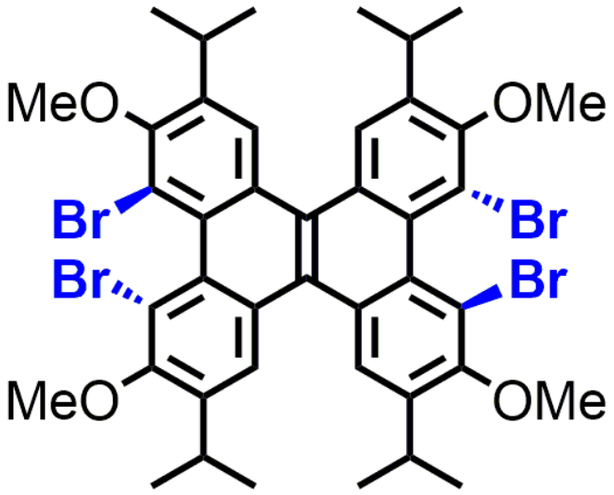
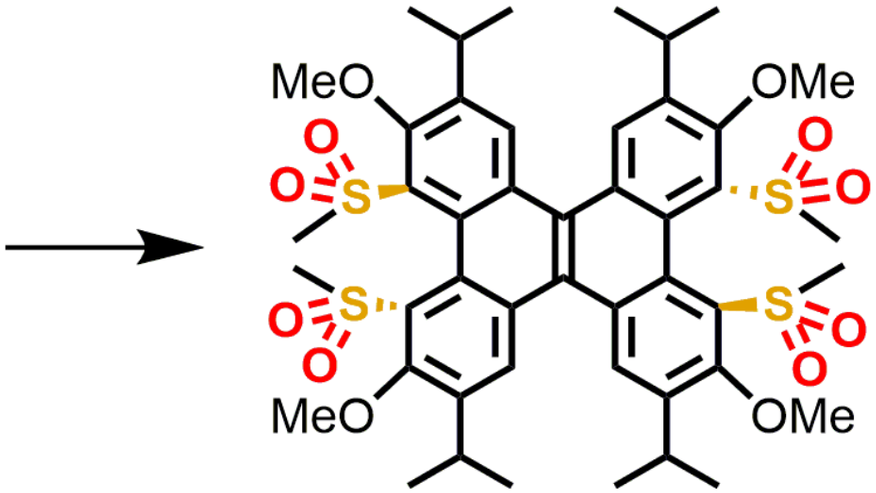
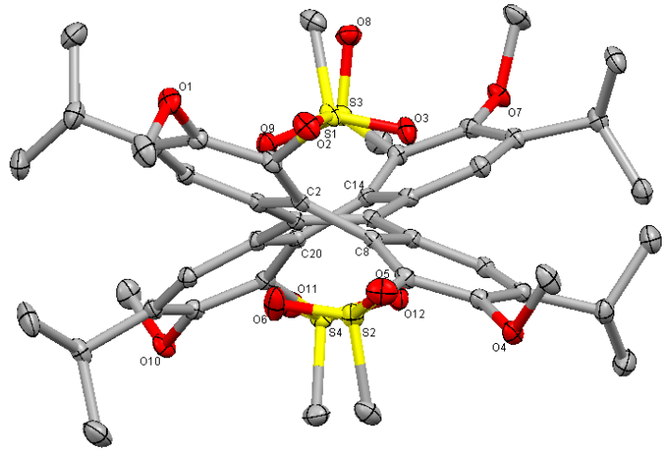
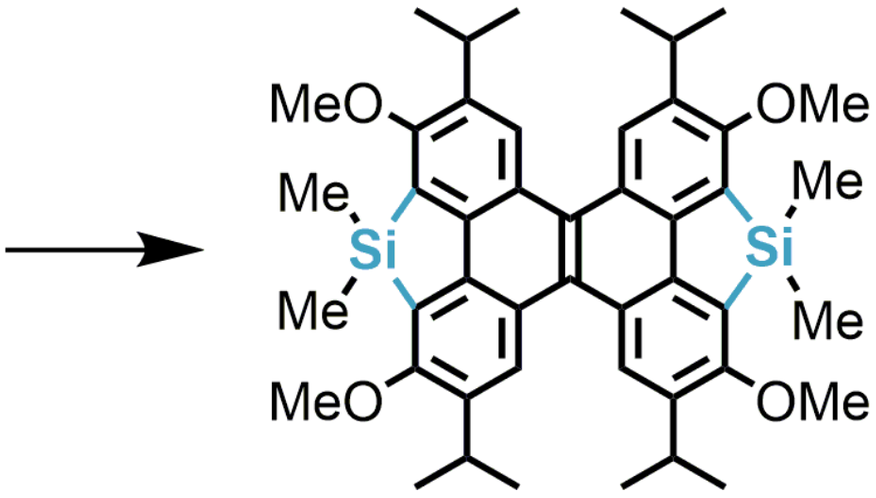
Relevant Synthesis to Manipulating Non-Planarity in Dibenzo[*g*,*p*]chrysene: Substitution Reactions at the *Bay*

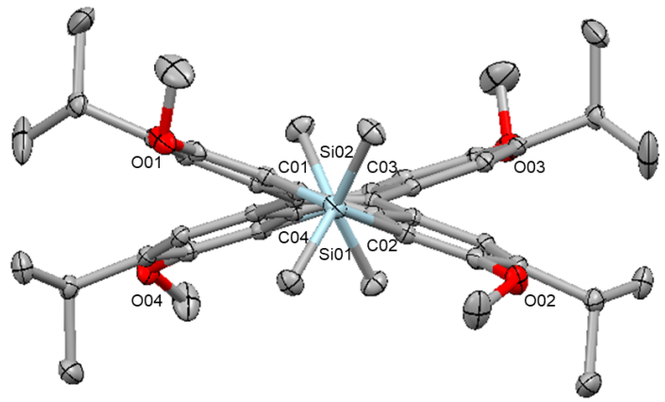






max. torsion angle, 57.4°

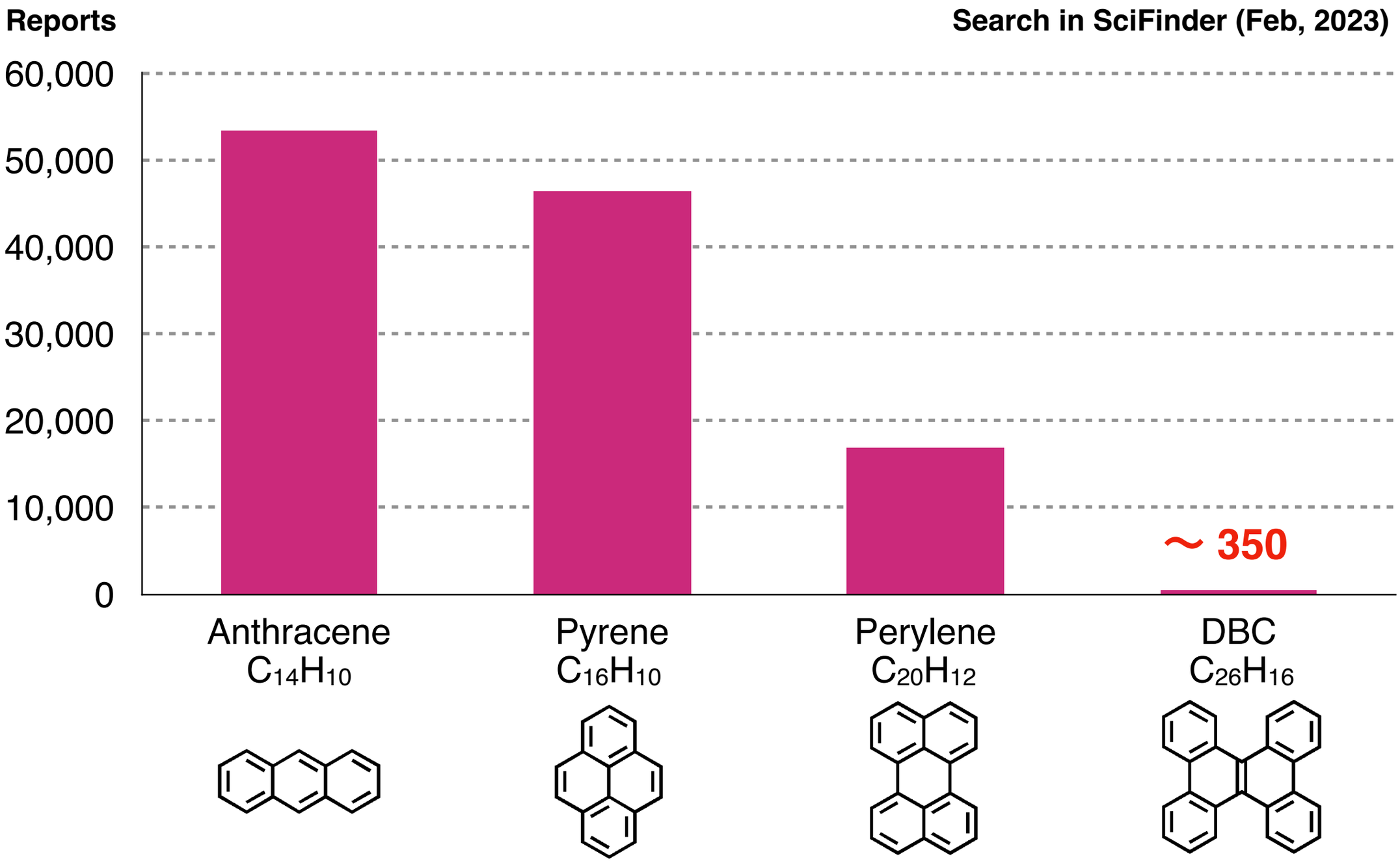




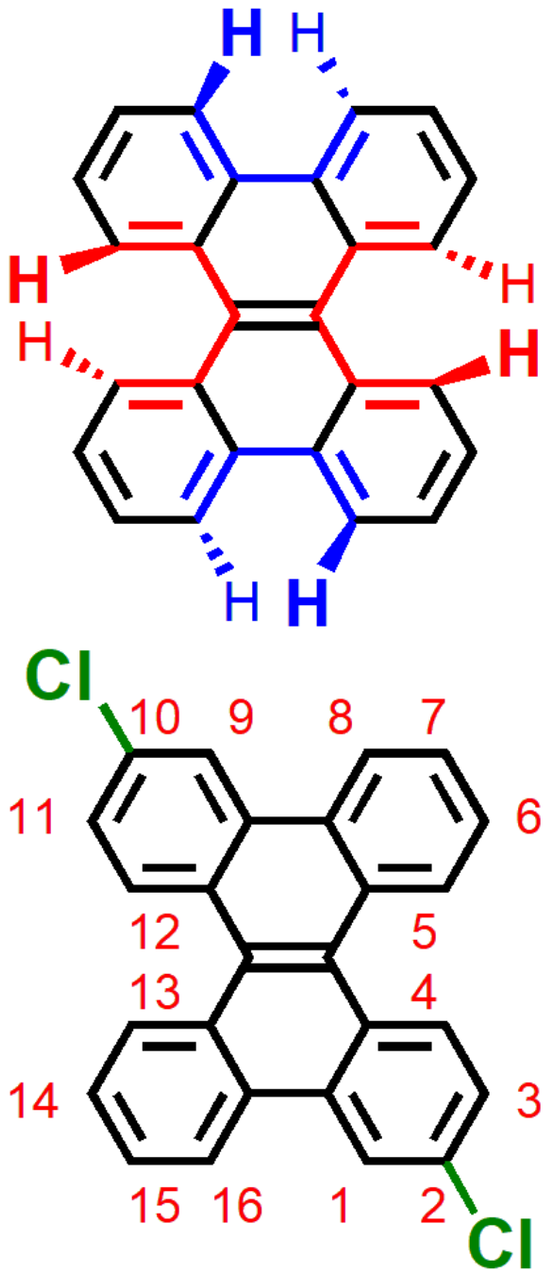
min. torsion angle, 31.8°

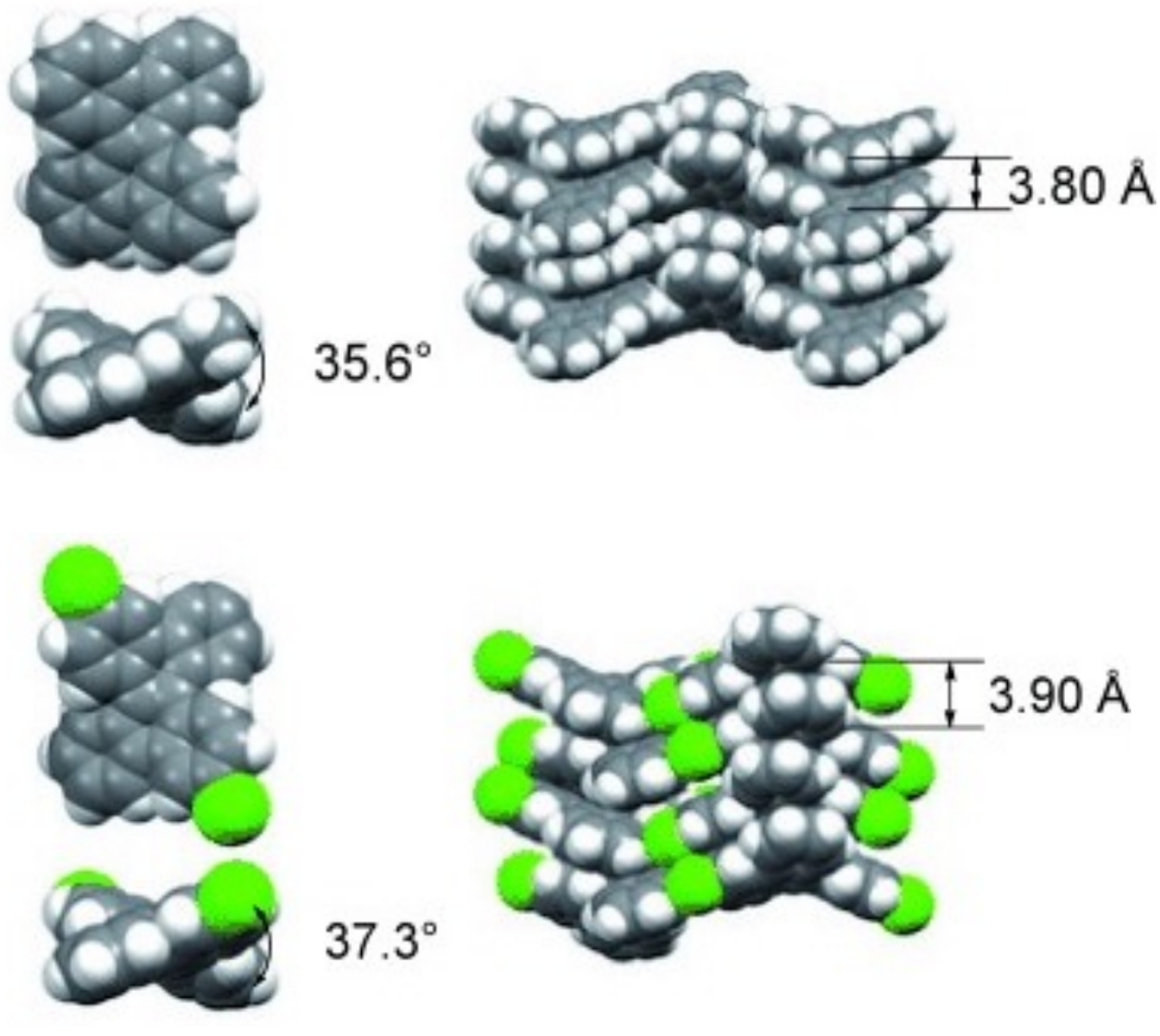
S. Kamiguchi, R. Akasaka, N. Yoshida, T. Imai, Y. Yamaoka, T. Amaya, T. Iwasawa, *Tetrahedron Lett.* **2022**, *92*, 153664.

General Background: Reports about DBC synthesis have been underrepresented so far, compared to Perylene etc.



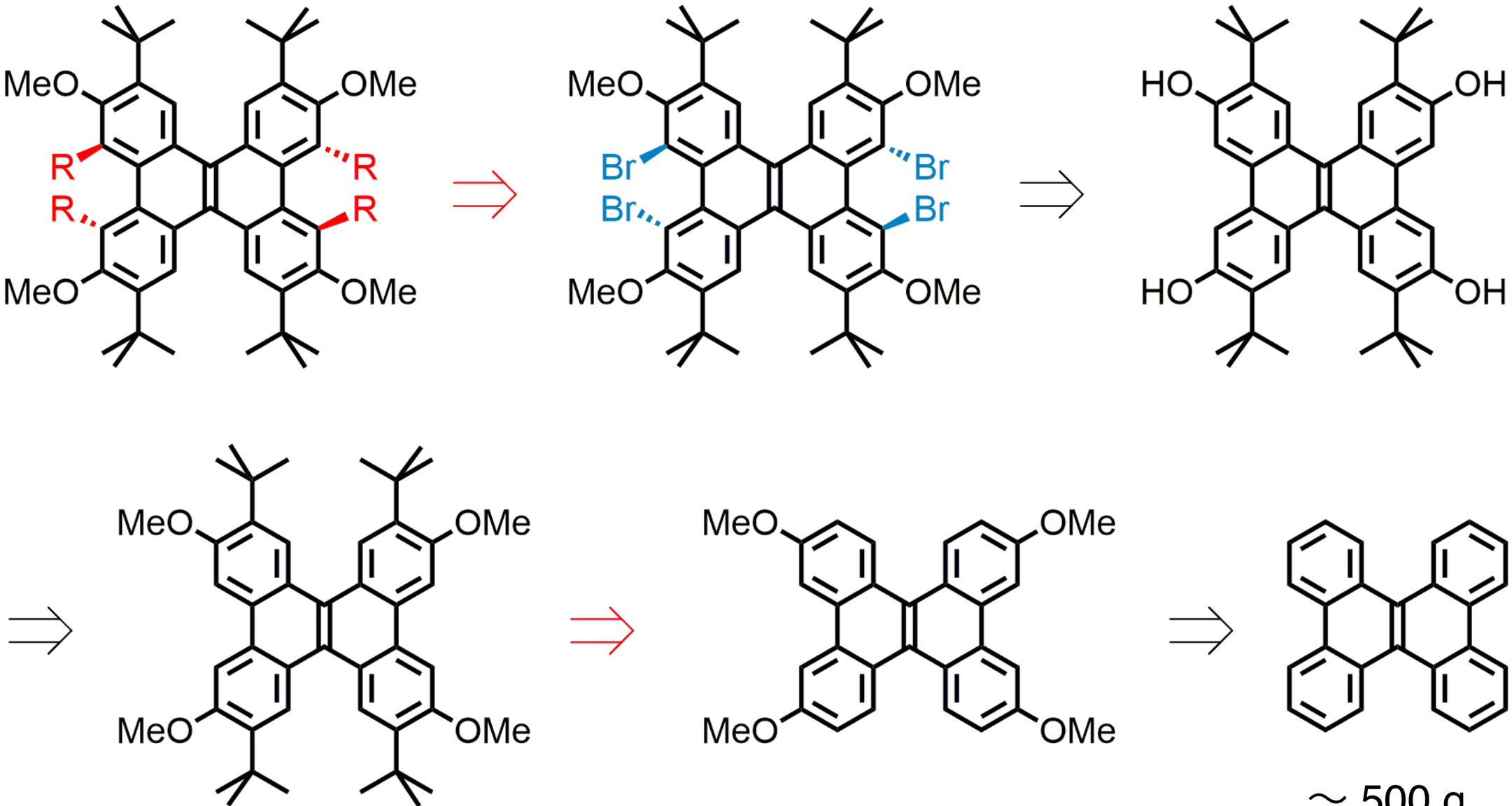
Background: DBC moiety has an essential characteristic structure that possesses a non-planar pi-conjugation.



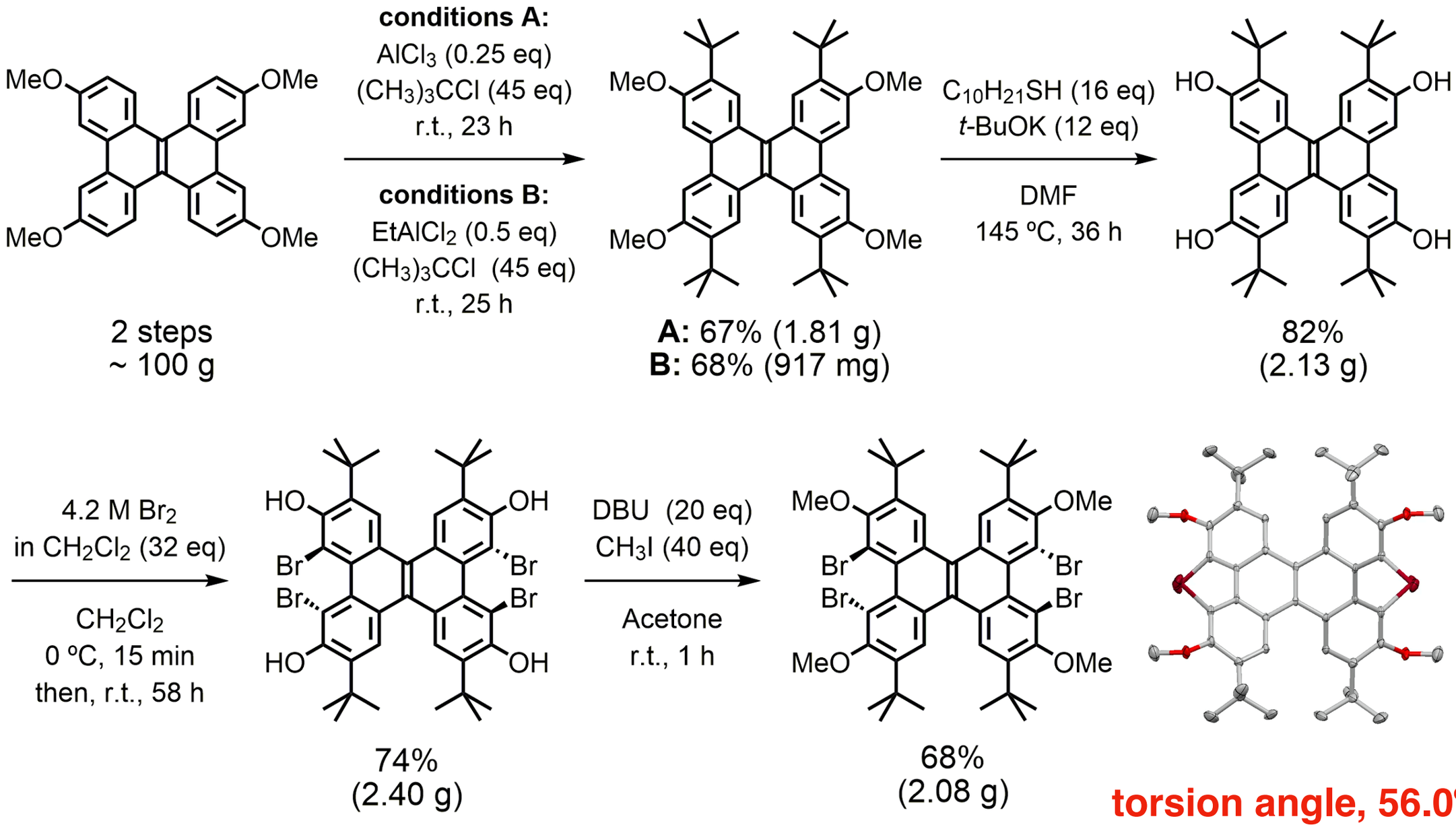


Y. Ueda, H. Tsuji, H. Tanaka, E. Nakamura, *Chem. Asia. J.* **2014**, *9*, 1623-1628.

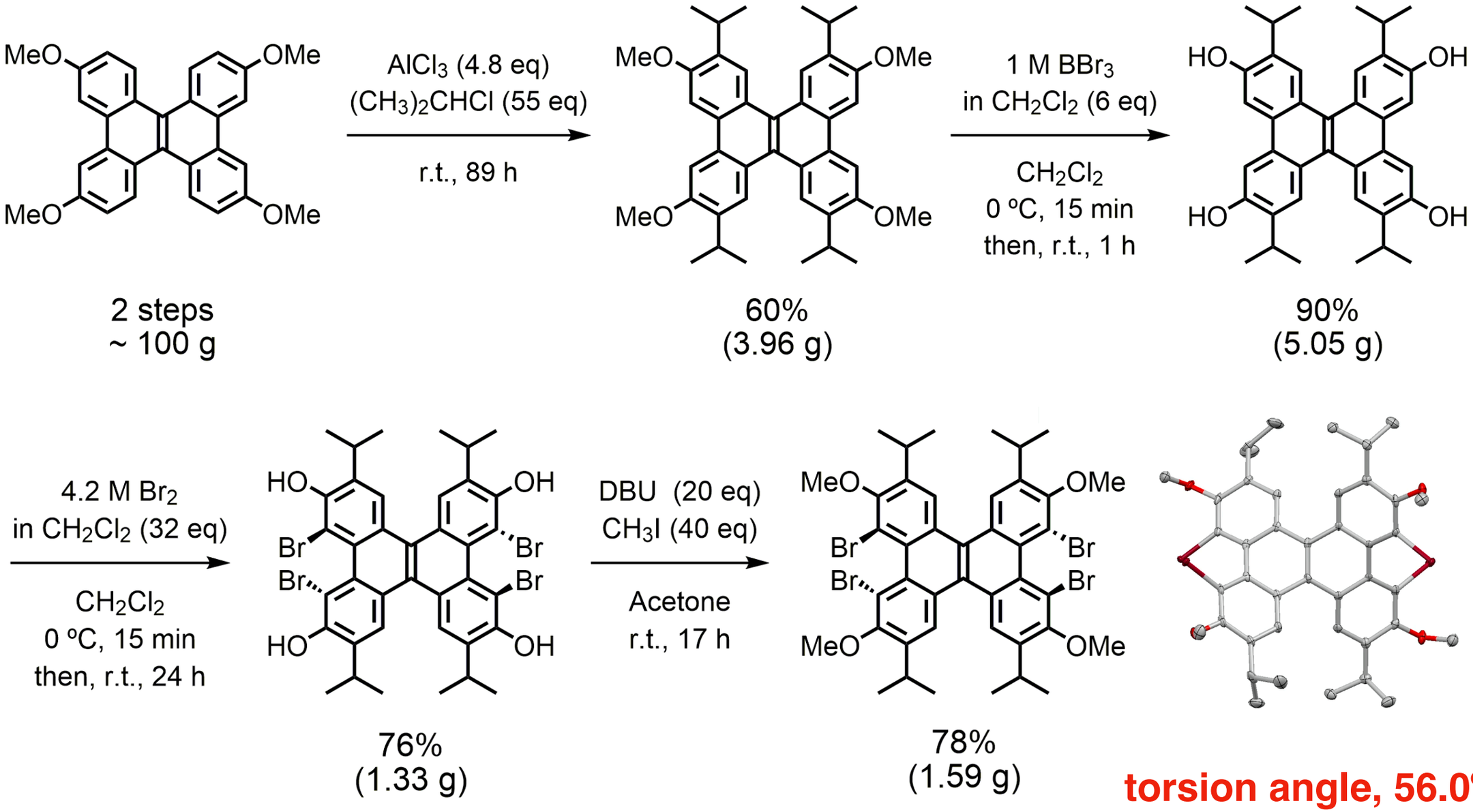
Approach: Is it possible to manipulate the non-planarity with torsion angles? Different non-planarity could provide different chemical property.



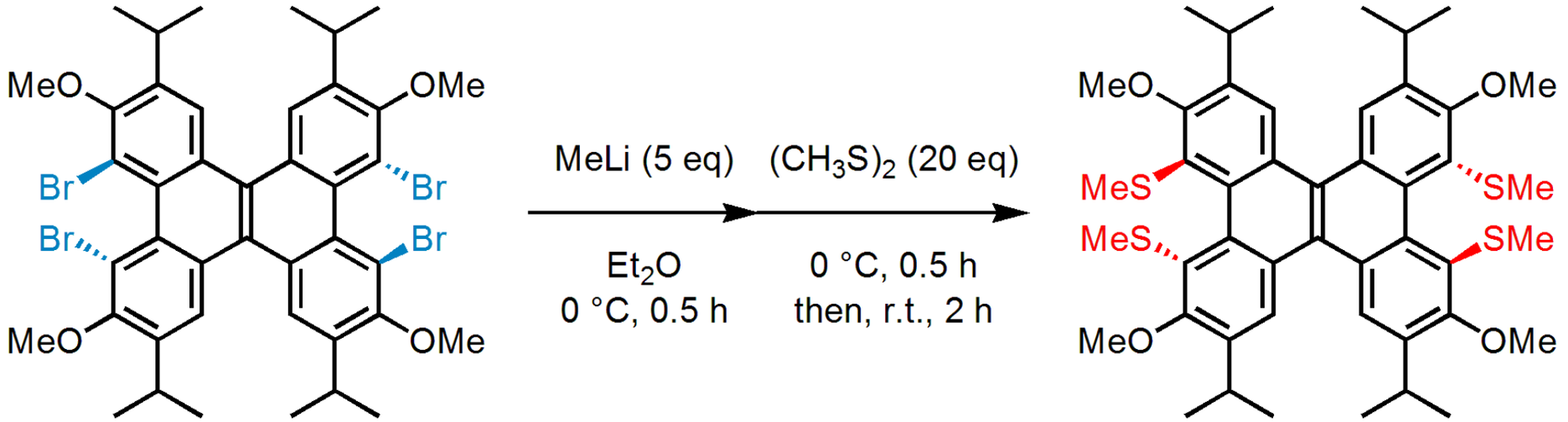
In real, synthesis of the starting tetra-bromide: Substitution of *tert*-Bu groups proceeded in gram-scale, although the products didn't show good solubility against my expectation.



***Iso*-propyl version**: the moieties attained much better solubility than the *tert*-Bu groups. Torsion angles between *i*-Pr and *t*-Bu substructures are the mostly same (56º).

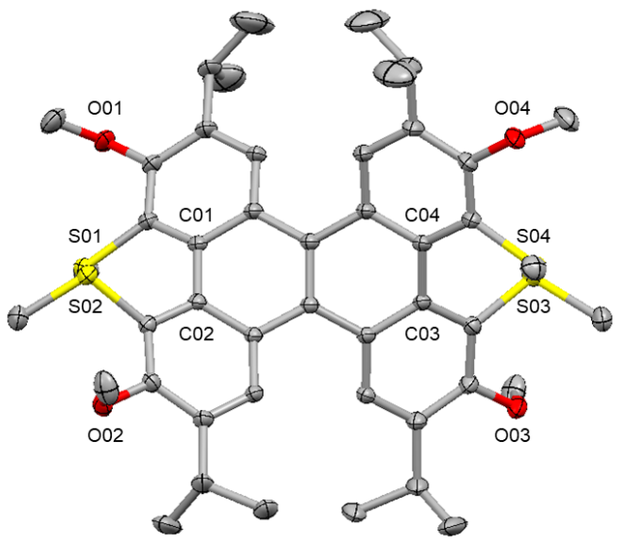


Activation by organolithium reagents: the lithium-halogen exchange reactions occurred smoothly, which enabled the desired substitution reactions.

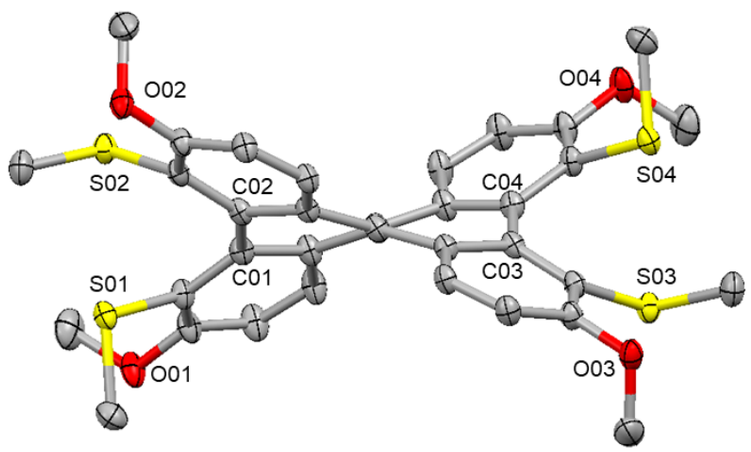


68%

torsion angle, 56.0°

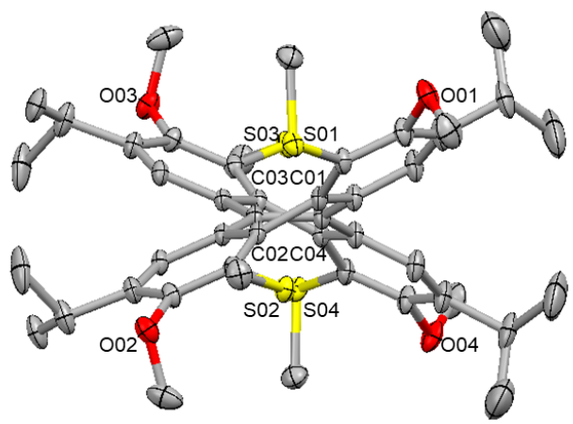


CCDC 2093676: Monoclinic
R_1 = 0.0484, GOF = 1.034



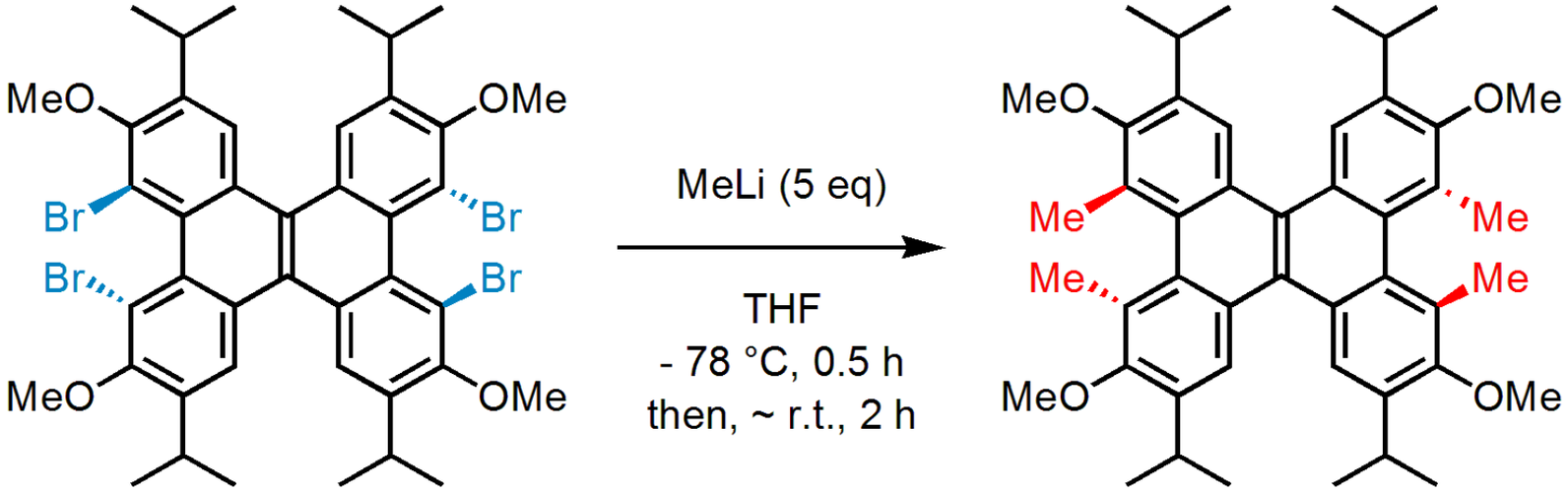
side view from the *fjord* region

torsion angle, 57.2°



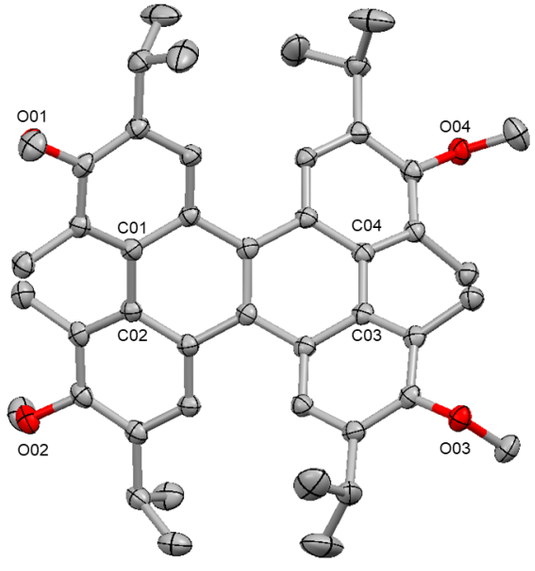
side view from the *bay* region

Me groups: Attaching the methyl groups into the bay regions was successful without the electrophilic MeI.



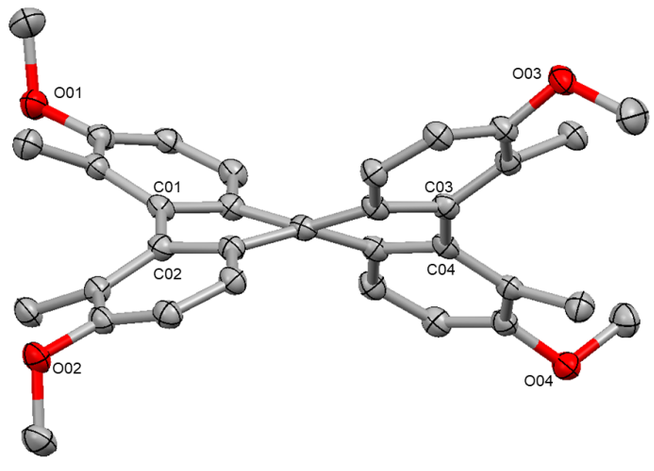
51%

torsion angle, 56.0°

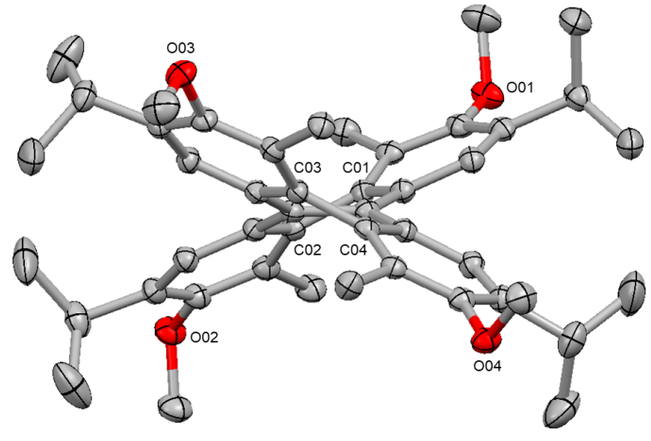


CCDC 2119962: Monoclinic
R_1 = 0.0636, GOF = 1.117

torsion angle, 55.4°

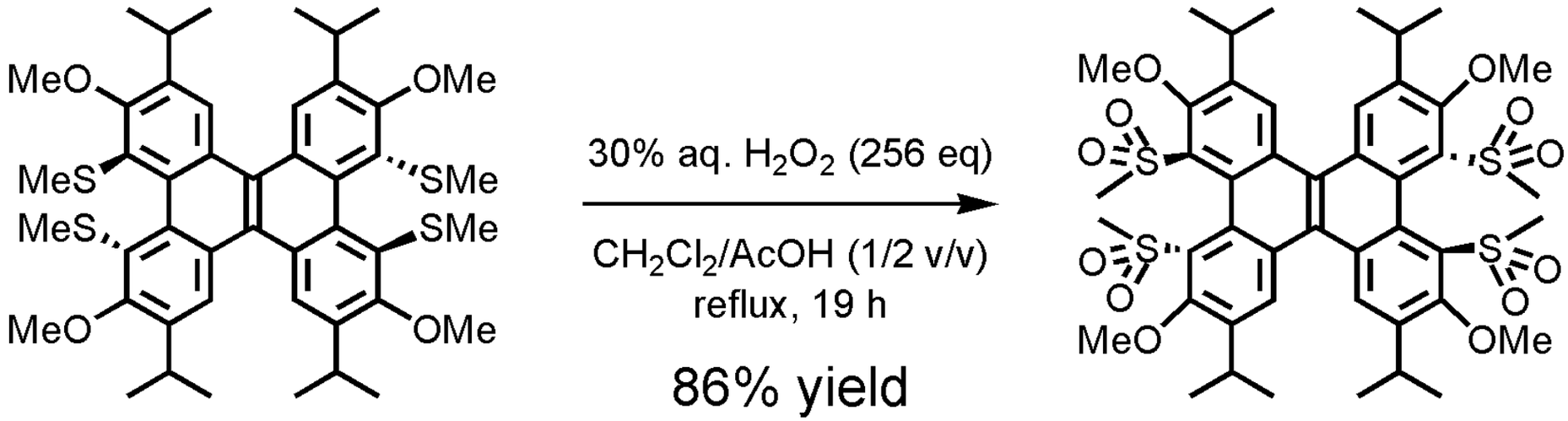


side view from the *fjord* region

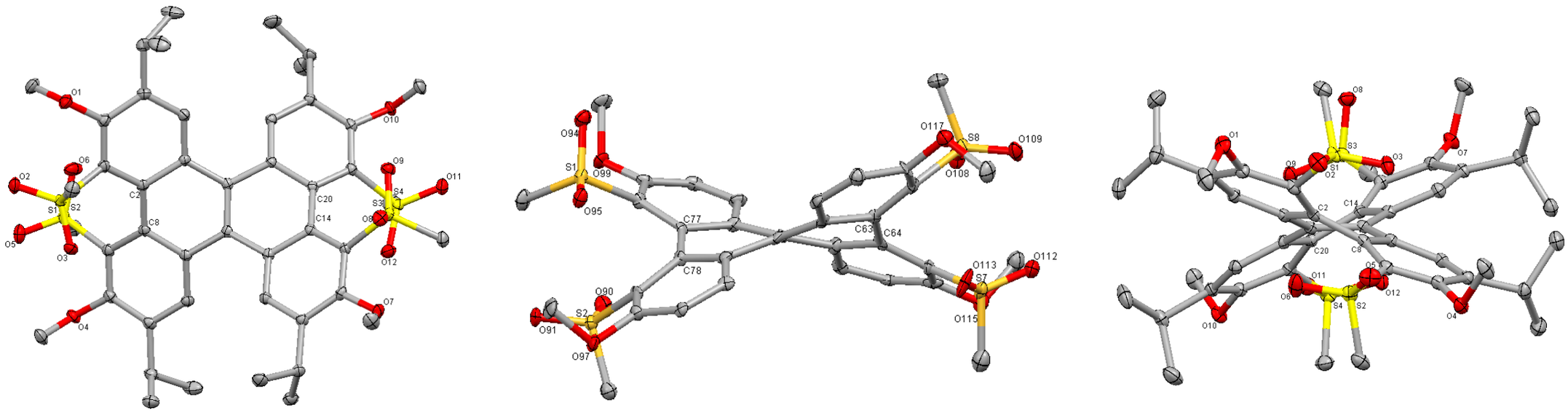


side view from the *bay* region

The much bulky substituent of SO_2Me groups were successfully induced into the *bay*: its torsion angle of 57.4º was comparable to that of 57.2º in the SMe moieties.



torsion angle, 57.2º **torsion angle, 57.4º**

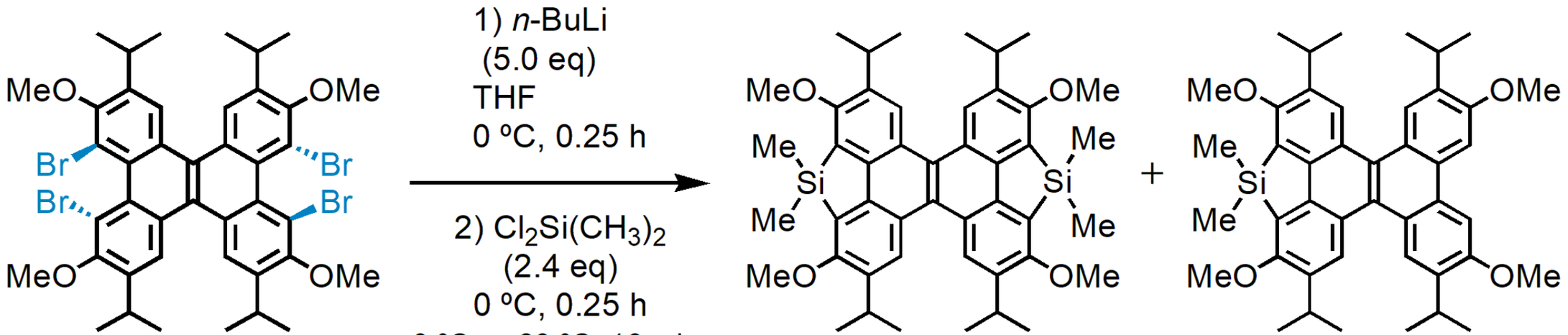


CCDC 2093960: Triclinic
R_1 = 0.0427, GOF = 1.070

side view from the *fjord* region

side view from the *bay* region

Double pentagons formation: We made a contrastive synthesis in which two five-membered rings were formed with the aid of silicon atoms.

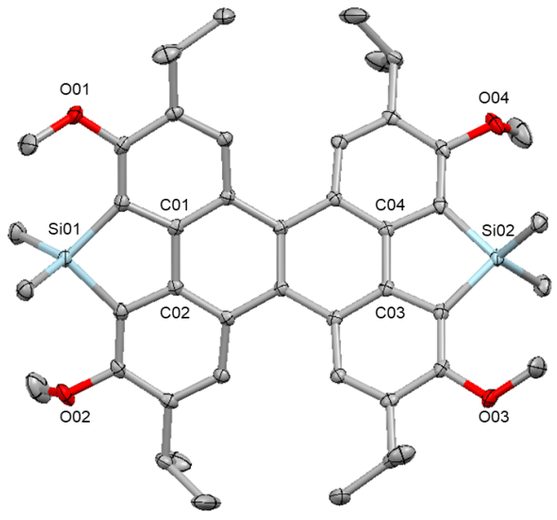


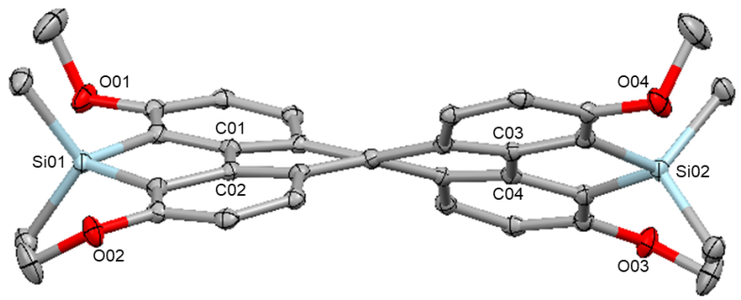
21%

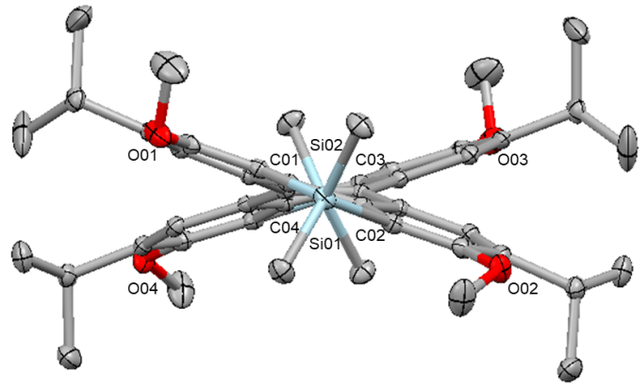
21%

torsion angle, 56.0º

torsion angle, 31.8º





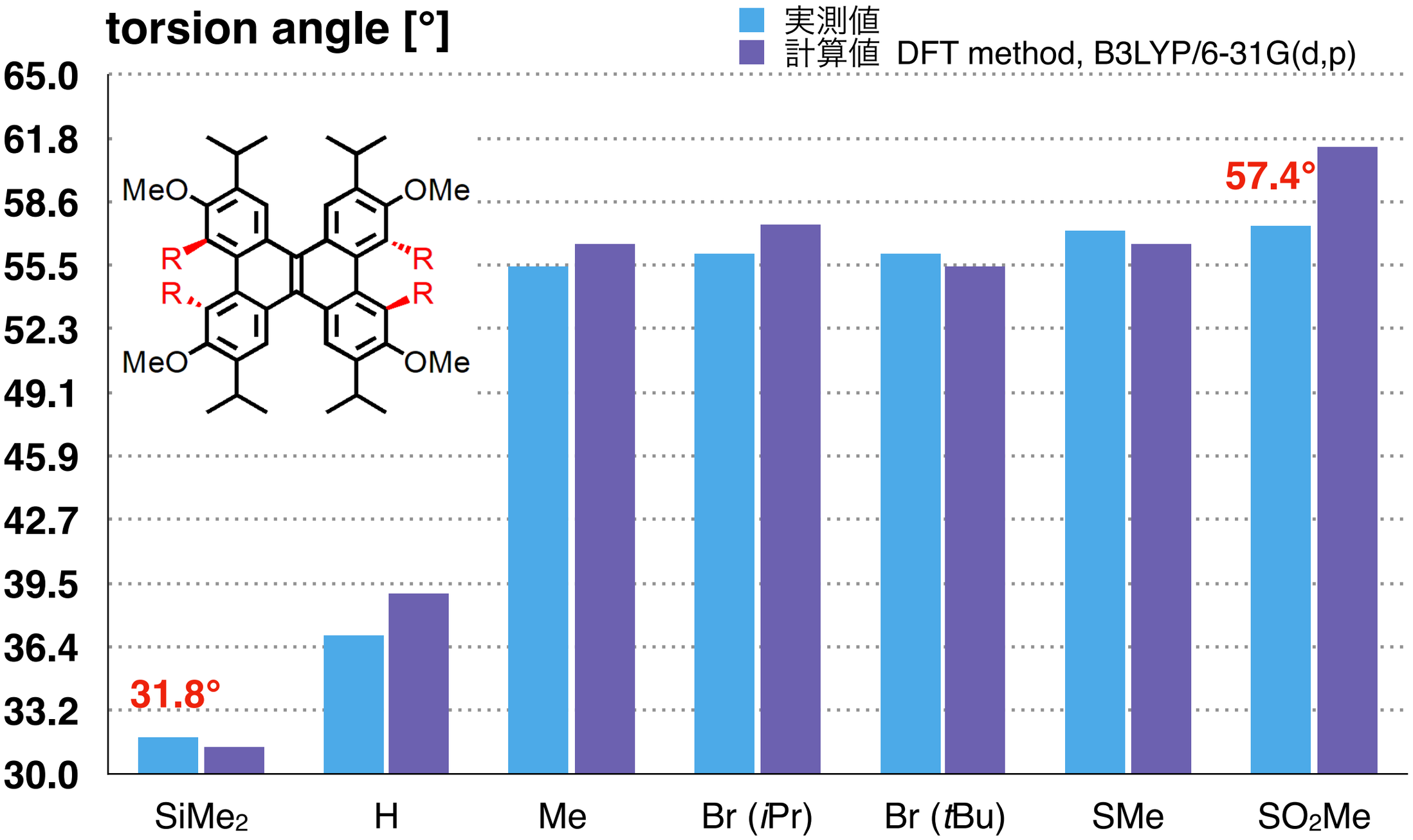


CCDC 2111352: Orthorhombic
R_1 = 0.0431, GOF = 1.072

side view from the *fjord* region

side view from the *bay* region

Correlation between substituents and torsion angles.



At least 26º can change in the angle: The DBC core has turned out to be flexibly movable in the range from 57º to 32º.