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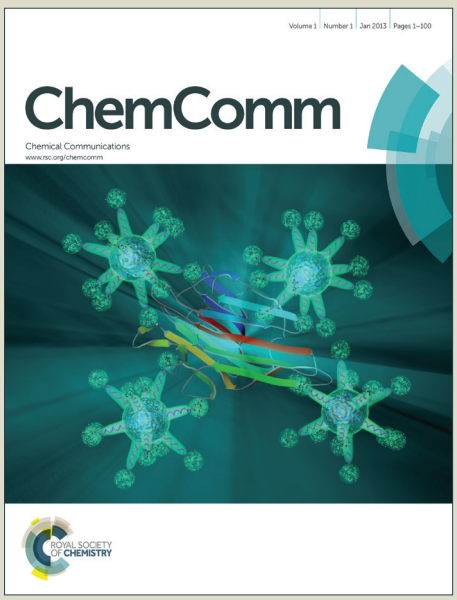

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Diversity-Oriented Synthesis of Acyclic Nucleosides via Ring-Opening of Vinyl Cyclopropanes with Purines†

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Hong-Ying Niu,*[a,b] Cong Du,[a] Ming-Sheng Xie,[a] Yong Wang,[a] Qian Zhang,[a] Gui-Rong Qu,[a] and Hai-Ming Guo*

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The diversity-oriented synthesis of acyclic nucleosides has been achieved via ring-opening of vinyl cyclopropanes with purines. With $Pd_2(dba)_3$·$CHCl_3$ as catalyst, the 1,5-ring-opening reaction proceeded well and afforded N9 adducts as the major form, in which the C=C bonds in the side chain were exclusively *E*-form. In the presence of $AlCl_3$, the 1,3-ring-opening reaction occurred smoothly, giving N9 adducts as the dominate products. Meanwhile, when MgI_2 was used as the catalyst, the 1,3-ring-opening reaction also worked well to form N7 adducts.

Acyclic nucleosides have attracted considerable attention due to their outstanding anti-virus activities.[1] Since 1977, Acyclovir was firstly reported as an antiherpes drug,[2] a series of acyclic nucleosides including Ganciclovir, Penciclovir and Famcidovir have been approved by FDA as anti-HIV agents (Fig.1).[3] For the construction of acyclic nucleosides, the direct strategy is utilizing the nucleophilicity of N9 in purines,[4] including alkylation,[5] aza-Michael reaction,[6] ring-opening of epoxide,[7] *N*-allylation,[8] and Mitsunobu reaction.[9] However, the ring-opening of vinyl cyclopropane with purine has never been reported to construct acyclic nucleosides.[10] The challenges for the ring-opening of vinyl cyclopropane with purine are as follows (Scheme 1): 1) the chemoselectivity between 1,3-ring-opening and 1,5-ring-opening modes in vinyl cyclopropane;[13-15] 2) the competitive nucleophilicity of N9 or N7 positions in purine;[16] 3) the *Z*- or *E*- forms of the C=C bond in the 1,5-ring-opening product.[17] In the context of our ongoing projects in modifying nucleosides,[18] herein, we describe the establishment of reaction conditions that enable the ring-opening of vinyl cyclopropane with purine to construct different acyclic nucleosides, which holds great promise in the area of diversity-oriented synthesis.

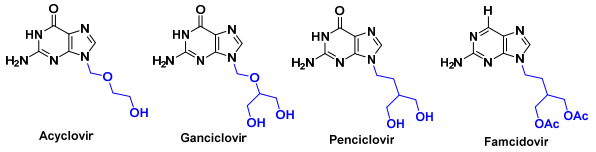
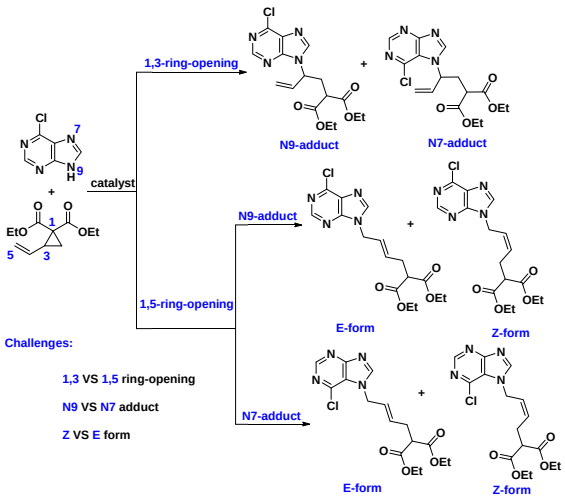


Fig. 1 Representative acyclic nucleosides approved by FDA as anti-HIV agents.

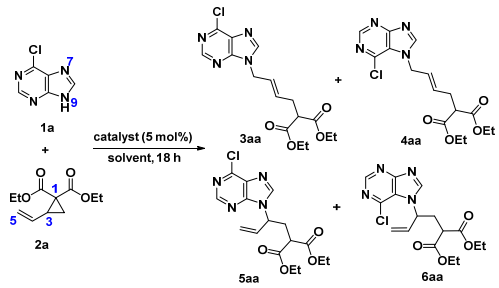


Scheme 1 Potential products for the ring-opening of vinyl cyclopropane with purine.

Initially, the reaction between 6-chloro-purine **1a** and vinyl cyclopropane **2a** was chosen as the model reaction (Table 1). When $Pd_2(dba)_3$ was used as the catalyst with DPPP as the ligand, the major product was 1,5-ring-opening N9-adduct **3aa** in 62% yield, along with 1,5-ring-opening N7-adduct **4aa**, 1,3-ring-opening adducts **5aa** and **6aa** in less than 5% total yield (entry 1). It should be noted that the C=C bond in the side chain of 1,5-ring-opening product **3aa** was exclusively *E*-form. Encouraged by the results, other palladium salts including $Pd(PPh_3)_4$, $Pd(dba)_2$, $Pd_2(dba)_3$·$CHCl_3$, $Pd(OAc)_2$, and $PdCl_2$ were screened, and a higher yield for **3aa** (66% yield) was achieved when $Pd_2(dba)_3$·$CHCl_3$ was employed (entries 2-6). After testing the ligand from DPPP to DIOP, the yield of **3aa** was increased to 71% (entries 4, 7-8). Subsequently, several solvents were examined, and dioxane was found as the best one to give **3aa** in 76% yield (entries 9-11). Increasing the reaction temperature from room temperatrue to 30 °C, up to 82% yield was obtained for **3aa**, along with the isomers **4aa**, **5aa**, and **6aa** (entry 12). While further increase of the reaction temperatrue to

40 °C led to a decrease of the yield of **3aa** (65%, entry 13). Thus, the optimal reaction conditions were 5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$-DIOP in dioxane at 30 °C (entry 12).

Table 1 Optimization of the reaction conditions[a]



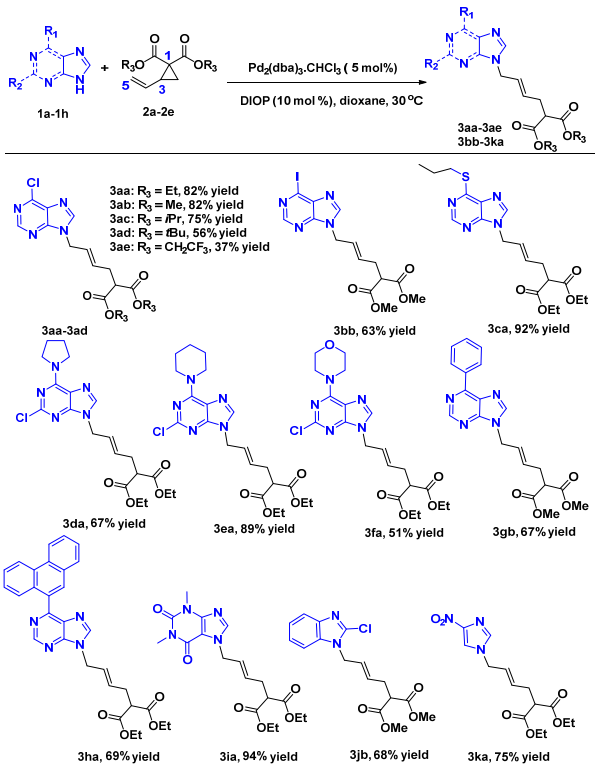
Entry	Catalyst	Ligand[b]	Solvent	T (°C)	Yield (**3aa**) (%)[c]	Yields (**4aa/5aa/6aa**) (%)[c]
1[d]	$Pd_2(dba)_3$	DPPP	THF	rt	62	1/2/trace
2	$Pd(PPh_3)_4$	DPPP	THF	rt	51	<5
3	$Pd(dba)_2$	DPPP	THF	rt	46	<5
4	$Pd_2(dba)_3{\cdot}CHCl_3$	DPPP	THF	rt	66	<5
5	$Pd(OAc)_2$	DPPP	THF	rt	NR[e]	-
6	$PdCl_2$	DPPP	THF	rt	NR[e]	-
7	$Pd_2(dba)_3{\cdot}CHCl_3$	DPPE	THF	rt	21	<5
8	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	THF	rt	71	<5
9	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	2-Me-THF	rt	51	<5
10	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	dioxane	rt	76	<5
11	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	$PhCF_3$	rt	62	<5
12[d]	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	dioxane	30	82	2/2/trace
13	$Pd_2(dba)_3{\cdot}CHCl_3$	DIOP	dioxane	40	65	<5

[a] Unless otherwise noted, the reaction conditions were: **2a** (0.1 mmol), **1a** (0.15 mmol, 1.5 equiv), metal (5 mol%), ligand (10 mol%), solvent (2.0 mL) at 30 °C for 18 h. [b] DPPP = 1,3-bis(diphenylphosphino) propane, DPPE = 1,2-Bis(diphenylphosphino)ethane, DIOP = (2S,3S)-(+)-1,4-Bis(diphenylphosphino)-2,3-O-isopropylidene-2,3-butanediol. [c] Isolated yield. [d] **2a** was used on a 1.0-mmol-scale. [e] NR = No reaction.

With the optimal conditions in hand, the generality of the 1,5-ring-opening reactions was explored (Scheme 2). Firstly, a series of vinyl cyclopropanes **2a-2e** with different ester groups were investigated, and the desired 1,5-ring opening products **3aa-3ae** were afforded in moderate to good yields. Next, several purine derivatives with halogen, alkyl sulfide, amine substituents at C2 or C6 positions participated well in the reaction (**3bb-3fa**). In the case of 6-phenyl-purine **1g** and 6-phenanthren-9-yl purine **1h**, the corresponding 1,5-ring-opening products **3gb** and **3ha** were obtained in moderate yields. To our delight, when other *N*-heterocycles such as xanthine derivative **1i**, 2-chloro-benzoimidazole **1j** and 4-nitro-imidazole **1k** were employed, the desired 1,5-ring-opening products could also be obtained in 94% yield (**3ia**), 68% yield (**3jb**), and 75% yield (**3ka**), respectively.

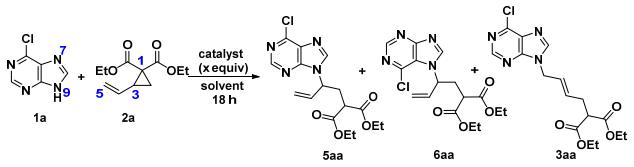
Subsequently, the 1,3-ring-opening reaction of vinyl cyclopropane with purine was examined (Table 2). When $Sc(OTf)_3$, $In(OTf)_3$, $Cu(OTf)_2$, or $Mg(OTf)_2$ was used as catalyst in THF at 60 °C, the reaction did not occur (entries1-4). With $Ni(OTf)_2$ as catalyst, only trace amount of 1,3-ring-opening product **5aa** was observed (entry 5). Luckily, when MgI_2 was tested as catalyst, the 1,3-ring-opening N7-adduct **6aa** was obtained in 35% yield (entry 6). Thus, several solvents were screened, and a higher yield of **6aa** was obtained with dioxane as solvent, along with trace amount of **5aa** (entries 6-9). Then, the reaction temperature was further investigated and 85 °C was selected as the best one (entries 9-12). Next, the ratio of the reactants was examined (entries 11, 13-14). When 5.0 equiv of vinyl cyclopropane **2a** was used, the major product **6aa** was obtained in 72% yield (entry 14). Thus, the optimized N7-adduct of 1,3-ring-opening reaction conditions were 10 mol% MgI_2 with 5.0 equiv of **2a** in dioxane at 85 °C (entry 14).

Scheme 2 Sope of the 1,5-ring-opening reactions.[a]



[a] Reaction conditions: **2** (0.1 mmol), **1** (0.15 mmol, 1.5 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%), DIOP (10 mol %), dioxane (2.0 mL) at 30 °C for 18 h, and the yields were referred to isolated yield.

Table 2 Optimization of the 1,3-ring-opening reaction conditions[a]

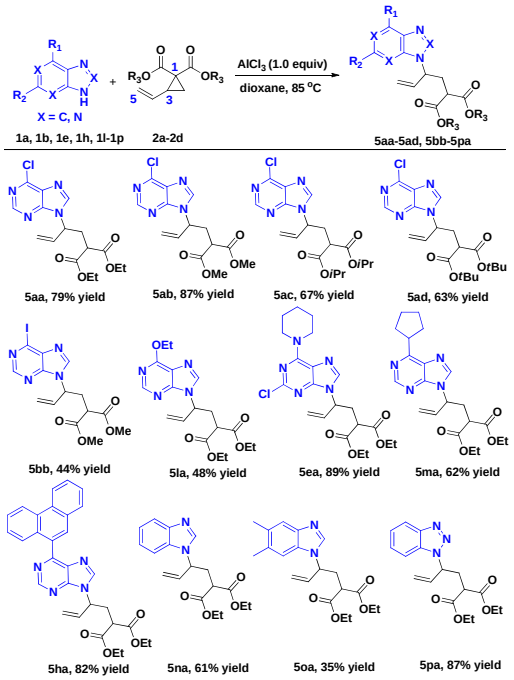


Entry	Catalyst	x (equiv)	Solvent	T (°C)	**2a** (equiv)	Yield (**5aa**) (%)[b]	Yield (**6aa**) (%)[b]	Yield (**3aa**) (%)[b]
1	$Sc(OTf)_3$	0.1	THF	60	3	0	0	0
2	$In(OTf)_3$	0.1	THF	60	3	0	0	0
3	$Cu(OTf)_2$	0.1	THF	60	3	0	0	0
4	$Mg(OTf)_2$	0.1	THF	60	3	0	0	0
5	$Ni(OTf)_2$	0.1	THF	60	3	trace	0	0
6	MgI_2	0.1	THF	60	3	0	35	0
7	MgI_2	0.1	$CHCl_3$	60	3	0	trace	0
8	MgI_2	0.1	toluene	60	3	0	trace	0
9	MgI_2	0.1	dioxane	60	3	trace	48	0
10	MgI_2	0.1	dioxane	70	3	trace	56	0
11	MgI_2	0.1	dioxane	85	3	4	67	0
12	MgI_2	0.1	dioxane	100	3	trace	24	0
13	MgI_2	0.1	dioxane	85	4	8	69	trace
14[c]	MgI_2	0.1	dioxane	85	5	17	72	trace
15	$AlCl_3$	0.1	dioxane	85	3	trace	0	0
16	$AlCl_3$	0.5	dioxane	85	3	52	14	0
17	$AlCl_3$	1.0	dioxane	85	3	79	trace	0

[a] Unless otherwise noted, reaction conditions: **1a** (0.1 mmol), **2a** (3-5 equiv), catalyst (x equiv), solvent (2.0 mL) for 18 h. [b] Isolated yield. [c] **1a** was used on a 1.0-mmol-scale.

Fortunately, it was found that the 1,3-ring-opening N9-adduct **5aa** could be obtained in 52% yield when 0.5 equiv of $AlCl_3$ was employed (entries 15-16). Increasing the amount of $AlCl_3$ to 1.0 equiv, the N9-adduct **5aa** was obtained in 79% yield (entry 17). As a result, the optimial reaction condition for N9-adduct **5aa** was 1.0 equiv $AlCl_3$ with 3.0 equiv of **2a** in dioxane at 85 °C (entry 17).

Scheme 3 Scope of the 1,3-ring-opening reactions in the presence of $AlCl_3$.[a]

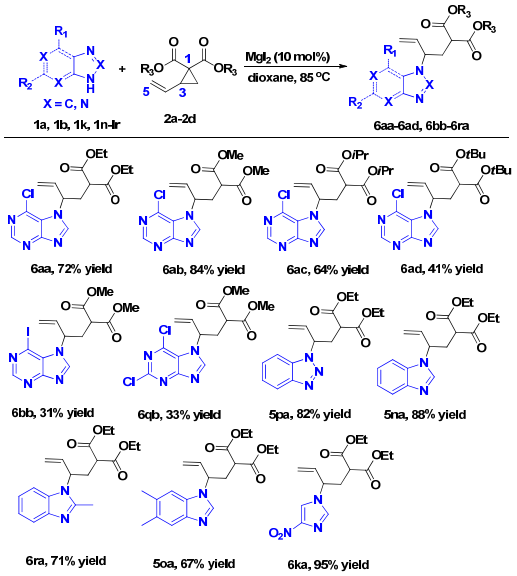


[a] Reaction conditions: **1** (0.1 mmol), **2** (0.3 mmol, 3.0 equiv), $AlCl_3$ (0.1 mmol, 1.0 equiv), dioxane (2.0 mL) at 85 °C for 18 h, and the yields were referred to isolated yields.

Next, with $AlCl_3$ as the catalyst, the substrate scope of 1,3-ring-opening reaction was investigated (Scheme 3). When several vinyl cyclopropanes with different ester groups were explored, the corresponding 1,3-ring opening products **5aa**-**5ad** were obtained in good yields. When 6-iodo-purine **1b**, 6-ethoxy-purine **1l** and 2-chloro-6-piperidinyl purine **1e** were employed, the N9-adducts **5bb**, **5la** and **5ea** were afforded in moderate to good yields. In the case of 6-cyclopentyl purine **1m** and 6-phenanthren-9-yl purine **1h**, the 1,3-ring-opening reactions proceeded well, delivering the desired products **5ma** and **5ha** in 62% yield and 82% yield, respectively. In addition, other *N*-heterocycles including benzoimidazole **1n**, 5,6-dimethyl-benzoimidazole **1o**, and benzotriazole **1p** were also suitable nucleophiles.

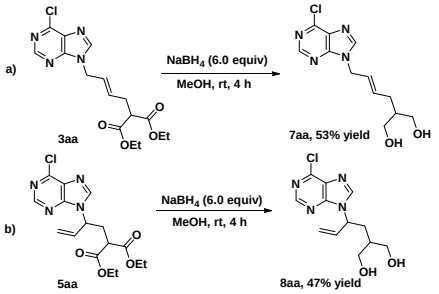
Then, in the presence of catalytic amount of MgI_2, the generality of the 1,3-ring-opening reactions was also explored (Scheme 4). Firstly, several vinyl cyclopropane with different ester groups were investigated (**2a-2d**), and a higher yield was obtained for vinyl cyclopropane with methyl ester (**6ab**). When vinyl cyclopropanes with isopropyl or tertbutyl ester groups were used, the yields decreased slightly (**6ac**-**6ad**). With 6-iodo-purine **1b** and 2,6-dichloro-purien **1q** as nucleophiles, the 1,3-ring-opening N7-adducts **6bb** and **6qb** were obtained in low yields. Subsequently, benzotriazole **1p** and benzoimidazole **1n** were explored, and the desired 1,3-ring-opening products **5pa** and **5na** were obtained in excellent yields. In the case of 2-methyl-benzoimidazole **1r** and 5,6-dimethyl-benzoimidazole **1o**, the addition reactions proceeded well, giving the adducts **6ra** and **5oa** in 71% and 67% yields, respectively. In addition, 5-nitroimidazole **1k** was also a suitable nucleophile, giving the adduct **6ka** in 95% yield.

Scheme 4 Scope of the 1,3-ring-opening reactions in the presence of MgI_2.[a]



[a] Reaction conditions: **1** (0.1 mmol), **2** (0.5 mmol, 5.0 equiv), MgI_2 (10 mol%), dioxane (2.0 mL) at 85 °C for 18 h, and the yields were referred to isolated yields.

Subsequently, hydrogenation of the ring-opening products **3aa** and **5aa** were carried out (Scheme 5). In the presence of $NaBH_4$, the hydrogenation of 1,5-ring-opening product **3aa** and 1,3-ring-opening product **5aa** proceeded well, affording the desired acyclic nucleosides **7aa** and **8aa** in 53% yield and 47% yield, respectively. For the control experiments and proposed mechanism of Pd, Al, and Mg catalyzed ring-opening reactions, see ESI for details.



Scheme 5 Reduction of **3aa** and **5aa** to the corresponding acyclic nucleosides.

In summary, we have estabilised the diversity-oriented synthesis of acyclic nucleosides via ring-opening of vinyl cyclopropanes with purines. These ring-opening reactions exhibited high chemo- and regioselectivity. With $Pd_2(dba)_3{\cdot}CHCl_3$ as the catalyst, the 1,5-ring-opening reaction proceeded well, affording the N9 adducts in moderate to excellent yields (15 examples, up to 94% yield), in which the C=C bonds in the side chain were exclusively *E*-form. In the presence of $AlCl_3$, the 1,3-ring-opening reaction happened smoothly, giving N9 adducts as the major products (12 examples, up to 89% yield). Furthermore, when MgI_2 was used as the catalyst, the 1,3-ring-opening reaction also worked well to form N7 adducts(11 examples, up to 95% yield). And acyclic

nucleosides could be easily obtained from the ring-opening products via reduction reaction.

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Notes and references

[a]*Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, P. R. China; E-mail: niu_hy@163.com; guohm518@hotmail.com*
[b]*School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, China.*
†Electronic Supplementary Information (ESI) available: Experimental details and analytical data of the products. See DOI: 10.1039/b000000x/

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