

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

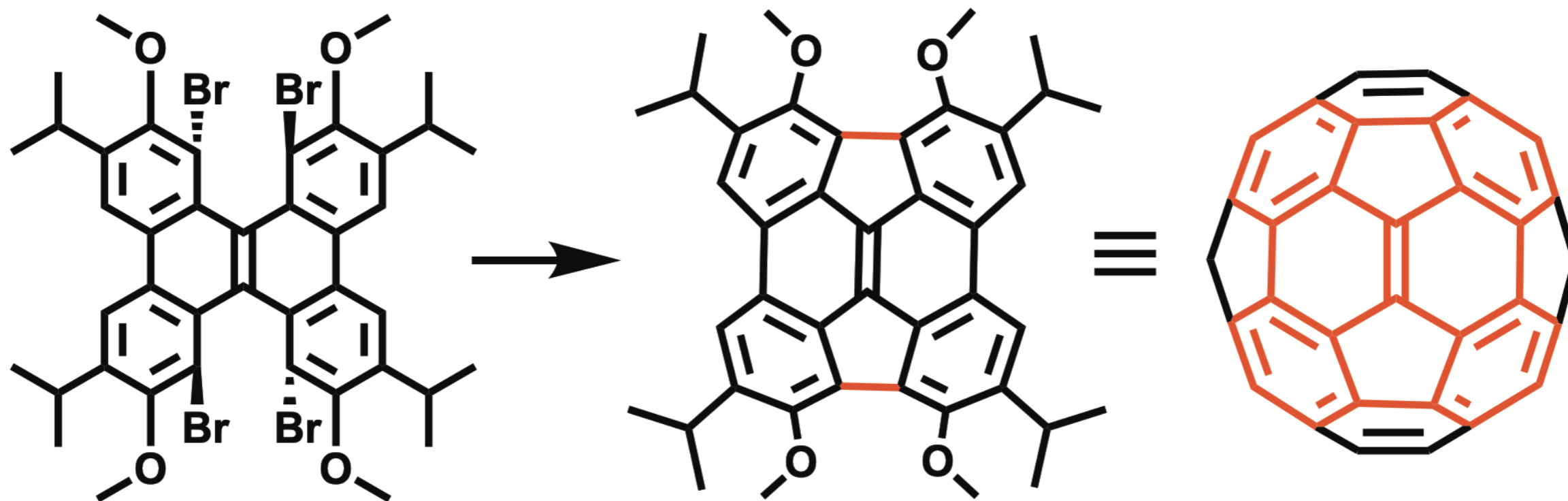
ジインデノクリセン型バッキーボウルの 液相合成・構造解析

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.

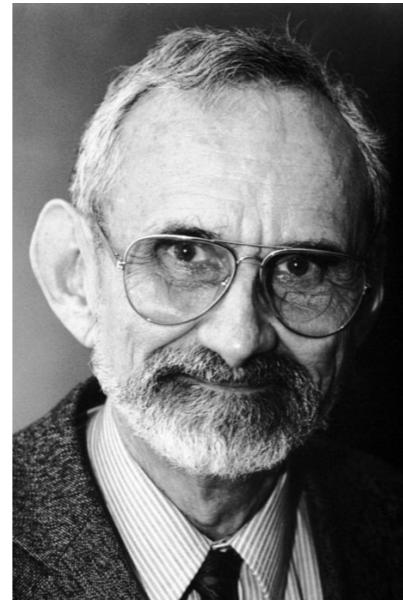
General background: C₆₀ fragments are commonly referred to as “buckybowls”, buckybowls in which unique opto-electronic properties appear sharp.

C₆₀: Buckminsterfullerene

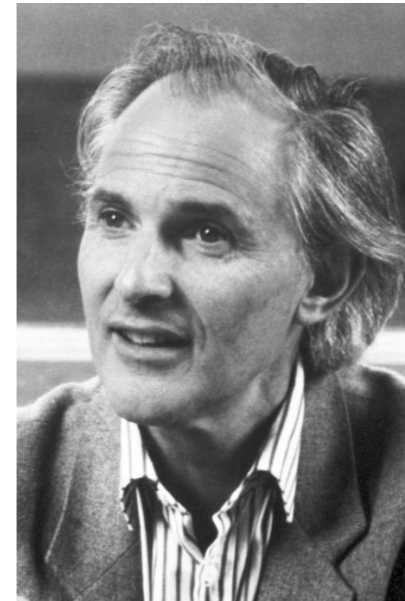


Acc. Chem. Res. **1992**, 25, 3.

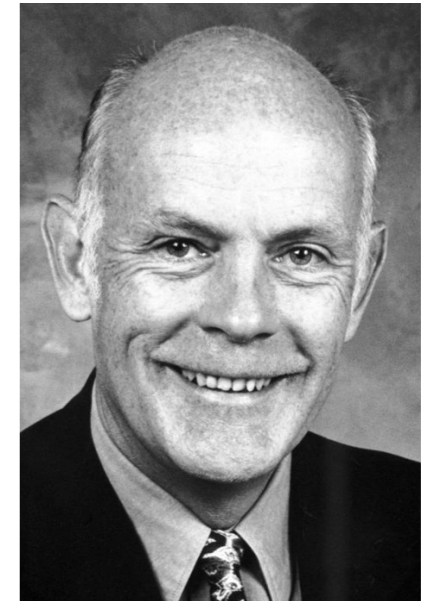
Nobel Prize in Chemistry 1996.



Robert F. Curl Jr.



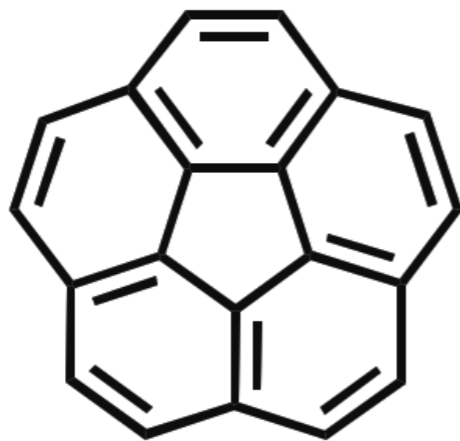
Sir Harold W. Kroto



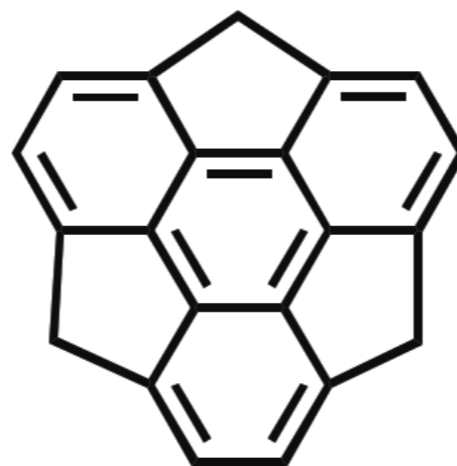
Richard E. Smalley

Photo from the Nobel Foundation archive.

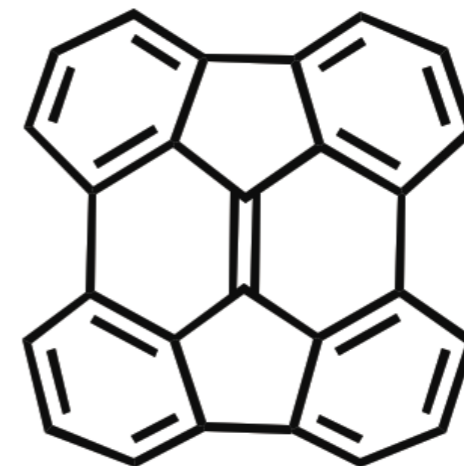
Buckybowls



Corannulene
1966, Lawton, Barth

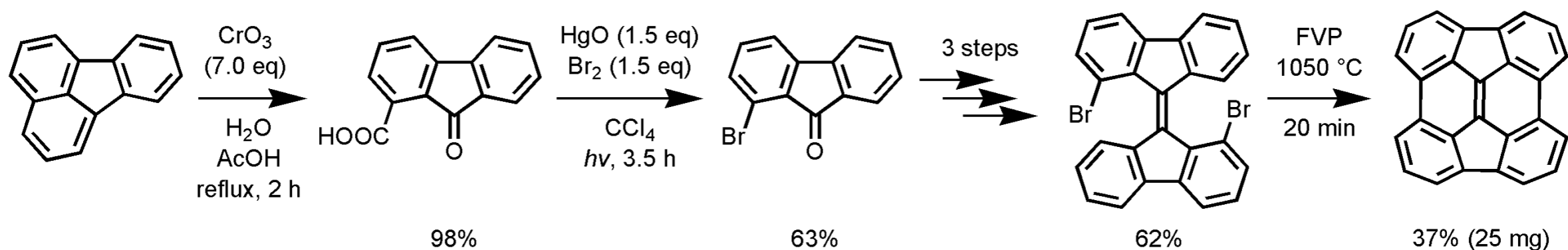


Sumanene
2003, Sakurai, Hirao

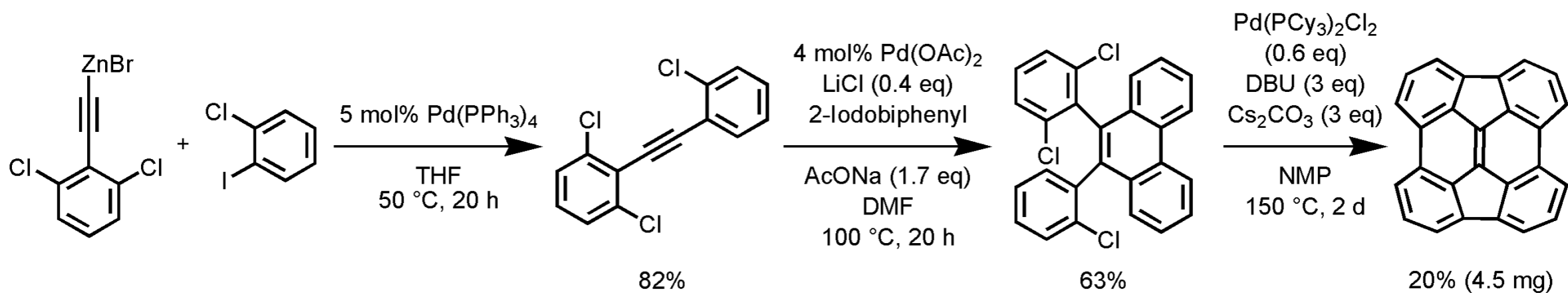


Diindeno[1,1-b]chrysene
2002, Scott

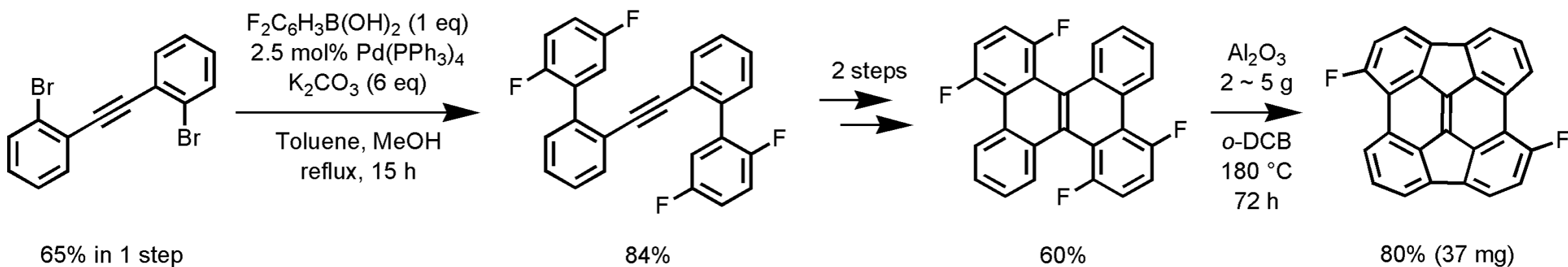
Background: While two outstanding corannulene and sumanene have been famed, DIC is underrepresented owing to the low productivity.



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

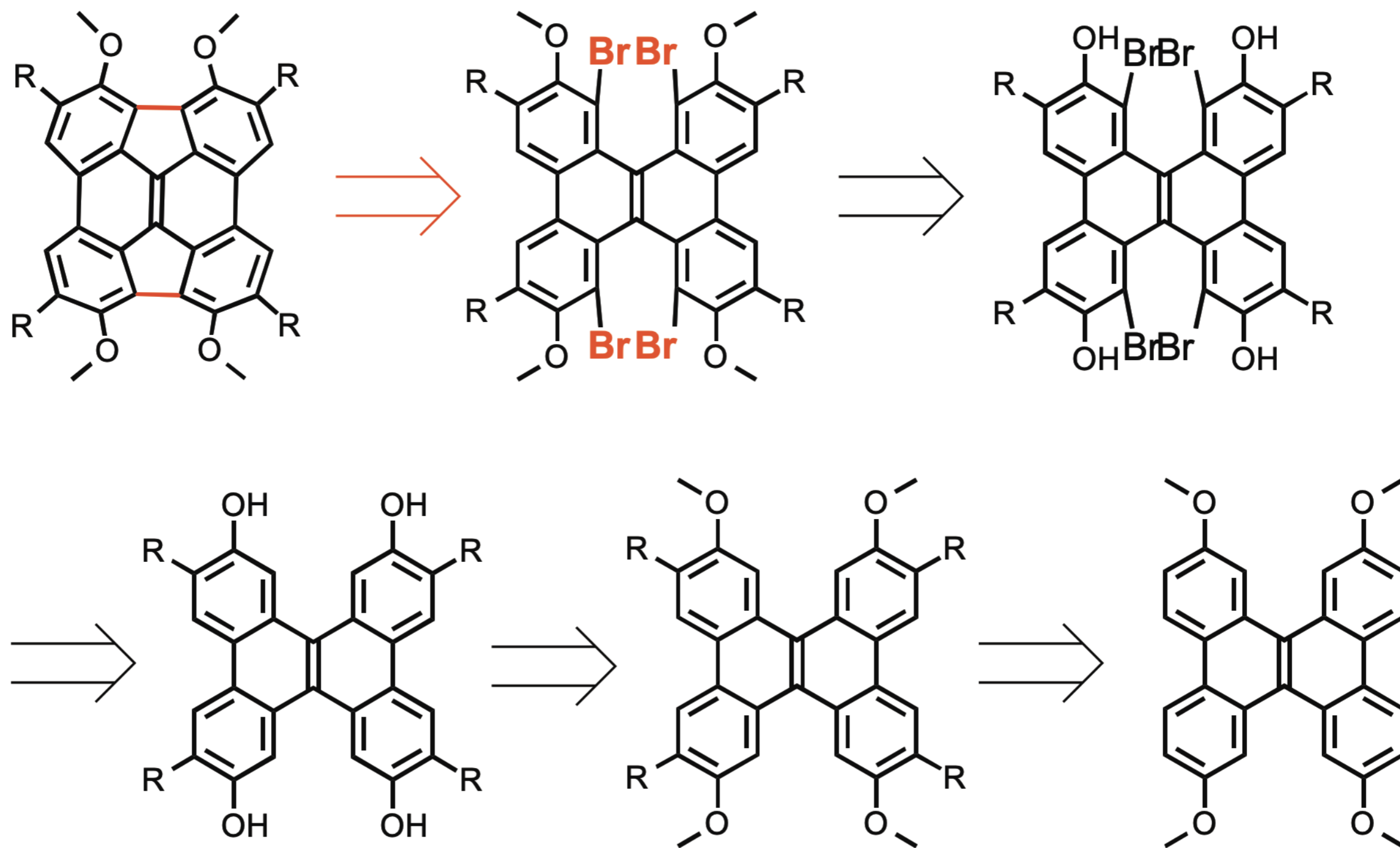


H. I. Chang, H. T. Huang, C. H. Huang, M. Y. Kuo, Y. T. Wu, *Chem. Commun.* **2010**, *46*, 7241-3.

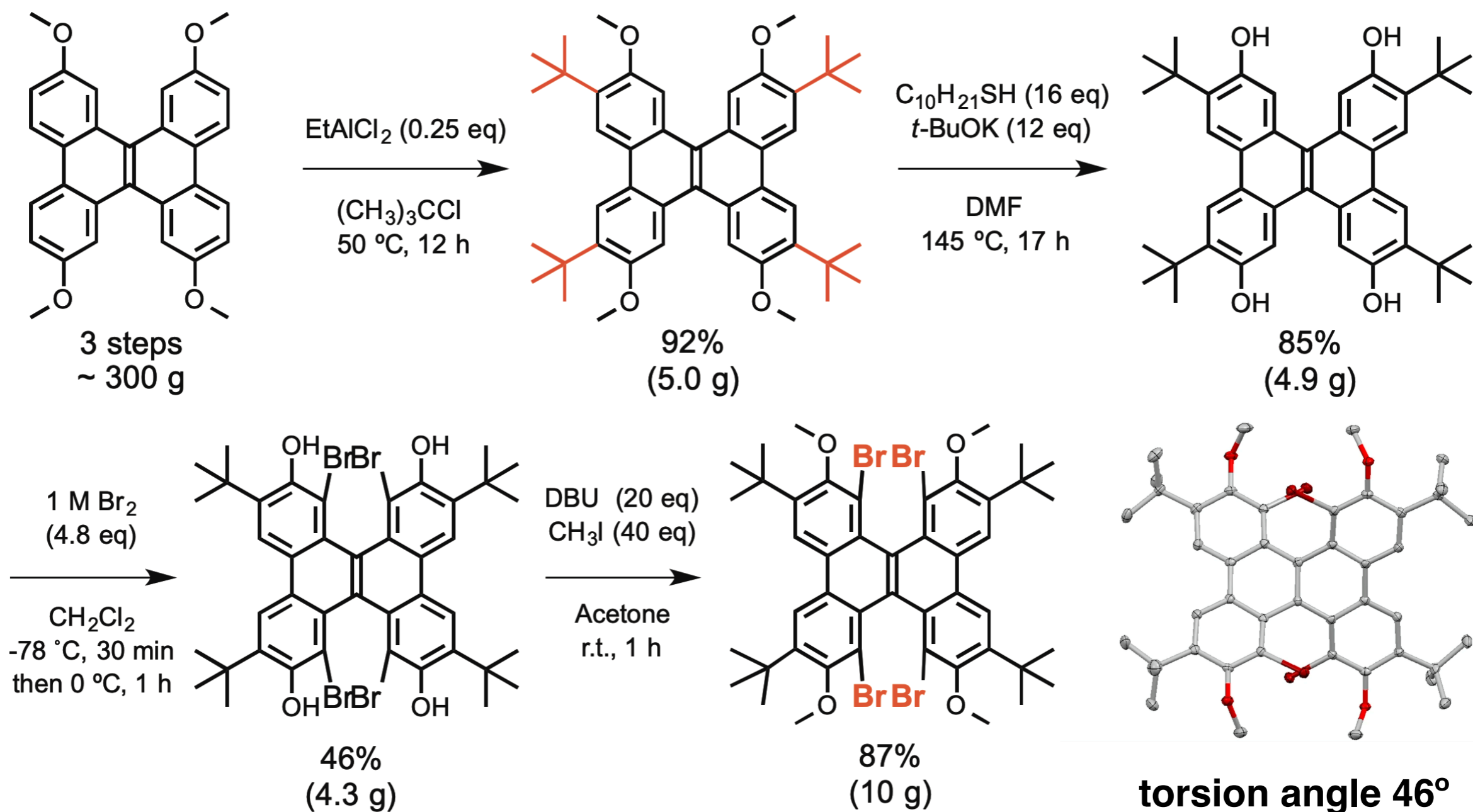


V. Akhmetov, M. Feofanov, S. Troyanov, K. Amsharov, *Chem. Eur. J.* **2019**, *25*, 7607-12.

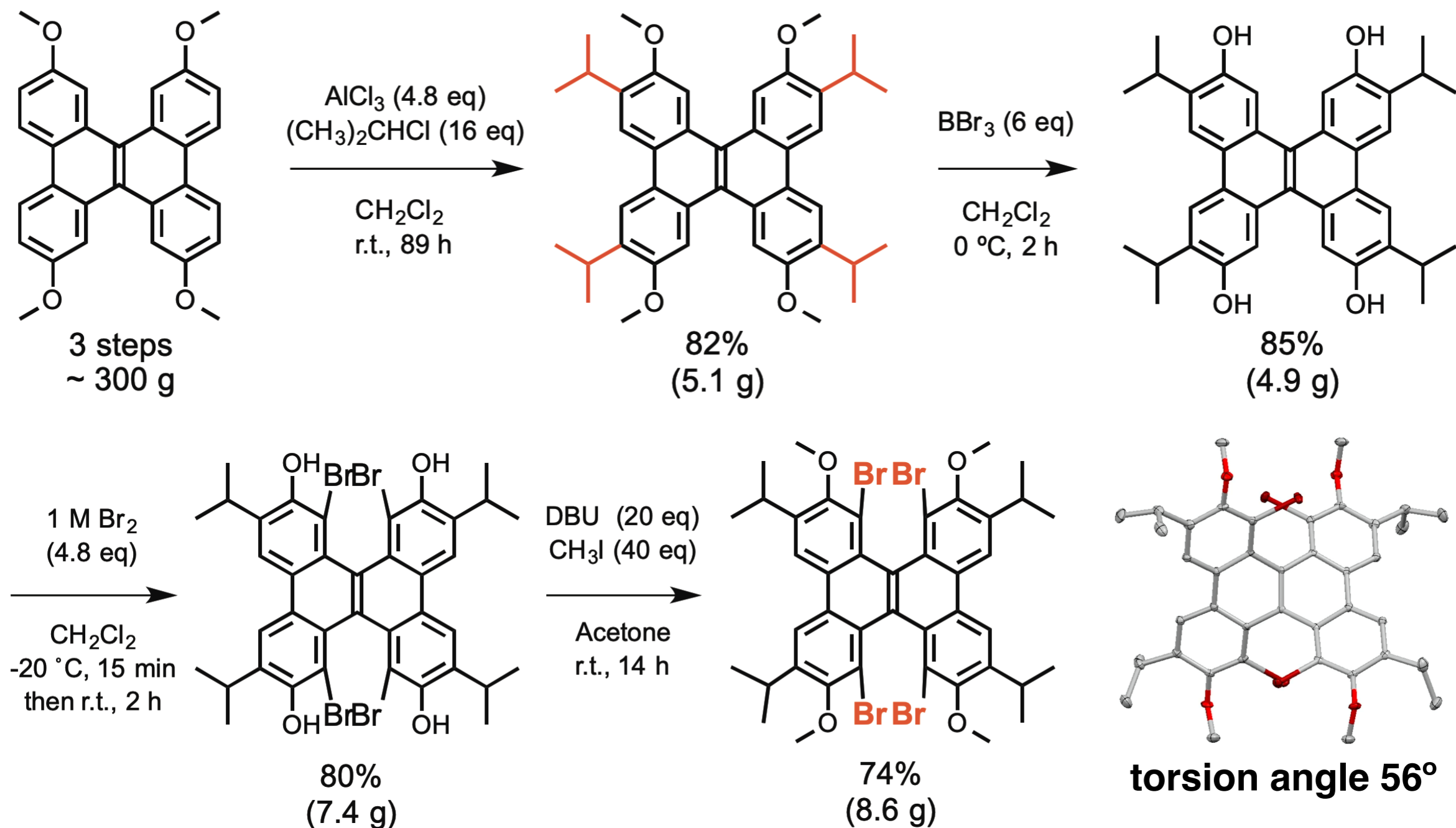
Retro-synthetic approach: Double ring-closures in the dibenzo[*g,p*]chrysene form the skeletal bucky bowl.



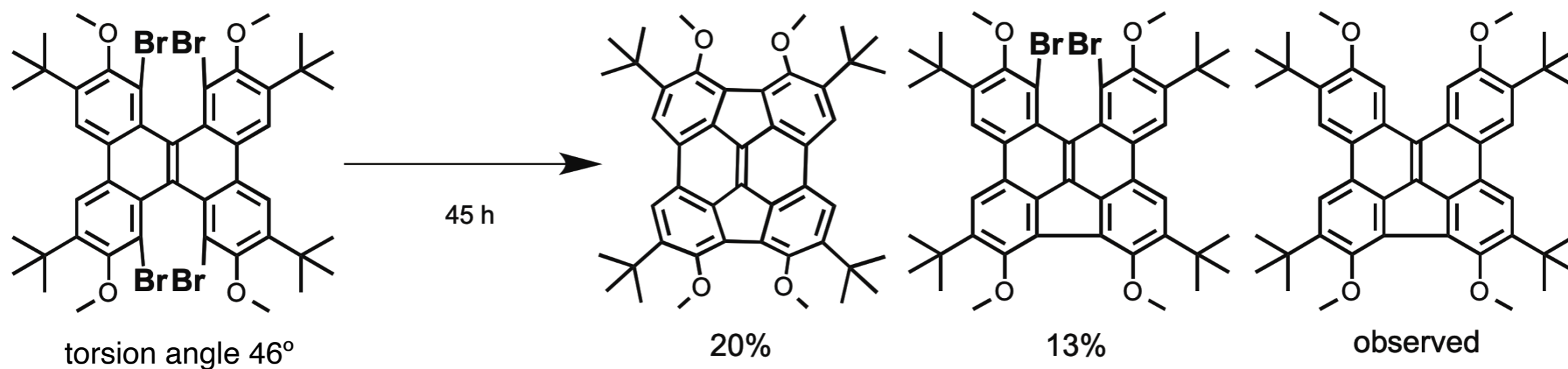
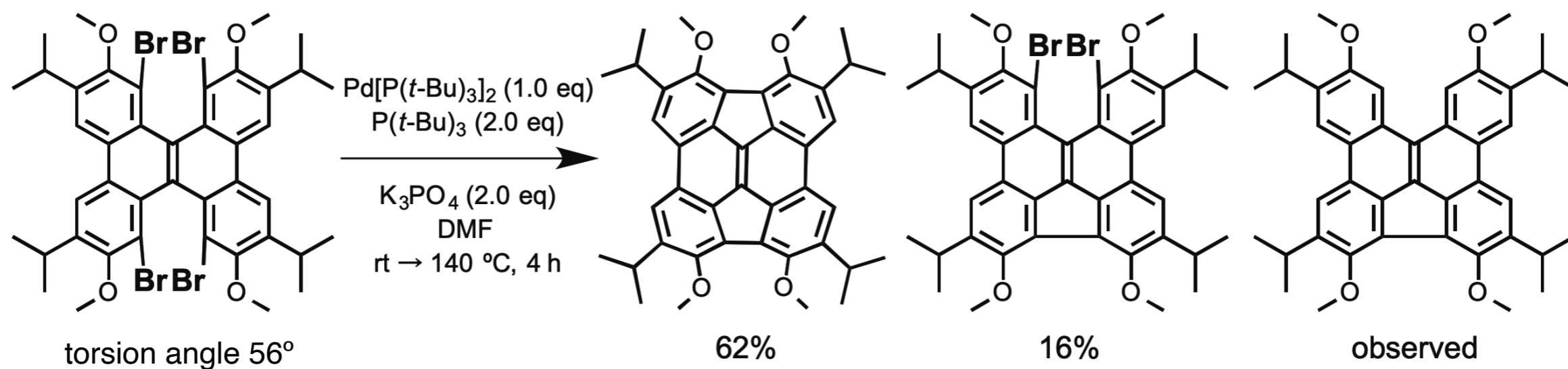
Precursor synthesis: Dibenzo[*g,p*]chrysene having four *tert*-butyls, four methyl ethers, and four bromines was prepared.



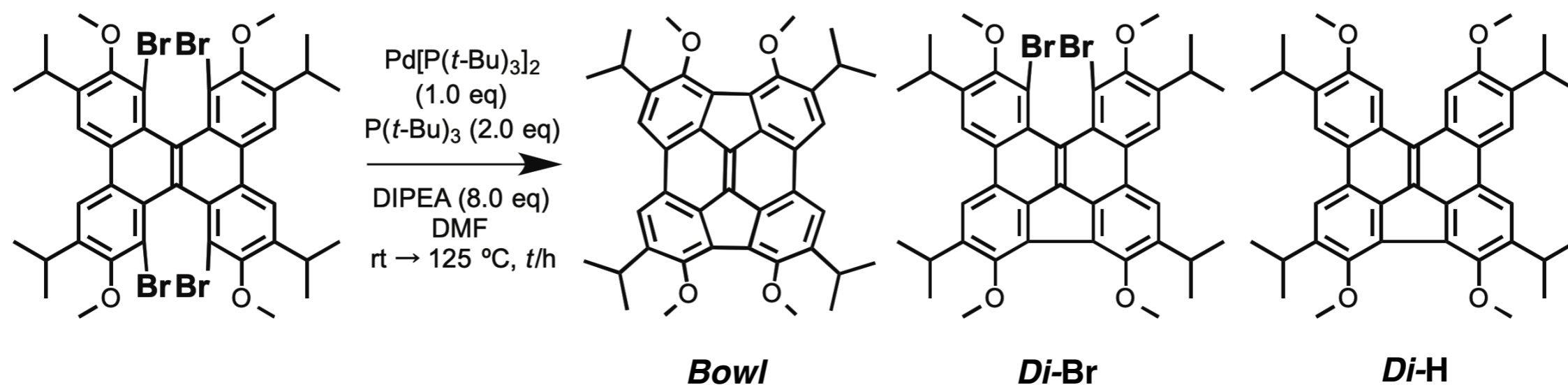
Precursor synthesis: Dibenzo[*g,p*]chrysene having four *iso*-propyls, four methyl ethers, and four bromines was prepared.



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

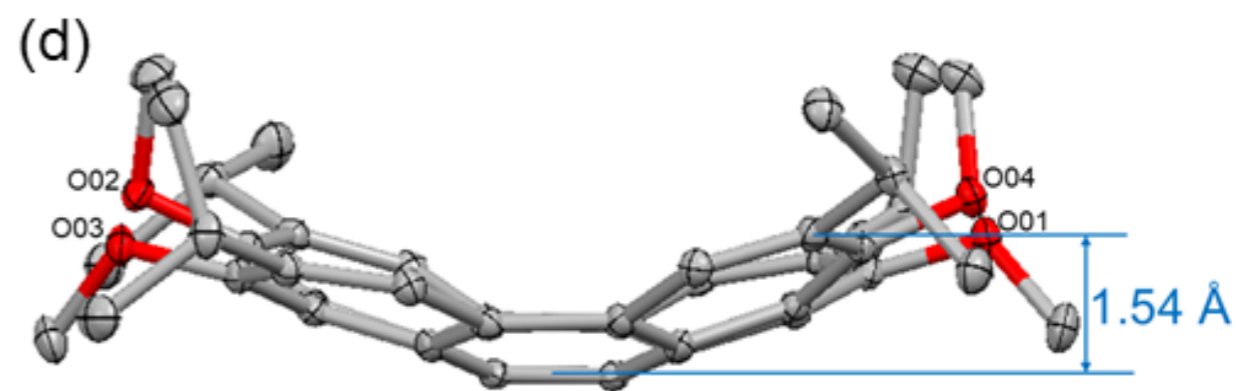
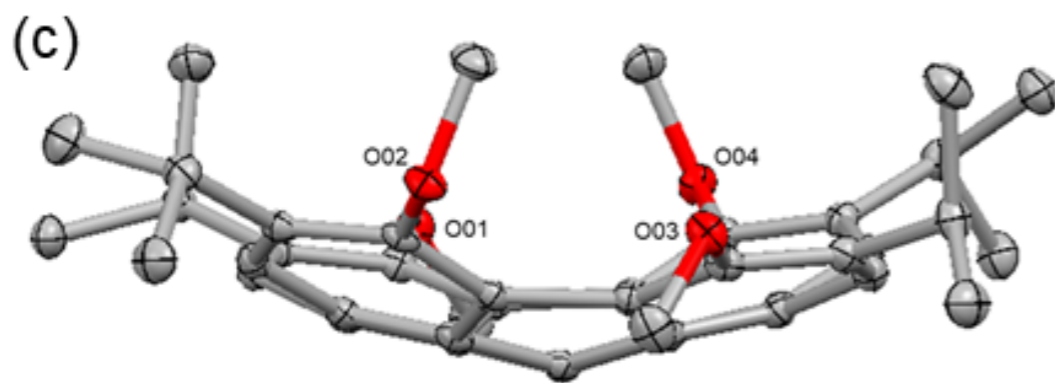
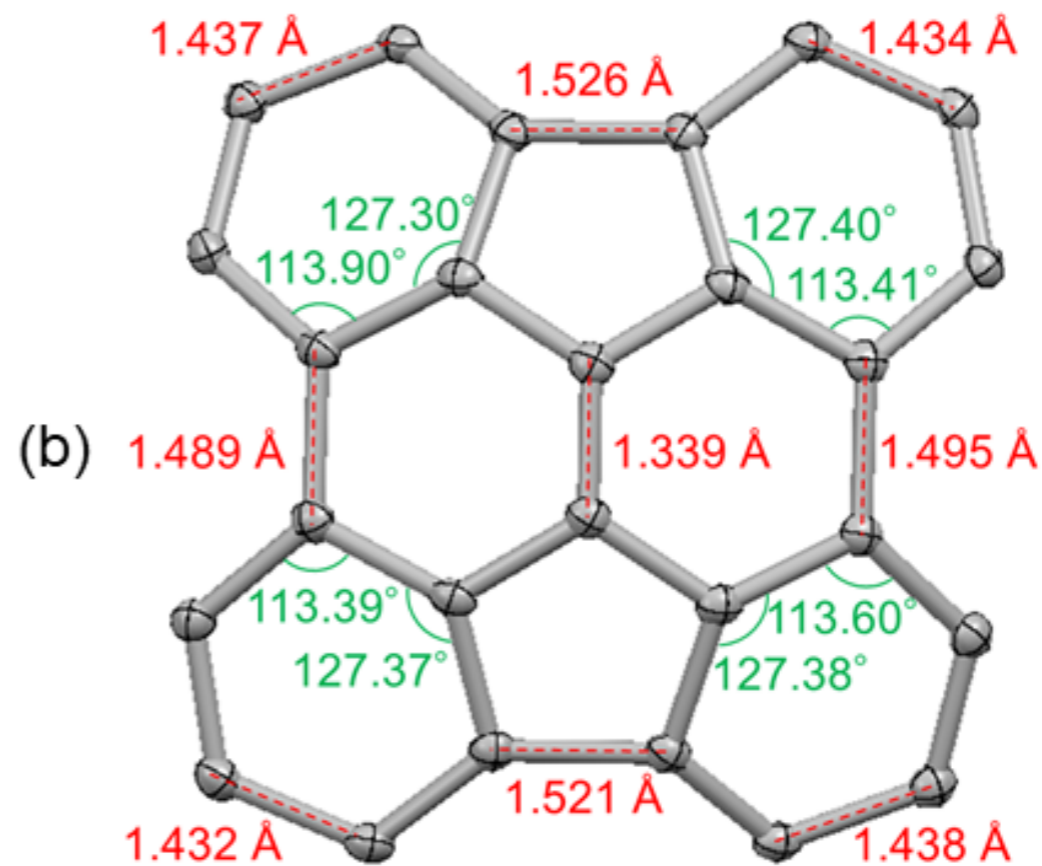
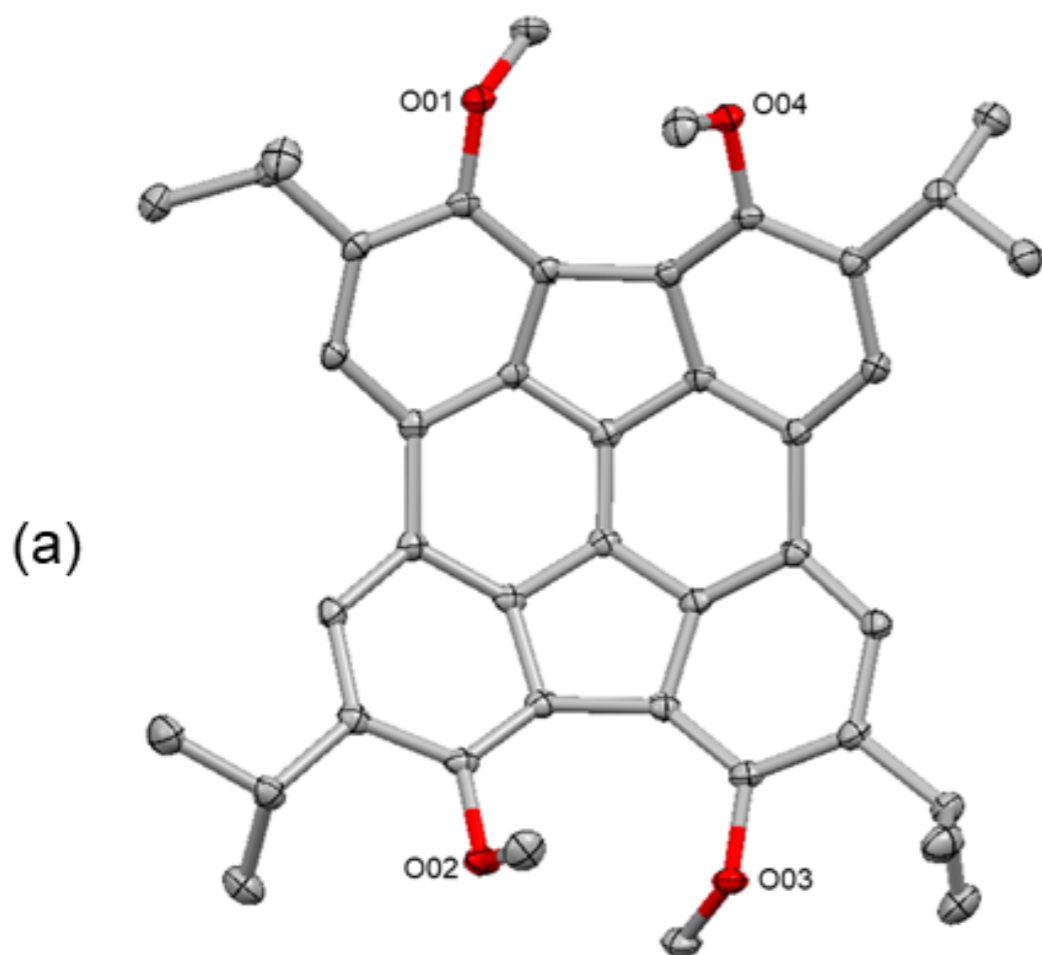


Gram-scale synthesis: the solution-processable protocol went well without serious loss of chemical yields.

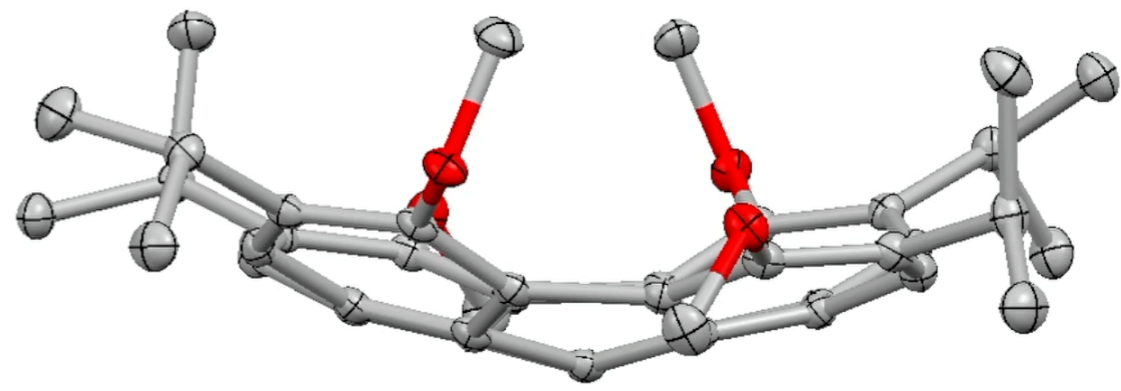
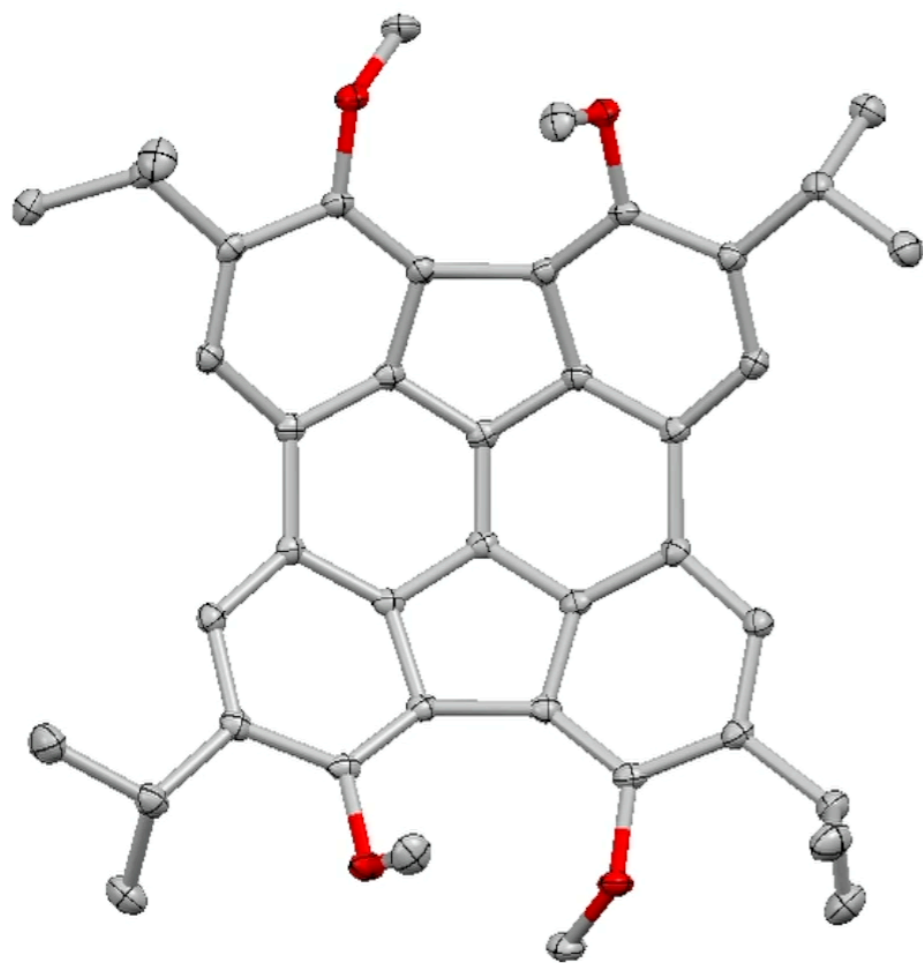


Scale		t/h	%Yield		
mmol	gram		<i>Bowl</i>	<i>Di-Br</i>	<i>Di-H</i>
0.15	0.14	1	68	0	25
0.45	0.42	1	67	3	5
1.4	1.3	2	66	0	10
2.7	2.5	2	66 (1.1 g)	0	14
5.4	5.1	2	62 (2.1 g)	0	19

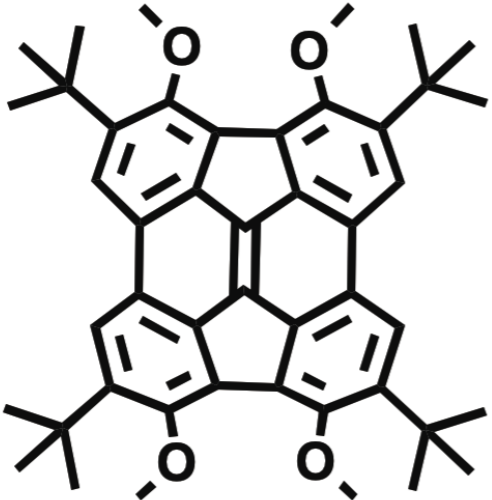
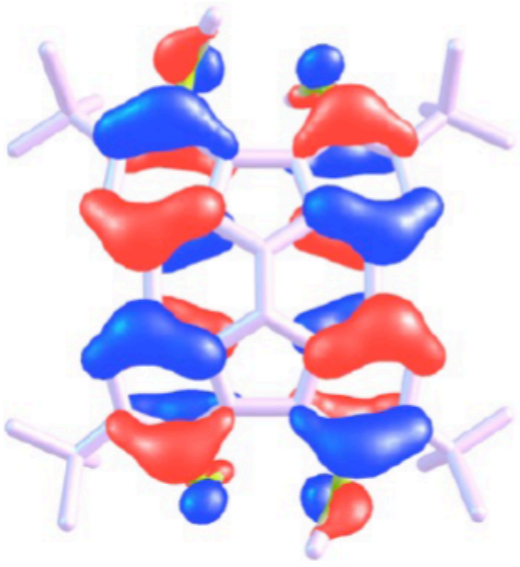
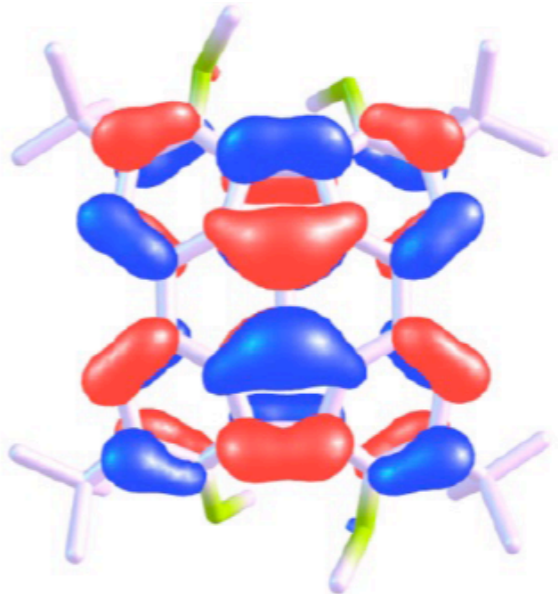
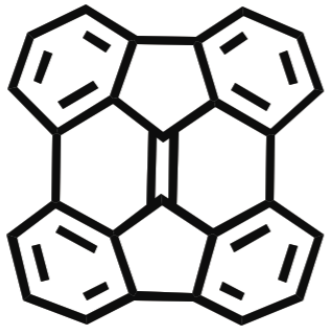
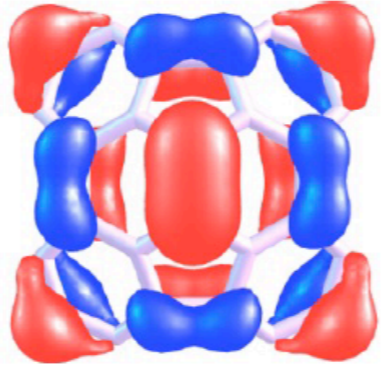
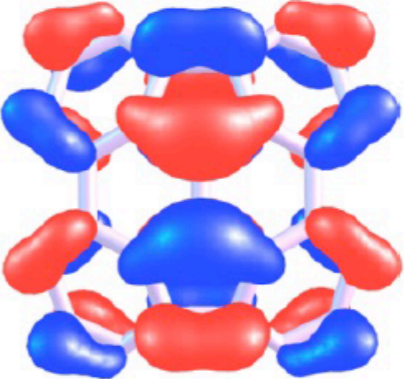
X-ray structure: result of 6:6-bond length 1.34 Å, bowl depth 1.54 Å.



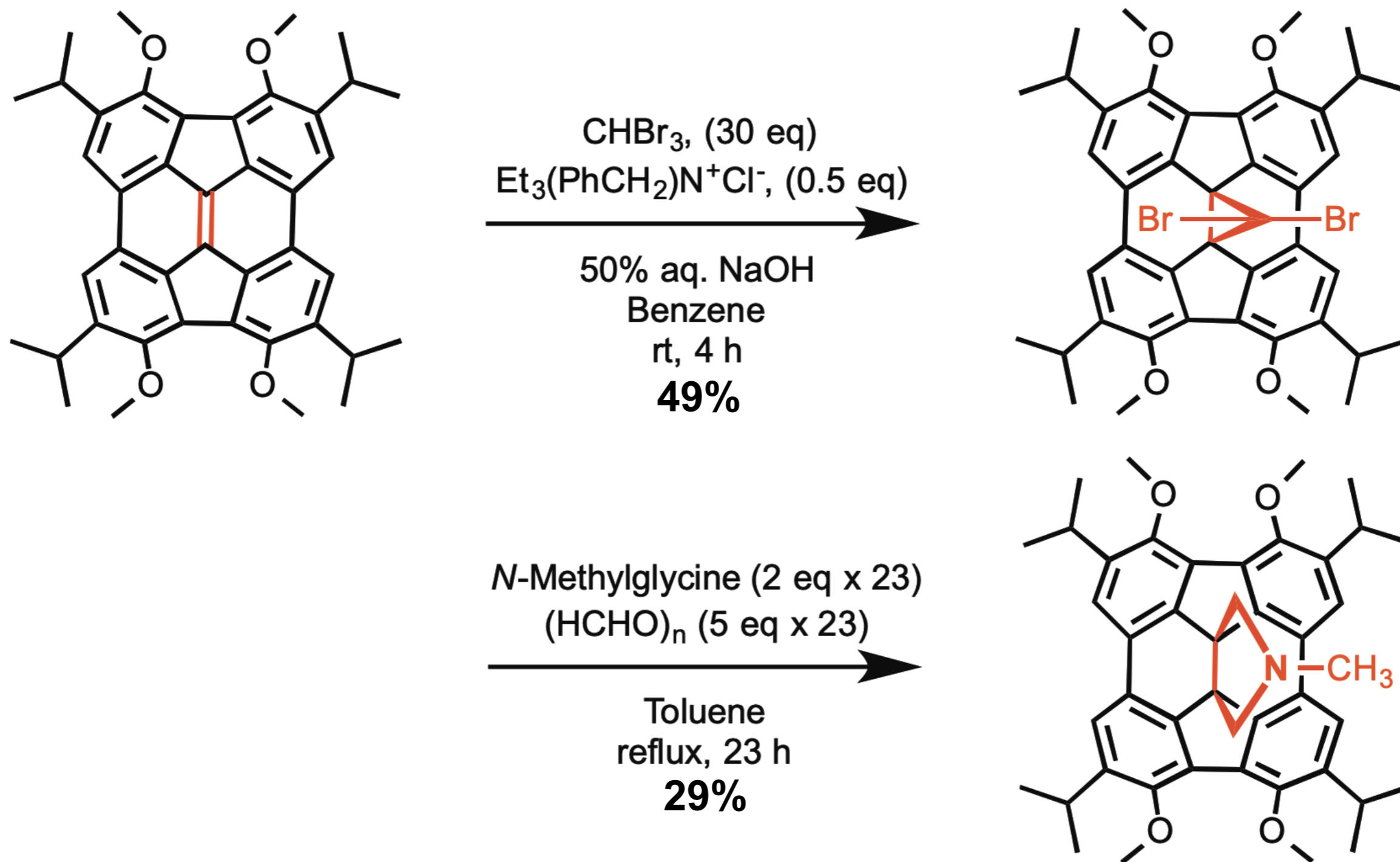
X-ray structure: result of a gently curved pi-surface (*i*-Pr)



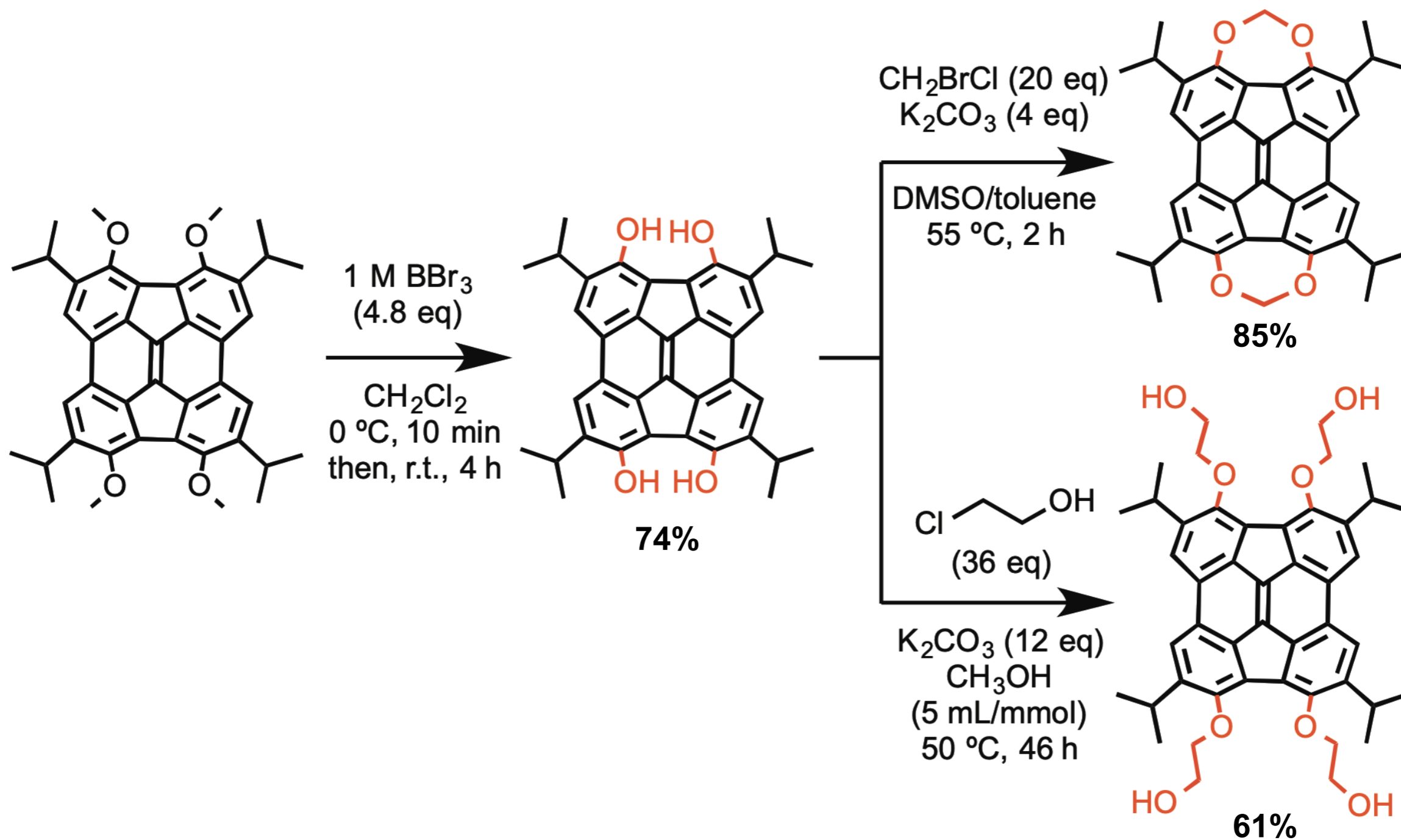
HOMO/LUMO Mappings (DFT method, B3LYP/6-31G(d,p))

	HOMO	LUMO
		
Energy [eV]	-5.34	-1.84
HOMO-LUMO gap	3.50	
		
Energy [eV]	-5.80	-1.98
HOMO-LUMO gap	3.82	

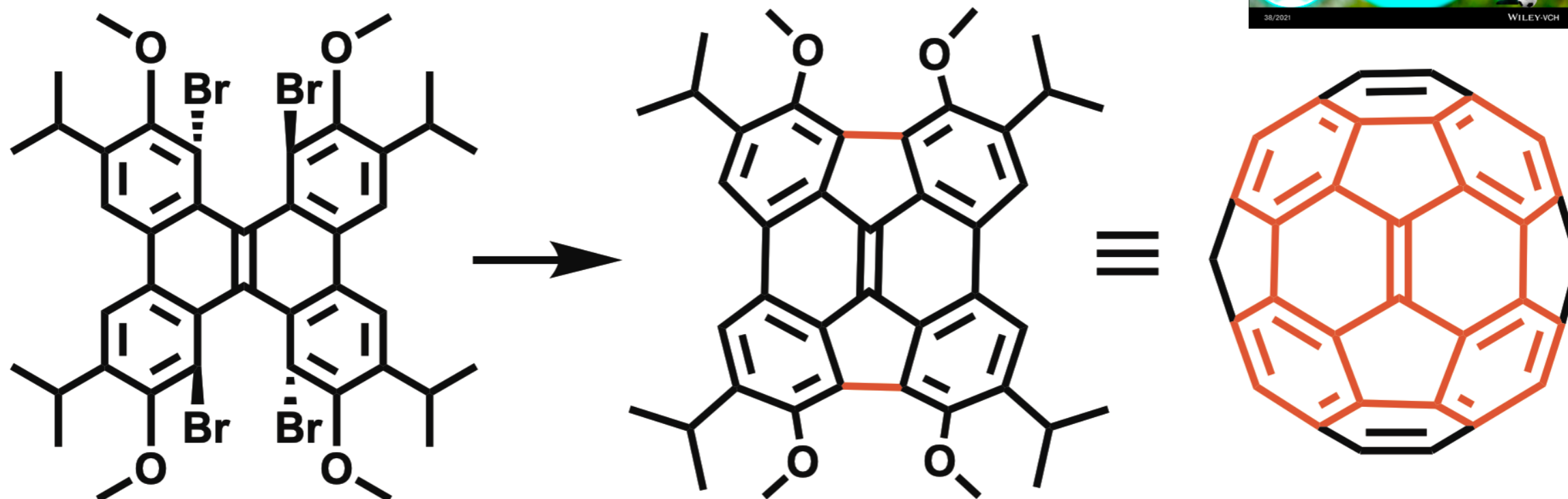
Further transformation in the 6:6-bond: the conventional cyclopropanation with *in situ* carbene and cycloaddition with *in situ* ylide were accomplished.



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

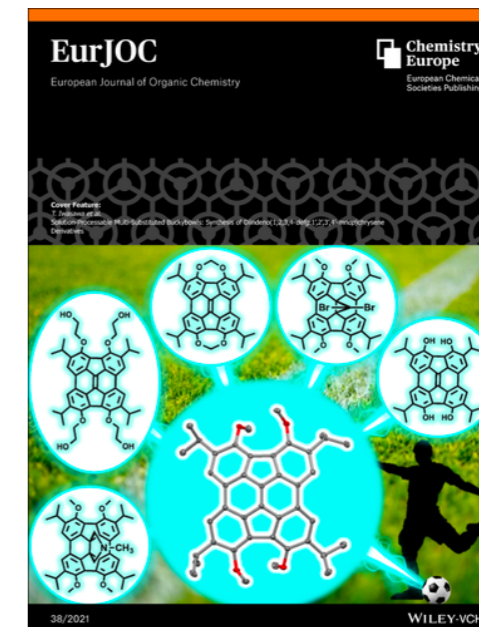


Summary: Solution-phase synthesis of the DIC-typed buckybowls was achieved in gram scale.



Up to 2.1 g

Buckybowl



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