Supporting Information

Ruthenium(II)-Catalyzed Regioselective C-H Hydroxymethylation of N-Aryl-Azaindoles with Paraformaldehyde

Siqi Li, a, b Yang Yu, a* Yaxi Yang, b,c and Bing Zhou b,c*

a Department of Chemistry, College of Sciences, Shanghai University, 99 Shangda Road, Shanghai 200444, PR China

b State Key Laboratory of Drug Research, Department of Medicinal Chemistry, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zu Chong Zhi Road, Shanghai 201203, PR China

c University of Chinese Academy of Sciences, Beijing 100049, PR China

E-mail address: zhoubing@simm.ac.cn (B. Zhou), yangyu2017@shu.edu.cn (Y. Yu).

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**General Information:**

Mass spectra and high-resolution mass spectra were measured on a Finnigan MAT-95 mass spectrometer. $^1$H and $^{13}$C NMR spectra were determined on Bruker AM-300, Bruker AM-400, Bruker AM-500 instruments using tetramethylsilane as internal reference. Data are presented as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, m = multiplet), J = coupling constant in hertz (Hz). Silica gel 60H (200 – 300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated.

**Mechanistic study**

(a) Procedure for H/D exchange experiment:

A mixture of 1a (0.2 mmol), [RuCl$_2$(p-cymene)]$_2$ (5 mol %), AgSbF$_6$ (20 mol %), NaH$_2$PO$_4$ (20 mol %), DCE: D$_2$O = 10: 1 (2 mL) in sealed tube and the mixture was stirred at 60 °C for 30 min. The solvent was removed under reduced pressure and the residue was purified the residue by silica gel chromatograph to recovery 1a.
A mixture of 1a (0.2 mmol), 2a (0.6 mmol, 3 equiv), [RuCl₂(p-cymene)]₂ (5 mol %), AgSbF₆ (20 mol %), NaH₂PO₄ (20 mol %) were dissolved in DCE: D₂O (10: 1) (2 mL) in sealed tube and the mixture was stirred at 60 ℃ for 2 h. The solvent was removed under reduced pressure to give the residue which was purified the residue by silica gel chromatograph to give 1a-dₙ and 3a.
(b) Competitive experiment:

A mixture of 1b (0.1 mmol), 1e (0.1 mmol), 2a (0.1 mmol), [RuCl₂(p-cymene)]₂ (5 mol %), AgSbF₆ (20 mol %), NaH₂PO₄ (20 mol %) were dissolved in DCE (1 ml) in sealed tube and the mixture was stirred at 60 °C for 36 h. The solvent was removed under reduced pressure and the residue was purified the residue by silica gel chromatograph to give 3b and 3e (3.7:1).
$^1$H and $^{13}$C NMR Spectrum of Compounds

Compound 3a
Compound 3b
Compound 3c
Compound 3d
Compound 3e
Compound 3g
Compound 3h
Compound 3j
Compound 3k
Compound 3l
Compound 3n
Compound 4a
Compound 4b