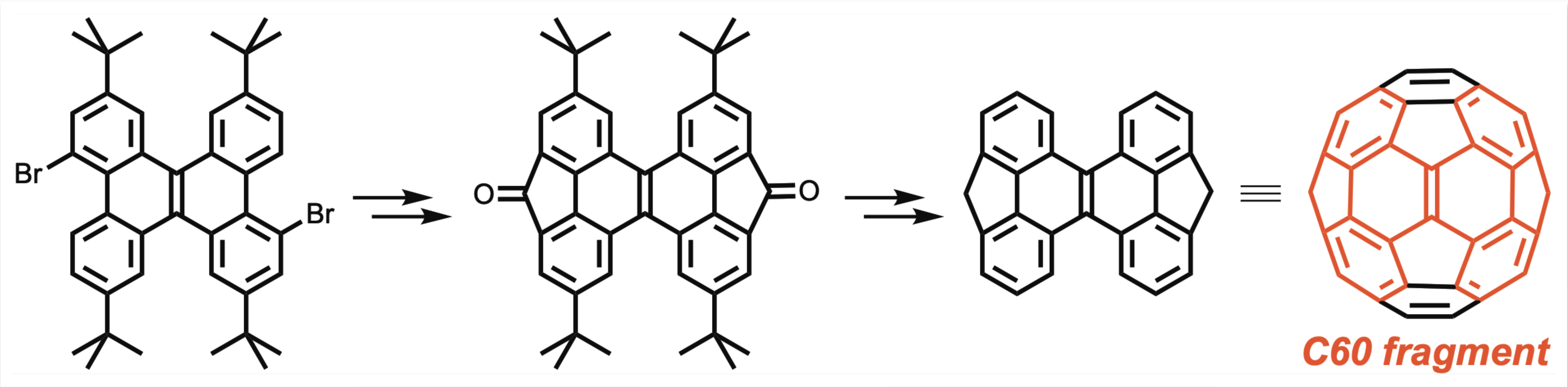
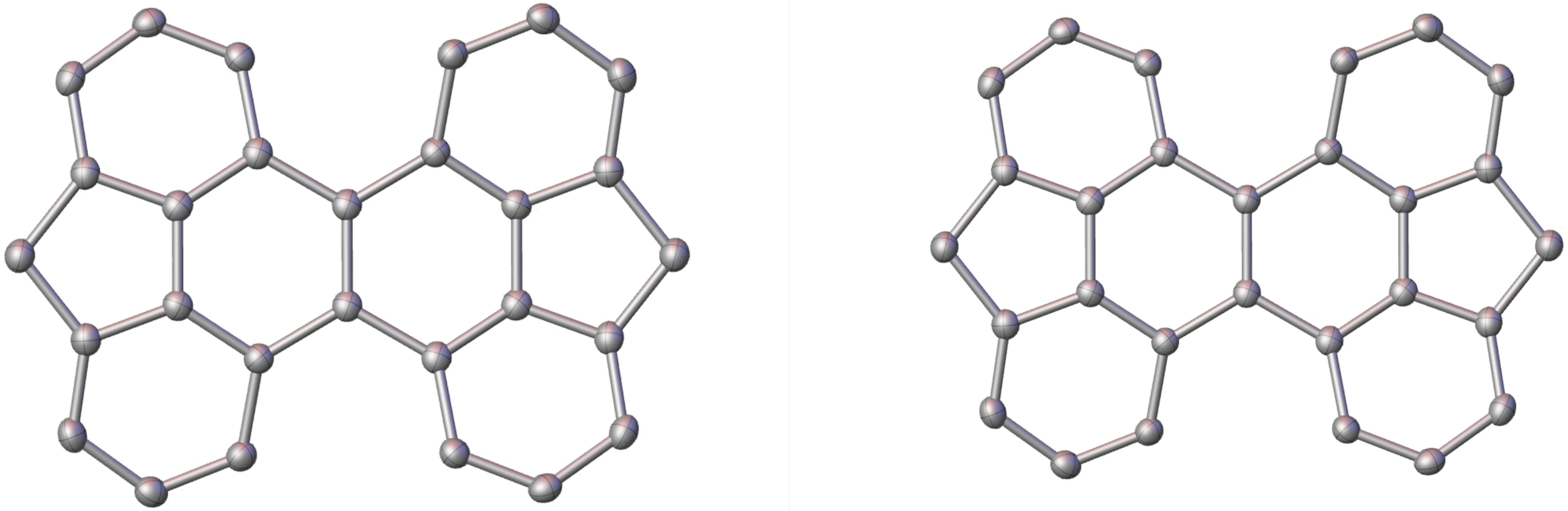
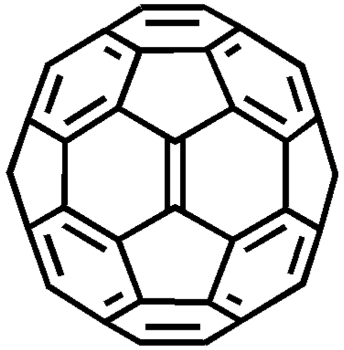
Solution-Compatible Synthesis of C_{60} Fragmentary Octacycles



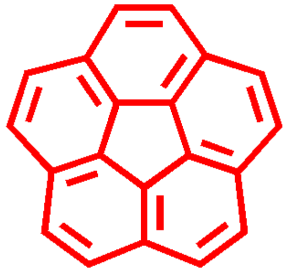


N. Yoshida, *et al.*, *Eur. J. Org. Chem.* **2023**, e202300407. Doi: 10.1002/ejoc.202300407

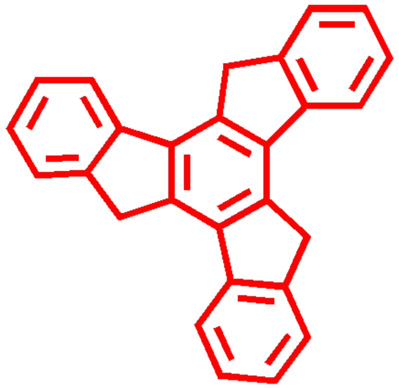
General background: C60-fragments include the monumental *Corannulene*, *Sumanene*, and *Truxene*, those three have served as leading molecules in ongoing research for curved, fused, and pi-extended polyaromatic molecules .



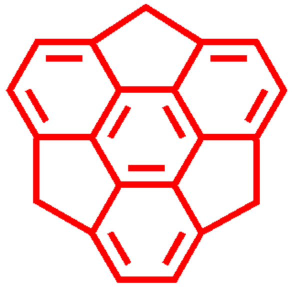
C_{60}
Buckminsterfullerene
1985 Kroto, Smalley, Curl



Corannulene
$C_{20}H_{10}$
1966 Lawton, Barth
¥42,000/100 mg (TCI)

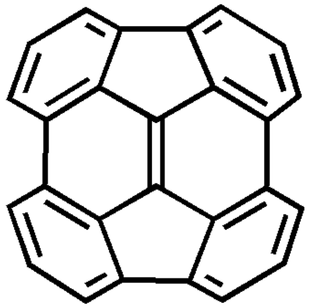


Truxene
$C_{27}H_{18}$
1984 Hartke
¥36,000/g (TCI)

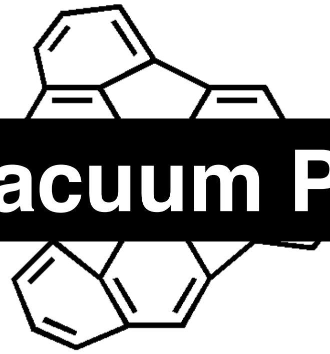


Sumanene
$C_{21}H_{12}$
2003 Sakurai, Hirao
¥100,000/100 mg (TCI)

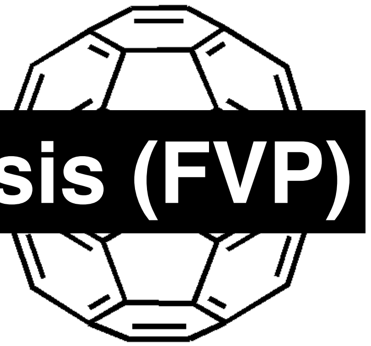
Flash Vacuum Pyrolysis (FVP)



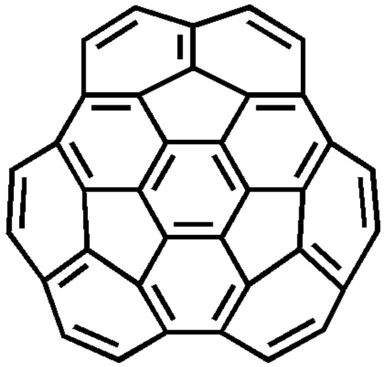
Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene
$C_{26}H_{12}$
2002 Scott



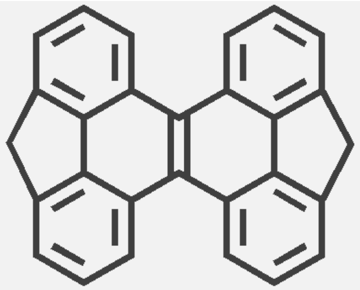
Hemifullerene
$C_{30}H_{12}$
1995 Rabideau, **1997** Scott



[5,5]fulvalene circulene
$C_{30}H_{12}$
1997 Scott



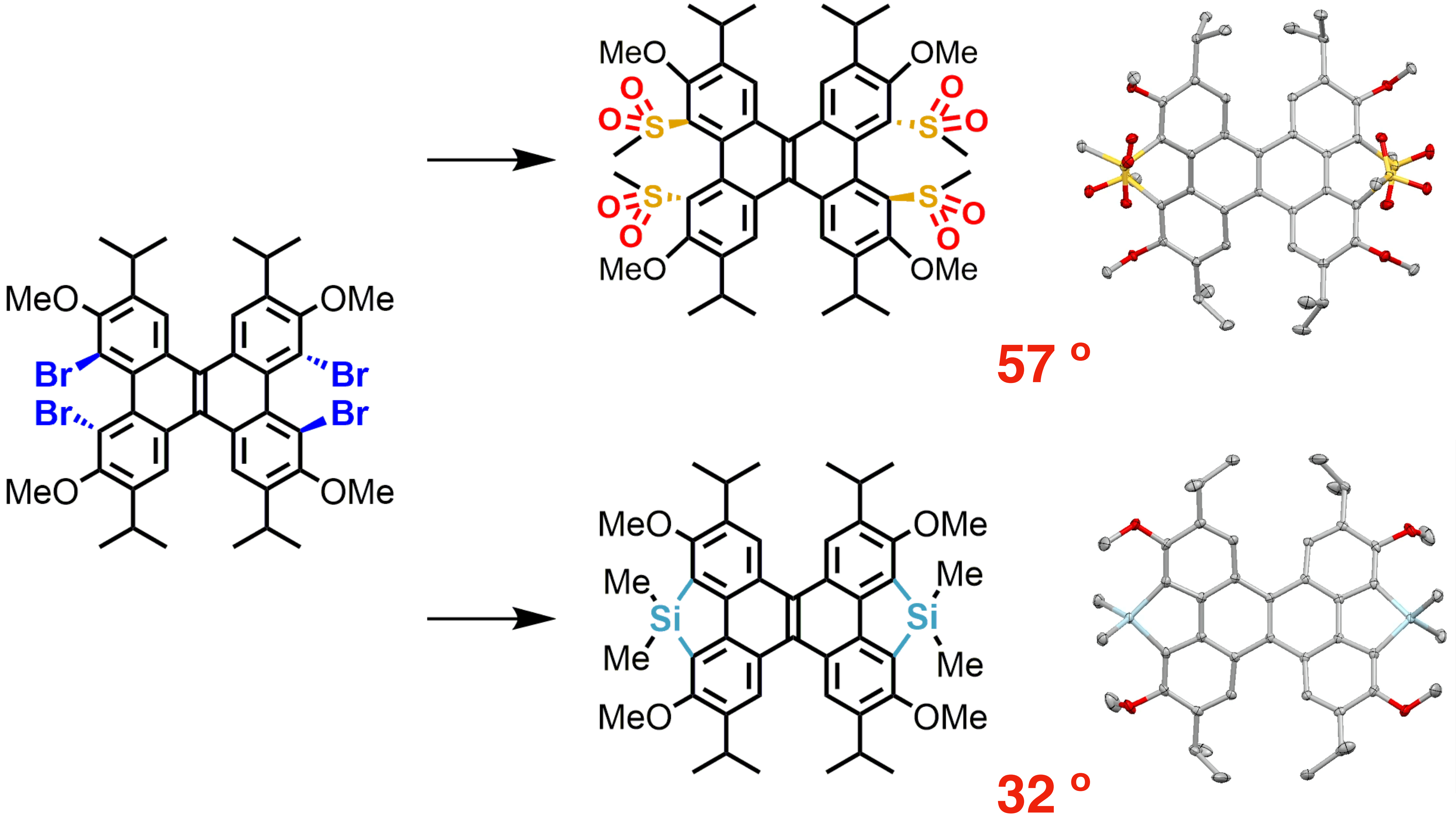
Circumtrindene
$C_{36}H_{12}$
1996 Hagen, **2000** Scott



4,11-dihydrodiindeno[7,1,2-*ghi*:7',1',2'-*pqr*]chrysene

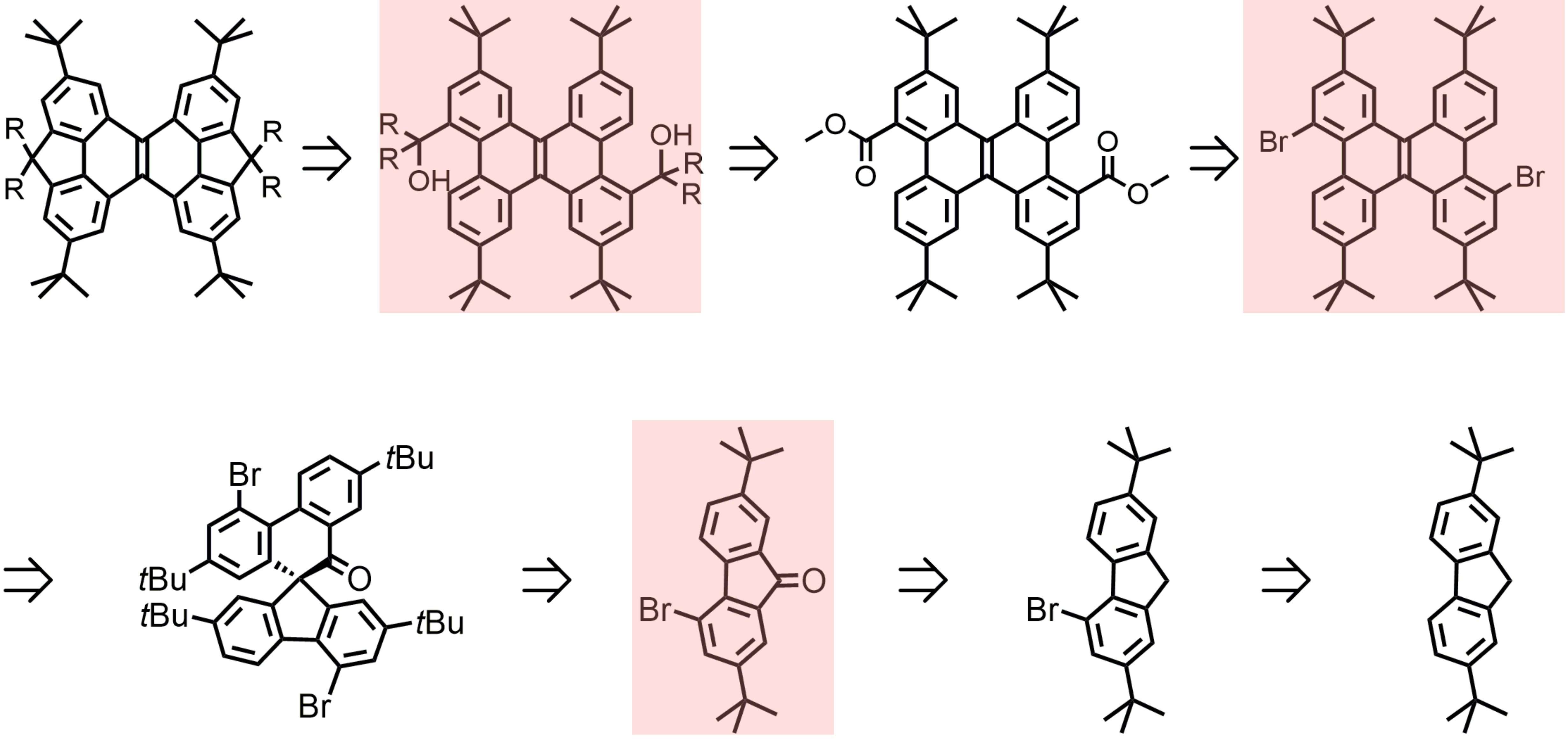
Simple yet unachievable octacycle

Our background: Relevant synthesis to manipulating non-planarity in dibenzo[*g*,*p*]chrysene was studied, and the hexacycle was flexibly movable in a range of 25°. ***Can carbon atoms bridge over the Bay?***



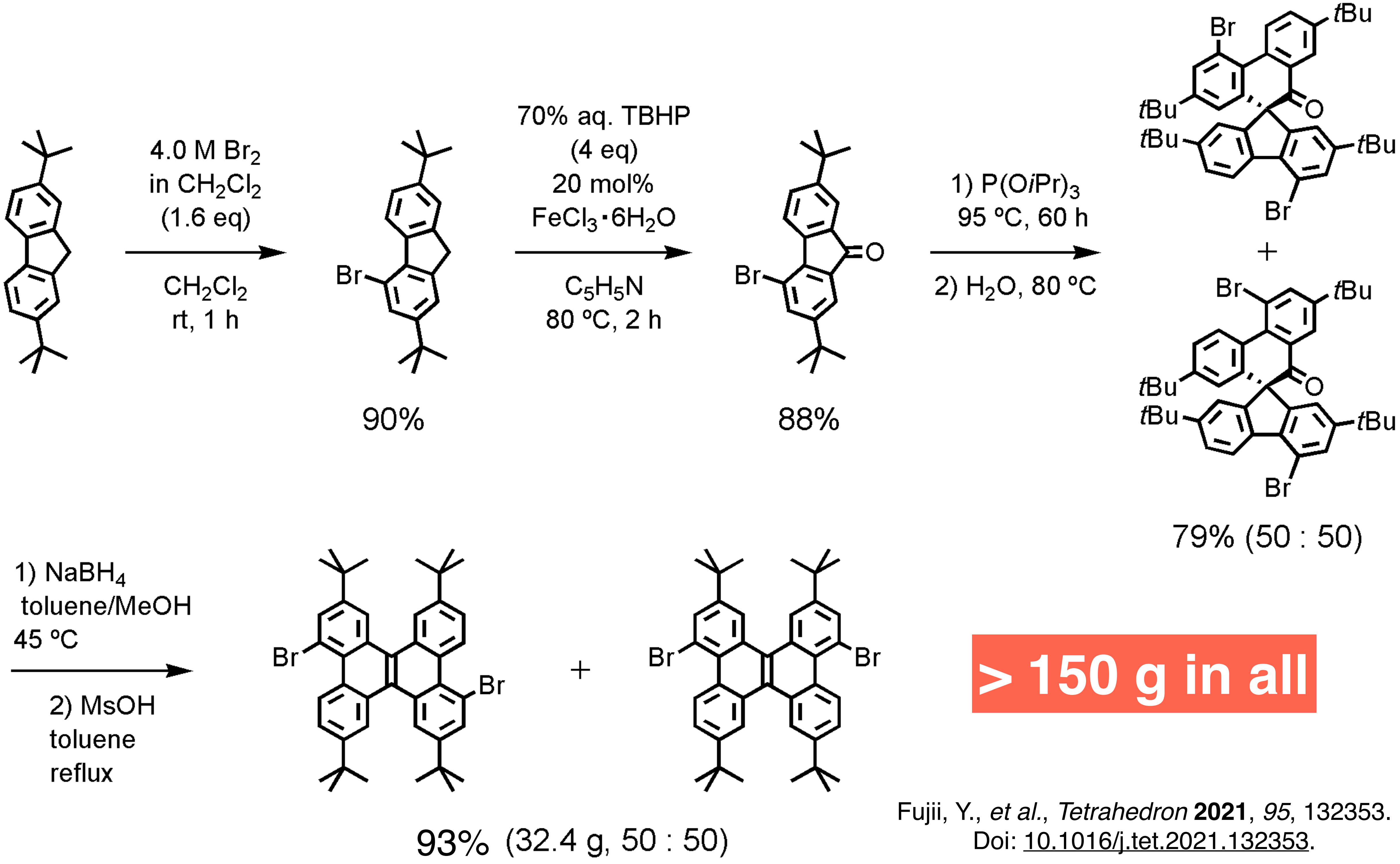
S. Kamiguchi, et al., *Tetrahedron Lett.* **2022**, *92*, 153664.

Can carbon atoms bridge over the Bay? **:** Our strategy lies in solution-phase bottom-up approach, in which Friedel-Crafts intra-molecular cyclization gives an opportunity of forming a C$_{60}$ fragmentary octacycle.



Readily Commercially Available (BLD ¥ 54900 / 500 g)

Scalable preparation of starting dibromo-DBCs: The readily commercially available 2,7-di-*tert*-butyl-fluorenes were employed, and four steps achieved more than 100 grams of the isomers.

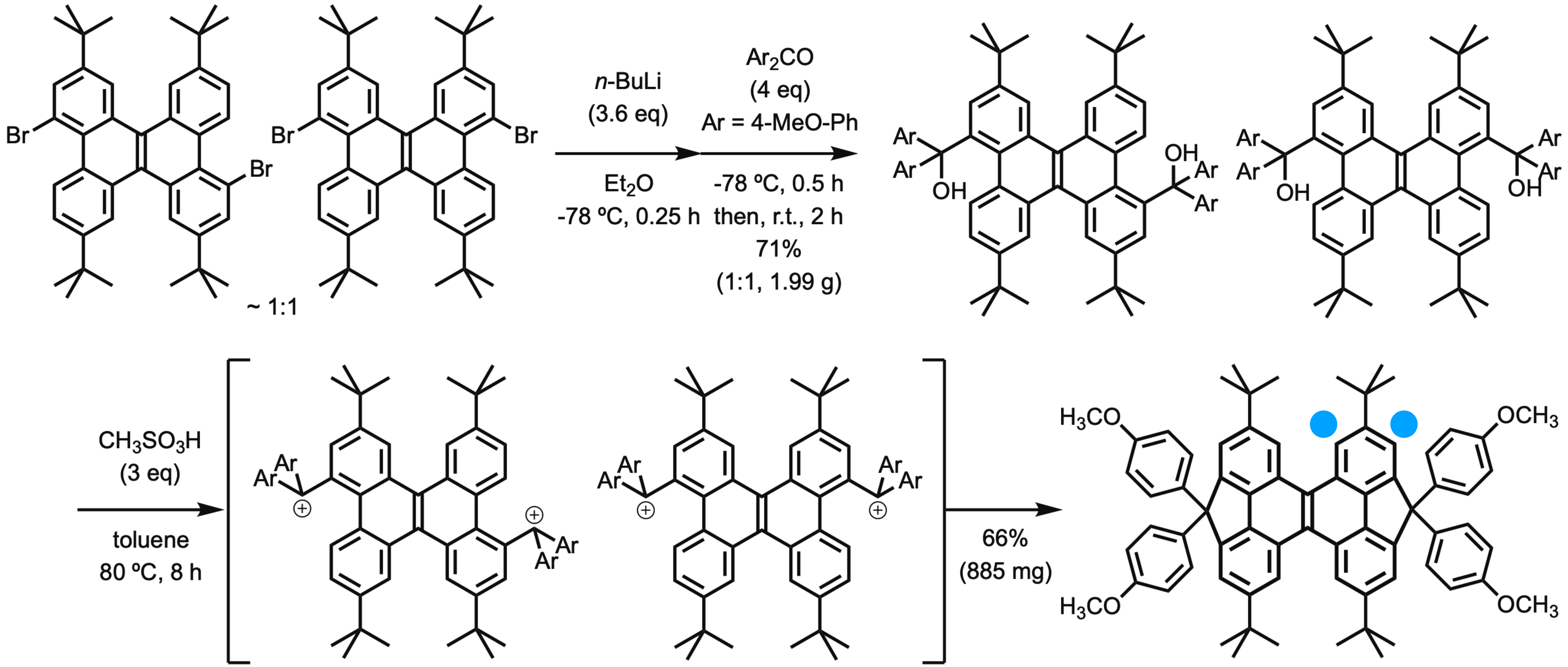


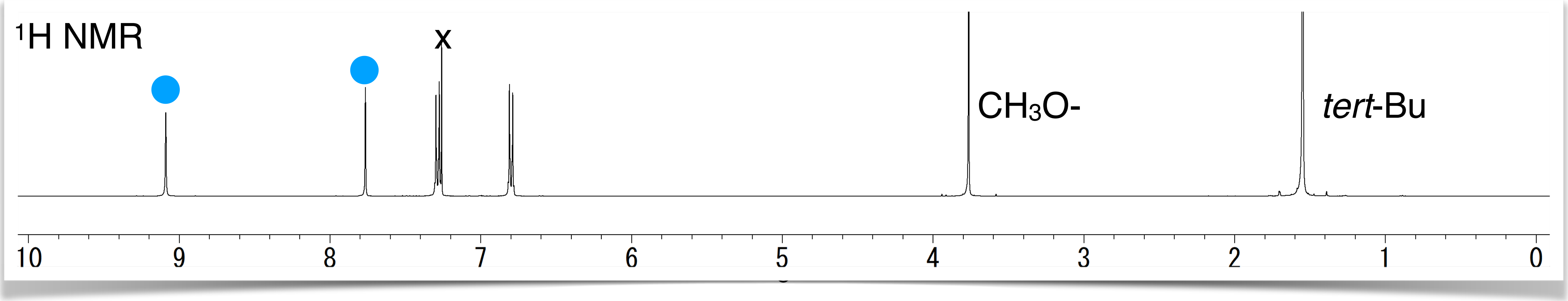
> 150 g in all

Fujii, Y., *et al.*, *Tetrahedron* **2021**, *95*, 132353.
Doi: 10.1016/j.tet.2021.132353.

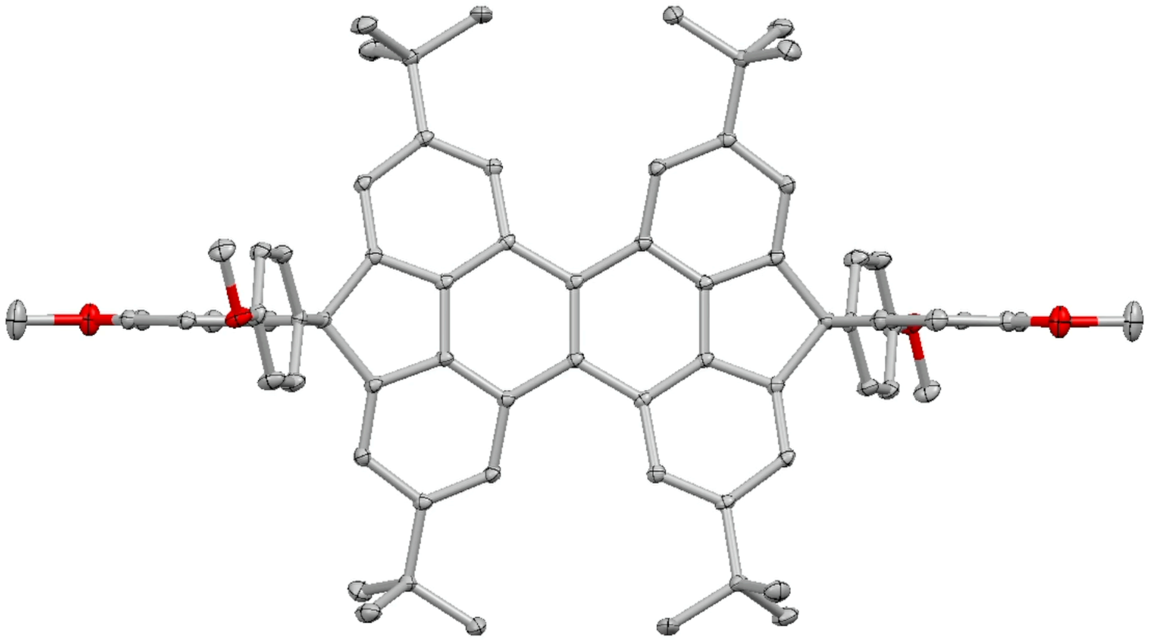
The first synthesis of a C_{60} fragmentary octacyclic framework:

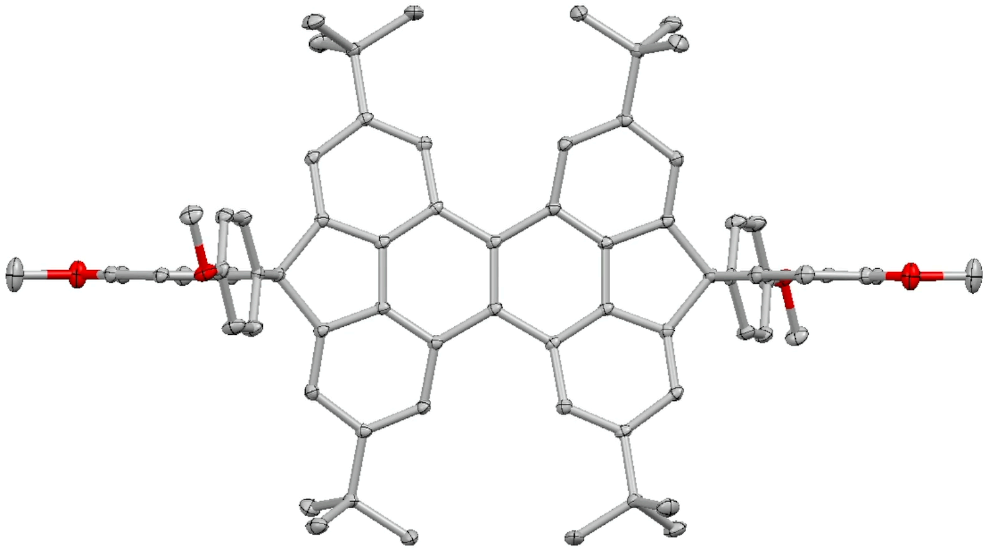
Conventional Friedel-Crafts alkylation was successfully carried out.

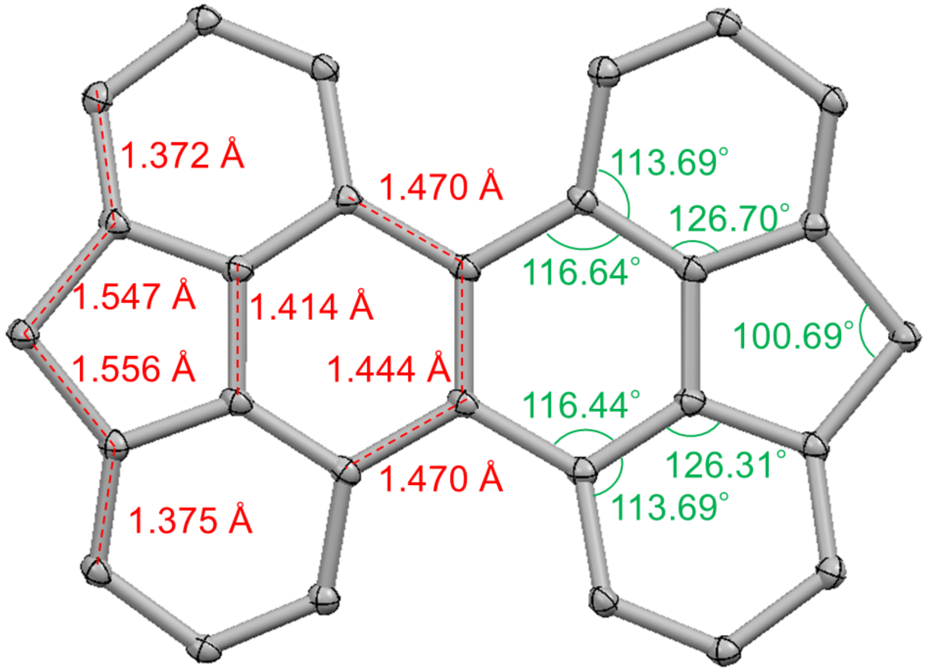


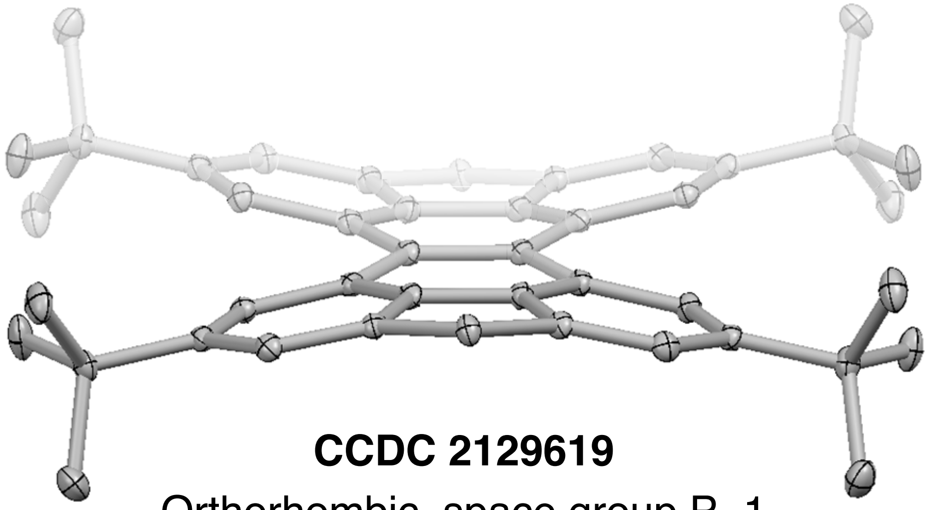


X-ray structure, result of a *saddle*-shaped octacycle: Indeed, we were very happy to confirm *sp*3-carbons tying two *Bay*-aryls.





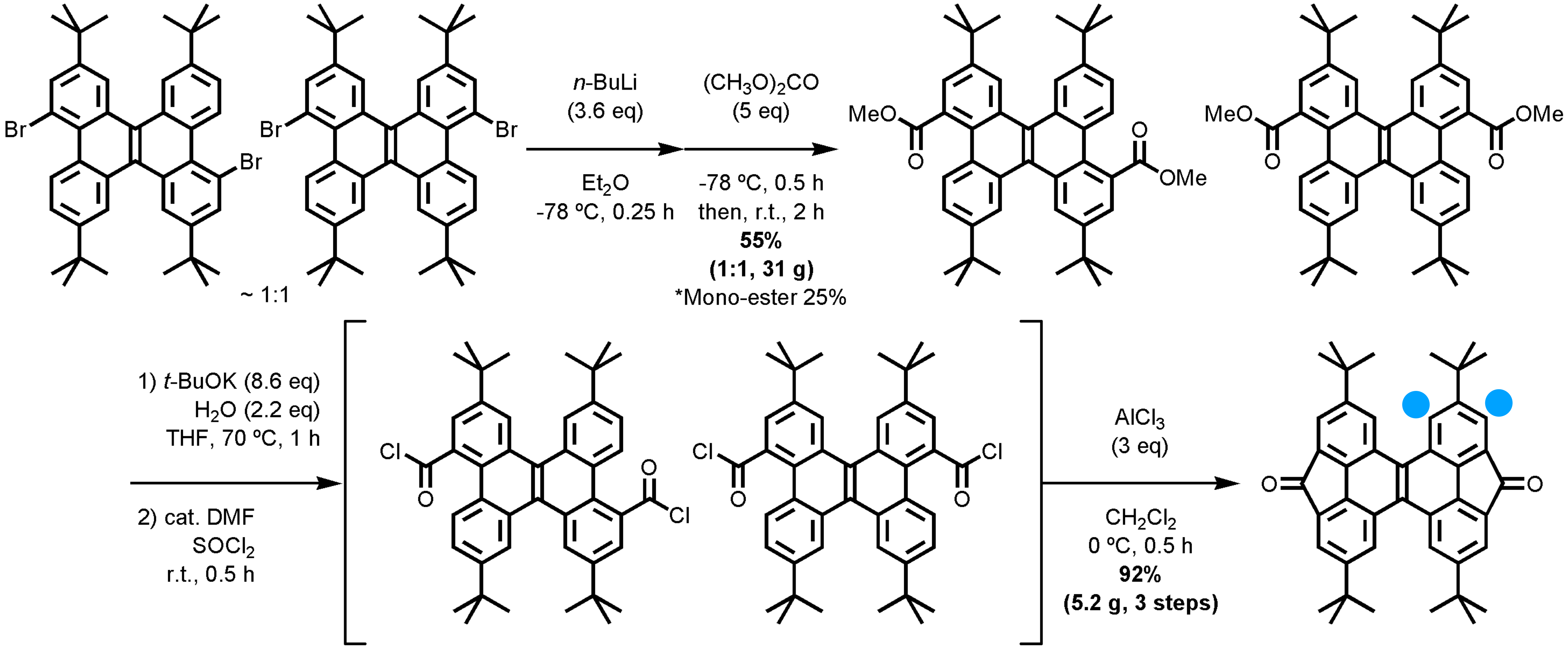


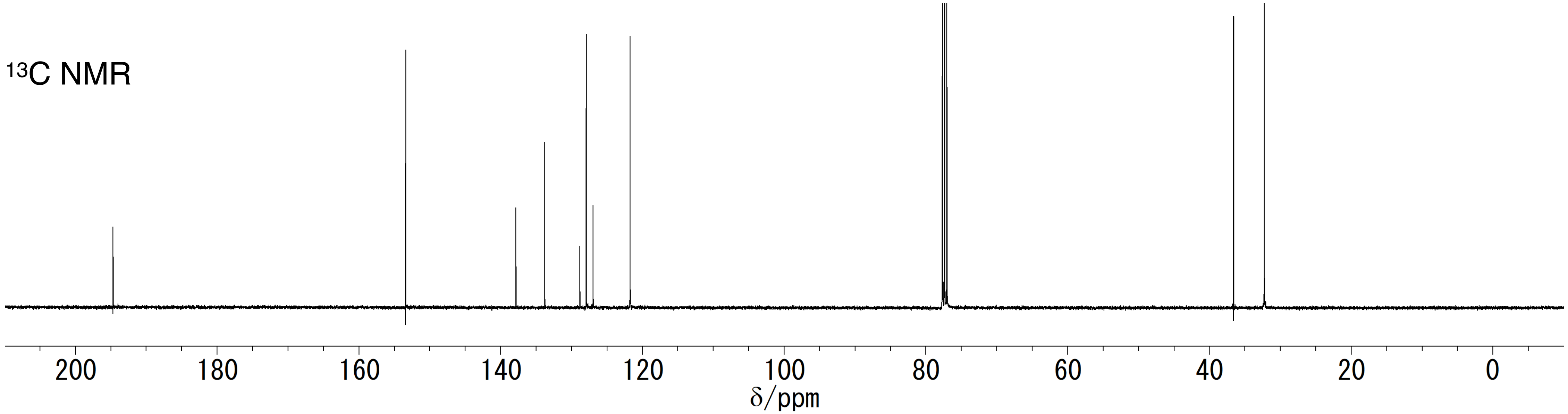


CCDC 2129619
Orthorhombic, space group P -1
R_1 = 0.0721, wR_2= 0.2178, GOF = 1.086
Torsion angle, 20.03(11)°
(Computational, 21.56°)

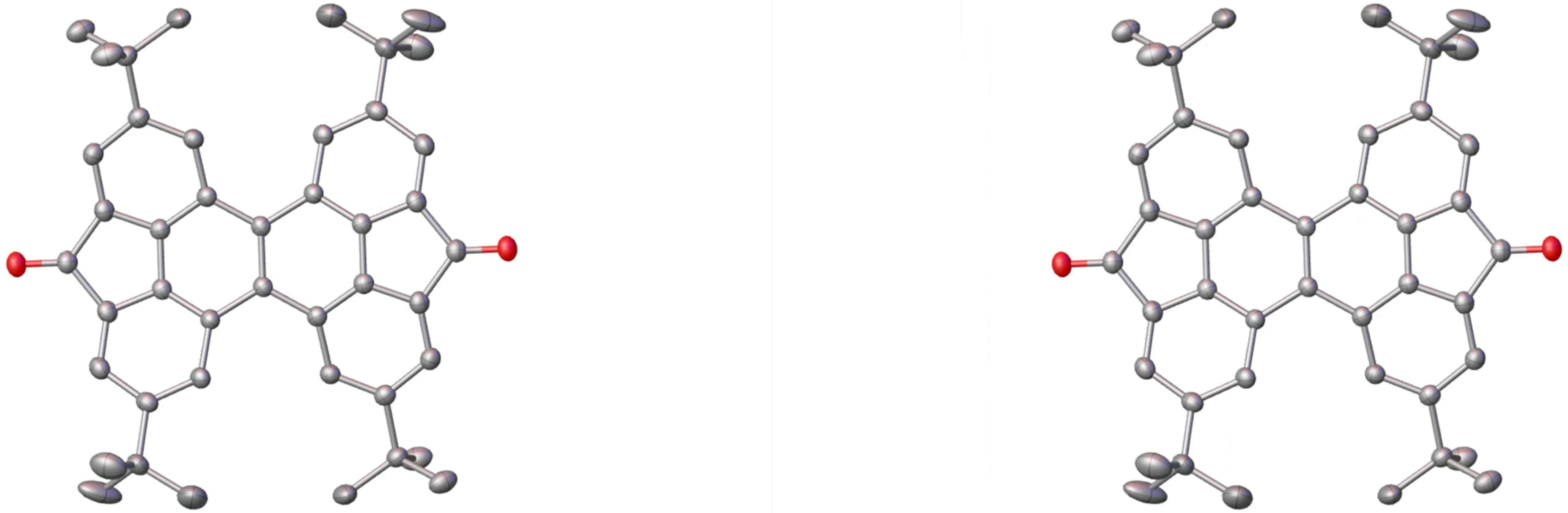
Can sp²-carbons tie the two Bay-aryls?

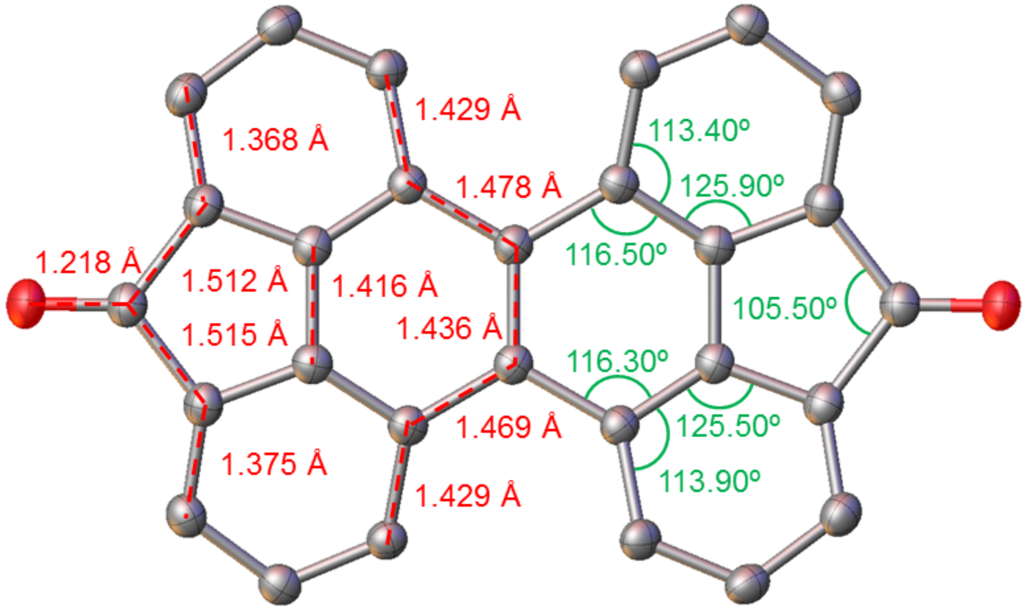
— Yes, carbonyls can bridge across the *Bay*-regions.

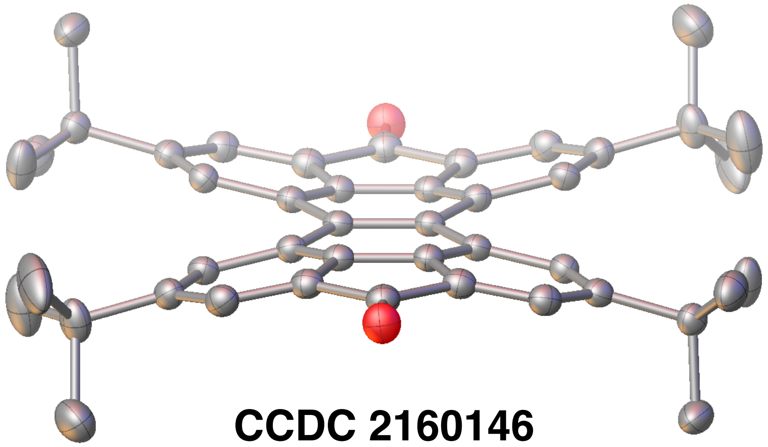




X-ray structure, result of a saddle-shaped octacycle: Indeed, we were glad to confirm *carbonyl*s tying the two *Bay*-aryls.

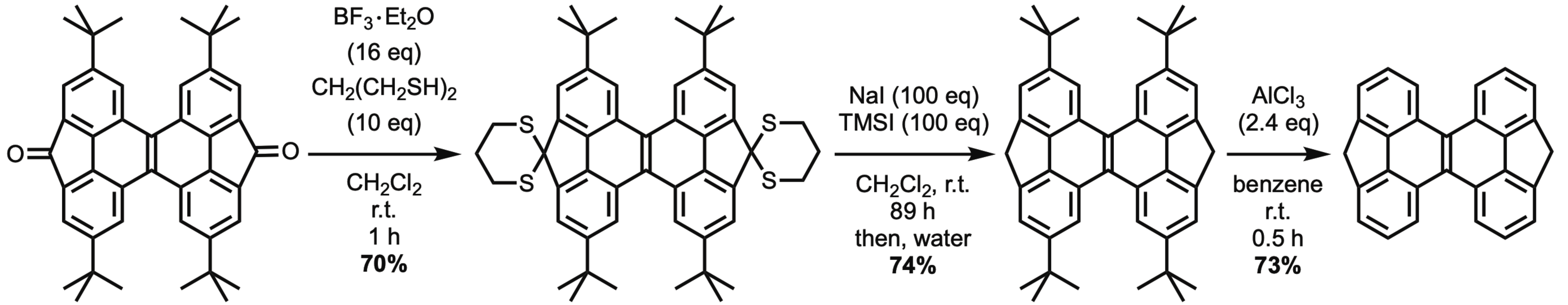


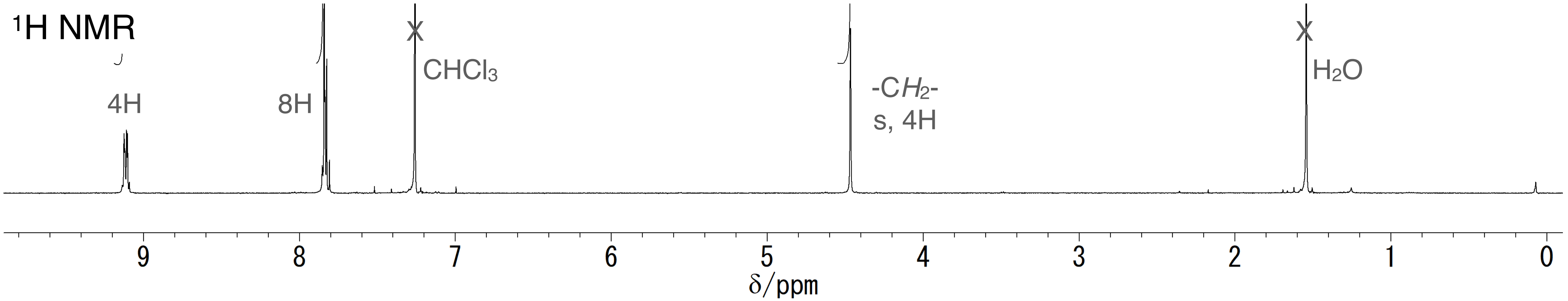


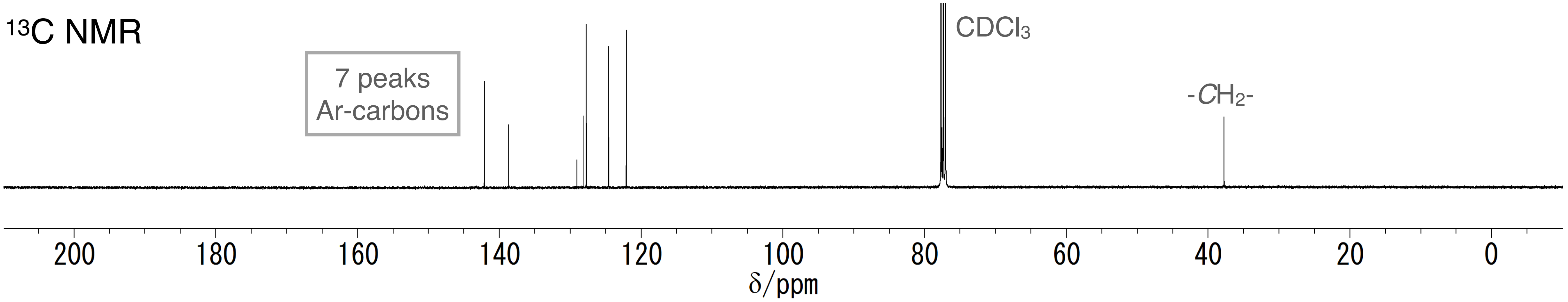


CCDC 2160146
Monoclinic, space group P 1 2/c 1
R_1 = 0.0733, wR_2= 0.2156, GOF = 1.067
Torsion angle, 20.83(12)º
(Computational, 20.90º)

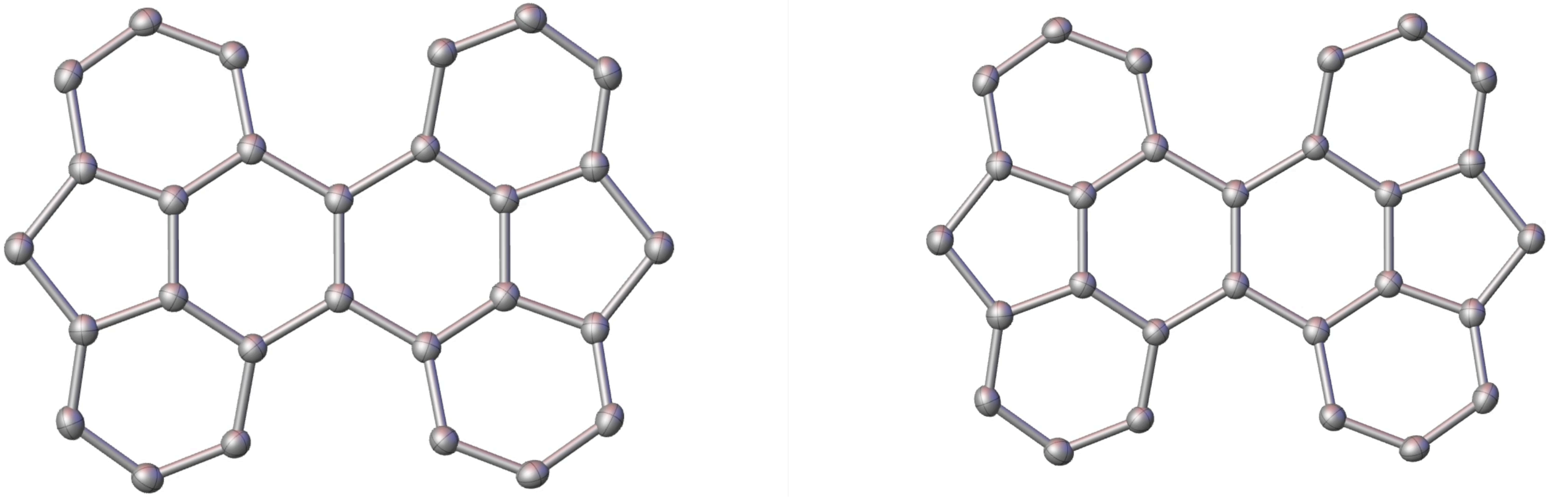
Deprotection of two carbonyls and fourfold alkyls: Synthesis of 4,11-dihydrodiindeno[*7,1,2-ghi:7’,1’,2’-pqr*]chrysene was achieved.

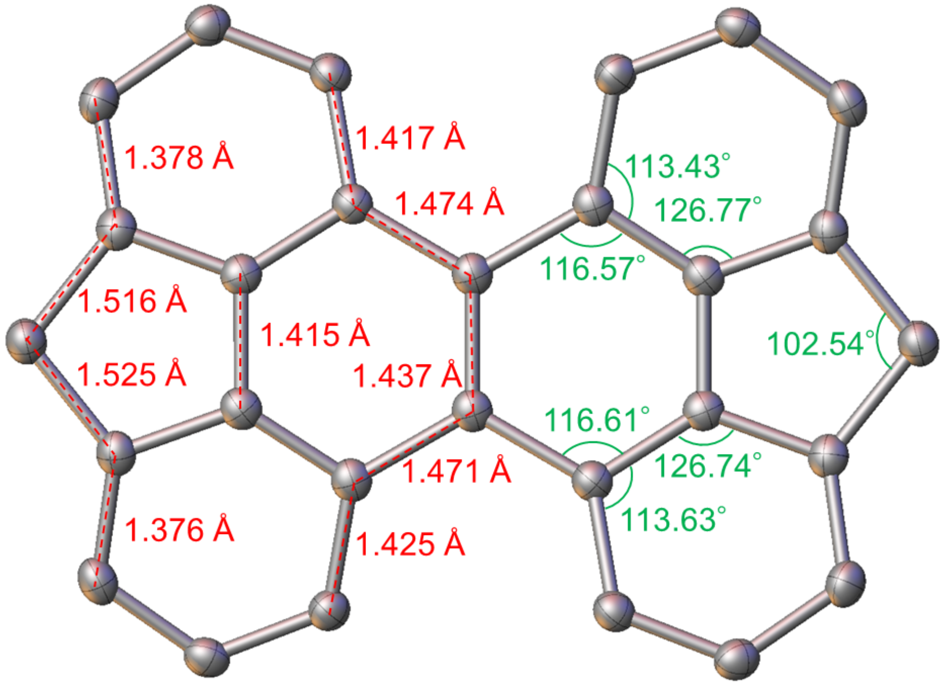


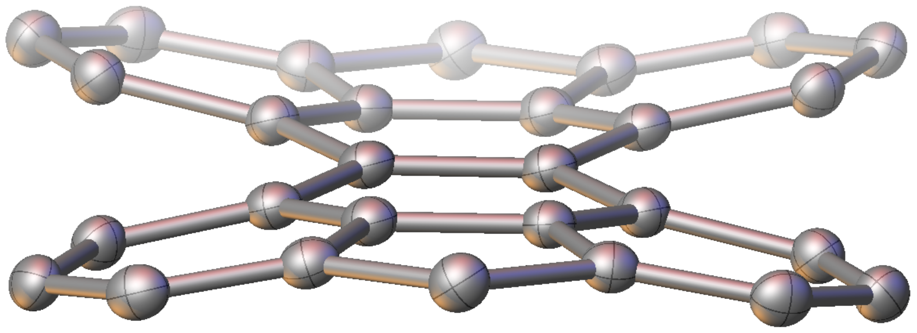




X-ray structure, a result of gently curved saddle-shape: Prepared by slow evaporation of CH_3CN (6 mL) solution of the sample (3 mg).

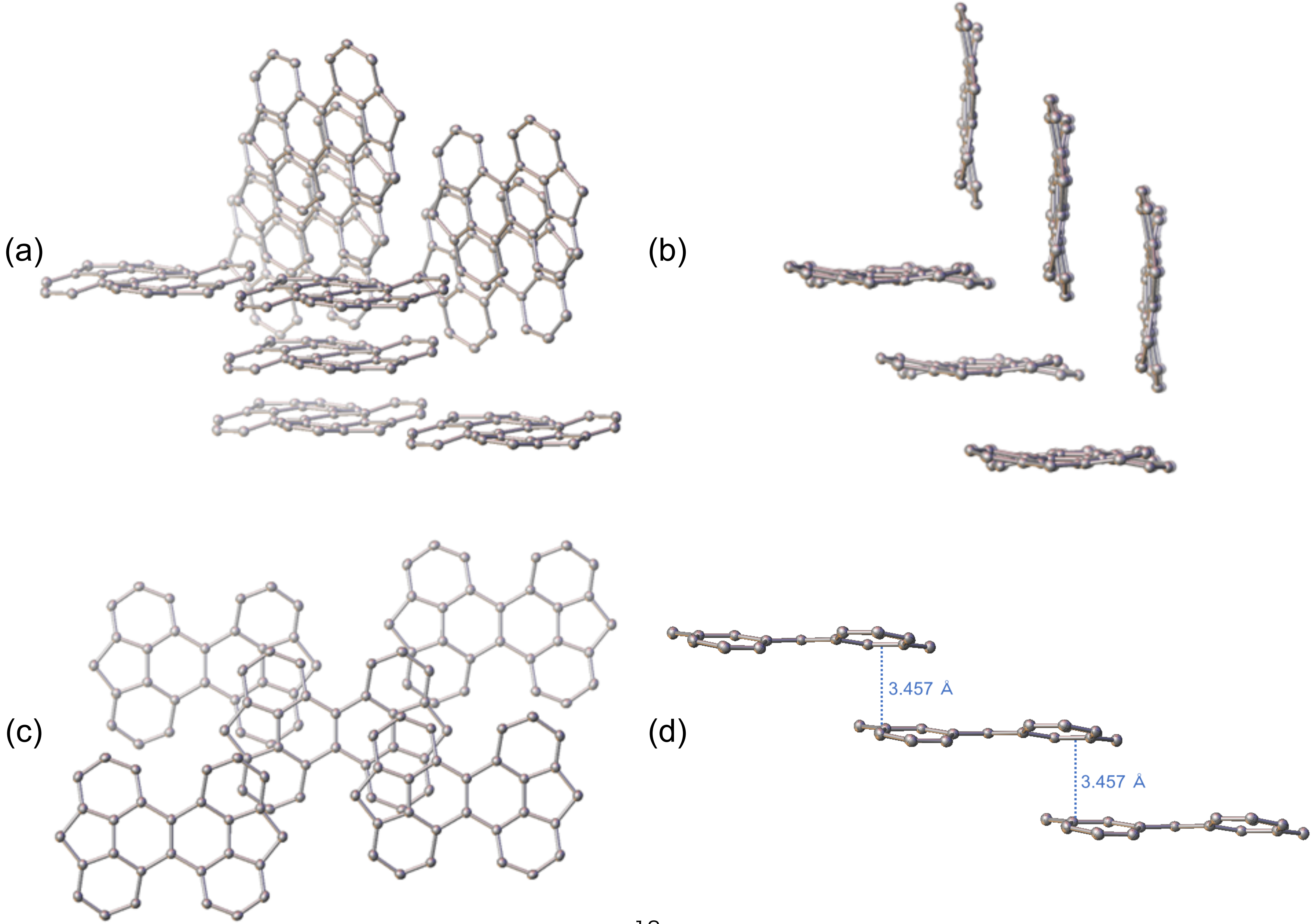




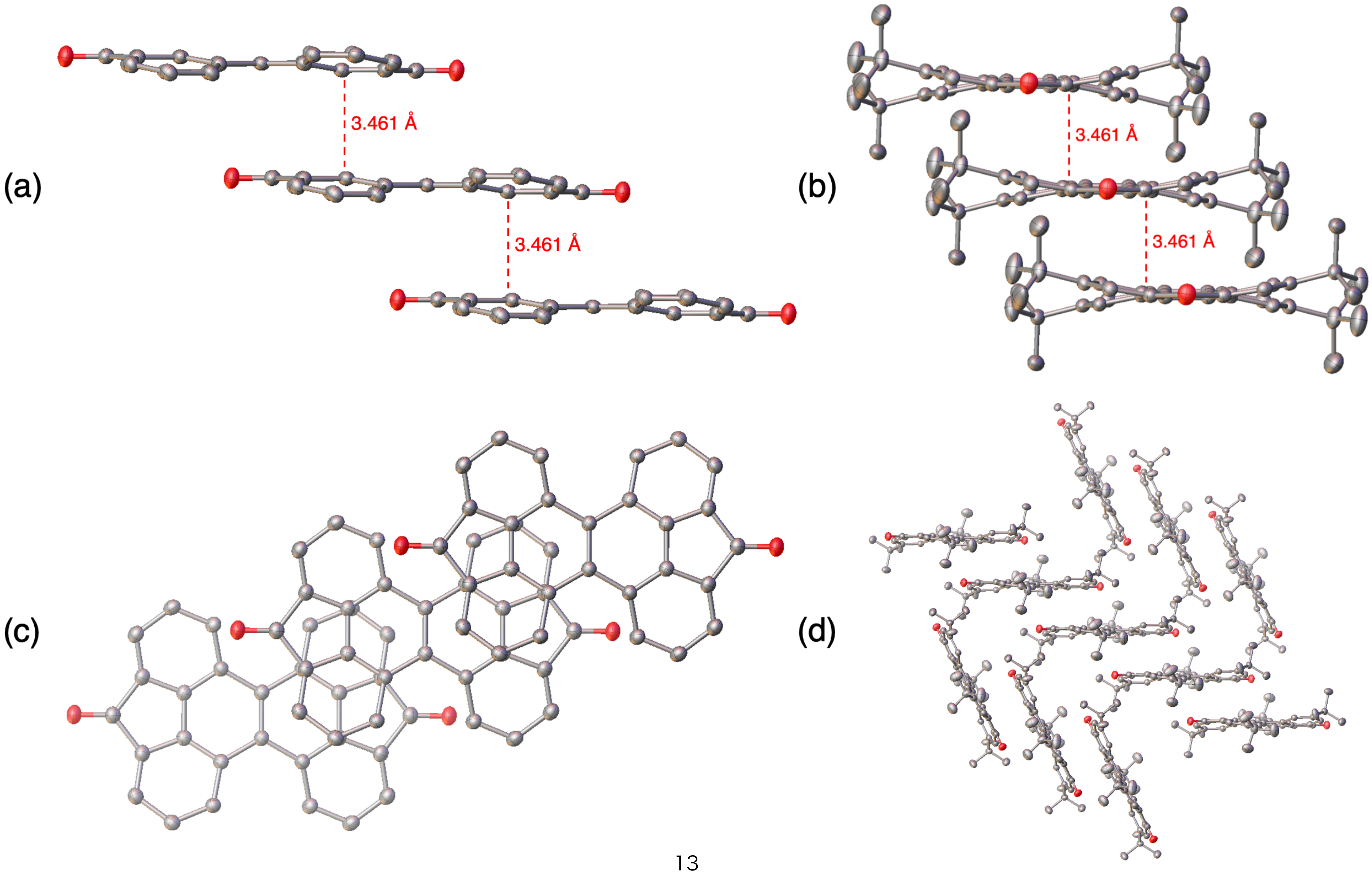


CCDC 2207864
Monoclinic, space group P 1 2/c 1
$R_1 = 0.0450$, $wR_2 = 0.1329$, GOF = 1.134
Torsion angle, 19.89(6)°
(Computational, 18.56°)

Packing views of an unsubstituted octacycle: The *unsubstituted* is totally and interestingly square to each array.

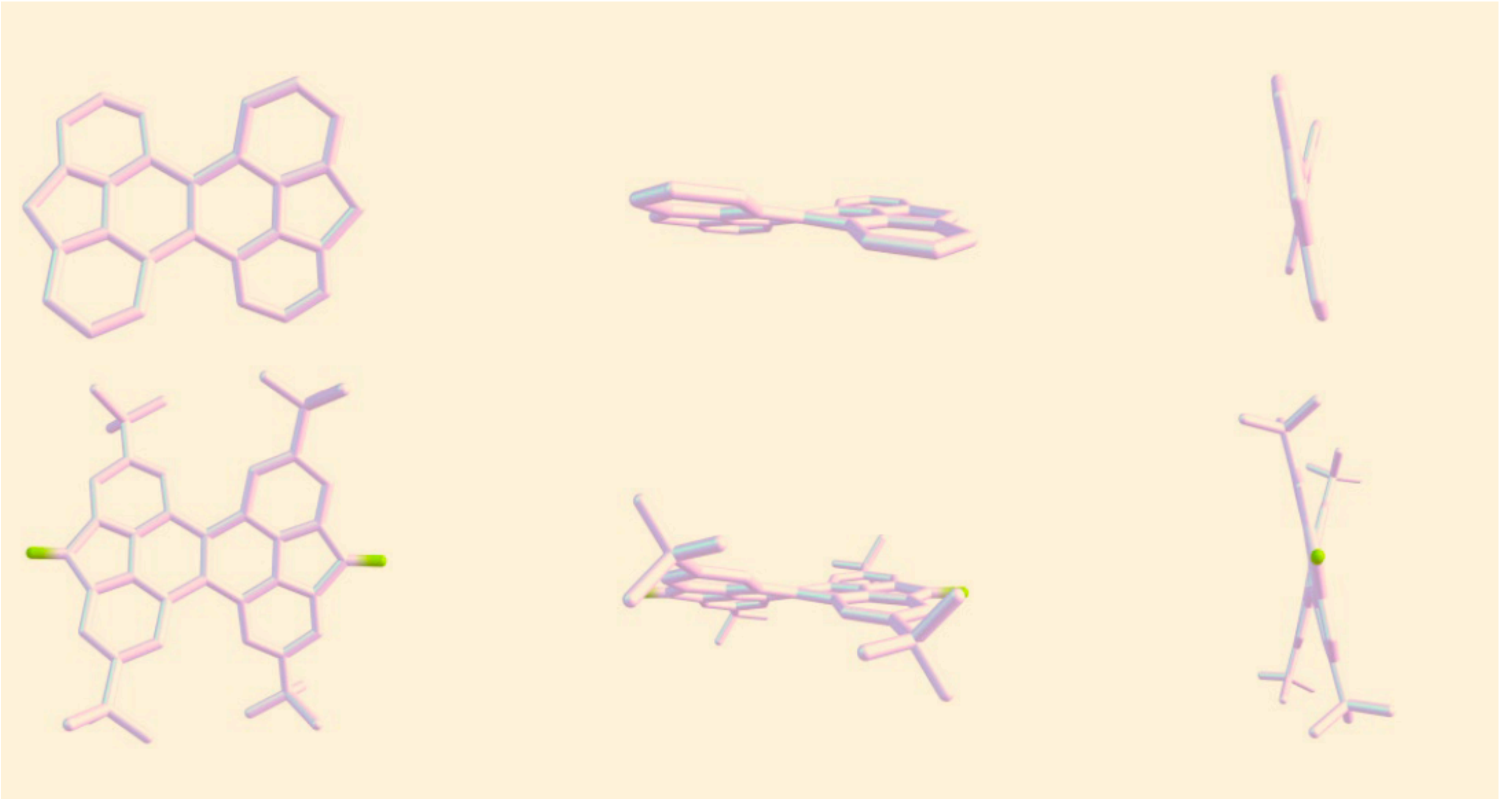


Packing views of the octacycle: The diketone is formed in a zig-zag. The interlayer distance is the mostly same as that of the unsubstituted.

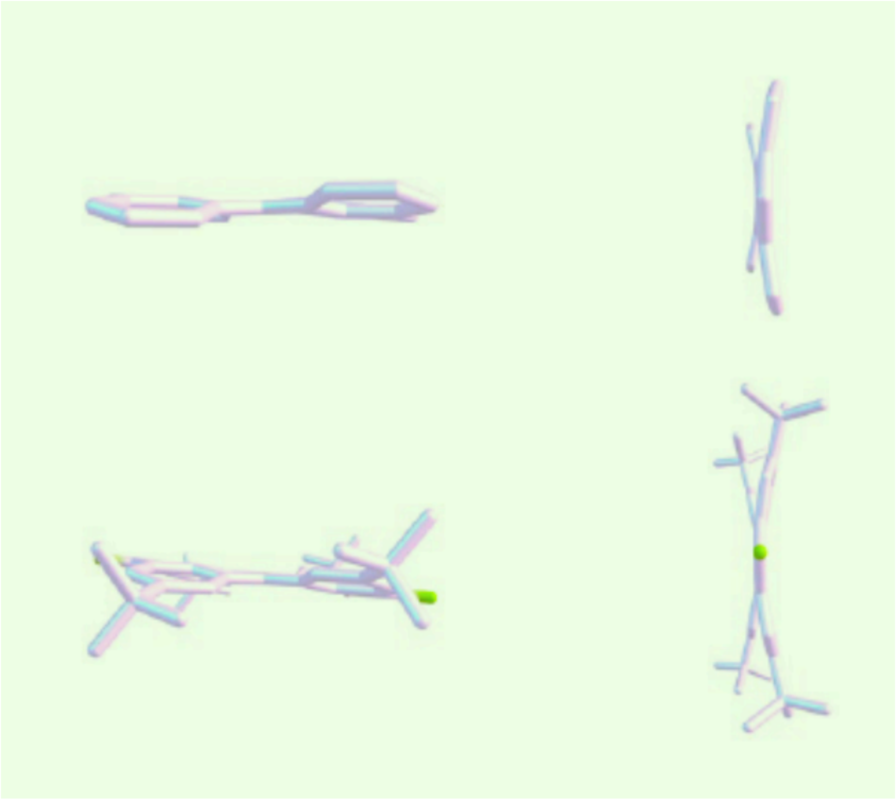


Energy difference between D_2 (twisted) and C_{2h} (saddled) symmetry of the DFT-optimized ones: The twisted form is 1.9 kcal/mol stable as compared to the saddle shape (a hydrogen bonding, 2 ~ 7 kcal/mol).

D_2 (Twisted)

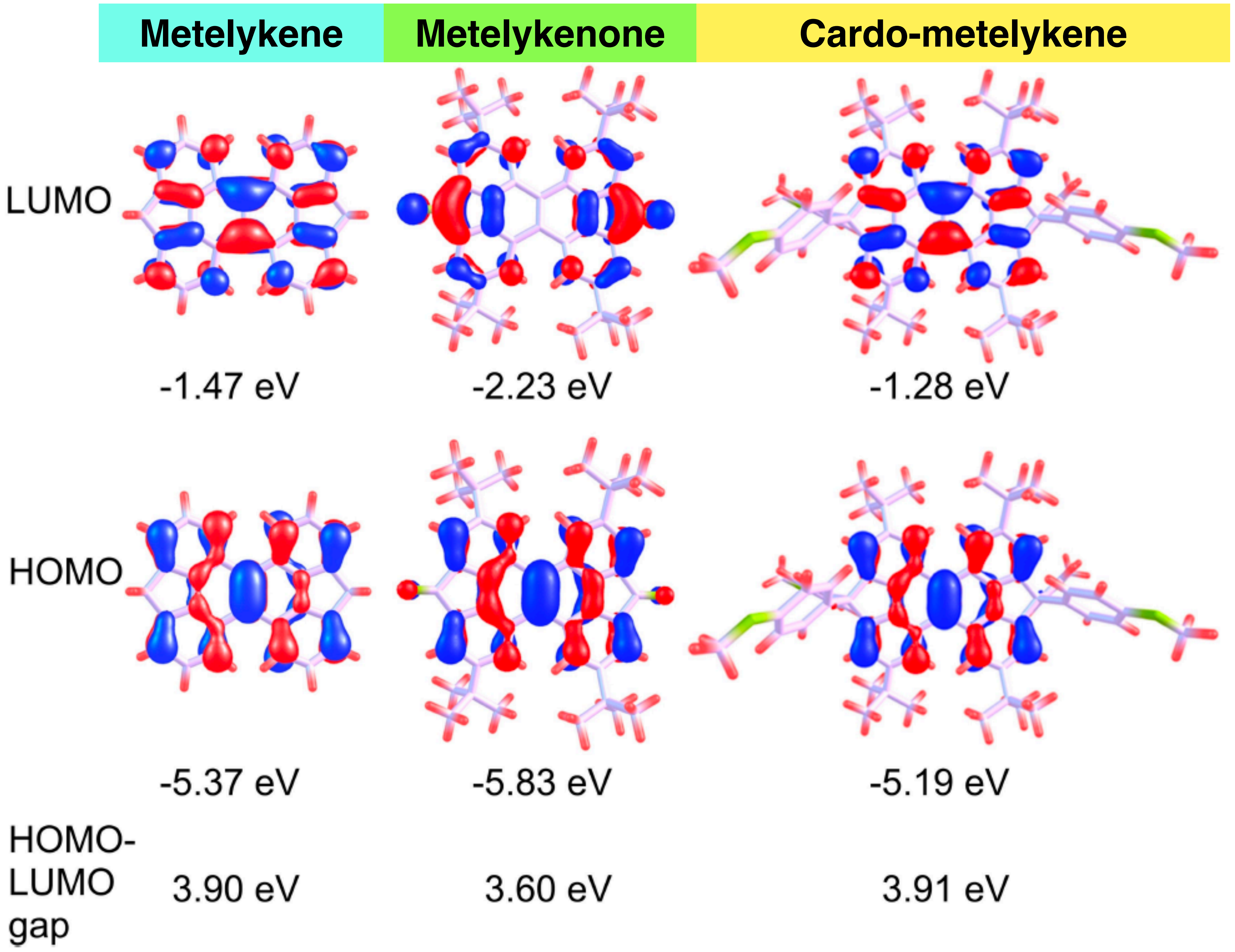


C_{2h} (Saddle)



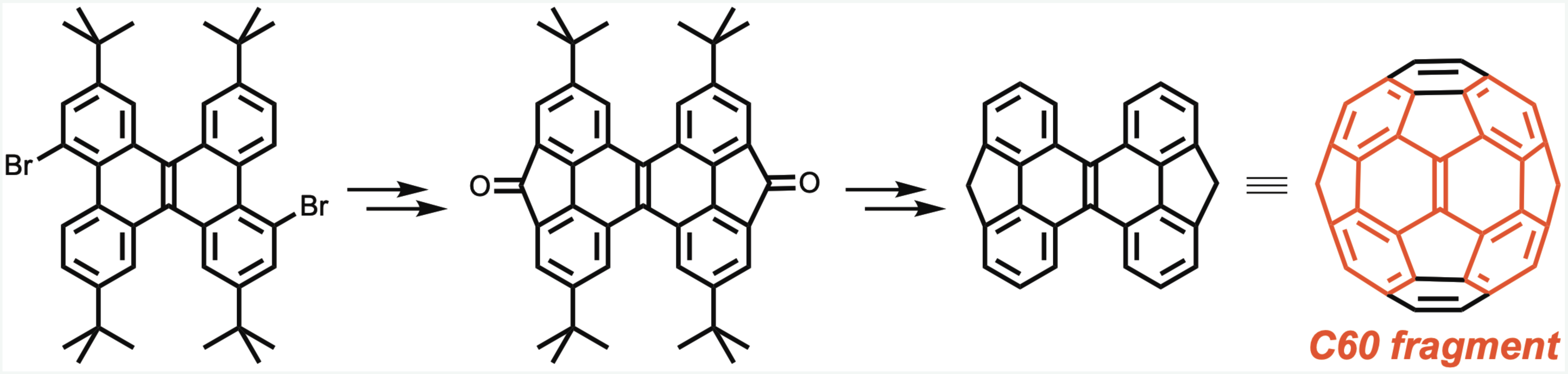
Point group	Energy difference [kcal/mol]	
	Metelykene	Metelykenone
D_2 (Twisted)	**-1.87**	**-1.94**
C_{2h} (Saddle)	**0**	**0**

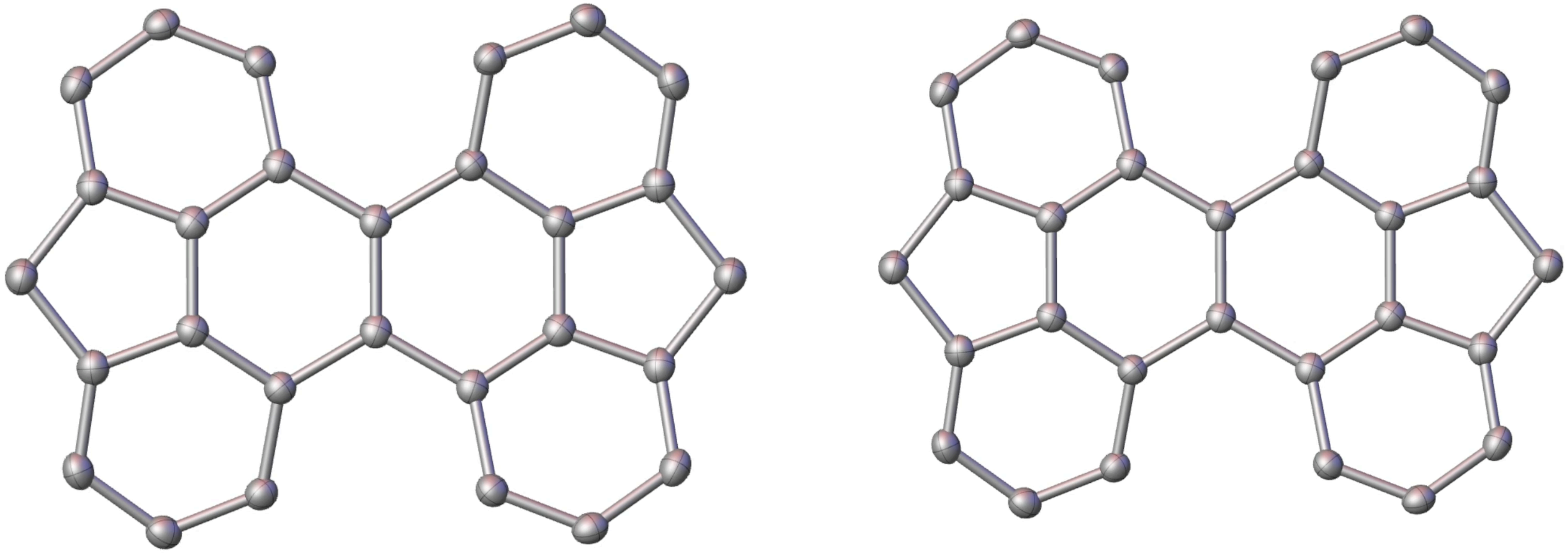
Frontier orbitals mappings and energies, calculated at the B3LYP/6-31G(d,p) level of theory.

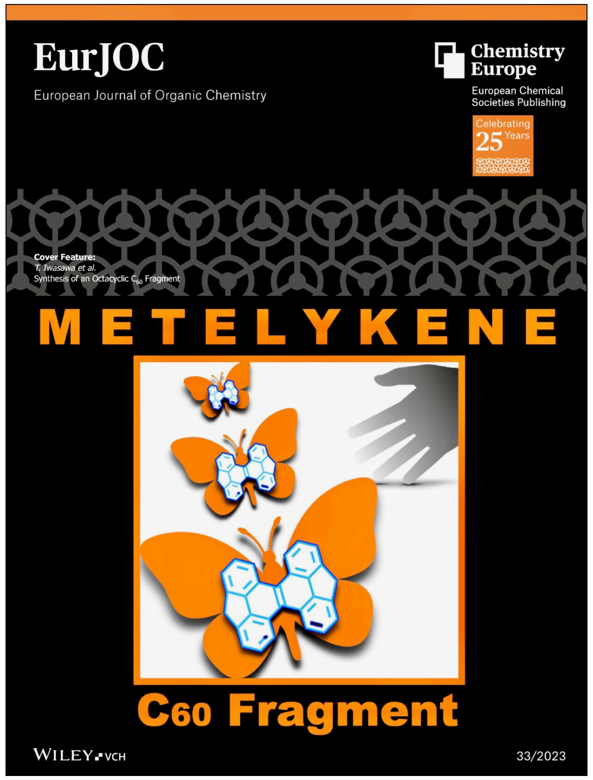


	Metelykene	**Metelykenone**	**Cardo-metelykene**
LUMO	-1.47 eV	-2.23 eV	-1.28 eV
HOMO	-5.37 eV	-5.83 eV	-5.19 eV
HOMO-LUMO gap	3.90 eV	3.60 eV	3.91 eV

Summary: The straightforward synthesis of C_{60} fragmentary octacycles has been achieved. The formation of two five-membered rings along with crystallographic analyses stands alone in the area of synthetic chemistry.







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