

## Support Information

# Catalytic Activity of Palladium (II) Complex Modified on Multi-Wall Carbon Nano Tube: As an Efficient Catalyst for Asymmetric Suzuki Coupling

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### 1-1 Materials and methods

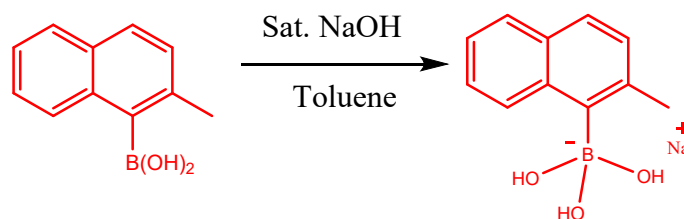
IR spectra were taken by a FT-IR Shimadzu of the Nicolet Instrument Corporation spectrophotometer. XRD powder patterns were acquired on a XRD Rigaku Ultima IV X-ray diffractometer with a copper anode and a graphite monochromator using Cu K $\alpha$  radiation, taking data from  $2\theta = 2.5^\circ$  to  $80^\circ$  at a scan rate of  $0.03^\circ/\text{s}$  and operating parameters of 40 kV and 80 mA. Thermal behavior was determined by Thermo Gravimetric Analysis (TGA) which was carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) placed in 70  $\mu\text{L}$  alumina pans were heated under airflow of 40 mL/min between 35 and 600  $^\circ\text{C}$  with a heating rate of 10  $^\circ\text{C}/\text{min}$ . Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were taken on a FEI NOVA Nano SEM 450 thermal field emission scanning electron microscope.

Graphs related to HPLC with the help of the device High Performance Liquid Chromatography model AZURA Educational HPLC System controlled by ClarityChrom Chromatography Software. Thin layer chromatography on precoated silica gel fluorescent 254 nm (0.2 mm) were used for monitoring the reaction progresses.

## 1-2 Carbon-Carbon coupling reaction of 1-iodo-2-methylnaphthalene and 1-bromo-2-methylnaphthalene with sodium borate salt

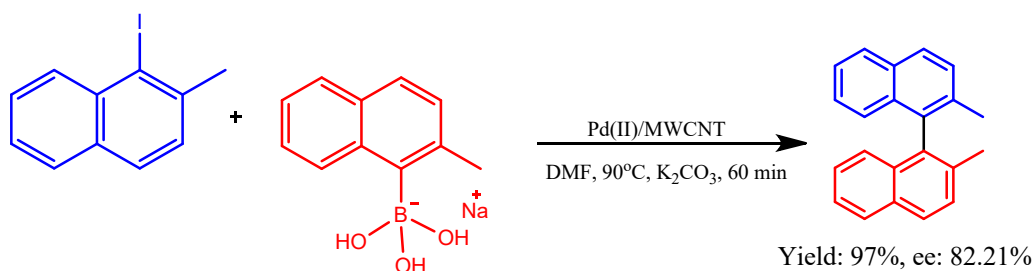
The sodium borate salt was then prepared from the boronic acid by the below method

(yield 99%):



**Scheme 1.** Preparation of sodium trihydroxy(2-methylnaphthalen-1-yl)borate salt

Sodium borate salt was obtained as a white powder solid after drying under vacuum. In this part a subsequent Suzuki coupling towards the racemic product was performed using the same borate salt but with 1-iodo-2-methylnaphthalene as the halide partner and after forming the product after purification was identified to measure the percentage of enantiomer.



**Scheme 2.** Asymmetric Suzuki coupling of sodium trihydroxy(2-methylnaphthalen-1-yl)borate and 1-iodo-2-methylnaphthalene

Product efficiency obtained calculated for the crystalline solid obtained was 58%. In this reaction it could be clearly seen that the use of an iodide coupling partner produced a much improved result. To review and process the information obtained from the reaction a sample of the impure product was nonetheless analysed by chiral HPLC.

## Azura

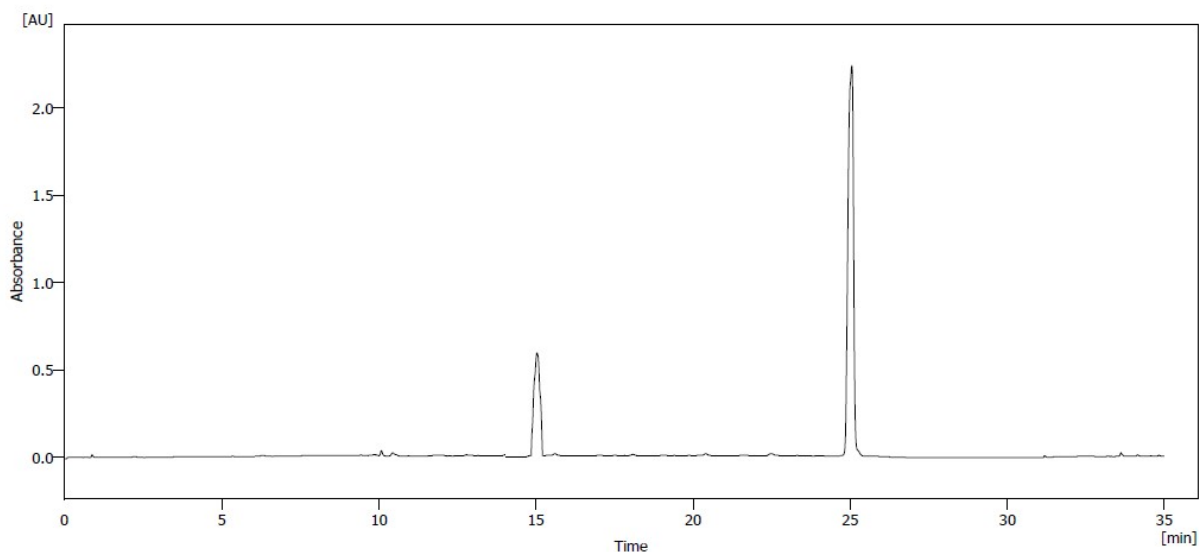
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## Sample Description:

Sample ID : SUZUKI  
Sample : SUZUKI

Column	: Chiralcel OC-H	Detection	: 230 nm
Mobile Phase	: Hexane:EtOH	Temperature	: RT
Flow Rate	: 0.5	Pressure	:
Note	: KOUHDAREH(QC MANAGER)		



**Figure 1.** Chiral HPLC trace of sodium trihydroxy(2-methylnaphthalen-1-yl)borate obtained from the symmetric coupling reaction using 1-iodo-2-methylnaphthalene

Two atropisomeric forms of coupled product were separated and identified as the first and last peaks as a result approximate calculation revealed that they were present in racemic proportions which was expected for this symmetric coupling.

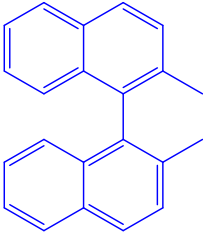
The following formula is used for the percentage of isomers:

$$\frac{A_S}{A_{Total}} \times 100 = \text{Enantiomeric excess}\%$$

$A_S$ : peak response of sample from the Sample solution

A<sub>Total</sub>: peak response of Total from the Sample solution

Chiral HPLC separation conditions and retention times of isomers:

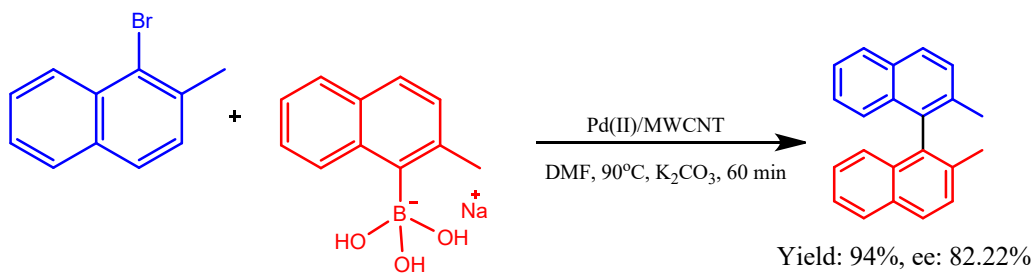
Compound	Column	Mobile phase Hexane/EtOH	Flow rate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers
	A*	80/20	1.0	15.1	25.1	17.79%&82.21%

A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.



**Figure 2.** Chiralcel OC-H column

In the next part a subsequent Suzuki coupling towards the racemic product was performed using the same borate salt but with 1-bromo-2-methylnaphthalene as the halide partner and after forming the product after purification was identified to measure the percentage of enantiomer.



**Scheme 3.** Asymmetric Suzuki coupling of sodium trihydroxy(2-methylnaphthalen-1-yl)borate and 1-bromo-2-methylnaphthalene

After purification of the reaction product, its detection was performed by Chiral HPLC separation technique.

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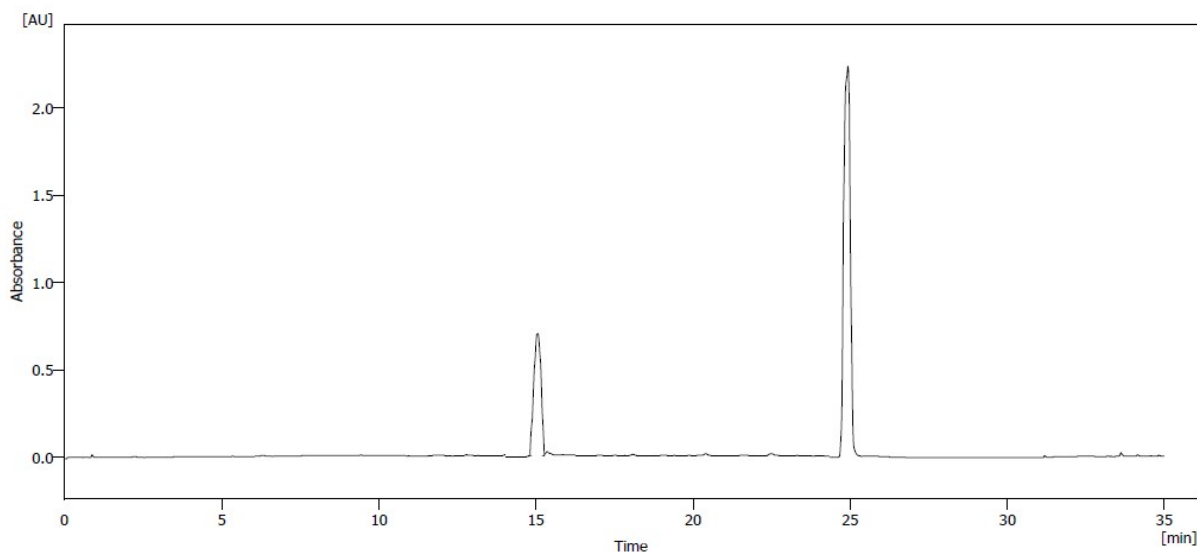
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Clarity	: 7.4.2.107, Demo: 0, SN: 015-47547		

## Sample Description:

Sample ID : SUZUKI  
 Sample : SUZUKI

Column	: Chiralcel OC-H	Detection	: 230 nm
Mobile Phase	: Hexane/EtOH	Temperature	: RT
Flow Rate	: 0.5	Pressure	:
Note	: KOUHDAREH(QC MANAGER)		

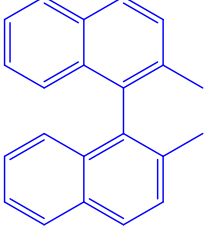


**Figure 3.** Chiral HPLC trace of sodium trihydroxy(2-methylnaphthalen-1-yl)borate obtained from the symmetric coupling reaction using 1-bromo-2-methylnaphthalene

Two atropisomeric forms of coupled product were separated After calculating and processing the results, it is as follows.

Chiral HPLC separation conditions and retention times of isomers:

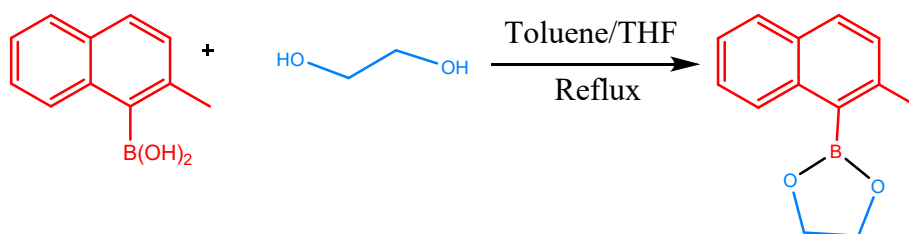
Compound	Column	Mobile phase Hexane/EtOH	Flowrate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers

	A*	80/20	1.0	15.1	25.1	17.78%&82.22%
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A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.

### 1-2 Carbon-Carbon coupling reaction of 1-iodo-2-methylnaphthalene and 1-bromo-2-methylnaphthalene with (ethylene glycol) boronate ester

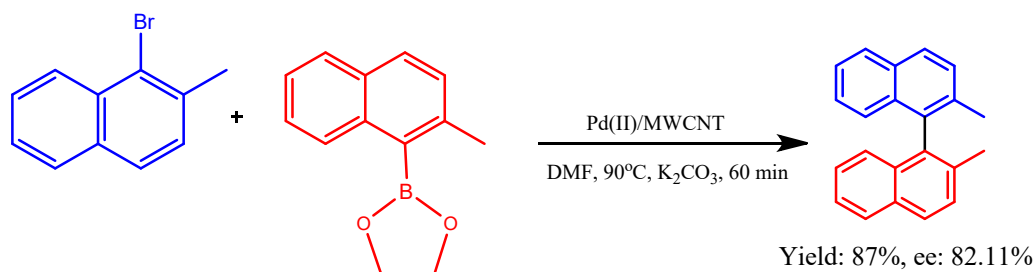
Composition synthesis direction (ethylene glycol) boronate ester in this step boronic acid was also converted to its (ethylene glycol) boronate ester analogue, via a slightly modified protocol employing a solvent mixture of 1:4 toluene/THF.



**Scheme 4.** Preparation of 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane

After heating under reflux for 60h, the product 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane was isolated initially as a viscous pale yellow oil which solidified upon standing to give an off-white waxy solid in good yield (yield 92%). This compound was used in the synthesis of complementary steps.

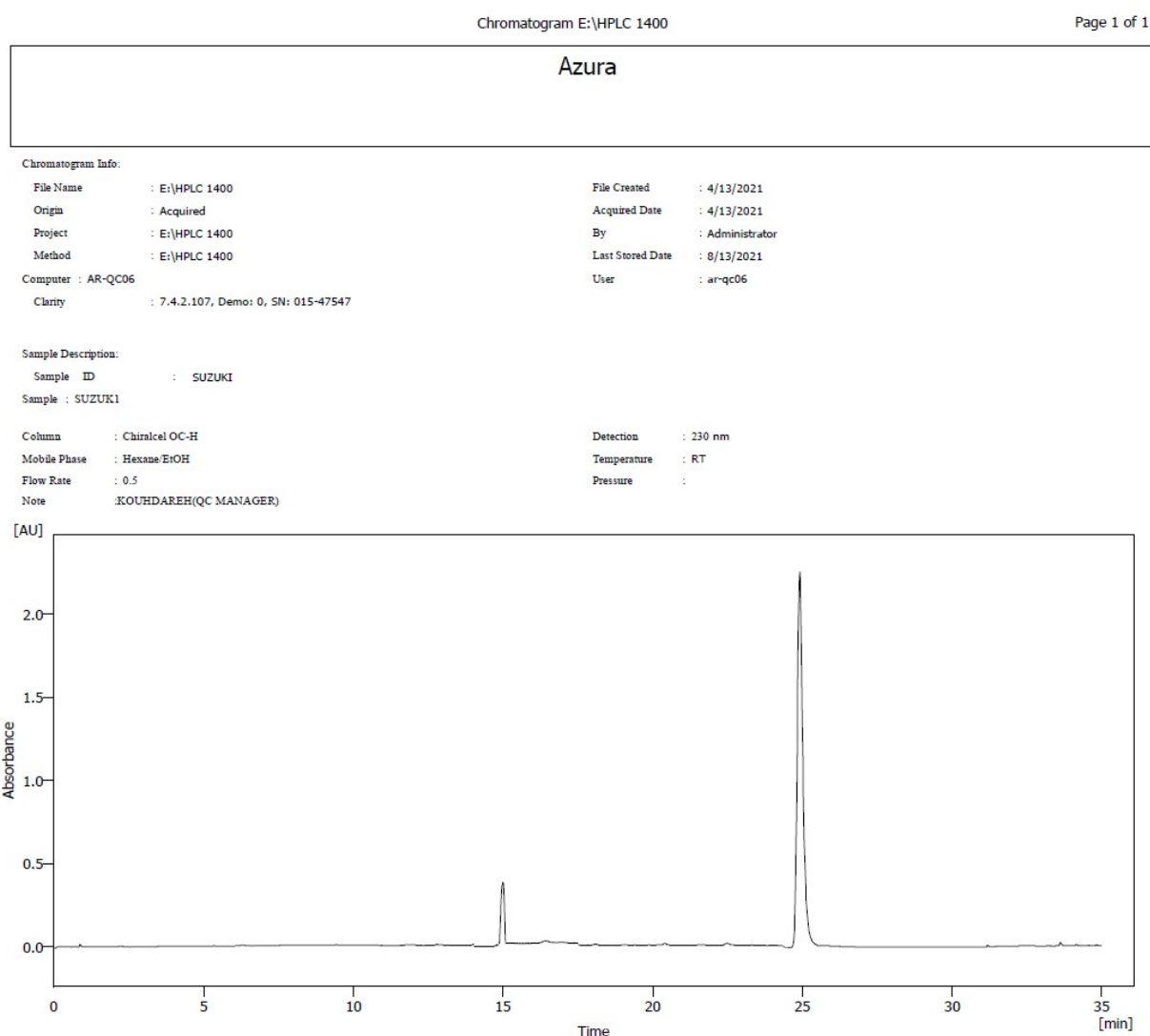
The first Suzuki coupling towards the racemic product 2,2'-dimethyl-1,1'-binaphthalene was carried out using 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-bromo-2-methylnaphthalene.



**Scheme 5.** Attempted asymmetric Suzuki coupling of 2,2'-dimethyl-1,1'-binaphthalene using 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-bromo-2-methylnaphthalene

Based on the results of the corresponding reaction efficiency the rate of the coupling reaction was evidently very slow from the poor conversion observed, likely due to the less reactive nature of the boronate ester substrate. Based on the results of the corresponding reaction efficiency the rate of the coupling reaction was evidently very slow from the poor conversion observed, likely due to the less reactive nature of the boronate ester substrate. The reaction efficiency was not as desirable (yield 24%). A very small amount of the reaction product was difficult to separate and purify and was duly analysed by chiral HPLC.

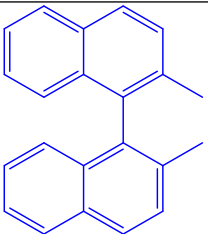
Chiral HPLC separation conditions and retention times of isomers:



**Figure 4.** Chiral HPLC trace of 2,2'-dimethyl-1,1'-binaphthalene obtained from asymmetric coupling reaction using 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-bromo-2-methylnaphthalene

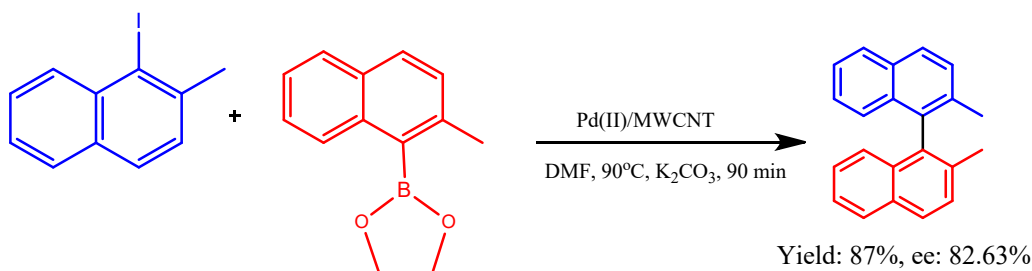


Based on the resulting calculations of the spectrum Chiral HPLC of the difference in the areas equal the peaks revealed an enantiomeric excess of 81%.

Compound	Column	Mobile phase Hexane/EtOH	Flowrate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers
	A*	80/20	1.0	15.1	25.1	17.89%&82.11%

A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.

In the next reaction of this class it could be clearly seen that the use of an iodide coupling partner produced a much improved result. To review and process the information obtained from the reaction a sample of the impure product was nonetheless analyzed by chiral HPLC.



**Scheme 6.** Attempted asymmetric Suzuki coupling towards 2,2'-dimethyl-1,1'-binaphthalene using 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-iodo-2-methylnaphthalene

The efficiency of this reaction was also not favorable and the product yielded little (yield 36%). A very small amount of the reaction product was difficult to separate and purify and was duly analysed by chiral HPLC.

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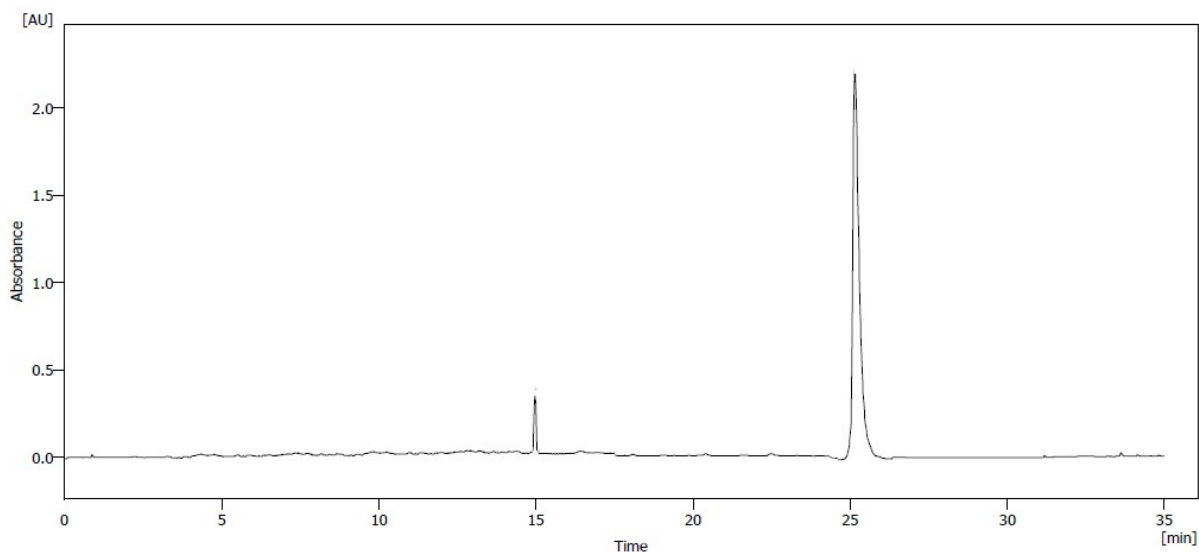
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## Sample Description:

Sample ID : SUZUKI  
 Sample : SUZUKI

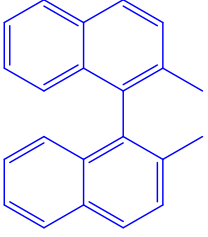
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Mobile Phase	: Hexane/EtOH	Temperature	: RT
Flow Rate	: 0.5	Pressure	:
Note	: KOUHDAREH(QC MANAGER)		



**Figure 5.** Chiral HPLC trace of 2,2'-dimethyl-1,1'-binaphthalene obtained from asymmetric coupling reaction using 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-iodo-2-methylnaphthalene

Based on the resulting calculations of the spectram Chiral HPLC of the difference in the areas equal the peaks revealed an enantiomeric excess of 81%.

Compound	Column	Mobile phase Hexane/EtOH	Flowrate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers

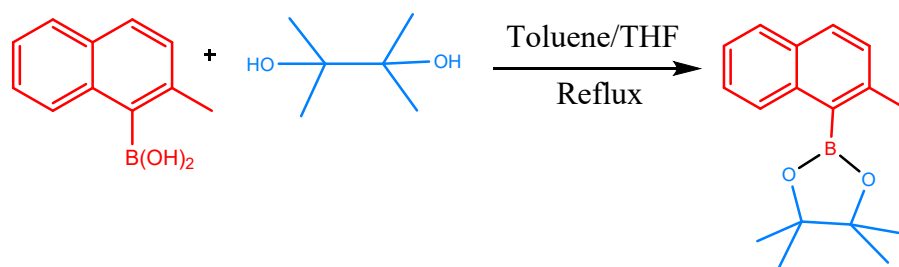
	A*	80/20	1.0	15.1	25.1	17.37%&82.63%
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A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.

Products from the Suzuki reaction based on 2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane material do not have good material efficiency. The reason for this decrease in efficiency is the difficulty of (ethylene glycol) boronate ester reaction conditions.

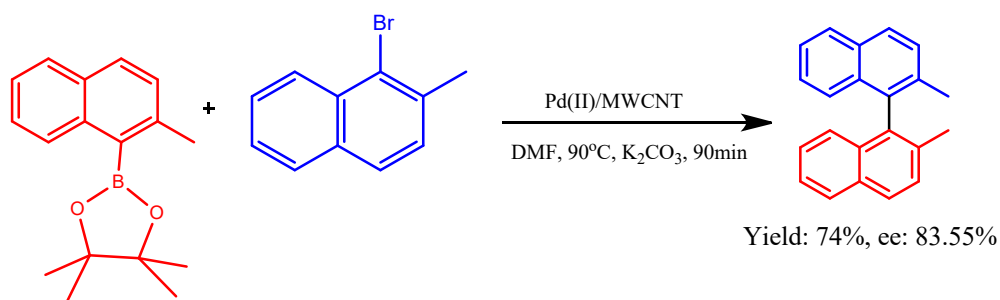
### 1-3. Carbon-Carbon coupling reaction of 1-iodo-2-methylnaphthalene and 1-bromo-2-methylnaphthalene with (pinacol) boronate ester

Preparation of the (pinacol) boronate ester was also undertaken, which was obtained by a successful reaction of boronic acid under the required standard conditions (yield 90%).



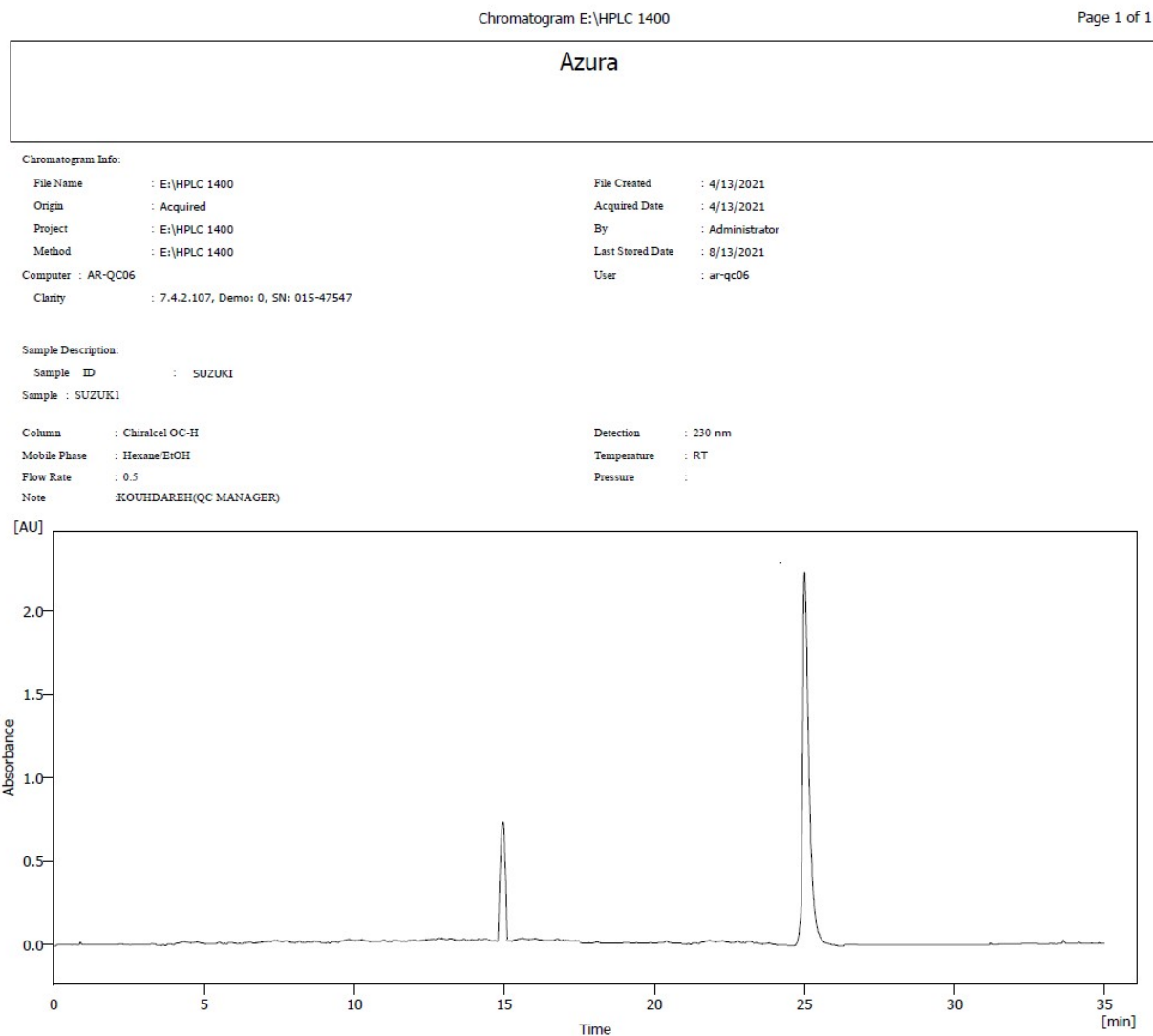
**Scheme 7.** Preparation of 4,4,5,5-tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane

After the reaction mixture was heated under reflux for 48 h, the boronate ester product (pinacol) boronate ester was isolated from extractions with Chloroform as an off-white waxy solid. In this section to review the following symmetric Suzuki reaction towards biaryl was attempted using the (pinacol) boronate ester coupling partner.



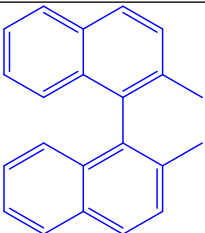
**Scheme 8.** Attempted asymmetric Suzuki coupling towards 2,2'-dimethyl-1,1'-binaphthalene using 4,4,5,5-tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-bromo-2-methylnaphthalene

This reaction has very little efficiency and is difficult to perform, which could be due to the spatial inhibition of methyl groups around the boron atom (yield 18%). After separation and purification of the reaction product, we analyzed the reaction product by Chiral HPLC analysis to identify and process the enantiomeric information.



**Figure 6.** Chiral HPLC trace of 2,2'-dimethyl-1,1'-binaphthalene obtained from asymmetric coupling reaction using 4,4,5,5-tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-bromo-2-methylnaphthalene

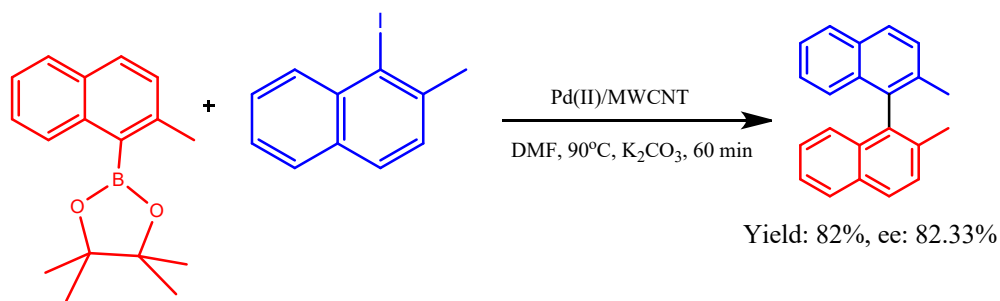
Two atropisomeric forms of coupled product were separated. After calculating and processing the results, it is as follows.

Compound	Column	Mobile phase Hexane/EtOH	Flowrate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers
	A*	80/20	1.0	15.1	25.1	17.67%&82.33%

A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.

This reaction was found to have produced an impressive enantiomeric excess of 81.91%, the highest reported value for this particular compound. The increased steric bulk of the (pinacol) boronate ester group appeared to improve the selectivity, although at a very poor conversion rate. In the next reaction of could be clearly seen that the use of an iodide coupling partner produced a much improved result. To review and process the information obtained from the reaction a sample of the impure product was nonetheless analysed by chiral HPLC.

The result of the next reaction with the iodide compound is as follows:



**Scheme 9.** Attempted asymmetric Suzuki coupling towards 2,2'-dimethyl-1,1'-binaphthalene using 4,4,5,5-tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-iodo-2-methylnaphthalen

## Azura

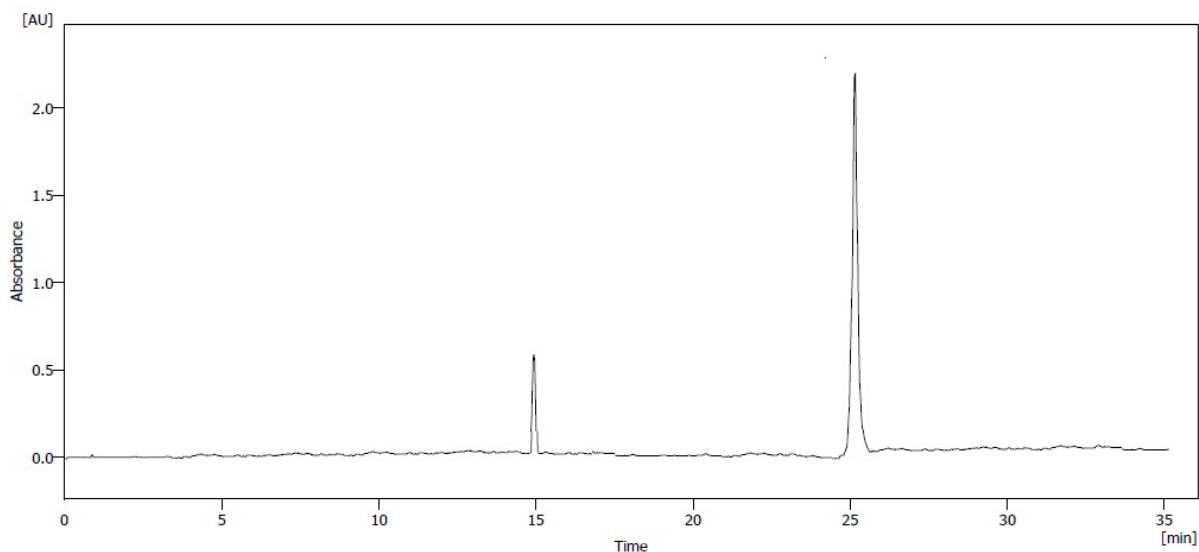
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Clarity	: 7.4.2.107, Demo: 0, SN: 015-47547		

## Sample Description:

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Sample : SUZUKI

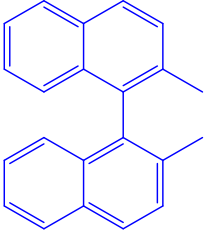
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Flow Rate	: 0.5	Pressure	:
Note	: KOUHDAREH(QC MANAGER)		



**Figure 7.** Chiral HPLC trace of 2,2'-dimethyl-1,1'-binaphthalene obtained from asymmetric coupling reaction using 4,4,5,5-tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane and 1-iodo-2-methylnaphthalene

The results of processing the spectra of this reaction are as follows:

Compound	Column	Mobile phase Hexane/EtOH	Flowrate (mL/min)	RT Isomer (a)(min)	RT Isomer(b)(min)	Ratio of isomers

	A*	80/20	1.0	15.1	25.1	16.45%&83.55%
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A\*: Chiralcel OC-H column by Daicel Chemical Ind. Detected at 230 nm.