Supplementary material

Crystallographic Information

Table S 1: Crystallographic data for compounds **4**-**8**.

	4	**5**	**6**	**7**	**8**
Formula	$C_{24}H_{21}BrN_2NiO_2 \cdot CHCl_3$	$C_{28}H_{29}BrN_2NiO_2$	$C_{30}H_{33}BN_2NiO_4$	$C_{34}H_{41}BN_2NiO_4$	$C_{48}H_{42}N_4Ni_2O_4 \cdot 2(C_5H_5N)$ (C_6H_6)
Weight [g/mol]	627.41	564.15	555.10	611.21	1092.58
Temperature [K]	100.1(1)	100.1(1)	100.1(1)	100.1(1)	100.1(1)
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Space group	$P\bar{1}$	$P2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.3441(2)	24.5626(2)	15.4727(4)	14.4687(1)	16.4203(2)
b [Å]	17.1747(3)	6.7022(1)	13.7843(3)	24.9127(2)	8.0156(1)
c [Å]	23.5777(4)	31.2584(3)	14.1565(3)	17.5423(2)	20.0126(3)
α [°]	84.506(1)	-	-	-	-
β [°]	76.205(1)	95.08(1)	114.416(3)	92.753(1)	10.66(1)
γ [°]	76.103(1)	-	-	-	-
V [Å^3]	5089.85(15)	5125.61(7)	2749.28(11)	6315.90(10)	2588.55(6)
Z	8	8	4	8	2
D [Mg/m^3]	1.638	1.462	1.341	1.286	1.402
μ [mm^{-1}]	2.67	2.34	0.74	0.65	0.79
F(000)	2528	2320	1168	2592	1144
θ [°]	1.8 – 27.4	2.2 – 35.5	2.9 - 25	1.4 – 28.5	2.2 – 32.8
h	-17 → 17	-39 → 39	-18 → 13	-19 → 19	-25 → 25
k	-22 → 22	-10 → 8	-15 → 16	-32 → 33	-12 → 12
l	-30 → 30	-43 → 51	-12 → 16	-22 → 23	-31 → 30
Reflexes	105227	103118	13164	105742	66118
Indep. refl. (I>2σ)	22932 (15397)	21035 (16132)	4844 (4344)	15108 (11096)	9902 (7237)
R_{int}	0.077	0.023	0.028	0.043	0.049
Refinement	FMLS on F^2	FMLS on F^2	FMLS on F^2	FMLS on F^2	FMLS on F^2
Parameter	1237	625	377	816	356
R_1 (I>2σ)	0.041	0.032	0.048	0.038	0.041
wR_2	0.090	0.085	0.120	0.103	0.109
ρ_{min}/ρ_{max}[e/ Å^3]	-0.60/1.14	-0.58/1.19	-0.84/0.96	-0.38/0.37	-0.39/0.53
CCDC	1053849	1053735	1053850	1053745	1053865

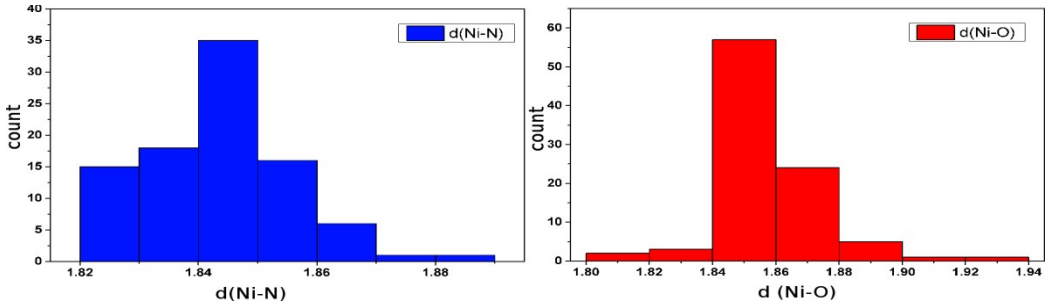


Figure S 1: Histograms for Ni-N and Ni-O bond-lengths taken from 93 Nickel(II)salophene-complexes published in the CCDC.

Table S2: Selected bond-lengths in the crystal-structures and the relaxed structures acquired by DFT-calculations of 4-8. Bond-lengths are given in Angströms.
*) The bond-lengths are averaged over more than one molecule in the asymmetric unit. #) Torsion-angle of

	4*		**5***		**6**		**7***		**8**	
d_{Ni-N1}	1.8624(26)	1.8826	1.8593(10)	1.8861	1.8556(23)	1.8817	1.8602(15)	1.8806	1.8607(12)	1.8628
d_{Ni-N2}	1.8605(26)	1.8798	1.8525(10)	1.8711	1.8549(25)	1.8803	1.8505(15)	1.8715	1.8580(13)	1.8626
d_{Ni-O1}	1.8501(22)	1.8606	1.8441(09)	1.8629	1.8437(22)	1.8605	1.8418(12)	1.8627	1.8425(11)	1.8577
d_{Ni-O2}	1.8458(22)	1.8558	1.8370(09)	1.8562	1.8330(19)	1.8569	1.8315(13)	1.8574	1.8368(11)	1.8562
d_{N1-C7}	1.3011(40)	1.3057	1.3052(15)	1.3051	1.2987(39)	1.3062	1.3086(23)	1.3056	1.3116(19)	1.3276
d_{N2-C14}	1.3037(40)	1.3090	1.3060(15)	1.3091	1.3047(37)	1.3086	1.3109(23)	1.3087	1.3107(19)	1.3284
$d_{C4-C4'}$	-	-	-	-	-	-	-	-	1.4831(29)	1.4848
d_{C4-B1}	-	-	-	-	1.5508(50)	1.5438	1.5406(27)	1.5444	-	-
$á_{O1-Ni1-N1}$	95.03(11)	94.64	95.41(04)	94.72	95.17(10)	94.69	95.50(06)	94.76	95.29(05)	95.20
$á_{O2-Ni1-N2}$	95.11(11)	94.72	94.66(04)	94.21	95.06(10)	94.69	94.66(06)	94.20	95.15(05)	95.26
$á_{O2-Ni1-O1}$	84.01(11)	84.82	83.84(04)	85.10	83.52(10)	84.80	83.67(06)	85.09	83.43(05)	82.98
$á_{N2-Ni1-N1}$	85.95(11)	85.82	86.16(04)	85.97	86.31(10)	85.82	86.22(06)	85.96	86.18(05)	86.58
$Ó_{á}$	360.10	360.00	360.07	360.00	360.06	360.00	360.04	360.00	360.05	360.01
$\phi_{C3-C4-B1-O4}$	-	-	-	-	4.3	4.5	4.1	3.7	0.0#	36.3#

UV/Vis data

Table S 3: Parameters for the Gauss-fits of the UV/Vis-spectra of compounds **4**-**9**/**10**. max: Peak-maximum (nm), wdt: Full-width-half-maximum (nm), h: Peak-height, A: Peak-area.

	band 1				band 2				band 3				band 4				band 5			
	max	wdt	ht	A	max	wdt	h	A	max	wdt	h	A	max	wdt	h	A	max	wdt	h	A
4	519	88.3	3.7	3.5	494	41.4	3.5	1.6	445	88.3	6.6	6.2	384	17.7	6.7	1.3	373	51.9	23	13
5	530	82.2	3.6	3.1	496	42.4	3.8	1.7	445	88.3	6.8	6.4	383	21.2	7.0	1.6	371	59.0	20	13
6	525	88.3	2.6	2.1	491	51.6	4.8	2.6	447	88.3	7.9	7.4	382	17.7	8.2	1.6	370	50.0	27	14
7	529	87.6	2.4	2.2	493	55.8	4.8	2.9	445	88.3	7.1	6.7	382	17.7	8.1	1.5	371	53.6	25	14
8	534	76.5	12	9.8	502	42.4	12	5.6	456	63.4	1.6	11	387	17.7	21	3.9	377	63.0	54	36
9/10	533	76.5	11	9.0	503	38.7	8.4	3.5	459	78.0	15	13	387	17.7	19	3.6	376	61.8	50	33

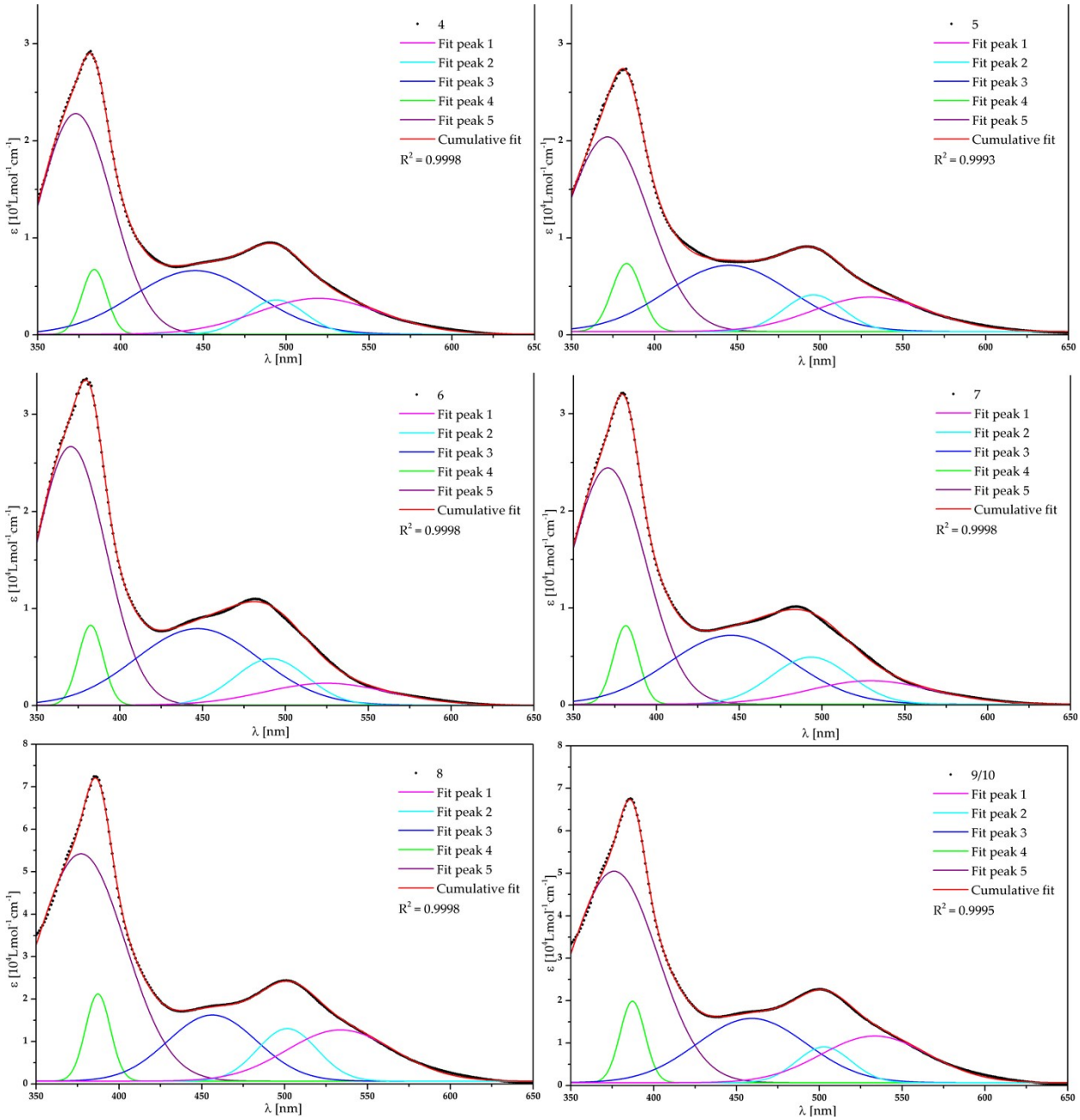


Figure S 2: Experinmental UV/Vis-spectra including the Gaussian deconvolution. Top-left: **4**, top, right: **5**, middle-left: **6**, middle-right: **7**, bottom-left: **8**, bottom-right: **9/10**.

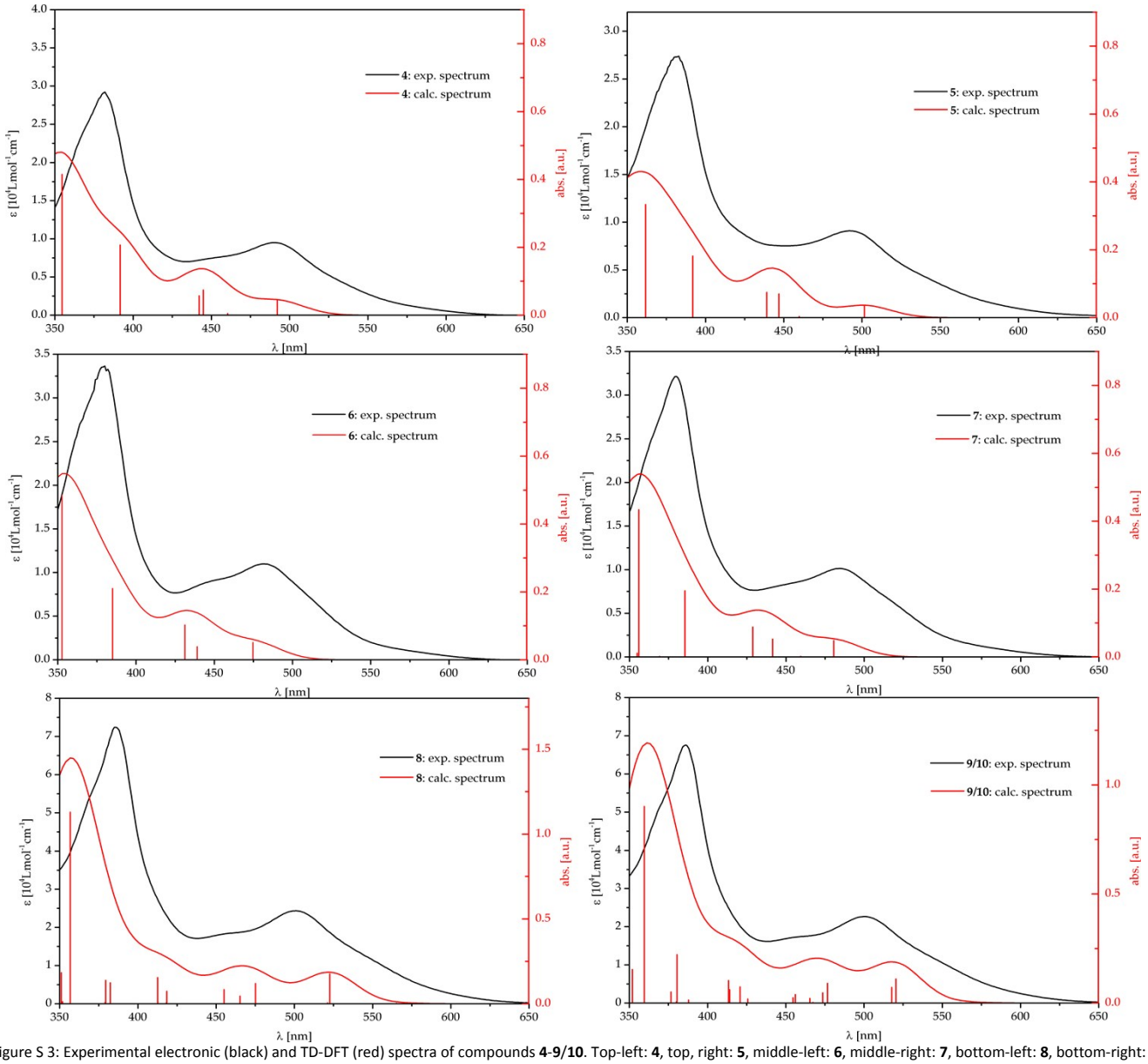


Figure S 3: Experimental electronic (black) and TD-DFT (red) spectra of compounds **4**-**9**/**10**. Top-left: **4**, top, right: **5**, middle-left: **6**, middle-right: **7**, bottom-left: **8**, bottom-right: **9**/**10**.

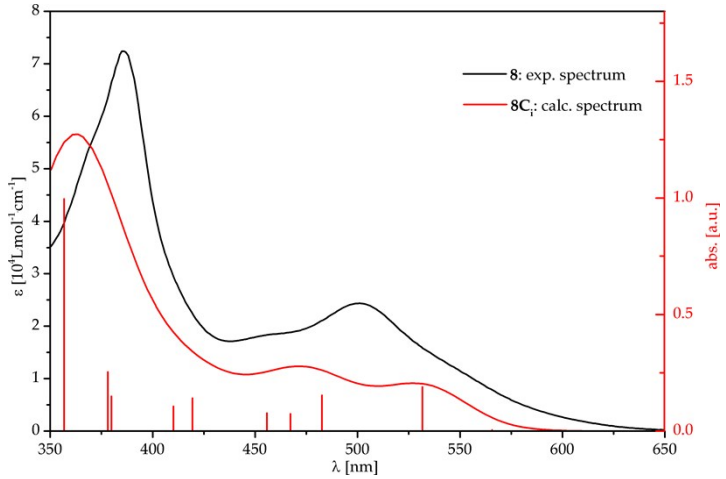


Figure S 4: Experimental electronic (black) and TD-DFT (red) spectra of compound **8** Ci.

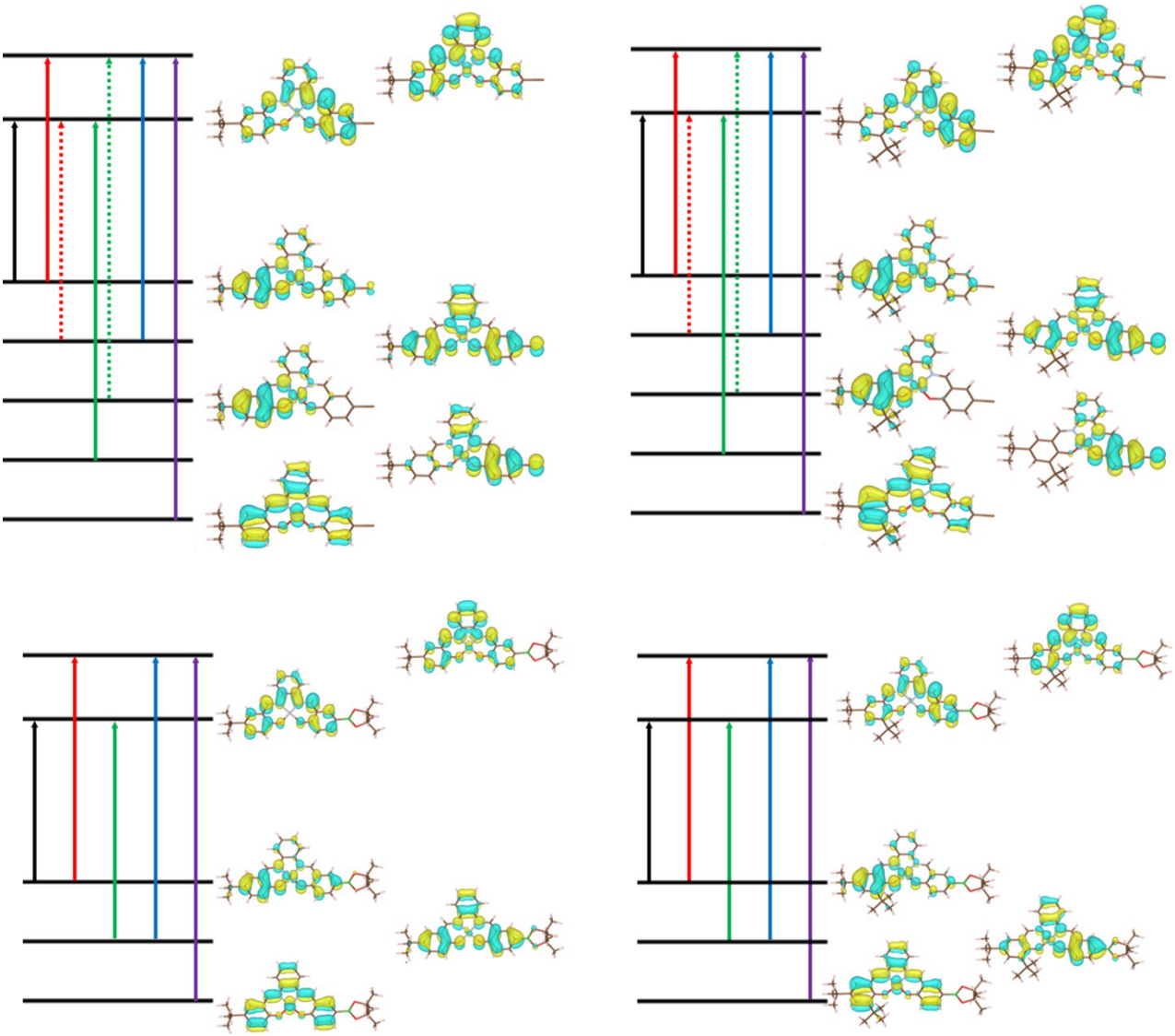


Figure S 5: NTOs for the mononuclear compounds. Top-left: **4**, top, right: **5**, bottom-left: **6**, bottom right: **7**. The five transition represented in each diagram correspond to the observed absorption-bands in the experimental UV/Vis-Spectra.

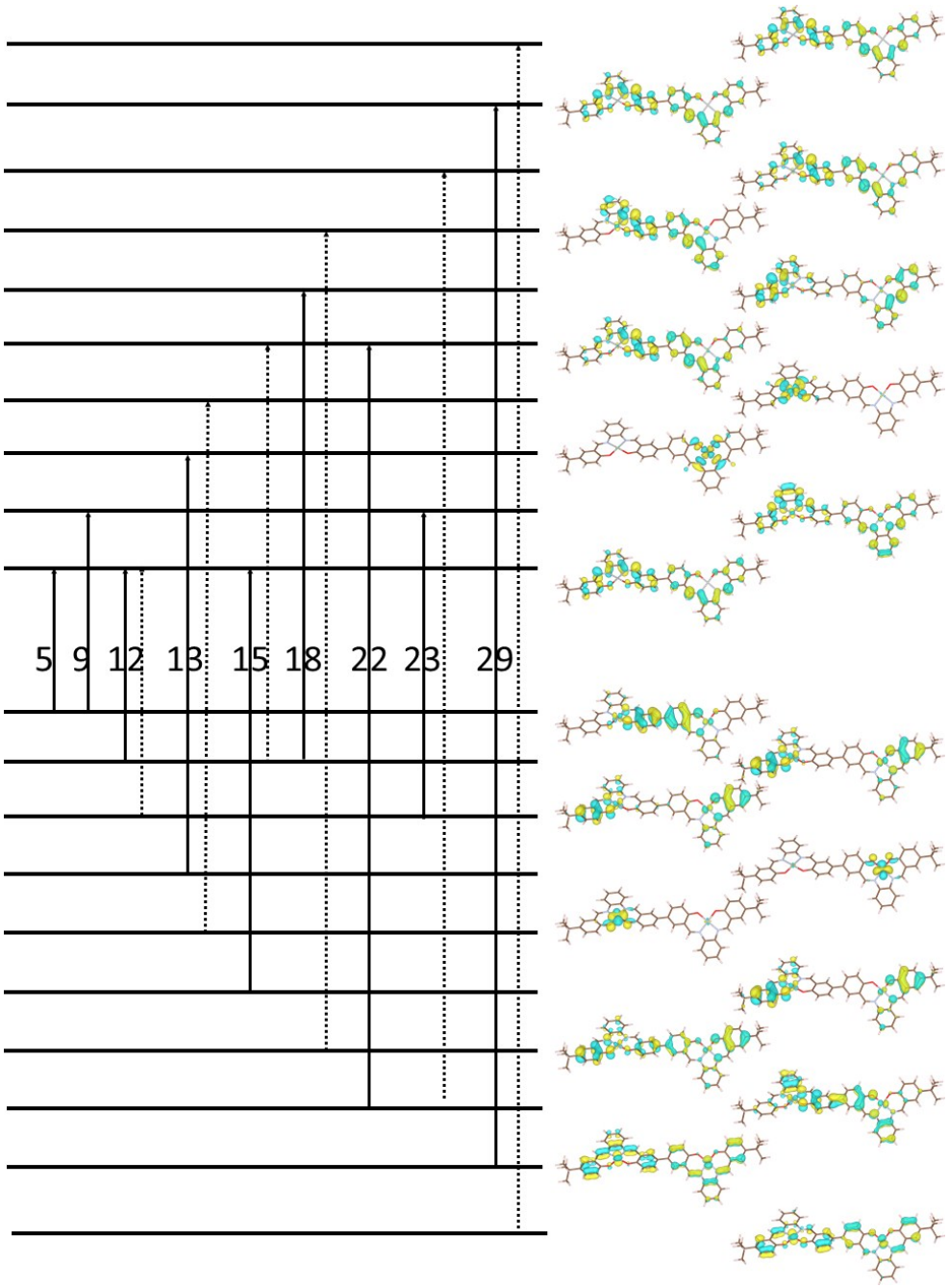


Figure S 6: NTOs for the dinuclear compound **8**. The observed electronic transitions are represented.

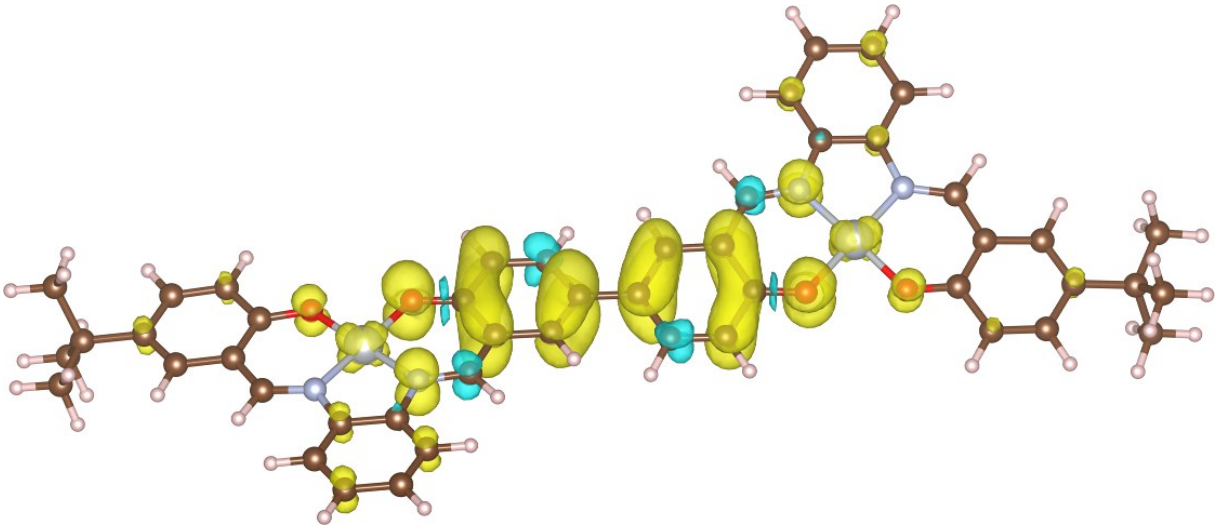
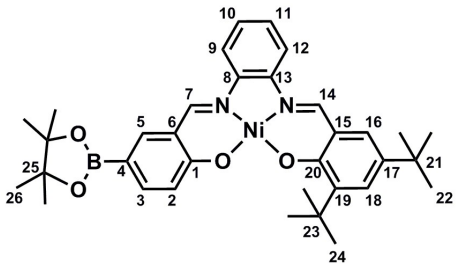


Figure S 7: DFT-spin density of the hypothetical monocation **8**$^{+}$.

NMR-Data

Table S 4: Selected ^{1}H (^{13}C) chemical shifts for compounds **4-11**. Data are given in ppm. Due to poor solubility no ^{13}C data is available for **9-11.** The ^{13}C shifts of the C4-atom in compounds **4** and **6** couldn't be determined.

	4	**5**	**6**	**7**	**9+10**	**11**
C1	- (-)	 (166.8)	 (169.8)	 (170.2)	- (-)	- (-)
C20	- (-)	 (166.3)	 (166.4)	 (165.6)	- (-)	- (-)
C7	8.56 (155.4)	8.60 (154.9)	8.62 (156.2)	8.67 (156.0)	8.68, 8.61	8.71
C14	8.50 (156.1)	8.47 (155.9)	8.56 (155.8)	8.52 (155.8)	8.49, 8.47	8.55
C2	6.79 (124.1)	6.77 (124.0)	6.84 (~121)	6.84 (121.4)	6.98, 6.91	6.99-6.96
C3	7.23 (136.7)	7.25 (137.4)	7.53 (140.6)	7.55 (140.3)	- (-)	- (-)
C4	- (-)	- (106.0)	- (-)	- (122.0)	- (-)	- (-)
C5	7.54 (134.5)	7.55 (135.3)	7.92 (143.7)	7.95 (143.7)	- (-)	- (-)
C16	7.35 (128.2)	~7.2 (127.3)	7.37 (129.1)	7.23 (127.8)	- (-)	- (-)
C17	- (137.8)	- (137.1)	- (137.8)	- (137.2)	- (-)	- (-)
C18	7.36 (133.4)	7.39 (130.6)	7.35 (134.1)	7.39 (130.5)	- (-)	- (-)
C19	6.84 (121.7)	- (141.1)	6.85 (~121)	- (141.3)	6.86 (-)	- (-)



Scheme S1: Numbering-pattern for NMR-peak-assignment.

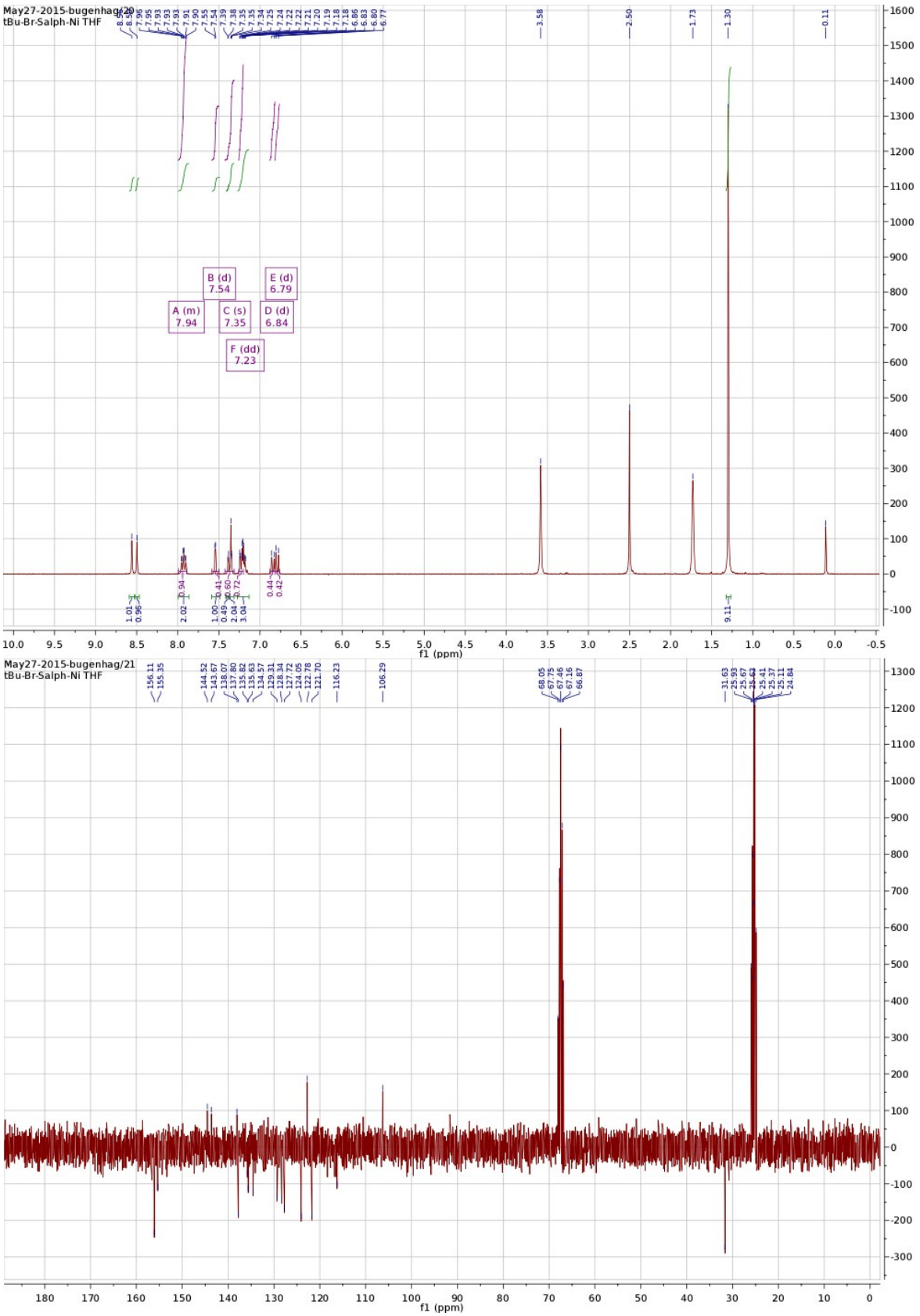


Figure S8: ^{1}H (top) and ^{13}C-DEPTQ (bottom)-spectra of **4** measured in THF-d_8.

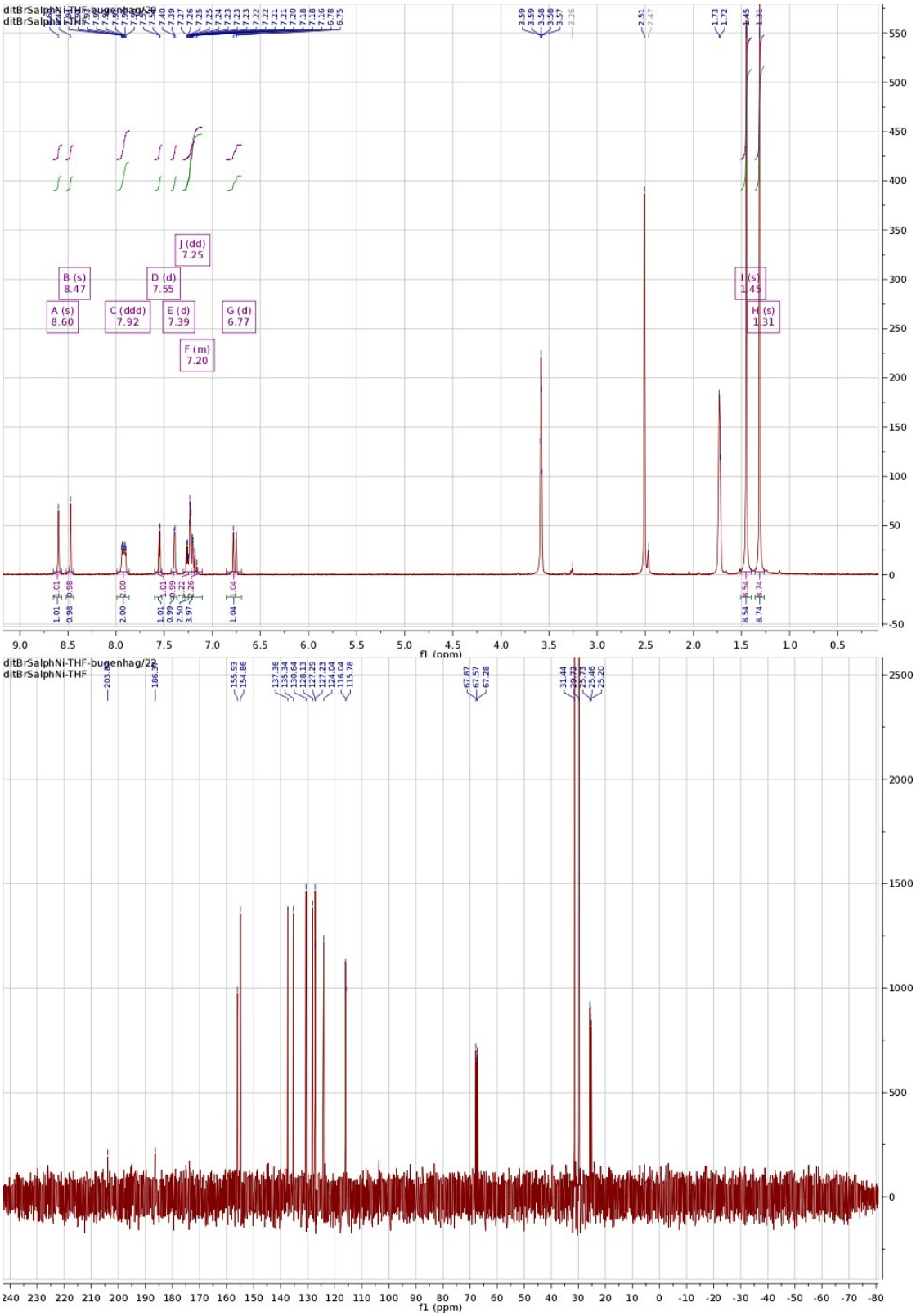


Figure S9: ^{1}H (top) and ^{13}C-DEPT135 (bottom)-spectra of **5** measured in THF-d_8.

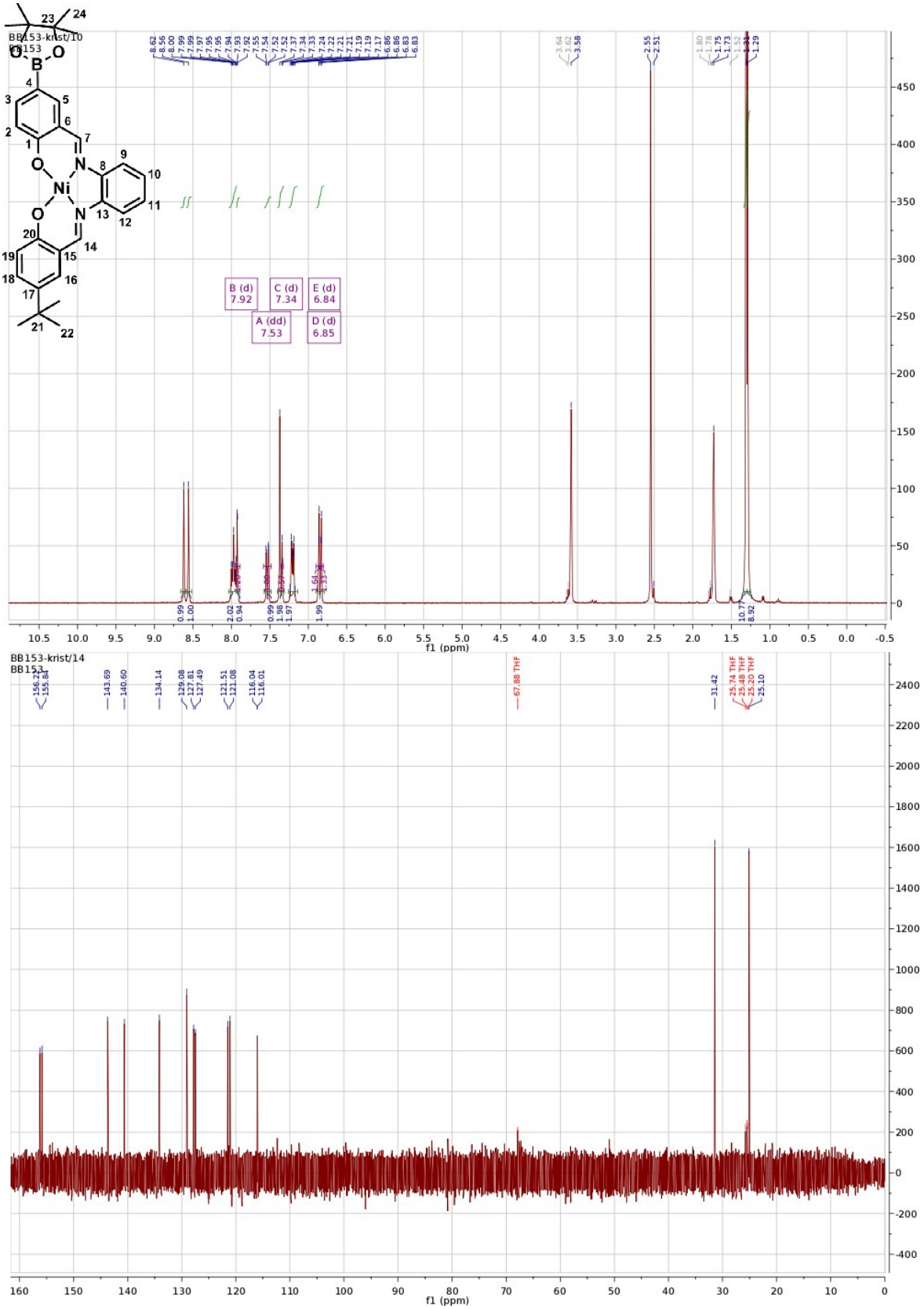


Figure S10: ^{1}H (top) and ^{13}C (bottom)-spectra of **6** measured in THF-d_8.

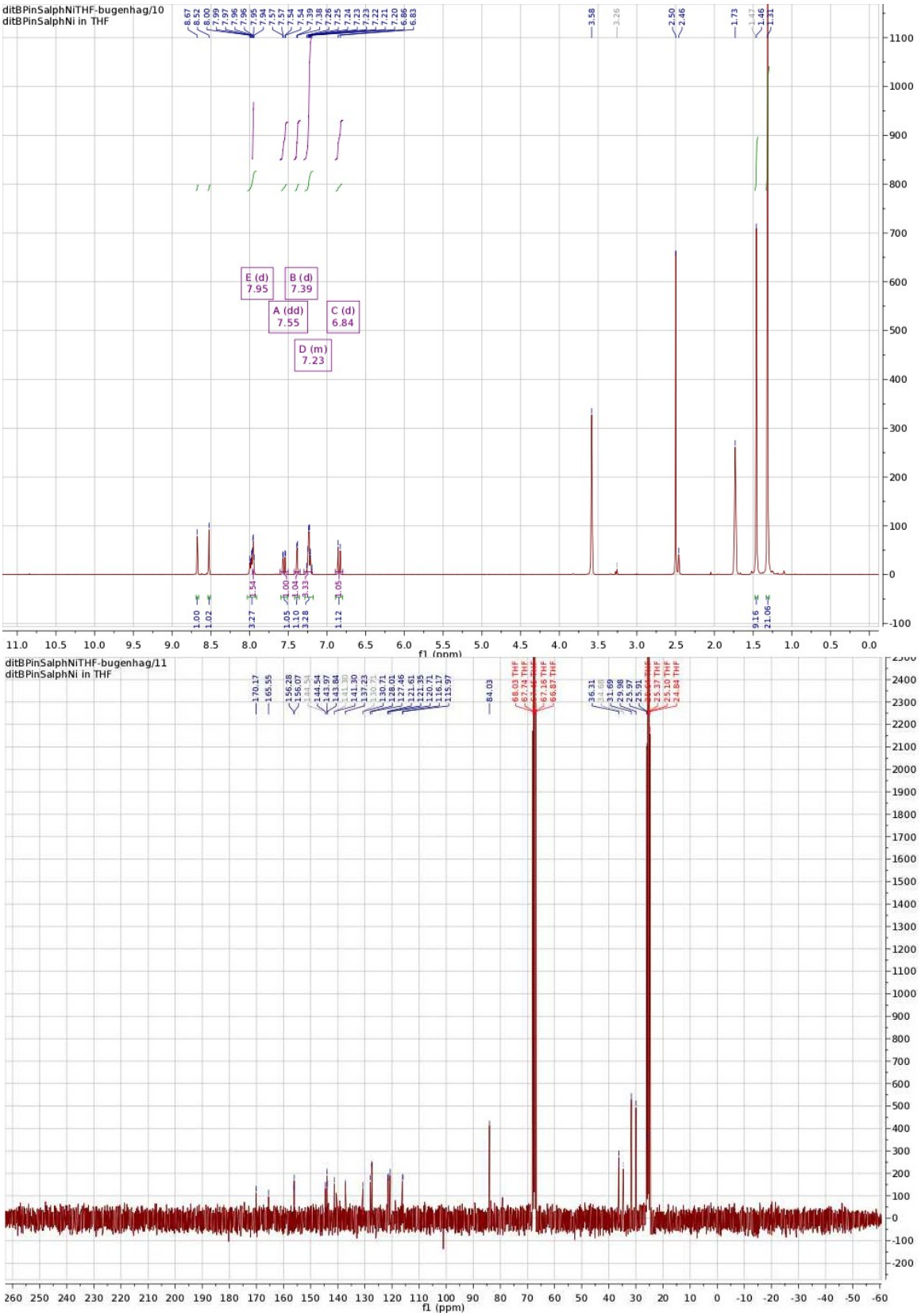


Figure S11: ^{1}H (top) and ^{13}C (bottom)-spectra of **6** measured in THF-d_8.

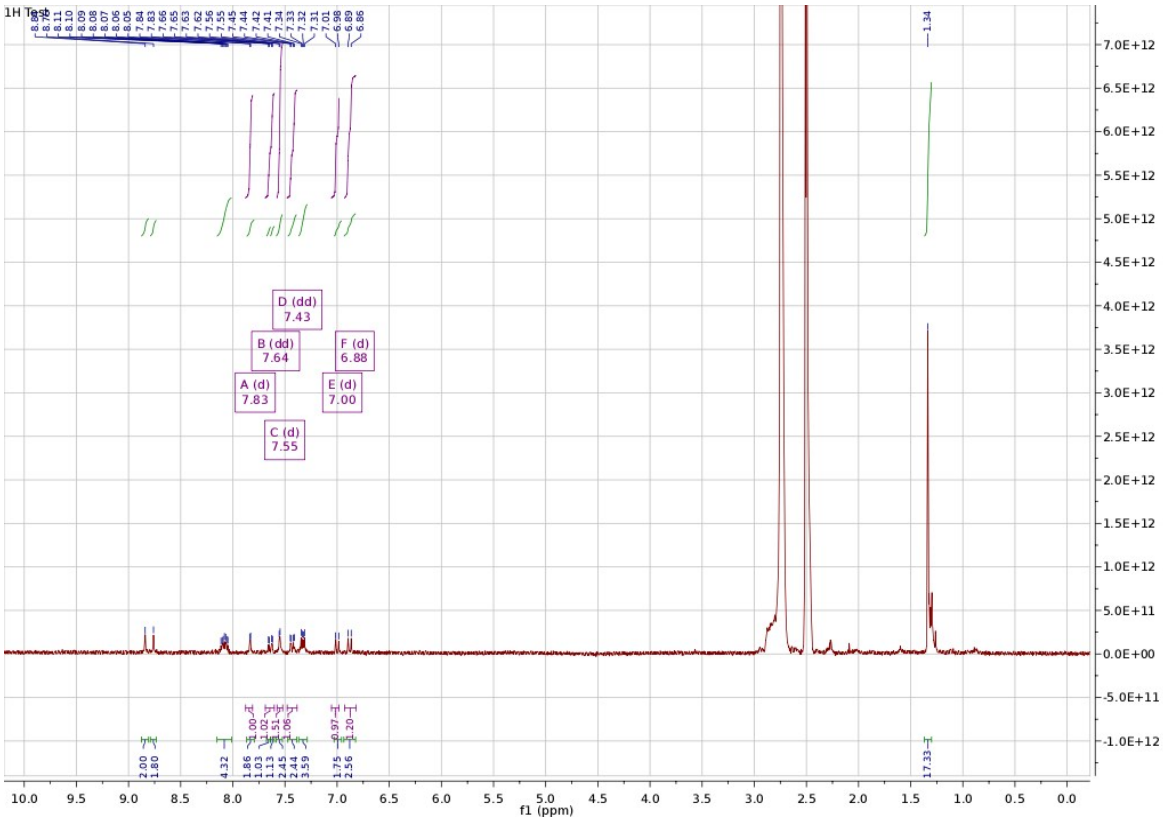


Figure S 81: ^{1}H-NMR-spectra of **8** measured in DMSO-d_6.

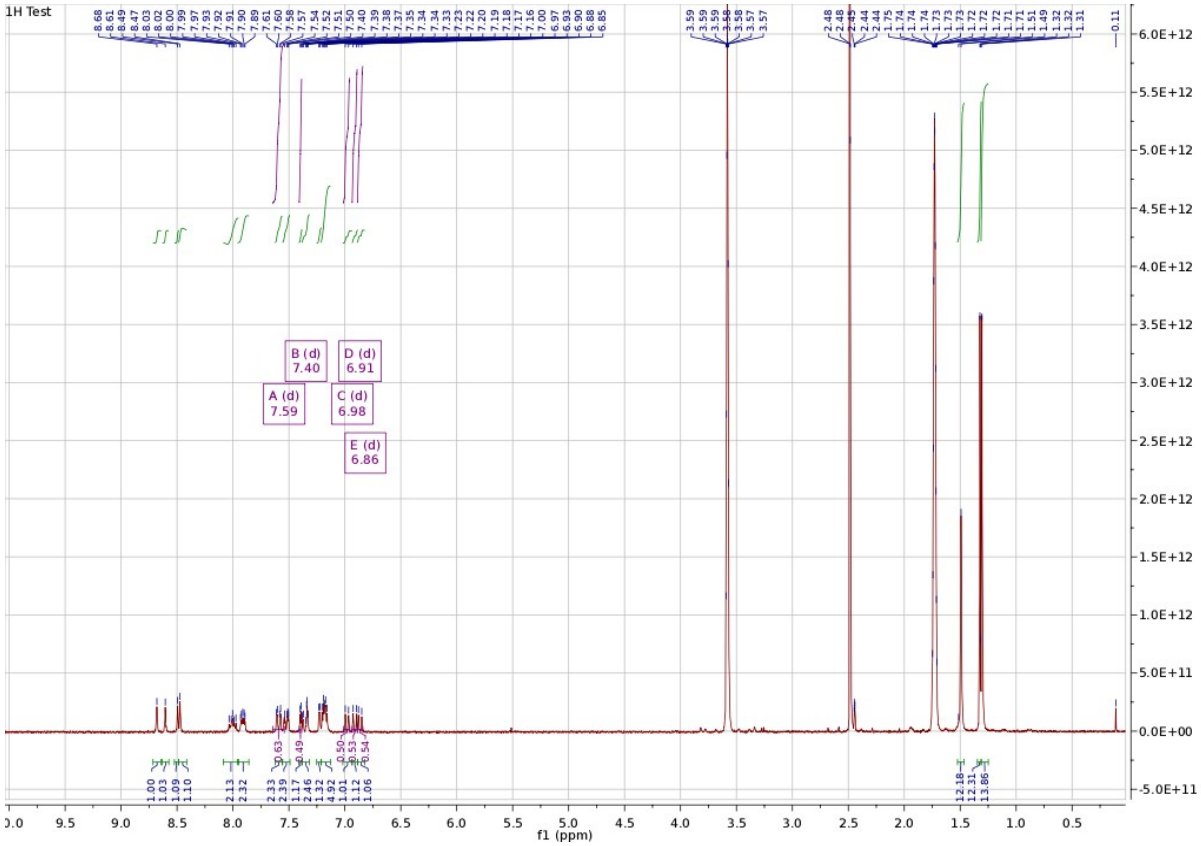


Figure S12: ^{1}H-NMR-spectra of **9/10** measured in THF-d_8.

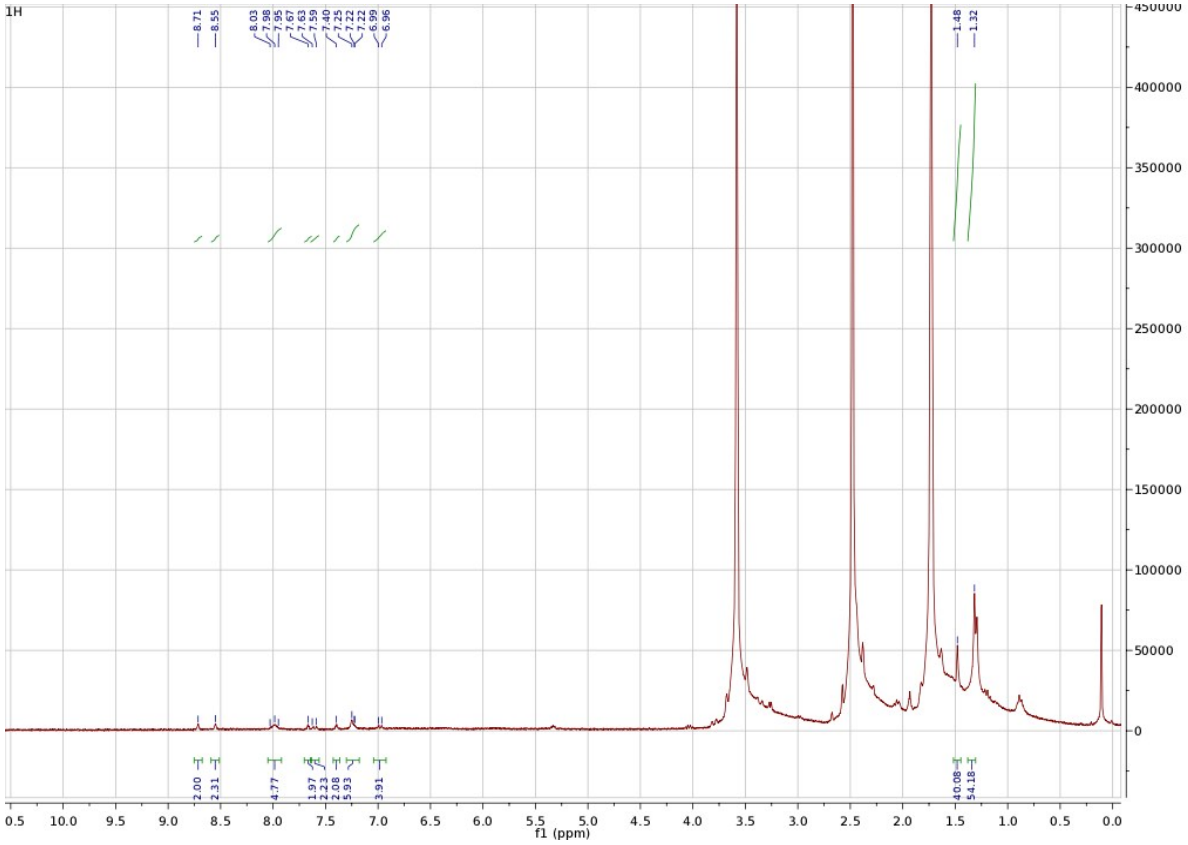


Figure S13: ^{1}H-NMR-spectra of **11** measured in THF-d_8.

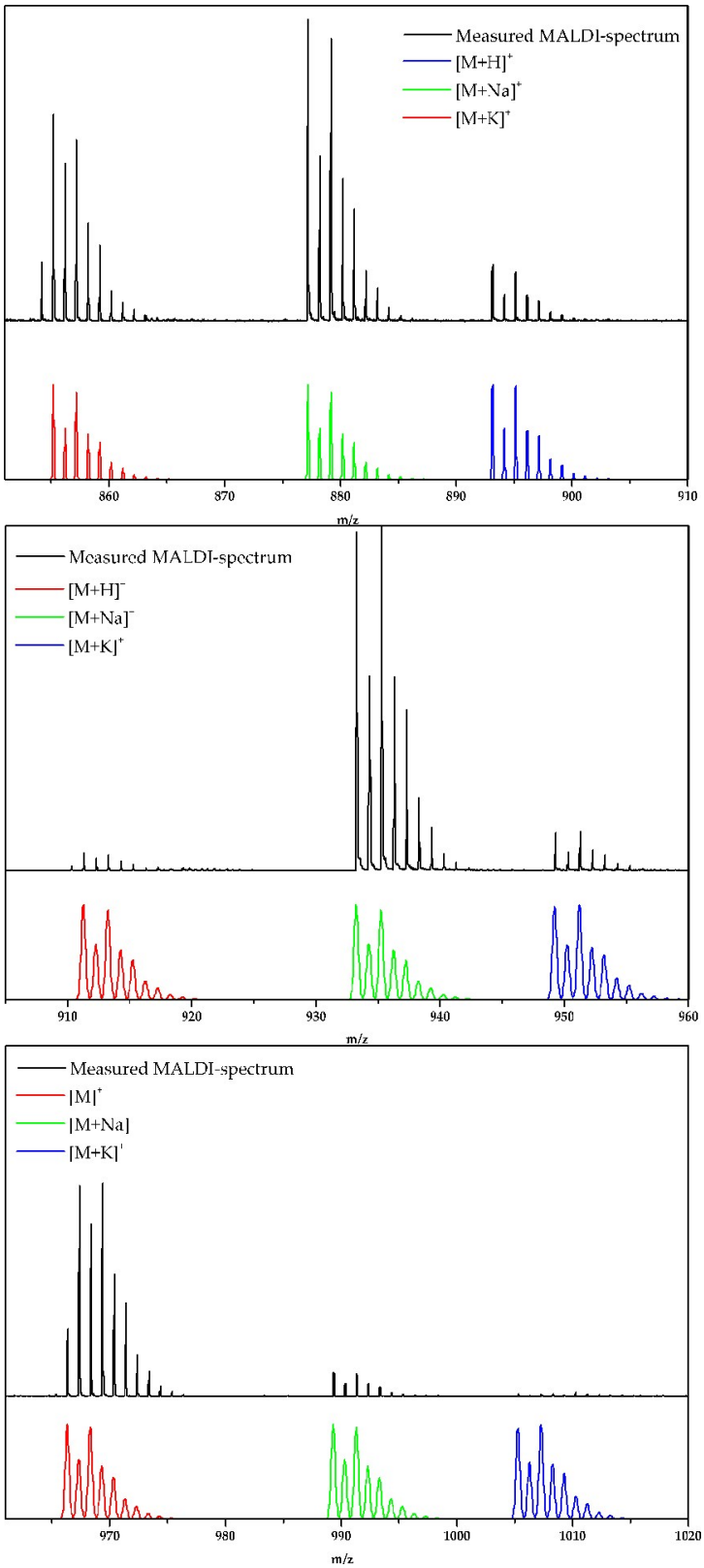


Figure S14: MALDI-MS-spectra of **8** (top), **9**/**10** (middle) and **11** (bottom). Black: experimental spectrum. red, green, blue: Simulated spectra of $[M]^+$ or $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$.

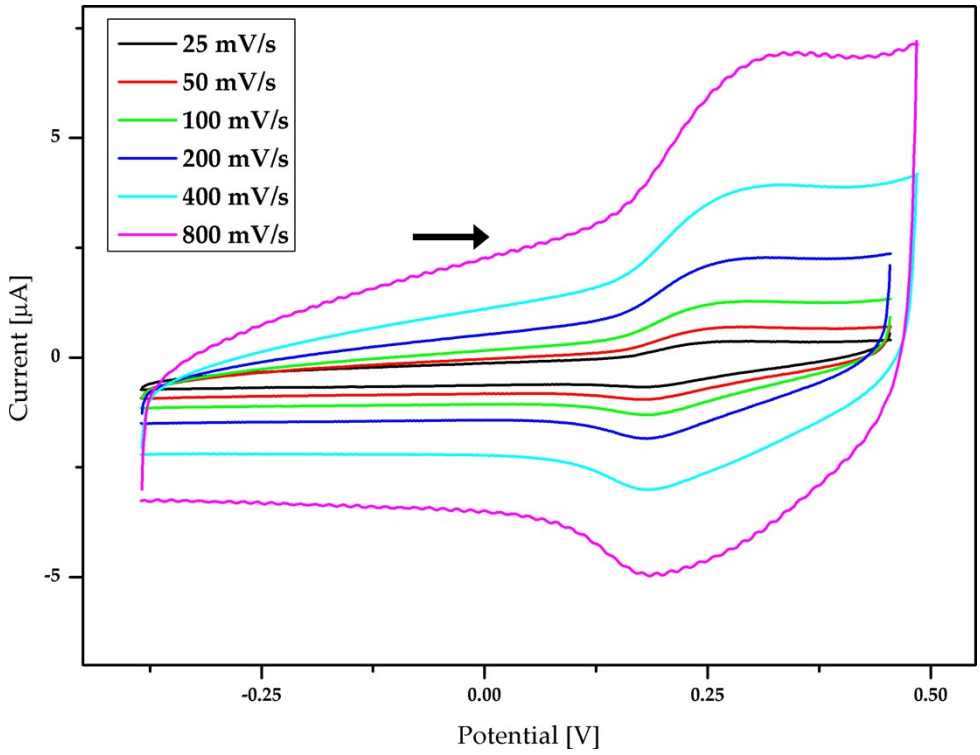


Figure S15: Cyclovoltammogram of the first Red/Ox-process of 11 at different scan-rates (dichloromethane, 0.1 M TBAP as supporting electrolyte, vs Fc^{+}/Fc).