Solution-Phase Synthesis of Diindeno(1,2,3,4-*defg*:1’,2’,3’,4’-*mnop*)chrysene Derivatives

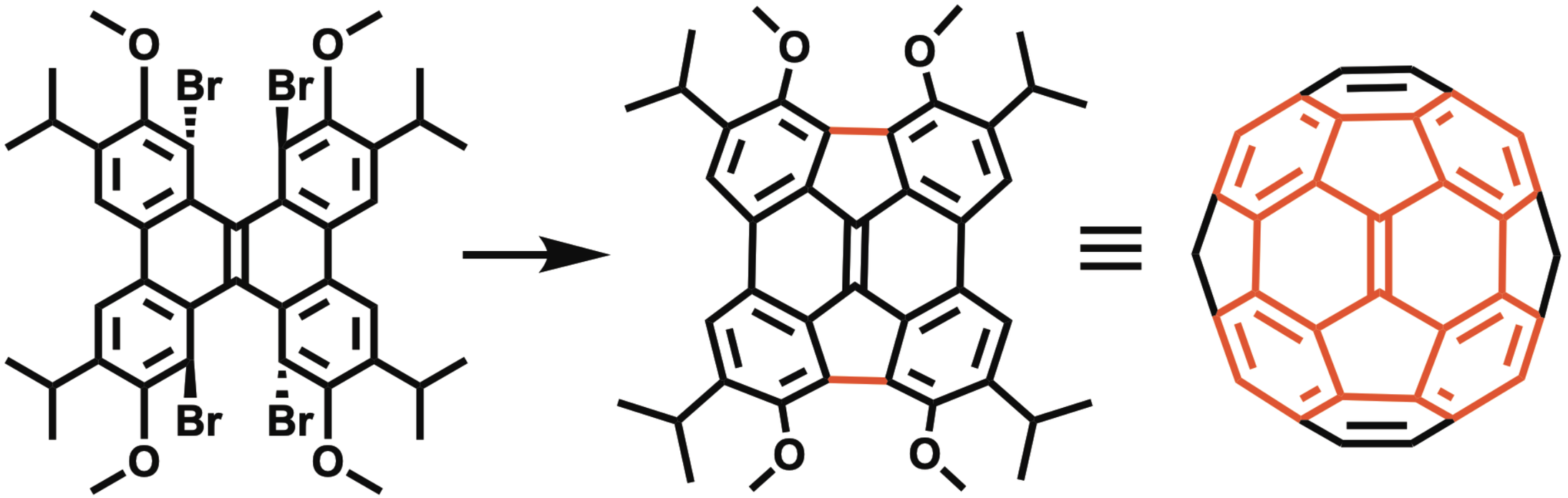
八環性バッキーボウルの液相ボトムアップ合成

龍谷大学大学院 理工学研究科 物質化学専攻

岩澤　研究室

赤阪　龍平

Solution-Phase Synthesis of Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene Derivatives



Up to 2.1 g

Buckybowl

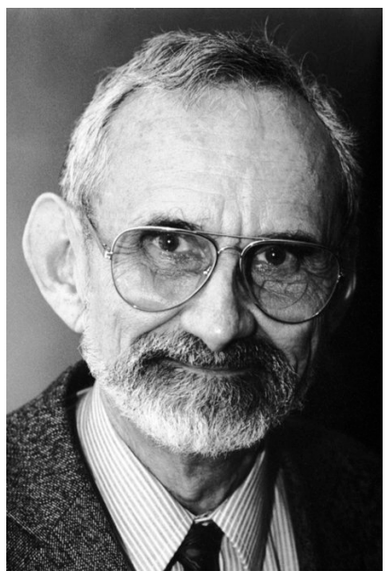
N. Yoshida, R. Akasaka, Y. Awakura, T. Amaya, T. Iwasawa, *Eur. J. Org. Chem.* **2021**, 5343-5347.

General background: C60 fragments are commonly referred to as “buckybowls”, buckybowls in which unique opto-electronic properties appear sharp.

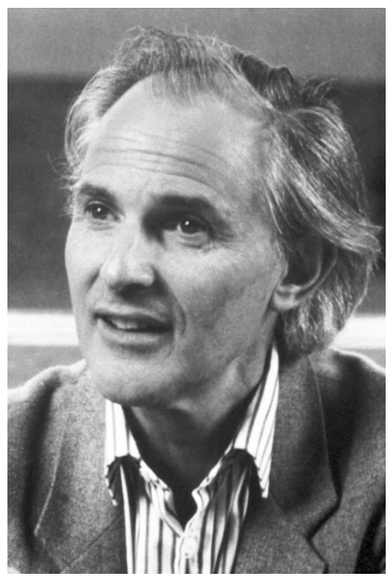
C_{60}: Buckminsterfullerene

Acc. Chem. Res. **1992**, *25*, *3*.

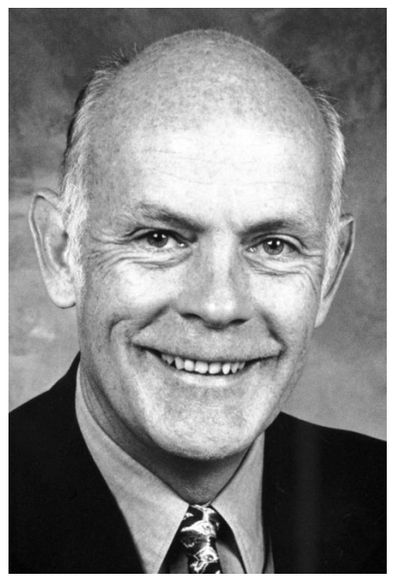
Nobel Prize in Chemistry 1996.



Robert F. Curl Jr.



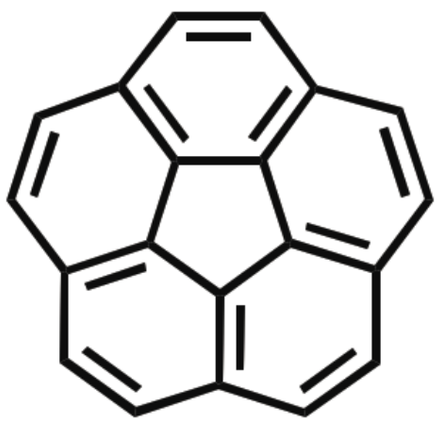
Sir Harold W. Kroto



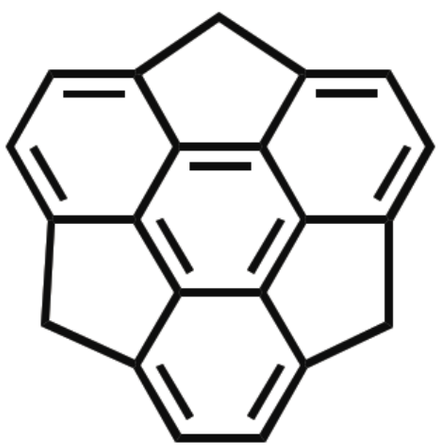
Richard E. Smalley

Photo from the Nobel Foundation archive.

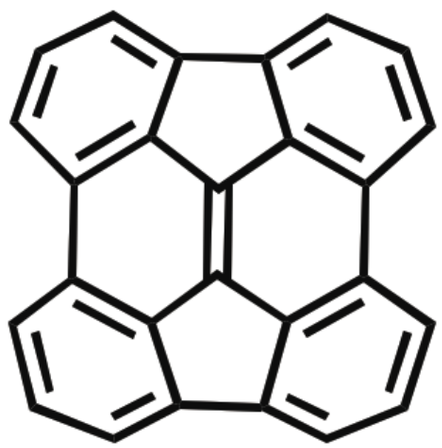
Buckybowls



Corannulene
1966, Lawton, Barth

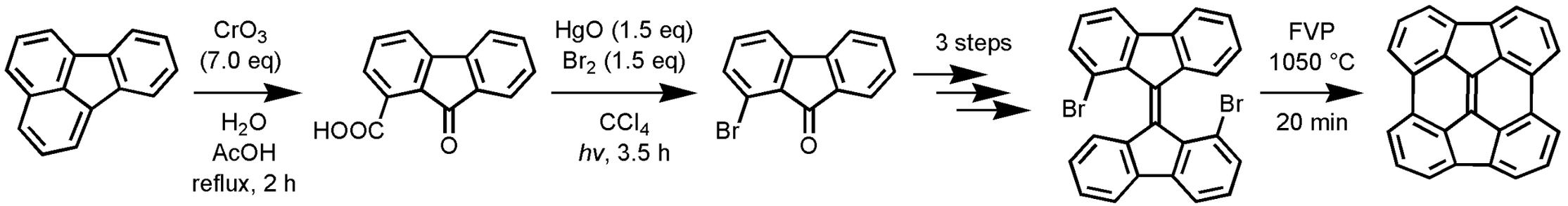


Sumanene
2003, Sakurai, Hirao



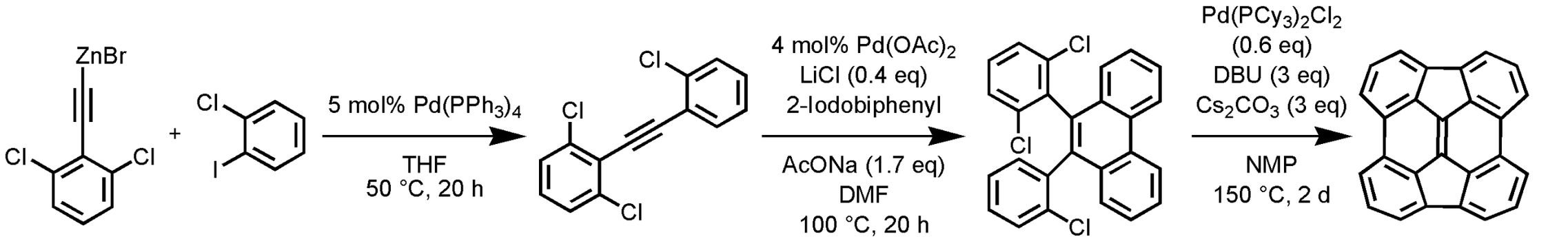
Diindenochrysene
2002, Scott

Background: While two outstanding corannulene and sumanene have been famed, DIC is underrepresented owing to the low productivity.



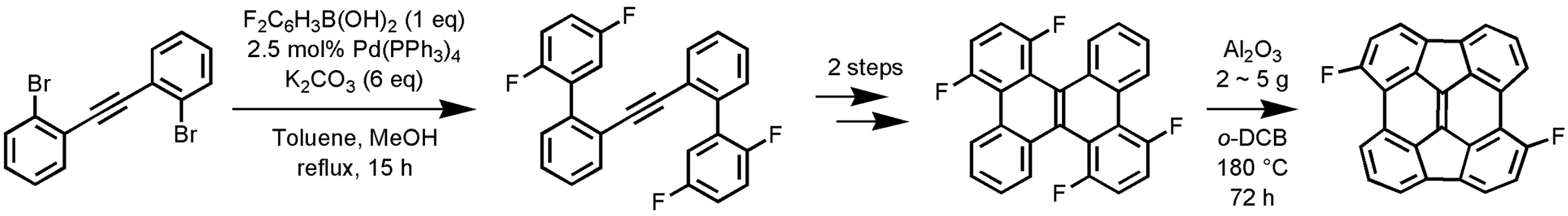
98% 63% 62% 37% (25 mg)

H. E. Bronstein, N. Choi, L. T. Scott, *J. Am. Chem. Soc.* **2002**, *124*, 8870-5.



82% 63% 20% (4.5 mg)

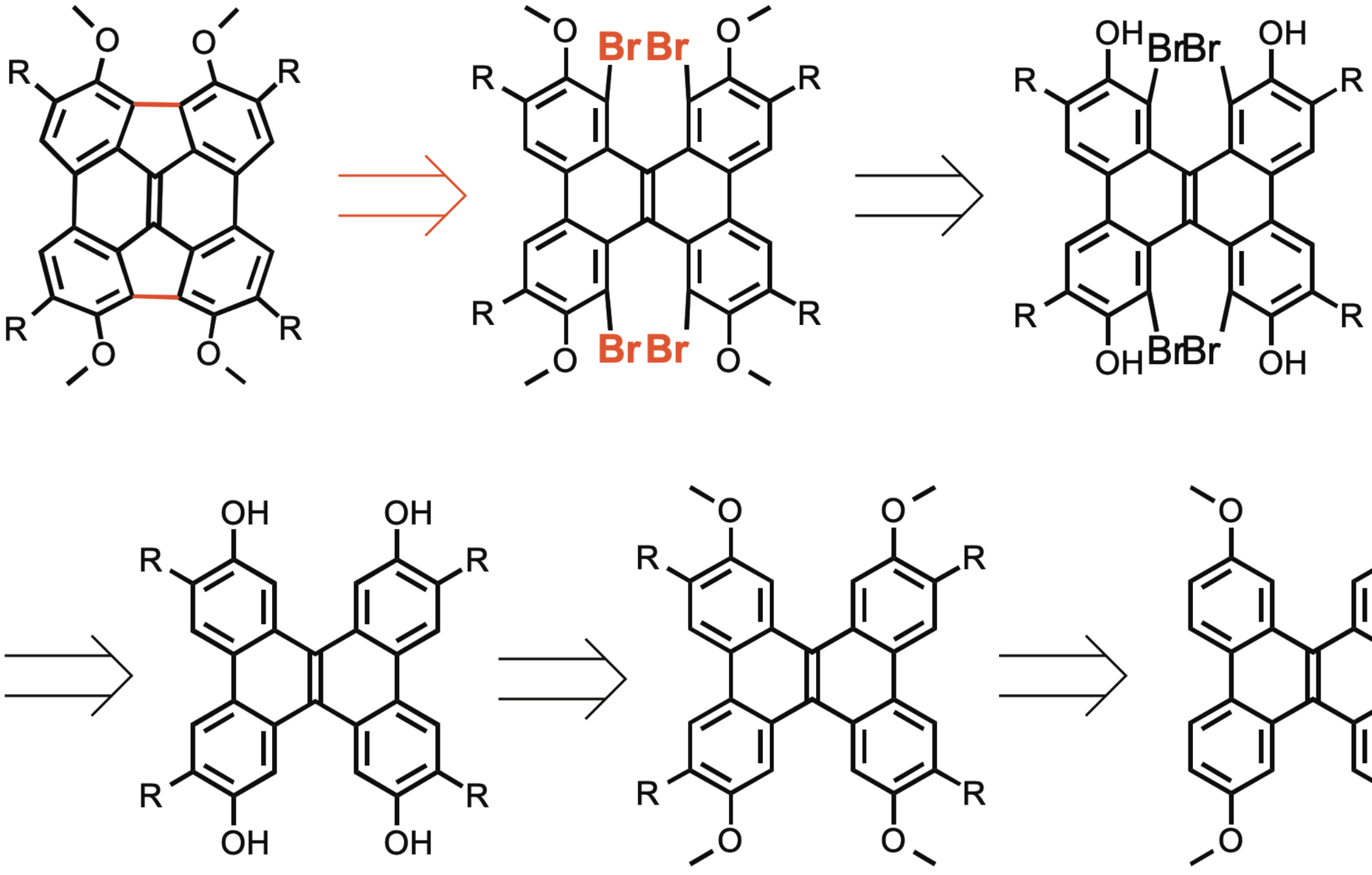
H. I. Chang, H. T. Huang, C. H. Huang, M. Y. Kuo, Y. T. Wu, *Chem. Commun.* **2010**, *46*, 7241-3.



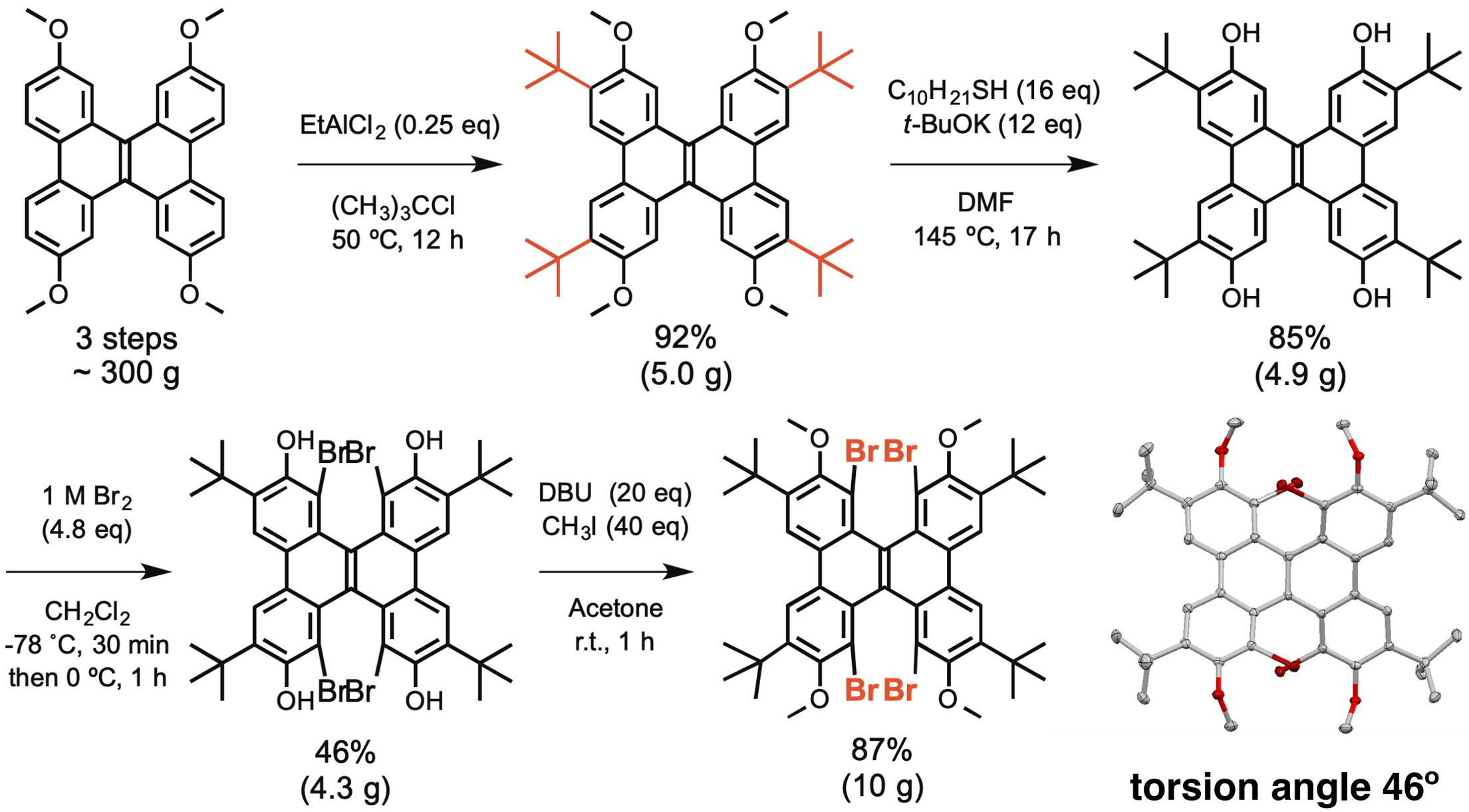
65% in 1 step 84% 60% 80% (37 mg)

V. Akhmetov, M. Feofanov, S. Troyanov, K. Amsharov, *Chem. Eur. J.* **2019**, *25*, 7607-12.

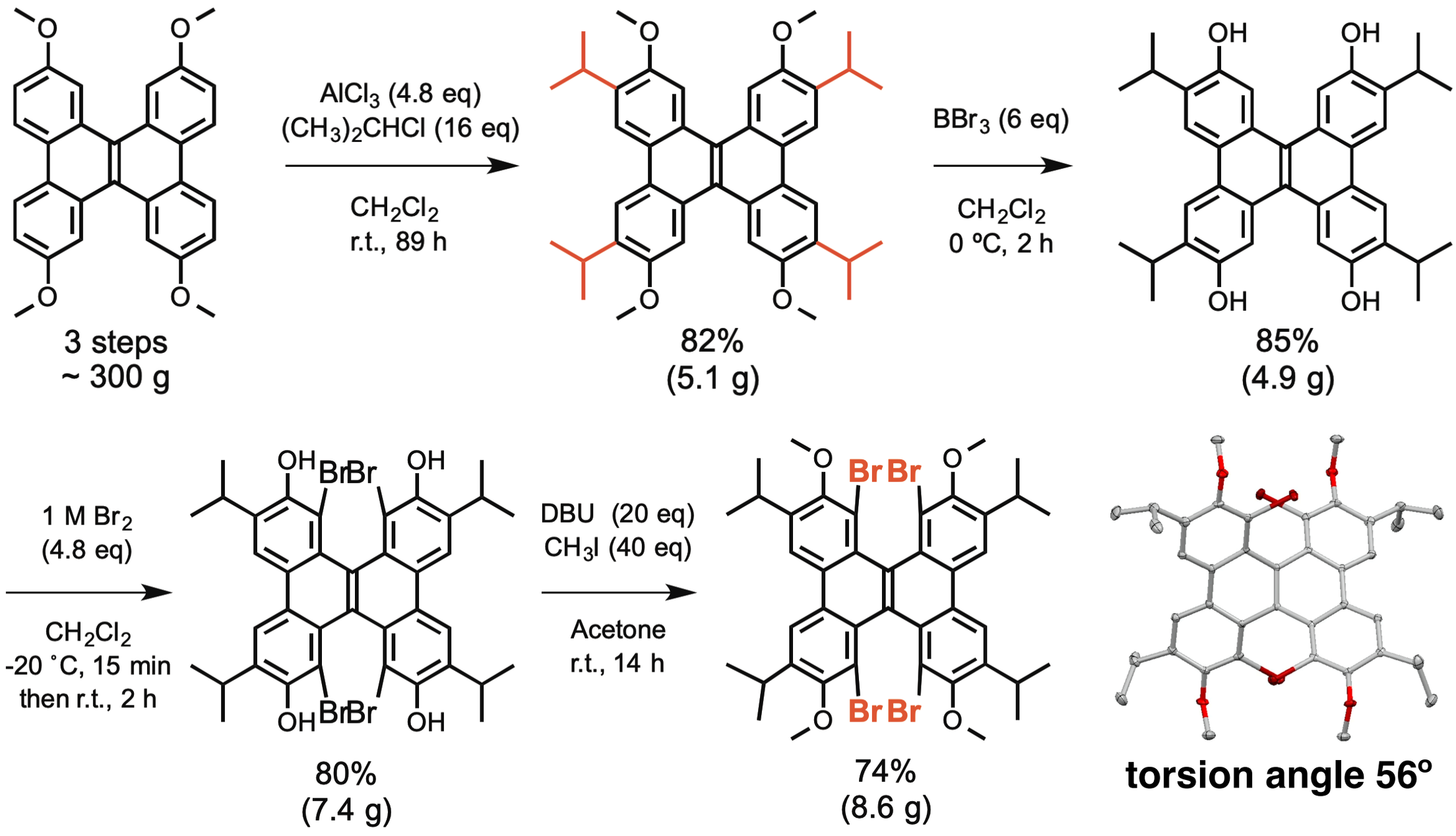
Retro-synthetic approach: Double ring-closures in the dibenzo[*g*,*p*]chrysene form the skeletal buckybowl.



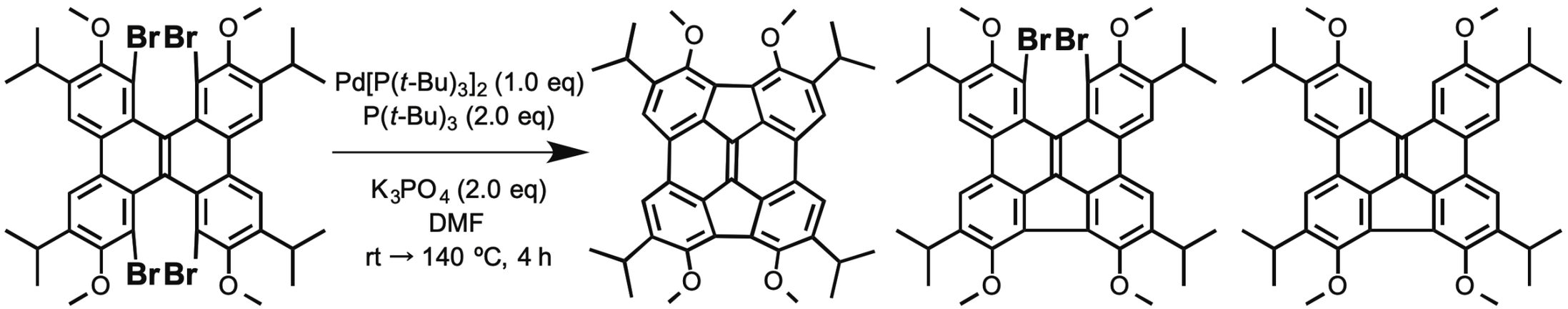
Precursor synthesis: Dibenzo[*g*,*p*]chrysene having four *tert*-butyls, four methyl ethers, and four bromines was prepared.



Precursor synthesis: Dibenzo[*g*,*p*]chrysene having four *iso*-propyls, four methyl ethers, and four bromines was prepared.



Ring-closing reactions: Preliminary experiments led to identification of a base set of the starting condition, in which Pd[P(*t*-Bu)$_3$]$_2$ was effective at 140 °C.



torsion angle 56°

62%

16%

observed

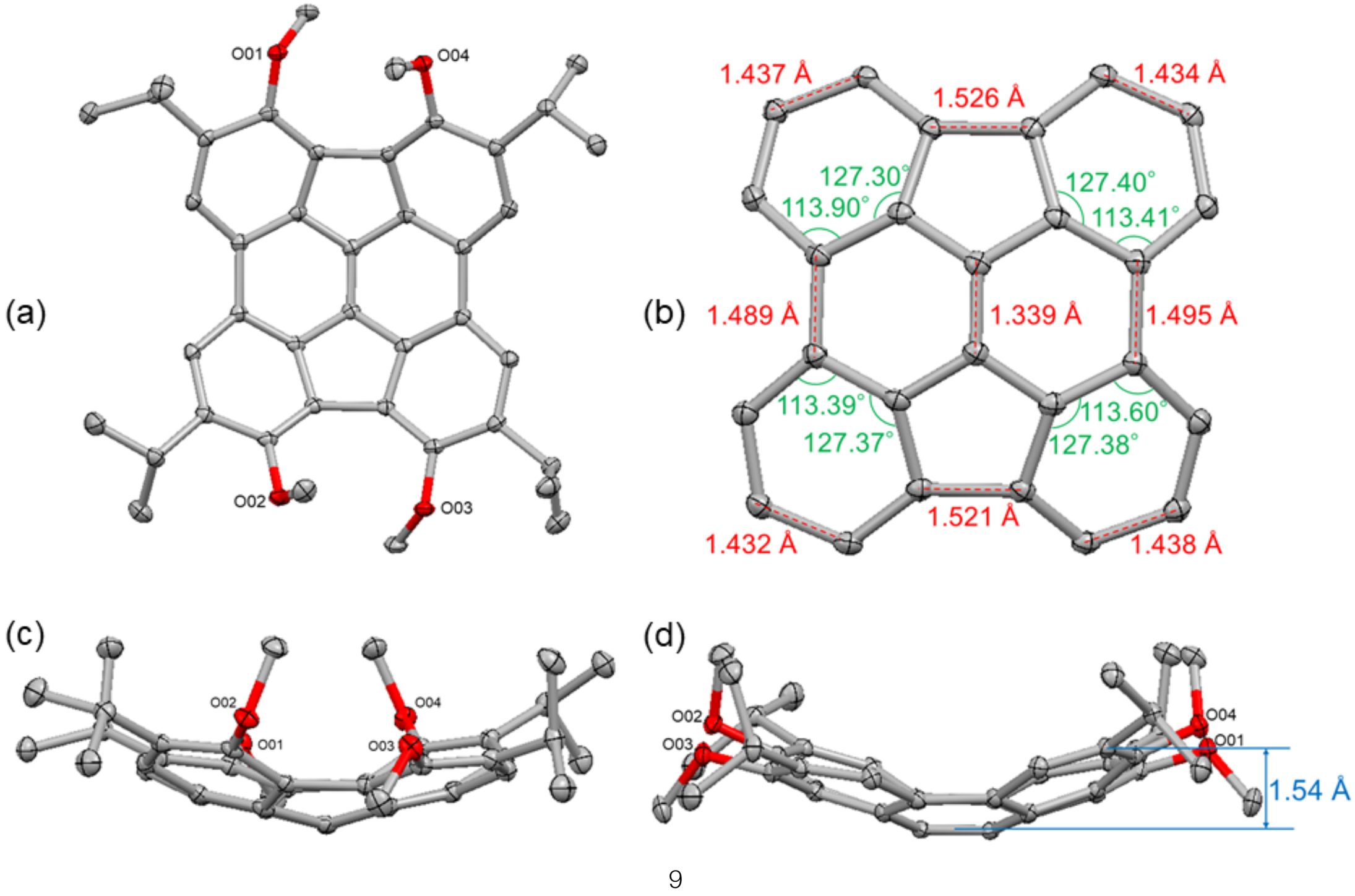
torsion angle 46°

20%

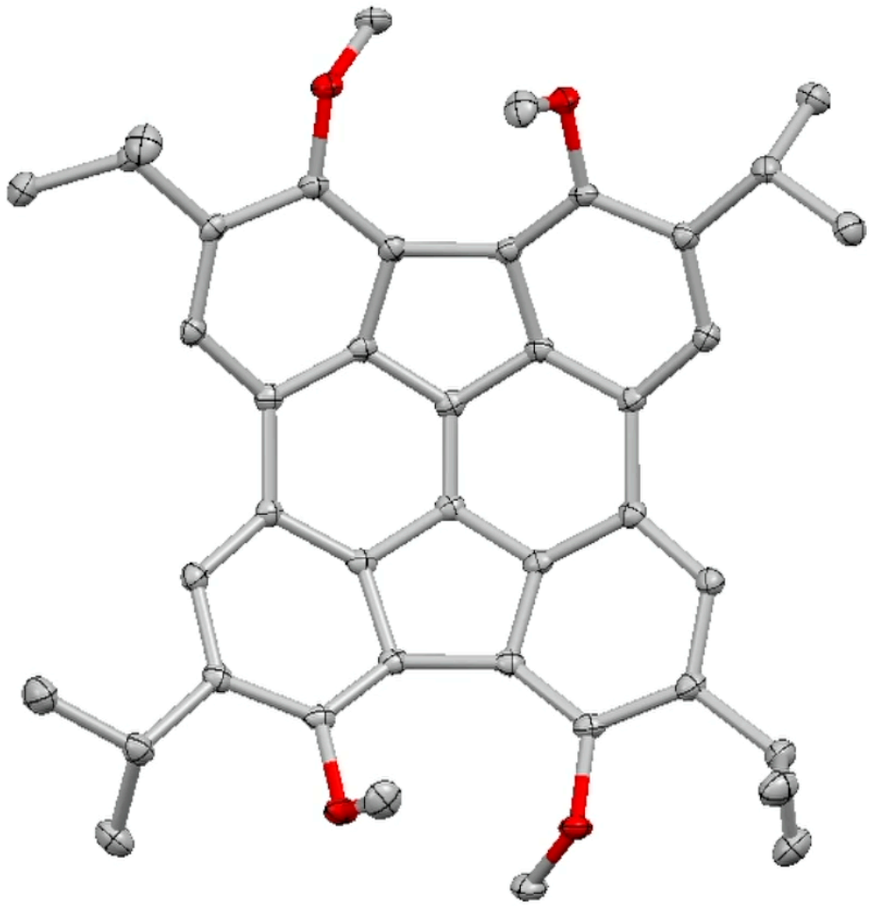
13%

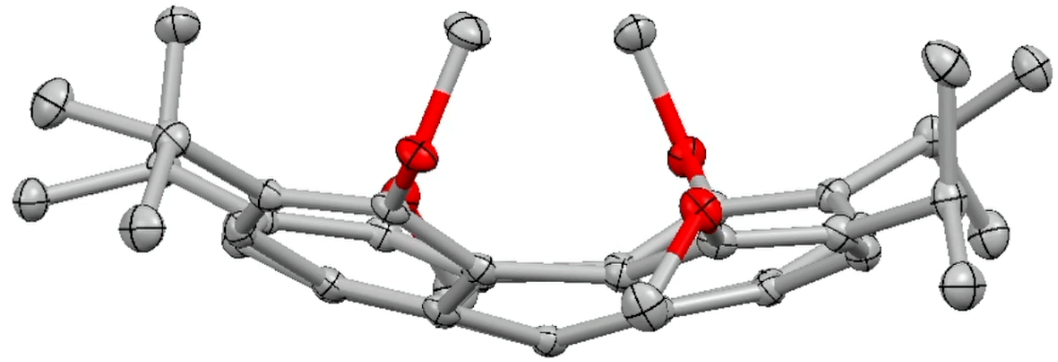
observed

X-ray structure: result of 6:6-bond length 1.34 Å, bowl depth 1.54 Å.

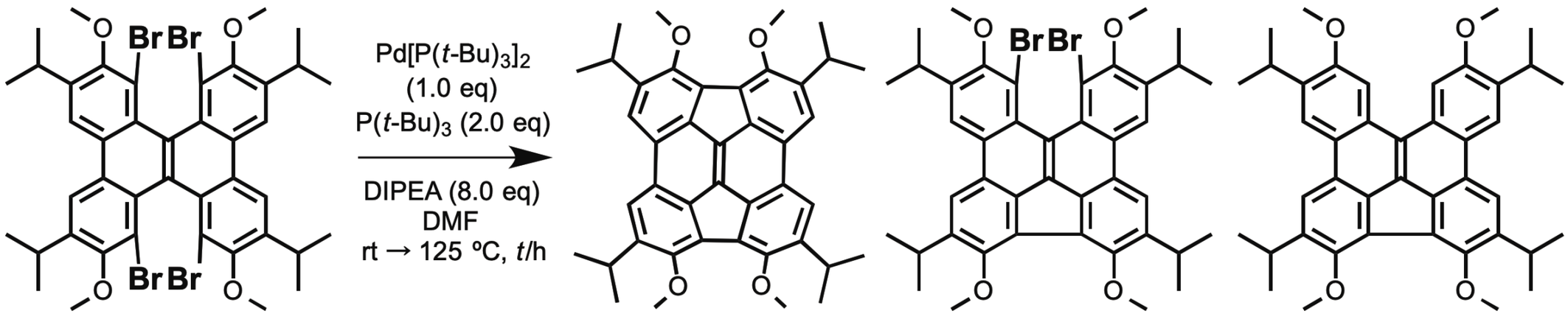


X-ray structure: result of a gently curved pi-surface (*i*-Pr)





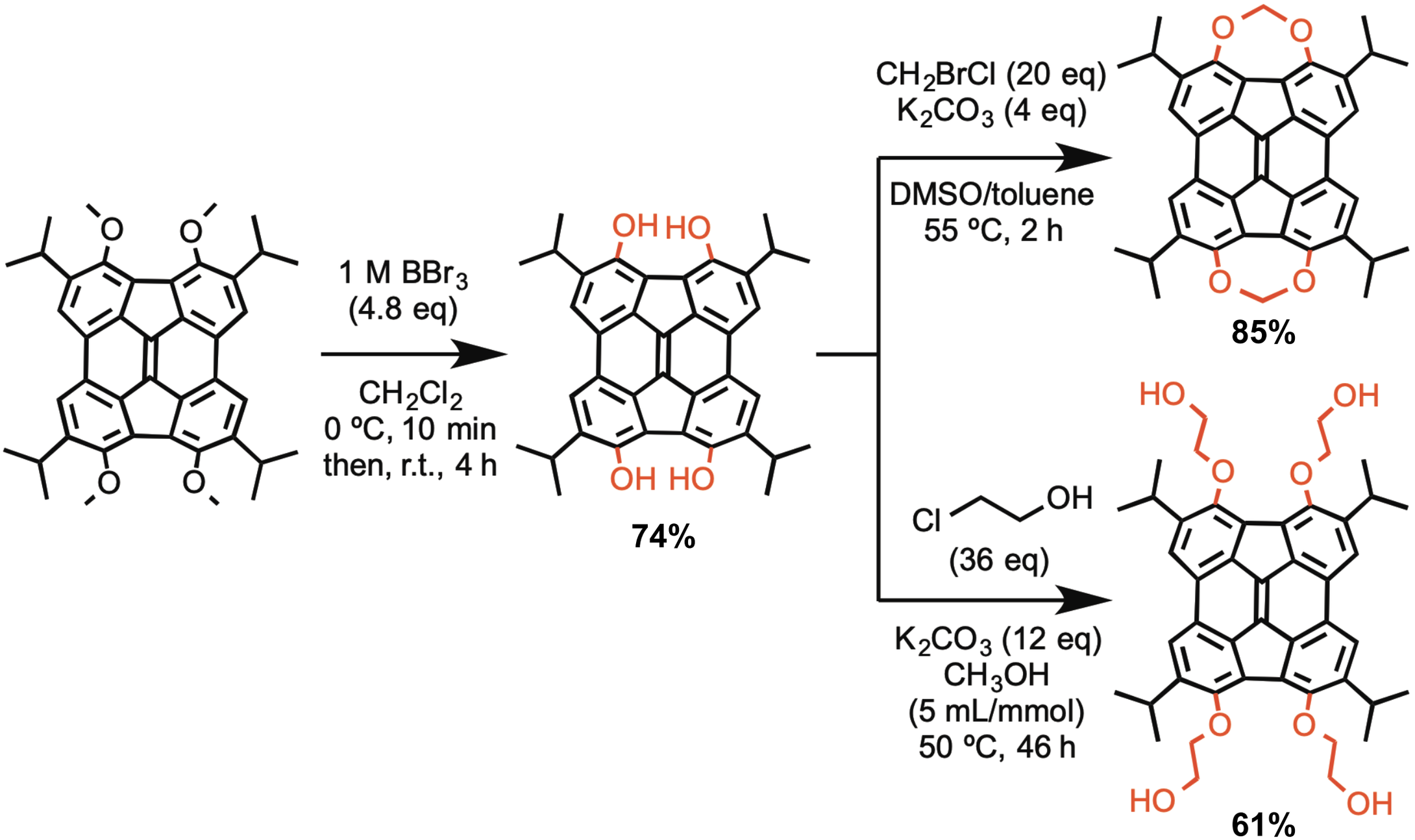
Gram-scale synthesis: the solution-processable protocol went well without serious loss of chemical yields.



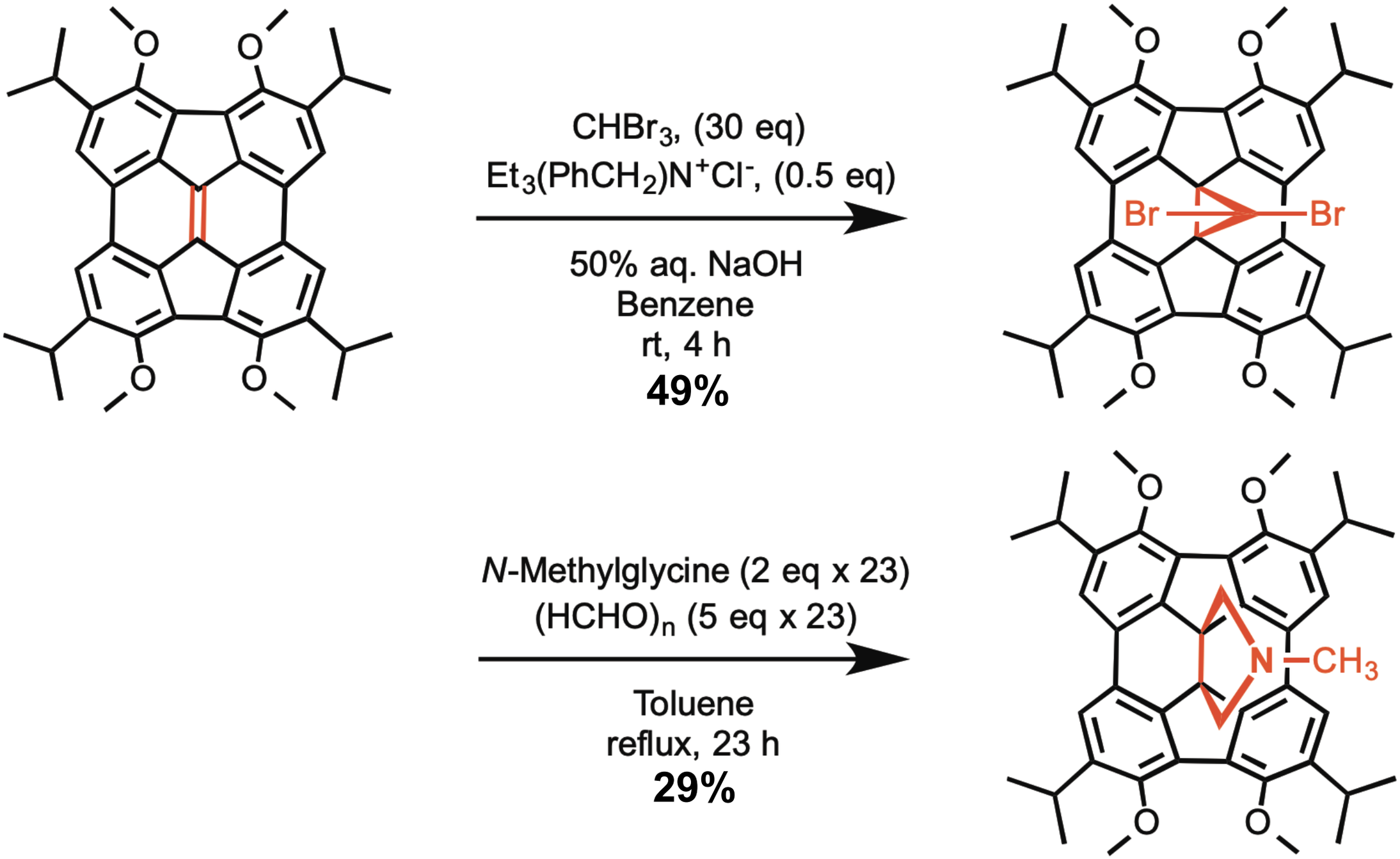
Bowl ***Di*-Br** ***Di*-H**

Scale		*t*/h	%Yield		
mmol	gram		***Bowl***	***Di*-Br**	***Di*-H**
0.15	0.14	1	68	0	25
0.45	0.42	1	67	3	5
1.4	1.3	2	66	0	10
2.7	2.5	2	66 (1.1 g)	0	14
5.4	5.1	2	62 (2.1 g)	0	19

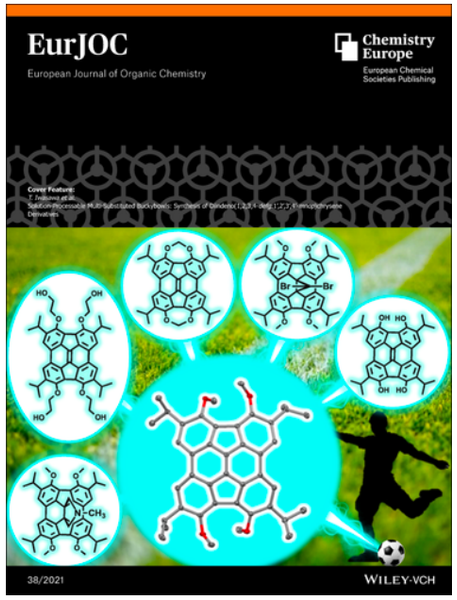
Further transformation in the methoxy groups: Demethylation, methylene-bridge, and hydroxy ethyl ether were carried out.

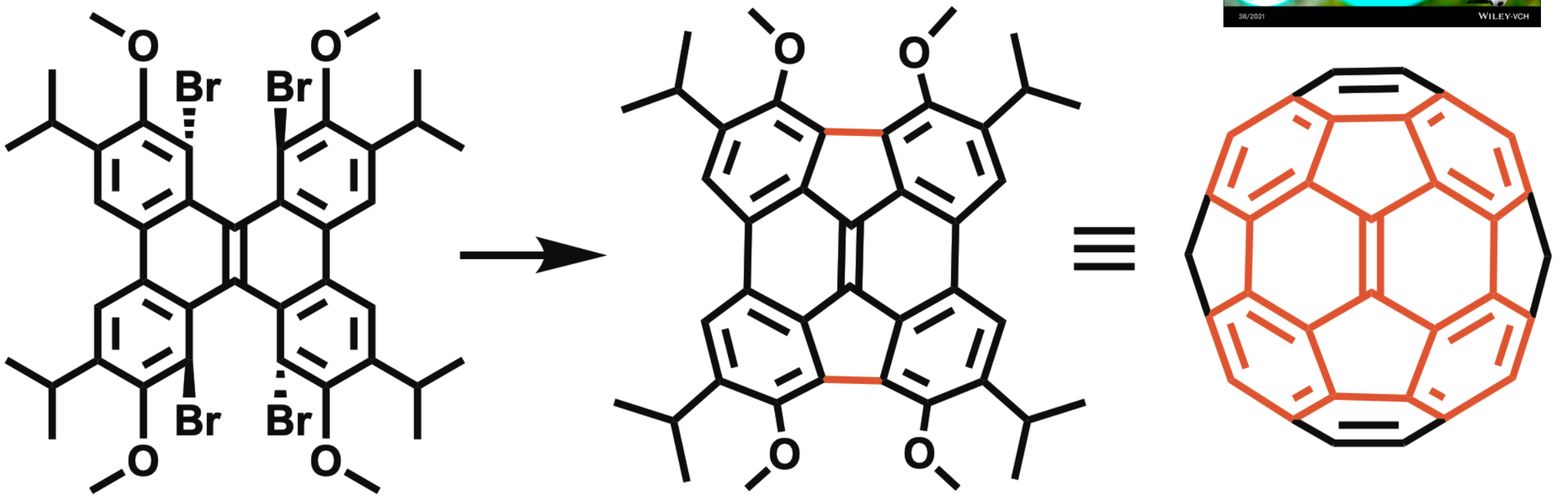


Further transformation in the 6:6-bond: the conventional cyclopropanation with *in situ* carbene and cycloaddition with *in situ* ylide were accomplished.



Summary: Solution-phase synthesis of the DIC-typed buckybowl was achieved in gram scale.





Up to 2.1 g

Buckybowl

N. Yoshida, R. Akasaka, Y. Awakura, T. Amaya, T. Iwasawa, *Eur. J. Org. Chem.* **2021**, 5343-5347.