

Supporting Information

Nickel-Catalyzed Molybdenum-Promoted Carbonylative Synthesis of Benzophenones

Jin-Bao Peng,^{*,†} Fu-Peng Wu,[†] Da Li,[†] Xinxin Qi,[†] Jun Ying[†] and Xiao-Feng Wu^{*,†,‡}

[†]Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, People's Republic of
China

[‡]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, Rostock 18059,
Germany

*E-mail: pengjb_05@zstu.edu.cn

*E-mail: xiao-feng.wu@catalysis.de

Table of Contents

1. Optimization of the Reaction Condition	S2
2. Copy of ¹H and ¹³C NMR Spectra of Products	S4

1. Optimization of the Reaction Condition

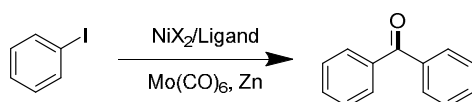


Table S1. Screening of Ni catalysts

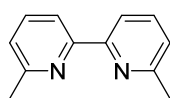
Entry	Condition	Yield (%)
1	NiCl ₂	64
2	NiBr₂	70
3	NiI ₂	69
4	Ni(cod) ₂	21
5	NiCl ₂ •glyme	63
6	Ni(acac) ₂	57

Reaction conditions: Iodobenzene (0.5 mmol), catalyst (5 mol%), dtbbpy (5 mol%), Mo(CO)₆ (1 equiv), Zn (3 equiv), dioxane (2 mL), 120 °C, 16 h.

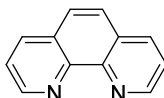
Table S2. Screening of the ligands

Entry	Condition	Yield (%)
1	dtbbpy	70
2	bpy	63
3	L1	62
4	L2	50
5	L3	70
6	PCy ₃	28
7	Xantphos	50

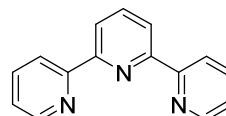
Reaction conditions: Iodobenzene (0.5 mmol), NiBr₂ (5 mol%), ligand (5 mol%), Mo(CO)₆ (1 equiv), Zn (3 equiv), dioxane (2 mL), 120 °C, 16 h.



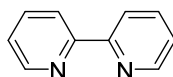
L1



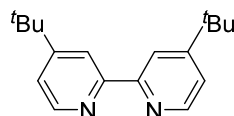
L2



L3



bpy



dtbbpy

Table S3. Screening of solvents

Entry	Condition	Yield (%)
1	Dioxane	70
2	THF	17
3	DMF	3
4	Toluene	17
5	Acetonitrile	0
6	Acetone	0
7	Ethyl acetate	29
8 ^[b]	Dioxane	74

Reaction conditions: Iodobenzene (0.5 mmol), NiBr₂ (5 mol%), dtbbpy (5 mol%), Mo(CO)₆ (1 equiv), Zn (3 equiv), solvent (2 mL), 120 °C, 16 h. [b] 1 mmol Iodobenzene.

Table S4. Screening of other conditons

Entry	Condition	Yield (%)
1	standard	74
2	dtbbpy (3.8 mol%, L:Ni=1.5:1)	74
3	dtbbpy (5.0 mol%, L:Ni=2.0:1)	65
4	dtbbpy (7.5 mol%, L:Ni=3.0:1)	69
5	NiBr ₂ (2.0 mol%), dtbbpy (2.0 mol%)	15
6	NiBr ₂ (1.0 mol%), dtbbpy (1.0 mol%)	9
7	Dioxane (0.5 mL), 16 h	74
8	Dioxane (0.5 mL), 24 h	60
9	Dioxane (0.5 mL), 10 h	82
10	Dioxane (0.5 mL), 8 h	86
11	Dioxane (0.5 mL), 6 h	90(86) ^[b]
12	Dioxane (0.5 mL), 4 h	79
13	Dioxane (0.5 mL), 2 h	69

Reaction conditions: Iodobenzene (1 mmol), NiBr₂ (2.5 mol%), dtbbpy (2.5 mol%), Mo(CO)₆ (0.5 equiv), Zn (1.5 equiv), dioxane (2 mL), 120 °C, 16 h. [b] isolated yield.

Table S5. Screening of CO source

Entry	Condition	Yield (%)
1	Mo(CO) ₆	90
2	Cr(CO) ₆	35
3	Fe ₃ (CO) ₁₂ (0.25 equvi)	0
4	No NiBr ₂ and dtbbpy	24

Reaction conditions: Iodobenzene (1 mmol), NiBr₂ (2.5 mol%), dtbbpy (2.5 mol%), Mo(CO)₆ (0.5 equiv), Zn (1.5 equiv), dioxane (2 mL), 120 °C, 6 h.

2. Copy of ^1H and ^{13}C NMR Spectra of Products

