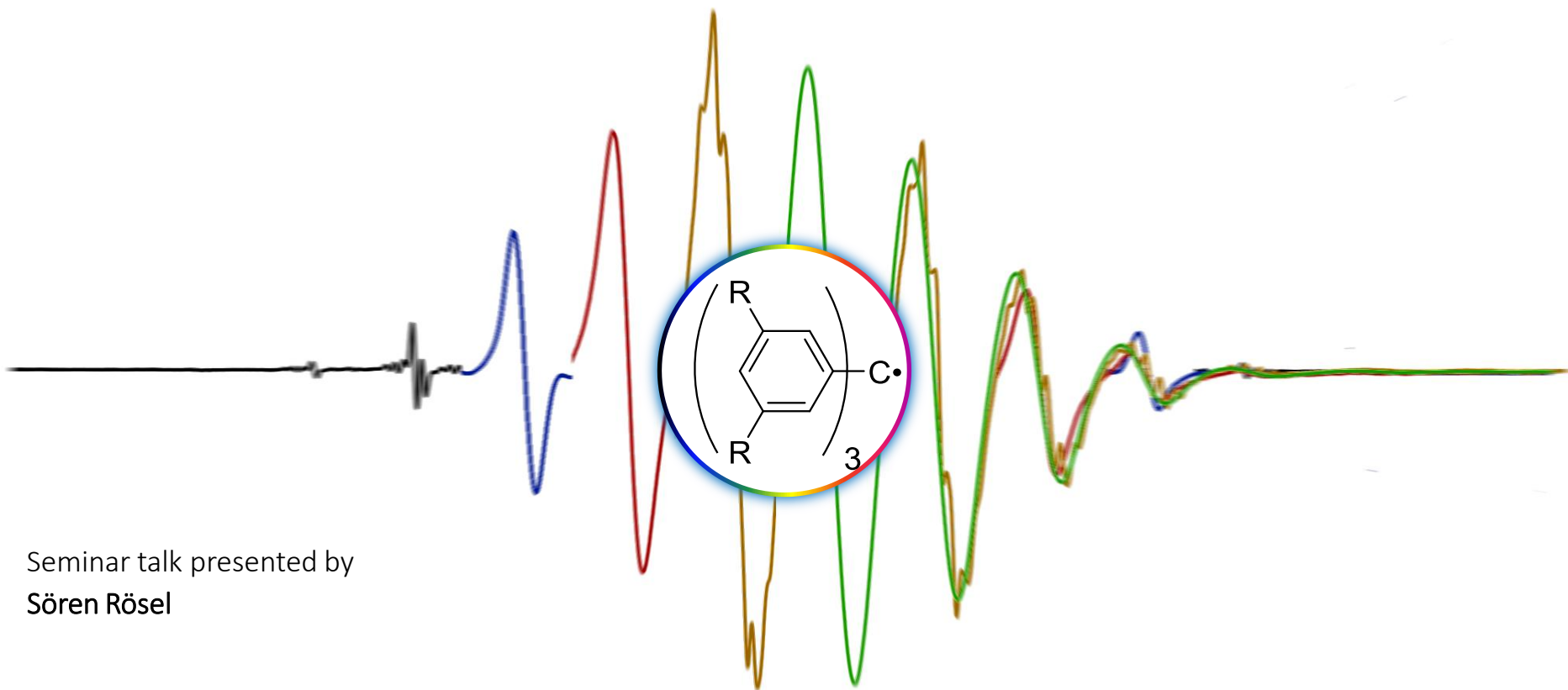


On Dispersion: What Can We Learn from Hexaphenylethanes?



Seminar talk presented by
Sören Rösel

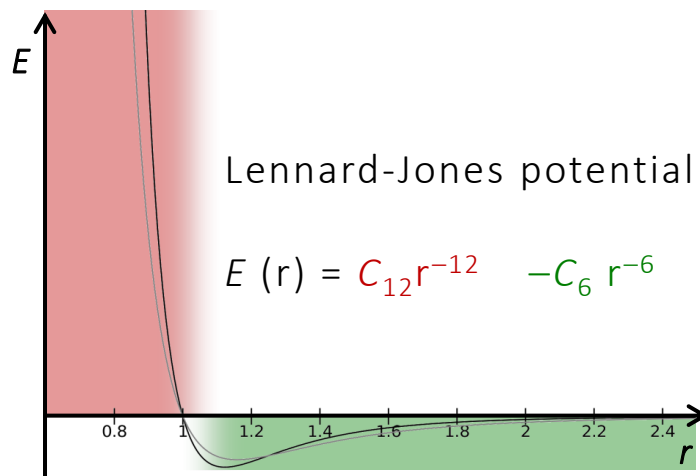
April 20st, 2018

AG Schreiner
Institute of Organic Chemistry
Justus-Liebig University Giessen

Intermolecular Forces in Chemistry

The non-covalent interaction:
A sum of many:

- Pauli Repulsion
- Keesom force
- Debye force
- London dispersion



Fritz London (1937):

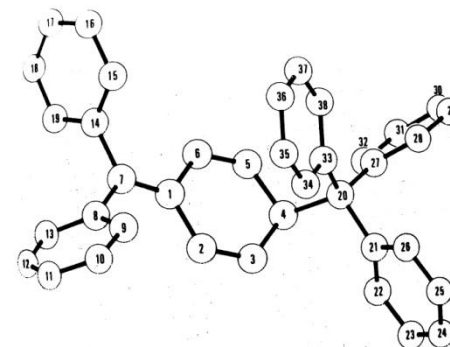
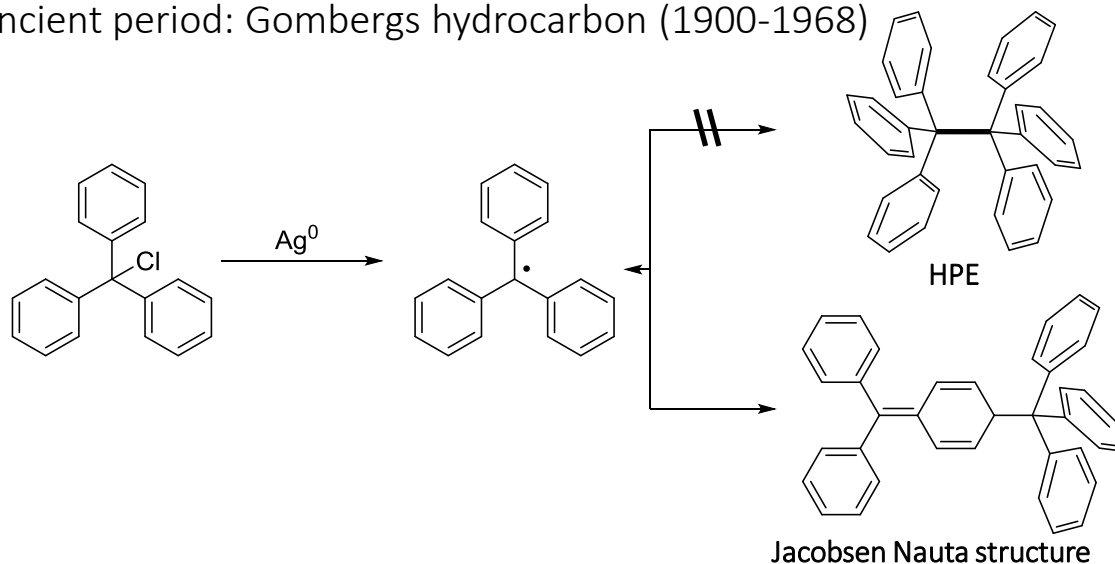
TABLE III.—THE THREE CONSTITUENTS OF THE VAN DER WAALS' FORCES.

	$\mu \cdot 10^{18}$.	$\alpha \cdot 10^{24}$.	$h\nu_0$ (Volts).	Orientation Effect Keesom	Induction Effect Debye	Dispersion Effect
CO .	0.12	1.99	14.3	0.0034	0.057	67.5
HI .	0.38	5.4	12	0.35	1.68	382
HBr .	0.78	3.58	13.3	6.2	4.05	176
HCl .	1.03	2.63	13.7	18.6	5.4	105
NH ₃ .	1.5	2.21	16	84	10	93
H ₂ O .	1.84	1.48	18	190	10	47

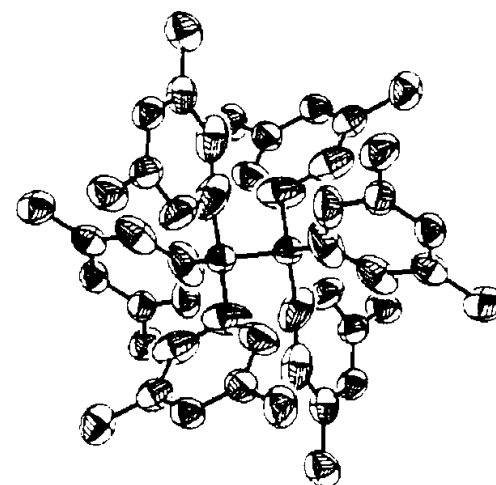
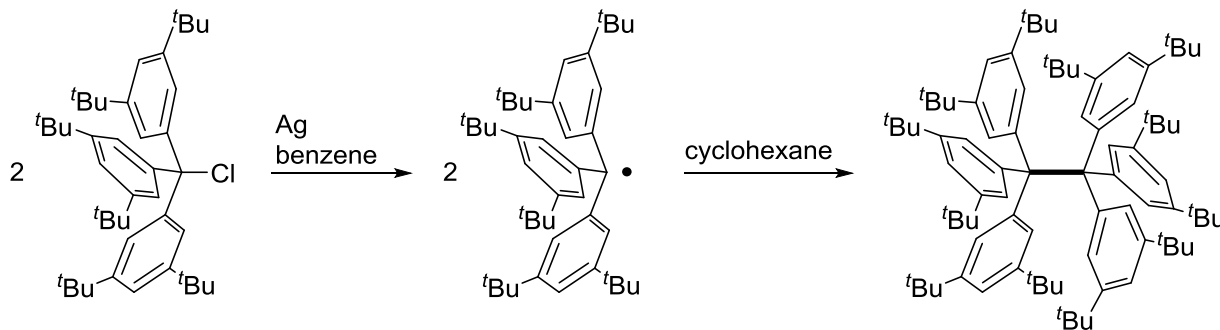
It is seen that the induction effect is in all cases practically negligible, and that even in such a strong dipole molecule as HCl the permanent dipole moments give no noticeable contribution to the Van der Waals' attraction. Not earlier than with NH₃ does the orientation effect become comparable with the dispersion effect, which latter seems in no case to be negligible.

A Brief History of Hexaphenylethane

Ancient period: Gombergs hydrocarbon (1900-1968)

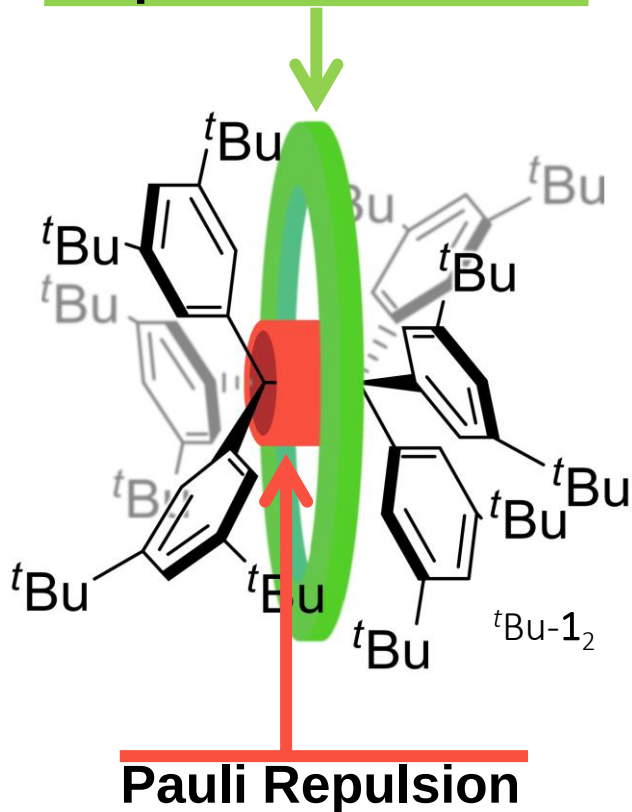


Late period: Unbridged hexaphenylethane derivatives (1978-1988)

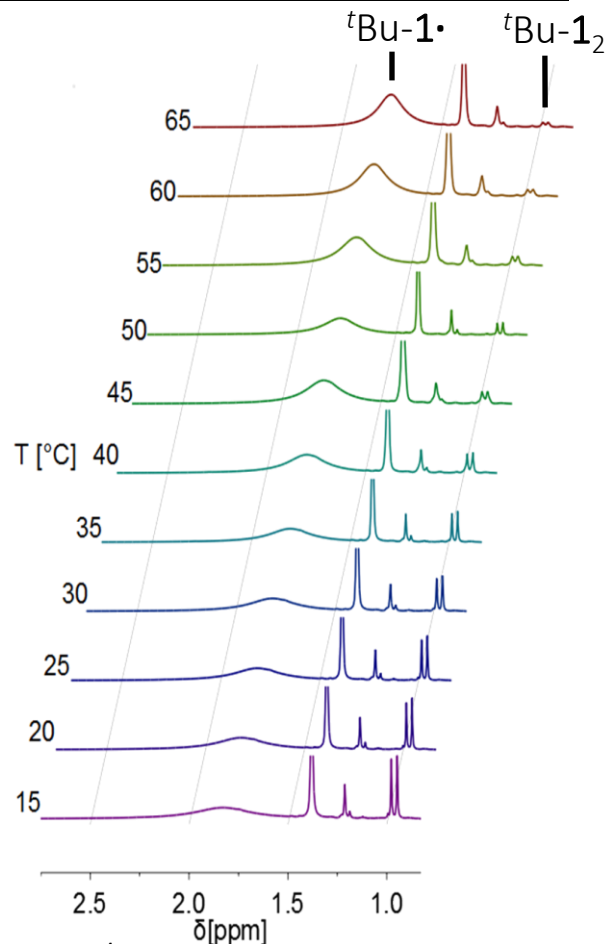


Hexa(3,5-di-*tert*-butylphenyl)ethane – the Prototype

Dispersion Attraction



computational	E_{disp}	ΔG_d^{298}
B3LYP-D3(BJ)/cc-pVDZ	67.7	10.5
TPSS-D3/TZVPP	61.6	+1 to +5
PWPB95-D3/QZVP(-g,-f)		-3 to +1



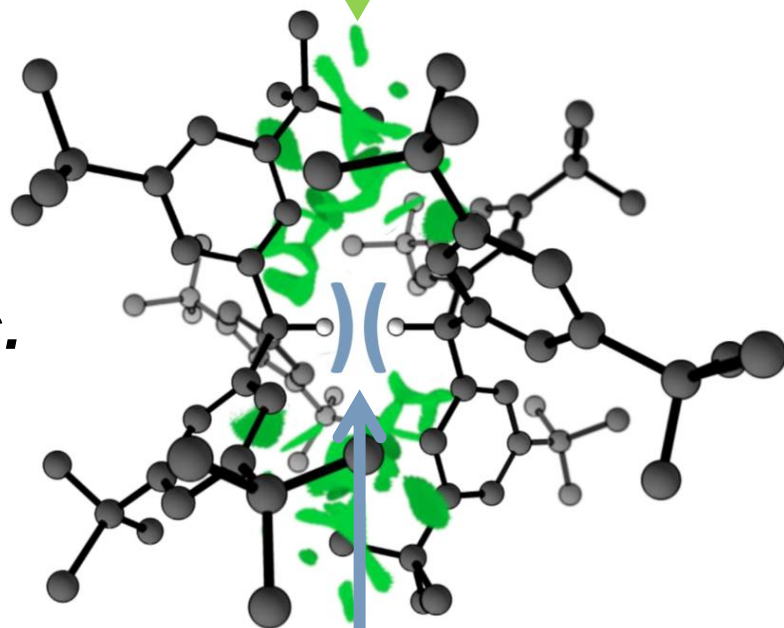
experimental	
$\Delta H_d =$	7.9(3) kcal mol ⁻¹ (10% of Ethane)
$T\Delta S_d^{298} =$	9.5(3) kcal mol ⁻¹
$\Delta G_d^{298} =$	-1.6(5) kcal mol ⁻¹

Tri(3,5-di-*tert*-butylphenyl)methane – a LD Bound Dimer

Dispersion Attraction

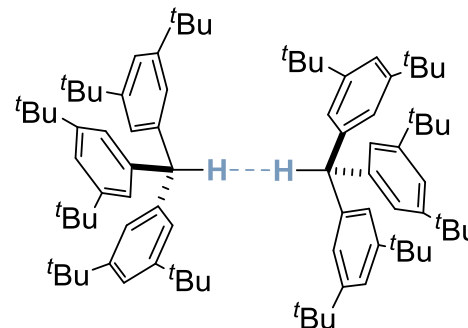


VS.

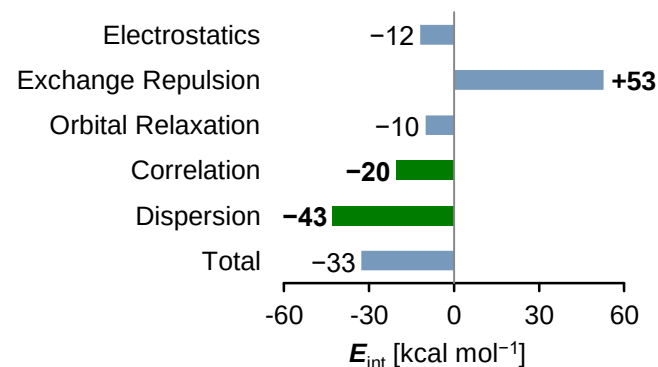


Pauli Repulsion

$$\begin{aligned} r(\text{H}\cdots\text{H}) &= 1.566(5) \text{ \AA} \\ \Delta r_{\text{vdW}} &= -0.84 \text{ \AA} \\ &(\text{NRD-structure!}) \end{aligned}$$

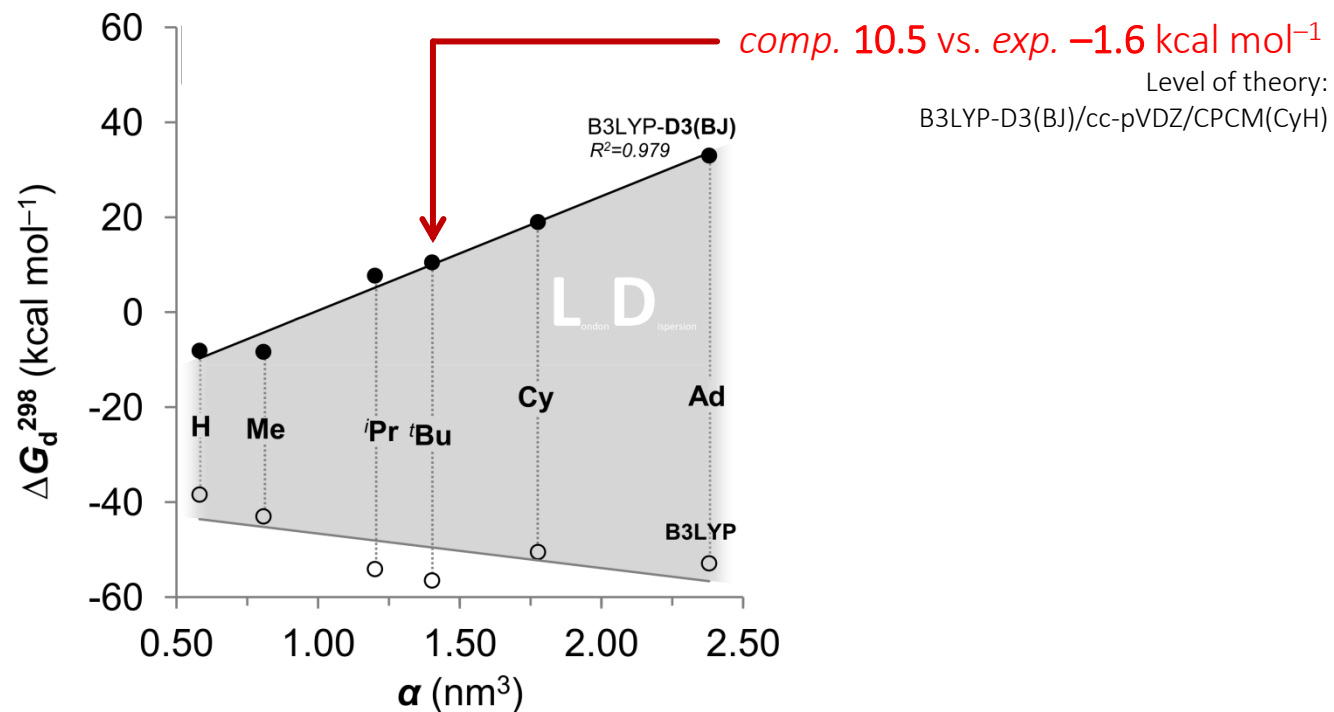
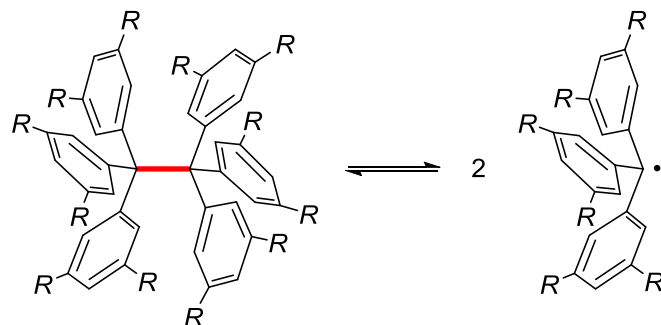


Energy Decomposition Analysis

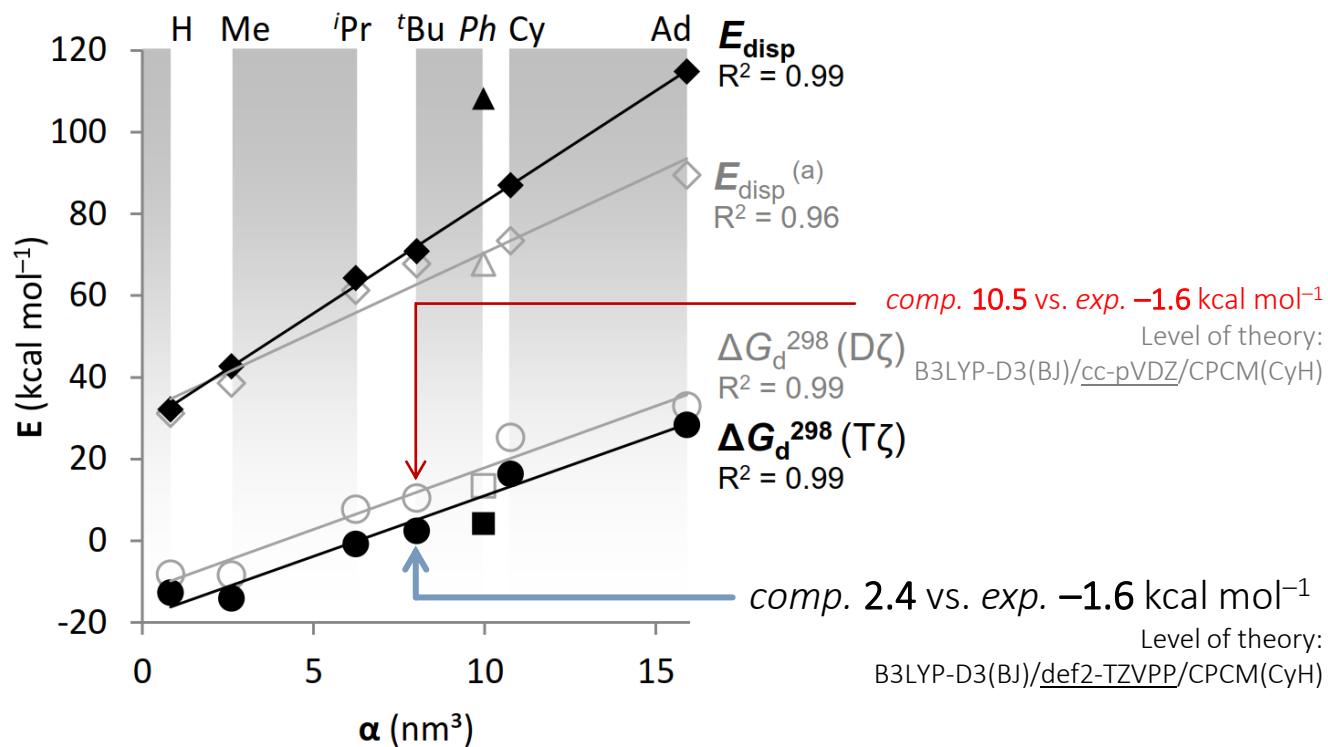
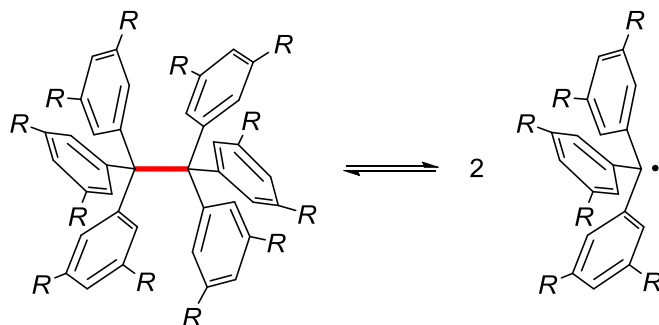


B3LYP-D3(BJ)/def2-TZVPP

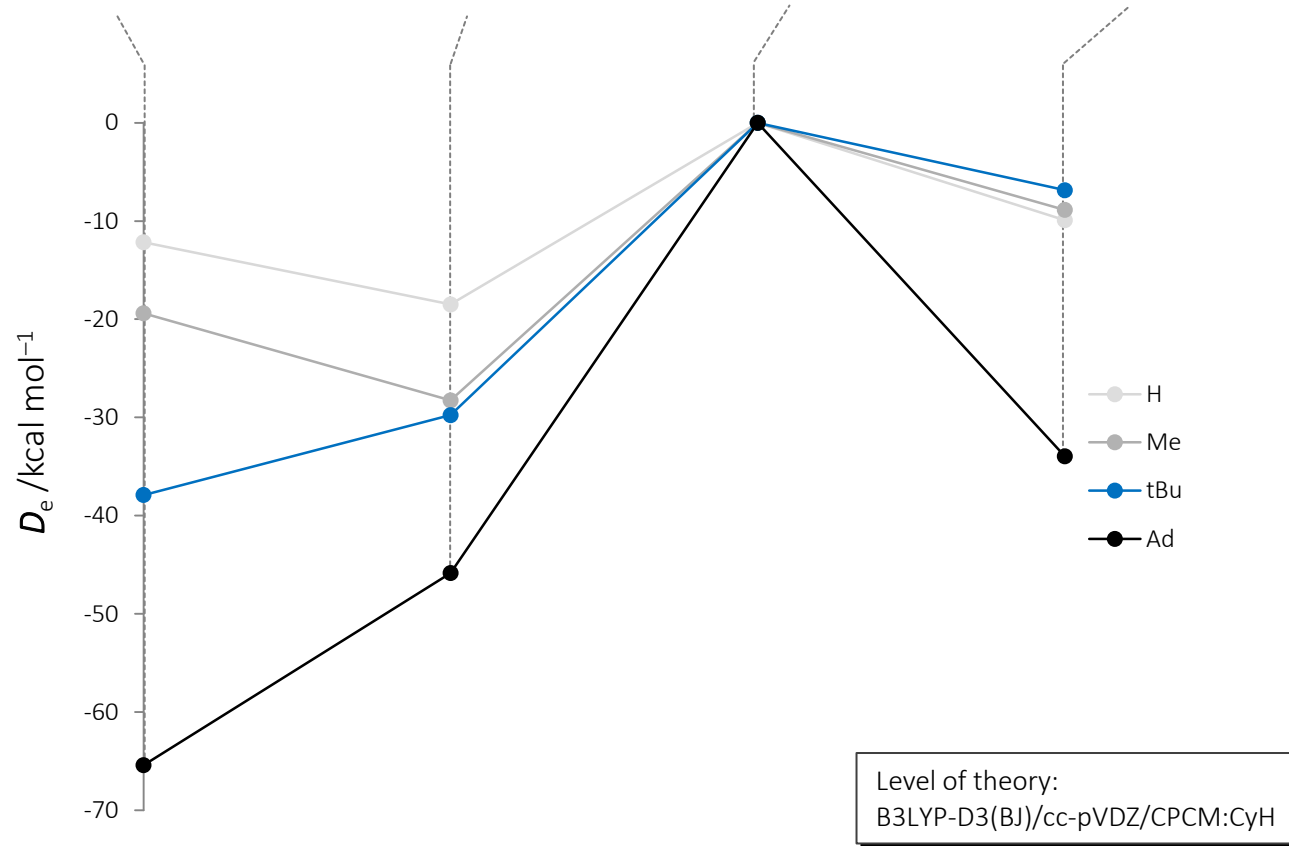
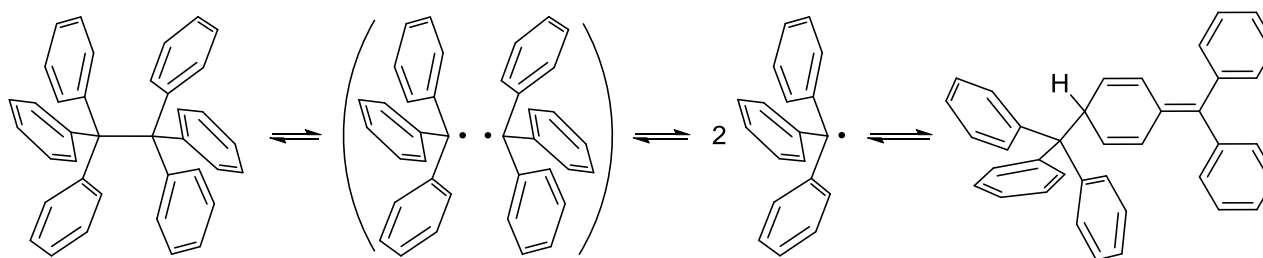
HPE as a Dispersion Balance



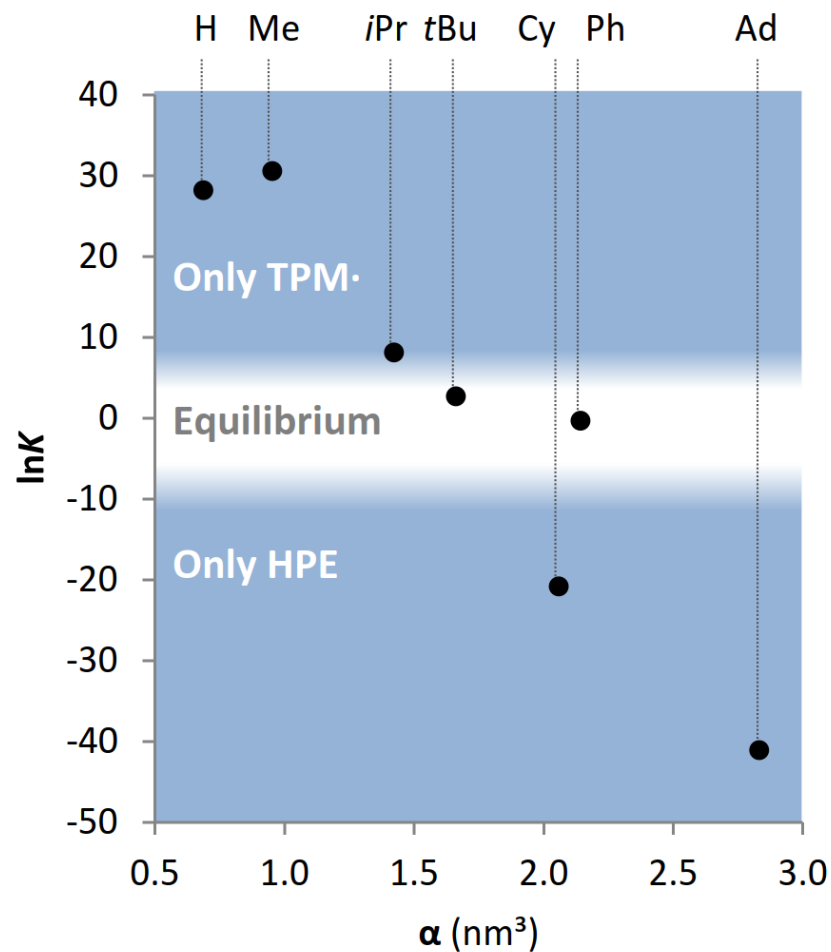
Improved Computations



Comparison to the Jacobsen-Nauta Structure



What Derivatives Might be Observable?



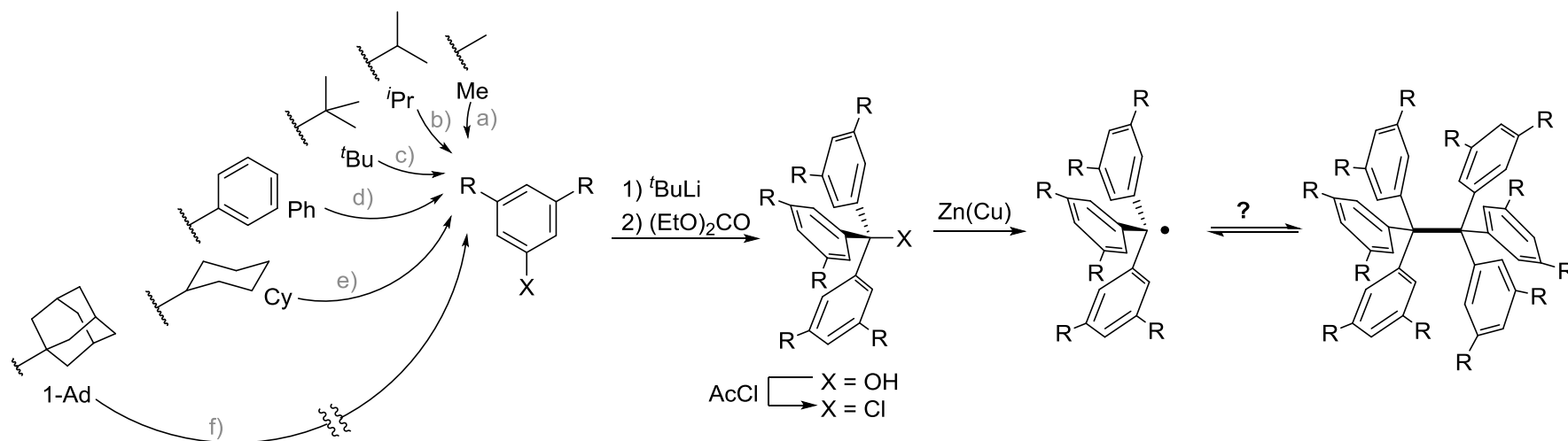
0) In all cases HPE is preferred over JNS

1) **H-**, **Me**, and **iPr**-HPE should not form

2) **tBu**- and **Ph**-HPE should exist in equilibrium with their monomers

3) **Cy**- and **Ad**-HPE should be stable

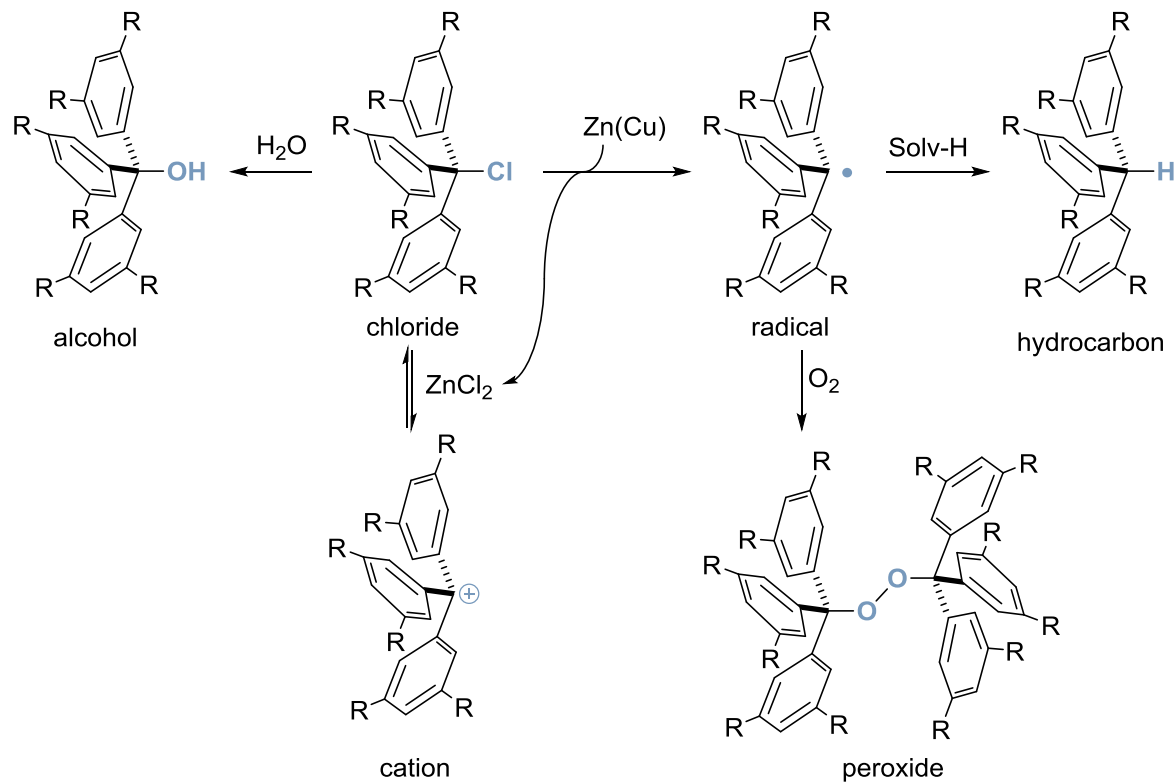
Synthesis



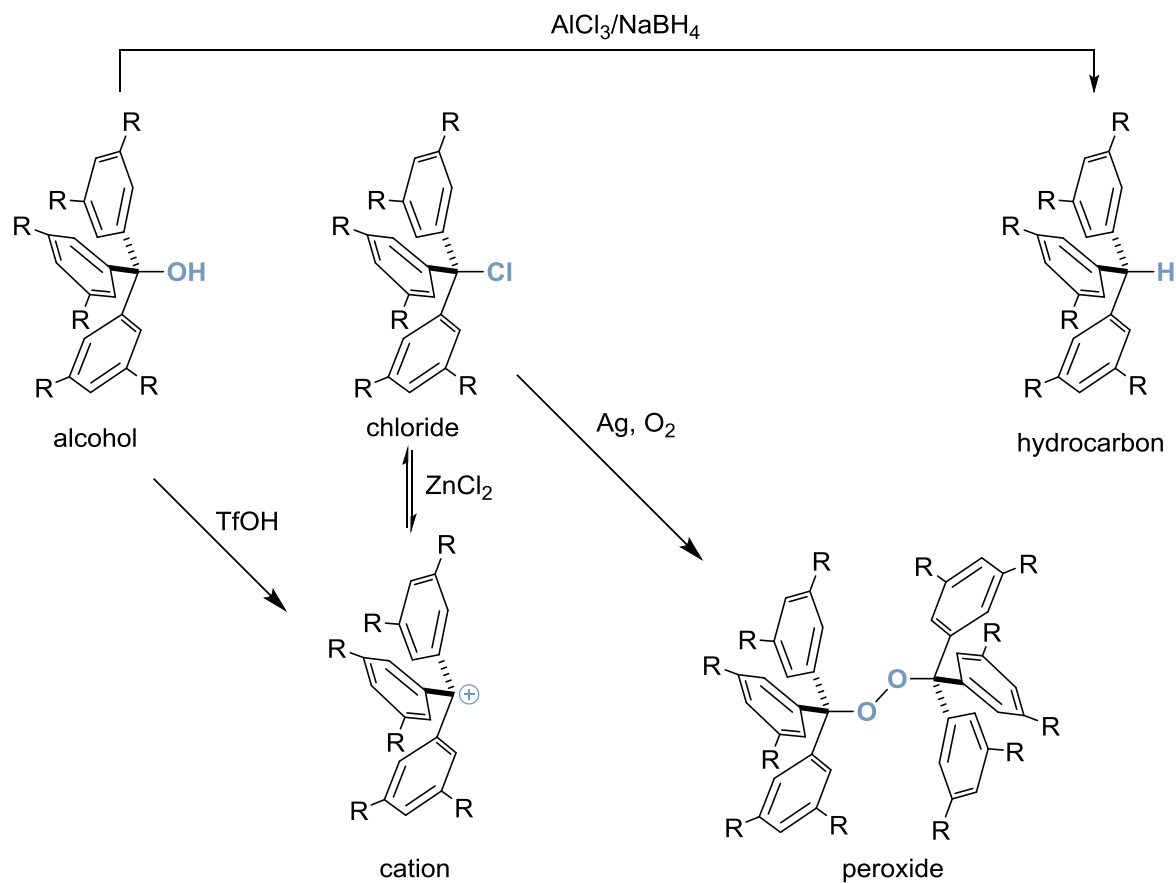
* Curved arrow length
is proportional to
consumed lifetime

a) commercially available, b) from $\text{X} = \text{NO}_2$, c) Friedel-Crafts-alkylation/bromination d) Suzuki to $\text{C}_6\text{H}_3\text{Br}_3$,
e) Negishi to $\text{C}_6\text{H}_3\text{Br}_2\text{Cl}$, then Li^0 , then I_2 , f) Negishi to $\text{C}_6\text{H}_3\text{Br}_2\text{TMS}$, then I_2 and AgOCCF_3

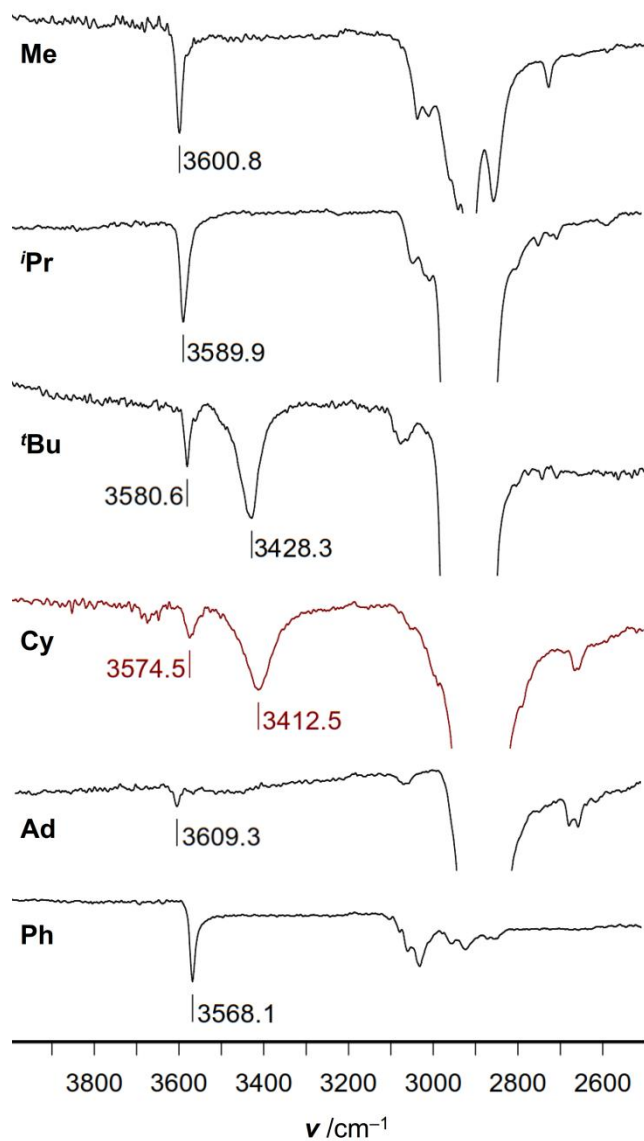
Possible Side Products of Radical Formation



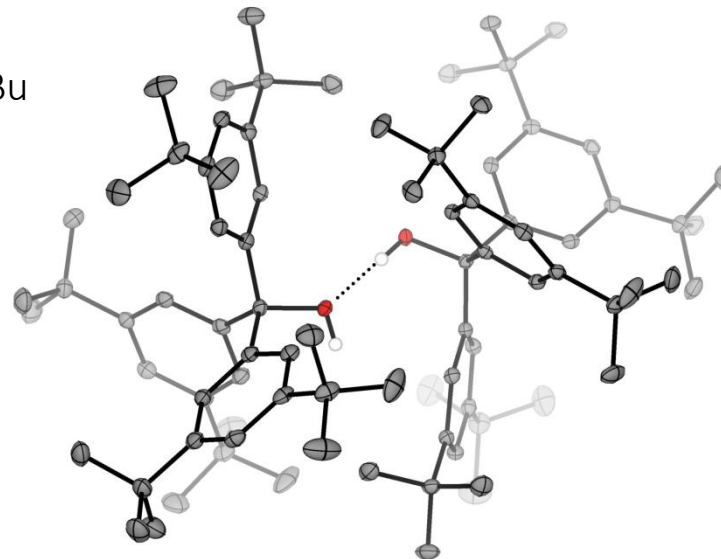
Side Product Synthesis



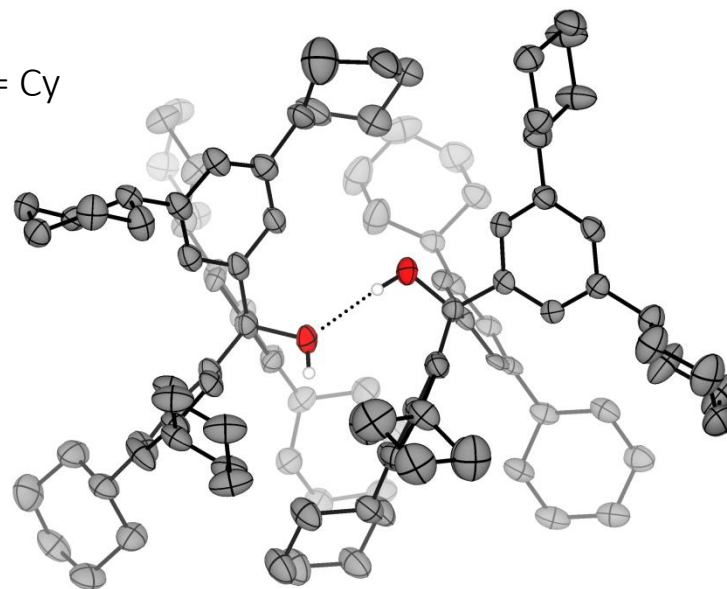
The Triphenylmethanols



R = *t*Bu

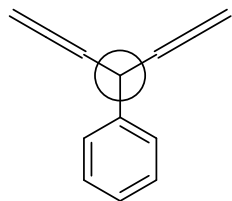


R = Cy

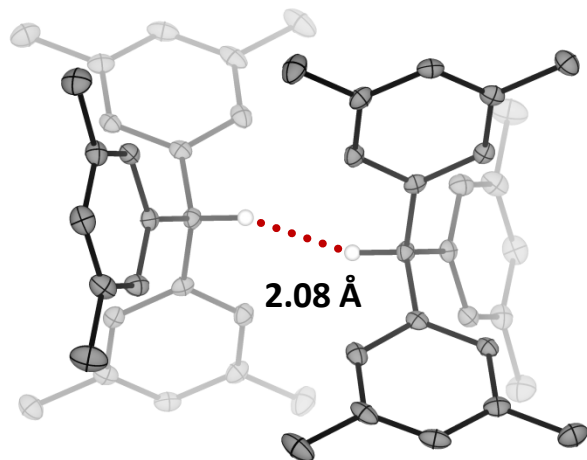


Triphenylmethane Arrangements

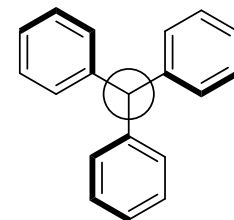
Me ($B \cdot B$)



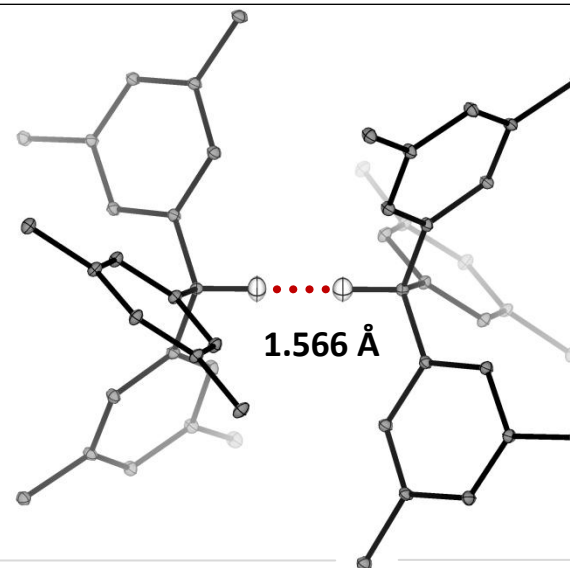
B -rotamer



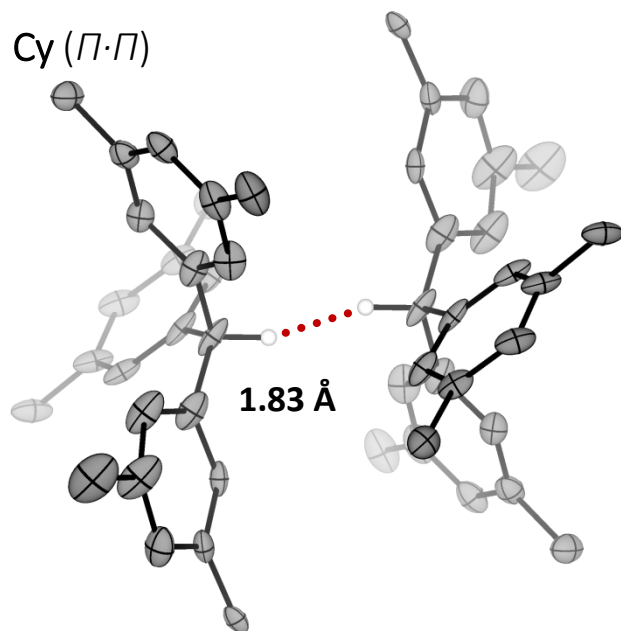
t Bu ($\Pi \cdot \Pi$)



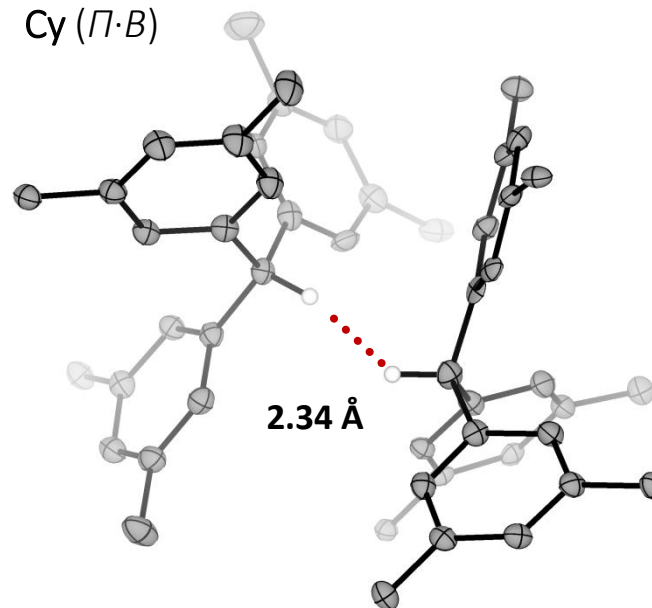
Π -rotamer



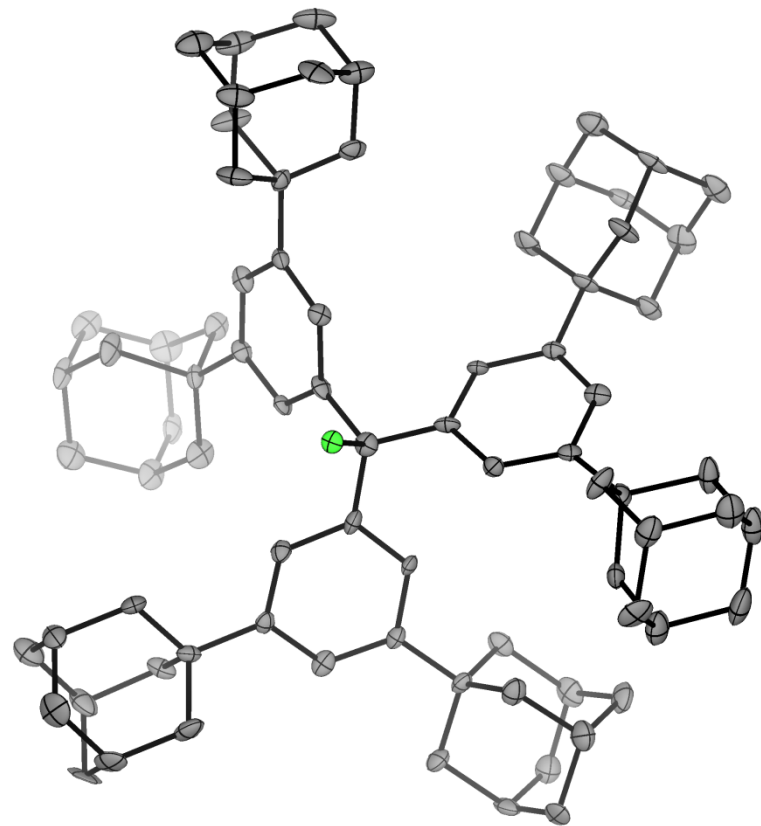
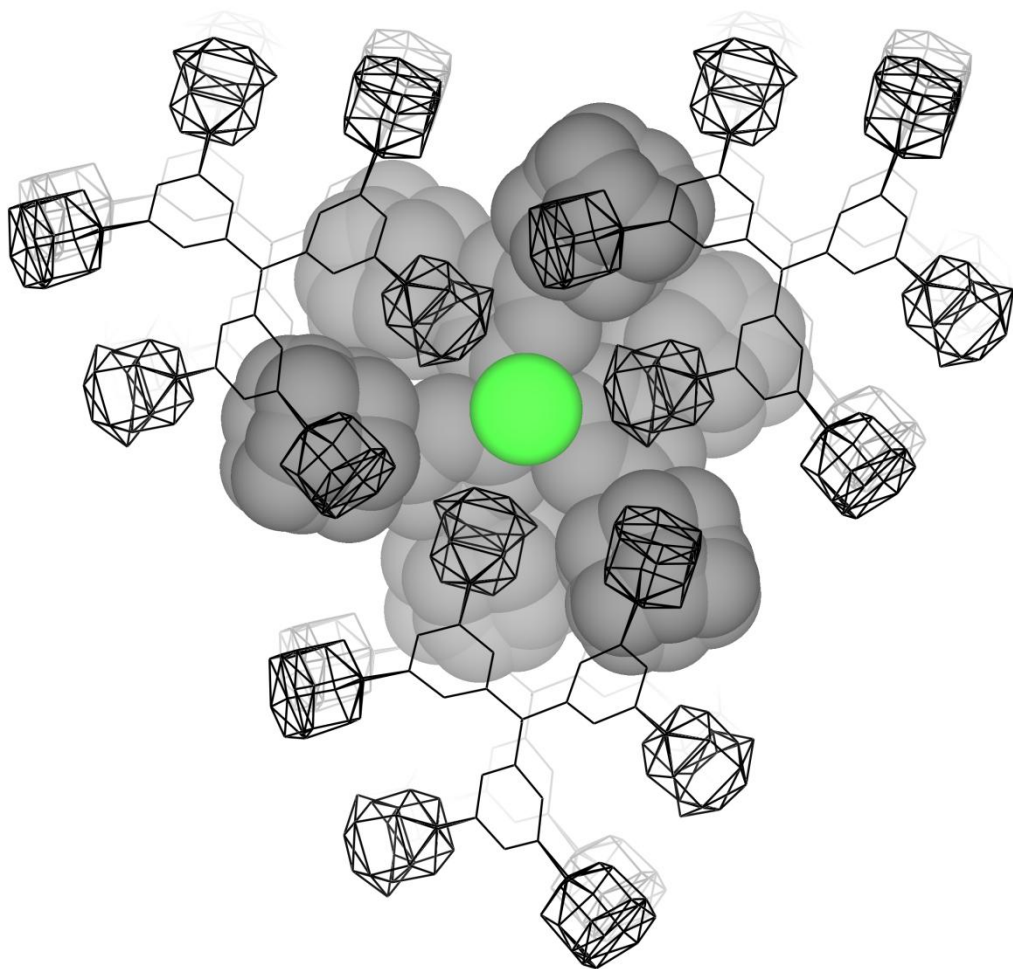
Cy ($\Pi \cdot \Pi$)



Cy ($\Pi \cdot B$)

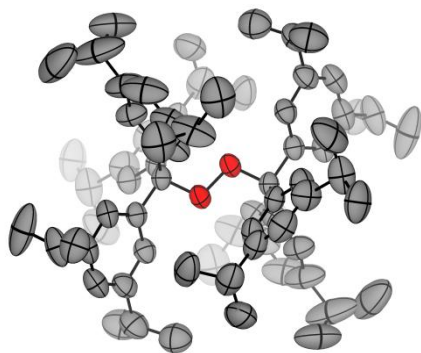


Triphenylmethyl chlorides

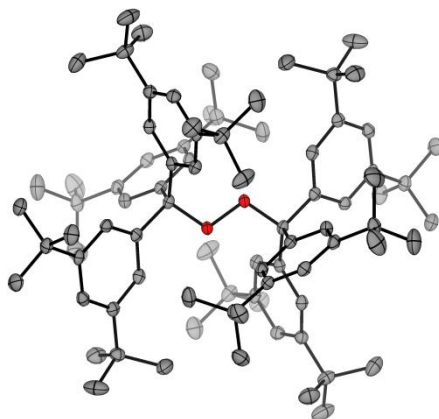


all-*meta* 1-Ad trityl chloride

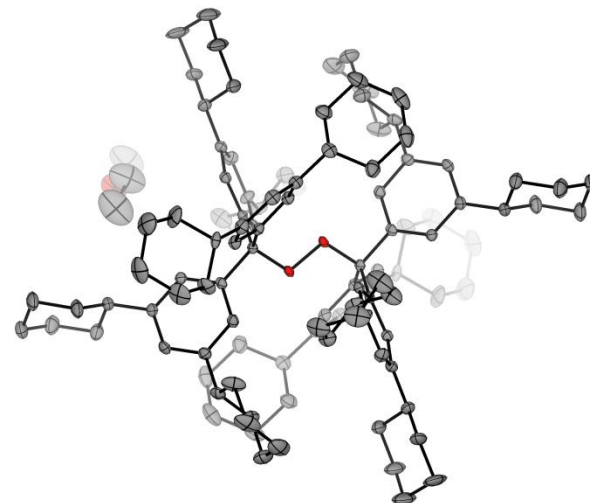
Bis Trityl Peroxides: Bench stable HPE Models



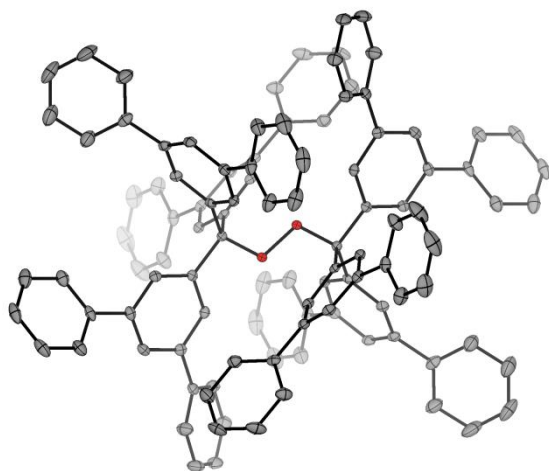
*i*Pr



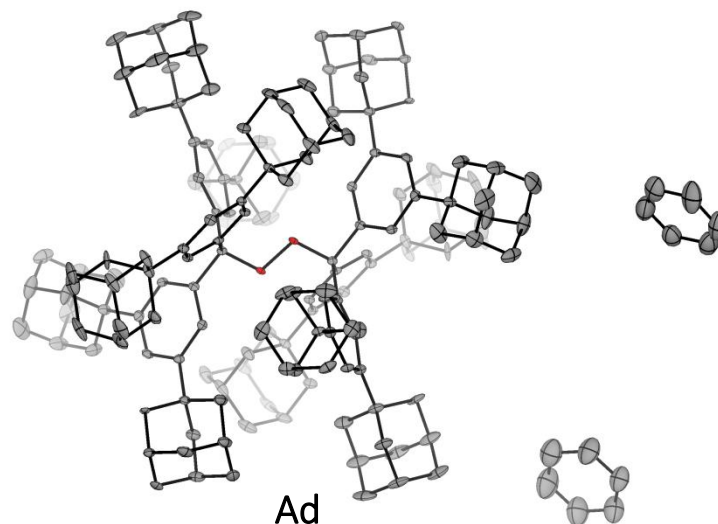
*t*Bu



Cy

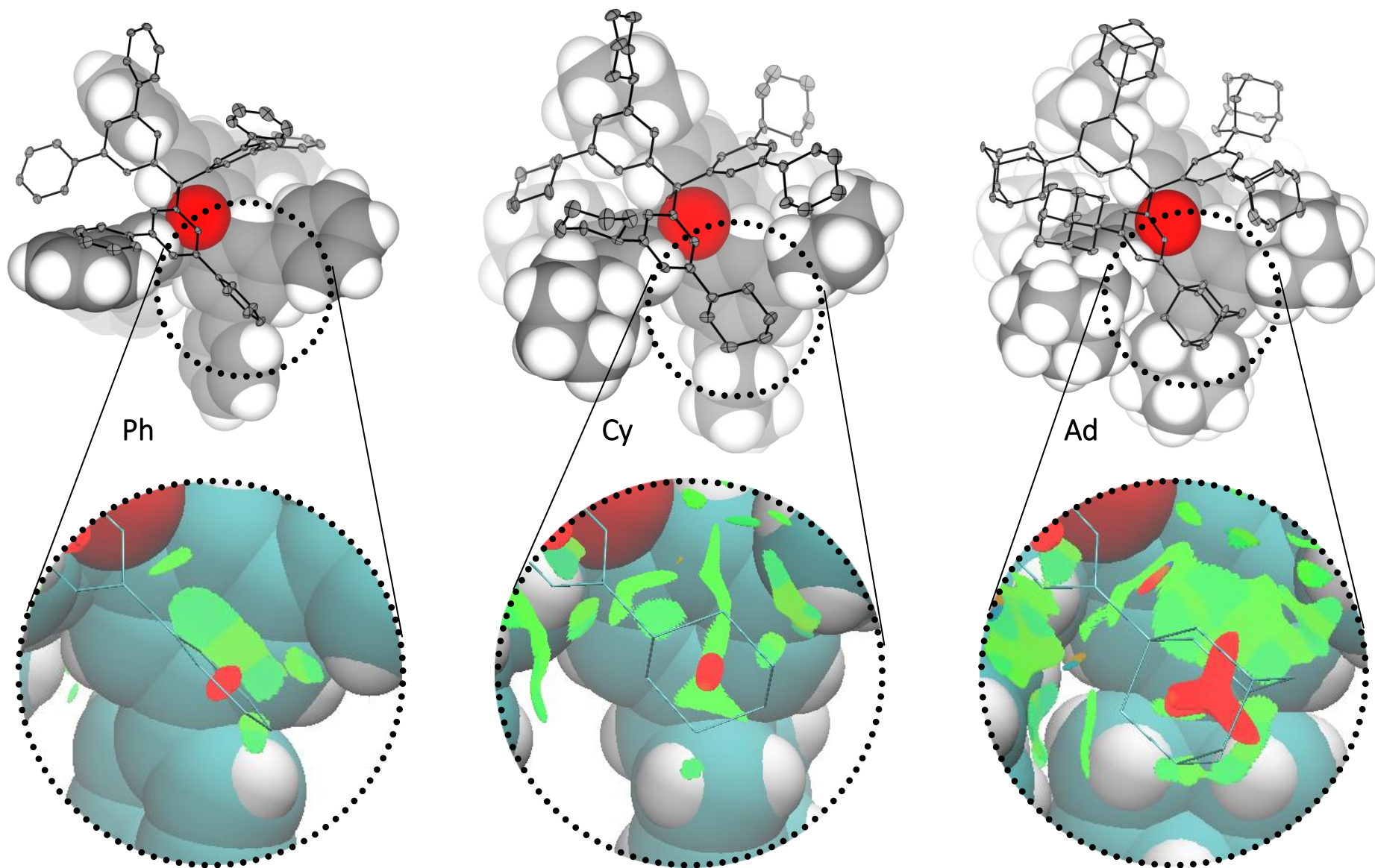


Ph

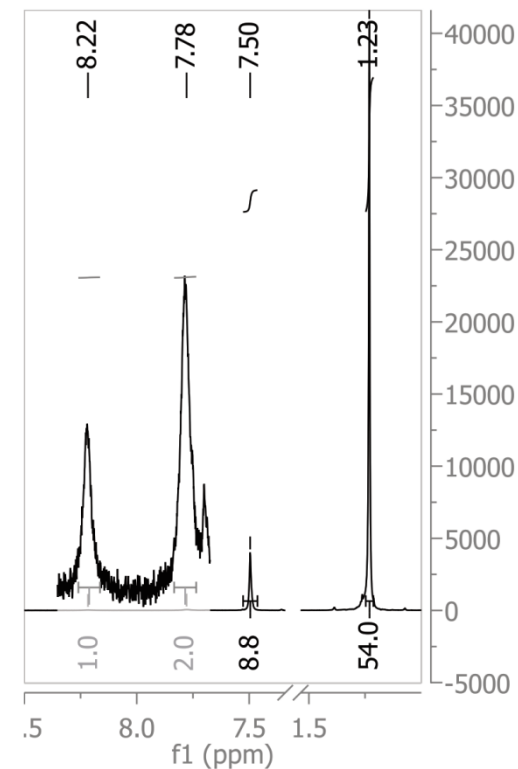
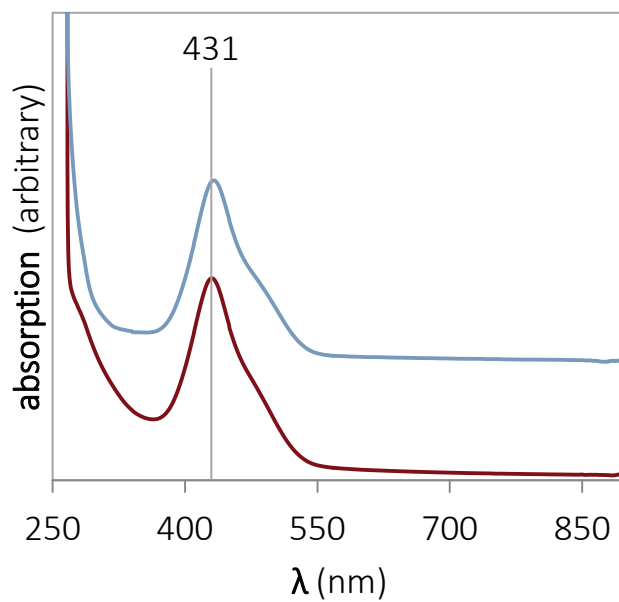
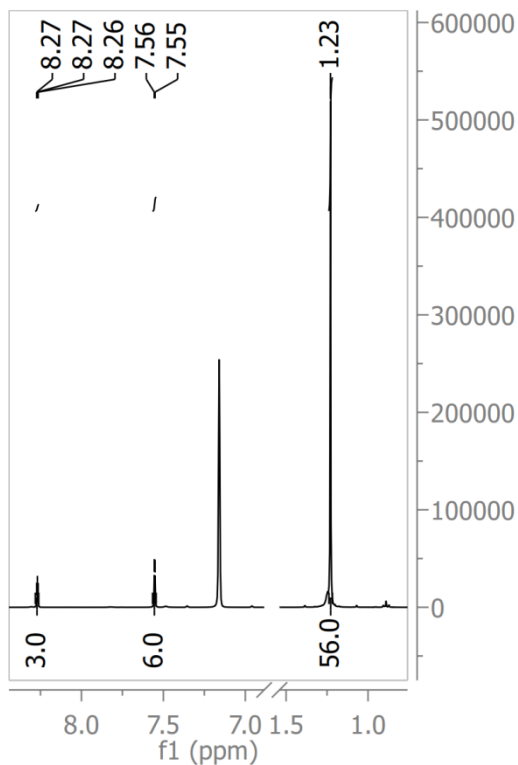
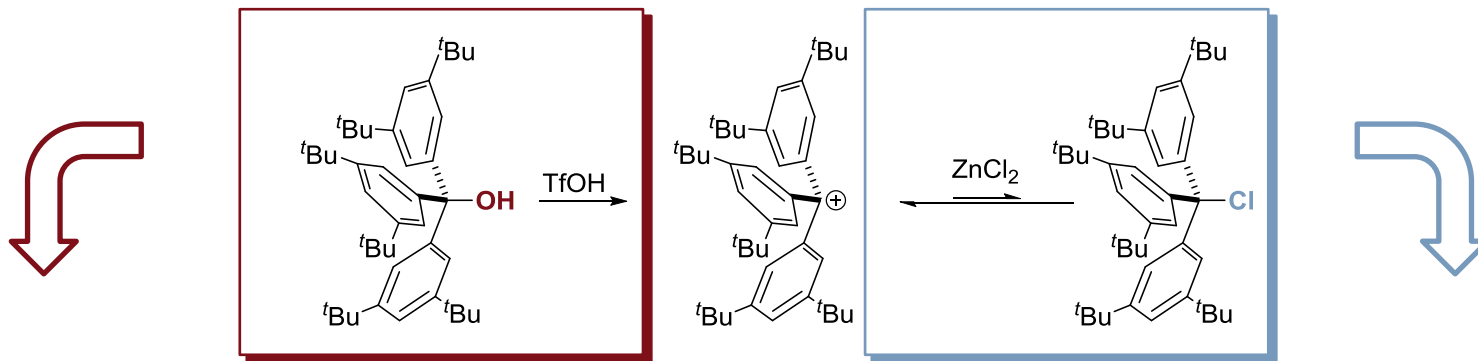


Ad

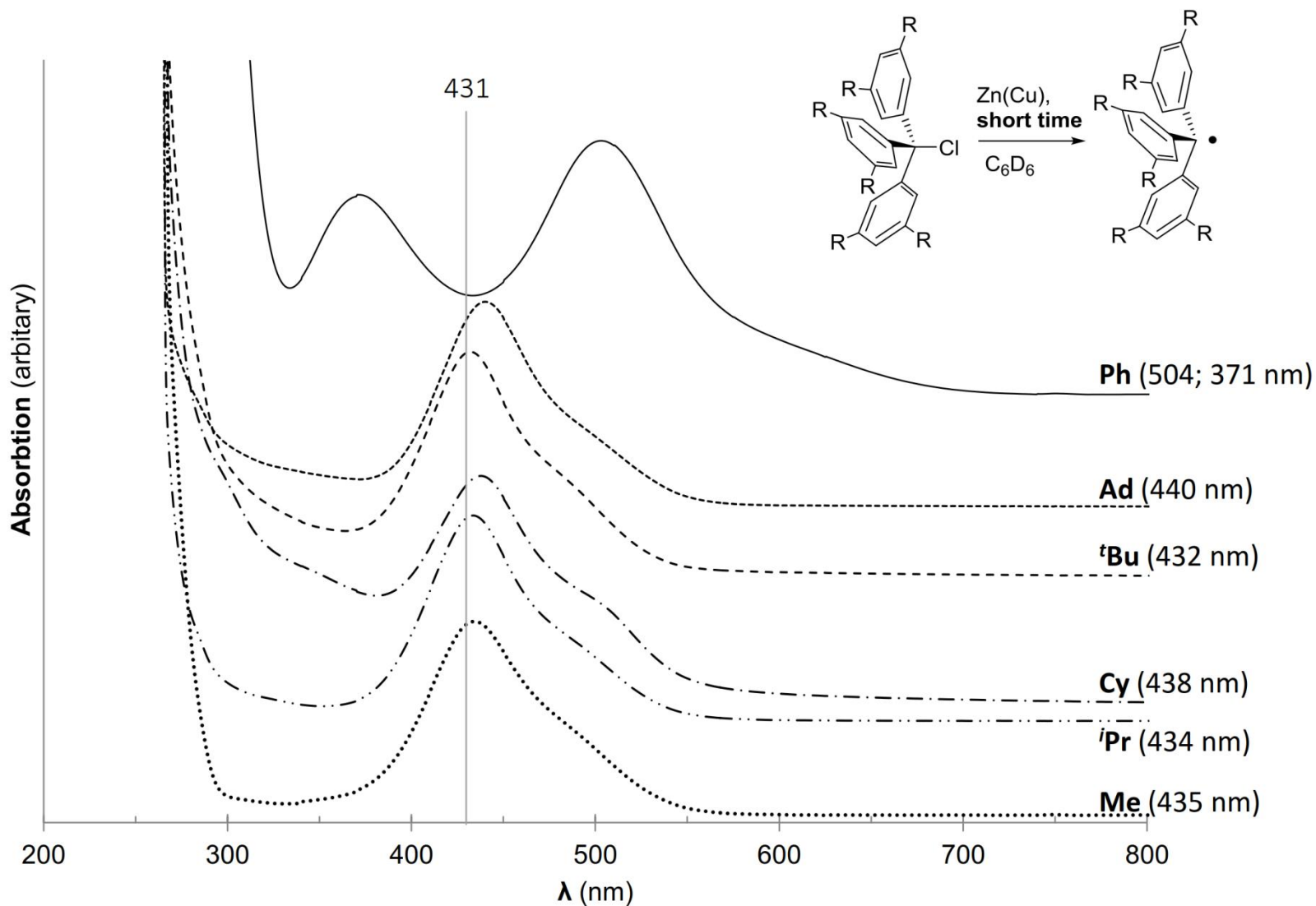
Bis Trityl Peroxides: Bench stable HPE Models



All-*meta* ^tBu Trityl Carbocation



All-*meta* Trityl Radical Solutions in Benzene



The color originate from the carbocation species present in the mixture

The True UV-Vis of All-*meta* ^tBu Trityl Radical

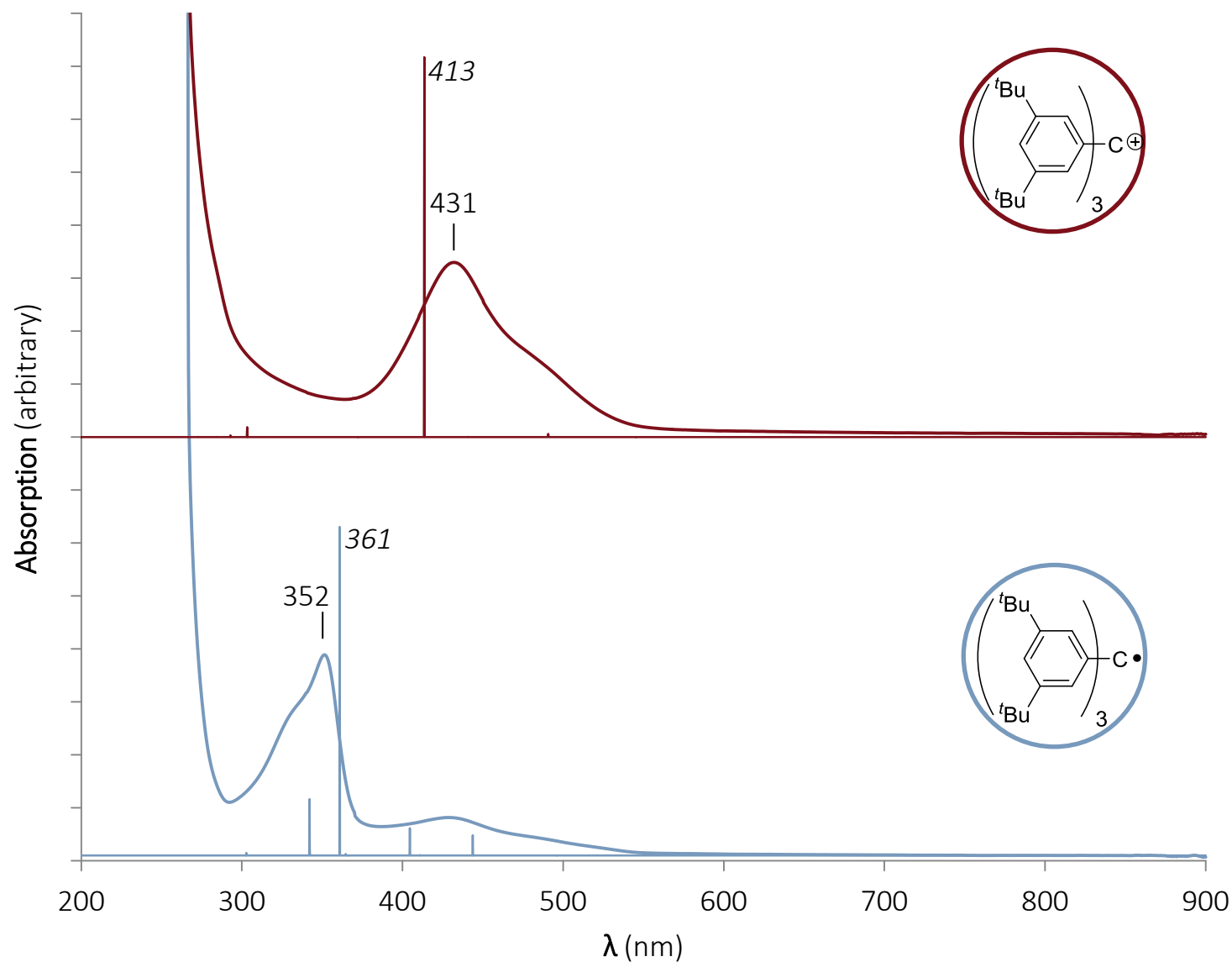
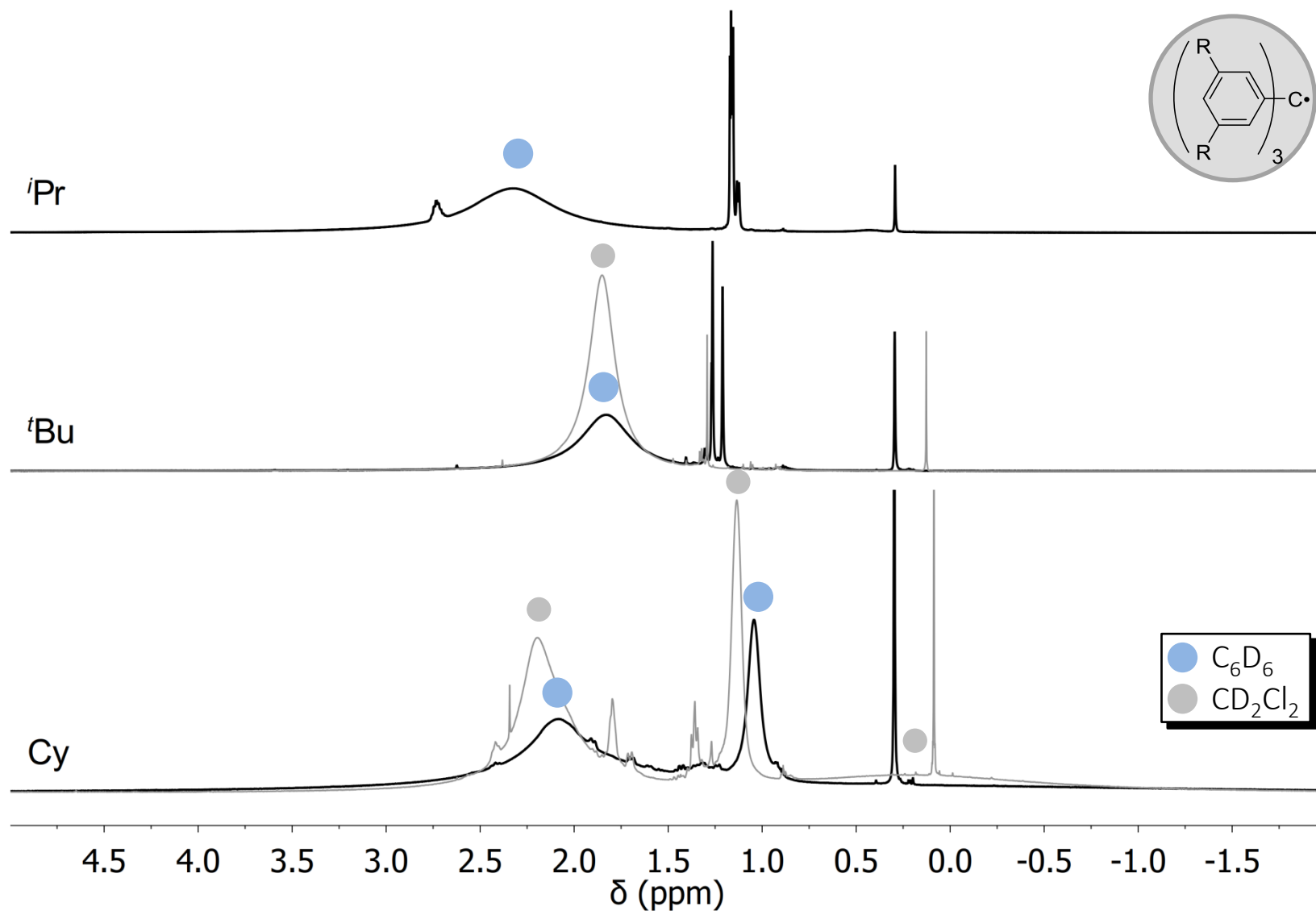


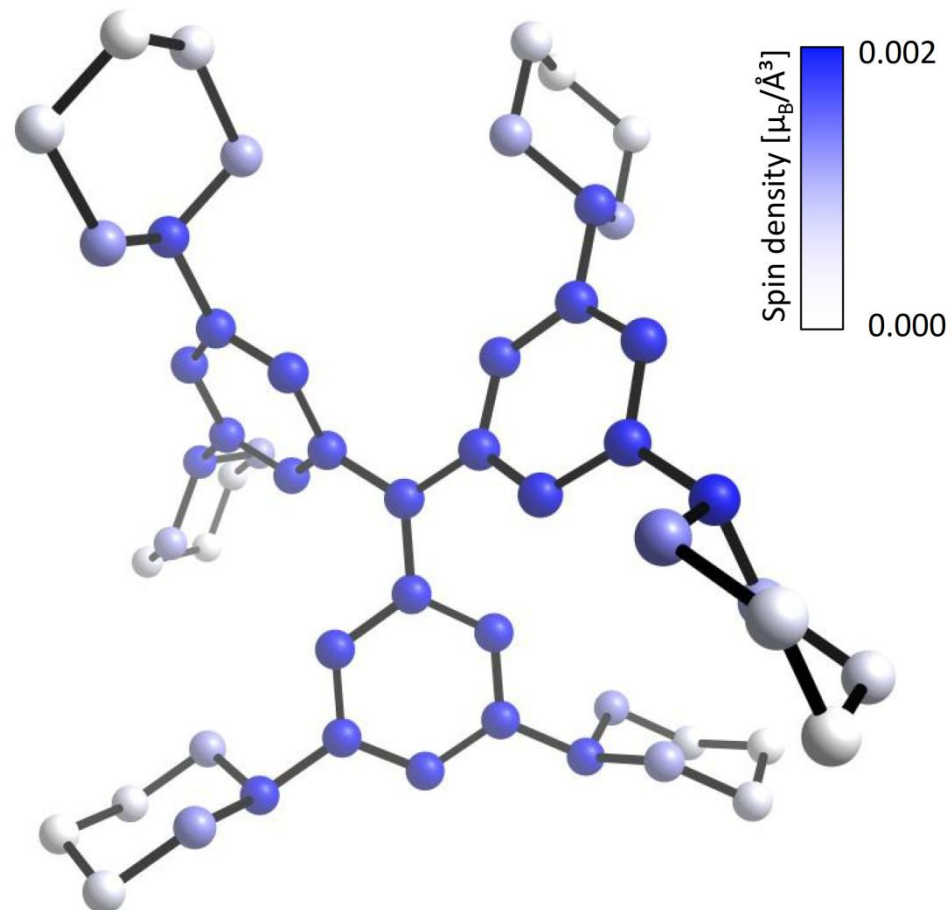
Figure 1 displays six EPR spectra of various nitroxide radicals, arranged in a 3x2 grid. Each spectrum is labeled with a chemical structure and its corresponding hyperfine splitting constants. The x-axis for all spectra is the magnetic field in Gauss (G), ranging from 324.5 to 328.5 G.

- Top Left:** Phenyl radical (Ph) with a hyperfine splitting constant of $a(9H) = 2.63$ G.
- Top Right:** Cyclohexyl radical (Cy) with a hyperfine splitting constant of $a(9H) = 2.60$ G.
- Middle Left:** 1-Adamantyl radical (1-Ad) with hyperfine splitting constants of $a(9H) = 2.57$ G and $a(6H) = 2.80$ G.
- Middle Right:** Isopropyl radical (iPr) with hyperfine splitting constants of $a(9H) = 2.57$ G and $a(6H) = 2.80$ G.
- Bottom Left:** Methyl radical (Me) with hyperfine splitting constants of $a(9H) = 2.57$ G and $a(18H) = 2.80$ G.
- Bottom Right:** A central structure (a phenyl ring with two R groups and a central carbon radical) with hyperfine splitting constants of $a(9H) = 2.57$ G and $a(6H) = 2.80$ G.

Trityl Radical Solutions in Benzene



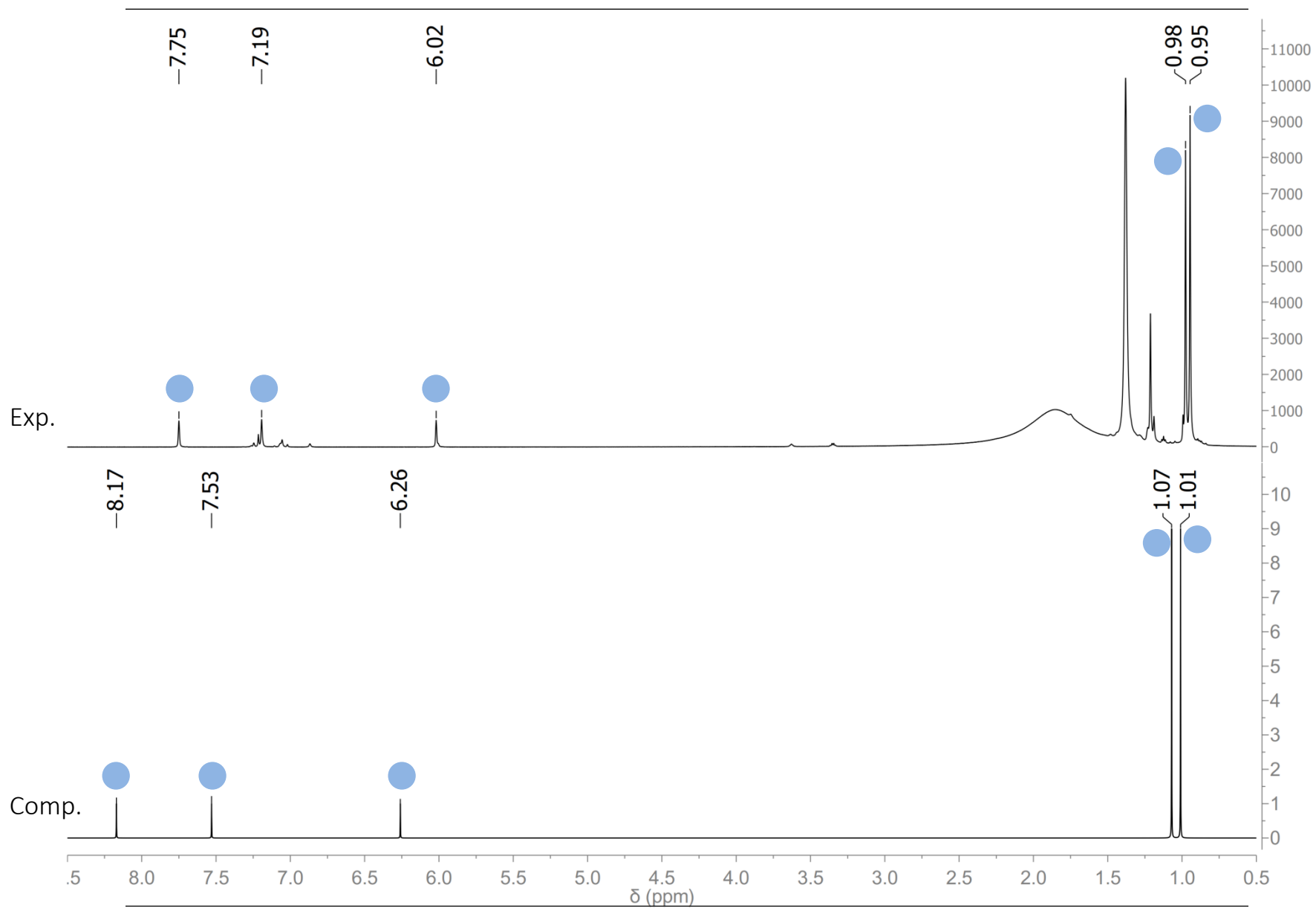
Spin Densities in Trityl Radicals



	Me	<i>i</i> Pr	Cy	<i>t</i> Bu	Ad	Ph
Trityl core						
<i>p</i>	0.14	0.13	0.13	0.14	0.15	0.13
<i>m</i>	0.12	0.12	0.06	0.06	0.06	0.06
<i>o</i>	0.06	0.06	0.12	0.12	0.13	0.12
<i>i</i>	0.11	0.11	0.11	0.11	0.11	0.11
<i>central</i>	0.62	0.62	0.62	0.61	0.60	0.64
Substituent						
α	0.005	0.004	0.004	0.004	0.004	0.008
β		0.001	0.001	0.001	0.001	0.006
γ			0.000		0.000	0.003
δ			0.000		0.000	0.006

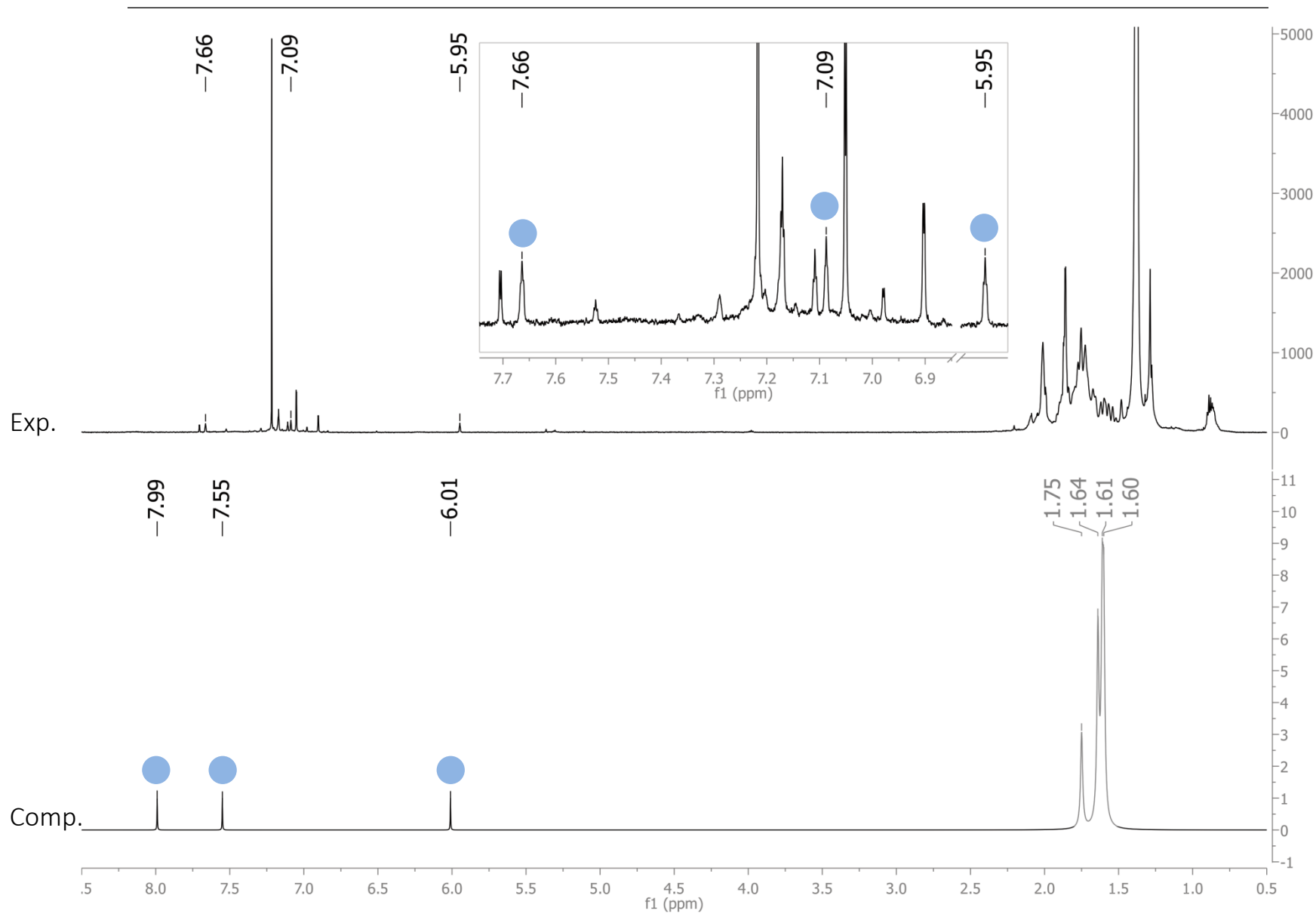
Is There any Life Sign of Hexaphenylethane?

^1H -NMR of $t\text{BuHPE}$ in C_6D_{12}



Top: ^1H NMR @ 277 K,
Bottom: GAIO:B3LYP/6-31G(d,p)/CPCM:CyH

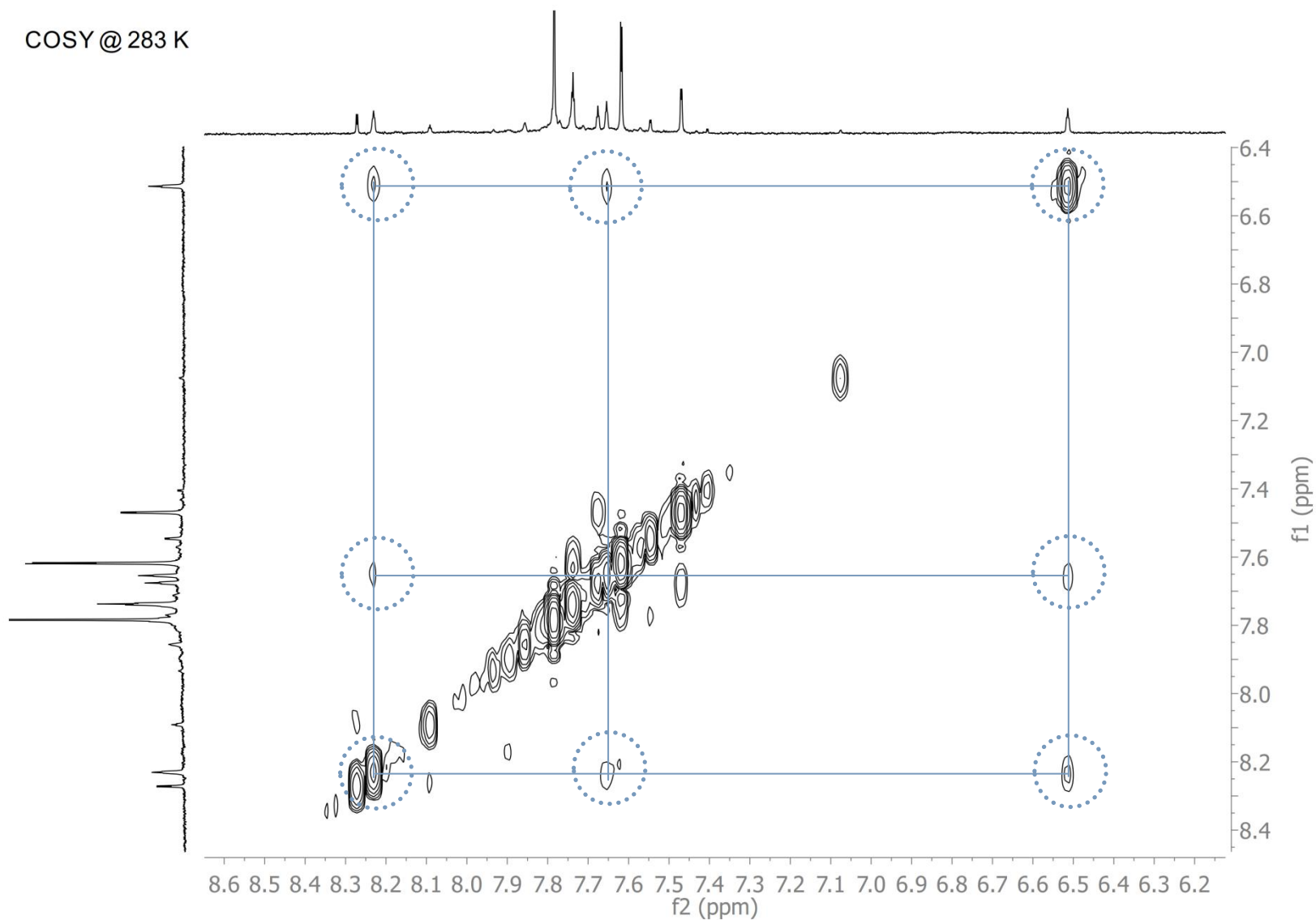
^1H -NMR of AdHPE in C_6D_{12}



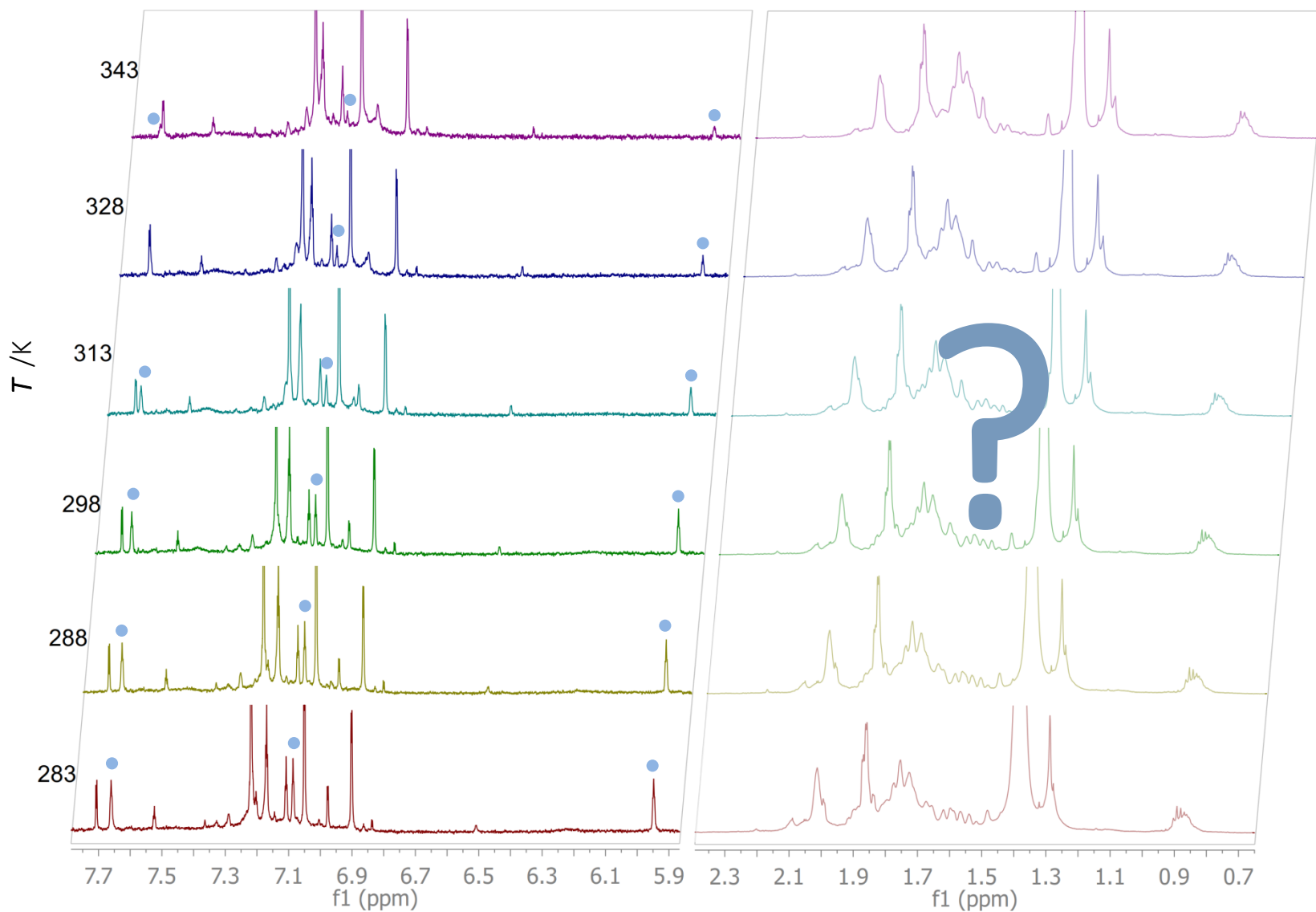
Top: ^1H NMR @ 288 K,
Bottom: GIAO:B3LYP/6-31G(d,p)/CPCM:CyH

^1H -COSY of AdHPE in C_6D_{12}

COSY @ 283 K



^1H -VT-NMR of AdHPE in C_6D_{12}



Half the information – enough to get the bond energy?

- Established:

Both species visible for $t\text{Bu}$ -HPE $\rightarrow$ van't Hoff plot to get ΔG_d , ΔH_d and ΔS_d

- Incomplete new data:

Only **Ad**-HPE visible $\rightarrow$ van't Hoff plot inapplicable!

- Raw solution:

- 1) Assume *any* general sigmoid decay of HPEs with temperature.
- 2) Fit to data $\rightarrow$ “initial” HPE concentration.
- 3) Get radical concentration *via* $[\text{Radical}] = 2([\text{HPE}_0] - [\text{HPE}])$
- 4) Apply established scheme.

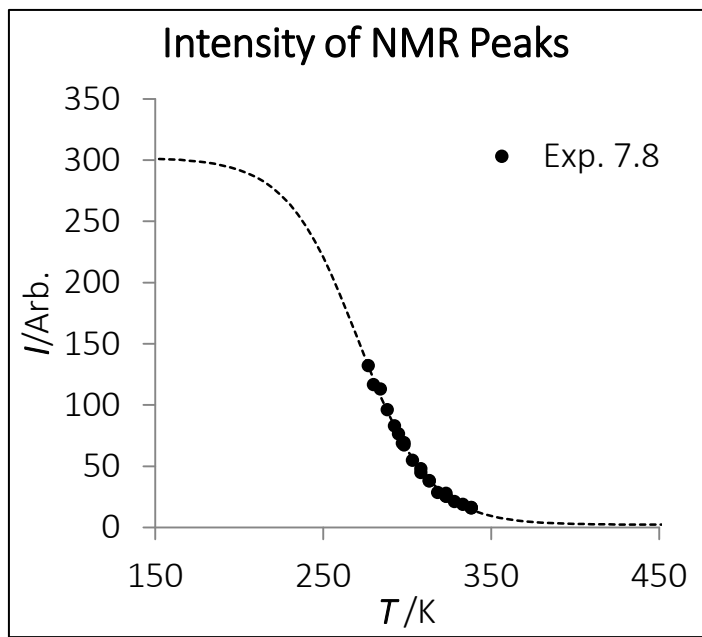
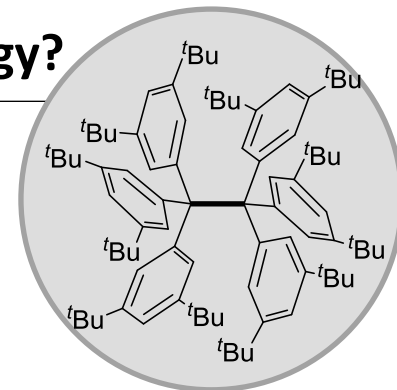
- Solid solution:

Establish the sigmoid curve *ab initio* and derive data directly from equation.

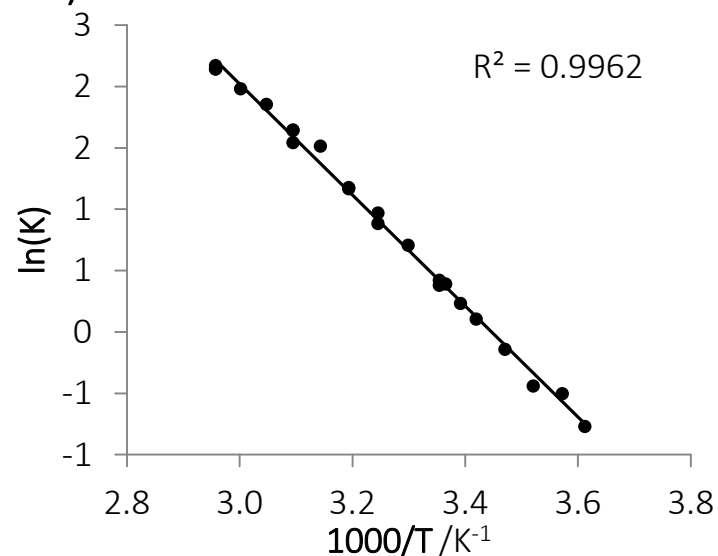
Half the information – enough to get the bond energy?

Raw solution:

- 1) Assume *any* general sigmoid decay of HPEs with temperature.
- 2) Fit to data → “initial” HPE concentration (I_0).
- 3) Get radical concentration *via* $[\text{Radical}] = 2([\text{HPE}_0] - [\text{HPE}])$
- 4) Apply established scheme.



3+4) Van't Hoff Plot



1)

$$I(T) = a + \frac{I_0 - a}{1 + e^{(T-b)c^{-1}}}$$

$$\begin{aligned} \Delta H_d^{298} &= 9.00(12) \text{ kcal mol}^{-1} \\ T\Delta S_d^{298} &= 9.24(1) \text{ kcal mol}^{-1} \\ \Delta G_d^{298} &= -0.25(13) \text{ kcal mol}^{-1} \end{aligned}$$

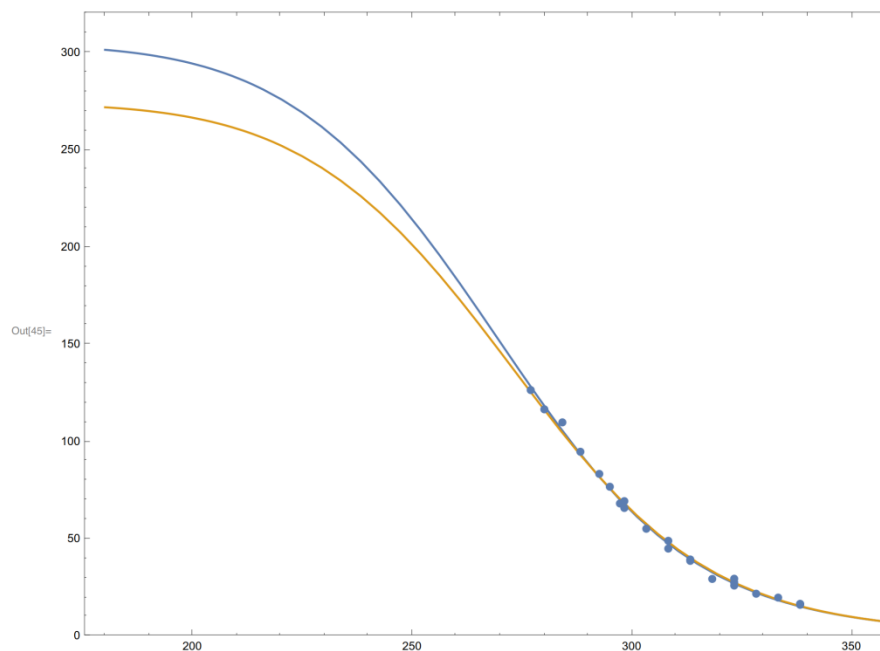
Half the information – enough to get the bond energy?

Solid solution:

Establish the sigmoid curve *ab initio* and get data directly from equation.



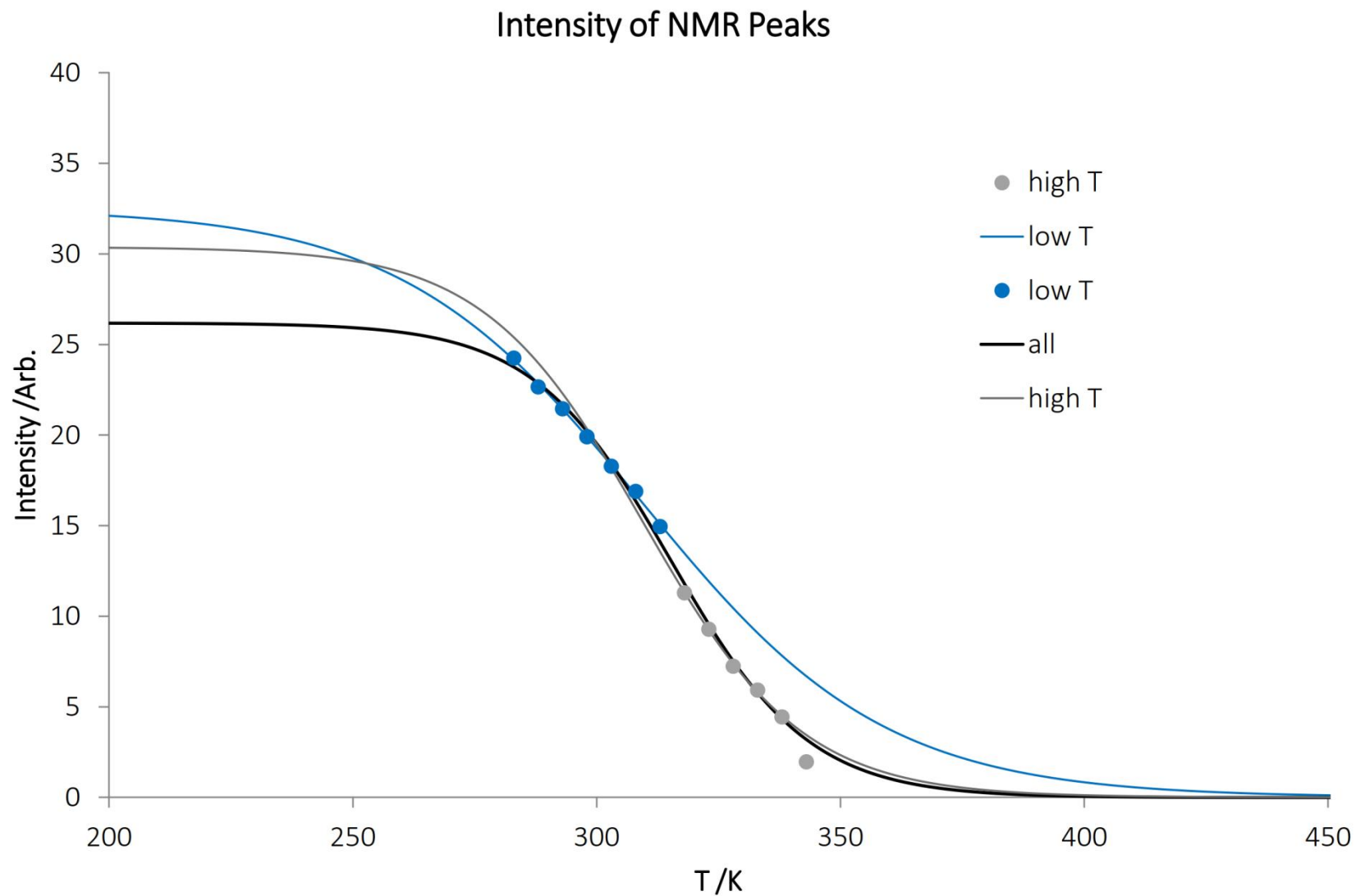
$$f(T) = \ln \left[\frac{(I_0 - I_2)^2}{I_2} \right] = \ln \left(\frac{I_0 K_0}{4C_0} \right) - \left(\frac{\Delta H^\circ}{R} \right) \frac{1}{T}$$



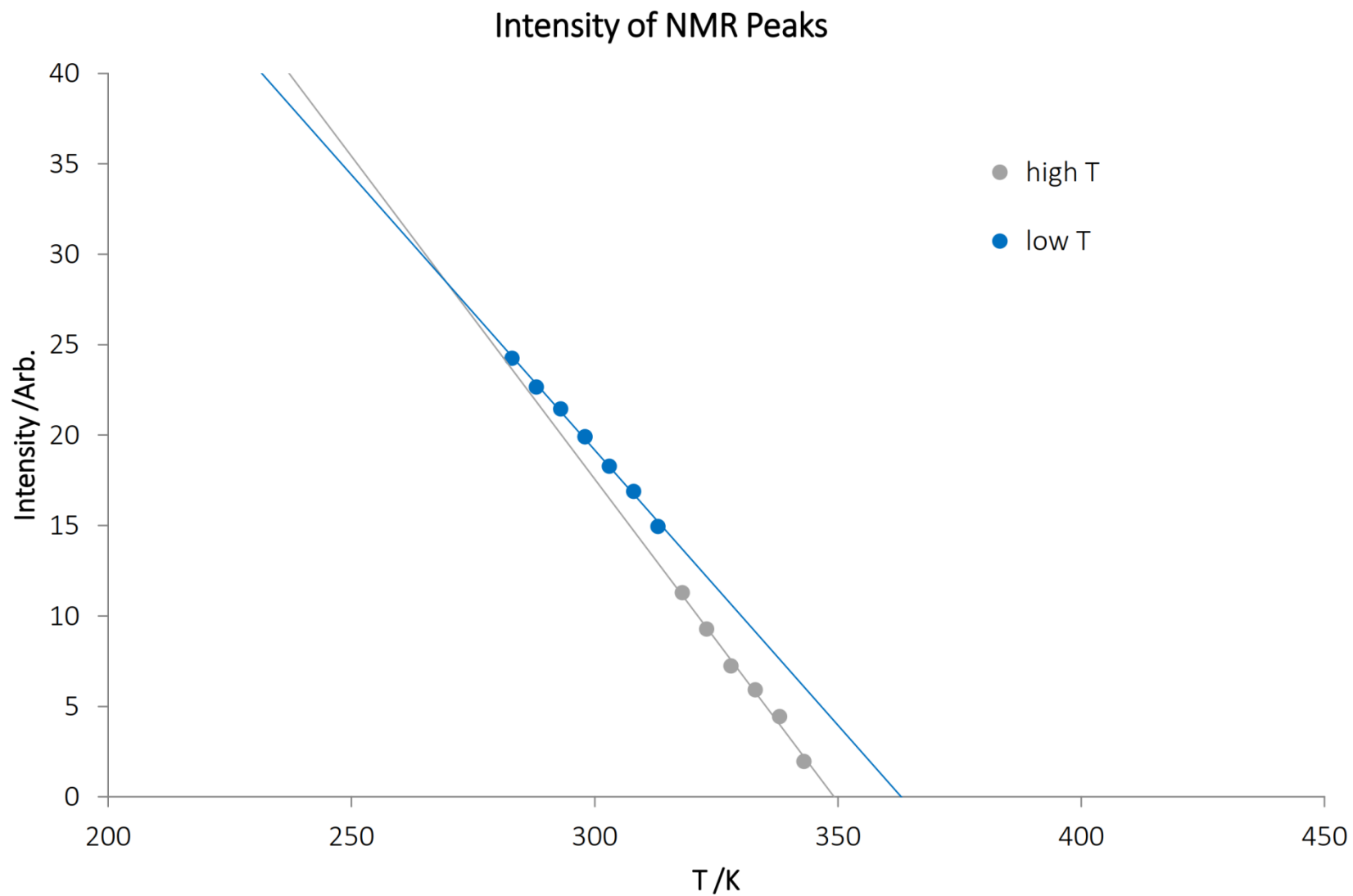
```
I0 fit = 304.1728216    deltaH0 (kJ/mol) = 39.5844    B0 (micromolar) = 0.01073893882
I0 uncertainty = 29.6149    deltaH0 uncertainty = 1.97433    B0 uncertainty = 0.00690778
```

$$\Delta H_d^{298} = 9.5(5) \text{ kcal mol}^{-1}$$

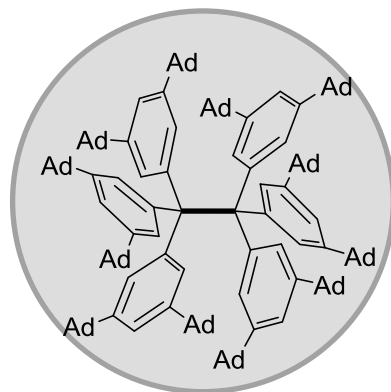
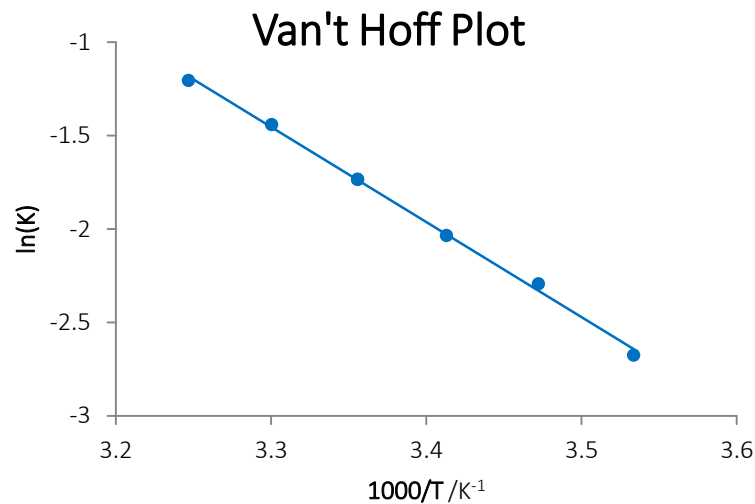
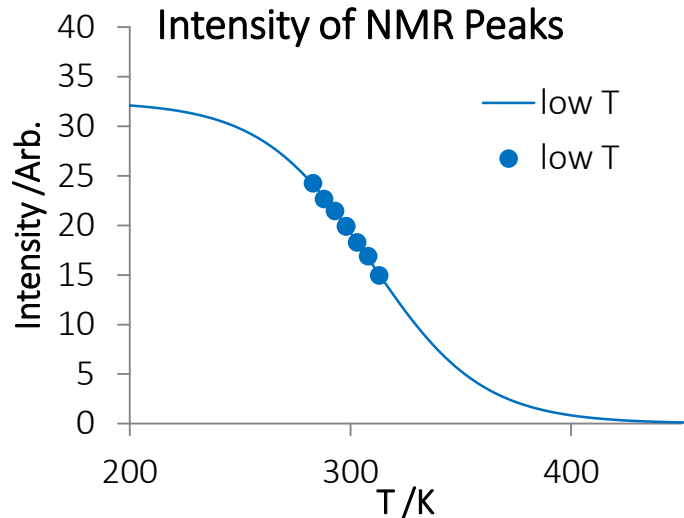
VT NMR of all-*meta* Ad HPE



VT NMR of all-*meta* Ad HPE



Half the information – enough to get the bond energy!



Ad

raw
10.1(2)
9.1(1)
1.0(3)

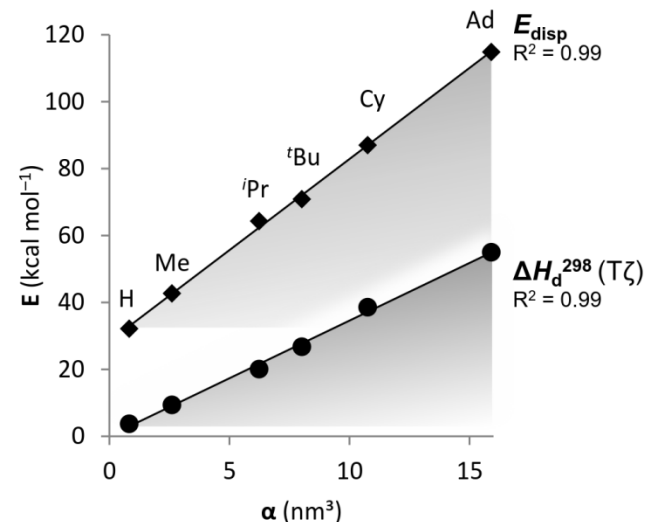
Summary

Prediction and assumptions

- ^tBuHPE bare a weak central bond and in equilibrium dissociates
→ applicable as molecular balance
- Linear relationship between polarizability and ΔG_d (ΔH_d)
→ differences are a measure of London Dispersion ($\Delta\Delta H_{LD}$)

Findings

- Numerous all-*meta* subs. trityl derivatives bind in a head-to-head fashion
- Color originate from carbocations
- Substitution barely influence the electronic properties (UV-Vis/EPR/NMR)
- Large solubility issues for larger derivatives ($M > 1000$ u)
- Radicals visible in NMR if spin density is negligible (obscured for Ad)
- Only evidence found for ^tBu- and Ad-HPE
- new method established to determine ΔH_d^{298}
- $\Delta H_{d,exp.}^{298}$ (Ad-HPE) unreliable yet



¹³ C NMR /central carbon	δ /ppm
Me	57.5
iPr	58.2
Cy	58.3
^t Bu	58.7
Ad	59.5
Ph	58.1

Summary

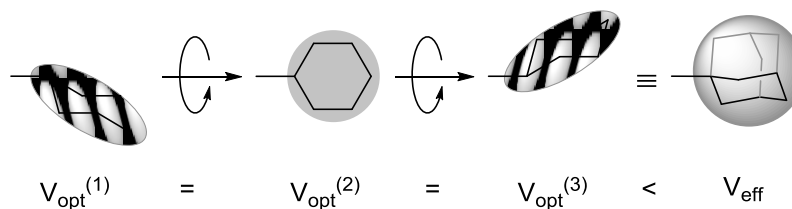
Conclusions:

- experimental:
 - a. HPE fail as a LD balance due to too large energy differences
 - b. rigidity of and fit between the substituents most important for HPE stability:
 - ^tBu and Ad are superior DEDs,
 - ^tBu favorable due to accessibility and solubility

- Computational

- a. Optimized structures fail to describe experiment:

- a) Continuous movement $\rightarrow$ lowered $\alpha_{\text{eff}} = \alpha/V_{\text{eff}}$

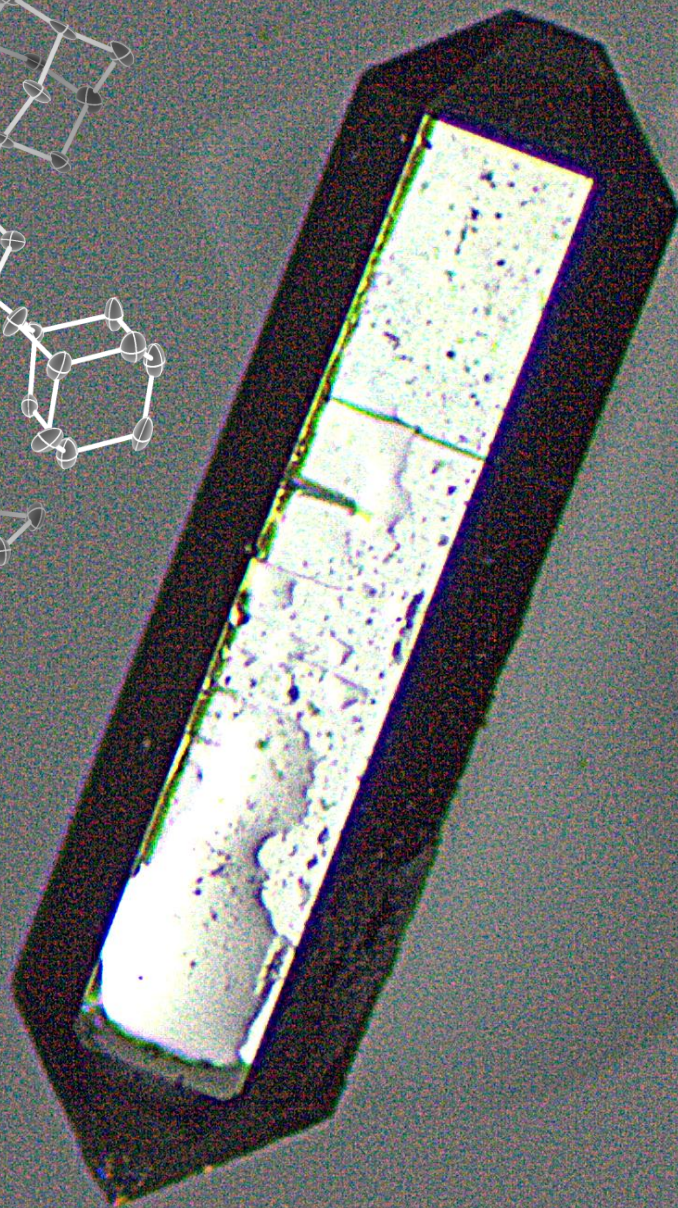
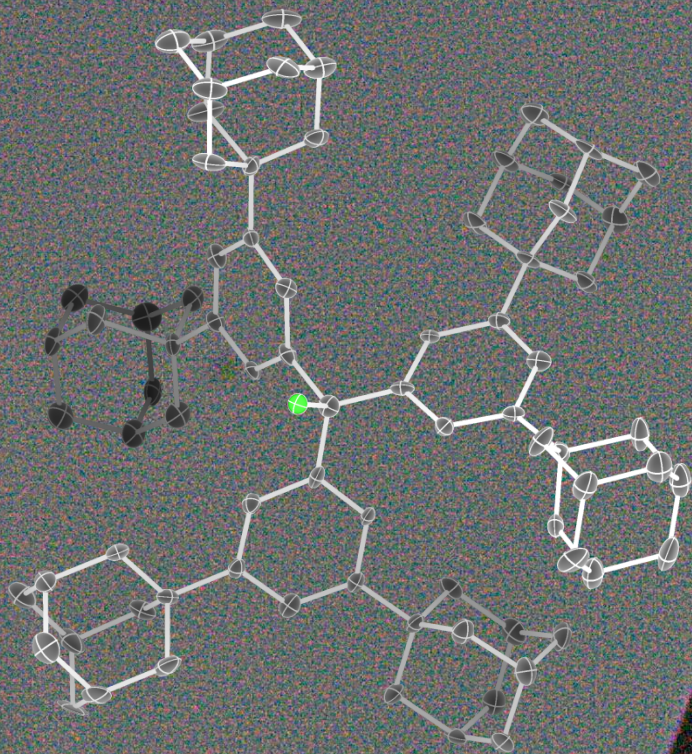


- b) Boltzmann-like treatment of conformers/rotamers still too expensive.

- b. $\Delta H_{\text{d,exp.}}^{298}$ is attenuated regarding $\Delta H_{\text{d,comp.}}^{298}$:

poor theoretical description of solubility and solutions

$\Delta H_{\text{d,exp.}}^{298}$ 7.9–9.5 kcal mol ⁻¹ $\Delta H_{\text{d,comp.}}^{298}$ 28.8 kcal mol ⁻¹
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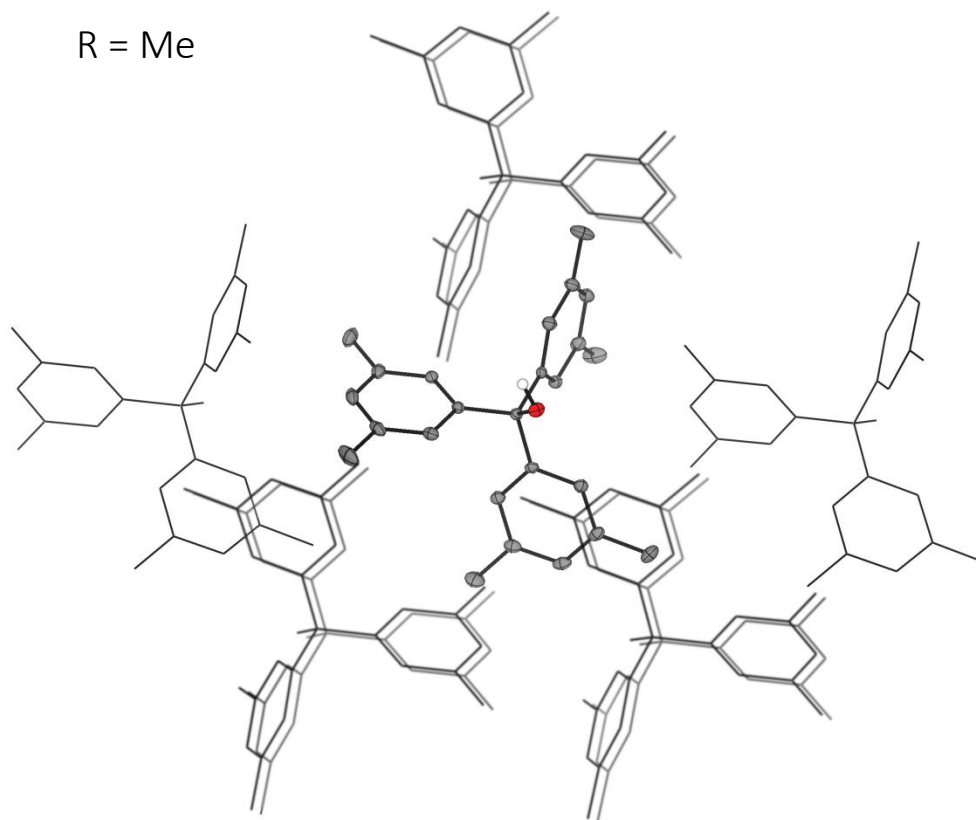
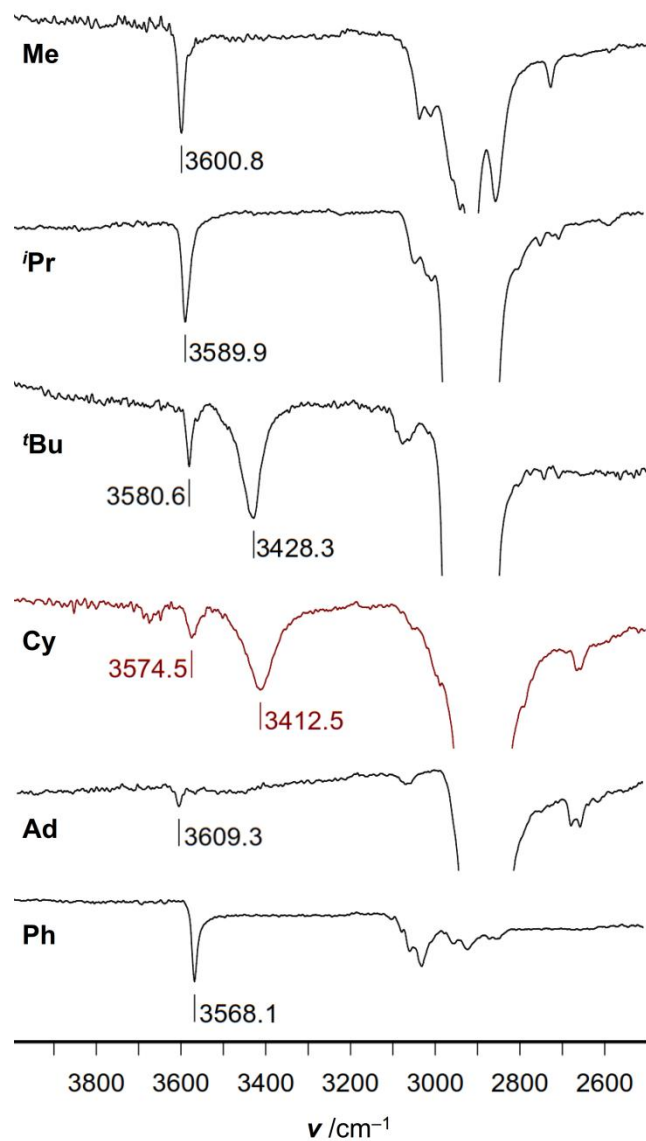
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The Triphenylmethanols



isolated hydroxyl group

Triphenylmethane arrangements

