Synthesis of cyclooctatetraene-based molecular balances

C106

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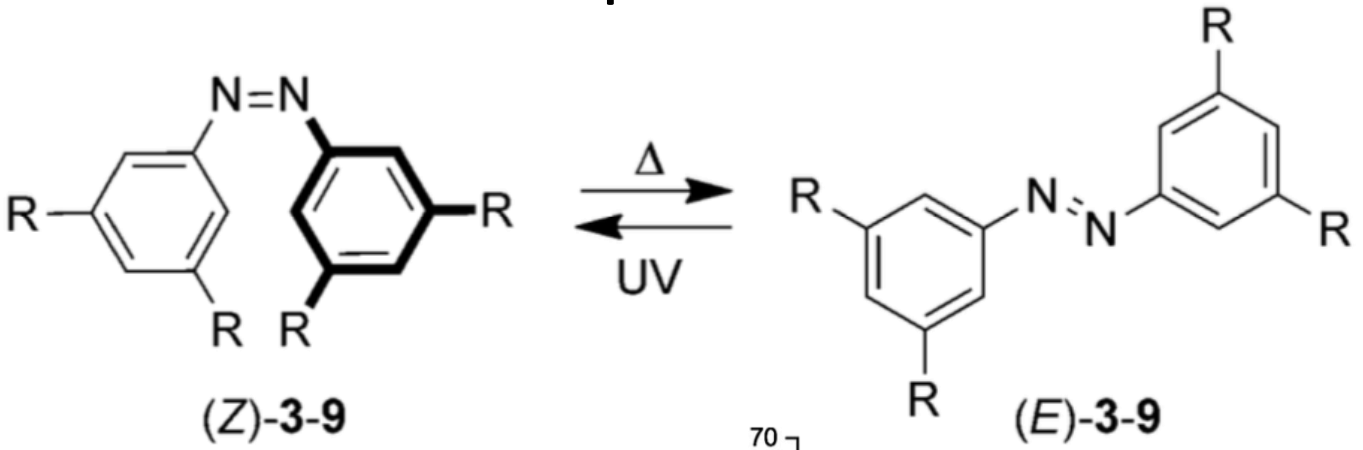
London Dispersion Force



(*Z*)-**3**-**9** (*E*)-**3**-**9**

3: R = H
4: R = *t*Bu
5: R = Me
6: R = *i*Pr
7: R = Cy
8: R = Ad
9: R = Ph

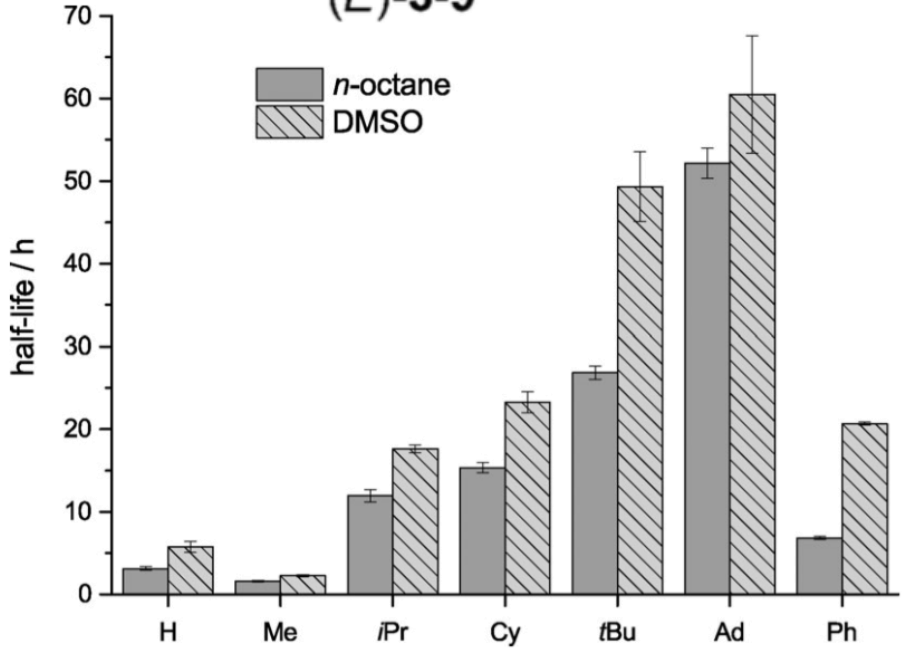
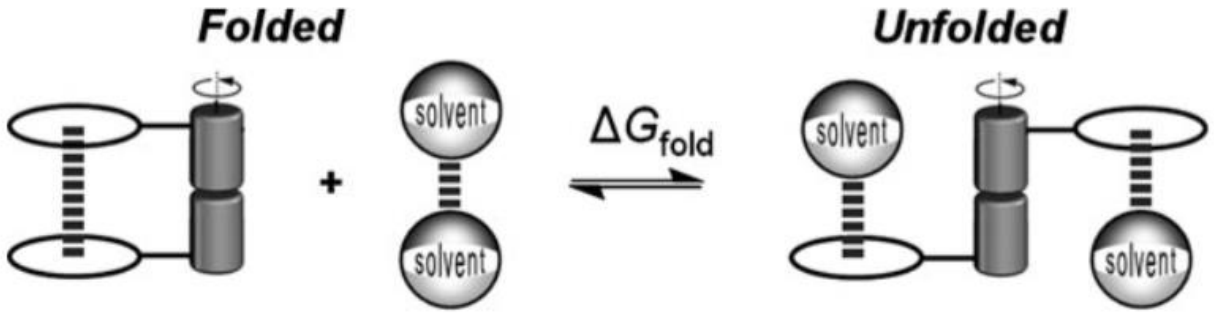
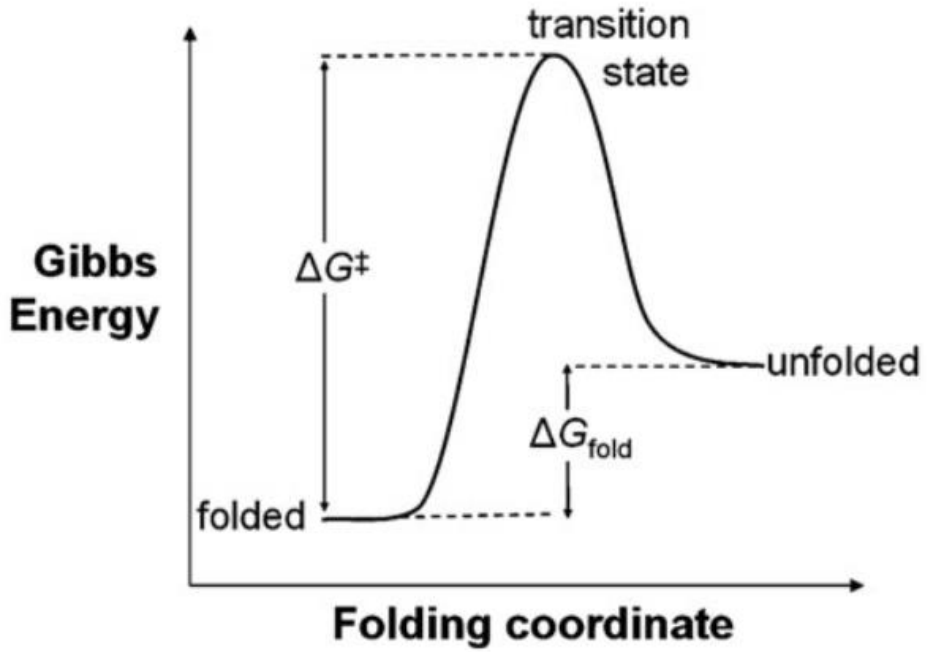


Figure 1. Half-lives of azobenzenes **3**–**9** measured in *n*-octane and DMSO at 53 °C.

L. Schweighauser, M. A. Strauss, S. Bellotto, H. A. Wegner, *Angew. Chem. Int. Ed.* **2015**, *54*, 13436–13439.

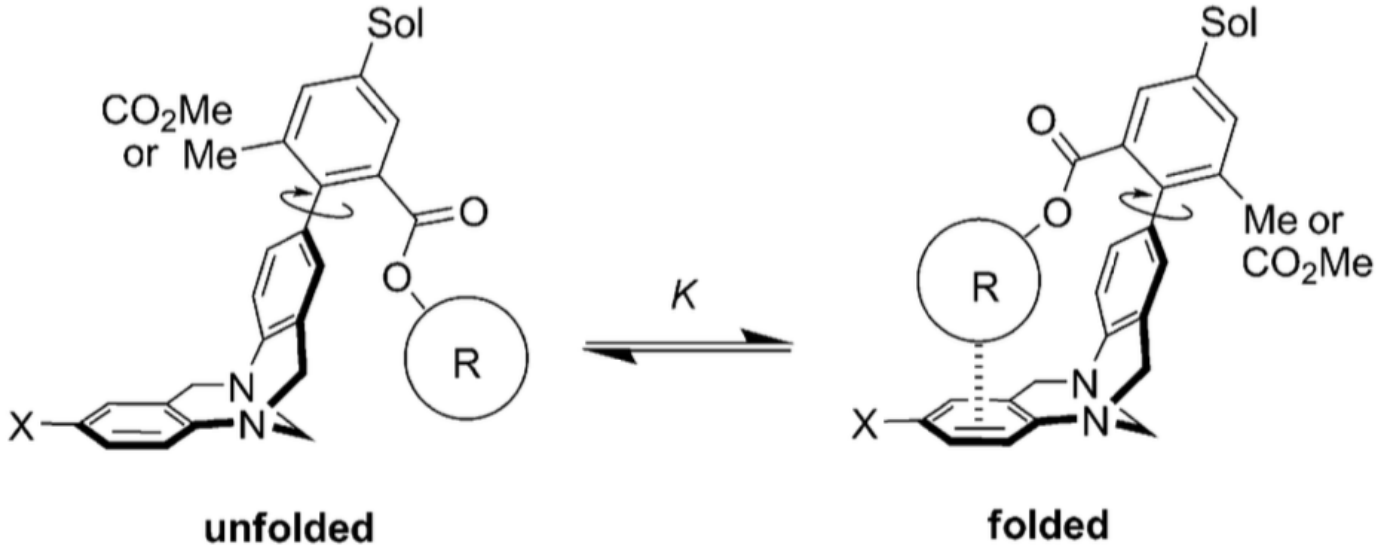
What is a molecular balance?





I. K. Mati, S. L. Cockroft, *Chem. Soc. Rev.* **2010**, *39*, 4195–4205.

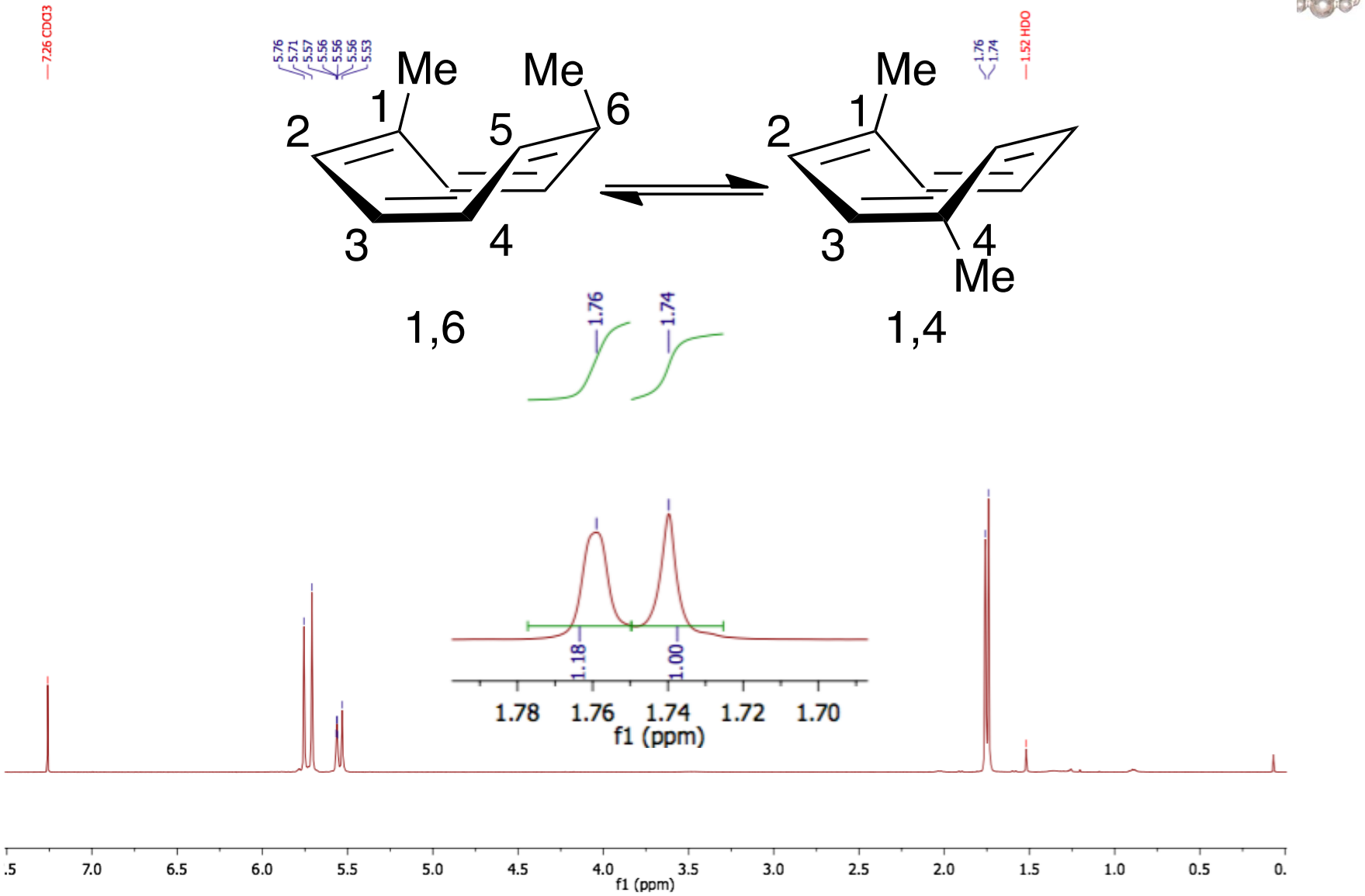
A variety of molecular balances



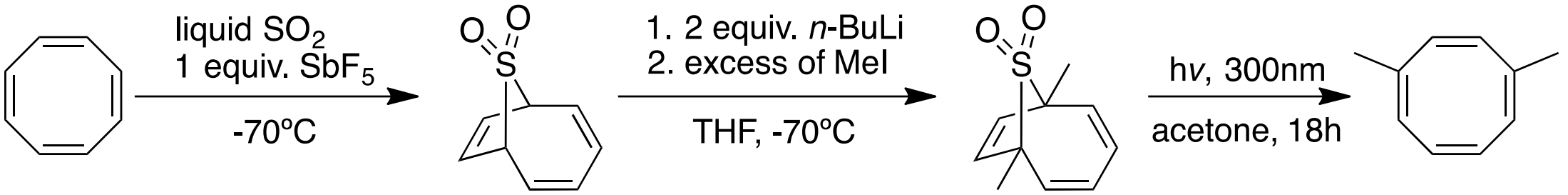
R = Me, *i*-Pr, *t*-Bu, cyclohexyl, 1-adamantyl, 2-adamantyl, substituted phenyl rings

S. Paliwal, S. Geib and C. S. Wilcox, *J. Am. Chem. Soc.* **1994**, 116, 4497–4498.
B. Bhayana and C. S. Wilcox, *Angew. Chem. Int. Ed.* **2007**, *46*, 6833–6836.

Our work


7.26 CDCl3
5.76
5.71
5.57
5.56
5.56
5.56
5.53
Me
Me
1
2
5
6
3
4
1,6
1.76
1.74
1.52 HDO
Me
1
2
3
4
Me
1,4
1.18
1.00
1.78
1.76
1.74
1.72
1.70
f1 (ppm)
f1 (ppm)

1,4-dimethylcyclooctatetraene



lit.[1]: 95%
SM: 23%

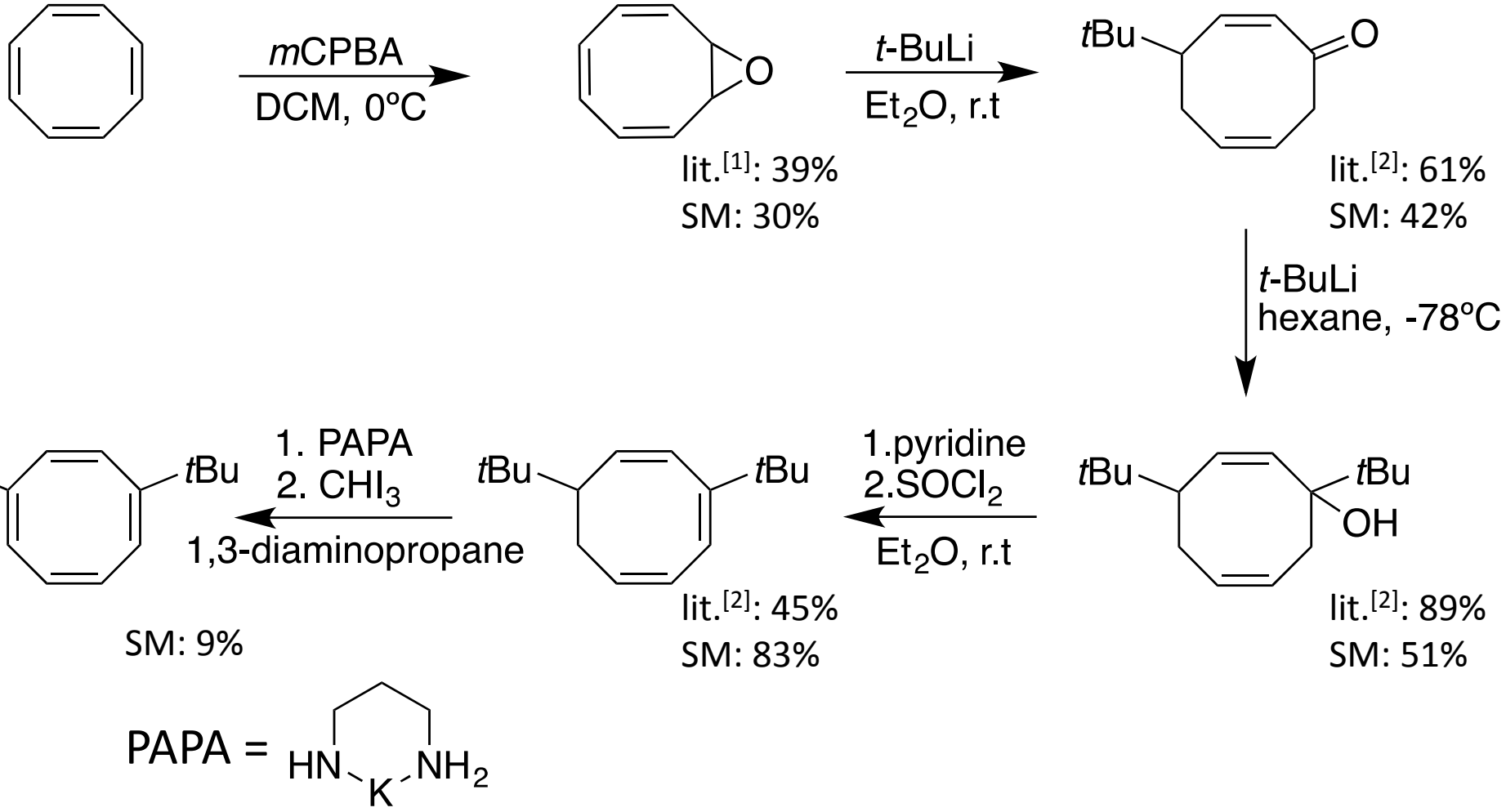
lit.[2]: quant.
SM: 86%

lit.[2]: quant.
SM: 37%

[1] J. Gasteiger, R. Huisgen, *J. Am. Chem. Soc.* **1972**, *94*, 6541-6543.

[2] L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, M. Oku, *J. Am. Chem. Soc.* **1974**, *96*, 5806-5815.

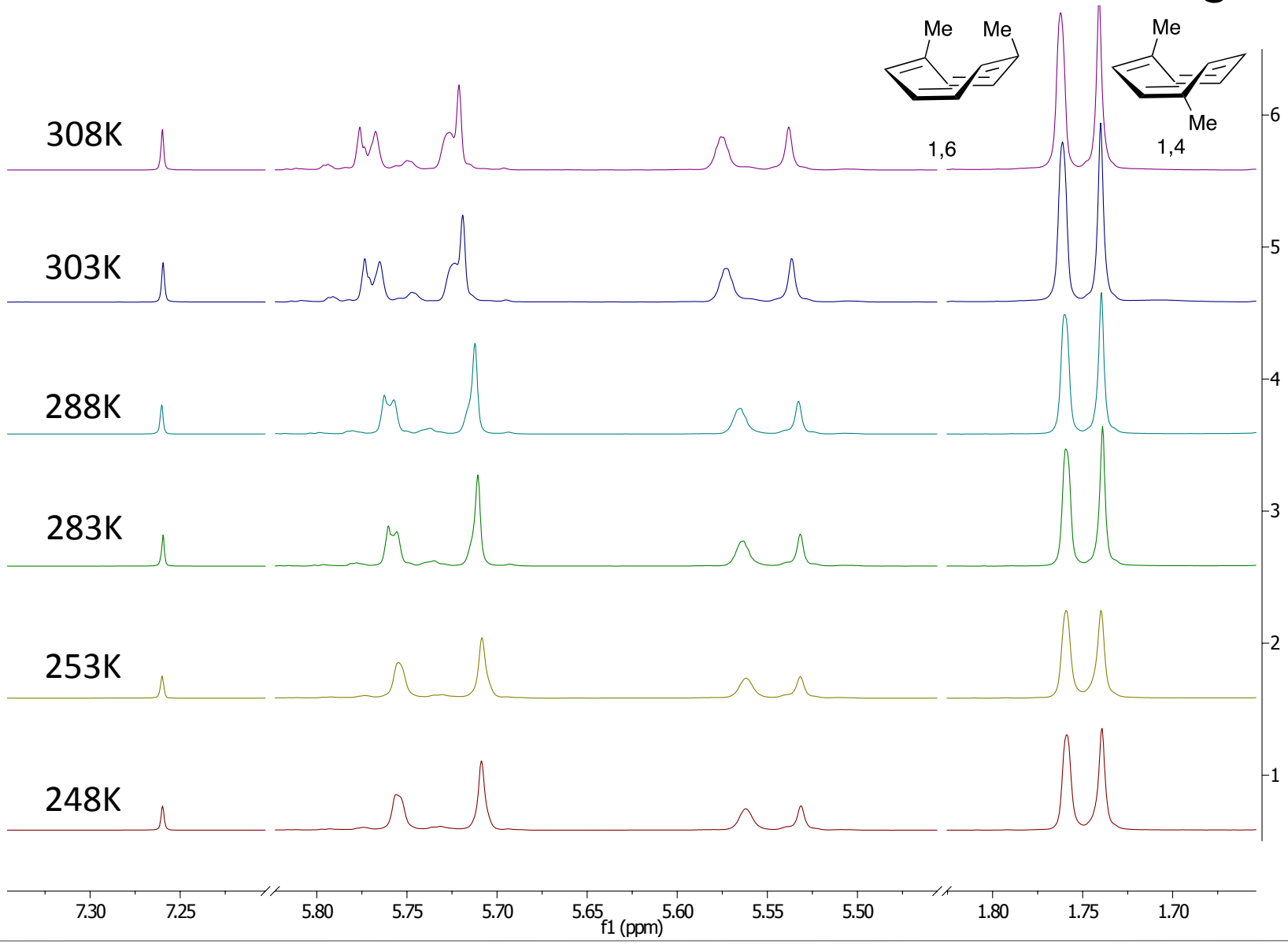
1,4-di-*tert*-butylcyclooctatetaene



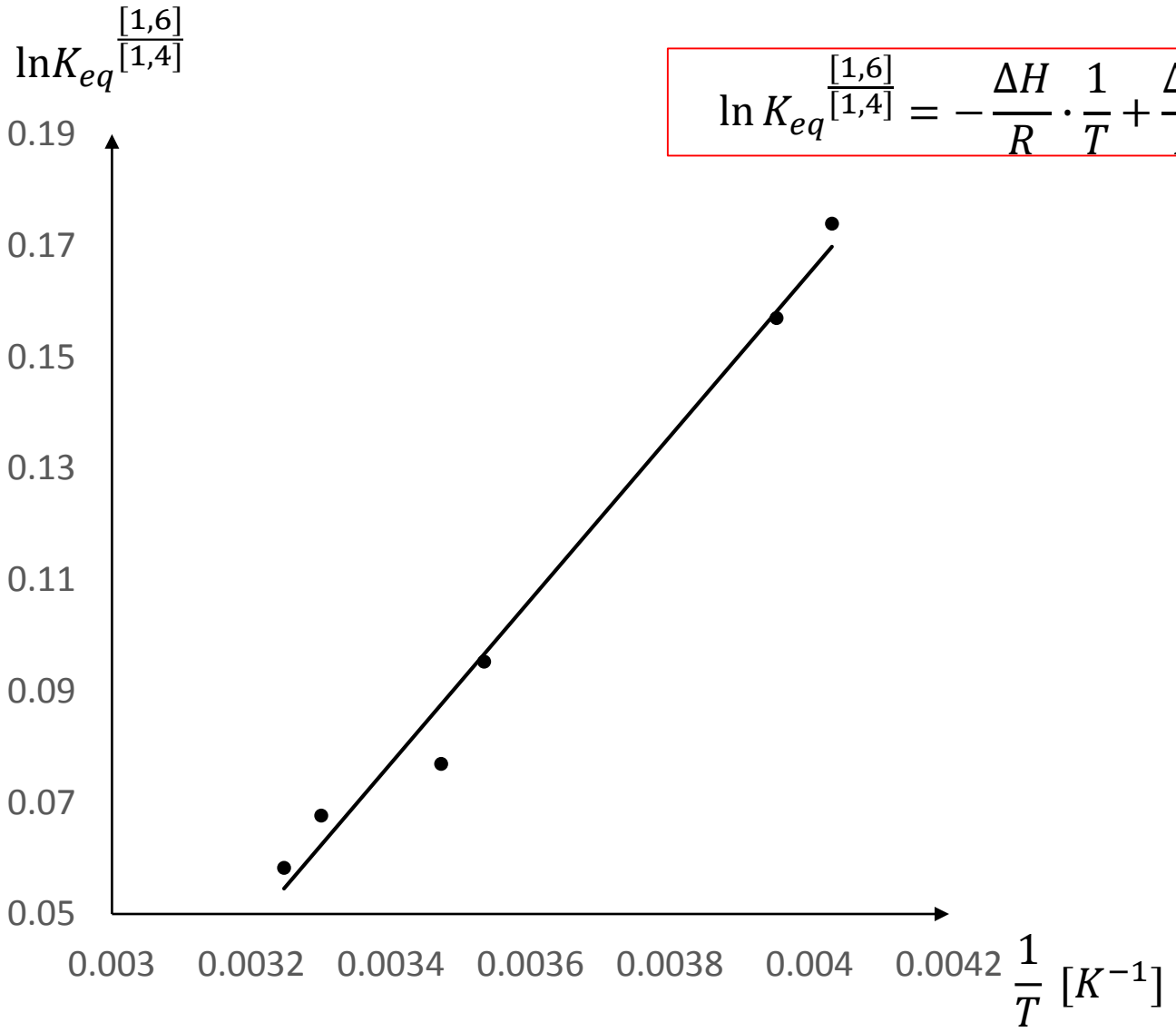
[1] A. C. Cope, B. D. Tiffany, *J. Am. Chem. Soc.* **1951**, *73*, 4158-4161.

[2] M. J. Miller, M. H. Lyttle, A. Streitwieser, *J. Org. Chem.* **1981**, *46*, 1977-1984.

Dimetylcyclooctatetaraene in $CDCl_3$

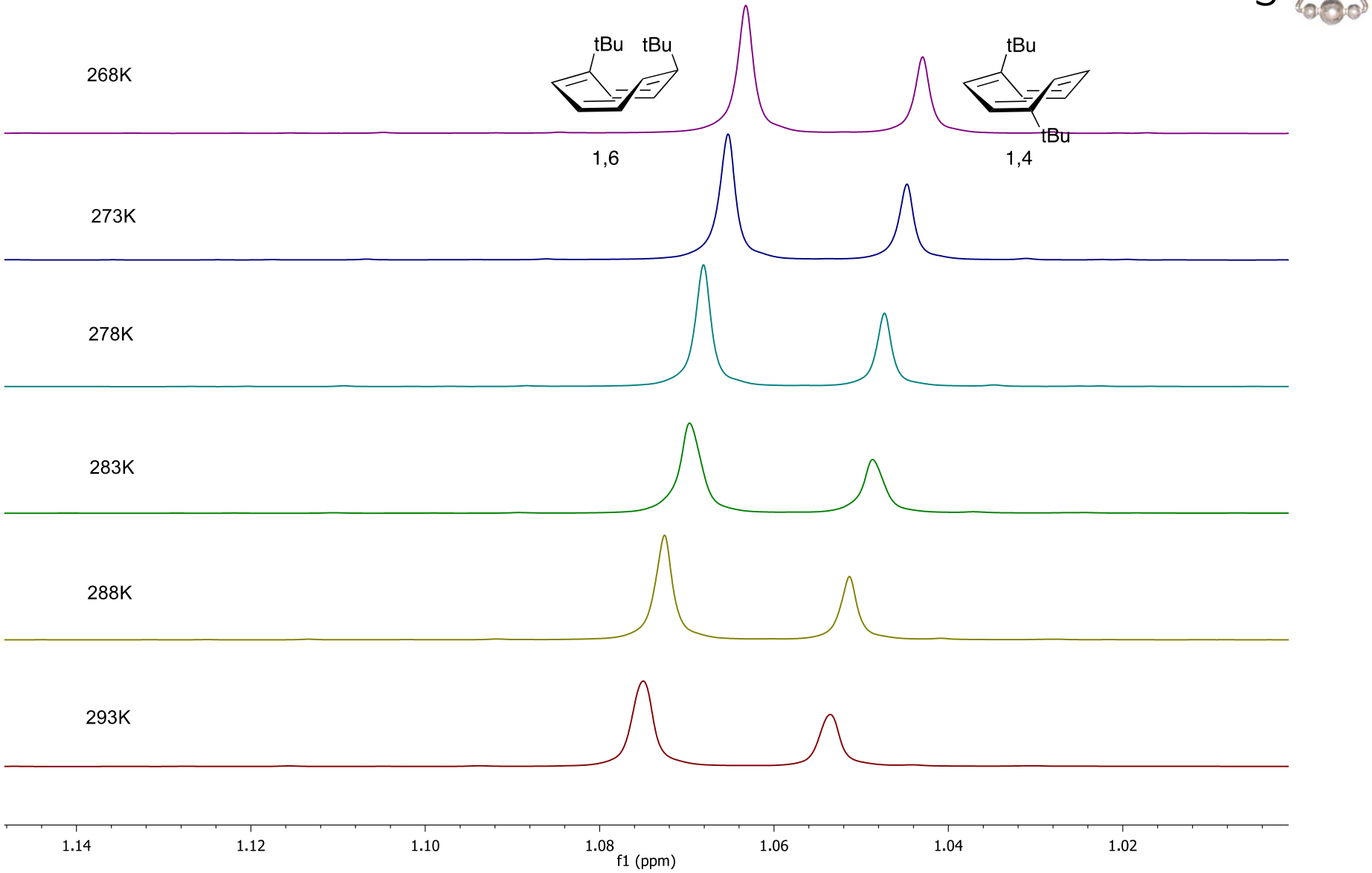


Dimetylcyclooctatetaraene in $CDCl_3$



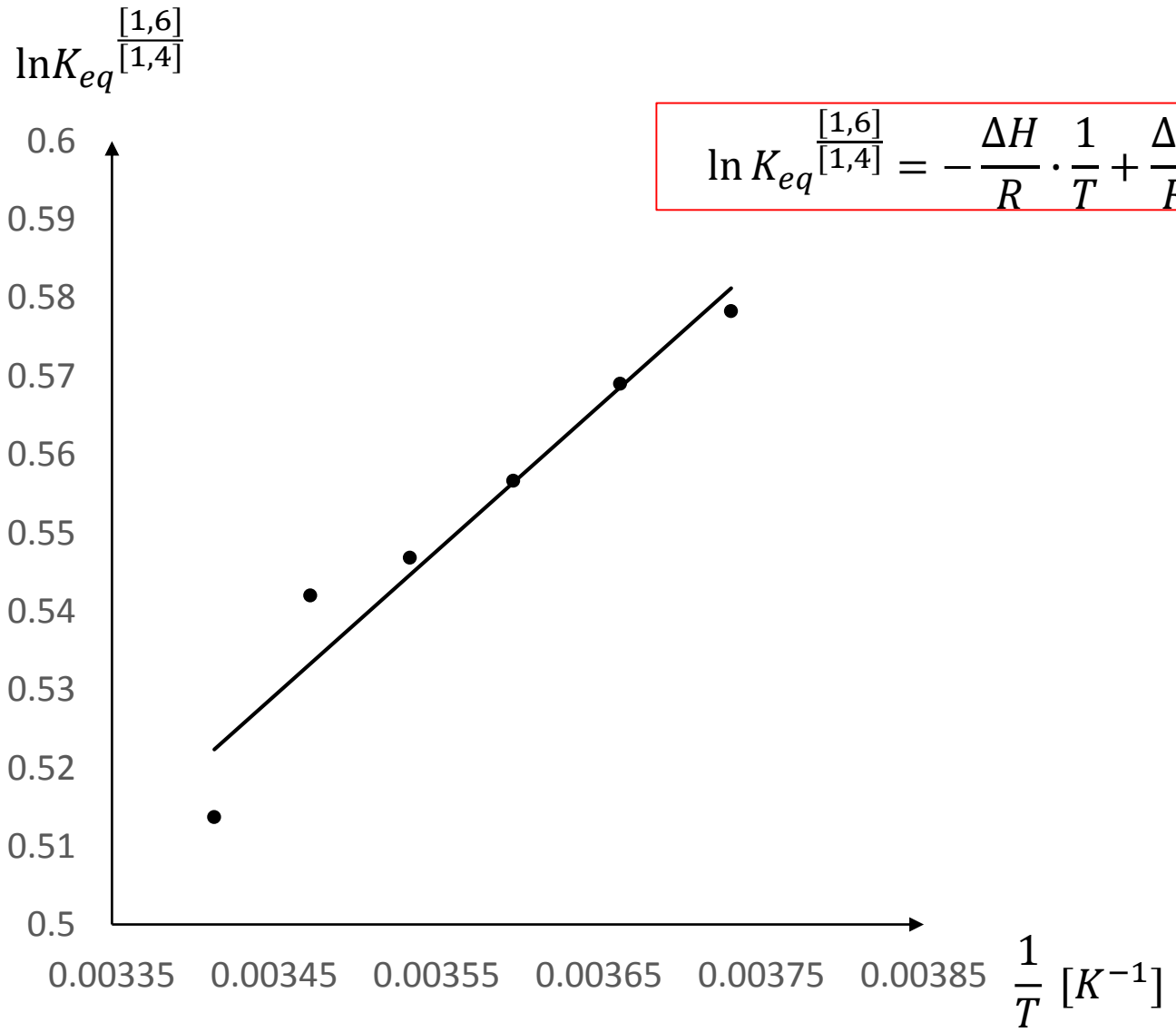
$$\ln K_{eq}^{\frac{[1,6]}{[1,4]}} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$$

Di-*tert*-butylcyclooctatetaraene in $CDCl_3$

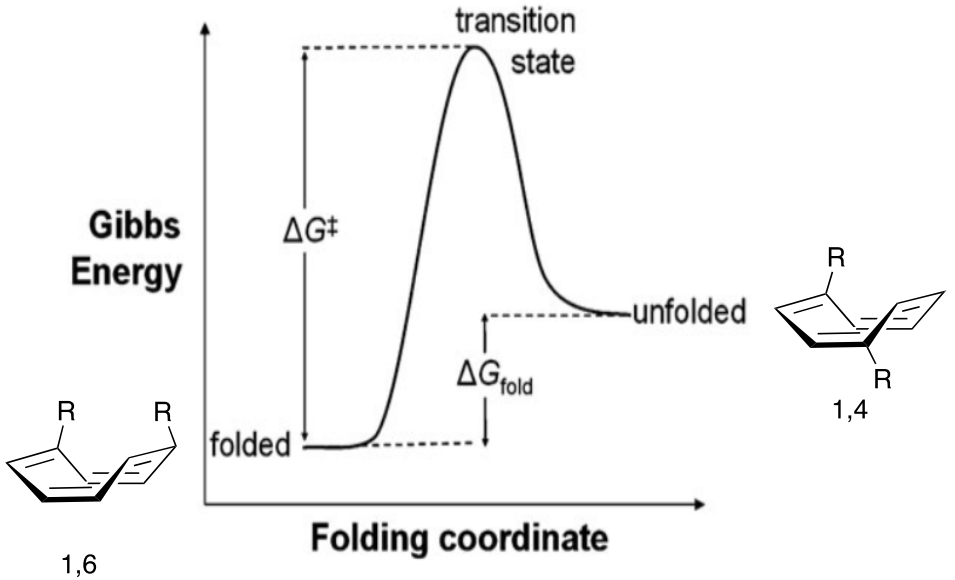


Di-*tert*-butylcyclooctatetaraene in $CDCl_3$

$$\ln K_{eq}^{\frac{[1,6]}{[1,4]}} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$$



Results



R	Solvent	ΔH [kcal·mol^{-1}]	ΔS [cal·mol^{-1}·K^{-1}]	$\Delta G_{\mathrm{fold}}^{293\mathrm{K}}$ [kcal·mol^{-1}]	R^2 [%]
Me	$CDCl_3$	-0.29	-0.84	-0.05	99
t-Bu	$CDCl_3$	-0.37	-0.22	-0.30	94

Comparison

R	Solvent	ΔH [kcal·mol^{-1}]	ΔS [cal·mol^{-1}·K^{-1}]	$\Delta G_{\text{fold}}^{293\text{K}}$ [kcal·mol^{-1}]	K_{eq}^{293K}
Me	$CDCl_3$	-0.29	-0.84	-0.05	1.10
Me[1]	C_6D_6	-0.05	-0.3	-0.08	1.15
t-Bu	$CDCl_3$	-0.37	-0.22	-0.30[a]	1.67[a]
t-Bu[1]	$CDCl_3$	-1.14	+2.5	-0.39[a]	1.93[a]
t-Bu[2]	$CDCl_3$	-1.07	N/A	-0.43[a]	N/A
t-Bu[3]	$CDCl_3$	-1.17	N/A	-0.48[a]	2.08[a]

[a] At 298K

[1] J. E. Anderson, P. A. Kirsch, *J. Chem. Soc. PERKIN TRANS.* 2, **1992**, 1951-1957

[2] M. H. Lyttle, A. Streitwieser Jr., R. Q. Klutz, *J. Am. Chem. Soc.* **1981**,103,3232

[3] L. A. Paquette, G. J. Hefferon, R. Samodral, Y. Hanzawa, *J. Org.Chem.* **1983**,48, 1262

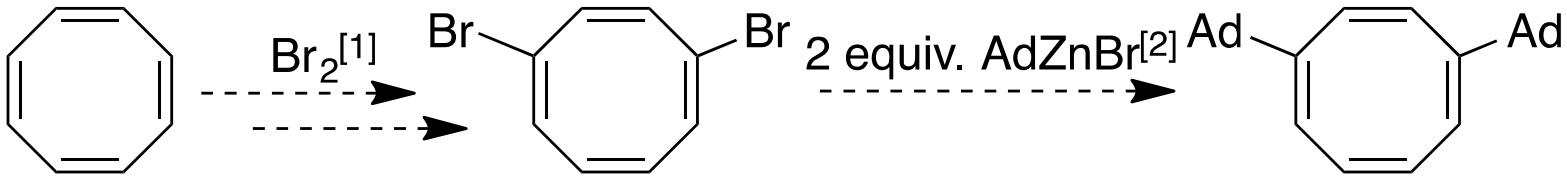
Conclusion

- Dimethylcycloocatetraene ✓
- Di-*tert*-butylcyclooctatetaraene ✓
- Measurements in $CDCl_3$

Outlook

- Screening of solvents

- Synthesis of di-adamantylcyclooctatetraene



[1] L. A. Paquette, S. V Ley, R. H. Meisinger, R. K. Russell, M. Oku, *J. Am. Chem. Soc.* **1974**, *96*, 5806–5815.
[2] C. Sämann, V. Dhayalan, P. R. Schreiner, P. Knochel, *Org. Lett.* **2014**, *16*, 2418–2421.

Acknowledgement

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Danke und Aufwiedersehen!