

Cationic Nickel porphyrinoids with unexpected reactivity

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Supporting Information (SI)

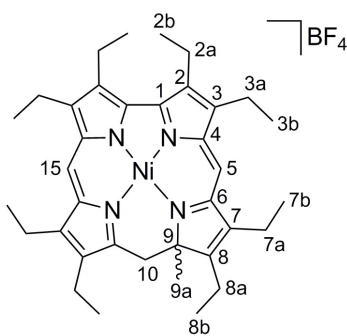
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1. General remarks

All reagents were purchased from commercial sources and used as received. The solvents for extraction and flash chromatography were distilled prior to use. 2,2'-Bidipyrrin complexes **5** and **6** were prepared as described.^[1] NMR spectra were obtained on Bruker AVII 600, AVIII 400, AVII 300 or DPX 200 spectrometer at room temperature in the given solvent (CDCl₃). Chemical shifts (δ) were given in ppm with reference to residual solvent signals ¹H NMR: CHCl₃ (7.26 ppm), ¹³C NMR: CDCl₃ (77.0 ppm). Splitting patterns are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). UV/Vis spectra were obtained on a Varian Cary 50 Scan spectrophotometer. The wavelengths of the UV-vis bands' maxima are given in nm. High resolution ESI⁺ mass spectra were recorded on an IonSpec Ultima instrument in MeCN, m/z values are given for the most abundant isotopes only. Low resolution ESI⁺ mass spectra were recorded on a LCQ-Deca Finnigan instrument in MeCN, m/z values are given for the most abundant isotopes only. EPR spectra were recorded on a Bruker ESP-300 (X-band) spectrometer. X-Ray intensity data was collected at 100(2) K using an Oxford Diffraction Nova A (CuK α) instrument. The single crystal was mounted in inert perfluoroether oil on top of a glass fiber. The structure was solved by direct methods with SIR-92.^[2] Refinements were carried out by full-matrix least squares techniques against all F² using SHELXL-97.^[3] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1057061. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

2. Preparation and analytical data for nickel 9-methylisocorrole **7**

Nickel(II)-2,2'-bidipyrrin **5** (50 mg, 0.1 mmol) was dissolved in 50 mL dichloromethane under nitrogen atmosphere in an UV/Vis protected flask and stirred für 10 min followed by addition of AgBF₄ (49 mg, 0.25 mmol). The reaction



mixture was stirred for 60 min at room temperature before the addition of solid NH₄Br (81 mg, 0.84 mmol) was accomplished and another 60 min reaction time. Thereafter the solution was filtered to remove excess of NH₄Br and solid AgBr. The solvent was removed under reduced pressure and the crude product was purified by the addition of 10 mL abs. methanol and filtration of the generated suspension. The solvent is removed under reduced pressure and the product was recrystallized from chloroform /*n*-hexane to give the nickel 9-methylisocorrole **7** (42 mg, 0.04 mmol, 55%) as dark blue/black needles.

^1H NMR (300 MHz, CD_2Cl_2): δ = 6.67 (s, 1H, H15), 6.16 (s, 1H, H5), 3.49 (d, J = 16.4 Hz, 1H, H10a), 2.65-2.60 (m, 1H, H8a), 2.60-2.51 (m, 10H, H2a, H3a, H7a, H8a, H13a, H17a), 2.51-2.43 (m, 4H, H2a, H12a, H18a), 2.43-2.36 (m, 1H, H12a), 1.74 (d, J = 16.5 Hz, 1H, H10b), 1.22 (m, 6H, H8b, H2b), 1.20 (t, J = 7.7 Hz, 3H, H18b), 1.18-1.14 (m, 12H, H3b, H7b, H13b, H17b), 1.13 (s, 3H, H9a), 1.10 (t, J = 7.6 Hz, 3H, H12b). ^{13}C NMR (150 MHz, CDCl_3): δ = 179.4 (C11), 172.3 (C8), 170.3 (C4), 168.6 (C6), 153.7 (C17), 152.5 (C7), 150.6 (C19), 145.4 (C16), 144.6 (C14), 143.2 (C1), 142.0 (C18), 140.7 (C13), 140.2 (C2), 140.1 (C12), 138.0 (C3), 118.2 (C15), 103.8 (C5), 77.9 (C9), 36.6 (C10), 27.1 (C9a), 19.7 (C8a), 18.9 (C3a), 18.8 (C7a), 18.3 (C17a), 18.2 (C13a), 17.5 (C2a), 17.4 (C18a), 17.3 (C3b), 17.2 (C12a), 16.6 (C17b), 16.5 (C18b), 16.0 (C2b), 15.6 (C7b), 15.1 (C12b), 15.0 (C13b), 13.5 (C8b). ^{11}B NMR (96 MHz, CDCl_3): δ = -0.71; ^{19}F NMR (188 MHz, CDCl_3): δ = -154.4; UV/Vis (CH_2Cl_2): λ_{max} : 340, 379 (sh), 550 (sh), 589, 630 (sh), 986; HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{47}\text{Ni}_4$: 593.3149, found: 593.3151 Δ = 0.2 mmu;

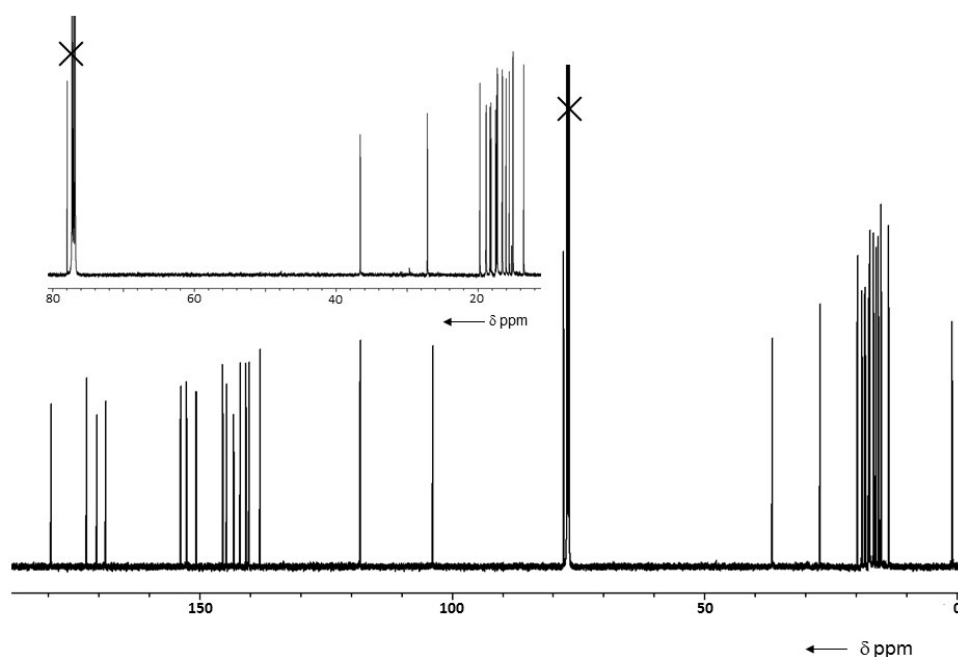


Fig. S1: ^{13}C NMR spectrum (150 MHz, CDCl_3) of nickel 9-methylisocorrole **7**.

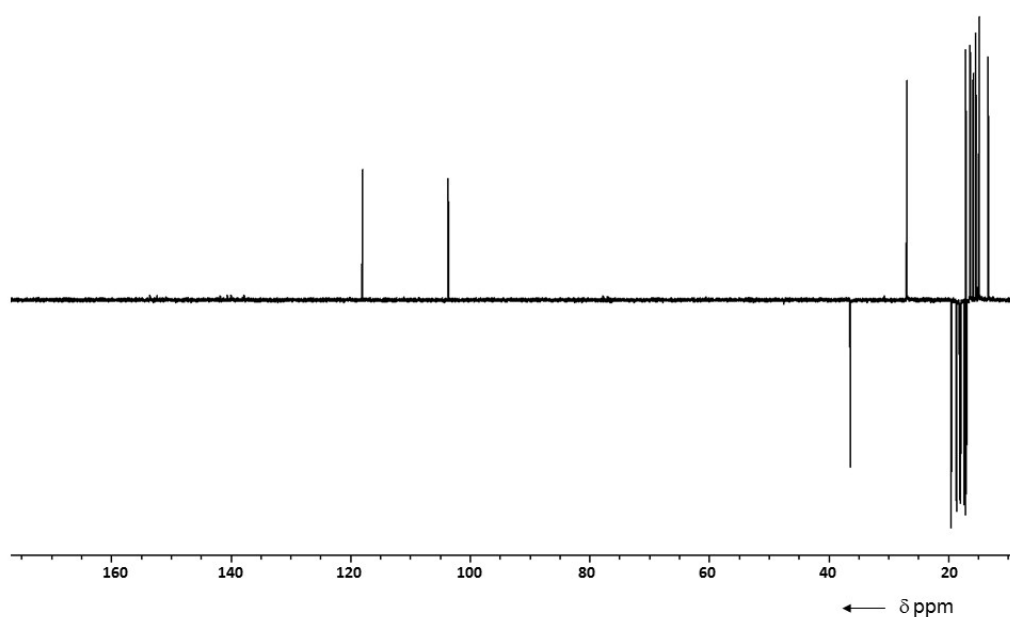


Fig. S2: ^{13}C NMR DEPT spectrum (150 MHz, CDCl_3) of nickel 9-methylisocorrole **7**.

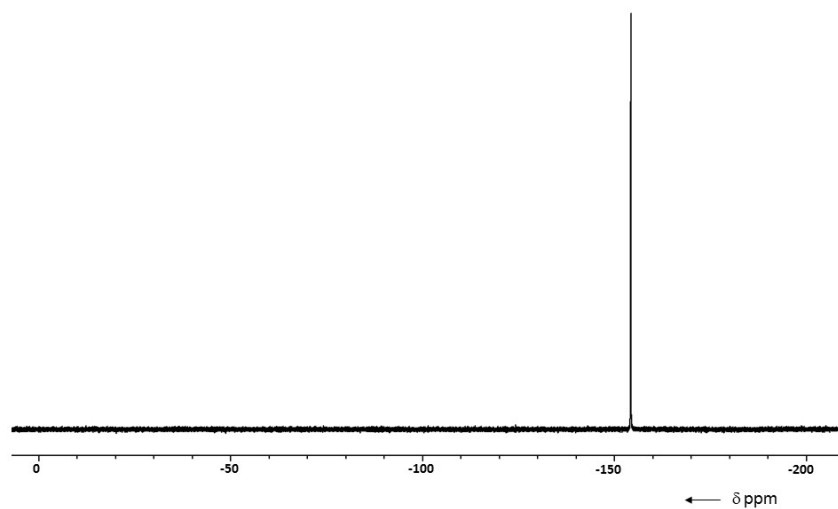


Fig. S3: ^{19}F NMR spectrum (188 MHz, CDCl_3) of nickel 9-methylisocorrole **7**.

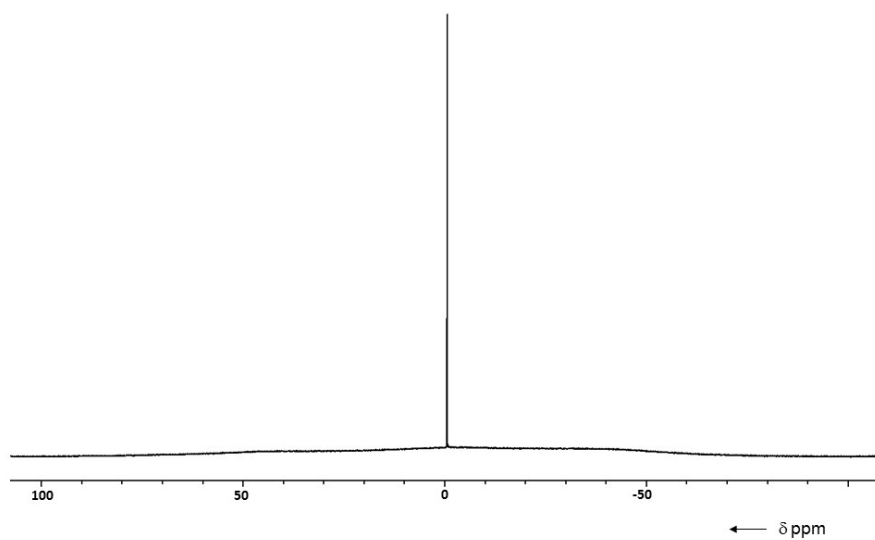


Fig. S4: ^{11}B NMR spectrum (96 MHz, CDCl_3) of 9-methylisocorrole **7**.

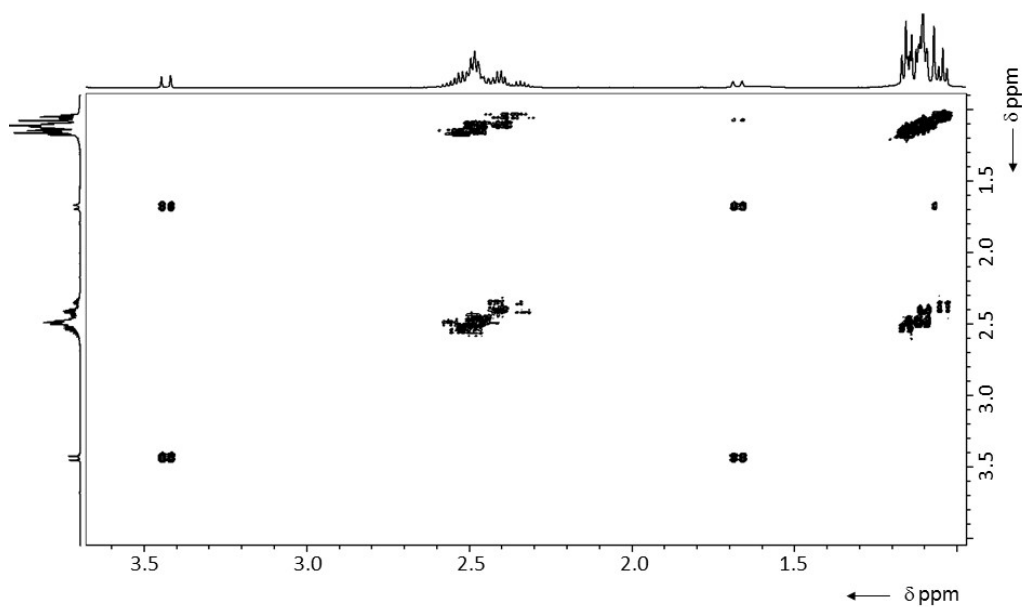


Fig. S5: ^1H , ^1H COSY spectrum of nickel 9-methylisocorrole **7**; aliphatic region details.

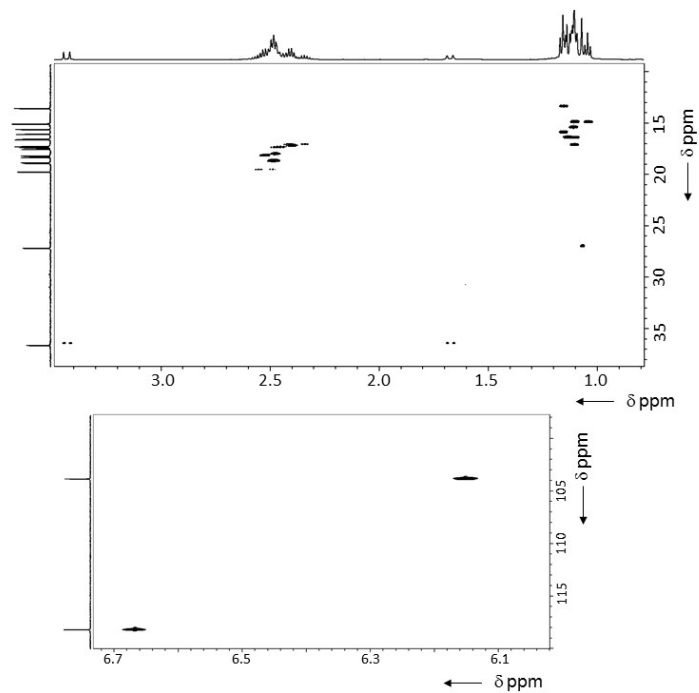


Fig. S6: ^1H , ^{13}C HSQC spectrum of nickel 9-methylisocorrole **7**; at the top: aliphatic region details; at the bottom: aromatic region details.

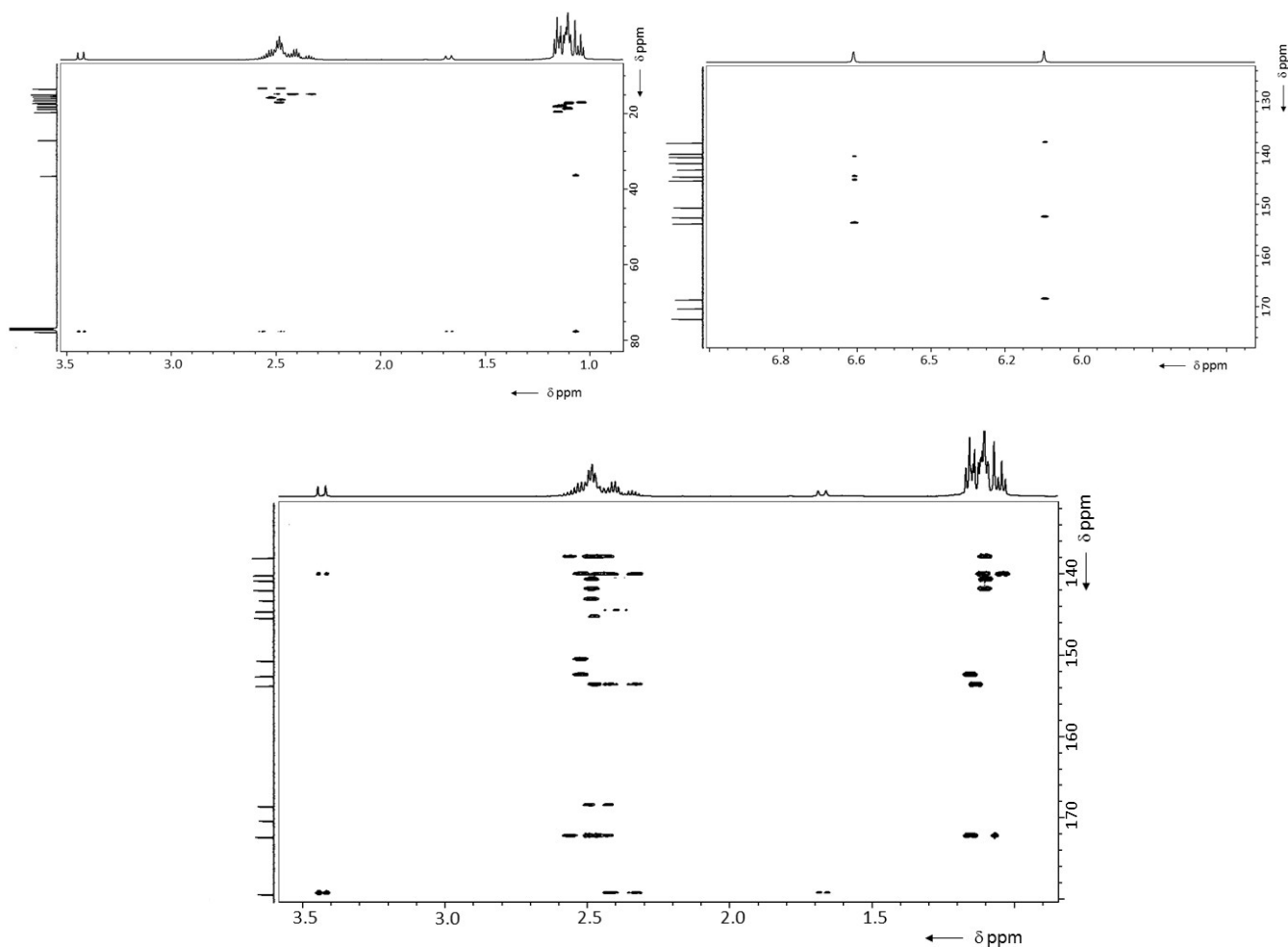
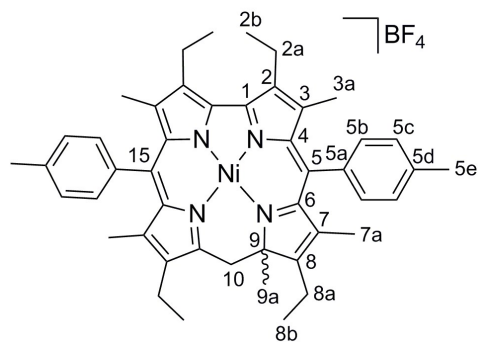


Fig. S7: ^1H , ^{13}C HMBC spectrum of nickel 9-methylisocorrole **7**; at the top left: aliphatic region details; at the top right: aromatic region details; at the bottom: aliphatic ^1H /aromatic ^{13}C region details.

3. Preparation and analytical data for nickel 9-methylisocorrole **8**



Nickel(II)-2,2'-bidipyrrin **6** (60 mg, 0.08 mmol) was dissolved in 50 mL dichloromethane under nitrogen atmosphere in an UV/Vis protected flask and stirred for 10 min followed by addition of AgBF_4 (33 mg, 0.17 mmol). The reaction mixture was stirred for 60 min at room temperature before the addition of solid NH_4Br (81 mg, 0.84 mmol) was accomplished and another 60 min reaction time. Thereafter the solution was filtered to remove excess of NH_4Br and solid AgBr from the solution. The solvent was removed under reduced pressure and the crude product was

purified by the addition of 10 mL abs. methanol and filtration of the generated suspension. The solvent is removed under reduced pressure and the product was recrystallized from dichloromethane /*n*-hexane to give the nickel 9-methylisocorrole **8** (48 mg, 0.06 mmol, 76%) as dark blue nearly black needles.

^1H NMR (300 MHz, CD_2Cl_2): δ = 7.30-6.99 (m, 8H, H5b, H5c, H15b, H15c), 3.25 (d, J = 16.1 Hz, 1H, H10a), 2.45-2.33 (m, 4H, H2a, H18a), 2.36 (s, 6H, H5e), 2.33-2.23 (m, 3H, H12a, H8a), 2.19-2.11 (m, 1H, H8a), 1.58 (d, J = 16.1 Hz, 1H, H10b), 1.24 (s, 3H, H13a), 1.17 (s, 3H, H17a), 1.10 (s, 3H, H9a), 1.08 (s, 3H, H3a), 1.02 (s, 3H, H7a), 0.99 (t, J = 7.7 Hz, 3H, H12b), 0.96 (t, J = 7.5 Hz, 3H, H18b), 0.94 (t, J = 7.6 Hz, 3H, H2b), 0.90 (t, J = 7.7 Hz, 3H, H8b). ^{13}C NMR (150 MHz, CDCl_3): δ = 175.7, 174.6, 170.5, 169.2, 150.0, 148.8, 148.7, 144.4, 143.5, 142.6, 141.4, 141.3, 140.9, 140.3, 140.1, 136.5, 134.4, 132.8, 131.5, 130.5 (CH_{Ar}), 130.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 126.2, 36.5 (C10), 25.3 (C9a), 21.5 (C5e), 20.2 (C12a), 19.1 (C2a oder C18a), 18.9 (C2a oder C18a), 17.5 (C8a), 16.2 (C2b), 14.7 (C18b), 14.6 (C8b), 14.0 (C17a), 13.3 (C13a), 12.9 (C12b), 12.8 (C3a), 11.3 (C7a). ^{11}B NMR (96 MHz, CDCl_3): δ = -0.80. ^{19}F NMR (188 MHz, CDCl_3): δ = -153.7. UV/Vis (CH_2Cl_2): λ_{max} : 331, 378 (sh), 556 (sh), 598, 642 (sh) 871, 973; HRMS (ESI): m/z calcd for $\text{C}_{46}\text{H}_{51}\text{NiN}_4$: 717.3462, found: 717.3468 Δ = 0.6 mmu.

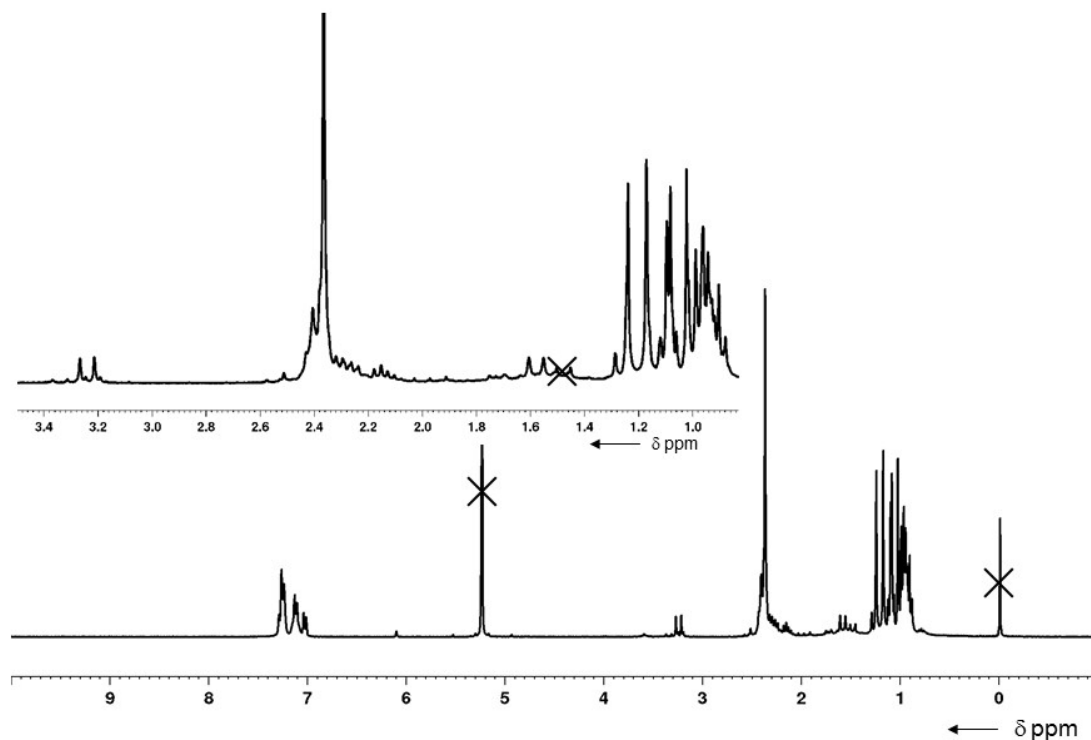


Fig. S8: ^1H NMR spectrum (600 MHz, CD_2Cl_2) of Nickel 9-methylisocorrole **8**.

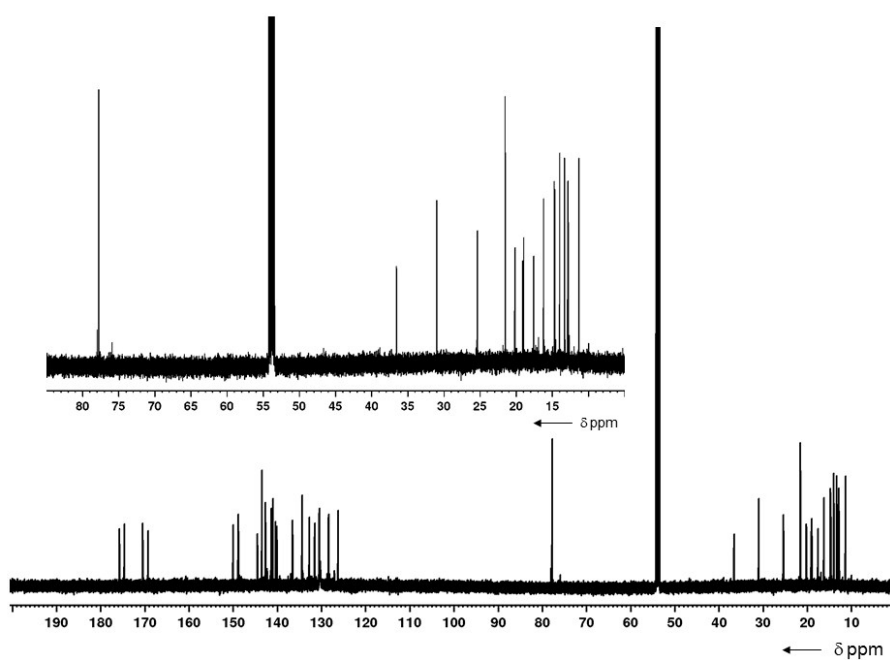


Fig. S9: ^{13}C NMR spectrum (150 MHz, CD_2Cl_2) of Nickel 9-methylisocorrole **8**.

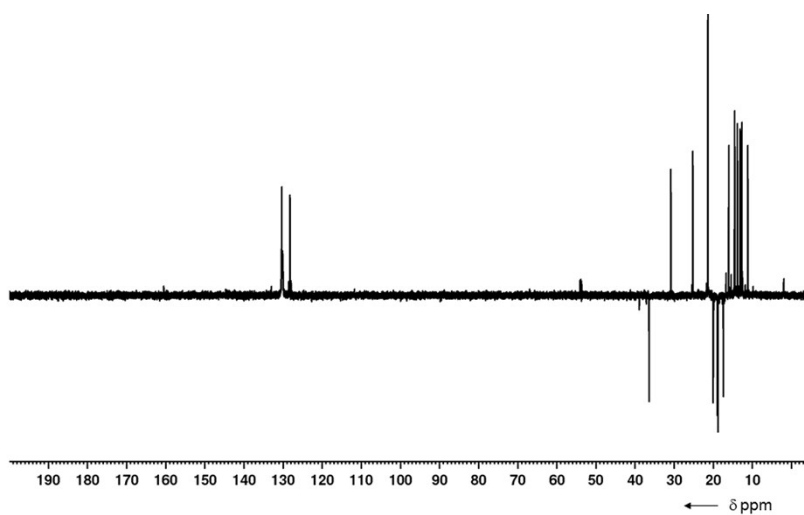


Fig. S10: ^{13}C NMR DEPT spectrum (150 MHz, CD_2Cl_2) of Nickel 9-methylisocorrole **8**.

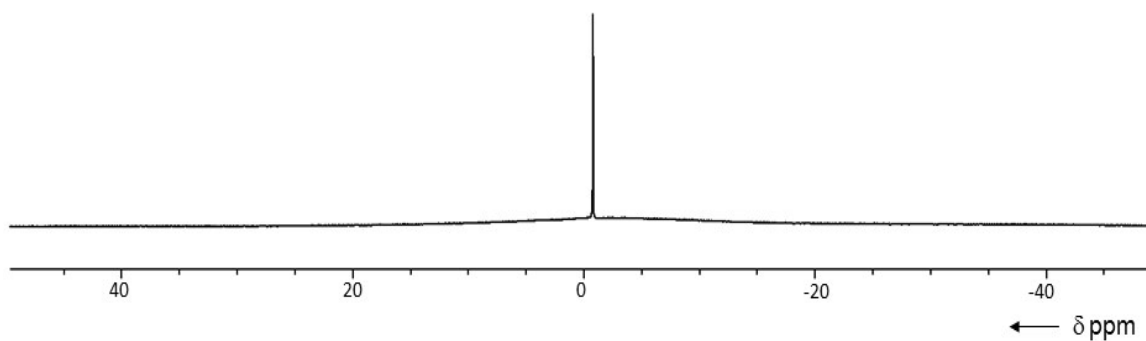


Fig. S11: ^{11}B NMR spectrum (96 MHz, CDCl_3) of Nickel 9-methylisocorrole **8**.

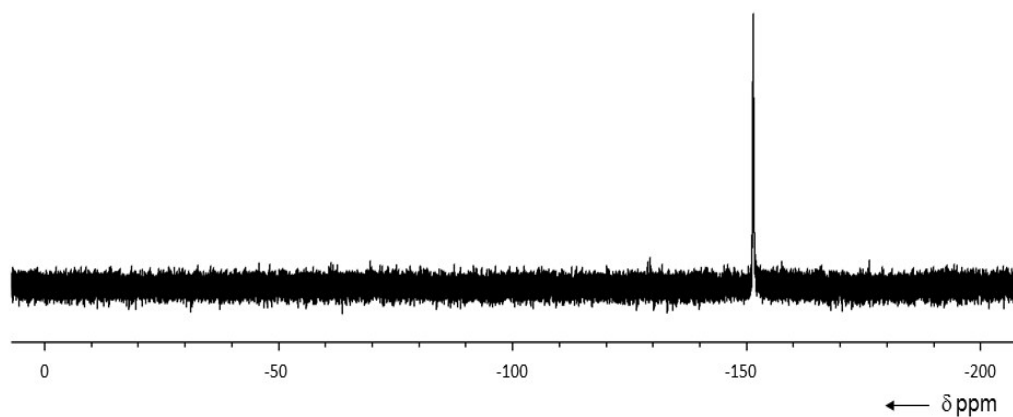


Fig. S12: ^{19}F NMR spectrum (88 MHz, CDCl_3) of Nickel 9-methylisocorrole **8**.

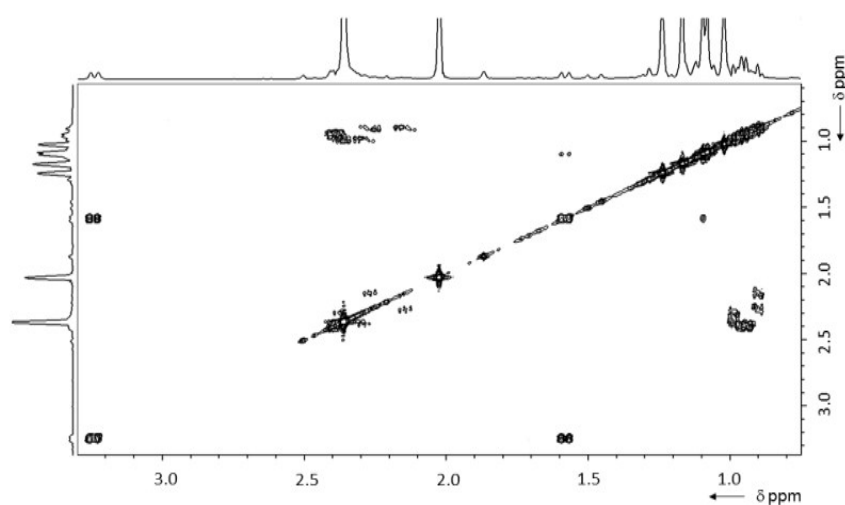


Fig. S13: $^1\text{H},^1\text{H}$ COSY spectrum of Nickel 9-methylisocorrole **8**; aliphatic region details.

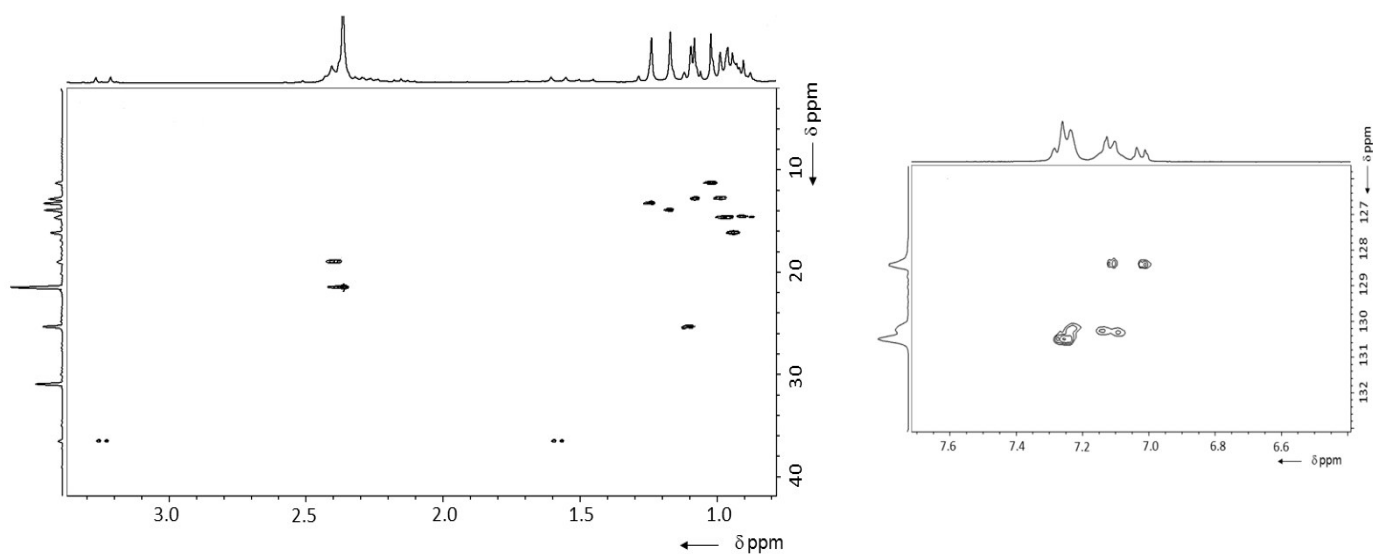


Fig. S14: $^1\text{H},^{13}\text{C}$ HSQC spectrum of Nickel 9-methylisocorrole **8**; left: aliphatic region details; right: aromatic region details.

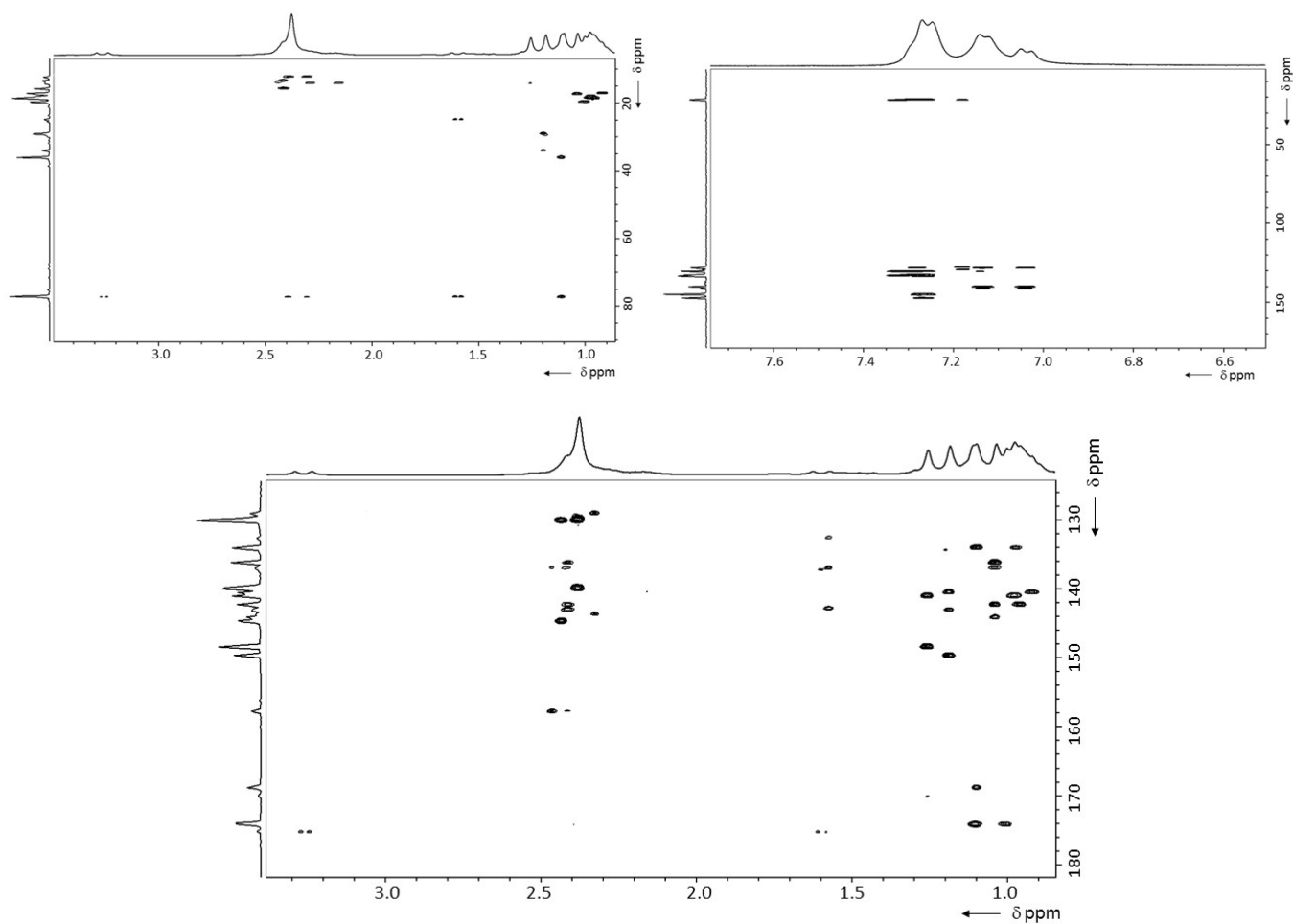


Fig. S15: ^1H , ^{13}C HMBC spectrum of Nickel 9-methylisocorrrole **8**; top left: aliphatic region details; top right: aromatic region details; bottom: aliphatic ^1H /aromatic ^{13}C region details.

4. UV/Vis and EPR spectra of reduced **7'** and **8'**

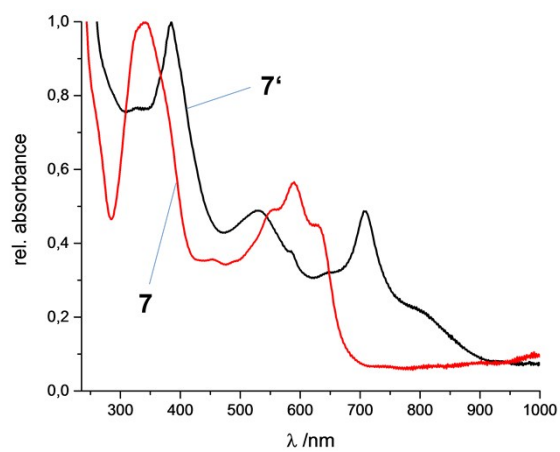


Fig. S16: UV/Vis spectra of **7** (THF) and of **7'** (THF, reduced with Na/Hg).

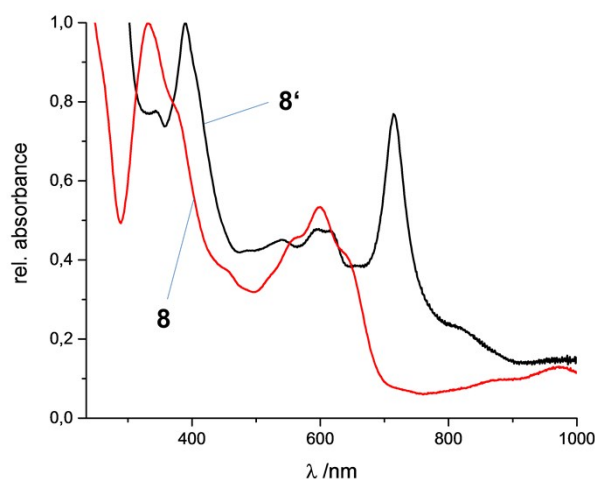


Fig. S17: UV/Vis spectra of **8** (THF) and of **8'** (THF, reduced with Na/Hg).

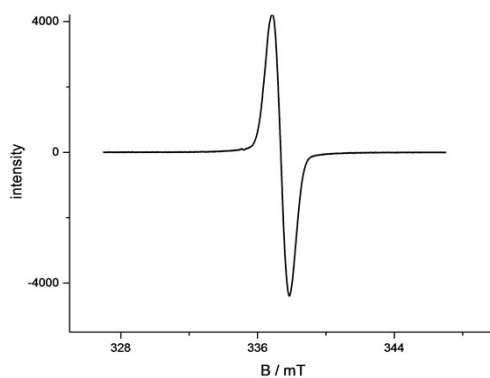


Fig. S18: X-band EPR spectrum (THF, reduced with Na/Hg, 10 K) of **8'**.

5. DFT calculations

Computational details: For the prediction of the electronic properties of the respective nickel corrinoid radical **7'** a geometry optimization with subsequent normal mode analysis was carried out. For all calculations the B3LYP hybrid density functional^[4] as implemented in the Gaussian 09 set of programs^[5] was employed. All atoms except nickel were described by a polarized valence basis set of triple zeta quality (TZVP) developed by *Ahlrichs et al.*^[6] as implemented in Gaussian 09. For nickel the well-tempered basis set (WTBS) from *Huzinaga et al.*^[7] was used. For the graphical representation of the relevant molecular orbitals, cube-files have been exported from the Gaussian calculations, which were then visualized by ChemDraw 3D. Percentual contributions of the molecular orbitals have been computed with the program GaussSum^[8].

Atom coordinates (xyz) for one-electron reduced nickel corrinoid 7':

C	2.54640	0.65070	-0.27380	C	1.36520	2.53320	-0.22820
C	3.49660	1.73830	-0.28970	C	0.20550	3.30690	-0.24760
C	2.75370	2.91170	-0.26850	H	0.31620	4.38320	-0.29260

C	-1.09410	2.80530	-0.25190	C	-5.53430	3.13180	0.76420
C	-2.30840	3.55560	-0.38610	H	-5.44330	2.25220	1.40540
C	-3.34520	2.63470	-0.44290	H	-6.59830	3.33140	0.61260
C	-2.74210	1.34650	-0.33640	H	-5.10540	3.97650	1.30690
C	-3.43250	0.01680	-0.40990	C	-2.90770	-0.59930	2.00150
H	-3.37420	-0.36270	-1.43680	H	-2.46520	-1.35780	2.64760
H	-4.49110	0.14950	-0.18130	H	-3.94150	-0.43530	2.31290
C	-2.84420	-1.06070	0.52690	H	-2.35700	0.33140	2.12940
C	-3.51130	-2.41940	0.39040	C	-4.98190	-2.64780	0.58630
C	-2.56270	-3.33730	0.12470	H	-5.39580	-1.85800	1.21900
C	-1.27120	-2.63730	0.00610	H	-5.13810	-3.58190	1.13330
C	-0.03100	-3.27470	-0.22540	C	-5.78200	-2.70660	-0.72780
H	-0.02610	-4.34710	-0.35540	H	-5.68700	-1.78020	-1.29620
C	1.17270	-2.57720	-0.27640	H	-6.84290	-2.86940	-0.52420
C	2.52950	-3.04510	-0.48520	H	-5.43030	-3.52070	-1.36370
C	3.35370	-1.93050	-0.49240	C	-2.71890	-4.81740	-0.02490
C	2.50050	-0.78540	-0.27250	H	-3.74800	-5.13090	0.15010
C	4.99670	1.66040	-0.28780	H	-2.08010	-5.35590	0.68070
H	5.39730	2.40640	-0.98130	H	-2.43760	-5.14800	-1.02890
H	5.32010	0.69650	-0.67410	C	2.91070	-4.48520	-0.64930
C	5.63130	1.88320	1.09560	H	3.85630	-4.55810	-1.19200
H	5.42520	2.88800	1.46650	H	2.16620	-4.98560	-1.27650
H	6.71590	1.75750	1.05030	C	3.03660	-5.25310	0.67890
H	5.23730	1.17640	1.82800	H	3.81280	-4.81790	1.31090
C	3.26190	4.32370	-0.27360	H	3.29320	-6.30020	0.49920
H	4.29680	4.33440	-0.62410	H	2.10070	-5.22400	1.23960
H	2.69410	4.91050	-1.00330	C	4.83930	-1.95350	-0.70440
C	3.18740	5.03040	1.09130	H	5.13800	-1.10550	-1.32340
H	2.15920	5.08500	1.45310	H	5.09550	-2.84180	-1.28700
H	3.57560	6.04960	1.02110	C	5.66460	-1.96410	0.59230
H	3.77010	4.49680	1.84400	H	5.43760	-1.09910	1.21600
C	-2.40760	5.04740	-0.44350	H	6.73520	-1.95240	0.37290
H	-3.39090	5.36490	-0.79300	H	5.45060	-2.85800	1.18080
H	-1.66530	5.47850	-1.11970	N	1.29540	1.17790	-0.22660
H	-2.25120	5.50220	0.54010	N	-1.41310	1.45060	-0.21060
C	-4.81410	2.91810	-0.57730	N	-1.44820	-1.32790	0.16450
H	-4.95670	3.80610	-1.19970	N	1.21490	-1.23210	-0.14170
H	-5.30080	2.10190	-1.11860	Ni	-0.15670	0.01900	-0.08370

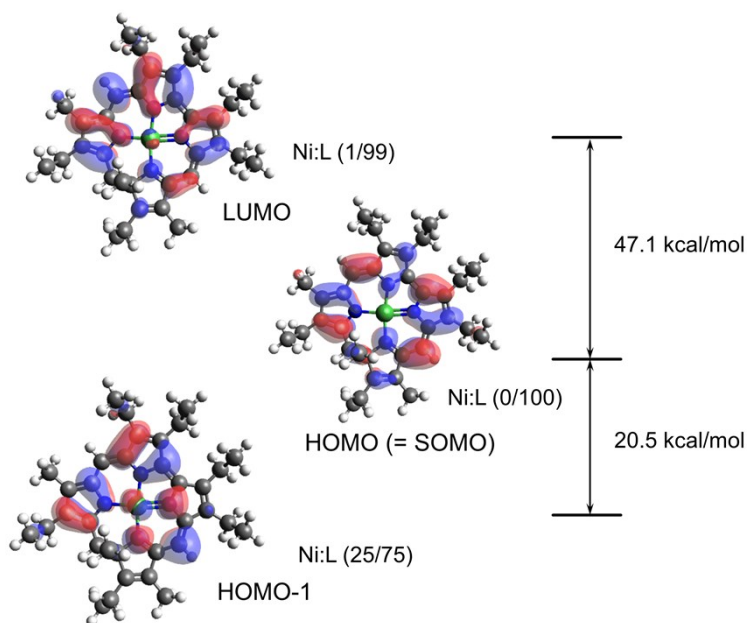


Fig. S19: Calculated LUMO, HOMO (= SOMO) and HOMO-1 with percentual contribution (Nickel:ligand) of 1e⁻-reduced **7**⁺.

6. Catalysis

Catalytic studies were investigated via coupled GC-MS on a GCMS-QP2010SE (Shimadzu) in positive EI mode (70 eV, 60 – 700 m/z). A ZB-5MS GUARDIAN column (30 m × 0.25 mm × 0.25 μm) and Helium as carrier gas were employed. The same temperature program (start at 50°C for 3 min, then heating by 12°C/min up to 300°C and keeping up for 8 min) was used for all measurements.

Typical catalytic reactions were conducted as follows: In a 10 mL rbf containing arylhalide (1 equiv, 134 μmol) in dry solvent (4 mL) the catalyst **7** or **8** (1 – 5 mol%), followed by the Grignard compound (1.5 – 5 equiv) was added and stirred under a blanket of nitrogen. For analysis, an aliquot (0.3 mL) of the reaction solution is diluted with diethylether (0.6 mL) and quenched with phosphoric acid (5% in water, 1 mL). An aliquot of the resulting organic layer (0.3 mL) is filtered on Celite and added to 1 mL of a decane standard (solution of decane (53.7 mg) in diethylether (50 mL)). GC measurements were performed on these solutions.

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