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Original scientific paper

Synthesis and process optimization of Boscalid by catalyst Pd-PEPPSI-IPr$^{\text{DtBu-An}}$

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Abstract: The purpose of this research was to reduce the amount of noble metal palladium catalyst and improve the catalytic performance in the Suzuki–Miyaura cross-coupling reaction, which is the key step in the synthesis of Boscalid. Taking *o*-bromonitrobenzene and *p*-chlorophenylboronic acid as raw materials, three kinds of Pd-PEPPSI-IPr catalysts were synthesized and employed in the Suzuki reaction, and then the biaryl product was subjected to reduction and condensation reaction to give Boscalid. Under the optimal reaction conditions, the result showed that the catalytic system exhibits highest catalytic efficiency under aerobic conditions, giving the 2-(4-chlorophenyl)nitrobenzene in over 99 % yield. Moreover, the Pd-PEPPSI-IPr$^{\text{DtBu-An}}$ catalyst was minimized to 0.01 mol%. The synthesis process was mild, the post-treatment was simple, and the production cost was reduced, which makes it suitable for industrial production.

Keywords: Boscalid; Suzuki reaction; Pd-PEPPSI-IPr$^{\text{DtBu-An}}$ synthesis.

INTRODUCTION

Boscalid has the advantages of low toxicity, high efficiency and no cross-resistance with other fungicides.[1] It has significant therapeutic effects on gray mold, black spot and powdery mildew.[2] It also has the advantages of rapid absorption, low environmental pollution, obvious therapeutic effect, resistance to rain erosion, rapid diffusion, safe crops, and long duration.[3] Boscalid was introduced into the market by BASF® in 2003, the current total production volume of this fungicide is more than 1000 t year^{-1}.[4] Boscalid has very broad application prospects in the world's agricultural sector. It would be of great value to develop a more efficient route suitable for the synthesis of Boscalid. Currently, the main production cost of Boscalid is the palladium catalyst that catalyzes the Suzuki reaction.[5,6] Cost reduction could be achieved by minimizing the amount of noble metal palladium catalyst and not using iodine-containing reagents. In accordance with the industrial synthesis method of Boscalid, the synthesis of 2-(4-chloro-

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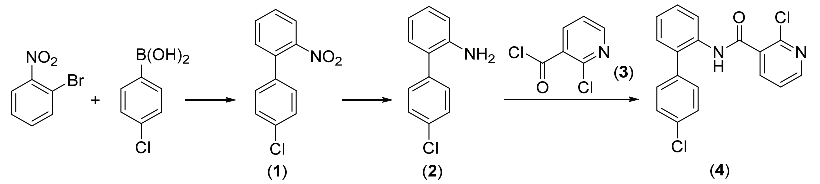
phenyl)nitrobenzene with halogenated nitrobenzene as the raw material is low cost and the method is mature.[3,4,7,8] Although it is suitable for industrial production, a noble metal, such as $Pd(PPh_3)_4$, is necessary as a catalyst in the Suzuki reaction.[5,9] In the reduction path of the traditional method, palladium carbon hydrogenation is used although the cost is higher and the operation is very complicated.[10] In this study, Pd-PEPPSI-IPr$^{DtBu-An}$ (1,2-di(*tert*-butyl)acenaphthyl(DtBu-An)-based Pd-PEPPSI) catalyst was used to increase the catalytic efficiency in the key step of the Suzuki reaction, and a more economic reduction method was used to reduce the manufacturing cost of Boscalid (Scheme 1).



Scheme 1. The synthesis route of Boscalid (**4**).

EXPERIMENTAL

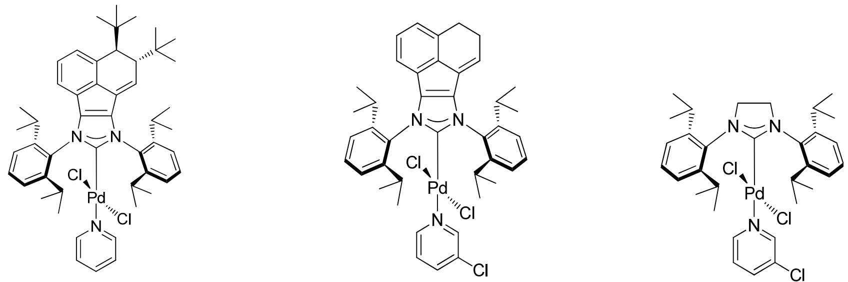
Materials and apparatus

o-Bromonitrobenzene and *p*-chlorophenylboronic acid were purchased from Shanghai DaRui Fine Chemical Co. Ltd. The ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ using a Bruker Avance III HD 400 MHz spectrometer with tetramethylsilane (TMS) as the internal standard; chemical shifts are expressed in ppm. Melting points were determined on an X-4 apparatus. Thin layer chromatography (TLC) was performed on commercial GF_{254} silica-backed plates. The optimization of the reaction conditions was performed in a WATTECSTM WP-RH-1020 parallel reactor. Gas chromatographic analysis was performed on a Shimadzu GC-2010 plus chromatograph with a flame ionization detector. The mass spectra were recorded on a Thermo Scientific™ ISQ-7000 GC–MS.

Analytical and spectral data are given in Supplementary material to this paper.

Structure of the Pd-PEPPSI-IPr catalysts

Pd-PEPPSI-IPr$^{DtBu-An}$, Pd-PEPPSI-IPr^{An} and Pd-PEPPSI-IPr (Scheme 2) were synthesized according to literature reports.[11-13]



Pd-PEPPSI-IPr$^{DtBu-An}$ (**Cat1**) Pd-PEPPSI-IPr^{An} (**Cat2**) Pd-PEPPSI-IPr (**Cat3**)

Scheme 2. The structure of Suzuki–Miyaura cross-coupling catalysts.

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*Synthesis of 2-chloronicotinoyl chloride (**3**)*

2-Chloronicotinic acid (2.36 g, 14.97 mmol) and thionyl chloride (10 mL) were added to a 50 mL single-mouth bottle and refluxed for 4 h. The tail gas was absorbed by an alkali sodium hydroxide solution. The reaction process was detected by TLC. When the consumption of 2-chloronicotinic acid was completed, the excess thionyl chloride was directly distilled off using a rotary evaporator, and then 10 mL anhydrous dichloromethane was added. A large amount of brown crystals precipitated on cooling the solution down to room temperature. The yield of the crystals was 2.64 g (98.5 %), m.p.: 56–57 °C.

*Synthesis of 2-(4-chlorophenyl)nitrobenzene (**1**)*

o-Bromonitrobenzene (20.20 g, 100 mmol), *p*-chlorophenylboronic acid (16.40 g, 105 mmol), anhydrous Na_2CO_3 (15.90 g, 150 mmol), anhydrous AcONa (2.46 g, 30 mmol) and TBAB (1.00 g) were added to C_2H_5OH/H_2O (3:1 volume ratio, 100 mL) as solvent in a 250 mL single port flask with a magnetic stir bar. A catalytic amount (0.01 mol % of **Cat1** (0.9 mg, 0.1 mmol) was added to the mixture, which was then stirred for 24 h at 90 °C. After completion of the reaction, the reaction mixture was cooled to room temperature, and 200 mL of ethyl acetate for extraction was added. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and the filtrate was a yellow liquid. The filtrate was concentrated to give the crude product, then recrystallization from ethanol gave 23.17 g of pale yellow crystals, yield 99.2 %.

*Synthesis of the 2-(4-chlorophenyl)aniline (**2**)*

2-(4-Chorophenyl)nitrobenzene (9.35 g, 40 mmol) and ethyl acetate (100 mL) were added to a 250 mL three-necked flask and stirred to dissolve completely. Then zinc powder (15.70 g, 240 mmol) was added to the reaction mixture and the reactants were heated to the required temperature of 70 °C, and a mixed solution of 40 mL of concentrated hydrochloric acid and 20 mL of AcOH was added dropwise over a period of 1 h under a protection of N_2 atmosphere. After the reaction was finished (about 3 h), the reaction mixture was cooled to room temperature, ammonia water was added slowly to adjust pH 10. The mixture was allowed to stir for another 1 h at room temperature, and then 100 mL ethyl acetate was added for extraction. The aqueous phase was further extracted by 50 mL of ethyl acetate, and the organic phases were combined, dried over anhydrous Na_2SO_4 and filtered. Finally, the filtrate was concentrated to give a pale yellow oily liquid. The oily liquid 2-(4-chlorophenyl)aniline (8.00 g) was purified by column chromatography, yield 98%.

*Synthesis of the Boscalid (**4**)*

In a dry 250 mL three-necked flask, 2-(4-chlorophenyl)aniline (2.04 g, 10 mmol), dry dichloromethane (30 mL) and anhydrous K_2CO_3 (2.12 g, 20 mmol) were well stirred and then cooled to 10 °C. 2-Chloronicotinoyl chloride (2 mL) dissolved in dichloromethane (2.64 g) was added dropwise into the mixture. After completion of the dropwise addition, the reaction was continued at room temperature for 1 h. 2-(4-Chlorophenyl)aniline was monitored by TLC. The reaction was terminated when the raw material had been consumed or almost none remained, the solution was washed with 30 mL of water and 20 mL of 10 % hydrochloric acid, and finally with 30 mL of water. The organic phase was separated and dried over anhydrous Na_2SO_4. The filtrate was concentrated to give 3.43 g of crude yellow solid Boscalid in 100 % yield. Recrystallization from absolute ethanol gave 3.25 g of Boscalid in 95.04% yield.

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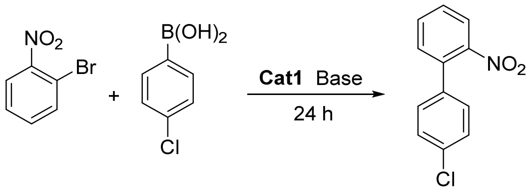
RESULTS AND DISCUSSION

The reaction conditions were investigated and optimized with special regard to the Suzuki reaction, the type of reducing agent on the reduction reaction, the type of acid binding agent on the synthesis of Boscalid and the amount of 2-chloronicotinoyl chloride.

Optimization of the reaction conditions in the Suzuki reaction

First, the catalytic performance of **Cat1** in the Suzuki reaction was explored (Scheme 3). None of the solvents were further purified and the cross-coupling reaction was performed under aerobic conditions.



Scheme 3. Scheme for the Suzuki coupling reaction.

The reaction conditions, *i.e.*, solvent, acid, base, reaction temperature, reaction time and catalyst dosage, were investigated. As shown in Table I, initially, in the conditions of C_2H_5OH/H_2O (3:1) as solvent and reaction for 24 h at 90 °C were considered. The amount of the catalyst used was 0.01 mol %. In addition, the effects of acid and alkali treatment on the coupling reaction were studied (entry 1-11, Table I). Under alkaline reaction conditions, the yield was higher than under acid reaction conditions. Unexpectedly, when AcONa and Na_2CO_3 were used in combination, the yield of the reaction reached 99.2 % (Table I, entry 3), while with K_2CO_3, Na_2CO_3, AcOK+Na_2CO_3, KOH and AcONa, the reactions were also successfully coupled with the yields of 21 to 88 % (entries 4–11, Table I).

The results indicated that the weak base Na_2CO_3 was the best in the reaction with AcONa. Subsequently, various solvents were screened (Table I, entries 12–18) and it was found that the solvent C_2H_5OH/H_2O (3:1) showed the highest yield. When the ratio of alcohol to water reached 6:1, the yield decreased to 86.57 % (Table I, entry 16).

When using a single solvent, such as EtOH, toluene, 1,4-dioxane, DMA, MeOH, THF, *etc*., the strategy did not yield the highest biaryl product. Moreover, the effect of a lowered temperature was not satisfactory giving a yield of 43.49 % (Table I, entry 19). Next, increasing the reaction temperature to 130 °C was tried, but the yield dropped to 77.75 % (Table I, entry 20). To our delight, under the optimal reaction conditions, lowering the amount of catalyst from 0.05 to 0.01 mol % gave little difference in the yield of 99 % (Table I, entries 3, 22, 23).

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Nevertheless, further lowering of the amount of catalyst to 0.008 mol % reduced the yield to 86.11 % (Table I, entry 21). In conclusion, the superior Suzuki reaction conditions were obtained, that is, AcONa+Na_2CO_3 was used as the base, C_2H_5OH/H_2O (3:1) as the solvent, the amount of **Cat1** catalytic was 0.01 mol %, and reaction conditions were 90 °C for 24 h under aerobic conditions.

TABLE I. Optimization of the conditions in the Suzuki reaction; reaction conditions: *o*-bromonitrobenzene (1 mmol) and *p*-chlorophenylboronic acid (1.05 mmol) in TBAB (0.01 g) stirred at required temperature for 24 h

Entry	T / °C	Solvent	Acid	Base	c_{Cat1} / mol%	Yield, %
1	90	EtOH[a]	PivOH[c]	/	0.01	89.41
2	90	EtOH[a]	AcOH[d]	/	0.01	89.63
3	90	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.01	99.20
4	90	EtOH[a]	/	K_2CO_3	0.01	21.77
5	90	EtOH[a]	/	Na_2CO_3	0.01	77.81
6	90	EtOH[a]	/	AcOK[f]+Na_2CO_3	0.01	62.19
7	90	EtOH[a]	/	AcOK[f]+K_2CO_3	0.01	76.70
8	90	EtOH[a]	/	AcONa[e]+K_2CO_3	0.01	79.87
9	90	EtOH[a]	/	KOH	0.01	28.11
10	90	EtOH[a]	/	AcOK[f]	0.01	76.37
11	90	EtOH[a]	/	AcONa[g]	0.01	88.27
12	90	Toluene	/	AcONa[e]+Na_2CO_3	0.01	23.28
13	90	DMA	/	AcONa[e]+Na_2CO_3	0.01	3.90
14	90	1,4-dioxane	/	AcONa[e]+Na_2CO_3	0.01	56.74
15	90	MeOH	/	AcONa[e]+Na_2CO_3	0.01	72.70
16	90	EtOH[b]	/	AcONa[e]+Na_2CO_3	0.01	86.57
17	90	THF	/	AcONa[e]+Na_2CO_3	0.01	37.45
18	90	EtOH	/	AcONa[e]+Na_2CO_3	0.01	93.54
19	60	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.01	43.49
20	130	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.01	77.75
21	90	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.008	86.11
22	90	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.02	99.30
23	90	EtOH[a]	/	AcONa[e]+Na_2CO_3	0.05	99.32

[a] $V_{(EtOH:H2O)}$ = 3:1 (3 mL); [b] $V_{(EtOH:H2O)}$ = 6:1 (3 mL); [c] 60 % mol L^{-1} PivOH (0.1 mL); [d] 30 % mol L^{-1} AcOH (4 drops); [e] 30 % mol L^{-1} AcONa (0.1 mL); [f] AcOK (1.5 equiv); [g] AcONa (1.5 equiv.)

The catalytic efficiency of the four kinds of catalyst, $Pd(PPh_3)_4$, **Cat1**, **Cat2** and **Cat3** was tested under the optimized reaction conditions for *o*-bromonitrobenzene (1 mmol) and *p*-chlorophenylboronic acid (1.05 mmol) at 90 °C for 24 h. AcONa and Na_2CO_3 were used as the base, C_2H_5OH/H_2O (3:1) as the solvent, the amount of catalyst was 0.01 mol %. The results are presented in Table II.

As can be seen from the Table II, the catalytic performance of **Cat1** (99.20 %) was significantly better than that of **Cat2** (80.36 %), **Cat3** (70.85 %) and $Pd(PPh_3)_4$ (56.34 %). As shown in Fig. 1, the 1,2-di-*tert*-butyl group on **Cat1** provides steric hindrance to the axial position of the acenaphthyl on the back-

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bone, which hinders the rotation of the C_{ar}–N bond, thereby protecting the Pd atom from exposure to air and preventing the formation of unreactive NHCs-Pd (O–O) peroxo complexes. It could be speculated that large substituents on the backbone would prolong the life of catalyst and increase the efficiency of the cross-coupling reaction. Therefore, **Cat1** was selected as the Pd source due to its high efficiency.

TABLE II. Synthesis of **1** promoted by Pd-PEPPSI-IPr

Entry	Catalyst	Amount of catalyst, mol%	Yield, %
1	None	0	34.25
2	$Pd(PPh_3)_4$	0.01	56.34
3	**Cat1**	0.01	99.20
4	**Cat2**	0.01	80.36
5	**Cat3**	0.01	70.85

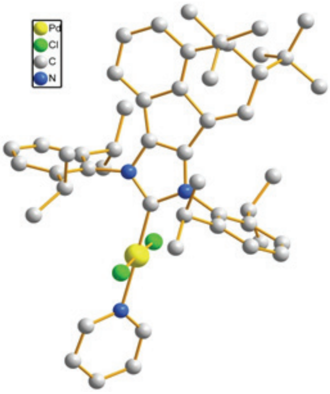

Fig. 1. X-Ray structure of **Cat1**. All H atoms are omitted and displacement ellipsoids are drawn at the 30 % probability level.

The effort of reducing agent on the reduction reaction

Hydrogen and Pd/C could be used as reducing agents for the reduction reaction, however, although the yield is extremely high, the reaction conditions are too harsh. Iron powder could also be used as the reducing agent for this reaction, the reaction conditions are mild, but considering that iron sludge pollutants, such as ferric hydroxide, are generated in the solution, the post-processing is more difficult.

In order to investigate the reduction reaction of 2-(4-chlorophenyl)nitrobenzene, zinc powder or iron powder were used as reducing agents at 70 °C for 4 h. The obtained results are presented in Table III.

As indicated in Table III, as the amount of reducing agent increases, the reduction yield of iron powder and zinc powder can reach up to 98 %. However, the post-processing is cumbersome in the course of the reaction with iron powder. Zinc hydroxide is more convenient to treat after the reduction reaction because it

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can be dissolved in ammonia. As a result, zinc powder was chosen as the reducing agent, and at a reactant ratio of 1:6 gives **2** in excellent yield.

TABLE III. Effect of reducing agent on the reduction reaction

Entry	Reducing agent	The mole ratio	Product yield, %
1	Zn	1	20.36
2	Zn	4	83.59
3	Zn	6	98.34
4	Fe	6	97.85

The effort of the type of acid binding agent on the synthesis of Boscalid

Reaction conditions: 2-(4-chlorophenyl)aniline (10 mmol) and 2-chloronicotinoyl chloride(2.64 g) in acid binding agent (20 mmol) stirred at room temperature for 2 h.

In the last step, the coupling of acid **3** and amine **2** should be performed in anhydrous conditions. All reagents and solvents need to be anhydrous to avoid the decomposition of 2-chloronicotinoyl chloride, otherwise the synthesis yield of Boscalid will be affected. The advantage of choosing an inorganic base as the acid binding agent is to improve greatly the yield and purity of Boscalid.

It can be seen from the data in Table IV, the reaction yields are significantly increased by replacing the organic base by an inorganic base. When Na_2CO_3 and K_2CO_3 are used as acid binding agents, the reaction afforded almost the same yields, but Na_2CO_3 is cheaper than K_2CO_3. Therefore, Na_2CO_3 was chosen as the acid binding agent.

TABLE IV. Results of the type of the acid-binding agent on the yield of Boscalid

Entry	Acid binding agent	Yield, %
1	Et_3N	62.13
2	Na_2CO_3	95.04
3	K_2CO_3	94.58

The effort of amount of 2-chloronicotinoyl chloride

The results depicted in Table V show that the highest yield of Boscalid 95.04 % could be acquired when the amount of 2-chloronicotinoyl chloride is increased

TABLE V. Effect of the amount of 2-chloronicotinoyl chloride; reaction conditions: 2-(4--chlorophenyl)aniline (2.04 g) and Na_2CO_3 (20 mmol) stirred at room temperature for 2 h

Entry	Amount of **2**, mmol	Amount of **3**, mmol	Product yield, %
1	10	11(1:1.1)	56.66
2	10	12(1:1.2)	64.32
3	10	13(1:1.3)	74.18
4	10	14(1:1.4)	78.92
5	10	15(1:1.5)	95.04
6	10	16(1:1.6)	90.01

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to 15 mmol, that is, with a 2-(4-chlorophenyl)aniline:2-chloronicotinoyl chloride ratio of 1:1.5.

CONCLUSIONS

The general route for the total synthesis of Boscalid has been widely reported in the literature, including three separate steps: Suzuki reaction, reduction reaction and condensation reactions. BASF® using *o*-chloronitrobenzene as the starting material, its reaction requires a large amount of expensive palladium catalysts and harsh conditions, such as high temperature, anhydrous and oxygen-free conditions, *etc.*[1] Glasnov *et al.*[5] reported a continuous and efficient method for synthesis of Boscalid, the Suzuki coupling reaction was catalyzed by $Pd(PPh_3)_4$, the reduction reaction under the catalysis of Pt/C, and condensation reaction under the conditions of microwave heating, the reaction conditions are harsh. Schwarze *et al.*[15] reported environmentally friendly solvents for the synthesis of Boscalid, the Suzuki reaction was catalyzed by water-soluble homogeneous Pd/ /SPhos, together with the easily recyclable heterogeneous $PtIr@TiO_2$, the condensation reaction under the conditions of triethylamine, the catalysts used are not easily available. Audun Drageset *et al.*[16] reported a three step continuous/ /semi-flow process for synthesis of Boscalid, the Suzuki coupling reaction was catalyzed by $Pd(PPh_3)_4$, in the reduction reaction $NaBH_4/CoSO_4\cdot7H_2O$ were used as reduction reagents, and condensation reaction under conditions of ethyl acetate as the reaction medium with pyridine as the amine base. It is not easy to separate the product. Balaram S. Takale *et al.*[17] reported a sustainable 1-pot, 3-step synthesis of Boscalid, the Suzuki coupling reaction was catalyzed by nanomicelles in water at a very low loading (0.07 ppm or 0.07 mol %) of $Pd(OAc)_2$. In the reduction reaction, carbonyl iron powder (CIP) was used, the acylation reaction was performed under the conditions of *i*-Pr_2Net. The catalysts of the method are not readily available.

In summary, Boscalid is synthesized in this paper through three-step reaction. In the first step of the Suzuki reaction, the optimum synthesis conditions are 0.01 mol % catalytic amount of Pd-PEPPSI-IPr$^{\text{DtBu-An}}$ catalyzed with *o*-bromonitrobenzene and *p*-chlorophenylboronic acid as raw materials, with C_2H_5OH/H_2O (3:1) as solvent, $AcONa+Na_2CO_3$ as the base, the phase transfer agent TBAB was added during the reaction, under aerobic conditions at 90 °C for 24 h. In the second step of the reduction reaction, the commonly used Pd/C was replaced by zinc powder to reduce costs and adapt to industrial production. In the last step of the coupling of acid **3** and amine **2**, compared with other synthesis usually carried out at high temperature or long time, in this paper sodium carbonate was used in a room temperature reaction for a short time. It could be seen from the experimental results that the reaction yields of each step were high, the reaction conditions were mild, using low-cost raw materials, and the amount of

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catalyst used is small. This method for producing the bactericide Boscalid can reduce greatly the cost in industrial production, and is expected to promote industrial production.

SUPPLEMENTARY MATERIAL

Analytical and spectral data of the synthesized compounds are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/index, or from the corresponding author on request.

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ИЗВОД

ОПТИМИЗАЦИЈА СИНТЕЗЕ БОСКАЛИДА УПОТРЕБОМ КАТАЛИЗАТОРА PD-PEPPSI-IPr$^{\text{DtBu-An}}$

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Циљ рада је био да се смањи количина паладијумског катализатора и да се унапреди његова каталитичка ефикасност у реакцији укрштеног Сузуки–Мијура (Suzuki–Miyaura), куповања која представља кључни корак у синтези Боскалида. Три типа Pd-PEPPSI-IPr катализатора су примењена у Сузукијевој реакцији куповања *o*-бромнитробензена и *p*-хлорфенилборонске киселине као полазних једињења. Добијени би-арилни производ је редукован и коришћен у реакцији куповања да би био добијен Боскалид. Под оптималним реакционим условима, резултати показују да каталитички систем има највећу каталитичку ефикасност под аеробним условима, при чему се 2-(4-хлорфенил)нитробензен добија у приносу од 99 %. Додатно, количина Pd-PEPPSI-IPr$^{\text{DtBu-An}}$ катализатора је смањена на 0,01 mol %. Реакциони услови су благи, обрада реакционе смеше је једноставна и трошкови производње су смањени, што поступак чини погодним за индустријску производњу.

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