Synthesis of organic molecules directed towards organic materials

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Introduction

Organic semiconductors are often more lightweight and low-cost than inorganic semiconductors. Thienoacenes has an interest as a OFETs because of planar conformation permitting π recovering. Thienoacene derivatives have already been synthesized by the laboratory such as benzodithienofuran[1]. Boron atom is a good electron acceptor because of its empty p-orbital. This property is very interisting in the thienoacenes synthesis and later for the organic field-effect transistor materials[2].

The theme of this work is to develop a methodology to synthesize dithienooxaborine derivatives.

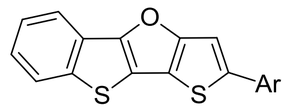


Figure 1 : Benzodithienofuran

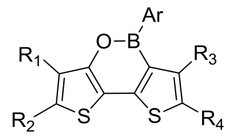
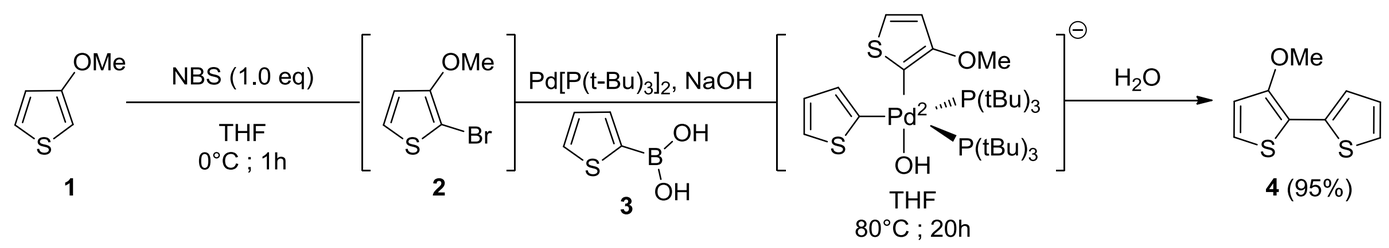


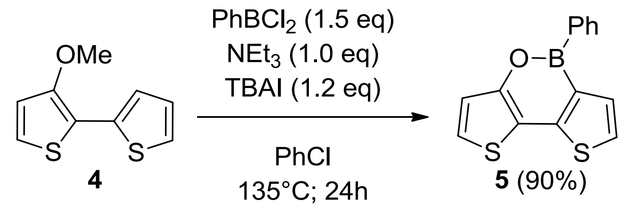
Figure 2 : Dithienooxaborine

Synthesis of starting material : Suzuki-Miyaura cross coupling



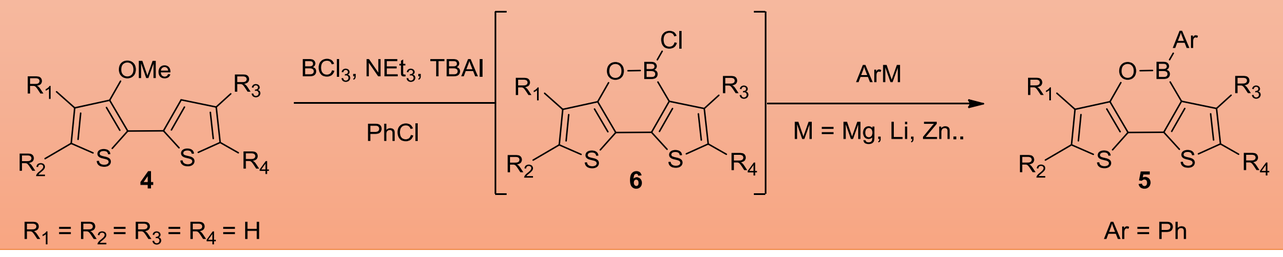
1 **2** **3**

First pathway



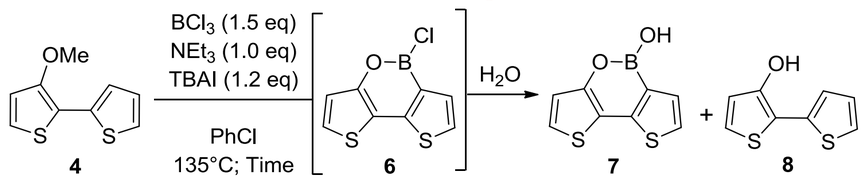
4

Object : Intermediate functionalisation



4 **6** **5**

Synthesis of the intermediate



4 **6** **7** **8**

Entry	Time (h)	7[a] (%)	8[a] (%)
1	12	87	12
2	22	88	10
3	24	95	-
4	48	90	-
5[b]	58	-	-

[a] : Isolated yield [b] : Solvent = THF ; Temperature = 70°C

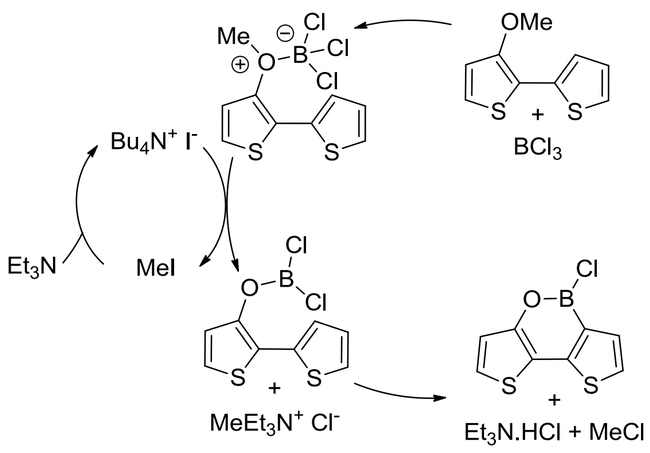
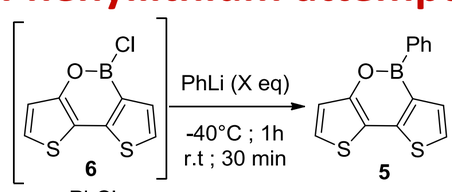


Figure 3 : Intermediate mecanism

6 could not be isolated directly but if **7** was produced, **6** was necesairely produced within 24h in 91-95% yields

Phenyllithium attempts



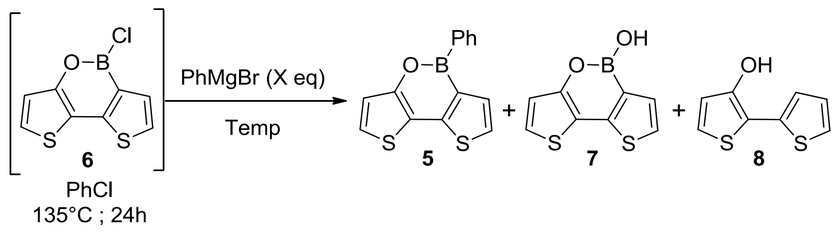
6 **5**

Entry	Time (h)	X (eq)	5[a] (%)
1	24	1.6	11
2	24	2.0	14
3	24	2.0	9
4	12	2.0	24
5	12	3.0	12

[a] : Isolated yield

PhLi was too reactive and the melting point of PhCl ($-45^{o}C$) was too high

Grignard reagent attempts



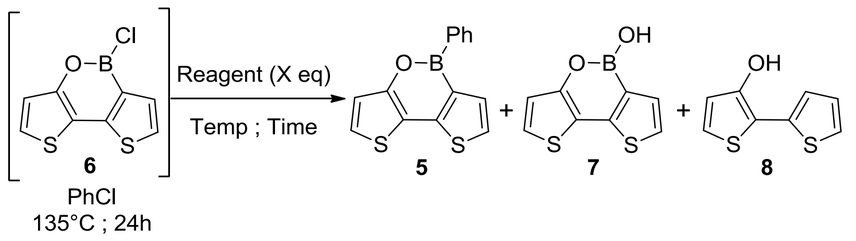
6 **5** **7** **8**

Entry	X (eq)	Temp (°C)	5[a] (%)	7[a] (%)	8[a] (%)
1	1.0	r.t	10	n.d	n.d
2	2.0	0	24	36	25
3	2.5	0	57	22	21
4	3.0	-17	45	12	6
5	3.5	0	19	14	47

[a] : Isolated yield n.d : not determined

PhMgBr was also too reactive, it produced the deboronation by-product **8**

Zinc reagent attempts



6 **5** **7** **8**

Entry	Reagent	X (eq)	Temp (°C)	Time	5[a] (%)	7[a] (%)	8[a] (%)
1	PhZnBr	2.5	r.t	15h	11	23	10
2	PhZnCl	4.7	rt	2h	19	48	4
3	PhZnCl	4.7	r.t	19h	41	44	5
4	Ph_2Zn	4.7	r.t	20 min	26	17	1
5	Ph_2Zn	2.6	r.t	2h	41	n.d	4

[a] : Isolated yield n.d : not determined

Zinc reagent did not make the deboronation by-product **8**

Conclusion

Synthesis of the intermediate was achieved with 95% yield. The nucleophile substitution step has given more problem than expected probably because PhLi and PhMgBr were too reactive. Zinc reagent gave the desired product selectively. The yield would be much better by further optimization.

This internship was a great opportunity to sharpen my scientific mindset, broaden my horizons about another culture and above all enable me to discover more about molecular chemistry.

I thank Associate Professor Koichi Mitsudo for his supervision ; my sponsor Michem, JSPS Alumni, Ile de France for the funding of this internship and the laboratory for the funding of the housing.

Advantages & Inconvenients

+	−
Schedule	Language wall
Life environment	Mosquitos
Laboratory's social life	Fruits and vegetable expensive
Nice co-workers	

References

(1) Mitsudo, K.; Kurimoto, Y.; Mandai, H.; Suga, S. *Org. Lett.* **2017**, *19* (11), 2821–2824.
(2) Lepeltier, M.; Lukoyanova, O.; Jacobson, A.; Jeeva, S.; Perepichka, D. F. *Chem. Commun.* **2010**, *46* (37), 7007–7009.