Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information (ESI)

## Reversible Photo-, Metallo- and Thermo-induced Morphological Dynamics of Bis-acylhydrazones

**Lars Ratjen and Jean-Marie Lehn***

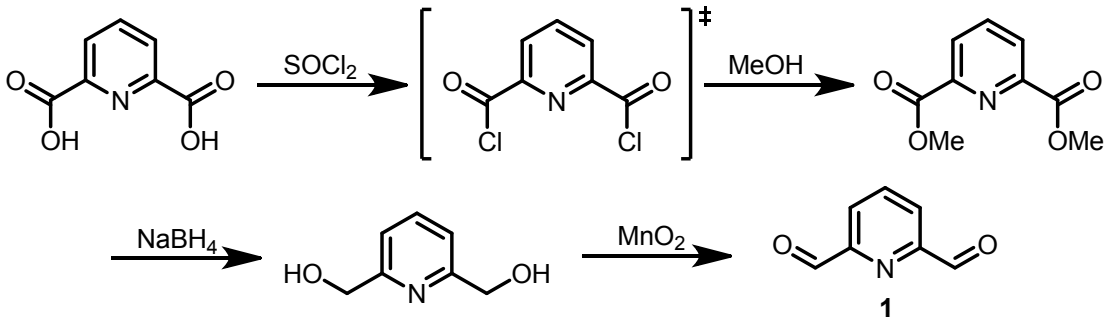
**NMR:** The NMR spectra were recorded on *Bruker* Avance 400 (400 MHz for $^{1}H$ and 100 MHz for $^{13}C$) and *Bruker* Avance III plus 400 (400 MHz for $^{1}H$, 100 MHz for $^{13}C$, 88.8 Mhz for $^{113}Cd$) NMR equipment. The spectra were referenced to the residual natural solvent peaks as reported by Nudelmann et al. (*J. Org. Chem.* **1997**, *62*, 7512-7515). For NMR-spectra recorded in $X/CD_3CN$, the $CH_3CN$-peak was chosen for calibration if not stated otherwise.

**MS:** ESI-MS measurements were conducted on *Bruker* Micro-TOF instruments.

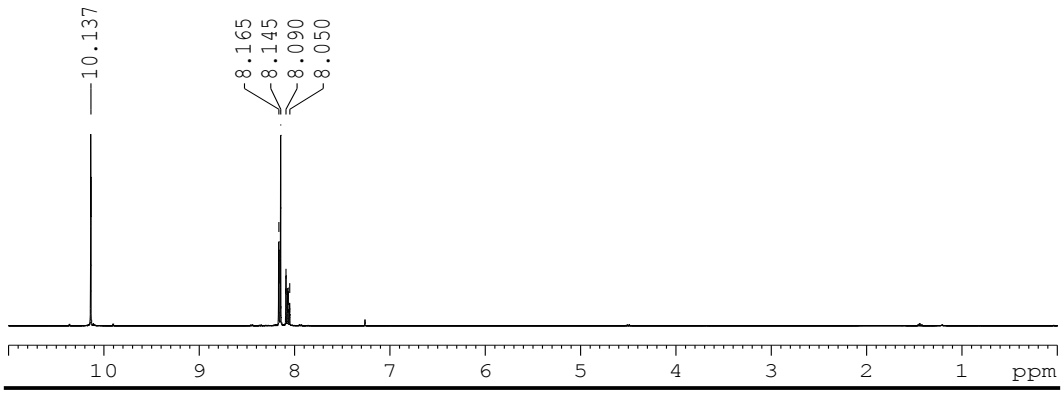
**UV-Irradiation:** All irradiations were performed with a Müller Elektronik Optik Light Source Model LAX 1000 / SVX 1000 and a xenon short arc lamp XBO 1000 W / HS OFR from Osram. Experiments were conducted in a thermostated glass bath at 25°C

**Chemicals and reagents and glassware:** Unless otherwise stated, chemicals and reagents for synthesis, as well as solvents for synthesis were utilized as delivered from commercial suppliers.

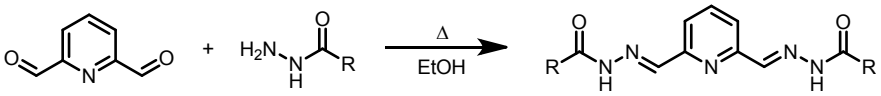
Dialdehyde **1** was prepared according to literature procedures (Cram et al., *J. Am. Chem. Soc.* **1977**, *99*, 6392-6398 and Reedijk et al., *Inorg. Chem.* **2008**, *47*, 6964-6973), the spectra of **1** correspond to the ones reported.




$^{1}H$-NMR-Spectrum ($CDCl_3$) of compound **1**:



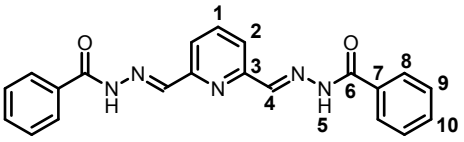
**Formation of Bisacylhydrazones**




The 2,6-pyridinedialdehyde and the corresponding hydrazide were mixed in a molar ratio of 1:2, suspended in EtOH [0.033 M] and heated to reflux temperature overnight (12-16 h). Subsequently the solvent was removed in vacuo, leading to the desired bisacylhydrazones which were used without further purification.

● Compound **1**-Ph:

**$^{1}$H-NMR (400 MHz, $CD_3CN$ DMSO-$d^6$ 3:1, δ in ppm):**
7.51 (t, 4H, -CH-**9**, 3J = 7.4 Hz), 7.58 (t, 2H, -CH-**10**, 3J = 7.2 Hz), 7.86-7.88 (m, 1H, -CH-**1**), 7.93 (d, 4H, -CH-**8**, 3J = 7.5 Hz), 7.97-7.98 (m, 2H -CH-**2**), 8.48 (s, 2H, -CH-**4**), 11.81 (s, 2H, -NH-**5**).



Chemical Formula: $C_{21}H_{17}N_5O_2$
Exact Mass: 371,138
Molecular Weight: 371,392

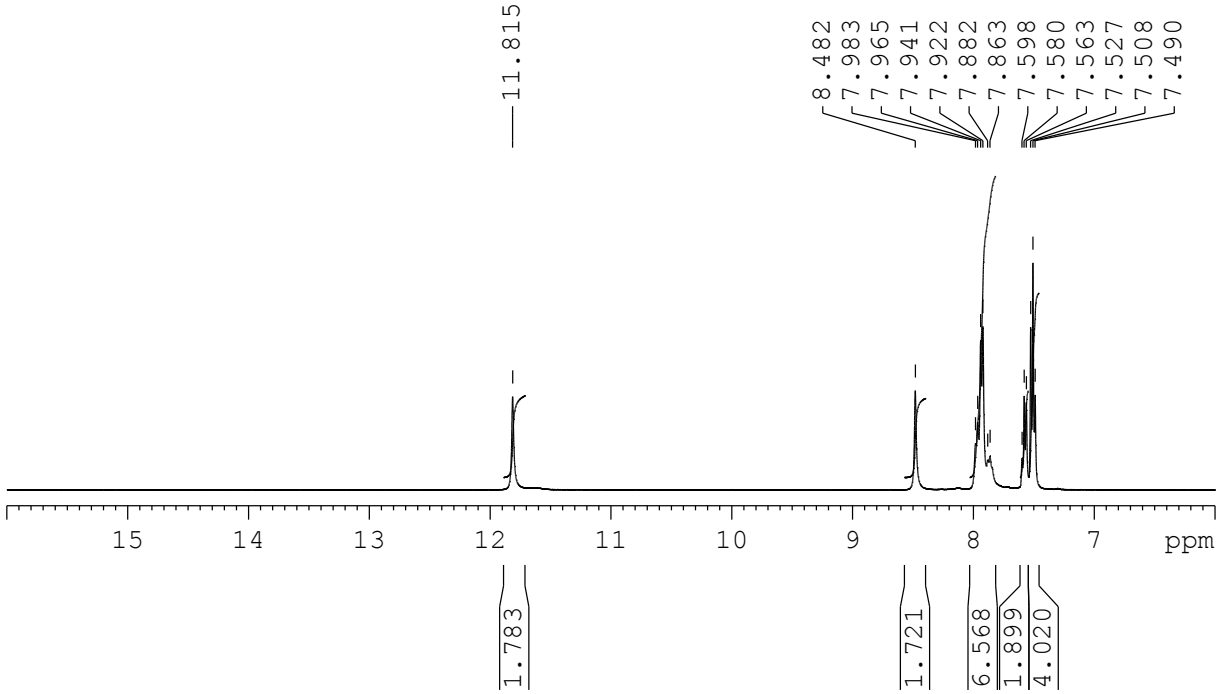
**$^{13}$C-NMR (100 MHz, $CD_3CN$ DMSO-$d^6$ 3:1, δ in ppm):**
120.50(-C**2**), 127.83 (-C**8**), 128.51 (-C**9**), 131.91 (-C**10**), 133.58 (-C**7**), 137.40 (-C**1**), 147.76 (-C**4**), 153.67 (-C**3**), 163.94 (-C**6**).

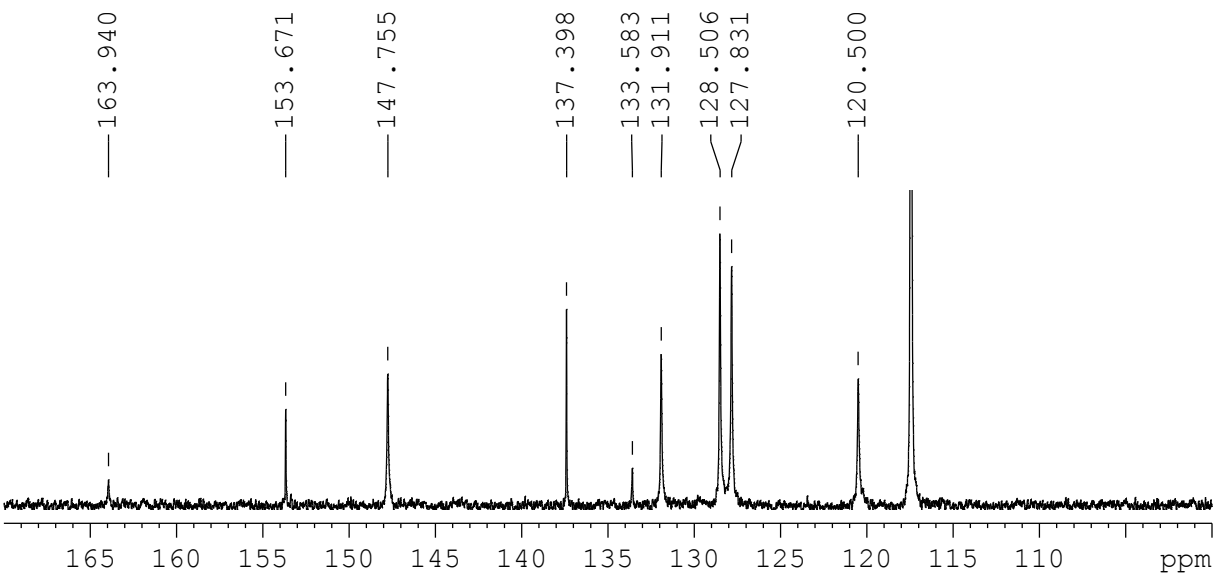
**MS (ESI-pos) m/z (M+Na):** 394.126.

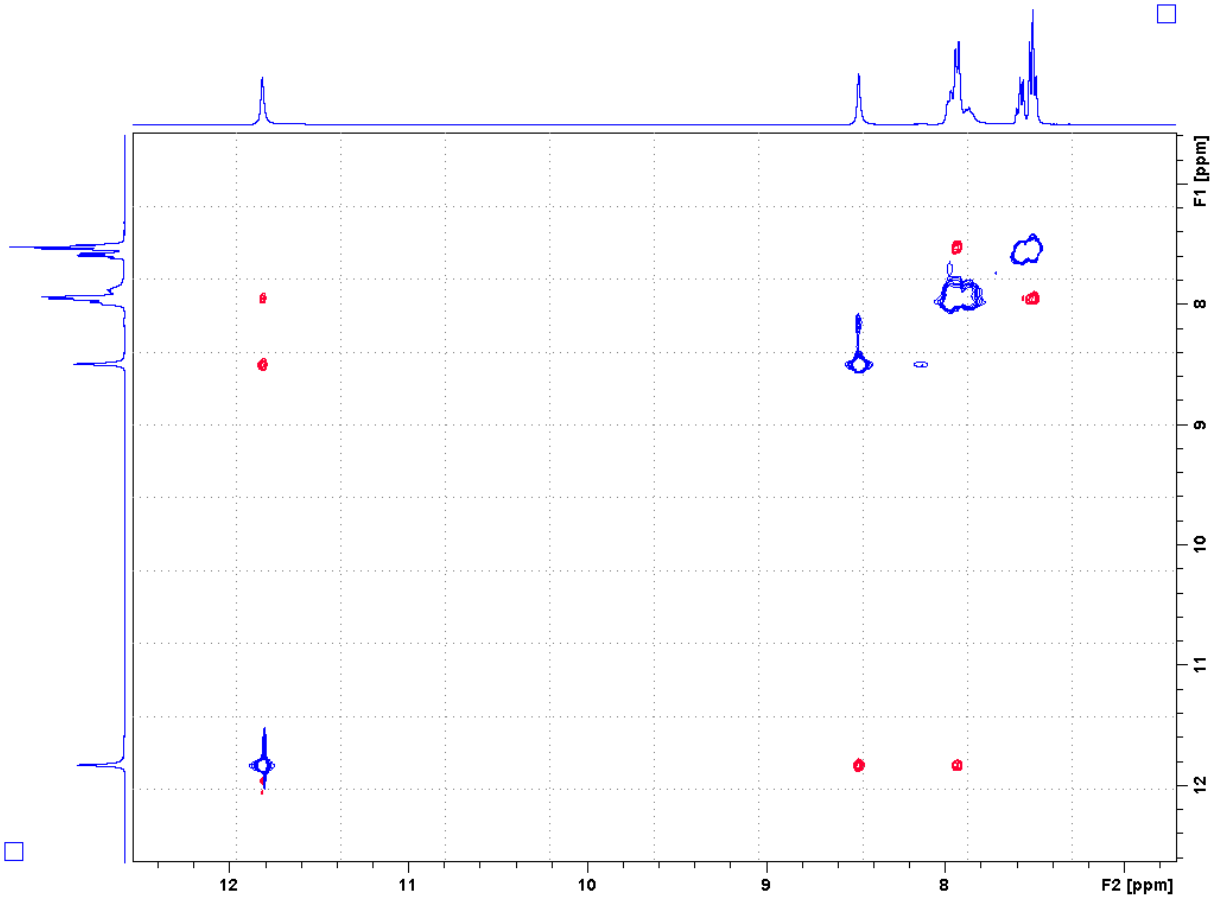
**M.P.**: 259-263°C.

**Elemental analysis** $C_{21}H_{17}N_5O_2$ (in %), calcd. C: 67.91; H: 4.61; N: 18.86.

found. C: 67.62; H: 4.58; N: 18.64.

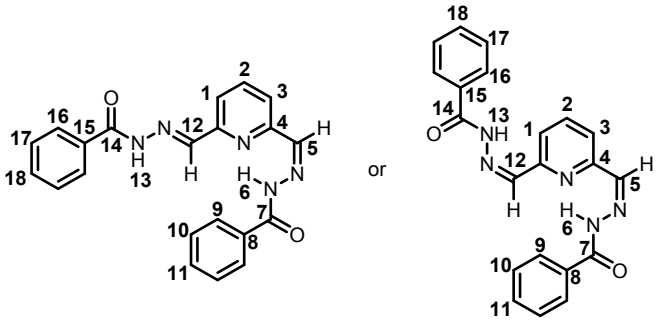



163.940
153.671
147.755
137.398
133.583
131.911
128.506
127.831
120.500
165
160
155
150
145
140
135
130
125
120
115
110
ppm

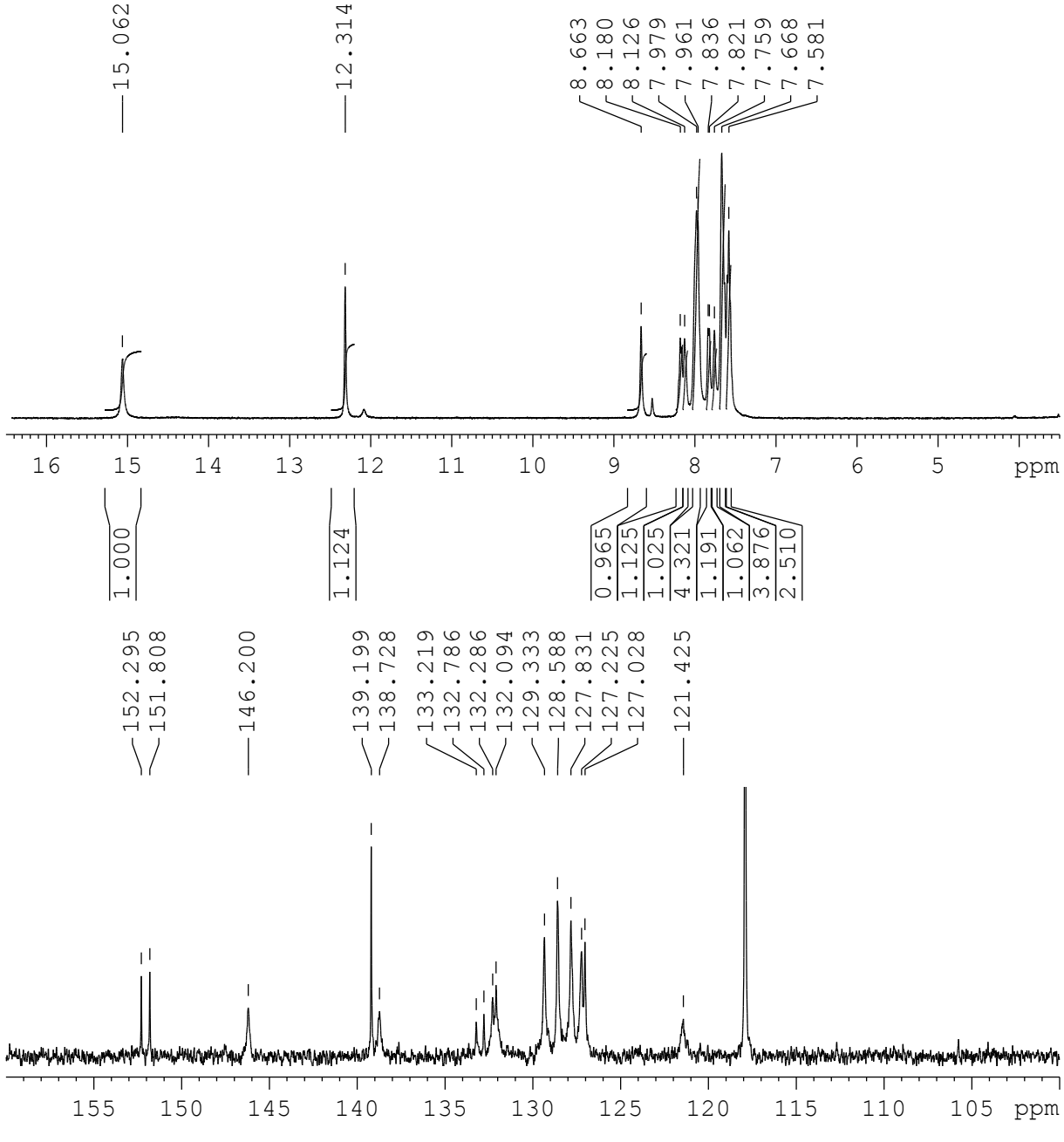

F1 [ppm]
8
9
10
11
12
12
11
10
9
8
F2 [ppm]

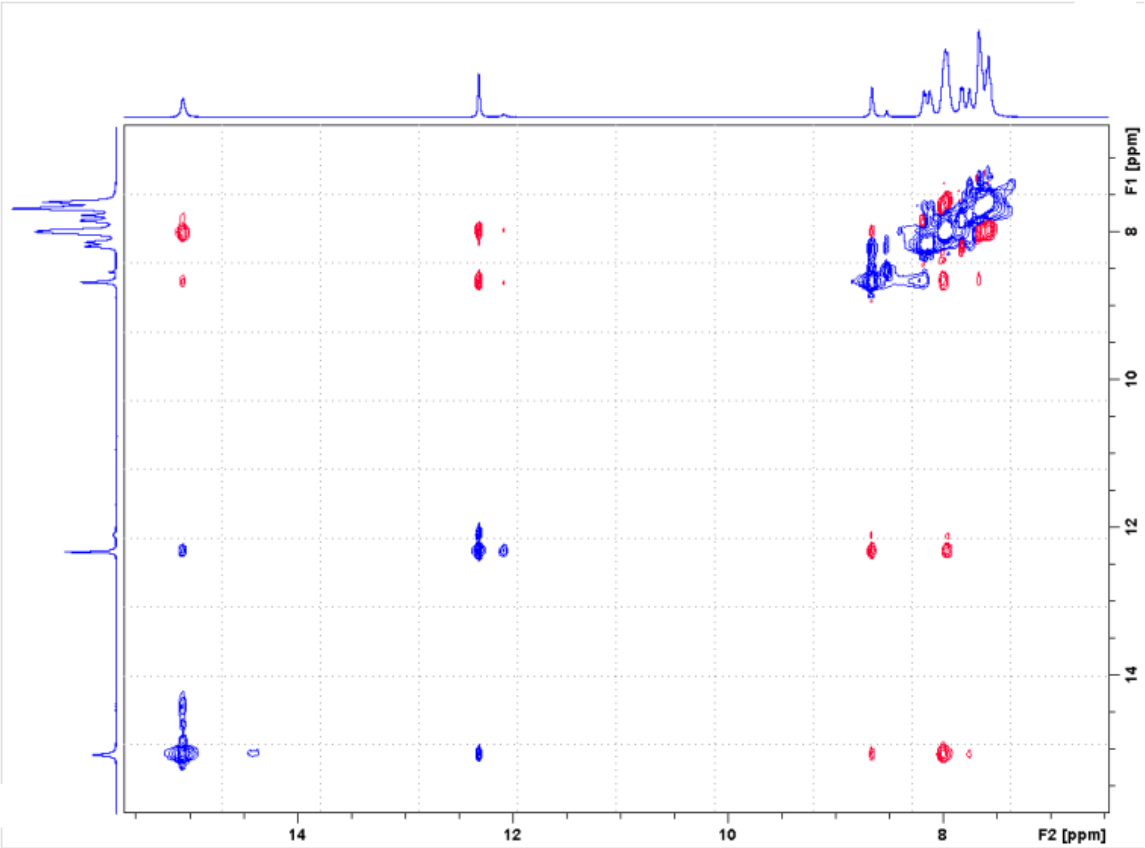
*EZ*-**1**-Ph:

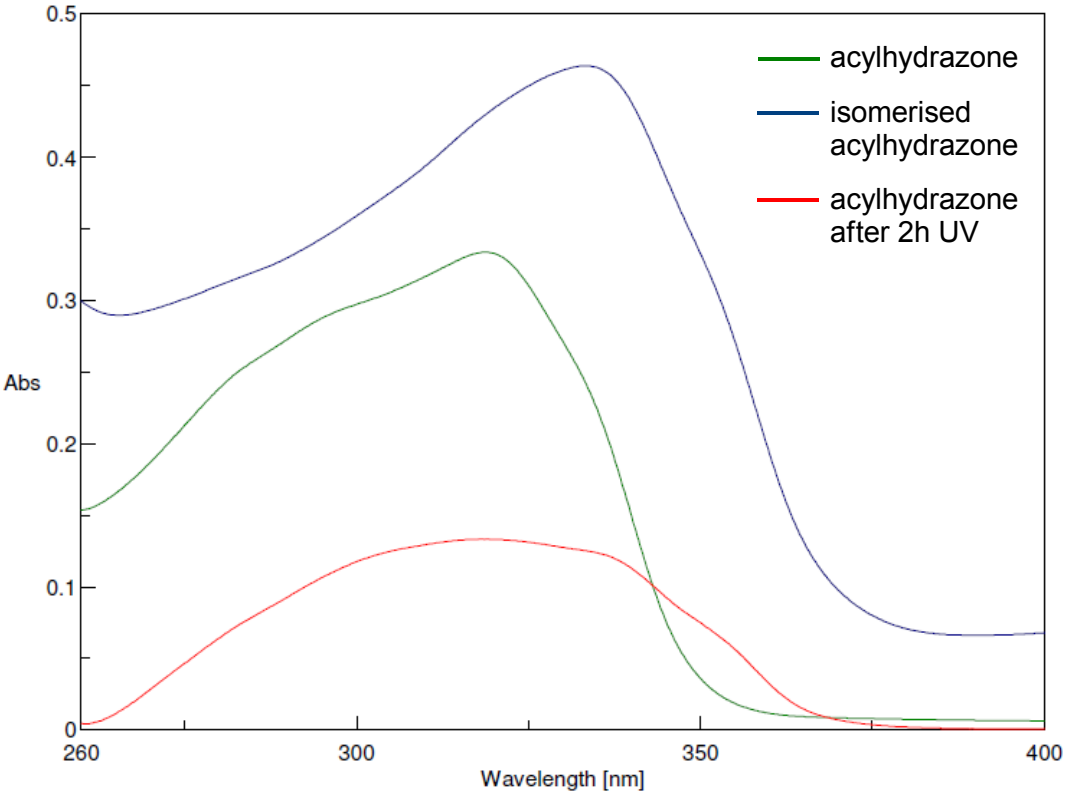
**$^{1}$H-NMR (400 MHz, DMSO-d$^{6}$/CD$_3$CN 8:1, δ in ppm):** 7.58-7.67 (m, 6H, -CH-**11,** -CH-**18**, -CH-**10,** -CH-**17**), 7.76 (s, 1H, -CH-**5**), 7.83 (d, 1H, 3J = 6.2 Hz, -CH-**3**), 7.96-7.98 (m, 4H, -CH-**9**, -CH-**16**), 8.13-8.18 (m, 2H, -CH-**1**, -CH-**2**), 8.66 (s, 1H, -CH-**12**), 12.31 (s, 1H, -CH-**13**), 15.06 (s, 1H, -CH-**6**).



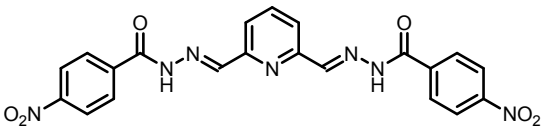

**$^{13}$C-NMR (100 MHz, DMSO-d$^{6}$/CD$_3$CN 8:1, δ in ppm):** The $^{13}$C-NMR-Signals could not be unambiguously assigned and appeared with significant broadening.




F1 [ppm]
8
10
12
14
14
12
10
8
F2 [ppm]


acylhydrazone
isomerised acylhydrazone
acylhydrazone after 2h UV
Abs
0.5
0.4
0.3
0.2
0.1
0
260
300
350
400
Wavelength [nm]

● Compound **1**-$NO_2$:



Chemical Formula: $C_{21}H_{15}N_7O_6$
Exact Mass: 461,108
Molecular Weight: 461,387

**$^1$H-NMR (400 MHz, DMSO-d$^6$, δ in ppm):** 7.98-8.05 (m, 3H), 8.17 (d, 4H, 3J = 7.6 Hz), 8.37 (d, 4H, 3J = 7.9 Hz), 8.52 (s, 2H), 12.31 (s, 2H).

**$^{13}$C-NMR (100 MHz, DMSO-d$^6$, δ in ppm):** 120.95, 123.76, 129.33, 137.86, 138.77, 148.58, 149.44, 153.09, 161.87.

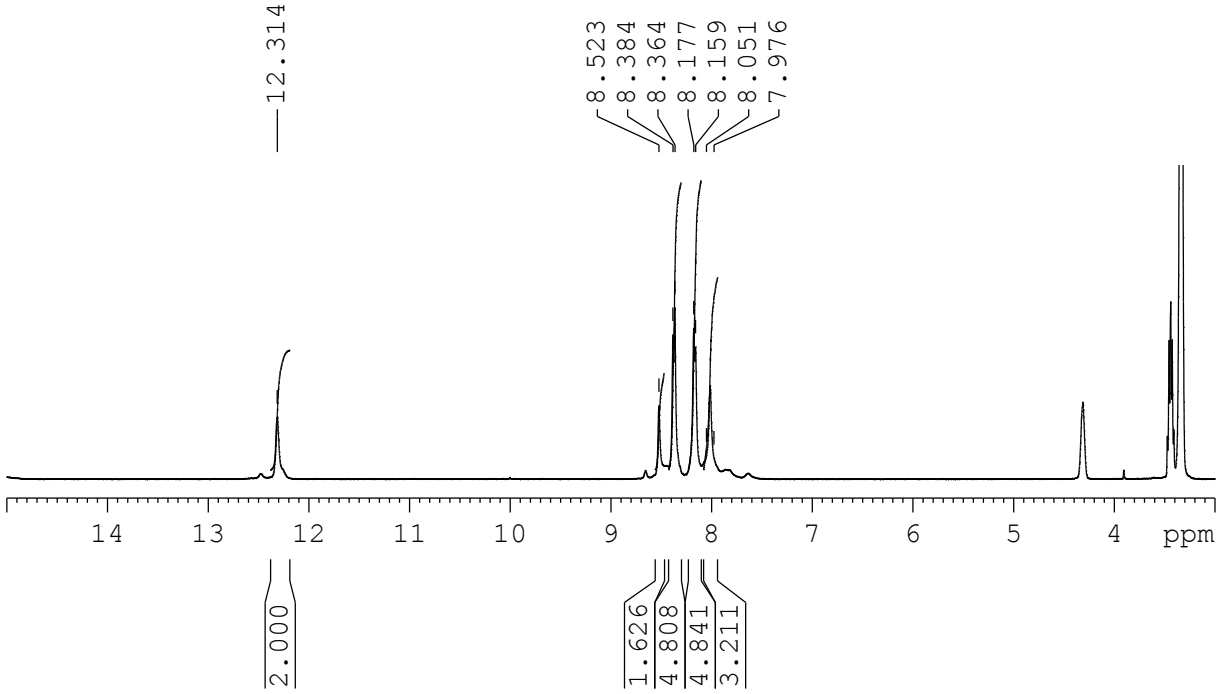
**MS (ESI-pos) m/z (M+Na):** 484.096.

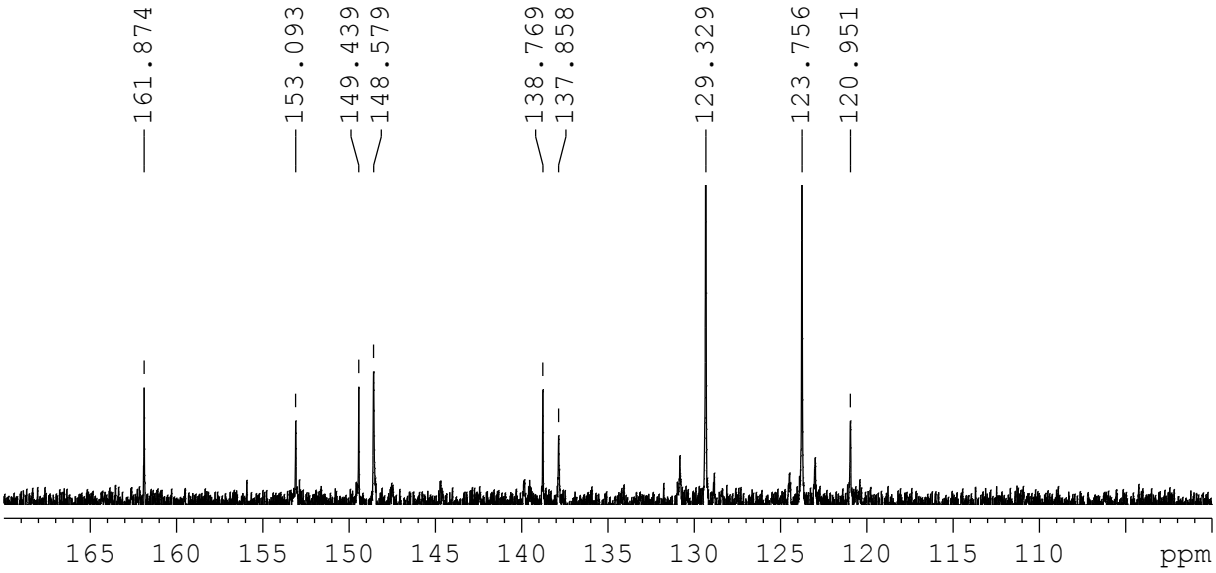
**M.P.:** >300°C.

The compound was almost insoluble in any organic solvent, including DMSO, therefore the NMR-signals are very broad and badly resolved.

**Elemental analysis** $C_{21}H_{15}N_7O_6 + H_2O$ (in %), calcd. C: 52.61; H: 3.57; N: 20.45.

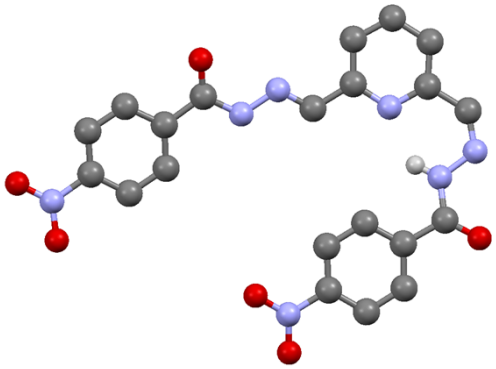
found. C: 52.63; H: 3.65; N: 20.31.






**X-Ray:** A crystal suitable for structure determination could be obtained for the isomerized material *EZ*-**1**-$NO_2$. For this purpose DMSO was heat saturated with the crude reaction product of **1**-$NO_2$ and after several days crystals formed, which proved to be EZ-**1**-$NO_2$.

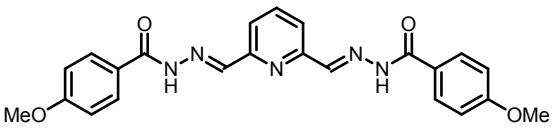
Structure *EZ*-1-$NO_2$, for details see **CCDC 1016567** (Cambridge Crystallographic Data Centre):



Formula: C21 H15 N7 O6,C2 H6 O1 S1
Unit Cell Parameters: a 9.4719(4) b 11.4442(5) c 11.8275(6) P-1

● Compound **1**-MeO:

**$^1$H-NMR (400 MHz, DMSO-d$^6$, δ in ppm):** 3.84 (s, 6H), 7.08 (d, 4H, 3J = 8.8 Hz), 7.94 (d, 4H, 3J = 9.0 Hz), 7.96-7.99 (m, 3H), 8.50 (s, 2H), 11.98 (s, 2H).




Chemical Formula: $C_{23}H_{21}N_5O_4$
Exact Mass: 431,159
Molecular Weight: 431,444

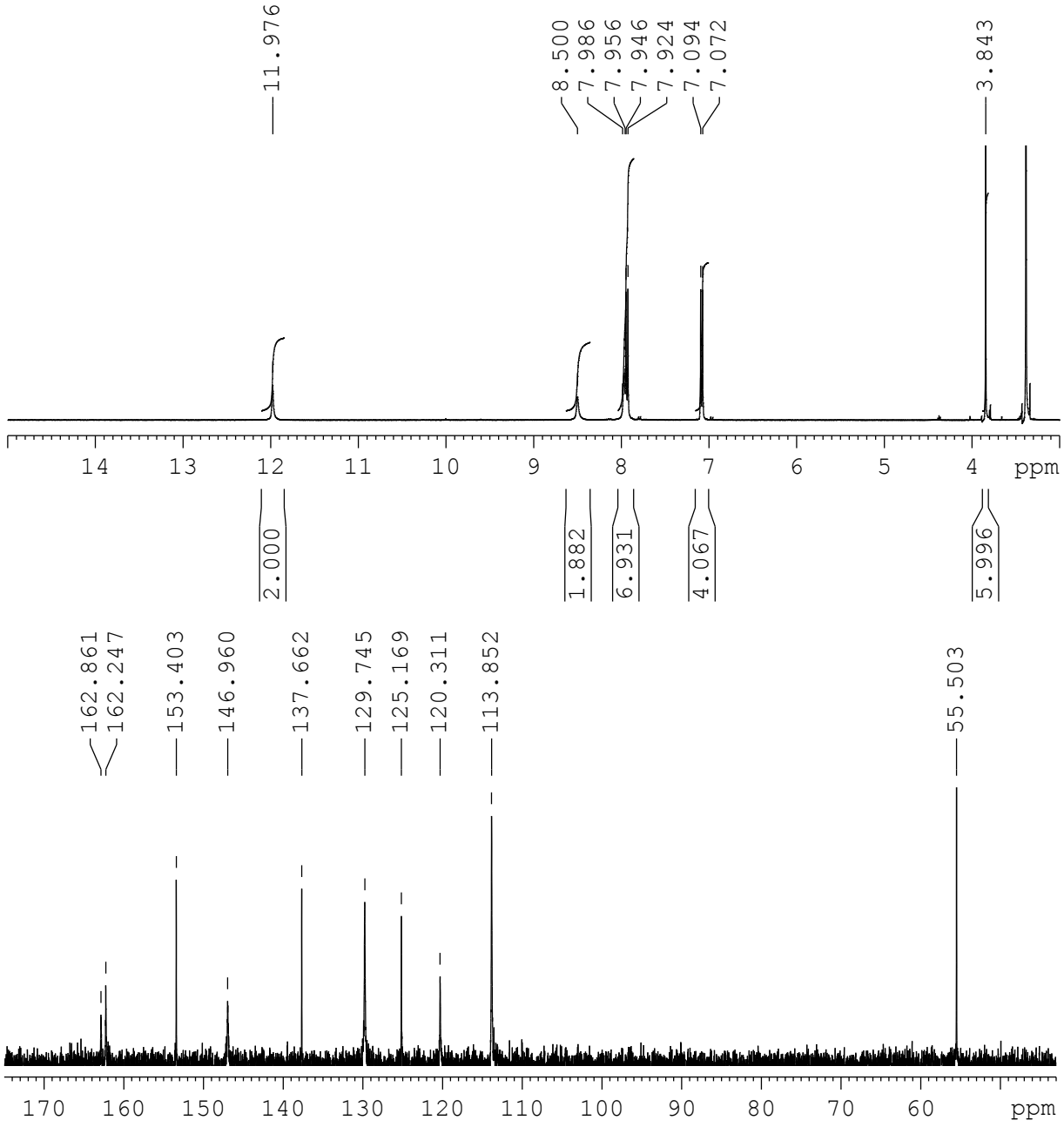
**$^{13}$C-NMR (100 MHz, DMSO-d$^6$, δ in ppm):**
55.50, 113.85, 120.31, 125.17, 129.75, 137.66, 146.96, 153.40, 162.25, 162.86.

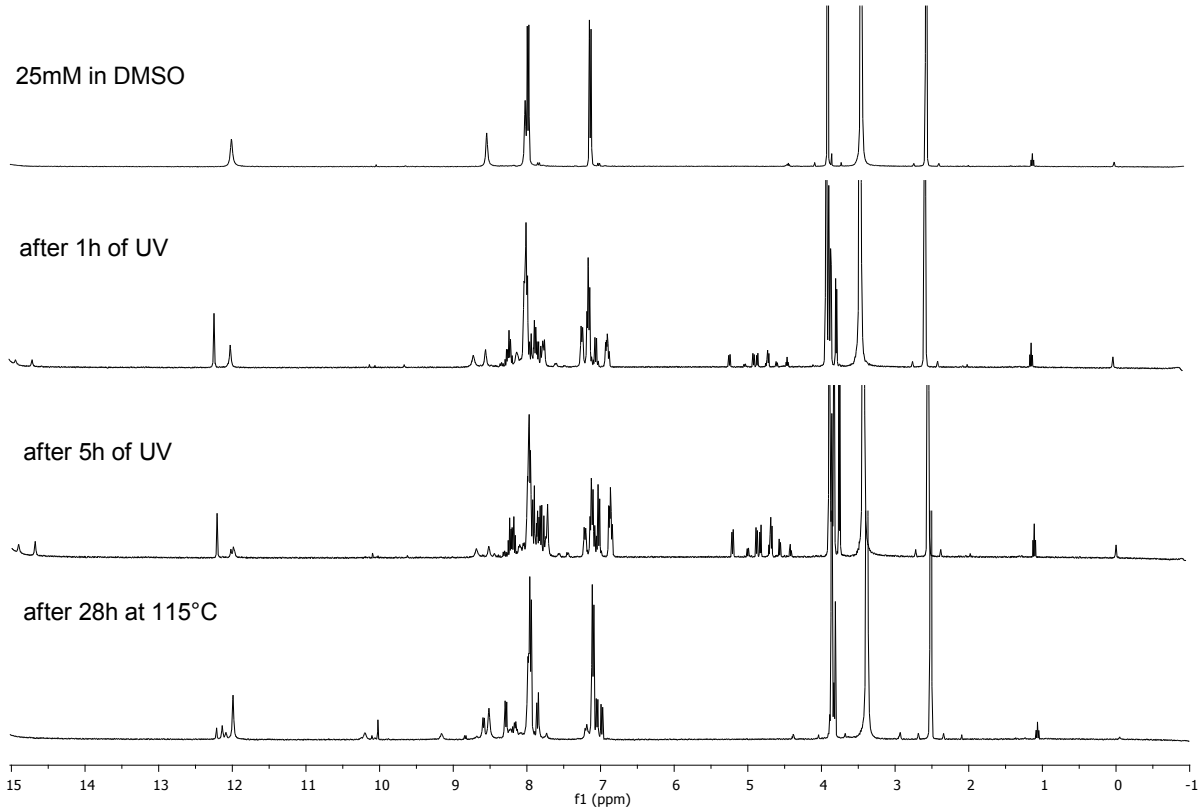
**MS (ESI-pos) m/z (M+Na):** 454.146.

**M.P.:** 268-271°C.

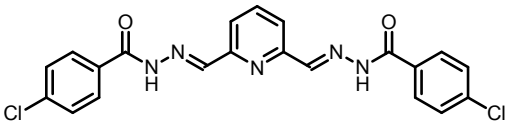
**Elemental analysis** $C_{23}H_{21}N_5O_4$ (in %), calcd. C: 64.03; H: 4.91; N: 16.23.

found. C: 63.71; H: 4.95; N: 15.98.






● Compound **1**-Cl:




Chemical Formula: $C_{21}H_{15}Cl_2N_5O_2$
Exact Mass: 439,060
Molecular Weight: 440,282

**$^{1}$H-NMR (400 MHz, DMSO-d$^{6}$, δ in ppm):** 7.63 (d, 4H, 3J = 8.3 Hz), 7.95-8.00 (m, 7H), 8.50 (s, 2H), 12.16 (s, 2H).

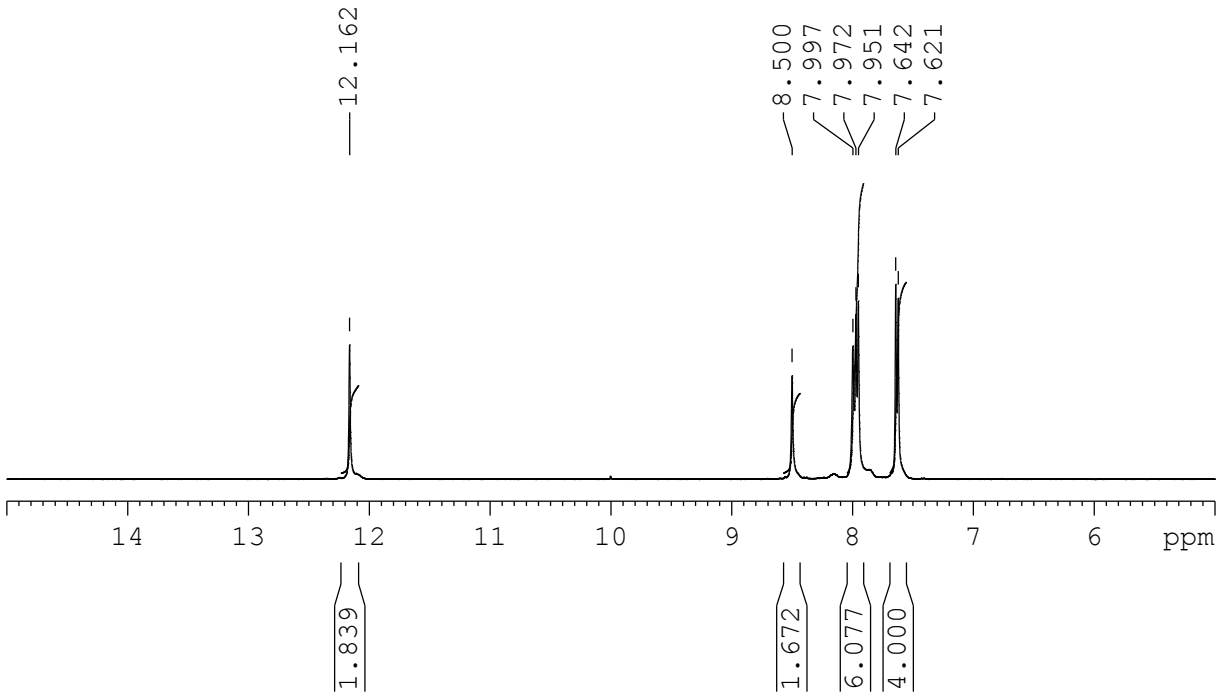
**$^{13}$C-NMR (100 MHz, DMSO-d$^{6}$, δ in ppm):** 120.69, 128.74, 129.73, 131.87, 136.93, 137.79, 147.84, 153.24, 162.44.

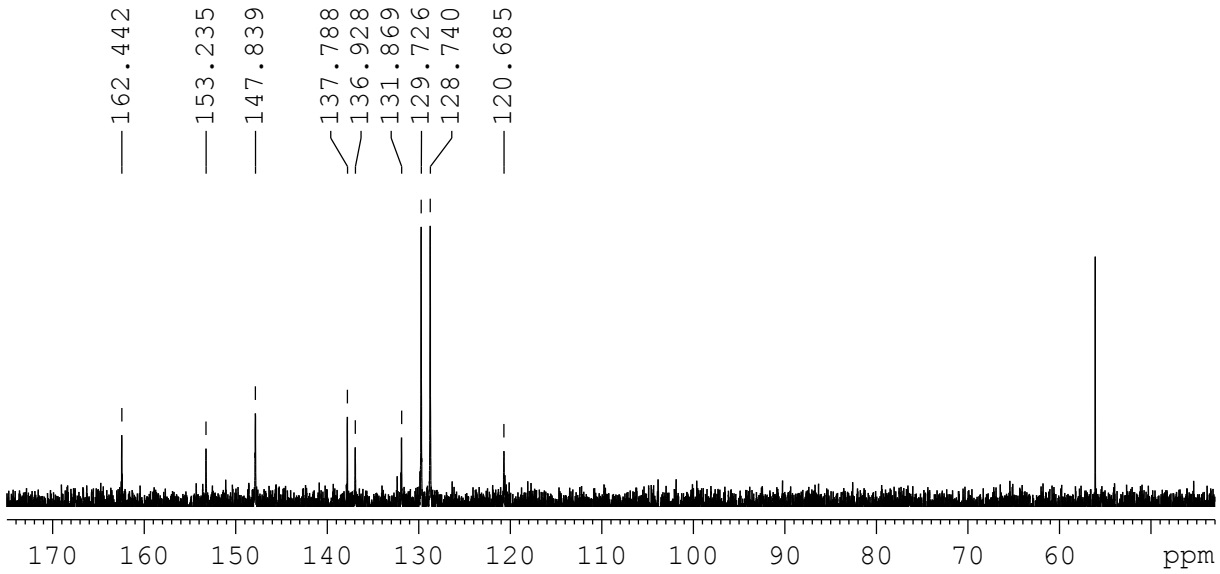
**MS (ESI-pos) m/z (M+Na):** 462.046.

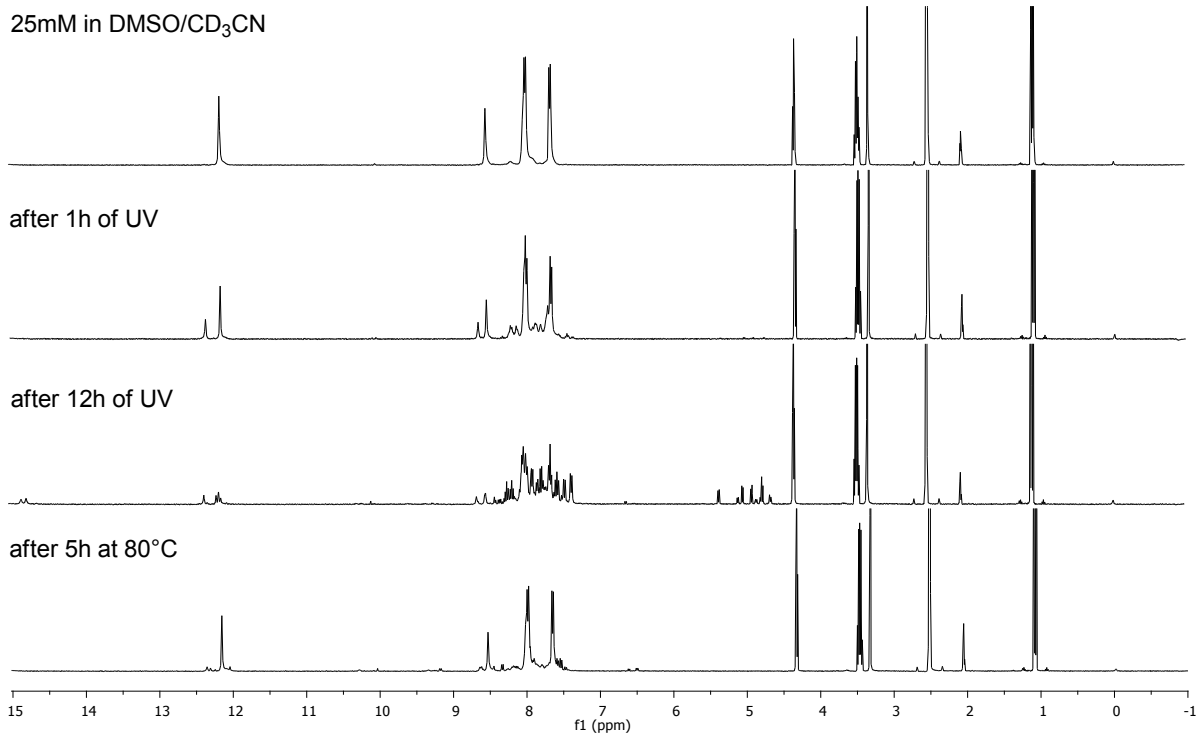
**M.P.:** >300°C.

**Elemental analysis** $C_{21}H_{15}Cl_2N_5O_2$ (in %), calcd. C: 57.29; H: 3.43; N: 15.91.

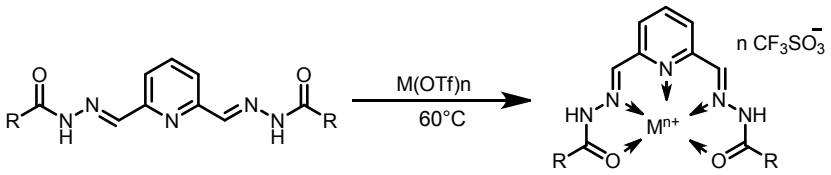
found. C: 56.89; H: 3.49; N: 15.88.


12.162
8.500
7.997
7.972
7.951
7.642
7.621
14
13
12
11
10
9
8
7
6
ppm
1.839
1.672
6.077
4.000


162.442
153.235
147.839
137.788
136.928
131.869
129.726
128.740
120.685
170
160
150
140
130
120
110
100
90
80
70
60
ppm



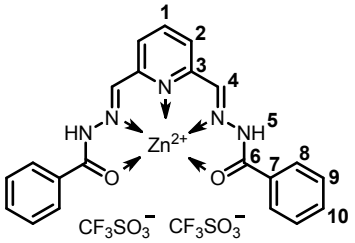

## Formation of 5-point-binding complexes using bisacylhydrazones as ligands




The ligand and the metal triflate are mixed in the appropriate solvent and reacted at 60°C. Completion of the complex formation could be easily followed by NMR.

● Compound **1**-Ph(Zn):

**$^{1}$H-NMR (400 MHz, $CD_3CN$/DMSO-$d^6$ 3:1, δ in ppm):** 7.67 (t, 4H, -CH-**9**, 3J = 7.5 Hz), 7.77 (t, 2H, -CH-**10**, 3J = 7.3 Hz), 8.00 (d, 2H, -CH-**2**, 3J = 7.8 Hz), 8.17 (d, 4H, -CH-**8**, 3J = 7.6 Hz), 8.27 (t, 1H, -CH-**1**, 3J = 7.5 Hz), 8.59 (s, -CH-**4**, 2H), 13.98 (bs, 2H, -NH-**5**).



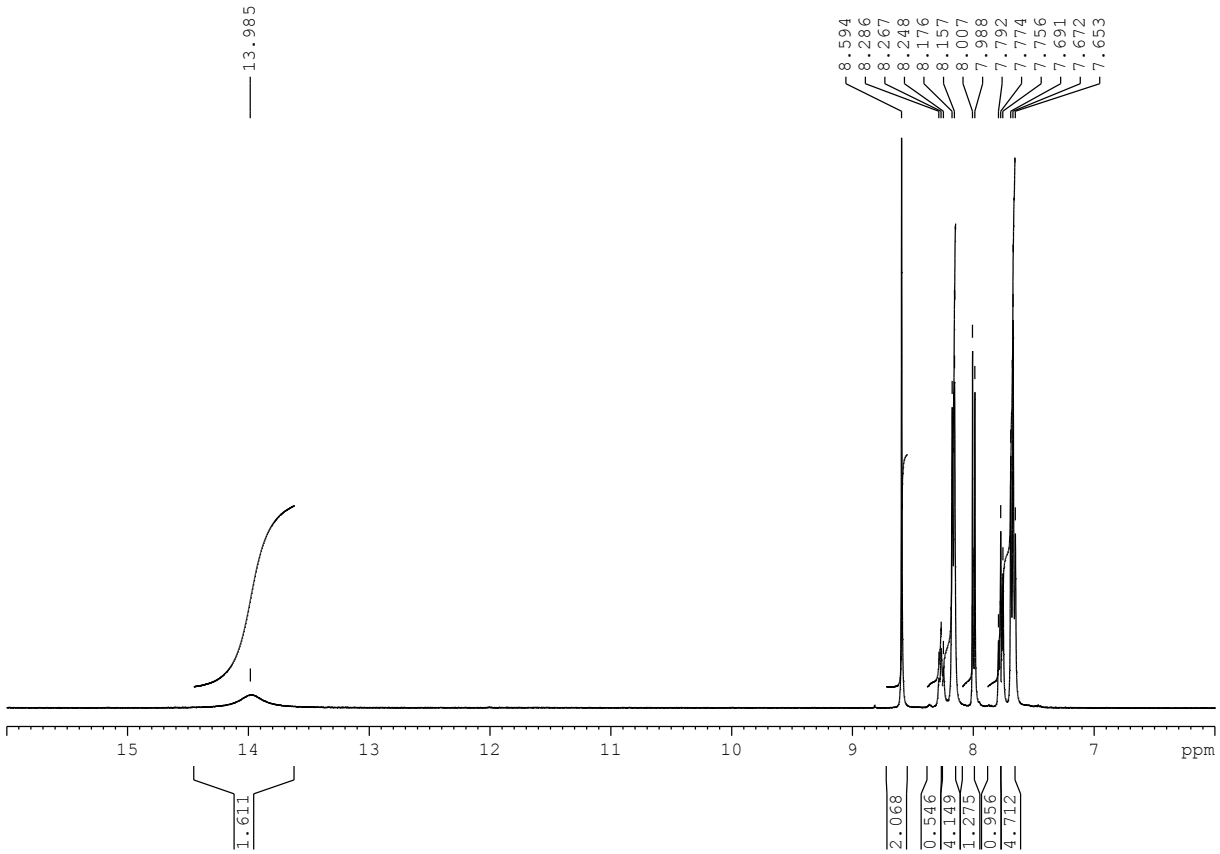

Chemical Formula: $C_{23}H_{17}F_6N_5O_8S_2Zn$
Exact Mass: 732,971
Molecular Weight: 734,910

**$^{13}$C-NMR (100 MHz, $CD_3CN$/DMSO-$d^6$ 3:1, δ in ppm):**121.12 (q, $\underline{C}F_3$, $^{C\text{-}F}J$ = 321.3 Hz), 127.09 (-C**2**) 128.51 (-C**9**), 129.30 (-C**8**), 129.81(-C**7**), 134.30 (-C**10**), 140.47 (-C**4**), 142.62 (-C**1**), 147.10 (-C**3**), 167.21 (-C**6**).

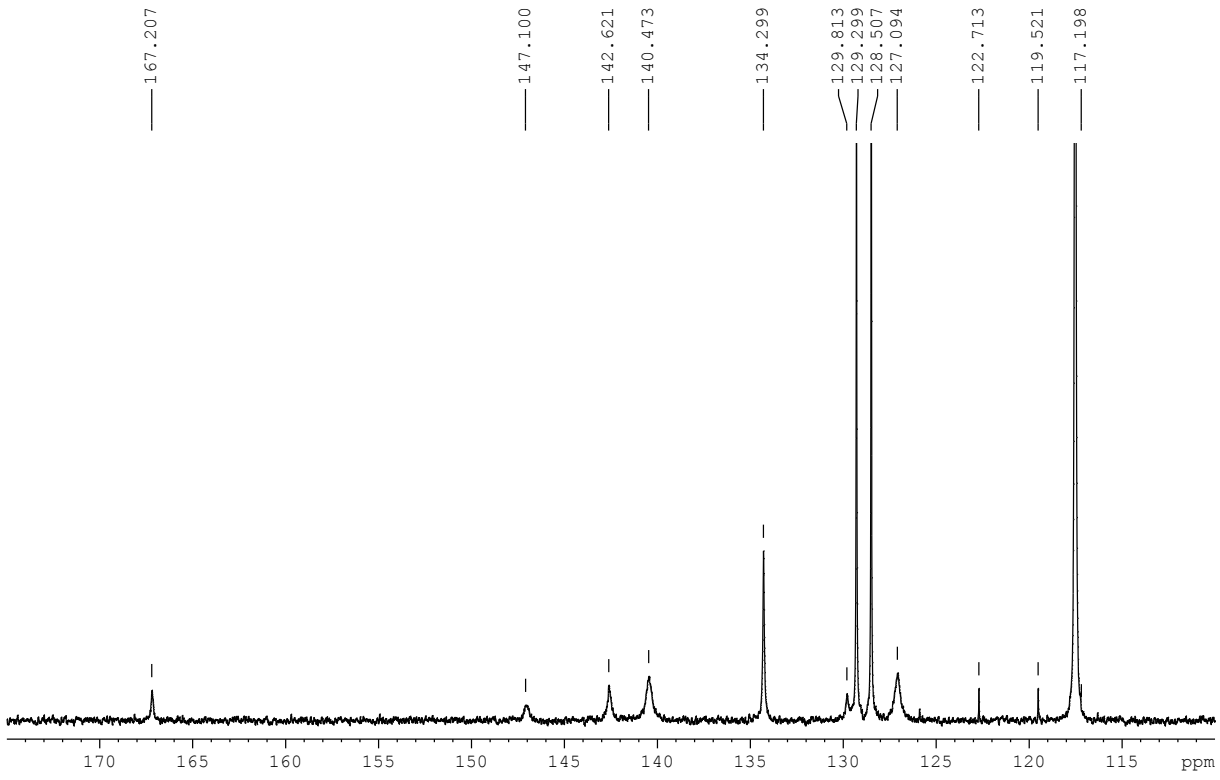
**MS (ESI-pos) m/z:** 584.016 ($Zn^{2+}L\cdot TfO^-$), 434.057 ($Zn^{2+}$L-H), 217.534 ($Zn^{2+}$L/2).

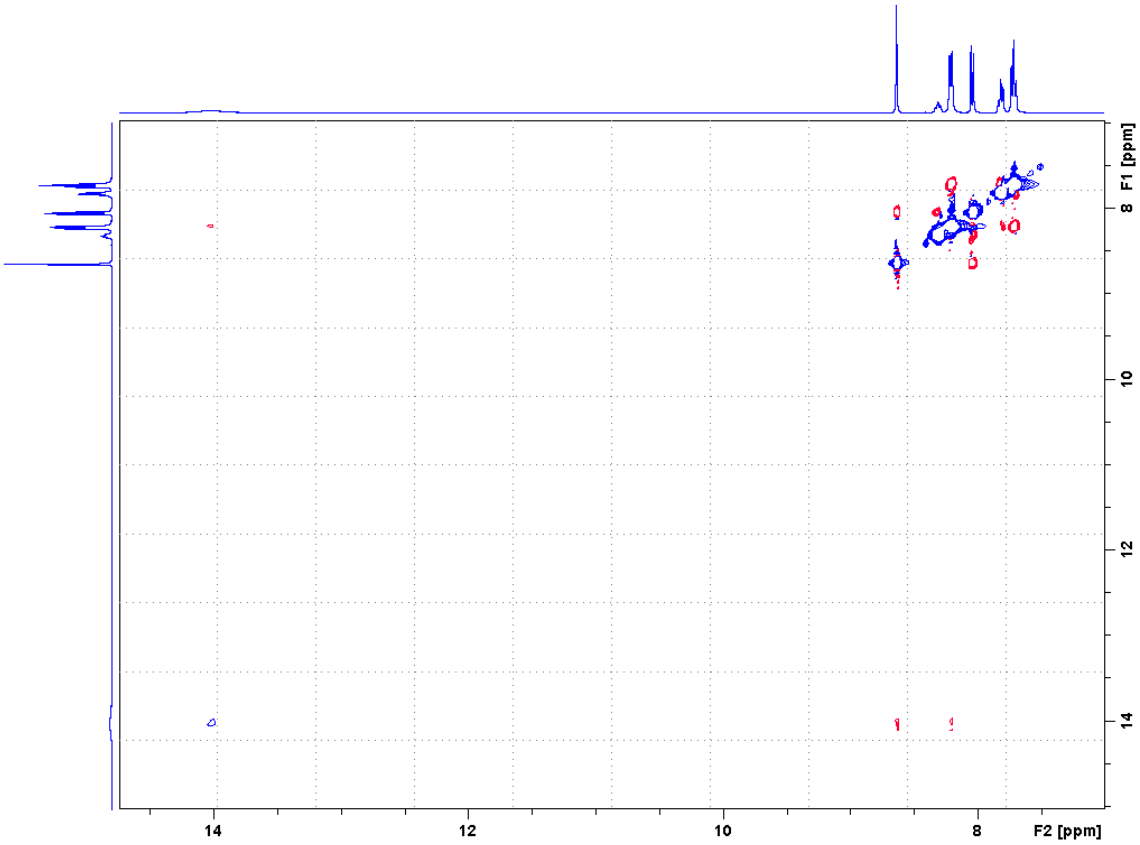
**HRMS (ESI-pos) m/z:** calcd. 217.533, found 217.534 ($Zn^{2+}$L/2).

Calibrated on CD3CN:



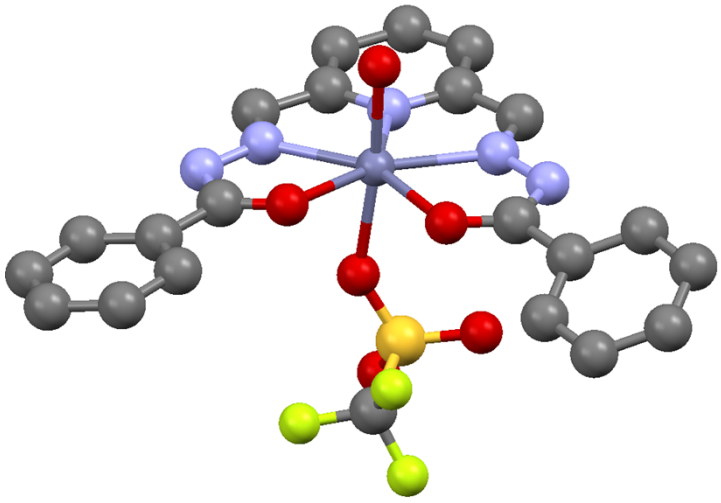

Calibrated on DMSO:





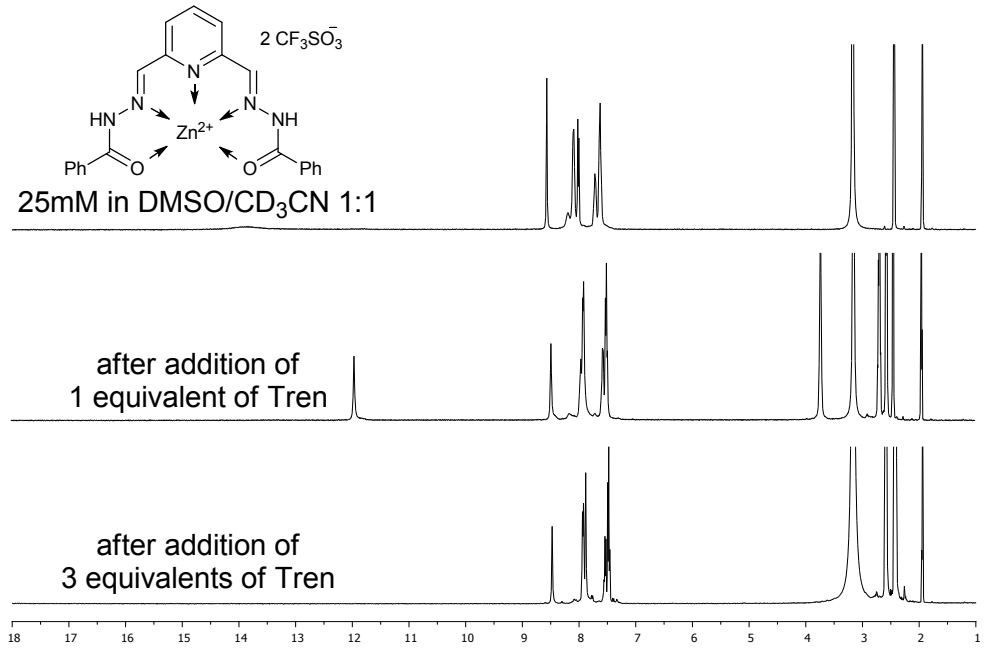

**X-Ray:**

Structure 1-Ph(Zn), for details see **CCDC 1016568** (Cambridge Crystallographic Data Centre):

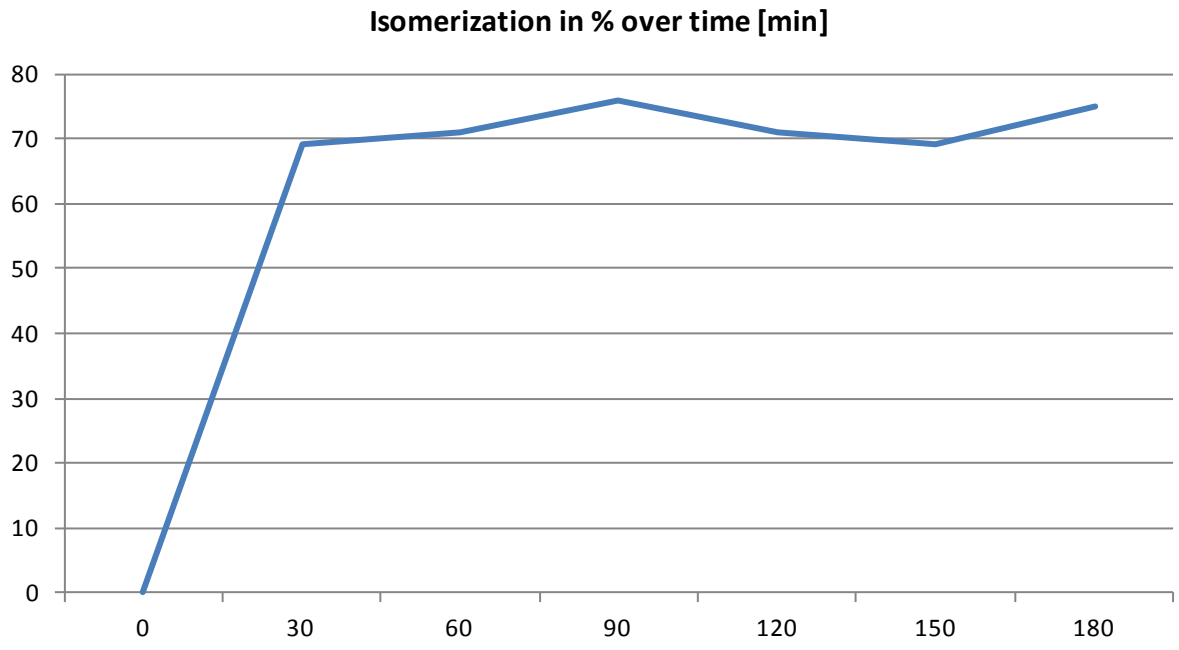


Formula: C22 H19 F3 N5 O6 S1 Zn1 1+,C1 F3 O3 S1 1-,C2 H3 N1
Unit Cell Parameters: a 10.9296(5) b 21.0471(10) c 14.9451(7) P21/c

Titration of complex **1**-Ph(Zn) with Tren:

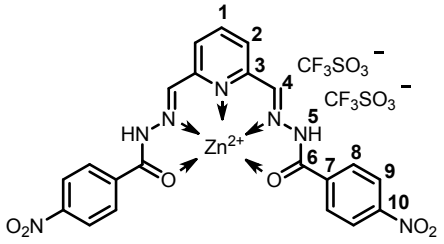



Reaching the photostationary point in the photoswitching of **1**-Ph(Zn):



● Compound **1**-$NO_2$(Zn):

**$^1$H-NMR (400 MHz, $CD_3CN$ δ in ppm):** 8.05 (d, 2H, -CH-**2**, 3J = 8.2 Hz), 8.33 (d, 4H, -CH-**8**, 3J = 9.1 Hz), 8.34-8.37 (m, -CH-**1**, 1H), 8.46 (d, 4H, -CH-**9**, 3J = 8.9 Hz), 8.72 (s, 2H, -CH-**4**), 12.75 (bs, 2H, -NH-**5**).

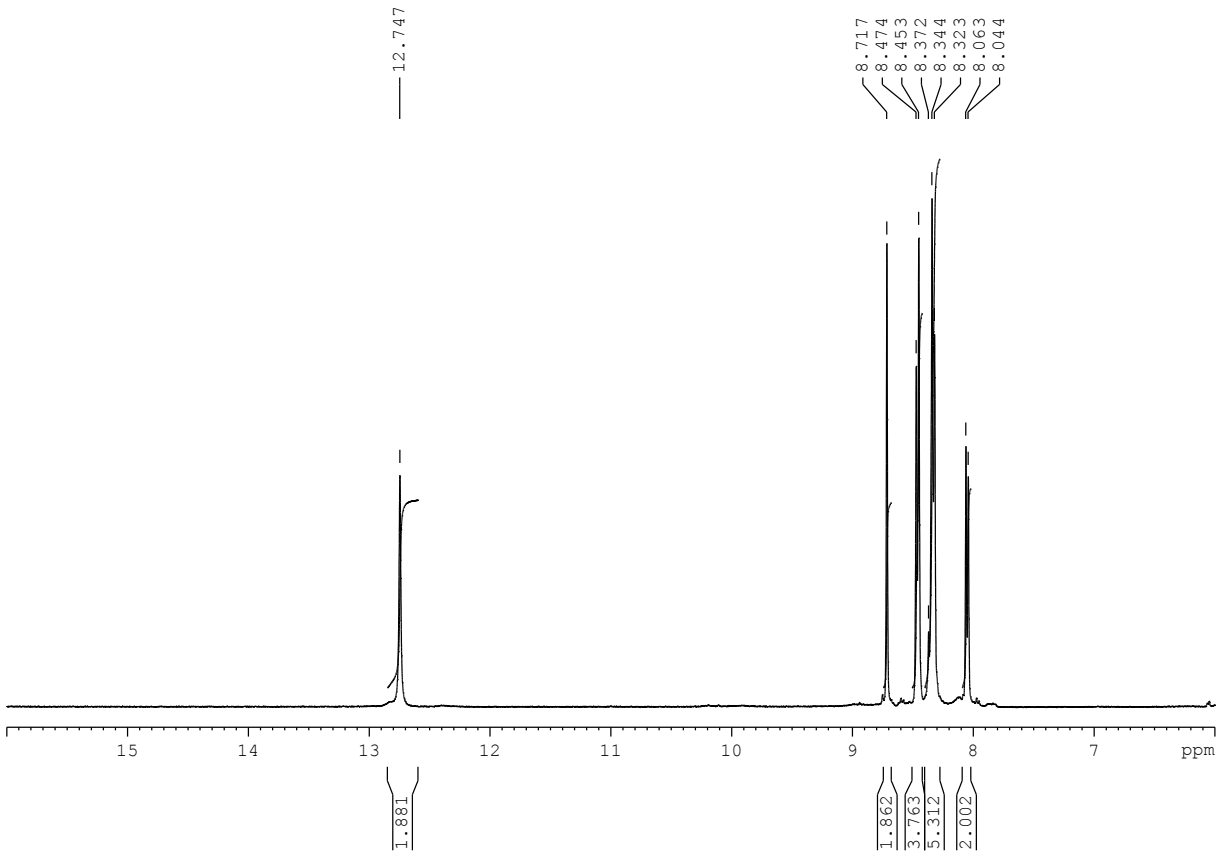


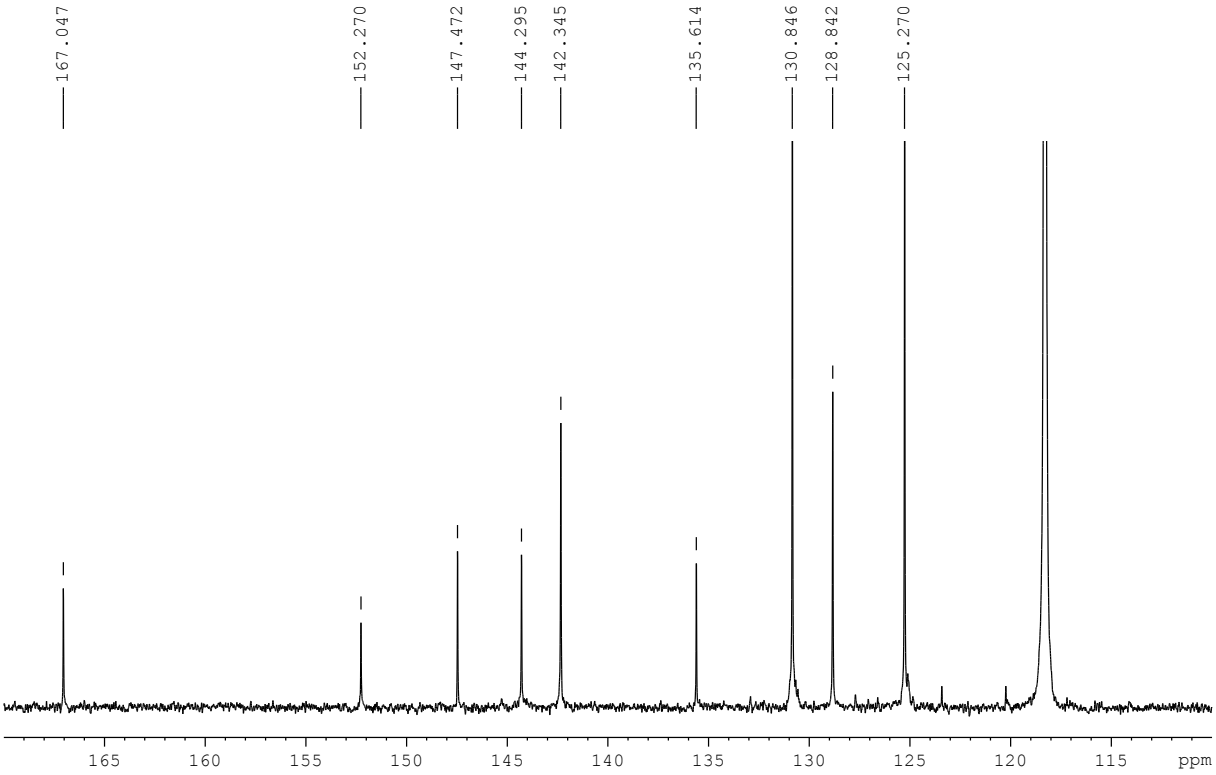

Chemical Formula: $C_{23}H_{15}F_6N_7O_{12}S_2Zn$
Exact Mass: 822,942
Molecular Weight: 824,905

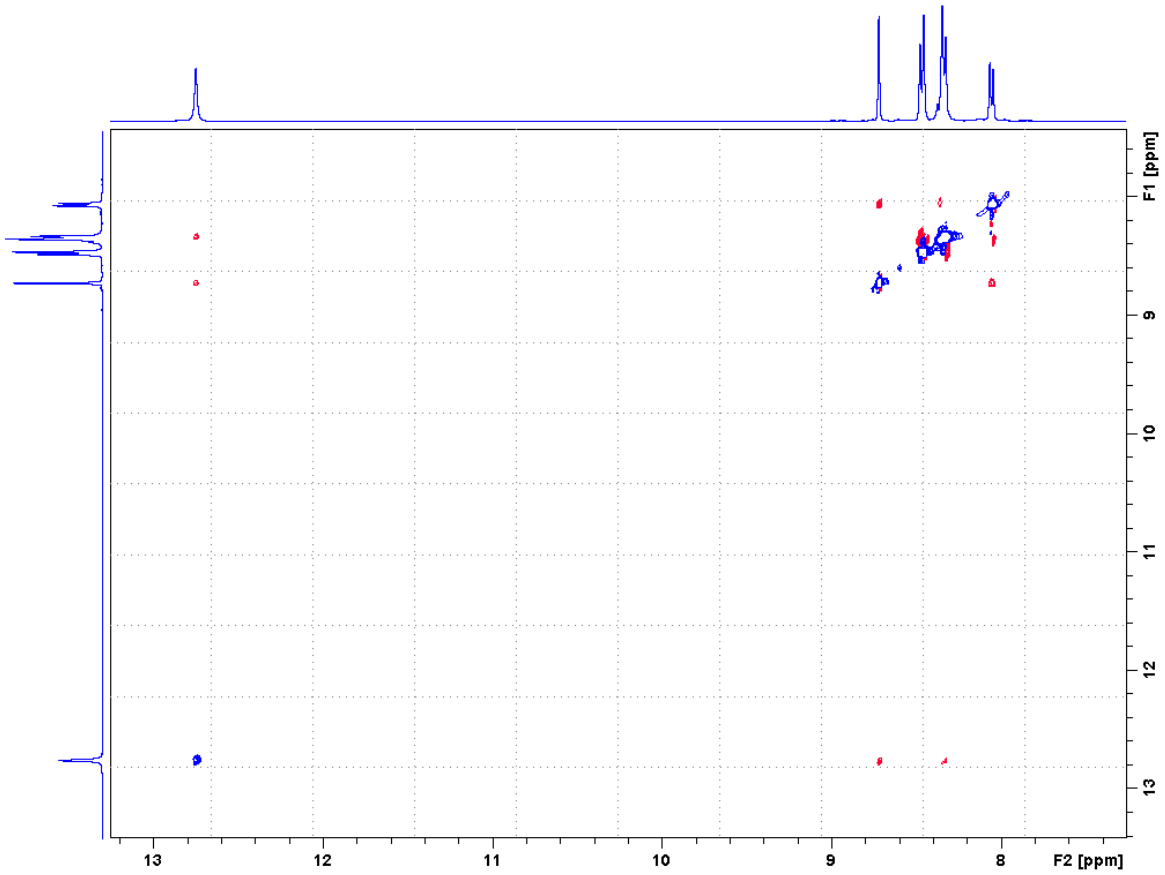
**$^{13}$C-NMR (100 MHz, $CD_3CN$ δ in ppm):** 125.27 (-C**9**), 128.84 (-C**2**), 130.85 (-C**8**), 135.61 (-C**7**), 142.35 (-C**4**), 144.30 (-C**1**), 147.47 (-C**3**), 152.27 (-C**10**), 167.05 (-C**6**).

**MS (ESI-pos) m/z:** 524.027 ($Zn^{2+}$L-H).

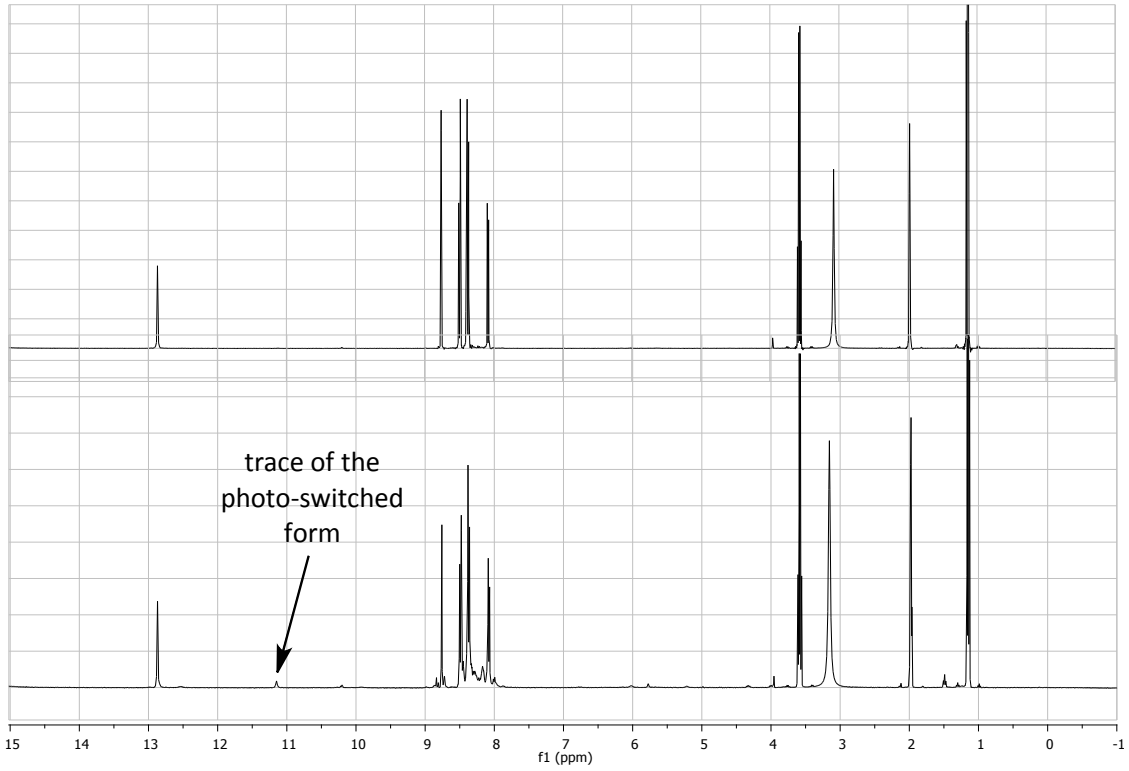
**HRMS (ESI-pos) m/z:** calcd. 524.029, found 524.027 ($Zn^{2+}$L-H).



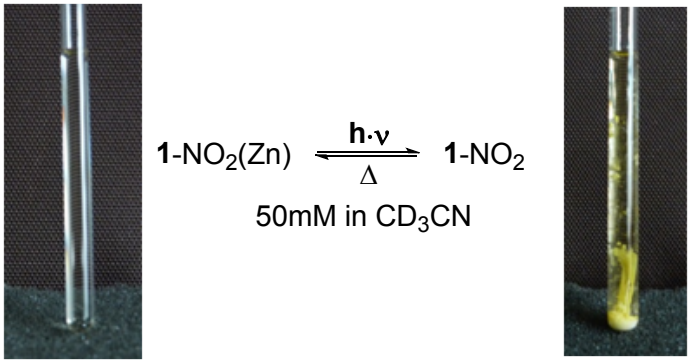

167.047
152.270
147.472
144.295
142.345
135.614
130.846
128.842
125.270
165
160
155
150
145
140
135
130
125
120
115
ppm


F1 [ppm]
9
10
11
12
13
13
12
11
10
9
8
F2 [ppm]

$^1$H-NMR-spectrum (400 MHz, $CD_3CN$, 50mM) of the complex before (up) and after irradiation with UV-light (overnight) upon which a solid formed (bottom).

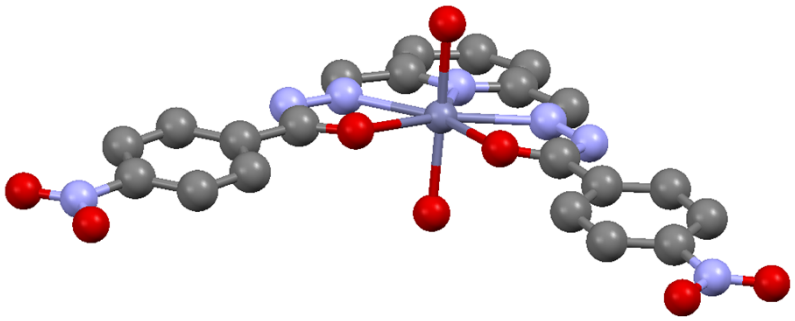



The intriguingly low solubility of the bisacylhydrazone **1**-$NO_2$ could be demonstrated for the complex **1**-$NO_2$(Zn). When formed in pure $CD_3CN$ (which is not able to dissolve **1**-$NO_2$ only), UV-irradiation led to the immediate precipitation of a white solid. This process could equally be reversed by heating the sample to 80°C upon which clearance of the solution could be observed:



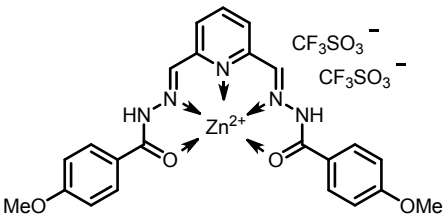
**X-Ray:**

Structure 1-$NO_2$(Zn), for details see **CCDC 1016569** (Cambridge Crystallographic Data Centre):



Formula: C21 H19 N7 O8 Zn1 2+,2(C1 F3 O3 S1 1-),2(C2 H3 N1)
Unit Cell Parameters: a 17.2793(4) b 20.0343(5) c 11.3521(3) C2/m

● Compound **1**-MeO(Zn):



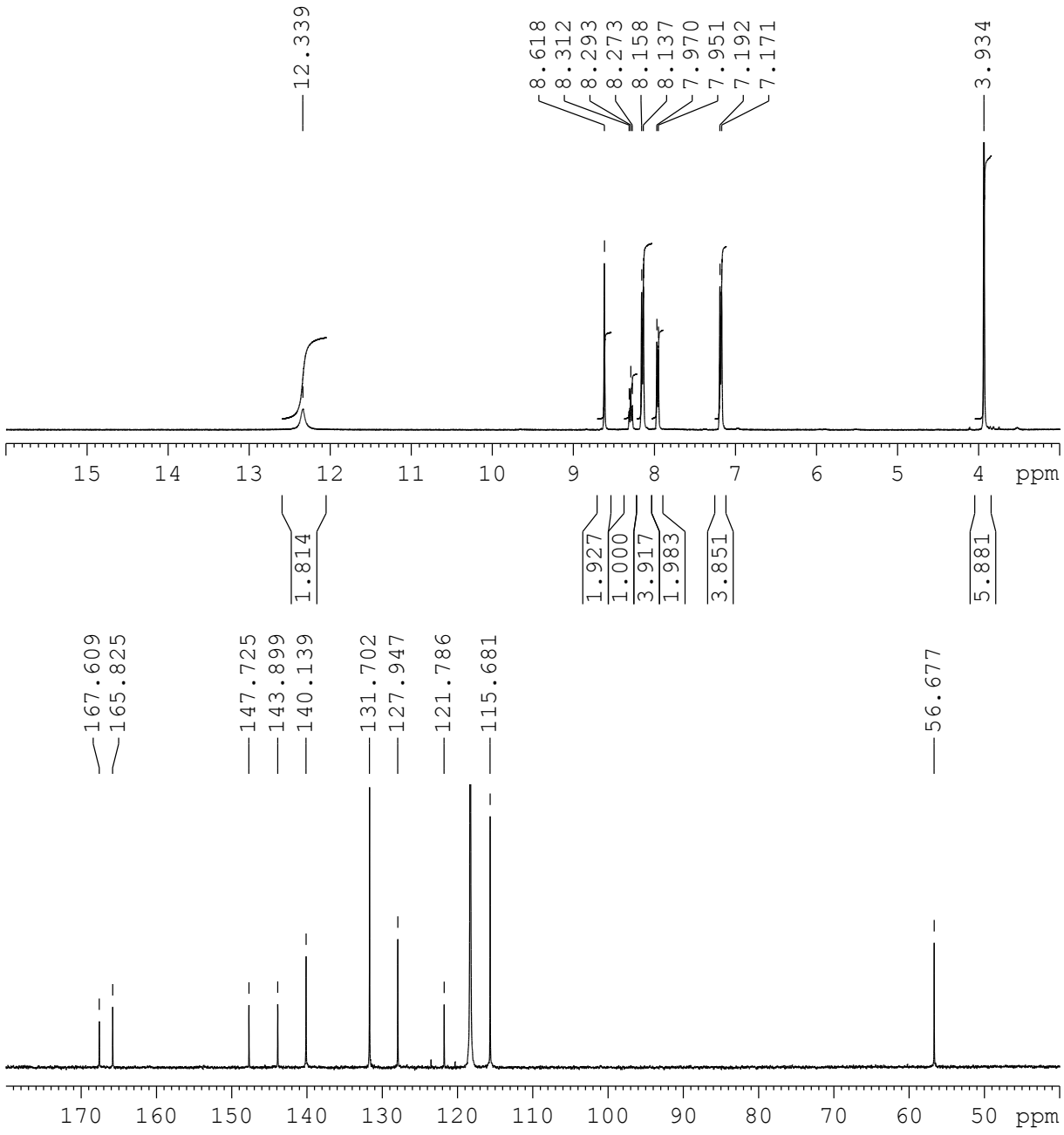

Chemical Formula: $C_{25}H_{21}F_6N_5O_{10}S_2Zn$
Exact Mass: 792,993
Molecular Weight: 794,962

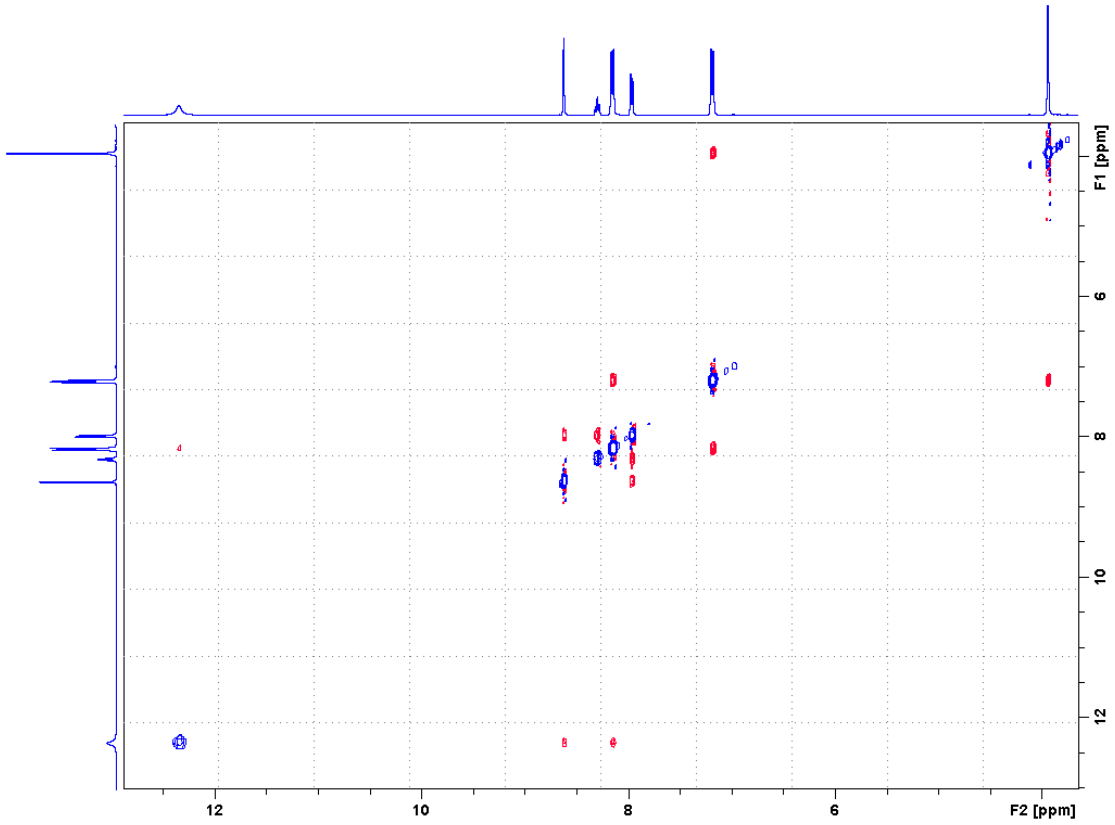
**$^1$H-NMR (400 MHz, $CD_3CN$ δ in ppm):** 3.93 (s, 6H), 7.18 (d, 4H, $^3J$ = 8.9 Hz), 7.96 (d, 2H, $^3J$ = 7.8 Hz), 8.15 (d, 4H, $^3J$ = 8.8 Hz), 8.29 (t, 1H = $^3J$ = 7.7 Hz), 8.62 (s, 2H), 12.34 (bs, 2H).

**$^{13}$C-NMR (100 MHz, $CD_3CN$ δ in ppm):** 56.68, 115.68, 121.79, 127.95, 131.70, 140.14, 143.90, 147.73, 165.83, 167.61.

**MS (ESI-pos) m/z:** 494.079 ($Zn^{2+}$L-H), 454.147 ($Zn^{2+}$L-frag.).

**HRMS (ESI-pos) m/z:** calcd. 247.544, found 247.542 ($Zn^{2+}$L/2).


12.339
8.618
8.312
8.293
8.273
8.158
8.137
7.970
7.951
7.192
7.171
3.934
15
14
13
12
11
10
9
8
7
6
5
4
ppm
1.814
1.927
1.000
3.917
1.983
3.851
5.881
167.609
165.825
147.725
143.899
140.139
131.702
127.947
121.786
115.681
56.677
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm



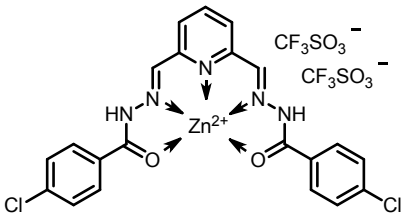

● Compound **1**-Cl(Zn):

**$^{1}$H-NMR (400 MHz, $CD_3CN$ δ in ppm):** 7.69 (d, 4H, 3J = 8.7 Hz), 8.00 (d, 2H, 3J = 7.8 Hz), 8.13 (d, 4H, 3J = 8.8 Hz), 8.32 (t, 2H, 3J = 7.7 Hz), 8.67 (s, 2H), 12.60 (bs, 2H).

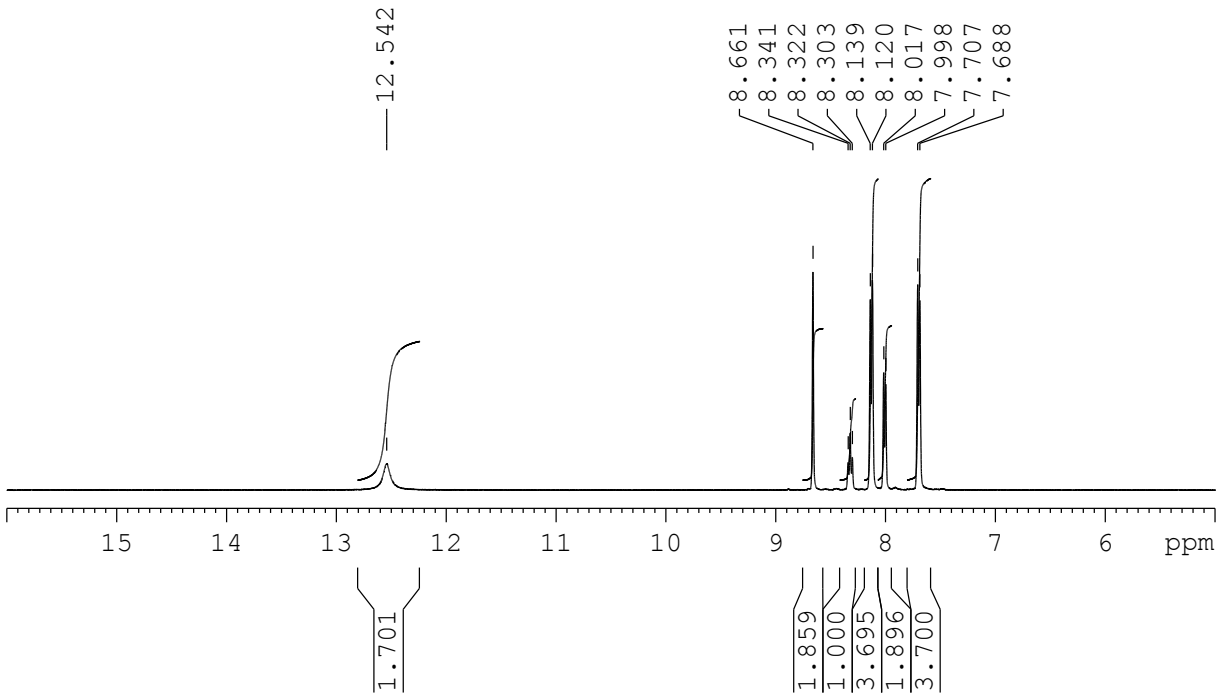
**$^{13}$C-NMR (100 MHz, $CD_3CN$ δ in ppm):** 129.03, 129.34, 131.14, 131.69, 141.90, 142.03, 144.71, 148.18, 168.13.

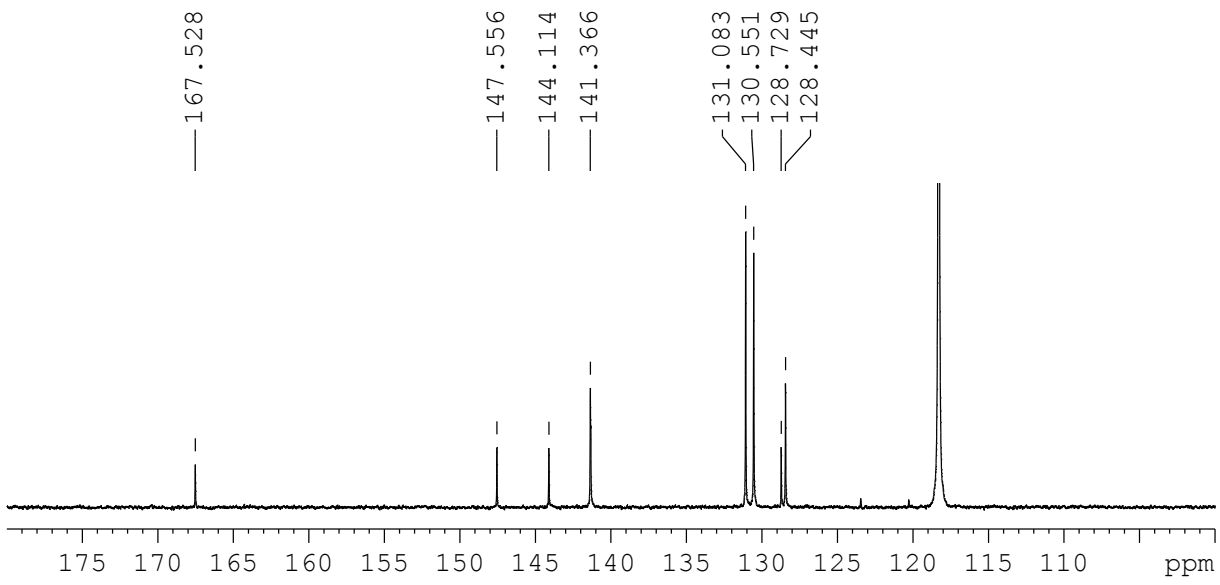
**MS (ESI-pos) m/z:** 653.935 ($Zn^{2+}L\cdot TfO^-$), 503.975 ($Zn^{2+}L$), 252.492 ($Zn^{2+}L/2$).

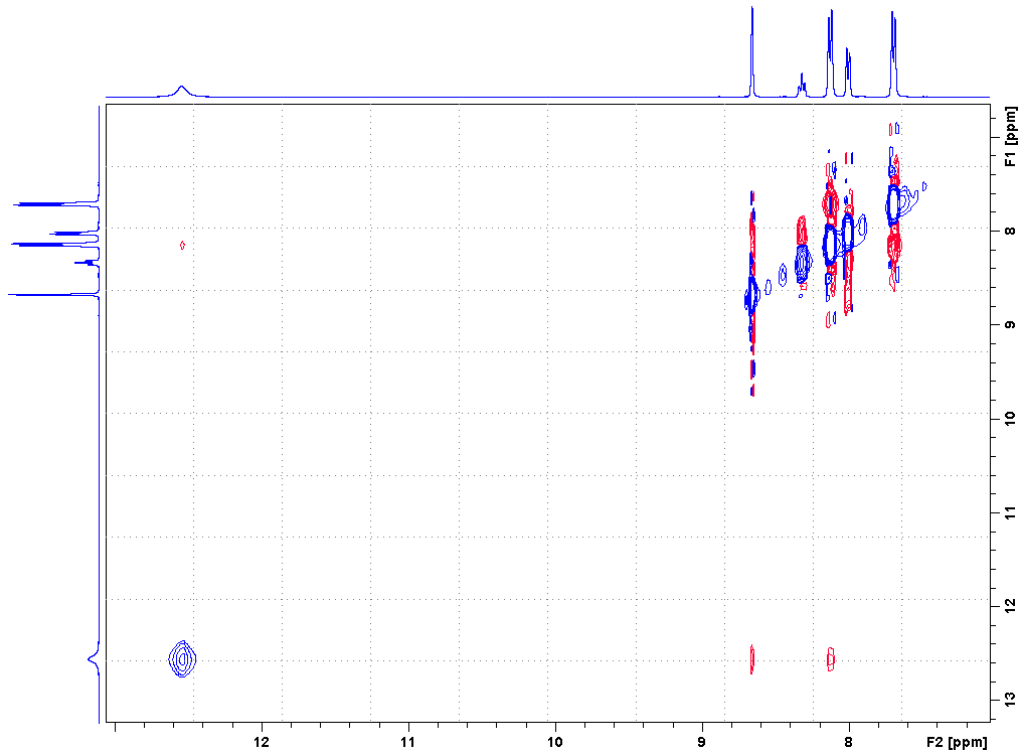
**HRMS (ESI-pos) m/z:** calcd. 252.492, found 252.494 ($Zn^{2+}L/2$).




Chemical Formula: $C_{23}H_{15}Cl_2F_6N_5O_8S_2Zn$
Exact Mass: 800,893
Molecular Weight: 803,800


12.542
8.661
8.341
8.322
8.303
8.139
8.120
8.017
7.998
7.707
7.688
15
14
13
12
11
10
9
8
7
6
ppm
1.701
1.859
1.000
3.695
1.896
3.700

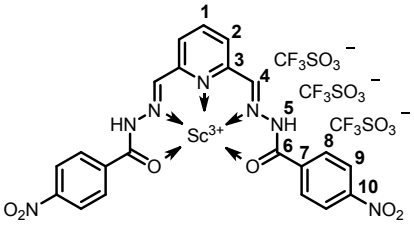

167.528
147.556
144.114
141.366
131.083
130.551
128.729
128.445
175
170
165
160
155
150
145
140
135
130
125
120
115
110
ppm




● Compound **1**-$NO_2$(Sc):

**$^{1}$H-NMR (400 MHz, $CD_3CN$ δ in ppm):** 4.56 (bs), 8.37-8.42 (m, 6H), 8.50 (d, 4H, 3J = 8.7 Hz), 8.63 (t, 1H, 3J = 7.7 Hz), 9.06 (s, 2H).

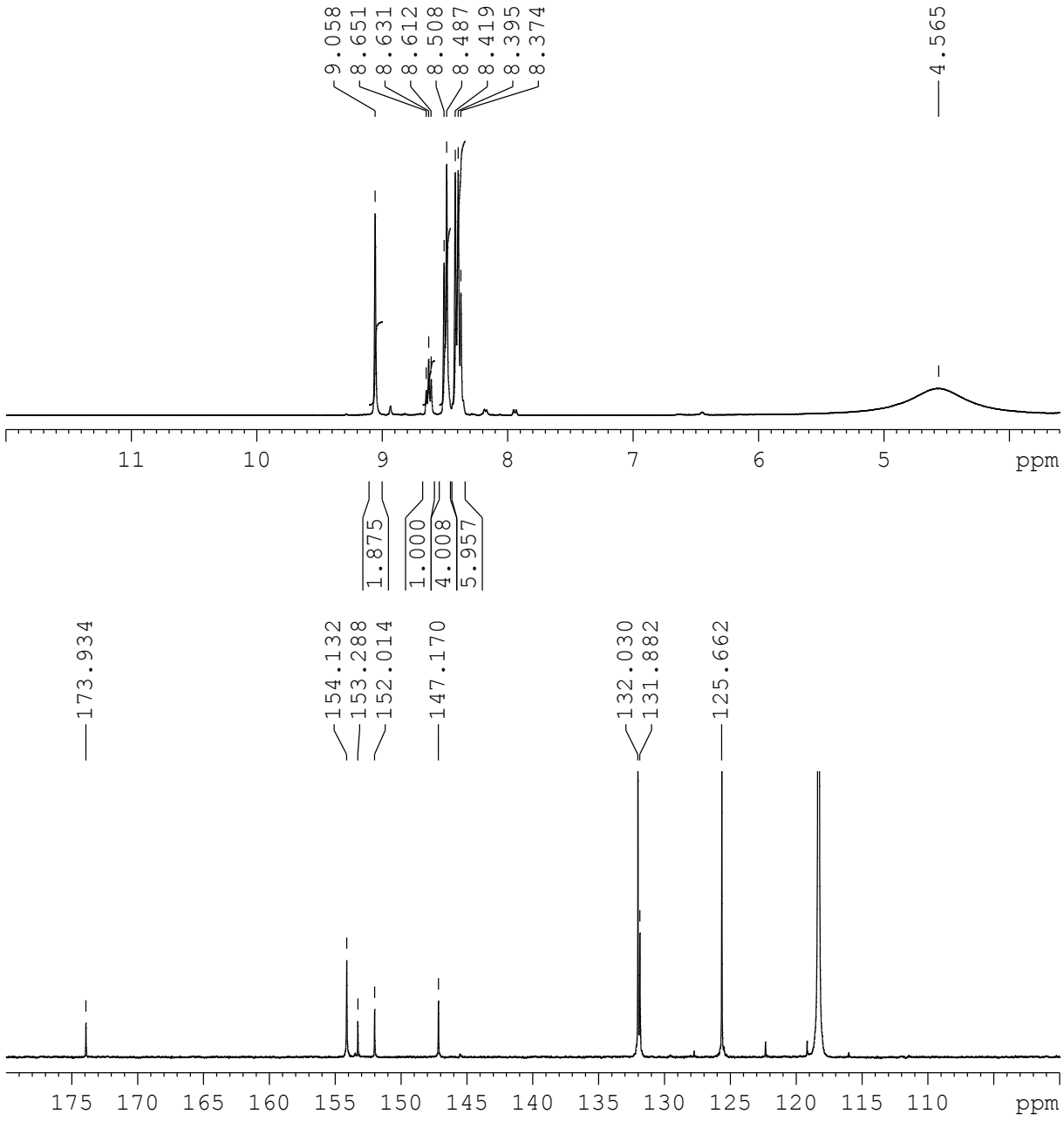
**$^{13}$C-NMR (100 MHz, $CD_3CN$ δ in ppm):** 125.66, 131.88, 132.03, 147.17, 152.01, 153.29, 154.13, 173.93.

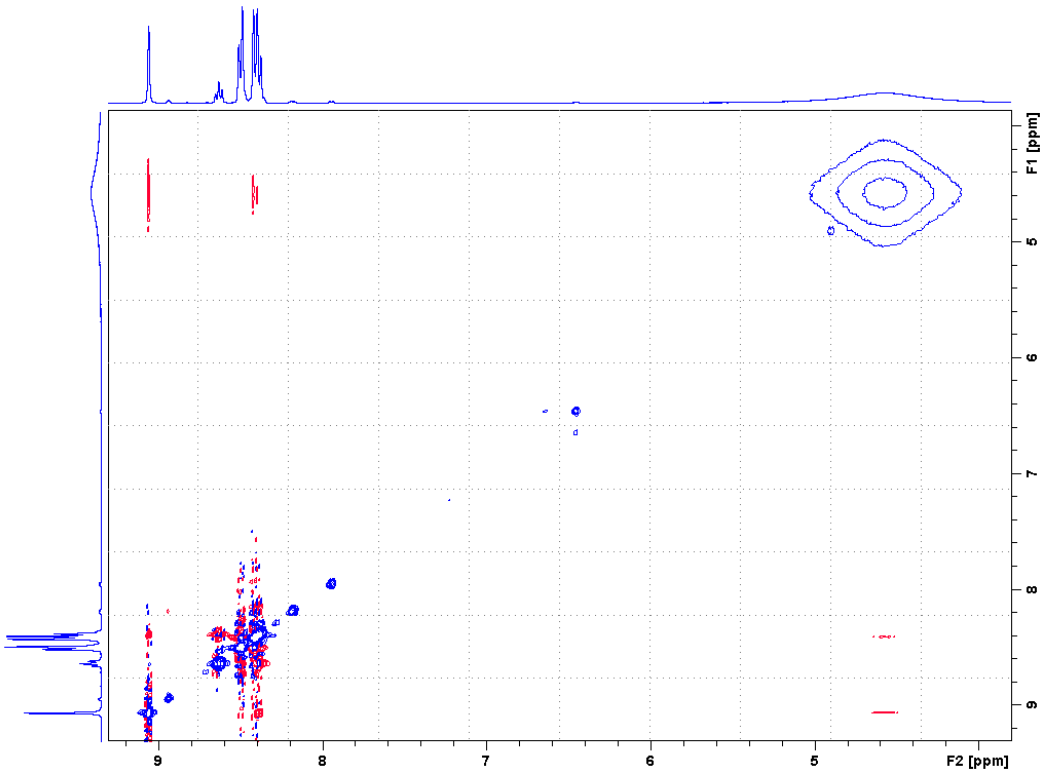



Chemical Formula: $C_{24}H_{15}F_9N_7O_{15}S_3Sc$
Exact Mass: 952,920
Molecular Weight: 953,550

**MS (ESI-pos) m/z:** ($Sc^{3+}$L-TfO) 803.962, ($Sc^{3+}$L-2·TfO-H) 654.005.

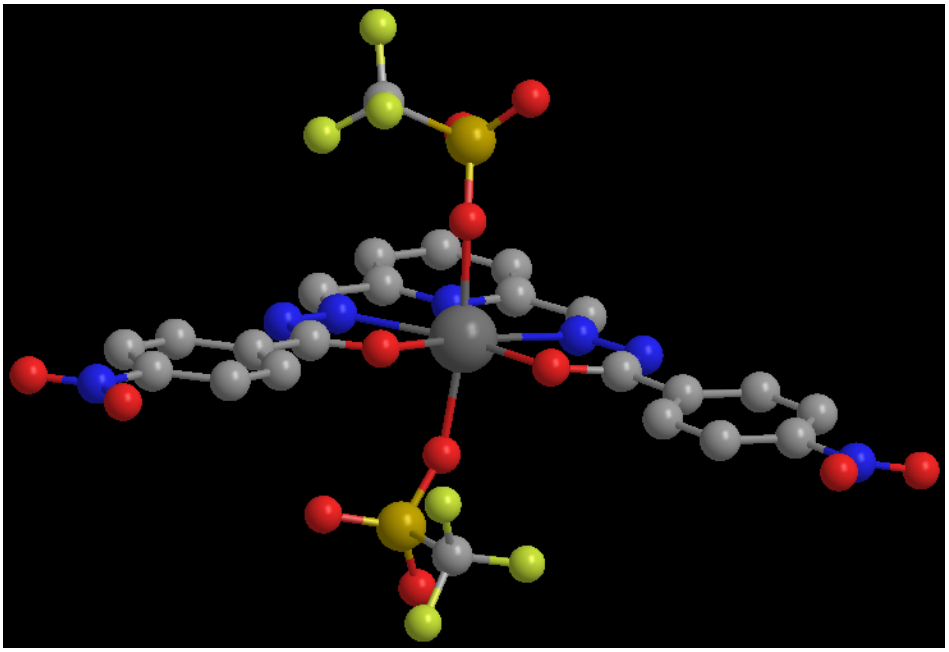
**HRMS (ESI-pos) m/z:** calcd. 654.008, found 654.005 ($Sc^{3+}$L-2·TfO-H).


9.058
8.651
8.631
8.612
8.508
8.487
8.419
8.395
8.374
4.565
11
10
9
8
7
6
5
ppm
1.875
1.000
4.008
5.957
173.934
154.132
153.288
152.014
147.170
132.030
131.882
125.662
175
170
165
160
155
150
145
140
135
130
125
120
115
110
ppm




**X-Ray:**

Structure 1-$NO_2$(Sc), for details see **CCDC 1016566** (Cambridge Crystallographic Data Centre):



Formula: C23 H14 F6 N7 O12 S2 Sc1,C2 H3 N1

Unit Cell Parameters: a 10.3540(3) b 13.4658(7) c 13.6487(6) P-1