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Cyclization

Unprecedented Oxycyanation of Methylenecyclopropanes for the Facile Synthesis of Benzoxazine Compounds Containing a Cyano Group

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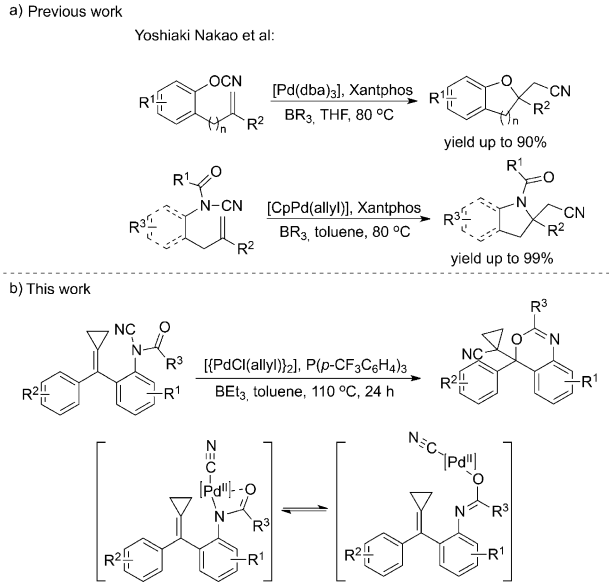
Abstract: A novel intramolecular oxycyanation of methylenecyclopropanes is reported that proceeds through oxidative cleavage of the N–CN bond and subsequent palladium transfer from N to O of the amide group. A range of substituted benzo[*d*][1,3]oxazines with a cyano group are readily furnished by this newly developed oxycyanation reaction. Tris(4-trifluoromethylphenyl)phosphine as a ligand has been found to be crucial to effectively promote the transformation with high chemo- and regioselectivity. Moreover, the reaction outcome can be significantly affected by the electronic effect of the acyl group attached to the nitrogen atom of methylenecyclopropanes. When R^3 is a chloromethyl group, the pyrrolo[2,3-*b*]quinoline derivative is obtained by thermal-induced [3+2] cycloaddition of methylenecyclopropane to the methanediimine intermediate.

Benzoxazines are an important class of organic compounds that are found in a number of thermoset materials,[1] optoelectronic materials, and pharmaceuticals.[2] Some of benzoxazine-containing compounds also show antibacterial or analgesic activity. Meanwhile, nitriles, which can serve as versatile synthetic intermediates for esters, amides, amines, aldehydes, and carboxylic acids, also play a pivotal role in organic synthesis. Accordingly, the development of novel and efficient synthetic methods for heterocyclic compounds containing a cyano group has been largely concerned in synthetic organic chemistry.[3,4] Metal-catalyzed cyanation reactions of unsaturated compounds, such as alkenes and alkynes, to access a variety of nitriles in highly chemo- and stereoselective manners have thus gained much interest. The silylcyanation,[5] germylcyanation,[6] stannylcyanation,[7] borylcyanation,[8] carbocyanation,[9] thiocyanation,[10] bromocyanation,[11] oxycyanation,[3] and most recently aminocyanation[4,12] of alkynes and/or alkenes have been realized by using a transition metal as catalyst to give nitriles containing a functional group at the β-position to the cyano group. Most cyano-functionalization reactions rely on the cleavage of the functional group (FG)–CN bonds by electron-rich late-transition-metal complexes, such as nickel(0), palladium(0), and platinum(0), through oxidative addition as a key step in their proposed catalytic cycles. For example, in 2012 and 2014, Nakao and co-workers reported the intramolecular oxycyanation and aminocyanation of alkenes by cooperative Pd/BPh_3 catalysis (Scheme 1 a).[3,4] Although the oxycyanation



Scheme 1. Metal-catalyzed cyanation reactions of unsaturated compounds.

of alkenes by cooperative Pd/BPh_3 catalysis has been disclosed, the oxycyanation of alkenes caused by the oxidative cleavage of the N–CN bond and the subsequent palladium transfer from N to O of the amide group has never been reported. In this paper, we wish to report the intramolecular oxycyanation reaction of cyanamido group substituted methylenecyclopropanes[13,14] catalyzed cooperatively by a palladium catalyst and BEt_3, providing useful benzoxazine derivatives incorporating a cyano group (Scheme 1 b).

The aniline-tethered alkylidenecyclopropanes were prepared according to the previous literature.[15] With these substrates in hand, we first examined the intramolecular oxycyanation reac-

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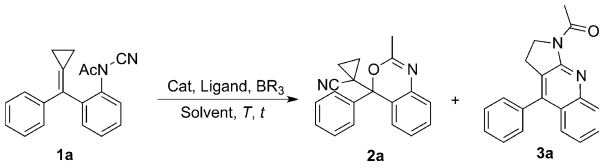
Table 1. Optimization of the reaction conditions.[a]



1a 2a 3a

Entry	Cat.	Ligand	Lewis acid	Solvent	*T* [°C]	Conv. [%]	Yield [%][b]	
							2a	**3a**
1	[{PdCl(allyl)}$_2$]	Xantphos	BEt_3	toluene	110	93	34	trace
2	[{PdCl(allyl)}$_2$]	PPh_3	BEt_3	toluene	110	80	68	trace
3	[{PdCl(allyl)}$_2$]	P(*p*-$CH_3OC_6H_4)_3$	BEt_3	toluene	110	82	63	trace
4	[{PdCl(allyl)}$_2$]	dppf	BEt_3	toluene	110	99	44	24
5	[{PdCl(allyl)}$_2$]	$PPhMe_2$	BEt_3	toluene	110	52	49	trace
6	**[{PdCl(allyl)}$_2$]**	**P(*p*-$CF_3C_6H_4)_3$**	**BEt_3**	**toluene**	**110**	**99**	**92 (89)**	**7 (6)**
7	[{PdCl(allyl)}$_2$]	–	BEt_3	toluene	110	83	35	trace
8	–	–	BEt_3	toluene	110	70	<10	trace
9	–	–	BEt_3	toluene	110	62	<10	trace
10	$Pd(OAc)_2$	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	110	88	26	trace
11	[$Pd_2(dba)_3$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	110	82	31	trace
12	$PdCl_2$	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	110	82	51	trace
13	[$Pd(OAc)_2(Py)_2$]	–	BEt_3	toluene	110	79	37	trace
14	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BPh_3	toluene	110	91	65	trace
15	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	$Zn(OTf)_2$	toluene	110	98	40	10
16	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	–	toluene	110	89	13	trace
17	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	DMF	110	99	26	trace
18	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	dioxane	110	69	33	trace
19	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	130	99	64	trace
20	[{PdCl(allyl)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	150	99	57	5
21	[$Ni(cod)_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	110	93	79	trace
22	[{RhCl(cod)}$_2$]	P(*p*-$CF_3C_6H_4)_3$	BEt_3	toluene	110	92	82 (77)	trace
23	[$Ru(C_5H_5)_2$]	–	BEt_3	toluene	110	96	78	trace

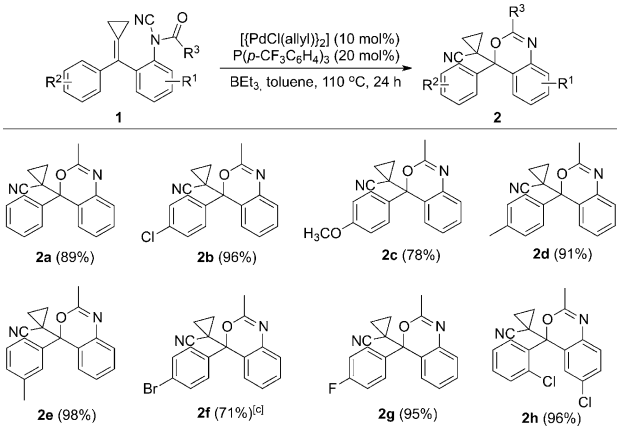
[a] Reaction conditions: **1** (0.1 mmol), catalyst (10 mol%), ligand (20–40 mol%) and Lewis acid (40 mol%) in solvent (1.0 mL) stirred for 24 h under Ar. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The isolated yield is shown in parentheses.

tion in the presence of various transition-metal catalysts. We found that when the reaction was carried out in toluene at 110 °C, two new compounds could be formed in the presence of the palladium catalyst and BEt_3. This result encouraged us to more carefully examine the reaction outcomes.

Initial examinations using **1a** as the substrate were aimed at determining the reaction outcome and subsequently optimizing the reaction conditions. The results are summarized in Table 1. Product **2a** was obtained in 34% yield as the major product with concomitant formation of thermal-induced [3+2] cycloaddition adduct **3a** in 3% yield (see Table 4), when the reaction was carried out in toluene under the catalysis of [{PdCl(allyl)}$_2$] (10 mol%) with Xantphos ligand and triethylborane Lewis acid at 110 °C for 24 h (Table 1, entry 1). We next screened different phosphine ligands, such as PPh_3, P(*p*-$CH_3OC_6H_4)_3$, dppf, $PPhMe_2$, P(*p*-$CF_3C_6H_4)_3$ (entries 2–7). It was found that P(*p*-$CF_3C_6H_4)_3$ combined with [{PdCl(allyl)}$_2$] gave the desired product **2a** in 89% isolated yield along with only trace of **3a**. Without the palladium catalyst and phosphine ligand or in the absence of palladium catalyst, phosphine ligand, and Lewis acid, yields of **2a** were less than 10% (entries 8–9). Subsequent examination of palladium catalysts using P(*p*-$CF_3C_6H_4)_3$ as the ligand did not give better results (entries 10–12). The combination of $Pd(OAc)_2$/Py also did not facilitate the formation of **2a** (entry 13). The examination of Lewis acid effects revealed that triethylborane was the Lewis acid of choice (entries 14–15). More importantly, the reaction only gave **2a** in 13% yield in the absence of triethylborane (entry 16), indicating that triethylborane plays a crucial role in activating the N–CN bond.[3,4] After screening of solvents, we found that toluene was the best one for this reaction (entries 17–18). Further studies were focused on the reaction temperature effect, and we found that the intramolecular oxycyanation was sensitive to the reaction temperature and the best results were obtained at 110 °C (entries 19–20). Other transition-metal catalysts, such as [$Ni(cod)_2$], [{RhCl(cod)}$_2$], and [bis(cyclopentadienyl)ruthenium], were also tested, but inferior results were obtained (entries 21–23). Finally, we identified [{PdCl(allyl)}$_2$] as the best catalyst for this reaction (for more details on the optimization of reaction conditions, see the Supporting Information).

With the optimized reaction conditions in hand, we next investigated the generality of this intramolecular oxycyanation reaction, and the results are shown in Table 2. As for substrate **1**, in which $R^1 = H$, $R^3 = Me$, both electron-withdrawing (**1b**, **1f**–**1g**) and -donating (**1c**–**1d**) substituents at the *para*-position of aromatic rings were tolerated, providing the corresponding products (**2b**–**2d** and **2f**–**2g**) in good to excellent yields. In addition, an electron-donating (**1e**) substituent at the *meta*-position of the aromatic ring also afforded the desired product (**2e**) in excellent yield. Importantly, we also found that

Table 2. Substrate scope for palladium-catalyzed intramolecular oxycyanation of methylenecyclopropanes with different aryl groups.[a,b]



[a] Reaction conditions: **1** (0.2 mmol), [{PdCl(allyl)}$_2$] (10 mol%), P(*p*-$CF_3C_6H_4$)$_3$ (20 mol%) and BEt_3 (40 mol%) are stirred in toluene (1 mL) for 24 h under Ar. [b] Isolated yield. [c] 15% of **1f** was recovered.

two electron-withdrawing group substituted **1h** was also suitable for this reaction, affording the desired product **2h** in excellent yield. The structures of **2b** and **2h** were unambiguously confirmed by X-ray diffraction. Their ORTEP drawings are shown in Figure 1 and the corresponding CIF data are presented in the Supporting Information.[16]

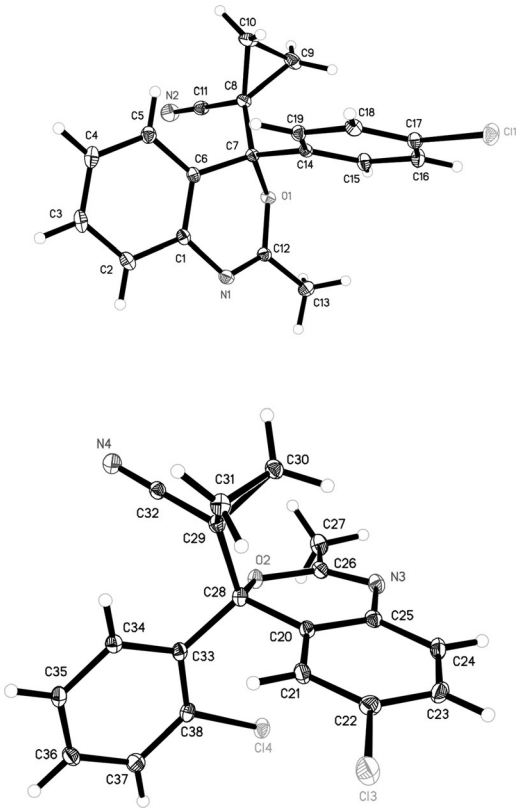
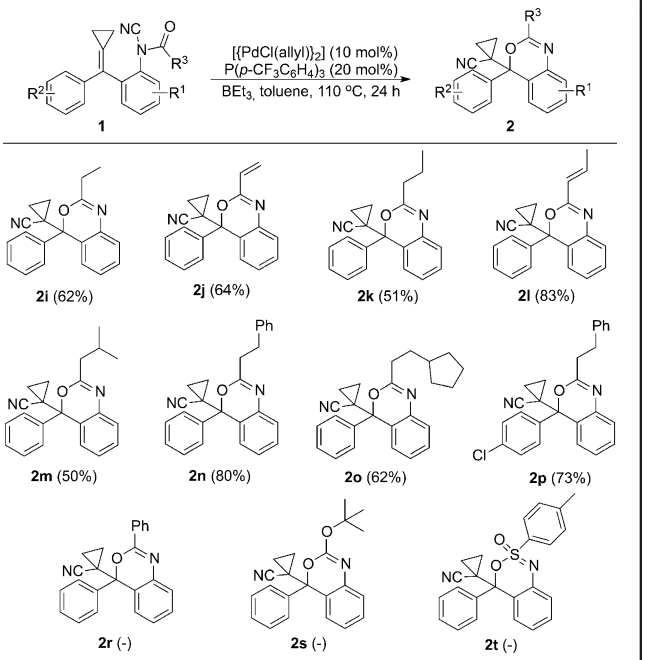


Figure 1. ORTEP drawings of **2b** and **2h** (the thermal ellipsoids are set at a 30% probability level).

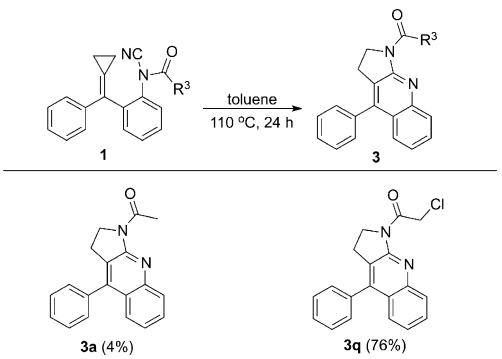
Table 3. Substrate scope for palladium-catalyzed intramolecular oxycyanation methylenecyclopropanes with different acyl substituents.[a,b]



[a] Reaction conditions: **1** (0.1 mmol), [{PdCl(allyl)}$_2$] (10 mol%), P(*p*-$CF_3C_6H_4$)$_3$ (20 mol%) and BEt_3 (40 mol%) are stirred in toluene (1 mL) for 24 h under Ar. [b] Isolated yield.

To further extend the substrate scope of this reaction, a variety of alkyl-, alkenyl- and aryl-substituted acyl groups incorporated substrates were examined (Table 3). As expected, for both alkyl- and alkenyl-substituted acyl groups (**1i**–**1m**), such as propionyl, acrylyl, butyryl, (*E*)-2-butenoyl, or isovaleryl instead of acetyl, the reaction occurred effectively, affording the corresponding products (**2i**–**2m**) in moderate to good yields. Furthermore, we found that when a phenyl- or cyclopentyl-substituted acyl group (**1n**–**1p**) was introduced in substrate **1**, the reaction proceeded smoothly to furnish the desired products **2n**–**2p** in 62–80% yields. It should be noted that in the cases of substrates **1n** and **1o**, the thermal-induced reaction

Table 4. The thermal-induced reaction.[a,b]



[a] Reaction conditions: **1** (0.1 mmol) is stirred in toluene (1 mL) for 24 h. [b] Isolated yield.

products **3n** and **3o** were obtained in 16 and 27% yield, respectively. Disappointingly, when the benzoyl-, *tert*-butyl acetate-, and tosyl-substituted substrates (**1r**–**1t**) were subjected to the catalytic system, no reaction occurred. Notably, we found that the thermal-induced [3+2] cycloaddition of substrate **1a** gave product **3a** in low yield in toluene at 110 °C (Table 4). The structure of **3a** was determined by X-ray diffraction.[16] Its ORTEP drawing is shown in Figure 2. Interestingly, with an electron-withdrawing group (such as Cl) at α-position of the carbonyl group, the corresponding product **3q** was obtained in 76% yield (Table 4, **3q**).

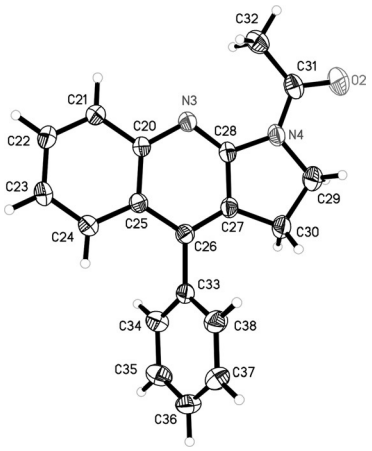
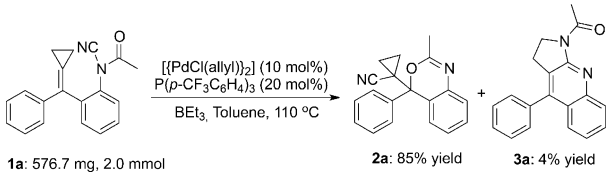


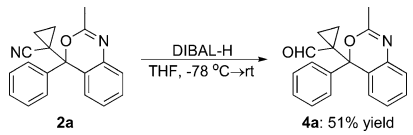
Figure 2. ORTEP drawing of **3a** (the thermal ellipsoids are set at a 30% probability level).

To examine the practicality of this new synthetic method, scale-up experiment was carried out as shown in Scheme 2. The use of **1a** (2.0 mmol) afforded the desired products **2a** and **3a** in 85 and 4% yield, respectively, without notable erosion of yields, demonstrating that the current method is suitable for the preparation of benzoxazine building blocks in practical organic synthesis. To illustrate the synthetic utility of the obtained products, we further developed a transformation of **2a** to the corresponding aldehyde upon treating **2a** with DIBAL-H in THF at −78 °C, giving the desired aldehyde **4a** in 51% yield (Scheme 3).

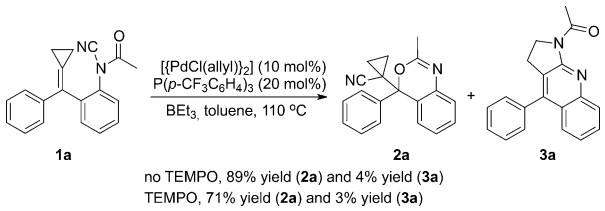


Scheme 2. Scale-up experiment.

To gain mechanistic insights into the intramolecular oxycyanation reaction, a control experiment was performed as shown in Scheme 4. The control experiment confirmed that the reaction under the optimized conditions was almost unaffected by the addition of the radical inhibitor, such as 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO; 2.0 equiv), rendering unlikely the intervention of a radical pathway.

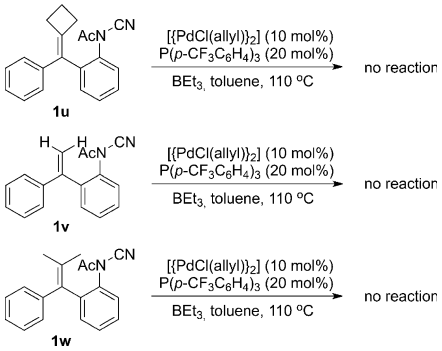


Scheme 3. Transformation of product **2a**.



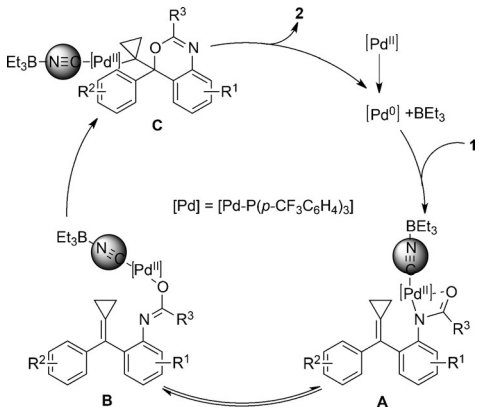
Scheme 4. Control experiments of **1a** in the presence of TEMPO.

Further control experiments were conducted as shown in Scheme 5. Substrates **1u**, **1v**, and **1w** without cyclopropane moiety, could not be converted into the desired products under the standard conditions, indicating that the strained small ring plays an important role in the intramolecular oxycyanation reaction.



Scheme 5. Control experiments of **1u**, **1v**, and **1w** under the standard conditions.

Based on the previous reports[4] and the control experiments, a plausible reaction mechanism is proposed in Scheme 6. The reaction is initiated by the oxidative addition of the N–CN bond in **1** to Pd^0, giving intermediate **A**. Subsequently, a palladium transfer from N to O of the amide group takes place in intermediate **A** to give oxypalladium species **B**. Then, oxypalladation takes place in an *exo*-trig manner to give species **C**, which undergoes reductive elimination to afford **2** as well as the catalytically active palladium and boron species. The Lewis acid catalyst is crucial for the oxidative addition of N–CN bonds, it has also been shown to promote $C(sp^3)$ –CN bond-forming reductive elimination from palladium(II) through coordination of a cyano group to Lewis acid.[17] As for product **3**, it can be obtained by 1,3-acyl migration, consecutive 6π-electrocyclization and the subsequent rearrangement.[18]



Scheme 6. Proposed reaction mechanism.

In summary, we have developed a novel intramolecular oxycyanation through the amide isomerization by palladium/boron cooperative catalysis. The process enabled the formation of a variety of substituted benzoxazine compounds containing a cyano group in good to excellent yields. Furthermore, the reaction is substrate dependent and the pyrrolo[2,3-*b*]quinoline derivative is obtained by thermal-induced [3+2] cycloaddition between the methylenecyclopropane and methanediimine intermediate when R^3 is a chloromethyl group. Further development of the enantioselective oxycyanation and more detailed mechanistic studies are in process in our laboratory.

Acknowledgement

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Keywords: amides · benzoxazines · intramolecular oxycyanation · palladium · synthetic methods

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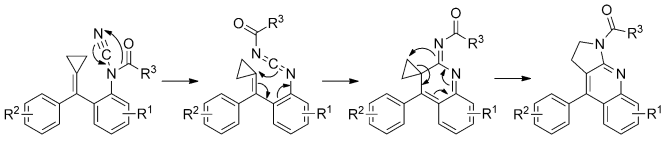

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