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Electronic Supplementary Information

Electronic, steric and catalytic properties of N-heterocyclic carbene rhodium(I) complexes linked to (metallo)porphyrins

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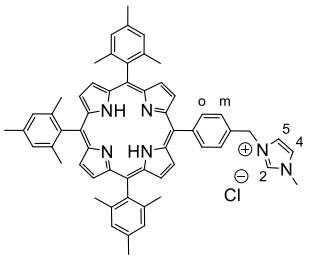
Experimental section

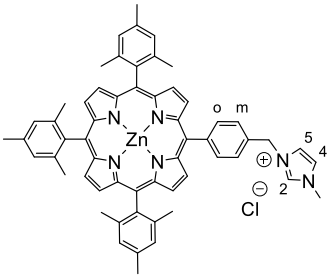
Materials. Reactions that needed inert atmosphere were performed under argon using Schlenk techniques and oven-dried glassware. All solvents were obtained from commercial suppliers and used as received. Dry THF was obtained by a PureSolve MD5 solvent purification system from Innovative Technology. Trifluoroacetic acid and pyrrole distilled under reduced pressure before use were purchased from Fluorochem. Boron trifluoride diethyl etherate (46%), paraformaldehyde (95%), phenyllithium 1.9 M in dibutyl ether, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (98%), sodium nitrite (99.9%), sodium hydride (99%) and 1-methylimidazole were purchased from Sigma Aldrich. Zinc acetate dihydrate (97%), 2,4,6-trimethylbenzaldehyde (98%), nickel(II) bis(acetylacetonate) (95%), *p*-tolualdehyde (98%), dimethyl carbonate (99%), imidazole (99%), iodomethane (99%), potassium hexafluorophosphate (95%) were purchased from Alfa Aesar. Potassium *tert*-butoxide (97%) was purchased from TCI and 2,3,5,6-tetrachloro-1,4-benzoquinone from Fluka (97%). Chloro(1,5-cyclooctadiene)rhodium(I) dimer was purchased from Alfa Aesar. TLC were carried out on Merck DC Kieselgel 60 F-254 aluminium sheets and spots were visualized with UV-lamp (λ = 254/365 nm) if necessary. Purifications were performed by silica gel Geduran® Si 60 for column chromatography (Merck 40−63 µM). Compound **IMe** was synthesized following the procedure described in the literature.[1] Porphyrin **2H-1** was synthesized following Lindsey's procedure.[2] Porphyrins **Ni-2**, **2H-2** and **Zn-2** were synthesized following our previously reported procedures.[3] Porphyrins **Ni-B-BF$_4$**, **2H-B-BF$_4$** and **Zn-B-BF$_4$** were synthesized following our previously reported procedures.[4] Rhodium(I) complexes **Ni-B-Rh(cod)Cl**, **2H-B- Rh(cod)Cl** and **Zn-B- Rh(cod)Cl** were synthesised following our previously reported procedures.[4,5] Porphyrin **Ni-3** was synthesized following our previously reported procedure.[6] Porphyrin **2H-3** and **Zn-3** were synthesized following our previous reported procedure.[7]

Instrument and methods. NMR spectroscopy and mass spectrometry were performed at the Laboratoire de Mesures Physiques of the University of Montpellier. ^{1}H, COSY, ROESY, HSQC, HMBC, ROESY ^{13}C{^{1}H}, ^{19}F spectra were recorded on Bruker 400 MHz Avance III HD, 500 MHz Avance III or 600 MHz Avance III spectrometers at 298 K. CD_2Cl_2, $CDCl_3$, and DMSO-d_6 solvents were purchased from Eurisotop, France and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the residual non-deuterated solvent as an internal standard. Chemical shifts (δ) are expressed in ppm from the residual non-deuterated solvent signal and coupling constants values (J) are expressed in Hz. Abbreviations used for ^{1}H NMR spectra are as follows: s, singlet; d, doublet; t, triplet; m, multiplet, br, broad. High resolution mass spectra analysis (HRMS) were recorded on a ESI Bruker MicroTof QII instrument in positive/negative modes or ESI-TOF Q instruments in positive/negative modes. UV-visible absorption spectra were recorded with a JASCO V-750 UV−visible spectrophotometer in 10 mm quartz cells (Hellma); λ_{max} is expressed in nm and molar extinction coefficients ε (L.mol^{-1}.cm^{-1}) are expressed as log ε. GC measurements were performed using Agilent 8860 GC with a FID detector and a column HP-5 (0.320 mm x 30 m x 0.25 µm).

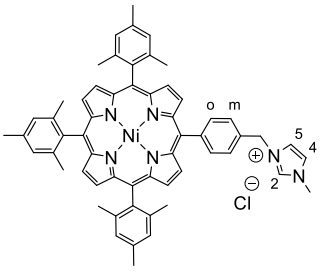
Synthesis and characterization of new compounds



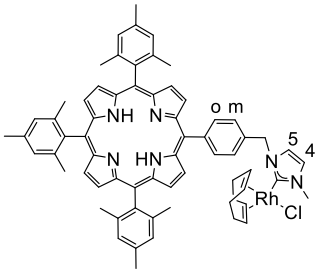
Synthesis of 2H-A-Cl. In a 250 mL two neck round bottom flask, **2H-1** (820 mg, 1.038 mmol, 1 eq) was added and degassed with argon. The solid was dissolved in CH_3CN (70 mL) and stirred. Then, 1-methylimidazole (8.52 g, 101.33 mmol, 100 eq) was added and the mixture was heated at reflux for 24 hours. The progress of the reaction was monitored by TLC analysis. Once finished, the solvent was evaporated and the excess of 1-methylimidazole was removed by distillation. Recrystallization form CH_2Cl_2/Et_2O afforded porphyrin **2H-A-Cl** as a purple solid in 91% yield (822 mg, 0.943 mmol). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 11.40 (s, 1H, H_2), 8.76 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.67 (d, $^3J_{H,H}$ = 4.8 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.63 (br s, 4H, $H_{\beta\text{-}pyr}$), 8.27 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, H_o), 7.86 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, H_m), 7.45 (s, 1H, H_5), 7.30 (s, 1H, H_4), 7.29 (s, 6H, $H_{mes\ meta}$), 5.95 (s, 2H, CH_2), 4.15 (s, 3H, N-CH_3), 2.61 (s, 9H, $H_{methyl\ para}$), 1.86 (s, 6H, $H_{methyl\ ortho}$), 1.83 (s, 12H, $H_{methyl\ ortho}$), –2.62 (s, 2H, NH) ppm.**^{13}C{^{1}H} NMR** (100.1 MHz, CH_2Cl_2): δ 144.0, 140.1, 140.0, 139.9, 139.8, , 138.8, 138.6, 138.5, 135.9, 133.5, 131.0, 128.3, 127.8, 123.8, 122.3, 118.7, 118.6, 118.5, 37.3, 22.0, 21.9, 21.7 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 419 (3.82), 514 (2.70), 548 (2.24), 590 (2.14), 646 (2.01) nm. **HRMS** (ESI+): *m/z* calc for $C_{58}H_{55}N_6^+$ [M–Cl]$^+$: 835.4483, found: 835.4488



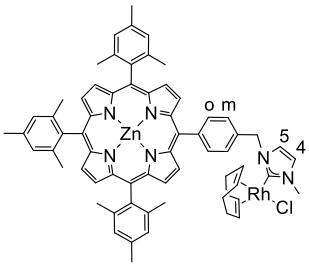
Synthesis of Zn-A-Cl. In a Schlenk tube, porphyrin **2H-A-Cl** (101 mg, 0.116 mmol, 1 eq) was added and degassed with argon/vacuum cycles. Chloroform was added (20 mL) and the obtained solution was stirred under argon. Then, a solution of $Zn(OAc)_2.2H_2O$ (28.0 mg, 0.127 mmol, 1.1 eq) in methanol (5 mL) was prepared and added under argon. The obtained mixture was stirred overnight for 16 hours. Metalation reaction was monitored by UV-visible absorption spectroscopy. Once finished, the solvent was evaporated and the solid residue was recrystallized from CH_2Cl_2/*n*-hexane giving porphyrin **Zn-A-Cl** as a purple solid in 96% yield (104 mg, 0.111 mmol). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.47 (s, 1H, H_2), 8.64 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.56 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.52 (m, 4H, $H_{\beta\text{-}pyr}$), 8.22 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, H_o), 8.09 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, H_5), 7.88 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, H_4), 7.77 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, H_m), 7.30 (d, $^3J_{H,H}$ = 3.2 Hz, 6H, $H_{mes\ meta}$), 5.79 (s, 2H, CH_2), 3.98 (s, 3H, N-CH_3), 2.57 (d, $^3J_{H,H}$ = 2.8 Hz, 9H, $H_{methyl\ para}$), 1.78 (s, 18H, $H_{methyl\ ortho}$) ppm. **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2): δ 150.3, 150.3, 149.9, 149.7, 144.8, 139.7, 139.7, 139.6, 139.6, 137.9, 137.8, 135.7, 132.4, 131.9, 131.4, 131.4, 130.8, 128.0, 128.0, 127.4, 123.8, 122.1, 119.1, 119.0, 118.7, 22.1, 21.8, 21.7, 21.6 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 429 (5.23), 562 (3.69), 601 (3.28) nm. **HRMS** (ESI+): *m/z* calc for $C_{58}H_{53}N_6Zn^+$ [M–Cl]$^+$: 897.3618, found: 897.3623



Synthesis of Ni-A-Cl. In a Schlenk tube, porphyrin **2H-A-Cl** (122 mg, 0.140 mmol, 1eq) was introduced and degassed with argon/vacuum cycles. Anhydrous toluene was added (20 mL) and the obtained solution was stirred under argon. Then, $Ni(acac)_2$ (71.9 mg, 0.280 mmol, 2 eq) was added and the mixture was heated at 40°C for 16 hours. Metalation reaction was monitored by UV-visible absorption spectroscopy. Once finished, the solvent was evaporated and the solid residue was recrystallized from CH_2Cl_2/*n*-hexane giving porphyrin **Ni-A-Cl** as a purple solid in 95% yield (123 mg, 0.132 mmol).**^{1}H NMR** (400 MHz, CD_2Cl_2): δ 11.45 (s, 1H, H_2), 8.71 (d, $^3J_{H,H}$ = 4.5 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.62 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.56 (br s, 4H, $H_{\beta\text{-}pyr}$), 8.27 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_o), 7.80 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_m), 7.44 (s, 1H, H_5), 7.29 (s, 1H, H_4), 7.29–7.23 (m, 6H, $H_{mes\ meta}$), 5.92 (s, 2H, CH_2), 4.15 (s, 3H, N-CH_3), 2.65 – 2.55 (m, 9H, $H_{methyl\ para}$), 1.87–1.76 (m, 18H, $H_{methyl\ ortho}$) ppm. **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2): δ 143.0, 142.9, 142.8, 139.4, 138.4, 137.5, 137.5, 135.0, 133.5, 132.5, 132.1, 132.0, 131.6, 128.2, 124.0, 122.4, 117.7, 117.7, 117.6, 21.6, 21.6 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 429 (4.76), 527 (3.61), 555 (2.95) nm. **HRMS** (ESI+): *m/z* calc for $C_{58}H_{53}N_6Ni^+$ [M–Cl]$^+$: 891.3680, found: 891.3685.



Synthesis of 2H-A-Rh(cod)Cl. Porphyrin **2H-A-Cl** (400 mg, 0.459 mmol, 1eq), $[Rh(cod)Cl]_2$ (159 mg, 0.322 mmol, 0.7 eq), and *t*-BuOK (72 mg, 0.643 mmol, 1.4 eq) were degassed under argon for 10 minutes. Then, anhydrous THF (150 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 97:3 (v:v)). Recrystallization from CH_2Cl_2/*n*-pentane afforded the porphyrin **2H-A-Rh(cod)Cl** as a purple solid in 45% yield (226 mg, 0.209 mmol. **^{1}H NMR** (600 MHz, CD_2Cl_2): δ 8.80 (d, $^3J_{H,H}$ = 4.8 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.67 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.63 (s, 4H, $H_{\beta\text{-}pyr}$), 8.22 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_o), 7.79 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_m), 7.30 (s, 6H, $H_{mes\ meta}$), 7.09 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_5), 7.02 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_4), 6.26 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.99 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.12–5.00 (m, 2H, C*H*-cod), 4.19 (s, 3H, N-CH_3), 3.54–3.43 (m, 2H, C*H*-cod), 2.62 (2s, 9H, $H_{methyl\ para}$), 2.59–2.39 (m, 4H, CH_2-cod), 2.08–1.96 (m, 4H, CH_2-cod), 1.87–1.85 (2s, 18H, $H_{methyl\ ortho}$), –2.59 (s, 2H, N*H*) ppm. **^{13}C{^{1}H} NMR** (150.9 MHz, CD_2Cl_2): δ 184.2 (d, $^1J_{Rh,C}$ = 51.5 Hz, *C*-Rh), 142.4, 140.0, 138.2, 138.6, 138.4, 137.2, 135.4, 128.3, 127.0, 123.3, 121.4, 119.2, 118.5, 118.4, 99.0 (br d, $^1J_{CH(cod)\text{-}Rh}$ = 8.1 Hz), 68.8 (br dd, $^1J_{CH(cod)\text{-}Rh}$ = 14.7 Hz), 38.3, 33.7, 33.4, 29.7, 29.3, 22.0, 21.9, 21.7 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 419 (5.56), 515 (4.41), 548 (3.93), 591 (3.88), 646 (3.66) nm. **HRMS** (ESI+): *m/z* calc for $C_{66}H_{67}ClN_6Rh^+$ $[M+H]^+$: 1081.4165, found: 1081.4171.



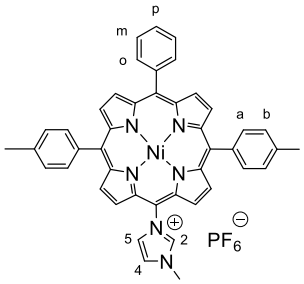
Synthesis of Zn-A-Rh(cod)Cl. Porphyrin **Zn-A-Cl** (80.0 mg, 0.0856 mmol, 1 eq), $[Rh(cod)Cl]_2$ (29.6 mg, 0.060 mmol, 0.7eq), and *t*-BuOK (14.4 mg, 0.128 mmol, 1.5 eq) were degassed under argon for 10 min. Then, anhydrous THF (30 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 95:5 (v:v)). Recrystallization from CH_2Cl_2/*n*-pentane afforded the porphyrin **Zn-A-Rh(cod)Cl** as a purple solid in 35% yield (34 mg, 0.0297 mmol). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ 8.85 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.72 (d, $^3J_{H,H}$ = 4.6 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.68 (s br, 4H, $H_{\beta\text{-}pyr}$), 8.22 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, H_o), 7.76 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, H_m), 7.29 (s, 6H, $H_{mes\ meta}$), 7.10 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_5), 7.03 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_4), 6.25 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.98 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.06–4.97 (m, 2H, CH_{cod}), 4.18 (s, 3H, N-CH_3), 3.51–3.44 (m, 2H, CH_{cod}), 2.61 (s, 9H, $H_{methyl\ para}$), 2.36–2.32 (m, 4H, $CH_{2\ cod}$), 2.12–2.06 (m, 4H, $CH_{2\ cod}$), 1.83 (2s, 18H, $H_{methyl\ ortho}$) ppm. **^{13}C{^{1}H} NMR NMR** (150.9 MHz, CD_2Cl_2) δ 183.5, (d, $^1J_{Rh,C}$ = 51.0 Hz) 143.0, 143.0, 142.93, 142.8, 141.3, 139.4, 138.3, 137.6, 137.5, 137.1, 134.5, 132.6, 132.0, 132.0, 131.9, 131.5, 128.2, 127.1, 123.2, 121.3, 118.4, 117.6, 117.4, 98.9 (br dd, $^1J_{CH(cod)\text{-}Rh}$ = 3.5 and 7.1 Hz), 68.8 (br dd, $^1J_{CH(cod)\text{-}Rh}$ = 7.4 and 17.8 Hz), , 38.2, 33.7, 33.3, 30.2, 29.6, 29.3, 28.5, 21.6, 21.6 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 420 (5.66), 549 (4.23), 576 (3.38) nm. **HRMS** (ESI+): *m/z* calc for $C_{66}H_{64}N_6RhZn^+$ $[M–Cl]^+$: 1107.3533, found: 1107.3541.

Synthesis of Ni-A-Rh(cod)Cl. Porphyrin **Ni-A-Cl** (80.0 mg, 0.0862 mmol, 1eq), $[Rh(cod)Cl]_2$ (29.8 mg, 0.060 mmol, 0.7 eq), and and *t*-BuOK (14.5 mg, 0.129 mmol, 1.5 eq) were degassed under argon for 10 min. Then, anhydrous THF (30 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 95:5 (v:v)). Recrystallization from CH_2Cl_2/*n*- afforded the porphyrin **Ni-A-Rh(cod)Cl** as a purple solid in 38% yield (37 mg, 0,0325 mmol). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ 8.70 (d, $^3J_{H,H}$ = 4.8 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.56 (d, $^3J_{H,H}$ = 4.8 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.54 (s, 4H, $H_{\beta\text{-}pyr}$), 8.02 (d, $^3J_{H,H}$= 8.0 Hz , 2H, H_o), 7.71 (d, $^3J_{H,H}$ =8.0 Hz , 2H, H_m), 7.22 (s, 6H, $H_{mes\ meta}$), 7.03 (d, $^3J_{H,H}$ = 1.8 Hz,1H, H_5), 7.00 (d, $^3J_{H,H}$ = 1.8 Hz,1H, H_4), 6.24 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.90 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, CH_2), 5.06–4.98 (m, 2H, CH_{cod}), 4.16 (s, 3H, N-CH_3), 3.49–3.40 (m, 2H, CH_{cod}), 2.55 (2s, 9H, $H_{methyl\ para}$), 2.47–2.40 (m, 4H, $CH_{2\ cod}$), 2.07–1.94 (m, 4H, $CH_{2\ cod}$), 1.80 (s, 18H, $H_{methyl\ ortho}$) ppm. **^{13}C{^{1}H} NMR NMR** (150.9 MHz, CD_2Cl_2): δ 183.6, (d, $^1J_{Rh,C}$ = 51.2 Hz) 150.3, 150.3, 143.2, 139.7, 139.7, 138.0, 136.8, 135.2, 132.5, 131.51, 131.4, 130.9, 129.1, 128.1, 126.7, 123.2, 121.4, 120.0, 119.2, 119.1, 98.9 (br dd, $^1J_{CH(cod)\text{-}Rh}$ = 6.8 Hz), 68.8 (br dd, $^1J_{CH(cod)\text{-}Rh}$ = 13.1 and 17.5 Hz), 38.2, 33.7, 33.4, 29.6, 29.3, 28.5, 25.1, 22.0, 21.9, 21.7 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 420 (5.68), 527(4.13), 555 (3.46) nm. **HRMS** (ESI+): *m/z* calc for $C_{66}H_{64}N_6NiRh^+$ $[M–Cl]^+$: 1101.3595, found: 1101.3571.

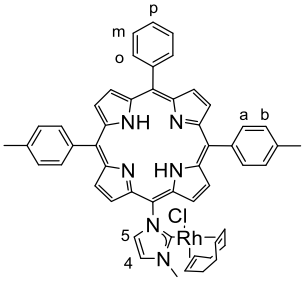
Synthesis of porphyrin 2H-C-PF_6. Porphyrin **2H-3** (152 mg, 0.240 mmol, 1 eq) was dissolved in dry THF (40 mL) under argon atmosphere. Then, iodomethane (1.50 mL, 24.02 mmol, 100 eq) was added and the reaction mixture was stirred at 40°C for 16 hours under argon atmosphere. Once finished according to TLC analysis, a solution of KPF_6 (221 mg, 1.20 mmol, 5 eq) in water (10 mL) was added dropwise and the reaction was stirred at room temperature for 2 hours. Then, the mixture was concentrated and the resulting solid was filtered off and washed with *n*-pentane to give porphyrin **2H-C-PF_6** as a purple solid in 96% yield (182 mg, 0.229 mmol). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 9.37 (s br, 1H, H_2), 9.07 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.92 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$) 8.89 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$) 8.72 (d, $^3J_{H,H}$ = 4.8 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.42 (s br, 1H, H_5), 8.20 (d, $^3J_{H,H}$ = 7.1 Hz, 2H, H_o), 8.14-8.05 (m, 4H, H_a), 7.93 (s br, 1H, H_4), 7.87-7.76 (m, 3H, H_m and H_p), 7.65-7.60 (m, 4H, H_b), 4.47 (s, 3H, N-CH_3), 2.71 (s, 6H, $CH_{3\ tolyl}$), -2.85 (s, 2H, NH) ppm. **^{13}C{^{1}H} NMR** (150.9 MHz, DMSO-d_6): δ 142.5, 140.9, 137.8, 137.5, 134.4, 134.3, 130.2, 128.5, 127.9, 127.1, 123.3, 123.0, 121.8, 108.7, 36.8, 21.1 ppm. **^{19}F NMR** (376.5 MHz, CD_2Cl_2): δ –73.8 ppm (d, $^1J_{F,P}$ = 711.2 Hz). ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 418 (5.64), 514 (4.26), 549 (3.79), 586 (3.77), 641 (3.47) nm. **MS** (ESI+): *m/z* calc for $C_{44}H_{35}N_6^+$ $[M–PF_6]^+$: 647.29, found 647.29. **MS** (ESI–): *m/z* calc for PF_6^-: 144.96, found 144.97.

Synthesis of porphyrin Zn-C-PF_6. Porphyrin **Zn-3** (142 mg, 0.204 mmol, 1 eq) was dissolved in dry THF (40 mL) under argon atmosphere. Then, iodomethane (1.30 mL, 20.40 mmol, 100 eq) was added and the reaction mixture was stirred at 40°C for 16 hours under argon atmosphere. Once finished according to TLC analysis, a solution of KPF_6 (188 mg, 1.02 mmol, 5 eq) in water (10 mL) was added dropwise and the reaction was stirred at room temperature for 2 hours. Then, the mixture was concentrated and the resulting solid was filtered off and washed with *n*-pentane to give porphyrin **Zn-C-PF_6** as a purple solid in 90% yield (158 mg, 0.184 mmol). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 9.41 (s br, 1H, H_2), 9.13 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.99 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.97 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.77 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.44 (s br, 1H, H_5), 8.21–8.17 (m, 2H, H_o), 8.13-8.00 (m, 4H, H_a), 7.91 (s br, 1H, H_4), 7.86–7.74 (m, 3H, H_m and H_p), 7.64–7.55 (m, 4H, H_b), 4.47 (s, 3H, N-CH_3), 2.72 (s, 6H, $CH_{3\ tolyl}$) ppm. **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2): δ 165.8, 152.2, 151.4, 151.1, 147.1, 142.7, 141.0, 139.4, 138.3, 135.3, 135.1, 135.0, 134.9, 133.6, 133.2, 131.0, 130.1, 128.4, 128.0, 127.2, 126.6, 123.9, 123.2, 108.0, 63.5, 38.0, 30.2, 21.8 ppm.

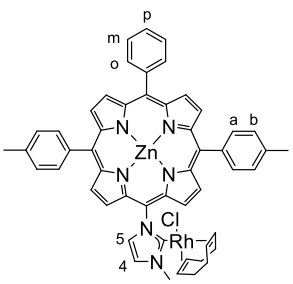
^{19}F NMR (376.5 MHz, CD_2Cl_2): δ –72.8 ppm (d, $^1J_{F,P}$ = 707.8 Hz) ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 427 (5.66), 557(4.25), 600 (3.77) nm. **MS** (ESI+): *m/z* calc for $C_{44}H_{33}N_6Zn^+$ $[M–PF_6]^+$: 709.21, found: 709.16. **MS** (ESI–): *m/z* calc for PF_6^-: 144.96, found 144.97.



Synthesis of porphyrin Ni-C-PF$_6$. Porphyrin **Ni-3** (154 mg, 0.223 mmol, 1 eq) was dissolved in dry THF (40 mL) under argon atmosphere. Then, iodomethane (1.39 mL, 22.34 mmol, 100 eq) was added and the reaction mixture was stirred at 40°C for 16 hours under argon atmosphere. Once finished according to TLC analysis, a solution of KPF_6 (205.6 mg, 1.12 mmol, 5 eq) in water (10 mL) was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. Then, the mixture was concentrated and the resulting solid was filtered off and washed with *n*-pentane to give porphyrin **Ni-C-PF$_6$** as a purple solid in 92% yield (174 mg, 0.205 mmol). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 9.78 (s br, 1H, H_2), 8.94 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.81 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.79 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.67 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, $H_{\beta\text{-}pyr}$), 8.20 (t, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, H_5), 8.01 (d, $^3J_{H,H}$ = 6.6 Hz, 2H, H_o), 7.91 (t, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, H_4), 7.88 (d, $^3J_{H,H}$ = 7.3 Hz, 4H, H_a), 7.79–7.68 (m, 3H, H_m and H_p), 7.53 (d, $^3J_{H,H}$ = 7.3 Hz, 4H, H_b), 4.50 (s, 3H, N-CH_3), 2.65 (s, 6H, $CH_{3\ tolyl}$) ppm. **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2): δ 145.1, 144.5, 144.2, 141.03, 140.8, 140.5, 138.9, 137.6, 135.5, 134.3, 133.9, 133.6, 130.0, 128.8, 128.4, 127.6, 127.3, 123.9, 122.1, 38.70, 27.5, 21.8 ppm. **^{19}F NMR** (376.5 MHz, CD_2Cl_2): δ –72.8 ppm (d, $^1J_{F,P}$ = 711.2 Hz). **UV-Vis** (DMSO)**:** λ_{max} (log ε) = 413 (4.91), 526 (3.74), 555 (3.34) nm. **MS** (ESI+): *m/z* calc for $C_{44}H_{33}N_6Ni$ $[M–PF_6]^+$: 703.21, found 703.21. **MS** (ESI–): *m/z* calc for PF_6^-: 144.96, found 144.97.



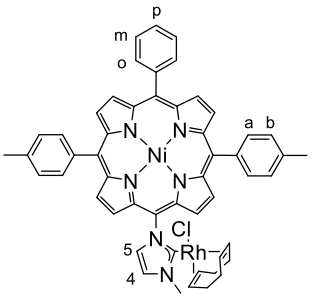
Synthesis of porphyrin H2-C-Rh(cod)Cl. Porphyrin **2H-C-PF$_6$** (103 mg, 0.1299 mmol, 1 eq), $[Rh(cod)Cl]_2$ (52.8 mg, 0.1071 mmol, 0.8 eq) and *t*-BuOK (17.5 mg, 0.1559 mmol, 1.2 eq) were degassed under argon for 10 min. Then, anhydrous THF (45 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 98:2 (v:v)). The first red fraction was collected and concentrated to give porphyrin **Ni-C-Rh(cod)Cl** a purple solid in 61% yield (71 mg, 0.0795 mmol). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ 9.72 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.99 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.91 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.89 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.86 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.82 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.81 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.48 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.24–8.18 (m br, 3H, $2H_o$+$1H_a$,), 8.11–8.05 (m br, 3H,H_a), 8.00 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, H_5), 7.84–7.74 (m, 3H, $2H_m$+$1H_p$), 7.63 (d br, $^3J_{H,H}$ = 8.2 Hz, 1H, H_b),7.58 (d, $^3J_{H,H}$ = 8.2 Hz, 3H, H_b), 7.42 (d, $^3J_{H,H}$ = 1.8 Hz, H_4), 4.62 (m, 1H, H_{cod}), 4.57 (s, 3H, N-CH_3), 4.32 (m, 1H, H_{cod}), 3.63 (m, 1H, H_{cod}), 2.71 (2s, 6H, $CH_{3\ tolyl}$), 2.37 (m, 1H, H_{cod}), 1.94 (m, 1H, H_{cod}), 1.72 (m, 1H, H_{cod}), 1.62 (m, 1H, H_{cod}), 1.20 (m, 1H, H_{cod}), 0.82–0.75 (m, 1H, H_{cod}), 0.20 (m, 1H, H_{cod}), 0.00 (m, 1H, H_{cod}), -1.04 (m, 1H, H_{cod}), –2.67 (s, 2H, NH) ppm. **^{13}C{^{1}H} NMR** (150.9 MHz, CD_2Cl_2): δ 189.4 (d, $^1J_{Rh,C}$ = 51.2 Hz), 142.5, 139.2, 138.4, 135.2, 135.1, 135.0, 130.9, 128.5, 128.3, 128.1, 127.3, 122.4, 121.9, 121.8, 121.5, 115.4, 97.5 (d, $^1J_{CH(cod)\text{-}Rh}$ = 6.6 Hz), 97.2 (d, $^1J_{CH(cod)\text{-}Rh}$ = 7.0 Hz), 68.5 (d, $^1J_{CH(cod)\text{-}Rh}$ = 14.4 Hz), 66.8 (d, $^1J_{CH(cod)\text{-}Rh}$ = 13.8 Hz), 39.7, 35.2, 29.9, 29.0, 27.6, 21.8 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 418 (5.14), 520 (4.26), 593 (3.83), 649 (3.49) nm. **HRMS** (ESI+): *m/z* calc for $C_{52}H_{46}N_6Rh$ $[M\text{-}Cl]^+$: 857.2833, found 857.2849.



Synthesis of porphyrin Zn-C-Rh(cod)Cl. Porphyrin **Zn-C-PF$_6$** (101 mg, 0.1180 mmol, 1 eq), $[Rh(cod)Cl]_2$ (48.0 mg, 0.0973 mmol, 0.8 eq) and *t*BuOK (15.9 mg, 0.1417 mmol, 1.2 eq) were degassed under argon for 10 min. Then, anhydrous THF (45 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 98:2 (v:v)). The first red fraction was collected and

concentrated to give a purple solid in 66% yield (75 mg, 0.0784 mmol). **^{1}H NMR** (600 MHz, CD_2Cl_2): δ 9.63 (d br, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 9.00 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.99 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.96-8.93 (m, 4H, $H_{\beta\text{-}pyrr}$), 8.62 (d, $^3J_{H,H}$ = 4.7 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.24-8.19 (m br, 3H, H_o+H_a), 8.13-8.03 (2m br, 3H, H_a), 7.99 (s, $^3J_{H,H}$ = 1.9 Hz, 1H, H_5), 7.81-7.77 (m, 3H, H_m+H_p), 7.63-7.57 (m br, 4H, H_b), 7.43 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_4), 4.61 (m, 1H, H_{cod}), 4.58 (s, 3H, N-CH_3), 4.21 (m, 1H, H_{cod}), 3.64 (m, 1H, H_{cod}), 2.70 (s, 6H, $CH_{3\ tolyl}$), 2.37 (m, 1H, H_{cod}), 2.00–1.86 (m, 2H, 2H_{cod}), 1.67–1.56 (m, 1H, H_{cod}), 1.14-1.09 (m, 1H, H_{cod}), 0.51 (m, 1H, H_{cod}), 0.28 (m, 1H, H_{cod}), 0,09 (m, 1H, H_{cod}), –0.89 (m, 1H, H_{cod}) ppm. **^{13}C{^{1}H} NMR** (125.7 MHz, CD_2Cl_2): δ 188.6 (br d, $^1J_{Rh,C}$ = 63.4 Hz), 152.4, 151.8, 151.1, 150.7, 150.5, 150.3, 143.1, 140.0, 138.0, 135.0, 134.9, 133.5, 133.4, 132.9, 132.7, 132.6, 132.5, 130.9, 128.1, 128.0, 127.8, 127.1, 121.1, 97.1 (br d, $^1J_{CH(cod)\text{-}Rh}$ = 29.8 Hz, 2 $CH_{(cod)}$), 68.4 (d, $^1J_{CH(cod)\text{-}Rh}$ = 17.1 Hz), 66.9 (d, $^1J_{CH(cod)\text{-}Rh}$ = 12.7 Hz), 39.5, 35.0, 31.4, 28.8, 27.7, 21.7 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 413 (5.14), 532 (4.20), 560 (3.82) nm. **HRMS** (ESI+): *m/z* calc for $C_{52}H_{46}N_6Rh$ [M-Cl]$^+$: 919.1962, found 919.1968.

Synthesis of porphyrin Ni-C-Rh(cod)Cl. Porphyrin **Ni-C-PF$_6$** (122 mg, 0.1436 mmol, 1 eq), $[Rh(cod)Cl]_2$ (53.1 mg, 0.1077 mmol, 0.75 eq) and *t*BuOK (20.7 mg, 0.1844 mmol, 1.3 eq) were degassed under argon for 10 min. Then, anhydrous THF (45 mL) was added and the reaction mixture was stirred at room temperature under argon atmosphere for 16 hours. Once finished according to TLC analysis, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 98:2 (v:v)). The first red fraction was collected and concentrated to give porphyrin **Ni-C-Rh(cod)Cl** a purple solid in 72% yield (99 mg, 0.1042 mmol).



^{1}H NMR (600 MHz, CD_2Cl_2): δ 9.49 (d, $^3J_{H,H}$ = 5.0 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.84 (d, $^3J_{H,H}$ = 5.0 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.81 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.78 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.76 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.76 (s, 2 $H_{\beta\text{-}pyrr}$), 8.44 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, $H_{\beta\text{-}pyrr}$), 8.04 (d br, $^3J_{H,H}$ = 7.1 Hz, 2H, H_o), 7.92 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H_5) 7.95–7.85 (m, 4H, H_a), 7.76–7.68 (m, 3H, 2H_m and 1H_p), 7.55–7.50 (m, 4H, H_b), 7.37 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, H_4), 4.56 (m, 1H, H_{cod}), 4.48 (s, 3H, N-CH_3), 4.26 (m, 1H, H_{cod}), 3.53 (m, 1H, H_{cod}), 2.65 (2s, 3+3H, $CH_{3\ tolyl}$), 2.33 (m, 1H, H_{cod}), 1.95 (m, 1H, H_{cod}), 1.63 (m, 2H, 2H_{cod}), 1.26 (m, 1H, H_{cod}), 0.85 (m, 1H, H_{cod}), 0.37 (m, 1H, H_{cod}), 0.20 (m, 1H, H_{cod}), –0.62 (m, 1H, H_{cod}) ppm. **^{13}C{^{1}H} NMR** (150.9 MHz, CD_2Cl_2): δ 189.3 (d, $^1J_{Rh,C}$ = 51.3 Hz), 145.2, 144.7, 144.1, 143.5, 143.6, 143.6, 143.5, 142.6, 141.3, 138.4, 138.2, 134.2, 134.2, 133.9, 133.7, 133.1, 132.9, 132.8, 132.7, 130.0, 128.5, 128.3, 128.2, 128.1, 127.5, 121.7, 121.1, 120.9, 120.6, 115.8, 97.6 (d, $^1J_{CH(cod)\text{-}Rh}$ = 8.0 Hz), 97.3 (d, $^1J_{CH(cod)\text{-}Rh}$ = 8.0 Hz), 68.3 (d, $^1J_{CH(cod)\text{-}Rh}$ = 16.0 Hz), 66.8 (d, $^1J_{CH(cod)\text{-}Rh}$ = 15.1 Hz), 39.5, 35.0, 30.3, 29.0, 27.8, 21.8 ppm. **UV-Vis** (DMSO): λ_{max} (log ε) = 413 (5.17), 532 (4.20), 560 (3.82) nm. **HRMS** (ESI+): *m/z* calc for $C_{52}H_{44}N_6NiRh$ [M-Cl]$^+$: 913.2030 found 913.2034.

Synthesis of complexes M^1-Rh-(CO)$_2$Cl. Rhodium(I) complexes **M^1-A-Rh(cod)Cl**, **M^1-B-Rh(cod)Cl** and **M^1-C-Rh(cod)Cl** were dissolved and stirred in CH_2Cl_2 (10^{-3} M in 5 mL). Then, carbon monoxide was bubbled through the solutions for 15 minutes and the corresponding rhodium(I) complexes **M^1-A-Rh(CO)$_2$Cl**, **M^1-B-Rh(CO)$_2$Cl** and **M^1-C-Rh(CO)$_2$Cl** were obtained. These complexes were not isolated and aliquots of the reaction mixtures were sampled for IR spectroscopy analyses. Carbonyl stretching frequencies were found to be in the range 2080-2082 and 2000-2002 cm^{-1}. These data are in agreement with those reported in the literature for known complexes of the type *cis*-[(NHC)RhCl(CO)$_2$].[8]

Spectra of new compounds

Porphyrin 2H-A-Cl

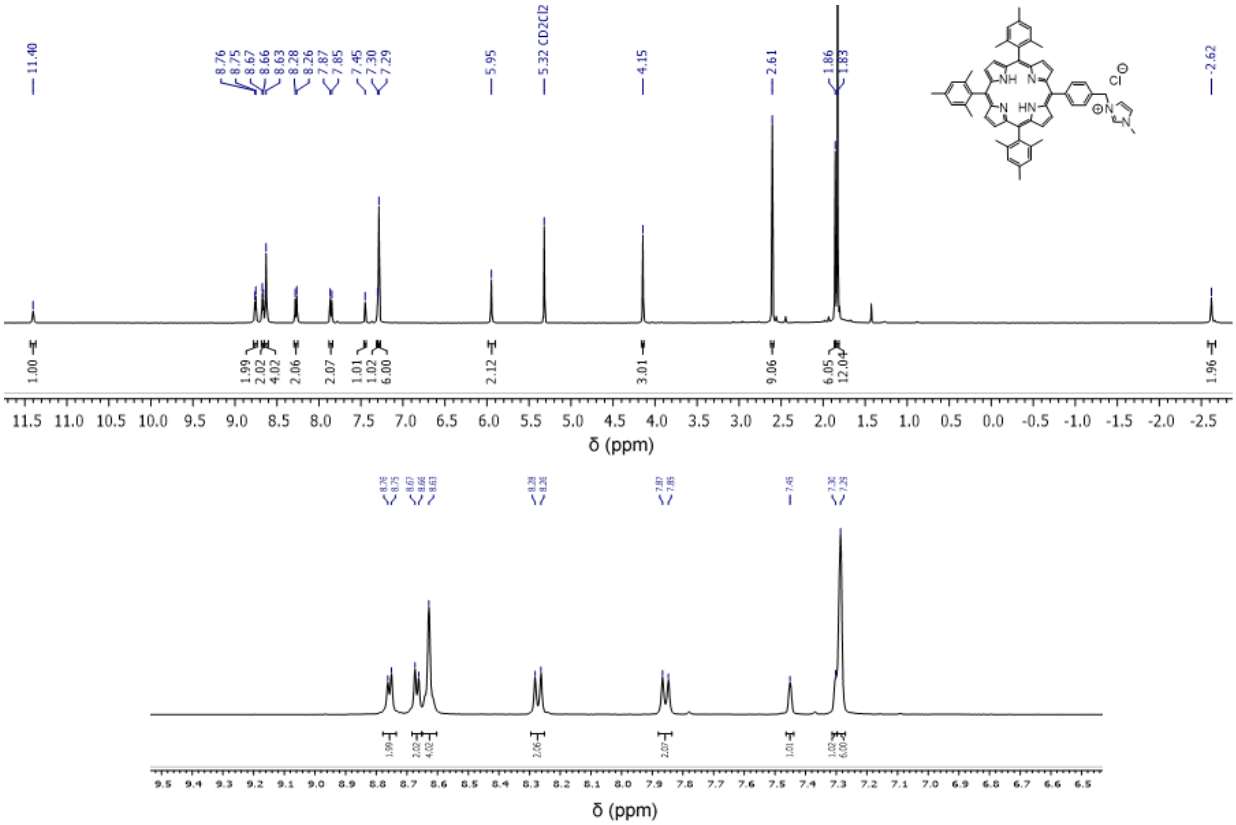


Figure S1. Full range (top) and partial (bottom) ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of **2H-A-Cl**

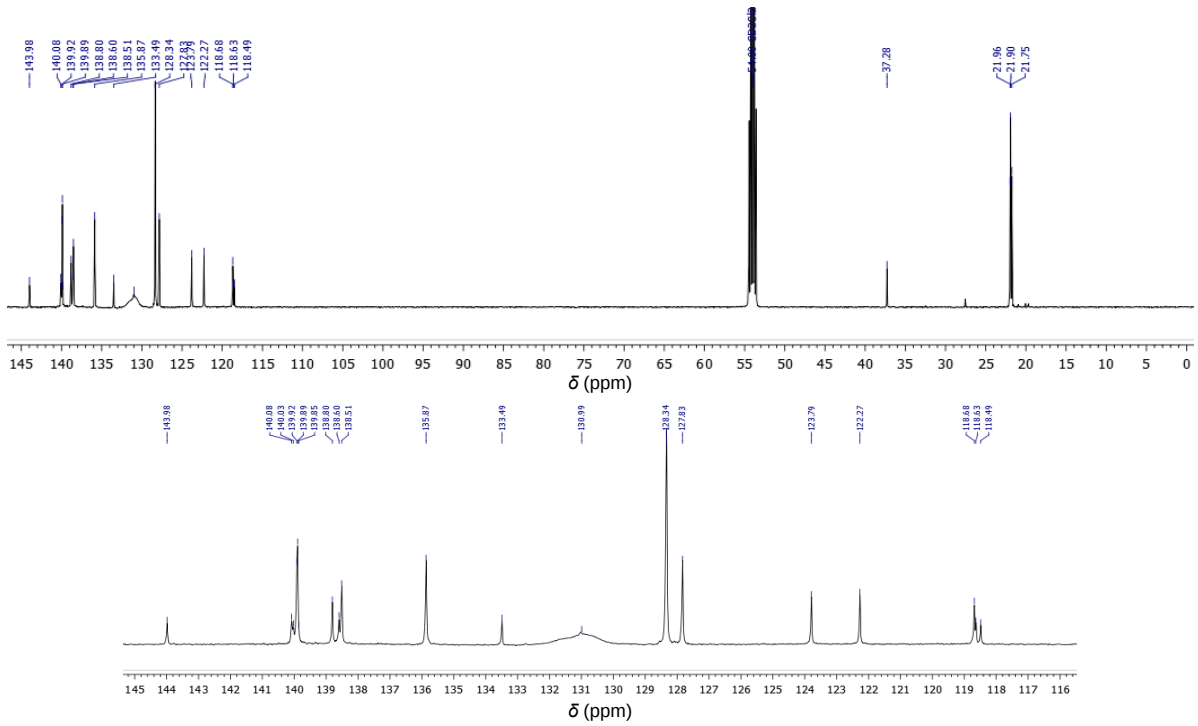


Figure S2. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, CD_2Cl_2) of **2H-A-Cl**

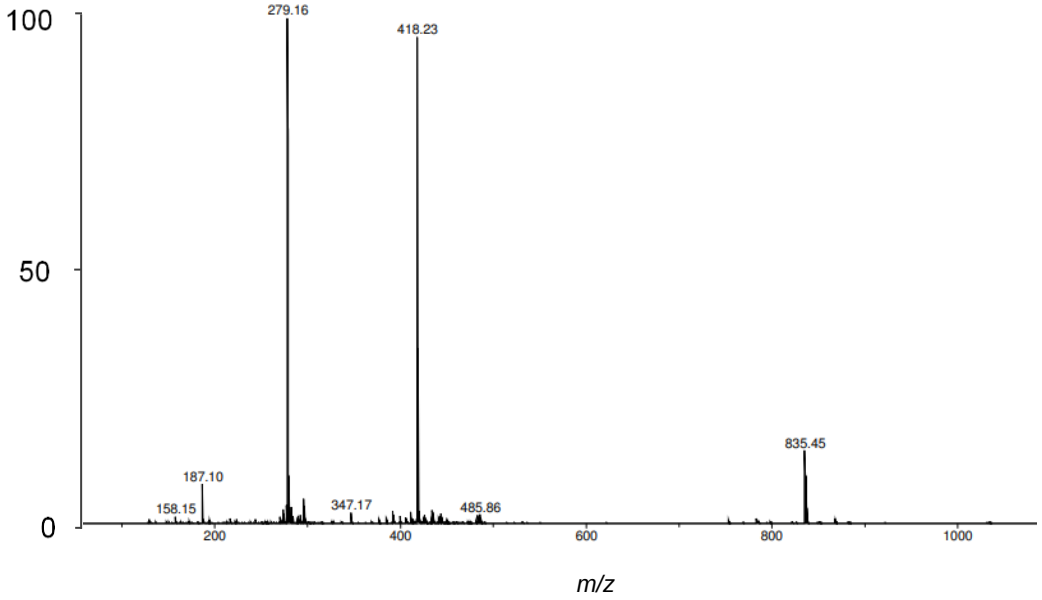


Figure S3. ESI-TOF (positive mode) mass spectrum of **2H-A-Cl**

Porphyrin Zn-A-Cl

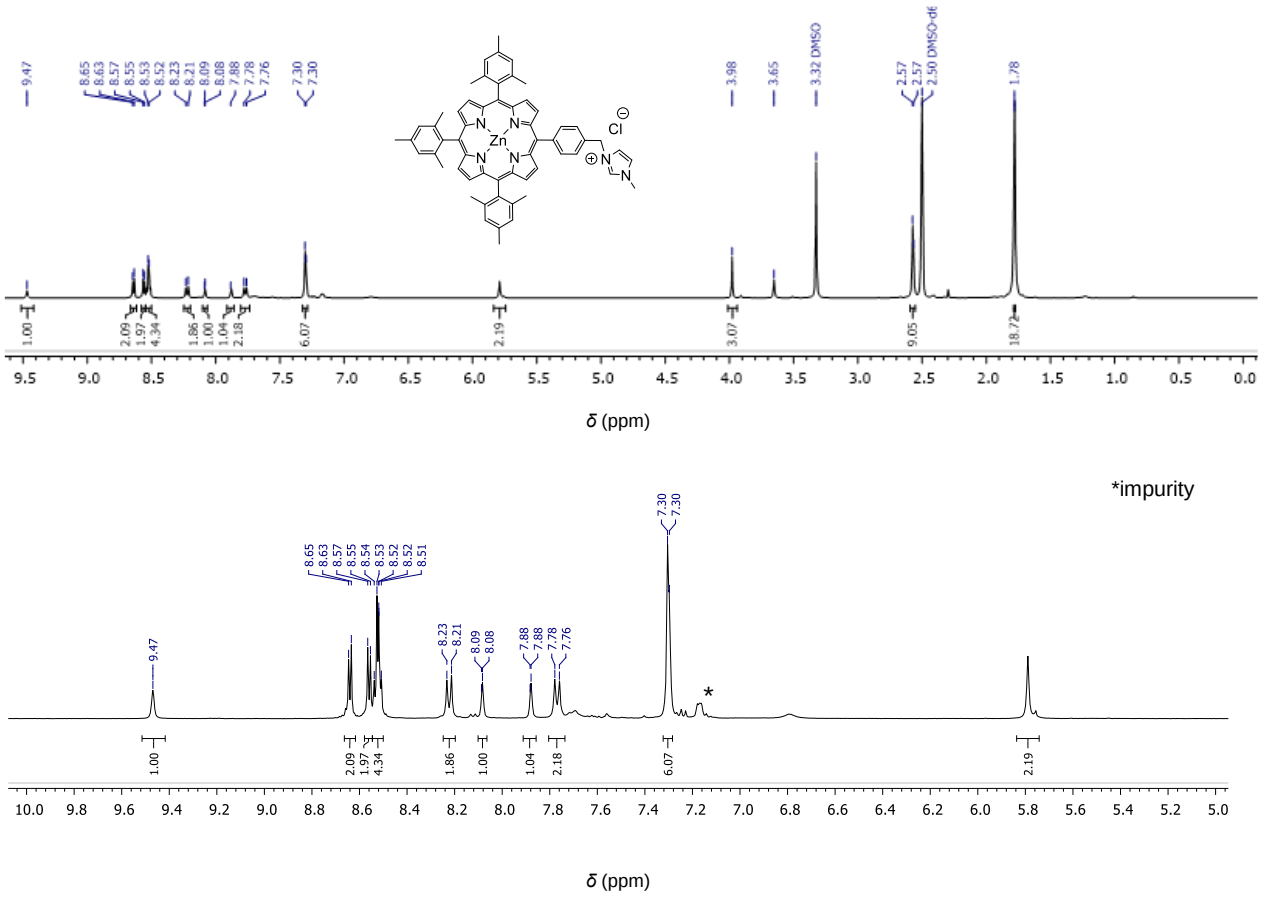


Figure S4. Full range (top) and partial (bottom) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **Zn-A-Cl**

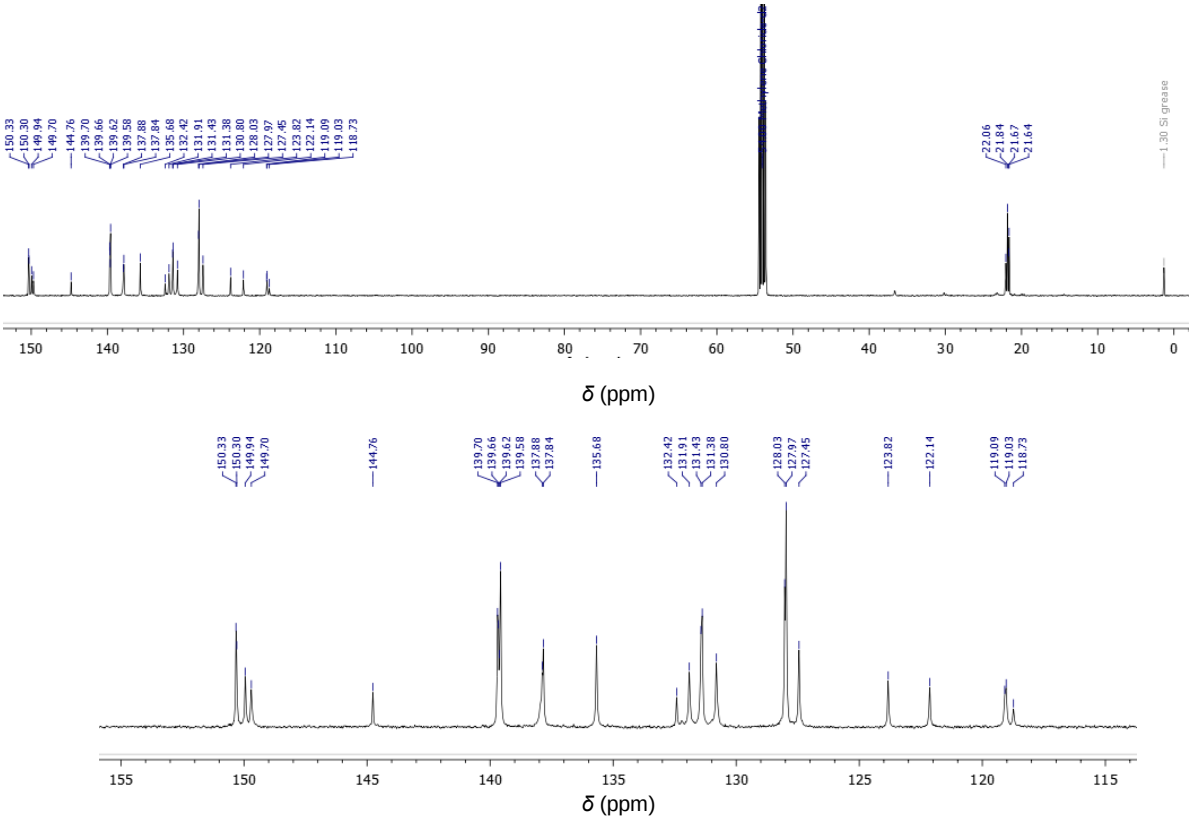


Figure S5. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, CD_2Cl_2) of **Zn-A-Cl**

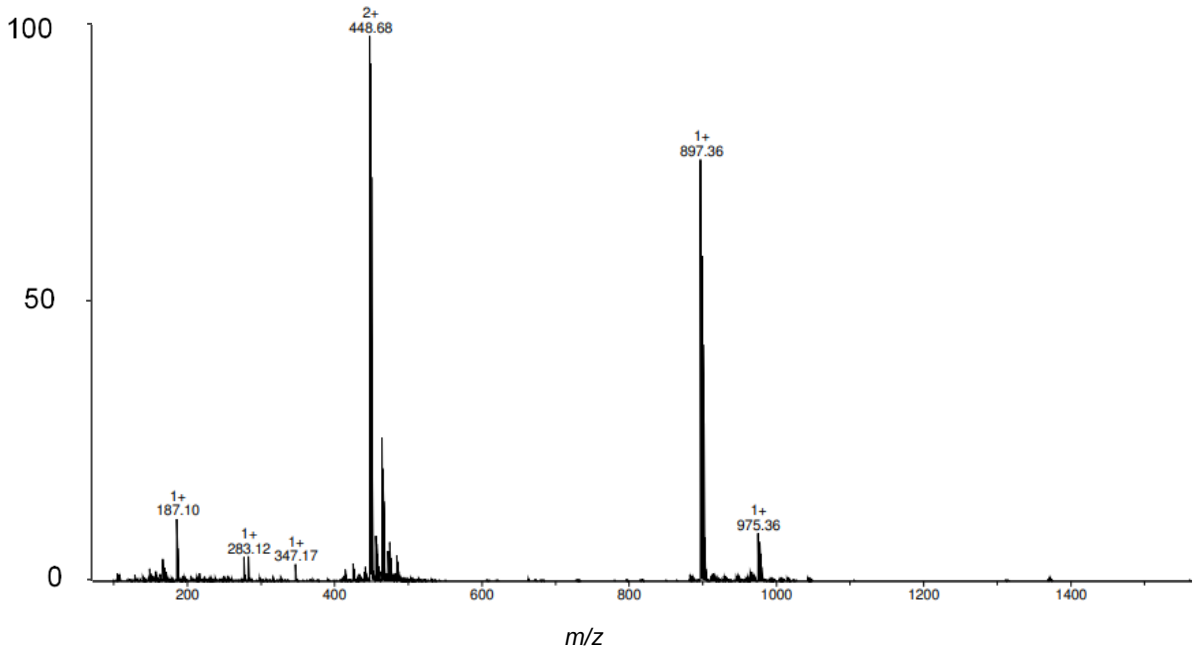
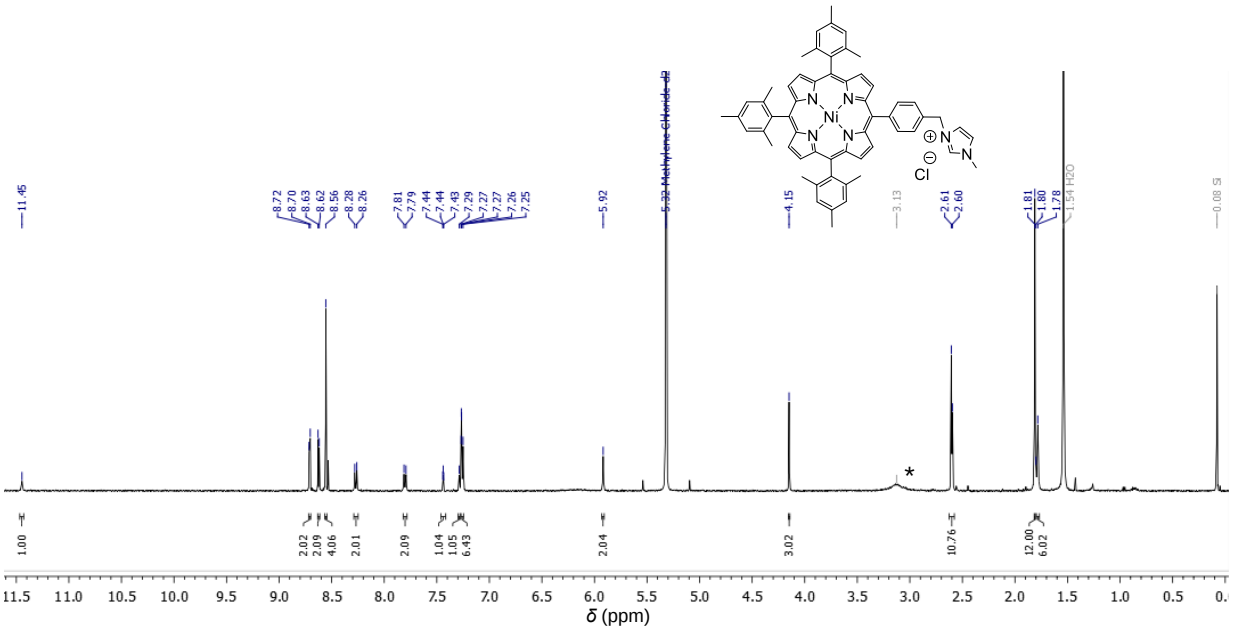


Figure S6. ESI-TOF (positive mode) mass spectrum of **Zn-A-Cl**

Porphyrin Ni-A-Cl



*impurity

Figure S7. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **Ni-A-Cl**

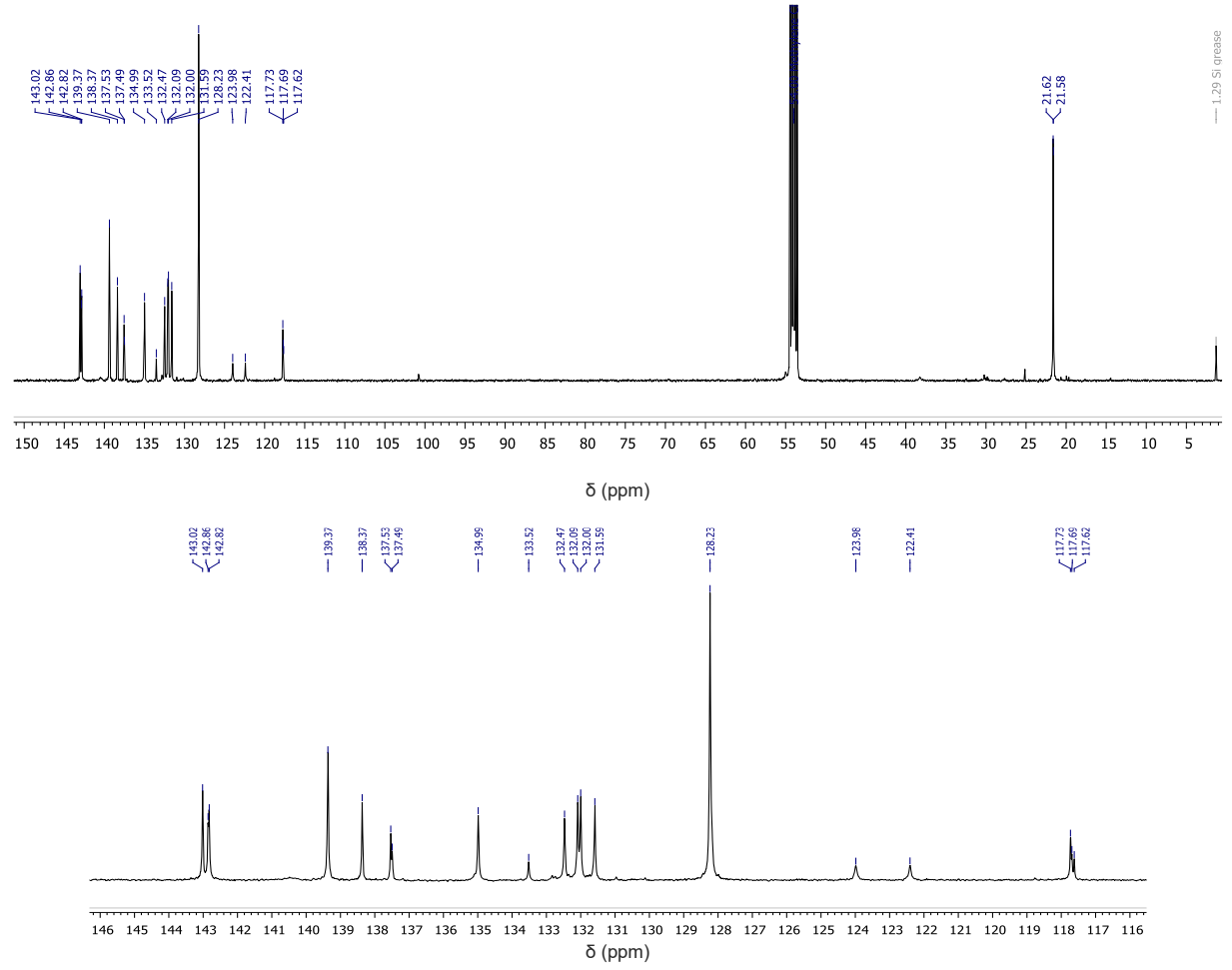


Figure S8. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, CD_2Cl_2) of **Ni-A-Cl**

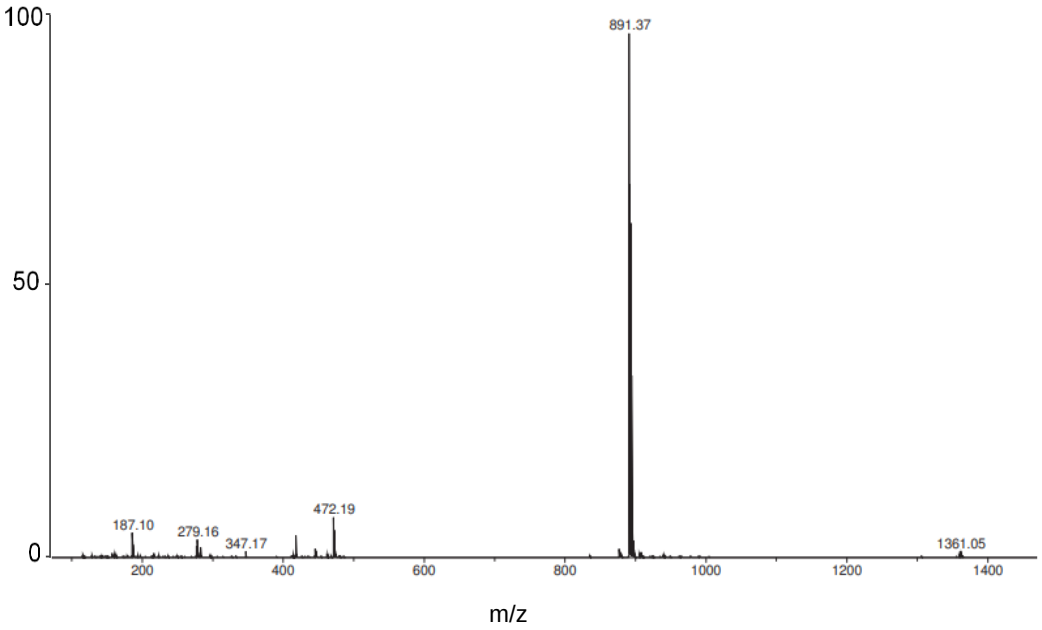


Figure S9. ESI-TOF (positive mode) mass spectrum of **Ni-A-Cl**

Porphyrin 2H-A-Rh(cod)Cl

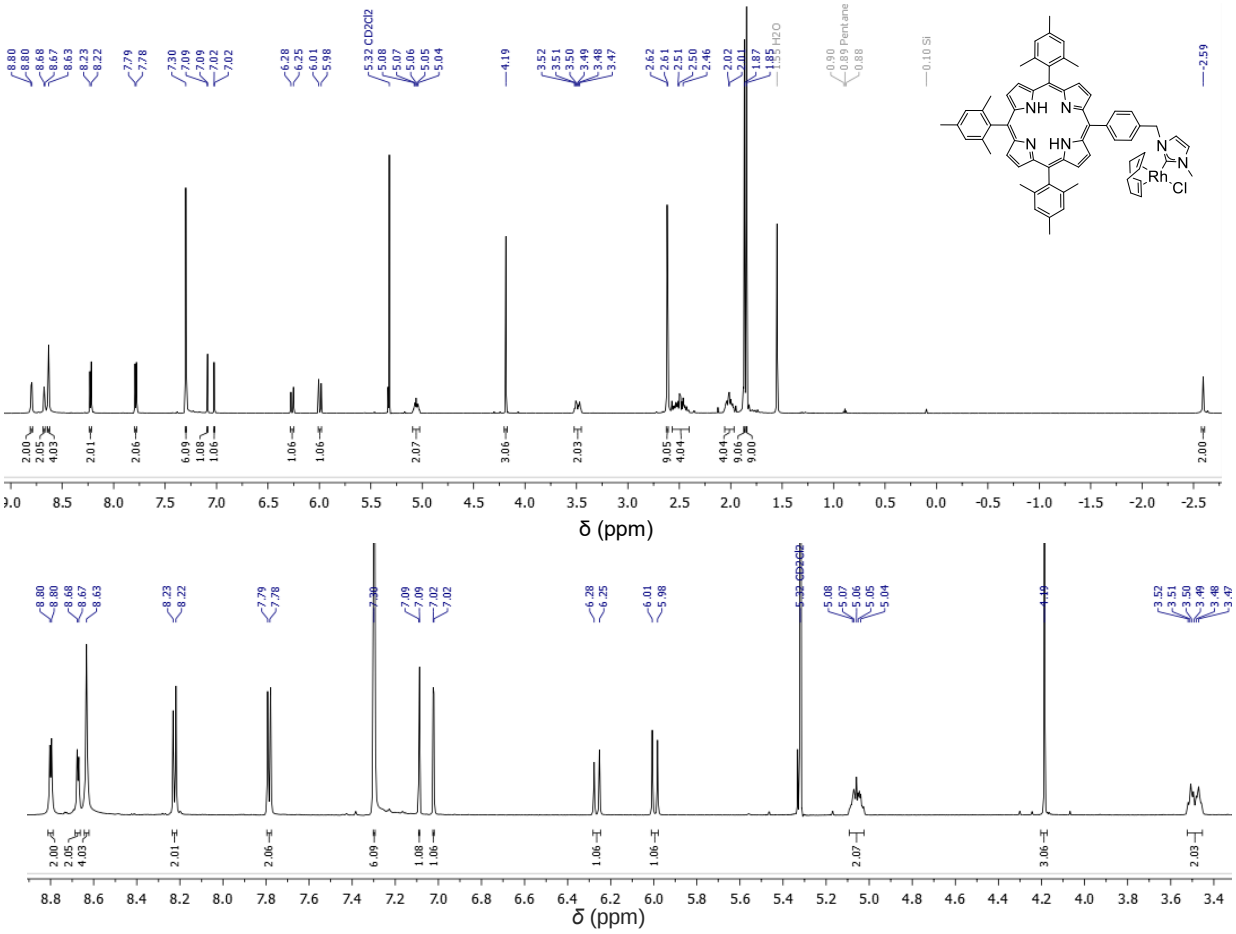


Figure S10. Full range (top) and partial (bottom) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

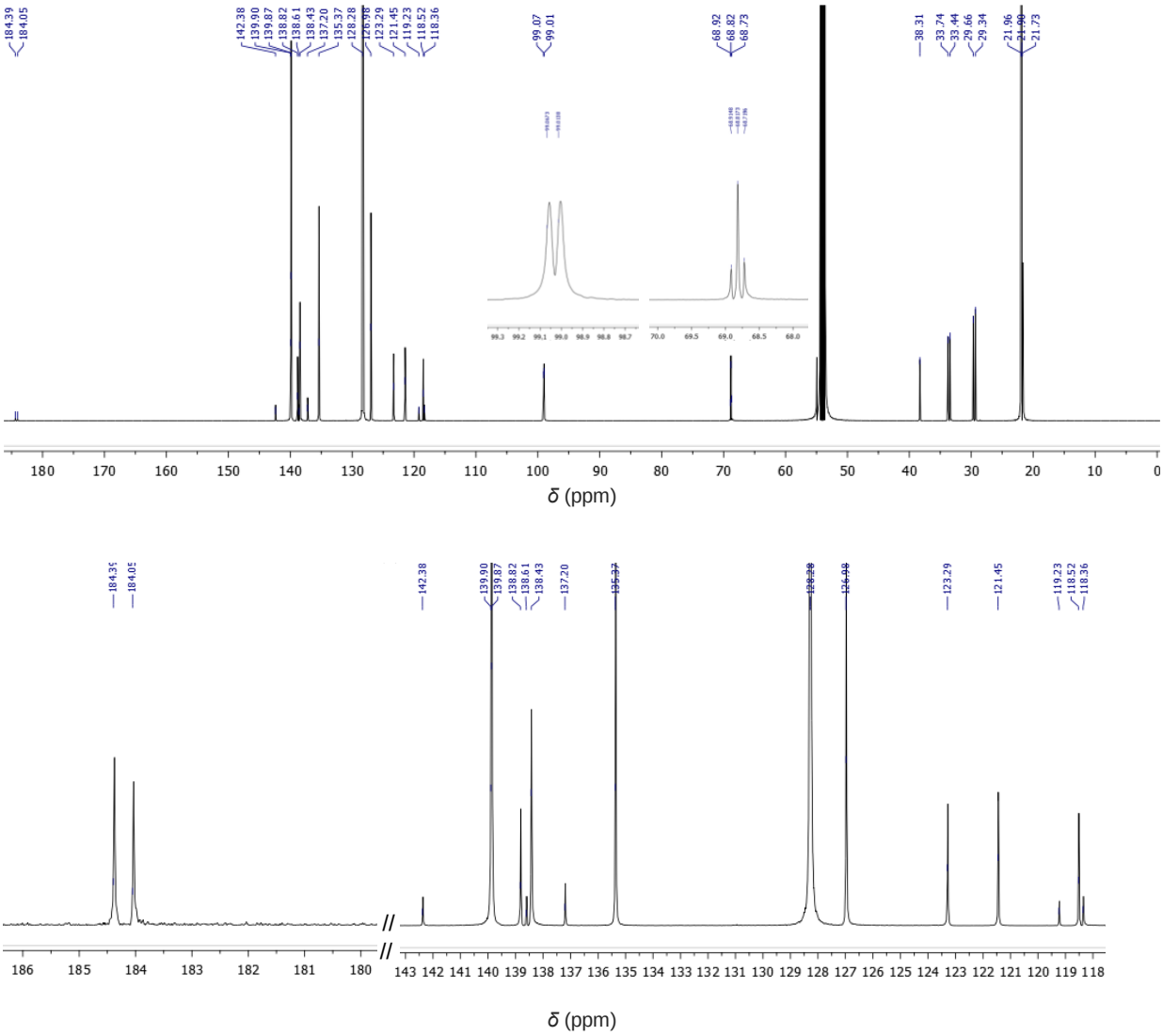


Figure S11. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

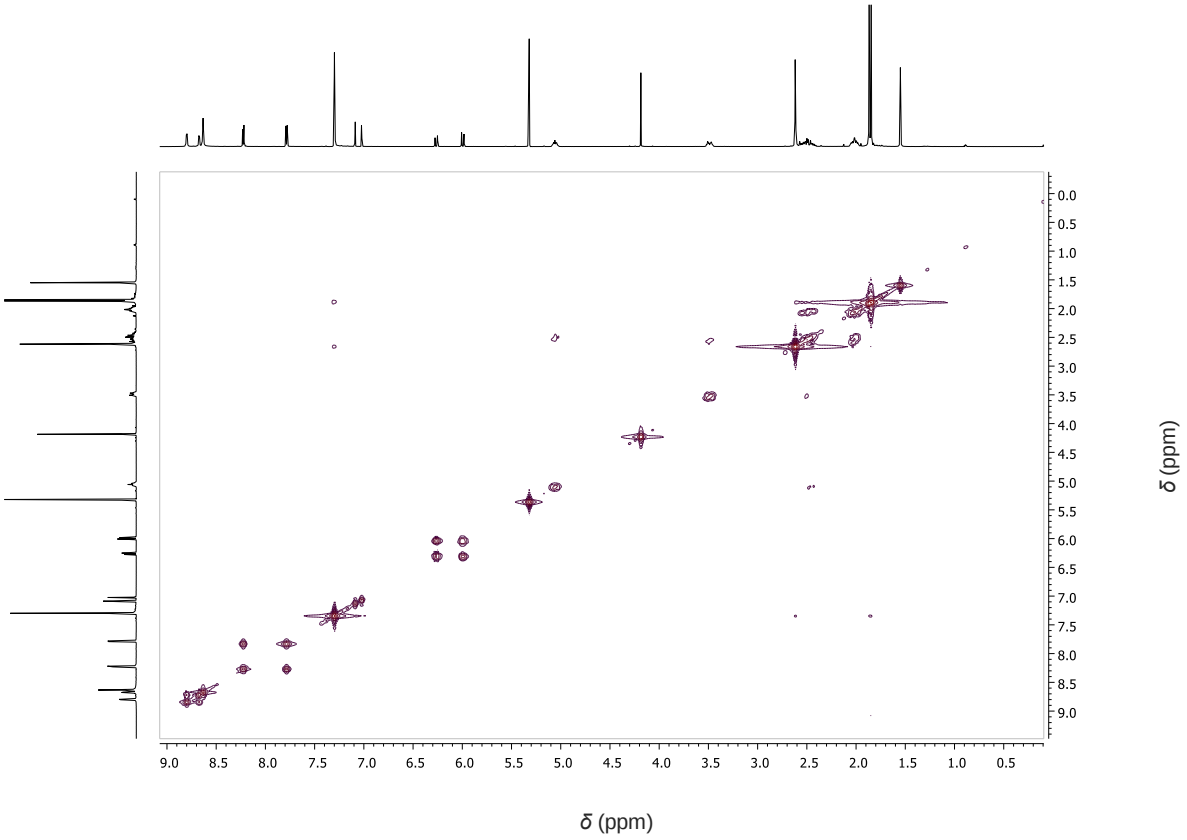


Figure S12. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

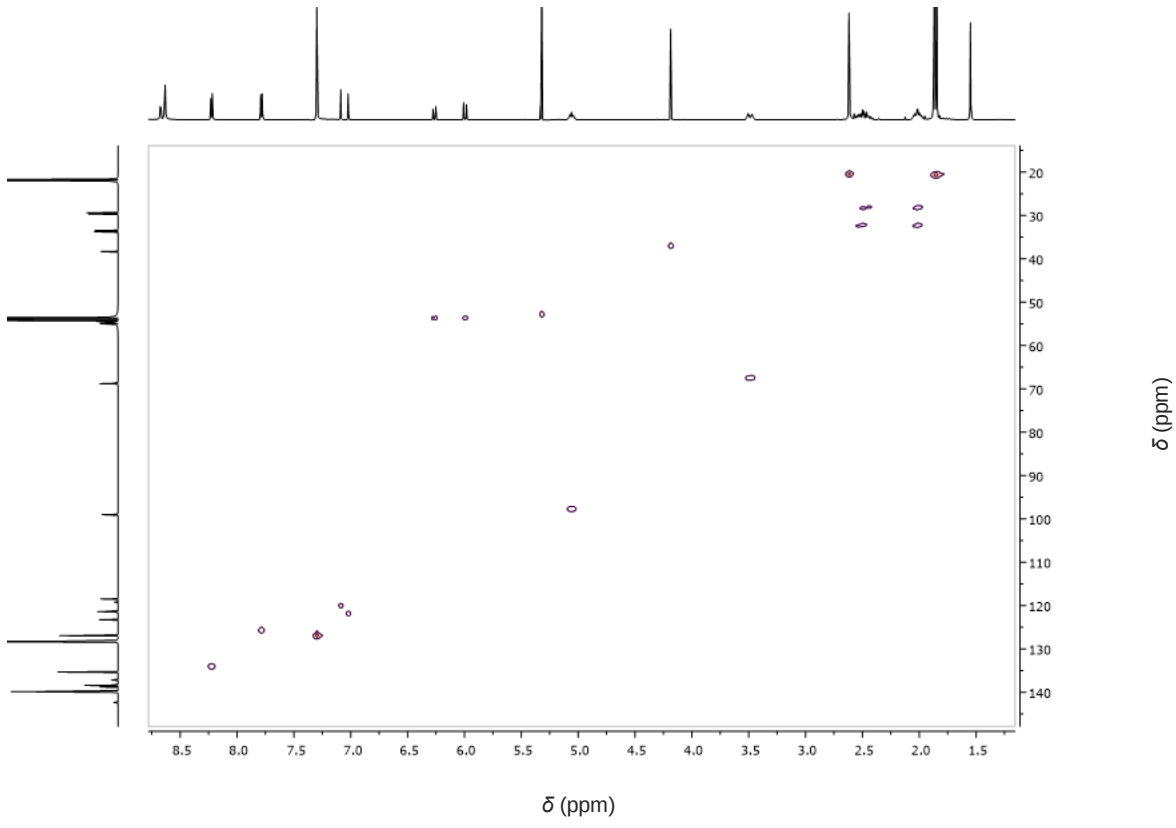


Figure S13. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR spectrum (600 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

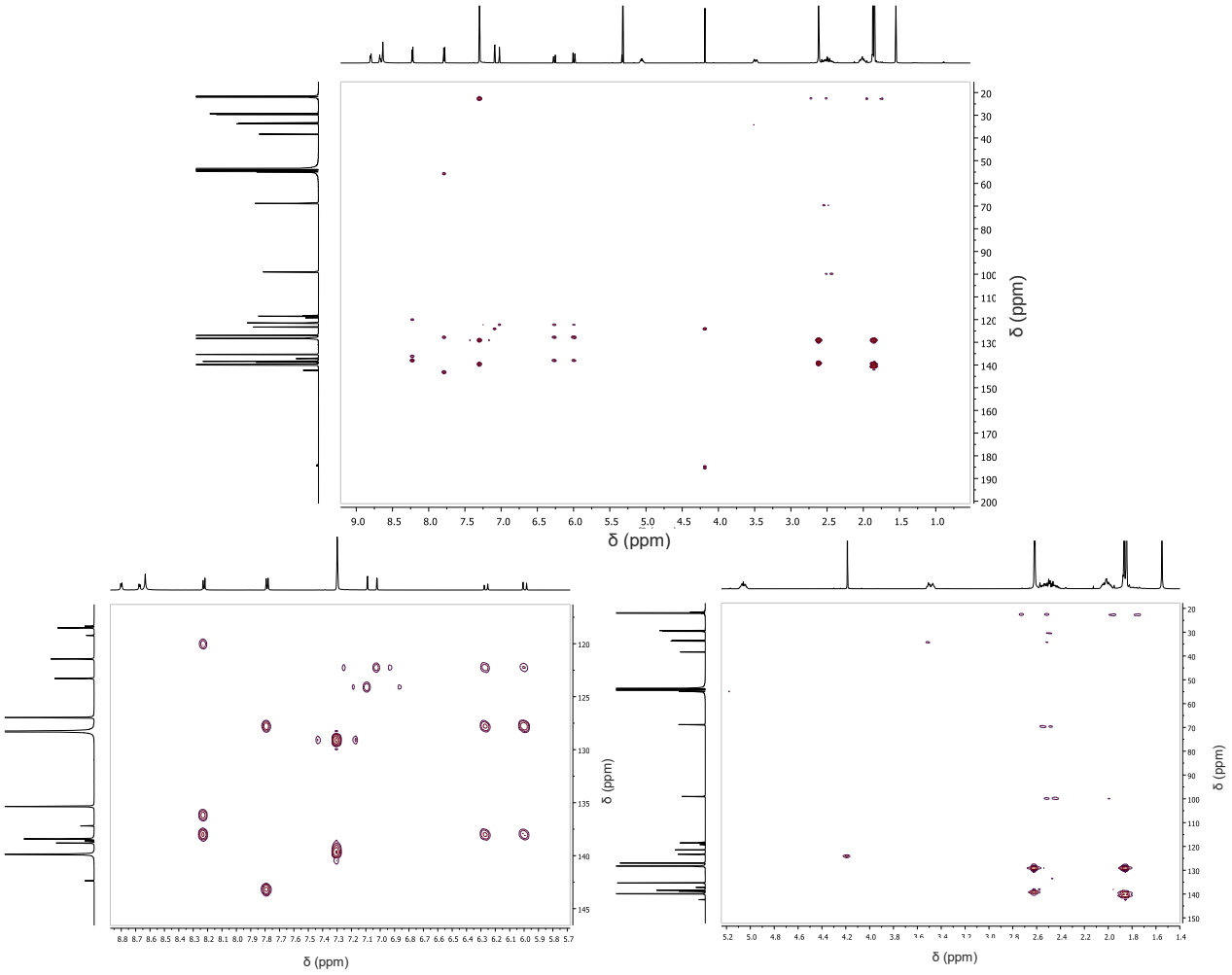


Figure S14. Full range (top), partial (bottom) ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR spectra (600 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

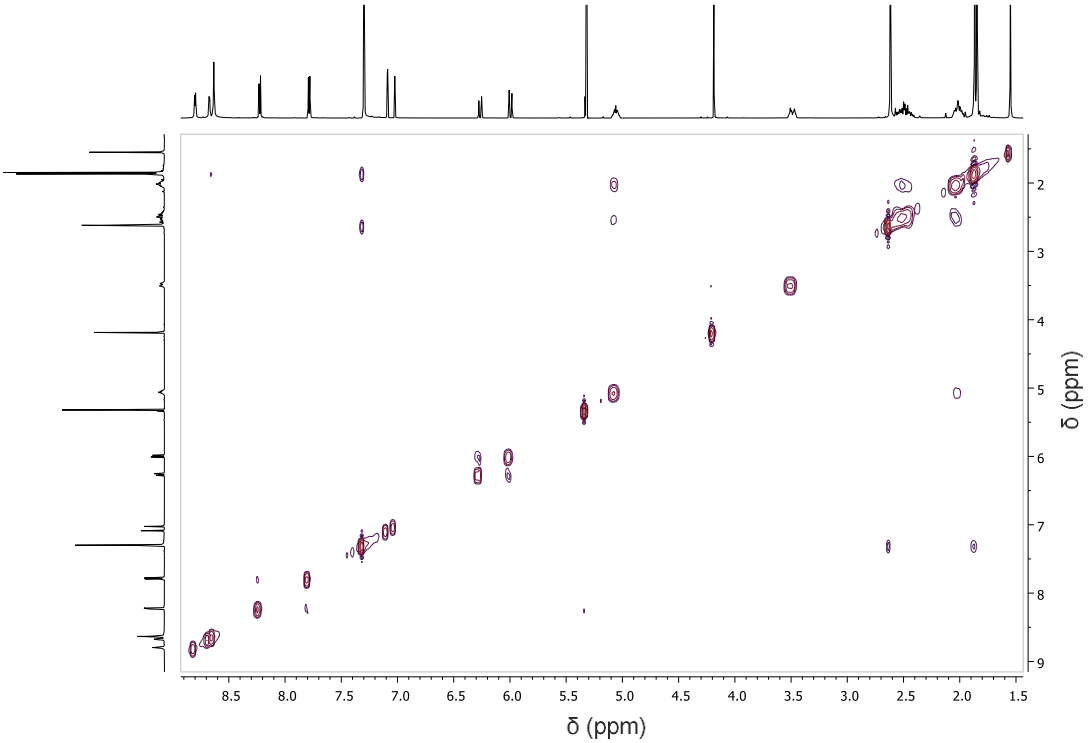


Figure S15. ^{1}H-^{1}H ROESY NMR spectra (600 MHz, CD_2Cl_2) of **2H-A-Rh(cod)Cl**

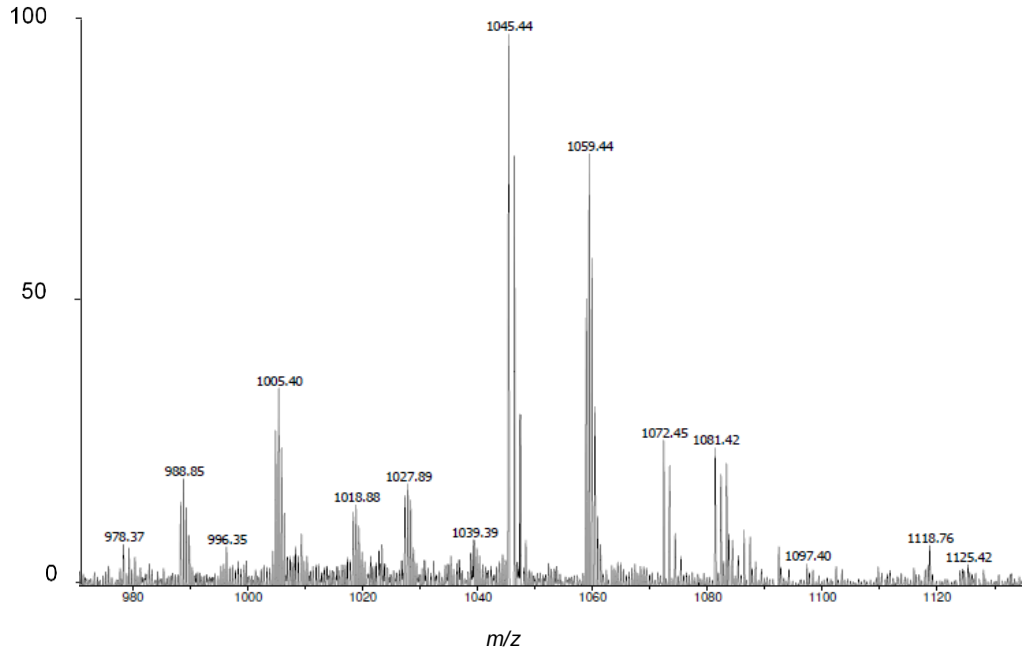


Figure S16. ESI-TOF (positive mode) mass spectrum of **2H-A-Rh(cod)Cl**

Porphyrin Zn-A-Rh(cod)Cl

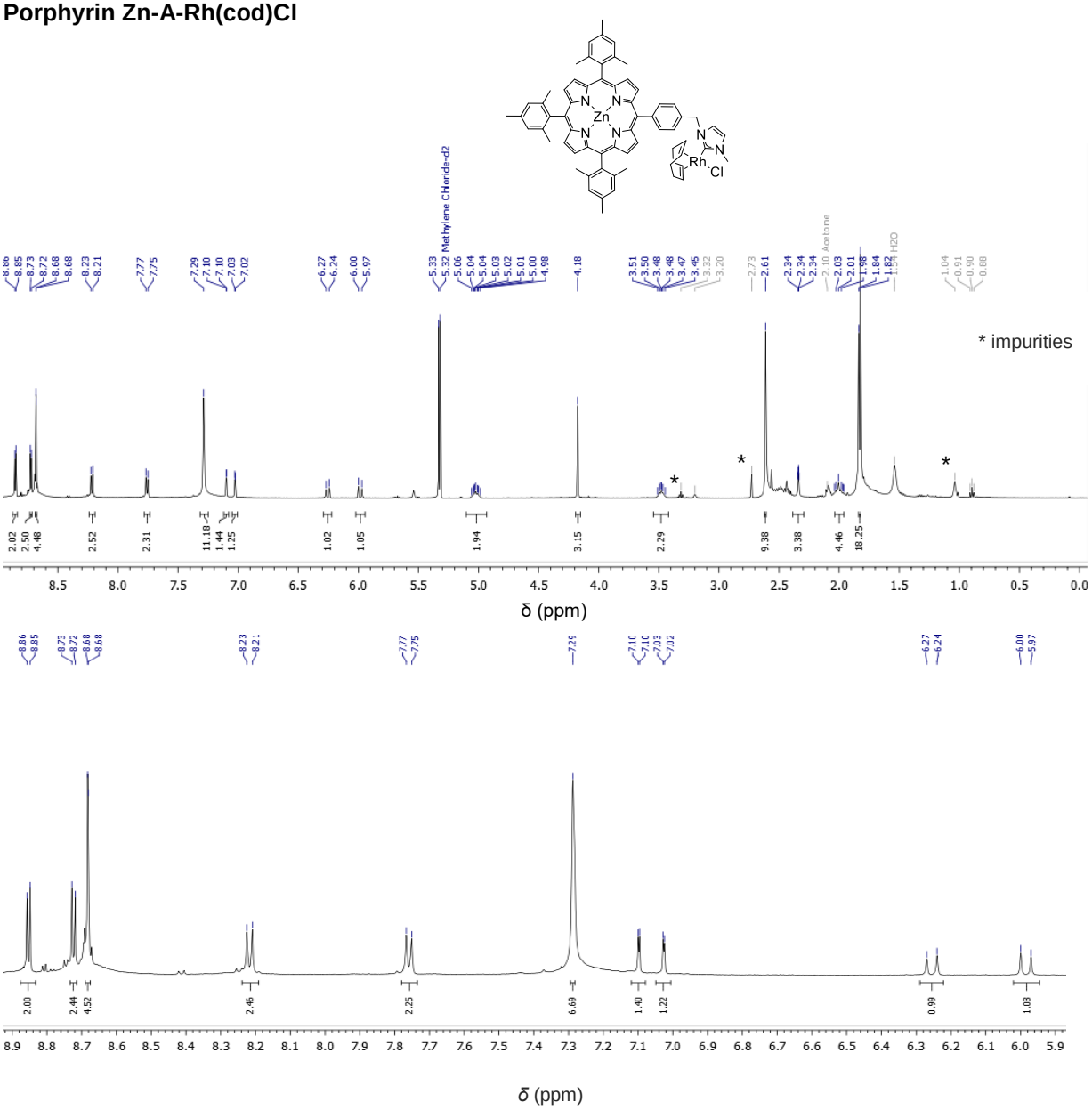


Figure S17. Full range (top) and partial (bottom) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of **Zn-A-Rh(cod)Cl**

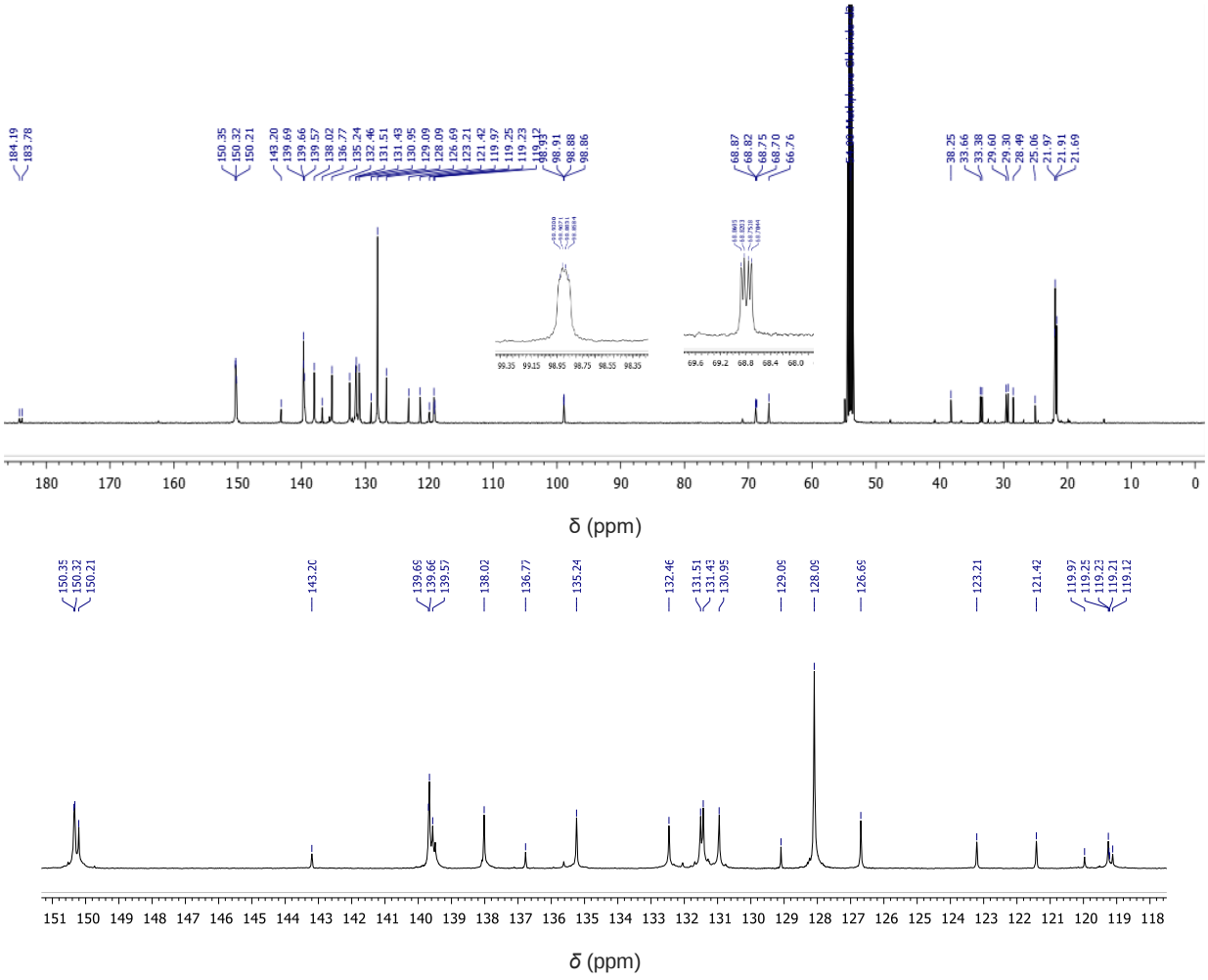


Figure S18. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **Zn-A-Rh(cod)Cl**

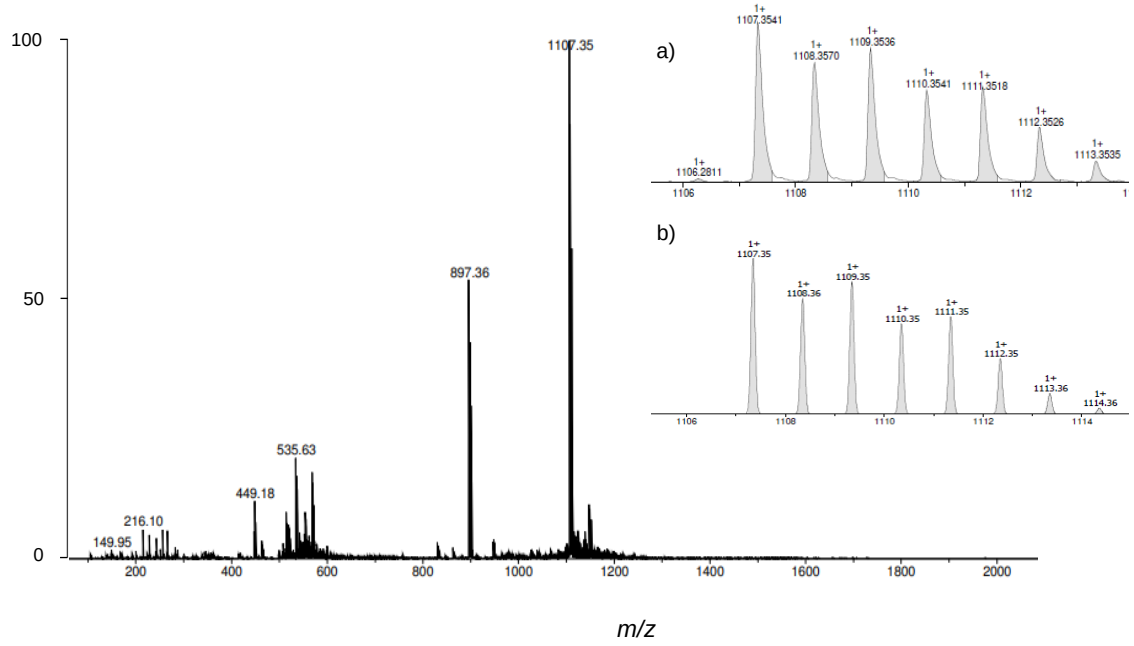
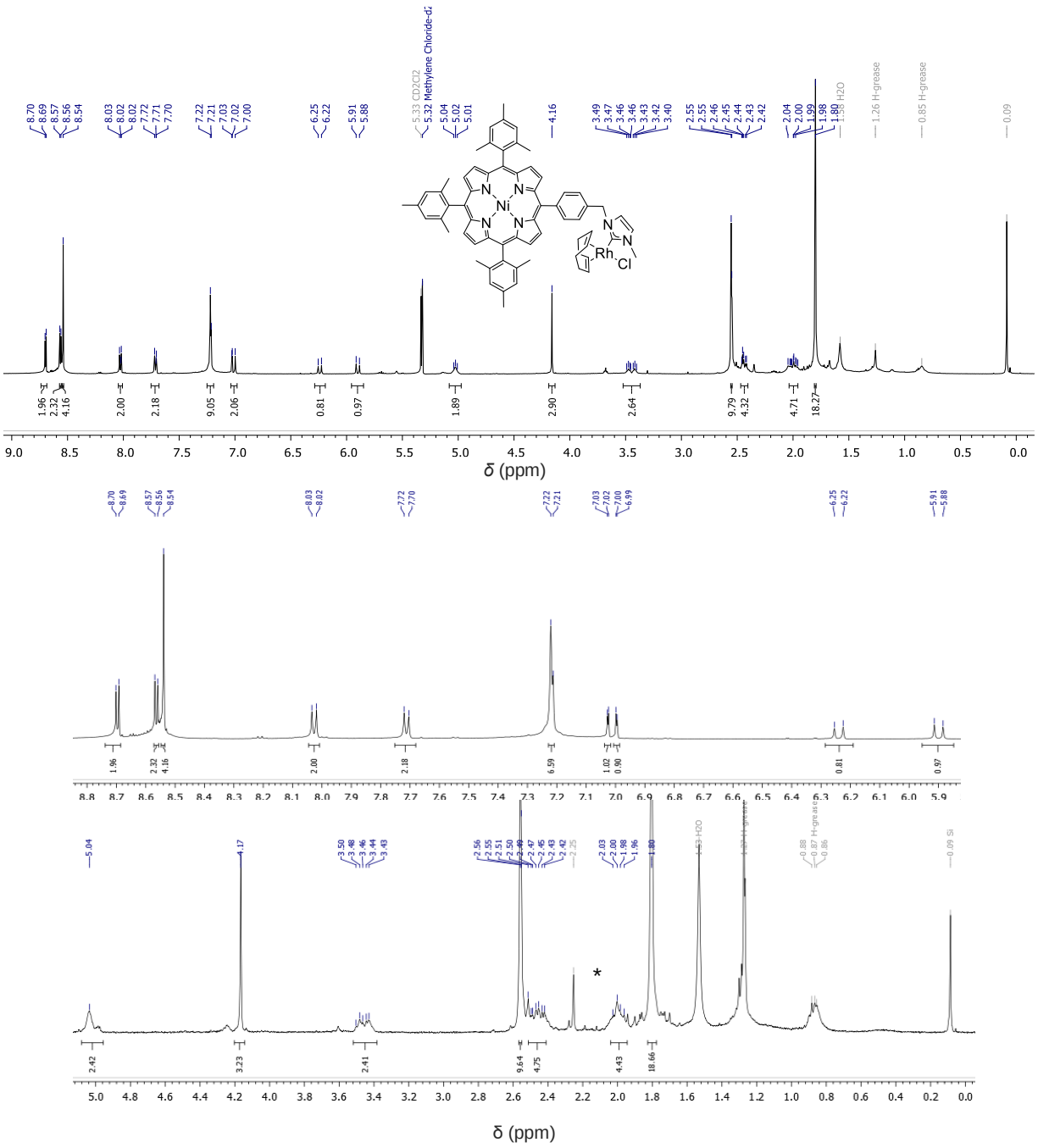


Figure S19. ESI-TOF (positive mode) mass spectrum (left) of **Zn-A-Rh(cod)Cl**. Experimental (a) and calculated (b) isotopic patterns (right)

Porphyrin Ni-A-Rh(cod)Cl



*Impurity

Figure S20. Full range (top) and partial (bottom) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **Ni-A-Rh(cod)Cl**

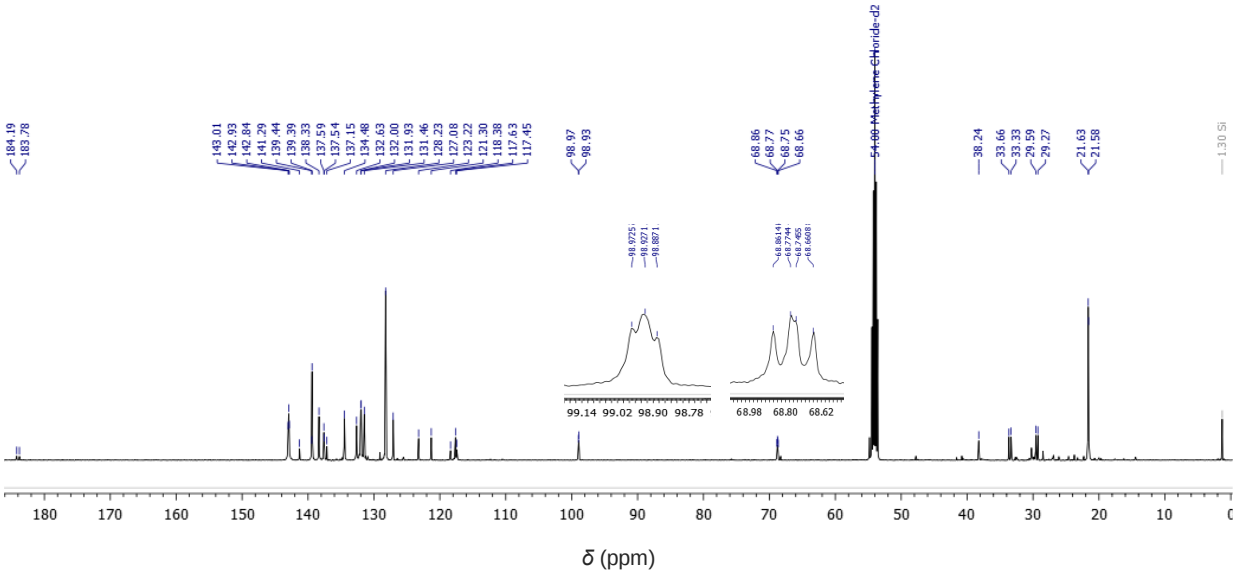


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **Ni-A-Rh(cod)Cl**

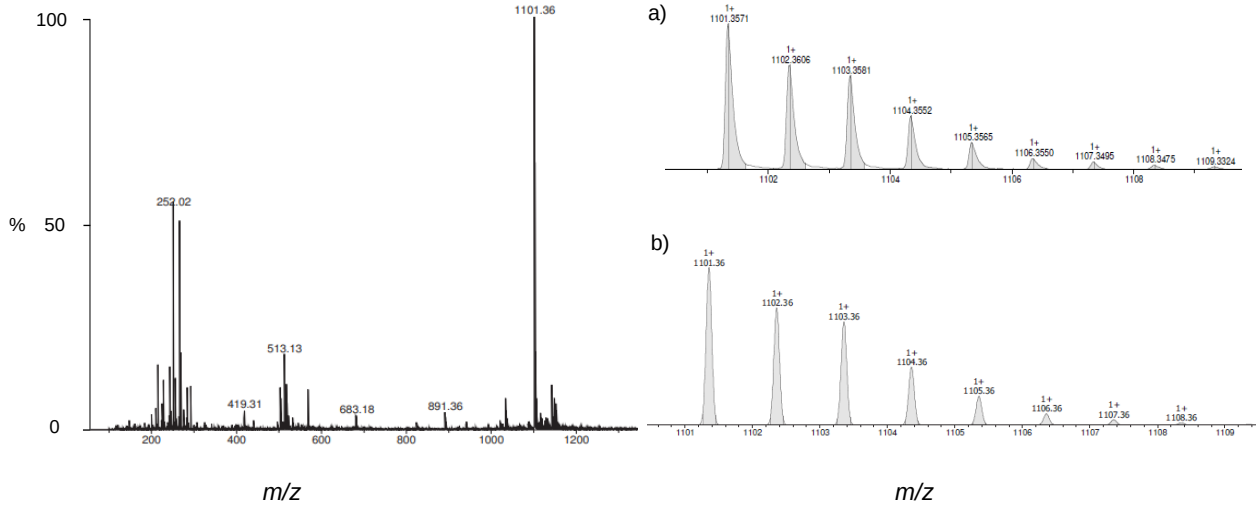


Figure S22. ESI-TOF positive mode mass spectrum (left) of **Ni-A-Rh(cod)Cl**. Experimental (a) and calculated (b) isotopic patterns

Porphyrin 2H-C-PF$_6$

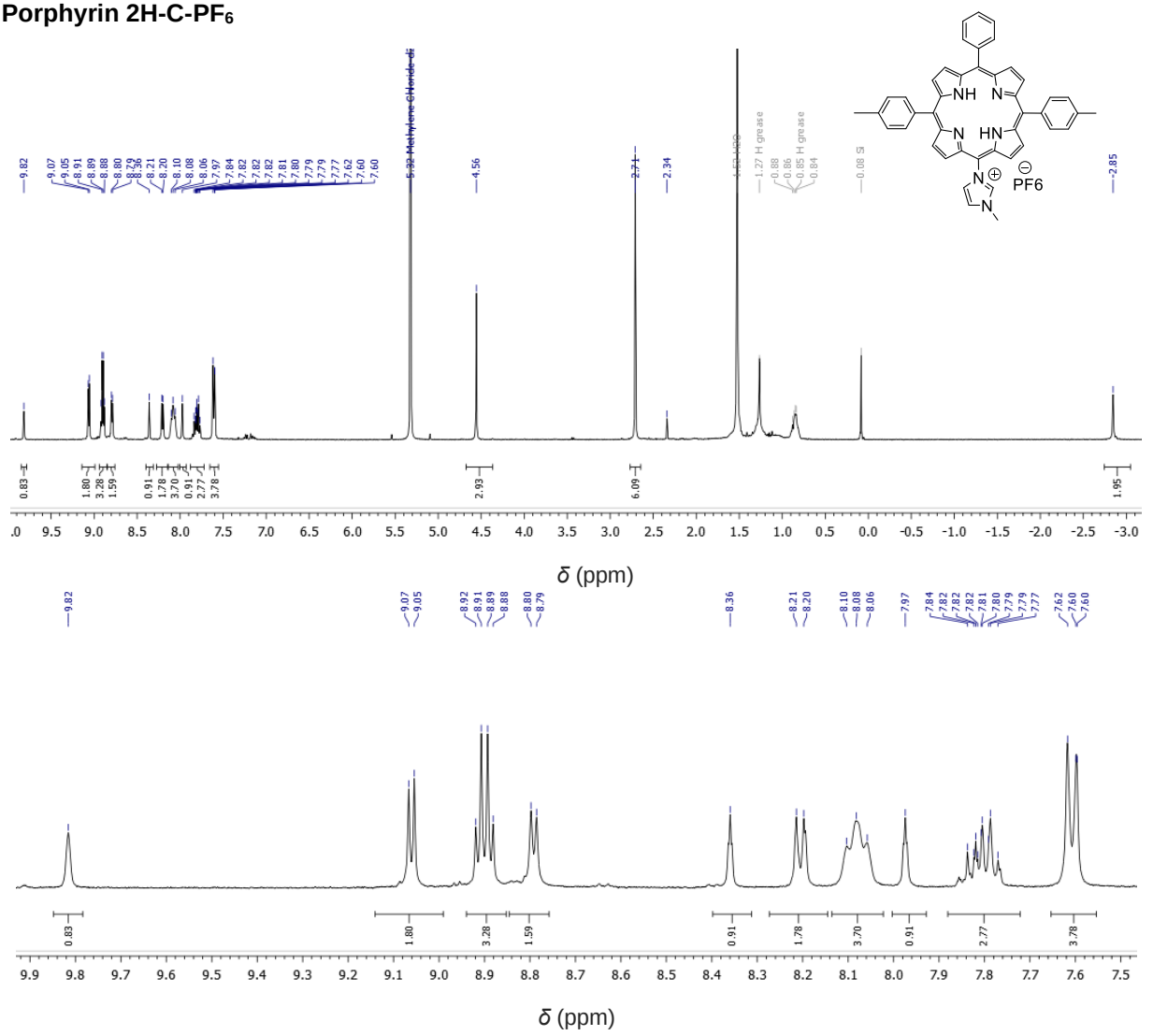


Figure S23. Full range (top) and partial (bottom) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **2H-C-PF$_6$**

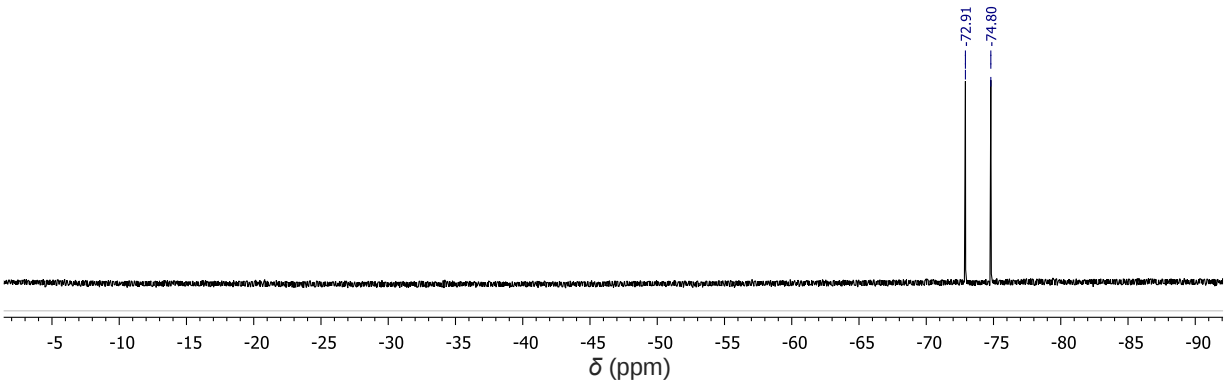


Figure S24. ^{19}F {^{1}H} spectrum (376.5 MHz, CD_2Cl_2) of **2H-C-PF$_6$**

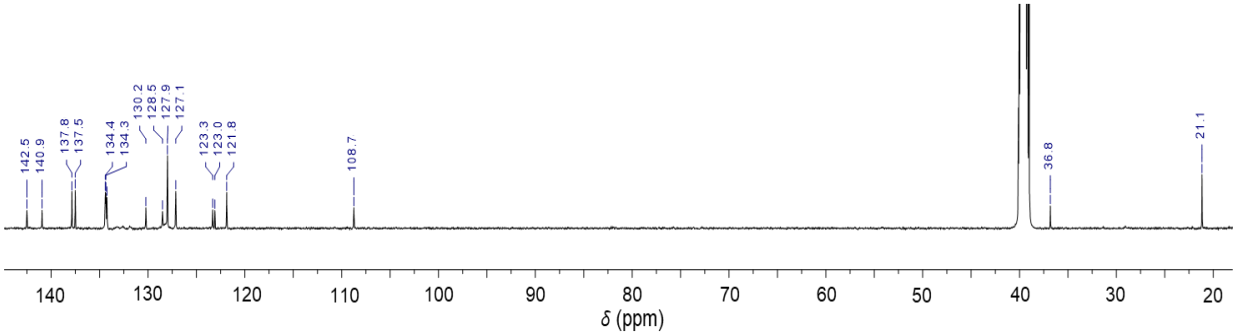


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, DMSO-d_6) of **2H-C-PF$_6$**

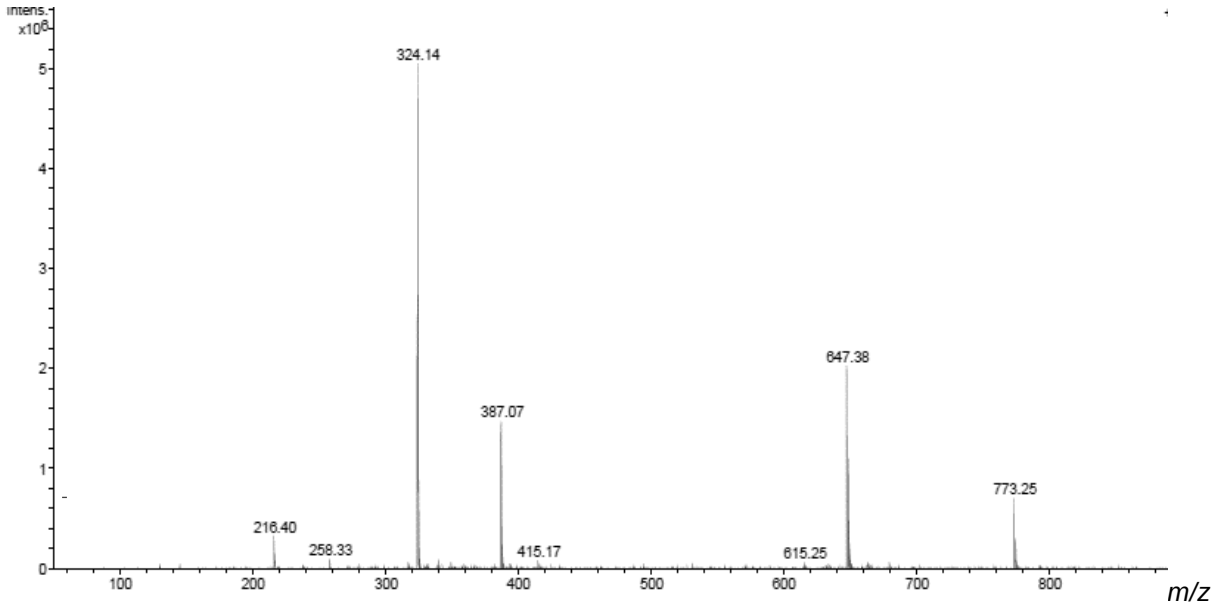


Figure S26. ESI-TOF positive mode mass spectrum of porphyrin **2H-C-PF$_6$**

Porphyrin Zn-C-PF$_6$

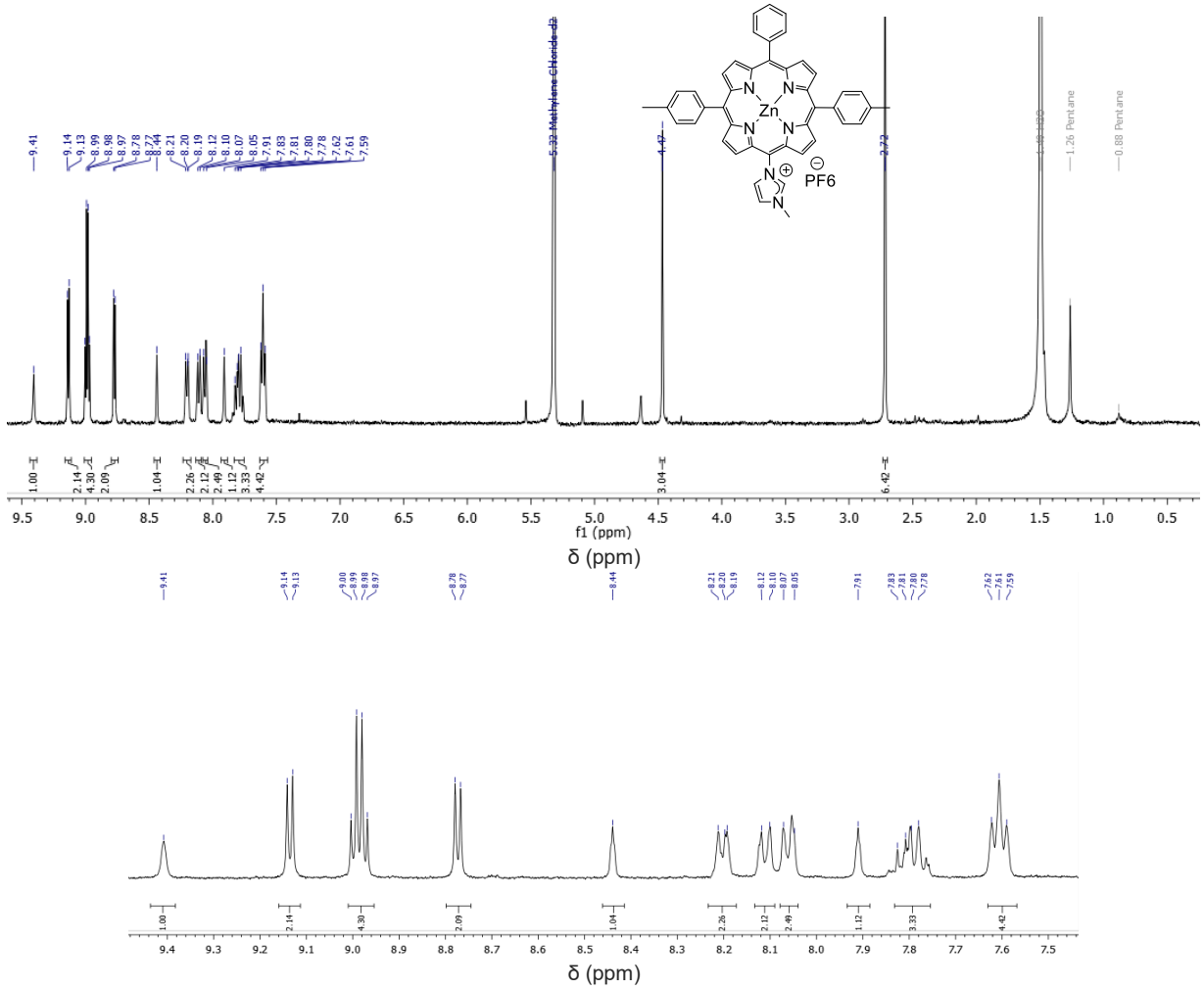


Figure S27. Full range (top) and partial (bottom)^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **Zn-C-PF$_6$**

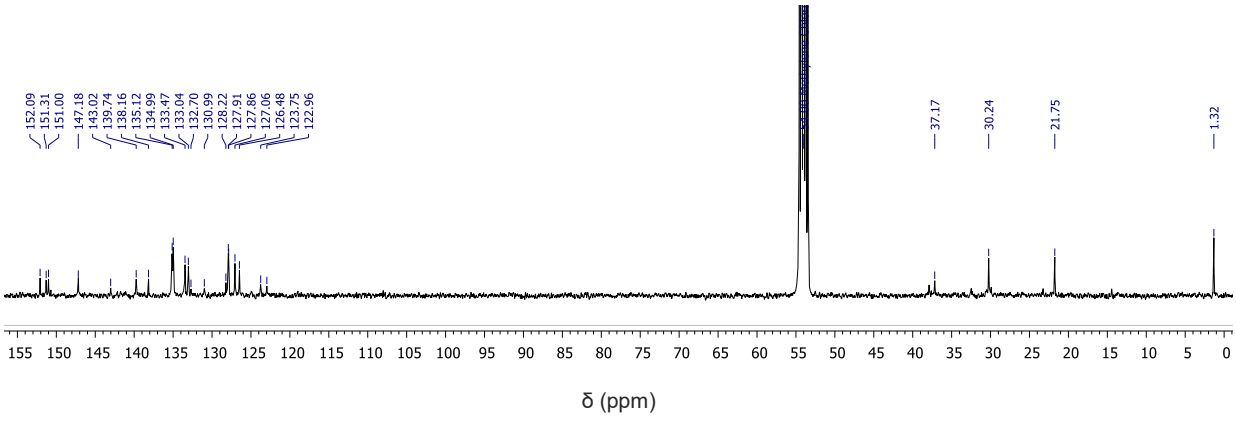


Figure S28. $^{13}C\{^1H\}$ NMR spectrum (125.7 MHz, CD_2Cl_2) of **Zn-C-PF$_6$**

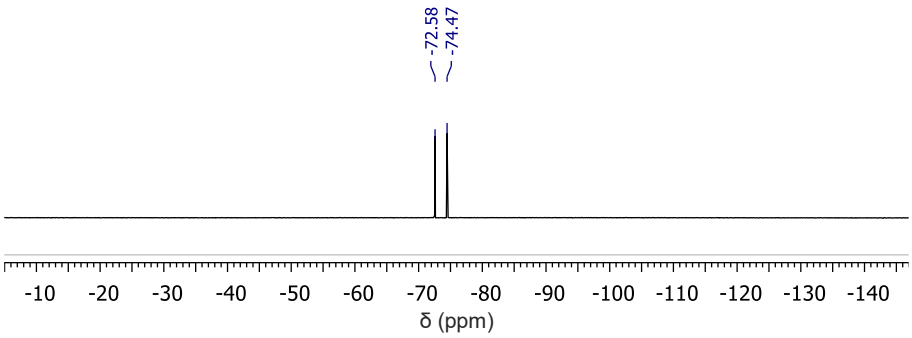


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum (376.5 MHz, CD_2Cl_2) of **Zn-C-PF$_6$**

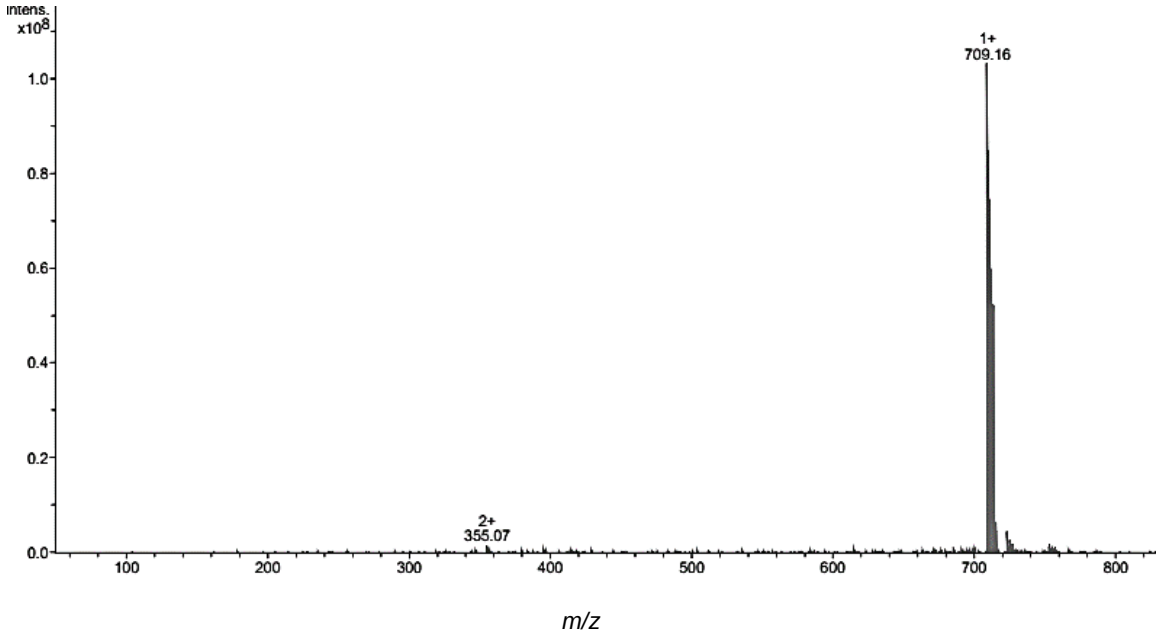


Figure S30. ESI-TOF (positive mode) mass spectrum of **Zn-C-PF$_6$**

Porphyrin Ni-C-PF$_6$

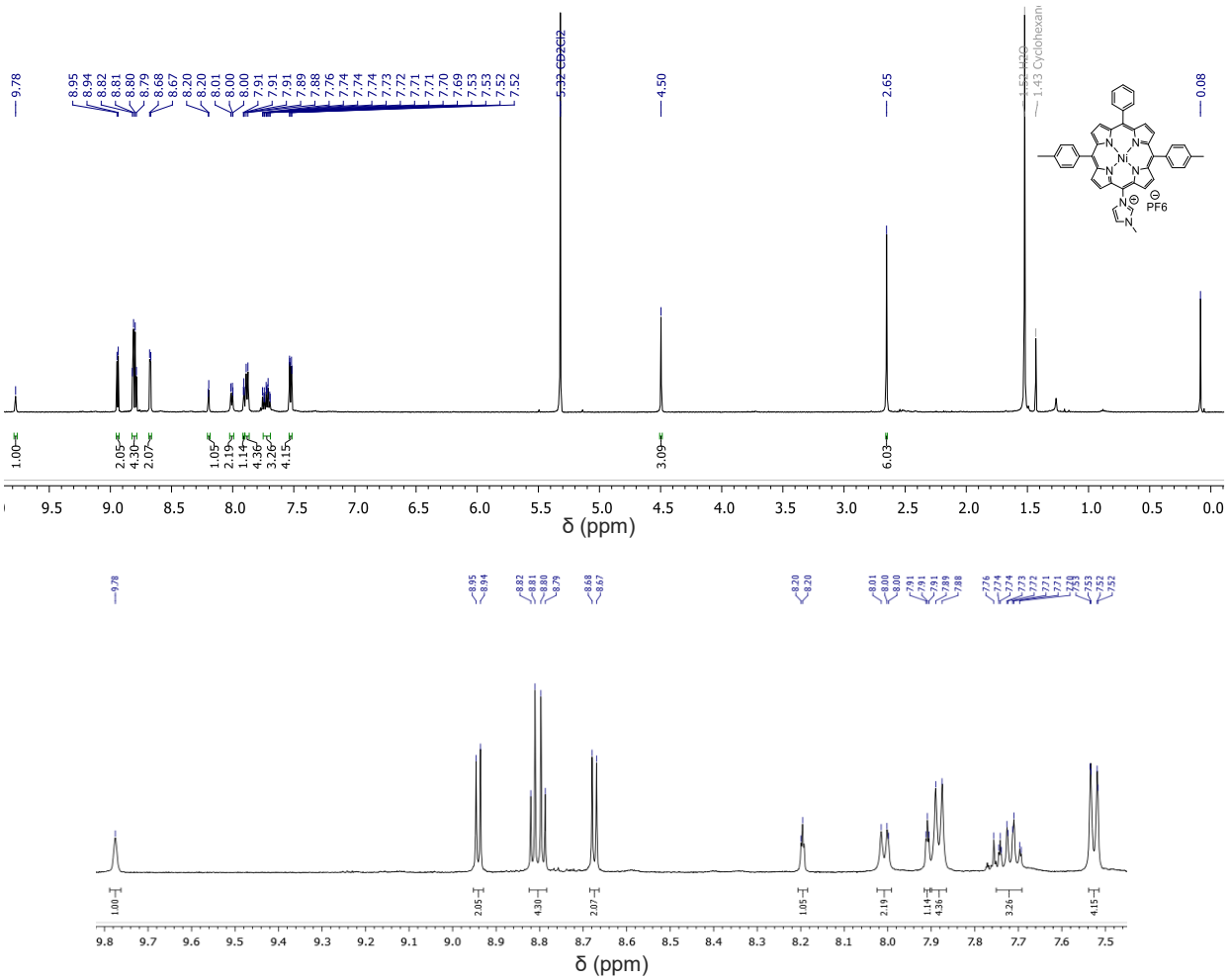


Figure S31. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **Ni-C-PF$_6$**

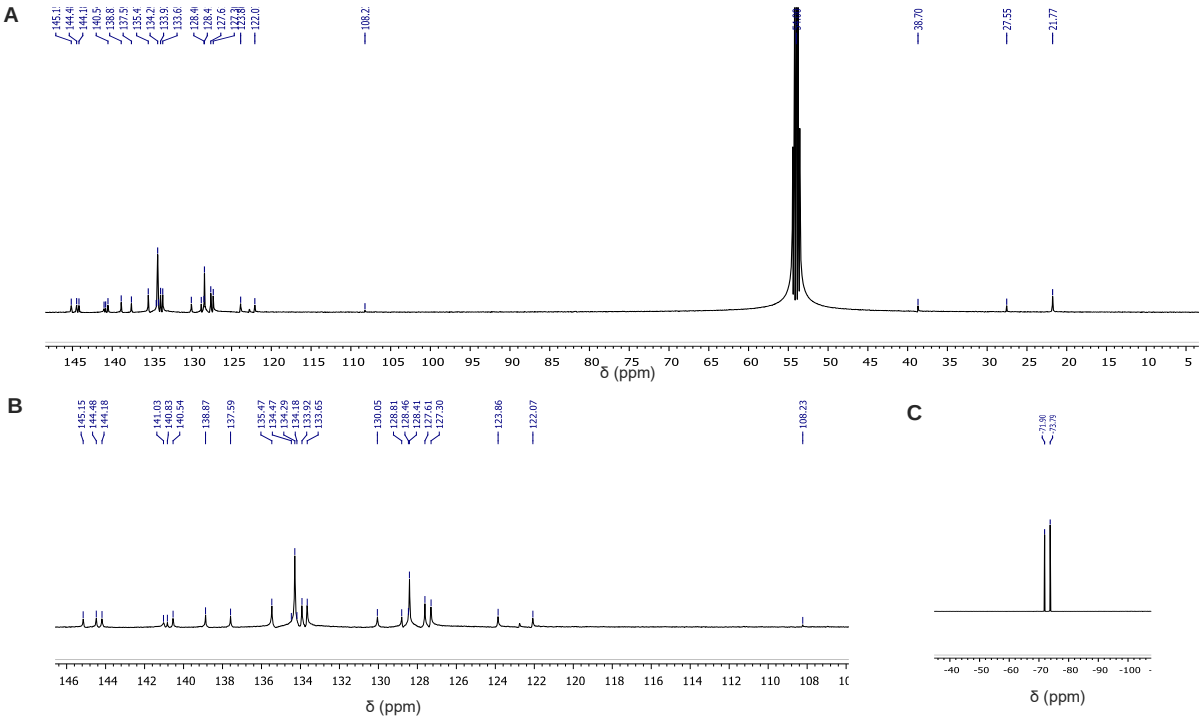


Figure S32. A) Full range B) Partial ^{13}C{^{1}H} NMR spectrum (125.7 MHz, CD_2Cl_2) of **Ni-C-PF$_6$**. C) ^{19}F {^{1}H} (376.5 MHz, CD_2Cl_2) of **Ni-C-PF$_6$**

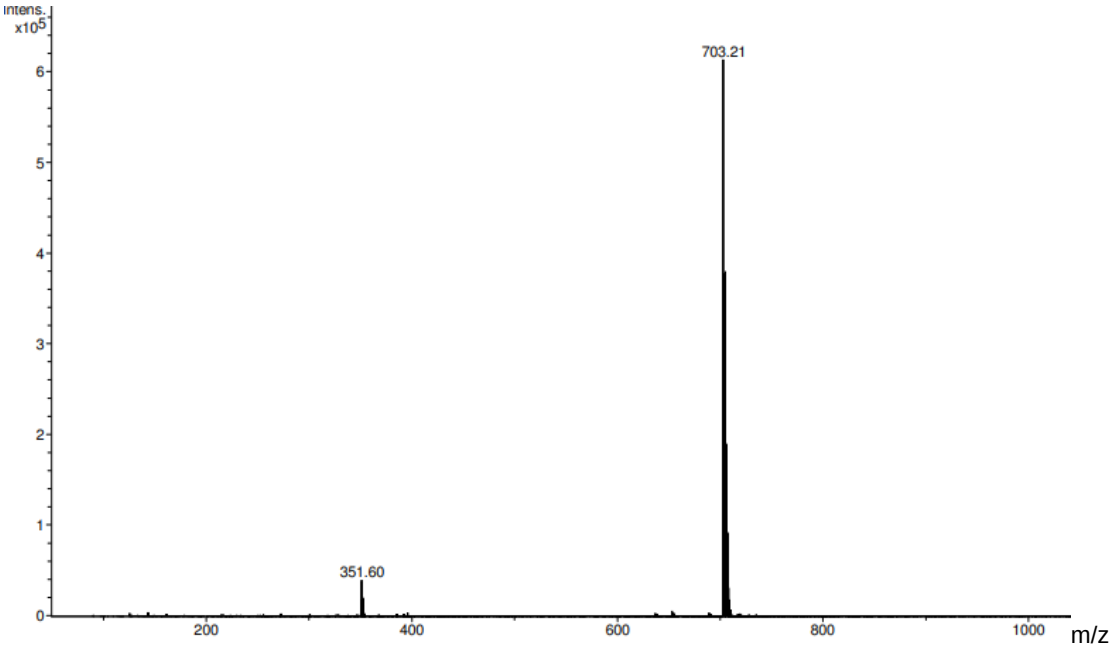


Figure S33. ESI-TOF (positive mode) mass spectra of **Ni-C-PF_6**

Porphyrin 2H-C-Rh(cod)Cl

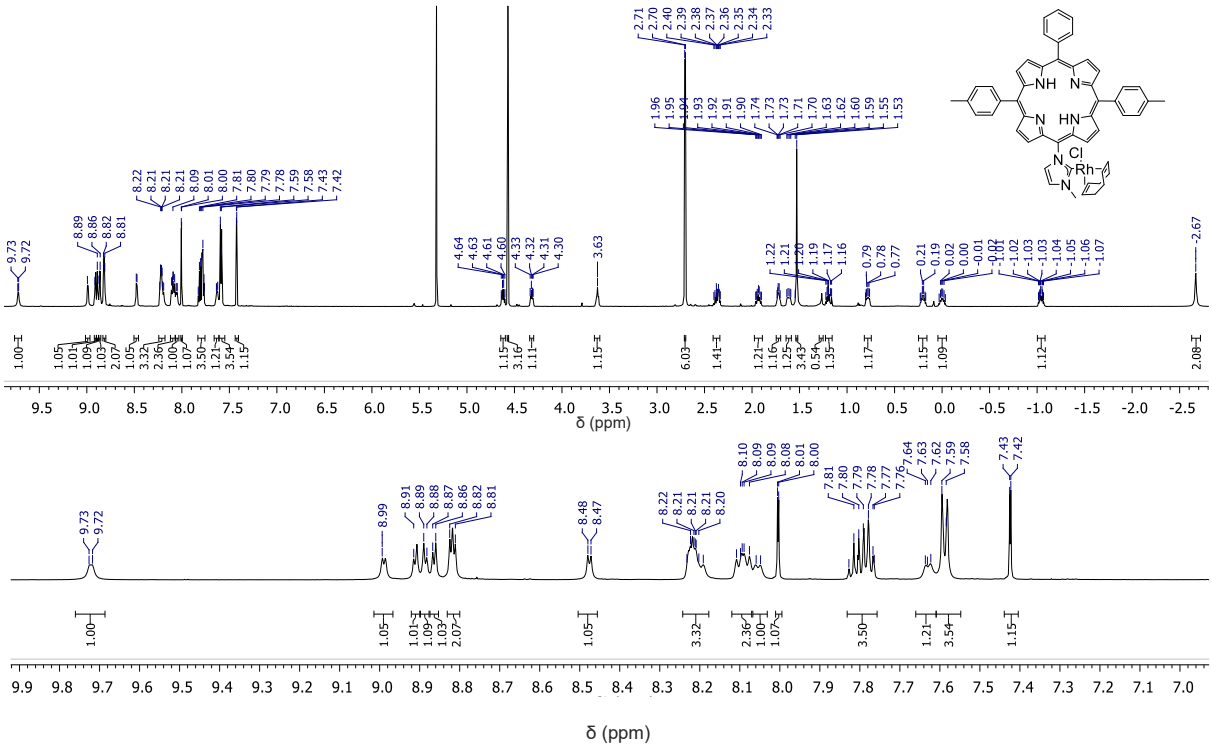


Figure S34: Full range (top) and partial (bottom) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of **2H-C-Rh(cod)Cl**

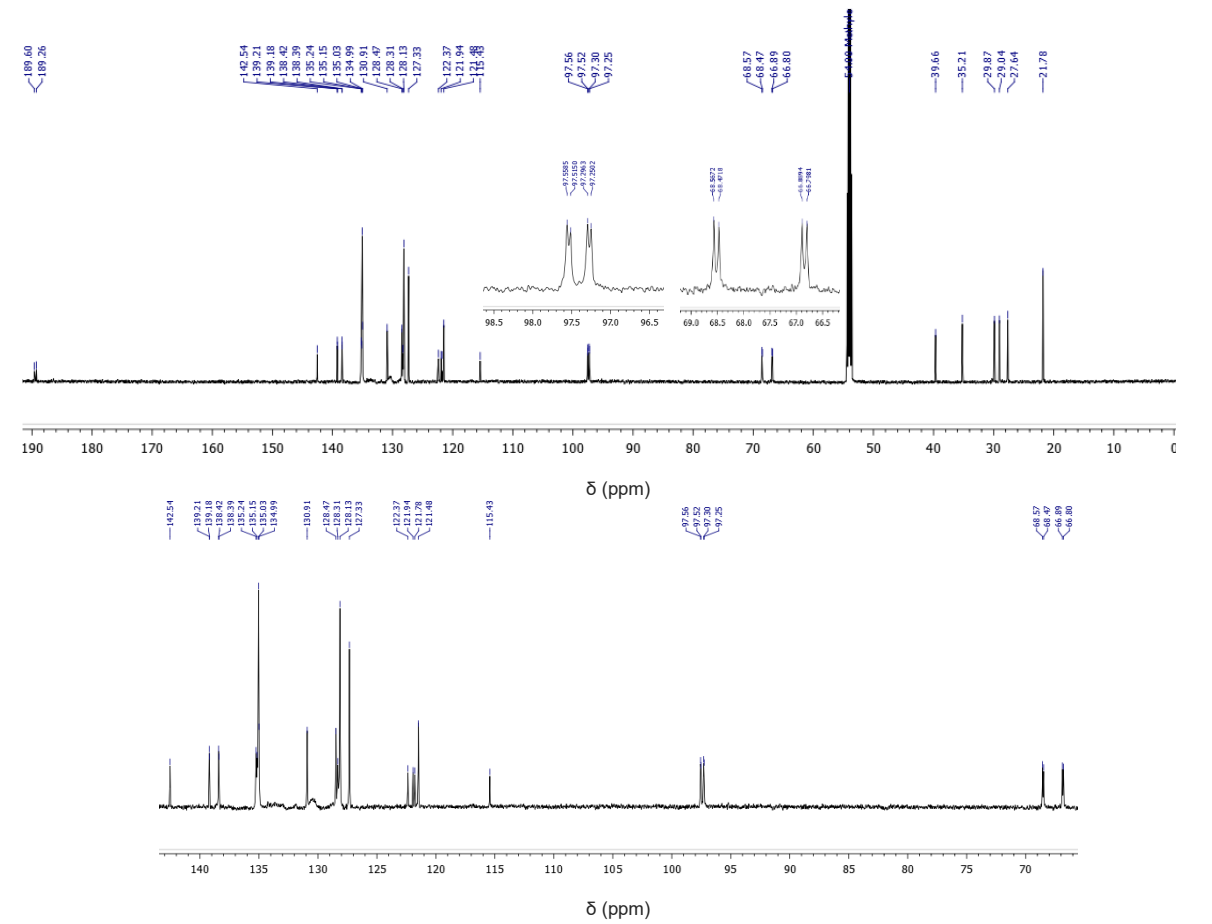


Figure S35. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **2H-C-Rh(cod)Cl**

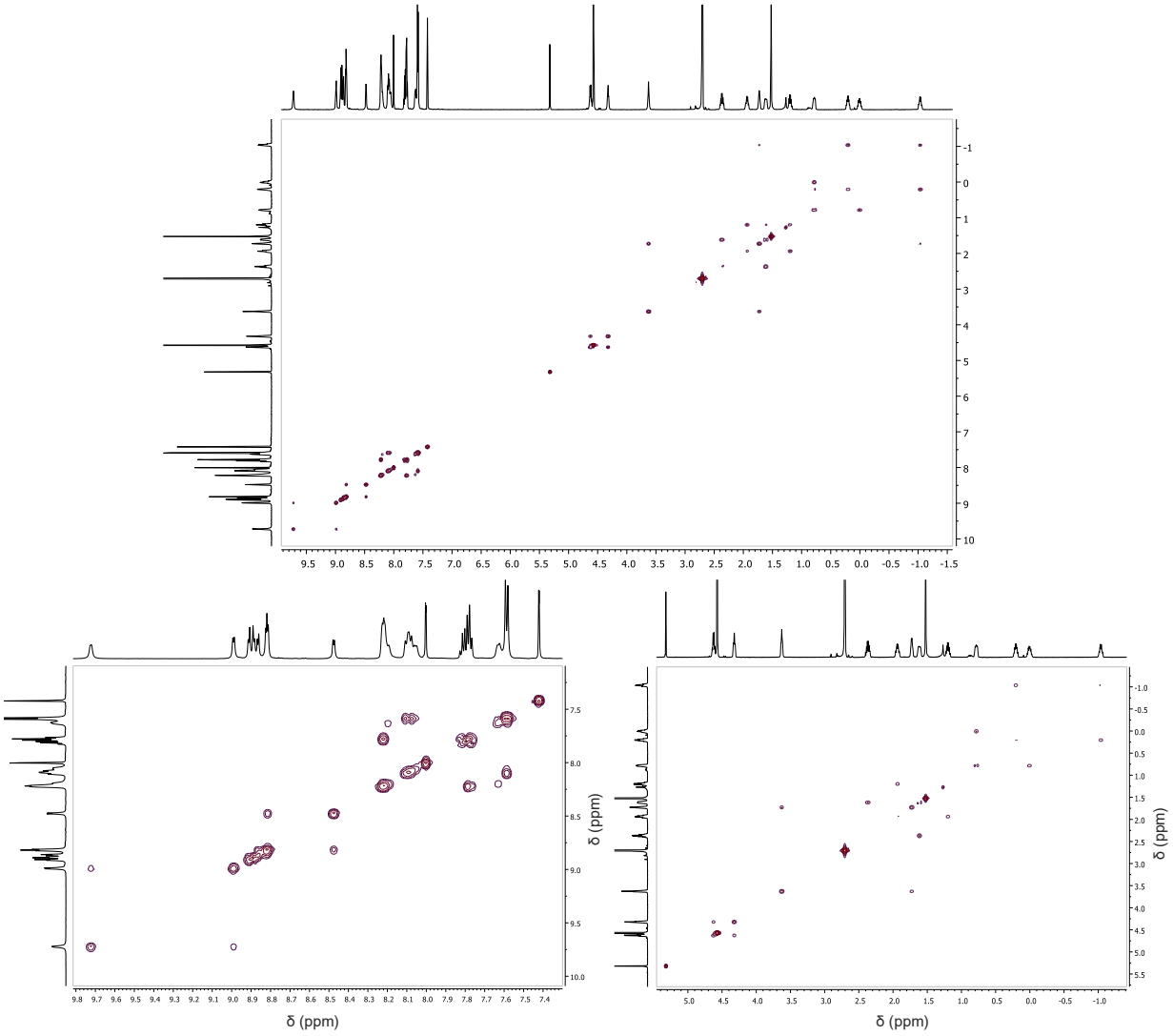


Figure S36. Full range (top) and partial (bottom) ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_2Cl_2) of **2H-C-Rh(cod)Cl**

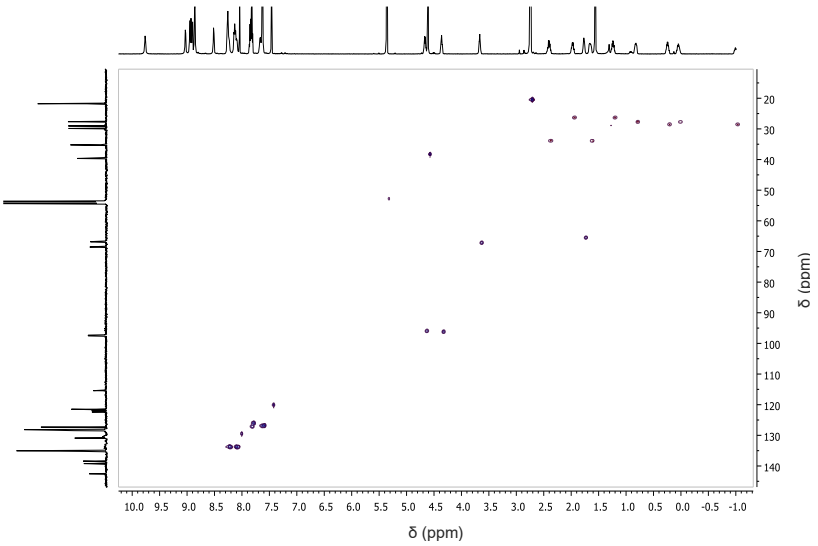


Figure S37. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR spectrum (600 MHz, CD_2Cl_2) of **2H-C-Rh(cod)Cl**

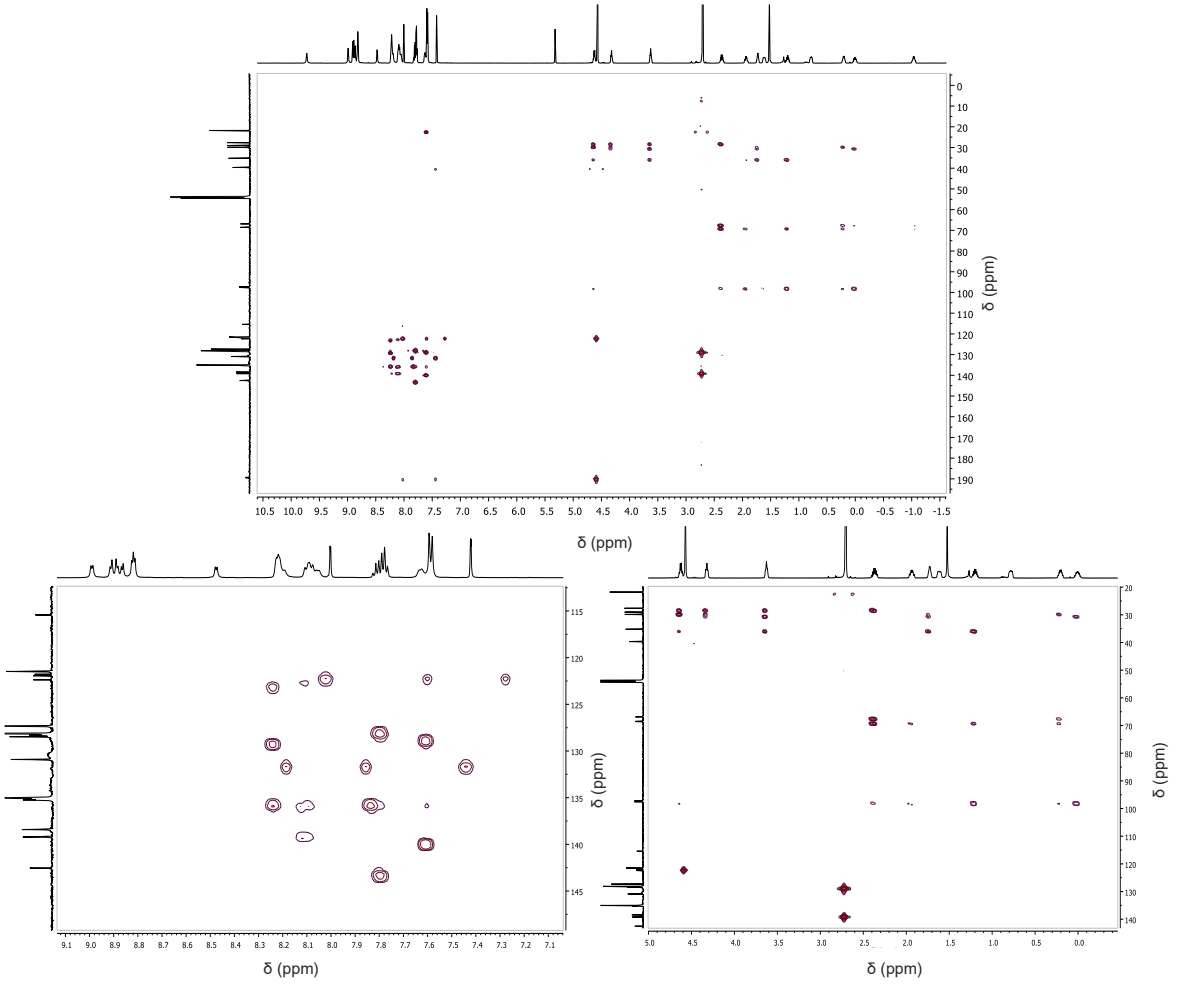


Figure S38. Full range (top) and partial (bottom) ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR spectrum (600 MHz, CD_2Cl_2) of **2H-C-Rh(cod)Cl**

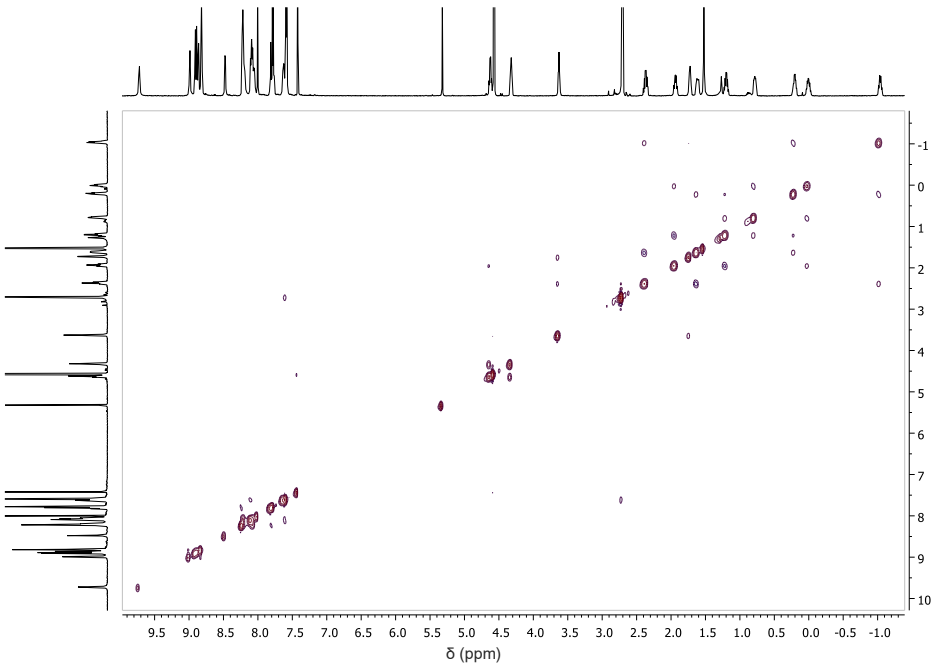


Figure S39. ^{1}H-^{1}H ROESY NMR spectra (600 MHz, CD_2Cl_2)

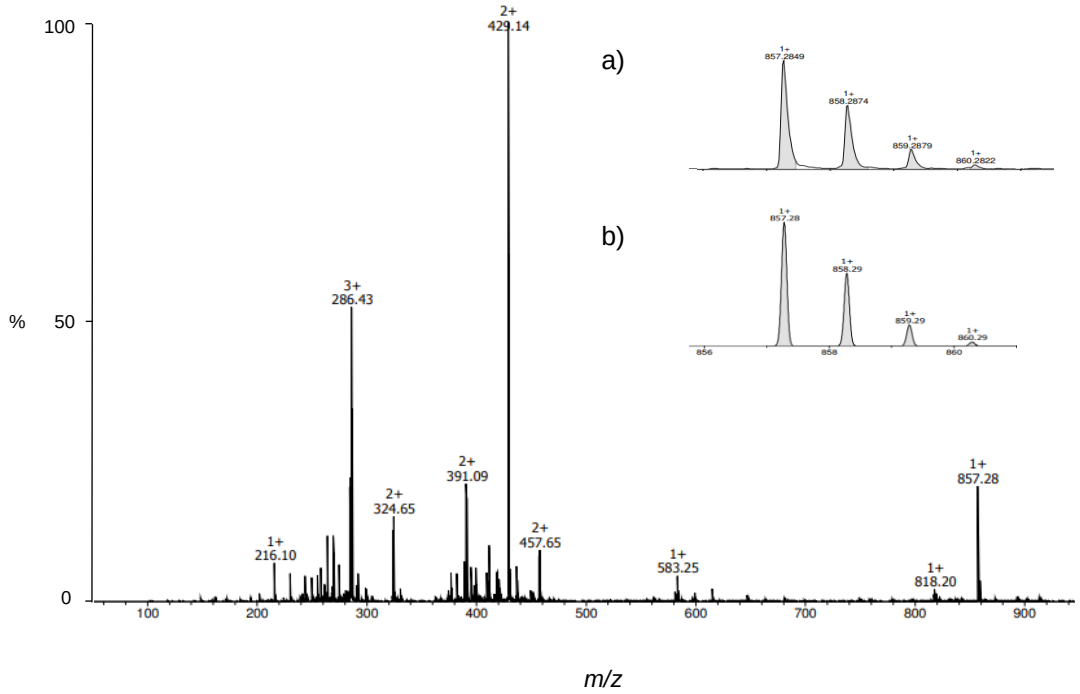


Figure S40. ESI-TOF (positive mode) mass spectrum of **2H-C-Rh(cod)Cl** (left). Experimental (a) and theoretical (b) isotopic patterns (right)

Porphyrin Zn-C-Rh(cod)Cl

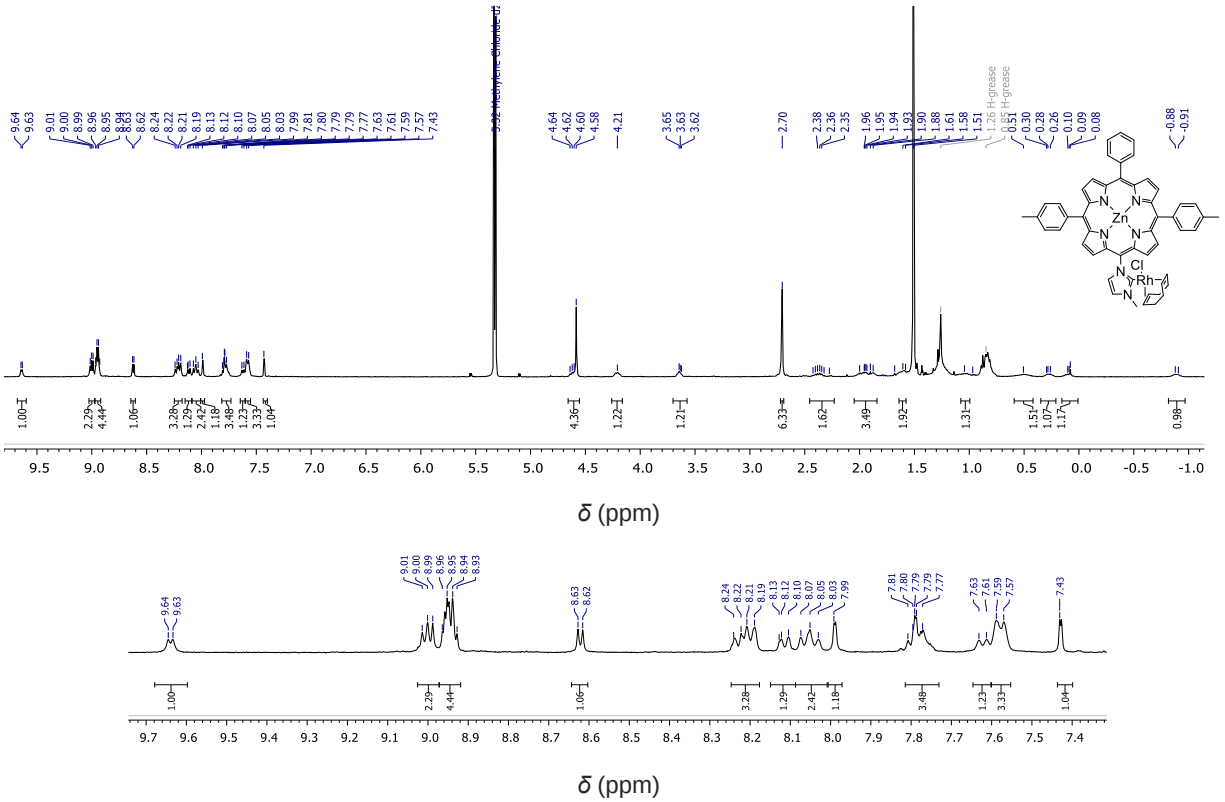


Figure S41. Full range (top) and partial (bottom) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of **Zn-C-Rh(cod)Cl**

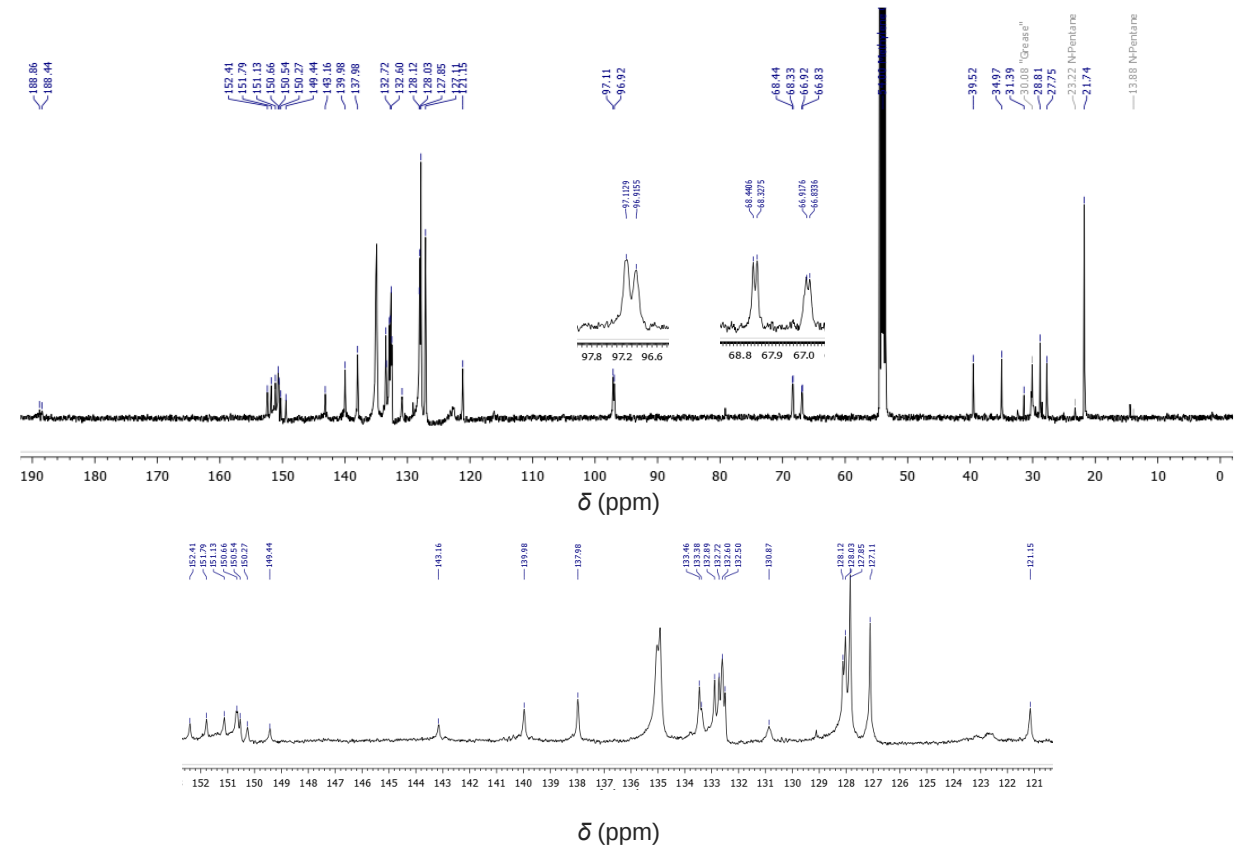


Figure S42. Full range (top) and partial $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **Zn-C-Rh(cod)Cl**

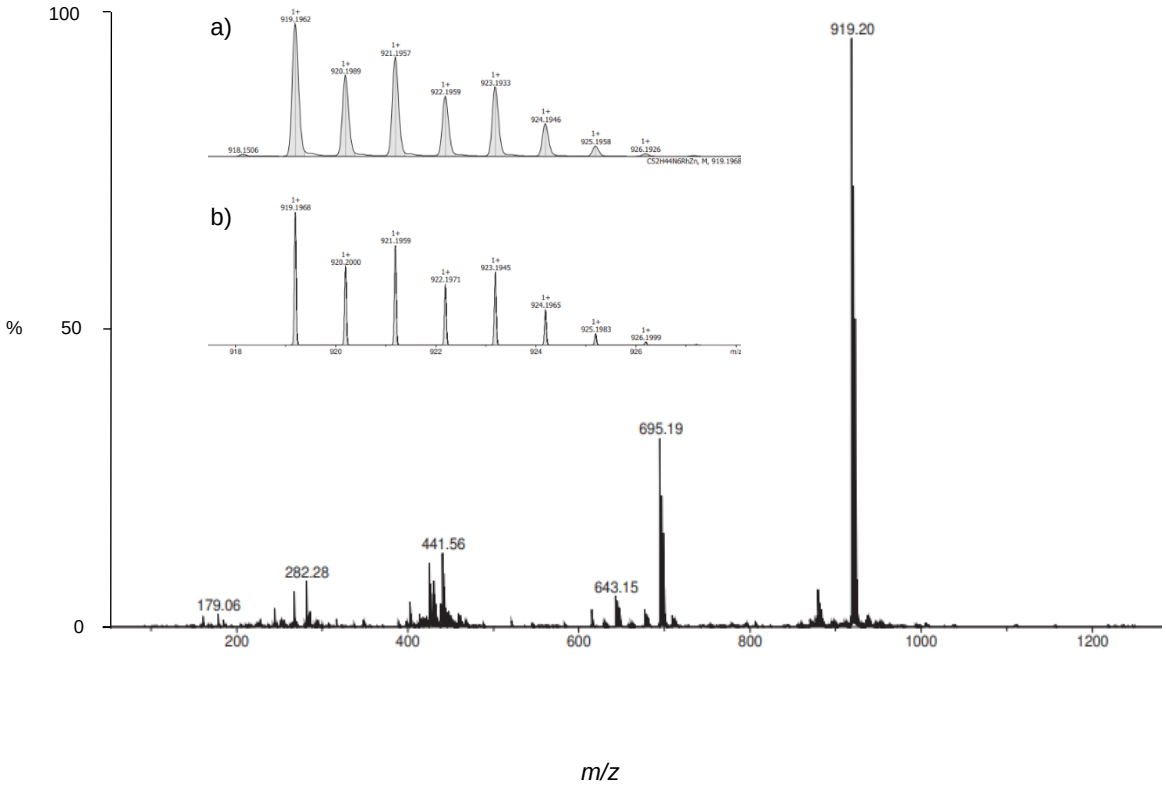


Figure S43. ESI-TOF (positive mode) mass spectrum of porphyrin **Zn-C-Rh(cod)Cl** (right)**.** Experimental (a) and theoretical (b) isotopic patterns (left)

Porphyrin Ni-C-Rh(cod)Cl

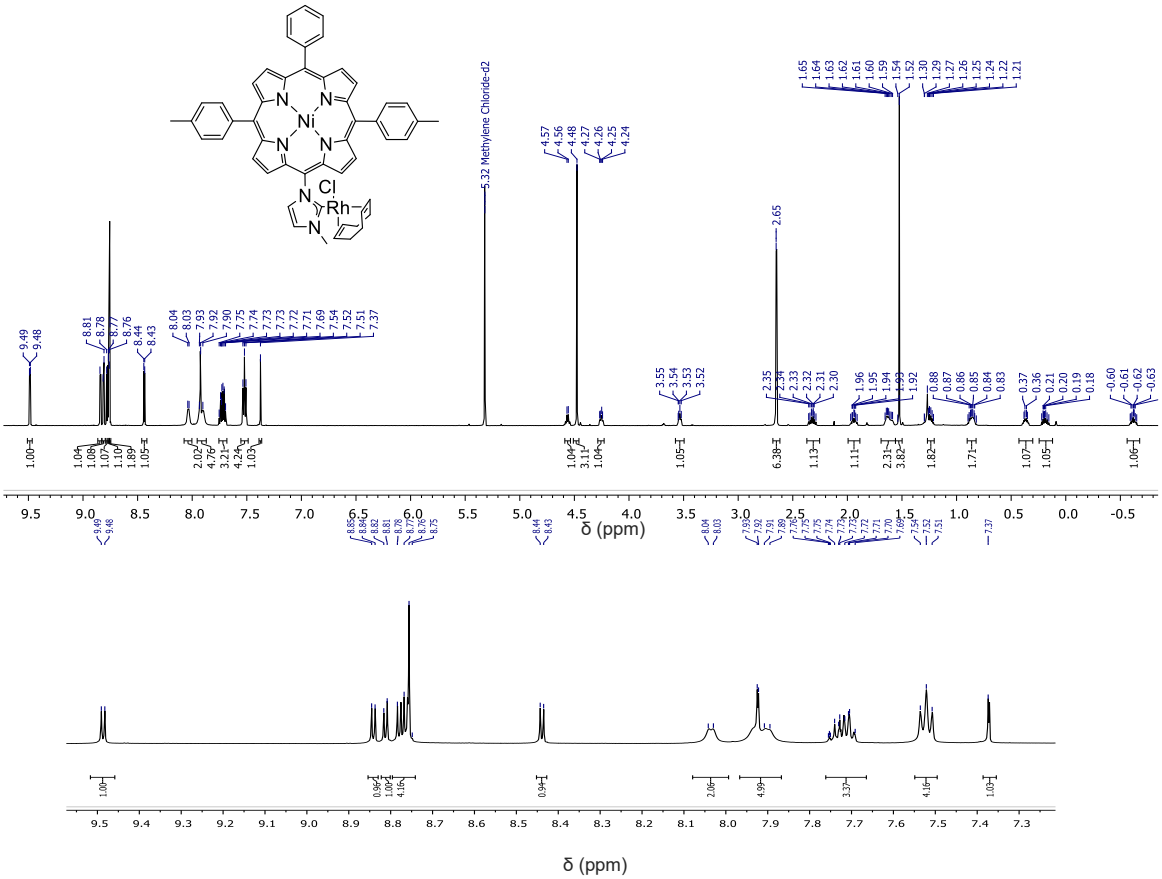


Figure S44. Full range (top) and partial (bottom) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of **Ni-C-Rh(cod)Cl**

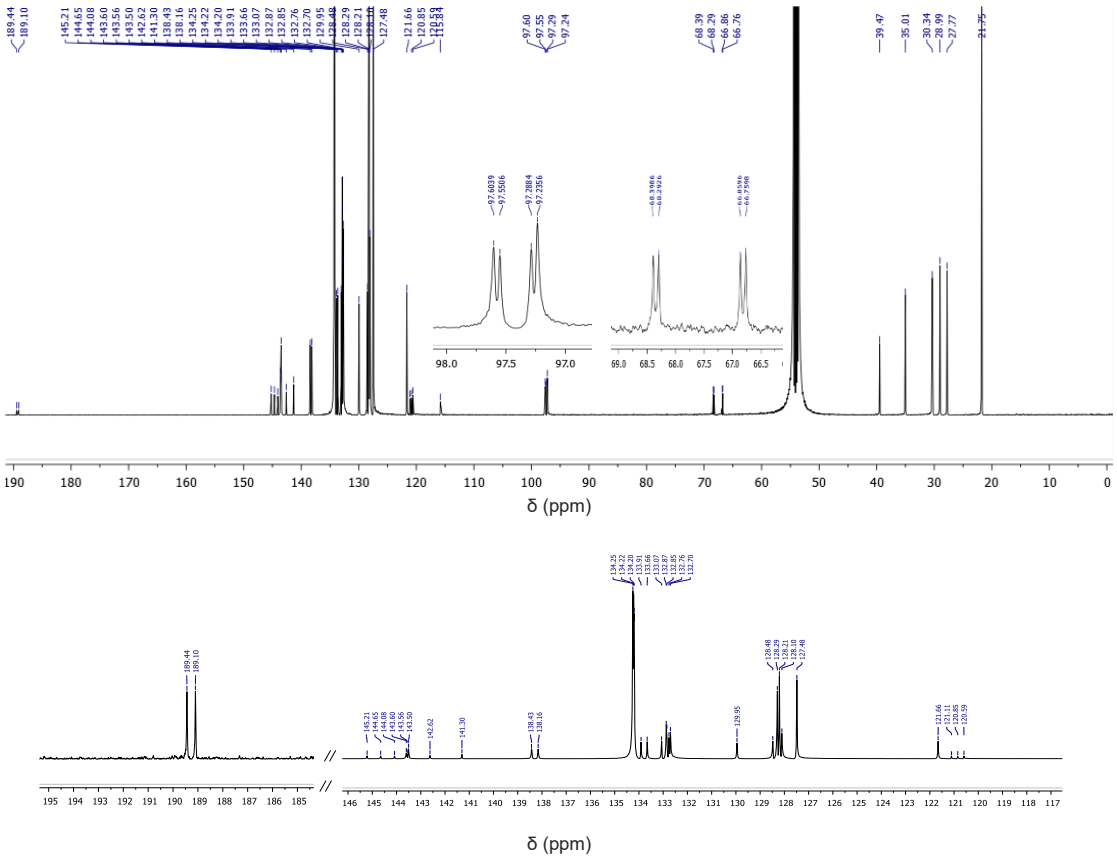


Figure S45. Full range (top) and partial (bottom) $^{13}C\{^{1}H\}$ NMR spectrum (150.9 MHz, CD_2Cl_2) of **Ni-C-Rh(cod)Cl**

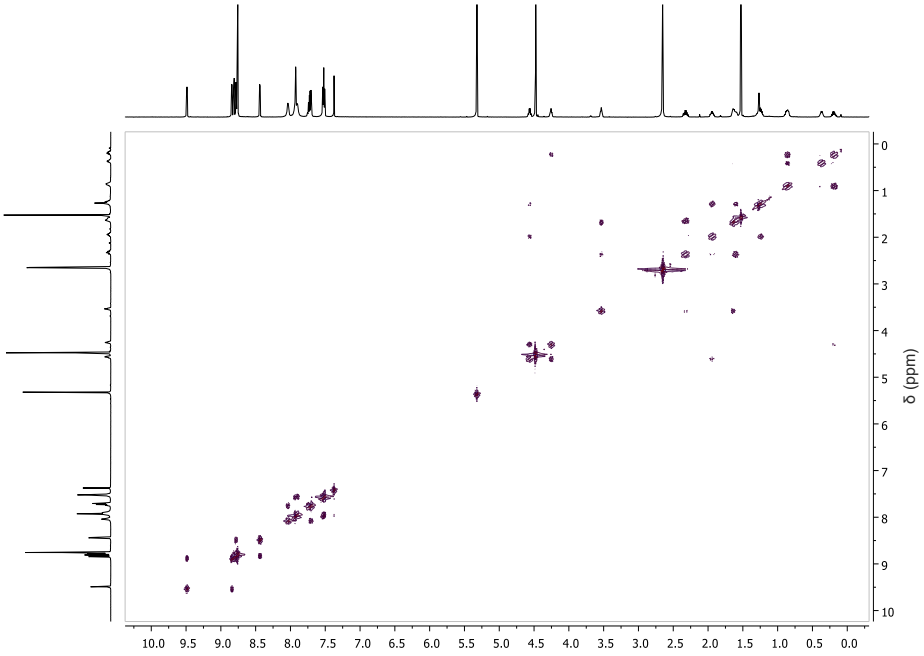


Figure S46. Full range ^{1}H-^{1}H COSY NMR spectra (600 MHz, CD_2Cl_2) of porphyrin Ni-C-Rh(cod)Cl

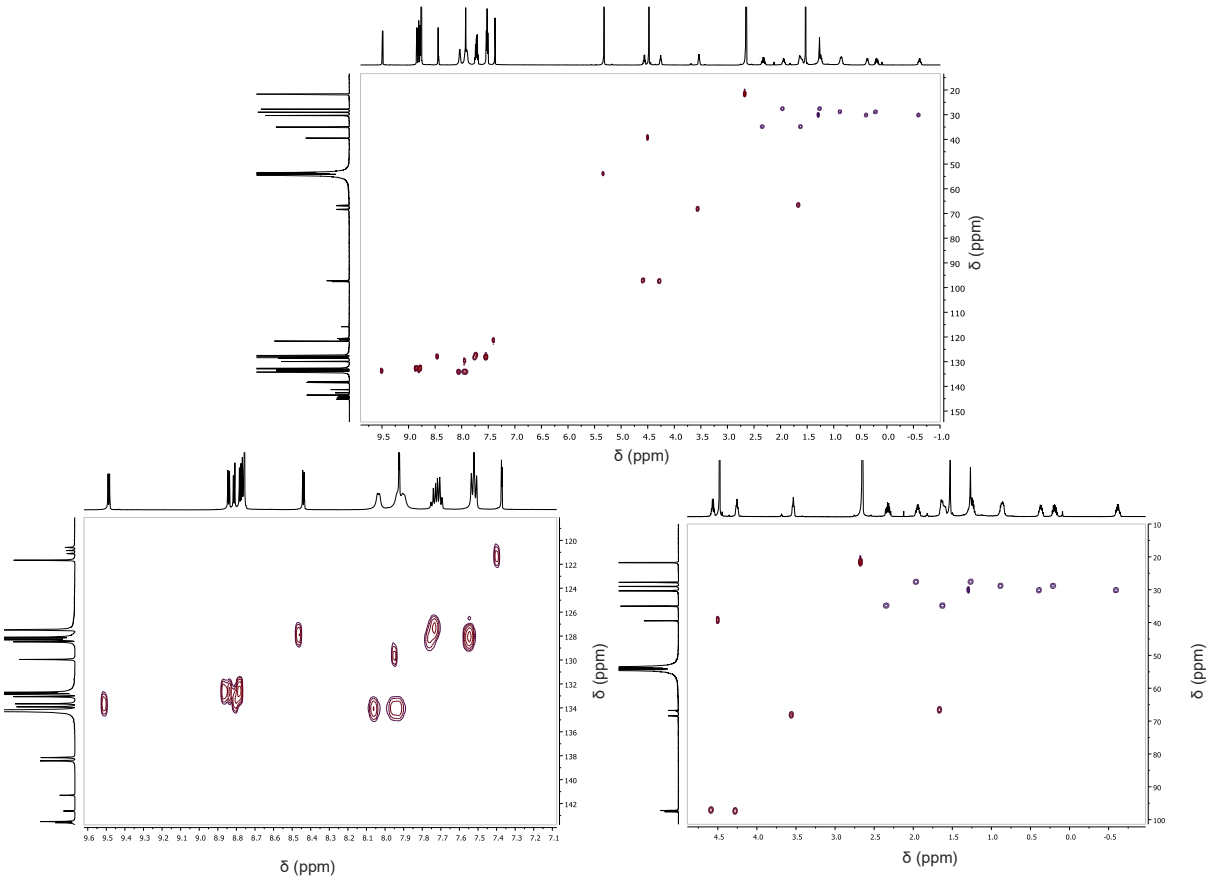


Figure S47. Full range (top) and partial (bottom) ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR spectrum (600 MHz, CD_2Cl_2) of **Ni-C-Rh(cod)Cl**

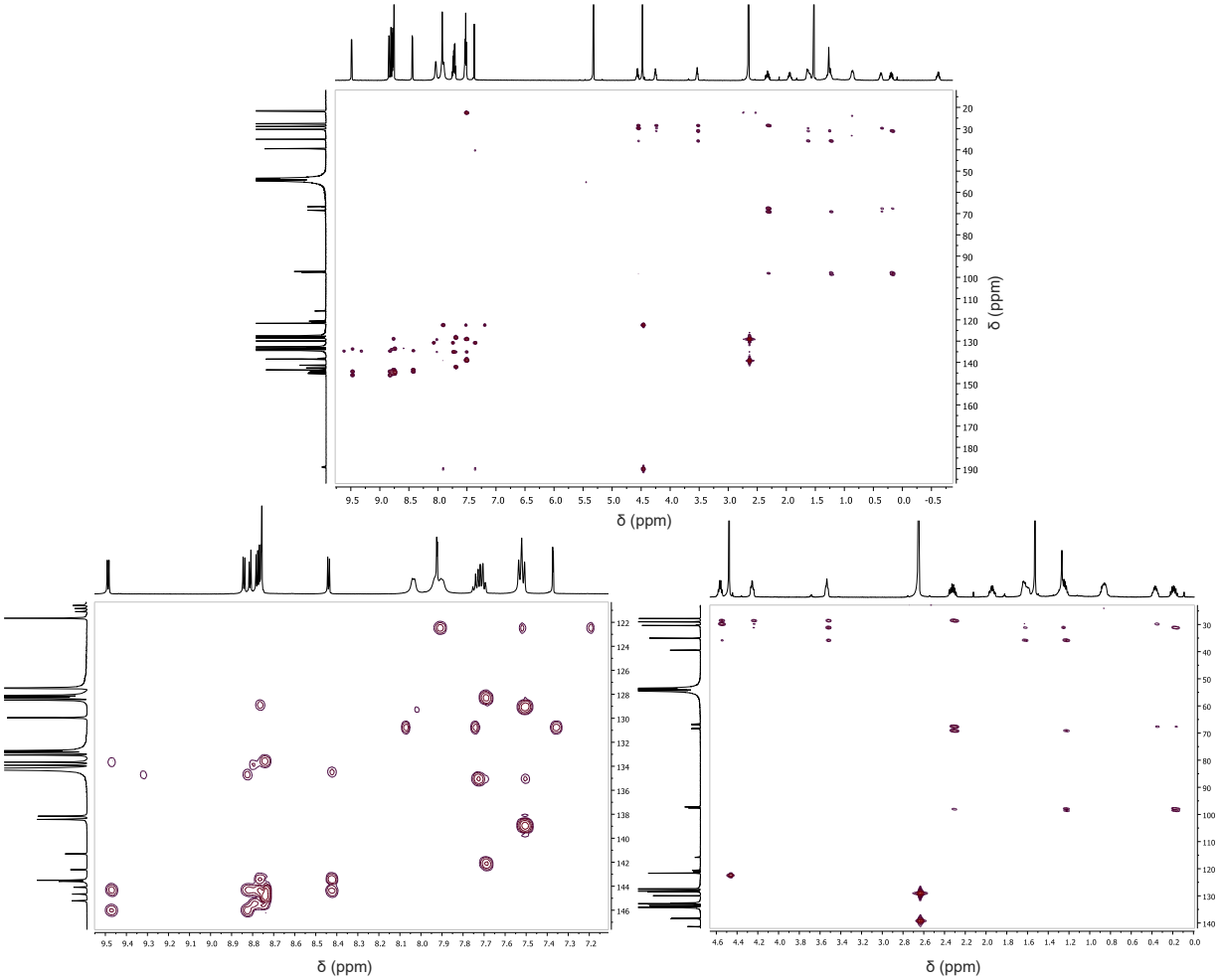


Figure S48. Full range (top) and partial (bottom) ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR spectrum (600 MHz, CD_2Cl_2) of **Ni-C-Rh(cod)Cl**

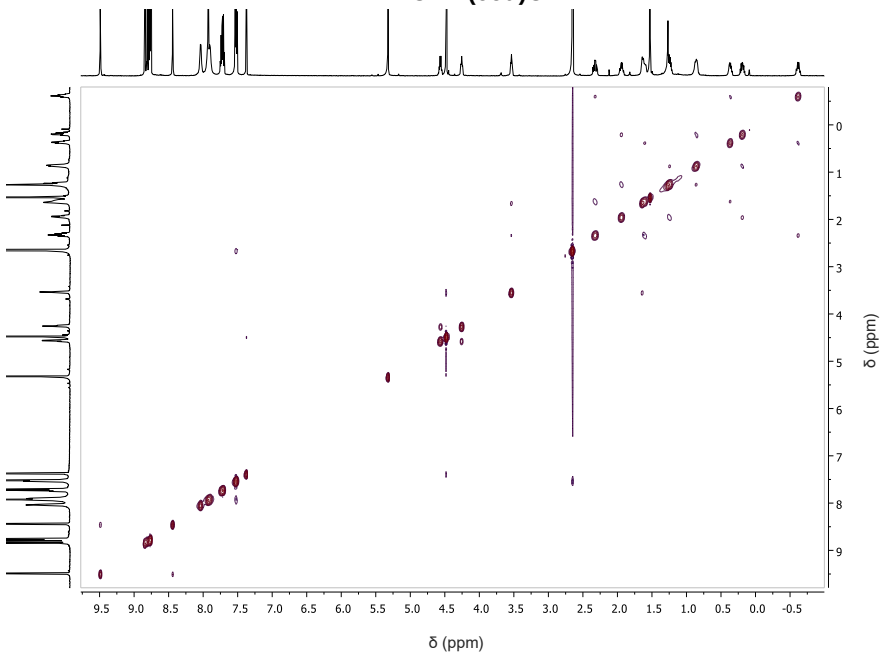


Figure S49. Full range ^{1}H-^{1}H ROESY NMR spectrum (600 MHz, CD_2Cl_2) of **Ni-C-Rh(cod)Cl**

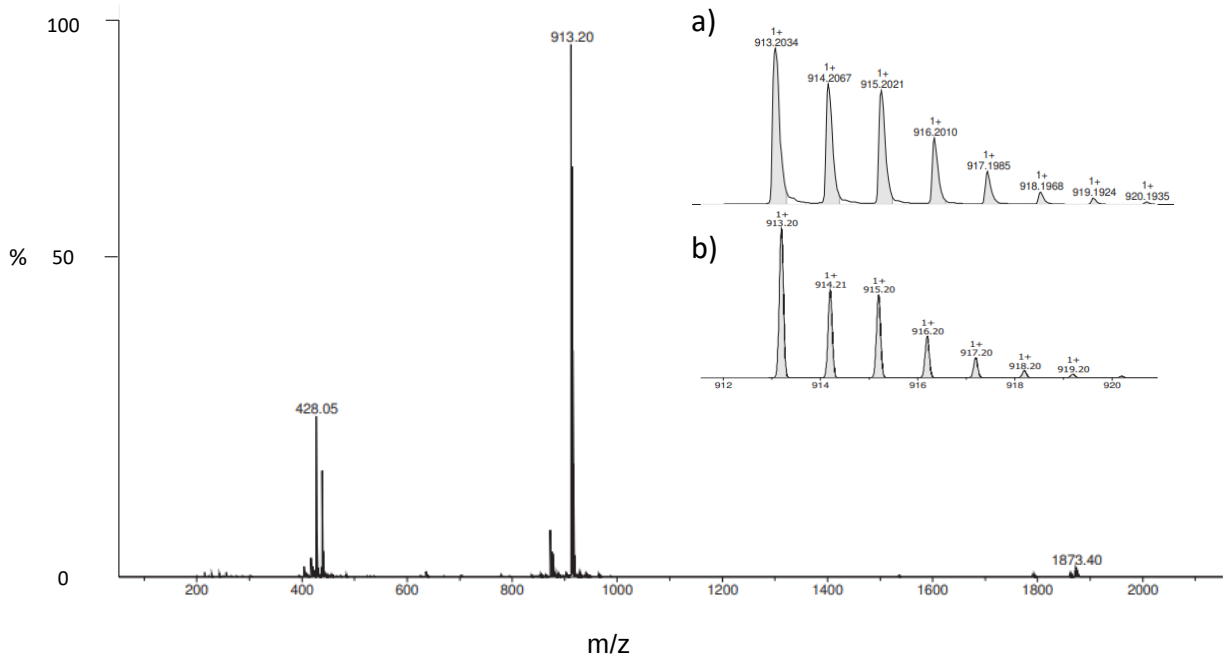


Figure S50. ESI-TOF (positive mode) mass spectrum of **Ni-C-Rh(cod)Cl** (left). Experimental (a) and calculated (b) isotopic patterns (right)

DFT optimized geometries

Gaussian16 has been used to perform quantum mechanical calculations.[9] B3LYP[10,11], including Grimme's dispersion correction for nonbonding interactions was employed using atom pair-wise additive scheme[12], the DFT-D3 method. The Stuttgart/Dresden (SDD) valence basis set and effective core potential have been used for Rh atom[13] in conjunction with the 6-31G** basis set for rest of the atoms. Full geometry optimizations, without any constrains, have been carried out in implict toluene (ε = 2.4), the solvent used for the catalytic experiments, using the PCM continuum solvation model as implemented in Gaussian 16[14].

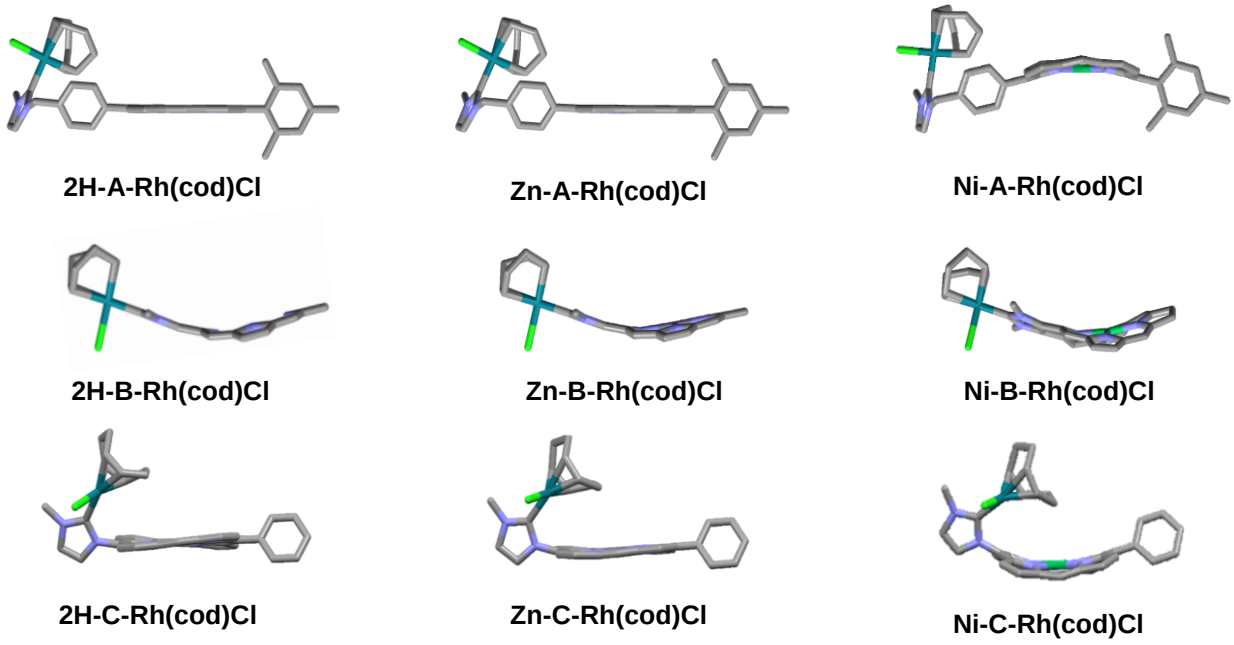


Figure S51. DFT optimized structures of complexes **M^1-A-Rh(cod)Cl**, **M^1-B-Rh(cod)Cl** and **M^1-C-Rh(cod)Cl** with M^1 = 2H, Zn and Ni (meso p-tolyl groups and H omitted for clarity).

Topographic steric maps

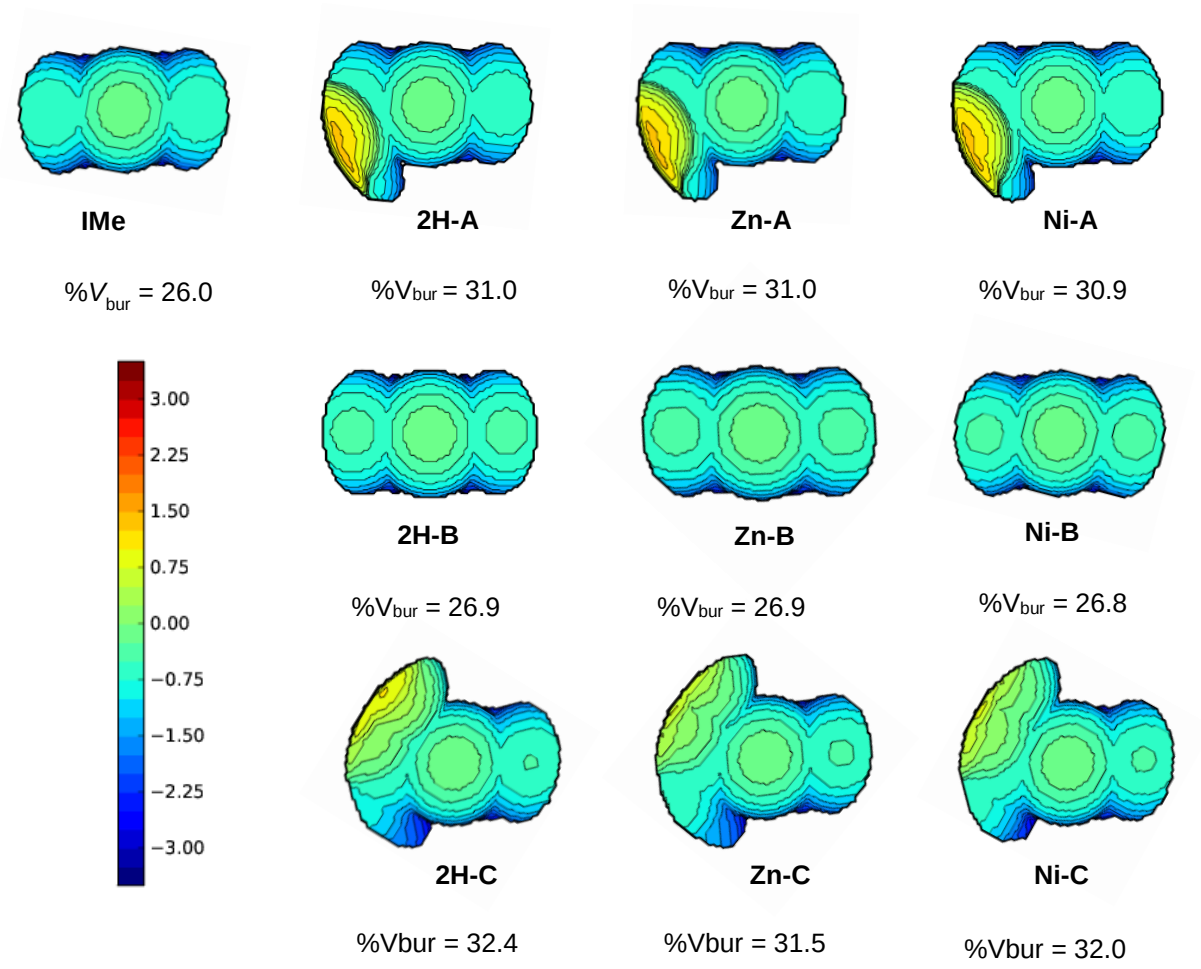
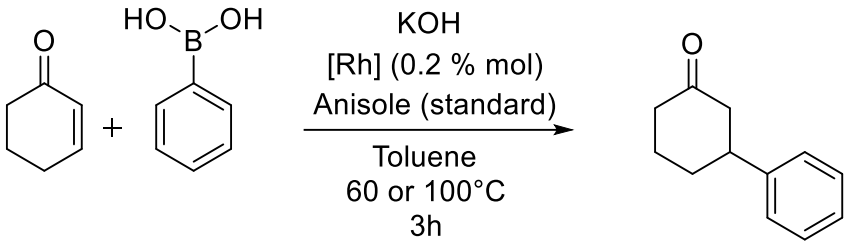


Figure S52. Steric maps of the complexes **M[1]-A-Rh(cod)Cl**, **M[1]-B-Rh(cod)Cl** and **M[1]-C-Rh(cod)Cl** with M[1] = 2H, Zn and Ni in optimized geometries of the corresponding complexes calculated with the SambVca 2.1 tool with the following standard inputs: Bondi radii 1.17 Å, Rh─C_{NHC} 2.00 Å, r_{sphere} = 3.50 Å, mesh spacing 0.10 Å, H atoms excluded.[15]

Catalytic studies

General procedure for catalytic studies



Cyclohex-2-en-1-one (48.0 mg, 0.499 mmol, 1eq) and anisole (54.0 mg, 0.499 mmol, 1eq) used as internal standard were dissolved in anhydrous toluene (2 mL) in a degassed 10 mL vial. Phenylboronic acid (121.7 mg, 0.999 mmol, 2 eq) was added under argon and the mixture was stirred until complete dissolution. KOH (5.2 mg, 0.093 mmol, 0.2 eq) and the catalyst (0.2% mol, 0.998 µmol) were added under argon and the mixture was protected from light and stirred at 60 or 100°C for 3 hours. Conversion of cyclohex-2-en-1-one was monitored by gas chromatography (GC) analyses. Conversions of the cyclohex-2-en-1-one and yields of 3-phenylcyclohexan-1-one after 3 hours were determined by gas GC analyses and by ^{1}H NMR spectroscopy. All reactions were performed minimum in triplicate with reproducible results.

Monitoring of the reactions by gas chromatography (GC)

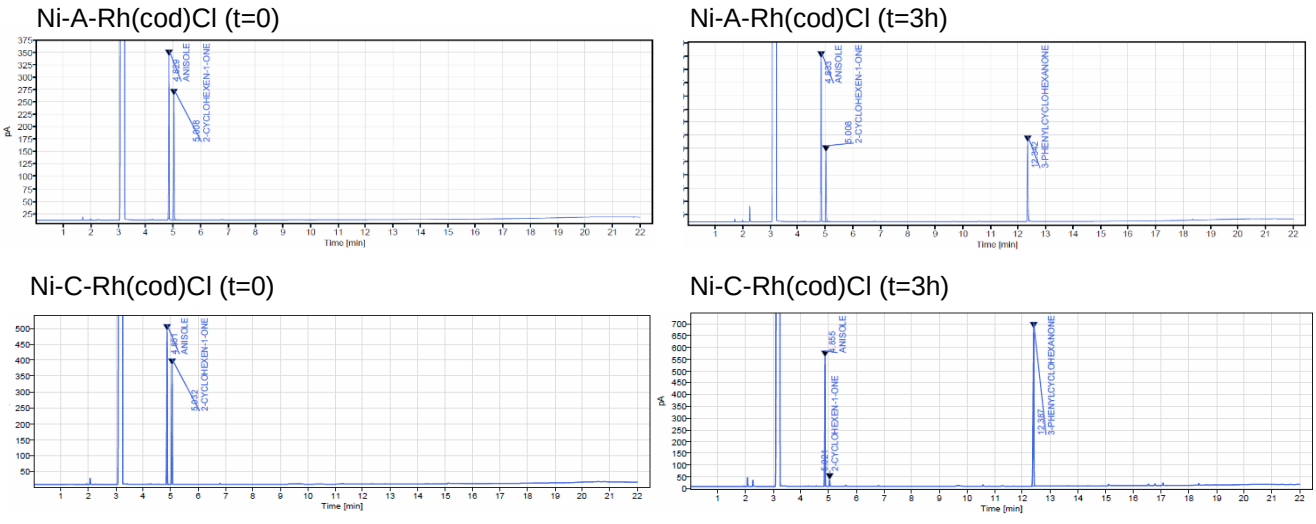


Figure S53. GC chromatograms obtained from reaction mixtures with **Ni-A-Rh(cod)Cl** (top) and **Ni-C-Rh(cod)Cl** (bottom) at 100°C with t=0 (left) and t=3h (right).

Time profile of the reactions

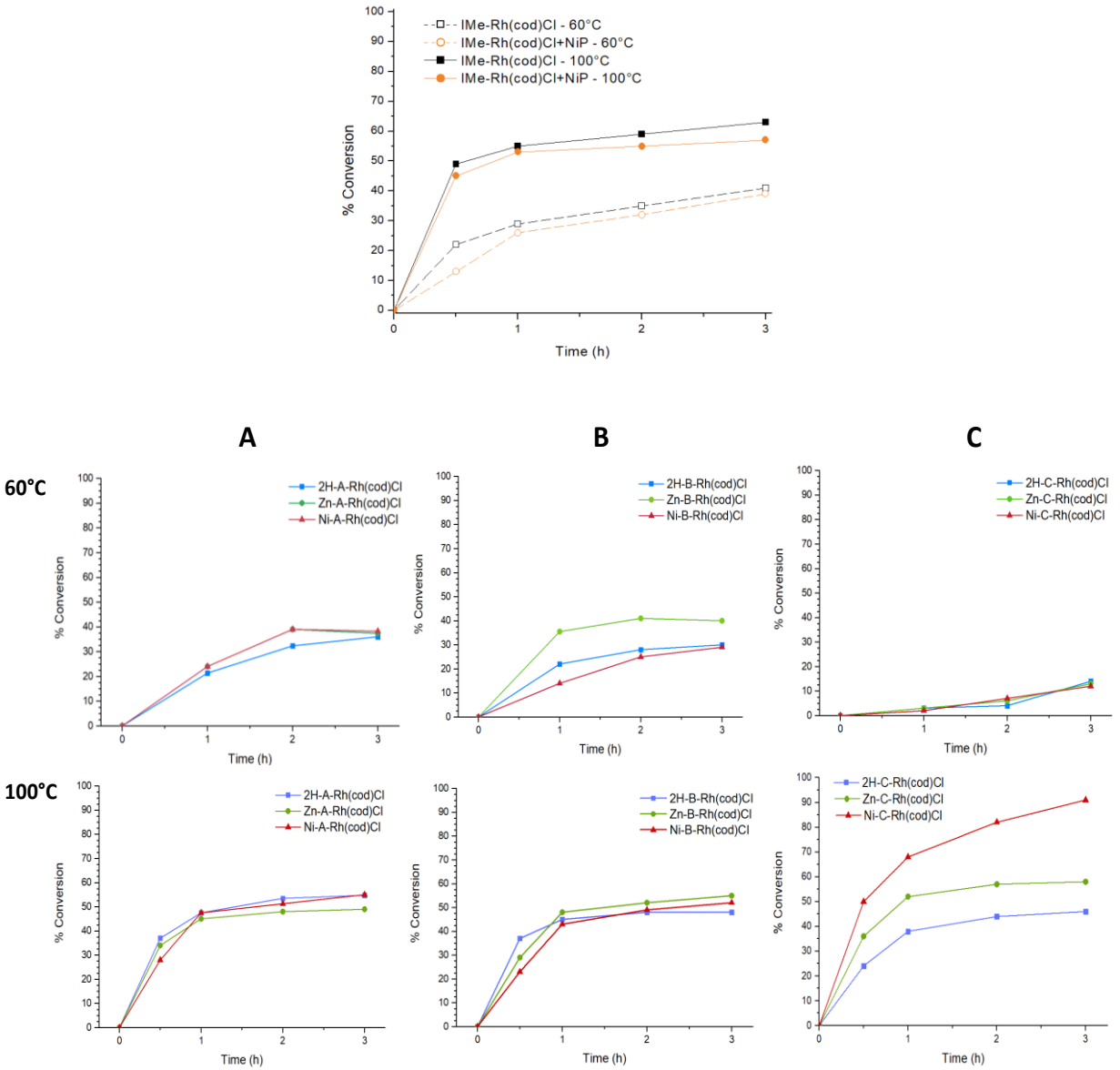
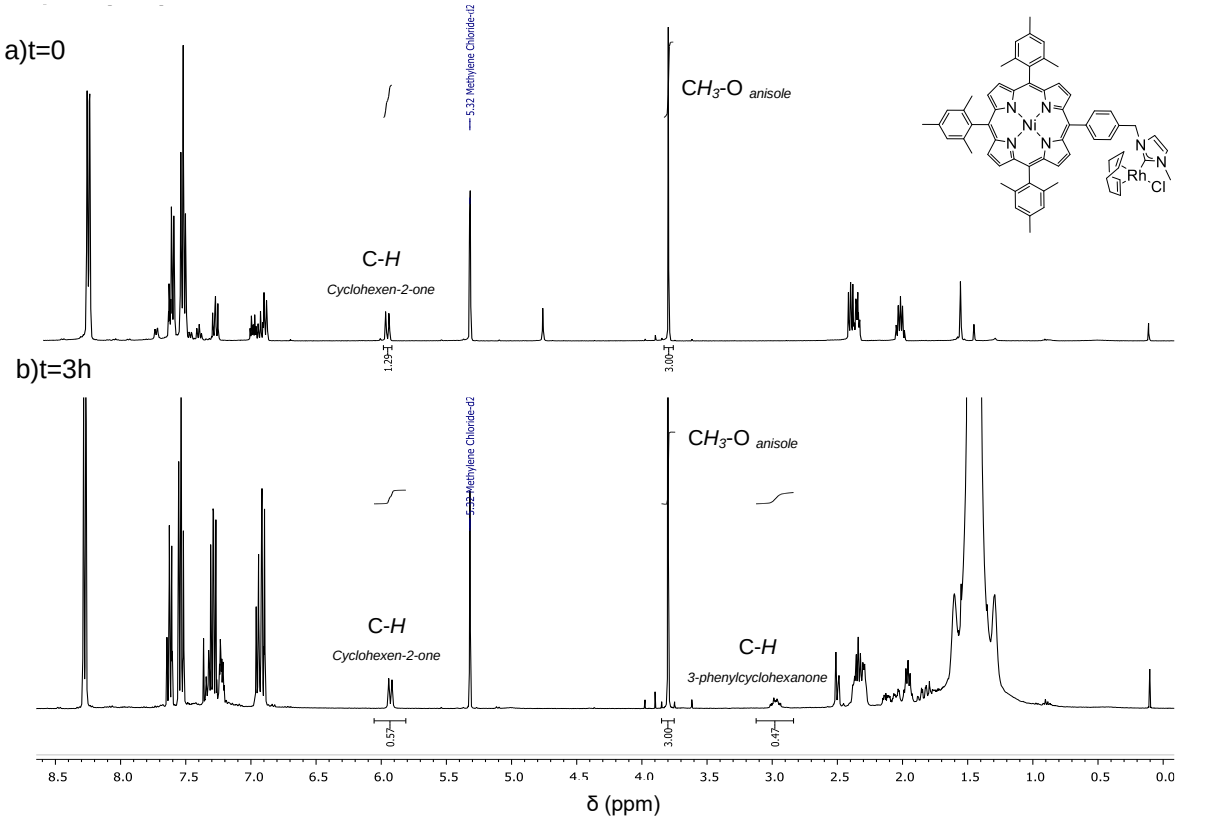


Figure S54: Time profiles of the conjugated addition of phenylboronic acid to cyclohexen-2-one catalysed by **IMe-Rh(cod)Cl** (black), **IMe-Rh(cod)Cl + NiP** (orange) at 60°C and 100°C (top); Time profiles of the same reaction catalysed by **M^1-A-Rh(cod)Cl**, **M^1-B-Rh(cod)Cl** and **M^1-C-Rh(cod)Cl** (M^1 =2H in blue, Zn in green and Ni in red) at 60°C and 100°C.

Monitoring of the reactions by ^{1}H NMR spectroscopy

Ni-A-Rh(cod)Cl



Ni-C-Rh(cod)Cl

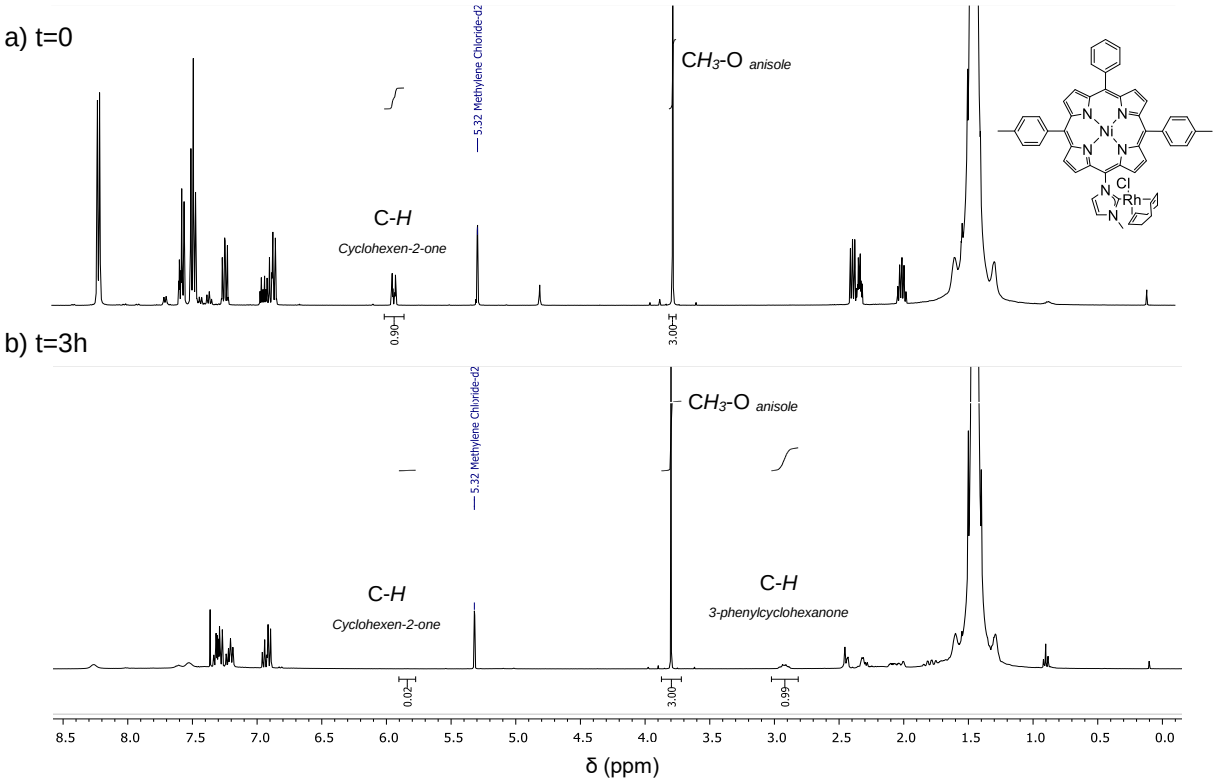


Figure S55. ^{1}H NMR spectra of the reaction mixtures with **Ni-A-Rh(cod)Cl** (top) and **Ni-C-Rh(cod)Cl** (bottom) complexes at t = 0 (up) and t = 3 hours (down). A drop of the reaction mixtures was taken at t = 0 and t = 3h and diluted with CD_2Cl_2 for ^{1}H NMR spectroscopy analysis.

Monitoring of the catalysis reactions by UV-visible absorption spectroscopy

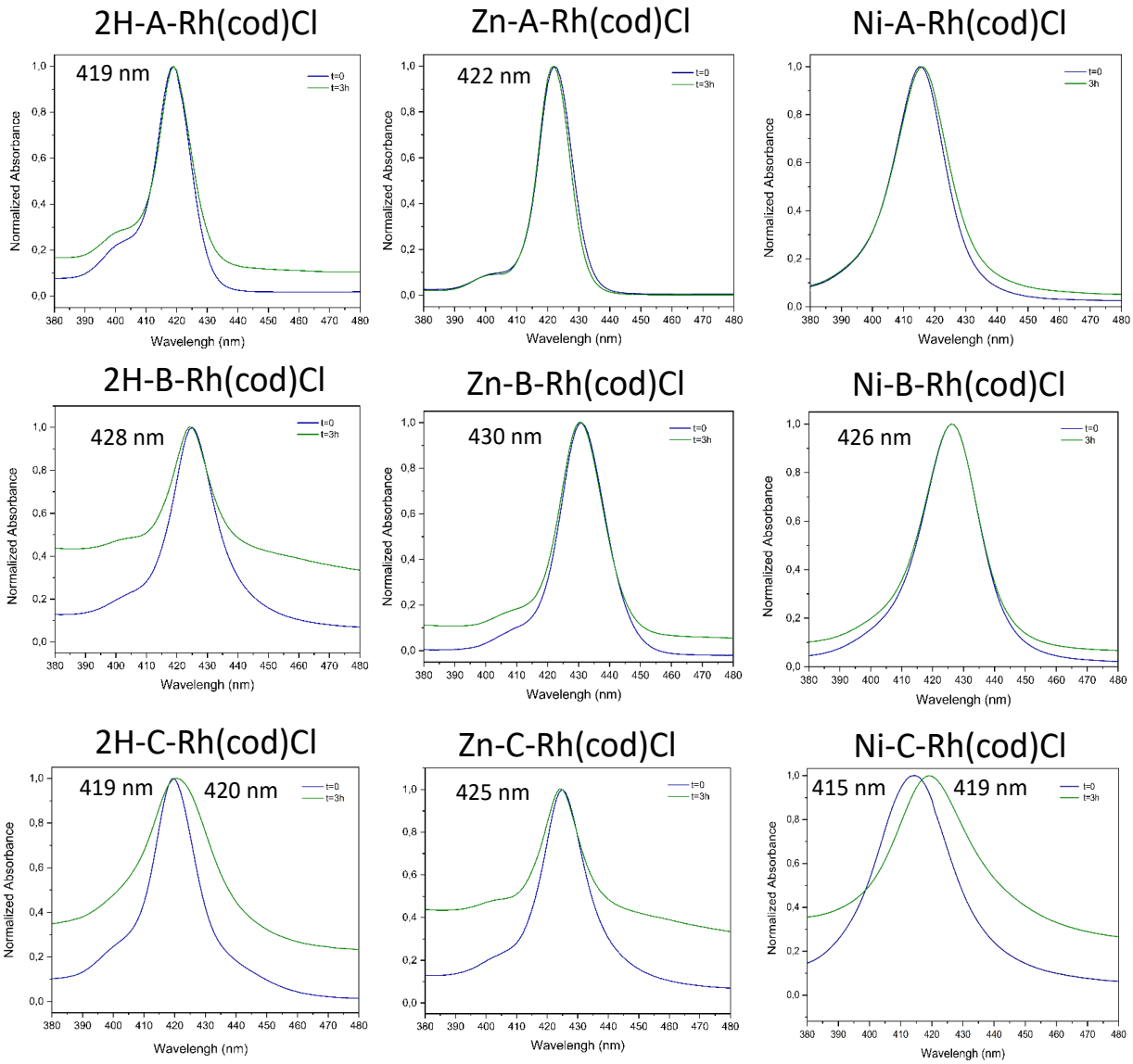


Figure S56. UV-visible absorption spectra in CH_2Cl_2 of the reaction mixtures of the conjugated addition of phenylboronic acid to cyclohexen-2-one at 100°C catalysed by **M[1]-A-Rh(cod)Cl**, **M[1]-B-Rh(cod)Cl** and **M[1]-C-Rh(cod)Cl** (M^1 = Ni, Zn, 2H) at t = 0, blue and t = 3h, green.

Stability of 2H-C-Rh(cod)Cl and Ni-C-Rh(cod)Cl

Catalysts **M[1]-C-Rh(cod)Cl** (M1=Ni or 2H) (10 mg) were dissolved in toluene (15 mL) and mixed with KOH (100 eq), heated to 100°C for 3h. At t= 0.5h and t= 3h, 7mL of the reaction mixture were take-off and concentrated for $^{13}C\{^{1}H\}$ NMR spectroscopy, UV-visible absorption spectroscopy and Electrospray Ionization Time-of-Flight mass spectrometry.

Monitoring of the stability of complexes 2H-C-Rh(cod)Cl and Ni-C-Rh(cod)Cl by $^{13}C\{^{1}H\}$ NMR spectroscopy

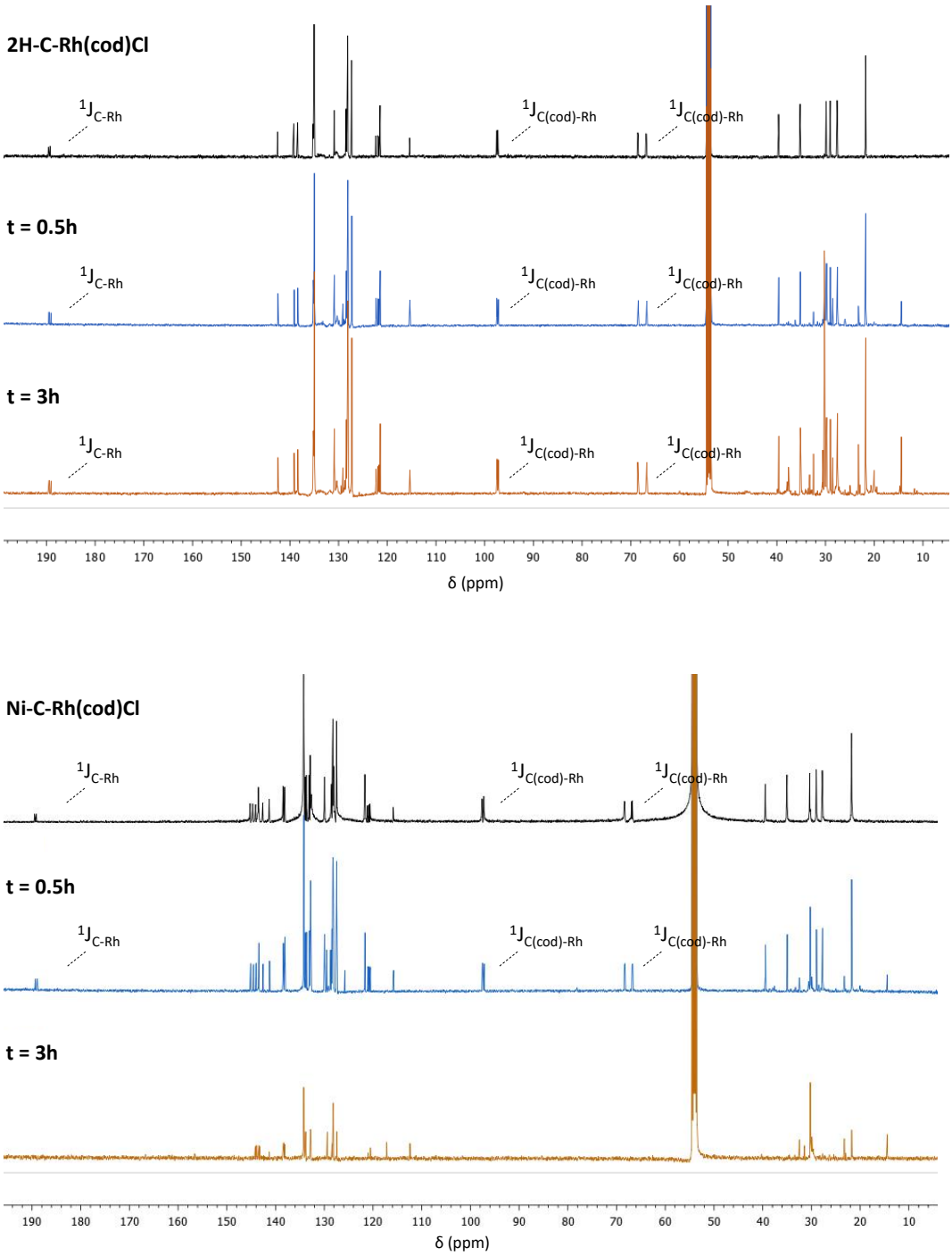


Figure S57. Monitoring of the stability of complexes **2H-C-Rh(cod)Cl** (top) and **Ni-C-Rh(cod)Cl** (bottom) in the presence of KOH (100 eq) in toluene at 100 °C (t = 0, black; t = 0.5 h, blue; t = 3 h, orange) by $^{13}C\{^{1}H\}$ NMR spectroscopy (500 MHz, CD_2Cl_2).

Monitoring of the stability of Ni-C-Rh(cod)Cl by UV-visible absorption spectroscopy

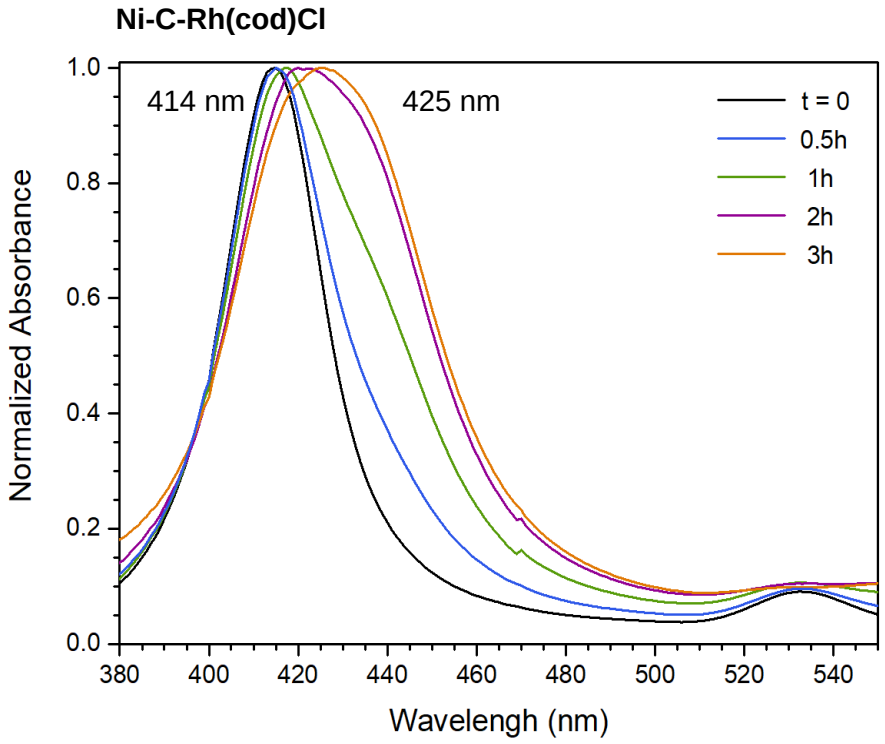


Figure S58: Monitoring of the stability of complex **Ni-C-Rh(cod)Cl** in the presence of KOH (100 eq) in toluene at 100 °C (t = 0, black; t = 0.5 h, blue; t = 1h, green, t = 2h, purple, t = 3h, orange) by UV-visible absorption spectroscopy in CH_2Cl_2.

Monitoring of the stability of complexe Ni-C-Rh(cod)Cl by Electrospray Ionization Time-of-Flight mass spectrometry.

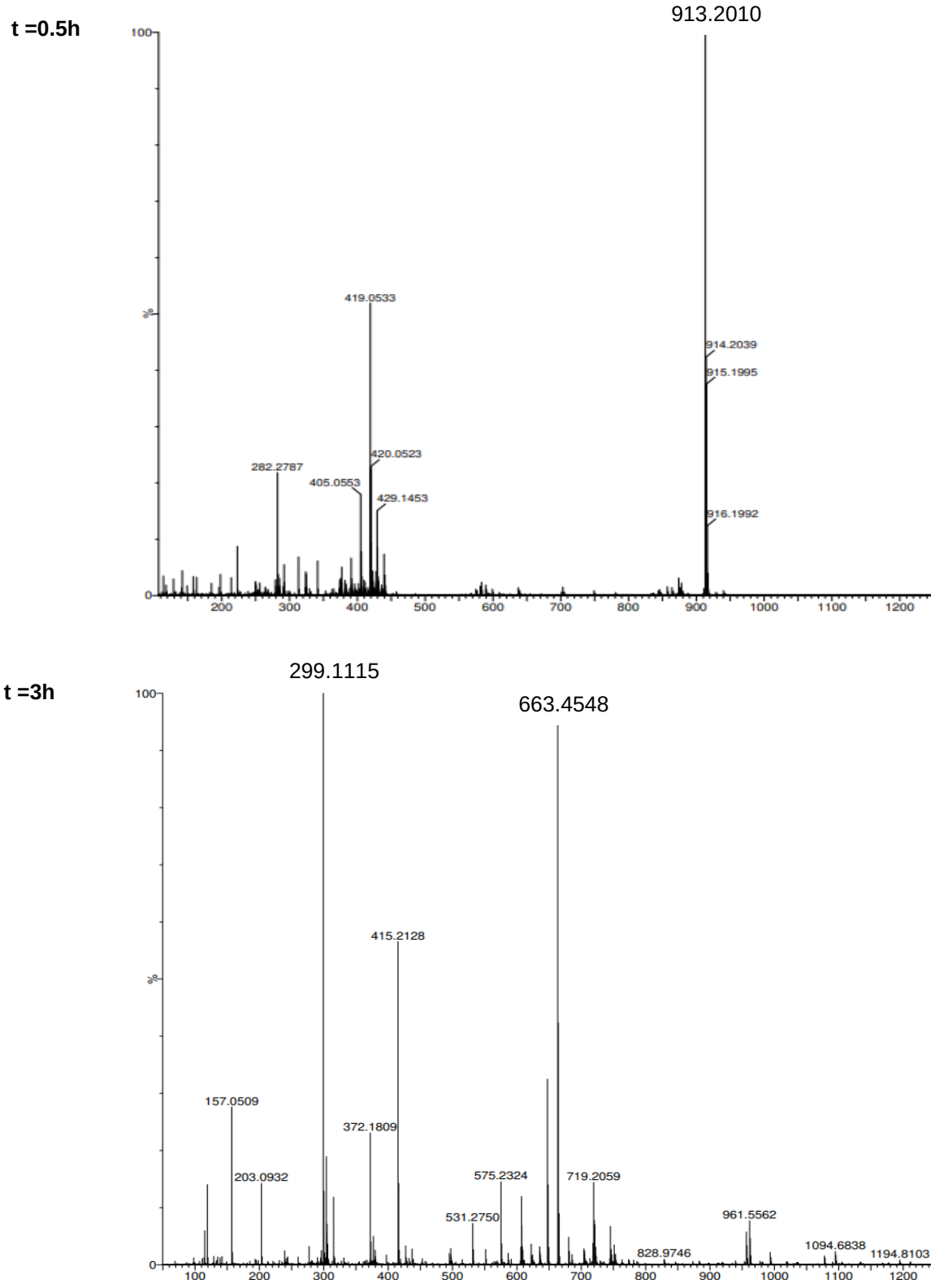


Figure S59: Monitoring of the stability of complex **Ni-C-Rh(cod)Cl** (*m/z* calc for $C_{52}H_{44}N_6NiRh$ $[M\text{-}Cl]^+$: 913.2030) in the presence of KOH (100 eq) in toluene at 100 °C (t = 0.5h (top) and t = 3h (bottom), by ESI-TOF mass spectrometry.

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