Tetrahedron 69 (2013) 1476–1480

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A silver(I)–rhodium(I) cooperative catalysis in the reaction of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane

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ARTICLE INFO

Article history:
Received 11 November 2012
Received in revised form 30 November 2012
Accepted 7 December 2012
Available online 17 December 2012

Keywords:
N′-(2-Alkynylbenzylidene)hydrazide
H-Pyrazolo[5,1-*a*]isoquinoline-1-carbaldehyde
(Triphenylphosphine)rhodium(I) chloride
Silver triflate
2-Vinyloxirane

ABSTRACT

A novel and efficient route to *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehydes via a tandem reaction of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane is described. The reaction proceeds through a silver(I)–rhodium(I) cooperative catalysis.

1. Introduction

Recently, cooperative catalysis as a powerful approach has been demonstrated in organic transformations.[1] The merging of two or more catalysts in one pot would enable the reactivities of reactants, leading to the successful transformations. Examples of combination of metal catalyst and organocatalyst, or two metal catalysts have been appeared.[1]

Currently, continuous efforts have been focused on the preparation of biologically and pharmaceutically important *N*-heterocyclic compounds in the drug discovery process.[2] During our efforts for the combinatorial synthesis of *N*-heterocycles with privileged scaffolds, we are interested in *H*-pyrazolo[5,1-*a*]isoquinoline compounds, which show promising biological acitivities.[3] Although there are several methods for the synthesis of *H*-pyrazolo[5,1-*a*]isoquinolines,[4] an efficient approach for the generation of diverse *H*-pyrazolo[5,1-*a*]isoquinolines is in great demand. If a carbonyl group (such as aldehyde) could be installed in the skeleton of *H*-pyrazolo[5,1-*a*]isoquinoline (Fig. 1), a small library of diverse *H*-pyrazolo[5,1-*a*]isoquinolines would be expected.

Recently, we found that *N*′-(2-alkynylbenzylidene)hydrazide could work as a good reactant for the construction of *H*-pyrazolo[5,1-*a*]isoquinolines.[5] Initially, we designed a tandem reaction for the formation of *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehydes via a silver/iron co-catalyzed reaction of *N*′-(2-alkynylbenzylidene)hydrazides with tertiary amines (Scheme 1). This proposed route was inspired by Li's work for the synthesis of β-1,3-dicarbonyl aldehydes,[6] in which α,β-unsaturated aldehyde was the key intermediate generated by tertiary amine oxidation in situ. However, the installation of aldehyde into the *H*-pyrazolo[5,1-*a*]isoquinoline scaffold was failed based on this strategy.[7] Thus, we shifted our focus on 2-vinyloxirane, which could serve as the precursor for the introduction of aldehyde in the presence of transition metal catalyst (such as rhodium salt) as well. The proposed pathway is present in Scheme 2.

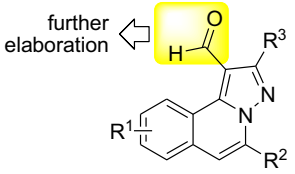

Fig. 1. Diverse *H*-pyrazolo[5,1-*a*]isoquinolines.

We conceived that an oxidative addition of rhodium(I) to 2-vinyloxirane would occur first to generate intermediate **B1**. An equilibrium between **B1** and **B3** via allylic rhodium complex would be existed. In the meantime, silver triflate-catalyzed 6-*endo* cyclization of *N*′-(2-alkynylbenzylidene)hydrazide **1** would give

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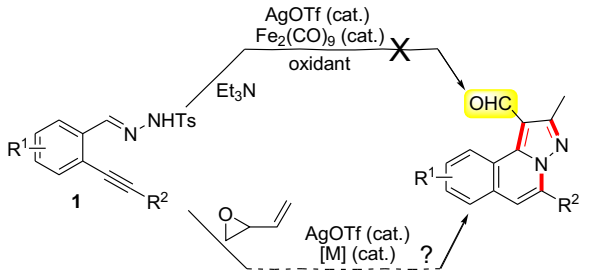
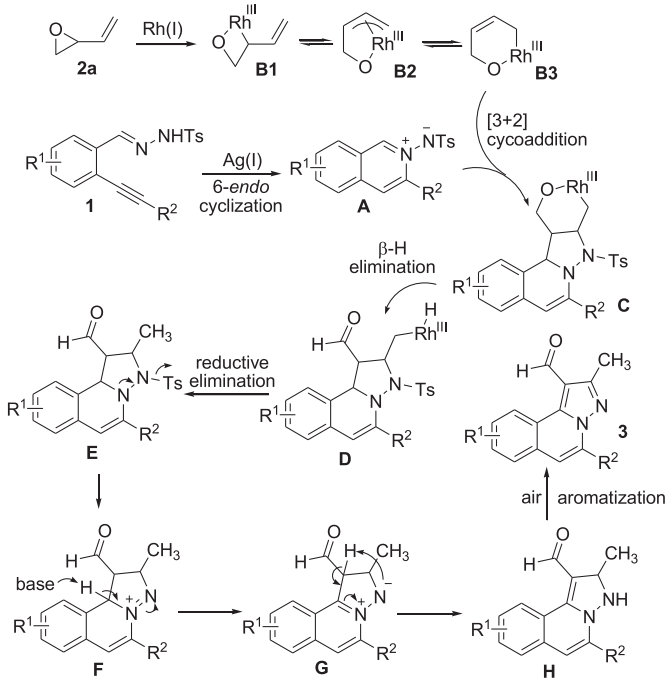
http://dx.doi.org/10.1016/j.tet.2012.12.018



Scheme 1. A proposed route to *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehydes.



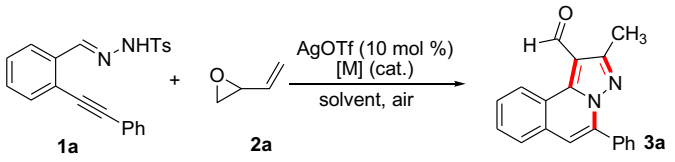
Scheme 2. A possible mechanism for the reaction of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane.

rise to isoquinolinium-2-yl amide **A**,[5] which would then undergo a [3+2] cycloaddition with intermediate **B3** to generate rhodium(III) species **C**. After β-hydrogen elimination and reductive elimination, aldehyde **E** would be produced. The subsequent rearrangement with the release of tosyl group would happen to afford intermediate **H**, which would then produce *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehyde **3** via aromatization in air (Scheme 2).

2. Results/discussion

With the above consideration in mind, we started to explore the possibility of this transformation. The initial studies were conducted with a model reaction of *N*′-(2-alkynylbenzylidene)hydrazide **1a** with 2-vinyloxirane **2a**. Only isoquinolinium-2-yl amide was obtained in the absence of an additional transition metal catalyst (Table 1, entry 1). A trace amount of product was detected when $Rh(OAc)_2$ was added as the co-catalyst (Table 1, entry 2). Interestingly, the expected compound **3a** was formed in 41% yield when the reaction was performed in the presence of $Rh(PPh_3)_3Cl$ (10 mol %) at room temperature (Table 1, entry 3). The structure of compound **3a** was confirmed by X-ray diffraction analysis

Table 1
Initial studies for the tandem reaction of *N*′-(2-alkynylbenzylidene)hydrazide **1a** with 2-vinyloxirane **2a**



Entry	[M] (cat.)	T (°C)	Solvent	Yield[a] (%)
1	—	25	DCE	Trace
2	$Rh(OAc)_2$ (10 mol %)	25	DCE	Trace
3	$Rh(PPh_3)_3Cl$ (10 mol %)	25	DCE	41
4	$Pd(PPh_3)_4$ (10 mol %)	25	DCE	13
5	CuI (10 mol %)	25	DCE	7
6	$Au(PPh_3)Cl$ (10 mol %)	25	DCE	Trace
7	$Rh(PPh_3)_3Cl$ (10 mol %)	50	DCE	77
8	$Rh(PPh_3)_3Cl$ (10 mol %)	50	THF	46
9	$Rh(PPh_3)_3Cl$ (10 mol %)	50	MeCN	65
10	$Rh(PPh_3)_3Cl$ (10 mol %)	50	DCM	57
11	$Rh(PPh_3)_3Cl$ (10 mol %)	50	Toluene	30
12	$Rh(PPh_3)_3Cl$ (10 mol %)	50	1,4-Dioxane	17
13	$Rh(PPh_3)_3Cl$ (2 mol %)	50	DCE	32
14	$Rh(PPh_3)_3Cl$ (5 mol %)	50	DCE	58

[a] Isolated yield based on *N*′-(2-alkynylbenzylidene)hydrazide **1a**.

concurrently (Fig. 2, also see Supplementary data). We also tested other transition metal salts, such as $Pd(PPh_3)_4$, CuI, and $Au(PPh_3)_3Cl$ (Table 1, entries 4–6). However, the results were inferior. The yield was dramatically increased to 77% when the reaction occurred at 50 °C (Table 1, entry 7). We further examined the reaction in various solvents, and no better results were obtained (Table 1, entries 8–12). The yield was lower when the amount of $Rh(PPh_3)_3Cl$ was decreased (Table 1, entries 13 and 14).

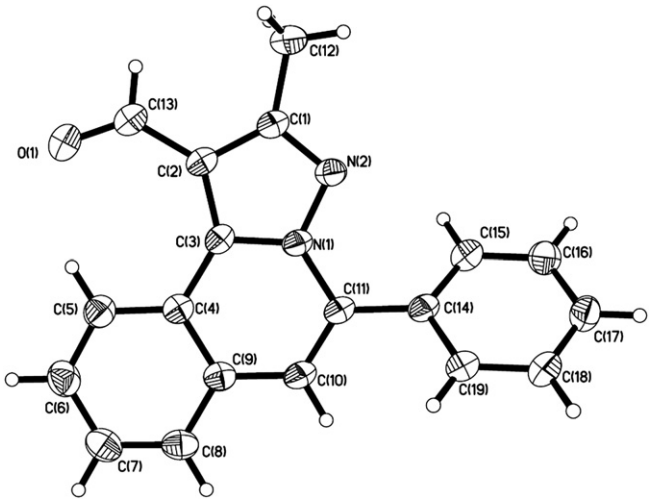
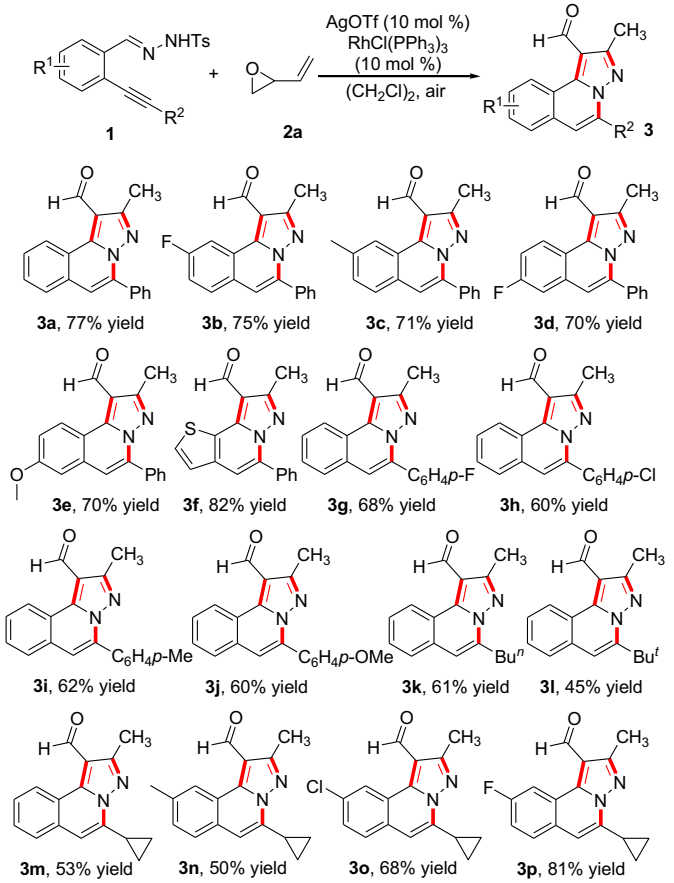


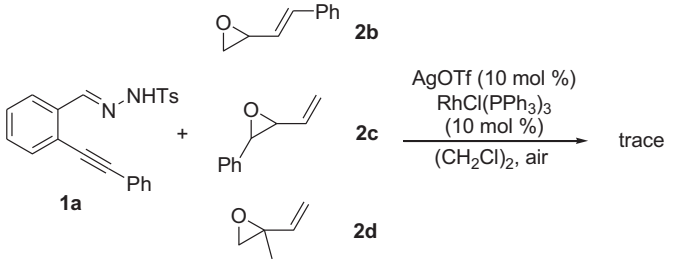
Fig. 2. X-ray ORTEP illustration of *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehyde **3a**.

Under the optimal conditions as mentioned in Table 1 (entry 7), we then explored the scope and generality of this silver(I)–rhodium(I) cooperative catalysis in the tandem reaction[1d,8] of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane. The results are presented in Scheme 3. This transformation shows high efficiency, which leads to the corresponding *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehyde **3** in moderate to good yields. Different functional groups were compatible during the conversion. Additionally, the thienyl-substituted *N*′-(2-alkynylbenzylidene)hydrazide

was a suitable substrate as well, giving rise to the desired product **3f** in 82% yield. However, the reactions failed to furnish the expected products under the standard conditions when *N*′-(2-alkynylbenzylidene)hydrazide **1a** reacted with 2-vinyloxiranes **2b**–**d** (Scheme 4). This might be due to the steric hindrance of 2-vinyloxiranes, which hampered the efficiency of the reaction.



Scheme 3. Synthesis of *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehydes via a tandem reaction of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane.



Scheme 4. Reactions of *N*′-(2-alkynylbenzylidene)hydrazide **1a** with other 2-vinyloxiranes.

3. Conclusions

In summary, we have described a silver(I)–rhodium(I) cooperative catalysis in the reaction of *N*′-(2-alkynylbenzylidene) hydrazide with 2-vinyloxirane. During the tandem process, multiple bonds are formed and *H*-pyrazolo[5,1-*a*]isoquinoline-1-carbaldehydes could be obtained in moderate to good yields under mild conditions. The presence of carbonyl group in the scaffold of *H*-pyrazolo[5,1-*a*]isoquinoline could be further elaborated, which would allow the generation of diverse *H*-pyrazolo[5,1-*a*]isoquinolines. Currently, construction of other *N*-heterocycles using the strategy of cooperative catalysis is under investigation in our laboratory.

4. Experimental section

4.1. General procedure of the tandem reaction of *N*′-(2-alkynylbenzylidene)hydrazide with 2-vinyloxirane

Silver triflate (0.03 mmol, 7.7 mg) was added to a solution of *N*′-(2-alkynylbenzylidene)hydrazide **1** (0.3 mmol) in DCE (2.0 mL), and the solution was stirred at 70 °C under N_2 for 2 h. Subsequently, $RhCl(PPh_3)_3$ (0.03 mmol, 28 mg) and 2-vinyloxirane **2a** (0.45 mmol, 32 mg) were added. The reaction was stirred at 50 °C under air. After completion of the reaction as indicated by TLC, the solvent was evaporated and the residue was purified on silica gel by flash column chromatograph (eluting with PE/EA=8/1) to afford the product **3**.

4.1.1. 2-Methyl-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3a***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.70–7.67 (m, 1H), 7.85–7.83 (m, 2H), 7.80–7.78 (m, 1H), 7.70–7.68 (m, 2H), 7.54–7.52 (m, 3H), 7.25 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.5, 156.1, 139.9, 137.8, 133.1, 131.2, 130.0, 129.7, 129.5, 128.3, 127.7, 127.5, 126.8, 123.5, 115.6, 114.1, 13.2; HRMS calcd for $C_{19}H_{14}N_2NaO^+$ $[M+Na]^+$: 309.0998, found 309.0996.

4.1.2. 9-Fluoro-2-methyl-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3b***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H), 9.61–9.58 (m, 1H), 7.83–7.56 (m, 3H), 7.54–7.528 (m, 3H), 7.45–7.41 (m, 1H), 7.24 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 161.4 (d, $^1J_{CF}$=251.1 Hz), 156.6, 139.4, 137.5, 133.1, 129.9, 129.8, 129.26, 128.4, 128.1, 125.0, 115.5, 115.0, 114.3, 113.2 (d, $^2J_{CF}$=24.6 Hz), 13.3; HRMS calcd for $C_{19}H_{14}FN_2NaO^+$ $[M+Na]^+$: 327.0904, found 327.0906.

4.1.3. 2,9-Dimethyl-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3c***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H), 9.41 (s, 1H), 7.84–7.82 (m, 2H), 7.69 (d, J=8.0 Hz, 1H), 7.52–7.51 (m, 4H), 7.21 (s, 1H), 2.70 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 156.1, 139.8, 138.0, 137.1, 133.3, 131.7, 129.8, 129.7, 129.2, 128.2, 126.8, 123.2, 115.8, 115.3, 114.14, 22.0, 13.5; HRMS calcd for $C_{20}H_{16}N_2NaO^+$ $[M+Na]^+$: 323.1155, found 323.1167.

4.1.4. 8-Fluoro-2-methyl-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3d***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 1H), 9.60–9.56 (m, 1H), 7.82–7.81 (m, 2H), 7.78–7.74 (m, 1H), 7.53–7.52 (m, 3H), 7.44–7.40 (m, 1H), 7.23 (s, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.4, 161.3 (d, $^1J_{CF}$=247.4 Hz), 156.5, 139.2, 137.3, 132.9, 129.7, 129.0, 128.3, 127.9, 124.9, 115.3, 114.9, 114.2, 113.0 (d, $^2J_{CF}$=24.6 Hz), 13.1; HRMS calcd for $C_{19}H_{13}FN_2NaO^+$ $[M+Na]^+$: 327.0904, found 327.0917.

4.1.5. 8-Methoxy-2-methyl-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3e***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21 (s, 1H), 9.67–9.65 (m, 1H), 7.83–7.81 (m, 2H), 7.52–7.50 (m, 3H), 7.27–7.24 (m, 1H), 7.15 (s, 1H), 7.10–7.09 (m, 1H), 3.92 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.2, 160.7, 156.3, 140.0, 138.2, 133.4, 129.8, 128.2, 117.9, 117.4, 115.4, 114.9, 113.3, 107.5, 107.0, 55.3, 12.9; HRMS calcd for $C_{20}H_{16}N_2NaO_2^+$ $[M+Na]^+$: 339.1104, found 339.1109.

4.1.6. H-Pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3f***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 7.83 (d, J=6.0 Hz, 2H), 7.72 (d, J=5.2 Hz, 1H), 7.53–7.51 (m, 3H), 7.43 (d, J=5.2 Hz, 1H), 7.37 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 154.9, 139.1, 138.0, 137.4, 133.2, 131.4, 129.7, 129.5, 128.3, 127.2, 123.4, 111.3, 111.0,

12.7; HRMS calcd for $C_{17}H_{12}N_2NaOS^+$ $[M+Na]^+$: 315.0563, found 315.0587.

4.1.7. 5-(4-Fluorophenyl)-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3g***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 9.68–9.66 (m, 1H), 7.85–7.77 (m, 3H), 7.70–7.68 (m, 2H), 7.22–7.19 (m, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 163.4 (d$^1J_{CF}$=249.5 Hz), 156.3, 140.0, 136.9, 131.8, 131.2, 130.2, 129.2, 127.9, 127.7, 127.0, 123.6, 115.8, 115.2 (d, $^2J_{CF}$=22.8 Hz), 114.3, 13.1; HRMS calcd for $C_{19}H_{13}FN_2NaO^+$ $[M+Na]^+$: 327.0904, found 327.0906.

4.1.8. 5-(4-Chlorophenyl)-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3h***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 9.68–9.66 (m, 1H), 7.39 (d, J=8.4 Hz, 3H), 7.71–7.69 (m, 2H), 7.50 (d, J=8.4 Hz, 2H), 7.24 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 156.3, 139.0, 136.8, 135.6, 131.5, 131.1, 130.2, 128.5, 128.0, 127.7, 127.0, 123.7, 115.9, 115.4, 114.3, 13.0; HRMS calcd for $C_{19}H_{13}ClN_2NaO^+$ $[M+Na]^+$: 343.0609, found 343.0627.

4.1.9. 2-Methyl-5-p-tolylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3i***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H), 9.70–9.68 (m, 1H), 7.81–7.78 (m, 1H), 7.74 (d, J=8.0 Hz, 2H), 7.70–7.68 (m, 2H), 7.34 (d, J=8.0 Hz, 2H), 7.25 (s, 1H), 2.71 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 156.3, 140.0, 139.7, 138.1, 131.4, 130.1, 129.7, 129.3, 128.9, 127.7, 126.9, 123.5, 115.6, 115.1, 114.2, 21.5, 13.1; HRMS calcd for $C_{20}H_{16}N_2NaO^+$ $[M+Na]^+$: 323.1155, found 323.1181.

4.1.10. 5-(4-Methoxyphenyl)-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3j***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 9.68–9.64 (m, 1H), 7.81–7.75 (m, 3H), 7.67–7.65 (m, 2H), 7.21 (s, 1H), 7.04 (d, J=8.0 Hz, 2H), 3.89 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 160.7, 156.3, 140.1, 137.9, 131.5, 131.3, 130.1, 127.6, 126.9, 125.6, 123.5, 115.4, 114.9, 114.2, 113.7, 55.6, 13.2; HRMS calcd for $C_{20}H_{16}N_2NaO_2^+$ $[M+Na]^+$: 339.1104, found 339.1122.

4.1.11. 5-Butyl-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3k***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.30 (s, 1H), 9.59 (d, J=7.2 Hz, 1H), 7.73–7.61 (m, 3H), 7.04 (s, 1H), 3.18 (t, J=7.6 Hz, 2H), 2.75 (s, 3H), 1.90–1.82 (m, 2H), 1.54–1.48 (m, 2H), 1.01 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 156.0, 139.5, 139.2, 131.3, 129.8, 127.4, 127.0, 126.3, 123.0, 114.2, 112.8, 30.7, 29.0, 22.4, 14.09, 13.0; HRMS calcd for $C_{17}H_{18}N_2NaO^+$ $[M+Na]^+$: 289.1311, found 289.1342.

4.1.12. 5-tert-Butyl-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3l***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H), 9.60 (d, J=8.4 Hz, 1H), 7.76–7.74 (m, 1H), 7.68–7.62 (m, 2H), 7.16 (s, 1H), 2.76 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 154.8, 146.0, 140.8, 131.3, 129.7, 127.2, 126.8, 123.2, 113.3, 111.7, 111.2, 36.2, 28.4, 13.2; HRMS calcd for $C_{17}H_{18}N_2NaO^+$ $[M+Na]^+$: 289.1311, found 289.1345.

4.1.13. 5-Cyclopropyl-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3m***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 9.69 (d, J=8.0 Hz, 1H), 7.69–7.61 (m, 3H), 6.83 (s, 1H), 2.78–2.71 (m, 4H), 1.24–1.21 (m, 2H), 0.95–0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 156.1, 140.6, 139.5, 131.3, 129.8, 127.4, 126.9, 126.3, 122.8, 114.3, 109.7, 13.4, 11.2, 7.7; HRMS calcd for $C_{16}H_{14}N_2NaO^+$ $[M+Na]^+$: 273.0998, found 273.1015.

4.1.14. 5-Cyclopropyl-2,9-dimethylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3n***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 1H), 9.32 (s, 1H), 7.58 (d, J=8.0 Hz, 1H), 7.46 (d, J=7.6 Hz, 1H), 6.80 (s, 1H), 2.78–2.69 (m, 4H), 2.56 (s, 3H), 1.23–1.19 (m, 2H), 0.93–0.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 156.0, 139.7, 137.1, 131.4, 129.2, 126.8, 126.2, 122.9, 114.2, 109.6, 22.1, 13.2, 11.2, 7.6; HRMS calcd for $C_{17}H_{16}N_2NaO^+$ $[M+Na]^+$: 287.1155, found 287.1172.

4.1.15. 9-Chloro-5-cyclopropyl-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3o***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21 (s, 1H), 9.66 (s, 1H), 7.54–7.53 (m, 2H), 6.74 (s, 1H), 2.76–2.68 (m, 4H), 1.24–1.21 (m, 2H), 0.94–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.2, 156.3, 140.9, 138.3, 132.5, 130.2, 129.4, 127.4, 126.8, 123.5, 114.2, 108.9, 13.2, 11.5, 7.9; HRMS calcd for $C_{16}H_{13}ClN_2NaO^+$ $[M+Na]^+$: 307.0609, found 307.0634.

4.1.16. 5-Cyclopropyl-9-fluoro-2-methylH-pyrazolo[5,1-a]isoquinoline-1-carbaldehyde ***3p***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21 (s, 1H), 9.46 (dd, J=10.8, 1.8 Hz, 1H), 7.65–7.62 (m, 1H), 7.39–7.34 (m, 1H), 6.79 (s, 1H), 2.77–2.69 (m, 4H), 1.25–1.22 (m, 2H), 0.91–0.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 160.7 (d, $^1J_{CF}$=246.5 Hz), 156.3, 139.9, 138.7, 127.9, 123.8, 118.6, 114.1, 112.80 (d, $^2J_{CF}$=23.9 Hz), 109.3, 13.1, 11.5, 7.7; HRMS calcd for $C_{16}H_{13}FN_2NaO^+$ $[M+Na]^+$: 291.0904, found 291.0929.

Acknowledgements

Financial support from National Natural Science Foundation of China (Nos. 21032007, 21172038) is gratefully acknowledged.

Supplementary data

Experimental procedure, characterization data, ^{1}H and ^{13}C NMR spectra of compounds **3**, and a CIF file of compound **3a** are available. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.018. These data include MOL files and InChiKeys of the most important compounds described in this article.

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