Exploring new structures for the development of CPL-dyes based on flexible bis(BODIPY)s

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Introduction and background

CPL

Circularly Polarized Luminiscence:
Differential emission of left and right-hand polarized light

Importance

High resolution provided by the circular polarization of the light

Development of smarter materials for useful technologies:

3D display

Information storage and processing Spintronics-based devices

Imaging (ellipsometry-based tomography)

Specific interaction with chiral mater → control of the morphology in nanomaterials
detection of chiral environments (chiral sensing)

Asymmetric photochemistry

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Introduction and background

CPL

$$g_{lum} = \frac{\Delta I}{\frac{1}{2} I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}$$

$-2 < g_{lum} < +2$

Highest values of g_{lum}: lanthanide complexes (low fluorescence quantum yield)

Simple organic molecules (CPL-SOMs):

- Small size → physiological CPL applications
- Excellent solvent solubility → CPL-active dye-doped inclusion materials

CPL-SOMs are rare

- Low g_{lum} values: $10^{-5} – 10^{-3}$
- Small number of chiral designs (highly inefficient synthesis)

New structural designs are necessary, with:

- High CPL activity
- High emission efficiency
- Synthetic accessibility

→ Low-cost effective materials

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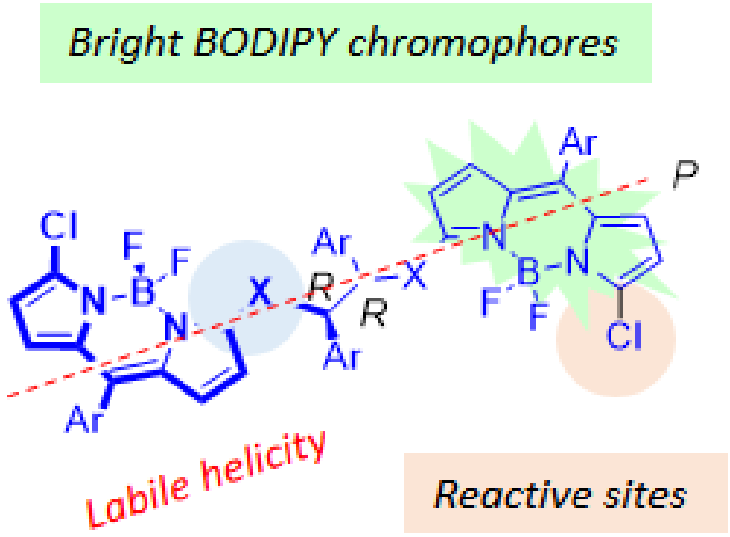
Introduction and background

Helically labile bis(haloBODIPYs): an advantageous platform for the development of CPL-SOMs



A **new structural design** for CPL-SOMs.
All-in-one:

- synthetic accessibility
- capacity for reversing the polarization handedness
- helical lability
- reactive functional groups making possible photophysics modulation

Ray, C.; Sánchez-Carnerero, E. M.; Moreno, F.; Maroto, B. L.; Agarrabeitia, A. R.; Ortiz, M. J.; López-Arbeloa, Í.; Bañuelos, J.; Cohovi, K. D.; Lunkley, J. L.; Muller, G.; de la Moya Cerero, S. *Chem.-Eur. J.* **2016,** *22*, 8805-8808

Exploring new structures for the development of CPL-dyes based on flexible bis(BODIPY)s

Objectives

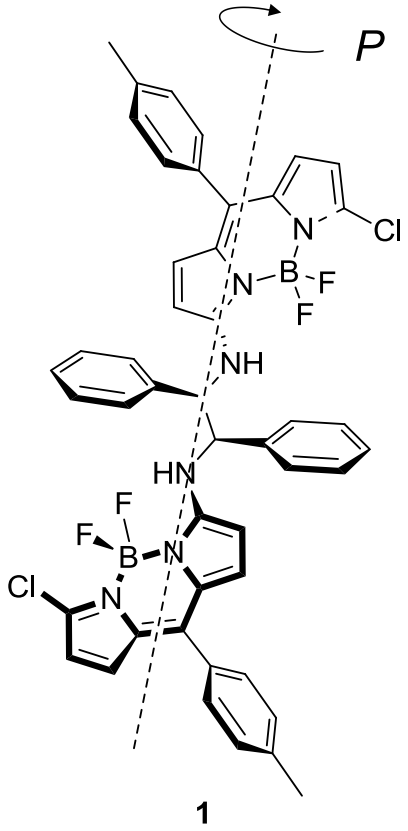
Synthetic strategies for the modification of the parent structure

↓

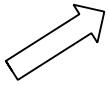
Structure-activity relationships studies

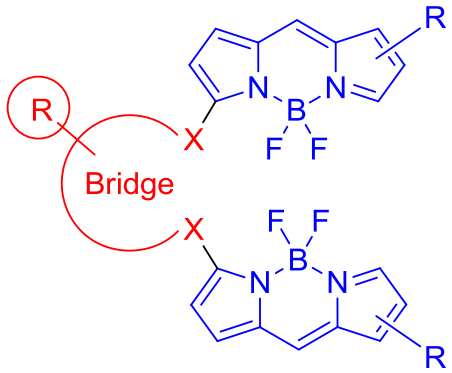
↓

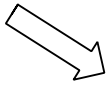
Towards the optimization of theCPL properties

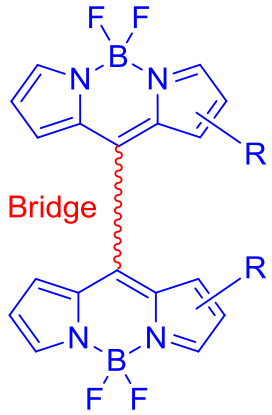


1









Strategy 1

Modify the **dihedral angle** (Sterical hindrance and rigidity in the flexible bridge)

Strategy 2

Explore **new positions** for the connection of the chromophores

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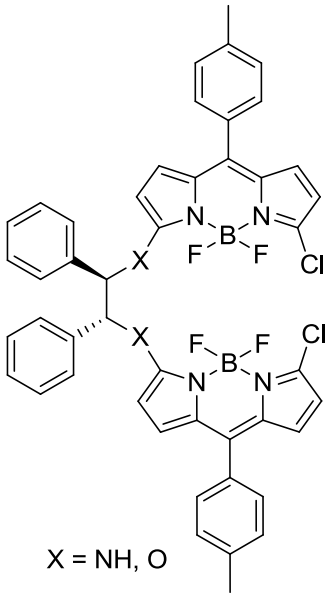
Results

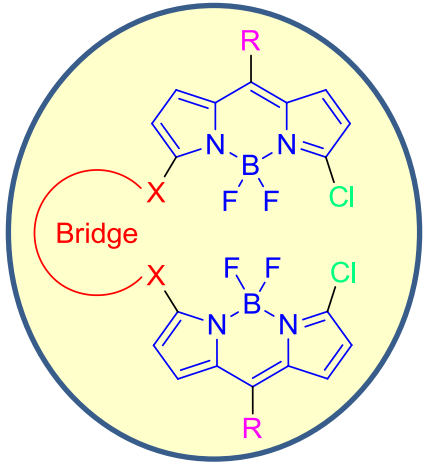
Strategy 1

Modify the diedral angle

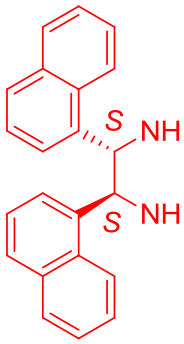
Based on:



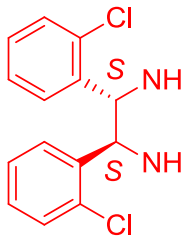
de la Moya Cerero, S. and col. *Chem.-Eur. J.* **2016,** *22*, 8805.



1: R = *p*-tolyl; Bridge = a
2: R = *p*-tolyl; Brigde = b
3: R = *p*-tolyl; Brigde = c
4: R = *p*-tolyl; Bridge = d
5: R = mesityl; Bridge = d
6: R = CF_3; Bridge = d
7: R = *p*-tolyl; Bridge = e



a



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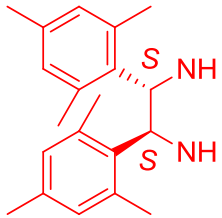

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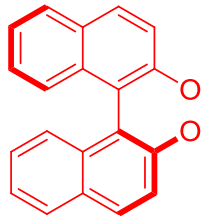
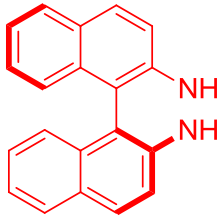


d



e

Sterical hindrance

Rigidity

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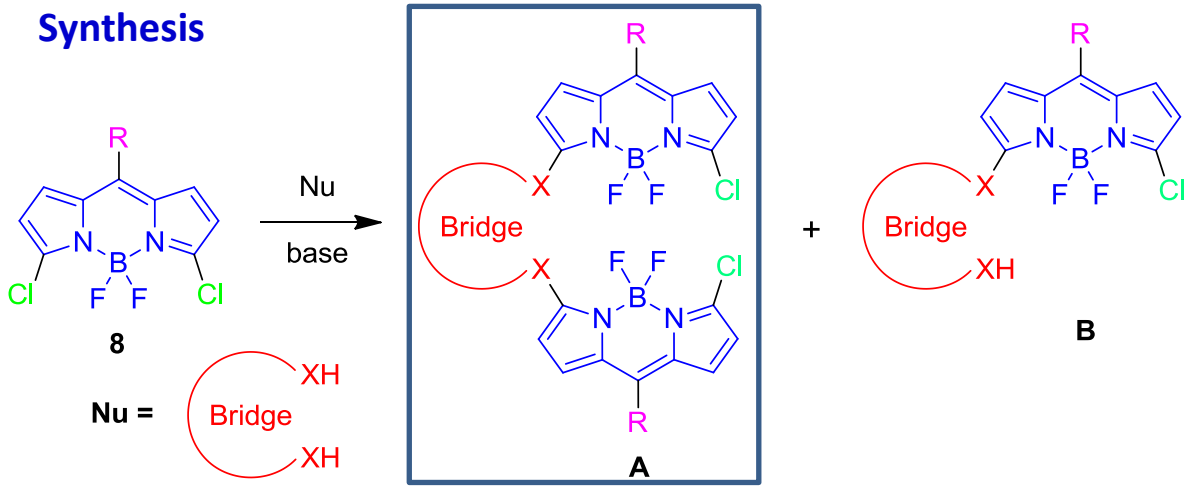
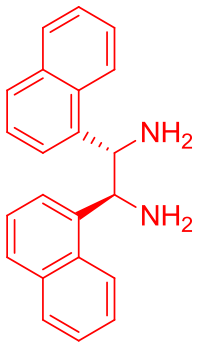
Results

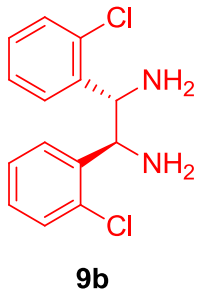
Synthesis

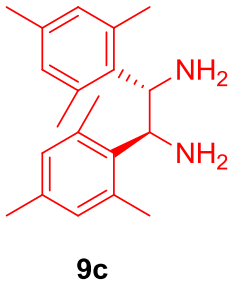
Strategy 1

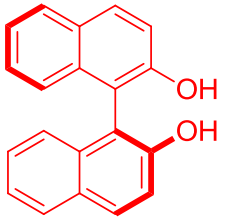


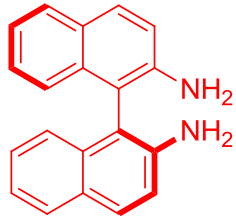
Nu:











R	Nu	base	solvent	temperature	Bis(BODIPY) (% yield)	BODIPY (% yield)
p-tolyl	**9a**	Et_2PrN	dioxane	reflux	**1A** (traces)*	**1B** (71)
p-tolyl	**9b**	Et_2PrN	CH_3CN	reflux	**2A** (38)	**2B** (32)
p-tolyl	**9c**	Et_2PrN	CH_3CN	reflux	**3A** (54)	**3B** (36)
p-tolyl	**9d**	K_2CO_3	CH_3CN	reflux	**4A**§ (52)	**4B**§ (-)
mesityl	**9d**	K_2CO_3	CH_3CN	reflux	**5A**§ (87)	**5B**§ (-)
CF_3	**9d**	K_2CO_3	CH_3CN	reflux	**6A**§ (82)	**6B**§ (-)
p-tolyl	**9e**	K_2CO_3	CH_3CN	reflux	**7A**§ (82)	**7B**§ (-)

§ Ray, C.; Banuelos, J.; Arbeloa, T.; Maroto, B. L.; Moreno, F.; Agarrabeitia, A. R.; Ortiz, M. J.; Lopez-Arbeloa, I.; de la Moya, S., *Dalton Transactions* **2016,** *45*, 11839

* **1A** was obtained from **1B** with excess of 3,5-dichloroBODIPY under the same conditions (65% yield)

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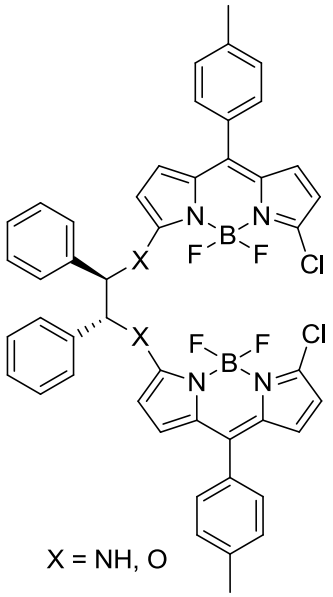
Results

Strategy 2

Explore new positions for the connection of the chromophores

Based on:



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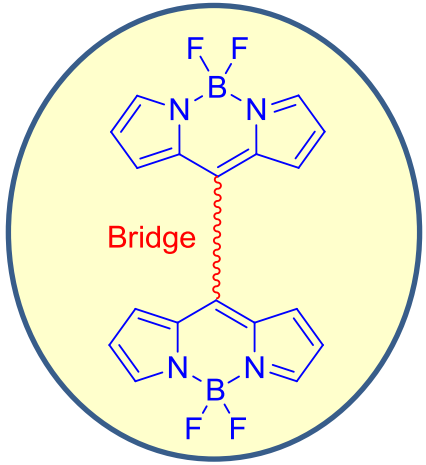
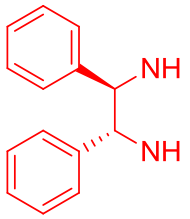
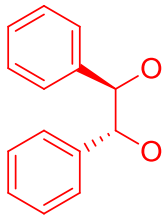


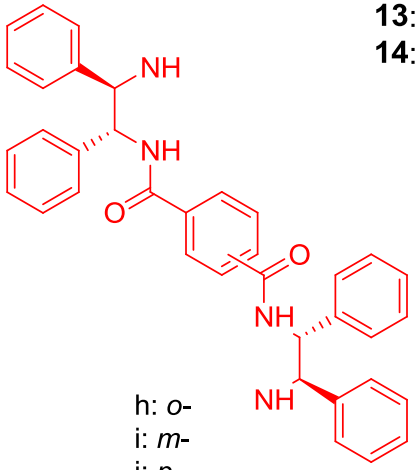
10: Bridge = f
11: Brigde = g
12: Brigde = h
13: Bridge = i
14: Bridge = j



f



g



h: *o*-
i: *m*-
j: *p*-

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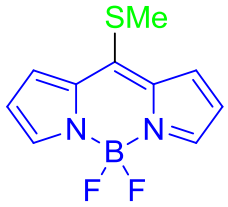
Results

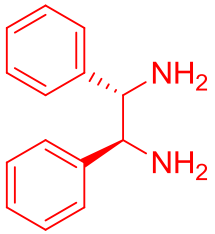
Synthesis

Strategy 2



15

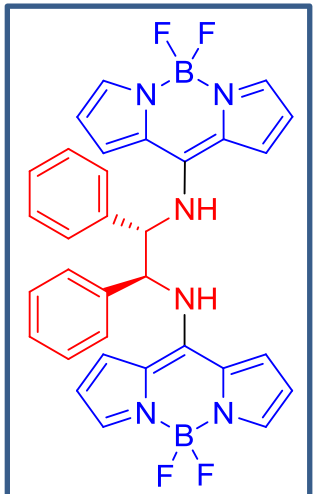
+



9f

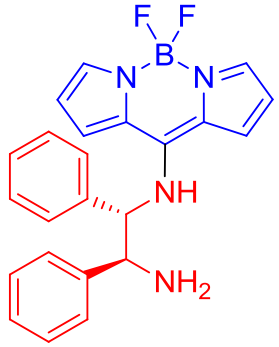
DMAP

DCM, Δ



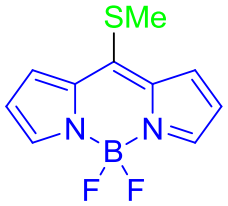
10A

+



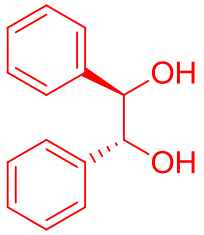
10B

15 / 9f ratio	Yield of 10A (%)	Yield of 10B (%)
2:1	17 borsm: 26	46 borsm: 72
1:1	-	98



15

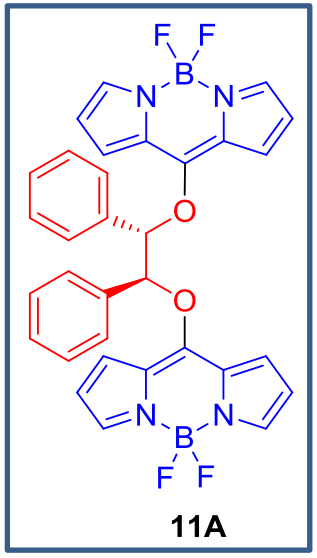
+



9g

CuI, Na_2CO_3

CH_3CN, 55 °C



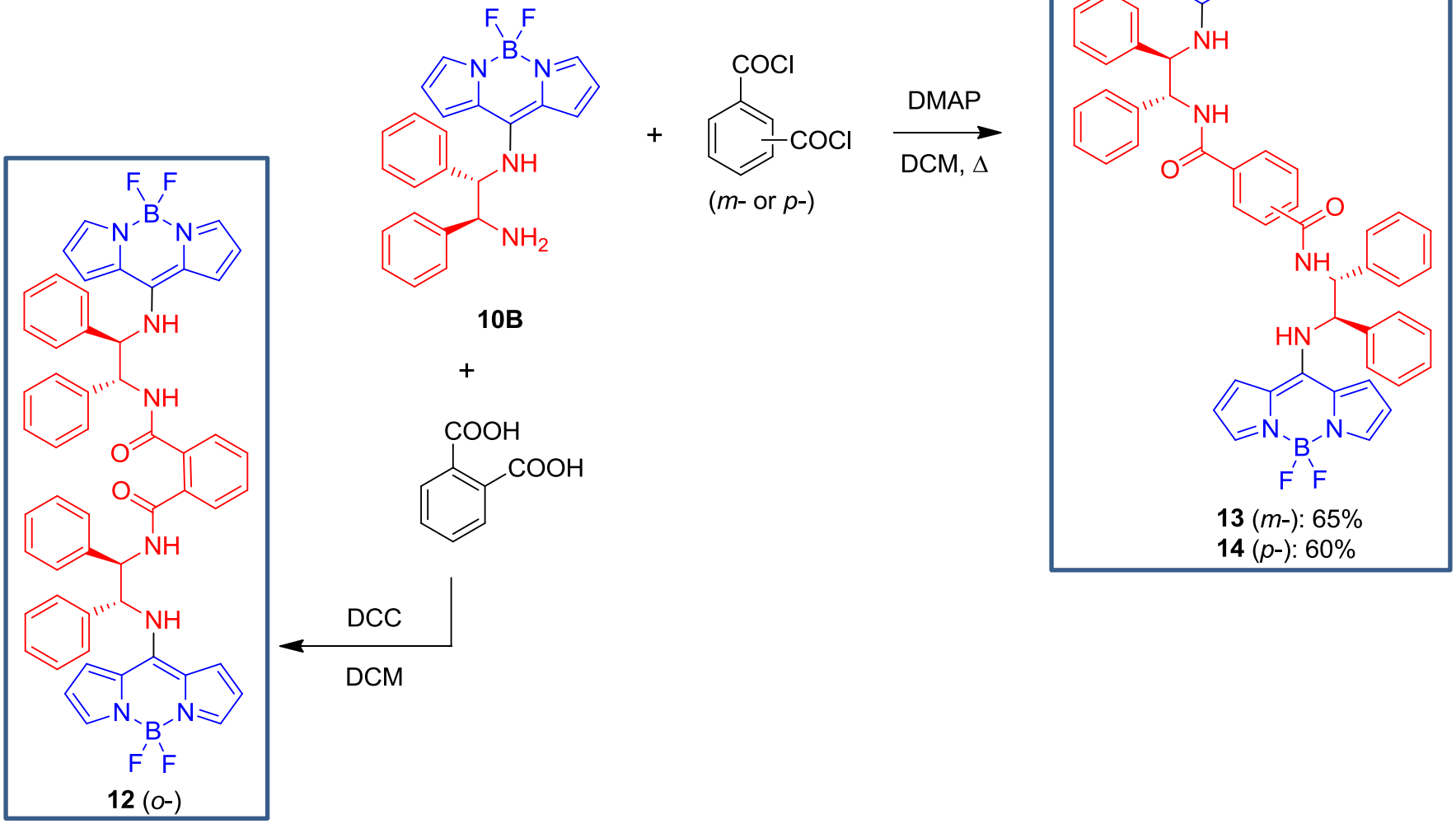
11A

Exploring new structures for the development of CPL-dyes based on flexible bis(BODIPY)s

Results

Synthesis

Strategy 2



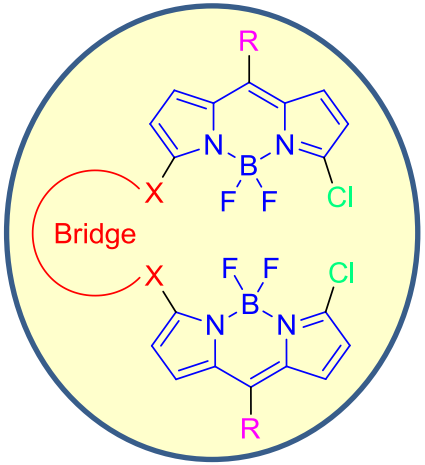
Exploring new structures for the development of CPL-dyes based on flexible bis(BODIPY)s

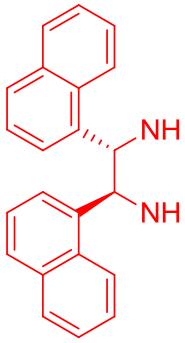
Conclusions

New series of chiral conformationally labile helical bis(BODIPY)s for studying structure - CPL activity relationships

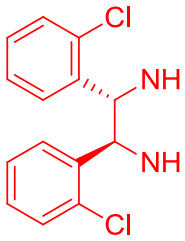
Strategy 1

Dihedral angle

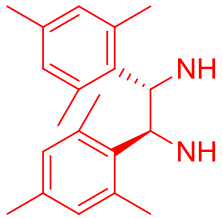




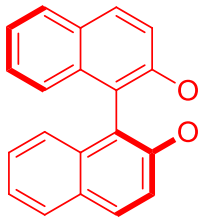
a



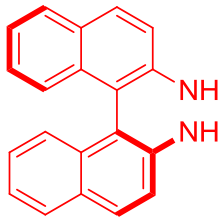
b



c



d

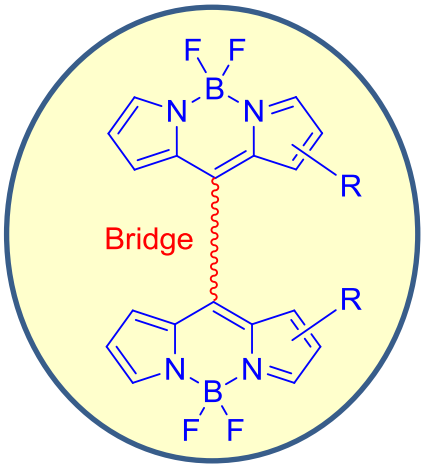


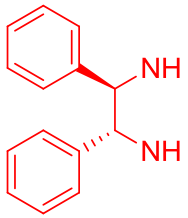
e

R = *p*-tolyl, mesityl, CF_3

Strategy 2

New positions





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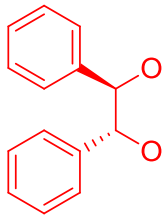

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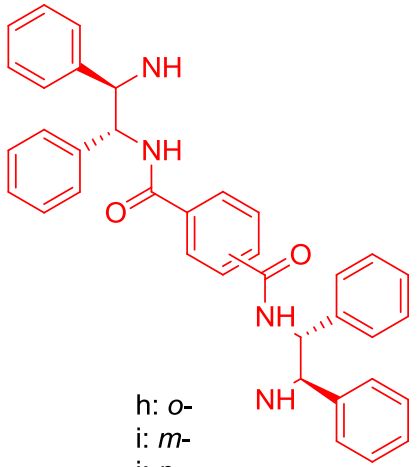

h: *o*-
i: *m*-
j: *p*-

Optimized CPL properties??