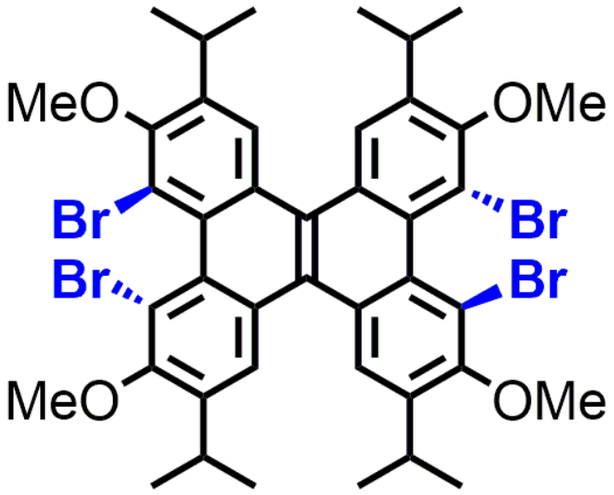
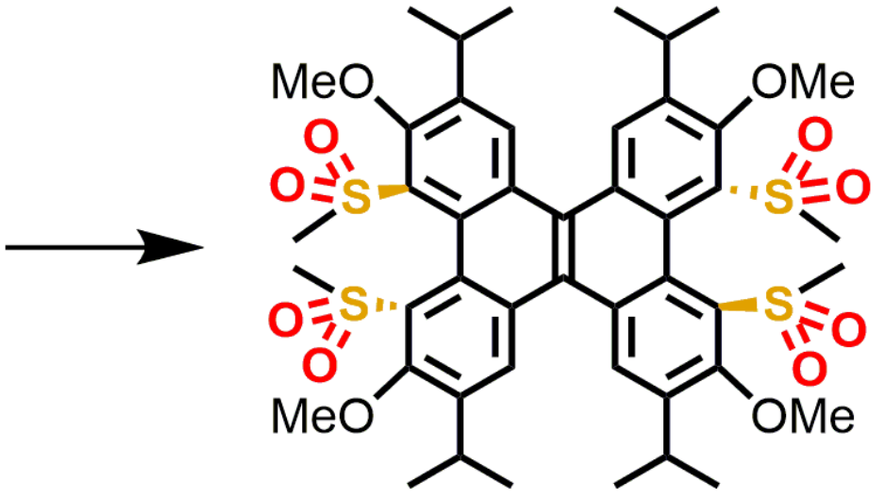
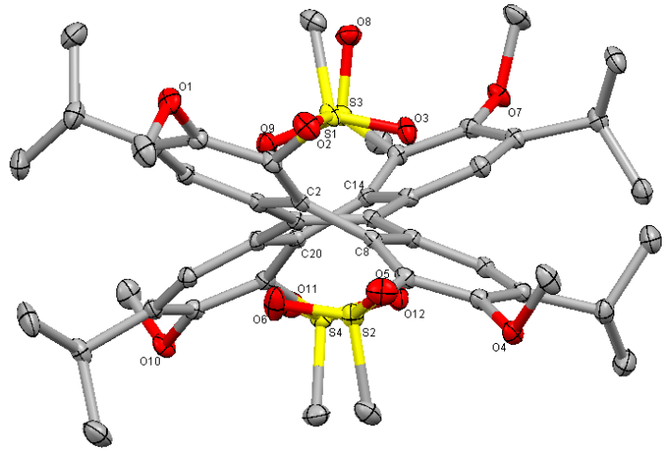
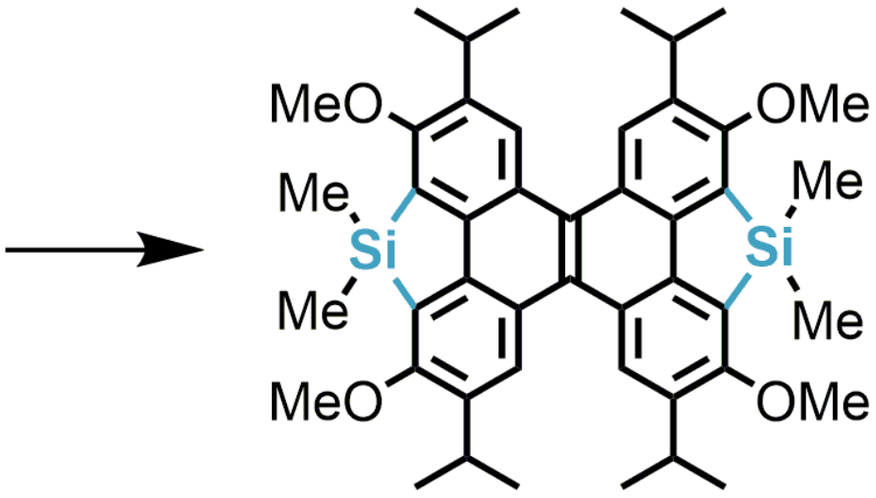
# Relevant Synthesis to Manipulating Non-Planarity in Dibenzo[*g*,*p*]chrysene: Substitution Reactions at the *Bay*

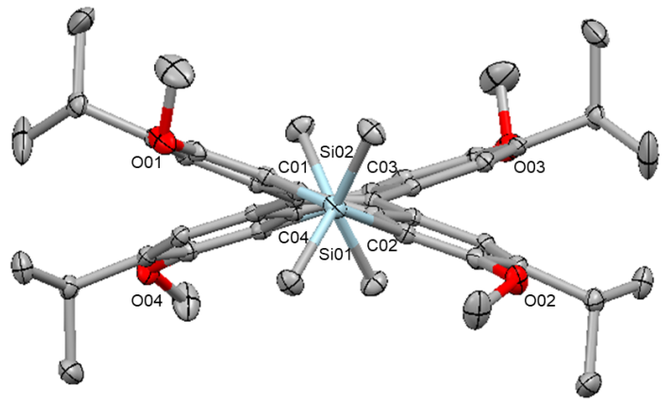



**max. torsion angle, 57.4°**

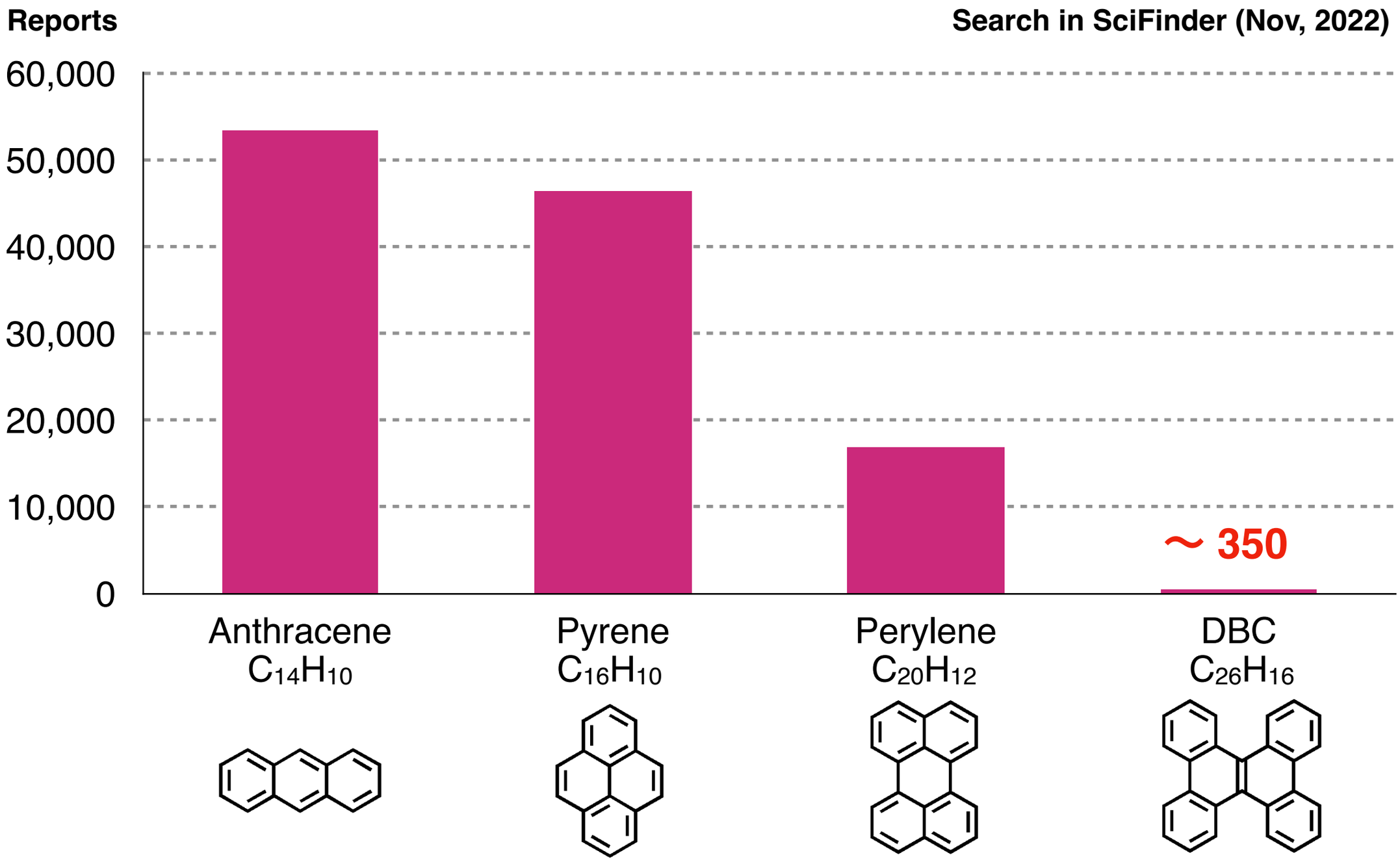


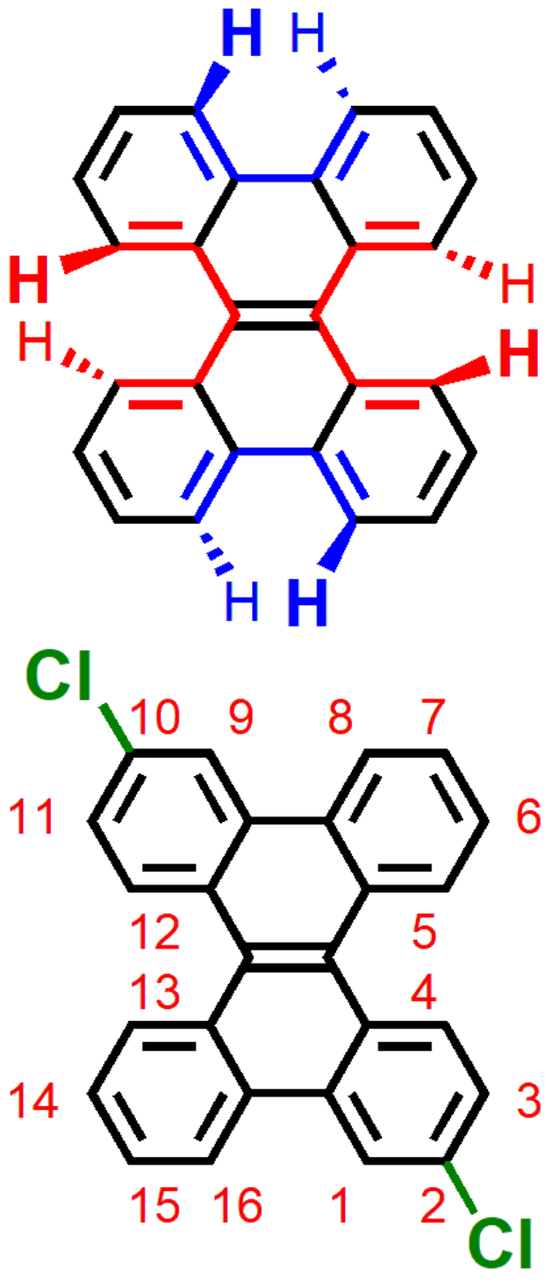

**min. torsion angle, 31.8°**

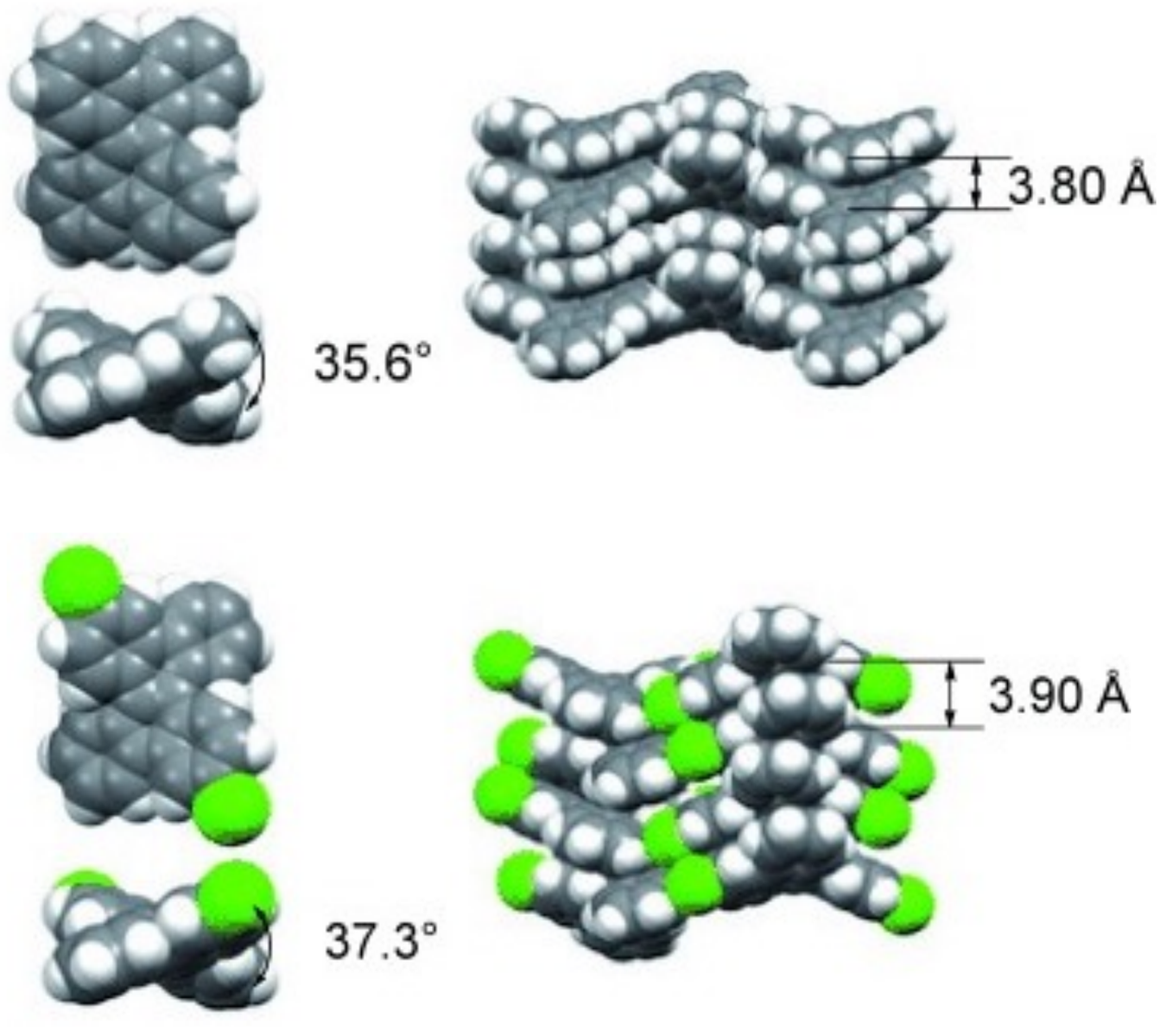
S. Kamiguchi, R. Akasaka, N. Yoshida, T. Imai, Y. Yamaoka, T. Amaya, T. Iwasawa, *Tetrahedron Lett.* **2022**, *92*, 153664.

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



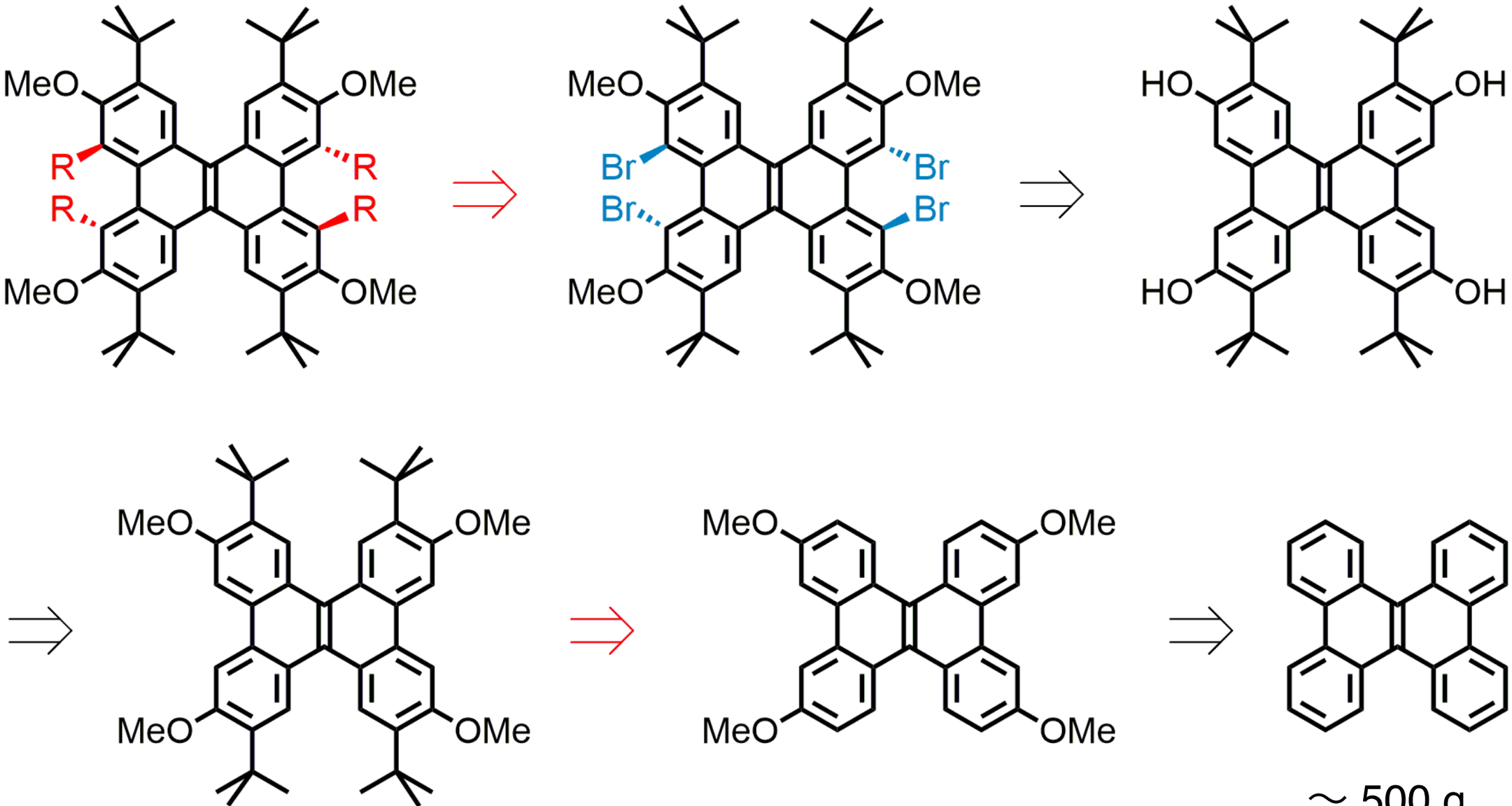
**Background**: DBC moiety has an essential characteristic structure that possesses a non-planar pi-conjugation.



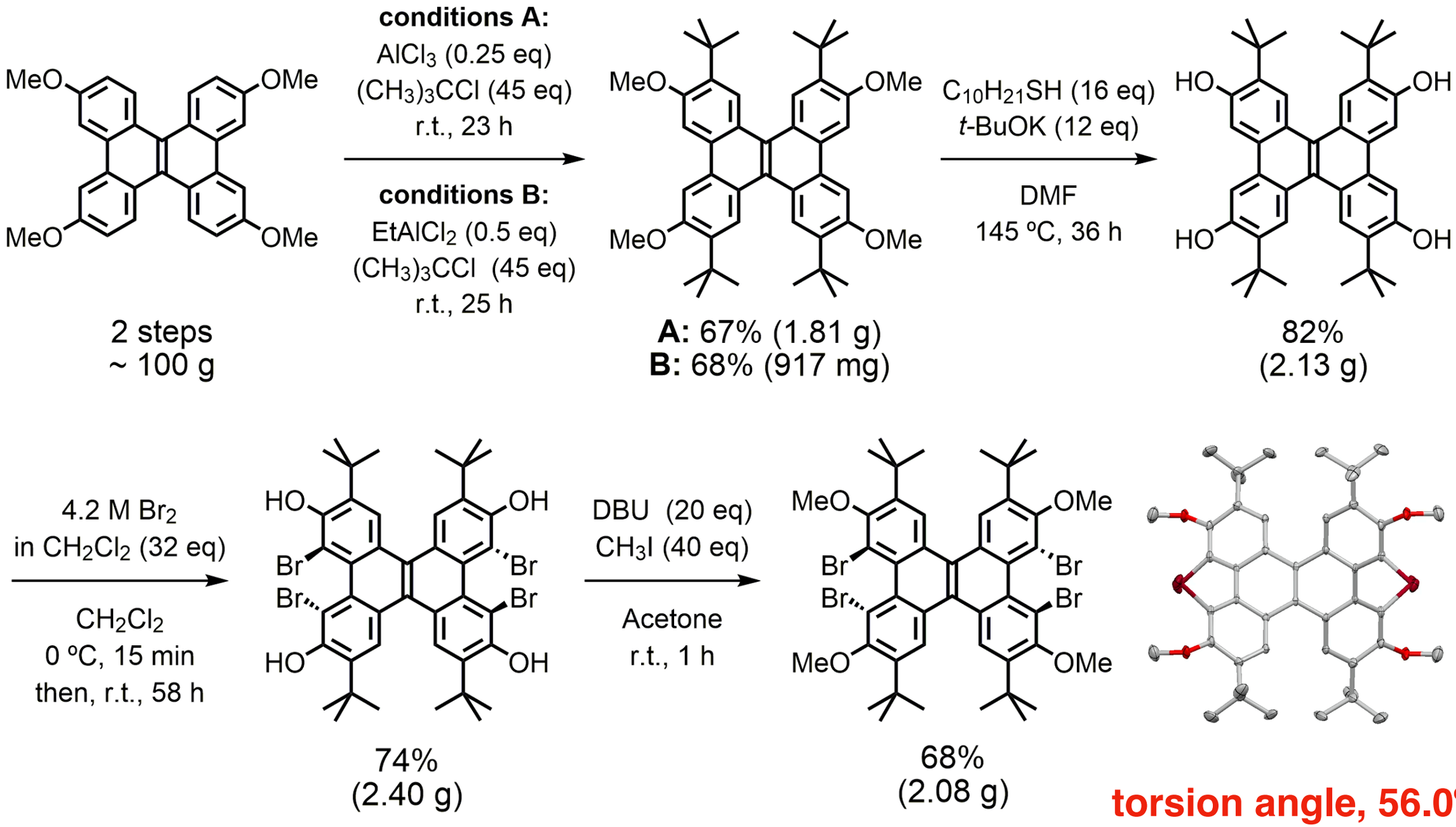




Y. Ueda, H. Tsuji, H. Tanaka, E. Nakamura, *Chem. Asia. J.* **2014**, *9*, 1623-1628.

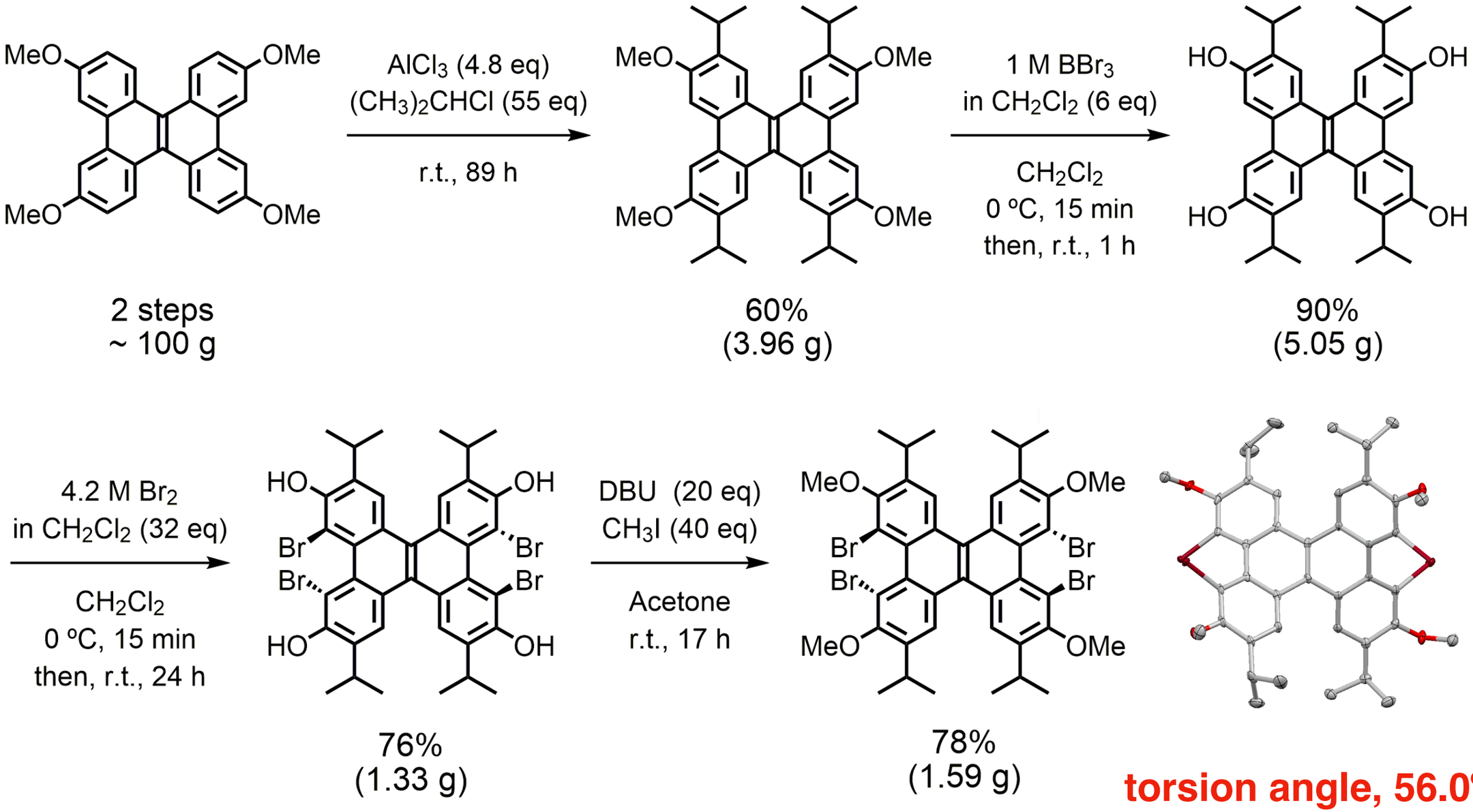
**Approach**: Is it possible to manipulate the non-planarity with torsion angles? Different non-planarity could provide different chemical property.



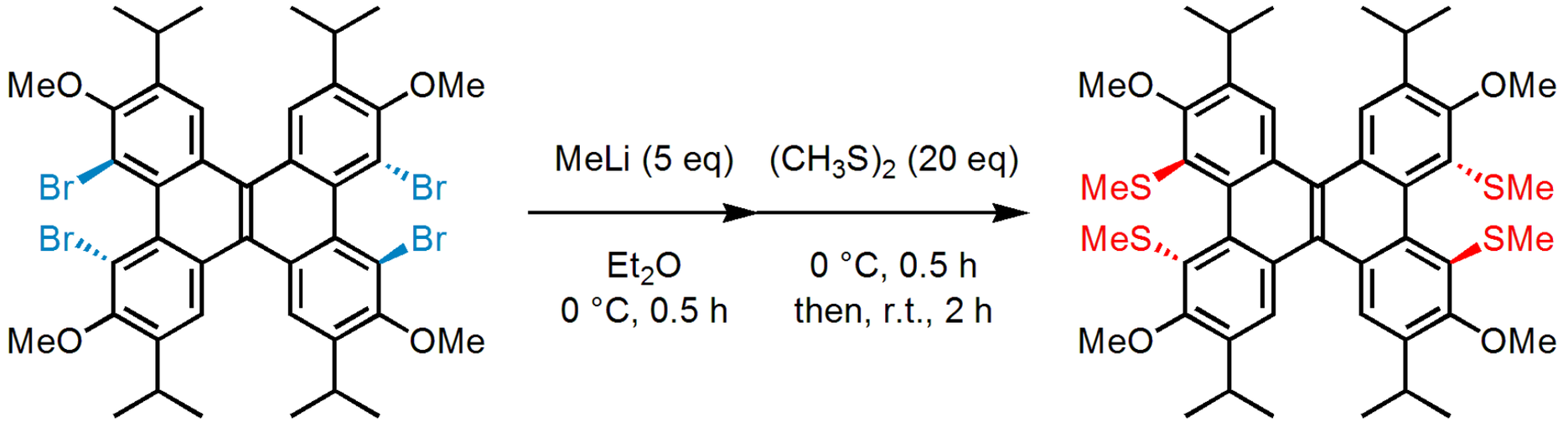
**In real, synthesis of the starting tetra-bromide**: Substitution of *tert*-Bu groups proceeded in gram-scale, although the products didn't show good solubility against my expectation.



***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).

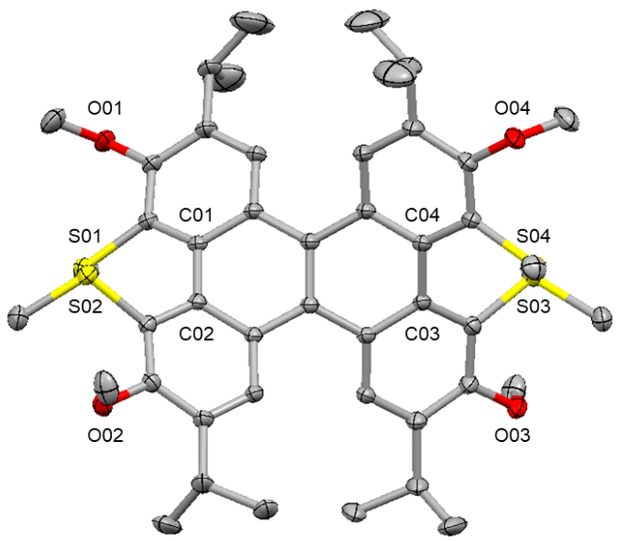


**Activation by organolithium reagents**: the lithium-halogen exchange reactions occurred smoothly, which enabled the desired substitution reactions.

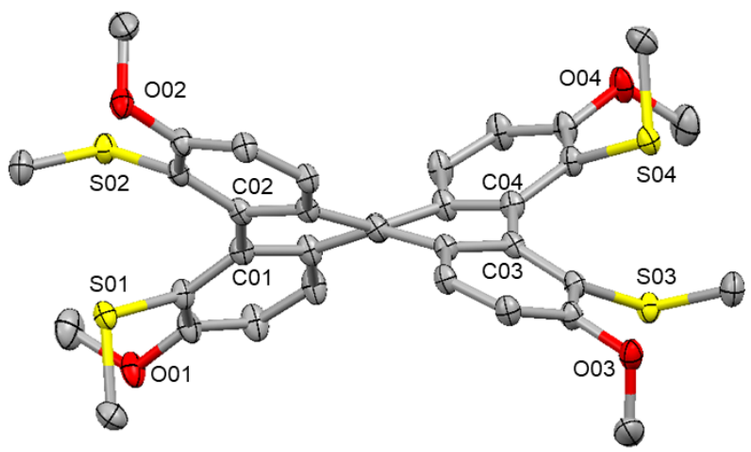



68%

**torsion angle, 56.0°**

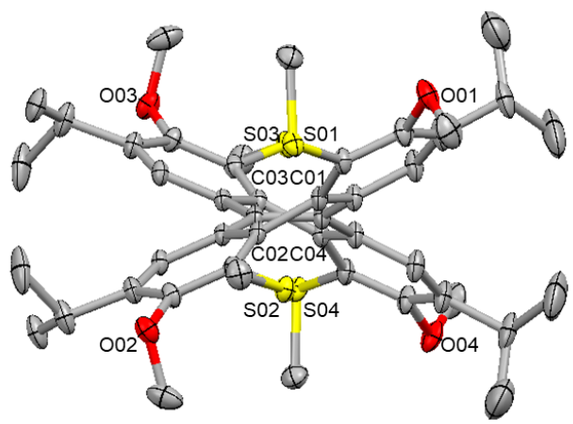



**CCDC 2093676**: Monoclinic
$R_1$ = 0.0484, GOF = 1.034



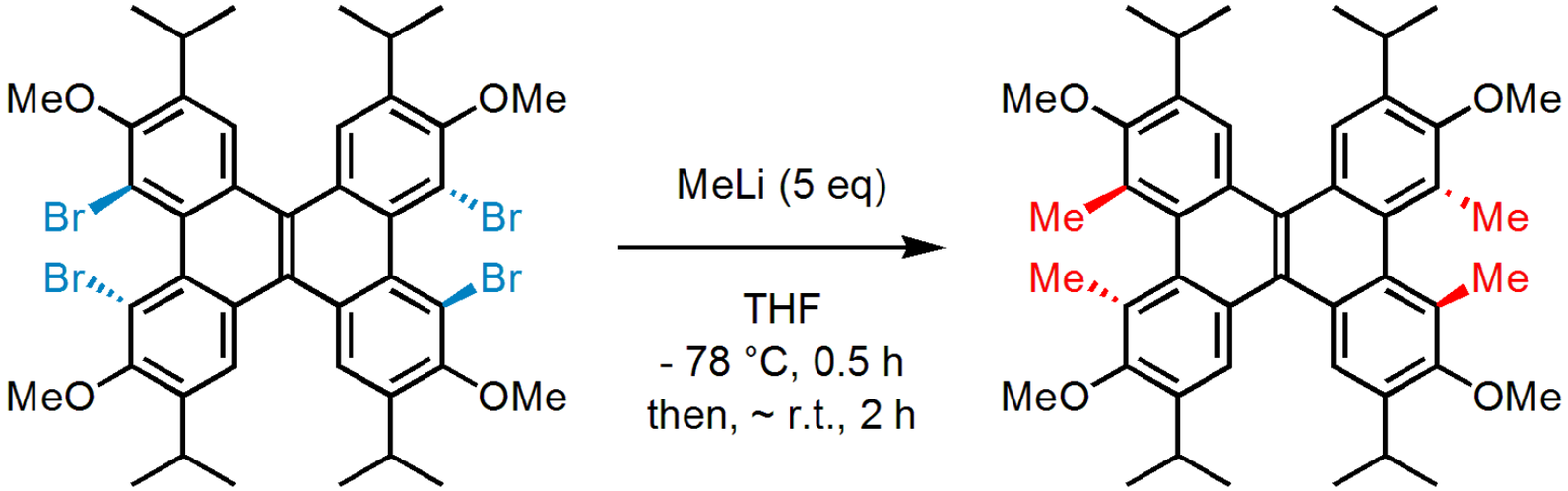

side view from the *fjord* region

**torsion angle, 57.2°**



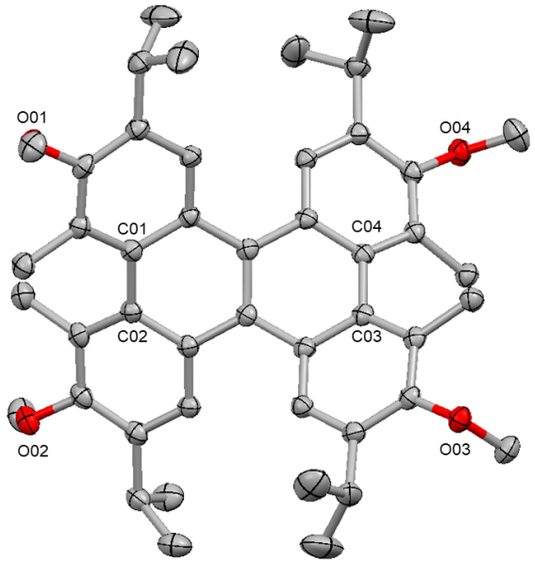

side view from the *bay* region

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



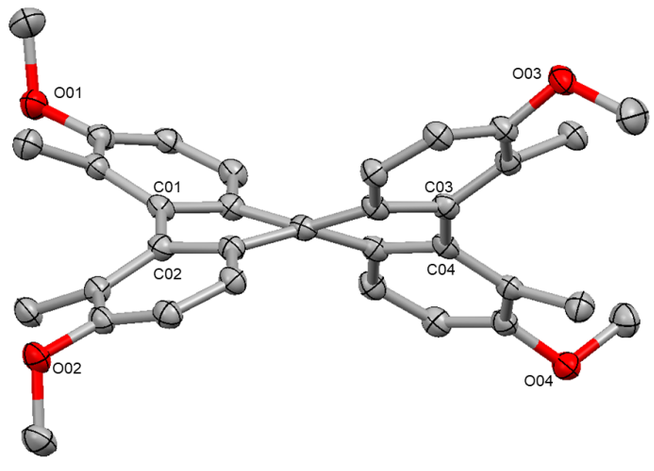

51%

**torsion angle, 56.0°**

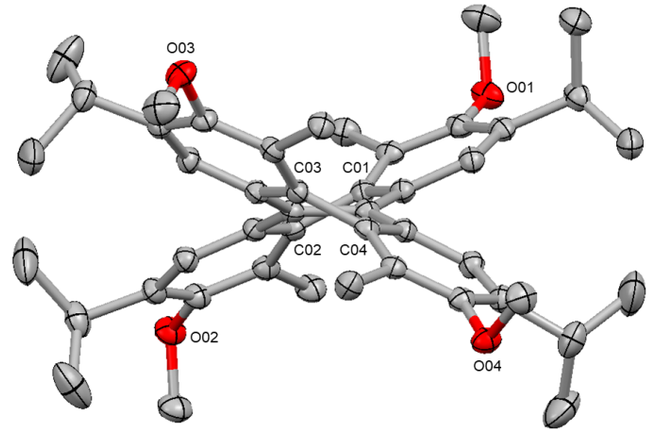



**CCDC 2119962**: Monoclinic
$R_1$ = 0.0636, GOF = 1.117

**torsion angle, 55.4°**

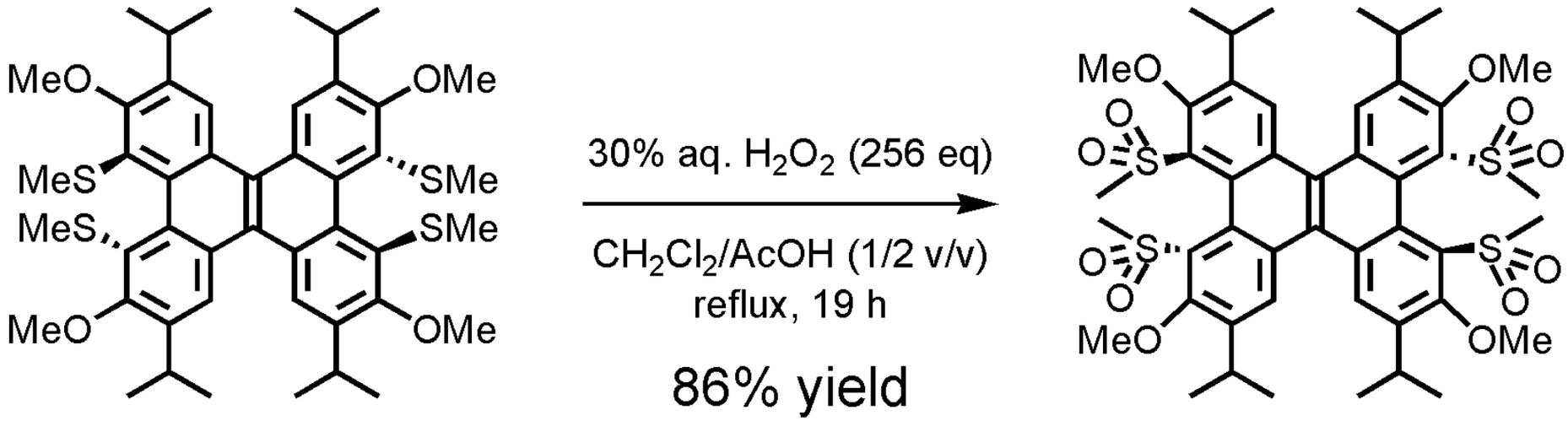



side view from the *fjord* region

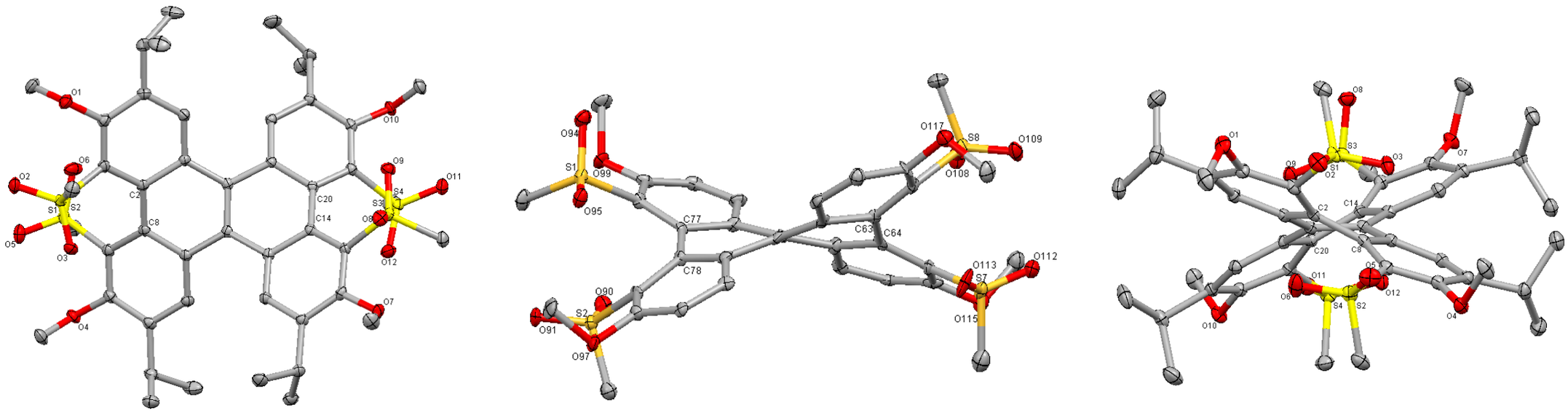



side view from the *bay* region

**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**

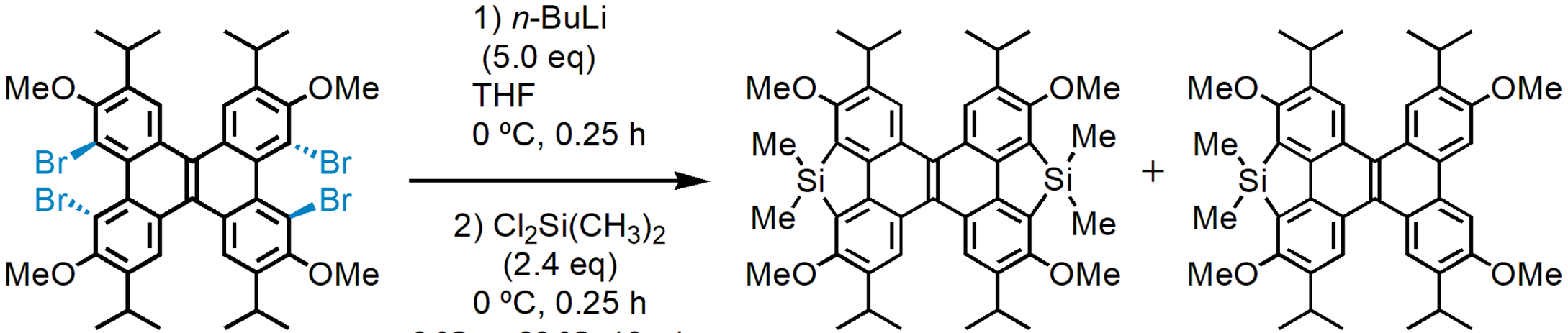


**CCDC 2093960**: Triclinic
$R_1$ = 0.0427, GOF = 1.070

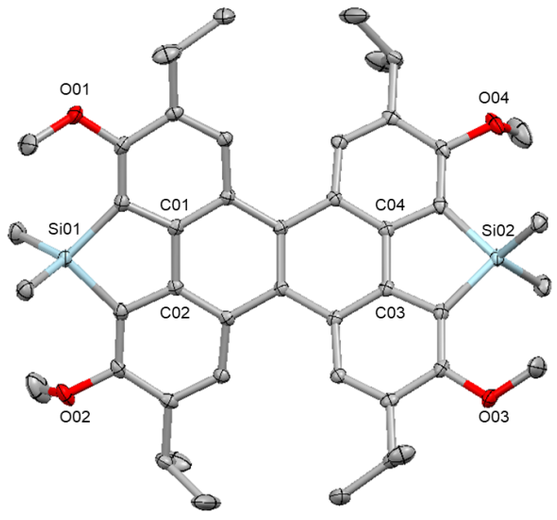
side view from the *fjord* region

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.

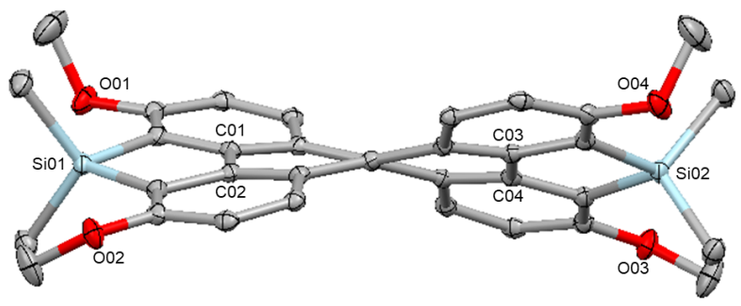



**torsion angle, 56.0º**

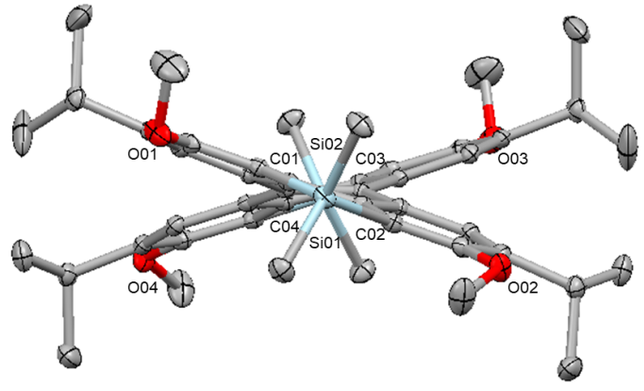



**CCDC 2111352:** Orthorhombic
$R_1$ = 0.0431, GOF = 1.072

**torsion angle, 31.8º**

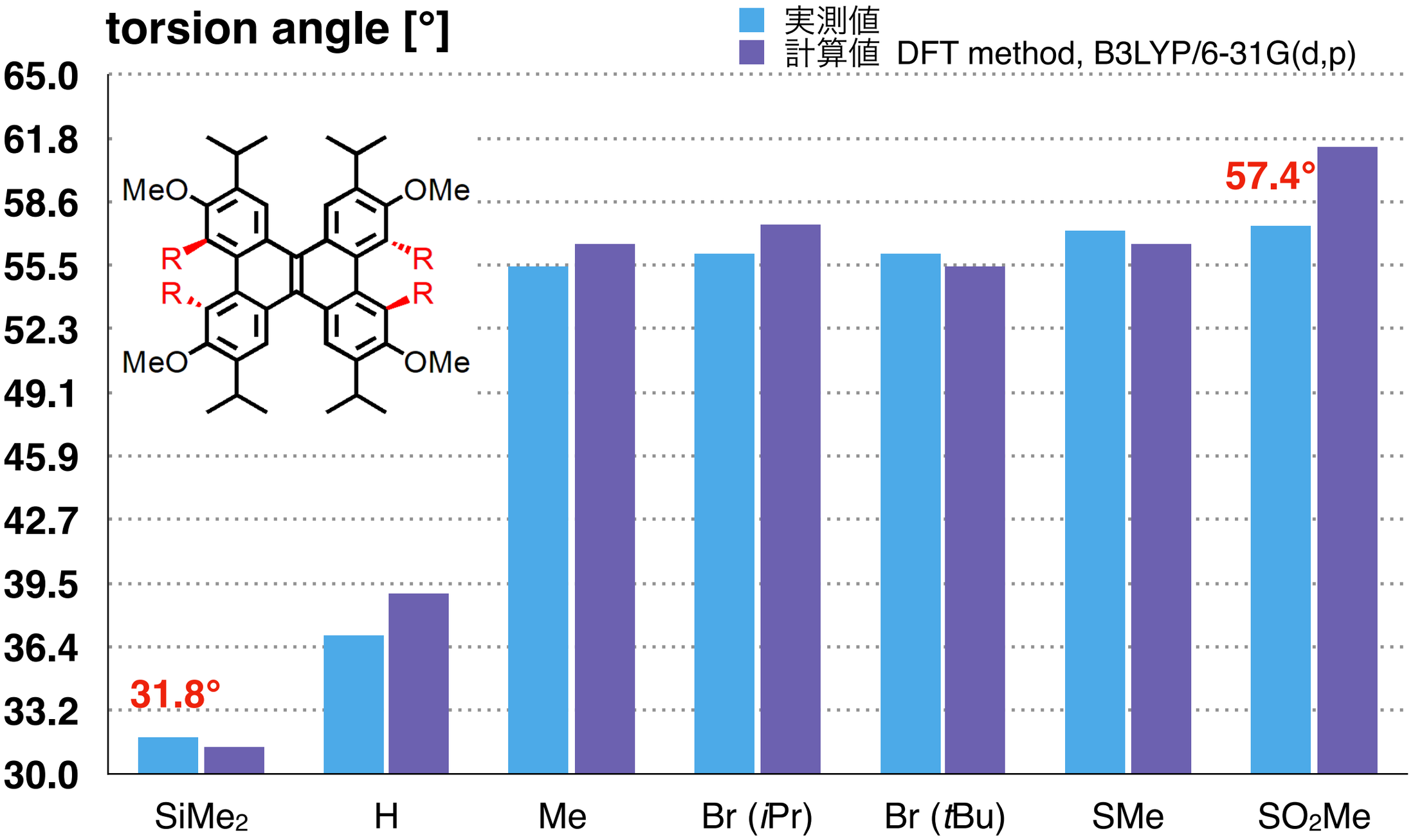



side view from the *fjord* region




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.