Electronic Supplementary Information (ESI) for

Boron-nitrogen substituted perylene through photocyclisation

Matthias Müller,[a] Stefan Behnle,[a] Cäcilia Maichle-Mössmer[b] and Holger F. Bettinger*[,a]

[a]*Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. Fax: +49 7071/29-5244; Tel: +49 7071/29-72072; E-mail: Holger.Bettinger@uni-tuebingen.de*
[b]*Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany.*

Experimental section

General. All experiments were performed in quartz glass ware (transparent for UV light) under anhydrous conditions using nitrogen as protective gas. Dry toluene and THF was collected from a MBraun SPS-800 solvent purification system while dry cyclohexane was purchased from Acros and used as received. Iodine was purchased as spherical perls. All NMR spectra were recorded on Bruker DRX 250 and AMX 600 spectrometers. The NMR spectra were measured at room temperature in CD_2Cl_2 that was purchased from Deutero GmbH. The spectra were referenced to residual solvent signals (^1H, ^{13}C: $SiMe_4$)[1] and externally (^{11}B: $BF_3{\cdot}OEt_2$). Solid state NMR spectra were received from a Bruker DSX250 (primary ref: TMS and $BF_3{\cdot}OEt_2$, secondary ref: ^{13}C glycin (*C*OOH, 176.03 ppm); ^{11}B $NaBH_4$ (-42.06 ppm)). Electron impact ionisation mass spectrometry (EI-MS) as well as high resolution mass spectrometry was done on a Finnigan MAT MAT95 (EI-HRMS) whereas LDI-TOF was performed on a Bruker Daltonics autoflex. Infrared spectra were measured on a Bruker Tensor 27, UV-Vis spectra on a Perkin Elmer Lambda 1050, and fluorescence spectra on a Varian CARY Eclipse spectrometer. Melting points (uncorrected) were measured on a Büchi B-540. Irraditions have been carried out with a low pressure mercury vapor (lpmv) lamp (Pen-Ray UVP 3SC-9 series) or a Newport high pressure mercury vapor (hpmv) lamp (500 watts) with suitable housing and collimation setup. Dichroic mirrors (Newport, 1.5 inch, flange size) are used to cut out specific wavelength ranges from the lamp spectrum (product numbers; 66215 (200 nm – 30 μm); 66231 (240 – 255 nm); 66216 (280 – 400 nm); 66219 (420 – 630 nm)).

The precursors **3**[2] and **5**[3] are synthesized according to literature procedures. $h_{1/2}$ is the Full Width at Half Maximum which is determined by a Lorentzian fit with TopSpin 2.1 (Bruker) and given in Hertz (Hz). TopSpin 2.1 was also used for the deconvolution of ^{11}B spectra.

Dibenzo[fg,ij]-1,3,4a,2,4,12b-triazatriboratriphenyleno[1,2,3,4-rst]-13,13b,13a,14-diazadiborapentaphen, 1

A quartz flask is charged with 32.4 mg (0.06 mmol) **3** and dissolved in 90 ml of dry toluene (0.68 µmol/ml). Then, 297 µl (3.66 mmol) dry THF and 51.5 mg (0.20 mmol) iodine were added and the solution was irradiated with the hpmv lamp for 16 h. The solution turned slightly green and was quenched by the addition of 80 ml of sat. sodium sulfite solution. The colorless organic phase was dried over sodium sulfate and the solvent evaporated. After the addition of 4 ml of acetone to the yellow crude product the resulting suspension was centrifugated three times 5 min at 13.4 krpm each. The collected off-white sediment **1** was dried under a nitrogen stream (14.0 mg, 43 %).

To scale up the reaction 166.3 mg (0.31 mmol) **3**, 236.9 mg (0.94 mmol) iodine and 1.52 ml (18.80 mmol) THF were dissolved in 500 ml toluene and irradiated for 63 h with a hpmv lamp equipped with a dichroic mirror (200 nm – 30 µm). Yield: 82.5 mg of **1** (50 %).

Up to now, it is neither possible to recrystallize the sample nor to do column chromatography (with dichloromethane on silica gel; leads to decomposition).

m.p. 348-350 °C; δ_H(600 MHz; CD_2Cl_2) 7.09 (1 H, m), 7.15 (1 H, m), 7.21 (1 H, m), 7.28 (1 H, m), 7.32 (1 H, m), 7.38 (1 H, m), 7.56-7.61 (4 H, m), 7.71 (1 H, m), 7.86 (1 H, m), 7.93 (1 H, m), 8.01 (1 H, m), 8.29 (1 H, m), 8.30 (1 H, m), 8.35 (1 H, m), 8.39-8.41 (3 H, m), 8.57 (2 H, m); δ_C(151 MHz; CD_2Cl_2) 120.3, 121.2, 122.5, 123.6, 123.7, 124.1, 124.1, 124.7, 125.0, 125.4, 125.4, 125.6, 125.9, 126.0, 126.4, 126.6, 126.6, 127.1, 127.2, 127.3, 128.2, 131.8, 132.2, 132.9, 134.2, 135.8, 139.7, 139.9, 140.6, 140.7, 140.9, 141.5, 143.0, 145.9 (solubility too low to resolve all peaks, see spectrum); δ_C(solid-state, 50 MHz, Rf =10000 Hz) 121.0, 125.0, 133.3, 136.0, 141.1; δ_B(80 MHz; CD_2Cl_2) 31.2 ($h_{1/2}$ 694); LDI-MS (TOF) m/z: 619 (M + $C_4H_{10}O_2^+$, 9 %), 529 (100, M^+); δ_B(solid-state, 64 MHz, Rf =10000 Hz) due to 3 boron nuclei pattern is too complex to assign δ_{iso}, C_Q and η; EI-MS (70 eV, sector field) m/z: 529 (M^+, 100 %), 512 (20), 525 (M – 4H), 262 (45, $[M - 6\ H]^{2+}$), 256 (20); EI-HRMS (M^+, 70 eV,

sector field) found: 529.20350, calc. for $C_{36}H_{22}B_3N_3$: 529.20929; IR (KBr) cm^{-1}: 654w, 679w, 756m, 800w, 824w, 867w, 1047w, 1169w, 1262w, 1317m, 1375vs, 1446m, 1481m, 1495m, 1561w, 1575w, 1601m, 3061w; UV-Vis (DCM) nm: 257, 292, 330, 350, 369; (toluene) 297, 331, 351, 370; (cyclohexan) 215, 229, 262, 292, 329, 349, 367; fluorescence (DCM, 5 mm slit): 375, 393, 411, 435 nm, ex. 247, 261, 292, 330, 350, 369 nm; (cyclohexan) 371, 389, 409, 431, 460 nm, ex. 231, 260, 290, 328, 349, 367 nm.

16-Hydroxy-dibenzo[b,n]-1,12a,12,12b-diazadiboraperylen, 2

A solution of 68.8 mg (0.13 mmol) **1** in 50 ml of dichloromethane is charged with 50 ml of methanol. The colorless suspension is stirred at room temperature for 70 h while a slightly brownish solution is formed. The solvent is removed completely, the residue suspended in 6 ml of acetone and centrifuged twice 5 min at 13.4 krpm each run. A minor amount of solid material is discarded (sediment, ca. 1-2 mg) and the centrifugate is liberated from the solvent by evaporation. A column chromatrography on an automated system (15 µm silica gel, dichloromethane) is performed afterwards yielding 39.5 mg **2** (82 %).

On crystallization scale, the hydrolysis reaction of **1** can also be run in wet CH_2Cl_2, yielding crystals showing NMR spectra and X-ray structures in full accordance with **2**.

m.p. 267-269 °C; δ_H(600 MHz; CD_2Cl_2) 5.96 (1 H, s), 7.20 (1 H, m), 7.32 (1 H, m), 7.42-7.45 (2 H, m), 7.59 (1 H, m), 7.80 (1 H, m), 7.90 (1 H, m), 8.01 (1 H, m), 8.30 (1 H, m), 8.33-8.36 (2 H, m), 8.46 (1 H, m), 8.48 (1 H, m), 8.51 (1 H, m), 9.55 (1 H, br s); δ_B(80 MHz; CD_2Cl_2) 30.8 ($h_{1/2}$ 272, 48 %), 34.2 ($h_{1/2}$ 292, 52 %); EI-HRMS (M^+, 70 eV, sector field) found: 370.14291, calc. for $C_{24}H_{16}B_2N_2O$: 370.14488; IR (KBr) cm^{-1}: 722w, 754s, 1202m, 1300m, 1368s, 1424s, 1474m, 1493m, 1513m, 1573m ,1604m, 3395m, 3627m; UV-vis (DCM) nm: 259, 271, 283, 296, 324, 337, 352, 369; fluorescence (DCM, 5 mm slit): 345, 386, 399, 424, 485 nm, ex. 243, 250, 259, 269, 283, 295, 325, 337, 352, 369 nm.

X-Ray Crystallography

Crystals of **2** were grown from a solution of **1** in DCM and methanol. One of those crystals was measured on an APEX II DUO with Cu radiation. The system crystallizes in an orthorhombic metric with spacegroup $P2_12_12_1$ and cell constantes a = 5.28903(3), b = 15.6927(8), c = 20.2461(1) A. The structure was solved by direct methodes and successively refined against F^2. This resulted in a $wR_2 = 0.0902$ an $R_1 = 0.0335$ for reflections I>2sigma. The CCDC 987402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

#	Reaction conditions (starting material, irrad. source, solvent, oxidant/additives, concentration, filter, irrad. time)	isolated yields
1)	**3**, lpmv, toluene, iodine (3.3 eq.), THF (60 eq.), 0.58 µmol/ml	**3**
2)	**3**, lpmv, toluene, cyclohexene (6 eq.), 0.61 µmol/ml	**3**
3)	**3**, hpmv, toluene, cyclohexene (6 eq.), 0.62 µmol/ml, no mirror	**3**
4)	**3**, hpmv, toluene, iodine (3.4 eq.), THF (60 eq.), 0.68 µmol/ml, no mirror	43 wt% **1**
5)	**3**, hpmv, toluene, iodine (1.1 eq.), THF (60 eq.), 0.67 µmol/ml, no mirror	27 wt% **1**
6)	**3**, hpmv, toluene, iodine (3.0 eq.), propylene oxide (60 eq.), 0.79 µmol/ml, full arc	44 wt% mixt. **1** + **3**
7)	**3**, hpmv, toluene, iodine (30 eq.), THF (60 eq.), 0.68 µmol/ml, full arc	49 Gew.% mixt. **1** + **3**
8)	**5**, hpmv, toluene, iodine (3 eq.), THF (60 eq.), 0.70 µmol/ml, full arc	14 wt% **5**
9)	**3**, hpmv, cyclohexane, iodine (3.0 eq.), THF (60 eq.), 0.24 µmol/ml, full arc, 66 h	61 wt% **1**
10)	**3**, hpmv, toluene, iodine (3.0 eq.), THF (60 eq.), 0.68 µmol/ml, 280-400 nm	42 wt% mixt. **1** (66 %) + **3** (34 %)
11)	**3**, hpmv, toluene, iodine (3.1 eq.), THF (60 eq.), 0.69 µmol/ml, 420-630 nm	68 wt% mixt. **1** (15 %) + **3** (85 %)
12)	**3**, hpmv, toluene, iodine (3.0 eq.), THF (60 eq.), 0.66 µmol/ml, 240-255 nm	79 wt% **3**
13)	**3**, hpmv, toluene, iodine (3.0 eq.), THF (60 eq.), 0.94 µmol/ml, full arc	44 wt% mixt. **1** (45 %) + **3** (55 %)
14)	**1**, hpmv, cyclohexane, iodine (3.0 eq.), THF (60 eq.), 0.26 µmol/ml, full arc, 62 h	72 wt% **1**
15)	**3**, hpmv, toluene, DDQ (4.0 eq.), 0.71 µmol/ml	46 wt% **3**
16)	**3**, hpmv, cyclohexane, benzophenone (4.0 eq.), 0.35 µmol/ml, full arc	30 wt% **3**
17)	**3**, hpmv, toluene, iodine (3.0 eq.), THF (60 eq.), 0.67 µmol/ml, full arc, 160 h	47 wt% **1**
18)	**3**, hpmv, 500 ml toluene, iodine (3.0 eq.), THF (60 eq.), 0.63 µmol/ml, full arc, 63 h	50 wt% **1**

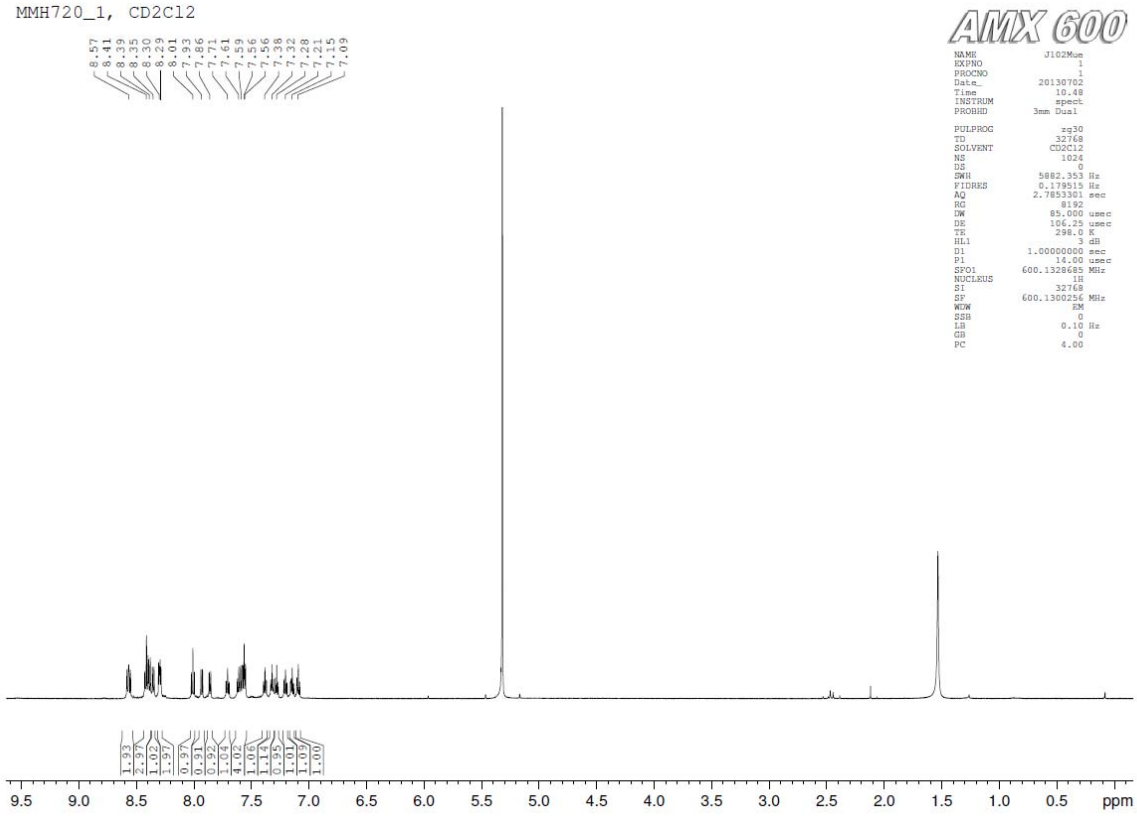
Lpmv: low pressure mercury vapor lamp

Hpmv: high pressure mercury vapor lamp

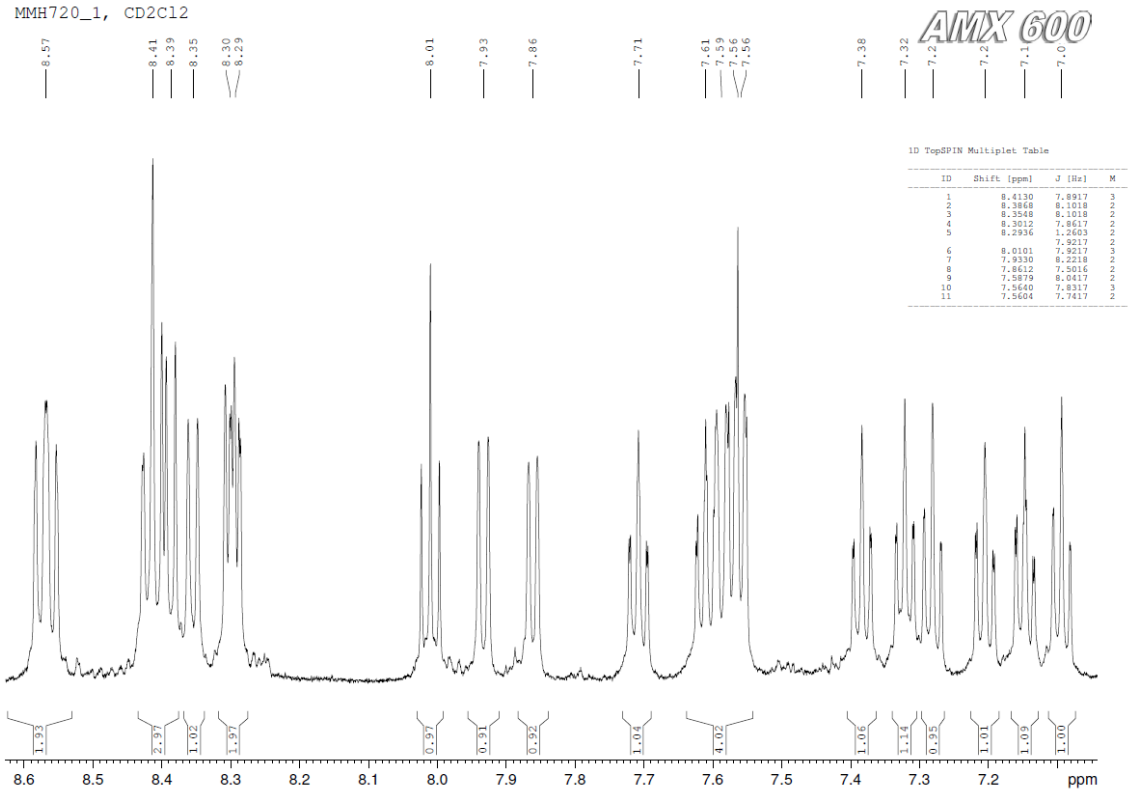
Full arc: dichroic mirror (200 nm – 30 µm)

Irradiation time: 15-20 h, if not stated otherwise

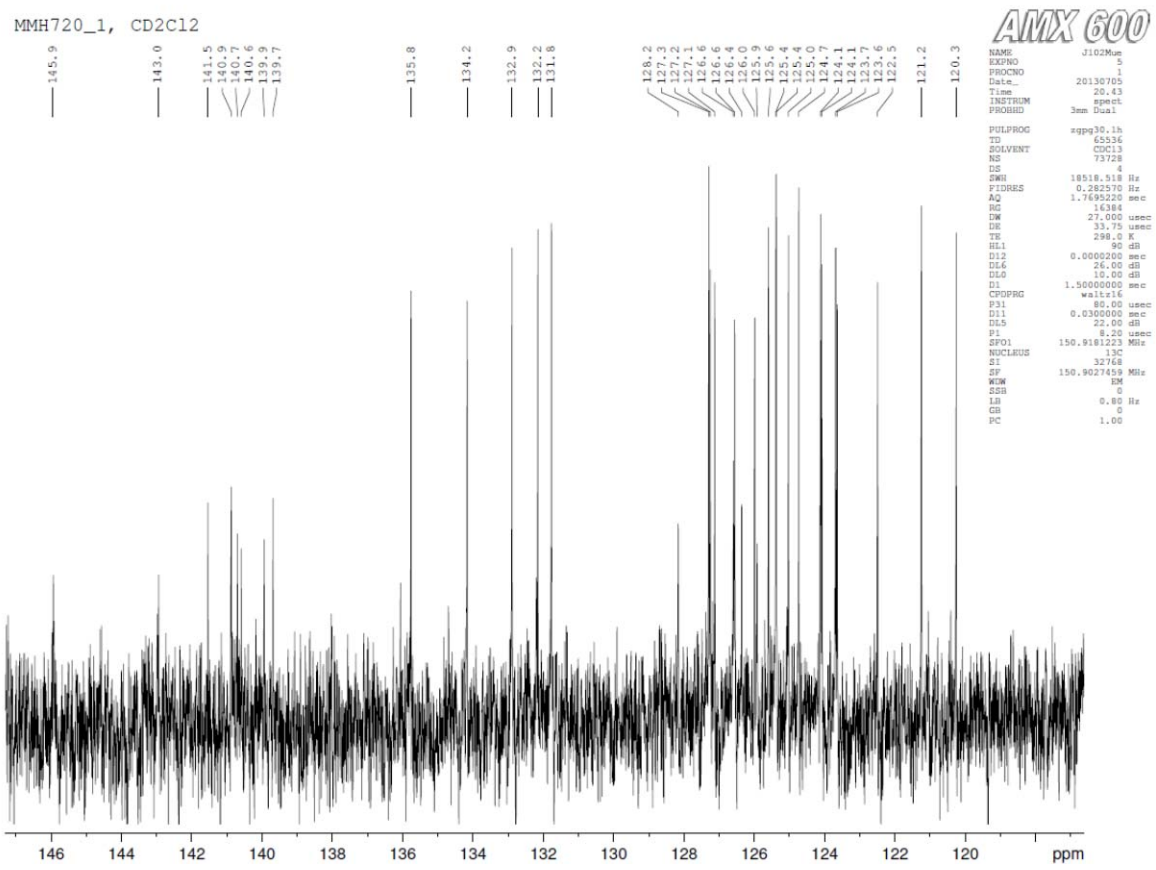
Condition 11): Formation of (1) may be due to the low but non neglectable transmittance of the dichroic mirror (420 – 630 nm) in the region of 280 to 400 nm.



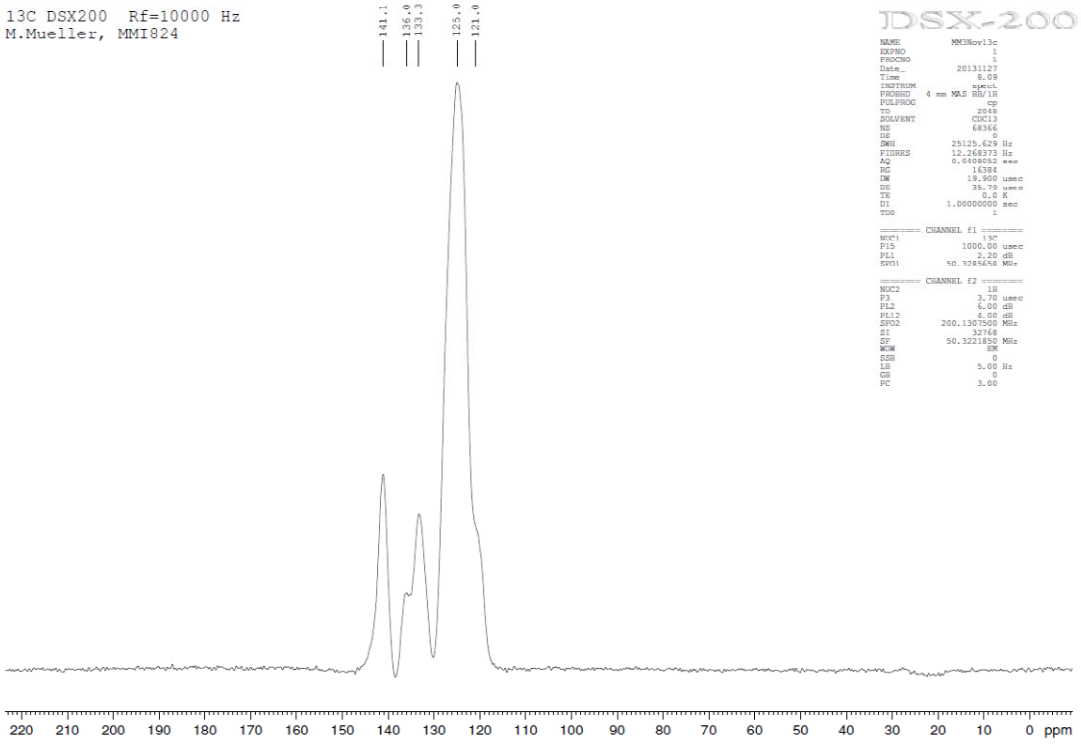
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **1**



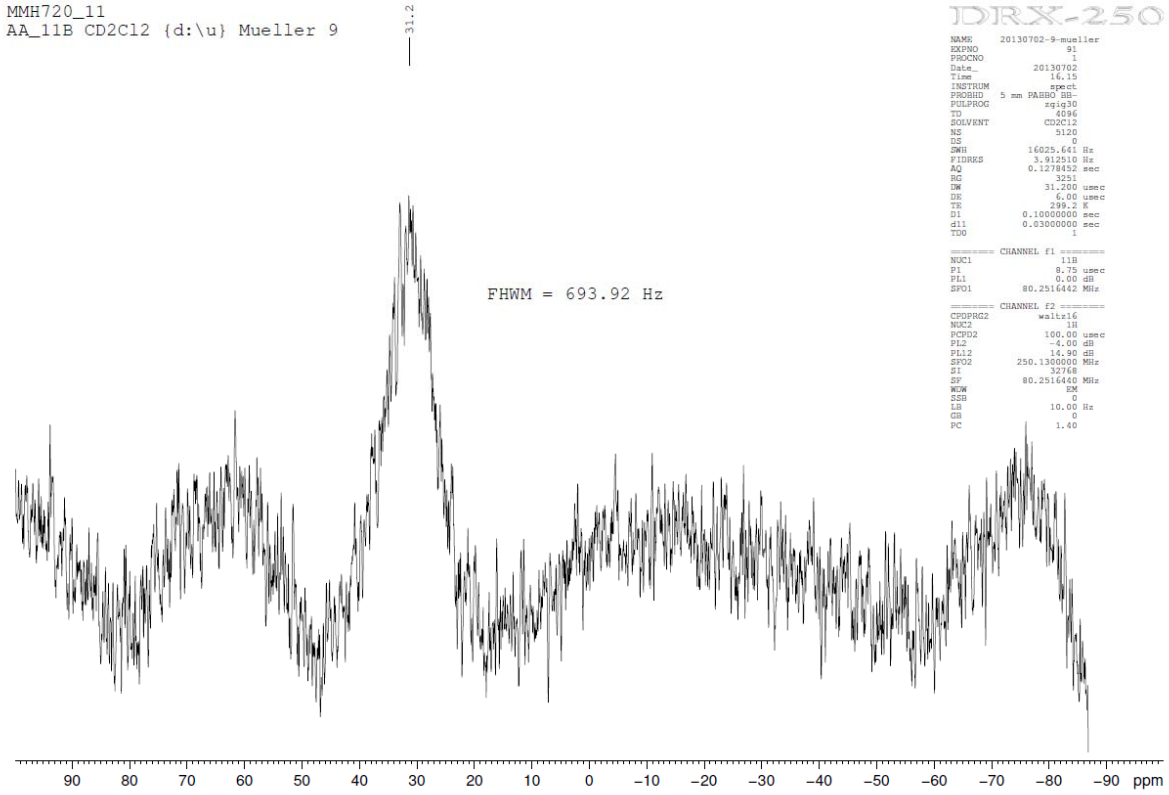
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **1** (enlarged)



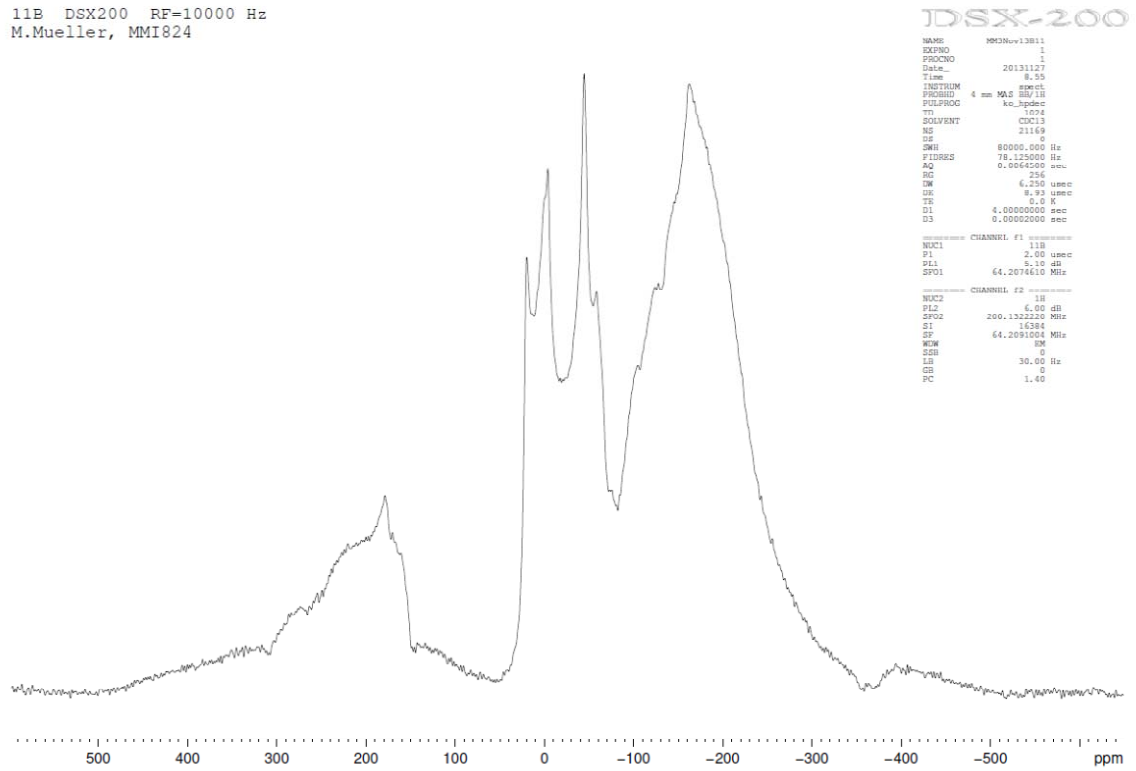
$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2) spectrum of **1**, 73 k scans, no better resolution (on the available setup) possible



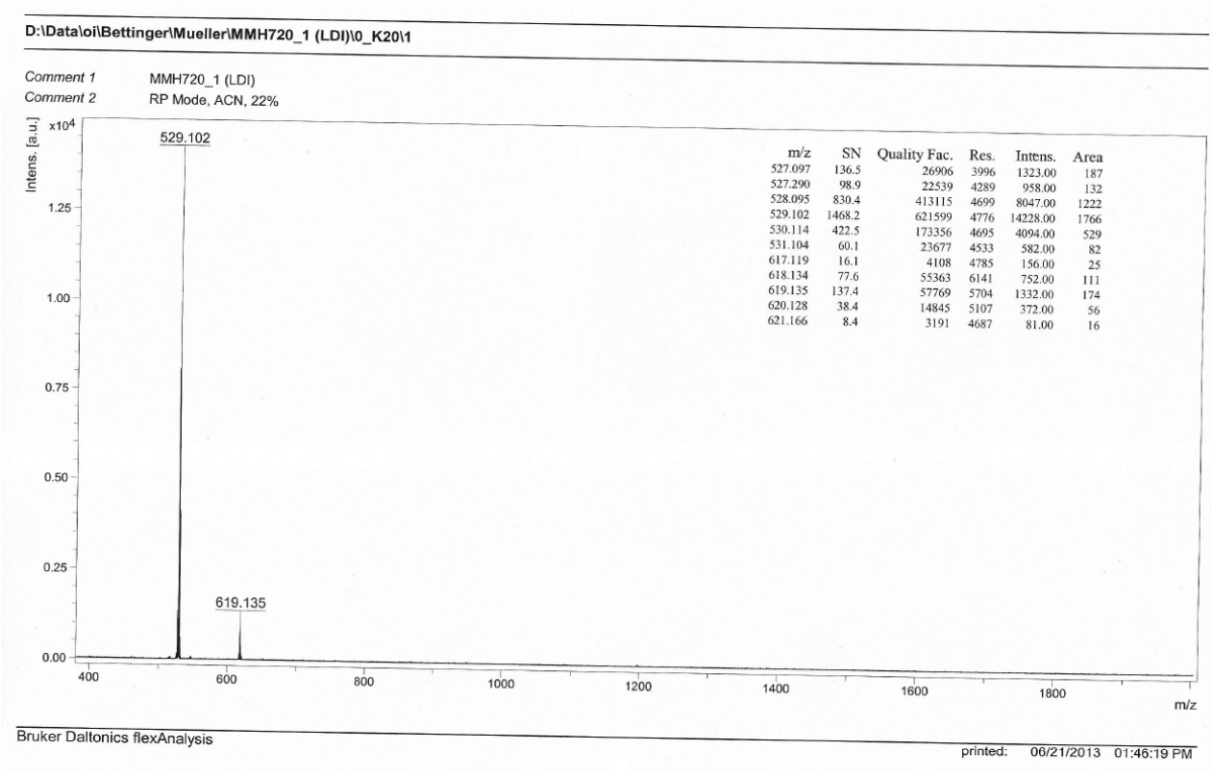
$^{13}C\{^{1}H\}$ (50 MHz, Rf = 10000 Hz) solid stated NMR spectrum of **1**



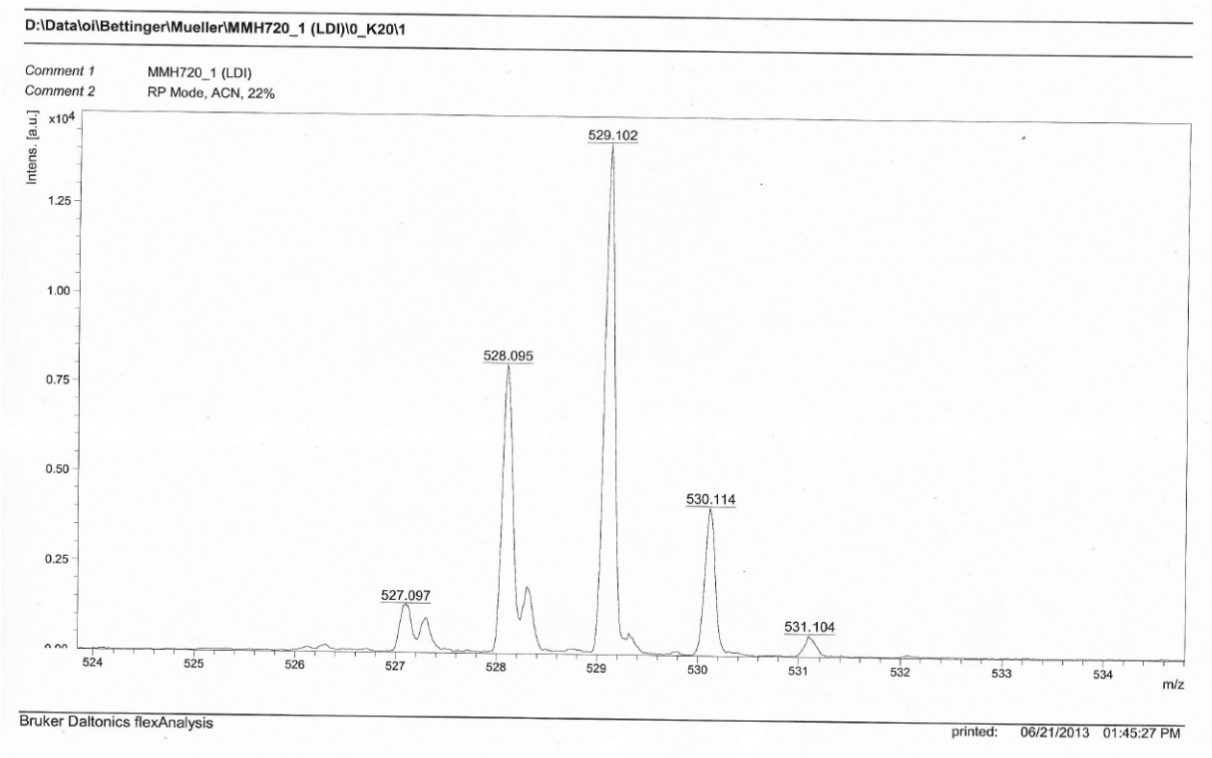
$^{11}B\{^{1}H\}$ NMR (80 MHz, CD_2Cl_2) spectrum of **1** (5 k scans)



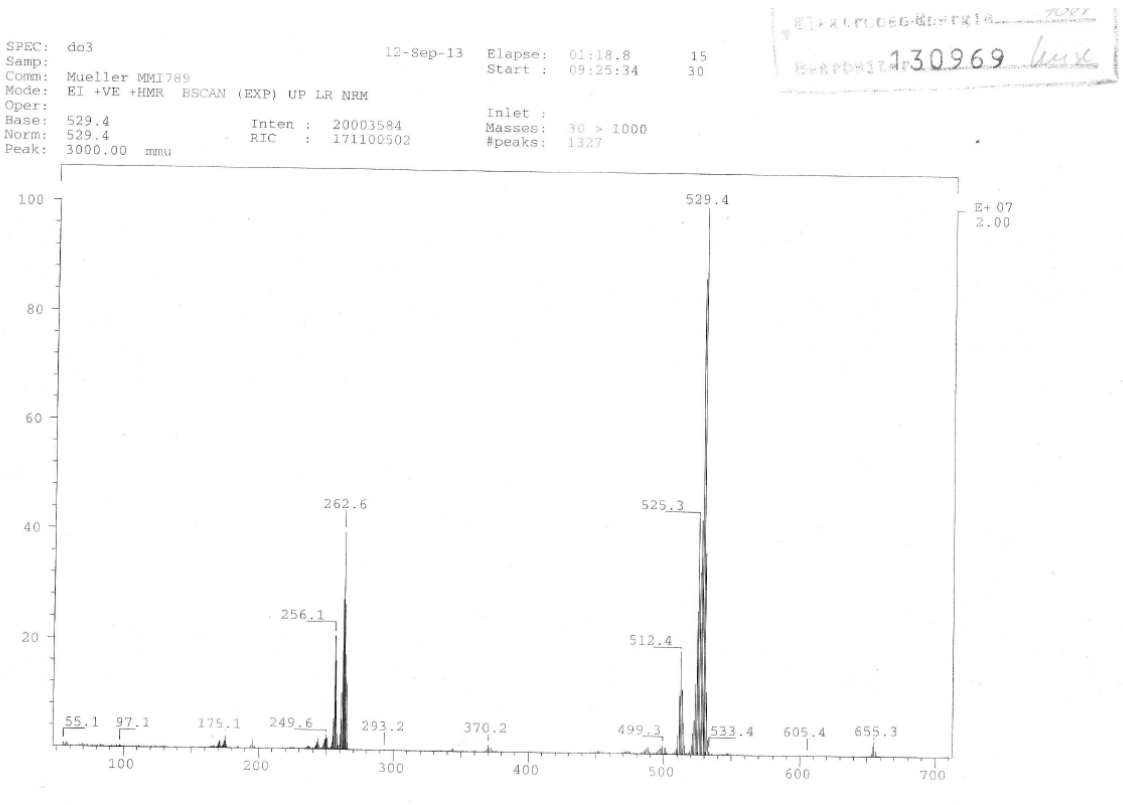
$^{11}B\{^{1}H\}$ solid state NMR (64 MHz, Rf = 10000 Hz) spectrum of **1**



LDI-TOF (reflectron, ACN as solvent) of **1**



LDI-TOF (enlarged) of **1**



EI-MS (70 eV) of **1**

M a s s e n f e i n b e s t i m m u n g

Name: Müller Probenbezeichnung: **MMI789**

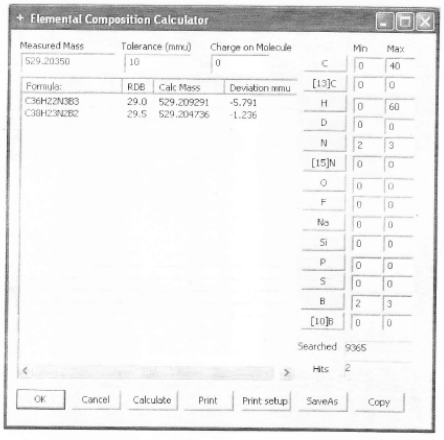
Ionisierungsmethode: **EI** ..X... **FAB** .....

Referenz - Ion und seine **exakte Masse:**

$C_{12}F_{21}$ 543 542,96651

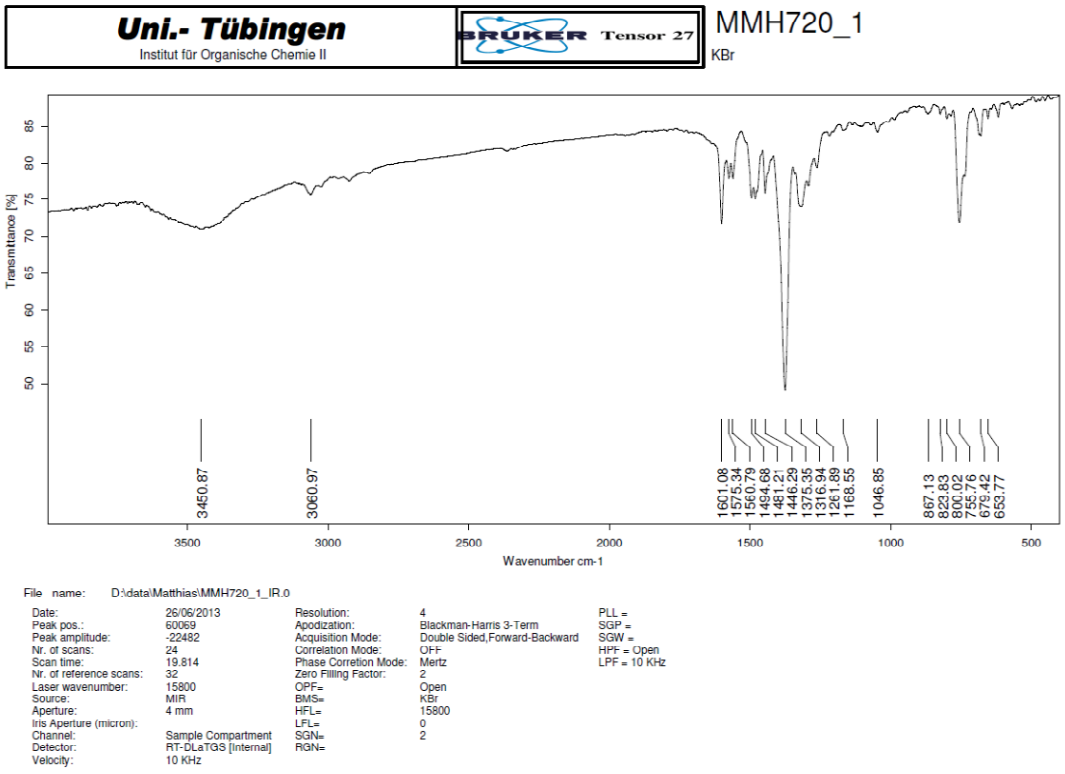
die **gefundene exakte Masse** erhält man zu: **529,20350**

damit ergibt/ergeben sich folgende **Elementkombination(en)** :

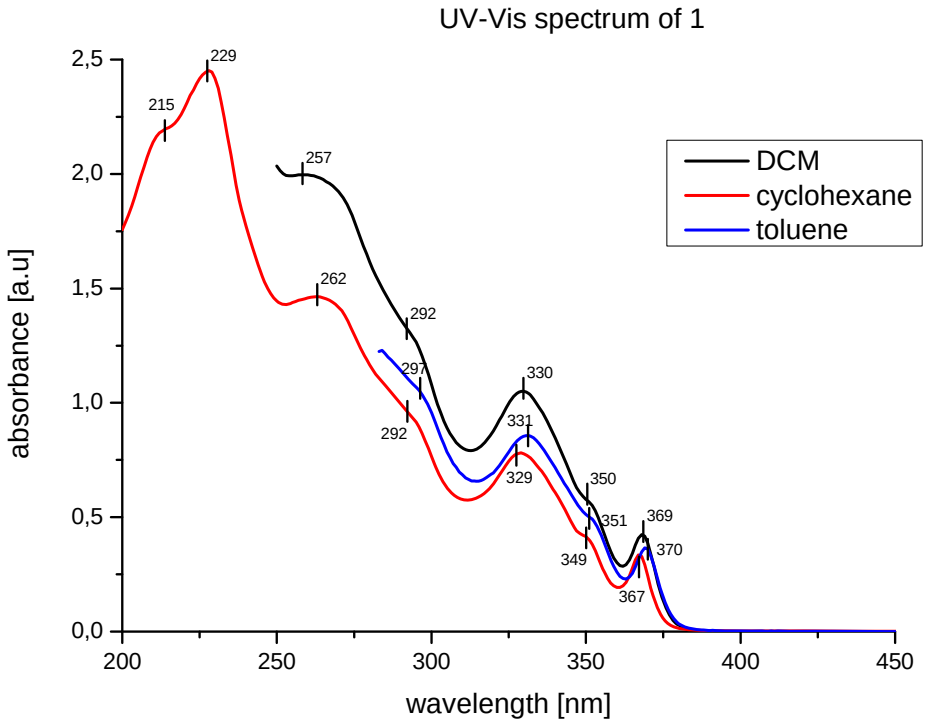


Datum 17. Sep. 2013 MS - Nummer 130968 Bearbeiter

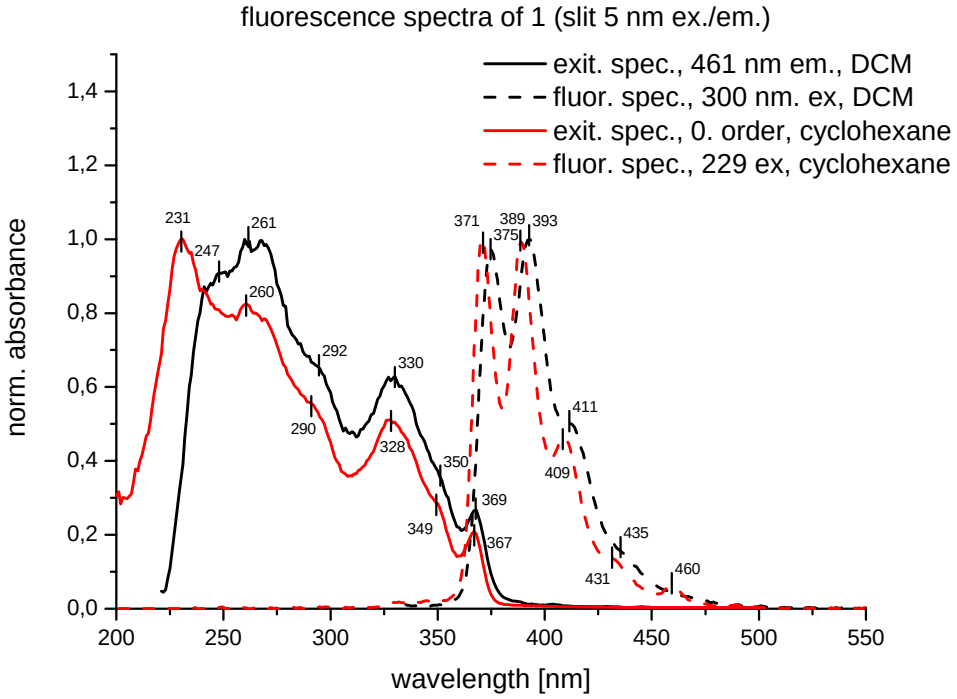
Exact mass determination (EIMS, 70 eV) of **1**



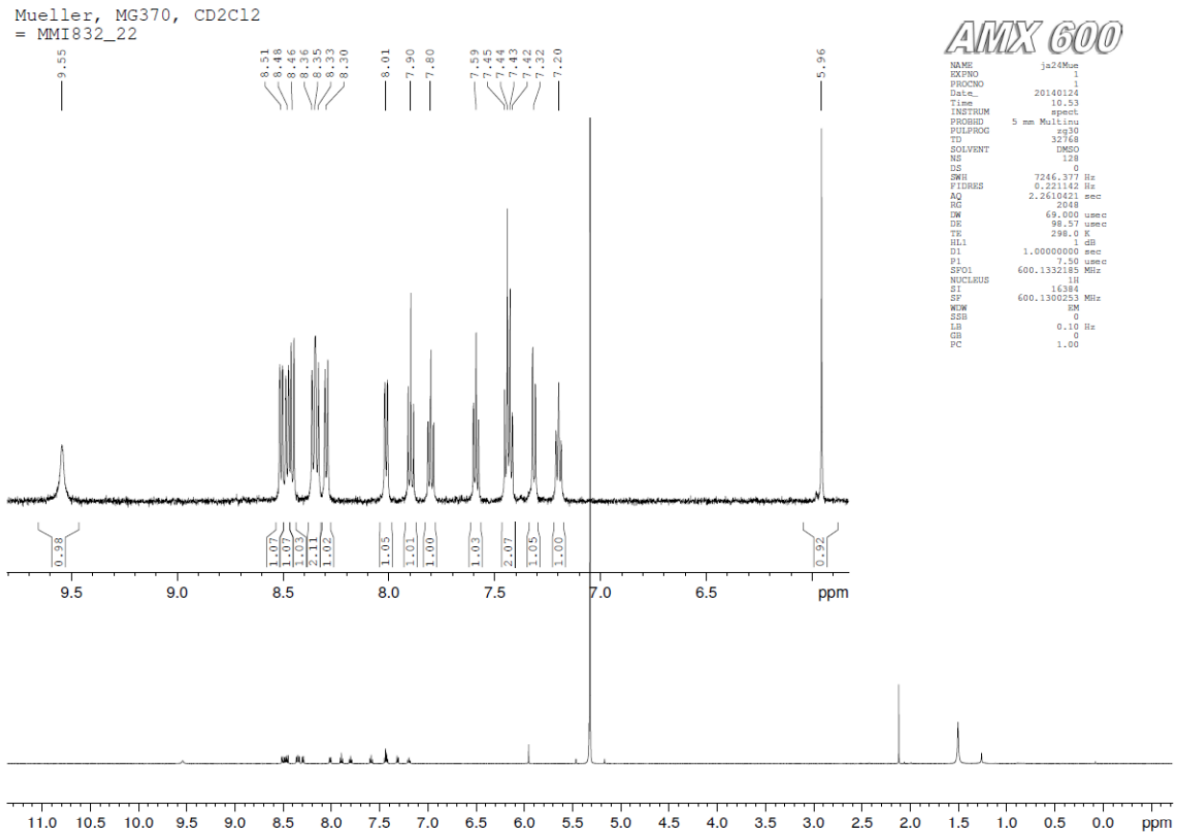
IR (KBr in cm^{-1}) spectrum of **1**



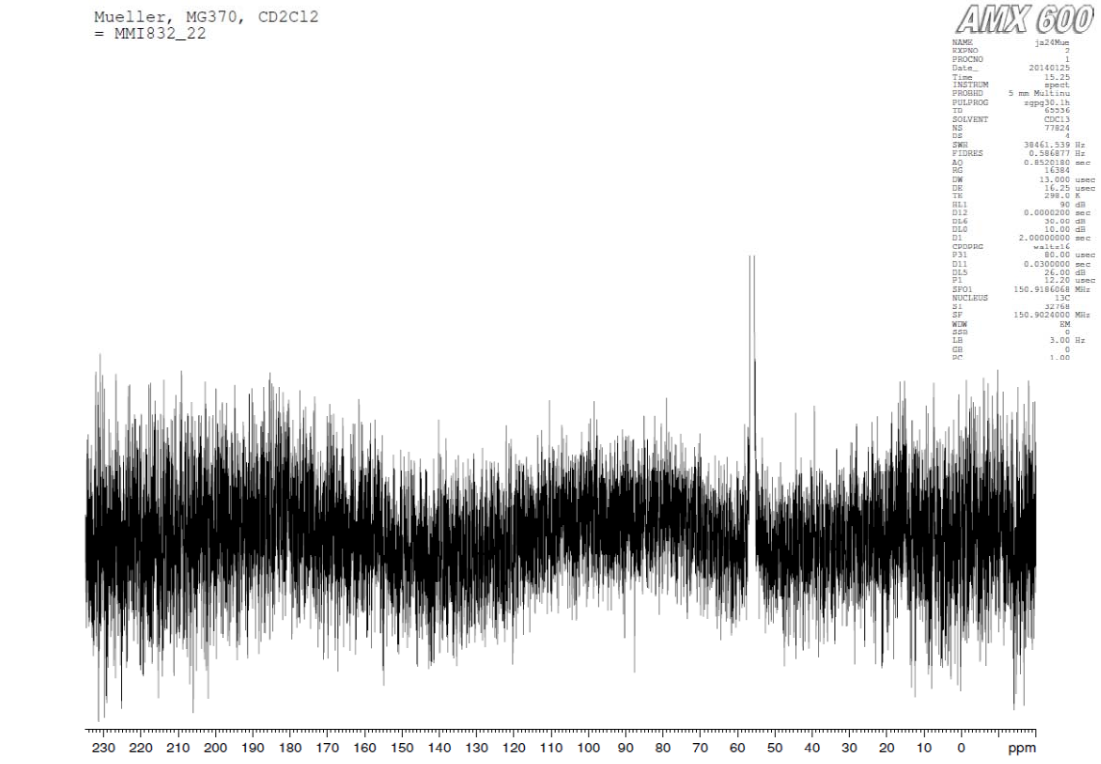
UV-Vis spectrum of **1** (267 nm/min, 2 nm slit, in nm) in different solvents



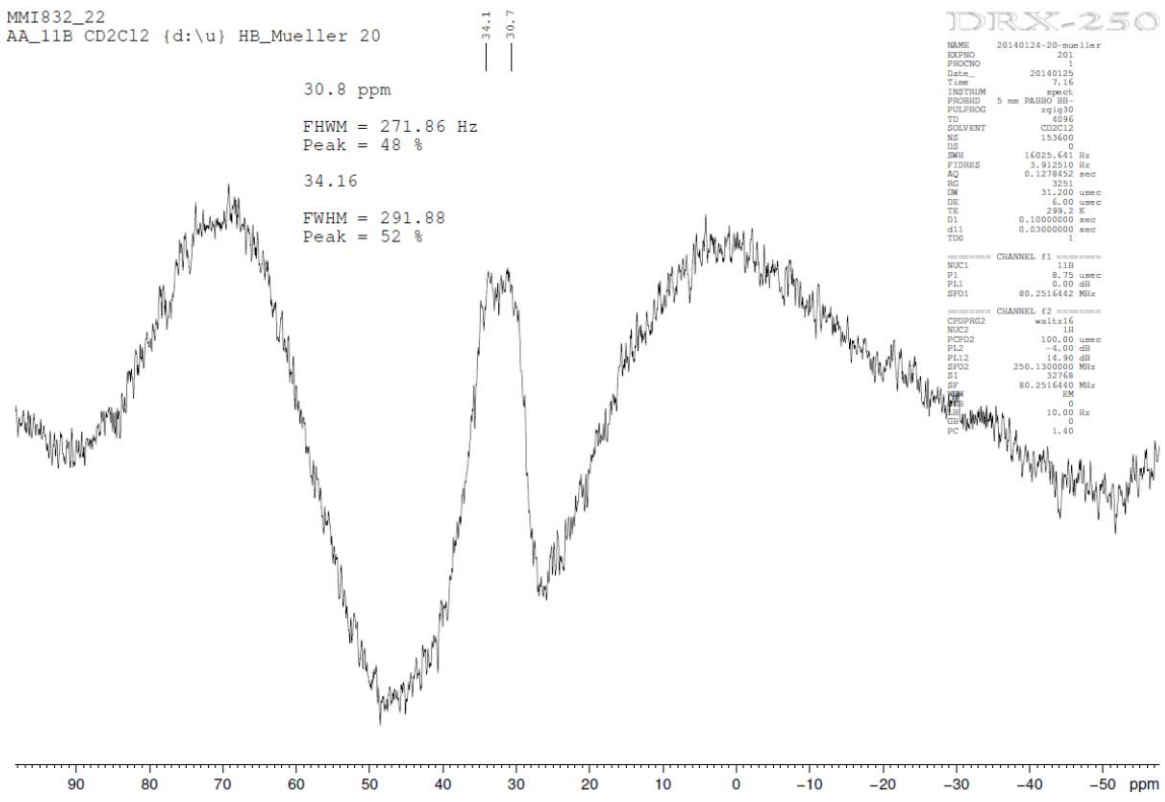
Fluorescence spectra of **1**, different solvents (in nm)



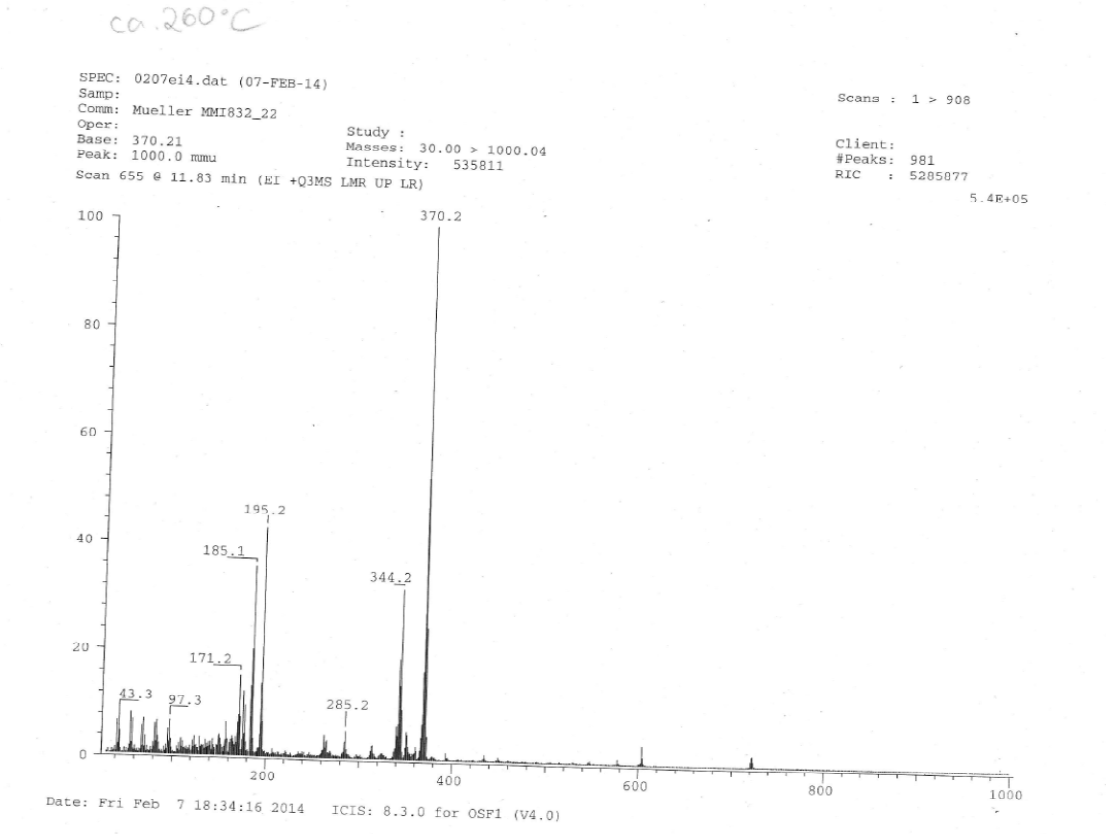
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **2**



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) spectrum, 78 k scans of **2**



$^{11}B\{^{1}H\}$ NMR (80 MHz, CD_2Cl_2) spectrum, 154 k scans of **2**



EI MS (70 eV) of **2**

Name: Müller Probenbezeichnung: **MMI832_22**

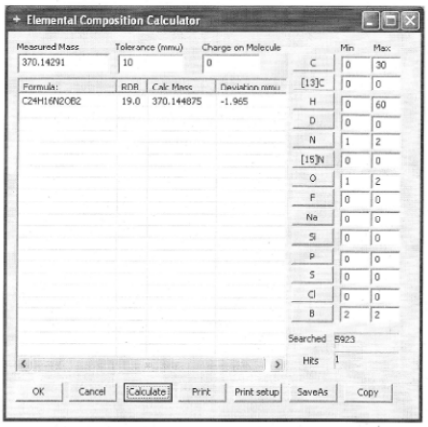
Ionisierungsmethode: **EI** ..X... **FAB** .....

Referenz - Ion und seine **exakte Masse:**

C_8F_{15} 381 380,97607

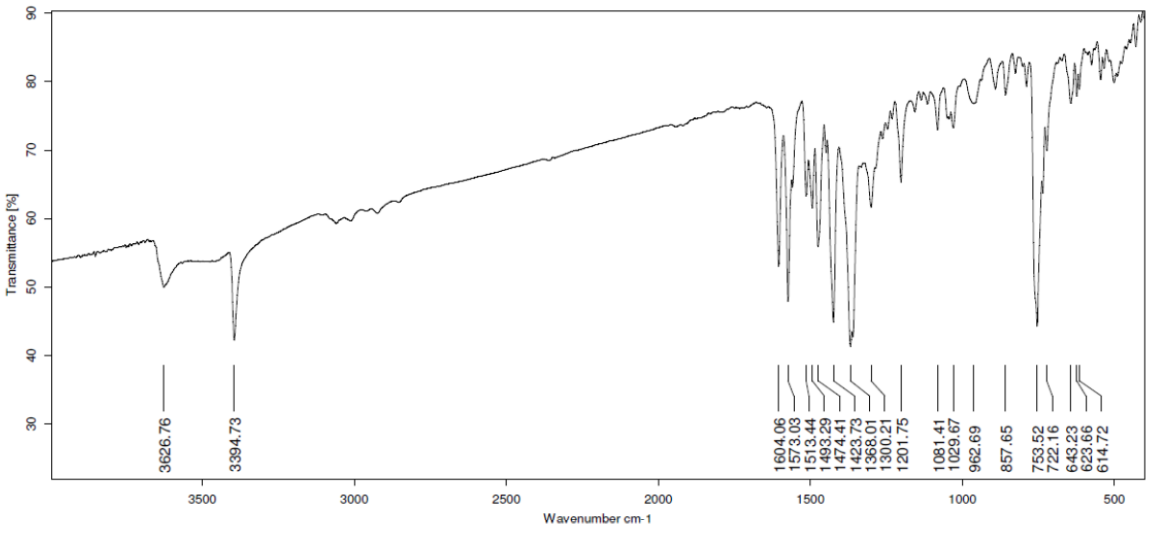
die **gefundene exakte Masse** erhält man zu: **370,14291**

damit ergibt/ergeben sich folgende **Elementkombination(en)** :

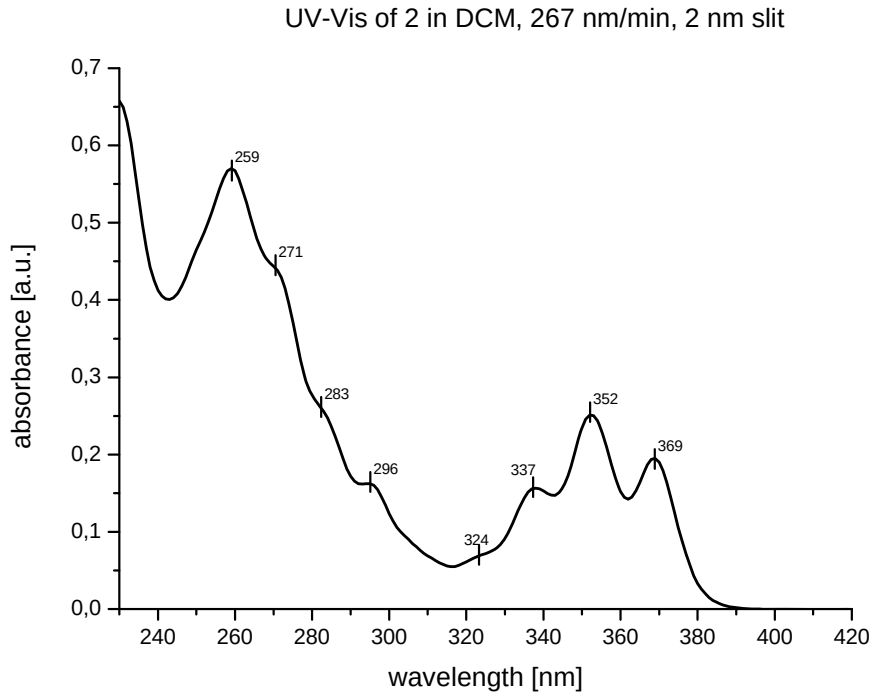


Datum 10. Feb. 2014 MS - Nummer 140202 Bearbeiter .....

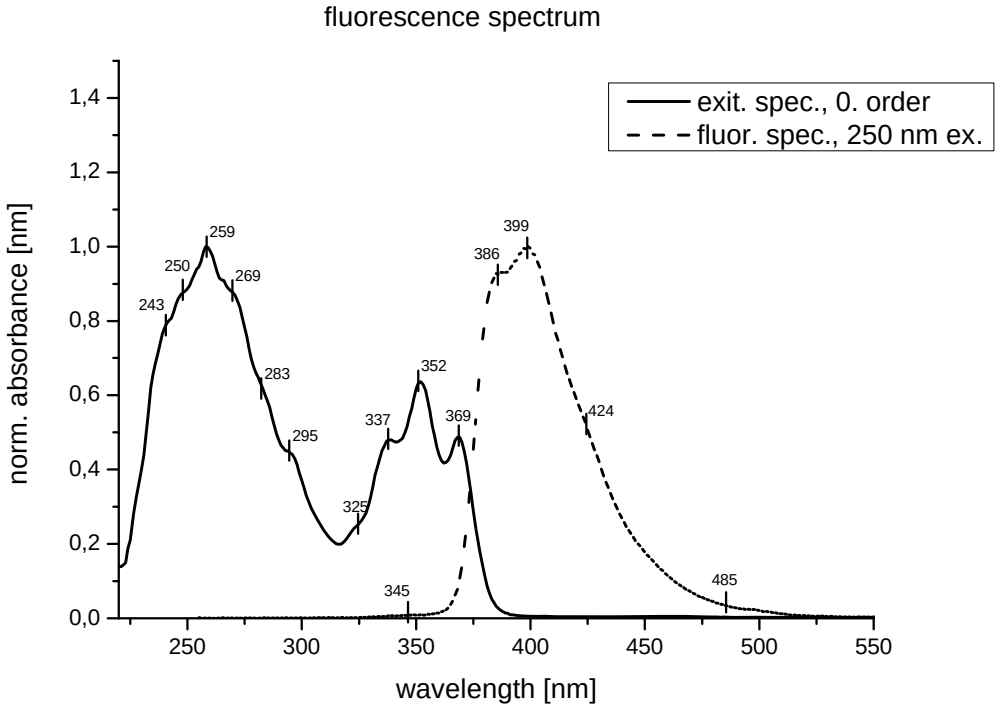
Exact mass determination (HRMS-EI, 70 eV) of **2**



IR (KBr in cm^{-1}) of **2**



UV-Vis spectrum of **2** in DCM, 267 nm/min, 2 nm slit (in nm)



fluorescence spectrum of **2** in DCM (in nm)

References

1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

2 a) S. Biswas, M. Müller, C. Tönshoff, K. Eichele, C. Maichle-Mössmer, A. Ruff, B. Speiser and H. F. Bettinger, *Eur. J. Org. Chem.*, 2012, **2012**, 4634; b) R. Köster, H. Bellut and S. Hattori, *Liebigs Ann. Chem.*, 1968, **720**, 1; c) R. Köster, K. Iwasaki, S. Hattori and Y. Morita, *Liebigs Ann. Chem.*, 1968, **720**, 23.

3 M. Müller, C. Maichle-Mössmer, P. Sirsch and H. F. Bettinger, *ChemPlusChem*, 2013, **78**, 988.