



# Intramolekulares $\pi$ -stacking

Skilizium – Hospental (CH) – 06/03/2016

Marvin Linnemannstöns & Sebastian Blomeyer



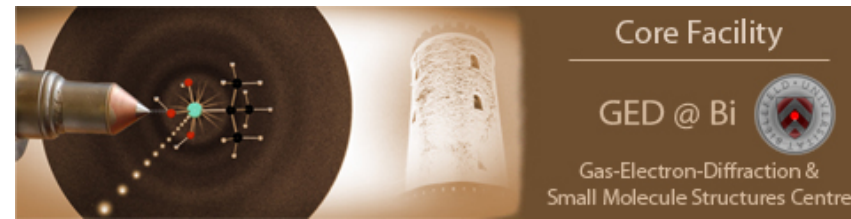
# Einleitung



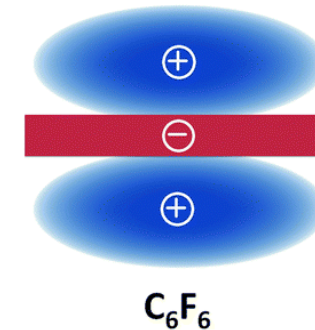
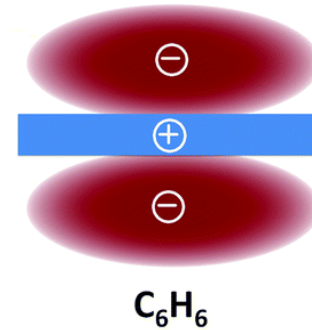
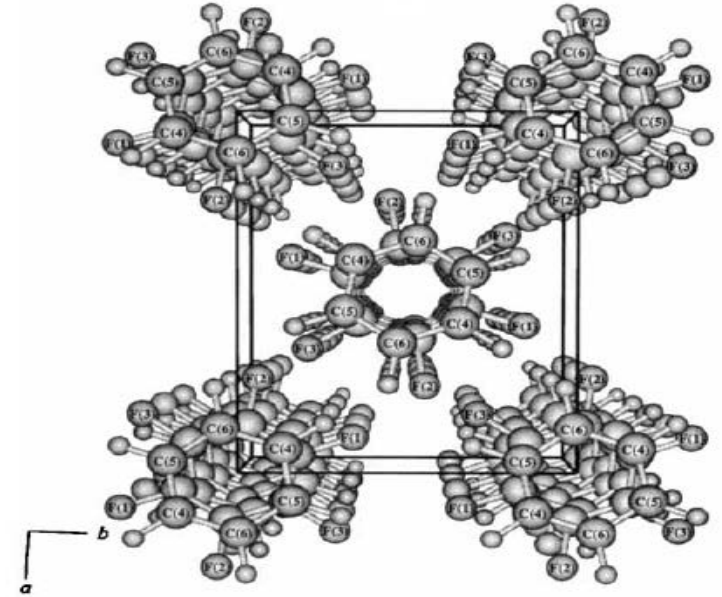
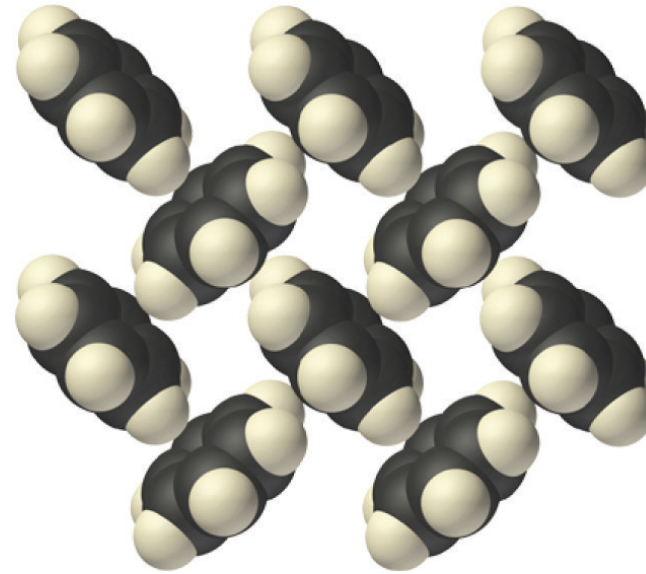
Art der Wechselwirkung	Energie [kJ mol <sup>-1</sup> ]
Ion-Ion	ca. 250
Wasserstoffbrücken	ca. 40
Permanente Dipol-Dipol	ca. 25
fluktuierender Dipol	ca. 10

- Fluktuierende Dipol–Dipol-WW → London'sche Dispersionskräfte
- Dispersive Wechselwirkung scheinbar am schwächsten

# Einleitung



- $\sigma$ - $\sigma$ -Wechselwirkungen
- $\sigma$ - $\pi$ -Wechselwirkungen
- $\pi$ - $\pi$ -Wechselwirkungen



[2] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, P. M. Deya, *Chem. Phys. Chem.* **2003**, 4, 1344–1348.

[3] J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 1655–1657.



# Ziel

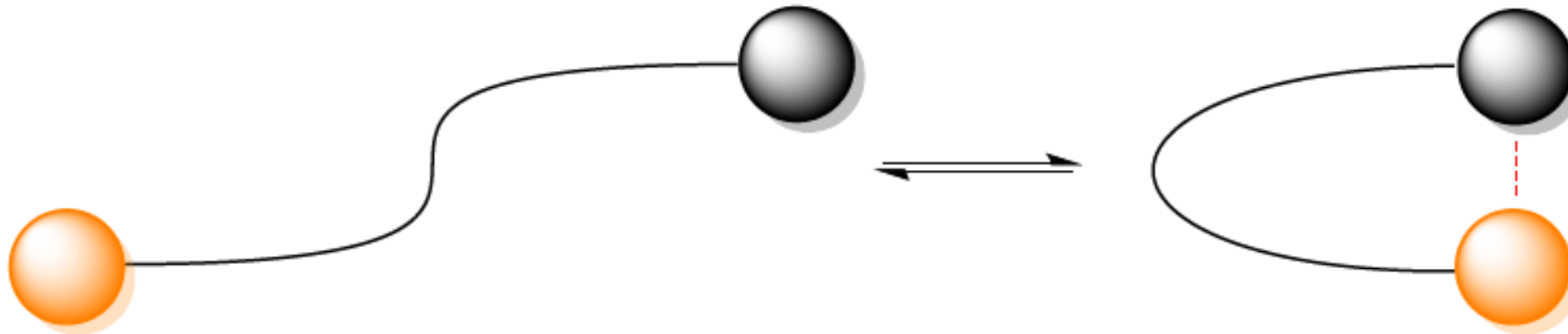


- Verbindungen mit zwei unterschiedlichen aromatischen Systemen
- Verwendung einer möglichst kurzen, flexiblen Linkereinheit

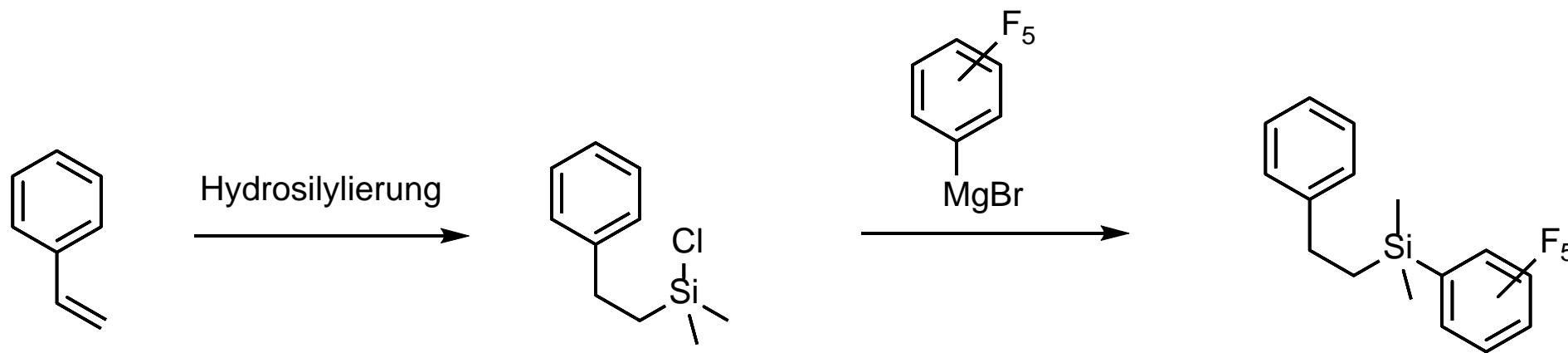
# Ziel



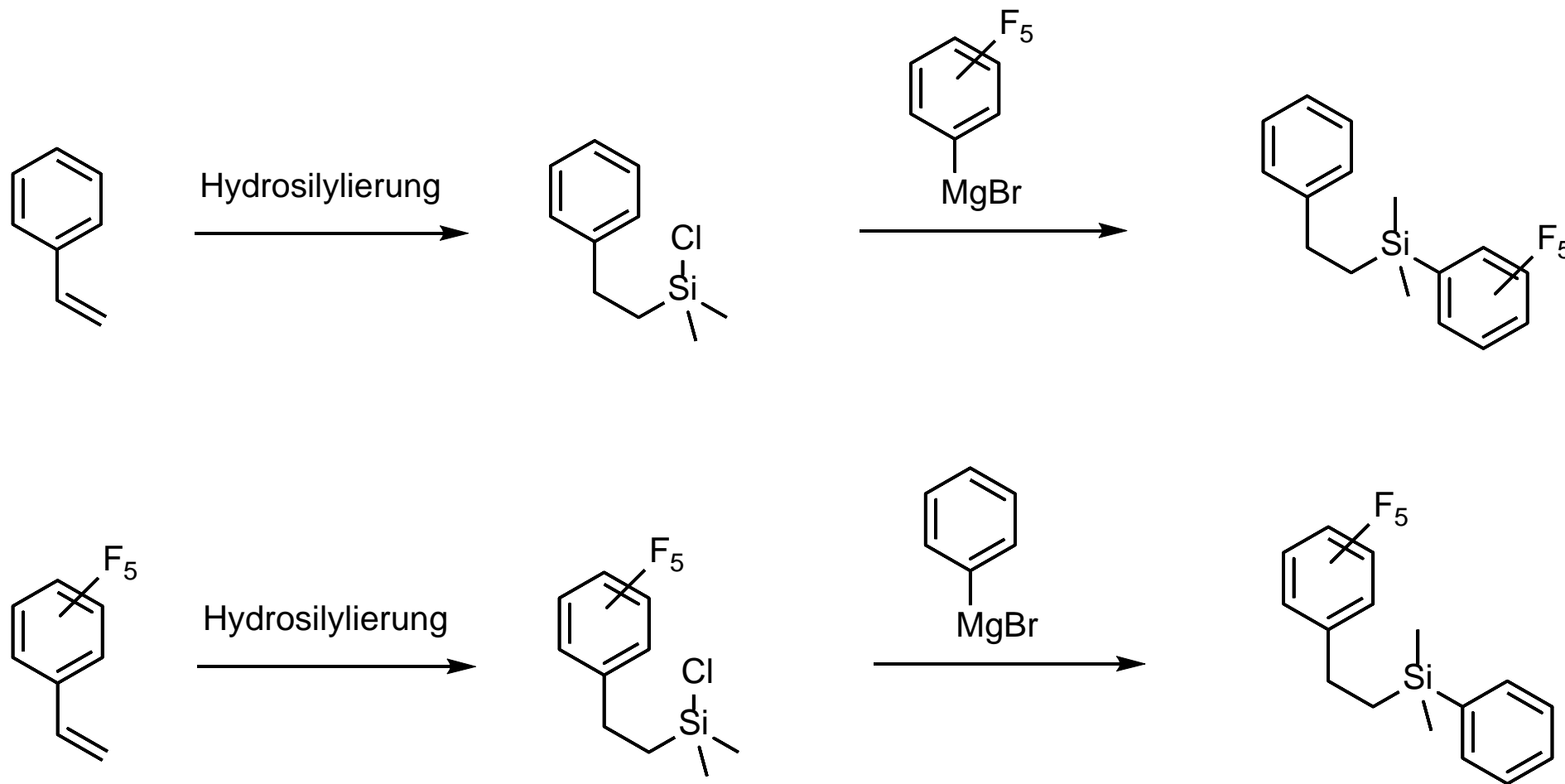
- Verbindungen mit zwei unterschiedlichen aromatischen Systemen
- Verwendung einer möglichst kurzen, flexiblen Linkereinheit



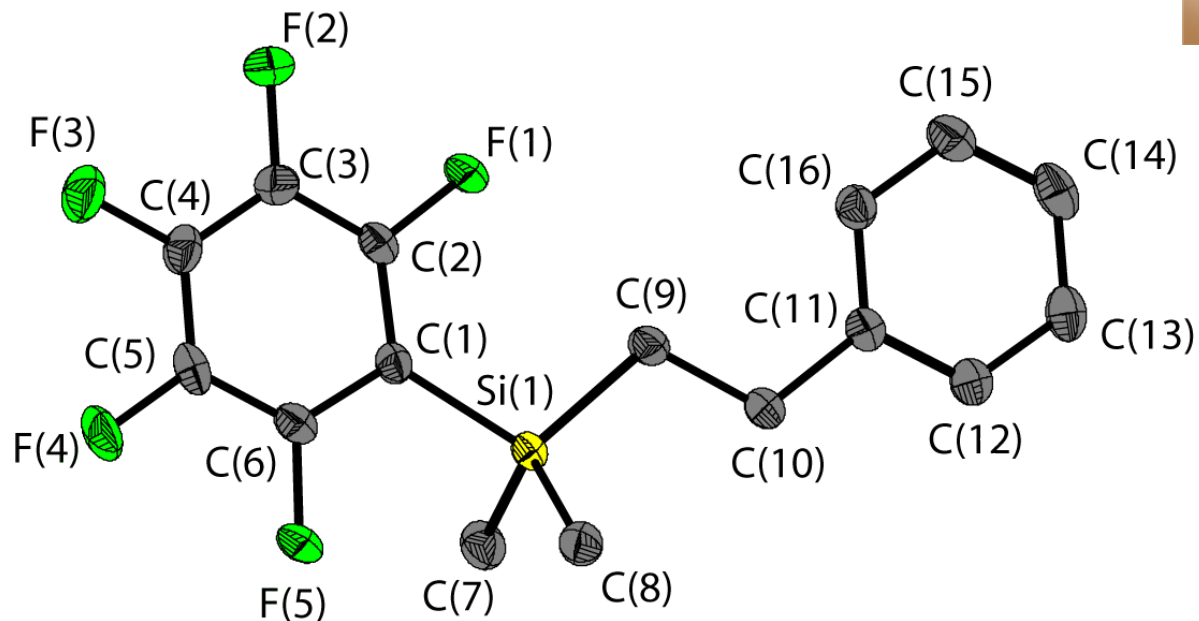
# Synthese



# Synthese



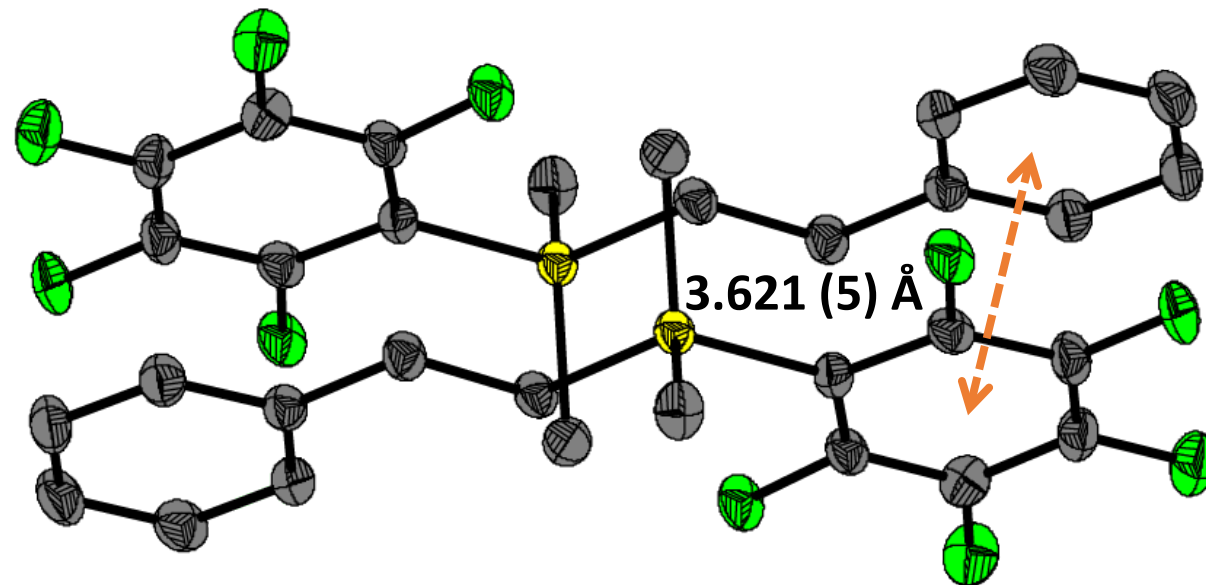
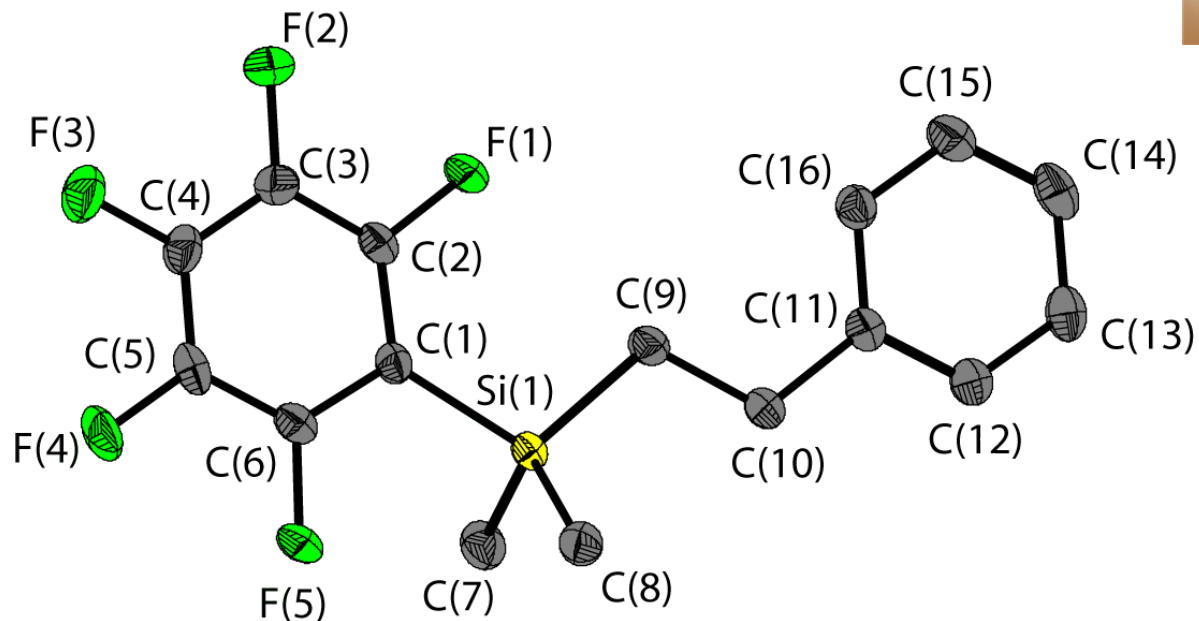
# Molekülstruktur im Kristall



A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
C(6)	C(1)	Si(1)	1.394(4)	119.4(2)
C(1)	Si(1)	C(9)	1.912(3)	109.4(1)
Si(1)	C(9)	C(10)	1.973(3)	112.9(2)
C(9)	C(10)	C(12)	1.528(4)	116.1(2)

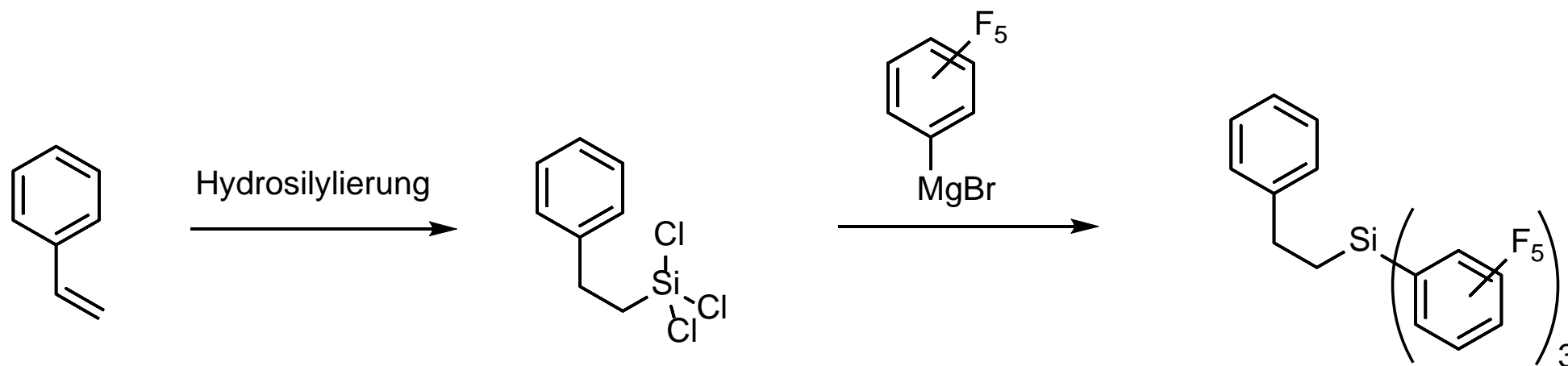


# Molekülstruktur im Kristall

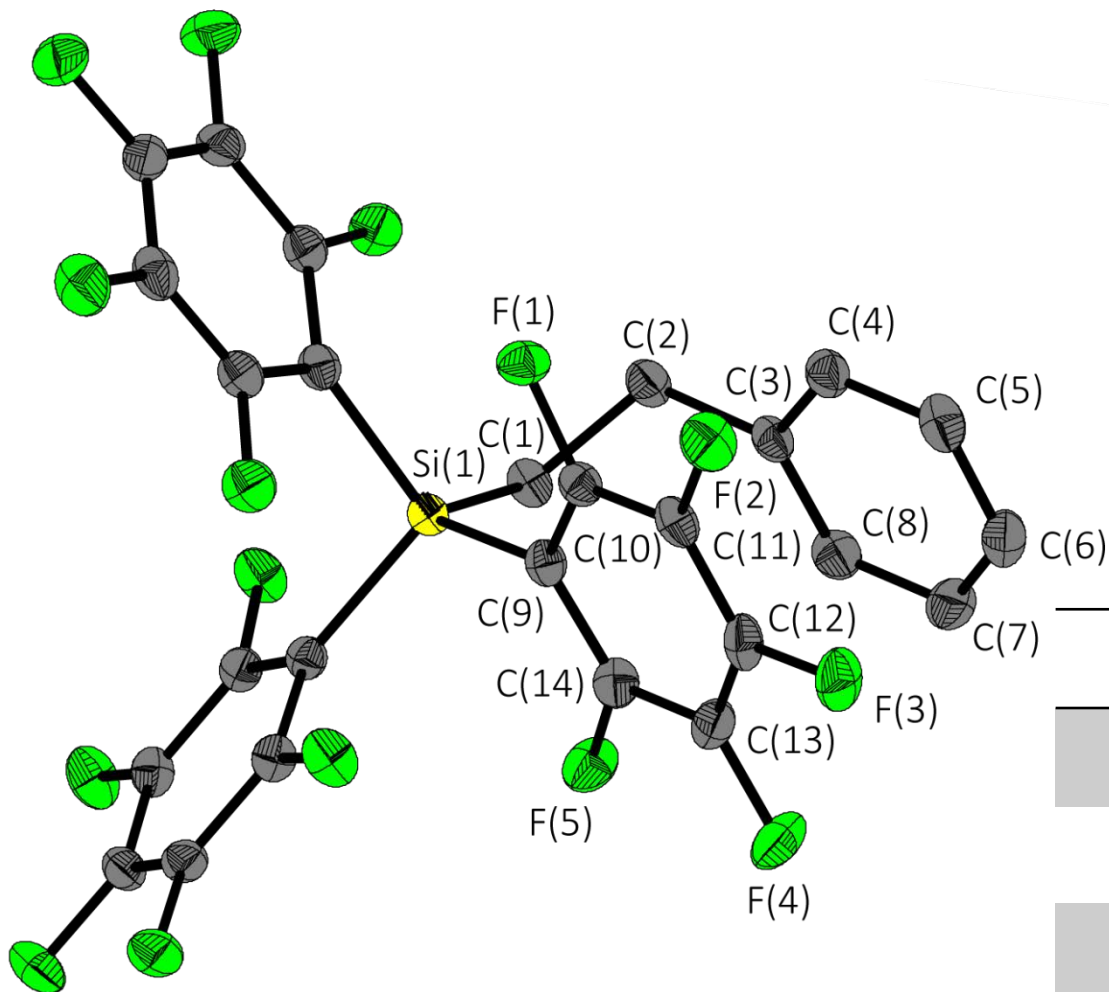


A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
C(6)	C(1)	Si(1)	1.394(4)	119.4(2)
C(1)	Si(1)	C(9)	1.912(3)	109.4(1)
Si(1)	C(9)	C(10)	1.973(3)	112.9(2)
C(9)	C(10)	C(12)	1.528(4)	116.1(2)

# Synthese



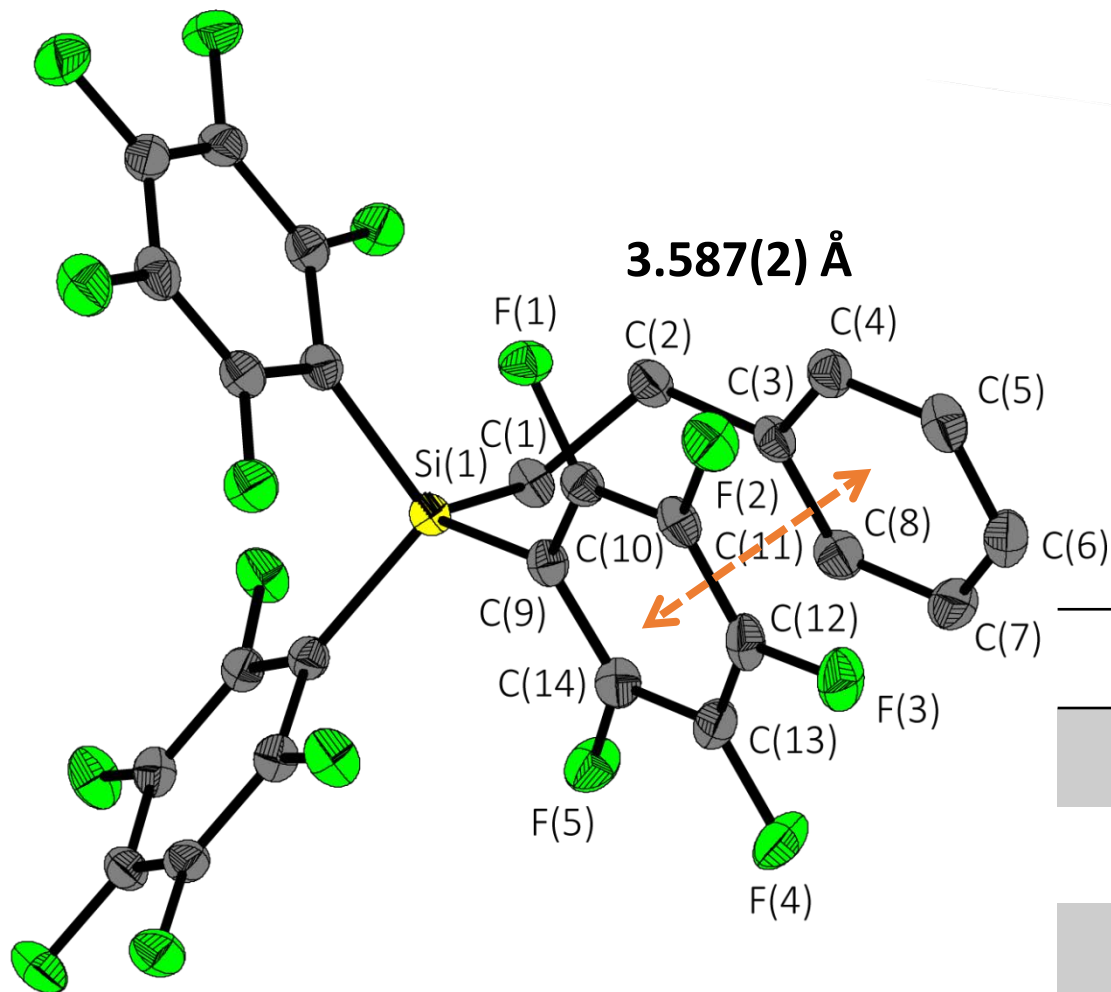
# Molekülstruktur im Kristall



A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
Si(1)	C(1)	C(2)	1.864(1)	116.7(1)
C(1)	C(2)	C(3)	1.546(2)	115.2(1)
C(9)	Si(1)	C(1)	1.889(1)	108.4(1)



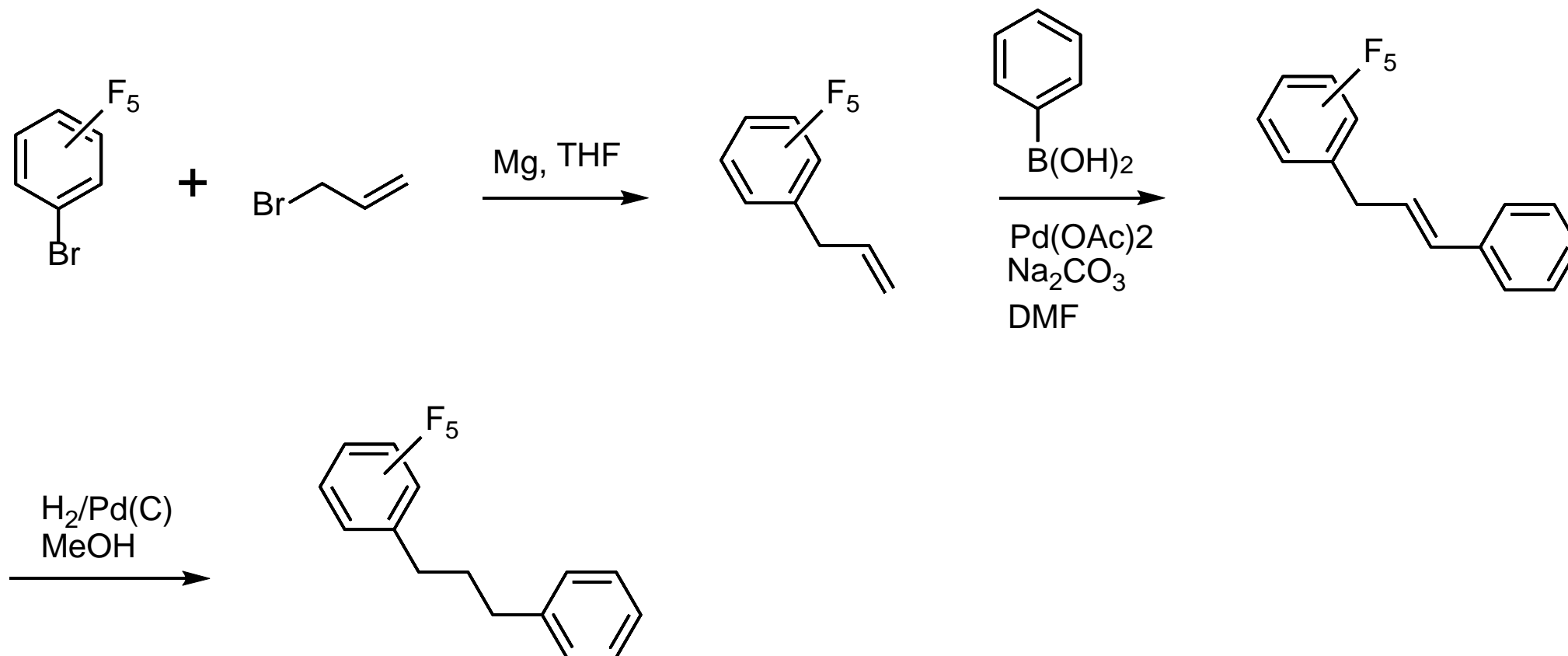
# Molekülstruktur im Kristall



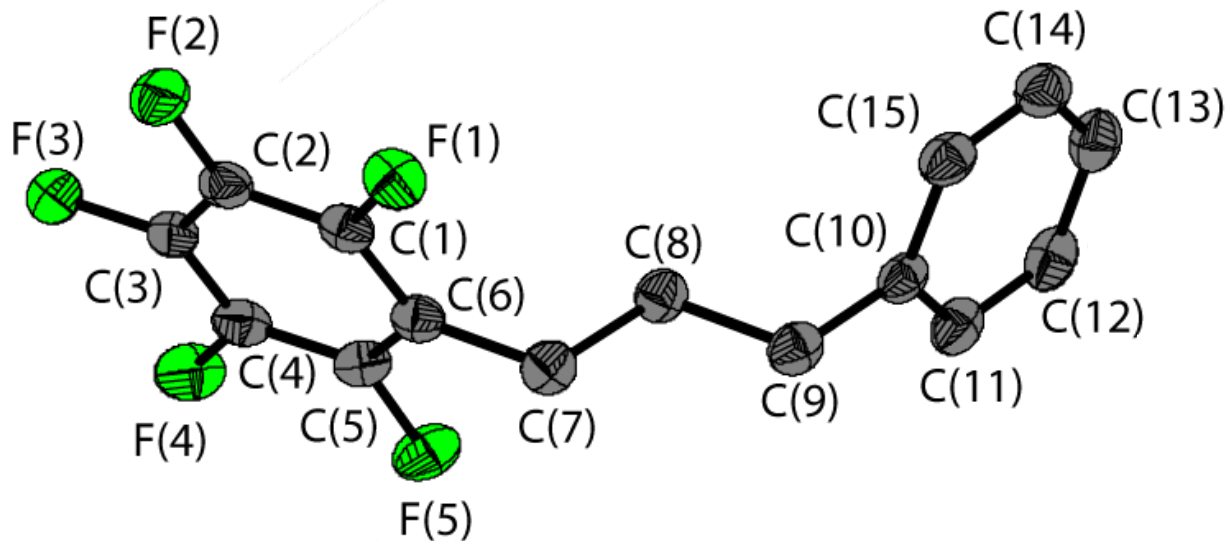
A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
Si(1)	C(1)	C(2)	1.864(1)	116.7(1)
C(1)	C(2)	C(3)	1.546(2)	115.2(1)
C(9)	Si(1)	C(1)	1.889(1)	108.4(1)



# Synthese



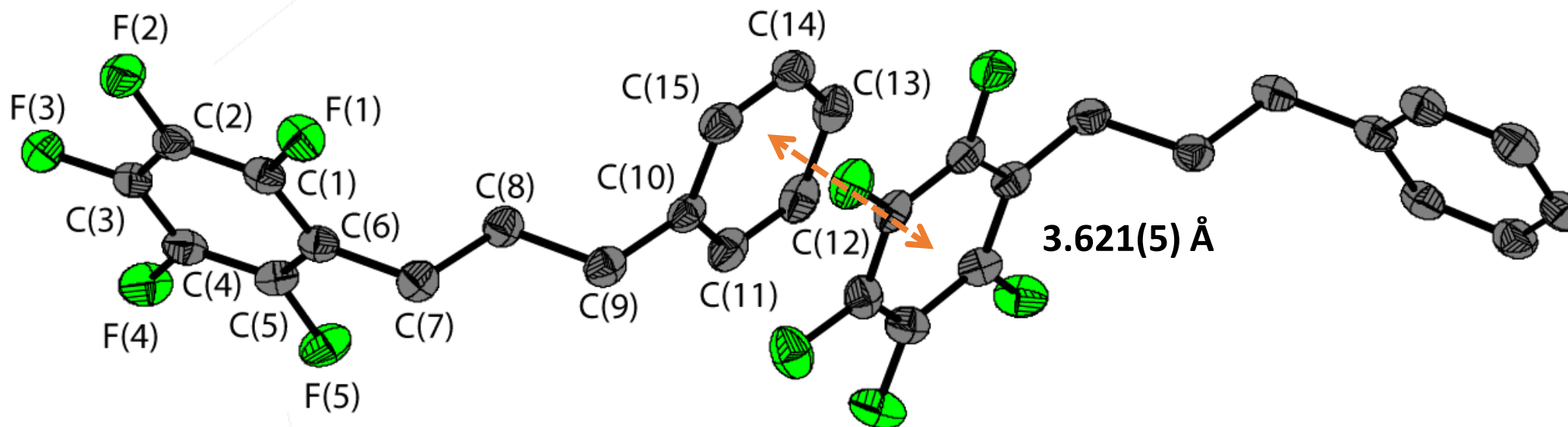
# Molekülstruktur im Kristall



A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
C(1)	C(6)	C(7)	1.390(2)	122.8(2)
C(6)	C(7)	C(8)	1.507(2)	111.8(1)
C(7)	C(8)	C(9)	1.531(2)	113.0(1)
C(8)	C(9)	C(10)	1.511(2)	111.1(1)



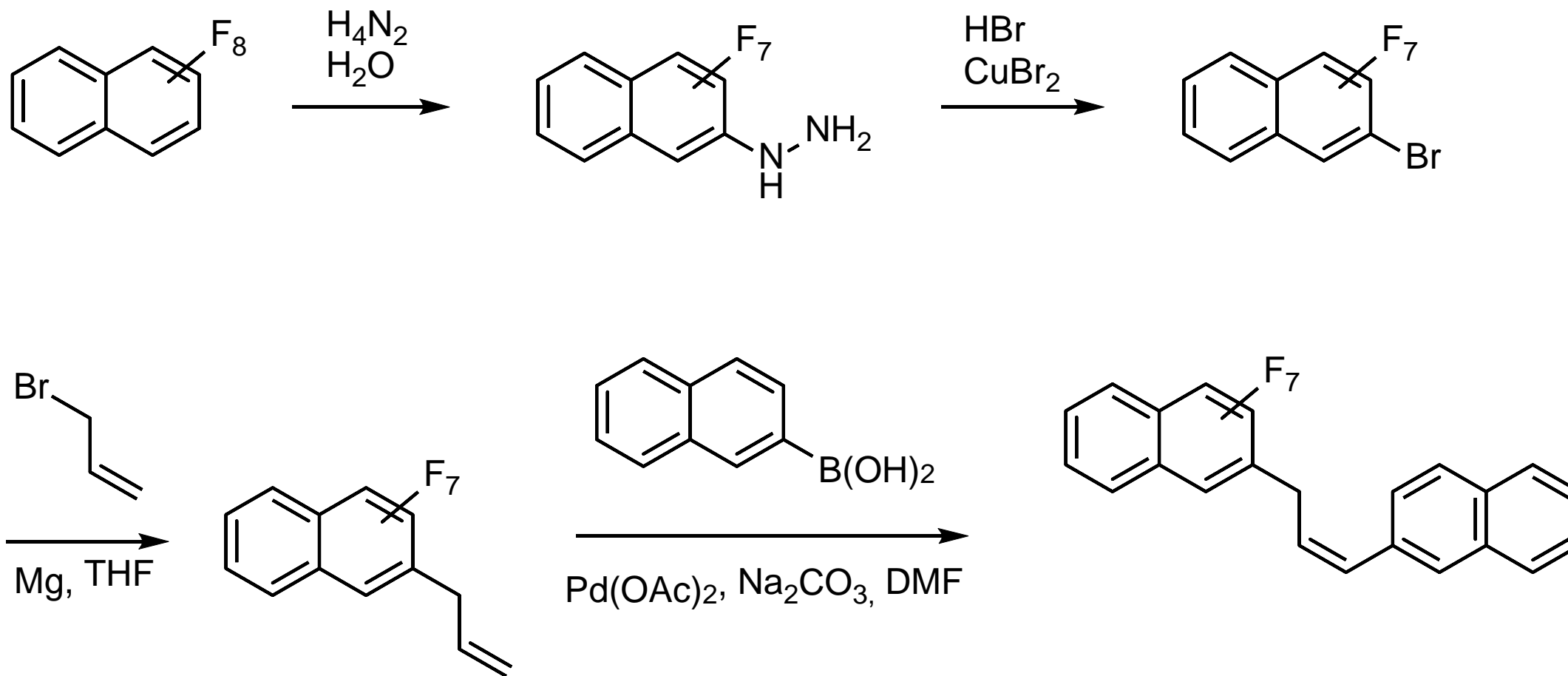
# Molekülstruktur im Kristall



A	B	C	$d(AB)$ [Å]	$\angle(ABC)$ [°]
C(1)	C(6)	C(7)	1.390(2)	122.8(2)
C(6)	C(7)	C(8)	1.507(2)	111.8(1)
C(7)	C(8)	C(9)	1.531(2)	113.0(1)
C(8)	C(9)	C(10)	1.511(2)	111.1(1)



# Synthese



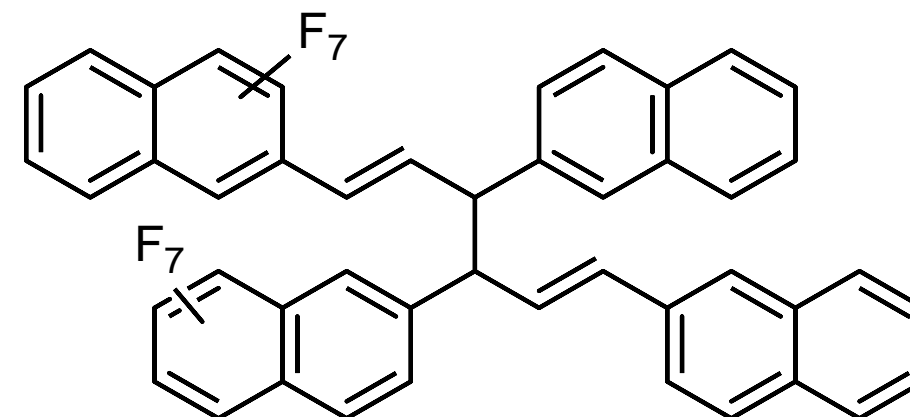
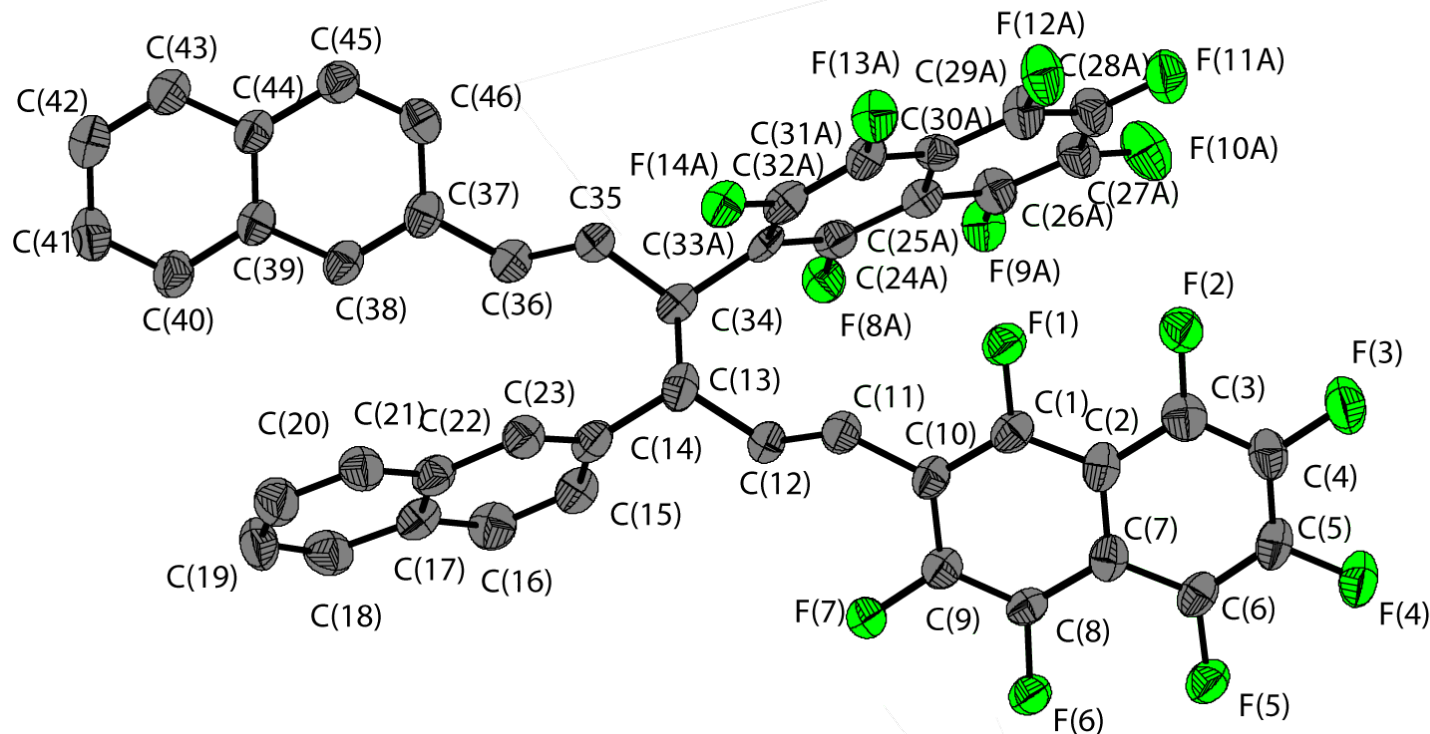
[4] B. Gehring, C. R. Patrick, J. C. Tatlow, *J. Chem. Soc.* **1962**, 186–190.

[5] J. Marks, Tobin, Li Liting, *Organometallics*, **1998**, 17, 3996–4003





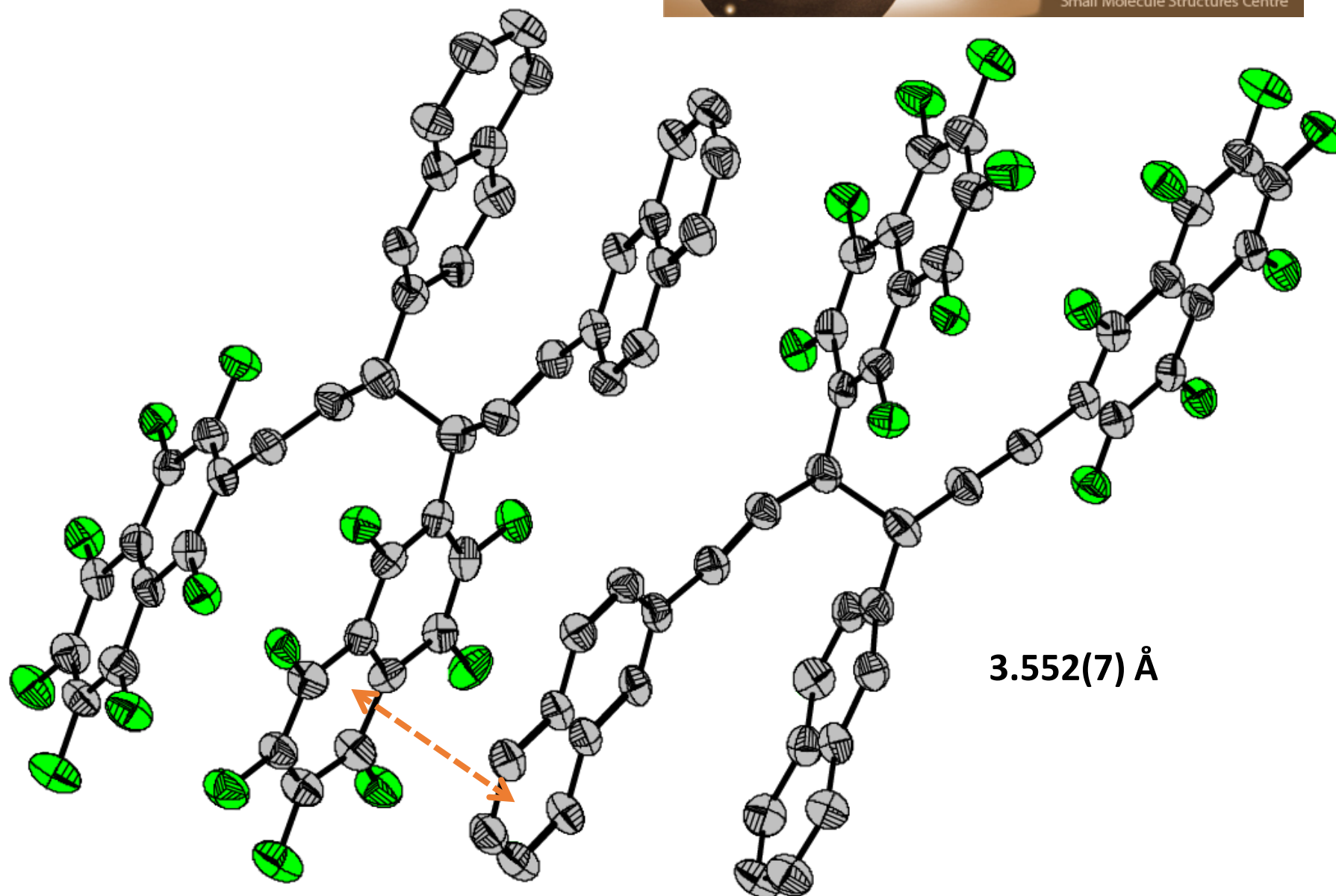
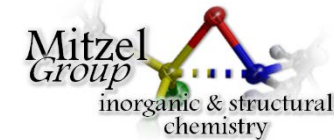
# Molekülstruktur im Kristall

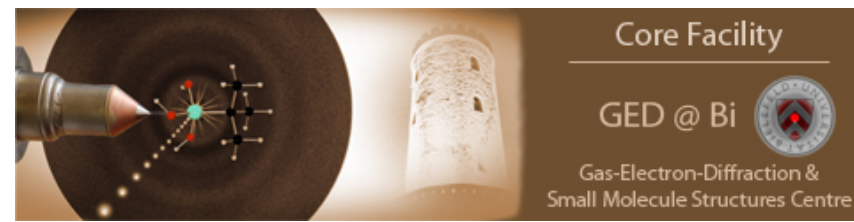


A	B	C	$d(AB)$ [Å]	$d(BC)$ [Å]	$\angle(ABC)$ [°]
C(11)	C(12)	C(13)	1.342(2)	1.507(10)	121.8(8)
C(34)	C(35)	C(36)	1.515(10)	1.340(10)	121.2(7)
C(14)	C(13)	C(34)	1.514(11)	1.610(12)	106.7(6)



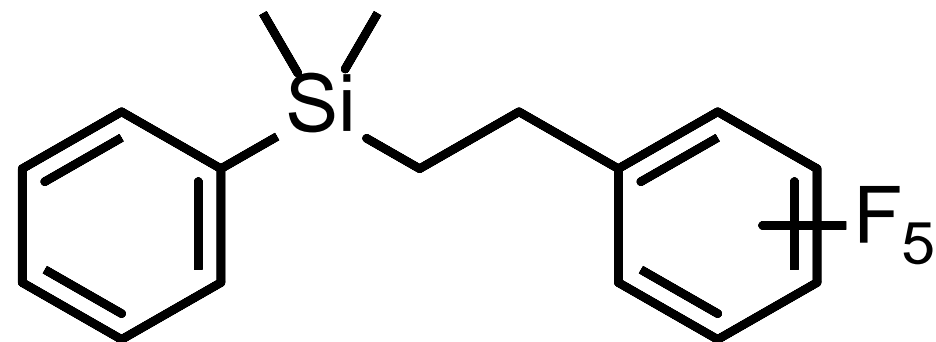
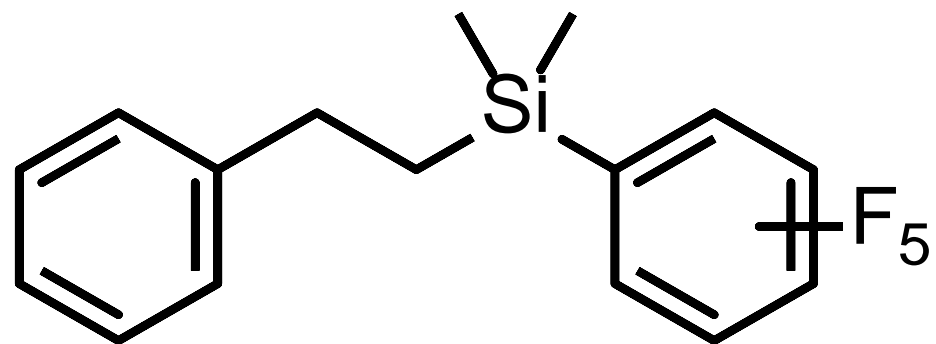
# Molekülstruktur im Kristall





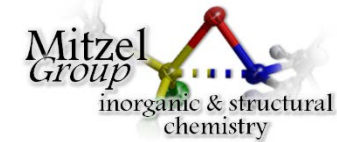
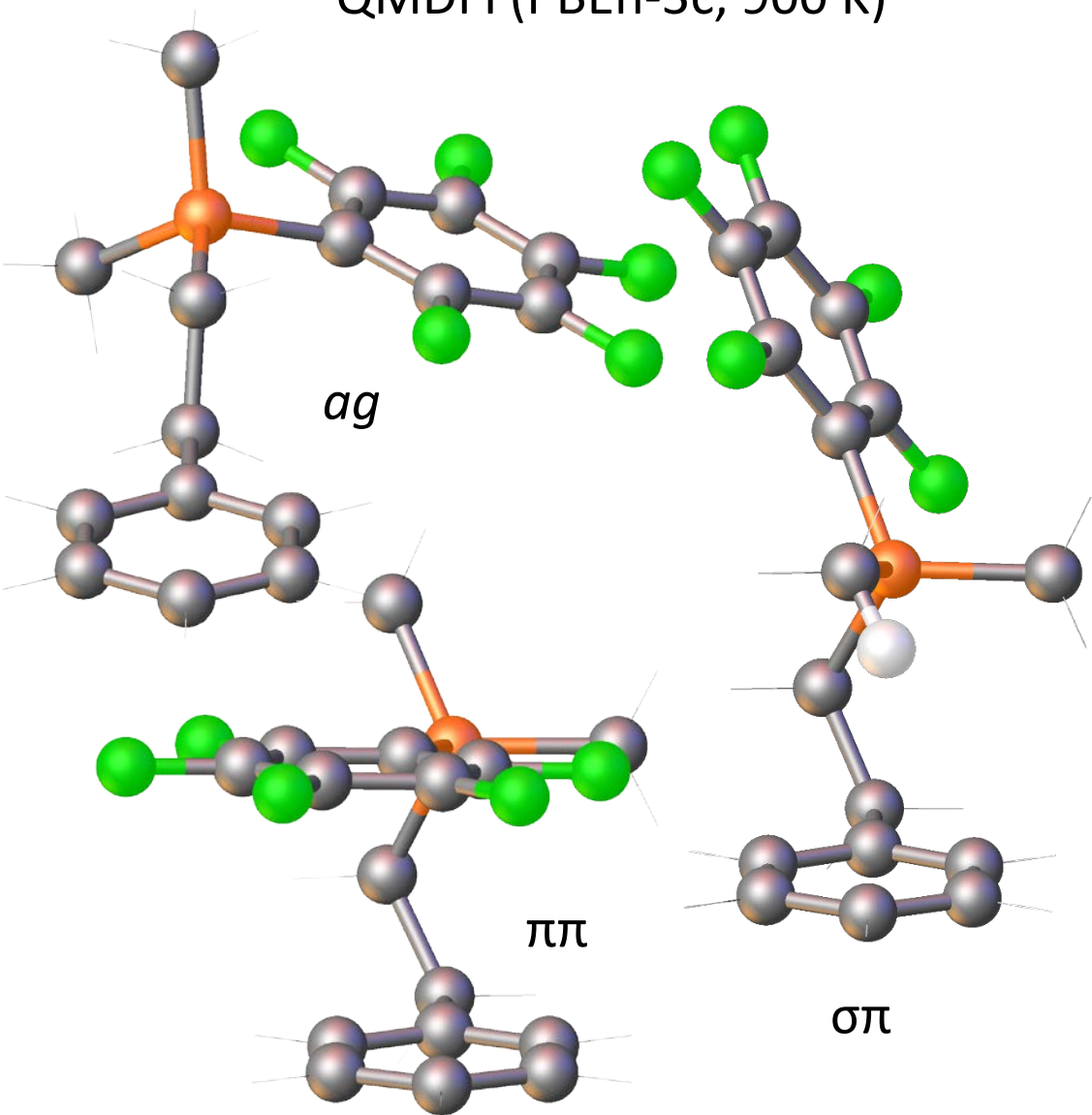
Weiter mit Teil 2





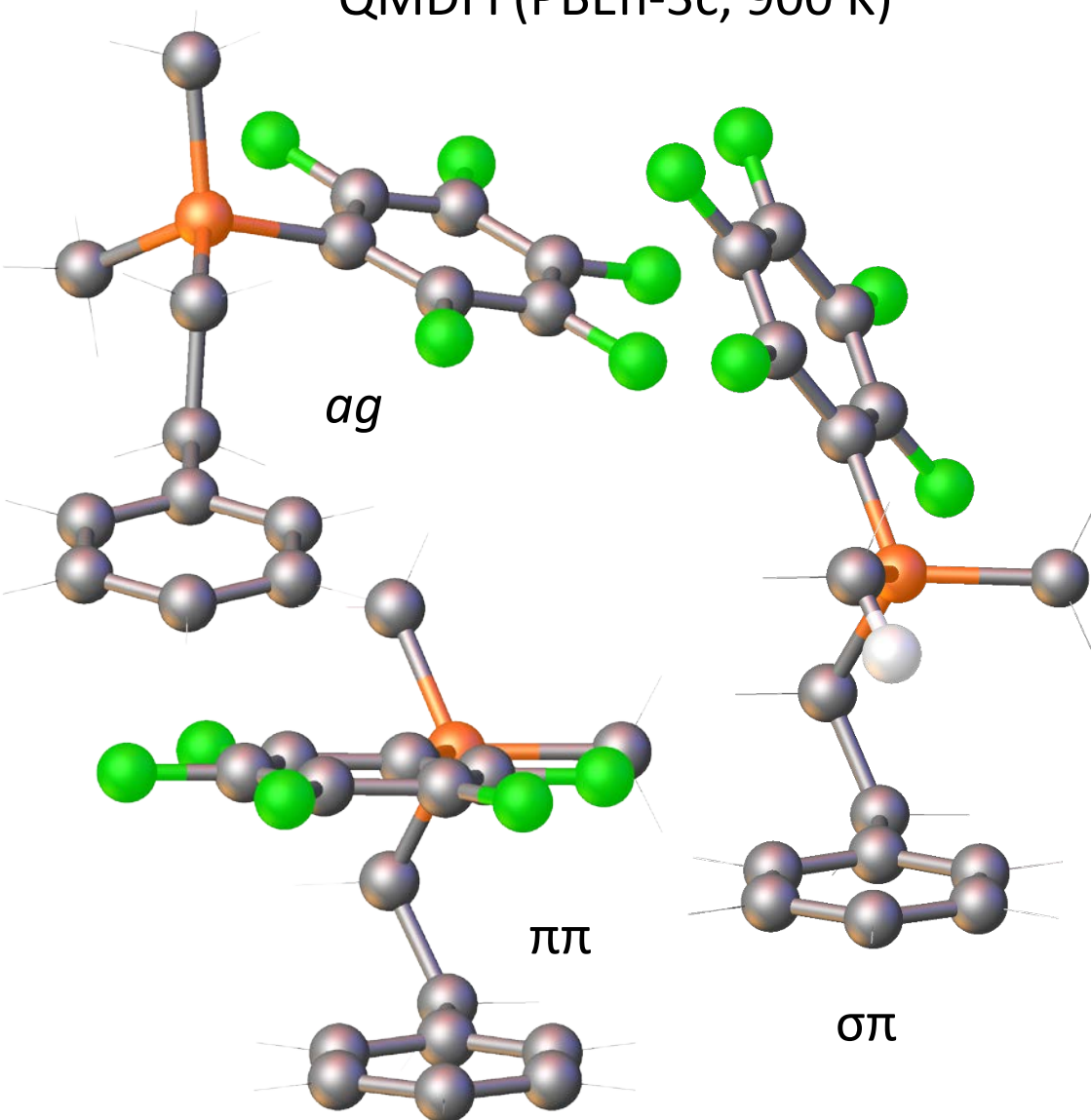
# CCSi/SiCC – QC

QMDFE(PBEh-3c, 900 K)



# CCSi/SiCC – QC

QMDFP(PBEh-3c, 900 K)



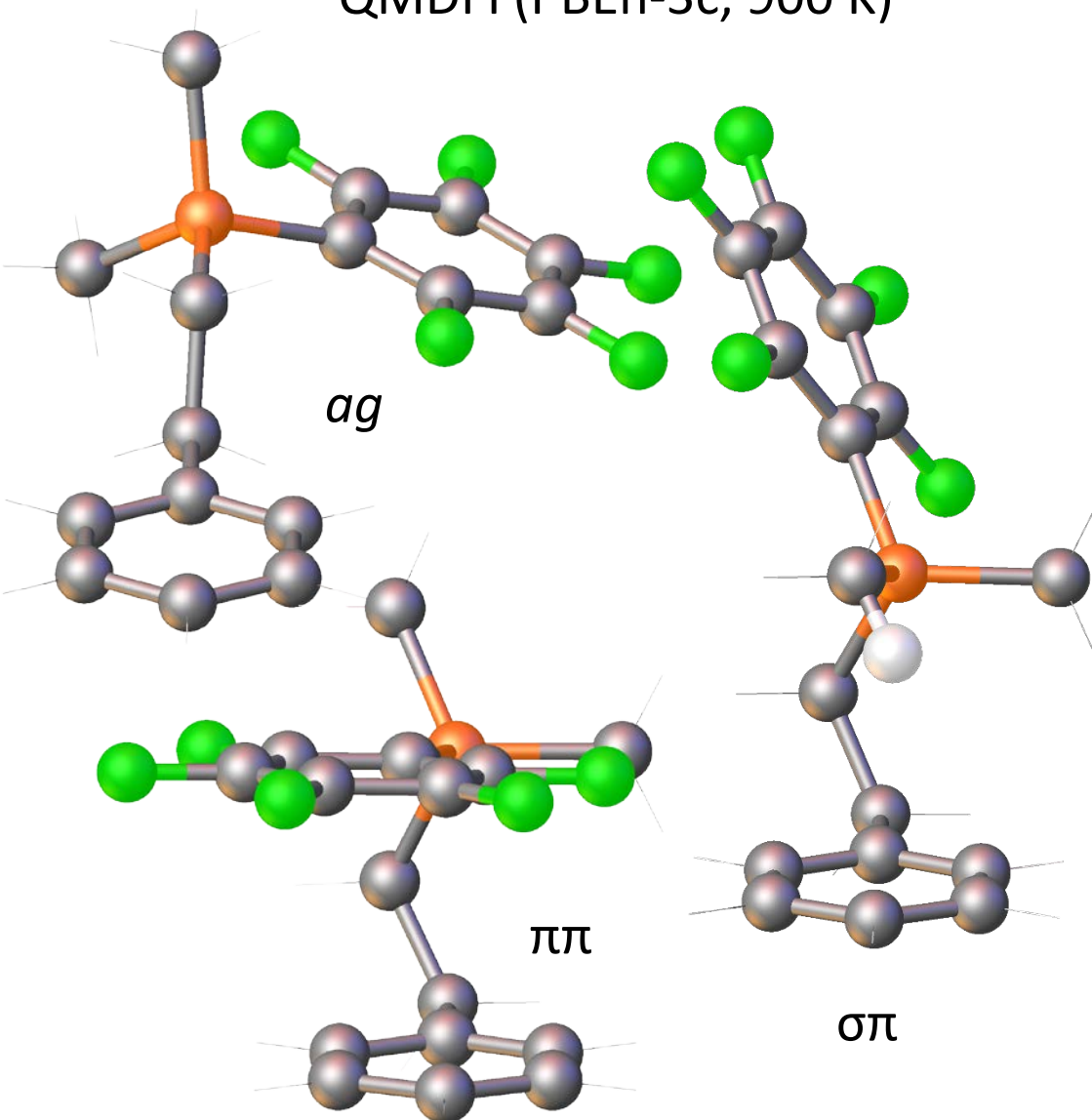
$\Delta E$ [kJ mol <sup>-1</sup> ]	
ag	17.7
σπ	13.9
ππ	0
$d_{\text{centr-centr}}$ (ππ)	3.57 Å
$d_{\text{centr-H}}$ (σπ)	2.74 Å

TPSS-D3BJ(abc)/def2-TZVP



# CCSi/SiCC – QC

QMDFE(PBEh-3c, 900 K)

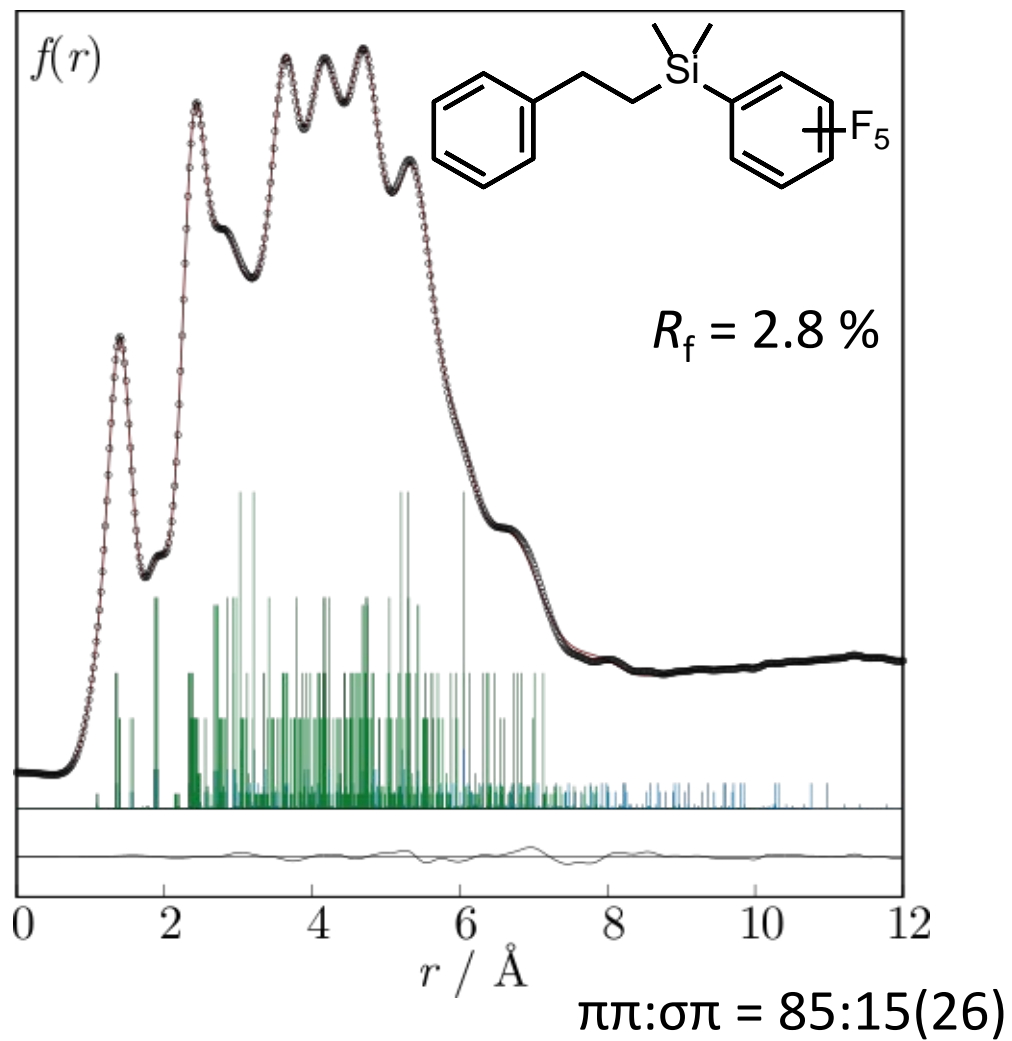


$\Delta E$ [kJ mol <sup>-1</sup> ]		
<i>ag</i>	17.7	14.3
$\sigma\pi$	13.9	16.5
$\pi\pi$	0	0
$d_{\text{centr-centr}} (\pi\pi)$	3.57 Å	3.53 Å
$d_{\text{centr-H}} (\sigma\pi)$	2.74 Å	2.84 Å

TPSS-D3BJ(abc)/def2-TZVP

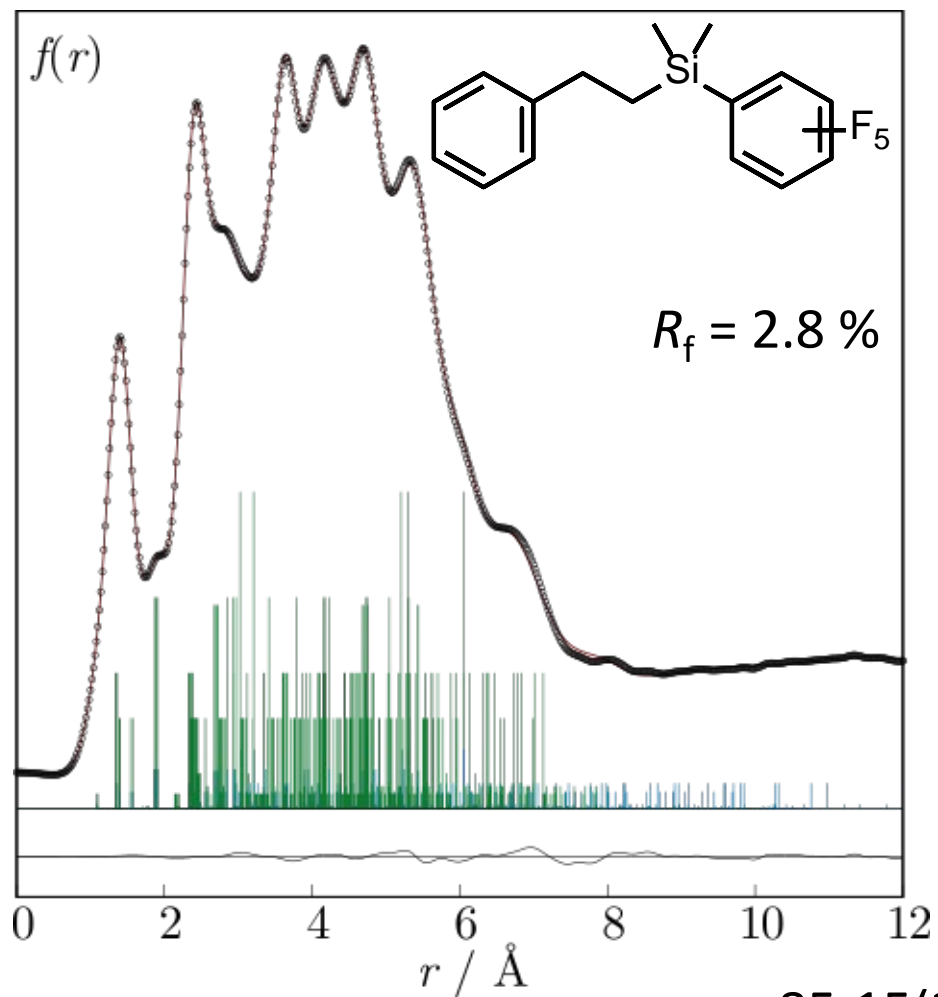


# CCSi/SiCC – GED

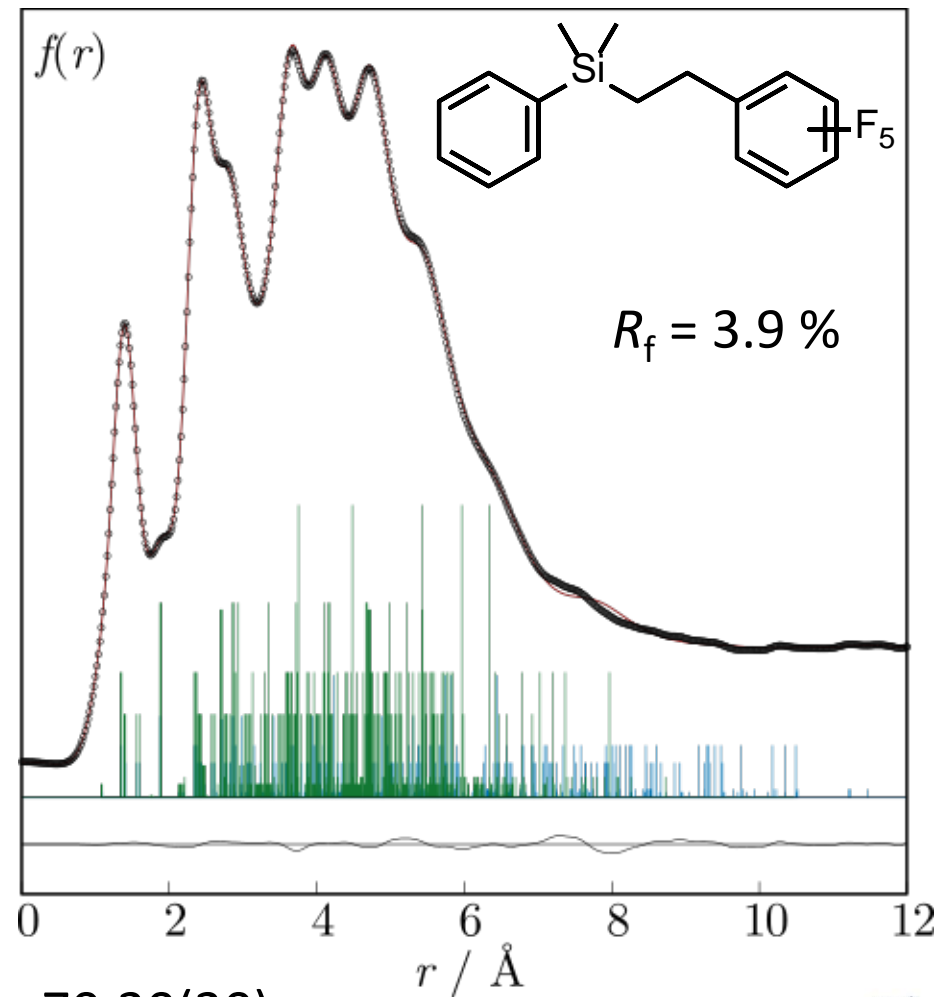




# CCSi/SiCC – GED



$\pi\pi:\sigma\pi = 85:15(26)$



$\pi\pi:\sigma\pi = 70:30(30)$



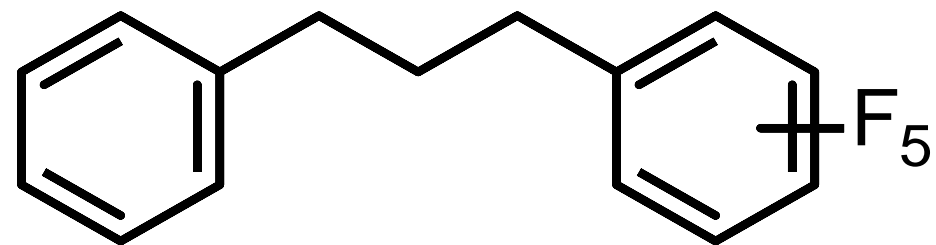
Core Facility

GED @ Bi 

Gas-Electron-Diffraction & Small Molecule Structures Centre

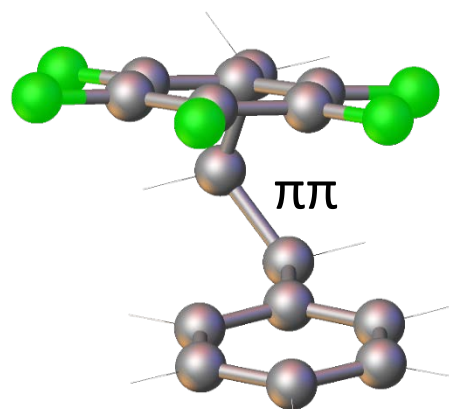
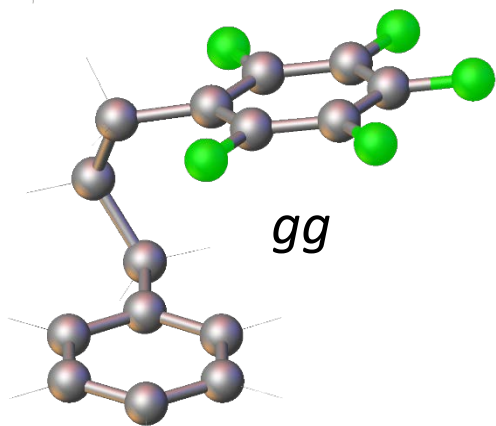
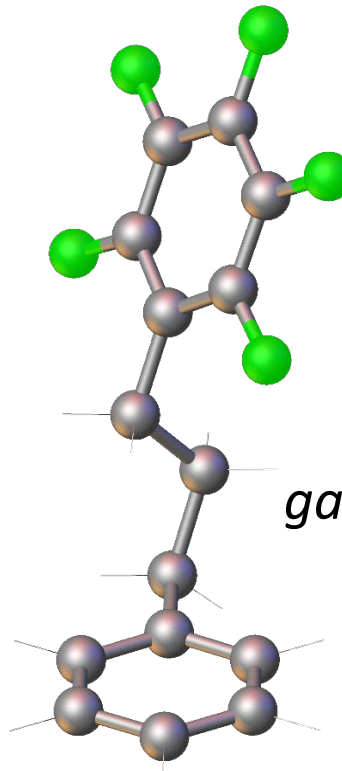
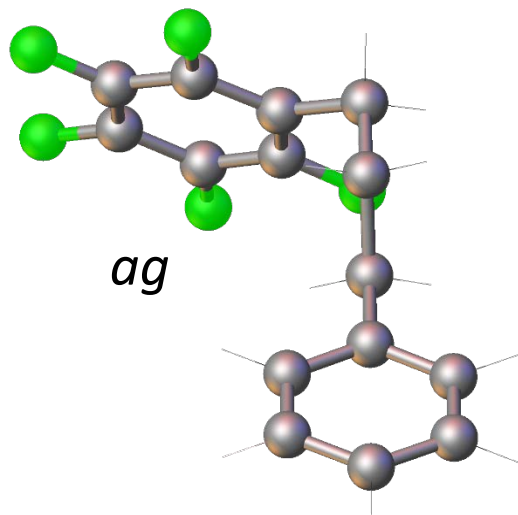
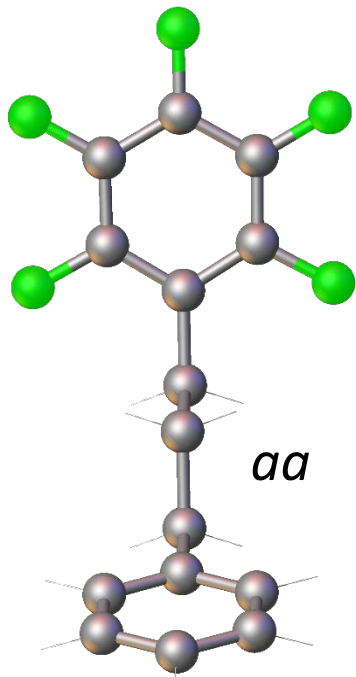


Mitzel  
Group  
inorganic & structural  
chemistry



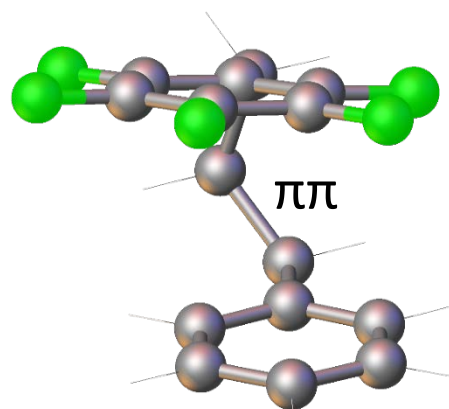
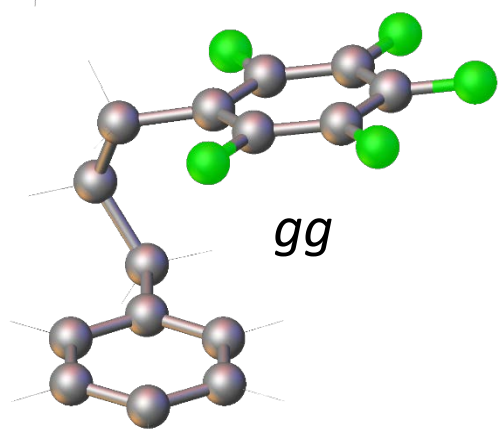
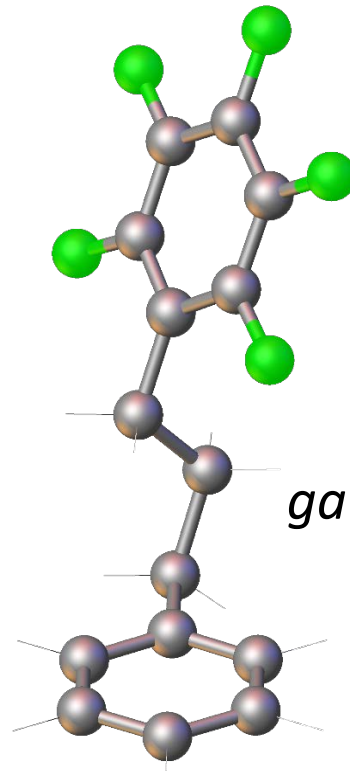
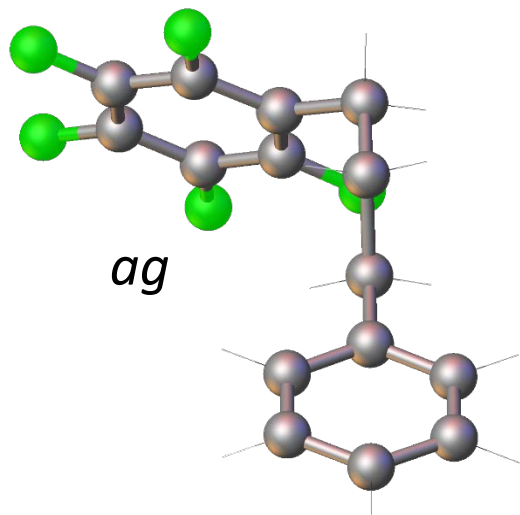
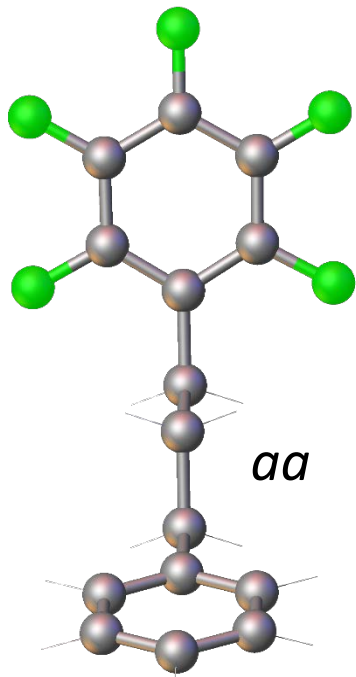
# CCC – QC

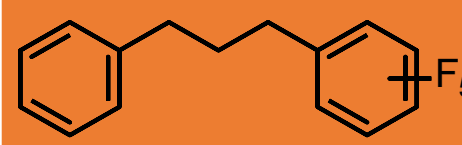
QMDF (PBEh-3c, 900 K)



# CCC – QC

QMDFFF(PBEh-3c, 900 K)

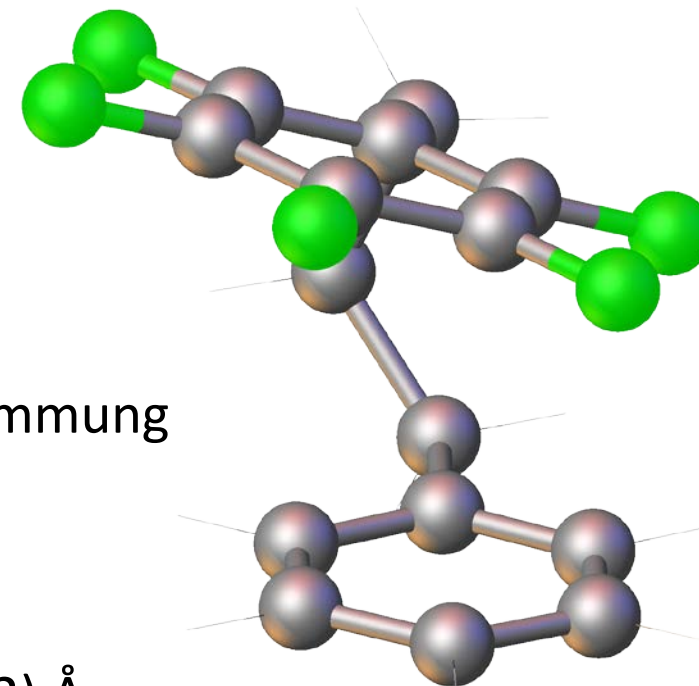
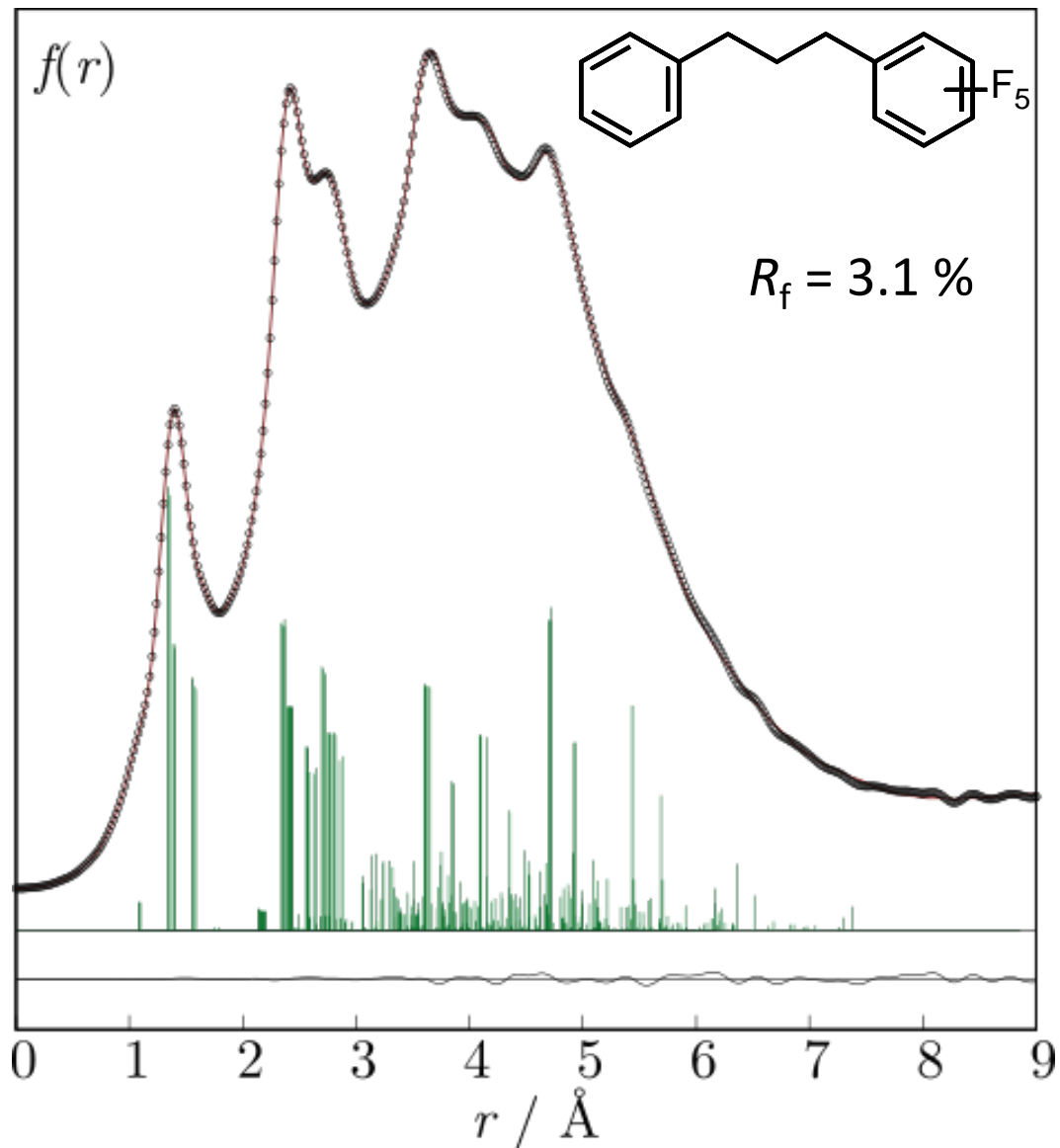


$\Delta E$ [kJ mol <sup>-1</sup> ]	
<i>aa</i>	10.7
<i>ag</i>	10.1
<i>ga</i>	10.1
<i>gg</i>	9.4
$\pi\pi$	0
$d_{\text{centr-centr}} (\pi\pi)$	3.57 Å

TPSS-D3BJ(abc)/def2-TZVP



# CCC – GED



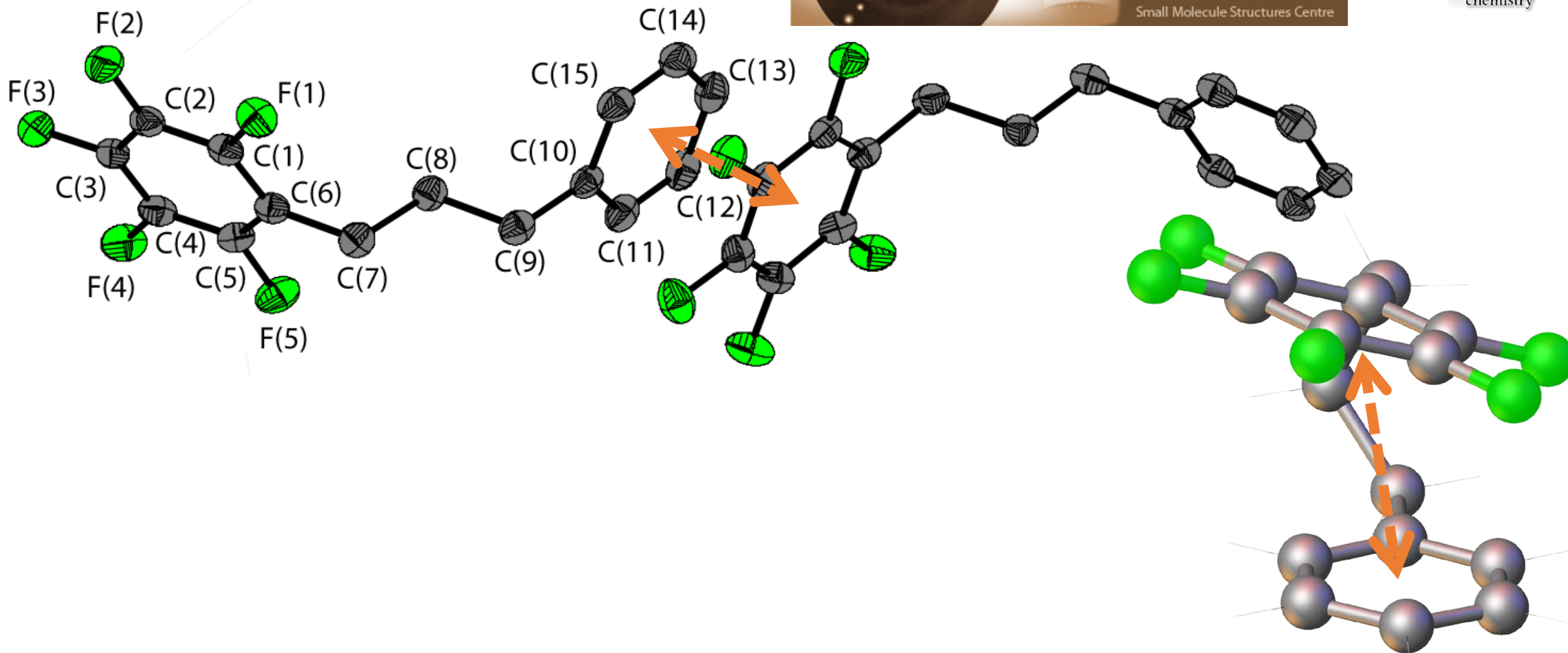
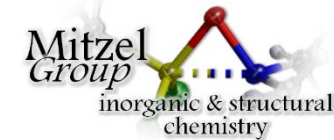
beste Übereinstimmung  
Exp.  $\leftrightarrow$  Theor.:  
100 %  $\pi\pi$

$$d_{\text{centr-centr}} = 3.47(2) \text{ \AA}$$

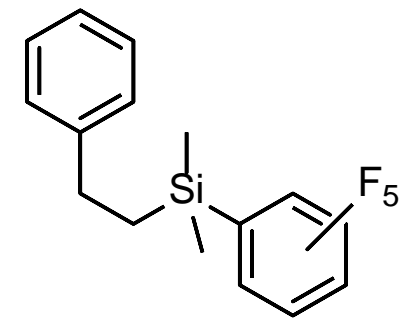
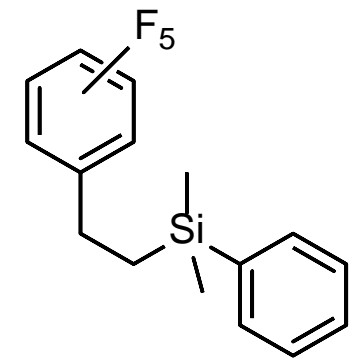
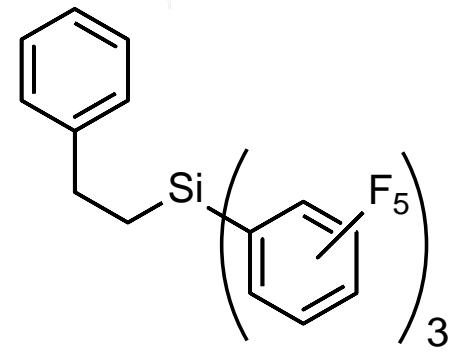
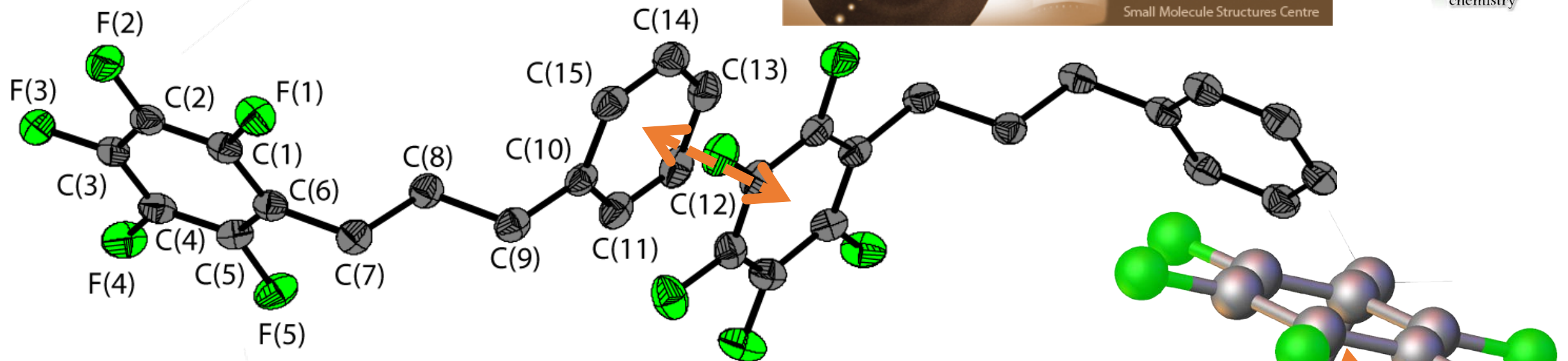
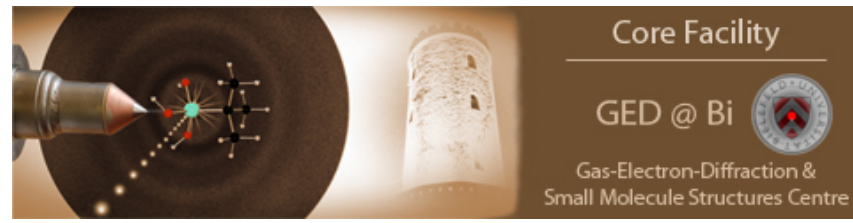
$C_6$ -Ebenen  $17(6)^\circ$  verkippt



# Zusammenfassung



# Zusammenfassung



Synthese 😊  
 XRD 😊  
 GED...?

