



# Synthesis and Properties of New Fluorescent Biarylboronic Acids

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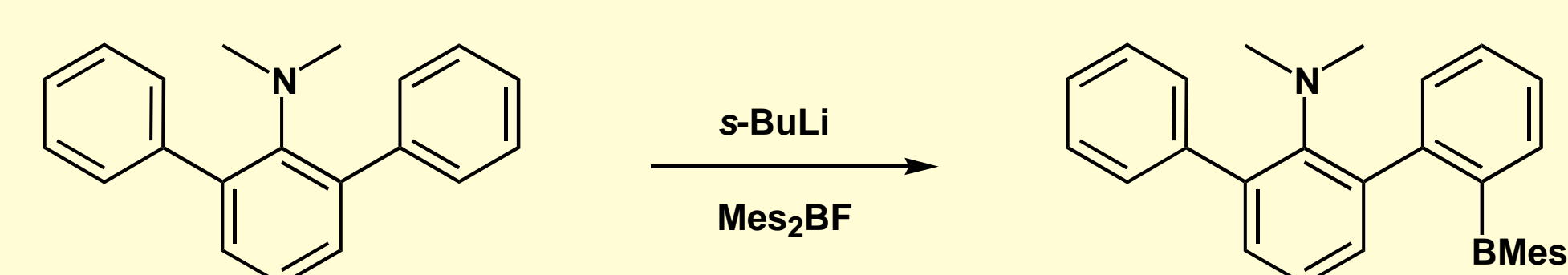
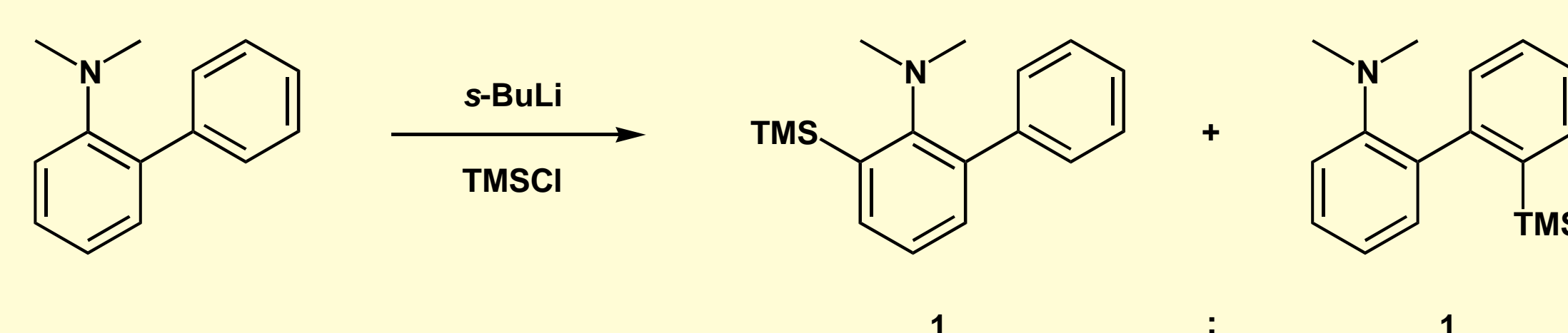
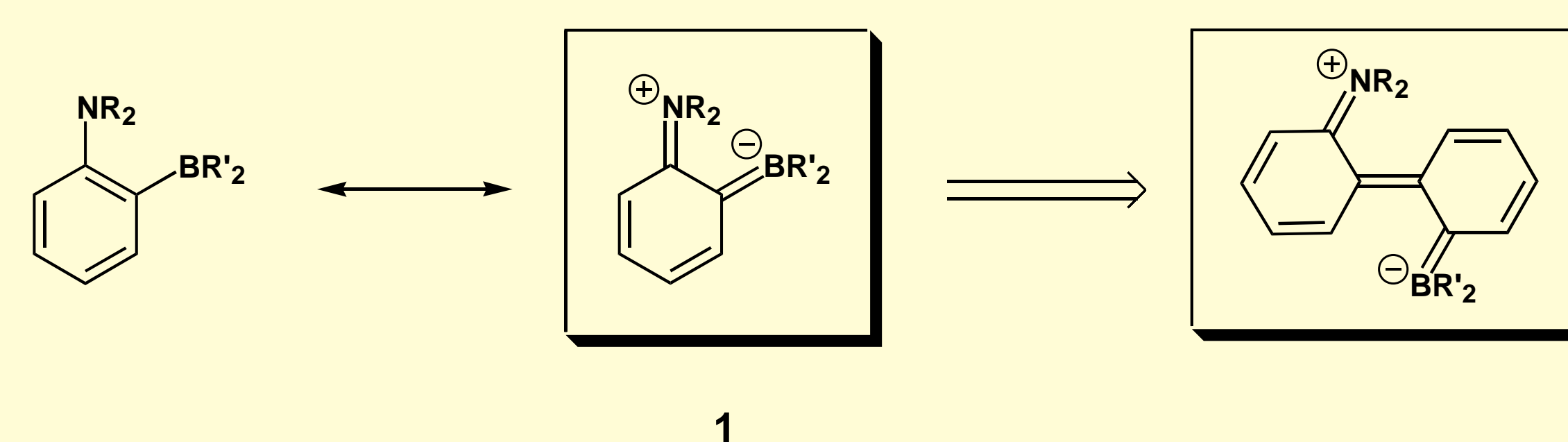
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## Introduction

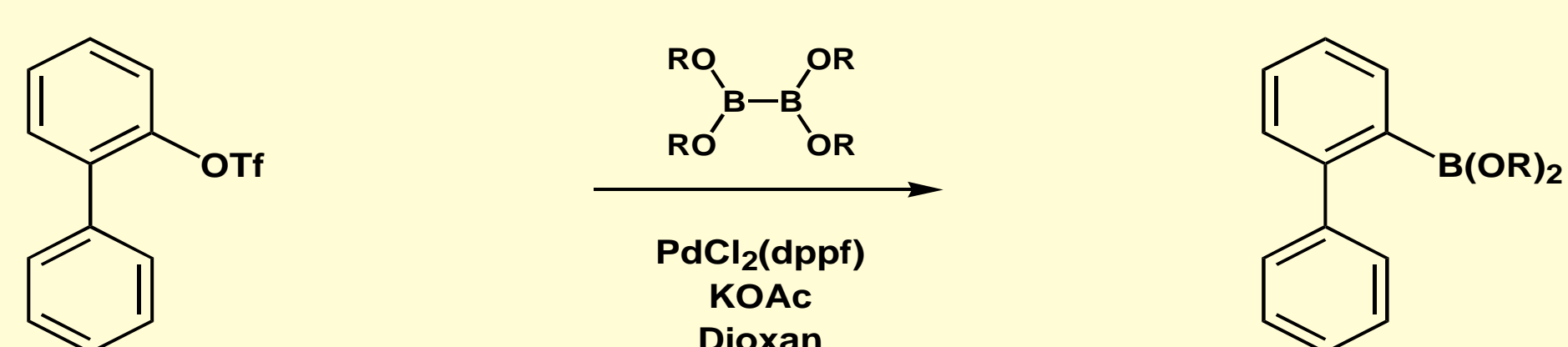
Recently, we have tried to apply the directed *ortho*-lithiation to the synthesis of borylated biaryls as an extension to the synthesis of (2-dialkylaminophenyl)diarylboranes<sup>[1]</sup>. Test reactions on 2-dimethylaminobiphenyl gave a mixture of both possible lithiation products; therefore, a symmetrical terphenyl was introduced to give *N,N*-dimethyl-2-(*o*-dimesitylborylphenyl)-5-phenylanilin as the sole product. However, for the synthesis of 4-amino-4'-boryl biphenyls having a *para*-conjugated chromophoric system **2** compared to the *ortho*-conjugated system **1** a different approach is needed. The use of transition metal cross coupling reactions opens a

1. convergent
2. stereoselective
3. high yield

approach to new functionalized B,N push-pull systems. The introduction of a boronic ester can be done by a palladium-catalyzed borylation reaction with diboron compounds<sup>[2]</sup> in higher yield and purity compared to the classical anion chemistry. The reaction has also been used

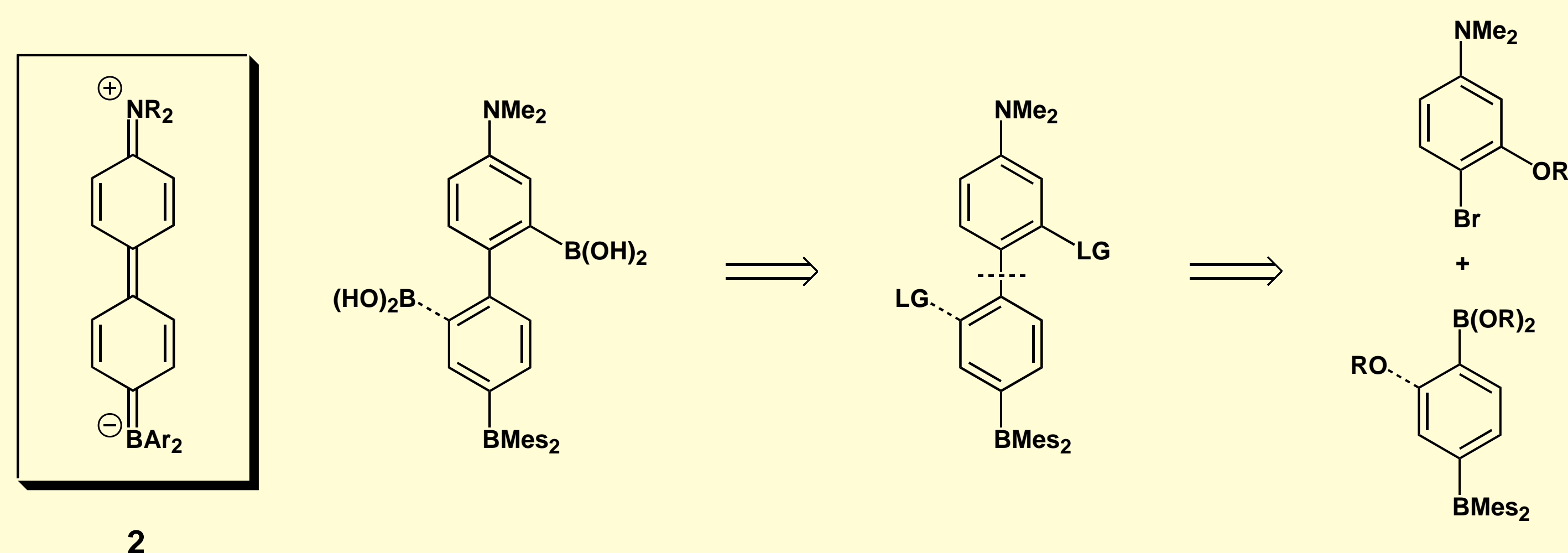


Directed metallation to *ortho*-B,N biaryls

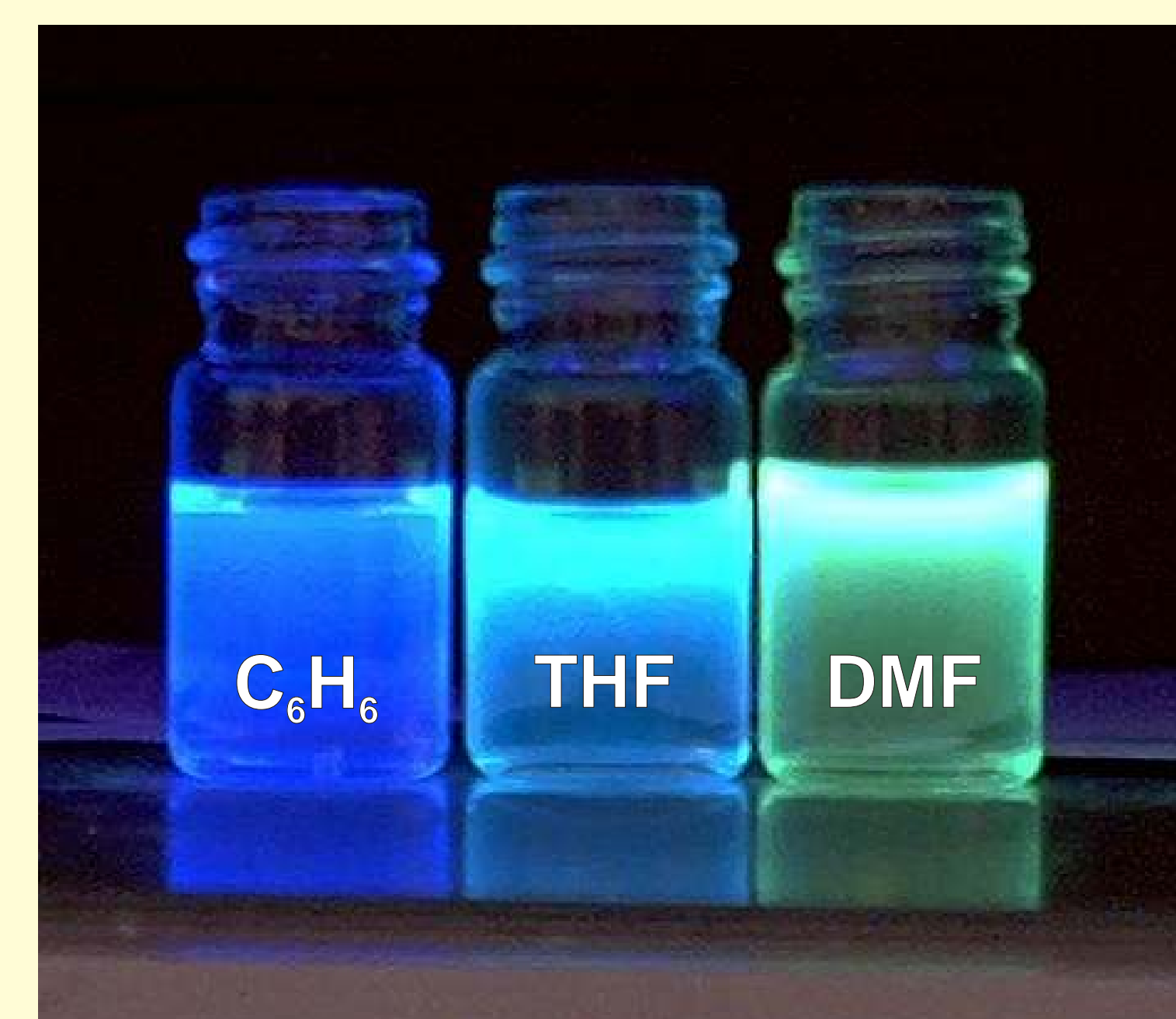


R	t (h)	yield (%)
	36	24 %
	12	91 %

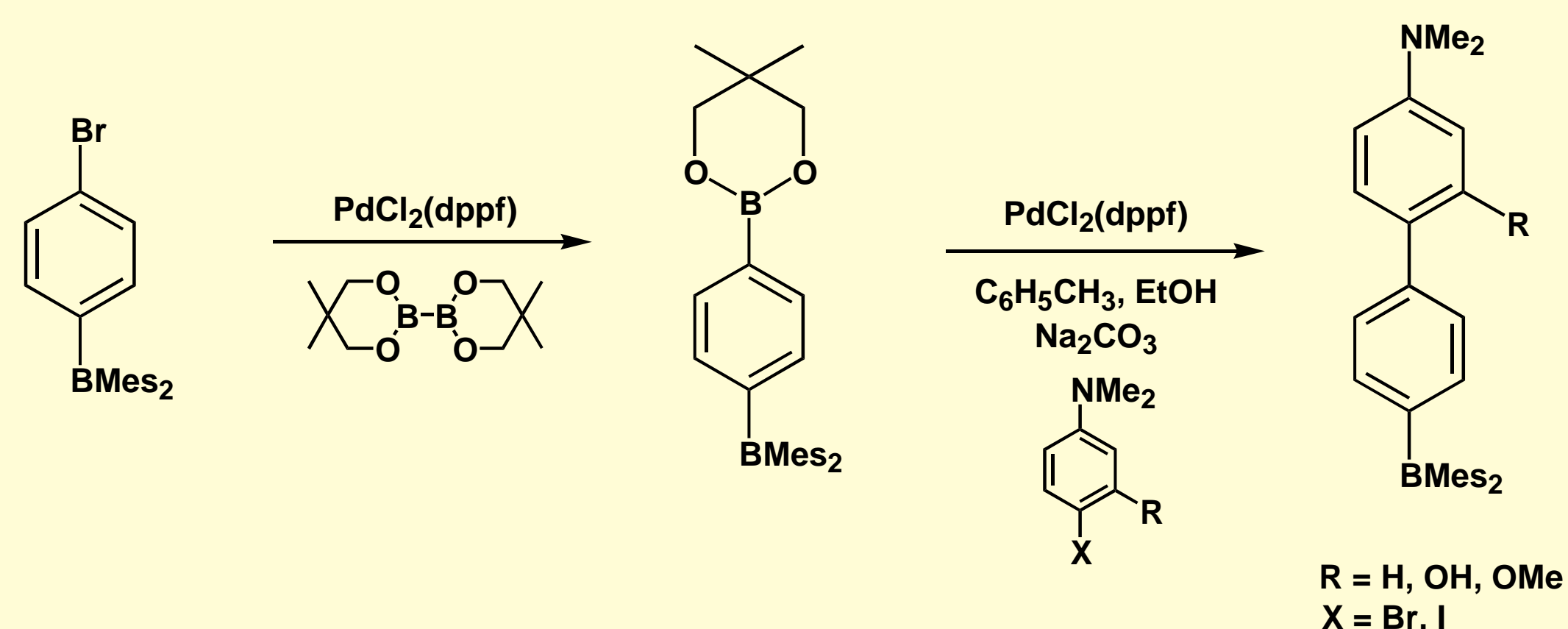
High yield synthesis of biphenylboronates



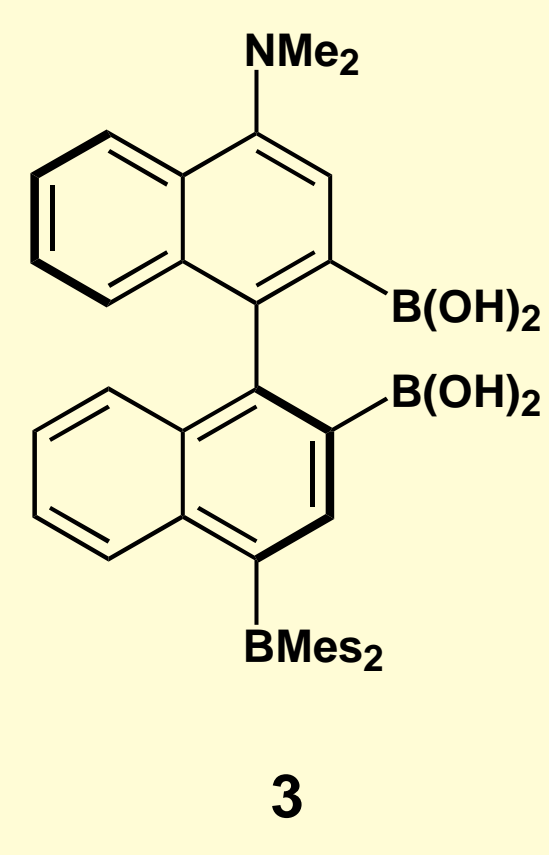
Synthetic strategy to *para*-B,N biaryls



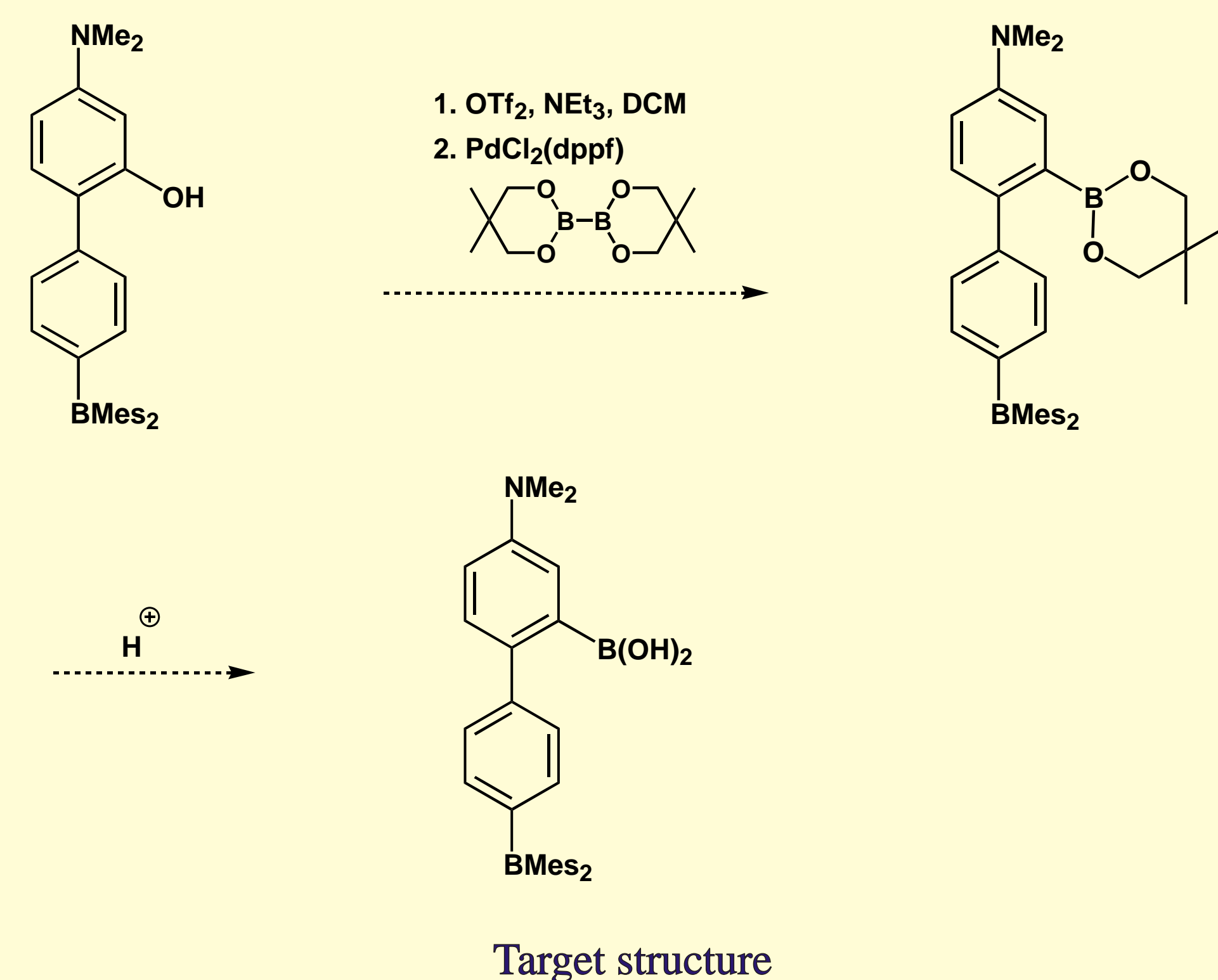
Fluorescence of 4-dimethylamino-4'-dimesitylboryl-biphenyl in different solvents



Boronate selective coupling reaction



Target structure



Target structure

## Summary

We have presented a new synthetic approach to fluorescent 4-amino-4'-boryl biaryls by a boronate selective *Suzuki*-coupling of *p*-(dimesitylboryl)phenylboronates with haloarenes under the employed reaction conditions the triarylboronyl unit is not attacked whereas non-sterically hindered triarylboranes like tri-1-naphthylborane give coupling products in good yields<sup>[3]</sup>. To allow the use for enantioselective sensor applications more sterically hindered, optically active systems like borane **3** are desirable. We are currently investigating the scope of the

## References

- [1] K. Albrecht, V. Kaiser, R. Boese, J. Adams, D.E. Kaufmann, *J. Chem. Soc. Perkin Trans.2* **2000**, 2153-2157.
- [2] a) T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508-7510. b) T. Ishiyama, Y. Itoh, T. Kitano, N. Miyaura, *Tetrahedron Lett.* **1997**, *38*, 3447-3450.
- [3] N. A. Bumagin, D. A. Tsarev, *Tetrahedron Lett.* **1998**, *44*, 8155-8158.