Supporting Information

Optimised Synthesis of Monoanionic Bis(NHC)-Pincer Ligand Precursors and their Li-Complexes

Eva Jürgens[a], Kai N. Buys[b], Anna-Theresa Schmidt[a], Samantha K. Furfari[b], Marcus L. Cole[b*], Michael Moser[c], Frank Rominger[c], Doris Kunz[a,c*]

[a] Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

[b] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia.

[c] Organisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Im Neuenheimer Feld 250, D-69120 Heidelberg, Germany

Content:

1. General information S. 2
2. NMR-spectra of the bis(imidazolium) salts **5b-i** S. 3
3. Concentration and residual water dependency of the NH and 2'-CH chemical shifts S. 13
4. NMR-spectra of the Li(bimca) complexes **6** S. 15
5. Crystallographic data S. 23

(1) General information:

All reagents were purchased from Sigma-Aldrich, abcr or Fluka and used without further purification. Degassed tetrahydrofuran, *n*-hexane and *n*-pentane were purchased from Sigma-Aldrich and dried using the solvent purification system SPS-800 (MBraun). Deuterated THF-d_8 was purchased from Deutero, refluxed over sodium, distilled, and degassed. DMSO-d_6 was degassed and dried using several batches of molecular sieves (3 Å) and stored over molecular sieves (3 Å).

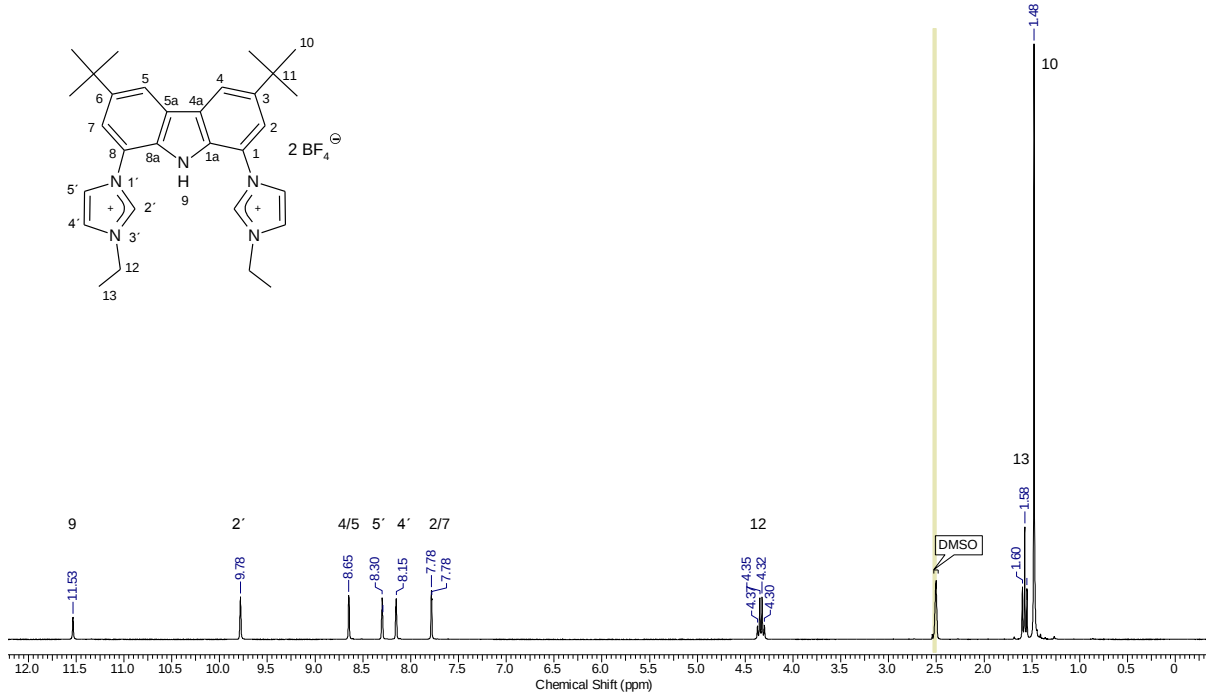
The synthesis of the lithium compounds was carried out under an argon atmosphere in dried and degassed solvents using Schlenk technique or a glove box. The imidazolium salt **5a** was synthesized according to the literature procedure.[1] ^{1}H, ^{13}C, 2D NMR experiments were recorded using a Bruker ARX 250 and AVANCE II +400 spectrometer. All chemical shifts are reported in ppm and calibrated to TMS on the basis of the residual proton signal as an internal standard. ^{7}Li chemical shifts are reported in ppm and calibrated to a 9.7 M LiCl solution in D_2O as external standard. The assignment of peaks was made using 2D NMR correlation spectra. IR spectra were recorded on a Bruker Vertex70 instrument. Mass spectra were recorded on a Thermo Finnigan TSQ 70.

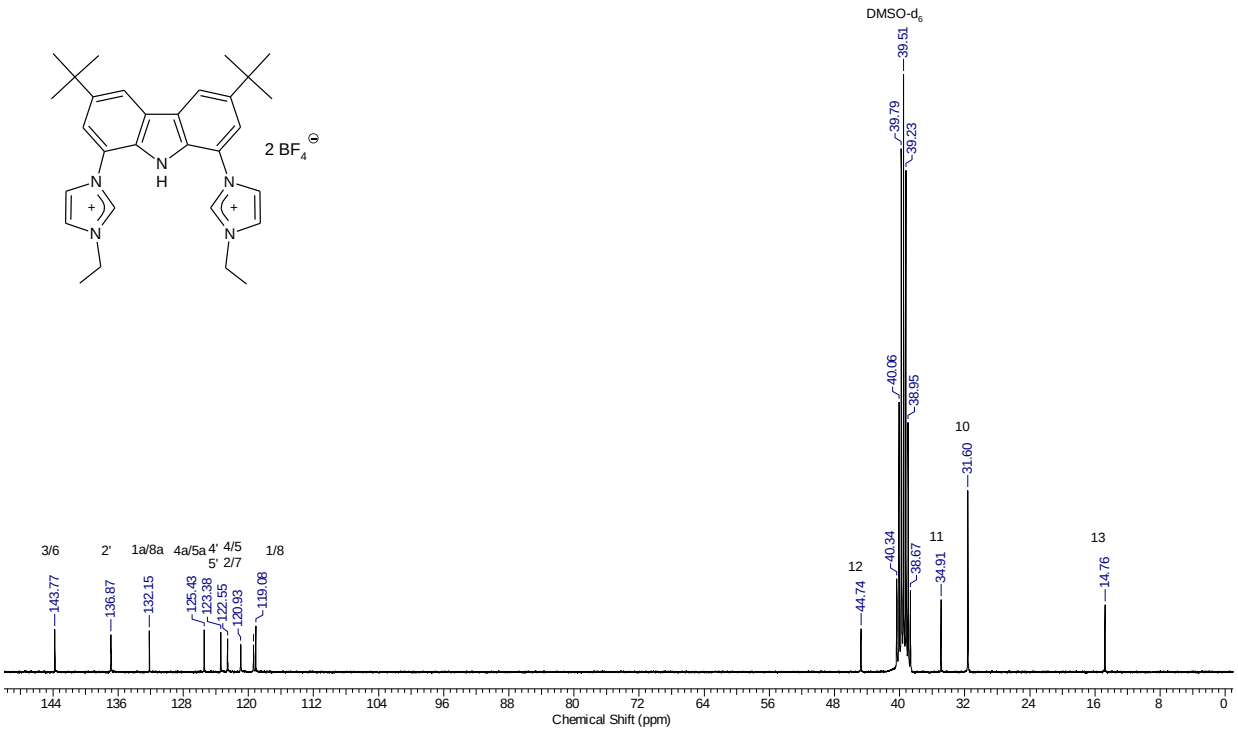
[1] M. Moser, B. Wucher, F. Rominger, D. Kunz, *Organometallics*, 2007, **26**, 1024–1030.

(2) ^{1}H- and ^{13}C-NMR spectra of the bis(imidazolium) salts 5b-5i

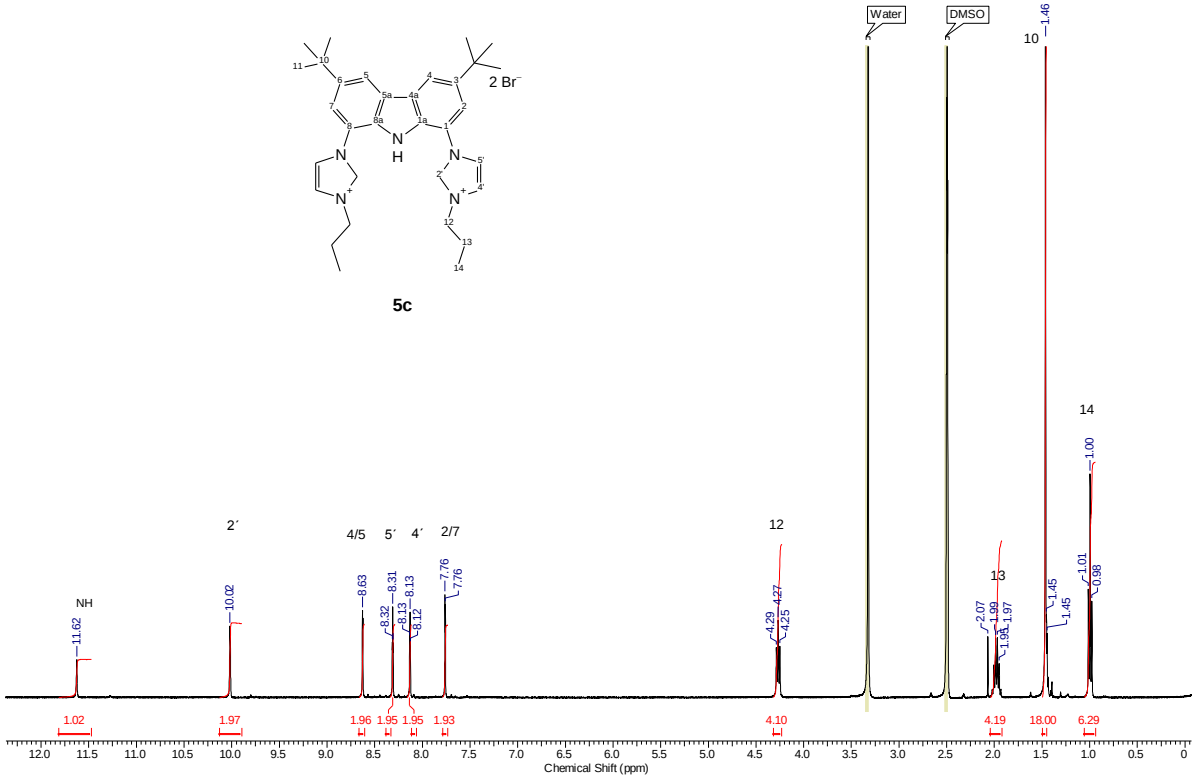
All NMR-spectra were recorded at ambient temperature in DMSO-d_6 as solvent.

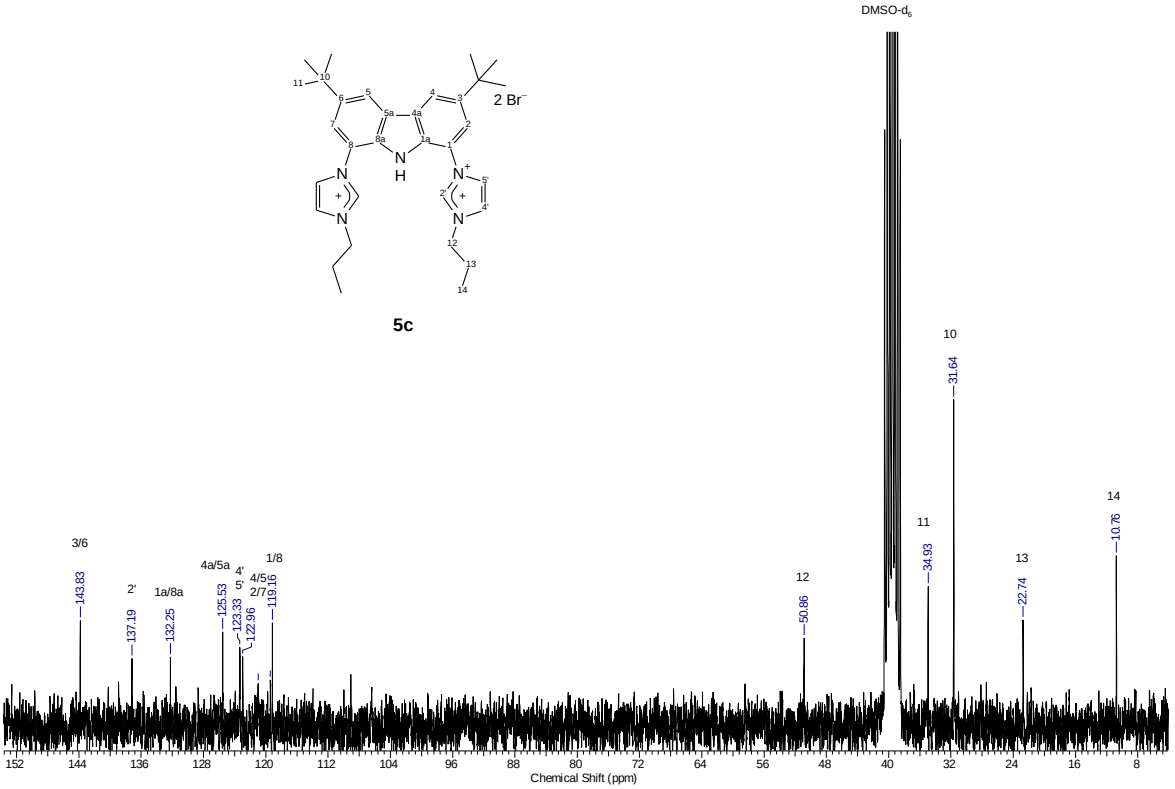
H(bimca^{Et})2HBF$_4$ (**5b**)



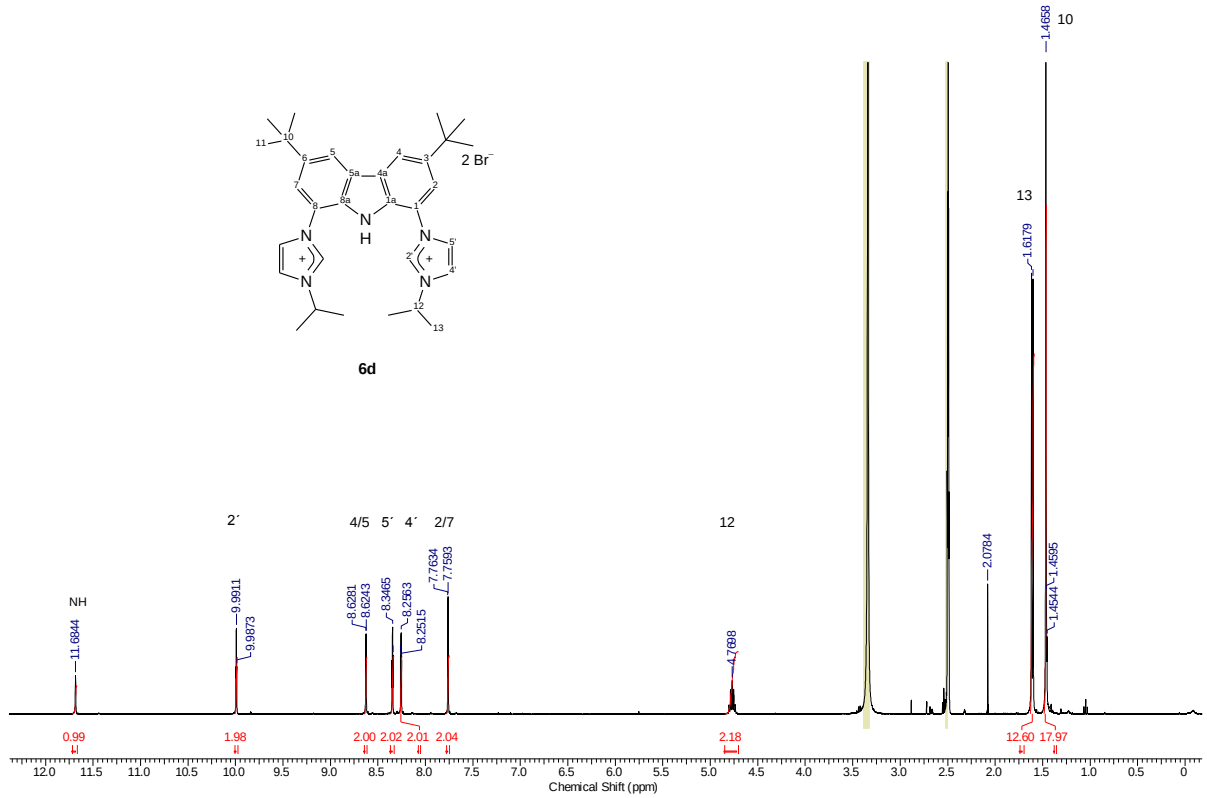


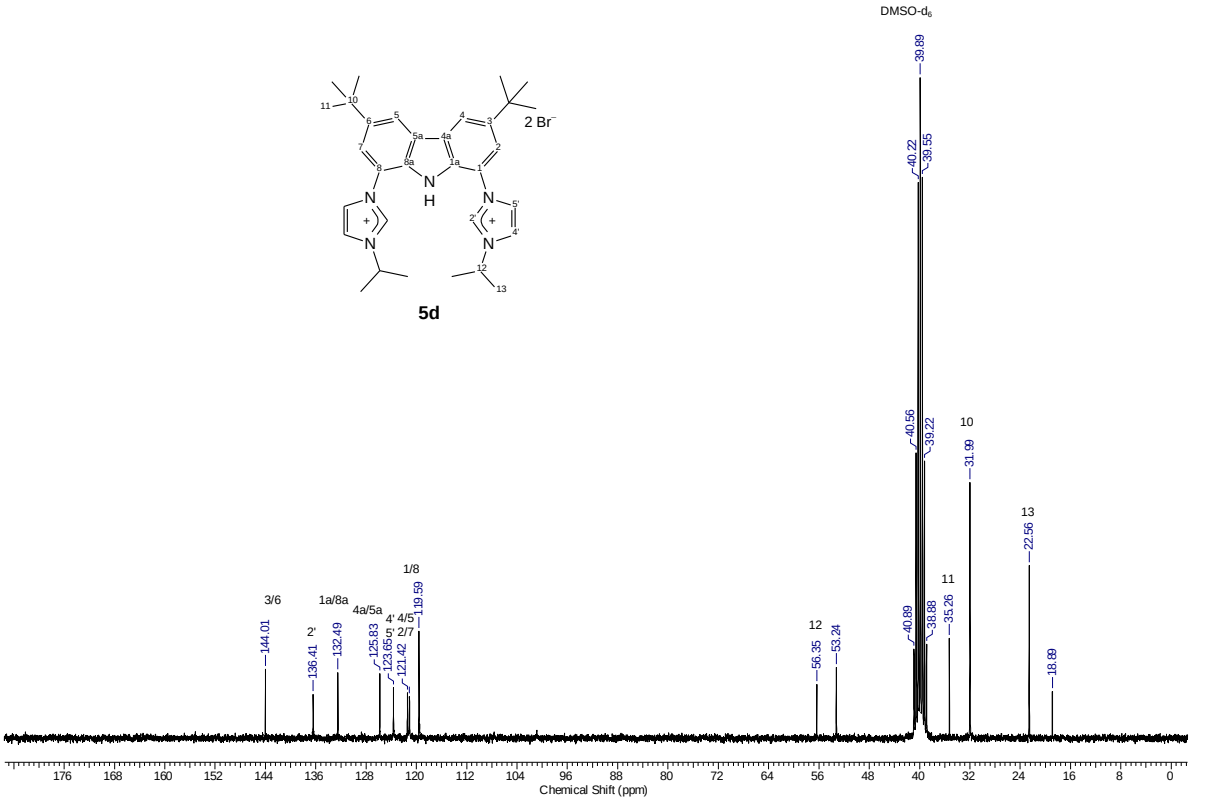
H(bimca^{nPr})2HBr (**5c**)



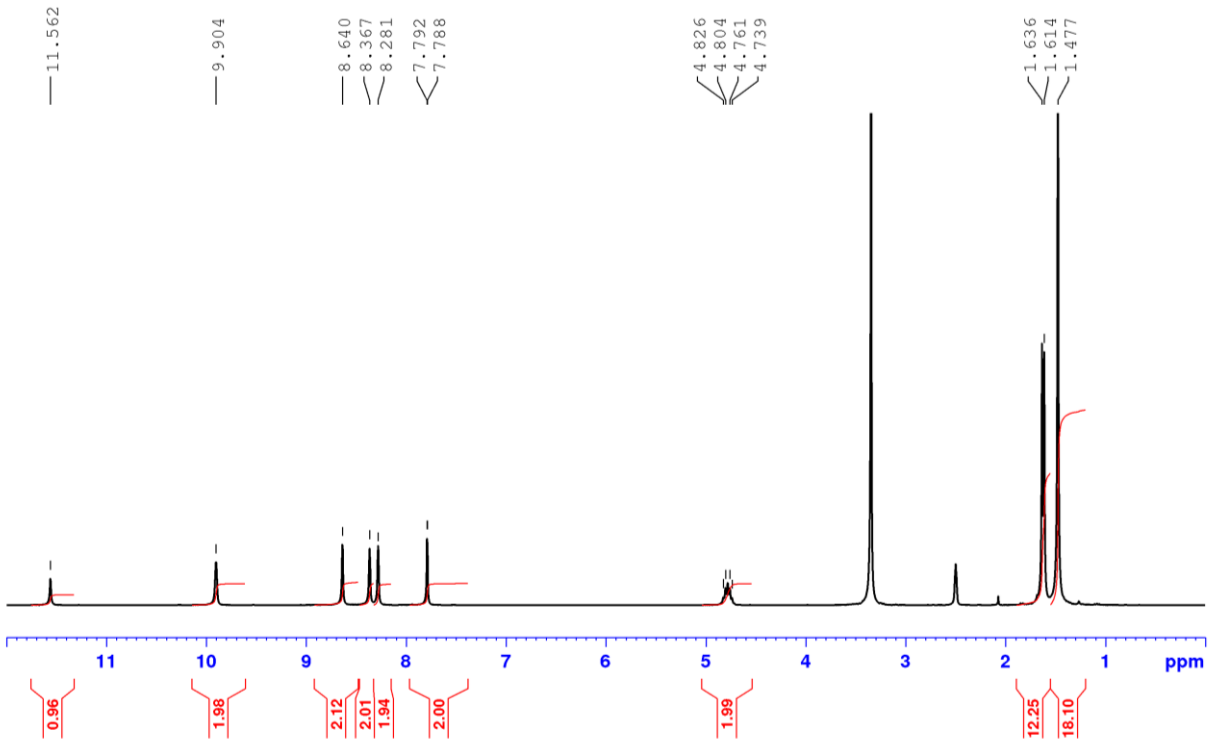


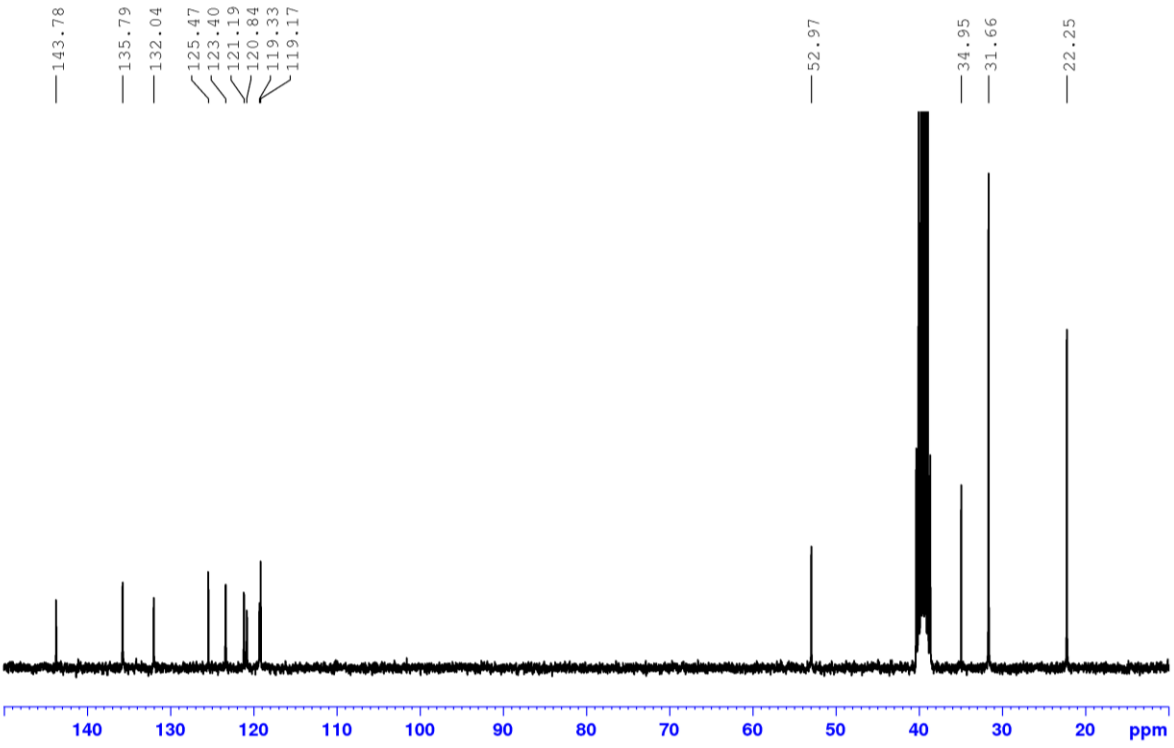
H(bimca^{iPr})2HBr (**5d**)



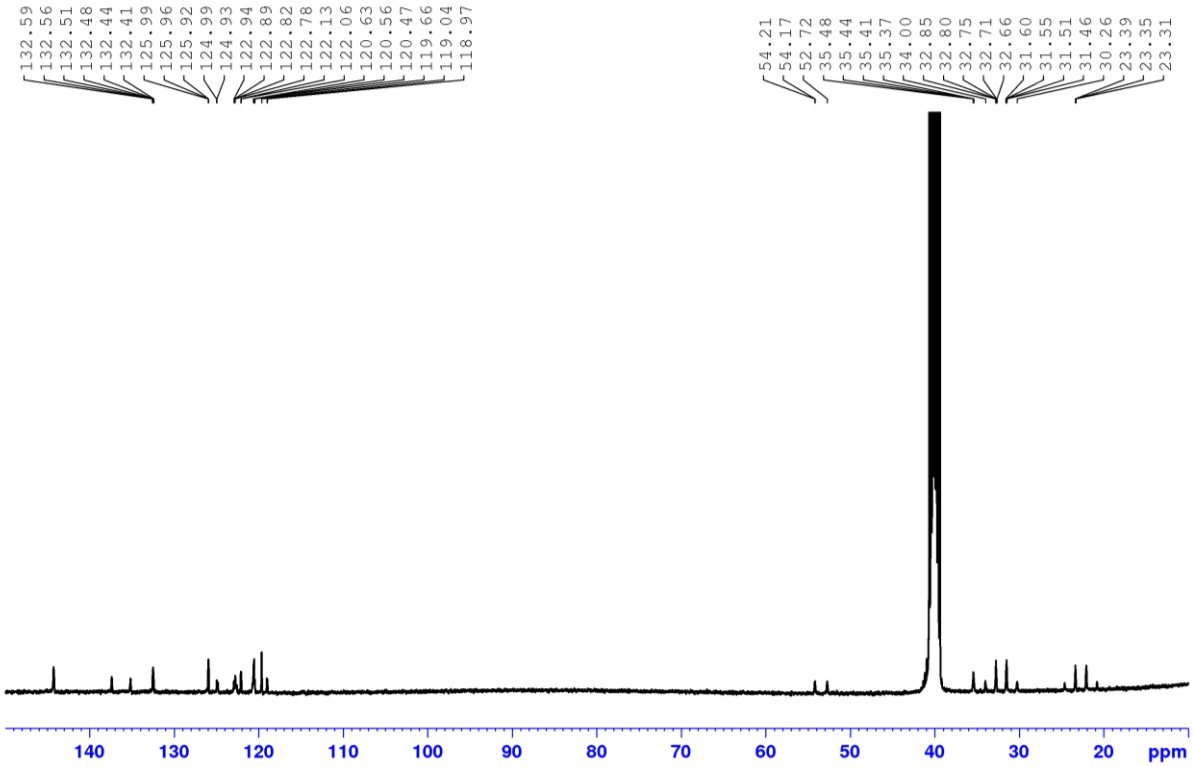


H(bimca^{iPr})2HI (**5d'**)

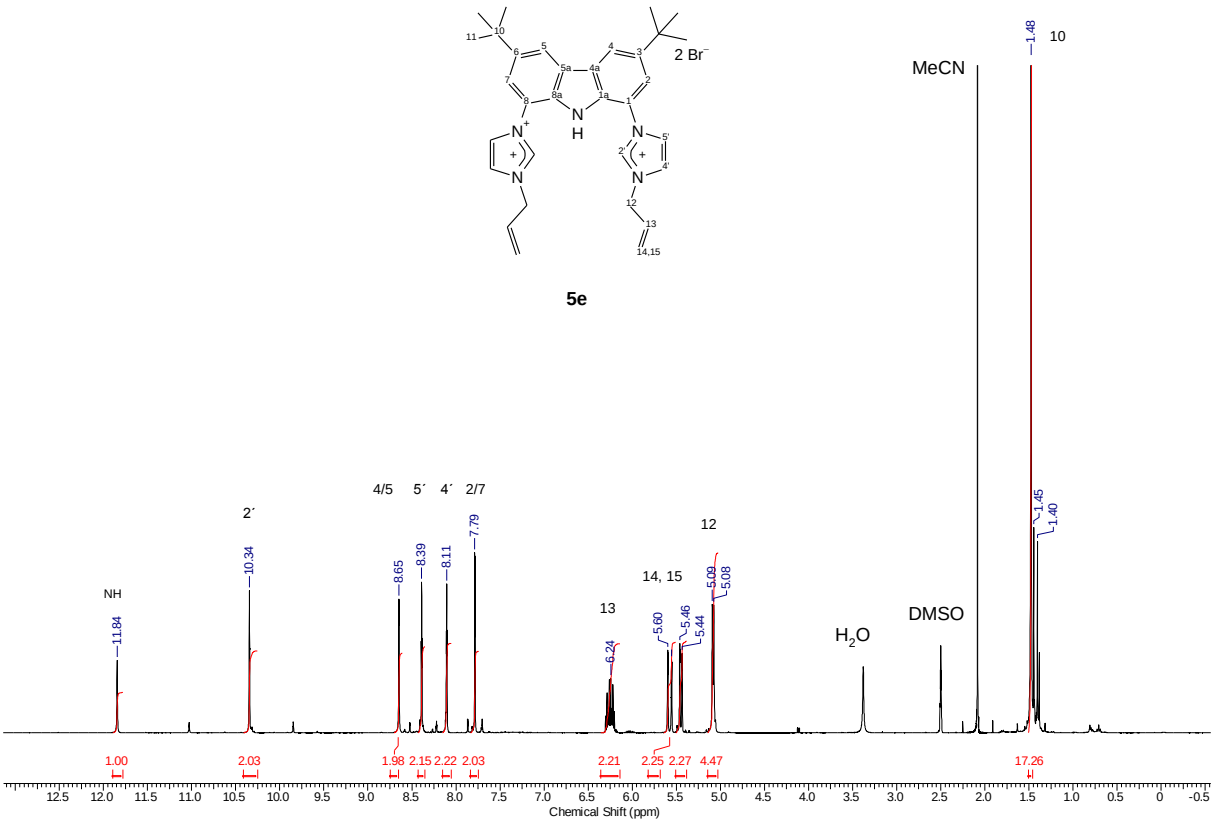


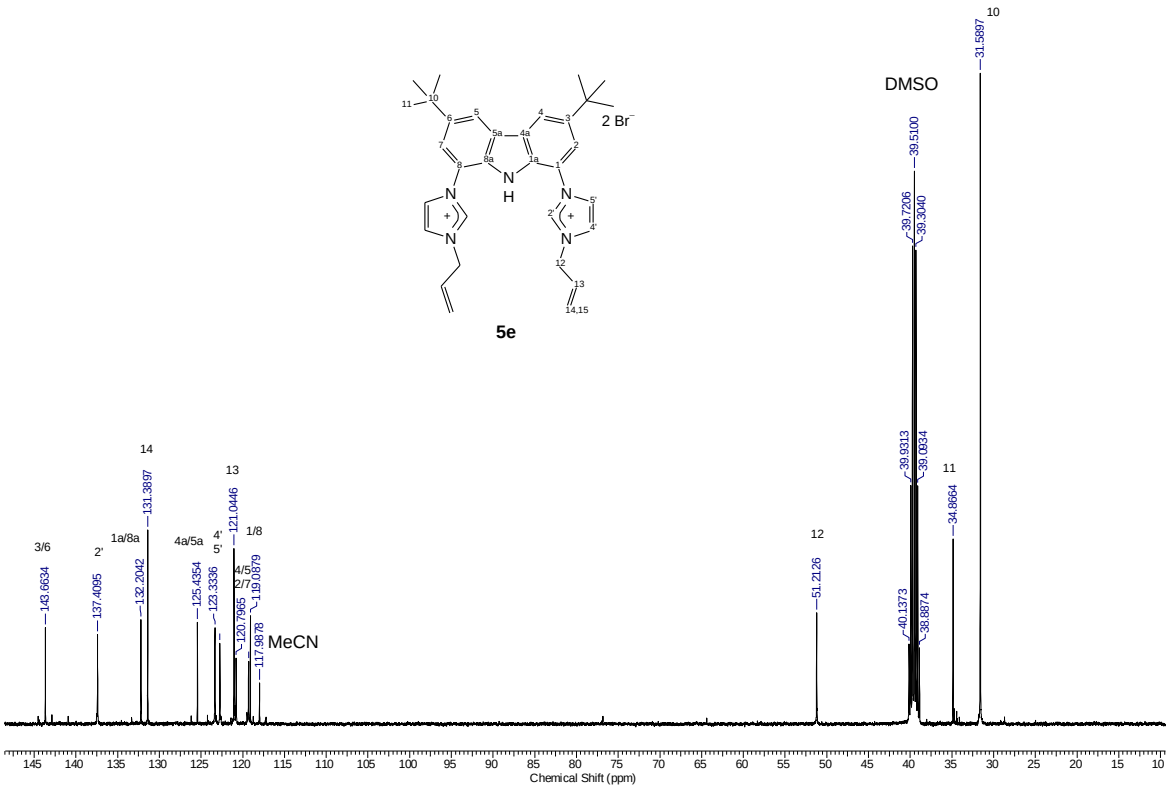


H(bimca^{iPr})2HI (**5d'**) ^{13}C NMR (^{1}H coupled)

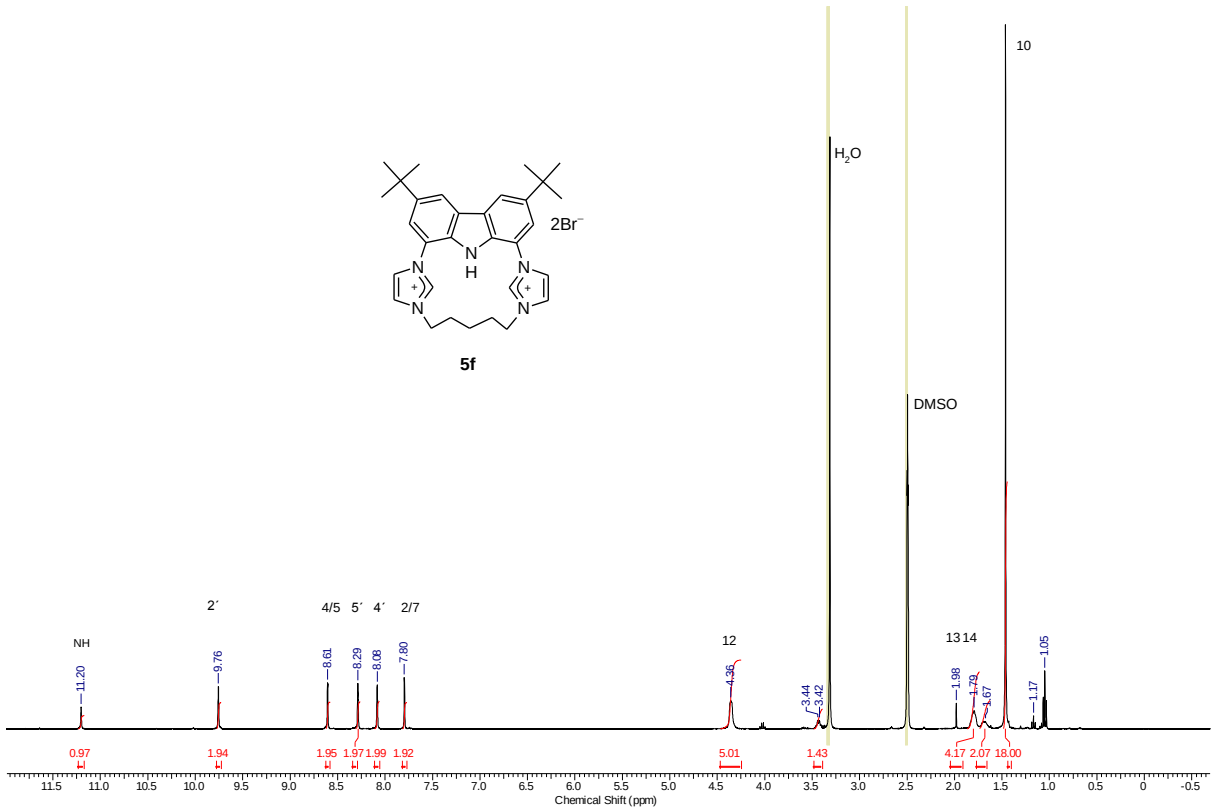


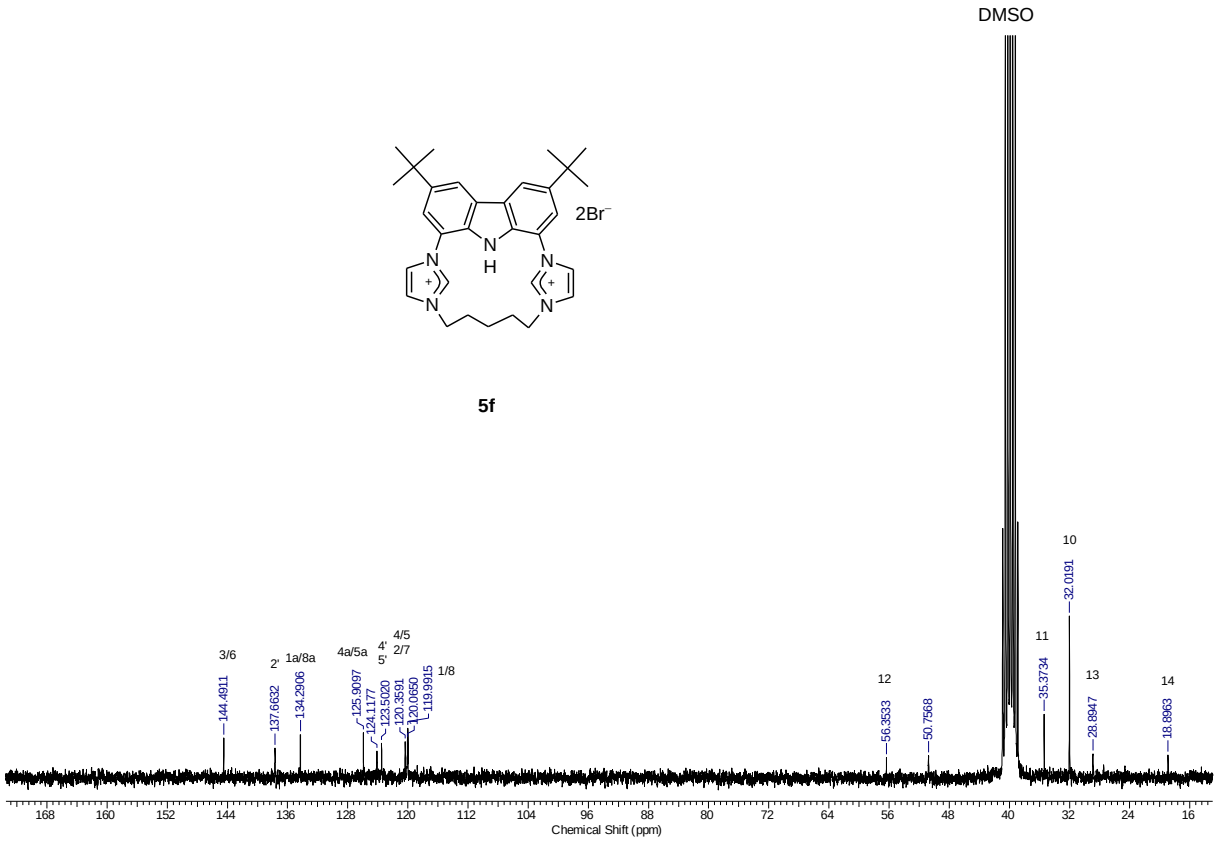
H(bimca^{Allyl})2HBr (**5e**)



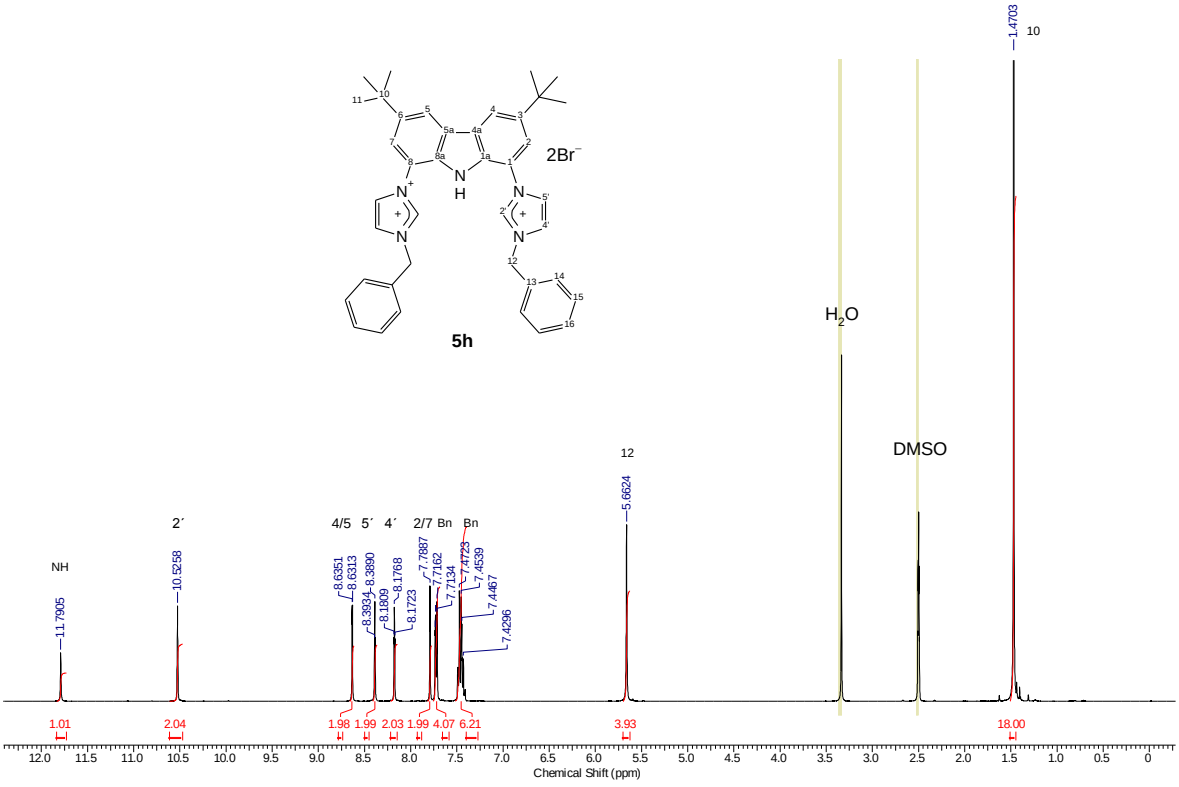


H(bimca^{C5})2HBr (**5f**)

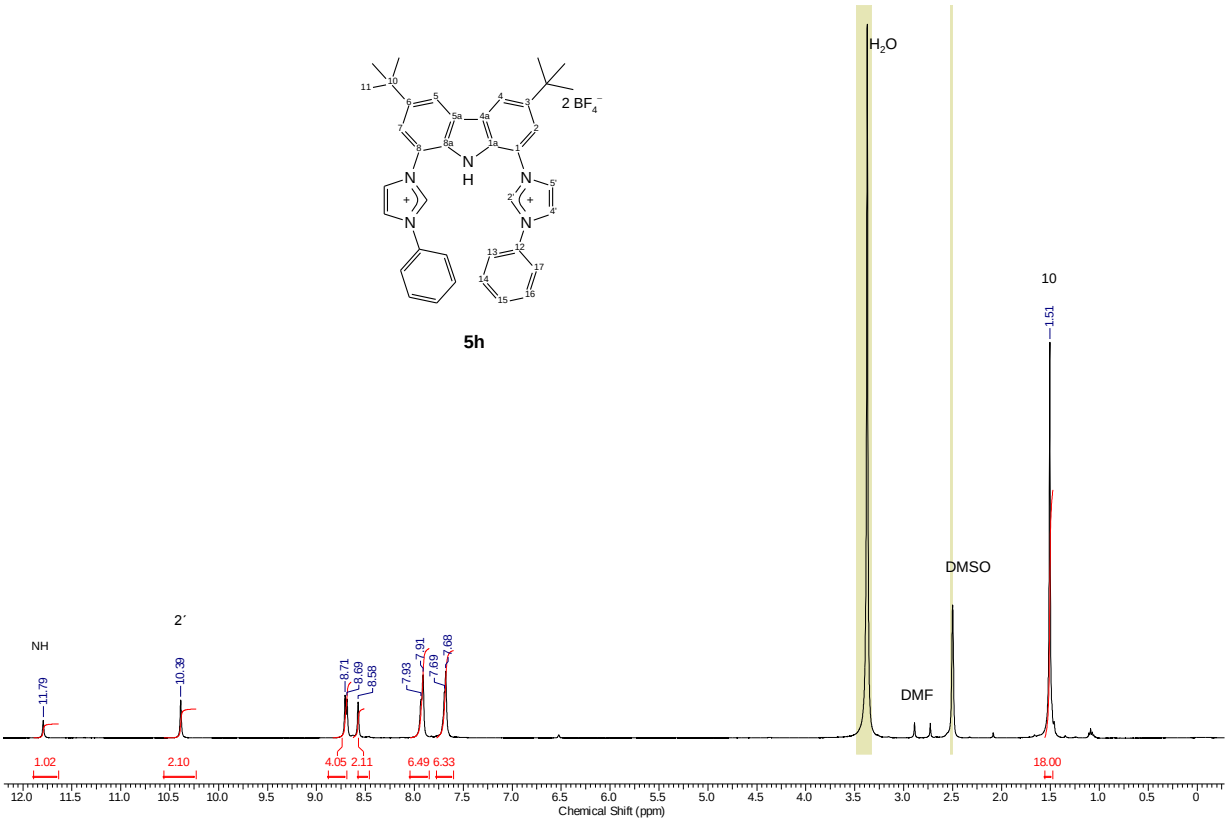


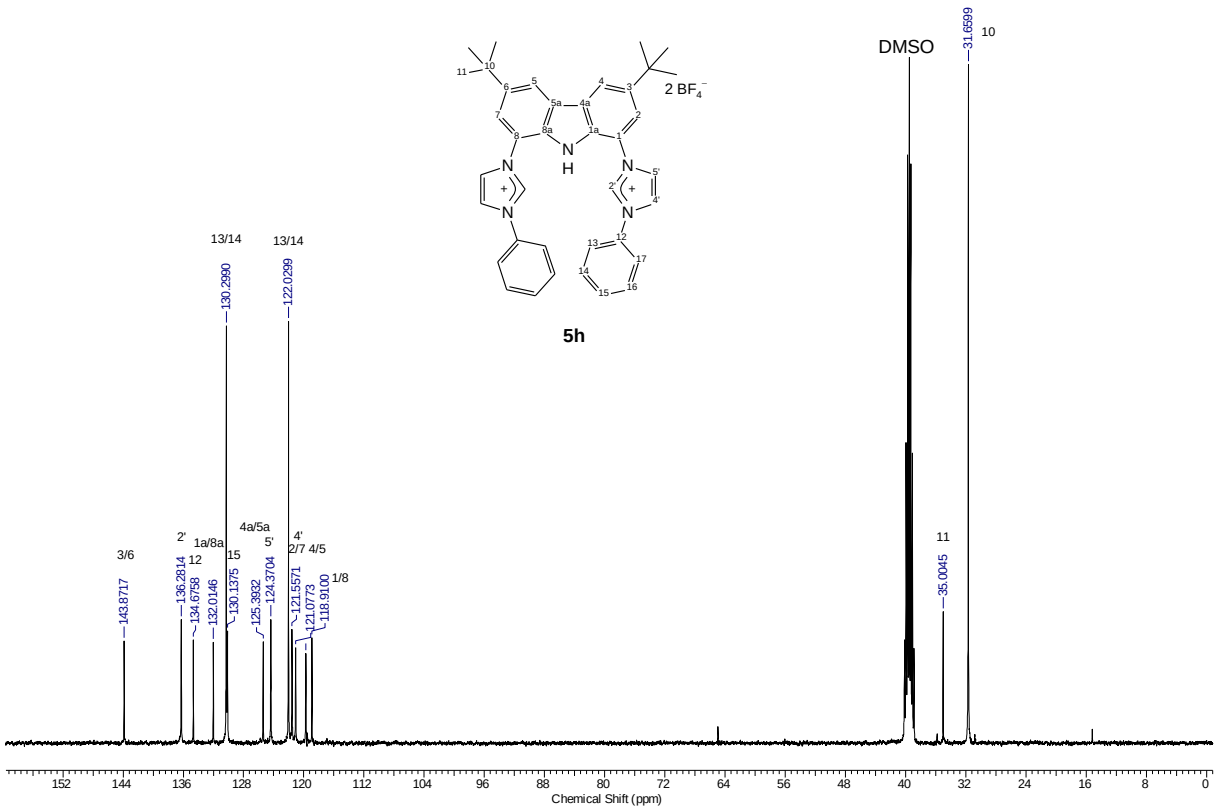


H(bimca^{Benzyl})2HBr (**5g**)

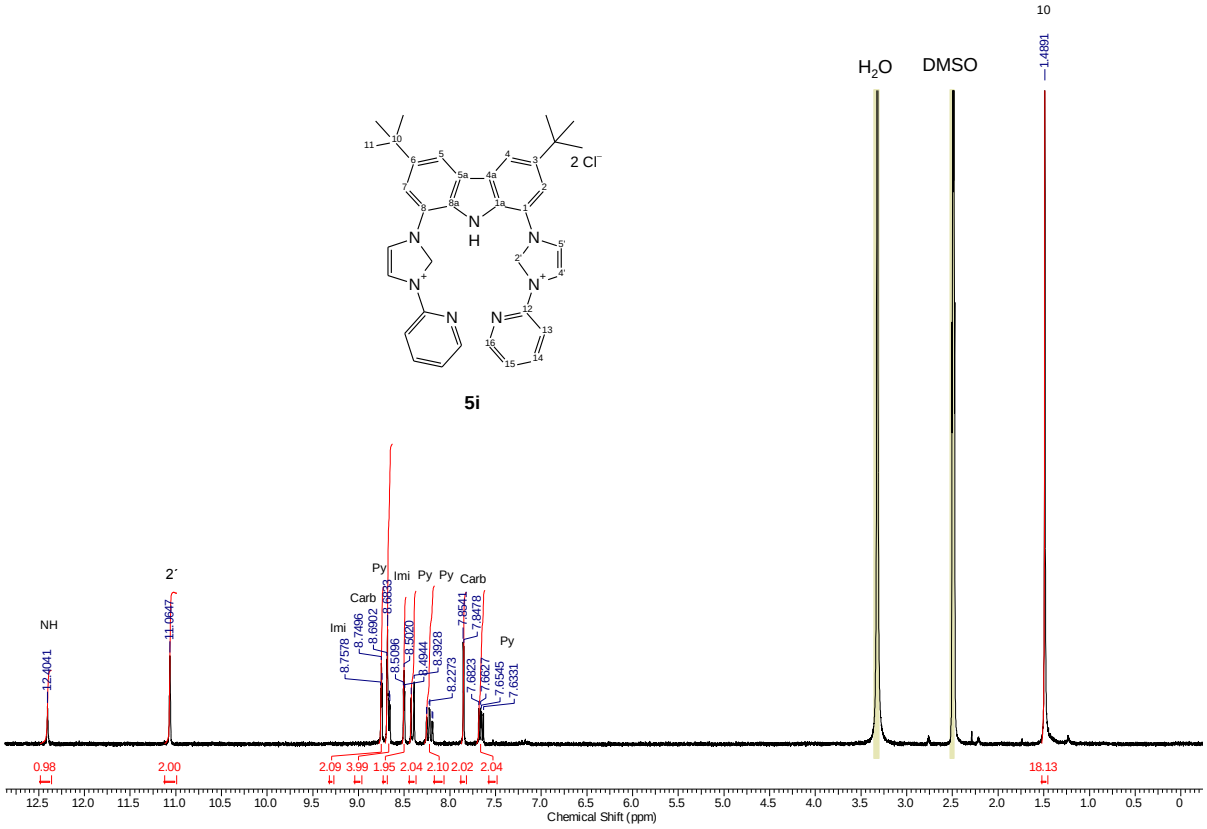


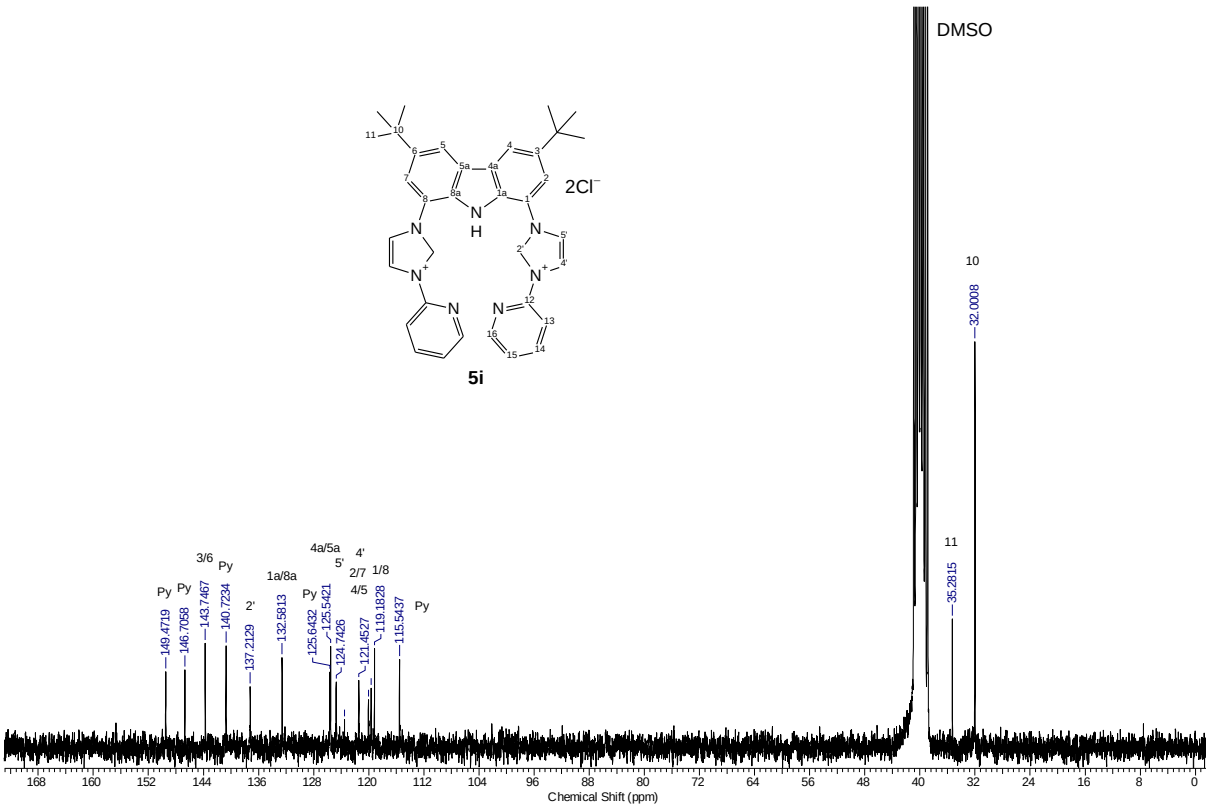
H(bimca^{Phenyl})2HBF$_4$ (**5h**)





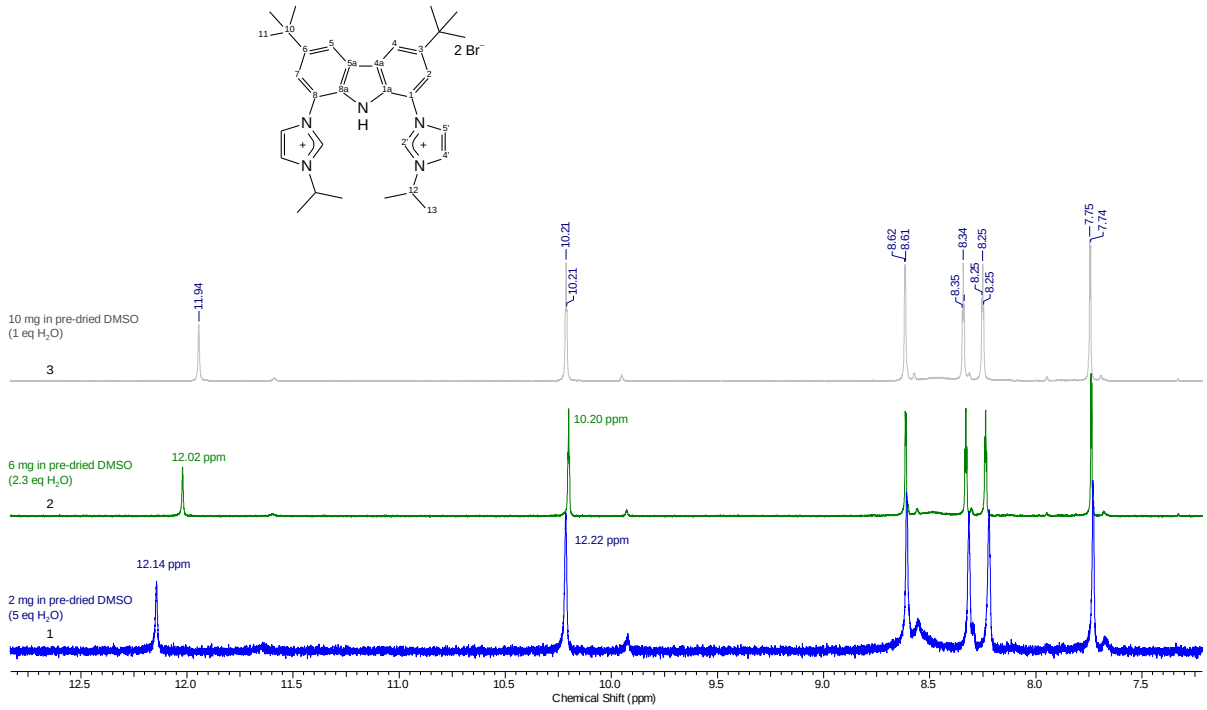
H(bimca^{Pyridyl})2HCl (**5i**)



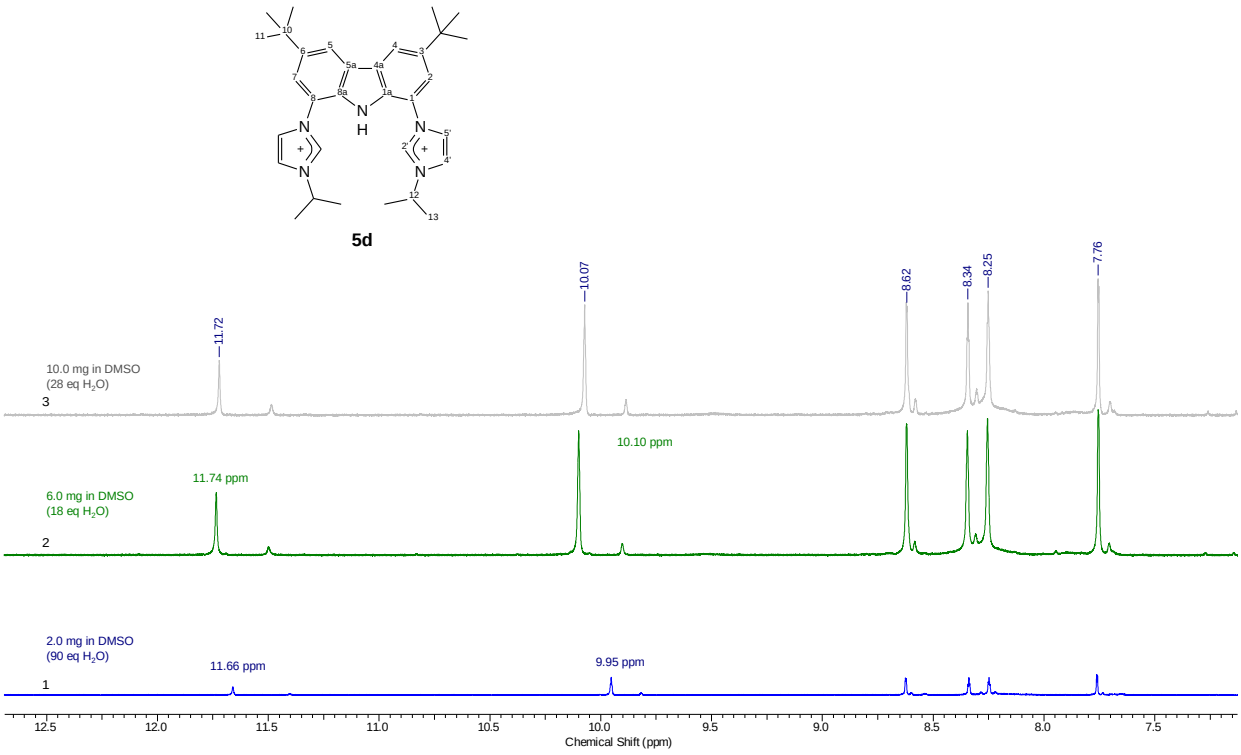


(3) Concentration and residual water dependency of the NH and 2'-CH chemical shifts.

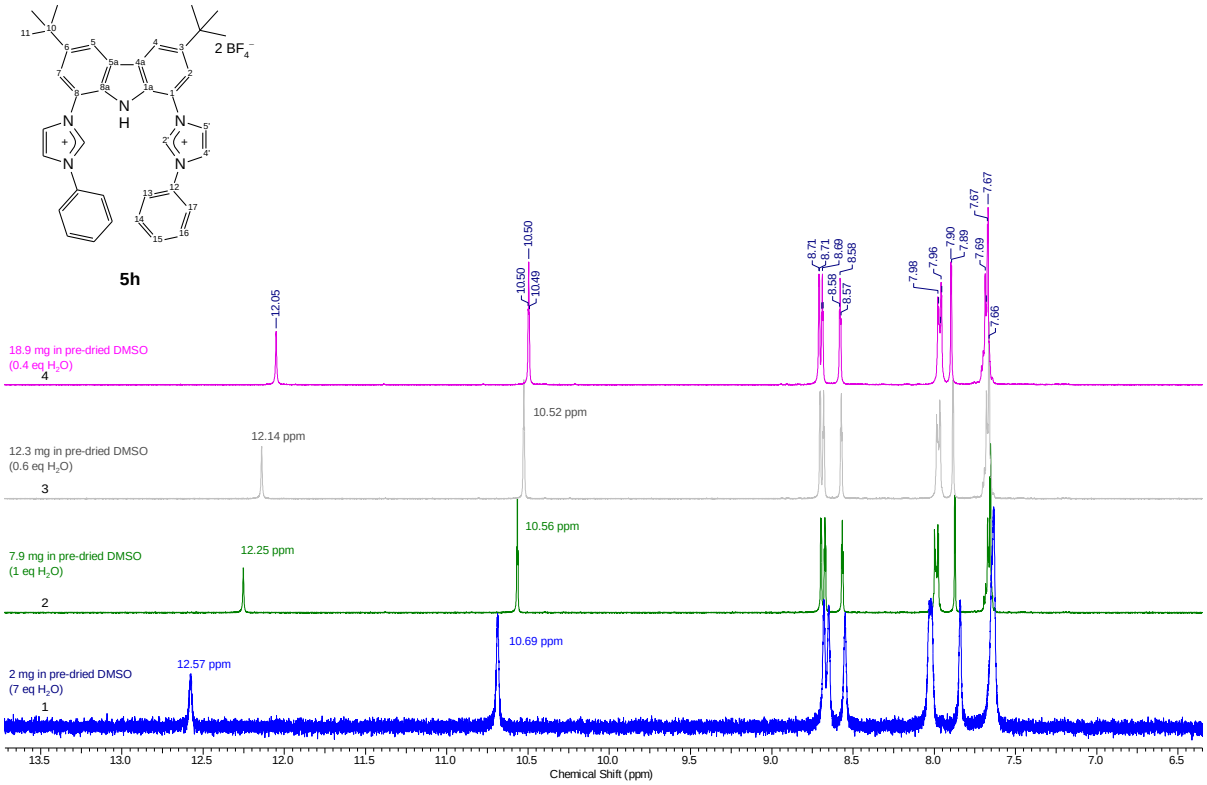
Concentration dependence of **5d** in pre-dried DMSO-d_6



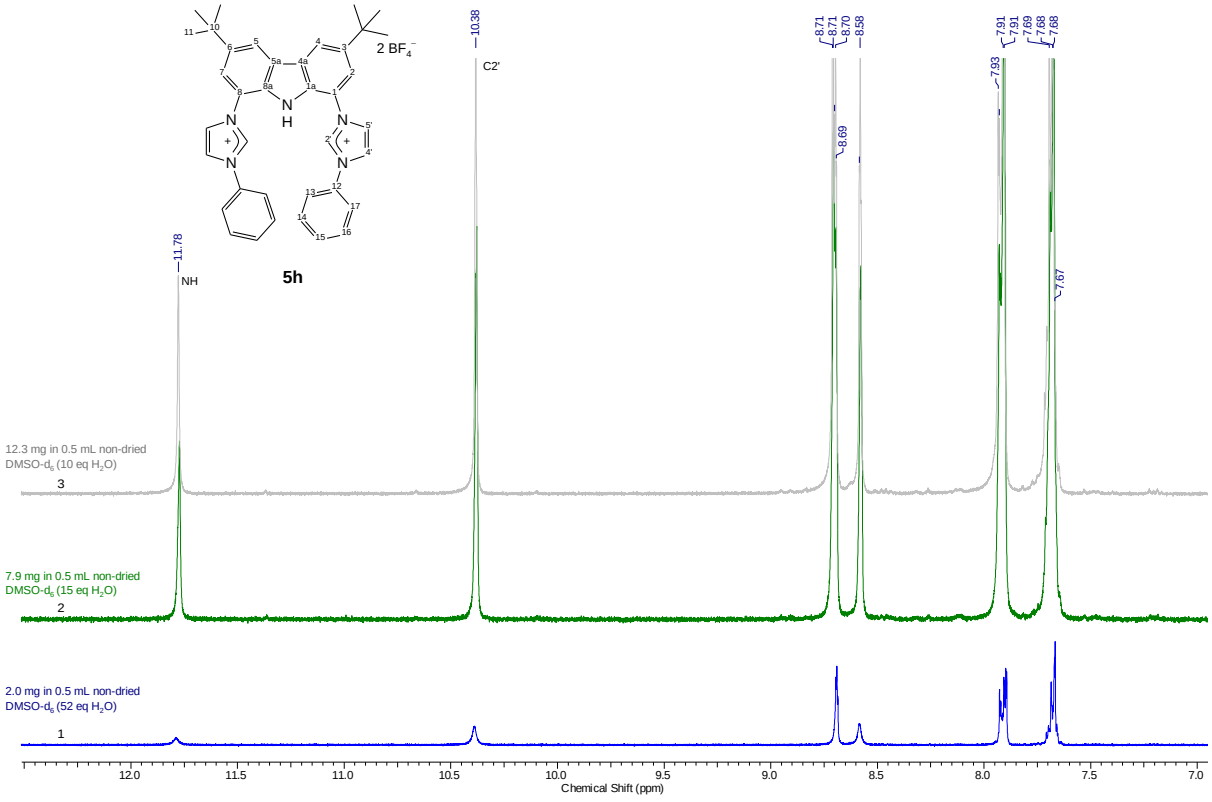
Concentration dependence of **5d** in „regular" DMSO-d_6



Concentration dependence of **5h** in pre-dried DMSO-d_6



Concentration dependence of **5d** in „regular“ DMSO-d_6



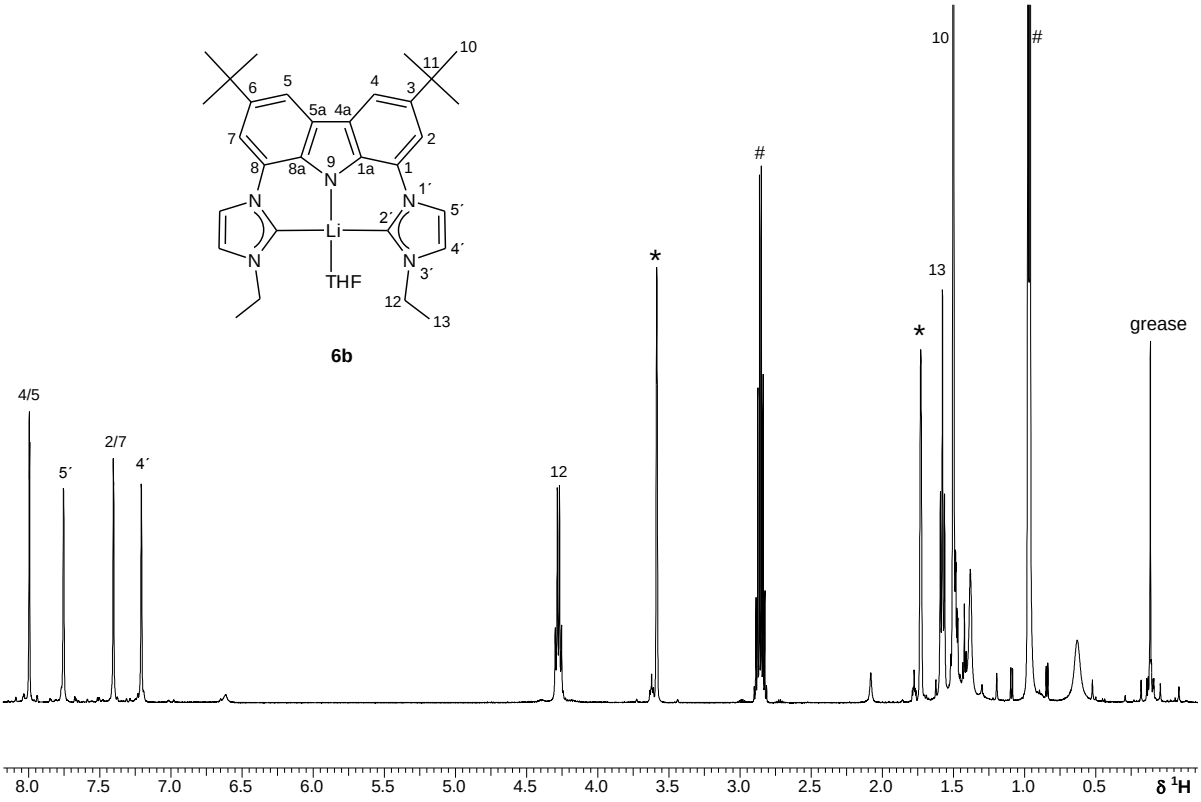
The analysis shows a pronounced contration dependence on the substrate with pre-dried DMSO-d_6. If more than 10 eq H_2O are present, this substrate dependance becomes negliglibe. The NH and the 2'-CH signals are shifted low field in pre-dried DMSO-d_6.

(4) NMR-spectra of the Li(bimca) complexes 6

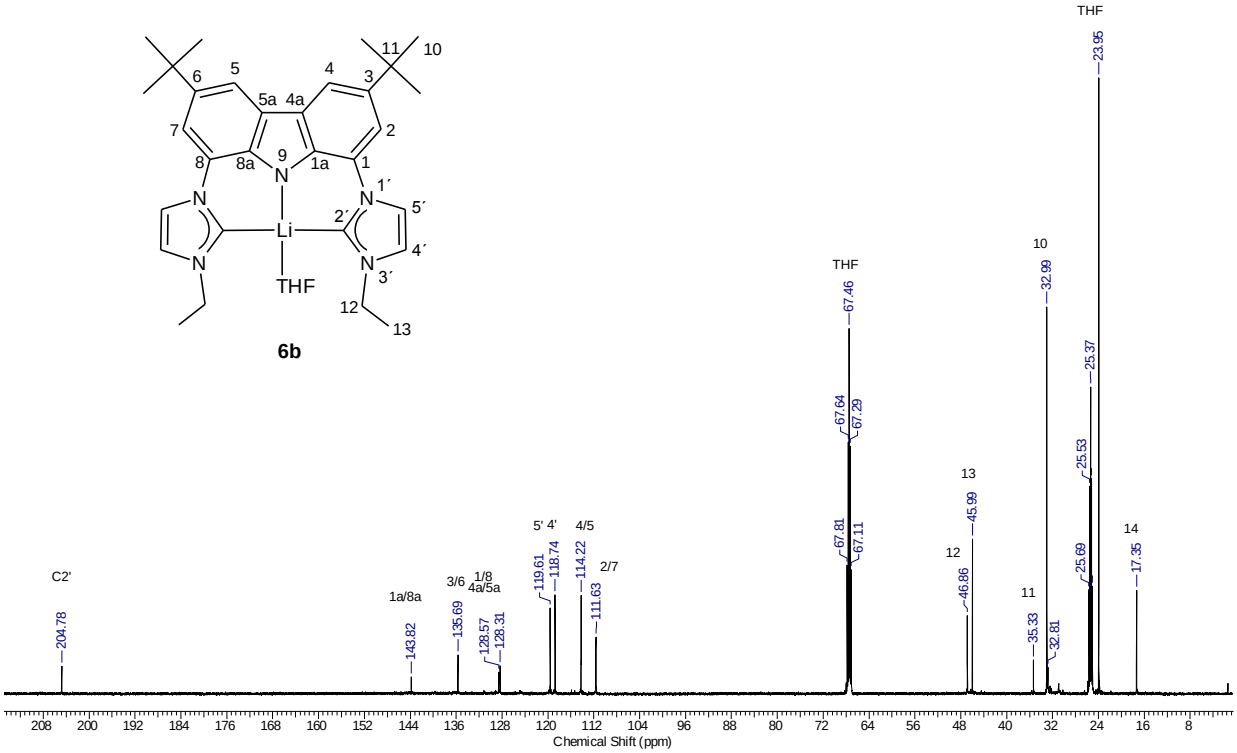
All NMR-spectra were recorded at ambient temperature in thf-d_8 as solvent. Signals in the ^{1}H-NMR spectra at 1.12 (t) resp. 3.38 (q) and 15.5 resp. 66.1 ppm are due to inclusion of diethyl ether in the solid methyllithium (used as base). The signal at 0.19 ppm (^{1}H-NMR spectrum) can be explained by the formation of methane from methyllithium after deprotonation of the imidazolium salt. The signal for methyllithium can be found at –0.10 ppm, whereas the signal for silicon grease is found at 0.19 ppm.

Peaks visible in the ^{13}C-NMR-spectrum at 257, 212, 167, 121, 77, 32 and -15 ppm are “Ghost-Peaks” which appear as a result of the special pulse frequence (UDEFT method) enhancing the intensity of the quaternary carbon atoms.

Li(bimca^{Et}) (**6d**)

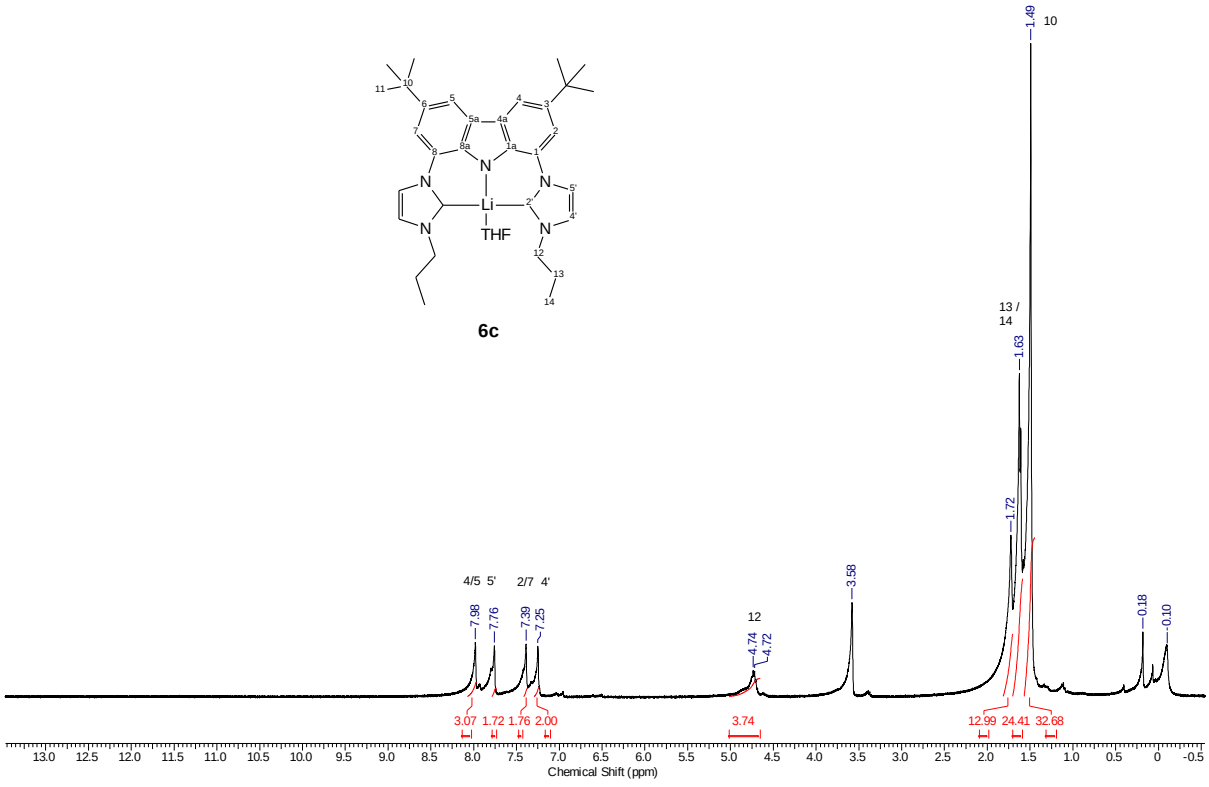


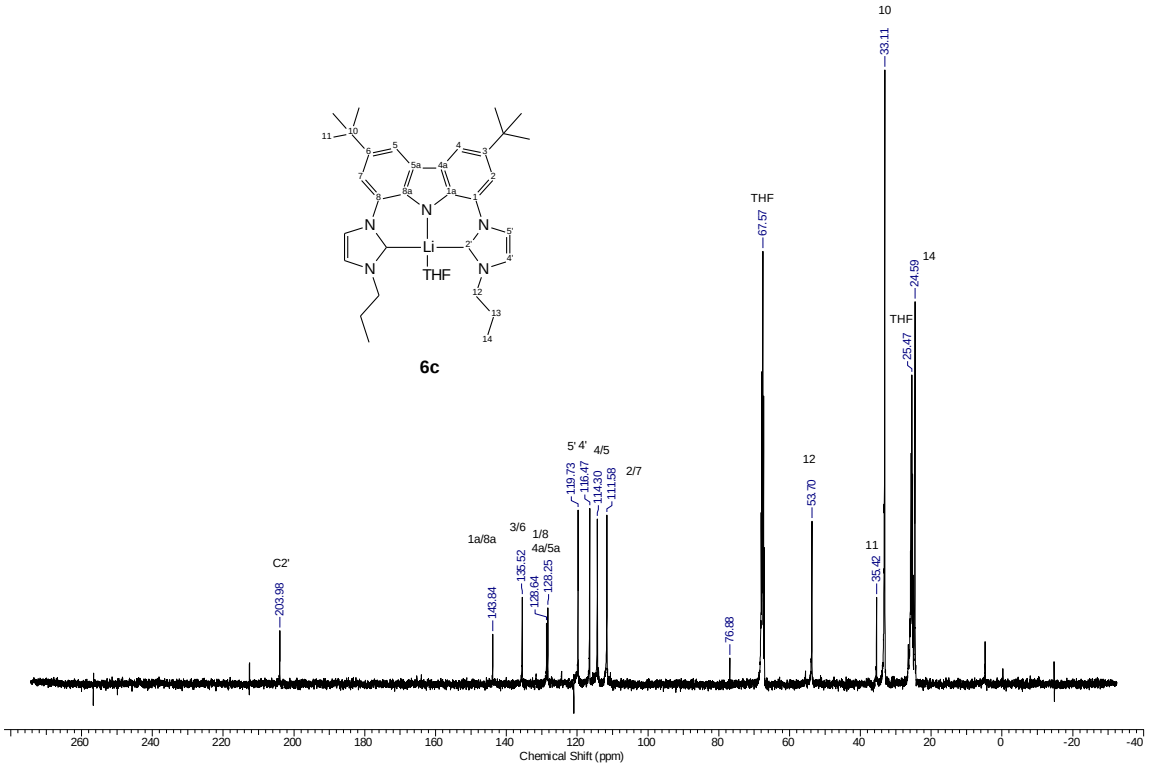
* THF-d_7, # (diisopropylamine).



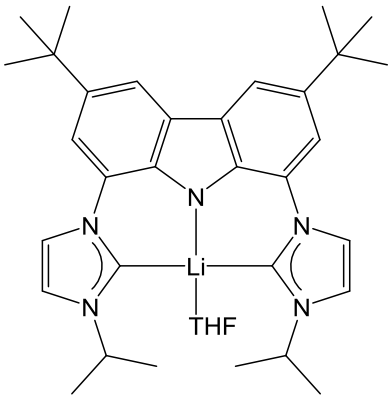
From an NMR experiment in which the deprotonation was carried out with methyl lithium.

Li(bimca^{nProp}) (**6c**)

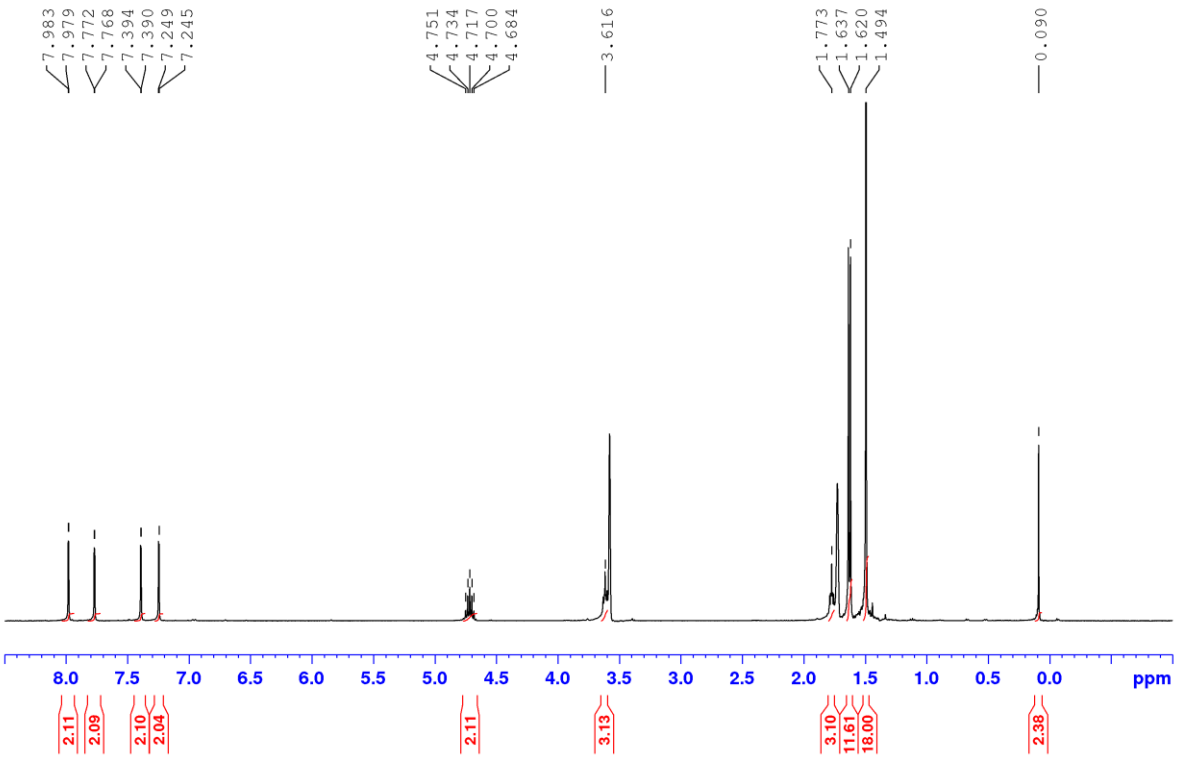




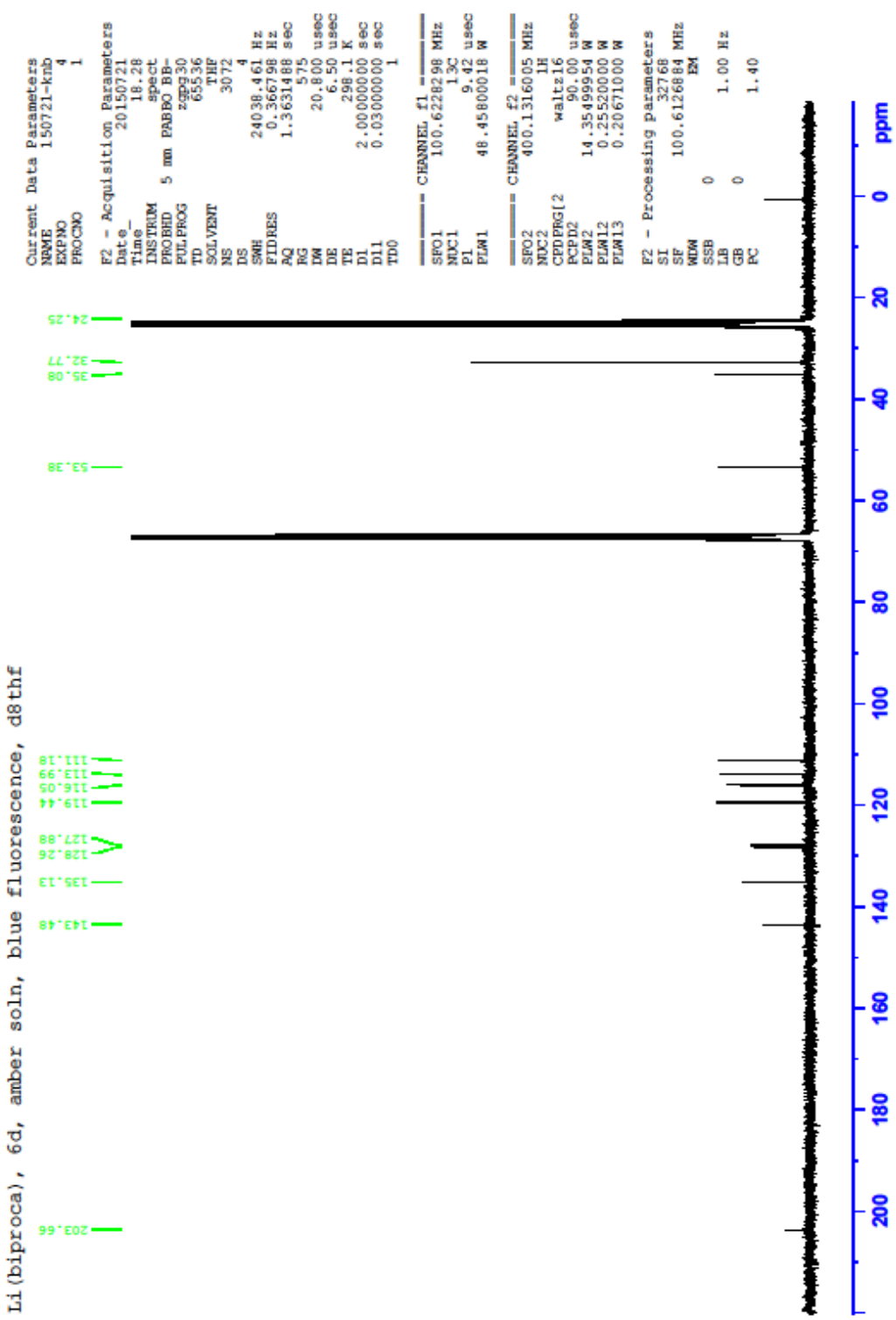
Li(bimca^{iPr}) (**6d**)



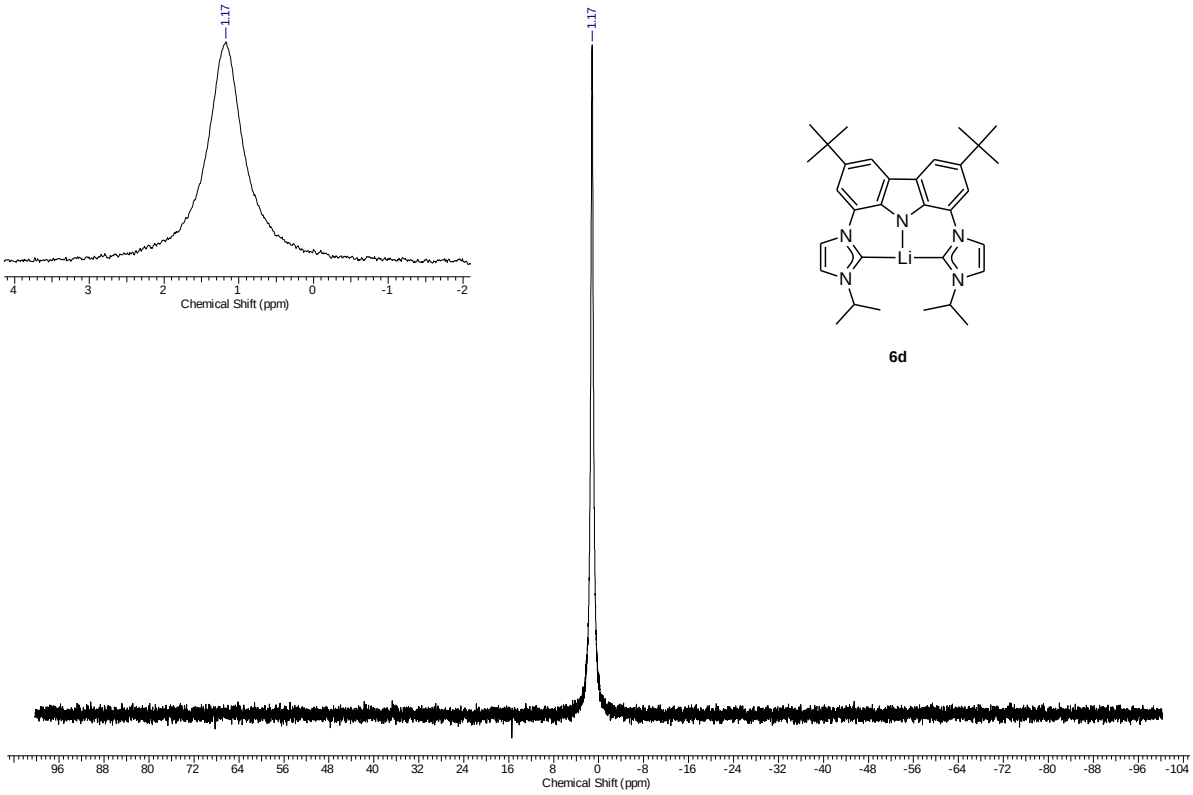
6d



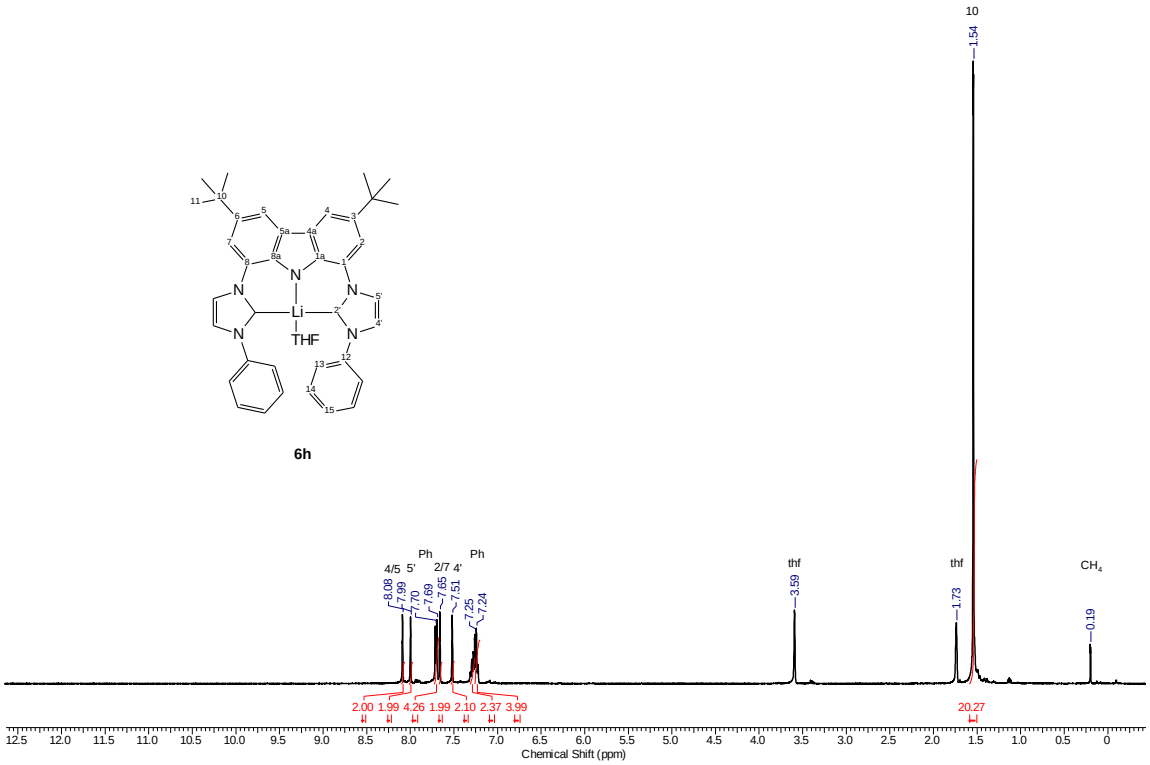
Singlet at 0.09 ppm due to grease.

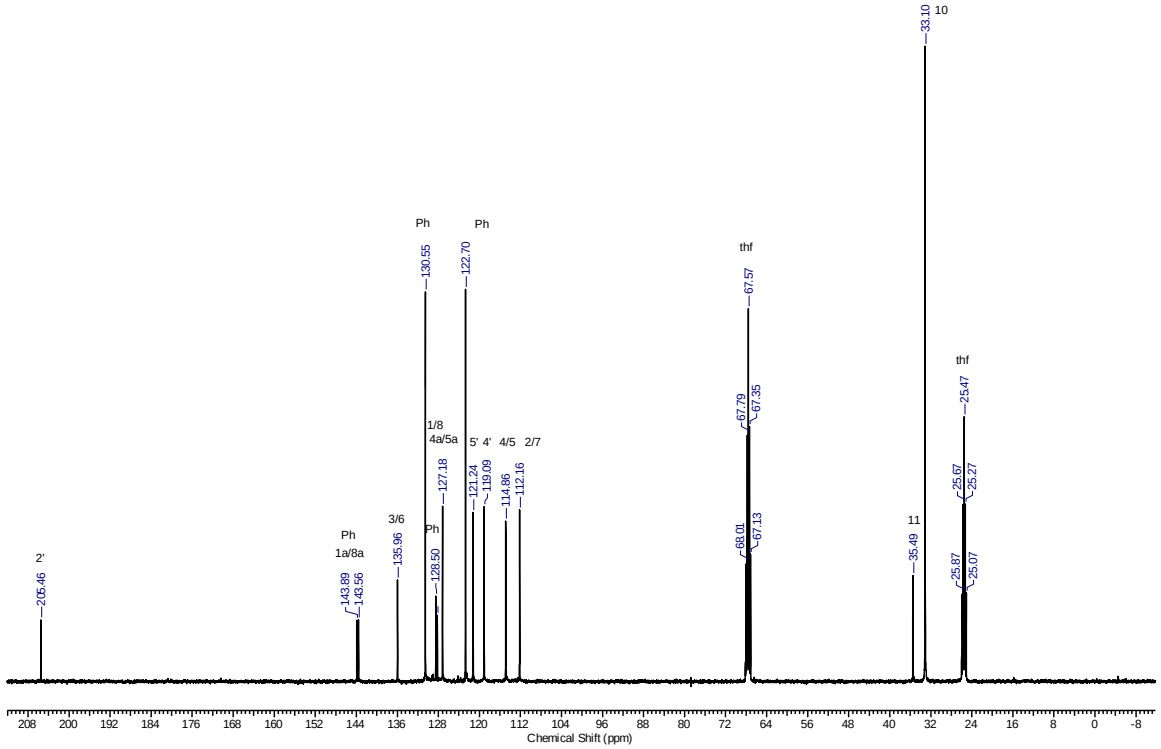

Li(biproca), 6d, amber soln, blue fluorescence, d8thf
Current Data Parameters
NAME 150721-kmb
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150721
Time 18.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT THF
NS 3072
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 575
DW 20.800 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6228298 MHz
NUC1 13C
P1 9.42 usec
PLW1 48.45800018 W
CHANNEL f2
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 14.35499954 W
PLW12 0.25520000 W
PLW13 0.20671000 W
F2 - Processing parameters
SI 32768
SF 100.6126884 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
24.25
32.77
35.08
53.38
111.18
113.99
116.05
119.44
127.88
128.26
135.13
143.48
203.66
ppm
0
20
40
60
80
100
120
140
160
180
200

$^{7}Li\{^{1}H\}$ NMR of compound **6d**

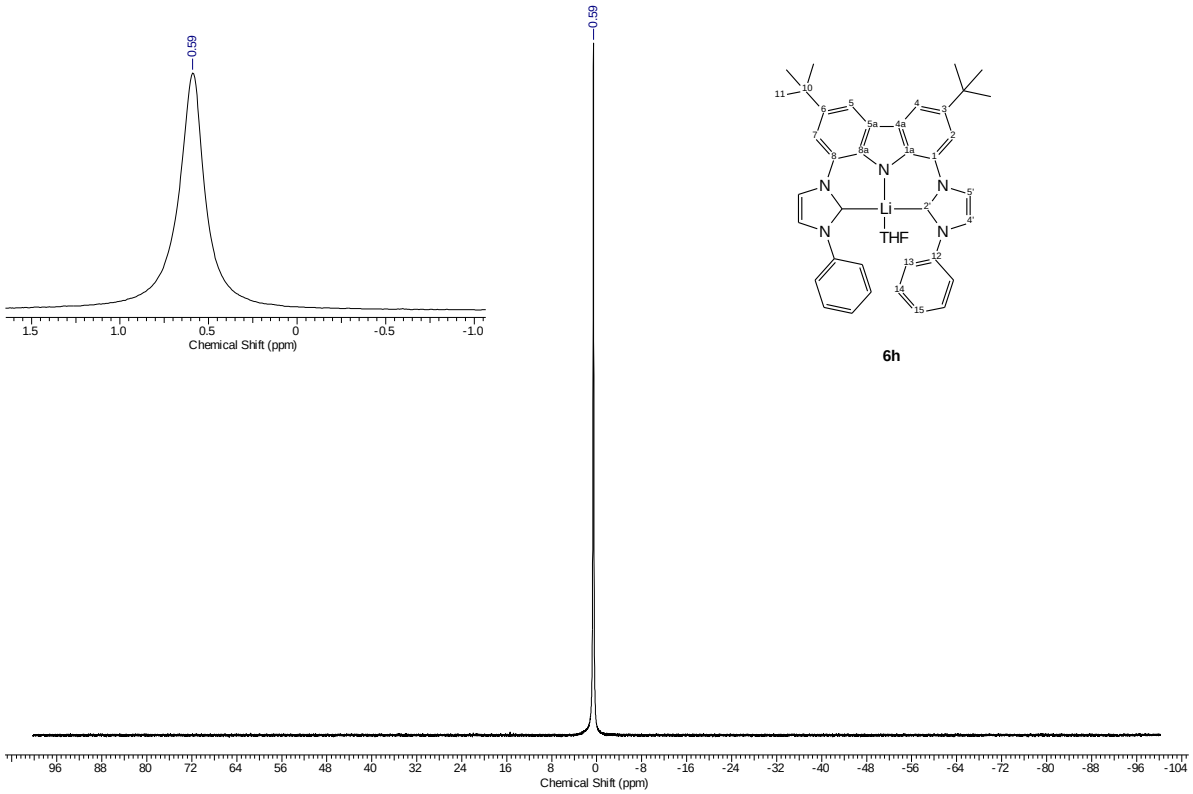


Li(bimca^{Phenyl}) (**6h**)



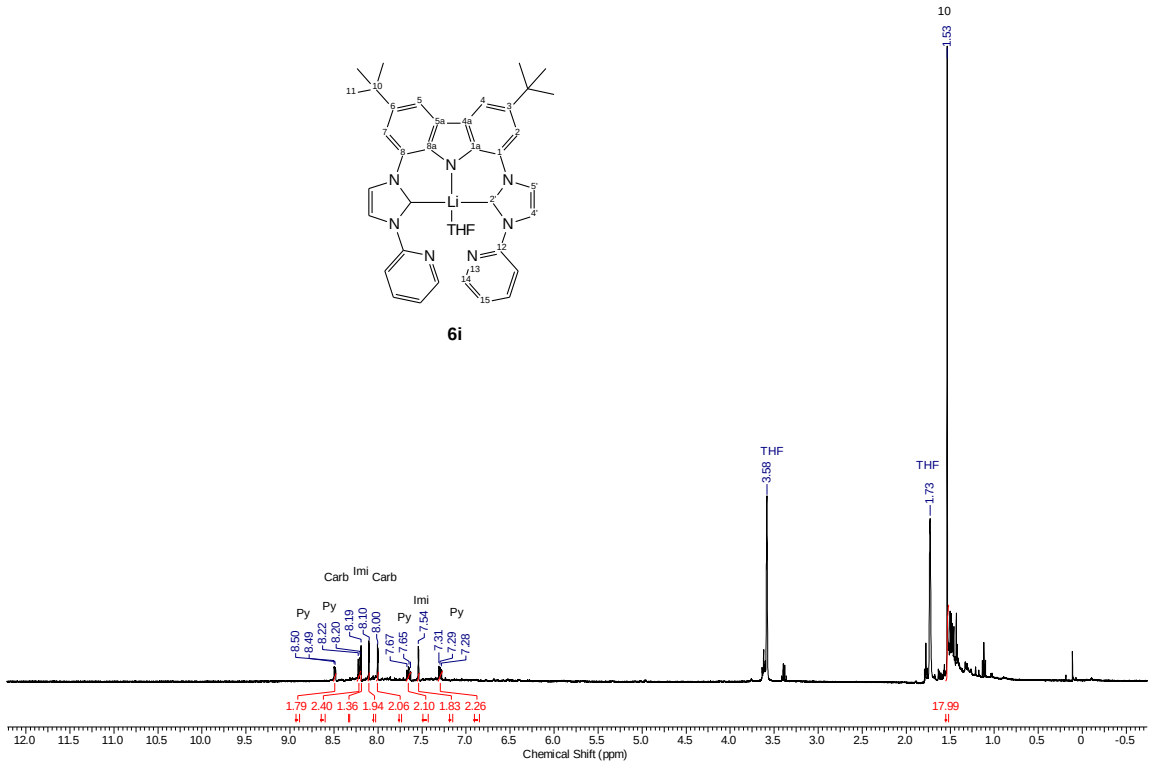


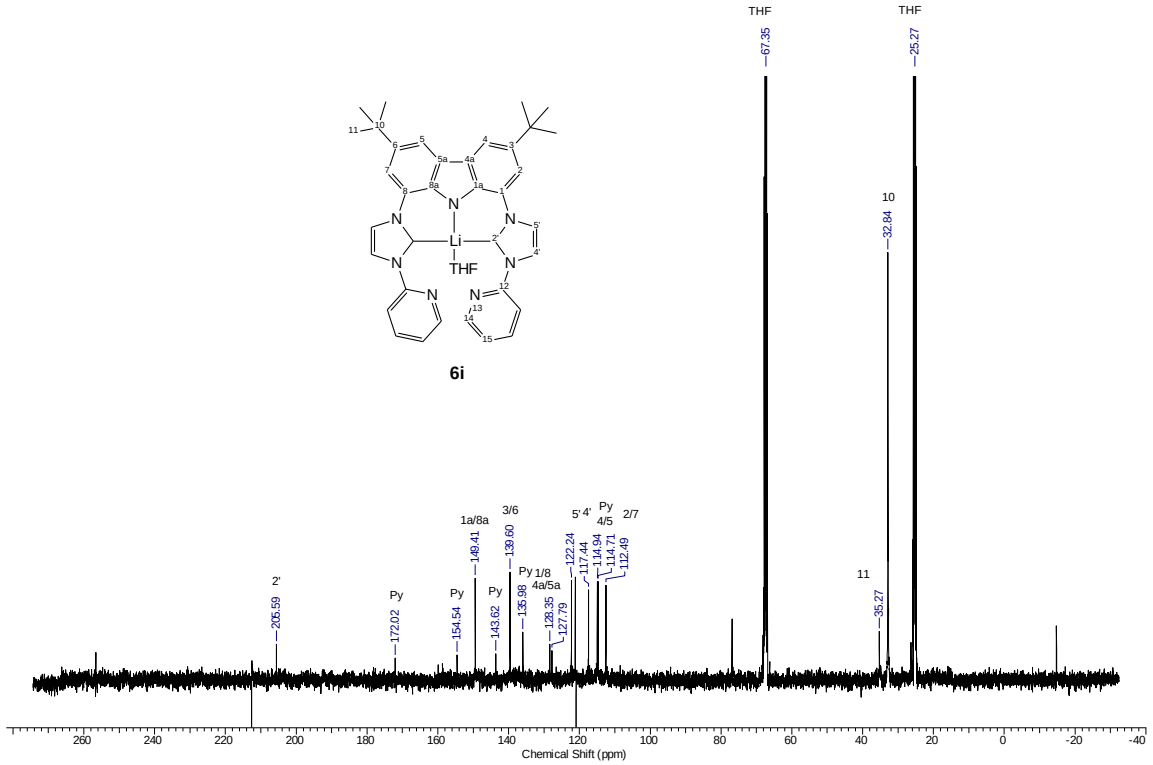
$^{7}Li\{^{1}H\}$ NMR of compound **6h**:



6h

Li(bimca^{Pyridyl}) (**6i**)

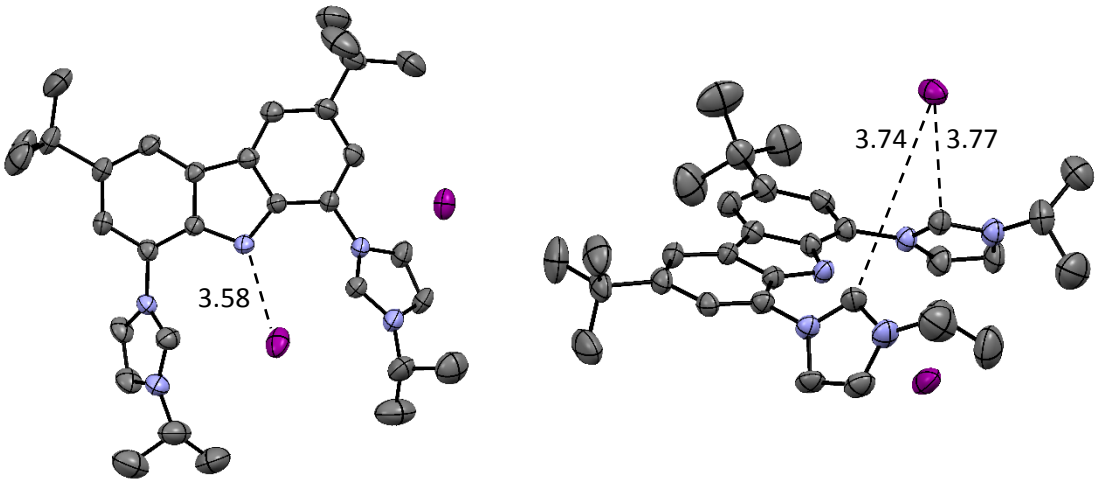




(5) Crystallographic Data:

Data collection for the crystal structures was carried out on a Bruker APEX Duo CCD with an Incoatec ImS Microsource with a Quazar MX mirror, using MO K_α radiation (λ = 0.71073 Å) and a graphite monochromator in both cases. Corrections for absorption effects were applied using SADABS[2]. All structures were solved by direct methods using SHELXS and refined using SHELXL[3,4]. Further details of the refinement and crystallographic data are given in the respective CIF-files. The listed CCDC numbers contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic DATA Center via www.ccdc.cam.ac.uk/data_request/cif.

CCDC 1472375	compound **5b**	Hbimca^{Et}2HBF$_4$
CCDC 1472369	compound **5d**	Hbimca^{iPr}2HBr
CCDC 1501070	compound **5d'**	Hbimca^{iPr}2HI
CCDC 1472370	compound **5e**	Hbimca^{Allyl}2HBr
CCDC 1472371	compound **5f**	Hbimca^{C5}2HBr
CCDC 1472372	compound **5g**	Hbimca^{Bn}2HBr
CCDC 1472373	compound **5h**	Hbimca^{Ph}2HBF$_4$
CCDC 1472374	compound **6d**	Li(bimca^{iPr})



Two views of the molecular structure of **5d'** (Hbimca^{iPr}2HI) (molecule A): Atoms are shown with anisotropic atomic displacement parameters at the 50 % probability level. All hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

[2] G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin **2001**.
[3] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.,* 2011, **44**, 1281–1284.
[4] G. M. Sheldrick, *Acta Crystallogr.,* 2013, **A69**, 74–81.