

Anindya S. Manna[†], Rajesh Nandi[†], Prakash K. Mandal[†], Tanmoy Ghosh[†], Debabrata Barman[†], Dilip K. Maiti^{*†}
[†]Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata - 700009, WB, India.

Chem condensation product, isoindolin-1-imine (N), in 1 : 2 ratio



$\text{R} = \text{Ar}, \text{CH}_2\text{Ar}, \text{Ts}$

N, 85-95% yield

Reaction scheme for the synthesis of indole derivatives:

Starting materials: **2,6-diformyl-1-R-benzene** (R-substituted benzene ring with two aldehyde groups at positions 2 and 6) and **R-NH₂**.

Reaction conditions: **Ni(II), 10 mol%**.

Three reaction pathways are shown:

- Pathway 1:** **ACN, reflux, 1hr** → **Product N** (Indole derivative with R group at position 2 and R group on the nitrogen atom) **N, 85-95% yield**.
- Pathway 2:** **Toluene, 100°C, 2hr** → **Product N2** (Indole derivative with R group at position 2 and R group on the nitrogen atom) **N2, 75-80% yield**.
- Pathway 3:** **Toluene, 70°C, 3hr** → **Product N1** (Indole derivative with R group at position 2 and R group on the nitrogen atom) **N1, 35-55% yield**.

Substrate Scope(N1).

N1, 35-55% yield

Entry	Catalyst	mol%	Solvent	Temperature Conditions	Time(h)	Yield(%)
1	Zn(OTf) ₂	20	ACN	Reflux	24	NR ^a
2	Ni(OTf) ₂	20	ACN	Reflux	12	NR
3	NiCl ₂ ·4H ₂ O	20	ACN	Reflux	10	NR
4	Ru(p-cymene)Cl ₂	20	ACN	Reflux	8	NR
7	Ni(OAc) ₂ ·4H ₂ O	20	ACN	Reflux	2.5	NR
5	AgOTf	20	ACN	Reflux	10	NR
6	Ni(acac) ₃ ·2H ₂ O	20	ACN	Reflux	10	NR
7	Ni(OAc) ₂ ·4H ₂ O	20	ACN	Reflux	2.5	NR
8	Ni(OAc) ₂ ·4H ₂ O	20	Toluene	130 °C	3	60
9	Ni(OAc) ₂ ·4H ₂ O	20	Toluene	100 °C	2.5	70
10	Ni(OAc) ₂ ·4H ₂ O	15	Toluene	100 °C	2.5	80
11	Ni(OAc) ₂ ·4H ₂ O	10	Toluene	100 °C	3	85
12	Ni(OAc) ₂ ·4H ₂ O	5 ^b	Toluene	100 °C	3	70
13	Ni(OAc) ₂ ·4H ₂ O	10	Benzene	100 °C	4	70
14	Ni(OAc) ₂ ·4H ₂ O	10	ACN	70 °C ^c	12	NR
15	Ni(OAc) ₂ ·4H ₂ O	10	1,4-Dioxane	100 °C	8	NR
16	Ni(OAc) ₂ ·4H ₂ O	10	EDC	100 °C	6	35
17	Ni(OAc) ₂ ·4H ₂ O	10	DCM	80 °C	4	40
18	Ni(acac) ₃ ·2H ₂ O	10	Toluene	100 °C	4	65
19	Ni(OTf) ₂	10	Toluene	100 °C	6	50
20	NiCl ₂ ·4H ₂ O	10	Toluene	100 °C	6	60

❖ & Most importantly, we have developed a unique efficient switching method to prepare synthetically important moieties staring from same point.