Restricting rotation of triple bond through π-stacking interactions in molecular hinges

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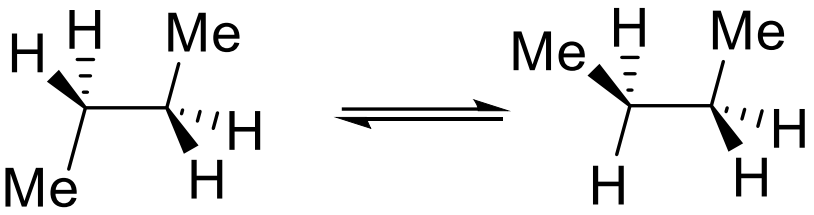
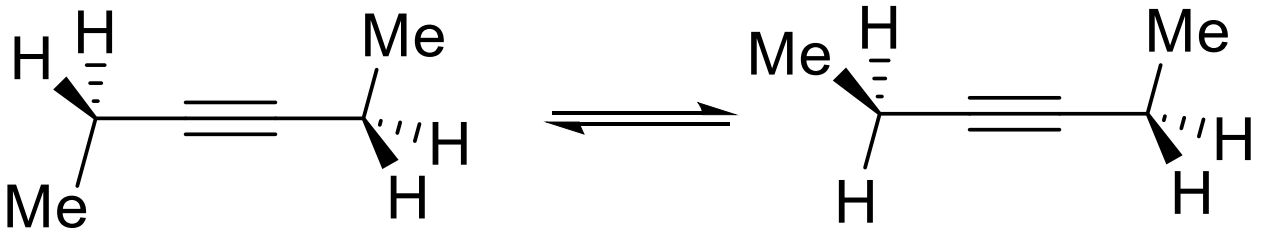
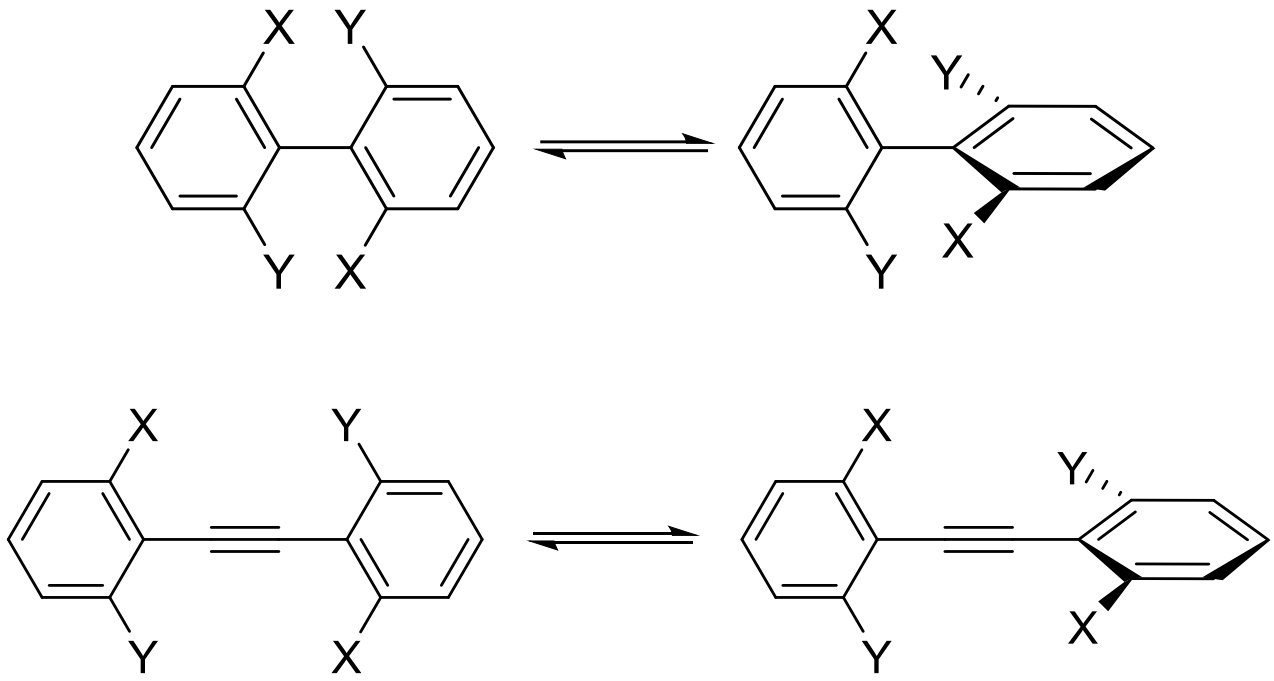




Organic stereochemistry is dominated by stereochemistry of C-C and C=C


X
Y
Y
X
X
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Y
X
X
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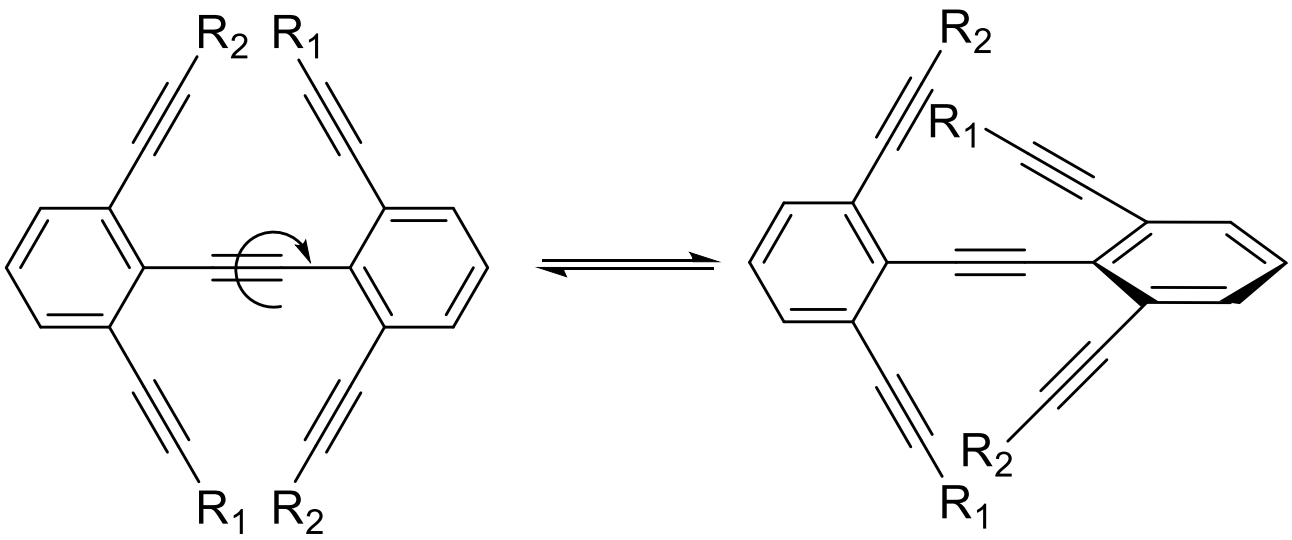
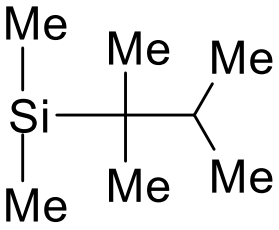
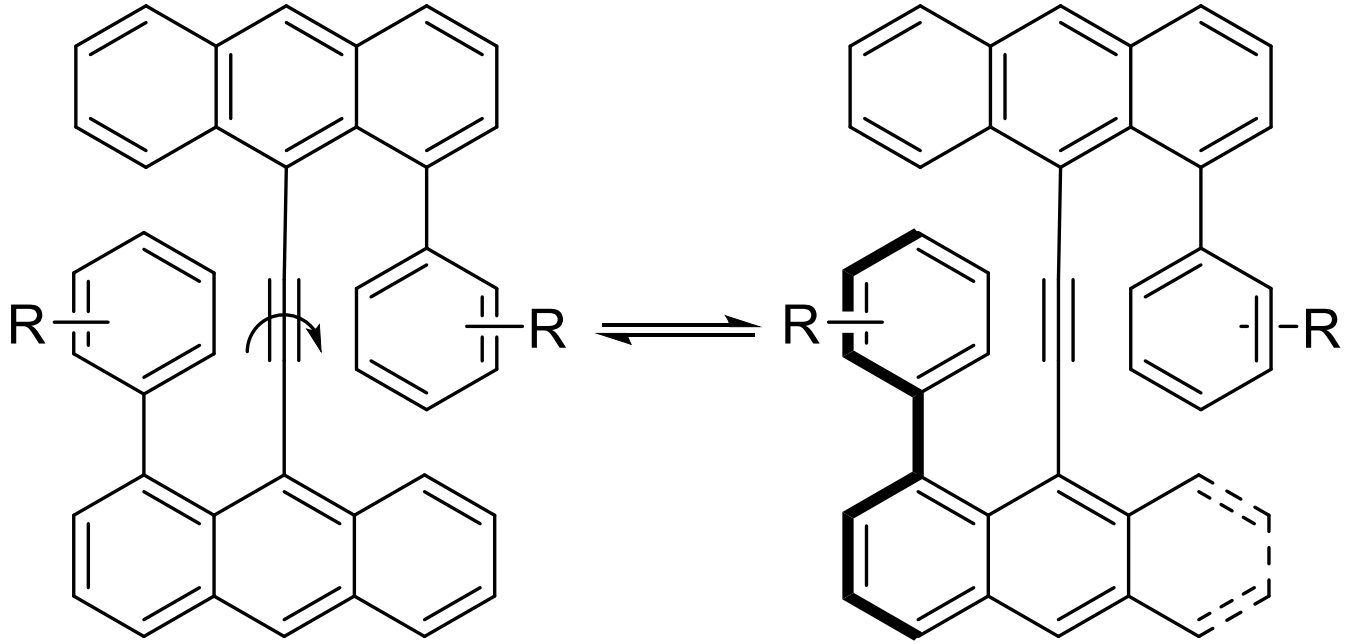
Y
X



$R_1 = Si(Me)_3$ $R_2 =$ 

Rotational barrier = 78 kJ/mole

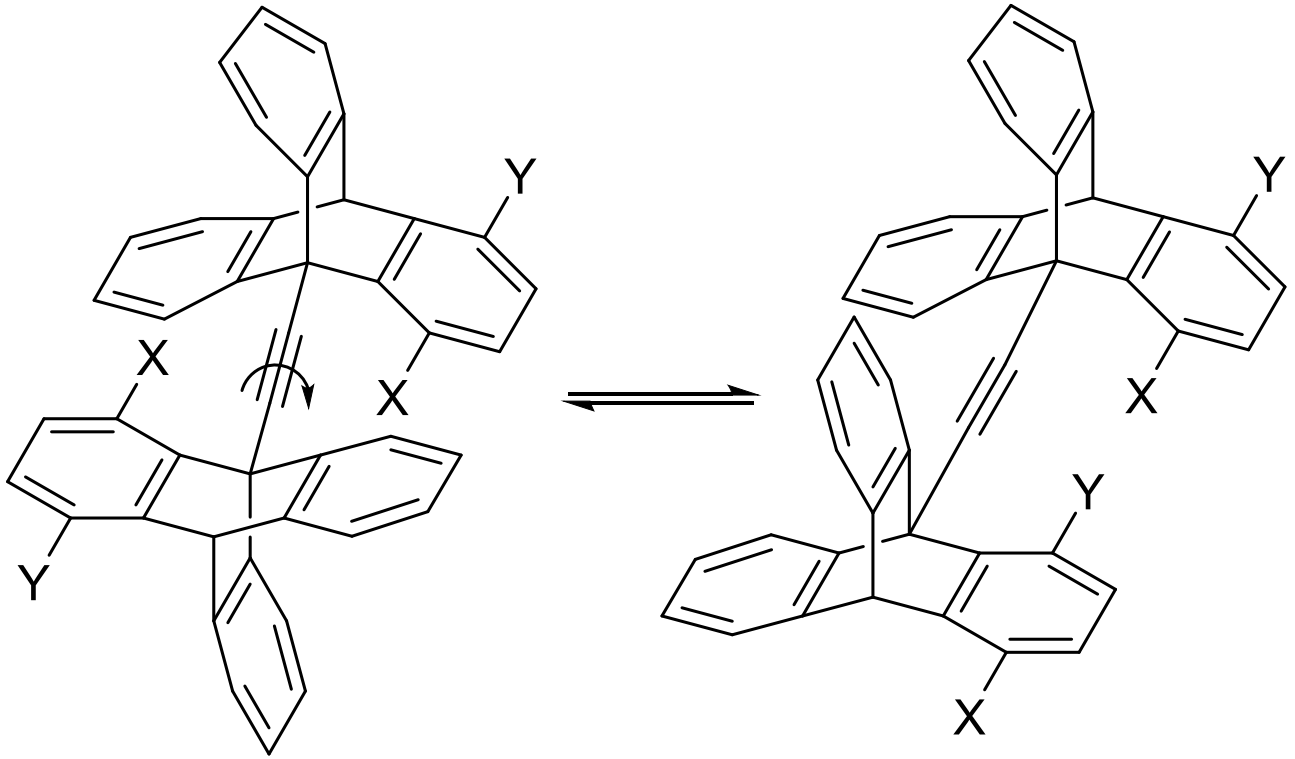
Vollhardt, K. P. C.; Chem. Commun., 2005, 2606.



R = 4-Me, 4-*i*-Pr, 4-*t*-Bu

Activation barrier: 45-51 kJ/mole

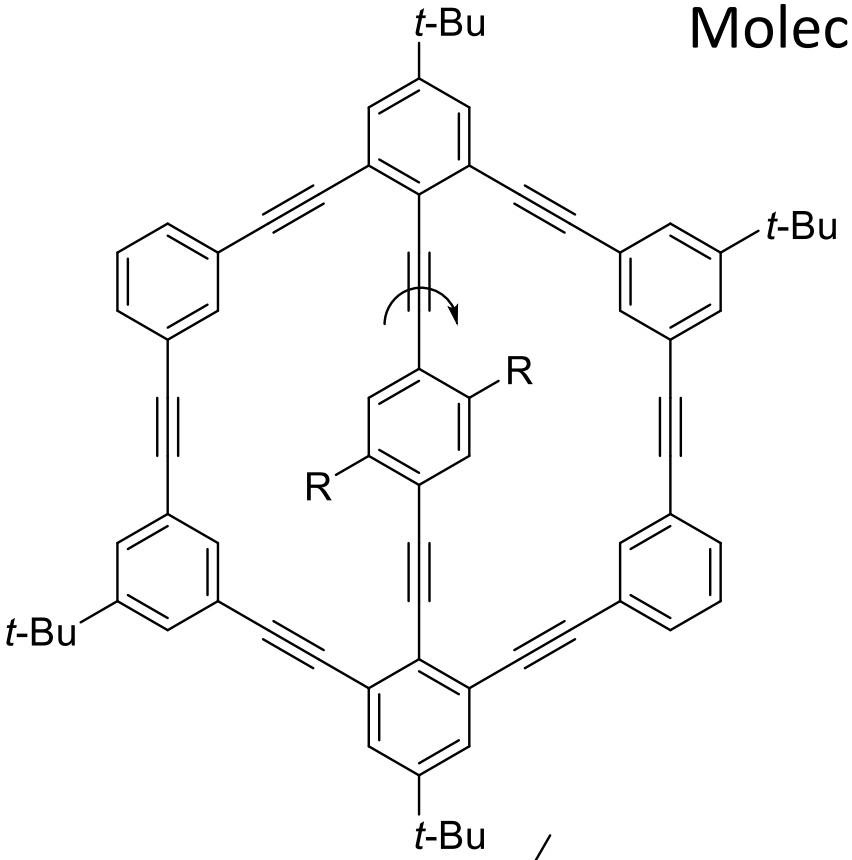
Toyota, S., et.al., *Tetrahedron Lett*, **2003**, *44*, 7775; *Bull. Chem. Soc. Jpn*, **2005**, *78*, 917.



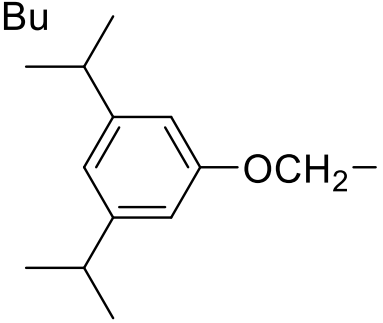
For various X and Y activation barrier range from 42-79 kJ/mole

Vögtle, F., *et.al., Angew. Chem. Int. Ed*., **1979**, *18*, 159.
Toyota, S., *et.al., Bull. Chem. Soc. Jpn*, **2000**, *73*, 205 and 2591.
Toyota, S., *et.al., Tetrahedron Lett*., **2001**, *57*, 3521.

Molecular turnstile



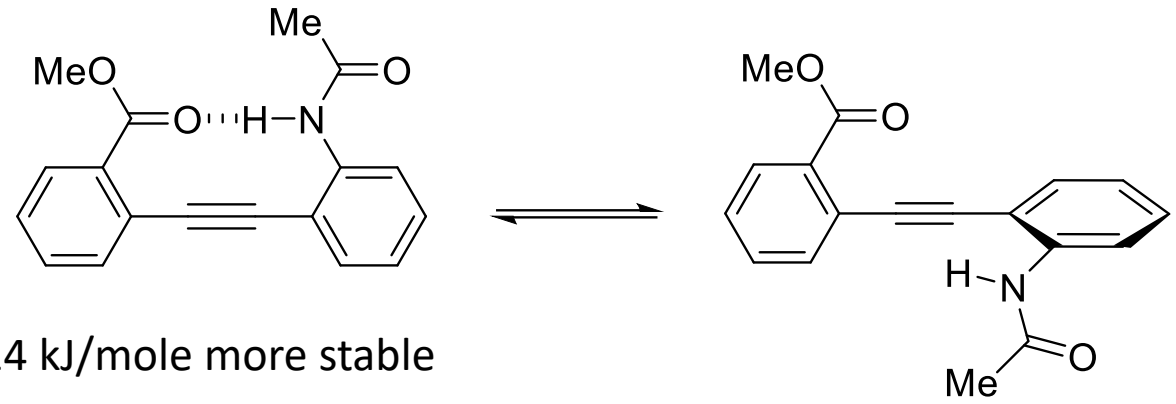
R = CH_3OCH_2-



Barrier = 86.2 kJ / mole

Moore, J. S., *et.al., J. Am. Chem. Soc*., **1995**, *117*, 10662.

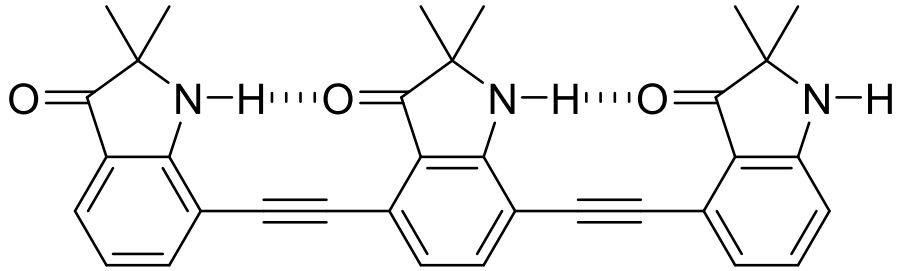
Restricting rotations and freezing conformations through weak bondings.



24 kJ/mole more stable

Activation barrier for rotation 30 kJ/mole , 12 times more than diphenylethyne

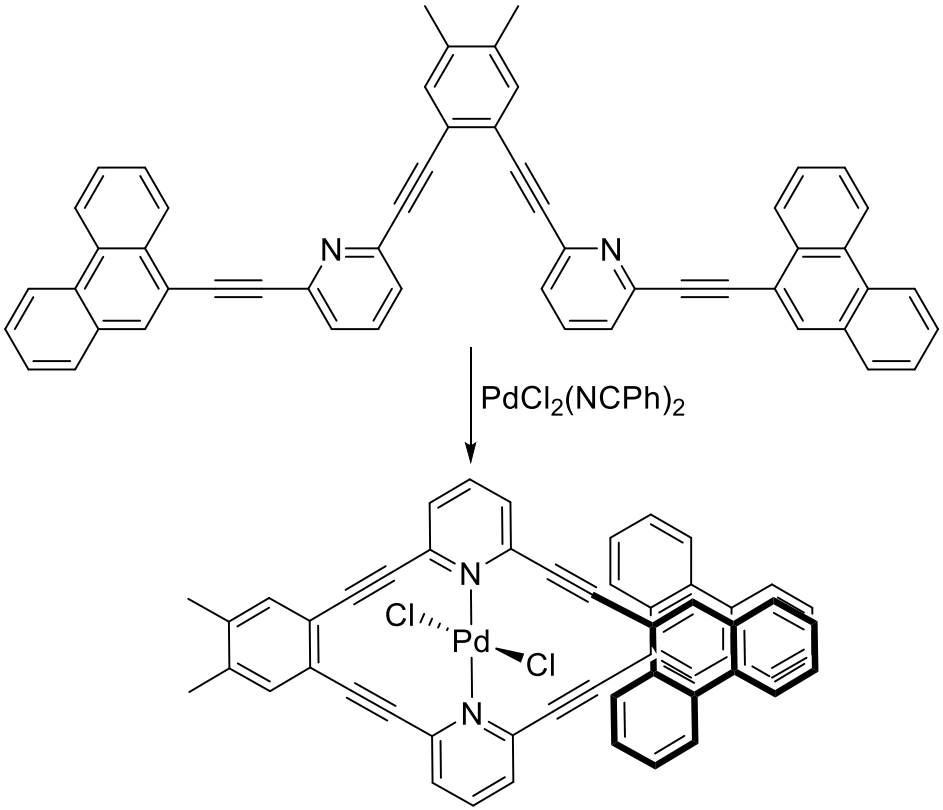
Yang, X. et.al; *chem. commun*., **2003**, 56; *J. Am. Chem. Soc*., **2004**, *126*, 3148

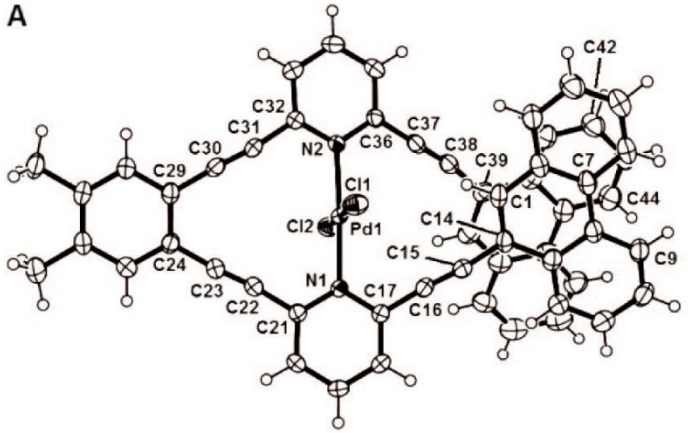


extended H-bonding

Hamilton, A. D. *et.al., J. Am. Chem. Soc.* **2009**, *131*, 4566.

Covalent bond mediated restriction of conformational mobility

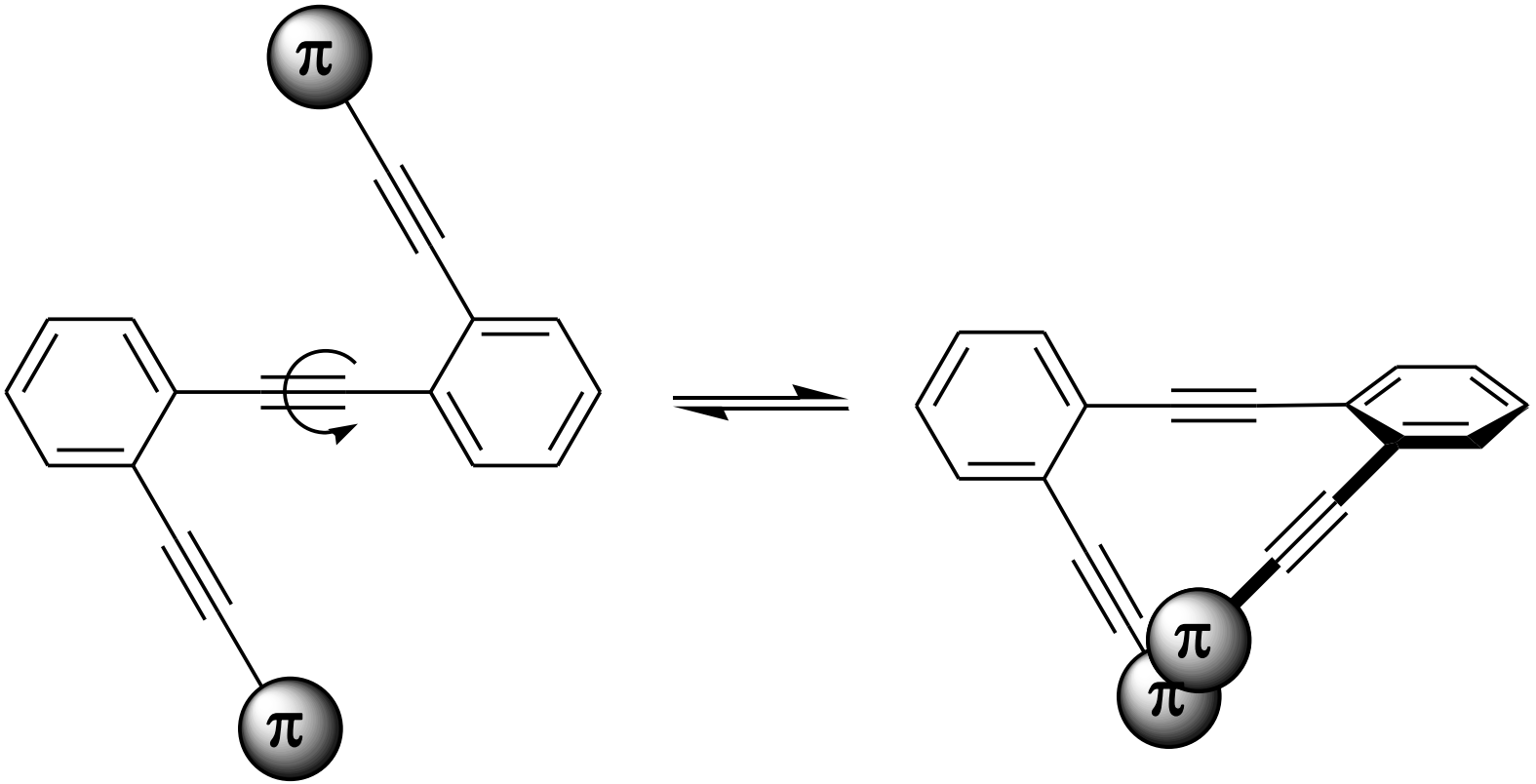




E. Bosch, *et. al., J. Org. Chem*. **2008**, *73*, 3931-3934

Why not use weak non-covalent forces instead of repulsion to restrict bond rotation?

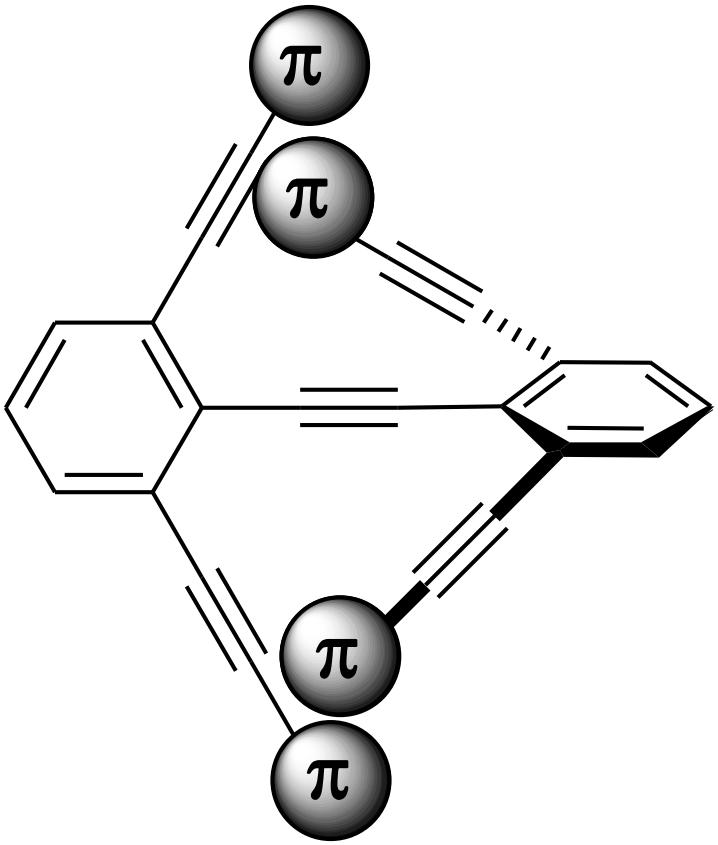
The concept of stabilization through π–π interaction



open form

π-stacked form

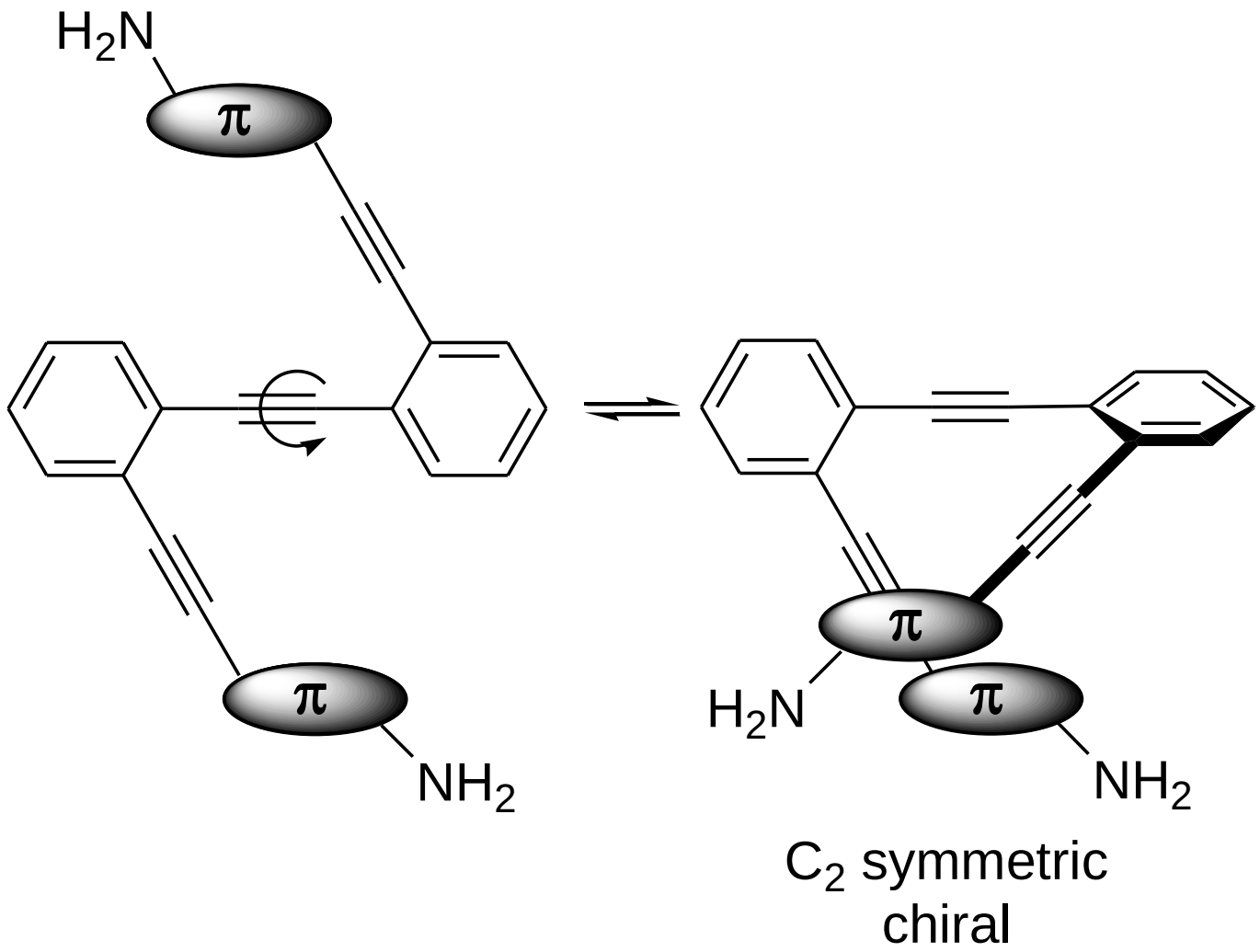
Inter-locked π-Stacking System



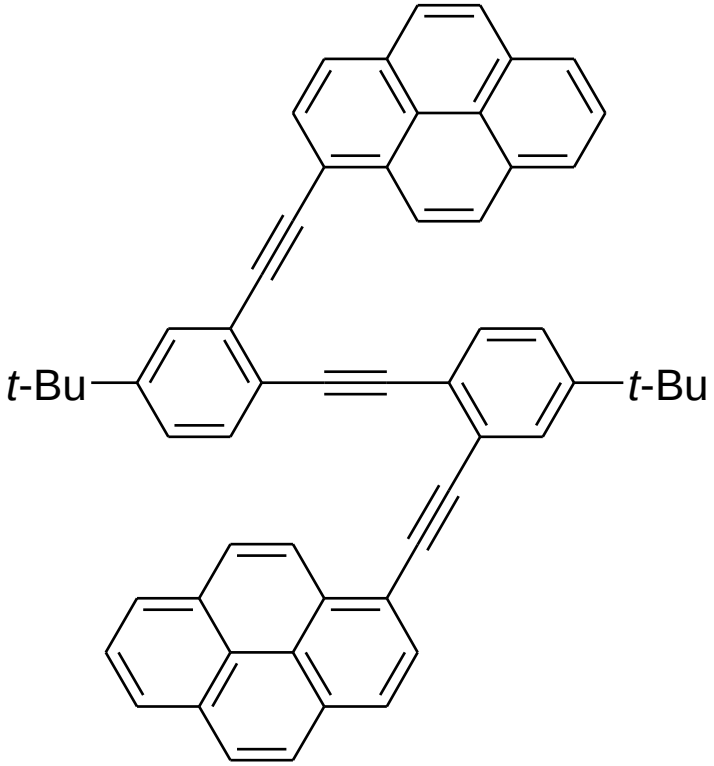
multiple π-stacked systems

Questions to be addressed:

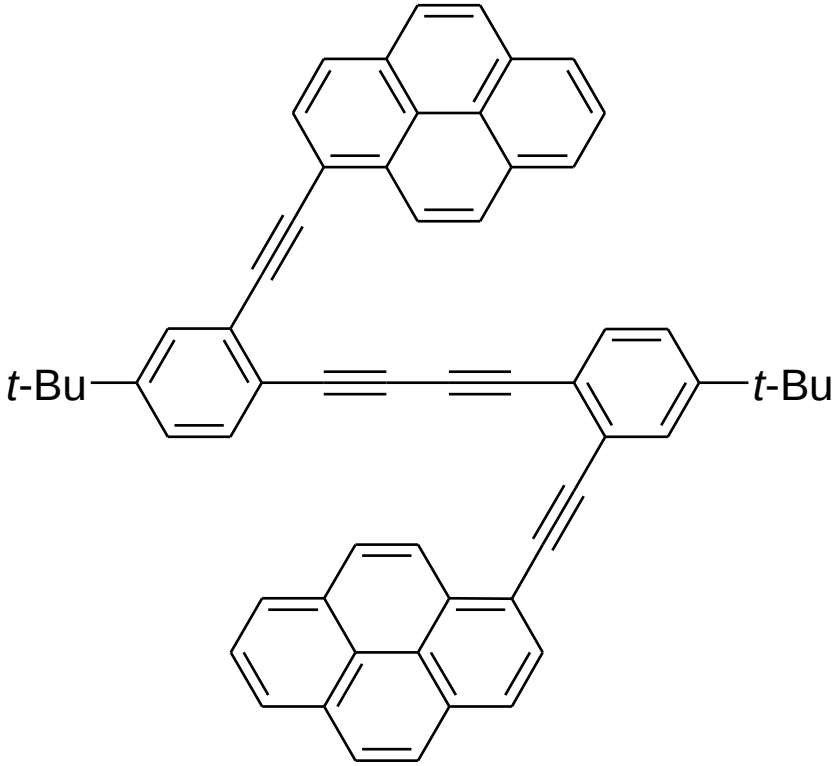
- Can π–stacking interaction stabilize rotational isomers?
- Can multiple π-stacking interactions lead to restricted rotation of the acetylenic bond?
- How much is the stabilization arising due to π-stacking interaction?
- What is the population distribution of the conformational isomers arising out of restricted rotation of the acetylenic bond?
- What are the geometric factors that can result in strong π- stacking interactions leading to isolation of rotational isomers?
- Can atropisomers be resolved in acetylenic systems?


H2N
π
π
NH2
π
π
H2N
NH2
C2 symmetric
chiral

TARGETS WITH ETHYNYLPYRENE ARMS

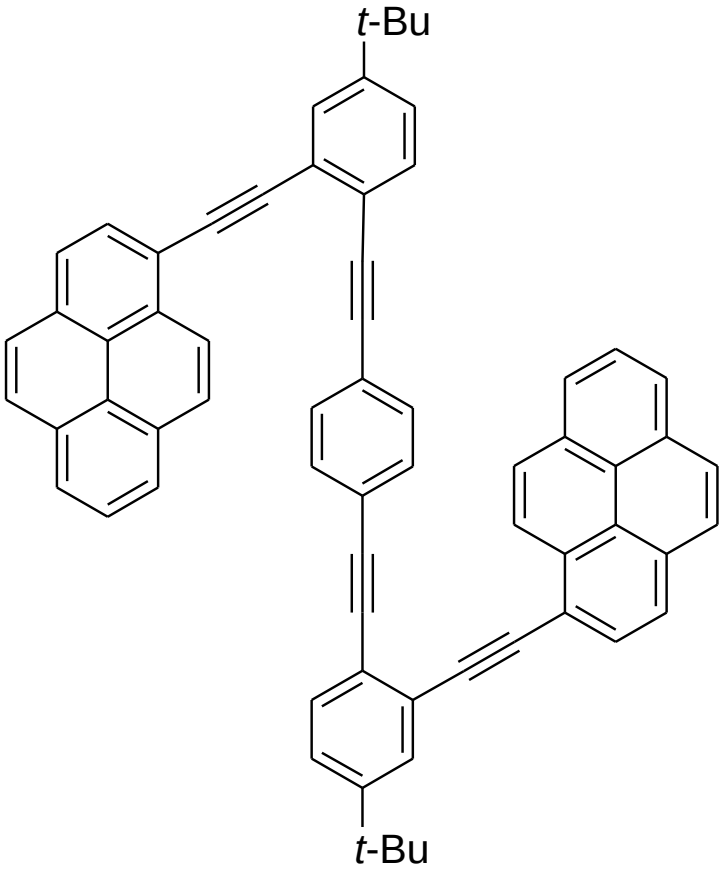


1



2

Two more targets with *p*-phenylene spacer as probes



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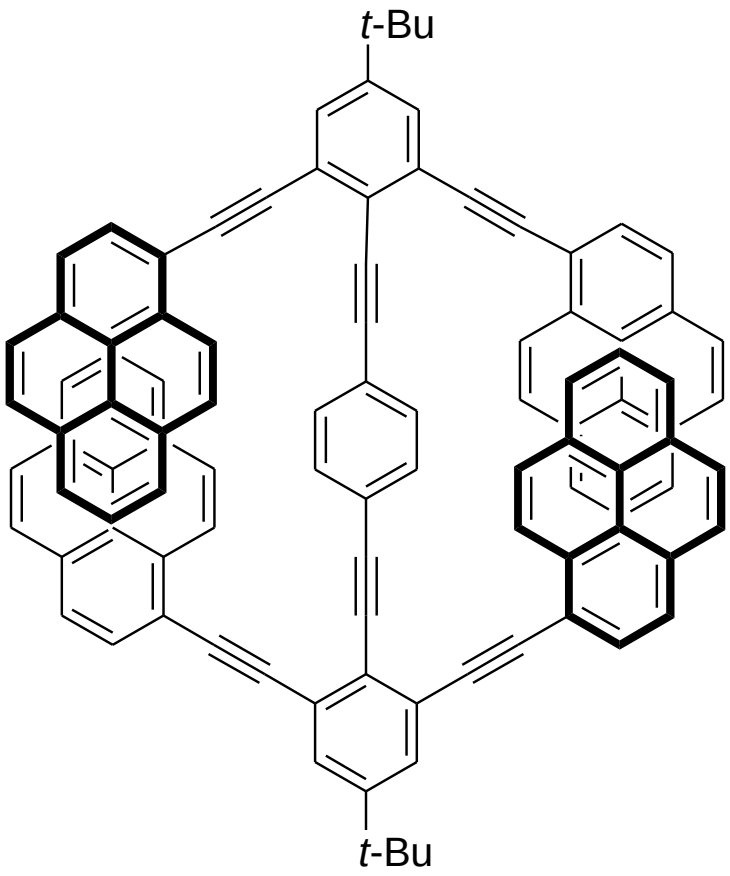
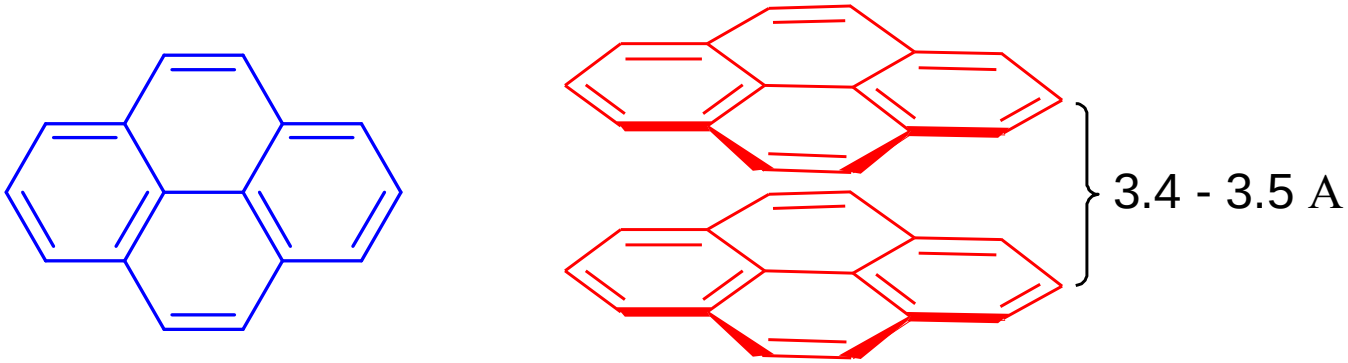


4

Why pyrene?



Pyrene – prototypical fluorescent molecule

Pyrene derivatives - widely used fluorescent probe

Pyrene template - used in supramolecular chemistry

Photophysical properties - well understood

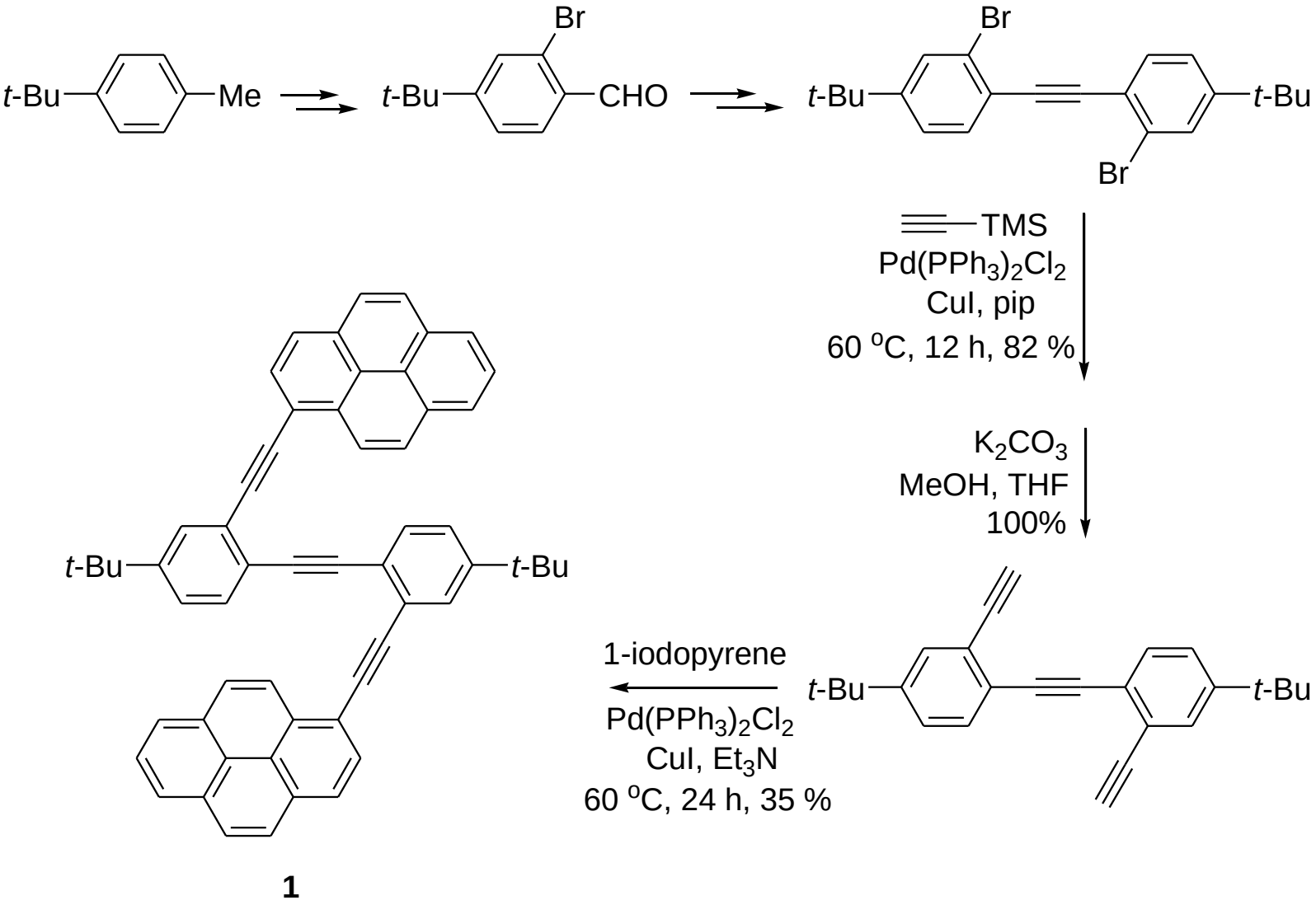
-monomer and excimer emission – well characterized

Applications – sensors – molecular photonics devices

Static excimer – preorganization in the ground state – π–π stacking in the GS

Dynamic excimer – interaction in the excited state after diffusional encounter

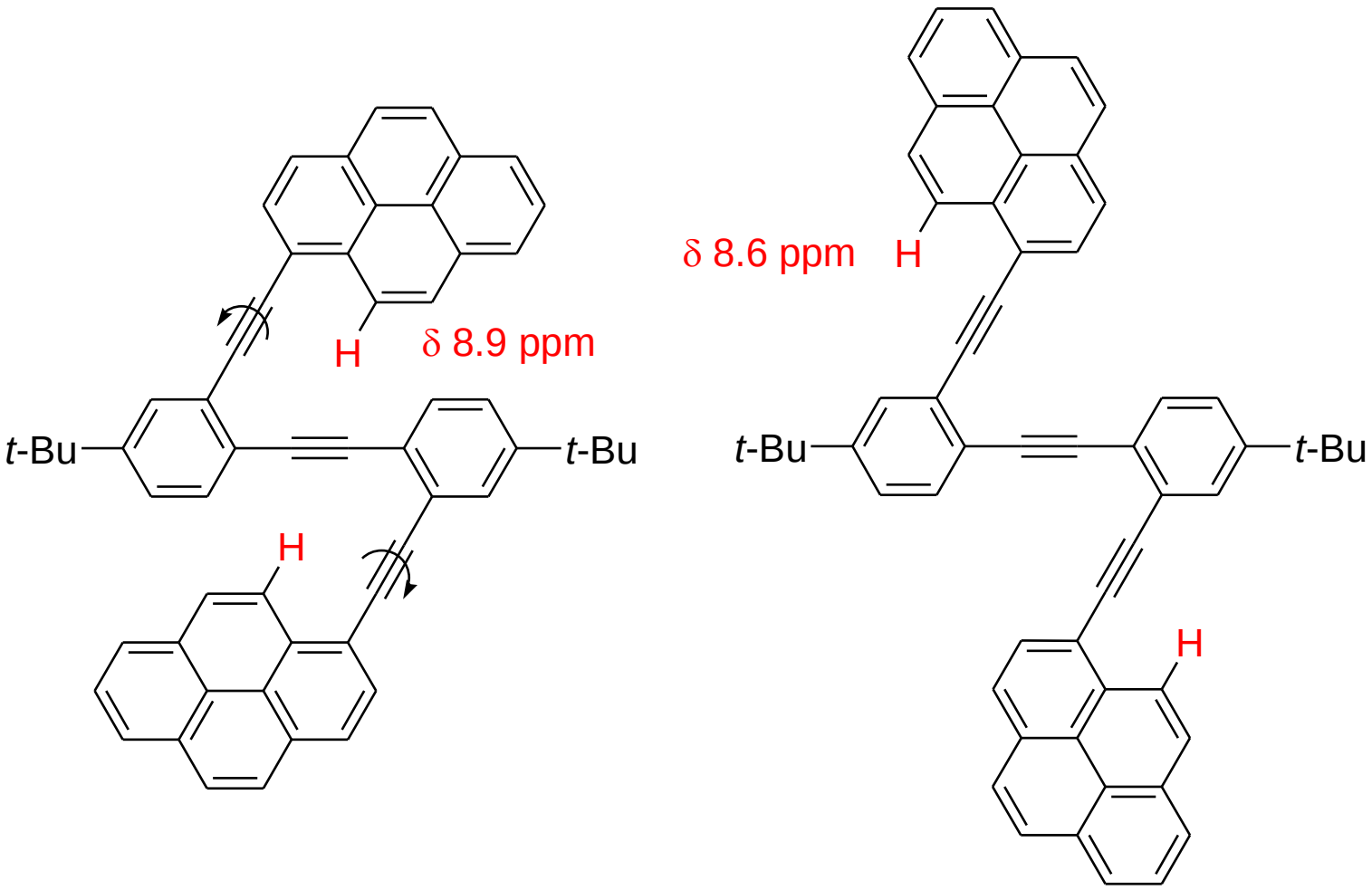
SYNTHESIS



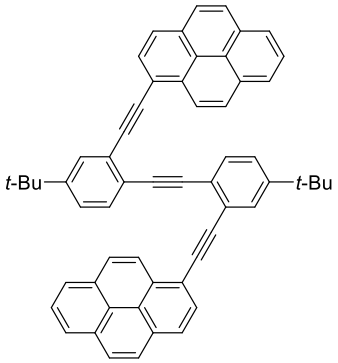
1

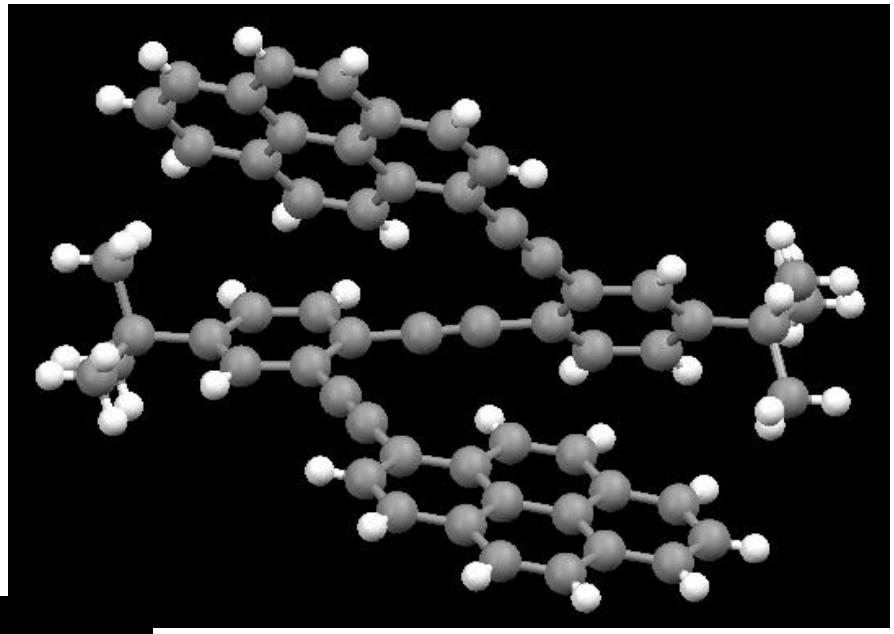
S. Sankararaman, Unpublished work

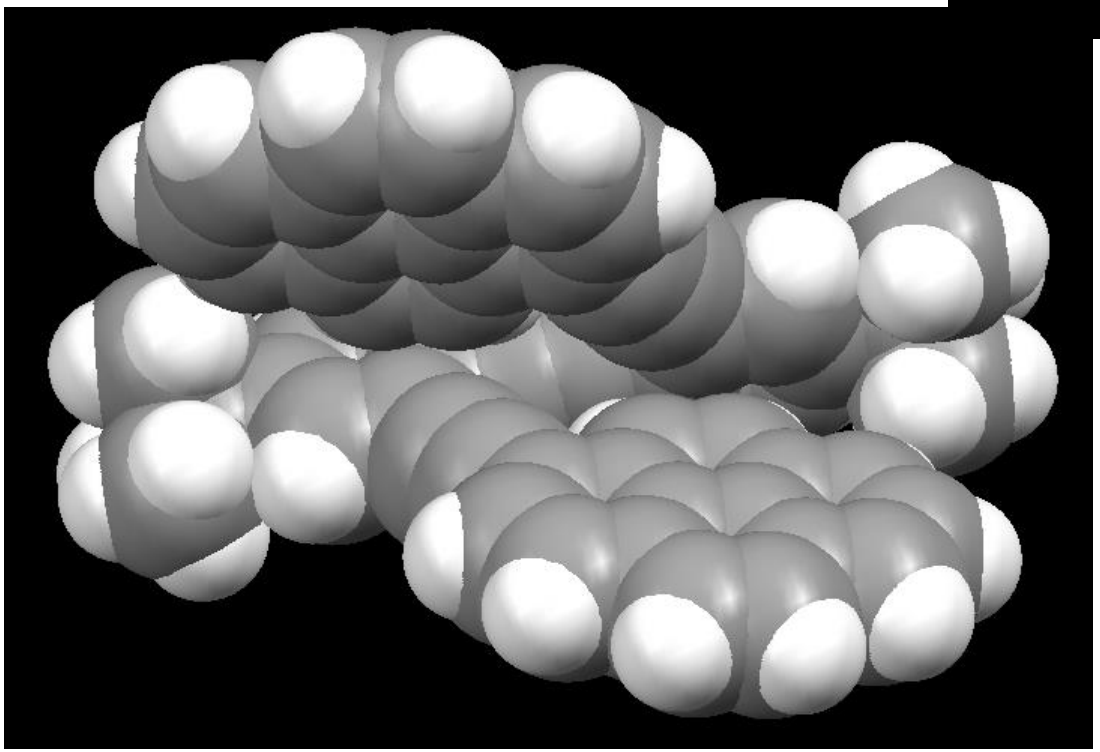
Orientation of the ethynylpyrene units



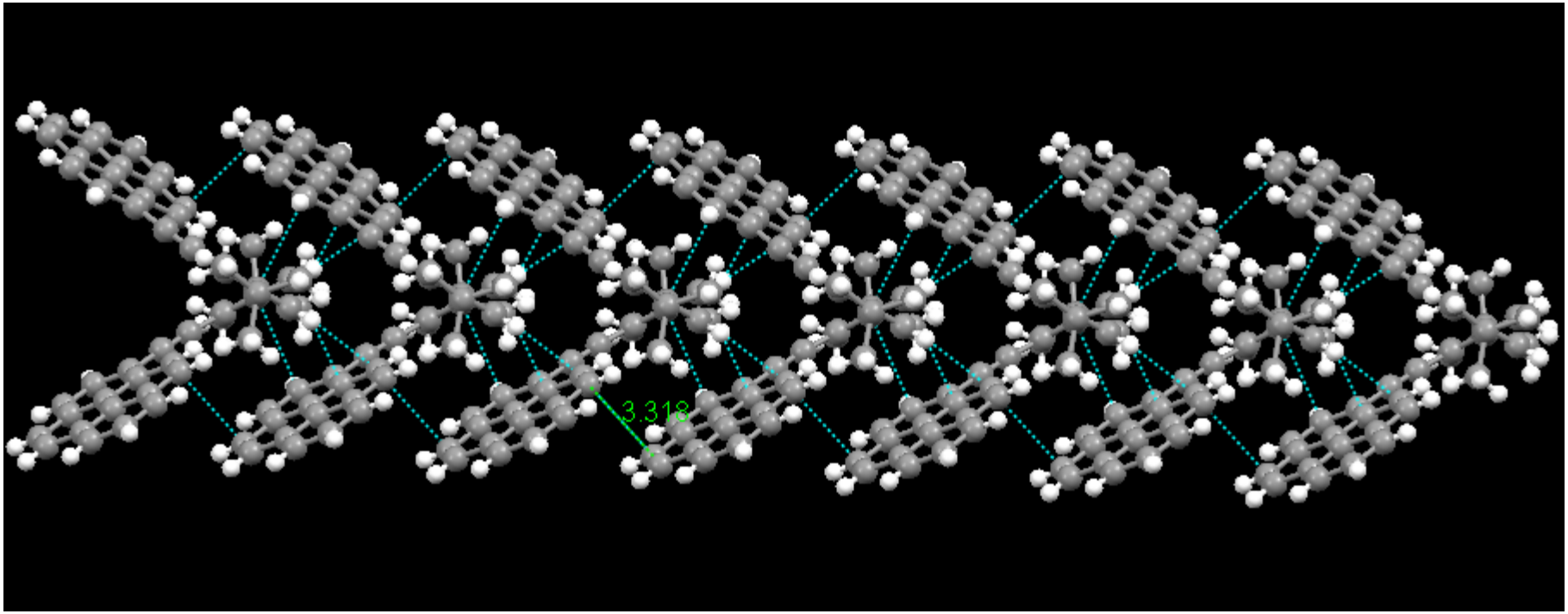
X-ray structure of





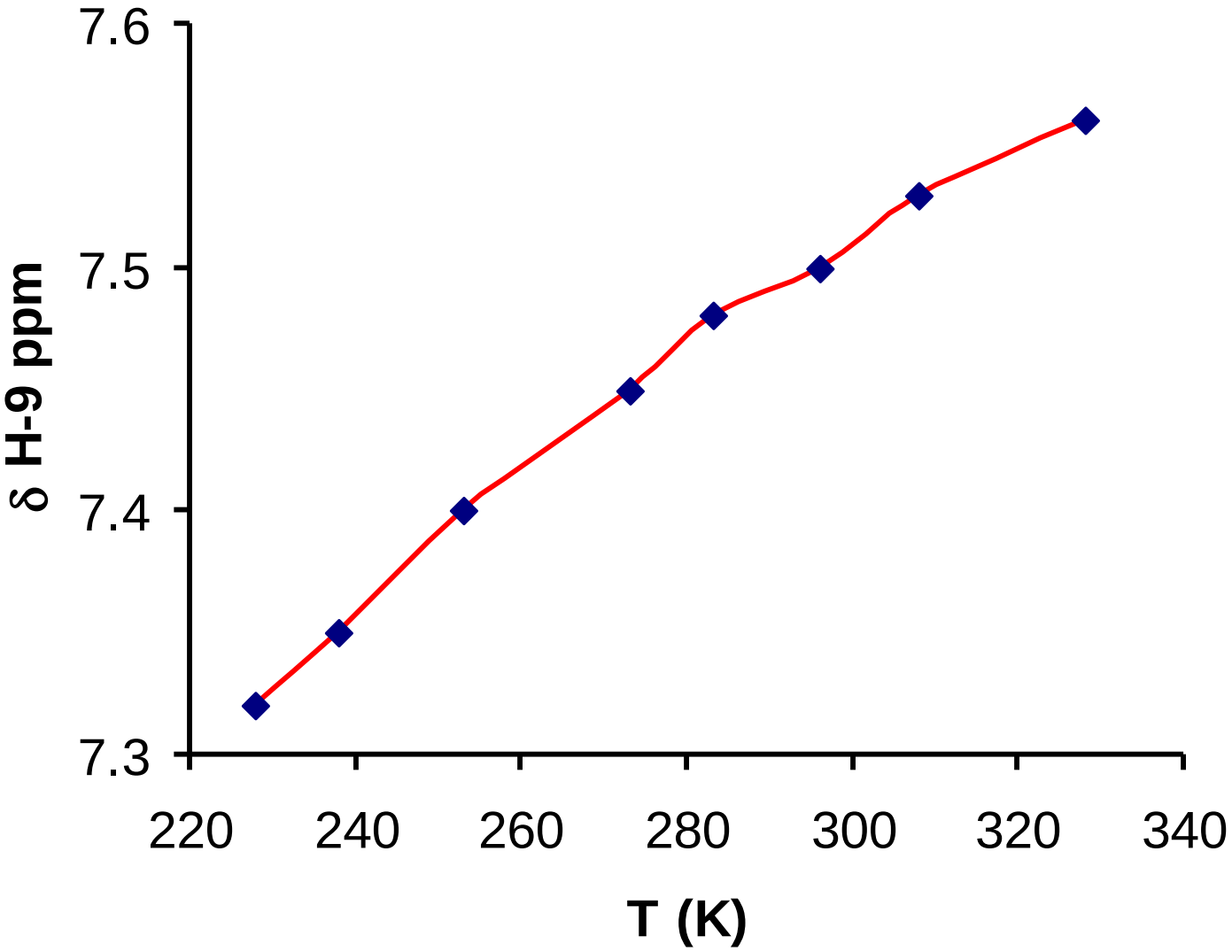


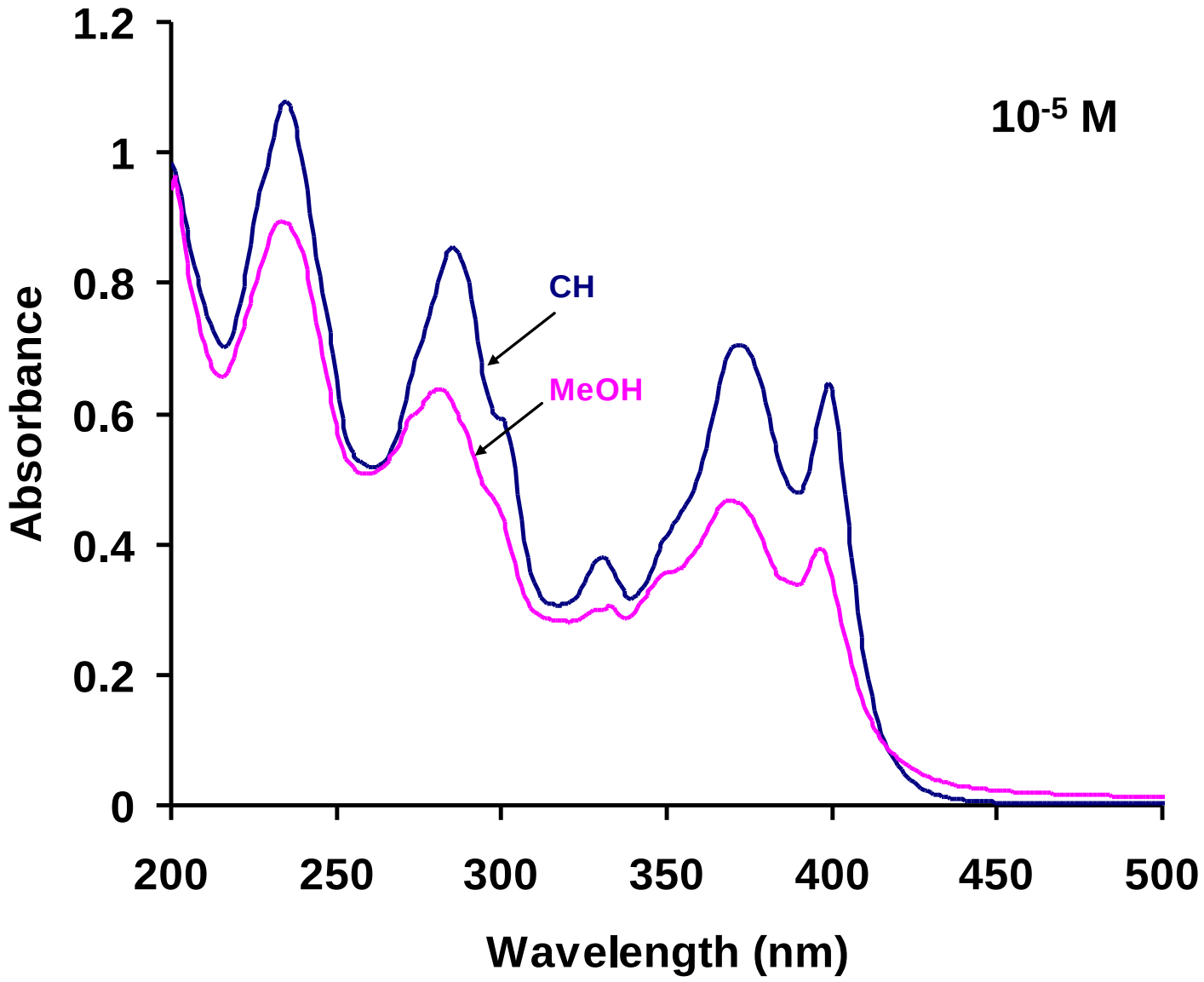
Packing of 1 in the crystal lattice

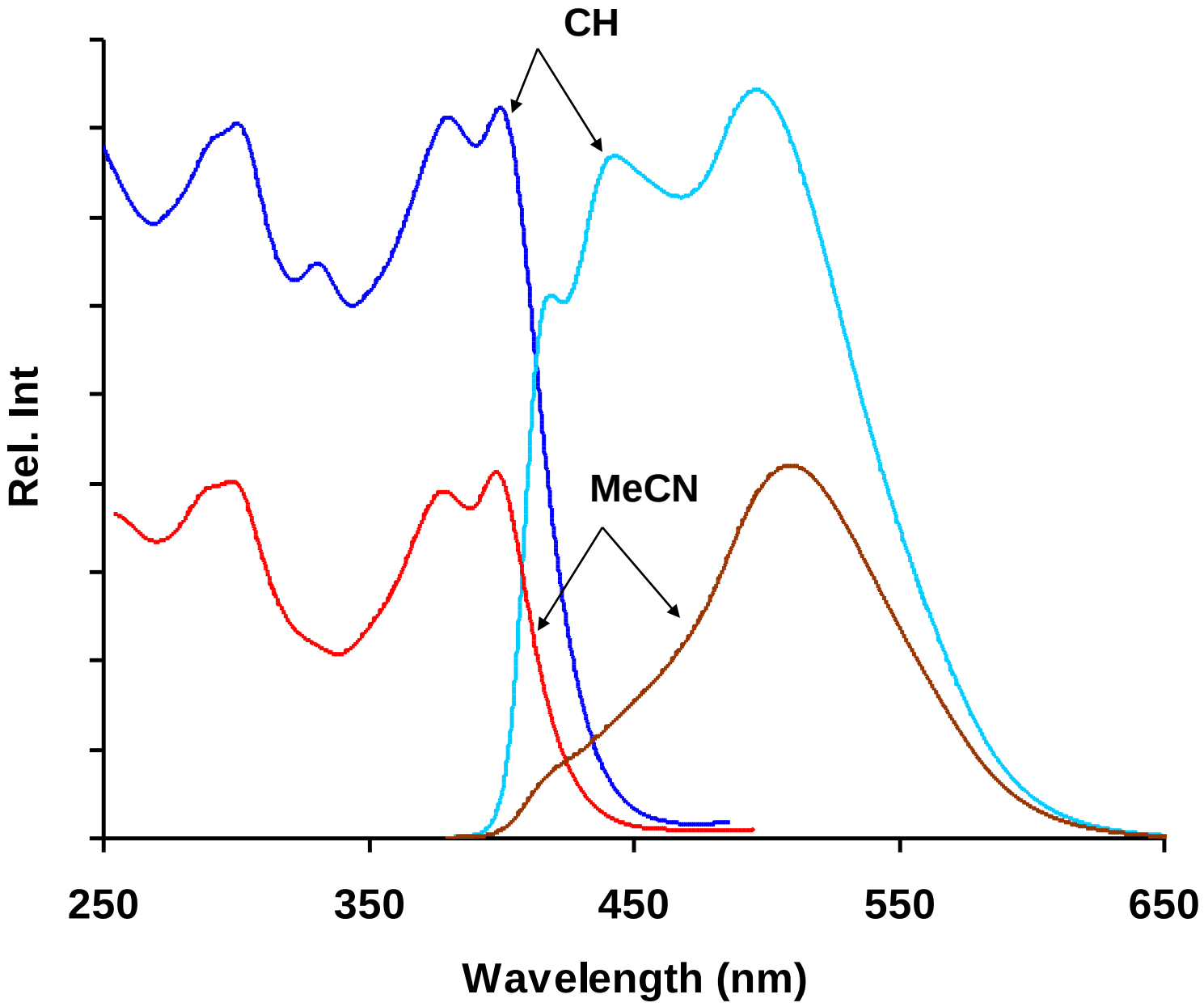


Distance between adjacent parallel pyrene planes = 3.202 Å

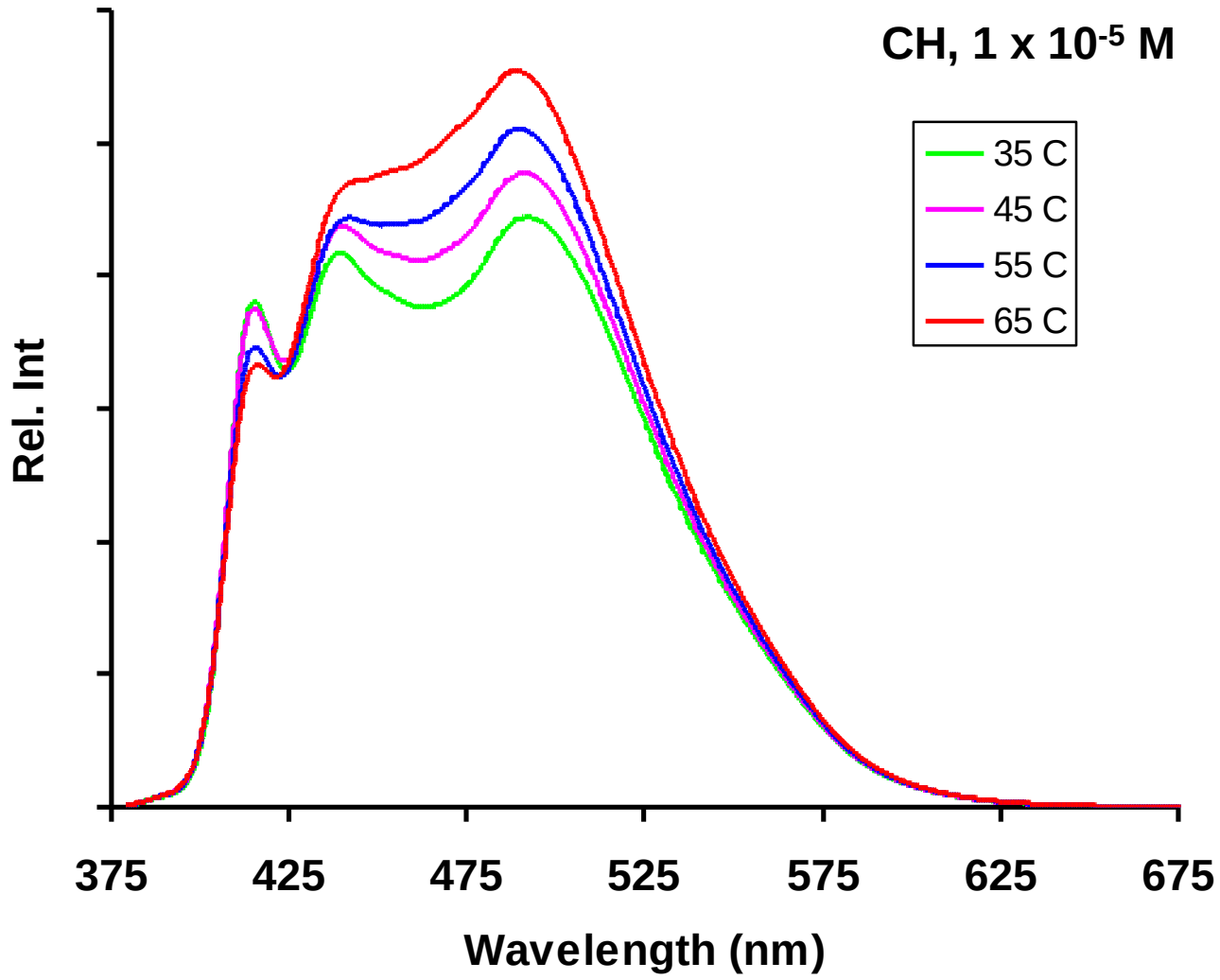
Temperature dependence of chemical shift of H-9 proton of pyrene

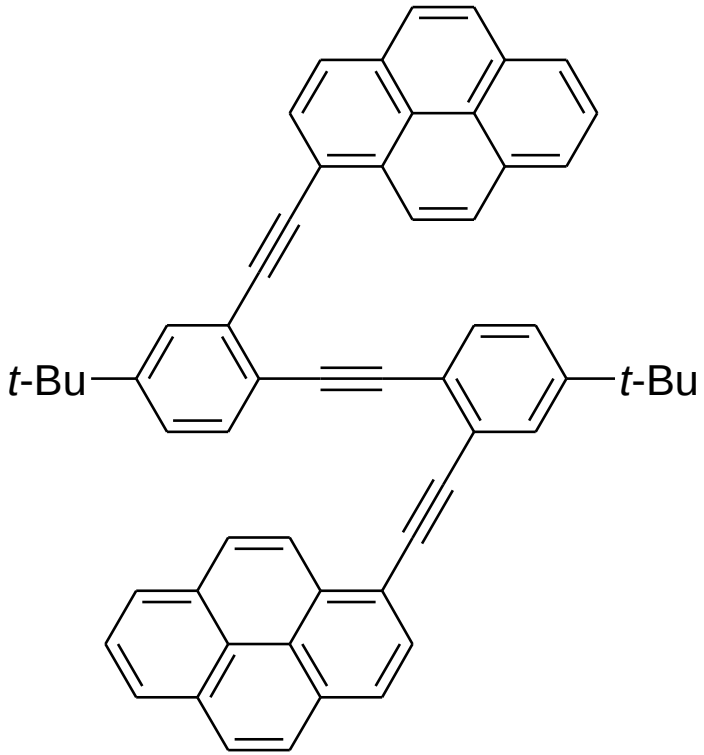



1.2
1
0.8
0.6
0.4
0.2
0
Absorbance
200
250
300
350
400
450
500
Wavelength (nm)
CH
MeOH
10-5 M

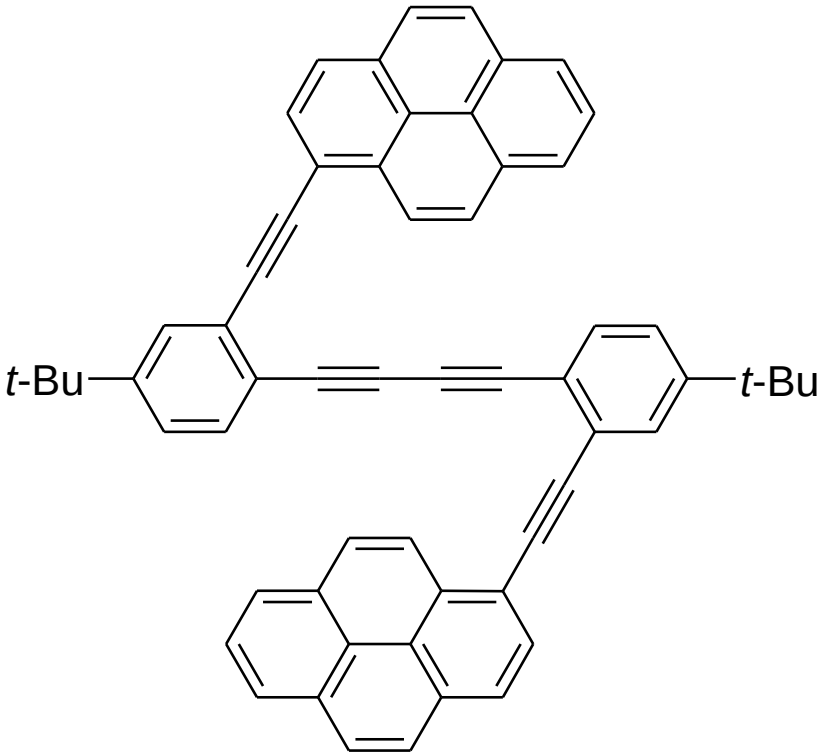

CH
MeCN
Rel. Int
250
350
450
550
650
Wavelength (nm)

Temperature dependence of fluorescence emission



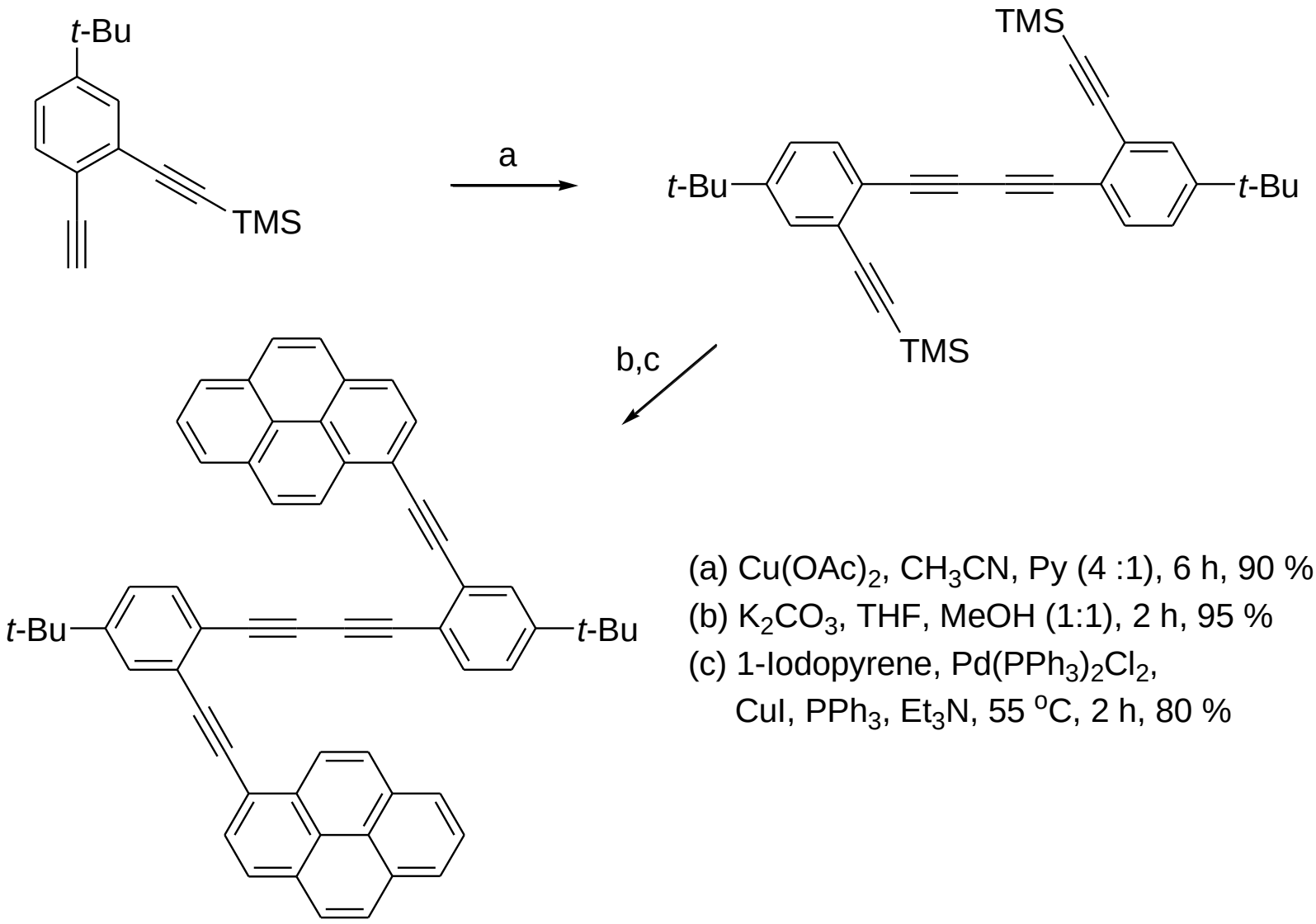


1



2

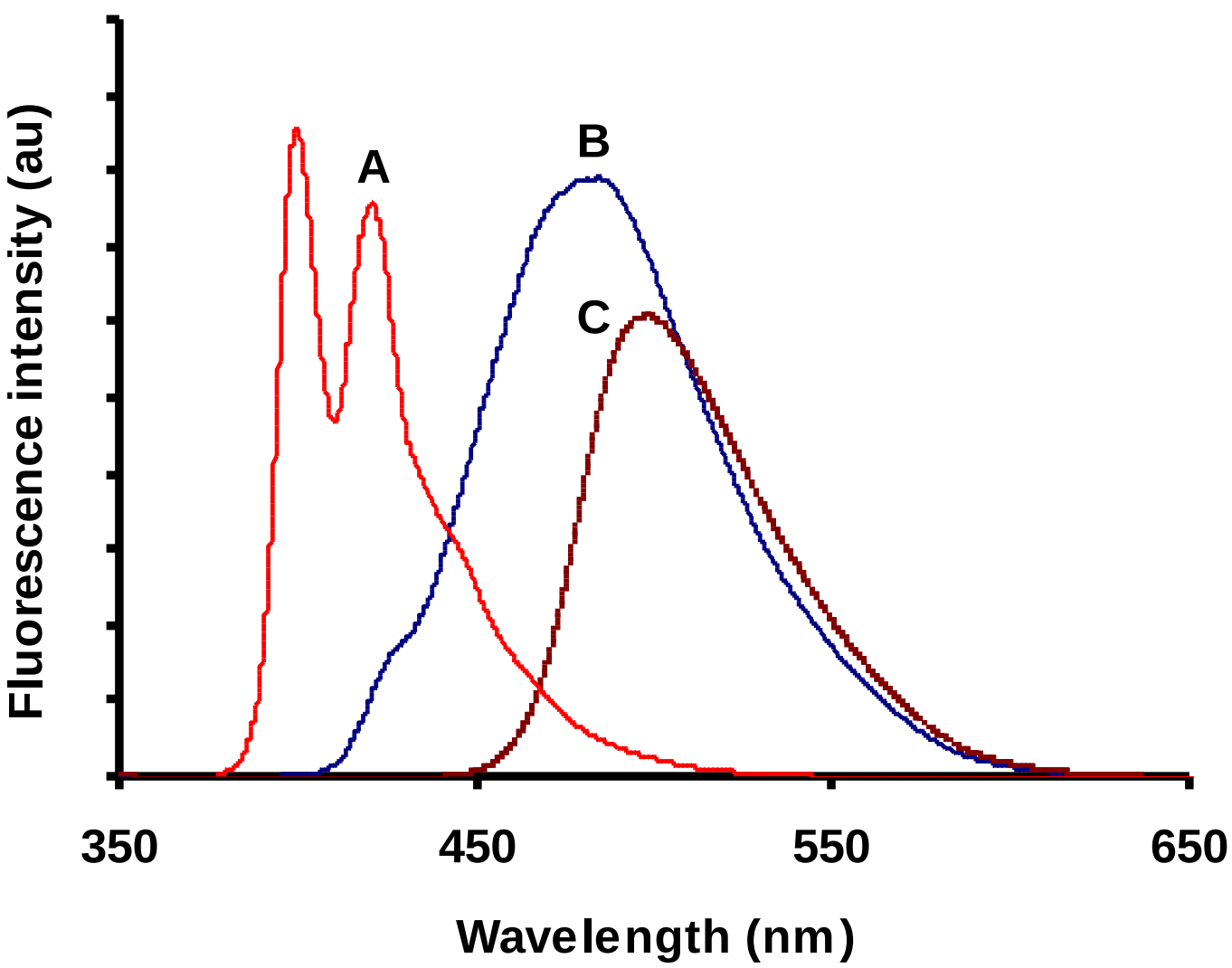
SYNTHESIS

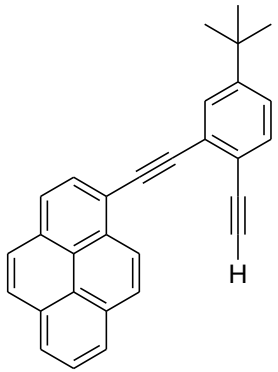


(a) $Cu(OAc)_2$, CH_3CN, Py (4 :1), 6 h, 90 %

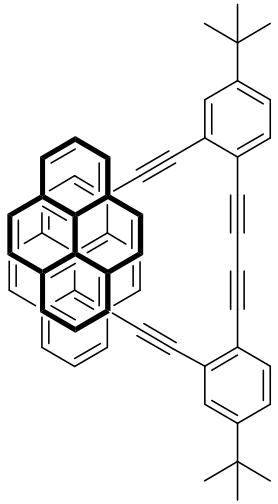
(b) K_2CO_3, THF, MeOH (1:1), 2 h, 95 %

(c) 1-Iodopyrene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, 55 ^oC, 2 h, 80 %





A



B

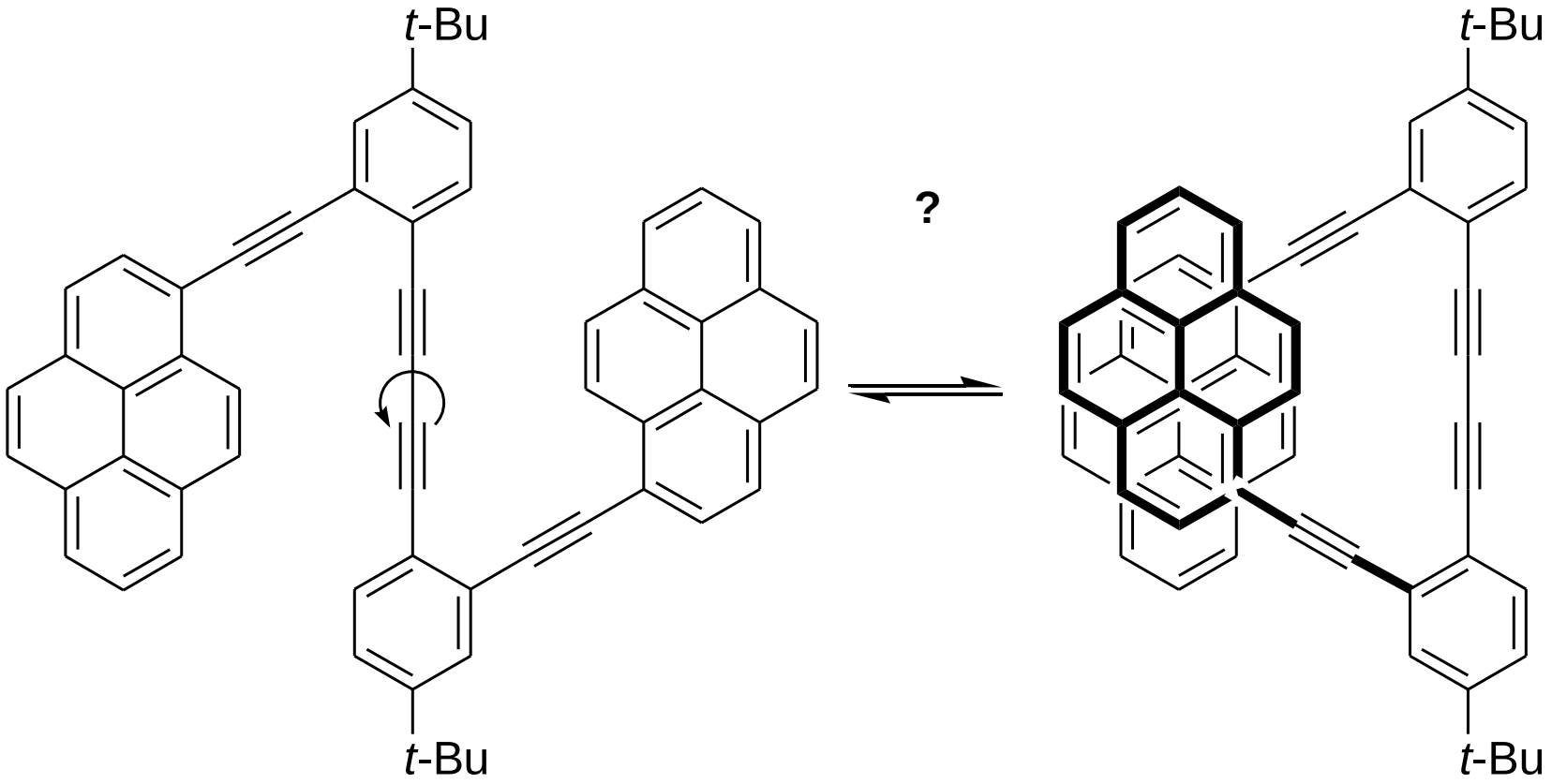
Red = A, Blue = B (CH_2Cl_2), Brown = B (solid state)

G. Venkataramana, *J. Org. Chem*. **2008**, *73*, 2404-2407

Is there an equilibrium between the OPEN and CLOSED forms ?

Conformational isomers arising out of acetylenic bond rotation

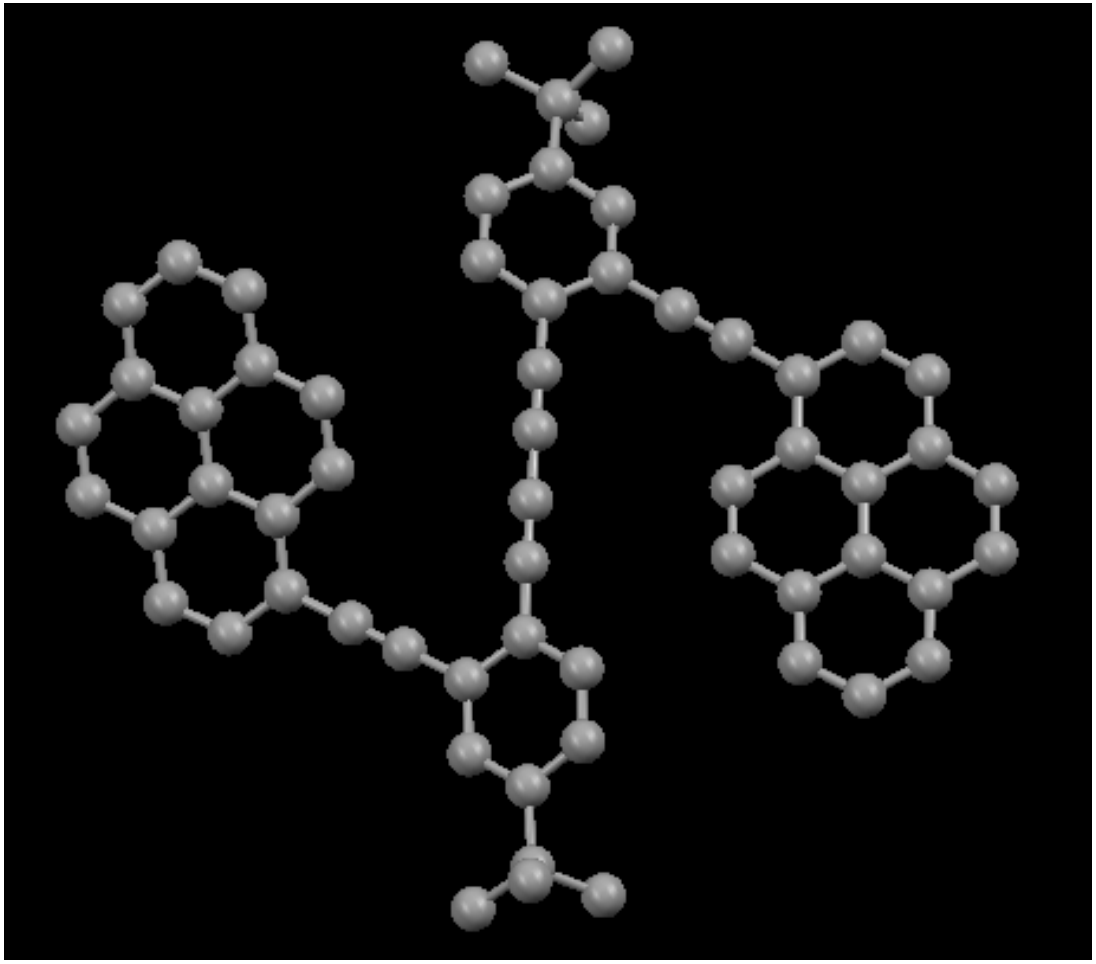
The first example of structural characterization!

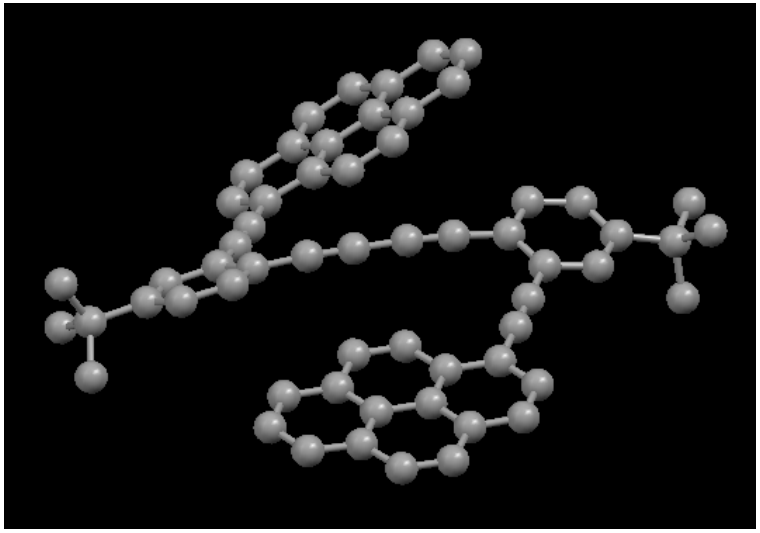


open form

closed form

X-ray structure of the OPEN form





Triclinic, P-1

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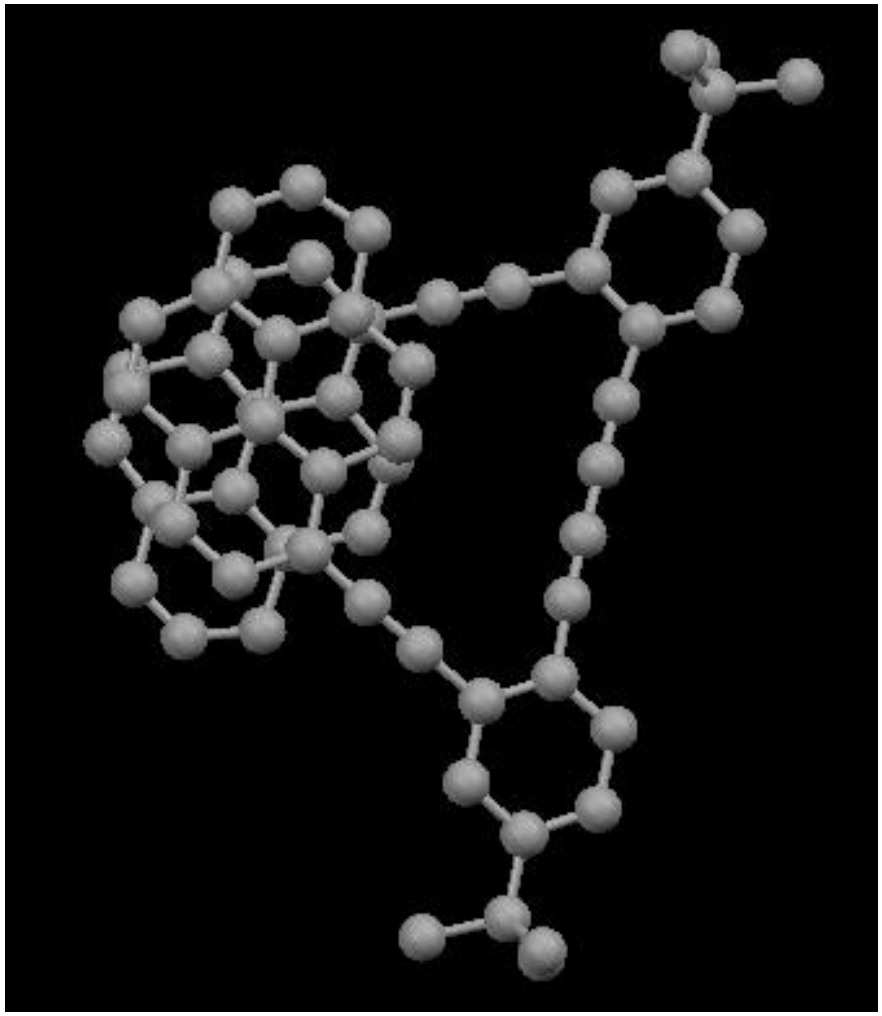
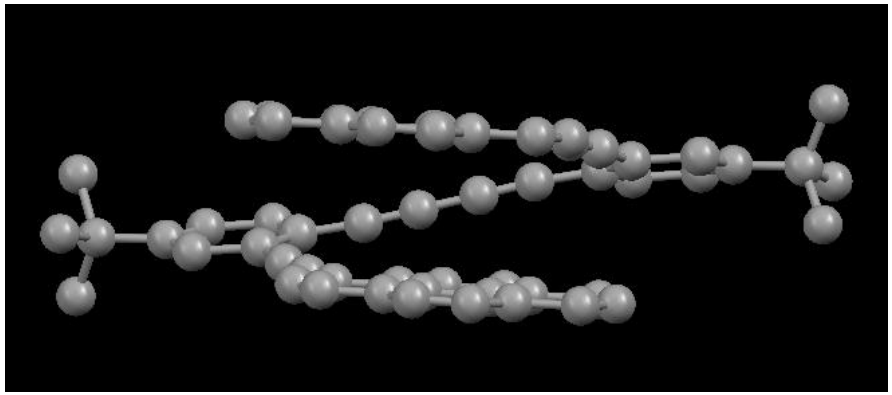
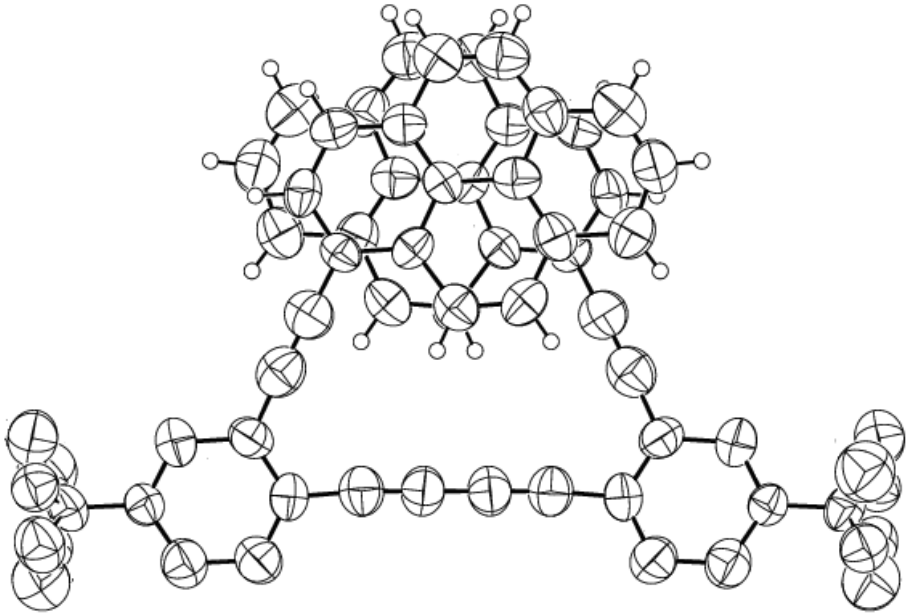
X-ray structure of the CLOSED form

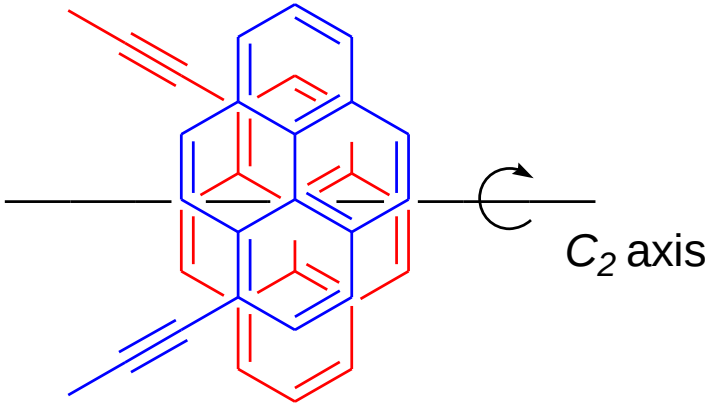




Orthorhombic, Pbcn

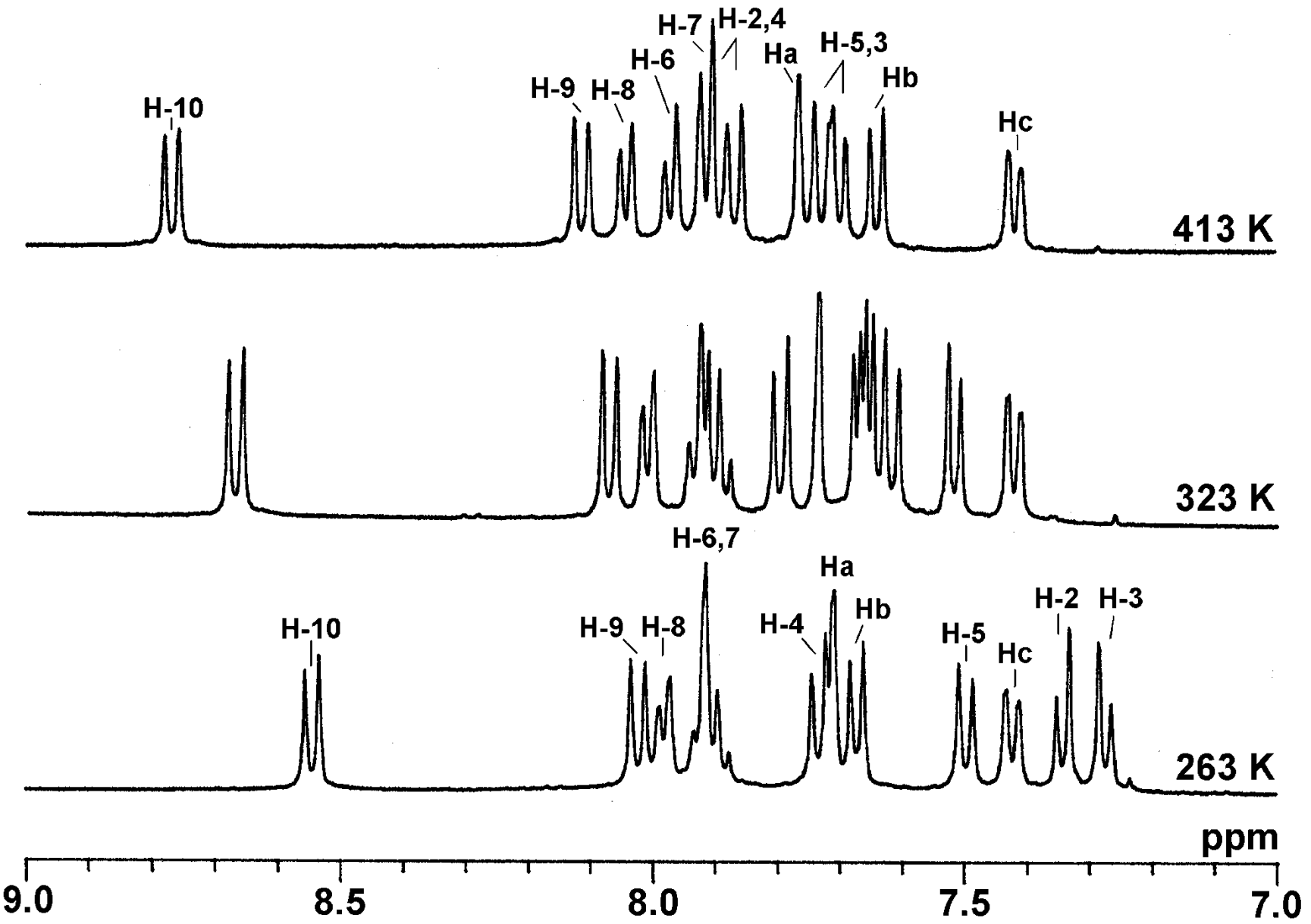
Distance between pyrene planes = 3.34 Å



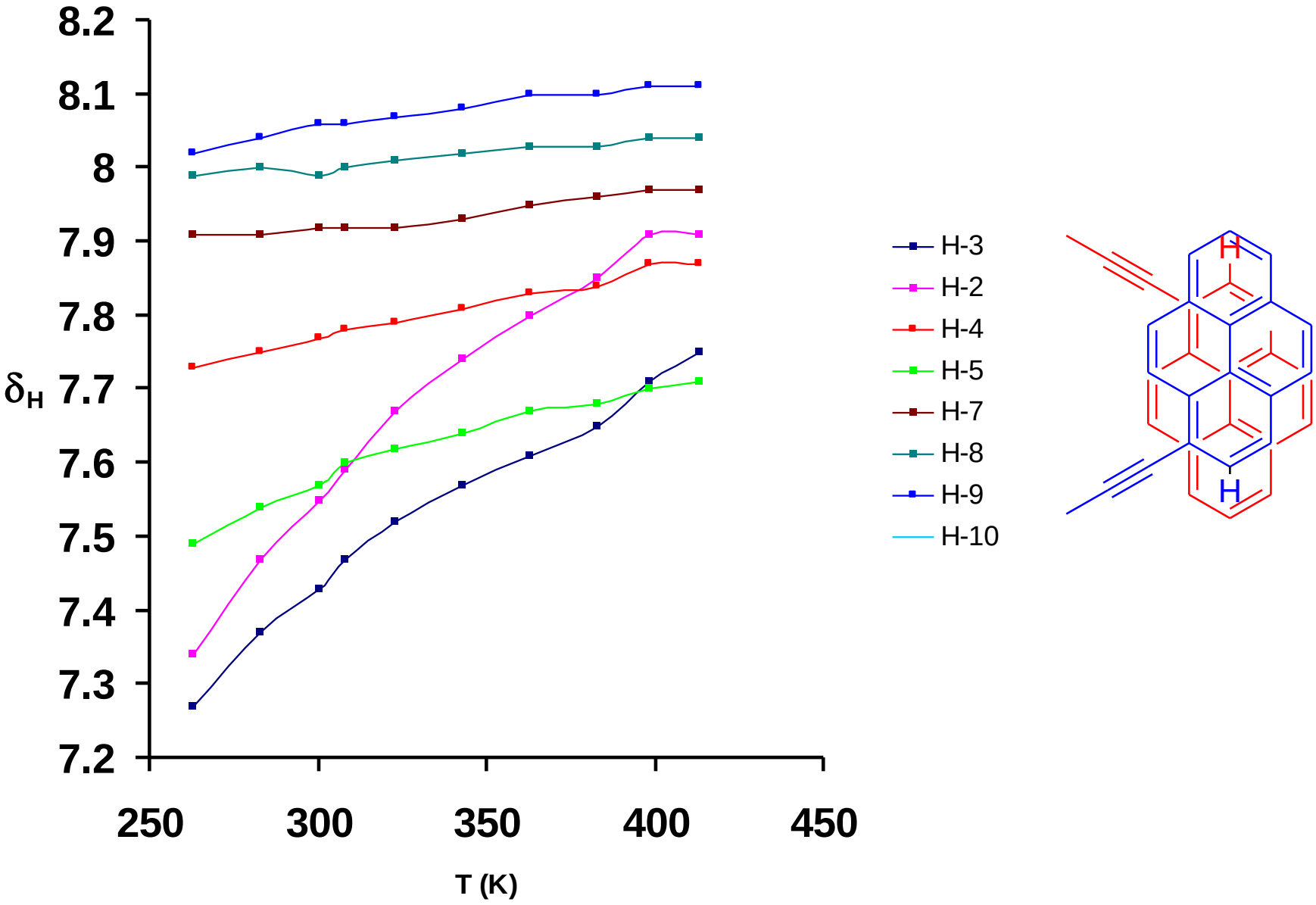


How about in solution?

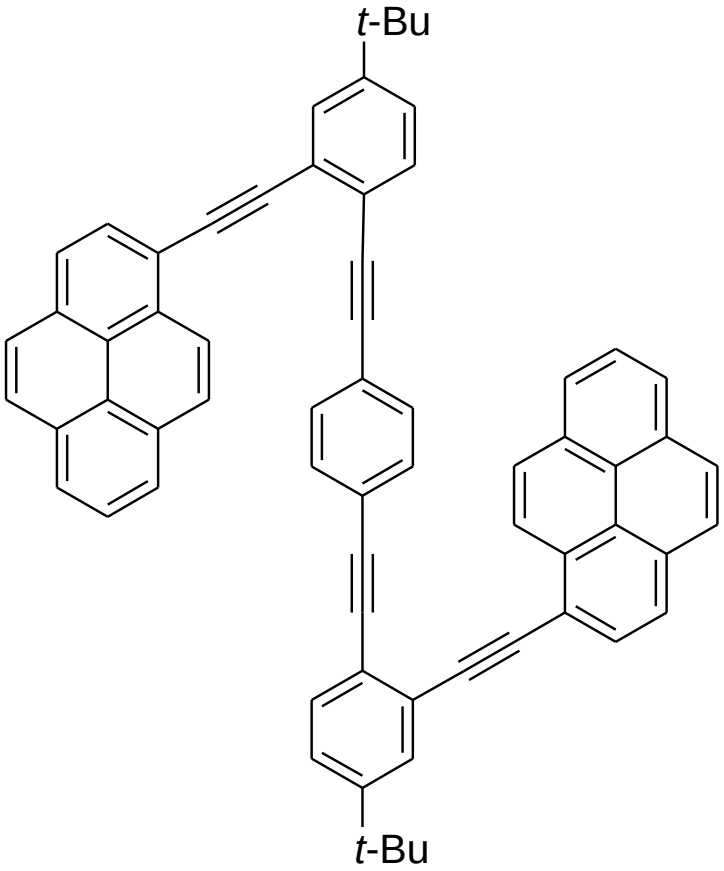
Temperature dependence of chemical shift of pyrene protons



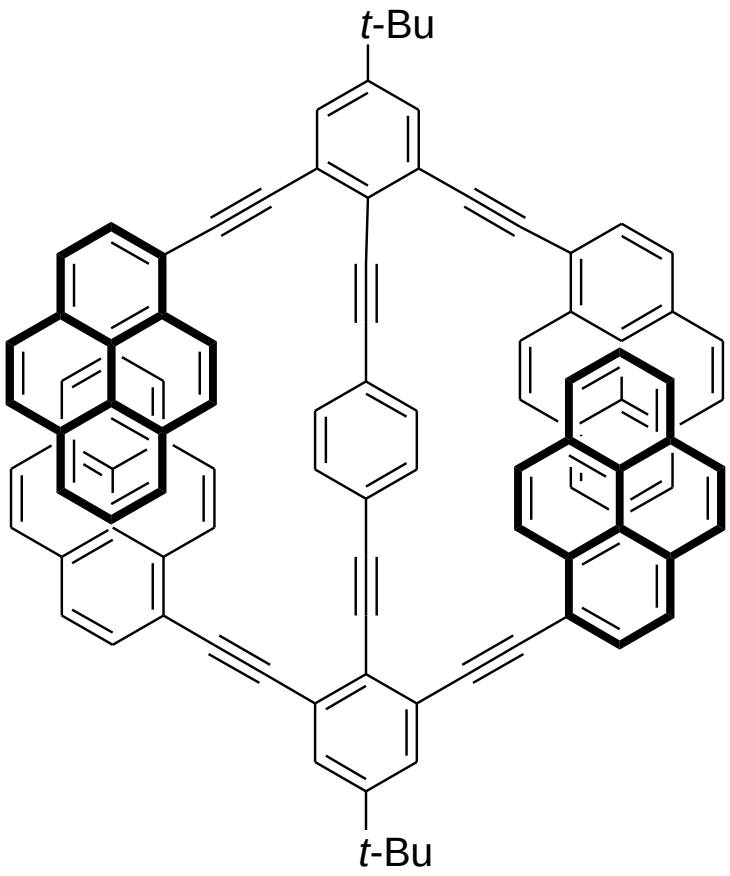
Temperature dependence of chemical shift of pyrene protons



Two more targets with *p*-phenylene spacer as probes

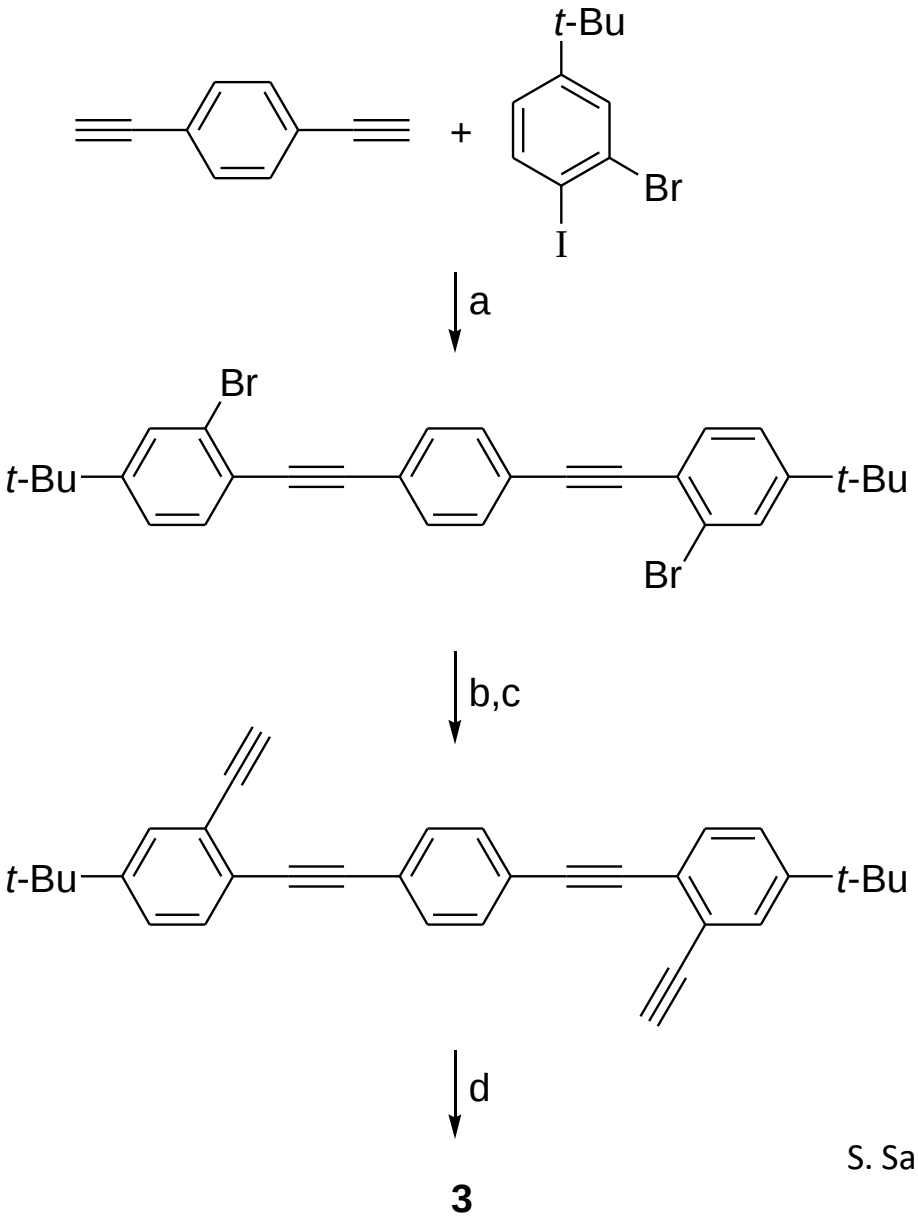


3



4

SYNTHESIS



3

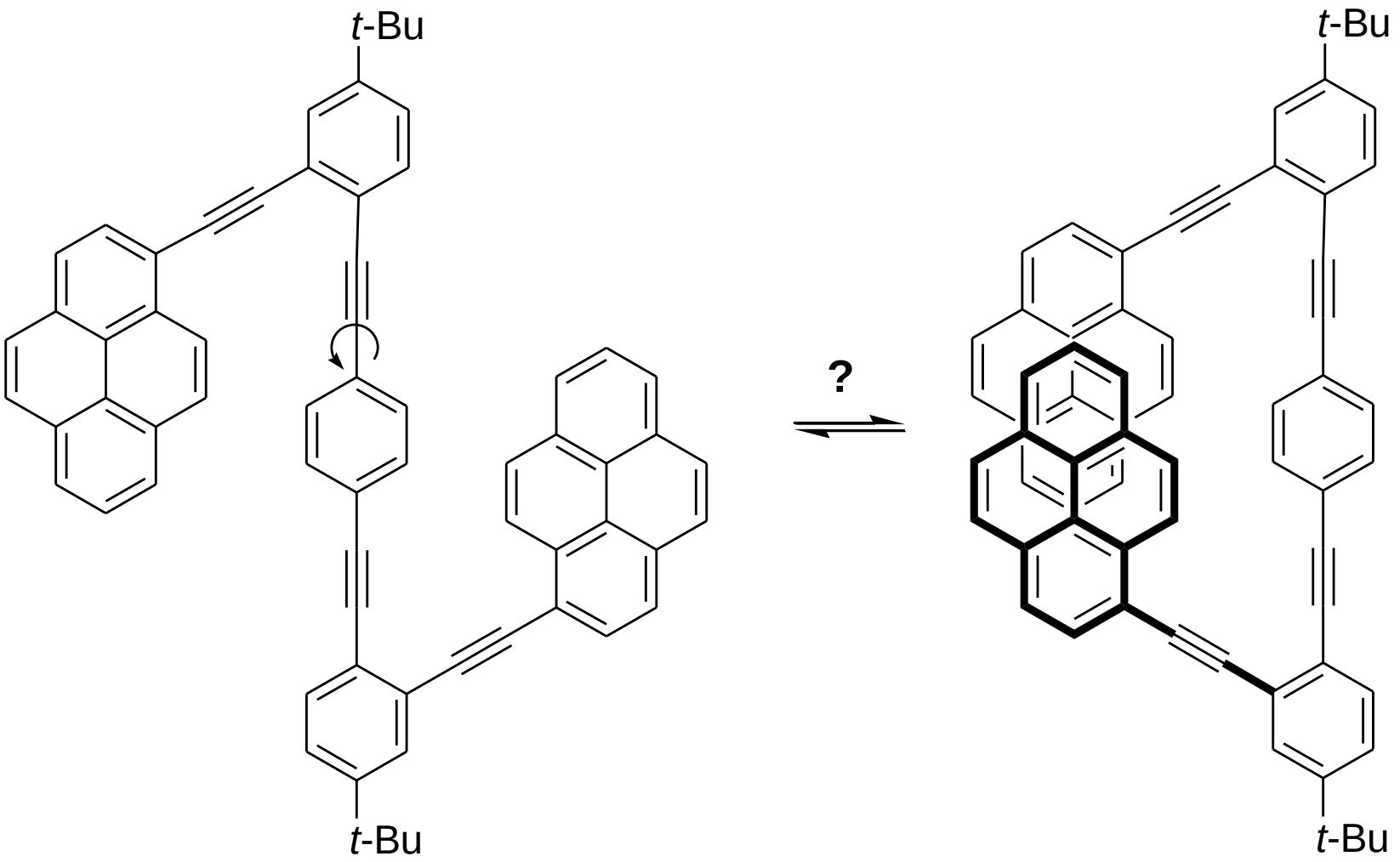
a) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N
rt, 2h, 83 %

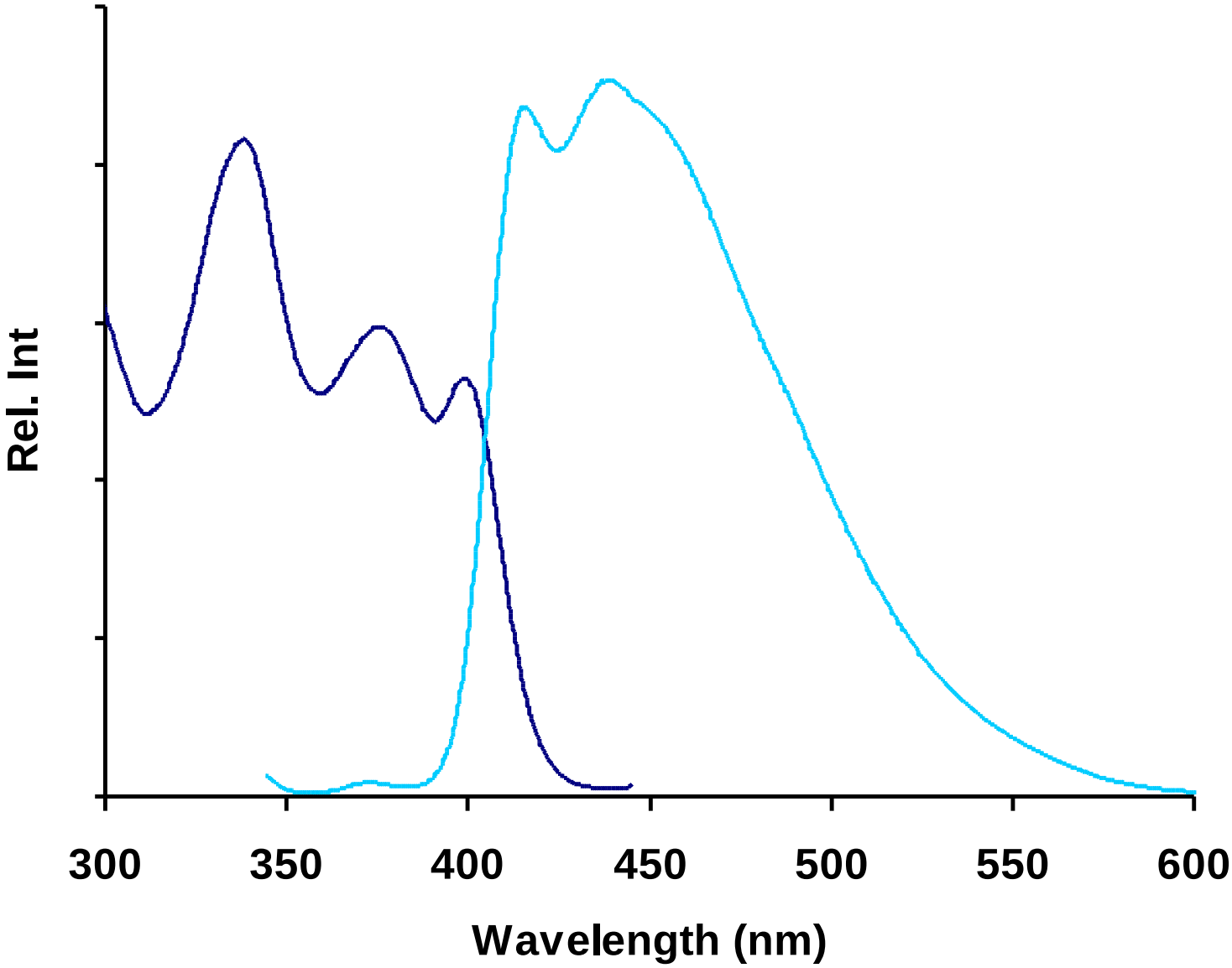
b) $Pd(PPh_3)_2Cl_2$, CuI, pip
60 ^oC, 8 h, 86 %

c) K_2CO_3, MeOH, THF
rt, 1 h, 93 %

d) 1-iodopyrene, $Pd(PPh_3)_2Cl_2$, CuI
Et_3N, 60 ^oC, 4 h, 60 %

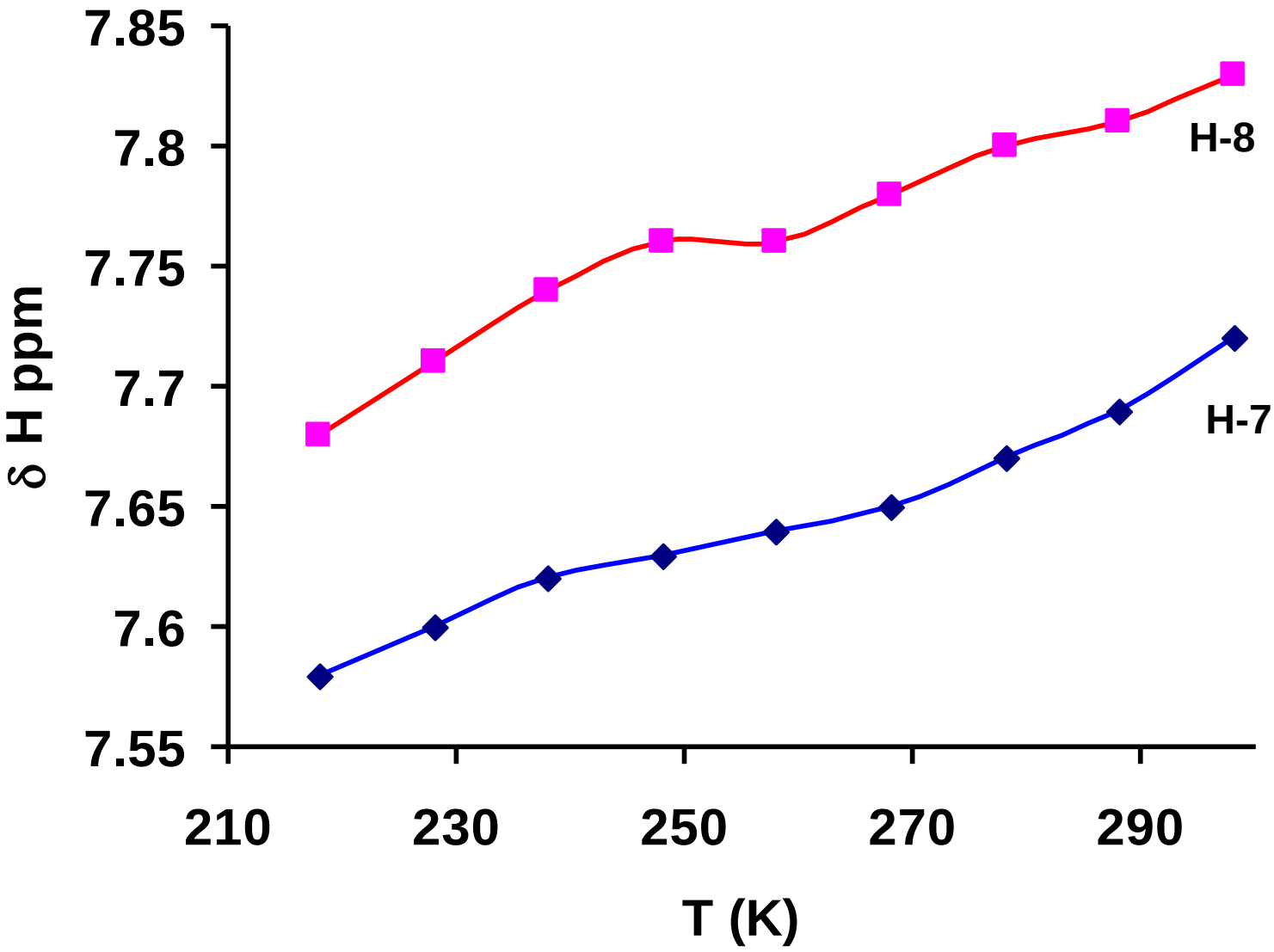
S. Sankararaman, unpublished work


t-Bu
t-Bu
?
t-Bu
t-Bu

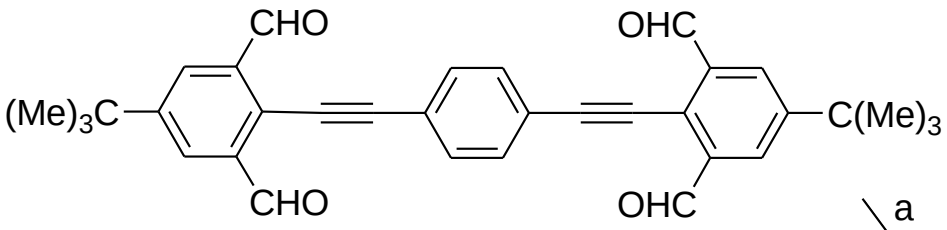


Excitation (λ_{em} 445 nm) (_____)
fluorescence emission (λ_{ex} 334 nm) (_____), CH, 1 x 10^{-7} M

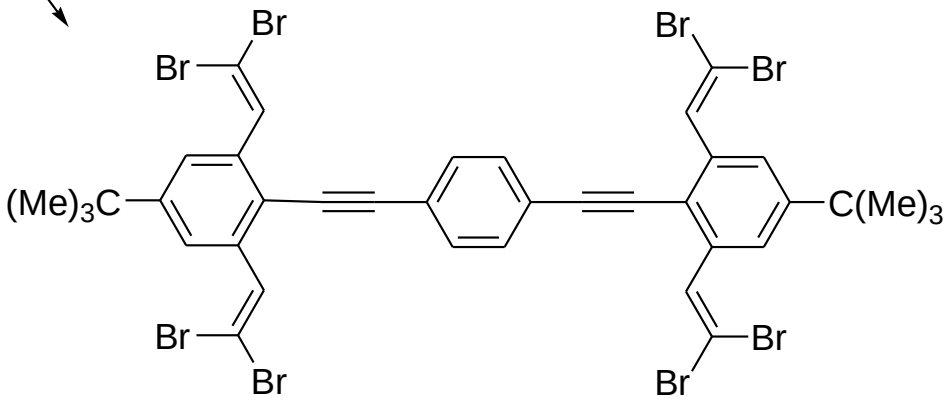
Temperature dependence of chemical shift of pyrene protons



SYNTHESIS OF A TETRA PYRENYL HINGE

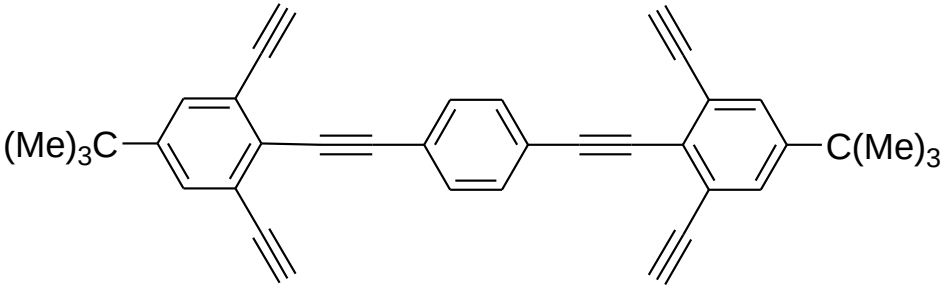


a

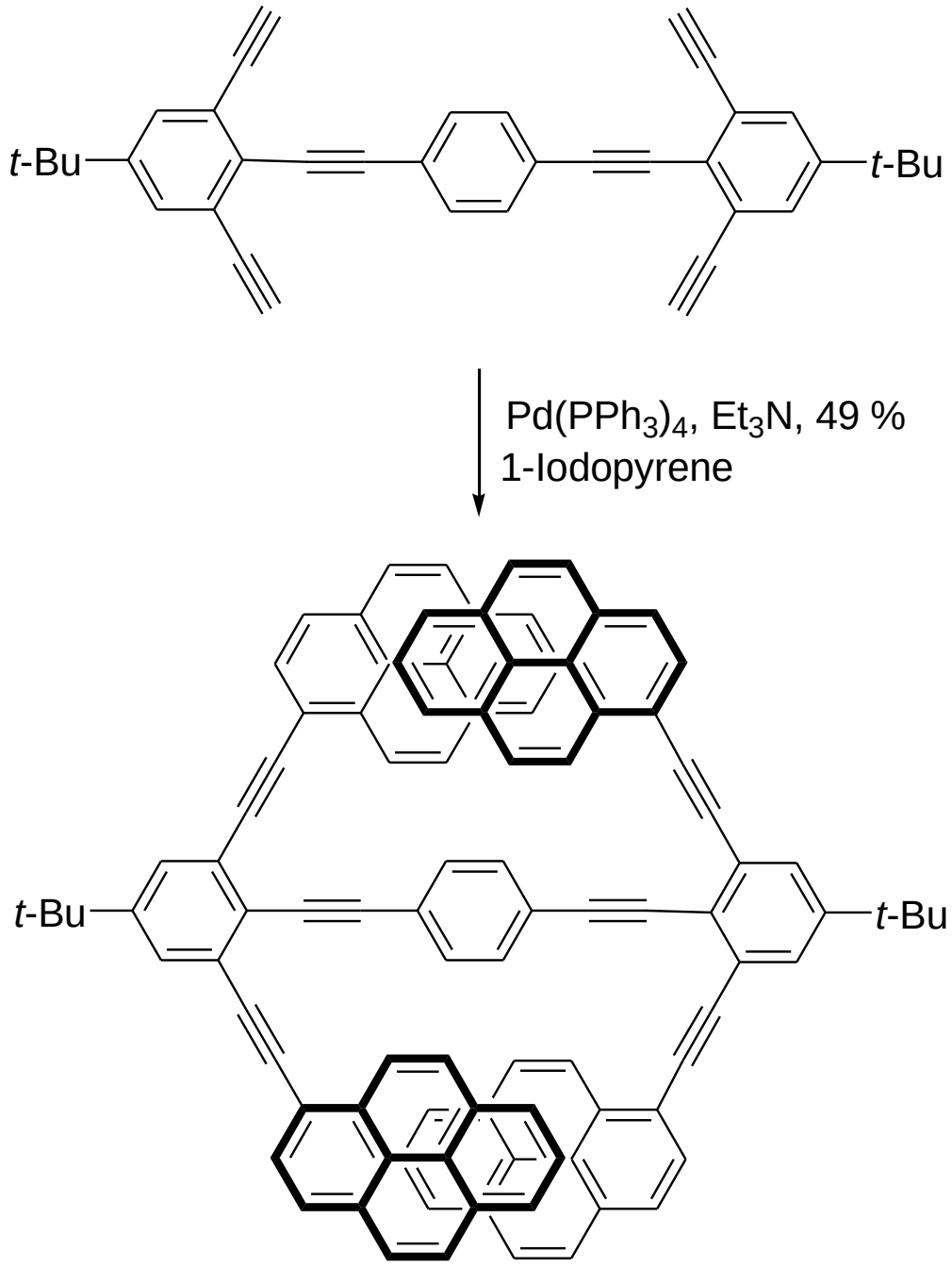


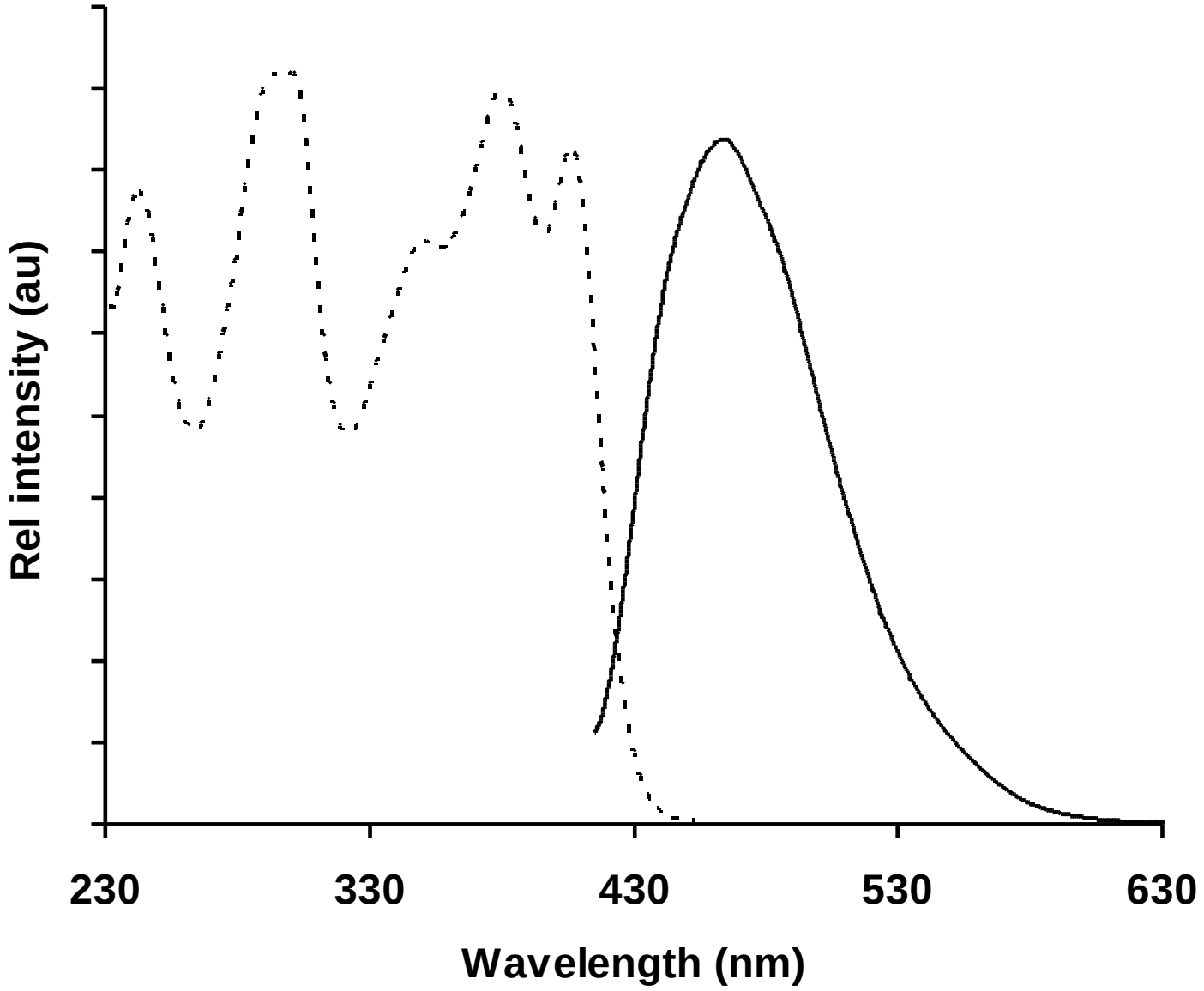
(a) CBr_4, Ph_3P, Zn, CH_2Cl_2, 25 ^oC, 75%.

LDA, THF, -78 ^oC, 80 %

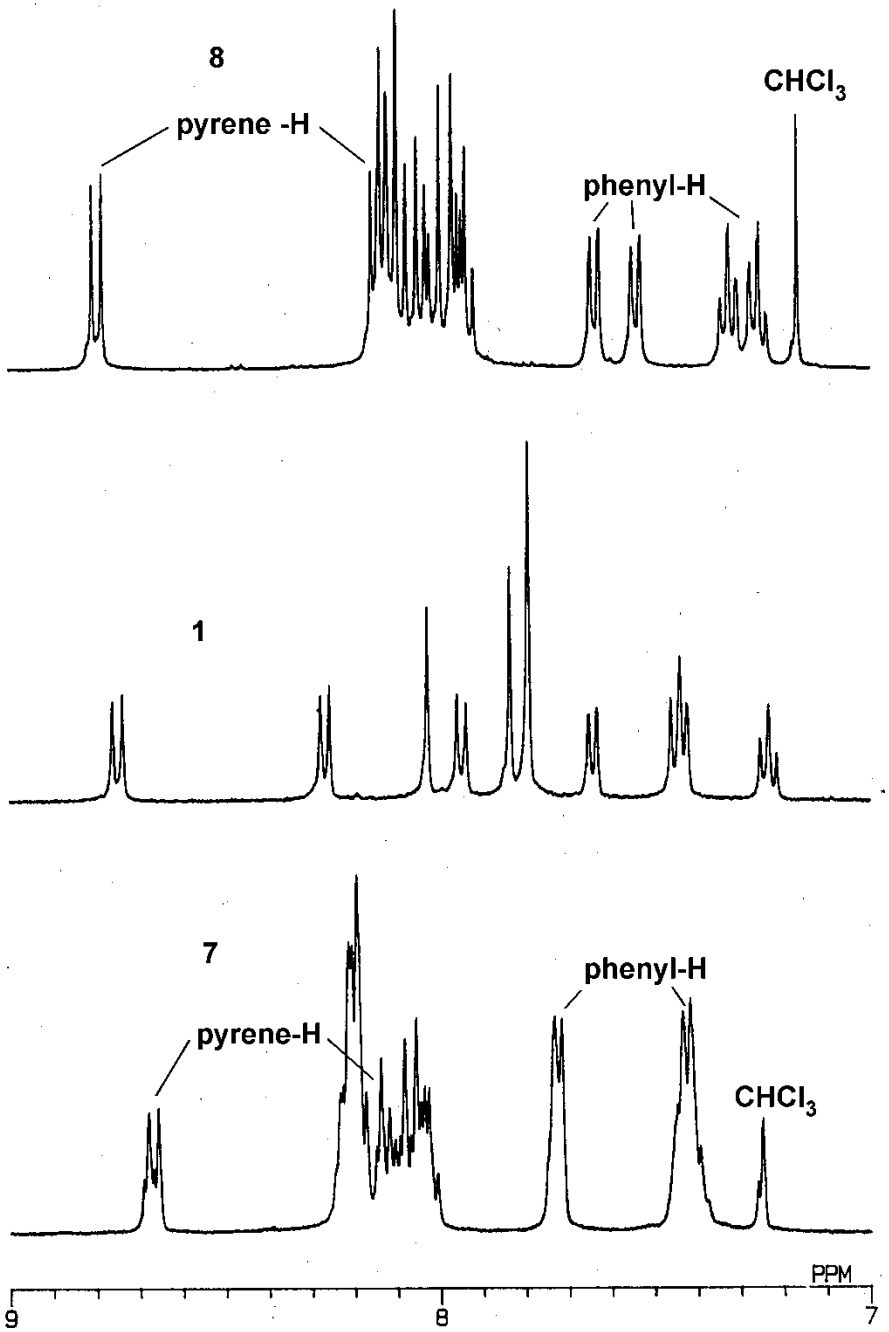


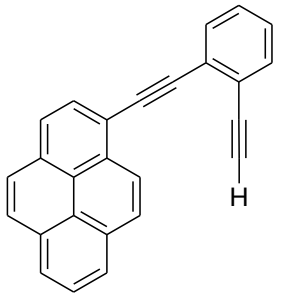
R. Nandy, *J. Org. Chem*. **2007**, *72*, 938-944

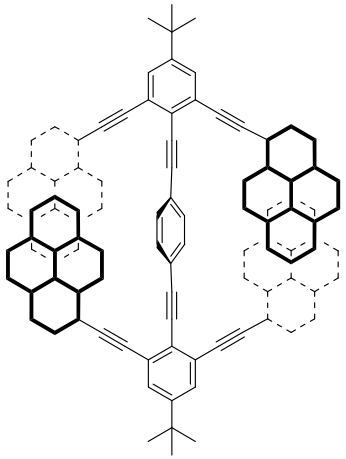

t-Bu
t-Bu
Pd(PPh3)4, Et3N, 49 %
1-Iodopyrene
t-Bu
t-Bu

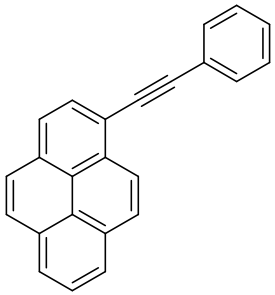


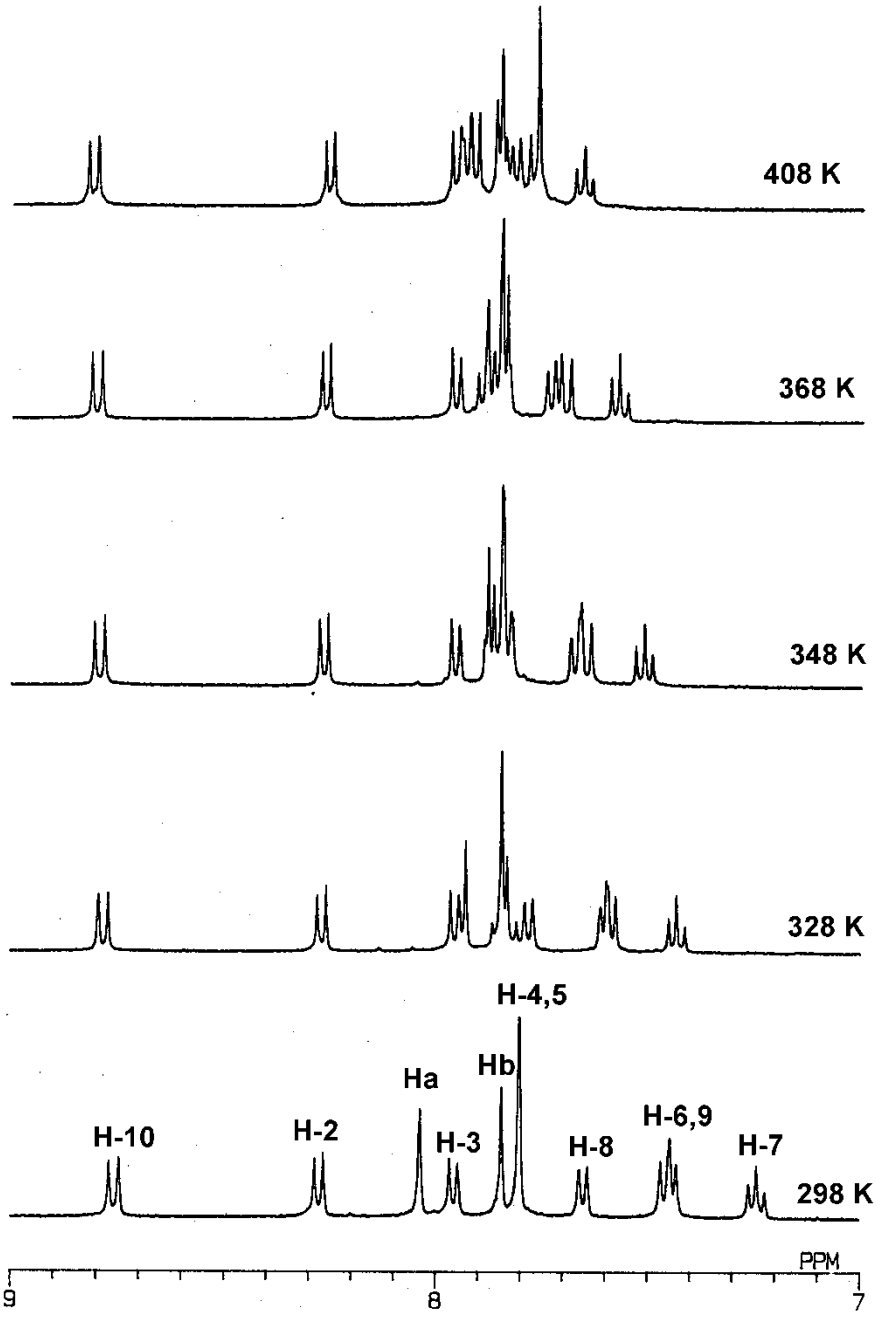
Excitation (λ_{em} 463 nm) (--------)
fluorescence emission (λ_{ex} 347 nm) (____) (1 x 10^{-5} M in CH_2Cl_2)

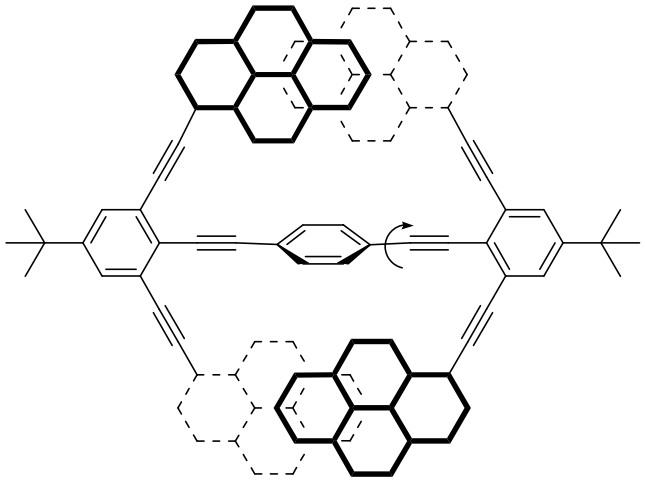

8
pyrene -H
phenyl-H
CHCl3
1
7
pyrene-H
phenyl-H
CHCl3
PPM
9
8
7

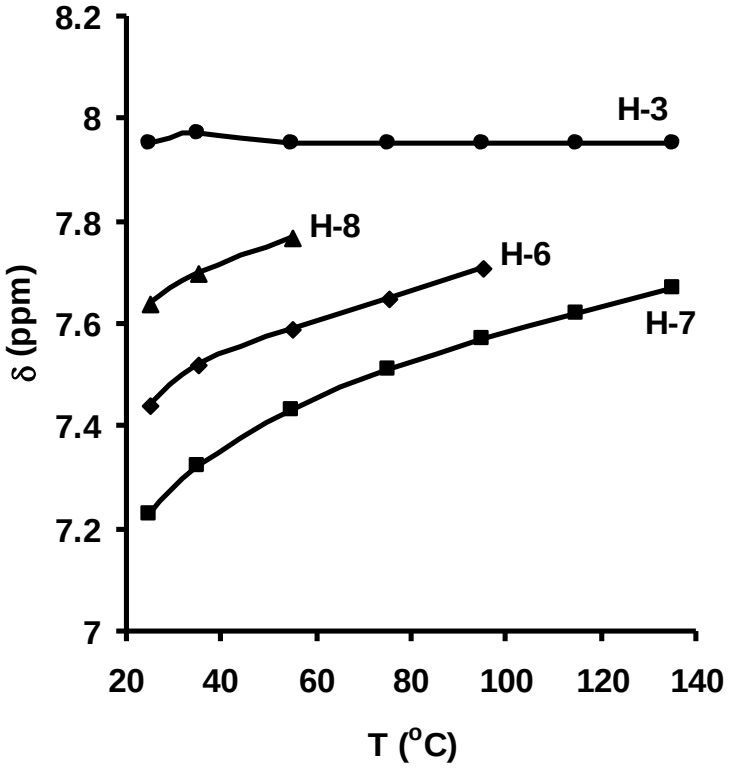

H

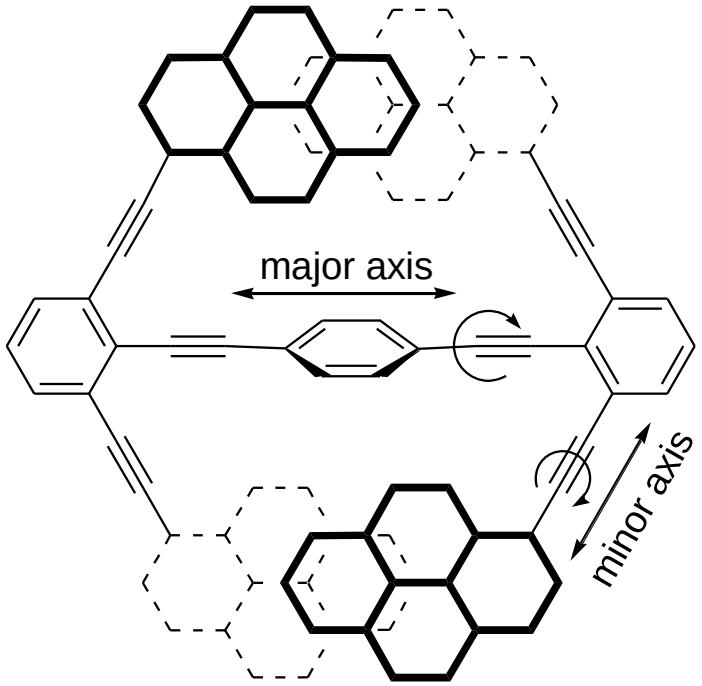





408 K
368 K
348 K
328 K
298 K
H-4,5
Hb
Ha
H-10
H-2
H-3
H-8
H-6,9
H-7
PPM
9
8
7

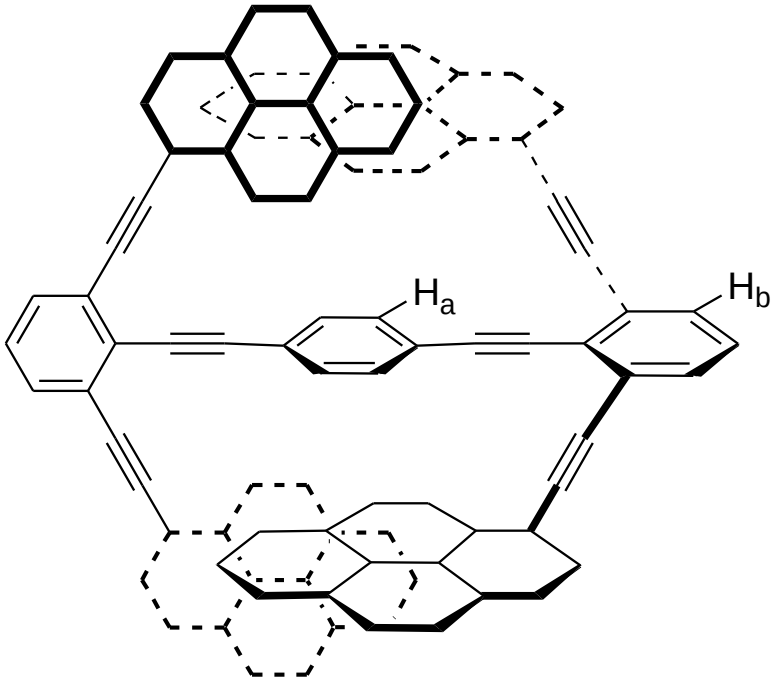


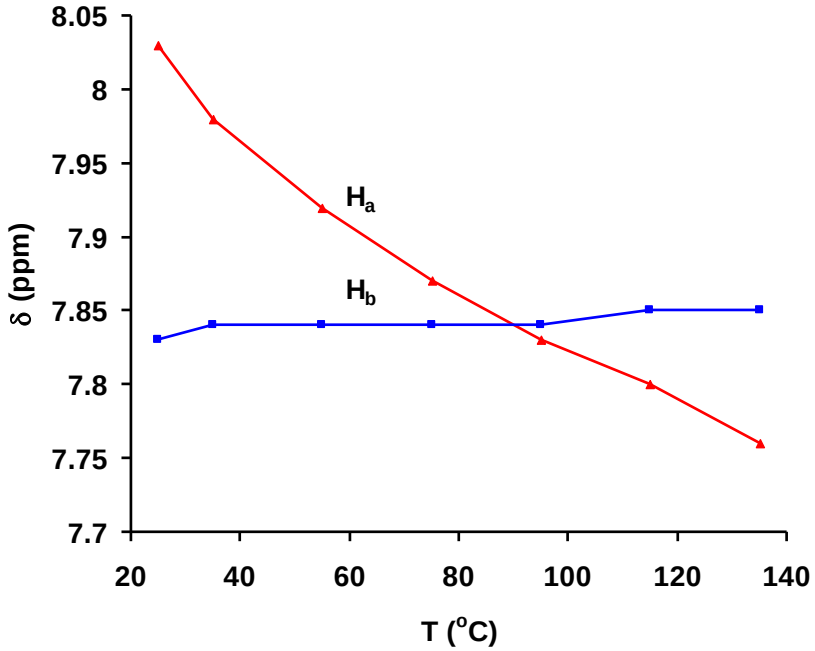

8.2
8
7.8
7.6
7.4
7.2
7
δ (ppm)
H-3
H-8
H-6
H-7
20
40
60
80
100
120
140
T (°C)



I

rotation along
the major axis





R. Nandy, *J. Org. Chem*. **2007**, *72*, 938-944

How about triphenylene as an aromatic unit?

Triphenylene is very different from pyrene

It does not form π-stacked dimer in the ground state

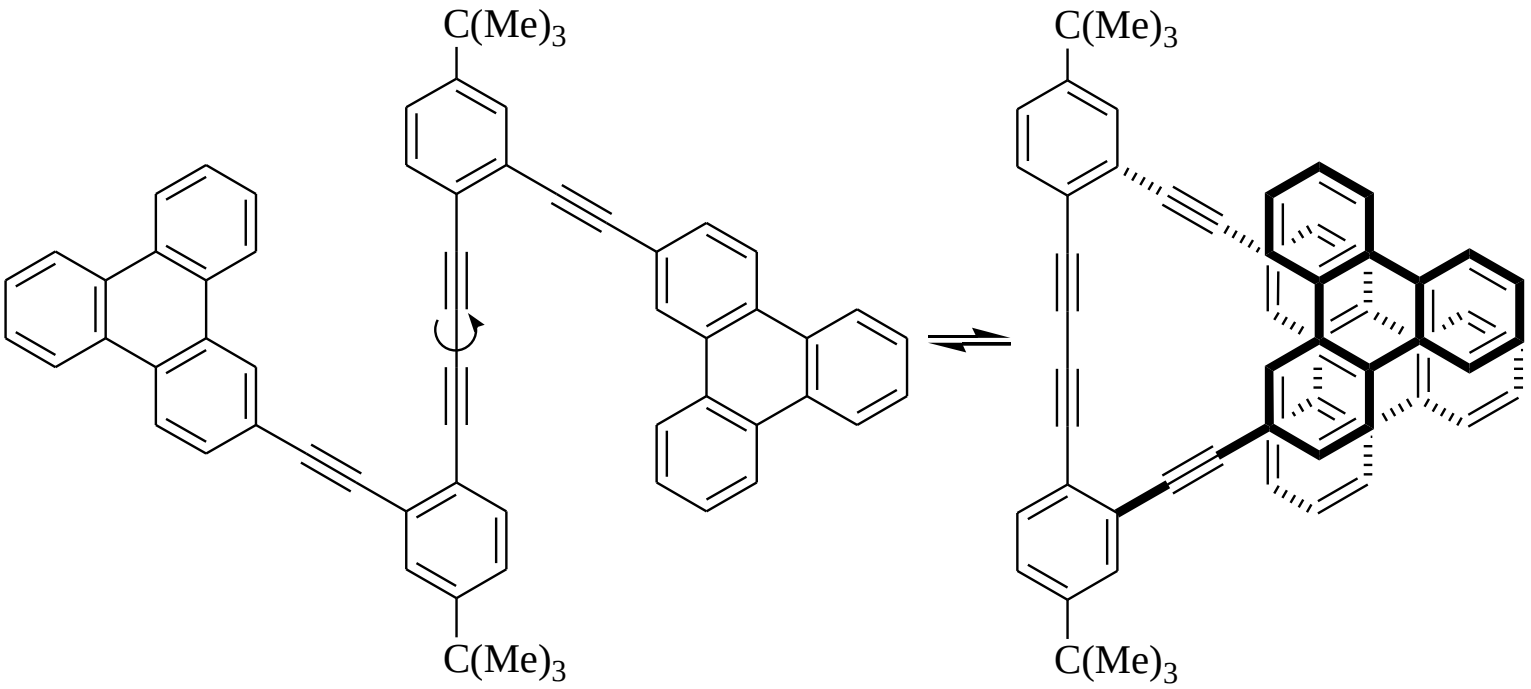
In solution no excimer emission

How about triphenylene in constrained environments?

Excimer emission in solid state

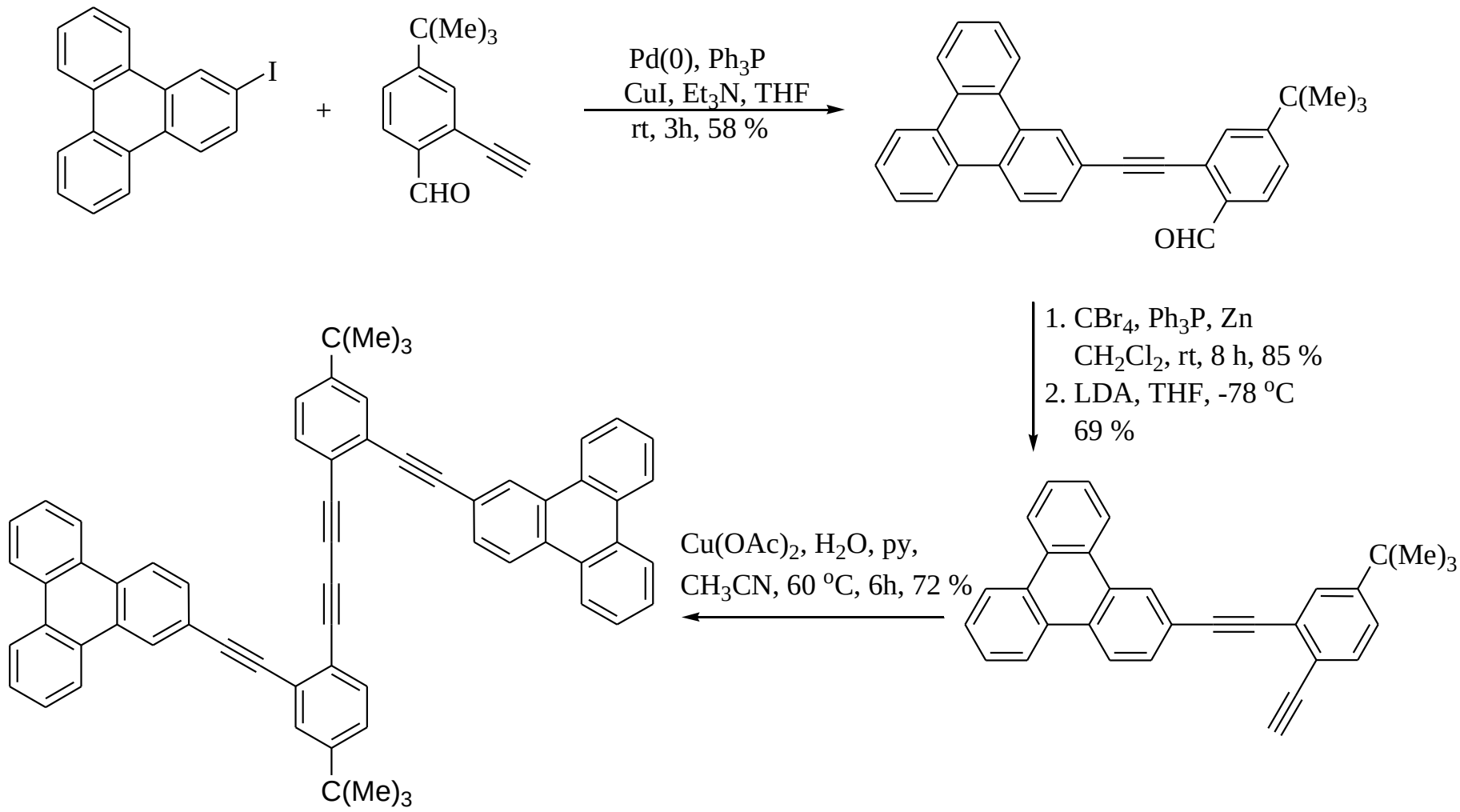
Excimer emission in derivatives that form organogels

(Ikeda, M.; Takeuchi, M.; Shinkai, S. *Chem. Commun*, 2003, 1354–1355).

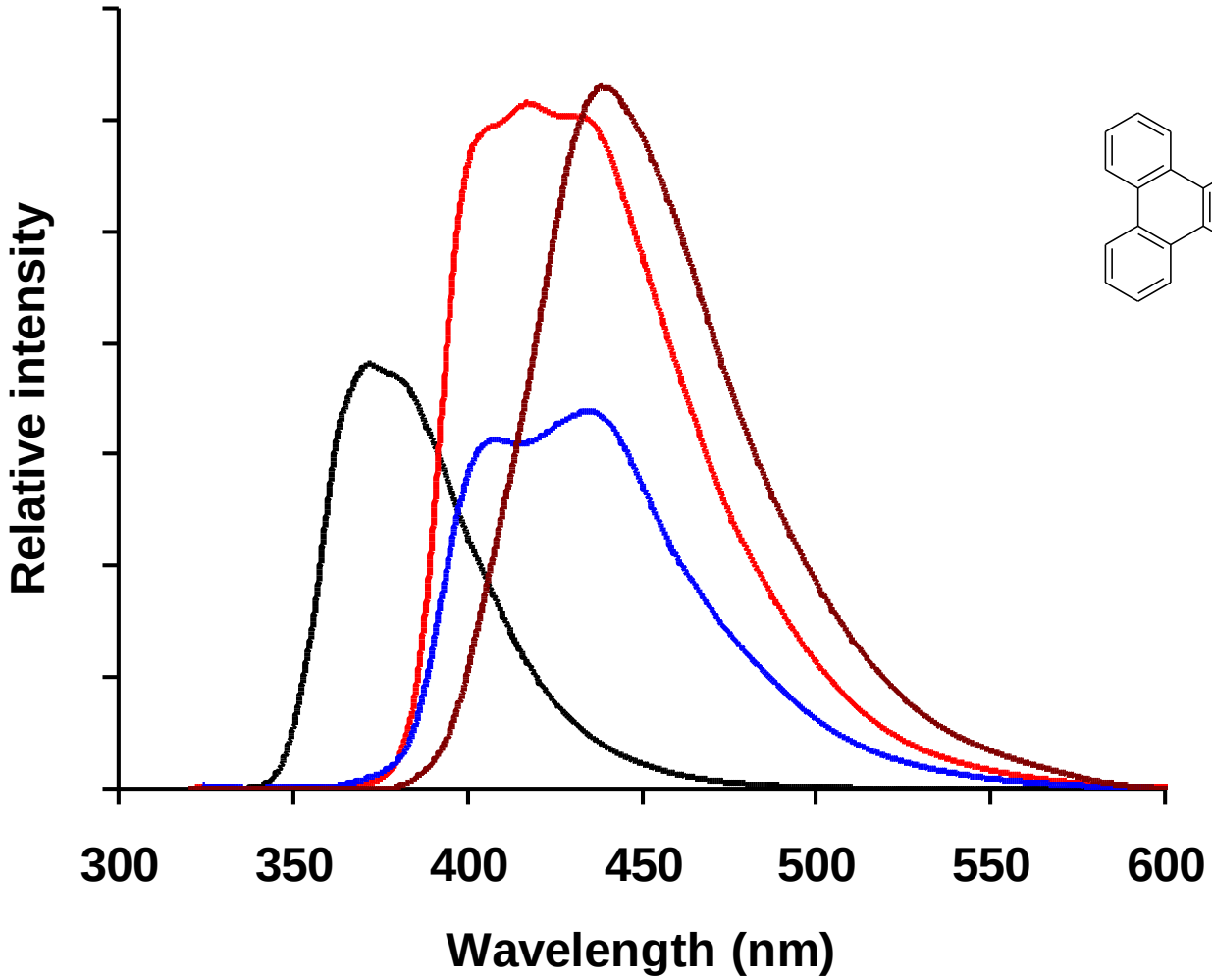


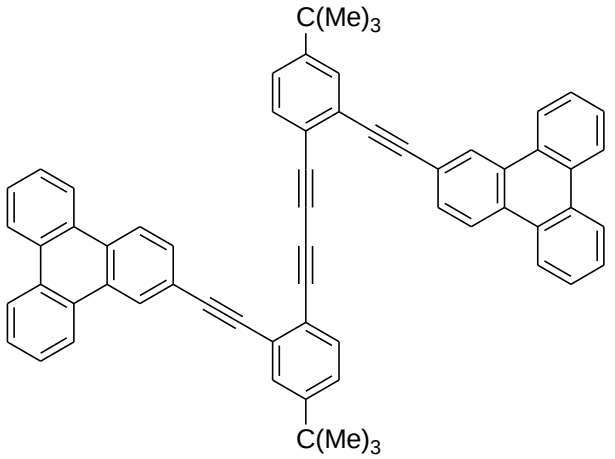
1a **1b**

R. Nandy, *Org. Biomol. Chem.*, **2010**, *8*, 2260-2266.

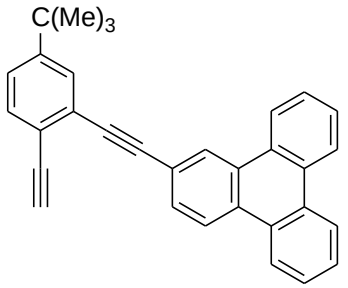


R. Nandy, *Org. Biomol. Chem.*, **2010**, *8*, 2260-2266.



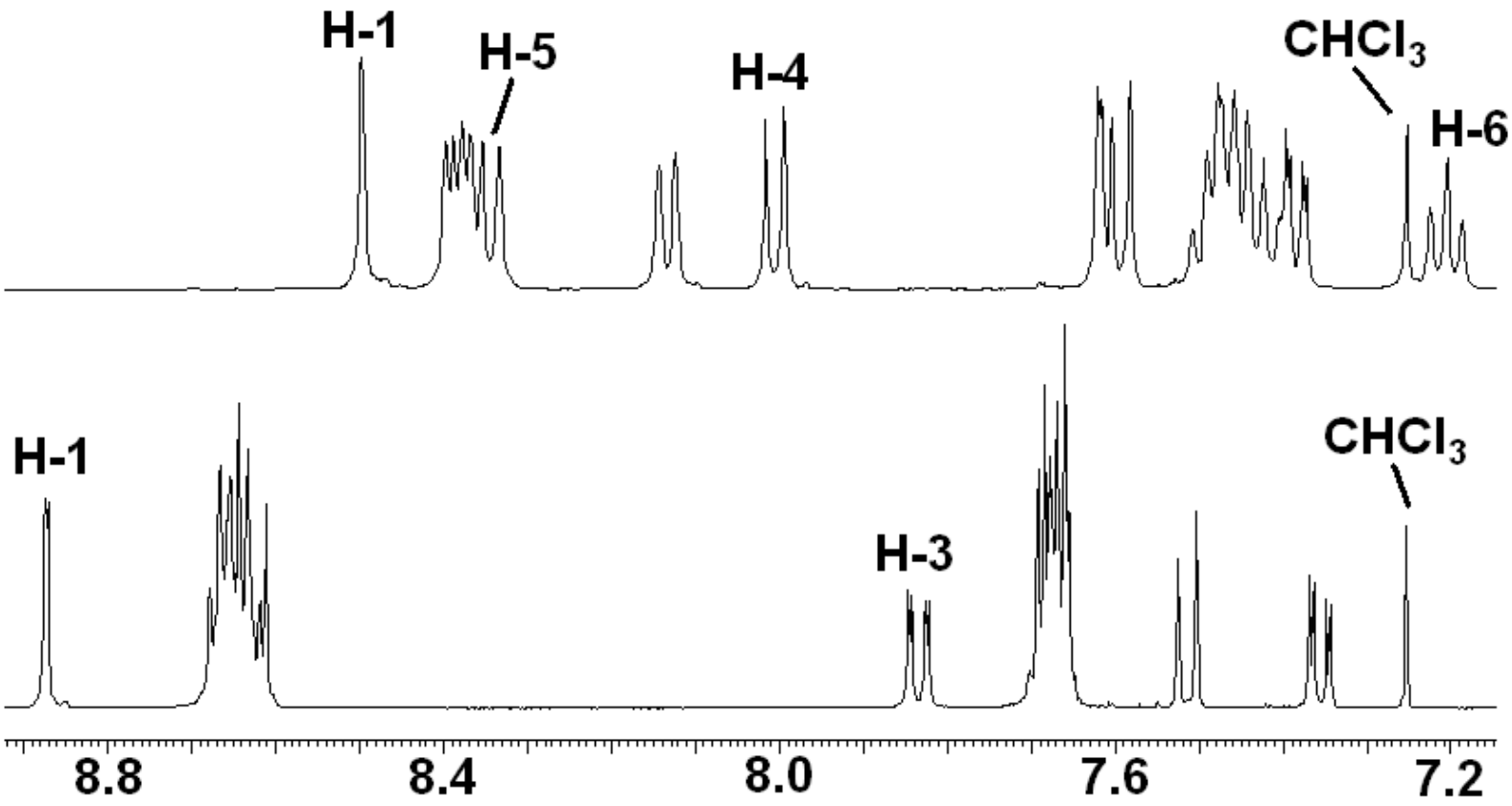


1

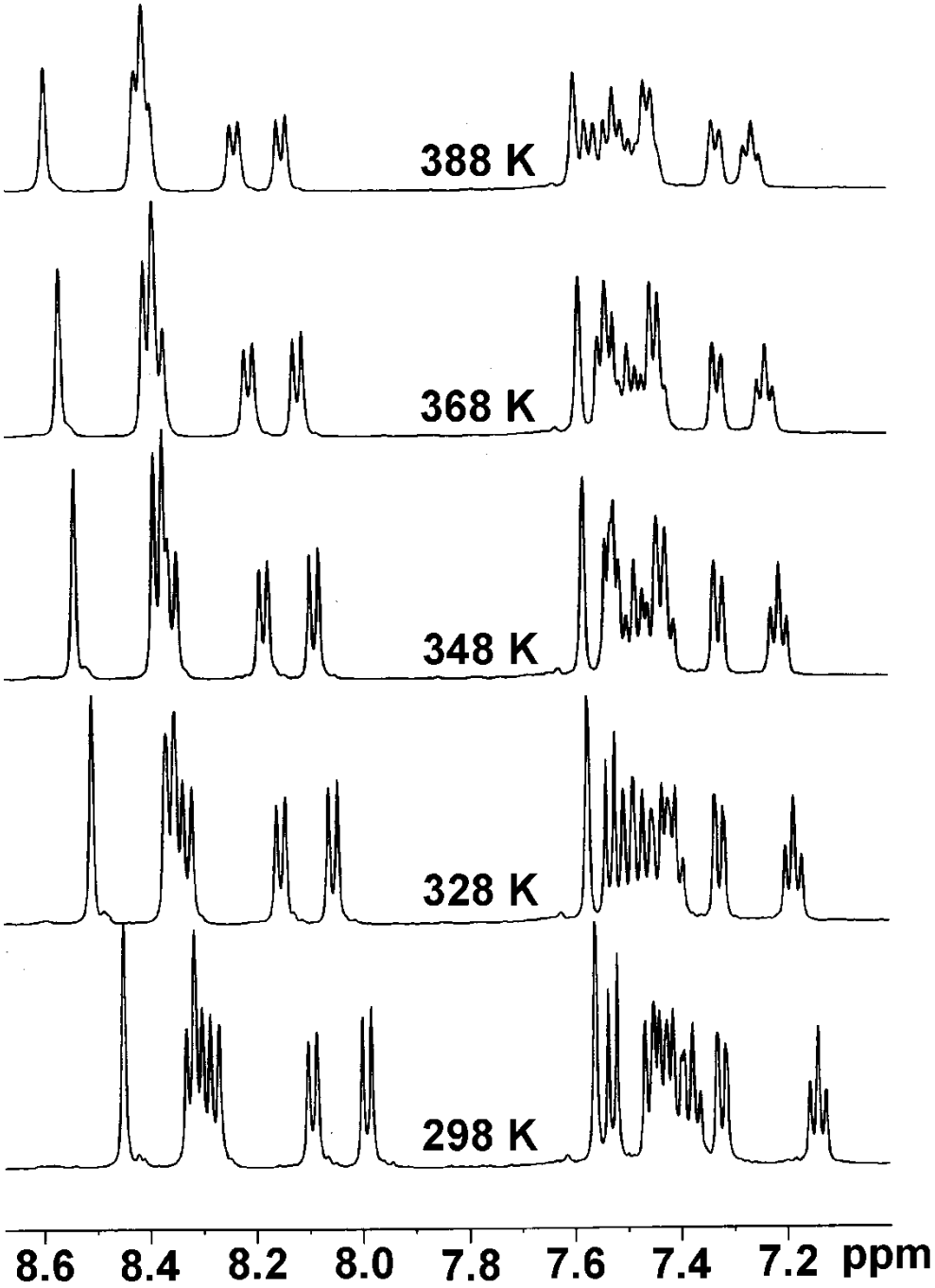


2

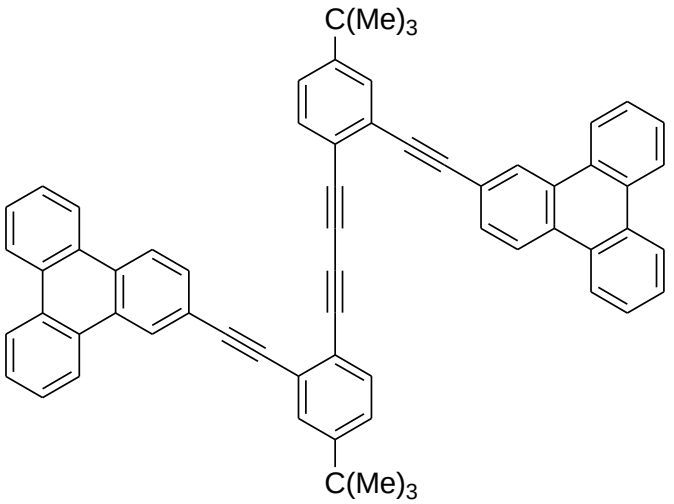
Fluorescence emission spectrum of 10^{-5} M solution of **1** in CH_2Cl_2 (red), in cyclohexane (blue) and **2** in CH_2Cl_2 (black) and of **1** in solid state (brown). λ_{ex} 310 nm.



Comparison of ^{1}H NMR spectra of 1 (top) and 2 (bottom) in $CDCl_3$.

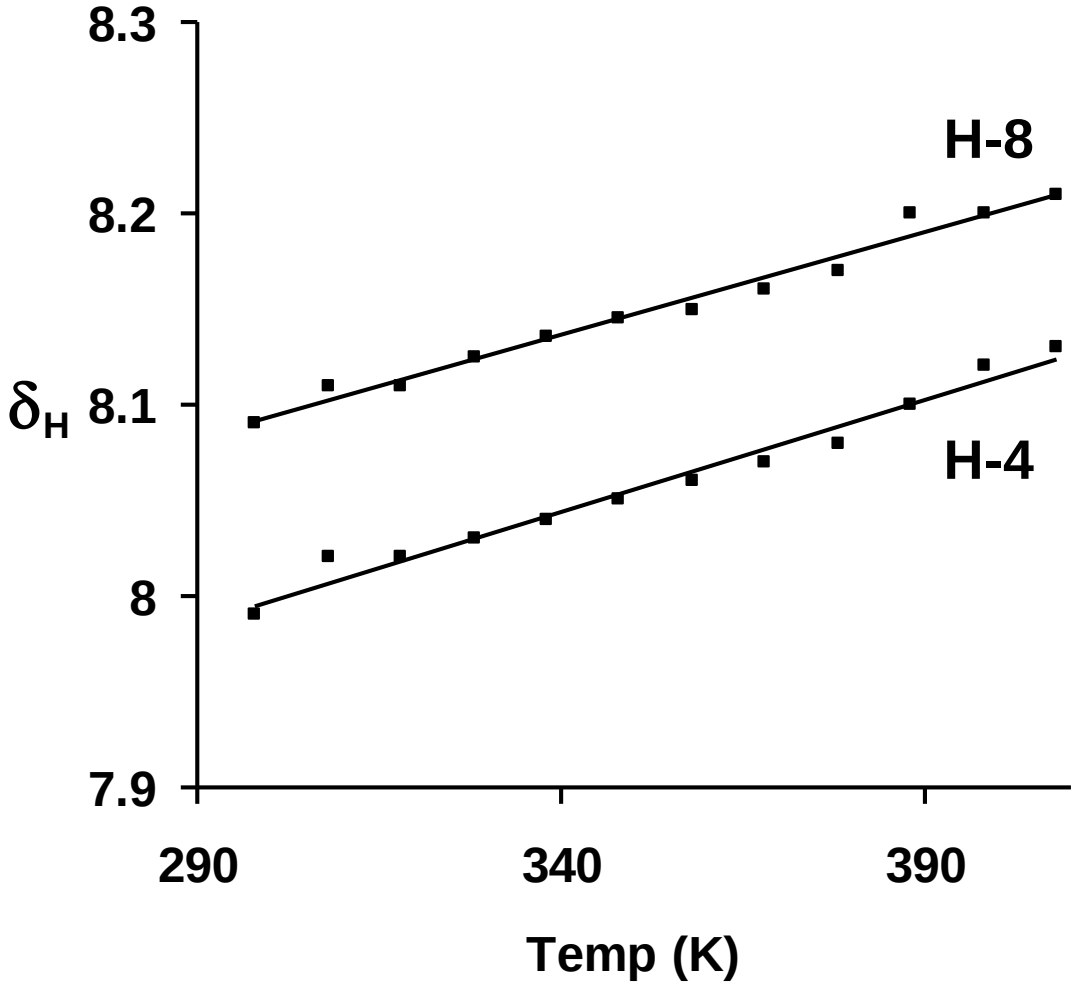


VT-^{1}NMR spectra of



1

Effect of temperature on chemical shift of H-4 and H-8 protons of 1



“NOTHING EVOLVES IN ISOLATION”

Dr. G. Venkataramana, Dr. R. Nandy

Dr. M. S. Moni, SAIF, IIT Madras (NMR data)
Dr. B. Varghese, SAIF, IIT Madras (X-ray crystallography)

A. Mohan (NMR) and Shantha Nair, Esakki Muthu (ESI-MS)
V. Ramkumar (XRD)

Department of Chemistry and SAIF, IIT Madras

DST (New Delhi), CSIR (New Delhi)

Thank you