Electronic Supporting Information

Effective stabilization of a planar phosphorus(III) center embedded in a porphyrin-based fused aromatic skeleton

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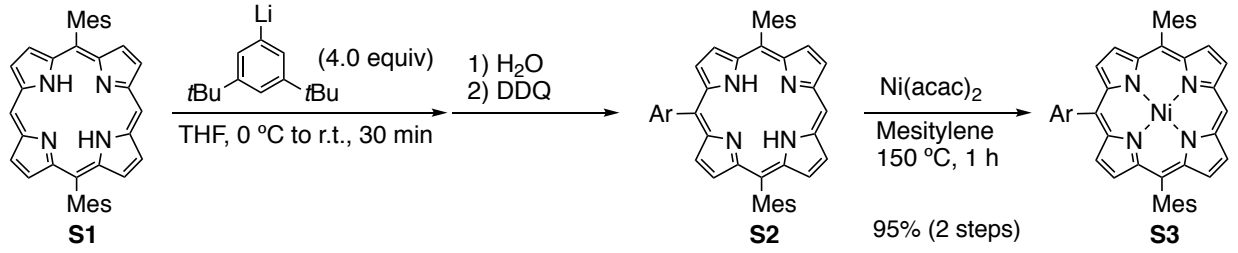
Contents

1. Instrumentation and Materials

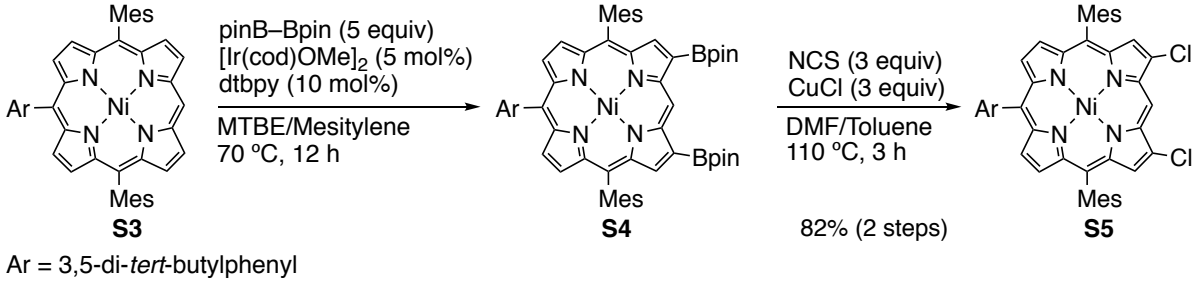
^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{31}P NMR (243 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts were reported as delta scale in ppm relative to $CHCl_3$ (δ = 7.26) and $CHDCl_2$ (δ = 5.31) for ^{1}H NMR, to $CDCl_3$ (δ = 77.16) for ^{13}C NMR, and to H_3PO_4 (δ = 0.00) for ^{31}P NMR. UV/Vis absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. High-resolution APCI-TOF mass spectra were taken on a Bruker micrOTOF. X-Ray single crystal diffraction analyses were performed on a Rigaku XtaLAB P200 apparatus at –180 °C using two-dimensional detector PILATUS 100K/R with Cu-K_α radiation (λ = 1.54187 Å). The structures were solved by direct method SIR-97 and refined by SHELXL-97 program.[S1] Redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 660. Magnetic susceptibility was measured for the powder sample with the temperature range from 2 to 300 K at 0.5 T magnetic field by a Quantum Design MPMS-2S instrument. Toluene and *o*-dichlorobenzene (*o*-DCB) were distilled from CaH_2. THF and ether was purified by passing through a neutral alumina column under N_2. $CHCl_3$ was purified by passing through alumina column. Methyl *tert*-butyl ether (MTBE) and mesitylene were dried over activated MS4A under N_2. Anhydrous dimethylacetamide (DMA) was purchased from Sigma Aldrich. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental Procedures and Compound Data



Synthesis of S3: To a Schlenk tube containing Li shot (210 mg, 30 mmol) and dry ether (6.0 mL), 1-bromo-3,5-di-*tert*-butylbenzene (2.8 g, 10 mmol in 6.0 mL of ether) was slowly added under argon atmosphere. After the solution was stirred at room temperature for 1 h, the resulting solution of 3,5-di-*tert*-butylphenyllithium was transferred to a Schlenk tube containing 5,15-dimesitylporphyrin **S1** (1.1 g, 2.0 mmol) and dry THF (60 mL) at 0 ºC under argon atmosphere. After the reaction mixture was stirred at 0 ºC for 10 min and then at room temperature for 30 min, H_2O (2.0 mL) was added. After stirring at room temperature for 10 min, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.3 g, 10 mmol) was added. After further stirring at room temperature for 30 min, the reaction mixture was passed through alumina column eluting with CH_2Cl_2. After removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography eluting with CH_2Cl_2/hexane and then dissolved in mesitylene (70 mL), To the obtained mesitylene solution of **S2**, $Ni(acac)_2$ (2.1 g, 7.0 mmol) was added. After stirring at 150 °C for 1 h, the reaction mixture was passed through silica gel column eluting with CH_2Cl_2. After removal of the solvent *in vacuo*, recrystallization from CH_2Cl_2/methanol gave **S3** (1.5 g, 1.9 mmol, 95%).

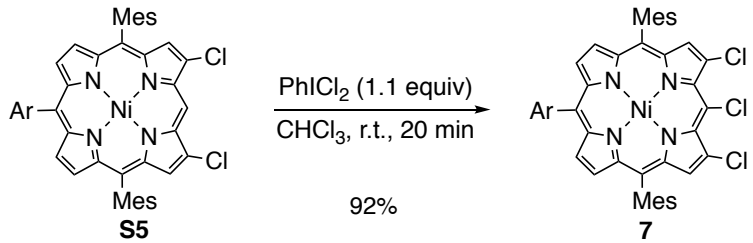
S3: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.79 (s, 1H, *meso*), 9.10 (d, *J* = 4.6 Hz, 2H, β), 8.79 (d, *J* = 4.2 Hz, 2H, β), 8.72 (d, *J* = 4.6 Hz, 2H, β), 8.63 (d, *J* = 5.0 Hz, 2H, β), 7.91 (d, *J* = 1.4 Hz, 2H, Ar-*o*), 7.72 (t, *J* = 1.6 Hz, 1H, Ar-*p*), 7.22 (s, 4H, Mes), 2.58 (s, 6H, Mes), 1.82 (s, 12H, Mes), and 1.47 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 148.95, 143.03, 142.97, 142.83, 142.65, 140.38, 139.22, 137.79, 137.57, 132.89, 132.47, 131.52, 130.93, 129.14, 127.89, 121.14, 120.57, 117.07, 104.25, 35.16, 31.84, 21.56, and 21.53 ppm; HR-APCI-TOF-MS: *m/z* = 790.3586. Calcd for $C_{52}H_{52}N_4{}^{58}Ni$: 790.3551 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 408 (2.5×10^5), and 521 (1.8×10^4) nm.



Ar = 3,5-di-*tert*-butylphenyl

Synthesis of S5: A Schlenk tube containing **S3** (633 mg, 0.80 mmol), $(Bpin)_2$ (1.02 g, 4.0 mmol), $[Ir(cod)OMe]_2$ (26 mg, 0.040 mol), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) (20 mg, 0.080 mmol) was filled with argon, and then charged with dry mesitylene (4.0 mL) and dry MTBE (12 mL). After stirring at 70 °C for 12 h, the reaction mixture was passed through short silica gel column eluting with CH_2Cl_2. After removal of the solvent *in vacuo*, the product **S4** was obtained by recrystallization from CH_2Cl_2/methanol. Then, **S4** was dissolved in *N*,*N*-dimethylformamide (DMF) (80 mL) and toluene (40 mL). To the resulting solution, *N*-chlorosuccinimide (NCS) (322 mg, 2.4 mmol) and CuCl (238 mg, 2.4 mmol) were added. After stirring at 110 °C for 3 h, the reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution, extracted with hexane, washed with water and brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **S5** (565 mg, 0.66 mmol, 82%).

S5: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.13 (s, 1H, *meso*), 8.74 (d, *J* = 4.6 Hz, 2H, β), 8.59 (d, *J* = 4.6 Hz, 2H, β), 8.56 (s, 2H, β), 7.88 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.72 (s, 1H, Ar-*p*), 7.22 (s, 4H, Mes), 2.58 (s, 6H, Mes), 1.80 (s, 12H, Mes), and 1.47 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.14, 143.84, 143.02, 140.49, 139.94, 139.24, 139.10, 138.20, 136.82, 133.50, 133.14, 131.53, 129.06, 128.21, 128.06, 121.54, 121.39, 117.58, 98.25, 35.18, 31.82, 21.56, and 21.52 ppm; HR-APCI-TOF-MS: *m/z* = 858.2764. Calcd for $C_{52}H_{50}N_4{}^{35}Cl_2{}^{58}Ni$: 858.2771 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (2.5×10^5) and 526 (1.5×10^4) nm.

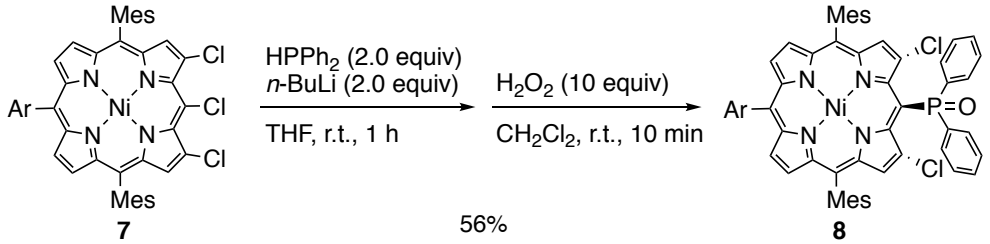


Ar = 3,5-di-*tert*-butylphenyl

Synthesis of 7: To a flask containing **S5** (516 mg, 0.60 mmol) dissolved in $CHCl_3$ (30 mL), a suspension of $PhICl_2$ (180 mg, 0.66 mmol) in 30 mL of $CHCl_3$ was added. After stirring at room temperature for 20 min, the reaction mixture was passed through short silica gel column eluting with CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **7** (493 mg, 0.55 mmol, 92%).

7: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.62 (d, *J* = 4.6 Hz, 2H, β), 8.49 (s, 2H, β), 8.44 (d, *J* = 5.0 Hz, 2H, β), 7.78 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.69 (s, 1H, Ar-*p*), 7.18 (s, 4H, Mes), 2.55 (s, 6H, Mes), 1.83 (s, 12H, Mes), and 1.44 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.39, 144.02, 142.11, 139.02, 138.99, 138.30, 137.74, 136.16, 134.78, 134.16, 133.23, 132.25, 132.50, 128.76, 128.09, 121.53, 120.40, 117.17, 110.48, 35.16,

31.78, 21.50, and 21.44 ppm; HR-APCI-TOF-MS: *m/z* = 892.2376. Calcd for $C_{52}H_{49}N_4{}^{35}Cl_3{}^{58}Ni$: 892.2382 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 425 (1.9×10^5) and 543 (1.5×10^4) nm.

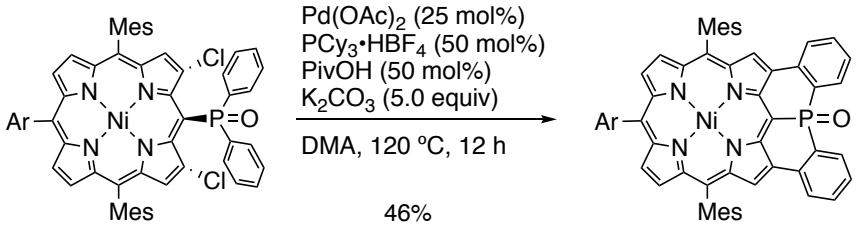


7 56% **8**

Ar = 3,5-di-*tert*-butylphenyl

Synthesis of 8: To a Schlenk tube containing diphenylphosphine ($HPPh_2$, 103 μL, 0.60 mmol) and dry THF (3.0 mL), *n*-BuLi (1.6 M in hexane, 0.37 mL, 0.60 mmol) was slowly added at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 20 min, the resulting solution was transferred to a Schlenk tube containing 3,5,7-trichloroporphyrin **7** (269 mg, 0.30 mmol) and dry THF (15 mL) at room temperature under argon atmosphere. After stirring at room temperature for 1 h, the reaction mixture was quenched by aqueous NH_4Cl solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (30 mL). To the CH_2Cl_2 solution, H_2O_2 (30% in water, 0.3 mL, 3 mmol) was added. After stirring at room temperature for 10 min, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **8** (177 mg, 167 μmol, 56%).

8: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.60 (d, *J* = 4.6 Hz, 2H, β), 8.31 (s, 1H, Ar-*o*), 8.29 (d, *J* = 5.0 Hz, 2H, β), 8.02 (s, 2H, β), 7.70 (s, 1H, Ar-*p*), 7.44 (s, 1H, Ar-*o*), 7.22 (s, 2H, Mes), 7.02 (t, *J* = 7.3 Hz, 2H, Ph), 6.99 (s, 2H, Mes), 6.75 (broad, 4H, Ph), 6.49 (broad, 4H, Ph), 2.48 (s, 6H, Mes), 2.16 (s, 6H, Mes), 1.54 (s, 9H, *tert*-butyl), 1.37 (s, 9H, *tert*-butyl), and 1.29 (s, 6H, Mes) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.54, 145.72, 145.67, 143.92, 142.85, 139.49, 139.34, 138.77, 138.35, 138.05 (d, *J* = 5.8 Hz), 135.74, 135.52, 134.37, 133.05, 130.99, 130.84 (d, *J* = 8.7 Hz), 129.98, 128.04 (d, *J* = 14.5 Hz), 127.16 (d, *J* = 11.6 Hz), 125.68, 121.86, 119.82, 94.53 (d, *J* = 110 Hz), 35.21, 31.80, 21.44, 21.23, and 21.11 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 12.90 ppm; HR-APCI-TOF-MS: *m/z* = 1058.3152. Calcd for $C_{64}H_{59}ON_4{}^{35}Cl_2P^{58}Ni$: 1058.3163 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 447 (1.8×10^5), 594 (9.1×10^3), and 625 (1.5×10^4) nm.



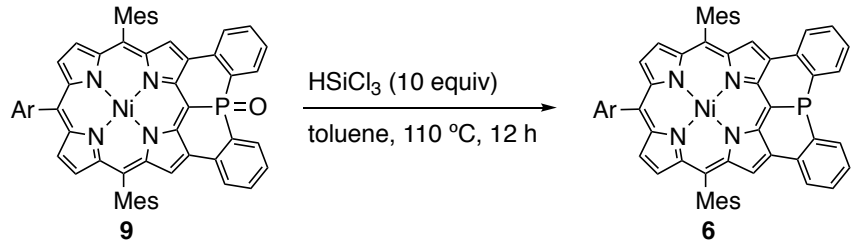
8

Ar = 3,5-di-*tert*-butylphenyl

9

Synthesis of 9: A Schlenk tube containing **8** (127 mg, 0.12 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), $PCy_3 \cdot HBF_4$ (22 mg, 0.060 mmol), PivOH (6.0 mg, 0.060 mmol), and K_2CO_3 (84 mg, 0.60 mmol) was filled with argon, and then charged with dry DMA (12 mL). After stirring at 120 °C for 12 h, the reaction mixture was quenched with water, extracted with hexane/CH_2Cl_2, washed with water twice and brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **9** (54 mg, 55 μmol, 46%).

9: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.68 (s, 2H, β), 8.56 (dd, *J* = 7.8 and 11.0 Hz, 2H, P-Ph), 8.50 (d, *J* = 5.0 Hz, 2H, β), 8.28 (d, *J* = 4.4 Hz, 2H, β), 8.24 (dd, *J* = 7.8 and 4.6 Hz, 2H, P-Ph), 8.19 (s, 1H, Ar-*o*), 7.67 (s, 1H, Ar-*p*), 7.65 (t, *J* = 7.8 Hz, 2H, P-Ph), 7.56 (t, *J* = 7.3 Hz, 2H, P-Ph), 7.44 (s, 1H, Ar-*o*), 7.32 (s, 2H, Mes), 7.08 (s, 2H, Mes), 2.56 (s, 6H, Mes), 2.31 (s, 6H, Mes), 1.51 (s, 9H, *tert*-butyl), 1.39 (s, 6H, Mes), and 1.37 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.19 (broad), 145.08, 143.93, 142.08, 140.81 (d, *J* = 7.2 Hz), 139.54, 139.12, 138.74 (d, *J* = 8.6 Hz), 138.52, 138.23, 136.08, 135.63 (d, *J* = 7.2 Hz), 134.00, 132.50, 132.05, 131.03, 128.84 (d, *J* = 10.1 Hz), 128.46, 128.23, 127.92, 127.66, 126.97 (d, *J* = 8.5 Hz), 125.24, 121.60, 120.61, 96.36 (d, *J* = 107 Hz), 35.16, 31.78, 21.88, 21.54, and 21.27 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 0.88 ppm; HR-APCI-TOF-MS: *m/z* = 986.3623. Calcd for $C_{64}H_{57}ON_4P^{58}Ni$: 986.3629 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 455 (1.4×10^5), 594 (9.8×10^3), and 643 (1.4×10^4) nm.



9

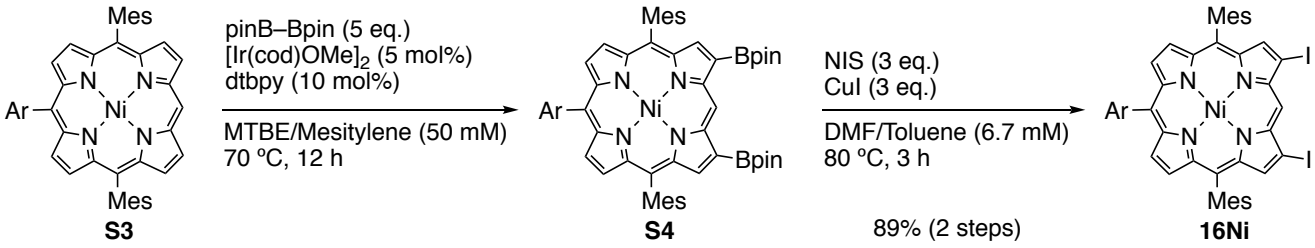
Ar = 3,5-di-*tert*-butylphenyl

6

Synthesis of 9: A Schlenk tube containing **9** (30 mg, 30 μmol) was filled with argon, and then charged with dry toluene (1.5 mL) and $HSiCl_3$ (0.20 M in toluene, 1.5 mL, 30 μmol). After stirring at 110 °C for 12 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal

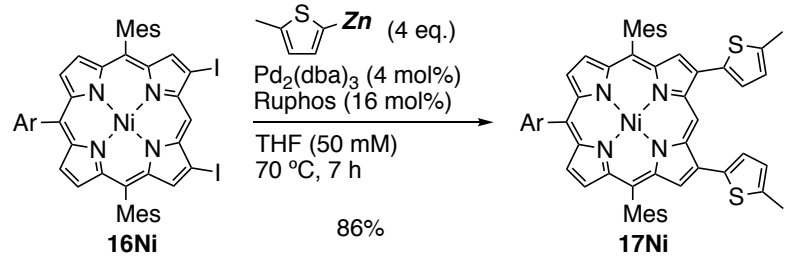
of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **6** (18 mg, 19 μmol, 65%).

6: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 9.03 (s, 2H, β), 8.69 (m, 4H, β(2H) and Ph(2H)), 8.61 (d, *J* = 7.4 Hz, 2H, Ph), 8.54 (d, *J* = 5.0 Hz, 2H, β), 8.39 (s, 1H, Ar-*o*), 7.72 (m, 4H, Ph), 7.67 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.40 (s, 2H, Mes), 7.38 (s, 1H, Ar-*o*), 7.09 (s, 2H, Mes), 2.58 (s, 6H, Mes), 2.45 (s, 6H, Mes), 1.55 (s, 9H, *tert*-butyl), 1.35 (s, 9H, *tert*-butyl), and 1.28 (s, 6H, Mes) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.13, 144.04, 142.52, 140.90, 140.13, 140.01, 139.28 (broad), 137.88, 137.13, 136.33, 134.16, 132.95, 131.73, 130.63, 129.04, 128.86, 128.05, 127.61, 126.64, 122.47, 121.12, 118.68, 117.35, 113.75, 35.17, 31.83, and 21.59 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –20 ppm (broad); HR-APCI-TOF-MS: *m/z* = 970.3671. Calcd for $C_{64}H_{57}N_4P^{58}Ni$: 970.3680 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 456 (1.7×10^5), 564 (1.8×10^4), and 611 (7.8×10^3) nm.



Synthesis of 16Ni: A Schlenk tube containing **S3** (791 mg, 1.0 mmol), $(Bpin)_2$ (1.27 g, 5.0 mmol), $[Ir(cod)OMe]_2$ (33 mg, 0.050 mmol), and dtbpy (27 mg, 0.10 mmol) was filled with argon, and then charged with dry mesitylene (5.0 mL) and dry MTBE (15 mL). After stirring at 70 ºC for 12 h, the reaction mixture was passed through short silica gel column eluting with CH_2Cl_2. After removal of the solvent *in vacuo*, the borylated porphyrin **S4** was obtained by recrystallization from CH_2Cl_2/methanol. Then, **S4** was dissolved in DMF (100 mL) and toluene (50 mL). To the resulting solution, *N*-iodosuccinimide (NIS) (675 mg, 3.0 mmol) and CuI (570 mg, 3.0 mmol) were added. After stirring at 80 ºC for 3 h, the reaction mixture was diluted with toluene (400 mL), washed with aqueous NH_4Cl solution, aqueous $Na_2S_2O_3$ solution, water, and brine, and dried over Na_2SO_4. After passed through short silica gel column eluting with toluene, the solvent was removed *in vacuo*. Recrystallization from CH_2Cl_2/methanol gave **16Ni** (930 mg, 0.89 mmol, 89%).

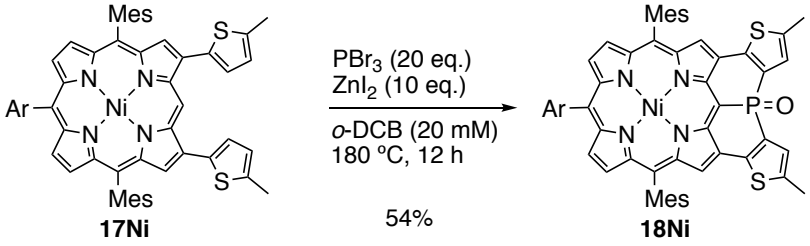
16Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.96 (s, 1H, *meso*), 8.92 (s, 2H, β), 8.73 (d, *J* = 5.0 Hz, 2H, β), 8.59 (d, *J* = 5.0 Hz, 2H, β), 7.87 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.72 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.23 (s, 4H, Mes), 2.59 (s, 6H, Mes), 1.80 (s, 12H, Mes), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.13, 143.98, 143.17, 142.86, 142.61, 139.86, 139.62, 139.13, 138.18, 136.73, 133.51, 131.80, 129.01, 128.04, 121.38, 121.28, 116.86, 106.10, 92.04, 35.17, 31.80, and 21.54 ppm; HR-APCI-TOF-MS: *m/z* = 1042.1502. Calcd for $C_{52}H_{50}N_4I_2^{58}Ni$: 1042.1473 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 418 (2.3×10^5), 529 (1.5×10^4), and 559 nm (6.0×10^3).



Ar = 3,5-di-*tert*-butylphenyl

Synthesis of 17Ni: To a Schlenk tube containing 2-bromo-5-methylthiophene (0.20 mL, 1.76 mmol) and dry THF (8.0 mL), *n*-BuLi (1.6 M hexane solution, 1.00 mL, 1.6 mmol) was slowly added at –80 ºC under argon atmosphere. After the reaction mixture was stirred at –80 °C for 1 h, $ZnCl_2$•tmeda (445 mg, 1.76 mmol) was added and further stirred for 1 h at room temperature. To the resulting thienylzinc solution, **16Ni** (417 mg, 0.40 mmol), $Pd_2(dba)_3$ (15 mg, 0.016 mmol), and Ruphos (30 mg, 0.064 mmol) were added. After stirred at 70 ºC for 7 h, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **17Ni** (339 mg, 0.34 mmol, 86%).

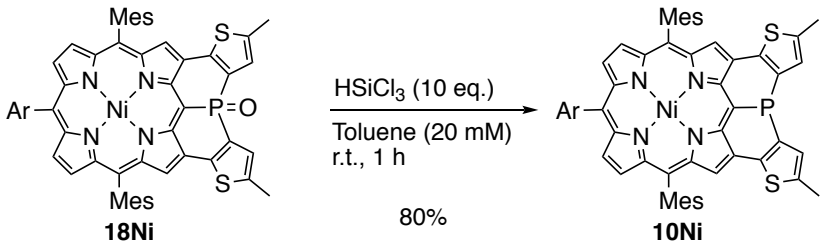
17Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.55 (s, 1H, *meso*), 8.73 (d, *J* = 4.6 Hz, 2H, β), 8.64 (s, 2H, β), 8.56 (d, *J* = 4.6 Hz, 2H, β), 7.90 (d, *J* = 1.4 Hz, 2H, Ar-*o*), 7.71 (s, 1H, Ar-*p*), 7,61 (d, *J* = 3.2 Hz, 2H, thienyl), 7.21 (s, 4H, Mes), 7.04 (d, *J* = 2.3 Hz, 2H, thienyl), 2.69 (s, 6H, thienyl), 2.58 (s, 6H, Mes), 1.84 (s, 12H, Mes), and 1.47 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.03, 143.35, 142.90, 141.67, 141.24, 140.75, 140.14, 139.18, 139.10, 137.84, 137.26, 135.89, 133.08, 131.14, 129.06, 128.32, 127.96, 127.94, 126.86, 121.18, 120.42, 117.09, 103.31, 35.16, 31.83, 21.58, and 15.72 ppm; HR-APCI-TOF-MS: *m/z* = 982.3625. Calcd for $C_{62}H_{60}N_4{}^{58}NiS_2$: 982.3607 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 426 (1.9×10^5), 537 (2.0×10^4), and 569 (1.2×10^4) nm.



Synthesis of 18Ni: A Schlenk tube containing **17Ni** (197 mg, 0.20 mmol) and ZnI_2 (636 mg, 2.0 mmol) was filled with argon, and then charged with dry *o*-DCB (10 mL) and PBr_3 (0.40 mL, 4.0 mmol). After stirring at 180 ºC for 12 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After removal of CH_2Cl_2 *in vacuo*, H_2O_2 (30% in water, 0.4 mL, 4 mmol) was added to the resulting *o*-DCB solution. After stirring at room temperature for 10 min, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the

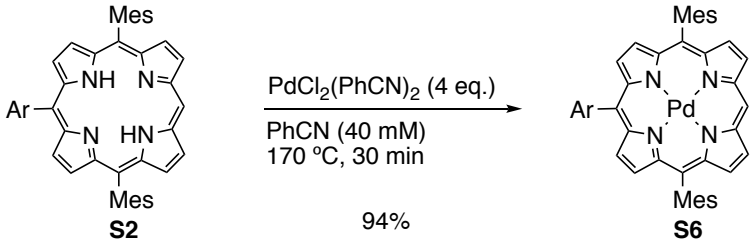
residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from $CHCl_3$/MeCN gave **18Ni** (110 mg, 107 μmol, 54%).

18Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.32 (d, *J* = 4.6 Hz, 2H, β), 8.12-8.08 (broad, 1H, Ar-*o*), 8.08 (d, *J* = 4.6 Hz, 2H, β), 8.02 (s, 2H, β), 7.67 (s, 1H, Ar-*p*), 7.46-7.42 (broad, 1H, Ar-*o*), 7.29 (s, 4H, Mes), 7.05 (s, 2H, thienyl), 2.61 (s, 6H, thienyl), 2.55 (s, 6H, Mes), 2.26 (s, 6H, Mes), 1.52-1.48 (broad, 9H, *tert*-butyl), 1.46 (s, 6H, Mes), and 1.40-1.36 (broad, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.6-149.2 (broad), 145.46, 143.76, 142.79, 142.68, 142.37, 142.33, 139.40, 138.87, 138.37, 138.18, 135.73, 135.56 (d, *J* = 8.6 Hz), 133.76, 130.44, 128.20, 127.87, 127.77 (d, *J* = 114 Hz), 126.42, 126.33, 125.75 (d, *J* = 15.0 Hz), 121.62, 120.80, 96.74 (d, *J* = 113 Hz), 35.15, 31.76, 21.75, 21.50, 21.20, and 15.46 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –3.71 ppm HR-APCI-TOF-MS: *m/z* = 1026.3047. Calcd for $C_{62}H_{57}N_4{}^{58}NiS_2PO$: 1026.3059 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 470 (1.0×10^5), 647 (8.7×10^3), and 706 (1.1×10^4) nm.



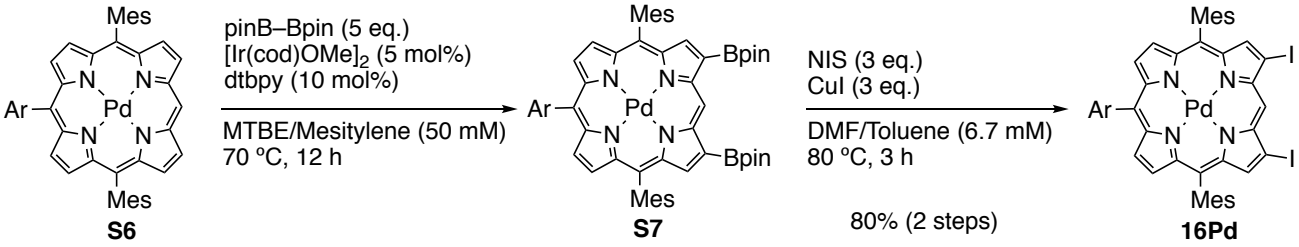
Synthesis of 10Ni: A Schlenk tube containing **18Ni** (10 mg, 10 μmol) was filled with argon, and then charged with and $HSiCl_3$ (0.2 M toluene solution, 0.50 mL, 0.10 mmol). After stirring at room temperature for 1 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2 and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2. Recrystallization from CH_2Cl_2/MeCN gave **10Ni** (8.0 mg, 8.0 μmol, 80%).

10Ni: ^{1}H NMR (600 MHz, $CDCl_3$, –40 °C): δ = 8.71 (d, *J* = 4.6 Hz, 2H, β), 8.59 (s, 2H, β), 8.53 (d, *J* = 4.6 Hz, 2H, β), 8.41 (s, 1H, Ar-*o*), 7.66 (t, *J* = 2.1 Hz, 1H, Ar-*p*), 7.60 (s, 2H, thienyl), 7.42 (s, 2H, Mes), 7.36 (s, 1H, Ar-*o*), 7.09 (s, 2H, Mes), 2.78 (s, 6H, thienyl), 2.60 (s, 6H, Mes), 2.49 (s, 6H, Mes), 1.55 (s, 9H, *tert*-butyl), 1.33 (s, 9H, *tert*-butyl), and 1.21 (s, 6H, Mes) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –15.4 ppm (broad); UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 457 (9.4×10^4) and 574 (1.9×10^4) nm.



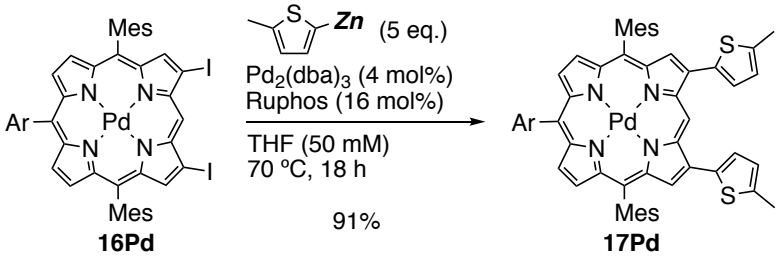
Synthesis of S6: A flask containing **S2** (735 mg, 1.0 mmol), $PdCl_2(PhCN)_2$ (1.54 g, 4.0 mmol), and PhCN (25 mL, 40 mM) was warmed to 170 °C and stirred for 30 min. After the reaction mixture was cooled to room temperature, addition of MeOH (60 mL) gave red precipitation. Then, the resulting precipitate was filtered, washed with MeOH, and recrystallized from $CHCl_3$/MeOH to obtain pure red solids of **S6** (788 mg, 0.94 mmol, 94%).

S6: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.13 (s, 1H, *meso*), 9.20 (d, *J* = 4.6 Hz, 2H, β), 8.83 (d, *J* = 5.0 Hz, 2H, β), 8.79 (d, *J* = 4.6 Hz, 2H, β), 8.68 (d, *J* = 5.0 Hz, 2H, β), 8.05 (d, *J* = 1.8 Hz, 2H, Ar-*o*) 7.77 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.28 (s, 4H, Mes), 2.63 (s, 6H, Mes), 1.82 (s, 12H, Mes), and 1.51 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 148.87, 141.52, 141.44, 141.34, 141.17, 140.95, 139.40, 138.12, 137.86, 131.96, 131.47, 130.41, 129.73, 129.68, 127.93, 123.05, 121.15, 119.39, 106.12, 35.22, 31.90, 21.71, and 21.63 ppm; HR-APCI-TOF-MS: *m/z* = 836.3256. Calcd for $C_{52}H_{52}N_4{}^{104}Pd$: 836.3227 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 408 (2.1×10^5), 517 (1.8×10^4), and 549 (3.2×10^3) nm.



Synthesis of 16Pd: A Schlenk tube containing **S6** (671 mg, 0.80 mmol), $(Bpin)_2$ (1.01 g, 4.0 mmol), $[Ir(cod)OMe]_2$ (26 mg, 0.040 mmol), and dtbpy (22 mg, 0.080 mmol) was filled with argon, and then charged with dry mesitylene (4.0 mL) and dry MTBE (12 mL). After stirring at 70 °C for 12 h, the reaction mixture was passed through short silica gel column eluting with CH_2Cl_2. After removal of the solvent *in vacuo*, the product **S7** was obtained by recrystallization from CH_2Cl_2/methanol. Then, **S7** was dissolved in DMF (80 mL) and toluene (40 mL). To the resulting solution, NIS (540 mg, 2.4 mmol) and CuI (456 mg, 2.4 mmol) were added. After stirring at 80 ºC for 3 h, the reaction mixture was diluted with toluene (400 mL), washed with aqueous NH_4Cl solution, aqueous $Na_2S_2O_3$ solution, water, and brine, and dried over Na_2SO_4. After passed through short silica gel column eluting with toluene, the solvent was removed *in vacuo*. Recrystallization from $CHCl_3$/methanol gave **16Pd** (695 mg, 0.64 mmol, 80%).

16Pd: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.28 (s, 1H, *meso*), 9.00 (s, 2H, β), 8.78 (d, *J* = 5.0 Hz, 2H, β), 8.65 (d, *J* = 5.0 Hz, 2H, β), 8.01 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.77 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.28 (s, 4H, Mes), 2.63 (s, 6H, Mes), 1.81 (s, 12H, Mes), and 1.50 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR was not obtained due to the poor solubility; HR-APCI-TOF-MS: *m/z* = 1088.1160. Calcd for $C_{52}H_{50}N_4I_2{}^{104}Pd$: 1088.1160 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (2.1×10^5), 525 (2.2×10^4), and 552 nm (5.2×10^4).

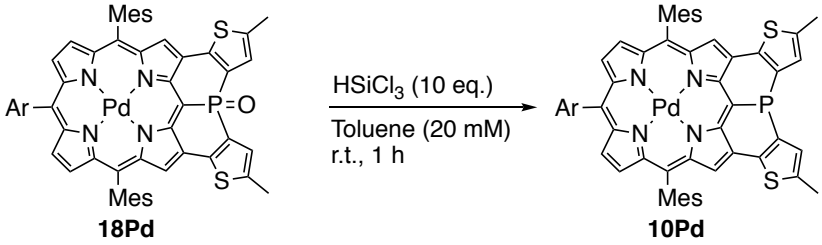


Synthesis of 17Pd: To a Schlenk tube containing 2-bromo-5-methylthiophene (0.31 mL, 2.8 mmol) and dry THF (10 mL), *n*-BuLi (1.6 M hexane solution, 1.60 mL, 2.5 mmol) was slowly added at –80 ºC under argon atmosphere. After the reaction mixture was stirred at –80 °C for 1 h, $ZnCl_2$·tmeda (696 mg, 2.8 mmol) was added and further stirred for 1 h at room temperature. To the resulting thienylzinc solution, **16Pd** (546 mg, 0.50 mmol), $Pd_2(dba)_3$ (18 mg, 0.020 mmol), and Ruphos (37 mg, 0.080 mmol) were added. After stirred at 70 °C for 18 h, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **17Pd** (469 mg, 0.45 mmol, 91%).

17Pd: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.94 (s, 1H, *meso*), 8.78 (d, *J* = 4.6 Hz, 2H, β), 8.72 (s, 2H, β), 8.62 (d, *J* = 4.6 Hz, 2H, β), 8.04 (d, *J* = 1.4 Hz, 2H, Ar-*o*), 7.79 (d, *J* = 2.3 Hz, 2H, thienyl), 7.77 (s, 1H, Ar-*p*), 7.27 (s, 4H, Mes), 7.10 (d, *J* = 2.3 Hz, 2H, thienyl), 2.73 (s, 6H, thienyl), 2.62 (s, 6H, Mes), 1.85 (s, 12H, Mes), and 1.51 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 148.93, 141.91, 141.82, 141.64, 140.80, 139.93, 139.41, 139.35, 138.23, 137.95, 137.91, 135.88, 132.10, 129.80, 129.62, 128.21, 127.99, 127.22, 126.89, 122.97, 121.17, 119.57, 104.49, 35.22, 31.89, 21.75, 21.63, and 15.77 ppm; HR-APCI-TOF-MS: *m/z* = 1028.3264. Calcd for $C_{62}H_{60}N_4{}^{104}PdS_2$: 1028.3294 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 424 (1.6×10^5), 533 (2.5×10^4), and 566 (1.2×10^4) nm.

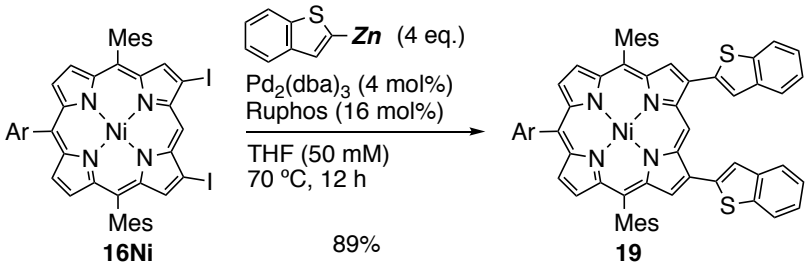
Synthesis of 18Pd: A Schlenk tube containing **17Pd** (206 mg, 0.20 mmol) and ZnI_2 (636 mg, 2.0 mmol) was filled with argon, and then charged with dry *o*-DCB (10 mL) and PBr_3 (0.40 mL, 4.0 mmol). After stirring at 180 °C for 12 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **18Pd** (114 mg, 106 μmol, 53%).

18Pd: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.40 (d, *J* = 4.6 Hz, 2H, β), 8.19 (d, *J* = 4.6 Hz, 2H, β), 8.13 (s, 2H, β), 8.03 (s, 1H, Ar), 7.76 (s, 1H, Ar), 7.73 (s, 1H, Ar), 7.38 (s, 2H, thienyl), 7.30 (s, 2H, Mes), 7.16 (s, 2H, Mes), 2.65 (s, 6H, thienyl), 2.59 (s, 6H, Mes), 2.11 (s, 6H, Mes), 1.63 (s, 6H, Mes), 1.50 (s, 9H, *tert*-butyl), and 1.45 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.23 (d, *J* = 24.6 Hz), 143.86, 143.34 (d, *J* = 11.6 Hz), 142.72 (d, *J* = 17.3 Hz), 142.14, 141.77 (d, *J* = 8.7 Hz), 141.47, 139.64, 139.50, 138.54, 138.25, 136.50, 133.59 (d, *J* = 8.7 Hz), 132.85, 129.28, 128.94, 128.80, 128.53, 128.21, 127.93, 125.82 (d, *J* = 13.0 Hz), 124.92, 123.00, 121.58, 100.50 (d, *J* = 108 Hz), 35.17, 31.80, 31.77, 21.85, 21.55, 21.45, and 15.46 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –1.84 ppm; HR-APCI-TOF-MS: *m/z* = 1073.2713. Calcd for $C_{62}H_{57}N_4{}^{104}PdS_2PO$: 1073.2758 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 388 (4.4×10^4), 468 (1.2×10^5), 633 (9.0×10^3), and 687 (1.1×10^4) nm.



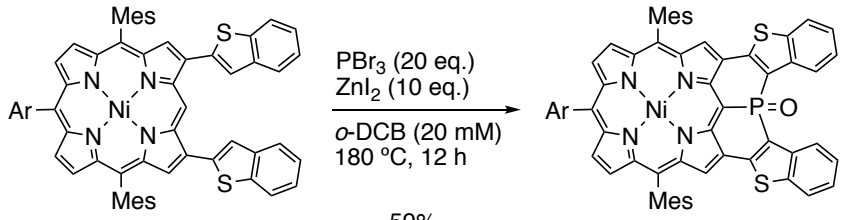
Synthesis of 10Pd: A Schlenk tube containing **18Pd** (11 mg, 10 μmol) was filled with argon, and then charged with $HSiCl_3$ (0.20 M toluene solution, 0.50 mL, 0.10 mmol). After stirring at room temperature for 1 h, the reaction mixture was dried *in vacuo.* Then, the crude mixture was sequentially passed through short alumina column and silica gel column eluting with thoroughly degassed CH_2Cl_2 under argon atmosphere. Removal of the solvent *in vacuo* gave analytically pure amorphous of **10Pd**. Because **10Pd** was quite sensitive to air, all spectroscopic measurements were conducted under argon atmosphere.

10Pd: ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ = 8.80 (d, *J* = 2.8 Hz, 2H, β), 8.78 (d, *J* = 5.0 Hz, 2H, β), 8.62 (d, *J* = 5.0 Hz, 2H, β), 8.05 (s, 2H, Ar-*o*), 7.82 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 7.80 (s, 2H, thienyl), 7.34 (s, 4H, Mes), 2.87 (s, 6H, thienyl), 2.66 (s, 6H, Mes), 1.87 (s, 12H, Mes), and 1.51 (s, 18H, *tert*-butyl) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –8.32 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 459 (8.4 × 10^4), 483 (1.3 × 10^5), 573 (2.3 × 10^4), and 618 (8.1 × 10^3) nm



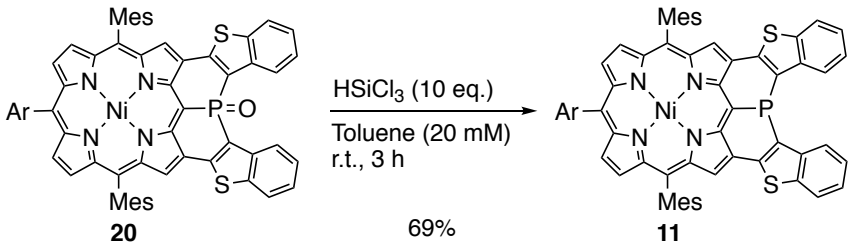
Synthesis of 19: To a Schlenk tube containing 2-bromobenzothiophene (469 mg, 2.2 mmol) and dry THF (10 mL), *n*-BuLi (1.6 M hexane solution, 1.25 mL, 2.0 mmol) was slowly added at –80 ºC under argon atmosphere. After the reaction mixture was stirred at –80 °C for 1 h, $ZnCl_2$·tmeda (557 mg, 2.2 mmol) was added and further stirred for 1 h at room temperature. To the resulting arylzinc solution, **16Ni** (522 mg, 0.50 mmol), $Pd_2(dba)_3$ (18 mg, 0.020 mmol), and Ruphos (37 mg, 0.080 mmol) were added. After stirred at 70 °C for 12 h, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **19** (472 mg, 0.25 mmol, 89%).

19: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.82 (s, 1H, *meso*), 8.83 (s, 2H, β), 8.74 (d, *J* = 5.0 Hz, 2H, β), 8.59 (d, *J* = 5.0 Hz, 2H, β), 8.11 (s, 2H, benzothiophene), 7.97 (d, *J* = 7.2 Hz, 2H, benzothiophene), 7.94 (d, *J* = 7.2 Hz, 2H, benzothiophene), 7.90 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.73 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.46 (d, *J* = 7.2 Hz, 2H, benzothiophene), 7.43 (d, *J* = 7.2 Hz, 2H, benzothiophene), 7.24 (s, 4H, Mes), 2.60 (s, 6H, Mes), 1.87 (s, 12H, Mes), and 1.48 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.15, 143.78, 143.20, 141.31, 141.05, 140.90, 140.70, 140.03, 139.19, 138.62, 138.10, 138.04, 137.05, 133.40, 131.60, 129.82, 129.04, 128.08, 124.81, 124.72, 124.63, 124.46, 123.99, 122.34, 121.33, 120.75, 117.65, 103.31, 35.19, 31.85, and 21.60 ppm; HR-APCI-TOF-MS: *m/z* = 1054.3619. Calcd for $C_{68}H_{60}N_4{}^{58}NiS_2$: 1054.3607 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 430 (2.0 × 10^5), 538 (2.2 × 10^4), and 572 (1.3 × 10^4) nm.



Synthesis of 20: A Schlenk tube containing **19** (211 mg, 0.20 mmol) and ZnI_2 (636 mg, 2.0 mmol) was filled with argon, and then charged with dry *o*-DCB (10 mL) and PBr_3 (0.40 mL, 4.0 mmol). After stirring at 180 °C for 12 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After removal of CH_2Cl_2 *in vacuo*, H_2O_2 (30% in water, 0.4 mL, 4 mmol) was added to the resulting *o*-DCB solution. After stirring at room temperature for 10 min, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **20** (130 mg, 0.12 mmol, 59%).

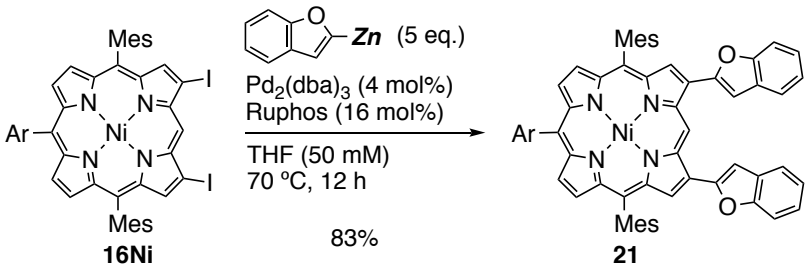
20: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.35 (d, *J* = 4.6 Hz, 2H, β), 8.32 (m, 2H, benzo), 8.28 (s, 2H, β), 8.12 (d, *J* = 4.6 Hz, 2H, β), 7.93 (m, 2H, benzo), 8.11 (s, 1H, Ar-*o*), 7.65 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.45-7.41 (m, 4H, benzo), 7.40 (s, 1H, Ar-*o*), 7.33 (s, 2H, Mes), 7.07 (s, 2H, Mes), 2.56 (s, 6H, Mes), 2.37 (s, 6H, Mes), 1.49 (s, 9H, *tert*-butyl), 1.41 (s, 6H, Mes), and 1.34 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.6-149.2, 146.43 (d, *J* = 11.5 Hz), 145.75, 144.23, 142.43, 142.08 (d, *J* = 8.6 Hz), 140.02 (d, *J* = 14.3 Hz), 139.68 (d, *J* = 13.0 Hz), 139.33, 138.67, 138.45 (d, *J* = 5.7 Hz), 135.60 (d, *J* = 8.8 Hz), 135.43, 134.04, 130.95, 128.99, 128.31, 128.00, 126.63, 126.03, 125.93, 125.84, 125.35, 125.12, 122.58, 121.77, 121.63, 98.21 (d, *J* = 111 Hz), 35.16, 31.76, 21.92, 21.52, and 21.21 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –0.37 ppm; HR-APCI-TOF-MS: *m/z* = 1098.3048. Calcd for $C_{68}H_{57}N_4{}^{58}NiOPS_2$: 1098.3059 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 476 (1.1×10^5), 665 (7.9×10^3), and 723 (8.4×10^3) nm.



Synthesis of 11: A Schlenk tube containing **20** (22 mg, 20 μmol) was filled with argon, and then charged with $HSiCl_3$ (0.20 M toluene solution, 1.0 mL, 0.20 mmol). After stirring at room temperature for 3 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4.

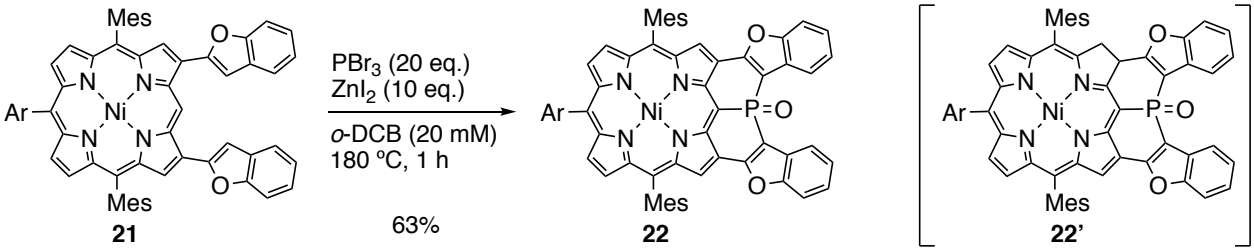
After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from $CHCl_3$/MeCN gave **11** (15 mg, 14 μmol, 69%).

11: ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ = 8.90 (d, *J* = 3.2 Hz, 2H, β), 8.71 (d, *J* = 5.0 Hz, 2H, β), 8.55 (d, *J* = 5.0 Hz, 2H, β), 8.47 (d, *J* = 7.3 Hz, 2H, benzo), 8.14 (d, *J* = 7.8 Hz, 2H, benzo), 7.92-7.85 (broad, 2H, Ar-*o*), 7.76 (s, 1H, Ar-*p*), 7.59-7.52 (m, 4H, benzo), 7.30 (s, 4H, Mes), 2.63 (s, 6H, Mes), 1.94-1.82 (broad, 12H, Mes), and 1.48 (s, 18H, *tert*-butyl) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –17.05 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 473 (1.1 × 10^5), 581 (2.0 × 10^4), and 632 (7.6 × 10^3) nm.



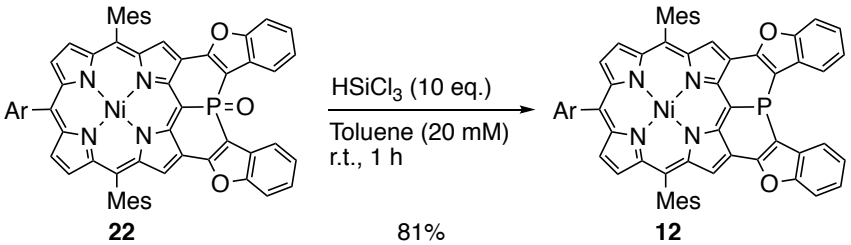
Synthesis of 21: To a Schlenk tube containing benzofuran (0.18 mL, 1.7 mmol) and dry THF (6.0 mL), *n*-BuLi (1.6 M hexane solution, 0.94 mL, 1.5 mmol) was slowly added at –40 ºC under argon atmosphere. After the reaction mixture was stirred at room temperature for 1 h, $ZnCl_2$·tmeda (417 mg, 1.7 mmol) was added and further stirred for 1 h at room temperature. To the resulting arylzinc solution, **16Ni** (313 mg, 0.30 mmol), $Pd_2(dba)_3$ (11 mg, 0.012 mmol), and Ruphos (22 mg, 0.048 mmol) were added. After stirred at 70 ºC for 12 h, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **21** (255 mg, 0.25 mmol, 83%).

21: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.31 (s, 1H, *meso*), 9.00 (s, 2H, β), 8.72 (d, *J* = 5.0 Hz, 2H, β), 8.58 (d, *J* = 5.0 Hz, 2H, β), 7.89 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.82 (d, *J* = 7.8 Hz, benzofuran, 2H), 7,78 (m, 4H, benzofuran), 7.72 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 7.46 (t, *J* = 7.4 Hz, 2H, benzofuran), 7.40 (t, *J* = 7.4 Hz, 2H, benzofuran), 7.26 (s, 4H, Mes), 2.62 (s, 6H, Mes), 1.88 (s, 12H, Mes), and 1.48 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 155.63, 153.21, 149.15, 143.99, 143.27, 141.58, 140.03, 139.98, 139.23, 138.05, 137.11, 134.28, 133.34, 131.60, 129.74, 129.03, 128.34, 128.08, 124.94, 123.47, 121.39, 121.32, 120.70, 117.90, 111.52, 106.13, 103.67, 35.18, 31.83, and 21.62 ppm; HR-APCI-TOF-MS: *m/z* = 1022.4044. Calcd for $C_{68}H_{60}N_4{}^{58}NiO_2$: 1022.4064 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 435 (1.6 × 10^5), 545 (2.1 × 10^4), and 580 (1.4 × 10^4) nm.



Synthesis of 22: A Schlenk tube containing **21** (123 mg, 0.12 mmol) and ZnI_2 (382 mg, 1.2 mmol) was filled with argon, and then charged with dry *o*-DCB (6.0 mL) and PBr_3 (0.24 mL, 2.4 mmol). After stirring at 180 °C for 1 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of CH_2Cl_2 *in vacuo*, H_2O_2 (30% in water, 0.4 mL, 4 mmol) was added to the resulting *o*-DCB solution. After stirring at room temperature for 10 min, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue which includes **22** and its reduced form **22'** (proposed structure) were separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2/hexane. Then, the obtained **22'** (30 mg, 0.028 mmol) was dissolved in $CHCl_3$ (10 mL), oxidized to **22** with DDQ (7.0 mg, 0.031 mmol) at 50 ºC for 30 min, and separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **22** (81 mg, 0.076 mmol, 63%).

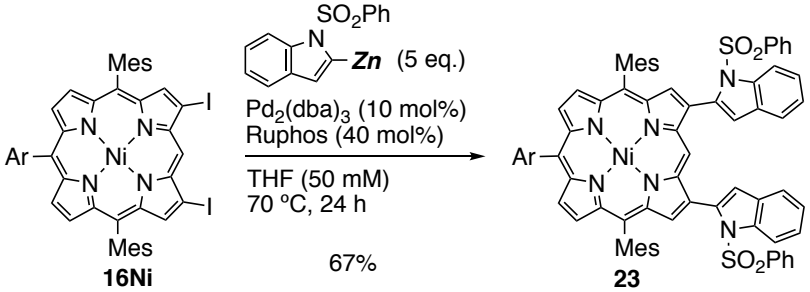
22: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.37 (s, 2H, β), 8.33 (d, *J* = 5.0 Hz, 2H, β), 8.31 (d, *J* = 7.8 Hz, 2H, benzo), 8.10 (d, *J* = 5.0 Hz, 2H, β), 8.09 (s, 1H, Ar-*o*), 7.65 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.62 (d, *J* = 7.8 Hz, 2H, benzo), 7.50 (t, *J* = 7.2 Hz, 2H, benzo), 7.45 (t, *J* = 7.2 Hz, 2H, benzo), 7.41 (s, 1H, Ar-*o*), 7.30 (s, 2H, Mes), 7.04 (s, 2H, Mes), 2.54 (s, 6H, Mes), 2.33 (s, 6H, Mes), 1.49 (s, 9H, *tert*-butyl), 1.44 (s, 6H, Mes), and 1.35 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 157.76 (d, *J* = 8.8 Hz), 155.84 (d, *J* = 13.0 Hz), 149.8-149.3 (broad) 145.92, 144.35, 142.55, 142.47, 139.33, 138.49, 138.43, 138.29, 135.36, 134.18, 131.37 (d, *J* = 4.3 Hz), 130.95, 128.58, 128.29, 127.99, 127.27, 126.93 (d, *J* = 7.2 Hz), 126.24, 124.71, 122.29, 121.82, 111.92, 107.91, 107.05, 96.99 (d, *J* = 116 Hz), 35.17, 31.75, 21.82, 21.49, and 21.19 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 2.45 ppm; HR-APCI-TOF-MS: *m/z* = 1066.3482. Calcd for $C_{68}H_{57}N_4{}^{58}NiO_3P$: 1066.3516 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 473 (1.1×10^5), 671 (7.7×10^3), and 732 (8.6×10^3) nm.



Synthesis of 12: A Schlenk tube containing **22** (21 mg, 20 μmol) was filled with argon, and then charged with and $HSiCl_3$ (0.20 M toluene solution, 1.0 mL, 0.20 mmol). After stirring at room temperature for 1 h, the reaction mixture

was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/MeCN gave **12** (17 mg, 16 μmol, 81%).

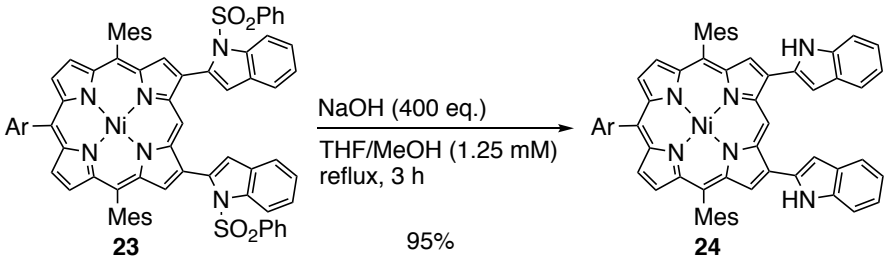
12: ^{1}H NMR (600 MHz, $CDCl_3$, –40 °C): δ = 9.07 (d, *J* = 3.2 Hz, 2H, β), 8.75 (d, *J* = 5.0 Hz, 2H, β), 8.61 (d, *J* = 4.6 Hz, 2H, β) 8.52 (d, *J* = 7.8 Hz, 2H, benzo), 8.43 (s, 1H, Ar-*o*), 7.84 (d, *J* = 7.8 Hz, 2H, benzo), 7.68 (s, 1H, Ar-*p*), 7.63 (d, *J* = 7.8 Hz, 2H, benzo), 7.58 (d, *J* = 7.8 Hz, 2H, benzo), 7.43 (s, 2H, Mes), 7.35 (s, 1H, Ar-*o*), 7.08 (s, 2H, Mes), 2.60 (s, 6H, Mes), 2.52 (s, 6H, Mes), 1.56 (s, 9H, *tert*-butyl), 1.34 (s, 9H, *tert*-butyl), and 1.23 (s, 6H, Mes); ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –25.38 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 468 (1.0×10^5), 580 (2.0×10^4), and 628 (8.1×10^3) nm.



Synthesis of 23: To a Schlenk tube containing 1-phenylsulfonyl-indole (424 mg, 1.7 mmol) and dry THF (6.0 mL), *n*-BuLi (1.6 M hexane solution, 0.94 mL, 1.5 mmol) was slowly added at –80 °C under argon atmosphere. After the reaction mixture was stirred at –80 ºC for 1 h, $ZnCl_2$·tmeda (417 mg, 1.7 mmol) was added and further stirred for 1 h at room temperature. To the resulting solution, **16Ni** (313 mg, 0.30 mmol), $Pd_2(dba)_3$ (27 mg, 0.030 mmol), and Ruphos (56 mg, 0.12 mmol) were added. After stirred at 70 °C for 24 h, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **23** (262 mg, 0.20 mmol, 67%).

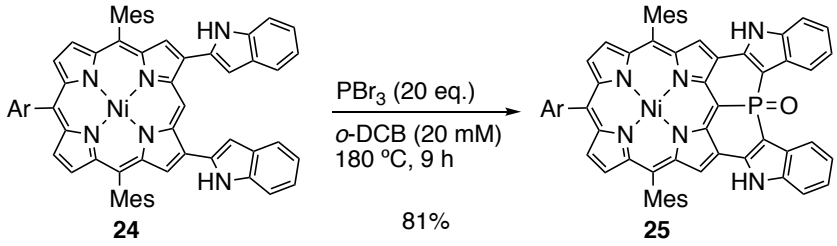
23: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.67 (s, 1H, *meso*), 8.82 (s, 2H, β), 8.78 (d, *J* = 5.0 Hz, 2H, β), 8.65 (d, *J* = 4.6 Hz, 2H, β), 8.35 (d, *J* = 7.8 Hz, 2H, indole), 7.93 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7,74 (s, 1H, Ar-*p*), 7.60 (d, *J* = 7.2 Hz, 2H, indole), 7.41 (t, *J* = 7.2 Hz, 2H, indole), 7.36 (t, *J* = 7.2 Hz, 2H, indole), 7.22 (d, *J* = 7.2 Hz, 4H, Ph), 7.09 (s, 2H, indole), 7.02 (t, *J* = 7.2 Hz, 2H, Ph), 6.79 (t, *J* = 7.2 Hz, 4H, Ph), 2.60 (s, 6H, Mes), 1.93 (s, 12H, Mes), and 1.49 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.08, 143.78, 143.24, 142.45, 141.14, 140.24, 139.25, 139.07, 137.97, 137.50, 137.29, 135.80, 135.18, 133.42, 133.10, 132.66, 131.35, 131.32, 129.13, 128.40, 128.01, 126.66, 125.28, 124.75, 121.25, 121.11, 120.69, 118.22, 117.92, 116.98, 103.89, 35.19, 31.86, and 21.60

ppm; HR-APCI-TOF-MS: *m/z* = 1300.4197. Calcd for $C_{80}H_{70}N_6{}^{58}NiO_4S_2$: 1300.4248 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε $[M^{-1}cm^{-1}]$) = 424 (2.2×10^5), 533 (2.2×10^4), and 566 (1.1×10^4) nm.



Synthesis of 24: To a flask containing **23** (260 mg, 0.20 mmol) dissolved in THF (80 mL), MeOH (80 mL) and NaOH (3.2 g, 80 mmol) were added and the resulting reaction mixture was stirred for 3 h at reflux. Then, the reaction mixture was quenched with aqueous NH_4Cl solution, extracted with AcOEt, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, recrystallization from CH_2Cl_2/methanol gave **24** (195 mg, 0.19 mmol, 95%).

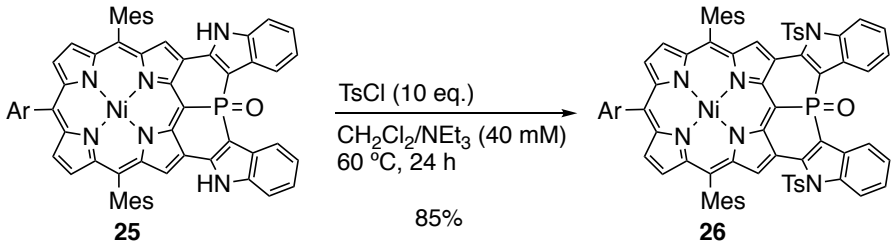
24: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.87 (s, 1H, *meso*), 8.86 (s, 2H, NH), 8.76 (s, 2H, β), 8.74 (d, *J* = 5.0 Hz, 2H, β), 8.59 (d, *J* = 5.0 Hz, 2H, β), 7.90 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.83 (d, *J* = 7.8 Hz, 2H, indole), 7.73 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.55 (d, *J* = 7.8 Hz, 2H, indole), 7.48 (s, 2H, indole), 7.32 (t, *J* = 7.2 Hz, 2H, indole), 7.26 (s, 4H, Mes), 7.23 (t, *J* = 7.2 Hz, 2H, indole), 2.61 (s, 6H, Mes), 1.87 (s, 12H, Mes), and 1.48 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.08, 143.78, 143.24, 142.45, 141.14, 140.24, 139.25, 139.07, 137.97, 137.50, 137.29, 135.80, 135.18, 133.42, 133.10, 132.66, 131.35, 131.32, 129.13, 128.40, 128.01, 126.66, 125.28, 124.75, 121.25, 121.11, 120.69, 118.22, 117.92, 116.98, 103.89, 35.19, 31.86, and 21.60 ppm; HR-APCI-TOF-MS: *m/z* = 1020.4356. Calcd for $C_{68}H_{62}N_6{}^{58}Ni$: 1020.4384 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε $[M^{-1}cm^{-1}]$) = 431 (1.4×10^5), 541 (2.1×10^4), and 578 (1.5×10^4) nm.



Synthesis of 25: A Schlenk tube containing **24** (184 mg, 0.18 mmol) was filled with argon, and then charged with dry *o*-DCB (9.0 mL) and PBr_3 (0.36 mL, 3.6 mmol). After stirring at 180 °C for 9 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After

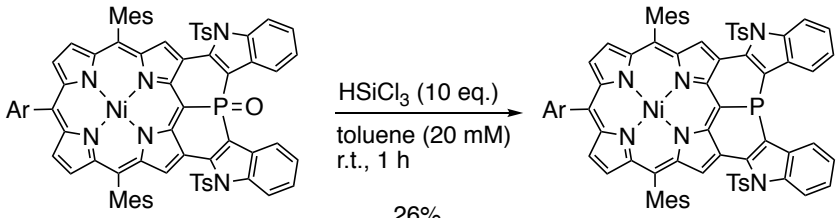
removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from $CHCl_3$/methanol gave **25** (155 mg, 0.15 mmol, 81%).

25: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.85 (s, 2H, NH), 8.37 (d, *J* = 7.2 Hz, 2H, indole), 8.35 (d, *J* = 4.6 Hz, 2H, β), 8.15 (s, 2H, β), 8.12 (d, *J* = 4.6 Hz, 2H, β), 8.16-8.11 (broad, 1H, Ar-*o*), 7.68 (s, 1H, Ar-*p*), 7.46-7.41 (broad, 1H, Ar-*o*), 7.40 (d, *J* = 7.2 Hz, 2H, indole), 7.31 (s, 2H, Mes), 7.31-7.26 (m, 4H, indole), 7.06 (s, 2H, Mes), 2.55 (s, 6H, Mes), 2.33 (s, 6H, Mes), 1.53-1.47 (broad, 9H, *tert*-butyl), 1.47 (s, 6H, Mes), and 1.42-1.36 (broad, 9H, *tert*-butyl) ppm. ^{13}C NMR was not obtained due to the poor solubility. ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 0.73 ppm; HR-APCI-TOF-MS: *m/z* = 1064.3809. Calcd for $C_{68}H_{59}N_6{}^{58}NiOP$: 1064.3836 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 432 (7.3×10^4), 472 (8.8×10^4), 663 (6.7×10^3), and 723 (6.1×10^3) nm.



Synthesis of 26: A Schlenk tube containing **25** (64 mg, 0.060 mmol) and TsCl (115 mg, 0.60 mmol) was filled with argon, and then charged with dry CH_2Cl_2 (1.5 mL) and NEt_3 (0.15 mL). After stirring at 60 °C for 24 h, the reaction mixture was quenched by water, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/methanol gave **26** (70 mg, 0.051 mmol, 85%).

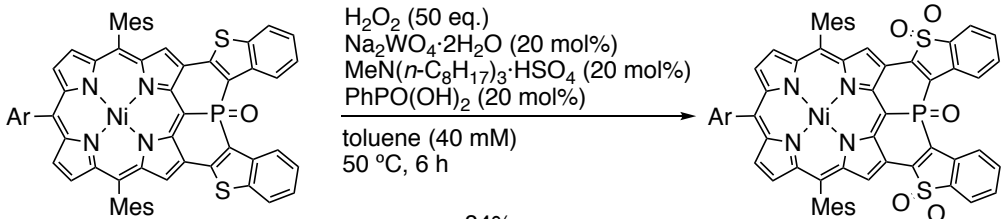
26: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.74 (s, 2H, β), 8.30 (d, *J* = 8.4 Hz, 2H, benzo), 8.27 (d, *J* = 4.6 Hz, 2H, β), 8.05 (s, 1H, Ar-*o*), 8.03 (d, *J* = 5.0 Hz, 2H, β), 7.75 (d, *J* = 7.8 Hz, 2H, benzo), 7.64 (s, 1H, Ar-*p*), 7.46-7.42 (m, 6H, benzo (2H) and *N*-Ts 4H)), 7.39 (s, 1H, Ar-*o*), 7.30-7.26 (m, 4H, benzo (2H) and Mes (2H)), 7.08 (s, 2H, Mes), 7.02 (d, *J* = 8.2 Hz, 4H, *N*-Ts), 2.58 (s, 6H, Mes), 2.21 (s, 6H, *N*-Ts), 2.20 (s, 6H, Mes), 1.47 (s, 9H, *tert*-butyl), 1.41 (s, 6H, Mes), and 1.35 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.6-149.3 (broad), 145.77, 145.03, 144.22, 143.66 (d, *J* = 10.1 Hz), 141.97, 141.76 (d, *J* = 15.9 Hz), 140.59 (d, *J* = 11.6 Hz), 139.23, 138.54, 138.29, 138.18, 135.62, 135.21, 134.72, 133.95, 131.29 (d, *J* = 5.1 Hz), 130.74, 129.90, 129.37 (d, *J* = 8.7 Hz), 128.28, 127.95, 127.20, 126.61, 126.51, 125.18, 122.52, 122.41, 121.79, 117.03, 116.53, 115.70, 94.42 (d, *J* = 115 Hz), 35.16, 31.75, 21.76, 21.65, 21.60, and 21.21 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –2.91 ppm; HR-APCI-TOF-MS: *m/z* = 1064.3766. Calcd for $C_{68}H_{59}N_6{}^{58}NiOP$: 1064.3836 $[M–2(Ts)+2H]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 479 (1.0×10^5), 683 (7.1×10^3), and 746 (7.1×10^3) nm.



26 **13**

Synthesis of 13: A Schlenk tube containing **26** (27 mg, 20 μmol) was filled with argon, and then charged with $HSiCl_3$ (0.20 M toluene solution, 1.0 mL, 0.20 mmol). After stirring at room temperature for 1 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **13** (7.0 mg, 5.2 μmol, 26%).

13: ^{1}H NMR (600 MHz, CD_2Cl_2, –40 °C): δ = 9.48 (d, *J* = 3.2 Hz, 2H, β), 8.72 (d, *J* = 4.6 Hz, 2H, β), 8.56 (d, *J* = 5.0 Hz, 2H, β), 8.49 (d, *J* = 8.3 Hz, 2H, indole), 8.42 (s, 1H, Ar-*o*), 7.67 (s, 3H, Ar-*p* (1H) and indole(2H)), 7.51 (t, *J* = 7.6 Hz, 2H, indole) 7.45 (s, 2H, Mes), 7.39-7.33 (m, 6H, indole (2H) and *N*-Ts (4H)), 7.30 (s, 1H, Ar-*o*), 7.11 (s, 2H, Mes), 6.84 (d, *J* = 8.3 Hz, 4H, *N*-Ts), 2.63 (s, 6H, Mes), 2.50 (s, 6H, Mes), 2.07 (s, 6H, *N*-Ts), 1.55 (s, 9H, *tert*-butyl), 1.35 (s, 9H, *tert*-butyl), and 1.20 (s, 6H, Mes) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –32.73 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 472 (9.7×10^4), 583 (1.8×10^4), and 631 (7.9×10^3) nm.

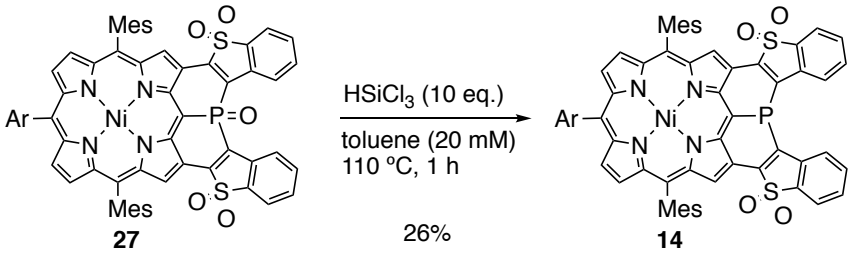


20 **27**

Synthesis of 27: A Schlenk tube containing **20** (132 mg, 0.12 mmol), $Na_2WO_4 \cdot 2H_2O$ (7.9 mg, 0.024 mmol), $MeN(n\text{-}C_8H_{17})_3 \cdot HSO_4$ (11.2 mg, 0.024 mmol), and $PhPO(OH)_2$ (3.8 mg, 0.024 mmol) was filled with argon, and then charged with dry toluene (3.0 mL) and H_2O_2 (30% in water, 0.60 mL, 6.0 mmol). After stirring at 50 °C for 6 h, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/MeOH gave **27** (118 mg, 0.101 mmol, 84%).

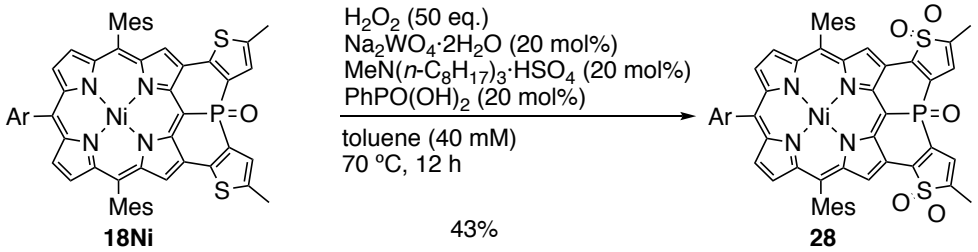
27: ^{1}H NMR (600 MHz, $CDCl_3$, –30 °C): δ = 8.45 (s, 2H, β), 8.20 (d, *J* = 4.6 Hz, 2H, β), 8.00 (broad, 3H, Ar-*o* (1H) and benzo (2H)), 7.97 (d, *J* = 5.0 Hz, 2H, β), 7.91 (m, 2H, benzo), 7.69 (m, 4H, benzo), 7.65 (s, 1H, Ar-*p*), 7.35 (s, 1H, Ar-*o*), 7.26 (s, 2H, Mes), 7.02 (s, 2H, Mes), 2.51 (s, 6H, Mes), 2.32 (s, 6H, Mes), 1.47 (s, 9H, *tert*-butyl), 1.46 (s, 6H, Mes), and 1.35 (s, 9H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.9-149.7 (broad), 147.32,

145.48, 144.97 (d, J = 5.8 Hz), 143.07 (d, J = 7.2 Hz), 142.87, 138.91 (d, J = 7.2 Hz), 138.05, 137.82, 135.72 (d, J = 5.8 Hz), 134.73, 134.04, 133.90, 131.82, 130.53, 130.16 (d, J = 7.2 Hz), 129.71, 128.61, 128.33, 128.2-127.8 (broad), 127.51 (d, J = 10.1 Hz), 126.51, 125.78, 125.17, 124.47, 122.75, 122.26, 93.68 (d, J = 119 Hz), 35.17, 31.71, 21.82, 21.48 and, 21.21 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 1.00 ppm; HR-APCI-TOF-MS: *m/z* = 1162.2836. Calcd for $C_{68}H_{57}N_4{}^{58}NiO_5PS_2$: 1162.2856 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 377 (5.2×10^4), 504 (1.0×10^5), 600 (6.0×10^3), 682 (5.9×10^3), 753 (6.9×10^3), and 823 (7.0×10^3) nm.



Synthesis of 14: A Schlenk tube containing **27** (12 mg, 0.010 mmol) was filled with argon, and then charged with $HSiCl_3$ (0.20 M toluene solution, 0.50 mL, 0.10 mmol). After stirring at 110 °C for 1 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, recrystallization from CH_2Cl_2/hexane gave **14** (3.0 mg, 2.6 μmol, 26%).

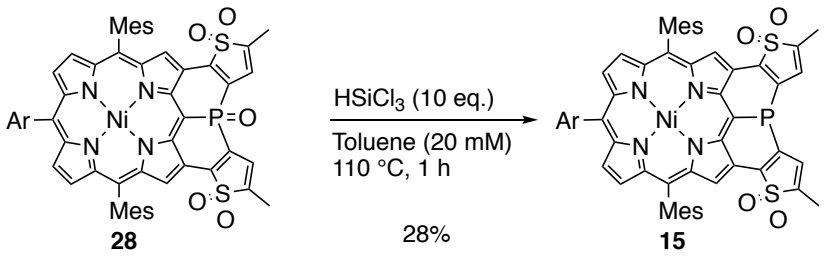
14: ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ = 9.20 (d, J = 5.0 Hz, 2H, β), 8.76 (d, J = 5.0 Hz, 2H, β), 8.61 (d, J = 5.0 Hz, 2H, β), 8.09 (d, J = 7.3 Hz, 2H, benzo), 7.99 (d, J = 7.3 Hz, 2H, benzo), 7.88 (s, 2H, Ar-*o*), 7.79 (m, 3H, Ar-*p* (1H) and benzo (2H)), 7.73 (t, J = 7.3 Hz, 2H, benzo), 7.32 (s, 4H, Mes), 2.63 (s, 6H, Mes), 1.87 (s, 12H, Mes), and 1.48 (s, 18H, *tert*-butyl) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –20.93 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 385 (4.9×10^4), 429 (5.0×10^4), 498 (6.4×10^4), 594 (1.7×10^4), and 647 (7.6×10^3) nm.



Synthesis of 28: A Schlenk tube containing **18Ni** (62 mg, 0.060 mmol), $Na_2WO_4{\cdot}2H_2O$ (4.0 mg, 0.012 mmol), $MeN(n\text{-}C_8H_{17})_3{\cdot}HSO_4$ (5.6 mg, 0.012 mmol), and $PhPO(OH)_2$ (1.9 mg, 0.012 mmol) was filled with argon, and then charged with dry toluene (1.5 mL) and H_2O_2 (30% in water, 0.30 mL, 3.0 mmol). After stirring at 70 °C for 12 h, the reaction mixture was quenched by aqueous $Na_2S_2O_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After

removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with AcOEt/CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane gave **28** (28 mg, 0.026 mmol, 43%).

28: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.16 (s, 2H, β), 8.10 (d, *J* = 5.0 Hz, 2H, β), 7.98-7.92 (broad, 1H, Ar-*o*), 7.87 (d, *J* = 4.6 Hz, 2H, β), 7.67 (s, 1H, Ar-*p*), 7.41-7.34 (broad, 1H, Ar-*o*), 7.22 (s, 2H, Mes), 7.01 (s, 2H, Mes), 6.85 (m, 2H, thiophene 1,1-dioxide), 2.50 (s, 6H, Mes), 2.35 (s, 6H, thiophene 1,1-dioxide), 2.23 (s, 6H, Mes), 1.54 (s, 6H, Mes), and 1.50-1.35 (broad, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.9-149.7 (broad), 147.48, 145.50, 143.90 (d, *J* = 8.7 Hz), 142.92, 142.05 (d, *J* = 7.6 Hz), 140.79 (d, *J* = 7.2 Hz), 138.86, 138.74, 137.89, 137.71, 134.58, 133.90, 133.53, 131.51, 130.23, 128.58, 128.29, 128.00 (d, *J* = 10.1 Hz), 127.8-127.5 (broad), 125.90, 122.26, 120.41 (d, *J* = 5.8 Hz), 119.57 (d, *J* = 110 Hz), 93.62 (d, *J* = 115 Hz), 35.16, 31.69, 22.78, 21.70, 21.44, 21.18, 14.25, and 9.99 ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –1.52 ppm; HR-APCI-TOF-MS: *m/z* = 1090.2849. Calcd for $C_{62}H_{57}N_4{}^{58}NiO_5PS_2$: 1090.2856 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 398 (5.1 × 10^4), 506 (8.4 × 10^4), 606 (5.1 × 10^3), 695 (5.5 × 10^3), 779 (6.0 × 10^3), and 842 (5.7 × 10^3) nm.



Synthesis of 15: A Schlenk tube containing **28** (11 mg, 0.010 mmol) was filled with argon, and then charged with $HSiCl_3$ (0.20 M toluene solution, 0.50 mL, 0.10 mmol). After stirring at 110 °C for 1 h, the reaction mixture was quenched by aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, recrystallization from CH_2Cl_2/hexane gave **15** (3.0 mg, 2.8 μmol, 28%).

15: ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ = 9.06 (d, *J* = 5.0 Hz, 2H, β), 8.78 (d, *J* = 5.0 Hz, 2H, β), 8.62 (d, *J* = 5.0 Hz, 2H, β), 7.88 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.78 (d, *J* = 1.9 Hz, 1H, Ar-*p*), 7.32 (t, *J* = 2.3 Hz, 2H, thiophene 1,1-dioxide), 7.30 (s, 4H, Mes), 2.61 (s, 6H, Mes), 2.51 (d, *J* = 1.9 Hz, 6H, thiophene 1,1-dioxide), 1.83 (s, 12H, Mes), and 1.50 (s, 18H, *tert*-butyl) ppm; ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = –17.96 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 391 (4.7 × 10^4), 440 (6.2 × 10^4), 484 (5.4 × 10^4), 588 (1.6 × 10^4), and 638 (6.7 × 10^3) nm.

3. NMR spectra

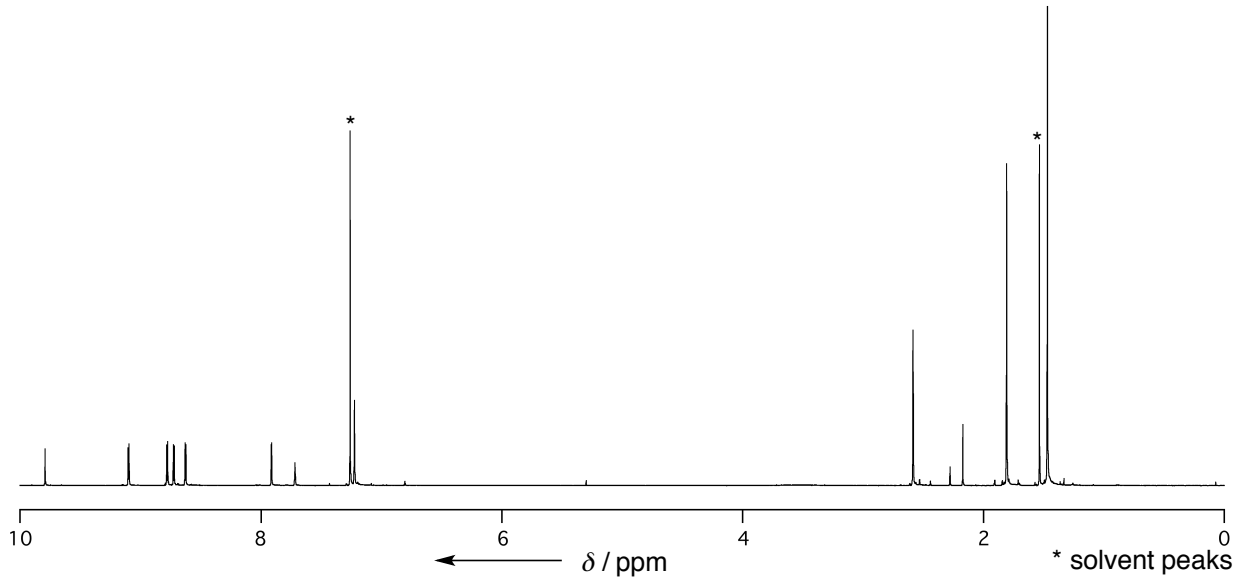


Figure S1. ^{1}H NMR spectrum of **S3** in $CDCl_3$ at 25 ºC.

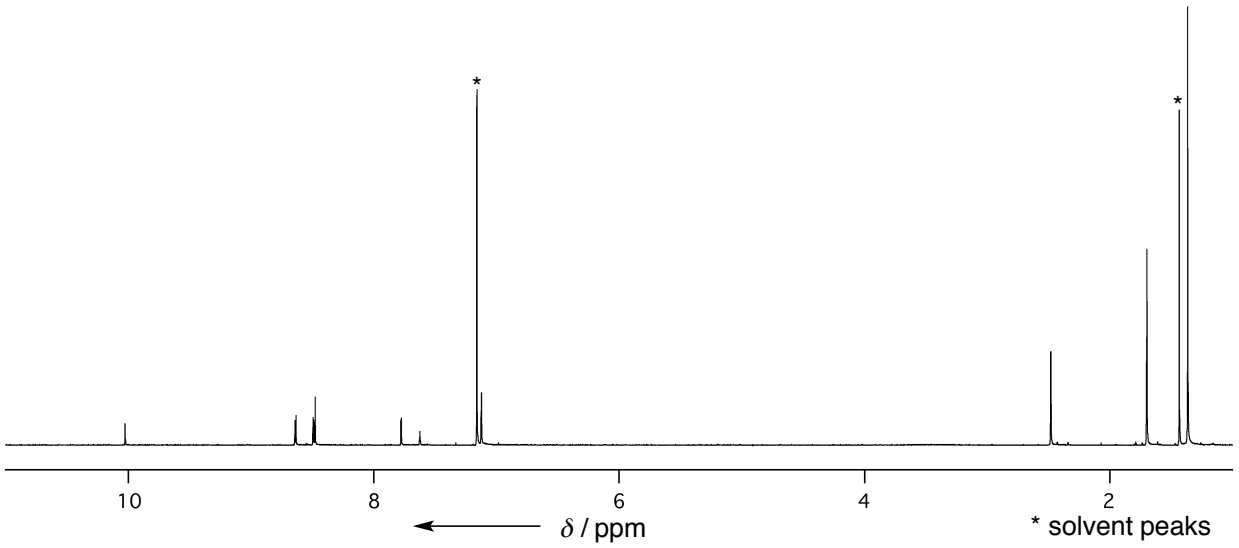


Figure S2. ^{1}H NMR spectrum of **S5** in $CDCl_3$ at 25 ºC.

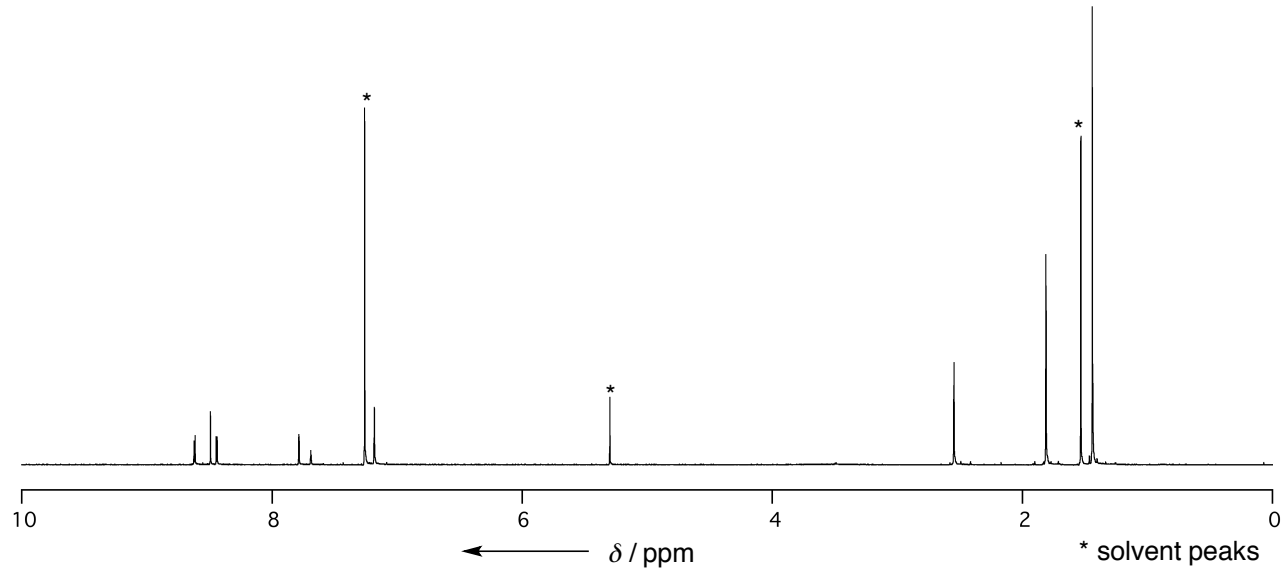


Figure S3. ^{1}H NMR spectrum of **7** in $CDCl_3$ at 25 ºC.

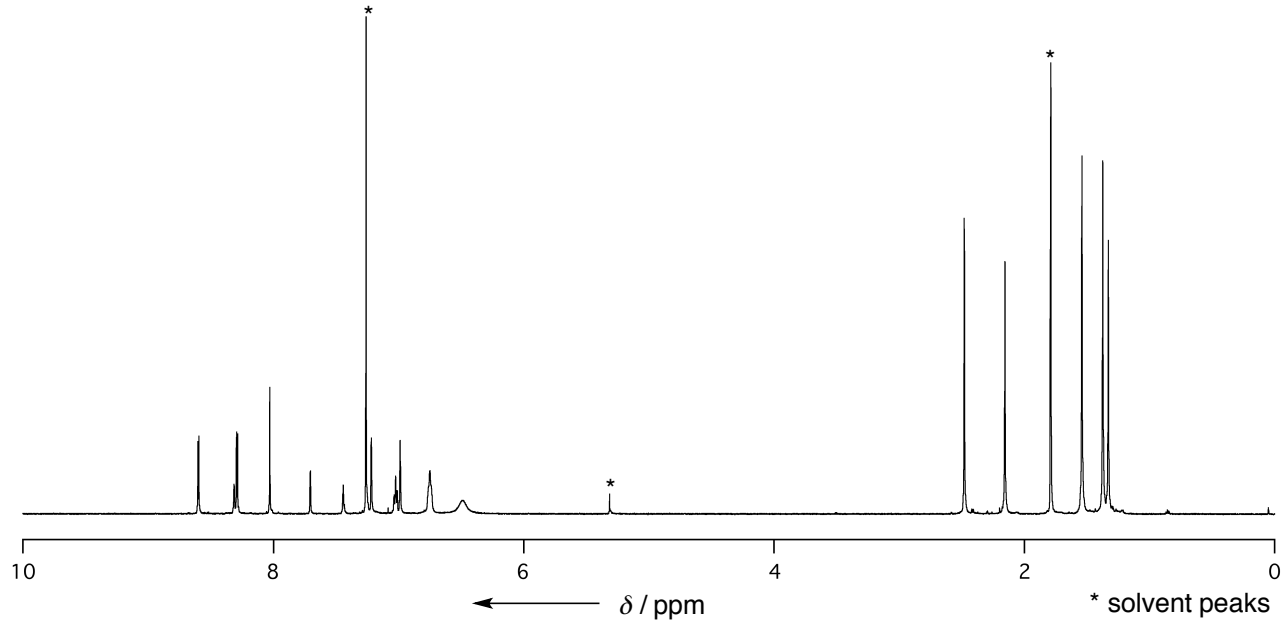


Figure S4. ^{1}H NMR spectrum of **8** in $CDCl_3$ at –30 ºC.

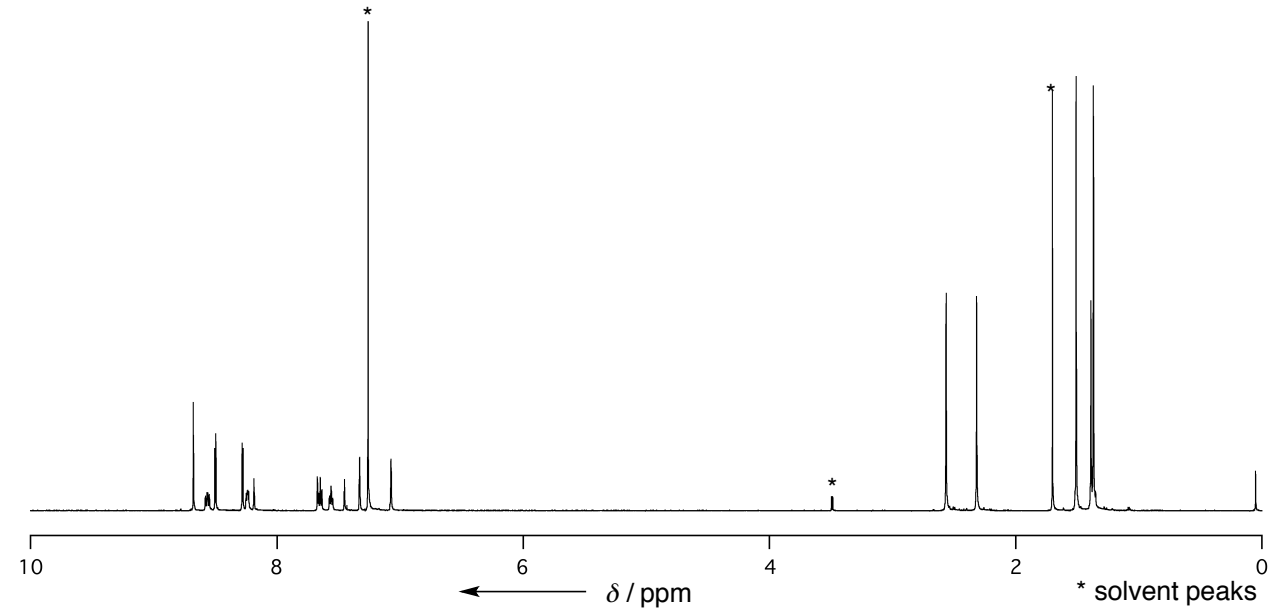


Figure S5. ^{1}H NMR spectrum of **9** in $CDCl_3$ at –30 ºC.

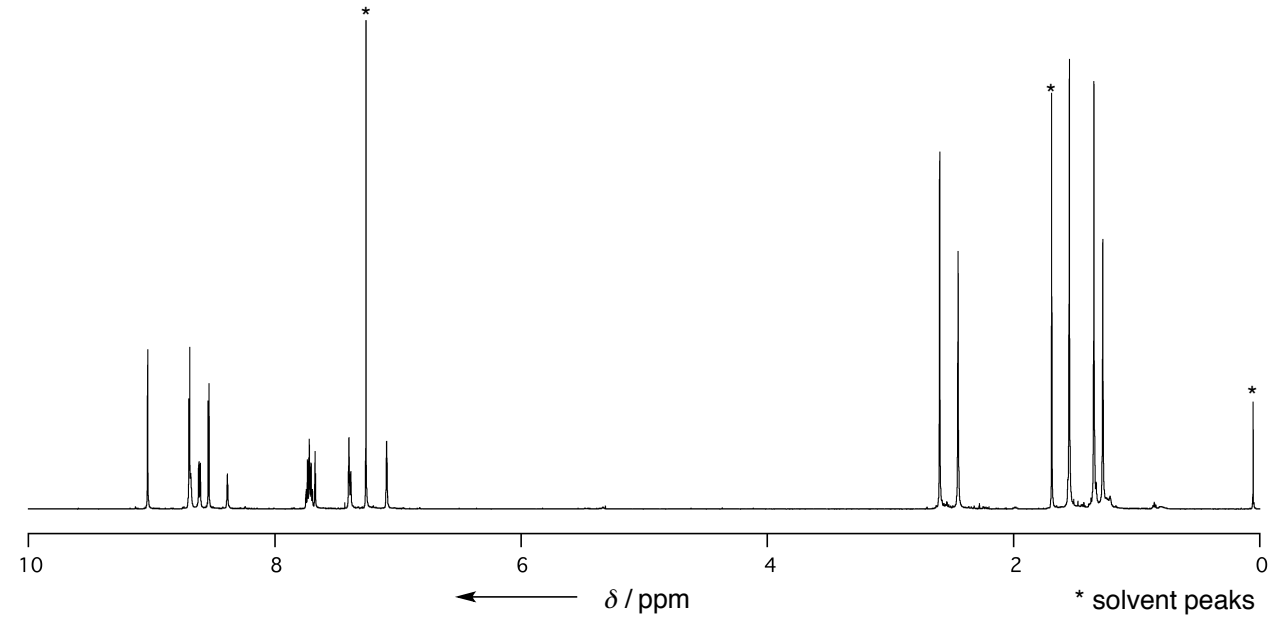


Figure S6. ^{1}H NMR spectrum of **6** in $CDCl_3$ at –30 ºC.

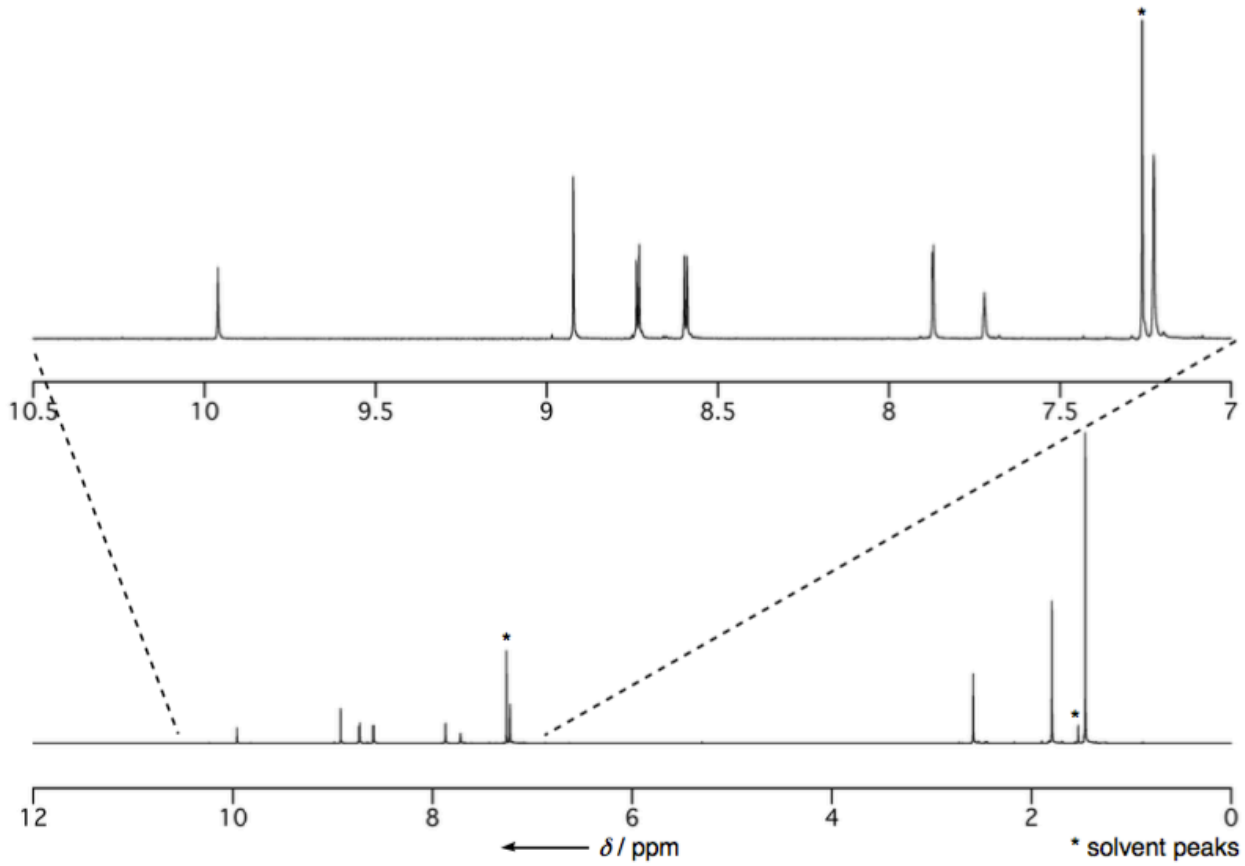


Figure S7. ^{1}H NMR spectrum of **16Ni** in $CDCl_3$ at 25 ºC.

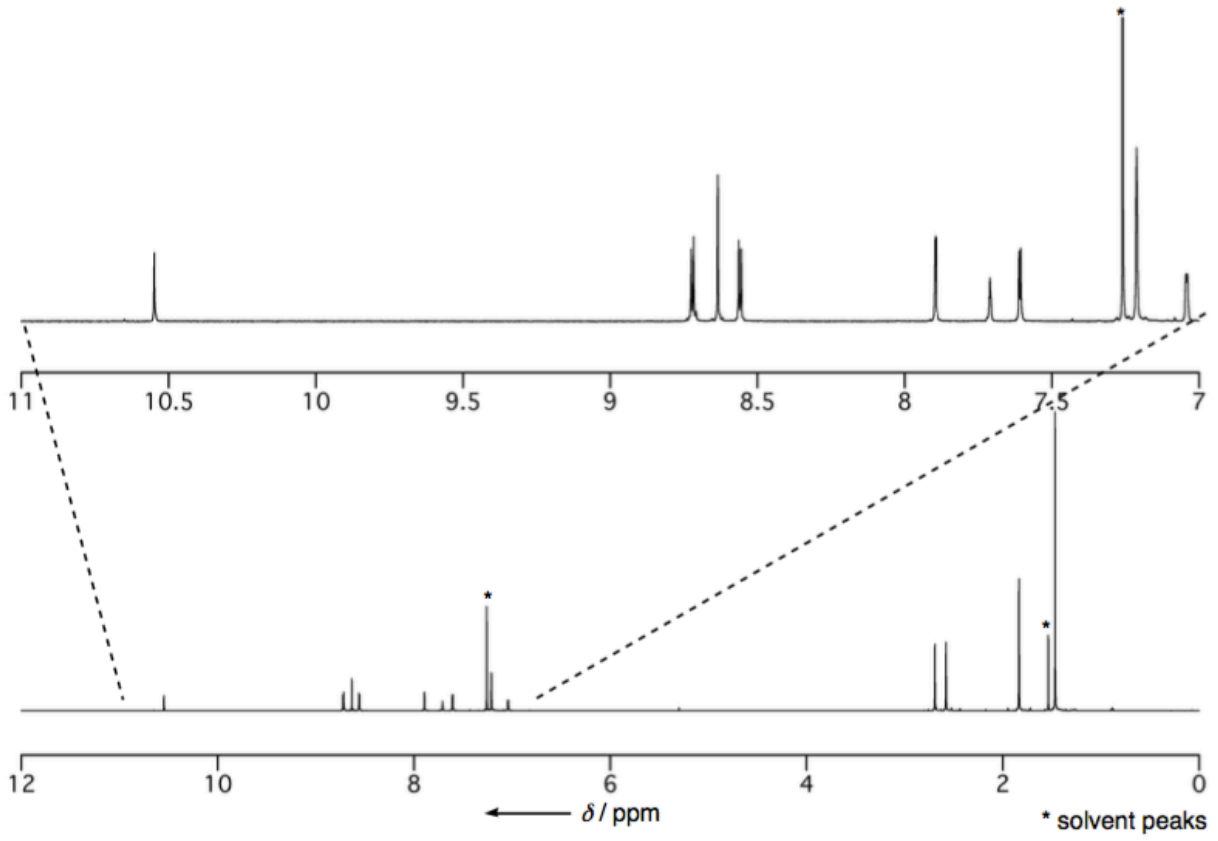


Figure S8. ^{1}H NMR spectrum of **17Ni** in $CDCl_3$ at 25 ºC.

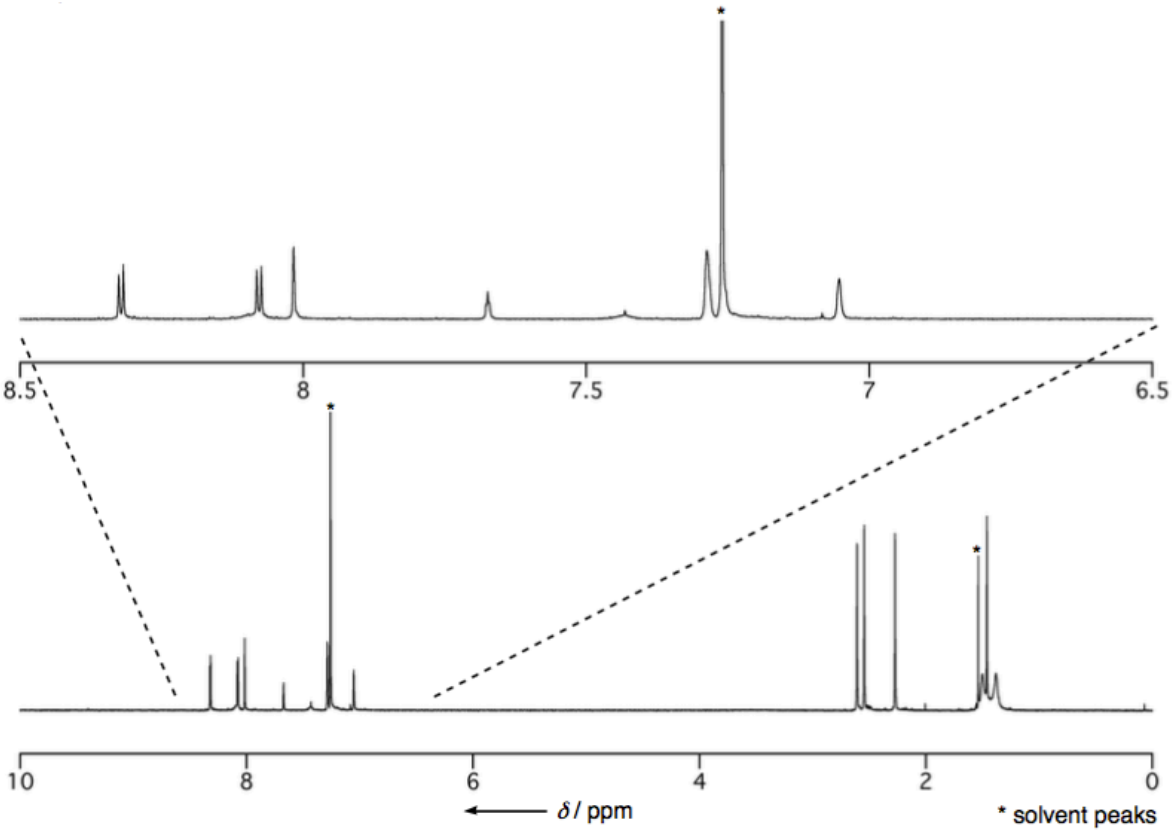


Figure S9. ^{1}H NMR spectrum of **18Ni** in $CDCl_3$ at 25 ºC.

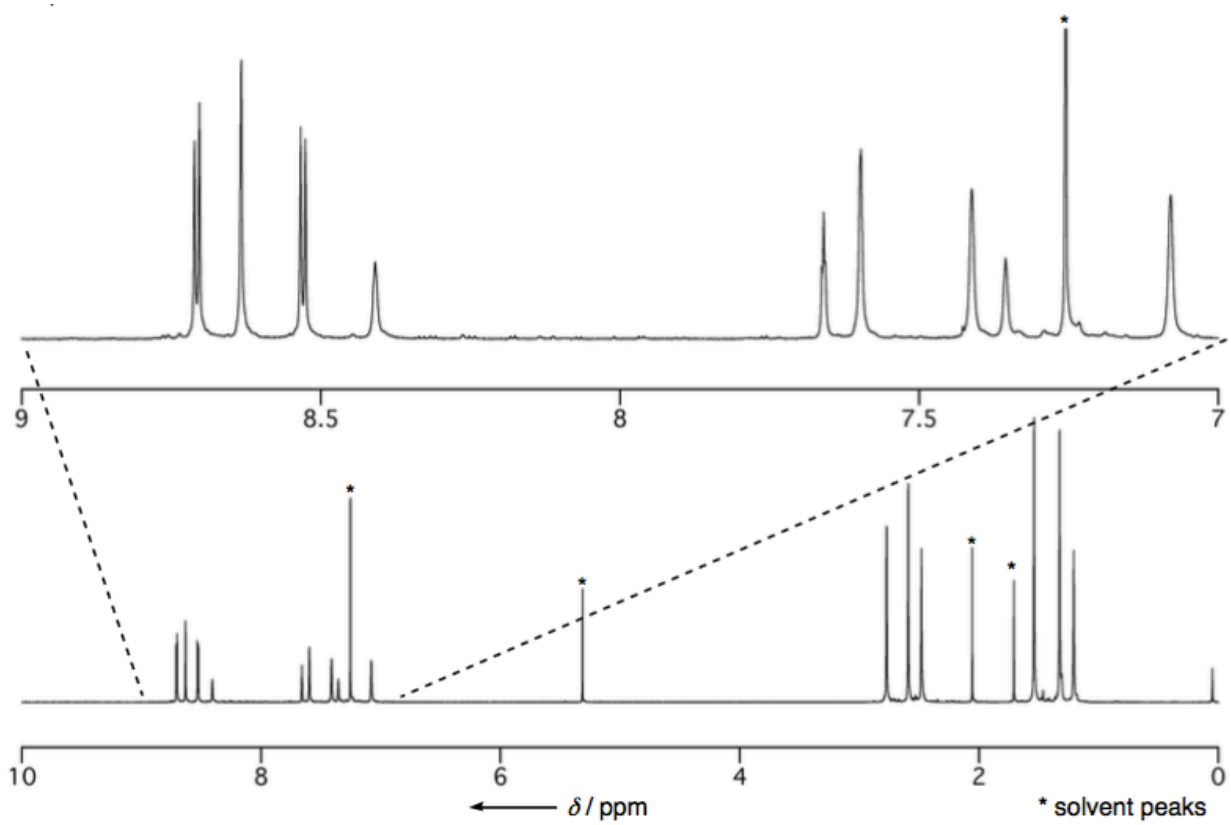


Figure S10. ^{1}H NMR spectrum of **10Ni** in $CDCl_3$ at –40 ºC.

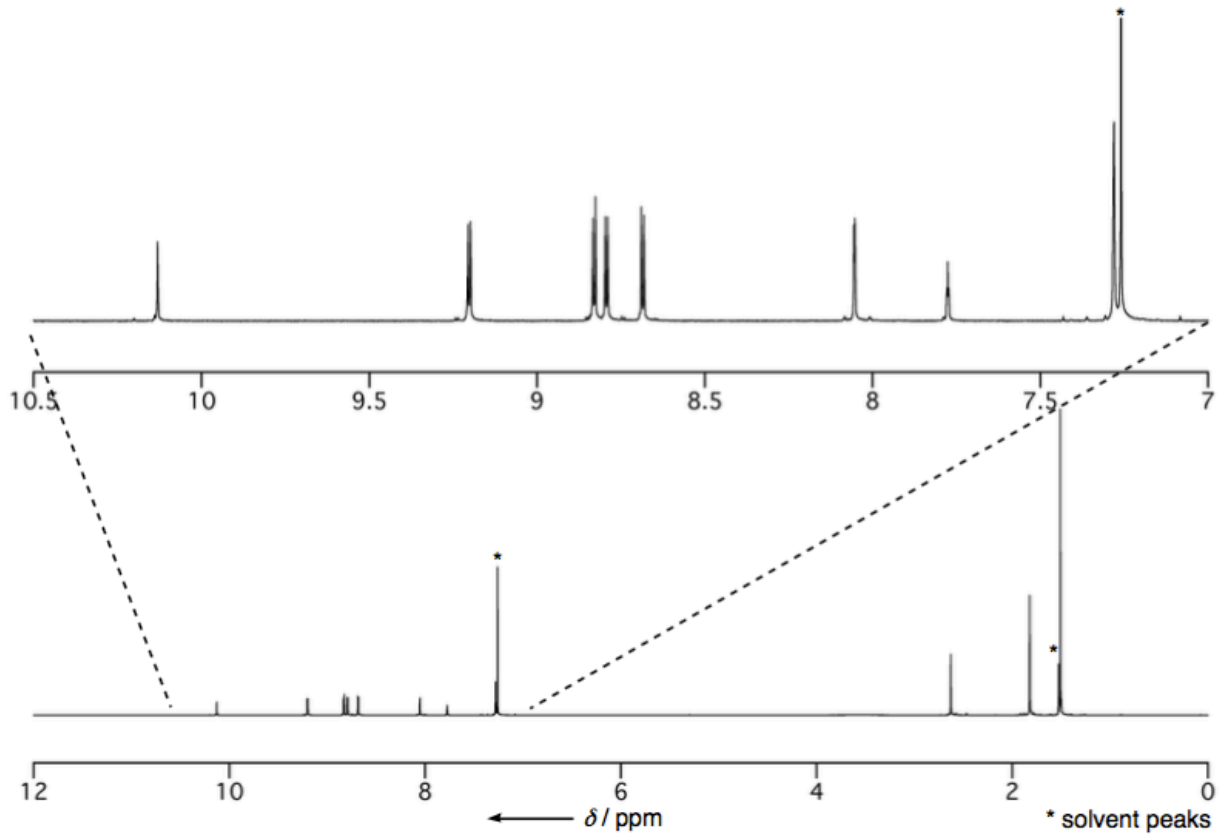


Figure S11. ^{1}H NMR spectrum of **S6** in $CDCl_3$ at 25 ºC.

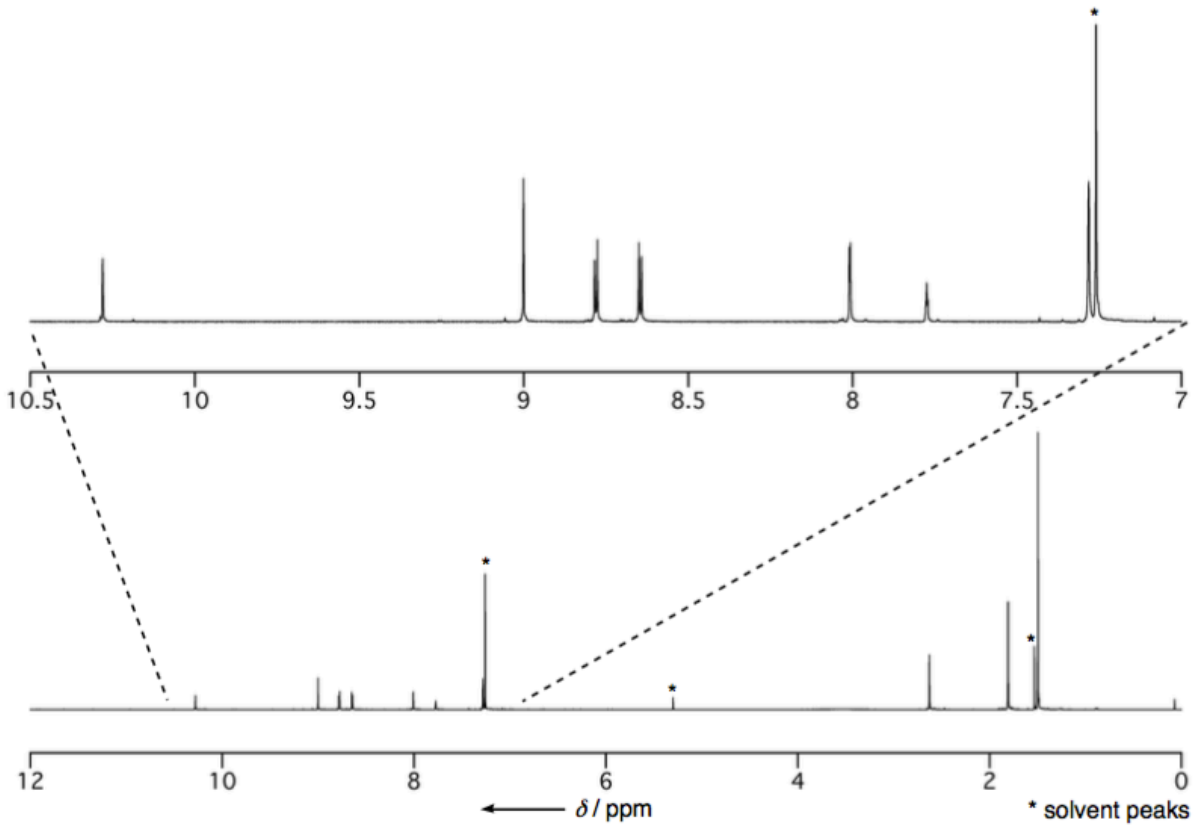


Figure S12. ^{1}H NMR spectrum of **16Pd** in $CDCl_3$ at 25 ºC.

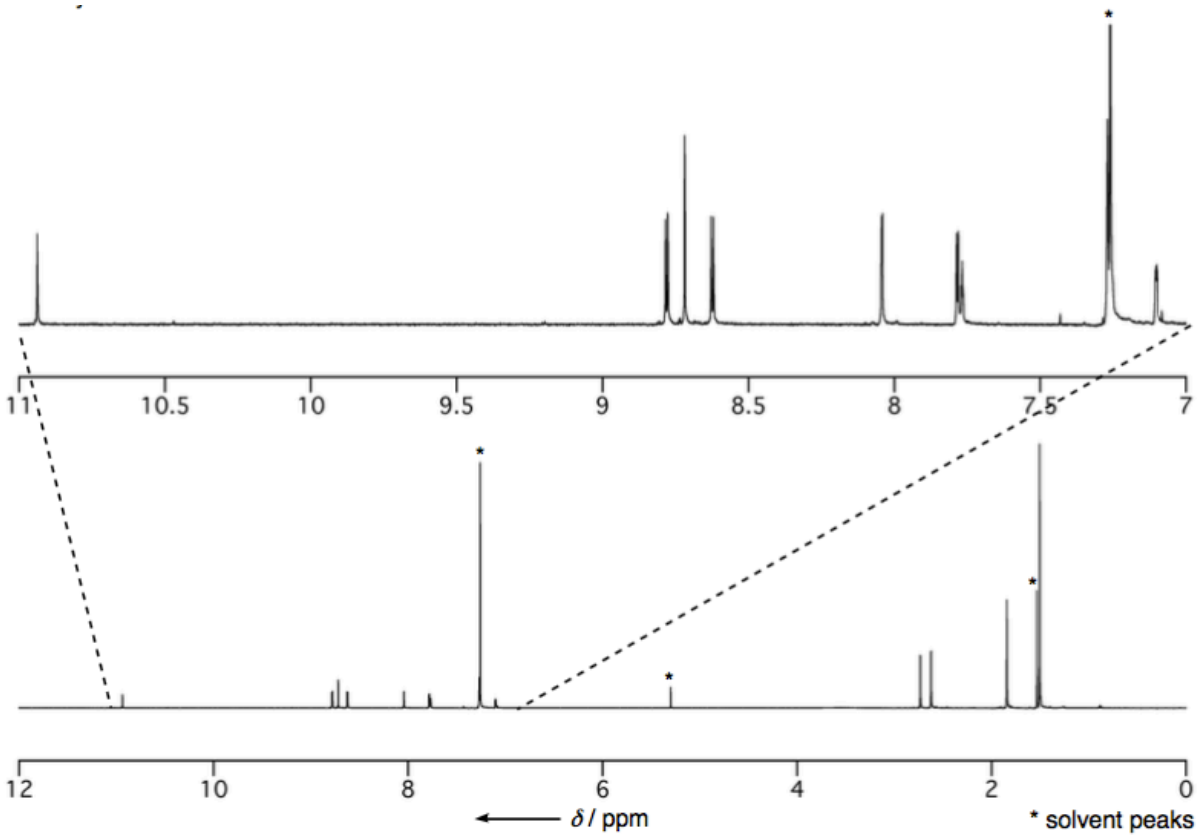


Figure S13. ^{1}H NMR spectrum of **17Pd** in $CDCl_3$ at 25 ºC.

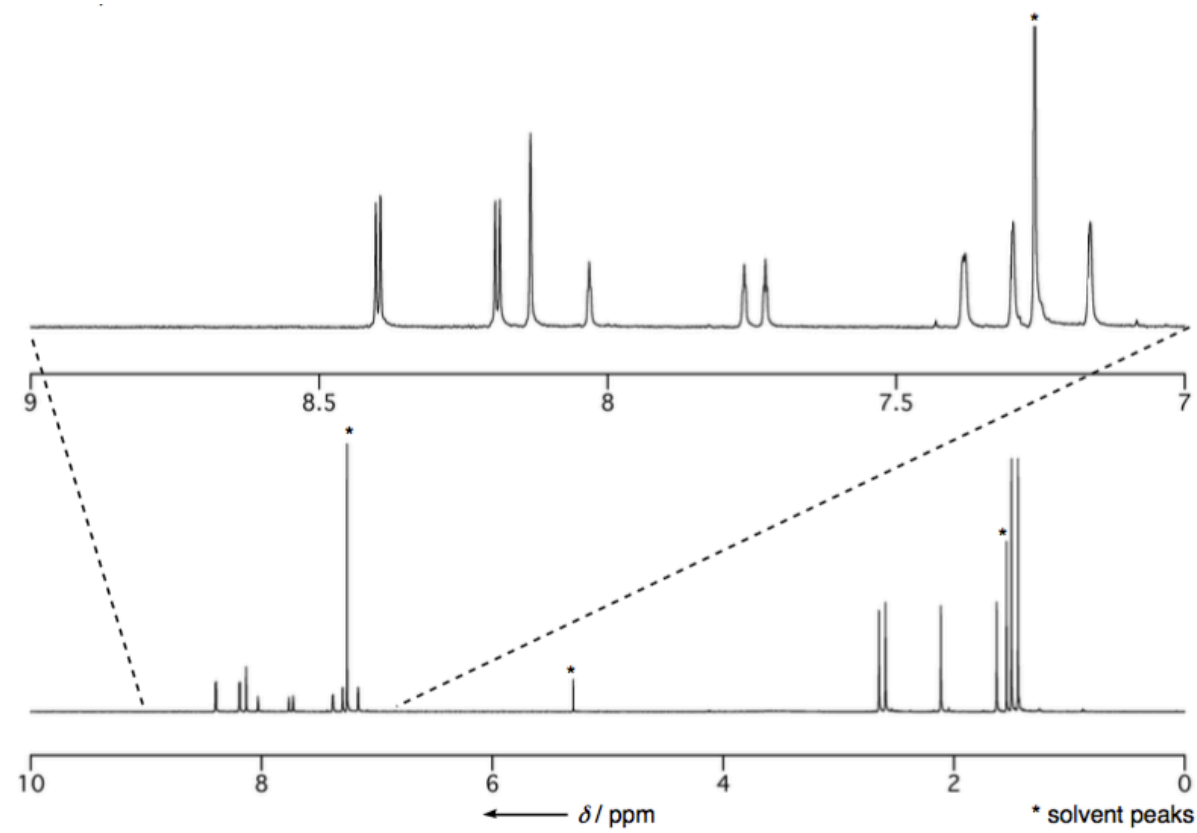


Figure S14. ^{1}H NMR spectrum of **18Pd** in $CDCl_3$ at 25 ºC.

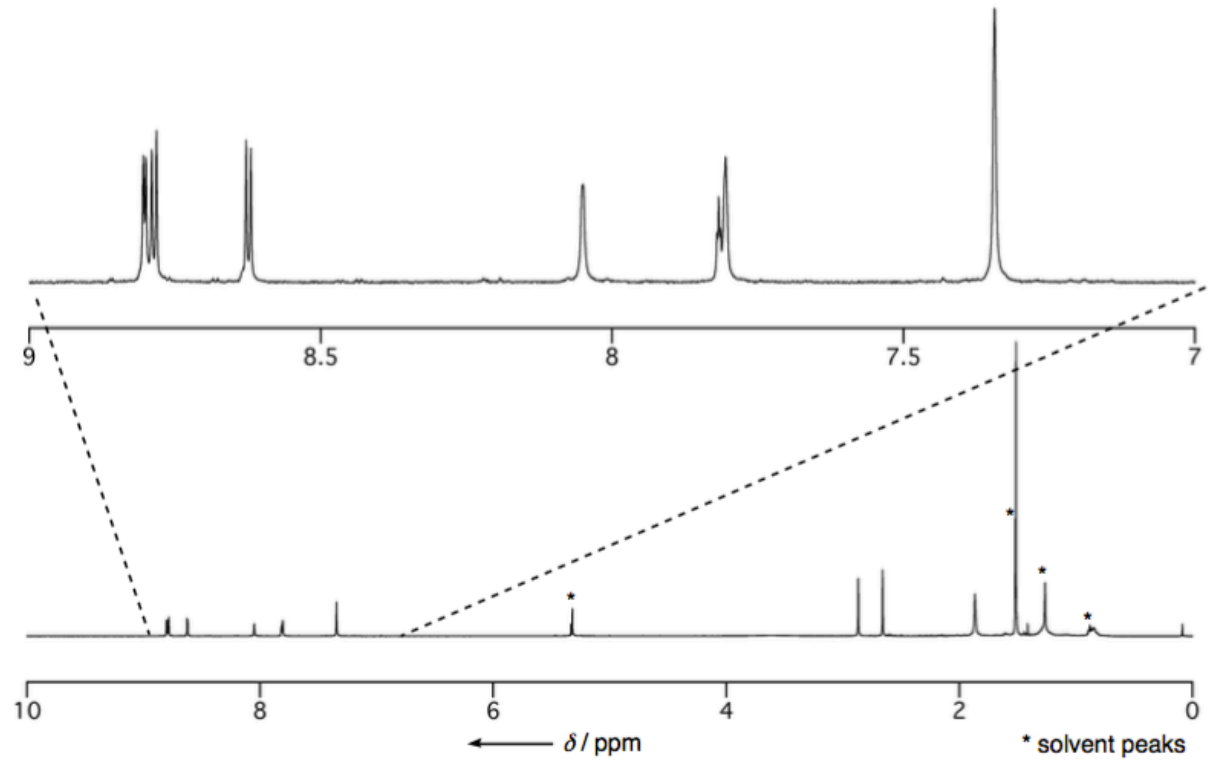


Figure S15. ^{1}H NMR spectrum of **10Pd** in CD_2Cl_2 at 25 ºC.

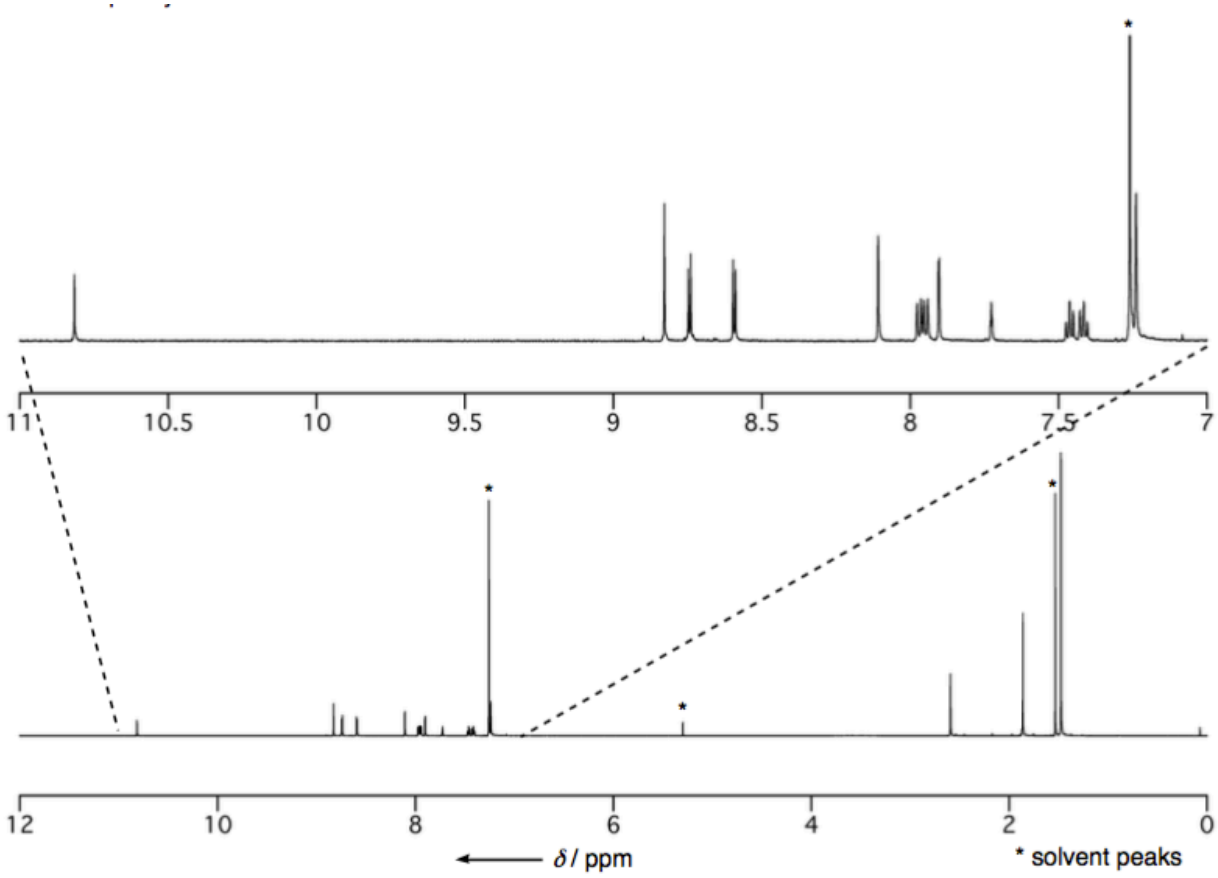


Figure S16. ^{1}H NMR spectrum of **19** in $CDCl_3$ at 25 ºC.

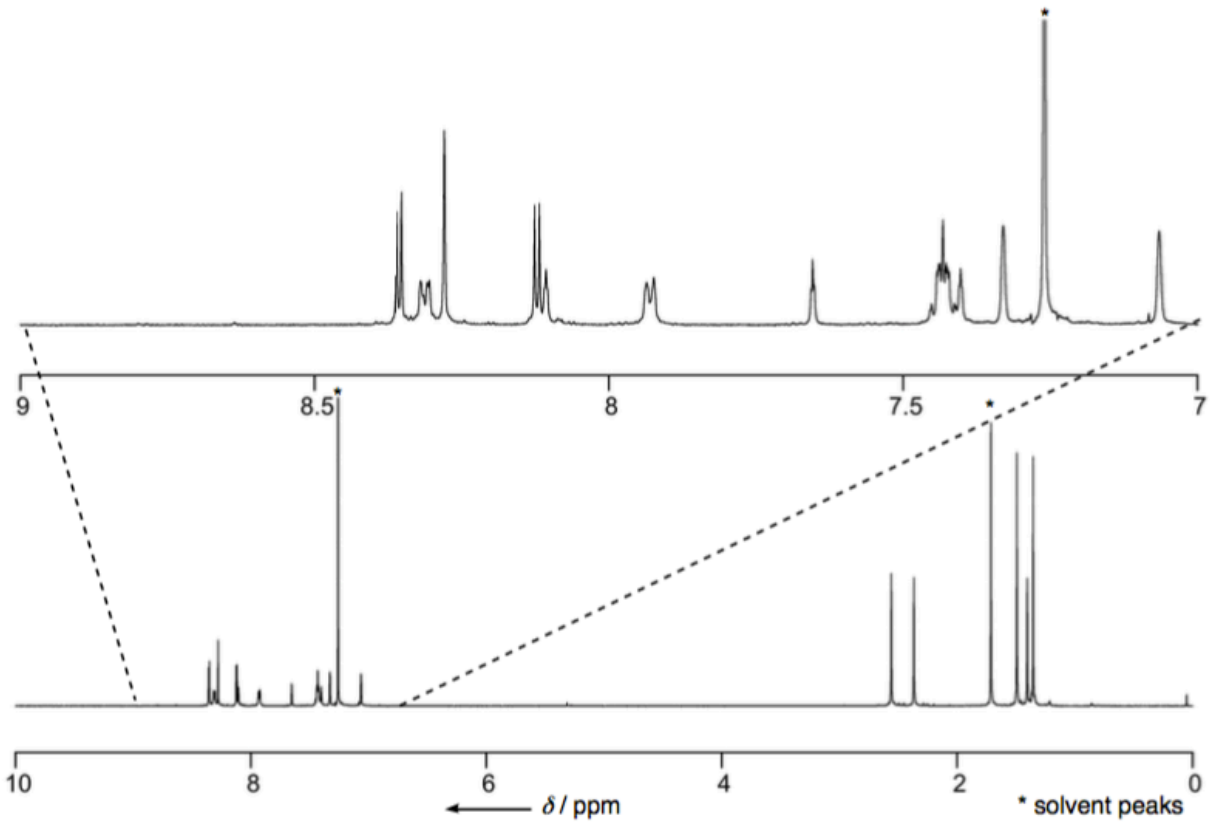


Figure S17. ^{1}H NMR spectrum of **20** in $CDCl_3$ at –30 ºC.

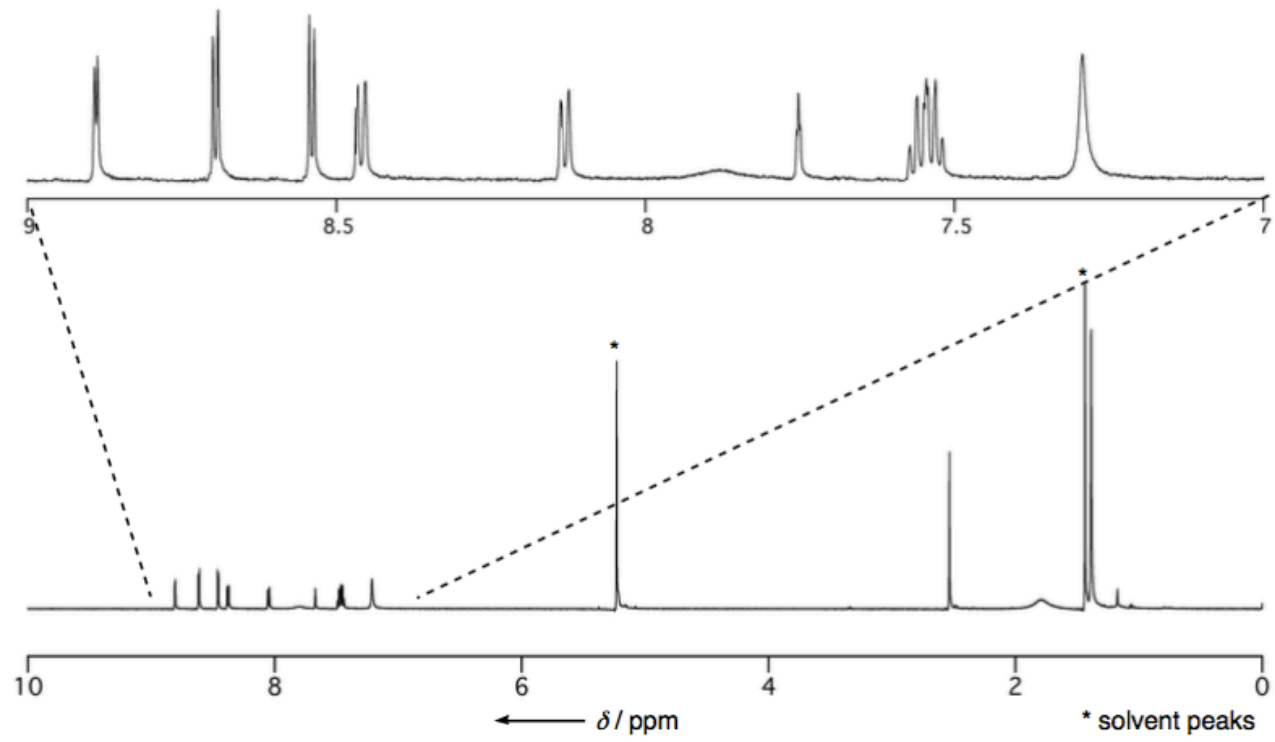


Figure S18. ^{1}H NMR spectrum of **11** in CD_2Cl_2 at 25 ºC.

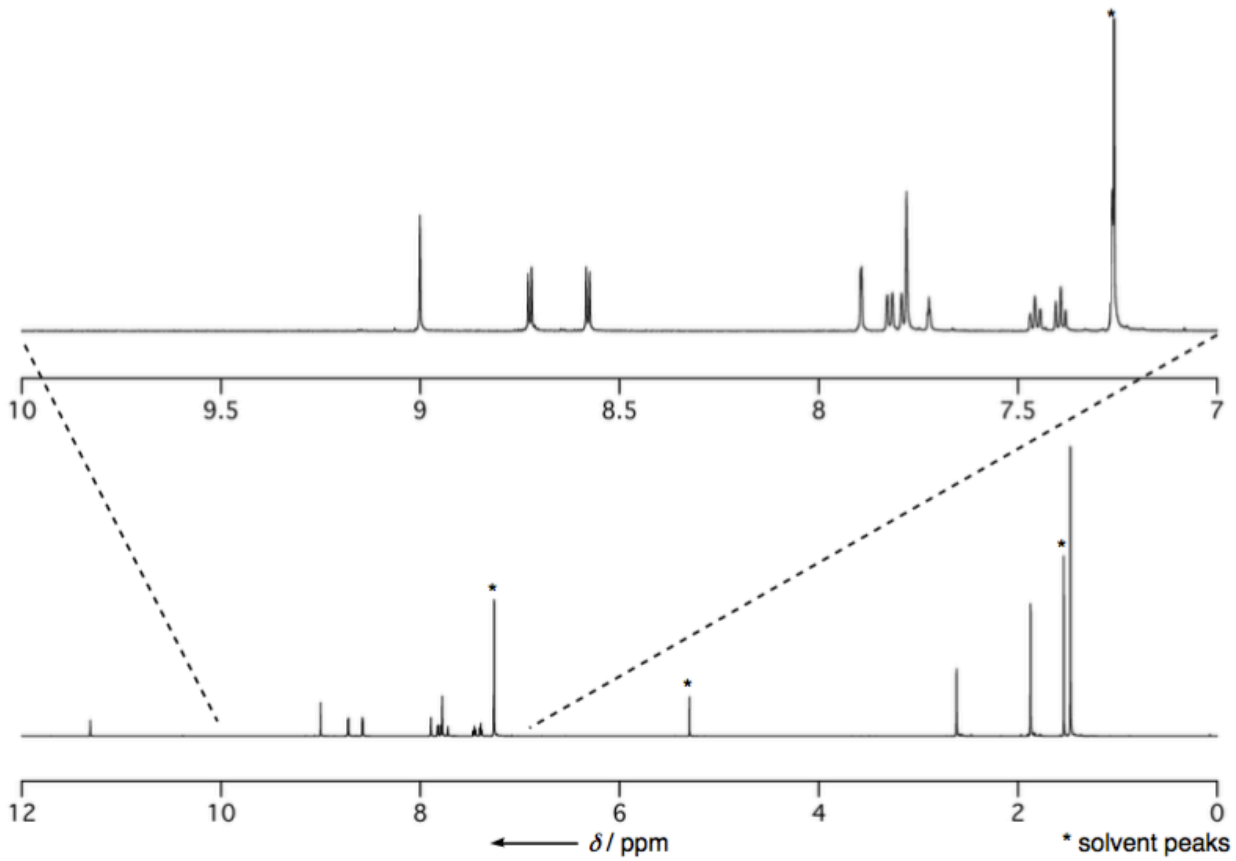


Figure S19. ^{1}H NMR spectrum of **21** in $CDCl_3$ at 25 ºC.

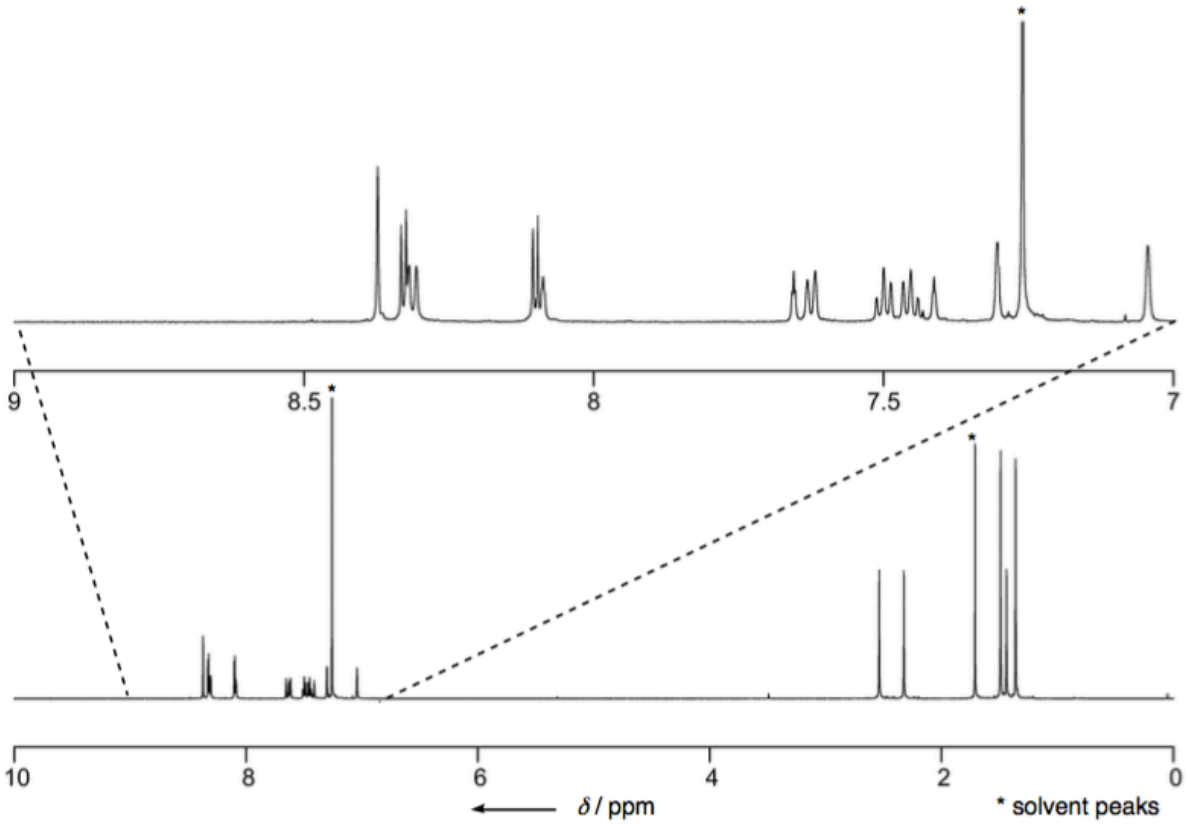


Figure S20. ^{1}H NMR spectrum of **22** in $CDCl_3$ at –30 ºC.

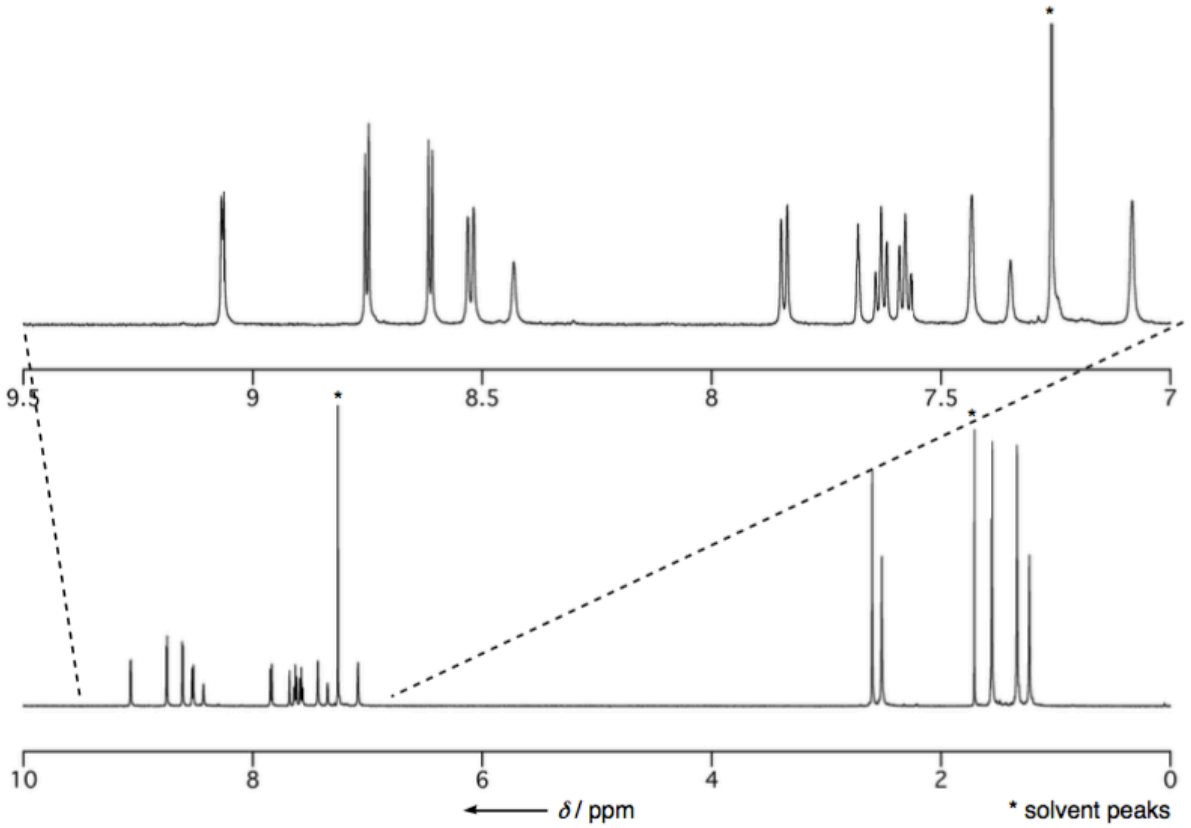


Figure S21. ^{1}H NMR spectrum of **12** in $CDCl_3$ at –40 ºC.

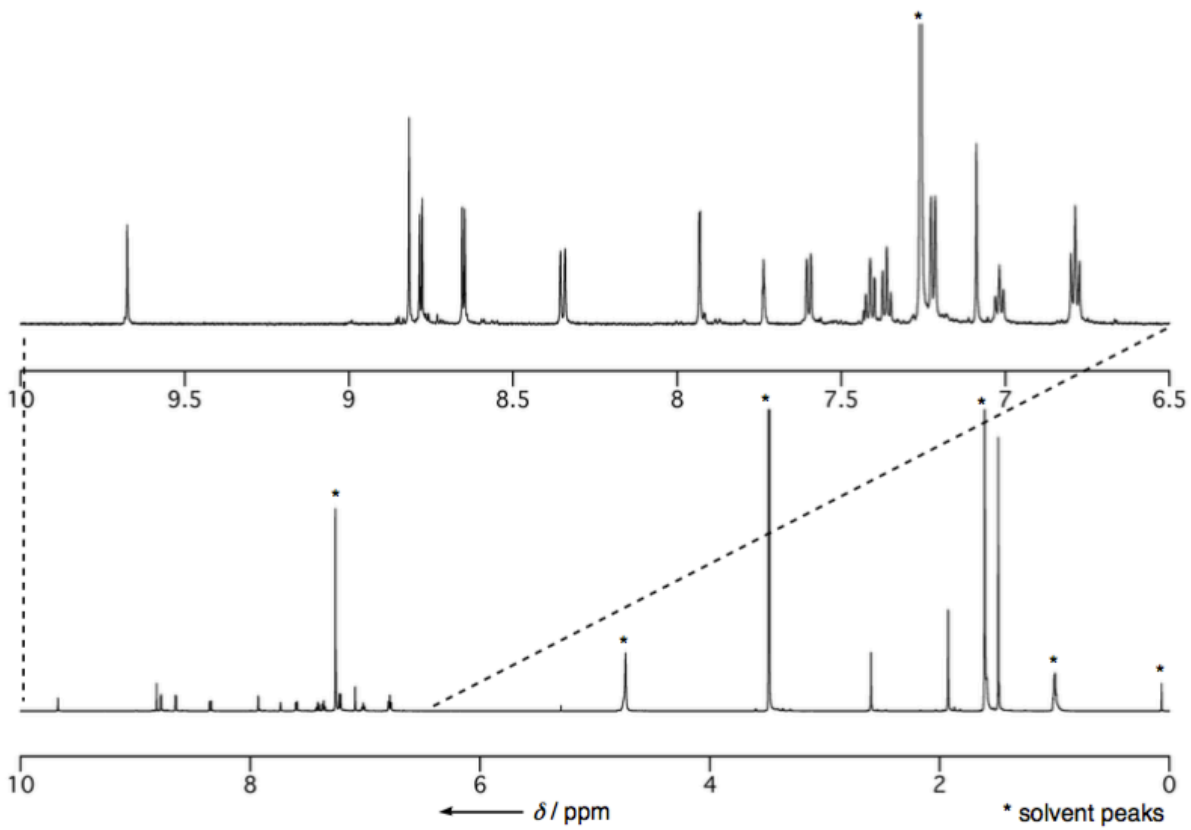


Figure S22. ^{1}H NMR spectrum of **23** in $CDCl_3$ at 25 ºC.

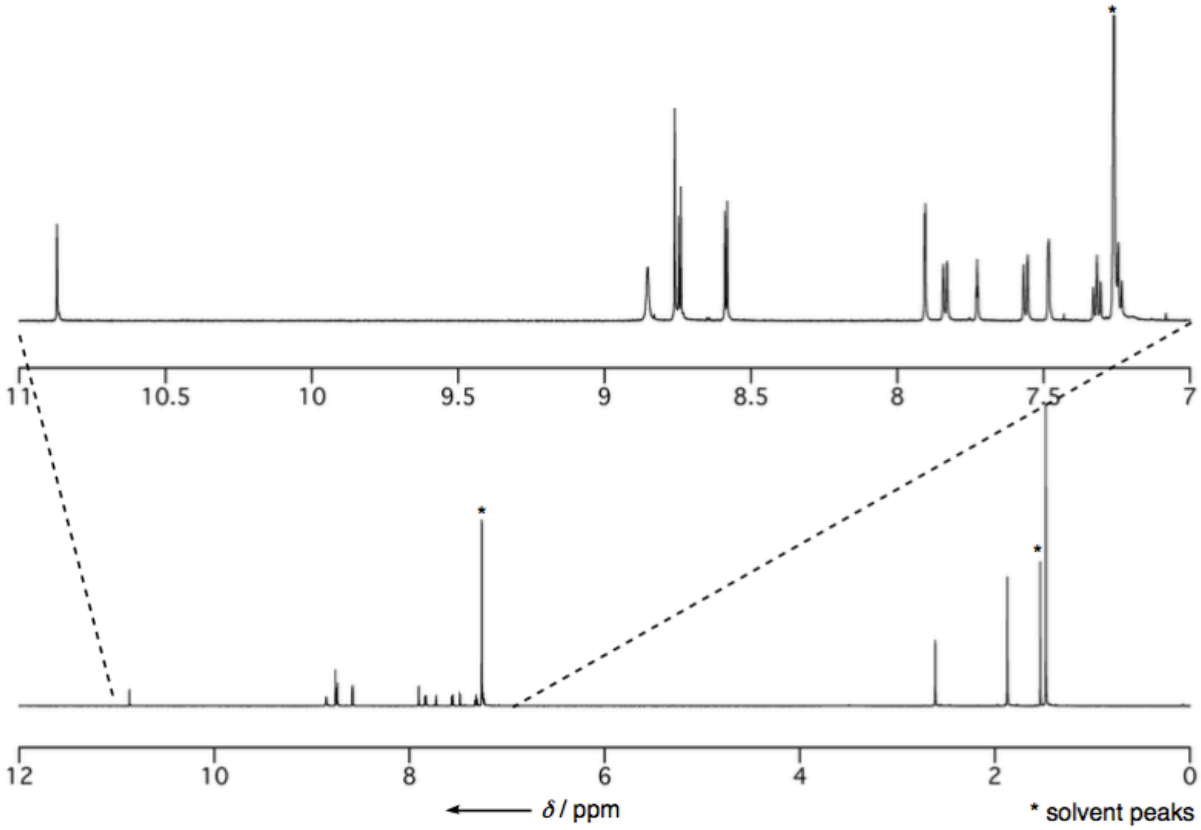


Figure S23. ^{1}H NMR spectrum of **24** in $CDCl_3$ at 25 ºC.

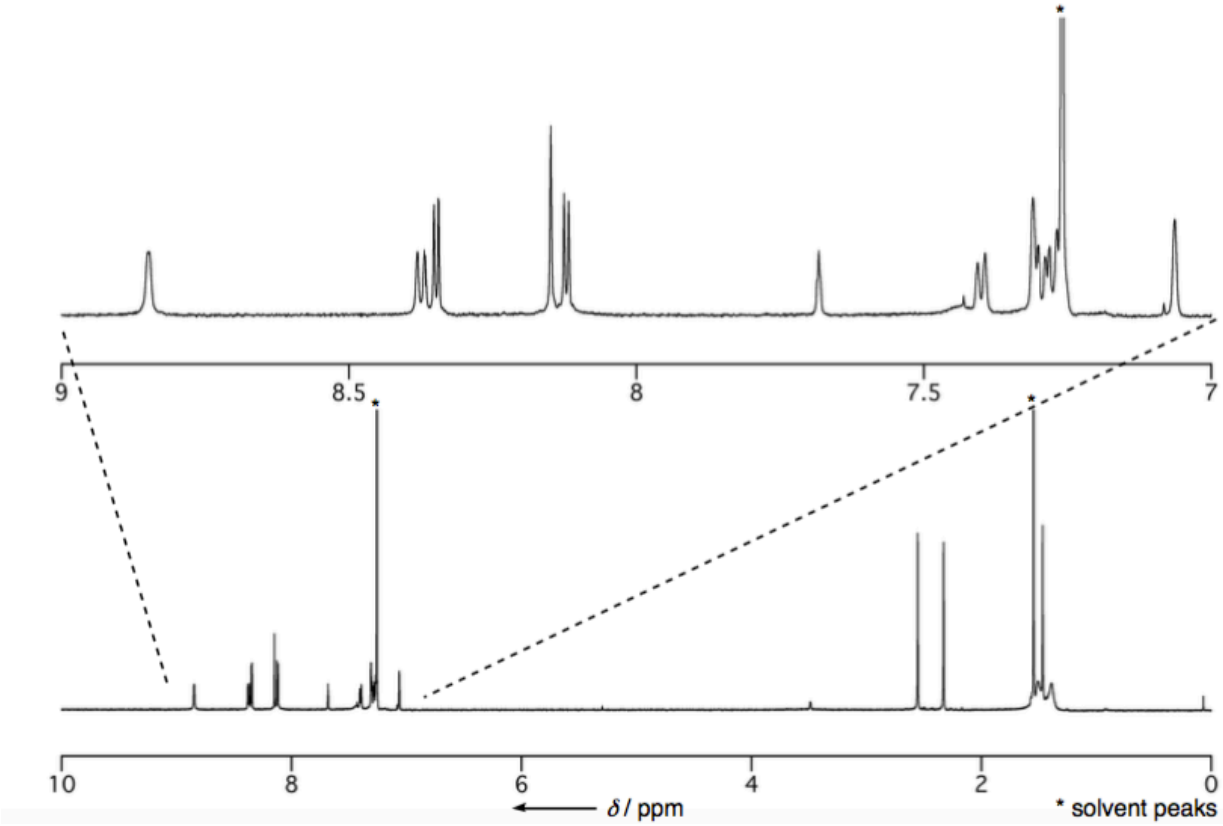


Figure S24. ^{1}H NMR spectrum of **25** in $CDCl_3$ at 25 ºC.

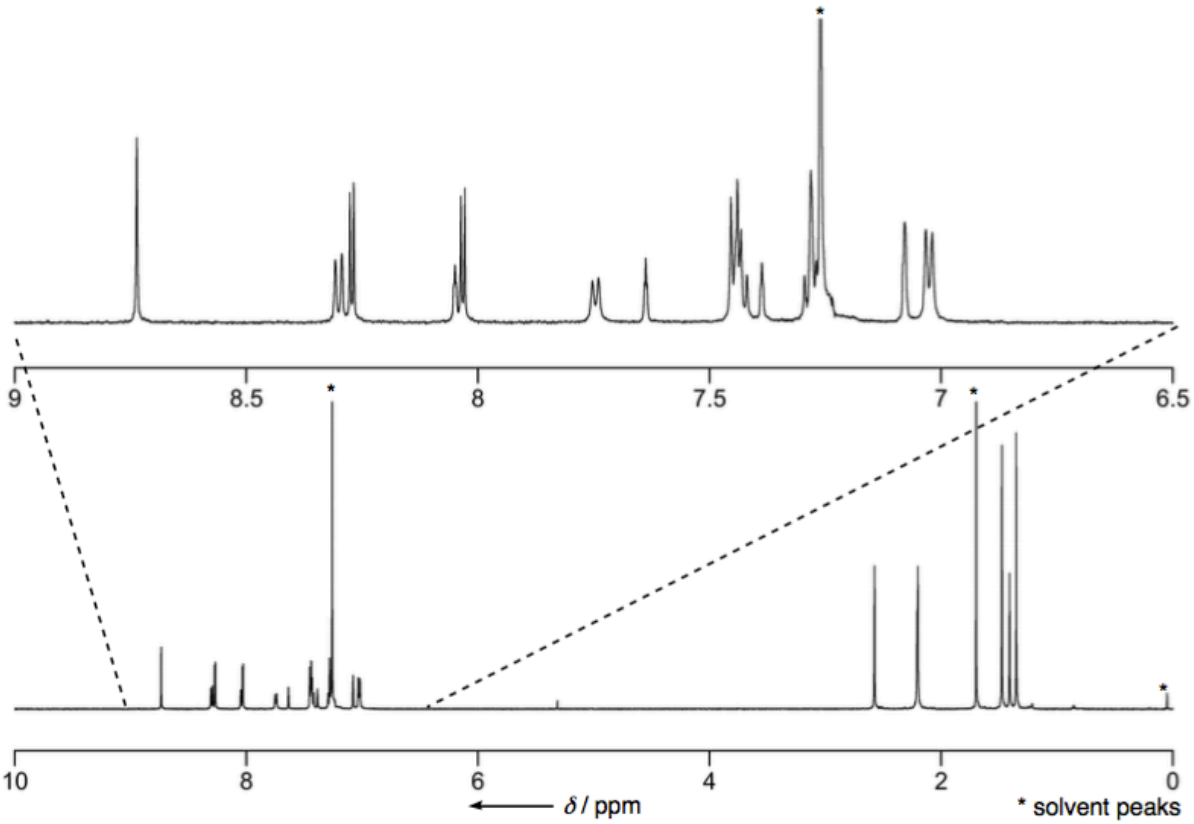


Figure S25. ^{1}H NMR spectrum of **26** in $CDCl_3$ at –30 ºC.

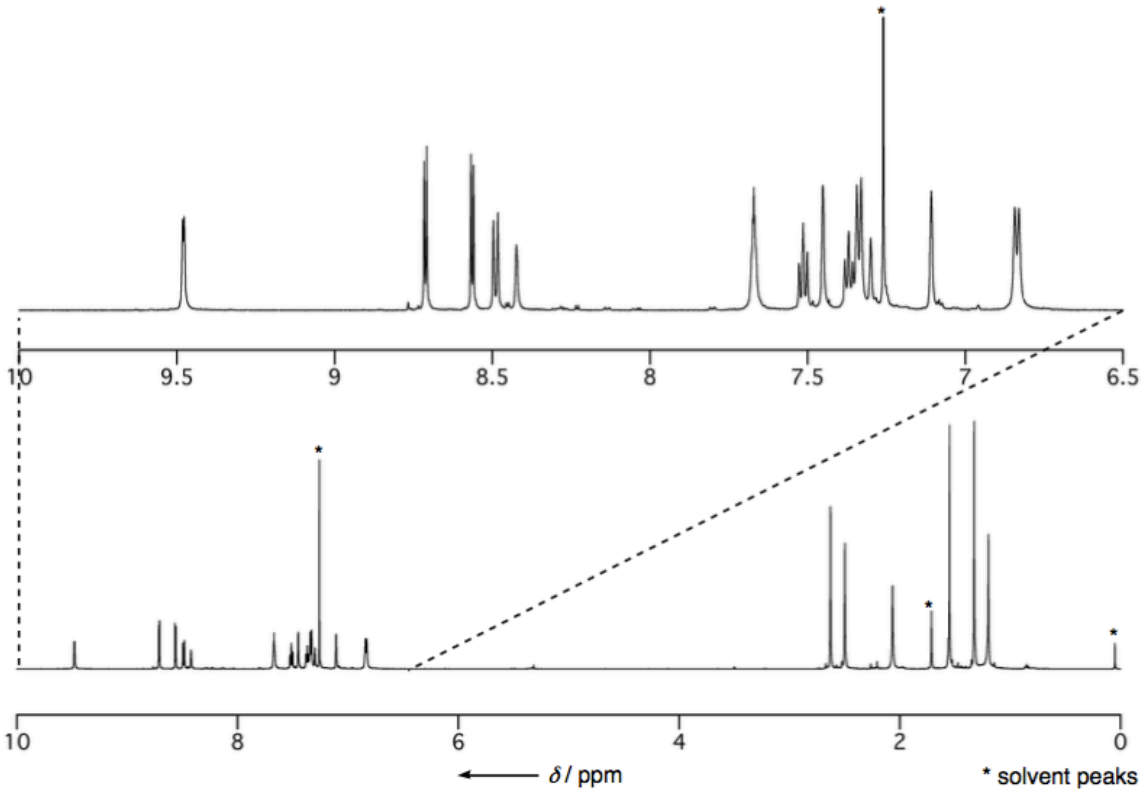


Figure S26. ^{1}H NMR spectrum of **13** in $CDCl_3$ at –40 ºC.

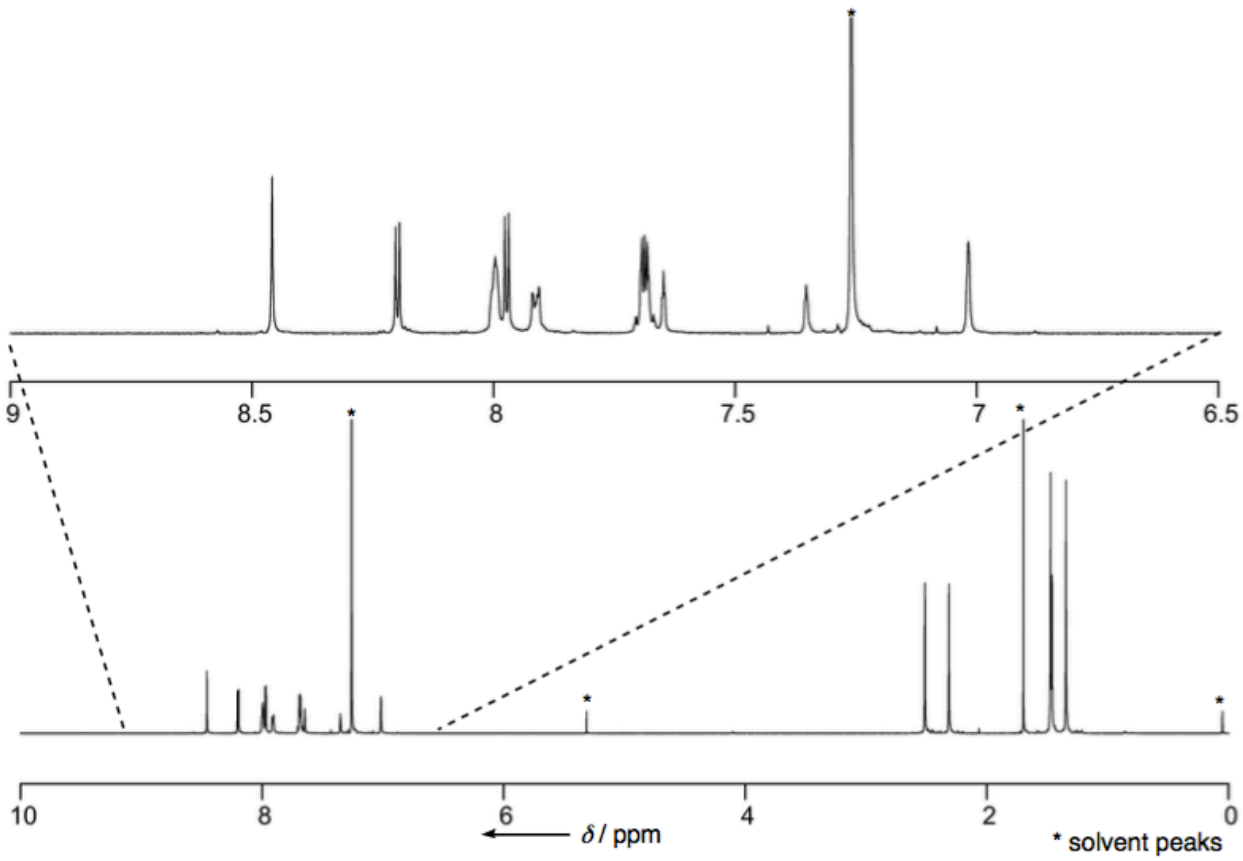


Figure S27. ^{1}H NMR spectrum of **27** in $CDCl_3$ at –30 ºC.

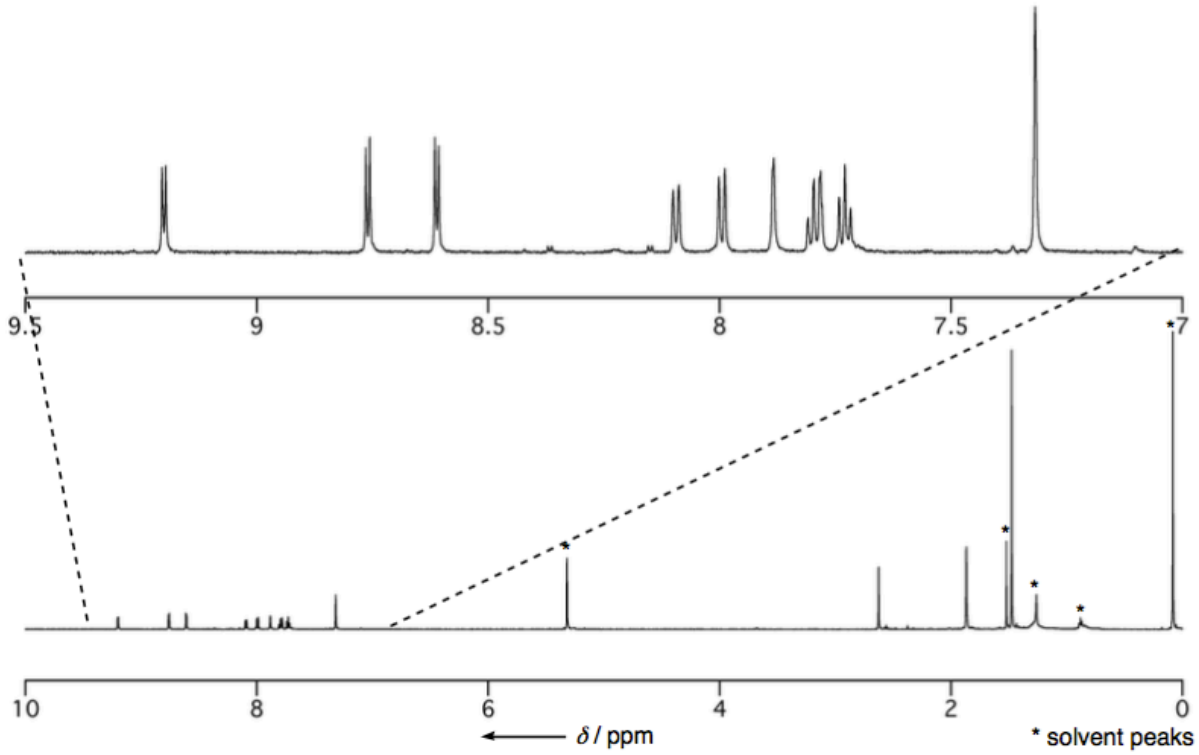


Figure S28. ^{1}H NMR spectrum of **14** in CD_2Cl_2 at 25 ºC.

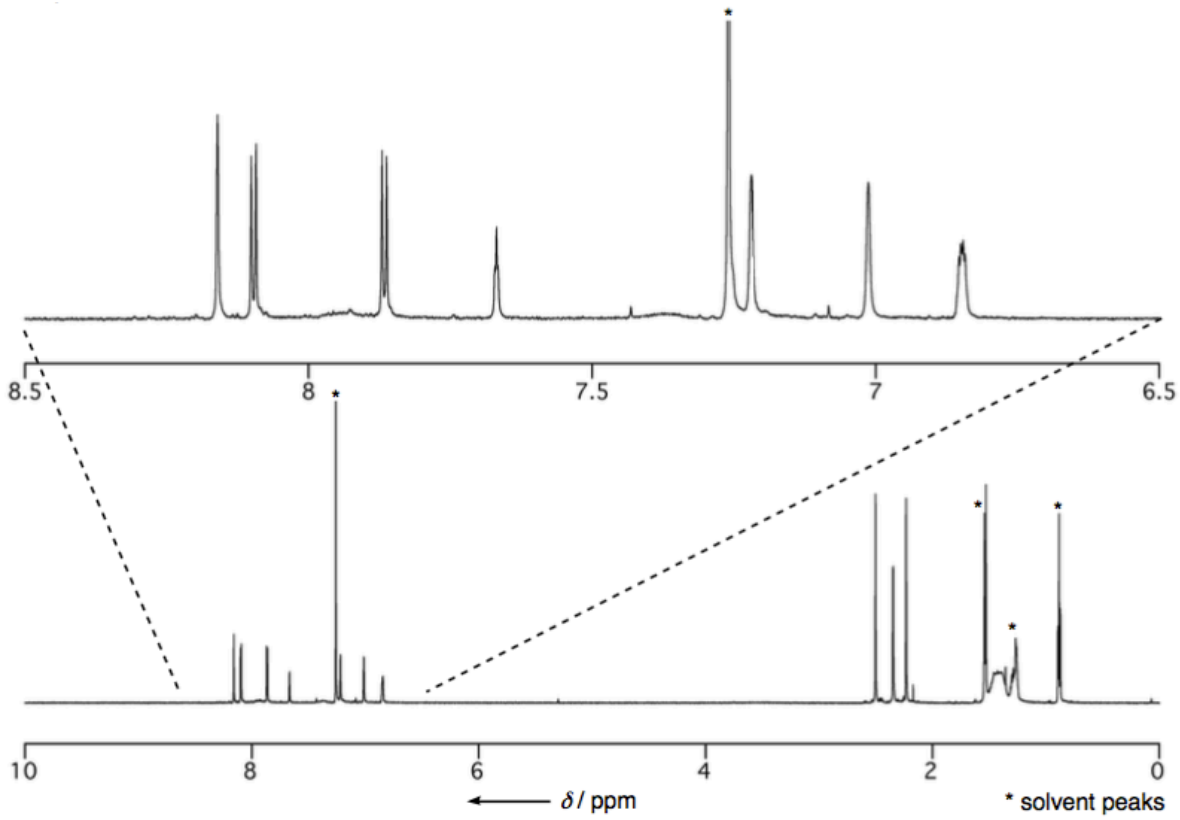


Figure S29. ^{1}H NMR spectrum of **28** in $CDCl_3$ at 25 ºC.

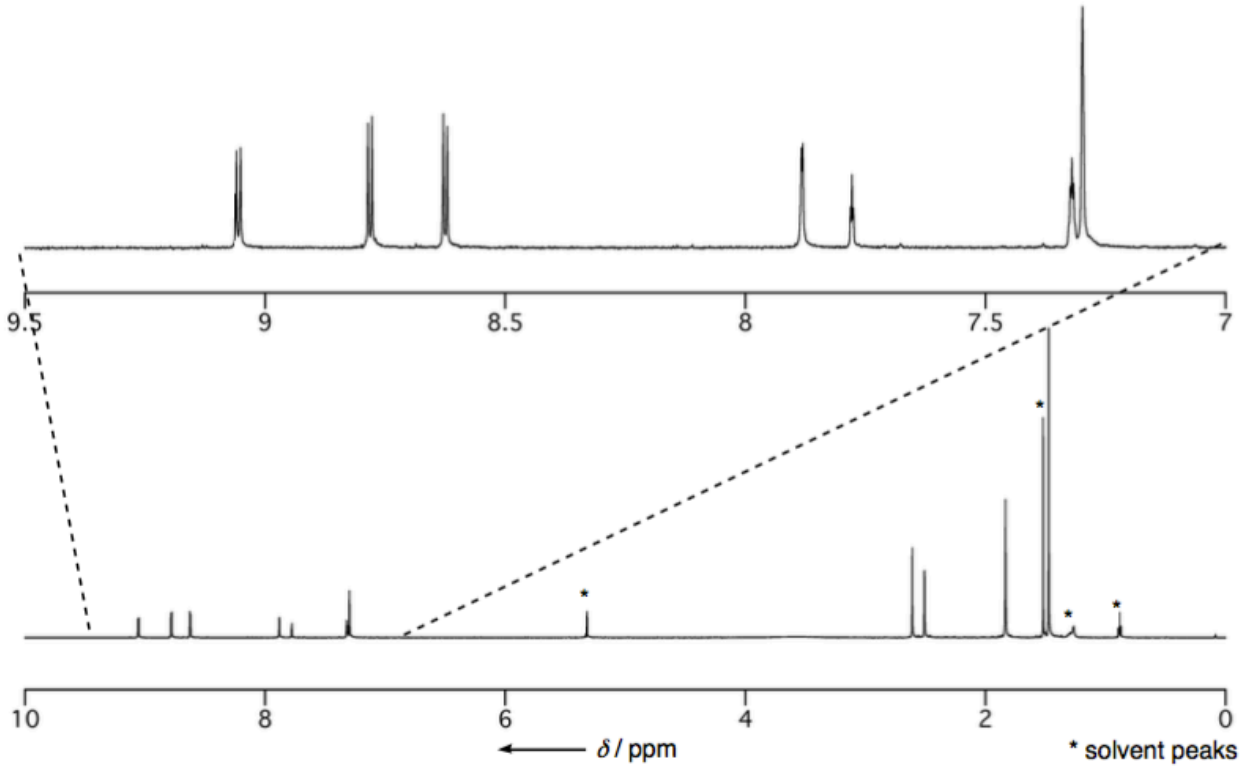


Figure S30. ^{1}H NMR spectrum of **15** in CD_2Cl_2 at 25 ºC.

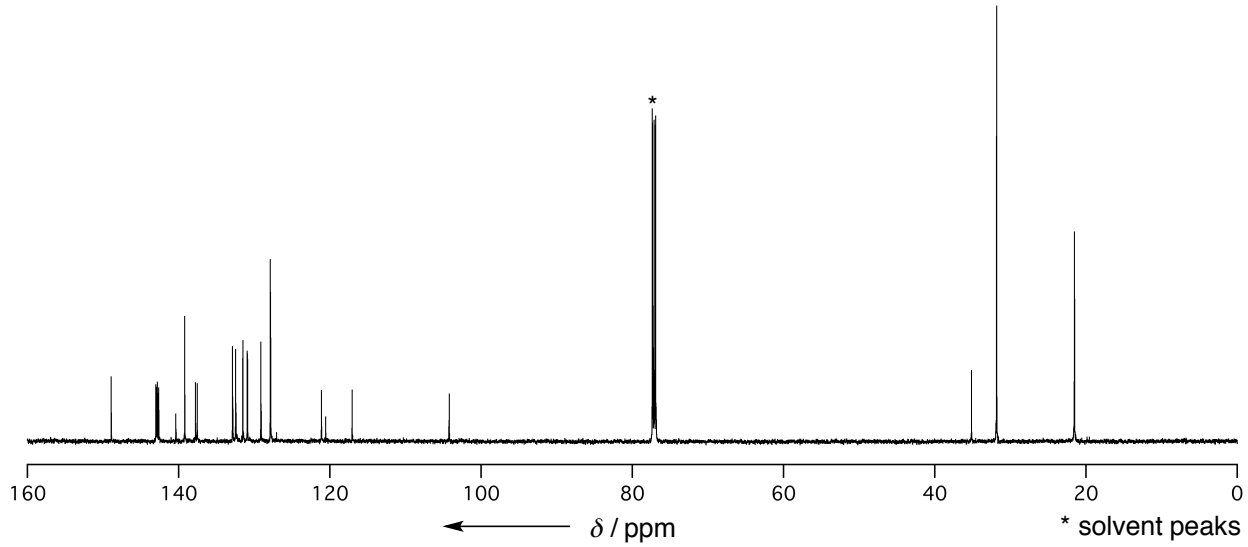


Figure S31. ^{13}C NMR spectrum of **S3** in $CDCl_3$ at 25 ºC.

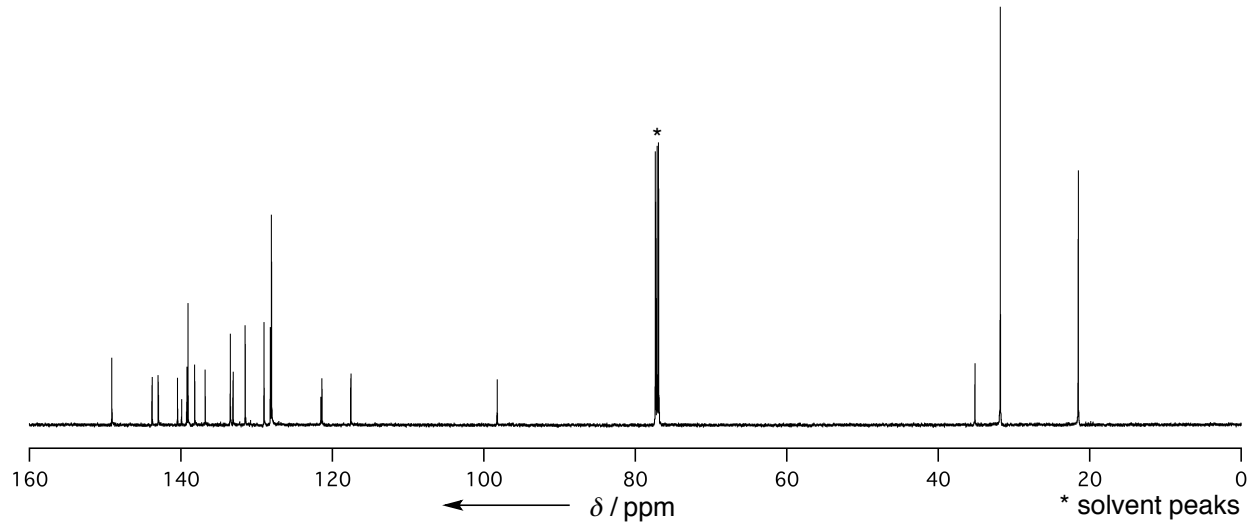


Figure S32. ^{13}C NMR spectrum of **S5** in $CDCl_3$ at 25 ºC.

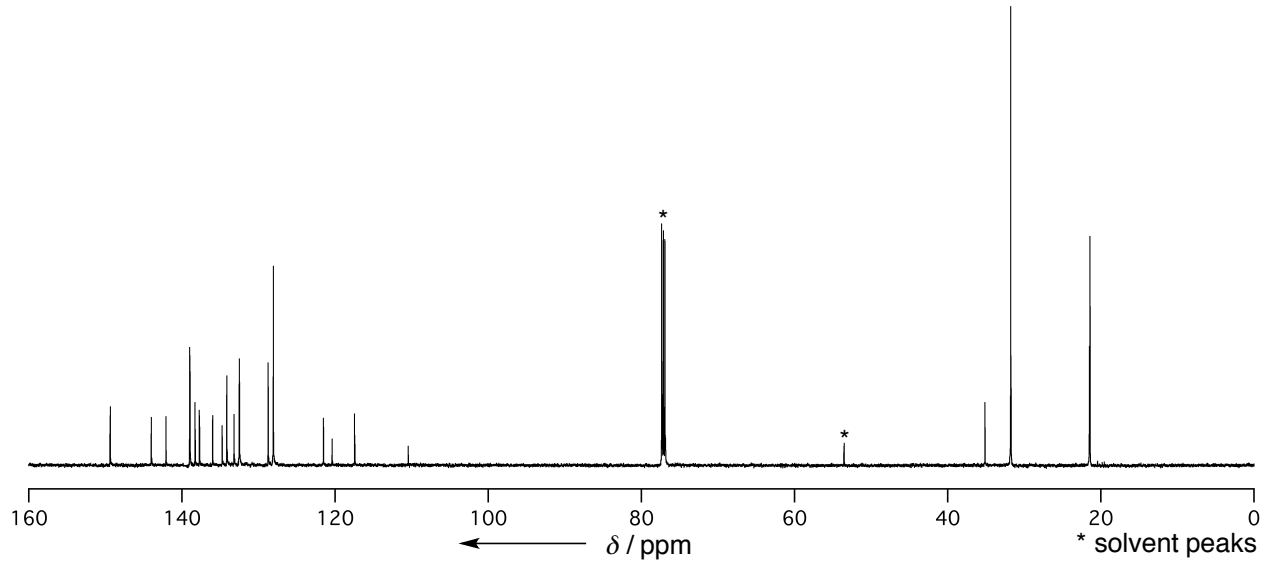


Figure S33. ^{13}C NMR spectrum of **7** in $CDCl_3$ at 25 ºC.

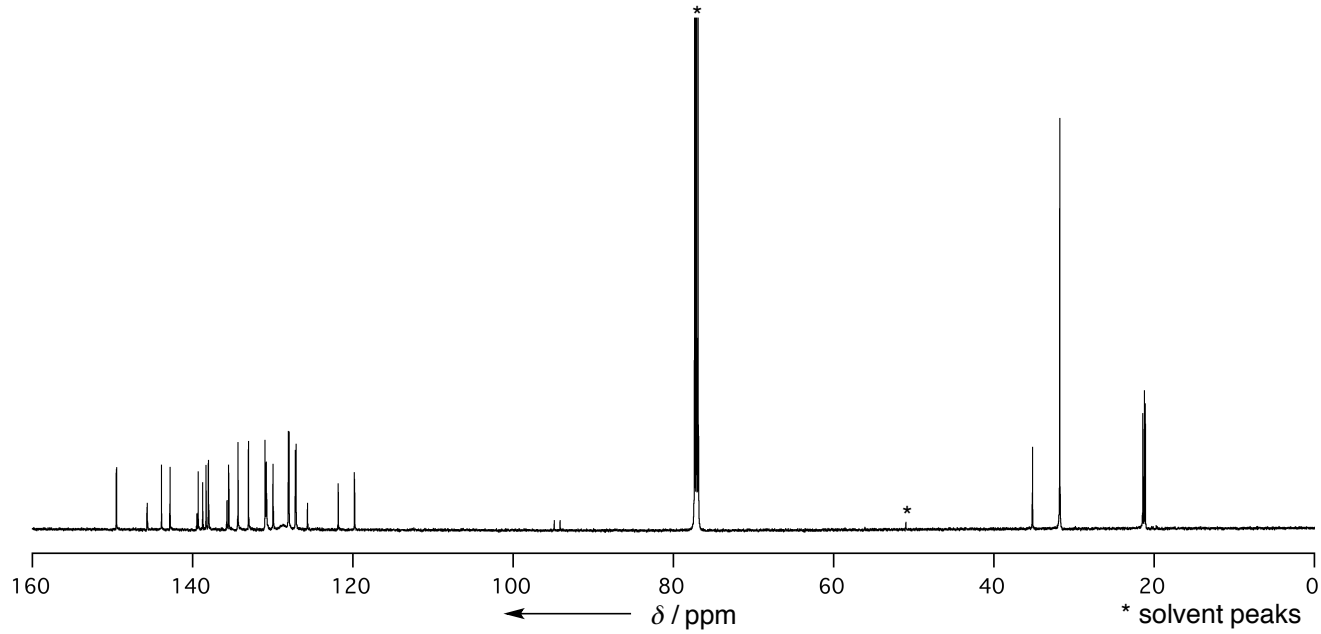


Figure S34. ^{13}C NMR spectrum of **8** in $CDCl_3$ at 25 ºC.

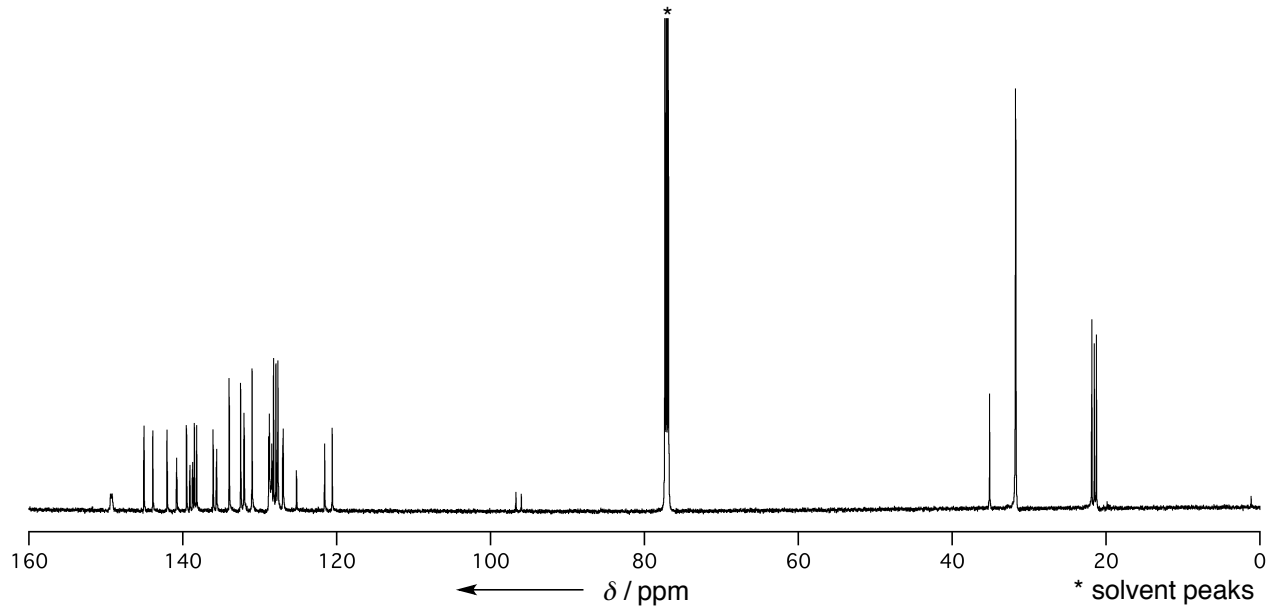


Figure S35. ^{13}C NMR spectrum of **9** in $CDCl_3$ at 25 ºC.

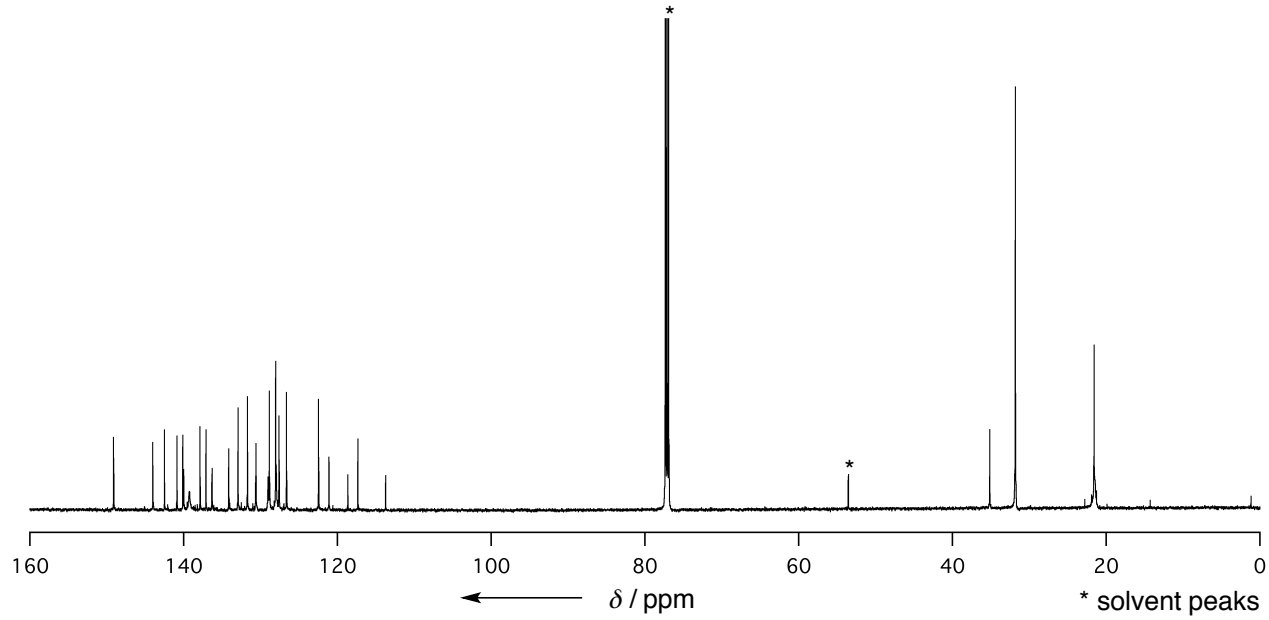


Figure S36. ^{13}C NMR spectrum of **6** in $CDCl_3$ at 25 ºC.

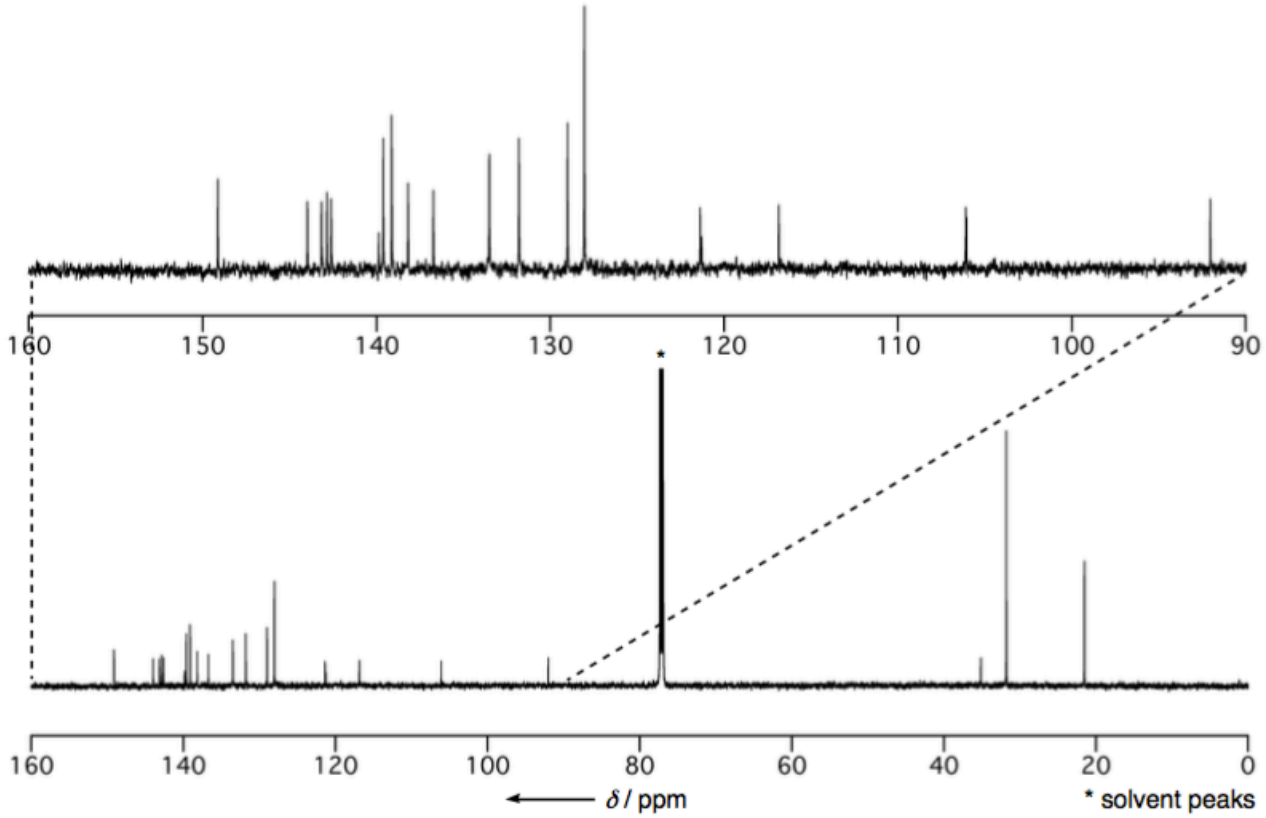


Figure S37. ^{13}C NMR spectrum of **16Ni** in $CDCl_3$ at 25 ºC.

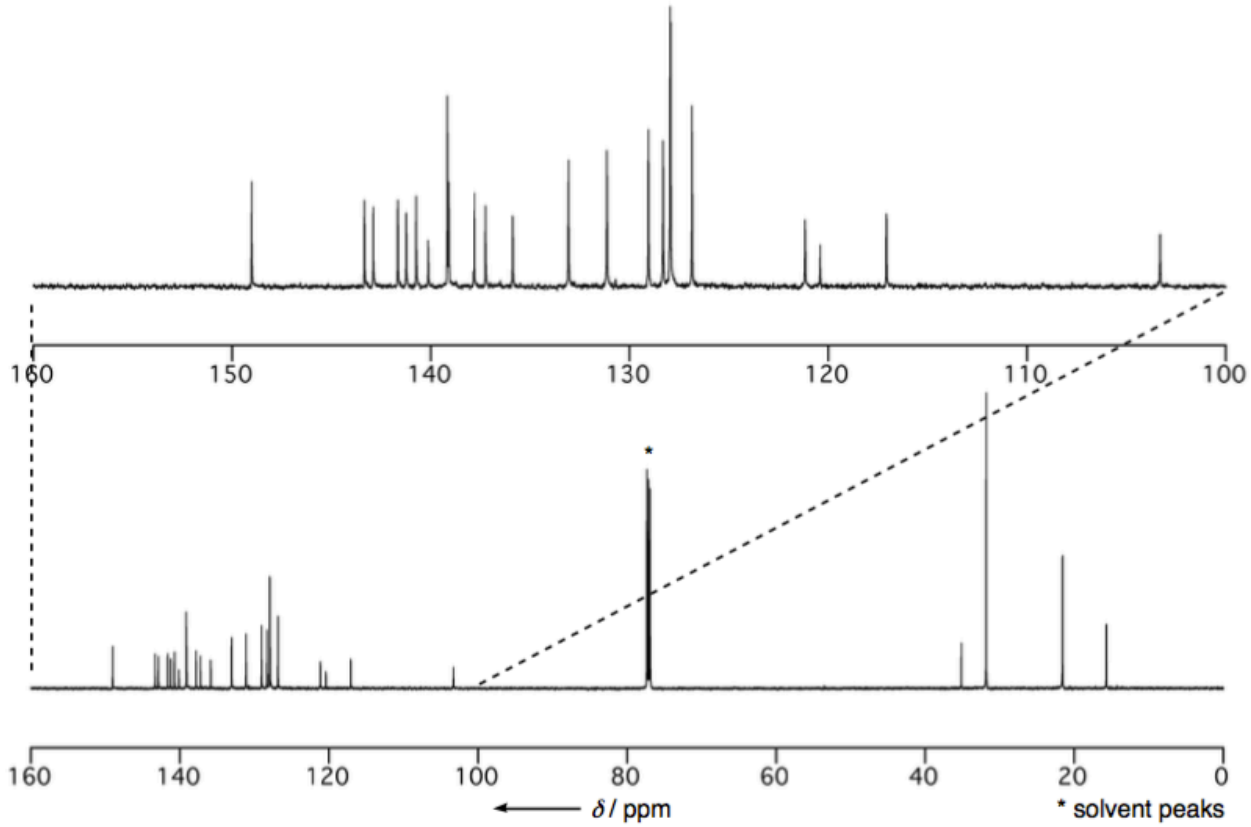


Figure S38. ^{13}C NMR spectrum of **17Ni** in $CDCl_3$ at 25 ºC.

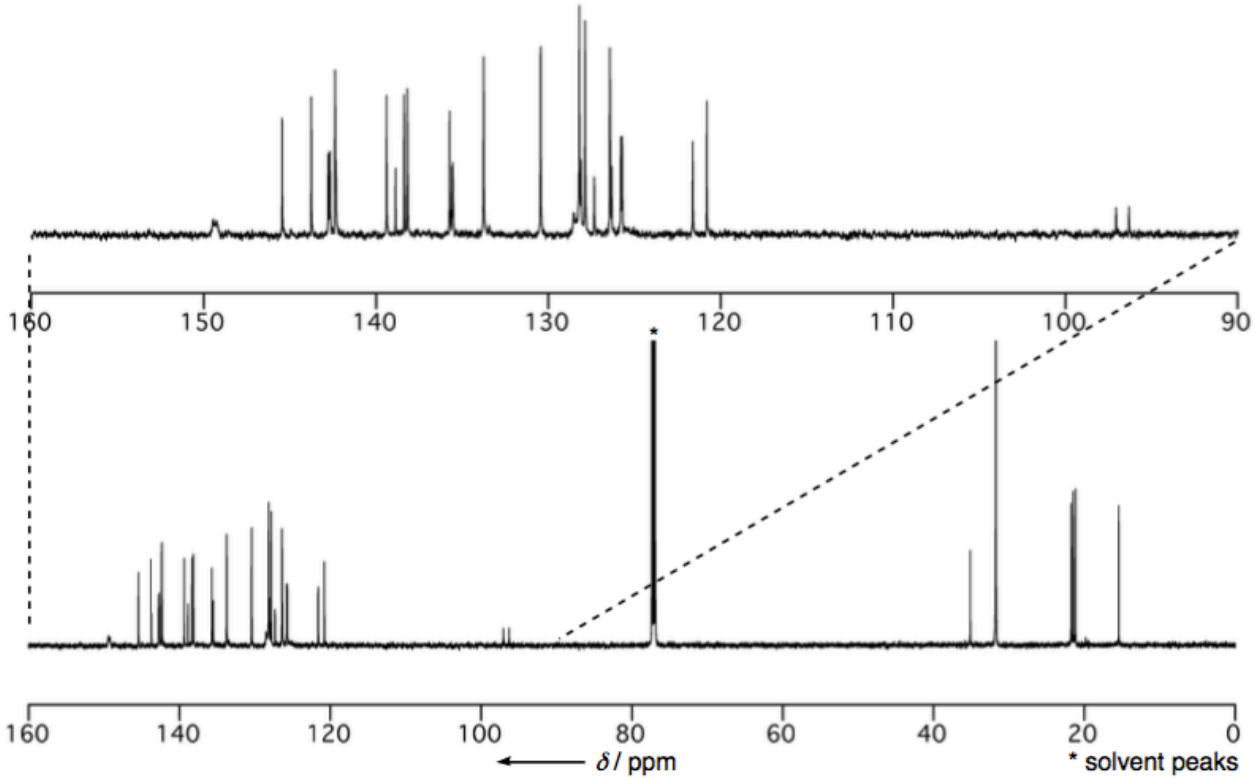


Figure S39. ^{13}C NMR spectrum of **18Ni** in $CDCl_3$ at 25 ºC.

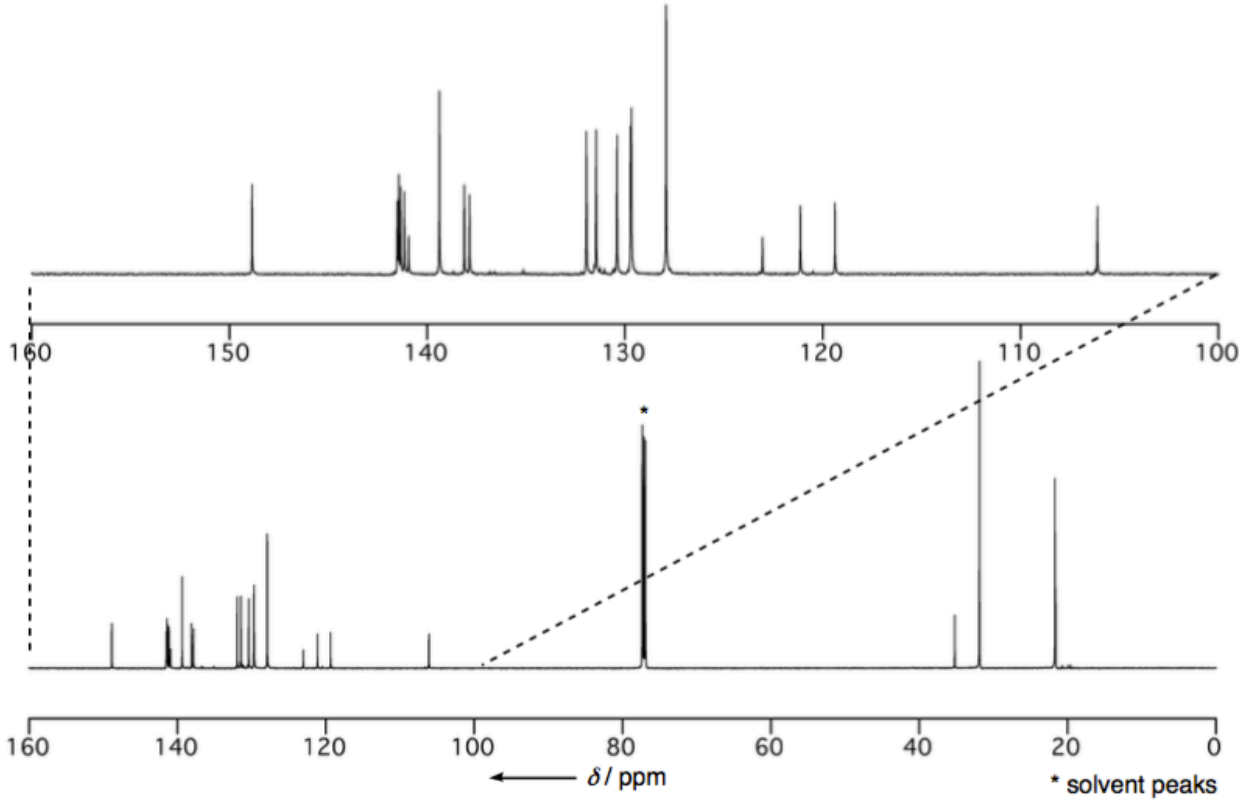


Figure S40. ^{13}C NMR spectrum of **S6** in $CDCl_3$ at 25 ºC.

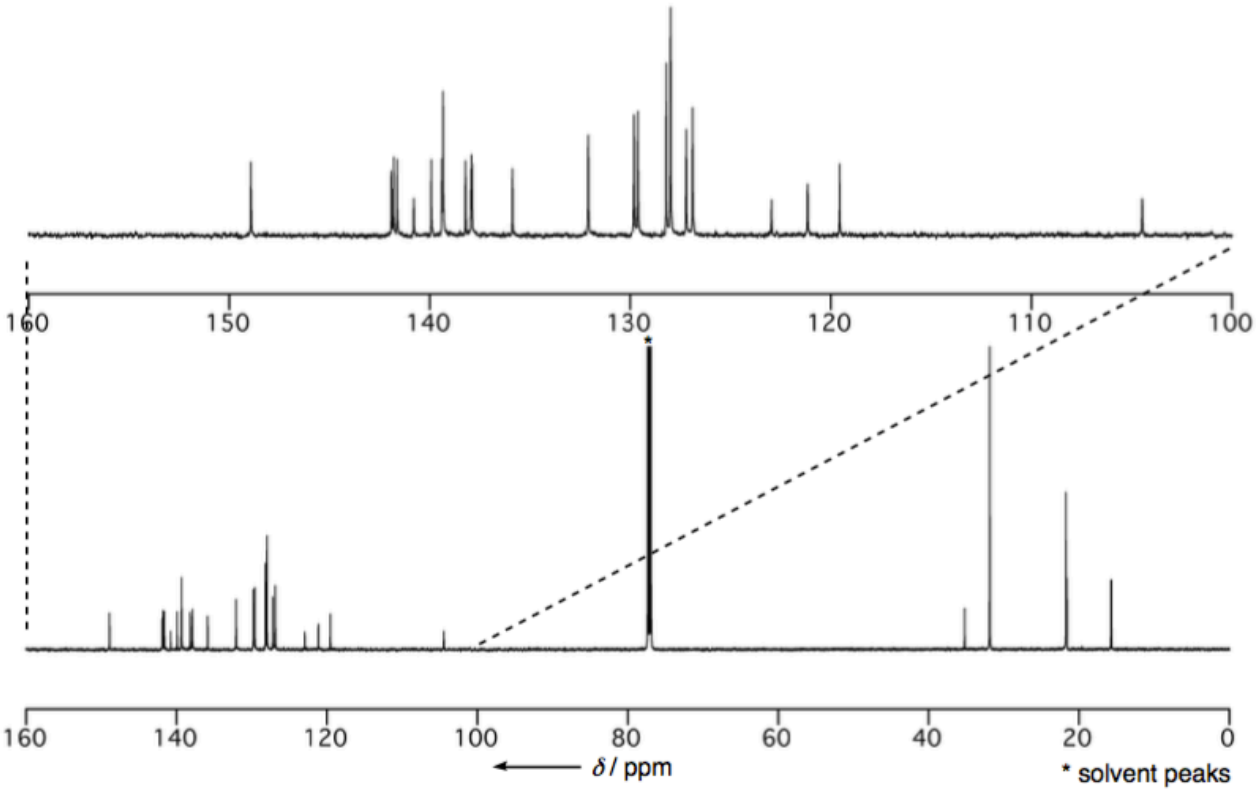


Figure S41. ^{13}C NMR spectrum of **17Pd** in $CDCl_3$ at 25 ºC.

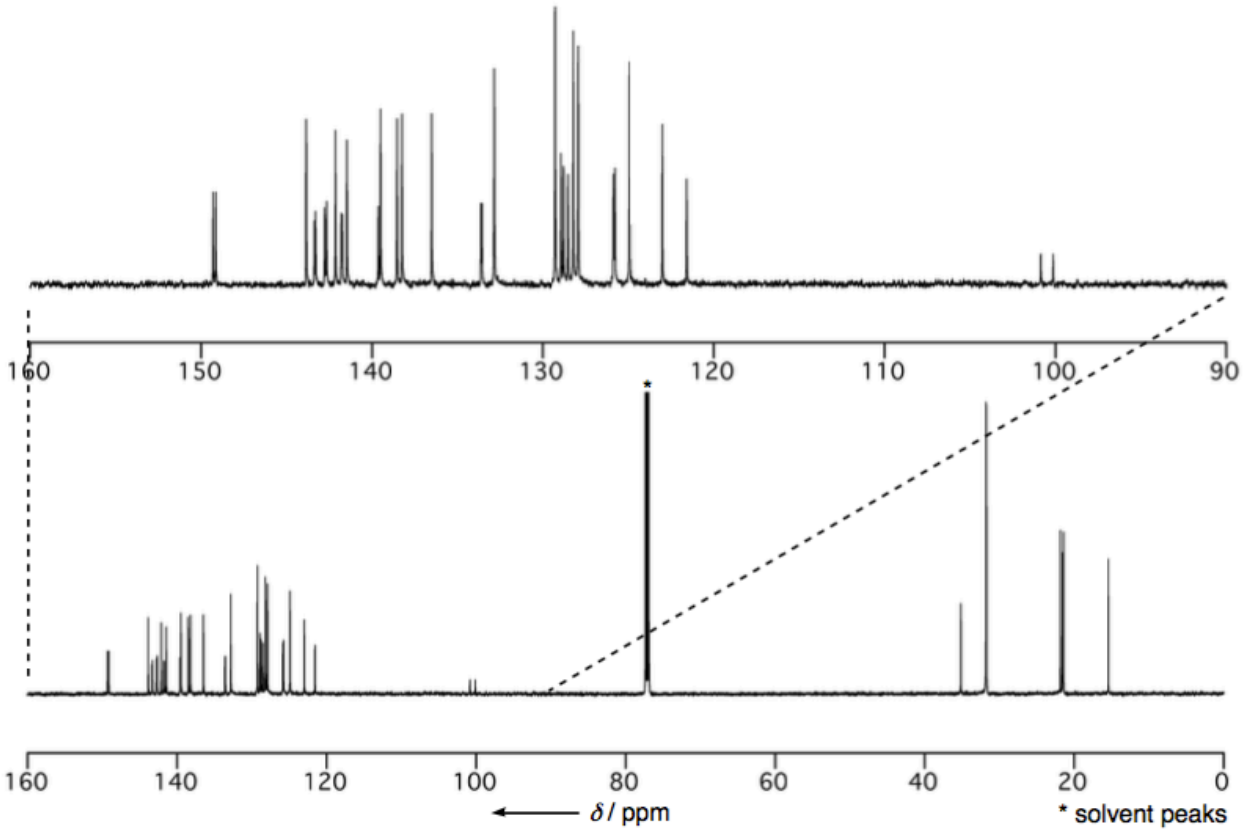


Figure S42. ^{13}C NMR spectrum of **18Pd** in $CDCl_3$ at 25 ºC.

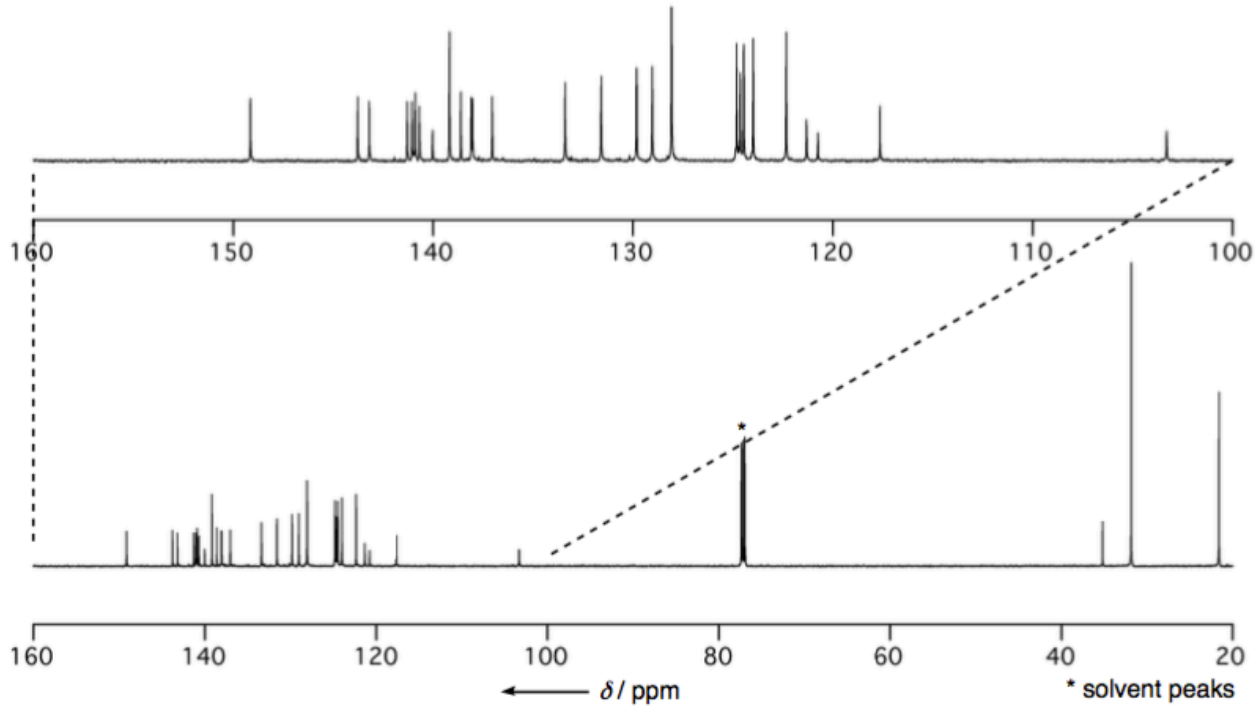


Figure S43. ^{13}C NMR spectrum of **19** in $CDCl_3$ at 25 ºC.

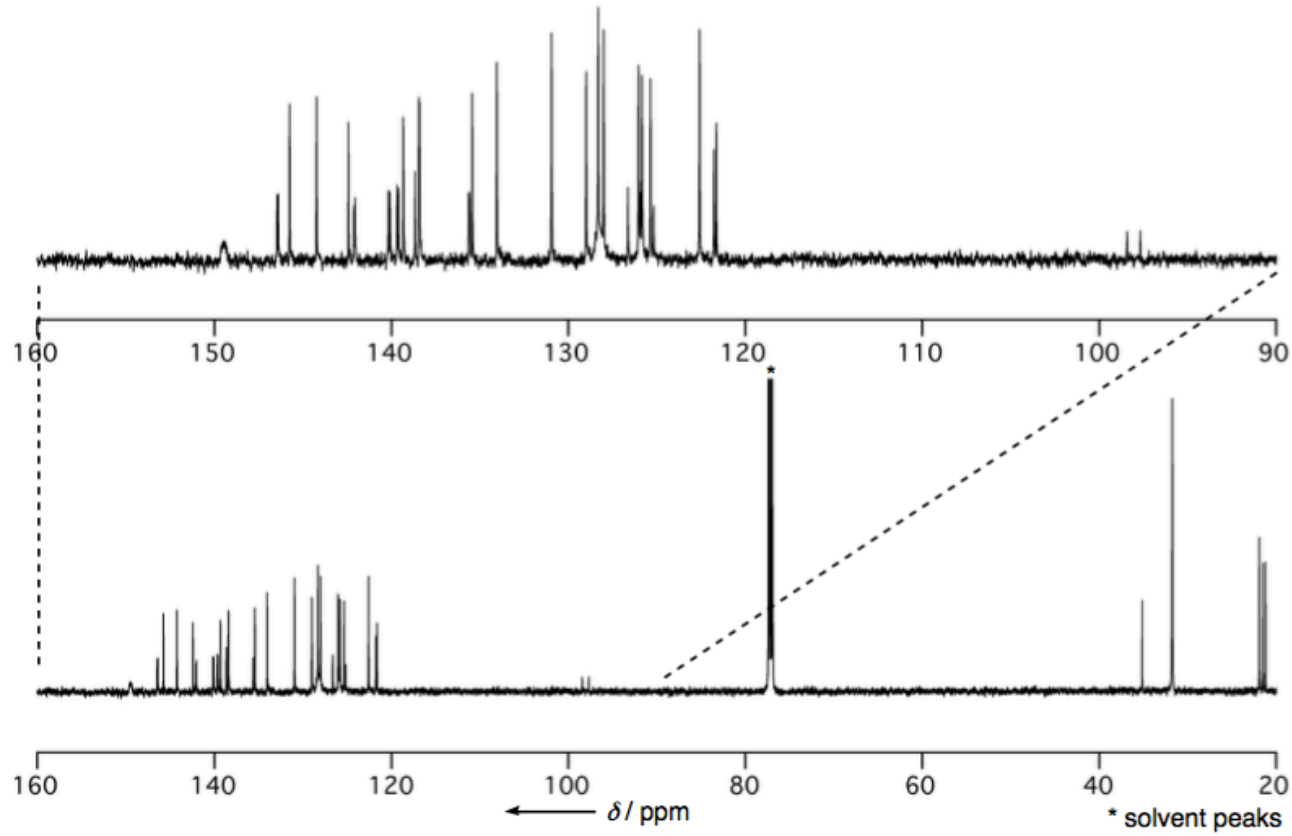


Figure S44. ^{13}C NMR spectrum of **20** in $CDCl_3$ at 25 ºC.

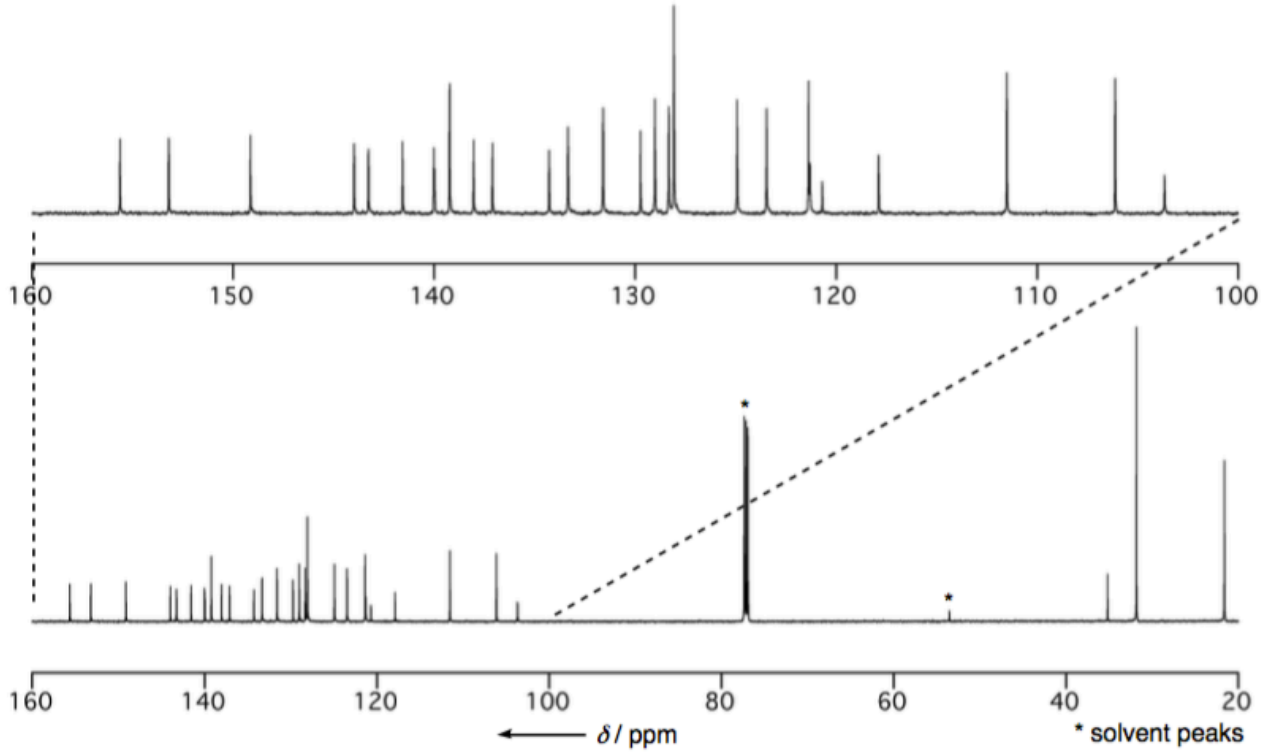


Figure S45. ^{13}C NMR spectrum of **21** in $CDCl_3$ at 25 ºC.

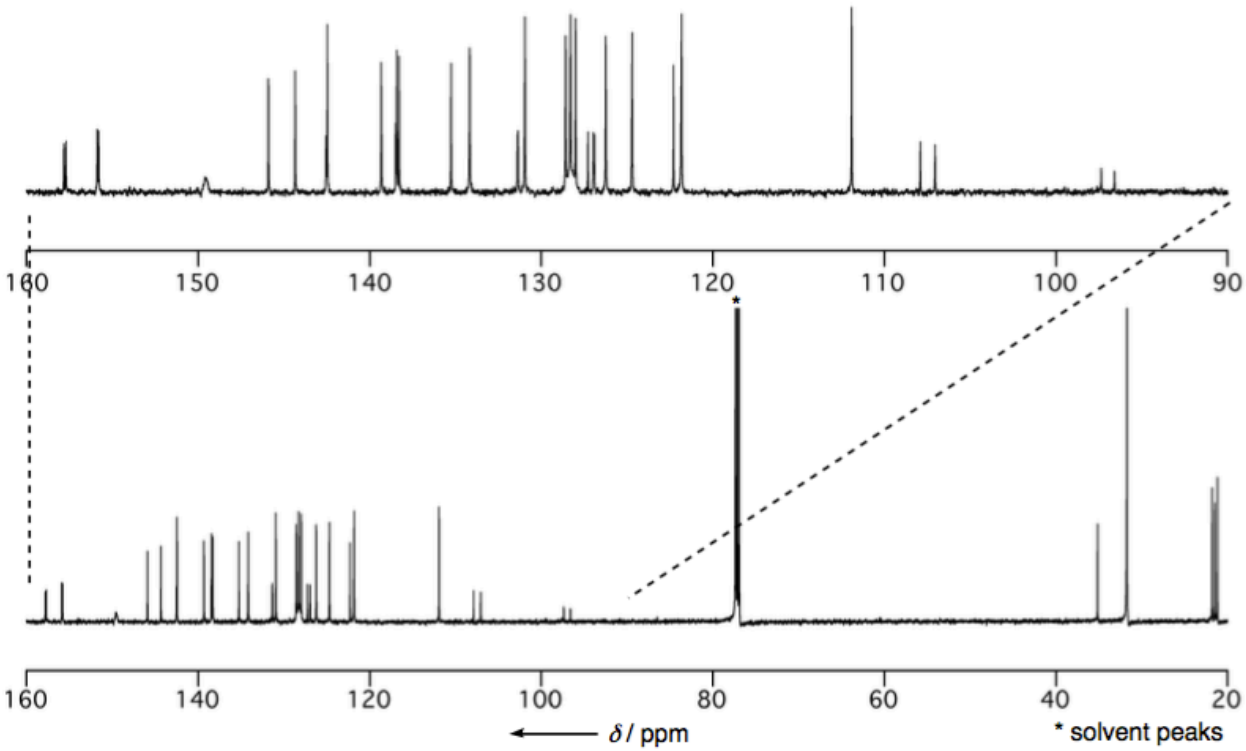


Figure S46. ^{13}C NMR spectrum of **22** in $CDCl_3$ at 25 ºC.

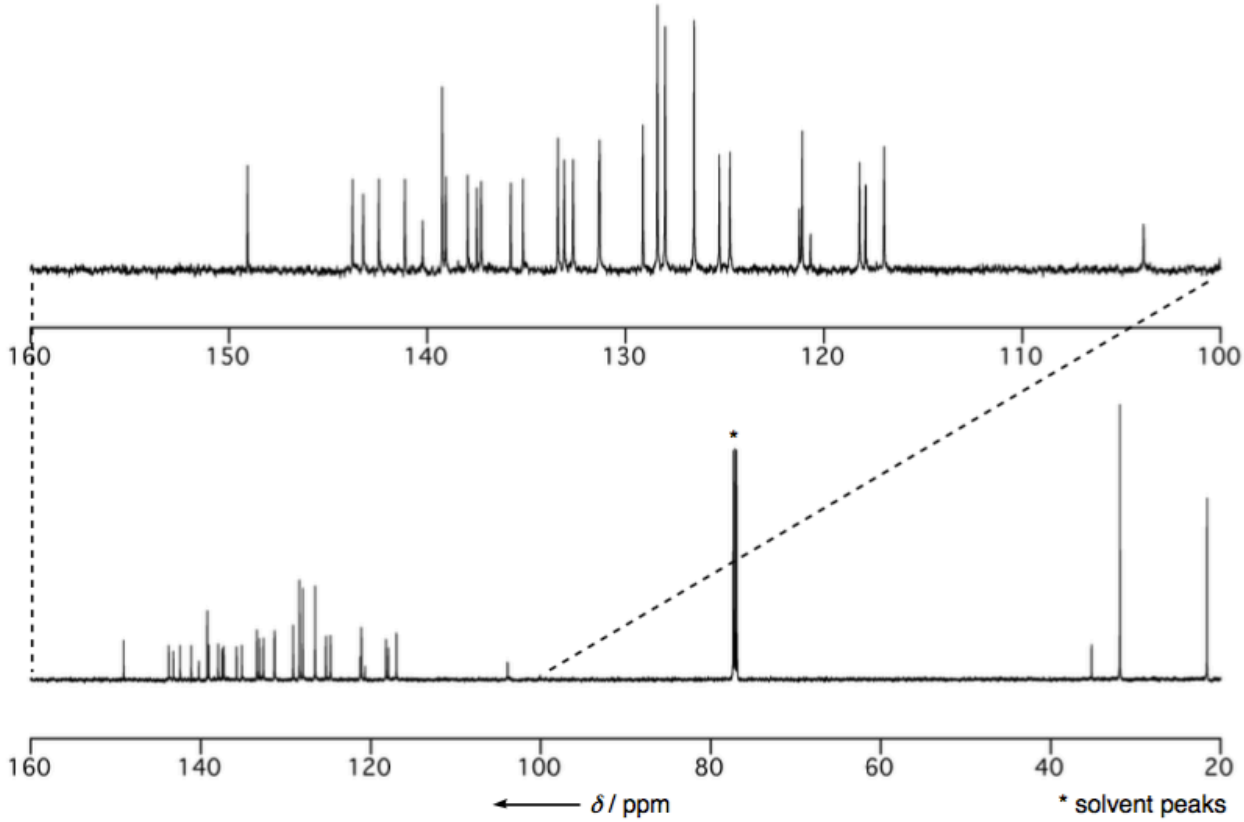


Figure S47. ^{13}C NMR spectrum of **23** in $CDCl_3$ at 25 ºC.

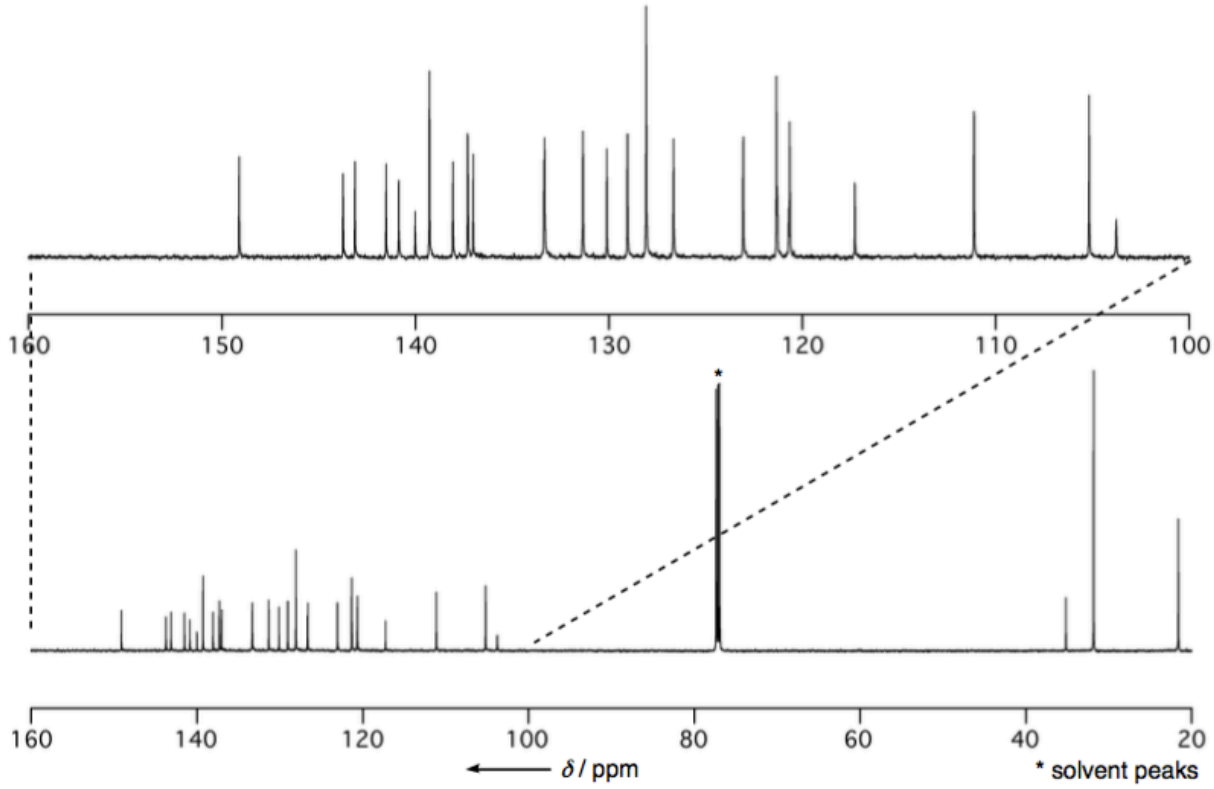


Figure S48. ^{13}C NMR spectrum of **25** in $CDCl_3$ at 25 ºC.

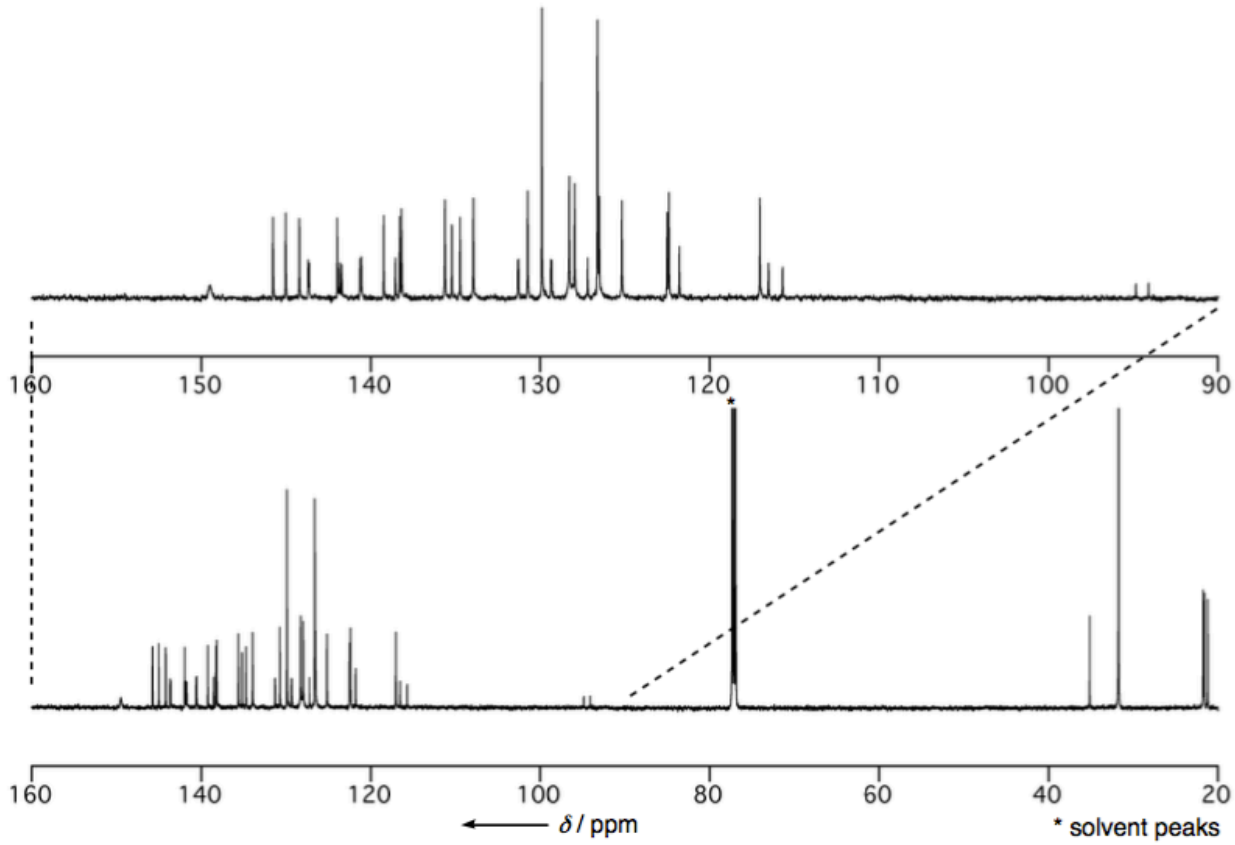


Figure S49. ^{13}C NMR spectrum of **26** in $CDCl_3$ at 25 ºC.

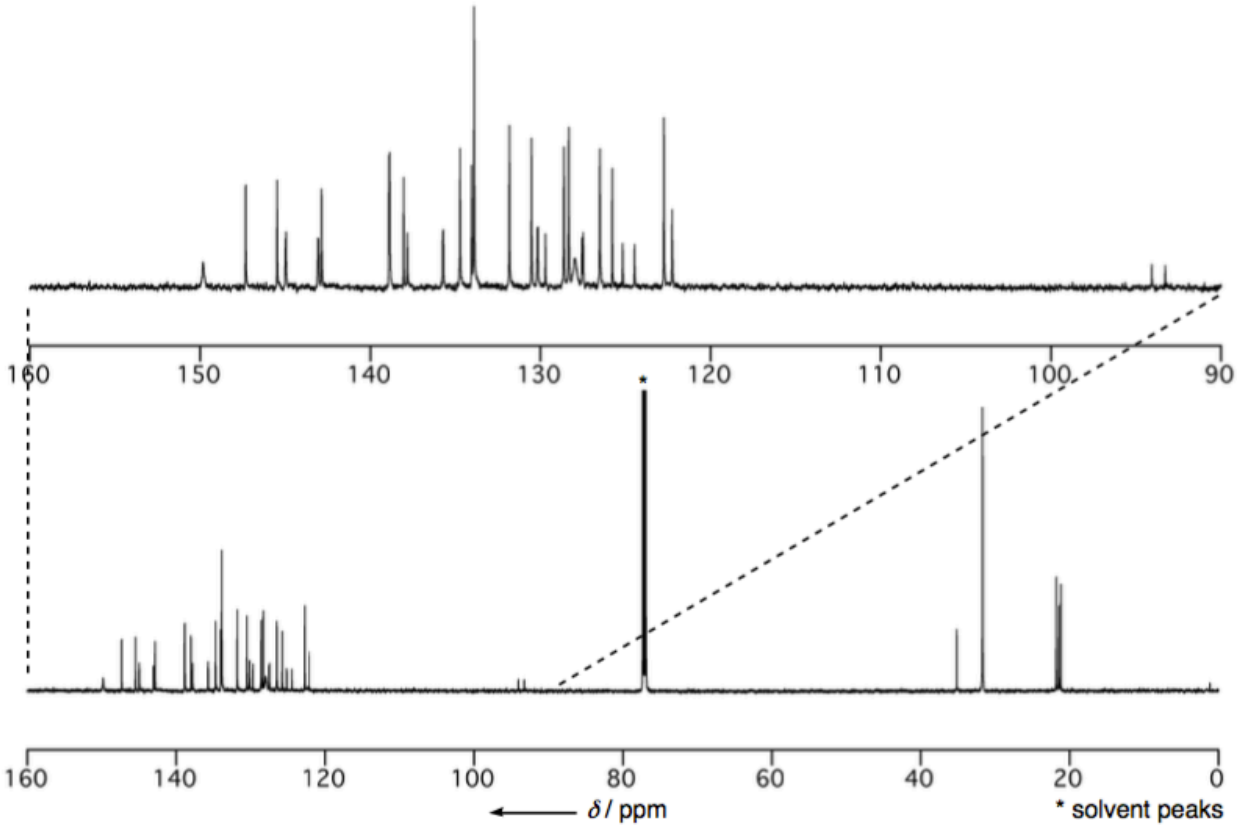


Figure S50. ^{13}C NMR spectrum of **27** in $CDCl_3$ at 25 ºC.

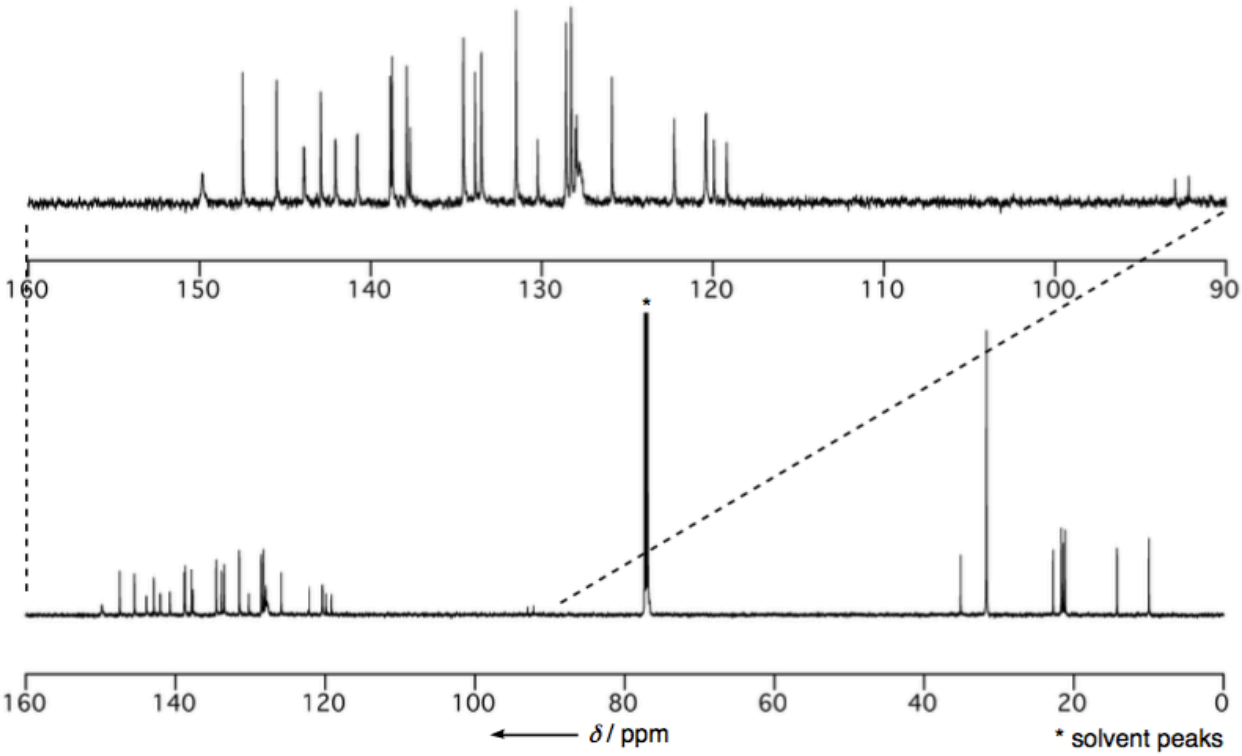


Figure S51. ^{13}C NMR spectrum of **28** in $CDCl_3$ at 25 ºC.

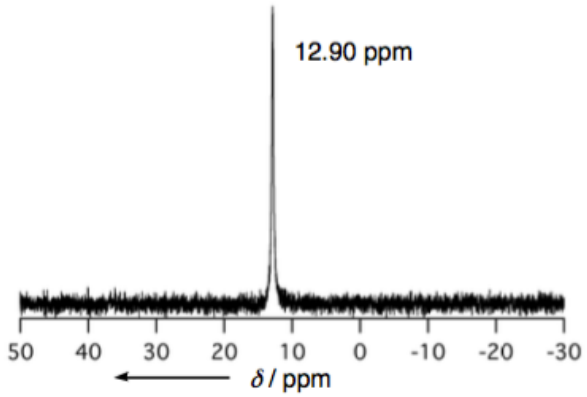


Figure S52. ^{31}P NMR spectrum of **8** in $CDCl_3$ at 25 ºC.

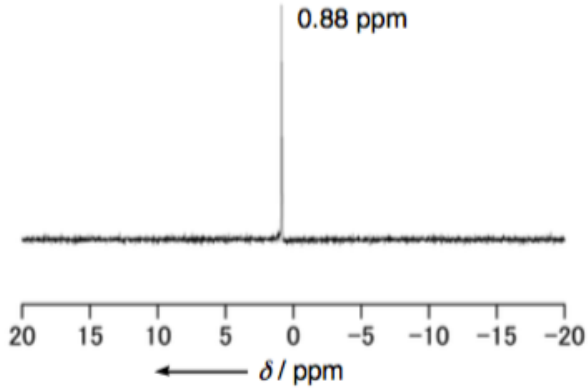


Figure S53. ^{31}P NMR spectrum of **9** in $CDCl_3$ at 25 ºC.

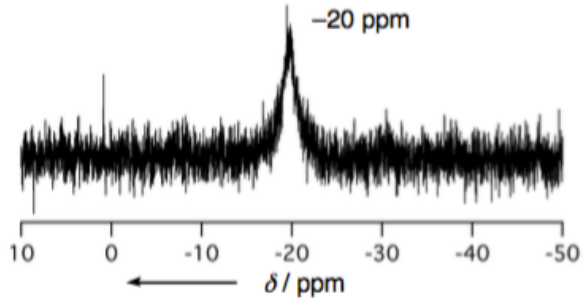


Figure S54. ^{31}P NMR spectrum of **6** in $CDCl_3$ at 25 ºC.

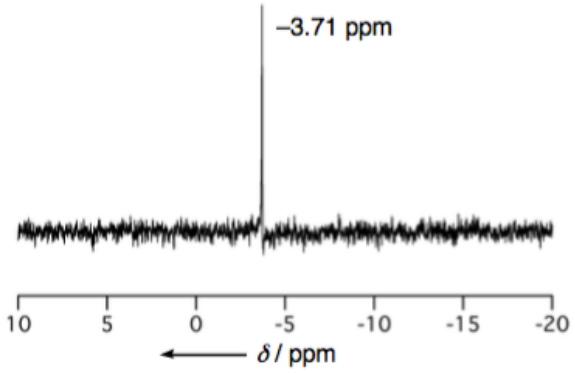


Figure S55. ^{31}P NMR spectrum of **18Ni** in $CDCl_3$ at 25 ºC.

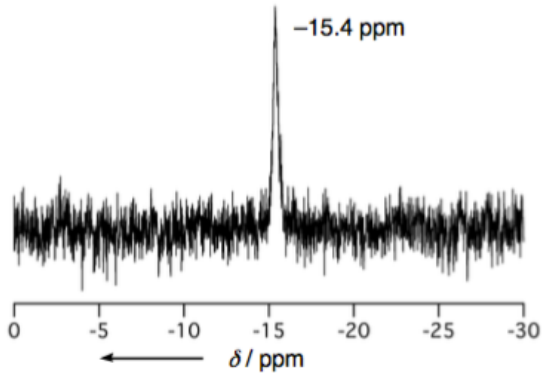


Figure S56. ^{31}P NMR spectrum of **10Ni** in $CDCl_3$ at 25 ºC.

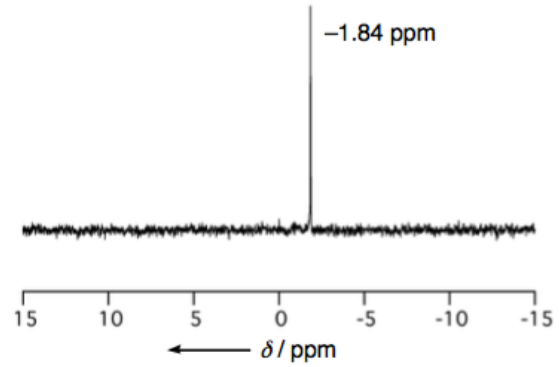


Figure S57. ^{31}P NMR spectrum of **18Pd** in $CDCl_3$ at 25 ºC.

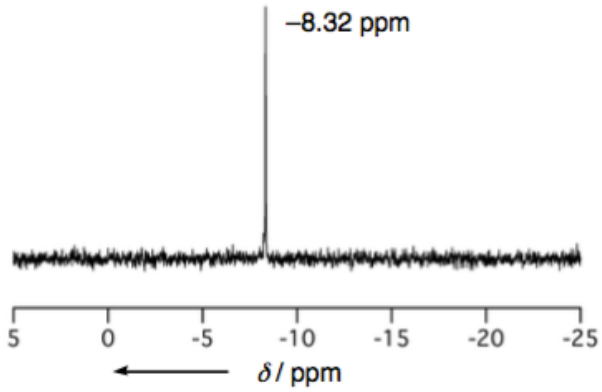


Figure S58. ^{31}P NMR spectrum of **10Pd** in $CDCl_3$ at 25 ºC.

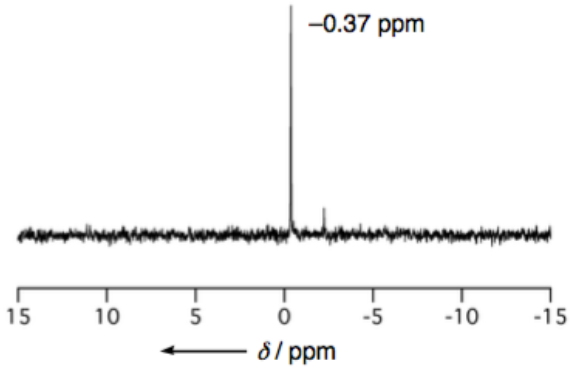


Figure S59. ^{31}P NMR spectrum of **20** in $CDCl_3$ at 25 ºC.

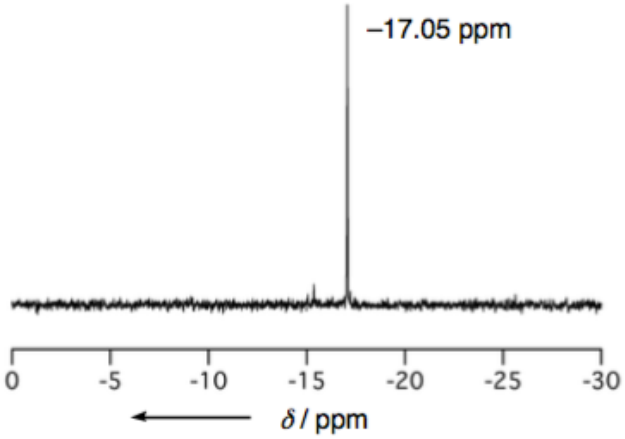


Figure S60. ^{31}P NMR spectrum of **11** in $CDCl_3$ at 25 ºC.

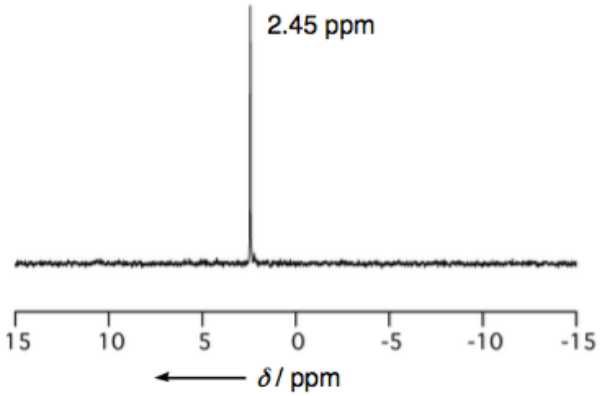


Figure S61. ^{31}P NMR spectrum of **22** in $CDCl_3$ at 25 ºC.

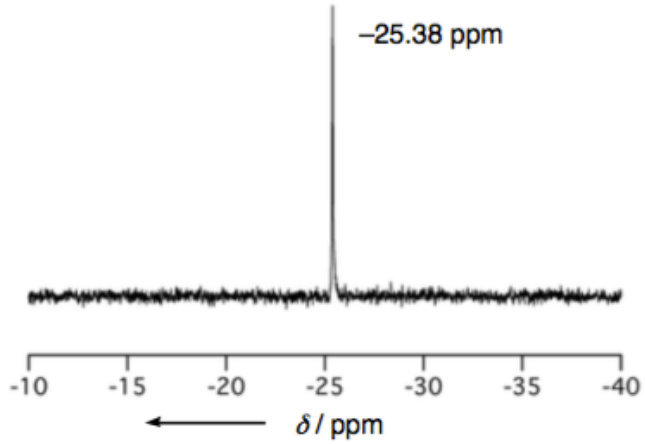


Figure S62. ^{31}P NMR spectrum of **12** in $CDCl_3$ at 25 ºC.

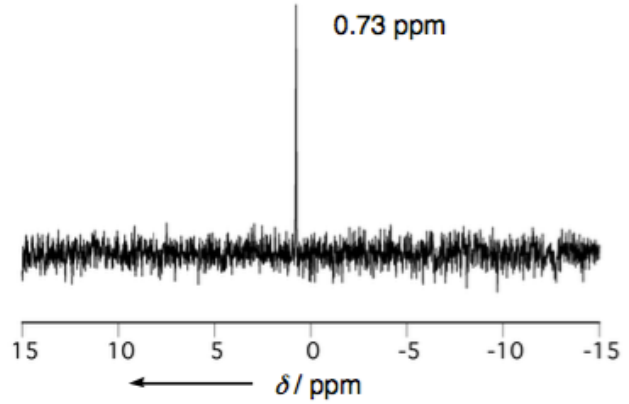


Figure S63. ^{31}P NMR spectrum of **25** in $CDCl_3$ at 25 ºC.

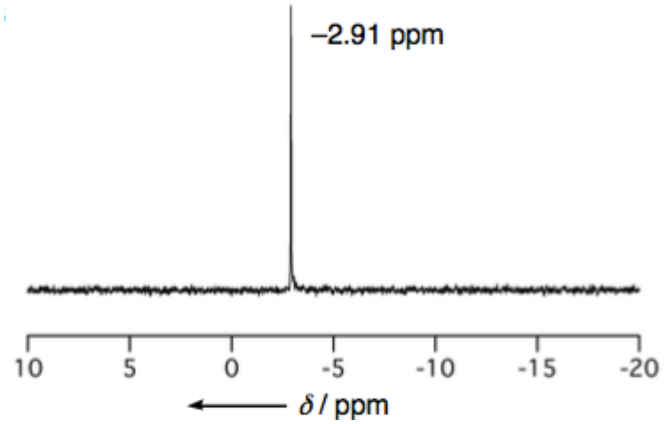


Figure S64. ^{31}P NMR spectrum of **26** in $CDCl_3$ at 25 ºC.

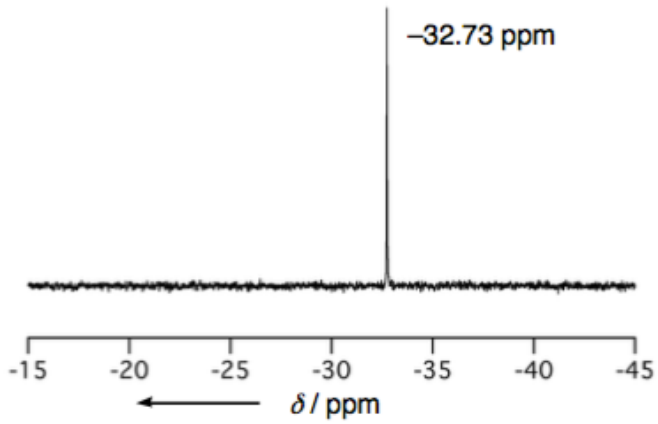


Figure S65. ^{31}P NMR spectrum of **13** in $CDCl_3$ at 25 ºC.

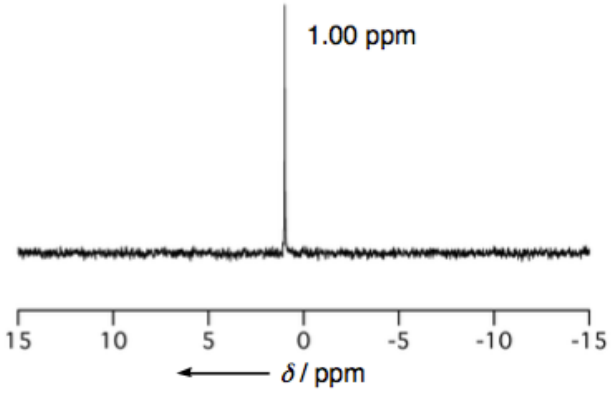


Figure S66. ^{31}P NMR spectrum of **27** in $CDCl_3$ at 25 ºC.

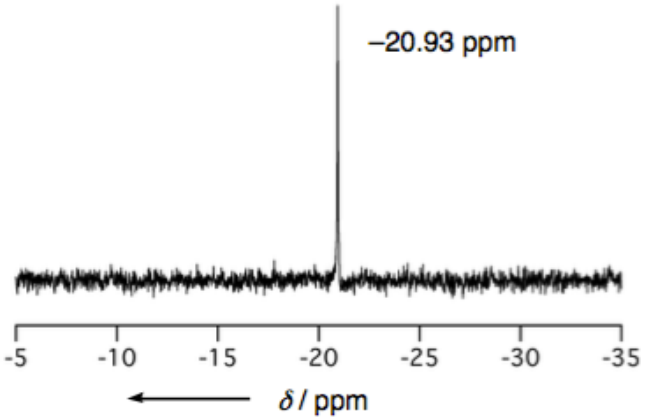


Figure S67. ^{31}P NMR spectrum of **14** in $CDCl_3$ at 25 ºC.

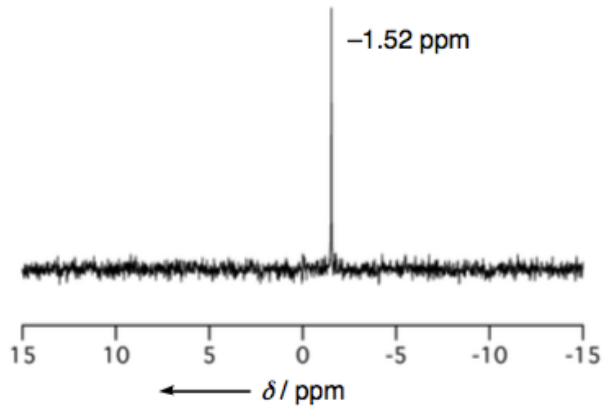


Figure S68. ^{31}P NMR spectrum of **28** in $CDCl_3$ at 25 ºC.

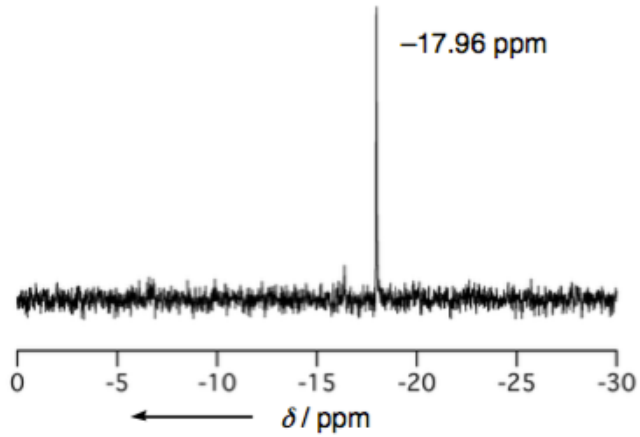


Figure S69. ^{31}P NMR spectrum of **15** in $CDCl_3$ at 25 ºC.

4. High Resolution Mass Spectra

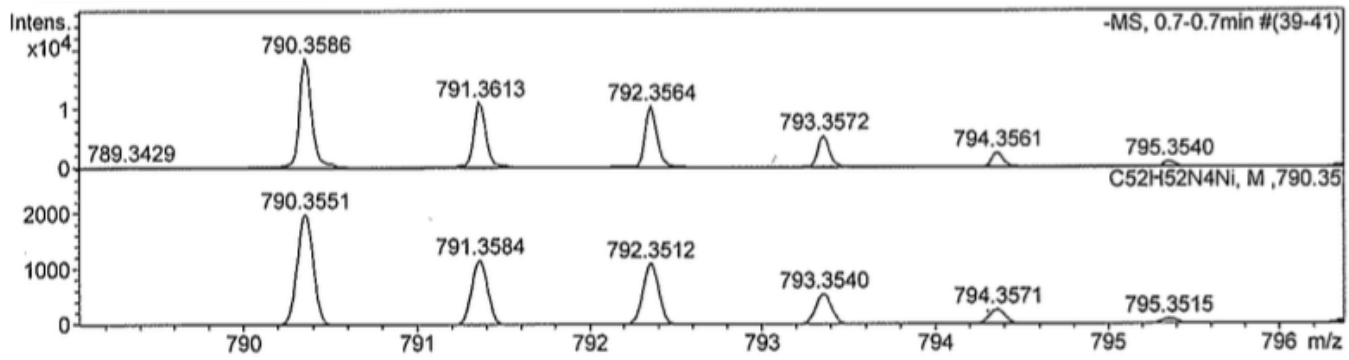


Figure S70. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **S3**.

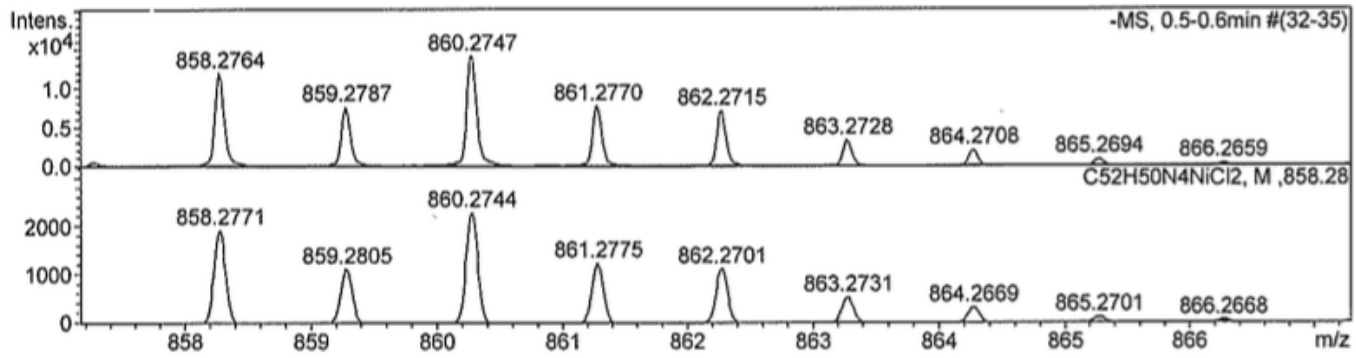


Figure S71. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **S5**.

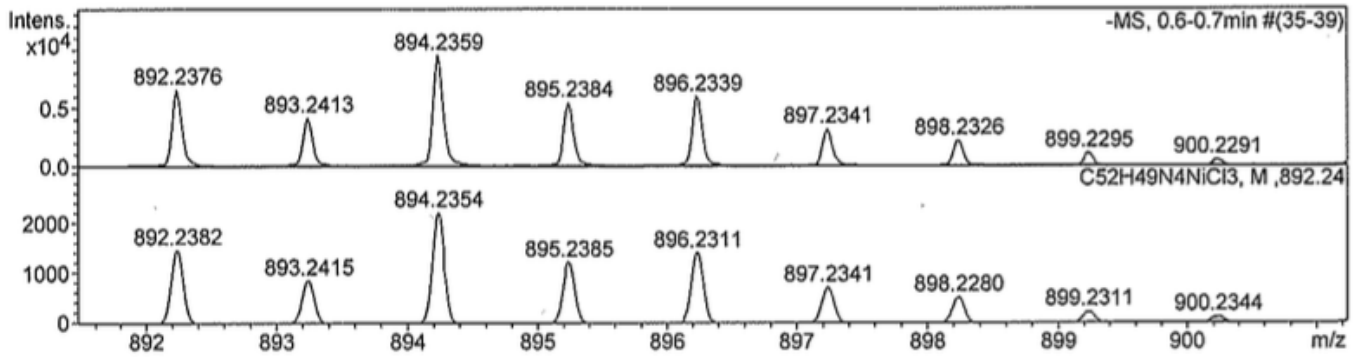


Figure S72. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **7**.

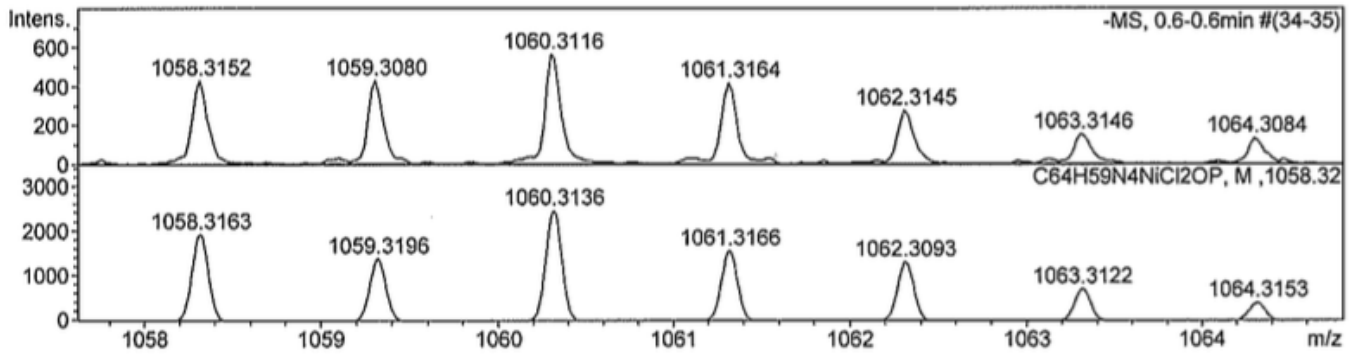


Figure S73. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **8**.

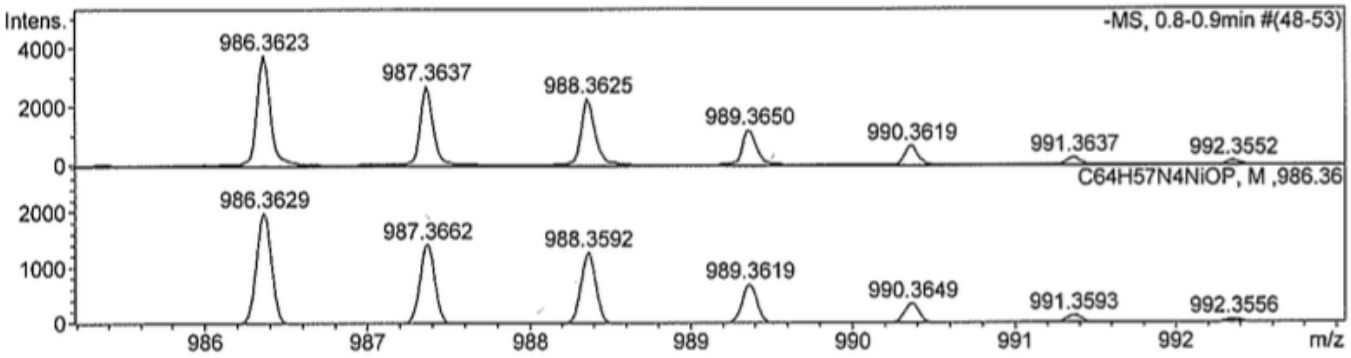


Figure S74. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **9**.

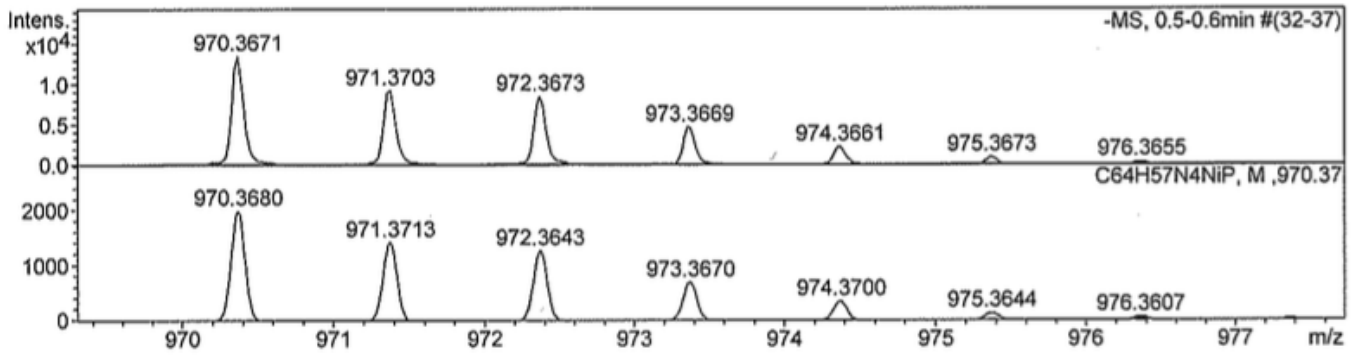


Figure S75. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **6**.

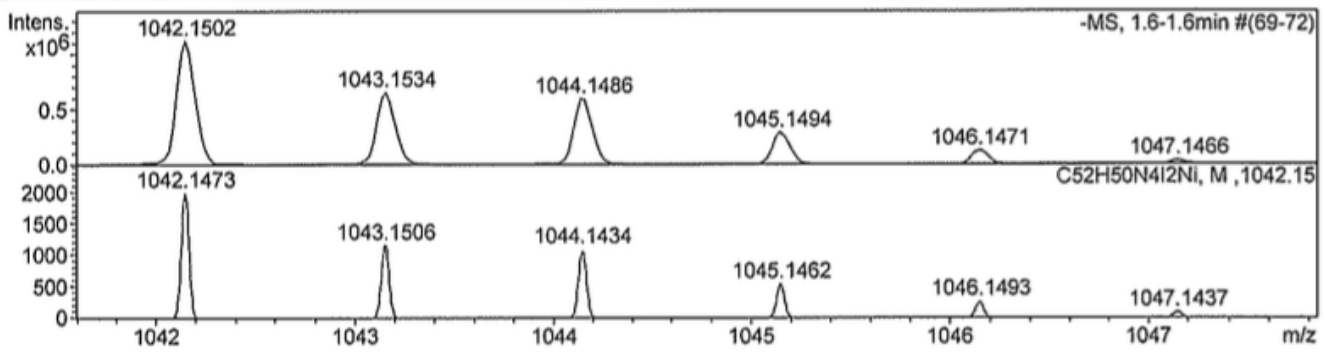


Figure S76. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **16Ni**.

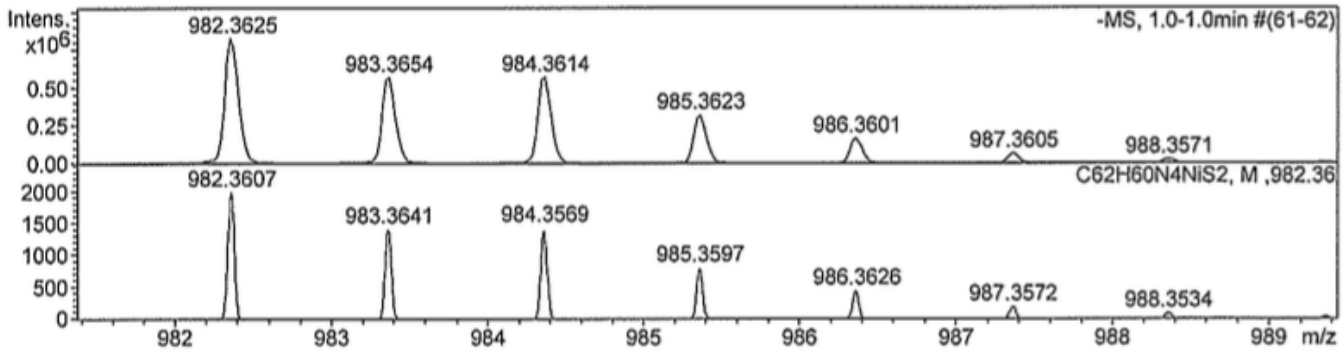


Figure S77. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **17Ni**.

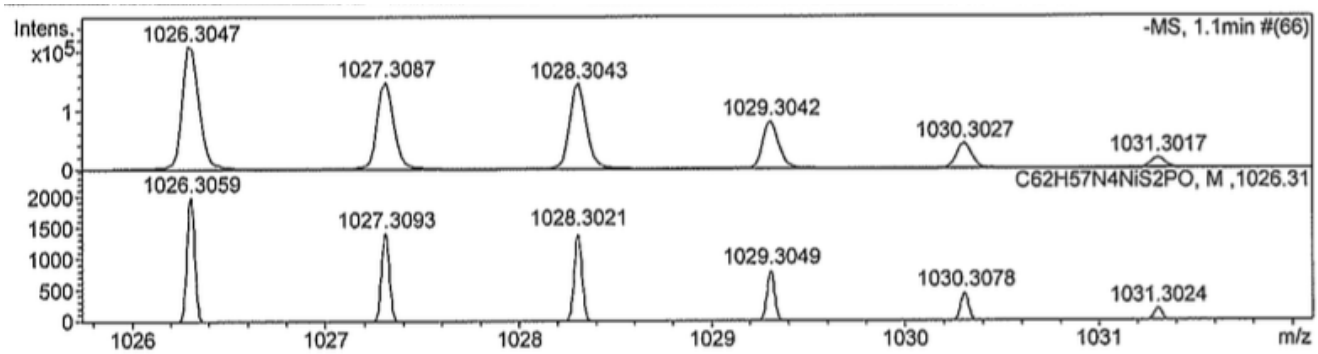


Figure S78. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **18Ni**.

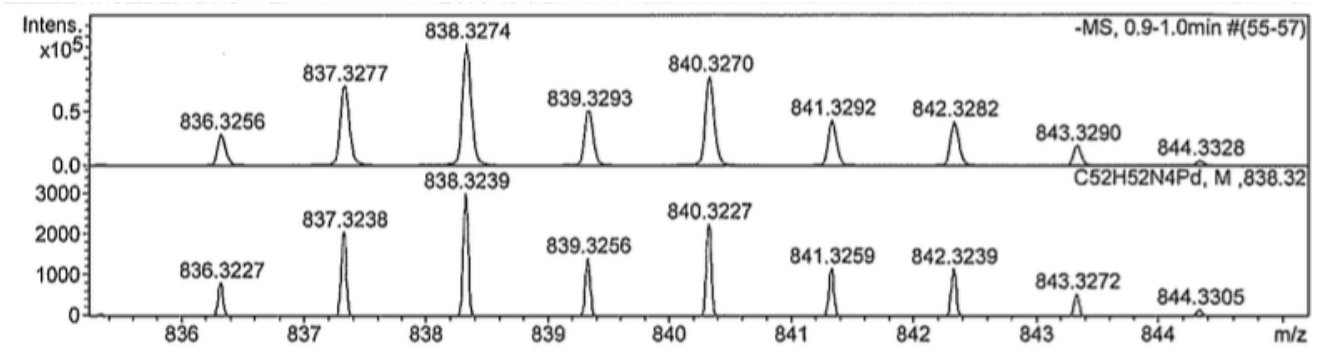


Figure S79. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **S6**.

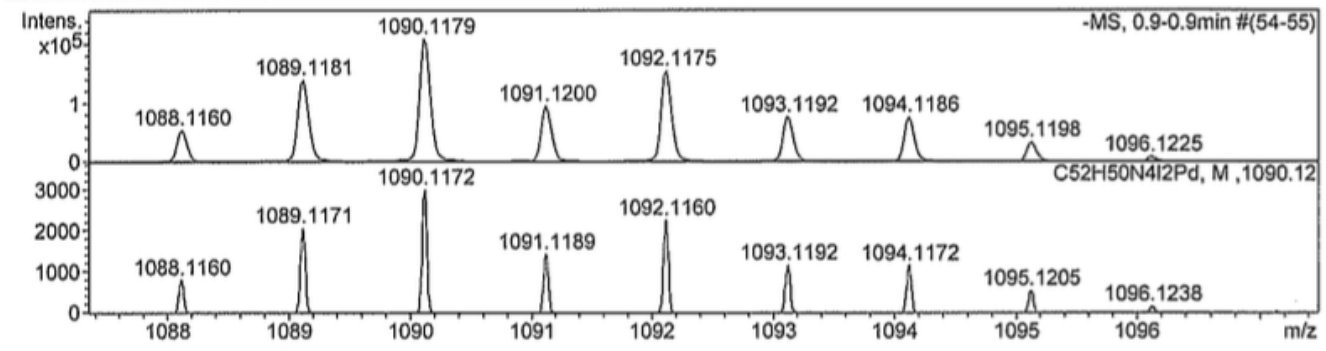


Figure S80. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **16Pd**.

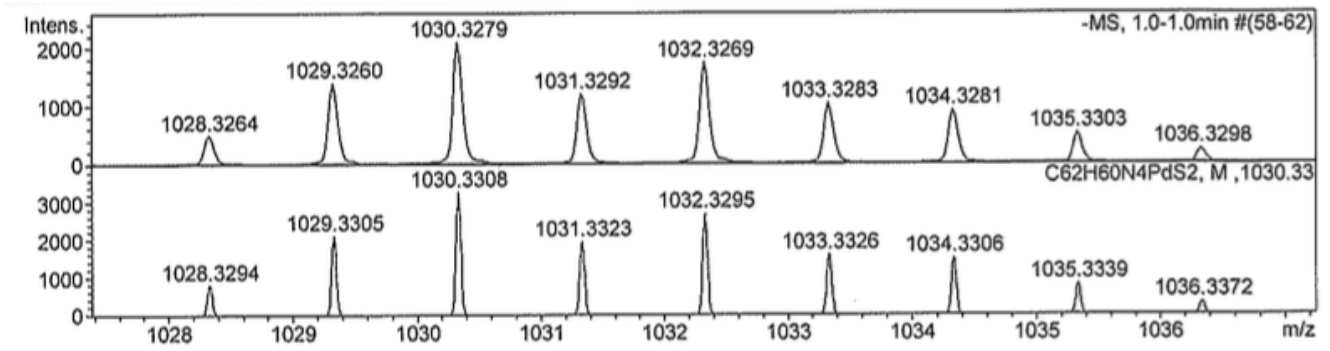


Figure S81. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **17Pd**.

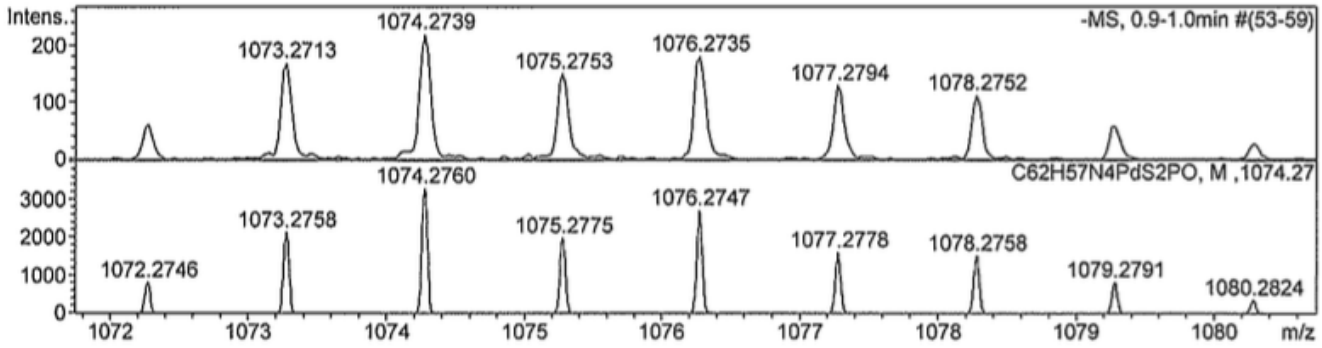


Figure S82. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **18Pd**.

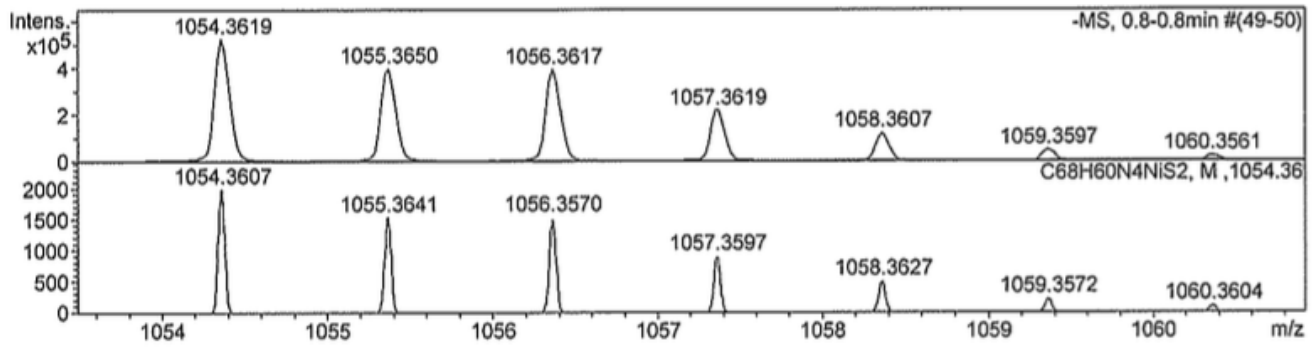


Figure S83. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **19**.

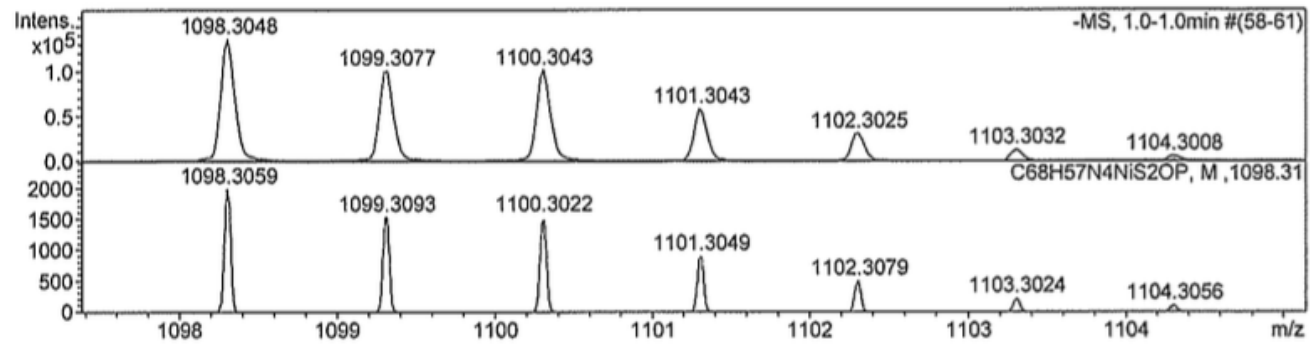


Figure S84. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **20**.

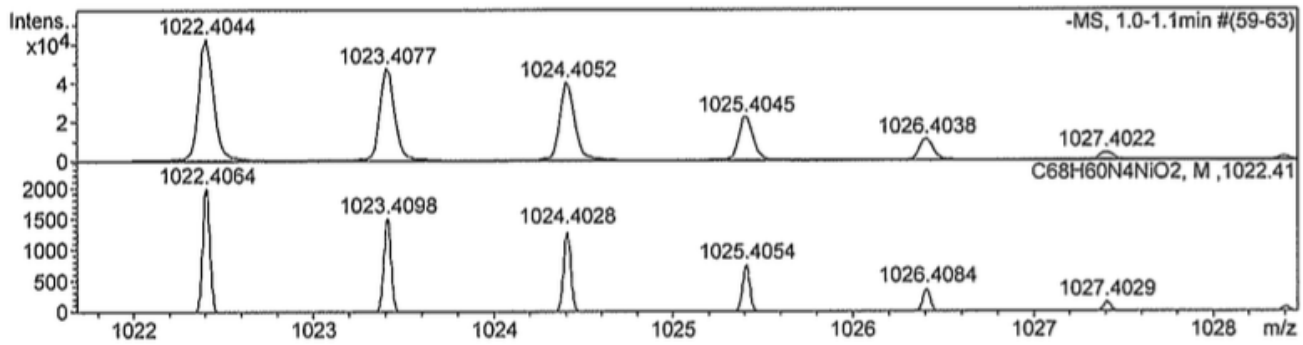


Figure S85. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **21**.

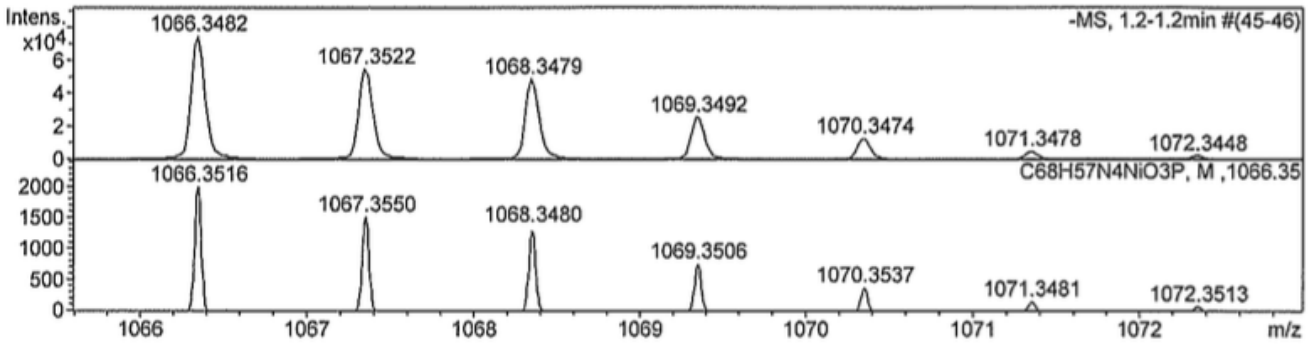


Figure S86. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **22**.

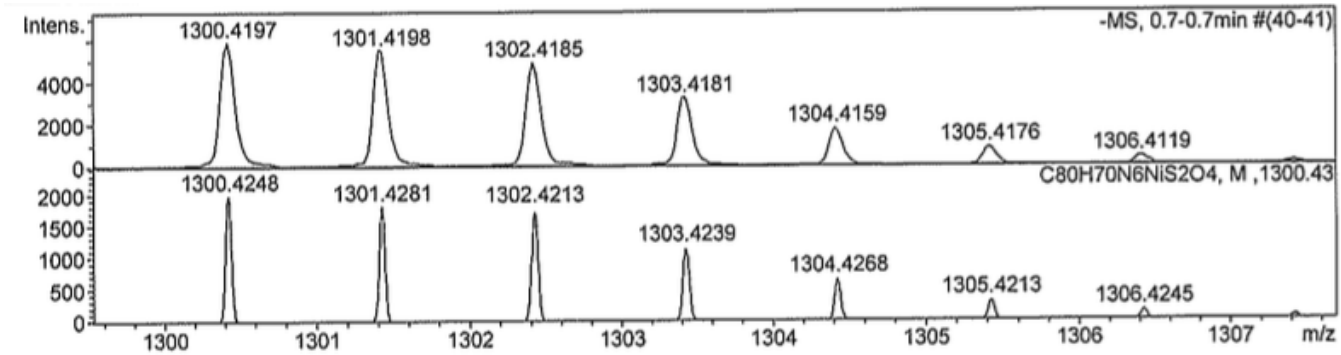


Figure S87. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **23**.

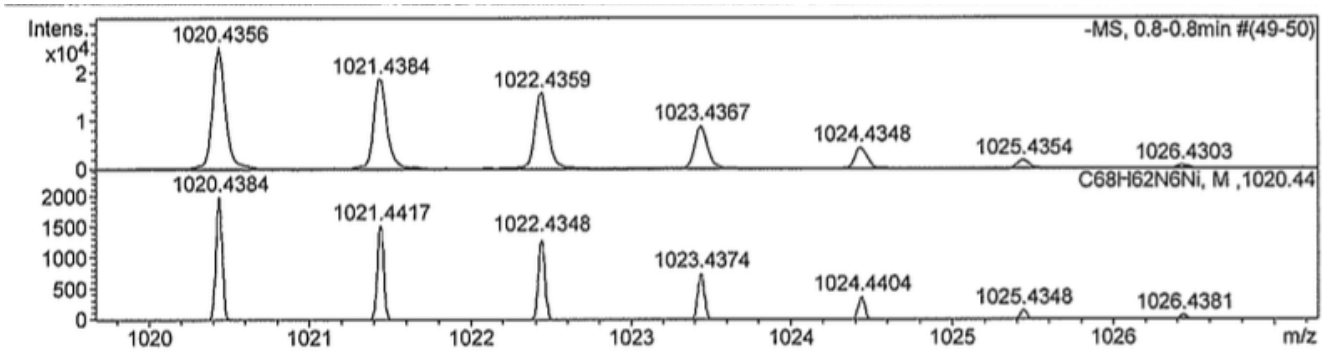


Figure S88. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **24**.

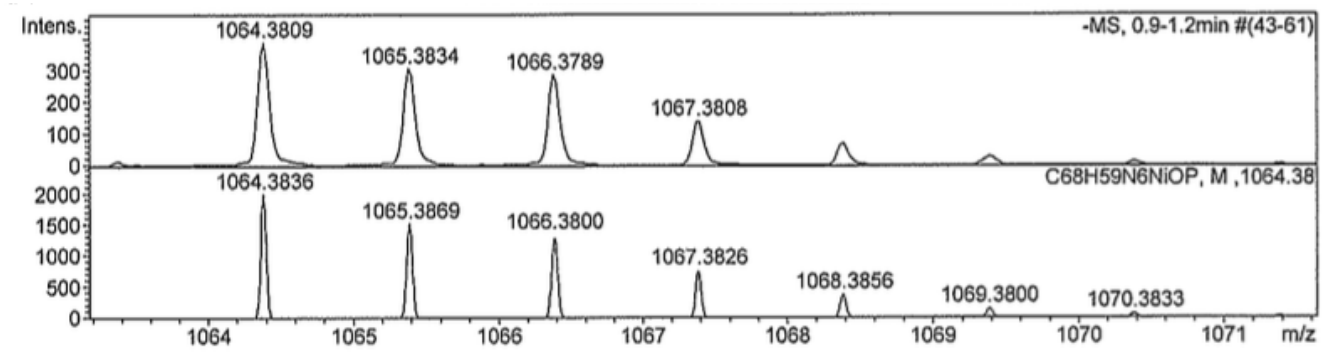


Figure S89. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **25**.

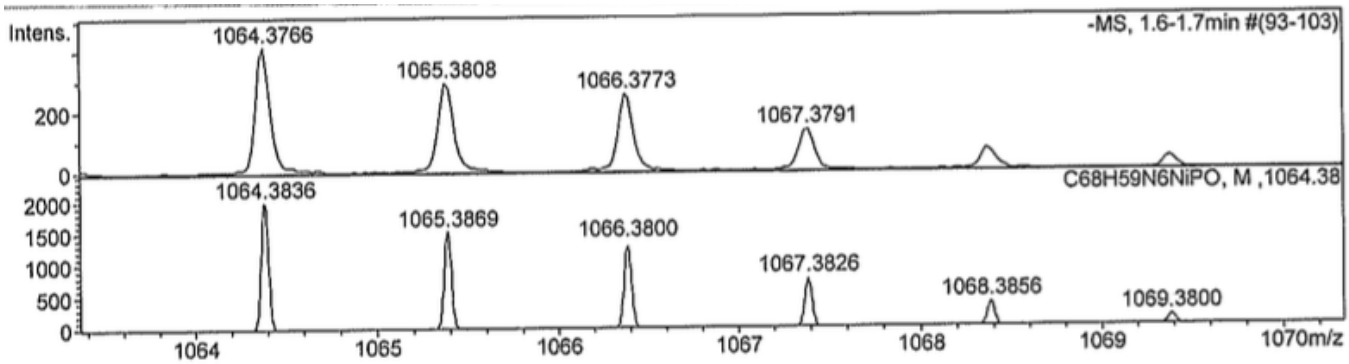


Figure S90. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **26**.

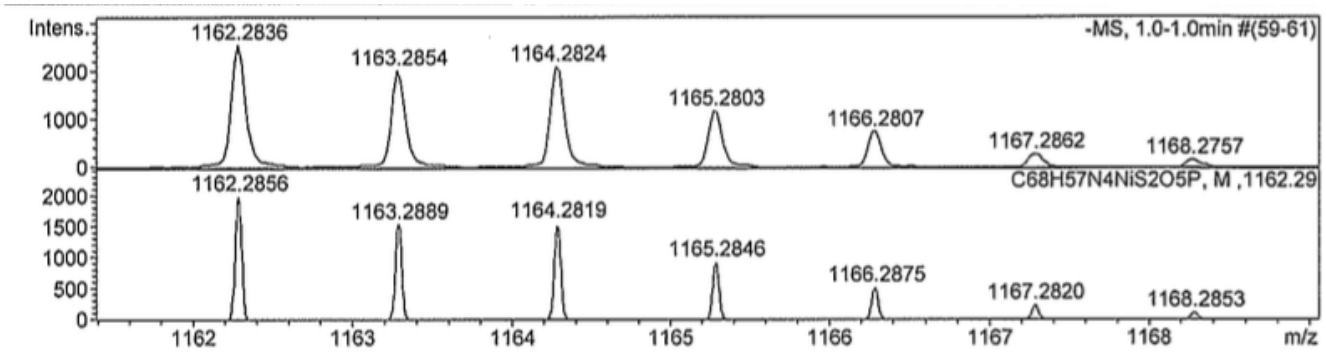


Figure S91. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **27**.

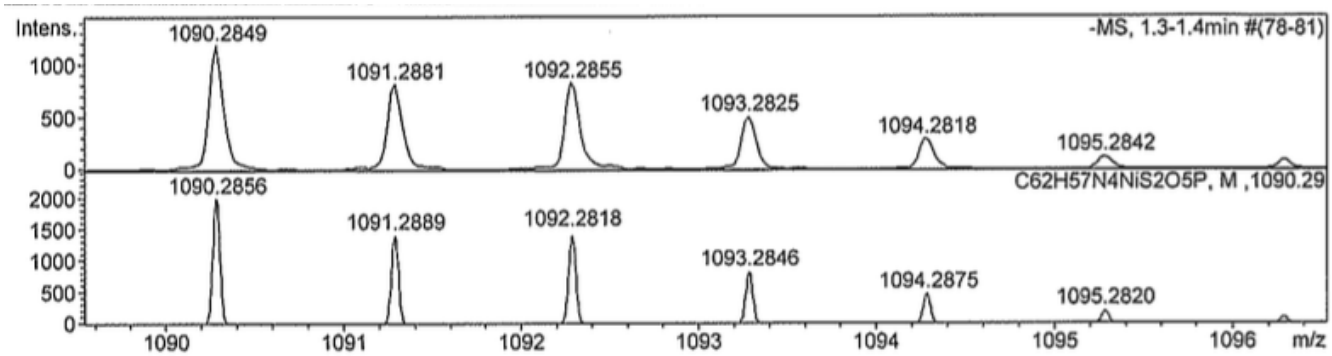


Figure S92. Observed (top) and simulated (bottom) HR-APCI-TOF MS of **28**.

5. X-Ray Crystal Structures

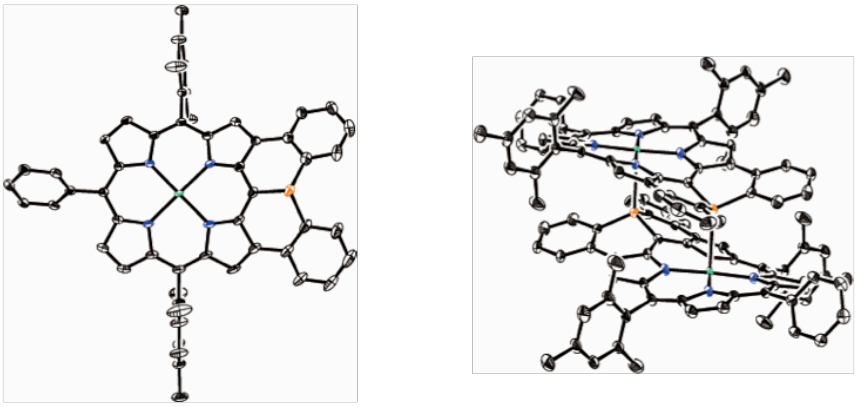


Figure S93. X-Ray crystal structure of **6**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

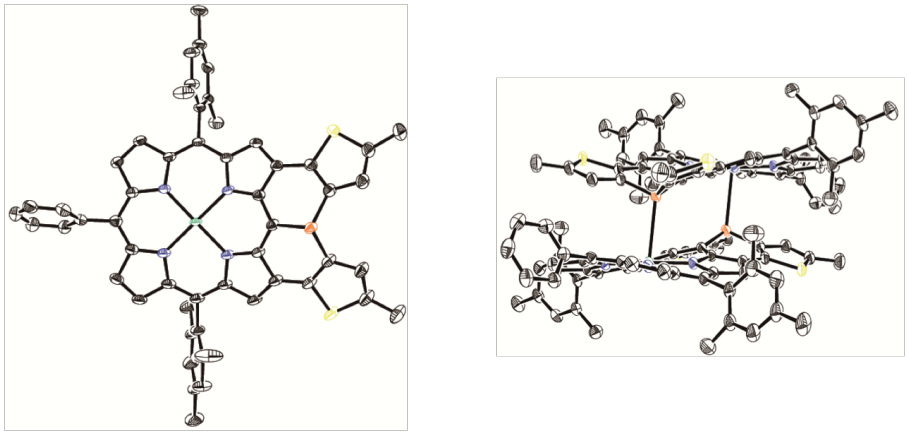


Figure S94. X-Ray crystal structure of **10Ni**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

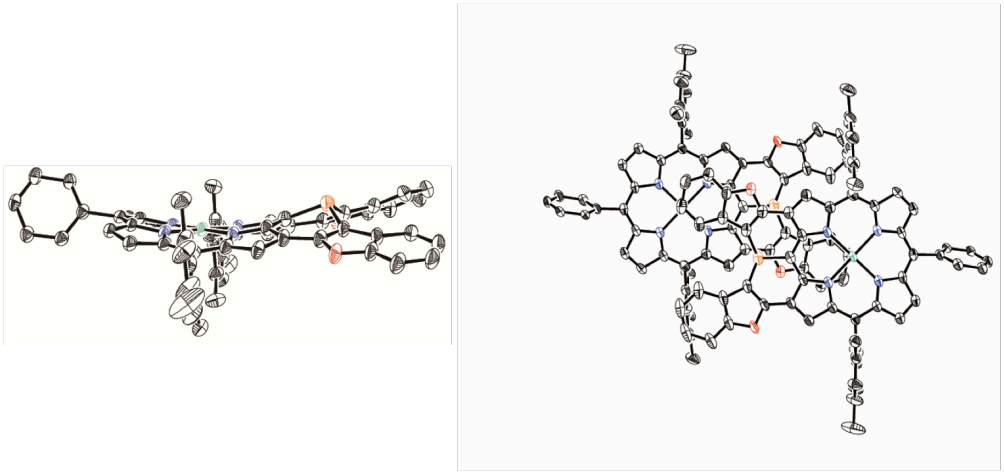


Figure S95. X-Ray crystal structure **12**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

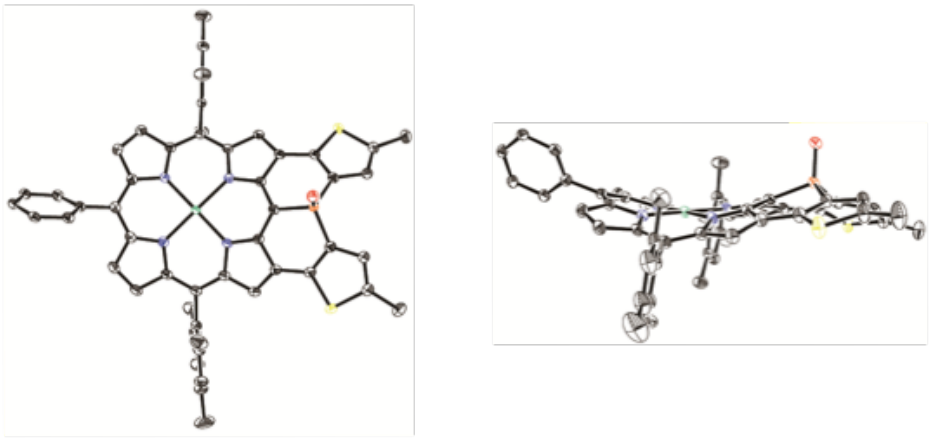


Figure S96. X-Ray crystal structure of **18Ni**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

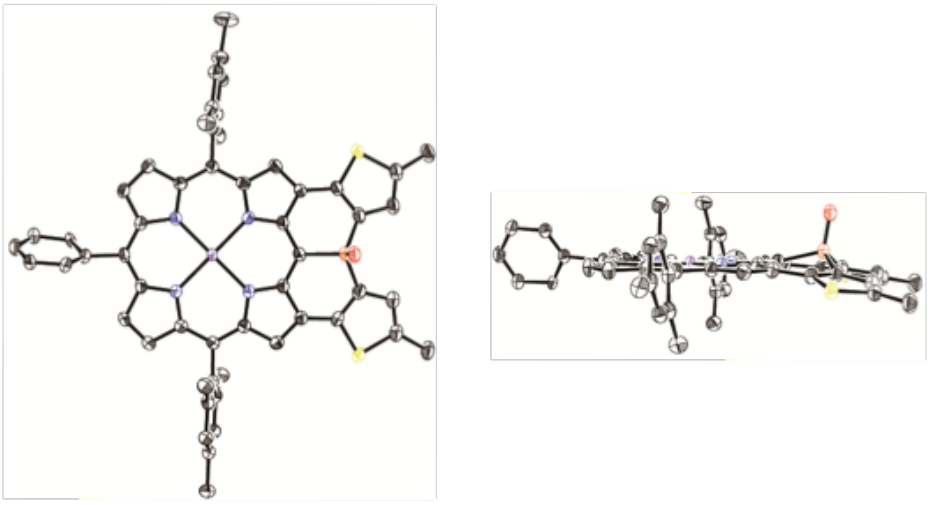


Figure S97. X-Ray crystal structure of **18Pd**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

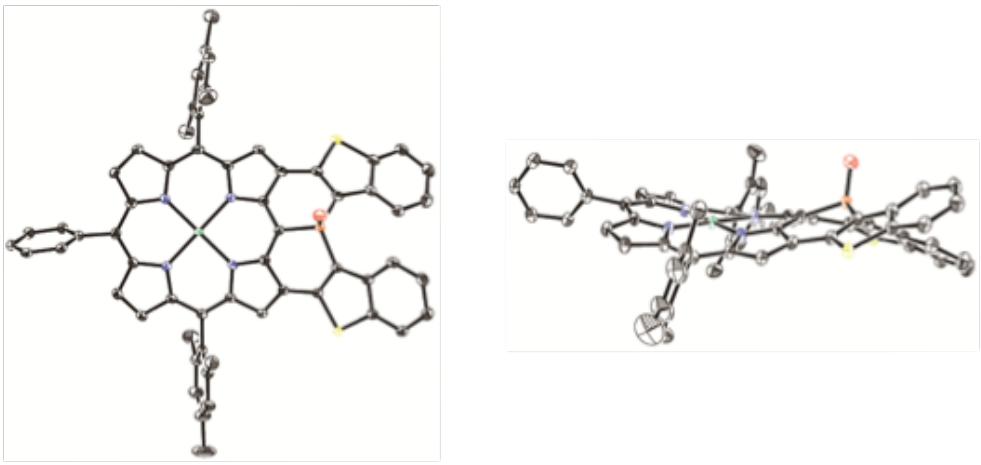


Figure S98. X-Ray crystal structure **20**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

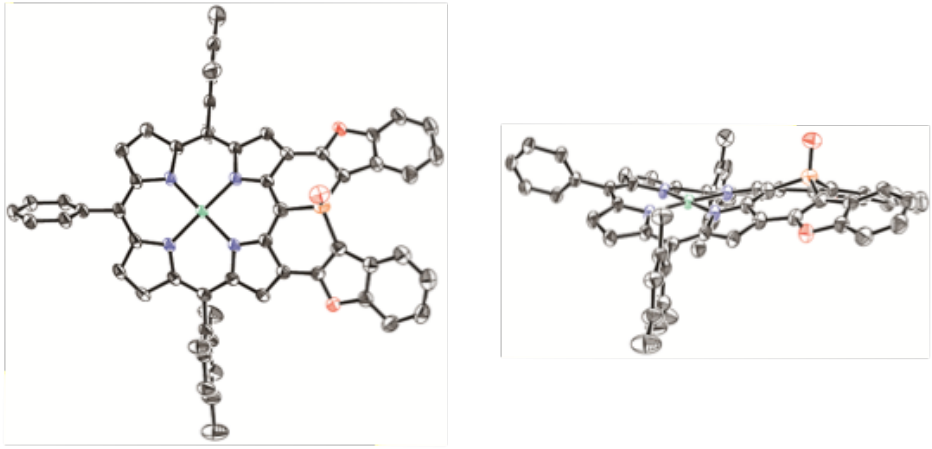


Figure S99. X-Ray crystal structure of **22**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

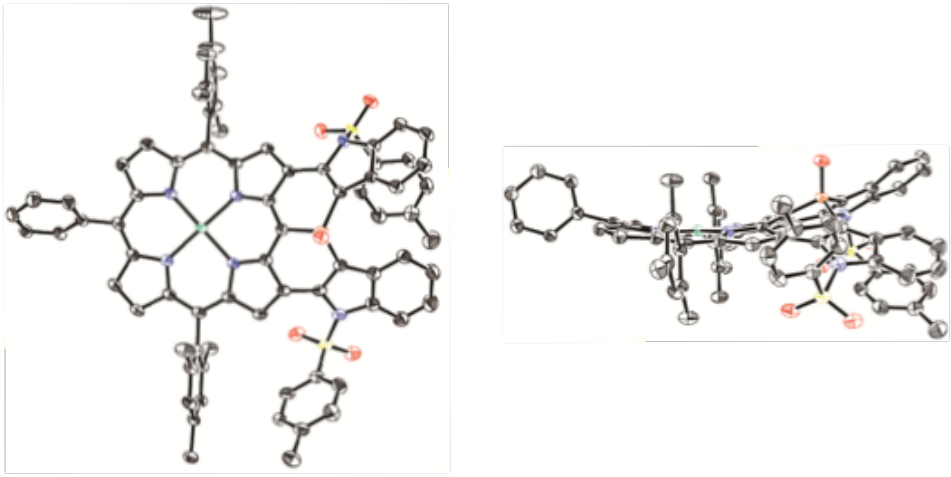


Figure S100. X-Ray crystal structure of **26**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

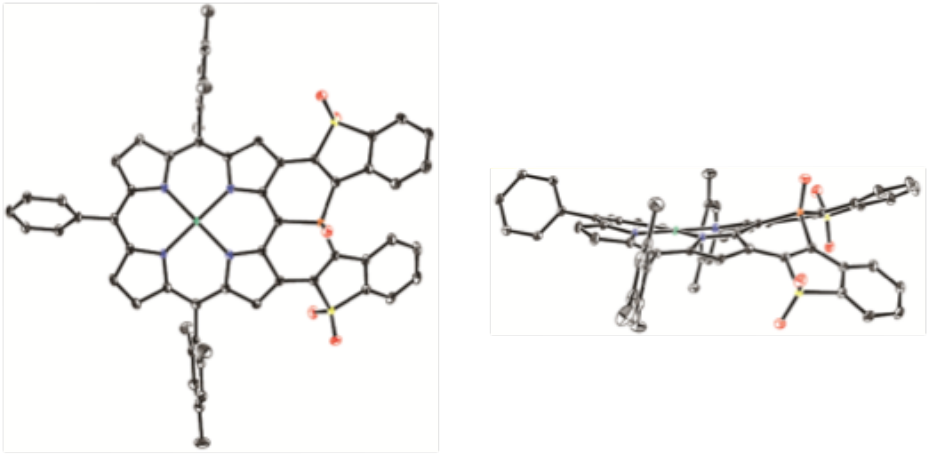


Figure S101. X-Ray crystal structure of **27**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

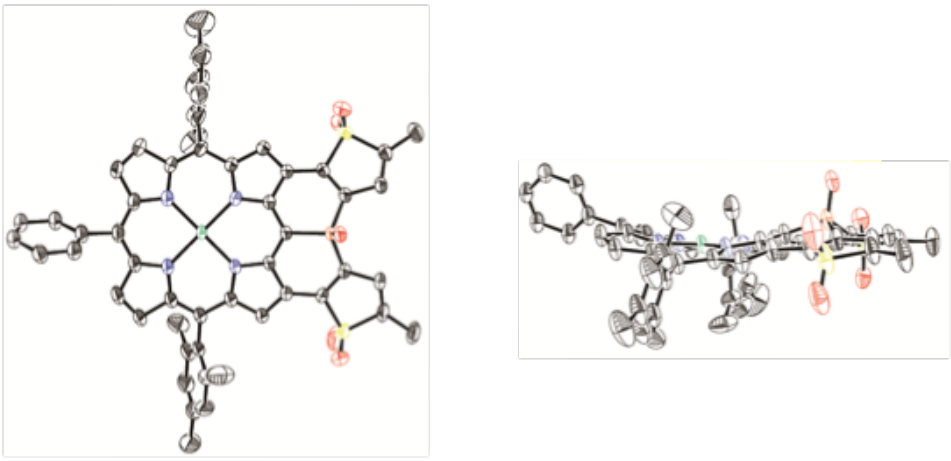


Figure S102. X-Ray crystal structure **28**. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, *tert*-butyl groups, and hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinements for **6**, **10Ni**, and **12**.

Compound	**6**	**10Ni**	**12**
Empirical Formula	$C_{66}H_{59}N_4NiP$	$C_{74}H_{69}N_4NiPS_2$	$C_{80}H_{69}N_4NiO_2P$
Mw	1210.55	1168.13	1208.07
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	*P* 2_1/*c* (No.14)	*P* 2_1/*c* (No.14)	*P* 2_1/*c* (No.14)
a	12.6212(19) Å	12.9016(19) Å	17.046(2) Å
b	16.578(2) Å	16.642(2) Å	11.8202(17) Å
c	27.567(4) Å	28.249(5) Å	31.451(5) Å
α	90°	90°	90°
β	95.009(3)°	95.324(6)°	97.756(4)°
γ	90°	90°	90°
Volume	5749.1(14) $Å^3$	6039.1(16) $Å^3$	6279.0(15) $Å^3$
Z	4	4	4
Density (calcd.)	1.399 g/cm^3	1.285 g/cm^3	1.278 g/cm^3
Completeness	0.985	0.989	0.978
Goodness-of-fit	1.079	1.010	1.085
R_1 [$I>2\sigma(I)$]	0.0723	0.0553	0.0768
wR_2 [$I>2\sigma(I)$]	0.2098	0.1562	0.1947
R_1 (all data)	0.0835	0.0606	0.0910
wR_2 (all data)	0.2218	0.1609	0.2023
Solvent System	$CHCl_3$/MeOH	C_6H_6/MeOH	C_6H_6/MeCN
CCDC No.	1572116	1572117	1572118

Table S2. Crystal data and structure refinements for **18Ni**, **18Pd**, and **20**.

Compound	**18Ni**	**18Pd**	**20**
Empirical Formula	$C_{75}H_{72}N_6NiOPS_2$	$C_{65}H_{60}N_5OCl_4NiPPdS_2$	$C_{71.65}H_{57}N_4OCl_{14.59}NiPS_2$
Mw	1227.18	1270.47	1660.94
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	*C* 2/*c* (No.15)	*P* 2_1/*a* (No.14)	*P* -1 (No.2)
a	41.875(9) Å	13.476(3) Å	14.070(3) Å
b	12.116(2) Å	18.301(3) Å	15.707(3) Å
c	33.342(7) Å	25.301(5) Å	18.170(3) Å
α	90°	90°	96.635(3)°
β	127.805(4)°	103.474(6)°	103.033(7)°
γ	90°	90°	104.706(2)°
Volume	13366(5) $Å^3$	6068(2) $Å^3$	3719.8(12) $Å^3$
Z	8	4	2
Density (calcd.)	1.220 g/cm^3	1.391 g/cm^3	1.483 g/cm^3
Completeness	0.982	0.967	0.966
Goodness-of-fit	1.024	1.037	1.050
R_1 [$I>2\sigma(I)$]	0.0435	0.0613	0.0674
wR_2 [$I>2\sigma(I)$]	0.1173	0.1726	0.1875
R_1 (all data)	0.0494	0.0696	0.0847
wR_2 (all data)	0.1210	0.1789	0.1989
Solvent System	C_6H_6/MeCN	CCl_4/MeCN	CCl_4/MeCN
CCDC No.	1572119	1572120	1572121

Table S3. Crystal data and structure refinements for **22** and **26**.

Compound	**22**	**26**
Empirical Formula	$C_{70}H_{58.89}N_4O_3Cl_6NiP_2$	$C_{85.77}H_{73.77}N_6O_{7.59}Cl_3NiPS_2$
Mw	2266.44	1570.17
Crystal System	Monoclinic	Monoclinic
Space Group	*P* $2_1/n$ (No.14)	*P* $2_1/c$ (No.14)
a	15.250(2) Å	15.0591(17) Å
b	23.282(3) Å	27.873(3) Å
c	18.497(3) Å	18.771(2) Å
α	90°	90°
β	104.562(4)°	101.374(3)°
γ	90°	90°
Volume	6356.4(16) $Å^3$	7724.2(15) $Å^3$
Z	4	4
Density (calcd.)	1.365 g/cm^3	1.350 g/cm^3
Completeness	0.989	0.967
Goodness-of-fit	1.087	1.067
R_1 [$I>2\sigma(I)$]	0.0687	0.0809
wR_2 [$I>2\sigma(I)$]	0.1992	0.2261
R_1 (all data)	0.0836	0.0941
wR_2 (all data)	0.2087	0.2385
Solvent System	$CHCl_3$/MeOH	CH_2Cl_2/MeOH
CCDC No.	1572122	1572123

Table S4. Crystal data and structure refinements for **27** and **28**.

Compound	**27**	**28**
Empirical Formula	$C_{73}H_{57}N_4O_5Cl_{20}NiPS_2$	$C_{73}H_{68}N_4O_{5.5}NiPS_2$
Mw	1933.02	1243.11
Crystal System	Triclinic	Monoclinic
Space Group	*P* -1 (No.2)	*C* 2/*c* (No.15)
a	14.5544(7) Å	28.316(5) Å
b	16.0580(5) Å	16.521(2) Å
c	19.2527(17) Å	32.462(6) Å
α	80.1620(10)°	90°
β	86.521(12)°	109.086(5)°
γ	67.319(8)°	90°
Volume	4090.5(5) $Å^3$	14351(4) $Å^3$
Z	2	8
Density (calcd.)	1.569 g/cm^3	1.151 g/cm^3
Completeness	0.959	0.985
Goodness-of-fit	1.007	1.025
R_1 [$I>2\sigma(I)$]	0.0422	0.0634
wR_2 [$I>2\sigma(I)$]	0.1225	0.1986
R_1 (all data)	0.0474	0.0760
wR_2 (all data)	0.1250	0.2087
Solvent System	CCl_4/MeOH	THF/hexane
CCDC No.	1572124	1572125

6. Absorption Spectra

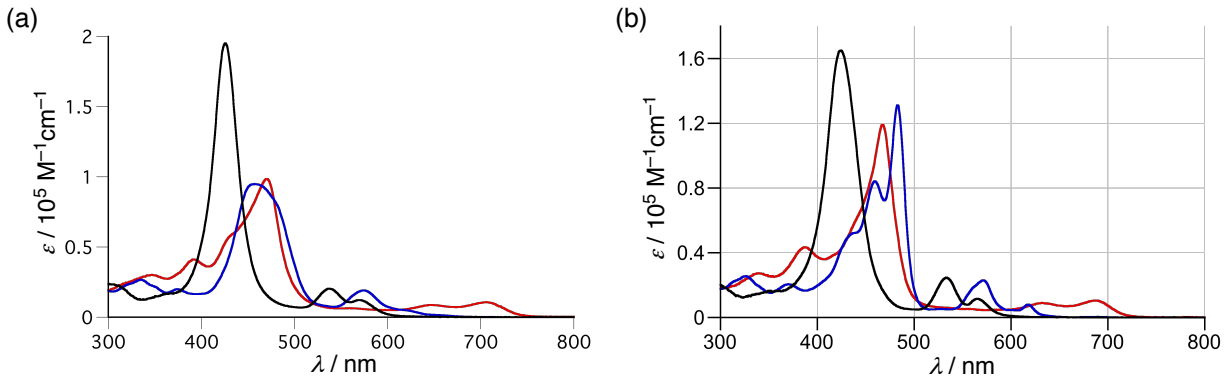


Figure S103. Absorption spectra of **17Ni** (a, black), **18Ni** (a, red), **10Ni** (a, blue), **17Pd** (b, black), **18Pd** (b, red), and **10Pd** (b, blue) in CH_2Cl_2.

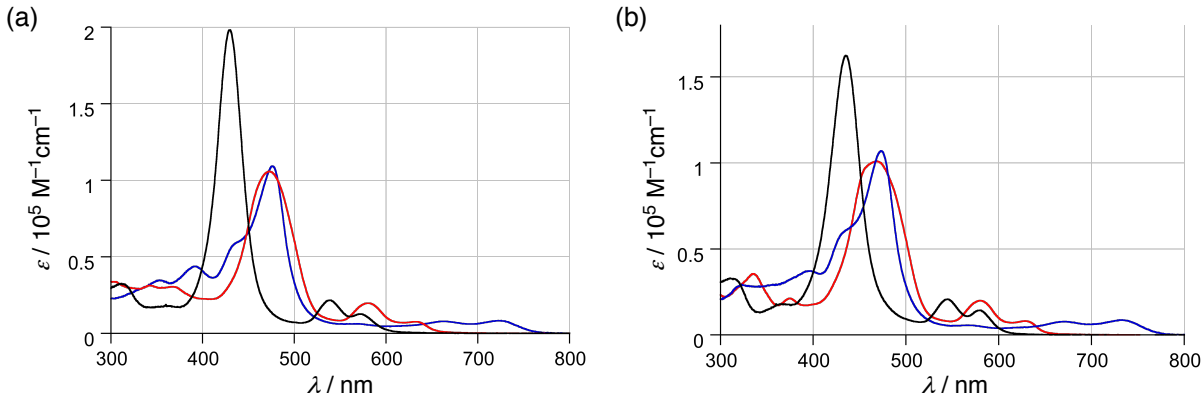


Figure S104. Absorption spectra of **19** (a, black), **20** (a, blue), **11** (a, red), **21** (b, black), **22** (b, blue), and **12** (b, red) in CH_2Cl_2.

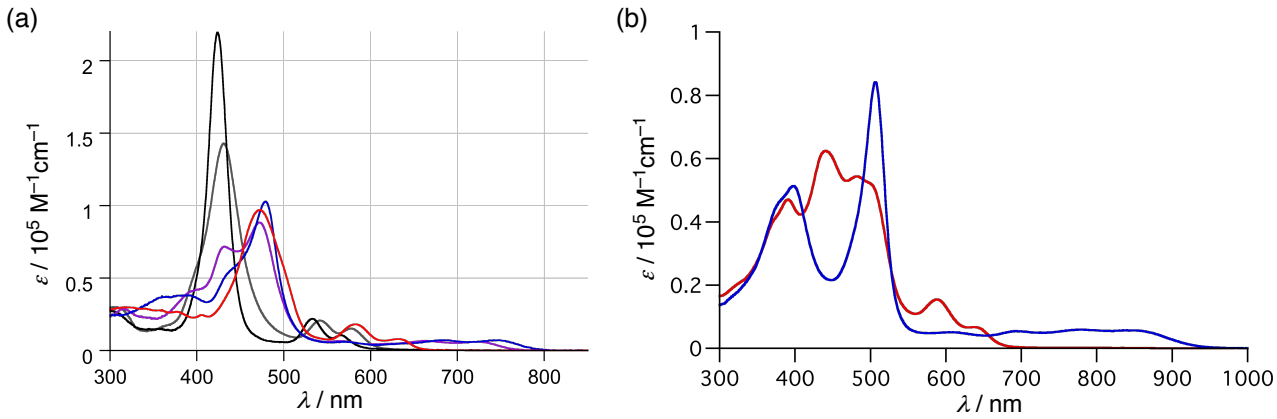


Figure S105. Absorption spectra of **23** (a, black), **24** (a, gray), **25** (a, violet), **26** (a, blue), **13** (a, red), **28** (b, blue), and **15** (b, red) in CH_2Cl_2.

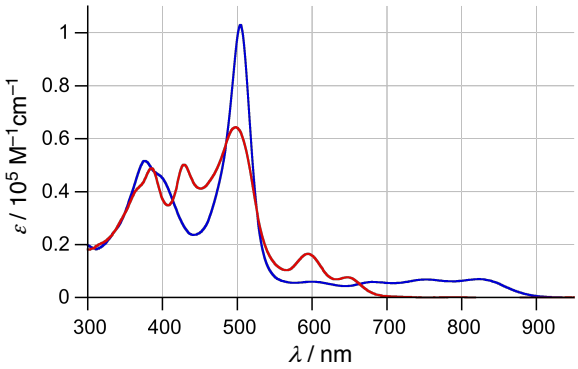
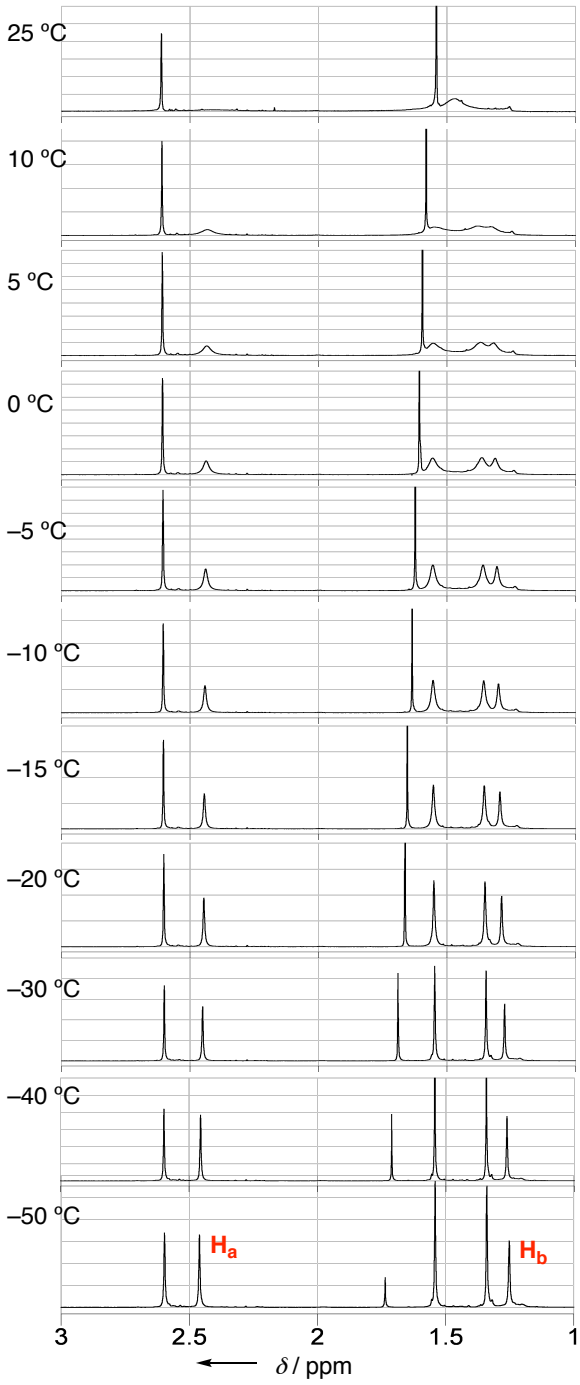
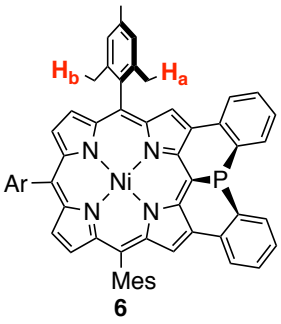


Figure S106. Absorption spectra of **27** (blue) and **14** (red) in CH_2Cl_2.

7. Determination of Pyramidal Inversion Barriers





6

Eyring equation

$$\ln(k/T) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln(k_B/h) + \frac{\Delta S^{\ddagger}}{R}$$

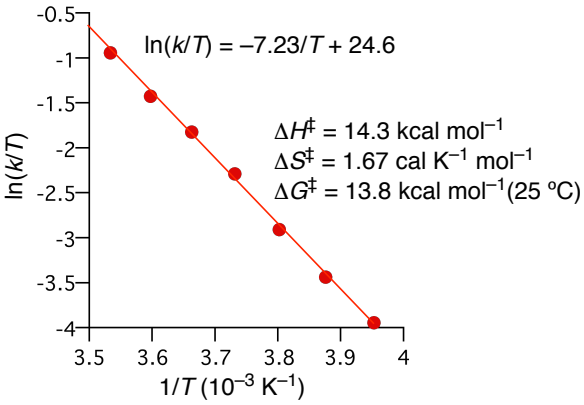
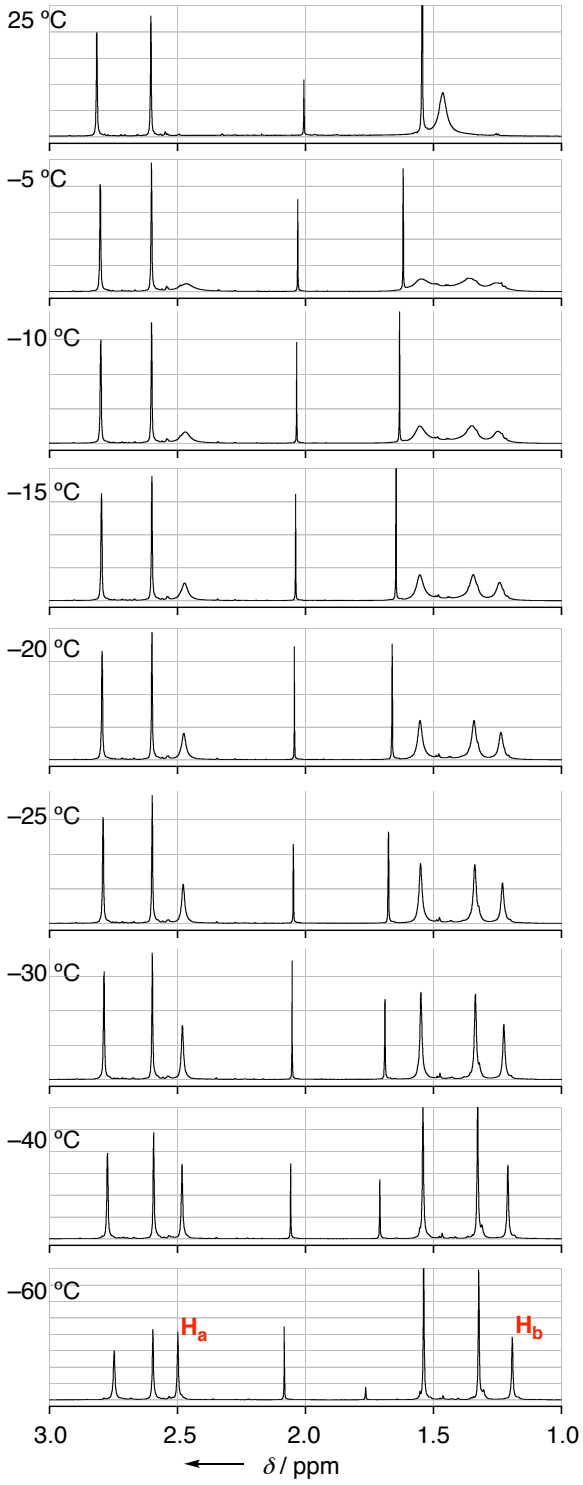
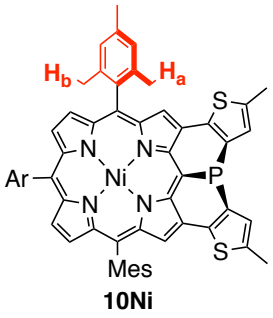


Figure S107. Temperature dependent ^{1}H NMR spectra of **6** in $CDCl_3$ and Eyring plot for determination of the pyramidal inversion barrier.





10Ni

Eyring equation

$$\ln(k/T) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln(k_B/h) + \frac{\Delta S^{\ddagger}}{R}$$

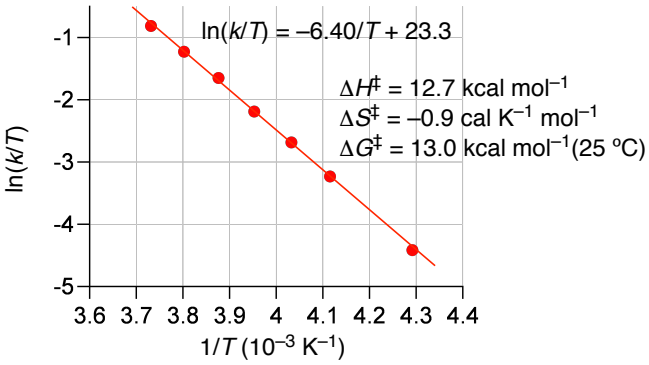
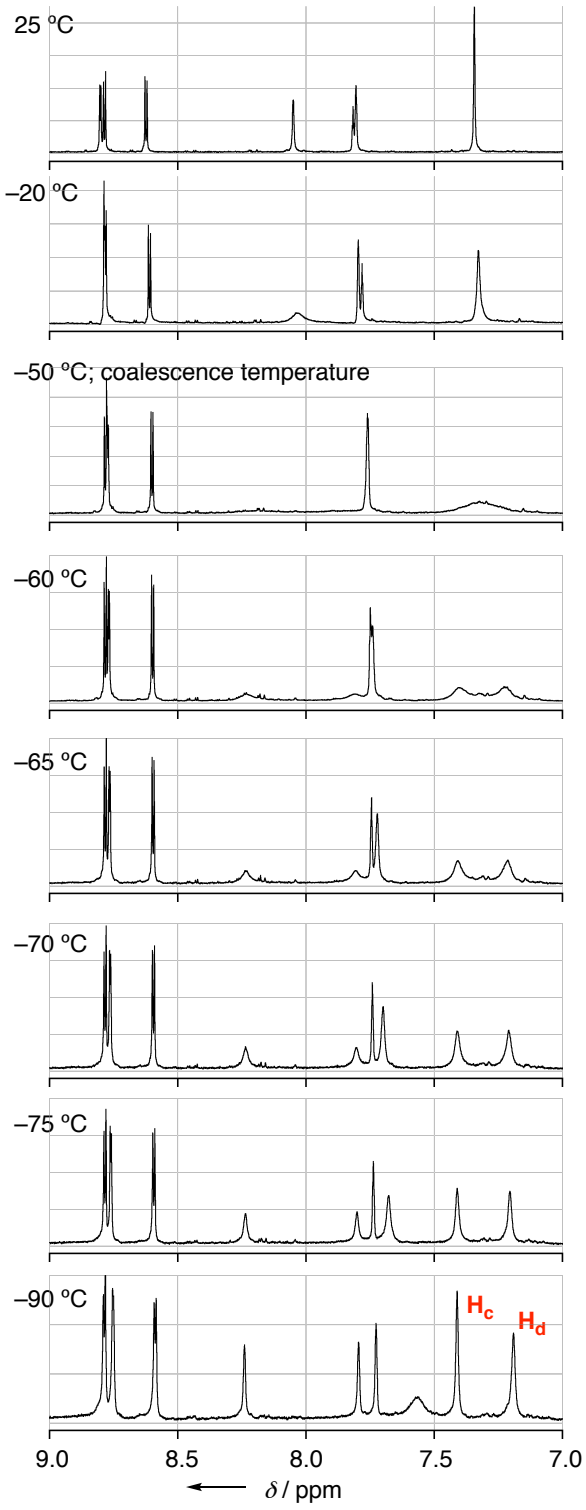
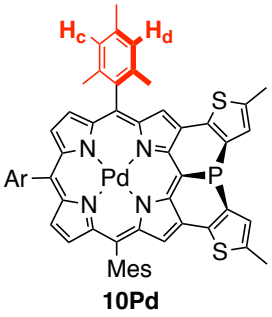


Figure S108. Temperature dependent ^{1}H NMR spectra of **10Ni** in $CDCl_3$ and Eyring plot for determination of the pyramidal inversion barrier.





10Pd

Eyring equation

$$\ln(k/T) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln(k_B/h) + \frac{\Delta S^{\ddagger}}{R}$$

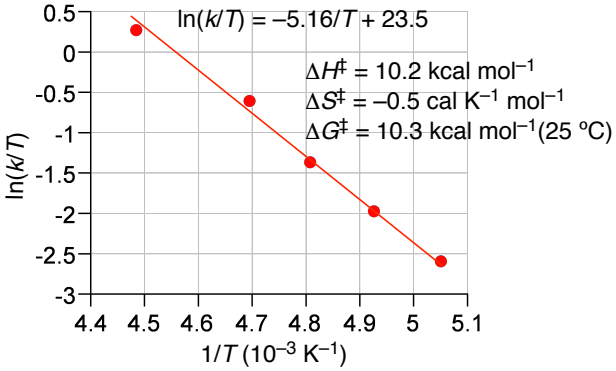
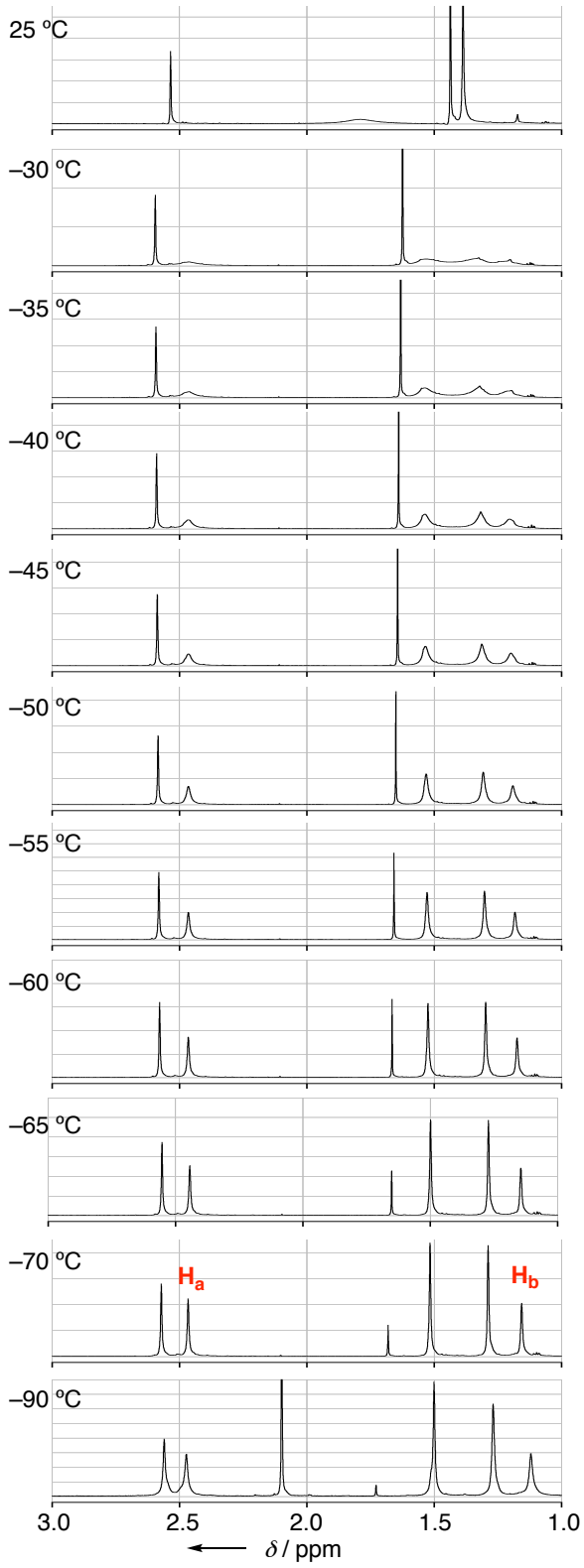
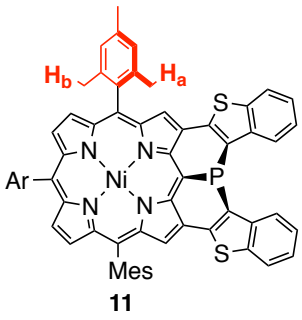


Figure S109. Temperature dependent ^{1}H NMR spectra of **10Pd** in CD_2Cl_2 and Eyring plot for determination of the pyramidal inversion barrier.





11

Eyring equation

$$\ln(k/T) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln(k_B/h) + \frac{\Delta S^{\ddagger}}{R}$$

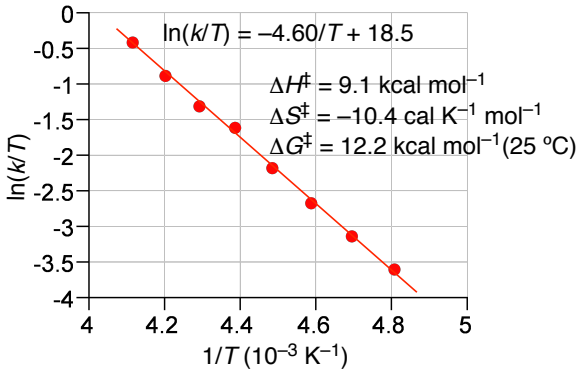
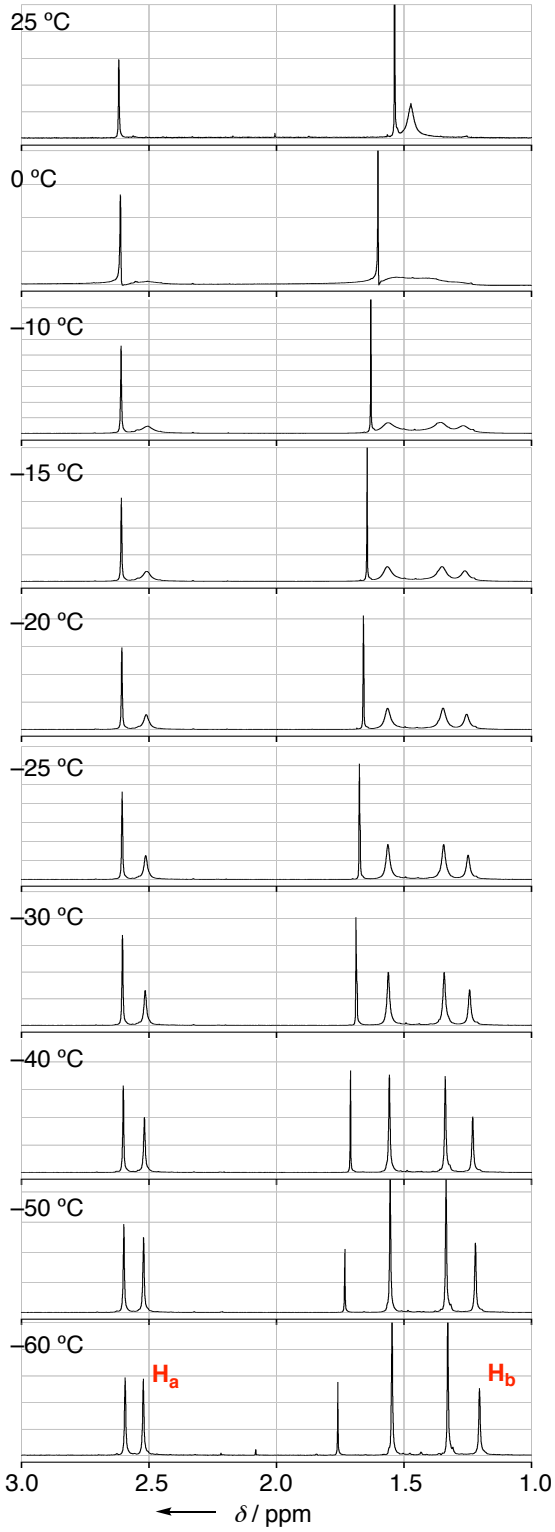
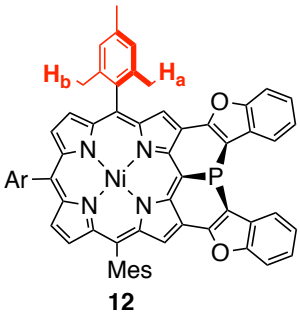


Figure S110. Temperature dependent ^{1}H NMR spectra of **11** in CD_2Cl_2 and Eyring plot for determination of the pyramidal inversion barrier.





12

Eyring equation

$$\ln(k/T) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln(k_B/h) + \frac{\Delta S^{\ddagger}}{R}$$

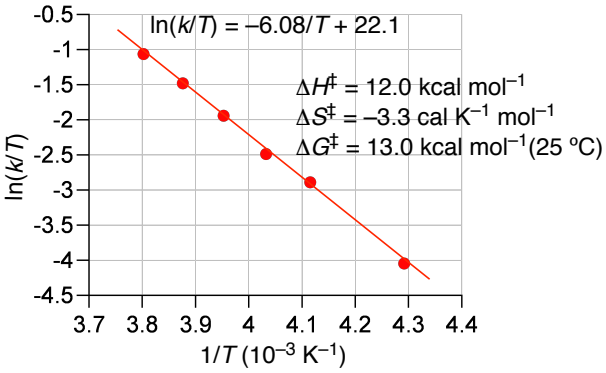


Figure S111. Temperature dependent ^{1}H NMR spectra of **12** in $CDCl_3$ and Eyring plot for determination of the pyramidal inversion barrier.

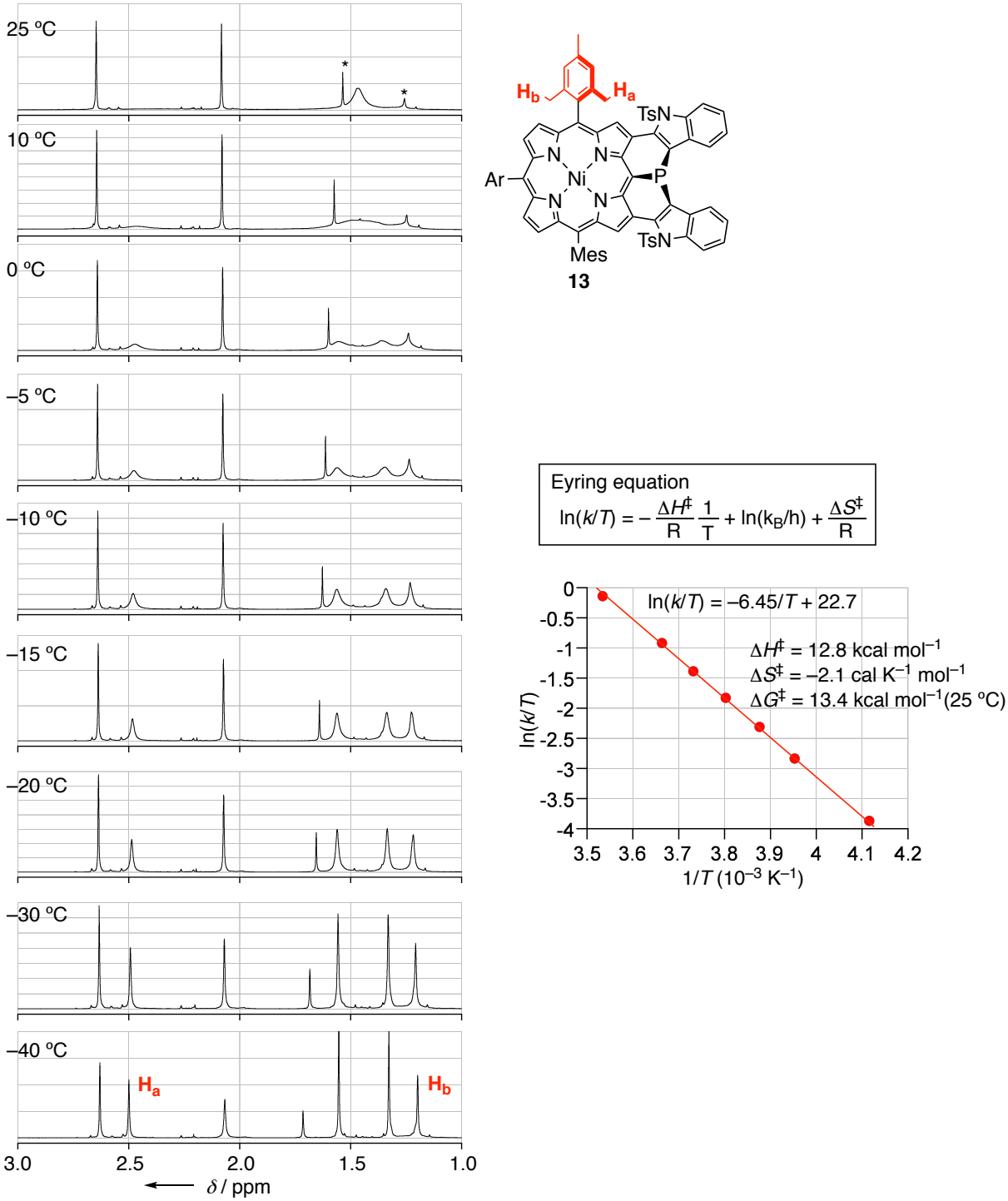
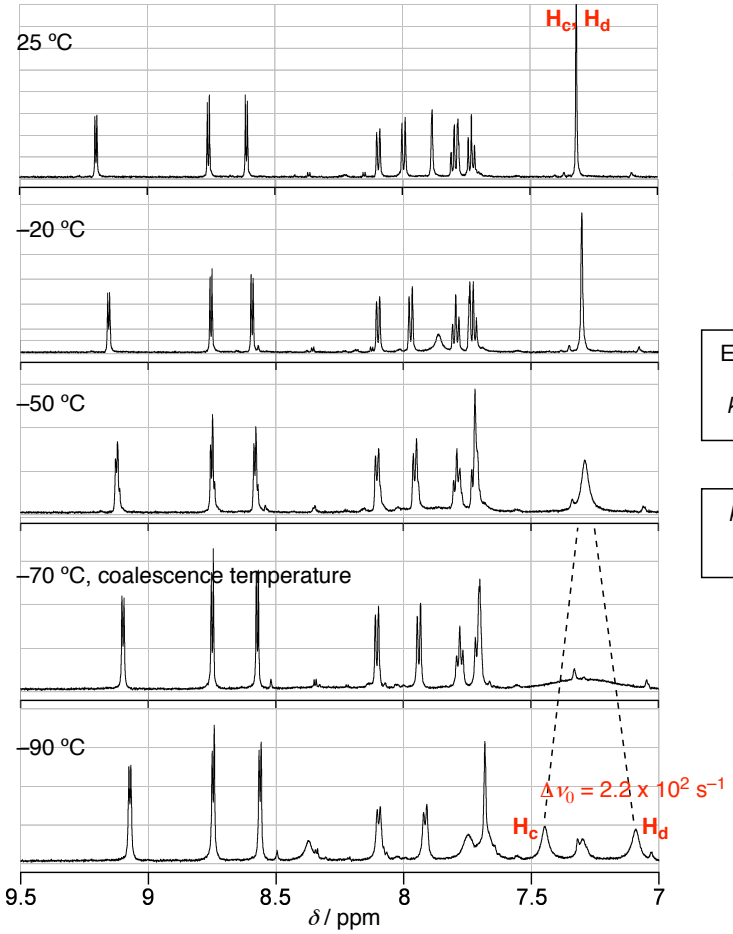
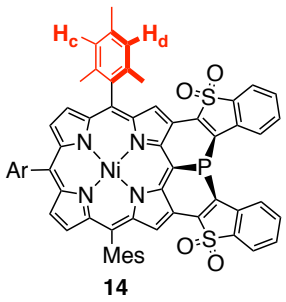


Figure S112. Temperature dependent ^{1}H NMR spectra of **13** in $CDCl_3$ and Eyring plot for determination of the pyramidal inversion barrier.





14

Eyring equation

$$k_{Tc} = \frac{k_B T_C}{h} \exp\left(-\frac{\Delta G^{\ddagger}_{Tc}}{RT_C}\right)$$

T_C: coalescence temperature
k_{Tc}: rate constant at coalescence

$k_{Tc} = 2.22 \times \Delta\nu_0$ (s^{-1}) $\Delta\nu_0$: peak separation

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$k = 4.9 \times 10^2$ s^{-1}, $\Delta G^{\ddagger}_{203} = 9.2$ kcal/mol

Figure S113. Temperature dependent ^{1}H NMR spectra of **14** in CD_2Cl_2 and determination of the pyramidal inversion barrier.

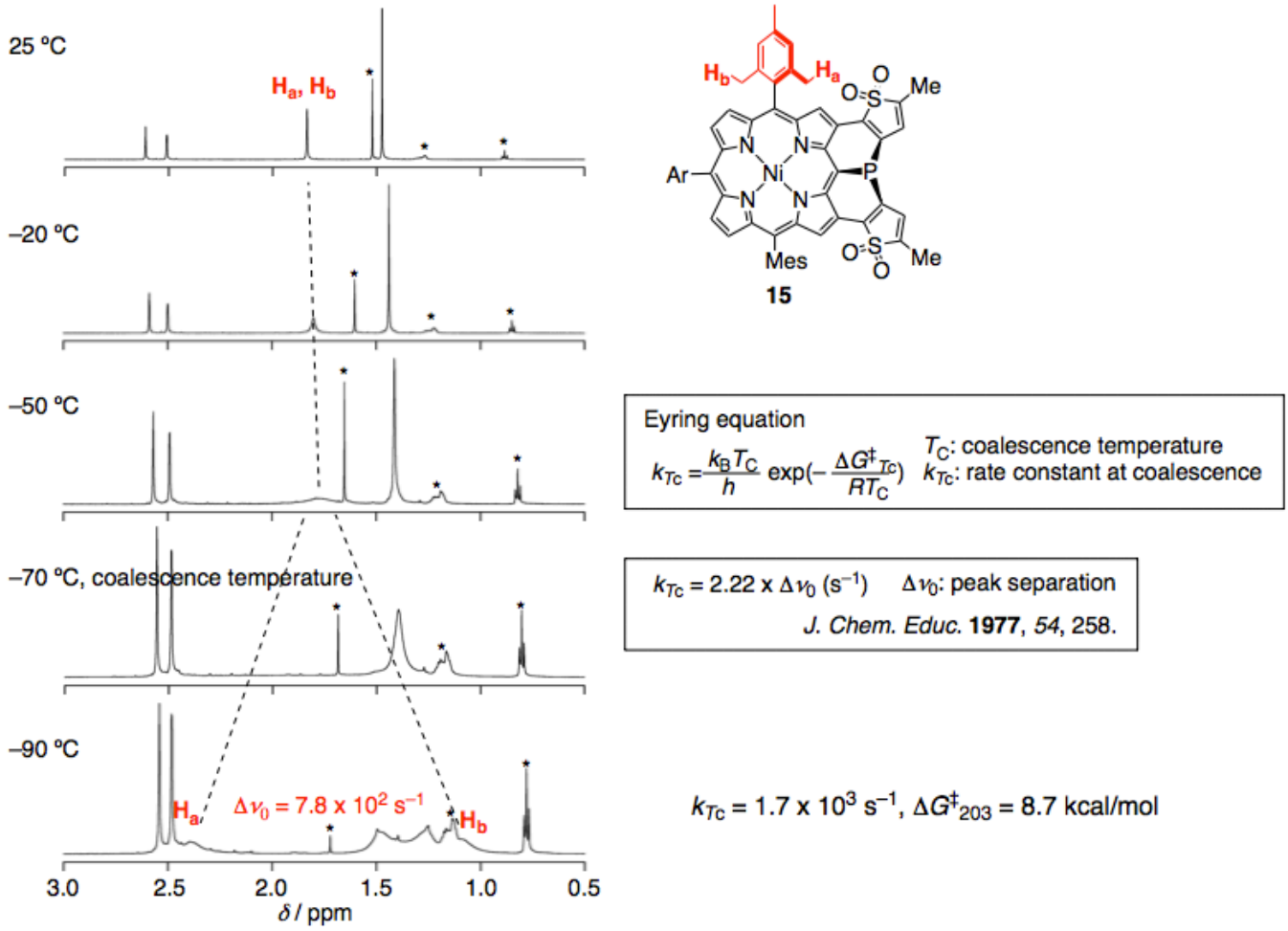


Figure S114. Temperature dependent ^{1}H NMR spectra of **15** in CD_2Cl_2 and determination of the pyramidal inversion barrier.

8. Electrochemical Properties

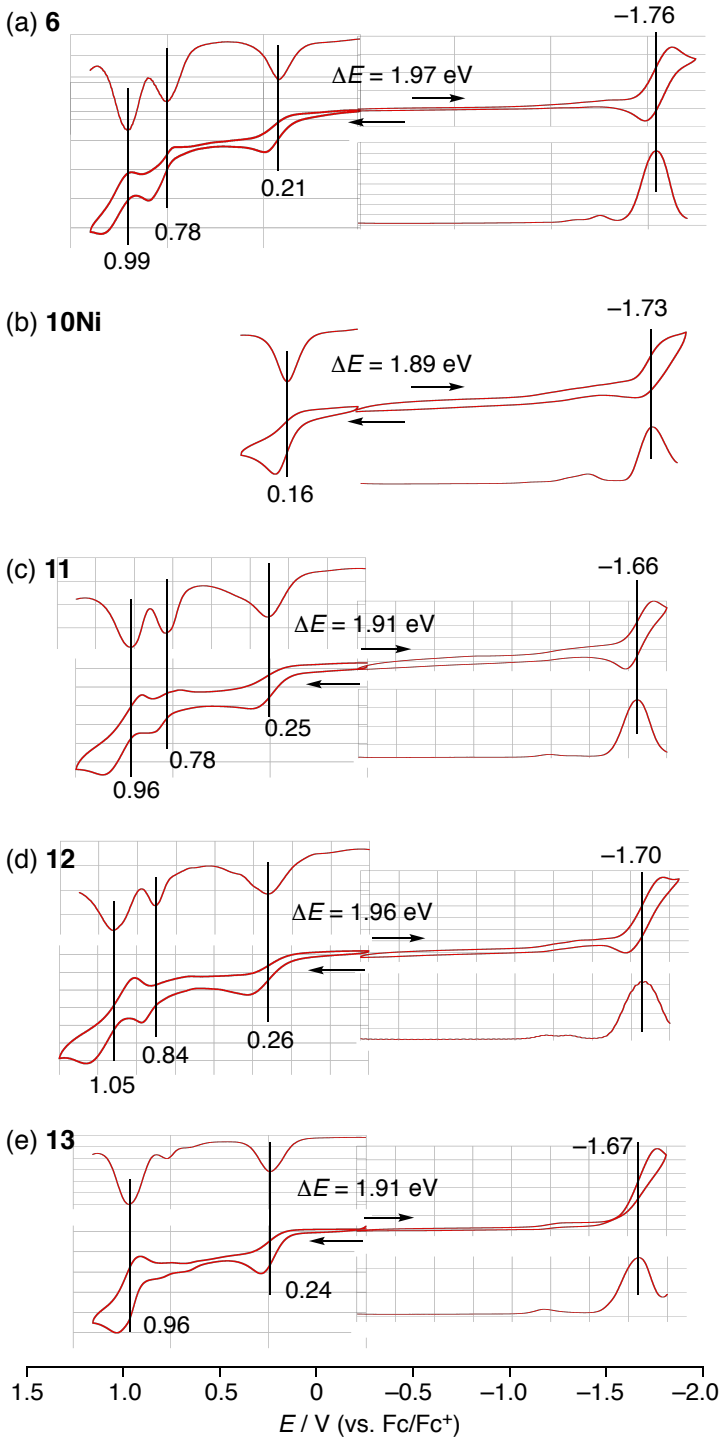


Figure S115. Cyclic voltammograms and differential pulse voltammograms of (a) **6**, (b) **10Ni**, (c) **11**, (d) **12**, and (e) **13** in anhydrous CH_2Cl_2. Potentials [V] vs ferrocene/ferrocenium cation. Scan rate, 0.05 Vs^{-1}; working electrode, glassy carbon; counter electrode, Pt wire; supporting electrolyte, 0.1 M Bu_4NPF_6.

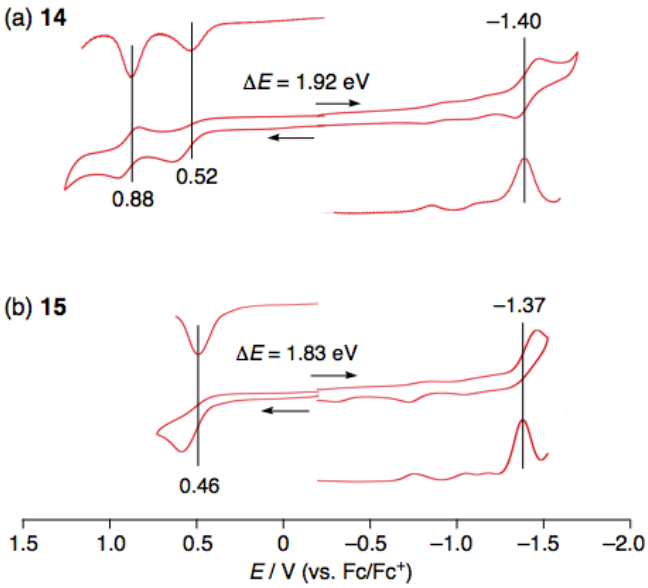


Figure S116. Cyclic voltammograms and differential pulse voltammograms of (a) **14** and (b) **15** in anhydrous CH_2Cl_2. Potentials [V] vs ferrocene/ferrocenium cation. Scan rate, 0.05 Vs^{-1}; working electrode, glassy carbon; counter electrode, Pt wire; supporting electrolyte, 0.1 M Bu_4NPF_6.

9. Temperature Dependent Magnetic Susceptibility

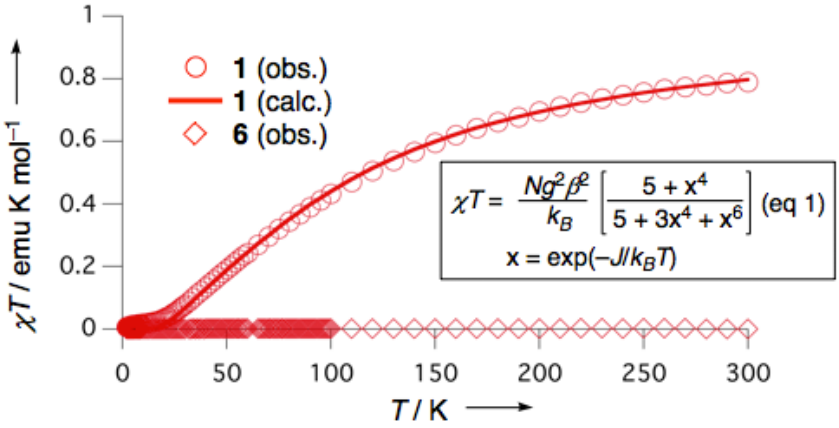


Figure S117. Temperature dependent magnetic susceptibility of **1** (circles), **6** (diamonds), and simulated χT value for **1** (solid line) which was calculated from eq 1 with fitted parameter of J_1/k_B = –44.7 K.

10. DFT Calculations

The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional)[S2] level, employing basis sets 6-31G(d) for C, H, O, N, S, and P and LANL2DZ for Ni and Pd using the *Gaussian 09* program.[S2] The initial geometries for optimization of **6**, **10Ni**, and **12**, were obtained from the X-ray structures. The initial geometries for optimization of **10Pd**, **11**, **14**, and **15** were obtained from X-ray structures of the corresponding phosphine oxide. *meso*-Aryl groups were replaced with phenyl groups to simplify the calculation. The planar transition structure was also calculated in the same level and is confirmed by one imaginary frequency corresponding to the pyramidal inversion. The nucleus independent chemical shift (NICS) values[S3] were obtained with the GIAO method at the B3LYP/6-31G(p) level.

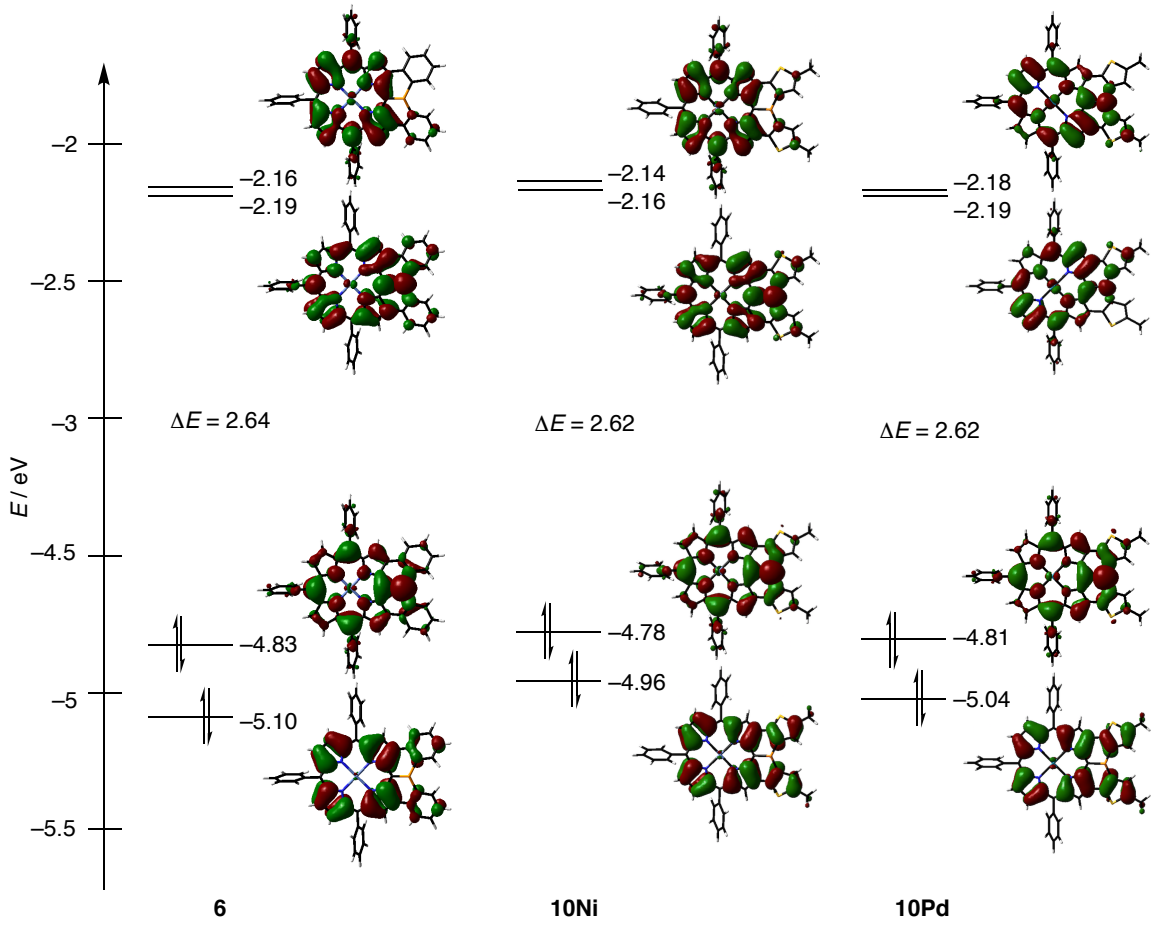


Figure S118. Energy diagram and representative Kohn-Sham orbitals of **6**, **10Ni**, and **10Pd.**

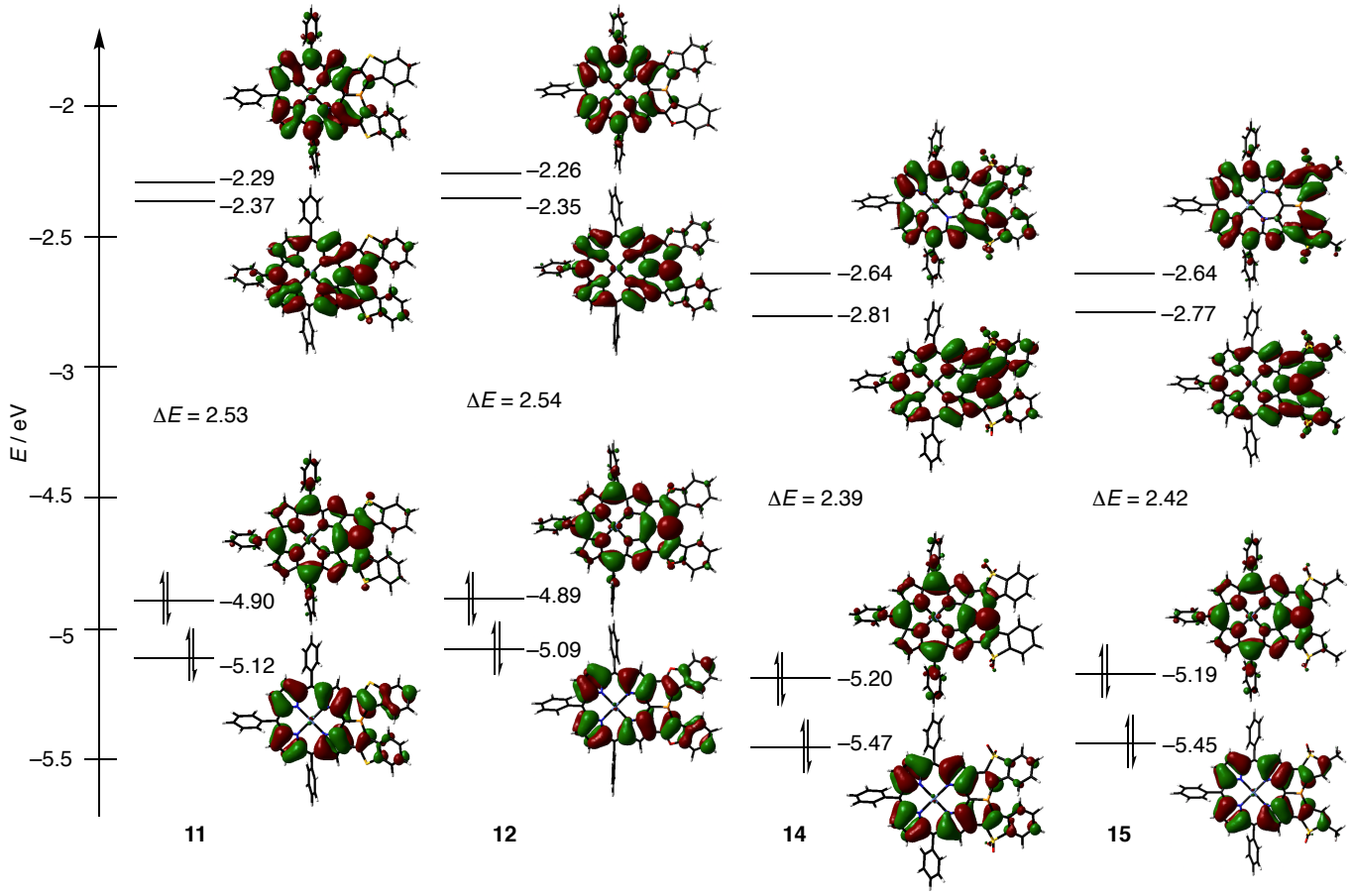


Figure S119. Energy diagram and representative Kohn-Sham orbitals of **11**, **12**, **14**, and **15.**

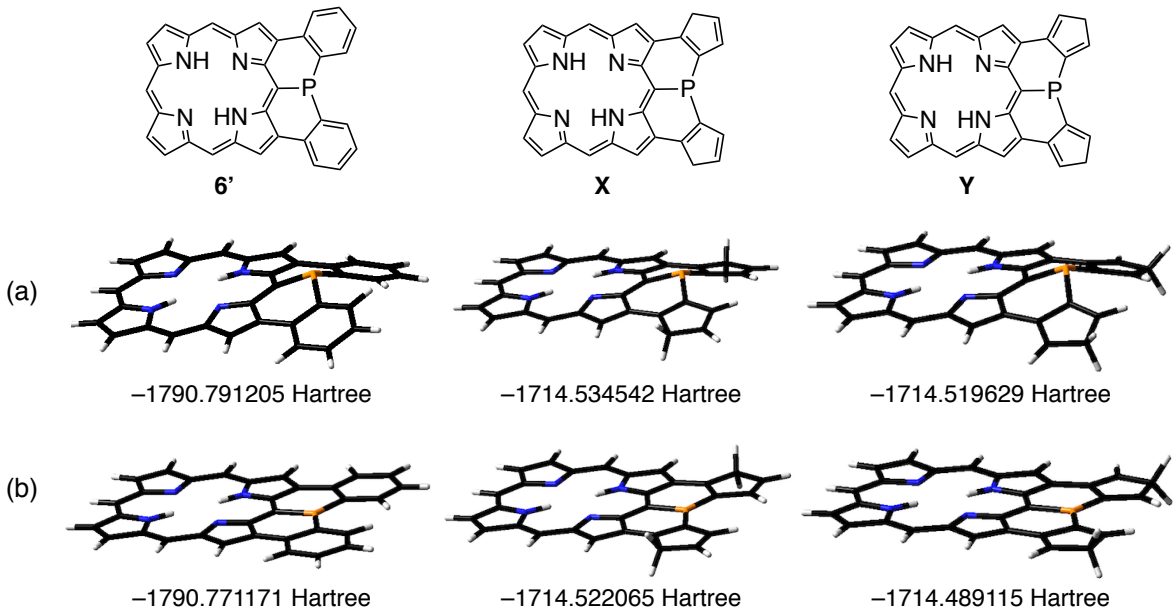
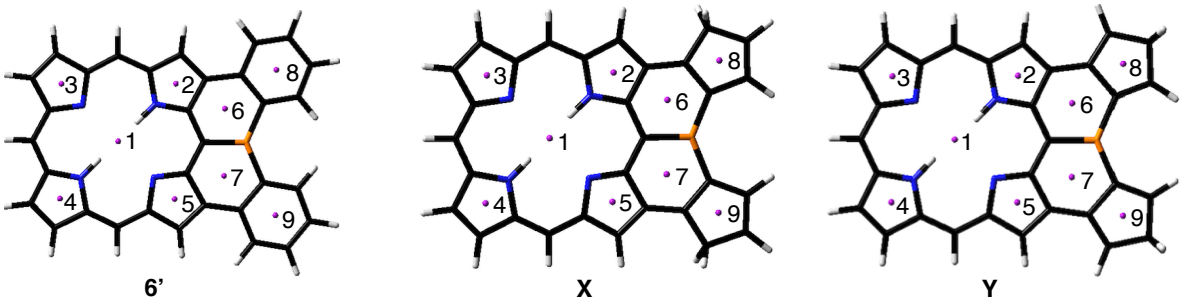


Figure S120. Optimized structures of **6'**, **X**, and **Y** (a) without symmetric restriction and (b) with symmetric restriction to C_s and sum of total energy and zero-point energy.



Compound (structure)	NICS(0) ppm								
	1	2	3	4	5	6	7	8	9
6' (pyramidal)	–14.18	–13.67	–2.85	–12.53	–5.80	+4.37	+2.97	–7.47	–7.80
6' (planar)	–11.78	–17.99	–2.43	–11.37	–14.09	–3.91	–5.92	–9.29	–10.20
X (pyramidal)	–14.28	–15.61	–2.98	–12.80	–9.45	+0.20	–1.12	+0.34	+0.73
X (planar)	–11.40	–19.67	–2.53	–11.26	–17.71	–10.15	–11.99	+0.43	+1.04
Y (pyramidal)	–14.13	–12.80	–2.82	–12.62	–2.91	+5.52	+5.59	–1.74	–2.05
Y (planar)	–11.45	–13.45	–2.63	–11.32	–4.35	+3.67	+3.62	–3.07	–3.35

Figure S121. NICS(0) values at various positions of **6'**, **X**, and **Y** in the pyramidal ground state and planar transition state.

11. References

[S1] SHELXL-97 and SHELXS-97, program for refinement of crystal structures from diffraction data, University of Goettingen, Goettingen (Germany); Sheldrick, G.; Schneider, T. *Methods Enzymol.* **1997**, *277*, 319.

[S2] (a) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. P.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc.: Wallingford, CT, 2009. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372; (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

[S3] (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.*, **1996**, **118**, 6317. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev*. **2005**, *105*, 3842.