Electronic Supplementary Material (ESI) for Dalton Transactions.

Substituent Effects in Pyridyl-Functionalized λ^3,σ^2-Phosphinines: A Fundamental and Systematic Study

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Supporting Information

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General Information:

The numbering of atoms in molecular structures in the crystal and NMR data is as shown in Figure S1.

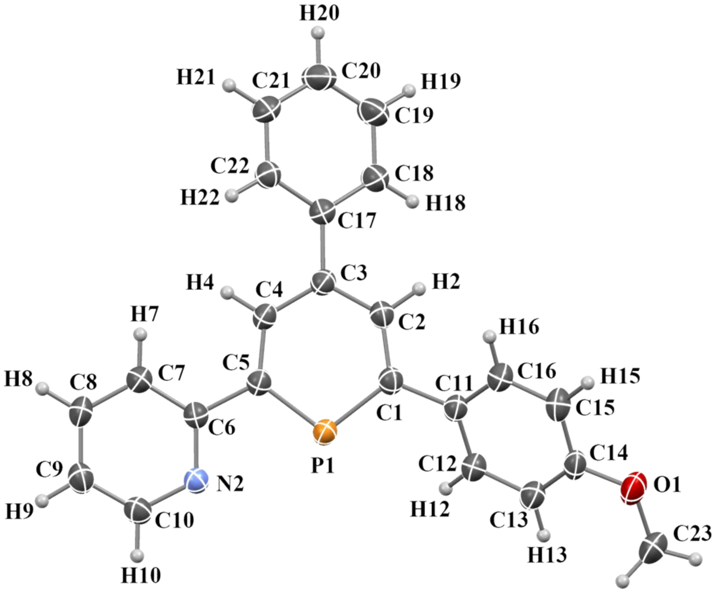

Figure S1: Numbering of the atoms.

Experimental Section

Experiments performed under an inert argon atmosphere were carried out using modified Schlenk techniques or in a MBraun dry box. All common chemicals were commercially available and purchased from Aldrich Chemical Co., ABCR, Alfa Aesar, Acros as well as Eurisol and were used as received. The synthesis and characterization of compounds **1-5a**, **1-4b,c,e** was already reported by us recently.[1-3] 1-phenyl-3-(4-fluorophenyl)prop-2-en-1-one, 1-phenyl-3-(4-trifluoromethyl-phenyl)prop-2-en-1-one, 1-phenyl-3-(4-methoxyphenyl)prop-2-en-1-one, 1-phenyl-3-(4-methylthiophenyl)prop-2-en-1-one, 1-(4-fluorophenyl)-3-phenylprop-2-en-1-one, 1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one, 1-(4-methylthiophenyl)-3-phenylprop-2-en-1-one (Chalcones)[1,2,4] and Tristrimethylsilylphosphane[5] were prepared according to the literature. For reactions under UV radiation a Philips HPK 125W high-pressure mercury vapor lamp was used. Dry or deoxygenated solvents were prepared using standard techniques or used from a MBraun MB SBS-800 solvent purification system. Tetrahydrofuran and diethyl ether were distilled under argon over potassium/benzophenone and sodium/benzophenone, respectively. For column chromatography silica 60M by Macherey-Nagel was used as stationary phase. The ^{1}H, ^{13}C{1H}, ^{19}F and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL EXZ400 (400 MHz), a JEOL ECX400 (400 MHz), a JEOL ECP500 (500 MHz), a Bruker AVANCE III 500 (500 MHz) or a Bruker AVANCE III 700 (700 MHz) FT spectrometer and chemical shifts are reported relative to the residual resonance of the deuterated solvents. The mass characterizations have been performed on an Agilent 6210 ESI-TOF instrument by Agilent Technologies with standard settings of 5 L/min, 4 kV and 15 psi for ESI-TOF and on a MAT 711 by Varian MAT with an electron energy of 0.8 mA for EI-MS. All other parameters have been optimized for each substance. IR spectra were measured on a Nicolet iS10 FTIR-ATR spectrometer by Thermo Scientific, UV-Vis spectra on a Cary 300 UV-Vis and fluorescence spectra on a Cary Eclipse spectrometer both by Agilent Technologies. Elemental analyses were performed with a vario MACRO cube by Elementar. Density Functional Theory (DFT) calculations were carried out at the B3LYP/6-311+G(d,p) level of theory with the Gaussian 09 program.[6] Full geometry optimization without any symmetry constraints was performed prior to the analysis of the electronic structure of the different phosphinine ligands. The nature of the stationary points was evaluated from the analytically computed harmonic modes. No imaginary frequencies were found for the optimized structures confirming that these correspond to local minima on the potential energy surface.

Diketones:

The respective chalcone (1 eq.), 2-acetylpyridine (1 eq.) and NaOH (1 eq.) were mixed with mortar and pestle until after around 10 min a sticky mixture was formed. The product was then recrystallized from water/ethanol 1:2.

3-(4-Methoxyphenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione: 1-Phenyl-3-(4-methoxyphenyl)-prop-2-en-1-one (6.0 g, 25 mmol), 2-acetylpyridine (2.9 mL, 3.1 g, 25 mmol) and NaOH (1.0 g, 25 mmol) gave the product (8.0 g, 22 mmol, 88%) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (dd, *J* = 16.5, 7.5 Hz, 1 H, H2), 3.43 (dd, *J* = 16.5, 6.8 Hz, 1 H, H2’), 3.60 (dd, *J* = 17.5, 6.8

Hz, 1 H, H4), 3.74 (dd, *J* = 17.5, 7.5 Hz, 1 H, H4'), 3.74 (s, 3 H, OMe), 4.08 (quin, *J* = 7.1 Hz, 1 H, H3), 6.80 (ms, 2 H, H19/21), 7.22 – 7.27 (m, 2 H, H18/22), 7.40 – 7.46 (m, 3 H, H9, H13/15), 7.50 – 7.56 (m, 1 H, H14), 7.79 (ddd, *J* = 7.8, 7.7, 1.7 Hz, 1 H, H8), 7.90 – 7.94 (m, 2 H, H12/16), 7.97 (ddd, *J* = 7.9, 1.1, 1.1 Hz, 1 H, H7), 8.64 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1 H, H10) ppm; ^{13}C{1H} NMR (101 MHz, CDCl3): δ = 36.0 (C3), 44.2 (C4), 45.6 (C2), 55.3 (OMe), 114.0 (C19/21), 121.9 (C7), 127.2 (C9), 128.2 (C12/16), 128.6 (C13/15 or C18/22), 128.6 (C13/15 or C18/22), 133.1 (C14), 136.4 (C17), 137.0 (C8), 137.1 (C11), 149.0 (C10), 153.5 (C6), 158.2 (C20), 198.0 (C1), 200.2 (C5) ppm; ESI-TOF (m/z): 382.1442 g/mol (calc.: 382.1414 g/mol) [M + Na]+; elemental analysis calc (%) for $C_{23}H_{21}NO_3$ (359.42 g/mol): C 76.86, H 5.89, N 3.90; found: C 76.60, H 5.87, N 3.62.

1-(4-Fluorophenyl)-3-phenyl-5-(2-pyridyl)pentane-1,5-dione: 1-(4-Fluorophenyl)-3-phenylprop-2-en-1-one (5.0 g, 22 mmol), 2-acetyl-pyridine (2.5 mL, 2.7 g, 22 mmol) and NaOH (0.9 g, 22 mmol) gave the product (3.4 g, 10 mmol, 44%) as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.32 (dd, *J* = 16.5, 7.5 Hz, 1 H, H2), 3.44 (dd, *J* = 16.5, 6.8 Hz, 1 H, H2'), 3.65 (dd, *J* = 17.7, 7.0 Hz, 1 H, H4), 3.76 (dd, *J* = 17.7, 7.1 Hz, 1 H, H4'), 4.10 (quin, *J* = 7.1 Hz, 1 H, H3), 7.09 (ms, 2 H, H13/15), 7.13 – 7.18 (m, 1 H, H20), 7.23 – 7.28 (m, 2 H, H19/21), 7.30 – 7.35 (m, 2 H, H18/22), 7.43 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1 H, H9), 7.78 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1 H, H8), 7.92 – 7.99 (m, 3 H, H7, H12/16), 8.64 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1 H, H10) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.4 (ms) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 36.8 (C3), 44.0 (C4), 45.2 (C2), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, C13/15), 121.9 (C7), 126.7 (C20), 127.3 (C9), 127.6 (C18/22), 128.6 (C19/21), 130.8 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz, C12/16), 133.5 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C11), 137.0 (C8), 144.2 (C17), 148.9 (C10), 153.3 (C6), 165.7 (d, $^{1}J_{C\text{-}F}$ = 254.5 Hz, C14), 197.1 (C1), 200.0 (C5) ppm; ESI-TOF (m/z): 348.1396 g/mol (calc.: 348.1400 g/mol) [M + H]+, 370.1256 g/mol (calc.: 370.1219 g/mol) [M + Na]+; elemental analysis calc (%) for $C_{22}H_{18}FNO_2$ (347.38 g/mol): C 76.06, H 5.22, N 4.03; found: C 75.99, H 5.28, N 3.74.

1-(4-Methoxyphenyl)-3-phenyl-5-(2-pyridyl)pentane-1,5-dione: 1-(4-Methoxy-phenyl)-3-phenyl-prop-2-en-1-one (6.5 g, 27 mmol), 2-acetylpyridine (3.1 mL, 3.2 g, 27 mmol) and NaOH (1.1 g, 27 mmol) gave the product (7.4 g, 21 mmol, 76%) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (dd, *J* = 16.4, 7.2 Hz, 1 H, H2), 3.41 (dd, *J* = 16.4, 7.1 Hz, 1 H, H2'), 3.63 (dd, *J* = 17.7, 6.7 Hz, 1 H, H4), 3.77 (dd, *J* = 17.7, 7.5 Hz, 1 H, H4'), 3.85 (s, 3 H, OMe), 4.11 (quin, *J* = 7.1 Hz, 1 H, H3), 6.90 (ms, 2 H, H13/15), 7.12 – 7.18 (m, 1 H, H20), 7.23 – 7.28 (m, 2 H, H19/21), 7.31 – 7.35 (m, 2 H, H18/22), 7.44 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1 H, H9), 7.79 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1 H, H8), 7.87 – 7.94 (m, 2 H, H12/16), 7.97 (ddd, J = 7.9, 1.1, 1.1 Hz, 1 H, H7), 7.64 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 36.8 (C3), 44.0 (C4), 45.0 (C2), 55.5 (OMe), 113.7 (C13/15), 121.9 (C7), 126.5 (C20), 127.2 (C9), 127.7 (C18/22), 128.6 (C19/21), 130.2 (C11), 130.5 (C12/16), 137.0 (C8), 144.5 (C17), 148.9 (C10), 153.4 (C6), 163.4 (C14), 197.2 (C1), 200.1 (C5) ppm; ESI-TOF (m/z): 382.1418 g/mol (calc.: 382.1414 g/mol) [M + Na]+; elemental analysis calc (%) for $C_{23}H_{21}NO_3$ (359.42 g/mol): C 76.86, H 5.89, N 3.90; found: C 76.93, H 5.93, N 3.77.

1-(4-Methylthiophenyl)-3-phenyl-5-(2-pyridyl)pentane-1,5-dione: 1-(4-Methylthio-phenyl)-3-phenyl-prop-2-en-1-one (7.0 g, 28 mmol), 2-acetylpyridine (3.2 mL, 3.5 g, 29 mmol) and NaOH (1.1 g, 28 mmol) gave the product (8.3 g, 22 mmol, 80%) as a pale yellow solid. ^{1}H NMR (400

MHz, $CDCl_3$): δ = 2.51 (s, 3 H, SMe), 3.30 (dd, *J* = 16.4, 7.3 Hz, 1 H, H2), 3.42 (dd, *J* = 16.4, 7.0 Hz, 1 H, H2'), 3.63 (dd, *J* = 17.7, 6.8 Hz, 1 H, H4), 3.76 (dd, *J* = 17.7, 7.3 Hz, 1 H, H4'), 4.10 (quin, *J* = 7.0 Hz, 1 H, H3) 7.13 – 7.18 (m, 1 H, H20), 7.21 – 7.28 (m, 4 H, H13/15, H19/21), 7.30 – 7.35 (m, 2 H, H18/22), 7.44 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1 H, H9), 7.79 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1 H, H8), 7.82 – 7.86 (ms, 2 H, H12/16), 7.97 (ddd, *J* = 7.9, 1.1, 1.1 Hz, 1 H, H7), 8.64 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 14.9 (SMe), 36.8 (C3), 44.0 (C4), 45.1 (C2), 121.9 (C7), 125.0 (C13/15), 126.6 (C20), 127.2 (C9), 127.7 (C18/22), 128.6 (C19/21 or C12/16), 128.7 (C19/21 or C12/16), 133.4 (C11), 137.0 (C8), 144.3 (C17), 145.8 (C14), 149.0 (C10), 153.4 (C6), 197.7 (C1), 200.1 (C5) ppm; ESI-TOF (m/z): 398.1222 g/mol (calc.: 398.1185 g/mol) [M + Na]+; elemental analysis calc (%) for $C_{23}H_{21}NO_2S$ (375.48 g/mol): C 73.57, H 5.64, N 3.73, S 8.54; found: C 76.18, H 5.54, N 3.34, S 8.71.

Pyrylium salts:

Under Argon the respective diketone (1 eq.) was mixed with 1,3-diphenylprop-2-en-1-one (1 eq.) and boron trifluoride diethyl etherate (8 eq.) was added. The mixture was heated to T = 70°C for 3 h and then slowly dropped into 400 mL diethyl ether. The precipitate was filtered off, dried, and recrystallized from methanol.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylpyrylium tetra-fluoroborate (**1d**): Diketone d (4.0 g, 11 mmol), 1,3-diphenylprop-2-en-1-one (2.3 g, 11 mmol) and BF_3 etherate (11.0 mL, 12.7 g, 89 mmol) gave the product (0.450 g, 1 mmol, 9%) as orange crystals after washing with chloroform and recrystallizing from acetonitrile. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 4.04 (s, 3 H, OMe), 7.32 (ms, 2 H, H19/21), 7.75 – 7.92 (m, 4 H, H13/15, H9, H14), 8.27 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1 H, H8), 8.61 – 8.67 (m, 4 H, H12/16, H18/22), 8.73 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1 H, H7), 8.99 – 8.98 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1 H, H10), 9.14 (d, *J* = 1.9 Hz, 1 H, H4), 9.18 (d, *J* = 1.9 Hz, 1 H, H2) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = 151.3 (s, $^{10}BF_4^-$), -151.4 (s, $^{11}BF_4^-$) ppm; ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO/(CD_3)_2SO$): δ = 56.7 (OMe), 114.1 (C4), 115.1 (C2), 116.6 (C19/21), 124.7 (C7), 125.1 (C17), 129.0 (C9), 129.5 (C12/16), 129.9 (C11), 130.5 (C13/15), 133.9 (C18/22), 135.7 (C14), 139.1 (C8), 147.3 (C6), 151.6 (C10), 165.3 (C3), 167.4 (C20), 167.8 (C5), 170.5 (C1) ppm; ESI-TOF (m/z): 340.1337 g/mol (calc.: 340.1332 g/mol) [M]+; elemental analysis calc (%) for $C_{23}H_{18}BF_4NO_2$ (443,26 g/mol): C 64.66, H 4.25, N 3.28; found: C 64.77, H 4.24, N 3.00.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)pyrylium tetrafluoro-borate (**1f**): Diketone f (3.4 g, 10 mmol), 1,3-diphenylprop-2-en-1-one (2.0 g, 10 mmol) and BF_3 etherate (9.5 mL, 11.0 g, 77 mmol) gave the product (0.886 g, 2 mmol, 22%) as yellow crystals. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 7.61 (mS, 2 H, H13/15), 7.79 – 7.94 (m, 4 H, H19/21, H9, H20), 8.30 (ddd, *J* = 7.9, 7.8, 1.7 Hz, 1 H, H8), 8.55 – 8.59 (m, 2 H, H18/22), 8.81 – 8.86 (m, 3 H, H12/16, H7), 9.02 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1 H, H10), 9.32 (d, *J* = 1.8 Hz, 1 H, H2 or H4), 9.32 (d, *J* = 1.8 Hz, 1 H, H2 or H4) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = -102.2 (mS), -151.3 (s, $^{10}BF_4^-$), -151.4 (s, $^{11}BF_4^-$) ppm; ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$): δ = 116.4 (C2 or C4), 117.7 (C2 or C4), 118.3 (d, $^{2}J_{\text{C-F}}$ = 22.7 Hz, C13/15), 125.3 (C7), 126.7 (d, $^{4}J_{\text{C-F}}$ = 3.0 Hz, C11), 129.6 (C9), 130.8 (C18/22), 131.1 (C19/21), 133.3 (d, $^{3}J_{\text{C-F}}$ = 10.1 Hz, C12/16), 133.8 (C17), 136.5 (C20), 139.5 (C8), 147.4 (C6), 152.0 (C10), 167.9 (C3), 168.0 (d, $^{1}J_{\text{C F}}$ = 259.6 Hz, C14), 169.7 (C1 or C5), 171.6 (C1 or C5) ppm; ESI-TOF (m/z): 328.1159 g/mol (calc.: 328.1132 g/mol) [M]+; elemental analysis calc (%) for $C_{22}H_{15}BF_5NO$ (415,16 g/mol): C 63.65, H 3.64, N 3.37; found: C 63.61, H 3.72, N 3.21.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxy)phenylpyrylium tetra-fluoroborate (**1g**): Diketone g (5.3 g, 15 mmol), 1,3-diphenylprop-2-en-1-one (3.1 g, 15 mmol) and BF_3 etherate (17.0 mL, 19.6 g, 138 mmol) gave the product (2.812 g, 7 mmol, 45%) as orange crystals. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 4.05 (s, 3 H, OMe), 7.36 (ms, 2 H, H13/15), 7.77 – 7.92 (m, 4 H, H19/21, H9, H20), 8.28 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1 H, H8), 8.49 – 8.53 (m, 2 H, H18/22), 8.71 – 8.78 (m, 3 H, H12/16, H7), 9.00 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1 H, H10), 9.16 (d, *J* = 1.8 Hz, 1 H, H4), 9.18 (d, *J* = 1.8 Hz, 1 H, H2) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = -151.5 (s, $^{10}BF_4^-$), -151.6 (s, $^{11}BF_4^-$) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2CO$): δ = 56.7 (OMe), 115.2 (C4), 116.7 (C2), 116.7 (C13/15), 122.2 (C11), 124.8 (C7), 129.3 (C9), 130.5 (C18/22), 131.0 (C19/21), 132.9 (C12/16), 134.0 (C17), 136.0 (C20), 139.3 (C8), 147.6 (C6), 152.0 (C10), 166.5 (C3), 167.4 (C14), 168.3 (C5), 172.7 (C1) ppm; ESI-TOF (m/z): 340.1360 g/mol (calc.: 340.1332 g/mol) [M]+; elemental analysis calc (%) for $C_{23}H_{18}BF_4NO_2$ (427,20 g/mol): C 64.66, H 4.25, N 3.28; found: C 64.21, H 4.30, N 2.91.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyrylium tetra-fluoroborate (**1h**): Diketone h (3.2 g, 9 mmol), 1,3-diphenylprop-2-en-1-one (2.0 g, 10 mmol) and BF_3 etherate (9.6 mL, 11.0 g, 78 mmol) gave the product (1.451 g, 3 mmol, 38%) as dark red crystals. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 2.69 (s, 3 H, SMe), 7.65 (ms, 2 H, H13/15), 7.78 – 7.93 (m, 4 H, H19/21, H9, H20), 8.29 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1 H, H8), 8.50 – 8.55 (m, 2 H, H18/22), 8.63 (ms, 2 H, H12/16), 8.77 (ddd, *J* = 7.9, 1.0, 1.0 Hz, 1 H, H7), 9.01 (ddd, J = 4.7, 1.7, 0.9 Hz, 1 H, H10), 9.21 (d, *J* = 1.8 Hz, 1 H, H4), 9.24 (d, *J* = 1.8 Hz, 1 H, H2) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = -151.5 (s, $^{10}BF_4^-$), -151.5 (s, $^{11}BF_4^-$) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2CO/(CD_3)_2SO$): δ = 14.3 (SMe), 115.3 (C4), 116.8 (C2), 124.9 (C7), 125.3 (C11), 126.5 (C13/15), 129.1 (C9), 130.2 (C12/16), 130.5 (C18/22), 130.7 (C19/21), 133.5 (C17), 135.9 (C20), 139.2 (C8), 147.3 (C6), 151.7 (C10 or C14), 151.7 (C10 or C14), 166.1 (C3), 168.1 (C5), 171.8 (C1) ppm; ESI-TOF (m/z): 356.1139 g/mol (calc.: 356.1104 g/mol) [M]+; elemental analysis calc (%) for $C_{23}H_{18}BF_4NOS$ (443,26 g/mol): C 62.32, H 4.09, N 3.16, S 7.23; found: C 62.29, H 4.10, N 3.07, S 7.35.

Pyridylphosphinines

The respective pyrylium salt (1 eq.) was stirred under argon in dry acetonitrile. Tris(trimethylsilyl)phosphane (2 eq.) was added dropwise. The solution was then heated to T = 85°C for 6 h. After evaporation of the solvent the product was purified first by column chromatography (petrol ether: ethyl acetate = 20:1 to 5:1) and subsequently by recrystallization from acetonitrile.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylphosphinine (**2d**): Pyrylium salt 1d (3.5 g, 8 mmol) and tris(trimethylsilyl)phosphane (4.1 g, 16 mmol) in acetonitrile (20 mL) gave the product (0.560 g, 1.5 mmol, 19%) as a slightly yellow-orange solid. ^{1}H NMR (500 MHz, DCM-d_2): δ = 3.87 (s, 3 H, OMe), 7.05 (ms, 2 H, H19/21), 7.32 (dd, *J* = 7.4 Hz, 4.8 Hz, 1 H, H9), 7.42 – 7.46 (m, 1 H, H14), 7.48 – 7.53 (m, 2 H, H13/15), 7.71 (ms, 2 H, H18/22), 7.75 – 7.79 (m, 2 H, H12/16), 7.82 (ddd, *J* = 7.7 Hz, 7.7 Hz, 1.9 Hz, 1 H, H8), 8.02 (dd, *J* = 8.0 Hz, 1.1 Hz, 1 H, H7), 8.23 (dd, *J* = 5.9 Hz, 1.3 Hz, 1 H, H2), 8.69 (dd, *J* = 5.7 Hz, 1.3 Hz, 1 H, H4), 8.73 (ddd, *J* = 4.7 Hz, 1.9 Hz, 0.9 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (126 MHz, DCM-d$_2$): δ = 55.9 (OMe), 115.0 (d, $^{6}J_{\text{C-P}}$ = 2.8 Hz, C19/21), 121.7 (d, $^{3}J_{\text{C-P}}$ = 14.0 Hz, C7), 123.4 (C9), 128.2 (d, $^{3}J_{\text{C-P}}$ = 12.8 Hz, C12/16), 128.5 (C14), 129.4 (C18/22), 129.5 (C13/15), 131.8 (d, $^{2}J_{\text{C-P}}$ = 13.5 Hz, C4), 133.0 (d, $^{2}J_{\text{C-P}}$ = 11.7 Hz, C2), 134.9 (d, $^{4}J_{\text{C-P}}$ = 3.1 Hz, C17), 137.5 (C8), 144.2 (d, $^{2}J_{\text{C-P}}$ = 24.6 Hz, C11), 144.3 (d, $^{3}J_{\text{C-P}}$ = 13.4 Hz, C3), 150.4 (C10), 159.8 (d, $^{2}J_{\text{C-P}}$ = 24.6 Hz, C6), 160.5 (C20), 169.9 (d, $^{1}J_{\text{C-P}}$ = 49.7 Hz, C1 or C5), 172.1 (d, $^{1}J_{\text{C-P}}$ = 50.2 Hz, C1 or C5) ppm; ^{31}P{^{1}H} NMR (162 MHz, DCM-d$_2$) δ = 183.9 ppm; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ = 184.2 ppm; ESI-TOF (m/z): 356.1236 g/mol (calc.: 356.1199 g/mol) [M + H]+.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine (**2f**): Pyrylium salt **1f** (3.4 g, 10 mmol) and tris(trimethylsilyl)phosphane (5.1 g, 21 mmol) in acetonitrile (24 mL) gave the product (0.515 g, 1.5 mmol, 18%) as a slightly yellow-orange solid. ^{1}H NMR (400 MHz, THF-d$_8$): δ = 7.20 – 7.27 (m, 2 H, H13/15), 7.29 – 7.34 (m, 1 H, H9), 7.38 – 7.43 (m, 1 H, H20), 7.47 – 7.53 (m, 2 H, H19/21), 7.77 – 7.85 (m, 5 H, H18/22, H12/16, H8), 8.11 – 8.15 (m, 1 H, H7), 8.27 (dd, *J* = 5.9, 1.2 Hz, 1 H, H2), 8.69 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1 H, H10), 8.90 (dd, *J* = 5.8, 1.3 Hz, 1 H, H4) ppm; ^{19}F NMR (377 MHz, THF-d$_8$): δ = -116.3 (ms) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d$_8$): δ = 115.5 (d, $^{2}J_{\text{C-F}}$ = 21.7 Hz, C13/15), 120.8 (d, $^{3}J_{\text{C-P}}$ = 16.0 Hz, C7), 122.8 (C9), 127.6 (C18/22), 127.9 (C20), 128.8 (C19/21), 129.3 (dd, $^{3}J_{\text{C-F}}$ = 8.2 Hz, $^{3}J_{\text{C-P}}$ = 12.9 Hz, C12/16), 131.4 (d, $^{2}J_{\text{C-P}}$ = 13.0 Hz, C4), 132.5 (d, $^{2}J_{\text{C-P}}$ = 11.7 Hz, C2), 136.6 (C8), 140.0 (d, $^{2}J_{\text{C-P}}$ = 25.6 Hz, C11), 142.1 (d, $^{4}J_{\text{C-P}}$ = 3.3 Hz, C17), 144.3 (d, $^{2}J_{\text{C-P}}$ = 13.7 Hz, C6), 149.8 (C10), 158.8 (d, $^{3}J_{\text{C-P}}$ = 25.5 Hz, C3), 163.2 (d, $^{1}J_{\text{C-F}}$ = 248.9 Hz, C14), 169.5 (d, $^{1}J_{\text{C-P}}$ = 50.5 Hz, C1 or C5), 170.3 (d, $^{1}J_{\text{C-P}}$ = 51.1 Hz, C1 or C5) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$) δ = 186.3 (d, $^{6}J_{\text{P-F}}$ = 2.6 Hz) ppm; ESI-TOF (m/z): 344.1003 g/mol (calc.: 344.0999 g/mol) [M + H]+.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)phosphinine (**2g**): Pyrylium salt **1g** (4.4 g, 10 mmol) and tris(trimethylsilyl)phosphane (5.5 g, 22 mmol) in acetonitrile (30 mL) gave the product (0.282 g, 0.8 mmol, 8%) as a slightly yellow-orange solid. ^{1}H NMR (400 MHz, THF-d$_8$): δ = 3.84 (s, 3 H, OMe), 7.01 – 7.06 (m, 2 H, H13/15), 7.28 – 7.32 (m, 1 H, H9), 7.37 – 7.43 (m, 1 H, H20), 7.46 – 7.52 (m, 2 H, H19/21), 7.72 – 7.84 (m, 5 H, H12/16, H18/22, H8), 8.11 – 8.16 (m, 1 H, H7), 8.23 – 8.27 (m, 1 H, H2), 8.67 – 8.70 (m, 1 H, H10), 8.85 – 8.88 (m, 1 H, H4) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d8): δ = 55.6 (OMe), 115.2 (C13/15), 121.8 (d, 3JC P = 16.6 Hz, C7), 123.7 (d, $^{5}J_{\text{C-P}}$ = 2.0 Hz, C9), 128.6 (d, $^{5}J_{\text{C-P}}$ = 1.7 Hz, C18/22), 128.7 (C20), 129.4 (d, $^{3}J_{\text{C-P}}$ = 13.4 Hz, C12/16), 129.8 (C19/21), 131.9 (d, $^{2}J_{\text{C-P}}$ = 13.1 Hz, C4), 132.9 (d, $^{2}J_{\text{C-P}}$ = 11.6 Hz, C2), 137.0 (d, $^{2}J_{\text{C-P}}$ = 25.2 Hz, C11), 137.6 (C8), 143.3 (d, $^{4}J_{\text{C-P}}$ = 3.3 Hz, C17), 145.1 (d, $^{3}J_{\text{C-P}}$ = 13.7 Hz, C3), 150.7 (C10), 160.0 (d, $^{2}J_{\text{C-P}}$ = 25.7 Hz, C6), 161.3 (d, $^{5}J_{\text{C-P}}$ = 2.1 Hz, C14), 170.4 (d, $^{1}J_{\text{C-P}}$ = 50.6 Hz, C5), 172.2 (d, $^{1}J_{\text{C-P}}$ = 50.8 Hz, C1) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$) δ = 185.8 ppm; ESI-TOF (m/z): 356.1236 g/mol (calc.: 356.1199 g/mol) [M + H]+.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine (**2h**): Pyrylium salt **1h** (5.0 g, 11 mmol) and tris(trimethylsilyl)phosphane (5.8 g, 23 mmol) in acetonitrile (30 mL) gave the product (0.897 g, 2.5 mmol, 22%) as a slightly yellow-orange solid. ^{1}H NMR (401 MHz, THF-d$_8$): δ = 2.52 (s, 3 H, SMe), 7.28 – 7.33 (m, 1 H, H9), 7.36 – 7.43 (m, 3 H, H13/15, H20), 7.47 – 7.52 (m, 2 H, H19/21), 7.72 – 7.76 (m, 2 H, H12/16), 7.77 – 7.84 (m, 3 H, H18/22, H8), 8.11 – 8.15 (m, 1 H, H7), 8.27 (dd, *J* = 5.8 Hz, 1.3 Hz, 1 H, H2), 8.69 (ddd, *J* = 4.8 Hz, 1.9 Hz, 1.0 Hz, 1 H, H10), 8.89 (dd, *J* = 5.8 Hz, 1.3 Hz, 1 H, H4) ppm; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 15.5 (SMe), 121.8 (d, JC P =

16.2 Hz, C7), 123.7 (d, JC P = 2.0 Hz, C9), 127.6 (C13/15), 128.6 (d, $J_{\text{C-P}}$ = 1.7 Hz, C18/22), 128.6 (C20), 128.8 (C12/16), 129.8 (C19/21), 132.3 (d, $J_{\text{C-P}}$ = 13.1 Hz, C4), 133.1 (d, $J_{\text{C-P}}$ = 11.8 Hz, C2), 137.7 (C8), 140.3 (d, $J_{\text{C-P}}$ = 2.3 Hz, C14), 141.1 (d, $J_{\text{C-P}}$ = 25.1 Hz, C11), 143.2 (d, $J_{\text{C-P}}$ = 3.2 Hz, C17), 145.2 (d, $J_{\text{C-P}}$ = 13.7 Hz, C3), 150.7 (C10), 159.9 (d, $J_{\text{C-P}}$ = 25.7 Hz, C6), 170.5 (d, $J_{\text{C-P}}$ = 50.5 Hz, C5), 171.8 (d, $J_{\text{C-P}}$ = 51.0 Hz, C1) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$) δ = 186.0 ppm; ESI-TOF (m/z): 372.1000 g/mol (calc.: 372.0970 g/mol) [M + H]+.

Bipyridines

To pyrylium salt (1 eq.) stirred in ethanol aqueous ammonia (large excess) was added. After a colour change to a red solution, a white solid precipitated after 10-30 min. The reaction was allowed to go to completion for two hours. Then the solid product was filtered off and dried under vacuum.

2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyridine (**3b**): **3b** has been synthesised before via a different synthetic pathway.[7] Pyrylium salt **1b** (0.199 g, 0.48 mmol) with ammonia (2.0 mL, 24% in water, 25 mmol) in ethanol (3 mL) gave the product (0.152 g, 0.47 mmol, 97%) as a colourless solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.20 (ms, 2 H), 7.34 (ddd, J = 7.4 Hz, 4.8 Hz, 1.3 Hz, 1 H), 7.44 – 7.56 (m, 3 H), 7.79 (ms, 2 H), 7.87 (ddd, J = 7.7 Hz, 7.7 Hz, 1.9 Hz, 1 H), 7.92 (d, J = 1.6 Hz, 1 H), 8.18 – 8.23 (m, 2 H), 8.61 (d, J = 1.6 Hz, 1 H), 8.67 – 8.74 (m, 2 H) ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -112.6 (ms) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 116.1 (d, $J_{\text{C-F}}$ = 21.6 Hz), 117.4, 118.4, 121.7, 124.0, 127.2, 128.9, 129.1 (d, $J_{\text{C-F}}$ = 8.2 Hz), 129.3, 134.9 (d, $J_{\text{C-F}}$ = 3.3 Hz), 137.1, 139.4, 149.1, 149.3, 156.3, 156.3, 157.3, 163.5 (d, $J_{\text{C-F}}$ = 248.9 Hz) ppm; ESI-TOF (m/z): 327.1304 g/mol (calc.: 327.1298 g/mol) [M + H]+.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyridine (**3c**): Pyrylium salt **1c** (0.199 g, 0.57 mmol) with ammonia (3.0 mL, 24% in water, 25 mmol) in ethanol (10 mL) gave the product (0.069 g, 0.18 mmol, 33%) as a colourless solid. ^{1}H NMR (700 MHz, DCM-d$_2$): δ = 7.38 (ddd, J = 7.4 Hz, 4.7 Hz, 1.2 Hz, 1 H), 7.47 – 7.51 (m, 1 H), 7.54 – 7.57 (m, 2 H), 7.80 – 7.82 (m, 2 H), 7.90 (ddd, J = 7.9 Hz, 7.4 Hz, 1.8 Hz, 1 H), 7.95 – 7.97 (m, 2 H), 8.02 (d, J = 1.6 Hz, 1 H), 8.22 – 8.25 (m, 2 H), 8.69 (ddd, J = 8.0 Hz, 1.1 Hz, 1.1 Hz, 1 H), 8.69 (d, J = 1.6 Hz, 1 H), 8.71 (ddd, J = 4.7 Hz, 1.8 Hz, 0.9 Hz, 1 H) ppm; ^{19}F NMR (376 MHz, DCM-d$_2$): δ = -62.8 ppm; ^{13}C{^{1}H} NMR (176 MHz, DCM-d$_2$): δ = 118.0, 119.0, 121.8, 124.6, 124.8 (q, $J_{\text{C-F}}$ = 271.9 Hz), 126.5 (q, $J_{\text{C-F}}$ = 3.9 Hz), 127.6, 128.3, 129.3, 129.9, 131.25 (q, JC F = 32.6 Hz), 137.5, 139.7, 143.1, 149.3, 149.7, 156.5, 157.2, 157.8 ppm; ESI-TOF (m/z): 399.1086 g/mol (calc.: 399.1084 g/mol) [M + Na]+.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylpyridine (**3d**): **3d** has been synthesised before via a different synthetic pathway.[7] Pyrylium salt **1d** (0.445 g, 1.04 mmol) with ammonia (2.5 mL, 24% in water, 32 mmol) in ethanol (10 mL) gave the product (0.466 g, 1.38 mmol, 98%) as a colourless solid. ^{1}H NMR (400 MHz, DCM-d$_2$): δ = 3.88 (s, 3 H), 7.07 (ms, 2 H), 7.36 (ddd, J = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1 H), 7.44 – 7.50 (m, 1 H), 7.51 – 7.57 (m, 2 H), 7.82 (ms, 2 H), 7.88 (ddd, J = 8.0 Hz, 7.5 Hz, 1.8 Hz, 1 H), 8.00 (d, J = 1.6 Hz, 1 H), 8.20 – 8.23 (m, 2 H), 8.64 (d, J = 1.6 Hz, 1 H), 8.68 (ddd, J = 8.0 Hz, 1.1 Hz, 1.1 Hz, 1 H), 8.71 (ddd, J = 4.8 Hz, 1.8 Hz, 0.9 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, DCM-d$_2$): δ = 56.0, 115.0, 117.3, 118.3, 121.7, 124.4, 127.5, 128.9, 129.2, 129.6, 131.4, 137.4, 140.1, 149.6, 150.2, 156.8, 156.9, 157.5, 161.2 ppm; ESI-TOF (m/z): 339.1510 g/mol (calc.: 339.1497 g/mol) [M + H]+, 361.1331 g/mol (calc.: 361.1317 g/mol) [M + Na]+.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyridine (**3e**): **3e** has been synthesised before via a different synthetic pathway.[8] Pyrylium salt **1e** (0.315 g, 0.71 mmol) with ammonia (2.0 mL, 24% in water, 25 mmol) in ethanol (3 mL) gave the product (0.236 g, 0.67 mmol, 94%) as a colourless solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.56 (s, 3 H, SMe), 7.33 – 7.40 (m, 3 H, H9, H19/21), 7.44 – 7.56 (m, 3 H, H14, H13/15), 7.75 – 7.79 (m, 2 H, H18/22), 7.84 – 7.90 (m, 1 H, H8), 7.96 (d, *J* = 1.4 Hz, 1 H, H2), 8.18 – 8.22 (m, 2 H, H12/16), 8.63 (d, *J* = 1.4 Hz, 1 H, H4), 8.67 – 8.71 (m, 1 H, H7), 8.72 (ddd, *J* = 4.7 Hz, 1.8 Hz, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 15.6 (SMe), 117.11 (C4), 118.3 (C2), 121.7 (C7), 124.0 (C9), 126.7 (C19/21), 127.2 (C12/16), 127.6 (C18/22), 128.9 (C13/15), 129.2 (C14), 135.3 (C17), 137.0 (C8), 139.6 (C11), 140.2 (C20), 149.2 (C10), 149.6 (C3), 156.4 (C5 or C6), 156.4 (C5 or C6), 157.3 (C1) ppm; ESI-TOF (m/z): 355.1278 g/mol (calc.: 355.1269 g/mol) [M + H]+, 377.1089 g/mol (calc.: 377.1088 g/mol) [M + Na]+.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)pyridine (**3f**): **3f** has been synthesised before via a different synthetic pathway.[30] Pyrylium salt **1f** (0.144 g, 0.35 mmol) with ammonia (1.0 mL, 24% in water, 13 mmol) in ethanol (2 mL) gave the product (0.088 g, 0.27 mmol, 78%) as a colourless solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.18 – 7.24 (m, 2 H), 7.33 (ddd, *J* = 7.4 Hz, 4.8 Hz, 1.2 Hz, 1 H), 7.44 – 7.54 (m, 3 H), 7.79 – 7.83 (m, 2 H), 7.85 (ddd, *J* = 7.7 Hz, 7.7 Hz, 1.8 Hz, 1 H), 7.91 (d, *J* = 1.6 Hz, 1 H), 8.16 – 8.22 (m, 2 H), 8.63 – 8.67 (m, 2 H), 8.71 – 8.74 (m, 1 H) ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -112.8 – -112.7 (m) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 115.7 (d, $J_{C\text{-}F}$ = 21.5 Hz), 117.6, 118.2, 121.5, 124.0, 127.3, 128.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.1, 129.2, 135.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 137.0, 138.7, 149.1, 150.4, 156.1, 156.3, 156.3, 163.7 (d, JC-F = 248.5 Hz) ppm; ESI-TOF (m/z): 327.1308 g/mol (calc.: 327.1298 g/mol) [M + H]+, 349.1127 g/mol (calc.: 349.1117 g/mol) [M + Na]+.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)pyridine (**3g**): **3g** has been synthesised before via a different synthetic pathway.[9] Pyrylium salt 1g (0.600 g, 1.40 mmol) with ammonia (2.5 mL, 24% in water, 32 mmol) in ethanol (3 mL) gave the product (0.152 g, 0.47 mmol, 97%) as a colourless solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.90 (s, 3 H), 7.06 (ms, 2 H), 7.34 (ddd, *J* = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1 H), 7.44 – 7.55 (m, 3 H), 7.81 – 7.84 (m, 2 H), 7.87 (ddd, *J* = 8.0 Hz, 7.5 Hz, 1.8 Hz, 1 H), 7.93 (d, *J* = 1.6 Hz, 1 H), 8.18 (ms, 2 H), 8.59 (d, *J* = 1.5 Hz, 1 H), 8.68 (ddd, *J* = 8.0 Hz, 1.1 Hz, 1.1 Hz, 1 H), 8.72 (ddd, *J* = 4.8 Hz, 1.8 Hz, 0.9 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 55.5, 114.2, 117.0, 117.9, 121.6, 123.9, 127.4, 128.5, 129.1, 129.1, 132.3, 137.0, 139.1, 149.2, 150.3, 156.2, 156.6, 156.9, 160.7 ppm; ESI-TOF (m/z): 339.1503 g/mol (calc.: 339.1497 g/mol) [M + H]+, 361.1318 g/mol (calc.: 361.1317 g/mol) [M + Na]+.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyridine (**3h**): Pyrylium salt **1h** (0.150 g, 0.34 mmol) with ammonia (2.5 mL, 24% in water, 32 mmol) in ethanol (10 mL) gave the product (0.095 g, 0.27 mmol, 79%) as a colourless solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.90 (s, 3 H, SMe), 7.35 (ddd, *J* = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1 H, H9), 7.40 (ms, 2 H, H13/15), 7.44 – 7.55 (m, 3 H, H20, H19/21), 7.80 – 7.84 (m, 2 H, H18/22), 7.87 (ddd, *J* = 8.0 Hz, 7.4 Hz, 1.8 Hz, 1 H, H8), 7.96 (d, J =

1.6 Hz, 1 H, H2), 8.13 – 8.17 (m, 2 H, H12/16), 8.62 (d, J = 1.5 Hz, 1 H, H4), 8.67 (ddd, J = 8.0 Hz, 1.1 Hz, 1.1 Hz, 1 H, H7), 8.72 (ddd, J = 4.8 Hz, 1.8 Hz, 0.9 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 15.7 (SMe), 117.5 (C4), 118.1 (C2), 121.6 (C7), 123.9 (C9), 126.5 (C13/15), 127.4 (C18/22), 127.5 (C12/16), 129.1 (C20), 129.1 (C19/21), 136.3 (C11), 137.0 (C8), 138.9 (C17), 140.0 (C14), 149.2 (C10), 150.4 (C3), 156.3 (C1 or C5 or C6), 156.4 (C1 or C5 or C6), 156.6 (C1 or C5 or C6) ppm; ESI-TOF (m/z): 355.1291 g/mol (calc.: 355.1264 g/mol) [M + H]+, 377.1113 g/mol (calc.: 377.1083 g/mol) [M + Na]+; elemental analysis calc (%) for $C_{23}H_{18}N_2S$ (354.47 g/mol): C 77.93, H 5.12, N 7.90, S 9.02; found: C 77.83, H 5.08, N 7.75, S 9.23.

P,N-tungsten tetracarbonyl complexes

In a Young-NMR-tube phosphinine (1 eq.) was dissolved in THF-d$_8$ (0.6 mL) and tungsten hexacarbonyl (1 eq.) was added. The tube was then irradiated with UV light until the ^{31}P{^{1}H} NMR spectrum showed complete conversion (15 - 20 h). After evaporation of all volatiles the product was recrystallized from acetonitrile (**4f-h**) or THF/diethyl ether (**4d**).

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylphosphinine-P,N-tungsten tetra-carbonyl (**4d**): Phosphinine 2d (27 mg, 0.08 mmol), THF-d8 (0.6 mL) and tungsten hexacarbonyl (27 mg, 0.08 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction recrystallization by slow diffusion of diethyl ether into THF gave the product (45 mg, 0.07 mmol, 91%) as a dark red solid. ^{1}H NMR (500 MHz, THF-d$_8$): δ = 3.85 (s, 3 H, OMe), 7.08 (ms, 2 H, H19/21), 7.32 – 7.36 (m, 1 H, H9), 7.43 – 7.48 (m, 1 H, H14), 7.52 – 7.57 (m, 2 H, H13/15), 7.75 (ms, 2H, H18/22), 7.96 – 7.99 (m, 2 H, H12/16), 8.04 – 8.09 (m, 1 H, H8), 8.47 (dd, J = 17.9, 1.5 Hz, 1 H, H2), 8.61 (d, J = 8.1 Hz, 1 H, H7), 8.82 (dd, J = 14.3, 1.5 Hz, 1 H, H4), 9.42 (ddd, J = 5.7, 1.7, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (126 MHz, THF-d$_8$): δ = 55.7 (OMe), 115.4 (C19/21), 121.8 (d, $J_{C\text{-}P}$ = 11.5 Hz, C7), 125.6 (d, $J_{C\text{-}P}$ = 3.8 Hz, C9), 129.0 (d, $^{3}J_{C\text{-}P}$ = 11.1 Hz, C12/16), 129.4 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, C14), 129.6 (d, $^{5}J_{C\text{-}P}$ = 2.4 Hz, C18/22), 130.1 (C13/15), 132.3 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, C4), 134.9 (d, $^{4}J_{C\text{-}P}$ = 4.6 Hz, C17), 138.1 (d, $^{2}J_{C\text{-}P}$ = 11.2 Hz, C2), 139.4 (C8), 140.6 (d, $^{2}J_{C\text{-}P}$ = 16.0 Hz, C11), 141.0 (d, $^{3}J_{C\text{-}P}$ = 21.2 Hz, C3), 158.4 (d, $^{4}J_{C\text{-}P}$ = 4.5 Hz, C10), 160.0 (d, $^{1}J_{C\text{-}P}$ = 14.3 Hz, C5), 160.7 (d, $^{1}J_{C\text{-}P}$ = 17.4 Hz, C1), 161.1 (d, $^{7}J_{C\text{-}P}$ = 0.8 Hz, C20), 162.1 (d, $^{2}J_{C\text{-}P}$ = 17.5 Hz, C6), 199.0 (d, $J_{C\text{-}P}$ = 11.0 Hz, CO$_{\text{axial}}$), 209.4 (d, $J_{C\text{-}P}$ = 5.1 Hz, CO$_{\text{equatorial}}$), 212.0 (d, $J_{C\text{-}P}$ = 41.7 Hz, CO$_{\text{equatorial}}$) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$) δ = 196.6 (s, $^{1}J_{P\text{-}W}$ = 274 Hz) ppm; FT-IR (solid ATR): (CO) 2015, 1973, 1891, 1857 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine-P,N-tungsten tetracarbonyl (**4f**): Phosphinine 2f (21 mg, 0.06 mmol), THF-d$_8$ (0.6 mL) and tungsten hexacarbonyl (22 mg, 0.06 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction recrystallization from acetonitrile gave the product (27 mg, 0.04 mmol, 69%) as a dark red solid. ^{1}H NMR (700 MHz, THF d$_8$): δ = 7.30 (ms, 2 H, H13/15), 7.35 – 7.38 (m, 1 H, H9), 7.42 – 7.45 (m, 1 H, H20), 7.50 – 7.54 (m, 2 H, H19/21), 7.78 – 7.81 (m, 2 H, H18/22), 8.00 (ddd, J = 8.9, 5.1, 1.6 Hz, 2 H, H12/16), 8.06 – 8.10 (m, 1 H, H8), 8.47 (dd, 3JH-P = 17.7, $^{4}J_{H\text{-}H}$ = 1.4 Hz, 1 H, H2), 8.63 (d, J = 8.2 Hz, 1 H, H7), 8.85 (dd, J = 14.4 Hz, J = 1.3 Hz, 1 H, H4), 9.42 (ddd, J = 5.6, 1.6, 0.7 Hz, 1 H, H10) ppm; ^{19}F NMR (376 MHz, THF-d$_8$): δ = -114.7 (ms) ppm; ^{13}C{^{1}H} NMR (176 MHz, THF-d$_8$): δ = 117.0 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz, C13/15), 121.8 (d, $^{3}J_{C\text{-}P}$ = 11.6 Hz, C7), 125.7 (d, $^{5}J_{C\text{-}P}$ = 3.5 Hz, C9), 128.5 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, C18/22), 128.9 (C20), 129.9 (C19/21), 131.0 (dd, $^{3}J_{C\text{-}F}$ = 8.4, $^{3}J_{C\text{-}P}$ =

10.9 Hz, C12/16), 132.6 (d, $^{2}J_{\text{C-P}}$ = 12.4 Hz, C4), 136.8 (dd, $^{2}J_{\text{C-P}}$ = 16.5 Hz, $^{4}J_{\text{C-F}}$ = 3.0 Hz, C11), 138.4 (d, $^{2}J_{\text{C-P}}$ = 10.9 Hz, C2), 139.5 (C8), 141.1 (d, $^{3}J_{\text{C-P}}$ = 21.2 Hz, C3), 142.7 (d, $^{4}J_{\text{C-P}}$ = 4.3 Hz, C17), 158.5 (d, $^{4}J_{\text{C-P}}$ = 4.4 Hz, C10), 159.4 (d, $^{1}J_{\text{C-P}}$ = 17.7 Hz, C1), 160.0 (d, $^{1}J_{\text{C-P}}$ = 14.5 Hz, C5), 162.0 (d, $^{2}J_{\text{C-P}}$ = 17.3 Hz, C6), 164.4 (dd, $^{1}J_{\text{C-F}}$ = 247.9 Hz, $^{5}J_{\text{C-P}}$ = 1.9 Hz, C14), 198.8 (d, $^{2}J_{\text{C-P}}$ = 10.9 Hz, CO_{axial}), 209.4 (d, $^{2}J_{\text{C-P}}$ = 4.9 Hz, $\text{CO}_{\text{equatorial}}$), 211.8 (d, $^{2}J_{\text{C-P}}$ = 41.8 Hz, $\text{CO}_{\text{equatorial}}$) ppm; $^{31}\text{P}\{^{1}\text{H}\}$ NMR (162 MHz, THF-d8): δ = 201.0 (d, $^{1}J_{\text{P-W}}$ = 278 Hz) ppm; FT-IR (solid ATR): (CO) 2009, 1902, 1870, 1840 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)phosphinine-P,N-tungsten tetra-carbonyl (**4g**): Phosphinine 2g (15 mg, 0.04 mmol), THF-d8 (0.6 mL) and tungsten hexacarbonyl (15 mg, 0.04 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction recrystallization from acetonitrile gave the product (21 mg, 0.03 mmol, 76%) as a dark red solid. ^{1}H NMR (400 MHz, THF d$_8$): δ = 3.85 (s, 3 H, OMe), 7.08 – 7.13 (m, 2 H, H13/15), 7.32 – 7.37 (m, 1 H, H9), 7.40 – 7.45 (m, 1 H, H20), 7.49 – 7.55 (m, 2 H, H19/21), 7.77 – 7.81 (m, 2H, H18/22), 7.91 – 7.96 (m, 2 H, H12/16), 8.03 – 8.09 (m, 1 H, H8), 8.44 (dd, *J* = 17.9, 1.2 Hz, 1 H, H2), 8.61 (d, *J* = 8.5 Hz, 1 H, H7), 8.80 (d, *J* = 14.3 Hz, 1 H, H4), 9.40 – 9.44 (m, 1 H, H10) ppm; $^{13}\text{C}\{^{1}\text{H}\}$ NMR (101 MHz, THF-d$_8$): δ = 55.7 (OMe), 115.6 (C13/15), 121.8 (d, $^{3}J_{\text{C-P}}$ = 11.6 Hz, C7), 125.6 (d, $^{5}J_{\text{C-P}}$ = 3.7 Hz, C9), 128.5 (d, $^{5}J_{\text{C-P}}$ = 2.5 Hz, C18/22), 128.8 (C20), 129.9 (C19/21), 130.1 (d, $^{3}J_{\text{C-P}}$ = 11.3 Hz, C12/16), 132.1 (d, $^{2}J_{\text{C-P}}$ = 12.5 Hz, C4), 132.8 (d, $^{2}J_{\text{C-P}}$ = 16.1 Hz, C11), 137.7 (d, $^{2}J_{\text{C-P}}$ = 10.6 Hz, C2), 139.4 (C8), 141.2 (d, $^{3}J_{\text{C-P}}$ = 21.0 Hz, C3), 142.9 (d, $^{4}J_{\text{C-P}}$ = 4.5 Hz, C17), 158.4 (d, $^{4}J_{\text{C-P}}$ = 4.5 Hz, C10), 160.0 (d, $^{1}J_{\text{C-P}}$ = 14.1 Hz, C5), 160.6 (d, $^{1}J_{\text{C-P}}$ = 17.0 Hz, C1), 161.7 (d, $^{5}J_{\text{C-P}}$ = 2.1 Hz, C14), 162.1 (d, $^{2}J_{\text{C-P}}$ = 17.3 Hz, C6), 198.9 (d, $^{2}J_{\text{C-P}}$ = 10.9 Hz, $^{1}J_{\text{C-W}}$ = 126.8 Hz, CO_{axial}), 209.5 (d, 2JC-P = 5.0 Hz, $\text{CO}_{\text{equatorial}}$), 212.1 (d, $^{2}J_{\text{C-P}}$ = 41.7 Hz, $\text{CO}_{\text{equatorial}}$) ppm; $^{31}\text{P}\{^{1}\text{H}\}$ NMR (162 MHz, THF-d$_8$) δ = 197.9 (s, $^{1}J_{\text{P-W}}$ = 274 Hz) ppm; FT-IR (solid ATR): (CO) 2006, 1883, 1852, 1827 (shoulder), 1810 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine-P,N-tungsten tetracarbonyl (4h): Phosphinine 2h (43 mg, 0.12 mmol), THF-d$_8$ (0.6 mL) and tungsten hexacarbonyl (41 mg, 0.12 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction recrystallization from acetonitrile gave the product (13 mg, 0.02 mmol, 17%) as a dark red solid. ^{1}H NMR (400 MHz, DCM d$_2$): δ = 2.55 (s, 3 H, SMe), 7.24 (ms, 1 H, H9), 7.41 – 7.46 (m, 2 H, H13/15), 7.46 – 7.9 (m, 1 H, H20), 7.52 – 7.58 (m, 2 H, H19/21), 7.68 – 7.73 (m, 2 H, H18/22), 7.87 (ms, 2 H, H16/22), 7.97 (dddd, *J* = 8.3, 7.4, 1.7, 1.0 Hz, 1 H, H8), 8.27 – 8. 32 (m, 1 H, H2), 8.37 (dd, *J* = 17.7, 1.3 Hz, 1 H, H7), 8.58 (dd, *J* = 14.2, 1.4 Hz, 1 H, H4), 9.38 (ddd, *J* = 5.7, 1.7, 0.8 Hz, 1 H, H10) ppm; $^{13}\text{C}\{^{1}\text{H}\}$ NMR (101 MHz, THF-d$_8$): δ = 15.3 (SMe), 121.8 (d, $^{3}J_{\text{C-P}}$ = 11.7 Hz, C7), 125.7 (d, $^{5}J_{\text{C-P}}$ = 3.9 Hz, C9), 127.5 (C13/15), 128.5 (d, $^{5}J_{\text{C-P}}$ = 2.5 Hz, C18/22), 128.9 (C20), 129.2 (d, $^{3}J_{\text{C-P}}$ = 11.4 Hz, C12/16), 129.9 (C19/21), 132.5 (d, $^{2}J_{\text{C-P}}$ = 12.8 Hz, C4), 136.9 (d, $^{2}J_{\text{C-P}}$ = 16.2 Hz, C11), 137.9 (d, $^{2}J_{\text{C-P}}$ = 10.9 Hz, C2), 139.4 (C8), 141.2 (d, $^{3}J_{\text{C-P}}$ = 20.8 Hz, C3), 141.4 (d, $^{5}J_{\text{C-P}}$ = 2.4 Hz, C14), 142.8 (d, $^{4}J_{\text{C-P}}$ = 4.5 Hz, C17), 158.4 (d, $^{4}J_{\text{C-P}}$ = 3.4 Hz, C10), 160.1 (d, $^{1}J_{\text{C-P}}$ = 17.4 Hz, C1 or C5), 160.1 (d, $^{1}J_{\text{C-P}}$ = 14.1 Hz, C1 or C5), 162.0 (d, $^{2}J_{\text{C-P}}$ = 17.7 Hz, C6), 198.9 (d, $J_{\text{C-P}}$ = 11.1 Hz, CO_{axial}), 209.5 (d, $J_{\text{C-P}}$ = 5.5 Hz, $\text{CO}_{\text{equatorial}}$), 212.0 (d, $J_{\text{C-P}}$ = 41.8 Hz, $\text{CO}_{\text{equatorial}}$) ppm; $^{31}\text{P}\{^{1}\text{H}\}$ NMR (162 MHz, THF-d$_8$) δ = 199.2 (s, $^{1}J_{\text{P-W}}$ = 278 Hz) ppm; FT-IR (solid ATR): (CO) 2016, 1975, 1893, 1859 cm^{-1}.

N,N-tungsten tetracarbonyl complexes

2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (**5b**): Bipyrydine **3b** (40 mg, 0.12 mmol), MeCN-d$_4$ (0.6 mL) and tungsten hexacarbonyl (38 mg, 0.11 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction, the product (47 mg, 0.08 mmol, 70%) was filtrated from the reaction mixture as dark red crystals. ^{1}H NMR (400 MHz, DCM d$_2$): δ = 7.25 – 7.32 (m, 2 H, H19/21), 7.42 – 7.47 (m, 1 H, H9), 7.54 – 7.64 (m, 5 H, H14, H13/15, H12/16), 7.73 – 7.76 (m, 1 H, H2), 7.79 – 7.84 (m, 2 H, H18/22), 8.00 – 8.07 (m, 1 H, H8), 8.28 – 8.32 (m, 1 H, H7), 8.34 (d, J = 1.9 Hz, 1 H, H4), 9.29 – 9.33 (m, 1 H, H10) ppm; ^{19}F NMR (376 MHz, DCM-d$_2$): δ = -110.8 (tt, $J_{\text{F-H}}$ = 8.6, 5.2 Hz) ppm; ^{13}C{^{1}H} NMR (101 MHz, DCM-d$_2$): δ = 117.1 (d, $^{2}J_{\text{C-F}}$ = 22.0 Hz, C19/21), 119.3 (d, $^{6}J_{\text{C-F}}$ = 0.6 Hz, C4), 123.8 (C7), 125.1 (d, $^{6}J_{\text{C-F}}$ = 0.7 Hz, C2), 126.4 (C9), 128.9 (C12/16 or C13/15), 129.0 (C12/16 or C13/15), 129.8 (d, $^{3}J_{\text{C-F}}$ = 8.7 Hz, C18/22), 130.1 (C14), 133.0 (d, $^{4}J_{\text{C-F}}$ = 3.3 Hz, C17), 137.8 (C8), 143.1 (C11), 149.0 (C3), 153.6 (C10), 157.5 (C5 or C6), 157.5 (C5 or C6), 163.5 (C1), 163.7 (d, $^{1}J_{\text{C-F}}$ = 250.8 Hz, C20), 202.5 ($^{1}J_{\text{C-W}}$ = 133.2 Hz, CO$_{\text{axial}}$), 210.9 ($^{1}J_{\text{C-W}}$ = 163.6 Hz, CO$_{\text{equatorial}}$), 217.4 ($^{1}J_{\text{C-W}}$ = 172.8 Hz, CO$_{\text{equatorial}}$) ppm; FT-IR (solid ATR): (CO) 2000, 1872, 1853, 1802, 1783 cm^{-1}.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (**5c**): Bipyrydine 3c (16 mg, 0.04 mmol), MeCN-d$_4$ (0.6 mL) and tungsten hexacarbonyl (15 mg, 0.04 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction, the solution was filtered and recrystallization of the solids by slow diffusion of diethyl ether into a THF solution gave the product (25 mg, 0.04 mmol, 87%) as dark red crystals. ^{1}H NMR (700 MHz, DCM-d$_2$): δ = 7.46 (ddd, J = 7.5, 5.5, 1.2 Hz, 1 H, H9), 7.55 – 7.60 (m, 3 H, H13/15, H14), 7.60 – 7.63 (m, 2 H, H12/16), 7.79 (d, J = 1.9 Hz, 1 H, H2), 7.85 (d, J = 8.2 Hz, 2 H, H19/21), 7.93 (d, J = 8.1 Hz, 2 H, H18/22), 8.04 (ddd, J = 8.2, 7.6, 1.6 Hz, 1 H, H8), 8.31 (d, J = 8.3 Hz, 1 H, H7), 8.37 (d, J = 1.8 Hz, 1 H, H4), 9.33 (ddd, J = 5.5, 1.5, 0.8 Hz, 1 H, H10) ppm; ^{19}F NMR (376 MHz, DCM-d$_2$): δ = -63.0 (s) ppm; ^{13}C{^{1}H} NMR (176 MHz, DCM d$_2$): δ = 119.6 (C4), 123.9 (C7), 124.5 (q, $^{1}J_{\text{C-F}}$ = 271.3 Hz, CF$_3$), 125.5 (C2), 126.6 (C9), 127.0 (q, $^{3}J_{\text{C-F}}$ = 3.8 Hz, C19/21), 128.3 (C18/22), 128.9 (C12/16), 129.1 (C13/15), 130.2 (C14), 132.4 (q, $^{2}J_{\text{C-F}}$ = 32.7 Hz, C20), 137.8 (C8), 140.6 (C17), 143.0 (C11), 148.5 (C3), 153.7 (C10), 157.3 (C5 or C6), 157.8 (C5 or C6), 165.2 (C1), 202.4 ($^{1}J_{\text{C-W}}$ = 133.3 Hz, CO$_{\text{axial}}$), 210.8 ($^{1}J_{\text{C-W}}$ = 163.7 Hz, CO$_{\text{equatorial}}$), 217.4 (1JC-W = 172.0 Hz, CO$_{\text{equatorial}}$) ppm; FT-IR (solid ATR): (CO) 1997, 1887, 1877, 1867, 1848, 1805 cm^{-1}.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (**5d**): Bipyrydine 3d (15 mg, 0.04 mmol), MeCN-d$_4$ (0.6 mL) and tungsten hexacarbonyl (16 mg, 0.05 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction, the reaction mixture was filtrated. Recrystallization of the solids by slow evaporation of a THF solution gave the product (17 mg, 0.03 mmol, 60%) as dark red crystals. ^{1}H NMR (400 MHz, THF d$_8$): δ = 3.87 (s, 3 H, OMe), 7.10 (ms, 2 H, H19/21), 7.45 – 7.54 (m, 4 H, H14, H13/15, H9), 7.57 – 7.62 (m, 2 H, H12/16), 7.90 (ms, 1 H, H2), 7.98 (ms, 2H, H18/22), 8.09 (ddd, J = 8.2, 7.5, 1.7 Hz, 1 H, H8), 8.64 – 8.68 (m, 1 H, H7), 8.70 (d, J = 1.9 Hz, 1 H, H4), 9.32 (ddd, J = 5.5, 1.6, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d$_8$): δ = 55.7 (OMe), 115.6 (C19/21), 119.2 (C4), 124.4 (C2), 124.7 (C7), 126.7 (C9), 129.1 (C17), 129.2 (C12/16 or C13/15), 129.3 (C12/16 or C13/15), 129.6 (C18/22), 130.2 (C14), 138.1 (C8), 143.9 (C11), 149.8 (C3), 153.8 (C10), 158.1 (C5 or C6), 158.5 (C5 or C6), 162.9 (C20), 165.2 (C1), 203.1 ($^1J_{C-W}$ = 133.1 Hz, CO_{axial}), 210.4 (1JC W = 162.4 Hz, $CO_{equatorial}$), 217.0 ($CO_{equatorial}$) ppm; FT-IR (solid ATR): (CO) 2015, 1971, 1891, 1857 cm^{-1}.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (**5e**): Bipyrydine 3e (20 mg, 0.06 mmol), THF-d_8 (0.6 mL) and tungsten hexacarbonyl (20 mg, 0.06 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction, all volatiles were evaporated under reduced pressure. Recrystallization from acetonitrile gave the product (8 mg, 0.01 mmol, 22%) as dark red crystals. ^{1}H NMR (400 MHz, DCM d_2): δ = 2.56 (s, 3 H, SMe), 7.39 – 7.46 (m, 3 H, H19/21, H9), 7.54 – 7.62 (m, 5 H, H12/16, H13/15, H14), 7.72 – 7.77 (m, 3 H, H18/22, H2), 8.02 (ddd, *J* = 8.1, 7.5, 1.6 Hz, 1 H, H8), 8.30 (ms, 1 H, H7), 8.36 (d, *J* = 1.8 Hz, 1 H, H4), 9.30 (ddd, *J* = 5.6, 1.6, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (176 MHz, THF-d_8): δ = 15.5 (SMe), 118.9 (C4), 123.8 (C7), 124.7 (C2), 126.4 (C9), 127.0 (C19/21), 127.9 (C18/22), 128.9 (C13/15), 129.0 (C12/16), 130.0 (C14), 132.7 (C17), 137.8 (C8), 143.2 (C20 or C11), 143.2 (C11 or C20), 149.3 (C3), 153.6 (C10), 157.5 (C5 or C6), 157.6 (C5 or C6), 164.9 (C1), 202.5 (d, J_{C-W} = 132.9 Hz, CO_{axial}), 211.0 ($CO_{equatorial}$), 217.4 ($CO_{equatorial}$) ppm; FT-IR (solid ATR): (CO) 1999, 1934, 1865, 1823 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)pyridine-N,N-tungsten tetracarbonyl (**5f**): Bipyrydine **3f** (41 mg, 0.13 mmol), THF-d_8 (0.6 mL) and tungsten hexacarbonyl (46 mg, 0.13 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction and removal of the solvent under reduced pressure, recrystallization by slow evaporation of a THF solution gave the product (28 mg, 0.05 mmol, 36%) as dark red crystals. ^{1}H NMR (400 MHz, DCM-d_2): δ = 7.26 (ms, 2 H, H13/15), 7.45 (ddd, *J* = 7.5, 5.5, 1.2 Hz, 1 H, H9), 7.55 – 7.63 (m, 5 H, H19/21, H20, H13/15), 7.76 – 7.84 (m, 3 H, H2, H18/22), 8.03 (ddd, *J* = 7.9, 7.9, 1.7 Hz, 1 H, H8), 8.31 (d, *J* = 8.2 Hz, 1 H, H7), 8.39 (d, *J* = 1.9 Hz, 1 H, H4), 9.29 – 9.33 (m, 1 H, H10) ppm; ^{19}F NMR (376 MHz, DCM-d_2): δ = 112.5 (tt, *J* = 8.7, 5.4 Hz) ppm; ^{13}C{^{1}H} NMR (101 MHz, DCM-d_2): δ = 116.0 (d, $^2J_{C-F}$ = 22.1 Hz, C13/15), 119.7 (C4), 123.8 (C7), 125.2 (C2), 126.5 (C9), 127.7 (C18/22), 130.1 (C19/21), 130.9 (d, $^3J_{C-F}$ = 8.7 Hz, C12/16), 131.0 (C20), 136.7 (C17), 137.9 (C8), 139.5 (d, $^4J_{C-F}$ = 3.4 Hz, C11), 150.2 (C3), 153.6 (C10), 157.5 (C5), 157.5 (C6), 163.8 (C1), 164.2 (d, $^1J_{C-F}$ = 248.2 Hz, C14), 202.4 ($^1J_{C-W}$ = 133.1 Hz, CO_{axial}), 211.1 ($CO_{equatorial}$), 217.3 ($CO_{equatorial}$) ppm; FT-IR (solid ATR): (CO) 2002, 1882, 1851, 1819 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)pyridine-N,N-tungsten tetracarbonyl (**5g**): Bipyrydine 3g (20 mg, 0.06 mmol), THF-d_8 (0.6 mL) and tungsten hexacarbonyl (24 mg, 0.07 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction and removal of the solvent under reduced pressure, recrystallization by slow diffusion of diethyl ether into a THF solution gave the product (15 mg, 0.02 mmol, 40%) as dark red crystals. ^{1}H NMR (400 MHz, DCM-d_2): δ = 3.90 (s, 3 H, OMe), 7.08 (ms, 2 H, H13/15), 7.43 (ddd, *J* = 7.6, 5.5, 1.3 Hz, 1 H, H9), 7.52 – 7.61 (m, 5 H, H13/15, H19/21, H20), 7.78 – 7.83 (m, 3 H, H2, H18/22), 8.02 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1 H, H8), 8.26 – 8.30 (m, 1 H, H7), 8.35 (d, *J* = 1.9 Hz, 1 H, H4), 9.31 (ddd, *J* = 5.5, 1.6, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (101 MHz, DCM-d_2): δ = 56.1 (OMe), 114.4 (C13/15), 119.3 (C4), 123.8 (C7), 125.3 (C2), 126.3 (C9), 127.7 (C18/22), 130.1 (C12/16 or C19/21), 130.3 (C19/21 or C12/16), 130.8 (C20), 136.0 (C11), 136.9 (C17), 137.7 (C8), 150.0 (C3), 153.6 (C10), 157.4 (C5 or C6), 157.8 (C5 or C6), 161.5 (C14), 164.8 (C1), 202.7 (1JC-W = 133.2 Hz, CO_{axial}), 211.1 ($CO_{equatorial}$), 217.4 ($CO_{equatorial}$) ppm; FT-IR (solid ATR): (CO) 1989, 1867, 1853, 1817 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyridine-N,N-tungsten tetracarbonyl (**5h**): Bipyrydine 3h (20 mg, 0.06 mmol), THF-d_8 (0.6 mL) and tungsten hexacarbonyl (20 mg, 0.06 mmol) were filled into a Young-NMR-tube. After irradiation with UV light until completion of the reaction and removal of the solvent under reduced pressure, recrystallization by slow diffusion of diethyl ether into a THF solution gave the product (3 mg, 0.005 mmol, 8%) as dark red crystals. ^{1}H NMR (700 MHz, DCM-d_2): δ = 2.57 (s, 3 H, SMe), 7.42 – 7.45 (m, 3 H, H9, H13/15), 7.54 (ms, 2 H, H12/16), 7.55 – 7.60 (m, 3 H, H20, H19/21), 7.78 (d, *J* = 1.9 Hz, 1 H, H4), 7.79 – 7.82 (m, 2 H, H18/22), 8.02 (ddd, J = 8.2, 7.6, 1.6 Hz, 1 H, H8), 8.29 (d, *J* = 8.2 Hz, 1 H, H7), 8.37 (d, *J* = 1.8 Hz, 1 H, H2), 8.31 (ddd, *J* = 5.5, 1.5, 0.8 Hz, 1 H, H10) ppm; ^{13}C{^{1}H} NMR (176 MHz, DCM-d_2): δ = 16.2 (SMe), 119.5 (C2), 123.8 (C7), 125.2 (C4), 126.4 (C9), 126.7 (C12/16), 127.7 (C18/22), 129.2 (C13/15), 130.1 (C19/21), 130.9 (C20), 136.9 (C17), 137.8 (C8), 139.8 (C11), 141.4 (C14), 150.1 (C3), 153.6 (C10), 157.5 (C6), 157.6 (C1), 164.4 (C5), 202.5 (d, $J_{C\text{-}W}$ = 133.3 Hz, CO_{axial}), 211.1 (d, $J_{C\text{-}W}$ = 164.0 Hz, $CO_{equatorial}$), 217.3 ($^1J_{C\text{-}W}$ = 172.3 Hz, $CO_{equatorial}$) ppm; FT-IR (solid ATR): (CO) 1991, 1873, 1850, 1816 cm^{-1}.

DFT Calculations:

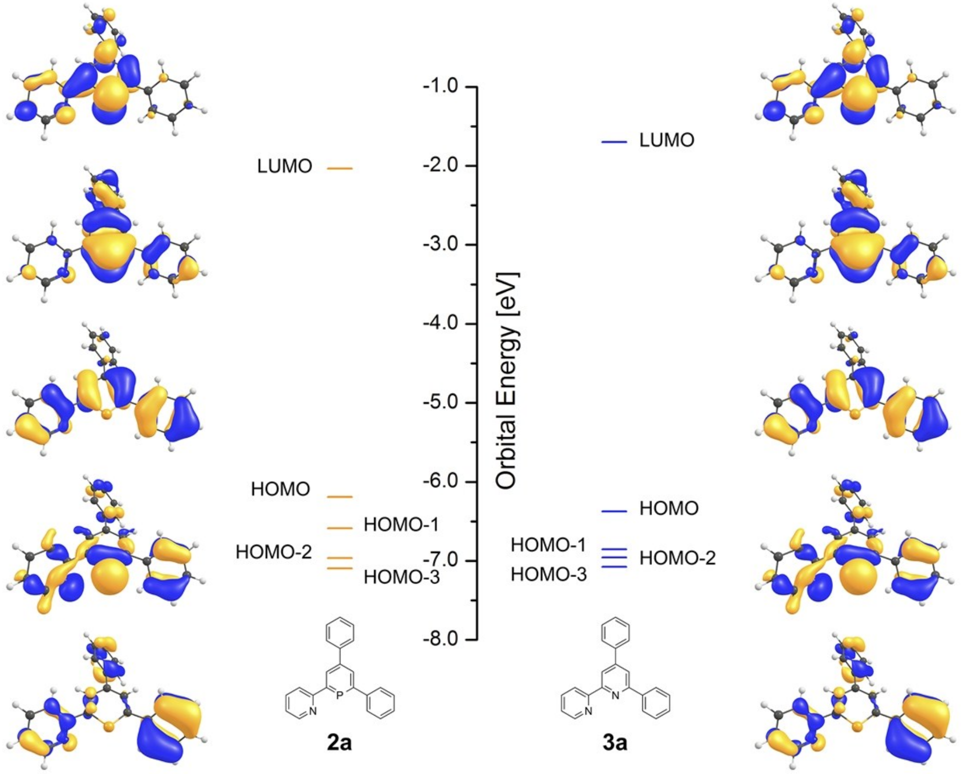

Figure S2: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2a** and **3a**.

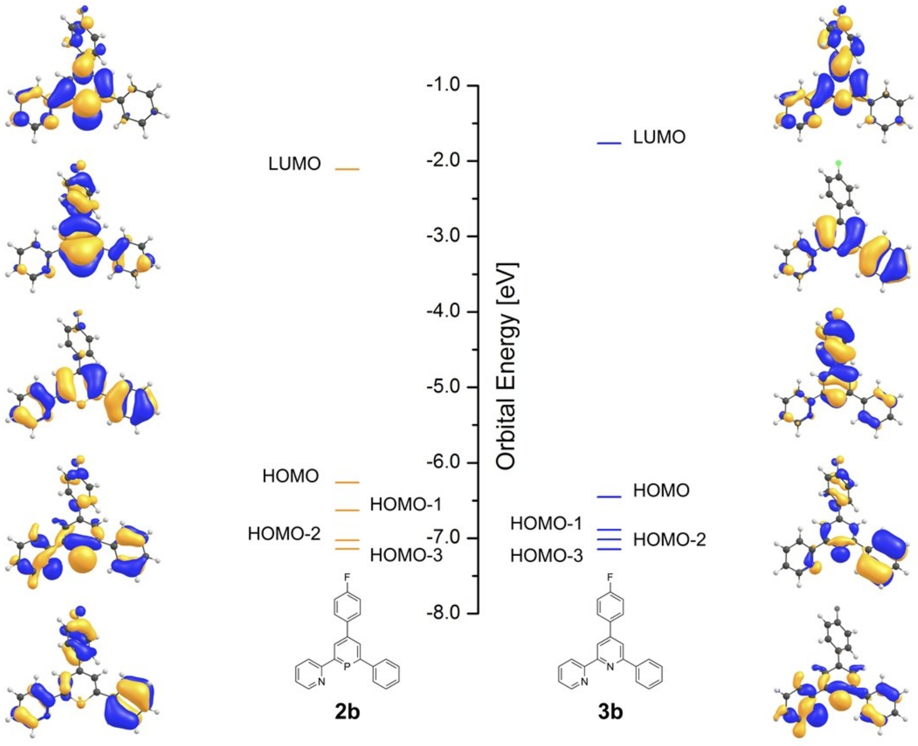

Figure S3: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2b** and **3b**.

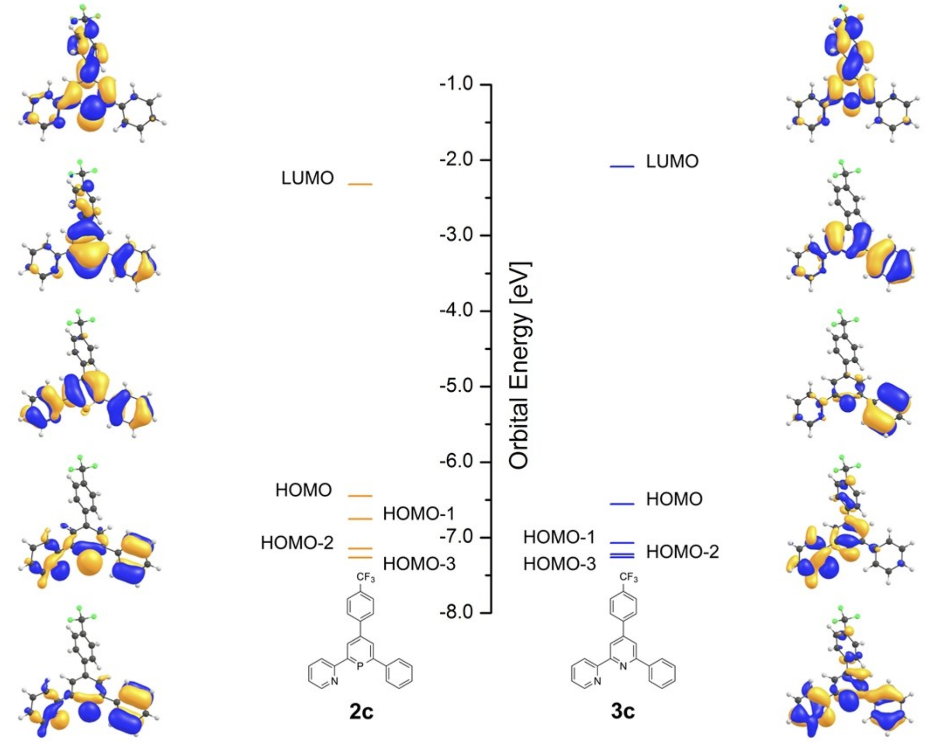

Figure S4: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2c** and **3c**.

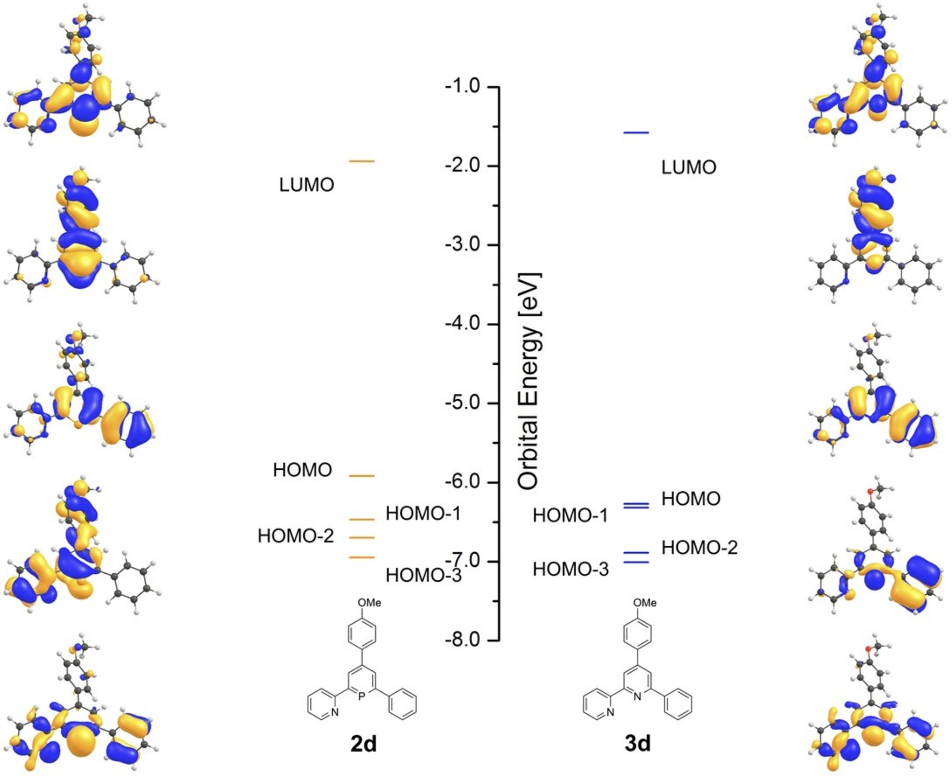

Figure S5: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2d** and **3d**.

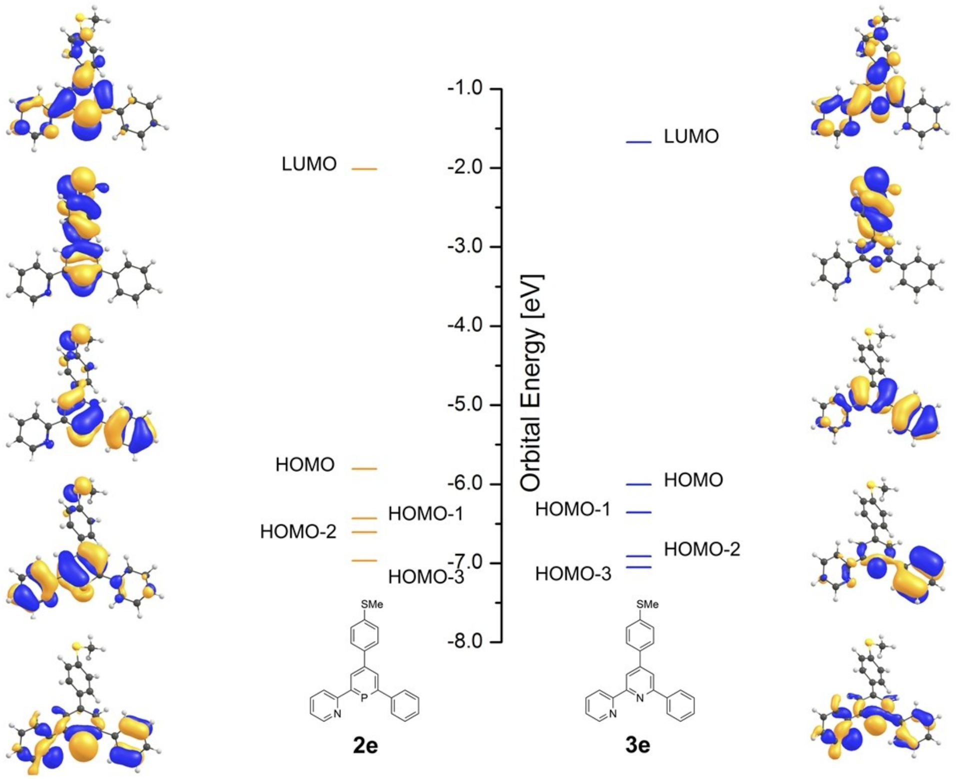

Figure S6: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2e** and **3e**.

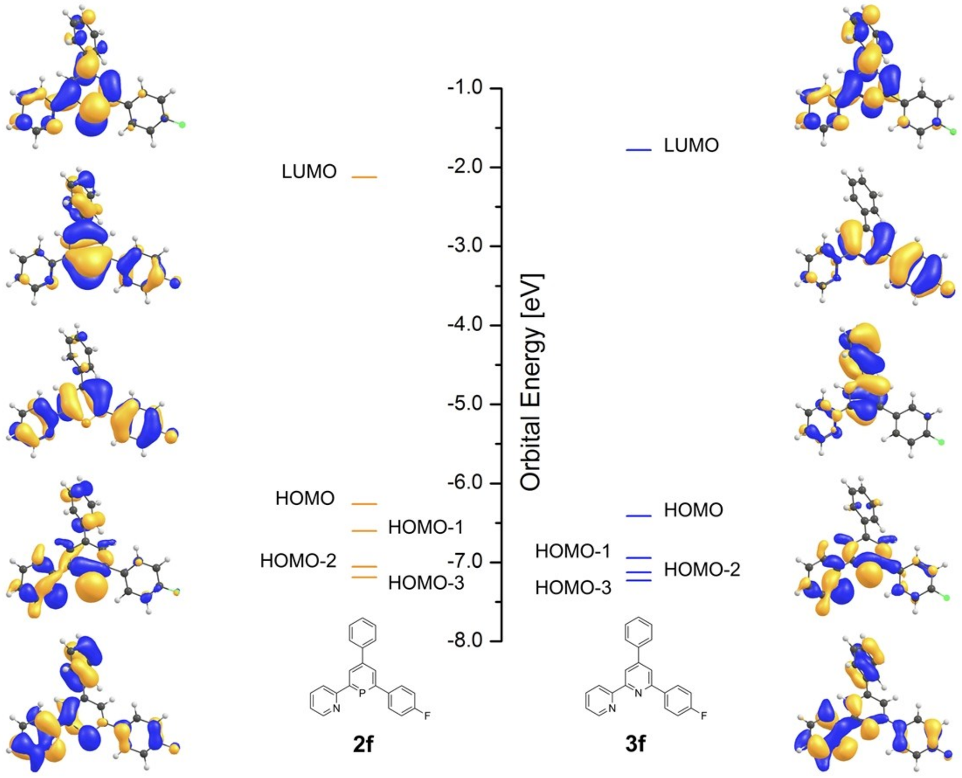

Figure S7: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2f** and **3f**.

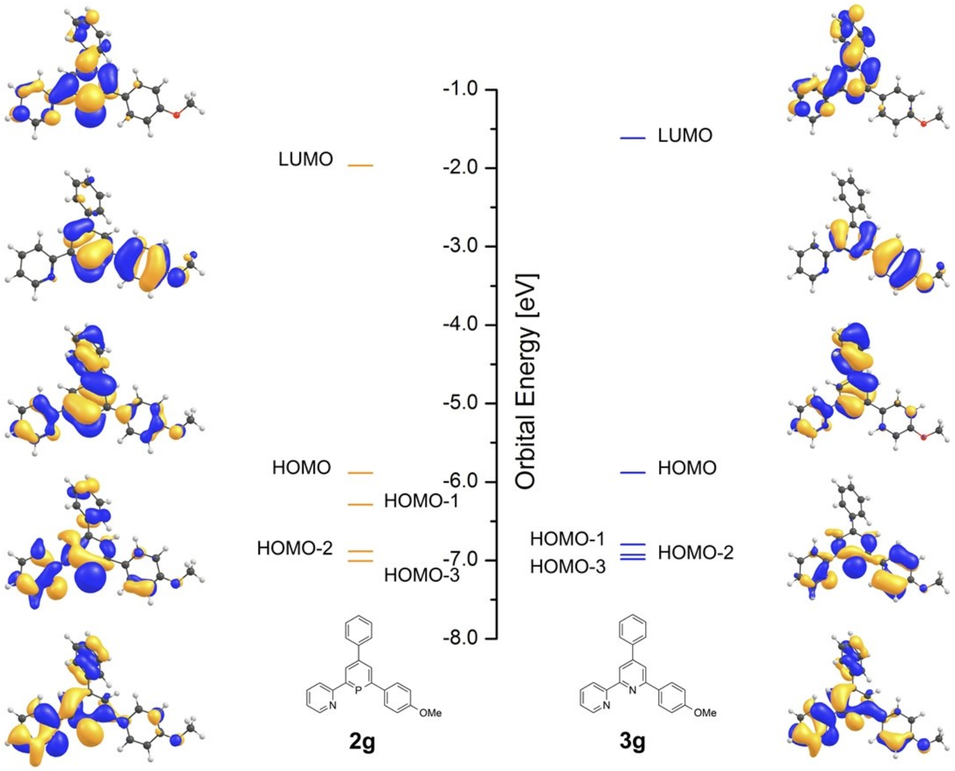

Figure S8: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2g** and **3g**.

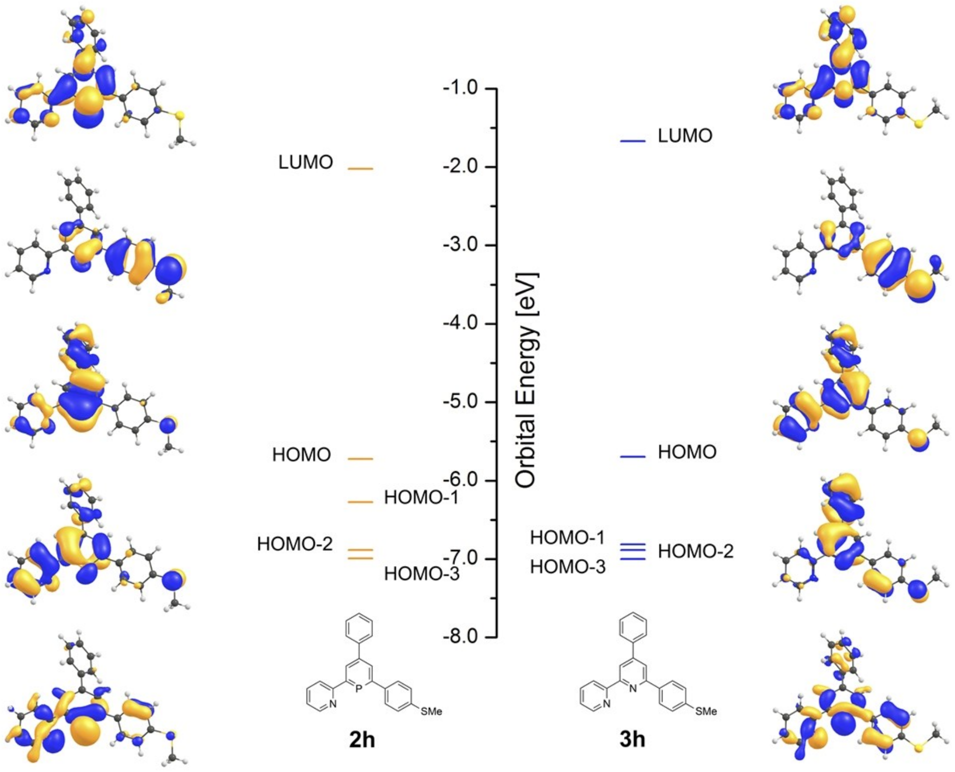

Figure S9: Energy levels of the LUMO to HOMO-3 for phosphinine- and bipyridine-derivative **2h** and **3h**.

Crystal Structure Determination:

2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyrylium tetrafluoroborate (1b)

Crystals suitable for X-ray diffraction were obtained from slow evaporation of an acetone solution.

Crystallographic data: $C_{22}H_{15}NOF$, BF_4, Fw = 415.16, 0.22×0.20×0.06 mm^3, yellow platelet, monoclinic, $P2_1/c$, a = 7.2677(2), b = 14.2809(3), c = 17.5498 (5) Å, β = 97.5668(9)°, V = 1805.62(8) Å^3, Z = 4, Dx = 1.527 gcm^{-3}, μ = 0.128 mm^{-1}. 28487 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} at a temperature of 100 K.[10] 2532 reflections were unique (R_{int} = 0.061). The structures were solved with SHELXS-2014[11] by using direct methods and refined with SHELXL-2014[11] on $F2$ for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 290 parameter were refined without restraints. R_1 = 0.040 for 2532 reflections with $I>2\sigma(I)$ and wR_2 = 0.100 for 3204 reflections, S = 1.048, residual electron density was between -0.23 and 0.22 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541815 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

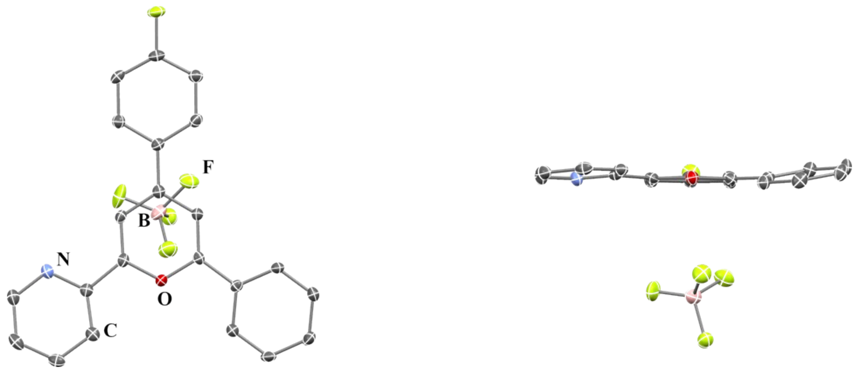

Figure S10: Molecular structure of **1b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyrylium tetrafluoroborate (1e)

Crystals suitable for X-ray diffraction were obtained by from a hot methanol solution.

Crystallographic data: $C_{23}H_{18}NOS$, BF_4, *F*w = 443.26, 0.21×0.13×0.09 mm^3, orange needle, triclinic, $P\bar{1}$, a = 8.1048(16), b = 11.553(2), c = 12.473(3) Å, α = 64.34(3)°, β = 81.29(3)°, γ = 77.44(3)°, V = 1025.4(5) Å^3, Z = 2, D_x = 1.436 gcm^{-3}, μ = 0.21 mm^{-1}. 11647 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK$_\alpha$ radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} at a temperature of 200 K.[10] 2875 reflections were unique (R_{int} = 0.055). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 280 parameters were refined without restraints. R_1 = 0.056 for 2875 reflections with $I>2\sigma(I)$ and wR_2 = 0.143 for 5484 reflections, S = 0.922, residual electron density was between -0.28 and 0.36 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541809 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

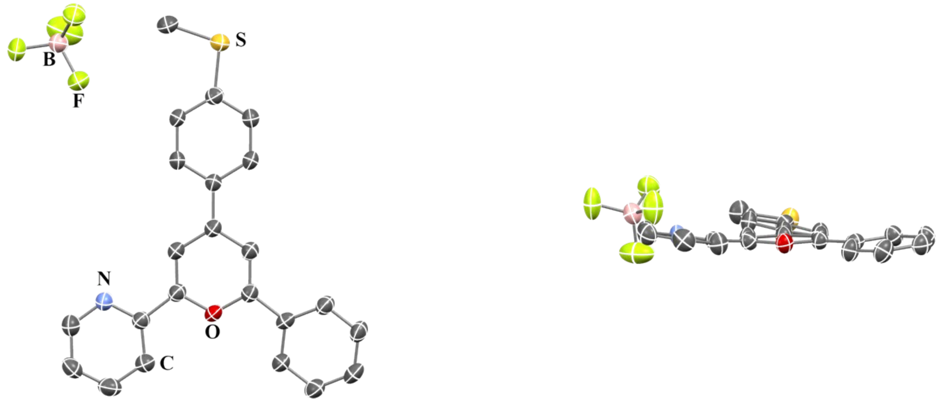

Figure S11: Molecular structure of **1e** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyrylium tetrafluoroborate (1h)

Crystals suitable for X-ray diffraction were obtained from slow evaporation of an acetone solution.

Crystallographic data: $C_{23}H_{18}NOS$, BF_4, *F*w = 443.25, 0.43×0.09×0.07 mm^3, red needle, monoclinic, *P2₁/c*, *a* = 10.0880(3), *b* = 26.1395(7), *c* = 7.7459(2) Å, *β* = 104.137(1)°, *V* = 1980.70(9) Å^3, *Z* = 4, *D*x = 1.468 gcm^{-3}, μ = 0.217 mm^{-1}. 17873 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} at a temperature of 100 K.[13] 2888 reflections were unique (R_{int} = 0.059). The structures were solved with SHELXS-2014[11] by using direct methods and refined with SHELXL-2014[11] on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 281 parameter were refined without restraints. R_1 = 0.053 for 2888 reflections with $I>2\sigma(I)$ and wR_2 = 0.125 for 3494 reflections, *S* = 1.054, residual electron density was between -0.70 and 1.09 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1542023 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

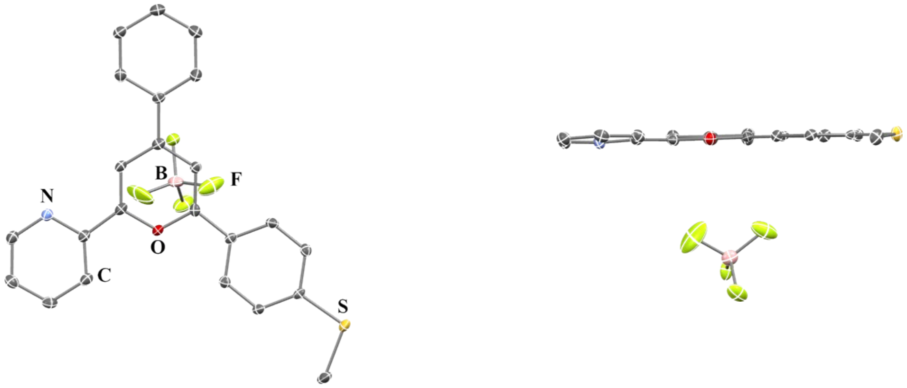

Figure S12: Molecular structure of **1h** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyridine (3c)

Crystals suitable for X-ray diffraction were obtained from a hot ethanol solution.

Crystallographic data: $C_{23}H_{15}F_3N_2$, Fw = 376.37, 0.65×0.06×0.05 mm^3, colourless needle, monoclinic, $P2_1/c$, a = 10.6860(3), b = 21.8463(5), c = 7.4437(1) Å, β = 92.658(1)°, V = 1735.86(7) $Å^3$, Z = 4, Dx = 1.440 gcm^{-3}, μ = 0.11 mm^{-1}. 16134 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 $Å^{-1}$ at a temperature of 100 K.[13] 2510 reflections were unique (R_{int} = 0.045). The structures were solved with SHELXS-2013[11] by using direct methods and refined with SHELXL-2013 on $F2$ for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 253 parameter were refined without restraints. R_1 = 0.043 for 2510 reflections with $I>2\sigma(I)$ and wR_2 = 0.108 for 3069 reflections, S = 1.035, residual electron density was between -0.32 and 0.49 $eÅ^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

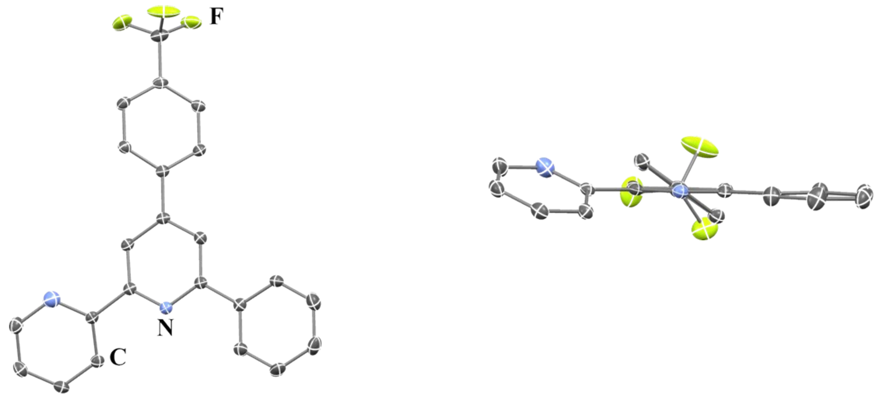

Figure S13: Molecular structure of **3c** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyridine (3h)

Crystals suitable for X-ray diffraction were obtained from a hot ethanol solution.

Crystallographic data: $C_{23}H_{18}N_2S$, *F*w = 354.45, 0.56×0.10×0.05 mm^3, colourless needle, monoclinic, *P2₁/c*, *a* = 19.3924(2), *b* = 5.14157(5), *c* = 18.1289 (2) Å, *β* = 99.9167(7)°, *V* = 1780.58(3) $Å^3$, *Z* = 4, *D*x = 1.322 gcm^{-3}, μ = 1.661 mm^{-1}. 10917 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (CuKα radiation, λ = 1.54178 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 $Å^{-1}$ at a temperature of 100 K.[13] 2518 reflections were unique (R_{int} = 0.068). The structures were solved with SHELXS-2014[11] by using direct methods and refined with SHELXL-2014 on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 236 parameter were refined without restraints. R_1 = 0.062 for 2518 reflections with $I>2\sigma(I)$ and wR_2 = 0.166 for 3146 reflections, *S* = 1.026, residual electron density was between -0.57 and 0.40 $eÅ^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541812 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

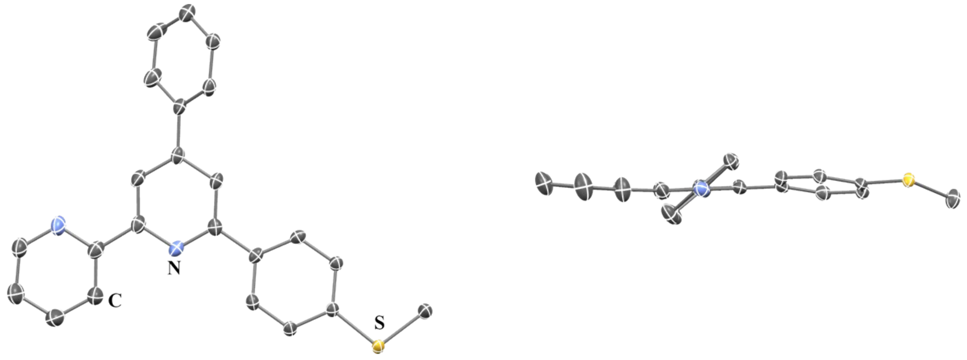

Figure S14: Molecular structure of **3h** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine-P,N-tungsten tetracarbonyl (4f)

Crystals suitable for X-ray diffraction were obtained from a hot tetrahydrofuran solution.

Crystallographic data: $C_{26}H_{15}FNO_4PW$, *F*w = 639.20, 0.38×0.04×0.04 mm^3, orange needle, orthorhombic, $Pna2_1$, a = 16.3244(17), b = 18.5970(12), c = 7.2964(5) Å, V = 2215.1(3) Å^3, Z = 4, D_x = 1.917 gcm^{-3}, μ = 5.33 mm^{-1}. 10058 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK$_\alpha$ radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.69 Å^{-1} at a temperature of 200 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.41–0.84 correction range).[10] 3832 reflections were unique (R_{int} = 0.042). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 309 parameters were refined with one restraint. R_1 = 0.041 for 3832 reflections with $I>2\sigma(I)$ and wR_2 = 0.102 for 5235 reflections, S = 0.949, residual electron density was between -1.18 and 1.15 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12] (Flack x parameter = -0.01(2)).[14]

CCDC-1541818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

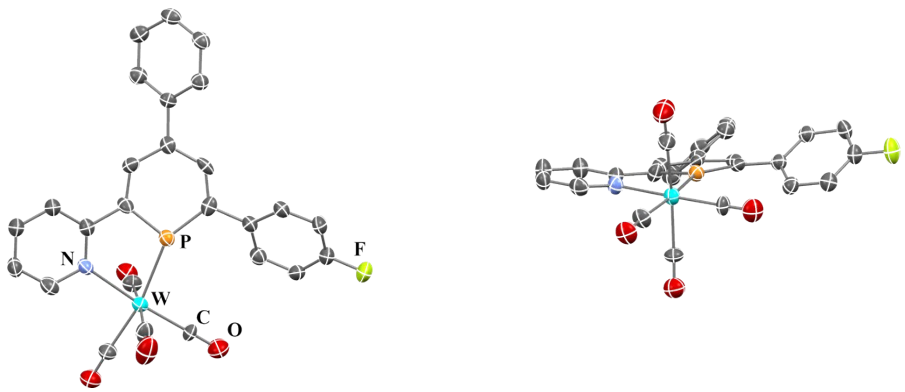

Figure S15: Molecular structure of **4f** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)phosphinine-P,N-tungsten tetracarbonyl (4g)

Crystals suitable for X-ray diffraction were obtained from a hot acetonitrile solution.

Crystallographic data: $C_{27}H_{18}NO_5PW$, *F*w = 651.23, 0.46×0.27×0.07 mm^3, red rhombus, monoclinic, *P2$_1$/n*, a = 8.2075(16), b = 18.297(4), c = 16.182(3) Å, β = 98.63(3)°, V = 2402.6(9) Å^3, Z = 4, D_x = 1.800 gcm^{-3}, μ = 4.91 mm^{-1}. 18474 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK$_\alpha$ radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.69 Å^{-1} at a temperature of 220 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.32–0.65 correction range).[10] 4729 reflections were unique (R_{int} = 0.038). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 317 parameters were refined without restraints. R_1 = 0.033 for 4729 reflections with $I>2\sigma(I)$ and wR_2 = 0.078 for 6473 reflections, S = 0.908, residual electron density was between -1.34 and 1.29 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541806 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

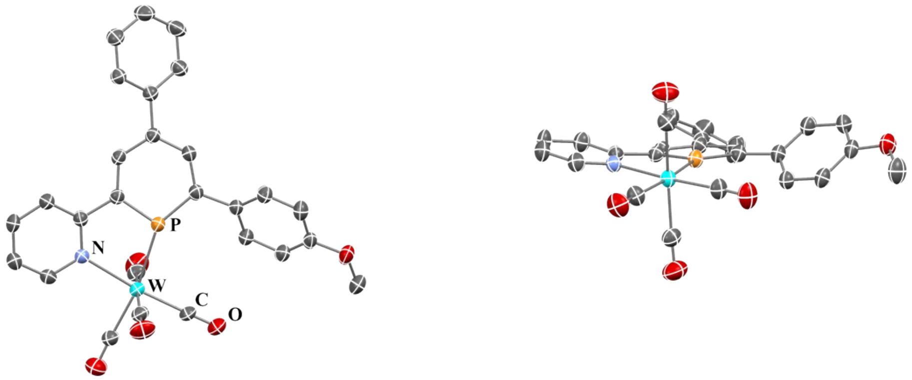

Figure S16: Molecular structure of **4g** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5b)

Crystals suitable for X-ray diffraction were obtained from the reaction mixture.

Crystallographic data: $2\times(C_{26}H_{15}FN_2O_4W)$, C_2H_3N, Fw =1285.53, $0.21\times0.18\times0.16$ mm^3, dark prism, tetragonal, $P4_12_12$, a = 11.888(1), b = 11.888(1), c = 32.757(5) Å, V = 4629.4(11) Å^3, Z = 4, D_x = 1.844 gcm^{-3}, μ = 5.04 mm^{-1}. 76012 reflections were measured by using a Bruker-AXS smart CCD area detector diffractometer (MoKα radiation, λ = 0.71073 Å)[13] up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.72 Å^{-1} at a temperature of 100 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the SADABS program[13] (0.65-0.75 correction range). 4729 reflections were unique (R_{int} = 0.052). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97[11] on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 330 parameters were refined without restraints. R_1 = 0.042 for 4534 reflections with $I>2\sigma(I)$ and wR_2 = 0.086 for 7093 reflections, S=1.138, residual electron density was between -2.13 and 1.40 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12] (Flack x parameter = 0.007(17)).[14]

CCDC-1541814 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

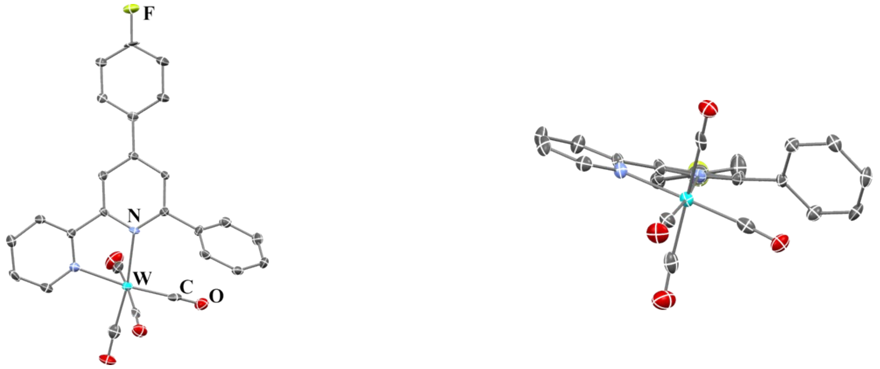

Figure S17: Molecular structure of **5b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5c)

Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution.

Crystallographic data: $C_{27}H_{15}F_3N_2O_4W$, Fw = 672.25, 0.42×0.20×0.07 mm^3, colourless block, monoclinic, $P2_1/c$, a = 14.5198(7), b = 17.2400(9), c = 19.1014(10) Å, β = 99.3220(14)°, V = 4718.3(4) Å^3, Z = 8, Dx = 1.893 gcm^{-3}; μ = 4.96 mm^{-1}. 78726 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.72 Å^{-1} at a temperature of 100 K.[13] The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the SADABS program[13] (0.34–0.75 correction range). 13202 reflections were unique (R_{int} = 0.037). The structures were solved with SHELXS-2013[11] by using direct methods and refined with SHELXL-2013 on $F2$ for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 667 parameter were refined without restraints. R_1 = 0.019 for 13202 reflections with $I>2\sigma(I)$ and wR_2 = 0.044 for 14451 reflections, S = 1.049, residual electron density was between -1.49 and 0.84 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541819 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

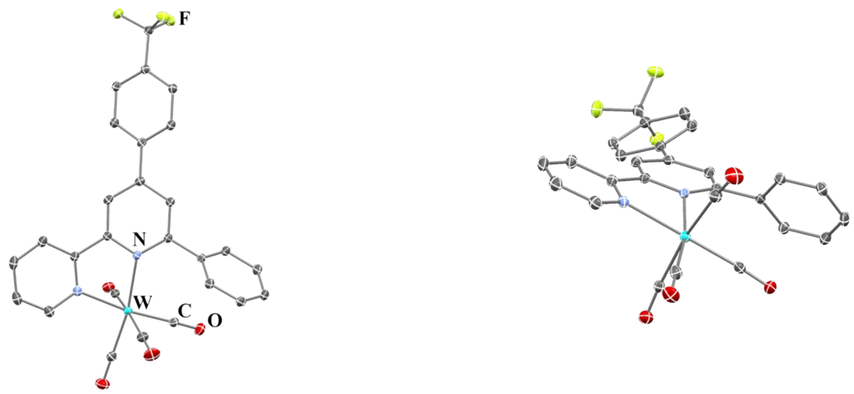

Figure S18: Molecular structure of **5c** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5d)

Crystals suitable for X-ray diffraction were obtained from slow evaporation of a tetrahydrofuran solution.

Crystallographic data: $C_{27}H_{18}N_2O_5W$, *F*w = 634.27, 0.37×0.22×0.14 mm^3, red block, monoclinic, $P2_1/n$, a = 8.1178(16), b = 16.843(3), c= 16.736(3) Å, β = 90.90(3)°,V = 2288.0(7) Å^3, Z = 4, D_x = 1.841 gcm^{-3}, μ = 5.09 mm^{-1}. 11284 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK$_\alpha$ radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} at a temperature of 220 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.31–0.53) correction range.[10] 3231 reflections were unique (R_{int} = 0.043). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 317 parameters were refined without restraints. R_1 = 0.044 for 3231 reflections with $I>2\sigma(I)$ and wR_2 = 0.104 for 4005 reflections, S = 1.175, residual electron density was between -1.61 and 2.82 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541813 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

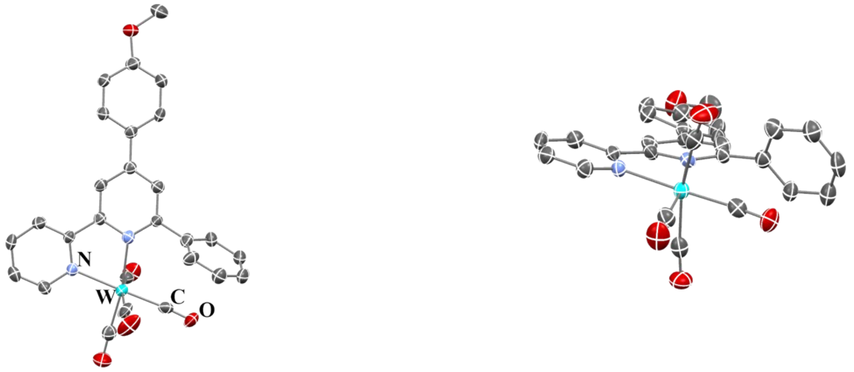

Figure S19: Molecular structure of **5d** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5e)

Crystals suitable for X-ray diffraction were obtained from an acetonitrile solution.

Crystallographic data: $C_{27}H_{18}N_2O_4SW$, *F*w = 650.34, 0.30×0.25×0.20 mm^3, red cube, monoclinic, *P2$_1$/n*, *a* = 7.8635(6), *b* = 16.7687(9), *c* = 18.1335(12) Å, *β* = 98.182(6)°, *V* = 2366.8(3) Å^3, *Z* = 4, D_x = 1.825 gcm^{-3}, *μ* = 5.01 mm^{-1}. 18073 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK$_\alpha$ radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.69 Å^{-1} at a temperature of 200 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.35–0.45 correction range).[10] 4616 reflections were unique (R_{int} = 0.050). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 318 parameters were refined without restraints. R_1 = 0.034 for 4616 reflections with $I>2\sigma(I)$ and wR_2 = 0.078 for 6352 reflections, *S* = 0.944, residual electron density was between -1.10 and 1.37 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

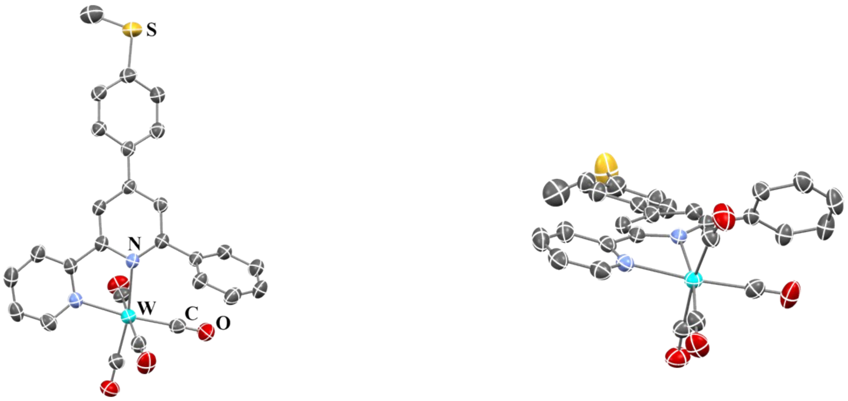

Figure S20: Molecular structure of **5e** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)pyridine-N,N-tungsten tetracarbonyl (5f)

Crystals suitable for X-ray diffraction were obtained from slow evaporation of tetrahydrofuran. *Crystallographic data*: $C_{26}H_{15}FN_2O_4W$, *F*w = 622.24, 0.55×0.15×0.04 mm^3, red platelet, triclinic, $P\bar{1}$, *a* = 7.611(2), *b* = 13.016(4), *c* = 13.175(4) Å, α = 79.773(6)°, *β* = 73.331(6), γ = 83.135(6)°, *V* = 1227.2(6) Å^3, *Z* = 2, *D*x = 1.684 gcm^{-3}, μ = 4.75 mm^{-1}. 15071 reflections were measured by using a Bruker-AXS smart CCD area detector diffractometer (MoKα radiation, λ = 0.71073 Å)[13] up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.72 Å^{-1} at a temperature of 100 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the SADABS program[13] (0.49–0.75 correction range). 6419 reflections were unique (R_{int} = 0.018). The structures were solved with SHELXS-2013[11] by using direct methods and refined with SHELXL-2013 on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displace–ment parameters. The positions of the hydrogen atoms were calculated for idealized positions. 307 parameter were refined without restraints. R_1 = 0.018 for 6419 reflections with $I > 2\sigma(I)$ and wR_2 = 0.046 for 6890 reflections, *S* = 1.062, residual electron density was between -0.77 and 1.29 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

SQUEEZE RESULTS (APPEND TO CIF)[15]

Note: Data are Listed for all Voids in the P1 Unit Cell i.e. Centre of Gravity, Solvent Accessible Volume, Recovered number of Electrons in the Void and Details about the Squeezed Material.

```
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1 -0.039  0.000  0.000      184       37 ' '
_platon_squeeze_details
```

The general procedure (based on a preliminary implementation of the technique) has been described as the 'BYPASS procedure' by Sluis and Spek.[16]

CCDC-1541810 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

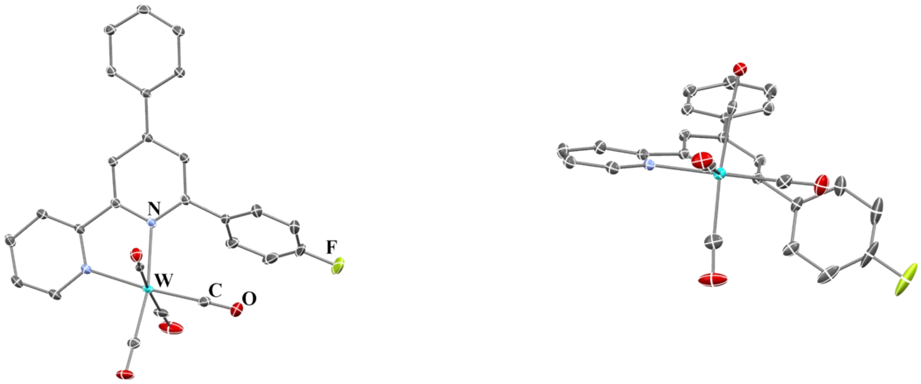

Figure S21: Molecular structure of **5f** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)pyridine-N,N-tungsten tetracarbonyl (5g)

Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution.

Crystallographic data: $C_{27}H_{18}N_2O_5W$, *F*w = 634.27, 0.42 0.29×0.05 mm^3, red plate, monoclinic, *P2₁/c*, *a*= 8.3701(5), *b* = 16.0053(7), *c* = 17.5299(11) Å, *β* = 92.967(5)°, *V* = 2345.3(2) Å^3, *Z* = 4, D_x = 1.796 gcm^{-3}, μ = 4.97 mm^{-1}. 22039 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK_α radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.69 Å^{-1} at a temperature of 200 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.17–0.59 correction range).[10] 4837 reflections were unique (R_{int} = 0.044). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 318 parameters were refined without restraints. R_1 = 0.026 for 4837 reflections with $I>2\sigma(I)$ and wR_2 = 0.063 for 6186 reflections, *S* = 0.934, residual electron density was between -0.95 and 0.82 eÅ^{-3}. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541816 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

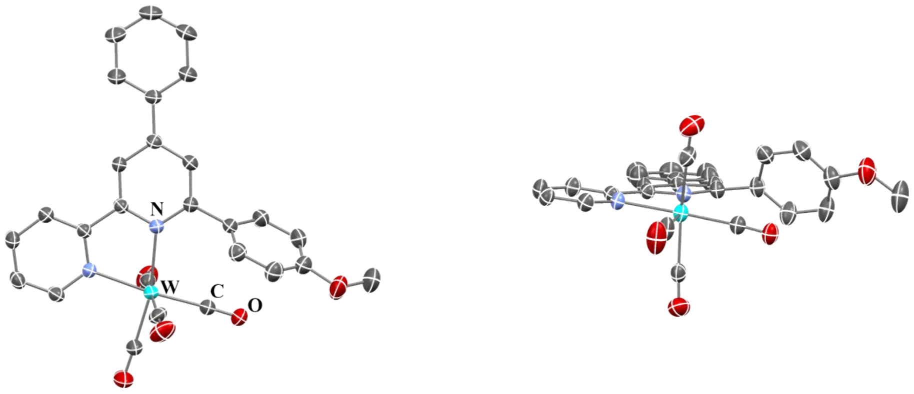

Figure S22: Molecular structure of **5g** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyridine-N,N-tungsten tetracarbonyl (5h)

Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution.

Crystallographic data: $C_{27}H_{18}FN_2O_4SW$, *F*w = 650.34, 0.14×0.11×0.09 mm^3, red block, monoclinic, $P2_1/c$, a = 8.4430(17), b = 16.193(3), c = 17.514(4) Å, β = 92.85(3)°, V = 2391.5(9) $Å^3$, Z = 4, D_x = 1.806 gcm^{-3}, μ = 4.96 mm^{-1}. 17632 reflections were measured by using a Stoe IPDS 2T diffractometer with a rotating anode (MoK_α radiation, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.69 $Å^{-1}$ at a temperature of 220 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.58–0.77 correction range).[10] 2551 reflections were unique (R_{int} = 0.090). The structures were solved with SHELXS-97[11] by using direct methods and refined with SHELXL-97 on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 308 parameters were refined without restraints. R_1 = 0.041 for 2551 reflections with $I > 2\sigma(I)$ and wR_2 = 0.081 for 6431 reflections, S = 0.730, residual electron density was between -3.67 and 1.22 $eÅ^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[12]

CCDC-1541817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

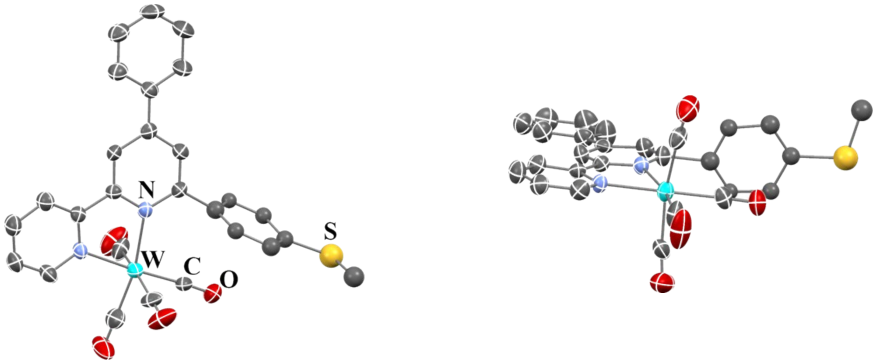

Figure S23: Molecular structure of **5h** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. The MeS-phenyl ring is disordered.

NMR Spectra:

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylphosphinine (2d)

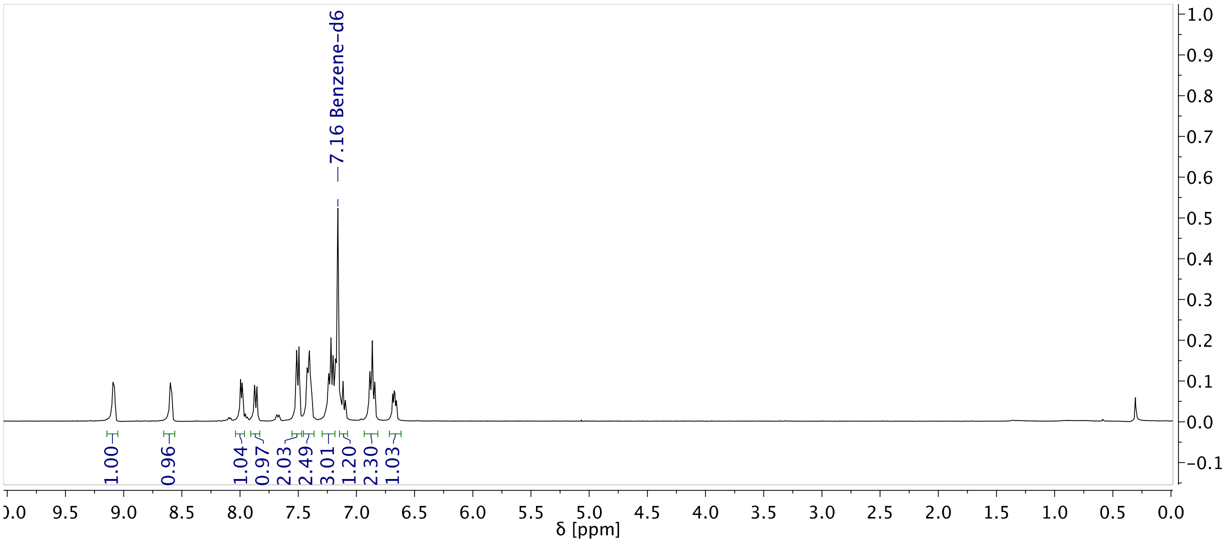

Figure S24: ^{1}H NMR spectrum of phosphinine **2d**.

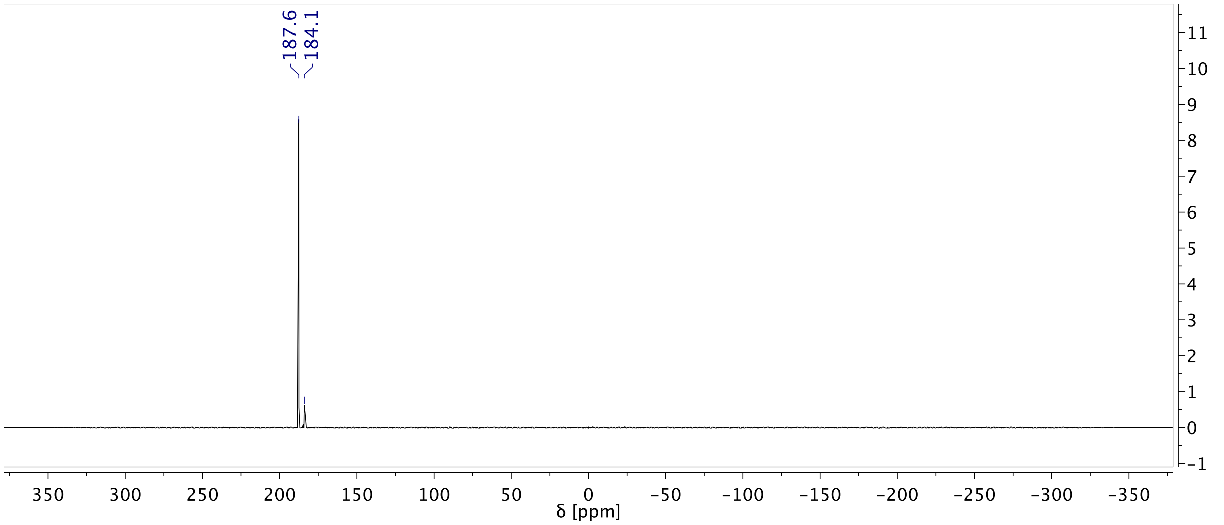

Figure S25: ^{31}P NMR spectrum of phosphinine **2d**.

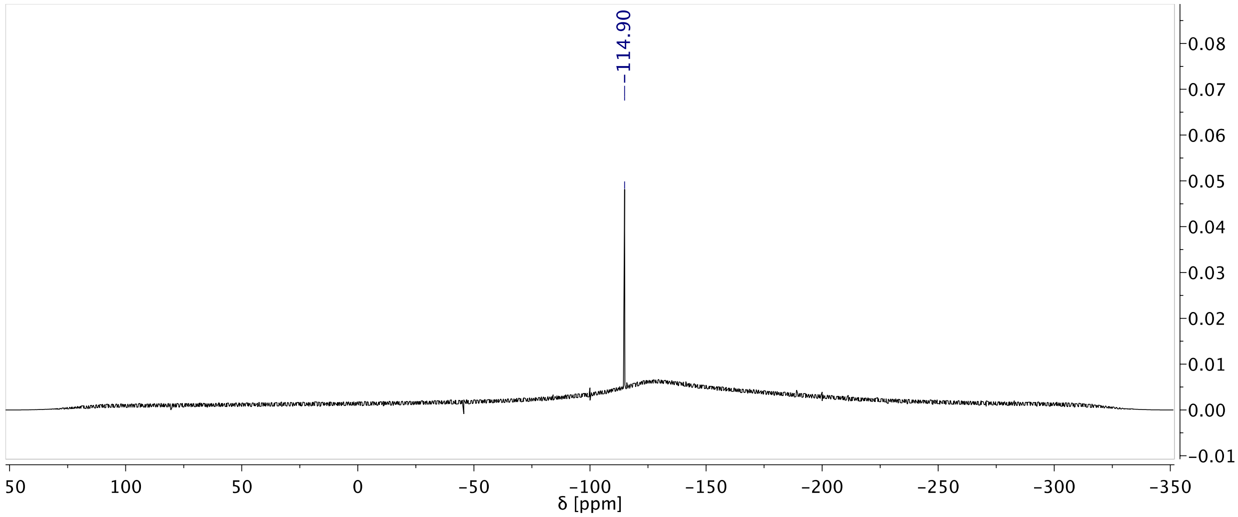

Figure S26: ^{19}F NMR spectrum of phosphinine **2d**.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine (2f)

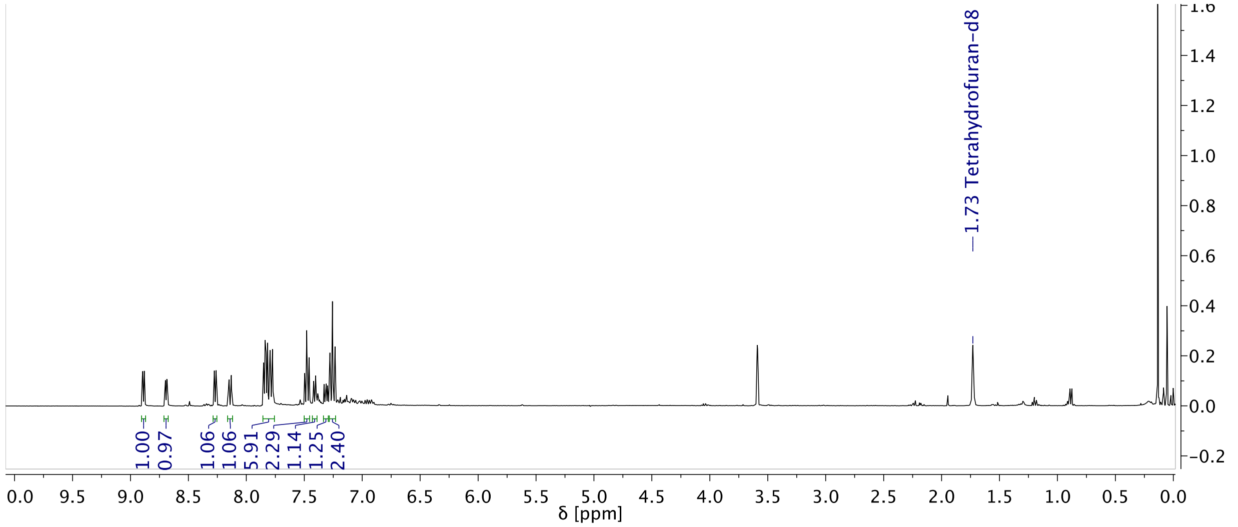

Figure S27: ^{1}H NMR spectrum of phosphinine **2f**.

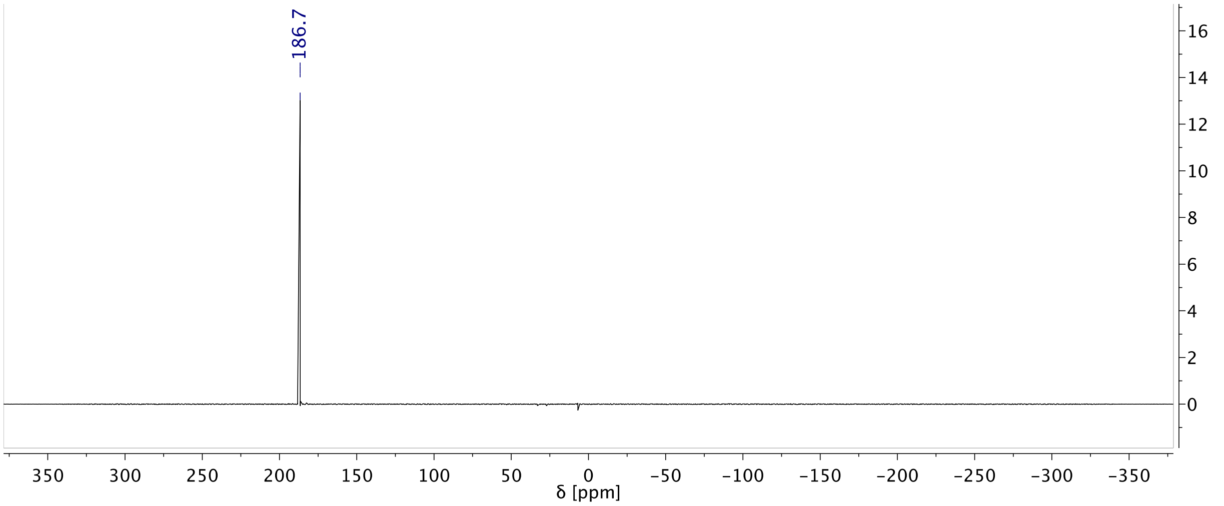

Figure 28: ^{31}P NMR spectrum of phosphinine **2f**.

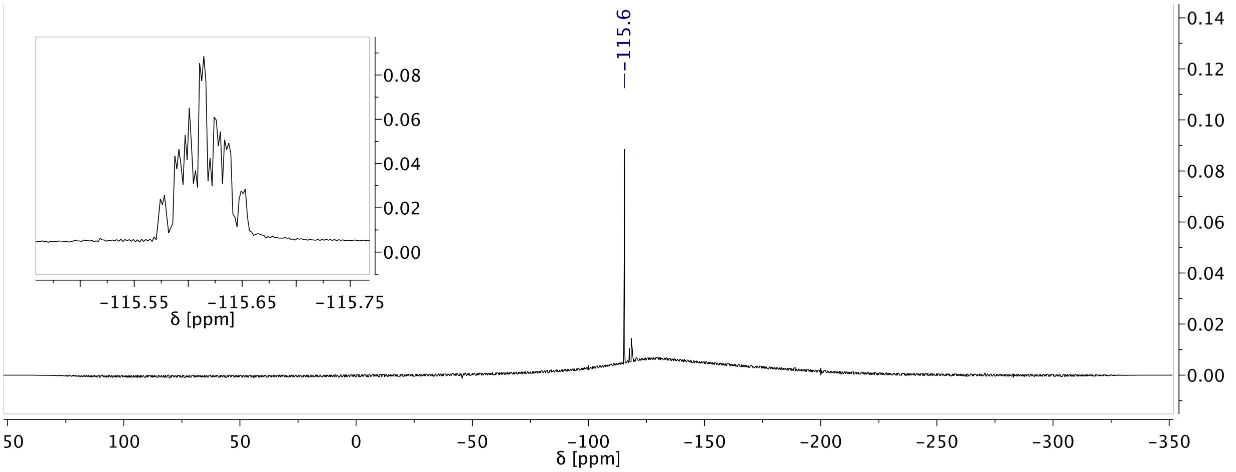

Figure 29: ^{19}F NMR spectrum of phosphinine **2f**.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)phosphinine (2g)

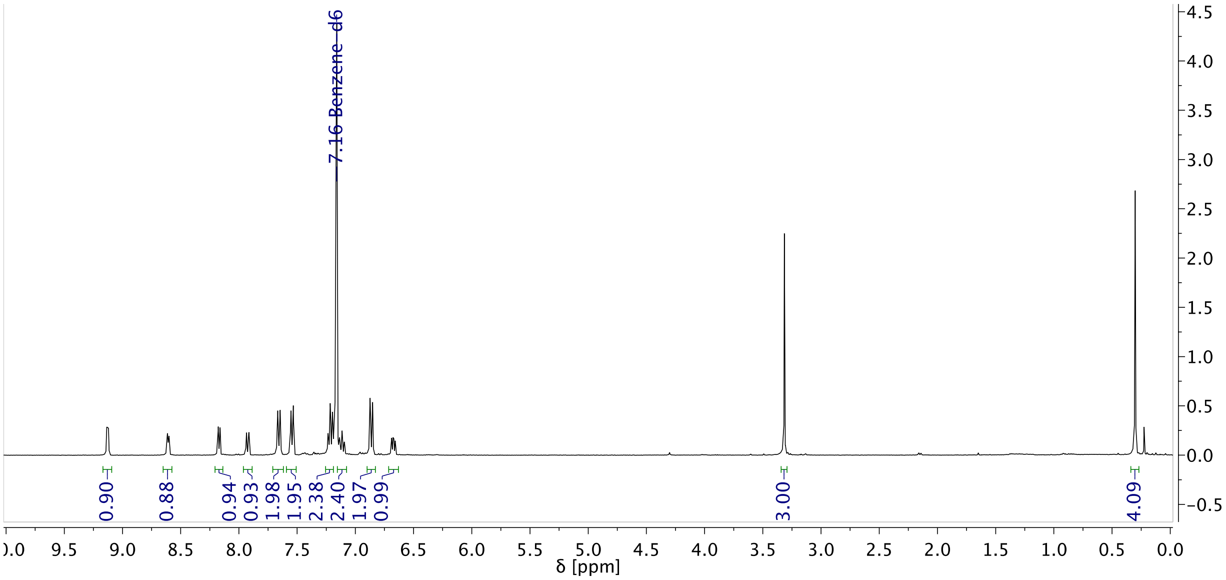

Figure 30: ^{1}H NMR spectrum of phosphinine **2g**.

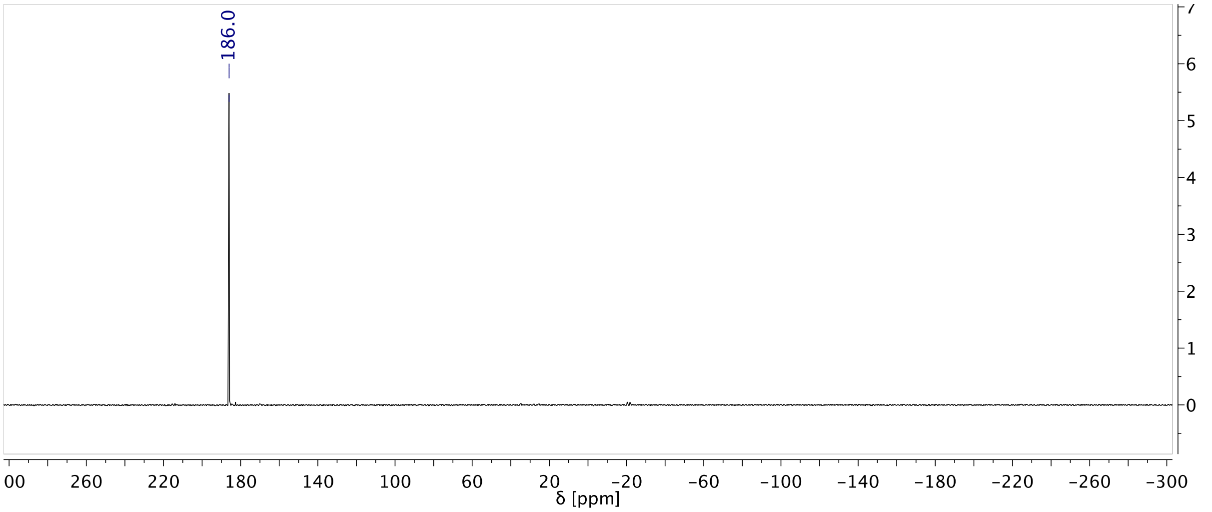

Figure 31: ^{31}P NMR spectrum of phosphinine **2g**.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine (2h)

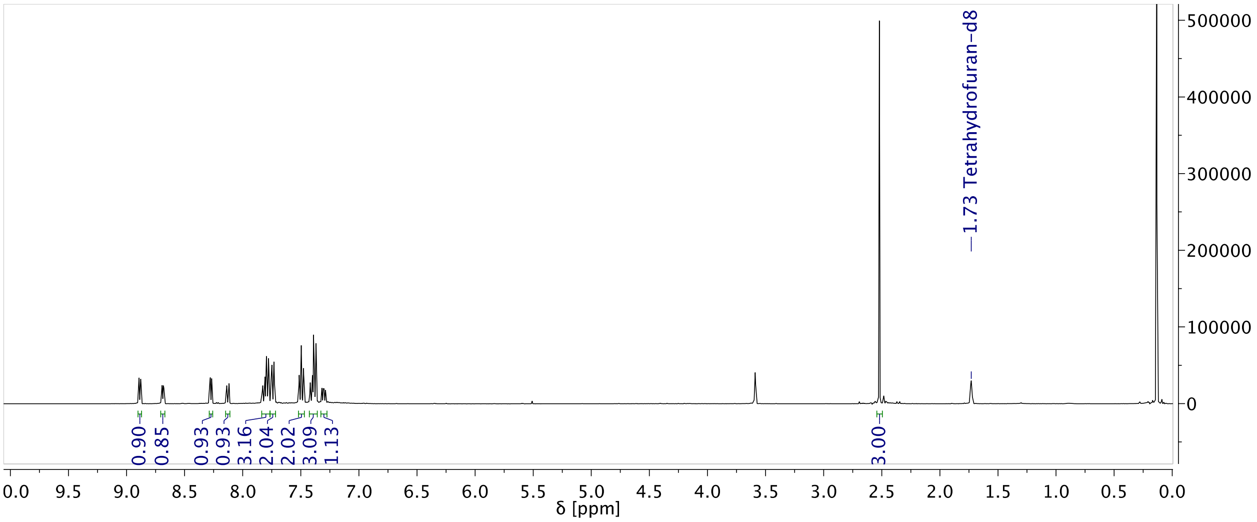

Figure 32: ^{1}H NMR spectrum of phosphinine **2h**.

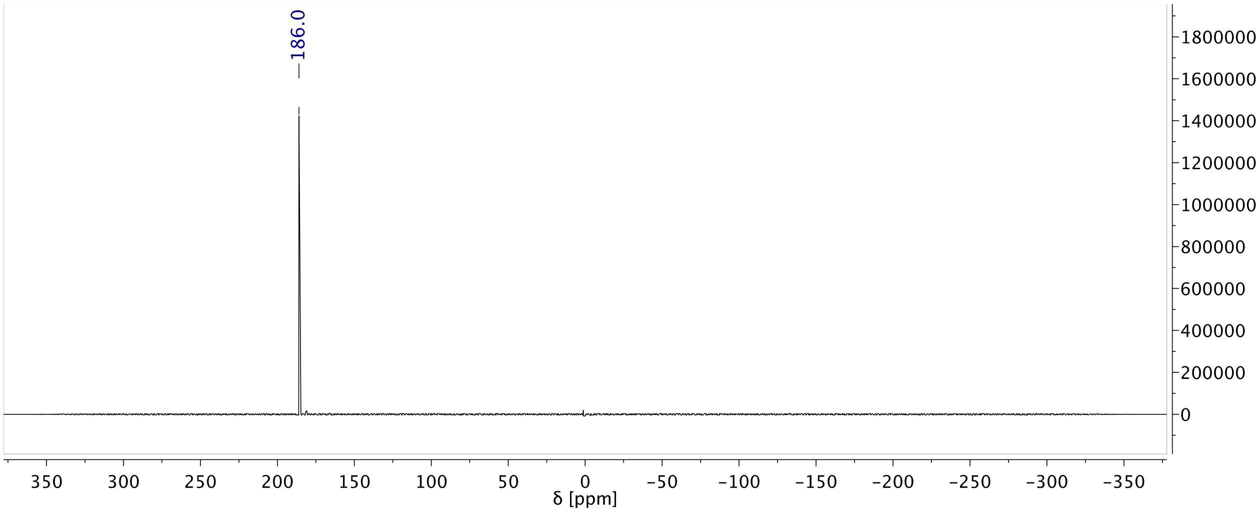

Figure 33: ^{31}P NMR spectrum of phosphinine **2h**.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylphosphinine-P,N-tungsten tetra-carbonyl (4d)

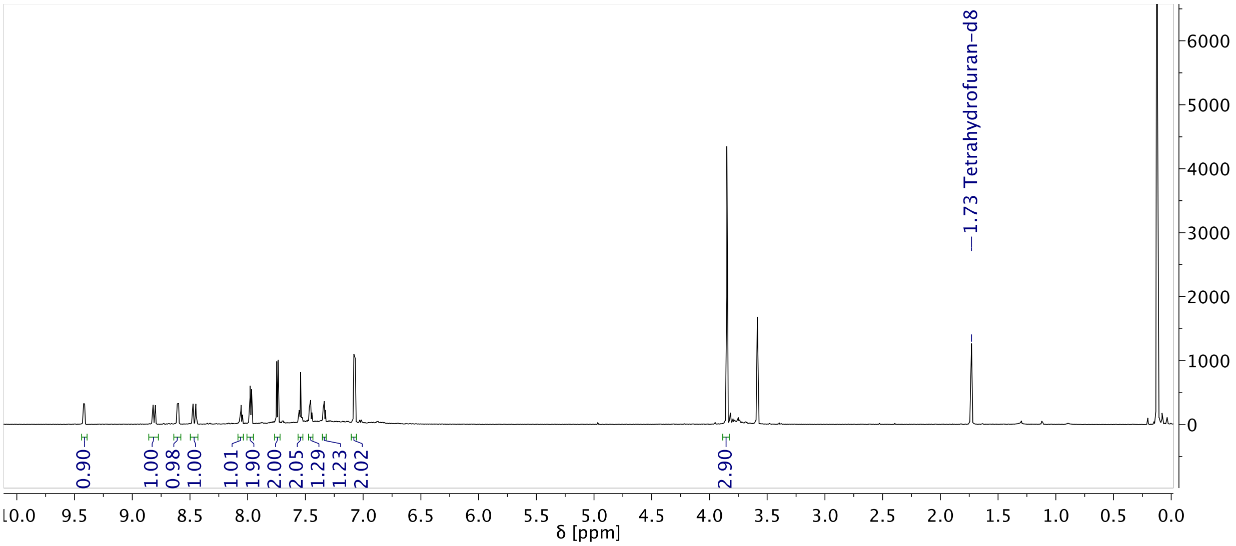

Figure 34: ^{1}H NMR spectrum of tungsten complex **4d**.

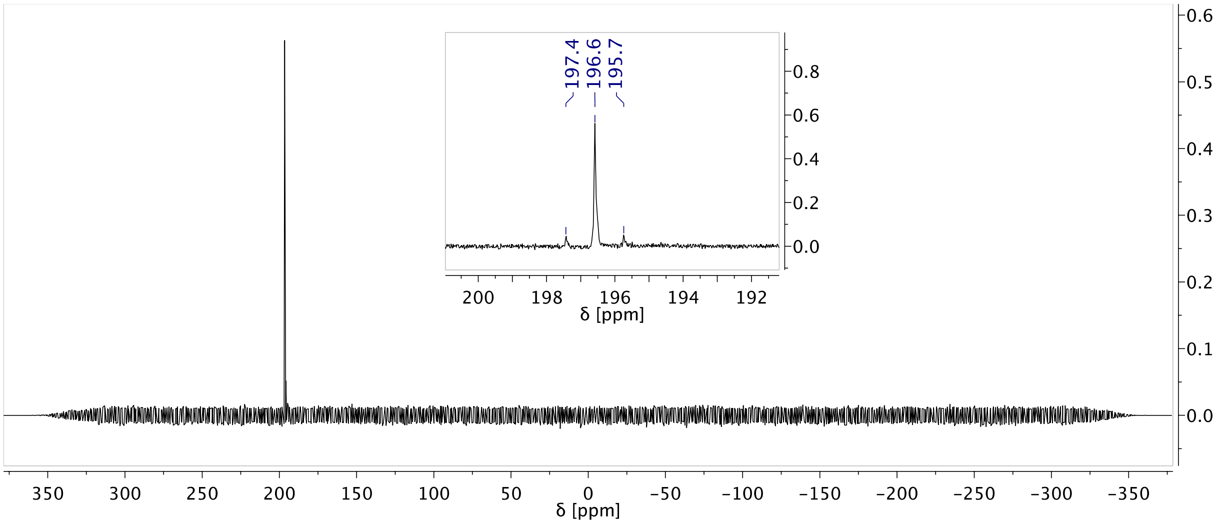

Figure 35: ^{31}P NMR spectrum of tungsten complex **4d**.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine-P,N-tungsten tetracarbonyl (4f)

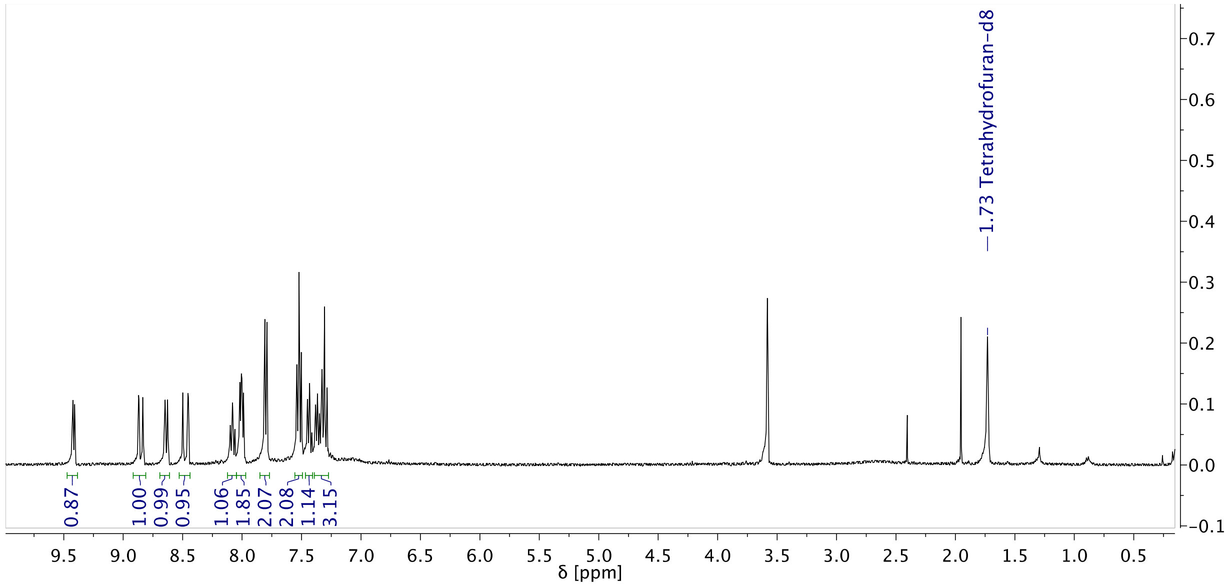

Figure 36: ^{1}H NMR spectrum of tungsten complex **4f**.

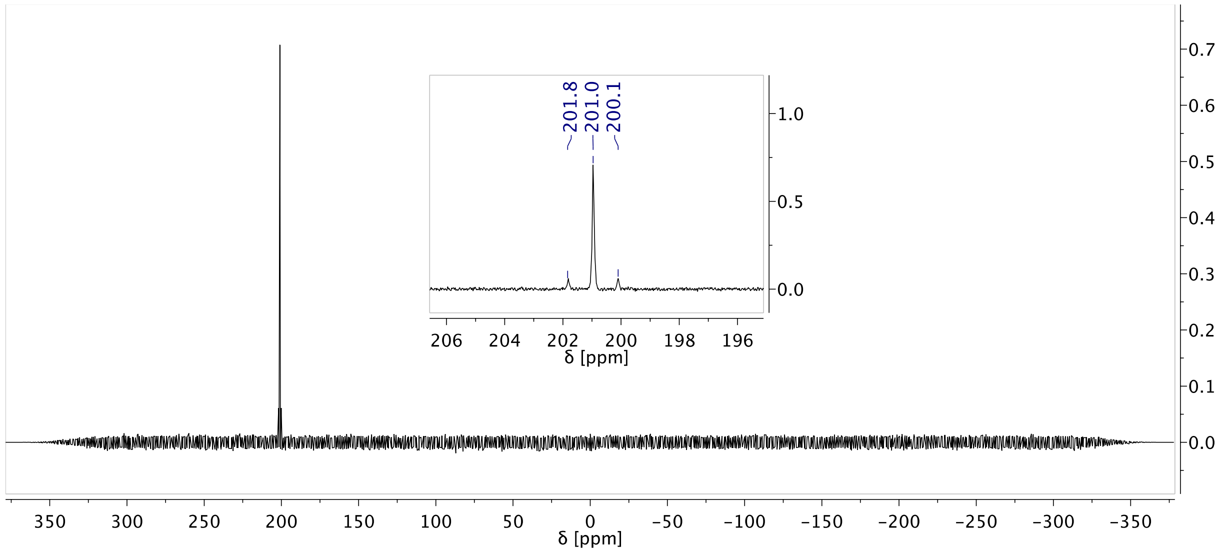

Figure 37: ^{31}P NMR spectrum of tungsten complex **4f**.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)phosphinine-P,N-tungsten tetra-carbonyl (4g)

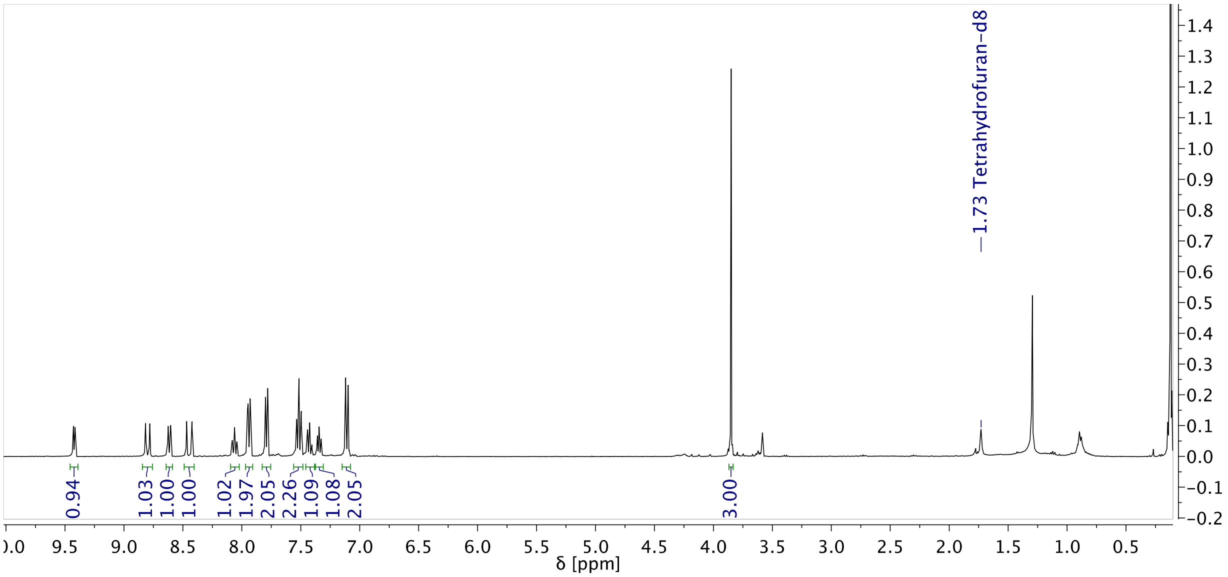

Figure 38: ^{1}H NMR spectrum of tungsten complex **4g**.

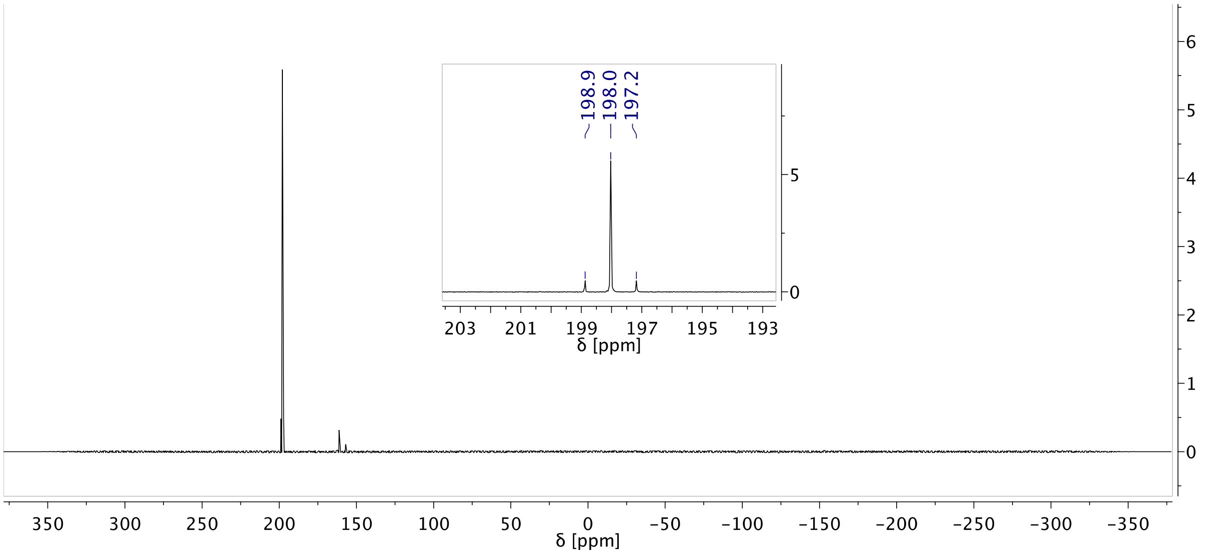

Figure 39: ^{31}P NMR spectrum of **4g**.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine-P,N-tungsten tetracarbonyl (4h)

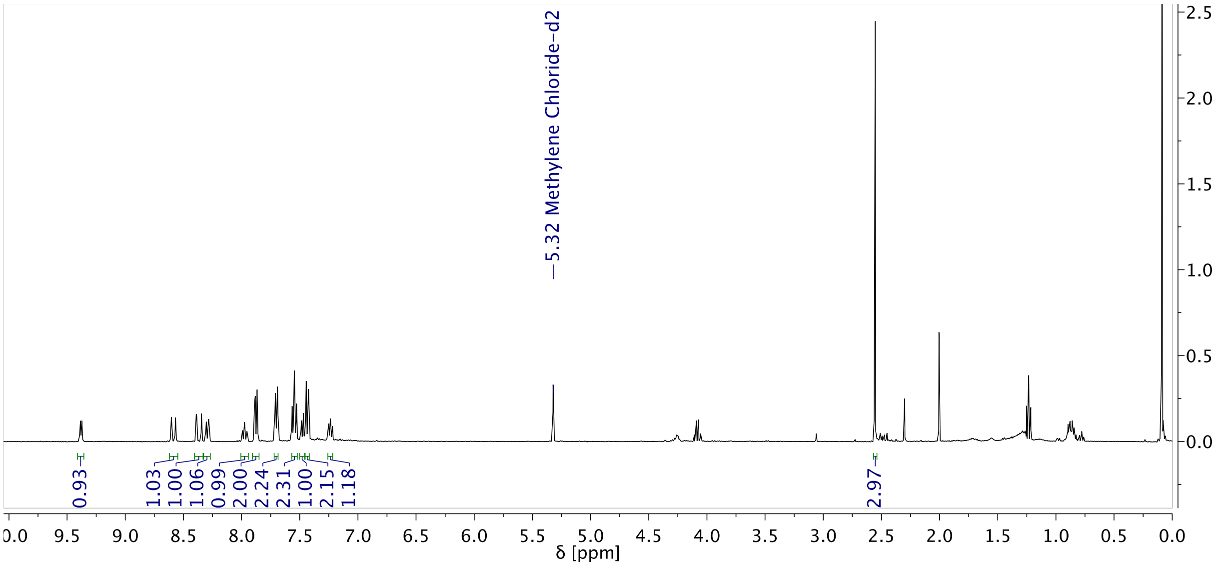

Figure 40: ^{1}H NMR spectrum of tungsten complex **4h**.

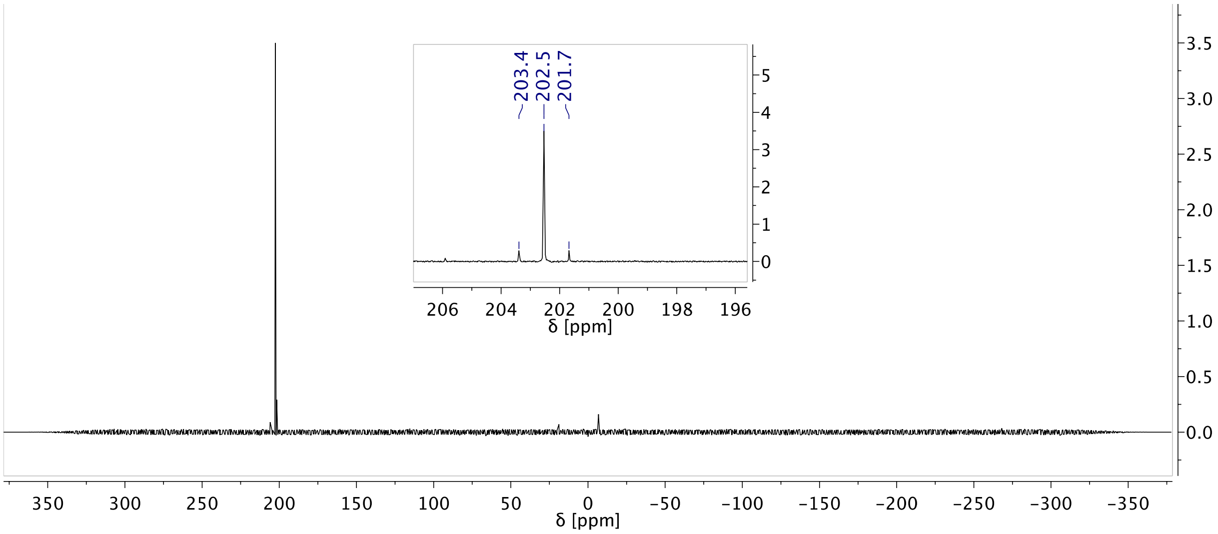

Figure 41: ^{31}P NMR spectrum of tungsten complex **4h**.

2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5b)

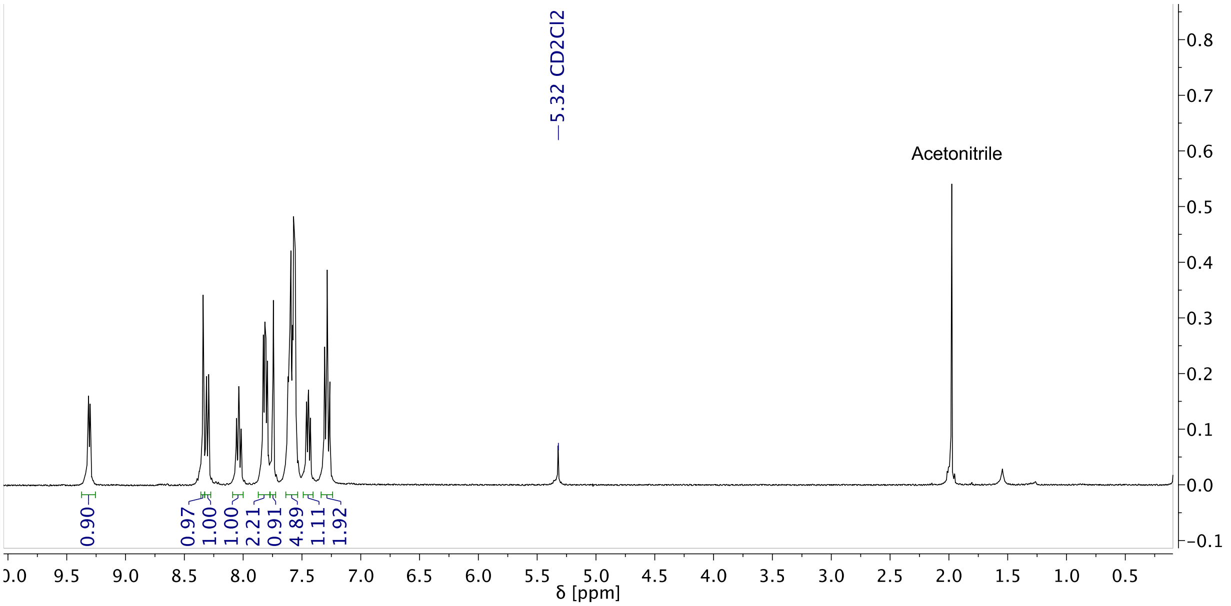

Figure 42: ^{1}H NMR spectrum of tungsten complex **5b**.

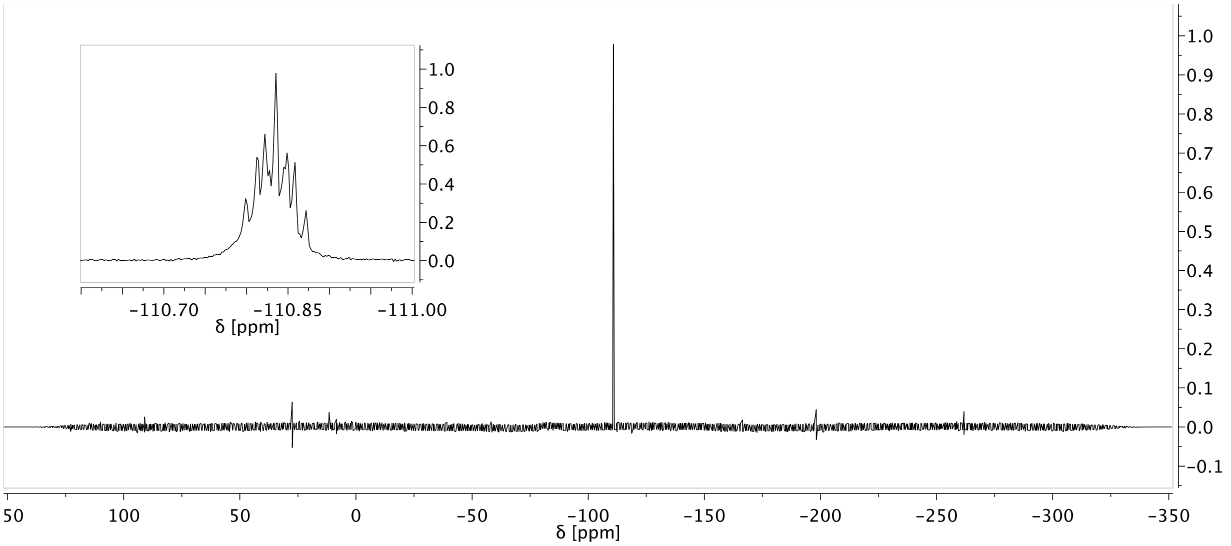

Figure 43: ^{19}F NMR spectrum of tungsten complex **5b**.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5c)

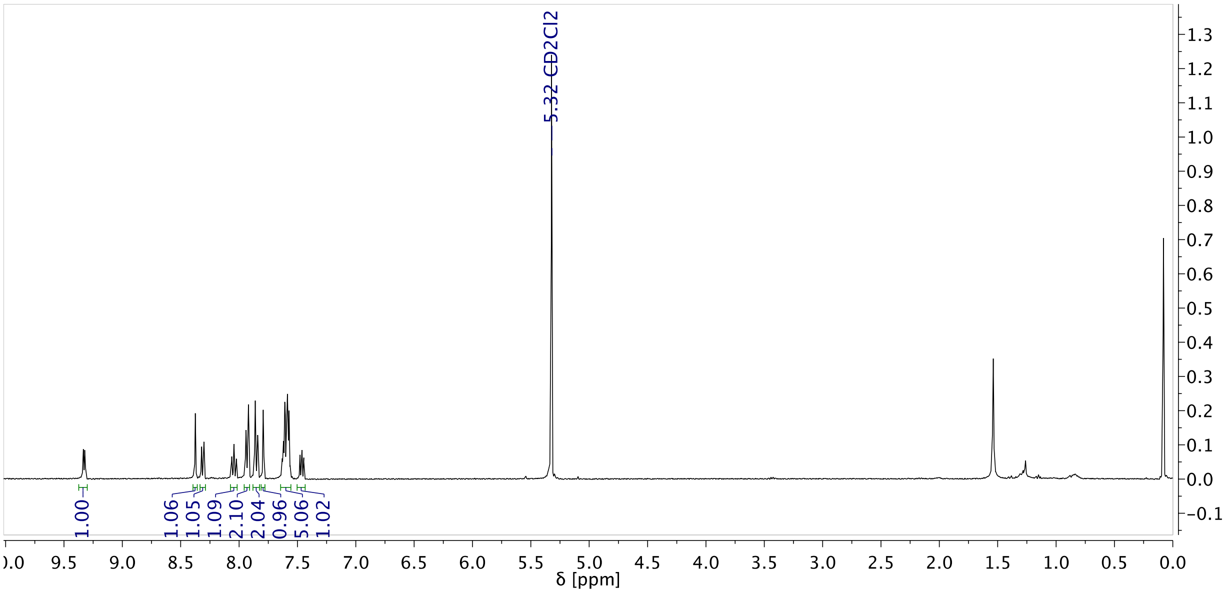

Figure 44: ^{1}H NMR spectrum of tungsten complex **5c**.

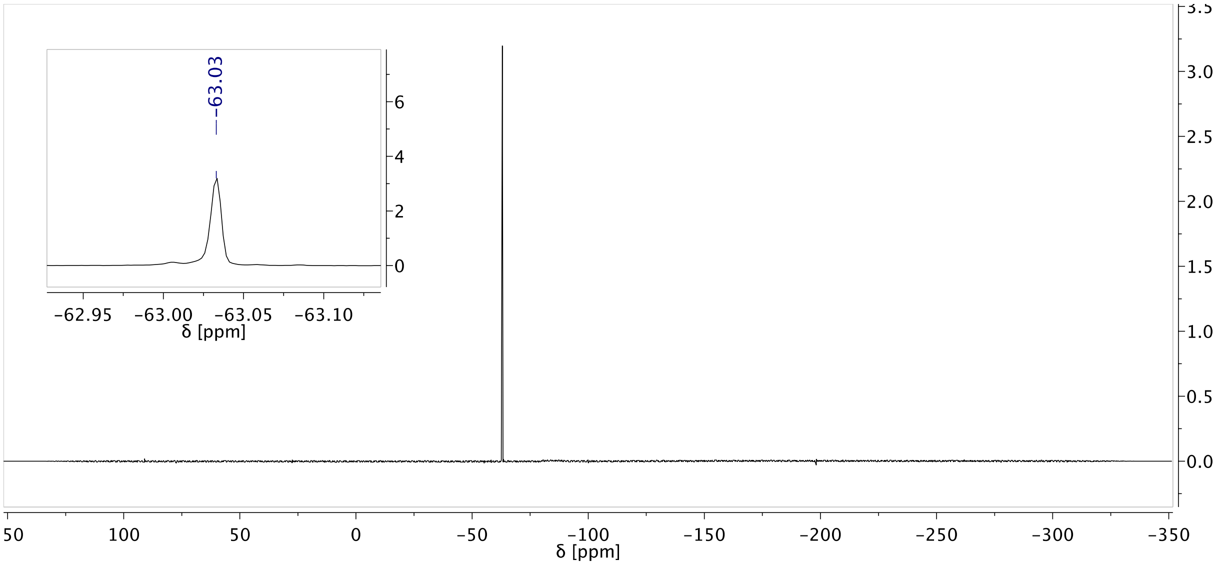

Figure 45: ^{19}F NMR spectrum of tungsten complex **5c**.

2-(2-Pyridyl)-4-(4-methoxyphenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5d)

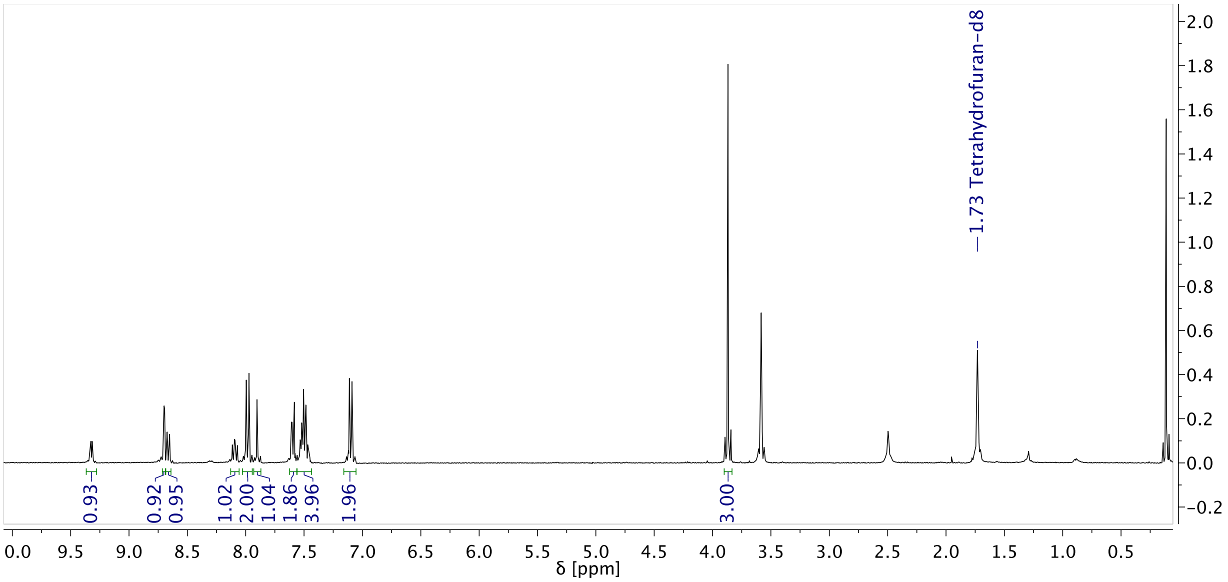

Figure 46: ^{1}H NMR spectrum of tungsten complex **5d**.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyridine-N,N-tungsten tetracarbonyl (5e)

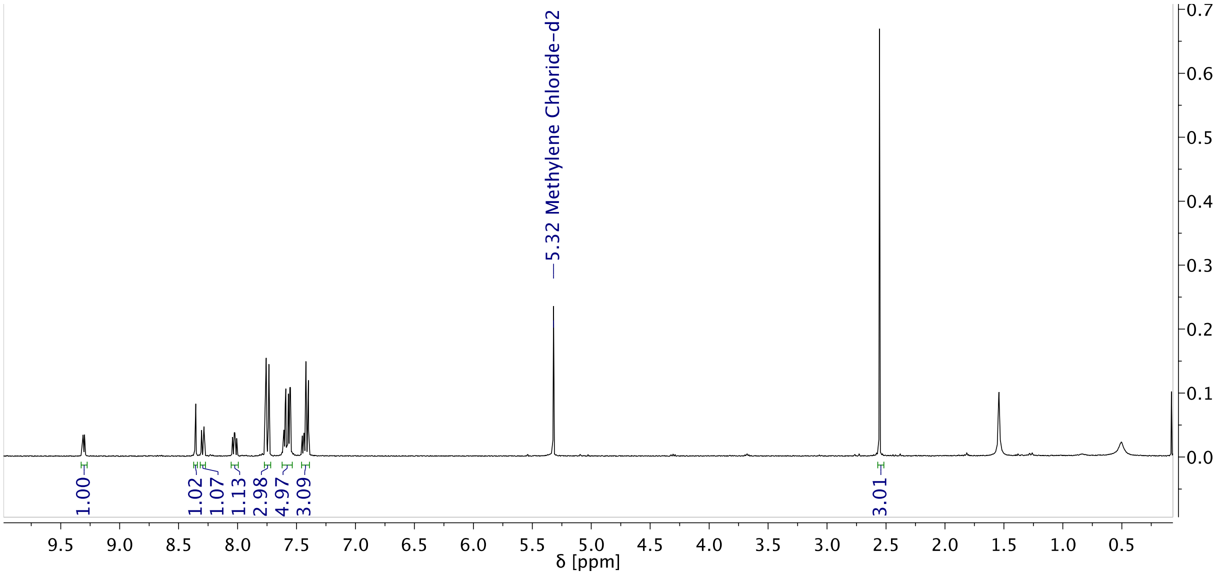

Figure 47: ^{1}H NMR spectrum of tungsten complex **5e**.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)pyridine-N,N-tungsten tetracarbonyl (5f)

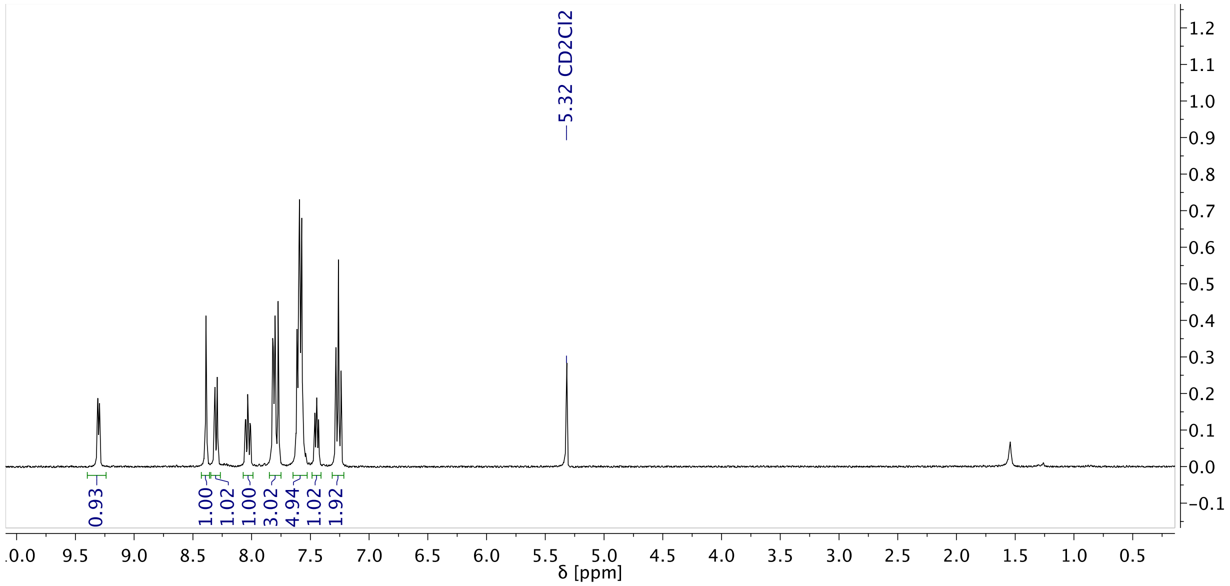

Figure 48: ^{1}H NMR spectrum of tungsten complex **5f**.

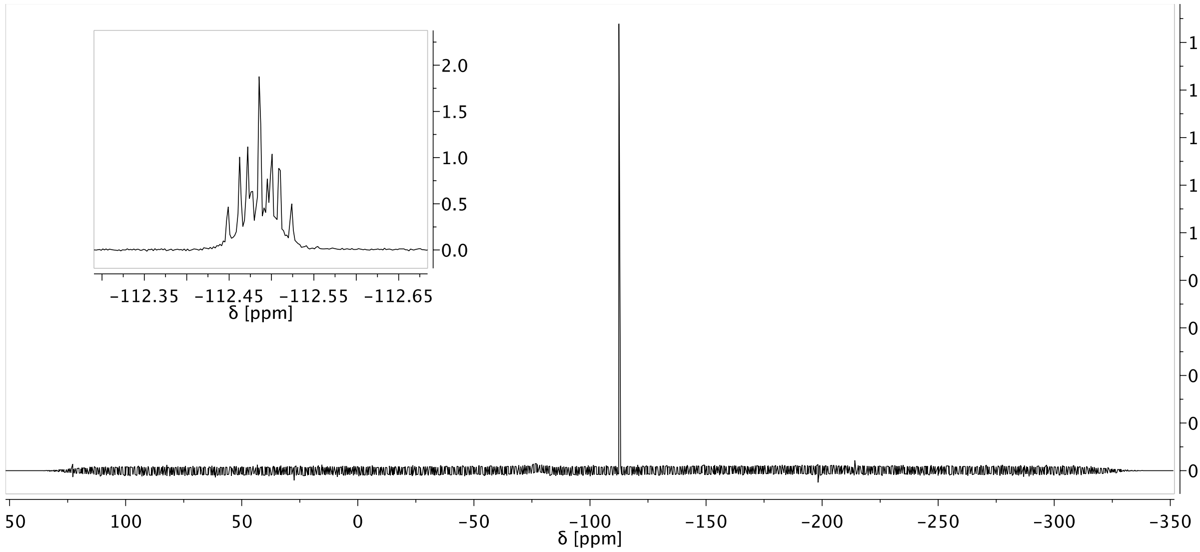

Figure 49: ^{19}F NMR spectrum of tungsten complex **5f**.

2-(2-Pyridyl)-4-phenyl-6-(4-methoxyphenyl)pyridine-N,N-tungsten tetracarbonyl (5g)

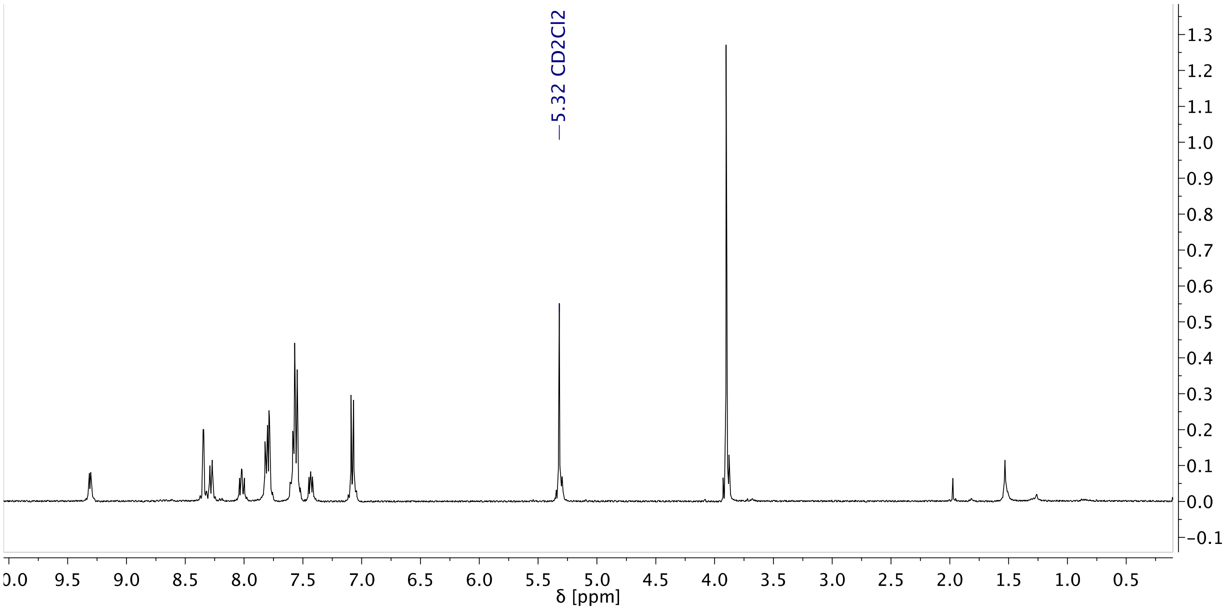

Figure 50: ^{1}H NMR spectrum of tungsten complex **5g**.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)pyridine-N,N-tungsten tetracarbonyl (5h)

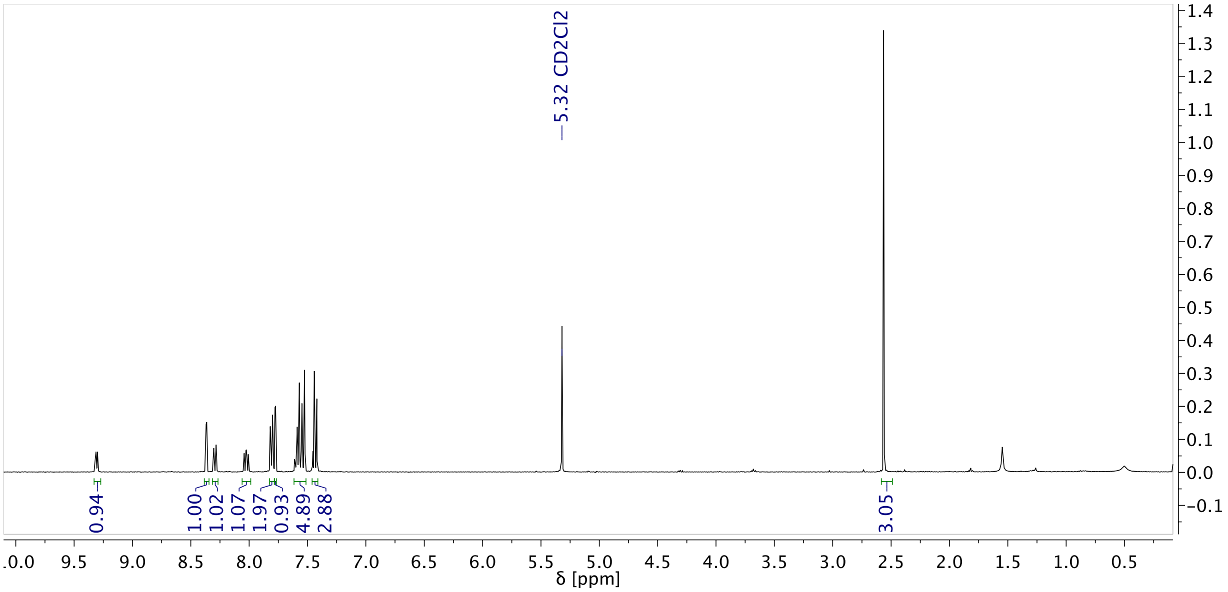

Figure 51: ^{1}H NMR spectrum of tungsten complex **5h**.

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