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# Palladium-catalysed asymmetric cascade transformations of 4-alken-2-ynyl carbonates to construct complex frameworks†

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As a class of readily available and multifunctional building blocks, the chemistry of 4-alken-2-ynyl carbonates remains to be explored. Presented herein is a palladium-catalysed cascade transformative reaction between 4-alken-2-ynyl carbonates and *ortho*-functionalised activated alkenes. Achiral 1,1-bisalkyl-4-alken-2-ynyl carbonates undergo highly regioselective propargylic substitution with *ortho*-hydroxyphenyl-tethered activated alkenes, and an auto-tandem vinylogous addition, unusual central-carbon Tsuji–Trost alkylation, protonation and  $\beta$ -H elimination process is followed to furnish fused and spirocyclic frameworks with high structural complexity. Even kinetic transformations with racemic 1-monoalkylated 4-alken-2-ynyl carbonates can be accomplished in the assemblies with *ortho*-aminophenyl-tethered activated alkenes to afford the analogous alkaloid architectures. This palladium-catalysed auto-tandem protocol exhibits excellent chemo-, regio-, stereoselectivity and reaction efficacy, and substantial functionality compatibility is also observed.

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## Introduction

Owing to their ready availability and versatile reactivity, propargylic substrates have emerged as valuable reagents in organic synthesis.<sup>1</sup> Upon the oxidative addition of propargylic alcohol derivatives with transition metals, the formed allenyl or propargyl metal species can undergo a variety of transformations, such as allenylation,<sup>2</sup> 1,3-dienylation,<sup>3</sup> propargylation<sup>4</sup> and others,<sup>5</sup> to afford structurally diverse products, even enantioselectively. In addition, pre-installation of a pendent alkene moiety into propargylic skeleton, as in 4-alken-2-ynyl carbonates **1**, would further enrich the transformative potential, since more reactive sites might be envisaged upon activation by transition metals. In this regard, Ma recently revealed that vinylidene- $\pi$ -allyl palladium intermediates **I**, which were generated *in situ* from 1,1-bisalkyl-substituted 4-alken-2-ynyl carbonates **1** and Pd<sup>0</sup>, could undergo Tsuji–Trost-type reaction with stabilized carbon-centred nucleophiles to furnish achiral 1,2,3-butatrienes with exclusive linear selectivity.<sup>6</sup>

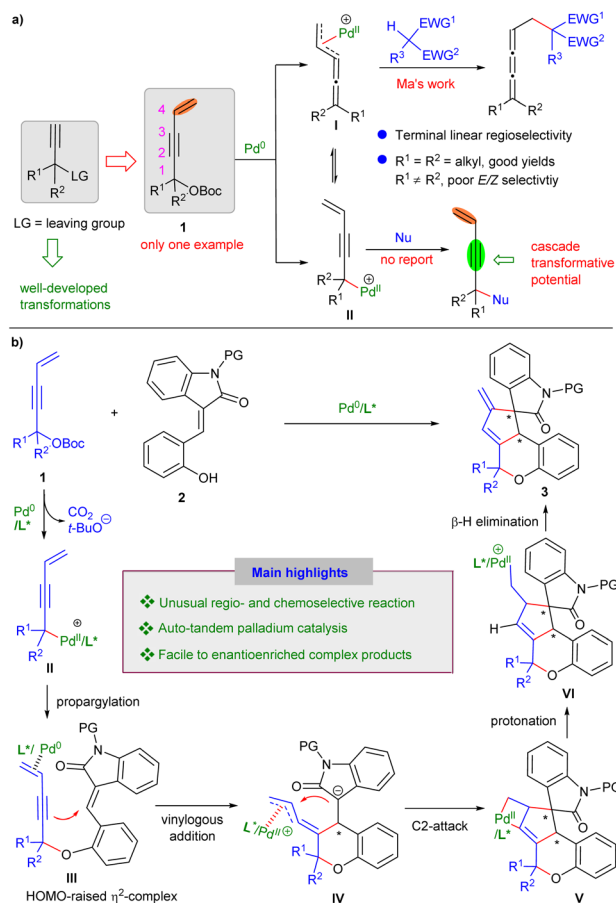
Unfortunately, the reactivity of racemic propargylic substrates ( $R^1 \neq R^2$ ) was not well investigated in this work, and poor *E/Z* selectivity was observed for the sole example. In addition, switching the regioselectivity of nucleophilic substitution to the more sterically hindered C1 position *via* potential species **II** is a formidable challenge, but would provide valuable opportunities in latent reaction design owing to the versatile features of the enyne products (Scheme 1a).<sup>7</sup> Taking advantage of the multiple catalytic roles of palladium,<sup>8</sup> here, we would like to present an unprecedented cascade transformative reaction between 4-alken-2-ynyl carbonates **1** and *ortho*-functionalised activated alkenes, such as 3-olefinic oxindoles **2**. As outlined in Scheme 1b, the oxidative addition of Pd<sup>0</sup> to carbonates **1** would generate propargylic palladium complexes **II**. In sharp contrast to Ma's work, exclusive C1-regioselective substitution with *O*-centered nucleophiles was observed to deliver multifunctional propargylated intermediates **III**. By employing our recently developed  $\pi$ -Lewis base catalysis,<sup>9</sup> Pd<sup>0</sup> further enhanced the nucleophilicity of the alkyne moiety by forming  $\eta^2$ -complexes with increased highest occupied molecular orbital (HOMO) energy levels, thus facilitating intramolecular vinylogous addition to the 3-olefinic oxindole motif to produce ene- $\pi$ -allyl-Pd intermediates **IV**. Intriguingly, an unusual nucleophilic attack on the central carbon of  $\pi$ -allylpalladium-type species occurred to afford palladacyclobutanes **V**.<sup>10</sup> Subsequent protonation and  $\beta$ -H elimination delivered fused and spirocyclic architectures **3** with high molecular complexity.<sup>3,11</sup> It is noteworthy that highly regio-, chemo- and enantioselective assemblies were achieved in this palladium-based auto-tandem catalysis.<sup>12</sup>

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† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic data for new compounds, NMR and HRMS spectra, and HPLC chromatograms, CIF files of enantiopure **3o**, **12g** and racemic **17**, **18**, **20** (CIF). CCDC 2381131–2381135. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4sc07823c>





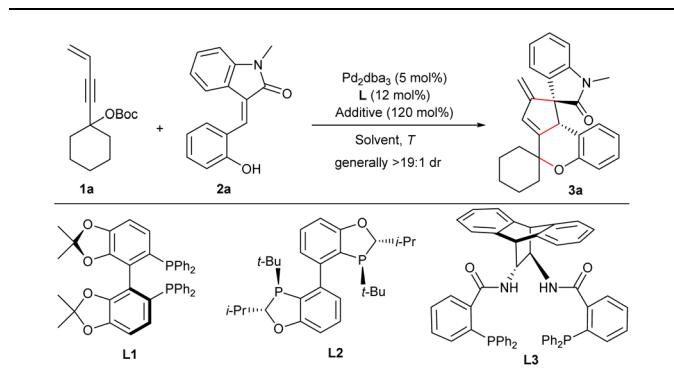
**Scheme 1** Typical reaction pathways of propargylic derivatives and our design for palladium-catalysed cascade transformations of 4-alken-2-ynyl carbonates. (a) Transformations from propargylic substrates to 4-alken-2-ynyl carbonates. (b) This work: Pd<sup>0</sup>-catalysed cascade transformations of 4-alken-2-ynyl carbonates.

## Results and discussion

### Reaction optimisation

The reaction of 4-alken-2-ynyl carbonate **1a** and (*E*)-3-(2-hydroxybenzylidene)oxindole **2a** was initially examined in MeCN at 80 °C. The reaction proceeded smoothly in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, and product **3a** was obtained straightforwardly in a good yield through the proposed pathway as virtually a single diastereomer (Table 1, entry 1). Next, we turned our attention to the enantioselective synthesis of **3a**. After a brief survey of various chiral ligands, we quickly found that bisphosphine ligands exhibited good catalytic performance for the current transformations.<sup>13</sup> Fair enantioselectivity was observed for ligands **L1** and **L2** in combination with Pd<sub>2</sub>dba<sub>3</sub> (entries 2 and 3), and ligand **L3** having an anthracene diamine backbone substantially boosted both the efficiency and enantiocontrol (entry 4). Lowering the temperature enhanced the enantioselectivity, although a longer time was required to achieve better conversions (entry 5). A solvent survey suggested enantiocontrol was slightly improved in polar solvents (entries 6–8), and a higher yield was obtained in diluted DMA (entry 9).

**Table 1** Screening conditions for the asymmetric auto-tandem reaction<sup>a</sup>



Entry	L	Solvent	T (°C)	t (h)	Additive	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1 <sup>d</sup>	—	MeCN	80	36	—	78	—
2	<b>L1</b>	MeCN	80	24	—	56	29
3	<b>L2</b>	MeCN	80	24	—	33	58
4	<b>L3</b>	MeCN	80	24	—	63	74
5	<b>L3</b>	MeCN	50	48	—	63	85
6	<b>L3</b>	NMP	50	48	—	58	87
7	<b>L3</b>	DMF	50	48	—	62	85
8	<b>L3</b>	DMA	50	48	—	57	88
9 <sup>e</sup>	<b>L3</b>	DMA	50	48	—	60	88
10 <sup>e</sup>	<b>L3</b>	DMA	50	48	KHCO <sub>3</sub>	73	89
11 <sup>e,f</sup>	<b>L3</b>	DMA	45	60	KHCO <sub>3</sub>	72	91
12 <sup>e,f,g</sup>	<b>L3</b>	DMA	45	60	KHCO <sub>3</sub>	48	91

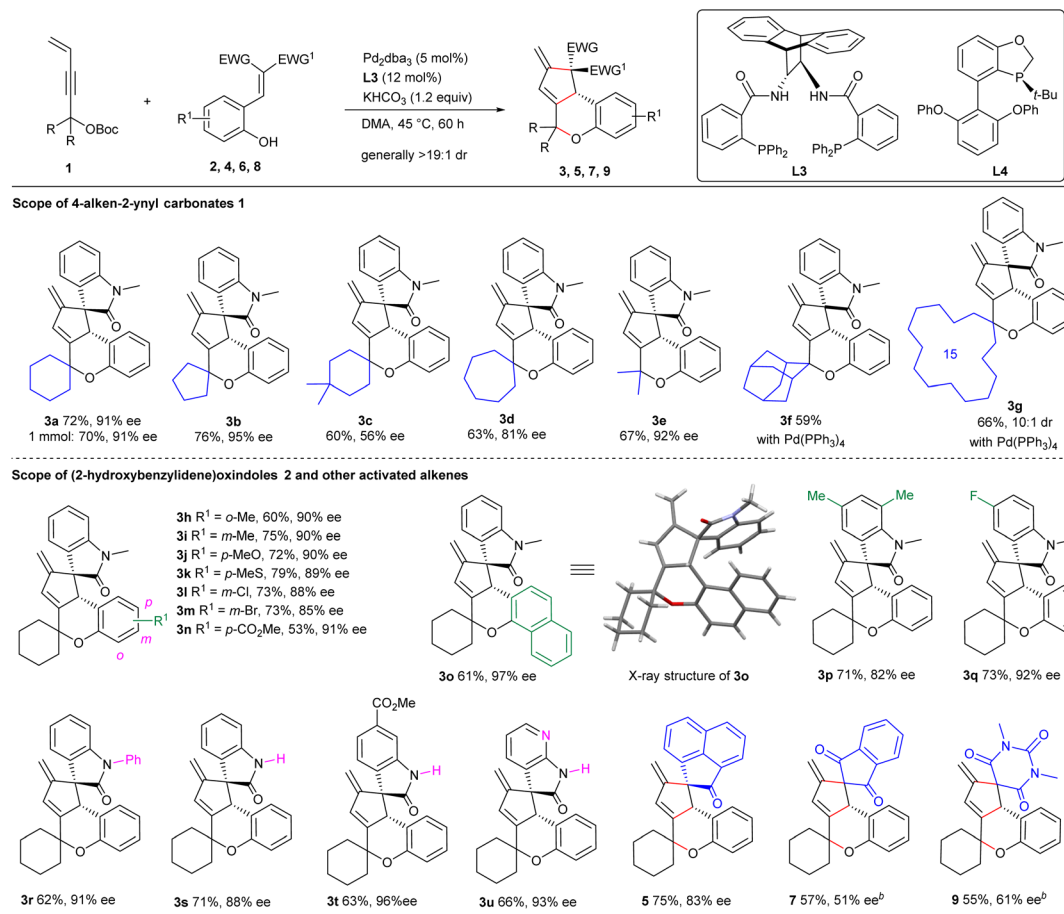
<sup>a</sup> Unless noted otherwise, reactions were performed with carbonate **1a** (0.1 mmol), alkene **2a** (0.12 mmol), Pd<sub>2</sub>dba<sub>3</sub> (5 mol%), ligand **L** (12 mol%) and additive (1.2 equiv.) in degassed solvent (1.0 mL) under Ar. <sup>b</sup> Yield of the isolated product. <sup>c</sup> Determined by HPLC analysis on a chiral stationary phase, and >19:1 dr was generally obtained through <sup>1</sup>H NMR analysis. <sup>d</sup> With Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%). <sup>e</sup> In DMA (2.0 mL). <sup>f</sup> With **1a** (0.15 mmol) and **2a** (0.1 mmol). <sup>g</sup> With Pd<sub>2</sub>dba<sub>3</sub> (2.5 mol%) and **L3** (6 mol%).

Then, several additives were screened,<sup>13</sup> and KHCO<sub>3</sub> was found to be beneficial to the yield (entry 10). A satisfactory yield with an excellent ee value was finally obtained by employing 1.5 equivalents of carbonate **1a** at 45 °C (entry 11), whereas the yield was reduced significantly when using 2.5 mol% of Pd<sub>2</sub>dba<sub>3</sub> (entry 12).

### Substrate scope and limitations

Under the optimised conditions, the scope of the 3-vinyl propargylic carbonates **1** was first explored in the reactions with (*E*)-3-(2-hydroxybenzylidene)oxindole **2a** under the catalysis of Pd<sub>2</sub>dba<sub>3</sub>/**L3** with KHCO<sub>3</sub> as an additive. As summarised in Scheme 2, an array of carbonates **1** derived from different cyclic ketones reacted smoothly with **2a**, generally affording the corresponding products **3a–3d** in moderate yields with remarkable diastereo- and enantioselectivity, even in a 1.0 mmol scale reaction (product **3a**), whereas a moderate ee value was observed for product **3c** bearing a 4,4-dimethylcyclohexane moiety. Pleasingly, product **3e** having *gem*-dimethyl groups was furnished with comparably good results. Unfortunately, no





**Scheme 2** Substrate scope of asymmetric auto-tandem reaction of achiral 4-alken-2-ynyl carbonates **1** and diverse activated alkenes.<sup>a</sup>Unless noted otherwise, reactions were performed with carbonate **1** (0.15 mmol), activated alkene (0.1 mmol), Pd<sub>2</sub>dba<sub>3</sub> (5 mol%), L3 (12 mol%) and KHCO<sub>3</sub> (1.2 equiv.) in degassed dry DMA (2.0 mL) at 45 °C for 60 h under Ar; yields refer to the isolated product; dr was determined by <sup>1</sup>H NMR analysis of the crude product; ee was determined by HPLC analysis on a chiral stationary phase.<sup>b</sup>With L4 (20 mol%) in toluene (1.0 mL) at 80 °C for 24 h.

apparent conversion was observed when using propargylic carbonates bearing an admantyl or cyclopentadecyl group, while racemic **3f** and **3g** could be obtained in moderate yields catalysed by Pd(PPh<sub>3</sub>)<sub>4</sub>. Next, the scope of functionalized alkenes **2** was evaluated (Scheme 2). Substrates with a broad range of electron-donating and -withdrawing groups at various positions of the phenyl or oxindole unit were well tolerated, generally affording the desired products **3h–3q** in moderate yields with high levels of enantioselectivity. Notably, similarly good data were obtained for (7-aza)oxindoles **2** having an *N*-phenyl or even a free NH group (products **3r–3u**).

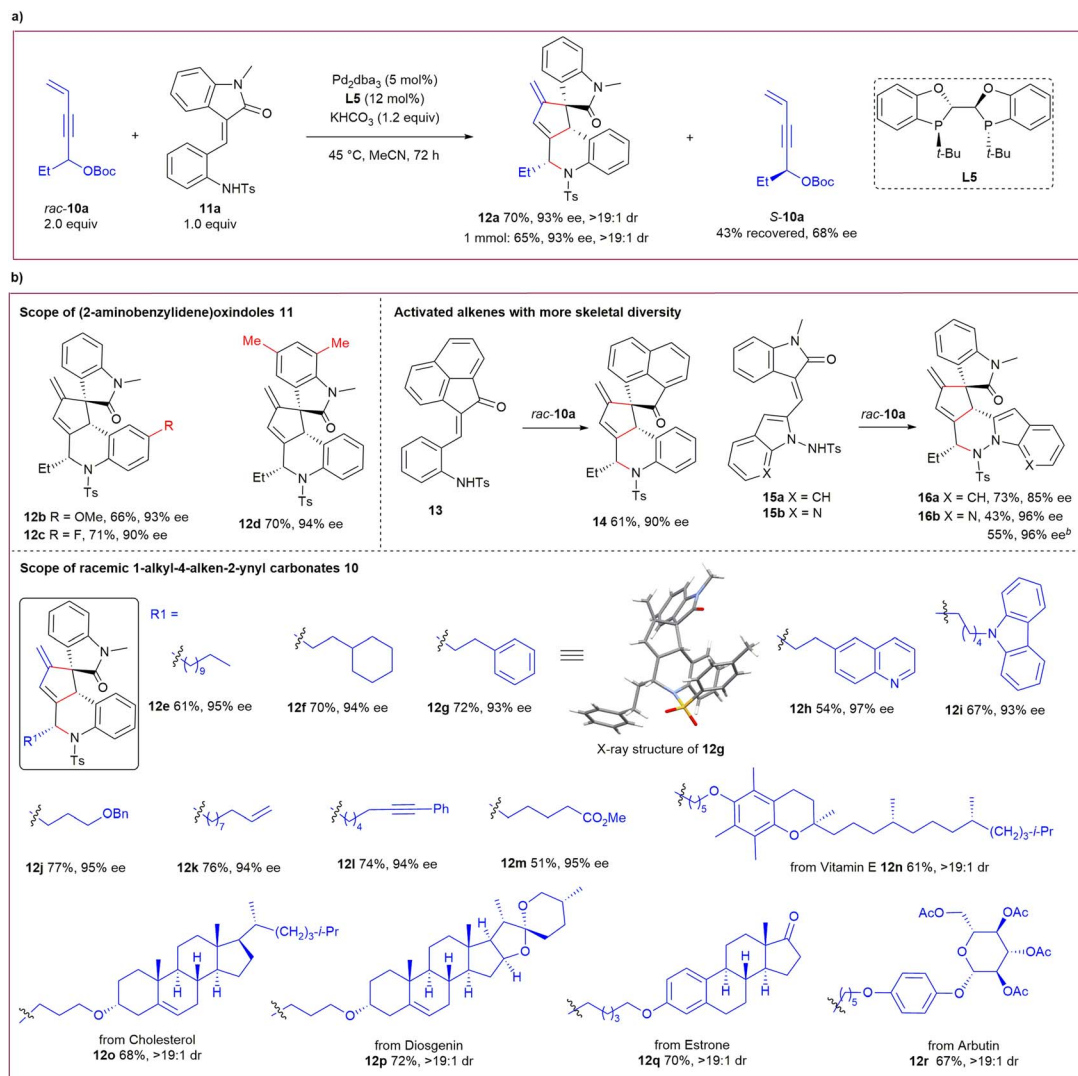
In addition to 3-olefinic oxindoles **2**, activated alkenes derived from other skeletons were also applicable. As outlined in Scheme 2, benzylideneacenaphthenone **4** was successfully assembled with carbonate **1a** to deliver **5** in good yield and enantioselectivity under the standard conditions. Moreover, both activated alkenes **6** and **8** condensed from 1,3-indandione and barbituric acid with salicylaldehyde, respectively, proved to be reliable counterparts in the reactions with **1a** under the catalysis of Pd<sub>2</sub>dba<sub>3</sub>/L4, albeit with moderate enantiocontrol (products **7** and **9**). These results not only showcased the

robustness of the current catalytic strategy, but also enriched the structural diversity of the frameworks constructed.

The successful cascade transformations of achiral 1,1-bisalkyl-substituted 4-alken-2-ynyl carbonates **1** inspired us to investigate the potential application of more challenging racemic propargylic carbonates. As illustrated in Scheme 3a, gratifyingly, 1-ethyl carbonate *rac*-**10a** (2 equiv.) could be efficiently utilised in similar asymmetric cascade transformations with (2-aminobenzylidene) oxindole **11a** catalysed by Pd<sub>2</sub>dba<sub>3</sub> and ligand L5, furnishing an analogous alkaloid architecture **12a** in a moderate yield with excellent stereoselectivity, even on a larger scale. In addition, simultaneous kinetic resolution for recovered *rac*-**10a** was observed, albeit with moderate enantioselectivity.<sup>14</sup>

The substrate scope for this type of kinetic transformation is substantial. As summarised in Scheme 3b, good yields and high enantioselectivity were uniformly obtained for activated alkenes **11** with different substituents on the aryl unit under the standard catalytic conditions (products **12b–12d**). Activated alkene **13** and newly designed **15** smoothly participated in the reactions with *rac*-**10a** to produce complex frameworks **14** and **16a–**





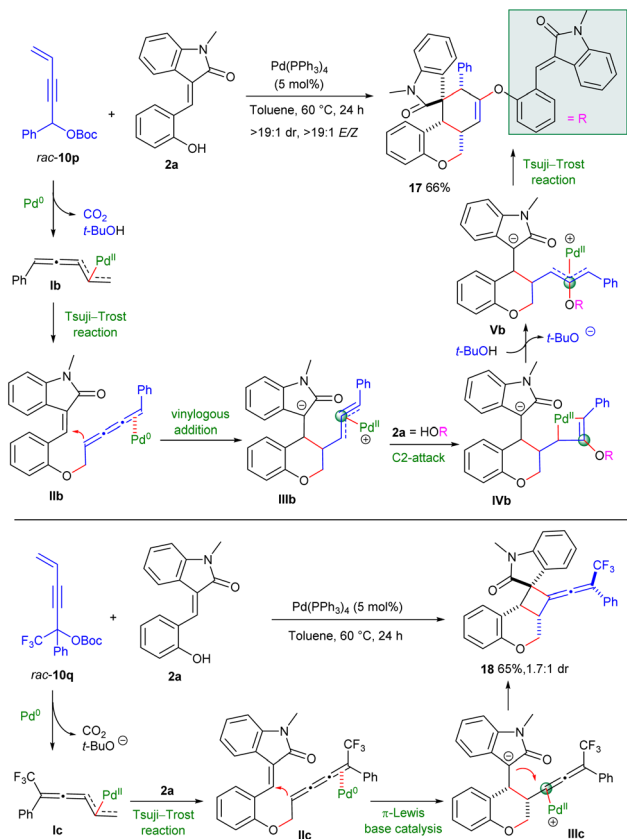
Scheme 3 Substrate scope for kinetic transformations of racemic 1-alkyl-substituted 4-alken-2-ynyl carbonates **10**.<sup>a</sup>(a) Kinetic transformations of racemic 1-alkyl-4-alken-2-ynyl carbonates *via* auto-tandem catalysis. (b) Substrate scope investigation.<sup>a</sup>Unless noted otherwise, reactions were performed with racemic carbonate **10** (0.2 mmol), activated alkene (0.1 mmol), Pd<sub>2</sub>dba<sub>3</sub> (5 mol%), L5 (12 mol%) and KHCO<sub>3</sub> (1.2 equiv.) in degassed MeCN (1.0 mL) at 45 °C for 72 h under Ar; <sup>b</sup>With *rac*-**10a** (0.3 mmol).

**16b** with high efficiency. Importantly, a spectrum of racemic propargylic carbonates **10** with diverse 1-alkyl substitutions, including those bearing various functionalities, were compatible in the reactions with activated alkene **11a**, yielding products **12e–12m** with high enantiocontrol. This method also provides an efficient tool for the late-stage modification of bioactive molecules. A broad range of chiral drugs (or their fragments) containing a 3-vinyl motif were competent in this process, which led to the complex products **12n–12r** in moderate yields with excellent diastereoselectivity.

Of particular note, 1-phenyl-substituted carbonate *rac*-**10p** underwent *O*-allylic alkylation with (*E*)-3-(2-hydroxybenzylidene)oxindole **2a** with distinct terminal regioselectivity under the catalysis of Pd(PPh<sub>3</sub>)<sub>4</sub>,<sup>6</sup> probably resulting from the generation of thermally more stable 1-phenyl allenyl- $\pi$ -allyl species **1b**. The formed 1,2,3-butatriene intermediate **11b** could be similarly HOMO-activated by Pd(0) *via* a  $\pi$ -Lewis base pattern, thus

facilitating intramolecular vinylogous addition to the 3-olefinic oxindole motif. Interestingly, the resultant  $\eta^3$ -propargylpalladium species **11b** was C2-attacked by another molecule of **2a**, delivering palladacyclobutene intermediate **11b**. Subsequent protonation and intramolecular Tsuji–Trost reaction of **11b** would furnish spirocyclic product **17** with high diastereo- and *E/Z*-selectivity (Scheme 4).<sup>5</sup> Moreover, tertiary propargylic carbonate *rac*-**10q** was found to undergo similar Tsuji–Trost reaction/vinylogous addition with **2a** efficiently through intermediates **11c** and **11c**, respectively, whereas the formed  $\eta^1$ -allenylpalladium moiety of **11c** was intramolecularly captured by enolate to provide intriguing cyclobutane-fused chromanone **18** having a tetrasubstituted exocyclic allene motif in a moderate yield with fair diastereoselectivity.<sup>2g–i</sup> Although the asymmetric variants were not applicable at the current stage, these explorations clearly demonstrated the versatile reactivity of 4-alken-2-ynyl carbonates and significantly enriched the product diversity.

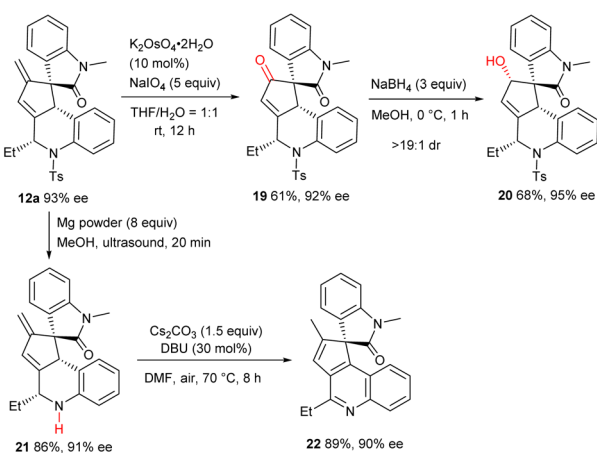




Scheme 4 Divergent transformations of 1-aryl-4-alken-2-ynyl carbonates.

### Synthetic transformations

Further transformations successfully exemplified the synthetic utility of the multifunctional products. As depicted in Scheme 5, osmium-catalysed oxidative cleavage of the terminal olefin moiety of **12a** afforded ketone **19** in a moderate yield, which was further reduced to alcohol **20** with exclusive diastereoselectivity. Additionally, the *N*-Ts group was efficiently removed to deliver amine **21**, and fused quinoline **22** was obtained in high yield *via*



Scheme 5 Transformations of product **12a**.

a base-promoted isomerization/oxidative aromatization process. It should be noted that the spirooxindole-fused polycycles and their derivatives are core subunits of many bioactive natural products and drug candidates.<sup>15</sup>

## Conclusions

In summary, we successfully developed a cascade transformative reaction between 4-alken-2-ynyl carbonates and *ortho*-functionalized activated alkenes under auto-tandem palladium catalysis. This process showed high regio-, chemo-, and stereoselectivity through integrating classical palladium-mediated nucleophilic substitution with our newly uncovered  $\pi$ -Lewis base catalysis into a one-pot fashion. Both achiral 1,1-bisalkyl- and racemic 1-alkyl-4-alken-2-ynyl carbonates with broad substitution patterns underwent C1-selective propargylation to afford enyne intermediates, and fused and spirocyclic frameworks with high structural complexity were finally furnished enantioselectively upon tandem palladium catalysis, which proceeded *via* a cascade vinylogous addition, unusual central carbon Tsuji-Trost alkylation, protonation and  $\beta$ -H elimination process. In contrast, 1-aryl-substituted 4-alken-2-ynyl carbonates favoured terminal substitution to generate 1,2,3-butatriene intermediates, and regiodivergent transformations gave distinct polycyclic architectures, albeit in a racemic pattern. This work exhibits the versatile reaction potential of multifunctional 4-alken-2-ynyl carbonates, which offer a platform to construct structurally complex compounds *via* auto-tandem catalysis. More results will be reported in due course.

## Data availability

The data that support the findings of this study are available in the ESI† or on request from the corresponding author.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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