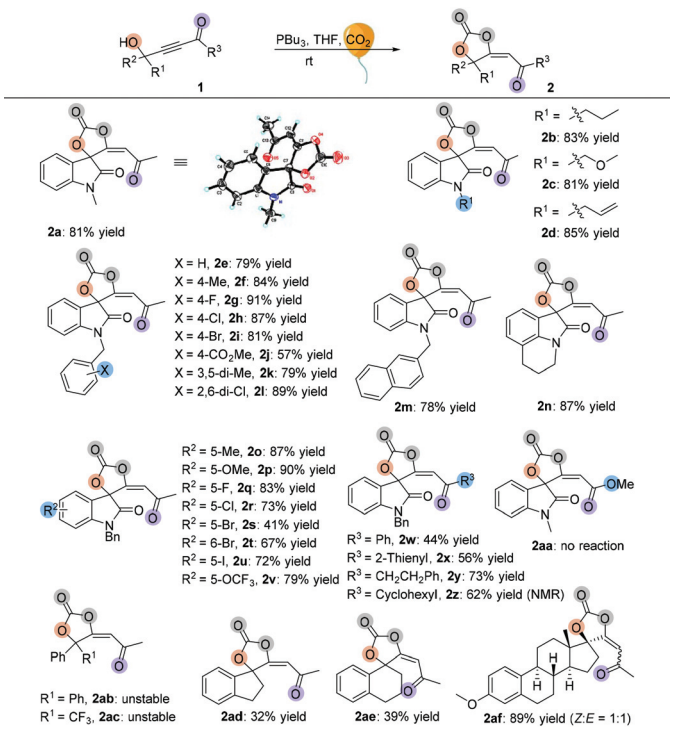
Table 1 Cycloaddition of CO_2 with isatin-derived γ-hydroxyl alkynone **1a** catalyzed by phosphine[a]



Entry[a]	Cat.	Solvent	Temp (°C)	Time (h)	Yield % of **2a**[b]
1	**PBu_3**	**THF**	**rt**	**3**	**81**
2	PBu_3	DCM	rt	3	64
3	PBu_3	MeOH	rt	3	—[c]
4	PBu_3	Et_2O	rt	3	Trace
5	PBu_3	MTBE	rt	3	40
6	PBu_3	EA	rt	3	56
7	PBu_3	THF[d]	rt	3	32
8	PMe_3	THF	rt	3	Complex
9	PMe_3Ph	THF	rt	3	66
10	$PMePh_2$	THF	rt	3	53
11	$PEtPh_2$	THF	rt	3	60
12	PPh_3	THF	rt	3	Trace
13	DMAP	THF	rt	3	20
14	DABCO	THF	rt	3	31
15	K_2CO_3	THF	rt	3	nr

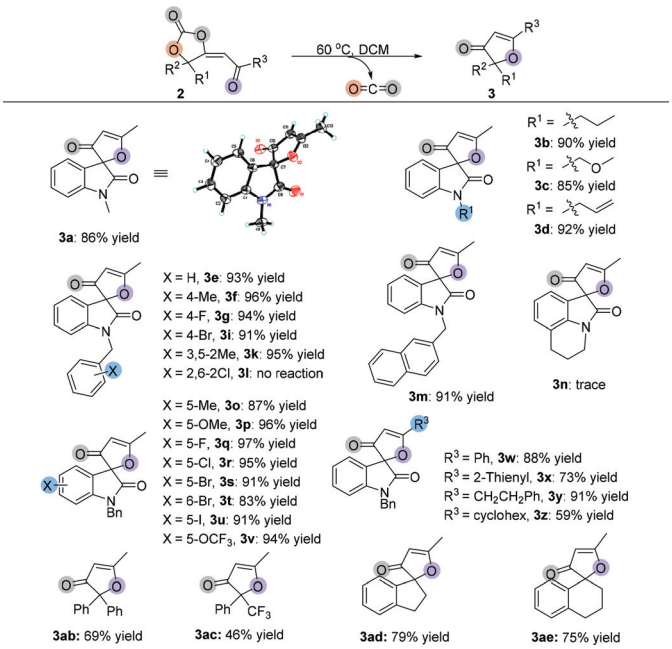
[a] The reaction was carried out using **1a** (0.1 mmol) and cat. (0.02 mmol) in the indicated solvent (0.5 mL) in a Schlenk tube at the indicated temperature under a CO_2 atmosphere. [b] Determined by ^1H NMR analysis of the crude reaction mixture by using 1,3,5-trimethoxybenzene as an internal standard. [c] Only product **3a** was obtained in 49% yield. [d] 1 mL THF was used and 56% **1a** was recovered.

Table 2 Substrate scope for cycloaddition of CO_2 with γ-hydroxyl alkynones catalyzed by phosphine[a]



[a] The reaction was carried out using **1** (0.3 mmol) and PBu_3 (0.06 mmol), in THF (1.5 mL) in a Schlenk tube at the indicated temperature.

Table 3 Substrate scope of the decarboxylative cyclization of cyclic carbonates **2**[a]



[a] The reaction was carried out using **2** (0.2 mmol) in DCM (2.0 mL) in a Schlenk tube at the indicated temperature.

Having established the optimal reaction conditions, we next surveyed the substrate scope of the reaction by using a range of γ-hydroxyl alkynones **1** (Table 2). First, we examined isatin-derived substrates **1** with different *N*-alkyl groups. It was found that methyl, *n*-propyl, methyloxymethyl and allyl group substituted 3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-ones **1a–1d** afforded the desired spirocarbonates **2a–2d** in the range of 81–85% yields. Using the benzyl group substituted 3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one **1e** as the substrate also gave the corresponding product **2e** in 79% yield. Changing the substituents on the benzyl moiety afforded the corresponding products **2f–2l** in yields ranging from 57% to 91%; only the 4-CO_2Me substituted product **2j** was isolated in 57% yield. Replacing the benzyl group by a naphthalen-2-ylmethyl group (**1m**) did not significantly influence the reaction, giving **2m** in 78% yield. 4*H*-Pyrrolo[3,2,1-ij]quinoline-derived substrate **1n** was also tolerated, affording the corresponding product **2n** in 87% yield.

Next, substrates **1o–1v** having different substituents on the isatin moiety were examined. Substrates **1o** and **1p** containing electron-donating groups (Me, OMe) afforded the corresponding products in higher yields (87% yield and 90% yield) than substrates **1q–1v** containing electron-withdrawing groups such as F, Cl, Br, I and OCF_3 groups (41% yield to 83% yield). When R^3 groups were phenyl and 2-thienyl groups, the desired products **2w** and **2x** were only obtained in 44% and 56% yields, respectively; using the CH_2CH_2Ph group instead of the methyl group could also give the desired product **2y** in 73% yield. However, it is hard to isolate cyclohexyl group substi-

tuted product **2z** from the reaction mixture, perhaps due to its instability. The NMR spectrum of the crude reaction solution indicated that 62% of **2z** was produced. Propiolate-derived substrate **1aa** failed to give the desired product **2aa**. Other types of γ-hydroxyl alkynones were also investigated. Firstly, acyclic substrates **1ab** and **1ac** were synthesized, however, the corresponding products **2ab** and **2ac** were unstable and easily converted to furanones **3ab** and **3ac** (see Table 3). Under the standard conditions, both carbocyclic products **2ad** and **2ae** were successfully obtained in 32% and 39% yields, respectively, with exclusive *E*-configurations. Interestingly, using ethinylestradiol-derived substrate **1af** smoothly gave a pair of separable products containing a *cis* isomer and a *trans* isomer in 89% total yield, presumably due to the steric effect.

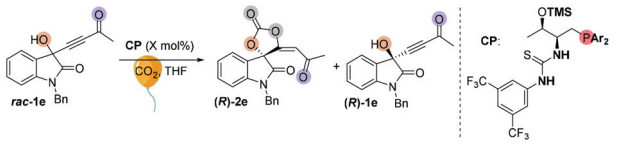
After investigation of the substrate scope, we noted that the cyclic carbonate products **2** could easily release CO_2 upon heating and obtained a diversity of furanones **3** in excellent yields. Subsequently, we examined the decarboxylative cyclization of cyclic carbonate products **2** at 60 °C. As shown in Table 3, changing the groups on the oxindole moiety with methyl, *n*-propyl, methyloxymethyl and allyl groups did not affect the product yields, giving the desired products **3a–3d** in the range of 85%–92% yields. Most of the benzyl group substituted isatin-derived spirocarbonates could release CO_2 and give the corresponding isatin-derived furanones in excellent yields. However, cyclic carbonate products **2** having sterically hindered substituents could not undergo the reaction; spirocarbonates **2l** and **2af** were stable upon heating, and none of the desired products **3l** and **3af** were detected. Naphthalen-2-ylmethyl substituted substrate **2m** could smoothly give **3m** in 91% yield; however, the transformation of 4*H*-pyrrolo[3,2,1-ij] quinoline-derived spirocarbonate **2n** failed under identical conditions. These results suggested that the more rigid multicyclic systems or the larger sterically hindered groups would lead to less degree of rotational freedom of these non-reactive substrates and subsequently block out their rearrangements. Fortunately, either substrates containing electron-donating groups (Me, OMe) or substrates containing electron-withdrawing groups (F, Cl, Br, I and OCF_3) could give the corresponding products in excellent yields. On changing the R^3 groups, furanones **3w–3y** containing a phenyl group, 2-thienyl group and CH_2CH_2Ph substituted group were obtained in 73%–91% yields; even cyclohexyl group substituted furanone **3z** could be isolated in 59% yield after two-step transformations. Similarly, acyclic furanones **3ab** and **3ac** were isolated in 69% yield and 46% yield, respectively, suggesting that the furanones are thermodynamically more stable than spirocarbonates. Five- or six-membered carbocyclic furanones **3ad** and **3ae** were also obtained in 79% yield and 75% yield under the standard conditions, respectively.

Kinetic resolution investigations

We initially screened a variety of chiral phosphines **CP1–CP14** by using racemic **1e** with CO_2 (balloon, 1 atm) in THF. The results are summarized in Tables S1 and S2.† Preliminary investigations showed that Lu's catalyst **CP14** gave the highest yield; however, as compared with other catalysts (Table SI†), the enantioselectivity remained low ($s < 5$) (Table 4, entry 1). We then focused our attention on improving the stereoselectivity by developing new chiral phosphine catalysts. Based on Lu and Pfaltz's work,[23k] we introduced a series of different substituents into the aryl group substituents on the phosphine atom and synthesized a series of new bifunctional chiral phosphines. When 30 mol% **N-CP1** was used as a catalyst, the extra two methyl groups could significantly improve the enantioselectivity of spirocarbonate (up to 80% ee) and the *s*-factor was up to 7.8; reducing the amount of catalyst would result in lower conversion rates and lower *s*-factors (entries 2–4). Due to the excess steric hindrance, *tert*-butyl group substituted catalyst **N-CP2** could not promote the reaction either at −40 °C or at −20 °C (entries 5 and 6). Next, we introduced methoxy groups into the phenyl ring to improve the nucleophilicity of catalysts. However, the DTBM type catalyst **N-CP3** and 4-methoxyl group substituted **N-CP4** showed almost the same selectivities as that of using **CP14** as the catalyst (entries 7 and 8). The highly nucleophilic 3,5-dimethoxy groups substituted phosphine catalyst **N-CP5** could catalyze the reaction at −60 °C, affording (*R*)-**2e** in 32% yield with 84% ee; however, (*R*)-**1e** was isolated with only 84% ee, which showed a low selectivity (s = 2.9) (entries 9–11). Finally, using 4-methoxy-3,5-dimethylphenyl group substituted catalyst **N-CP6** could increase the selectivity slightly; (*R*)-**2e** was isolated in 42% yield with 86% ee, (*R*)-**1e** was simultaneously isolated in 51% yield with 64% ee and the *s*-factor was up to 9.5 (entries 12 and 13). Interestingly, employing 2-MeTHF as a solvent could further improve the enantioselectivity of (*R*)-**1e** up to 90% ee, which encouraged us to continue to explore the way to improve the selectivity of the reaction. Adding 2.0 mL 2-MeTHF was essential to avoid **1e** from precipitating at low temperature (entry 14). After further screening of catalyst loading (entries 15 and 16), we found that the use of 15 mol% of **N-CP-6** [1-((2*S*,3*R*)-1-(bis(4-methoxy-3,5-dimethylphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea] could improve this kinetic resolution process to a higher selectivity (s = 24.6) as well as 54% conversion; unreacted (*R*)-**1e** could be recovered in 46% yield with 91% ee, and (*R*)-**2e** was isolated in 49% yield with 81% ee. The investigations on solvent effects are summarized in Table S3 in the ESI.†

The generality of this chiral phosphine-catalyzed kinetic resolution process was then investigated. A wide range of substrates having different substituents on the oxindole backbones were also well tolerated in our catalytic system (Table 5). We first tested the effects of protecting groups on the nitrogen atom (Table 5, entries 1–3); substrates **1b–1d** containing *n*-propyl, methyloxymethyl and allyl groups worked as well as the Bn protected substrate **1e**, giving the desired products (*R*)-**1b–1d** and (*R*)-**2b–2d** with good selectivities (s = 17.0–20.6). On changing the substituents on the benzyl group, the reactions proceed to about 50% conversion, which afforded the corresponding products **2e–2i** in ee values ranging from 81% to 90%, and the best *s*-factor was up to 24.5 (entries 4–8). Next, substrates **1o**, **1p** and **1v** with various substituents on the oxi-

Table 4 Catalyst screening for the kinetic resolution[a]



Entry[a]	CP		Temp (°C)	Time (h)	Conv. (%)	Yield[b] (%)		ee[c] (%)		
	CP (*X* mol%)	Ar				(*R*)-**2e**	(*R*)-**1e**	(*R*)-**2e**	(*R*)-**1e**	*s*-Factor[d]
1	**CP14** (20)		−40	12	31	29	69	68	20	3.1
2	**N-CP1** (10)		−40	12	37	29	63	85	22	2.7
3	**N-CP1** (20)		−40	12	49	40	51	84	55	5.5
4	**N-CP1** (30)		−40	12	57	48	43	80	75	7.8
5	**N-CP1** (20)		−40	12	Trace	—	—	—	—	—
6	**N-CP1** (20)		−20	24	Trace	—	—	—	—	—
7	**N-CP1** (20)		−40	12	49	41	51	61	43	3.9
8	**N-CP1** (20)		−40	12	48	40	52	70	40	3.7
9	**N-CP1** (10)		−60	12	Trace	—	—	—	—	—
10	**N-CP1** (20)		−60	12	39	32	61	84	25	2.9
11	**N-CP1** (20)		−40	12	49	42	51	77	45	4.2
12	**N-CP1** (20)		−40	12	33	33	67	86	42	2.2
13	**N-CP1** (30)		−60	12	49	42	51	86	64	9.5
14[e]	**N-CP1** (20)		−40	12	63	52	37	80	90	5.4
15[e]	**N-CP1 (15)**		**−40**	**12**	**54**	**49**	**46**	**81**	**91**	**24.6**
16[e]	**N-CP1** (10)		−40	12	53	46	47	80	88	23.2

[a] The reaction was carried out using *rac*-**1e** (0.1 mmol) and cat. (0.015–0.03 mmol), in THF (0.5 mL) in a Schlenk tube at the indicated temperature. [b] Isolated yields. [c] The ee value was determined by HPLC analysis using a chiral stationary phase. [d] Selectivity (*s*-factor) calculated as $s = \ln[(1 - C)(1\text{-eeSM})]/\ln[(1 - C)(1 + \text{eeSM})]$. [e] 2.0 mL 2-MeTHF was used.

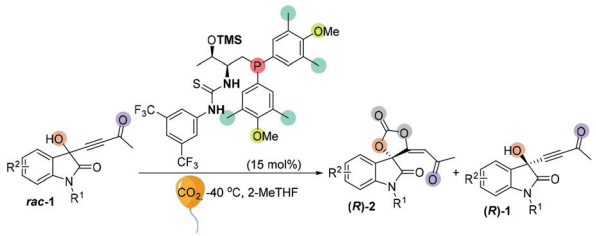
ndole moiety were examined. Substrates **1o** and **1p** containing electron-donating groups (Me, OMe) afforded the corresponding products in higher selectivities (*s* = 22.9 and 20.2) than substrate **1v** containing an electron-withdrawing group such as OCF_3 (entries 9–11). The substrates containing electron-withdrawing groups showed lower conversion and reactivity, probably due to the difficulty in regenerating the catalyst. 4*H*-Pyrrolo[3,2,1-ij]quinoline-derived substrate **1n** was recovered with an excellent enantioselectivity in up to 96% ee, and (*R*)-**2n** was isolated with 92% ee, which proceeded to 44% conversion with *s* = 38.6 (entry 12). Other substrates could not produce the desired products with excellent selectivities and the results are summarized in Table S4 of the ESI.†

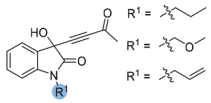
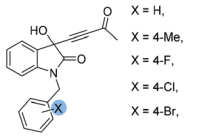
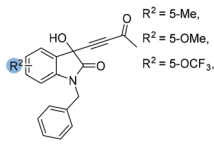
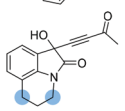
Several optically active spirocarbonates were used to investigate whether the configuration retention of the chiral quaternary carbon center could be realized during decarboxylative cyclization, because it could afford optically active furanones. The results are summarized in Table 6. Allyl group protected furanone **3d** was obtained in 89% yield with 82% ee, which completely maintained the chirality. Moreover, 4-methylbenzyl and 4-fluorobenzyl groups protected furanones **3f** and **3g** were also obtained in high yields with high ee values. However, partial racemization was observed during the transformation of 4-bromobenzyl spirocarbonates, suggesting that the decarboxylative cyclization might go through a carbocationic intermediate. Finally, **2o** gave the desired product **3o** in 81% ee with 95% es. **2v** also underwent partial racemization and afforded the corresponding product **3v** in 76% ee with 88% es.

Mechanistic studies

To gain some insights into the reaction mechanism, several deuterium-labeling experiments were performed at different temperatures. The reaction of **1a** with CO_2 was first carried out in the presence of D_2O (10 equiv.) under the standard reaction conditions. The reaction became sluggish to give the corresponding partially deuterated addition product [D]-**2a** in 65% yield along with 84% deuterium incorporation at the olefinic position (Scheme 2a). After heating, [D]-**3a** was obtained in 86% yield along with 80% deuterium incorporation at the olefinic position. Under the standard reaction conditions, using 53% O–H deuterated [D]-**1a** as a substrate produced the corresponding deuterated product [D]-**2a′** in 81% yield with 52% D content incorporated at the olefinic position, respectively (Scheme 2a). The deuterium incorporation at the olefinic position proved the H-shift process shown in Scheme 2b. Then, we performed an ^{18}O-labeling experiment with ^{18}O-**1a** under the standard reaction conditions and obtained ^{18}O-**2a** in 80% yield with 2% ^{18}O incorporation, which afforded **3a** with no ^{18}O

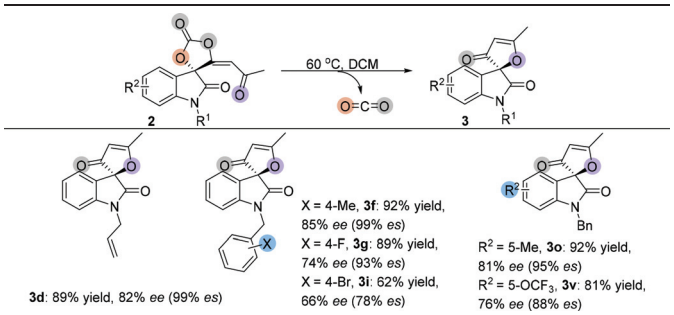
Table 5 Substrate scope for the kinetic resolution[a]



Entry[a]	Starting materials	Time (h)	Conv. (%)	Yield[b] (%)		ee[c] (%)		*s*-Factor[d]
				(*R*)-**2**	(*R*)-**1**	(*R*)-**2**	(*R*)-**1**	
1	 R¹ =	**1b**: 12	59	49	41	82	97	20.6
2	R¹ =	**1c**: 12	51	41	49	87	81	17.0
3	R¹ =	**1d**: 12	60	52	40	79	97	18.6
4	 X = H,	**1e**: 12	54	49	46	81	91	24.6
5	X = 4-Me,	**1f**: 12	51	42	49	85	80	18.5
6	X = 4-F,	**1g**:12	55	46	45	90	93	24.5
7	X = 4-Cl,	**1h**: 12	49	40	51	84	76	19.4
8	X = 4-Br,	**1i**: 12	53	41	47	85	83	19.6
9	 R² = 5-Me,	**1o**: 12	54	40	46	85	90	22.9
10	R² = 5-OMe,	**1p**: 12	53	42	47	90	86	20.2
11	R² = 5-OCF₃,	**1v**: 12	50	41	50	86	65	9.3
12		**1n**: 12	44	47	46	92	96	38.6

[a] The reaction was carried out using *rac*-**1** (0.1 mmol) and cat. (0.015 mmol) in the indicated solvent (2.0 mL) in a Schlenk tube at the indicated temperature. [b] Isolated yields. [c] The ee value was determined by HPLC analysis using a chiral stationary phase. [d] Selectivity (*s*-factor) calculated as $s = \ln[(1 - C)(1\text{-eeSM})]/\ln[(1 - C)(1 + \text{eeSM})]$.

Table 6 Substrate scope for the decarboxylative cyclization of chiral cyclic carbonate products 2[a–d]

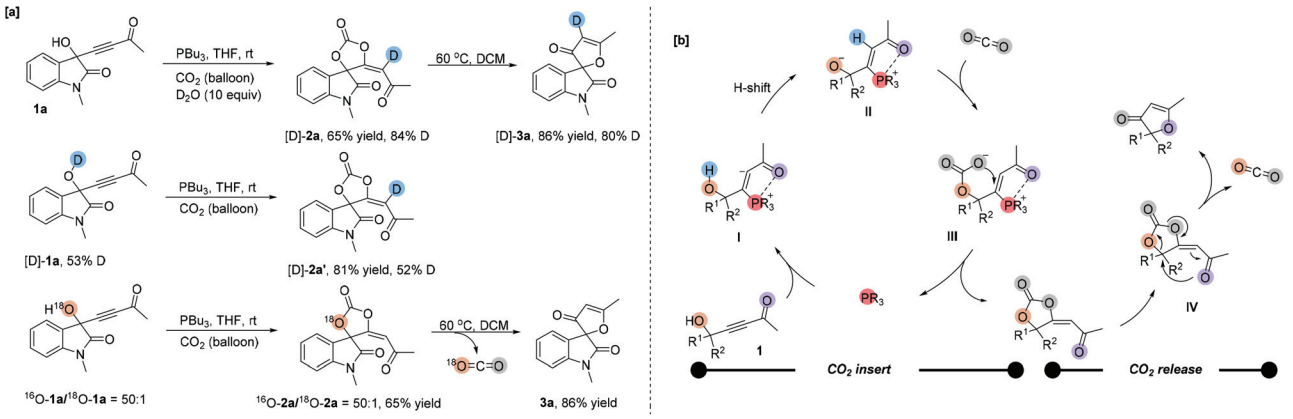


[a] The reaction was carried out using **2** (0.05 mmol) in DCM (1.0 mL) in a Schlenk tube at the indicated temperature. [b] Isolated yields. [c] The ee value was determined by HPLC analysis using a chiral stationary phase. [d] The enantiospecificity (es) = (ee of product/ee of starting material) × 100%.

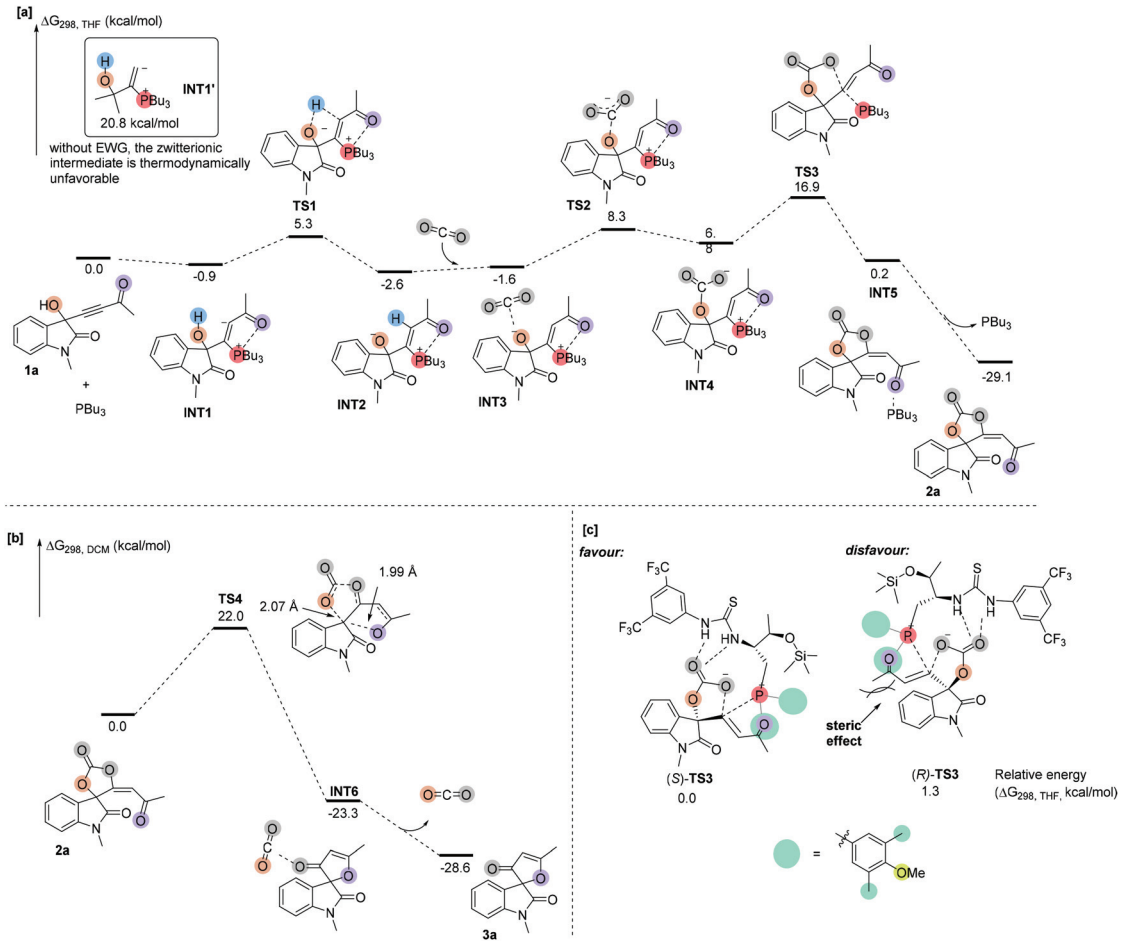
incorporation after heating. These results indicated that the oxygen atom of the carbonyl group in furanones **3** originated from CO_2.

We proposed the following mechanism depicted in Scheme 2b to account for the reaction outcomes. The reaction starts with the addition of tertiary phosphine to the γ-hydroxyl alkynone **1** to afford a zwitterionic intermediate **I**. Then the carbanion abstracts the proton from the hydroxyl group to form another zwitterionic intermediate **II**. The oxygen anion moiety of intermediate **II** directly attacks carbon dioxide, generating an intermediate **III**, which undergoes a cyclization to furnish product **2a** and the phosphine catalyst. Upon heating, the C–O bond of carbonate is cleaved and the oxygen atom of the carbonyl group attacks the quaternary carbon center simultaneously. With the release of CO_2, the furanone **3** is generated.

In order to understand the detailed reaction mechanism, we performed DFT calculations on the suggested reaction pathways. We first investigated the proposed reaction pathway for the PBu_3-catalyzed reaction of **1a** and CO_2 to produce **2a**, and the solvation Gibbs free energy profiles in THF are shown in Scheme 3a. As shown in Scheme 3a, the addition of catalyst PBu_3 to **1a** leads to the formation of zwitterionic intermediate **INT1**, which is exergonic by 0.9 kcal mol^{-1}. For comparison, we calculated the relative stability of **INT1′** without any EWG group, which is highly endergonic and indicates that the inter-



Scheme 2 Isotope-labeling experiments and proposed mechanism.



Scheme 3 Mechanistic studies on the proposed reaction pathways.

mediate **INT1′** is unstable at room temperature. These calculation results indicated that the substrate having an EWG group plays a key role in stabilizing the important zwitterionic intermediates and facilitates the following CO_2 fixation process. The proton from the hydroxyl group is transferred to the carbanion moiety of intermediate **INT1** to generate an intermediate **INT2** *via* **TS1**, which is located 6.2 kcal mol^{-1} above the intermediate **INT1**; converting **INT1** to **INT2** is exergonic by 1.7 kcal mol^{-1}, indicating that this step is thermodynamically favorable. This result agrees with the finding in deuterium-labeling experiments in which the deuterium incorporation can be found at the olefinic position of product **2a** (see Scheme 2a). Subsequently, **INT2** is associated with CO_2 to produce a complex **INT3**. On passing through transition state

TS2 with an activation free energy of 9.9 kcal mol^{-1}, **INT3** undergoes addition to furnish an intermediate **INT4**, which is endergonic by 8.4 kcal mol^{-1}. **INT4** undergoes cyclization *via* **TS3** with an energy barrier of 10.1 kcal mol^{-1} to afford a product complex **INT5**; the energy barrier of the cyclization step is not very high, probably due to the fact that the carbanion moiety in **INT4** is the highly electrophilic center. The cleavage of complex **INT5** gives product **2a** and PBu_3. The calculation results revealed that the phosphine catalyst acts as a nucleophilic organocatalyst and the CO_2 fixation is a stepwise cyclization process. All energy barriers along the proposed reaction pathway are not larger than 16.9 kcal mol^{-1}, which are in line with the experiment performed at room temperature. The proposed reaction pathway for the reaction of **2a** to afford **3a** was also investigated, and the solvation Gibbs free energy profiles in DCM are shown in Scheme 3b. The carbonyl group of **2a** attacks the quaternary carbon center and the C–O bond of the carbonate moiety undergoes concerted cleavage *via* transition state **TS4** to afford the product complex **INT6**. Transition state **TS4** is located 22.0 kcal mol^{-1} above **2a**. The structure of transition state **TS4** clearly demonstrates that the carbon–oxygen bond is extended to 2.07 Å, and the distance is about 1.99 Å between the quaternary carbon center and oxygen atom, indicating that the carbonyl group attacking the quaternary carbon center and the cleavage of the carbonate moiety is a concerted process. Finally, cleavage of the complex **INT6** to yield the separate components **3a** and CO_2 is exothermic by 15.3 kcal mol^{-1}. This transition state **TS4** may account for a partial racemization process in the reaction of chiral cyclic carbonates **2**; it is hard to control the stereoselectivity in the process of carbonyl group attacking due to the opening of the oxygen heterocycle.

In order to understand the origin of enantioselectivity, we investigated the relative energies of key transition states (*R*)-**TS3** and (*S*)-**TS3** using (*R*)-**1a** and (*S*)-**1a** as substrates, respectively (Scheme 3c). The energy of transition states (*S*)-**TS3** involving (*S*)-**1a** is lower than that of (*R*)-**TS3** and of the kinetic resolution of cycloaddition of CO_2 involving (*R*)-**1a** by 1.3 kcal mol^{-1}, indicating that (*S*)-**1a** reacts faster than (*R*)-**1a**. The calculation results agree with the stereochemical findings in experiments. Sterically hindered benzene ring substituents on the phosphine atom probably provide more powerful stereocontrol. In transition state (*R*)-**TS3**, the steric hindrance between the benzene moiety of (*R*)-**1a** and the tertiary phosphine moiety in chiral phosphine probably leads to its higher energy. On the other hand, in transition state (*S*)-**TS3**, the benzene moiety of (*S*)-**1a** was far away from the tertiary phosphine moiety in chiral phosphine and this transition state was more favored to give the corresponding product (*R*)-**2**.

Conclusions

In conclusion, we have first disclosed the phosphine-catalyzed CO_2 fixation of γ-hydroxyl alkynones, affording a series of spirocarbonates **2** in moderate to good yields. The CO_2 fixation process could perform at room temperature under ambient pressure and the very broad substrate generality brought simple and quick synthesis of a variety of skeleton spirocarbonates. Moreover, the spirocarbonates **2** could easily release CO_2 under heating conditions and obtain diverse furanones **3** in excellent yields. In addition, we have developed a new series of sterically hindered and highly nucleophilic bifunctional amino acid-derived phosphine catalysts and realized the first example of chiral phosphine catalyzed kinetic resolution of propargyl alcohols *via* carbon dioxide fixation, which has the *s*-factor up to 38.6. The detailed mechanistic studies were conducted by isotope-labeling experiments and DFT calculations. Further applications of the phosphine-catalyzed CO_2 fixation reactions are underway in our lab.

Computational methods

All DFT calculations were performed with the Gaussian 09 program. The geometries of all minima and transition states have been optimized at the M06/6-31+G(d) level of theory.[35] The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima or first-order saddle points on the respective potential energy surfaces. All transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory to further authenticate the transition states. The conformational space of flexible systems has first been searched manually. Thermochemical corrections at 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The solvent effect was estimated by the IEFPCM method with radii and nonelectrostatic terms for the SMD solvation model[36] in THF (ε = 7.4257) or DCM (ε = 8.93). Solution-phase single point energy calculations were performed at the M06/6-311+G(d,p) level based on the gas phase optimized structures.

Conflicts of interest

There are no conflicts to declare.

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