A Modular Synthetic Route to Monofunctionalized Porphyrin Architectures.

Gernot Heitmann, Marcel Dommaschk, Roland Löw and Rainer Herges

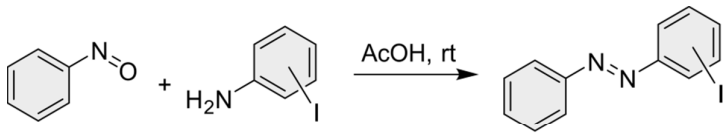
Table of Contents

I. Synthesis of halogenated azo compounds 6, 8 and 9

I.1 Synthesis of azobenzenes 6

The iodinated azobenzenes **6** were prepared according to a literature-known procedure.[1] Nitrosobenzene was reacted with the respective iodo aniline in a Mills reaction under acidic conditions (see scheme S1).

Scheme S1. Synthesis of iodinated azobenzenes 6.

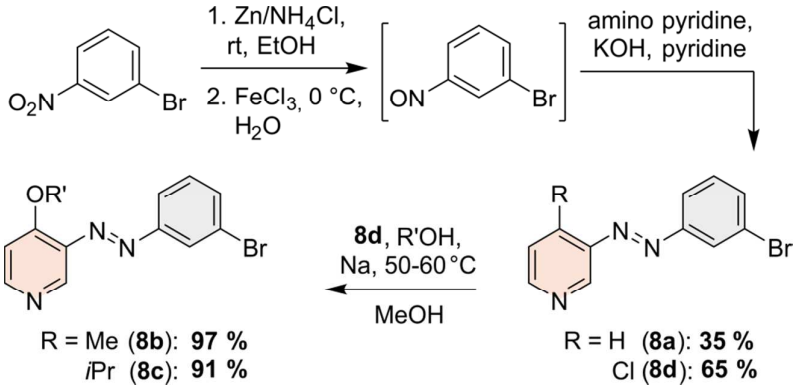


o-I (**6a**): **29 %**
m-I (**6b**): **97 %**
p-I (**6c**): **83 %**

I.2 Synthesis of azopyridines 8

Azopyridine-based switching units **8a** and **8d** are obtained via a Mills reaction under basic conditions of *in-situ* prepared 3-bromonitrobenzene with the respective 3-aminopyridine (see scheme S2). The chlorinated azopyridine **8d** gives the ether-functionalized azopyridines **8b** and **8c** upon nucleophilic aromatic substitution with the respective alcohol.

Scheme S2. Synthesis of azopyridine switching units 8.



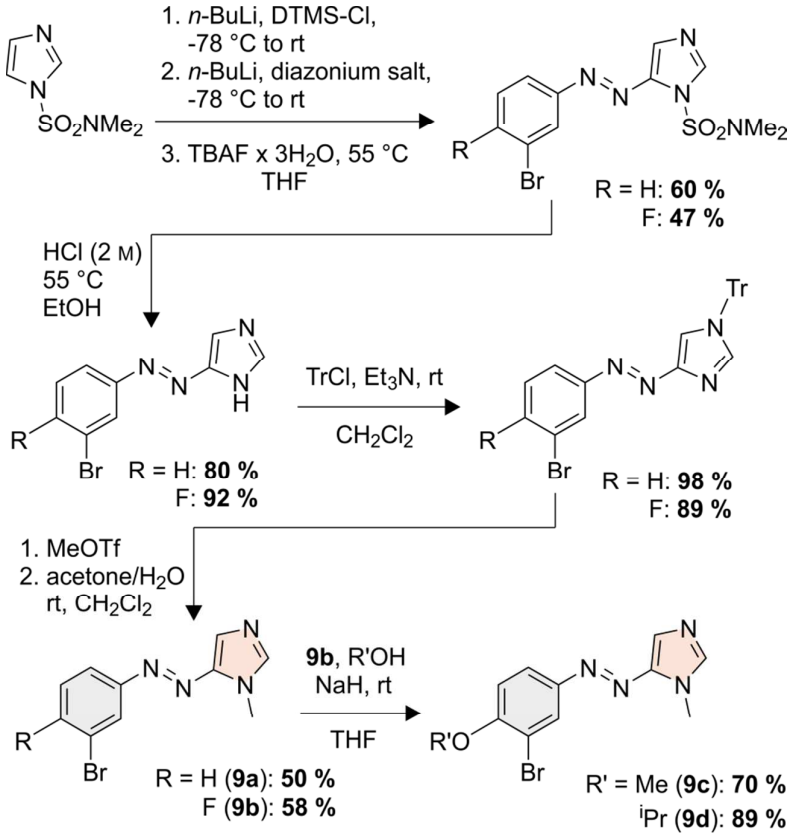
R = Me (**8b**): **97 %**
*i*Pr (**8c**): **91 %**

R = H (**8a**): **35 %**
Cl (**8d**): **65 %**

I.3 Synthesis of azoimidazoles 9

The synthesis of azoimidazole-based switching units **9** (see Scheme S3) starts from *N*,*N*-dimethylsulfamoyl protected imidazole which is *in-situ* silyl-protected in 2-position and consequently reacted with the respective diazonium salt after *in-situ* lithiation in 5-position. After stepwise deprotection an unsubstituted azoimidazole is obtained, which is regioselectively trityl-protected to give a 1,4-substitution pattern on the imidazole ring. Subsequent methylation and trityl-deprotection yields the desired 1-methyl-5-phenylazoderivatives **9a** and **9b**. The fluorinated derivative **9b** can further be modified by nucleophilic aromatic substitution with an alcohol, which gives the ether derivatives **9c** and **9d**.

Scheme S3. Synthesis of azo-*N*-methylimidazole switching units 9.



II. Experimental Section

II.1 General Information

Commercially available solvents and starting materials were used as received. THF was distilled from benzophenone-Na. Dichloromethane was distilled from CaH_2. Column chromatography was carried out using 0.04 – 0.063 mm mesh silica gel (Merck). R_f values were determined by thin layer chromatography on Polygram® Sil G/UV_{254} (Macherey-Nagel, 0.2 mm particle size).

NMR spectra were measured in Schott Economic NMR tubes using deuterated solvents (Deutero). The degree of deuteration is given in parentheses. Chemical shifts are calibrated to residual protonated solvent signals (^{1}H: δ (acetone-d_6) = 2.05 ppm, δ (DMSO-d_6) = 2.50 ppm, δ ($CDCl_3$) = 7.26 ppm, δ (CD_2Cl_2) = 5.32 ppm, δ (methanol-d_4) = 3.31 ppm; ^{13}C: δ (acetone-d_6) = 29.84 ppm, δ (DMSO-d_6) = 39.52 ppm, δ ($CDCl_3$) = 77.16 ppm, δ (CD_2Cl_2) = 53.84 ppm, δ (methanol-d_4) = 49.00 ppm; deuteration grade 99.8 %). Reference for ^{19}F NMR spectra is CCl_3F to which the spectrometer frequency is calibrated. The signal multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad signal). ^{13}C NMR and ^{19}F NMR spectra were measured ^{1}H-decoupled. Measurements were performed with a Bruker DRX 500 (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz, ^{19}F NMR: 470 MHz, ^{11}B NMR: 160 MHz) and a Bruker AV 600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz).

The high resolution (HR) mass spectra were measured with an AccuTOF by co. Jeol (EI). Low resolution mass spectra were measured with an AccuTOF by co. Jeol (EI), a LCQ Classic by co. Thermo Finnigan (ESI) or an AutoflexSpeed by co. Bruker (MALDI-TOF).

Infrared spectra were recorded on a Perkin-Elmer ATR spectrometer with a Golden-Gate-Diamond-ATR A531-G for neat samples. Signal intensities were abbreviated with w (weak), m (medium), s (strong) and vs (very strong). Broad signals are additionally labeled with br.

UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda-14 spectrophotometer with a Büchi thermostat using quartz cells of 1 cm path length.

The amount of carbon, hydrogen, sulfur and nitrogen in a compound was determined with a CHNS-Elementaranalysator Euro EA 3000 Series by co. Euro Vector.

Melting points were measured with a Melting Point B-540 (Büchi).

II.2 Synthetic procedures

General Procedure A: Suzuki cross coupling of precursor 5 with azobenzenes 6 and azopyridines 8. The porphyrin precursor **5** and the halogenated azo compound (1.3-2.0 equiv.) were weighted out in a round-bottomed flask and set under nitrogen atmosphere. Toluene (4.4 mL per 28.1 µmol **5**) and Ethanol (1.6 mL per 28.1 µmol **5**) were added and the solution was treated with aqueous (1 mL per 28.1 µmol **5**) potassium carbonate (3.3 equiv.) and catalytic amounts of tetrakis(triphenylphosphine)palladium(0). The reaction mixture was stirred at 90-95 °C overnight under an atmosphere of nitrogen. After cooling to room temperature water was added and the mixture was extracted with dichloromethane twice. The combined organic layer were dried over magnesium sulfate and the solvent was removed under reduced pressure.

General Procedure B: Suzuki cross coupling of precursor 5 with azoimidazoles 9. The porphyrin precursor **5** and the azoimidazole-based switching unit (1.3-1.6 equiv.) were weighted out in a round-bottomed flask and set under nitrogen atmosphere. Dry 1,4-dioxane (~12 mL per 50 µmol **5**) was added and the solution was treated with aqueous (1.3 mL per 50 µmol **5**) cesium carbonate (3 equiv.) and catalytic amounts of $PdCl_2$(dppf). The reaction mixture was stirred at 90-95 °C overnight under an atmosphere of nitrogen. After cooling down to room temperature an excess of ethyl acetate was added and the mixture was filtrated over diatomaceous earth. The organic layer was washed twice with water, dried over magnesium sulfate and the solvent was removed under reduced pressure.

5-(Phenyl-2'-(boronic acid pinacol ester))-10,15,20-tris(pentafluorophenyl)-porphyrin (4). A solution of 2-formylphenylboronic acid pinacol ester (**1**) (564 mg, 2.43 mmol), pentafluoro-benzaldehyde (**2**) (1.42 g, 7.29 mmol) and freshly distilled pyrrole (**3**) (700 µL, 10.1 mmol) in degassed dichloromethane (400 mL) was treated with borontrifluoride diethyl etherate (150 µL, 1.19 mmol) and the reaction mixture was stirred overnight at 37 °C under an atmosphere of nitrogen. Chloranil (1.90 g, 7.73 mmol) was added and stirring at 37 °C was continued overnight. The reaction mixture was filtrated over diatomaceous earth and the solvent was removed in vacuo. Purification via column chromatography on silica gel (*n*-pentane/dichloromethane, 9:1 → 6:4, R_f = 0.20) gave a purple solid (580 mg, 574 µmol, 24 %).

Mp: 221 °C.

FT-IR (layer): υ = 3324 (w), 3316 (w), 2977 (w), 1650 (w), 1595 (w), 1567 (w), 1517 (s), 1495 (vs), 1480 (s), 1437 (m), 1402 (m), 1387 (m), 1353 (s), 1317 (s), 1267 (m), 1246 (w), 1230 (w), 1165 (m), 1143 (m), 1116 (m), 1082 (m), 1072 (m), 1061 (m), 1043 (m), 985 (vs), 936 (m), 918 (vs), 857 (m), 832 (w), 804 (s), 758 (s), 750 (s), 738 (s), 703 (m), 660 (m), 636 (m), 580 (m), 569 (m), 556 (w), 548 (w), 539 (w), 528 (w), 518 (m), 503 (w), 496 (m), 483 (w), 469 (w), 427 (m), 412 (m) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.30 (s, br, 4H, Por*H*,), 9.17 (s, br, 2H, Por*H*), 8.80 (d, ^{3}J = 3.75 Hz, 2H, Por*H*), 8.34-8.28 (m, 1H, PorCC*H*), 8.23-8.17 (m, 1H, PorCCC*H*), 7.95-7.86 (m, 2H, PorCCCHC*H*, PorCCHC*H*), 0.14 (s, 12H, 4x -CH_3) ppm.

^{13}C NMR (125 MHz, acetone-d_6, 300 K): δ = 147.1 (Por*C*), 135.6 (PorC*C*H), 134.7 (PorCC*C*H), 129.7 (PorCCH*C*H), 128.7 (PorCCCH*C*H), 126.2 (PorC*C*), 83.6 (-*C*(CH_3)$_2$), 23.9 (-C(*C*H_3)$_2$) ppm. The C atoms of the porphyrin and the C atoms of the pentafluorophenyl substituents cannot be assigned.

^{19}F NMR (470 MHz, acetone-d_6, 300 K): δ = -139.83 to -139.96 (m, 2F, Por-Ar-*o*-*F*), -140.00 (dd, ^{3}J = 23.7 Hz, ^{4}J = 7.81 Hz, 2F, Por-Ar-*o*-*F*), -140.21 (dd, ^{3}J = 23.8 Hz, ^{4}J = 7.79 Hz, 2F, Por-Ar-*o*-*F*), -155.80 (t, ^{3}J = 20.4 Hz, 3F, Por-Ar-*p*-*F*), -164.56 to -164.89 (m, 6F, Por-Ar-*m*-*F*) ppm.

^{11}B NMR (160 MHz, CD_2Cl_2, 300 K): δ = 30.45 (s, 1B, -*B*Pin) ppm.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{50}H_{26}F_{15}BN_4O_2$, 1010.1909; found 1010.1889 (-2.0 ppm).

Anal. Calcd for $C_{50}H_{26}BF_{15}N_4O_2$: C, 59.43; H, 2.59; N, 5.54. Found: C, 59.64; H, 2.60; N, 5.57.

5-(Phenyl-2'-(boronic acid pinacol ester))-10,15,20-tris(pentafluorophenyl)-Ni(II)-porphyrin (5). The metal free precursor porphyrin **4** (426 mg, 422 μmol) was dissolved in toluene (45 mL) and treated with nickel(II)acetylacetonate (1.08 g, 4.22 mmol). The resulting mixture was stirred at reflux and the progress of the reaction was followed by MALDI-TOF-MS. After 4 days, no starting material was detectable and the reaction mixture was evaporated to dryness. Purification via column chromatography on silica gel (chloroform, R_f = 0.73) gave a purple solid (420 mg, 394 μmol, 93 %).

Mp: 207 °C.

FT-IR (layer): υ = 2978 (w), 1652 (w), 1595 (w), 1519 (s), 1487 (s), 1434 (m), 1350 (s), 1320 (m), 1270 (w), 1215 (w), 1168 (w), 1144 (m), 1117 (w), 1077 (m), 1061 (m), 1006 (m), 987 (vs), 960 (m), 941 (s), 928 (s), 857 (m), 842 (m), 802 (m), 764 (s), 745 (m), 726 (m), 702 (m), 660 (m), 544 (w), 491 (w), 412 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.19-9.15 (m, 4H, Por*H*,), 9.05 (d, ^{3}J = 4.95 Hz, 2H, Por*H*), 8.80 (d, ^{3}J = 5.00 Hz, 2H, Por*H*), 8.25 (ddd, ^{3}J = 7.43 Hz, ^{4}J = 1.22 Hz, ^{4}J = 0.60 Hz, 1H, PorCC*H*), 8.08 (ddd, ^{3}J = 7.49 Hz, ^{4}J = 1.63 Hz, ^{4}J = 0.60 Hz, 1H, PorCCC*H*), 7.88 (td, ^{3}J = 7.52 Hz, ^{4}J = 1.58 Hz, 1H, PorCCHC*H*), 7.82 (td, ^{3}J = 7.51 Hz, ^{4}J = 1.23 Hz, 1H, PorCCCHC*H*), 0.14 (s, 12H, 4x -CH_3) ppm.

^{13}C NMR (125 MHz, acetone-d_6, 300 K): δ = 146.1 (Por*C*CH), 145.6 (*C*-Por), 144.2 (*C*-Por), 143.9 (*C*-Por), 143.7 (*C*-Por), 135.2 (*C*H-Por), 134.6 (PorCC*C*H), 134.2 (PorC*C*H), 133.5 (*C*H-Por), 133.2 (*C*H-Por), 132.3 (*C*H-Por), 129.8 (PorCCH*C*H), 128.7 (PorCCCH*C*H), 124.6 (PorC*C*CH), 103.6 (*C*-

Por), 102.8 (*C*-Por), 83.5 (-*C*$(CH_3)_2$), 23.9 (-C(*C*$H_3)_2$) ppm. The the C atoms of the pentafluorophenyl substituents could not be assigned.

^{19}F NMR (470 MHz, acetone-d_6, 300 K): δ = -139.94 (dd, ^3J = 24.0 Hz, ^4J = 7.75 Hz, 1F, Por-Ar-*o*-*F*), -140.09 to -140.30 (m, 5F, Por-Ar-*o*-*F*), -155.86 (t, ^3J = 20.4 Hz, 3F, Por-Ar-*p*-*F*), -164.51 to -164.74 (m, 6F, Por-Ar-*m*-*F*) ppm.

^{11}B NMR (160 MHz, CD_2Cl_2, 300 K): δ = 30.27 (s, 1B, -*B*Pin) ppm.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{50}H_{24}F_{15}BN_4O_2Ni$, 1066.1106; found 1066.1109 (+0.2 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 294 (4.146), 403 (5.357), 522 (4.193), 556 (4.003) nm.

Anal. Calcd for $C_{50}H_{24}BF_{15}N_4O_2Ni$: C, 56.27; H, 2.27; N, 5.25. Found: C, 56.90; H, 2.25; N, 5.34.

***o*-Iodoazobenzene (6a).**[1] 2-Iodoaniline (3.65 g, 16.7 mmol) and nitrosobenzene (3.26 g, 30.4 mmol) were stirred in acetic acid (180 mL) overnight at room temperature. The solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica gel (*n*-pentane/dichloromethane, 3:1). The product was obtained as a red solid (1.48 g, 4.80 mmol, 29 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.04 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, ICC*H*), 8.02 (d, ^3J = 7.7 Hz, 2H, N_2CC*H*), 7.66 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, ICCC*H*), 7.55 (t, ^3J = 7.4 Hz, 2H, N_2CCHC*H*), 7.51 (t, ^3J = 7.1 Hz, 1H, N_2CCHCHC*H*), 7.43 (td, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 1H, ICCCHC*H*), 7.17 (td, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, ICCHC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 152.3 (N_2*C*), 151.3 (IC*C*), 139.8 (IC*C*H), 132.2 (ICCHC*H*), 131.6 (N_2CCHCHC*H*), 129.2 (N_2CCHC*H*), 128.9 (ICCCHC*H*), 123.5 (N_2C*C*H), 117.3 (ICC*C*H), 102.5 (I*C*) ppm.

Anal. Calcd for $C_{12}H_9N_2I$: C, 46.78; H, 2.94; N, 9.09. Found: C, 46.79; H, 2.80; N, 9.06.

***m*-Iodoazobenzene (6b).**[1] 3-Iodoaniline (5.08 g, 23.2 mmol) and nitrosobenzene (3.23 g, 30.2 mmol) were stirred in acetic acid (250 mL) overnight at room temperature. The solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica gel (dichloromethane). The product was obtained as an orange solid (6.96 g, 22.6 mmol, 97 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.25 (t, ^4J = 1.7 Hz, 1H, ICC*H*C), 7.92 (d, ^3J = 8.0 Hz, 2H, N_2CC*H*), 7.92 (ddd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, ^4J = 1.1 Hz, 1H, ICCHCC*H*), 7.80 (ddd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, ^4J = 1.0 Hz, 1H, ICC*H*CH), 7.55-7.48 (m, 3H, N_2CCHC*H*, N_2CCHCHC*H*), 7.28 (t, ^3J = 7.9 Hz, 1H, ICCHC*H*) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$, 300 K): δ = 153.4 (ICCH*C*), 152.3 (N_2C), 139.5 (IC*C*HCH), 131.5 (N_2CCHCHC*H*), 130.6 (IC*C*HC), 130.6 (ICCH*C*H), 129.2 (N_2CCH*C*H), 123.5 (ICCHC*C*H), 123.0 (N_2C*C*H), 94.6 (I*C*) ppm.

Anal. Calcd for $C_{12}H_9N_2I$: C, 46.78; H, 2.94; N, 9.09. Found: C, 47.03; H, 2.84; N, 9.13.

***p*-Iodoazobenzene (6c).**[1] 4-Iodoaniline (4.38 g, 20.0 mmol) and nitrosobenzene (2.14 g, 20.0 mmol) were stirred in acetic acid (100 mL) overnight at room temperature. The precipitate was filtered of and recrystallized from ethanol. The product was obtained as an orange solid (5.14 g, 16.7 mmol, 83 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.91 (d, ^3J = 7.9 Hz, 2H, N_2CC*H*), 7.87 (d, ^3J = 8.6 Hz, 2H, ICC*H*), 7.66 (d, ^3J = 8.6 Hz, 2H, ICCHC*H*), 7.52 (t, ^3J = 7.0 Hz, 2H, N_2CCHC*H*), 7.49 (t, ^3J = 7.1 Hz, 1H, N_2CCHCHC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 152.0 (N_2C), 151.5 (ICCHCH*C*), 138.4 (IC*C*H), 131.4 (N_2CCHCH*C*H), 129.2 (N_2CCH*C*H), 124.5 (ICCH*C*H), 123.0 (N_2C*C*H), 97.6 (I*C*) ppm.

Anal. Calcd for $C_{12}H_9N_2I$: C, 46.78; H, 2.94; N, 9.09. Found: C, 46.49; H, 2.80; N, 9.04.

5-(Biphenyl-*o*-azobenzene)-10,15,20-tris(pentafluorophenyl)-nickel(II)porphyrin (7a). The Ni-porphyrin precursor **5** (30 mg, 28.1 µmol) and 2-iodoazobenzene (**6a**)[1] (40 mg, 130 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. The product was purified by column chromatography (cyclohexane/ethyl acetate = 9:1, R_f = 0.40). The product was obtained as a purple solid (29.6 mg, 26.4 µmol, 94%).

Mp: 171 °C.

FT-IR (layer): υ = 1650 (w), 1517 (m), 1486 (s), 1351 (w), 1167 (w), 1080 (w), 1060 (m), 986 (vs), 959 (m), 940 (s), 927 (s), 841 (w), 802 (w), 763 (vs), 702 (m), 687 (m), 539 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.20-8.48 (m, br, 8H, Por*H*), 8.33 (dd, ^3J = 7.0 Hz, ^4J = 1.7 Hz, 1H, PorCC*H*), 7.91-7.86 (m, 2H, PorCCHC*H*, PorCCCHC*H*), 7.74-7.73 (m, 2H *o*Ph*H*), 7.66 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, PorCCC*H*), 7.63-7.60 (m, 3H, *m*Ph*H*, *p*Ph*H*), 7.10 (dd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, 1H, N_2CC*H*), 6.96 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, N_2CCC*H*), 6.61 (td, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1H, N_2CCHC*H*), 6.45 (dd, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1H, N_2CCCHC*H*) ppm.

^{19}F NMR (470 MHz, acetone-d_6, 300 K) δ = -139.00 to -139. 60 (m, br, 2F, *o*Ar*F*), -139.78 (dd, ^3J = 23.5 Hz, ^5J = 7.2 Hz, 1F, *o*Ar*F*), -140.27 (dd, ^3J = 23.6 Hz, ^5J = 7.1 Hz, 1F, *o*Ar*F*), -140.35 to -140.45 (m, br, 2F, *o*Ar*F*), -155.69 to -155.80 (m, 3F, *p*Ar*F*), -164.41 to -164.70 (m, 6F, *m*Ar*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **7a** did not provide sufficient signal

intensities. Therefore, the **^{13}C-NMR (125 MHz, acetone-d$_6$, 300 K)** spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HRMS (EI, TOF-Q) *m/z*: $[M]^+$ calcd for $C_{56}H_{21}F_{15}N_6Ni$ 1120.0942, found: 1120.0924.

Anal. Calcd for $C_{56}H_{21}F_{15}N_6Ni$: C, 59.97; H, 1.89; N, 7.49. Found: C, 60.17; H, 2.14; N, 7.44.

$t_{1/2}$ of *cis* isomer (acetone, 20 °C): 86 h.

5-(Biphenyl-*m*-azobenzene)-10,15,20-tris(pentafluorophenyl)-nickel(II)porphyrin (7b). The Ni-porphyrin precursor **5** (30 mg, 28.1 µmol) and 3-iodoazobenzene (**6b**)[1] (30 mg, 97.4 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. The product was purified by column chromatography (cyclohexane/ethyl acetate = 9:1, R_f = 0.34). The product was obtained as a purple solid (30.3 mg, 27.0 µmol, 97%).

Mp: 186 °C.

FT-IR (layer): υ = 2964 (w), 1711 (w), 1517 (s), 1486 (vs), 1430 (m), 1349 (m), 1319 (w), 1261 (w), 1166 (w), 1080 (m), 1060 (m), 986 (vs), 959 (m), 939 (s), 926 (m), 802 (m), 762 (vs), 696 (s), 657 (w), 621 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d$_6$, 300 K): δ = 9.16 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 9.13 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 9.06 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 8.97 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 8.30 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.4 Hz, 1H, PorCC*H*C), 7.95 (td, ^{3}J = 7.7 Hz, ^{4}J = 1.4 Hz, 1H, PorCCCHC*H*), 7.89 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.5 Hz, 1H, PorCCC*H*), 7.83 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1H, PorCCHC*H*), 7.29 (t, ^{4}J = 1.9 Hz, 1H, N_2CC*H*), 7.28 (tt, ^{3}J = 7.4 Hz, ^{4}J = 1.3 Hz, 1H, *p*Ph*H*), 7.18 (t, ^{3}J = 7.9 Hz, 2H, *m*Ph*H*), 7.16 (ddd, ^{3}J = 7.8 Hz, ^{4}J = 1.9, 1.1 Hz, 1H, N_2CC*H*CH), 7.08 (ddd, ^{3}J = 7.8 Hz, ^{4}J = 1.9, 1.1 Hz, 1H, N2CCHCC*H*), 6.93 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.3 Hz, 2H, *o*Ph*H*), 6.80 (t, ^{3}J = 7.8 Hz, 1H, N_2CCHC*H*) ppm.

^{13}C NMR (125 MHz, acetone-d$_6$, 300 K): δ = 152.5 (*C*-*i*Ph), 152.3 (N_2C), 148.3 (C_6F_5), 146.3 (C_6F_5), 145.2 (*C*-Por), 144.3 (*C*-Por), 144.2 (PorC*C*CH), 143.9 (*C*-Por), 143.8 (*C*-Por), 142.9 (N_2CCH*C*CH), 139.8 (C_6F_5), 139.0 (Por*C*CH), 137.8 (C_6F_5), 136.0 (PorC*C*H), 135.1 (*C*H-Por), 133.7 (*C*H-Por), 133.5 (*C*H-Por), 132.9 (*C*H-Por), 132.5 (N_2C*C*H), 131.7 (*C*-*p*Ph), 130.6 (PorCC*C*H), 130.4 (PorCCCH*C*H), 129.6 (*C*-*m*Ph), 129.3 (N_2CCH*C*H), 127.3 (PorCCH*C*H), 122.9 (N2CCHC*C*H, *C*-*o*Ph), 122.7 (N_2C*C*HC), 121.5 (*C*-Por), 115.5 (C_6F_5), 103.8 (*C*-Por), 103.1 (*C*-Por) ppm.

^{19}F NMR (470 MHz, acetone-d$_6$, 300 K) δ = -139.33 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.9 Hz, 2F, *o*Ar*F*), -139.83 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.9 Hz, 1F, *o*Ar*F*), -139.96 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.9 Hz, 1F, *o*Ar*F*), -140.33 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.8 Hz, 2F, *o*Ar*F*), -155.73 (t, ^{3}J = 20.5 Hz, 2F, *p*Ar*F*), -155.77 (t, ^{3}J = 20.3 Hz,

1F, *p*Ar*F*), -164.32 (ddd, ^{3}J = 23.6, 20.5 Hz, ^{5}J = 8.0 Hz, 2F, *m*Ar*F*), -164.47 to -164.65 (m, 2F, *m*Ar*F*), -164.67 (ddd, ^{3}J = 23.5, 20.5 Hz, ^{5}J = 8.0 Hz, 2F, *m*Ar*F*) ppm.

HRMS (EI, TOF-Q) *m/z*: $[M]^{+}$ calcd for $C_{56}H_{21}F_{15}N_6Ni$ 1120.0942, found: 1120.0922.

$t_{1/2}$ of *cis* isomer (acetone, 20 °C): 642 h.

5-(Biphenyl-*p*-azobenzene)-10,15,20-tris(pentafluorophenyl)-nickel(II)porphyrin (7c). The Ni-porphyrin precursor **5** (30 mg, 28.1 µmol) and 4-iodoazobenzene (**6c**)[1] (15 mg, 48.7 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. The product was purified by column chromatography (cyclohexane/ethyl acetate = 9:1, R_f = 0.31). The product was obtained as a purple solid (29.1 mg, 25.9 µmol, 93%).

Mp: 370 °C.

FT-IR (layer): υ = 1517 (s), 1486 (s), 1352 (m), 1086 (w), 986 (vs), 957 (m), 924 (s), 852 (w), 802 (m), 763 (vs), 700 (m), 867 (m), 571 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.16-9.13 (m, 4H, Por*H*), 9.05 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 8.97 (d, ^{3}J = 5.0 Hz, 2H, Por*H*), 8.26 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, 1H, PorCC*H*), 7.93 (td, ^{3}J = 7.7 Hz, ^{4}J = 1.4 Hz, 1H, PorCCCHC*H*), 7.85 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.4 Hz, 1H, PorCCC*H*), 7.82 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H, PorCCHC*H*), 7.47-7.45 (m, 2H, *o*Ph*H*), 7.31-7.28 (m, 3H, *m*Ph*H*, *p*Ph*H*), 7.12 (d, ^{3}J = 8.8 Hz, 2H, N_2CC*H*), 7.08 (d, ^{3}J = 8.8 Hz, 2H, N_2CCHC*H*) ppm.

^{13}C NMR (125 MHz, acetone-d_6, 300 K): δ = 153.1 (*C*-*i*Ph), 151.2 (N_2C), 148.2 (C_6F_5), 146.3 (C_6F_5), 145.2 (*C*-Por), 145.0 (N_2CCHCH*C*), 144.3 (*C*-Por, PorC*C*CH), 143.8 (*C*-Por), 142.3 (C_6F_5), 139.9 (C_6F_5), 139.0 (Por*C*CH), 137.9 (C_6F_5), 136.3 (PorC*C*H), 135.2 (*C*H-Por), 133.8 (*C*H-Por), 133.5 (*C*H-Por), 132.9 (*C*H-Por), 131.8 (*C*-*p*Ph), 130.9 (N_2C*C*H), 130.6 (PorCC*C*H), 130.3 (PorCCCH*C*H), 129.8 (*C*-*m*Ph), 127.4 (PorCCH*C*H), 123.2 (*C*-*o*Ph), 122.7 (N_2CCH*C*H), 121.5 (*C*-Por), 115.5 (C_6F_5), 103.8 (*C*-Por), 103.1 (*C*-Por) ppm.

^{19}F NMR (470 MHz, acetone-d_6, 300 K) δ = -139.44 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.8 Hz, 2F, *o*Ar*F*), -139.85 (dd, ^{3}J = 23.7 Hz, ^{5}J = 7.9 Hz, 1F, *o*Ar*F*), -140.05 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.6 Hz, 1F, *o*Ar*F*), -140.32 (dd, ^{3}J = 23.6 Hz, ^{5}J = 7.7 Hz, 2F, *o*Ar*F*), -155.70 (t, ^{3}J = 20.6 Hz, 2F, *p*Ar*F*), -155.74 (t, ^{3}J = 20.4 Hz, 1F, *p*Ar*F*), -164.36 (ddd, ^{3}J = 23.6, 20.6 Hz, ^{5}J = 7.9 Hz, 2F, *m*Ar*F*), -164.44 to -164.57 (m, 2F, *m*Ar*F*), -164.65 (ddd, ^{3}J = 23.6, 20.6 Hz, ^{5}J = 7.9 Hz, 2F, *m*Ar*F*) ppm.

HRMS (EI, TOF-Q) *m/z*: $[M]^{+}$ calcd for $C_{56}H_{21}F_{15}N_6Ni$ 1120.0942, found: 1120.0973.

$t_{1/2}$ of *cis* isomer (acetone, 20 °C): 387 h.

3-(3'-Bromophenylazo)pyridine (8a)[2] and **3-(3'-bromophenylazo)-4-methoxypyridine (8b)**[3] were synthesized and characterized as previously reported.

3-(3'-Bromophenylazo)-4-isopropoxypyridine (8c). Sodium (1.00 g, 44 mmol) was dissolved in isopropanol (150 mL). 3-(3'-bromophenylazo)-4-chloropyridine (700 mg, 2.36 mmol) was added and the solution was stirred overnight at 60 °C. The major amount of the solvent was removed under reduced pressure. Water were added and the aqueous layer was extracted with dichloromethane twice. The combined organic layers were dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified via column chromatography on silica gel (ethyl acetate). The product was obtained as an orange solid (689 mg, 2.15 mmol, 91 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.63 (s, 1H, Py*H*-2), 8.49 (d, ^3J = 5.8 Hz, 1H, Py*H*-6), 8.03 (t, ^4J = 1.9 Hz, 1H, N_2CCHC), 7.88 (ddd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, ^4J = 1.1 Hz, 1H, N_2CCHCH), 7.61 (ddd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, ^4J = 1.0 Hz, 1H, $N_2CCHCCH$), 7.41 (t, ^3J = 8.0 Hz, 1H, N_2CCHCH), 7.00 (d, ^3J = 5.0 Hz, 1H, Py*H*-5), 4.85 (sept, ^3J = 6.1 Hz, 1H, $OCH(CH_3)_2$), 1.50 (d, ^3J = 6.1 Hz, 1H, $OCH(CH_3)_2$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 160.8 (Py*C*-4), 153.9 (N_2C), 153.1 (Py*C*-6), 139.5 (Py*C*-2), 138.7 (Py*C*-3), 133.9 ($N_2CCHCCH$), 130.5 (N_2CCHCH), 125.1 (N_2CCHC), 123.3 (N_2CCHCH), 110.1 (Br-*C*), 72.2 ($OCH(CH_3)_2$) , 22.0 ($OCH(CH_3)_2$) ppm.

MS (EI): m/z (%) = 319 (5) $[M]^{\bullet+}$, 182 (10) $[BrPhN_2]^{\bullet+}$, 152 (59) $[BrPh]^{\bullet+}$, 149 (100) $[M\text{-}PhBrN]^{\bullet+}$.

Anal. Calcd for $C_{14}H_{14}BrN_3O$: C, 52.52; H, 4.41; N, 13.12. Found: C, 52.78; H, 4.41; N, 13.31.

5-(3′-Bromophenylazo)-1-methylimidazole (9a). 4-(3'-Bromophenylazo)-1-(triphenylmethyl)-imidazole[4] (381 mg, 772 µmol) was dissolved in dry methylene chloride (12 mL) under an atmosphere of nitrogen and methyl trifluoromethanesulfonate (140 µL, 1.24 mmol) was added via syringe. The solution was stirred at room temperature overnight. Acetone/H_2O (2:1, 36 mL) was added and stirring was continued for 4 h at 40 °C. Saturated sodium bicarbonate solution (5 mL) was added, layers were separated and the aqueous layer was extracted twice with dichloromethane (each 20 mL). The combined organic layers were dried over magnesium sulfate and were evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, R_f = 0.25) gave an orange solid (103 mg, 389 µmol, 50 %).

Mp: 105 °C.

FT-IR (layer): υ = 3081 (m), 2360 (w), 1719 (w), 1566 (m), 1522 (m), 1503 (m), 1460 (m), 1432 (m), 1400 (m), 1340 (s), 1281 (m), 1234 (s), 1211 (m), 1125 (s), 1052 (m), 992 (m), 904 (s), 882 (s), 860 (s), 781 (ss), 680 (ss), 675 (m), 670 (m), 641 (ss), 571 (m), 530 (s) cm^{-1}.

^{1}H NMR (600 MHz, DMSO-d_6, 298 K): δ = 8.03 (s, 1H, 2-*H*), 7.94 (s, 1H, 2′-*H*), 7.83 (d, ^{3}J = 7.92 Hz, 1H, 6′-*H*), 7.69 (d, ^{3}J = 7.92 Hz, 1H, 4′-*H*), 7.57 (s, 1H, 4-*H*), 7.53 (t, ^{3}J = 7.95 Hz, 1H, 5′-*H*), 3.94 (s, 3H, -CH_3) ppm.

^{13}C NMR (150 MHz, DMSO-d_6, 298 K): δ = 153.7 (*C*-3′), 144.8 (*C*-5), 142.6 (*C*-2), 133.0 (*C*-4′), 131.4 (*C*-5′), 123.8 (*C*-4), 123.6 (*C*-6), 123.5 (*C*-11), 123.1 (*C*-7), 32.3 (-*C*H_3) ppm.

MS (EI, 70 eV): m/z (%) = 266.0/264.0 (57/58) $[M]^{\bullet+}$, 186.0/184.0 (13/14) $[PhBrN_2+H]^{\bullet+}$, 157.0/155.0 (35/37) $[PhBr]^{\bullet+}$, 109 (100) $[M\text{-}PhBr]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{10}H_9N_4{}^{79}Br$, 264.0011; found 264.0010 (-0.3 ppm); calcd for $C_{10}H_9N_4{}^{81}Br$, 265.9990; found 265.9990 (±0 ppm).

5-(3′-Bromo-4’-fluorophenylazo)-1-methylimidazole (9b). Step 1: 3-Bromo-4-fluorobenzenediazonium tetrafluoroborate. A solution of 3-bromo-4-fluoroaniline (3.00 g, 15.8 mmol) in a mixture of ethanol and tetrafluoroboric acid (50 wt-%) (60 mL, 7:3) was cooled to 0 °C and isopentylnitrite (2.55 mL, 18.9 mmol) was added dropwise over 10 min. Diethyl ether (210 mL) was added and stirring at 0 °C was continued for 45 min. The precipitate was filtered off and washed thoroughly with diethyl ether (300 mL) before being dried in vacuo. The desired product (2.74 g, 9.49 mmol, 60 %) was obtained as a white solid which is thermally unstable and therefore was used in the following step immediately after preparation.

FT-IR (layer): υ = 3101 (w), 2301 (m), 1569 (m), 1474 (m), 1413 (w), 1307 (w), 1272 (m), 1135 (w), 1027 (vs, br), 891 (m), 857 (m), 825 (s), 733 (m), 559 (m), 524 (m), 464 (m), 403 (s) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.28 (dd, $^{4}J_{H\rightarrow F}$ = 5.63 Hz, $^{4}J_{H\rightarrow H}$ = 2.58 Hz, 1H, 2-*H*), 9.03 (ddd, $^{3}J_{H\rightarrow H}$ = 9.21 Hz, $^{4}J_{H\rightarrow F}$ = 3.91 Hz, $^{4}J_{H\rightarrow H}$ = 2.59 Hz, 1H, 6-*H*), 8.03 (dd, $^{3}J_{H\rightarrow H}$ = 9.20 Hz, $^{3}J_{H\rightarrow F}$ = 7.95 Hz, 1H, 5-*H*) ppm.

^{13}C NMR (125 MHz, acetone-d_6, 300 K): δ = 167.6 (d, ^{1}J = 268.3 Hz, *C*-4), 139.6 (d, ^{3}J = 4.01 Hz, *C*-2), 137.1 (d, ^{3}J = 11.8 Hz, *C*-6), 121.1 (d, ^{2}J = 26.4 Hz, *C*-5), 113.4 (s, *C*-1), 112.6 (d, ^{2}J = 24.6 Hz, *C*-3) ppm.

^{11}B NMR (160 MHz, acetone-d_6, 300 K): δ = -0.95 (1B, *B*F_4^-) ppm.

^{19}F NMR (470 MHz, acetone-d_6, 300 K): δ = -81.64 (s, 1F, 4-*F*), -150.86 (s, 1F, B*F*$_4^-$), -150.92 (s, 3F, B*F*$_4^-$) ppm.

MS (EI, 70 eV): m/z (%) = 191.9/193.9 (100/98) $[C_6H_3BrF_2]^{\bullet+}$.

HR-MS (EI): m/z $[M]^{\bullet+}$ calcd for $C_6H_3{}^{79}BrF_2$, 191.9386; found 191.9394 (+4.1 ppm); calcd for $C_6H_3{}^{81}BrF_2$, 193.9366; found 193.9375 (+4.6 ppm).

Diazonium tetrafluoroborates undergo a Baltz Schiemann reaction during the vaporization process in EI-MS. Therefore, only the fluorinated derivative is found.

Step 2: 5-(3'-Bromo-4'-fluorophenylazo)-1-(*N*,*N*-dimethylsulfamoyl)imidazole. 1-(*N*,*N*-Dimethyl-sulfamoyl)imidazole[5] (1.00 g, 5.71 mmol) was dissolved in dry THF (30 mL) and cooled to -78 °C. *n*-Butyllithium (2.30 mL, 5.75 mmol, 2.5 M in *n*-hexane) was added dropwise over a period of 15 minutes. After 30 minutes of stirring at -78 °C, dimethylthexylchlorosilane (1.24 mL, 6.31 mmol) was added. The reaction mixture was stirred at -78 °C for 60 minutes and at room temperature for 15 hours. It was again cooled to -78 °C and *n*-butyllithium (2.50 mL, 6.25 mmol, 2.5 M in *n*-hexane) was added dropwise over a period of 10 minutes. After 30 minutes of stirring at -78 °C, 3-bromo-4-fluorobenzenediazonium tetrafluoroborate (1.65 g, 5.71 mmol) was added as a solid in one portion, and the reaction mixture immediately turned from light yellow to deep red. It was stirred at -78 °C for 60 minutes and at room temperature for 5 hours. Then, half saturated aqueous sodium bicarbonate solution (30 mL) was added, layers were separated and the aqueous layer was extracted once with THF (40 mL). The combined organic layers were treated with tetra-*n*-butylammoniumfluoride trihydrate (1.95 g, 6.18 mmol) and the mixture was stirred at 55 °C for 90 min and at room temperature for 15 hours. Then, half saturated aqueous sodium bicarbonate solution (60 mL) was added, layers were separated and the aqueous layer was extracted three times with chloroform (each 40 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The resulting crude product was purified via column chromatography on silica gel (methylene chloride, 10 vol-% ethyl acetate, R_f = 0.42 (*cis*) & 0.33 (*trans*)). The desired product was obtained as orange solid (1.02 g, 2.71 mmol, 47 %).

Mp: 110 °C.

FT-IR (layer): υ = 3130 (w), 3070 (w), 3030 (w), 2947 (w), 1582 (w), 1482 (m), 1451 (m), 1390 (s), 1375 (s), 1340 (m), 1289 (m), 1255 (s), 1238 (m), 1182 (m), 1159 (vs), 1118 (s), 1091 (vs), 1033 (m), 980 (s), 887 (m), 844 (s), 820 (m), 759 (m), 729 (vs), 704 (m), 634 (m), 594 (s), 584 (vs), 575 (vs), 544 (vs), 536 (vs), 514 (vs), 473 (vs), 447 (m) cm^{-1}.

^{1}H NMR (600 MHz, CD_2Cl_2, 300 K): δ = 8.13 (s, 1H, 2-*H*), 8.07 (dd, $^4J_{H\rightarrow F}$ = 6.48 Hz, $^4J_{H\rightarrow H}$ = 2.34 Hz, 1H, 2′-*H*), 7.83 (ddd, $^3J_{H\rightarrow H}$ = 8.76 Hz, $^4J_{H\rightarrow F}$ = 4.62 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 6′-*H*), 7.50 (s, 1H, 4-*H*), 7.30 (dd(t), $^3J_{H\rightarrow F}$ = 8.40 Hz, $^3J_{H\rightarrow H}$ = 8.40 Hz, 1H, 5′-*H*), 2.97 (s, 6H, N(CH_3)$_2$) ppm.

^{13}C NMR (150 MHz, CD_2Cl_2, 300 K): δ = 161.2 (d, ^1J = 253.7 Hz, *C*-4′), 150.3 (s, *C*-1′), 145.3 (s, *C*-5), 141.8 (*C*-2), 128.1 (s, *C*-2′), 124.6 (d, ^3J = 7.73 Hz, *C*-6′), 119.8 (s, *C*-4), 117.6 (d, ^2J = 24.0 Hz, *C*-5′), 110.5 (d, ^2J = 23.0 Hz, *C*-3′), 38.7 (s, N(*C*H_3)$_2$) ppm.

^{19}F NMR (470 MHz, CD_2Cl_2, 300 K): δ = -103.30 ppm.

MS (EI, 70 eV): m/z (%) = 377.0/375.0 (18/17) $[M]^{\bullet+}$, 270.0/268.0 (36/37) $[M\text{-}SO_2N(CH_3)_2+H]^{\bullet+}$, 175.0/173.0 (32/32) $[PhFBr]^{\bullet+}$, 108.0 (100) $[SO_2N(CH_3)_2]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{11}H_{11}N_5O_2FS^{79}Br$, 374.9801; found 374.9800 (-0.2 ppm); calcd for $C_{11}H_{11}N_5O_2FS^{81}Br$, 376.9780; found 376.9780 (±0 ppm).

Step 3: 4(5)-(3'-Bromo-4'-fluorophenylazo)imidazole. The sulfamoyl-protected azoimidazole (857 mg, 2.28 mmol) was dissolved in ethanol (30 mL) and ethanolic hydrochloric acid (4 M, 30 mL) was added. The reaction mixture was stirred at 55 °C for 1 hour, then cooled to 0 °C and potassium hydroxide solution (40 %, 12 mL) was added dropwise. The solution was treated with saturated aqueous sodium bicarbonate solution (80 mL) and stirring at 0 °C was continued for 15 minutes. Methylene chloride (100 mL) was added and the layers were separated. The aqueous layer was extracted twice with methylene chloride (50 mL) and the combined organic layers were dried over magnesium sulfate before being evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, $R_f = 0.14$) gave the desired deprotected azoimidazole (564 mg, 2.10 mmol, 92 %) as yellow powder.

Mp: 229 °C (decomp.).

FT-IR (layer): υ = 1592 (w), 1515 (w), 1487 (m), 1432 (vs), 1391 (m), 1324 (m), 1255 (s), 1228 (s), 1175 (m), 1149 (m), 1121 (m), 1093 (m), 1035(m), 1003 (s), 914 (m), 837 (vs), 822 (s), 798 (s), 755 (s), 707 (m), 688 (w), 668 (m), 623 (vs), 578 (m), 552 (m), 541 (m) cm^{-1}.

^{1}H NMR (600 MHz, CD_3OD, 300 K): δ = 8.11 (dd, $^4J_{H\rightarrow F}$ = 6.54 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 2′-*H*), 7.90 (ddd, $^3J_{H\rightarrow H}$ = 8.73 Hz, $^4J_{H\rightarrow F}$ = 4.59 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 6′-*H*), 7.86 (s, br, 1H, 5(4)-*H*), 7.83 (s, br, 1H, 2-*H*), 7.38 (dd(t), $^3J_{H\rightarrow F}$ = 8.52 Hz, $^3J_{H\rightarrow H}$ = 8.52 Hz, 1H, 5′-*H*) ppm. The *N*H signal is not found due to fast proton-deuterium exchange in CD_3OD.

^{13}C NMR (150 MHz, CD_3OD, 300 K): δ = 161.4 (d, ^1J = 250.2 Hz, *C*-4′), 155.0 (s, *C*-4(5)), 151.4 (s, *C*-1′), 138.0 (*C*-2), 127.5 (s, *C*-2′), 125.5 (d, ^3J = 6.45 Hz, *C*-6′), 119.4 (s, *C*-5(4)), 118.0 (d, ^2J = 24.0 Hz, *C*-5′), 110.6 (d, ^2J = 22.7 Hz, *C*-3′) ppm.

^{19}F NMR (470 MHz, CD_3OD, 300 K): δ = -107.51 ppm.

MS (EI, 70 eV): m/z (%) = 270.0/268.0 (49/50) $[M]^{\bullet+}$, 174.9/172.9 (40/42) $[PhFBr]^{\bullet+}$, 95.0 (100) $[C_3H_3N_4]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_9H_6N_4{}^{79}Br$, 267.9760; found 267.9763 (+1.2 ppm); calcd for $C_9H_6N_4{}^{81}Br$, 269.9739; found 269.9748 (+3.3 ppm).

Anal. Calcd for $C_9H_6BrFN_4$: C, 40.17; H, 2.25; N, 20.82. Found: C, 39.76; H, 2.27; N, 20.70.

Step 4: 4-(3'-Bromo-4'-fluorophenylazo)-1-(triphenylmethyl)imidazole. A suspension of 4(5)-(3'-

bromo-4'-fluorophenylazo)imidazole (512 mg, 1.90 mmol) and triphenylchloromethane (557 mg, 2.00 mmol) in methylene chloride (25 mL) was treated with triethylamine (342 µL, 2.47 mmol). Stirring at room temperature for 19 hours gave a deep red solution. Half saturated sodium bicarbonate solution (30 mL) was added, layers were separated and the aqueous layer was extracted twice with methylene chloride (each 30 mL). The combined organic layers were dried over magnesium sulfate and evaporated to dryness. Purification of the crude product via column chromatography on silica gel (cyclohexane/ethyl acetate, 7:3, R_f = 0.38) gave a yellow solid (863 mg, 1.69 mmol, 89 %).

Mp: 85 °C.

FT-IR (layer): υ = 3088 (w), 3060 (w), 3032 (w), 2295 (w), 1582 (w), 1526 (w), 1480 (m), 1444 (s), 1393 (w), 1353 (w), 1323 (w), 1296 (m), 1252 (m), 1230 (m), 1155 (w), 1116 (s), 1087 (m), 1035 (m), 1001 (w), 991 (w), 927 (w), 887 (w), 866 (m), 838 (m), 823 (m), 755 (s), 742 (vs), 699 (vs), 677 (s), 656 (s), 639 (m), 619 (w), 586 (w), 555 (w), 539 (m), 508 (m), 491 (w), 474 (m) cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 8.06 (dd, $^4J_{H\rightarrow F}$ = 6.55 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 2′-*H*), 7.83 (ddd, $^3J_{H\rightarrow H}$ = 8.76 Hz, $^4J_{H\rightarrow F}$ = 4.64 Hz, $^4J_{H\rightarrow H}$ = 2.44 Hz, 1H, 6′-*H*), 7.56 (d, ^4J = 1.45 Hz, 1H, 5-*H*), 7.53 (d, ^4J = 1.45 Hz, 1H, 2-*H*), 7.42-7.36 (m, 9H, *m*-Tr-*H*, *p*-Tr-*H*), 7.27-7.19 (m, 7H, 5′-*H*, *o*-Tr-*H*) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ = 160.4 (*C*-4′, identified by HMBC), 153.6 (s, *C*-4), 150.5 (s, *C*-1′), 142.2 (s, *C*-*i*-Tr), 139.8 (s, *C*-2), 130.2 (s, *C*-*o*-Tr), 128.8 (s, *C*-*p*-Tr), 128.7 (s, *C*-*m*-Tr), 126.6 (s, *C*-2′), 125.0 (d, ^3J = 7.70 Hz, *C*-6′), 122.4 (s, *C*-5), 117.1 (d, ^2J = 23.7 Hz, *C*-5′), 110.1 (d, ^2J = 22.4 Hz, *C*-3′), 76.7 (s, *C*Ph_3) ppm.

^{19}F NMR (470 MHz, CD_2Cl_2, 300 K): δ = -106.06 ppm.

MS (ESI-TOF, methanol): m/z (%) = 534.8/532.8 (93/100) $[M+Na]^+$, 243.1 (67) $[CPh_3]^+$.

Anal. Calcd. for $C_{28}H_{21}N_4Br$ (492.09): cal. C 65.76, H 3.94, N 10.96, found C 66.52, H 4.43, N 11.19 %.

Step 5: 5-(3′-Bromo-4'-fluorophenylazo)-1-methylimidazole (9b). The tritylated phenylazo-imidazole (410 mg, 802 µmol) was dissolved in dry methylene chloride (12 mL) and methyl trifluoromethanesulfonate (100 µL, 882 µmol) was added under an atmosphere of nitrogen. It was stirred at room temperature for 40 min, followed by the addition of acetone/H_2O (1:1, 24 mL) and further stirring at room temperature for 30 min. Saturated sodium bicarbonate solution (3 mL) was added, layers were separated and the aqueous layer was extracted twice with dichloromethane (each 20 mL). The combined organic layers were dried over magnesium sulfate and were evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, R_f = 0.15) gave a yellow solid (132 mg, 466 µmol, 58 %).

Mp: 112 °C.

FT-IR (layer): υ = 3118 (w), 3090 (w), 3052 (w), 3031 (w), 2958 (w), 2360 (w), 2291 (w), 1650 (w), 1581 (m), 1515 (m), 1506 (m), 1474 (s), 1424 (m), 1409 (s), 1387 (m), 1377 (w), 1339 (s), 1301 (m), 1281 (m), 1257 (s), 1244 (s), 1221 (s), 1207 (s), 1171 (m), 1118 (vs), 1067 (m), 1036 (s), 950 (m), 905 (m), 850 (s), 814 (vs), 762 (m), 707 (m), 696 (m), 660 (vs), 640 (vs), 579 (m), 561 (m), 544 (s), 519 (m), 472 (vs) cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 8.07 (dd, $^4J_{H\rightarrow F}$ = 6.55 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 2′-*H*), 7.82 (ddd, $^3J_{H\rightarrow H}$ = 8.75 Hz, $^4J_{H\rightarrow F}$ = 4.65 Hz, $^4J_{H\rightarrow H}$ = 2.40 Hz, 1H, 6′-*H*), 7.62 (s, 1H, 2-*H*), 7.55 (d, ^4J = 0.75 Hz, 1H, 4-*H*), 7.27 (dd, $^3J_{H\rightarrow H}$ = 8.73 Hz, $^3J_{H\rightarrow F}$ = 8.13 Hz, 1H, 5′-*H*), 3.94 (d, ^4J = 0.55 Hz, 3H, -CH_3) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ = 160.4 (d, ^1J = 251.6 Hz, *C*-4′), 150.5 (s, *C*-1′), 145.6 (s, *C*-5), 141.7 (*C*-2), 126.5 (s, *C*-2′), 124.8 (d, ^3J = 7.71 Hz, *C*-6′), 124.5 (s, *C*-4), 117.2 (d, ^2J = 23.9 Hz, *C*-5′), 110.3 (d, ^2J = 22.8 Hz, *C*-3′), 32.9 (s, -*C*H_3) ppm.

^{19}F NMR (470 MHz, CD_2Cl_2, 300 K): δ = -105.45 ppm.

MS (EI, 70 eV): m/z (%) = 284.0/282.0 (86/88) $[M]^{\bullet+}$, 204.0/202.0 (18/20) $[PhFBrN_2+H]^{\bullet+}$, 175.0/173.0 (46/47) $[PhFBr]^{\bullet+}$, 109.1 (100) $[C_4H_5N_4]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{10}H_8N_4F^{79}Br$, 281.9916; found 281.9914 (-0.7 ppm); calcd for $C_{10}H_8N_4F^{81}Br$, 283.9896; found 283.9895 (-0.4 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 205 (4.138), 247 (3.872), 361 (4.314) nm.

5-(3′-Bromo-4’-methoxyphenylazo)-1-methylimidazole (9c). Under an atmosphere of nitrogen methanol (17.2 µL, 424 µmol) was dissolved in dry DMF (4 mL) and sodium hydride (12.7 mg, 318 µmol, 60% in mineral oil) was added. After 30 min of stirring at room temperature, the fluorinated phenylazoimidazole **9b** (30.0 mg, 106 µmol) was added and stirring at room temperature was continued overnight. The reaction mixture was diluted with diethyl ether (20 mL) and washed once with half saturated ammonium chloride solution (20 mL) and once with water (20 mL). The aqueous layer was extracted twice with diethyl ether (each 15 mL) and the combined organic layers were dried over magnesium sulfate and evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, R_f = 0.13) gave an orange solid (22.0 mg, 74.5 µmol, 70 %).

Mp: 121 °C.

FT-IR (layer): υ = 3102 (w), 2945 (w), 2841 (w), 1657 (w), 1589 (m), 1505 (m), 1493 (s), 1484 (s), 1467 (m), 1440 (m), 1341 (m), 1269 (s), 1260 (s), 1251 (s), 1224 (s), 1165 (m), 1139 (m), 1108 (vs), 1039 (s), 1011 (s), 909 (m), 890 (m), 873 (m), 846 (m), 832 (s), 805 (vs), 747 (m), 712 (m), 694 (m), 671 (m), 661 (s), 645 (s), 579 (s), 555 (s), 532 (vs), 510 (vs) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 8.06 (d, ^4J = 2.40 Hz, 1H, 2′-*H*), 7.88 (dd, ^3J = 8.75 Hz, ^4J = 2.35 Hz, 1H, 6′-*H*), 7.79 (s, br, 1H, 2-*H*), 7.44 (d, ^4J = 0.80 Hz, 1H, 4-*H*), 7.26 (d, ^3J = 8.80 Hz, 1H, 5′-*H*), 4.01-3.99 (m, 6H, -OCH_3, NCH_3) ppm.

^{13}C NMR (125 MHz, acetone-d_6, 300 K): δ = 158.6 (*C*-4′), 148.5 (*C*-1′), 146.1 (*C*-5), 142.2 (*C*-2), 126.1 (*C*-6′), 125.7 (*C*-2′), 123.5 (*C*-4), 113.1 (*C*-5′), 113.0 (*C*-3′), 57.1 (O*C*H$_3$), 32.6 (N*C*H$_3$) ppm.

MS (EI, 70 eV): m/z (%) = 296.0/294.0 (99/100) $[M]^{\bullet+}$, 281.0/279.0 (4/4) $[M\text{-}CH_3]^{\bullet+}$, 216.0/214.0 (13/14) $[PhOCH_3BrN_2+H]^{\bullet+}$, 187.0/185.0 (38/38) $[PhOCH_3Br]^{\bullet+}$, 109.1 (79) $[C_4H_5N_4]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{11}H_{11}N_4O^{79}Br$, 294.0116; found 294.0116 (+0.1 ppm); calcd for $C_{11}H_{11}N_4O^{81}Br$, 296.0096; found 296.0099 (+1.2 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 256 (3.951), 370 (4.422) nm.

5-(3′-Bromo-4’-isopropoxyphenylazo)-1-methylimidazole (9d). Under an atmosphere of nitrogen isopropanol (25.0 µL, 324 µmol) was dissolved in dry THF (3 mL) and sodium hydride (8.00 mg, 200 µmol, 60% in mineral oil) was added. After 30 min of stirring at room temperature, the fluorinated phenylazoimidazole **9b** (32.0 mg, 113 µmol) was added and stirring at room temperature was continued for 16 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed once with half saturated ammonium chloride solution (20 mL) and three times with water (each 20 mL). The organic layer was dried over magnesium sulfate and evaporated to dryness. Purification via column chromatography on silica gel (ethyl acetate, R_f = 0.31) gave an orange solid (30.0 mg, 92.8 µmol, 82 %).

Mp: 100 °C.

FT-IR (layer): υ = 3105 (w), 3082 (w), 3039 (w), 2978 (m), 2965 (w), 2928 (w), 2870 (w), 1710 (w), 1589 (m), 1564 (m), 1514 (w), 1499 (m), 1479 (s), 1463 (s), 1427 (m), 1413 (w), 1383 (w), 1373 (m), 1345 (m), 1336 (m), 1313 (w), 1282 (s), 1273(s), 1249 (s), 1225 (vs), 1165 (m), 1147 (s), 1135 (m), 1114 (vs), 1104 (vs), 1066 (m), 1033 (s), 947 (s), 909 (s), 888 (s), 861 (s), 841 (s), 815 (vs), 757 (m), 716 (m), 685 (w), 674 (m), 666 (vs), 650 (s), 592 (s), 585 (s), 554 (s), 488 (m), 456 (m) cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 8.07 (d, ^4J = 2.40 Hz, 1H, 2′-*H*), 7.80 (dd, ^3J = 8.78 Hz, ^4J = 2.38 Hz, 1H, 6′-*H*), 7.57 (s, 1H, 2-*H*), 7.46 (d, ^4J = 0.80 Hz, 1H, 4-*H*), 7.03 (d, ^3J = 8.90 Hz, 1H, 5′-*H*), 4.69 (sept., ^3J = 5.99 Hz, 1H, -OC*H*$(CH_3)_2$), 3.93 (s, 3H, NCH_3), 1.42 (d, 3J = 6.05 Hz, 1H, -OCH(C$H_3)_2$) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ = 156.8 (*C*-4′), 147.8 (*C*-1′), 145.7 (*C*-5), 140.9 (*C*-2), 125.9 (*C*-2′), 125.3 (*C*-6′), 122.8 (*C*-4), 114.7 (*C*-5′), 114.4 (*C*-3′), 72.8 (O*C*H$(CH_3)_2$), 32.7 (s, N*C*H$_3$), 22.1 (OCH(*C*H$_3)_2$) ppm.

MS (EI, 70 eV): m/z (%) = 324.0/322.0 (38/38) $[M]^{\bullet+}$, 282.0/280.0 (85/85) $[M\text{-}C_3H_7+H]^{\bullet+}$,

202.0/200.0 (8/9) $[C_6H_3OHBrN_2+H]^{\bullet+}$, 172.9/170.9 (12/12) $[C_6H_3OHBr]^{\bullet+}$, 109.1 (100) $[C_4H_5N_4]^{\bullet+}$.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{13}H_{15}N_4O^{79}Br$, 322.0429; found 322.0429 (±0 ppm); calcd for $C_{13}H_{15}N_4O^{81}Br$, 324.0409; found 324.0402 (-2.1 ppm).

5-(Biphenylazopyridine)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (10a).[2] The Ni-porphyrin precursor **5** (30.0 mg, 28.1 µmol) and 3-(3'-bromophenylazo)pyridine (**8a**)[2] (14.7 mg, 56.2 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. Purification via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1, R_f = 0.36 (*cis*-isomer), 0.23 (*trans*-isomer)) gave a purple solid (31.0 mg, 27.6 µmol, 98 %).

^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.15 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 9.12 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 9.08 (d, ^3J = 5.6 Hz, 1H, Py*H*-6), 9.01 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 8.99 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 8.91 (s, 1H, Py*H*-2), 8.40 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H, PorCC*H*), 8.07 (dd, ^3J = 8.2 Hz, ^3J = 5.1 Hz, 1H, Py*H*-5), 8.00 (td, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 1H, PorCCHC*H*), 7.92-7.87 (m, 3H, PorCCHC*H*, PorCCC*H*, Py*H*-4), 7.30 (ddd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, ^4J = 1.1 Hz, 1H, N_2CCHCC*H*), 7.30 (t, ^4J = 1.8 Hz, 1H, N_2CC*H*CCH), 7.13 (ddd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1H, N_2CC*H*CHCH), 6.86 (t, ^3J = 8.0 Hz, 1H, N_2CCHC*H*CH) ppm.

^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -139.75 (dd, ^3J = 23.7 Hz, ^5J = 7.6 Hz, 1F, Por-Ar-*o*-*F*), -139.88 (dd, ^3J = 23.4 Hz, ^5J = 7.5 Hz, 2F, Por-Ar-*o*-*F*), -140.47 (dd, ^3J = 23.6 Hz, ^5J = 7.4 Hz, 1F, Por-Ar-*o*-*F*), -140.57 (dd, ^3J = 23.6 Hz, ^5J = 7.5 Hz, 2F, Por-Ar-*o*-*F*), -155.58 (t, ^3J = 20.6 Hz, 2F, Por-Ar-*p*-*F*), -155.65 (t, ^3J =20.6 Hz, 1F, Por-Ar-*p*-*F*), -164.28 to -164.39 (m, 3F, Por-Ar-*m*-*F*), -164.43 to -164.62 (m, 3F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **10b** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

The analytical data are in accordance with the reported data for pyridine record player **10a**.[2]

5-(Biphenylazo-methoxypyridine)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (10b).[3] The Ni-porphyrin precursor **5** (290 mg, 272 µmol) and 3-(3'-bromophenylazo)-4-methoxypyridine (**8b**)[3] (103 mg, 353 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. Purification via column chromatography on silica gel (cyclohexane/ethyl acetate, 3:2, R_f = 0.13) gave a purple solid (297 mg, 258 µmol, 95 %).

^{1}H NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.15-9.13 (m, 4H, Por-*H*), 9.05 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 8.99 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 8.93 (dd, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, Py*H*-6), 8.45 (d, ^4J = 1.2 Hz, 1H, Py*H*-2), 8.33 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H, PorCC*H*), 8.01 (td, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, PorCCHC*H*), 7.90 (td, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H, PorCCHC*H*), 7.88 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, PorCCC*H*), 7.87 (d, ^3J = 7.0 Hz, 1H, Py*H*-5), 7.64 (t, ^4J = 1.8 Hz, 2H, N_2CC*H*CCH), 7.15 (m, 2H, N_2CCHCC*H*, N_2CC*H*CHCH), 6.73 (t, ^3J = 8.0 Hz, 1H, N_2CCHC*H*CH), 4.11 (s, 3H, OCH_3) ppm.

^{19}F NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -139.77 (dd, ^3J = 23.8 Hz, ^5J = 7.8 Hz, 1F, Por-Ar-*o*-*F*), -139.88 (dd, ^3J = 23.6 Hz, ^5J = 7.3 Hz, 2F, Por-Ar-*o*-*F*), -140.22 (dd, ^3J = 23.3 Hz, ^5J = 7.2 Hz, 2F, Por-Ar-*o*-*F*), -140.47 (dd, ^3J = 23.5 Hz, ^5J = 7.3 Hz, 1F, Por-Ar-*o*-*F*), -155.59 (t, ^3J = 20.7 Hz, 2F, Por-Ar-*p*-*F*), -155.66 (t, ^3J =20.5 Hz, 1F, Por-Ar-*p*-*F*), -164.29 to -164.53 (m, 5F, Por-Ar-*m*-*F*), -164.61 (ddd, ^3J = 23.5 Hz, ^3J = 20.5 Hz, ^5J = 7.8 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **10b** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

MS (ESI-TOF, methanol): m/z (%) = 1152 (100) $[M+H]^+$.

The analytical data are in accordance with the reported data for methoxypyridine record player **10b**.[3]

5-(Biphenylazo-isopropoxypyridine)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (10c). The Ni-porphyrin precursor **5** (30.0 mg, 28.1 µmol) and 3-(3'-bromophenylazo)-4-isopropoxy-pyridine (**8c**) (18 mg, 56.2 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure A. Purification via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1, R_f = 0.39 (*cis*-isomer), 0.08 (*trans*-isomer)) gave a purple solid (30.0 mg, 25.4 µmol, 90 %).

Mp: 186.9°C.

FT-IR (layer): υ = 1733 (w), 1652 (w), 1595 (w), 1518 (s), 1486 (s), 1341 (w), 1299 (w), 1243 (w), 1187 (w), 1071 (m), 1053 (m), 985 (vs), 955 (m), 937 (s), 926 (s), 839 (w), 801 (m), 761 (s), 745 (m), 703 (m), 659 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.15-9.13 (m, 4H, Por-*H*), 9.05 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 9.00 (d, ^3J = 5.1 Hz, 2H, Por-*H*), 8.88 (dd, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, Py*H*-6), 8.43 (d, ^4J = 1.3 Hz, 1H, Py*H*-2), 8.34 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, PorCC*H*), 8.01 (td, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, PorCCCHC*H*), 7.91 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, PorCCHC*H*), 7.89 (d, ^3J = 7.8 Hz, 1H, Py*H*-5), 7.87 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, PorCCC*H*), 7.69 (t, ^4J = 1.8 Hz, 1H, N_2CC*H*CCH),

7.12 (ddd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, ^4J = 1.1 Hz, 1H, $N_2CCHCCH$), 7.10 (ddd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1H, $N_2CCHCHCH$), 6.71 (t, ^3J = 7.9 Hz, 1H, $N_2CCHCHCH$), 5.22 (sept, ^3J = 6.1 Hz, 1H, $OCH(CH_3)_2$, 1.33 (d, ^3J = 6.1 Hz, 6H, $OCH(CH_3)_2$ ppm.

^{19}F NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -139.75 (dd, ^3J = 23.4 Hz, ^5J = 6.7 Hz, 1F, Por-Ar-*o*-*F*), -139.82 (dd, ^3J = 23.6 Hz, ^5J = 6.5 Hz, 2F, Por-Ar-*o*-*F*), -140.21 (dd, ^3J = 23.8 Hz, ^5J = 7.1 Hz, 2F, Por-Ar-*o*-*F*), -140.52 (dd, ^3J = 23.7 Hz, ^5J = 7.4 Hz, 1F, Por-Ar-*o*-*F*), -155.59 (t, ^3J = 20.4 Hz, 2F, Por-Ar-*p*-*F*), -155.66 (t, ^3J = 20.4 Hz, 1F, Por-Ar-*p*-*F*), -164.34 (ddd, ^3J = 23.4 Hz, ^3J = 20.4 Hz, ^5J = 7.4 Hz, 1F, Por-Ar-*m*-*F*), -164.34 to -164.50 (m, 4F, Por-Ar-*m*-*F*), -164.65 (ddd, ^3J = 23.7 Hz, ^3J = 20.4 Hz, ^5J = 7.4 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **10c** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{58}H_{26}F_{15}N_7NiO$, 1179.1313; found 1179.1314 (+0.1 ppm).

5-(Biphenylazo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (11a).[4] The Ni-porphyrin precursor **5** (20.0 mg, 18.7 µmol) and 5-(3'-bromophenylazo)-1-methylimidazole (**9a**) (8.00 mg, 30.2 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure B for reactions with azoimidazole-based switching units. Purification of the obtained crude product was achieved via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1→1:1→2:3, R_f = 0.68 (*cis*) & 0.40 (*trans*)) and yielded a purple solid (19.0 mg, 16.9 µmol, 90 %).

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 10.47-9.07 (m, 8H, Por-*H*), 8.27 (d, ^3J = 7.20, 1H, PorCC*H*), 7.99 (t, ^3J = 7.65 Hz, 1H, PorCCCHC*H*), 7.92 (dd, ^3J = 7.80 Hz, ^3J = 1.06 Hz, 1H, PorCCC*H*), 7.87 (t, ^3J = 7.25 Hz, 1H, PorCCHC*H*), 7.34 (s, br, 1H, N_2CC*H*CPh), 7.08 (d, ^3J = 7.60 Hz, 1H, N_2CCHCC*H*), 6.94 (d, ^3J = 7.95 Hz, 1H, N_2CC*H*CHCH), 6.71 (t, ^3J = 7.80 Hz, 1H, N_2CCHC*H*CH), 3.01 (s, br, 3H, -NCH_3) ppm.

The ^{1}H NMR signals experience strong line broadening which is due to intermolecular coordination. The imidazole protons are too broad and cannot be assigned. Deuterated trifluoroacetic acid (TFA-d, 25 µL) was added to protonate the imidazole and consequently inhibit intermolecular coordination.

^{1}H NMR (500 MHz, acetone-d6, TFA-d, 300 K): δ = 9.17-9.12 (m, 4H, Por-*H*), 9.10 (s, br, 1H, CH_3NC*H*N), 9.05 (d, ^3J = 4.95 Hz, 2H, Por-*H*), 8.99 (d, ^3J = 5.05 Hz, 2H, Por-*H*), 8.36-8.33 (m, 1H, PorCC*H*), 8.03-7.98 (m, 1H, PorCCCHC*H*), 7.92-7.87 (m, 2H, PorCCC*H*, PorCCHC*H*), 7.50 (d, ^{4}J = 1.45 Hz, 1H, N_2CC*H*N), 7.36-7.32 (m, 2H, N_2CC*H*CPh, $N_2CCHCPhC$*H*), 7.14 (ddd, ^3J = 7.94 Hz, ^4J =

1.86 Hz, ^4J = 1.19 Hz, 1H, $N_2CCHCHCH$), 6.90 (t, ^3J = 8.13 Hz, 1H, $N_2CCHCHCH$), 3.53 (s, 3H, NCH_3) ppm.

^{19}F NMR (470 MHz, acetone-d6, TFA-d, 300 K): δ = -139.69 (dd, ^3J = 23.7 Hz, ^4J = 7.58 Hz, 1F, Por-Ar-*o*-*F*), -140.02 (dd, ^3J = 23.4 Hz, ^4J = 7.38 Hz, 2F, Por-Ar-*o*-*F*), -140.20 (dd, ^3J = 23.2 Hz, ^4J = 6.71 Hz, 2F, Por-Ar-*o*-*F*), -140.63 (dd, ^3J = 23.6 Hz, ^4J = 6.28 Hz, 1F, Por-Ar-*o*-*F*), -155.55 (t, ^3J = 20.3 Hz, 2F, Por-Ar-*p*-*F*), -155.61 (t, ^3J = 20.4 Hz, 1F, Por-Ar-*p*-*F*), -164.27 (ddd, ^3J = 23.5 Hz, ^3J = 20.5 Hz, ^4J = 8.21 Hz, 1F, Por-Ar-*m*-*F*), -164.34 to -164.57 (m, 4F, Por-Ar-*m*-*F*), -164.67 (ddd, ^3J = 23.5 Hz, ^3J = 20.1 Hz, ^4J = 8.05 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **11a** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (150 MHz, acetone-d_6, TFA-d, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{54}H_{21}F_{15}N_8Ni$, 1124.1003; found 1124.0989 (-1.2 ppm).

The analytical data are in accordance with the reported data for *N*-methylimidazole record player **11a**.[4]

5-(Biphenyl-*p*-fluoro-azo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)nickel(II)porphyrin (11b). The Ni-porphyrin precursor **5** (19.5 mg, 18.3 µmol) and 5-(3'-bromo-4'-fluorophenylazo)-1-methylimidazole (**9b**) (7.50 mg, 26.5 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure B for reactions with azoimidazole-based switching units. Purification of the obtained crude product was achieved via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1→3:2→2:3, R_f = 0.70 (*cis*) & 0.46 (*trans*)) and yielded a purple solid (17.2 mg, 15.0 µmol, 82 %).

Mp: 250 °C (decomp.).

FT-IR (layer): υ = 1752 (w), 1651 (w), 1518 (s), 1486 (vs), 1430 (m), 1342 (m), 1211 (w), 1164 (w), 1114 (m), 1060 (m), 985 (vs), 956 (m), 938 (vs), 839 (m), 800 (m), 762 (vs), 744 (s), 703 (s), 646 (m), 614 (w), 572 (w) cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6, 300 K): δ = 9.76 (s, br, 8H, Por-*H*,), 8.36 (d, ^3J = 7.26 Hz, 1H, PorCC*H*), 8.00 (t, ^3J = 7.74 Hz, 1H, PorCCCHC*H*), 7.94 (t, ^3J = 7.08 Hz, 1H, PorCCHC*H*), 7.88 (d, ^3J = 7.62 Hz, 1H, PorCCC*H*), 7.31 (d, $^4J_{H\rightarrow F}$ = 4.92 Hz, 1H, $N_2CCHCCO$), 6.93 (s, br, 1H, $N_2CCHCHCO$), 6.62 (dd(t), $^3J_{H\rightarrow F}$ = 9.00 Hz, $^3J_{H\rightarrow H}$ = 9.00 Hz, 1H, $N_2CCHCHCO$), 3.07 (s, br, 3H, NCH_3) ppm.

The ^{1}H NMR signals experience strong line broadening which is due to intermolecular coordination. The imidazole protons are too broad and cannot be assigned. Deuterated trifluoroacetic acid (TFA-d, 25 µL) was added to protonate the imidazole and consequently inhibit intermolecular coordination.

^{1}H NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.15 (dd, ^{4}J = 1.43 Hz, ^{4}J = 0.68 Hz, 1H, CH_3NCHN), 9.14-9.12 (m, 4H, Por-*H*), 9.08 (d, ^{3}J = 5.00 Hz, 2H, Por-*H*), 9.01 (d, ^{3}J = 4.95 Hz, 2H, Por-*H*), 8.44 (dd, ^{3}J = 7.50 Hz, ^{4}J = 1.10 Hz, 1H, PorCC*H*), 8.01 (td, ^{3}J = 7.70 Hz, ^{4}J = 1.48 Hz, 1H, PorCCCHC*H*), 7.96 (td, ^{3}J = 7.57 Hz, ^{4}J = 1.50 Hz, 1H, PorCCHC*H*), 7.86 (d, ^{3}J = 7.80 Hz, 1H, PorCCC*H*), 7.52 (d, ^{4}J = 1.50 Hz, 1H, N_2CCHN), 7.41 (dd, $^{4}J_{H\rightarrow F}$ = 6.88 Hz, $^{4}J_{H\rightarrow H}$ = 2.53 Hz, 1H, $N_2CCHCCO$), 7.17 (ddd, $^{3}J_{H\rightarrow H}$ = 8.77 Hz, $^{4}J_{H\rightarrow F}$ = 4.73 Hz, $^{4}J_{H\rightarrow H}$ = 2.58 Hz, 1H, $N_2CCHCHCO$), 6.75 (dd(t), $^{3}J_{H\rightarrow H}$ = 9.08 Hz, $^{3}J_{H\rightarrow F}$ = 9.08 Hz, 1H, $N_2CCHCHCO$), 3.73 (d, ^{4}J = 0.50 Hz, 3H, NCH_3) ppm.

^{19}F NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -107.32 (s, 1F, $N_2CCHCCF$), -139.68 (dd, ^{3}J = 23.7 Hz, ^{4}J = 7.22 Hz, 1F, Por-Ar-*o*-*F*), -140.11 to -140.30 (m, 4F, Por-Ar-*o*-*F*), -140.69 (dd, ^{3}J = 23.7 Hz, ^{4}J = 7.22 Hz, 1F, Por-Ar-*o*-*F*), -155.60 (t, ^{3}J = 20.3 Hz, 2F, Por-Ar-*p*-*F*), -155.67 (t, ^{3}J = 20.3 Hz, 1F, Por-Ar-*p*-*F*), -164.28 (ddd, ^{3}J = 23.1 Hz, ^{3}J = 20.5 Hz, ^{4}J = 7.84 Hz, 1F, Por-Ar-*m*-*F*), -164.34 to -164.55 (m, 4F, Por-Ar-*m*-*F*), -164.69 (ddd, ^{3}J = 23.3 Hz, ^{3}J = 20.6 Hz, ^{4}J = 7.93 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **11b** did not provide sufficient signal intensities. Therefore, the **^{13}C-NMR (150 MHz, acetone-d_6, 300 K)** spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{54}H_{20}F_{16}N_8Ni$, 1142.0909; found 1142.0865 (-3.9 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 298 (4.240), 405 (5.272), 524 (4.138), 557 (3.965) nm.

5-(Biphenyl-*p*-methoxy-azo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)nickel(II)-porphyrin (11c). The Ni-porphyrin precursor **5** (20.0 mg, 18.7 µmol) and 5-(3'-bromo-4'-methoxyphenylazo)-1-methylimidazole (**9c**) (7.20 mg, 24.4 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure B for reactions with azoimidazole-based switching units. The general procedure B for Suzuki cross coupling reactions with azoimidazole-based switching units was applied using 5-(3'-bromo-4'-methoxyphenylazo)-1-methylimidazole (**9c**) (7.20 mg, 24.4 µmol). Purification of the obtained crude product was achieved via column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1→3:2→2:3, R_f = 0.68 (*cis*) & 0.39 (*trans*)) and yielded a purple solid (20.0 mg, 17.3 µmol, 93 %).

Mp: >400 °C.

FT-IR (layer): υ = 1751 (w), 1651 (w), 1517 (s), 1486 (vs), 1430 (m), 1345 (m), 1260 (m), 1112 (m), 1060 (m), 985 (vs), 956 (m), 938 (vs), 801 (m), 762 (vs), 744 (m), 703 (s), 660 (w), 507 (m) cm^{-1}.

^{1}H NMR (600 MHz, acetone-d_6, 300 K): δ = 9.35 (s, br, 8H, Por-*H*,), 8.34 (d, ^3J = 7.08 Hz, 1H, PorCC*H*), 7.93 (td, ^3J = 7.80 Hz, ^4J = 1.25 Hz, 1H, PorCCCHC*H*), 7.87 (td, ^3J = 7.69 Hz, ^4J = 1.32 Hz, 1H, PorCCHC*H*), 7.75 (dd, ^3J = 7.80 Hz, ^4J = 1.26 Hz, 1H, PorCCC*H*), 7.48 (d, ^4J = 2.34 Hz, 1H, N_2CC*H*CCO), 6.90 (dd, ^3J = 8.70 Hz, ^4J = 2.16 Hz, 1H, N_2CC*H*CHCO), 6.23 (d, ^3J = 8.76 Hz, 1H, N_2CCHC*H*CO), 3.51 (s, br, 3H, NCH_3), 3.03 (s, 3H, OCH_3) ppm.

The ^{1}H NMR signals experience strong line broadening which is due to intermolecular coordination. The imidazole protons are too broad and cannot be assigned. Deuterated trifluoroacetic acid (TFA-d, 20 µL) was added to protonate the imidazole and consequently inhibit intermolecular coordination.

^{1}H NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.18 (dd, ^4J = 1.40 Hz, ^4J = 0.60 Hz, 1H, CH_3NC*H*N), 9.14-9.10 (m, 4H, Por-*H*), 9.08-9.02 (m, 4H, Por-*H*), 8.40 (dd, ^3J = 7.41 Hz, ^4J = 1.50 Hz, 1H, PorCC*H*), 7.94 (td, ^3J = 7.65 Hz, ^4J = 1.53 Hz, 1H, PorCCCHC*H*), 7.91 (td, ^3J = 7.54 Hz, ^4J = 1.53 Hz, 1H, PorCCHC*H*), 7.74 (dd, ^3J = 7.61 Hz, ^4J = 1.48 Hz, 1H, PorCCC*H*), 7.55 (d, ^4J = 1.50 Hz, 1H, N_2CC*H*N), 7.53 (d, ^4J = 2.50 Hz, 1H, N_2CC*H*CCO), 7.07 (dd, ^3J = 8.83 Hz, ^4J = 2.53 Hz, 1H, N_2CC*H*CHCO), 6.37 (d, ^3J = 8.95 Hz, 1H, N_2CCHC*H*CO), 3.95 (d, ^4J = 0.47 Hz, 3H, NCH_3), 3.20 (s, 3H, OCH_3) ppm.

^{19}F NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -139.67 (dd, ^3J = 23.8 Hz, ^4J = 7.65 Hz, 1F, Por-Ar-*o*-*F*), -140.11 to -140.42 (m, 4F, Por-Ar-*o*-*F*), -140.67 (dd, ^3J = 22.9 Hz, ^4J = 6.64 Hz, 1F, Por-Ar-*o*-*F*), -155.54 to -155.73 (m, 3F, Por-Ar-*p*-*F*), -164.24 to -164.64 (m, 5F, Por-Ar-*m*-*F*), -164.72 (ddd, ^3J = 23.2 Hz, ^3J = 20.7 Hz, ^4J = 7.84 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **11c** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (150 MHz, acetone-d_6, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{55}H_{23}F_{15}N_8ONi$, 1154.1109; found 1154.1073 (-3.1 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 405 (5.290), 524 (4.168), 557 (4.004) nm.

5-(Biphenyl-*p*-isopropoxy-azo-*N*-methylimidazole)-10,15,20-tris(pentafluorophenyl)nickel(II)-porphyrin (11d). The Ni-porphyrin precursor **5** (20.0 mg, 18.7 µmol) and 5-(3'-bromo-4'-isopropoxyphenylazo)-1-methylimidazole (**9d**) (7.55 mg, 23.3 µmol) were deployed for a Suzuki cross-coupling reaction according to the general procedure B for reactions with azoimidazole-based switching units. Purification of the obtained crude product was achieved via column chromatography

on silica gel (cyclohexane/ethyl acetate, 4:1→3:2→2:3, R_f = 0.70 (*cis*) & 0.46 (*trans*)) and yielded a purple solid (14.6 mg, 12.3 µmol, 66 %).

Mp: >400 °C.

FT-IR (layer): υ = 2975 (w), 2932 (w), 1651 (w), 1591 (w), 1518 (s), 1486 (s), 1431 (w), 1345 (m), 1257 (m), 1223 (w), 1164 (w), 1129 (w), 1109 (m), 1075 (m), 1060 (m), 986 (vs), 956 (m), 938 (s), 926 (s), 839 (w), 801 (m), 762 (s), 744 (m), 703 (m), 665 (w), 647 (w), 600 (w), 573 (w), 517 (w) cm^{-1}.

^{1}H NMR (600 MHz, acetone-d_6, 300 K): δ = 9.49 (s, br, 8H, Por-*H*,), 8.31 (d, ^3J = 7.32 Hz, 1H, PorCC*H*), 7.90 (t, ^3J = 7.65 Hz, 1H, PorCCCHC*H*), 7.85 (t, ^3J = 7.38 Hz, 1H, PorCCHC*H*), 7.76 (d, ^3J = 7.68 Hz, 1H, PorCCC*H*), 7.33 (s, 1H, N_2CC*H*CCO), 6.89 (d, ^3J = 8.28 Hz, 1H, N_2CC*H*CHCO), 6.44 (d, ^3J = 8.76 Hz, 1H, N_2CCHC*H*CO), 4.39 (sept., ^3J = 6.01 Hz, 1H, OC*H*$(CH_3)_2$), 3.28 (s, br, 3H, NCH_3), 0.97 (s, br, 6H, OCH(CH_3)$_2$) ppm.

^{19}F NMR (470 MHz, acetone-d_6, 300 K): δ = -139.4 to -139.8 (m, 3F, Por-Ar-*o*-*F*), -140.0 to -140.40 (m, 3F, Por-Ar-*o*-*F*), -155.6 to -155.9 (m, 3F, Por-Ar-*p*-*F*), -164.2 to -164.8 (m, 6F, Por-Ar-*m*-*F*) ppm.

The ^{1}H NMR signals experience strong line broadening which is due to intermolecular coordination. The imidazole protons are too broad and cannot be assigned. Deuterated trifluoroacetic acid (TFA-d, 20 µL) was added to protonate the imidazole and consequently inhibit intermolecular coordination.

^{1}H NMR (500 MHz, acetone-d_6, TFA-d, 300 K): δ = 9.13 (dd, ^4J = 1.45 Hz, ^4J = 0.65 Hz, 1H, CH_3NC*H*N), 9.12-9.09 (m, 4H, Por-*H*), 9.09-9.06 (m, 4H, Por-*H*), 8.38 (dd, ^3J = 7.48 Hz, ^4J = 1.50 Hz, 1H, PorCC*H*), 7.93 (td, ^3J = 7.69 Hz, ^4J = 1.50 Hz, 1H, PorCCCHC*H*), 7.88 (td, ^3J = 7.54 Hz, ^4J = 1.49 Hz, 1H, PorCCHC*H*), 7.75 (dd, ^3J = 7.70 Hz, ^4J = 1.50 Hz, 1H, PorCCC*H*), 7.43 (d, 4J = 1.55 Hz, 1H, N_2CC*H*N), 7.40 (d, ^4J = 2.55 Hz, 1H, N_2CC*H*CCO), 7.09 (dd, ^3J = 8.83 Hz, ^4J = 2.58 Hz, 1H, N_2CC*H*CHCO), 6.58 (d, ^3J = 8.88 Hz, 1H, N_2CCHC*H*CO), 4.49 (sept., ^3J = 6.08 Hz, 1H, OC*H*$(CH_3)_2$), 3.83 (d, ^4J = 0.50 Hz, 3H, NCH_3), 1.04 (s, br, 6H, OCH(CH_3)$_2$) ppm.

^{19}F NMR (470 MHz, acetone-d_6, TFA-d, 300 K): δ = -139.66 (dd, ^3J = 23.6 Hz, ^4J = 7.93 Hz, 1F, Por-Ar-*o*-*F*), -140.04 to -140.55 (m, 4F, Por-Ar-*o*-*F*), -140.65 (dd, ^3J = 23.0 Hz, ^4J = 7.55 Hz, 1F, Por-Ar-*o*-*F*), -155.58 (t, ^3J = 20.3 Hz, 2F, Por-Ar-*p*-*F*), -155.67 (t, ^3J = 20.3 Hz, 1F, Por-Ar-*p*-*F*), -164.31 (ddd, ^3J = 23.6 Hz, ^3J = 20.4 Hz, ^4J = 7.88 Hz, 1F, Por-Ar-*m*-*F*), -164.43 (s, br, 2F, Por-Ar-*m*-*F*), -164.59 (ddd, ^3J = 23.6 Hz, ^3J = 20.7 Hz, ^4J = 7.84 Hz, 2F, Por-Ar-*m*-*F*), -164.73 (ddd, ^3J = 23.6 Hz, ^3J = 20.5 Hz, ^4J = 7.91 Hz, 1F, Por-Ar-*m*-*F*) ppm.

Due to the highly diluted NMR samples, the large number of quarternary C atoms and the large number of ^{19}F-coupled C atoms, ^{13}C NMR spectroscopy of **11d** did not provide sufficient signal intensities. Therefore, the **^{13}C NMR** (150 MHz, acetone-d_6, 300 K) spectrum was not analyzable. However, ^{1}H-^{13}C correlation experiments (HMBC, HSQC) confirmed the assignments of the ^{1}H-NMR signals.

HR-MS (EI, TOF-Q): m/z $[M]^{\bullet+}$ calcd for $C_{57}H_{27}F_{15}N_8ONi$, 1182.1422; found 1182.1407 (-1.3 ppm).

UV-vis (CH_3CN): λ_{max} (lg ε) = 405 (5.290), 524 (4.169), 557 (3.987) nm.

III. NMR Spectra

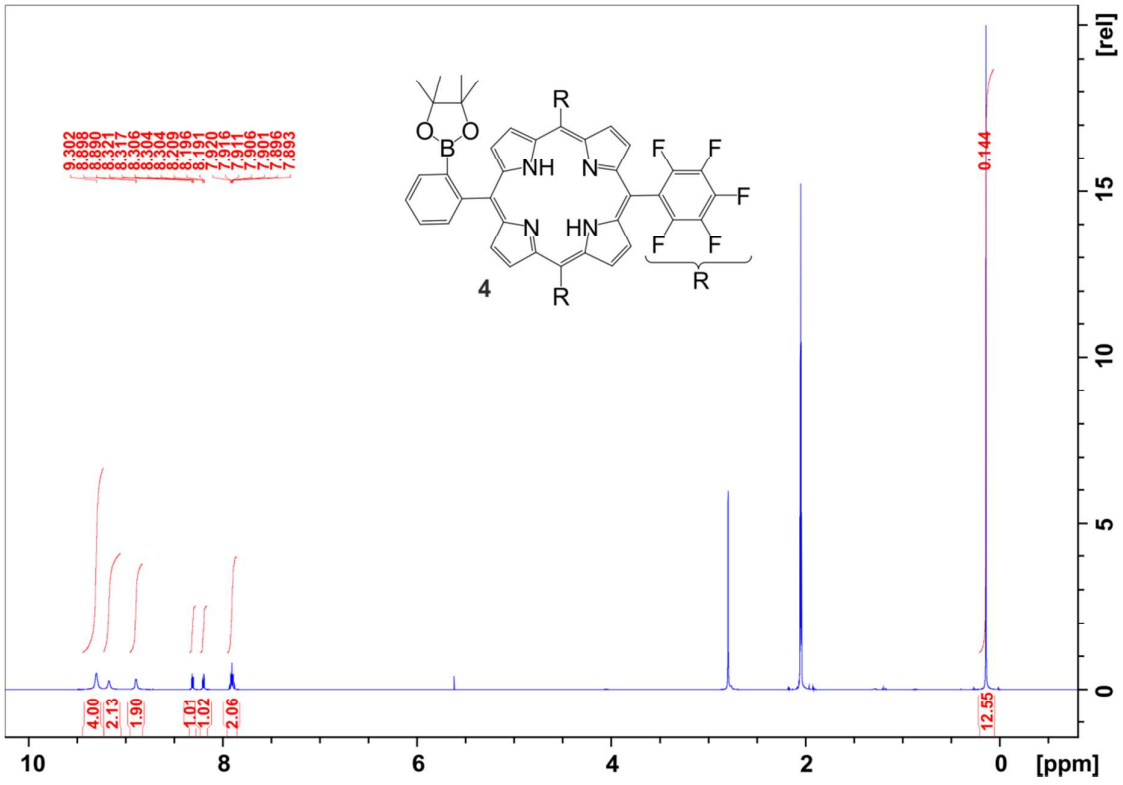


Figure S1. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **4**.

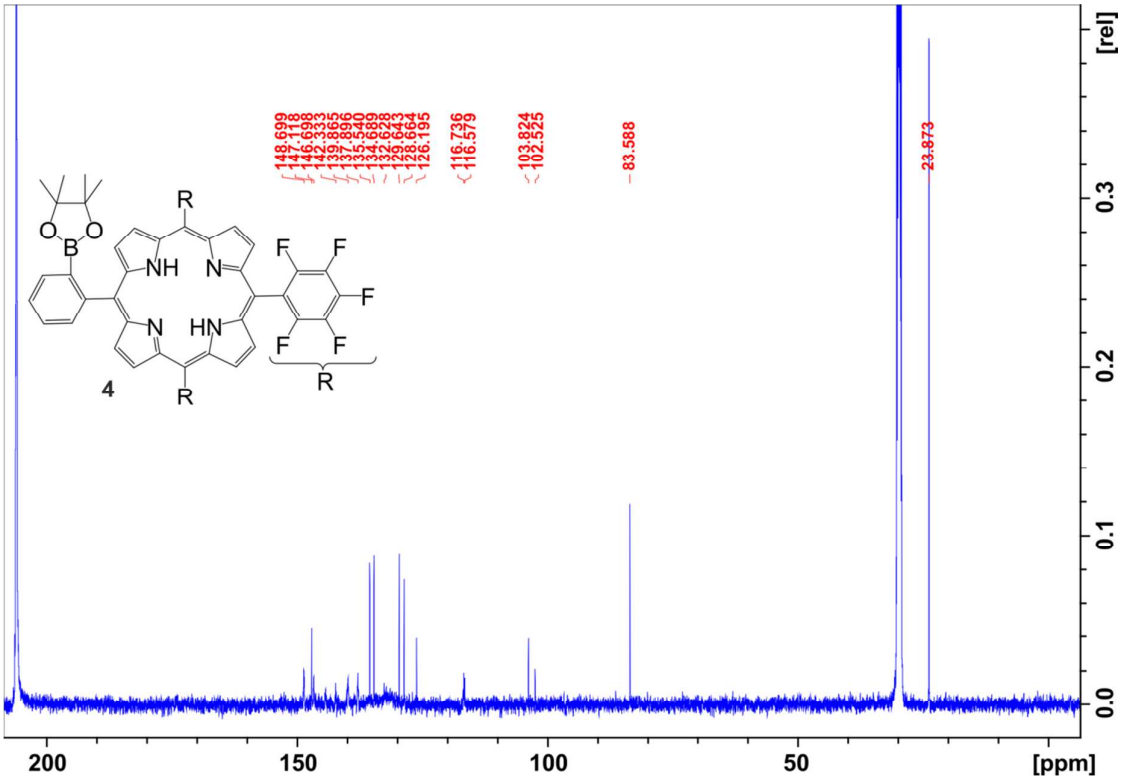


Figure S2. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **4**.

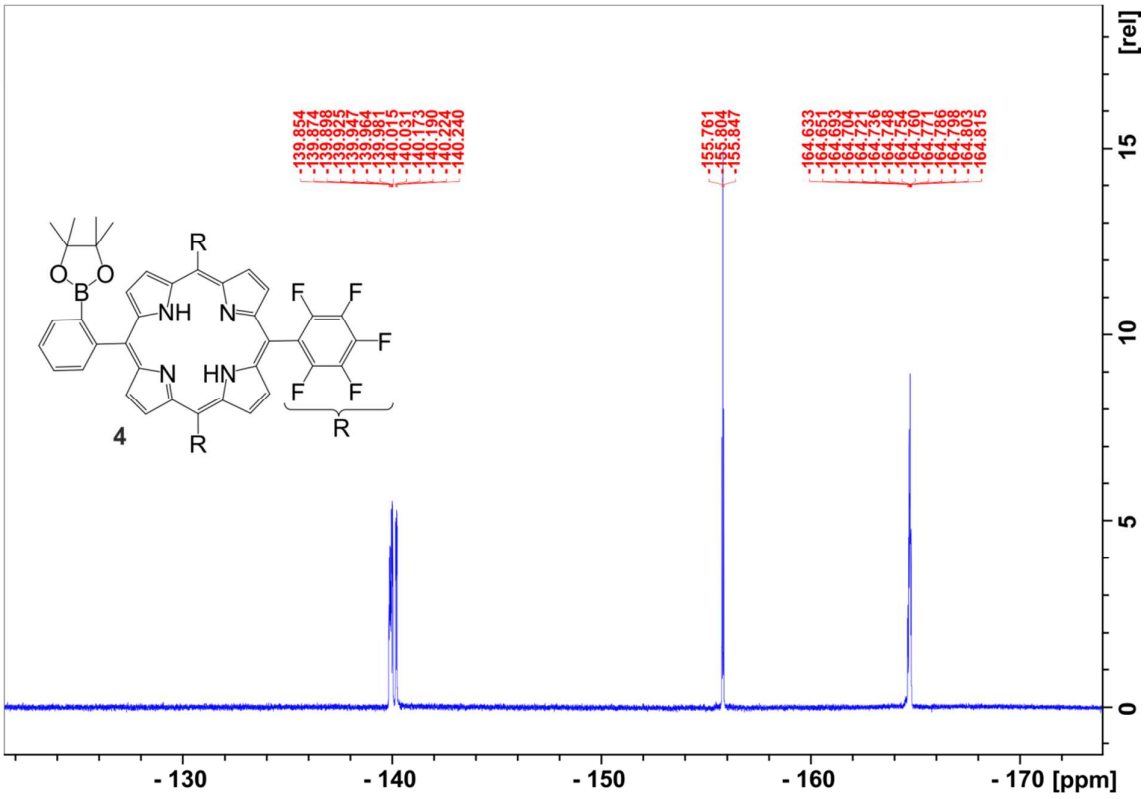


Figure S3. ^{19}F-NMR (470 MHz, acetone-d_6, 300 K) spectrum of **4**.

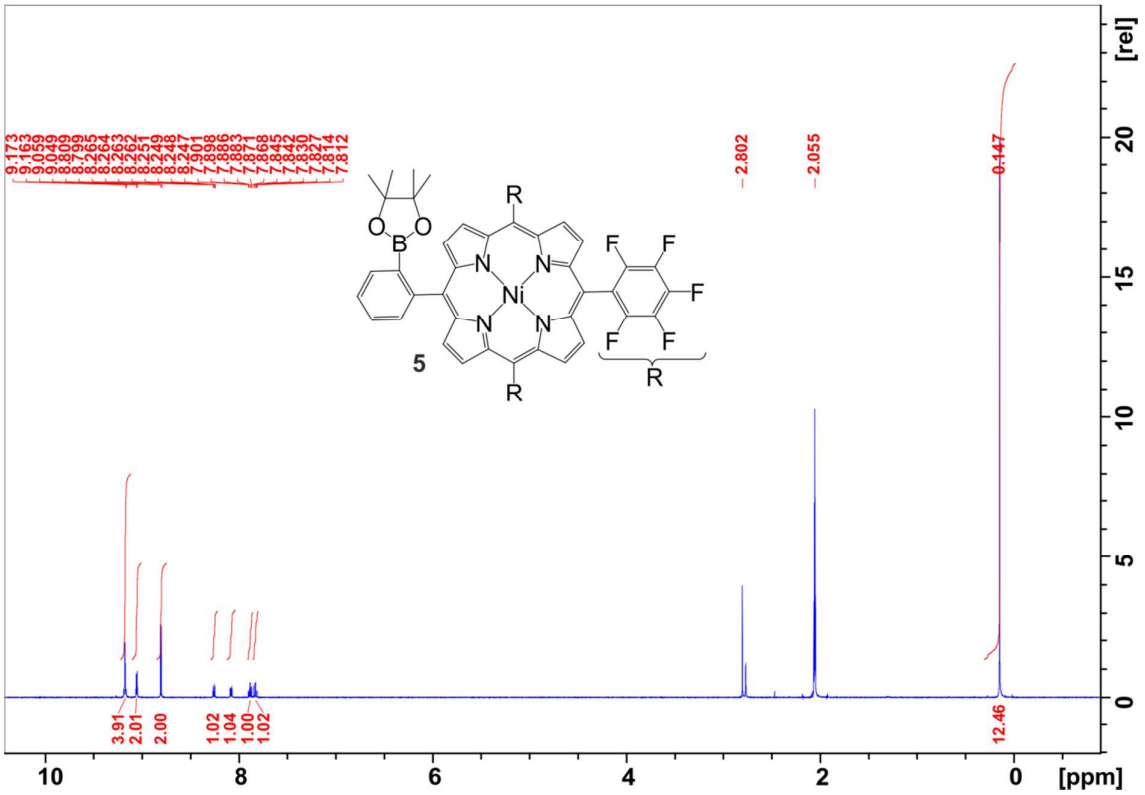


Figure S4. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **5**.

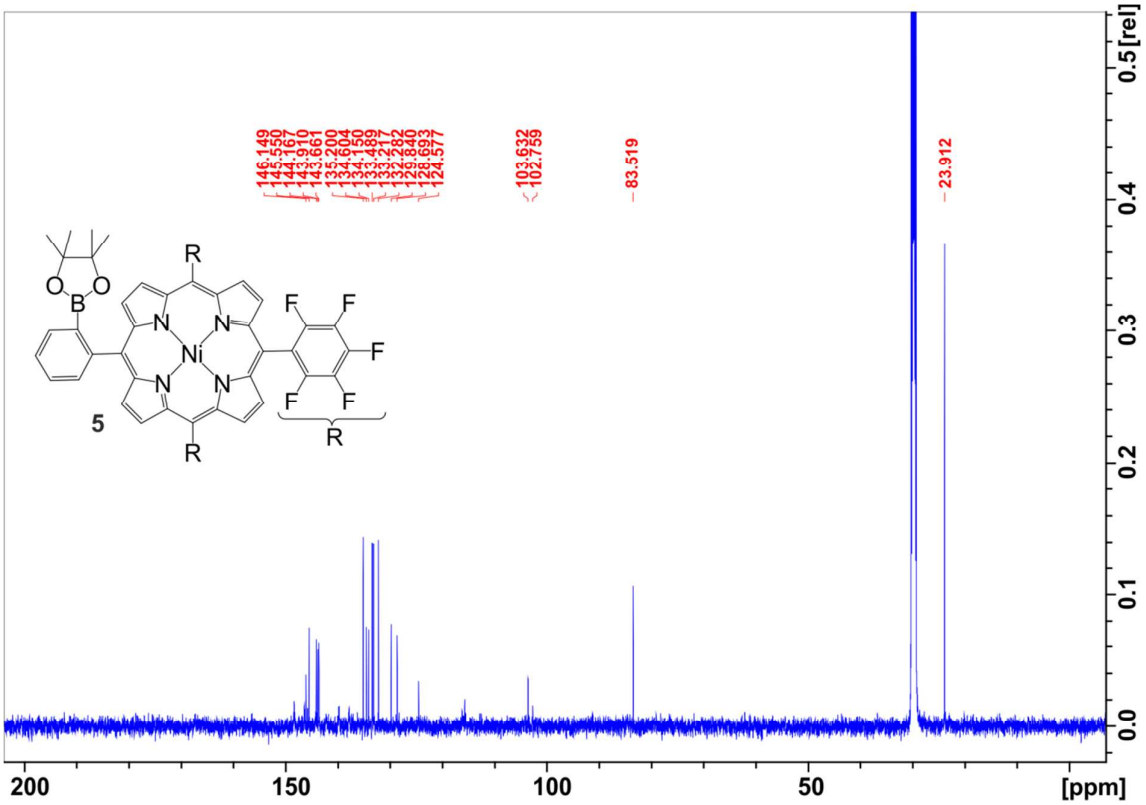


Figure S5. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **5**.

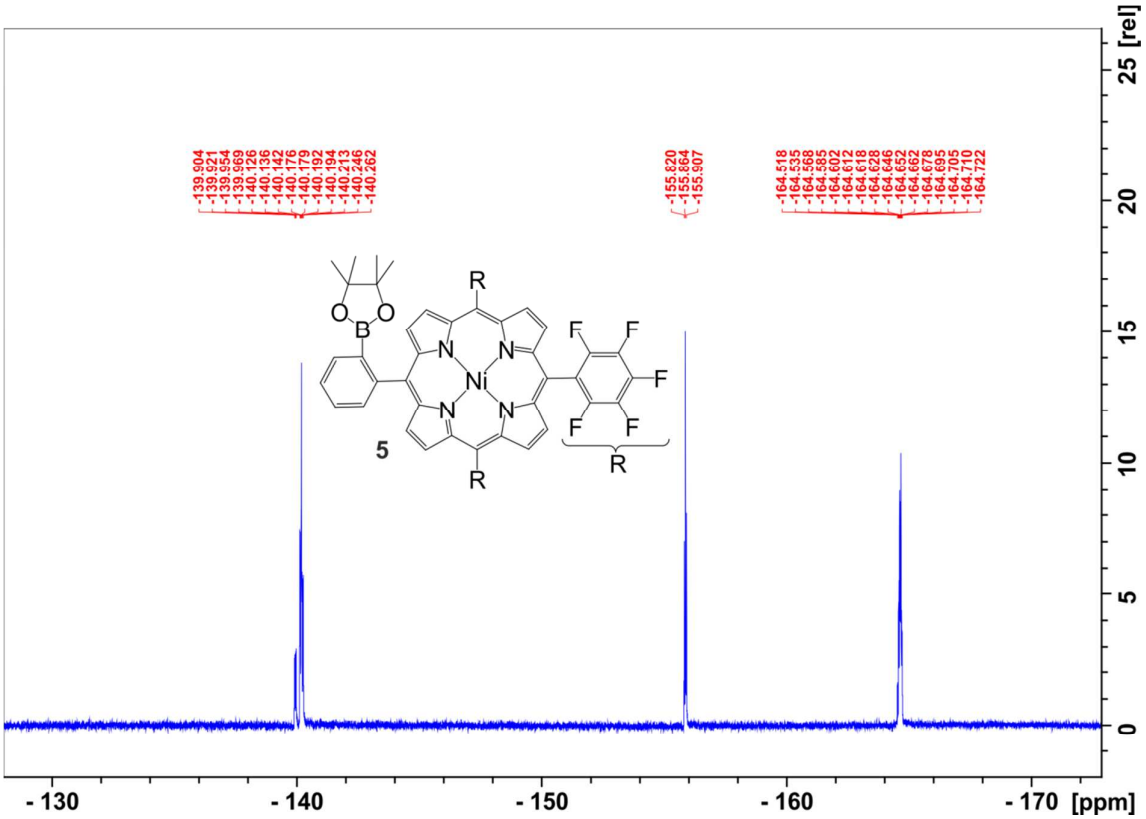


Figure S6. ^{19}F-NMR (470 MHz, acetone-d_6, 300 K) spectrum of **5**.

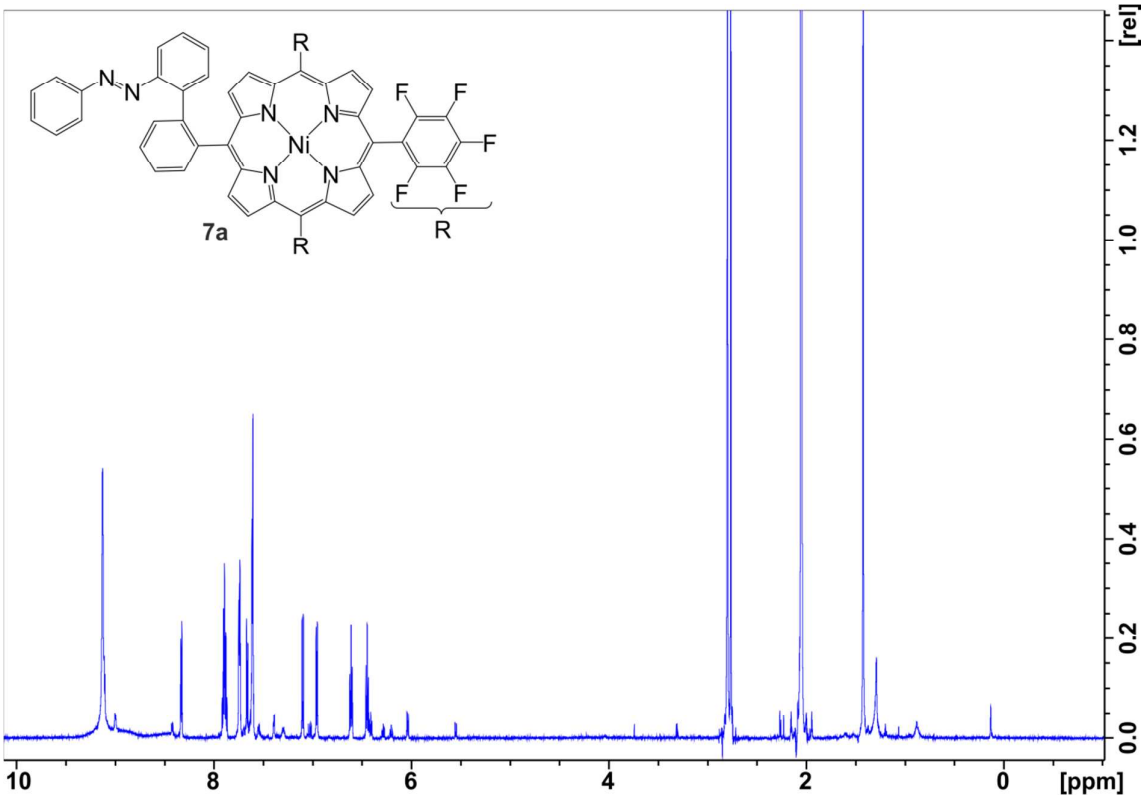


Figure S7. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **7a**.

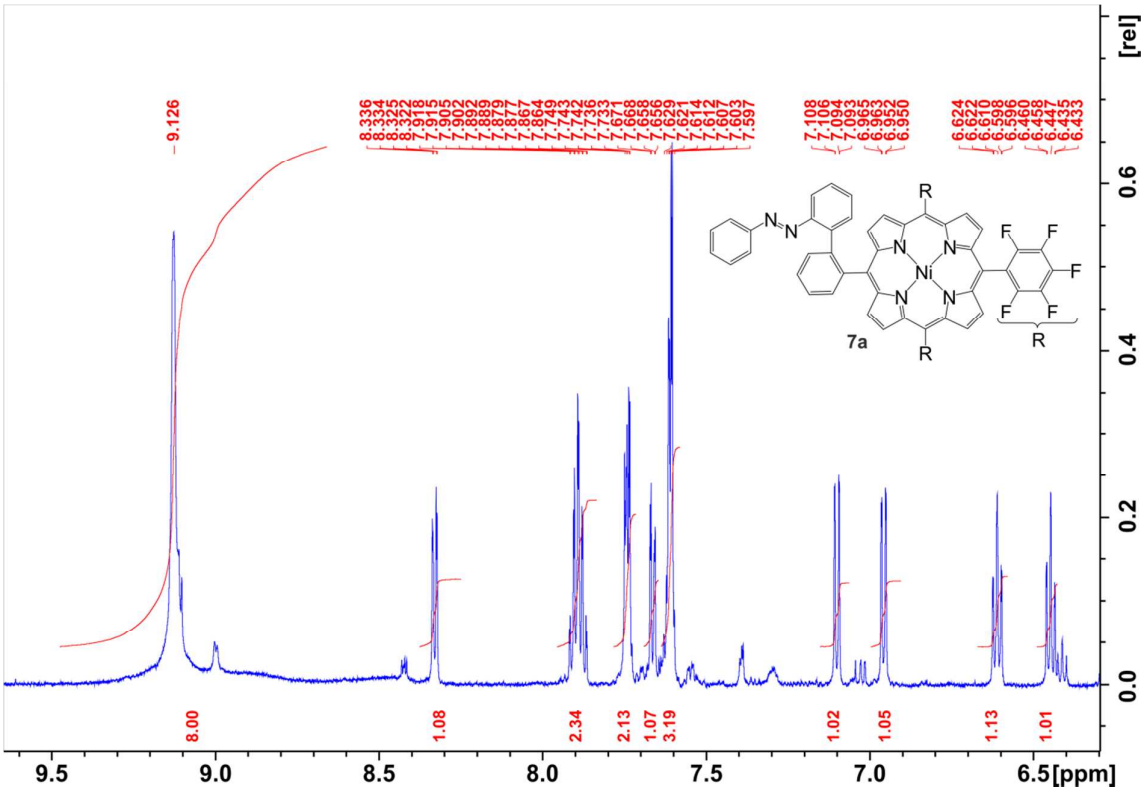


Figure S8. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum (aromatic region) of **7a**.

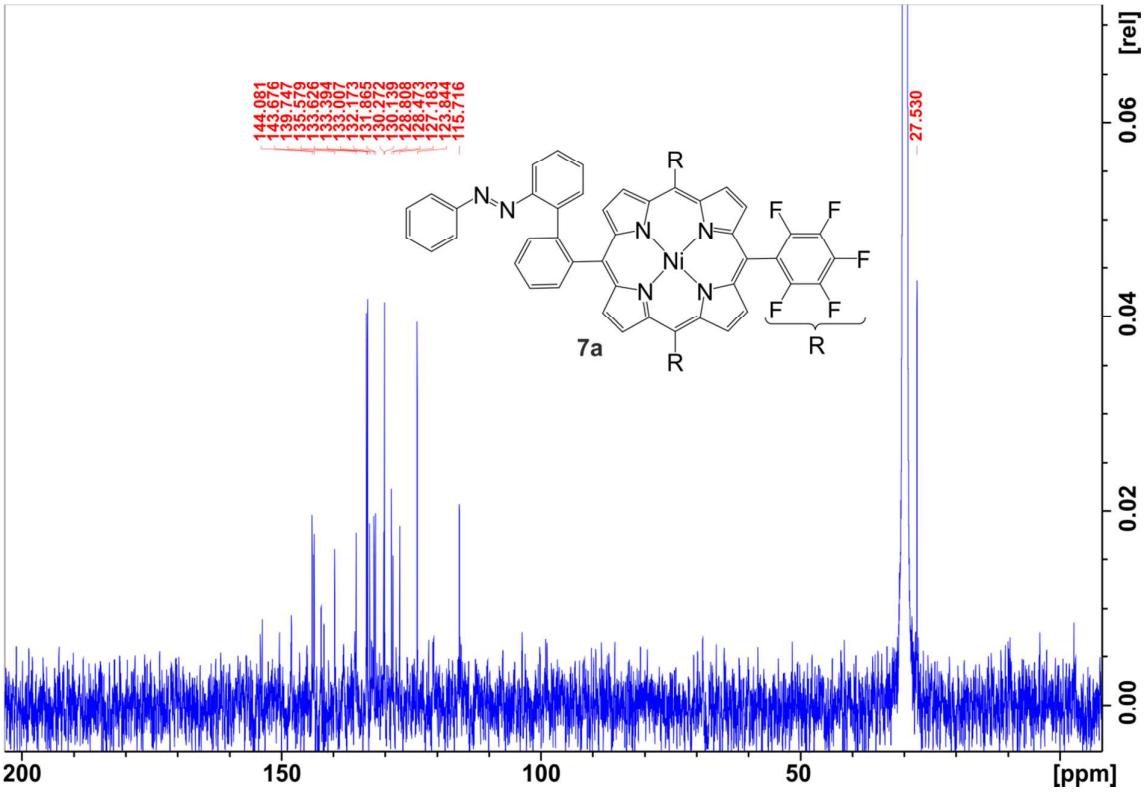


Figure S9. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **7a**.

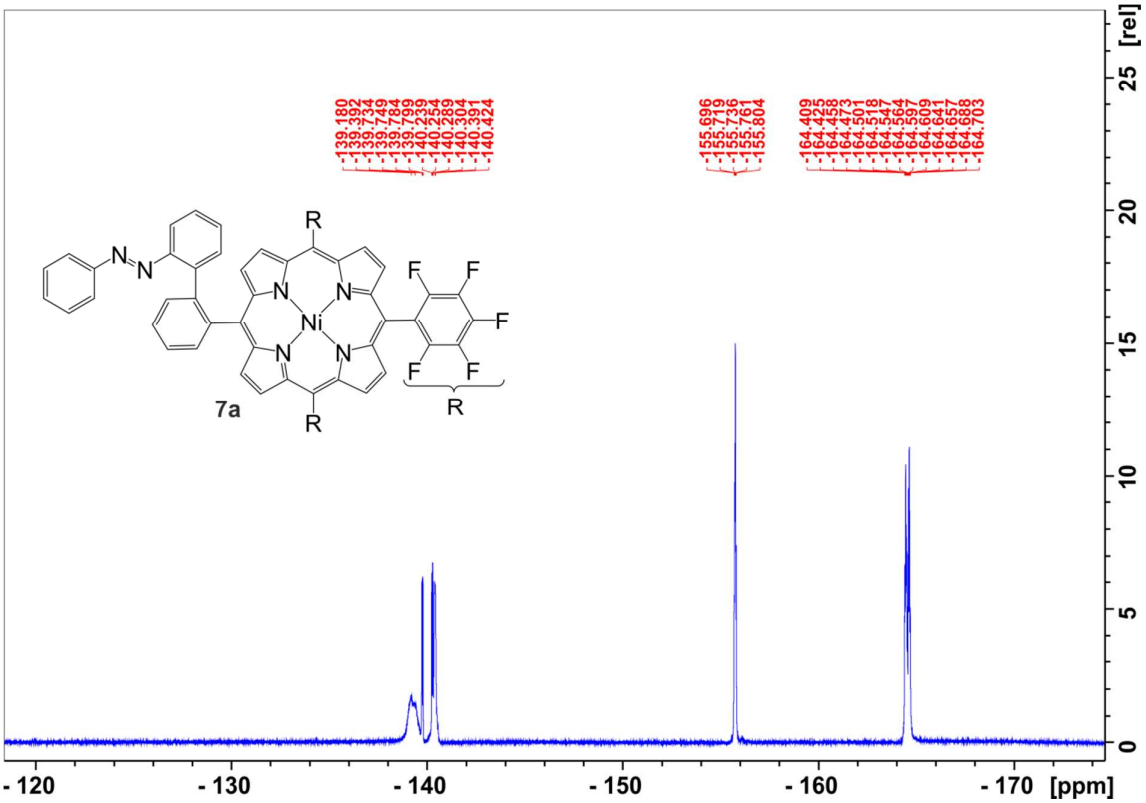


Figure S10. ^{19}F-NMR (470 MHz, acetone-d_6, 300 K) spectrum of **7a**.

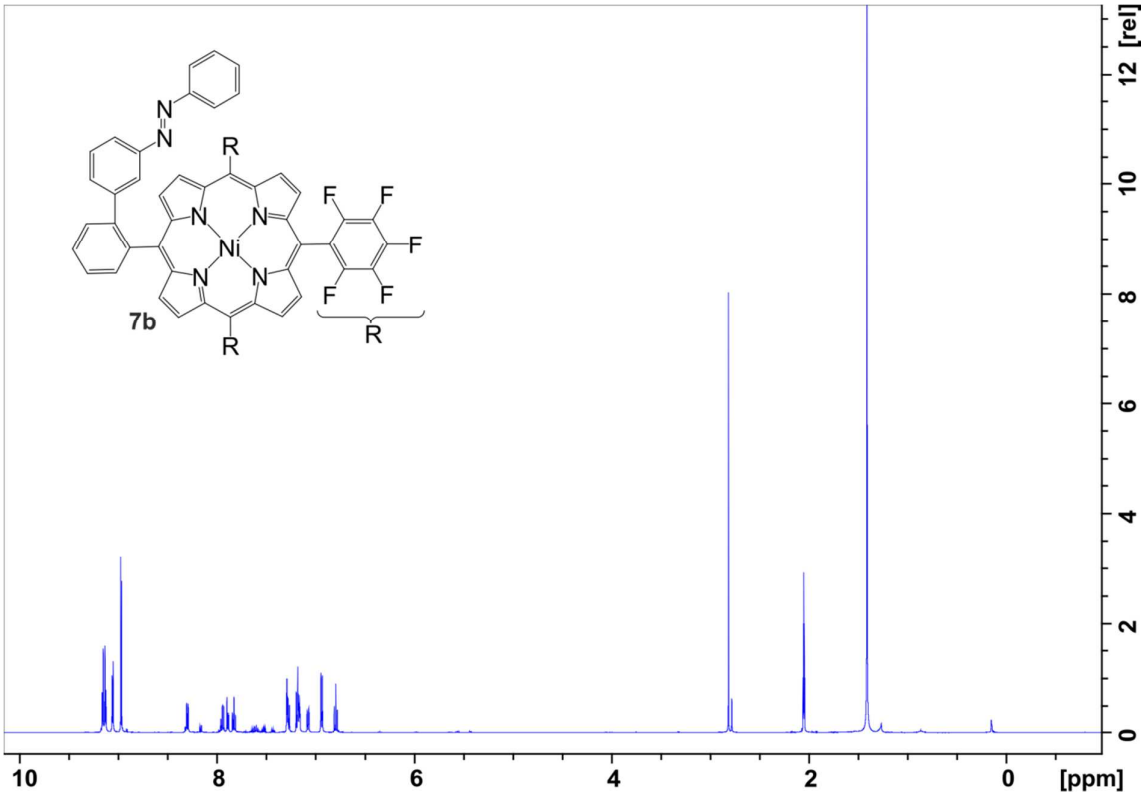


Figure S11. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **7b**.

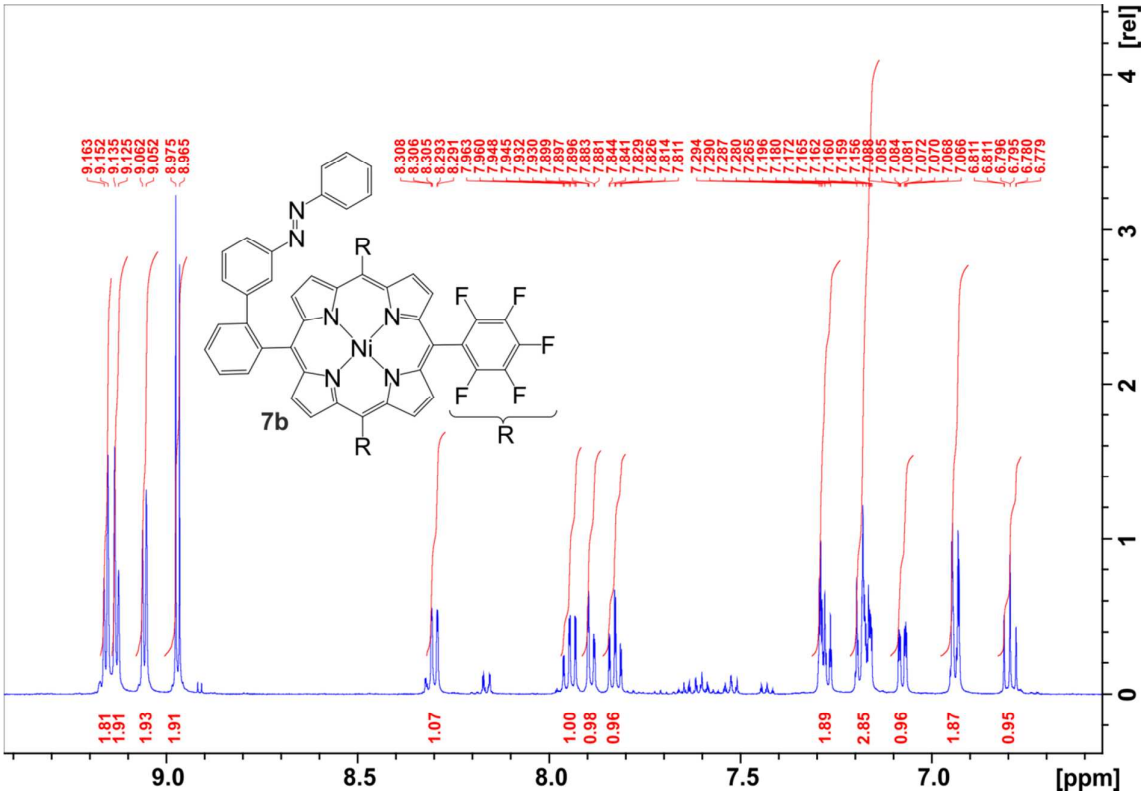


Figure S12. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum (aromatic region) of **7b**.

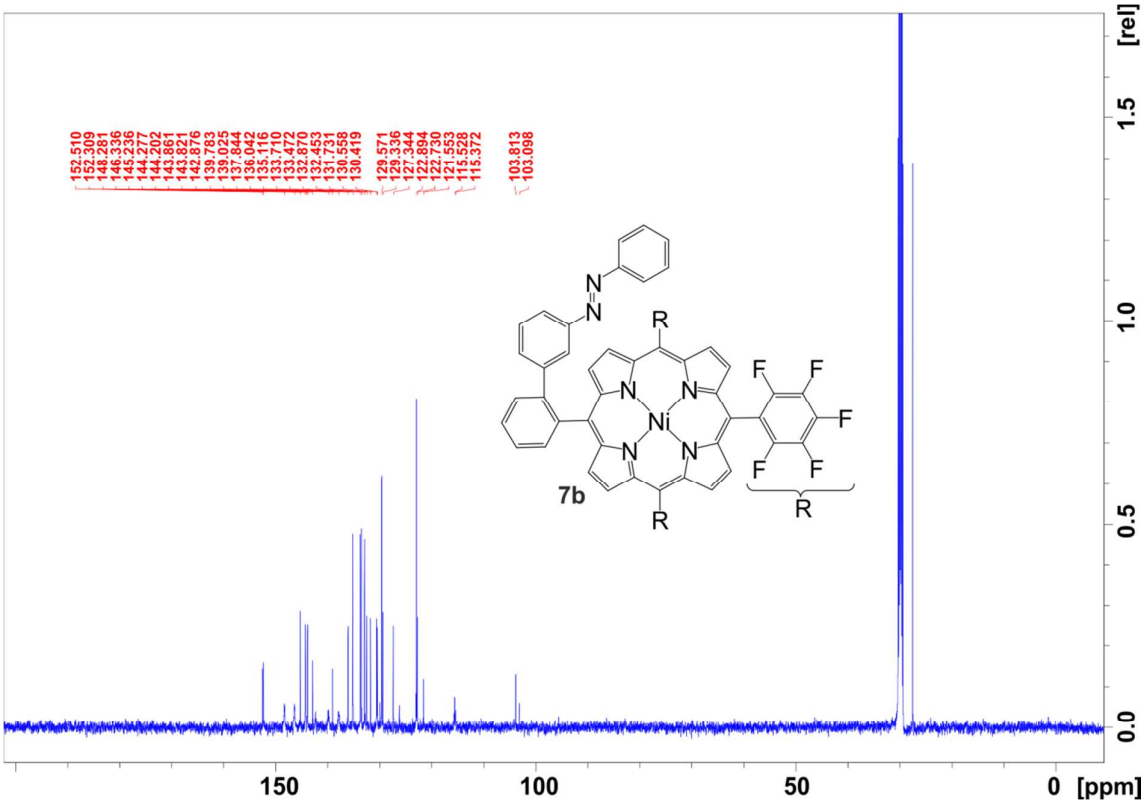


Figure S13. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **7b**.

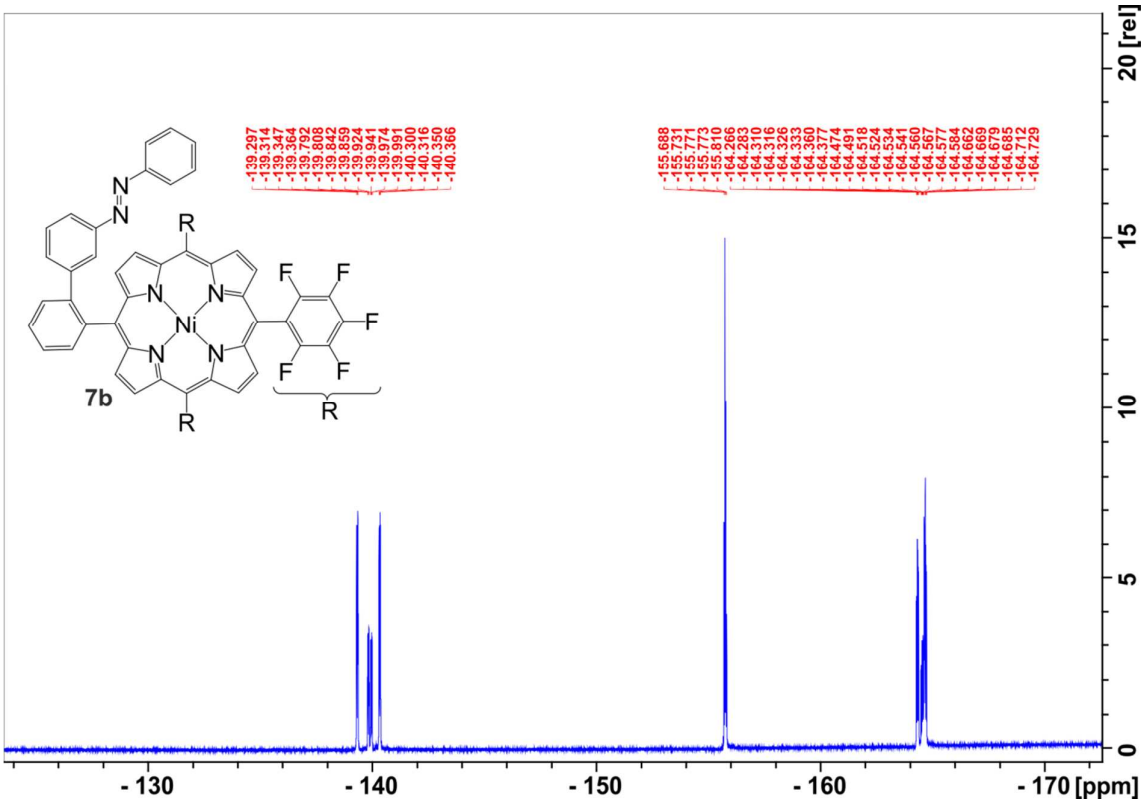


Figure S14. ^{19}F-NMR (470 MHz, acetone-d_6, 300 K) spectrum of **7b**.

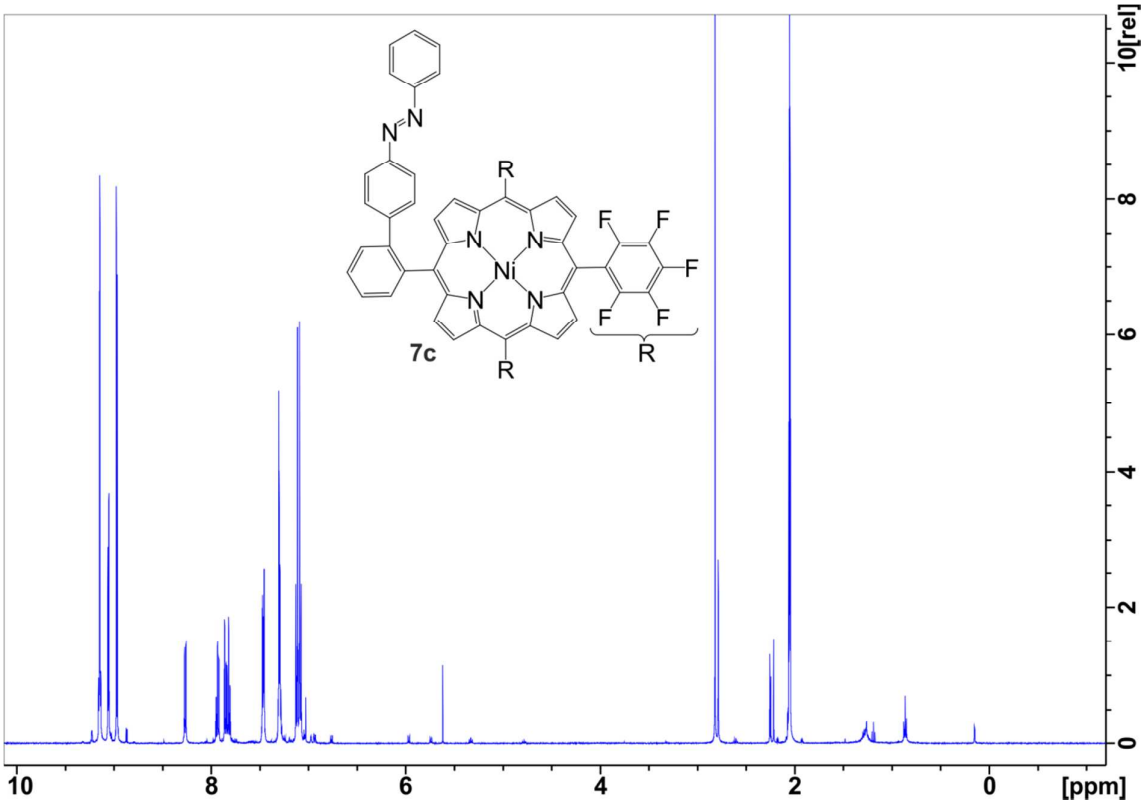


Figure S15. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **7c**.

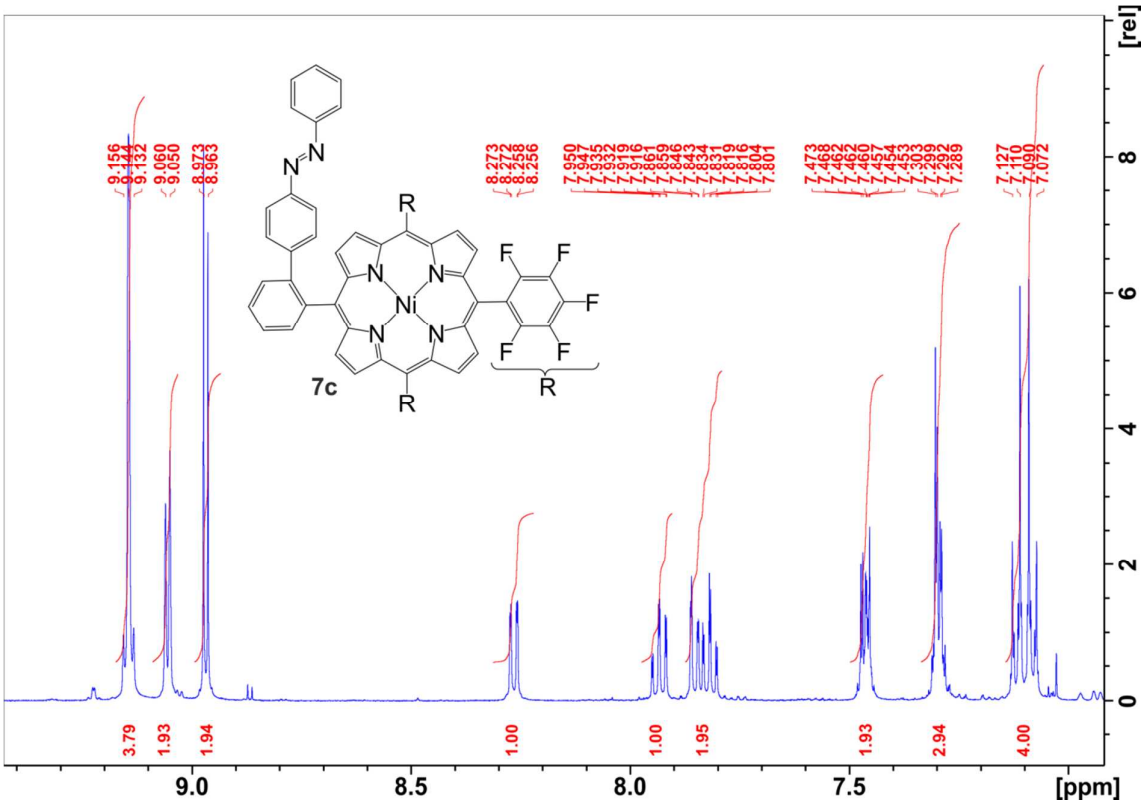


Figure S16. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum (aromatic region) of **7c**.

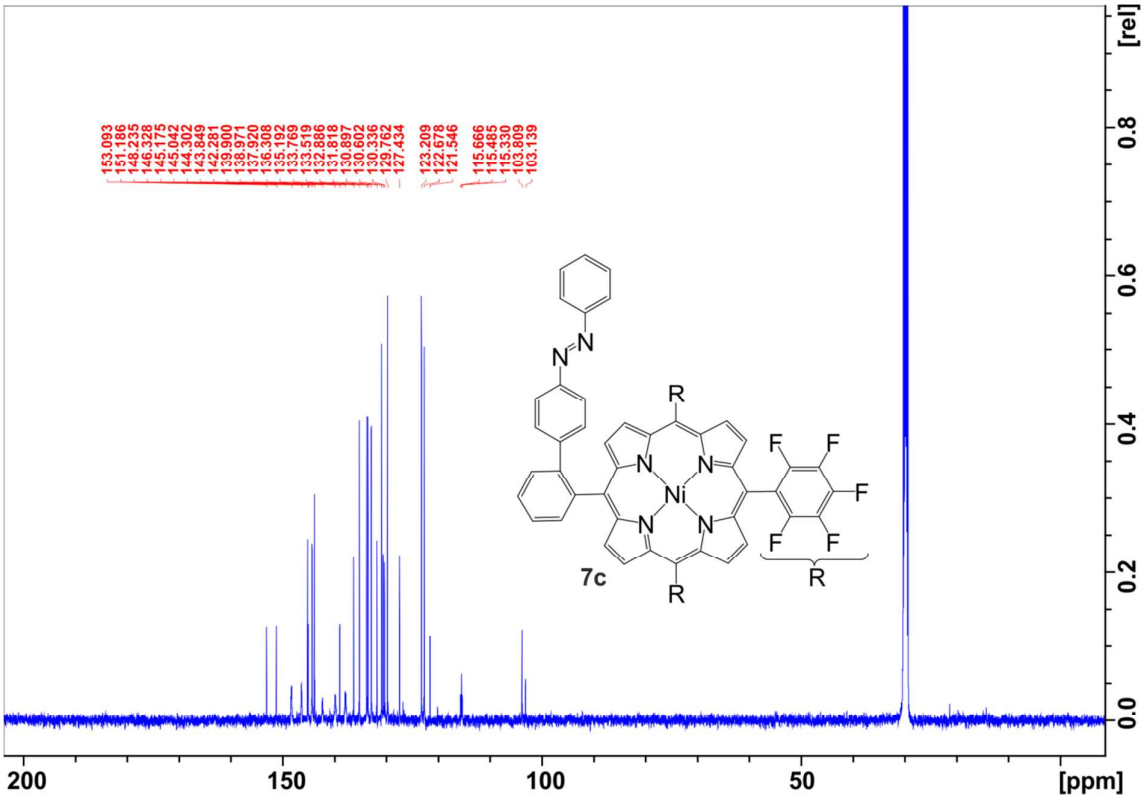


Figure S17. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **7c**.

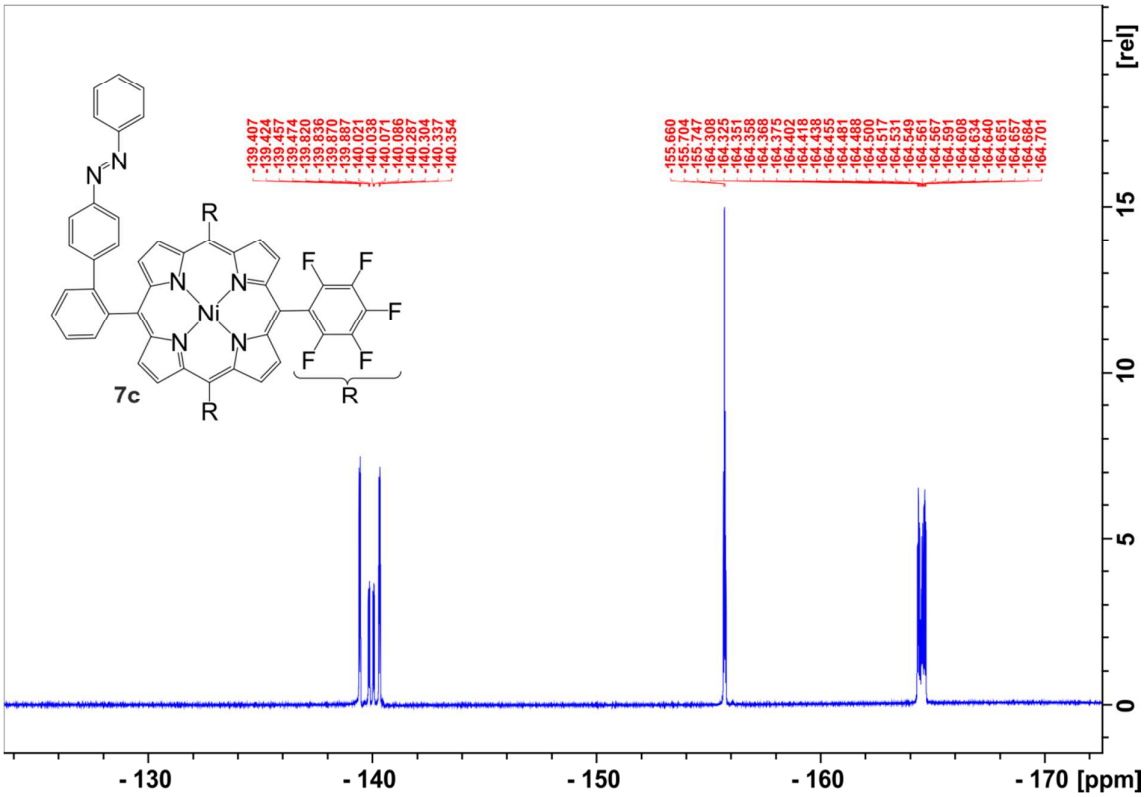


Figure S18. ^{19}F-NMR (470 MHz, acetone-d_6, 300 K) spectrum of **7c**.

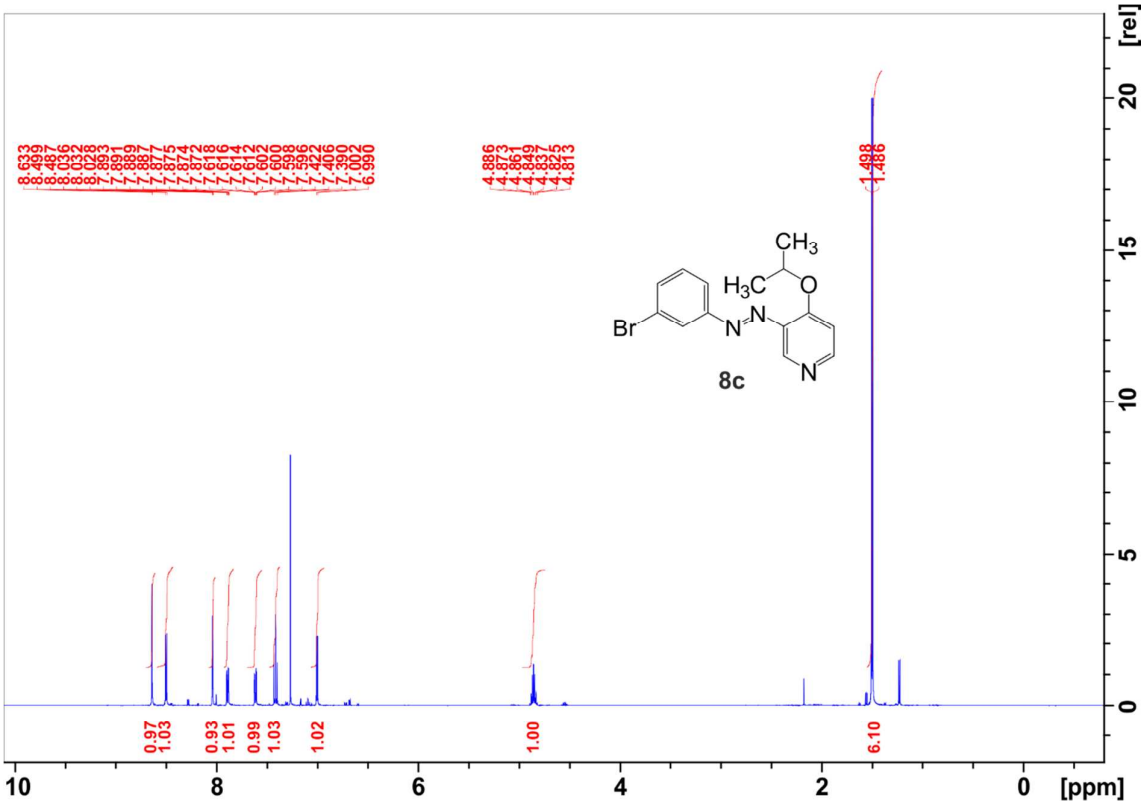


Figure S19. ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **8c**.

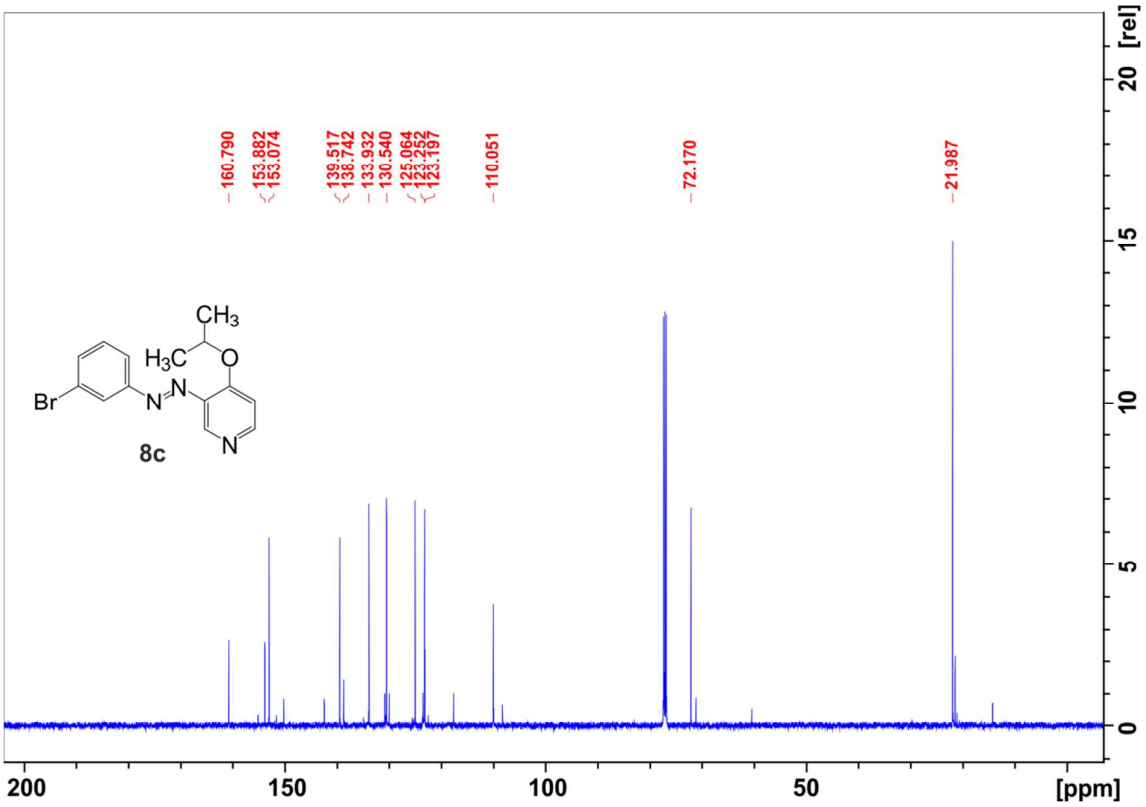


Figure S20. ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K) spectrum of **8c**.

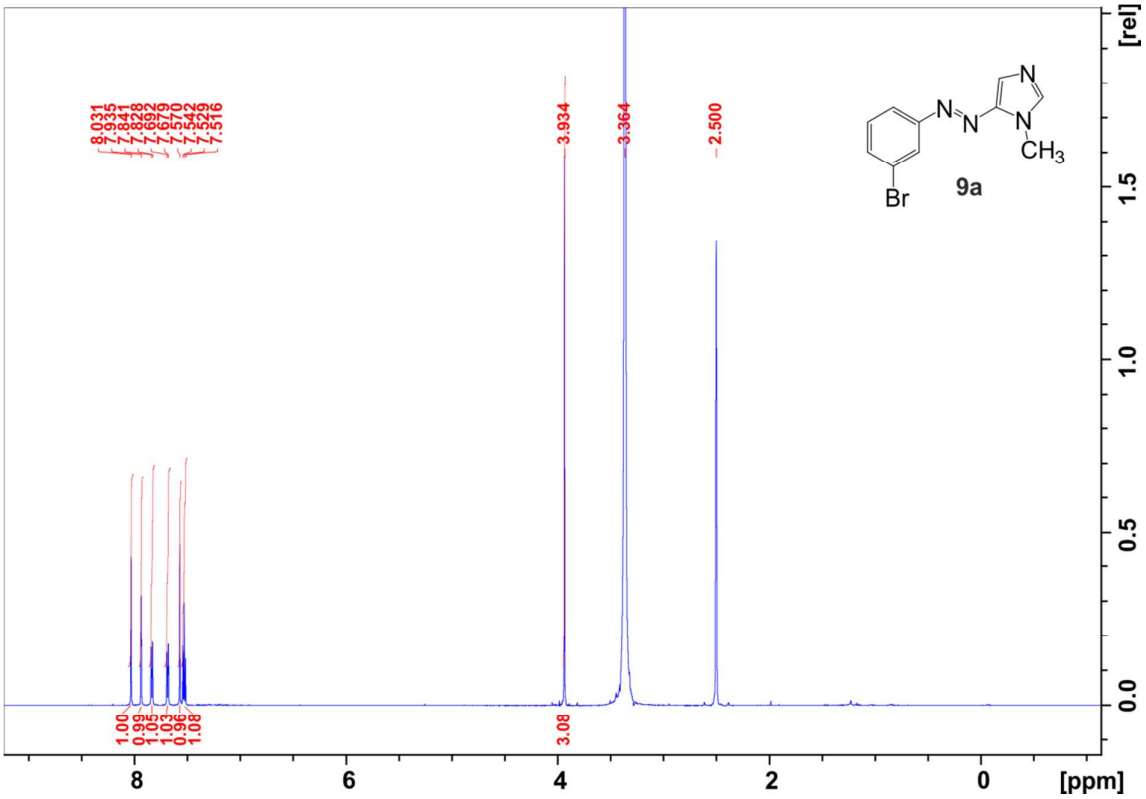


Figure S21. ^{1}H-NMR (600 MHz, DMSO-d_6, 298 K) spectrum of **9a**.

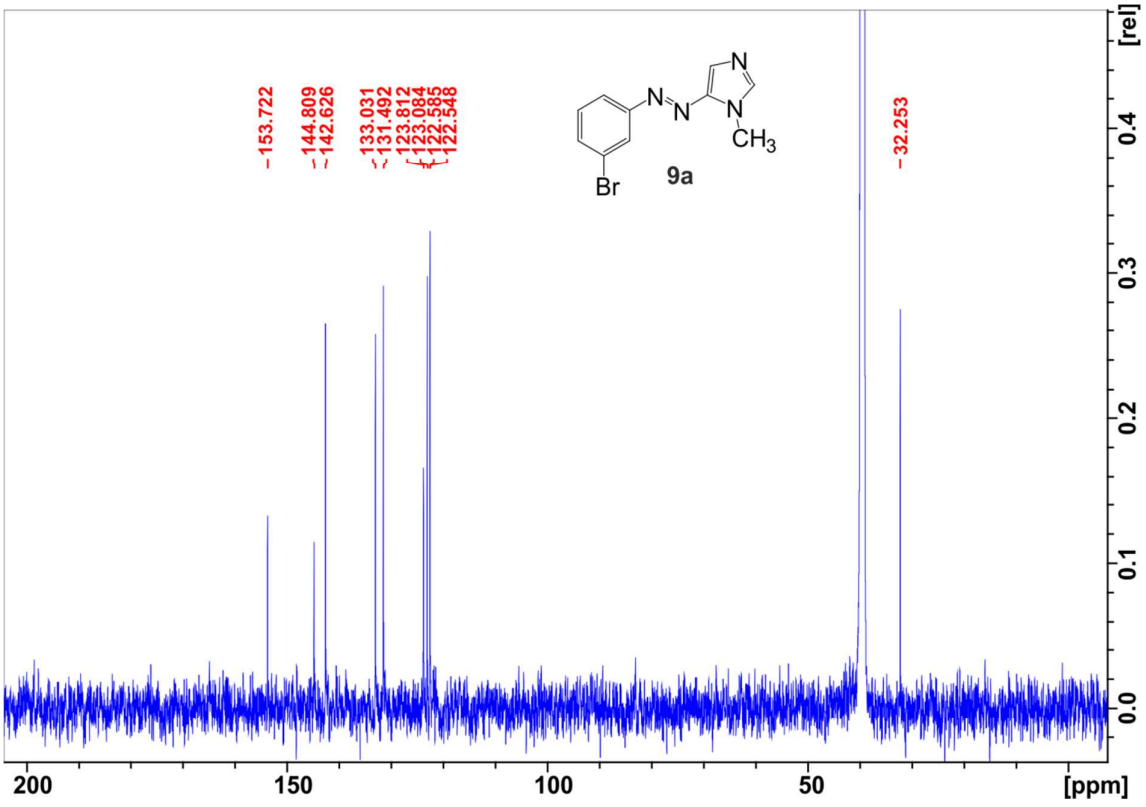


Figure S22. ^{13}C-NMR (150 MHz, DMSO-d_6, 298 K) spectrum of **9a**.

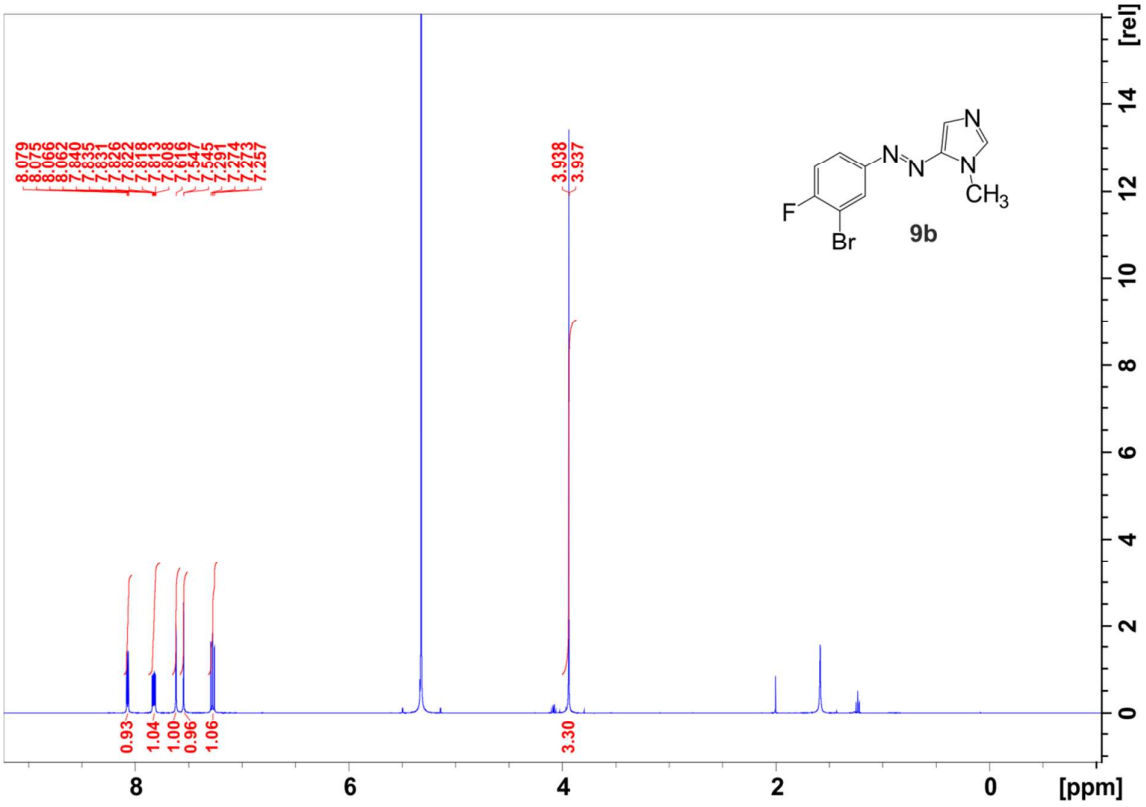


Figure S23. ^{1}H-NMR (500 MHz, CD_2Cl_2, 300 K) spectrum of **9b**.

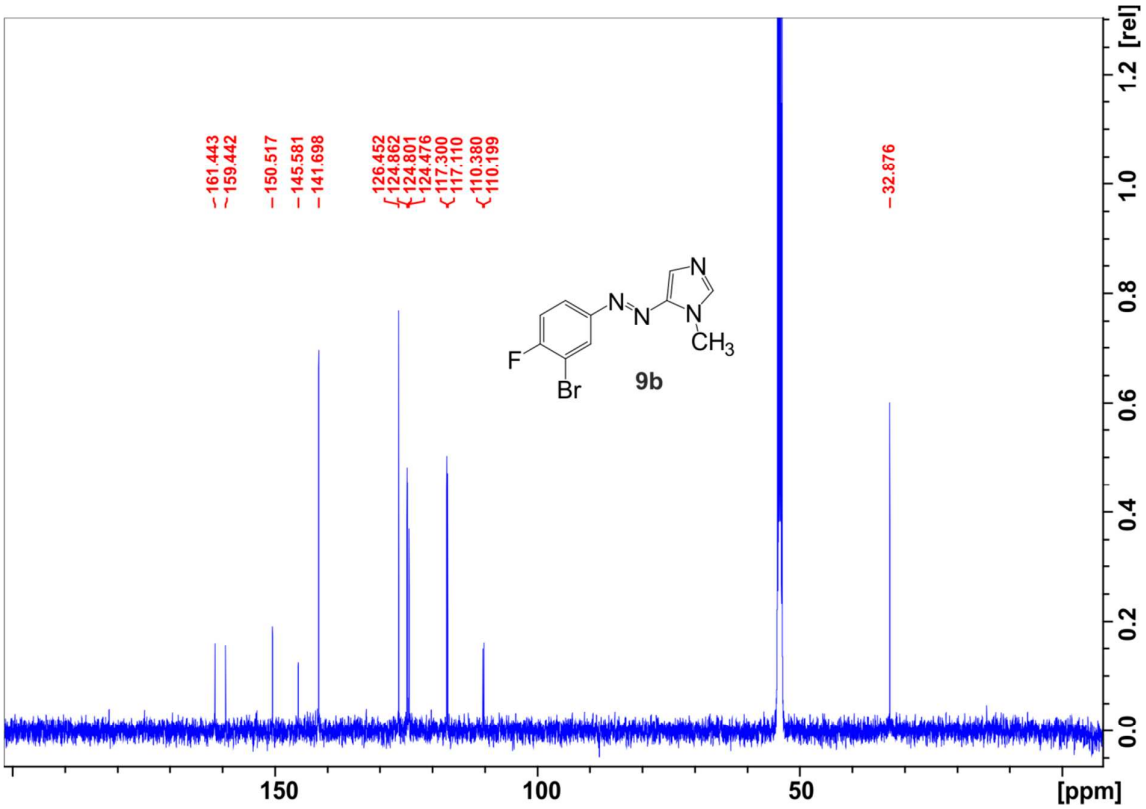


Figure S24. ^{13}C-NMR (125 MHz, CD_2Cl_2, 300 K) spectrum of **9b**.

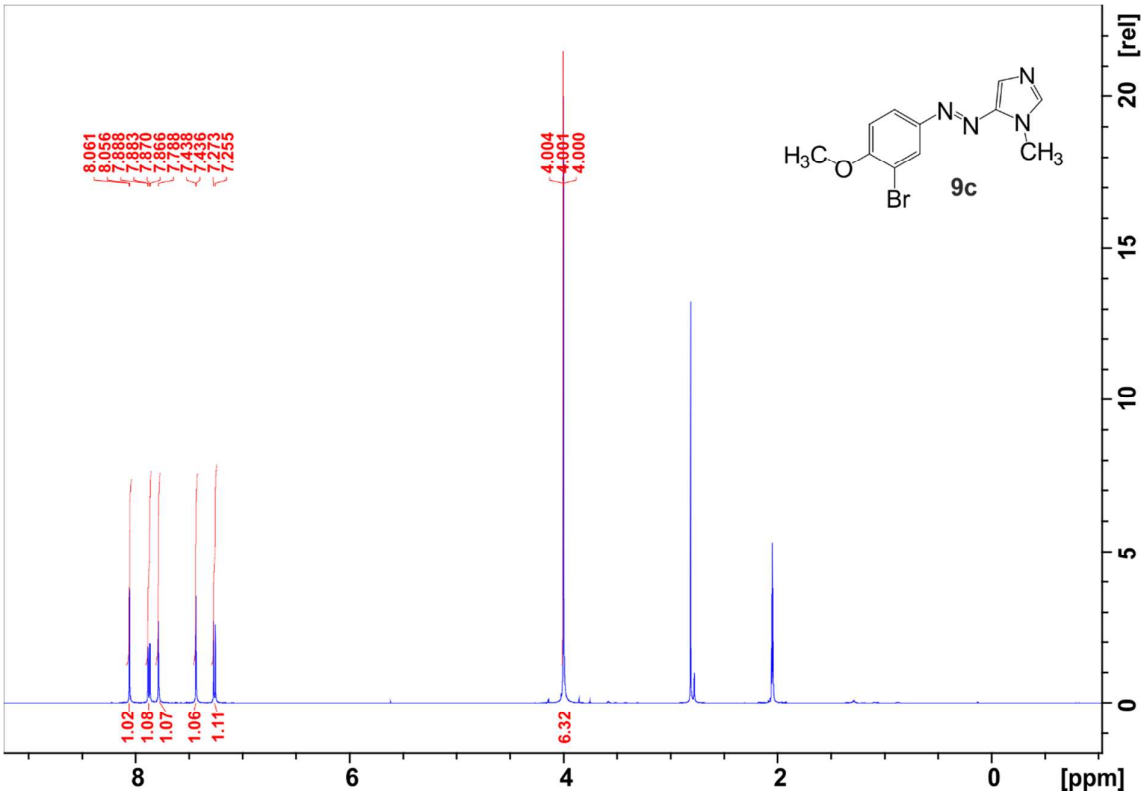


Figure S25. ^{1}H-NMR (500 MHz, acetone-d_6, 300 K) spectrum of **9c**.

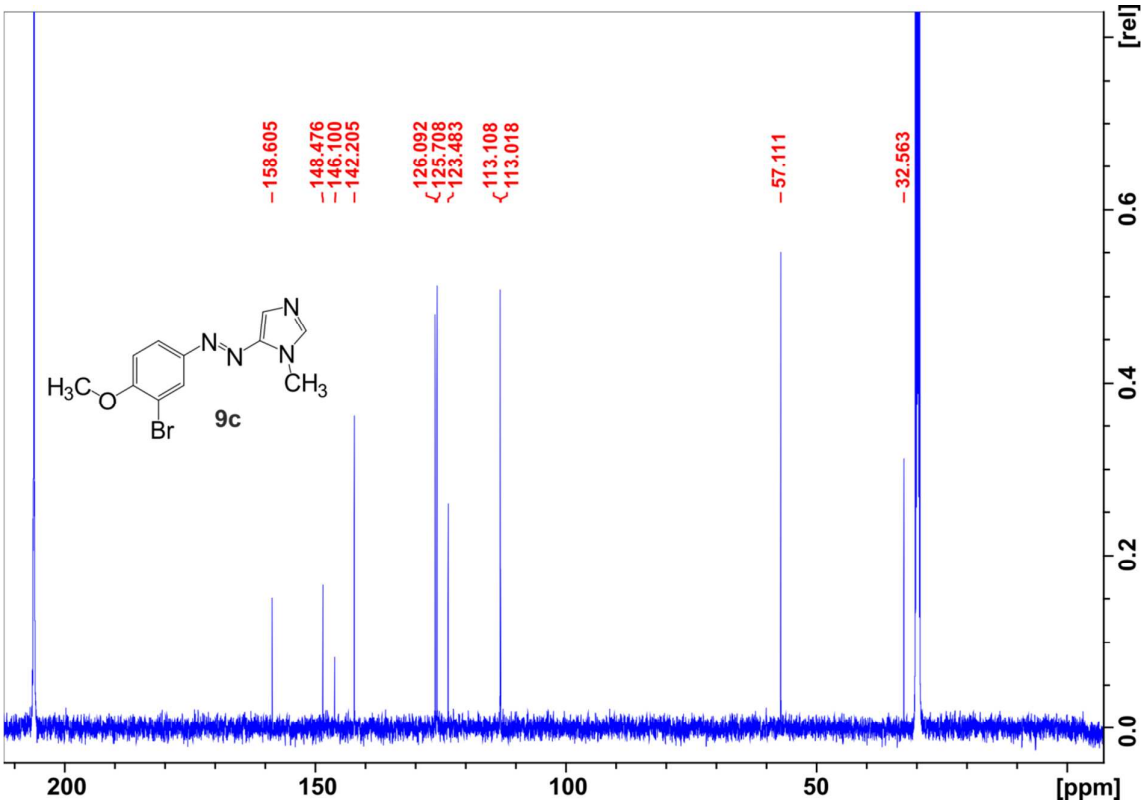


Figure S26. ^{13}C-NMR (125 MHz, acetone-d_6, 300 K) spectrum of **9c**.

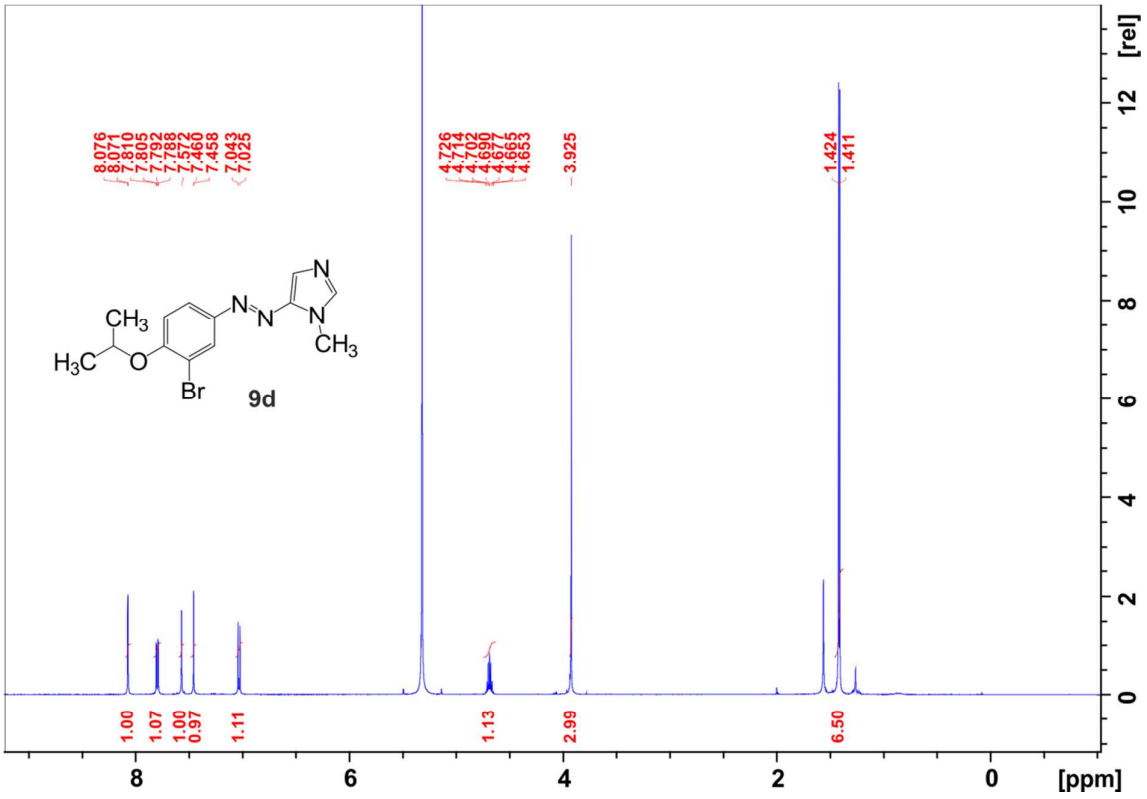


Figure S27. ^{1}H-NMR (500 MHz, CD_2Cl_2, 300 K) spectrum of **9d**.

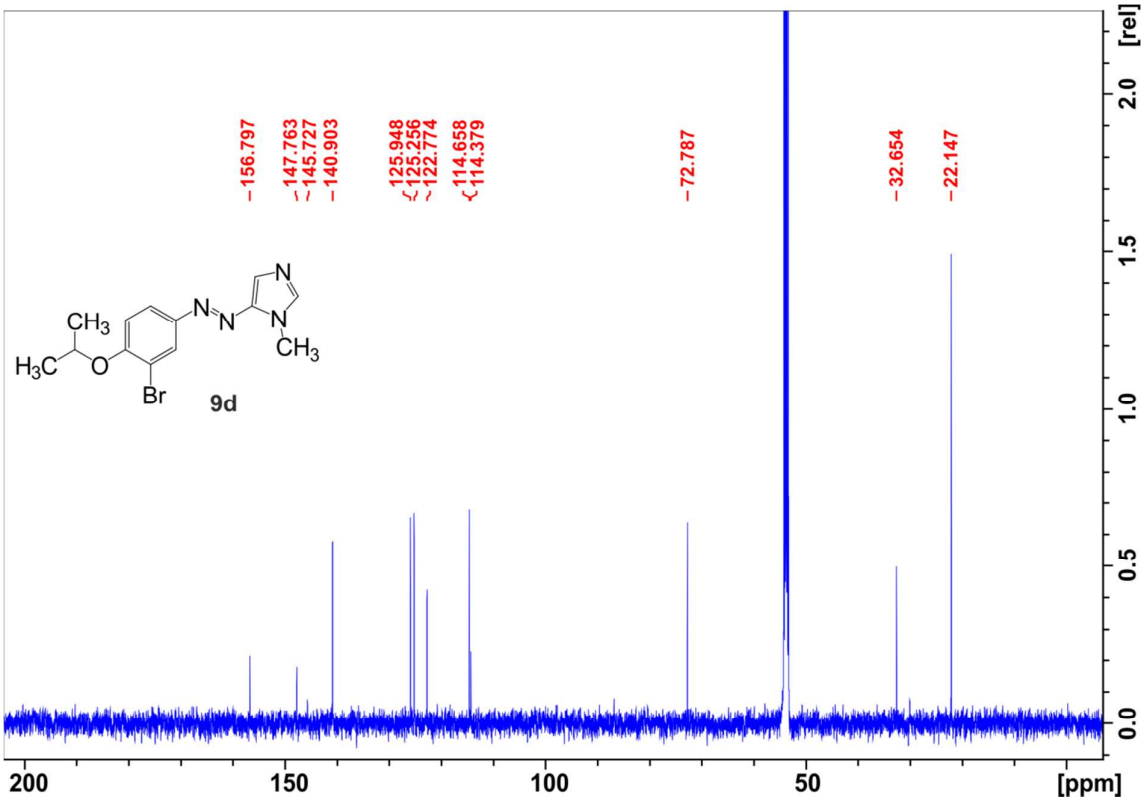


Figure S28. ^{13}C-NMR (125 MHz, CD_2Cl_2, 300 K) spectrum of **9d**.

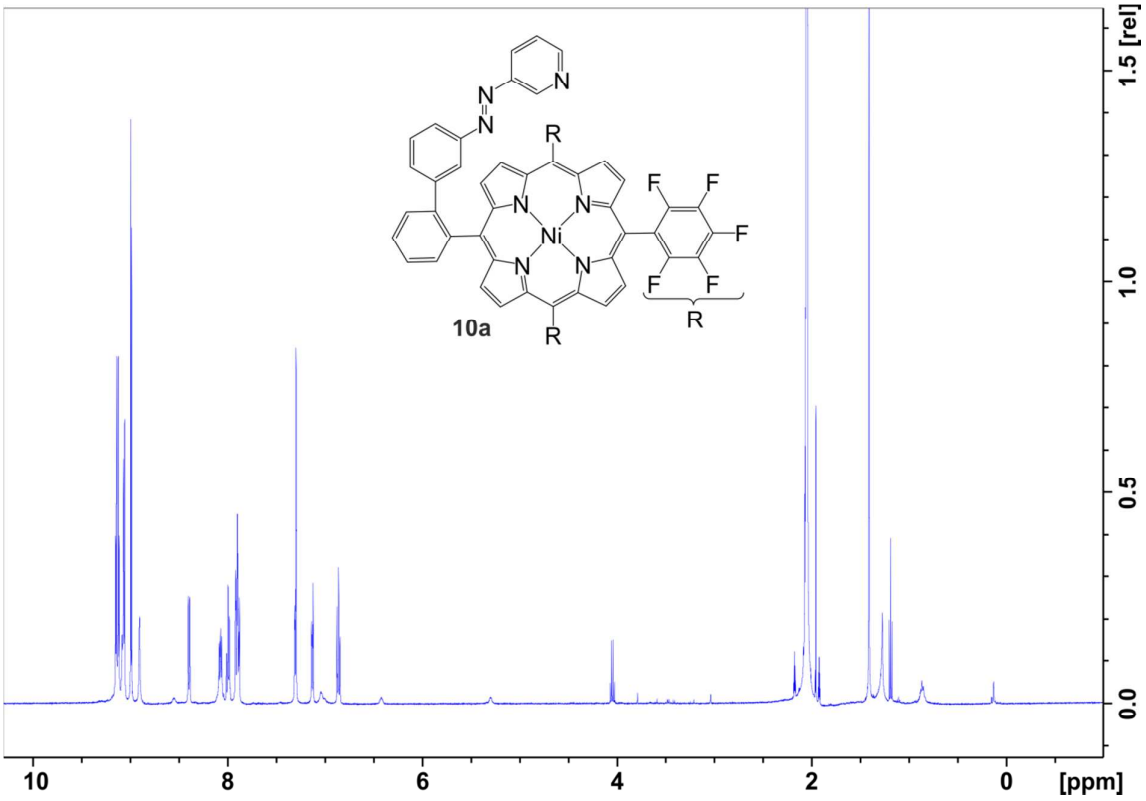


Figure S29. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10a**.

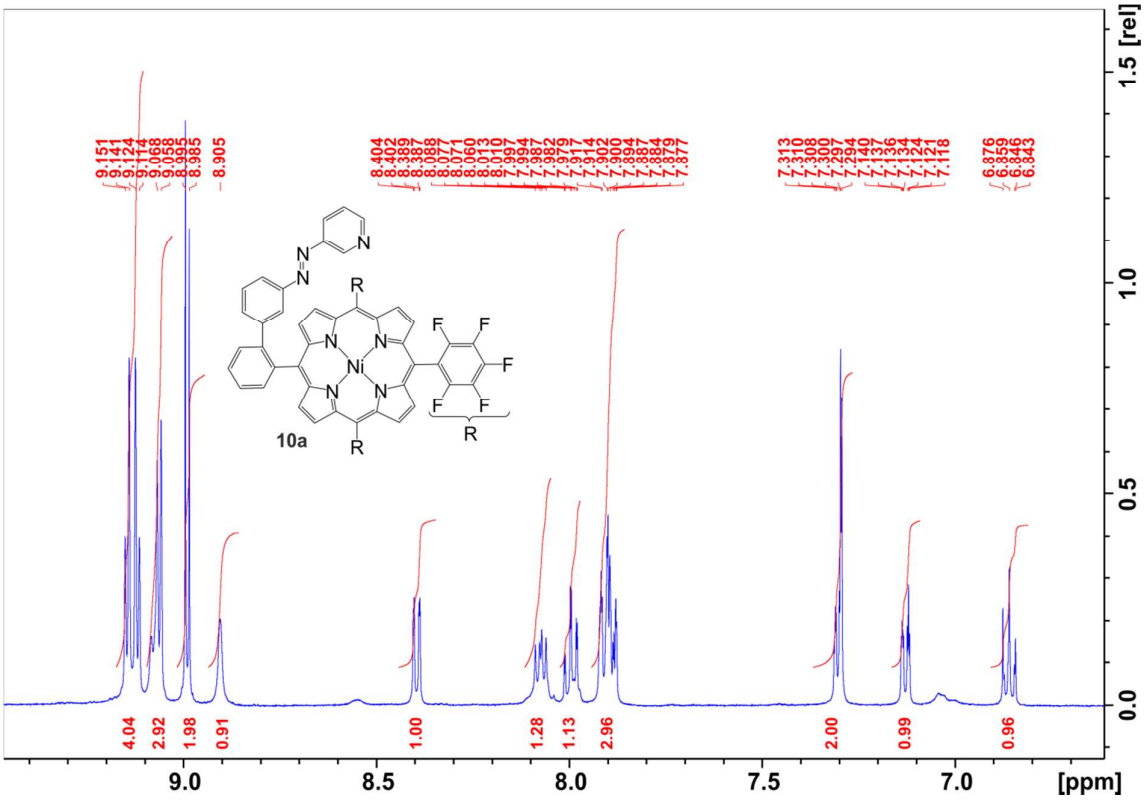


Figure S30. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **10a**.

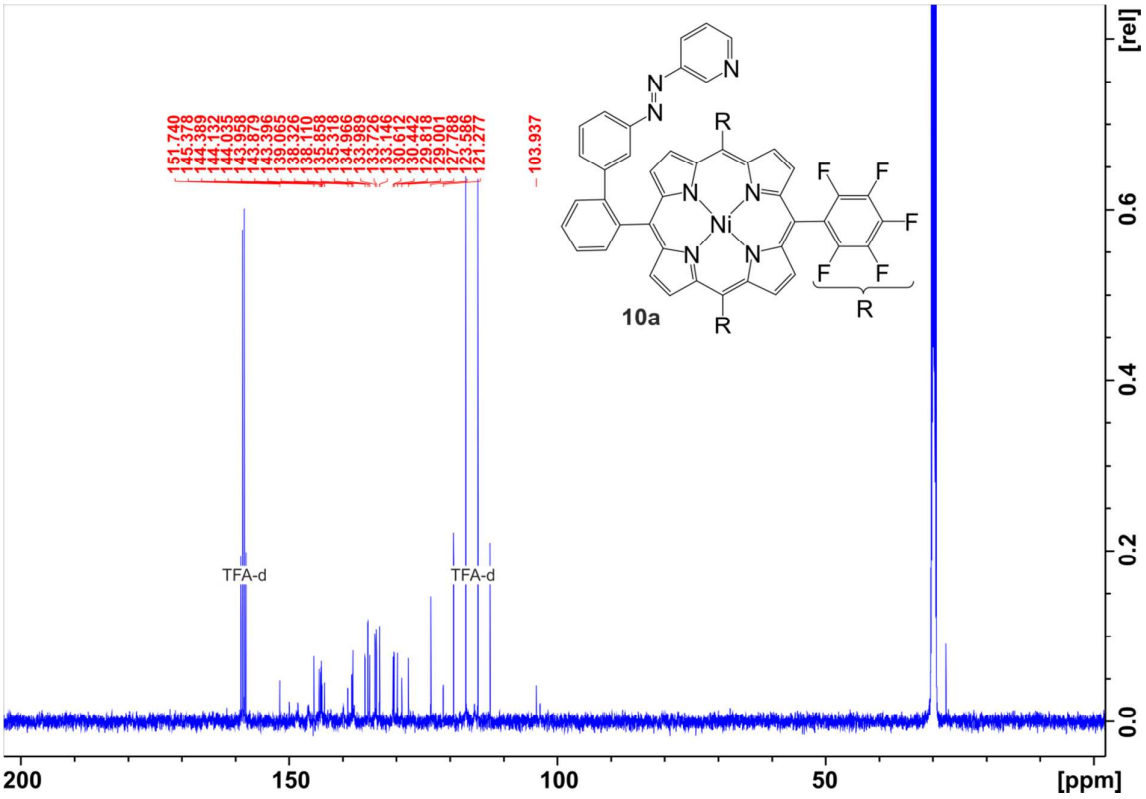


Figure S31. ^{13}C-NMR (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10a**.

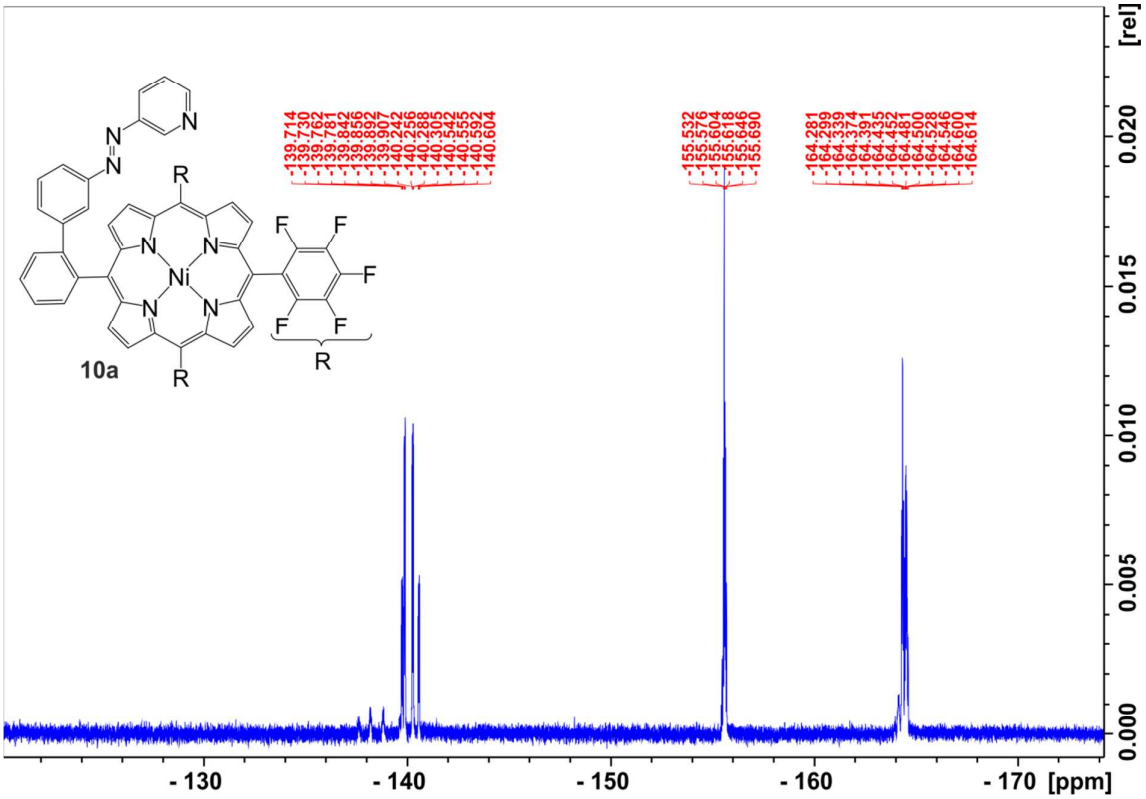


Figure S32. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10a**.

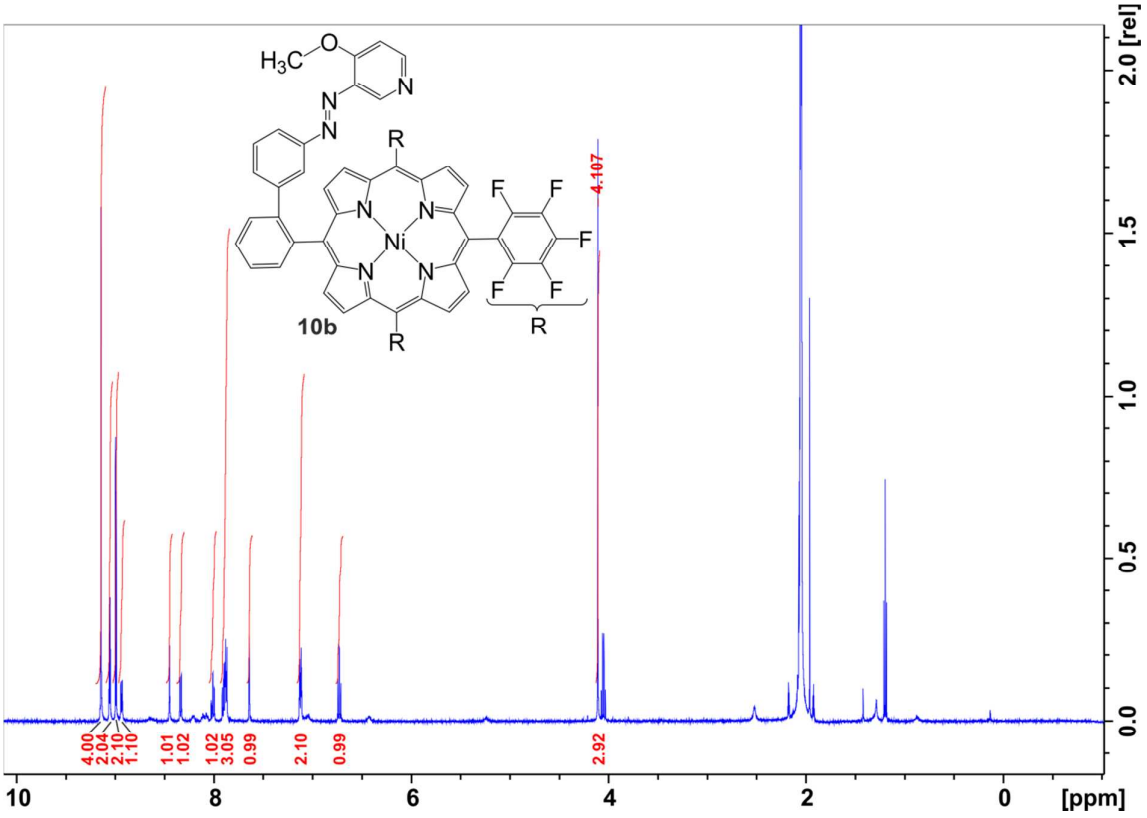


Figure S33. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10b**.

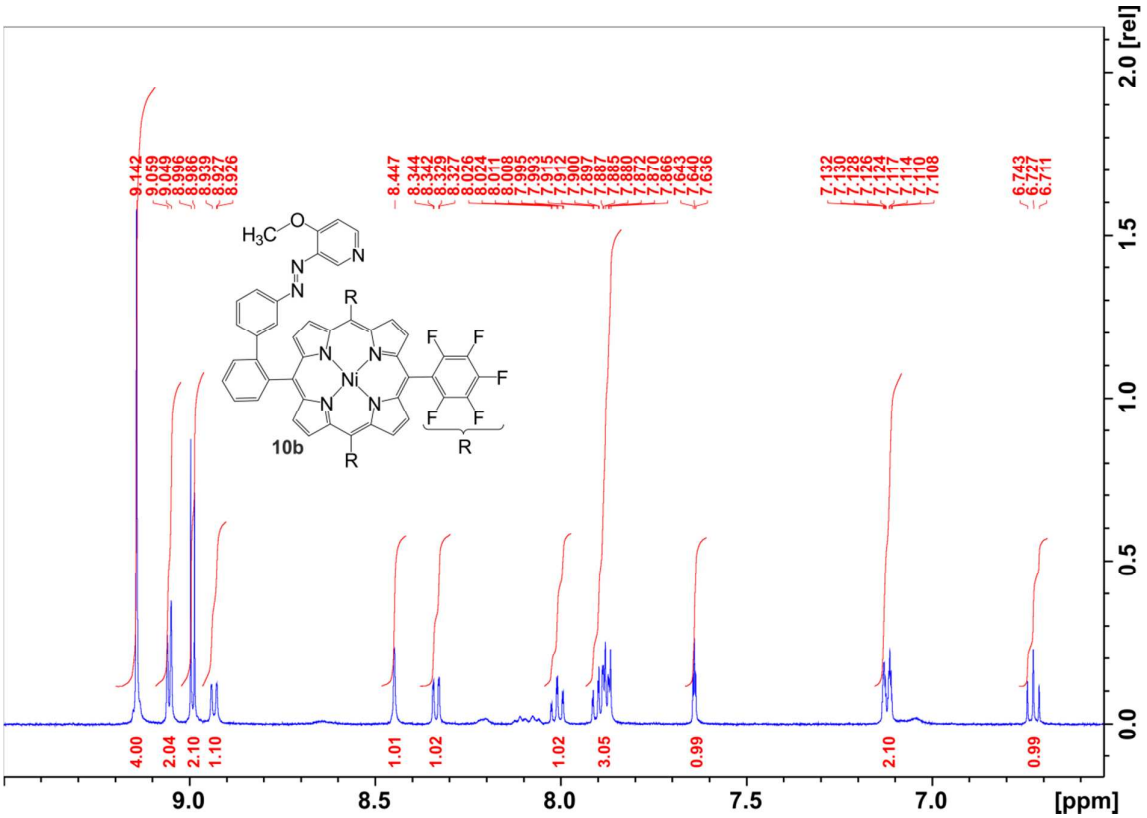


Figure S34. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **10b**.

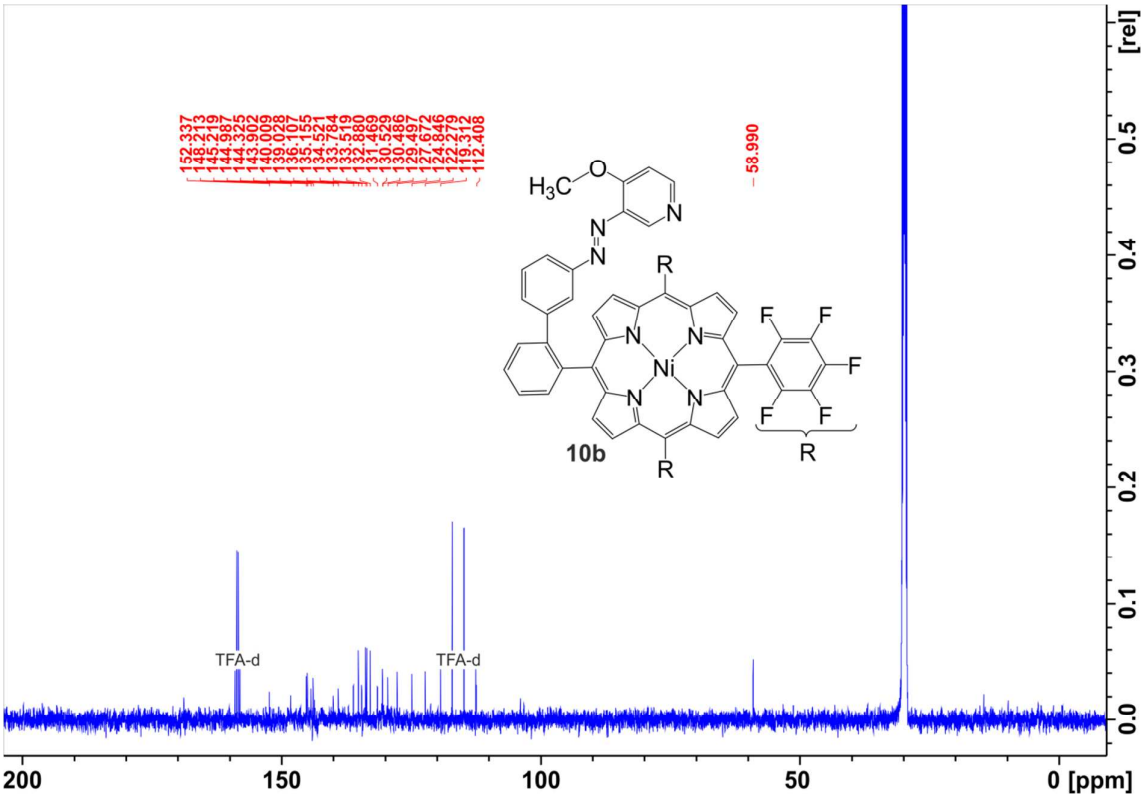


Figure S35. ^{13}C-NMR (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10b**.

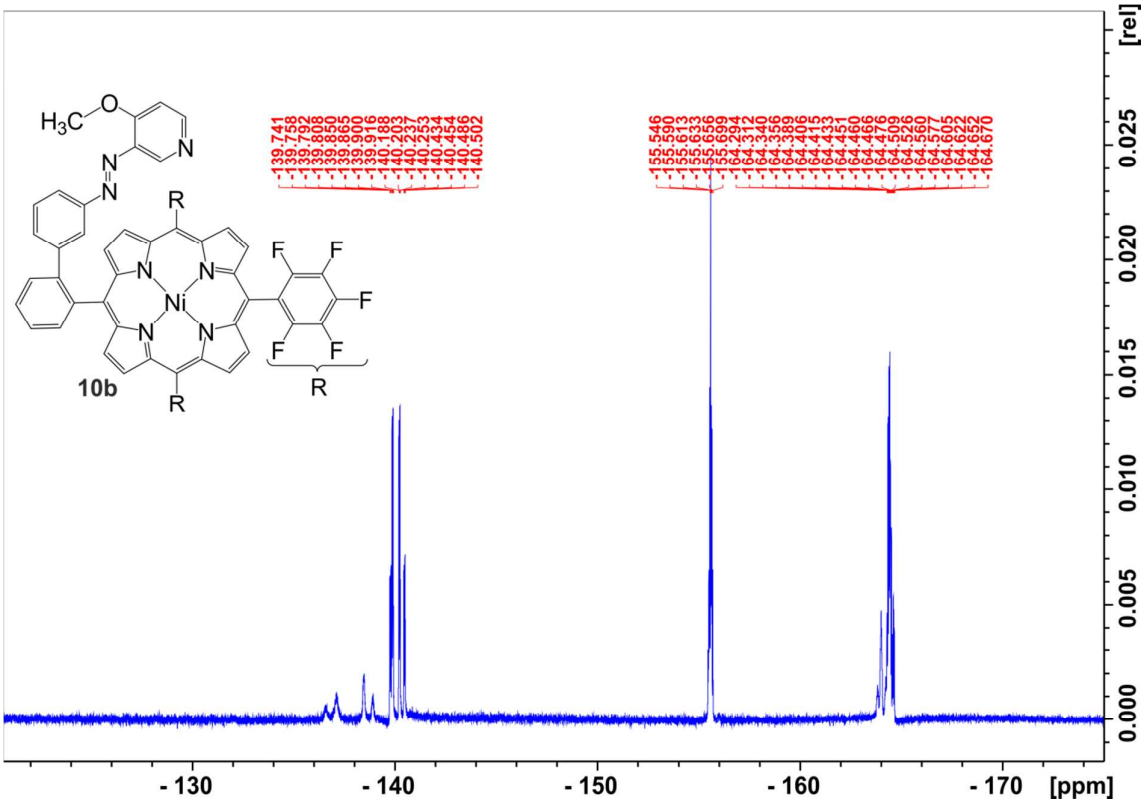


Figure S36. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10b**.

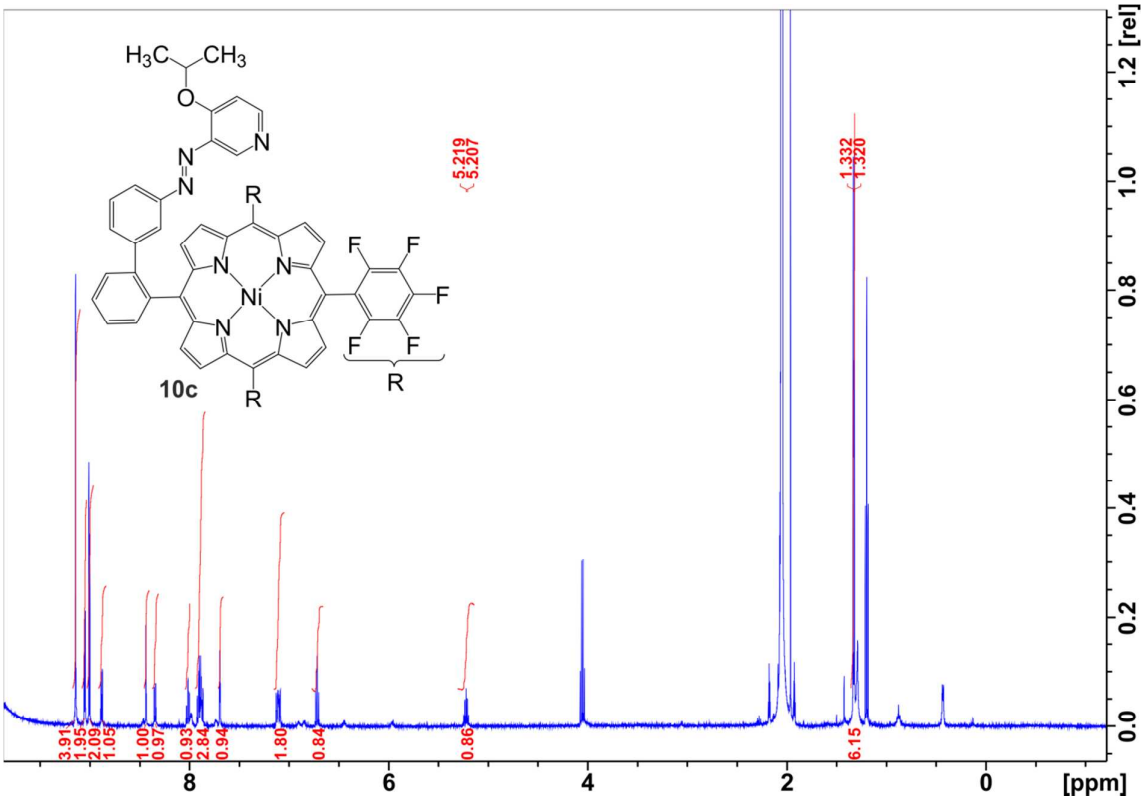


Figure S37. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10c**.

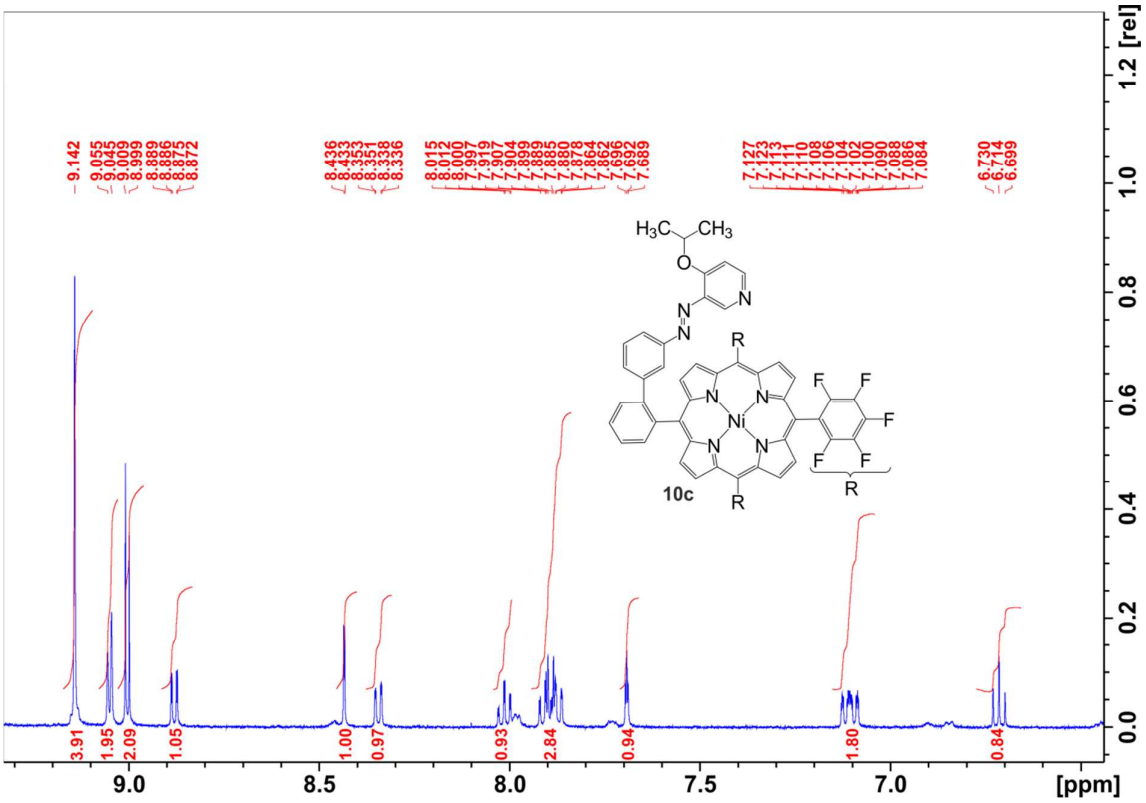


Figure S38. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **10c**.

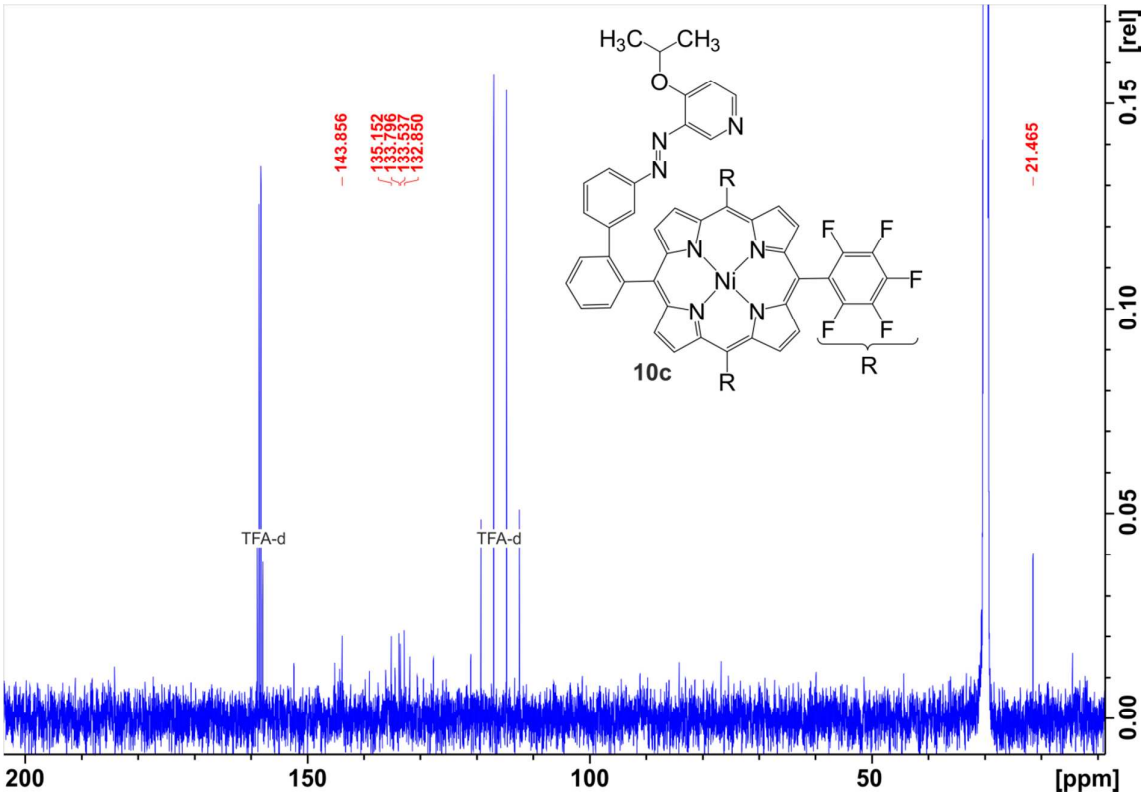


Figure S39. ^{13}C-NMR (125 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10c**.

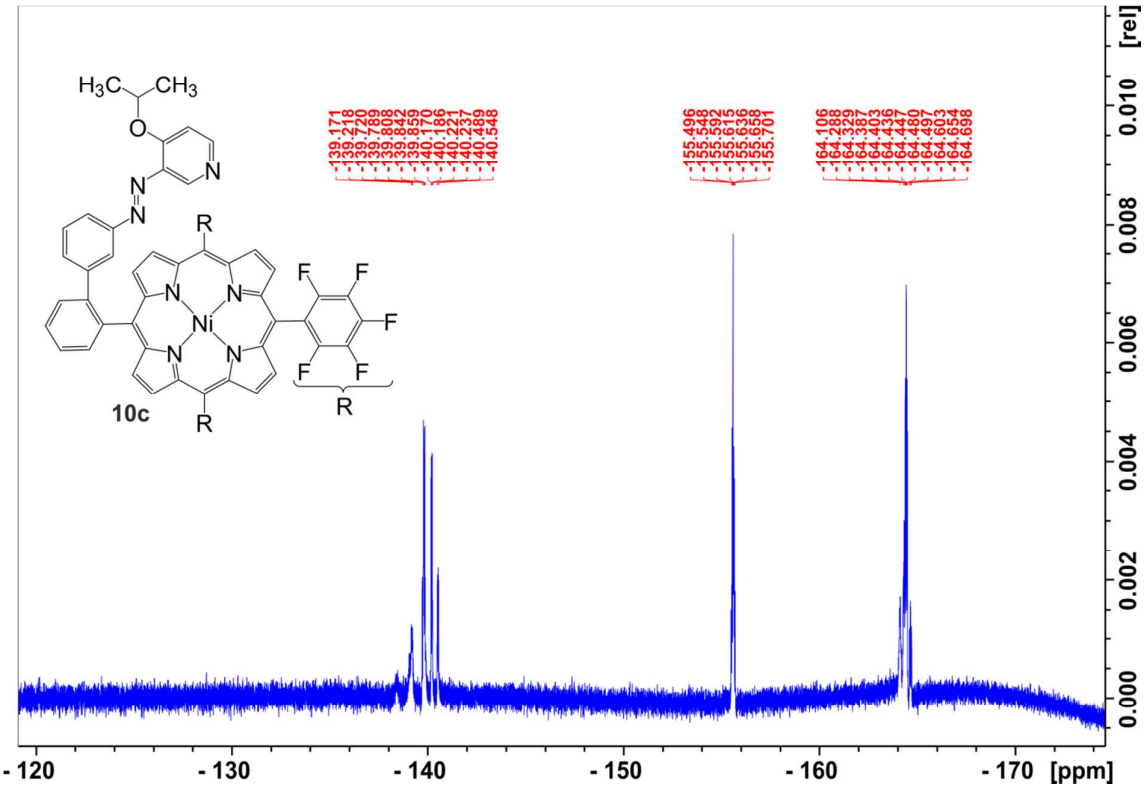


Figure S40. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **10c**.

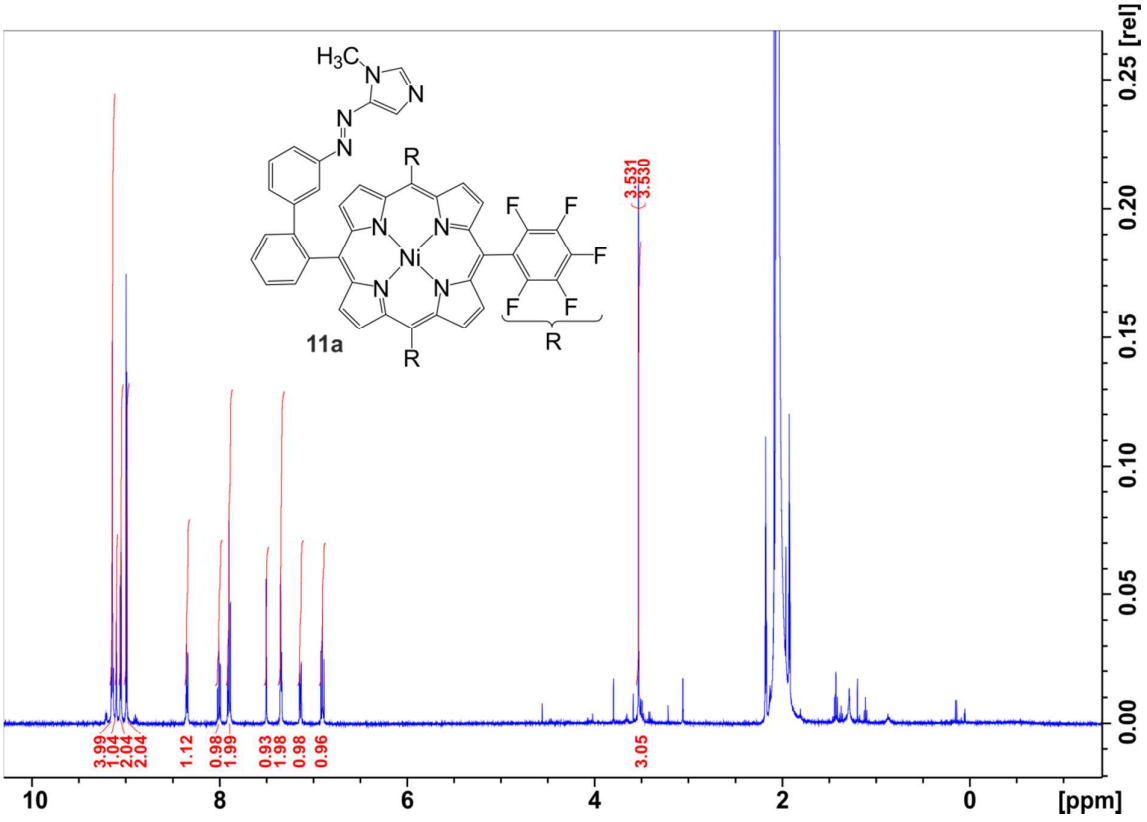


Figure S41. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11a**.

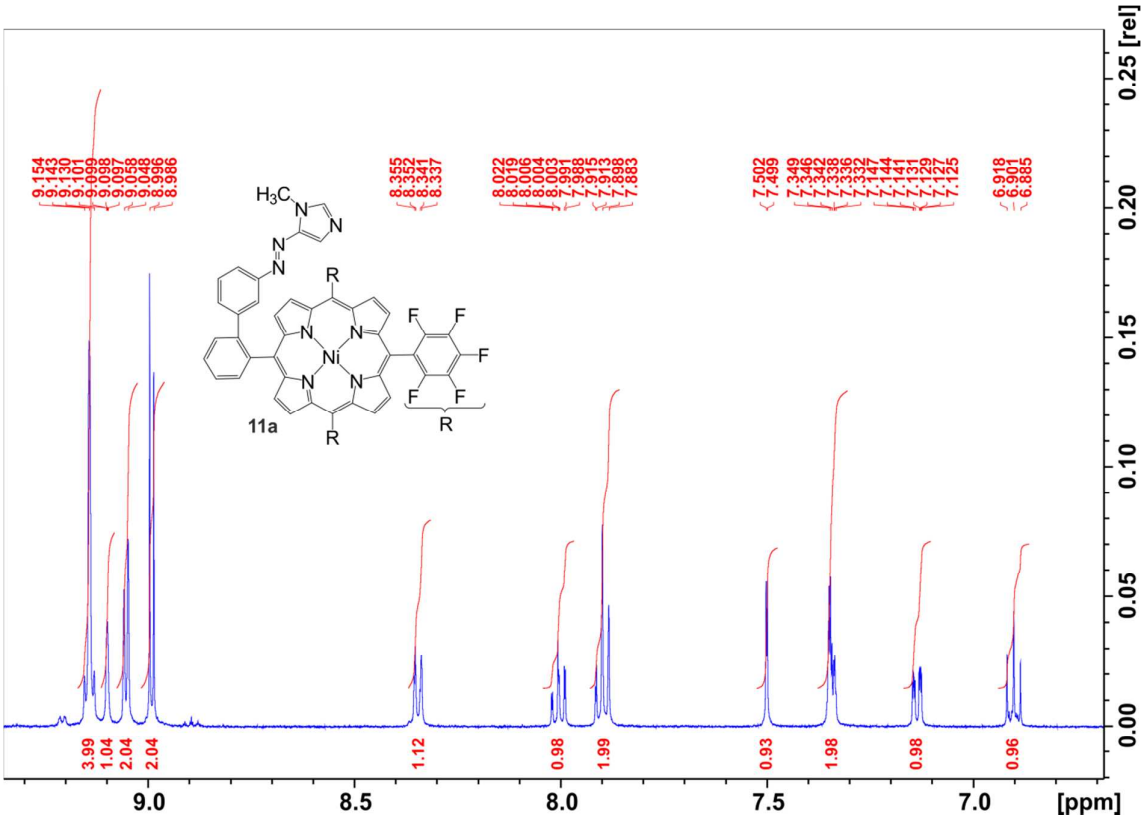


Figure S42. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **11a**.

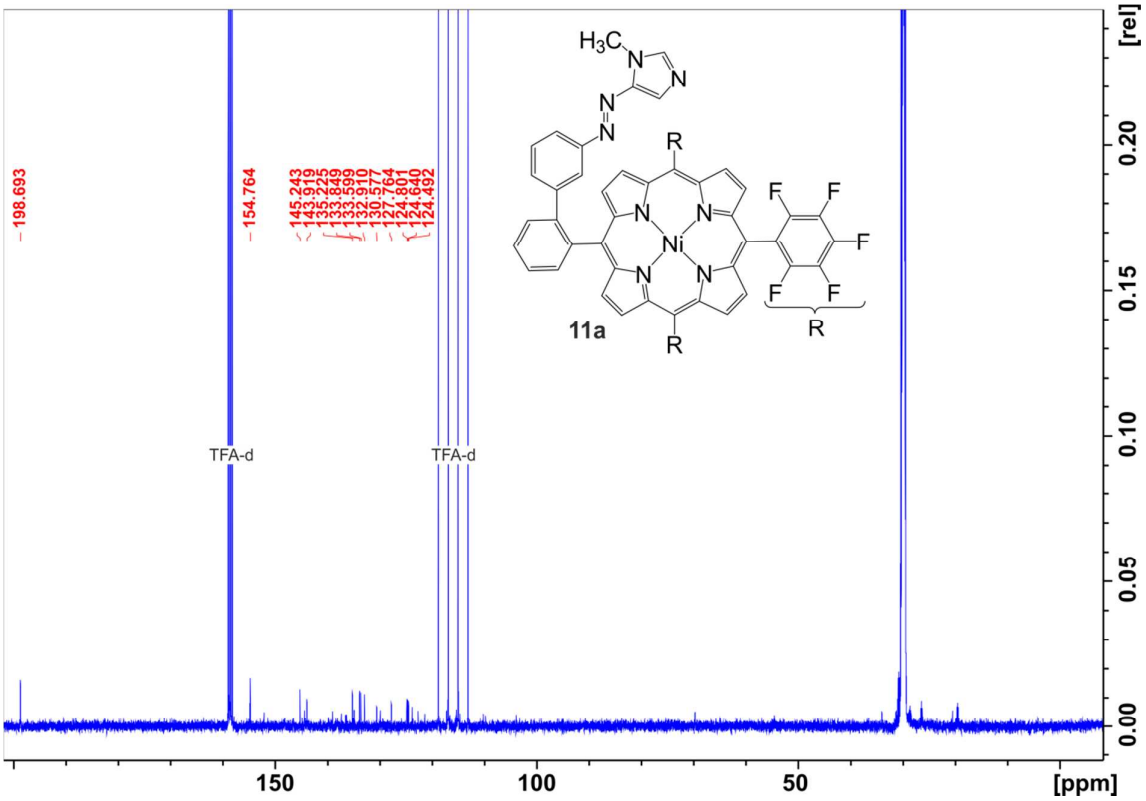


Figure S43. ^{13}C-NMR (150 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11a**.

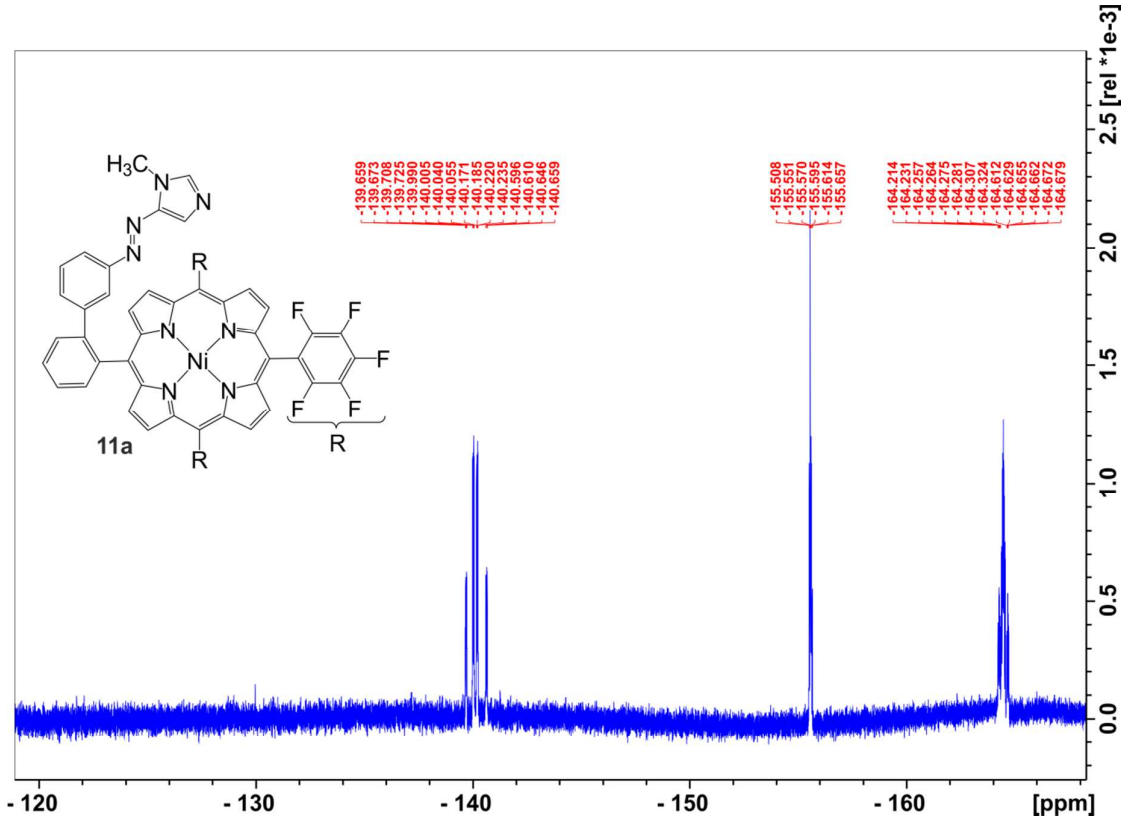


Figure S44. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11a**.

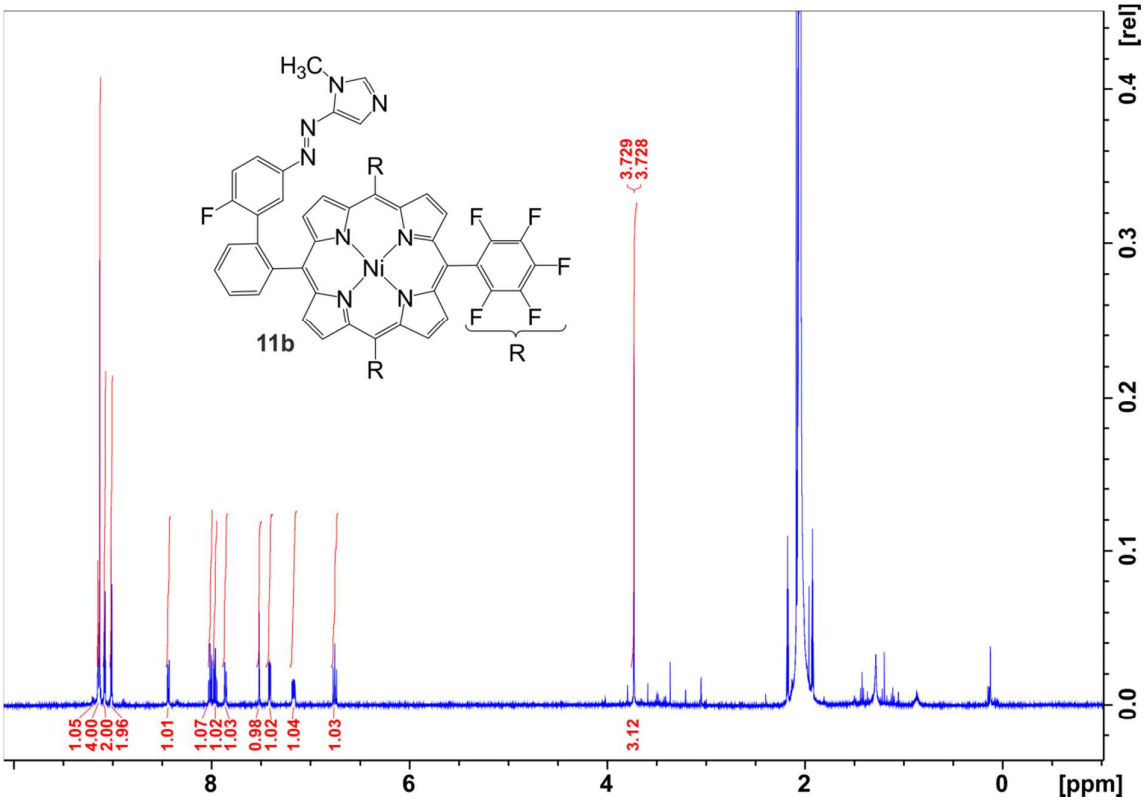


Figure S45. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11b**.

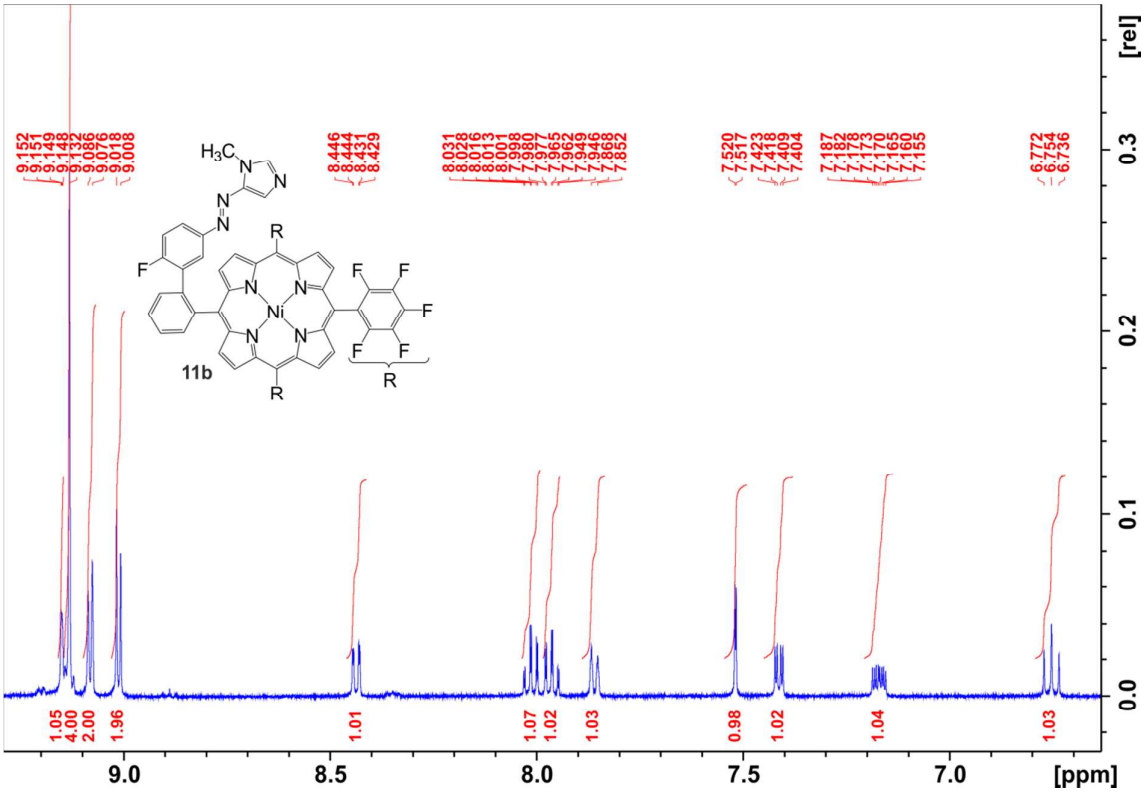


Figure S46. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **11b**.

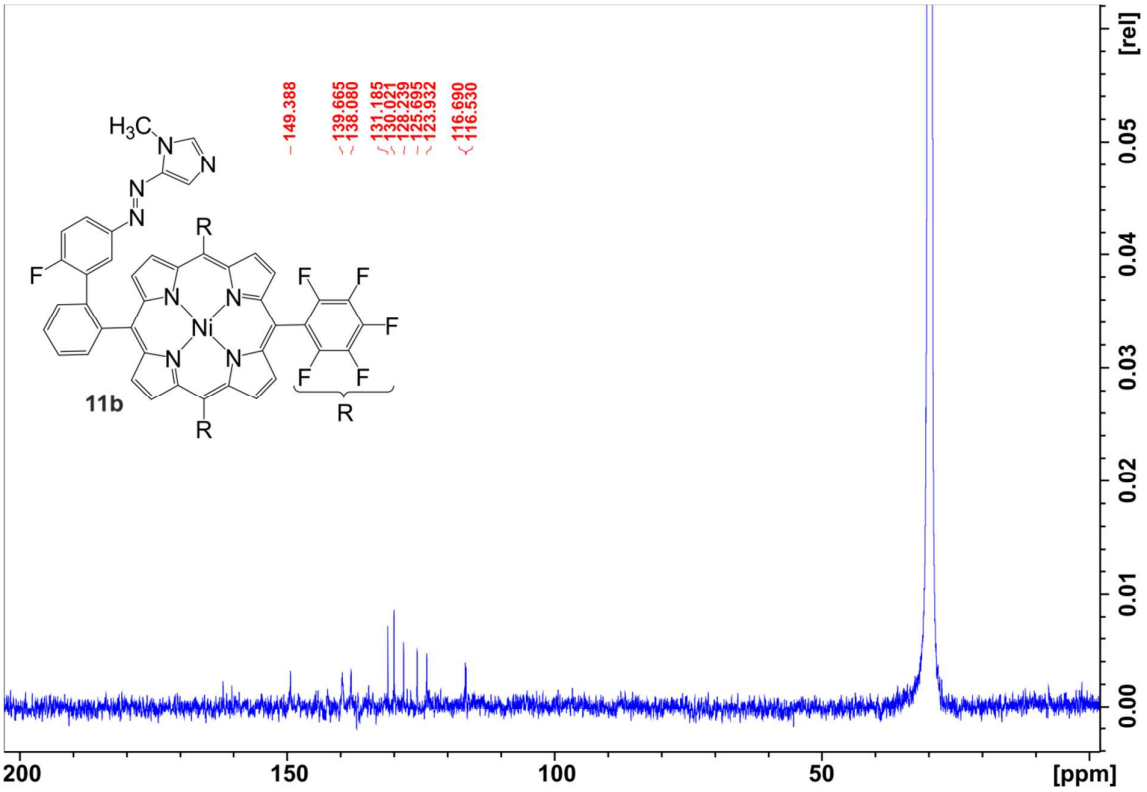


Figure S47. ^{13}C-NMR (150 MHz, acetone-d$_6$, 300 K) spectrum of **11b**.

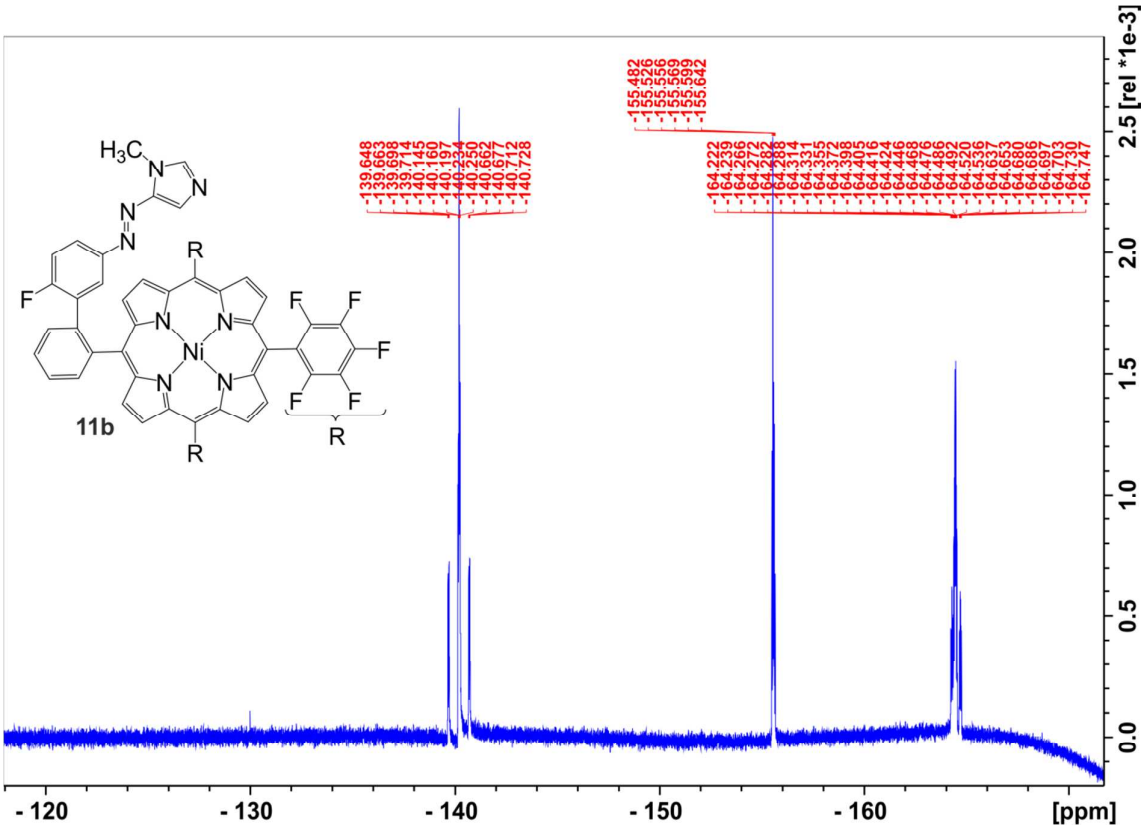


Figure S48. ^{19}F-NMR (470 MHz, acetone-d$_6$, TFA-d, 300 K) spectrum of **11b**.

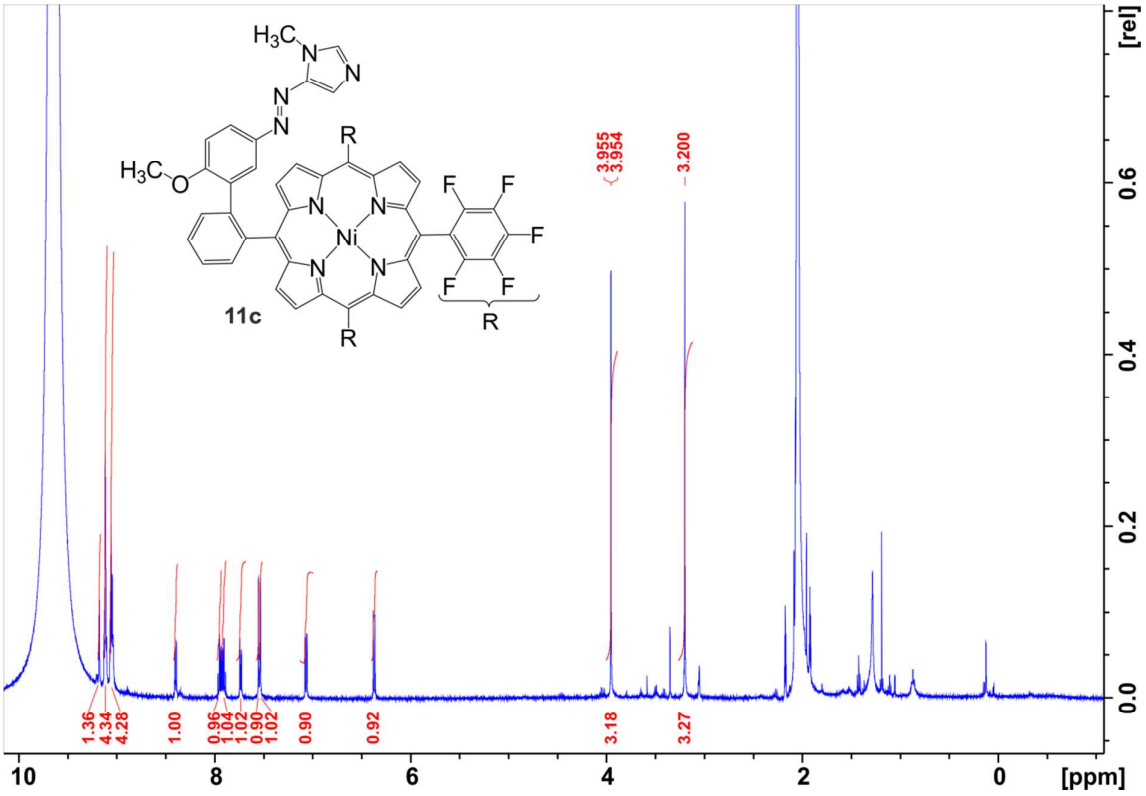


Figure S49. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11c**.

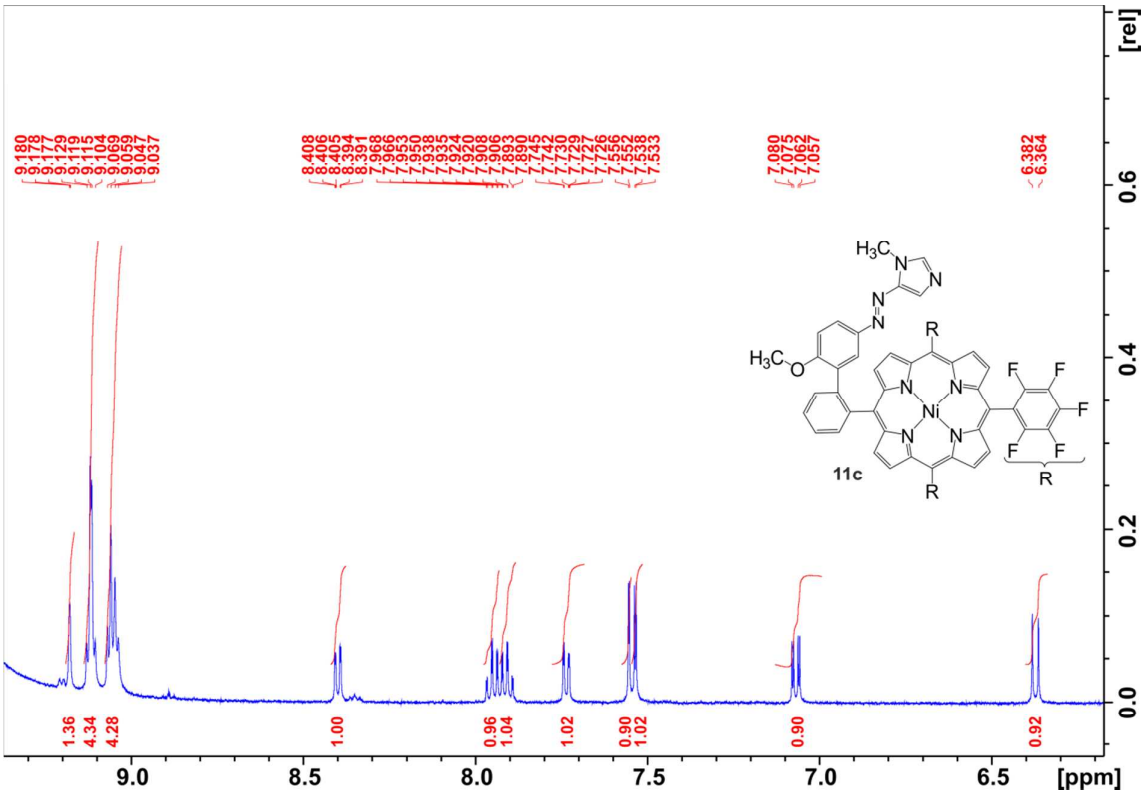


Figure S50. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **11c**.

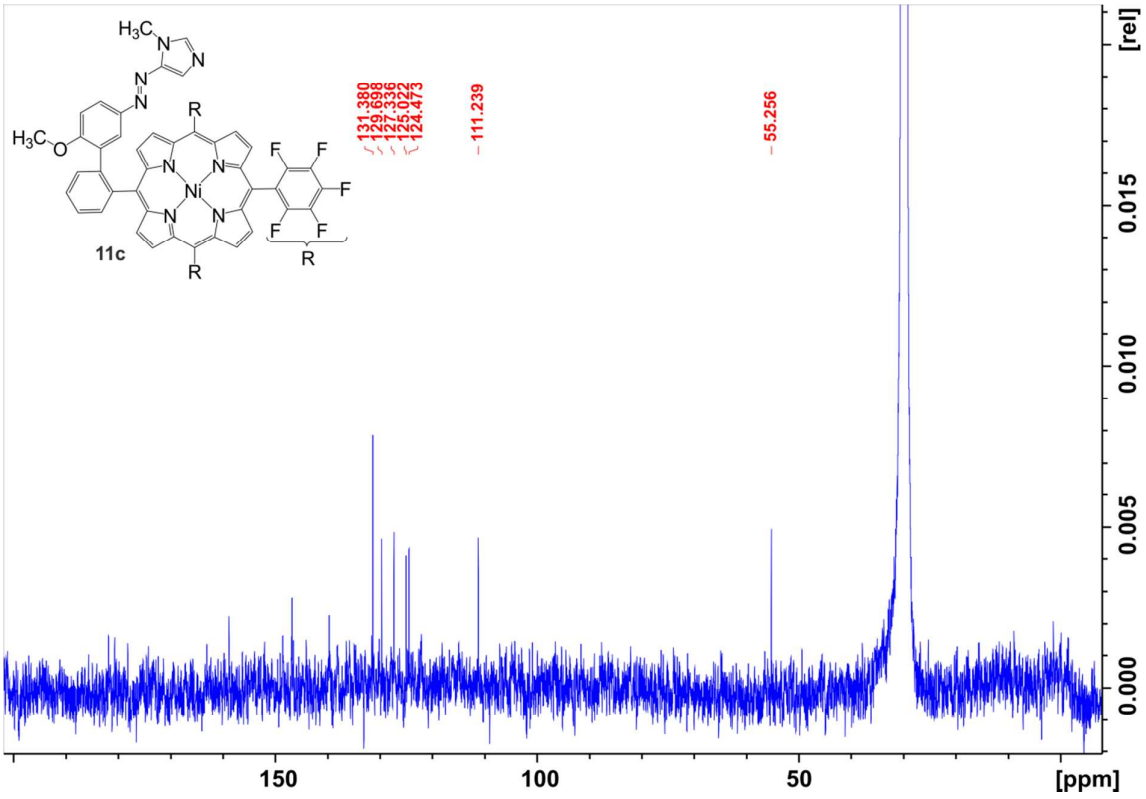


Figure S51. ^{13}C-NMR (150 MHz, acetone-d_6, 300 K) spectrum of **11c**.

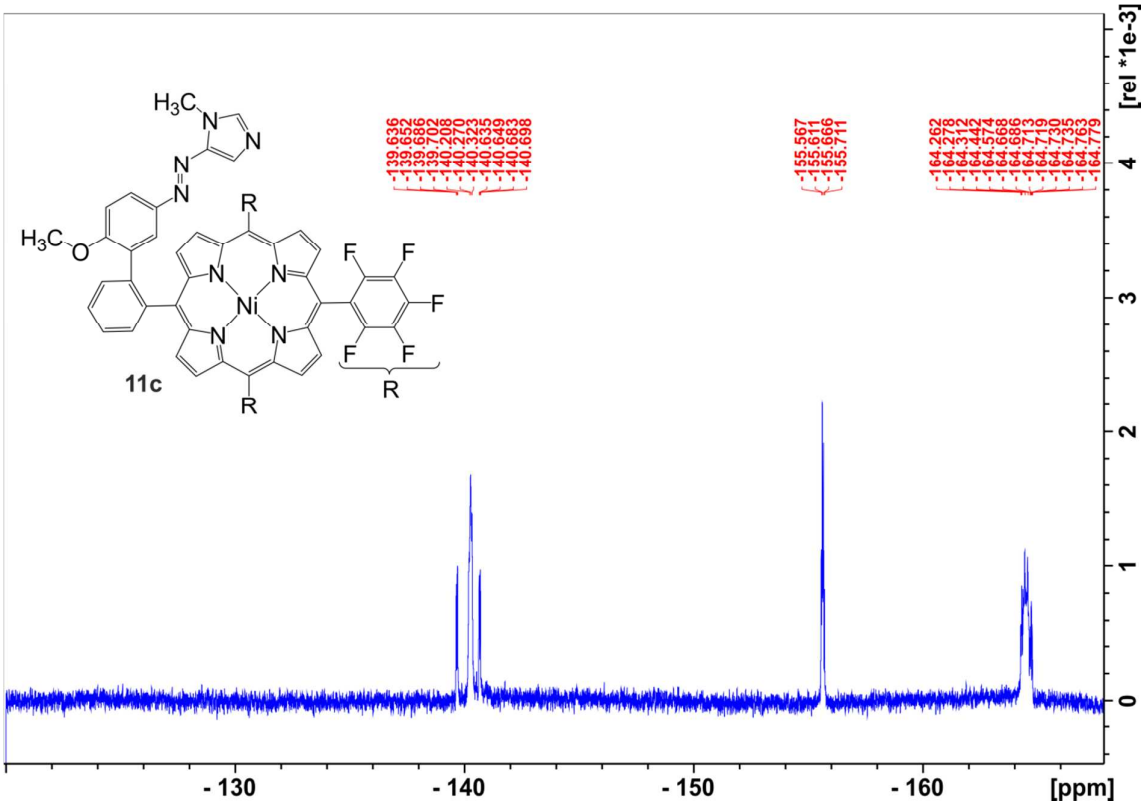


Figure S52. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11c**.

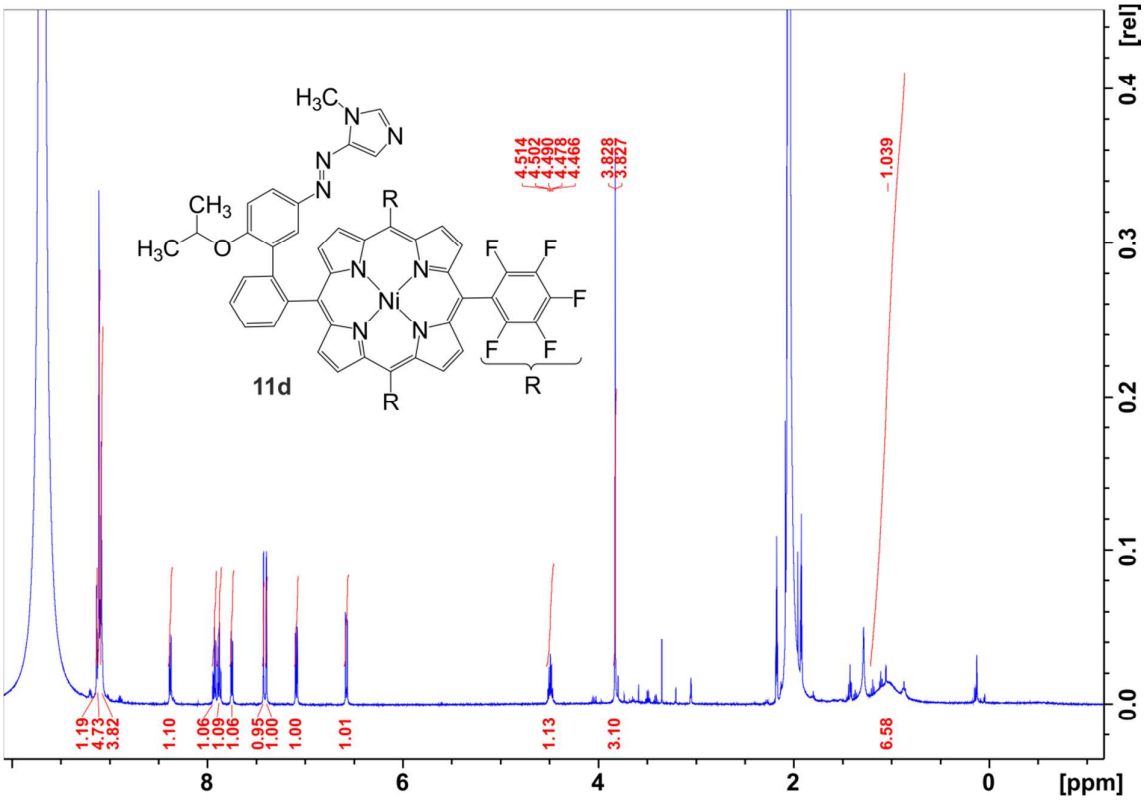


Figure S53. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11d**.

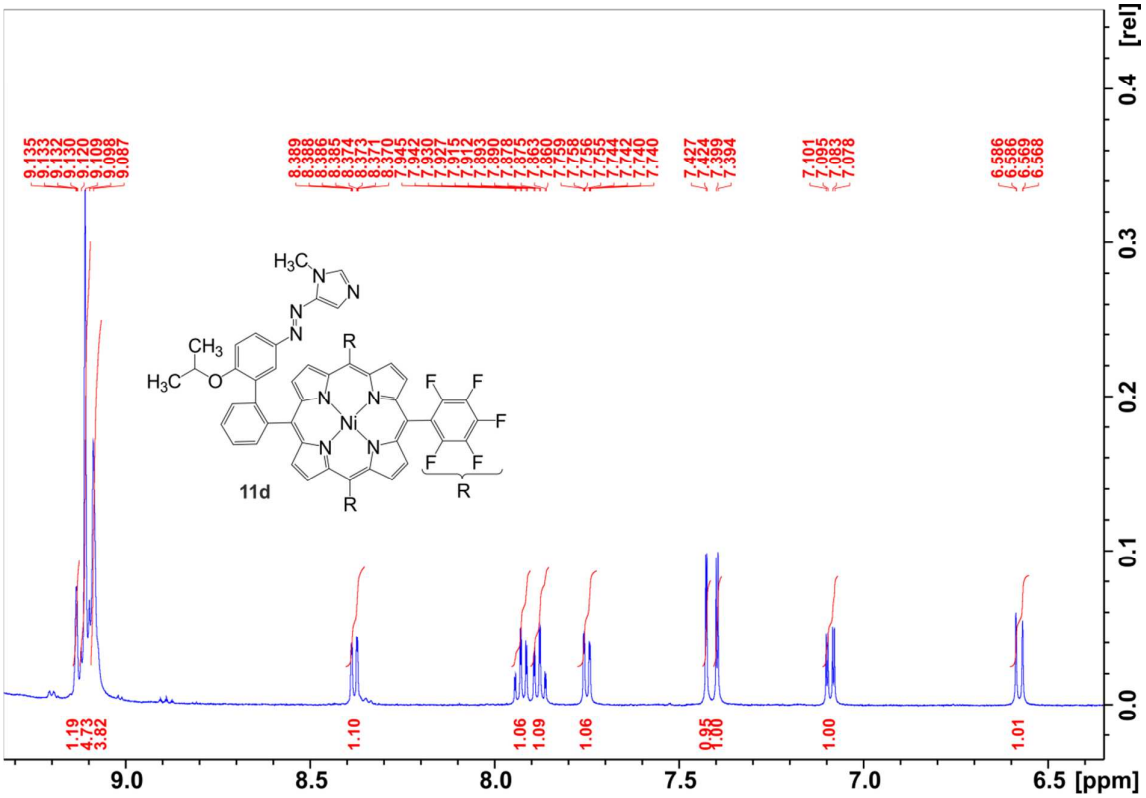


Figure S54. ^{1}H-NMR (500 MHz, acetone-d_6, TFA-d, 300 K) spectrum (aromatic region) of **11d**.

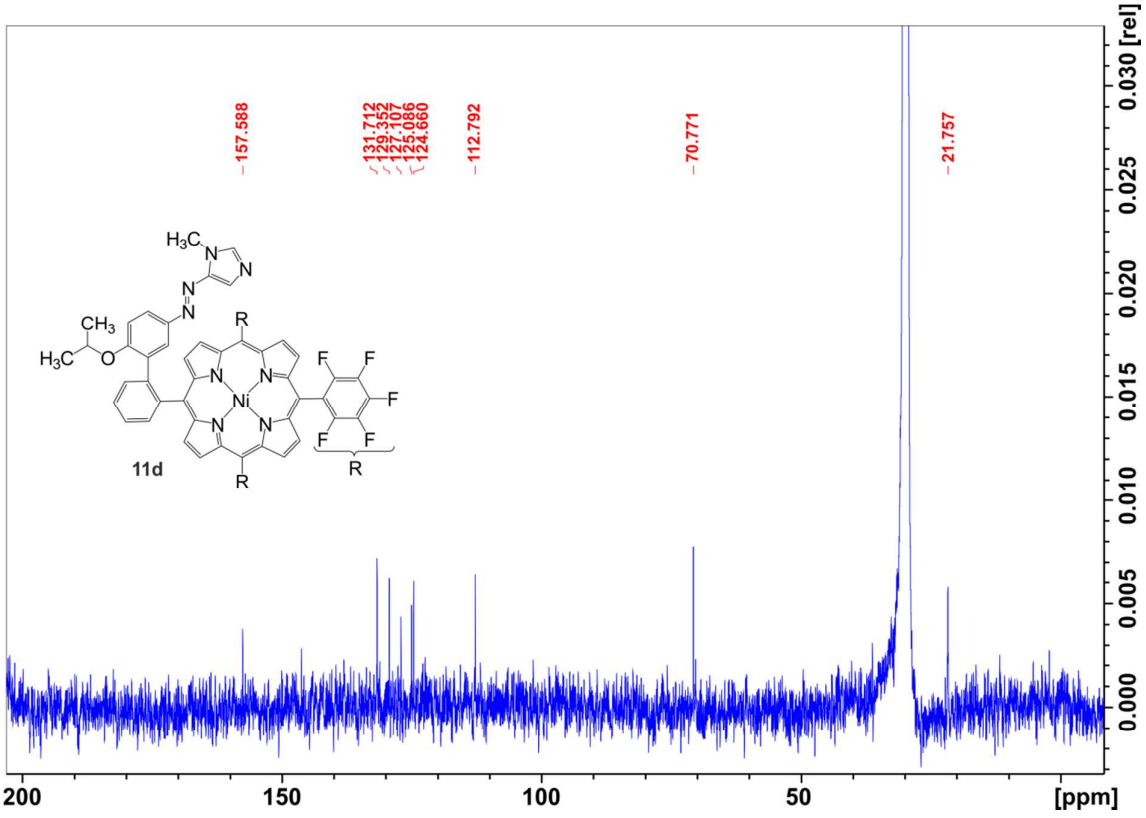


Figure S55. ^{13}C-NMR (150 MHz, acetone-d_6, 300 K) spectrum of **11d**.

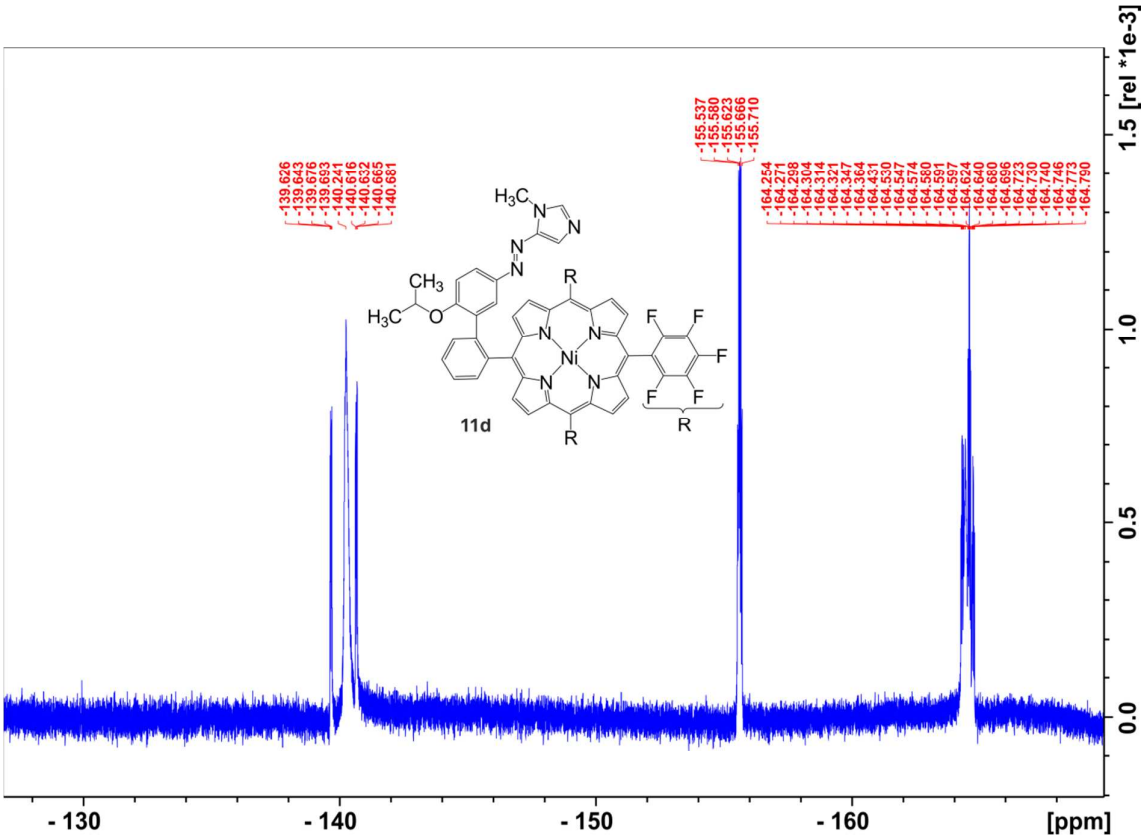


Figure S56. ^{19}F-NMR (470 MHz, acetone-d_6, TFA-d, 300 K) spectrum of **11d**.

IV. Literature

(1) Strueben, J.; Lipfert, M.; Springer, J.-O.; Gould, C. A.; Gates, P. J.; Sönnichsen, F. D.; Staubitz, A. *Chemistry - A European Journal* **2015**, *21*, 11165–11173.

(2) Venkataramani, S.; Jana, U.; Dommaschk, M.; Sönnichsen, F. D.; Tuczek, F.; Herges, R. *Science* **2011**, *331*, 445–448.

(3) Dommaschk, M.; Peters, M.; Gutzeit, F.; Schütt, C.; Näther, C.; Sönnichsen, F. D.; Tiwari, S.; Riedel, C.; Boretius, S.; Herges, R. *J. Am. Chem. Soc.* **2015**, *137*, 7552–7555.

(4) Heitmann, G.; Schütt, C.; Gröbner, J.; Huber, L. M.; Herges, R. *Dalton Trans.* **2016**, *45*, 11407–11412.

(5) Chadwick, D. J.; Ngochindo, R. I. *J. Chem. Soc. Perkin Trans. 1* **1984**, 481–486.