Electronic Supplementary Information

Synthesis of stable free base secochlorins and their corresponding metal complexes from *meso*-tetraarylporphyrin derivatives

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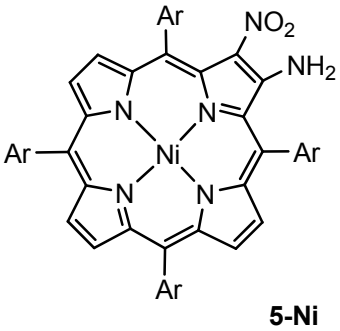
I. EXPERIMENTAL DETAILS

^{1}H NMR spectra were recorded on Brucker DPX 200 MHz and Brucker Avance 300 MHz spectrometers. NMR spectra were reported downfield to $SiMe_4$ and referenced to chloroform peak (δ = 7.29 ppm). Abbreviations for ^{1}H NMR spectra used are as follows: s, singlet; d, doublet; m, multiplet. UV-visible spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer in quartz cells and CH_2Cl_2 was used as solvent. IR spectra were recorded on an Avatar 320 FT-IR spectrometer as KBr discs. High resolution mass spectra were recorded on a Q-Tof Waters 2001 MS instrument. All reagents and solvents were of the commercial reagent grade and were used without further purification. Dry CH_2Cl_2 was obtained by distilling over P_2O_5. THF was obtained by distilling over CaH_2, then Na/benzophenone. Preparative separations were performed by silica gel flash column chromatography (Baeckeroot-Labo 60M).

II. SYNTHESES OF THE COMPOUNDS

Synthesis of nickel(II) 2-amino-3-nitroporphyrin 5-Ni

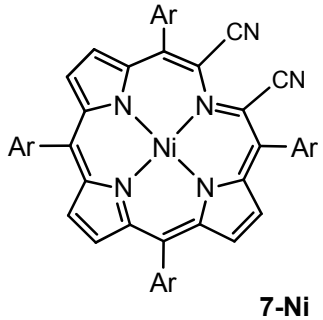


5-Ni

Ar = 4-*t*BuPh

The synthesis of this compound was previously reported. See: S. Richeter, A. Hadj-Aïssa, C. Taffin, A. van der Lee and D. Leclercq, *Chem. Commun.,* 2007, 2148-2150; J. -F Lefebvre, D. Leclercq, J.-P. Gisselbrecht and S. Richeter, *Eur. J. Org. Chem.*, 2010, 1912-1920.

Synthesis of nickel(II) 2,3-dicyano-2,3-secochlorin 7-Ni



7-Ni

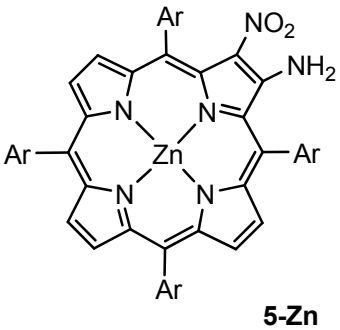
Ar = 4-*t*BuPh

To a degassed solution of the 2-amino-3-nitroporphyrin **5-Ni** (362 mg, 0.38 mmol) and palladium on activated carbon 10% (15 mg) in a dichloromethane (100 mL) /methanol (10 mL) mixture, sodium borohydride (360 mg, 9.63 mmol) was added and the mixture was stirred under argon at room temperature for 1h. The

completion of the reduction was verified by silica gel TLC (one red spot corresponding to the 2,3-diaminoporphyrin **6-Ni**). After evaporation of the solvents, the residue was filtered through a pad of celite with chloroform. The solid obtained after evaporation of chloroform was immediately dissolved in dichloromethane (100 mL) and (diacetoxyiodo)benzene (250 mg, 0.78 mmol) was added. The reaction mixture was stirred for 10 minutes and the completion of the reduction was verified by silica gel TLC (one green spot corresponding to the 2,3-dicyano-2,3-secochlorin **7-Ni**). Then, the solvent was evaporated, and the residue was purified by silica gel column chromatography (dichloromethane/*n*-pentane 1:1). Crystallization from a CH_2Cl_2/*n*-pentane mixture afforded the nickel(II) 2,3-dicyano-2,3-secochlorin **7-Ni** in 75% yield (262 mg).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$): δ = 8.35 (d, J = 4.9 Hz, 2H, pyrrole), 8.13 (s, 2H, pyrrole), 7.92 (d, J = 4.9 Hz, 2H, pyrrole), 7.81 – 7.56 (m, 16H, Ar *meso*), 1.50 (s, 18H, *t*-Bu), 1.45 (s, 18H, *t*-Bu) ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 451 (101 000), 661 (16 000 L.mol^{-1}.cm^{-1}) nm. **^{13}C{^{1}H} NMR** (50.3 MHz, 25°C, $CDCl_3$, 25°C): δ = 152.1, 151.8, 147.5, 144.4, 140.4, 135.4, 134.88, 133.9, 133.4, 132.8, 131.7, 131.1, 129.9, 125.3, 124.6, 121.1, 120.7, 120.5, 35.0, 35.0, 31.6, 31.6 ppm. **IR** (KBr): ν = 2211 (C≡N) cm^{-1}. **HR-MS** (ESI-TOF$^+$) $C_{60}H_{59}N_6Ni^+$ $[M+H]^+$: calcd. *m/z* = 921.4155; found 921.4166. **Elem. Anal.** (%) $C_{60}H_{58}N_6Ni \bullet 1.5H_2O$: calcd. C 75.95, H 6.48, N 8.86; found C 75.99, H 6.60, N 8.62.

Synthesis of zinc(II) 2-amino-3-nitroporphyrin 5-Zn



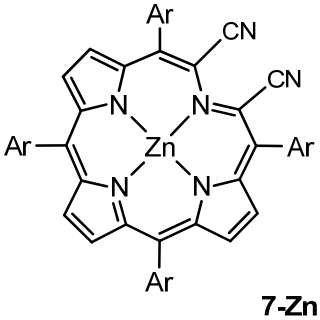
5-Zn

Ar = 4-*t*BuPh

The 2-amino-3-nitroporphyrin **5-Ni** (378 mg, 0.40 mmol) was dissolved in a TFA/H_2SO_4 (12 mL / 3 mL) mixture and the solution was stirred at room temperature for 30 minutes. It was then poured on ice, diluted with chloroform (200 mL), neutralized with saturated K_2CO_3 and washed with water. The organic layer was separated, dried with $MgSO_4$ and evaporated. The residue was dissolved in THF (100 mL), $Zn(OAc)_2.2H_2O$ (750 mg) was added and the mixture was refluxed for one hour. After evaporation of THF, the residue was purified by silica gel column chromatography (dichloromethane/*n*-pentane, from 1:1 to 2:1). Crystallization from CH_2Cl_2/MeOH afforded the zinc(II) 2-amino-3-nitroporphyrin **5-Zn** as a green solid in 47% (178 mg).

^{1}H NMR (200 MHz, 25°C, $CDCl_3/CD_3OD$ 9:1): broad signals indicative of aggregation presumably due to the formation of oligomeric or polymeric materials through NH_2---Zn coordination bonds. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 446 (117 000), 572 (9 500), 514 (8 000 L.mol^{-1}.cm^{-1}) nm. **HR-MS** (ESI-TOF$^+$) $C_{60}H_{61}N_6O_2Zn^+$ $[M+H]^+$: calcd. *m/z* = 961.4147; found 961.4128. **Elem. Anal.** (%) $C_{60}H_{60}N_6O_2Zn\bullet H_2O$: calcd. C 73.49, H 6.37, N 8.57; found C 73.50, H 6.95, N 8.61.

Synthesis of zinc(II) 2,3-dicyano-2,3-secochlorin 7-Zn



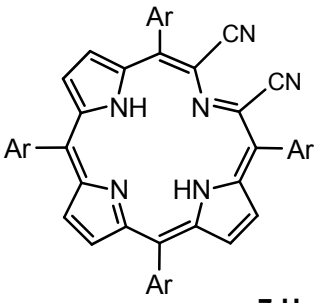
7-Zn

Ar = 4-*t*BuPh

Same procedure as for secochlorin **7-Ni**, using the zinc(II) 2-amino-3-nitroporphyrin **5-Zn** (178 mg, 0.19 mmol) as starting material. The 2,3-dicyano-2,3-secochlorin **7-Zn** was purified by silica gel column chromatography (dichloromethane/*n*-pentane from 3:2 to 4:1) and obtained in 78% yield (134 mg) as a green solid after crystallization from a CH_2Cl_2/*n*-pentane mixture.

^{1}H NMR (200 MHz, 25°C, $CDCl_3/CD_3OD$ 1:1): δ = 8.41 (d, J = 4.6 Hz, 2H, pyrrole), 8.25 (s, 2H, pyrrole), 7.95 (d, J = 4.6 Hz, 2H, pyrrole), 7.84 (d, J = 8.0 Hz, 4H, Ar *meso*), 7.77 (d, J = 8.0 Hz, 4H, Ar *meso*), 7.61 – 7.55 (m, 8H, Ar *meso*), 1.46 (s, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu) ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 443 (183 000), 554 (4 500), 593 (7 000), 645 (21 000 L.mol^{-1}.cm^{-1}) nm. **IR** (KBr): ν = 2208 (C≡N) cm^{-1}. **HR-MS** (ESI-TOF$^+$) $C_{60}H_{59}N_6Zn^+$ $[M+H]^+$: calcd. *m/z* = 927.4093; found: 927.4071. **Elem. Anal.** (%) $C_{60}H_{58}N_6Zn\bullet 3H_2O$: calcd. C 73.34, H 6.57, N 8.55; found C 73.38, H 6.96, N 8.35.

Synthesis of free base 2,3-dicyano-2,3-secochlorin 7-H_2



7-H_2

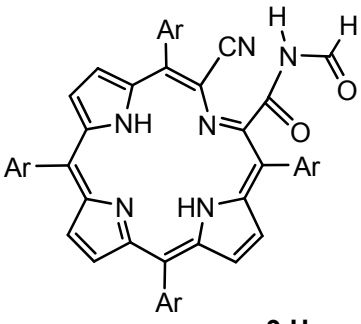
Ar = 4-*t*BuPh

A solution of zinc(II) 2,3-dicyano-2,3-secochlorin **7-Zn** (102 mg, 0.11 mmol) in dichloromethane (25 mL) was prepared and trifluoroacetic acid (2 mL) was added in small portions. The reaction mixture was stirred at room temperature for 30 minutes and poured on ice. Then, dichloromethane (100 mL) was added. The mixture was neutralized with saturated K_2CO_3 and washed with water. The organic layer was separated, dried with $MgSO_4$

and evaporated. The crude product was purified by silica gel column chromatography (dichloromethane/*n*-pentane from 2:3 to 1:1). Crystallization from a CH_2Cl_2/CH_3OH afforded the free base 2,3-dicyano-2,3-secochlorin **7-H$_2$** in 95% yield (90 mg).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$): δ = 8.64 (d, J = 4.8 Hz, 2H, pyrrole), 8.44 (s, 2H, pyrrole), 8.32 (d, J = 4.8 Hz, 2H, pyrrole), 7.98 (d, J = 8.2 Hz, 4H, Ar *meso*), 7.94 (d, J = 8.2 Hz, 4H, Ar *meso*), 7.73 (d, J = 8.2 Hz, 4H, Ar *meso*), 7.71 (d, J = 8.2 Hz, 4H, Ar *meso*), 1.56 (s, 18H, *t*-Bu), 1.52 (s, 18H, *t*-Bu), -0.38 (s, 2H, inner NH) ppm. **^{13}C{^{1}H} NMR** (50.3 MHz, 25°C, $CDCl_3$, 25°C): δ = 155.2, 152.2, 151.6, 139.1, 137.5, 137.3, 137.1, 134.7, 134.5, 134.0, 129.3, 128.5, 128.4, 126.0, 125.1, 124.3, 121.1, 119.2, 35.1, 35.1, 31.7, 31.7, 29.9 ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 435 (162 000), 559 (8 000), 619 (10 000), 684 (5 500). **IR** (KBr): ν = 2202 (C≡N) cm^{-1}. **HR-MS** (ESI-TOF$^+$) $C_{60}H_{61}N_6^+$ $[M+H]^+$: calcd. *m/z* = 865.4958; found: 865.4967. **Elem. Anal.** (%) $C_{60}H_{60}N_6 \bullet 2H_2O$: calcd. C 79.97, H 7.16, N 9.33; found C 79.54, H 7.73, N 9.14.

Synthesis of free base secochlorin 9-H$_2$



9-H$_2$

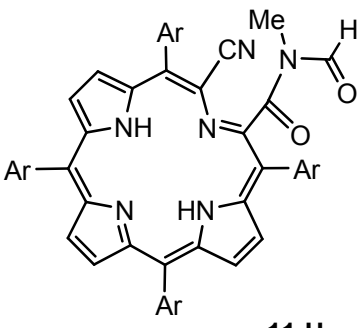
Ar = 4-*t*BuPh

The synthesis of the nickel(II) porphyrin fused to one imidazole ring **8-Ni** was previously described (See: J. -F Lefebvre, D. Leclercq, J.-P. Gisselbrecht and S. Richeter, *Eur. J. Org. Chem.*, 2010, 1912-1920). The nickel(II) porphyrin fused to one imidazole ring **8-Ni** (270 mg, 0.22 mmol) was dissolved in a TFA/H_2SO_4 (7.5 mL / 2.5 mL) mixture and the solution was stirred at room temperature for 30 minutes. It was then poured on ice, diluted with chloroform (150 mL), neutralized with saturated K_2CO_3, washed with water, dried (Na_2SO_4), and evaporated. Dichloromethane (200 mL) was added to the residue in round bottom flask of 1L and the mixture was vigorously stirred under visible light irradiation (halogen lamp, 250 W) for 15 hours. The solvent was evaporated and the residue was purified by silica gel column chromatography (dichloromethane). A first green fraction was collected corresponding to the free base secochlorin **9-H$_2$**, followed by a purple fraction corresponding to the free base imidazole **8-H$_2$**. After evaporation of the solvent, the free base secochlorin **9-H$_2$** and the free base imidazole **8-H$_2$** were respectively obtained in 24% yield (62 mg) and 48% yield (121 mg).

Secochlorin 9-H_2. **^{1}H NMR** (300 MHz, 25°C, $CDCl_3$): δ = 9.20 (d, J = 9.7 Hz, 1H, C*H*O), 8.59 (broad d, 1H, pyrrole), 8.55 (broad d, 1H, pyrrole), 8.43 (broad d, 1H, pyrrole), 8.40 (s, 2H, pyrrole), 8.39 (broad s, 1H NH), 8.22 (broad d, 1H, pyrrole), 8.25 – 7.50 (m, 16H, Ar *meso*), 1.57 (s, 18H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), -0.03 (broad s, 2H, inner N*H*) ppm. **^{13}C{^{1}H} NMR** (50.3 MHz, 25°C, $CDCl_3$): δ = 168.1 (*C*=O), 161.9 (*C*=O), 155.1, 154.3, 152.2, 151.5, 147.1, 140.8, 138.8, 137.7, 137.6, 137.2, 137.2, 136.7, 134.40, 134.1, 134.0, 132.1, 130.4, 129.2, 128.8, 128.0, 127.5, 126.4, 125.9, 125.6, 125.0, 124.4, 124.2, 120.7, 120.3, 114.2, 35.1, 35.0, 31.7, 31.7, 31.5 ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 435 (135 000), 561sh (7 500), 601 (10 000), 684 (7 500 L.mol^{-1}.cm^{-1}) nm. **IR** (KBr): ν = 2206 (C≡N), 1733 (C=O), 1682 (C=O) cm^{-1}. **HR-MS** (ESI-TOF$^+$) $C_{61}H_{63}N_6O_2^+$ $[M+H]^+$: calcd. *m/z* = 911.5013; found: 911.5004.

Free base imidazole 8-H_2. **^{1}H NMR** (200 MHz, 25°C, $CDCl_3$): δ = 9.00 (d, J = 4.8 Hz, 2H, pyrrole), 8.88 (d, J = 4.8 Hz, 2H, pyrrole), 8.85 (s, 2H, pyrrole), 8.22 (d, J = 8.3 Hz, 4H, Ar *meso*), 8.20 (d, J = 8.3 Hz, 4H, Ar *meso*), 8.01 (s, 1H, CH imidazole), 7.90 (d, J = 8.2 Hz, 4H, Ar *meso*), 7.80 (d, J = 8.3 Hz, 4H, Ar *meso*), 1.69 (s, 18H, *t*-Bu), 1.65 (s, 18H, *t*-Bu), -2.89 (s, 2H, internal NH) ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 420 (351 000), 516 (16 000), 552 (9 500), 587 (7 000), 644 (3 000 L.mol^{-1}.cm^{-1}) nm. **ESI$^+$ MS** $C_{61}H_{63}N_6^+$: calcd. 879.51; found 879.5. This compound is continuously converted into secochlorin **9-H_2** upon prolonged storage in solution or solid state, but is enough stable to be properly characterized.

Synthesis of free base secochlorin 11-H_2



11-H_2

Ar = 4-*t*BuPh

The synthesis of the nickel(II) porphyrin fused to one N-methylimidazole ring **10-Ni** was previously described (See: J. -F Lefebvre, D. Leclercq, J.-P. Gisselbrecht and S. Richeter, *Eur. J. Org. Chem.*, 2010, 1912-1920). The nickel(II) porphyrin fused to one imidazole ring **10-Ni** 152 mg, 0.16 mmol) was dissolved in a TFA/H_2SO_4 (7.5 mL / 2.5 mL) mixture and the solution was stirred at room temperature for 30 minutes. It was then poured on ice, diluted with chloroform (150 mL),

neutralized with saturated K_2CO_3, washed with water, dried (Na_2SO_4), and evaporated. Dichloromethane (200 mL) was added to the residue in round bottom flask of 1L and the mixture was vigorously stirred under visible light irradiation (halogen lamp, 250 W) for 15 hours. The solvent was evaporated and the residue was purified by silica gel column chromatography (dichloromethane). A first green fraction was collected corresponding to the free base secochlorin **11-H$_2$**, followed by a purple fraction corresponding to the free base imidazole **10-H$_2$**. After evaporation of the solvent, the free base secochlorin **11-H$_2$** and the free base imidazole **10-H$_2$** were respectively obtained in 72% yield (106 mg) and 5% yield (7 mg).

Secochlorin 11-H$_2$. ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ = 9.75 (s, 1H, C*H*O), 8.64 (d, *J* = 5.1 Hz, 1H, pyrrole), 8.64 (d, *J* = 5.1 Hz, 1H, pyrrole), 8.52 (d, *J* = 5.1 Hz, 1H, pyrrole), 8.49 (s, 2H, pyrrole), 8.27 (d, 1H, *J* = 5.1 Hz, 1H, pyrrole), 8.25 – 7.35 (m, 16H, Ar *meso*), 3.05 (s, 3H, N-C*H*$_3$), 1.60 (s, 9H, *t*-Bu), 1.59 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu), 1.48 (s, 9H, *t*-Bu), -0.70 (broad s, 2H, inner N*H*) ppm. **^{13}C{^{1}H} NMR** (50.3 MHz, 25°C, $CDCl_3$, 25°C): δ = 172.5 (*C*=O), 164.1 (*C*=O), 156.1, 154.1, 153.0, 152.3, 151.6, 151.4, 151.4, 148.0, 141.0, 138.2, 137.8, 137.5, 137.4, 137.3, 137.1, 137.0, 134.8, 134.4, 134.2, 133.7, 132.3, 131.0, 128.2, 127.7, 127.6, 127.0, 125.1, 125.0, 124.3, 124.3, 124.0, 124.0, 123.0, 119.4, 113.1, 35.1, 35.0, 35.0, 35.0, 31.7, 31.7, 31.7, 31.5 ppm. **UV/vis** (CH_2Cl_2): λ_{max} (ε) = 430 (160 000), 547 sh (8 500), 598 (12 000), 666 (6 000 L.mol^{-1}.cm^{-1}) nm. **IR** (KBr): ν = 2191 (C≡N), 1731 (C=O), 1660 (C=O) cm^{-1}. **HR-MS** (ESI-TOF$^+$) $C_{62}H_{65}N_6O_2^+$ $[M+H]^+$: calcd. *m/z* = 925.5169; found: 925.5162.

Free base imidazole 10-H$_2$. This compound is continuously converted into secochlorin **11-H$_2$**.

III. COMPUTATIONAL STUDIES

The LanL2DZ effective core potential and a valence basis set were used to describe the metal ions. Solvent effects were taken into account by the PCM model. All the calculations were carried out using the Gaussian 09 packag, Gaussian 09, Revision A02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.

F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

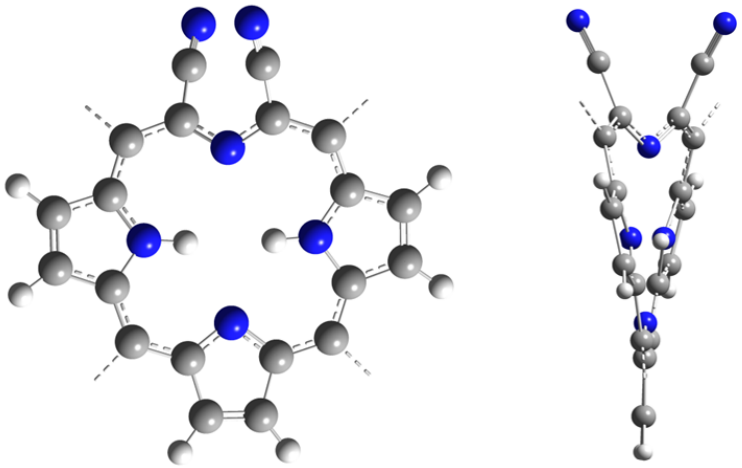


Fig. S1 Top (left) and side (right) views of the optimized structures of secochlorins **7-H$_2$**.

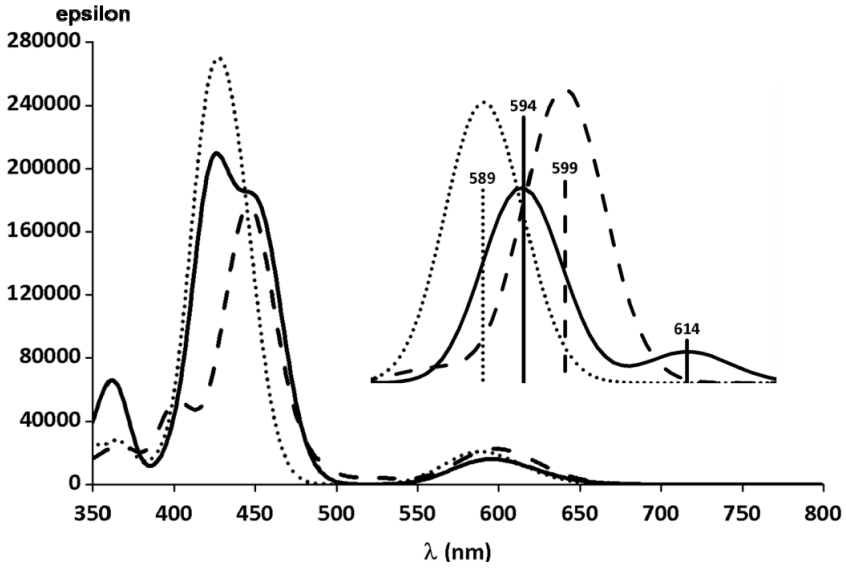
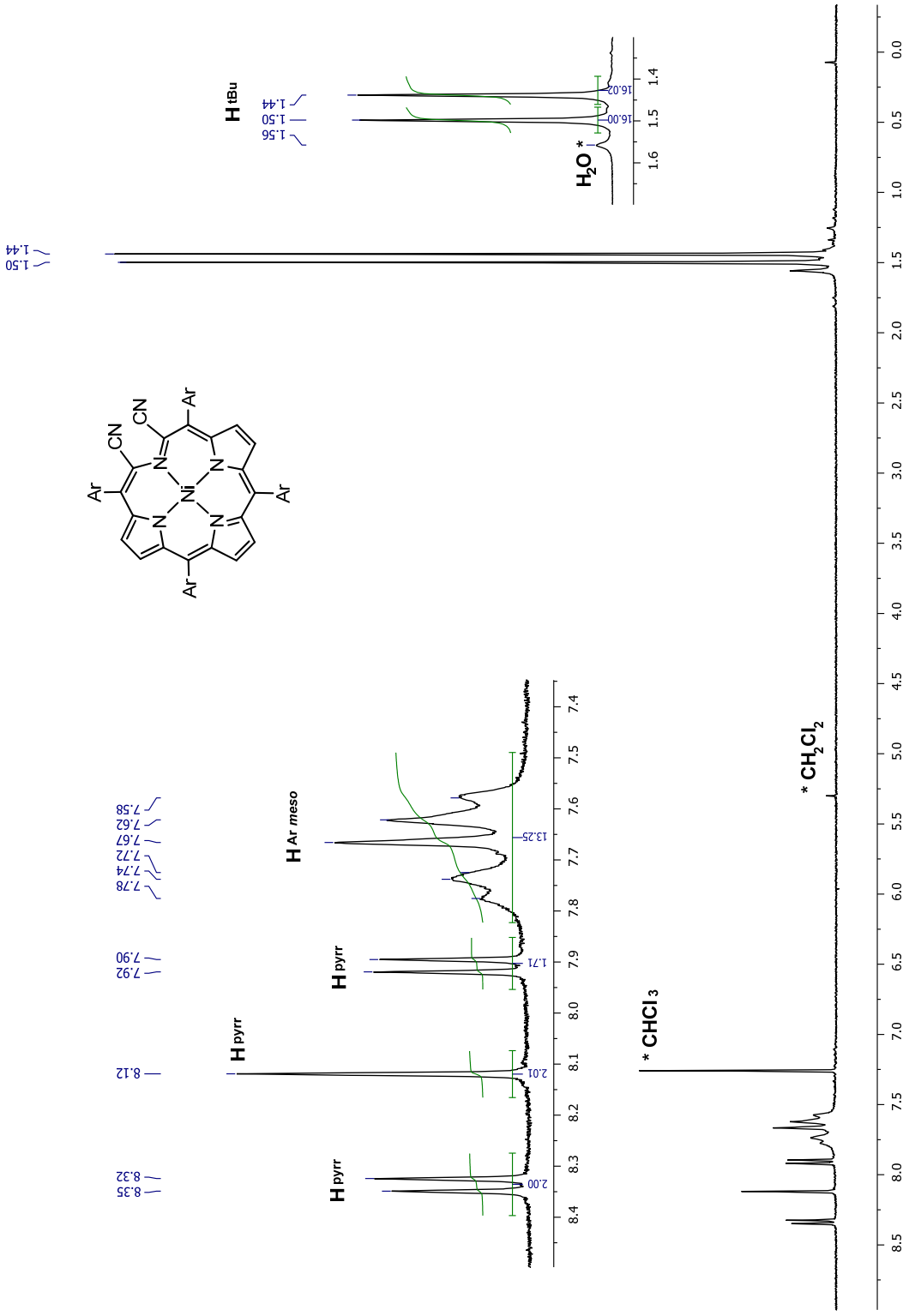


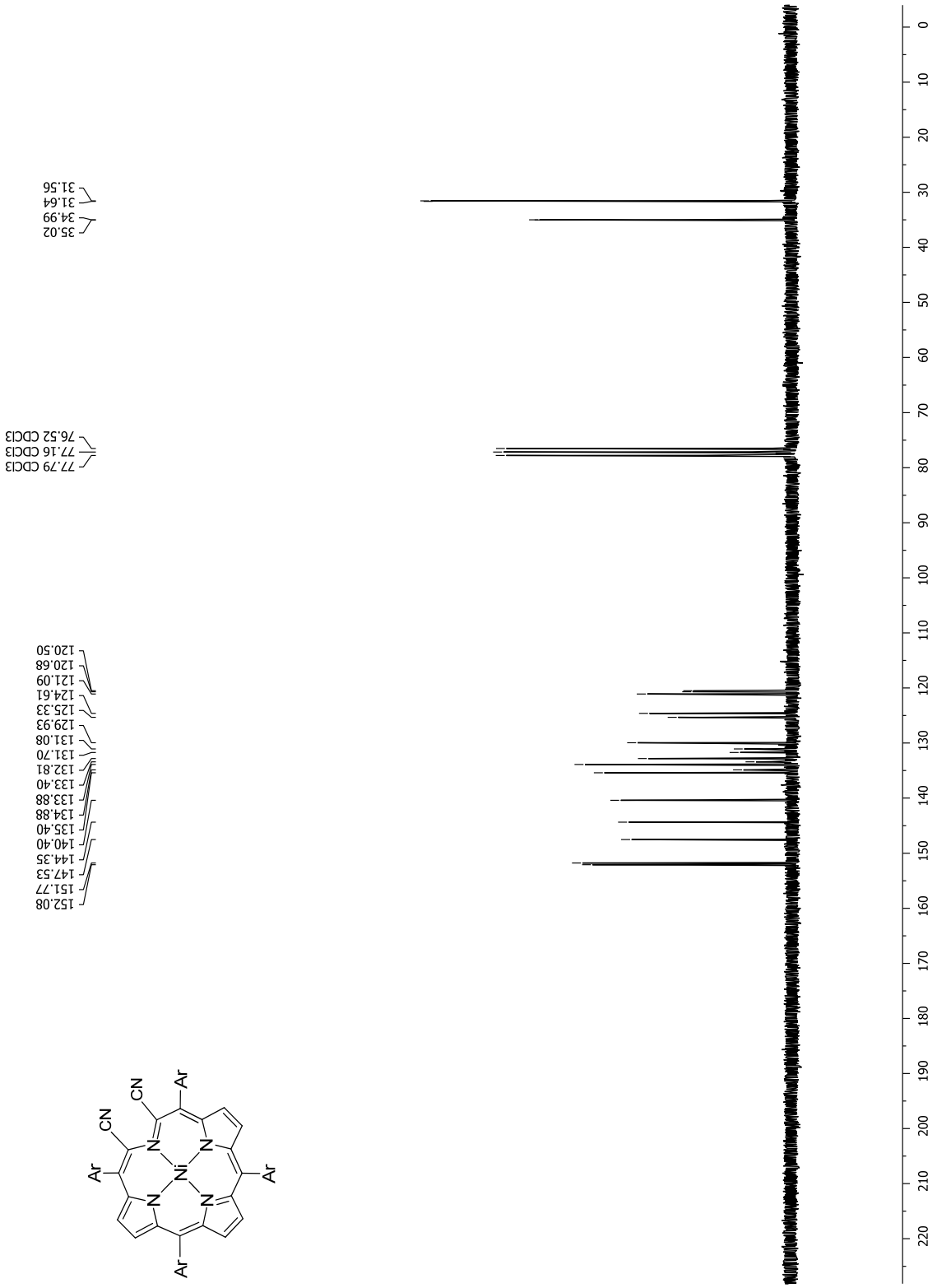
Fig. S2 Computed UV-Vis spectra of **7-Ni** (dashed), **7-Zn** (dotted) and **7-H$_2$** (full) - zoom on the Q bands (the peak width is smaller compared to the full spectrum, for a better visualisation, and the associated oscillator strengths are represented by the vertical bars).

III. COPIES OF ^{1}H AND 13C{^{1}H} NMR SPECTRA OF NEW COMPOUNDS

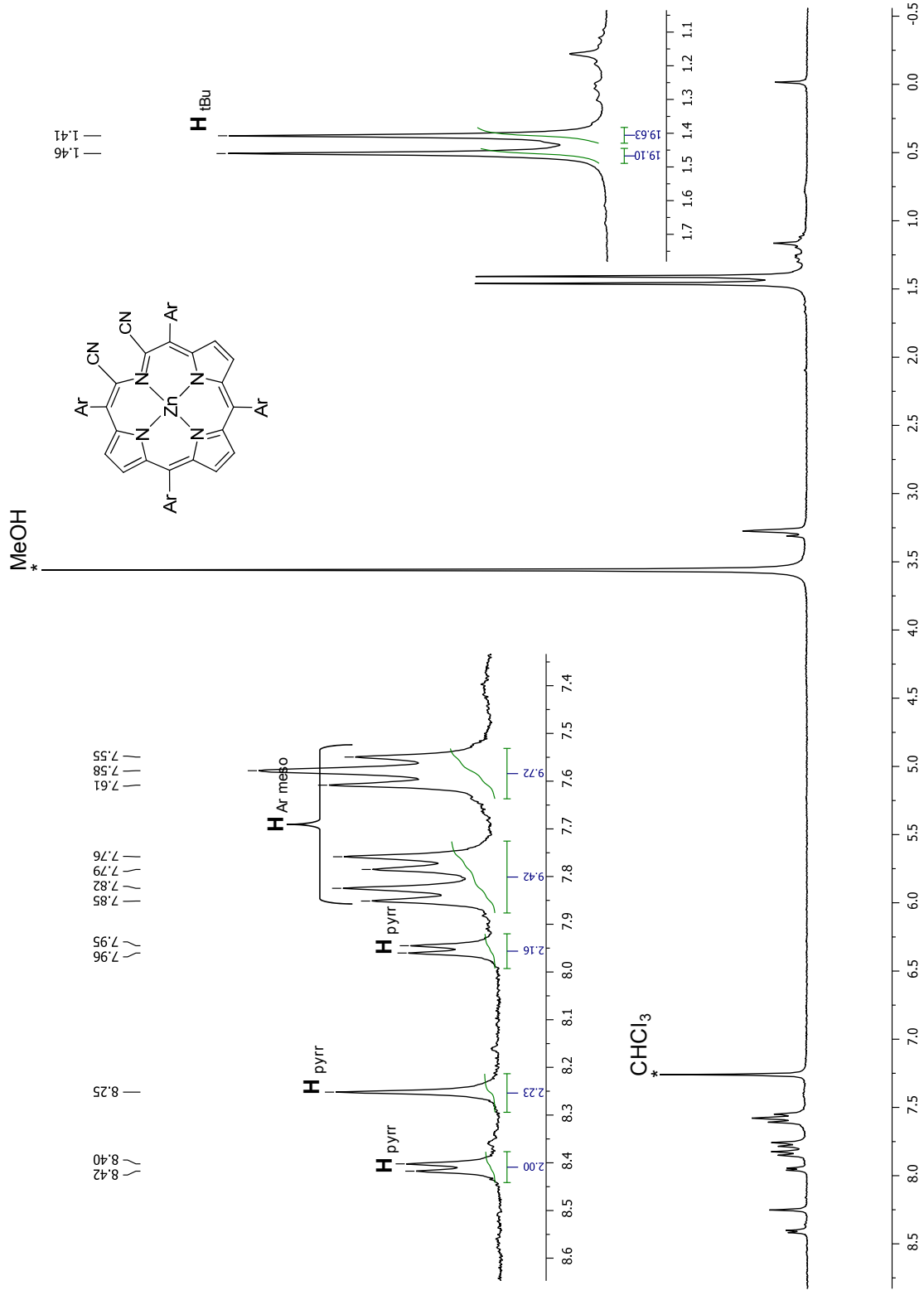
^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25°C) of 7-Ni



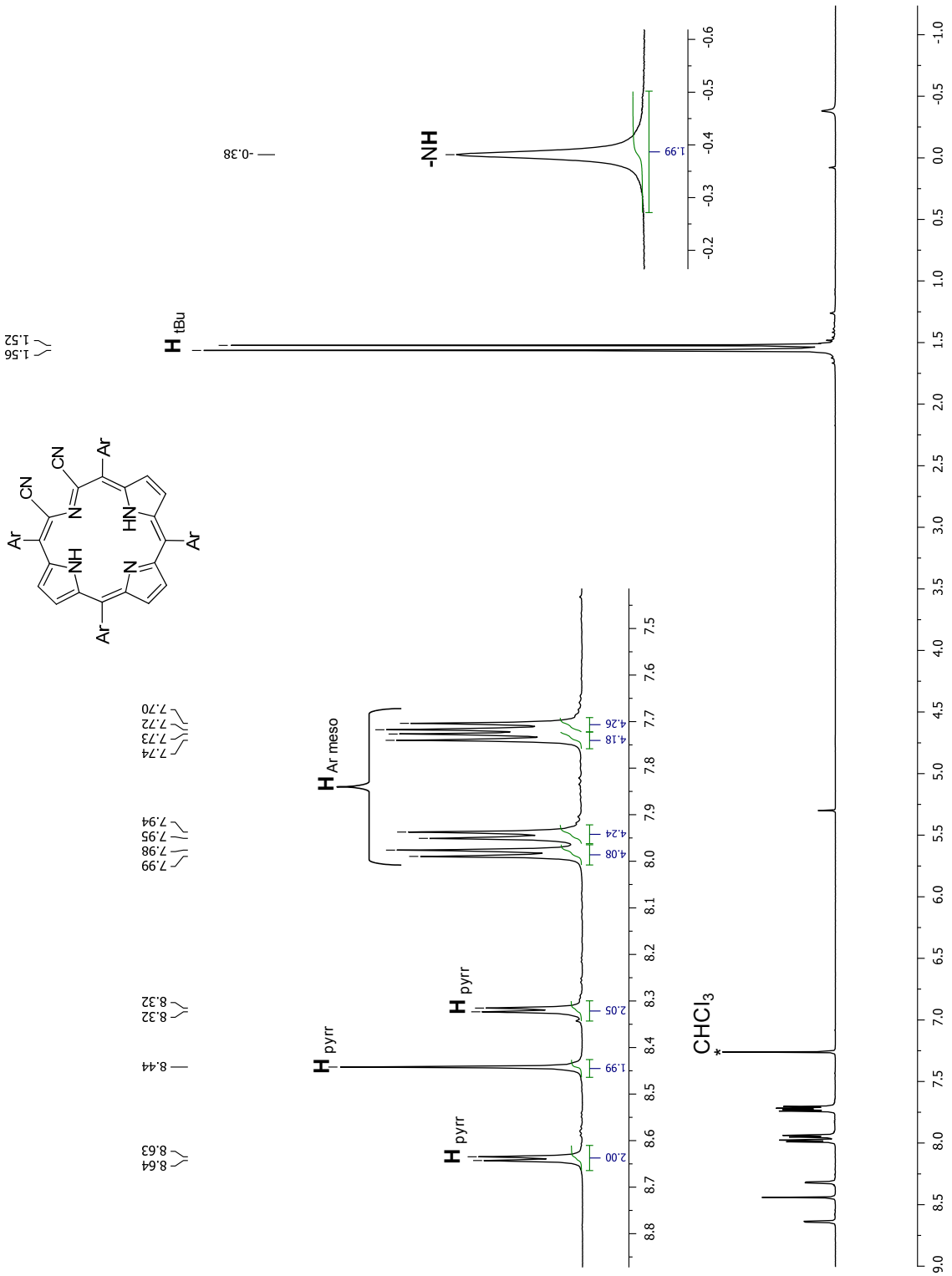
$^{13}C\{^{1}H\}$ NMR spectrum (50.3 MHz, $CDCl_3$, 25°C) of 7-Ni



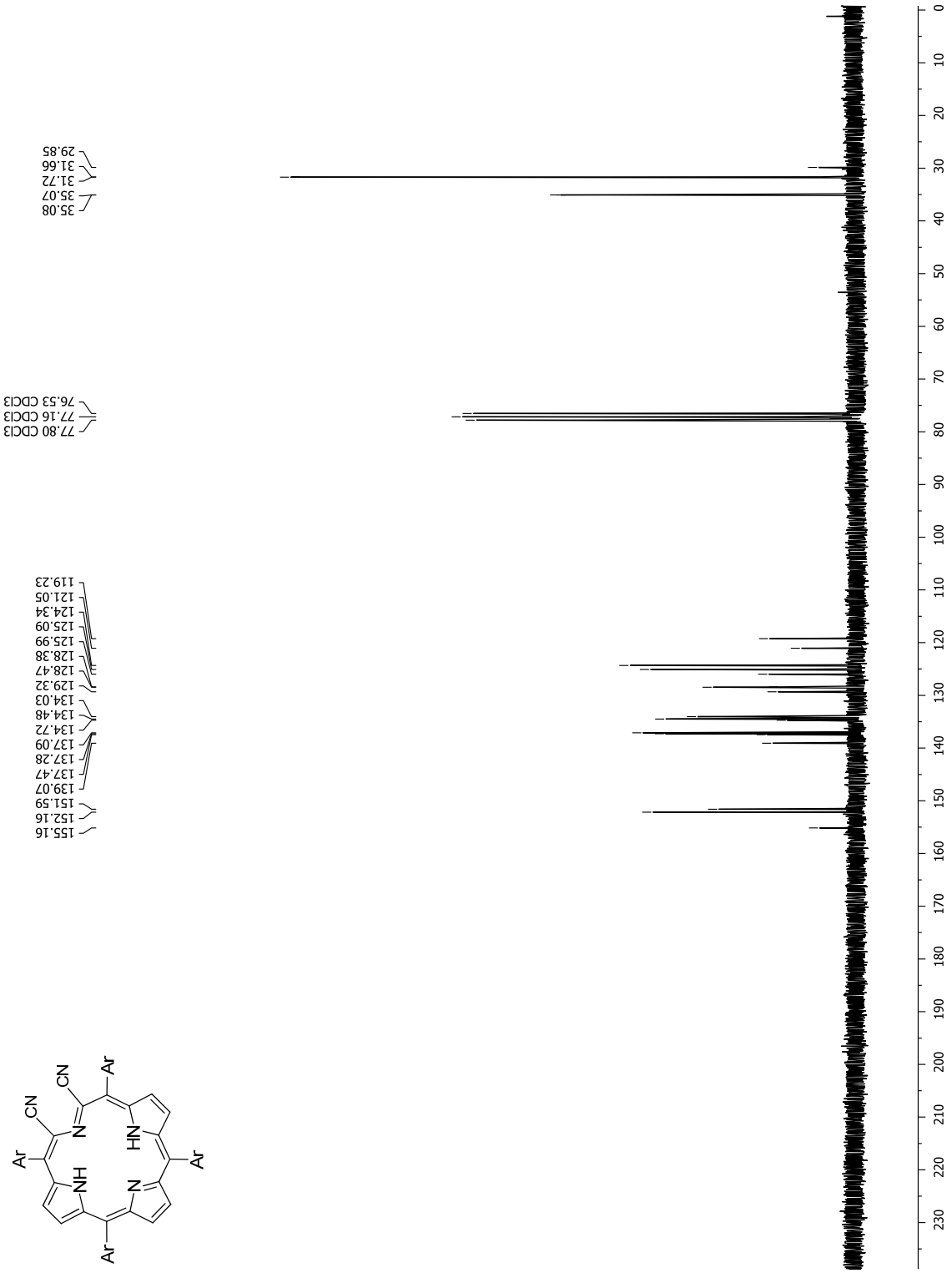
^{1}H NMR spectrum (200 MHz, $CDCl_3$ + CD_3OD 1:1, 25°C) of 7-Zn



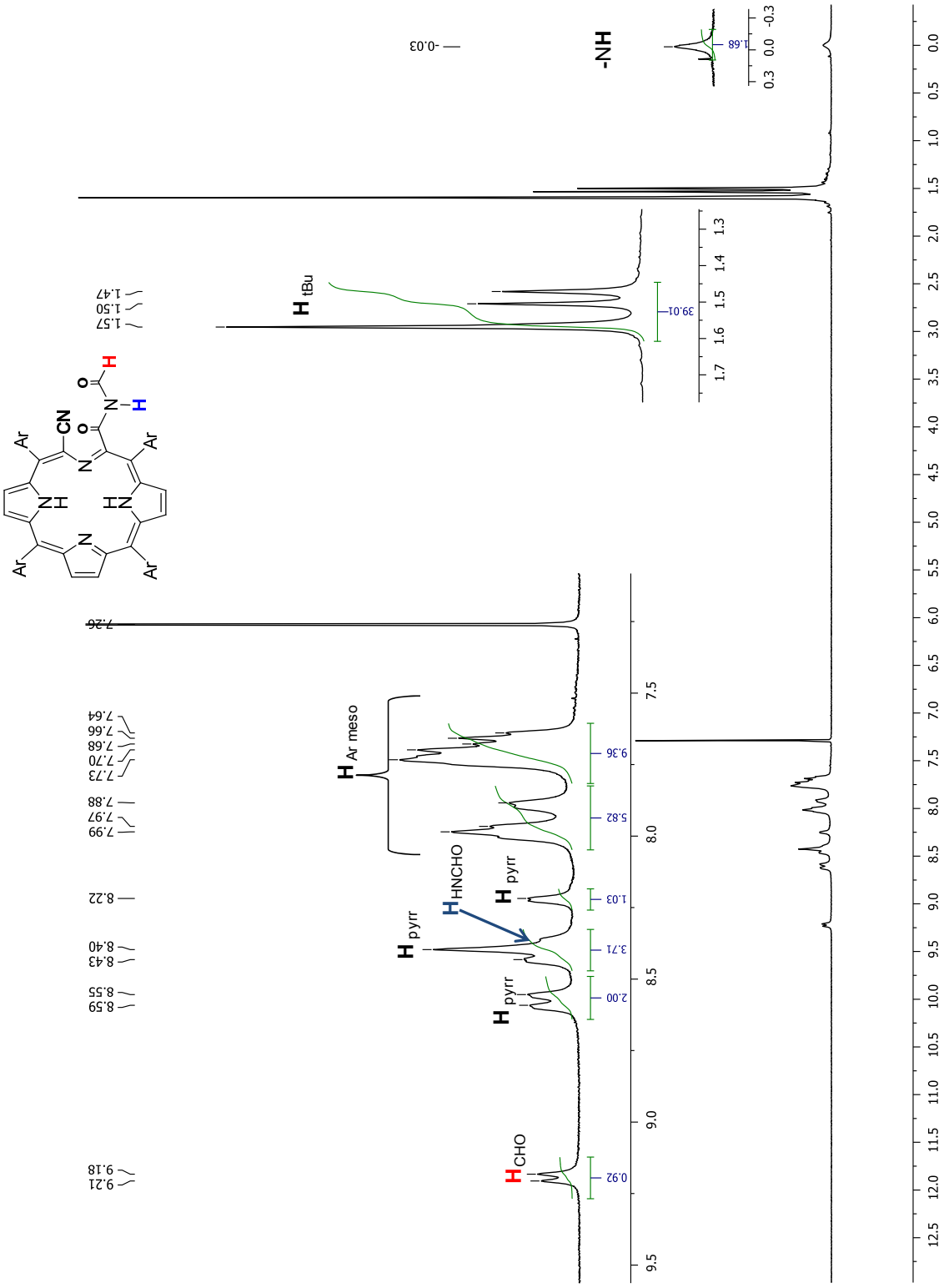
^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25°C) of 7-H_2



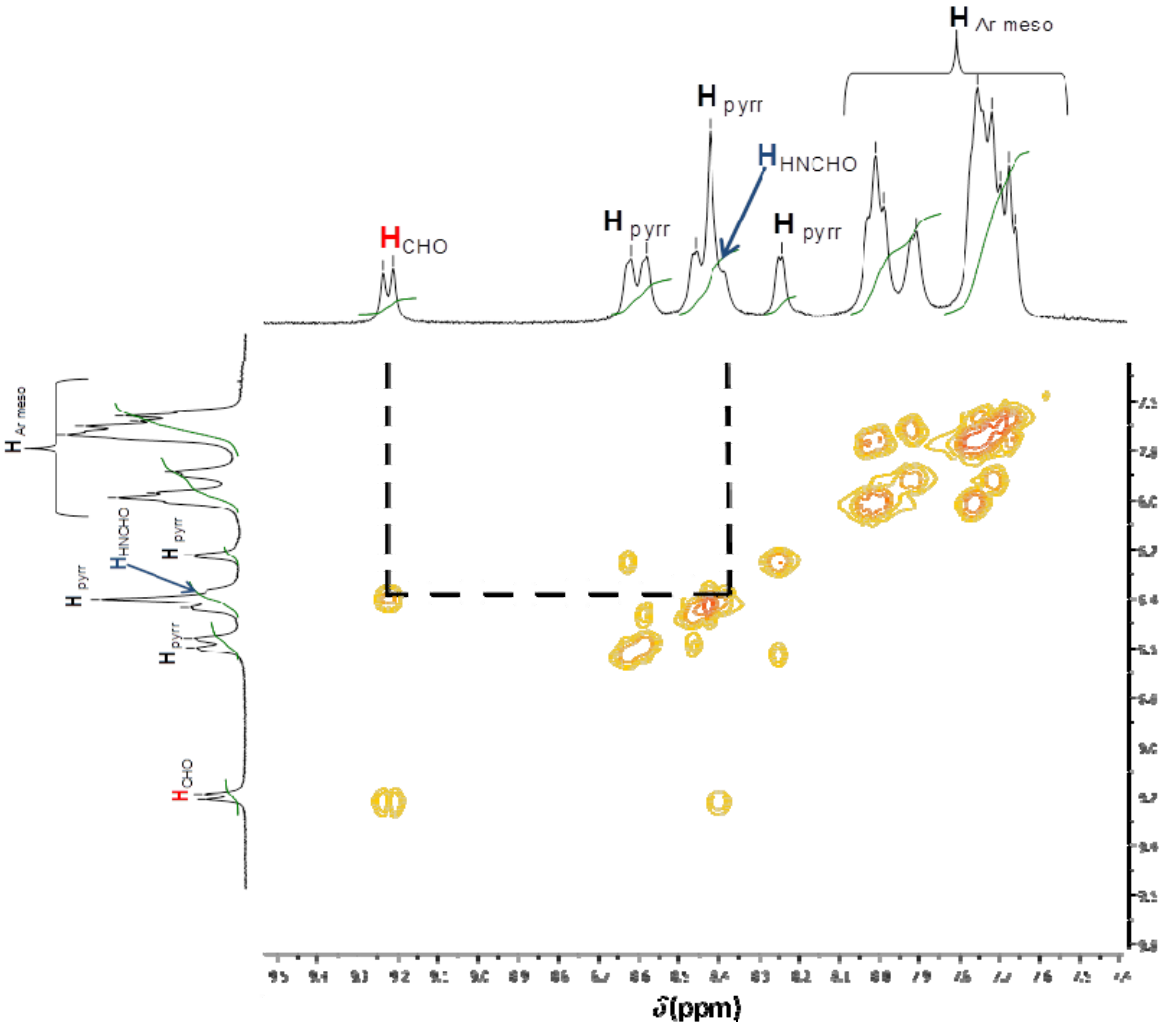
$^{13}C\{^{1}H\}$ NMR spectrum (50.3 MHz, $CDCl_3$, 25°C) of 7-H_2



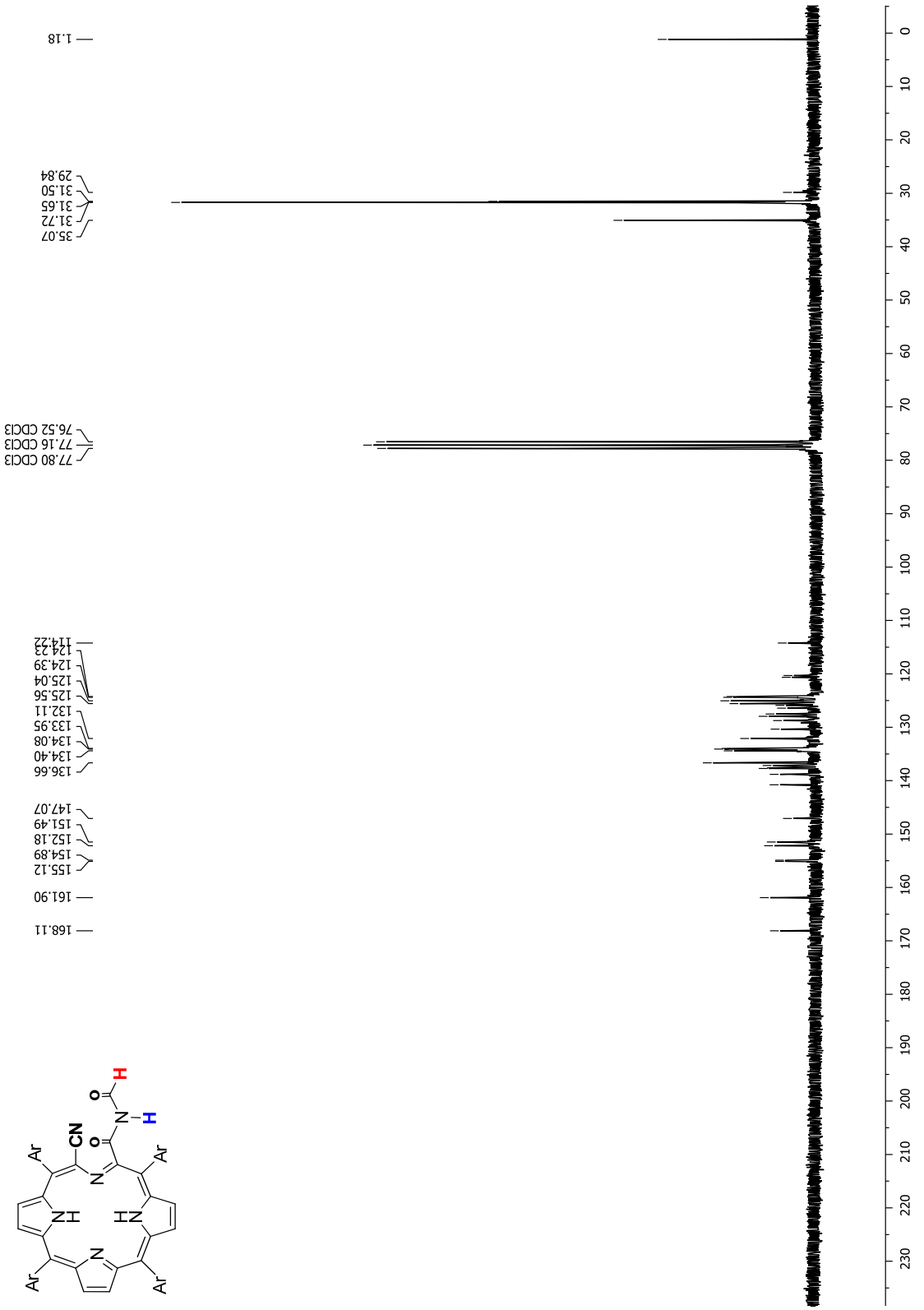
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of 9-H_2



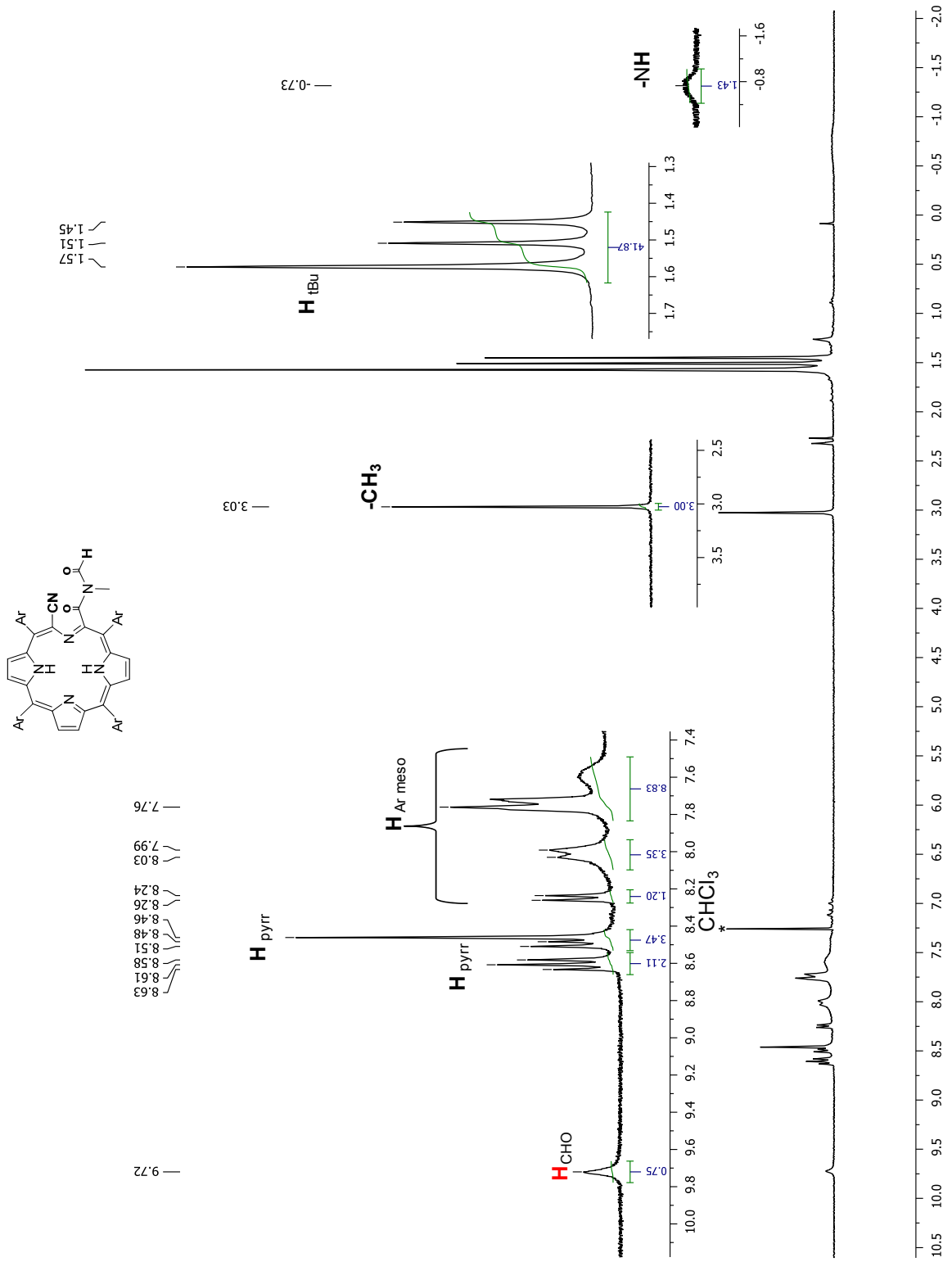
COSY 2D ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of 9-H_2



$^{13}C\{^{1}H\}$ NMR spectrum (50.3 MHz, $CDCl_3$, 25°C) of 9-H_2



^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of 11-H_2



$^{13}C\{^{1}H\}$ NMR spectrum (50.3 MHz, $CDCl_3$, 25°C) of 11-H_2