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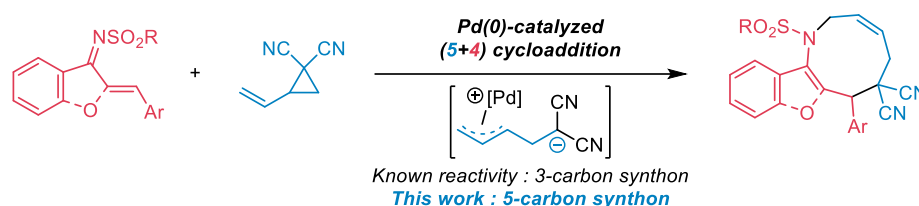
# Vinylcyclopropanes as All-Carbon 1,5-Dipoles: A Reactivity Switch for Palladium-Catalyzed (5+4) Cycloadditions

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Supporting Information Placeholder

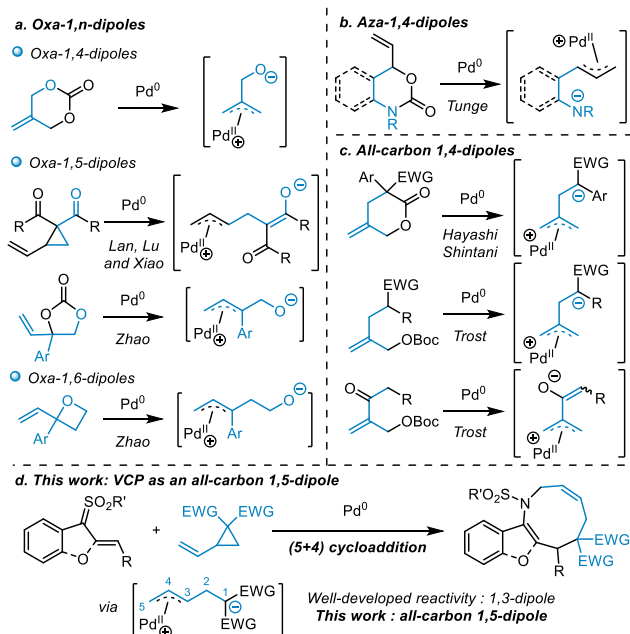


**ABSTRACT:** Azonanes were prepared by a palladium-catalyzed (5+4) cycloaddition between activated vinylcyclopropanes and 1-azadienes. During this process, the vinylcyclopropane partner displayed an unusual reactivity and behave as an all-carbon 1,5-dipole. A *N,N*-bidentate ligand was required to inhibit the formation of thermodynamic (3+2) cycloadducts.

When a multitude of methods describes the preparation of 3 to 7 membered-rings, the synthesis of medium-sized (8 to 11) heterocycles<sup>1,2</sup> remains a more demanding task because of the high entropy and enthalpy associated with the cyclization process.<sup>3</sup> Our group is interested in the design of new cycloaddition strategies for the preparation of these important structures and we focused our attention on the design and reactivity of 1,*n*-dipoles (*n*≥4) whose application for medium-rings synthesis is still limited.<sup>4</sup>

Transition-metal catalyzed cycloadditions relying on Tsuji-Trost chemistry has recently emerged as a valuable approach towards  $\pi$ -allyl-Pd<sup>II</sup> 1,*n*-zwitterionic dipoles.<sup>5-7</sup>

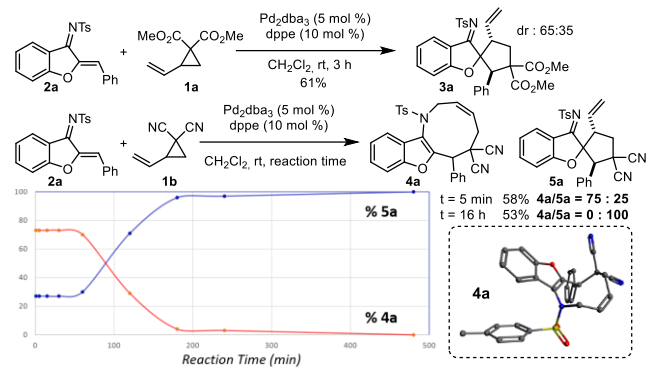
Following the pioneering work of Zhao, vinyl ethylene carbonates (and, to a lesser extent, the corresponding oxiranes) have recently gathered a growing attention as readily available oxa-1,5-dipole precursors (Scheme 1a).<sup>8,9</sup> The relevance of nitrogenated heterocycles prompted organic chemists to study new aza-dipoles.<sup>10</sup> Tunge and others demonstrated the versatility of vinyl benzoxazinones in a wide array of Pd-catalyzed (4+*n*) cycloadditions (Scheme 1b).<sup>11</sup> The negative charge of the zwitterionic  $\pi$ -allyl-Pd<sup>II</sup> intermediates could also be stabilized as a soft enolate by electron withdrawing neighboring groups and cycloadditions of all-carbon 1,4-dipoles were pioneered by Hayashi and Shintani using  $\gamma$ -methylidene- $\delta$ -valerolactones as readily available substrates.<sup>12</sup> Recently, the group of Trost designed two acyclic substrates, precursors of trimethylenemethane homologues, allowing for the enantioselective formation of diversely substituted cyclohexanes<sup>13</sup> and cyclohexanones<sup>14</sup> (Scheme 1c). To the best of our knowledge,



Scheme 1. 1,*n*-dipoles (*n*≥4) in Tsuji-Trost chemistry.

cycloadditions of all-carbon 1,5-dipoles relying on Tsuji-Trost chemistry have not been disclosed yet.<sup>15</sup> Acknowledging that such zwitterionic intermediates could contribute to the preparation of new medium-sized cyclic structures, we envisioned to involve VCPs as their precursors.

While these substrates have been well established as 3-carbon synthons in Pd(0) catalysis,<sup>16</sup> we anticipated that steric hindrance at the nucleophilic site of a cycloaddition partner would promote a faster cyclization step at the C<sub>5</sub> carbon. Herein we report a kinetically-controlled Pd-catalyzed (5+4) cycloaddition of activated vinylcyclopropanes with 1-azadienes<sup>8a,8b,9a</sup> for the synthesis of azonane heterocycles (Scheme 1d).



Scheme 2. Preliminary studies

To conduct this study, we initially involved VCP **1a** bearing two methyl ester groups and benzofuran-derived 1-azadiene **2a** as test substrates. Under usual conditions (Pd<sub>2</sub>dba<sub>3</sub>, dppe, CH<sub>2</sub>Cl<sub>2</sub>, rt), we observed the formation of spiro compound **3a** originating from a (3+2) cycloaddition involving the VCP as a nucleophilic 1,3-dipole and the C=C bond of the azadiene as an electrophilic 1,2-dipole.<sup>17</sup> A remarkably different outcome was observed with VCP **1b** bearing two cyano electron-withdrawing groups. Under the same conditions, a fast transformation (<1 min) was observed and furnished the expected 9-membered ring **4a**<sup>18</sup> as a major product along with a mixture of diastereomers of the cyclopentane spiro compound **5a** (**4a/5a** = 75:25). Interestingly, **5a** was the only cycloadduct observed after 4 hours (rt) and a careful monitoring of the **4a/5a** ratio by <sup>1</sup>H NMR spectroscopy revealed that (5+4) cycloadduct **4a** was gradually converted to (3+2) cycloadduct **5a** under these reaction conditions (Scheme 2).

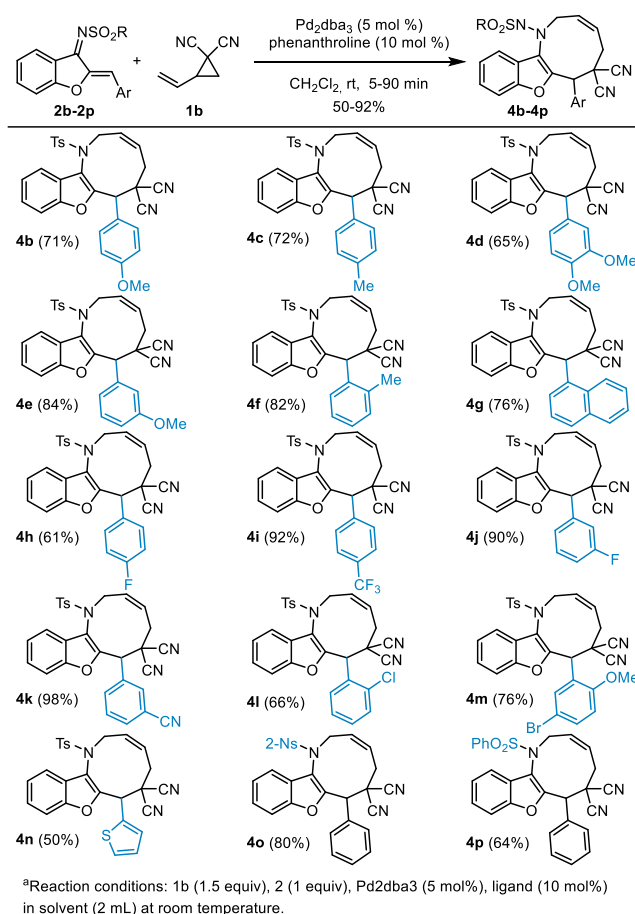
After this encouraging preliminary result, an array of solvents was tested but did not allow for a more selective formation of 9-membered azonane **4a** (Table 1, Entry 1-5). Gratifyingly, a Pd<sub>2</sub>dba<sub>3</sub>/*N,N*-bidentate ligand catalytic system led to the exclusive formation of the (5+4) cycloadduct **4a** (**4a/5a** > 96:4) which was isolated in good yield (74%) using phenanthroline as ligand (Table 1, Entry 7) and, in this case, no conversion of **4a** to **5a** was observed after 16 hours (Table 1, Entry 8). These conditions proved to be suitable for the gram-scale synthesis (1.10 g, 73%) of **2a** (Table 1, Entry 9). It is worth pointing out that VCP **1a** bearing two methyl esters was exclusively converted to the corresponding spiro compound under these conditions, highlighting the importance of the two cyano groups.<sup>19</sup>

Table 1. Optimization of the reaction conditions<sup>a</sup>

Entry	Ligand	Solvent	<b>4a/5a</b>	Yield (%)
1	dppe	CH <sub>2</sub> Cl <sub>2</sub>	75:25	58 <sup>b</sup>
2	dppe	Toluene	72:28	42 <sup>b</sup>
3	dppe	Methanol	65:35	41 <sup>b</sup>
4	dppe	Et <sub>2</sub> O	65:35	62 <sup>b</sup>
5	dppe	Acetone	63:37	56 <sup>b</sup>
6	bipyridine	CH <sub>2</sub> Cl <sub>2</sub>	> 96:4	64 <sup>c</sup>
<b>7<sup>d</sup></b>	<b>phenanthroline</b>	<b>CH<sub>2</sub>Cl<sub>2</sub></b>	<b>&gt; 96:4</b>	<b>74<sup>c</sup></b>
8 <sup>e</sup>	phenanthroline	CH <sub>2</sub> Cl <sub>2</sub>	> 96:4	71 <sup>c</sup>
9 <sup>f</sup>	phenanthroline	CH <sub>2</sub> Cl <sub>2</sub>	> 96:4	73 <sup>c</sup>

<sup>a</sup>Reaction conditions: **1b** (0.075 mmol), **2a** (0.05 mmol), Pd<sub>2</sub>dba<sub>3</sub> (0.0025 mmol), ligand (0.005 mmol) in solvent (0.5 mL) at room temperature. <sup>b</sup>NMR yields <sup>c</sup>isolated yields. <sup>d</sup>Reaction time: 5 min. <sup>e</sup>Reaction time: 16 h. <sup>f</sup>**2a** (3.00 mmol), Reaction time: 5 min.

Having these optimized conditions in hand, we then examined the scope of this (5+4) cycloaddition by involving benzofuran-derived azadienes bearing an array of aromatic substituents at position C<sub>4</sub>. Electron-rich phenyl groups were well tolerated and azonane with *p*-anisyl (**4b**), *p*-tolyl (**4c**), 3,4-dimethoxyphenyl (**4d**) and *m*-methoxyphenyl (**4e**) groups were smoothly generated. Steric hindrance on this aromatic group had little influence on this cycloaddition as azadienes **2f** (82%) and **2g** (76%) with an *o*-tolyl and a 1-naphthyl group, respectively, were readily converted to the corresponding nine-membered heterocycles. We continued to question the importance of the electronic properties of this aromatic moiety and demonstrated that electron-withdrawing substituents such as a fluorine (**4h**) or a trifluoromethyl (**4i**) group at the *para* position could be installed. Substitutions at the *meta* position (3-F for **2j** and 3-CN for **2k**) were also tolerated as the expected azonanes **4j** (90%) and **4k** (98%) were generated in high yields. Halogen atoms are susceptible to alter the course of this reaction as an oxidative insertion of the Pd<sup>0</sup> catalyst can occur. We were pleased to observe the efficient formation of azonanes **4l** (2-Cl, 66%) and **4m** (5-Br-2-OMe, 76%). Under the same reaction conditions, azadiene **2n** (50%) bearing an electron-rich 2-thiophenyl group was converted to the expected nine-membered ring.

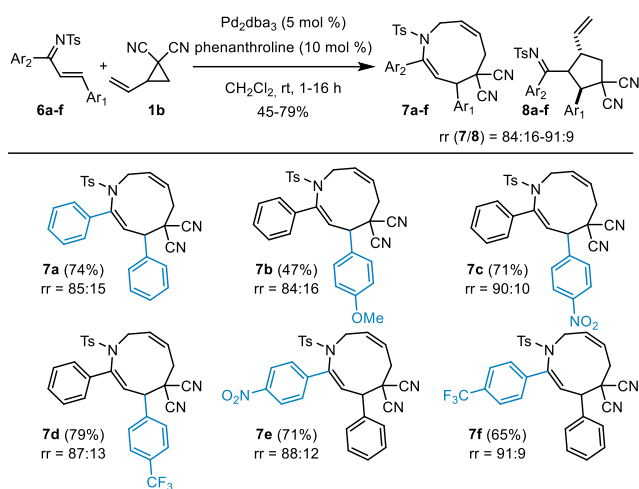


**Scheme 3. Formation of benzofuran-fused azonanes<sup>a</sup>**

Finally, the reactivity of benzofuran-derived azadienes with different sulfonamide groups was examined and 2-nitrosulfonamide **4o** (80%) as well as benzenesulfonamide **4p** (64%) were isolated (Scheme 3).

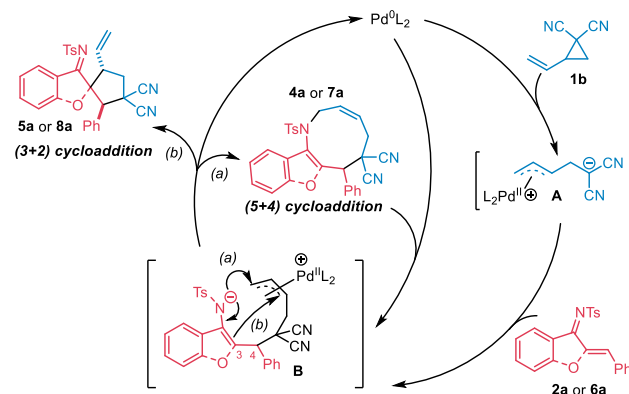
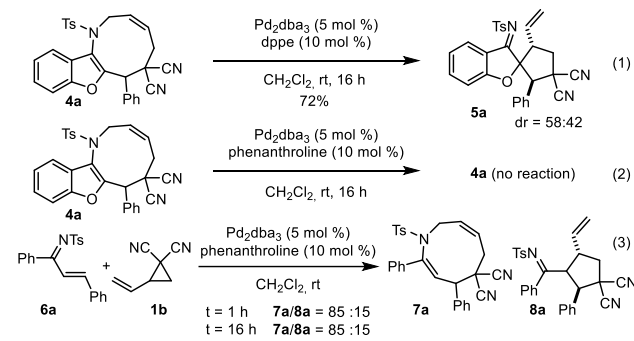
We then focused our attention towards linear 1-azadienes **6a-f** derived from various chalcones. These substrates present an ambitious challenge as the (5+4) cycloaddition does not come with an aromatization step driving the azadiene to act as a 4-atoms synthon rather than a 2-atom synthon. We first interrogated the behavior of *N*-Ts-azadiene **6a** derived from benzylideneacetophenone and were pleased to observe that the nine-membered heterocycle remained the major product under the previously optimized reaction conditions as a 85:15 mixture of the expected (5+4) cycloadduct **7a** along with cyclopentane **8a** was obtained (74%). The presence of an electron-rich aryl Ar<sub>1</sub>, substituted with a methoxy group at the *para* position, did not influence the **7b/8b** (84:16) isomeric ratio but the mixture was isolated in a moderate yield of 47%. Electron-withdrawing groups on Ar<sub>1</sub> restored the

reactivity: azonanes **7c** and **7d** were isolated as the major products with a better selectivity of 90:10 and 87:13, respectively. The ease of preparation of acyclic 1-azadienes bearing different Ar<sub>2</sub> aryl groups allowed us to further review the scope of this monocyclic azonane synthesis. In this case, electrophilic partners with an electron-deficient *p*-nitrophenyl and *p*-trifluoromethylphenyl substituents also reacted promptly to generate **7e** (**7e/8e** = 88:12) and **7f** (**7f/8f** = 91:9) with similar selectivities, showing that electronic properties of these 1-azadienes had little influence on the outcome of the transformation (Scheme 4).



#### Scheme 4. (5+4) cycloadditions of linear 1-azadienes.<sup>a</sup>

A mechanistic rationale was proposed for this (5+4) process relying on Tsuji-Trost chemistry (Scheme 5). After *in situ* formation of the active 14 electrons complex Pd<sup>0</sup>L<sub>2</sub> (L<sub>2</sub> = phen or dppe), its complexation (not shown) with the alkene moiety of VCP **1b** is then followed by an oxidative addition to generate zwitterionic Pd<sup>II</sup>-π-allyl complex **A**. A Michael addition into azadiene **2a** then generates the key Pd<sup>II</sup>-π-allyl complex intermediate **B**. The formation of the observed nine-membered ring **4a** could result from pathway (a) after addition of the sulfonamide anion, acting as a bulky soft nucleophile, to the terminal carbon of the π-allyl moiety. An alternative pathway (b) involving the nucleophilic addition of the C<sub>3</sub> carbon onto the substituted carbon of the π-allyl Pd<sup>II</sup> complex would then lead to the spiro (3+2) cycloadduct **5a**, observed as the side product of the transformation when L<sub>2</sub> = dppe. In this case, the complete conversion of **4a** to **5a** after 4 h (see Scheme 2) could be explained by the ring-opening of kinetic product **4a** and regeneration of zwitterionic intermediate **B** which then cyclizes towards the thermodynamic product **5a** (Scheme 5, Eq 1). When L<sub>2</sub> = phenanthroline, the complete selectivity for the 9-membered ring **4a** (Scheme 5, Eq 2) could be explained by an inhibition of pathway (b) but could also result from a forbidden ring-opening step. We finally established that the lower selectivity for monocyclic azonane **7a** (1 h, **7a/8a** = 85:15) did not evolve after an extended reaction time (Scheme 5, Eq 3), suggesting that no subsequent ring-opening of **7a** (and by analogy **4a**) occurs with a *N,N*-bidentate ligand.



**Scheme 5. Control experiments and proposed mechanism.**

In this study, we reported a Pd-catalyzed (5+4) cycloaddition between an activated vinylcyclopropane and 1-azadienes as the electrophilic partner to furnish azonanes, a nine-membered *N*-heterocycle. During this process, the VCP acts as a 5-atom synthon and a *N,N*-ligand was necessary to achieve a complete selectivity and avoid the formation of the undesired thermodynamic product originating from a competing (3+2) process. Mechanistic investigations are underway to better understand the selectivity of this transformation with the aim of involving VCPs in other (5+n) cycloadditions.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and NMR spectra for all new compounds (PDF)

### Crystallographic data

CCDC 2058000 (**4a**) contains the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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## Notes

The authors declare no competing financial interest.

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