

ARYL-3-HYDROXY PROPIONIC ACID – A VERSATILE CHIRAL BUILDING BLOCK FOR LIQUID CRYSTALS

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The chiral LC structures are often achieved by introducing either a cholesterol mesogenic unit or a methyl branch group utilising commercial enantiopure starting material. [1] The structural variations of materials with a cholesterol mesogenic unit are limited what diminishes detailed investigation of structure-property relations. Furthermore, incorporation of the methyl group causes steric repulsion and destabilizes liquid-crystalline properties. [2] Our research is focused on the development of a novel chiral aryl-3-hydroxy propanoate building block capable of upgrading into various shapes of chiral molecules (Fig. 1). This structural element is less spacious than the methyl group allowing for better interaction between mesogenic units and its conformational freedom is reduced due to hydrogen bonding. Here we describe the synthetic pathway to novel chiral aryl-3-hydroxy propanoate building block (Fig. 2). Novel materials could be obtained in racemic and in chiral forms as exemplified by bent-shaped cyanobiphenyl-based dimers.

Synthesis

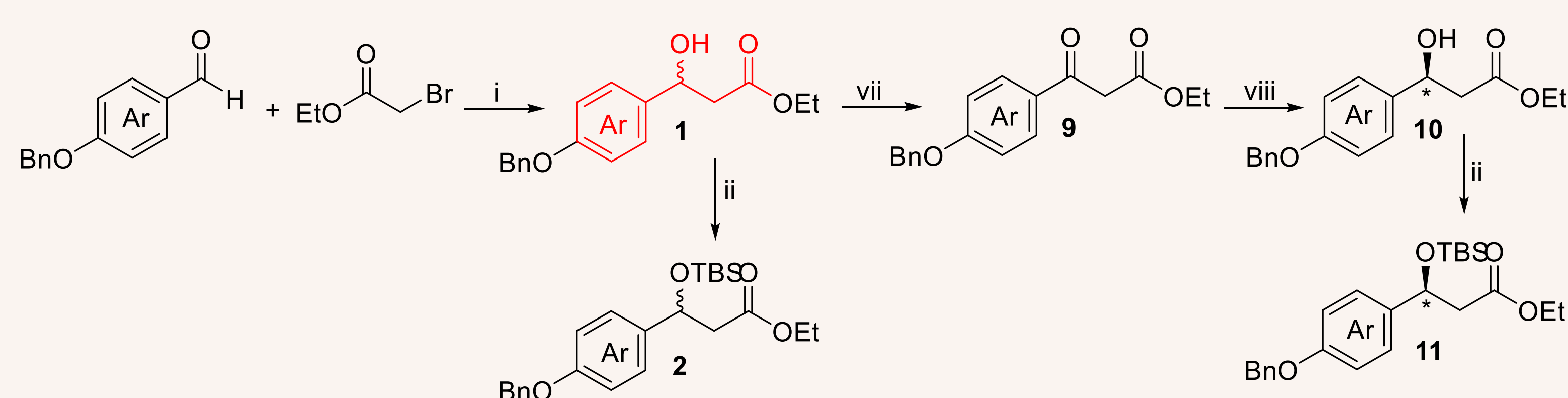


Fig. 2 Synthetic pathway of racemic and chiral aryl-3-hydroxy propanoate building block: i) Zn, TMSCl, benzene, Et₂O, 2 h, r.t.; ii) TBSCl, imidazole, DMF, 24 h, r.t.; vii) Jones reagent, acetone, 30 min, r.t.; viii) Ru cat, ligand, HCOOC/Et₃N=5/2, DMF, 40 °C, 20 h.

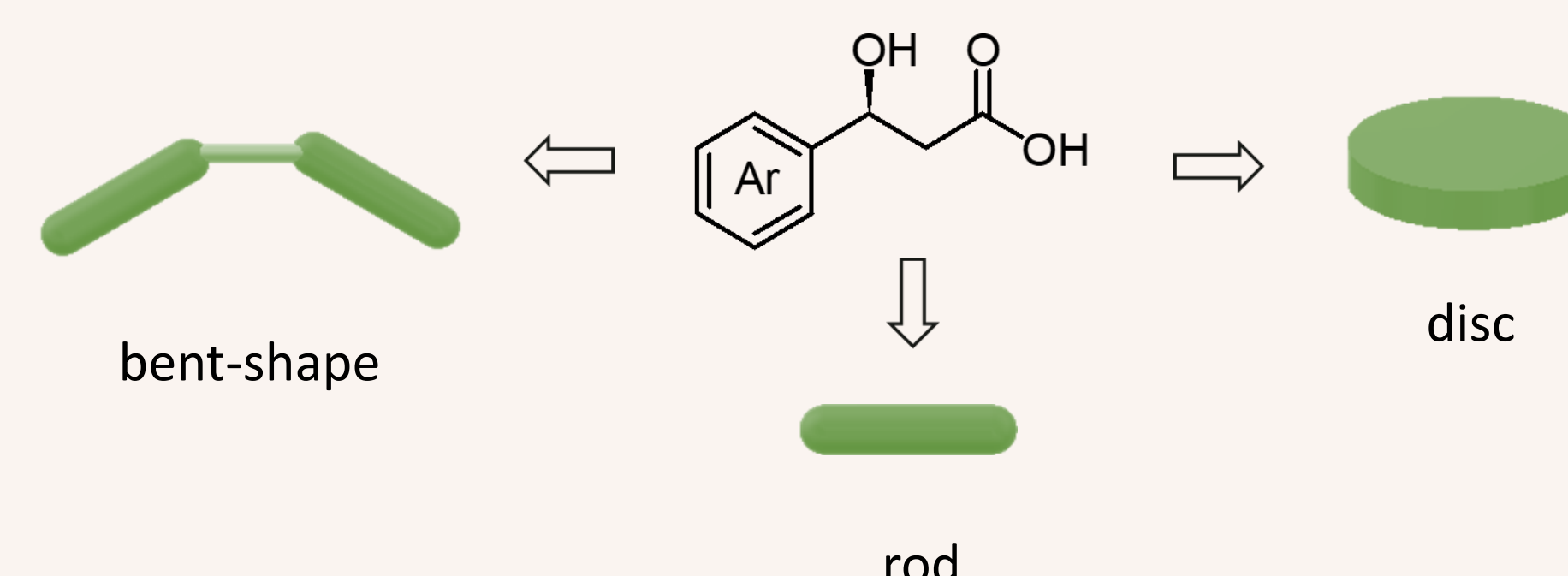
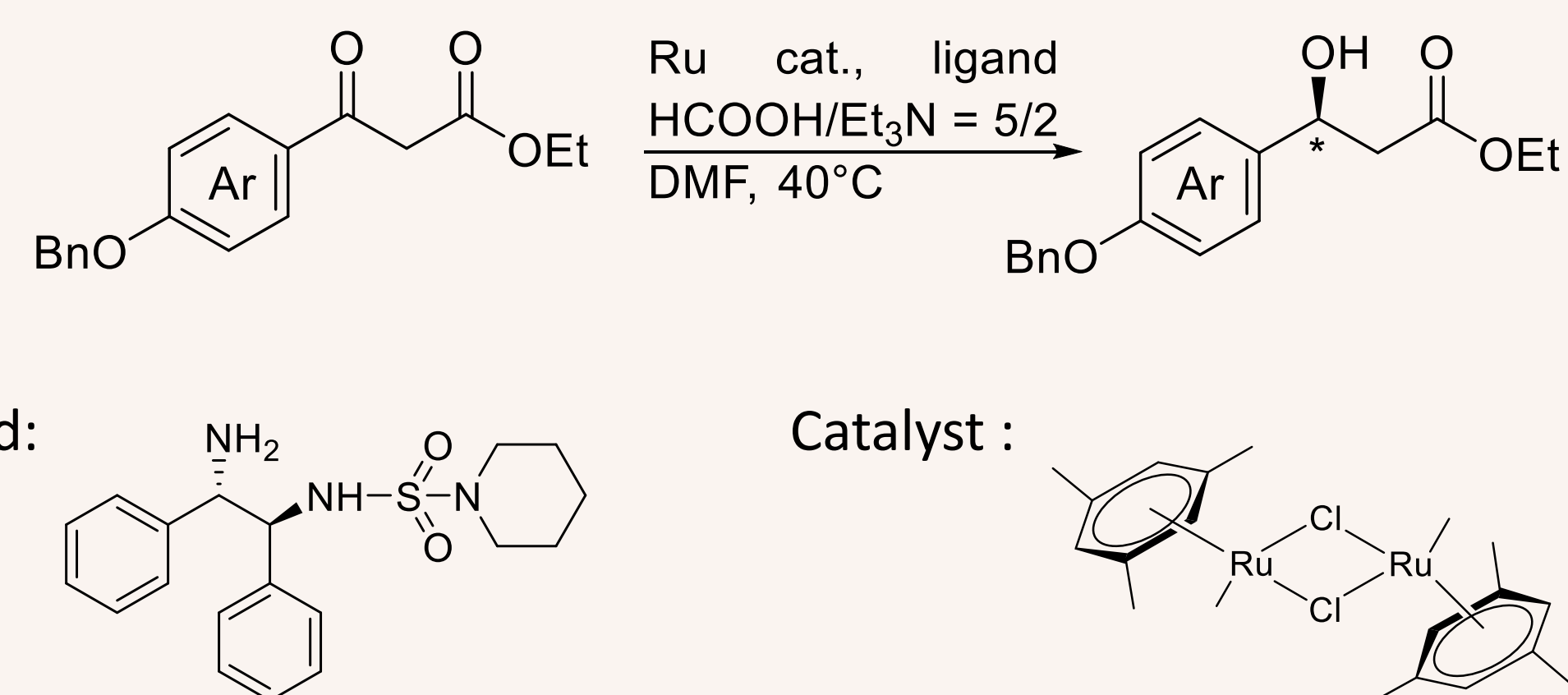


Fig. 1 Various shapes of liquid crystal molecules containing chiral aryl-3-hydroxy propanoate building block



Mesomorphic behaviour

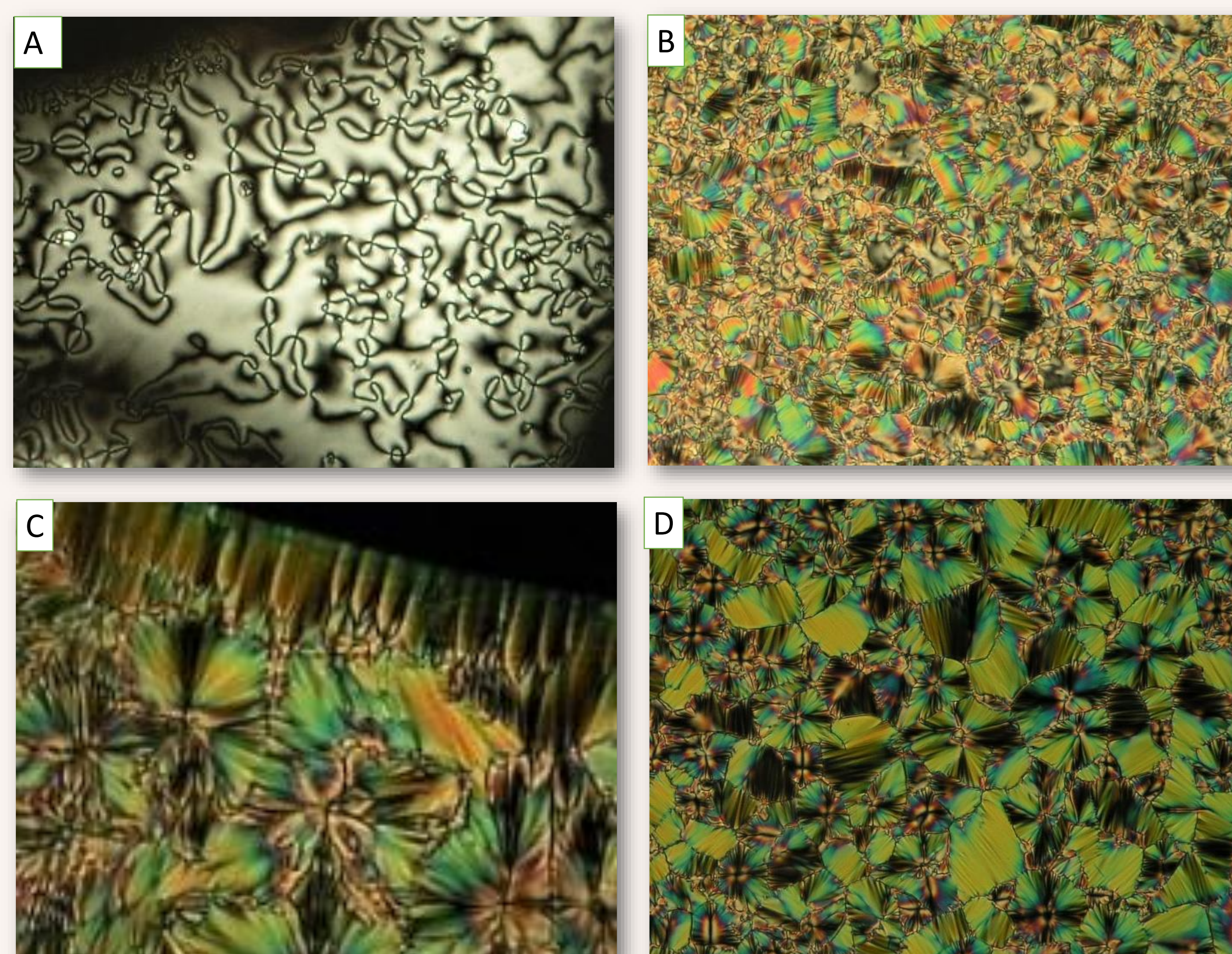


Fig. 4 Schlieren (A) and fan-shaped (B) texture obtained on cooling of a *rac*-**8** and focal conic (C) and fan-shaped (D) texture of a (*S*)-**8**.

Table 2. Transition temperatures and enthalpies in italics for racemic and chiral dimers **8**

Dimer	Transition temperatures (°C) and enthalpies (kJ mol ⁻¹)
<i>rac</i> - 8	Cr • 85 (SmC _A • 21) • I 17.08 ^[a] 2.75 ^[b]
(<i>S</i>)- 8	Cr • 84 (SmX* • 24) • I 36.65 ^[a] 2.78 ^[b]

Cr: crystalline phase; SmC_A: anticlinic smectic C phase; SmX*: unknown smectic chiral phase; I: isotropic liquid; (•): monotropic phase; [a]: combined enthalpies; [b]: obtained on cooling.

Conclusion

- The targeted molecules *rac*-**8** and (*S*)-**8** were synthesized using the same convergent approach
- The *rac*-**8** exhibits a monotropic SmC_A phase with characteristic schlieren and fan-shaped texture
- Focal conic and fan-shaped texture were obtained from (*S*)-**8**, but the exact phase is yet to be determined; SmC_A* is presumed
- Cr phase of *rac*-**8** is more stable than Cr chiral phase, but LC phase of (*S*)-**8** is more stable than LC phase of *rac*-mixture.
- This building block enables investigation of the structure-property relation as well as a correlation between chiralities of different origin and discovery of novel liquid crystalline phases

References

- Donaldson T., Staesche H., Lu Z. B., *et al.*, *Liq. Cryst.* **37** (2010) 1097.
- Goodby J. W., Davis E. J., Mandle R. J., *et al.*, *Isr. J. Chem.* **52** (2012) 863.

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Table 1. Time, yield and ee of various aryl-3-hydroxy propanoate building blocks with [RuCl₂(mesitylene)]₂

Ar	Time (h)	Yield (%)	ee (%)
phenyl	3 h	81	90
naphthyl	3 h	92	95
biphenyl	3 h	82	97

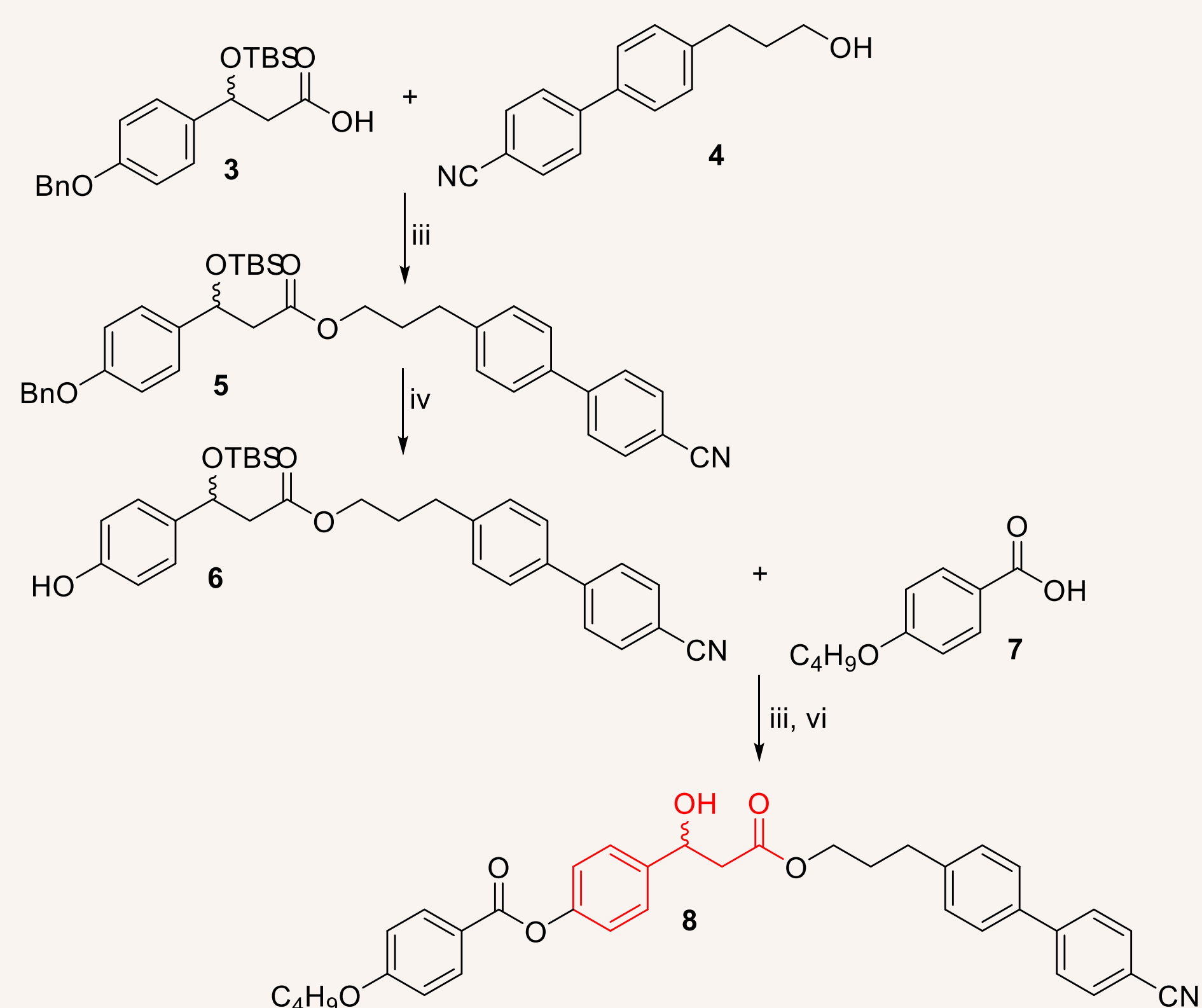


Fig. 3 Synthesis of a racemic mixture of a bent-shaped molecule containing phenyl-3-hydroxy propanoate building block. A chiral molecule (*S*)-**8** is synthesized following the same synthetic route: iii) 1. (COCl)₂, toluene, DMF, 1.5 h, r.t., 2. DMAP, Et₃N, CH₂Cl₂, 2 h, r.t.; iv) Pd/C, cyclohexene, EtOH, 24 h, 100 °C; vi) TBAF, THF, 3.5 h, r.t.