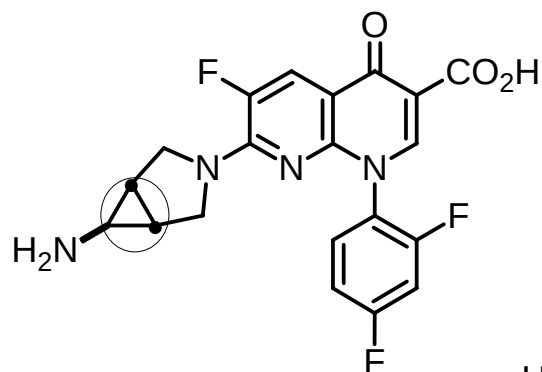
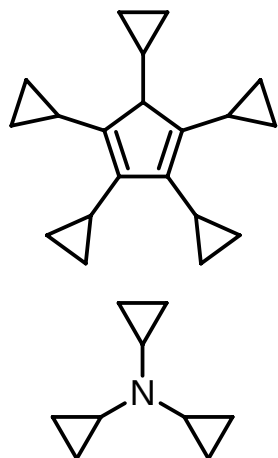
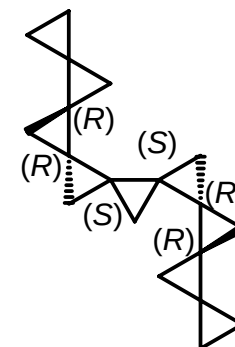
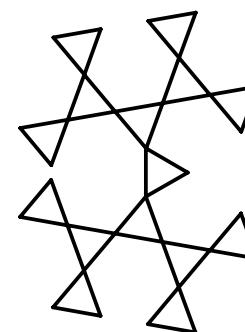
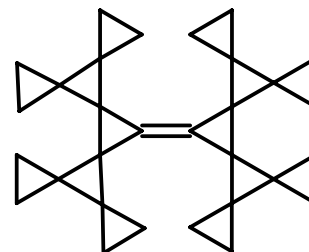
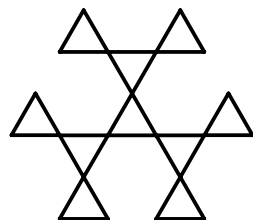
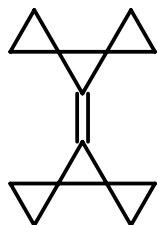
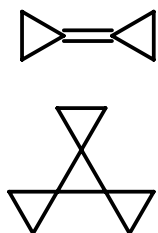


Small Rings: A World of Wonders and Benefits

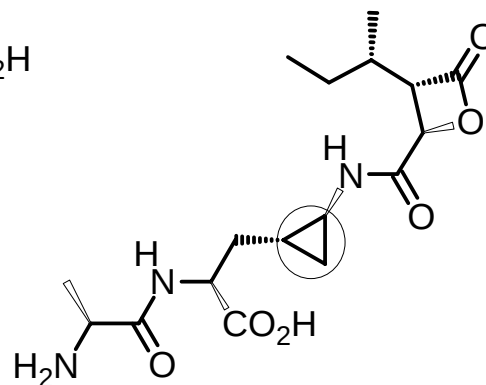
Unusual Architectures

Armin de Meijere

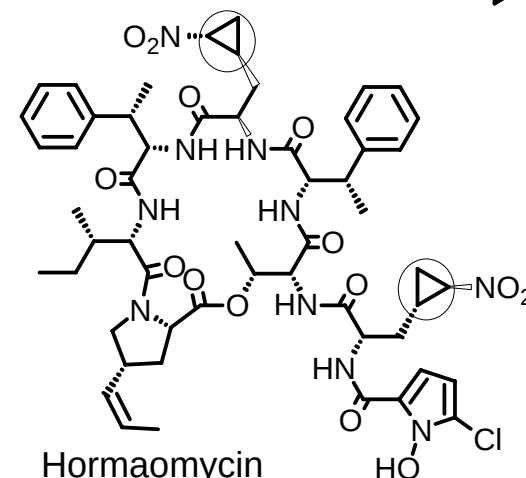
Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen,
Tammannstr. 2, 37077 Göttingen, Germany
e-mail: Armin.deMeijere@chemie.uni-goettingen.de
<http://www.gwdg.de/~ucoc/adm>



Trovafloxacin (PFIZER)

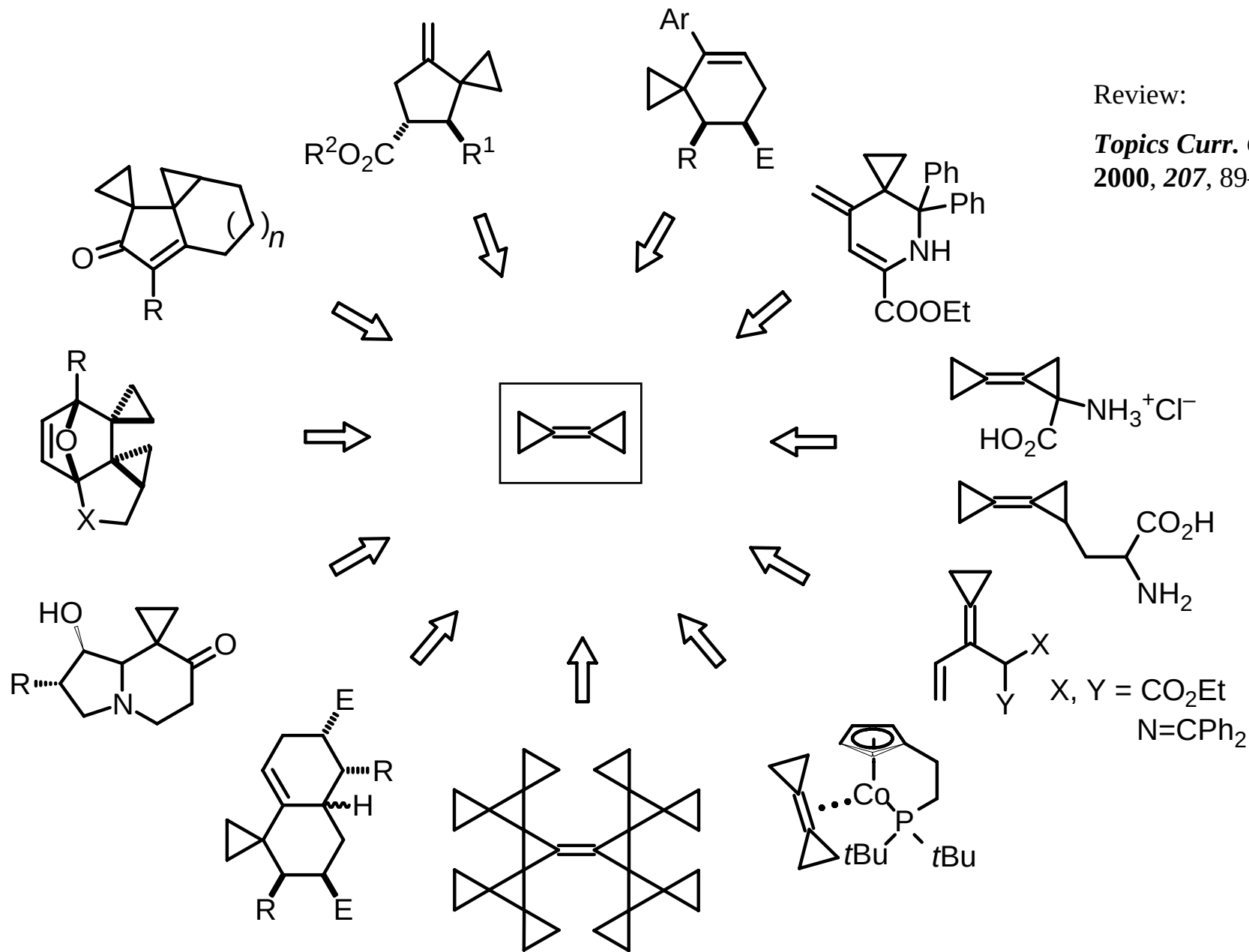


Belactosin A

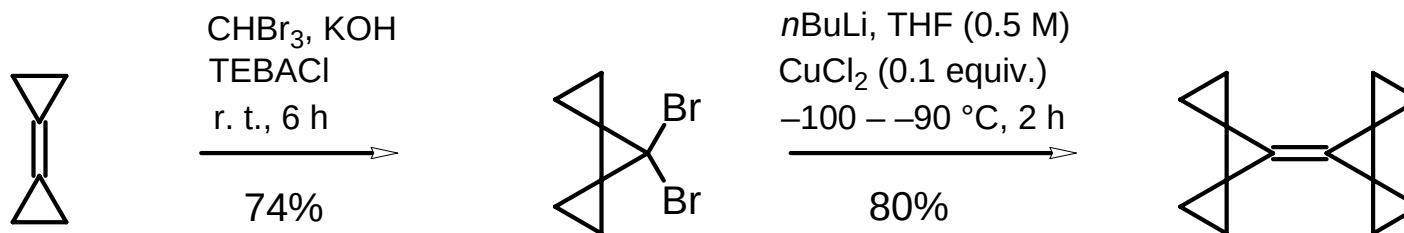


Hormaomycin

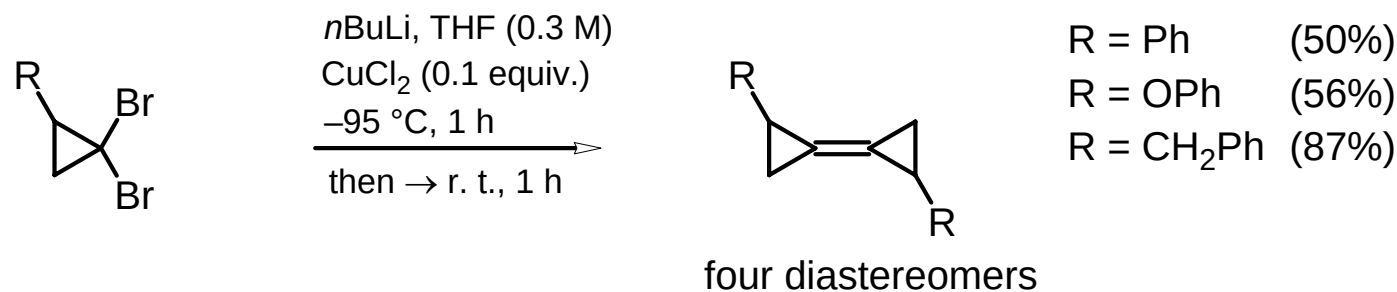
Bicyclopropylidene: A Highly Compact Multifunctional Building Block



Improved Synthesis of 7,7'-Bi(trispiro[2.0.2.1]heptylidene)

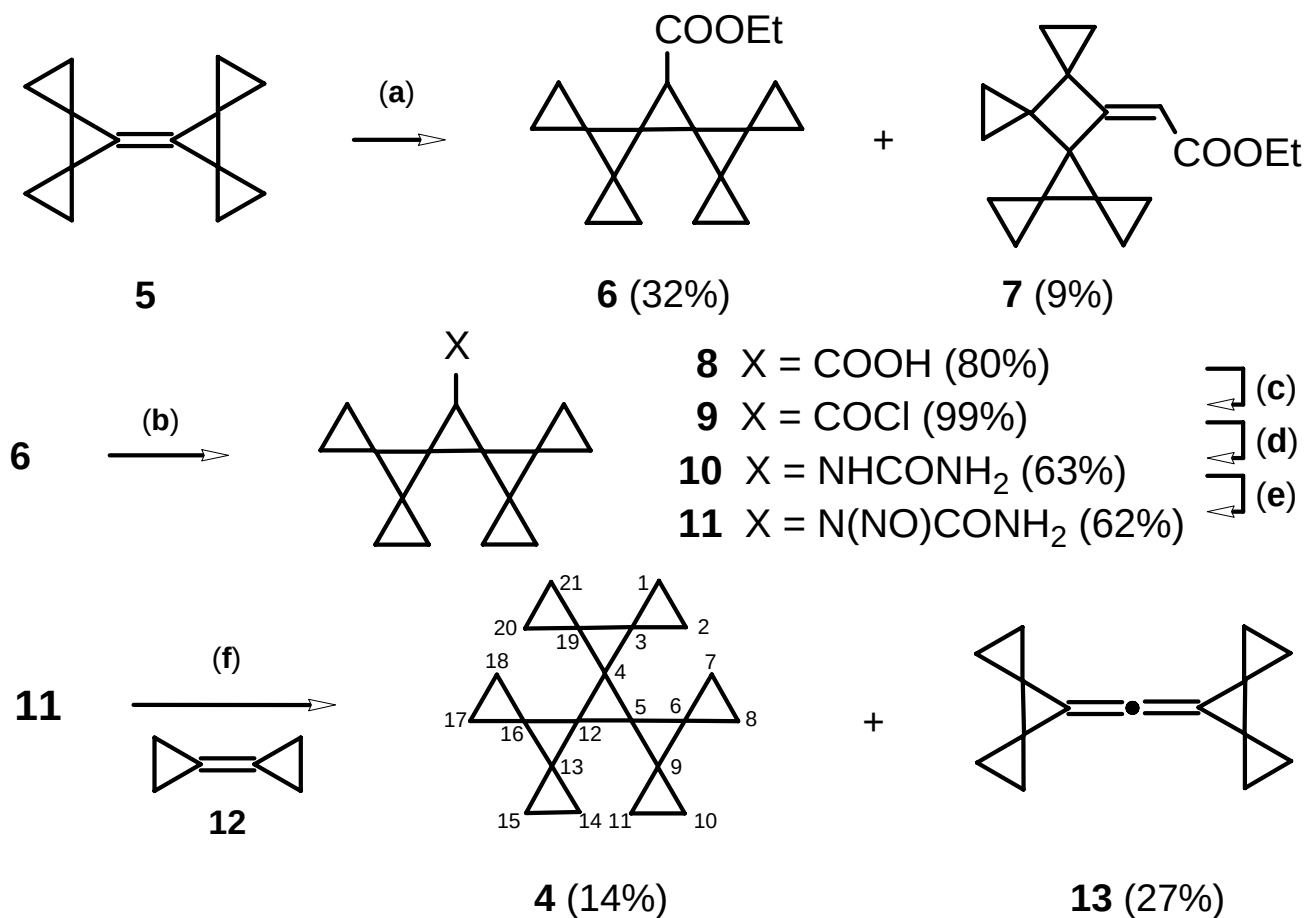


M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Bucholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem. Int. Ed.* **2000**, 39, 2495–2498.



Cf. T. Loosli, M. Borer, I. Kulakowska, A. Minger, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1995**, 78, 1144; M. Borer, T. Loosli, A. Minger, M. Neuenschwander, P. Engel, *ibid.* **1995**, 78, 1311.

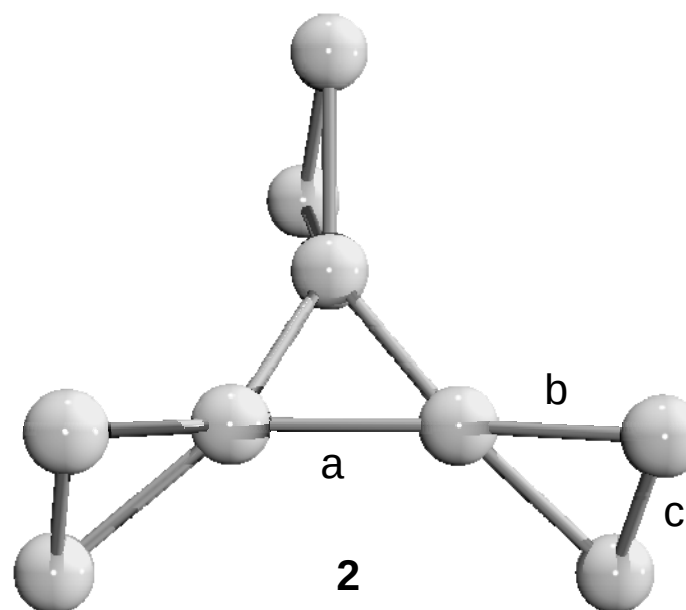
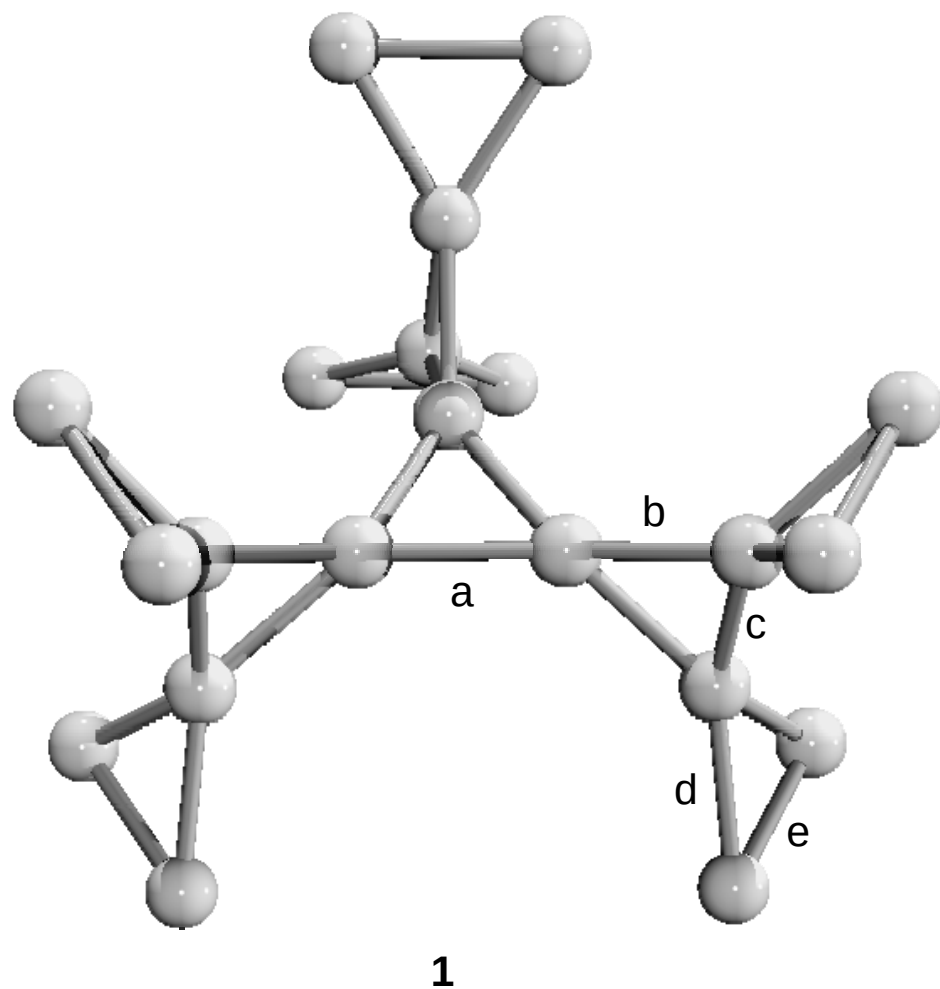
Perspirocyclopropanated [3]Rotane – A [10]Triangulane



a) 2 N₂CHCOOEt, CH₂Cl₂, [Rh(OAc)₂]₂ (1 mol %), 0 °C, 12 h. **b)** 1.2 NaOH, H₂O, 100 °C, 6 h. **c)** SOCl₂, 80 °C, 2 h. **d)** 1) NaN₃, Me₂CO, 2 h; 2) C₆H₆, 80 °C, 2 h; 3) NH₃. **e)** N₂O₄, Et₂O, 0 °C, 2 h. **f)** 10 NaOMe, 0 °C, 10 h.

S. I. Kozhushkov, T. Haumann, R. Boese, A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 401–403.

Crystal Structure of Perspirocyclopropane[3]rotane

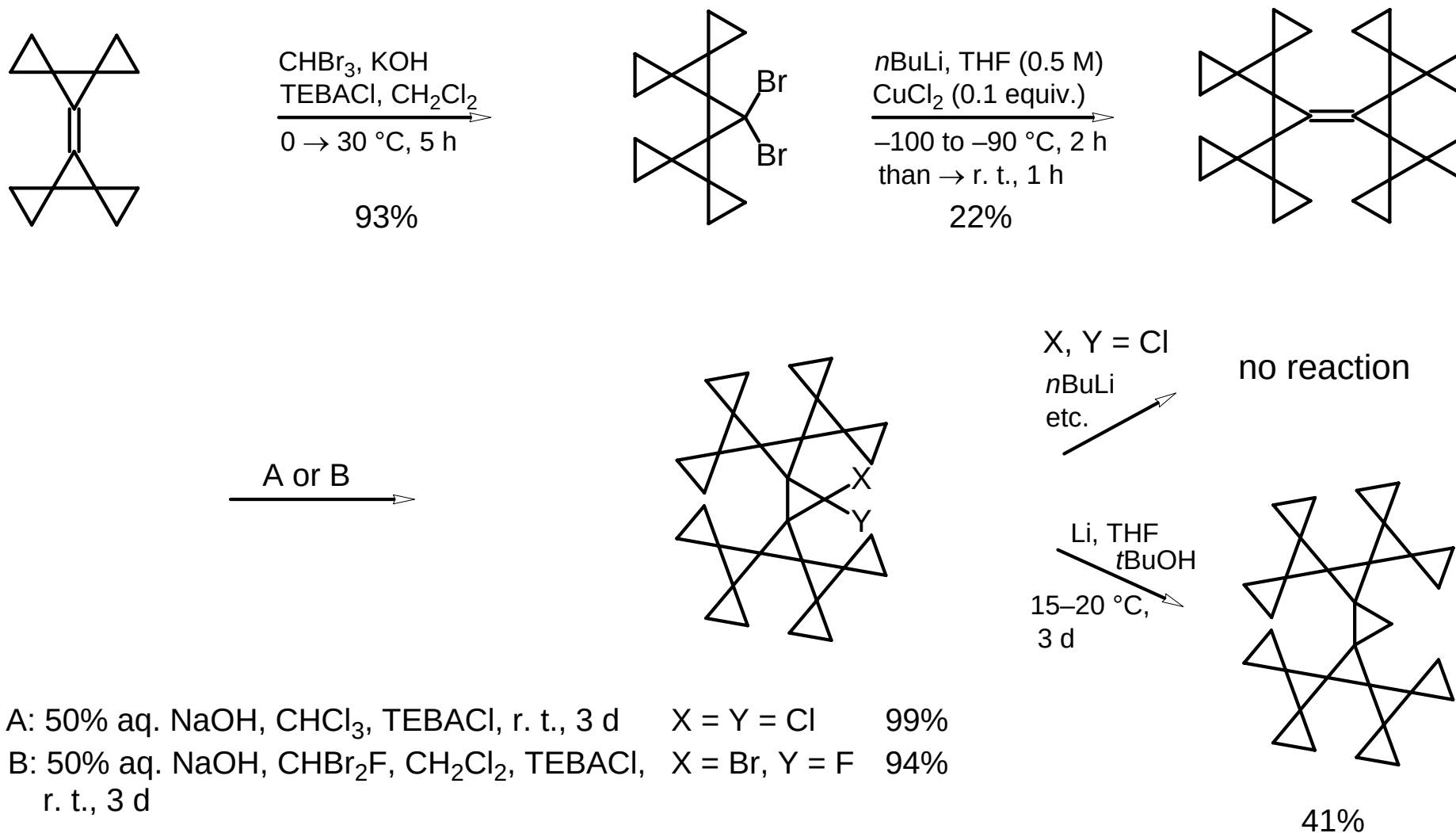


Bond	1 [Å]	2 [Å]
a	1.484(1)	1.475(2)
b	1.479(1)	1.477(1)
c	1.476(2)	1.525(2)
d	1.481(1)	---
e	1.529(1)	---

S. I. Kozhushkov, T. Haumann, R. Boese, A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 401.

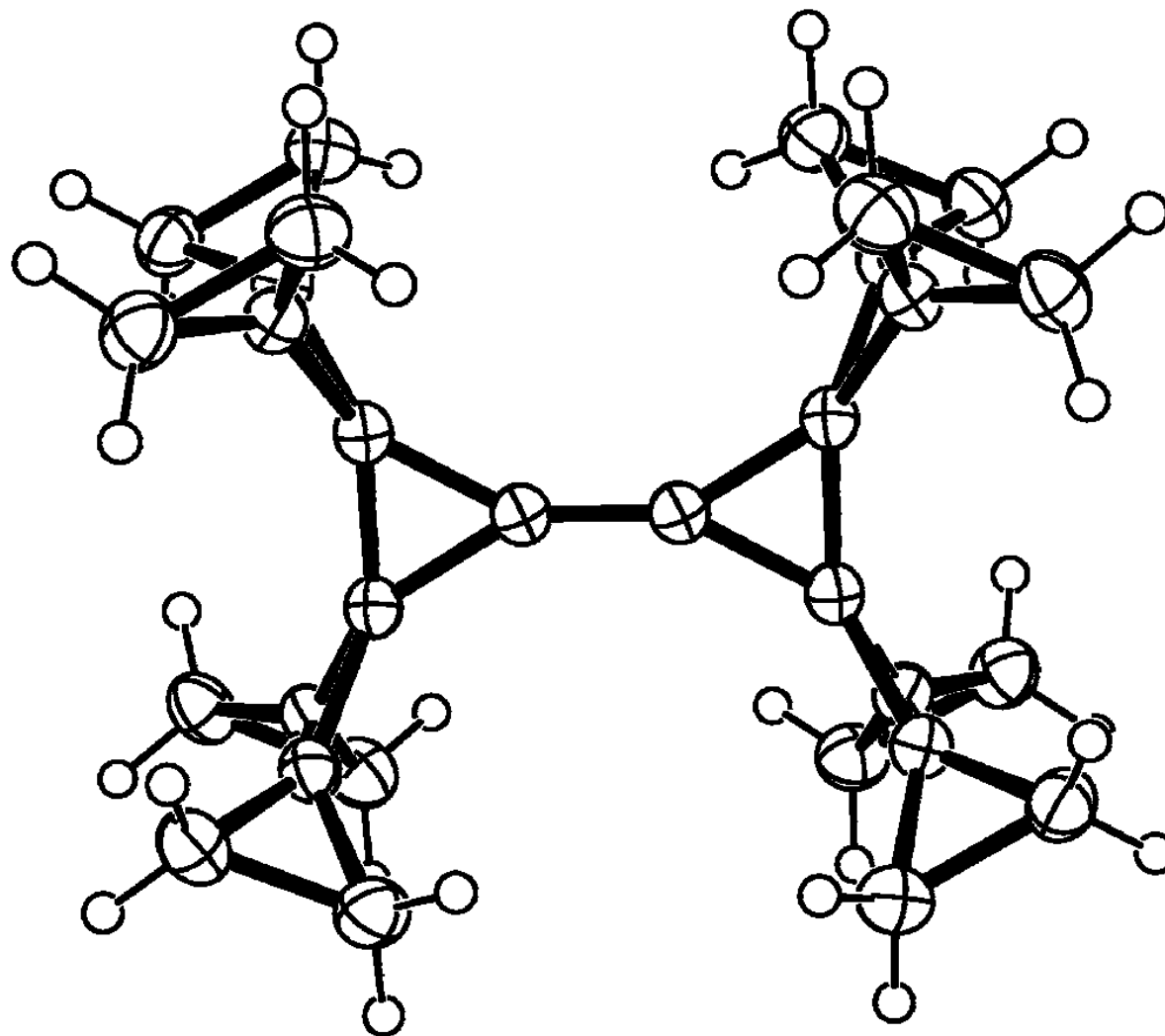
R. Boese, T. Miebach, A. de Meijere, *J. Am. Chem. Soc.* **1991**, 113, 1743.

Reaching for a New Record: A Third-Generation Bicyclopropylidene and a Branched [15]Triangulane



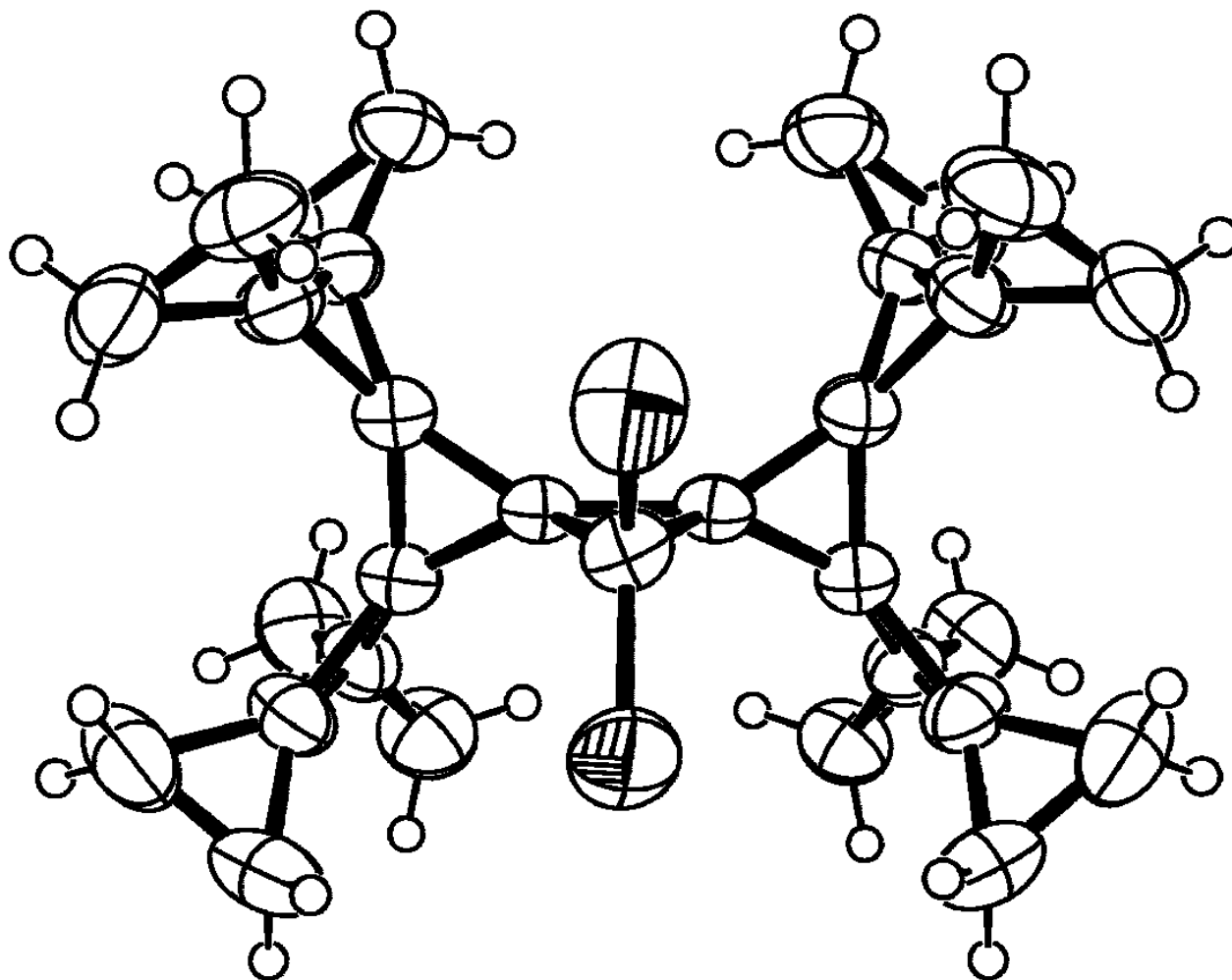
M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Bucholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem. Int. Ed.* **2000**, 39, 2495–2498.

Third-Generation Bicyclopropylidene !



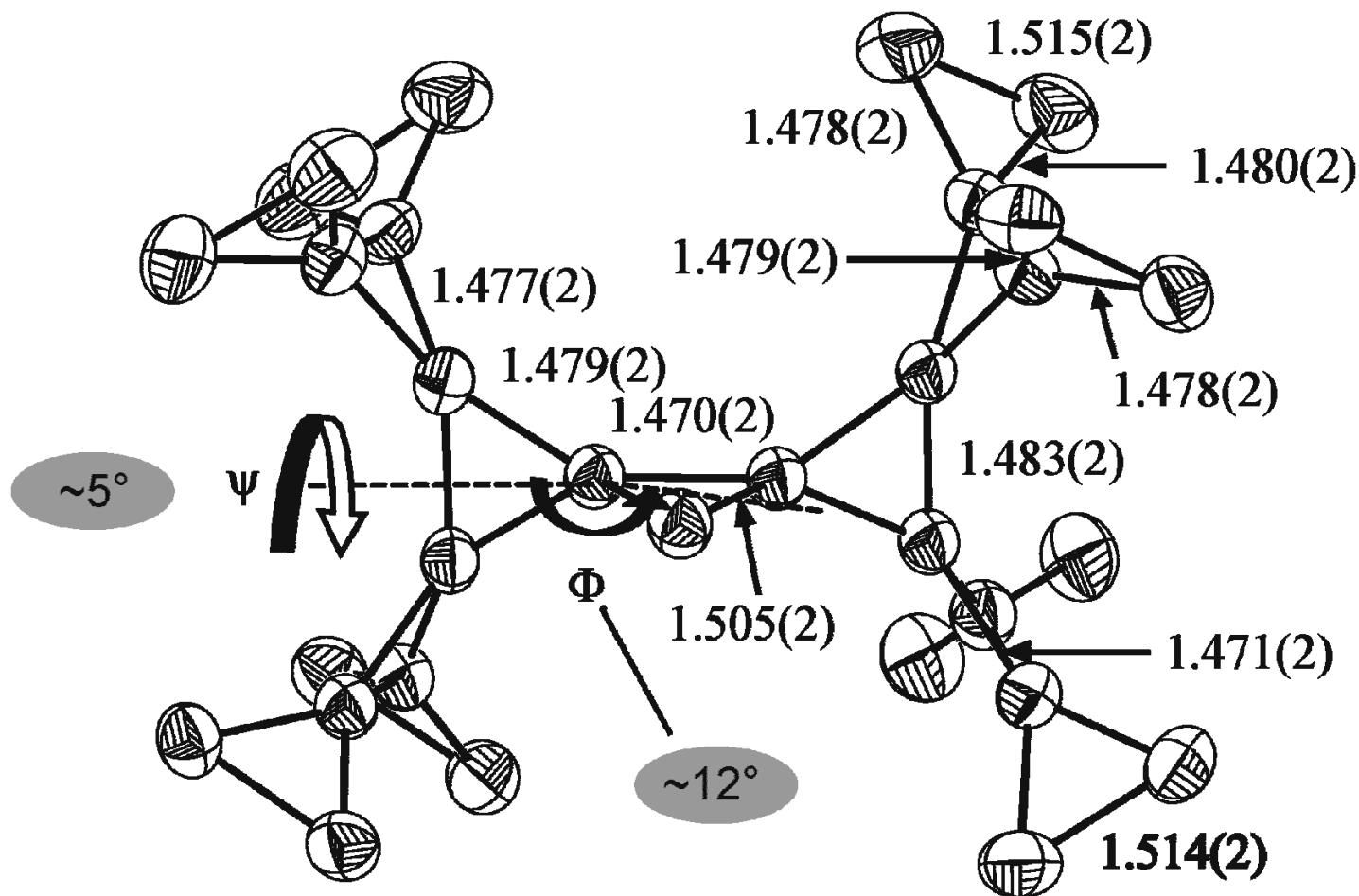
M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Bucholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem. Int. Ed.* **2000**, 39, 2495–2498.

An Overcyclopropanated Dichlorotrispiro[2.0.2.1]heptane !



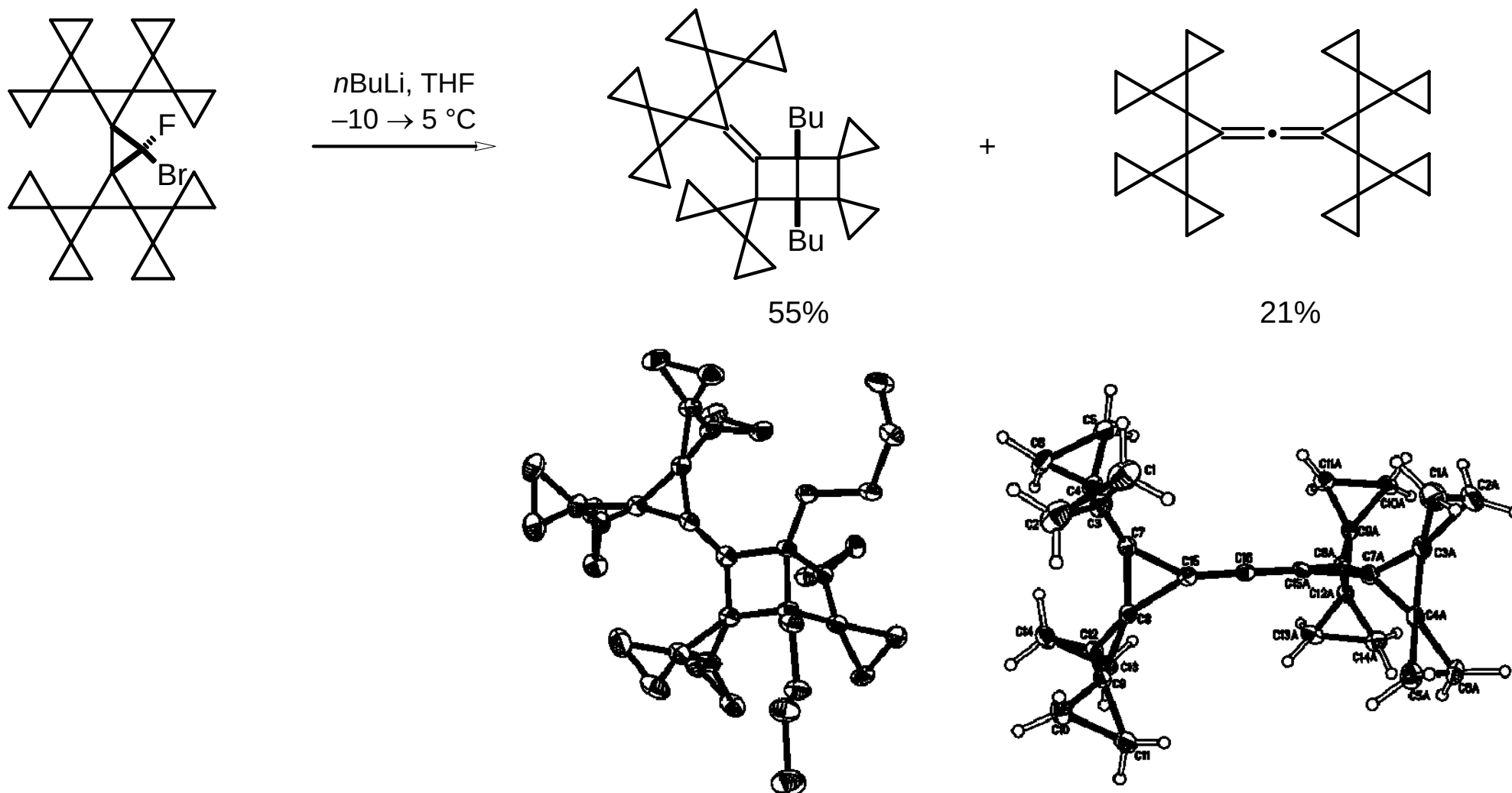
M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Bucholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem. Int. Ed.* **2000**, 39, 2495–2498.

Branched [15]Triangulane



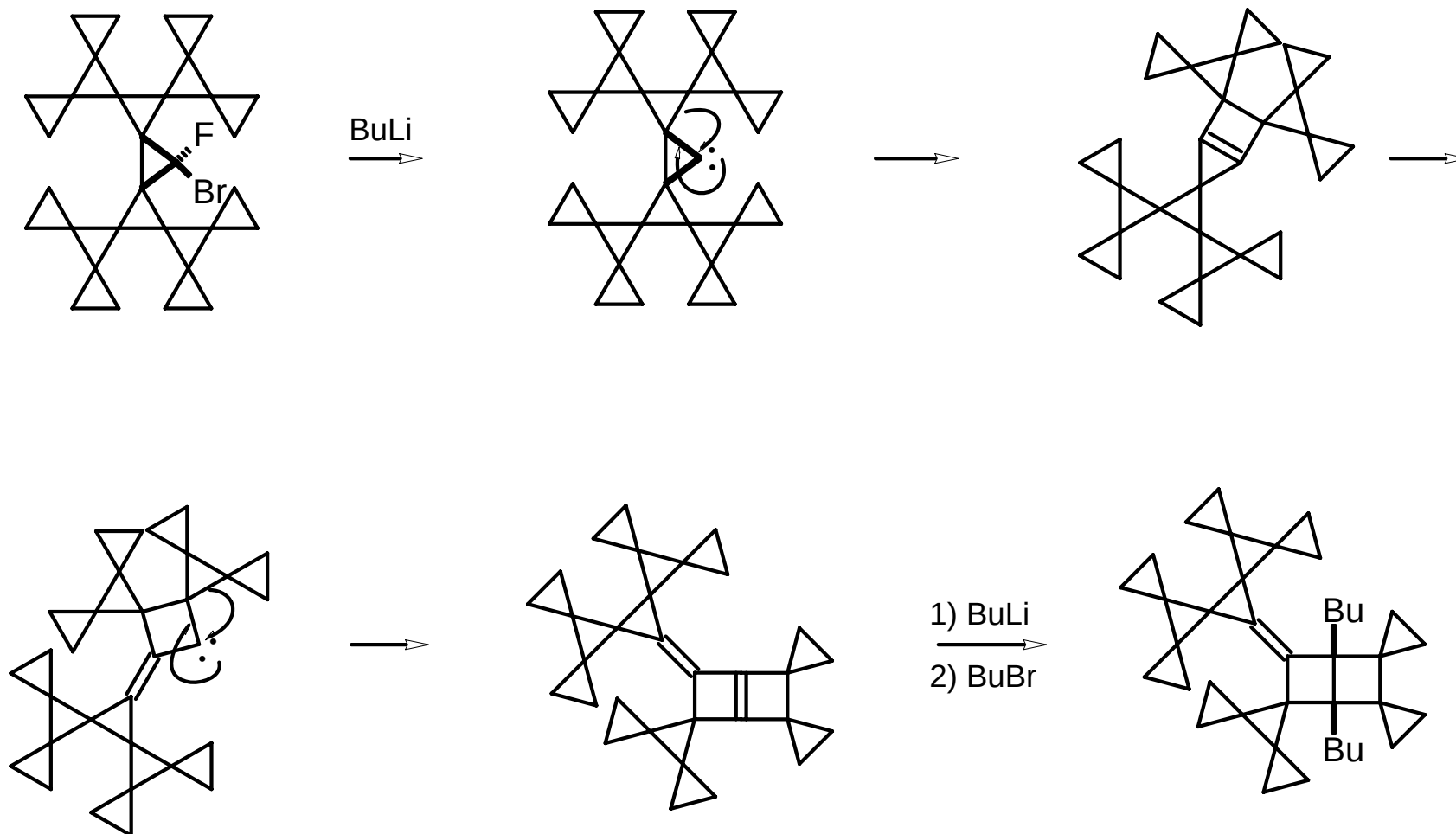
M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Bucholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem. Int. Ed.* **2000**, 39, 2495–2498.

At Last: A Cume Question



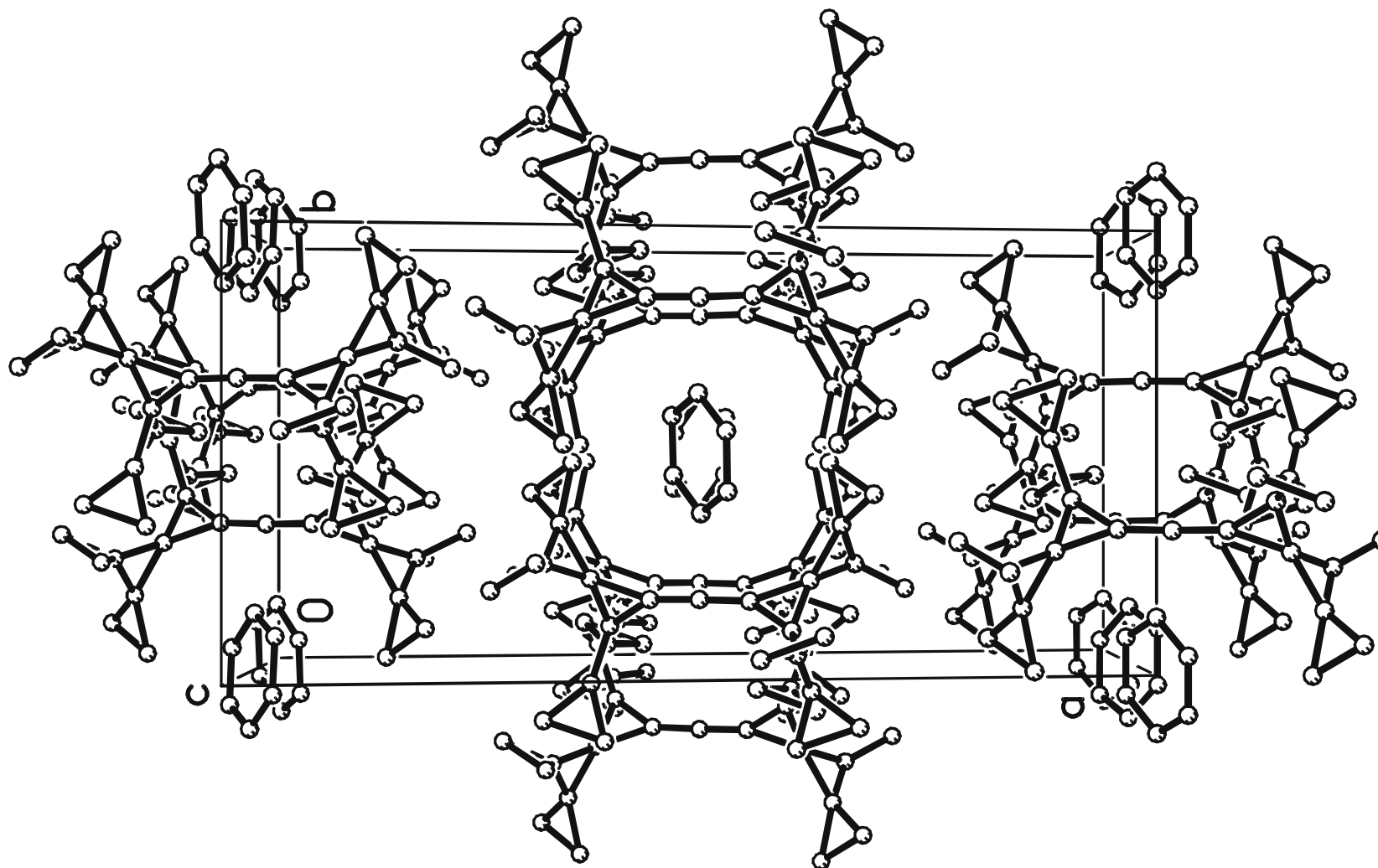
A. de Meijere, M. von Seebach, S. Zöllner, S. I. Kozhushkov, V. N. Belov, R. Boese, T. Haumann, J. Benet-Buchholz, D. S. Yufit, J. A. K. Howard, *Chem. Eur. J.* **2001**, 7, 4021–4034.

And the Most Probable Answer



A. de Meijere, M. von Seebach, S. Zöllner, S. I. Kozhushkov, V. N. Belov, R. Boese, T. Haumann, J. Benet-Buchholz, D. S. Yufit, J. A. K. Howard, *Chem. Eur. J.* **2001**, 7, 4021–4034.

Supramolecular in the Crystal

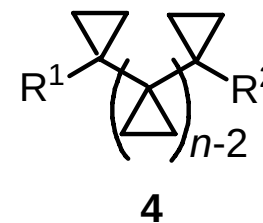
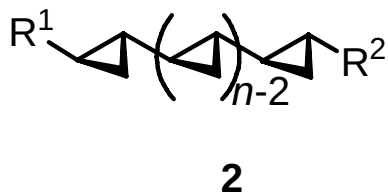
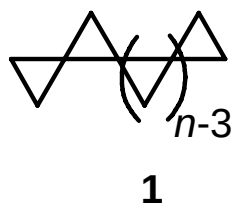


M. von Seebach, S. Kozhushkov, D. S. Yufit, A. de Meijere 1999–2000

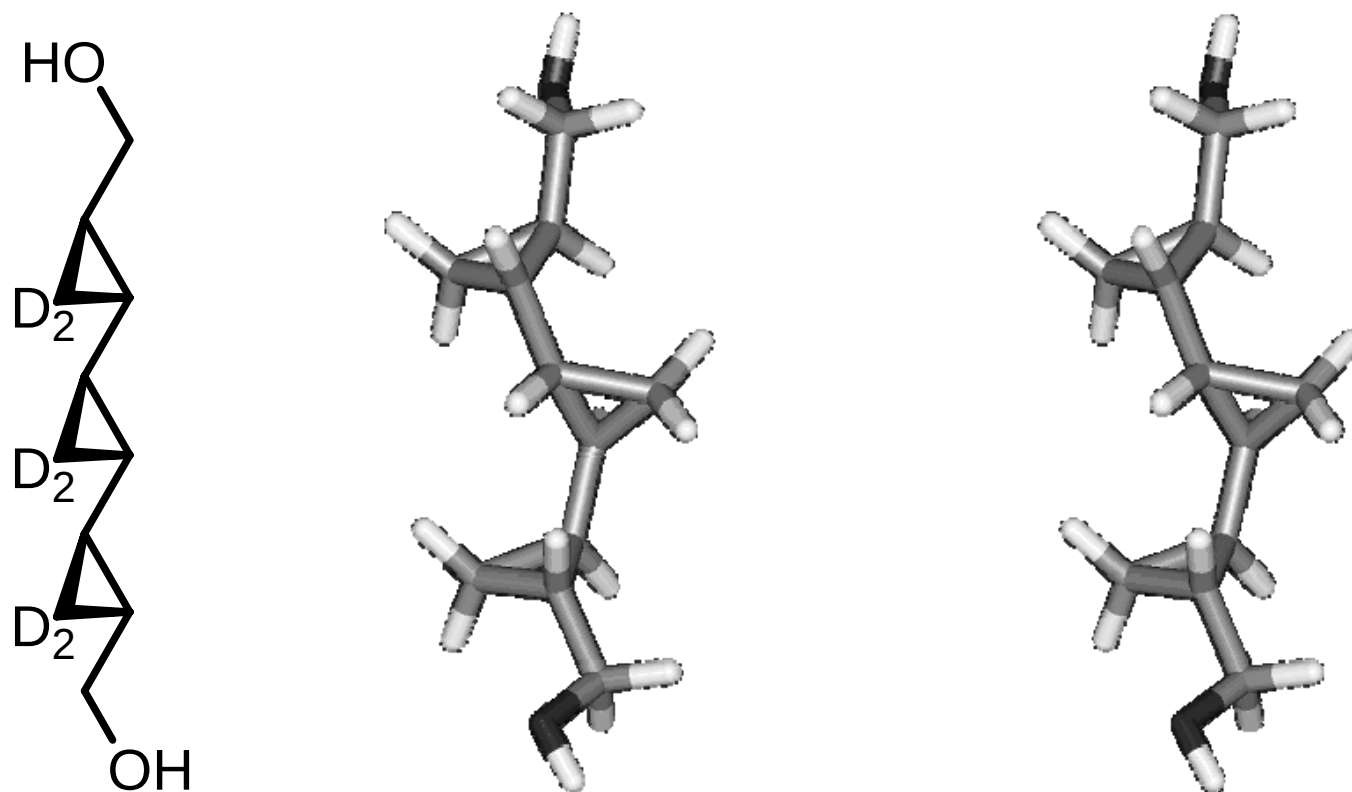
1,1'-Linked Cyclopropane Derivates: The Helical Conformation of Quinquecyclopropanol

*Takuya Kurahashi, Sergei I. Kozhushkov, Heiko Schill, Kathrin Meindl, Stephan Rühl and Armin de Meijere**

Dedicated to Professor Kenneth B. Wiberg on the occasion of his 80th birthday



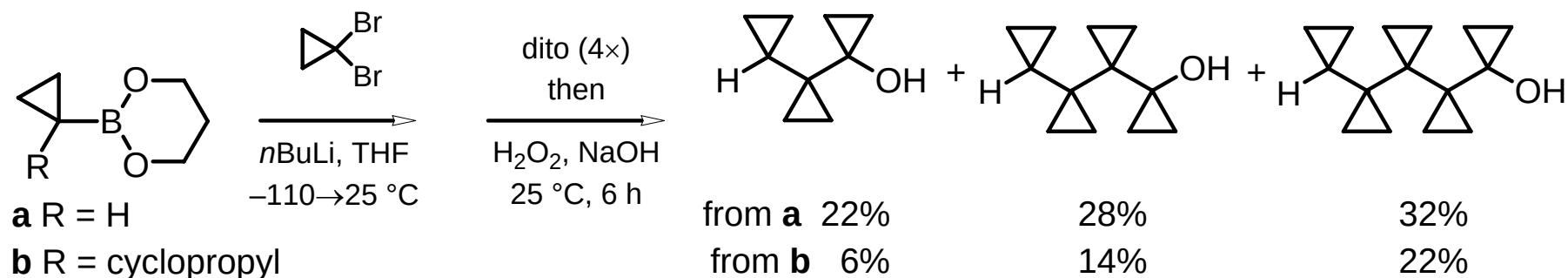
Helical Conformation of Tercyclopropanedimethanol in Solution



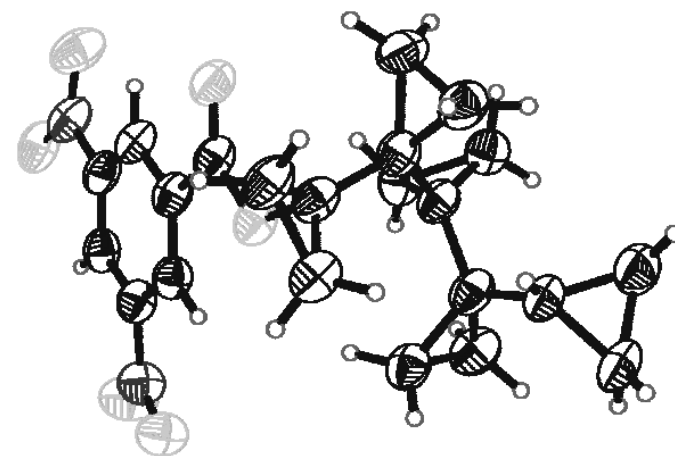
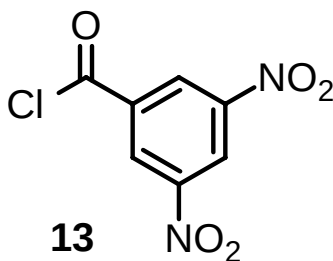
Preferred interunit dihedral angle of $+40^\circ$ from NMR coupling constants,
NOE intensities as evaluated by DFT calculations

A. G. M. Barrett, R. A. James, G. E. Morton, P. A. Procopiou, A. de Meijere, C. Griesinger, U. M. Reinscheid, *J. Org. Chem.* **2006**, 71, 2756–2759.

Synthesis of 1,1'-Linked Quinquecyclopropanol

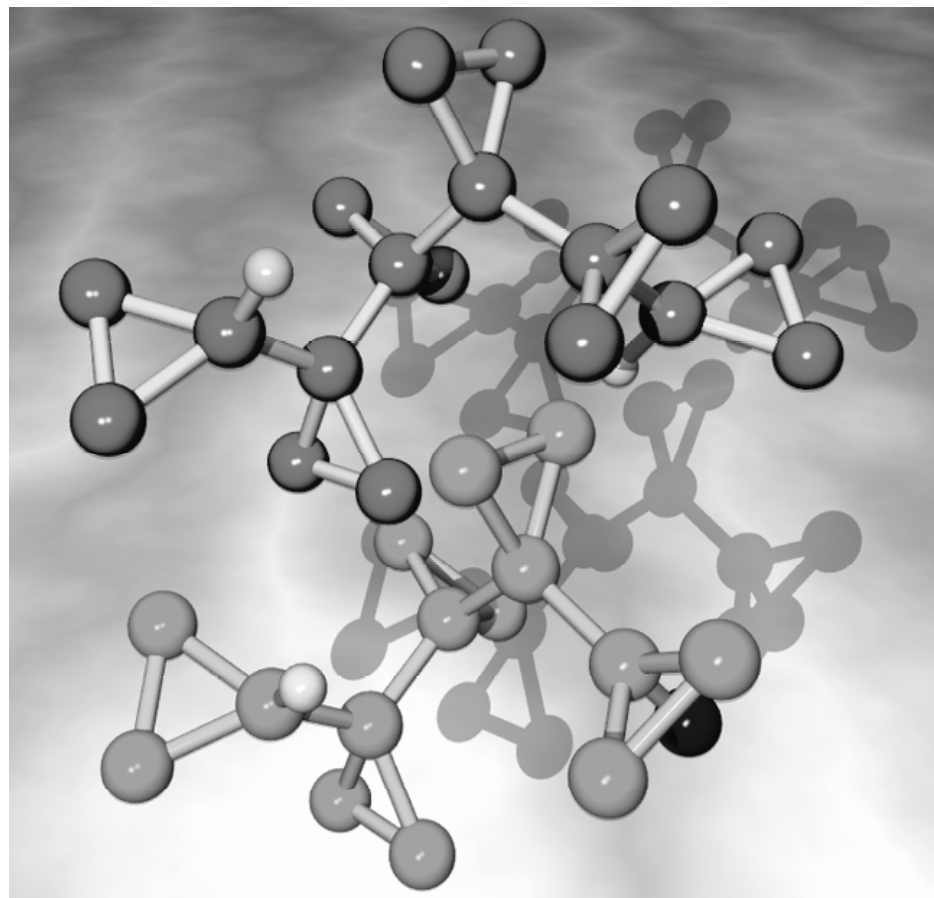


13, Py, DMAP
 40 °C, 30 h
 67%

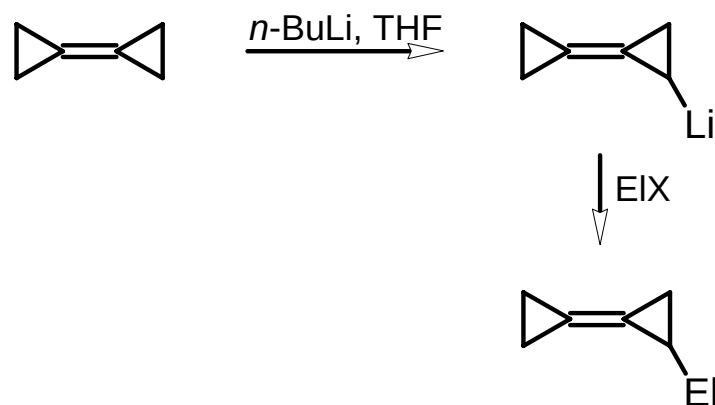
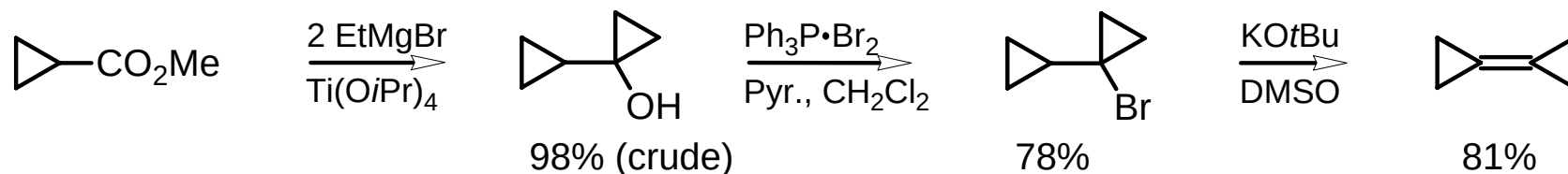


T. Kurahashi, S. I. Kozhushkov, A. de Meijere et al., *Angew. Chem.Int. Ed.* **2007**, 46, 6545.

Structures of Sexicyclopropane (in the Gas Phase) and a Quinquecyclopropane Derivative (in the Crystal)



Versatile New Synthesis of Bicyclopropylidene and its Derivatives

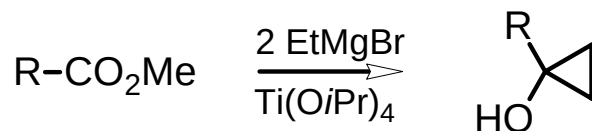


EIX	X	%
Me ₃ SiCl	SiMe ₃	85
(PhS) ₂	SPh	77
C ₂ Cl ₆	Cl	73
(CH ₂ Br) ₂	Br	65
<i>n</i> -C ₇ H ₁₅ I	<i>n</i> Hept	74
1) CO ₂ 2) H ⁺	CO ₂ H	95
Me ₂ CO	Me ₂ CHOH	82

A. de Meijere, S. I. Kozhushkov, T. Späth, N. S. Zefirov *J. Org. Chem.* **1993**, *58*, 502–505.

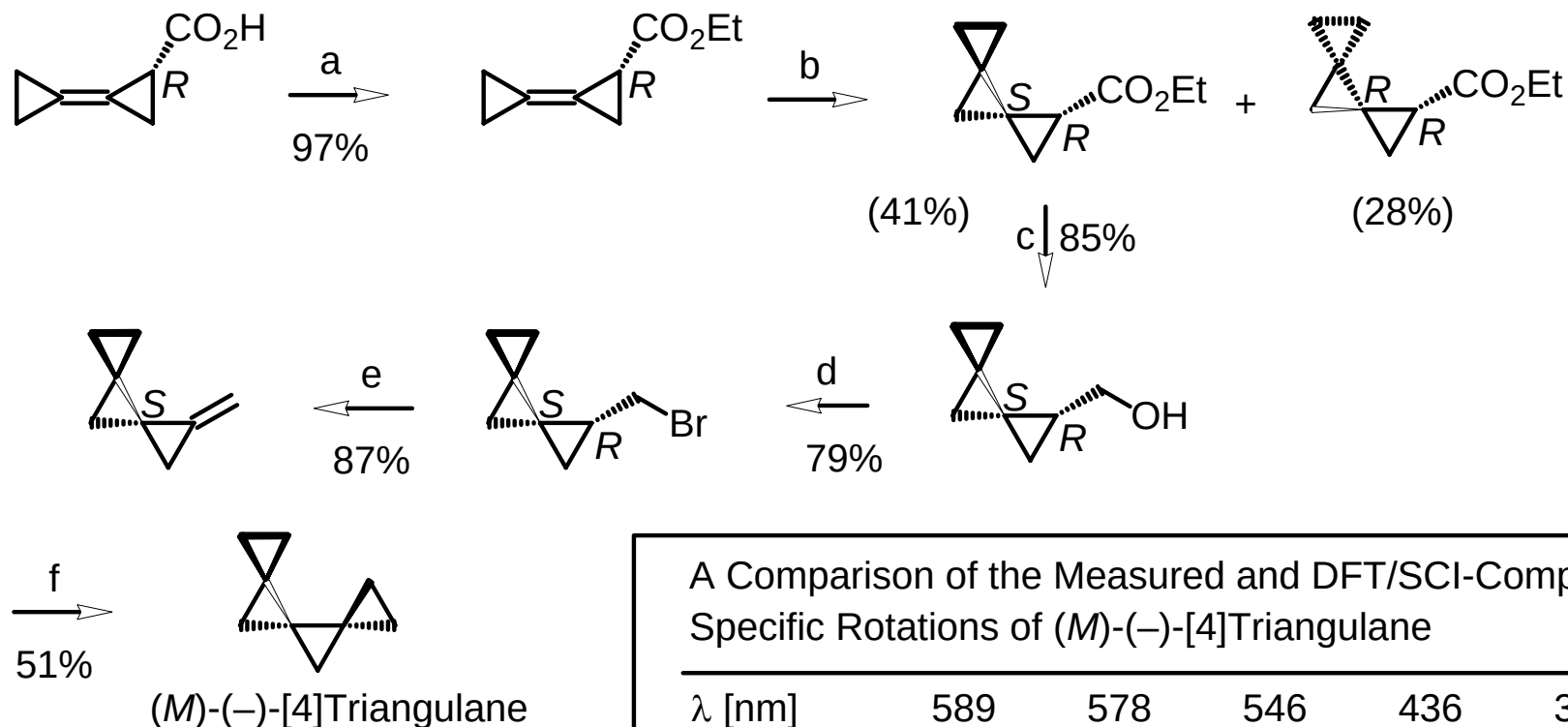
A. de Meijere, S. I. Kozhushkov, N. S. Zefirov, *Synthesis* **1993**, 681–683.

A. de Meijere, S. I. Kozhushkov, T. Späth, *Org. Synth.* **2000**, *78*, 142–151.



O. G. Kulinkovich et al., *Synthesis* **1991**, 234.

Enantiomerically Pure (*M*)-[4]Triangulane



A Comparison of the Measured and DFT/SCI-Computed Specific Rotations of (*M*)-(-)-[4]Triangulane

λ [nm]	589	578	546	436	365
$[\alpha]_D^{20}$	-192.7	-201.3	-229.7	-400.2	-648.2
Computed	-241.0	-250.2	-283.8	-466.0	-703.7

a: $\text{BF}_3 \cdot \text{Et}_2\text{O}$, EtOH, 78 °C, 2 h. – b: CH_2I_2 , Zn, DME, ultrasound, 80 °C, 2 h. – c: LiAlH_4 , Et_2O . – d: $\text{Ph}_3\text{P} \cdot \text{Br}_2$, Py, CH_2Cl_2 , -10 °C, 1.5 h, then 20 °C, 7 h. – e: $t\text{BuOK}$, DMSO, 20 °C, 14 h. – f: CH_2N_2 , $\text{Pd}(\text{OAc})_2$, Et_2O , -5 °C.

A. de Meijere, A. F. Khlebnikov, R. R. Kostikov, S. I. Kozhushkov, P. R. Schreiner, A. Wittkopp, D. S. Yufit, *Angew. Chem.* **1999**, *111*, 3682–3685; *Angew. Chem. Int. Ed.* **1999**, *38*, 3474–3477.

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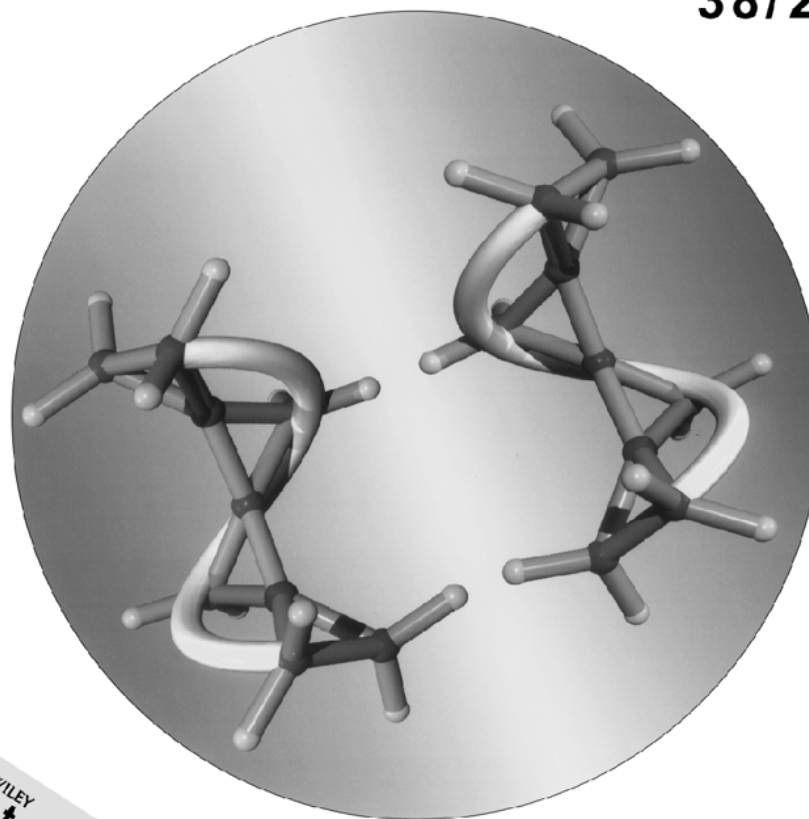
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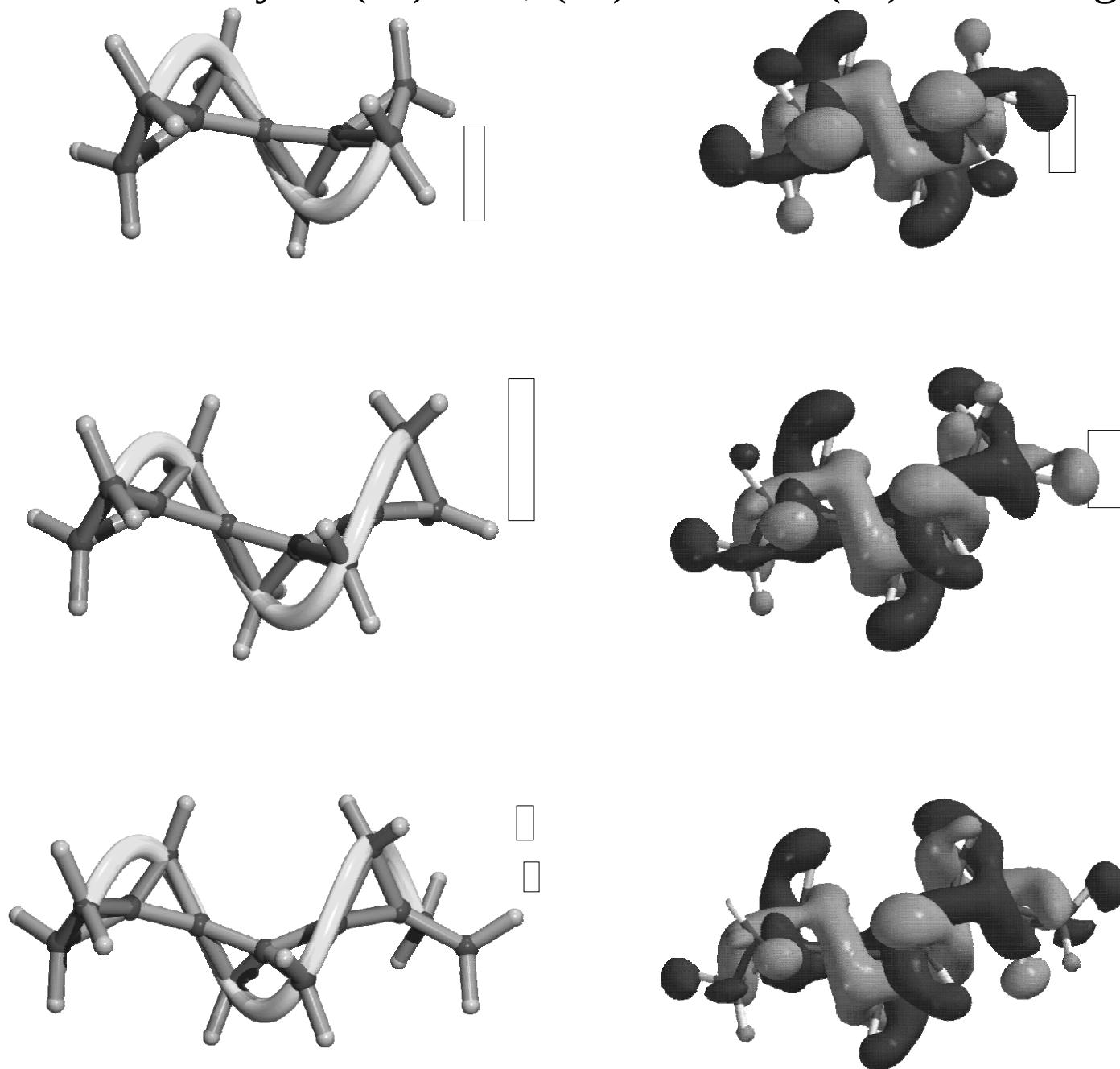
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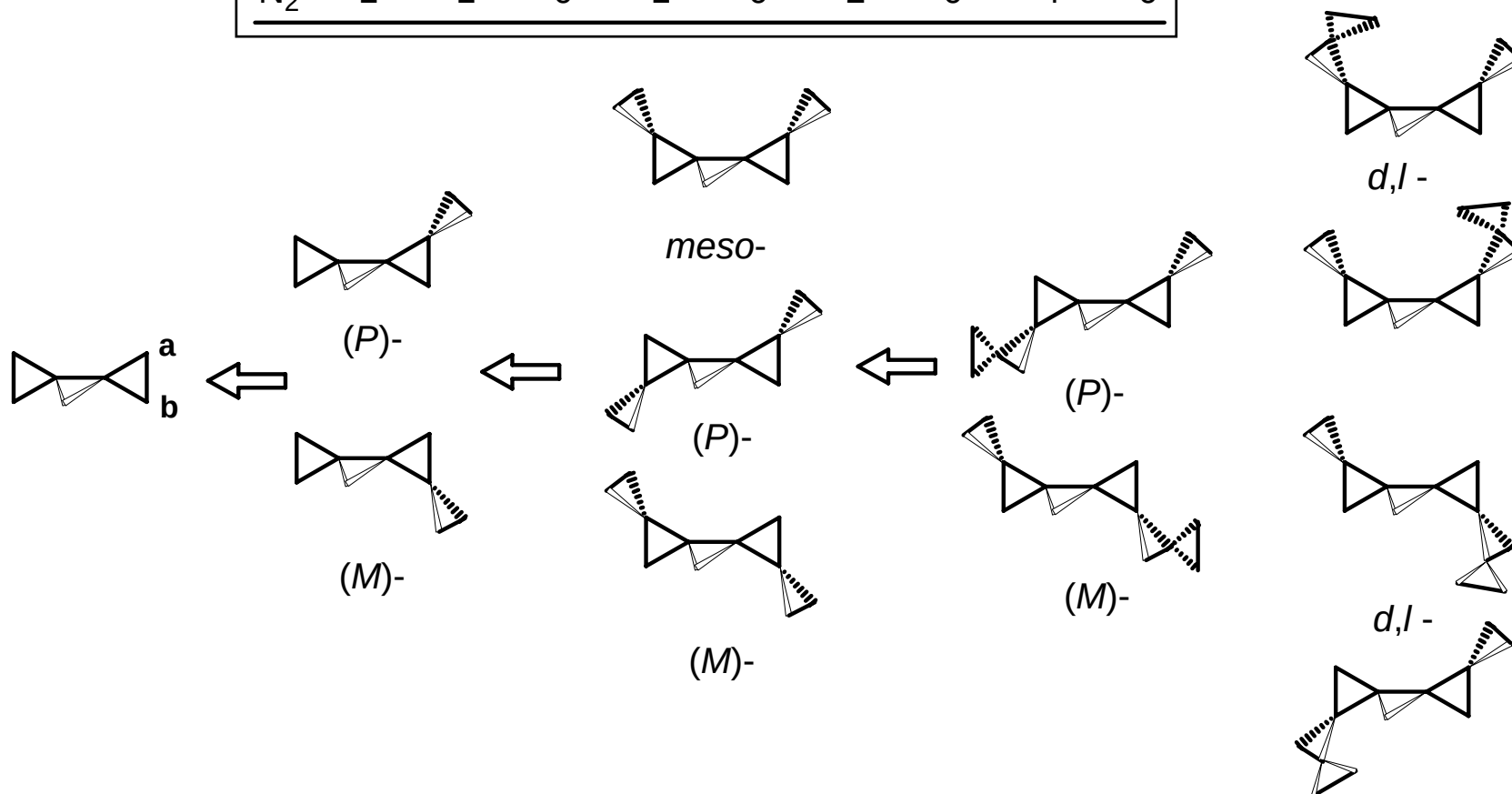
ACIEF5 38 (23) 3403-3570 (1999) • ISSN 1433-7851 • Vol. 38 • No. 23 • December 3, 1999

The Helicity of (M)-[4]-, (M)-[5]- and (M)-[6]Triangulane



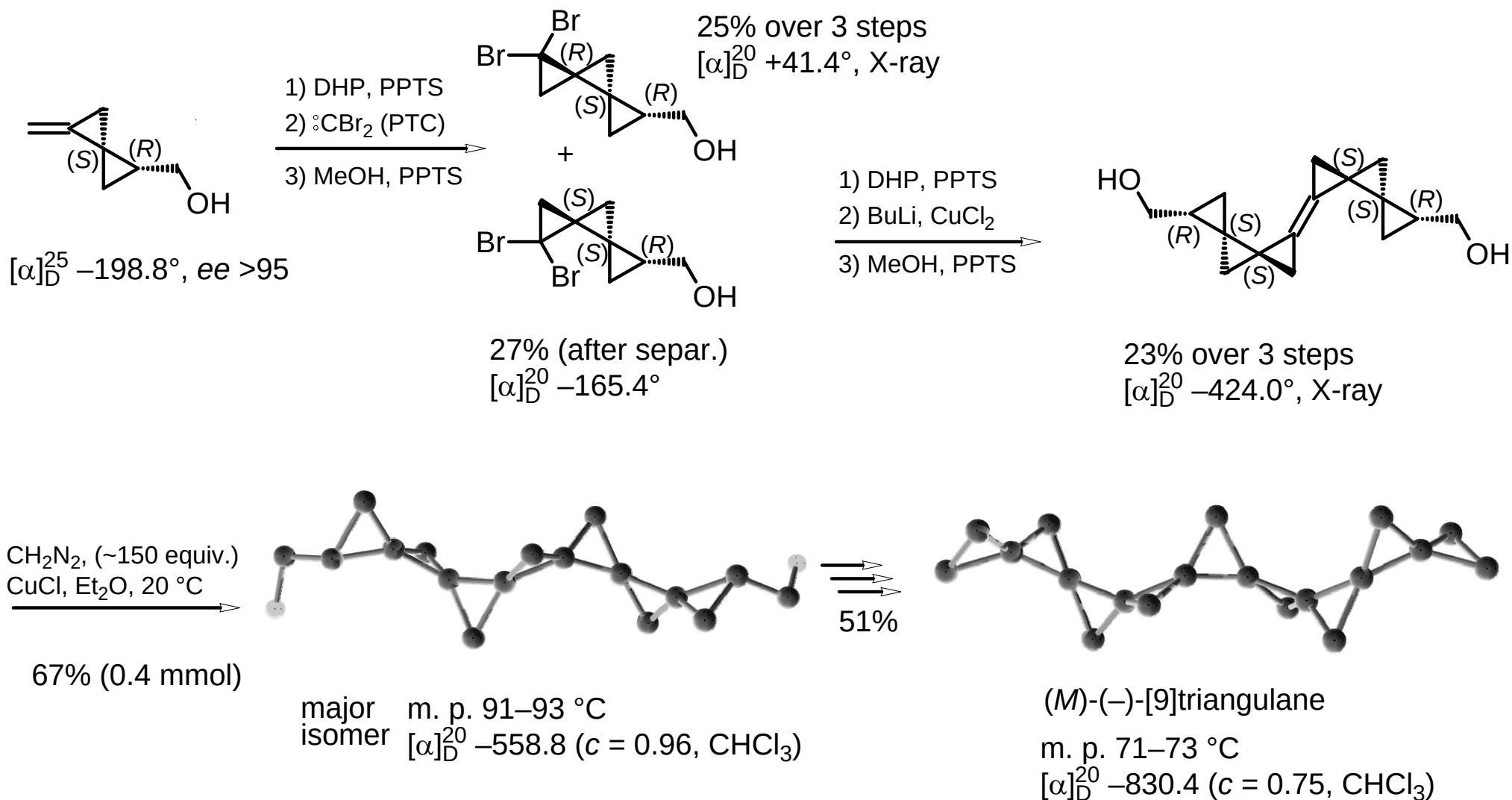
Number of Enantiomeric Pairs (N_1) and Achiral Stereoisomers (N_2) of $[n]$ Triangulanes^[1]

n	2	3	4	5	6	7	8	9	10
N_1	0	0	1	1	3	4	10	16	36
N_2	1	1	0	1	0	2	0	4	0



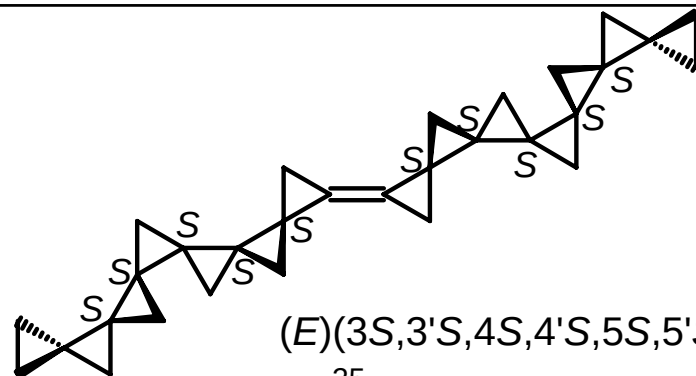
[1] N. S. Zefirov et al. *J. Am. Chem. Soc.* 1990, **112**, 7702.

Convergent Synthesis of (*M*)-[9]Triangulane



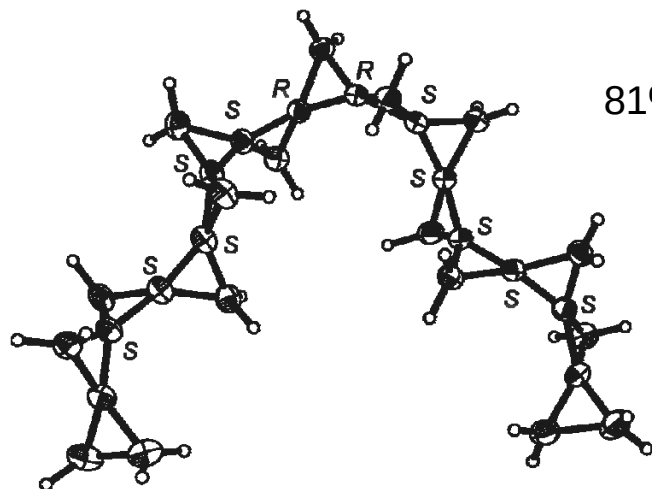
A. de Meijere, A. F. Khlebnikov, S. I. Kozhushkov, K. Miyazawa, D. Frank, P. R. Schreiner, C. Rinderspacher, D. S. Yufit, J. A. K. Howard, *Angew. Chem. Int. Ed.* **2004**, *43*, 6553–6557.

A Horseshoe-Shaped and the Straight Helical [15]Triangulane in Enantiomerically Pure Form



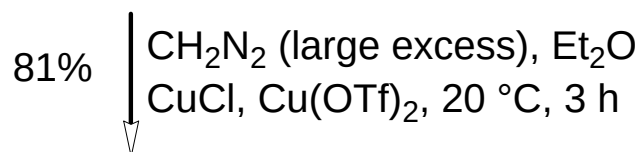
(*E*)(3*S*,3'*S*,4*S*,4'*S*,5*S*,5'*S*,6*S*,6'*S*,7*S*,7'*S*)-**38**

$[\alpha]_{\text{D}}^{25} -1446$ ($c = 0.525$, CHCl_3)

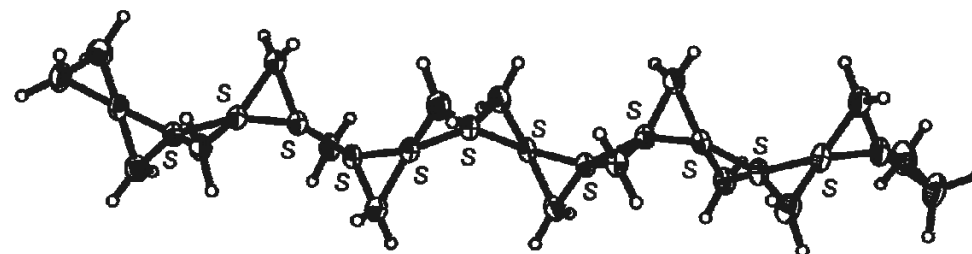


(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**

$[\alpha]_{\text{D}}^{25} -721.8$ ($c = 0.257$, CHCl_3)



+



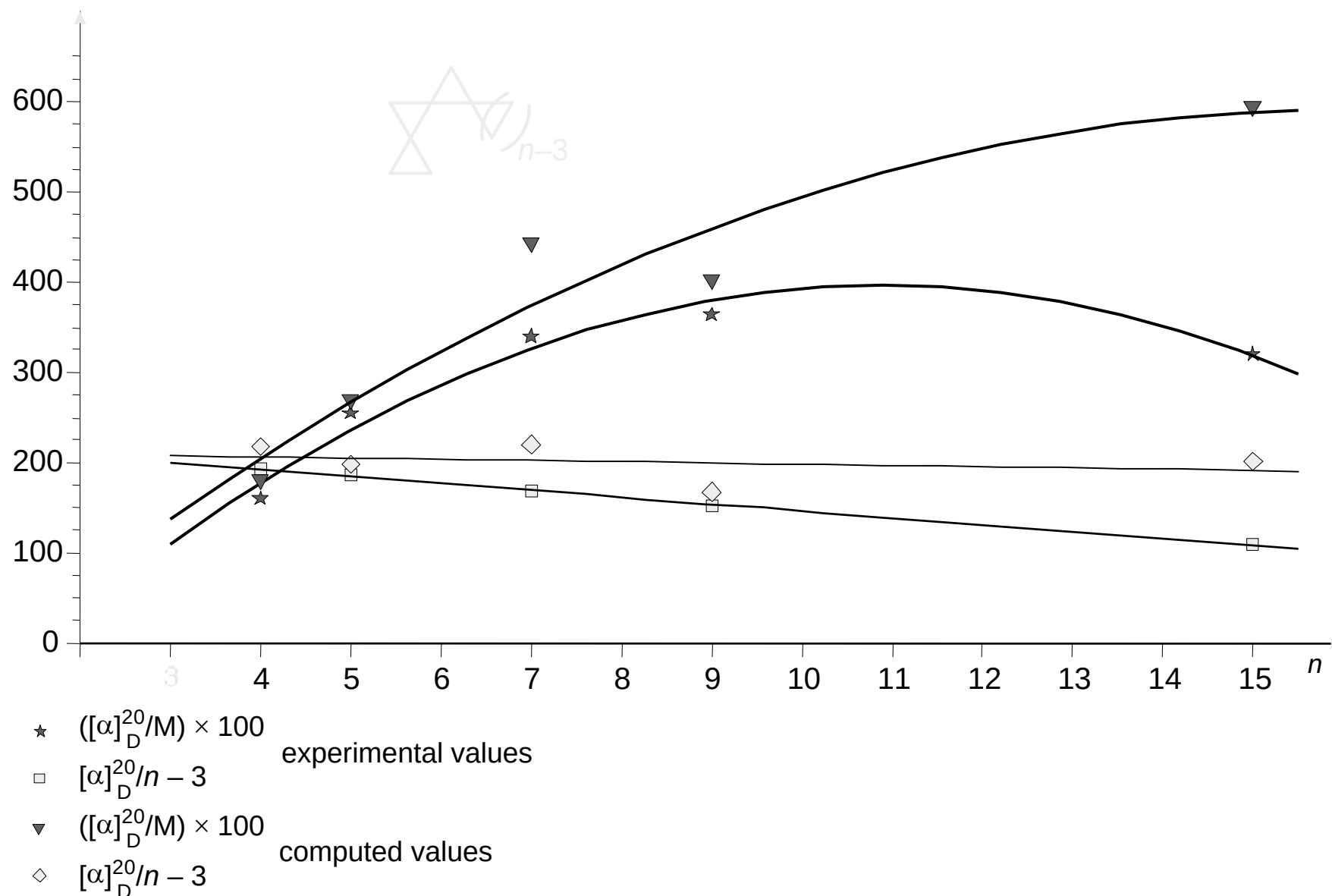
overall length ~2 nm

(4*S*,5*S*,6*S*,7*S*,8*S*,9*S*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**

$[\alpha]_{\text{D}}^{25} -1302.5$ ($c = 0.362$, CHCl_3)

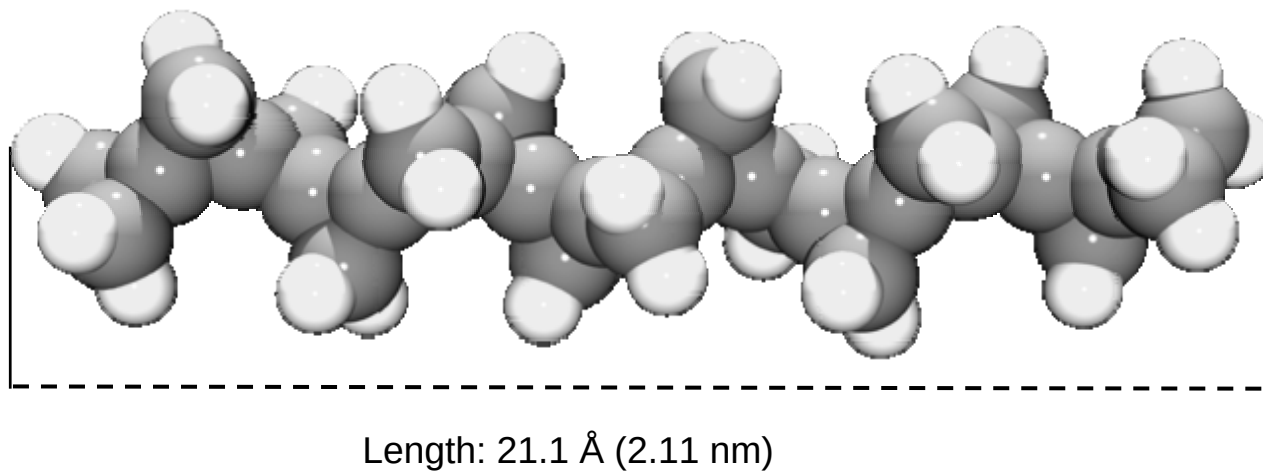
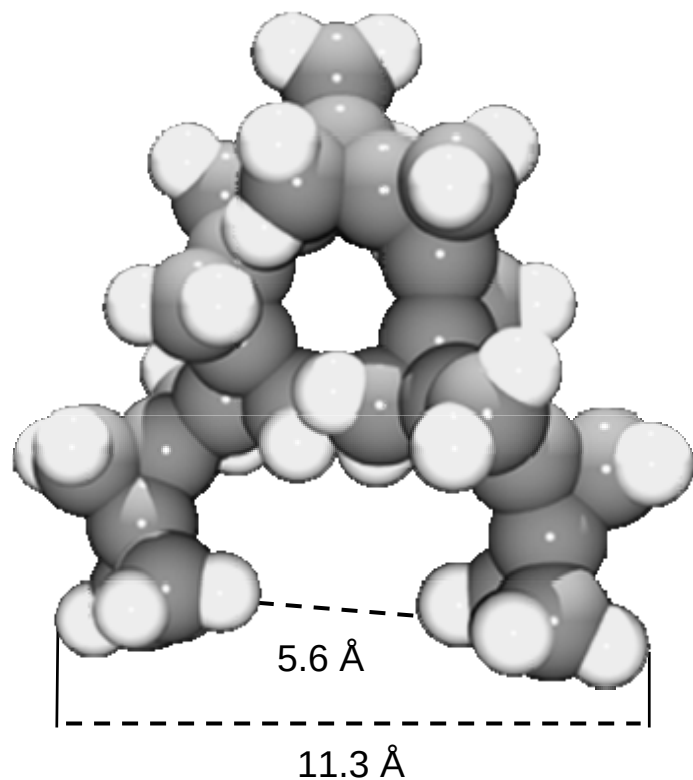
A. de Meijere, A. F. Khlebnikov, S. I. Kozhushkov, et al., *Chem. Eur. J.* **2006**, in press.

Normalized Rotations of $[n]$ Triangulanes (σ - $[n]$ Helicenes)



A. Khlebnikov, S. I. Kozhushkov, D. S. Yufit, K. Miyazawa, D. Frank, A. de Meijere 2005

A Helical Horseshoe and a Helical Stick



A. de Meijere, A. F. Khlebnikov, S. I. Kozhushkov, D. S. Yufit, J. A. K. Howard, T. Kurahashi, K. Miyazawa, D. Frank, P. R. Schreiner, C. Rinderspacher, *Chem. Eur. J.* **2006**, in press.

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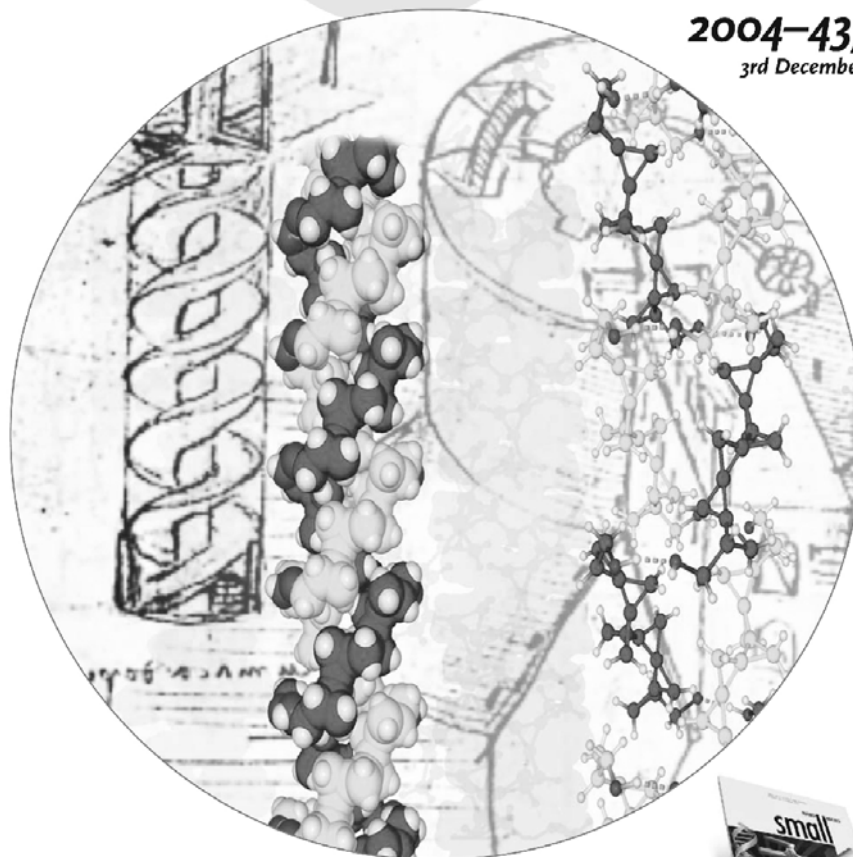
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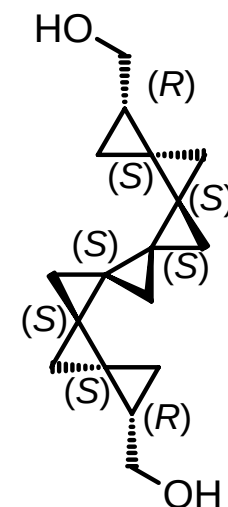
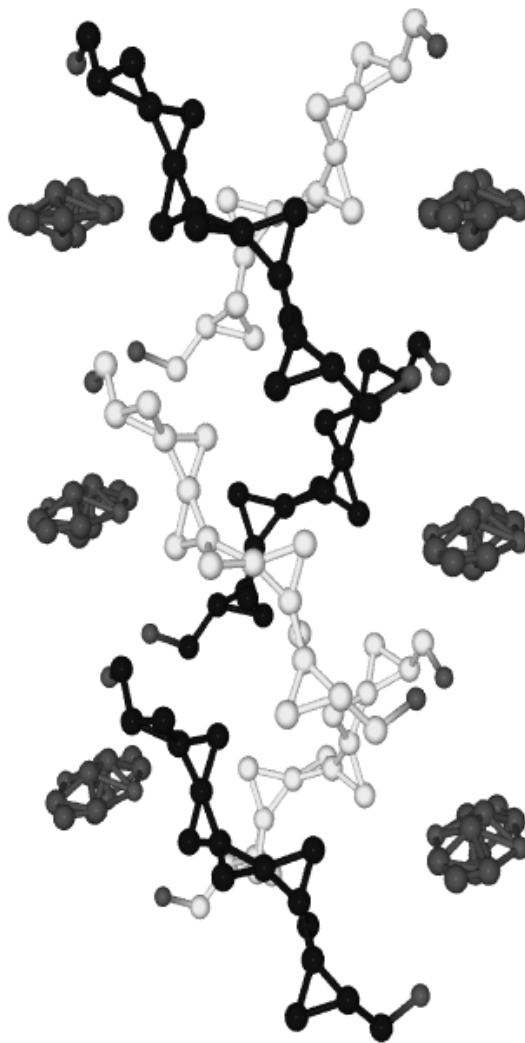
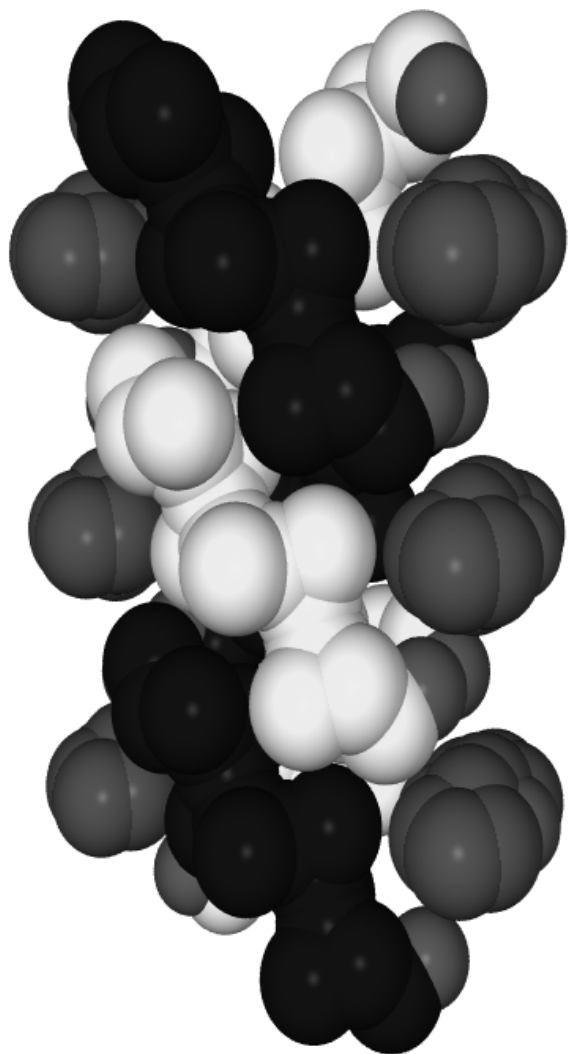
ACIEFS 43 (47) 6391–6564 (2004) · ISSN 1433–7851 · Vol. 43 · No. 47 · December 3, 2004



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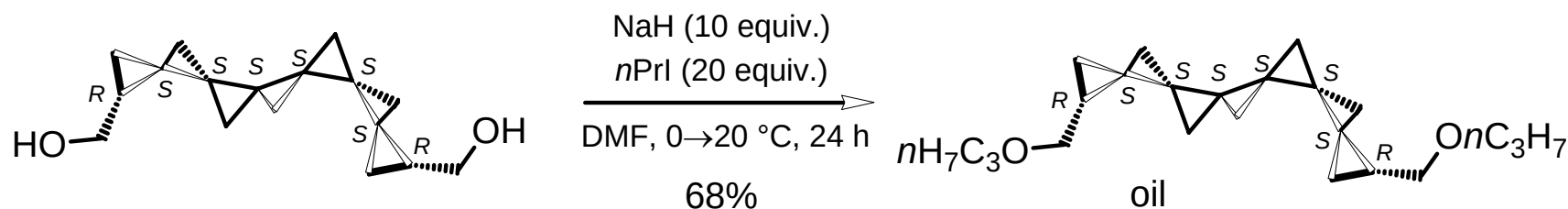
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... and a Remarkable Case of Self-Organization



A. de Meijere, A. F. Khlebnikov, S. I. Kozhushkov, K. Miyazawa, D. Frank, P. R. Schreiner, C. Rinderspacher, D. S. Yufit, J. A. K. Howard, *Angew. Chem.* **2004**, *116*, 6715–6719; *Angew. Chem. Int. Ed.* **2004**, *43*, 6553–6557.

Liquid Crystalline Properties of (1*R*,9*R*)-(M)-(-)-[7]Triangulane-1,9-dimethanol and Derivatives?

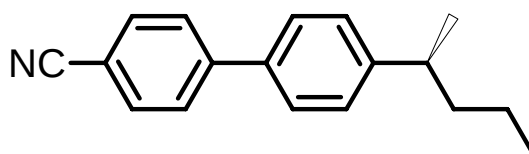


m. p. 129–131 °C, $[\alpha]_{\text{D}}^{20} = -660.0$ ($c = 1.04$, CHCl_3)

HTP = $\sim 13\mu\text{m}^{-1}$

(in base nematic mixture ZLI-1132², Merck)

HTP = $17.7\mu\text{m}^{-1}$



common in the
display industry

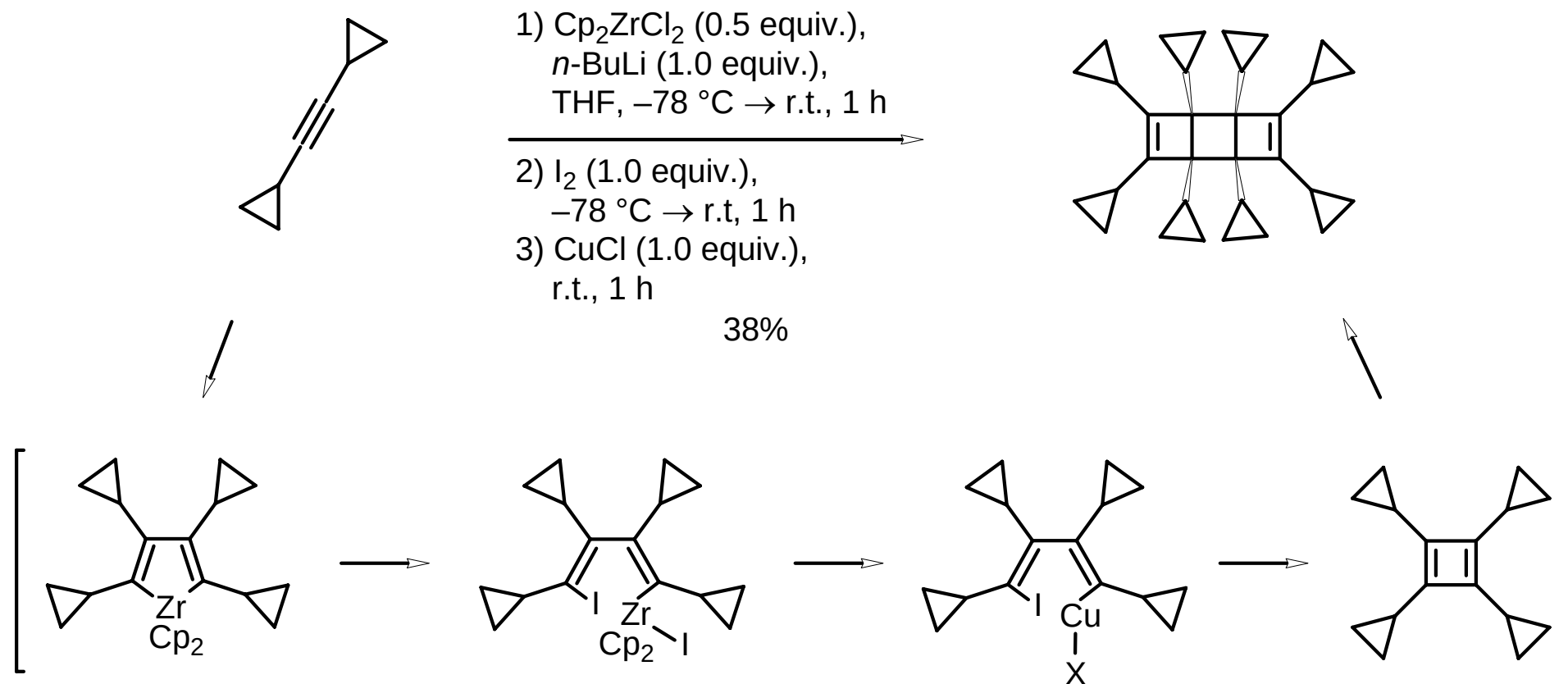
(*S*)-4-cyano-4'-(2-methylbutyl)-1,1'-biphenyl

HTP = $6.6\mu\text{m}^{-1}$

HTP = helical twisting power

S. I. Kozhushkov, K. Miyazawa, A. de Meijere 2004

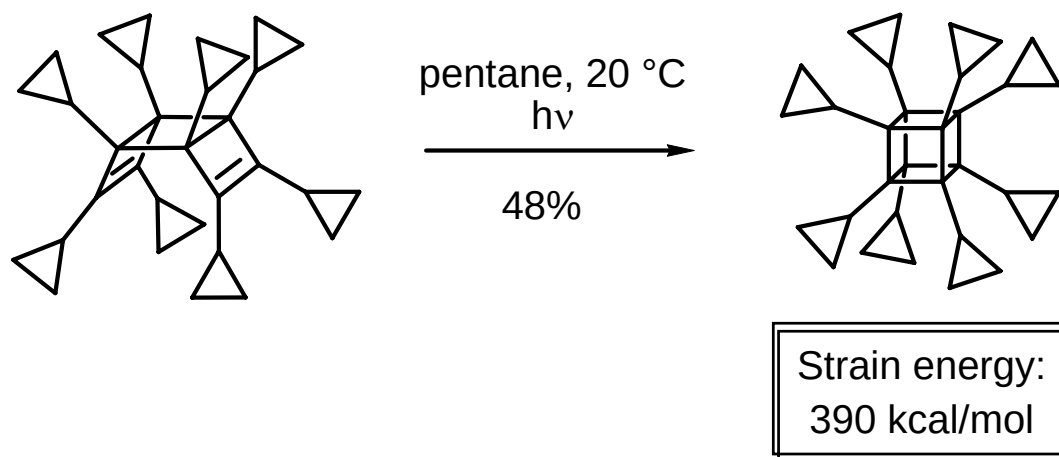
***syn*-Octacyclopropyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene for Fun**



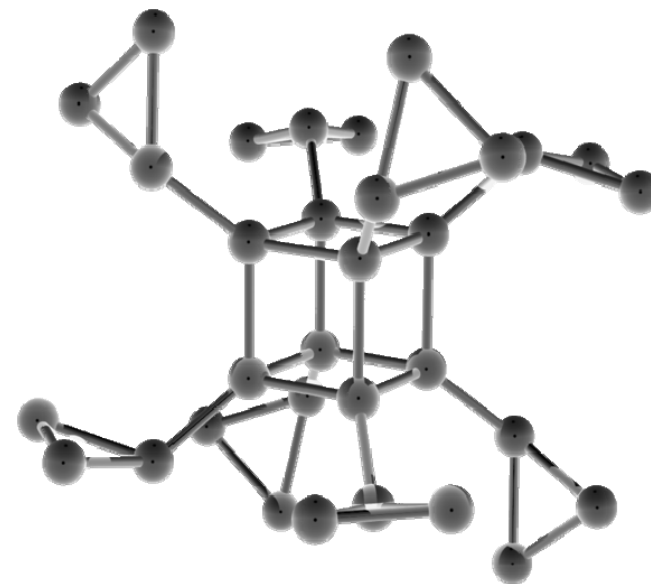
S. Redlich, D. Frank, A. de Meijere 2006, to be published.

Real Fun and Energy – Octacyclopropylcubane

Dedicated to Professor Philip E. Eaton on the occasion of his 70th birthday



Dec. >250 °C
Stable towards AgBF_4 , $[\text{Rh}(\text{COD})\text{Cl}]_2$
 $E_{1/2}$ (SCE) = 2.15 V (irrev.)
For comparison cubane $E_{1/2}$ (SCE) = 1.73 V

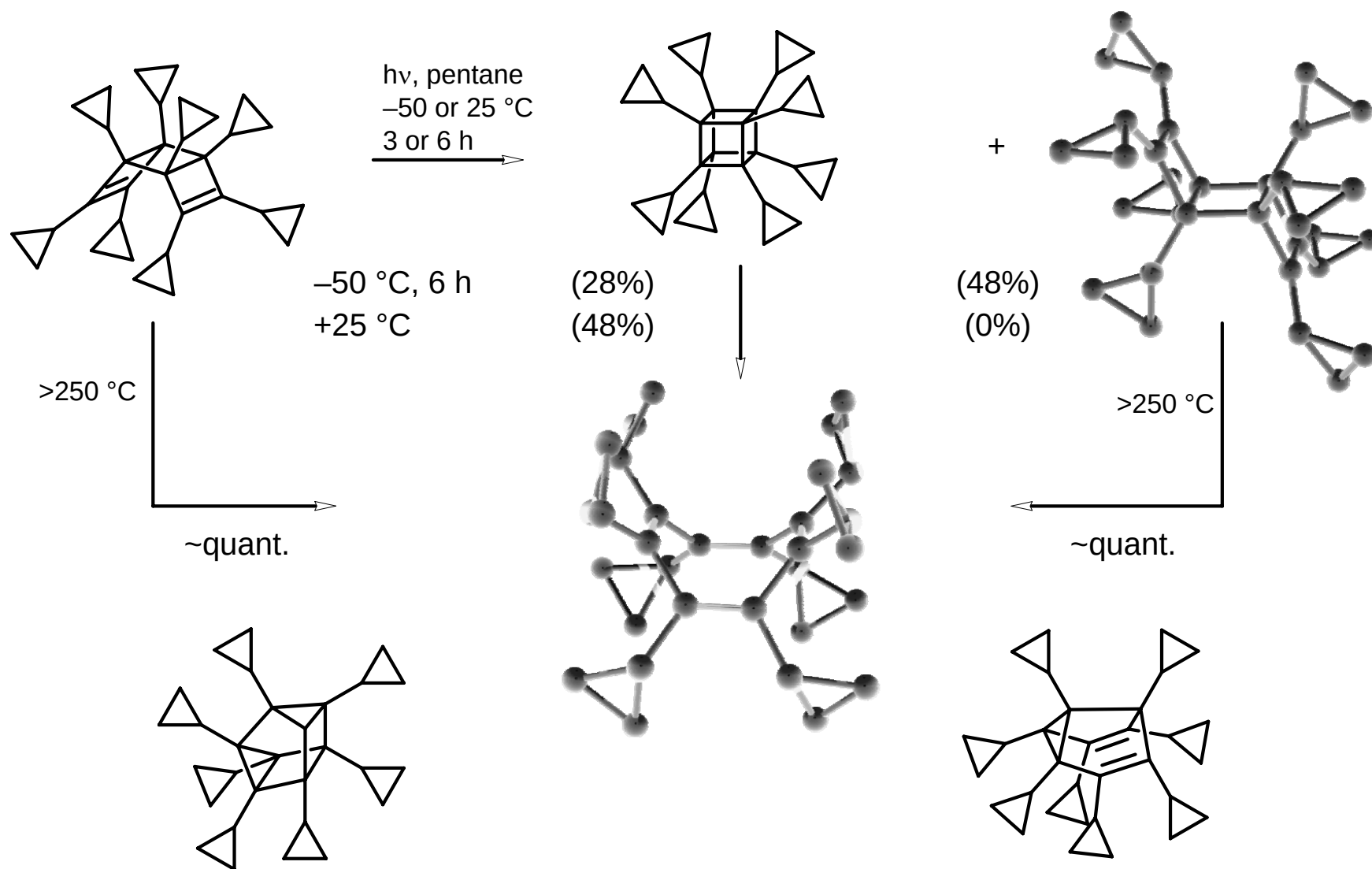


For reviews on cubane and its derivatives see:

- 1) P. E. Eaton, *Angew. Chem.* **1992**, 104, 1447–1462.
- 2) G. W. Griffin, A. P. Marchand, *Chem. Rev.* **1989**, 89, 997–1010.

A. de Meijere, S. Redlich, D. Frank, J. Magull, A. Hofmeister, H. Menzel, B. König, J. Svoboda, *Angew. Chem. Int. Ed.* **2007**, 46, in press.

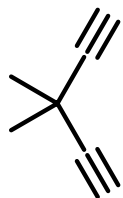
Temperature Dependence of the Photochemical Transformation of Octa-propyl-syn-tricyclooctadiene



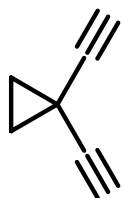
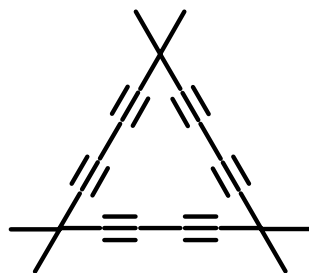
A. de Meijere, S. Redlich, D. Frank, et al. *Angew. Chem. Int. Ed.* **2007**, 46, 4574–4576.

Expected Increased Homoconjugation in Completely Spirocyclopropanated Macrocyclic Oligodiacetylenes

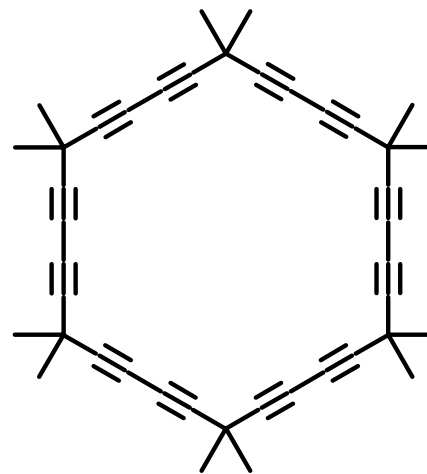
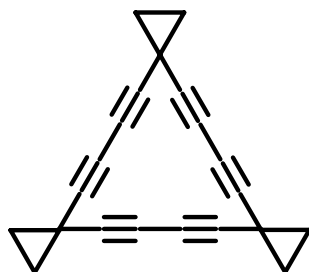
IE(π) from
PE Spectra



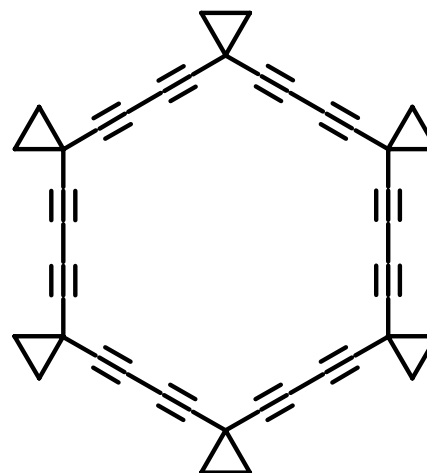
$$\Delta \text{IE}(\pi) = 0.6 \text{ eV}$$



$$\Delta \text{IE}(\pi) = 1.4 \text{ eV}$$

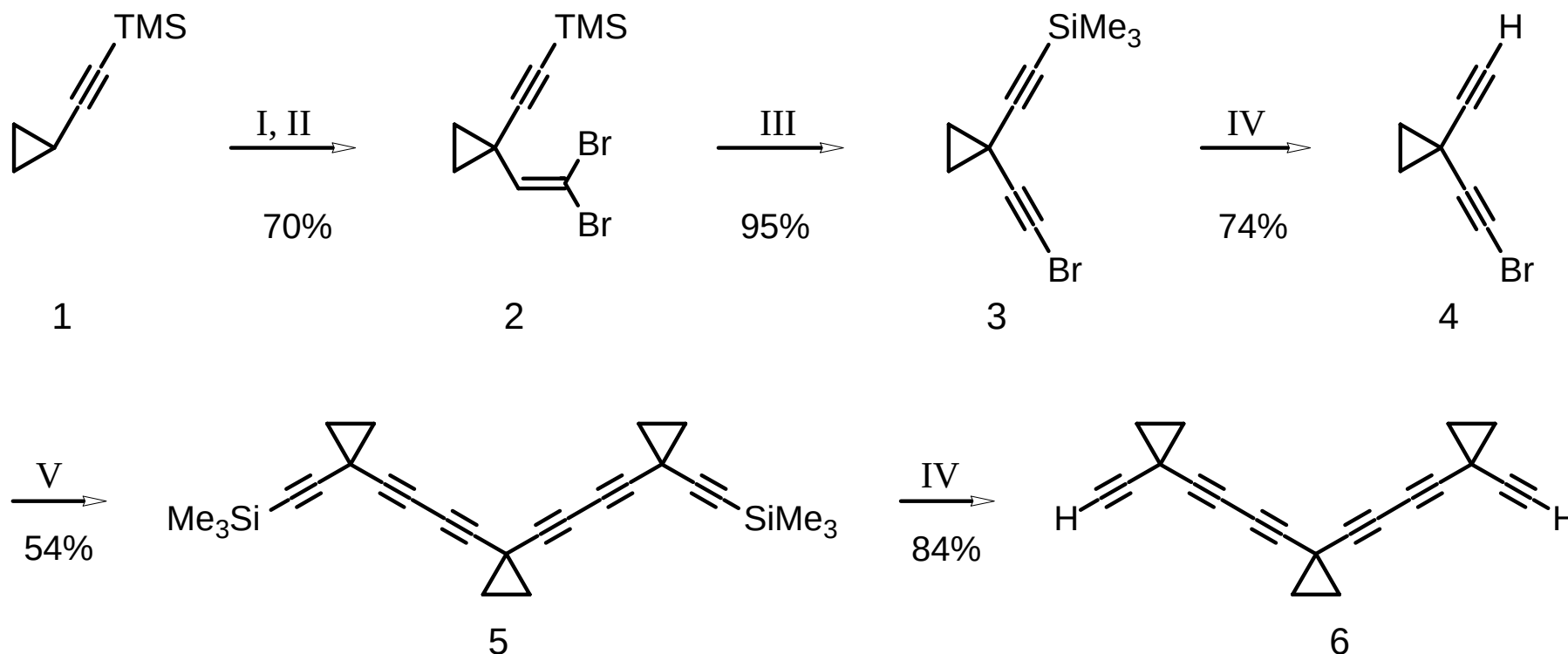


[1]



[1] L. T. Scott, M. J. Cooney, D. Johnels, *J. Am. Chem. Soc.* **1990**, *112*, 4054.

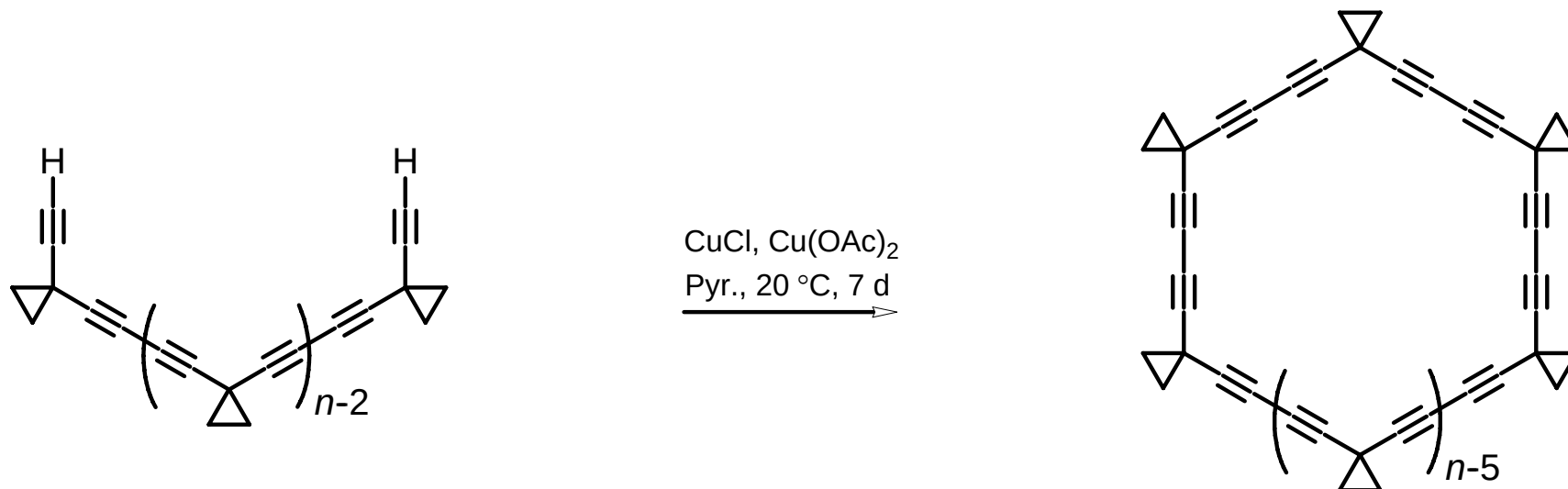
En Route to Perspirocyclopropanated Macrocyclic Oligodiacetylenes



I: 1) *n*-BuLi, Et₂O, 20 °C, 14 h; 2) DMF, 0 °C. – **II:** Zn, Ph₃P, CBr₄, CH₂Cl₂, 20 °C, 30 h. – **III:** *t*-BuOK, THF, –78 °C, 5 h. – **IV:** 3 equiv. KF • 2H₂O, DMF, 20 °C, 3h. – **V:** 1) 2 equiv. *n*-BuLi, Et₂O, 0 °C, 0.5 h; 2) 2 equiv. CuCl, THF, 0 °C, 2 h; 3) 2 equiv. **3**, pyridine, 20 °C, 4 h.

A. de Meijere, S. I. Kozhushkov, C. Puls, T. Haumann, R. Boese, M. J. Cooney, L. T. Scott, *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 869–871.

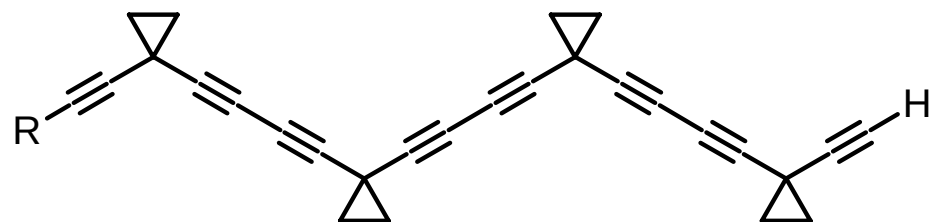
Completely Spirocyclopropanated Macrocyclic Oligodiacetylenes "Expanded [n]Rotanes"



Acyclic Precursor [n]	Exploding [n]Rotane [n]					
[2] + [3]	[5] : 35%	[6] : 20%	[7] : 13%	[8] : 3%	[9] : trace	
[3]	[6] : 39%	[9] : 8%				
[3] + [4]	[6] : 28%	[7] : 44%	[8] : 14%	[9] : trace		
[4]	[8] : 46%	[12] : 1%				
[5]	[5] : 70%	[10] : 0.2%				

A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott,
Chem. Eur. J. **1995**, *1*, 124–131.

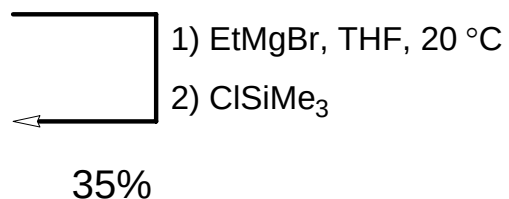
The Exploding [8]Rotane



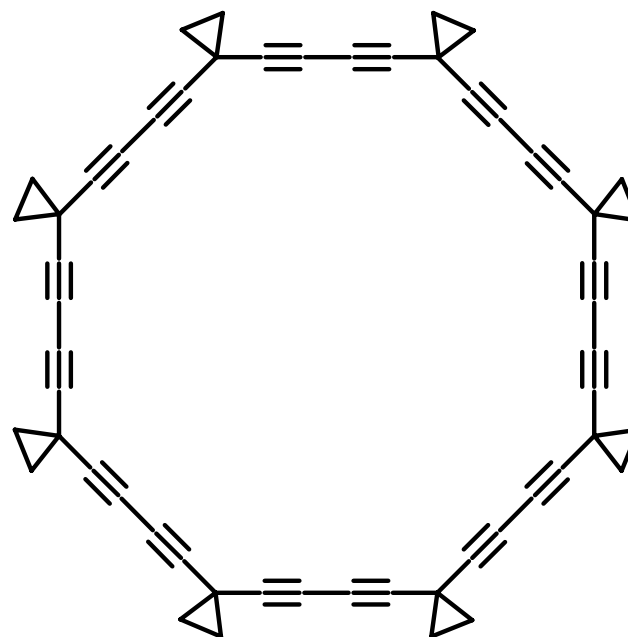
CuCl, Cu(OAc)₂
Pyr., 20 °C, 3 d

R = H

R = SiMe₃



55%



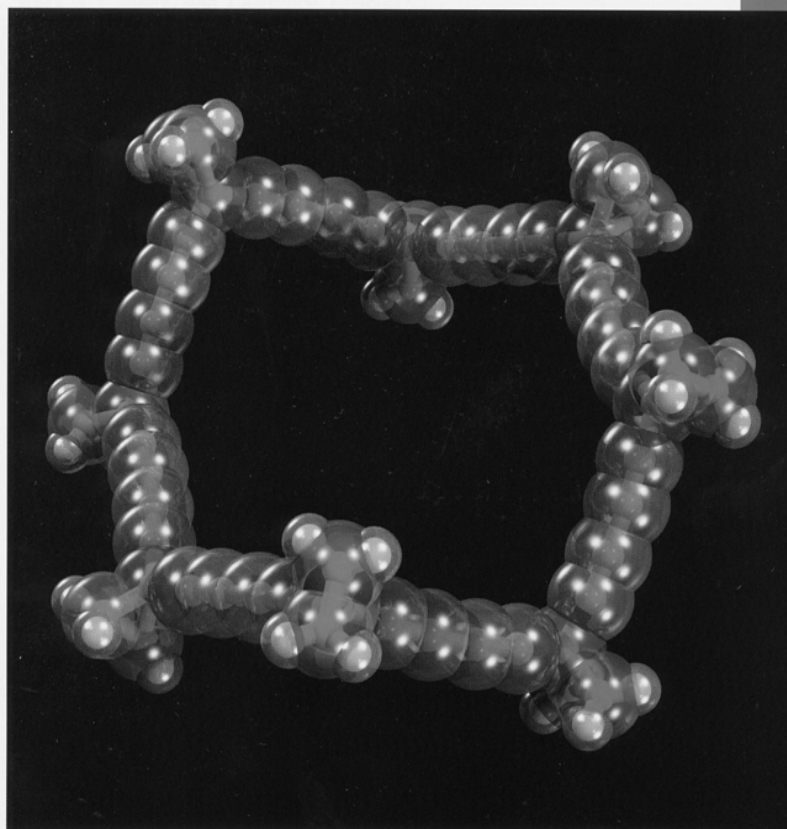
A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott,
Chem. Eur. J. **1995**, *1*, 124–131.

CHEMISTRY

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1/2

1995



Contributions by:

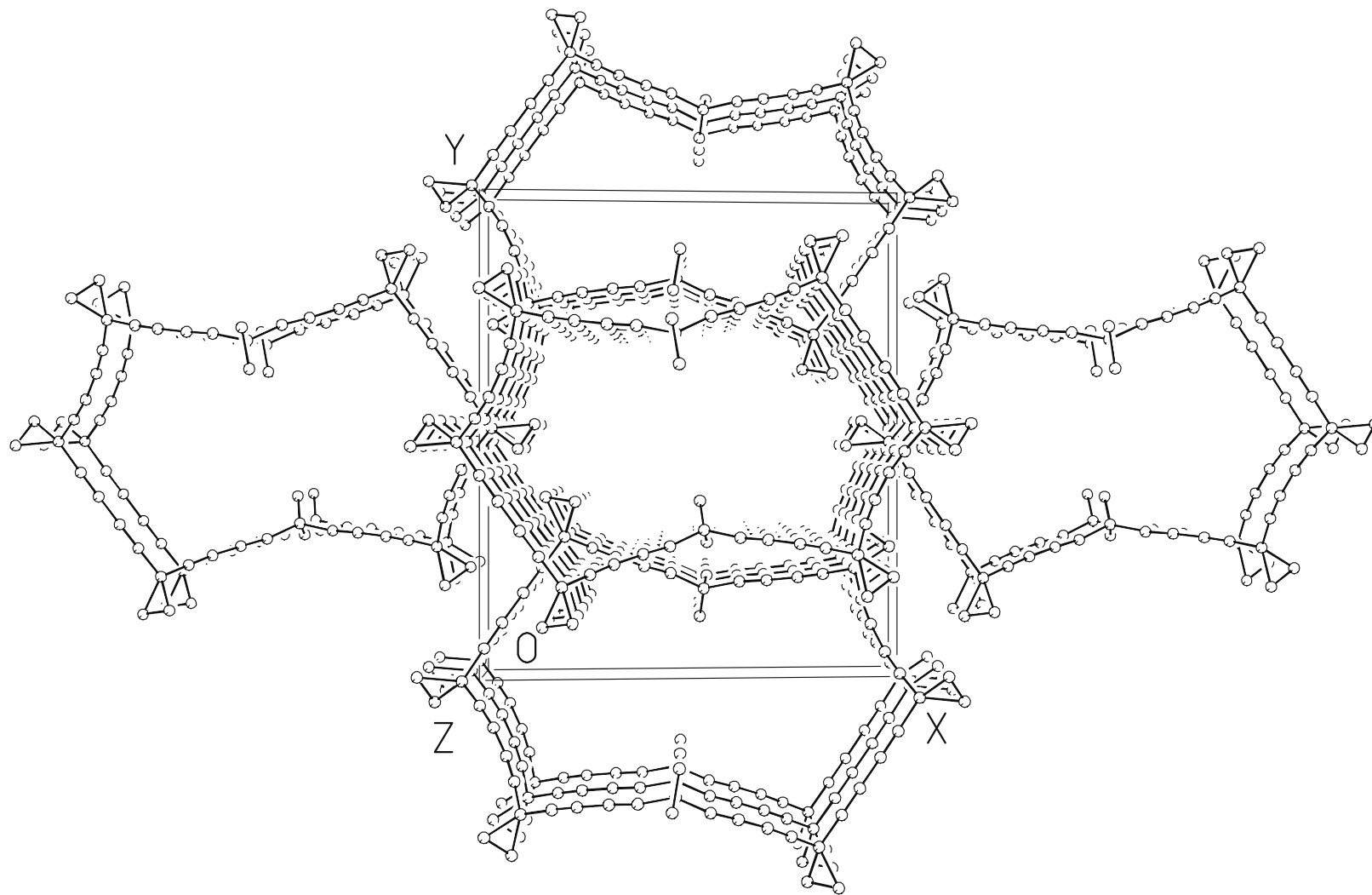
F. Diederich · R. Dronskowski · A. de Meijere/L. T. Scott · D. N. Reinhoudt ·
P. A. Jacobs · H. Waldmann



CEUJED 1 (2) 107-156 (1995) · ISSN 0947-6539 · Vol. 1 · No. 2 · May 1995

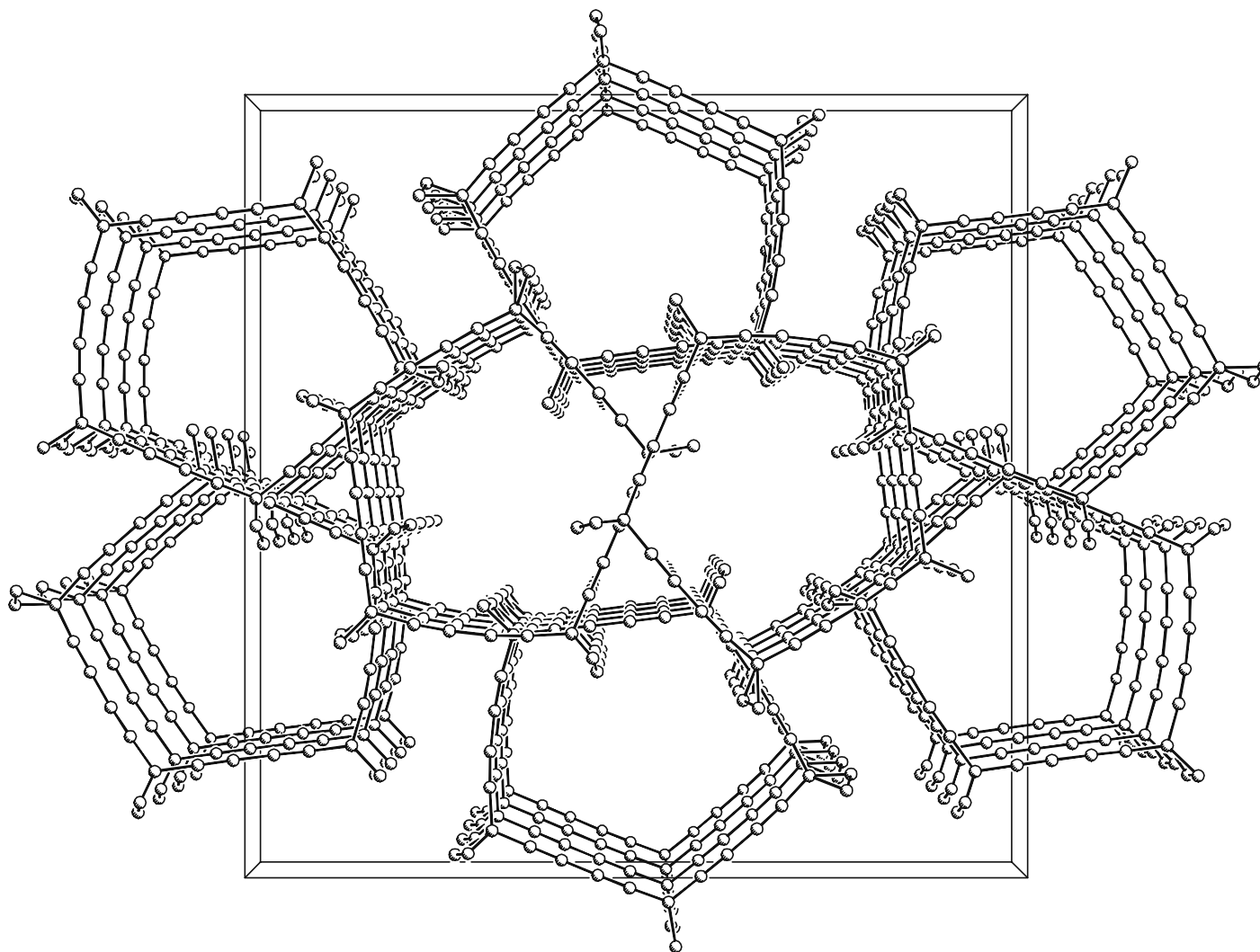
CEJ_1995

Crystal Packing of Exp[8]rotane



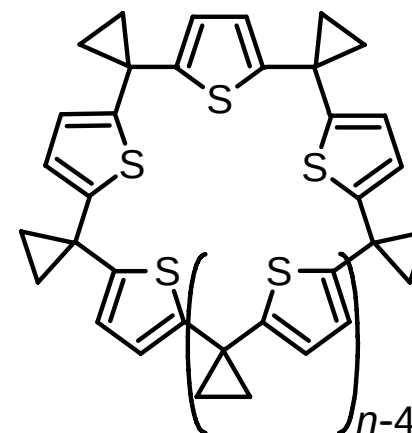
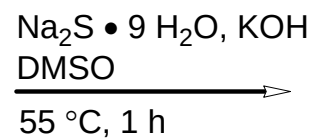
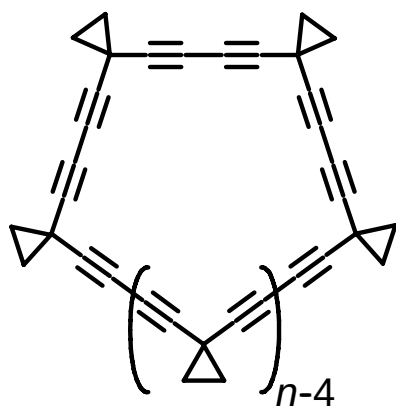
A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, *Chem. Eur. J.* **1995**, *1*, 124–131.

Crystal Packing of Exp[5]rotane



A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, *Chem. Eur. J.* **1995**, *1*, 124–131.

Cyclopropyl-Spaced Cyclic Oligothiophenes



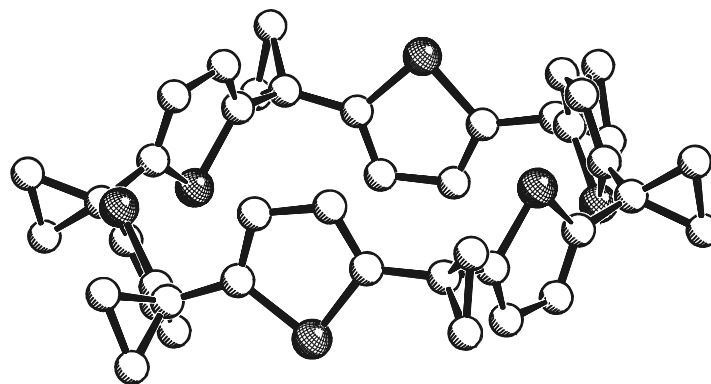
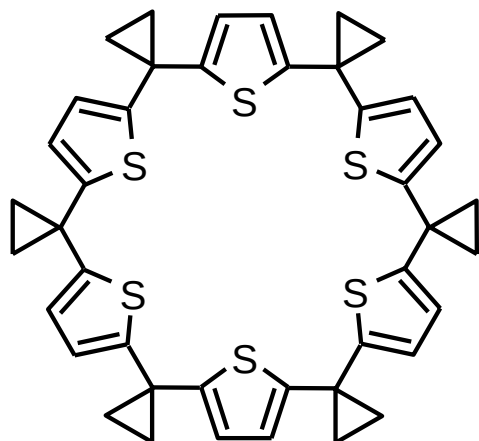
$n = 5$ 22%

$n = 6$ 59%

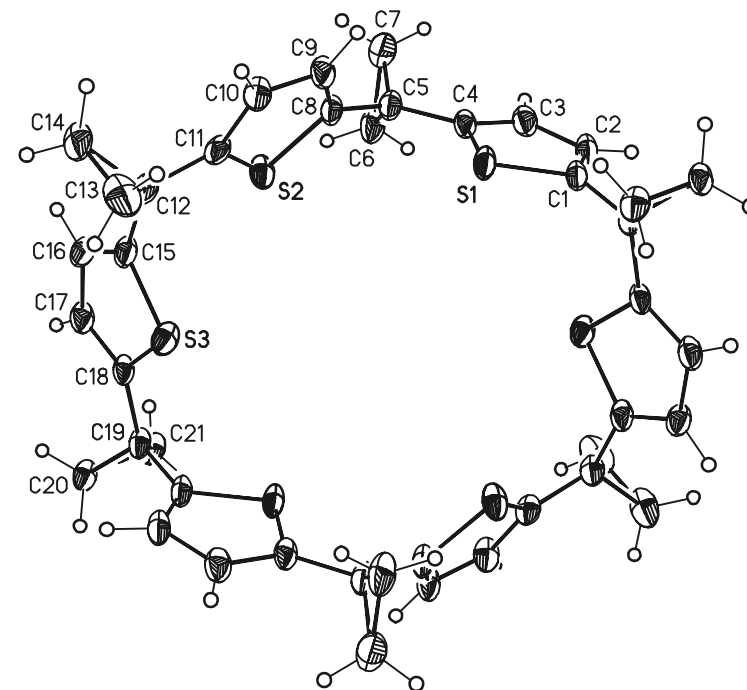
$n = 7$ 58%

S. I. Kozhushkov, T. Haumann, R. Boese, B. Knieriem, S. Scheib, P. Bäuerle, A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 781–783.

A Crown of Thiophenes ?

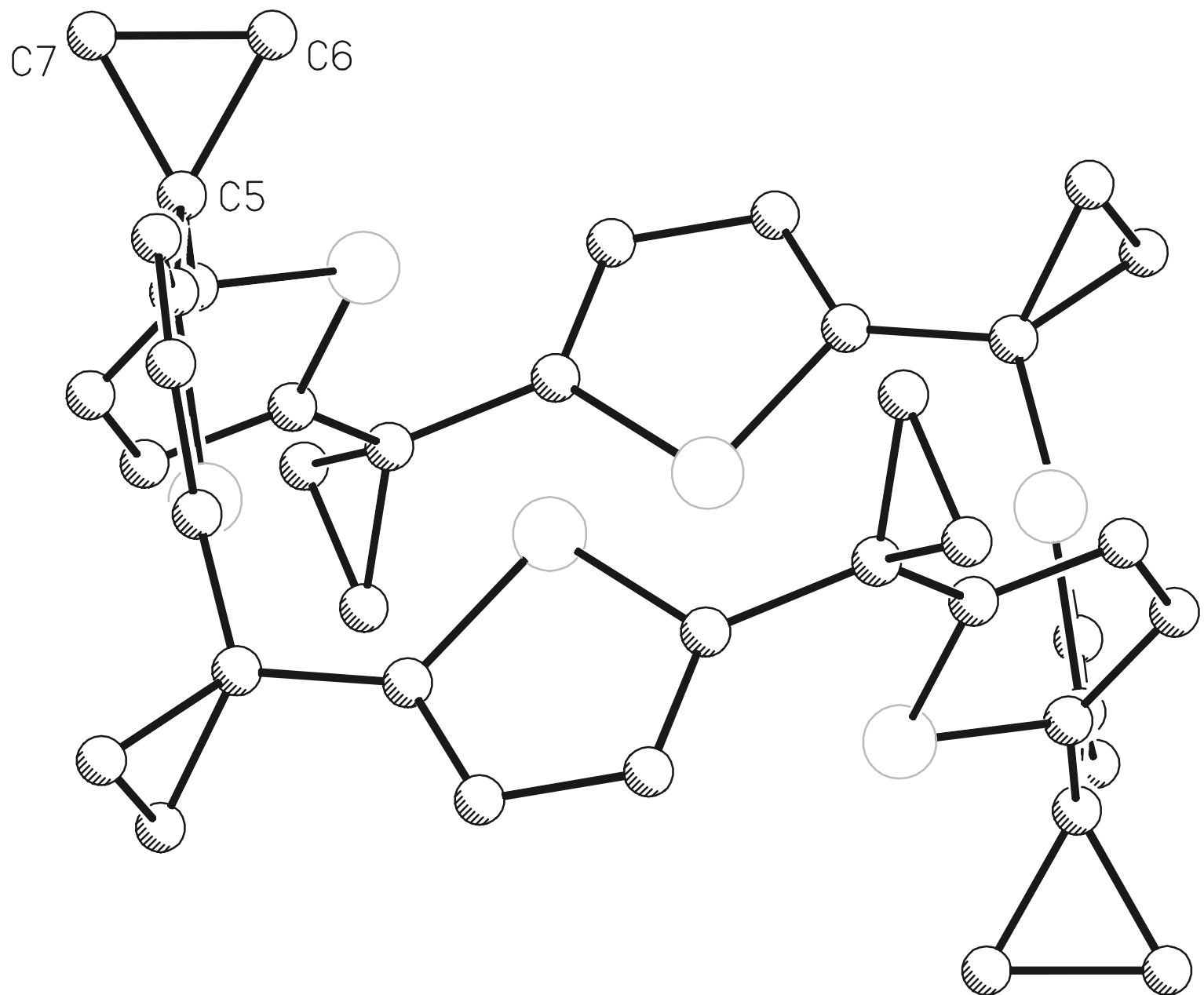


MM 2 calculation

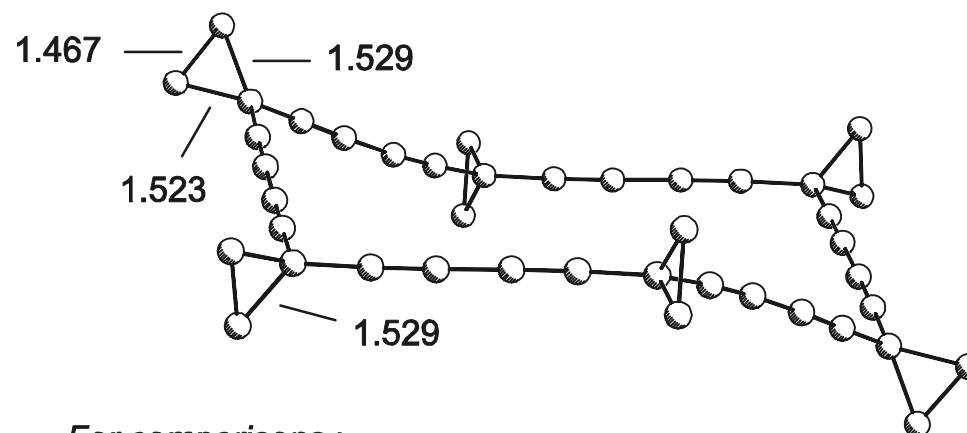
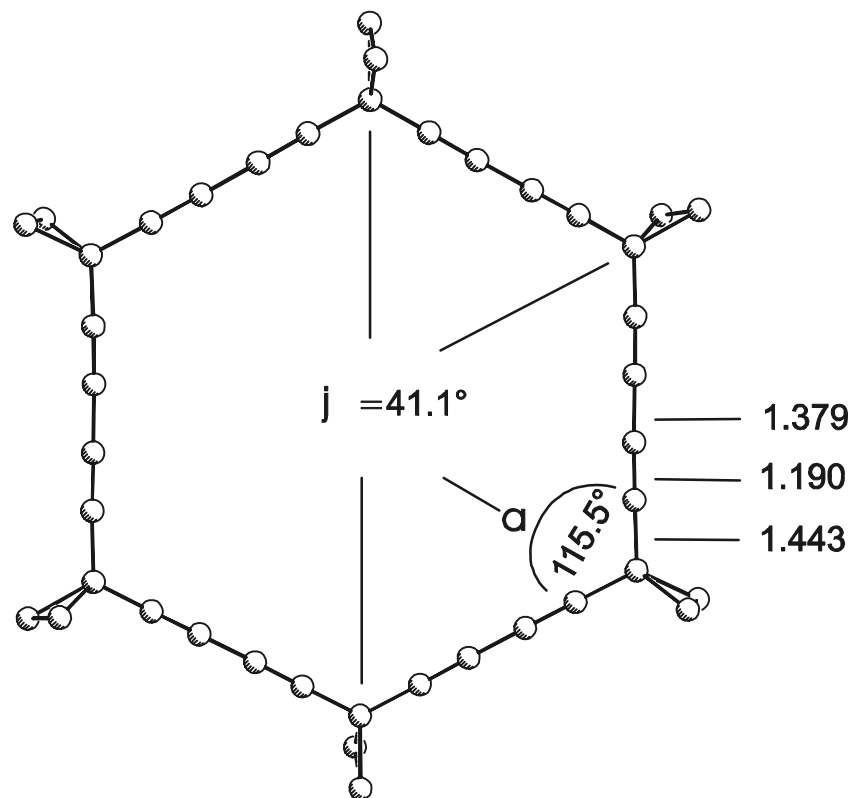


X-Ray structure Analysis

S. I. Kozhushkov, T. Haumann, R. Boese, B. Knieriem, S. Scheib, P. Bäuerle, A. de Meijere, *Angew. Chem.* **1995**, *107*, 859–862;
Angew. Chem. Int. Ed. Engl. **1995**, *34*, 781–783.



Hexaspiro[2.4.2.4.2.4.2.4.2.4]dotetraconta-4,6,11,13,18,20,25,27,32,34,39,41-dodecayne – – The Exploding [6]Rotane (Exp[6]rotane)



For comparisons :

Cyclohexane $j = 55.1^\circ$, $\alpha = 111.4^\circ$

[6]Rotane $j = 54.6^\circ$, $\alpha = 111.5^\circ$

A. de Meijere, S. Kozhushkov, C. Puls, T. Haumann, R. Boese, M. J. Cooney, L. T. Scott,
Angew. Chem. Int. Ed. Engl. **1993**, 33, 869–871.

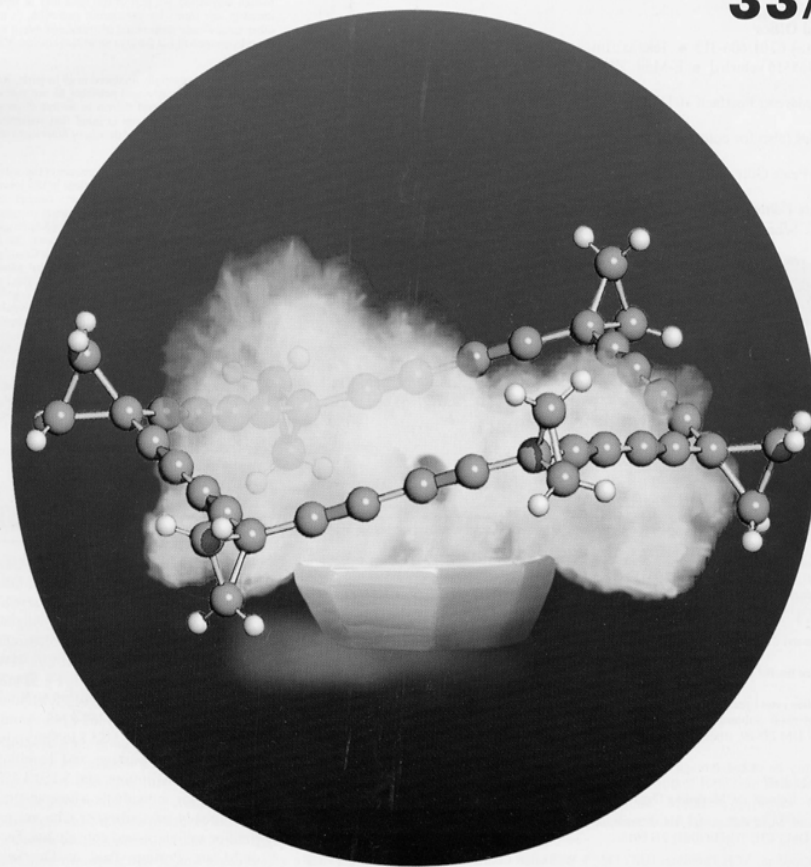
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International Edition in English

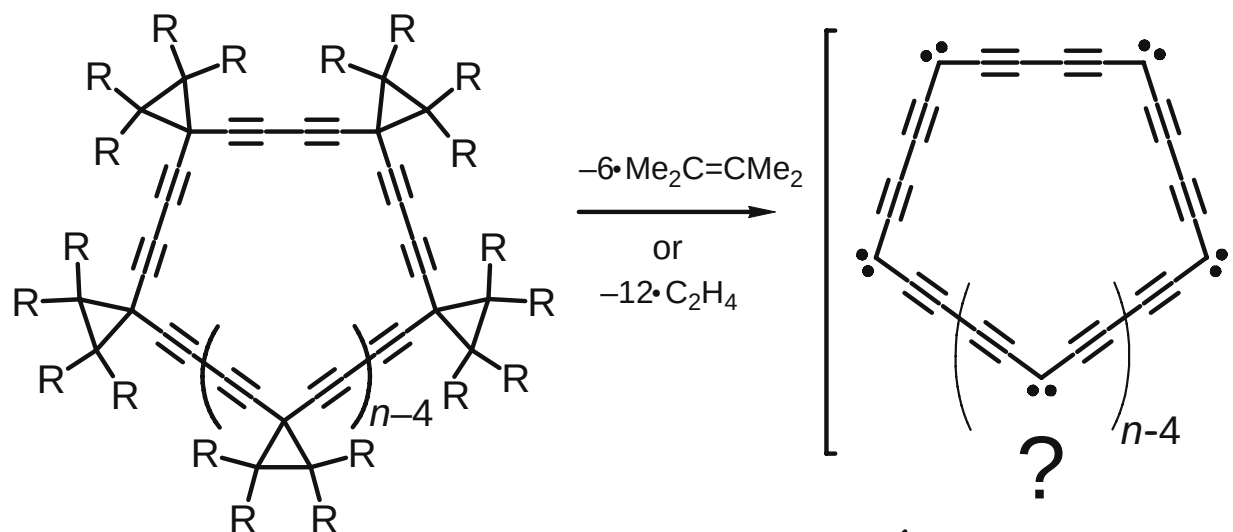
1994
33/8



Reviews: Cyclodextrins · Structure Correlation Method
Highlights: Methane Monooxygenase · Fullercages

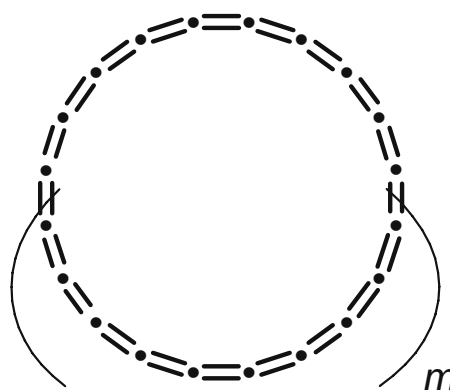
ACIEAY 33 (8) 793-902 (1994) · ISSN 0570-0833 · Vol. 33 · No. 8 · Mai 2, 1994

Potential Approaches to Cyclo-C₃₀ and Cyclo-C₆₀ Carbon Clusters



30 $\text{R} = \text{Me}, n = 6$
32 $\text{R} = \text{H}, n = 12$

34 $n = 6$
35 $n = 12$



36 *cyclo-C₃₀* ($m = 2$)
37 *cyclo-C₆₀* ($m = 5$)

Coworkers

Bicyclopropylidenes and Triangulanes

Thomas Späth
Stefan Bräse
Hanno Nüske

Rene Scheurich
Lars Arve
Baris Yucel

Small Ring Architectures

Sergei I. Kozhushkov

Ingo Emme
Stefan Redlich

Heiko Schill
Daniel Frank

Natural Products and Analogues

Markus Kordes
Boris D. Zlatopolskiy
Oleg V. Larionov
Sergei I. Kozhushkov

Collaborations

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Prof. Alexander F. Khlebnikov
Dr. Kazutoshi Miyazawa, Chisso Corp.
Dr. Mazen Es-Sayed, BAYER AG
Prof. Axel Zeeck, Göttingen

Prof. Christian Griesinger, Göttingen
Dr. Uwe Reinscheid
Prof. Stefan Bräse, Karlsruhe

X-ray Crystal Structures

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Dr. Dimitri S. Yufit, Durham
Prof. George Sheldrick, Göttingen
Prof. Jörg Magull, Göttingen

Computations

Prof. Peter R. Schreiner, Gießen

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