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Supporting Information

Synthesis of Ni^{II} and Al^{III} 10-azacorroles through coordination-induced cyclisation involving 1,2-migration

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Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm), acetone-d_6 (δ = 2.050 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm), acetone-d_6 (δ = 29.84 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Compounds **1a** was prepared according to the previous report.[1]

Synthesis and Compound Data

meso-Mesityl-α,α'-dichlorodipyrrin 1b

A two-necked flask containing *meso*-mesityl-dipyrromethane (1.32 g, 5.00 mmol) was evacuated and then refilled with N_2. To the flask, dry THF (75.0 mL) was added and the solution was cooled to –78 °C. After *N*-chlorosuccinimide (1.34 g, 10.0 mmol) was added to the solution, the mixture was stirred for 1 h. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.14 g, 5.02 mmol) was added. The resulting mixture was stirred at –78 °C for 10 min then warmed to room temperature. After stirring for additional 20 min, the reaction mixture was filtered through a short pad of alumina column (EtOAc as an eluent) and then evaporated. Purification by silica-gel column chromatography with CH_2Cl_2/hexane afforded the title compound in 57% (946 mg, 2.86 mmol) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 12.1 (br s, 1H, NH), 6.91 (s, 2H, Mes), 6.32 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.18 (d, J = 4.0 Hz, 2H,

pyrrole-β) 2.34 (s, 3H, *p*-Me), 2.07 (s, 6H, *o*-Me) ppm; ^{13}C NMR ($CDCl_3$): δ 141.4, 139.0, 138.5, 138.1, 137.0, 131.6, 128.8, 128.1, 117.2, 21.3, 20.0 ppm; HR-MS (ESI-MS): *m/z* = 331.0771, calcd for $(C_{18}H_{17}N_2Cl_2)^+$ = 331.0763 [$(M + H)^+$].

_N_,_N_-Bis(*meso*-mesityl-1-bromodipyrrin-9-yl)-_N_-benzylamine 2a

A Schlenk tube containing **1a** (104 mg, 248 μmol), $Pd_2(dba)_3$•$CHCl_3$ (6.51 mg, 6.29 μmol), Xantphos (7.53mg, 12.8 μmol), and KO^{t}Bu (71.3 mg, 635 μmol) was evacuated and then refilled with N_2. To the tube, benzylamine (68.0 μL, 624 μmol), and dry and degassed toluene (3.50 mL) were added. The mixture was stirred at 80 °C for 12 h. The reaction mixture was passed through a short plug of silica ($CHCl_3$ as an eluent) and evaporated. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded the title compound in 64% (62.5 mg, 79.6 μmol) as a black solid. ^{1}H NMR (acetone-d_6): δ 12.8 (br s, 2H, NH), 7.49 (d, *J* = 7.0 Hz, 2H, Ph), 7.40 (dd, $J^1 = J^2$ = 7.8 Hz, 2H, Ph), 7.29 (t, *J* = 7.5 Hz, 1H, Ph), 6.98 (s, 4H, Mes), 6.72 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 6.53 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 6.23 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 5.93 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 5.48 (s, 2H, CH_2), 2.33 (s, 6H, *p*-Me), 2.12 (s, 12H, *o*-Me) ppm; ^{1}H NMR ($CDCl_3$): δ 12.6 (br s, 2H, NH), 7.47 (d, *J* = 7.0 Hz, 2H, Ph), 7.39 (dd, $J^1 = J^2$ = 7.8 Hz, 2H, Ph), 7.29 (t, *J* = 7.5 Hz, 1H, Ph), 6.90 (s, 4H, Mes), 6.55 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 6.53 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 6.14 (d, *J* = 3.5 Hz, 2H, pyrrole-β), 5.94 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 5.36 (s, 2H, CH_2), 2.34 (s, 6H, *p*-Me), 2.12 (s, 12H, *o*-Me) ppm; ^{13}C NMR (acetone-d_6): δ 160.2, 142.5, 138.8, 138.4, 137.8, 137.6, 134.1, 133.9, 133.6, 129.8, 128.7, 128.2, 127.3, 122.2, 116.8, 116.3, 116.0, 54.1, 21.2, 20.2 ppm; HR-MS (ESI-MS): *m/z* = 786.1627, calcd for $(C_{43}H_{40}N_5Br_2)^+$ = 786.1629 [$(M + H)^+$].

_N_,_N_-Bis(*meso*-mesityl-1-chlorodipyrrin-9-yl)-_N_-benzylamine 2b

A Schlenk tube containing **1b** (133 mg, 402 μmol), $Pd_2(dba)_3$•$CHCl_3$ (10.8 mg, 10.4 μmol), Xantphos (12.1 mg, 20.6 μmol), and KO^{t}Bu (113 mg, 1.00 mmol) was evacuated and then refilled with N_2. To the tube, benzylamine (37.0 μL, 340 μmol) and dry and degassed toluene (6.00 mL) were added. The mixture was stirred at 75 °C for 11 h. The reaction mixture was passed through a short plug of silica ($CHCl_3$ as an eluent) and evaporated. Purification by silica-gel column chromatography with EtOAc/hexane afforded **2b** in 29% (40.0 mg, 57.4 μmol) as a black solid. ^{1}H NMR ($CDCl_3$): δ 12.7 (br s, 2H, NH), 7.43 (d, J = 7.0 Hz, 2H, Ph), 7.38 (dd, $J^1 = J^2$ = 7.8 Hz, 2H, Ph), 7.29 (t, J = 7.3 Hz, 1H, Ph), 6.91 (s, 4H, Mes), 6.49 (d, J = 5.0 Hz, 2H, pyrrole-β), 6.37 (d, J = 4.5 Hz, 2H, pyrrole-β), 6.07 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.03 (d, J = 4.0 Hz, 2H, pyrrole-β), 5.27 (s, 2H, CH_2), 2.34 (s, 6H, *p*-Me), 2.13 (s, 12H, *o*-Me) ppm; ^{13}C NMR ($CDCl_3$): δ 158.2, 140.7, 137.5, 137.4, 135.5, 134.2, 132.9, 132.8, 131.5, 129.1, 127.9, 127.6, 126.5, 122.3, 113.5, 112.9, 53.8, 21.3, 20.1 ppm; HR-MS (ESI-MS): *m/z* = 696.2686, calcd for $(C_{43}H_{40}N_5Cl_2)^+$ = 696.2655 [$(M + H)^+$].

_N_,_N_-Bis(*meso*-phenyl-1-bromodipyrrin-9-yl)-1'-bromo-1''-phenyl-_N_-benzylamine 2c

A Schlenk tube containing **2a** (32.9 mg, 41.9 μmol) and $Pd(PPh_3)_4$ (6.33 mg, 5.48 μmol) was evacuated and then refilled with N_2. To the tube, $PhSnBu_3$ (14.0 μL, 42.4 μmol) and dry and degassed toluene (4.00 mL) were added. The mixture was stirred at 110 °C for 15 h. The reaction mixture was passed through a short plug of silica ($CHCl_3$ as an eluent) and evaporated. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded **2c** in 16% (5.30 mg, 6.77 μmol) as a black solid. ^{1}H NMR ($CDCl_3$): δ 12.6 (br s, 1H, NH), 12.4

(br s, 1H, NH), 7.60 (d, J = 7.0 Hz, 2H, Bn), 7.42 (dd, $J^1 = J^2$ = 7.8 Hz, 2H, Bn), 7.36-7.38 (m, 2H, Ph), 7.30 (t, J = 7.3 Hz, 1H, Bn), 7.09-7.15 (m, 3H, Ph), 6.94 (s, 2H, Mes), 6.93 (d, J = 5.0 Hz, 1H, pyrrole-β), 6.91 (s, 2H, Mes), 6.84 (d, J = 4.5 Hz, 1H, pyrrole-β), 6.70 (d, J = 4.5 Hz, 1H, pyrrole-β), 6.58 (d, J = 4.5 Hz, 1H, pyrrole-β), 6.49 (dd, J^1 = 4.0 Hz, J^2 = 2.5 Hz, 1H, pyrrole-β), 6.08 (d, J = 3.5 Hz, 1H, pyrrole-β), 6.05 (dd, J^1 = 3.5 Hz, J^2 = 1.5 Hz, 1H, pyrrole-β), 5.86 (d, J = 4.0 Hz, 1H, pyrrole-β), 5.63 (s, 2H, CH_2), 2.37 (s, 3H, *p*-Me), 2.35 (s, 3H, *p*-Me), 2.17 (s, 6H, *o*-Me) 2.08 (s, 6H, *o*-Me) ppm; ^{13}C NMR (acetone-d_6): δ 165.2, 164.3, 146.9, 146.8, 139.8, 139.4, 138.5, 138.3, 137.9, 137.8, 136.3, 135.9, 134.9, 134.4, 134.2, 133.7, 133.4, 132.2, 131.9, 129.9, 129.8, 128.8, 128.7, 128.2, 128.1, 127.5, 127.5, 125.0, 121.1, 120.2, 120.2, 118.7, 114.0, 109.8, 53.8, 21.2, 21.2, 20.2, 20.2 ppm; HR-MS (ESI-MS): m/z = 784.2873, calcd for $(C_{49}H_{45}N_5Br)^+$ = 784.2844 [$(M + H)^+$].

N,N-Bis(*meso*-mesityl-1-bromodipyrrin-9-yl)-N-benzylamine Zn^{II} complex 3Zn

A flask containing **2a** (119 mg, 151 μmol), NaOAc (62.5 mg, 762 μmol), and $Zn(OAc)_2$•$2H_2O$ (166 mg, 756 μmol) was charged with MeOH (60 mL). The mixture was stirred at reflux for 3 h. The reaction mixture was extracted with EtOAc. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with EtOAc/hexane afforded **3a** in 98% (126 mg, 148 μmol) as a green solid. ^{1}H NMR ($CDCl_3$): δ 7.28–7.38 (m, 5H, Bn), 6.91 (s, 4H, Mes), 6.61 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.41 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.22–6.24 (m, 4H, pyrrole-β), 5.29 (d, J = 18 Hz, 1H, CH_2), 5.15 (d, J = 18 Hz, 1H, CH_2), 2.35 (s, 6H, Me), 2.22 (s, 6H, Me), 2.07 (s, 6H, Me) ppm; ^{13}C NMR ($CDCl_3$): δ 158.1, 141.0, 139.6, 138.7,

137.6, 137.4, 137.2, 136.4, 134.1, 133.7, 129.2, 129.0, 128.0, 127.8, 127.2, 126.0, 118.3, 110.9, 54.3, 21.3, 20.3, 19.8 ppm; HR-MS (ESI-MS): *m/z* = 850.0725, calcd for $(C_{43}H_{38}N_5Br_2Zn)^+$ = 850.0744 [$(M + H)^+$].

_N_,_N_-Bis(*meso*-mesityl-1-bromodipyrrin-9-yl)-_N_-benzylamine Cu^{II} complex 3Cu

A flask containing **2a** (118 mg, 150 μmol), NaOAc (62.1 mg, 757 μmol), and $Cu(OAc)_2•H_2O$ (150 mg, 751 μmol) was charged with MeOH (50 mL). The mixture was stirred at reflux for 3 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded **3Cu** in 96% (122 mg, 144 μmol) as a green solid. HR-MS (ESI-MS): *m/z* = 847.0769, calcd for $(C_{43}H_{38}N_5Br_2Cu)^+$ = 847.0768 [$(M + H)^+$].

_N_-Benzyl-2-bromo-5,15-dimesityl-10-azacorrole 4 and _N_-benzyl-5,15-dimesityl-10-azacorrole 5

A flask containing **2a** (39.1 mg, 49.8 μmol), NaOAc (20.5 mg, 250 μmol), and $NiCl_2•6H_2O$ (59.4 mg, 250 μmol) was charged with MeOH (20 mL). The mixture was stirred at reflux for 3 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded **4** in 67% (25.4 mg, 33.4 μmol) and **5** in 32% (11.0 mg, 16.1 μmol) as black solids. ^{1}H NMR (acetone-d_6) of **4**: δ 8.42 (d, *J* = 5.0 Hz, 1H, pyrrole-β), 8.38 (d, *J* = 5.0 Hz, 1H, pyrrole-β), 8.35 (d, *J* = 4.5 Hz, 1H, pyrrole-β), 8.18 (d, *J* = 5.0 Hz, 1H, pyrrole-β), 8.15 (d, *J* = 4.5 Hz, 1H, pyrrole-β), 7.81 (d, *J* = 4.5 Hz, 1H,

pyrrole-β), 7.73 (s, 1H, pyrrole-β), 7.25–7.31 (m, 7H), 7.21 (s, 4H, Mes), 2.51 (s, 6H, *p*-Me), 1.91 (s, 12H, *o*-Me) ppm; ^{13}C NMR ($CDCl_3$): δ 144.5, 144.0, 142.3, 138.5, 137.9, 137.7, 137.7, 135.0, 134.7, 133.5, 133.4, 133.3, 133.1, 132.9, 132.6, 129.3, 129.0, 128.3, 127.9, 127.9, 127.9, 127.8, 125.5, 125.2, 124.9, 117.8, 112.6, 111.9, 104.4, 57.2, 21.5, 21.1 ppm; HR-MS (ESI-MS): *m/z* = 762.1541, calcd for $(C_{43}H_{37}N_5BrNi)^+$ = 762.1560 [$(M + H)^+$].

_N_-Benzyl-5,15-dimesityl-2-phenyl-10-azacorrole 6

A flask containing **2c** (5.30 mg, 6.77 μmol), NaOAc (3.05 mg, 37.2 μmol), and $NiCl_2$•$6H_2O$ (8.86 mg, 37.3 μmol) was charged with MeOH (3 mL). The mixture was stirred at reflux for 4 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded **6** in 99% (5.08 mg, 6.70 μmol) as a black solid. ^{1}H NMR ($CDCl_3$): δ 8.30 (d, J = 4.5 Hz, 1H, pyrrole-β), 8.24 (dd, J^1 = 8.5 Hz, J^2 = 1.5 Hz, 2H), 8.14 (d, J = 4.5 Hz, 1H, pyrrole-β), 8.13 (d, J = 5.0 Hz, 1H, pyrrole-β), 7.97 (d, J = 5.0 Hz, 1H, pyrrole-β), 7.96 (d, J = 4.5 Hz, 1H, pyrrole-β), 7.91 (s, 1H, pyrrole-β), 7.84 (d, J = 4.0 Hz, 1H, pyrrole-β), 7.59–7.62 (m, 2H), 7.41–7.44 (m, 1H), 7.28–7.30 (m, 3H), 7.17–7.19 (m, 2H), 7.15 (s, 2H, Mes), 7.14 (s, 2H, Mes), 6.98 (s, 2H, CH_2), 2.53 (s, 3H, *p*-Me), 2.53 (s, 3H, *p*-Me), 1.96 (s, 6H, *o*-Me) 1.93 (s, 6H, *o*-Me) ppm; ^{13}C NMR ($CDCl_3$): δ 144.7, 143.9, 143.8, 142.5, 138.7, 138.6, 137.9, 137.7, 137.6, 137.1, 135.3, 135.0, 133.4, 133.3, 133.1, 132.6, 129.6, 129.2, 128.9, 128.3, 128.1, 127.8, 127.8, 127.7, 126.9, 125.5, 125.0, 122.5, 118.7, 111.9, 111.8, 57.2, 21.5, 21.1, 21.1 ppm; HR-MS (ESI-MS): *m/z* = 758.2792, calcd for $(C_{49}H_{42}N_5Ni)^+$ = 758.2788 [$(M + H)^+$].

Al^{III} 10-azacorrole 7

A two-necked flask containing **2a** (137 mg, 174 μmol) and $AlCl_3$ (239 mg, 1.80 mmol) was evacuated and then refilled with N_2. To the flask, dry pyridine (50 mL) was added. The mixture was stirred at reflux for 4 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. A Schlenk tube containing the residue, $Pd_2(dba)_3$•$CHCl_3$ (50.4 mg, 48.8 μmol), and Xphos (101 mg, 212 μmol) was evacuated and then refilled with N_2. To the tube, dry and degassed toluene (10.5 mL), Et_3N (1.5 mL), and HCOOH (500 μL, 13.2 mmol) were added. The mixture was stirred at 65 °C for 4 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with $CHCl_3$/MeOH followed by recrystallization with MeOH/H_2O afforded the title compound **7** in 67% (78.3 mg, 117 μmol) as a purple solid. ^{1}H NMR (CD_3OD): δ 8.57 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 8.42 (d, *J* = 5.0 Hz, 2H, pyrrole-β), 8.32 (d, 2H, *J* = 4.5 Hz pyrrole-β), 8.15 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 7.22–7.28 (m, 11H), 2.54 (s, 6H, Mes-*p*-Me), 1.91 (s, 12H, Mes-*o*-Me) ppm; ^{13}C NMR (CD_3OD): δ 149.9, 144.0, 139.7, 139.6, 139.4, 139.1, 138.2, 136.2, 133.1, 131.2, 130.0, 129.6, 129.0, 128.9, 126.6, 118.4, 113.7, 58.1, 21.5, 21.1 ppm; HR-MS (ESI-MS): *m*/*z* = 690.2753, calcd for $(C_{43}H_{38}N_5OAlNa)^+$ = 690.2784 [$(M + Na)^+$].

2-Boryl-5,15-dimesityl-10-azacorrole 8

A Schlenk tube containing bromoazacorrole **4** (38.0 mg, 49.9 μmol), $Pd_2(dba)_3$•$CHCl_3$ (2.61 mg, 2.52 μmol), Xphos (4.86 mg, 10.2 μmol), B_2pin_2 (39.2 mg, 154 μmol), and KOAc (14.7

mg, 150 μmol) was evacuated and then refilled with N_2. To the tube, dry 1,4-dioxane (2.00 mL) was added. The mixture was stirred at 110 °C for 2 h. The reaction mixture was filtered over a pad of Celite (CH_2Cl_2 as an eluent) and evaporated in vacuo. Purification by silica-gel column chromatography with CH_2Cl_2/hexane afforded **8** in 52% (20.8 mg, 25.7 μmol) as a black solid. ^{1}H NMR (acetone-d_6): δ 8.65 (d, J = 4.5 Hz, 1H, pyrrole-β), 8.34 (d, J = 5.0 Hz, 1H, pyrrole-β), 8.29 (d, J = 4.5 Hz, 1H, pyrrole-β), 8.16 (d, J = 5.0 Hz, 1H, pyrrole-β), 8.11 (s, 1H, pyrrole-β), 8.09 (d, J = 4.5 Hz, 1H, pyrrole-β), 7.76 (d, J = 4.5 Hz, 1H, pyrrole-β), 7.27–7.30 (m, 5H), 7.21 (s, 2H), 7.20 (s, 2H), 7.19 (s, 2H), 2.52 (s, 3H, *p*-Me), 2.51 (s, 3H, *p*-Me), 1.92 (s, 6H, *o*-Me), 1.92 (s, 6H, *o*-Me), 1.52 (s, 12H, Bpin) ppm; ^{13}C NMR (acetone-d_6): δ 149.9, 146.8, 145.8, 145.2, 139.6, 138.8, 138.6, 138.4, 136.0, 135.9, 134.5, 133.9, 133.8, 133.7, 133.4, 133.1, 129.8, 129.1, 128.7, 128.6, 128.6, 126.7, 126.4, 125.7, 125.0, 120.6, 118.8, 114.8, 113.7, 84.4, 57.6, 31.8, 25.5, 21.4, 21.1, 21.0 ppm; HR-MS (ESI-MS): m/z = 808.3345, calcd for $(C_{49}H_{49}N_5BO_2Ni)^+$ = 808.3336 [$(M + H)^+$].

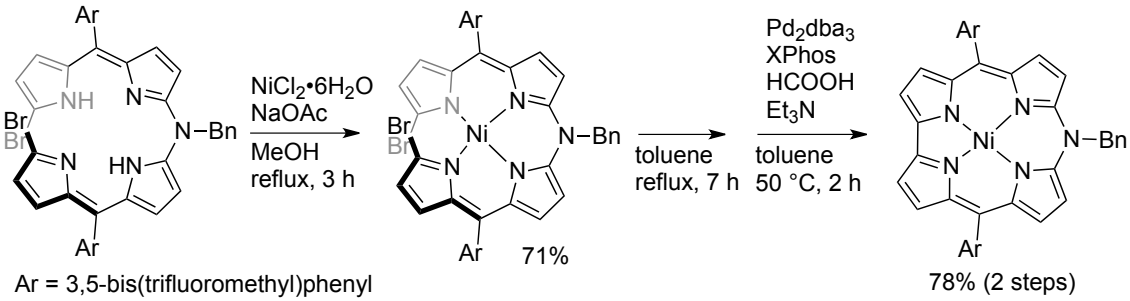
2,2'-Bridged 10-azacorrole dimer 9

A Schlenk tube containing bromoazacorrole **4** (22.3 mg, 29.2 μmol), 2,2'-bipyridyl (21.6 mg, 128 μmol), and $Ni(cod)_2$ (41.6 mg, 151 μmol) was evacuated and then refilled with N_2. To the tube, 1,5-dicyclooctadiene (15 μL, 143μmol) and dry DMF (2.00 mL) was added. The mixture was stirred at 60 °C for 4 h. The reaction mixture was extracted with EtOAc. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography with $CHCl_3$/hexane followed by recrystallization with $CHCl_3$/MeOH afforded **9** in 62% (12.4 mg, 9.10 μmol) as a green solid.

^{1}H NMR ($CDCl_3$): δ 8.62 (s, 2H, pyrrole-β), 8.22 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 8.19 (d, *J* = 5.0 Hz, 2H, pyrrole-β), 8.14 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 8.00 (d, *J* = 5.0 Hz, 2H, pyrrole-β), 7.98 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 7.78 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 7.29–7.32 (m, 6H, Bn), 7.23–7.25 (m, 4H, Bn), 7.18 (s, 4H, Mes), 7.13 (s, 4H, Mes-*m*), 7.01 (s, 4H, Bn), 2.52 (s, 12H, *p*-Me), 2.10 (s, 12H, *o*-Me), 1.93 (s, 12H, *o*-Me) ppm; ^{13}C NMR ($CDCl_3$): δ 143.8, 138.7, 138.6, 138.0, 137.7, 135.5, 135.4, 133.8, 133.5, 133.0, 132.4, 129.5, 129.2, 128.2, 127.9, 127.8, 127.7, 125.6, 124.9, 124.5, 118.8, 111.6, 57.2, 21.5, 21.5, 21.2, 21.1 ppm; HR-MS (ESI-MS): *m/z* = 1363.4749, calcd for $(C_{86}H_{73}N_{10}Ni_2)^+$ = 1363.4717 [$(M + H)^+$].

Isolation of nitrogen-bridged dipyrrin dimer Ni^{II} complex 3Ni

The nitrogen-bridged dipyrrin dimer Ni^{II} complex **3Ni** was isolated by using 3,5-bis(trifluoromethyl)phenyl substituents at the *meso*-positions. This Ni^{II} complex was converted into the corresponding azacorrole only by heating. The synthetic details and compound data were described below.



Scheme S1. Synthesis of *meso*-3,5-bis(trifluoromethyl)phenylazacorrole through isolation of Ni^{II} dipyrrin complex intermediate **3Ni**.

meso-3,5-Bis(trifluoromethyl)phenyl-α,α'-dibromodipyrrin

A two-necked flask containing *meso*-3,5-bis(trifluoromethyl)phenyldipyrromethane (537 mg, 1.50 mmol) was evacuated and then refilled with N_2. To the flask, dry THF (22.5 mL) was added and cool to –78 °C. NBS (530 mg, 2.98 mmol) was added to the solution in three portions every 15 min. After addition of all NBS, the solution was stirred for 1 h. Then DDQ (340 mg, 1.50 mmol) was added and stirred at –78 °C for 10 min and at room temperature for 20 min. The reaction mixture was subjected to alumina column chromatography (EtOAc as an eluent) and evaporated. Purification by silica-gel column chromatography with CH_2Cl_2/hexane afforded the title compound in 71% (545 mg, 1.06 mmol) as an orange solid. ^{1}H NMR ($CDCl_3$): δ 12.4 (br s, 1H, NH), 8.02 (s, 1H, Ar-*p*), 7.90 (s, 2H, Ar-*o*), 6.40 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 6.32 (d, *J* = 4.0 Hz, 2H, pyrrole-β) ppm; ^{13}C NMR ($CDCl_3$): δ 140.0, 137.8, 134.9, 131.8 (q, CF_3), 131.4, 130.6, 129.5, 126.4, 124.2, 123.3, 123.3, 123.3, 122.0, 121.8 ppm; ^{19}F NMR ($CDCl_3$): δ –66.0 ppm; HR-MS (ESI-MS): *m/z* = 514.9024, calcd for $(C_{17}H_9N_2Br_2F_6)^+$ = 514.9011 [$(M + H)^+$].

***N*,*N*-Bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)-*N*-benzylamine**

A Schlenk tube containing *meso*-3,5-bis(trifluoromethyl)phenyl-α,α-dibromodipyrrin (307 mg, 597 μmol), $Pd_2(dba)_3$•$CHCl_3$ (15.8 mg, 15.3 μmol), Xantphos (21.4 mg, 36.4 μmol), and ^{t}BuOK (167 mg, 1.49 mmol) was evacuated and then refilled with N_2. To the tube, benzylamine (60.0 μL, 552 μmol) and dry and degassed toluene (9.00 mL) were added. The mixture was stirred at 75 °C for 11 h. The reaction mixture was passed through a short plug of silica ($CHCl_3$ as an eluent) and evaporated. Purification by silica-gel column chromatography

with $CHCl_3$/hexane afforded the title compound in 37% (107 mg, 110 μmol) as a brown solid. ^{1}H NMR (acetone-d_6): δ 12.7 (br s, 2H, NH), 8.21 (s, 2H, Ar-*p*), 8.12 (s, 4H, Ar-*o*), 7.56 (d, J = 7.5 Hz, 2H, Ph), 7.44 (dd, $J^1 = J^2$ = 7.8 Hz, 2H, Ph), 7.32 (t, J = 7.5 Hz, 1H, Ph), 7.10 (d, J = 5.0 Hz, 2H, pyrrole-β), 6.87 (d, J = 5.0 Hz, 2H, pyrrole-β), 6.28 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.14 (d, J = 4.0 Hz, 2H, pyrrole-β), 5.63 (s, 2H, CH_2) ppm; ^{13}C NMR ($CDCl_3$): δ 163.9, 145.5, 138.8, 137.2, 135.9, 134.0, 131.6 (q, CF_3), 130.9, 130.0, 129.3, 127.8, 126.6, 126.5, 124.4, 122.7, 122.2, 120.3, 120.0, 114.4, 110.9, 53.6 ppm; ^{19}F NMR ($CDCl_3$): δ –66.0 ppm; HR-MS (ESI-MS): m/z = 974.0209, calcd for $(C_{41}H_{24}N_5Br_2F_{12})^+$ = 974.0185 [$(M + H)^+$].

_N_,_N_-Bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)-_N_-benzylamine Ni complex

A flask containing *N*,*N*-bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)-*N*-benzylamine (11.6 mg, 11.9 μmol), AcONa (4.43 mg, 54.0 μmol), and $NiCl_2$•$6H_2O$ (13.7 mg, 57.7 μmol) was charged with MeOH (4 mL). The mixture was stirred at reflux for 3 h. After the precipitated solid was washed with MeOH, the title compound was obtained in 71% (8.72 mg, 8.46 μmol) as a black solid. ^{1}H NMR (acetone-d_6): δ 8.26 (br s, 2H, Ar), 8.21 (s, 2H, Ar) 7.90 (br s, 2H, Ar) 7.38 (t, J = 7.3 Hz, 2H, Bn), 7.26–7.31 (m, 3H, Bn), 6.94 (d, J = 5.0 Hz, 2H, pyrrole-β), 6.62 (d, J = 5.0 Hz, 2H, pyrrole-β), 6.40 (d, J = 4.0 Hz, 2H, pyrrole-β), 6.08 (d, J = 4.0 Hz, 2H, pyrrole-β), 5.52 (d, J = 18 Hz, 1H, CH_2), 5.28 (d, J = 18 Hz, 1H, CH_2) ppm; ^{13}C NMR (acetone-d_6): δ 156.1, 139.8, 139.1, 137.2, 136.1, 135.5, 133.9, 133.9, 132.0, 131.8, 129.9, 128.7, 127.0, 125.6, 125.4, 123.6, 112.5, 54.3 ppm; ^{19}F NMR ($CDCl_3$): δ –65.8, –65.9 ppm; HR-MS (ESI-MS): m/z = 1029.9383, calcd for $(C_{41}H_{22}N_5Br_2F_{12}Ni)^+$ =

1029.9377 [$(M + H)^+$].

5,15-(3,5-Bis(trifluoromethyl)phenyl)-10-azacorrole.

A flask containing *meso*-3,5-bis(trifluoromethyl)phenyl Ni^{II} complex (10.1 mg, 9.80 μmol), was charged with toluene (7.00 mL). The mixture was stirred at reflux for 7 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The reaction mixture was passed through a short plug of silica ($CHCl_3$ as an eluent) and evaporated. A Schlenk tube containing the residue, $Pd_2(dba)_3$•$CHCl_3$ (2.42 mg, 2.34 μmol), and Xphos (5.56 mg, 11.7 μmol) was evacuated and then refilled with N_2. To the tube, dry and degassed toluene (3.50 mL), Et_3N (500 μL), and HCOOH (20 μL, 529 μmol) were added. The mixture was stirred at 50 °C for 2 h. The reaction mixture was evaporated. Purification by silica-gel column chromatography with $CHCl_3$/hexane afforded the title compound in 78% (6.69 mg, 7.69 μmol) as a black solid. ^{1}H NMR (acetone-d_6): δ 8.66 (s, 4H, Ar-*o*), 8.60 (d, *J* = 5.0 Hz, 2H, pyrrole-β), 8.60 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 8.50 (d, 2H, *J* = 5.0 Hz pyrrole-β), 8.43 (s, 2H, Ar-*p*), 8.12 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 7.33 (s, 2H, Bn) 7.26–7.27 (m, 3H, Bn), 7.15–7.17 (m, 2H, Bn) ppm; ^{13}C NMR (acetone-d_6): δ 145.7, 145.0, 142.4, 139.5, 134.0, 134.0, 133.6, 131.5, 131.3, 129.7, 128.8, 126.7, 126.3, 125.8, 125.3, 122.8, 119.2, 115.4, 58.1 ppm; ^{19}F NMR ($CDCl_3$): δ –65.7 ppm; HR-MS (ESI-MS): *m/z* = 870.1034, calcd for $(C_{41}H_{22}N_5F_{12}Ni)^+$ = 870.1032 [$(M + H)^+$].

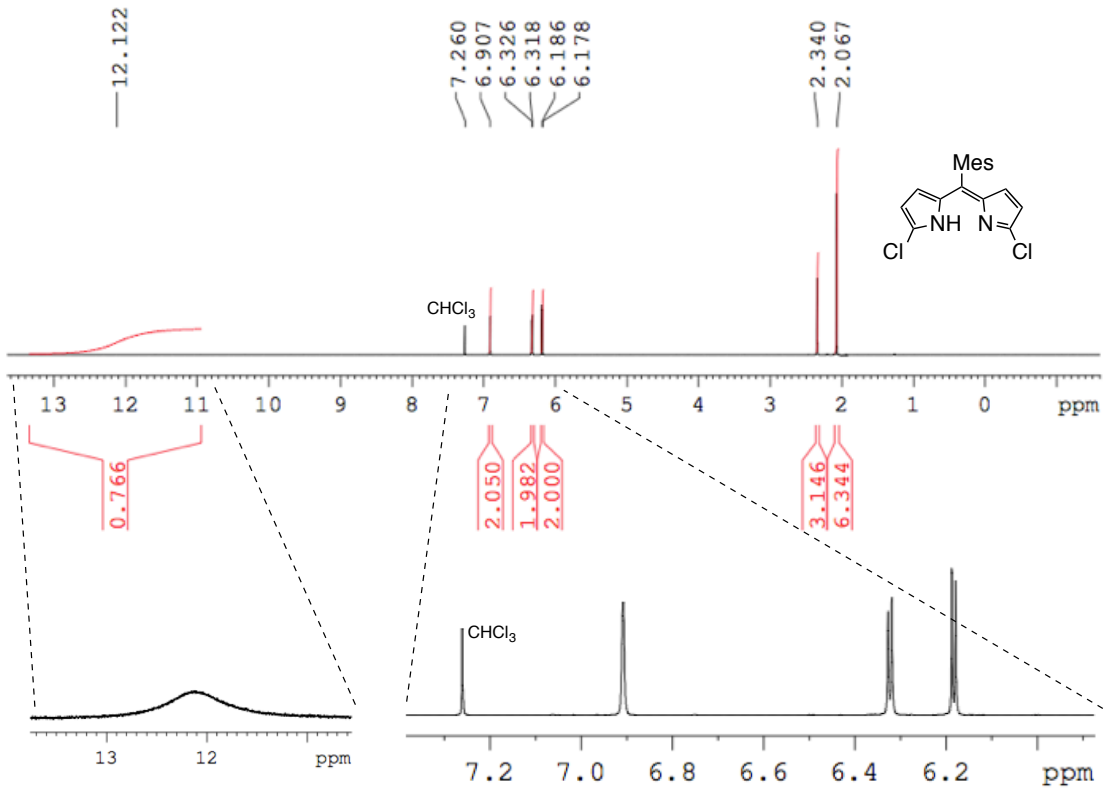


Fig S1. ^{1}H NMR spectrum of **1b** in $CDCl_3$.

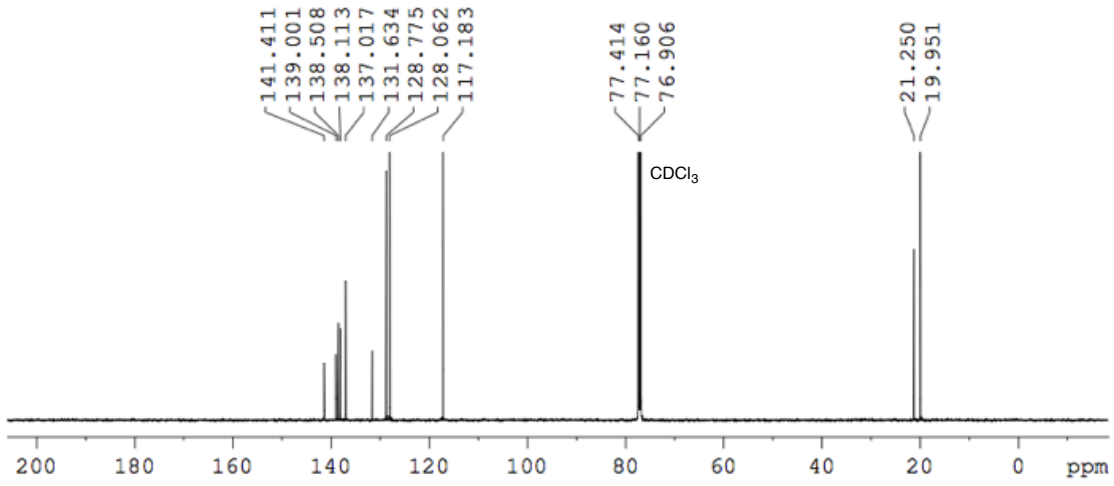


Fig S2. ^{13}C NMR spectrum of **1b** in $CDCl_3$.

* = solvents and impurities

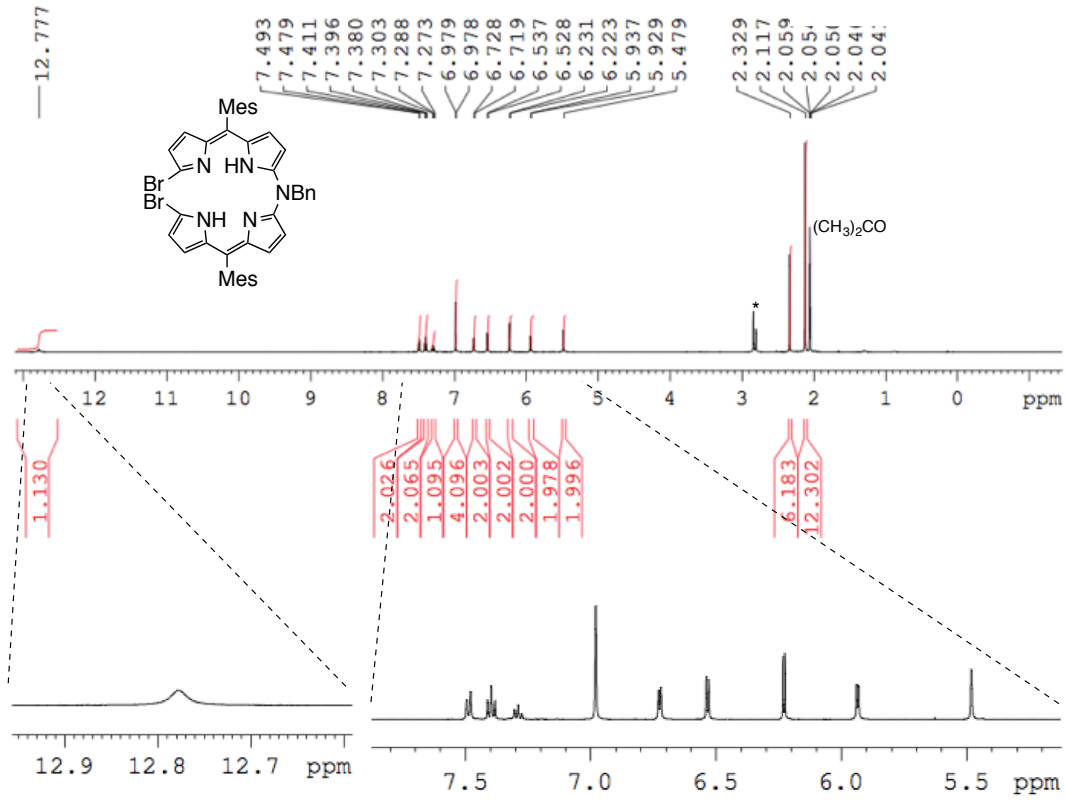


Fig S3. [1]H NMR spectrum of **2a** in acetone-d_6.

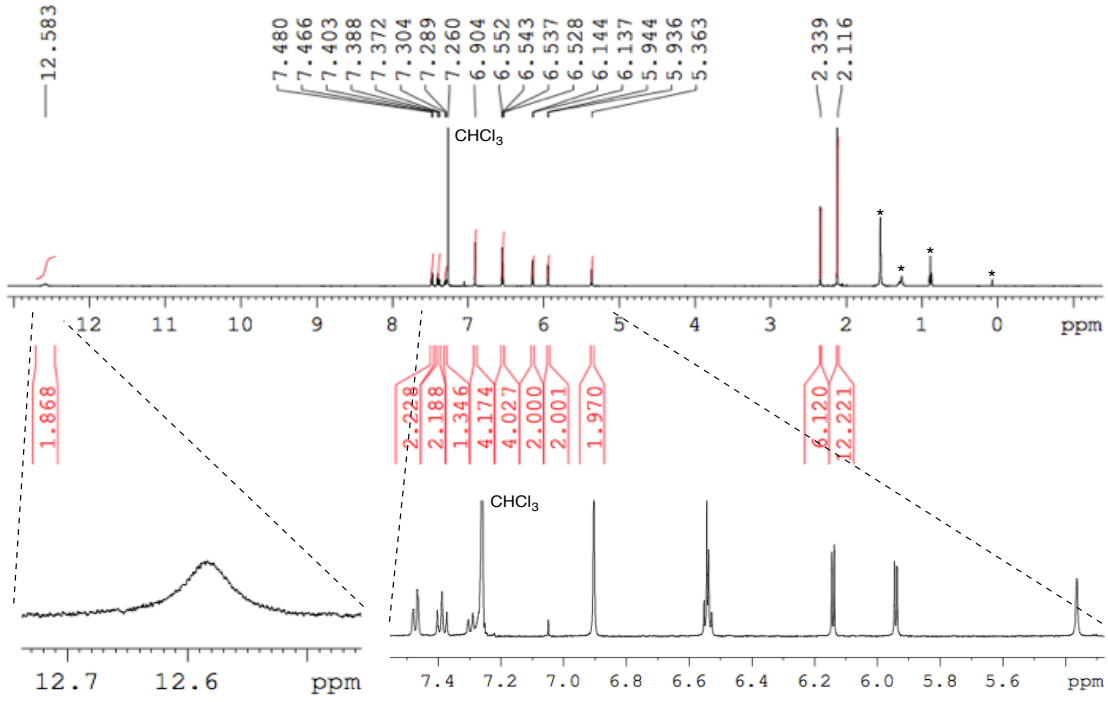


Fig S4. [1]H NMR spectrum of **2a** in $CDCl_3$.

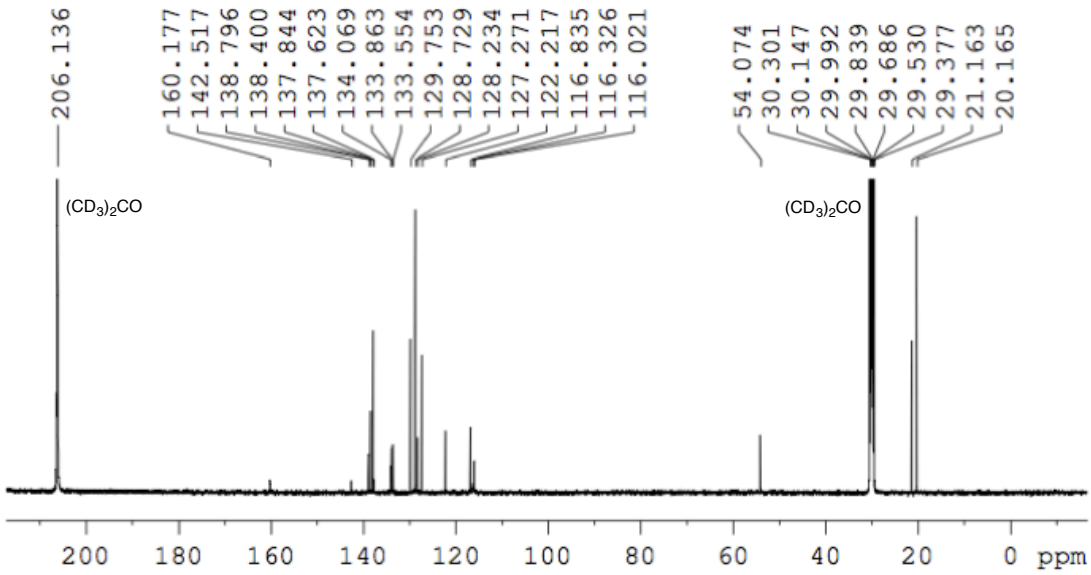


Fig S5. ^{13}C NMR spectrum of **2a** in acetone-d_6.

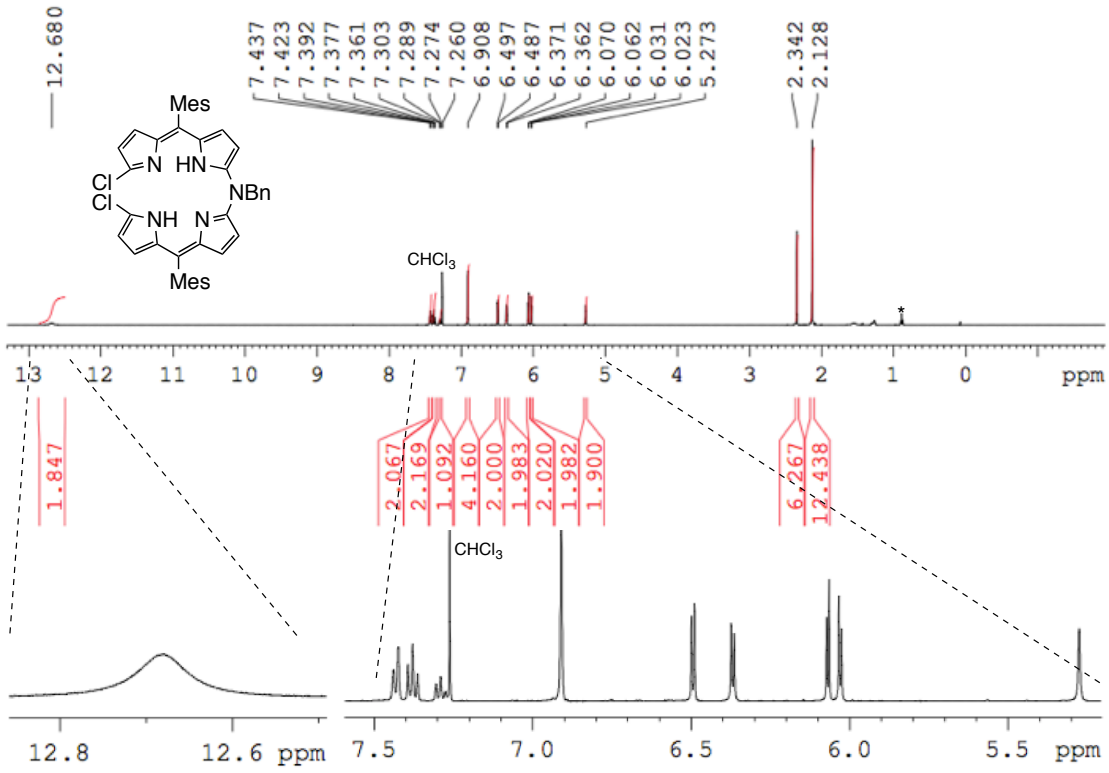


Fig S6. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

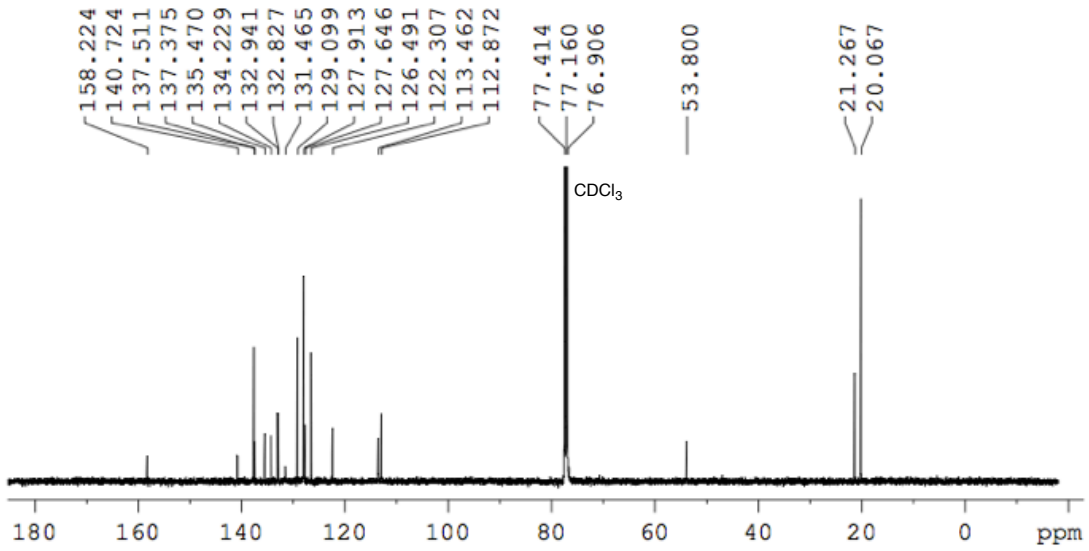


Fig S7. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

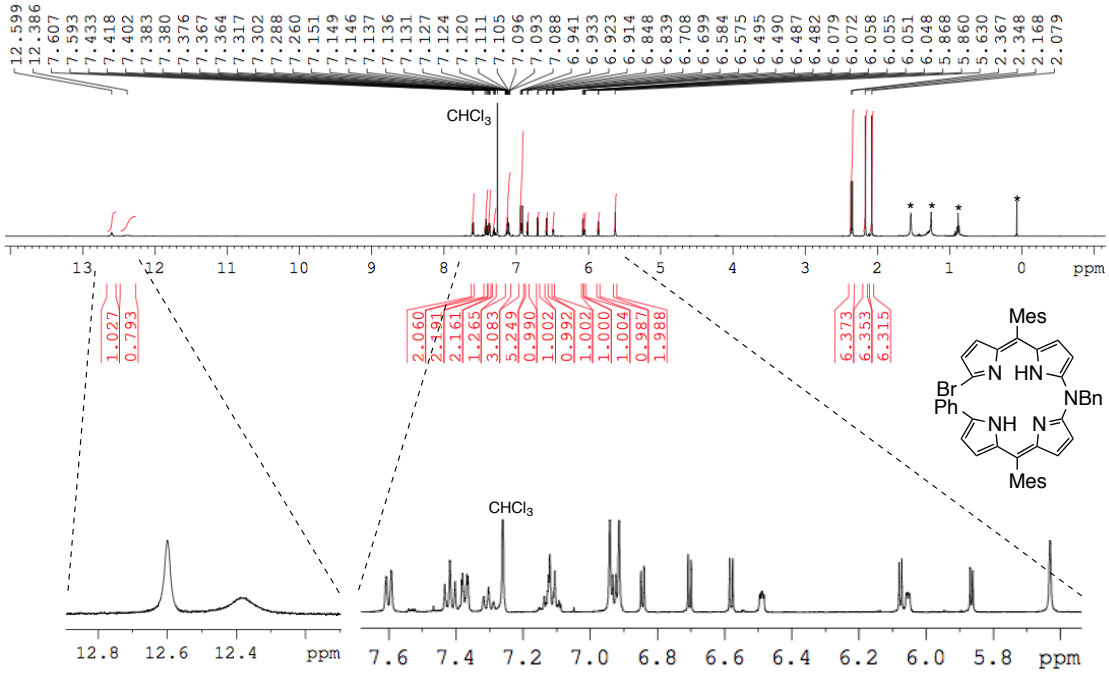


Fig S8. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

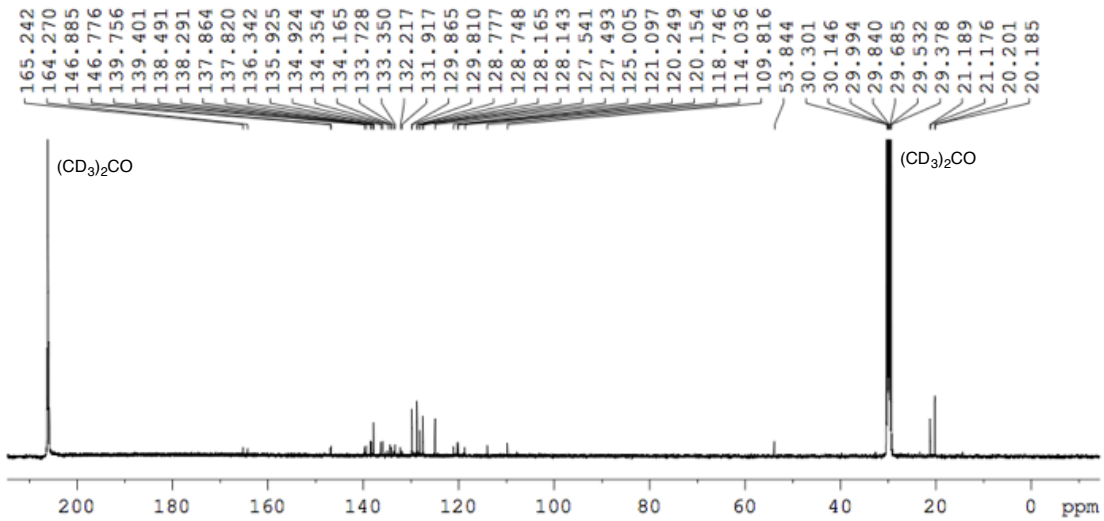


Fig S9. ^{13}C NMR spectrum of **2c** in acetone-d_6.

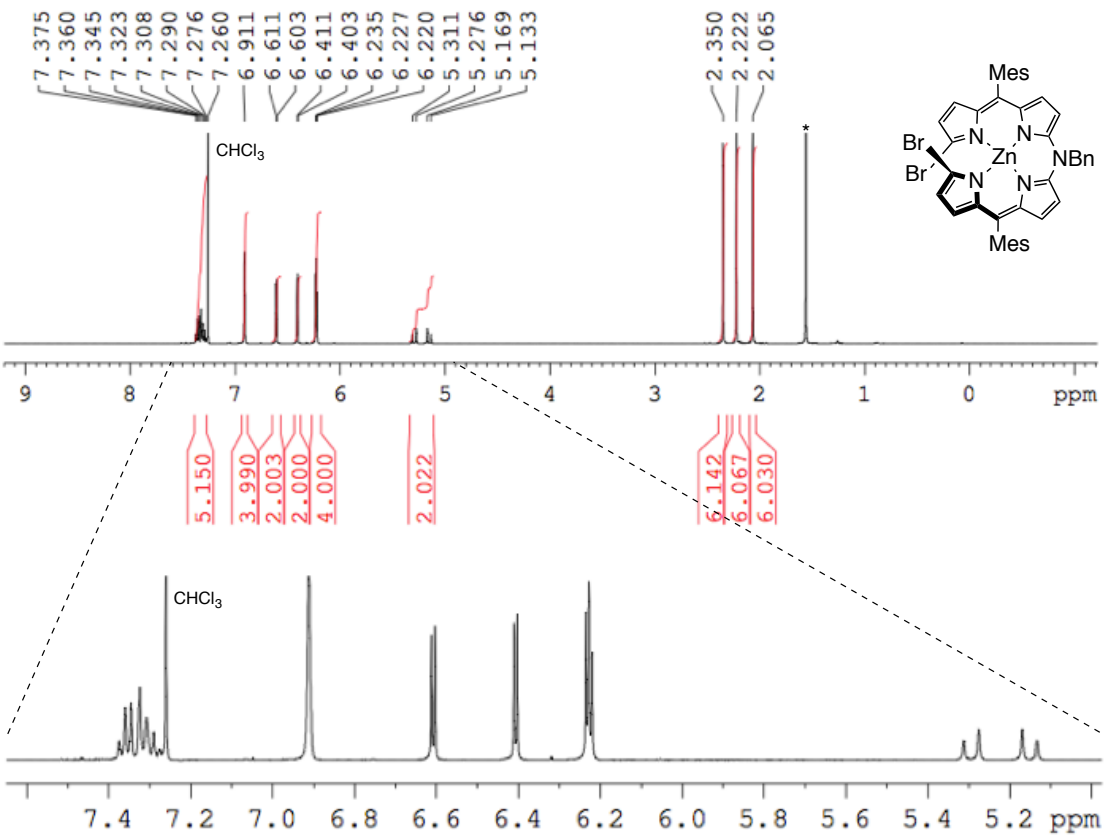


Fig S10. ^{1}H NMR spectrum of **3Zn** in $CDCl_3$.

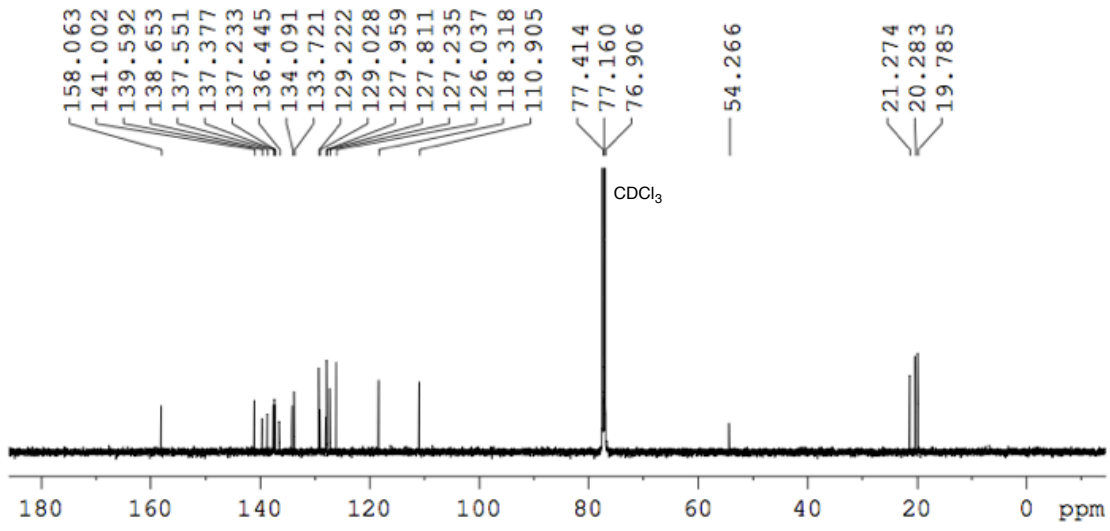


Fig S11. ^{13}C NMR spectrum of **3Zn** in $CDCl_3$.

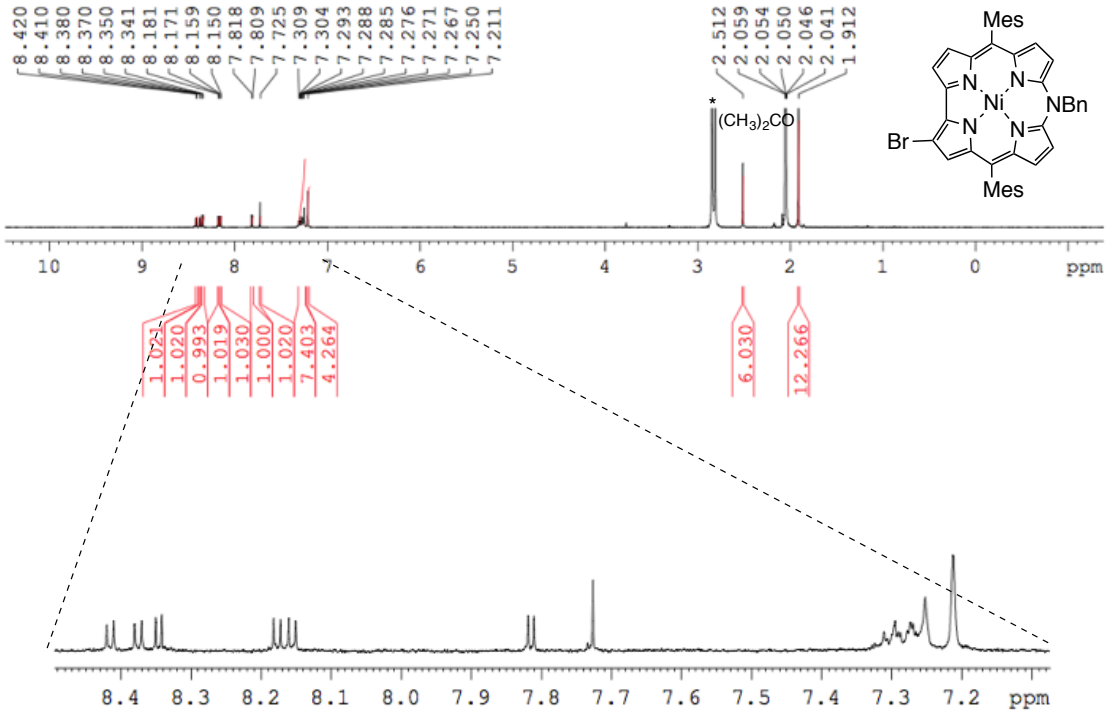


Fig S12. ^{1}H NMR spectrum of **4** in acetone-d_6.

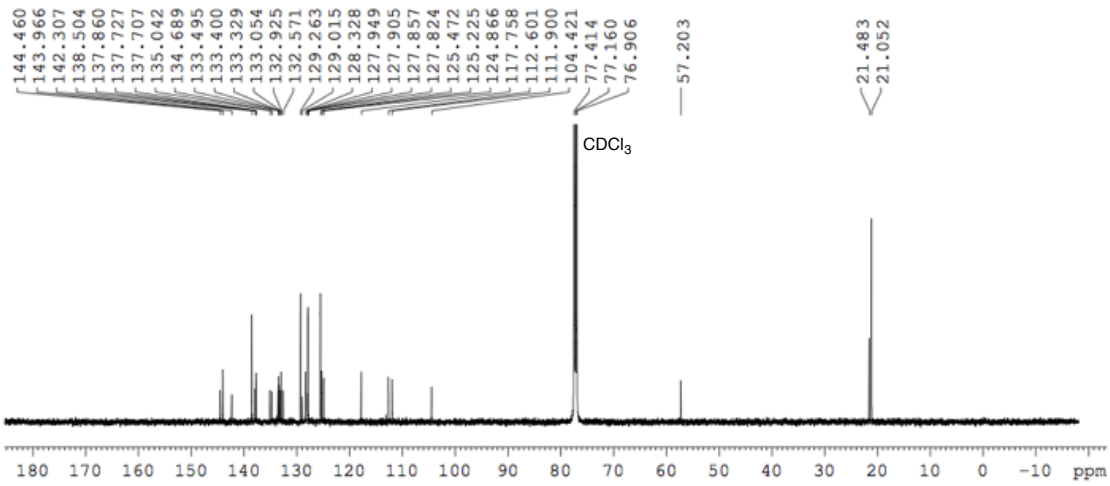


Fig S13. ^{13}C NMR spectrum of **4** in $CDCl_3$.

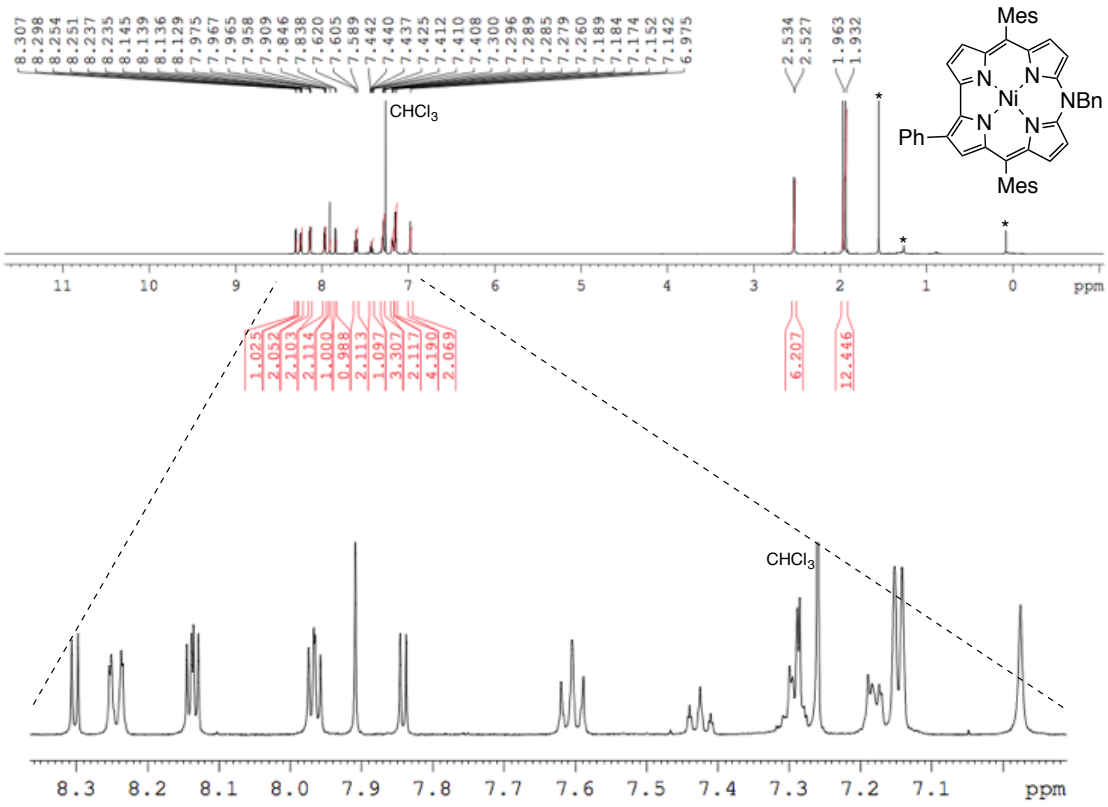


Fig S14. ^{1}H NMR spectrum of **6** in $CDCl_3$.

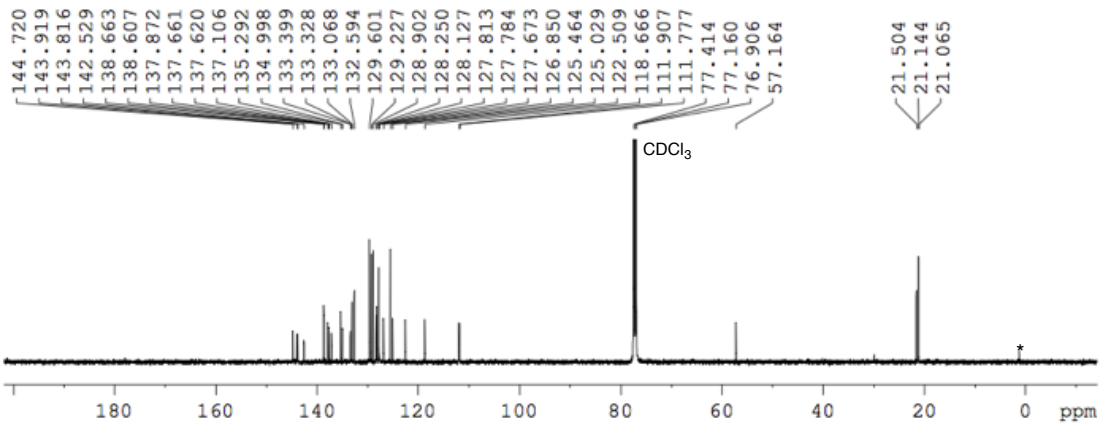


Fig S15. ^{13}C NMR spectrum of **6** in $CDCl_3$.

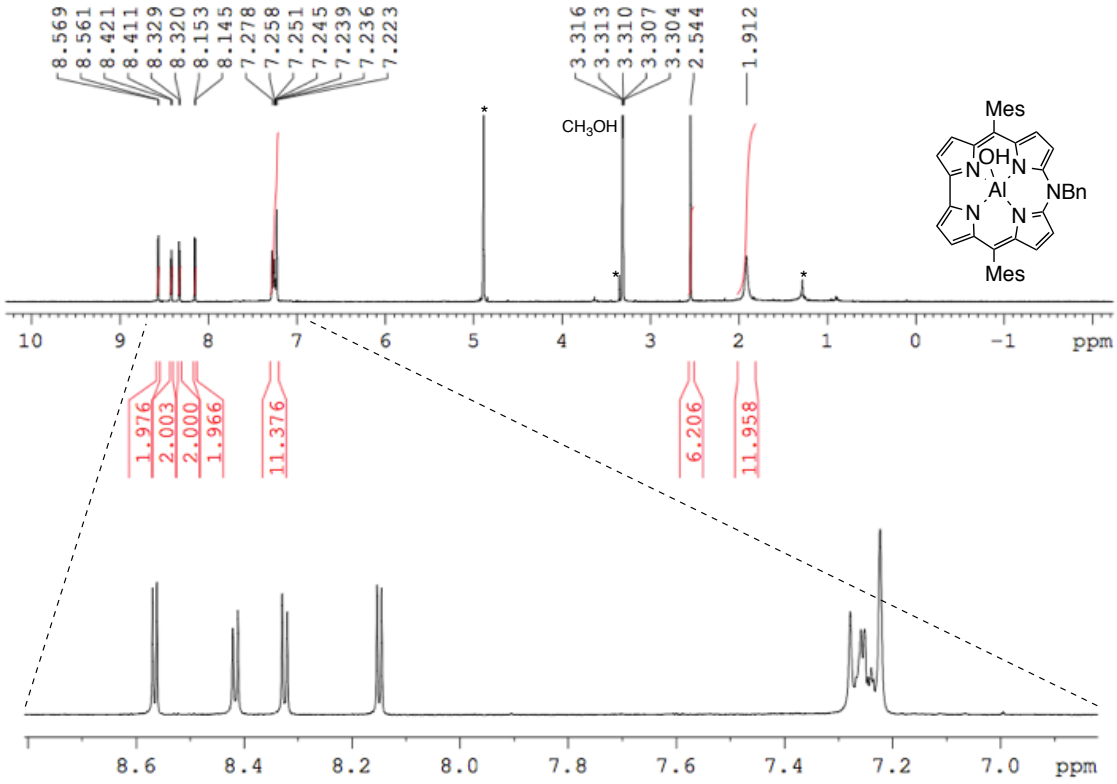


Fig S16. ^{1}H NMR spectrum of **7** in CD_3OD.

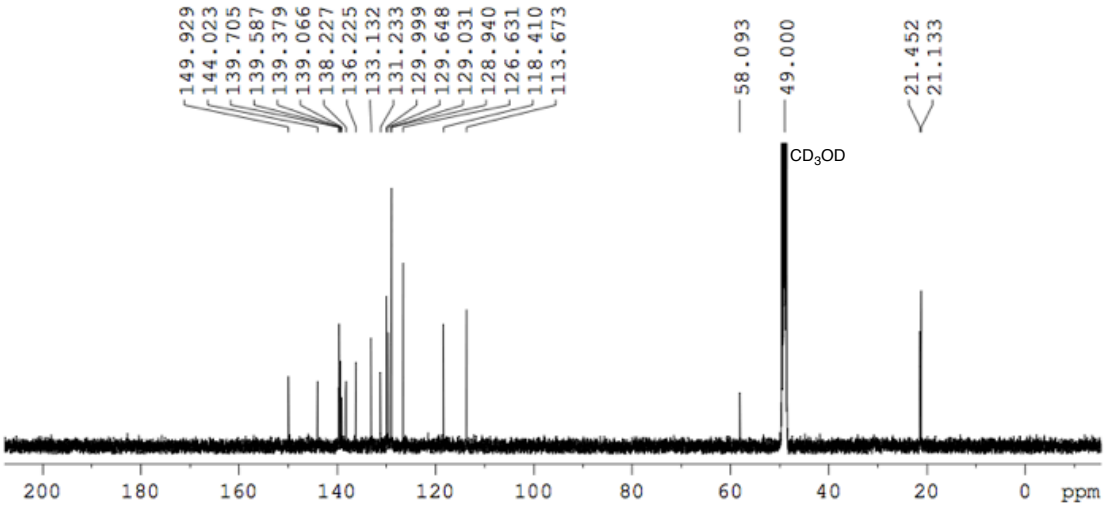


Fig S17. ^{13}C NMR spectrum of **7** in CD_3OD.

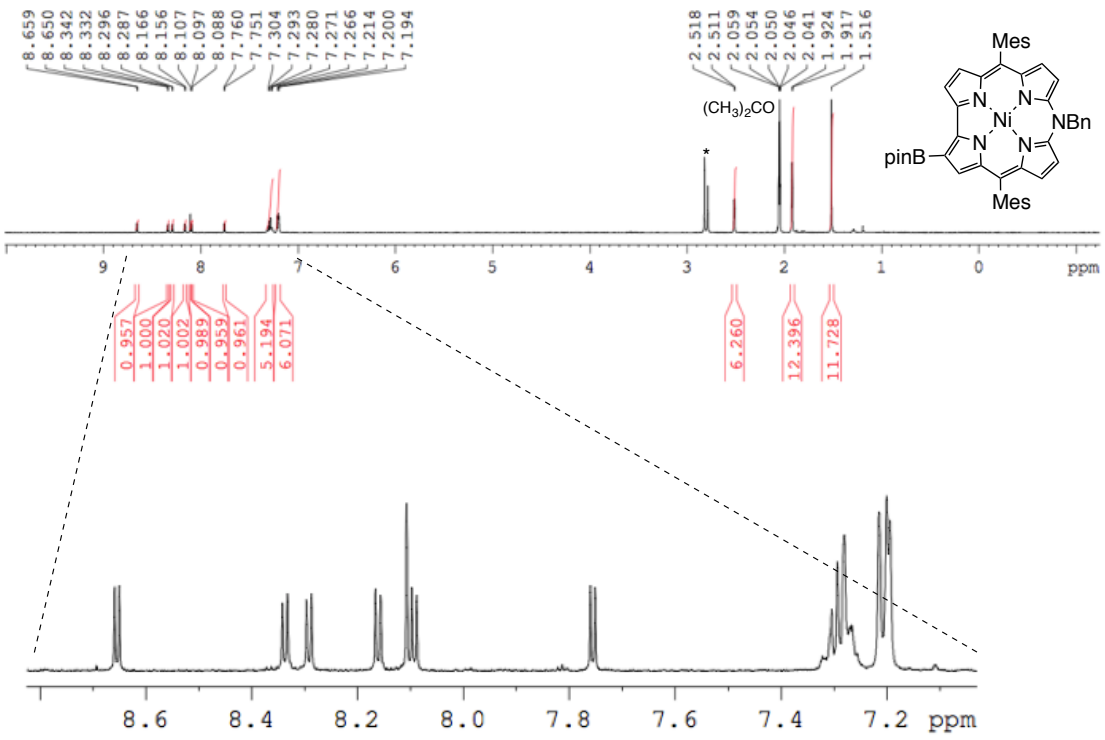


Fig S18. ^{1}H NMR spectrum of **8** in acetone-d_6.

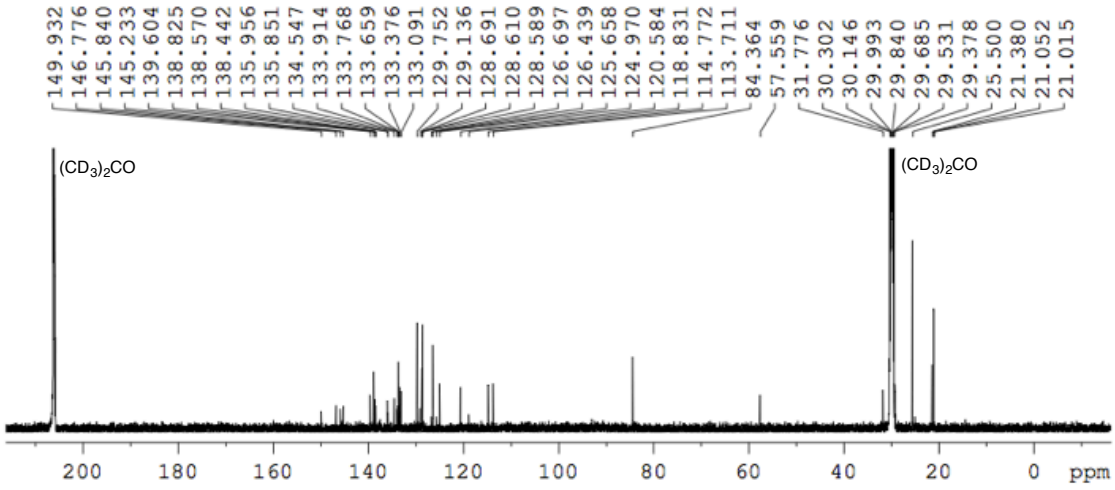


Fig S19. ^{13}C NMR spectrum of **8** in acetone-d_6.

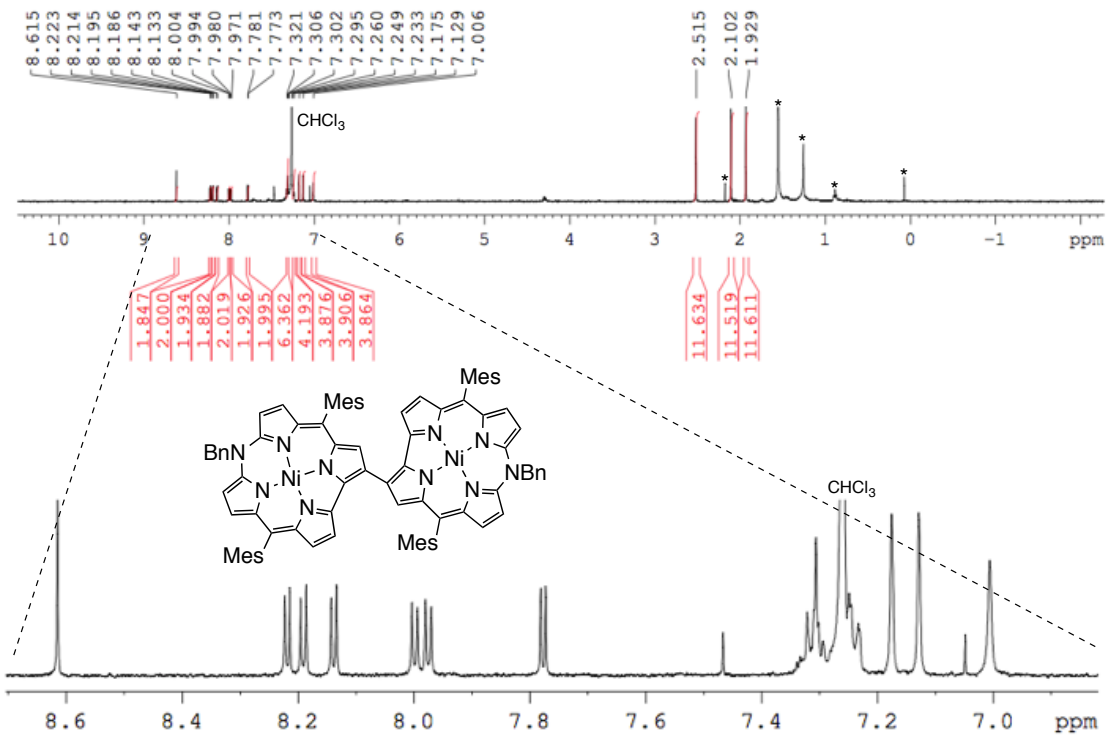


Fig S20. ^{1}H NMR spectrum of **9** in $CDCl_3$.

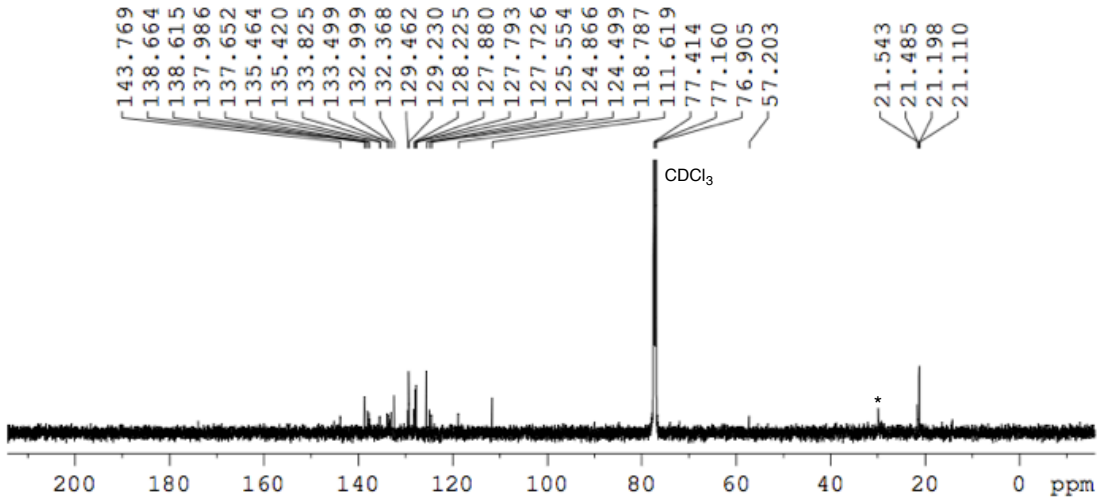


Fig S21. ^{13}C NMR spectrum of **9** in $CDCl_3$.

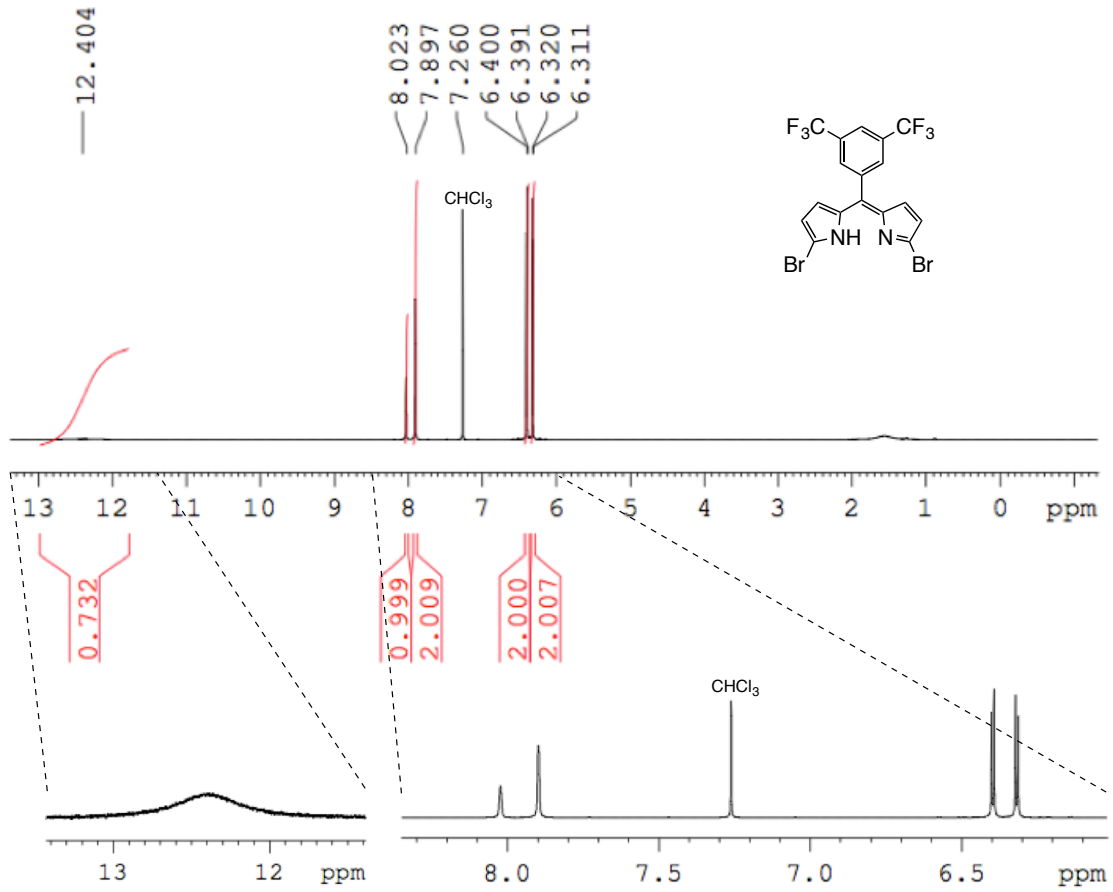


Fig S22. ^{1}H NMR spectrum of *meso*-3,5-bis(trifluoromethyl)phenyl-α,α'-dibromodipyrrin in $CDCl_3$.

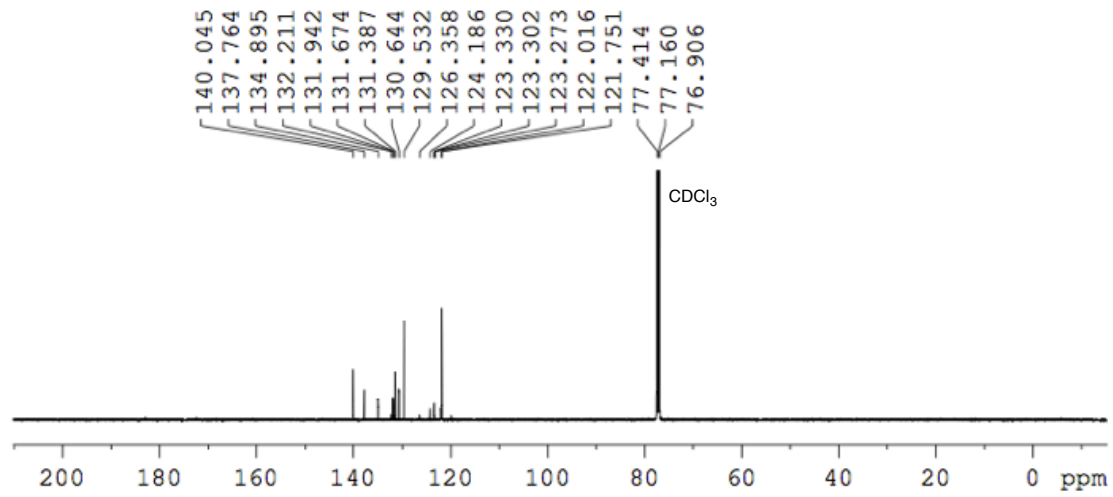


Fig S23. ^{13}C NMR spectrum of *meso*-3,5-bis(trifluoromethyl)phenyl-α,α'-dibromodipyrrin in $CDCl_3$.

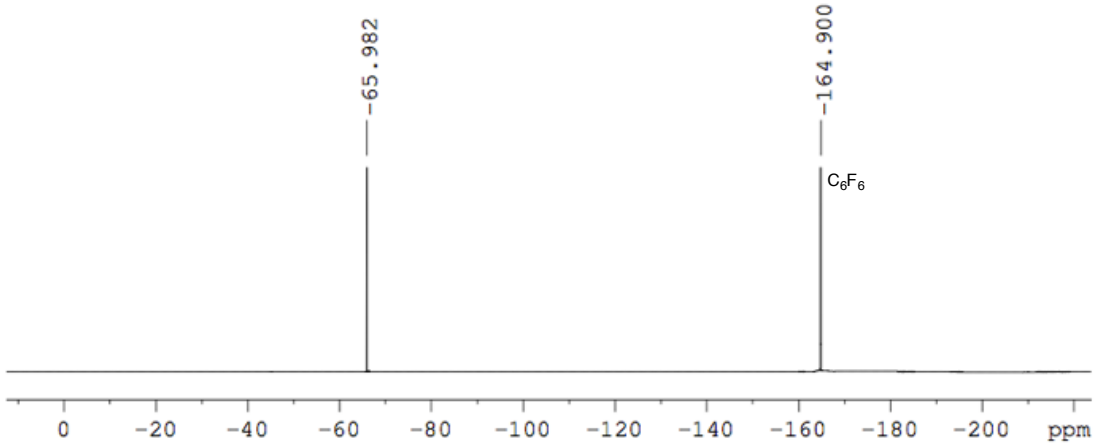


Fig S24. ^{19}F NMR spectrum of *meso*-3,5-bis(trifluoromethyl)phenyl-α,α'-dibromodipyrrin in $CDCl_3$.

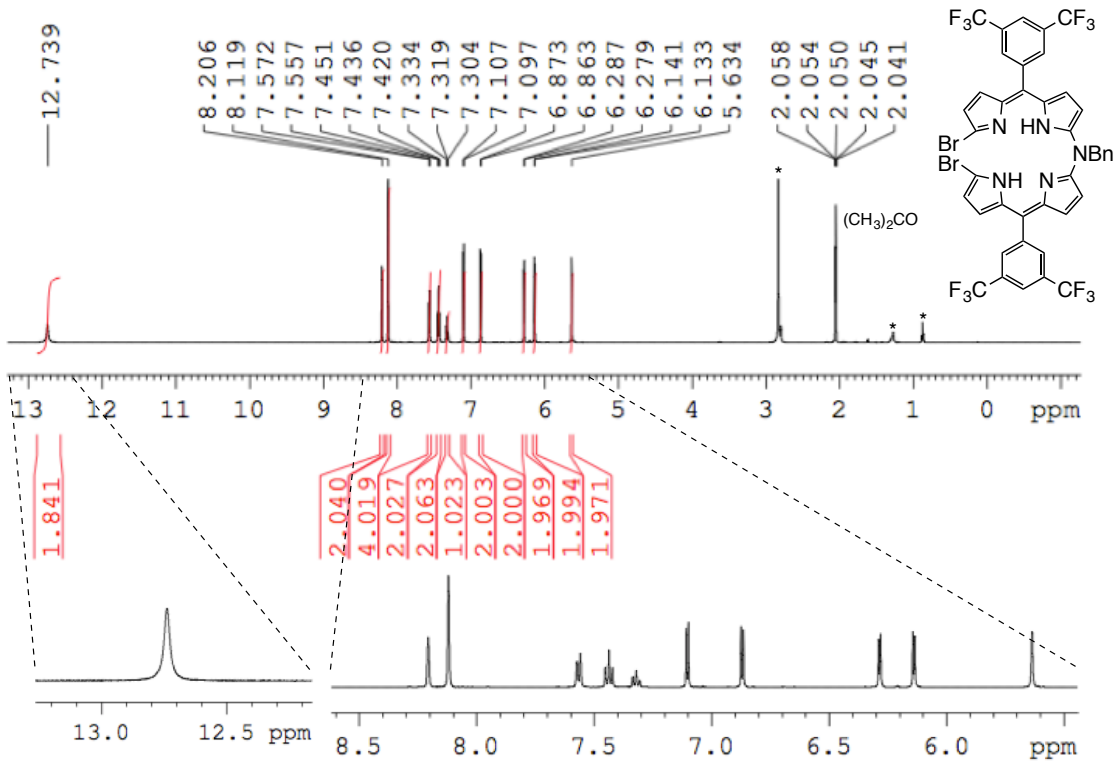


Fig S25. ^{1}H NMR spectrum of *N*,*N*-bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine in acetone-d_6.

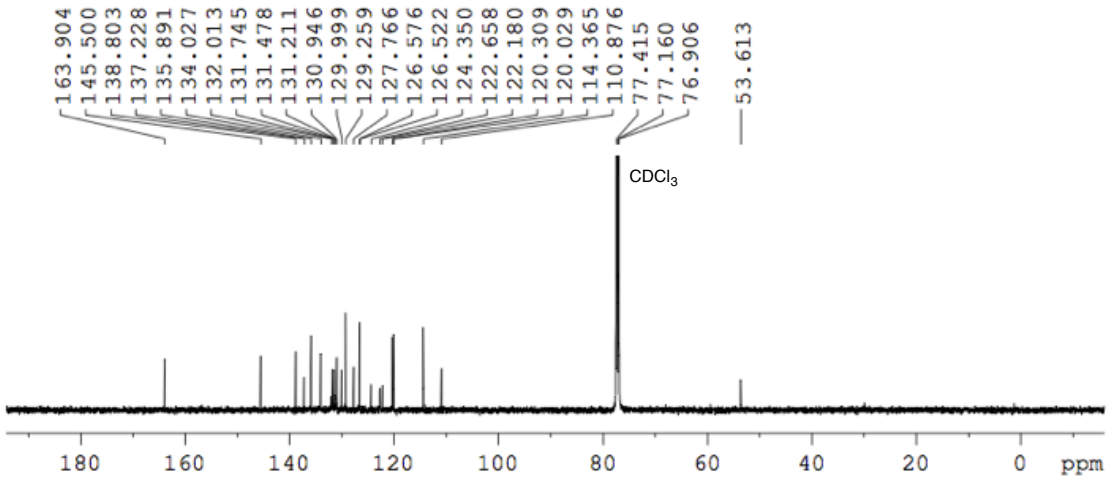


Fig S26. ^{13}C NMR spectrum of *N*,*N*-bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine in $CDCl_3$.

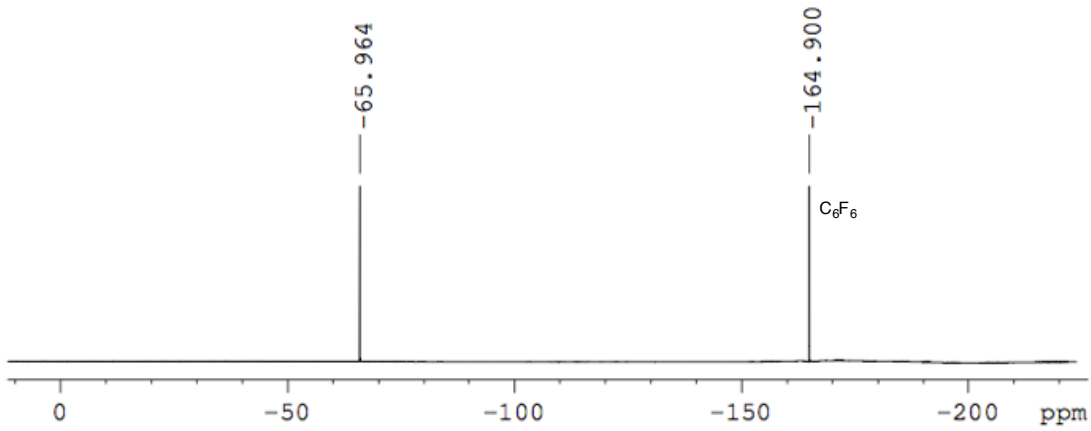


Fig S27. ^{19}F NMR spectrum of *N*,*N*-bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine in $CDCl_3$.

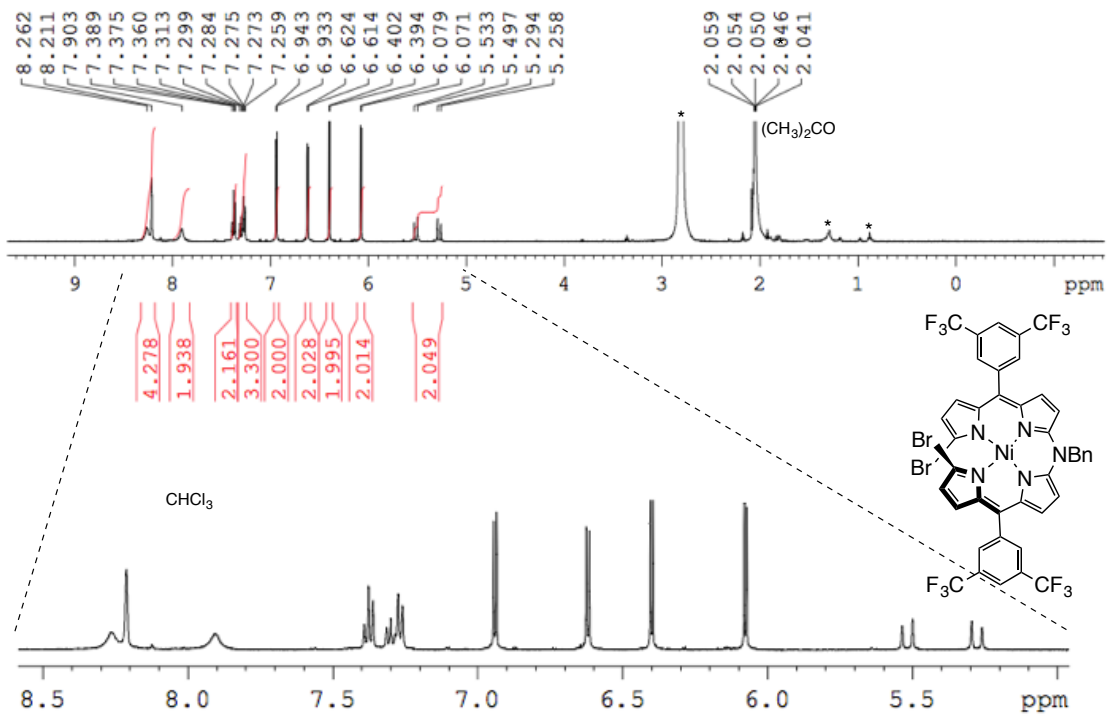


Fig S28. ^{1}H NMR spectrum of *N*,*N*-Bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine Ni complex in acetone-d_6.

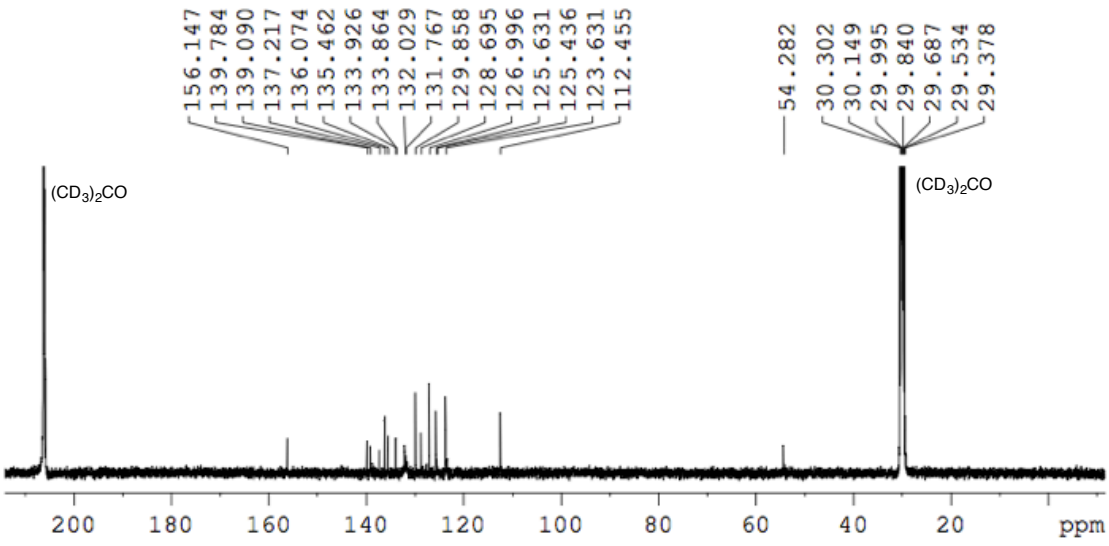


Fig S29. ^{13}C NMR spectrum of *N*,*N*-Bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine Ni complex in acetone-d_6.

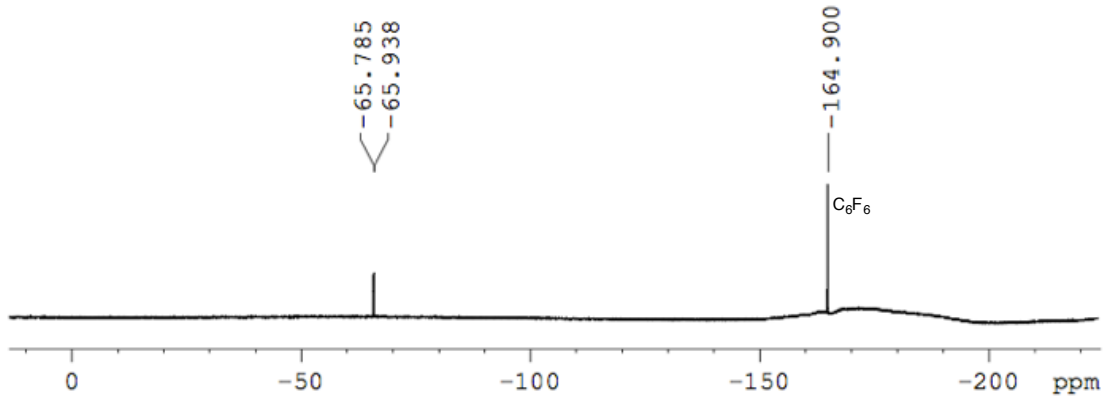


Fig S30. ^{19}F NMR spectrum of *N*,*N*-bis(*meso*-3,5-bis(trifluoromethyl)phenyl-1-bromodipyrrin-9-yl)- *N*-benzylamine Ni complex in $CDCl_3$.

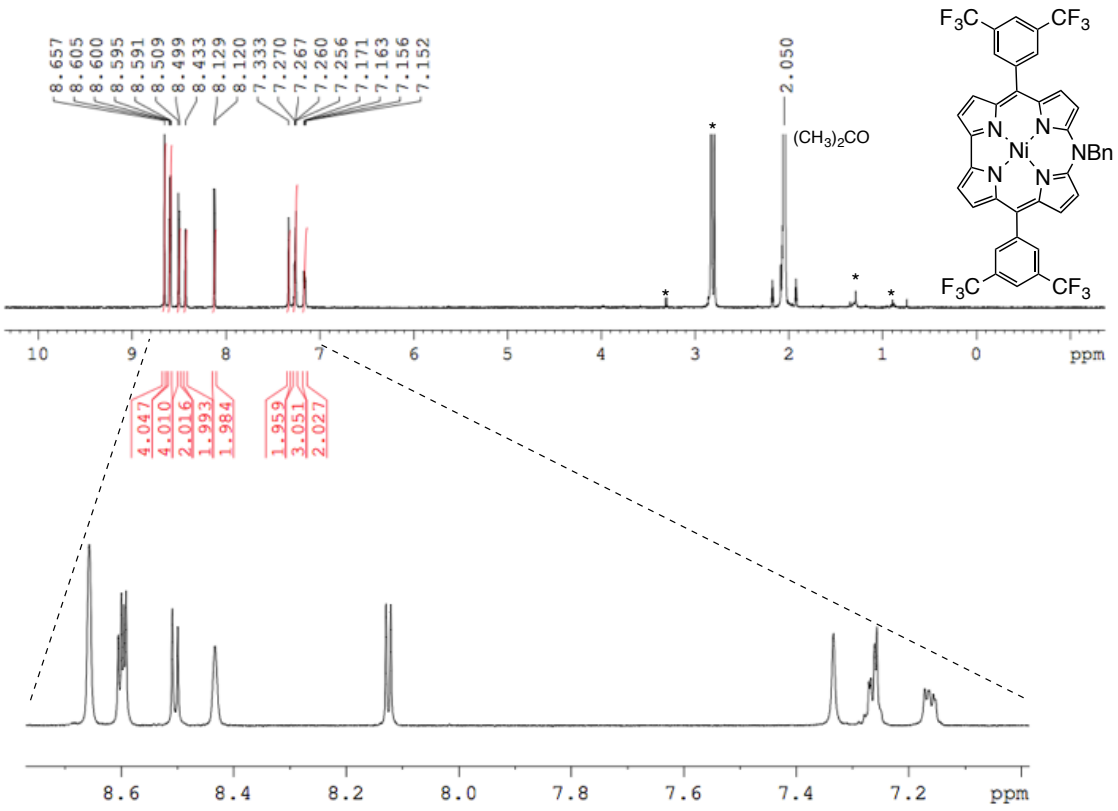


Fig S31. ^{1}H NMR spectrum of 5,15-(3,5-bis(trifluoromethyl)phenyl)-10-azacorrole in acetone-d_6.

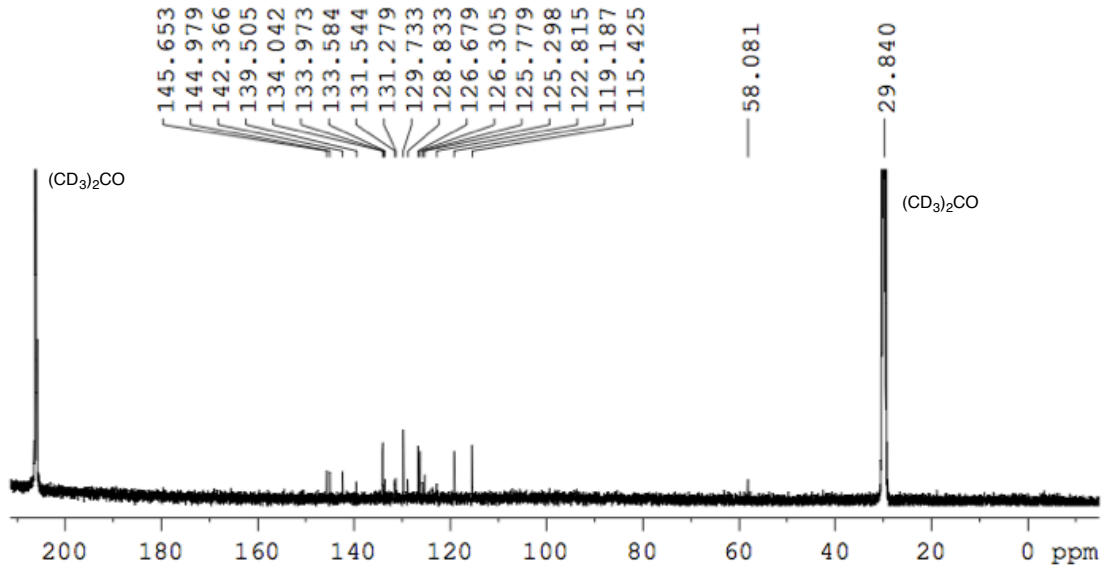


Fig S32. ^{13}C NMR spectrum of 5,15-(3,5-bis(trifluoromethyl)phenyl)-10-azacorrole in acetone-d_6.

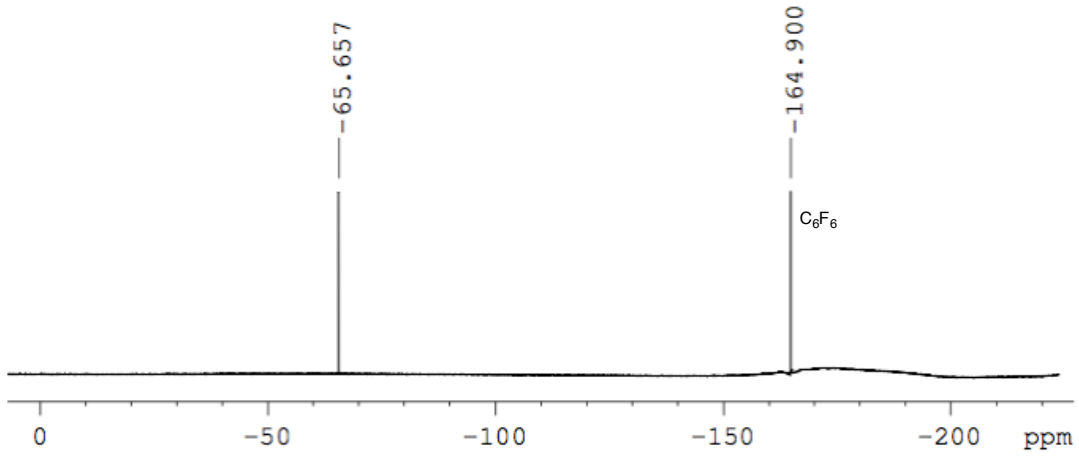


Fig S33. ^{19}F NMR spectrum of 5,15-(3,5-bis(trifluoromethyl)phenyl)-10-azacorrole in $CDCl_3$.

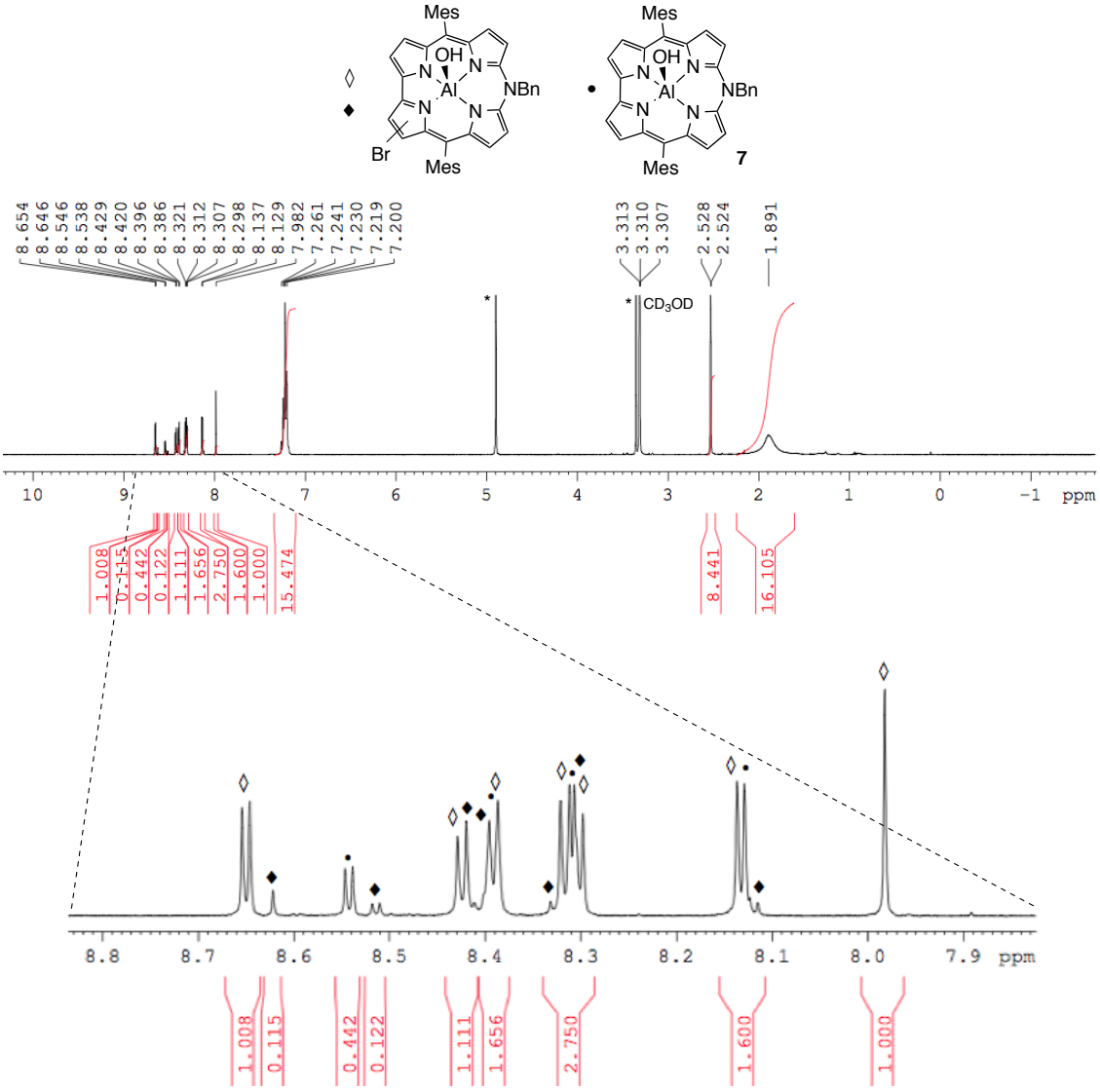


Fig S34. ^{1}H NMR spectra of the mixture obtained by the reaction with $AlCl_3$ in CD_2Cl_2.

Cyclic Voltammetry

The cyclic voltammogram and differential-pulse voltammogram of **5** and **7** were recorded on ALS electrochemical analyser 612C. Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three-electrode system was used and consisted of a platinum working electrode, a platinum wire and $Ag/AgClO_4$ as the reference electrode. The scan rate was 100 mVs^{-1}. The measurement was performed under nitrogen atmosphere. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

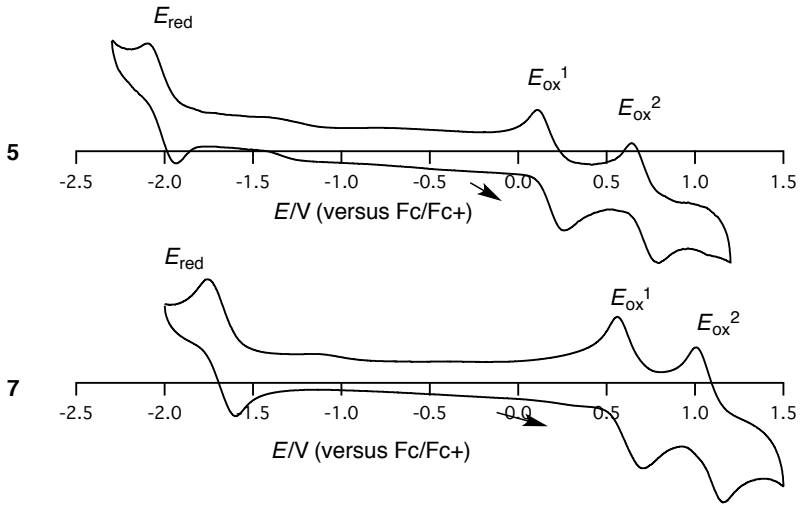


Fig. S35 Cyclic voltammograms of **5** and **7**.

Table S1. Results of electrochemical measurement for **5** and **7**.[a]

Compound	E_{red}	E_{ox}^{1}	E_{ox}^{2}	ΔE^{b}
5	–2.01	0.181	0.718	2.19
7	–1.89	0.426	0.871	2.33

a: unit: V, *b*: $\Delta E = E_{ox}^{1} - E_{red}$

Theoretical Calculations

All calculations were carried out using the Gaussian 09 program.[2] The geometries of all compounds for the mechanistic investigations were optimized by the DFT method with Zhao's M06-2X functional[3] and the 6-31G(d) basis set for C, H, N, and Br atoms and SDD for Ni. Mesityl substituents were replaced with hydrogen to reduce the calculation cost. The structures of the intermediates and transition states were obtained by hand-guesses. Full optimizations were performed without any symmetry restriction with the M06-2X/631SDD method. Zero-point energy and thermal energy corrections were conducted for all optimized structures, and the sums of electronic and thermal free energies were obtained. The zero-point energies were not scaled, and the enthalpic corrections were made at 298.150 K. Each transition state gave single imaginary frequency and IRC calculations supported the transition structure.

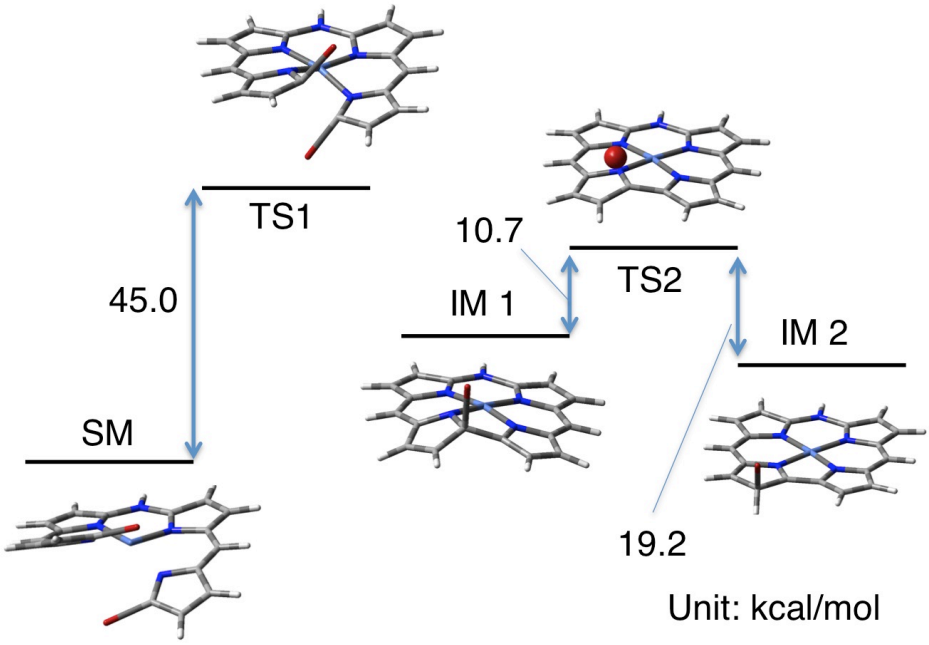


Fig S36. Energy profile for electrocyclization and 1,2-migration by DFT calculations. The calculations were performed at the M06-2X/6-31G(d) level.

Table S2. Summary of calculations on the electroncyclization/1,2-migration process of **3Ni**.

	3Ni	**TS1**
Energy (au)	–6279.613308	–6279.542662
Total Energy (au)	–6279.662114	–6279.590389
E_a (kcal/mol)		45.0

	IM I	**TS2**	**IM II**
Energy (au)	–3707.917140	–3707.900435	–3707.930149
Total Energy (au)	–3707.962407	–3707.945341	–3707.975947
E_a (kcal/mol)		10.7	

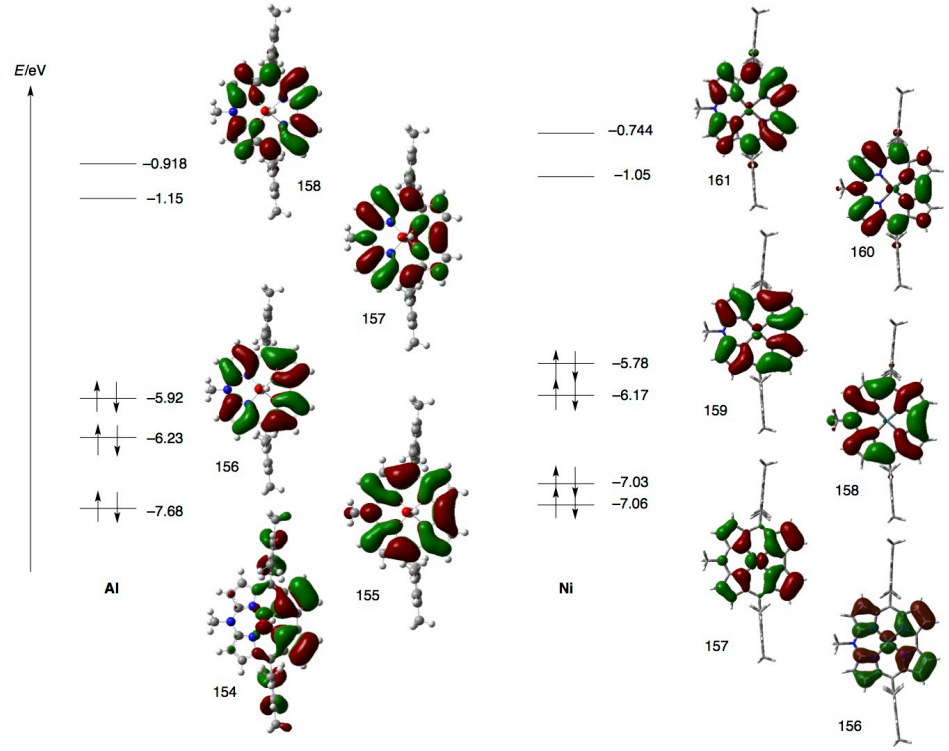


Fig S37. MO diagrams of Al^{III} azacorrole **7** and Ni^{II} azacorrole **5**.

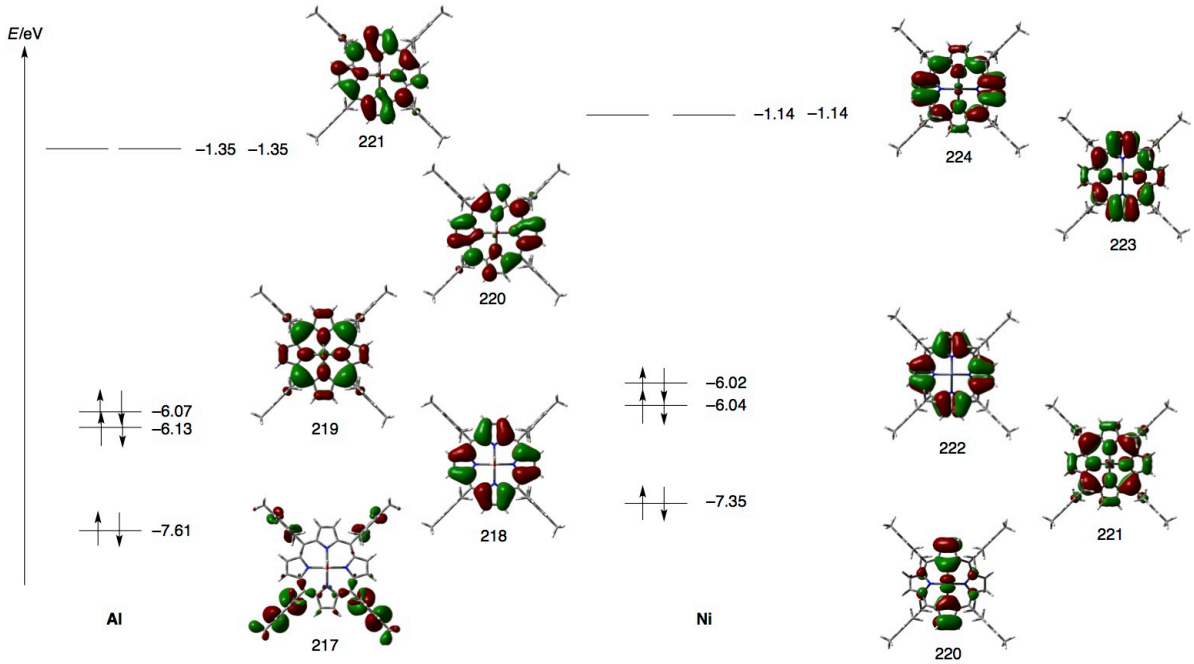


Fig S38. MO diagrams of Al^{III} TPP and Ni^{II} TPP.

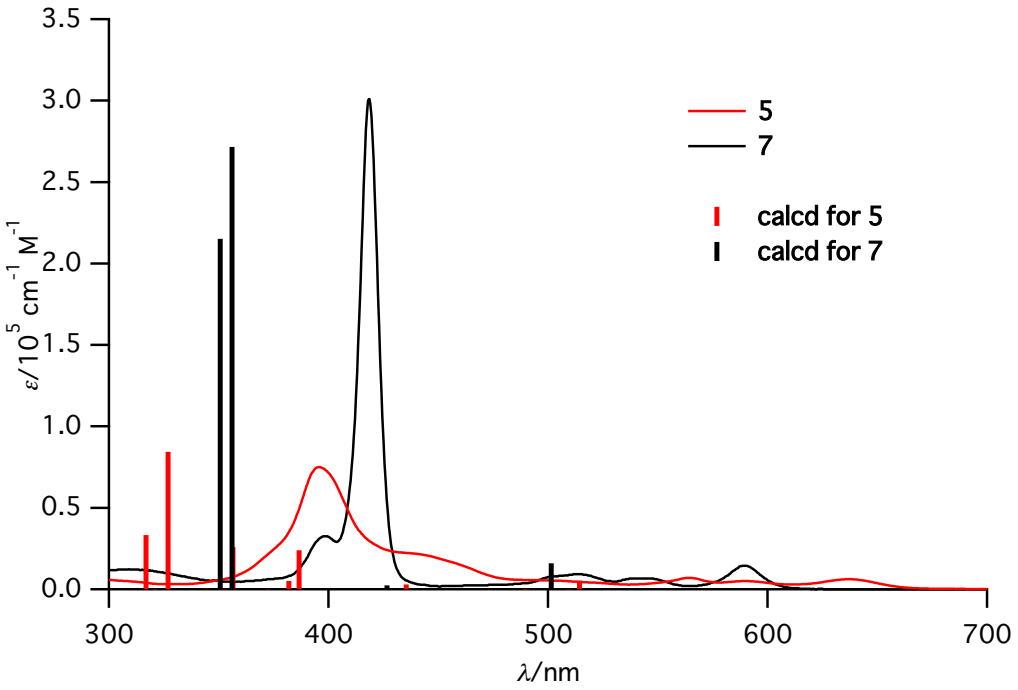


Fig S39. Calculated oscillator strengths of **5** and **7**.

Table S3. Summary of calculated oscillator strengths for compounds **5** and **7**.

compound	wavelength (nm)	oscillator strength	component	population
5	514.26	0.0542	158 → 161	–0.27757
			159 → 160	0.63241
	435.36	0.0313	157 → 160	0.19131
			158 → 160	0.30206
			159 → 161	0.59289
	386.53	0.2394	157 → 160	–0.41823
			158 → 160	0.52008
			159 → 161	–0.10831
	326.93	0.8454	156 → 160	–0.44106
			158 → 161	0.45884
			159 → 160	0.27599
7	501.39	0.0535	155 → 158	–0.36015
			156 → 158	0.60061
	426.54	0.0084	155 → 157	0.44108
			156 → 158	0.54352
	356.06	0.9053	155 → 157	0.54688
			156 → 158	–0.43930
	350.61	0.7176	154 → 157	0.13544
			155 → 158	0.57919
			156 → 157	0.35471

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