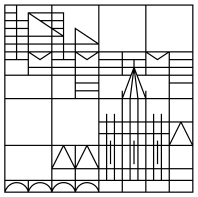
Universität Konstanz



Bent Pi-Systems

Johannes Bayer

21/03/2018

Introduction

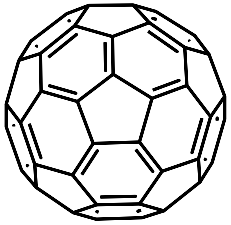
Euler‘s polyhedron formula for convex polyhedron:

$$V - E + F = 2$$

Polyhedron	Vertex	Edge	Face	V – E + F
cube	8	12	6	2
octahedron	6	12	8	2
dodecahedron	20	30	12	2
icosahedron	12	30	20	2
Fullerene-C_{60}	60	90	32	2

https://www.vismath.eu/de/blog/leonhard-euler/

Leonhard Euler
*1707 Basel
†1783 St. Petersburg

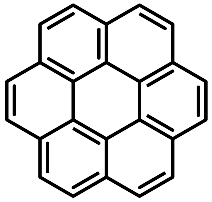


1

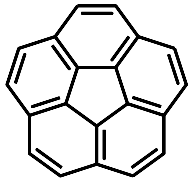
≙ 12 x  + 20 x 

Planar sheet of hexagons can be converted to a curved surface by inclusion of pentagons

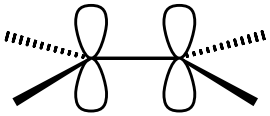
Introduction

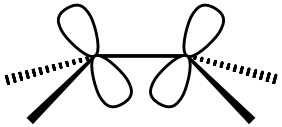


2
Coronene



3
Corannulene



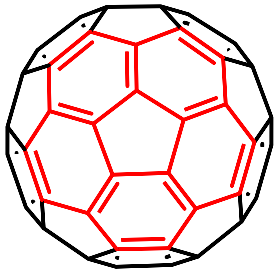


- Worse orbital overlap
- Increased s-character
- Lowered LUMO energy

Cho, H. Y; Scott L.T., *et Al. Beilstein J. Org. Chem.* **2014,** *10,* 956–968.

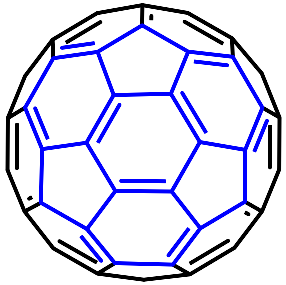
Bucky Bowls

The generic name of the bowl-shaped conjugated compounds corresponding to substructure of fullerenes and the cap structure of the carbon nanotube



1

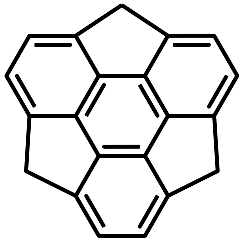
Fullerene



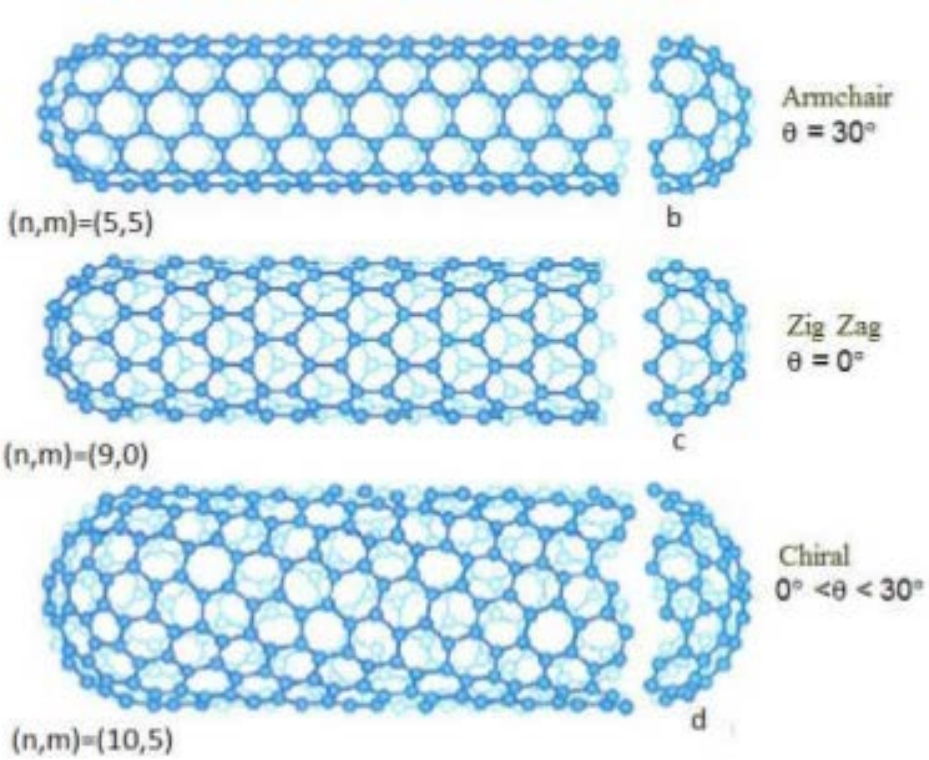
1

Fullerene

3
Corannulene



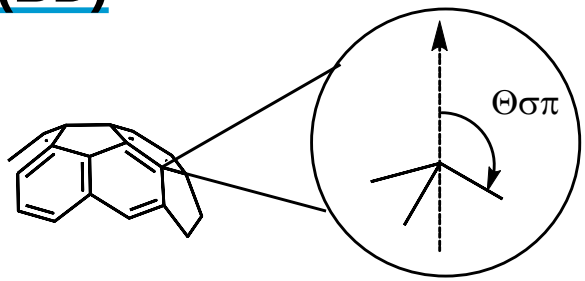
4
Sumanene

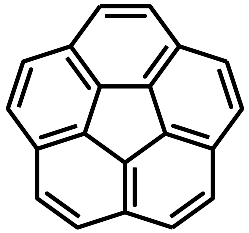


Choudhary, V. and Gupta A. (**2011**)*Carbon Nanotubes – Polymer Nanocomposites*. Rijeka, InTech.

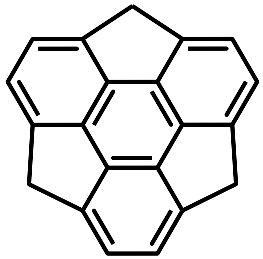
P-Orbital Axis Vector (POAV) and Bowl Depth (BD)

- POAV angle is defined as $\theta_{\sigma\pi} - 90$ °
- Indicates the extent of the pyramidalization

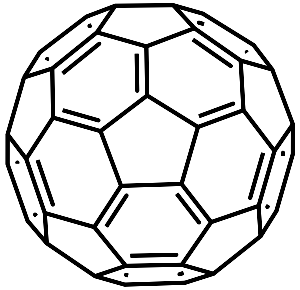




3



4

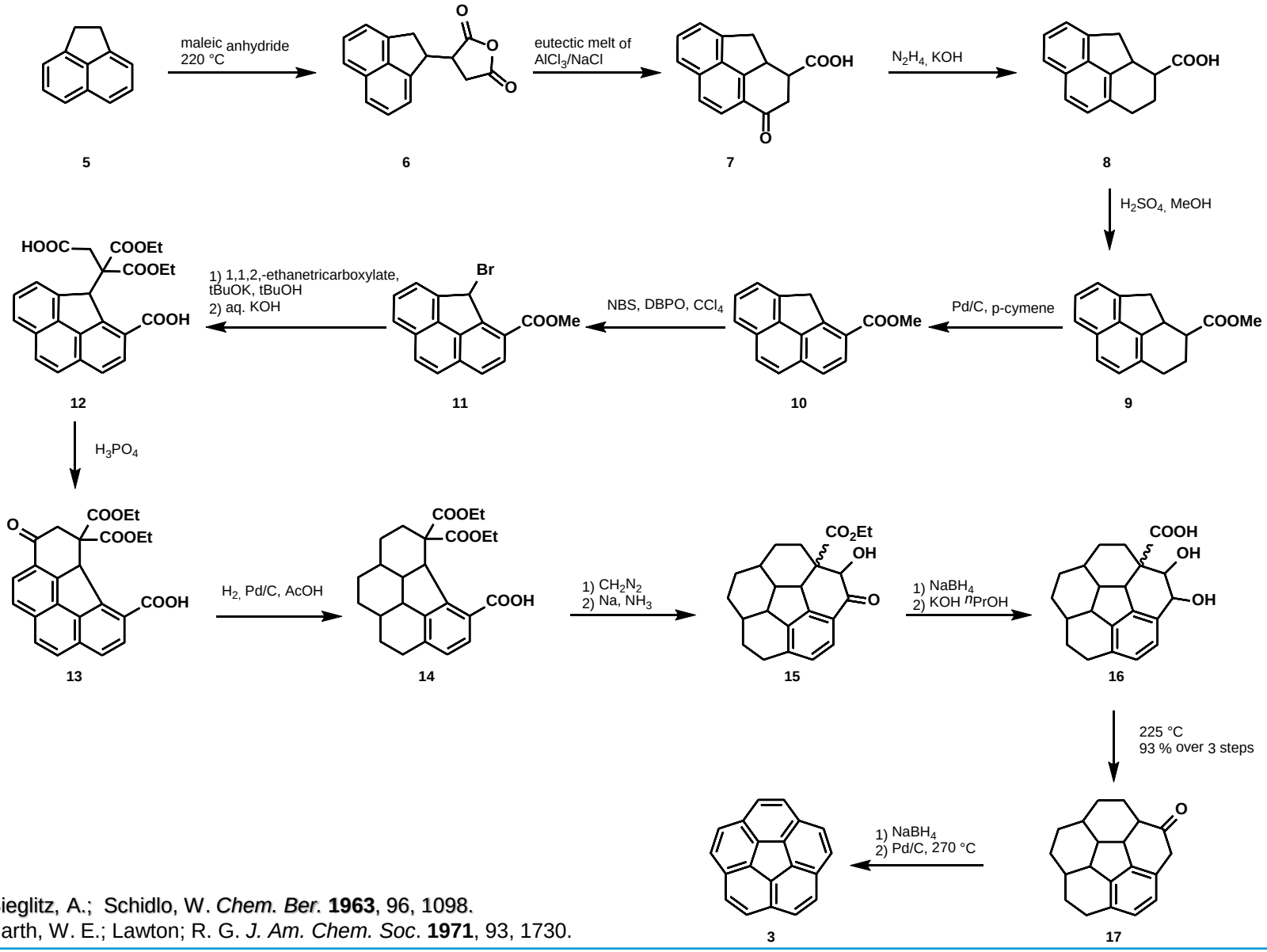


1

POAV:	8.4 °	8.7 °	11.6 °
BD:	0.89 Å	1.15 Å	

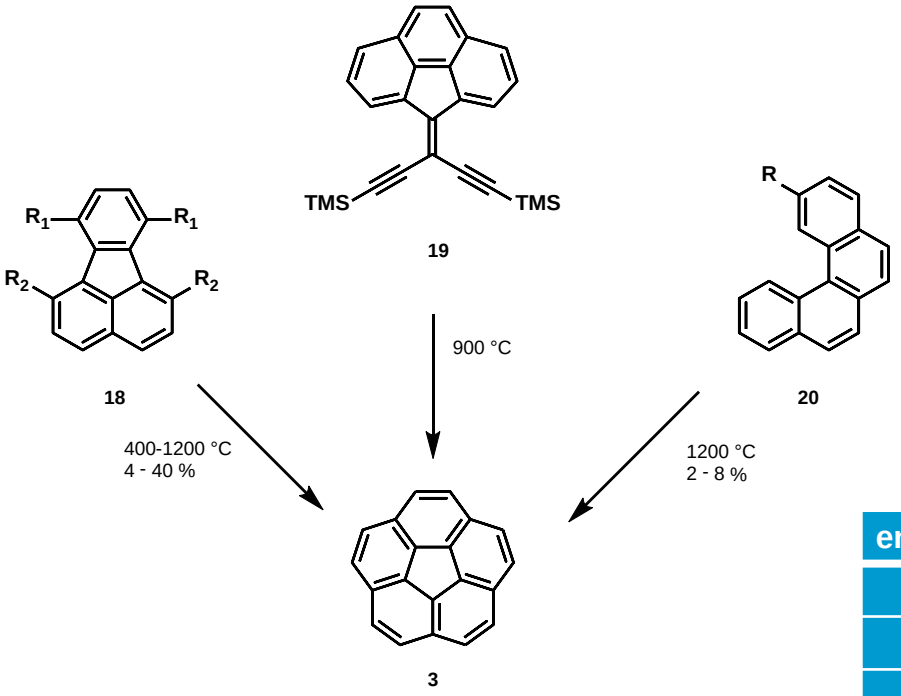
Andrzej, S. *et Al. J. Am. Chem. Soc.* **1996**, 118, 339-343.
Amaya, T. *et Al. Pure Appl. Chem.* **2010**, 82, 969-978.
Wu, Y.-T and Siegel, J.S. *Chem. Rev.* **2006**, 106, 4843-4867.

First Bucky Bowl Synthesis



Sieglitz, A.; Schidlo, W. *Chem. Ber.* **1963**, 96, 1098.
Barth, W. E.; Lawton; R. G. *J. Am. Chem. Soc.* **1971**, 93, 1730.

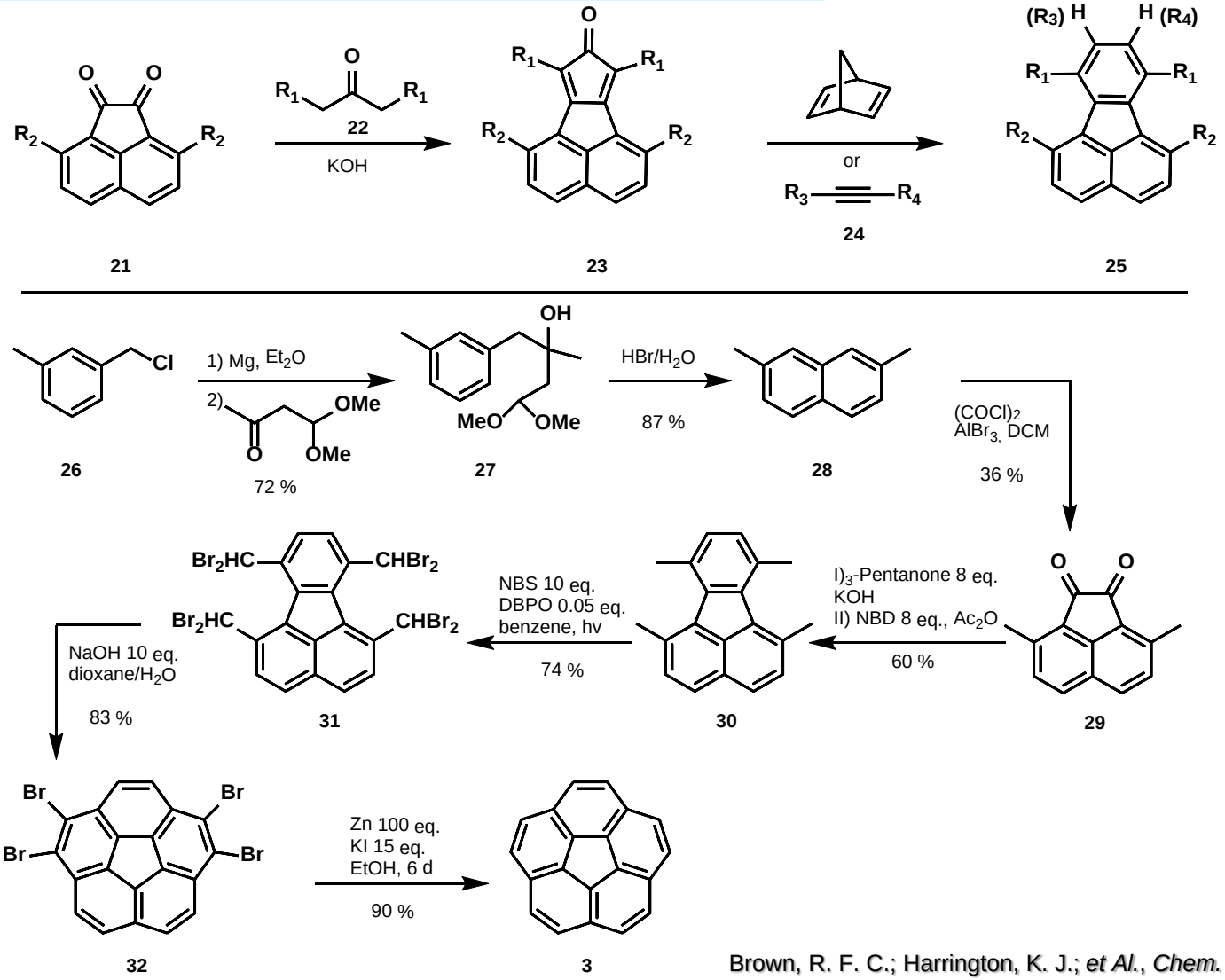
Access to Corannulene (3) by Pyrolysis



entry	S. M.	substitutents	temp. [°C]	yield [%]
1	18a	R_1: acetylene, R_2: H	1000	10
2	18b	R_1: TMSA, R_2: H	1000	36
3	18c	R_1: C(OTMS)=CH_2, R_2: H	1000	8
4	18d	R_1: CH=CHCl, R_2: H	1100	35 - 40
5	18e	R_1: CH=CBr_2, R_2: H	700-1000	4 - 23
6	18f	R_1 = R_2 : CH_2Br	1000	18
7	18g	Ar-CH_2-SO_2-CH_2-Ar	400	7
8	20a	R: vinyl	1200	2 - 4
9	20b	R: CCl=CH_2	1200	8
10	20c	R: CH=CHCl	1200	8
11	20d	R: C(OTMS)CH_2	1200	2 - 4

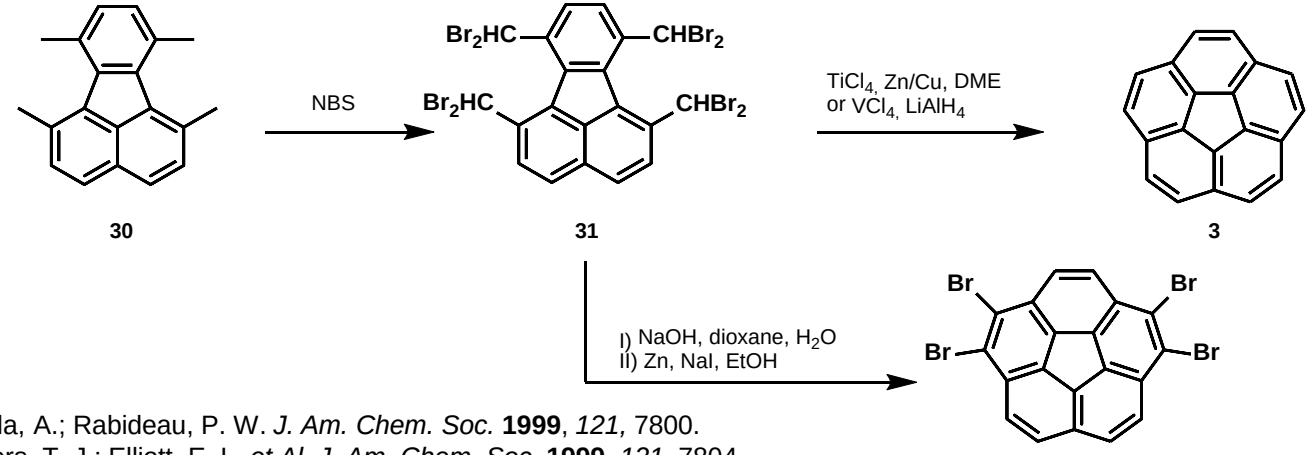
Scott, L.T., *et Al*., *J. Am. Chem. Soc.* **1991**, *113*, 7082.
Knölker, H.-J., *et Al., Tetrahedron Lett.* **1999**, *40*, 8075.
Liu, C.Z., *et Al., Tetrahedron Lett.* **1996**, *37*, 3437.
Cheng, P.-C., M.S. Thesis, University of Nevada, Reno, NV, **1992**.
Scott, L.T., *et Al., J. Am. Chem. Soc.* **1997**, *119,* 10963.
Scott, L.T., *et Al., J. Am. Chem. Soc.* **1992**, *114*, 1920.
Borchardt, A.; Siegel, J. S., *et Al., J. Am. Chem. Soc.* **1992**, *114*,192.
G. Mehta; G. Panda, *Tetrahedron Lett.* **1997**, *38*, 2145.

Synthesis of Fluoranthene Derivatives (25)



Brown, R. F. C.; Harrington, K. J.; *et Al.*, *Chem. Commun.* **1974**, 123.
Brown, R. F. C.; Eastwood, F.W.; *et Al.*, *J. Chem.* **1977**, *30*, 1757.
Brown, R. F. C.; Eastwood, F.W. *et Al.*, *J. Chem.* **1978**, *31*, 579.
Sygula, A.; Rabideau, P. W. *Tetrahedron* **2001**, 57, 3637.

Preparation of Corannulene Derivatives by Solution methods



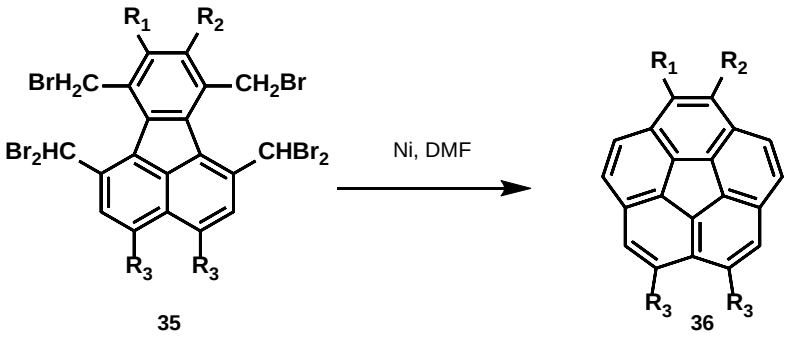
30 31 3 32

Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121,* 7800.
Seiders, T. J.; Elliott, E. L. *et Al. J. Am. Chem. Soc.* **1999**, *121*, 7804.
Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122,* 6323.

33 34

entry	S.M.	R	yield [%]
1	33a	R_1 = Me, R_2 = R_3 = H	24
2	33b	R_1 = H, R_2 = Me, R_3 = H	48
3	33c	R_1 = H, R_2 = Me, R_3 = Cl	45
4	33d	R_1 = R_2 = Me, R_3 = H	6

Seiders, T. J.; Elliott, E. L. *et Al. J. Am. Chem. Soc.* **1999**, *121*, 7804.

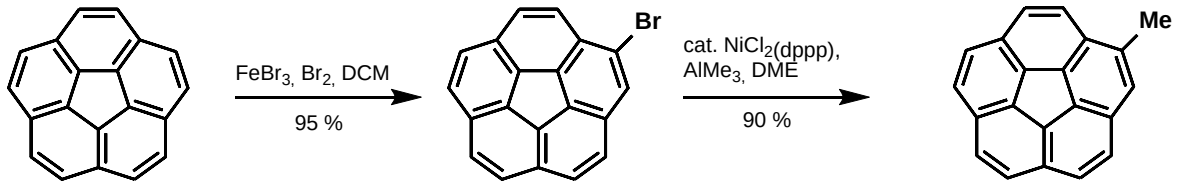


35 36

entry	S.M.	R	yield [%]
1	35a	R_1 = R_2 = CO_2Me, R_3 = H	60
2	35b	R_1 = R_2 = CO_2Me, R_3 = Cl	49
3	35c	R_1 = Ph, R_2 CO_2Me, R_3 = Cl	51

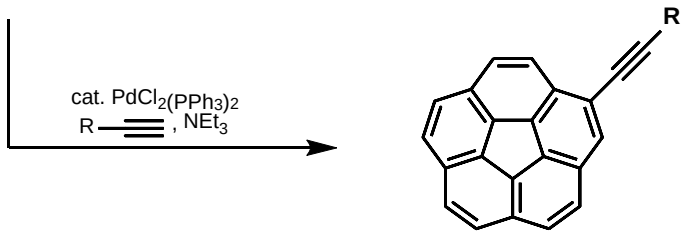
Wu, Y.-T.; Hayama, T., *et Al.* J. *Am. Chem. Soc.* **2006**, *128*, 6870.
Sygula, A.; Karlen, S., *et Al.* Org. *Lett.* **2002**, *4*, 3135.

Monosubstituted Corannulene Derivatives



3 37 38

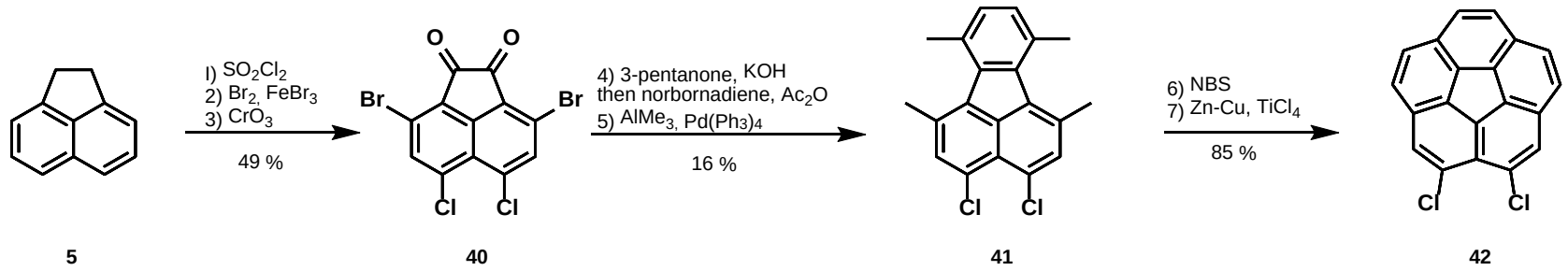
entry	product	R	yield [%]
1	39a	TMS	97
2	39b	Ph	67
3	39c	H	quant.
4	39d	corannulenyl	45
5	39e	F_5Ph	57



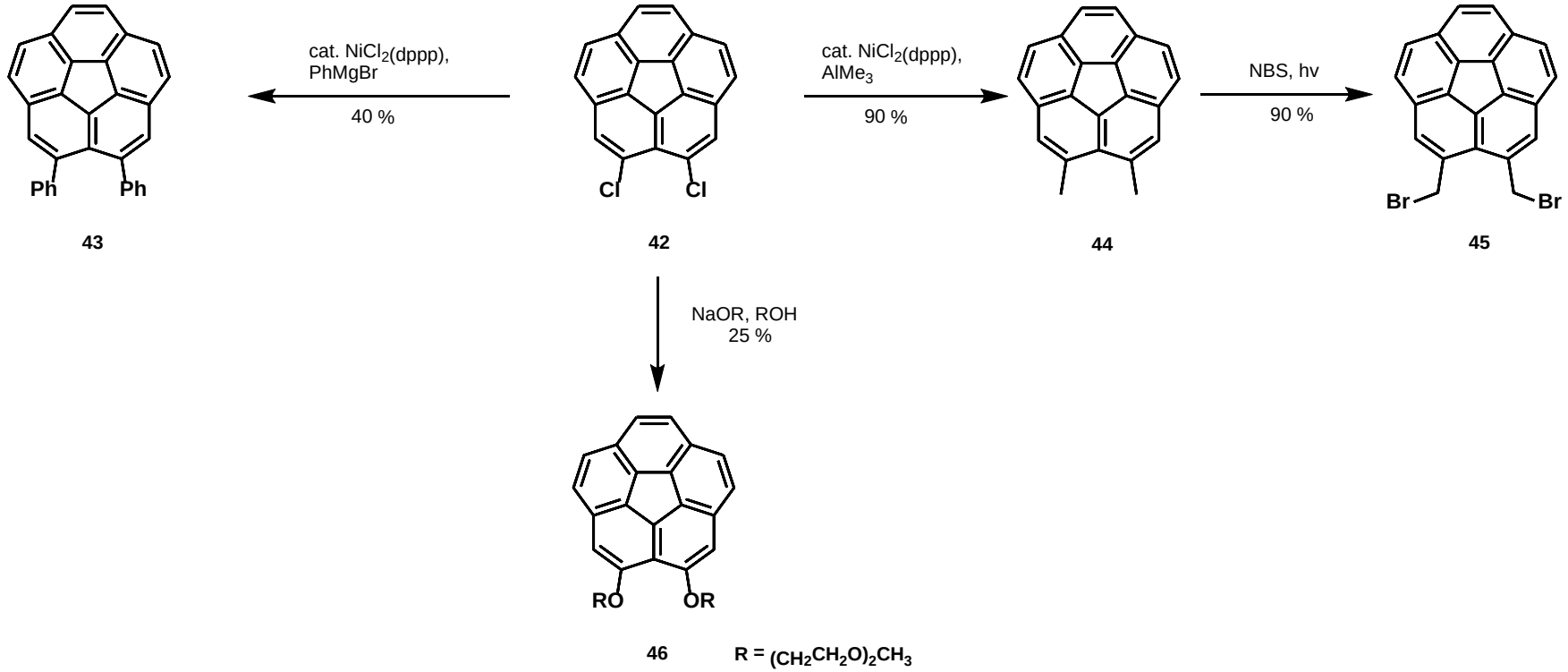
39

Jones, C. S.; Elliott, E.; Siegel, J. S. *Synlett.* **2004**, 187.

2,3-Disubstituted Corannulenes



5 **40** **41** **42**

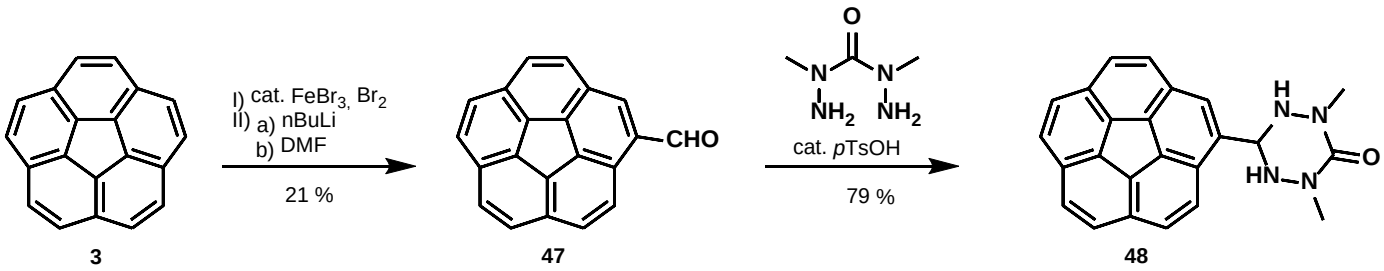


43 **42** **44** **45**

46 **R = $(CH_2CH_2O)_2CH_3$**

T. J. Seiders, J. S. Siegel *et Al.*, *J. Am. Chem. Soc.* **2001**, *123*, 517.

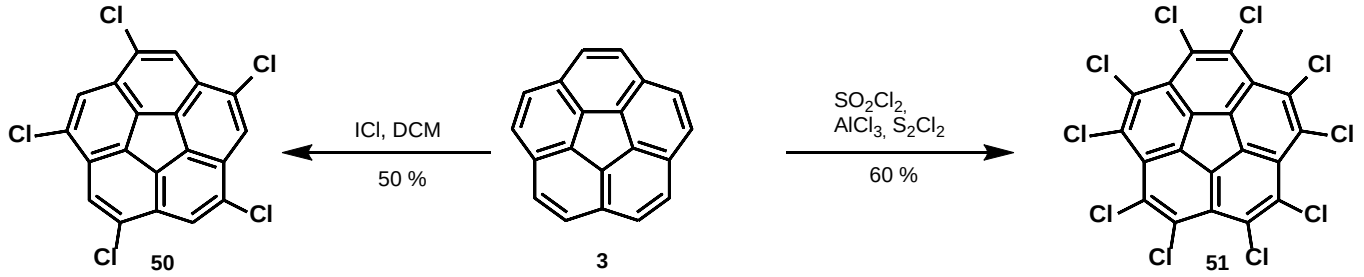
Stable Neutral Corannulene Radical



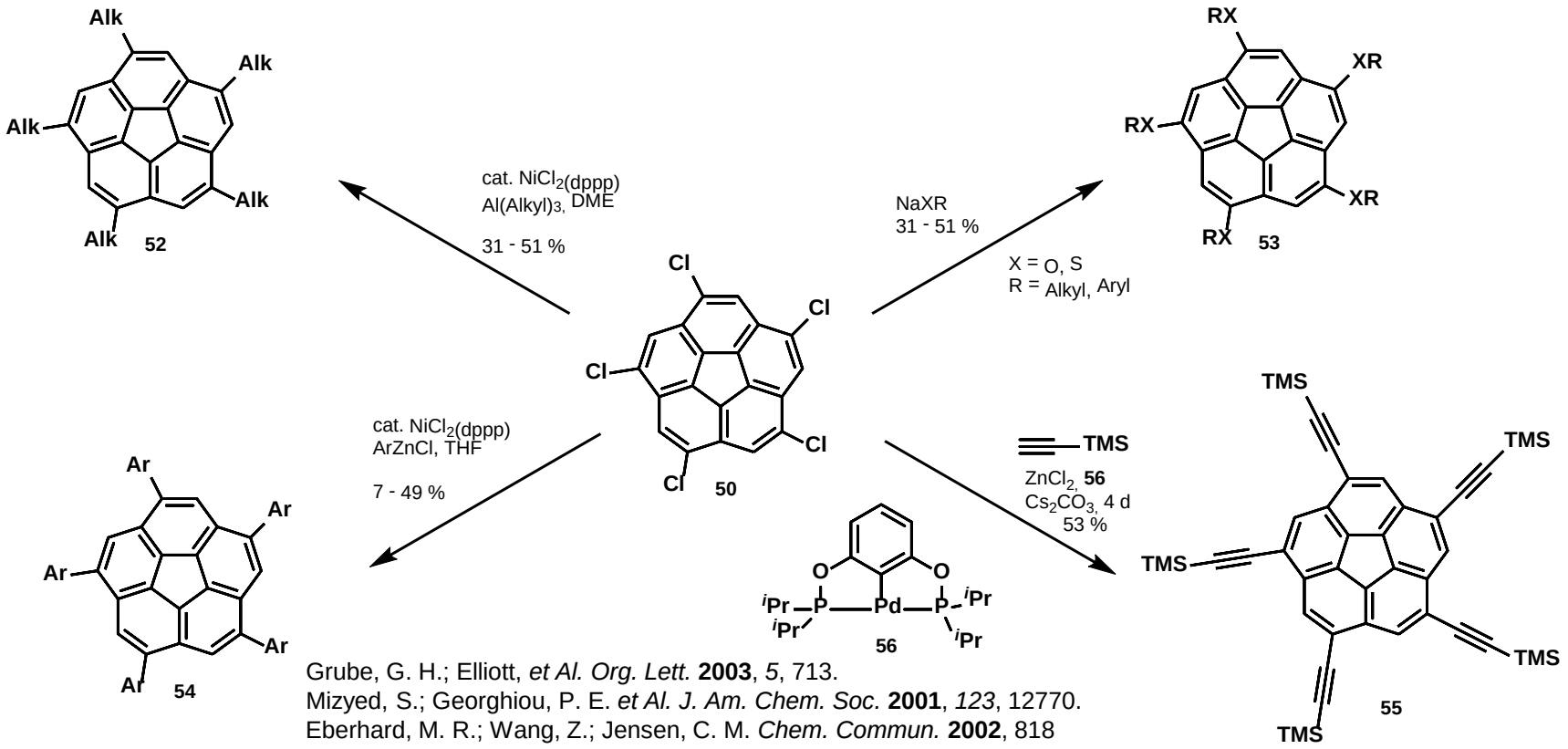
3 **47** **48** **49**

Morita, Y.; Nishida, S. *Et Al. Org. Lett.* **2004**, *6,* 1397.

Highly Substituted Corannulenes

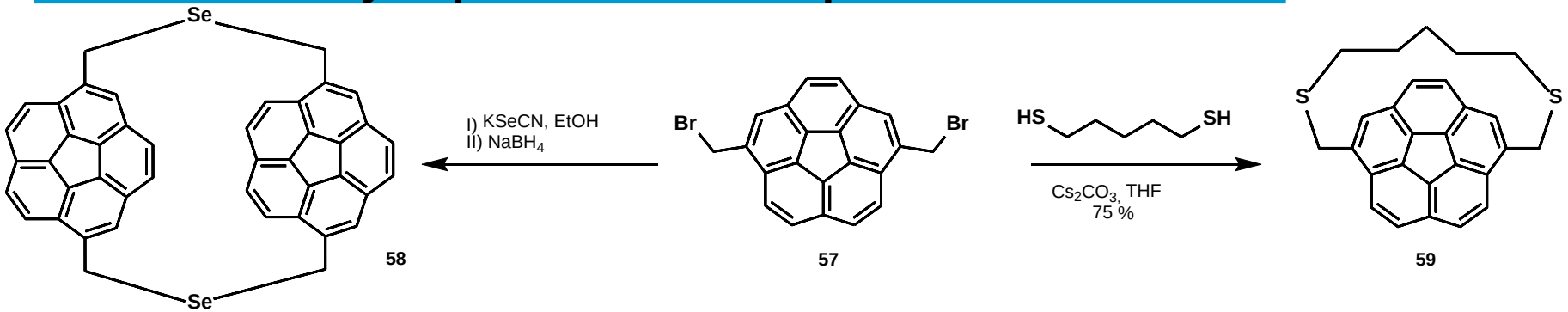


Huang, R.; Huang, W.; Wang, Y.; Tang, Z.; Zheng, L. *J. Am. Chem.Soc.* **1997**, *119*, 5954.
Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291.

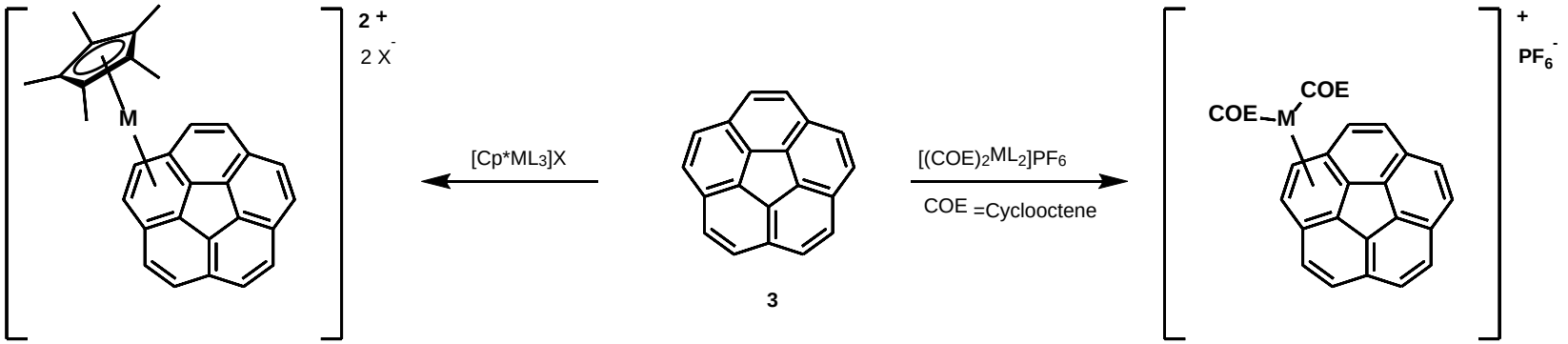


Grube, G. H.; Elliott, *et Al. Org. Lett.* **2003**, *5*, 713.
Mizyed, S.; Georghiou, P. E. *et Al. J. Am. Chem. Soc.* **2001**, *123*, 12770.
Eberhard, M. R.; Wang, Z.; Jensen, C. M. *Chem. Commun.* **2002**, 818

Corannulene Cyclophanes and Complexed Corannulenes



Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754.
Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *Tetrahedron* **2001**, *57*, 3737.

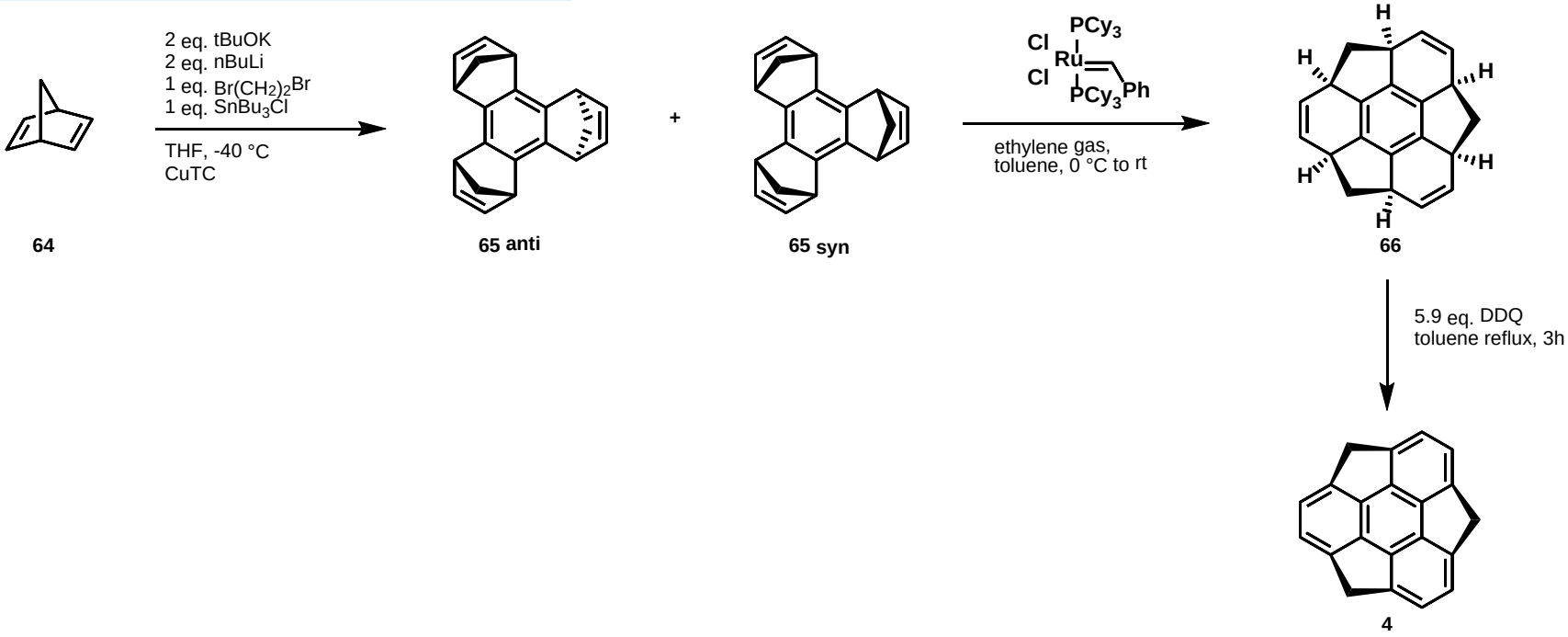


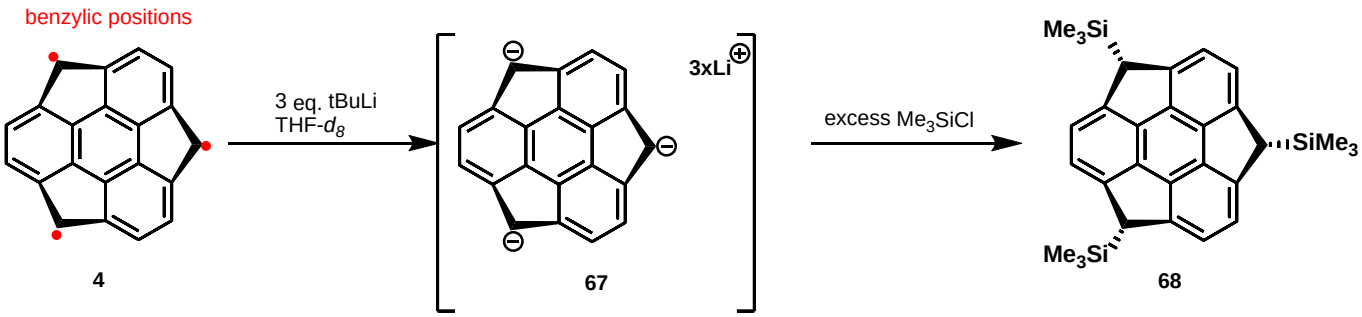
62a (M = Ru, L = MeCN, X = OTf)
62b (M = Ir, L = acetone, X = BF_4)

Seiders, T. J.; Siegel, J. S. *et Al. J. Am. Chem. Soc.* **1997**, *119*, 4781.
Alvarez, C. M.; Rabideau, P. W. *Et Al. Organometallics* **2003**, *22*, 624.
Siegel, J. S.; Baldridge, K. K. *et Al. J. Am. Chem. Soc.* **2006**, *128*, 10644.

63a (M = Rh)
63b (M = Ir)

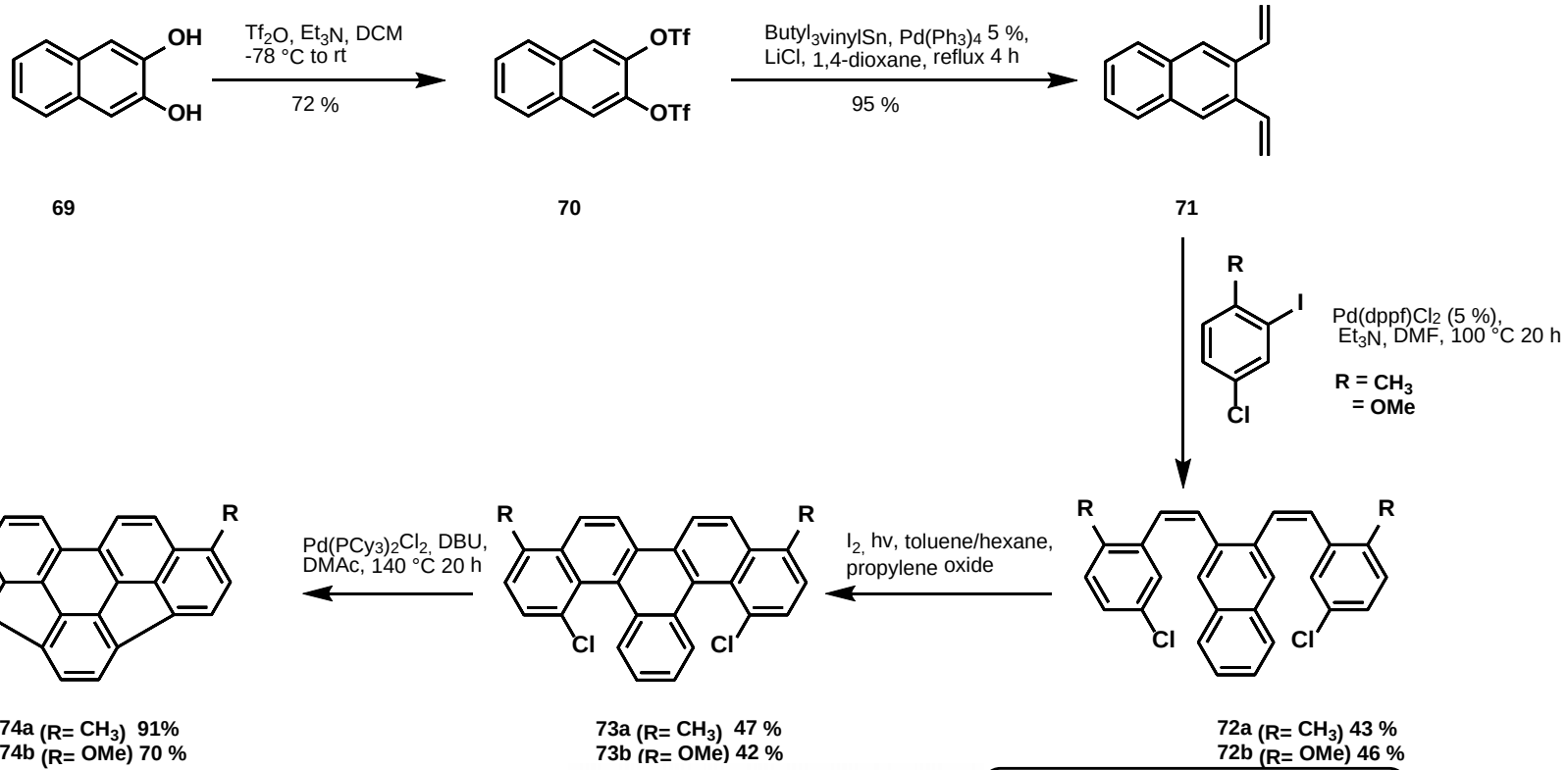
Synthesis of Sumanene (4)



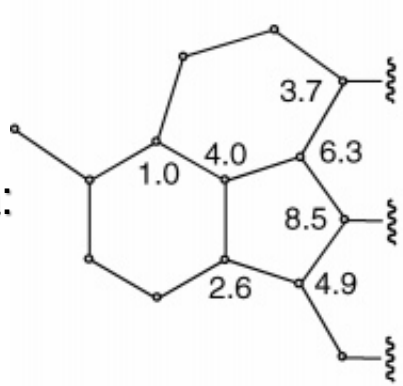


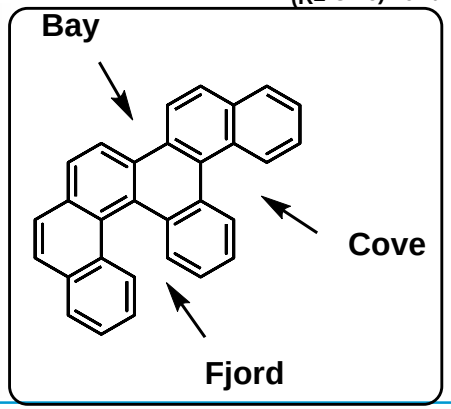
Sakurai, H; Daiko, T. *et Al. J. Am. Chem. Soc.* **2005**, 127, 11580-11581.

Synthesis of Indacenopicene



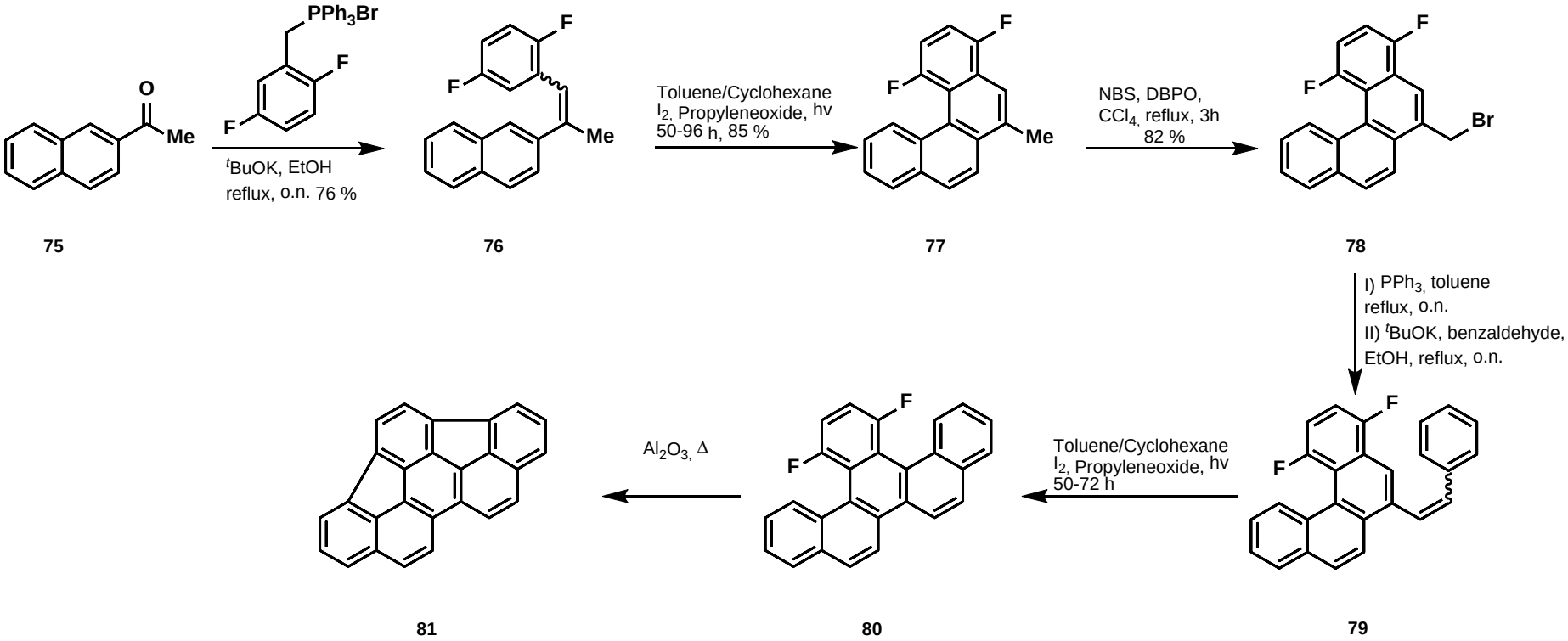
POAV pyramidalization of 74a:





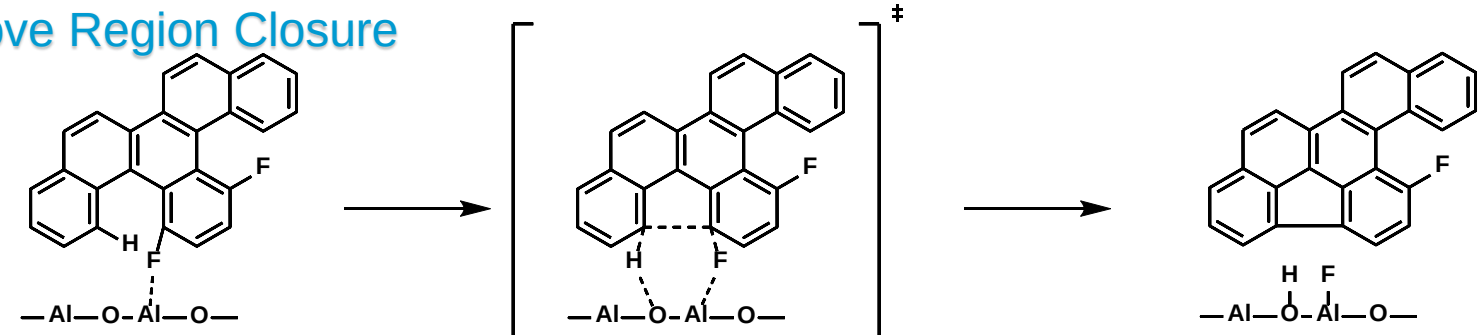
Wang, L.; Shevlin, P. B., *Org. Lett.,* **2000**, 2, 23.

Synthesis of Indacenopicene



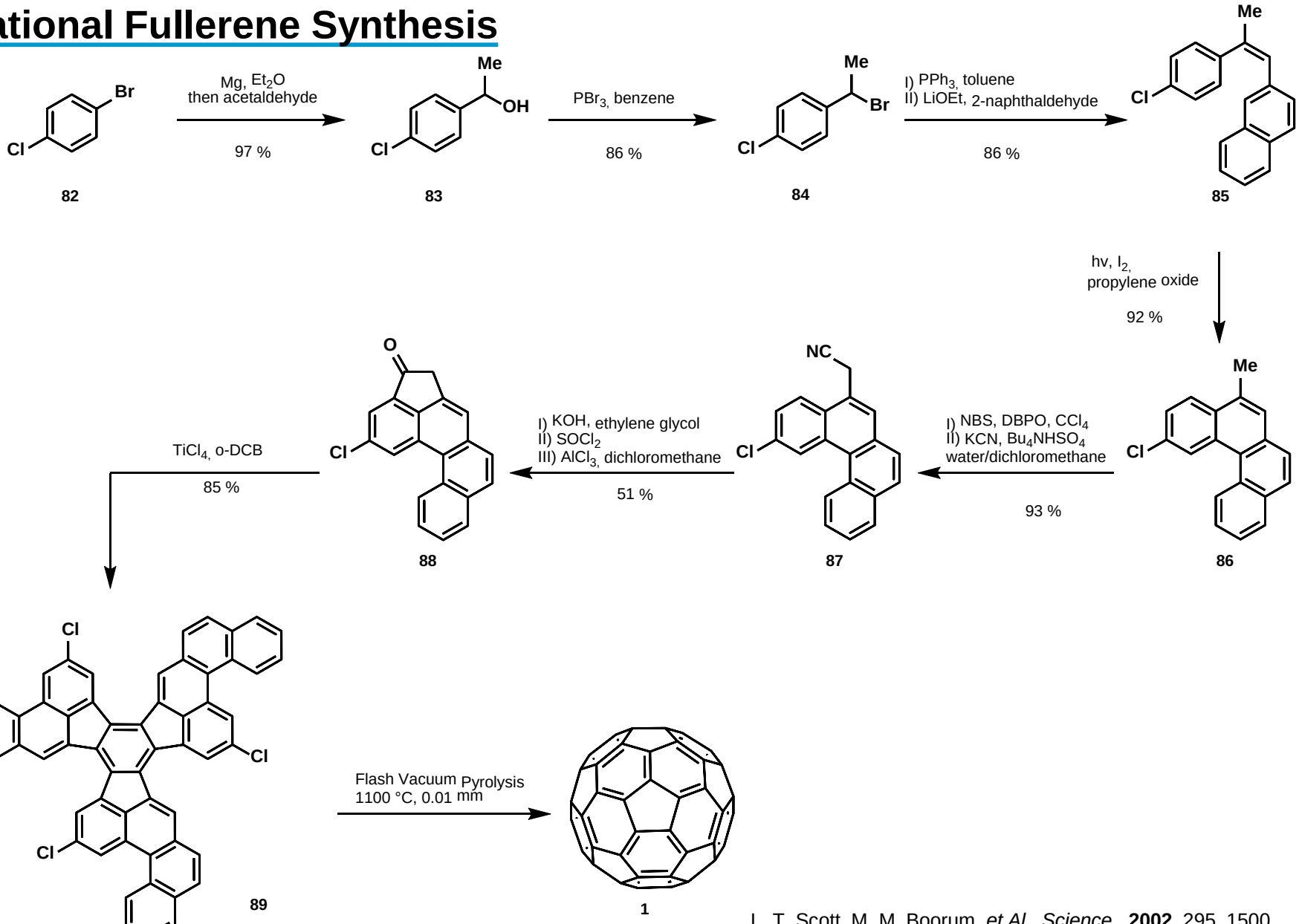
75 **76** **77** **78** **79** **80** **81**

Cove Region Closure



Amsharov, K. Y.; Kabdulov, M. A., *et Al. Angew. Chem.*, **2012**, 124, 4672

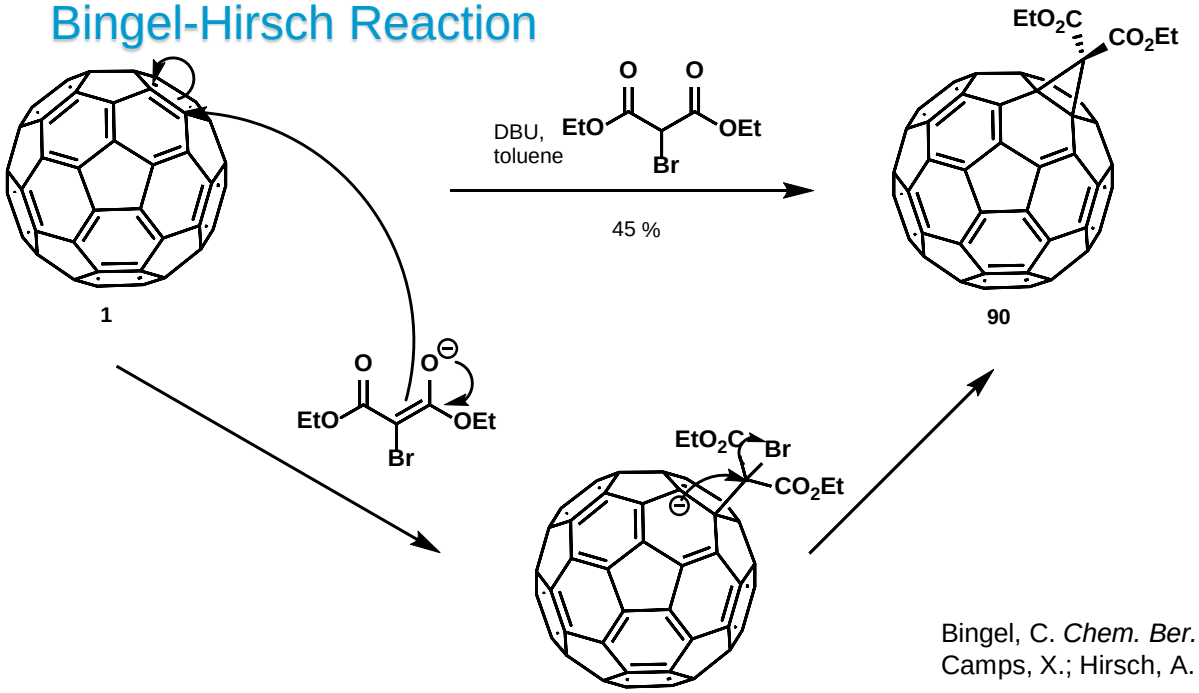
Rational Fullerene Synthesis



L. T. Scott, M. M. Boorum, *et Al*., *Science.,* **2002**, 295, 1500

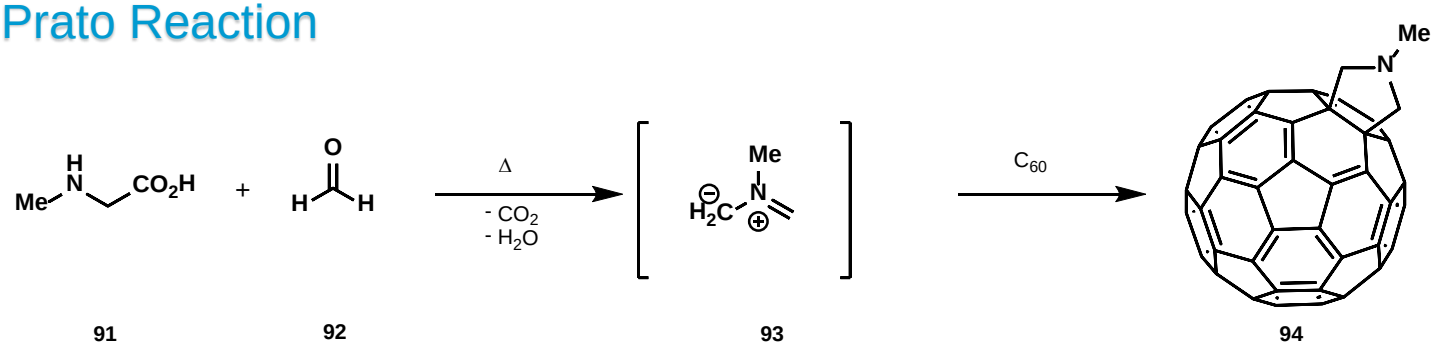
Covalent Functionalization of C60-Fullerene

Bingel-Hirsch Reaction



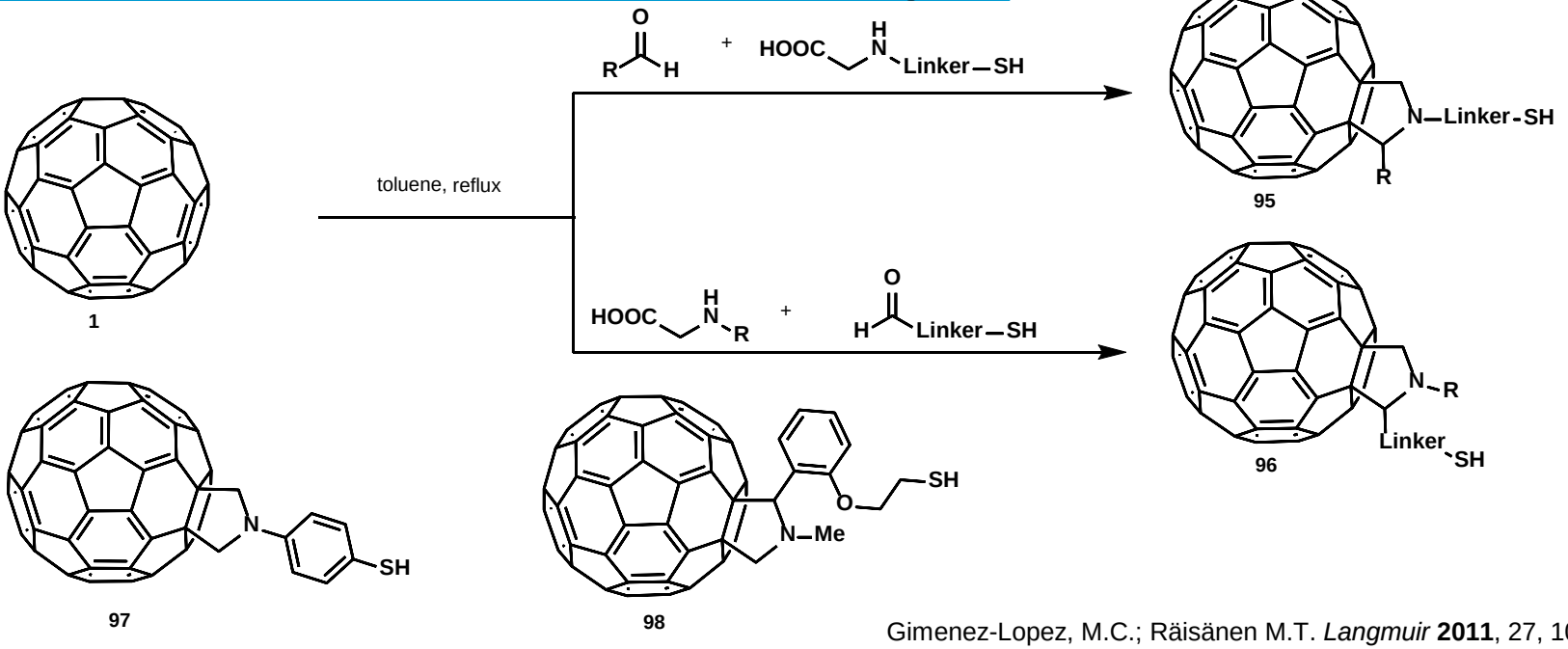
Bingel, C. *Chem. Ber.* **1993,** *126,* 1957–1959.
Camps, X.; Hirsch, A. *J. Chem. Soc., Perkin Trans. 1* **1997,** 1595–1596.

Prato Reaction

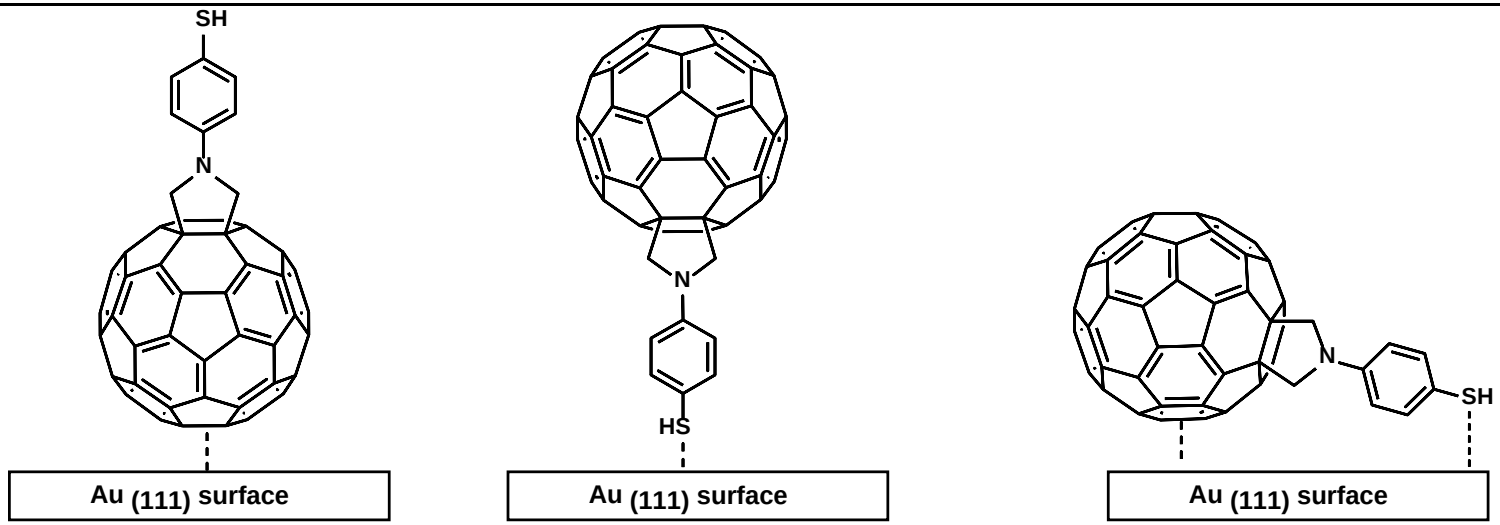


Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993,** *115,* 9798–9799.
Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998,** *31,* 519–526.

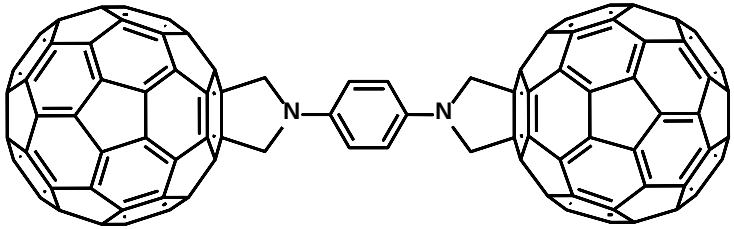
Applications: Self-Assembled Monolayers



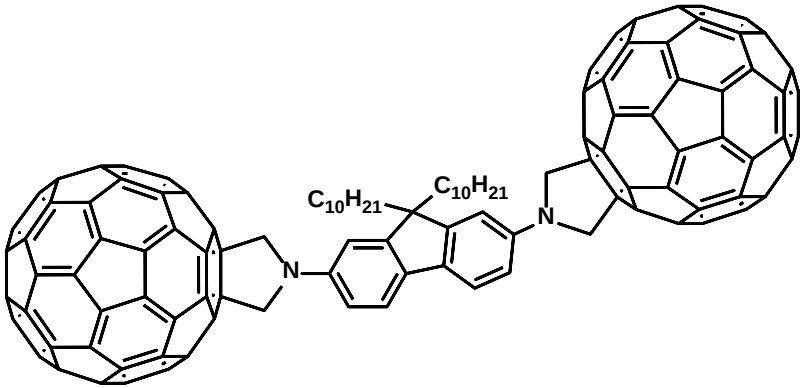
Gimenez-Lopez, M.C.; Räisänen M.T. *Langmuir* **2011**, 27, 10977–10985



Applications: Molecular Wires



99



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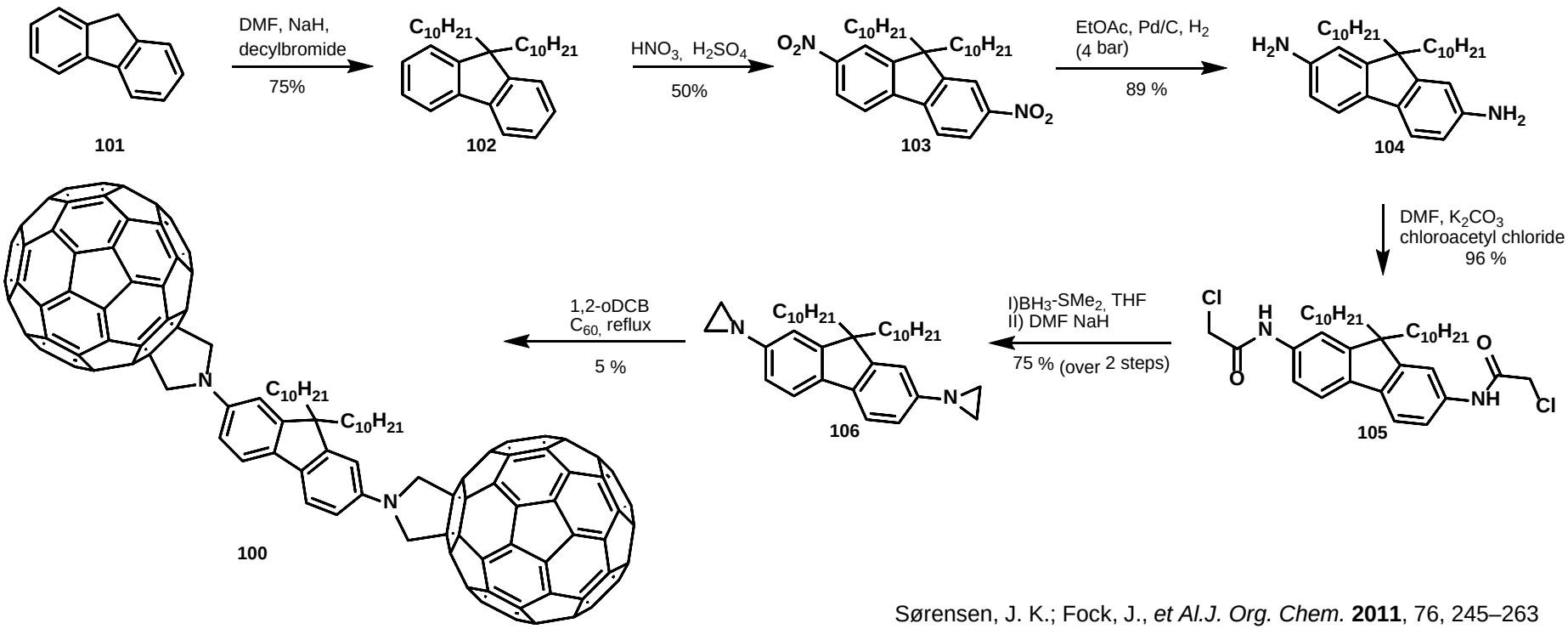

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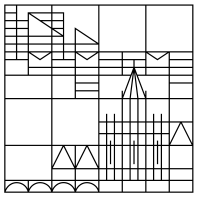

Thank you for your Attention!