Supporting Information: Modifications to the Aryl Group of dppf-Ligated Ni σ-Aryl Precatalysts: Impact on Speciation and Catalytic Activity in Suzuki-Miyaura Coupling Reactions

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SI. General Methods

Experiments were performed under an atmosphere of dinitrogen in an M-Braun glovebox or using standard Schlenk techniques, unless specified otherwise. Purging of the glovebox atmosphere was not performed between uses of pentane, benzene, toluene, diethyl ether, and THF; as such, trace amounts of the solvents may have been present in the box atmosphere and intermixed in the solvent bottles. All chemicals were used as received unless otherwise stated. Air- or moisture-sensitive liquids were transferred using stainless steel cannulae on a Schlenk line or in a glovebox. Solvents were dried via passage through a column of activated alumina and subsequently stored under dinitrogen. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Powdered K_3PO_4 was purchased from Acros Organics, finely ground using a mortar and pestle, heated in an oven at 120 °C for at least 24 hours and stored in a glove box. NMR spectra were recorded on Agilent-400, -500 or -600 MHz spectrometers at ambient probe temperatures unless otherwise stated. Chemical shifts are reported in ppm, with respect to residual internal protio solvent for ^{1}H and ^{13}C NMR spectra and $^{31}P\{^{1}H\}$ NMR spectra are referenced via the ^{1}H resonances based on the relative gyromagnetic ratios[1]. Gas Chromatography was performed on a ThermoFisher Trace 1300 GC apparatus equipped with a flame ionization detector and a Supelco fused silica capillary column (5 Å molecular sieves, 30 m x 0.53 mm) using the following parameters: flow rate 1.23 mL/min constant flow, column temperature 50 °C (held for 5 min), 20 °C/min increase to 300 °C (held for 5 min), total time 22.5 min. GC yields were calculated based on calibration curves generated using the independently synthesized biaryl product of interest. Naphthalen-1-yl sulfamate and 4-trifluoromethylphenyl sulfamate were prepared according to literature procedures.[2] **1-Cl**,[3] **1-Br**,[3] (dppf)Ni^{II}(2,4,6-triisopropylphenyl)(Br) (**16)**[4] and (dppf)$Ni^{0}(C_2H_4)$ (**18**)[5] were prepared according to literature precedent. X-Band EPR spectra were recorded on a Bruker ELEXSYS E500 EPR spectrometer equipped with a SHQ resonator and an Oxford ESR-900 helium-flow cryostat with the following settings: microwave frequency, 9.4 GHz; modulation frequency, 100 kHz; modulation amplitude, 10 G; sweep time, 84 s; conversion time, 41 ms; time constant 20 ms. 1 mM solutions of the samples of interest were prepared in the glovebox using toluene for a total of 200 µL of solution per tube. The tubes were sealed in the glovebox and immediately frozen in liquid nitrogen. Robertson Microlit Laboratories, Inc. performed the elemental analyses (inert atmosphere).

SII. Synthesis of Precatalysts

General Procedure for the Synthesis of Ni(II) Precatalysts

The compounds were synthesized by modification of the previously described literature method for the preparation of (dppf)Ni^{II}(*o*-tolyl)(Br) (**1-Br**) in all cases except (dppf)Ni^{II}(2-Me-4-NO_2Ph)(Br) (**7**), whose synthesis is detailed with its reported spectroscopic data.[3,4] (dppf)$Ni^{II}Br_2$ (**17**) (200 mg, 0.258 mmol) was added to a 100 mL Schlenk flask containing a stir bar. 10 mL of THF was transferred via cannula into the flask, and the contents were stirred until dissolution. The flask was cooled to 0 °C in an ice bath, after which the appropriate arylmagnesium bromide Grignard reagent (0.258 mmol) was added dropwise using a gas-tight syringe. The solutions turned from dark green to orange in all cases by the end of the addition. The flask was allowed to warm to room temperature, after which the THF was removed under vacuum to yield an orange residue. 5 mL of methanol was added to the flask, and the heterogeneous mixture was sonicated for 3 minutes until a uniform suspension was obtained. The flask was cooled in an ice bath for 15 minutes, and the resulting bright yellow solid was isolated by vacuum filtration and analyzed by ^{1}H, ^{31}P, ^{13}C, and ^{19}F (if applicable) NMR spectroscopy. For fluorine-containing species, we note that ^{1}J, ^{2}J, and ^{3}J(C-F) couplings could not be resolved in the $^{13}C\{^{1}H\}$ NMR spectra, in part because of the low solubility of the complexes, and as such, are not reported. Spectroscopic data is reported below.

*Spectroscopic Data for (dppf)Ni^{II}(1-naphthyl)(Br) (**2**)*

Yield: 64% (135.2 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 9.53 (d, J = 7.2 Hz, 1H), 8.72 (t, J = 8.3 Hz, 2H), 8.32 (t, J = 7.2 Hz, 2H), 8.09 (br s, 1H), 7.91 (t, J = 4.5 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.24 (m, 4H, partially obscured by solvent), 7.10 (m, 2H, partially obscured by solvent), 6.97 (m, 2H), 6.86 (m, 3H), 6.57 (t, J = 6.7 Hz, 1H), 6.43 (t, J = 6.4 Hz, 2H), 5.33 (s, 1H), 4.26 (s, 1H), 4.16 (s, 1H), 3.88 (s, 1H), 3.65 (s, 1H), 3.60 (s, 1H), 3.59 (s, 1H), 3.44 (s, 1H). The NMR spectrum is shown in Figure S7.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202 MHz, 25 °C): δ 32.0 (d, J = 28 Hz); 11.8 (d, J = 28 Hz) The NMR spectrum is shown in Figure S8.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 151 MHz, 25 °C): δ 140.1, 136.5, 136.1, 135.8, 135.5, 135.3, 134.7, 134.4, 134.1, 132.5, 131.7, 131.6, 131.5, 131.3, 131.1, 130.3, 130.0, 126.4, 124.8, 124.2, 123.4, 122.6,

77.1, 76.4, 76.1, 75.6, 74.6, 74.4, 74.3, 74.0, 74.0, 73.0, 72.4, 71.3. The NMR spectrum is shown in Figure S9.

Elemental Analysis: $C_{44}H_{35}BrFeNiP_2$ % Calc'd(Found): C: 64.44(64.57); H: 4.30(4.44); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-ethylphenyl)(Br) (**3**)*

Yield: 69% (141.4 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.65 (t, J = 6.4 Hz, 2H), 8.37 (br s, 2 H), 8.28 (t, J = 7.7 Hz, 2H), 7.79 (t, J = 4.4 Hz, 1H), 7.21 (m, 4H, obscured by solvent), 6.98 (m, 3H), 6.76 (m, 4H), 6.68 (m, 3H), 6.52 (d, J = 5.2 Hz, 1H), 5.31 (s, 1H), 4.15 (s, 1H), 4.00 (s, 2H), 3.84 (s, 1H), 3.69 (s, 1H), 3.66 (s, 1H), 3.60 (s, 1H), 3.46 (s, 1H), 2.84 (s, 1H), 1.42 (t, J = 6.3 Hz, 3H). The NMR spectrum is shown in Figure S10.

^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25 °C): δ 31.2 (d, 24 Hz), 11.0 (d, 26 Hz). The NMR spectrum is shown in Figure S11.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 136.8, 136.5, 135.8, 132.9, 131.6, 131.5, 131.4, 128.7, 128.4, 127.1, 126.8, 122.8, 75.4, 74.8, 74.7, 74.4, 74.0, 73.7, 73.6, 73.5, 73.4, 72.1, 70.9, 30.5, 14.1. The NMR spectrum is shown in Figure S12.

Elemental Analysis: $C_{42}H_{37}BrFeNiP_2$ % Calc'd(Found): C: 63.20(63.47); H: 4.67(4.45); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-trifluoromethylphenyl)(Br) (**4**)*

Yield: 63% (137.0 mg)

^{1}H NMR (*d*$_8$-toluene, 500 MHz, 25 °C): δ 8.64 (t, J = 8.3 Hz, 2H), 8.41 (br s, 1H), 8.36 (t, J = 8.8 Hz, 3H), 8.09 (t, J = 8.1 Hz, 1H), 7.22 (m, 3H, obscured by solvent), 7.12 (m, 1H), 6.99 (m, 4H), 6.78 (m, 2H), 6.66 (m, 3H), 6.45 (t, J = 6.5 Hz 1H), 5.50 (s, 1H), 4.16 (s, 1H), 4.02 (s, 1H), 3.84 (s, 1H), 3.62 (s, 1H), 3.58 (s, 1H), 3.52 (s, 1H), 3.40 (s, 1H). The NMR spectrum is shown in Figure S13.

^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25 °C): δ 31.2 (dq, J = 36 Hz, 8 Hz), 13.0 (36 Hz). The NMR spectrum is shown in Figure S14.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 136.87, 136.79, 136.59, 136.52, 135.67, 135.60, 135.51, 135.49, 135.05, 134.43, 134.14, 134.11, 133.87, 133.04, 132.99, 132.74, 131.73, 130.83, 130.23, 130.19, 128.72, 128.56, 128.52, 128.49, 128.47, 128.35, 128.22, 128.16, 128.14, 128.06, 127.98,

127.90, 127.81, 127.73, 127.61, 127.22, 127.15, 121.99, 121.98, 77.47, 77.28, 77.15, 76.44, 76.19, 75.86, 75.84, 74.84, 74.78, 73.92, 73.85, 73.46, 73.43, 72.28, 72.26, 71.05, 71.03. The NMR spectrum is shown in Figure S15.

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 470 MHz, 25 °C): δ -56.9 (d, J = 8 Hz). The NMR spectrum is shown in Figure S16.

Elemental Analysis: $C_{41}H_{32}BrF_3FeNiP_2$ % Calc'd(Found): C: 58.76(59.00); H: 3.85(4.01); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-methoxyphenyl)(Br) (**5**)*

Yield: 65% (133.6 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.73 (t, J = 9.7 Hz, 2H), 8.46 (br s, 2H), 8.36 (t, J = 11.2 Hz, 2H), 7.56 (t, J = 6.1 Hz, 1H), 7.29 (m, obscured by solvent), 7.02 (m, 3H), 6.89 (m, 3H), 6.65 (m, 4H), 5.73 (s, 1H), 5.37 (s, 1H), 4.11 (s, 1H), 4.08 (s, 1H), 3.86 (s, 1H), 3.78 (s, 1H), 3.70 (s, 1H) 3.68 (s, 1H), 3.58 (s, 1H), 3.42 (s, 3H). The NMR spectrum is shown in Figure S17.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202 MHz, 25 °C): δ 30.91 (d, J = 32 Hz), 10.14 (d, J = 34 Hz). The NMR spectrum is shown in Figure S18.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 25 °C): δ 159.37, 139.90, 139.83, 139.69, 139.61, 136.05, 135.36, 134.06, 134.01, 133.97, 133.94, 133.88, 133.86, 133.81, 131.79, 131.73, 131.30, 131.28, 128.69, 128.66, 128.48, 128.44, 128.39, 128.35, 128.31, 128.17, 128.14, 127.98, 127.73, 127.61, 127.57, 114.61, 78.37, 77.68, 77.62, 74.79, 74.69, 74.63, 74.35, 74.35, 74.25, 73.63, 73.61, 73.58, 73.56, 73.50, 72.75, 72.72, 54.87. The NMR spectrum is shown in Figure S19.

Despite repeated attempts this species did not pass elemental analysis.

*Spectroscopic Data for (dppf)Ni^{II}(2,4-xylyl)(Br) (**6**)*

Yield: 52% (108 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.66 (t, J = 6.8 Hz, 2H), 8.33 (br s, 1H), 8.26 (t, J = 9.2 Hz, 2H), 7.57 (t, J = 4.3 Hz, 1H), 7.21 (m, obscured by solvent), 6.97 (m, 3H), 6.82 (t, J = 6.7 Hz, 2H), 6.67 (m, 2H), 6.57 (d, J = 7.1 Hz, 1H), 6.28 (s, 1H), 5.26 (s, 1H), 4.15 (s, 1H), 4.02 (s, 1H), 3.84 (s, 1H), 3.72 (s, 1H), 3.67 (s, 1H), 3.60 (s, 1H), 3.45 (s, 1H), 2.84 (s, 3H), 2.08 (s, 3H). The NMR spectrum is shown in Figure S20.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202 MHz, 25 °C): δ 30.47 (d, 22 Hz), 11.12 (d, 23 Hz). The NMR spectrum is shown in Figure S21.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 151 MHz, 25 °C): δ 142.93, 136.79, 136.48, 135.75, 134.12, 133.17, 131.67, 131.36, 131.09, 129.97, 126.63, 125.03, 77.14, 75.42, 74.35, 74.04, 73.79, 73.33, 72.04, 70.97, 67.84, 27.50, 25.83, 20.51. The NMR spectrum is shown in Figure S22.

Elemental Analysis: $C_{42}H_{37}BrFeNiP_2$ % Calc'd(Found): C: 63.20(63.43); H: 4.67(4.97); N: <0.02(<0.02).

*Synthesis and Spectroscopic Data for (dppf)Ni^{II}(2-methyl-4-nitrophenyl)(Br) (**7**)*

To a 100 mL Schlenk flask containing a stir bar in a glove box was added (dppf)$Ni^0(C_2H_4)$ (**18**) (200 mg, 0.312 mmol) and 2-bromo-5-nitrotoluene (67.4 mg, 0.312 mmol, 1 equiv.). The flask was sealed and brought out onto a Schlenk line. Approximately 10 mL of toluene was added to the flask via cannula transfer, and the mixture was stirred at room temperature for one hour. After one hour, the solvent was removed under vacuum, and the resulting orange residue was triturated with methanol (3 mL) and the solid was collected by filtration. The solid was then sonicated in 3 mL of diethyl ether for 10 minutes, then filtered. The resulting solid was recrystallized from THF layered with hexanes at -15 °C.

Yield: 44% (114.3 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.52 (t, J = 8.1 Hz, 2H), 8.20 (t, J = 8.9 Hz, 2H), 8.12 (br s, 2H), 7.63 (m, 1H), 7.51 (m, 1H), 7.22 (m, J = 7.2 Hz, 6H), 7.00 (m, 2H), 6.93 (t, J = 7.0 Hz, 2H), 6.71 (m, 3H), 6.52 (t, J = 6.8 Hz, 2H), 5.11 (s, 1H), 4.11 (s, 1H), 4.05 (s, 1H), 3.83 (s, 1H), 3.63 (s, 1H), 3.58 (s, 1H), 3.55 (s, 1H), 3.38 (s, 1H), 2.78 (s, 3H). The NMR spectrum is shown in Figure S23.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 25 °C): δ 31.66 (d, J = 24 Hz), 11.75 (d, J = 26 Hz) The NMR spectrum is shown in Figure S24.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 151 MHz, 25 °C): δ 145.82, 143.17, 136.32, 136.15, 136.09, 135.66, 135.59, 133.89, 133.57, 132.69, 131.85, 130.45, 130.34, 129.44, 127.05, 126.98, 121.96, 117.71, 76.84, 75.51, 74.48, 74.09, 73.49, 72.50, 71.29, 27.48. The NMR spectrum is shown in Figure S25.

Elemental Analysis: $C_{41}H_{34}BrFeNiNO_2P_2$ % Calc'd(Found): C: 59.39(59.53); H: 4.13(4.65); N:1.69(1.42).

*Spectroscopic Data for (dppf)Ni^{II}(2-methyl-4-trifluoromethylphenyl)(Br) (**8**)*

Yield: 60% (132.3 mg)

^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.57 (t, J = 7.3 Hz, 2H), 8.22 (t, J = 6.9 Hz 2H), 7.69 (m, 1H), 7.21 (obscured by solvent), 7.04 (t, J = 7.0 Hz, 1H), 6.97 (m, 3H), 6.87 (d, J = 5.9 Hz, 1H), 6.81 (t, J = 5.9 Hz, 1H), 6.73 (m, 2H), 6.67 (m, 2H), 6.62 (s, 1H), 5.18 (s, 1H), 4.13 (s, 1H), 4.04 (s, 1H), 3.84 (s, 1H), 3.64 (s, 1H), 3.61 (s, 1H), 3.59 (s, 1H), 3.40 (s, 1H), 2.80 (s, 3H). The NMR spectrum is shown in Figure S26.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 31.72 (d, J = 29 Hz), 11.52 (d, J = 29 Hz). The NMR spectrum is shown in Figure S27.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 143.13, 136.52, 136.28, 136.21, 135.71, 135.64, 134.56, 134.44, 134.17, 134.05, 134.00, 133.82, 132.71, 132.65, 131.86, 131.72, 131.43, 130.34, 130.21, 129.08, 128.57, 128.50, 128.46, 128.35, 128.14, 127.98, 127.61, 127.07, 127.01, 124.67, 119.82, 110.41, 77.63, 77.07, 76.95, 76.21, 75.98, 75.51, 75.49, 74.51, 74.44, 74.17, 74.10, 73.96, 73.49, 73.46, 72.38, 72.36, 71.20. The NMR spectrum is shown in Figure S28.

^{19}F{^{1}H} NMR (C_6D_6, 470 MHz, 25 °C): δ -60.90 (s). The NMR spectrum is shown in Figure S29. Elemental Analysis: $C_{42}H_{34}BrF_3FeNiP_2$ % Calc'd(Found): C: 59.20(59.86); H: 4.02(4.36); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-methyl-4-methoxyphenyl)(Br) (**9**)*

Yield: 67% (142.5 mg)

^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 8.66 (t, J = 8.4 Hz, 2H), 8.35 (br s 2H), 8.28 (t, J = 8.8 Hz, 2H), 7.50j (dd, J = 4.1 Hz, J = 2.1 Hz,1H), 7.36 (s, 1H), 7.21 (obscured by solvent), 7.00 (m, 4H), 6.83 (m, 3H), 6.73 (m, 3H), 6.48 (d, J = 6.4 Hz, 1H), 6.26 (s, 1H), 5.25 (s, 1H), 4.14 (s, 1H), 4.00 (s, 1H), 3.83 (s, 1H), 3.73 (s, 1H), 3.66 (s, 1H), 3.61 (s, 1H), 3.45 (s, 1H), 3.32 (s, 3H), 2.83 (s, 3H). The NMR spectrum is shown in Figure S30.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 31.72 (d, J = 21 Hz), 11.52 (d, J = 22 Hz). The NMR spectrum is shown in Figure S31.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 136.81, 136.46, 135.77, 133.93, 133.17, 131.68, 131.40, 126.78, 117.00, 115.98, 113.26, 112.09, 111.33, 110.69, 77.09, 74.41, 74.02, 73.63, 72.00, 70.98, 54.85, 27.55, 23.10, 16.79. The NMR spectrum is shown in Figure S32.

Elemental Analysis: $C_{42}H_{37}BrFeNiOP_2$ % Calc'd(Found): C: 61.96(62.24); H: 4.58(4.25); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-methyl-5-trifluoromethylphenyl)(Br) (**10**)*

Yield: 68% (150.0 mg)

^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 8.52 (t, J = 5.6 Hz, 2H), 8.27 (t, J = 8.6 Hz, 2H), 8.17 (t, J = 6.3 Hz, 2H), 8.07 (d, J = 4.7 Hz, 1H), 7.22 (m, 4H, obscured by solvent), 7.13 (m, 3H), 6.94 (m, 5H), 6.80 (m, 2H), 6.68 (t, J = 7.0 Hz, 2H), 6.30 (d, J = 7.9 Hz, 1H), 5.12 (s, 1H), 4.18 (s, 1H), 4.11 (s, 1H), 3.86 (s, 1H), 3.63 (s, 1H), 3.58 (s, 2H), 3.41 (s, 1H), 2.90 (s, 3H). The NMR spectrum is shown in Figure S33.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 32.07 (d, J = 29 Hz), 11.44 (J = 28 Hz). The NMR spectrum is shown in Figure S34.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 157.54, 157.28, 156.98, 156.73, 146.96, 136.27, 136.19, 135.65, 135.58, 135.34, 134.96, 134.46, 134.19, 133.90, 133.66, 133.02, 132.13, 131.64, 131.33, 130.33, 130.17, 129.12, 128.56, 128.49, 128.41, 128.35, 127.19, 127.12, 125.79, 125.58, 125.13, 119.49, 77.54, 77.25, 76.77, 76.65, 76.30, 76.07, 75.36, 74.38, 74.31, 74.05, 73.31, 72.55, 71.35, 27.83. The NMR spectrum is shown in Figure S35.

^{19}F{^{1}H} NMR (C_6D_6, 470 MHz, 25 °C): δ -61.36 (s). The NMR spectrum is shown in Figure S36.

Elemental Analysis: $C_{42}H_{34}BrF_3FeNiP_2$ % Calc'd(Found): C: 59.20(59.71); H: 4.02(4.56); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2,6-xylyl)(Br) (**11**)*

Yield: 54% (111.2 mg)

Due to fluxional processes, the ^{1}H NMR spectrum was obtained at low temperature.

^{1}H NMR (*d*$_8$-toluene, 500 MHz, -50 °C): δ 9.47 (br s, 1H), 8.85 (t, J = 6.6 Hz, 3H), 7.24 (m, 4H), 7.10 (obscured by solvent), 6.88-6.78 (m, 6H), 6.64 (t, J = 7.1 Hz, 2H), 6.51 (br s, 1H), 6.29-6.22 (m, 2H), 5.67 (s, 1H), 4.22 (s, 1H), 3.80 (s, 1H), 3.77 (s, 1H), 3.61 (s, 1H), 3.53 (s, 1H), 3.44 (s, 1H), 3.39 (s, 1H), 3.30 (s, 3H), 3.18 (s, 3H). The NMR spectrum is shown in Figure S37.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 32.87 (d, J = 19 Hz); 10.94 (d, J = 19 Hz). The NMR spectrum is shown in Figure S38.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 25 °C): δ 140.52, 135.79, 134.80, 130.09, 127.32, 126.29, 123.46, 78.92, 77.10, 75.44, 75.16, 73.27, 71.97, 27.52. The NMR spectrum is shown in Figure S39.

Elemental Analysis: $C_{42}H_{37}BrFeNiP_2$ % Calc'd(Found): C: 63.20(62.73); H: 4.67(5.06); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2-trifluoromethyl-6-methylphenyl)(Br) (**12**)*

Yield: 72% (159.1 mg)

Due to fluxional processes, the ^{1}H, ^{31}P, and ^{19}F NMR spectra were obtained at low temperature. At low temperature, the species appears as two rotamers, in an approximately a 2:1 ratio. NMR data for both rotamers are reported.

^{1}H NMR (*d*$_8$-toluene, 500 MHz, -50 °C): δ 9.40 (t, J = 10.7 Hz, 2H), 9.32 (t, J = 10.0 Hz, 0.7H), 9.13 (t, J = 9.0 Hz, 0.5H), 8.86 (t, J = 6.7 Hz, 2H), 8.81 (t, J = 8.3 Hz, 1H), 7.52 (br s, 1.5H), 7.35 (t, J = 8.4 Hz, 2H), 7.23 (m, 5H), 7.03 (obscured by solvent), 6.85 (m, 8H), 6.70 (m, 5H), 6.50 (m, 3H), 6.35 (t, J = 6.6 Hz, j1H), 6.28 (d, J = 6.6 Hz, 0.6H), 6.10 (t, J = 7.9 Hz, 1H), 5.84 (s, 1H), 5.68 (s, 0.5H), 4.21 (s, 0.5H), 4.18 (s, 1H), 3.74 (s, 2H), 3.67 (s, 1H), 3.65 (s, 0.7H), 3.58 (s, 3H), 3.57 (s, 2H), 3.53 (s, 1H), 3.44 (s, 3H), 3.41 (s, 2H), 3.37 (s, 2H), 3.34 (s, 0.7H). The NMR spectrum is shown in Figure S40.

$^{31}P\{^{1}H\}$ NMR (*d*$_8$-toluene, 202 MHz, -50 °C): δ major isomer: 31.37 (dq, J = 37 Hz, 10 Hz), 12.66 (d, J = 38 Hz); minor isomer: 32.15 (d, J = 36 Hz), 13.43 (d, J = 36 Hz). The NMR spectrum is shown in Figure S41.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 151 MHz, 25 °C): δ 136.77, 135.11, 134.36, 133.73, 131.69, 131.42, 130.17, 124.52, 123.73, 122.91, 78.21, 77.94, 76.76, 76.54, 75.35, 74.82, 73.86, 73.36, 30.25. The NMR spectrum is shown in Figure S42.

$^{19}F\{^{1}H\}$ NMR (*d*$_8$-toluene, 376 MHz, -50 °C): δ major isomer: -50.2 (d, J = 10 Hz); minor isomer: -47.67 (s). The NMR spectrum is shown in Figure S43.

Elemental Analysis: $C_{42}H_{34}BrF_3FeNiP_2$ % Calc'd(Found): C: 59.20(58.89); H: 4.02(4.12); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2,6-dimethyl-4-fluorophenyl)(Br) (**13**)*

Yield: 89% (199.8 mg)

Due to fluxional processes, the ^{1}H NMR spectrum was obtained at low temperature.

^{1}H NMR (*d*$_{8}$-toluene, 400 MHz, -50 °C): δ 9.42 (br s, 2H), 8.80 (t, J = 7.2 Hz, 2H), 7.64 (dd, J = 4.5 Hz, J = 7.2 Hz, 1H), 7.22 (m, obscured by solvent), 7.11 (obscured by solvent), 6.87 (m, 4H), 6.80 (m, 3H), 6.72 (m, 2H), 6.57 (t, J = 10.6 Hz, 2H), 6.10 (m, 2H), 5.58 (s, 1H), 4.19 (s, 1H), 3.77 (s, 1H), 3.72 (s, 1H), 3.49 (s, 1H), 3.41 (s, 1H), 3.37 (s, 1H), 3.15 (s, 3H), 3.04 (s, 3H). The NMR spectrum is shown in Figure S44.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 32.64 (dd, J = 27 Hz, 2 Hz), 11.36 (dd, J = 27 Hz, 2 Hz). The NMR spectrum is shown in Figure S45.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 163.77, 162.21, 146.41, 146.17, 145.85, 145.61, 144.02, 141.02, 137.58, 135.67, 134.43, 134.17, 131.67, 130.18, 113.05, 112.95, 78.48, 78.21, 77.03, 76.80, 75.18, 73.38, 72.09, 65.94, 27.30, 15.62. The NMR spectrum is shown in Figure S46.

^{19}F{^{1}H} NMR (C_6D_6, 470 MHz, 25 °C): δ -127.62 (t, J = 10.33 Hz). The NMR spectrum is shown in Figure S47.

Elemental Analysis: $C_{42}H_{36}BrFFeNiP_2$ % Calc'd(Found): C: 61.81(62.06); H: 4.45(4.67); N: <0.02(<0.02).

Spectroscopic Data for (dppf)Ni^{II}(mesityl)(Br) ***(14)***

Yield: 75% (158.6 mg)

Due to fluxional processes, the ^{1}H NMR spectrum was obtained at low temperature.

^{1}H NMR (*d*$_{8}$-toluene, 500 MHz, -50 °C): δ 9.49 (br s, 1H), 8.85 (t, J = 7.0 Hz, 2H), 8.06 (br s, 2H), 7.24 (m, 4H), 7.10 (obscured by solvent), 6.88-6.79 (m, 6H), 6.55 (br s, 1H), 6.43 (br s, 1H), 6.17 (s, 1H), 6.02 (s, 1H), 5.66 (s, 1H), 4.21 (s, 1H), 3.79 (s, 1H), 3.76 (s, 1H), 3.60 (s, 1H), 3.55 (s, 1H), 3.44 (s, 1H), 3.39 (s, 1H), 3.25 (s, 3H), 3.13 (s, 3H), 2.16 (s, 3H). The NMR spectrum is shown in Figure S48.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25 °C): δ 32.53 (d, J = 19 Hz); 10.87 (d, J = 19 Hz). The NMR spectrum is shown in Figure S49.

^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 25 °C): δ 140.10, 135.79, 135.28, 134.97, 134.49, 131.94, 130.07, 130.07, 129.75, 127.21, 127.18, 75.43, 75.35, 75.14, 73.27, 73.21, 72.01, 71.91, 27.32, 20.35. The NMR spectrum is shown in Figure S50.

Elemental Analysis: $C_{43}H_{39}BrFeNiP_2$ % Calc'd(Found): C: 63.59(63.79); H: 4.84(4.66); N: <0.02(<0.02).

*Spectroscopic Data for (dppf)Ni^{II}(2,6-dimethyl-4-methoxyphenyl)(Br) (**15**)*

Yield: 76% (162.6 mg)

Due to fluxional processes, the ^{1}H NMR spectrum was obtained at low temperature.

^{1}H NMR (*d*$_{8}$-toluene, 500 MHz, -50 °C): δ 9.50 (br s, 1H), 8.85 (t, J = 6.9 Hz, 3H), 7.65 (dd, J = 2.9 Hz, J = 7.8 Hz, 1H), 7.23 (m, 5H), 7.10 (obscured by solvent), 6.87 (m, 4H), 6.78 (m, 4H), 6.52 (m, 3H), 6.21 (t, J = 10.3 Hz, 1H), 5.99 (s, 1H), 5.64 (s, 1H), 4.20 (s, 1H), 3.77 (s, 1H), 3.75 (s, 1H), 3.59 (s, 1H), 3.55 (s, 1H), 3.42 (s, 1H), 3.38 (s, 1H), 3.34 (s, 3H), 3.24 (s, 3H), 3.23 (s, 1H), 3.12 (s, 3H). The NMR spectrum is shown in Figure S51.

^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25 °C): δ 32.52 (d, J = 25 Hz), 11.05 (J = 25 Hz). The NMR spectrum is shown in Figure S52.

^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 25 °C): δ 158.81, 140.45, 140.05, 139.74, 139.50, 135.77, 134.75, 130.09, 128.48, 128.38, 128.35, 128.14, 127.98, 127.61, 127.27, 113.47, 113.44, 113.42, 113.40, 78.97, 78.94, 78.70, 77.42, 77.20, 75.14, 73.24, 71.95, 54.84, 27.52. The NMR spectrum is shown in Figure S53.

Despite repeated attempts this species did not pass elemental analysis.

SIII. Analysis of Catalyst Speciation in Situ via EPR Spectroscopy

General Procedure for EPR Spectroscopy

A stock solution containing naphthalen-1-yl sulfamate (0.266 mmol), naphthalene (0.133 mmol) and precatalyst (2.5 mol%, 0.00665 mmol) in 2 mL of toluene was prepared. 4-methoxyphenylboronic acid (50.0 mg, 0.333 mmol) and K_3PO_4 (127.2 mg, 0.599 mmol) were weighed into a 1-dram vial containing a stir bar. 1 mL of the stock solution was added via micropipette to the vial. The vial was tightly capped and removed from the glovebox. The vial was then placed in an aluminum heating block with a thermocouple at room temperature and stirred for 4 hours. In order to record an EPR spectrum, 61 µL of reaction mixture was removed from the catalytic reaction in a glovebox and added to an EPR tube along with 139 µL of toluene. The tube was sealed and removed from the glovebox and immediately frozen in liquid nitrogen. The EPR spectrum was then recorded.

X-Band EPR spectra were recorded at cryogenic temperatures (<15 K) on a Bruker ELEXSYS E500 EPR spectrometer equipped with a SHQ resonator and an Oxford ESR-900 helium-flow cryostat with the following settings: microwave frequency, 9.4 GHz; modulation frequency, 100 kHz; modulation amplitude, 10 G; sweep time, 84 s; conversion time, 41 ms; time constant 20 ms, power, 0.1-10 mW. The presence or absence of bromide-ligated nickel(I) species was verified by the septet hyperfine splitting pattern in $g_\perp$ from coupling to Br nuclei. Definitive identification was conducted by comparison of experimental spectra to the known spectra of (dppf)Ni^{I}Br and (dppf)Ni^{I}(sulfamate).[6] Representative comparisons are given in Figures S1A and S1B.

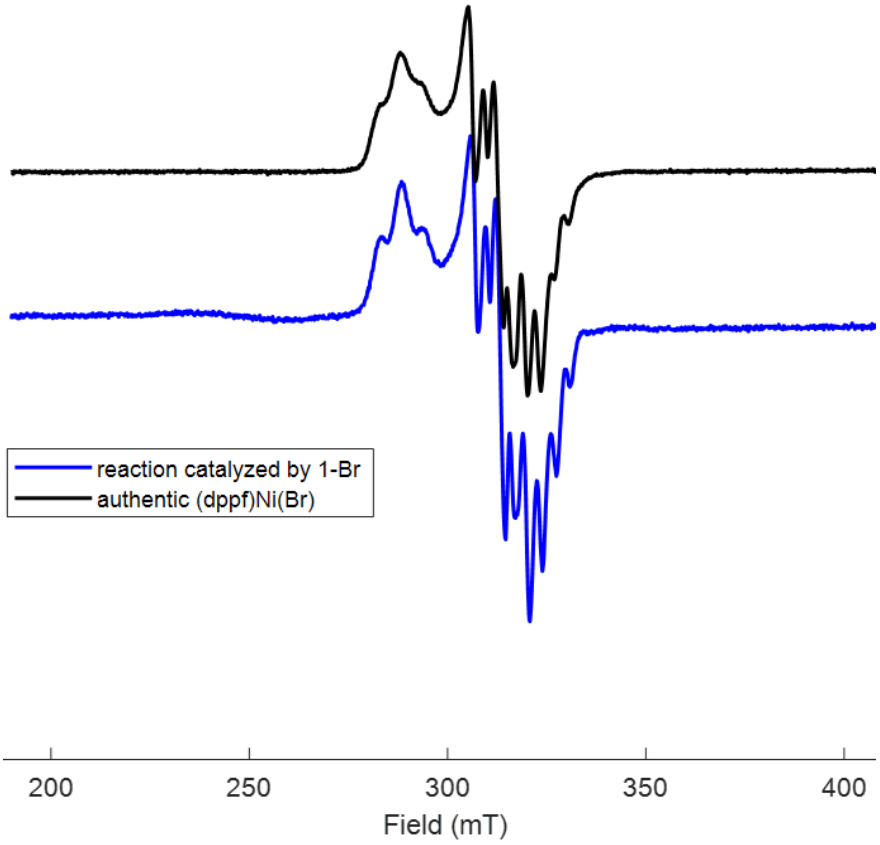


Figure S1A. Representative comparison of Ni(I) material identified by EPR spectroscopy in a reaction catalyzed by **1-Br** (blue trace) versus authentic (dppf)$Ni^{I}(Br)$[6] (black trace).

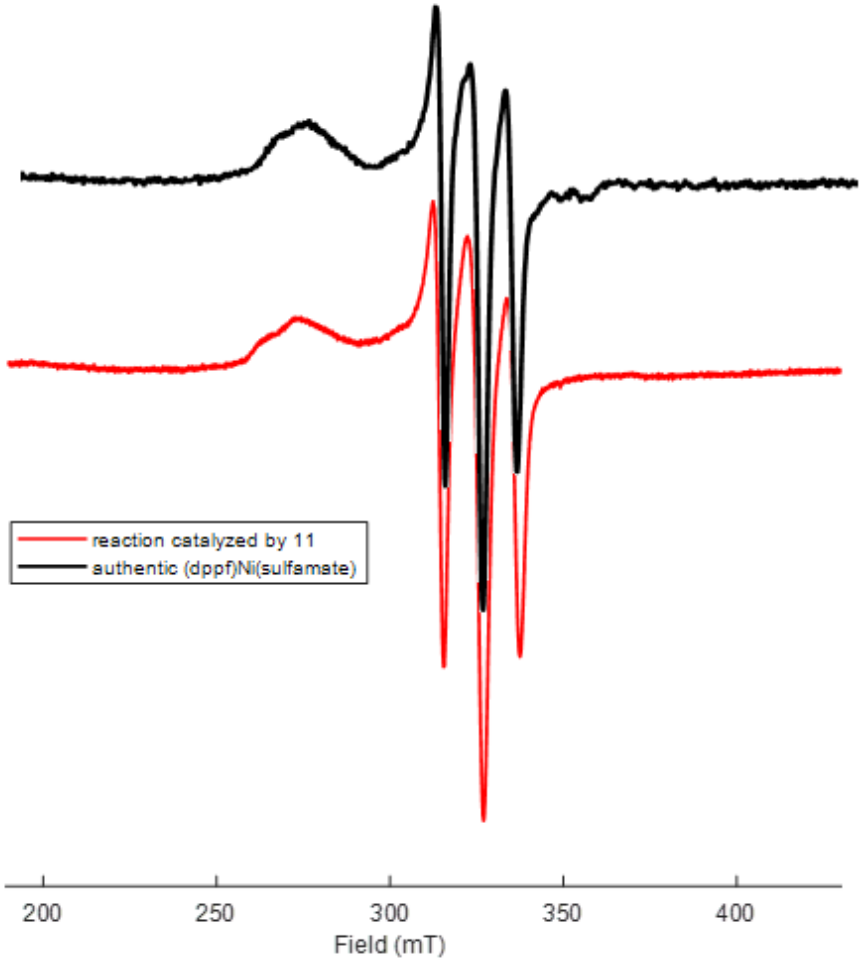


Figure S1B. Representative comparison of Ni(I) material identified by EPR spectroscopy in a reaction catalyzed by **11** (red trace) versus authentic (dppf)Ni^{I}(sulfamate)[6] (black trace).

SIV. Catalytic Performance of Precatalysts

General Procedure for Catalysis for Reactions A, A', A'', B, and D

A stock solution containing aryl sulfamate (0.266 mmol), naphthalene (0.133 mmol) and precatalyst (2.5 mol%, 0.00665 mmol) in 2 mL of toluene was prepared. Boronic acid and K_3PO_4 were weighed into a 1-dram vial containing a stir bar. 1 mL of the stock solution was added via micropipette to the vial. The vial was tightly capped and removed from the glovebox. The vial was then placed in an aluminum heating block with a thermocouple at room temperature and stirred for 4 hours. In order to prepare a GC sample, the reactions were quenched by exposure to air, after which 100-200 μL of the reaction mixture was added to a ~5 cm plug of silica and eluted with ethyl acetate. The yield of cross-coupled product was determined by gas chromatography, referenced to the naphthalene internal standard. All reactions were performed in duplicate and the reported yields are the average of two runs.

General Procedure for Catalysis for Reactions C and E

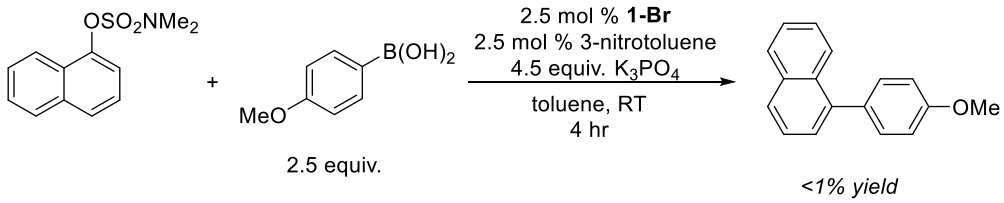
A stock solution containing aryl chloride (0.4 mmol), naphthalene (0.2 mmol) and precatalyst (2.5 mol%, 0.01 mmol) in 680 μL of 1,4-dioxane and 320 μL of benzene was prepared. Boronic acid (0.4 mmol, 2 equiv.) and K_3PO_4 (0.8 mmol, 4 equiv.) were weighed into a 1-dram vial containing a stir bar. 500 μL of the stock solution was added via micropipette to the vial. The vial was tightly capped and removed from the glovebox. The vial was then placed in an aluminum heating block with a thermocouple at room temperature and stirred for 4 hours. In order to prepare a GC sample, the reactions were quenched by exposure to air, after which 50-100 μL of the reaction mixture was added to a ~5 cm plug of silica and eluted with ethyl acetate. The yield of cross-coupled product was determined by gas chromatography, referenced to the naphthalene internal standard. All reactions were performed in duplicate and the reported yields are the average of two runs.

General Procedure for Spiking Experiments

A stock solution containing 1-naphthyl sulfamate (66.6 mg, 0.266 mmol), naphthalene (16.8 mg, 0.133 mmol, 0.5 equiv.) and precatalyst (2.5 mol%, 0.00665 mmol) in 2 mL of toluene was prepared. 4-methoxyphenylboronic acid (49.9 mg, 0.333 mmol, 2.5 equiv.) and K_3PO_4 (127.2 mg, 0.599 mmol, 4.5 equiv.) were weighed into a 1-dram vial containing a stir bar. 1 mL of the stock solution was added via micropipette to the vial. The vial was tightly capped and removed from the glovebox. The vial was then placed in an aluminum heating block with a thermocouple at room

temperature and stirred for 4 hours. Another stock solution was prepared, containing 1-naphthyl sulfamate (66.6 mg, 0.266 mmol) in 1 mL of toluene. After 4 hours, the vial was brought back into the glove box, after which 500 µL of the stock solution containing only 1-naphthyl sulfamate was added. The vial was capped tightly, removed from the glove box, and stirred in the aluminum heating block at room temperature for another 4 hours. In order to prepare a GC sample, the reactions were quenched by exposure to air, after which 50-100 µL of the reaction mixture was added to a ~5 cm plug of silica and eluted with ethyl acetate. The yield of cross-coupled product was determined by gas chromatography, referenced to the naphthalene internal standard. All reactions were performed in duplicate and the reported yields are the average of two runs.

Procedure for Catalysis in the Presence of 3-Nitrotoluene



A stock solution containing 1-naphthyl sulfamate (66.6 mg, 0.266 mmol), naphthalene (16.8 mg, 0.133 mmol, 0.5 equiv.) and **1-Br** (5.2 mg, 2.5 mol%, 0.00665 mmol) in 2 mL of toluene was prepared. 4-methoxyphenylboronic acid (49.9 mg, 0.333 mmol, 2.5 equiv.) and K_3PO_4 (127.2 mg, 0.599 mmol, 4.5 equiv.) were weighed into a 1-dram vial containing a stir bar. 1 mL of the stock solution was added via micropipette to the vial. 3-nitrotoluene (0.4 µL, 0.003325 mmol, 1 equiv. relative to precatalyst) was added to each vial via micropipette. The vial was tightly capped and removed from the glovebox. The vial was then placed in an aluminum heating block with a thermocouple at room temperature and stirred for 4 hours. In order to prepare a GC sample, the reactions were quenched by exposure to air, after which 50-100 µL of the reaction mixture was added to a ~5 cm plug of silica and eluted with ethyl acetate. The yield of cross-coupled product was determined by gas chromatography, referenced to the naphthalene internal standard. All reactions were performed in duplicate and the reported yields are the average of two runs.

SV. Correlation of Catalytic Results to % Buried Volume and Hammett Parameters

In order to determine any correlation between catalytic results and the steric/electronic effects on the precatalysts, the yields of the cross-coupled products were plotted against quantifiable metrics for either sterics or electronics. % Buried Volume was used to quantify sterics, while Hammett parameters were assigned to precatalysts substituted with moieties other than hydrogens in the para-position of the aryl group. Details regarding analyses as well as discussion of the resulting correlations are given below.

Correlation of Catalytic Results to % Buried Volume

% Buried Volume was determined using the SambVca 2.0 server[7] for all precatalysts characterized by X-ray crystallography. The coordinates for the molecules were generated from the .cif files obtained from crystallographic characterization.[4,8] The Ni atom was defined as the center of the sphere. The z-axis was defined as coincident with the Ni-Br bond, while the xz-plane was defined

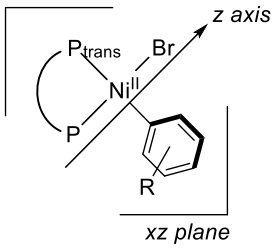


Figure S2. Definition of axes for % V_{bur} calculations.

Table S1. Tabulated % V_{Bur} for each precatalyst.

Species	% Vbur
1-Cl	92.6
2	92.7
3	93.3
4	95.1
5	92.3
6	92.7
7	92.4
8	92.5
10	93.4
12	96.4
13	95.6
14	96.6
16	97.8

as containing C_{aryl}, Ni, and Br (Figure S2). The bond radii were scaled by 1.17, and the radius of the sphere was set to 3.5 Å. Hydrogens were included in the model. The resulting % Buried Volume (% V_{Bur}) values are shown in Table S1.

Plotting yield of cross-coupled product as a function of % V_{Bur} for each reaction indicates no strong correlation between steric bulk on the precatalyst and catalytic efficiency, as indicated by regression analysis (Figure S3). For individual reactions, there is a weak correlation between sterics and catalytic efficiency. For example, the strongest correlation (R^2 = 0.2084) occurs in Reaction **B**, indicating a slight decrease in yield corresponding to an increase in steric bulk. However, this correlation is poor, and the overall conclusion from these correlations is that % V_{bur} is a poor metric in determining reaction yields for the reactions surveyed in this study.

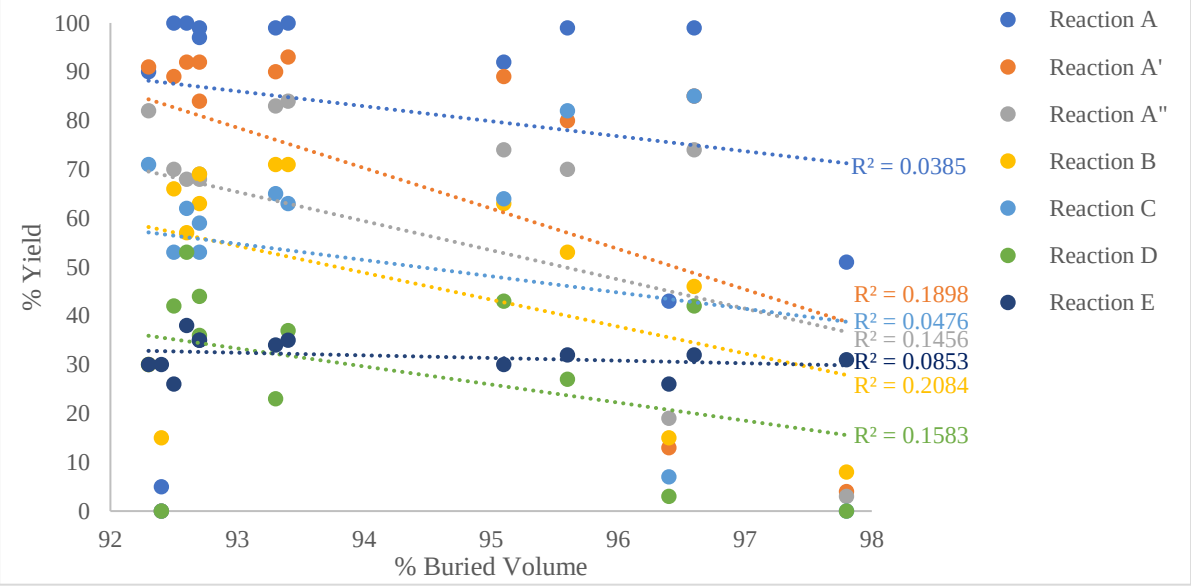


Figure S3. Regression analysis for the correlation of yield of cross-coupled product with % V_{Bur}.

Further interpretation can be conducted if precatalyst **7**, containing a nitro moiety in the 4-position, is excluded. Control experiments (*see SIV. Catalytic Performance of Precatalysts)* indicate that the nitroarene contributes to detrimental chemistry that renders **7** an inefficient precatalyst. Exclusion of the yields of **7** as an outlier in the analysis significantly improves the correlations, as determined by regression analysis (Figure S4). The slight trend now observed is that more steric bulk correlates with a lower yield of cross-coupled product for all reactions except reaction **E**. However, the correlations are still weak at best; as such, the conclusions remain the same- % V_{Bur} does not effectively track with reaction yield.

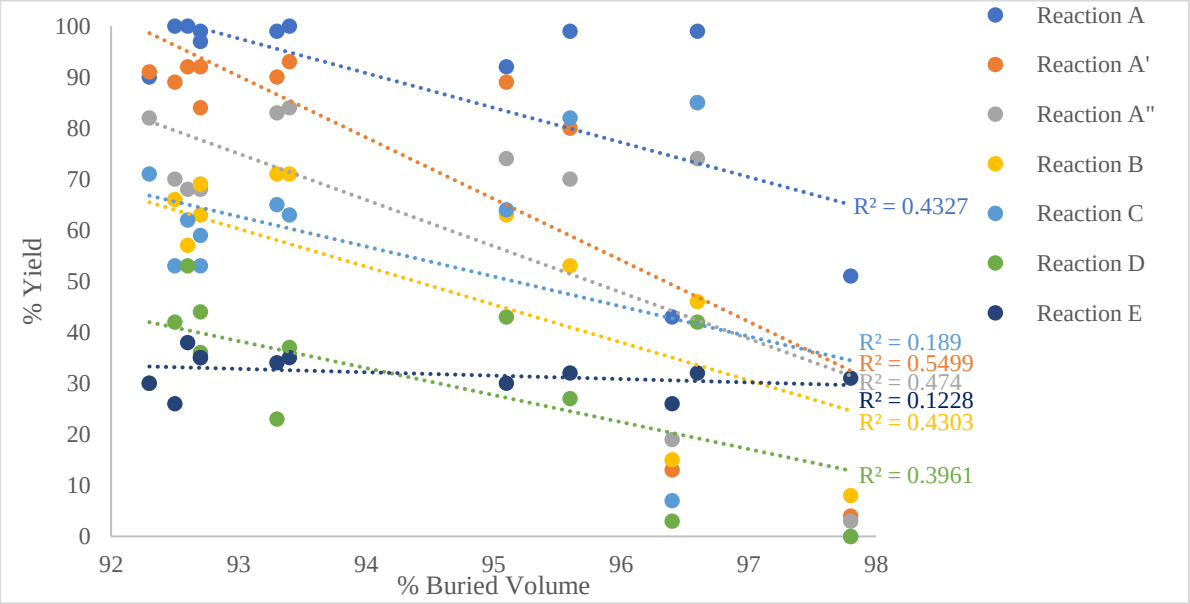


Figure S4. Regression analysis for the correlation of yield of cross-coupled product with % V_{Bur}, excluding data from **7**.

The effect of % V_{Bur} on yield can be re-evaluated by including only the nickel center and aryl unit in the calculated volume, in order to identify any possible correlation that is specifically due to the aryl group on the molecule. As such, the % V_{Bur} was recalculated, excluding every atom except the nickel center and the atoms pertaining to the appended aryl group. The defined axes in this regime are given in Figure S3, and the resulting % V_{Bur} values are given in Table S2.

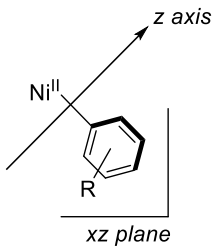


Figure S5. Definition of axes for % V_{bur} calculations, excluding all but the nickel center and aryl group.

Table S2. Tabulated % V_{Bur} for each precatalyst.

Species	% Vbur
1-Cl	37.1
2	37.0
3	37.7
4	39.7
5	36.7
6	37.6
7	37.1
8	37.5
10	37.5
12	43.2
13	41.0
14	40.9
16	42.6

Once again, there are no strong correlations between % V_{bur} and reaction yield (Figure S6). Weak negative correlations exist universally across all reactions, with the strongest correlation having an R^2 of only 0.26. The trend associated with the correlations is that an increase in steric bulk correlates with decreased reaction yields. Further, exclusion of the data of 7 also results in improved, but still weak negative correlations (Figure S7). However, the overall conclusion is that % V_{bur} is a poor predictor of reaction yield.

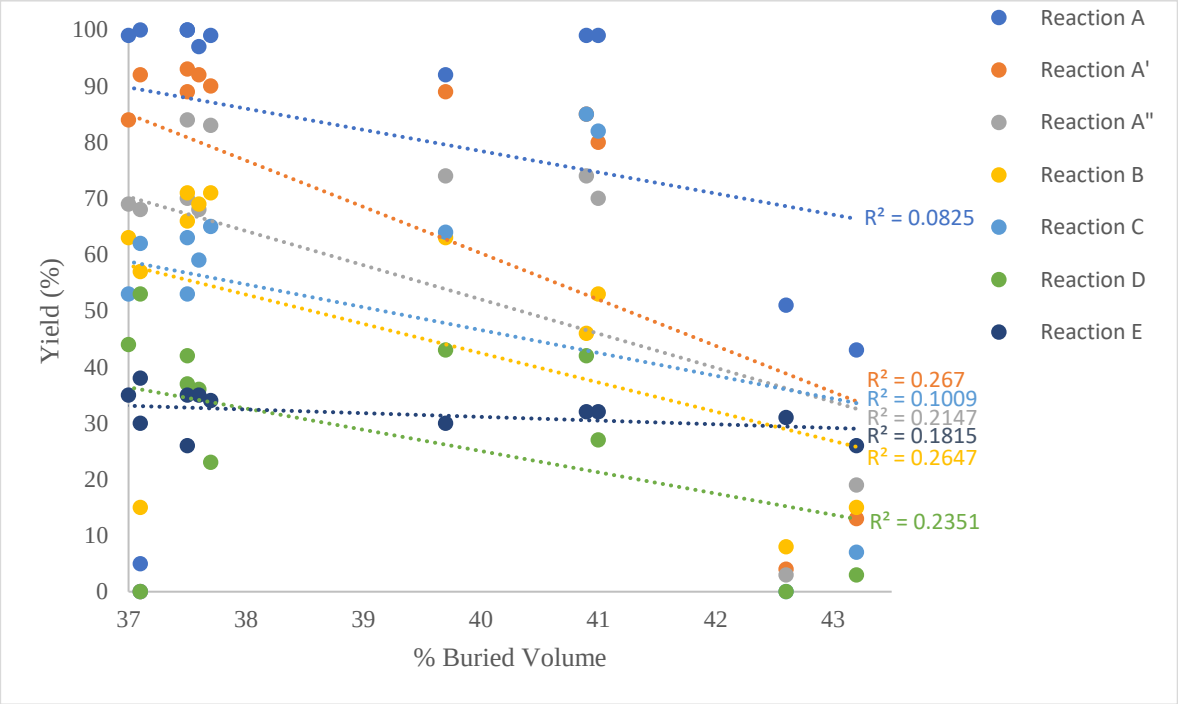


Figure S6. Regression analysis for the correlation of yield of cross-coupled product with % V_{Bur} for only the nickel and aryl atoms.

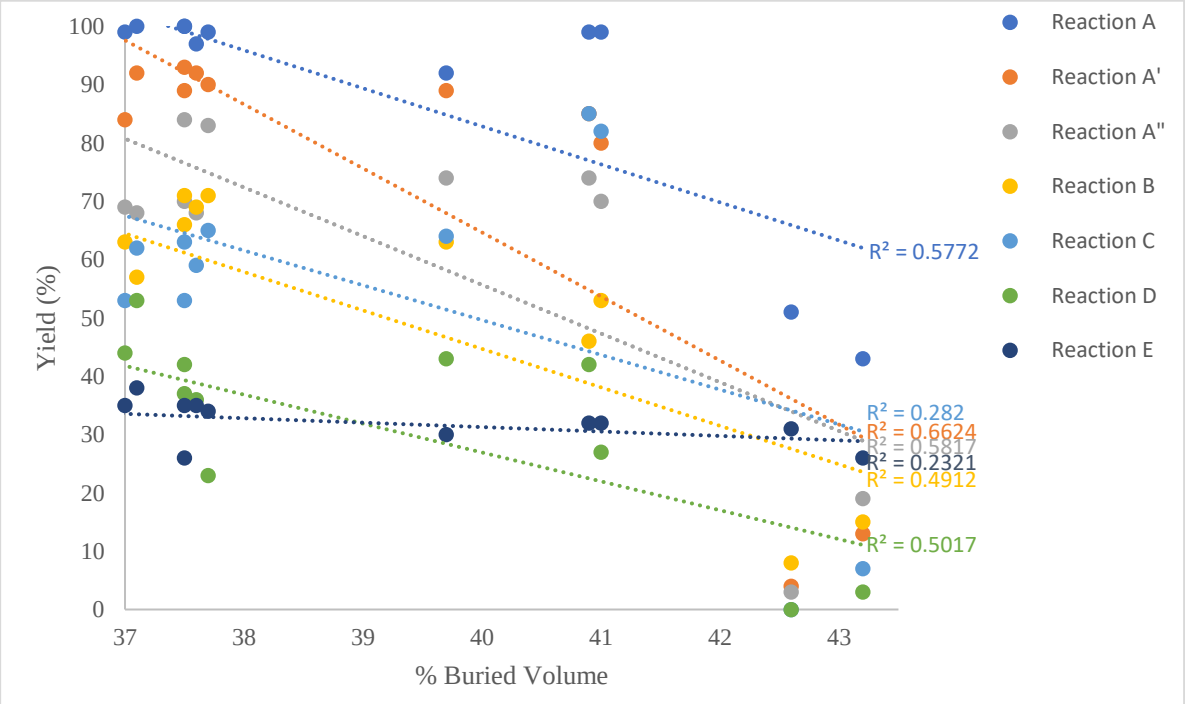


Figure S7. Regression analysis for the correlation of yield of cross-coupled product with % V_{Bur} for only the nickel and aryl atoms, excluding data from **7**.

Correlation of Catalytic Results to Hammett Parameters

In order to determine any correlations coming from Hammett parameters, a subset of the precatalyst suite was chosen. The subset contains precatalysts that are explicitly substituted in the para-position of the aryl ring- that is, the 2-, 2,5- and 2,6-substituted species were excluded from this analysis. Values for σ_p were taken from the literature.[9] The precatalysts chosen and corresponding Hammett parameters are given in Table S3.

Table S3. Tabulated Hammett parameters for 4-substituted precatalysts.

Species	σ_p
6	-0.17
7	0.78
8	0.54
9	-0.27
13	0.06
14	-0.17
15	-0.27

In agreement with the lack of correlations seen in the analysis of yield based on % V_{Bur}, there are no strong associations between Hammett parameters and yield of cross-coupled product for the reactions analyzed (Figure S8). Relatively weak correlations exist for reactions **A**, **A'**, **A"**, **C**, and **D**. The observed trend is a decrease in yield when more electron-withdrawing moieties are appended on the precatalyst. However, excluding the data originating from the performance of precatalyst **7** results in deterioration of all previous weak correlations seen in Figure S8 (Figure S9). In this regime, there are universally no correlations between electronics and reaction yield in all cases except reaction **B**. In reaction **B**, there appears to be a very weak positive correlation between electronics and reaction yield, indicating that more electron-withdrawing moieties on the precatalyst correlate with a higher reaction yield. This is more consistent with the global data from the heat map in Figure 5b, in which none of the methoxy-substituted (negative Hammett parameters) precatalysts were able to effectively catalyze reaction **B**. Overall, our results indicate that there is minimal to no association between Hammett parameters and reaction yield.

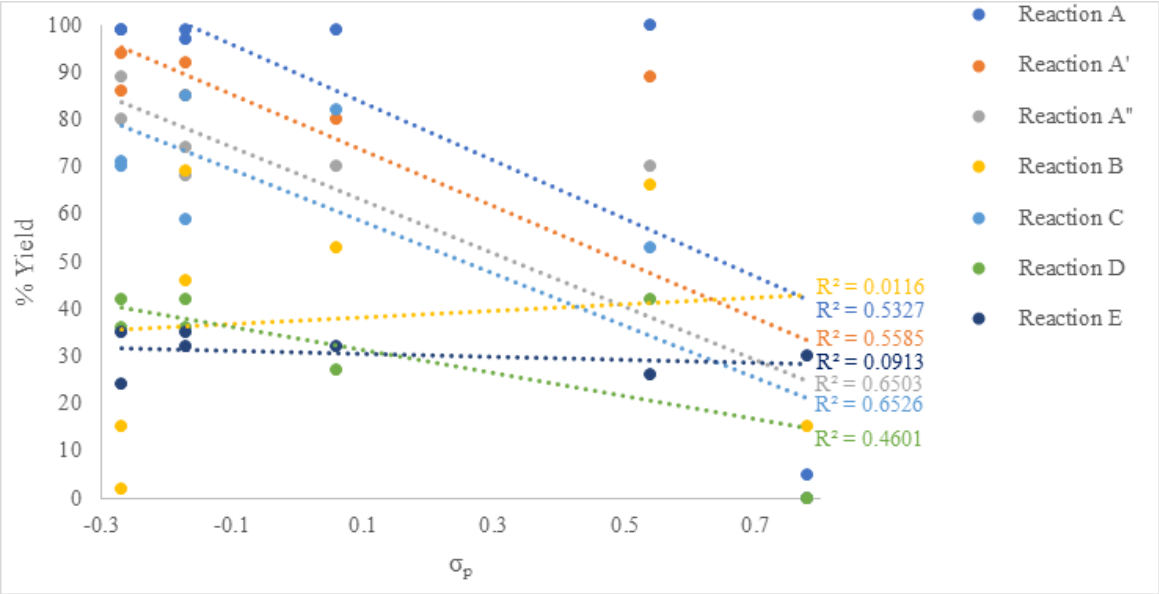


Figure S8. Regression analysis for the correlation of yield of cross-coupled product with σ_p.

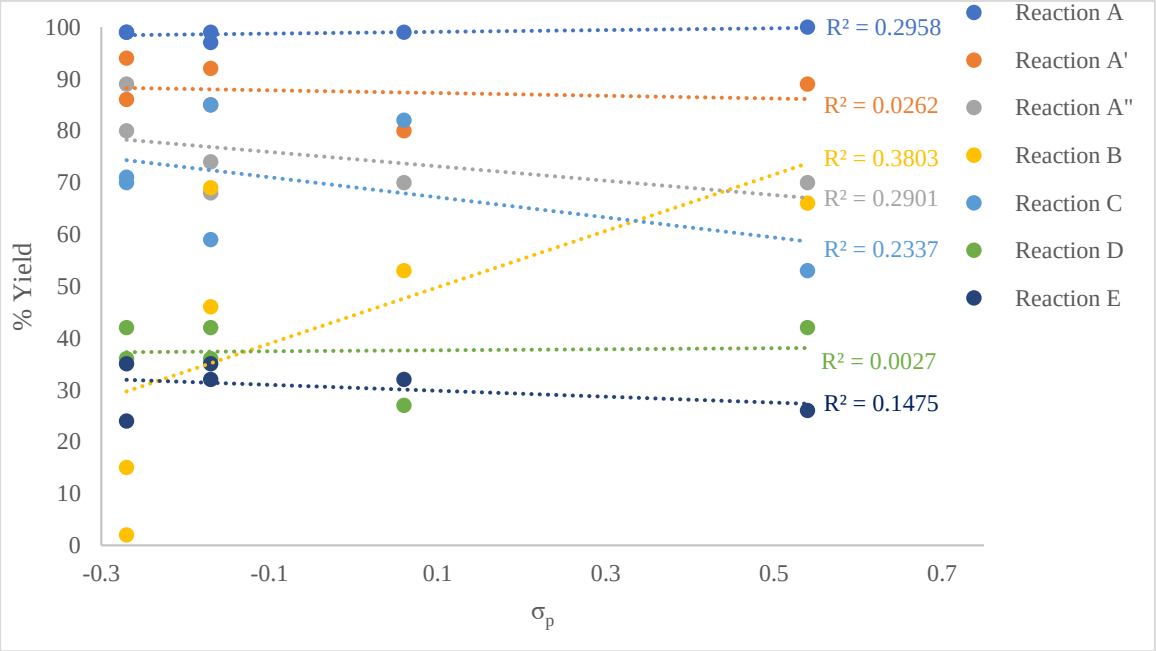


Figure S9. Regression analysis for the correlation of yield of cross-coupled product with σ_p, excluding data from **7.**

SVI. NMR Spectra

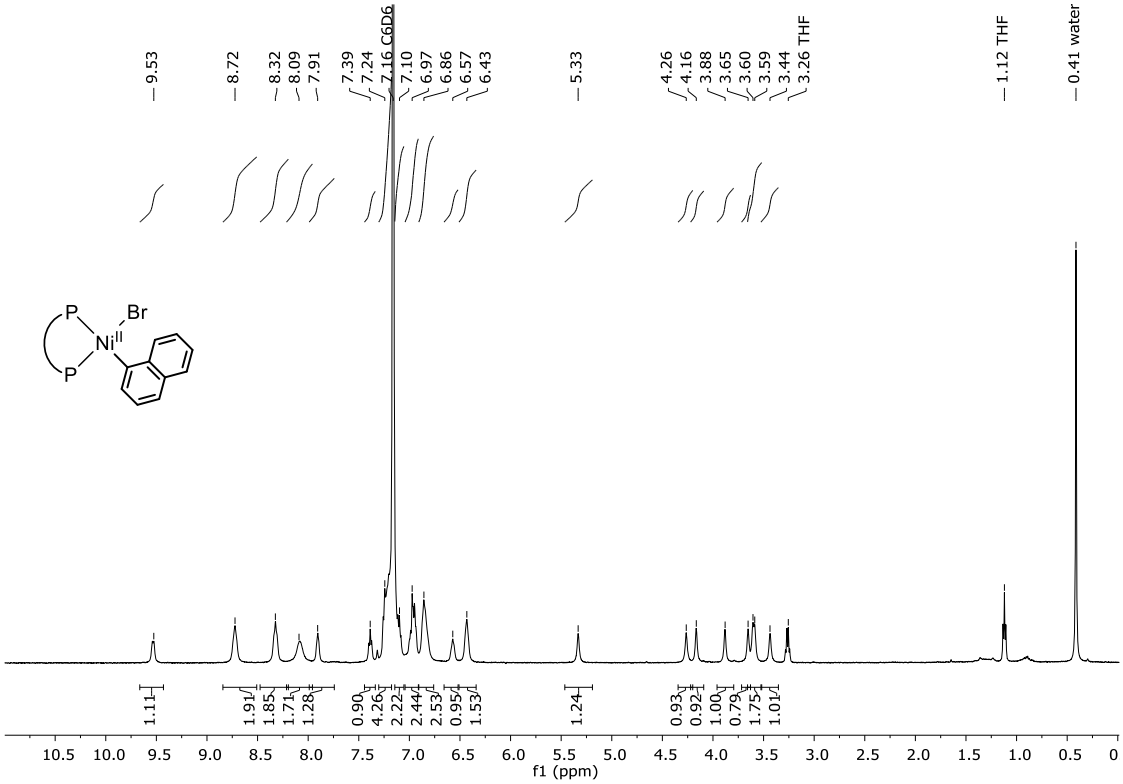


Figure S10. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(1-naphthyl)(Br), **2**.

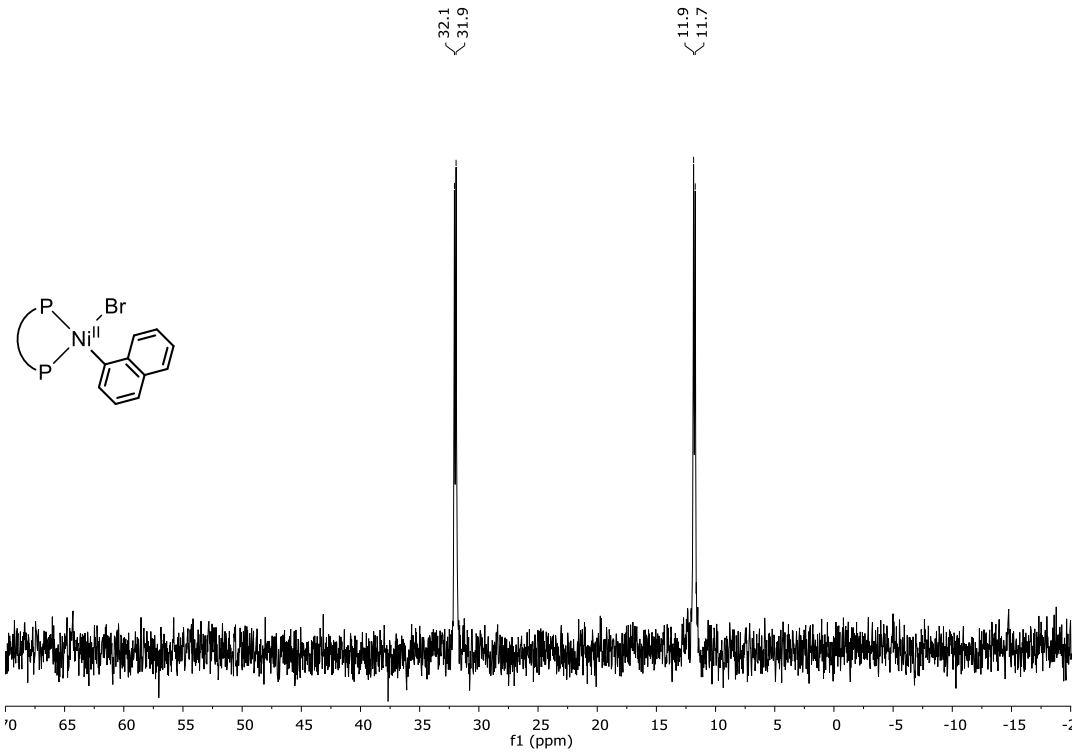


Figure S11. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(1-naphthyl)(Br), **2**.

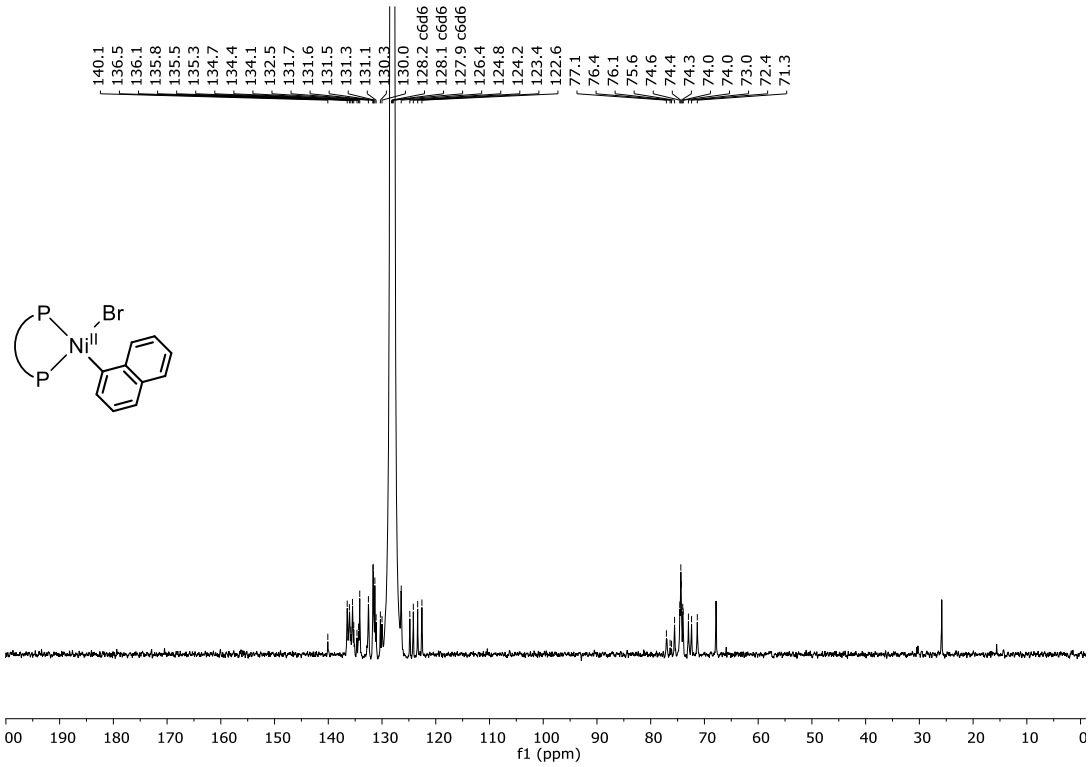


Figure S12. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(1-naphthyl)(Br), **2**.

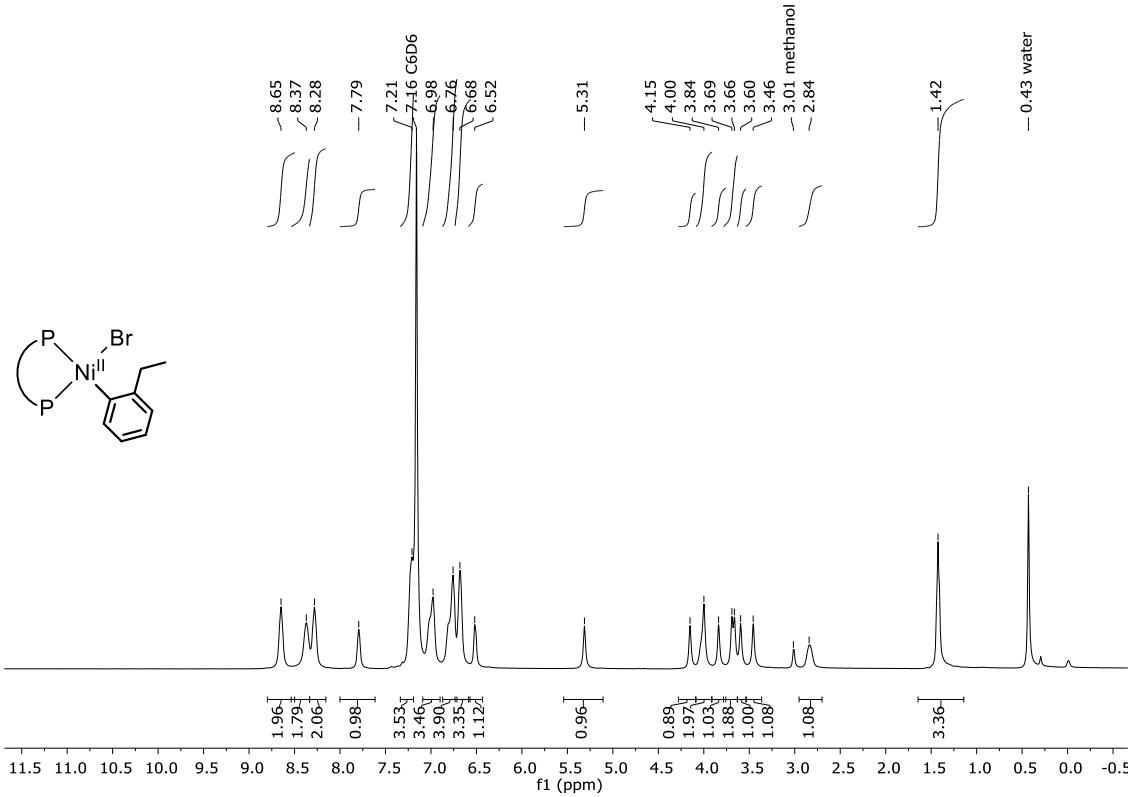


Figure S13. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-ethylphenyl)(Br), **3**.

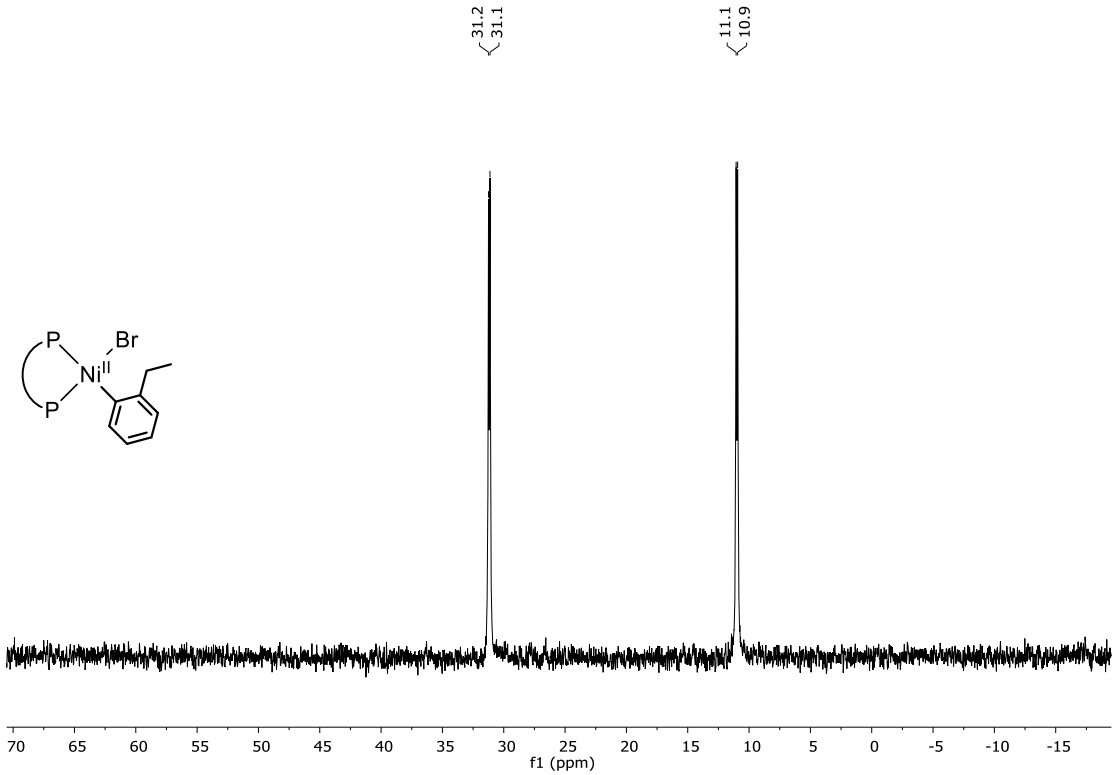


Figure S14. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-ethylphenyl)(Br), **3**.

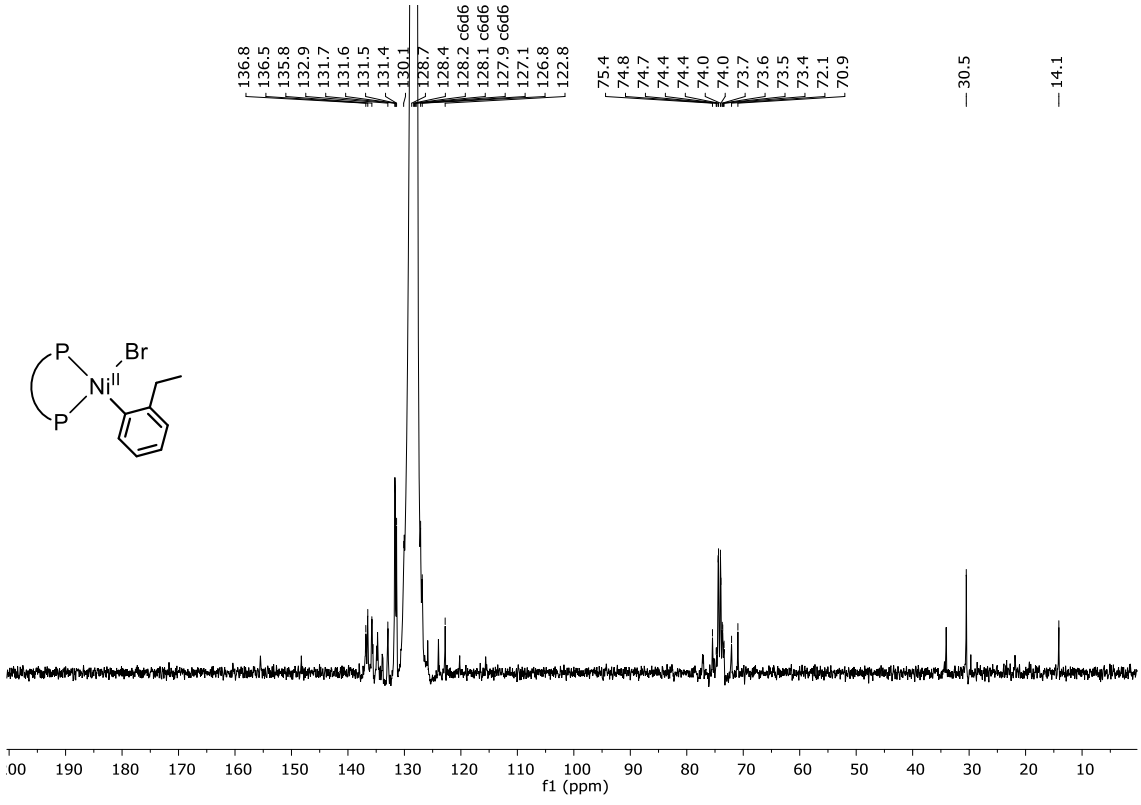


Figure S15. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-ethylphenyl)(Br), **3**.

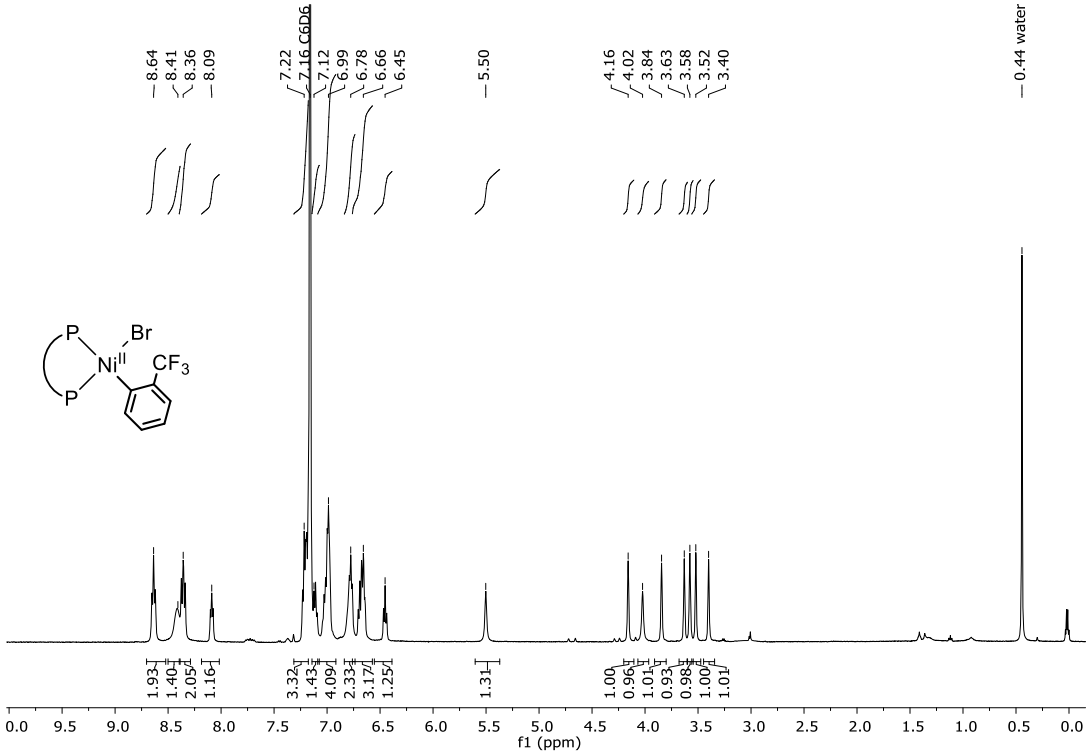


Figure S16. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-trifluoromethylphenyl)(Br), **4**.

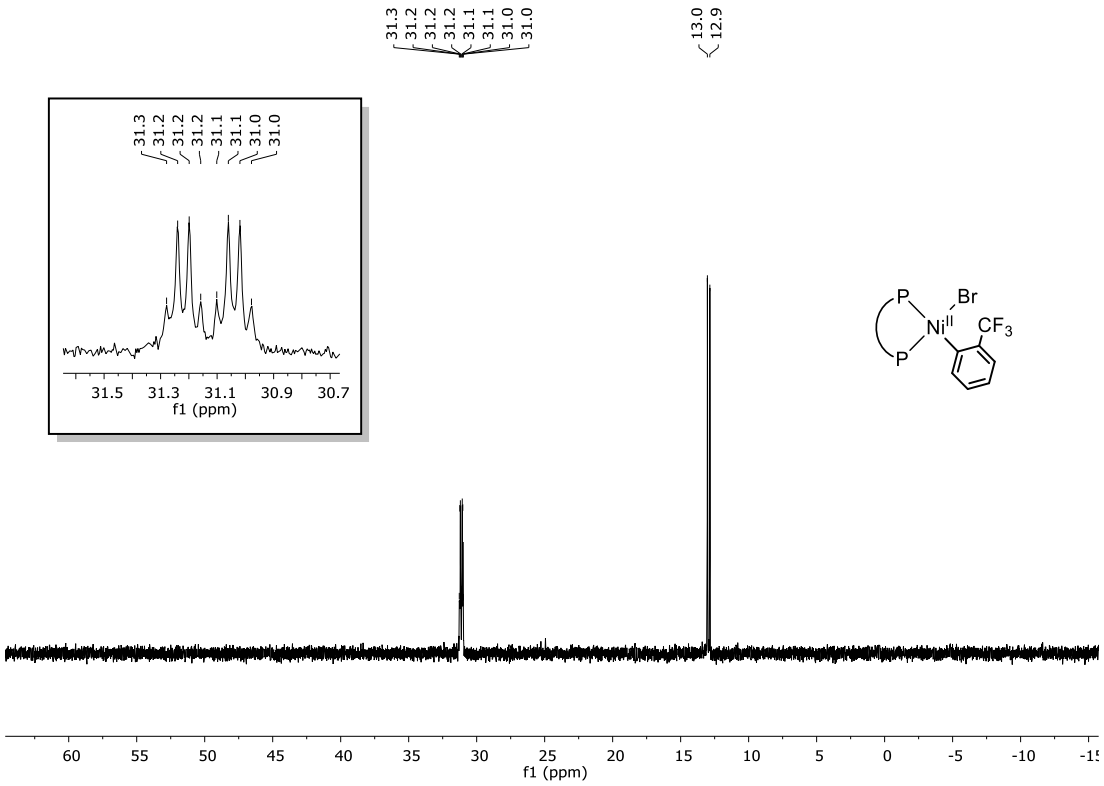


Figure S17. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-trifluoromethylphenyl)(Br), **4**.

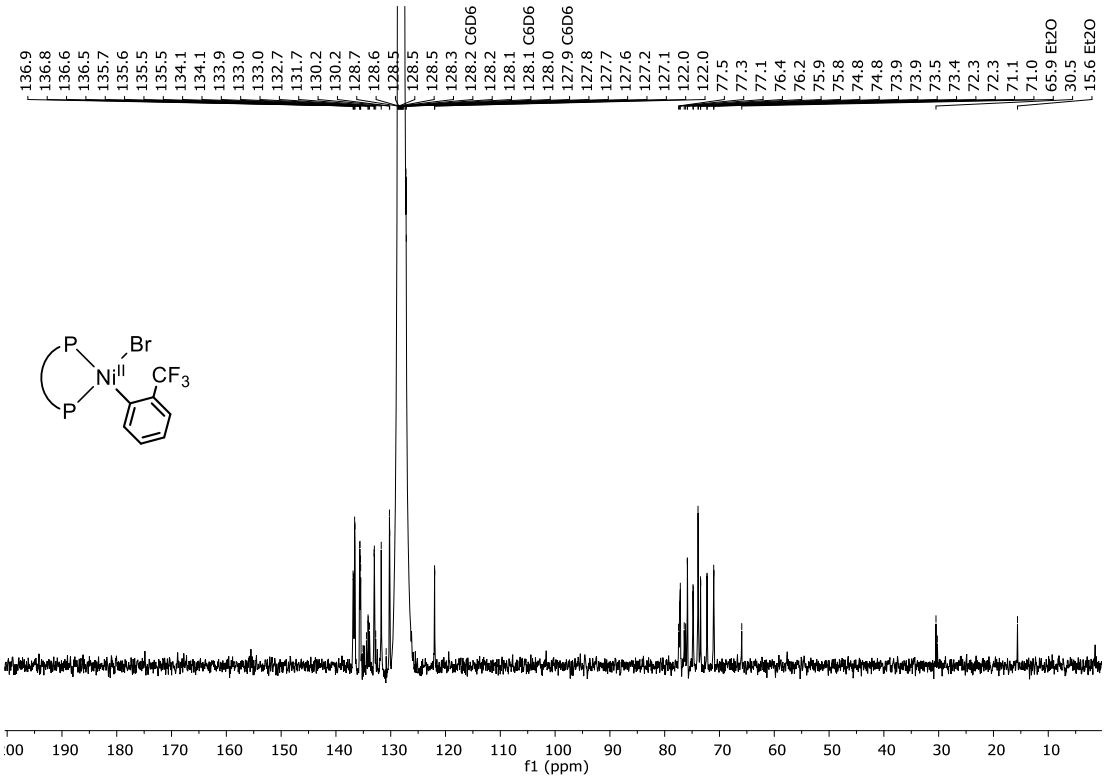


Figure S18. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-trifluoromethylphenyl)(Br), **4**.

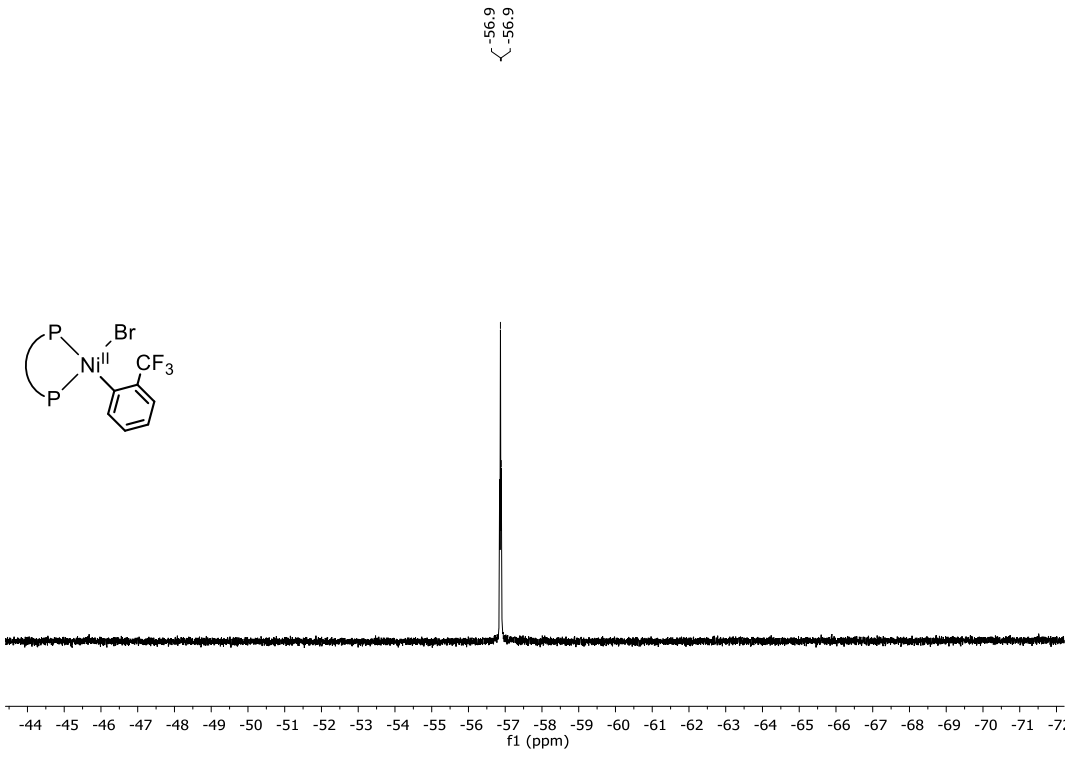


Figure S19. ^{19}F NMR spectrum (C_6D_6, 470 MHz, 25 °C) of (dppf)Ni^{II}(2-trifluoromethylphenyl)(Br), **4**.

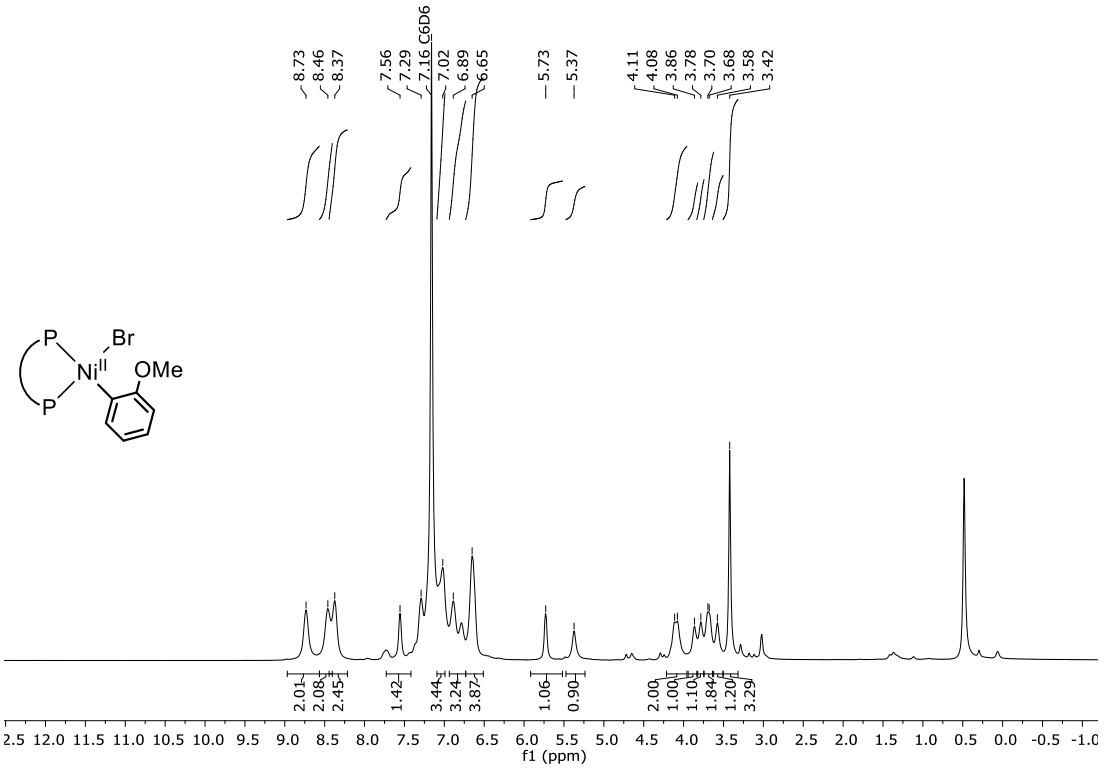


Figure S20. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-methoxyphenyl)(Br), **5**.

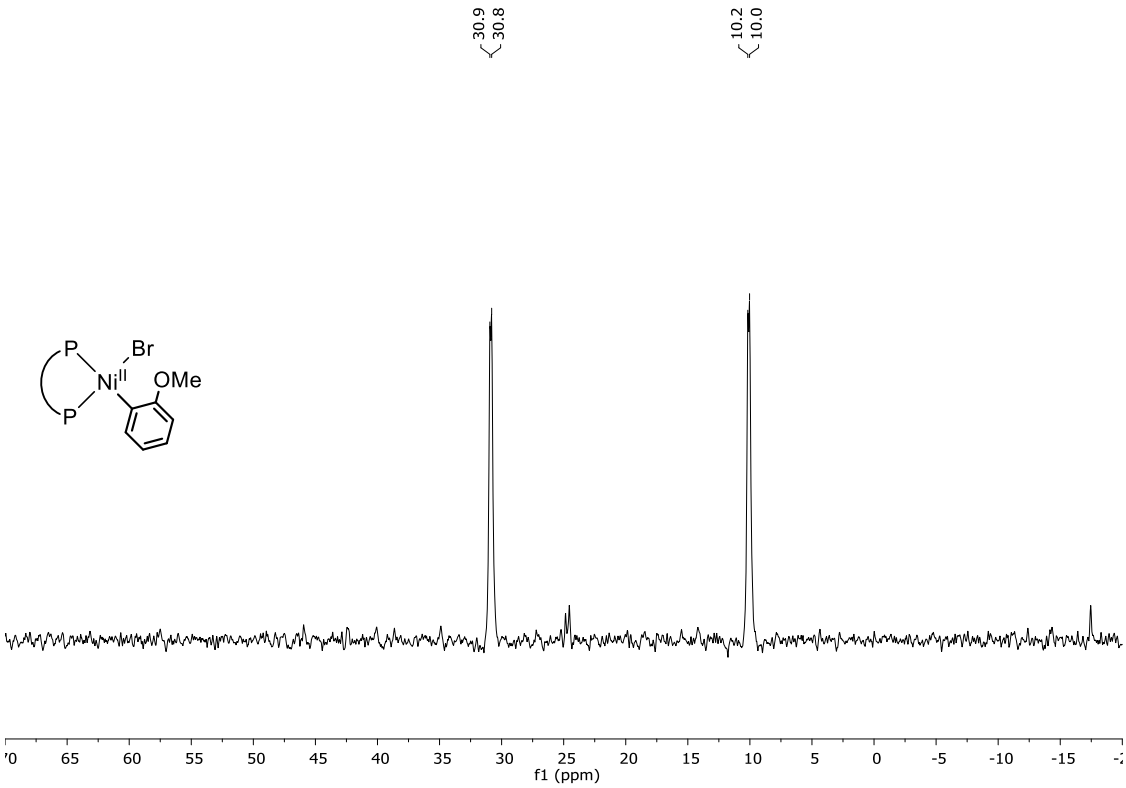


Figure S21. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-methoxyphenyl)(Br), **5**.

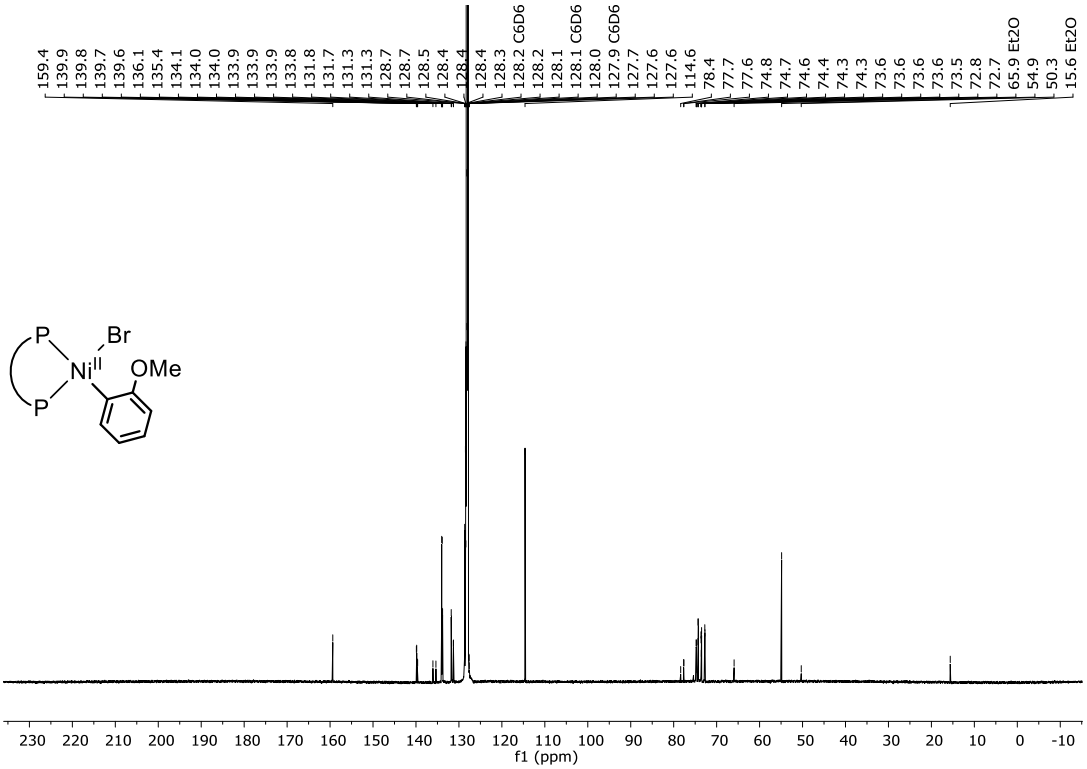


Figure S22. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-methoxyphenyl)(Br), **5**.

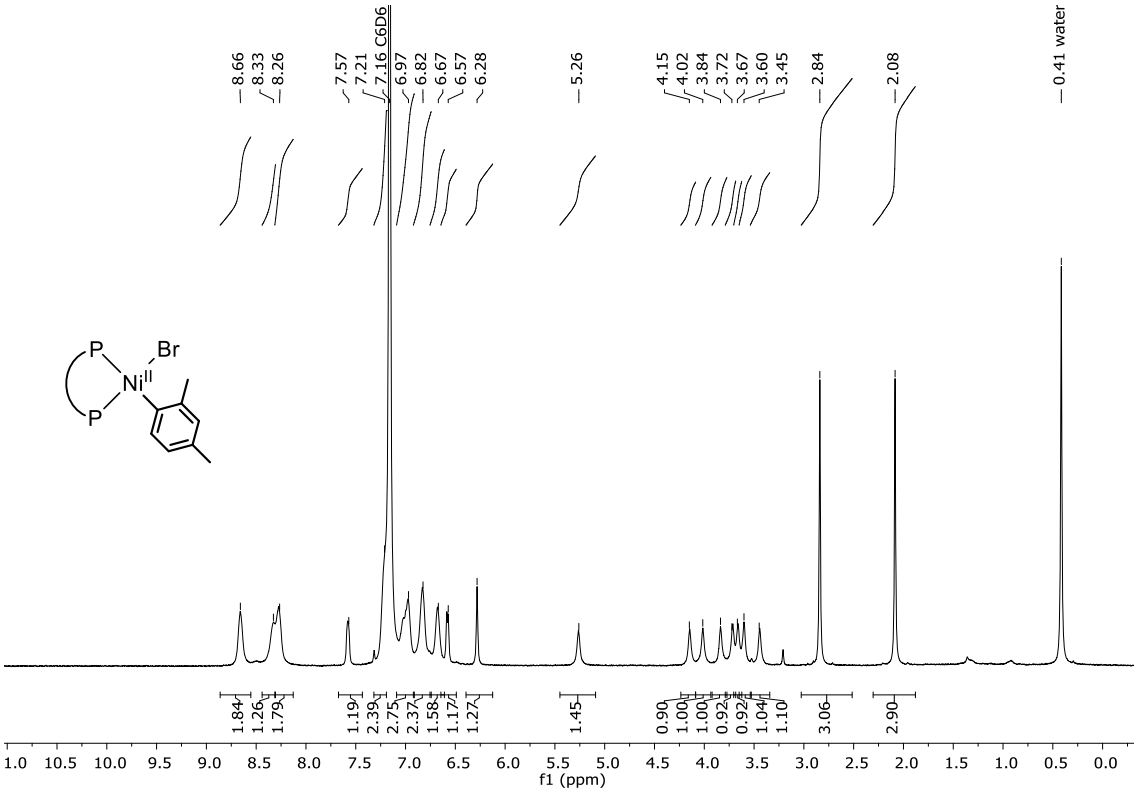


Figure S23. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2,4-xylyl)(Br), **6**.

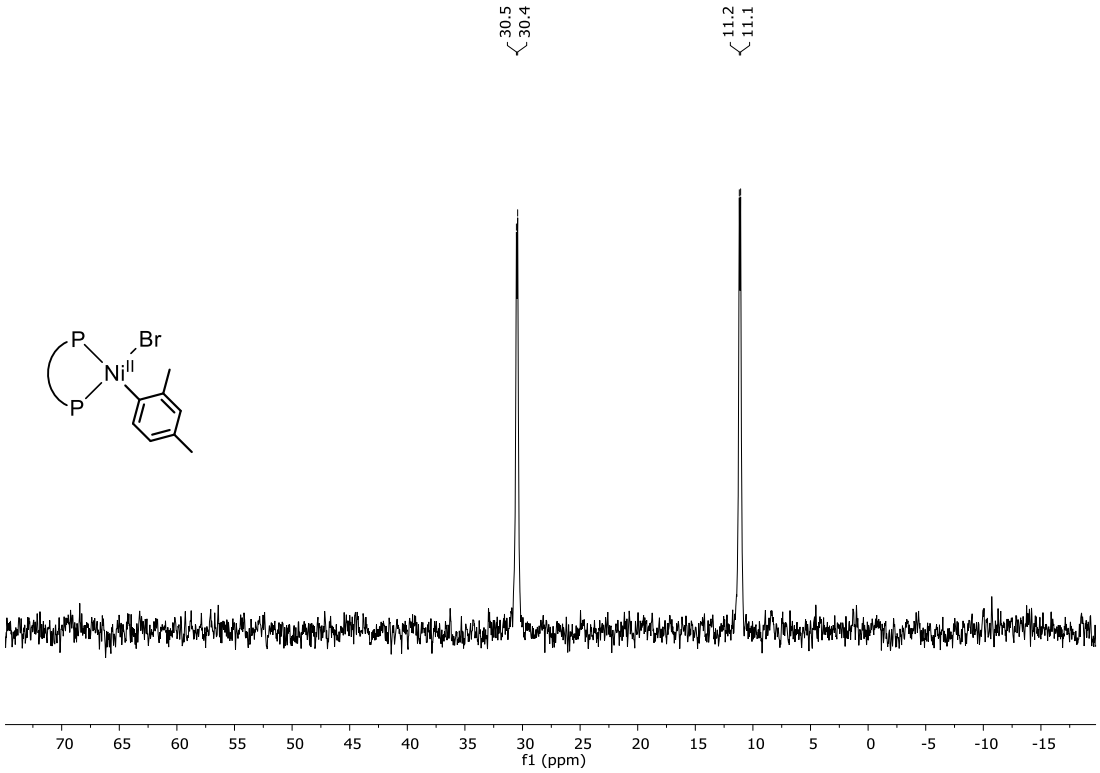


Figure S24. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2,4-xylyl)(Br), **6**.

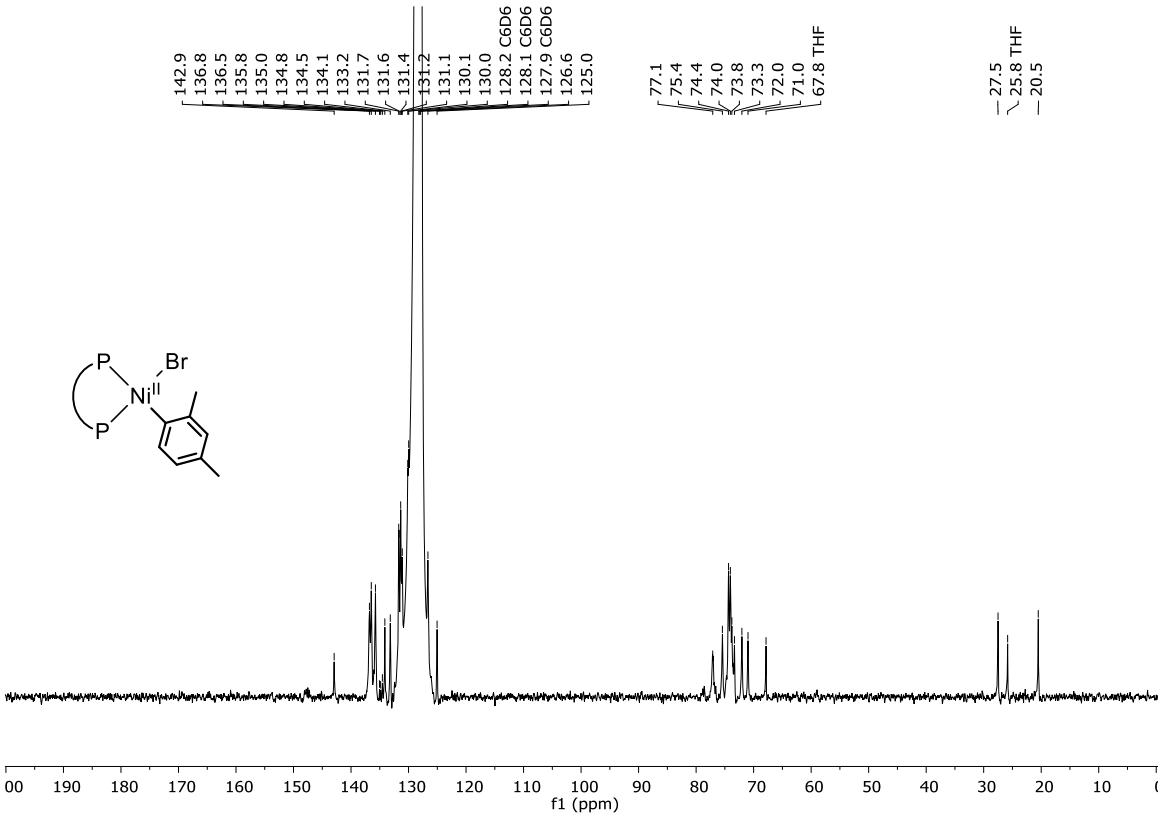


Figure S25. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2,4-xylyl)(Br), **6**.

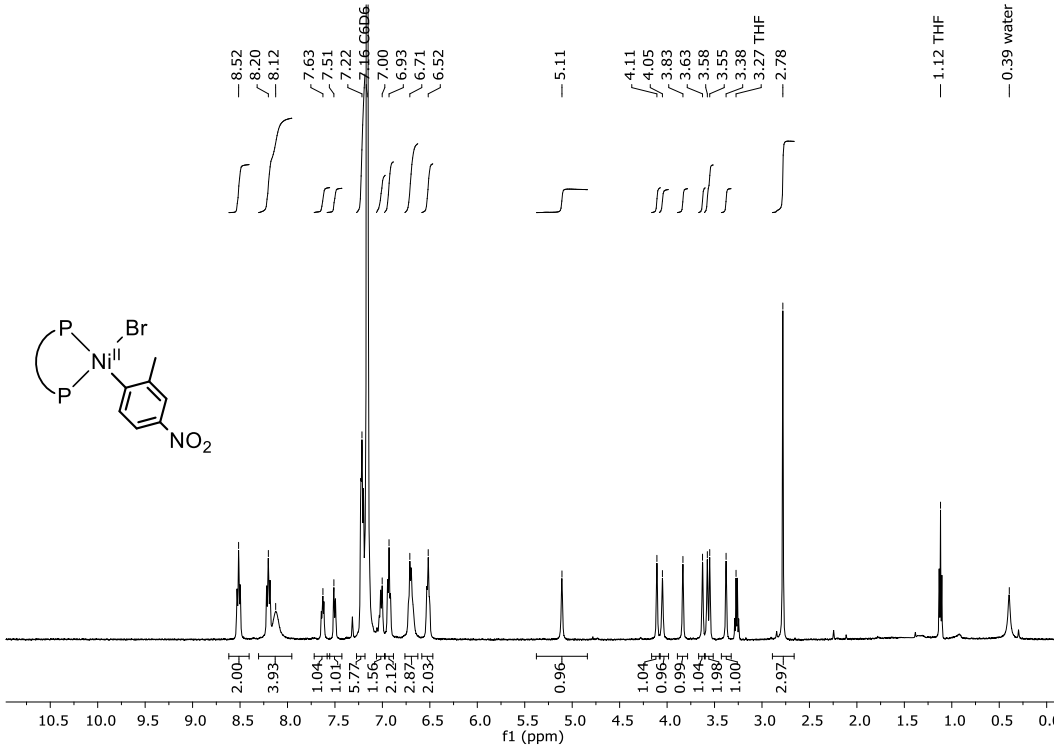


Figure S26. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-nitrophenyl)(Br), **7**.

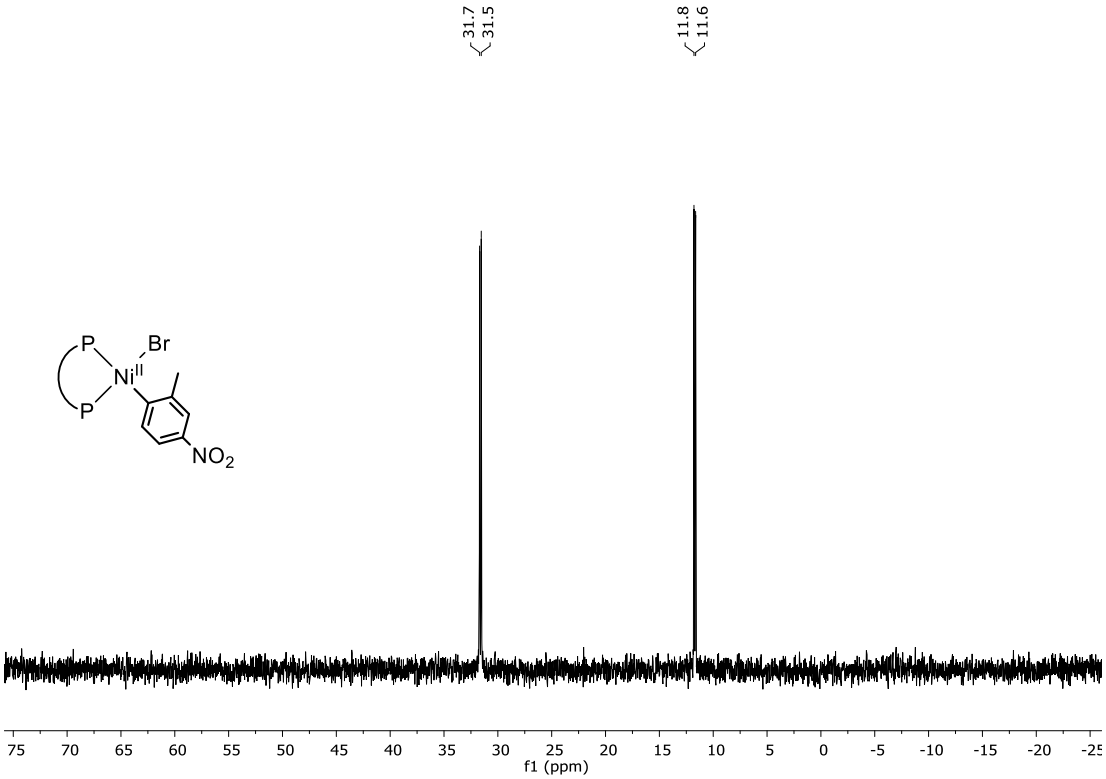


Figure S27. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-nitrophenyl)(Br), **7**.

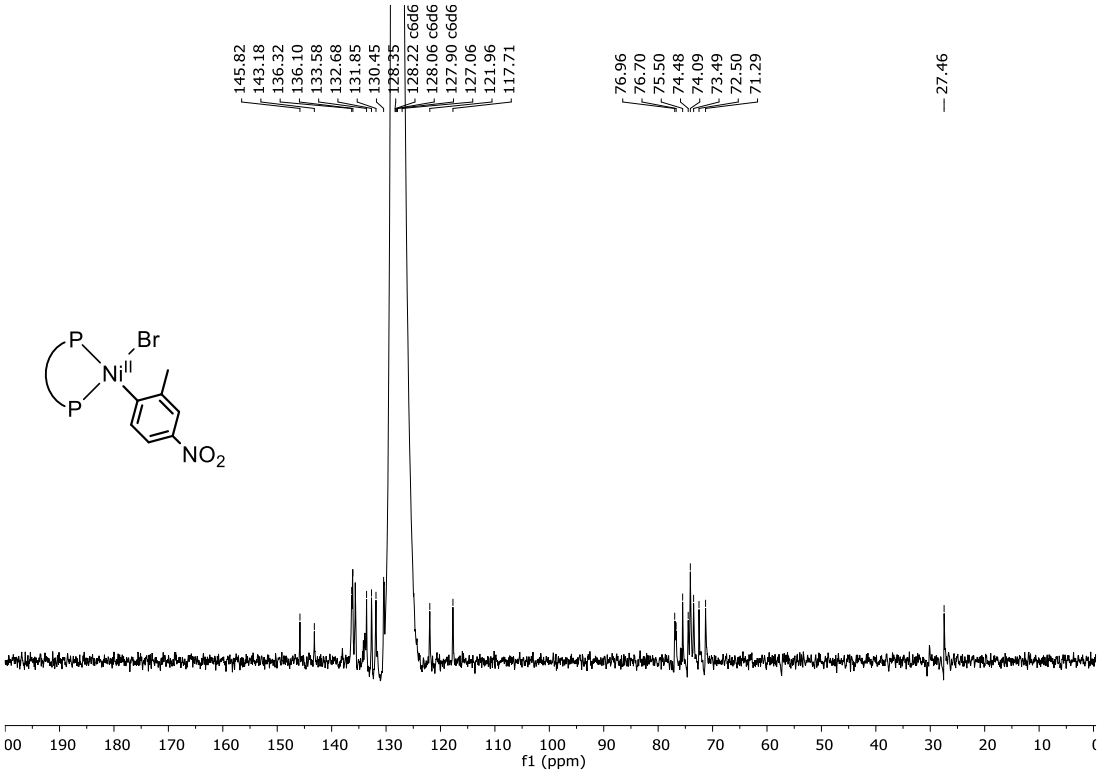


Figure S28. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-nitrophenyl)(Br), **7**.

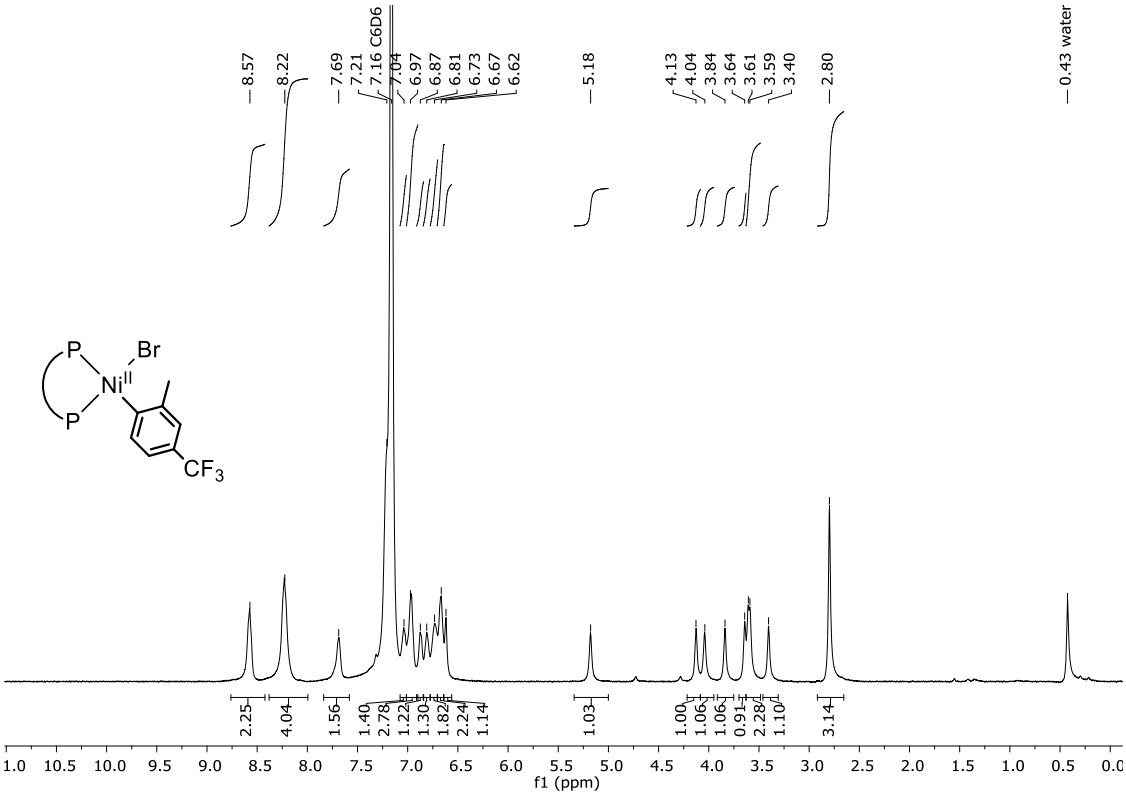


Figure S29. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-trifluoromethylphenyl)(Br), **8**.

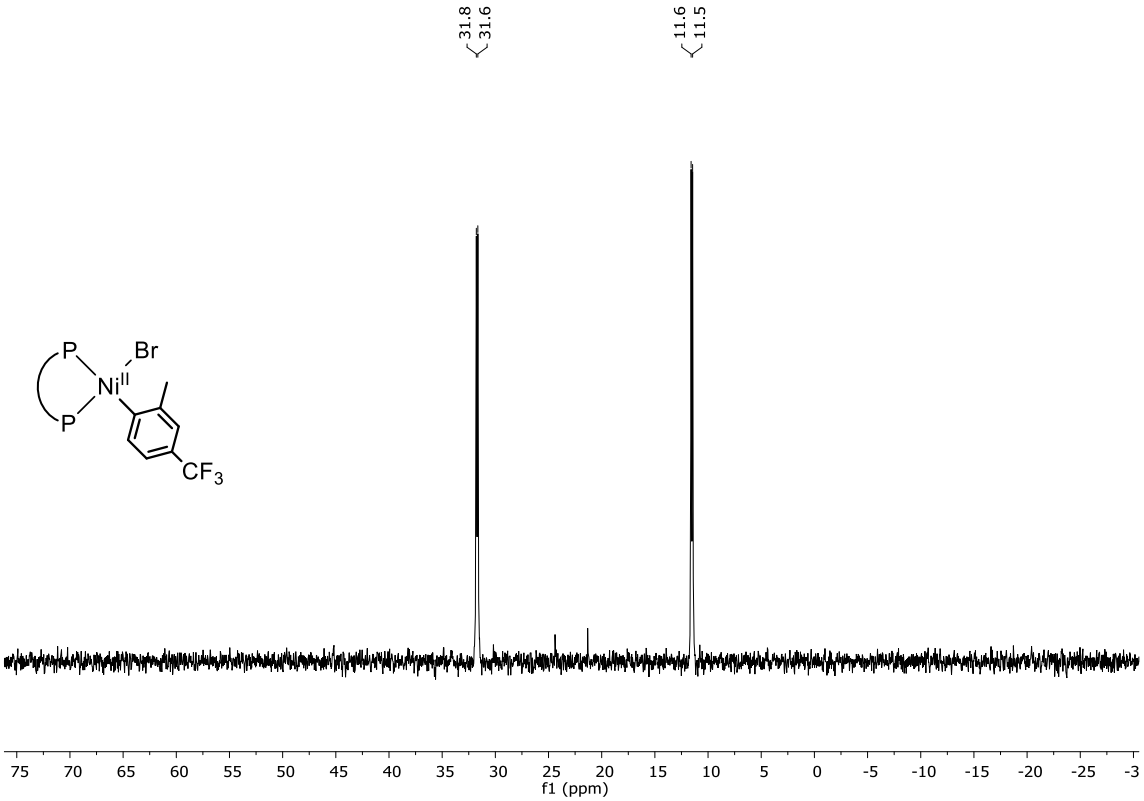


Figure S30. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-trifluoromethylphenyl)(Br), **8**.

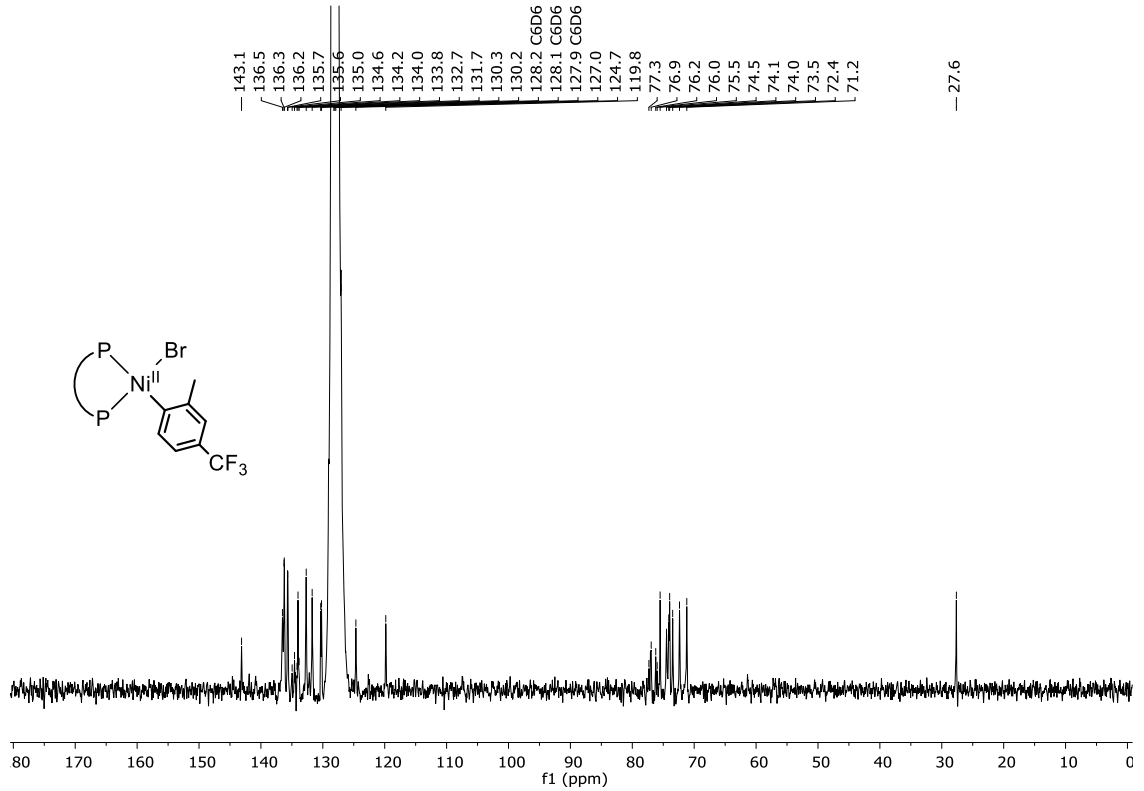


Figure S31. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-trifluoromethylphenyl)(Br), **8**.

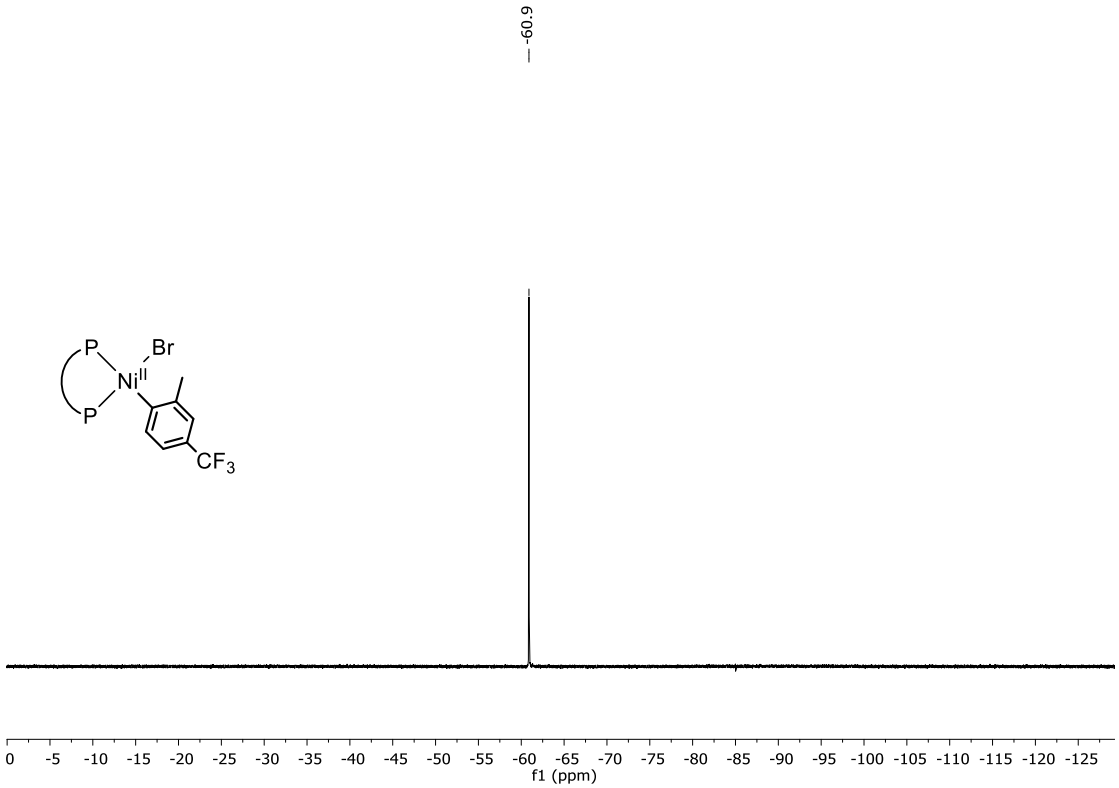


Figure S32. ^{19}F NMR spectrum (C_6D_6, 470 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-trifluoromethylphenyl)(Br), **8**.

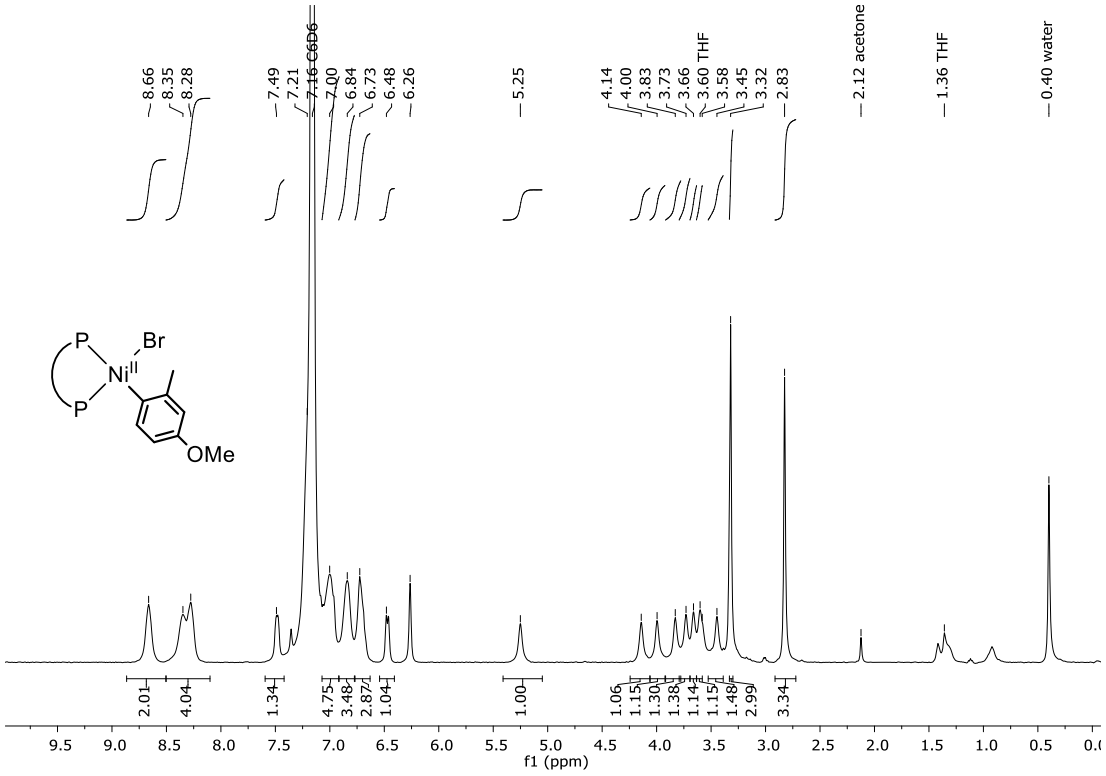


Figure S33. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-methoxyphenyl)(Br), **9**.

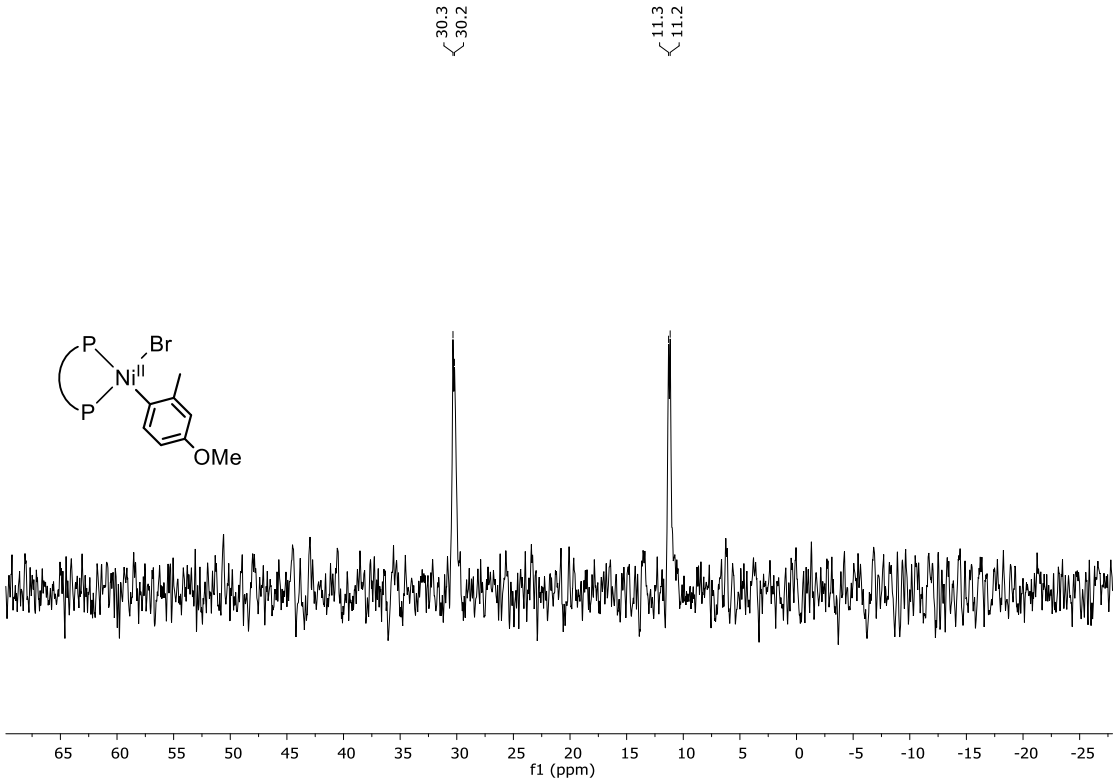


Figure S34. ^{31}P NMR spectrum (C_6D_6, 162 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-methoxyphenyl)(Br), **9**.

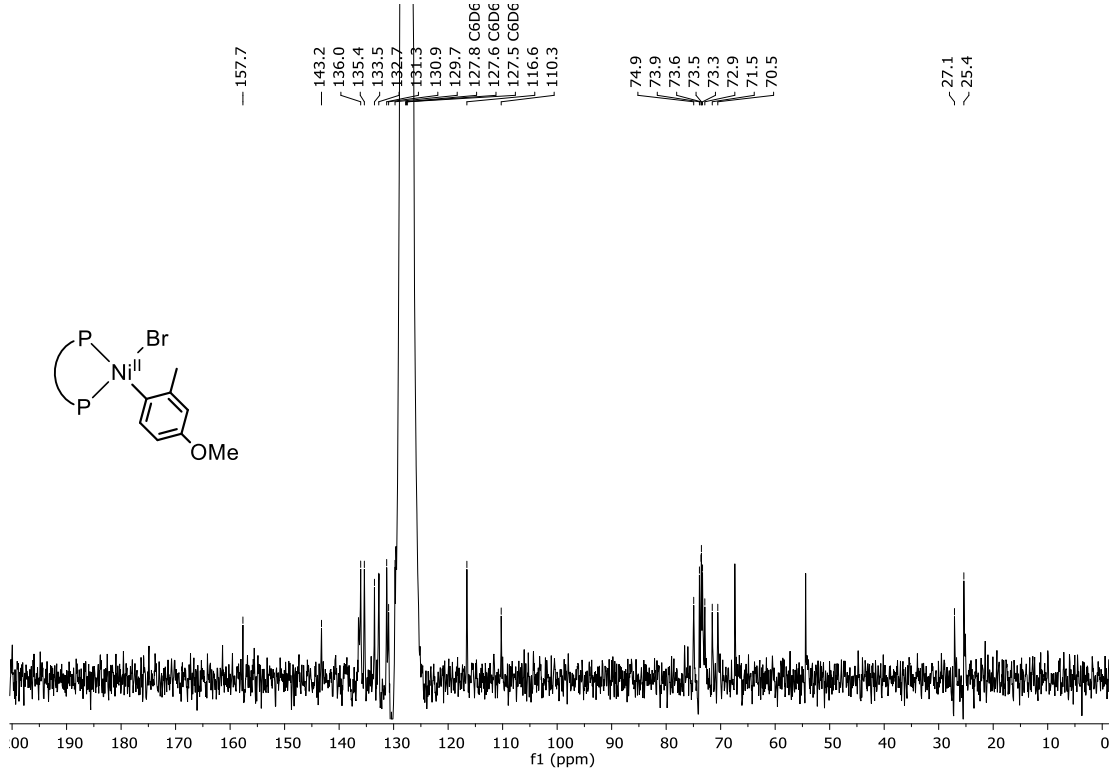


Figure S35. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-4-methoxyphenyl)(Br), **9**.

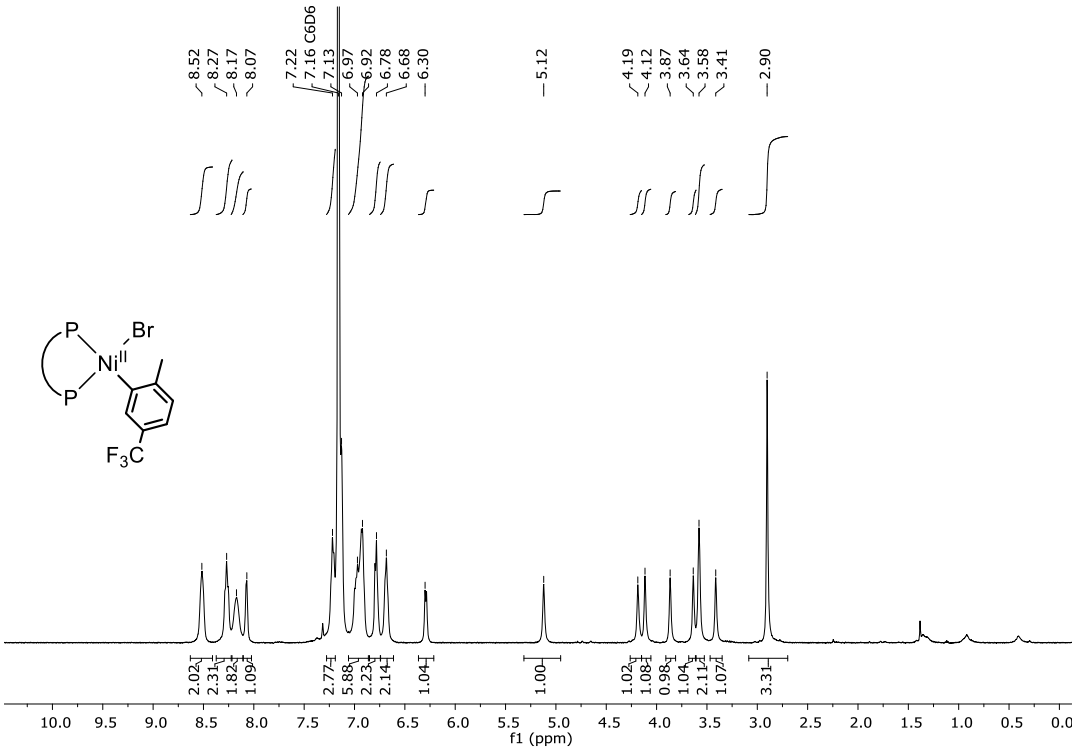


Figure S36. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-5-trifluoromethylphenyl)(Br), **10**.

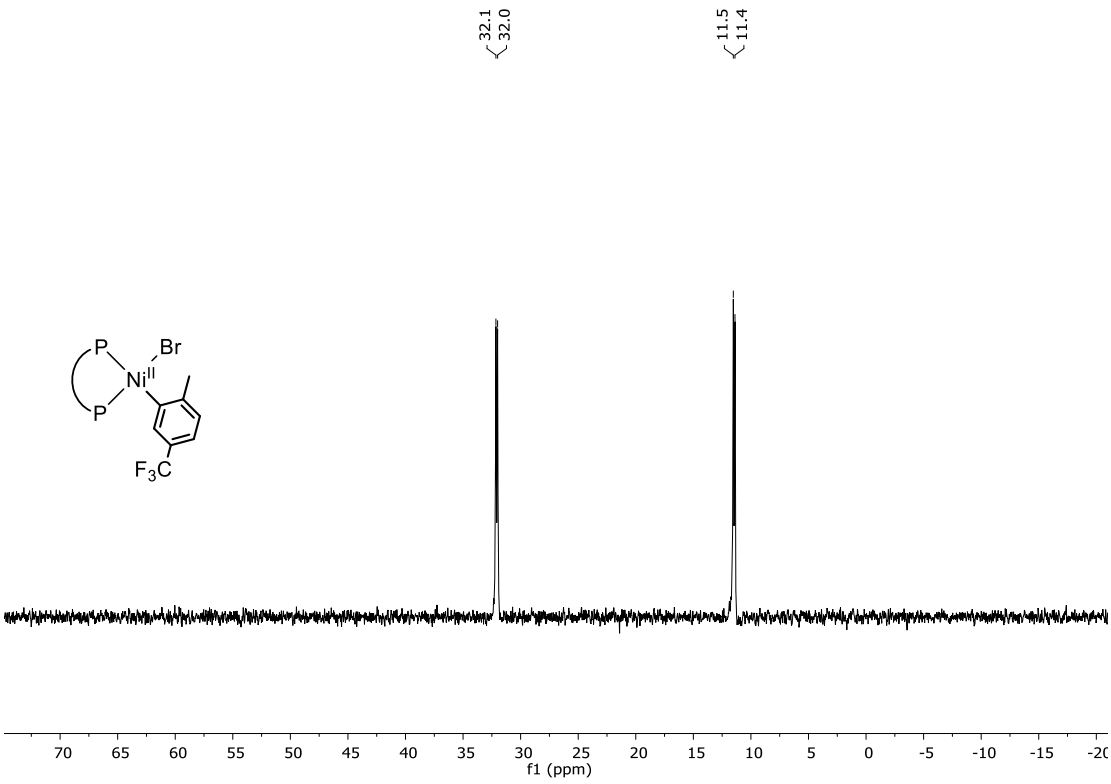


Figure S37. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-5-trifluoromethylphenyl)(Br), **10**.

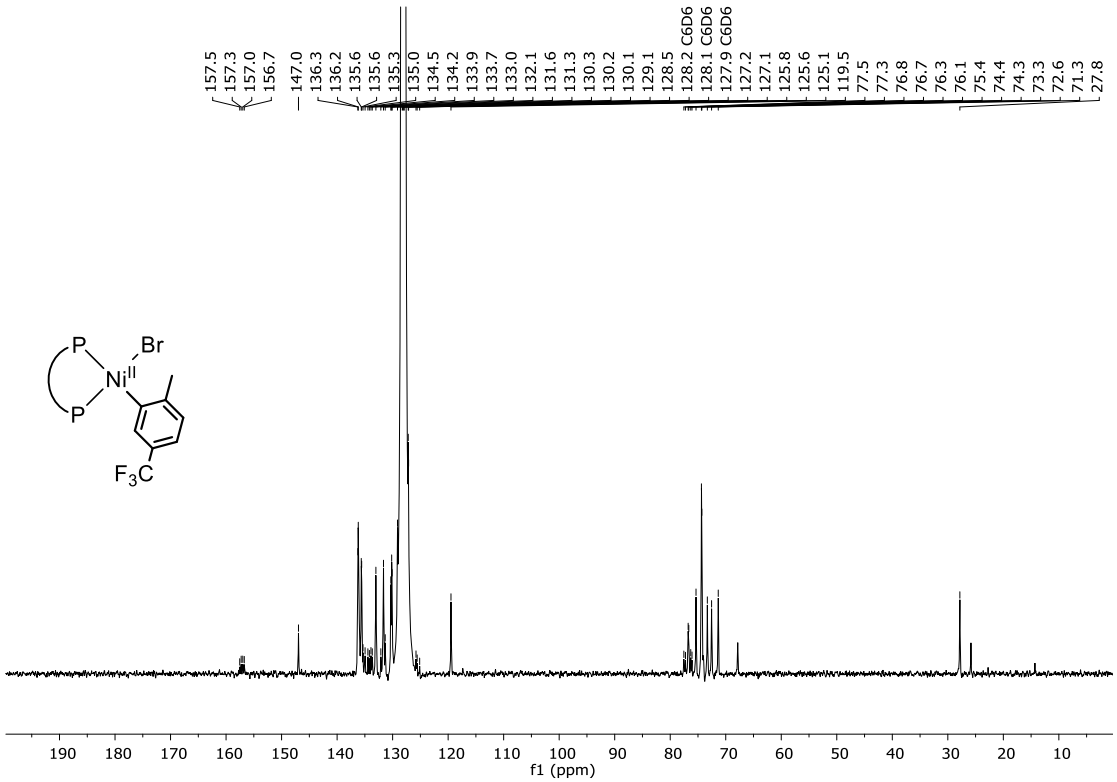


Figure S38. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-5-trifluoromethylphenyl)(Br), **10**.

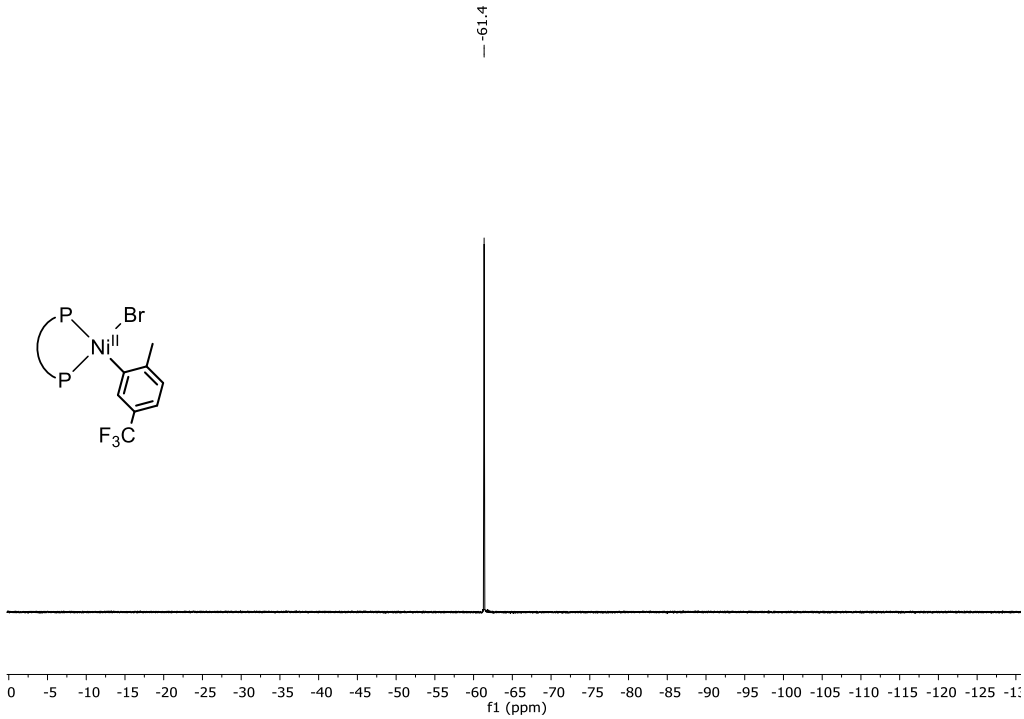


Figure S39. ^{19}F NMR spectrum (C_6D_6, 470 MHz, 25 °C) of (dppf)Ni^{II}(2-methyl-5-trifluoromethylphenyl)(Br), **10**.

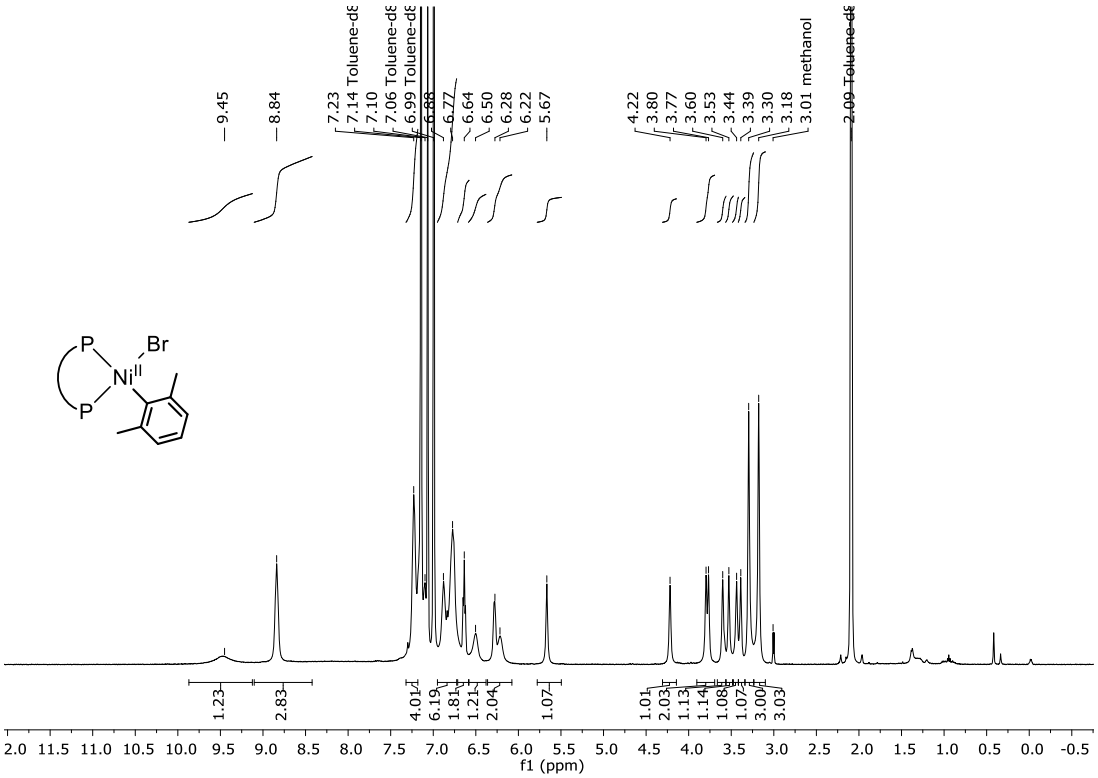


Figure S40. ^{1}H NMR spectrum (d_8-toluene, 500 MHz, -50 °C) of (dppf)Ni^{II}(2,6-xylyl)(Br), **11**.

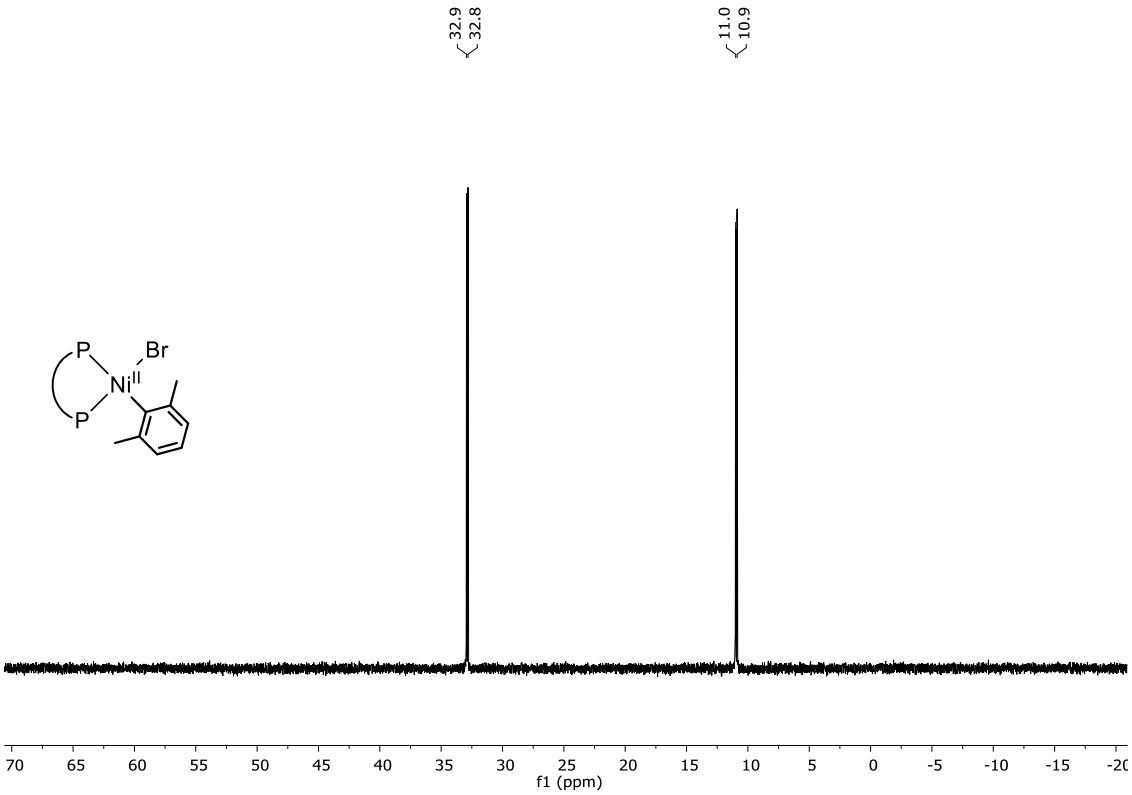


Figure S41. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2,6-xylyl)(Br), **11**.

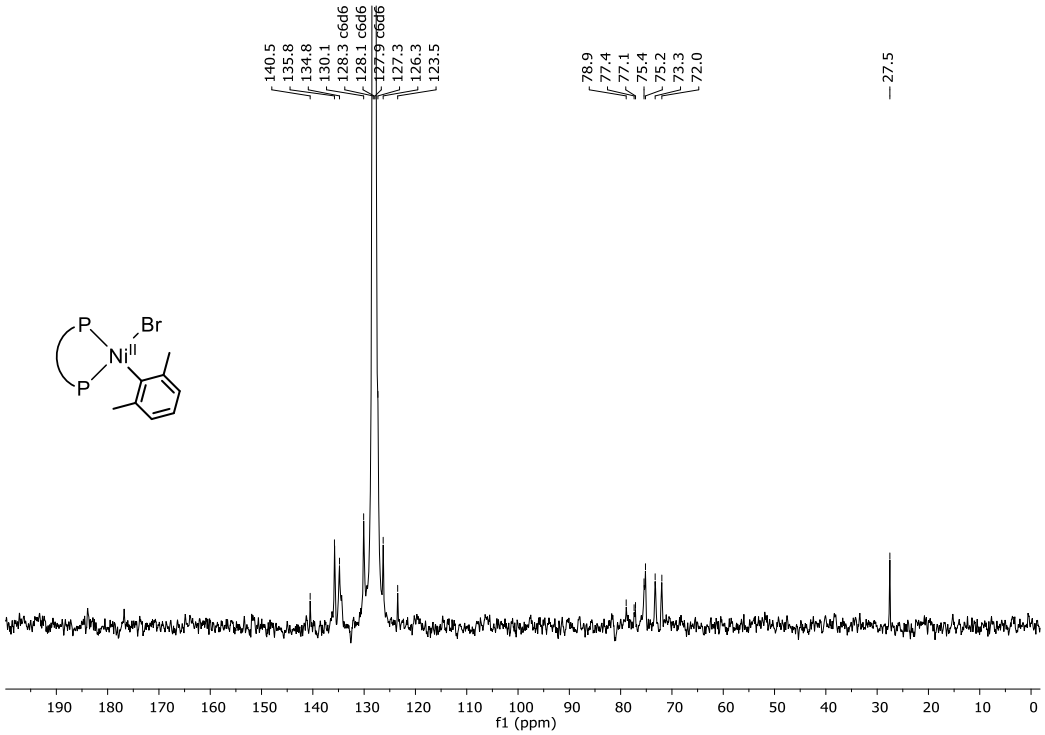


Figure S42. ^{13}C NMR spectrum (C_6D_6, 126 MHz, 25 °C) of (dppf)Ni^{II}(2,6-xylyl)(Br), **11**.

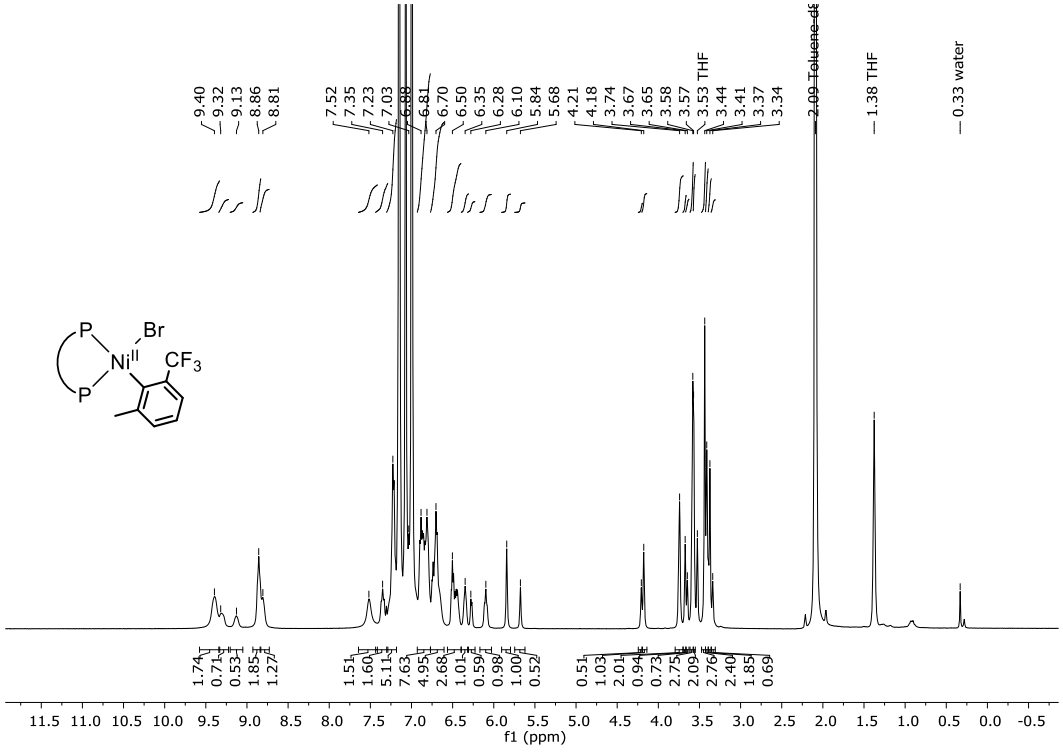


Figure S43. ^{1}H NMR spectrum (d_8-toluene, 500 MHz, -50 °C) of (dppf)Ni^{II}(2-trifluoromethyl-6-methylphenyl)(Br), **12**.

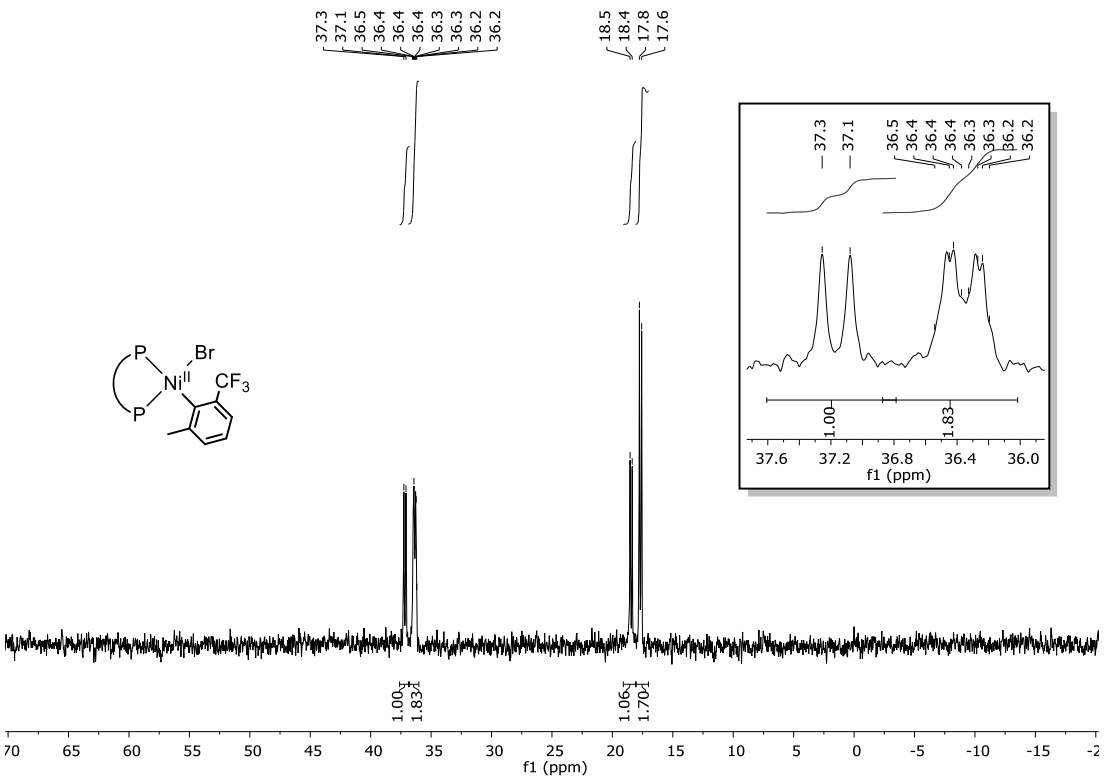


Figure S44. ^{31}P NMR spectrum (*d*$_8$-toluene, 202 MHz, -50 °C) of (dppf)Ni^{II}(2-trifluoromethyl-6-methylphenyl)(Br), **12**.

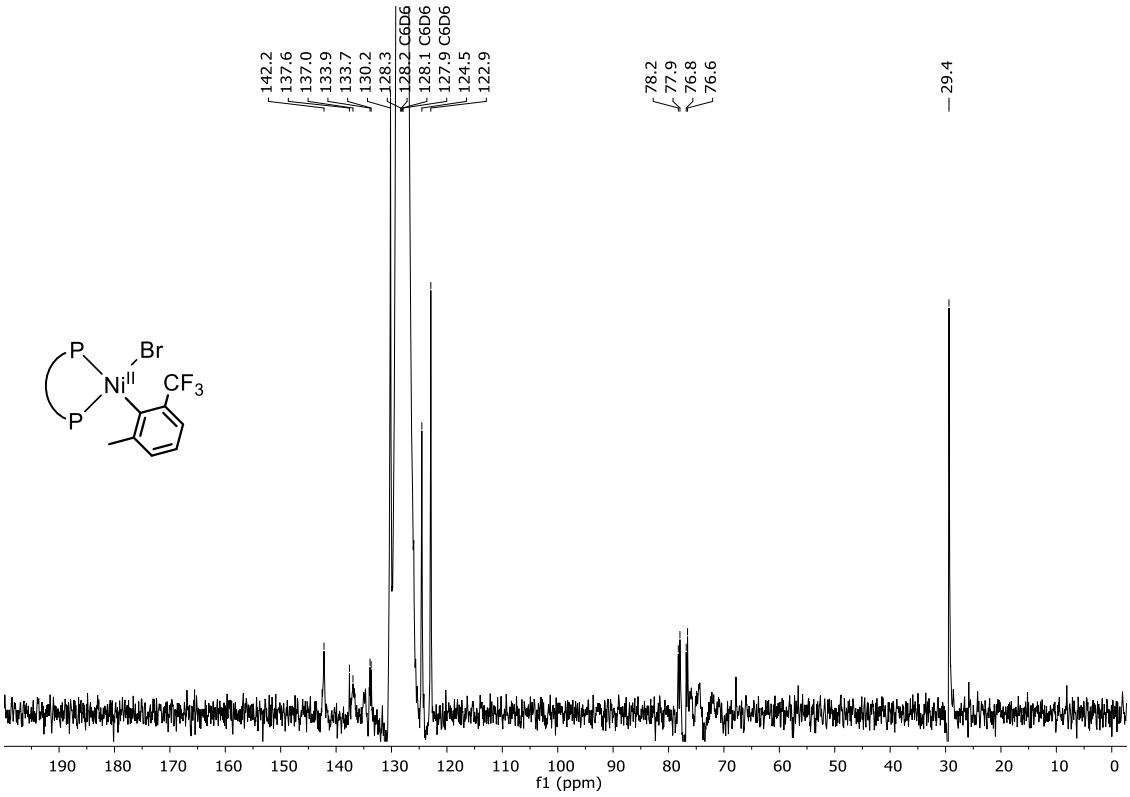


Figure S45. ^{1}H NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2-trifluoromethyl-6-methylphenyl)(Br), **12**.

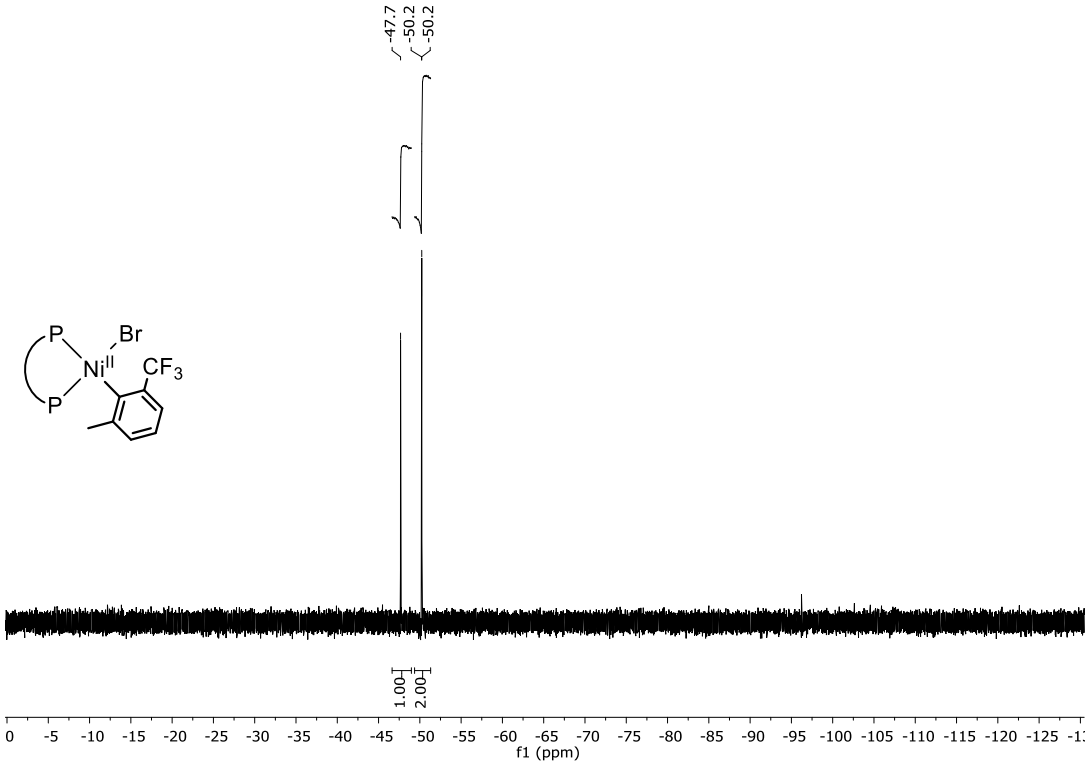


Figure S46. ^{19}F NMR spectrum (d_8-toluene, 376 MHz, -50 °C) of (dppf)Ni^{II}(2-trifluoromethyl-6-methylphenyl)(Br), **12**.

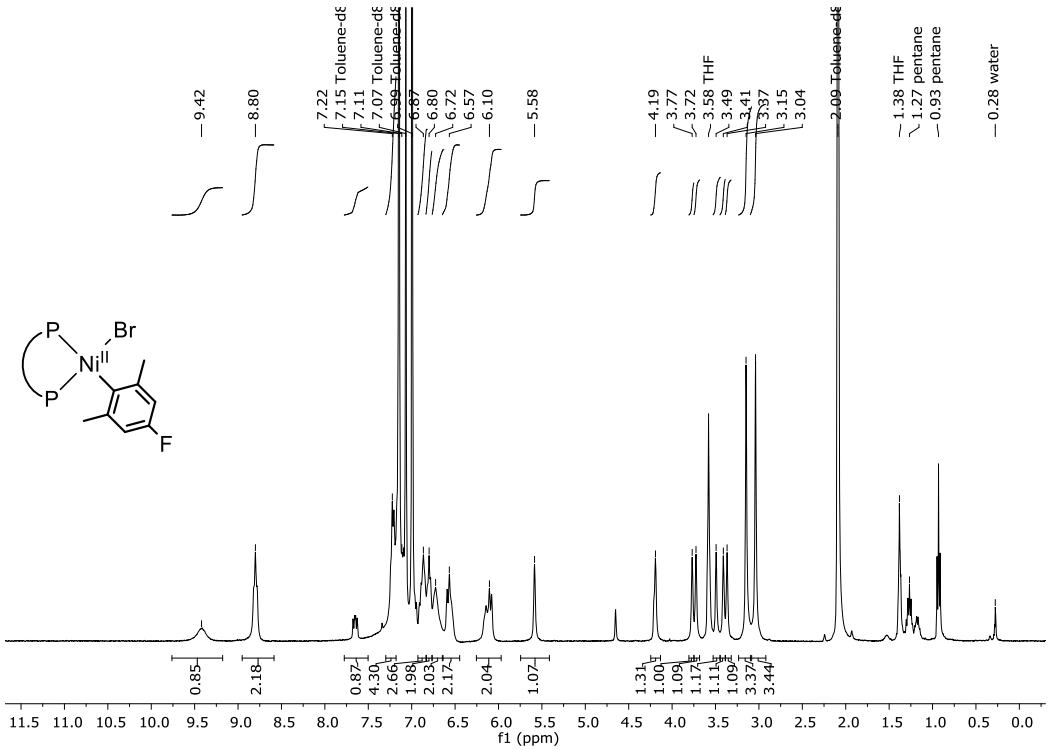


Figure S47. ^{1}H NMR spectrum (d_8-toluene, 400 MHz, -50 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-fluorophenyl)(Br), **13**.

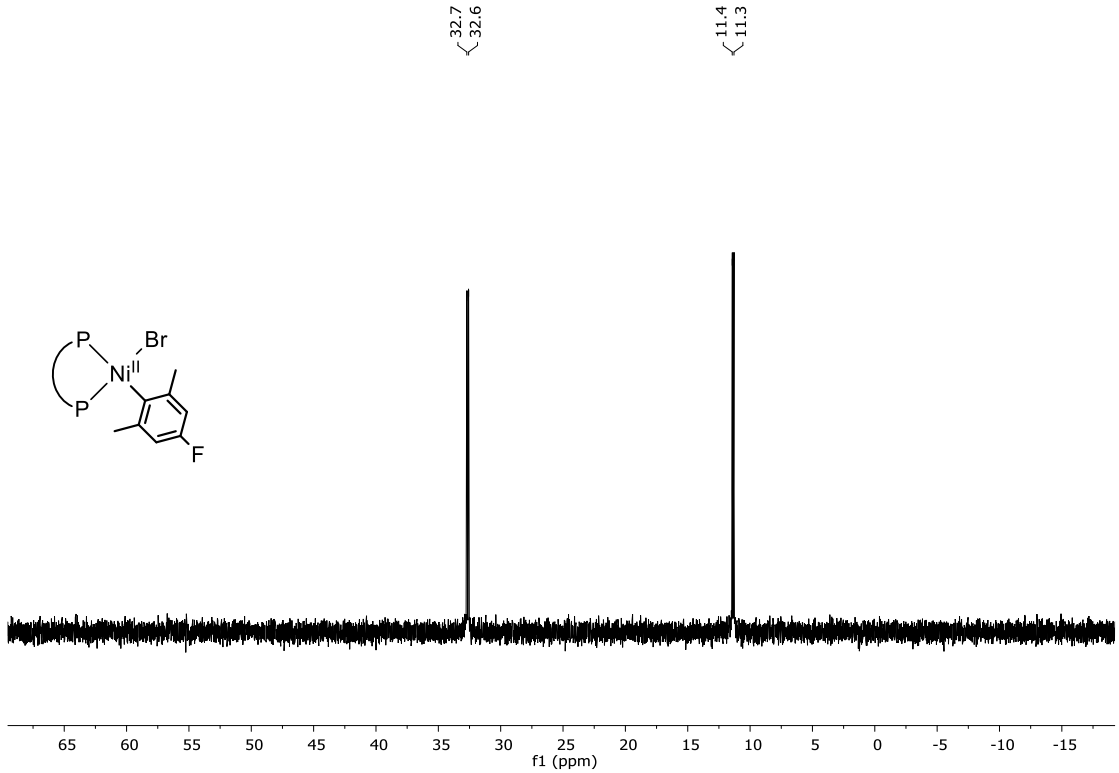


Figure S48. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-fluorophenyl)(Br), **13**.

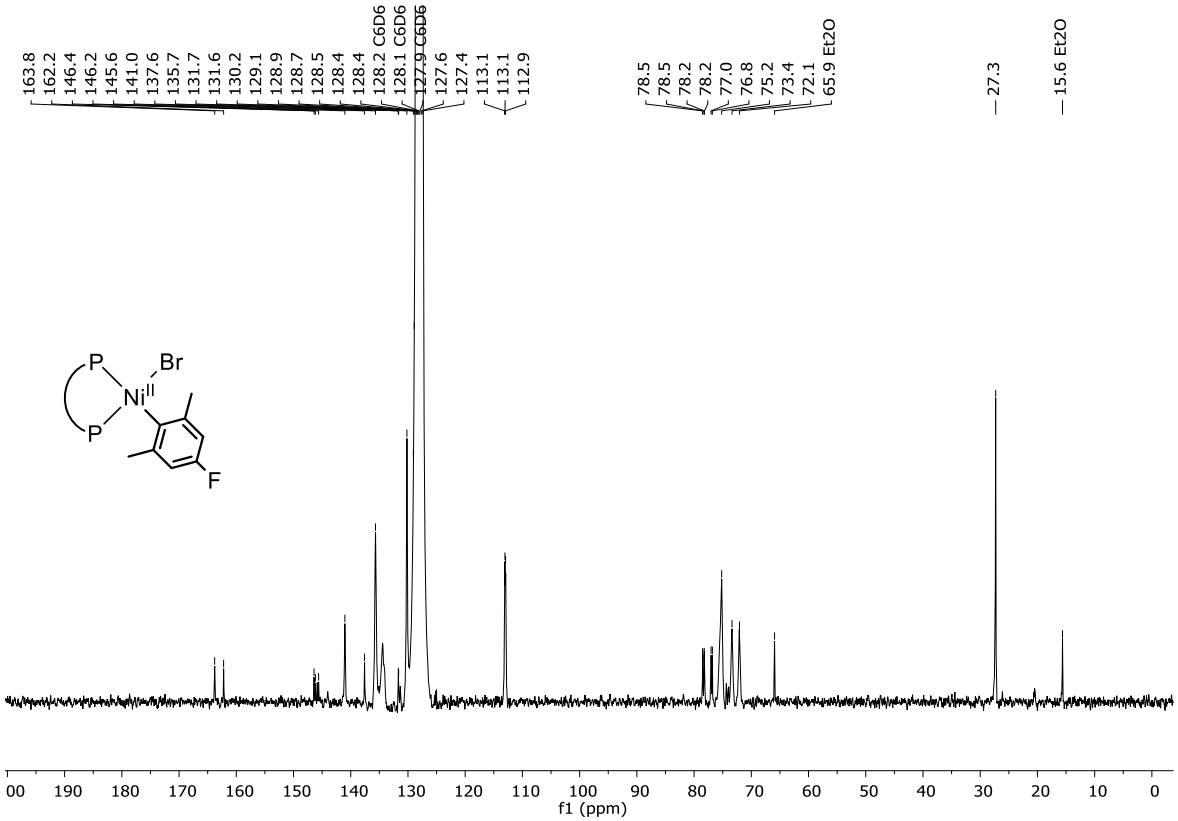


Figure S49. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-fluorophenyl)(Br), **13**.

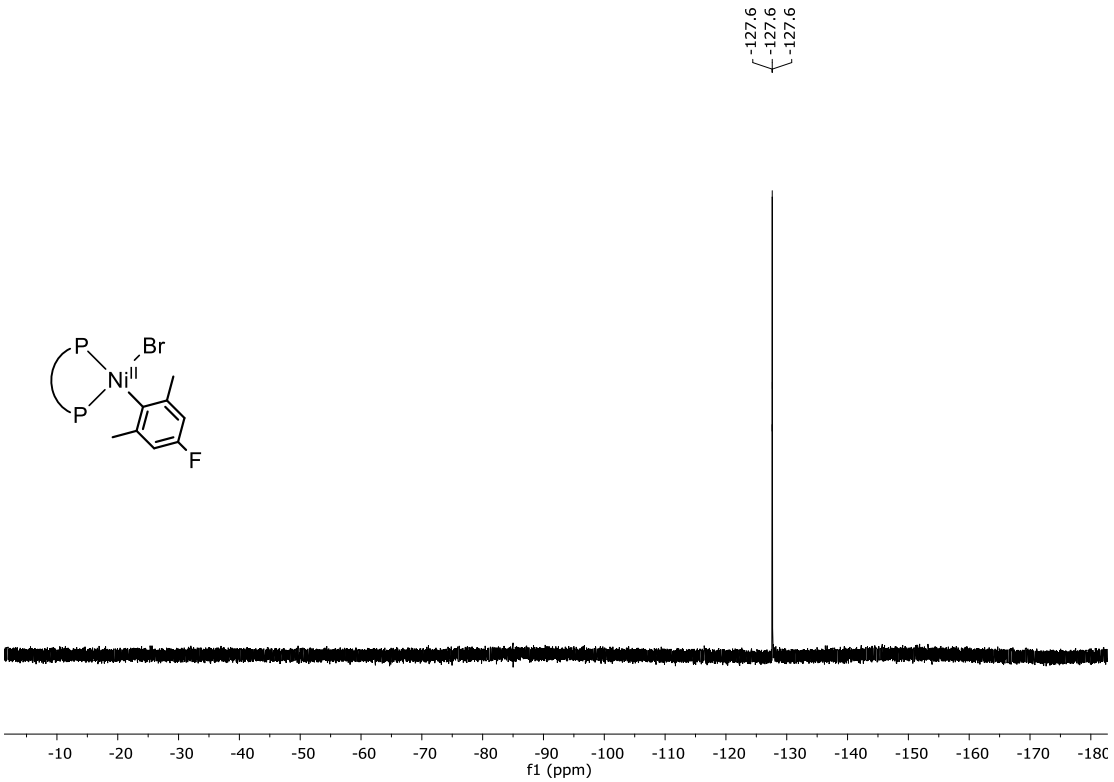


Figure S50. ^{19}F NMR spectrum (C_6D_6, 470 MHz, 25 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-fluorophenyl)(Br), **13**.

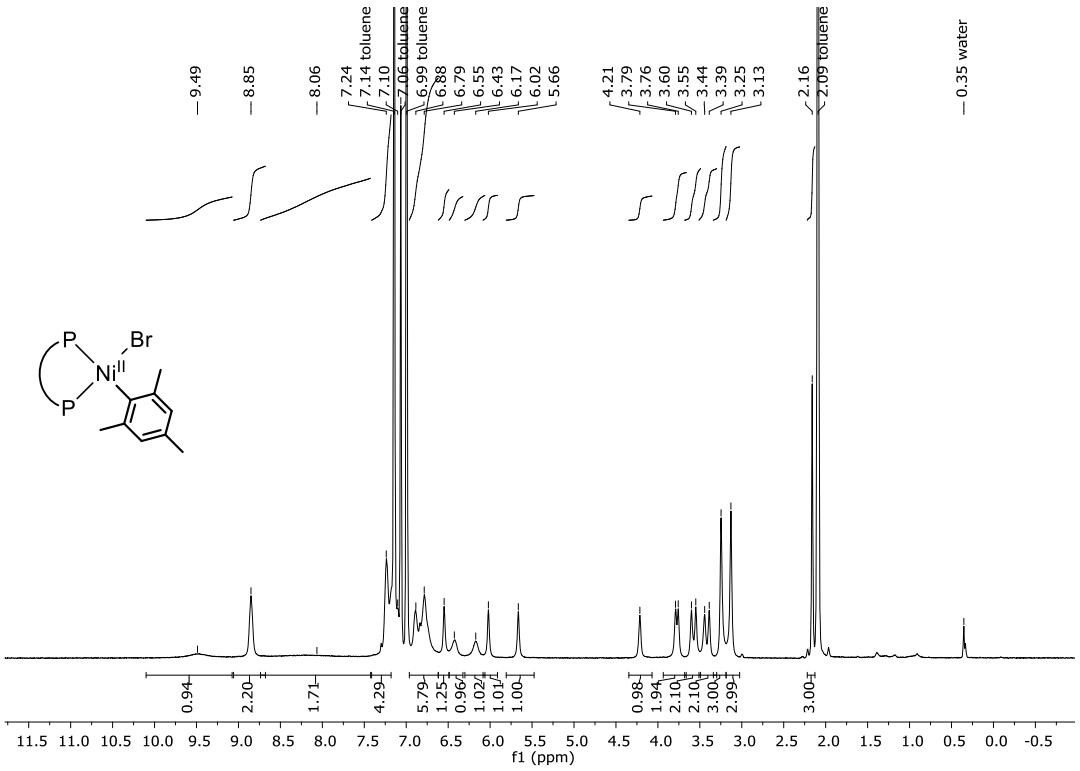


Figure S51. ^{1}H NMR spectrum (d_8-toluene, 500 MHz, -50 °C) of (dppf)Ni^{II}(mesityl)(Br), **14**.

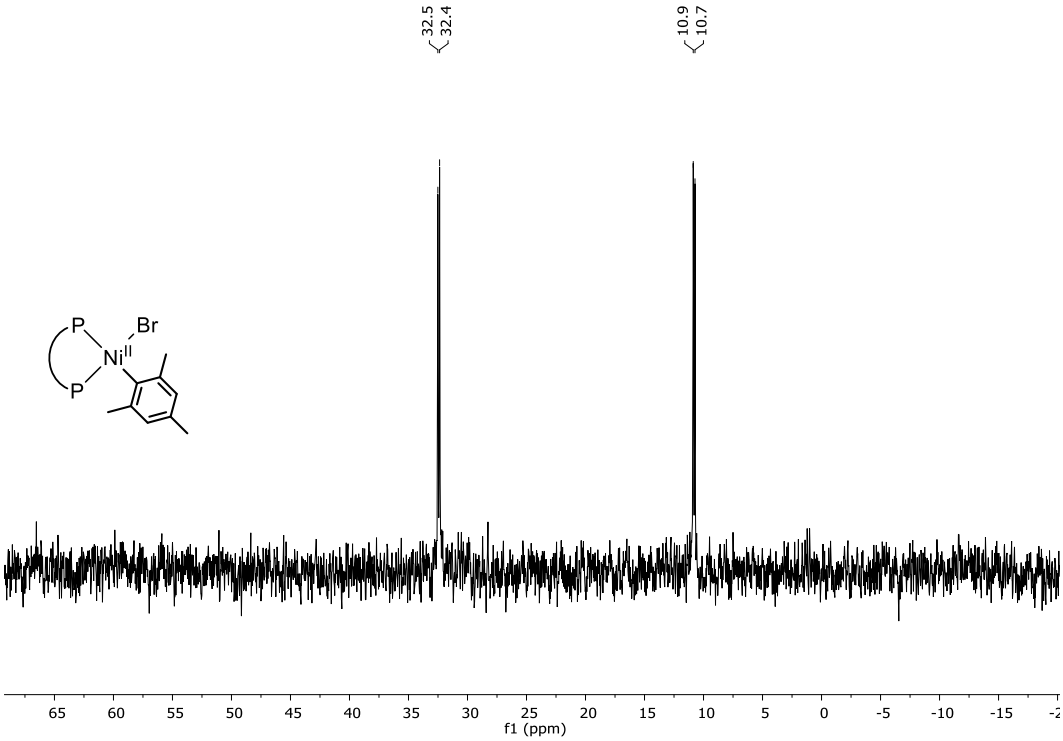


Figure S52. ^{31}P NMR spectrum (C_6D_6, 161 MHz, 25 °C) of (dppf)Ni^{II}(mesityl)(Br), **14**.

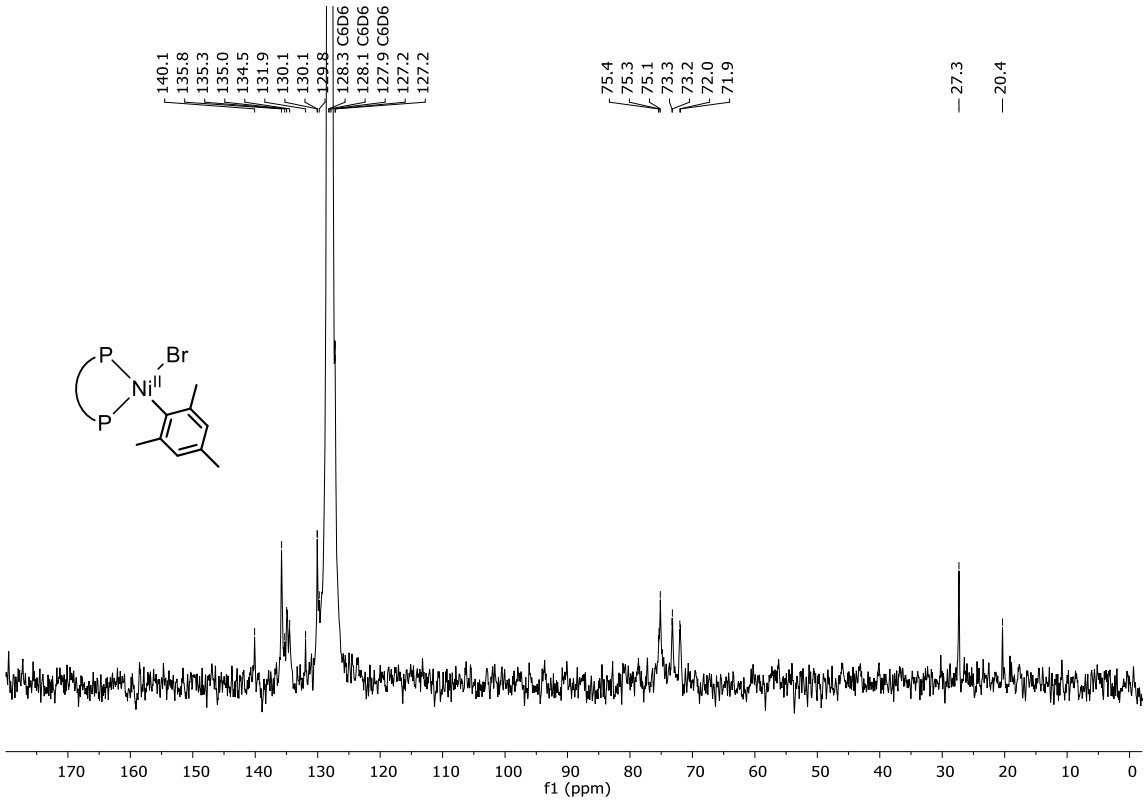


Figure S53. ^{13}C NMR spectrum (C_6D_6, 126 MHz, 25 °C) of (dppf)Ni^{II}(mesityl)(Br), **14**.

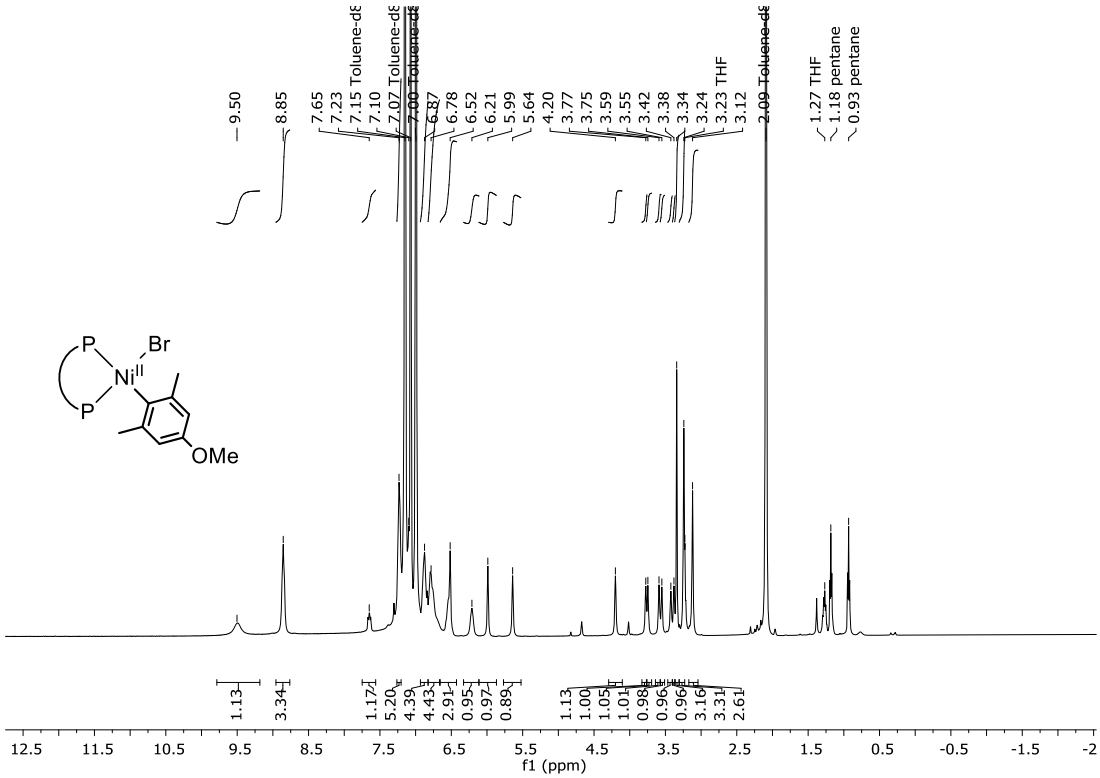


Figure S54. ^{1}H NMR spectrum (d_8-toluene, 500 MHz, -50 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-methoxyphenyl)(Br), **15**.

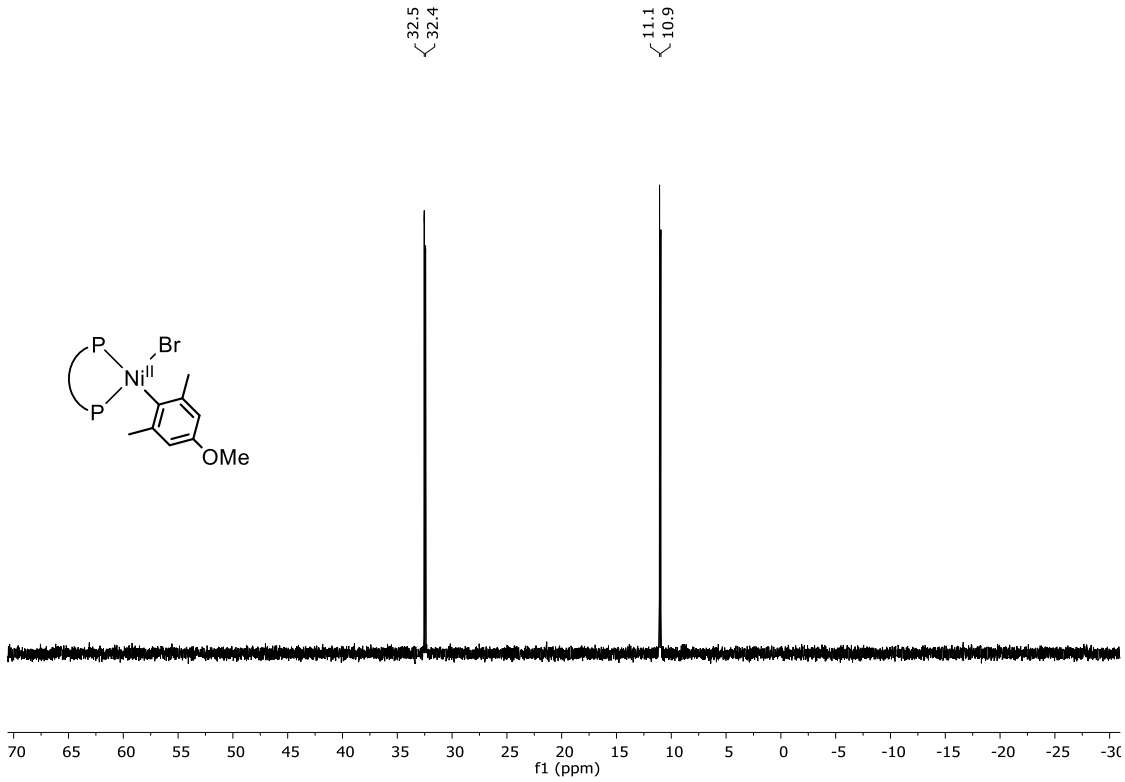


Figure S55. ^{31}P NMR spectrum (C_6D_6, 202 MHz, 25 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-methoxyphenyl)(Br), **15**.

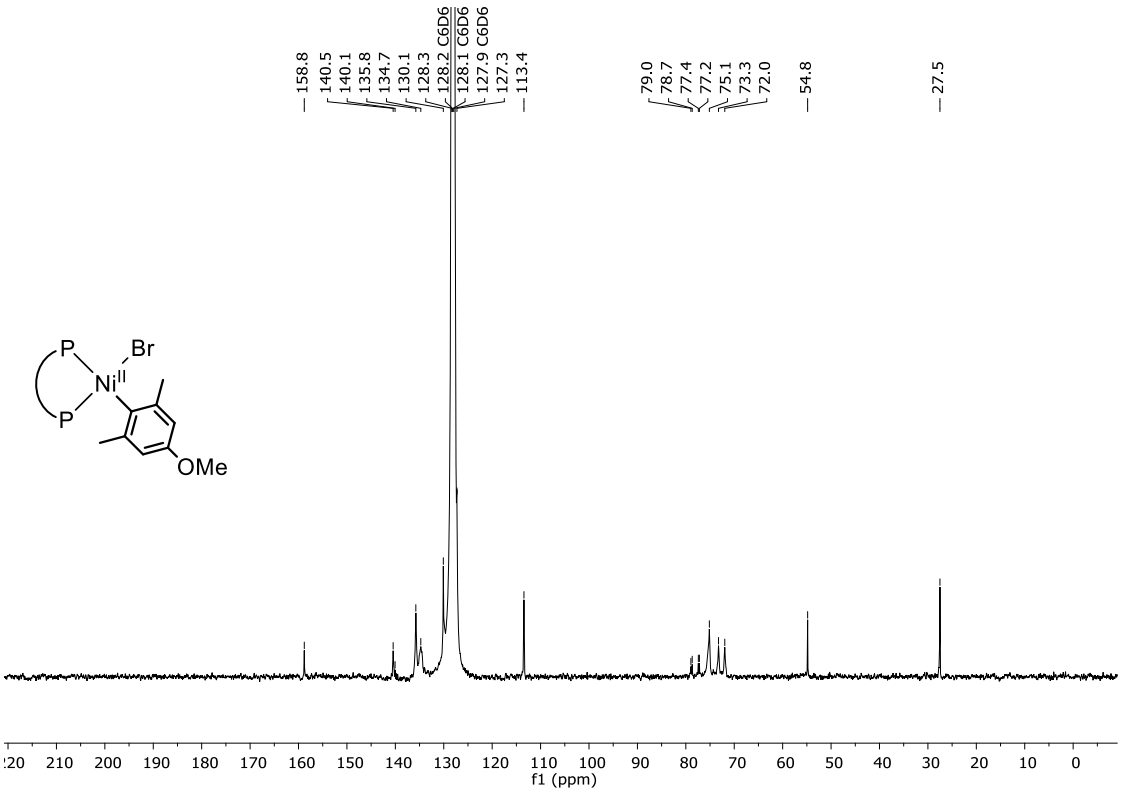


Figure S56. ^{13}C NMR spectrum (C_6D_6, 151 MHz, 25 °C) of (dppf)Ni^{II}(2,6-dimethyl-4-methoxyphenyl)(Br), **15**.

SVII. X-ray Diffraction Data

Further characterization of precatalysts was conducted through X-ray Crystallography. A comparison of relevant bond metrics for all catalysts crystallized is given in Table S4. Specific details regarding data collection and processing for each species is given below.

Table S4. Select bond lengths and angles of the crystallized precatalysts.

Species	Ni-C_{aryl} (Å)	Ni-P_{trans} (Å)	P-Ni-P (°)
2	1.924(6)	2.2871(14)	99.76(5)
3[a]	1.898(14), 1.905(14)	2.278(4), 2.281(4)	101.63(16), 102.43(16)
4	1.897(6)	2.2564(17)	101.39(6)
5[a]	1.896(18), 1.898(17)	2.274(6), 2.263(5)	100.08(19), 100.09(19)
6	1.890(7)	2.278(2)	102.54(8)
7[b]	1.87(3)	2.276(10)	102.0(3)
8	1.891(9)	2.280(3)	101.77(10)
10	1.888(4)	2.2616(13)	100.16(5)
12	1.932(4)	2.3172(11)	97.04(4)
13	1.914(2)	2.2957(7)	98.96(2)
14	1.906(6)	2.2460(17)	100.11(6)

[a] [b]Two sets of geometric parameters are included because there are two independent molecules in the unit cell. [b]Only low angle diffraction data used.

*X-ray Diffraction Data for (dppf)Ni(1-naphthyl)(Br) (**2**)*

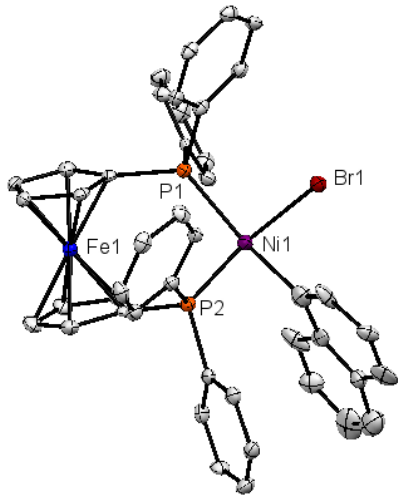


Figure S57. ORTEP of **2**, with ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization have been removed for clarity.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **2** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a

Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **2** (Figure S57). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL[11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Eight reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **2** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860562 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Crystal data and structure refinement for **2**.

Empirical formula	$C_{48}H_{43}BrFeNiOP_2$
Formula weight	892.23
Temperature/K	93.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.6607(7)
b/Å	15.1096(8)
c/Å	20.4830(12)
α/°	90
β/°	104.423(6)
γ/°	90
Volume/Å^3	3794.9(4)
Z	4
ρ_{calc}g/cm^3	1.562
μ/mm^{-1}	2.054
F(000)	1832.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.326 to 50.05
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-24 \le l \le 24$
Reflections collected	53514
Independent reflections	6688 [R_{int} = 0.1437, R_{sigma} = 0.0834]
Data/restraints/parameters	6688/0/487

Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.0990
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.1139

Table S6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	4123.7(4)	2867.5(3)	8049.4(2)	19.59(14)
Ni1	2993.6(5)	3369.5(4)	7052.1(3)	18.27(17)
Fe1	2962.8(6)	3470.2(5)	5000.1(3)	16.35(18)
P1	4442.6(10)	3327.7(9)	6572.7(6)	14.3(3)
P2	1790.6(11)	3947.4(9)	6240.7(6)	16.0(3)
C1	1908(5)	3531(4)	7552(3)	33.1(15)
C2	1129(4)	2919(4)	7582(3)	31.1(15)
C3	1149(5)	2059(4)	7206(3)	36.0(16)
C4	343(5)	1497(4)	7201(3)	28.6(14)
C5	-493(6)	1672(5)	7519(3)	49.5(19)
C6	-536(5)	2407(5)	7859(3)	47.2(18)
C7	295(4)	3010(4)	7900(3)	23.7(13)
C8	304(5)	3845(4)	8288(3)	43.2(18)
C9	1092(4)	4441(4)	8291(3)	24.3(13)
C10	1844(5)	4272(4)	7911(3)	30.7(15)
C11	4992(4)	2218(3)	6571(2)	15.1(11)
C12	6014(4)	2084(3)	6454(2)	19.3(12)
C13	6379(4)	1237(3)	6403(3)	24.0(13)
C14	5745(4)	528(4)	6463(3)	24.9(13)
C15	4746(4)	651(4)	6595(2)	22.9(13)
C16	4379(4)	1500(3)	6649(2)	18.2(12)
C17	5613(4)	3961(3)	7033(2)	16.6(11)
C18	6353(4)	3594(3)	7575(2)	18.9(12)
C19	7220(4)	4081(3)	7934(2)	18.8(12)
C20	7367(4)	4932(3)	7756(2)	19.6(12)
C21	6647(4)	5308(3)	7218(2)	17.6(11)
C22	5770(4)	4836(3)	6864(2)	17.4(11)
C23	2137(4)	5107(3)	6224(2)	16.5(11)
C24	3044(4)	5404(3)	6687(2)	16.6(11)
C25	3407(4)	6264(3)	6672(2)	20.4(12)
C26	2840(4)	6828(3)	6185(2)	21.4(12)
C27	1906(4)	6554(3)	5738(3)	22.6(12)
C28	1555(4)	5697(3)	5752(3)	19.7(12)
C29	368(4)	3958(3)	6245(2)	17.2(11)
C30	-299(4)	3253(3)	5983(2)	19.6(12)

C31	-1366(4)	3231(3)	6016(2)	20.3(12)
C32	-1776(4)	3915(4)	6320(3)	23.6(13)
C33	-1132(4)	4625(3)	6573(2)	19.1(12)
C34	-64(4)	4642(3)	6535(2)	19.8(12)
C35	4358(4)	3646(3)	5710(2)	14.0(11)
C36	3963(4)	4463(3)	5401(2)	17.0(11)
C37	3906(4)	4401(3)	4706(2)	17.2(11)
C38	4261(4)	3553(4)	4577(2)	20.3(12)
C39	4541(4)	3088(4)	5190(2)	20.1(12)
C40	1714(4)	3485(3)	5430(2)	15.1(11)
C41	1411(4)	3883(4)	4782(2)	20.9(12)
C42	1530(4)	3259(4)	4298(3)	24.1(13)
C43	1910(4)	2466(4)	4634(3)	21.1(12)
C44	2025(4)	2593(4)	5325(3)	19.8(12)
O1	2274(6)	8570(3)	5084(3)	87(2)
C45	1312(7)	9080(5)	4983(4)	65(2)
C46	1692(7)	10009(5)	5168(4)	65(2)
C47	2824(7)	10016(5)	5048(3)	59(2)
C48	3212(7)	9093(4)	5251(3)	56(2)

Table S7. Anisotropic Displacement Parameters ($Å^2×10^3$) for **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	17.6(3)	24.3(3)	16.7(3)	4.7(2)	4.0(2)	2.3(2)
Ni1	13.0(4)	24.8(4)	17.2(3)	7.5(3)	4.1(3)	0.9(3)
Fe1	16.1(4)	19.4(4)	13.8(4)	-0.8(3)	4.2(3)	-1.4(3)
P1	13.6(7)	15.9(7)	13.5(6)	1.0(6)	3.7(5)	-0.7(6)
P2	13.6(7)	18.3(7)	15.8(7)	2.5(6)	2.9(6)	-1.6(6)
C1	29(4)	40(4)	29(3)	13(3)	5(3)	8(3)
C2	19(3)	48(4)	26(3)	27(3)	4(3)	8(3)
C3	35(4)	20(3)	39(4)	9(3)	-15(3)	2(3)
C4	28(3)	21(3)	36(3)	3(3)	6(3)	4(3)
C5	60(5)	43(4)	44(4)	21(4)	11(4)	30(4)
C6	40(4)	55(5)	49(4)	26(4)	16(3)	13(4)
C7	19(3)	33(3)	19(3)	7(3)	3(2)	0(3)
C8	26(4)	56(5)	39(4)	15(3)	-7(3)	19(3)
C9	16(3)	25(3)	28(3)	0(3)	-1(3)	5(3)
C10	34(4)	34(3)	17(3)	-13(3)	-6(3)	16(3)
C11	16(3)	19(3)	9(2)	3(2)	0(2)	-2(2)
C12	14(3)	21(3)	23(3)	1(2)	3(2)	-2(2)
C13	21(3)	26(3)	28(3)	-1(3)	10(3)	5(3)
C14	31(3)	20(3)	26(3)	-6(3)	11(3)	2(3)

C15	26(3)	23(3)	19(3)	-7(2)	6(2)	-10(2)
C16	14(3)	22(3)	17(3)	0(2)	0(2)	2(2)
C17	17(3)	17(3)	17(3)	-2(2)	8(2)	-1(2)
C18	18(3)	20(3)	21(3)	6(2)	8(2)	2(2)
C19	11(3)	26(3)	18(3)	-1(2)	1(2)	4(2)
C20	16(3)	23(3)	20(3)	-6(2)	5(2)	0(2)
C21	20(3)	14(3)	21(3)	-2(2)	10(2)	-3(2)
C22	16(3)	23(3)	14(3)	-1(2)	6(2)	0(2)
C23	13(3)	21(3)	17(3)	-1(2)	6(2)	0(2)
C24	15(3)	22(3)	14(3)	3(2)	5(2)	3(2)
C25	21(3)	21(3)	17(3)	-6(2)	1(2)	-1(2)
C26	27(3)	17(3)	22(3)	-3(2)	10(3)	1(2)
C27	28(3)	21(3)	17(3)	4(2)	3(2)	3(3)
C28	16(3)	25(3)	20(3)	-2(2)	6(2)	0(2)
C29	14(3)	21(3)	16(3)	7(2)	4(2)	1(2)
C30	25(3)	21(3)	14(3)	-1(2)	5(2)	0(2)
C31	14(3)	25(3)	21(3)	0(2)	1(2)	-8(2)
C32	17(3)	30(3)	26(3)	4(3)	10(2)	1(3)
C33	19(3)	21(3)	19(3)	6(2)	8(2)	6(2)
C34	20(3)	22(3)	18(3)	7(2)	5(2)	2(2)
C35	9(3)	18(3)	14(3)	-1(2)	3(2)	-4(2)
C36	10(3)	21(3)	21(3)	1(2)	5(2)	-3(2)
C37	14(3)	22(3)	15(3)	5(2)	4(2)	-3(2)
C38	14(3)	34(3)	14(3)	-5(2)	7(2)	-6(2)
C39	14(3)	27(3)	19(3)	-1(2)	4(2)	-3(2)
C40	8(3)	19(3)	17(3)	1(2)	0(2)	-4(2)
C41	13(3)	28(3)	21(3)	3(2)	3(2)	0(2)
C42	21(3)	30(3)	18(3)	-2(3)	-1(2)	-6(3)
C43	20(3)	22(3)	20(3)	-5(2)	2(2)	-6(2)
C44	12(3)	25(3)	21(3)	-2(2)	2(2)	-7(2)
O1	103(5)	38(3)	99(5)	-5(3)	-12(4)	2(3)
C45	92(7)	48(5)	58(5)	12(4)	24(5)	-7(5)
C46	112(8)	44(5)	40(4)	5(4)	21(5)	17(5)
C47	93(7)	43(4)	30(4)	3(3)	-6(4)	-7(4)
C48	95(6)	42(4)	26(4)	-11(3)	4(4)	-12(4)

Table S8. Bond Lengths for **2**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	Ni1	2.3106(8)	C14	C15	1.370(7)
Ni1	P1	2.2871(14)	C15	C16	1.379(7)
Ni1	P2	2.1409(14)	C17	C18	1.380(7)
Ni1	C1	1.924(6)	C17	C22	1.394(7)

Fe1	C35	2.006(5)	C18	C19	1.372(7)
Fe1	C36	2.003(5)	C19	C20	1.362(7)
Fe1	C37	2.031(5)	C20	C21	1.367(7)
Fe1	C38	2.044(5)	C21	C22	1.365(7)
Fe1	C39	2.022(5)	C23	C24	1.370(7)
Fe1	C40	1.992(5)	C23	C28	1.384(7)
Fe1	C41	2.003(5)	C24	C25	1.381(7)
Fe1	C42	2.040(5)	C25	C26	1.371(7)
Fe1	C43	2.035(5)	C26	C27	1.367(7)
Fe1	C44	2.001(5)	C27	C28	1.372(7)
P1	C11	1.816(5)	C29	C30	1.382(7)
P1	C17	1.818(5)	C29	C34	1.373(7)
P1	C35	1.808(5)	C30	C31	1.369(7)
P2	C23	1.809(5)	C31	C32	1.374(7)
P2	C29	1.804(5)	C32	C33	1.369(7)
P2	C40	1.782(5)	C33	C34	1.373(7)
C1	C2	1.364(8)	C35	C36	1.421(7)
C1	C10	1.352(8)	C35	C39	1.422(7)
C2	C3	1.515(8)	C36	C37	1.409(7)
C2	C7	1.378(7)	C37	C38	1.405(7)
C3	C4	1.327(8)	C38	C39	1.405(7)
C4	C5	1.401(8)	C40	C41	1.420(7)
C5	C6	1.318(9)	C40	C44	1.434(7)
C6	C7	1.378(8)	C41	C42	1.404(7)
C7	C8	1.490(8)	C42	C43	1.406(7)
C8	C9	1.343(8)	C43	C44	1.400(7)
C9	C10	1.394(8)	O1	C45	1.412(9)
C11	C12	1.388(7)	O1	C48	1.397(9)
C11	C16	1.366(7)	C45	C46	1.501(10)
C12	C13	1.373(7)	C46	C47	1.513(11)
C13	C14	1.363(7)	C47	C48	1.503(9)

Table S9. Bond Angles for **2**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P1	Ni1	Br1	89.10(4)	C9	C8	C7	118.6(6)
P2	Ni1	Br1	169.84(5)	C8	C9	C10	118.9(6)
P2	Ni1	P1	99.76(5)	C1	C10	C9	126.6(6)
C1	Ni1	Br1	86.47(17)	C12	C11	P1	120.6(4)
C1	Ni1	P1	171.17(19)	C16	C11	P1	120.3(4)
C1	Ni1	P2	84.08(17)	C16	C11	C12	119.1(5)
C35	Fe1	C37	69.32(19)	C13	C12	C11	119.6(5)
C35	Fe1	C38	69.13(19)	C14	C13	C12	120.6(5)

C35	Fe1	C39	41.34(19)	C13	C14	C15	120.3(5)
C35	Fe1	C42	178.1(2)	C14	C15	C16	119.2(5)
C35	Fe1	C43	138.0(2)	C11	C16	C15	121.1(5)
C36	Fe1	C35	41.54(19)	C18	C17	P1	120.6(4)
C36	Fe1	C37	40.88(19)	C18	C17	C22	118.1(5)
C36	Fe1	C38	68.6(2)	C22	C17	P1	121.3(4)
C36	Fe1	C39	69.0(2)	C19	C18	C17	120.5(5)
C36	Fe1	C42	140.0(2)	C20	C19	C18	120.5(5)
C36	Fe1	C43	177.0(2)	C19	C20	C21	120.0(5)
C37	Fe1	C38	40.3(2)	C22	C21	C20	120.2(5)
C37	Fe1	C42	112.6(2)	C21	C22	C17	120.7(5)
C37	Fe1	C43	141.9(2)	C24	C23	P2	118.0(4)
C39	Fe1	C37	68.2(2)	C24	C23	C28	118.8(5)
C39	Fe1	C38	40.42(19)	C28	C23	P2	123.2(4)
C39	Fe1	C42	138.9(2)	C23	C24	C25	121.2(5)
C39	Fe1	C43	112.5(2)	C26	C25	C24	119.0(5)
C40	Fe1	C35	109.30(19)	C27	C26	C25	120.6(5)
C40	Fe1	C36	107.5(2)	C26	C27	C28	120.1(5)
C40	Fe1	C37	135.5(2)	C27	C28	C23	120.3(5)
C40	Fe1	C38	175.7(2)	C30	C29	P2	120.4(4)
C40	Fe1	C39	140.6(2)	C34	C29	P2	121.0(4)
C40	Fe1	C41	41.66(19)	C34	C29	C30	118.6(5)
C40	Fe1	C42	69.5(2)	C31	C30	C29	121.0(5)
C40	Fe1	C43	69.6(2)	C30	C31	C32	119.5(5)
C40	Fe1	C44	42.1(2)	C33	C32	C31	120.2(5)
C41	Fe1	C35	139.3(2)	C32	C33	C34	119.8(5)
C41	Fe1	C36	110.1(2)	C29	C34	C33	120.9(5)
C41	Fe1	C37	109.5(2)	P1	C35	Fe1	120.0(2)
C41	Fe1	C38	137.2(2)	C36	C35	Fe1	69.1(3)
C41	Fe1	C39	177.6(2)	C36	C35	P1	126.5(4)
C41	Fe1	C42	40.6(2)	C36	C35	C39	106.6(4)
C41	Fe1	C43	68.5(2)	C39	C35	Fe1	69.9(3)
C42	Fe1	C38	112.2(2)	C39	C35	P1	126.4(4)
C43	Fe1	C38	114.3(2)	C35	C36	Fe1	69.3(3)
C43	Fe1	C42	40.4(2)	C37	C36	Fe1	70.6(3)
C44	Fe1	C35	109.5(2)	C37	C36	C35	108.4(4)
C44	Fe1	C36	136.6(2)	C36	C37	Fe1	68.5(3)
C44	Fe1	C37	177.2(2)	C38	C37	Fe1	70.3(3)
C44	Fe1	C38	142.0(2)	C38	C37	C36	108.2(4)
C44	Fe1	C39	112.8(2)	C37	C38	Fe1	69.3(3)
C44	Fe1	C41	69.5(2)	C39	C38	Fe1	69.0(3)
C44	Fe1	C42	68.5(2)	C39	C38	C37	108.0(4)

C44	Fe1	C43	40.58(19)	C35	C39	Fe1	68.7(3)
C11	P1	Ni1	112.01(16)	C38	C39	Fe1	70.6(3)
C11	P1	C17	102.9(2)	C38	C39	C35	108.7(5)
C17	P1	Ni1	113.61(16)	P2	C40	Fe1	123.5(3)
C35	P1	Ni1	123.60(16)	C41	C40	Fe1	69.6(3)
C35	P1	C11	100.0(2)	C41	C40	P2	130.1(4)
C35	P1	C17	102.1(2)	C41	C40	C44	106.2(4)
C23	P2	Ni1	106.32(17)	C44	C40	Fe1	69.3(3)
C29	P2	Ni1	121.23(16)	C44	C40	P2	123.7(4)
C29	P2	C23	103.8(2)	C40	C41	Fe1	68.8(3)
C40	P2	Ni1	115.25(17)	C42	C41	Fe1	71.1(3)
C40	P2	C23	108.6(2)	C42	C41	C40	108.9(5)
C40	P2	C29	100.7(2)	C41	C42	Fe1	68.3(3)
C2	C1	Ni1	123.9(5)	C41	C42	C43	108.0(5)
C10	C1	Ni1	122.8(5)	C43	C42	Fe1	69.6(3)
C10	C1	C2	113.2(6)	C42	C43	Fe1	70.0(3)
C1	C2	C3	117.0(5)	C44	C43	Fe1	68.4(3)
C1	C2	C7	127.0(6)	C44	C43	C42	108.4(5)
C7	C2	C3	115.9(5)	C40	C44	Fe1	68.6(3)
C4	C3	C2	116.3(6)	C43	C44	Fe1	71.0(3)
C3	C4	C5	123.0(6)	C43	C44	C40	108.5(5)
C6	C5	C4	122.7(7)	C48	O1	C45	112.2(6)
C5	C6	C7	117.2(7)	O1	C45	C46	105.2(7)
C2	C7	C8	115.5(5)	C45	C46	C47	102.9(6)
C6	C7	C2	124.7(6)	C48	C47	C46	101.9(6)
C6	C7	C8	119.8(6)	O1	C48	C47	104.9(6)

*X-ray Diffraction Data for (dppf)Ni(2-ethylphenyl)(Br) (**3**)*

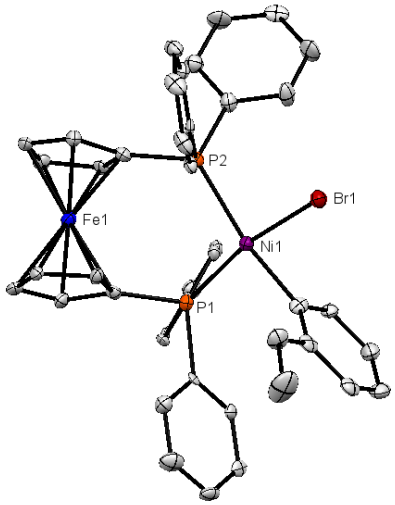


Figure S58. ORTEP of **3**, with ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization have been removed for clarity. Only one molecule present in the unit cell is shown.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **3** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **3** (Figure S58). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] Refined as a 2-component inversion twin. The contribution of the second twin component to the reflections was freely refined to 0.402(18). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The data was poor and required a global rigid bond restraint to prevent the thermal ellipsoids from converging to non-positive definite matrices. The thermal parameter of C92 and C93 were constrained to be identical. These atoms represent disordered positions in the THF molecule. The full numbering scheme of compound **3** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860567 contains the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S10. Crystal data and structure refinement for **3**.

Empirical formula	$C_{46}H_{45}BrFeNiOP_2$
Formula weight	870.23
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.7174(11)
b/Å	20.7385(10)
c/Å	14.7169(11)
α/°	90
β/°	116.752(10)
γ/°	90
Volume/Å^3	3738.5(5)
Z	4
ρ_{calc}g/cm^3	1.546
μ/mm^{-1}	2.083
F(000)	1792.0
Crystal size/mm^3	0.200 × 0.200 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.1 to 41.624
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 20$, $-14 \le l \le 14$
Reflections collected	34571
Independent reflections	7815 [R_{int} = 0.0941, R_{sigma} = 0.0704]
Data/restraints/parameters	7815/1057/944
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0667
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.0731

Table S11. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	4831.1(10)	4832.4(7)	-673.0(10)	18.7(4)
Ni1	4431.7(13)	3948.5(9)	70.4(13)	13.9(5)
Fe1	4786.4(15)	1937.0(10)	-27.3(14)	15.1(6)
P1	3666(3)	3220.3(19)	572(3)	14.0(10)
P2	5805(3)	3389(2)	-43(3)	14.6(10)
C1	3495(10)	4521(7)	322(10)	17(3)
C2	2502(10)	4694(7)	-403(10)	22(2)
C3	1882(10)	5145(7)	-170(10)	22(2)

C4	2267(11)	5405(7)	781(11)	26(4)
C5	3281(10)	5228(7)	1520(10)	26(3)
C6	3874(10)	4785(7)	1293(9)	17(3)
C7	2075(9)	4440(7)	-1465(10)	25(3)
C8	914(10)	4565(7)	-2186(10)	52(5)
C9	3576(9)	2444(7)	25(10)	13(3)
C10	3357(9)	2339(7)	-1002(10)	15(3)
C11	3320(9)	1672(7)	-1182(11)	15(3)
C12	3505(10)	1347(8)	-262(10)	18(3)
C13	3652(9)	1814(7)	468(10)	17(3)
C14	5996(10)	2538(7)	175(10)	16(3)
C15	6222(9)	2212(7)	1118(10)	15(3)
C16	6241(9)	1547(8)	945(11)	19(3)
C17	6062(9)	1448(8)	-62(10)	16(3)
C18	5930(10)	2038(7)	-534(10)	16(3)
C19	2265(9)	3326(7)	355(10)	14(3)
C20	1424(10)	3058(8)	-495(10)	21(4)
C21	351(10)	3165(8)	-692(11)	27(4)
C22	117(10)	3540(8)	-46(11)	21(3)
C23	954(10)	3801(7)	795(10)	17(3)
C24	2006(10)	3692(7)	988(11)	16(3)
C25	4385(9)	3120(7)	1935(9)	10(3)
C26	3936(10)	2789(7)	2466(10)	13(3)
C27	4506(10)	2722(7)	3504(10)	16(3)
C28	5535(10)	2983(8)	4006(10)	21(4)
C29	5980(10)	3300(7)	3507(10)	18(3)
C30	5416(9)	3367(7)	2459(11)	15(3)
C31	5732(10)	3427(7)	-1321(10)	14(3)
C32	6617(11)	3342(8)	-1481(11)	21(4)
C33	6536(11)	3346(8)	-2455(10)	21(4)
C34	5538(10)	3437(8)	-3266(11)	25(4)
C35	4631(11)	3510(8)	-3089(10)	22(4)
C36	4717(10)	3508(7)	-2128(10)	15(4)
C37	7174(10)	3684(7)	780(10)	18(3)
C38	7402(10)	4330(7)	974(10)	25(4)
C39	8440(10)	4538(7)	1583(10)	30(4)
C40	9274(10)	4119(7)	2016(9)	19(3)
C41	9070(10)	3485(8)	1813(11)	29(4)
C42	8037(9)	3255(8)	1217(10)	21(3)
Br2	9616.3(10)	5155.7(7)	4182.9(10)	19.6(4)
Ni2	9130.8(12)	6042.6(9)	4850.5(13)	14.4(5)
Fe2	9648.4(14)	8045.7(10)	4910.0(14)	16.3(6)

P3	10575(3)	6576(2)	4835(3)	14.4(10)
P4	8431(3)	6771.3(19)	5398(3)	14.2(10)
C43	8127(11)	5483(7)	5015(10)	20(3)
C44	7089(9)	5327(6)	4274(9)	16(3)
C45	6467(9)	4886(7)	4476(9)	20(3)
C46	6864(10)	4576(7)	5402(10)	22(3)
C47	7893(10)	4720(7)	6145(10)	20(3)
C48	8529(10)	5170(7)	5948(10)	19(3)
C49	6604(10)	5631(7)	3252(9)	20(3)
C50	6684(9)	5214(6)	2442(8)	27(3)
C51	10840(9)	7424(7)	5102(10)	14(3)
C52	10779(10)	7909(7)	4416(11)	18(3)
C53	10967(9)	8510(8)	4931(11)	16(3)
C54	11150(10)	8398(8)	5916(11)	21(3)
C55	11071(9)	7723(7)	6042(10)	13(3)
C56	8391(10)	7576(7)	4923(10)	14(3)
C57	8212(9)	7704(7)	3904(10)	16(3)
C58	8223(10)	8381(7)	3782(12)	23(3)
C59	8397(10)	8651(8)	4697(11)	25(3)
C60	8495(9)	8165(7)	5404(10)	18(3)
C61	10554(9)	6544(7)	3595(10)	12(3)
C62	11483(10)	6619(8)	3458(11)	20(4)
C63	11409(11)	6620(8)	2498(10)	25(4)
C64	10414(10)	6548(8)	1676(11)	23(4)
C65	9499(11)	6480(8)	1772(11)	22(4)
C66	9566(10)	6467(7)	2731(10)	18(4)
C67	11911(10)	6248(7)	5716(10)	16(3)
C68	12847(9)	6614(7)	6020(9)	15(3)
C69	13836(10)	6393(7)	6650(10)	22(4)
C70	13941(10)	5758(7)	6985(10)	22(3)
C72	13035(9)	5393(7)	6727(9)	20(3)
C73	12035(10)	5631(6)	6103(9)	17(3)
C74	7027(9)	6684(7)	5193(10)	12(3)
C75	6765(11)	6294(7)	5818(10)	19(4)
C76	5697(10)	6194(7)	5605(11)	24(4)
C77	4870(11)	6474(8)	4750(10)	26(4)
C78	5116(10)	6850(8)	4143(10)	22(4)
C79	6191(10)	6964(7)	4363(9)	16(3)
C80	9180(10)	6860(7)	6761(10)	17(3)
C81	10187(10)	6554(7)	7283(10)	16(3)
C82	10780(11)	6599(7)	8316(10)	22(4)
C83	10350(11)	6934(8)	8876(11)	24(4)

C84	9334(10)	7206(8)	8374(11)	24(4)
C85	8761(11)	7177(8)	7338(10)	21(4)
O1	7835(7)	9248(5)	6706(8)	33(3)
C86	6723(10)	9106(8)	6080(11)	34(4)
C87	6340(11)	9616(7)	5280(10)	28(3)
C88	6969(10)	10201(8)	5883(10)	27(3)
C89	8026(10)	9918(7)	6636(11)	31(4)
O2	3124(8)	708(5)	1817(9)	43(3)
C90	3129(10)	26(8)	1898(11)	32(4)
C91	1981(10)	-186(9)	1204(12)	46(4)
C92	1420(40)	390(20)	570(50)	64(16)
C93	1350(20)	423(12)	1250(40)	37(9)
C94	2065(12)	908(9)	1238(13)	44(4)

Table S12. Anisotropic Displacement Parameters ($Å^2×10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	20.0(7)	15.5(9)	22.2(8)	3.7(7)	10.9(7)	0.8(7)
Ni1	14.4(9)	11.9(11)	17.0(10)	0.8(8)	8.6(8)	0.7(8)
Fe1	14.0(11)	13.4(14)	17.0(11)	-0.3(11)	6.3(10)	2.2(9)
P1	15.0(18)	12(2)	14(2)	-1.1(17)	6.4(17)	-0.1(16)
P2	15.3(19)	14(2)	15(2)	0.7(16)	7.7(18)	-0.1(16)
C1	21(6)	19(7)	14(5)	5(5)	11(5)	3(5)
C2	22(5)	18(6)	28(4)	10(4)	14(4)	-2(4)
C3	22(5)	18(6)	28(4)	10(4)	14(4)	-2(4)
C4	25(7)	24(9)	40(7)	5(6)	24(6)	4(6)
C5	27(6)	21(8)	37(7)	-5(6)	21(6)	-3(6)
C6	18(6)	18(7)	21(6)	0(5)	14(5)	1(5)
C7	19(6)	24(8)	24(6)	6(5)	3(5)	6(6)
C8	30(7)	53(11)	43(9)	-11(8)	-10(7)	16(7)
C9	9(6)	13(5)	15(6)	1(4)	3(5)	-1(4)
C10	11(6)	11(6)	18(6)	-2(4)	3(5)	1(5)
C11	13(6)	14(7)	22(6)	-6(5)	10(5)	-2(5)
C12	11(6)	16(6)	28(6)	-1(5)	10(5)	2(5)
C13	15(6)	13(6)	24(6)	3(5)	10(5)	4(5)
C14	14(6)	15(5)	22(6)	0(4)	10(5)	-3(4)
C15	8(6)	16(7)	17(5)	-2(4)	2(5)	-4(5)
C16	13(6)	17(7)	24(6)	2(5)	5(5)	2(5)
C17	11(6)	13(7)	23(6)	-3(5)	7(5)	-1(5)
C18	16(6)	14(7)	21(6)	-2(5)	10(5)	-1(5)
C19	15(5)	7(7)	25(6)	1(5)	14(5)	-4(5)
C20	19(6)	19(9)	24(7)	1(6)	10(5)	2(5)

C21	16(6)	33(10)	26(7)	7(7)	5(5)	5(6)
C22	13(6)	21(9)	32(7)	12(6)	12(5)	8(5)
C23	21(6)	11(8)	26(7)	12(6)	15(5)	6(5)
C24	16(6)	8(8)	24(7)	4(6)	11(5)	2(5)
C25	12(5)	5(7)	16(5)	-3(5)	8(4)	-2(5)
C26	9(6)	9(8)	23(6)	-1(5)	8(5)	-3(5)
C27	22(6)	5(8)	23(6)	1(5)	12(5)	4(5)
C28	19(6)	20(9)	21(6)	1(6)	7(5)	2(5)
C29	16(6)	12(8)	22(6)	-6(5)	6(5)	-1(5)
C30	16(6)	7(8)	22(6)	-3(5)	8(5)	-1(5)
C31	19(5)	5(9)	18(5)	-3(5)	8(5)	-1(5)
C32	22(6)	18(10)	25(6)	-8(6)	13(5)	-4(6)
C33	21(6)	23(11)	24(6)	-9(6)	14(5)	-8(6)
C34	31(6)	30(12)	16(7)	-4(6)	13(5)	-10(6)
C35	28(6)	21(10)	15(6)	0(6)	7(6)	-10(6)
C36	19(6)	12(10)	15(6)	0(5)	9(5)	-3(5)
C37	20(5)	15(6)	17(7)	0(5)	6(5)	-1(4)
C38	20(6)	14(6)	28(8)	4(5)	-1(6)	1(5)
C39	18(6)	25(7)	35(8)	-9(6)	2(6)	-7(5)
C40	17(6)	35(7)	7(7)	2(5)	6(5)	-1(5)
C41	9(6)	35(8)	31(9)	-3(6)	-1(6)	0(5)
C42	18(5)	21(7)	24(8)	2(6)	9(5)	0(5)
Br2	19.2(8)	15.8(10)	26.5(8)	-5.7(7)	12.6(7)	-1.5(6)
Ni2	13.7(9)	12.3(11)	17.9(10)	-1.4(9)	7.8(9)	0.1(8)
Fe2	12.2(10)	13.6(14)	22.7(11)	2.8(11)	7.6(10)	1.9(9)
P3	14.7(18)	11(2)	17(2)	-0.5(17)	6.9(17)	1.0(16)
P4	14.1(19)	12(2)	18(2)	0.8(17)	8.4(17)	-0.2(16)
C43	21(6)	17(7)	24(6)	-3(5)	11(5)	0(5)
C44	18(6)	14(7)	20(5)	-7(5)	13(5)	-3(5)
C45	15(6)	20(7)	24(6)	2(5)	9(5)	0(5)
C46	27(6)	18(8)	27(6)	-1(5)	16(5)	-3(5)
C47	27(6)	18(8)	19(7)	3(6)	13(5)	9(5)
C48	25(7)	12(7)	24(6)	-13(5)	14(5)	1(6)
C49	21(7)	19(8)	21(6)	0(5)	10(5)	-5(6)
C50	24(7)	30(8)	23(6)	-12(6)	8(6)	-14(6)
C51	9(6)	16(5)	13(6)	-2(4)	2(5)	0(4)
C52	18(6)	14(7)	20(6)	4(5)	8(5)	0(5)
C53	5(6)	15(7)	27(7)	2(5)	7(5)	-2(5)
C54	17(6)	14(7)	29(6)	-3(5)	10(5)	0(5)
C55	9(5)	12(6)	18(5)	-1(5)	4(5)	-4(5)
C56	12(6)	11(6)	18(6)	2(4)	6(5)	2(4)
C57	8(6)	16(7)	23(6)	4(5)	6(5)	0(5)

C58	17(6)	18(7)	32(6)	12(5)	8(5)	1(5)
C59	16(6)	20(7)	37(7)	9(5)	10(6)	3(5)
C60	15(6)	14(7)	24(6)	0(5)	7(5)	0(5)
C61	15(5)	5(8)	19(5)	2(5)	10(4)	3(5)
C62	14(6)	27(10)	19(6)	0(6)	7(5)	2(6)
C63	26(6)	34(12)	21(6)	3(6)	16(5)	3(6)
C64	29(6)	22(11)	19(6)	7(6)	12(5)	10(6)
C65	18(6)	27(11)	15(6)	5(6)	4(5)	11(6)
C66	21(6)	10(10)	20(6)	-1(5)	8(5)	-4(5)
C67	16(5)	13(6)	17(7)	1(5)	6(5)	4(4)
C68	19(5)	15(7)	14(7)	2(5)	10(5)	4(5)
C69	16(6)	30(7)	19(8)	1(6)	6(5)	1(5)
C70	14(6)	35(7)	14(8)	9(6)	3(6)	9(5)
C72	19(6)	20(7)	16(7)	-4(5)	4(5)	6(5)
C73	18(6)	14(6)	15(7)	0(5)	5(5)	1(5)
C74	14(5)	6(8)	14(6)	-4(5)	5(4)	-3(5)
C75	22(6)	17(9)	21(7)	0(6)	12(5)	4(5)
C76	25(6)	16(9)	36(7)	0(6)	18(6)	-2(5)
C77	21(7)	28(9)	36(8)	-3(6)	18(6)	-3(6)
C78	14(6)	23(9)	28(7)	-2(6)	7(5)	0(5)
C79	20(6)	12(8)	19(7)	0(6)	12(5)	0(5)
C80	16(6)	16(8)	17(5)	-1(5)	5(4)	-2(5)
C81	17(6)	12(8)	19(6)	-1(5)	8(5)	-3(5)
C82	24(7)	22(9)	19(6)	5(6)	9(5)	-3(6)
C83	26(7)	28(9)	21(7)	-4(6)	12(6)	-16(6)
C84	24(6)	26(9)	26(6)	-7(6)	16(5)	-12(6)
C85	23(7)	18(9)	24(6)	-5(5)	13(5)	-10(6)
O1	32(5)	22(6)	38(6)	5(5)	11(5)	2(4)
C86	30(7)	22(8)	49(8)	2(6)	17(6)	0(6)
C87	23(7)	29(8)	36(7)	-1(5)	17(6)	1(5)
C88	29(7)	18(7)	35(7)	4(5)	16(6)	5(5)
C89	33(7)	22(7)	39(8)	2(6)	16(6)	0(5)
O2	37(5)	30(6)	55(7)	0(5)	15(5)	-7(4)
C90	29(6)	28(8)	44(8)	-1(6)	21(6)	-4(5)
C91	31(7)	34(7)	67(10)	-2(7)	16(7)	-5(6)
C92	50(15)	41(12)	74(19)	-3(10)	4(15)	2(9)
C93	24(9)	42(10)	40(20)	10(10)	10(10)	2(7)
C94	46(7)	32(8)	56(10)	6(7)	24(7)	3(6)

Table S13. Bond Lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.323(2)	Fe2	C51	1.999(14)

Ni1	C1	1.905(14)	Fe2	C52	2.007(15)
Ni1	P1	2.151(4)	Fe2	C55	2.026(12)
Ni1	P2	2.281(4)	Fe2	C60	2.032(14)
Fe1	C14	1.989(14)	Fe2	C59	2.034(15)
Fe1	C9	1.996(14)	Fe2	C58	2.035(13)
Fe1	C13	2.009(14)	Fe2	C53	2.036(14)
Fe1	C15	2.014(12)	Fe2	C54	2.055(13)
Fe1	C10	2.017(12)	P3	C51	1.804(15)
Fe1	C16	2.027(13)	P3	C61	1.813(15)
Fe1	C18	2.029(14)	P3	C67	1.833(13)
Fe1	C11	2.039(12)	P4	C56	1.801(15)
Fe1	C12	2.040(14)	P4	C80	1.805(13)
Fe1	C17	2.043(14)	P4	C74	1.819(13)
P1	C9	1.779(15)	C43	C44	1.387(16)
P1	C25	1.806(12)	C43	C48	1.388(19)
P1	C19	1.813(13)	C44	C45	1.371(17)
P2	C14	1.792(15)	C44	C49	1.483(17)
P2	C37	1.822(13)	C45	C46	1.378(18)
P2	C31	1.840(15)	C46	C47	1.374(16)
C1	C2	1.346(16)	C47	C48	1.393(19)
C1	C6	1.394(18)	C49	C50	1.516(17)
C2	C3	1.407(19)	C51	C52	1.40(2)
C2	C7	1.496(18)	C51	C55	1.415(19)
C3	C4	1.365(19)	C52	C53	1.42(2)
C4	C5	1.375(17)	C53	C54	1.38(2)
C5	C6	1.364(18)	C54	C55	1.42(2)
C7	C8	1.486(16)	C56	C60	1.386(19)
C9	C10	1.419(19)	C56	C57	1.431(19)
C9	C13	1.444(19)	C57	C58	1.417(19)
C10	C11	1.406(19)	C58	C59	1.38(2)
C11	C12	1.43(2)	C59	C60	1.41(2)
C12	C13	1.393(19)	C61	C62	1.39(2)
C14	C18	1.445(19)	C61	C66	1.389(16)
C14	C15	1.45(2)	C62	C63	1.37(2)
C15	C16	1.40(2)	C63	C64	1.365(17)
C16	C17	1.40(2)	C64	C65	1.33(2)
C17	C18	1.38(2)	C65	C66	1.374(19)
C19	C24	1.367(19)	C67	C73	1.378(18)
C19	C20	1.381(18)	C67	C68	1.382(18)
C20	C21	1.383(19)	C68	C69	1.334(17)
C21	C22	1.37(2)	C69	C70	1.390(19)
C22	C23	1.365(19)	C70	C72	1.355(17)

C23	C24	1.358(18)	C72	C73	1.355(16)
C25	C30	1.369(17)	C74	C79	1.373(18)
C25	C26	1.377(18)	C74	C75	1.388(19)
C26	C27	1.374(18)	C75	C76	1.369(19)
C27	C28	1.375(18)	C76	C77	1.386(18)
C28	C29	1.322(18)	C77	C78	1.339(19)
C29	C30	1.386(18)	C78	C79	1.380(18)
C31	C32	1.35(2)	C80	C85	1.386(19)
C31	C36	1.374(16)	C80	C81	1.394(18)
C32	C33	1.388(19)	C81	C82	1.367(18)
C33	C34	1.366(17)	C82	C83	1.39(2)
C34	C35	1.39(2)	C83	C84	1.37(2)
C35	C36	1.366(19)	C84	C85	1.367(19)
C37	C38	1.376(19)	O1	C86	1.413(15)
C37	C42	1.387(18)	O1	C89	1.425(18)
C38	C39	1.367(16)	C86	C87	1.49(2)
C39	C40	1.347(17)	C87	C88	1.521(19)
C40	C41	1.349(19)	C88	C89	1.493(17)
C41	C42	1.374(17)	O2	C94	1.376(16)
Br2	Ni2	2.320(3)	O2	C90	1.419(18)
Ni2	C43	1.898(14)	C90	C91	1.506(18)
Ni2	P4	2.133(4)	C91	C92	1.50(5)
Ni2	P3	2.278(4)	C91	C93	1.55(3)
Fe2	C57	1.987(12)	C92	C94	1.45(5)
Fe2	C56	1.988(14)	C93	C94	1.41(3)

Table S14. Bond Angles for **3**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C1	Ni1	P1	83.9(4)	C57	Fe2	C51	110.4(6)
C1	Ni1	P2	169.4(4)	C56	Fe2	C51	109.9(6)
P1	Ni1	P2	102.43(16)	C57	Fe2	C52	110.4(6)
C1	Ni1	Br1	85.6(4)	C56	Fe2	C52	138.6(6)
P1	Ni1	Br1	166.08(12)	C51	Fe2	C52	40.9(6)
P2	Ni1	Br1	89.37(13)	C57	Fe2	C55	139.4(6)
C14	Fe1	C9	108.4(6)	C56	Fe2	C55	110.4(6)
C14	Fe1	C13	139.1(6)	C51	Fe2	C55	41.2(5)
C9	Fe1	C13	42.3(6)	C52	Fe2	C55	68.7(6)
C14	Fe1	C15	42.4(6)	C57	Fe2	C60	68.9(6)
C9	Fe1	C15	109.6(6)	C56	Fe2	C60	40.3(5)
C13	Fe1	C15	110.9(6)	C51	Fe2	C60	138.3(6)
C14	Fe1	C10	109.0(6)	C52	Fe2	C60	178.9(6)
C9	Fe1	C10	41.4(5)	C55	Fe2	C60	111.3(5)

C13	Fe1	C10	69.3(6)	C57	Fe2	C59	67.7(6)
C15	Fe1	C10	138.6(6)	C56	Fe2	C59	68.2(6)
C14	Fe1	C16	69.8(6)	C51	Fe2	C59	177.9(6)
C9	Fe1	C16	139.0(6)	C52	Fe2	C59	140.1(6)
C13	Fe1	C16	111.7(6)	C55	Fe2	C59	139.9(6)
C15	Fe1	C16	40.7(6)	C60	Fe2	C59	40.6(6)
C10	Fe1	C16	178.8(6)	C57	Fe2	C58	41.2(5)
C14	Fe1	C18	42.2(6)	C56	Fe2	C58	69.9(6)
C9	Fe1	C18	139.0(6)	C51	Fe2	C58	139.5(6)
C13	Fe1	C18	178.6(6)	C52	Fe2	C58	111.6(6)
C15	Fe1	C18	69.6(6)	C55	Fe2	C58	179.3(6)
C10	Fe1	C18	111.2(6)	C60	Fe2	C58	68.5(6)
C16	Fe1	C18	67.8(6)	C59	Fe2	C58	39.5(6)
C14	Fe1	C11	137.5(6)	C57	Fe2	C53	139.1(6)
C9	Fe1	C11	69.4(5)	C56	Fe2	C53	178.3(6)
C13	Fe1	C11	68.5(6)	C51	Fe2	C53	68.8(6)
C15	Fe1	C11	179.0(6)	C52	Fe2	C53	41.1(6)
C10	Fe1	C11	40.6(5)	C55	Fe2	C53	67.9(6)
C16	Fe1	C11	140.2(6)	C60	Fe2	C53	140.0(6)
C18	Fe1	C11	111.0(6)	C59	Fe2	C53	113.1(6)
C14	Fe1	C12	177.9(6)	C58	Fe2	C53	111.8(6)
C9	Fe1	C12	69.8(6)	C57	Fe2	C54	178.2(6)
C13	Fe1	C12	40.2(5)	C56	Fe2	C54	139.4(6)
C15	Fe1	C12	139.0(6)	C51	Fe2	C54	68.7(6)
C10	Fe1	C12	68.9(6)	C52	Fe2	C54	67.9(6)
C16	Fe1	C12	112.3(6)	C55	Fe2	C54	40.8(5)
C18	Fe1	C12	138.5(6)	C60	Fe2	C54	112.8(6)
C11	Fe1	C12	41.0(6)	C59	Fe2	C54	113.2(7)
C14	Fe1	C17	69.4(6)	C58	Fe2	C54	138.6(6)
C9	Fe1	C17	177.8(6)	C53	Fe2	C54	39.3(5)
C13	Fe1	C17	139.2(6)	C51	P3	C61	99.5(7)
C15	Fe1	C17	68.6(6)	C51	P3	C67	99.7(6)
C10	Fe1	C17	139.2(6)	C61	P3	C67	104.9(6)
C16	Fe1	C17	40.4(6)	C51	P3	Ni2	124.1(5)
C18	Fe1	C17	39.6(6)	C61	P3	Ni2	111.9(4)
C11	Fe1	C17	112.3(6)	C67	P3	Ni2	114.2(5)
C12	Fe1	C17	112.3(6)	C56	P4	C80	103.9(7)
C9	P1	C25	106.9(6)	C56	P4	C74	100.5(6)
C9	P1	C19	100.2(6)	C80	P4	C74	103.0(6)
C25	P1	C19	102.5(6)	C56	P4	Ni2	116.8(5)
C9	P1	Ni1	115.1(5)	C80	P4	Ni2	111.3(5)
C25	P1	Ni1	110.8(5)	C74	P4	Ni2	119.3(5)

C19	P1	Ni1	119.8(5)	C44	C43	C48	118.6(13)
C14	P2	C37	100.8(6)	C44	C43	Ni2	126.1(10)
C14	P2	C31	99.2(7)	C48	C43	Ni2	115.1(10)
C37	P2	C31	103.4(6)	C45	C44	C43	120.3(11)
C14	P2	Ni1	123.2(5)	C45	C44	C49	117.6(10)
C37	P2	Ni1	114.7(5)	C43	C44	C49	122.1(12)
C31	P2	Ni1	112.8(4)	C44	C45	C46	121.2(12)
C2	C1	C6	119.1(13)	C47	C46	C45	119.5(13)
C2	C1	Ni1	122.8(10)	C46	C47	C48	119.6(12)
C6	C1	Ni1	118.1(9)	C43	C48	C47	120.8(12)
C1	C2	C3	119.4(12)	C44	C49	C50	113.4(11)
C1	C2	C7	121.0(13)	C52	C51	C55	107.7(13)
C3	C2	C7	119.5(11)	C52	C51	P3	127.1(11)
C4	C3	C2	121.0(12)	C55	C51	P3	125.1(11)
C3	C4	C5	119.5(14)	C52	C51	Fe2	69.8(8)
C6	C5	C4	119.3(13)	C55	C51	Fe2	70.4(8)
C5	C6	C1	121.8(12)	P3	C51	Fe2	121.8(6)
C8	C7	C2	118.3(12)	C51	C52	C53	107.9(13)
C10	C9	C13	106.2(12)	C51	C52	Fe2	69.2(8)
C10	C9	P1	124.0(11)	C53	C52	Fe2	70.6(9)
C13	C9	P1	129.7(11)	C54	C53	C52	108.5(15)
C10	C9	Fe1	70.1(8)	C54	C53	Fe2	71.1(9)
C13	C9	Fe1	69.4(8)	C52	C53	Fe2	68.3(8)
P1	C9	Fe1	127.2(7)	C53	C54	C55	108.3(15)
C11	C10	C9	108.9(14)	C53	C54	Fe2	69.6(8)
C11	C10	Fe1	70.6(7)	C55	C54	Fe2	68.5(8)
C9	C10	Fe1	68.5(7)	C51	C55	C54	107.5(14)
C10	C11	C12	108.1(14)	C51	C55	Fe2	68.4(7)
C10	C11	Fe1	68.9(7)	C54	C55	Fe2	70.7(8)
C12	C11	Fe1	69.5(7)	C60	C56	C57	107.5(13)
C13	C12	C11	107.7(14)	C60	C56	P4	129.8(11)
C13	C12	Fe1	68.7(8)	C57	C56	P4	122.7(11)
C11	C12	Fe1	69.5(8)	C60	C56	Fe2	71.5(8)
C12	C13	C9	109.0(13)	C57	C56	Fe2	68.9(8)
C12	C13	Fe1	71.1(8)	P4	C56	Fe2	125.7(7)
C9	C13	Fe1	68.4(8)	C58	C57	C56	108.1(14)
C18	C14	C15	105.8(13)	C58	C57	Fe2	71.2(8)
C18	C14	P2	128.5(11)	C56	C57	Fe2	68.9(7)
C15	C14	P2	125.7(11)	C59	C58	C57	106.6(15)
C18	C14	Fe1	70.4(8)	C59	C58	Fe2	70.2(8)
C15	C14	Fe1	69.7(8)	C57	C58	Fe2	67.6(7)
P2	C14	Fe1	123.1(7)	C58	C59	C60	110.3(15)

C16	C15	C14	107.4(14)	C58	C59	Fe2	70.3(9)
C16	C15	Fe1	70.2(7)	C60	C59	Fe2	69.6(8)
C14	C15	Fe1	67.9(7)	C56	C60	C59	107.5(13)
C15	C16	C17	109.1(15)	C56	C60	Fe2	68.2(8)
C15	C16	Fe1	69.2(8)	C59	C60	Fe2	69.8(9)
C17	C16	Fe1	70.4(8)	C62	C61	C66	117.6(13)
C18	C17	C16	108.8(15)	C62	C61	P3	122.9(10)
C18	C17	Fe1	69.6(9)	C66	C61	P3	119.5(10)
C16	C17	Fe1	69.2(8)	C63	C62	C61	120.3(12)
C17	C18	C14	108.9(13)	C64	C63	C62	119.6(14)
C17	C18	Fe1	70.8(9)	C65	C64	C63	122.1(15)
C14	C18	Fe1	67.4(8)	C64	C65	C66	118.8(13)
C24	C19	C20	118.2(12)	C65	C66	C61	121.6(14)
C24	C19	P1	121.8(10)	C73	C67	C68	116.9(12)
C20	C19	P1	119.9(11)	C73	C67	P3	122.3(10)
C19	C20	C21	120.1(15)	C68	C67	P3	120.8(11)
C22	C21	C20	120.3(13)	C69	C68	C67	122.8(14)
C23	C22	C21	119.2(12)	C68	C69	C70	118.9(13)
C24	C23	C22	120.4(15)	C72	C70	C69	119.6(12)
C23	C24	C19	121.8(13)	C73	C72	C70	120.4(13)
C30	C25	C26	118.7(11)	C72	C73	C67	121.2(13)
C30	C25	P1	119.5(11)	C79	C74	C75	118.3(12)
C26	C25	P1	121.8(9)	C79	C74	P4	120.2(11)
C27	C26	C25	120.3(12)	C75	C74	P4	121.3(10)
C26	C27	C28	119.4(14)	C76	C75	C74	120.5(12)
C29	C28	C27	121.1(13)	C75	C76	C77	119.9(15)
C28	C29	C30	120.1(12)	C78	C77	C76	120.0(13)
C25	C30	C29	120.4(14)	C77	C78	C79	120.5(13)
C32	C31	C36	120.5(14)	C74	C79	C78	120.8(14)
C32	C31	P2	122.2(10)	C85	C80	C81	117.3(12)
C36	C31	P2	117.1(10)	C85	C80	P4	122.9(10)
C31	C32	C33	121.3(13)	C81	C80	P4	119.6(12)
C34	C33	C32	119.1(14)	C82	C81	C80	121.9(15)
C33	C34	C35	118.8(14)	C81	C82	C83	119.5(13)
C36	C35	C34	121.9(13)	C84	C83	C82	119.0(13)
C35	C36	C31	118.4(13)	C85	C84	C83	121.1(15)
C38	C37	C42	117.5(12)	C84	C85	C80	121.1(13)
C38	C37	P2	122.4(10)	C86	O1	C89	109.7(10)
C42	C37	P2	120.1(12)	O1	C86	C87	105.0(12)
C39	C38	C37	121.1(13)	C86	C87	C88	101.6(11)
C40	C39	C38	121.3(14)	C89	C88	C87	103.0(12)
C39	C40	C41	118.4(12)	O1	C89	C88	106.8(11)

C40	C41	C42	122.2(14)	C94	O2	C90	108.5(11)
C41	C42	C37	119.5(15)	O2	C90	C91	105.6(12)
C43	Ni2	P4	84.8(5)	C92	C91	C90	106(2)
C43	Ni2	P3	169.2(4)	C90	C91	C93	99.4(16)
P4	Ni2	P3	101.63(16)	C94	C92	C91	101(3)
C43	Ni2	Br2	86.1(4)	C94	C93	C91	100.4(19)
P4	Ni2	Br2	170.22(13)	O2	C94	C93	108.7(17)
P3	Ni2	Br2	87.90(13)	O2	C94	C92	110(2)
C57	Fe2	C56	42.2(6)				

*X-ray Diffraction Data for (dppf)Ni(2-trifluoromethylphenyl)(Br) (**4**)*

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **4** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **4**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Seven reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **4** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860566 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S15. Crystal data and structure refinement for **4.**

Empirical formula	$C_{45}H_{40}BrF_3FeNiOP_2$
Formula weight	910.18
Temperature/K	93.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	13.6542(11)
b/Å	20.5256(11)
c/Å	14.8694(12)

α/°	90
β/°	116.959(10)
γ/°	90
Volume/Å^3	3714.4(6)
Z	4
ρ_{calc}g/cm^3	1.628
μ/mm^{-1}	2.112
F(000)	1856.0
Crystal size/mm^3	0.02 × 0.01 × 0.002
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.968 to 50.054
Index ranges	-16 ≤ h ≤ 16, -24 ≤ k ≤ 24, -17 ≤ l ≤ 17
Reflections collected	53046
Independent reflections	6548 [R_{int} = 0.1311, R_{sigma} = 0.0673]
Data/restraints/parameters	6548/0/487
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.0929
Final R indexes [all data]	R_1 = 0.0754, wR_2 = 0.1061

Table S16. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	7151.0(4)	7318.7(2)	1719.7(3)	17.53(13)
Ni1	6764.1(4)	6447.6(3)	2486.9(4)	12.82(15)
Fe1	7261.9(5)	4419.3(3)	2546.8(5)	14.27(16)
P1	6063.8(9)	5706.5(5)	3041.0(8)	12.6(3)
P2	8164.6(9)	5900.4(5)	2423.7(8)	13.7(3)
F1	4678(2)	6483.2(13)	832.2(19)	27.5(7)
F2	4241(2)	7464.7(14)	355(2)	33.8(7)
F3	3187(2)	6882.4(14)	708(2)	30.3(7)
C1	5844(4)	7038(2)	2734(3)	16.5(10)
C2	4803(4)	7248(2)	2063(4)	19.7(11)
C3	4235(4)	7704(2)	2334(4)	24.7(12)
C4	4689(4)	7958(2)	3279(4)	27.6(12)
C5	5733(4)	7771(2)	3957(4)	23.3(11)
C6	6299(4)	7328(2)	3696(3)	19.5(10)
C7	4245(4)	7021(2)	1012(4)	23.7(11)
C8	4650(4)	5811(2)	2817(3)	14.9(10)
C9	3803(4)	5529(2)	1983(3)	19.5(11)
C10	2734(4)	5644(2)	1774(4)	22.3(11)
C11	2493(4)	6034(2)	2389(4)	23.8(12)

C12	3317(4)	6314(2)	3215(4)	19.3(11)
C13	4395(4)	6205(2)	3432(3)	16.9(10)
C14	6801(3)	5620(2)	4393(3)	13.0(9)
C15	6361(4)	5294(2)	4929(3)	16.3(10)
C16	6933(4)	5242(2)	5961(3)	18.6(10)
C17	7954(4)	5524(2)	6457(3)	22.0(11)
C18	8403(4)	5851(2)	5939(3)	21.8(11)
C19	7825(4)	5906(2)	4910(3)	16.0(10)
C20	8119(4)	5921(2)	1182(3)	14.1(10)
C21	7116(4)	5996(2)	340(3)	18.4(10)
C22	7041(4)	5992(2)	-604(3)	21.4(11)
C23	7964(4)	5920(2)	-732(4)	23.9(11)
C24	8971(4)	5842(2)	97(4)	24.5(11)
C25	9040(4)	5838(2)	1041(3)	18.1(10)
C26	9503(4)	6237(2)	3272(3)	14.2(10)
C27	9617(4)	6870(2)	3618(3)	15.8(10)
C28	10632(4)	7127(2)	4219(3)	20.6(11)
C29	11555(4)	6757(2)	4489(3)	21.6(11)
C30	11456(4)	6122(2)	4174(3)	19.3(10)
C31	10441(4)	5863(2)	3573(3)	16.1(10)
C32	6003(3)	4903(2)	2552(3)	13.3(10)
C33	5803(3)	4768(2)	1551(3)	17.2(10)
C34	5822(4)	4092(2)	1437(4)	22.1(11)
C35	6022(4)	3803(2)	2361(4)	19.6(11)
C36	6124(3)	4298(2)	3046(3)	15.4(10)
C37	8441(3)	5046(2)	2702(3)	15.4(10)
C38	8385(4)	4545(2)	2031(4)	20.4(11)
C39	8569(4)	3948(2)	2541(3)	18.7(11)
C40	8771(4)	4070(2)	3538(4)	18.3(10)
C41	8697(3)	4748(2)	3644(3)	16.0(10)
O1	5440(3)	3221.8(17)	4307(3)	36.8(9)
C42	5544(4)	2550(2)	4181(4)	30.4(13)
C43	4461(4)	2303(2)	3413(4)	27.2(12)
C44	3889(4)	2910(3)	2872(4)	33.9(13)
C45	4324(5)	3401(3)	3699(4)	35.8(14)

Table S17. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	20.3(3)	13.8(2)	20.4(2)	3.8(2)	10.9(2)	0.9(2)
Ni1	13.3(3)	11.5(3)	15.0(3)	1.1(2)	7.6(2)	0.7(2)
Fe1	15.1(3)	12.0(3)	17.0(3)	-1.6(3)	8.5(3)	-0.1(3)

P1	13.7(6)	11.5(6)	13.2(6)	0.2(5)	6.5(5)	0.4(5)
P2	15.5(6)	11.8(6)	14.2(6)	0.2(5)	7.0(5)	0.1(5)
F1	27.4(16)	31.3(17)	20.4(15)	-3.5(13)	7.9(13)	3.1(13)
F2	28.7(17)	43.9(19)	26.3(16)	14.8(14)	10.2(13)	0.0(14)
F3	14.3(15)	45.3(19)	27.2(16)	8.1(14)	5.8(12)	1.4(13)
C1	21(3)	11(2)	22(3)	2(2)	14(2)	-1(2)
C2	25(3)	15(2)	29(3)	5(2)	20(2)	0(2)
C3	22(3)	23(3)	33(3)	13(2)	16(2)	6(2)
C4	39(3)	18(3)	39(3)	3(2)	29(3)	7(2)
C5	35(3)	20(3)	25(3)	-2(2)	23(2)	0(2)
C6	25(3)	14(2)	23(3)	2(2)	14(2)	-1(2)
C7	21(3)	27(3)	23(3)	5(2)	10(2)	4(2)
C8	20(3)	11(2)	16(2)	2.3(19)	10(2)	0.4(19)
C9	22(3)	20(3)	19(3)	3(2)	11(2)	1(2)
C10	16(3)	22(3)	25(3)	2(2)	6(2)	-1(2)
C11	16(3)	21(3)	37(3)	13(2)	15(2)	6(2)
C12	26(3)	9(2)	34(3)	4(2)	23(2)	4(2)
C13	19(2)	11(2)	20(2)	2.0(19)	8(2)	-4(2)
C14	15(2)	9(2)	14(2)	-0.8(18)	6.2(19)	5.2(19)
C15	19(2)	15(2)	16(2)	-1(2)	9(2)	-1(2)
C16	27(3)	12(2)	20(3)	5(2)	14(2)	5(2)
C17	26(3)	25(3)	14(2)	1(2)	8(2)	12(2)
C18	15(3)	22(3)	23(3)	-5(2)	4(2)	3(2)
C19	18(2)	11(2)	22(3)	0(2)	12(2)	4(2)
C20	19(2)	10(2)	10(2)	0.6(18)	3.9(19)	-1.8(19)
C21	25(3)	16(2)	20(3)	-2(2)	14(2)	2(2)
C22	21(3)	21(3)	16(3)	2(2)	3(2)	-2(2)
C23	38(3)	21(3)	17(3)	-4(2)	15(2)	-13(2)
C24	28(3)	23(3)	31(3)	-5(2)	20(2)	-4(2)
C25	21(3)	17(2)	17(2)	-1(2)	9(2)	-1(2)
C26	17(2)	12(2)	16(2)	0.7(18)	9(2)	-3.7(19)
C27	16(2)	16(2)	13(2)	2.2(19)	4(2)	3(2)
C28	25(3)	16(2)	21(3)	-2(2)	10(2)	-5(2)
C29	16(3)	31(3)	18(2)	-5(2)	8(2)	-9(2)
C30	19(3)	23(3)	18(3)	1(2)	11(2)	3(2)
C31	21(3)	15(2)	14(2)	0.4(19)	10(2)	-1(2)
C32	9(2)	12(2)	18(2)	-0.8(19)	5.2(19)	-0.6(18)
C33	11(2)	22(3)	15(2)	-1(2)	2.9(19)	1(2)
C34	21(3)	23(3)	24(3)	-9(2)	11(2)	0(2)
C35	17(3)	14(2)	32(3)	-4(2)	15(2)	-4(2)
C36	13(2)	14(2)	21(2)	2(2)	9(2)	2.9(19)
C37	13(2)	14(2)	24(3)	0(2)	12(2)	-3.0(19)

C38	23(3)	22(3)	23(3)	-4(2)	17(2)	-3(2)
C39	23(3)	8(2)	29(3)	-1(2)	15(2)	3(2)
C40	13(2)	17(2)	26(3)	2(2)	11(2)	1(2)
C41	13(2)	16(2)	20(3)	-2(2)	10(2)	-1(2)
O1	45(2)	24(2)	38(2)	-7.7(17)	15.6(19)	-8.5(18)
C42	26(3)	27(3)	37(3)	-1(2)	14(3)	-3(2)
C43	35(3)	24(3)	26(3)	-3(2)	17(2)	-6(2)
C44	28(3)	40(3)	35(3)	2(3)	16(3)	-4(3)
C45	42(4)	25(3)	50(4)	-1(3)	29(3)	7(3)

Table S18. Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3074(7)	C12	C13	1.374(6)
Ni1	P1	2.1497(12)	C14	C15	1.371(6)
Ni1	P2	2.2561(13)	C14	C19	1.384(6)
Ni1	C1	1.898(4)	C15	C16	1.375(6)
Fe1	C32	1.987(4)	C16	C17	1.374(6)
Fe1	C33	2.000(4)	C17	C18	1.359(6)
Fe1	C34	2.024(5)	C18	C19	1.372(6)
Fe1	C35	2.029(4)	C20	C21	1.383(6)
Fe1	C36	2.018(4)	C20	C25	1.375(6)
Fe1	C37	1.991(4)	C21	C22	1.360(6)
Fe1	C38	2.018(4)	C22	C23	1.366(7)
Fe1	C39	2.034(4)	C23	C24	1.378(7)
Fe1	C40	2.044(5)	C24	C25	1.364(6)
Fe1	C41	2.014(4)	C26	C27	1.380(6)
P1	C8	1.817(4)	C26	C31	1.383(6)
P1	C14	1.803(4)	C27	C28	1.369(6)
P1	C32	1.790(4)	C28	C29	1.367(6)
P2	C20	1.820(4)	C29	C30	1.370(6)
P2	C26	1.822(4)	C30	C31	1.371(6)
P2	C37	1.802(4)	C32	C33	1.413(6)
F1	C7	1.335(5)	C32	C36	1.413(6)
F2	C7	1.333(5)	C33	C34	1.400(6)
F3	C7	1.335(5)	C34	C35	1.404(6)
C1	C2	1.385(6)	C35	C36	1.401(6)
C1	C6	1.407(6)	C37	C38	1.410(6)
C2	C3	1.386(6)	C37	C41	1.420(6)
C2	C7	1.470(7)	C38	C39	1.403(6)
C3	C4	1.357(7)	C39	C40	1.402(6)
C4	C5	1.375(7)	C40	C41	1.410(6)
C5	C6	1.360(6)	O1	C42	1.407(6)

C8	C9	1.382(6)	O1	C45	1.423(6)
C8	C13	1.379(6)	C42	C43	1.489(7)
C9	C10	1.368(6)	C43	C44	1.497(7)
C10	C11	1.363(7)	C44	C45	1.488(7)
C11	C12	1.361(7)			

Table S19. Bond Angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Br1	168.27(4)	F2	C7	F3	104.7(4)
P1	Ni1	P2	101.33(5)	F2	C7	C2	112.9(4)
P2	Ni1	Br1	88.67(4)	F3	C7	C2	112.7(4)
C1	Ni1	Br1	85.46(13)	C9	C8	P1	120.2(3)
C1	Ni1	P1	85.94(13)	C13	C8	P1	121.0(3)
C1	Ni1	P2	166.93(14)	C13	C8	C9	118.7(4)
C32	Fe1	C33	41.50(17)	C10	C9	C8	120.2(4)
C32	Fe1	C34	69.30(18)	C11	C10	C9	120.4(5)
C32	Fe1	C35	69.05(18)	C12	C11	C10	120.1(4)
C32	Fe1	C36	41.31(17)	C11	C12	C13	120.2(4)
C32	Fe1	C37	109.41(18)	C12	C13	C8	120.4(4)
C32	Fe1	C38	138.16(18)	C15	C14	P1	121.7(3)
C32	Fe1	C39	178.47(18)	C15	C14	C19	118.8(4)
C32	Fe1	C40	139.73(18)	C19	C14	P1	119.4(3)
C32	Fe1	C41	110.79(18)	C14	C15	C16	120.7(4)
C33	Fe1	C34	40.71(18)	C15	C16	C17	119.4(4)
C33	Fe1	C35	68.48(19)	C18	C17	C16	120.8(4)
C33	Fe1	C36	69.02(18)	C17	C18	C19	119.6(4)
C33	Fe1	C38	110.27(19)	C18	C19	C14	120.7(4)
C33	Fe1	C39	138.51(18)	C21	C20	P2	119.0(3)
C33	Fe1	C40	178.42(19)	C25	C20	P2	122.6(3)
C33	Fe1	C41	139.13(18)	C25	C20	C21	118.4(4)
C34	Fe1	C35	40.55(19)	C22	C21	C20	120.9(4)
C34	Fe1	C39	111.64(19)	C21	C22	C23	120.2(4)
C34	Fe1	C40	139.50(19)	C22	C23	C24	119.8(4)
C35	Fe1	C39	112.46(18)	C25	C24	C23	119.8(4)
C35	Fe1	C40	112.65(19)	C24	C25	C20	121.0(4)
C36	Fe1	C34	68.52(18)	C27	C26	P2	121.6(3)
C36	Fe1	C35	40.51(17)	C27	C26	C31	118.1(4)
C36	Fe1	C38	179.3(2)	C31	C26	P2	120.3(3)
C36	Fe1	C39	140.02(18)	C28	C27	C26	121.1(4)
C36	Fe1	C40	112.56(18)	C29	C28	C27	120.2(4)
C37	Fe1	C33	109.63(19)	C30	C29	C28	119.6(4)
C37	Fe1	C34	138.10(19)	C29	C30	C31	120.4(4)

C37	Fe1	C35	178.09(19)	C30	C31	C26	120.6(4)
C37	Fe1	C36	138.94(18)	P1	C32	Fe1	125.5(2)
C37	Fe1	C38	41.18(18)	C33	C32	Fe1	69.7(2)
C37	Fe1	C39	69.07(18)	C33	C32	P1	124.0(3)
C37	Fe1	C40	69.24(18)	C33	C32	C36	107.3(4)
C37	Fe1	C41	41.52(18)	C36	C32	Fe1	70.5(2)
C38	Fe1	C34	110.94(19)	C36	C32	P1	128.7(3)
C38	Fe1	C35	139.33(18)	C32	C33	Fe1	68.8(2)
C38	Fe1	C39	40.52(18)	C34	C33	Fe1	70.6(3)
C38	Fe1	C40	68.15(19)	C34	C33	C32	108.4(4)
C39	Fe1	C40	40.22(17)	C33	C34	Fe1	68.7(3)
C41	Fe1	C34	179.6(2)	C33	C34	C35	107.9(4)
C41	Fe1	C35	139.84(19)	C35	C34	Fe1	69.9(3)
C41	Fe1	C36	111.81(18)	C34	C35	Fe1	69.6(3)
C41	Fe1	C38	68.73(19)	C36	C35	Fe1	69.3(3)
C41	Fe1	C39	68.25(18)	C36	C35	C34	108.4(4)
C41	Fe1	C40	40.65(17)	C32	C36	Fe1	68.2(2)
C8	P1	Ni1	117.82(14)	C35	C36	Fe1	70.2(3)
C14	P1	Ni1	112.10(15)	C35	C36	C32	108.0(4)
C14	P1	C8	103.1(2)	P2	C37	Fe1	121.9(2)
C32	P1	Ni1	116.30(15)	C38	C37	Fe1	70.4(3)
C32	P1	C8	100.6(2)	C38	C37	P2	127.5(4)
C32	P1	C14	105.2(2)	C38	C37	C41	107.1(4)
C20	P2	Ni1	113.02(15)	C41	C37	Fe1	70.1(2)
C20	P2	C26	104.8(2)	C41	C37	P2	125.3(3)
C26	P2	Ni1	112.66(15)	C37	C38	Fe1	68.4(2)
C37	P2	Ni1	124.63(14)	C39	C38	Fe1	70.4(3)
C37	P2	C20	99.4(2)	C39	C38	C37	108.4(4)
C37	P2	C26	99.8(2)	C38	C39	Fe1	69.1(3)
C2	C1	Ni1	127.8(4)	C40	C39	Fe1	70.3(3)
C2	C1	C6	115.9(4)	C40	C39	C38	108.4(4)
C6	C1	Ni1	116.2(3)	C39	C40	Fe1	69.5(3)
C1	C2	C3	121.8(5)	C39	C40	C41	107.7(4)
C1	C2	C7	122.4(4)	C41	C40	Fe1	68.5(3)
C3	C2	C7	115.8(4)	C37	C41	Fe1	68.4(2)
C4	C3	C2	120.5(5)	C40	C41	Fe1	70.8(3)
C3	C4	C5	119.2(5)	C40	C41	C37	108.3(4)
C6	C5	C4	120.8(5)	C42	O1	C45	108.2(4)
C5	C6	C1	121.8(5)	O1	C42	C43	108.1(4)
F1	C7	F3	105.4(4)	C42	C43	C44	102.9(4)
F1	C7	C2	114.4(4)	C45	C44	C43	101.8(4)
F2	C7	F1	105.9(4)	O1	C45	C44	105.2(4)

*X-ray Diffraction Data for (dppf)Ni(2-methoxyphenyl)(Br) (**5**)*

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **5** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **5**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The overall data quality was poor. The model reported here is intended to establish the atom connectivity of the target complex. The thermal parameters of each molecular model were globally restrained to behave as rigid bodies. Each cyclopentadienyl group and two aryl groups were constrained to have identical thermal parameters. The oxygen atoms of the THF groups are disordered over two positions with constrained occupancy distributions of 0.6/0.4. The full numbering scheme of compound **5** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S20. Crystal data and structure refinement for **5**.

Empirical formula	$C_{45}H_{43}BrFeNiO_2P_2$
Formula weight	872.20
Temperature/K	93(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.6336(9)
b/Å	14.7133(14)
c/Å	24.133(2)
α/°	82.664(8)
β/°	84.682(8)
γ/°	89.874(7)
Volume/Å^3	3728.5(6)

Z	4
ρ_{calc}g/cm^3	1.554
μ/mm^{-1}	2.091
F(000)	1792.0
Crystal size/mm^3	0.200 × 0.200 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.846 to 41.63
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	33581
Independent reflections	7802 [R_{int} = 0.2421, R_{sigma} = 0.1944]
Data/restraints/parameters	7802/1068/801
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0932, wR_2 = 0.1852
Final R indexes [all data]	R_1 = 0.1777, wR_2 = 0.2268

Table S21. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	10815.7(16)	8060.7(12)	8053.1(8)	31.8(6)
Ni1	9138.6(19)	8841.7(15)	7661.9(10)	25.8(6)
Fe1	5287(2)	9094.5(17)	8183.7(11)	27.4(7)
P1	7716(4)	9519(3)	7183(2)	24.8(12)
P2	8248(4)	8929(3)	8547(2)	28.6(12)
O1	8829(11)	7518(8)	6909(5)	39(3)
C1	10060(15)	8799(12)	6955(8)	32(3)
C2	9787(17)	8098(12)	6658(8)	35(4)
C3	10398(17)	7989(13)	6128(8)	43(5)
C4	11305(18)	8609(13)	5902(9)	48(5)
C5	11657(17)	9328(13)	6197(8)	44(5)
C6	11014(15)	9405(12)	6726(8)	33(4)
C7	8454(17)	6791(12)	6610(8)	43(5)
C8	6136(15)	9110(11)	7406(7)	26.7(17)
C9	4939(14)	9534(11)	7374(7)	26.7(17)
C10	4024(15)	8951(11)	7620(7)	26.7(17)
C11	4587(14)	8066(11)	7777(7)	26.7(17)
C12	5882(15)	8184(11)	7633(7)	26.7(17)
C13	6581(15)	9237(11)	8721(8)	29.7(17)
C14	6042(15)	10122(11)	8540(7)	29.7(17)
C15	4757(15)	10003(11)	8714(7)	29.7(17)
C16	4446(16)	9155(11)	8991(7)	29.7(17)
C17	5579(15)	8644(12)	8994(7)	29.7(17)

C18	7776(15)	9486(11)	6427(7)	24(3)
C19	7105(16)	8834(11)	6209(7)	29(4)
C20	7187(16)	8817(12)	5644(8)	33(4)
C21	7944(16)	9410(11)	5268(8)	33(4)
C22	8649(16)	10061(12)	5494(8)	34(4)
C23	8542(15)	10085(11)	6053(8)	27(4)
C24	7696(16)	10740(11)	7236(8)	30(4)
C25	8559(16)	11105(11)	7537(8)	35(4)
C26	8531(16)	12022(11)	7608(8)	35(5)
C27	7660(17)	12597(12)	7364(9)	44(5)
C28	6799(16)	12247(11)	7057(8)	35(4)
C29	6855(16)	11342(11)	6979(8)	34(4)
C30	8384(15)	7864(11)	8996(7)	22(3)
C31	9227(16)	7773(12)	9417(7)	34(4)
C32	9350(17)	6909(12)	9718(8)	37(5)
C33	8647(17)	6172(12)	9618(8)	35(5)
C34	7830(16)	6264(12)	9220(7)	32(4)
C35	7727(15)	7099(11)	8894(7)	27(4)
C36	9029(16)	9791(11)	8885(8)	32(4)
C37	10235(15)	10092(10)	8688(7)	26(4)
C38	10841(17)	10769(11)	8913(8)	35(4)
C39	10241(17)	11155(12)	9348(8)	35(4)
C40	9036(17)	10836(11)	9575(8)	32(4)
C41	8485(17)	10169(12)	9344(8)	36(4)
Br2	5775.7(16)	5625.5(12)	8099.5(8)	30.0(5)
Ni2	4121.1(19)	5023.1(14)	7684.0(10)	23.6(6)
Fe2	265(2)	4537.3(16)	8173.5(11)	24.6(7)
P3	2712(4)	4556(3)	7188(2)	21.5(11)
P4	3225(4)	4534(3)	8558(2)	23.9(12)
O2	3812(10)	6673(7)	6923(5)	36(3)
C42	5055(14)	5392(11)	6982(8)	26(3)
C43	4770(15)	6194(11)	6679(8)	28(4)
C44	5393(17)	6475(13)	6149(8)	38(4)
C45	6318(17)	5985(13)	5940(9)	45(5)
C46	6664(16)	5158(13)	6229(8)	38(4)
C47	6026(14)	4863(12)	6746(8)	29(4)
C48	3437(16)	7509(11)	6617(8)	39(5)
C49	1115(14)	4882(11)	7409(7)	23.3(16)
C50	853(14)	5685(11)	7651(7)	23.3(16)
C51	-470(14)	5732(11)	7781(7)	23.3(16)
C52	-1000(15)	4972(10)	7617(7)	23.3(16)
C53	-53(14)	4434(11)	7373(7)	23.3(16)

C54	1562(14)	4158(11)	8711(7)	25.1(16)
C55	571(14)	4650(11)	8984(7)	25.1(16)
C56	-566(15)	4167(10)	8971(7)	25.1(16)
C57	-273(14)	3393(11)	8696(7)	25.1(16)
C58	1048(14)	3362(11)	8544(7)	25.1(16)
C59	2771(15)	4900(11)	6437(7)	26(3)
C60	2119(15)	5660(11)	6215(7)	26(4)
C61	2197(18)	5946(13)	5640(8)	45(5)
C62	2975(16)	5452(13)	5291(8)	40(5)
C63	3652(16)	4720(12)	5508(8)	34(4)
C64	3568(16)	4442(12)	6069(8)	31(4)
C65	2718(14)	3313(11)	7236(7)	20(3)
C66	3580(15)	2838(11)	7543(7)	26(4)
C67	3549(16)	1876(12)	7613(8)	35(4)
C68	2682(16)	1421(13)	7377(8)	37(5)
C69	1836(16)	1871(12)	7062(8)	34(4)
C70	1868(14)	2830(11)	6961(7)	23(4)
C71	3258(15)	5405(11)	9019(8)	27.7(19)
C72	2788(14)	6269(11)	8858(8)	27.7(19)
C73	2701(14)	6934(12)	9209(8)	27.7(19)
C74	3104(14)	6774(12)	9717(8)	27.7(19)
C75	3543(14)	5935(11)	9919(8)	27.7(19)
C76	3615(14)	5261(12)	9568(7)	27.7(19)
C77	4036(15)	3517(11)	8896(8)	28.2(19)
C78	5253(15)	3339(11)	8694(8)	28.2(19)
C79	5812(15)	2517(11)	8939(7)	28.2(19)
C80	5191(15)	1955(11)	9364(7)	28.2(19)
C81	4003(15)	2164(11)	9549(8)	28.2(19)
C82	3431(16)	2955(11)	9315(7)	28.2(19)
O3	5570(30)	8940(18)	3900(13)	85(7)
O4	6370(30)	8680(20)	4304(18)	69(9)
C83	5080(20)	9236(14)	4385(10)	60(5)
C84	4226(19)	8515(13)	4700(9)	59(5)
C85	4730(20)	7639(14)	4513(10)	74(7)
C86	5840(20)	7956(16)	4134(12)	88(7)
O5	570(20)	6552(16)	3897(12)	71(6)
O6	1360(40)	6610(30)	4258(18)	75(10)
C87	870(20)	7433(16)	4152(12)	94(7)
C88	-240(20)	7583(16)	4506(12)	96(8)
C89	-760(20)	6646(14)	4690(11)	73(6)
C90	80(20)	6025(15)	4370(10)	68(6)

Table S22. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	12.7(11)	33.8(12)	48.1(14)	0.0(10)	-5.4(9)	4.4(8)
Ni1	9.6(13)	26.7(14)	40.3(16)	-1.2(11)	-3.0(11)	0.3(10)
Fe1	10.5(14)	29.7(16)	41.9(18)	-5.7(13)	0.3(12)	-1.3(11)
P1	9(2)	22(3)	42(3)	-3(2)	0(2)	-0.9(19)
P2	17(3)	23(3)	46(3)	-2(2)	-3(2)	-3(2)
O1	26(7)	44(7)	47(7)	-10(5)	-3(5)	-5(5)
C1	9(6)	38(7)	47(6)	-1(5)	-4(5)	7(5)
C2	22(8)	36(7)	46(7)	-1(6)	-7(6)	2(6)
C3	30(9)	50(9)	46(8)	1(6)	-3(6)	10(7)
C4	35(10)	55(10)	51(9)	4(7)	2(7)	6(7)
C5	19(9)	54(10)	54(9)	5(7)	3(7)	7(7)
C6	9(7)	40(8)	48(8)	6(6)	-6(6)	3(6)
C7	34(11)	46(9)	50(12)	-10(8)	-8(9)	-6(8)
C8	11(3)	26(4)	43(3)	-6(3)	1(3)	-4(3)
C9	11(3)	26(4)	43(3)	-6(3)	1(3)	-4(3)
C10	11(3)	26(4)	43(3)	-6(3)	1(3)	-4(3)
C11	11(3)	26(4)	43(3)	-6(3)	1(3)	-4(3)
C12	11(3)	26(4)	43(3)	-6(3)	1(3)	-4(3)
C13	17(3)	27(4)	44(3)	-6(3)	2(3)	-3(3)
C14	17(3)	27(4)	44(3)	-6(3)	2(3)	-3(3)
C15	17(3)	27(4)	44(3)	-6(3)	2(3)	-3(3)
C16	17(3)	27(4)	44(3)	-6(3)	2(3)	-3(3)
C17	17(3)	27(4)	44(3)	-6(3)	2(3)	-3(3)
C18	10(7)	22(7)	42(5)	-5(4)	0(4)	5(5)
C19	26(9)	27(8)	34(7)	-2(6)	-5(6)	-5(7)
C20	33(10)	33(9)	34(7)	1(6)	-7(6)	-4(7)
C21	26(10)	34(9)	37(8)	4(6)	-6(6)	4(7)
C22	22(9)	37(9)	41(7)	-3(6)	-1(6)	4(7)
C23	12(8)	27(8)	42(6)	-1(6)	-4(6)	1(6)
C24	19(8)	17(5)	53(9)	-3(5)	2(7)	0(4)
C25	26(8)	22(6)	55(11)	-1(6)	-2(8)	-2(5)
C26	18(8)	22(6)	64(12)	-7(7)	3(8)	2(5)
C27	25(9)	22(7)	85(13)	-9(7)	-8(9)	6(6)
C28	15(8)	21(6)	67(12)	-1(6)	7(8)	-2(6)
C29	18(8)	24(6)	57(11)	2(6)	3(8)	0(5)
C30	13(7)	22(5)	28(7)	-4(5)	8(5)	0(4)
C31	31(9)	31(7)	41(9)	-5(6)	-6(7)	2(6)
C32	31(9)	32(7)	47(10)	-1(6)	-8(8)	2(6)
C33	35(10)	29(7)	41(10)	0(6)	-4(8)	0(6)

C34	28(9)	27(7)	38(10)	2(6)	2(7)	1(6)
C35	23(9)	23(6)	35(9)	-4(5)	0(7)	0(5)
C36	27(6)	24(7)	46(8)	1(6)	-7(5)	-6(5)
C37	25(7)	8(7)	43(9)	12(6)	-10(6)	0(5)
C38	27(8)	20(8)	57(10)	0(7)	-6(7)	-5(6)
C39	32(8)	20(8)	54(10)	1(7)	-11(7)	1(6)
C40	33(8)	24(8)	40(9)	0(7)	-15(7)	-3(6)
C41	34(8)	27(9)	47(9)	-2(7)	-4(7)	-11(6)
Br2	10.9(10)	30.1(11)	49.8(14)	-7.1(10)	-3.8(9)	-3.5(8)
Ni2	5.7(12)	23.9(13)	40.8(16)	-4.2(11)	-0.4(11)	-2.3(10)
Fe2	6.2(14)	23.0(15)	43.5(18)	-0.4(13)	-2.1(12)	0.5(11)
P3	5(2)	21(2)	39(3)	-4(2)	-2(2)	-0.1(18)
P4	9(2)	23(3)	40(3)	-4(2)	0(2)	0.7(19)
O2	24(6)	29(6)	55(8)	-4(5)	-3(5)	5(5)
C42	7(6)	25(6)	47(6)	-7(4)	-3(4)	-8(4)
C43	14(7)	26(6)	45(7)	-8(5)	-9(5)	-6(5)
C44	30(9)	37(8)	48(8)	-7(6)	-2(6)	-9(6)
C45	30(9)	45(9)	60(9)	-9(7)	1(7)	-9(7)
C46	15(8)	45(9)	56(9)	-15(6)	-2(6)	-8(7)
C47	7(7)	28(7)	54(8)	-14(6)	-6(6)	-6(6)
C48	24(10)	34(8)	58(12)	-2(7)	-8(9)	2(7)
C49	4(3)	24(3)	41(3)	-2(3)	0(2)	3(2)
C50	4(3)	24(3)	41(3)	-2(3)	0(2)	3(2)
C51	4(3)	24(3)	41(3)	-2(3)	0(2)	3(2)
C52	4(3)	24(3)	41(3)	-2(3)	0(2)	3(2)
C53	4(3)	24(3)	41(3)	-2(3)	0(2)	3(2)
C54	8(3)	23(3)	43(3)	0(3)	-1(2)	3(2)
C55	8(3)	23(3)	43(3)	0(3)	-1(2)	3(2)
C56	8(3)	23(3)	43(3)	0(3)	-1(2)	3(2)
C57	8(3)	23(3)	43(3)	0(3)	-1(2)	3(2)
C58	8(3)	23(3)	43(3)	0(3)	-1(2)	3(2)
C59	21(8)	17(7)	39(5)	-4(4)	0(4)	-9(5)
C60	15(8)	17(7)	41(7)	4(5)	4(6)	-11(6)
C61	36(11)	49(9)	44(7)	7(6)	7(7)	1(8)
C62	27(10)	49(10)	41(8)	4(6)	1(7)	-4(7)
C63	20(9)	42(9)	40(7)	-6(6)	-3(6)	-11(7)
C64	21(9)	33(8)	39(6)	-6(6)	-1(6)	-3(7)
C65	6(7)	24(5)	30(8)	-4(4)	6(6)	1(4)
C66	14(8)	33(6)	30(9)	-5(6)	5(7)	5(5)
C67	14(8)	33(7)	57(11)	-5(6)	1(8)	4(5)
C68	15(9)	33(7)	61(12)	-3(7)	1(8)	1(6)
C69	15(8)	29(6)	60(12)	-9(6)	-2(8)	-1(5)

C70	8(7)	29(6)	33(9)	-9(6)	6(7)	3(5)
C71	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C72	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C73	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C74	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C75	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C76	8(4)	33(4)	45(5)	-12(4)	-5(3)	-1(3)
C77	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
C78	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
C79	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
C80	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
C81	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
C82	13(4)	28(4)	43(5)	-7(3)	-3(3)	1(3)
O3	94(17)	60(10)	99(13)	-19(9)	16(11)	-3(10)
O4	55(11)	39(11)	110(20)	5(12)	3(10)	18(8)
C83	50(11)	51(9)	80(13)	-11(8)	-12(9)	14(7)
C84	47(10)	51(9)	80(13)	-12(9)	-11(9)	13(7)
C85	71(12)	45(9)	103(16)	-11(8)	12(11)	6(7)
C86	80(12)	60(9)	121(15)	-17(9)	25(11)	1(8)
O5	47(14)	45(10)	112(14)	8(9)	7(10)	14(9)
O6	57(11)	52(11)	110(30)	-21(12)	10(11)	-18(9)
C87	71(12)	55(9)	147(17)	-7(10)	32(11)	-12(8)
C88	71(13)	59(10)	152(19)	-18(10)	28(13)	-13(8)
C89	45(11)	66(10)	107(15)	-14(10)	3(10)	-16(8)
C90	57(11)	51(9)	94(15)	-2(8)	-6(10)	-11(8)

Table S23. Bond Lengths for **5**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	Ni1	2.328(3)	Fe2	C57	2.019(16)
Ni1	C1	1.896(18)	Fe2	C52	2.033(16)
Ni1	P1	2.155(5)	Fe2	C50	2.036(16)
Ni1	P2	2.274(6)	Fe2	C55	2.040(18)
Fe1	C8	2.004(17)	Fe2	C56	2.049(17)
Fe1	C13	2.004(18)	Fe2	C58	2.054(16)
Fe1	C15	2.011(17)	Fe2	C51	2.075(16)
Fe1	C10	2.027(17)	P3	C59	1.814(18)
Fe1	C14	2.033(17)	P3	C49	1.814(16)
Fe1	C17	2.035(18)	P3	C65	1.818(16)
Fe1	C9	2.046(18)	P4	C71	1.803(17)
Fe1	C12	2.063(17)	P4	C54	1.844(16)
Fe1	C16	2.079(17)	P4	C77	1.860(17)

Fe1	C11	2.080(16)	O2	C43	1.369(19)
P1	C8	1.798(16)	O2	C48	1.428(19)
P1	C24	1.817(16)	C42	C43	1.36(2)
P1	C18	1.826(18)	C42	C47	1.41(2)
P2	C30	1.801(17)	C43	C44	1.40(2)
P2	C36	1.832(18)	C44	C45	1.32(2)
P2	C13	1.853(17)	C45	C46	1.39(2)
O1	C2	1.38(2)	C46	C47	1.38(2)
O1	C7	1.442(19)	C49	C50	1.40(2)
C1	C2	1.37(2)	C49	C53	1.42(2)
C1	C6	1.38(2)	C50	C51	1.42(2)
C2	C3	1.41(2)	C51	C52	1.37(2)
C3	C4	1.36(2)	C52	C53	1.41(2)
C4	C5	1.42(3)	C54	C58	1.41(2)
C5	C6	1.41(2)	C54	C55	1.43(2)
C8	C12	1.42(2)	C55	C56	1.41(2)
C8	C9	1.42(2)	C56	C57	1.41(2)
C9	C10	1.34(2)	C57	C58	1.42(2)
C10	C11	1.45(2)	C59	C60	1.39(2)
C11	C12	1.39(2)	C59	C64	1.41(2)
C13	C17	1.43(2)	C60	C61	1.39(2)
C13	C14	1.45(2)	C61	C62	1.40(2)
C14	C15	1.40(2)	C62	C63	1.37(2)
C15	C16	1.36(2)	C63	C64	1.36(2)
C16	C17	1.42(2)	C65	C66	1.37(2)
C18	C19	1.38(2)	C65	C70	1.41(2)
C18	C23	1.39(2)	C66	C67	1.40(2)
C19	C20	1.36(2)	C67	C68	1.35(2)
C20	C21	1.38(2)	C68	C69	1.35(2)
C21	C22	1.41(2)	C69	C70	1.40(2)
C22	C23	1.35(2)	C71	C72	1.39(2)
C24	C25	1.37(2)	C71	C76	1.40(2)
C24	C29	1.39(2)	C72	C73	1.37(2)
C25	C26	1.38(2)	C73	C74	1.33(2)
C26	C27	1.38(2)	C74	C75	1.37(2)
C27	C28	1.37(2)	C75	C76	1.38(2)
C28	C29	1.37(2)	C77	C82	1.34(2)
C30	C35	1.39(2)	C77	C78	1.38(2)
C30	C31	1.41(2)	C78	C79	1.43(2)
C31	C32	1.39(2)	C79	C80	1.35(2)
C32	C33	1.38(2)	C80	C81	1.35(2)
C33	C34	1.35(2)	C81	C82	1.39(2)

C34	C35	1.38(2)	O3	C83	1.36(3)
C36	C37	1.38(2)	O3	C86	1.52(3)
C36	C41	1.38(2)	O4	C86	1.33(4)
C37	C38	1.38(2)	O4	C83	1.61(4)
C38	C39	1.36(2)	C83	C84	1.48(3)
C39	C40	1.40(2)	C84	C85	1.50(3)
C40	C41	1.35(2)	C85	C86	1.46(3)
Br2	Ni2	2.334(3)	O5	C90	1.36(3)
Ni2	C42	1.898(17)	O5	C87	1.55(3)
Ni2	P3	2.167(5)	O6	C87	1.32(4)
Ni2	P4	2.263(5)	O6	C90	1.59(4)
Fe2	C49	1.983(17)	C87	C88	1.43(3)
Fe2	C54	2.010(17)	C88	C89	1.48(3)
Fe2	C53	2.018(17)	C89	C90	1.51(3)

Table S24. Bond Angles for **5**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C1	Ni1	P1	85.0(5)	C54	Fe2	C53	139.1(6)
C1	Ni1	P2	173.4(6)	C49	Fe2	C57	138.9(7)
P1	Ni1	P2	100.09(19)	C54	Fe2	C57	68.2(6)
C1	Ni1	Br1	86.7(5)	C53	Fe2	C57	112.1(7)
P1	Ni1	Br1	171.53(18)	C49	Fe2	C52	68.7(6)
P2	Ni1	Br1	88.32(15)	C54	Fe2	C52	177.5(7)
C8	Fe1	C13	109.8(7)	C53	Fe2	C52	40.8(6)
C8	Fe1	C15	137.9(7)	C57	Fe2	C52	114.3(6)
C13	Fe1	C15	67.9(7)	C49	Fe2	C50	40.7(6)
C8	Fe1	C10	68.3(7)	C54	Fe2	C50	110.4(7)
C13	Fe1	C10	178.1(7)	C53	Fe2	C50	68.5(7)
C15	Fe1	C10	113.5(7)	C57	Fe2	C50	178.6(6)
C8	Fe1	C14	108.3(7)	C52	Fe2	C50	67.0(6)
C13	Fe1	C14	42.2(6)	C49	Fe2	C55	138.6(6)
C15	Fe1	C14	40.4(6)	C54	Fe2	C55	41.5(6)
C10	Fe1	C14	138.0(7)	C53	Fe2	C55	179.4(6)
C8	Fe1	C17	140.2(7)	C57	Fe2	C55	68.0(7)
C13	Fe1	C17	41.6(6)	C52	Fe2	C55	138.6(6)
C15	Fe1	C17	66.9(7)	C50	Fe2	C55	111.4(7)
C10	Fe1	C17	139.9(6)	C49	Fe2	C56	178.4(7)
C14	Fe1	C17	70.2(7)	C54	Fe2	C56	68.7(6)
C8	Fe1	C9	41.0(6)	C53	Fe2	C56	139.4(6)
C13	Fe1	C9	140.0(7)	C57	Fe2	C56	40.5(6)
C15	Fe1	C9	112.9(7)	C52	Fe2	C56	112.9(6)

C10	Fe1	C9	38.5(6)	C50	Fe2	C56	139.8(6)
C14	Fe1	C9	110.9(7)	C55	Fe2	C56	40.3(6)
C17	Fe1	C9	178.3(6)	C49	Fe2	C58	109.8(7)
C8	Fe1	C12	40.8(6)	C54	Fe2	C58	40.7(6)
C13	Fe1	C12	111.0(7)	C53	Fe2	C58	111.4(7)
C15	Fe1	C12	178.2(6)	C57	Fe2	C58	40.8(6)
C10	Fe1	C12	67.6(7)	C52	Fe2	C58	141.4(6)
C14	Fe1	C12	137.9(6)	C50	Fe2	C58	137.9(6)
C17	Fe1	C12	113.3(7)	C55	Fe2	C58	69.1(7)
C9	Fe1	C12	66.9(7)	C56	Fe2	C58	68.9(6)
C8	Fe1	C16	176.7(7)	C49	Fe2	C51	68.4(6)
C13	Fe1	C16	68.6(7)	C54	Fe2	C51	138.8(6)
C15	Fe1	C16	38.9(6)	C53	Fe2	C51	67.8(7)
C10	Fe1	C16	113.2(7)	C57	Fe2	C51	141.1(6)
C14	Fe1	C16	68.5(7)	C52	Fe2	C51	39.0(6)
C17	Fe1	C16	40.4(6)	C50	Fe2	C51	40.3(6)
C9	Fe1	C16	138.5(7)	C55	Fe2	C51	111.7(7)
C12	Fe1	C16	142.3(6)	C56	Fe2	C51	112.9(6)
C8	Fe1	C11	68.3(6)	C58	Fe2	C51	178.0(7)
C13	Fe1	C11	138.2(7)	C59	P3	C49	100.9(8)
C15	Fe1	C11	142.4(6)	C59	P3	C65	102.3(8)
C10	Fe1	C11	41.4(6)	C49	P3	C65	106.9(7)
C14	Fe1	C11	176.6(7)	C59	P3	Ni2	121.4(5)
C17	Fe1	C11	112.3(7)	C49	P3	Ni2	113.6(6)
C9	Fe1	C11	66.7(7)	C65	P3	Ni2	110.3(6)
C12	Fe1	C11	39.3(6)	C71	P4	C54	99.7(8)
C16	Fe1	C11	114.9(7)	C71	P4	C77	106.7(8)
C8	P1	C24	105.8(8)	C54	P4	C77	100.5(7)
C8	P1	C18	101.1(8)	C71	P4	Ni2	112.2(6)
C24	P1	C18	102.9(8)	C54	P4	Ni2	123.6(6)
C8	P1	Ni1	114.1(6)	C77	P4	Ni2	112.3(6)
C24	P1	Ni1	111.0(6)	C43	O2	C48	117.7(14)
C18	P1	Ni1	120.4(5)	C43	C42	C47	117.2(17)
C30	P2	C36	105.4(8)	C43	C42	Ni2	119.2(13)
C30	P2	C13	102.1(8)	C47	C42	Ni2	123.5(14)
C36	P2	C13	99.3(8)	C42	C43	O2	114.9(16)
C30	P2	Ni1	111.5(5)	C42	C43	C44	121.3(17)
C36	P2	Ni1	112.2(6)	O2	C43	C44	123.8(17)
C13	P2	Ni1	124.3(6)	C45	C44	C43	121(2)
C2	O1	C7	117.8(14)	C44	C45	C46	121(2)
C2	C1	C6	117.8(18)	C47	C46	C45	118.5(18)
C2	C1	Ni1	117.7(14)	C46	C47	C42	121.2(18)

C6	C1	Ni1	124.4(15)	C50	C49	C53	108.0(14)
C1	C2	O1	114.8(17)	C50	C49	P3	122.3(12)
C1	C2	C3	123.5(18)	C53	C49	P3	129.7(13)
O1	C2	C3	121.7(17)	C50	C49	Fe2	71.7(10)
C4	C3	C2	118(2)	C53	C49	Fe2	70.5(9)
C3	C4	C5	121(2)	P3	C49	Fe2	124.1(9)
C6	C5	C4	118.5(18)	C49	C50	C51	108.3(14)
C1	C6	C5	121.1(19)	C49	C50	Fe2	67.6(9)
C12	C8	C9	105.9(14)	C51	C50	Fe2	71.3(9)
C12	C8	P1	121.7(12)	C52	C51	C50	107.4(15)
C9	C8	P1	132.3(13)	C52	C51	Fe2	68.9(9)
C12	C8	Fe1	71.8(10)	C50	C51	Fe2	68.4(9)
C9	C8	Fe1	71.1(10)	C51	C52	C53	110.2(15)
P1	C8	Fe1	124.9(9)	C51	C52	Fe2	72.2(10)
C10	C9	C8	110.0(16)	C53	C52	Fe2	69.0(9)
C10	C9	Fe1	70.0(11)	C52	C53	C49	106.1(15)
C8	C9	Fe1	67.9(10)	C52	C53	Fe2	70.2(10)
C9	C10	C11	108.5(15)	C49	C53	Fe2	67.9(10)
C9	C10	Fe1	71.5(10)	C58	C54	C55	109.2(14)
C11	C10	Fe1	71.3(10)	C58	C54	P4	124.9(12)
C12	C11	C10	106.0(15)	C55	C54	P4	125.9(12)
C12	C11	Fe1	69.7(9)	C58	C54	Fe2	71.3(10)
C10	C11	Fe1	67.3(9)	C55	C54	Fe2	70.4(9)
C11	C12	C8	109.2(15)	P4	C54	Fe2	121.4(9)
C11	C12	Fe1	71.0(10)	C56	C55	C54	107.4(15)
C8	C12	Fe1	67.4(10)	C56	C55	Fe2	70.2(10)
C17	C13	C14	108.1(14)	C54	C55	Fe2	68.1(10)
C17	C13	P2	127.4(13)	C55	C56	C57	107.4(14)
C14	C13	P2	124.1(12)	C55	C56	Fe2	69.5(10)
C17	C13	Fe1	70.3(10)	C57	C56	Fe2	68.6(10)
C14	C13	Fe1	70.0(10)	C56	C57	C58	110.2(15)
P2	C13	Fe1	120.3(9)	C56	C57	Fe2	70.9(10)
C15	C14	C13	103.7(15)	C58	C57	Fe2	70.9(9)
C15	C14	Fe1	68.9(10)	C54	C58	C57	105.8(14)
C13	C14	Fe1	67.8(10)	C54	C58	Fe2	68.0(9)
C16	C15	C14	114.1(16)	C57	C58	Fe2	68.3(9)
C16	C15	Fe1	73.2(10)	C60	C59	C64	118.3(17)
C14	C15	Fe1	70.7(10)	C60	C59	P3	121.4(13)
C15	C16	C17	106.5(15)	C64	C59	P3	120.1(14)
C15	C16	Fe1	67.8(10)	C61	C60	C59	121.7(17)
C17	C16	Fe1	68.1(10)	C60	C61	C62	117.8(19)
C16	C17	C13	107.5(15)	C63	C62	C61	121.0(19)

C16	C17	Fe1	71.5(10)	C64	C63	C62	121.0(19)
C13	C17	Fe1	68.1(10)	C63	C64	C59	120.3(18)
C19	C18	C23	117.6(17)	C66	C65	C70	119.5(15)
C19	C18	P1	121.1(13)	C66	C65	P3	118.6(13)
C23	C18	P1	121.2(13)	C70	C65	P3	121.9(12)
C20	C19	C18	119.7(17)	C65	C66	C67	119.4(16)
C19	C20	C21	123.3(18)	C68	C67	C66	120.6(17)
C20	C21	C22	116.7(18)	C67	C68	C69	121.4(18)
C23	C22	C21	119.7(18)	C68	C69	C70	120.1(17)
C22	C23	C18	123.1(17)	C69	C70	C65	118.7(16)
C25	C24	C29	117.0(16)	C72	C71	C76	115.0(16)
C25	C24	P1	119.5(13)	C72	C71	P4	119.7(14)
C29	C24	P1	123.5(14)	C76	C71	P4	124.9(13)
C24	C25	C26	121.0(17)	C73	C72	C71	122.1(18)
C27	C26	C25	120.6(18)	C74	C73	C72	120.4(18)
C28	C27	C26	119.2(17)	C73	C74	C75	121.6(18)
C29	C28	C27	119.5(18)	C74	C75	C76	117.9(18)
C28	C29	C24	122.4(18)	C75	C76	C71	122.9(17)
C35	C30	C31	119.3(16)	C82	C77	C78	120.8(17)
C35	C30	P2	119.2(13)	C82	C77	P4	120.4(13)
C31	C30	P2	121.3(13)	C78	C77	P4	118.7(14)
C32	C31	C30	117.9(17)	C77	C78	C79	117.0(16)
C33	C32	C31	121.2(18)	C80	C79	C78	121.6(16)
C34	C33	C32	120.8(18)	C81	C80	C79	119.1(17)
C33	C34	C35	119.8(18)	C80	C81	C82	120.6(17)
C34	C35	C30	121.0(17)	C77	C82	C81	120.9(16)
C37	C36	C41	115.9(17)	C83	O3	C86	98(2)
C37	C36	P2	120.2(15)	C86	O4	C83	96(3)
C41	C36	P2	123.8(14)	O3	C83	C84	109(2)
C36	C37	C38	122.4(18)	C84	C83	O4	101(2)
C39	C38	C37	119.5(18)	C83	C84	C85	104.3(18)
C38	C39	C40	119.5(18)	C86	C85	C84	102.5(18)
C41	C40	C39	118.8(18)	O4	C86	C85	111(3)
C40	C41	C36	123.7(18)	C85	C86	O3	106(2)
C42	Ni2	P3	85.1(5)	C90	O5	C87	99(2)
C42	Ni2	P4	173.4(5)	C87	O6	C90	99(3)
P3	Ni2	P4	100.08(19)	O6	C87	C88	114(3)
C42	Ni2	Br2	87.1(5)	C88	C87	O5	104(2)
P3	Ni2	Br2	172.02(18)	C87	C88	C89	104(2)
P4	Ni2	Br2	87.85(15)	C88	C89	C90	104.9(19)
C49	Fe2	C54	109.7(7)	O5	C90	C89	106(2)
C49	Fe2	C53	41.6(6)	C89	C90	O6	101(2)

*X-ray Diffraction Data for (dppf)Ni(2,4-xylyl)(Br) (**6**)*

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **6** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **6**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The crystal diffracted poorly, resulting in a low I/σ and a high value of RInt. Seven reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **6** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860563 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S25. Crystal data and structure refinement for **6**.

Empirical formula	$C_{46}H_{45}BrFeNiOP_2$
Formula weight	870.23
Temperature/K	93.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.2522(7)
b/Å	15.2797(7)
c/Å	20.2170(10)
α/°	90
β/°	96.736(5)
γ/°	90
Volume/Å^3	3758.7(3)
Z	4
ρ_{calc}g/cm^3	1.538
μ/mm^{-1}	2.072

F(000)	1792.0
Crystal size/mm^3	0.02 × 0.02 × 0.002
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.902 to 50.048
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	52841
Independent reflections	6634 [R_{int} = 0.1836, R_{sigma} = 0.0992]
Data/restraints/parameters	6634/0/471
Goodness-of-fit on F^2	0.933
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1353
Final R indexes [all data]	R_1 = 0.1098, wR_2 = 0.1613

Table S26. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	6540.0(6)	7058.0(4)	1908.6(3)	26.2(2)
Ni1	7002.4(7)	7673.3(5)	2955.3(4)	19.2(2)
Fe1	6887.6(7)	6935.7(6)	4935.6(4)	20.4(2)
P1	5805.6(14)	6735.8(11)	3369.9(8)	19.6(4)
P2	7707.1(14)	8357.6(10)	3829.4(8)	19.8(4)
C1	7873(5)	8453(4)	2516(3)	20.7(14)
C2	8942(5)	8221(4)	2404(3)	22.3(15)
C3	9542(6)	8792(4)	2069(3)	28.6(17)
C4	9126(6)	9594(4)	1824(3)	27.0(16)
C5	8068(6)	9791(4)	1923(3)	27.1(16)
C6	7456(6)	9240(4)	2266(3)	26.7(16)
C7	9379(6)	7359(4)	2637(4)	30.5(17)
C8	9833(6)	10198(5)	1474(4)	38.3(19)
C9	6097(5)	5606(4)	3201(3)	20.1(14)
C10	5337(6)	4965(4)	3289(3)	21.8(15)
C11	5533(6)	4100(4)	3154(3)	28.3(16)
C12	6498(6)	3876(4)	2927(4)	33.3(17)
C13	7272(6)	4493(5)	2842(3)	30.6(17)
C14	7077(6)	5367(4)	2981(3)	23.9(15)
C15	4383(5)	6809(4)	2989(3)	22.1(15)
C16	3561(5)	7173(4)	3314(3)	26.1(16)
C17	2494(6)	7194(4)	3010(3)	27.9(16)
C18	2237(6)	6857(4)	2381(3)	28.5(16)
C19	3052(5)	6490(4)	2064(3)	23.7(15)
C20	4114(5)	6461(4)	2360(3)	23.0(15)
C21	5761(5)	9261(4)	3643(3)	22.0(15)
C22	5027(6)	9905(4)	3778(3)	25.4(16)

C23	5297(6)	10504(4)	4273(3)	30.7(17)
C24	6304(6)	10461(4)	4641(3)	27.7(16)
C25	7048(5)	9833(4)	4518(3)	23.0(15)
C26	6774(5)	9212(4)	4024(3)	21.5(15)
C27	9030(5)	8925(4)	3847(3)	19.9(14)
C28	9994(6)	8509(4)	4071(3)	25.4(16)
C29	10979(6)	8915(5)	4036(3)	30.1(17)
C30	11035(6)	9744(5)	3794(3)	32.8(17)
C31	10073(6)	10170(5)	3581(3)	30.9(17)
C32	9076(6)	9771(4)	3602(3)	25.6(16)
C33	7974(5)	7699(4)	4561(3)	18.5(14)
C34	8298(5)	6806(4)	4545(3)	24.0(15)
C35	8439(5)	6492(4)	5199(3)	25.6(15)
C36	8211(5)	7164(4)	5625(3)	24.8(15)
C37	7939(5)	7911(4)	5239(3)	22.4(14)
C38	5625(5)	6681(4)	4244(3)	22.9(15)
C39	5367(5)	7393(4)	4647(3)	24.9(15)
C40	5436(5)	7088(4)	5311(3)	25.8(16)
C41	5724(5)	6205(4)	5322(3)	26.6(16)
C42	5839(5)	5940(4)	4669(3)	22.7(15)
O1	12417(5)	7263(3)	4789(3)	48.8(15)
C43	12210(7)	7514(5)	5439(4)	45(2)
C44	11489(7)	6827(5)	5653(4)	41(2)
C45	11812(8)	6003(5)	5304(4)	50(2)
C46	12570(7)	6324(5)	4822(4)	46(2)

Table S27. Anisotropic Displacement Parameters ($Å^2×10^3$) for **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	36.4(4)	27.5(4)	14.3(3)	-0.7(3)	1.8(3)	-7.1(3)
Ni1	26.5(5)	17.9(4)	13.2(4)	0.6(3)	1.9(3)	-0.5(4)
Fe1	26.6(5)	21.6(5)	13.0(5)	1.5(4)	2.1(4)	-1.3(4)
P1	28.0(10)	17.1(8)	13.3(8)	0.9(6)	1.0(7)	-0.4(7)
P2	27.1(10)	16.2(8)	15.9(8)	0.8(7)	2.5(7)	0.5(7)
C1	25(4)	18(3)	19(3)	-5(3)	1(3)	-7(3)
C2	31(4)	20(3)	16(3)	-2(3)	-1(3)	-2(3)
C3	32(4)	35(4)	19(4)	-13(3)	2(3)	-11(3)
C4	40(4)	27(4)	14(3)	-4(3)	5(3)	-10(3)
C5	34(4)	22(4)	23(4)	-3(3)	-9(3)	-5(3)
C6	40(4)	20(4)	20(4)	5(3)	3(3)	-8(3)
C7	26(4)	28(4)	38(4)	-8(3)	5(3)	4(3)
C8	45(5)	32(4)	38(5)	-4(3)	4(4)	-13(4)

C9	31(4)	18(3)	10(3)	1(3)	0(3)	2(3)
C10	35(4)	17(3)	14(3)	1(3)	3(3)	5(3)
C11	40(4)	18(4)	26(4)	3(3)	-3(3)	-11(3)
C12	46(5)	17(4)	36(4)	2(3)	-3(4)	9(4)
C13	28(4)	36(4)	25(4)	-6(3)	-6(3)	8(3)
C14	26(4)	23(4)	21(3)	1(3)	-3(3)	3(3)
C15	34(4)	13(3)	20(3)	2(3)	8(3)	-2(3)
C16	27(4)	32(4)	20(3)	-1(3)	5(3)	0(3)
C17	28(4)	33(4)	25(4)	0(3)	11(3)	1(3)
C18	26(4)	26(4)	32(4)	3(3)	-3(3)	-5(3)
C19	34(4)	21(3)	15(3)	-1(3)	1(3)	-3(3)
C20	33(4)	22(3)	15(3)	-3(3)	5(3)	-1(3)
C21	32(4)	20(3)	13(3)	2(3)	1(3)	-6(3)
C22	34(4)	24(4)	20(4)	6(3)	10(3)	0(3)
C23	46(5)	17(4)	32(4)	4(3)	20(4)	7(3)
C24	44(5)	23(4)	18(4)	0(3)	13(3)	0(3)
C25	28(4)	26(4)	16(3)	1(3)	7(3)	1(3)
C26	33(4)	14(3)	19(3)	5(3)	10(3)	0(3)
C27	31(4)	18(3)	10(3)	3(3)	0(3)	0(3)
C28	38(4)	24(4)	13(3)	0(3)	1(3)	0(3)
C29	23(4)	41(4)	25(4)	-5(3)	-5(3)	1(3)
C30	33(4)	38(4)	27(4)	-2(3)	3(3)	-10(4)
C31	40(5)	25(4)	29(4)	1(3)	9(3)	-2(4)
C32	38(4)	18(3)	20(4)	-3(3)	3(3)	3(3)
C33	24(4)	19(3)	14(3)	4(3)	5(3)	-2(3)
C34	28(4)	21(3)	22(4)	-8(3)	-1(3)	4(3)
C35	26(4)	29(4)	22(4)	7(3)	3(3)	2(3)
C36	29(4)	30(4)	14(3)	-1(3)	-3(3)	2(3)
C37	24(4)	22(3)	20(3)	0(3)	-2(3)	3(3)
C38	26(4)	23(3)	20(3)	1(3)	1(3)	-4(3)
C39	27(4)	28(4)	20(4)	1(3)	6(3)	-3(3)
C40	29(4)	34(4)	15(3)	-8(3)	6(3)	-7(3)
C41	31(4)	30(4)	19(4)	2(3)	4(3)	-9(3)
C42	31(4)	16(3)	21(3)	-3(3)	2(3)	0(3)
O1	74(4)	40(3)	35(3)	10(3)	20(3)	10(3)
C43	56(6)	51(5)	29(4)	-6(4)	9(4)	4(4)
C44	42(5)	51(5)	31(4)	3(4)	5(4)	-3(4)
C45	77(7)	34(5)	38(5)	-1(4)	9(4)	-7(5)
C46	45(5)	46(5)	47(5)	-2(4)	10(4)	-11(4)

Table S28. Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3241(10)	C15	C16	1.381(9)
Ni1	P1	2.2787(19)	C15	C20	1.383(8)
Ni1	P2	2.1456(18)	C16	C17	1.378(9)
Ni1	C1	1.889(6)	C17	C18	1.374(9)
Fe1	C33	1.986(6)	C18	C19	1.368(9)
Fe1	C34	1.993(7)	C19	C20	1.367(9)
Fe1	C35	2.030(7)	C21	C22	1.382(9)
Fe1	C36	2.041(6)	C21	C26	1.383(9)
Fe1	C37	2.018(6)	C22	C23	1.368(9)
Fe1	C38	1.998(6)	C23	C24	1.365(10)
Fe1	C39	2.011(7)	C24	C25	1.367(9)
Fe1	C40	2.027(7)	C25	C26	1.389(9)
Fe1	C41	2.038(6)	C27	C28	1.371(9)
Fe1	C42	2.023(6)	C27	C32	1.387(9)
P1	C9	1.804(6)	C28	C29	1.366(9)
P1	C15	1.825(7)	C29	C30	1.362(10)
P1	C38	1.809(6)	C30	C31	1.371(10)
P2	C26	1.809(6)	C31	C32	1.371(9)
P2	C27	1.834(7)	C33	C34	1.423(8)
P2	C33	1.787(6)	C33	C37	1.414(8)
C1	C2	1.401(9)	C34	C35	1.398(9)
C1	C6	1.379(9)	C35	C36	1.389(9)
C2	C3	1.370(9)	C36	C37	1.401(9)
C2	C7	1.479(9)	C38	C39	1.417(9)
C3	C4	1.394(9)	C38	C42	1.426(9)
C4	C5	1.368(9)	C39	C40	1.413(9)
C4	C8	1.500(9)	C40	C41	1.394(9)
C5	C6	1.369(9)	C41	C42	1.404(8)
C9	C10	1.376(9)	O1	C43	1.420(8)
C9	C14	1.379(9)	O1	C46	1.447(9)
C10	C11	1.376(9)	C43	C44	1.469(10)
C11	C12	1.362(10)	C44	C45	1.519(10)
C12	C13	1.362(10)	C45	C46	1.505(10)
C13	C14	1.391(9)			

Table S29. Bond Angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Br1	88.97(5)	C5	C6	C1	121.4(7)
P2	Ni1	Br1	168.13(6)	C10	C9	P1	120.3(5)
P2	Ni1	P1	102.56(7)	C10	C9	C14	118.8(6)

C1	Ni1	Br1	85.28(18)	C14	C9	P1	120.9(5)
C1	Ni1	P1	173.02(19)	C11	C10	C9	121.4(6)
C1	Ni1	P2	83.40(19)	C12	C11	C10	119.1(7)
C33	Fe1	C34	41.9(2)	C13	C12	C11	120.8(6)
C33	Fe1	C35	69.3(3)	C12	C13	C14	120.1(7)
C33	Fe1	C36	69.2(3)	C9	C14	C13	119.7(7)
C33	Fe1	C37	41.4(2)	C16	C15	P1	122.5(5)
C33	Fe1	C38	110.2(3)	C16	C15	C20	119.0(6)
C33	Fe1	C39	109.0(3)	C20	C15	P1	118.5(5)
C33	Fe1	C40	137.1(3)	C17	C16	C15	120.2(6)
C33	Fe1	C41	177.2(3)	C18	C17	C16	120.5(6)
C33	Fe1	C42	140.6(2)	C19	C18	C17	119.1(6)
C34	Fe1	C35	40.7(2)	C20	C19	C18	121.2(6)
C34	Fe1	C36	68.4(3)	C19	C20	C15	120.1(6)
C34	Fe1	C37	69.0(3)	C22	C21	C26	119.3(6)
C34	Fe1	C38	109.8(3)	C23	C22	C21	120.9(7)
C34	Fe1	C39	137.5(3)	C24	C23	C22	119.5(7)
C34	Fe1	C40	178.4(3)	C23	C24	C25	121.0(6)
C34	Fe1	C41	140.9(3)	C24	C25	C26	120.0(6)
C34	Fe1	C42	111.9(3)	C21	C26	P2	117.8(5)
C35	Fe1	C36	39.9(3)	C21	C26	C25	119.3(6)
C35	Fe1	C41	113.1(3)	C25	C26	P2	122.9(5)
C37	Fe1	C35	67.8(3)	C28	C27	P2	120.8(5)
C37	Fe1	C36	40.4(2)	C28	C27	C32	118.7(6)
C37	Fe1	C40	111.0(3)	C32	C27	P2	120.4(5)
C37	Fe1	C41	137.6(3)	C29	C28	C27	120.3(6)
C37	Fe1	C42	177.7(2)	C30	C29	C28	121.5(7)
C38	Fe1	C35	138.0(3)	C29	C30	C31	118.4(7)
C38	Fe1	C36	177.9(3)	C32	C31	C30	121.1(7)
C38	Fe1	C37	140.4(3)	C31	C32	C27	119.9(7)
C38	Fe1	C39	41.4(3)	P2	C33	Fe1	125.5(3)
C38	Fe1	C40	69.1(3)	C34	C33	Fe1	69.3(4)
C38	Fe1	C41	69.0(3)	C34	C33	P2	123.1(5)
C38	Fe1	C42	41.6(2)	C37	C33	Fe1	70.5(4)
C39	Fe1	C35	178.1(3)	C37	C33	P2	130.5(5)
C39	Fe1	C36	140.7(3)	C37	C33	C34	106.4(5)
C39	Fe1	C37	111.6(3)	C33	C34	Fe1	68.8(3)
C39	Fe1	C40	41.0(3)	C35	C34	Fe1	71.1(4)
C39	Fe1	C41	68.6(3)	C35	C34	C33	108.1(5)
C39	Fe1	C42	69.3(3)	C34	C35	Fe1	68.3(4)
C40	Fe1	C35	140.9(3)	C36	C35	Fe1	70.5(4)
C40	Fe1	C36	112.8(3)	C36	C35	C34	108.8(6)

C40	Fe1	C41	40.1(3)	C35	C36	Fe1	69.6(4)
C41	Fe1	C36	111.6(3)	C35	C36	C37	108.0(6)
C42	Fe1	C35	111.4(3)	C37	C36	Fe1	68.9(4)
C42	Fe1	C36	137.7(3)	C33	C37	Fe1	68.1(4)
C42	Fe1	C40	68.2(3)	C36	C37	Fe1	70.7(4)
C42	Fe1	C41	40.4(2)	C36	C37	C33	108.7(6)
C9	P1	Ni1	112.5(2)	P1	C38	Fe1	120.1(3)
C9	P1	C15	100.3(3)	C39	C38	Fe1	69.8(4)
C9	P1	C38	100.9(3)	C39	C38	P1	126.0(5)
C15	P1	Ni1	115.5(2)	C39	C38	C42	107.5(5)
C38	P1	Ni1	123.1(2)	C42	C38	Fe1	70.2(4)
C38	P1	C15	101.2(3)	C42	C38	P1	126.2(5)
C26	P2	Ni1	109.1(2)	C38	C39	Fe1	68.8(4)
C26	P2	C27	103.6(3)	C40	C39	Fe1	70.2(4)
C27	P2	Ni1	121.0(2)	C40	C39	C38	107.5(6)
C33	P2	Ni1	115.1(2)	C39	C40	Fe1	68.9(4)
C33	P2	C26	106.6(3)	C41	C40	Fe1	70.3(4)
C33	P2	C27	100.1(3)	C41	C40	C39	108.7(6)
C2	C1	Ni1	120.5(5)	C40	C41	Fe1	69.5(4)
C6	C1	Ni1	121.1(5)	C40	C41	C42	108.5(6)
C6	C1	C2	118.3(6)	C42	C41	Fe1	69.2(4)
C1	C2	C7	119.0(6)	C38	C42	Fe1	68.3(4)
C3	C2	C1	119.0(6)	C41	C42	Fe1	70.3(4)
C3	C2	C7	122.0(6)	C41	C42	C38	107.8(6)
C2	C3	C4	122.7(7)	C43	O1	C46	105.2(6)
C3	C4	C8	120.1(7)	O1	C43	C44	105.0(6)
C5	C4	C3	117.0(6)	C43	C44	C45	104.9(6)
C5	C4	C8	122.9(6)	C46	C45	C44	104.1(6)
C4	C5	C6	121.6(7)	O1	C46	C45	105.5(6)

*X-ray Diffraction Data for (dppf)Ni(2-methyl-4-nitrophenyl)(Br) (**7**)*

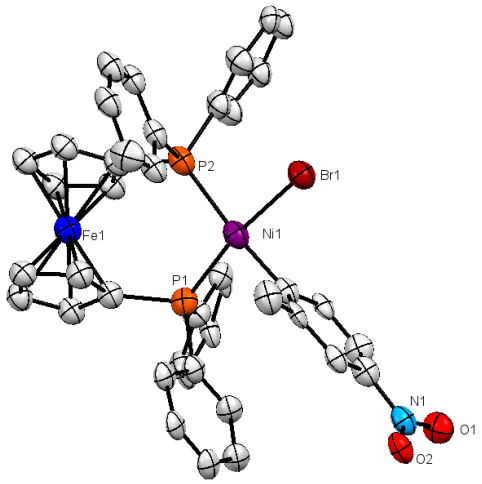


Figure S59. ORTEP of **7**, with ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization have been removed for clarity.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **7** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **7** (Figure S59). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] The model presented here was obtained from low angle data. The crystal weakly diffracted, but the connectivity of this model was determined from the low resolution Fourier map. This model is intended to establish only the connectivity of the compound that crystallized. Additionally, this data was refined as a 2-component twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.188(8). The HKLF5 data was generated by the program PLATON, and the twin law was found by TWINROTMAT. An anisotropic refinement was performed, which increased the number of refined parameters. Due to the small number of reflections collected and poor resolution, a global rigid body restraint was used in the refinement. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound **7** can be found in the full details of the X-ray structure

determination (CIF), which is included as Supporting Information. CCDC number 1860569 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S30. Crystal data and structure refinement for **7**.

Empirical formula	$C_{41}H_{34}BrFeNNiO_2P_2$
Formula weight	829.10
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.0139(13)
b/Å	11.9643(11)
c/Å	25.102(4)
α/°	90
β/°	103.138(13)
γ/°	90
Volume/Å^3	3513.7(7)
Z	4
ρ_{calc}g/cm^3	1.567
μ/mm^{-1}	6.467
F(000)	1688.0
Crystal size/mm^3	0.100 × 0.030 × 0.020
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.232 to 80.026
Index ranges	$-10 \leq h \leq 9$, $-9 \leq k \leq 9$, $-20 \leq l \leq 20$
Reflections collected	2113
Independent reflections	2113 [R_{int} = 0.2707, R_{sigma} = 0.0995]
Data/restraints/parameters	2113/510/444
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.1118, wR_2 = 0.2808
Final R indexes [all data]	R_1 = 0.1376, wR_2 = 0.3028

Table S31. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **7**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	5786(3)	6449(3)	2235.4(13)	48.9(13)
Ni1	6922(4)	4865(4)	2250.2(19)	43.1(17)
Fe1	7484(4)	2312(4)	1137.4(19)	46.4(17)
P1	8024(7)	3402(7)	2420(3)	45(2)
P2	6330(7)	4800(7)	1323(3)	44(2)

O1	9429(17)	6247(18)	4889(8)	56(6)
O2	8208(16)	5070(16)	5019(8)	47(5)
N1	8670(20)	5590(20)	4721(11)	43(7)
C1	7410(20)	5070(20)	3004(12)	40(5)
C2	6750(20)	4770(20)	3376(12)	36(7)
C3	7140(20)	4920(20)	3960(12)	38(7)
C4	8160(30)	5490(30)	4111(13)	45(8)
C5	8780(30)	5830(30)	3781(13)	46(8)
C6	8420(20)	5720(20)	3225(12)	36(7)
C7	5590(20)	4240(30)	3202(13)	53(8)
C8	7790(20)	2220(30)	1949(12)	41(4)
C9	6720(30)	1730(30)	1728(11)	45(5)
C10	6840(20)	840(30)	1371(12)	45(5)
C11	8030(20)	770(30)	1403(12)	46(5)
C12	8590(30)	1570(20)	1761(11)	43(5)
C13	6930(30)	3870(30)	877(12)	47(4)
C14	6360(30)	3070(20)	506(11)	46(5)
C15	7130(20)	2440(30)	301(12)	46(5)
C16	8280(30)	2880(30)	554(11)	46(5)
C17	8120(20)	3770(20)	909(12)	44(5)
C18	8120(20)	2690(30)	3084(12)	41(6)
C19	8960(20)	2950(30)	3553(11)	42(8)
C20	8970(20)	2430(30)	4035(12)	42(8)
C21	8080(20)	1670(20)	4056(12)	40(8)
C22	7280(30)	1450(20)	3610(12)	38(7)
C23	7250(20)	1910(20)	3097(12)	40(7)
C24	9480(20)	3800(30)	2408(12)	43(6)
C25	10440(20)	3100(30)	2647(11)	43(7)
C26	11550(30)	3360(30)	2607(12)	47(8)
C27	11700(30)	4340(30)	2337(12)	47(8)
C28	10790(20)	5010(20)	2089(11)	37(7)
C29	9730(20)	4760(30)	2165(11)	38(7)
C30	4800(20)	4350(20)	1129(13)	42(6)
C31	4380(20)	3770(20)	1497(13)	44(8)
C32	3320(30)	3250(30)	1369(14)	61(9)
C33	2650(30)	3470(30)	850(13)	50(8)
C34	3030(30)	4070(30)	487(13)	49(8)
C35	4120(20)	4530(20)	587(12)	44(7)
C36	6400(30)	6170(30)	1013(12)	45(6)
C37	5500(30)	6870(30)	857(12)	53(8)
C38	5630(30)	7940(20)	636(11)	41(7)
C39	6700(20)	8320(30)	594(12)	48(8)

C40	7670(30)	7570(30)	780(12)	48(8)
C41	7500(30)	6520(30)	971(13)	54(8)

Table S32. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **7**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	43(2)	46(3)	59(2)	0.3(19)	14.6(17)	5.1(19)
Ni1	35(3)	38(3)	58(3)	-1(3)	13(2)	2(3)
Fe1	41(3)	46(4)	53(3)	-1(2)	13(2)	1(3)
P1	36(4)	47(5)	52(5)	-4(4)	11(4)	-3(4)
P2	38(5)	37(5)	61(5)	0(4)	17(4)	0(4)
O1	52(12)	52(14)	66(12)	4(9)	16(9)	-12(10)
O2	49(12)	33(12)	66(11)	-2(9)	28(9)	2(10)
N1	36(13)	36(15)	63(9)	-1(8)	21(8)	5(9)
C1	29(10)	35(12)	57(7)	-1(6)	12(6)	2(8)
C2	36(10)	17(16)	59(8)	-2(8)	17(7)	7(10)
C3	32(11)	28(17)	59(9)	-2(8)	20(7)	3(11)
C4	35(12)	41(18)	62(9)	0(8)	20(7)	-1(11)
C5	32(12)	50(19)	59(9)	-1(9)	16(7)	-7(12)
C6	25(11)	24(15)	60(9)	-1(8)	12(7)	8(10)
C7	43(11)	50(20)	75(16)	-9(14)	20(10)	-4(12)
C8	35(9)	40(8)	50(6)	-1(5)	12(5)	-1(6)
C9	37(9)	45(9)	53(8)	-1(6)	12(6)	-1(6)
C10	41(9)	44(8)	50(10)	1(6)	10(7)	0(6)
C11	42(9)	43(7)	53(9)	-3(6)	12(7)	3(6)
C12	37(8)	41(8)	52(8)	0(6)	12(6)	0(6)
C13	40(8)	44(7)	57(8)	0(5)	15(6)	4(6)
C14	42(9)	44(9)	55(8)	2(6)	14(6)	5(6)
C15	41(10)	44(10)	54(7)	1(6)	14(6)	4(7)
C16	42(9)	45(10)	54(9)	2(7)	16(6)	5(7)
C17	38(8)	43(8)	53(10)	2(6)	15(7)	5(6)
C18	43(12)	39(12)	46(7)	-6(7)	19(7)	5(9)
C19	44(13)	42(16)	44(9)	1(9)	21(8)	-4(11)
C20	46(14)	43(17)	44(10)	0(9)	21(9)	-4(12)
C21	45(15)	39(17)	44(11)	-7(10)	28(9)	-2(12)
C22	43(14)	32(15)	46(11)	-9(10)	26(9)	7(11)
C23	42(13)	39(14)	45(11)	-8(9)	22(9)	6(11)
C24	33(7)	50(11)	47(14)	-1(9)	9(7)	-4(6)
C25	33(8)	43(13)	49(17)	-12(11)	-1(9)	-8(8)
C26	34(9)	31(15)	73(19)	-18(13)	7(9)	-8(9)
C27	32(11)	30(15)	80(20)	-18(13)	17(10)	-2(9)
C28	34(10)	28(13)	56(17)	-21(11)	25(11)	0(9)

C29	30(10)	47(12)	41(16)	-7(11)	14(9)	1(8)
C30	37(7)	27(14)	65(11)	-4(9)	17(6)	1(7)
C31	35(11)	34(17)	65(12)	0(11)	15(8)	0(10)
C32	43(12)	60(20)	81(15)	11(14)	11(9)	-15(13)
C33	42(12)	33(19)	76(15)	-1(13)	16(10)	-3(11)
C34	40(11)	34(19)	74(14)	0(12)	14(9)	-2(10)
C35	38(10)	31(17)	65(11)	-2(10)	15(8)	1(10)
C36	41(10)	38(8)	55(14)	-5(7)	5(9)	-8(7)
C37	44(11)	43(11)	70(20)	3(11)	10(10)	-6(8)
C38	40(12)	36(11)	45(17)	-10(11)	6(11)	-8(9)
C39	41(12)	36(12)	67(19)	-1(12)	11(13)	-8(9)
C40	40(12)	38(12)	60(20)	-5(12)	8(11)	-8(8)
C41	42(11)	42(12)	80(20)	2(12)	9(10)	-8(8)

Table S33. Bond Lengths for **7**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	Ni1	2.331(6)	C9	C10	1.42(4)
Ni1	C1	1.87(3)	C10	C11	1.42(4)
Ni1	P1	2.178(10)	C11	C12	1.39(4)
Ni1	P2	2.276(10)	C13	C14	1.40(4)
Fe1	C8	1.99(3)	C13	C17	1.42(4)
Fe1	C12	2.01(3)	C14	C15	1.39(4)
Fe1	C11	2.03(3)	C15	C16	1.47(4)
Fe1	C17	2.04(3)	C16	C17	1.42(4)
Fe1	C16	2.04(3)	C18	C19	1.40(4)
Fe1	C9	2.04(3)	C18	C23	1.40(4)
Fe1	C13	2.04(3)	C19	C20	1.36(4)
Fe1	C14	2.05(3)	C20	C21	1.42(4)
Fe1	C15	2.05(3)	C21	C22	1.33(4)
Fe1	C10	2.06(3)	C22	C23	1.39(4)
P1	C24	1.82(3)	C24	C29	1.36(4)
P1	C8	1.82(3)	C24	C25	1.44(4)
P1	C18	1.85(3)	C25	C26	1.40(4)
P2	C36	1.83(3)	C26	C27	1.38(4)
P2	C13	1.83(3)	C27	C28	1.39(4)
P2	C30	1.87(3)	C28	C29	1.36(3)
O1	N1	1.21(3)	C30	C31	1.34(4)
O2	N1	1.20(3)	C30	C35	1.43(4)
N1	C4	1.52(4)	C31	C32	1.39(4)
C1	C2	1.40(4)	C32	C33	1.39(4)
C1	C6	1.45(4)	C33	C34	1.32(4)
C2	C3	1.44(4)	C34	C35	1.39(4)

C2	C7	1.51(4)	C36	C37	1.36(4)
C3	C4	1.37(4)	C36	C41	1.41(4)
C4	C5	1.31(4)	C37	C38	1.42(4)
C5	C6	1.37(4)	C38	C39	1.39(4)
C8	C12	1.40(4)	C39	C40	1.46(4)
C8	C9	1.41(4)	C40	C41	1.38(4)

Table S34. Bond Angles for **7**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Ni1	P1	82.4(9)	C5	C4	C3	126(3)
C1	Ni1	P2	174.6(10)	C5	C4	N1	117(3)
P1	Ni1	P2	102.0(3)	C3	C4	N1	117(3)
C1	Ni1	Br1	87.7(9)	C4	C5	C6	121(3)
P1	Ni1	Br1	169.9(3)	C5	C6	C1	119(3)
P2	Ni1	Br1	88.1(3)	C12	C8	C9	106(3)
C8	Fe1	C12	41.0(11)	C12	C8	P1	129(2)
C8	Fe1	C11	69.1(12)	C9	C8	P1	125(2)
C12	Fe1	C11	40.1(10)	C12	C8	Fe1	70.4(17)
C8	Fe1	C17	110.0(12)	C9	C8	Fe1	71.5(17)
C12	Fe1	C17	111.6(12)	P1	C8	Fe1	126.0(16)
C11	Fe1	C17	139.3(11)	C8	C9	C10	110(3)
C8	Fe1	C16	138.5(12)	C8	C9	Fe1	67.6(17)
C12	Fe1	C16	111.9(12)	C10	C9	Fe1	70.4(17)
C11	Fe1	C16	111.9(12)	C11	C10	C9	105(3)
C17	Fe1	C16	40.8(11)	C11	C10	Fe1	68.5(18)
C8	Fe1	C9	40.9(11)	C9	C10	Fe1	69.1(18)
C12	Fe1	C9	67.2(11)	C12	C11	C10	109(3)
C11	Fe1	C9	67.4(12)	C12	C11	Fe1	69.5(18)
C17	Fe1	C9	139.3(12)	C10	C11	Fe1	70.9(18)
C16	Fe1	C9	179.1(12)	C11	C12	C8	110(3)
C8	Fe1	C13	110.3(12)	C11	C12	Fe1	70.4(17)
C12	Fe1	C13	139.5(12)	C8	C12	Fe1	68.6(17)
C11	Fe1	C13	179.5(12)	C14	C13	C17	108(3)
C17	Fe1	C13	40.8(11)	C14	C13	P2	128(2)
C16	Fe1	C13	68.5(12)	C17	C13	P2	123(2)
C9	Fe1	C13	112.2(12)	C14	C13	Fe1	70.3(18)
C8	Fe1	C14	138.6(12)	C17	C13	Fe1	69.5(17)
C12	Fe1	C14	179.6(13)	P2	C13	Fe1	120.2(16)
C11	Fe1	C14	140.2(12)	C15	C14	C13	110(3)
C17	Fe1	C14	68.2(12)	C15	C14	Fe1	70.3(17)
C16	Fe1	C14	68.2(12)	C13	C14	Fe1	69.6(17)
C9	Fe1	C14	112.7(12)	C14	C15	C16	107(3)

C13	Fe1	C14	40.2(11)	C14	C15	Fe1	70.1(17)
C8	Fe1	C15	178.1(12)	C16	C15	Fe1	68.4(16)
C12	Fe1	C15	140.9(12)	C17	C16	C15	107(3)
C11	Fe1	C15	112.5(12)	C17	C16	Fe1	69.6(17)
C17	Fe1	C15	69.5(12)	C15	C16	Fe1	69.4(16)
C16	Fe1	C15	42.2(11)	C16	C17	C13	108(3)
C9	Fe1	C15	138.5(11)	C16	C17	Fe1	69.6(17)
C13	Fe1	C15	68.0(12)	C13	C17	Fe1	69.7(17)
C14	Fe1	C15	39.5(10)	C19	C18	C23	122(3)
C8	Fe1	C10	69.8(12)	C19	C18	P1	123(2)
C12	Fe1	C10	68.2(12)	C23	C18	P1	116(2)
C11	Fe1	C10	40.6(11)	C20	C19	C18	120(3)
C17	Fe1	C10	179.8(13)	C19	C20	C21	118(3)
C16	Fe1	C10	139.3(12)	C22	C21	C20	120(3)
C9	Fe1	C10	40.5(11)	C21	C22	C23	124(3)
C13	Fe1	C10	139.3(12)	C22	C23	C18	115(3)
C14	Fe1	C10	112.0(12)	C29	C24	C25	116(3)
C15	Fe1	C10	110.7(12)	C29	C24	P1	122(2)
C24	P1	C8	101.6(14)	C25	C24	P1	121(2)
C24	P1	C18	105.7(14)	C26	C25	C24	122(3)
C8	P1	C18	101.3(14)	C27	C26	C25	117(3)
C24	P1	Ni1	109.3(11)	C26	C27	C28	122(3)
C8	P1	Ni1	119.8(10)	C29	C28	C27	118(3)
C18	P1	Ni1	117.3(10)	C24	C29	C28	124(3)
C36	P2	C13	102.7(14)	C31	C30	C35	121(3)
C36	P2	C30	106.7(14)	C31	C30	P2	118(2)
C13	P2	C30	99.7(14)	C35	C30	P2	121(2)
C36	P2	Ni1	111.7(10)	C30	C31	C32	123(3)
C13	P2	Ni1	124.7(10)	C31	C32	C33	116(3)
C30	P2	Ni1	109.6(10)	C34	C33	C32	122(3)
O2	N1	O1	123(3)	C33	C34	C35	123(3)
O2	N1	C4	117(3)	C34	C35	C30	115(3)
O1	N1	C4	121(3)	C37	C36	C41	120(3)
C2	C1	C6	116(3)	C37	C36	P2	124(2)
C2	C1	Ni1	123(2)	C41	C36	P2	116(2)
C6	C1	Ni1	120(2)	C36	C37	C38	121(3)
C1	C2	C3	123(3)	C39	C38	C37	121(3)
C1	C2	C7	123(3)	C38	C39	C40	117(3)
C3	C2	C7	114(3)	C41	C40	C39	120(3)
C4	C3	C2	114(3)	C40	C41	C36	121(3)

*X-ray Diffraction Data for (dppf)Ni(2-methyl-4-trifluoromethylphenyl)(Br) (**8**)*

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **8** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **8**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The crystal diffracted poorly, resulting in a low I/σ and a high value of RInt. Nine reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **8** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860568 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S35. Crystal data and structure refinement for **8**.

Empirical formula	$C_{46}H_{42}BrF_3FeNiOP_2$
Formula weight	924.20
Temperature/K	93.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3226(12)
b/Å	15.3912(11)
c/Å	20.3093(15)
α/°	90
β/°	93.380(8)
γ/°	90
Volume/Å^3	3845.2(5)
Z	4
ρ_{calc}g/cm^3	1.596
μ/mm^{-1}	2.041
F(000)	1888.0
Crystal size/mm^3	0.1 × 0.02 × 0.01

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.356 to 50.052
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	54043
Independent reflections	6796 [R_{int} = 0.2399, R_{sigma} = 0.1358]
Data/restraints/parameters	6796/0/497
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1105
Final R indexes [all data]	R_1 = 0.1379, wR_2 = 0.1321

Table S36. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	6662.3(7)	7930.0(4)	6887.7(3)	30.4(2)
Ni1	7056.7(8)	7285.0(5)	7905.4(4)	19.8(2)
Fe1	6984.3(8)	8007.0(6)	9889.0(4)	22.4(3)
P1	5917.5(16)	8243.5(11)	8372.0(8)	21.5(4)
P2	7697.0(15)	6570.9(11)	8752.1(8)	19.3(4)
F1	10210(6)	4194(4)	6722(2)	102(3)
F2	10054(5)	4901(3)	5861(3)	80(2)
F3	8940(5)	3976(4)	6085(3)	106(3)
C1	7831(5)	6459(4)	7429(3)	17.8(15)
C2	7312(6)	5727(4)	7185(3)	22.7(17)
C3	7843(6)	5127(4)	6814(3)	26.4(17)
C4	8896(6)	5266(4)	6682(3)	25.2(17)
C4	9474(6)	7421(4)	7487(3)	29.4(18)
C5	9526(7)	4616(5)	6336(4)	37(2)
C6	9431(6)	6002(4)	6914(3)	25.5(17)
C7	8906(6)	6616(4)	7279(3)	21.3(16)
C8	4503(6)	8166(4)	8039(3)	21.4(16)
C9	3693(6)	7796(4)	8386(3)	25.7(17)
C10	2639(6)	7788(4)	8132(4)	29.0(18)
C11	2379(6)	8144(4)	7520(4)	27.5(18)
C12	3188(6)	8499(4)	7168(3)	27.5(18)
C13	4244(6)	8519(4)	7426(3)	25.6(17)
C14	6199(6)	9375(4)	8194(3)	22.2(17)
C15	5436(6)	9997(4)	8313(3)	25.4(17)
C16	5627(7)	10856(4)	8162(3)	29.2(19)
C17	6562(7)	11081(4)	7899(3)	32.2(19)
C18	7345(7)	10473(5)	7789(3)	35(2)
C19	7155(6)	9604(4)	7945(3)	27.2(18)
C20	8953(6)	5956(4)	8723(3)	24.0(17)

C21	9919(6)	6322(5)	8944(3)	29.6(18)
C22	10882(6)	5863(5)	8910(3)	33.7(19)
C23	10881(7)	5045(5)	8657(4)	37(2)
C24	9927(7)	4679(5)	8435(3)	37(2)
C25	8949(6)	5127(4)	8464(3)	25.4(17)
C26	6727(6)	5756(4)	8965(3)	21.9(17)
C27	6971(6)	5124(4)	9434(3)	22.4(17)
C28	6207(7)	4504(4)	9562(4)	31.5(19)
C29	5209(7)	4491(4)	9228(4)	35(2)
C30	4972(6)	5108(4)	8756(3)	27.0(18)
C31	5731(6)	5737(4)	8627(3)	22.1(17)
C32	5749(6)	8295(4)	9248(3)	21.4(17)
C33	5473(6)	7598(4)	9659(3)	24.0(17)
C34	5536(6)	7890(4)	10318(3)	26.7(17)
C35	5881(6)	8768(4)	10314(3)	30.5(19)
C36	5993(6)	9015(4)	9664(3)	26.6(18)
C37	8300(6)	7744(4)	10512(3)	27.1(17)
C38	7975(6)	7012(4)	10146(3)	24.4(17)
C39	8000(5)	7212(4)	9466(3)	18.7(15)
C40	8373(6)	8092(4)	9427(3)	26.5(18)
C41	8541(6)	8395(5)	10075(3)	33.3(19)
O1	7761(7)	2349(6)	5080(3)	94(3)
C42	7323(9)	3205(9)	4915(7)	120(6)
C43	8145(10)	3615(9)	4513(5)	106(5)
C44	8571(10)	2848(9)	4153(6)	101(5)
C45	8513(11)	2088(8)	4578(5)	115(5)

Table S37. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **8**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	49.2(6)	27.0(4)	14.7(4)	1.6(3)	0.6(3)	14.3(4)
Ni1	31.1(6)	13.7(4)	14.3(4)	-0.1(4)	-0.8(4)	1.0(4)
Fe1	34.9(7)	18.3(5)	14.2(5)	-0.5(4)	1.6(5)	-0.2(5)
P1	35.6(13)	13.8(9)	14.9(9)	1.5(7)	1.1(9)	1.3(8)
P2	28.1(12)	12.8(9)	16.8(9)	-0.4(7)	-0.2(8)	-1.7(8)
F1	150(6)	111(5)	44(3)	0(3)	3(4)	109(5)
F2	138(5)	32(3)	79(4)	24(3)	87(4)	36(3)
F3	93(5)	70(4)	163(7)	-78(4)	71(5)	-19(4)
C1	20(4)	15(3)	18(4)	7(3)	0(3)	1(3)
C2	25(5)	24(4)	19(4)	3(3)	-1(3)	3(3)
C3	30(5)	25(4)	24(4)	-3(3)	0(4)	0(3)
C4	40(5)	23(4)	12(4)	3(3)	4(3)	8(4)

C4	25(5)	32(4)	32(4)	-3(3)	5(4)	-3(3)
C5	59(6)	21(4)	30(5)	7(4)	5(4)	10(4)
C6	23(5)	32(4)	22(4)	10(3)	2(3)	-1(3)
C7	34(5)	13(4)	17(4)	3(3)	-1(3)	2(3)
C8	33(5)	14(4)	17(4)	2(3)	2(3)	4(3)
C9	38(5)	13(4)	25(4)	7(3)	0(4)	-2(3)
C10	31(5)	17(4)	40(5)	-1(3)	13(4)	-3(3)
C11	19(4)	23(4)	40(5)	-2(3)	-2(4)	1(3)
C12	40(5)	17(4)	25(4)	-1(3)	-4(4)	6(4)
C13	34(5)	21(4)	22(4)	-2(3)	3(4)	8(3)
C14	38(5)	13(4)	16(4)	2(3)	9(3)	0(3)
C15	36(5)	16(4)	24(4)	0(3)	-1(3)	0(3)
C16	44(6)	24(4)	19(4)	-3(3)	-3(4)	6(4)
C17	51(6)	17(4)	29(4)	3(3)	1(4)	1(4)
C18	51(6)	36(5)	17(4)	3(3)	3(4)	-14(4)
C19	33(5)	20(4)	28(4)	-3(3)	4(4)	0(3)
C20	38(5)	18(4)	17(4)	1(3)	5(3)	3(3)
C21	37(5)	29(4)	22(4)	-1(3)	-5(4)	-6(4)
C22	26(5)	46(5)	29(4)	9(4)	1(4)	-6(4)
C23	41(6)	40(5)	31(5)	2(4)	-1(4)	14(4)
C24	61(7)	26(4)	26(4)	3(3)	10(4)	14(4)
C25	28(5)	23(4)	25(4)	-1(3)	3(3)	1(3)
C26	31(5)	16(4)	18(4)	-5(3)	-1(3)	-6(3)
C27	28(5)	15(4)	23(4)	-2(3)	4(3)	5(3)
C28	50(6)	17(4)	29(4)	0(3)	14(4)	6(4)
C29	52(6)	17(4)	37(5)	-7(3)	18(5)	-8(4)
C30	30(5)	24(4)	27(4)	-14(3)	7(4)	-3(3)
C31	38(5)	9(3)	20(4)	-7(3)	7(4)	-2(3)
C32	32(5)	13(3)	20(4)	1(3)	4(3)	1(3)
C33	24(4)	23(4)	25(4)	2(3)	9(3)	7(3)
C34	35(5)	31(4)	14(4)	6(3)	5(3)	4(4)
C35	47(6)	28(4)	17(4)	-2(3)	3(4)	11(4)
C36	35(5)	20(4)	25(4)	0(3)	1(4)	0(3)
C37	30(5)	32(4)	18(4)	-2(3)	-3(3)	-3(4)
C38	36(5)	23(4)	14(3)	2(3)	-3(3)	-5(3)
C39	17(4)	21(4)	18(4)	0(3)	-2(3)	1(3)
C40	35(5)	28(4)	17(4)	-2(3)	6(3)	-8(3)
C41	37(5)	28(4)	35(5)	-12(4)	8(4)	-12(4)
O1	113(7)	113(7)	57(5)	26(5)	5(5)	-43(5)
C42	52(8)	154(13)	149(13)	87(11)	-27(8)	-31(8)
C43	130(12)	151(13)	34(6)	39(7)	-4(7)	-88(10)
C44	94(10)	142(12)	65(8)	39(8)	-15(7)	-58(9)

C45	157(14)	146(13)	41(7)	39(8)	-13(8)	-49(11)

Table S38. Bond Lengths for **8**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3185(10)	C11	C12	1.375(9)
Ni1	P1	2.281(2)	C12	C13	1.374(9)
Ni1	P2	2.1512(19)	C14	C15	1.373(9)
Ni1	C1	1.890(6)	C14	C19	1.356(9)
Fe1	C32	1.994(7)	C15	C16	1.382(9)
Fe1	C33	1.995(7)	C16	C17	1.343(10)
Fe1	C34	2.040(7)	C17	C18	1.372(10)
Fe1	C35	2.026(7)	C18	C19	1.398(9)
Fe1	C36	2.010(7)	C20	C21	1.369(9)
Fe1	C37	2.038(7)	C20	C25	1.379(9)
Fe1	C38	2.008(7)	C21	C22	1.387(10)
Fe1	C39	1.983(6)	C22	C23	1.358(10)
Fe1	C40	2.004(7)	C23	C24	1.357(10)
Fe1	C41	2.024(7)	C24	C25	1.393(9)
P1	C8	1.837(7)	C26	C27	1.382(8)
P1	C14	1.816(6)	C26	C31	1.370(9)
P1	C32	1.804(6)	C27	C28	1.376(9)
P2	C20	1.818(7)	C28	C29	1.369(10)
P2	C26	1.802(7)	C29	C30	1.368(9)
P2	C39	1.775(6)	C30	C31	1.381(9)
F1	C5	1.292(8)	C32	C33	1.413(8)
F2	C5	1.272(8)	C32	C36	1.416(8)
F3	C5	1.307(9)	C33	C34	1.409(9)
C1	C2	1.373(9)	C34	C35	1.418(9)
C1	C7	1.396(9)	C35	C36	1.388(9)
C2	C3	1.381(9)	C37	C38	1.394(9)
C3	C4	1.357(9)	C37	C41	1.383(9)
C4	C5	1.472(9)	C38	C39	1.417(8)
C4	C6	1.380(9)	C39	C40	1.434(8)
C4	C7	1.473(9)	C40	C41	1.400(9)
C6	C7	1.385(9)	O1	C42	1.455(13)
C8	C9	1.378(9)	O1	C45	1.473(13)
C8	C13	1.378(8)	C42	C43	1.480(13)
C9	C10	1.370(9)	C43	C44	1.500(15)
C10	C11	1.378(9)	C44	C45	1.458(13)

Table S39. Bond Angles for **8**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Br1	89.52(5)	C4	C6	C7	120.9(7)
P2	Ni1	Br1	168.27(7)	C1	C7	C4	121.6(6)
P2	Ni1	P1	101.77(7)	C6	C7	C1	118.5(6)
C1	Ni1	Br1	85.24(18)	C6	C7	C4	119.9(7)
C1	Ni1	P1	171.7(2)	C9	C8	P1	122.6(5)
C1	Ni1	P2	83.87(19)	C13	C8	P1	118.1(5)
C32	Fe1	C33	41.5(2)	C13	C8	C9	119.3(7)
C32	Fe1	C34	69.2(3)	C10	C9	C8	120.7(6)
C32	Fe1	C35	69.2(3)	C9	C10	C11	120.1(7)
C32	Fe1	C36	41.4(2)	C12	C11	C10	119.3(7)
C32	Fe1	C37	177.0(3)	C13	C12	C11	120.6(7)
C32	Fe1	C38	140.2(3)	C12	C13	C8	120.0(7)
C32	Fe1	C40	108.7(3)	C15	C14	P1	119.5(5)
C32	Fe1	C41	137.3(3)	C19	C14	P1	120.3(5)
C33	Fe1	C34	40.9(2)	C19	C14	C15	120.2(6)
C33	Fe1	C35	69.0(3)	C14	C15	C16	120.1(7)
C33	Fe1	C36	69.2(3)	C17	C16	C15	119.7(7)
C33	Fe1	C37	141.3(3)	C16	C17	C18	121.2(7)
C33	Fe1	C38	111.4(3)	C17	C18	C19	119.1(7)
C33	Fe1	C40	136.2(3)	C14	C19	C18	119.6(7)
C33	Fe1	C41	176.9(3)	C21	C20	P2	120.0(5)
C35	Fe1	C34	40.8(3)	C21	C20	C25	119.3(7)
C35	Fe1	C37	112.3(3)	C25	C20	P2	120.7(6)
C36	Fe1	C34	68.3(3)	C20	C21	C22	120.2(7)
C36	Fe1	C35	40.2(2)	C23	C22	C21	120.6(7)
C36	Fe1	C37	138.1(3)	C24	C23	C22	119.5(8)
C36	Fe1	C41	111.8(3)	C23	C24	C25	121.0(7)
C37	Fe1	C34	113.6(3)	C20	C25	C24	119.4(7)
C38	Fe1	C34	110.8(3)	C27	C26	P2	122.3(6)
C38	Fe1	C35	138.0(3)	C31	C26	P2	118.9(5)
C38	Fe1	C36	178.0(3)	C31	C26	C27	118.8(6)
C38	Fe1	C37	40.3(2)	C28	C27	C26	119.6(7)
C38	Fe1	C41	67.7(3)	C29	C28	C27	121.4(7)
C39	Fe1	C32	109.4(3)	C30	C29	C28	119.0(7)
C39	Fe1	C33	107.9(3)	C29	C30	C31	120.0(7)
C39	Fe1	C34	136.1(3)	C26	C31	C30	121.1(7)
C39	Fe1	C35	176.8(3)	P1	C32	Fe1	120.4(4)
C39	Fe1	C36	140.3(3)	C33	C32	Fe1	69.3(4)
C39	Fe1	C37	69.3(3)	C33	C32	P1	126.5(5)
C39	Fe1	C38	41.6(2)	C33	C32	C36	106.9(6)

C39	Fe1	C40	42.2(2)	C36	C32	Fe1	69.9(4)
C39	Fe1	C41	69.3(3)	C36	C32	P1	126.2(5)
C40	Fe1	C34	177.1(3)	C32	C33	Fe1	69.2(4)
C40	Fe1	C35	140.8(3)	C34	C33	Fe1	71.3(4)
C40	Fe1	C36	111.6(3)	C34	C33	C32	108.5(6)
C40	Fe1	C37	68.5(3)	C33	C34	Fe1	67.9(4)
C40	Fe1	C38	69.4(3)	C33	C34	C35	107.4(6)
C40	Fe1	C41	40.7(3)	C35	C34	Fe1	69.1(4)
C41	Fe1	C34	142.2(3)	C34	C35	Fe1	70.1(4)
C41	Fe1	C35	113.7(3)	C36	C35	Fe1	69.3(4)
C41	Fe1	C37	39.8(3)	C36	C35	C34	108.2(6)
C8	P1	Ni1	113.5(2)	C32	C36	Fe1	68.7(4)
C14	P1	Ni1	114.1(2)	C35	C36	Fe1	70.5(4)
C14	P1	C8	100.2(3)	C35	C36	C32	109.0(6)
C32	P1	Ni1	123.2(2)	C38	C37	Fe1	68.7(4)
C32	P1	C8	101.8(3)	C41	C37	Fe1	69.5(4)
C32	P1	C14	100.9(3)	C41	C37	C38	108.0(6)
C20	P2	Ni1	120.8(2)	C37	C38	Fe1	71.0(4)
C26	P2	Ni1	109.2(2)	C37	C38	C39	108.8(6)
C26	P2	C20	102.9(3)	C39	C38	Fe1	68.2(4)
C39	P2	Ni1	114.8(2)	P2	C39	Fe1	126.1(4)
C39	P2	C20	100.2(3)	C38	C39	Fe1	70.2(4)
C39	P2	C26	107.6(3)	C38	C39	P2	131.3(5)
C2	C1	Ni1	119.8(5)	C38	C39	C40	106.5(5)
C2	C1	C7	119.4(6)	C40	C39	Fe1	69.7(4)
C7	C1	Ni1	120.6(5)	C40	C39	P2	122.2(5)
C1	C2	C3	121.3(7)	C39	C40	Fe1	68.1(4)
C4	C3	C2	119.4(7)	C41	C40	Fe1	70.4(4)
C3	C4	C5	121.7(7)	C41	C40	C39	107.0(6)
C3	C4	C6	120.4(6)	C37	C41	Fe1	70.6(4)
C6	C4	C5	117.8(7)	C37	C41	C40	109.7(6)
F1	C5	F3	100.6(7)	C40	C41	Fe1	68.9(4)
F1	C5	C4	113.3(6)	C42	O1	C45	109.1(8)
F2	C5	F1	106.9(8)	O1	C42	C43	104.9(11)
F2	C5	F3	105.0(7)	C42	C43	C44	101.8(11)
F2	C5	C4	115.8(6)	C45	C44	C43	108.2(10)
F3	C5	C4	113.8(7)	C44	C45	O1	104.2(11)

*X-ray Diffraction Data for (dppf)Ni(2-methyl-5-trifluoromethylphenyl)(Br) (**10**)*

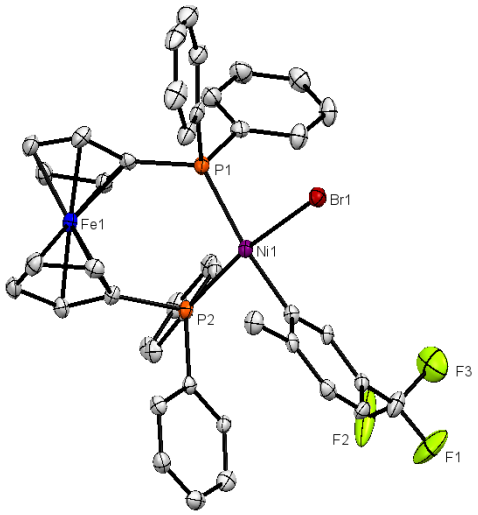


Figure S60. ORTEP of **10**, with ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization have been removed for clarity.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **10** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **10** (Figure S60). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). There is disorder in the position of the fluorine atoms that was not modelled in the refinement, as the model did not result in an improved fit of the data. The THF solvent in the crystal lattice lies on a special position, and only half of the molecule is present in the asymmetric unit. Six reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **10** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860570 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S40. Crystal data and structure refinement for **10**.

Empirical formula	$C_{44}H_{38}BrF_3FeNiO_{0.5}P_2$
Formula weight	888.15
Temperature/K	93.15
Crystal system	monoclinic
Space group	I2/a
a/Å	18.5727(8)
b/Å	9.4426(4)
c/Å	42.528(2)
α/°	90
β/°	93.412(4)
γ/°	90
Volume/Å^3	7445.1(6)
Z	8
ρ_{calc}g/cm^3	1.585
μ/mm^{-1}	2.104
F(000)	3616.0
Crystal size/mm^3	0.1 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.16 to 50.05
Index ranges	-22 ≤ h ≤ 22, -11 ≤ k ≤ 11, -50 ≤ l ≤ 50
Reflections collected	52026
Independent reflections	6581 [R_{int} = 0.1044, R_{sigma} = 0.0541]
Data/restraints/parameters	6581/0/475
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1167
Final R indexes [all data]	R_1 = 0.0715, wR_2 = 0.1334

Table S41. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **10**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	2989.1(2)	2158.3(5)	3957.7(2)	20.49(14)
Ni1	3996.9(3)	2793.7(6)	3688.4(2)	14.89(16)
Fe1	5647.3(3)	5787.6(6)	3834.2(2)	17.76(17)
P1	4591.5(6)	3385.1(12)	4149.3(3)	17.7(3)
P2	4779.9(6)	3395.4(11)	3364.8(3)	14.7(3)
F1	3135(2)	-1896(4)	2641.4(9)	63.1(11)
F2	4206.1(19)	-1451(4)	2813.6(13)	91.1(17)
F3	3466(2)	-2335(3)	3102.2(9)	57.8(10)
O1	7500	387(6)	5000	42.5(14)

C1	3506(2)	2012(4)	3327.6(10)	17.0(9)
C2	3665(2)	656(4)	3236.0(10)	16.1(9)
C3	3313(2)	46(4)	2974.8(10)	17.4(10)
C4	2783(2)	782(5)	2805.5(11)	21.2(10)
C5	2613(2)	2122(5)	2899.8(10)	20.2(10)
C6	2967(2)	2756(5)	3156.1(10)	17.3(9)
C7	3534(3)	-1366(5)	2874.4(12)	29.0(12)
C8	2785(2)	4235(5)	3246.5(11)	24.1(11)
C9	4542(2)	3518(5)	2948.1(10)	15.3(9)
C10	4574(2)	2357(5)	2747.7(10)	16.9(9)
C11	4382(2)	2482(5)	2434.2(11)	22.3(10)
C12	4149(2)	3753(5)	2311.0(11)	21.9(10)
C13	4111(2)	4902(5)	2504.0(11)	22.4(10)
C14	4311(2)	4793(5)	2819.6(10)	18.1(10)
C15	5554(2)	2228(4)	3384.3(10)	16.7(9)
C16	6088(2)	2370(5)	3174.3(11)	20.5(10)
C17	6712(2)	1592(5)	3212.2(11)	22.6(10)
C18	6810(3)	657(5)	3457.0(12)	25.3(11)
C19	6273(2)	486(5)	3663.0(11)	23.6(11)
C20	5646(2)	1265(4)	3625.8(11)	19.8(10)
C21	4053(2)	4397(5)	4410.9(11)	23.2(11)
C22	4160(3)	4303(5)	4732.9(11)	27.5(11)
C23	3807(3)	5207(6)	4924.9(13)	36.2(13)
C24	3350(3)	6214(6)	4793.7(13)	37.0(14)
C25	3233(3)	6306(6)	4474.2(13)	33.9(13)
C26	3582(2)	5387(5)	4279.6(12)	27.0(11)
C27	4888(3)	1816(5)	4369.1(10)	20.9(10)
C28	4505(2)	570(5)	4334.0(12)	25.7(11)
C29	4734(3)	-646(5)	4485.5(12)	29.7(12)
C30	5361(3)	-648(5)	4672.7(12)	29.0(12)
C31	5754(3)	573(5)	4708.7(12)	30.4(12)
C32	5521(3)	1797(5)	4556.6(11)	27.2(11)
C33	5400(2)	4458(5)	4176.2(10)	16.4(9)
C34	5436(2)	5876(5)	4293.5(11)	23.3(10)
C35	6129(3)	6393(5)	4255.4(11)	24.7(11)
C36	6535(2)	5328(5)	4121.0(11)	23.5(10)
C37	6089(2)	4136(5)	4073.7(10)	20.4(10)
C38	5148(2)	5123(4)	3432.8(10)	16.3(9)
C39	5849(2)	5624(5)	3375.2(10)	20.8(10)
C40	5894(3)	7059(5)	3467.4(11)	22.7(10)
C41	5232(3)	7446(5)	3579.9(11)	25.2(11)
C42	4767(2)	6275(5)	3560.4(10)	21.5(10)

C43	7629(3)	-505(7)	4734.6(12)	42.4(15)
C44	7493(6)	-1965(7)	4838.9(15)	76(3)

Table S42. Anisotropic Displacement Parameters ($Å^2×10^3$) for **10**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	16.7(2)	21.9(3)	23.3(3)	-2.81(18)	4.70(19)	-2.67(18)
Ni1	13.0(3)	13.0(3)	18.9(3)	-1.9(2)	2.5(2)	-1.1(2)
Fe1	17.5(3)	12.4(3)	23.3(4)	-1.6(3)	0.6(3)	-1.9(3)
P1	17.2(6)	15.3(6)	20.8(6)	-2.3(5)	2.6(5)	-3.2(5)
P2	13.6(5)	11.0(6)	19.7(6)	-1.6(4)	1.7(5)	-0.1(4)
F1	78(3)	39(2)	69(3)	-33.9(18)	-25(2)	10.7(19)
F2	39(2)	45(2)	196(5)	-69(3)	61(3)	-20.2(18)
F3	80(3)	23.6(18)	72(3)	2.0(17)	16(2)	14.5(18)
O1	35(3)	51(4)	42(3)	0	4(3)	0
C1	15(2)	15(2)	21(2)	0.8(18)	2.7(19)	-1.6(18)
C2	10(2)	15(2)	23(2)	-0.8(18)	2.2(18)	-3.4(18)
C3	17(2)	14(2)	22(2)	-1.4(18)	4.7(19)	-3.7(18)
C4	20(2)	24(3)	19(2)	-5.4(19)	-0.9(19)	-7(2)
C5	13(2)	24(3)	23(2)	5(2)	0.1(19)	-1.8(19)
C6	13(2)	16(2)	23(2)	0.7(18)	4.9(19)	-4.2(18)
C7	23(3)	24(3)	40(3)	-13(2)	2(2)	-6(2)
C8	21(2)	19(3)	32(3)	0(2)	0(2)	2(2)
C9	11(2)	16(2)	19(2)	0.6(18)	0.7(18)	-2.0(18)
C10	15(2)	15(2)	20(2)	-2.2(18)	3.3(18)	-3.8(18)
C11	16(2)	25(3)	27(3)	-6(2)	5(2)	0(2)
C12	15(2)	31(3)	20(2)	1(2)	0.4(19)	-2(2)
C13	20(2)	20(2)	27(3)	5(2)	0(2)	-3(2)
C14	18(2)	14(2)	22(2)	1.2(18)	3.8(19)	2.4(18)
C15	17(2)	11(2)	21(2)	-4.4(18)	-0.6(19)	1.4(18)
C16	20(2)	13(2)	29(3)	2.2(19)	1(2)	2.7(19)
C17	21(2)	16(2)	31(3)	-2(2)	8(2)	1(2)
C18	20(2)	18(2)	38(3)	-6(2)	1(2)	4(2)
C19	26(3)	13(2)	31(3)	0.1(19)	-2(2)	2(2)
C20	19(2)	13(2)	28(3)	-4.1(19)	5(2)	-4.2(19)
C21	19(2)	21(3)	29(3)	-7(2)	-1(2)	-8(2)
C22	27(3)	28(3)	27(3)	-8(2)	3(2)	-6(2)
C23	33(3)	42(3)	34(3)	-13(3)	7(2)	-10(3)
C24	27(3)	42(3)	44(3)	-26(3)	15(3)	-11(3)
C25	17(2)	34(3)	51(4)	-13(3)	5(2)	3(2)
C26	22(2)	26(3)	33(3)	-10(2)	2(2)	-5(2)
C27	25(3)	21(2)	17(2)	-2.3(18)	5(2)	-2(2)

C28	19(2)	21(3)	38(3)	-3(2)	1(2)	0(2)
C29	28(3)	13(2)	47(3)	1(2)	3(2)	0(2)
C30	31(3)	22(3)	34(3)	7(2)	5(2)	6(2)
C31	28(3)	35(3)	28(3)	7(2)	-3(2)	-2(2)
C32	27(3)	28(3)	26(3)	4(2)	-1(2)	-4(2)
C33	15(2)	17(2)	17(2)	3.2(18)	-0.6(18)	-0.2(18)
C34	23(2)	21(3)	26(3)	-7(2)	-2(2)	0(2)
C35	29(3)	18(2)	26(3)	-3(2)	-3(2)	-7(2)
C36	17(2)	23(3)	30(3)	5(2)	-2(2)	-3(2)
C37	18(2)	20(2)	23(2)	2.5(19)	-1.6(19)	-3.4(19)
C38	15(2)	13(2)	20(2)	-1.1(18)	-2.9(18)	0.1(18)
C39	23(2)	15(2)	24(2)	2.2(19)	2(2)	-2.0(19)
C40	25(3)	17(2)	26(3)	4(2)	-1(2)	-7(2)
C41	32(3)	13(2)	30(3)	-1.1(19)	-5(2)	-1(2)
C42	22(2)	20(2)	22(2)	2.6(19)	0(2)	3(2)
C43	32(3)	72(4)	24(3)	-1(3)	6(2)	4(3)
C44	131(7)	48(4)	50(4)	0(3)	11(5)	28(5)

Table S43. Bond Lengths for **10**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3303(7)	C10	C11	1.365(6)
Ni1	P1	2.2616(13)	C11	C12	1.369(7)
Ni1	P2	2.1378(12)	C12	C13	1.364(7)
Ni1	C1	1.888(4)	C13	C14	1.375(6)
Fe1	C33	1.995(4)	C15	C16	1.379(6)
Fe1	C34	2.017(5)	C15	C20	1.375(6)
Fe1	C35	2.036(5)	C16	C17	1.373(6)
Fe1	C36	2.039(5)	C17	C18	1.369(7)
Fe1	C37	2.011(4)	C18	C19	1.375(6)
Fe1	C38	1.995(4)	C19	C20	1.379(6)
Fe1	C39	2.015(5)	C21	C22	1.375(7)
Fe1	C40	2.042(5)	C21	C26	1.375(7)
Fe1	C41	2.029(5)	C22	C23	1.374(7)
Fe1	C42	2.003(4)	C23	C24	1.371(8)
P1	C21	1.812(5)	C24	C25	1.366(7)
P1	C27	1.820(5)	C25	C26	1.387(7)
P1	C33	1.810(4)	C27	C28	1.379(6)
P2	C9	1.804(4)	C27	C32	1.381(7)
P2	C15	1.810(4)	C28	C29	1.372(7)
P2	C38	1.785(4)	C29	C30	1.372(7)
F1	C7	1.302(6)	C30	C31	1.367(7)
F2	C7	1.292(6)	C31	C32	1.381(7)

F3	C7	1.344(6)	C33	C34	1.428(6)
O1	C43	1.440(6)	C33	C37	1.410(6)
O1	C43[1]	1.440(6)	C34	C35	1.395(6)
C1	C2	1.375(6)	C35	C36	1.400(7)
C1	C6	1.393(6)	C36	C37	1.404(6)
C2	C3	1.381(6)	C38	C39	1.421(6)
C3	C4	1.374(6)	C38	C42	1.423(6)
C3	C7	1.466(6)	C39	C40	1.412(6)
C4	C5	1.370(6)	C40	C41	1.395(7)
C5	C6	1.376(6)	C41	C42	1.401(6)
C6	C8	1.493(6)	C43	C44	1.475(9)
C9	C10	1.392(6)	C44	C44[1]	1.369(13)
C9	C14	1.381(6)			

[1]3/2-X,+Y,1-Z

Table S44. Bond Angles for **10**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Br1	90.16(4)	F1	C7	F3	102.3(4)
P2	Ni1	Br1	169.09(4)	F1	C7	C3	114.5(4)
P2	Ni1	P1	100.16(5)	F2	C7	F1	109.7(5)
C1	Ni1	Br1	86.31(13)	F2	C7	F3	103.6(5)
C1	Ni1	P1	171.17(14)	F2	C7	C3	113.9(4)
C1	Ni1	P2	83.96(13)	F3	C7	C3	111.7(4)
C33	Fe1	C34	41.71(18)	C10	C9	P2	122.3(3)
C33	Fe1	C35	69.10(18)	C14	C9	P2	119.8(3)
C33	Fe1	C36	69.06(18)	C14	C9	C10	117.9(4)
C33	Fe1	C37	41.19(17)	C11	C10	C9	120.8(4)
C33	Fe1	C38	108.08(18)	C10	C11	C12	120.5(4)
C33	Fe1	C39	136.22(18)	C13	C12	C11	119.6(4)
C33	Fe1	C40	176.92(18)	C12	C13	C14	120.5(4)
C33	Fe1	C41	141.01(19)	C13	C14	C9	120.7(4)
C33	Fe1	C42	110.69(18)	C16	C15	P2	120.7(3)
C34	Fe1	C35	40.25(18)	C20	C15	P2	120.0(3)
C34	Fe1	C36	68.05(19)	C20	C15	C16	119.1(4)
C34	Fe1	C40	141.35(19)	C17	C16	C15	120.4(4)
C34	Fe1	C41	113.2(2)	C18	C17	C16	120.5(4)
C35	Fe1	C36	40.19(19)	C17	C18	C19	119.4(4)
C35	Fe1	C40	113.57(19)	C18	C19	C20	120.2(4)
C36	Fe1	C40	111.82(19)	C15	C20	C19	120.3(4)
C37	Fe1	C34	68.80(19)	C22	C21	P1	121.7(4)
C37	Fe1	C35	68.12(19)	C22	C21	C26	120.0(5)

C37	Fe1	C36	40.57(18)	C26	C21	P1	118.0(4)
C37	Fe1	C39	109.72(18)	C21	C22	C23	120.4(5)
C37	Fe1	C40	137.68(19)	C24	C23	C22	119.6(5)
C37	Fe1	C41	177.7(2)	C25	C24	C23	120.5(5)
C38	Fe1	C34	137.25(18)	C24	C25	C26	120.1(5)
C38	Fe1	C35	177.15(18)	C21	C26	C25	119.4(5)
C38	Fe1	C36	139.76(18)	C28	C27	P1	120.0(4)
C38	Fe1	C37	110.15(18)	C28	C27	C32	117.9(4)
C38	Fe1	C39	41.49(17)	C32	C27	P1	122.0(4)
C38	Fe1	C40	69.26(18)	C29	C28	C27	121.3(4)
C38	Fe1	C41	69.15(18)	C30	C29	C28	120.2(5)
C38	Fe1	C42	41.69(18)	C31	C30	C29	119.5(5)
C39	Fe1	C34	177.91(18)	C30	C31	C32	120.2(5)
C39	Fe1	C35	140.95(19)	C31	C32	C27	120.9(5)
C39	Fe1	C36	111.90(19)	P1	C33	Fe1	122.1(2)
C39	Fe1	C40	40.72(18)	C34	C33	Fe1	70.0(3)
C39	Fe1	C41	68.26(19)	C34	C33	P1	124.6(3)
C41	Fe1	C35	112.67(19)	C37	C33	Fe1	70.0(3)
C41	Fe1	C36	138.74(19)	C37	C33	P1	128.7(3)
C41	Fe1	C40	40.09(19)	C37	C33	C34	106.6(4)
C42	Fe1	C34	110.77(19)	C33	C34	Fe1	68.3(3)
C42	Fe1	C35	138.36(19)	C35	C34	Fe1	70.6(3)
C42	Fe1	C36	178.55(19)	C35	C34	C33	108.2(4)
C42	Fe1	C37	140.09(18)	C34	C35	Fe1	69.1(3)
C42	Fe1	C39	69.32(18)	C34	C35	C36	108.6(4)
C42	Fe1	C40	68.50(19)	C36	C35	Fe1	70.0(3)
C42	Fe1	C41	40.67(19)	C35	C36	Fe1	69.8(3)
C21	P1	Ni1	113.78(15)	C35	C36	C37	107.9(4)
C21	P1	C27	106.0(2)	C37	C36	Fe1	68.7(3)
C27	P1	Ni1	111.20(15)	C33	C37	Fe1	68.8(3)
C33	P1	Ni1	123.63(15)	C36	C37	Fe1	70.8(3)
C33	P1	C21	98.8(2)	C36	C37	C33	108.7(4)
C33	P1	C27	101.4(2)	P2	C38	Fe1	125.4(2)
C9	P2	Ni1	120.88(14)	C39	C38	Fe1	70.0(3)
C9	P2	C15	103.4(2)	C39	C38	P2	128.5(3)
C15	P2	Ni1	112.21(15)	C39	C38	C42	107.0(4)
C38	P2	Ni1	114.02(15)	C42	C38	Fe1	69.4(2)
C38	P2	C9	99.8(2)	C42	C38	P2	124.5(3)
C38	P2	C15	104.7(2)	C38	C39	Fe1	68.5(3)
C43	O1	C43[1]	108.4(6)	C40	C39	Fe1	70.7(3)
C2	C1	Ni1	119.5(3)	C40	C39	C38	108.2(4)
C2	C1	C6	118.7(4)	C39	C40	Fe1	68.6(3)

C6	C1	Ni1	121.7(3)	C41	C40	Fe1	69.5(3)
C1	C2	C3	121.1(4)	C41	C40	C39	107.9(4)
C2	C3	C7	119.1(4)	C40	C41	Fe1	70.5(3)
C4	C3	C2	120.1(4)	C40	C41	C42	109.0(4)
C4	C3	C7	120.8(4)	C42	C41	Fe1	68.7(3)
C5	C4	C3	119.0(4)	C38	C42	Fe1	68.9(2)
C4	C5	C6	121.7(4)	C41	C42	Fe1	70.7(3)
C1	C6	C8	120.3(4)	C41	C42	C38	107.9(4)
C5	C6	C1	119.3(4)	O1	C43	C44	105.8(5)
C5	C6	C8	120.4(4)	C44[1]	C44	C43	107.9(4)

[1]3/2-X,+Y,1-Z

*X-ray Diffraction Data for (dppf)Ni(2-trifluoromethyl-6-methylphenyl)(Br) (**12**)*

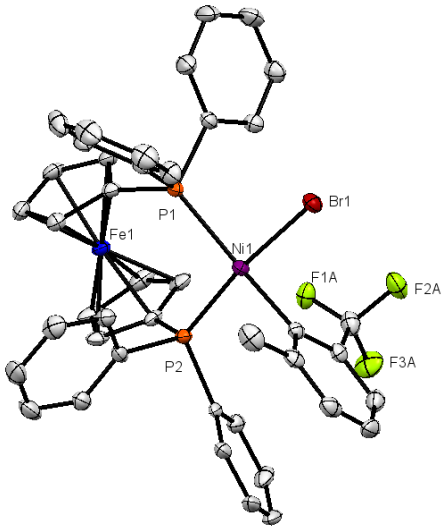


Figure S61. ORTEP of **12**, with ellipsoids shown at 50% probability. Disorder in the aryl ring, hydrogen atoms and solvent of crystallization have been removed for clarity.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **12** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **12** (Figure S61). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of

all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Both THF models are disordered. Atoms O1, C43, C44, C45, and C46 are disordered across the crystallographic 2-fold axis. The special position constraints were suppressed and the site occupancies were restrained to be 0.5. Chemically identical C-C and C-O bonds were restrained to be similar. The THF, as a group, was restrained to have similar tensor directions and behave as a rigid body. A similar approach was used for atoms O2, C47, C48, C49, and C50. The site occupancies were freely refined and fixed near their converged values of 0.5 for each atom. O2B did not refine well and required that the thermal parameters be constrained to the same value refined for O2A. Chemically identical C-C and C-O bonds were restrained to be similar. Each THF model, as a group, was restrained to have similar tensor directions and behave as a rigid body. The two, complementary models were distinguished with atom label suffixes "A" and "B". Based on the difference map there appeared to be a minor disordered position of the ortho CF3 group. The site occupancies of the CF3 groups were freely refined to converged values of 0.83/0.17. Atoms C7 and C8 were split in two. These two positions were then constrained to be identical in thermal and position parameters. The minor component fluorine atoms were constrained to have the same thermal parameters to their chemically identical counterparts. The full numbering scheme of compound **12** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860565 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S45. Crystal data and structure refinement for **12**.

Empirical formula	$C_{48}H_{46}BrF_{3.03}FeNiO_{1.5}P_2$
Formula weight	960.85
Temperature/K	93(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	23.8460(10)
b/Å	10.0157(4)
c/Å	34.4671(15)
α/°	90
β/°	95.897(4)
γ/°	90

Volume/Å^3	8188.4(6)
Z	8
ρ_{calc}g/cm^3	1.559
μ/mm^{-1}	1.921
F(000)	3938.0
Crystal size/mm^3	0.200 × 0.100 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.096 to 54.968
Index ranges	-30 ≤ h ≤ 30, -13 ≤ k ≤ 12, -44 ≤ l ≤ 44
Reflections collected	69711
Independent reflections	9370 [R_{int} = 0.1211, R_{sigma} = 0.0689]
Data/restraints/parameters	9370/116/591
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0942, wR_2 = 0.1105

Table S46. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **12**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	2830.2(2)	33.5(4)	3673.0(2)	22.50(11)
Ni1	3224.0(2)	2063.4(5)	3884.4(2)	15.05(12)
Fe1	2550.0(2)	5549.3(6)	4390.6(2)	16.99(13)
P1	2373.7(4)	3122.1(10)	3701.9(3)	15.9(2)
P2	3672.1(4)	3797.3(10)	4132.4(3)	14.7(2)
C1	3927.4(16)	1100(4)	3973.3(12)	17.8(8)
C2	4117.3(17)	480(4)	4325.7(12)	20.6(9)
C3	4644.6(19)	-127(4)	4384.7(13)	27.5(10)
C4	4997.9(18)	-137(4)	4095.5(15)	30.5(11)
C5	4816.0(18)	419(4)	3741.0(14)	26.4(10)
C6	4288.1(17)	1019(4)	3674.2(12)	21.1(9)
C9	2171.6(16)	4730(4)	3898.2(11)	17.5(9)
C10	2383.9(17)	6035(4)	3821.3(12)	20.5(9)
C11	2118.1(17)	6968(4)	4053.9(13)	24.6(10)
C12	1744.4(16)	6258(4)	4268.0(12)	22.9(9)
C13	1770.4(16)	4893(4)	4175.8(12)	20.1(9)
C14	3312.1(16)	4694(4)	4485.6(11)	17.3(9)
C15	3352.1(16)	6100(4)	4566.0(12)	21.8(9)
C16	3008.7(17)	6383(5)	4865.6(13)	28.5(11)
C17	2754.0(18)	5195(5)	4970.9(12)	26.9(10)
C18	2940.0(16)	4151(5)	4739.5(12)	23.4(10)
C19	2249.3(17)	3422(4)	3176.8(12)	19.5(9)
C20	2471.8(18)	2562(5)	2918.3(12)	25.8(10)

C21	2389(2)	2785(5)	2522.7(13)	32.4(11)
C22	2076(2)	3858(5)	2375.7(13)	36.1(12)
C23	1839(2)	4707(5)	2627.0(13)	34.1(12)
C24	1930.2(19)	4502(5)	3026.1(13)	26.9(10)
C25	1753.2(16)	2186(4)	3807.7(12)	19.2(9)
C26	1241.9(18)	2321(5)	3577.2(14)	30.6(11)
C27	760.5(19)	1746(5)	3690.6(15)	38.6(13)
C28	782.1(19)	1023(5)	4027.9(15)	34.4(12)
C29	1284.3(18)	856(4)	4255.6(13)	25.5(10)
C30	1770.5(17)	1443(4)	4147.6(12)	20.8(9)
C31	4361.1(16)	3554(4)	4409.3(12)	17.3(8)
C32	4405.5(17)	3448(4)	4812.9(12)	22.0(9)
C33	4919.1(19)	3162(4)	5017.9(14)	30.2(11)
C34	5388.6(18)	2979(4)	4824.9(15)	31.3(11)
C35	5346.6(17)	3093(4)	4424.2(15)	28.9(11)
C36	4836.0(16)	3383(4)	4214.3(14)	22.7(9)
C37	3816.4(16)	5039(4)	3773.0(12)	18.5(8)
C38	3564.6(16)	4924(4)	3392.6(12)	21.0(9)
C39	3631.0(19)	5917(5)	3120.3(13)	29.8(11)
C40	3946.0(19)	7035(5)	3228.2(15)	33.5(11)
C41	4209.4(18)	7141(5)	3601.0(15)	31.4(11)
C42	4152.4(17)	6145(4)	3870.0(13)	23.3(9)
F1A	3377.9(12)	1280(3)	4666.2(8)	26.7(7)
F2A	3492.7(13)	-834(3)	4643.4(9)	33.9(8)
F3A	4072.2(14)	365(3)	5006.0(9)	37.9(8)
C7A	3755(2)	358(4)	4649.3(13)	27.2(10)
C8A	4123(2)	1605(5)	3279.9(13)	32.8(11)
F1B	4412(6)	735(15)	3023(5)	33.9(8)
F2B	4503(7)	2697(17)	3248(4)	37.9(8)
F3B	3658(5)	1753(12)	3164(4)	26.7(7)
C7B	3755(2)	358(4)	4649.3(13)	27.2(10)
C8B	4123(2)	1605(5)	3279.9(13)	32.8(11)
O2A	3542(7)	3408(19)	1828(4)	116(4)
C47A	3916(9)	3940(30)	2194(6)	137(11)
C48A	4395(7)	3179(17)	2215(5)	97(6)
C49A	4369(6)	2147(12)	1982(4)	56(3)
C50A	4044(5)	2628(15)	1661(4)	46(3)
O2B	3657(8)	3695(18)	1676(4)	116(4)
C47B	3691(5)	4417(11)	2088(3)	38(2)
C48B	3934(7)	3469(11)	2363(3)	53(3)
C49B	4085(6)	2368(11)	2179(3)	52(3)
C50B	4121(10)	2600(20)	1800(4)	97(7)

O1	4509(5)	7665(9)	2327(3)	62(3)
C43	5028(10)	7062(9)	2555(8)	54(4)
C44	5280(9)	8259(15)	2746(6)	101(7)
C45	5184(5)	9310(11)	2446(4)	62(4)
C46	4620(7)	9074(16)	2274(5)	83(5)

Table S47. Anisotropic Displacement Parameters ($Å^2×10^3$) for **12**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	22.8(2)	17.8(2)	26.5(2)	-4.47(18)	0.18(16)	-4.44(18)
Ni1	14.4(2)	13.6(3)	16.7(3)	-0.9(2)	-0.27(19)	-2.1(2)
Fe1	12.3(3)	19.0(3)	19.1(3)	-1.1(3)	-1.1(2)	2.0(2)
P1	15.0(5)	15.7(5)	16.5(5)	1.2(4)	-1.4(4)	-2.8(4)
P2	11.3(5)	15.5(5)	16.9(5)	-1.8(4)	-0.3(4)	-0.1(4)
C1	16.5(19)	13(2)	23(2)	-3.6(17)	1.5(16)	-1.4(16)
C2	23(2)	14(2)	24(2)	-3.1(17)	0.7(17)	-1.6(17)
C3	32(2)	18(2)	31(2)	-0.5(19)	-7(2)	2(2)
C4	17(2)	19(2)	55(3)	-7(2)	-1(2)	4.0(19)
C5	23(2)	20(2)	38(3)	-8(2)	7(2)	-2.9(18)
C6	23(2)	18(2)	23(2)	-5.7(18)	1.9(17)	-5.1(18)
C9	13.0(18)	21(2)	18(2)	0.2(16)	-2.4(16)	-0.2(16)
C10	18(2)	21(2)	22(2)	1.6(18)	-1.1(17)	0.2(17)
C11	21(2)	19(2)	33(2)	0.3(19)	-4.8(18)	5.3(18)
C12	14(2)	27(2)	27(2)	-2.5(19)	-1.0(17)	6.8(18)
C13	12.4(18)	24(2)	24(2)	2.1(19)	-0.6(16)	1.0(18)
C14	13.2(19)	19(2)	18(2)	-4.4(16)	-3.5(15)	4.9(16)
C15	13.4(19)	25(2)	25(2)	-8.1(19)	-4.1(17)	-1.6(17)
C16	15(2)	38(3)	31(3)	-15(2)	-6.8(18)	6(2)
C17	21(2)	39(3)	21(2)	-1(2)	-0.2(17)	11(2)
C18	17(2)	31(2)	21(2)	6.0(19)	-3.6(17)	5.9(19)
C19	21(2)	17(2)	20(2)	0.8(17)	-3.4(17)	-9.3(17)
C20	31(2)	28(2)	18(2)	2.0(19)	1.9(18)	-4(2)
C21	38(3)	39(3)	19(2)	-3(2)	2(2)	-7(2)
C22	45(3)	43(3)	17(2)	9(2)	-8(2)	-14(3)
C23	48(3)	25(3)	27(3)	8(2)	-11(2)	-10(2)
C24	31(2)	25(2)	22(2)	2.1(19)	-6.9(19)	-5(2)
C25	17(2)	15(2)	25(2)	-2.5(17)	1.5(17)	-2.8(17)
C26	26(2)	29(3)	34(3)	10(2)	-8(2)	-5(2)
C27	19(2)	42(3)	51(3)	18(3)	-13(2)	-10(2)
C28	21(2)	37(3)	45(3)	8(2)	4(2)	-10(2)
C29	27(2)	27(2)	23(2)	5.0(19)	4.4(18)	-4.2(19)
C30	19(2)	22(2)	21(2)	-0.7(18)	1.2(17)	-3.1(18)

C31	14.7(19)	8.6(19)	27(2)	-1.9(17)	-5.6(16)	0.1(16)
C32	19(2)	16(2)	29(2)	-4.0(18)	-2.7(18)	2.4(17)
C33	31(3)	22(2)	33(3)	-3(2)	-17(2)	5(2)
C34	17(2)	19(2)	54(3)	-3(2)	-17(2)	1.3(19)
C35	13(2)	17(2)	56(3)	1(2)	1(2)	-1.3(17)
C36	15(2)	14(2)	39(3)	-0.8(19)	1.2(18)	-2.7(17)
C37	15.3(19)	13.3(19)	28(2)	-2.2(18)	5.7(16)	-1.2(17)
C38	17(2)	22(2)	24(2)	-0.7(19)	0.9(16)	-0.3(18)
C39	29(2)	37(3)	24(2)	7(2)	3.5(19)	1(2)
C40	29(2)	27(3)	47(3)	13(2)	11(2)	-3(2)
C41	25(2)	23(2)	48(3)	-4(2)	8(2)	-9(2)
C42	19(2)	19(2)	31(2)	-2.5(19)	3.3(18)	0.3(18)
F1A	33.2(17)	23.3(16)	24.7(16)	3.3(13)	8.5(13)	7.5(13)
F2A	38.5(19)	21.2(16)	44(2)	-0.9(14)	15.7(15)	-5.5(14)
F3A	39.5(19)	50(2)	22.8(17)	6.5(15)	-3.7(14)	3.0(16)
C7A	36(3)	19(2)	26(2)	-0.5(18)	0(2)	-2.0(19)
C8A	41(3)	33(3)	26(3)	-2(2)	11(2)	-6(2)
F1B	38.5(19)	21.2(16)	44(2)	-0.9(14)	15.7(15)	-5.5(14)
F2B	39.5(19)	50(2)	22.8(17)	6.5(15)	-3.7(14)	3.0(16)
F3B	33.2(17)	23.3(16)	24.7(16)	3.3(13)	8.5(13)	7.5(13)
C7B	36(3)	19(2)	26(2)	-0.5(18)	0(2)	-2.0(19)
C8B	41(3)	33(3)	26(3)	-2(2)	11(2)	-6(2)
O2A	134(6)	129(8)	80(6)	-18(6)	-13(5)	38(6)
C47A	145(12)	155(17)	100(13)	-51(13)	-44(10)	72(12)
C48A	111(10)	95(10)	73(8)	-7(7)	-47(8)	41(8)
C49A	62(7)	56(7)	42(6)	25(5)	-25(5)	11(6)
C50A	33(5)	53(7)	46(6)	13(5)	-16(4)	3(5)
O2B	134(6)	129(8)	80(6)	-18(6)	-13(5)	38(6)
C47B	43(6)	37(5)	32(5)	4(4)	-3(4)	-1(4)
C48B	64(8)	48(6)	43(6)	4(4)	-4(5)	16(5)
C49B	90(9)	24(5)	39(6)	-2(4)	-10(6)	19(5)
C50B	123(15)	110(11)	56(7)	-5(6)	6(7)	44(11)
O1	93(6)	52(5)	38(5)	10(4)	-5(4)	-13(5)
C43	60(6)	40(5)	65(12)	20(6)	22(6)	-19(6)
C44	119(14)	43(7)	127(11)	20(8)	-54(10)	-36(8)
C45	60(8)	35(5)	91(10)	2(6)	4(7)	-2(4)
C46	82(8)	53(7)	106(13)	24(6)	-22(8)	-19(5)

Table S48. Bond Lengths for **12**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	Ni1	2.3249(6)	C21	C22	1.375(7)

Ni1	C1	1.932(4)	C22	C23	1.375(7)
Ni1	P2	2.1681(11)	C23	C24	1.385(6)
Ni1	P1	2.3172(11)	C25	C30	1.385(6)
Fe1	C14	2.005(4)	C25	C26	1.392(6)
Fe1	C18	2.011(4)	C26	C27	1.377(6)
Fe1	C9	2.014(4)	C27	C28	1.366(7)
Fe1	C10	2.021(4)	C28	C29	1.373(6)
Fe1	C15	2.022(4)	C29	C30	1.385(6)
Fe1	C13	2.038(4)	C31	C36	1.386(6)
Fe1	C17	2.040(4)	C31	C32	1.388(6)
Fe1	C11	2.045(4)	C32	C33	1.380(6)
Fe1	C12	2.051(4)	C33	C34	1.372(7)
Fe1	C16	2.051(4)	C34	C35	1.379(7)
P1	C25	1.820(4)	C35	C36	1.382(6)
P1	C19	1.829(4)	C37	C42	1.387(6)
P1	C9	1.830(4)	C37	C38	1.390(6)
P2	C14	1.800(4)	C38	C39	1.387(6)
P2	C37	1.813(4)	C39	C40	1.378(6)
P2	C31	1.830(4)	C40	C41	1.375(7)
C1	C2	1.398(6)	C41	C42	1.378(6)
C1	C6	1.411(6)	F1A	C7A	1.295(5)
C2	C3	1.393(6)	F2A	C7A	1.347(5)
C2	C7B	1.484(6)	F3A	C7A	1.375(5)
C2	C7A	1.484(6)	F1B	C8B	1.464(15)
C3	C4	1.369(6)	F2B	C8B	1.431(17)
C4	C5	1.372(6)	F3B	C8B	1.150(11)
C5	C6	1.392(6)	O2A	C47A	1.564(15)
C6	C8B	1.495(6)	O2A	C50A	1.586(13)
C6	C8A	1.495(6)	C47A	C48A	1.371(14)
C9	C13	1.430(6)	C48A	C49A	1.307(13)
C9	C10	1.437(6)	C49A	C50A	1.373(11)
C10	C11	1.421(6)	O2B	C50B	1.587(14)
C11	C12	1.407(6)	O2B	C47B	1.589(12)
C12	C13	1.407(6)	C47B	C48B	1.422(12)
C14	C18	1.417(6)	C48B	C49B	1.340(11)
C14	C15	1.436(6)	C49B	C50B	1.338(13)
C15	C16	1.411(6)	O1	C46	1.451(15)
C16	C17	1.401(7)	O1	C43	1.521(18)
C17	C18	1.414(6)	C43	C44	1.466(15)
C19	C20	1.384(6)	C44	C45	1.477(15)
C19	C24	1.392(6)	C45	C46	1.432(14)
C20	C21	1.376(6)			

Table S49. Bond Angles for **12**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Ni1	P2	87.29(12)	C9	C10	Fe1	68.9(2)
C1	Ni1	P1	173.13(12)	C12	C11	C10	107.9(4)
P2	Ni1	P1	97.04(4)	C12	C11	Fe1	70.2(2)
C1	Ni1	Br1	85.94(12)	C10	C11	Fe1	68.6(2)
P2	Ni1	Br1	172.23(4)	C11	C12	C13	109.1(4)
P1	Ni1	Br1	90.06(3)	C11	C12	Fe1	69.7(2)
C14	Fe1	C18	41.33(16)	C13	C12	Fe1	69.4(2)
C14	Fe1	C9	106.48(16)	C12	C13	C9	108.1(4)
C18	Fe1	C9	111.08(17)	C12	C13	Fe1	70.4(2)
C14	Fe1	C10	110.20(16)	C9	C13	Fe1	68.4(2)
C18	Fe1	C10	141.34(17)	C18	C14	C15	106.9(4)
C9	Fe1	C10	41.73(16)	C18	C14	P2	126.7(3)
C14	Fe1	C15	41.78(16)	C15	C14	P2	126.4(3)
C18	Fe1	C15	69.28(18)	C18	C14	Fe1	69.5(2)
C9	Fe1	C15	133.73(16)	C15	C14	Fe1	69.7(2)
C10	Fe1	C15	108.03(17)	P2	C14	Fe1	126.1(2)
C14	Fe1	C13	134.35(17)	C16	C15	C14	107.8(4)
C18	Fe1	C13	109.94(17)	C16	C15	Fe1	70.8(2)
C9	Fe1	C13	41.34(16)	C14	C15	Fe1	68.5(2)
C10	Fe1	C13	69.18(17)	C17	C16	C15	108.6(4)
C15	Fe1	C13	174.80(17)	C17	C16	Fe1	69.6(2)
C14	Fe1	C17	69.20(16)	C15	C16	Fe1	68.7(2)
C18	Fe1	C17	40.85(17)	C16	C17	C18	108.2(4)
C9	Fe1	C17	142.79(18)	C16	C17	Fe1	70.4(3)
C10	Fe1	C17	175.46(19)	C18	C17	Fe1	68.5(2)
C15	Fe1	C17	68.38(18)	C17	C18	C14	108.5(4)
C13	Fe1	C17	114.62(18)	C17	C18	Fe1	70.7(2)
C14	Fe1	C11	141.68(17)	C14	C18	Fe1	69.1(2)
C18	Fe1	C11	176.93(17)	C20	C19	C24	118.3(4)
C9	Fe1	C11	69.44(16)	C20	C19	P1	120.1(3)
C10	Fe1	C11	40.92(16)	C24	C19	P1	121.6(3)
C15	Fe1	C11	112.70(18)	C21	C20	C19	120.8(4)
C13	Fe1	C11	68.32(17)	C22	C21	C20	120.6(5)
C17	Fe1	C11	137.13(18)	C21	C22	C23	119.5(4)
C14	Fe1	C12	174.56(17)	C22	C23	C24	120.1(5)
C18	Fe1	C12	136.92(17)	C23	C24	C19	120.6(4)
C9	Fe1	C12	68.79(16)	C30	C25	C26	118.9(4)
C10	Fe1	C12	68.31(17)	C30	C25	P1	119.5(3)
C15	Fe1	C12	143.53(17)	C26	C25	P1	121.2(3)

C13	Fe1	C12	40.26(16)	C27	C26	C25	120.3(4)
C17	Fe1	C12	112.73(17)	C28	C27	C26	120.3(4)
C11	Fe1	C12	40.17(17)	C27	C28	C29	120.4(4)
C14	Fe1	C16	69.11(16)	C28	C29	C30	120.0(4)
C18	Fe1	C16	68.30(19)	C29	C30	C25	120.2(4)
C9	Fe1	C16	174.26(17)	C36	C31	C32	119.6(4)
C10	Fe1	C16	135.42(19)	C36	C31	P2	119.9(3)
C15	Fe1	C16	40.53(16)	C32	C31	P2	120.3(3)
C13	Fe1	C16	144.40(17)	C33	C32	C31	120.1(4)
C17	Fe1	C16	40.04(19)	C34	C33	C32	120.3(4)
C11	Fe1	C16	111.50(19)	C33	C34	C35	119.7(4)
C12	Fe1	C16	115.78(17)	C34	C35	C36	120.7(4)
C25	P1	C19	103.34(18)	C35	C36	C31	119.5(4)
C25	P1	C9	97.38(18)	C42	C37	C38	118.4(4)
C19	P1	C9	101.49(19)	C42	C37	P2	121.9(3)
C25	P1	Ni1	114.63(14)	C38	C37	P2	119.6(3)
C19	P1	Ni1	113.10(14)	C39	C38	C37	120.7(4)
C9	P1	Ni1	123.95(13)	C40	C39	C38	119.8(4)
C14	P2	C37	104.88(19)	C41	C40	C39	119.9(4)
C14	P2	C31	100.30(18)	C40	C41	C42	120.4(4)
C37	P2	C31	102.97(18)	C41	C42	C37	120.7(4)
C14	P2	Ni1	114.61(14)	F1A	C7A	F2A	108.0(4)
C37	P2	Ni1	113.61(14)	F1A	C7A	F3A	106.1(4)
C31	P2	Ni1	118.61(13)	F2A	C7A	F3A	103.3(4)
C2	C1	C6	116.2(4)	F1A	C7A	C2	115.8(4)
C2	C1	Ni1	123.9(3)	F2A	C7A	C2	111.5(4)
C6	C1	Ni1	119.8(3)	F3A	C7A	C2	111.3(4)
C3	C2	C1	121.9(4)	F3B	C8B	F2B	118.0(10)
C3	C2	C7B	116.1(4)	F3B	C8B	F1B	111.3(10)
C1	C2	C7B	121.9(4)	F2B	C8B	F1B	93.9(9)
C3	C2	C7A	116.1(4)	F3B	C8B	C6	121.4(7)
C1	C2	C7A	121.9(4)	F2B	C8B	C6	105.1(7)
C4	C3	C2	120.7(4)	F1B	C8B	C6	102.7(7)
C3	C4	C5	118.9(4)	C47A	O2A	C50A	94.2(13)
C4	C5	C6	121.3(4)	C48A	C47A	O2A	104.7(13)
C5	C6	C1	120.8(4)	C49A	C48A	C47A	115.0(15)
C5	C6	C8B	117.9(4)	C48A	C49A	C50A	101.9(12)
C1	C6	C8B	121.2(4)	C49A	C50A	O2A	105.3(12)
C5	C6	C8A	117.9(4)	C50B	O2B	C47B	95.9(11)
C1	C6	C8A	121.2(4)	C48B	C47B	O2B	105.8(10)
C13	C9	C10	107.0(4)	C49B	C48B	C47B	110.1(10)
C13	C9	P1	124.6(3)	C50B	C49B	C48B	111.6(12)

C10	C9	P1	128.4(3)	C49B	C50B	O2B	105.6(13)
C13	C9	Fe1	70.3(2)	C46	O1	C43	107.6(10)
C10	C9	Fe1	69.4(2)	C44	C43	O1	100.4(11)
P1	C9	Fe1	123.9(2)	C43	C44	C45	104.1(13)
C11	C10	C9	107.9(4)	C46	C45	C44	104.0(12)
C11	C10	Fe1	70.4(2)	C45	C46	O1	106.5(11)

*X-ray Diffraction Data for (dppf)Ni(2,6-dimethyl-4-fluorophenyl)(Br) (**13**)*

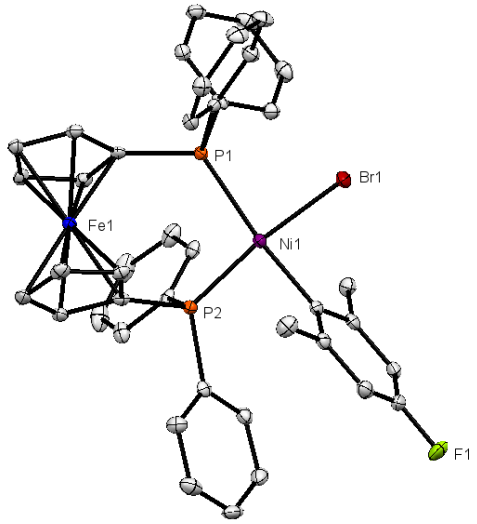


Figure S62. ORTEP of **13**, with ellipsoids shown at 50% probability. Hydrogen atoms and solvent of crystallization have been removed for clarity.

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **13** in THF layered with pentane at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **13** (Figure S62). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Ten reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **13** can be found in the full details of the X-ray structure determination (CIF), which

is included as Supporting Information. CCDC number 1860564 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S50. Crystal data and structure refinement for **13**.

Empirical formula	$C_{46}H_{44}BrFFeNiOP_2$
Formula weight	888.22
Temperature/K	93.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.7586(3)
b/Å	18.9665(5)
c/Å	17.0364(5)
α/°	90
β/°	104.395(3)
γ/°	90
Volume/Å^3	3680.16(18)
Z	4
ρ_{calc}g/cm^3	1.603
μ/mm^{-1}	2.122
F(000)	1824.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.37 to 50.054
Index ranges	$-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$
Reflections collected	52476
Independent reflections	6494 [R_{int} = 0.0547, R_{sigma} = 0.0273]
Data/restraints/parameters	6494/0/480
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0621
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.0672

Table S51. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **13**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	3604.3(2)	5185.8(2)	2664.0(2)	16.86(7)
Ni1	2738.1(3)	4108.5(2)	2794.2(2)	10.34(8)
Fe1	1282.1(3)	2487.9(2)	1184.6(2)	10.61(9)
P1	3289.2(5)	3737.0(3)	1660.4(4)	10.73(13)
P2	1908.6(5)	3156.9(3)	3058.0(4)	10.45(13)

F1	1655.7(14)	5358.9(8)	5758.3(9)	26.3(4)
C1	2405(2)	4500.8(12)	3748.4(14)	12.5(5)
C2	1325(2)	4816.2(12)	3693.6(15)	14.3(5)
C3	1072(2)	5109.3(13)	4375.2(15)	17.6(5)
C4	1912(2)	5083.4(13)	5087.6(15)	18.9(6)
C5	2986(2)	4798.3(13)	5156.7(15)	15.8(5)
C6	3246(2)	4504.5(13)	4479.7(14)	14.0(5)
C7	415(2)	4842.7(14)	2910.2(15)	20.6(6)
C8	4425(2)	4179.4(14)	4569.2(15)	17.0(5)
C9	4870(2)	3655.5(12)	1803.5(14)	12.8(5)
C10	5647(2)	3896.9(13)	2491.9(15)	15.9(5)
C11	6837(2)	3822.7(14)	2585.6(15)	19.8(6)
C12	7253(2)	3518.7(14)	1983.8(15)	18.9(6)
C13	6488(2)	3280.0(13)	1295.4(15)	17.1(5)
C14	5300(2)	3344.2(13)	1207.3(14)	14.8(5)
C15	2895(2)	4381.2(12)	847.0(14)	12.3(5)
C16	1741(2)	4461.2(13)	416.8(14)	14.7(5)
C17	1442(2)	4960.2(13)	-181.5(15)	17.4(5)
C18	2278(2)	5391.1(14)	-351.5(15)	19.7(6)
C19	3421(2)	5328.1(14)	83.1(15)	19.5(6)
C20	3728(2)	4823.5(13)	676.3(15)	17.0(5)
C21	1091(2)	3128.0(12)	3826.6(14)	12.8(5)
C22	-108(2)	3053.5(13)	3632.0(15)	17.5(5)
C23	-716(2)	3069.8(14)	4225.1(16)	21.3(6)
C24	-126(2)	3168.5(13)	5016.2(16)	21.2(6)
C25	1076(2)	3234.0(13)	5217.0(15)	20.2(6)
C26	1679(2)	3201.8(13)	4630.0(14)	15.2(5)
C27	3004(2)	2483.3(12)	3395.9(13)	12.3(5)
C28	4151(2)	2637.0(13)	3397.3(14)	15.1(5)
C29	4991(2)	2120.1(14)	3545.2(15)	20.2(6)
C30	4688(2)	1449.4(15)	3687.3(16)	25.6(6)
C31	3560(3)	1292.7(14)	3715.8(16)	26.2(7)
C32	2720(2)	1809.2(13)	3583.3(14)	17.7(6)
C33	2809(2)	2922.1(12)	1130.4(14)	11.6(5)
C34	2098(2)	2825.8(13)	333.4(14)	13.2(5)
C35	1838(2)	2106.8(13)	216.6(14)	13.7(5)
C36	2388(2)	1743.8(13)	925.3(14)	13.8(5)
C37	2997(2)	2239.7(13)	1484.7(14)	13.3(5)
C38	870(2)	2799.6(12)	2191.9(14)	11.5(5)
C39	500(2)	2094.1(13)	2012.8(14)	13.9(5)
C40	-303(2)	2088.4(14)	1247.6(15)	16.1(5)
C41	-442(2)	2779.3(14)	947.7(15)	16.1(5)

C42	271(2)	3221.8(13)	1527.8(14)	13.1(5)
O1	7538(2)	1668.7(13)	3384.7(13)	46.9(6)
C43	8496(3)	1228.0(17)	3698.4(19)	36.0(8)
C44	8445(4)	659(2)	3095(2)	56.0(11)
C45	7772(3)	958.7(17)	2322.7(19)	37.7(8)
C46	7244(4)	1598(2)	2542(2)	64.4(13)

Table S52. Anisotropic Displacement Parameters ($Å^2×10^3$) for **13**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	24.59(15)	10.24(13)	17.81(13)	-0.48(10)	9.18(10)	-3.87(10)
Ni1	11.89(16)	8.94(16)	10.72(15)	0.00(12)	3.83(12)	-0.77(12)
Fe1	9.84(17)	10.99(18)	11.24(17)	-0.97(13)	3.09(13)	-0.66(14)
P1	10.6(3)	10.8(3)	10.9(3)	0.2(2)	2.9(2)	-1.1(2)
P2	11.1(3)	10.2(3)	10.2(3)	0.1(2)	3.0(2)	-0.4(2)
F1	29.8(9)	31.5(9)	21.6(8)	-13.4(7)	13.7(7)	-3.2(7)
C1	15.9(13)	8.5(12)	14.8(12)	-0.3(9)	6.9(10)	-1.7(10)
C2	16.5(13)	9.8(12)	17.8(12)	0.3(10)	6.6(10)	-1.0(10)
C3	18.1(13)	12.8(13)	24.5(14)	-1.8(10)	10.0(11)	-0.4(10)
C4	26.8(15)	14.7(13)	19.2(13)	-6.4(10)	13.4(12)	-7.6(11)
C5	17.9(13)	14.2(13)	15.5(12)	-1.7(10)	4.3(10)	-6.6(11)
C6	16.2(13)	9.9(12)	16.8(13)	0.2(10)	6.0(10)	-4.2(10)
C7	19.9(14)	22.3(15)	19.1(13)	-0.3(11)	3.6(11)	4.9(11)
C8	17.2(13)	17.6(14)	15.6(13)	-1.3(10)	3.1(10)	-1.3(11)
C9	13.9(12)	10.4(12)	14.0(12)	4.0(9)	3.5(10)	-1.5(10)
C10	16.1(13)	17.2(13)	15.0(12)	0.6(10)	5.0(10)	-0.7(11)
C11	15.6(13)	22.3(14)	18.6(13)	1.0(11)	-1.4(11)	-3.7(11)
C12	12.0(12)	19.6(14)	24.9(14)	6.1(11)	4.4(11)	1.5(11)
C13	18.1(13)	16.1(13)	20.4(13)	0.6(11)	10.7(11)	1.3(11)
C14	15.9(13)	13.5(12)	15.1(12)	-1.0(10)	3.7(10)	-2.4(10)
C15	16.9(13)	11.3(12)	9.9(11)	-1.5(9)	5.3(10)	0.8(10)
C16	15.2(13)	13.3(13)	16.4(12)	-1.7(10)	5.4(10)	-2.7(10)
C17	16.5(13)	16.3(13)	18.7(13)	0.2(10)	3.1(11)	2.1(11)
C18	26.2(15)	17.4(14)	16.7(13)	7.3(10)	7.6(11)	3.6(11)
C19	20.5(14)	18.3(14)	22.2(14)	5.7(11)	9.8(11)	-1.2(11)
C20	16.6(13)	17.7(13)	17.2(13)	0.6(11)	4.8(10)	-2.5(11)
C21	16.7(13)	7.2(12)	15.0(12)	1.7(9)	5.1(10)	0.6(10)
C22	16.3(13)	20.6(14)	16.4(13)	1.9(10)	5.9(11)	1.0(11)
C23	17.8(14)	21.4(14)	27.5(15)	4.3(11)	11.0(12)	0.7(11)
C24	29.3(15)	18.0(14)	23.0(14)	1.6(11)	18.9(12)	1.2(12)
C25	32.1(16)	15.6(13)	14.5(13)	-1.2(10)	8.7(11)	-4.6(12)
C26	17.1(13)	12.5(13)	16.1(12)	1.3(10)	4.3(10)	-3.0(10)

C27	16.1(12)	12.9(12)	6.6(11)	-0.9(9)	0.0(9)	2.3(10)
C28	16.7(13)	16.7(13)	10.3(12)	-2.7(10)	0.3(10)	0.1(10)
C29	16.5(13)	24.8(15)	15.7(13)	-3.9(11)	-2.6(11)	6.0(11)
C30	27.0(15)	21.8(15)	21.6(14)	-2.6(11)	-6.2(12)	11.2(12)
C31	37.4(17)	13.5(14)	21.1(14)	1.8(11)	-5.0(13)	2.8(12)
C32	20.0(13)	14.8(13)	15.3(12)	1.4(10)	-1.0(11)	-1.5(11)
C33	10.4(12)	12.6(12)	13.4(12)	-2.0(10)	6.0(10)	-1.4(10)
C34	11.2(12)	17.9(13)	11.8(12)	0.2(10)	4.9(10)	-0.4(10)
C35	11.5(12)	15.8(13)	14.6(12)	-4.1(10)	4.8(10)	-1.9(10)
C36	11.8(12)	12.5(12)	18.3(12)	-4.2(10)	6.0(10)	1.2(10)
C37	9.7(12)	17.7(13)	12.4(12)	-1.5(10)	2.5(10)	1.4(10)
C38	11.4(12)	12.9(12)	11.6(12)	1.3(9)	5.3(10)	0.7(10)
C39	13.5(12)	13.8(13)	16.5(12)	-1.3(10)	7.7(10)	-2.2(10)
C40	12.2(12)	20.0(14)	18.3(13)	-6.7(10)	7.7(10)	-5.3(10)
C41	9.5(12)	22.7(14)	16.5(13)	-2.8(10)	4.3(10)	2.0(10)
C42	11.4(12)	15.4(13)	13.2(12)	-0.1(10)	4.6(10)	2.9(10)
O1	39.5(13)	62.9(16)	32.4(12)	-14.4(11)	-2.1(10)	27.7(12)
C43	35.9(18)	33.7(18)	35.0(17)	8.1(14)	2.4(14)	9.5(15)
C44	87(3)	45(2)	40(2)	6.2(17)	24(2)	31(2)
C45	37.4(18)	40.0(19)	35.0(18)	-4.7(15)	7.6(15)	-3.7(15)
C46	98(3)	56(3)	30.4(19)	-2.9(18)	0(2)	43(2)

Table S53. Bond Lengths for **13**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	Ni1	2.3182(4)	C13	C14	1.372(3)
Ni1	P1	2.2957(7)	C15	C16	1.380(3)
Ni1	P2	2.1515(7)	C15	C20	1.375(3)
Ni1	C1	1.914(2)	C16	C17	1.371(3)
Fe1	C33	1.998(2)	C17	C18	1.364(4)
Fe1	C34	2.031(2)	C18	C19	1.368(4)
Fe1	C35	2.051(2)	C19	C20	1.373(4)
Fe1	C36	2.041(2)	C21	C22	1.373(3)
Fe1	C37	2.009(2)	C21	C26	1.379(3)
Fe1	C38	1.985(2)	C22	C23	1.376(4)
Fe1	C39	2.010(2)	C23	C24	1.367(4)
Fe1	C40	2.039(2)	C24	C25	1.375(4)
Fe1	C41	2.043(2)	C25	C26	1.363(4)
Fe1	C42	2.010(2)	C27	C28	1.378(3)
P1	C9	1.820(2)	C27	C32	1.379(3)
P1	C15	1.819(2)	C28	C29	1.370(3)
P1	C33	1.808(2)	C29	C30	1.359(4)
P2	C21	1.808(2)	C30	C31	1.372(4)

P2	C27	1.804(2)	C31	C32	1.369(4)
P2	C38	1.797(2)	C33	C34	1.419(3)
F1	C4	1.356(3)	C33	C37	1.422(3)
C1	C2	1.386(3)	C34	C35	1.401(3)
C1	C6	1.385(3)	C35	C36	1.401(3)
C2	C3	1.385(3)	C36	C37	1.402(3)
C2	C7	1.490(3)	C38	C39	1.417(3)
C3	C4	1.362(4)	C38	C42	1.422(3)
C4	C5	1.352(4)	C39	C40	1.407(3)
C5	C6	1.382(3)	C40	C41	1.401(4)
C6	C8	1.490(3)	C41	C42	1.404(3)
C9	C10	1.374(3)	O1	C43	1.398(4)
C9	C14	1.376(3)	O1	C46	1.397(4)
C10	C11	1.375(4)	C43	C44	1.482(5)
C11	C12	1.369(4)	C44	C45	1.471(5)
C12	C13	1.366(4)	C45	C46	1.453(5)

Table S54. Bond Angles for **13**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Br1	88.127(19)	C5	C6	C1	119.8(2)
P2	Ni1	Br1	172.84(2)	C5	C6	C8	118.3(2)
P2	Ni1	P1	98.96(2)	C10	C9	P1	121.77(19)
C1	Ni1	Br1	85.77(7)	C10	C9	C14	119.0(2)
C1	Ni1	P1	173.59(7)	C14	C9	P1	119.24(18)
C1	Ni1	P2	87.12(7)	C9	C10	C11	120.4(2)
C33	Fe1	C34	41.22(9)	C12	C11	C10	120.0(2)
C33	Fe1	C35	68.79(9)	C13	C12	C11	120.0(2)
C33	Fe1	C36	69.31(10)	C12	C13	C14	120.0(2)
C33	Fe1	C37	41.56(10)	C13	C14	C9	120.6(2)
C33	Fe1	C39	139.35(10)	C16	C15	P1	120.61(19)
C33	Fe1	C40	177.46(10)	C20	C15	P1	120.71(19)
C33	Fe1	C41	137.60(10)	C20	C15	C16	118.6(2)
C33	Fe1	C42	109.36(10)	C17	C16	C15	120.5(2)
C34	Fe1	C35	40.13(10)	C18	C17	C16	120.4(2)
C34	Fe1	C36	67.92(10)	C17	C18	C19	119.7(2)
C34	Fe1	C40	139.00(10)	C18	C19	C20	120.1(2)
C34	Fe1	C41	113.28(10)	C19	C20	C15	120.7(2)
C36	Fe1	C35	40.03(10)	C22	C21	P2	121.83(19)
C36	Fe1	C41	143.05(10)	C22	C21	C26	118.8(2)
C37	Fe1	C34	68.49(10)	C26	C21	P2	119.36(19)
C37	Fe1	C35	67.76(10)	C21	C22	C23	120.7(2)
C37	Fe1	C36	40.50(9)	C24	C23	C22	119.9(2)

C37	Fe1	C40	140.55(10)	C23	C24	C25	119.7(2)
C37	Fe1	C41	176.22(10)	C26	C25	C24	120.2(2)
C37	Fe1	C42	135.83(10)	C25	C26	C21	120.6(2)
C38	Fe1	C33	109.40(10)	C28	C27	P2	118.11(18)
C38	Fe1	C34	141.55(10)	C28	C27	C32	119.3(2)
C38	Fe1	C35	174.26(10)	C32	C27	P2	122.36(19)
C38	Fe1	C36	134.31(10)	C29	C28	C27	120.6(2)
C38	Fe1	C37	107.15(10)	C30	C29	C28	119.6(3)
C38	Fe1	C39	41.54(10)	C29	C30	C31	120.5(3)
C38	Fe1	C40	69.07(10)	C32	C31	C30	120.2(3)
C38	Fe1	C41	69.32(10)	C31	C32	C27	119.7(3)
C38	Fe1	C42	41.69(9)	P1	C33	Fe1	120.12(12)
C39	Fe1	C34	176.56(10)	C34	C33	Fe1	70.63(13)
C39	Fe1	C35	136.59(10)	C34	C33	P1	128.66(18)
C39	Fe1	C36	108.80(10)	C34	C33	C37	106.4(2)
C39	Fe1	C37	109.86(10)	C37	C33	Fe1	69.64(13)
C39	Fe1	C40	40.66(10)	C37	C33	P1	124.73(18)
C39	Fe1	C41	68.56(10)	C33	C34	Fe1	68.15(13)
C39	Fe1	C42	69.28(10)	C35	C34	Fe1	70.70(14)
C40	Fe1	C35	112.93(10)	C35	C34	C33	108.5(2)
C40	Fe1	C36	113.23(10)	C34	C35	Fe1	69.16(14)
C40	Fe1	C41	40.16(10)	C34	C35	C36	108.6(2)
C41	Fe1	C35	115.84(10)	C36	C35	Fe1	69.59(14)
C42	Fe1	C34	114.07(10)	C35	C36	Fe1	70.38(14)
C42	Fe1	C35	143.91(10)	C35	C36	C37	107.7(2)
C42	Fe1	C36	175.58(9)	C37	C36	Fe1	68.54(14)
C42	Fe1	C40	68.13(10)	C33	C37	Fe1	68.80(13)
C42	Fe1	C41	40.54(10)	C36	C37	Fe1	70.96(14)
C9	P1	Ni1	113.94(8)	C36	C37	C33	108.8(2)
C15	P1	Ni1	111.28(8)	P2	C38	Fe1	124.06(13)
C15	P1	C9	102.58(11)	C39	C38	Fe1	70.15(14)
C33	P1	Ni1	124.34(8)	C39	C38	P2	129.97(18)
C33	P1	C9	100.14(11)	C39	C38	C42	107.2(2)
C33	P1	C15	101.82(11)	C42	C38	Fe1	70.08(13)
C21	P2	Ni1	121.81(8)	C42	C38	P2	122.83(18)
C27	P2	Ni1	109.63(8)	C38	C39	Fe1	68.31(13)
C27	P2	C21	102.34(11)	C40	C39	Fe1	70.80(14)
C38	P2	Ni1	113.29(8)	C40	C39	C38	107.8(2)
C38	P2	C21	102.02(11)	C39	C40	Fe1	68.55(14)
C38	P2	C27	106.28(11)	C41	C40	Fe1	70.07(14)
C2	C1	Ni1	119.21(18)	C41	C40	C39	108.8(2)
C6	C1	Ni1	120.99(18)	C40	C41	Fe1	69.78(14)

C6	C1	C2	119.7(2)	C40	C41	C42	107.9(2)
C1	C2	C7	121.1(2)	C42	C41	Fe1	68.46(14)
C3	C2	C1	120.1(2)	C38	C42	Fe1	68.23(13)
C3	C2	C7	118.8(2)	C41	C42	Fe1	71.00(14)
C4	C3	C2	118.3(2)	C41	C42	C38	108.3(2)
F1	C4	C3	118.3(2)	C46	O1	C43	107.8(3)
C5	C4	F1	118.6(2)	O1	C43	C44	106.3(3)
C5	C4	C3	123.1(2)	C45	C44	C43	105.0(3)
C4	C5	C6	119.0(2)	C46	C45	C44	105.2(3)
C1	C6	C8	121.9(2)	O1	C46	C45	109.4(3)

*X-ray Diffraction Data for (dppf)Ni(mesityl)(Br) (**14**)*

Crystals suitable for X-ray diffraction were grown from a concentrated solution of **14** in dichloromethane layered with hexanes at -15 °C. Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of **14**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software.[10] The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] The crystal chosen for data collection was twinned; as such, the reflections were integrated accounting for an approximately 11% contribution from a twin model. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The molecule of dichloromethane appearing in the asymmetric unit was disordered and was modelled by splitting the positions of the chlorines in the molecule, with each chlorine at half occupancy. Three reflections were omitted in which the Error/esd value was abnormally high. These reflections were located close to the beamstop. The full numbering scheme of compound **14** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1860572 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S55. Crystal data and structure refinement for **14**.

Empirical formula	$C_{44}H_{41}BrCl_2FeNiP_2$

Formula weight	897.08
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.4429(10)
b/Å	9.3655(3)
c/Å	18.4857(8)
α/°	90
β/°	106.677(5)
γ/°	90
Volume/Å^3	3722.1(3)
Z	4
ρ_{calc}g/cm^3	1.601
μ/mm^{-1}	2.232
F(000)	1832.0
Crystal size/mm^3	0.200 × 0.100 × 0.080
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.03 to 50.152
Index ranges	$-26 \leq h \leq 26$, $-11 \leq k \leq 11$, $-20 \leq l \leq 22$
Reflections collected	6561
Independent reflections	6561 [R_{int} = 0.1355, R_{sigma} = 0.0522]
Data/restraints/parameters	6561/0/483
Goodness-of-fit on F^2	1.174

Table S56. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **14**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	7572.8(3)	-480.9(6)	7526.2(4)	17.06(16)
Ni1	7195.8(3)	1777.1(8)	7100.7(4)	11.10(18)
Fe1	7907.0(4)	5391.8(9)	6226.6(5)	12.7(2)
P1	8182.0(7)	2557.9(17)	7380.1(8)	12.0(3)
P2	6705.8(7)	3703.7(16)	6639.4(8)	11.7(3)
C1	6391(3)	961(6)	6950(3)	12.2(12)
C2	6098(3)	343(6)	6263(3)	15.2(13)
C3	5505(3)	-194(6)	6127(3)	15.4(13)
C4	5190(3)	-152(6)	6664(3)	15.9(13)
C5	5504(3)	387(6)	7365(3)	16.2(13)
C6	6099(3)	919(7)	7521(3)	15.4(13)
C7	6427(3)	229(7)	5664(3)	18.2(13)
C8	4550(3)	-741(8)	6511(4)	25.2(15)
C9	6433(3)	1379(7)	8315(3)	17.5(13)

C10	8650(3)	1351(6)	7004(3)	16.4(13)
C11	9263(3)	1062(7)	7365(4)	20.9(14)
C12	9597(3)	131(8)	7043(4)	24.2(15)
C13	9319(3)	-498(7)	6369(4)	23.2(15)
C14	8703(3)	-197(7)	6003(4)	22.4(15)
C15	8370(3)	707(7)	6317(3)	17.5(13)
C16	8563(3)	2644(7)	8391(3)	15.3(13)
C17	9099(3)	3430(7)	8674(4)	20.2(14)
C18	9377(3)	3507(8)	9437(4)	22.8(15)
C19	9116(3)	2830(7)	9925(4)	22.1(15)
C20	8571(3)	2084(8)	9648(4)	25.9(16)
C21	8297(3)	1990(7)	8893(4)	21.8(14)
C22	6674(3)	4958(6)	7365(3)	14.7(13)
C23	7084(3)	4812(7)	8086(3)	15.5(13)
C24	7097(3)	5818(7)	8629(4)	21.7(14)
C25	6713(3)	6975(7)	8466(4)	21.5(14)
C26	6307(3)	7142(7)	7755(4)	18.3(14)
C27	6290(3)	6139(7)	7211(3)	16.2(13)
C28	5902(3)	3587(6)	6074(3)	13.7(12)
C29	5429(3)	3485(6)	6414(3)	14.8(13)
C30	4828(3)	3285(7)	5989(4)	17.8(13)
C31	4679(3)	3181(7)	5216(4)	20.4(14)
C32	5146(3)	3299(7)	4874(4)	20.5(14)
C33	5750(3)	3492(6)	5295(3)	16.5(13)
C34	8425(3)	4237(7)	7098(3)	14.3(13)
C35	8303(3)	5614(6)	7343(4)	17.8(13)
C36	8544(3)	6648(7)	6954(4)	20.3(14)
C37	8826(3)	5933(7)	6476(4)	18.9(14)
C38	8756(3)	4451(7)	6555(3)	14.8(13)
C39	7025(3)	4746(6)	6029(3)	13.8(12)
C40	7049(3)	6273(6)	5988(3)	14.7(13)
C41	7325(3)	6624(7)	5423(3)	18.7(14)
C42	7467(3)	5374(7)	5102(4)	19.4(14)
C43	7288(3)	4208(7)	5462(3)	14.6(13)
Cl1A	9596.6(17)	7669(5)	8541(2)	38.9(9)
Cl1B	9734(2)	9716(5)	9262(3)	49.2(11)
Cl2A	8841(6)	7920(12)	9536(7)	52(3)
Cl2B	8889(7)	7451(15)	9388(8)	101(5)
C44	9129(4)	8696(11)	8844(5)	49(2)

Table S57. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **14**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	15.3(3)	13.1(3)	23.2(3)	3.5(3)	6.2(3)	1.7(2)
Ni1	10.9(4)	10.6(4)	11.9(4)	1.1(3)	3.4(3)	0.6(3)
Fe1	13.6(4)	13.0(4)	12.0(4)	1.6(4)	4.3(3)	-0.1(3)
P1	11.8(7)	12.5(8)	12.0(7)	1.2(6)	3.8(6)	1.5(6)
P2	12.0(7)	12.3(8)	10.7(7)	0.0(6)	3.4(6)	0.4(6)
C1	14(3)	9(3)	12(3)	2(2)	3(2)	2(2)
C2	17(3)	10(3)	20(3)	4(2)	8(3)	3(2)
C3	18(3)	14(3)	12(3)	-1(2)	1(2)	0(3)
C4	17(3)	14(3)	18(3)	2(3)	6(3)	-3(2)
C5	18(3)	15(3)	17(3)	3(3)	7(3)	3(3)
C6	15(3)	15(3)	13(3)	2(2)	0(2)	3(2)
C7	21(3)	20(3)	16(3)	-4(3)	9(3)	-3(3)
C8	18(3)	32(4)	27(4)	-6(3)	9(3)	-9(3)
C9	15(3)	22(3)	17(3)	2(3)	6(3)	0(3)
C10	22(3)	12(3)	20(3)	1(3)	14(3)	-3(3)
C11	18(3)	23(4)	21(3)	0(3)	6(3)	4(3)
C12	13(3)	30(4)	33(4)	-1(3)	12(3)	3(3)
C13	22(3)	20(3)	35(4)	-2(3)	19(3)	1(3)
C14	27(4)	23(4)	18(3)	-4(3)	9(3)	-8(3)
C15	15(3)	19(3)	17(3)	1(3)	3(3)	-1(3)
C16	14(3)	20(3)	15(3)	-1(3)	8(2)	5(3)
C17	21(3)	24(4)	17(3)	0(3)	9(3)	-2(3)
C18	20(3)	32(4)	15(3)	-4(3)	2(3)	-6(3)
C19	22(3)	27(4)	16(3)	-2(3)	3(3)	2(3)
C20	34(4)	28(4)	17(3)	4(3)	11(3)	-3(3)
C21	20(3)	24(4)	20(3)	1(3)	5(3)	1(3)
C22	15(3)	12(3)	20(3)	-1(2)	8(3)	-6(2)
C23	10(3)	19(3)	17(3)	1(3)	4(2)	0(2)
C24	21(3)	29(4)	14(3)	-6(3)	2(3)	-9(3)
C25	21(3)	24(4)	21(3)	-7(3)	9(3)	-3(3)
C26	19(3)	15(3)	22(3)	0(3)	9(3)	0(3)
C27	14(3)	18(3)	16(3)	3(3)	3(2)	0(2)
C28	16(3)	10(3)	13(3)	0(2)	1(2)	-2(2)
C29	17(3)	12(3)	16(3)	-1(2)	5(3)	2(2)
C30	16(3)	13(3)	25(3)	-1(3)	6(3)	1(3)
C31	17(3)	12(3)	27(4)	-1(3)	-3(3)	-1(3)
C32	25(4)	16(3)	17(3)	-3(3)	0(3)	0(3)
C33	21(3)	10(3)	21(3)	0(3)	10(3)	1(3)
C34	8(3)	17(3)	15(3)	0(2)	0(2)	-3(2)

C35	18(3)	14(3)	18(3)	-2(3)	0(3)	-5(3)
C36	21(3)	17(3)	21(3)	1(3)	2(3)	-5(3)
C37	16(3)	21(3)	19(3)	2(3)	3(3)	-6(3)
C38	14(3)	20(3)	11(3)	2(3)	6(2)	1(3)
C39	13(3)	13(3)	13(3)	2(2)	1(2)	6(2)
C40	12(3)	12(3)	16(3)	1(2)	-1(2)	-2(2)
C41	17(3)	18(3)	21(3)	6(3)	6(3)	5(3)
C42	18(3)	23(3)	16(3)	2(3)	3(3)	-1(3)
C43	13(3)	16(3)	16(3)	-3(2)	5(2)	0(2)
Cl1A	24.4(18)	60(3)	27.9(19)	-3.7(18)	-0.2(15)	13.8(18)
Cl1B	43(2)	41(2)	51(3)	4(2)	-7(2)	5.5(19)
Cl2A	58(4)	63(5)	49(5)	22(4)	37(4)	15(4)
Cl2B	100(10)	115(11)	62(7)	45(7)	-18(5)	-49(7)
C44	53(6)	54(6)	39(5)	18(4)	10(4)	3(5)

Table S58. Bond Lengths for **14**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3291(9)	C14	C15	1.366(9)
Ni1	C1	1.906(6)	C16	C17	1.379(9)
Ni1	P2	2.1573(17)	C16	C21	1.382(9)
Ni1	P1	2.2460(17)	C17	C18	1.371(9)
Fe1	C39	2.001(6)	C18	C19	1.364(9)
Fe1	C43	2.008(6)	C19	C20	1.374(9)
Fe1	C34	2.010(6)	C20	C21	1.357(9)
Fe1	C35	2.010(6)	C22	C27	1.381(9)
Fe1	C40	2.024(6)	C22	C23	1.393(8)
Fe1	C38	2.027(6)	C23	C24	1.370(9)
Fe1	C42	2.029(6)	C24	C25	1.364(10)
Fe1	C41	2.032(6)	C25	C26	1.376(9)
Fe1	C36	2.033(6)	C26	C27	1.368(9)
Fe1	C37	2.043(6)	C28	C33	1.383(8)
P1	C34	1.791(6)	C28	C29	1.384(8)
P1	C10	1.811(6)	C29	C30	1.366(8)
P1	C16	1.819(6)	C30	C31	1.376(9)
P2	C39	1.789(6)	C31	C32	1.375(9)
P2	C22	1.799(6)	C32	C33	1.367(9)
P2	C28	1.810(6)	C34	C35	1.419(9)
C1	C2	1.378(8)	C34	C38	1.423(8)
C1	C6	1.394(8)	C35	C36	1.404(9)
C2	C3	1.376(8)	C36	C37	1.395(9)
C2	C7	1.501(8)	C37	C38	1.410(9)
C3	C4	1.375(8)	C39	C40	1.434(8)

C4	C5	1.380(9)	C39	C43	1.435(8)
C4	C8	1.489(8)	C40	C41	1.398(9)
C5	C6	1.377(9)	C41	C42	1.389(9)
C6	C9	1.505(8)	C42	C43	1.396(9)
C10	C11	1.374(9)	Cl1A	C44	1.636(10)
C10	C15	1.383(9)	Cl1B	C44	1.658(11)
C11	C12	1.390(9)	Cl2A	C44	1.748(14)
C12	C13	1.357(10)	Cl2B	C44	1.724(17)
C13	C14	1.382(9)			

Table S59. Bond Angles for **14**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Ni1	P2	85.61(18)	C5	C6	C1	119.3(6)
C1	Ni1	P1	173.65(18)	C5	C6	C9	119.3(5)
P2	Ni1	P1	100.11(6)	C1	C6	C9	121.3(5)
C1	Ni1	Br1	85.56(17)	C11	C10	C15	119.2(6)
P2	Ni1	Br1	170.92(6)	C11	C10	P1	123.1(5)
P1	Ni1	Br1	88.82(5)	C15	C10	P1	117.7(5)
C39	Fe1	C43	41.9(2)	C10	C11	C12	120.2(6)
C39	Fe1	C34	107.3(2)	C13	C12	C11	120.3(6)
C43	Fe1	C34	113.0(2)	C12	C13	C14	119.5(6)
C39	Fe1	C35	110.0(2)	C15	C14	C13	120.7(6)
C43	Fe1	C35	142.5(2)	C14	C15	C10	120.1(6)
C34	Fe1	C35	41.3(2)	C17	C16	C21	118.6(6)
C39	Fe1	C40	41.7(2)	C17	C16	P1	121.0(5)
C43	Fe1	C40	69.4(2)	C21	C16	P1	120.3(5)
C34	Fe1	C40	133.6(2)	C18	C17	C16	120.5(6)
C35	Fe1	C40	107.1(3)	C19	C18	C17	120.1(6)
C39	Fe1	C38	135.9(2)	C18	C19	C20	119.7(6)
C43	Fe1	C38	111.8(2)	C21	C20	C19	120.6(6)
C34	Fe1	C38	41.3(2)	C20	C21	C16	120.5(6)
C35	Fe1	C38	68.7(3)	C27	C22	C23	118.5(6)
C40	Fe1	C38	174.8(2)	C27	C22	P2	121.7(5)
C39	Fe1	C42	69.2(2)	C23	C22	P2	119.5(5)
C43	Fe1	C42	40.5(2)	C24	C23	C22	120.2(6)
C34	Fe1	C42	144.7(3)	C25	C24	C23	120.3(6)
C35	Fe1	C42	173.9(3)	C24	C25	C26	120.3(6)
C40	Fe1	C42	68.1(3)	C27	C26	C25	119.7(6)
C38	Fe1	C42	116.3(2)	C26	C27	C22	121.0(6)
C39	Fe1	C41	69.2(2)	C33	C28	C29	118.4(6)
C43	Fe1	C41	68.2(3)	C33	C28	P2	120.9(5)
C34	Fe1	C41	173.6(2)	C29	C28	P2	120.5(4)

C35	Fe1	C41	133.9(3)	C30	C29	C28	120.6(6)
C40	Fe1	C41	40.3(2)	C29	C30	C31	120.8(6)
C38	Fe1	C41	144.8(2)	C32	C31	C30	118.9(6)
C42	Fe1	C41	40.0(3)	C33	C32	C31	120.6(6)
C39	Fe1	C36	140.1(3)	C32	C33	C28	120.7(6)
C43	Fe1	C36	176.9(3)	C35	C34	C38	106.5(5)
C34	Fe1	C36	69.3(2)	C35	C34	P1	127.1(5)
C35	Fe1	C36	40.6(2)	C38	C34	P1	126.4(5)
C40	Fe1	C36	110.7(3)	C35	C34	Fe1	69.3(4)
C38	Fe1	C36	68.4(3)	C38	C34	Fe1	70.0(3)
C42	Fe1	C36	136.5(3)	P1	C34	Fe1	123.5(3)
C41	Fe1	C36	109.7(3)	C36	C35	C34	109.0(6)
C39	Fe1	C37	176.1(3)	C36	C35	Fe1	70.6(4)
C43	Fe1	C37	138.2(2)	C34	C35	Fe1	69.3(3)
C34	Fe1	C37	68.8(2)	C37	C36	C35	107.7(6)
C35	Fe1	C37	67.8(3)	C37	C36	Fe1	70.4(4)
C40	Fe1	C37	141.6(3)	C35	C36	Fe1	68.8(4)
C38	Fe1	C37	40.5(2)	C36	C37	C38	108.8(6)
C42	Fe1	C37	113.3(3)	C36	C37	Fe1	69.6(4)
C41	Fe1	C37	114.8(3)	C38	C37	Fe1	69.1(3)
C36	Fe1	C37	40.0(3)	C37	C38	C34	107.9(5)
C34	P1	C10	100.2(3)	C37	C38	Fe1	70.4(4)
C34	P1	C16	99.6(3)	C34	C38	Fe1	68.7(3)
C10	P1	C16	105.6(3)	C40	C39	C43	106.3(5)
C34	P1	Ni1	125.6(2)	C40	C39	P2	127.3(5)
C10	P1	Ni1	110.5(2)	C43	C39	P2	126.3(5)
C16	P1	Ni1	113.1(2)	C40	C39	Fe1	70.0(3)
C39	P2	C22	102.9(3)	C43	C39	Fe1	69.3(3)
C39	P2	C28	100.4(3)	P2	C39	Fe1	127.2(3)
C22	P2	C28	102.9(3)	C41	C40	C39	107.8(6)
C39	P2	Ni1	117.0(2)	C41	C40	Fe1	70.2(4)
C22	P2	Ni1	112.1(2)	C39	C40	Fe1	68.3(3)
C28	P2	Ni1	119.2(2)	C42	C41	C40	109.0(6)
C2	C1	C6	118.8(5)	C42	C41	Fe1	69.9(4)
C2	C1	Ni1	119.0(4)	C40	C41	Fe1	69.5(3)
C6	C1	Ni1	122.1(4)	C41	C42	C43	108.9(6)
C3	C2	C1	120.2(6)	C41	C42	Fe1	70.1(4)
C3	C2	C7	119.5(6)	C43	C42	Fe1	69.0(3)
C1	C2	C7	120.2(5)	C42	C43	C39	108.0(5)
C4	C3	C2	121.9(6)	C42	C43	Fe1	70.6(4)
C3	C4	C5	117.3(6)	C39	C43	Fe1	68.8(3)
C3	C4	C8	121.4(6)	Cl1B	C44	Cl2B	118.0(7)

C5	C4	C8	121.2(6)	Cl1A	C44	Cl2A	114.5(6)
C6	C5	C4	122.2(6)				

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