CHEMISTRY
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Authors: Aniruddha Biswas, Souradip Sarkar, and Rajarshi Samanta

To be cited as: *Chem. Eur. J.* 10.1002/chem.201806373

Link to VoR: http://dx.doi.org/10.1002/chem.201806373

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Rh(III)-Catalyzed Straightforward Synthesis of Benzophenanthroline and Benzophenanthrolinone Derivatives using Anthranils

Aniruddha Biswas, Souradip Sarkar and Rajarshi Samanta*[a]

Abstract: An efficient pot-economic and step-economic Rh(III)-catalyzed site-selective direct amination/annulation strategy was developed for the synthesis of benzophenanthroline derivatives using quinoline *N*-oxides and anthranils. The method was further extended to the synthesis of nitrogen-containing extended π-conjugated benzophenanthrolinone derivatives. Late-stage functionalizations of cinchonidine and cinchophen derivatives and synthesis of a bioactive quinolino-indole were furnished.

In contemporary organic synthesis, efficiency and environmental sustainability are the key factors. To address these issues, effective approaches like “step-economic” and “pot-economic” synthesis has emerged rapidly due to its simplicity and applicability in minimizing waste and reaction time.[1] Among nitrogen-containing polyaromatic hydrocarbons (PAHs), [1,10]phenanthroline and [1,10]phenanthrolin-one are frequent motifs in many pharmaceuticals, natural products, organic materials and ligands for catalysis (Figure 1).[2,3] Especially, these scaffolds are used as potential ligands in gold catalysed transformations.[3m-3o]

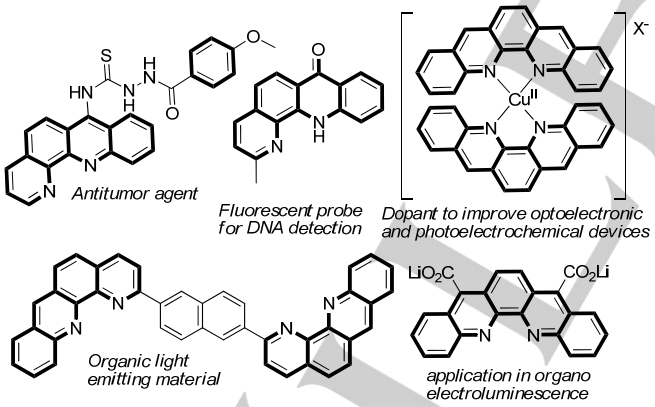
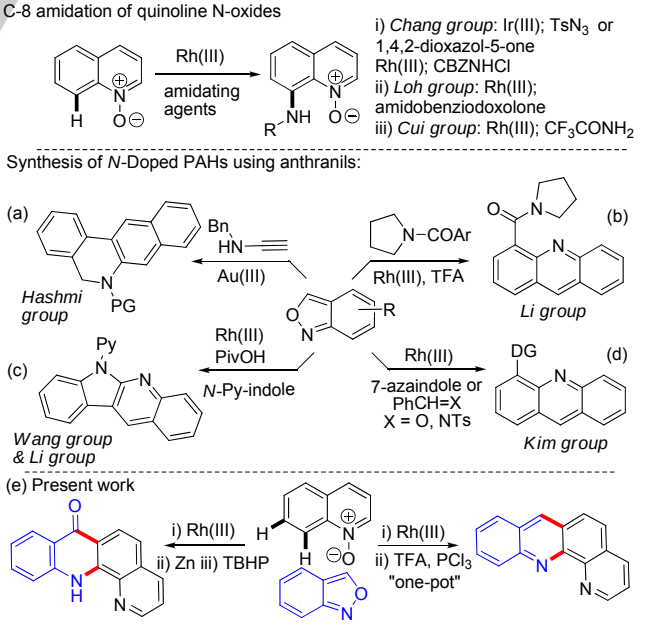


Figure 1: Important benzo[1,10]phenanthroline and benzo[1,10]phenanthrolin-one scaffolds

However, reported methods for their synthesis are in-general multistep procedures and suffer from poor yields or poor functional group tolerance.[2e-2g,4] Arguably, site-selective C-H functionalization/annulation is one of the best methods to access *N*-doped PAHs in a straightforward, facile and efficient manner.[5,6] Retrosynthetically, direct C8-aryl amination of quinoline derivative followed by condensation or oxidative coupling can provide the desired *N*-PAHs. Direct site-selective C-H bond functionalizations of quinoline are recent subject of interest.[7] Especially, a significant progress has been made on direct introduction of various functional groups at its C8 position by others[8] and us[9]. In pioneering work, Chang’s group elegantly established C8-amidation of quinoline *N*-oxides under Ir(III)[10] and Rh(III)[11] catalysis using various amidating sources. Loh and co-workers also established an Rh(III)-catalyzed alternative strategy for the C8-amidation of quinoline *N*-oxide using amidobenziodoxolone as the coupling partner.[12] Very recently, Cui’s group described another Rh(III)-catalyzed C8-amidation of quinoline *N*-oxide using commercially available trifluoroacetamide.[13] Recently, benzo[*c*]isoxazoles (anthranils) were highly admired as a bifunctional arylaminating agent under redox-neutral conditions for the direct aryl amination of sp^2 and sp^3 C-H bonds[14, 15] and straightforward construction of *N*-PAHs.[16-19]



Scheme 1. Direct amination/annulation strategies for *N*-containing extended π-conjugated systems.

[a] A. Biswas, S. Sarkar and Dr. R. Samanta
Department of Chemistry
Indian Institute of Technology Kharagpur
Kharagpur 721302, India
E-mail: rsamanta@chem.iitkgp.ac.in

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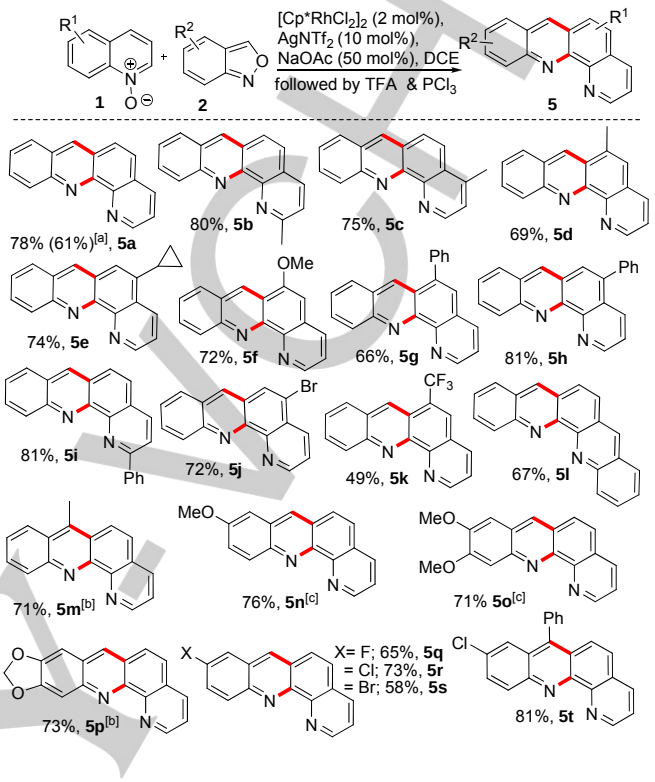
In a recent report, Hashmi and co-workers elegantly studied Au(III)-catalyzed construction of 2-amino pyrroles and quinoline-based polyazaheterocycles (Scheme 1a).[16a] In interesting developments, Li's group described Rh(III)-Catalyzed amination/annulation of arenes/heteroarenes using anthranils (Scheme 1b & c).[17] Wang's group independently revealed a tandem Rh(III)-catalyzed amination/annulation strategy to synthesize indoloquinoline derivatives (Scheme 1c).[18] Kim's group also extensively studied Rh(III)-catalyzed synthesis of acridine derivatives using various coupling partners (Scheme 1d).[19] However, as per best of our knowledge, there is no report for the synthesis of benzophenanthroline and benzophenanthrolin-one class of *N*-doped PAHs using pot and step-economic efficient strategy. Intrigued by our latest studies on step-economic synthesis of *N*-containing extended π-conjugated systems[9][20], we envisioned that similar idea might help us to obtain our desired *N*-containing extended π-conjugated systems. Herein, we report Rh(III)-catalyzed site-selective direct strategies for the pot-economic construction of benzophenanthroline and step-economic synthesis of benzophenanthrolin-one (Scheme 1e).

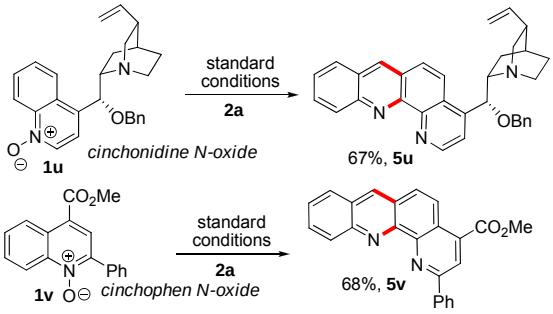
Our investigation started with the reaction of quinoline *N*-oxide (**1a**) with anthranil (**2a**) under different catalytic conditions. During the initial screening of suitable transition metal catalyst, $[Cp^*RhCl_2]_2$ was found out to be the best one in presence of $AgNTf_2$ additive surpassing the other known transition metal catalysts like $[Ru(p\text{-cymene})Cl_2]_2$, $[Cp^*IrCl_2]_2$, $[Cp^*Co(CO)I_2]$ with 46% isolated yield of **3a** (see ESI table 1, entries 1-4). For further improvement of the yield of **3a**, various acetate additives were tested. With our great pleasure, NaOAc was found to be the best one (see ESI table 1, entries 5-9) in DCE solvent with 89% isolated yield of **3a**. Other solvents did not turn out be effective except THF with 74% yield of **3a** (see ESI table 1, entries 10-14). As the aryl amination reaction didn't proceed with satisfactory yield in the presence of an acid additive (important for annulations), we planned for sequential addition of required reagents in one pot strategy for the synthesis of our desired benzo[*b*][1,10]phenanthroline (**5a**). To optimize the yield of annulated product **5a** in the same reaction system, we added TFA followed by PCl_3 (see ESI table 1, entries 15-18) with 71% of isolated yield. More simply, both TFA (8 equiv) and PCl_3 (4 equiv) were added together after complete formation of **3a** and reaction was continued for 12 h. Gladly, the isolated yield of the desired product **5a** was found to be best with 78% (see ESI table 1, entry 19) while the yield of **5a** got decreased under less reaction time (see ESI table 1, entry 20).

Our preliminary investigations focused on the synthesis of benzophenanthroline derivatives having electronically and sterically variable functional groups. Initially, different quinoline *N*-oxides were surveyed (Scheme 2, **5a**-**5l**). Alkyl groups and electron donating methoxy group were well tolerated during the operation (Scheme 2, **5a**-**5f**). Interestingly, a promising scope with more extended conjugated systems also synthesized in very good yields (Scheme 2, **5g**-**5i**). Next, the halogen also firmly accommodated under the optimized conditions keeping the window open for further modifications (Scheme 2, **5j**). Scope with electron withdrawing CF_3 group also generated albeit in moderate yield (Scheme 2, **5k**). Gratifyingly, another important class of *N*-containing heterocycle, that is, acridine *N*-oxide also provided the monoarylaminated/annulated product **5l** selectively in good yield.



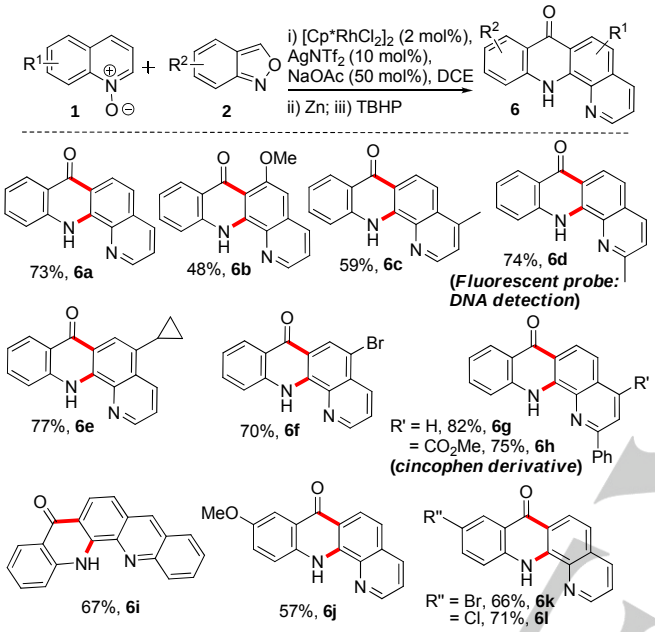
Scheme 2. Scope of benzophenanthroline *via* direct C8-arylamination/annulation strategy. Reaction Conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), $AgNTf_2$ (10 mol%), NaOAc (50 mol%), DCE (0.2 M), 18-24 h, 110 °C, Then TFA (8 equiv) and PCl_3 (4 equiv), 6-8 h 110 °C; [a] reaction was done in 2 mmol scale; [b] Reaction temperature: 150 °C; [c] NaOAc (1 equiv) used.

Additionally, the structure of **5b and 5l** were unequivocally confirmed *via* the comparison of known literature data.[2g, 4a] Next, the scope with different anthranil derivatives was explored. Pleasingly, anthranils with different electronic and steric properties provided the desired benzophenanthroline derivatives with good to excellent yields (Scheme 2, **5m**-**5t**).



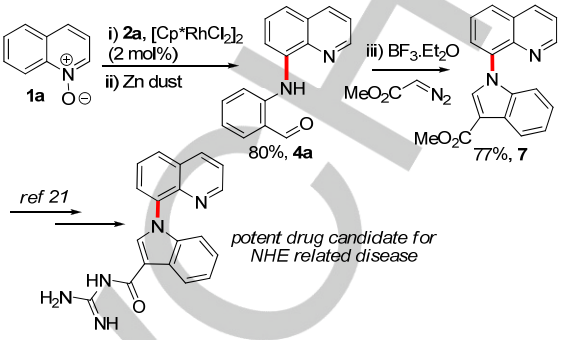
Scheme 3. Late-stage modification of cinchonidine and cinchophen derivative

Further, to demonstrate the application of the developed method late-stage modifications were carried out on more complex bioactive molecules. Notably, cinchonidine *N*-oxide substrate was modified to its benzophenanthroline derivative in 67% yield under the developed reaction conditions (Scheme 3, **5u**). This compound can be an important strategic platform to generate useful bifunctional catalysts. The method was further extended towards the modification of another drug molecule cinchophen derivative in good yield under the optimized conditions (Scheme 3, **5v**).



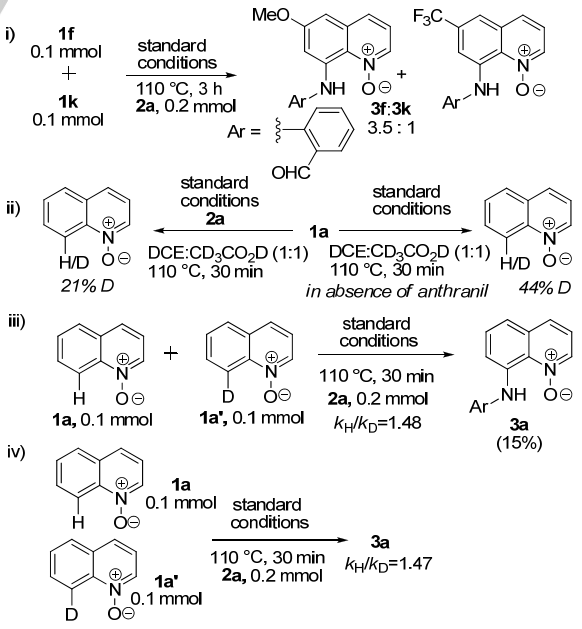
Scheme 4. Scope of benzophenanthrolinone via C8-amination/oxidative coupling based strategy. Reaction conditions: i) **1** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), $AgNTf_2$ (10 mol%), NaOAc (50 mol%), DCE (0.2 M), 18-24 h, 110 °C; ii) **3** (amount obtained from step i), 1:1 THF & 30% aq. NH_4Cl solution (5 mL), Zn dust (7 equiv w.r.t. **1**), 10 min, rt; iii) **4** (amount obtained from step ii), DCE, TBHP in decane (5 equiv w.r.t. **1**), 110°C, 6-12 h. Yields were determined after three steps.

Furthermore, we hypothesized that the developed C8-arylamination can be forwarded to the construction of important benzophenanthrolinone[3] core in step-economic fashion. Hence, the crucial Rh(III)-catalyzed C8-aryl amination of quinoline *N*-oxides, followed by zinc-mediated deoxygenation and subsequent TBHP based oxidative coupling led to the formation of expected benzophenanthrolinone moiety (Scheme 4). A brief survey of the substrate scope revealed that the generation of this *N*-doped extended π-conjugated core (*N*-PAHs) via our strategy is quite general having different substitutions both in *N*-oxide as well as in anthranil part. Electron donating alkyl or methoxy group at the quinoline core survived with very good yields (Scheme 4, **6a**-**6e**). Next, Compound **6d,** known as a fluorescent probe in DNA detection was synthesized using this unified strategy.[2h] Further, halogen or electron withdrawing groups in quinoline moiety also firmly tolerated under the developed conditions (**6f**-**6h**). More conjugated acridine *N*-oxide also provided the monoarylaminated/oxidatively coupled derivative **6i** in good yield. Various anthranils were also explored for the construction of benzophenanthrolinone core (**6j**-**6l**).



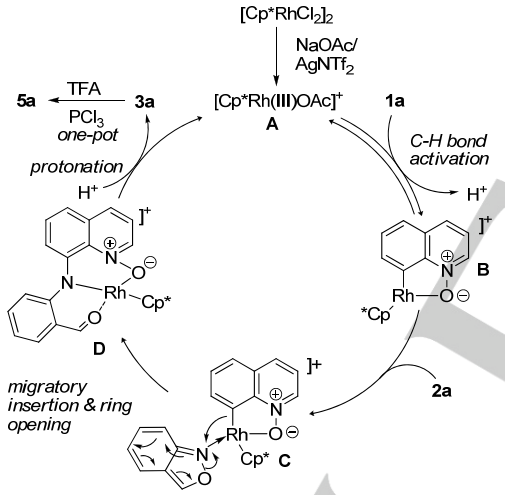
Scheme 5. Step-economic synthesis of an advanced intermediate of the potent drug candidate. Reaction conditions: i) **1** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgNTf_2$ (10 mol%), NaOAc (50 mol%), DCE (0.2 M), 18 h, 110 °C; ii) Zn dust (7 equiv), THF: aq. NH_4Cl (1:1, 5 mL), 10 min, rt. iii) **4a** (0.1 mmol), $BF_3.Et_2O$ (0.12 mmol), N_2=$CHCO_2Me$ (0.5 mmol), DCM, 0 °C-rt, 2 h.

To delineate another practical utility of the developed protocol, a drug candidate used for NHE related disease was developed (Scheme 5) under the optimized conditions.[21] First, the crucial Rh(III)-catalyzed C8-arylamination of quinoline *N*-oxide (**1a**) followed by Zn-mediated deoxygenation was performed to obtain the 2-aminoaldehyde compound **4a** which was further converted into the known substituted indole derivative **7** *via* [1,2]-aryl shift.[22] This advanced precursor **7** can be transformed into the potent drug candidate by literature known steps.[21]



Scheme 6. Control experiments for mechanistic studies

Numbers of control experiments were carried out to figure out more insight of the developed protocol (Scheme 6). First, substituted quinoline *N*-oxides **1f** and **1k** were treated with **2a** under optimized conditions to know the electronic preference. The outcome of the competition experiment shows that the rate of the reaction favours the electron-rich *N*-oxide over the electron-poor one (Scheme 6i). Next, treatment of **1a** with CD_3CO_2D as the co-solvent in the absence or presence of **2a** afforded significant H/D scrambling at the C8-position (Scheme 6ii) under optimized conditions. These results reveal that C-H activation step at C8-position is highly reversible and the further step ahead the C-H metalation is faster. Further, both competitive and parallel experiments with quinoline *N*-oxide (**1a**) and 8-$d_1$quinoline *N*-oxide (**1a'**) were performed to reveal whether C-H bond metalation is the rate determining step or not (Scheme 6 iii-iv). The obtained KIE (~1.5) suggests that C-H bond cleavage might not be involved in the rate determining step. Based on control experiments and previous literature[14, 15], a plausible mechanism for this unified Rh(III)-catalyzed straightforward strategy is proposed for the synthesis of benzophenanthroline and benzophenanthrolinone derivatives (Scheme 7).



Scheme 7. Plausible mechanism

First, the active catalyst **A** is generated from $[Cp^*RhCl_2]_2$ in the presence of NaOAc and $AgNTf_2$. Next, the acetate assistated C8-selective C-H bond metalation provides five-membered rhodacycle **B**. Further, nucleophilic nitrogen center of anthranil coordinates with **B** to afford the intermediate **C**. Subsequent ring opening and migratory insertion of nitrenoid species delivers intermediate **D** which further undergoes protodematalation to obtain compound **3a** with the regenration of active Rh(III)-catalyst. Finally, the trifluoroacetic acid mediated annulation and PCl_3 triggered deoxygentaion leads to our desired benzophenanthroline derivative **5a**. In another case, Zn based deoxygentaion of **3a** followed by TBHP mediated oxidative coupling offers desired benzophenanthrolinone compound **6a**.

In conclusion, we have accomplished a one-pot Rh(III)-catalyzed site-selective direct arylamination/annulation strategy for the synthesis of benzophenanthroline derivatives using isoxazoles as coupling partner. The method has been extended to the step-economic synthesis of benzophenanthrolinone derivatives and bioactive quinolino indole scaffold. Late-stage functionalizations of bioactive quinoline scaffolds were carried out. The application of benzophenanthroline derivatives as an ligand in catalytic reactions is currently underway in our laboratory.

Experimental Section

Quinoline *N*-oxide **1a** (29 mg, 0.2 mmol) was dissolved in 1 mL of dry DCE in a 10 mL sealed tube. Then $[Cp^*RhCl_2]_2$ (2 mol%, 2.4 mg) followed by $AgNTf_2$ (10 mol%, 7.8 mg), NaOAc (50 mol% 8.2 mg) and anthranil (**2a**, 45.5 mg, 0.4 mmol) were added to the solution. The reaction mixture was stirred for 18 h at 110 °C. After the mixture was cooled to room temperature, CF_3COOH (121 µL, 8 equiv.) and PCl_3 (70 µL, 4 equiv.) were added to the same reaction mixture and stirred for 12 h at 110 °C. After the completion of reaction, the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL) and neutralized using saturated $NaHCO_3$ solution. The organic layer was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography to obtain the pure products **5a**.

Acknowledgements

We thank CSIR, India for financial assistance through EMR project [02(0323)/17/EMR-II] and fellowship (AB). UGC, India is acknowledged for fellowship (SS). Authors appreciate DST, India (SR/FST/CSII-026/2013) for 500 MHz NMR facility and CRF(IIT Kharagpur) for the analytical facility.

Keywords: C-H Amination/Annulation • Anthranil • Rh(III)-catalysis • N-PAHs • Step-economic

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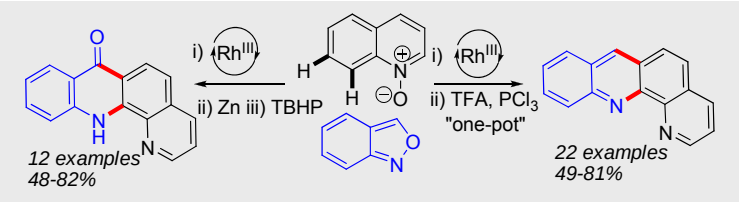

Rh(III)-catalyzed site-selective straightforward synthesis of benzophenanthroline and benzophenanthrolinone derivatives

*Aniruddha Biswas, Souradip Sarkar and Rajarshi Samanta**

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Rh(III)-Catalyzed Straightforward Synthesis of Benzophenanthroline and Benzophenanthrolinone Derivatives using Anthranils