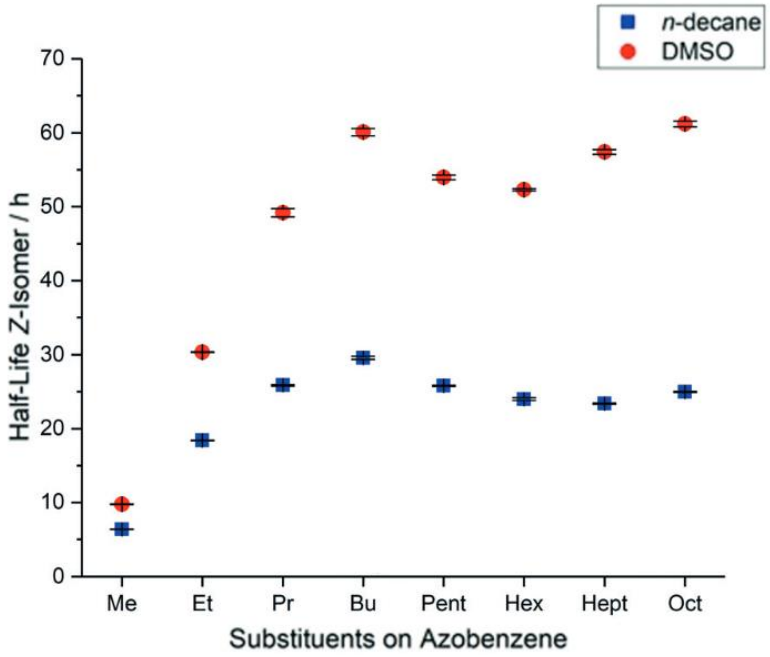
Probing London Dispersion in Solution with 2,2’-Substituted-9,9’-Bifluorenylidenes

Seminar talk presented by
Finn Wilming

November 22nd, 2019

Institute of Organic Chemistry
Justus-Liebig University Giessen


n-decane
DMSO
Half-Life Z-Isomer / h
0
10
20
30
40
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Me
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Pr
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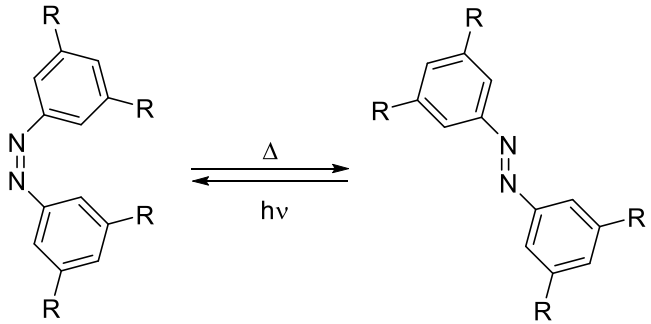
Hept
Oct
Substituents on Azobenzene


R
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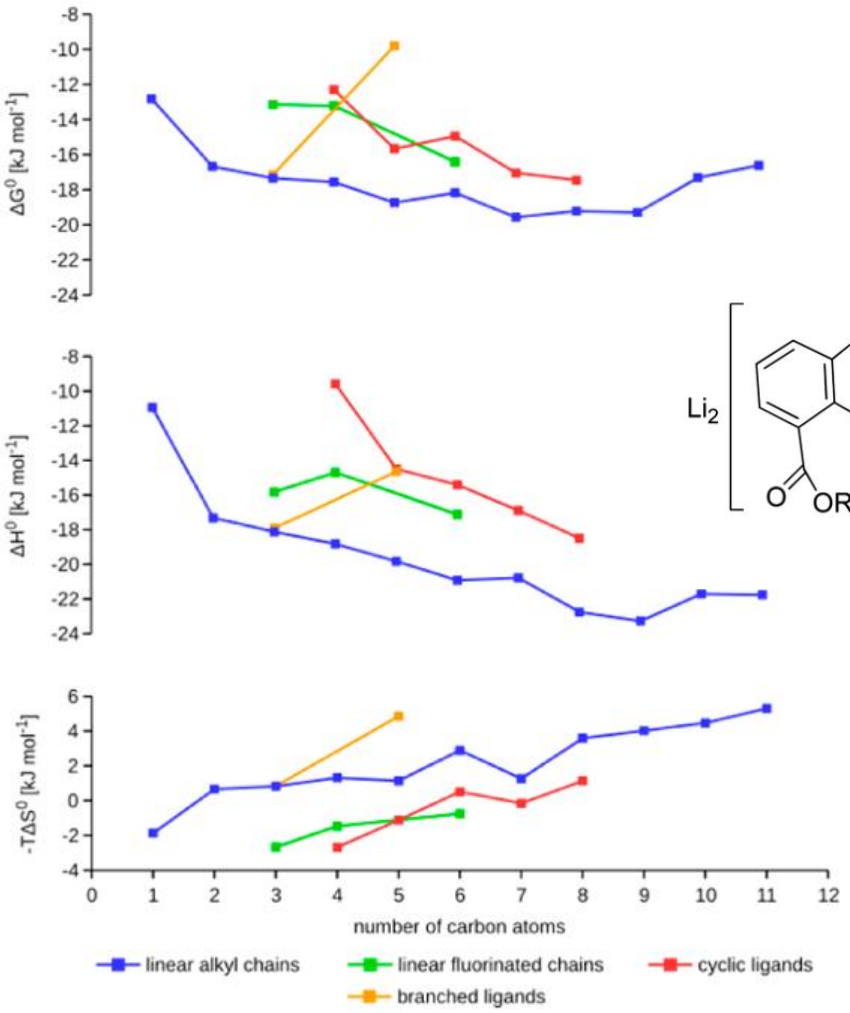
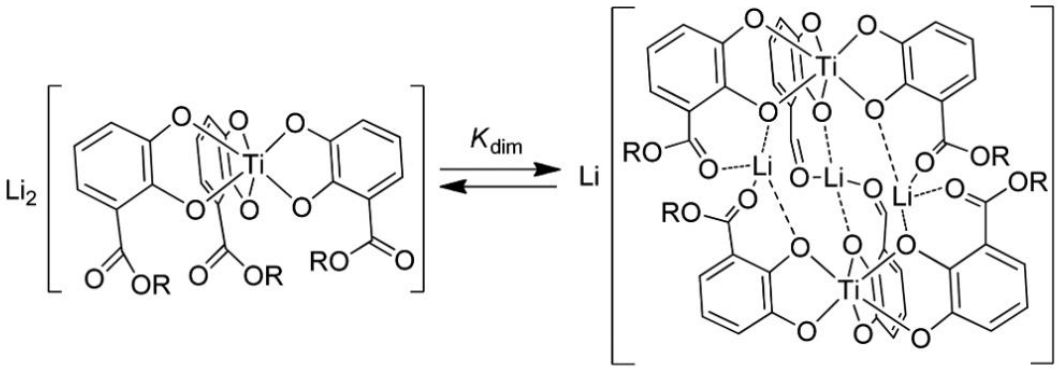
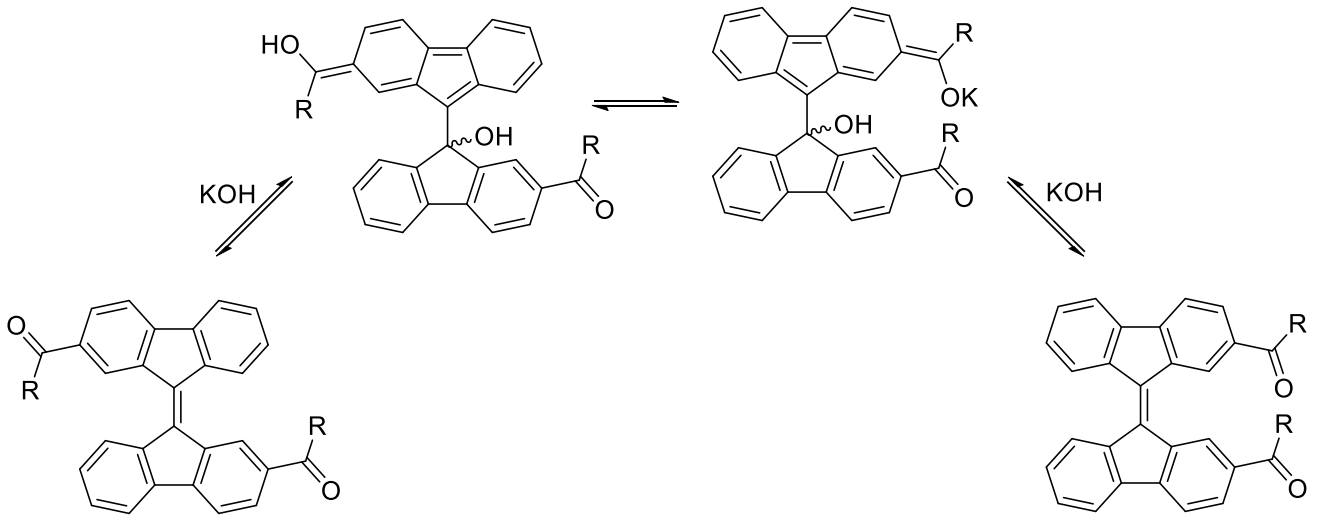
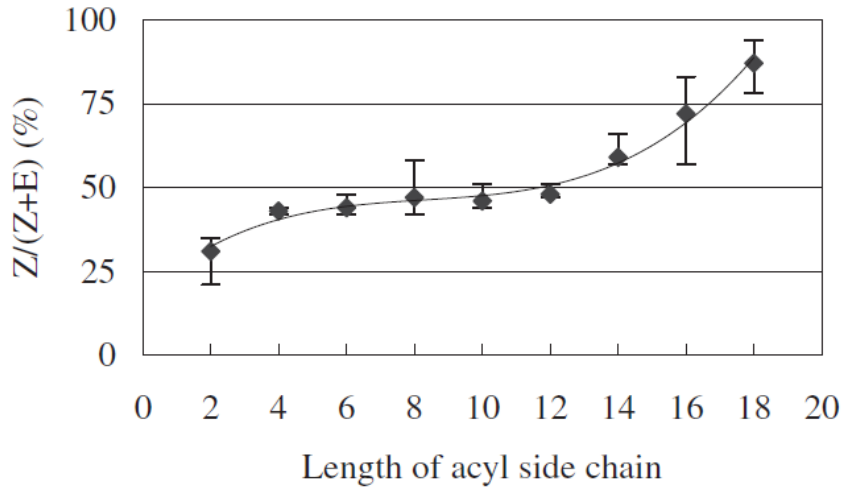


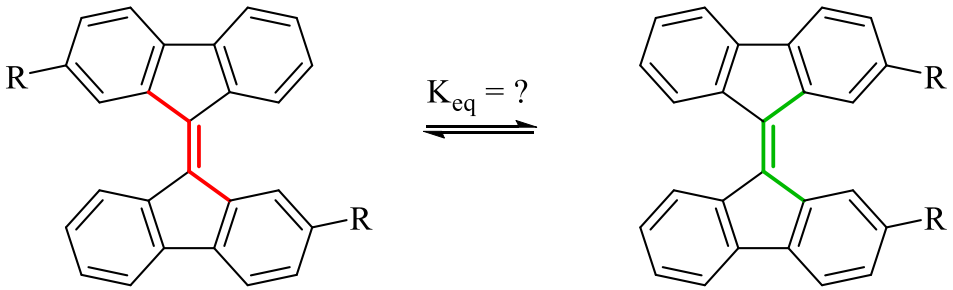


D. van Craen, W. H. Rath, M. Huth, L. Kemp, C. Räuber, J. M. Wollschläger, C. A. Schalley, A. Valkonen, K. Rissanen, M. Albrecht, *J. Am. Chem. Soc.* **2017**, *139*, 16959 – 16966.

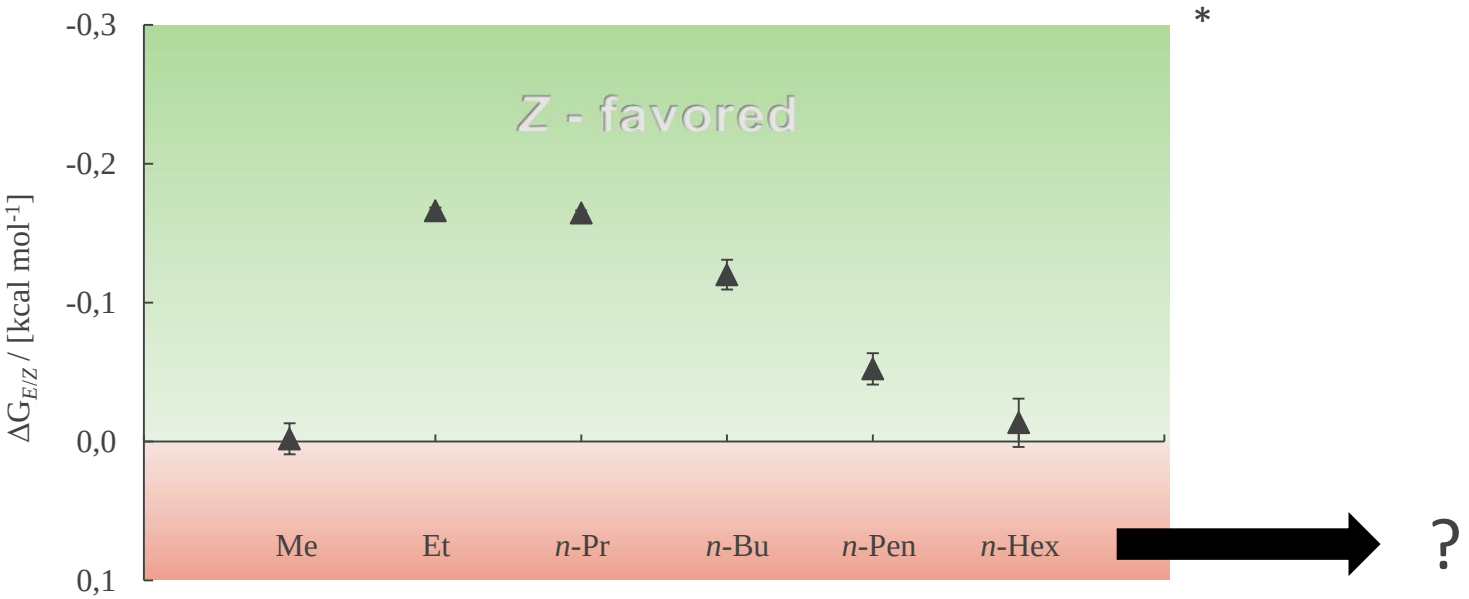




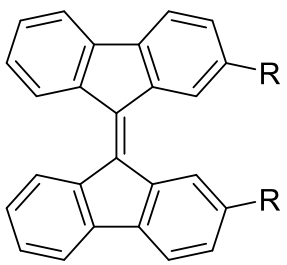
M. Minabe, A. Yamazaki, T. Imai. T. Takanezawa, M. Karikomi, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1758-1765.



E ***Z***



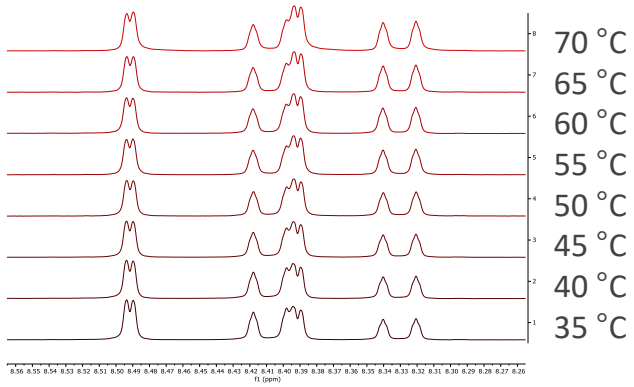
* Measurements were carried out after equilibration at 60 °C in $CDCl_3$



Linear:
Methyl – *n*-Nonyl

Branched, Cyclic:
iPr, Cy, Ph, tBu Ad, Dia.

15 Structures



8 Temperatures

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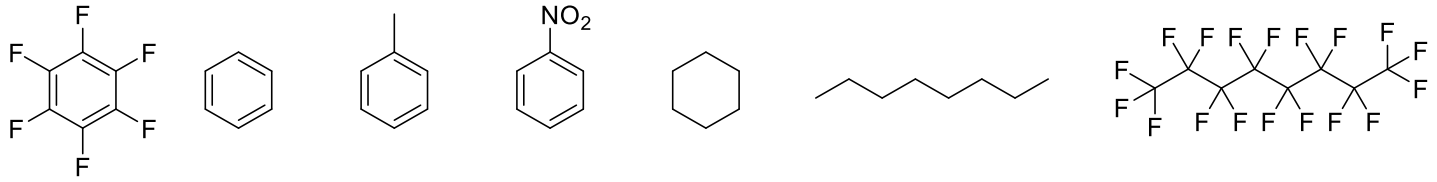
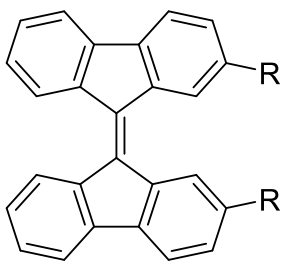


BP / °C	80	79	110	88	80	125	104
SP Scale*	0,623	0,793	0,782	0,891	0,683	0,650	≈0

7 Solvents

*J. Catalán, H. Hopf, *Eur. J. Org. Chem.* **2004**, 4694-4702. **All solvents are deuterated in every unmarked position.



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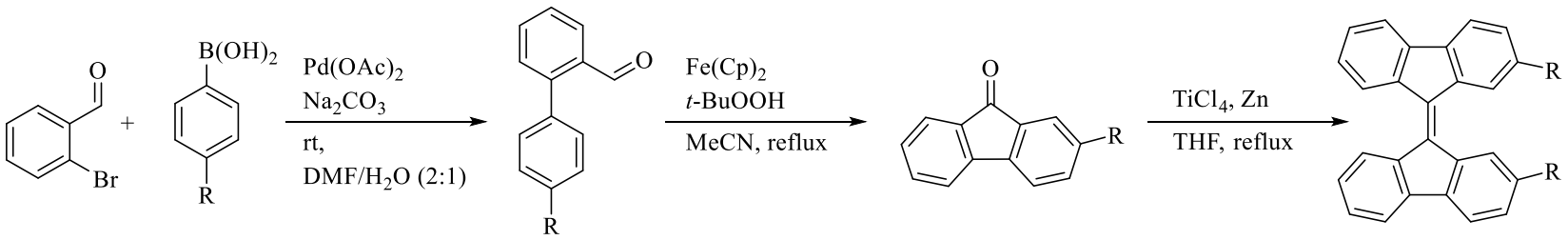
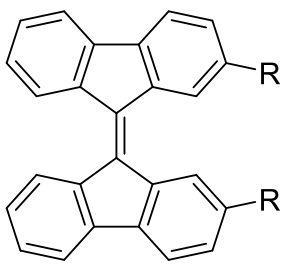
15 Structures

To do:

Gram Scale Synthesis

Crystal structures





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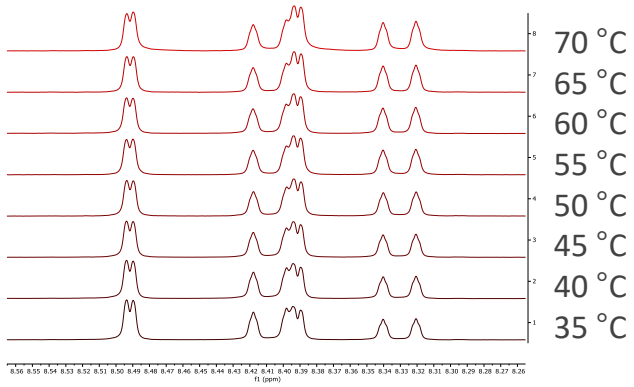

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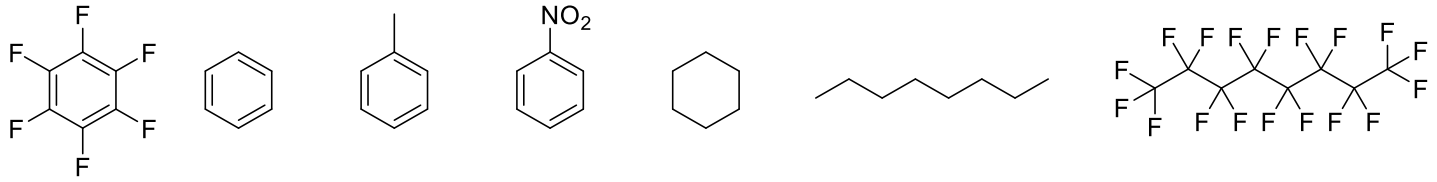

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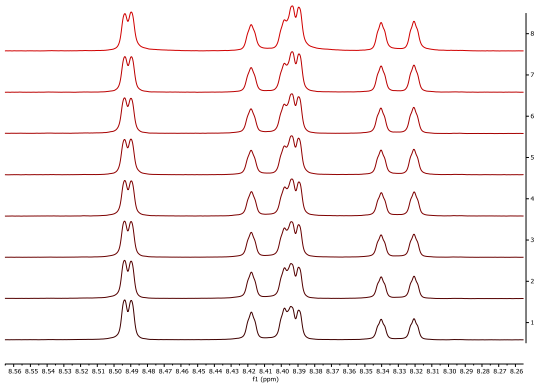
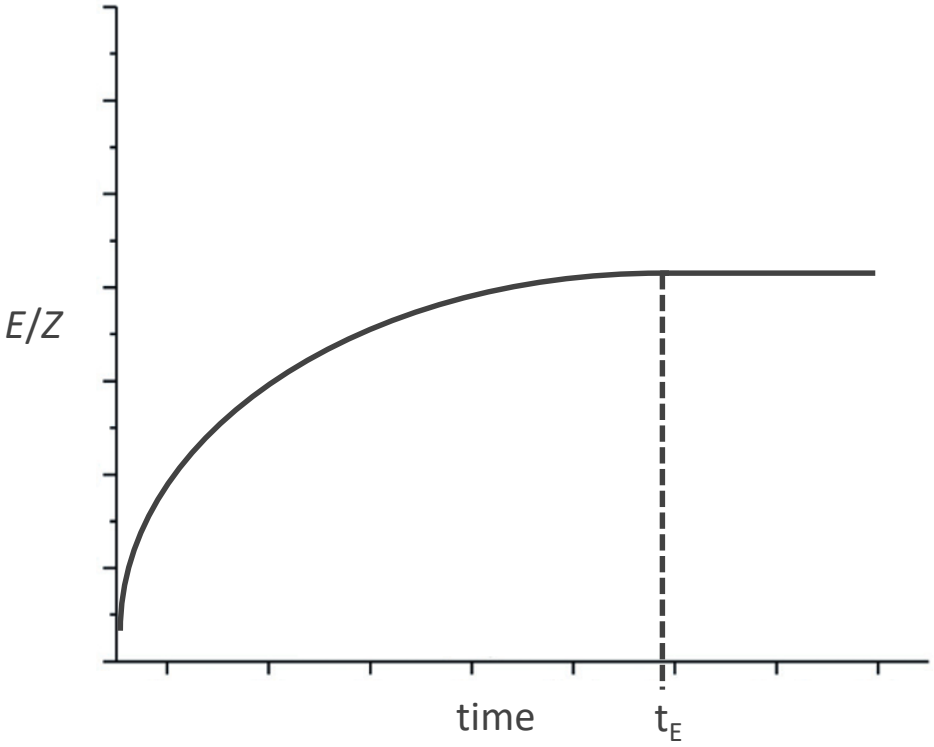
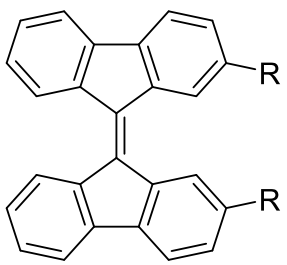
<u>To do:</u>

Understanding the kinetics of *E*/*Z* Isomerization to detemine t_E







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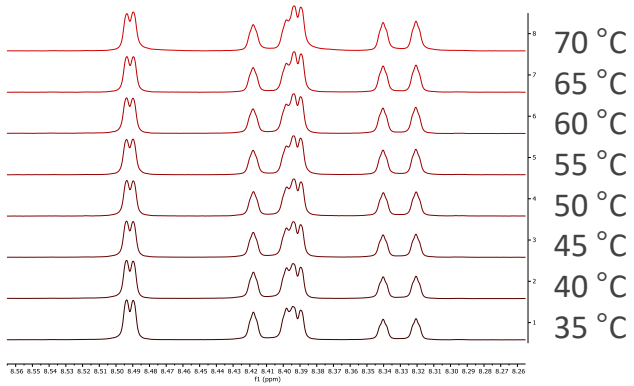

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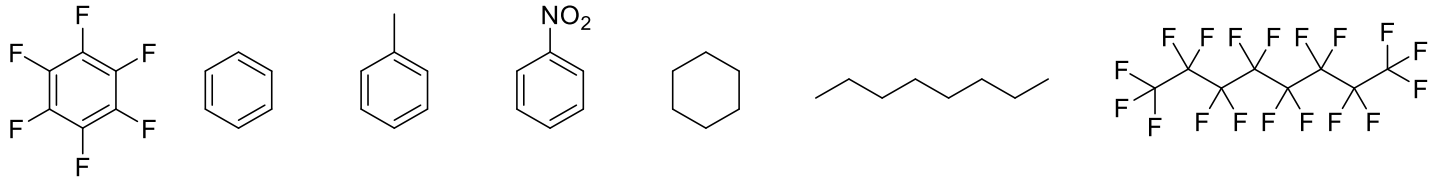

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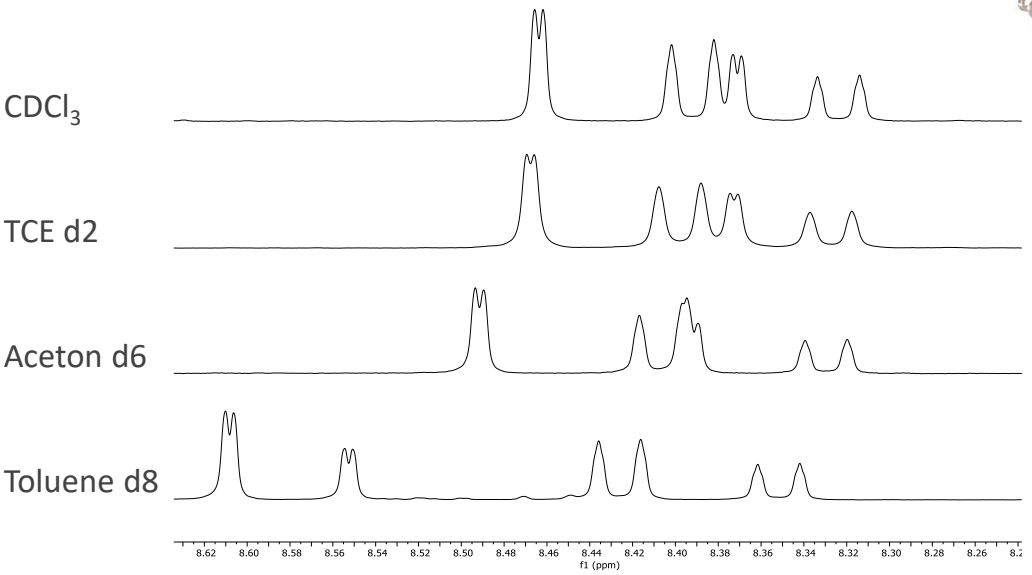
To do:

Understanding the kinetics of E/Z Isomerization

Solvent Screening

Locksignal for perfluorinated solvents



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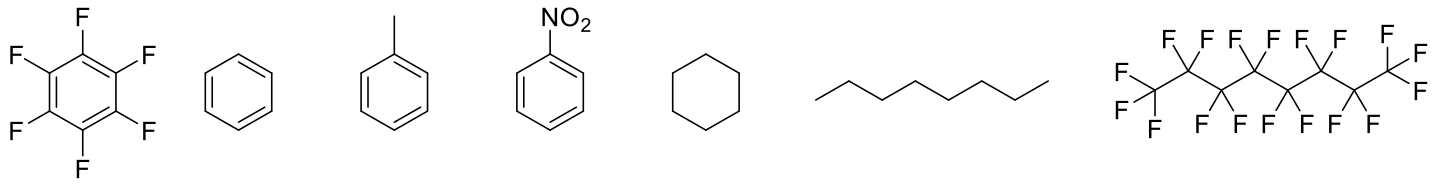

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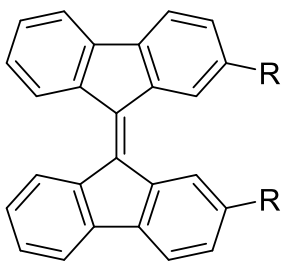

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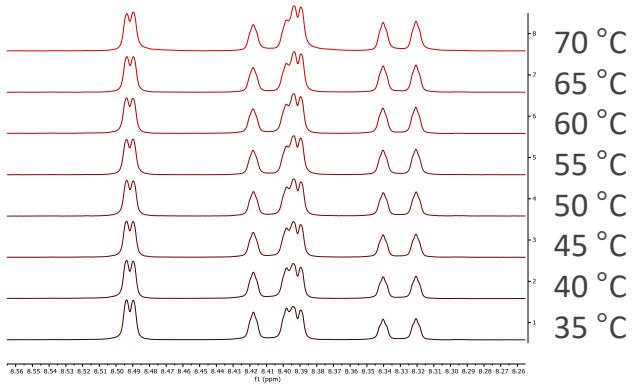

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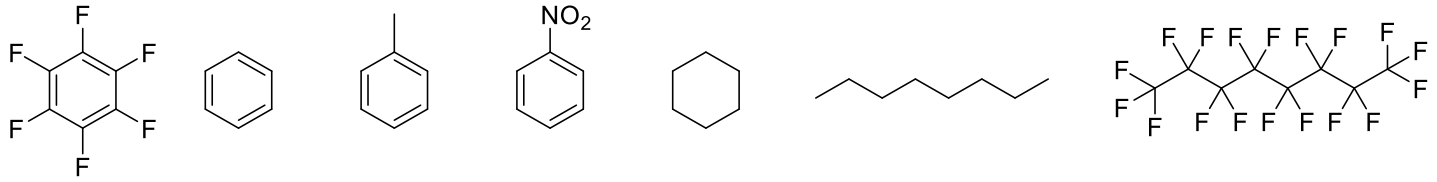

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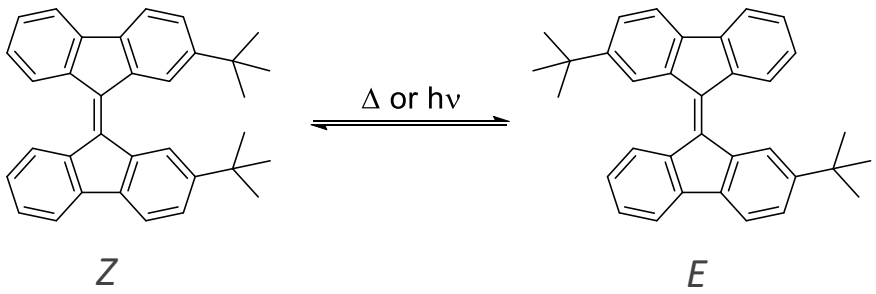
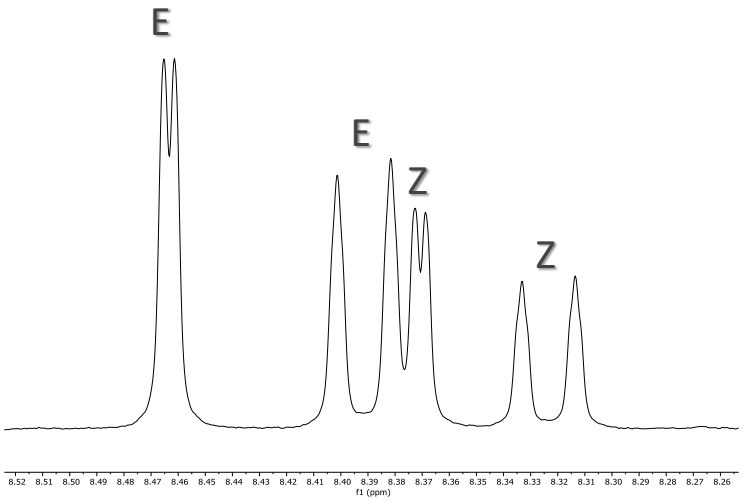
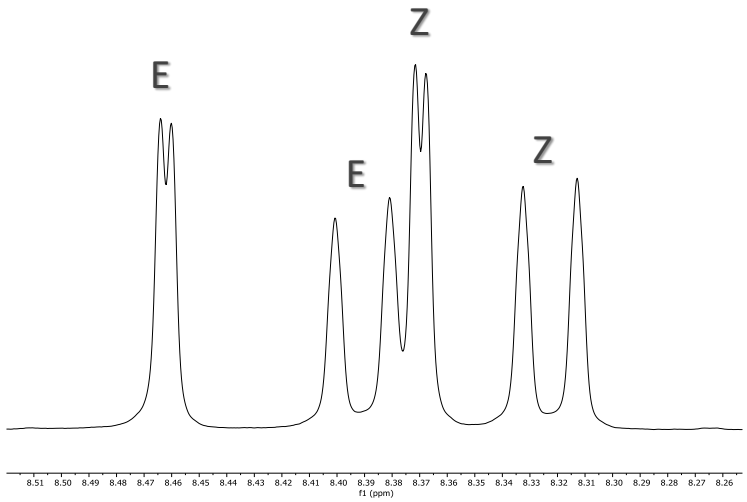
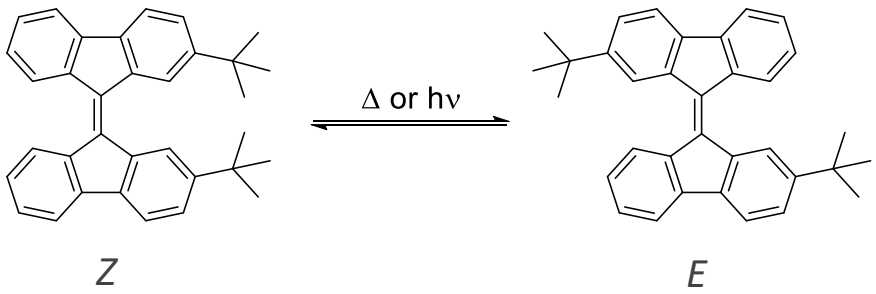


Thermal Treatment at 60 °C for 1h

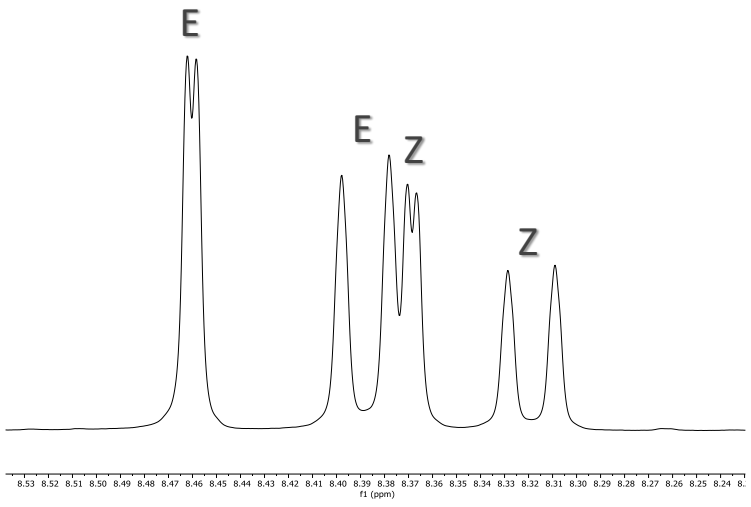


Irradiation at 0 °C for 72 h





„Thermal Treatment“ at 0 °C for 72h



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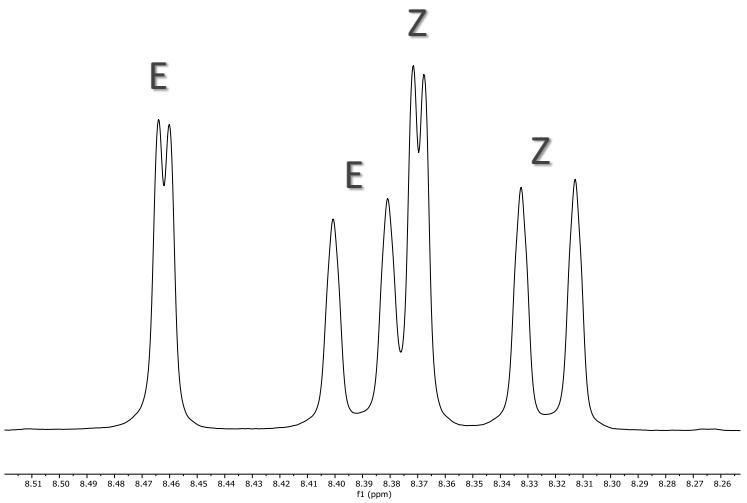
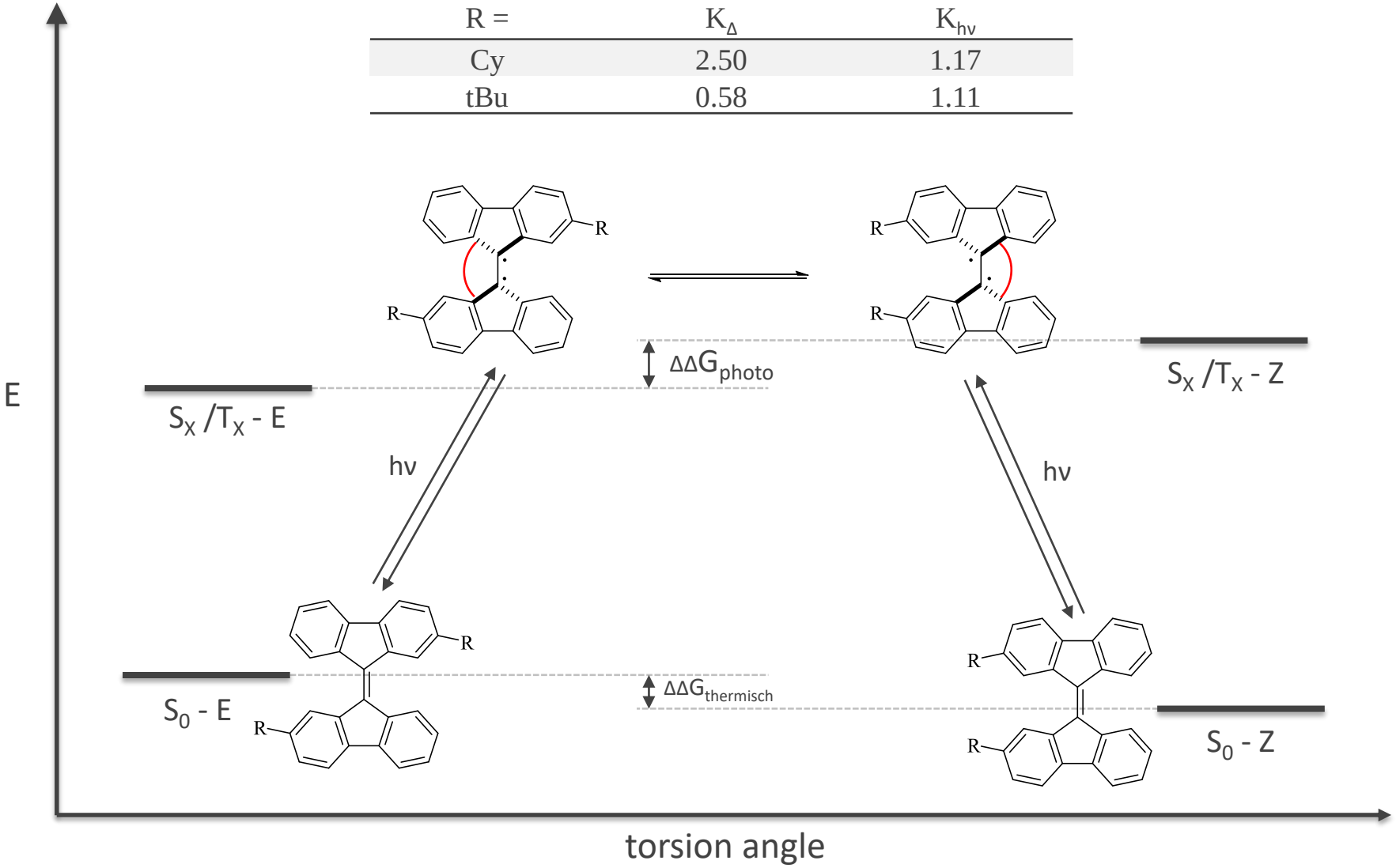
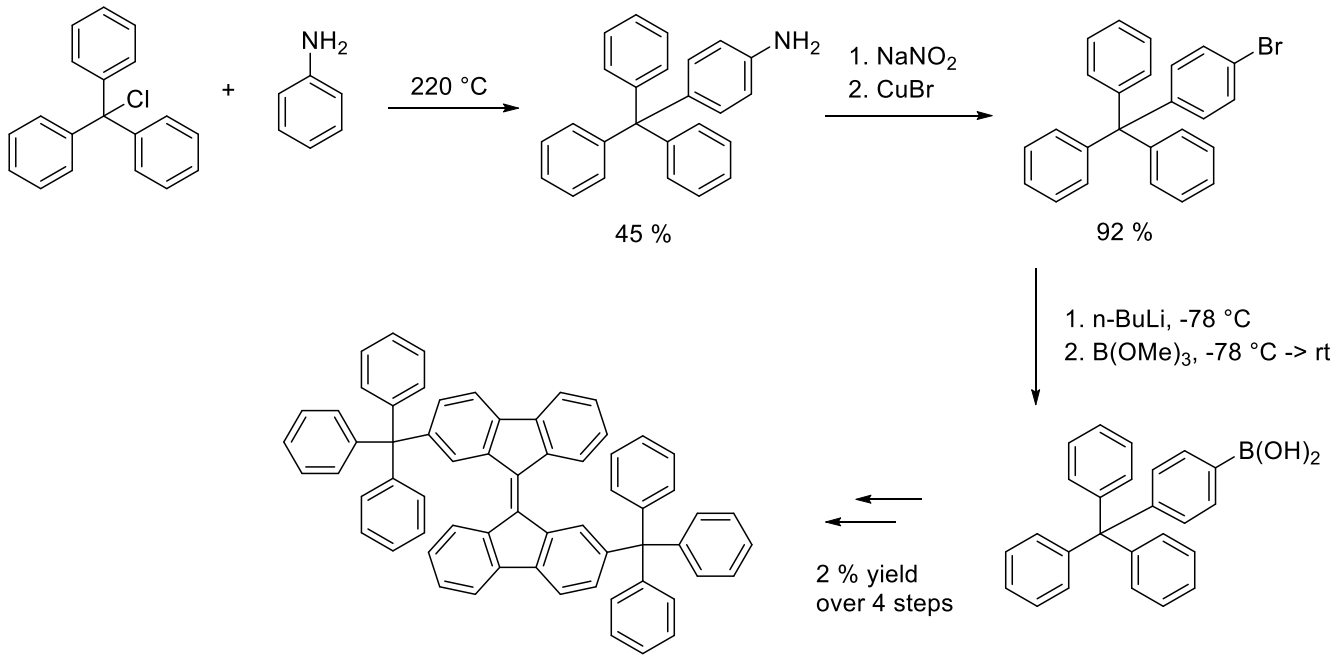
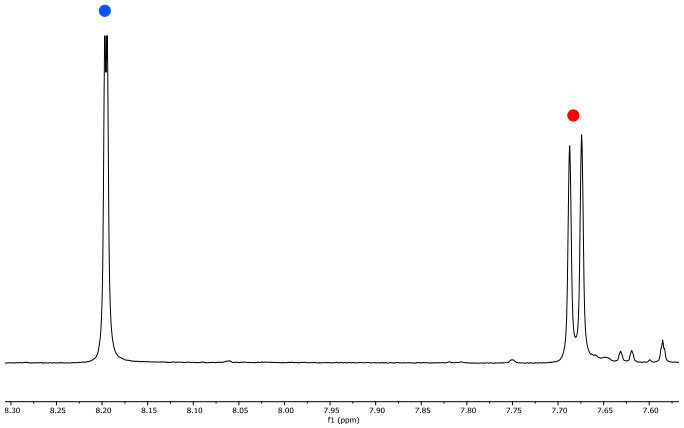


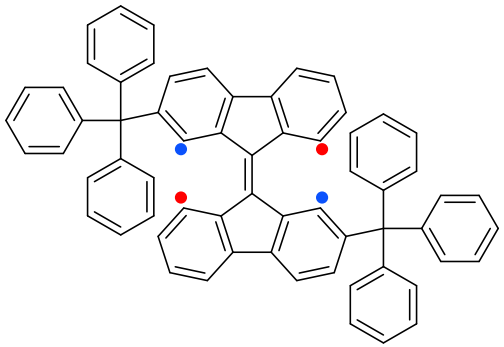
R =	K_{Δ}	K_{hv}
Cy	2.50	1.17
tBu	0.58	1.11

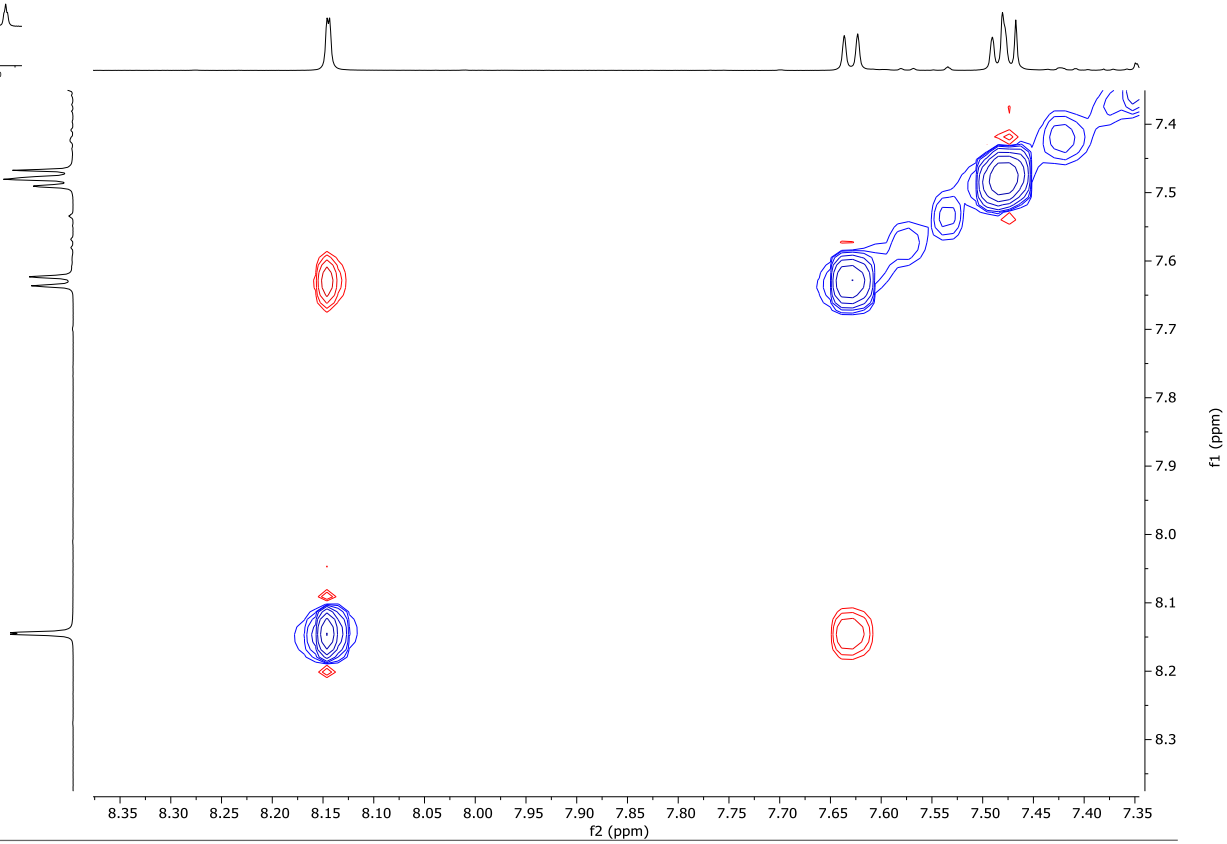



Cl
+
NH2
220 °C
NH2
45 %
1. NaNO2
2. CuBr
Br
92 %
1. n-BuLi, -78 °C
2. B(OMe)3, -78 °C -> rt
B(OH)2
2 % yield
over 4 steps

Part 3 – Synthesis of 2,2’-Trityl-9,9’-Bifluorenylidene







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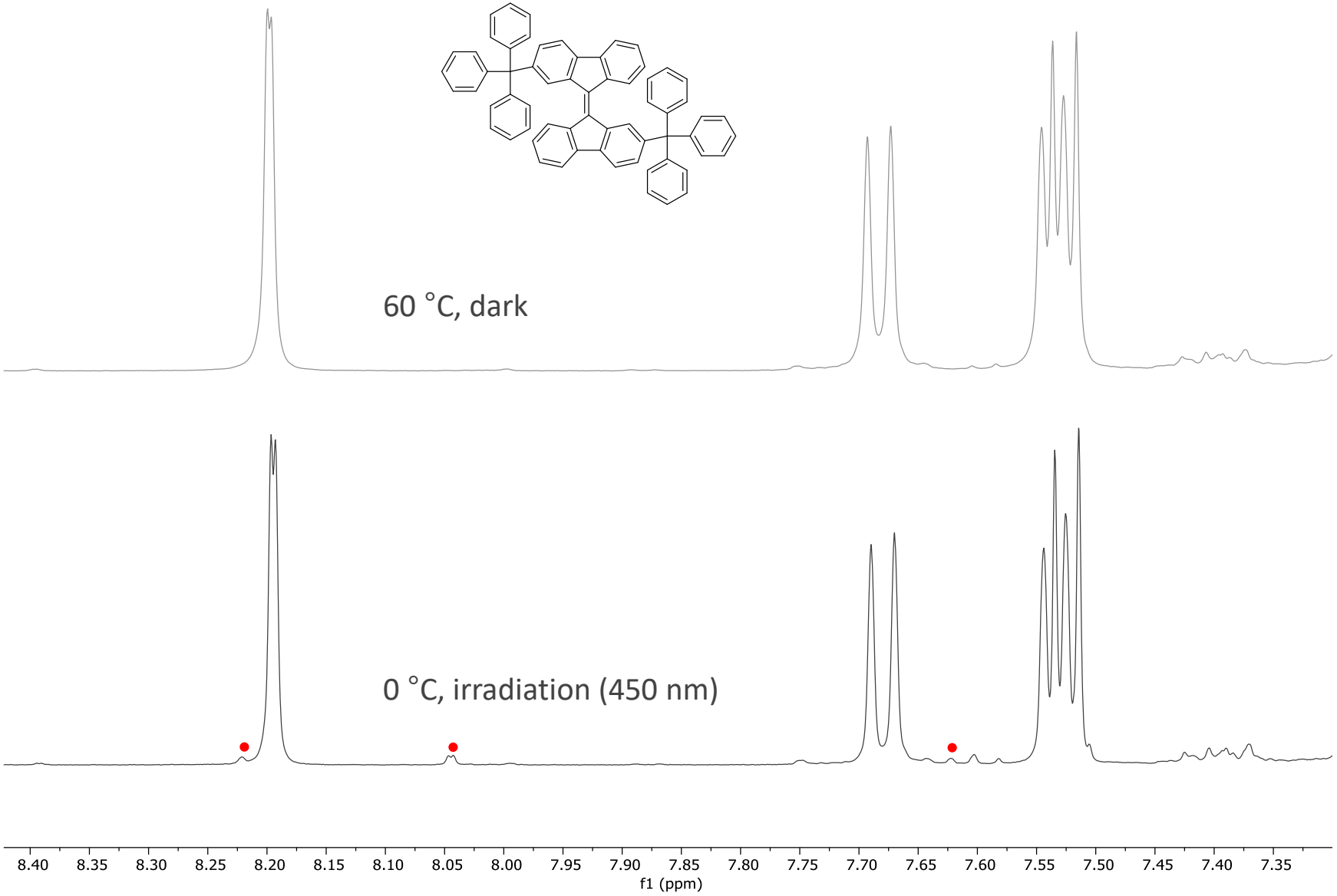
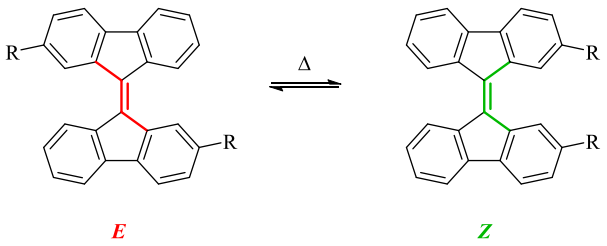
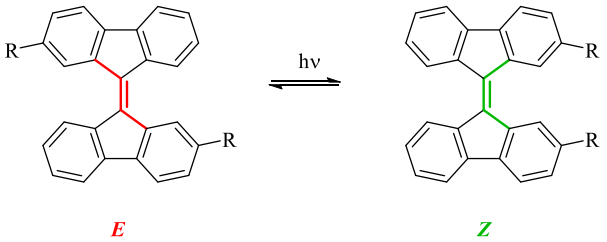


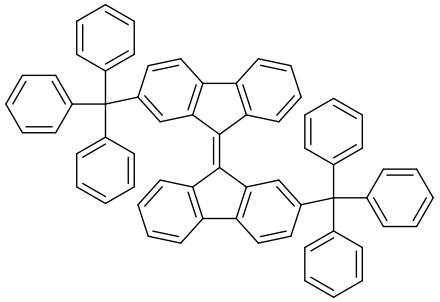
VT NMR experiments for linear, branched and cyclic substituents will start in early 2020.





Experimental data suggests, that the photochemically obtained E/Z values come from the equilibrium of two „excited state species“.

The Synthesis of 2,2‘-trityl-9,9‘-bifluorenylidene was successful. As expected, the *E*-Isomer is strongly favoured due to steric strain in the *Z*-Isomer.



Acknowledgements

Prof. Dr. Peter R. Schreiner

Lars, Jan, Lukas and Dennis for Discussions.

Lab B201

PRS Group