Synthetic Methods

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Allene Relay: Palladium-Catalyzed Bicyclization of Allene-Propargylic Carbonates with Geminal Bis(nucleophile)s**

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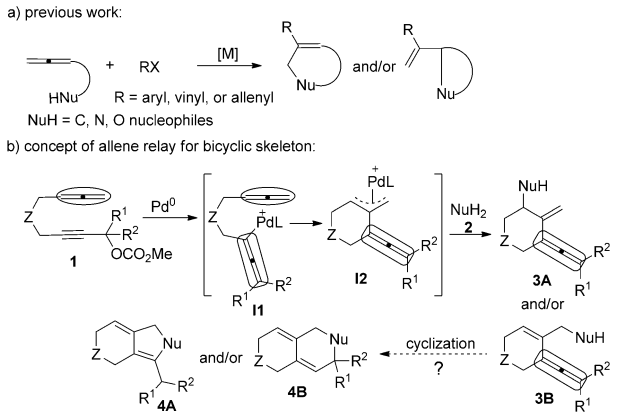
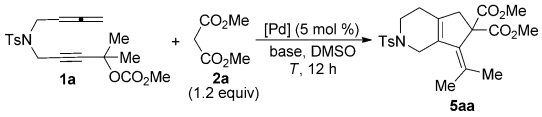
Rapid construction of molecular complexity from readily accessible starting materials is inarguably a subject of central importance in modern organic synthesis.[1] Accordingly, considerable progress has been made in this area over the last few decades by taking advantage of tandem reactions,[2] wherein two or more bond-forming transformations are involved in a single operation. On the other hand, with more and more efficient synthetic methods being developed,[3] allenes have now become a very important class of basic chemicals in organic synthesis, medicinal chemistry, and materials science.[4] Particularly, transition-metal-catalyzed cyclization reactions of allenes bearing a nucleophilic functionality have become a powerful way to construct a wide variety of hetero- and carbocycles (Scheme 1 a).[5] We envisaged that, under palladium(0) catalysis, the reaction of the allene-propargylic carbonate **1** with the geminal bis(nucleophile) **2** may afford the allene product **3B** over **3A** by cyclic carbopalladation of the allene moiety of the σ-allenyl palladium intermediate **I1**,[6,7] thus generating the π-allyl palladium species **I2**,[8] provided that the regioselectivity of the nucleophilic allylation can be controlled by steric effects (Scheme 1 b). Further cyclization of this in situ generated allene with a nucleophilic functionality (**3B**) may afford the fused bicyclic products **4A** and/or **4B**, which are ubiquitous structural units in many natural products and biologically active compounds.[9] Herein, we report the realization of such an allene relay concept, thereby providing an easy access to bicyclo[4.3.0] skeletons in a single step through three consecutive C–C bond formations.[10]



Scheme 1. Previous work and proposal of this work.

Our initial investigations were based on the reaction of the allene propargylic carbonate **1a** (Table 1).[11] After screening a range of nucleophiles and reaction conditions, we were pleased to find that the expected reaction of **1a** with dimethyl malonate (**2a**) was indeed realized in the presence of 5 mol% $[Pd(PPh_3)_4]$ and 2 equivalents of K_2CO_3 in DMSO at 70 °C after 12 hours. The fused bicyclic compound **5aa** having both C=C bonds migrate (compare **5aa** with **4A**) was obtained in 60% yield upon isolation (entry 1, Table 1).

Table 1: Optimization of reaction conditions.[a]



Entry	[Pd]	Base (*n* equiv)	*T* [°C]	Yield [%][b]
1[c]	$[Pd(PPh_3)_4]$	K_2CO_3 (2)	70	68 (60)
2	$[Pd(PPh_3)_4]$	Cs_2CO_3 (2)	70	51
3[c]	$[Pd(PPh_3)_4]$	K_3PO_4 (2)	70	78
4	$[Pd(PPh_3)_4]$	$K_3PO_4 \cdot 3H_2O$ (2)	70	70
5	$[Pd(PPh_3)_4]$	K_3PO_4 (2)	80	69
6[d]	$Pd(OAc)_2$	K_3PO_4 (2)	70	54
7[e]	$[Pd_2(dba)_3]\cdot CHCl_3$	K_3PO_4 (2)	70	45
8[f]	$[Pd(PPh_3)_4]$	K_3PO_4 (2)	70	69
9[g]	$[Pd(PPh_3)_4]$	K_3PO_4 (3)	70	83
10[g,h]	$[Pd(PPh_3)_4]$	K_3PO_4 (3)	90	80

[a] The reaction was carried out using **1a** (0.1 mmol), **2a** (0.12 mmol), $[Pd(PPh_3)_4]$ (5 mol%), and base (2 or 3 equiv) in the indicated solvent (1 mL) in a Schlenk tube at the indicated temperature for 12 h unless otherwise noted. [b] Determined by ^1H NMR analysis of the crude reaction mixture. Value in the parentheses is the yield of the isolated **5aa**. [c] The reaction was carried out on 0.2 mmol scale for **1a**. [d] $Pd(OAc)_2$ (5 mol%) and TFP (10 mol%) were used instead of $[Pd(PPh_3)_4]$. [e] $[Pd_2(dba)_3]\cdot CHCl_3$ (2.5 mol%) and TFP (10 mol%) were used instead of $[Pd(PPh_3)_4]$. [f] TBAI (10 mol%) was added. [g] **2a** (0.15 mmol) was used. [h] DMF (1 mL) was used as the solvent. dba = dibenzylideneacetone, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, TBAI = tetra-*n*-butylammonium iodide, TFP = tri(2′-furyl)phosphine.

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Encouraged by this exciting result, the influence of the critical reaction parameters was investigated and representative results are listed in Table 1. Among the bases surveyed, anhydrous K_3PO_4 was shown to be the best (entry 3). $K_3PO_4 \cdot 3H_2O$ was also effective, albeit with a diminished yield (entry 4). Elevating the temperature proved to be deleterious (entry 5), and changing the palladium catalysts (entries 6 and 7) or adding 10 mol% of TBAI as an additive (entry 8) all gave inferior results. Increasing the amount of **2a** to 1.5 equivalents and K_3PO_4 to 3 equivalents improved the yield of **5aa** to 83% as determined by ^{1}H NMR spectroscopy (entry 9). Interestingly, we noted that a comparable yield of **5aa** could also be obtained when the reaction was carried out in DMF at 90°C (entry 10). Therefore, 5 mol% $[Pd(PPh_3)_4]$, 1.5 equivalents of **2a**, and 3 equivalents of K_3PO_4 in DMSO at 70°C (or DMF at 90°C) were established as the standard reaction conditions for further study.

Having identified the optimal reaction conditions, we first examined the reactivity of various carbon nucleophiles with allene-propargylic carbonates (**1a–c**). The results are summarized in Table 2. The reaction of **1a** with the malonates **2a–c** all went smoothly, thus affording the corresponding bicyclic products **5aa–ac** in moderate to good yields (entries 1–4, Table 2). Besides malonates, a β-ketoester such as ethyl acetoacetate (**2d**) was also suitable for the reaction, thus furnishing the fused bicycle **5ad** in 58% yield (entry 5). It should be noted that the second cyclization step in this case was a C-attack-type process rather than the commonly observed O-attack-type process in the palladium-catalyzed cyclization reactions of 2-(2′,3′-allenyl)acetylacetates.[12] The structure of **5ad** was further confirmed by X-ray diffraction study (see Figure S1 in the Supporting Information).[13] Malonitrile (**2e**) seemed to be less reactive under the standard reaction conditions, however, when the reaction was carried out in DMF at 90°C, the corresponding product **5ae** was also obtained in 68% yield (entry 6). The allene-propargylic carbonates **1** may also be oxygen- (entries 7 and 8) and carbon-tethered (entry 9), thus affording **5ba**, **5bd**, and **5ca** in 85%, 65%, and 75% yields, respectively. The reaction may be easily conducted on a gram scale for **1a** (entry 2).

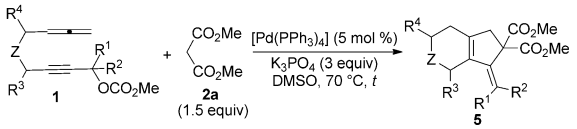
The scope of the allene-propargylic carbonates **1** was then explored (Table 3). In addition to linear carbonates (**1a–d**), carbonates of cyclic alcohols (**1e–g**) may also be utilized in this reaction (entries 2–4, Table 3). When secondary propargylic carbonates (**1h–j**) were subjected to the standard reaction conditions, the corresponding bicyclic products (*E*)-**5ha–ja** were obtained exclusively or as the major isomer as determined by ^{1}H NMR analysis of the crude reaction mixture, as well as NOE studies (entries 5–7). When R^3 or R^4 is replaced by an alkyl or phenyl group, good yields of **5ka–na** could also be obtained by extending the reaction time (entries 8–11).

Table 2: Palladium-catalyzed cyclization of the allene propargylic carbonates **1a–c** in the presence of the carbon nucleophiles **2a–e**.[a]

Entry	**1** Z	E^1	**2** E^2	Yield [%][b]
1	NTs (**1a**)	CO_2Me	CO_2Me (**2a**)	79 (**5aa**)
2[c]	NTs (**1a**)	CO_2Me	CO_2Me (**2a**)	74 (**5aa**)
3	NTs (**1a**)	CO_2Et	CO_2Et (**2b**)	80 (**5ab**)
4[d]	NTs (**1a**)	CO_2tBu	CO_2tBu (**2c**)	51 (**5ac**)
5	NTs (**1a**)	COMe	CO_2Et (**2d**)	58 (**5ad**)
6[e]	NTs (**1a**)	CN	CN (**2e**)	68 (**5ae**)
7	O (**1b**)	CO_2Me	CO_2Me (**2a**)	85 (**5ba**)
8	O (**1b**)	COMe	CO_2Et (**2d**)	65 (**5bd**)
9[f]	$C(CO_2Et)_2$ (**1c**)	CO_2Me	CO_2Me (**2a**)	75 (**5ca**)

[a] The reactions were carried out on 0.3 mmol scale of **1** in DMSO (3 mL) in a Schlenk tube at 70°C for 12 h unless otherwise noted. [b] Yield of isolated **5**. [c] The reaction was carried out on 3 mmol scale of **1a**. [d] Reaction time: 24 h. [e] The reaction was carried out in DMF (3 mL) at 90°C for 12 h. [f] Reaction time: 18 h. Ts = 4-toluenesulfonyl.

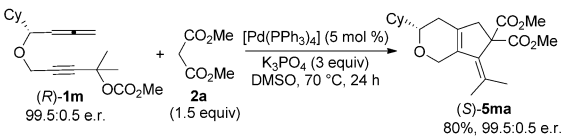
Table 3: Palladium-catalyzed cyclization of the allene propargylic carbonates **1d–n** with **2a**.[a]



Entry	**1** Z	R^1	R^2	R^3	R^4	t [h]	Yield [%][b]
1	NTs	Et	Et	H	H (**1d**)	12	80 (**5da**)
2	NTs	-$(CH_2)_4$-		H	H (**1e**)	12	78 (**5ea**)
3	NTs	-$(CH_2)_5$-		H	H (**1f**)	12	65 (**5fa**)
4	NTs	-$(CH_2)_6$-		H	H (**1g**)	12	70 (**5ga**)
5[c]	NTs	*t*Bu	H	H	H (**1h**)	24	67 [(*E*)-**5ha**]
6[c]	NTs	*i*Pr	H	H	H (**1i**)	12	69 [(*E*)-**5ia**][d]
7[c]	NTs	Cy	H	H	H (**1j**)	22	65 [(*E*)-**5ja**][d]
8[c]	NTs	Me	Me	Pr	H (**1k**)	24	66 (**5ka**)
9[c]	O	Me	Me	Pr	H (**1l**)	16	85 (**5la**)
10	O	Me	Me	H	Cy (**1m**)	24	78 (**5ma**)
11	O	Me	Me	H	Ph (**1n**)	27	74 (**5na**)

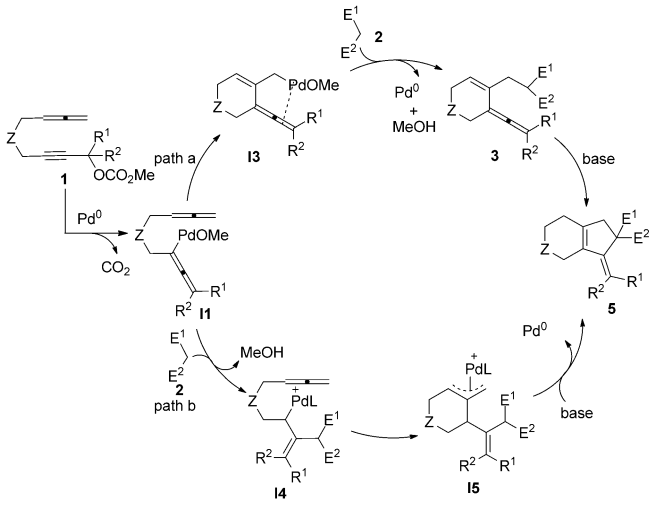
[a] The reactions were carried out on 0.3 mmol scale of **1** in DMSO (3 mL) in a Schlenk tube at 70°C unless otherwise noted. [b] Yield of isolated **5**. [c] The reaction was carried out in DMF (3 mL) at 90°C. [d] Contained minor *Z* isomer (ca. 6%). Cy = cyclohexyl.

When the optically active allene-propargylic carbonate (*R*)-**1m**, having a central chirality (99.5:0.5 e.r.), was subjected to the standard reaction conditions, (*S*)-**5ma** was obtained in 80% yield without any loss of enantiomeric purity (99.5:0.5 e.r.) [Eq. (1)].



(1)

A mechanism involving two different types of intermediates has been proposed as shown in Scheme 2. Oxidative addition of **1** with Pd^0 would afford the allenylpalladium intermediate **I1**,[6] which may undergo subsequent transformations by two possible pathways: a) intramolecular carbopalladation of the allene moiety generates the allyl



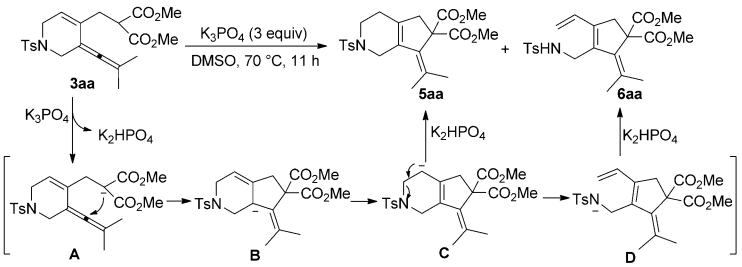
Scheme 2. Two possible pathways for the formation of **5**.

palladium species **I3**, which is regioselectively attacked by the geminal bis(nucleophile) **2** as a result of a steric effect, thus affording the monocyclization product **3** with concomitant regeneration of the catalytically active Pd^0. Further cyclization of the vinylallene **3** under basic conditions would then give the final bicyclic product **5**; b) the allenylpalladium intermediate **I1** is first attacked by the geminal bis(nucleophile) **2** to form the intermediate **I4**,[14] which then undergoes intramolecular carbopalladation of the allene moiety to furnish the π-allyl palladium species **I5**, which is then attacked by the nucleophilic moiety under basic conditions to yield the bicyclic product **5** and regenerate the Pd^0 catalyst.

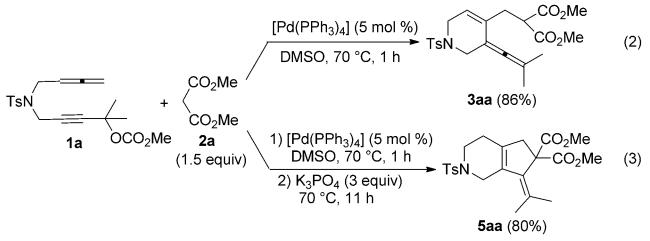
To gain further insight into the mechanism of this reaction, control experiments were conducted using **1a** and **2a** in the absence of base under otherwise identical reaction conditions. We were pleased to find that the monocyclization product **3aa** can be isolated in 86% yield [Eq. (2)]. Moreover, when the reaction was carried out in a one-pot, two-step manner as shown in Equation (3), **5aa** was obtained in a similar yield as that presented in entry 1 of Table 2. Therefore, the bicyclic product **5** is more likely formed from the monocyclization product **3** by path a (Scheme 2).

However, when **3aa** was heated in DMSO at 70°C for 11 hours in the presence of 3 equivalents of K_3PO_4, the bicyclic product **5aa** was formed in only 54% yield, as determined by ^{1}H NMR spectroscopy (entry 2, Table S1 in the Supporting Information), together with an unexpected byproduct (**6aa**), whose structure was confirmed by X-ray diffraction study.[13] Thus, we reasoned that the MeOH generated in situ in the first step (Scheme 2) may exert a profound influence on the second step of this transformation. Indeed, when 2 equivalents of MeOH were added, **5aa** was formed in 83% yield with only a trace amount of **6aa** being detected by ^{1}H NMR analysis (entry 4, Table S1). In the absence of MeOH, the intermediate **C**, generated from **3aa**, would undergo a slow protonation with inorganic salt K_2HPO_4 to afford the bicyclic product **5aa** or C–N bond cleavage to furnish the byproduct **6aa** via the intermediate **D**. In contrast, in the presence of MeOH, the intermediate **C** would undergo a fast protonation to yield **5aa**, thereby inhibited the formation of **6aa** (Scheme 3).

With a better understanding of the reaction mechanism, we turned to investigate the possibility of accessing optically active bicyclic products from enantioenriched axially chiral allene propargylic carbonates[15] by an axial-to-central chirality-transfer approach, which is undoubtedly a very challenging task as racemization of the **I2**-type π-allyl palladium species by a σ-π-σ process has been observed in previous studies.[5b,16]

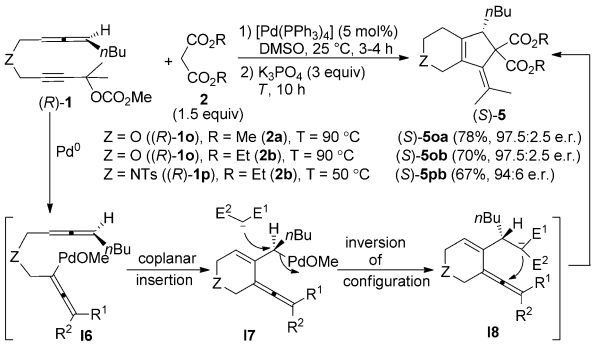


Scheme 3. Formation of **5aa** and **6aa** from **3aa**.



Fortunately, after much screening, we eventually found that when the reaction was carried out in a one-pot, two-step manner with the first step being conducted at room temperature (for racemization under the standard reaction conditions at 70°C or lower temperature; see Scheme S1 in the Supporting Information for details), the corresponding bicyclic products (*S*)-**5oa**–(*S*)-**5pb** may indeed be obtained in practical yields with only a slight decrease of enantiopurity (Scheme 4). The absolute configurations of these compounds have been tentatively assigned to be *S* based on the mechanism: coplanar *cis* insertion of the *n*-butyl-linked C=C bond in the allene moiety of **I6** followed by an instant nucleophilic substitution of η^1-**I7** by soft nucleophiles with inversion of the absolute configuration (Scheme 4).[17]

In conclusion, we have developed a highly efficient methodology for the synthesis of synthetically attractive fused bicyclic hetero- and carbocycles from allene-propargylic carbonates and geminal bis(nucleophile)s by an allene relay strategy. The ability to generate functionalized fused bicycles, including optically actives ones, from readily accessible starting materials in a single step is the most important feature of this process. Moreover, mechanistic studies uncov-



Scheme 4. Synthesis of optically active products by axial-to-central chirality transfer.

ered that the MeOH generated in situ in the first step played a critical role in the second step of this transformation. Being operationally simple and tolerating multiple sites of diversity with high efficiency of chirality transfer, this new methodology should be appealing to the modern synthetic and medicinal chemists. Further studies on expanding the scope of the reaction and synthetic applications are currently ongoing in our laboratory.

Experimental Section

Synthesis of **5aa**. Typical procedure: Anhydrous K_3PO_4 (197.4 mg, 0.9 mmol, 97%), $[Pd(PPh_3)_4]$ (17.4 mg, 0.015 mmol), **1a** (113.3 mg, 0.3 mmol), DMSO (3 mL), and **2a** (61.0 mg, 0.45 mmol, 98%) were sequentially added to a flame-dried Schlenk tube under an Ar atmosphere. The Schlenk tube was then sealed with a rubber septum and placed in a preheated oil bath at 70 °C with stirring for 12 h. The reaction mixture was cooled to room temperature, and H_2O (20 mL) and ethyl acetate (20 mL) were then added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford **5aa** (102.1 mg, 79%) as a white solid: m.p. 132–133 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 7.67$ (d, $J = 7.8$ Hz, 2H, Ar-H), 7.32 (d, $J = 8.4$ Hz, 2H, Ar-H), 4.00–3.96 (m, 2H, TsN$\underline{CH_2}$C=C), 3.74 (s, 6H, two CH_3 from CO_2Me), 3.21 (t, $J = 5.7$ Hz, 2H, TsN$\underline{CH_2}CH_2$), 2.92 (s, 2H, $CH_2C(CO_2Me)_2$), 2.43 (s, 3H, CH_3 from Ts), 2.27–2.22 (m, 2H, TsNCH$_2\underline{CH_2}$), 1.85 (s, 3H, one CH_3 from C=C$(CH_3)_2$), 1.71 ppm (s, 3H, one CH_3 from C=C$(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 171.6$, 143.6, 137.1, 135.7, 133.4, 131.3, 129.6, 128.5, 127.5, 62.6, 52.7, 46.8, 44.6, 42.2, 26.2, 24.3, 22.1, 21.4 ppm. MS (EI) *m/z* (%): 433 (M^+, 6.53), 91 (100). IR (neat): $\tilde{\nu} = 1737$, 1722, 1597, 1433, 1341, 1240, 1216, 1162, 1097, 1061 cm^{-1}. Elemental analysis calcd (%) for $C_{22}H_{27}NO_6S$: C 60.95, H 6.28, N 3.23, S 7.40; found: C 60.82, H 6.24, N 3.22, S 7.08.

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