Electronic Supplementary Material (ESI) for Chemical Communications.

Tuning the electronic effects of aromatic phosphorus heterocycles: An unprecedented phosphinine with significant P(π)-donor properties

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Supplementary Material

General remarks:

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. 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-methylthiophenyl)prop-2-en-1-one (**Chalcones b-d**)[S1] and Tristrimethylsilylphosphane[S2] as well as 2-(2-pyridyl)-4,6-diphenylphosphinine[S3] were prepared according to the literature. Dry or deoxygenated solvents were prepared using standard techniques or used from a MBraun solvent purification system. The ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectra were either recorded on a Varian Mercury 400 MHz spectrometeror on a JEOL ECX400 (400 MHz) spectrometer and chemical shifts are reported relative to the residual resonance in the deuterated solvents. The mass characterizations have been performed on an Agilent 6210 ESI-TOF instrument by Agilent Technologies, Santa Clara, CA, USA with standard settings of 5 L/min, 4 kV and 15 psi for ESI-TOF and on a MAT 711 by Varian MAT, Bremen, Germany with an electron energy of 0.8 mA for EI-MS. IR spectra were measured on a Nicolet iS10 FTIR-ATR spectrometer by Thermo Scientific. All other parameters have been optimized for each substance. For reactions under UV radiation a Philips HPK 125W high-pressure mercury vapor lamp was used. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr (Germany).

Synthetic procedures:

Diketones (1b-d)

The compounds were prepared according to a literature procedure for 3,5-diphenyl-1-(2-pyridyl)pentane-1,5-dione (**1a**).[S3] The respective chalcone, 2-acetylpyridine and NaOH 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-Fluorophenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1b)

1-Phenyl-3-(4-fluorophenyl)prop-2-en-1-one (**Chalcone b**, 5.4 g, 24 mmol), 2-acetylpyridine (2.7 mL, 2.9 g, 24 mmol) and NaOH (1.0 g, 24 mmol) gave the product (5.9 g, 17 mmol, 71%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (dd, J = 16.7 Hz, 7.1 Hz, 1 H), 3.46 (dd, J = 16.7 Hz, 7.1 Hz, 1 H,), 3.63 (dd, J = 17.6 Hz, 7.1 Hz, 1 H), 3.75 (dd, J = 17.6 Hz, 7.1 Hz, 1 H), 4.12 (quin, J = 7.1 Hz, 1 H), 6.94 (m_s, 2 H), 7.28 – 7.31 (m, 2 H), 7.42 – 7.47 (m, 3 H), 7.52 – 7.56 (m, 1 H), 7.80 (td, J = 7.8, 1.7 Hz, 1 H), 7.90 – 7.93 (m, 2 H), 7.97 (d, J = 7.9 Hz, 1 H), 8.65 (d, J = 6.3 Hz, 1 H) ppm; ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -116.5 – -116.6 (m) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 36.0, 44.1, 45.3, 115.4 (d, J_{C-F} = 21.2 Hz), 122.0, 127.4, 128.2, 128.7, 129.2 (d, J_{C-F} = 7.9 Hz), 133.2, 137.1, 140.0 (d, J_{C-F} = 3.7 Hz), 149.0, 153.3, 161.5 (d, J_{C-F} = 244.5 Hz), 198.5, 200.0 ppm; ESI-TOF (m/z): 370.1232 g/mol (calc.: 370.1214 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 76.00, H 4.92, N 3.94.

3-(4-Trifluoromethylphenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1c)

1-Phenyl-3-(4-trifluoromethylphenyl)prop-2-en-1-one (**Chalcone c**, 10.4 g, 38 mmol), 2-acetyl-pyridine (4.2 mL, 4.5 g, 37 mmol) and NaOH (1.5 g, 38 mmol) gave the product (10.1 g, 25 mmol, 68%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (dd, J = 17.1 Hz, 7.1 Hz, 1 H), 3.50 (dd, J = 17.1 Hz, 7.1 Hz, 1 H), 3.65 (dd, J = 17.9 Hz, 7.1 Hz, 1 H), 3.80 (dd, J = 17.8 Hz, 7.1 Hz, 1 H), 4.20 (quin, J = 7.1 Hz, 1 H), 7.41 – 7.58 (m, 8 H), 7.81 (td, J = 7.7, 1.7 Hz, 1 H), 7.90 – 7.94 (m, 2 H), 7.96 – 7.99 (m, 1 H), 8.63 – 8.66 (m, 1 H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.3 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 36.4, 43.7, 44.8, 121.9, 124.3 (q, J_{C-F} = 271.9 Hz), 125.5 (q, J_{C-F} = 3.8 Hz), 127.4, 128.1, 128.1, 128.7, 133.3, 136.9, 137.0, 148.5 (q, J_{C-F} = 1.4 Hz), 149.0, 153.2, 198.0, 199.7 ppm; ESI-TOF (m/z): 398.1360 g/mol (calc.: 398.1368 g/mol) $[M + H]^+$.

3-(4-Methylthiophenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1d)

1-Phenyl-3-(4-fluorophenyl)prop-2-en-1-one (**Chalcone d**, 7.7 g, 30 mmol), 2-acetylpyridine (3.4 mL, 3.7 g, 30 mmol) and NaOH (1.2 g, 30 mmol) gave the product (8.2 g, 22 mmol, 73%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 3.32 (dd, J = 16.8 Hz, 7.1 Hz, 1 H), 3.43 (dd, J = 16.8 Hz, 7.1 Hz, 1 H), 3.59 (dd, J = 17.6 Hz, 7.1 Hz, 1 H), 3.74 (dd, J = 17.6 Hz, 7.1 Hz, 1 H), 4.08 (quin, J = 7.1 Hz, 1 H) 7.14 (d, J = 8.1 Hz, 2 H), 7.22 – 7.27 (m, 2 H), 7.38 – 7.46 (m, 3 H), 7.49 – 7.55 (m, 1 H), 7.78 (td, J = 8.0, 1.7 Hz, 1 H), 7.88 – 7.92 (m, 2 H), 7.93–7.97 (m, 1 H), 8.63 (d, J = 10.4 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 16.1, 36.1, 43.9, 45.2, 121.9, 127.1, 127.3, 128.2, 128.2, 128.7, 133.1, 136.2, 137.0, 141.4, 149.0, 153.3, 198.5, 200.0 ppm; ESI-TOF (m/z): 398.1221 g/mol (calc.: 398.1185 g/mol) $[M + Na]^+$.

Pyrylium salts (2b-d)

The compounds were prepared according to a modified literature procedure for 3,5-diphenyl-1-(2-pyridyl)pentane-1,5-dione (**2a**).[S3] Under Argon the respective diketone (**1b-d**) was mixed with 1,3-diphenylprop-2-en-1-one and boron trifluoride diethyl etherate was added. The mixture was heated to 70 °C for 3h and then dropped into diethyl ether. The precipitate was filtered off, dried, and recrystallized from methanol.

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

Diketone **1b** (4,7 g, 14 mmol), 1,3-diphenylprop-2-en-1-one (2,8 g, 14 mmol) and BF_3 etherate (13.5 mL, 15.5 g, 109 mmol) gave the product (2,284 g, 6 mmol, 43%) as yellow crystals.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 7.60 (m_S, 2 H), 7.80 – 7.95 (m, 4 H), 8.31 (td, J = 7.9, 1.7 Hz, 1 H), 8.69 – 8.74 (m, 4 H), 8.82 (dt, J = 7.9 Hz, 1.0 Hz, 1 H), 9.00 – 9.03 (m, 1 H), 9.31 – 9.34 (m, 2 H) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = -102.8 (m_S), -151.3 (s), -151.4 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2SO$): δ = 114.7, 115.9, 116.9 (d, J_{C-F} = 22.0 Hz), 124.1, 128.1, 128.4 (d, J_{C-F} = 2.8 Hz), 128.5, 128.6, 129.5, 132.9 (d, J_{C-F} = 10.1 Hz), 135.5, 138.1, 145.9, 150.5, 163.9, 166.1 (d, J_{C-F} = 256.8 Hz), 167.4, 170.1 ppm; ESI-TOF (m/z): 328.1166 g/mol (calc.: 328.1132 g/mol) $[M]^+$.

2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyrylium tetrafluoroborate (2c)

Diketone **1c** (4.6 g, 12 mmol), 1,3-diphenylprop-2-en-1-one (2.4 g, 12 mmol) and BF_3 etherate (11 mL, 12.7 g, 89 mmol) were heated to 80 °C for 3 h and gave the product (1.9 g, 4 mmol, 34%) as yellow crystals.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 7.82 – 7.97 (m, 4 H), 8.14 (d, J = 8.2 Hz, 2 H), 8.32 (td, J = 7.8, 1.7 Hz, 1 H), 8.72 – 8.79 (m, 4 H), 8.86 (dt, J = 7.8, 1.7 Hz, 1 H), 9.02 – 9.05 (m, 1 H), 9.41 (d, J = 1.8 Hz, 1 H), 9.43 (d, J = 1.8 Hz, 1 H) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ = -63.6 (s), -151.3 (s), -151.4 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$): δ = 117.7, 119.1, 125.7, 127.7 (q, J_{C-F} = 3.7 Hz), 129.9, 130.3, 131.1, 131.5, 136.9, 139.5, 147.4, 152.2, 166.8, 170.5, 173.4 ppm; ESI-TOF (m/z): 378.1106 g/mol (calc.: 356.1100 g/mol) $[M]^+$.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyrylium tetrafluoroborate (2d)

Diketone **1d** (7.1 g, 19 mmol),1,3-diphenylprop-2-en-1-one (4.1 g, 20 mmol) and BF_3 etherate (20 mL, 23.0 g, 162 mmol) were heated to 80 °C for 6 h. The mixture was dropped into diethyl ether (400 mL). The precipitate was filtered off, dried and washed with chloroform (50 mL). Afterwards recrystallization of the solid from ethanol/methanol 2:1 gave the product (3.1 g, 7 mmol, 37%) as dark red crystals.

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ = 2.67 (s, 3 H), 7.59 – 7.64 (m, 2 H), 7.78 – 7.91 (m, 4 H), 8.27 (td, J = 7.8 Hz, 1.7 Hz, 1 H), 8.55 – 8.65 (m, 4 H), 8.70 (d, J = 7.9 Hz, 1 H), 8.99 – 9.01 (m, 1 H), 9.17 (d, J = 1.6 Hz, 1 H), 9.22 (d, J = 1.6 Hz, 1 H) ppm; ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ = -148.1 (s), -148.1 (s) ppm; ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2SO$): δ = 14.5, 114.4, 115.5,

124.8, 126.4, 128.2, 129.0, 129.4, 129.7, 130.4, 131.0, 135.7, 139.1, 147.1, 151.5, 151.6, 164.6, 167.6, 170.3 ppm; ESI-TOF (m/z): 356.1139 g/mol (calc.: 356.1104 g/mol) $[M]^+$.

Pyridylphosphinines (3c-d)

The compounds were prepared according to a modified literature procedure for 2-(2-Pyridyl)-4,6-diphenylphosphinine (**3a**).[S3] The respective pyrylium salt was stirred under argon in dry acetonitrile. Tris(trimethylsilyl)phosphane was added dropwise. The solution was then heated to 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-fluorophenyl)-6-phenylphosphinine (3b)

Pyrylium salt **2b** (6.4 g, 15 mmol) and Tris(trimethylsilyl)phosphane (8.1 g, 32 mmol) in acetonitrile (37 mL) gave the product (0.529 g, 1.5 mmol, 10%) as a slightly yellow-orange solid. ^{1}H NMR (400 MHz, THF-d_8): δ = 7.23 – 7.28 (m, 2 H), 7.29 – 7.34 (m, 1 H), 7.39 – 7.43 (m, 1 H), 7.45 – 7.51 (m, 2 H), 7.76 – 7.86 (m, 6 H), 8.12 – 8.16 (m, 1 H), 8.26 (dd, J = 6.0 Hz, 1.3 Hz, 1 H), 8.68 – 8.70 (m, 1 H), 8.89 (dd, J = 5.7 Hz, 1.3 Hz, 1 H) ppm; ^{19}F NMR (376 MHz, THF-d_8): δ = -115.6 (m_s) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 116.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 121.8 (d, $J_{C\text{-}P}$ = 16.5 Hz), 123.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 129.8, 130.5 (dd, $J_{C\text{-}F}$ = 8.2 Hz, $J_{C\text{-}P}$ = 1.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 13.0 Hz), 133.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 137.7, 139.4 (dd, $J_{C\text{-}F}$ = 3.2 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 144.0 (d, $J_{C\text{-}P}$ = 13.8 Hz), 144.5 (d, $J_{C\text{-}P}$ = 24.8 Hz), 150.8, 159.8 (d, $J_{C\text{-}P}$ = 25.6 Hz), 163.93 (dd, $J_{C\text{-}F}$ = 246.8 Hz, $J_{C\text{-}P}$ = 0.9 Hz), 170.6 (d, $J_{C\text{-}P}$ = 50.7 Hz), 172.6 (d, $J_{C\text{-}P}$ = 50.9 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ = 186.6 ppm; ESI-TOF (m/z): 344.1027 g/mol (calc.: 344.0999 g/mol) $[M + H]^+$.

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

Pyrylium salt **2c** (5.1 g, 11 mmol) and Tris(trimethylsilyl)phosphane (5.5 g, 22 mmol) in acetonitrile (24 mL) gave the product (0.214 g, 0.5 mmol, 5%) as a slightly yellow-orange solid. The NMR spectra still show impurities. However, the mass spectrum confirms the successful synthesis of **3c**.

^{1}H NMR (400 MHz, THF-d_8): δ = 7.25 – 7.29 (m, 1 H), 7.43 – 7.48 (m, 2 H), 7.75 – 7.82 (m, 6 H), 7.95 (d, J = Hz, 2 H), 8.11 (d, J = 8.2 Hz, 1 H), *8*.26 – 8.29 (m, 1 H), 8.67 – 8.70 (m, 1 H), 8.90 – 8.93 (m, 1 H) ppm; ^{19}F NMR (376 MHz, THF-d_8): δ = -62.9 ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 192.2 ppm; ESI-TOF (m/z): 394.0991 g/mol (calc.: 394.0967 g/mol) $[M + H]^+$.

2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylphosphinine (3d)

Pyrylium salt **2d** (5.3 g, 14 mmol) and Tris(trimethylsilyl)phosphane (6.7 g, 26 mmol) in acetonitrile (30 mL) gave the product (0.276 g, 0.7 mmol, 6%) as a slightly yellow-orange solid.

^{1}H NMR (400 MHz, THF-d_8): δ = 2.52 (s, 3 H), 7.28 – 7.33 (m, 1 H), 7.37 – 7.42 (m, 3 H), 7.45 – 7.50 (m, 2 H), 7.72 – 7.80 (m, 4 H), 7.82 (dd, J = 7.6 Hz, 1.9 Hz, 1 H), 8.11 – 8.15 (m, 1 H), 8.28 (dd, J = 6.0 Hz, 1.3 Hz, 1 H), 8.70 (ddd, J = 4.8 Hz, 1.9 Hz, 1.0 Hz, 1 H), 8.91 (dd, J = 5.7 Hz, 1.3 Hz, 1 H) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 15.5, 121.9 (d, J_{C-P} = 16.5 Hz), 123.9 (d, J_{C-P} = 2.0 Hz), 127.7, 128.6 (d, J_{C-P} = 13.0 Hz), 128.9 (d, J_{C-P} = 1.9 Hz), 129.0 (d, J_{C-P} = 1.7 Hz), 129.8, 132.1 (d, J_{C-P} = 13.1 Hz), 133.2 (d, J_{C-P} = 11.9 Hz), 137.8, 139.6 (d, J_{C-P} = 3.4 Hz), 140.4 (d, J_{C-P} = 1.0 Hz), 144.6, 144.7 (d, J_{C-P} = 38.4 Hz), 150.9, 160.0 (d, J_{C-P} = 25.7 Hz), 170.6 (d, J_{C-P} = 50.5 Hz), 172.6 (d, J_{C-P} = 50.8 Hz) ppm; ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ = 185.8 ppm; ESI-TOF (m/z): 372.0974 g/mol (calc.: 372.0970 g/mol) $[M + H]^+$.

P,N-tungsten tetracarbonyl complexes

In an Young-NMR-tube phosphinine (**3a-d**, 0.1 mmol) was dissolved in THF-d_8 (0.6 mL) and tungsten hexacarbonyl (0.1 mmol) was added. The tube was then treated with UV radiation until ^{31}P NMR showed complete conversion (15 - 20 h). After evaporation of all volatiles the product was recrystallized from acetonitril (**5b-d**) or THF/pentane (**5a**).

2-(2-Pyridyl)-4,6-diphenylphosphinine-P,N-tungsten tetracarbonyl (5a)

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.22 (dddd, $^{3}J_{H-H}$ = 7.3 Hz, $^{3}J_{H-H}$ = 5.9 Hz, $^{4}J_{H-H}$ = 1.3 Hz, $^{4}J_{H-P}$ = 1.3 Hz, 1 H), 7.52 (m, 6 H), 7.69 (m, 2 H), 7.95 (m, 3 H), 8.29 (d, $^{3}J_{H-H}$ = 8.6 Hz, 1 H), 8.39 (dd, $^{3}J_{H-P}$ = 17.8 Hz,, $^{4}J_{H-H}$ = 1.4 Hz, 1 H), 8.59 (dd, $^{3}J_{H-P}$ = 14.0 Hz, $^{4}J_{H-H}$ = 1.2 Hz, 1 H), 9.37 (ddd, $^{3}J_{H-H}$ = 5.6 Hz, $^{4}J_{H-H}$ = 1.6 Hz, $^{5}J_{H-P}$ = 0.8 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 120.5 (d, $^{2}J_{C-P}$ = 11.6 Hz), 124.8 (d, $^{3}J_{C-P}$ = 3.7 Hz) 127.9 (d, $^{4}J_{C-P}$ = 2.4 Hz), 128.4, 128.6 (d, $^{3}J_{C-P}$ = 11.0 Hz), 129.0 (d, $^{4}J_{C-P}$ = 1.9 Hz), 129.6 (d, $^{4}J_{C-P}$ = 3.2 Hz), 131.7 (d, $^{2}J_{C-P}$ = 12.4 Hz), 138.0 (d, $^{3}J_{C-P}$ = 11.0 Hz), 138.5, 139.9 (d, $^{2}J_{C-P}$ = 16.0 Hz), 140.2 (d, $^{1}J_{C-P}$ = 20.9 Hz), 142.1 (d, $^{4}J_{C-P}$ = 4.4 Hz), 157.9 (d, $^{4}J_{C-P}$ = 4.5 Hz), 159.1 (d, $^{2}J_{C-P}$ = 14.3 Hz), 160.1 (d, $^{1}J_{C-P}$ = 17.7 Hz), 161.3 (d, $^{2}J_{C-P}$ = 17.3 Hz), 198.3 (d, $^{2}J_{C-P}$ = 10.9 Hz), 209.7 (d, $^{2}J_{C-P}$ = 5.2 Hz), 211.3 (d, $^{2}J_{C-P}$ = 41.9 Hz) ppm; ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 203.4 (s, $^{1}J_{P-W}$ = 277 Hz) ppm; elemental analysis calc (%) for $C_{26}H_{16}NPO_4W$ (621.22 g/mol): C 50.27, H 2.60, N 2.25; found: C 50.10, H 2.82, N 2.37; FT-IR (solid ATR): $\tilde{\nu}$(CO) 2008, 1893, 1870, 1836 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine-P,N-tungsten tetracarbonyl (5b)

^{1}H NMR (400 MHz, THF-d_8): δ = 7.25 – 7.31 (m_s, 2 H), 7.34 – 7.39 (m, 1 H), 7.44 – 7.49 (m, 1 H), 7.52 – 7.57 (m, 2 H), 7.82 – 7.88 (m_s, 2 H), 7.96 – 8.00 (m, 2 H), 8.05 – 8.11 (m, 1 H), 8.47 (d, J = 17.7 Hz, 1 H), 8.63 (d, J = 8.3 Hz, 1 H), 8.83 (d, J = 14 Hz, 1 H), 9.41 – 9.44 (m_s, 1 H) ppm; ^{19}F NMR (376 MHz, THF-d_8): δ = -155.6 (m_s) ppm; ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 116.7 (d, J_{C-F} = 21.7 Hz), 121.8 (d, J_{C-P} = 11.6 Hz), 125.7 (d, J_{C-P} = 3.8 Hz), 129.0 (d, J_{C-P} = 11.2 Hz), 129.5 (d, J_{C-P} = 2.2 Hz), 130.1, 130.5 (dd, J_{C-F} = 8.3, J_{C-P} = 2.6 Hz), 132.5 (d,

$J_{C\text{-}P}$ = 13.5 Hz), 138.3 (d, $J_{C\text{-}P}$ = 10.8 Hz), 139.1 (dd, $J_{C\text{-}P}$ = 4.6 Hz, $J_{C\text{-}F}$ = 3.3 Hz), 139.4, 139.9 (d, $J_{C\text{-}P}$ = 21.1 Hz), 140.5 (d, $J_{C\text{-}P}$ = 15.9 Hz), 158.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 160.1 (d, $J_{C\text{-}P}$ = 13.9 Hz), 160.7 (d, $J_{C\text{-}P}$ = 17.3 Hz), 162.0 (d, $J_{C\text{-}P}$ = 17.5 Hz), 163.9 (dd, $J_{C\text{-}F}$ = 246.8 Hz, $J_{C\text{-}P}$ = 1.0 Hz), 198.9 (d, $J_{C\text{-}P}$ = 11.0 Hz), 209.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 212.0 (d, $J_{C\text{-}P}$ = 41.8 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8): δ = 201.0 (s, $^{1}J_{P\text{-}W}$ = 278 Hz) ppm; FT-IR (solid ATR): $\tilde{\nu}$(CO) 2012, 1893, 1877, 1840 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-trifluoromethylphenyl)phosphinine-P,N-tungsten tetracarbonyl (5c)

^{1}H NMR (400 MHz, THF-d_8): δ = 7.35 – 7.40 (m, 1 H), 7.45 – 7.50 (m, 1 H), 7.53 – 7.59 (m, 2 H), 7.85 (d, J = 8.2 Hz, 2 H), 7.97 – 8.05 (m, 4 H), 8.06 – 8.12 (m, 1 H), 8.53 (dd, J = 17.7 Hz, 1.3 Hz,1 H), 8.64 (d, J = 8.3 Hz, 1 H), 8.88 (dd, J = 14.3 Hz, 1.0 Hz, 1 H), 9.43 (m, 1 H) ppm; ^{19}F NMR (376 MHz, THF-d_8): δ = -63.1 ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8): δ = 121.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 125.5 (q, $J_{C\text{-}F}$ = 272.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 126.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.1 Hz), 129.2 (d, $J_{C\text{-}P}$ = 1.9 Hz), 129.6, 130.1, 130.5, 132.5 (d, $J_{C\text{-}P}$ = 12.2 Hz), 138.3 (d, $J_{C\text{-}P}$ = 10.7 Hz), 139.1 (d, $J_{C\text{-}P}$ = 20.9 Hz), 139.5, 140.4 (d, $J_{C\text{-}P}$ = 15.9 Hz), 146.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 158.5 (d, $J_{C\text{-}P}$ = 4.3 Hz), 160.1 (d, $J_{C\text{-}P}$ = 13.8 Hz), 160.6 (d, $J_{C\text{-}P}$ = 16.8 Hz), 161.9 (d, $J_{C\text{-}P}$ = 17.2 Hz), 198.7 (d, $J_{C\text{-}P}$ = 10.0 Hz), 209.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 211.5 (d, $J_{C\text{-}P}$ = 42.0 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8): δ = 206.3 (s, $^{1}J_{P\text{-}W}$ = 278 Hz) ppm; EI-MS (170 °C, m/z): 394.0991 g/mol (calc.: 689.0181 g/mol) $[M]^{\bullet+}$; FT-IR (solid ATR): $\tilde{\nu}$(CO) 2014, 1920, 1857 cm^{-1}.

2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine-P,N-tungsten tetracarbonyl (5d)

^{1}H NMR (400 MHz, THF-d_8): δ = 2.52 (s, 3 H), 7.31 – 7.36 (m, 1 H), 7.39 – 7.49 (m, 3 H), 7.52 – 7.58 (m, 2 H), 7.72 – 7.77 (m, 2 H), 7.95 – 8.01 (m, 2 H), 8.02 – 8.09 (m, 1 H), 8.47 (d, J = 17.9 Hz, 1 H), 8.60 (d, J = 8.2 Hz, 1 H), 8.81 (d, J = 14.3 Hz, 1 H), 9.42 (d, J = 5.6 Hz, 1 H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8): δ = 15.4, 121.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 125.6 (d, $J_{C\text{-}P}$ = 3.8 Hz), 127.6, 128.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 129.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 130.1, 132.2 (d, $J_{C\text{-}P}$ = 12.3 Hz), 130.0 (d, $J_{C\text{-}P}$ = 11.1 Hz), 139.0 (d, $J_{C\text{-}P}$ = 4.7 Hz), 139.4 (d, $J_{C\text{-}P}$ = 14.8 Hz), 140.5, 140.6 (d, $J_{C\text{-}P}$ = 8.5 Hz), 158.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 160.0 (d, $J_{C\text{-}P}$ = 14.2 Hz), 116.6 (d, $J_{C\text{-}P}$ = 17.3 Hz), 162.0 (d, $J_{C\text{-}P}$ = 17.4 Hz), 198.9 (d, $J_{C\text{-}P}$ = 11.0 Hz), 209.3 (d, $J_{C\text{-}P}$ = 5.0 Hz), 212.0 (d, $J_{C\text{-}P}$ = 41.8 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) δ = 199.7 (s, $^{1}J_{P\text{-}W}$ = 276 Hz) ppm; FT-IR (solid ATR): $\tilde{\nu}$(CO) 2014, 1971, 1889, 1859 cm^{-1}.

X-ray crystal structure analysis of 5b:

Crystals suitable for X-ray diffraction were obtained from a hot THF solution. *Crystallographic data*: $C_{26}H_{15}NO_4$ FPW; *F*w=639.21; 0.17×0.12×0.06 mm^3; red platelet, orthorhombic; *Pna*2$_1$ (no. 33); *a*=15.8144(16), *b*=19.0204(17), *c*=7.3213(9) Å; *V*=2202.2(4) Å^3; *Z*=4; D_x=1.928 gcm^{-3}; μ=5.35 mm^{-1}. 9573 reflections were measured by using a Stoe IPDS 2T diffractometer with a

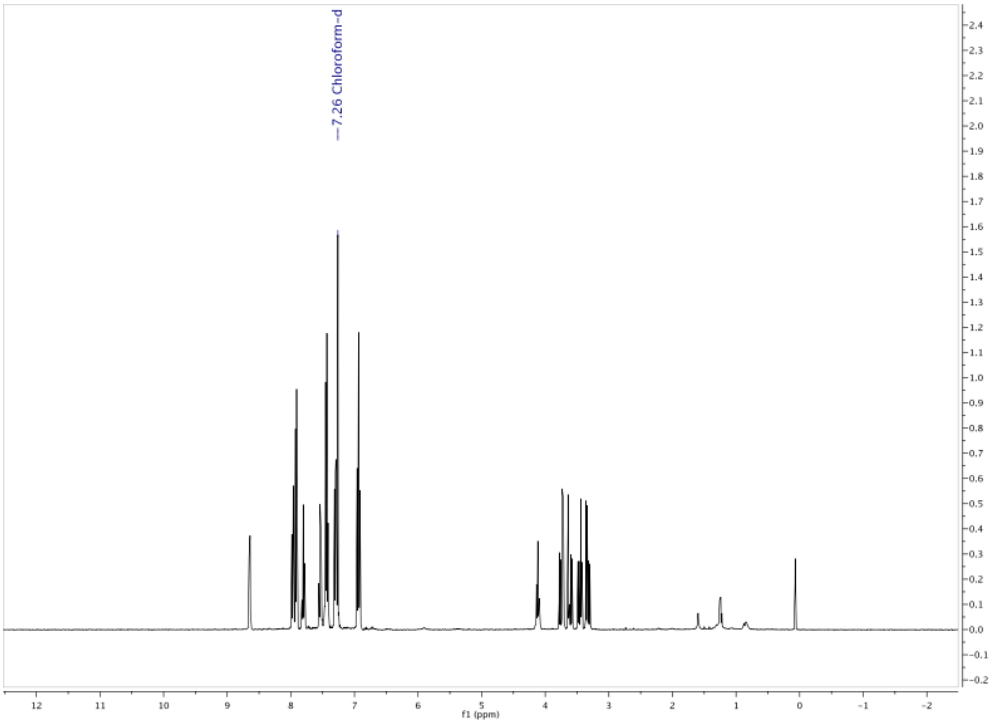
rotating anode (MoK_α radiation; λ=0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$=0.69 $Å^{-1}$ at a temperature of 210 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections by using the X-Red program (0.48–0.74 correction range).[S4] 5136 reflections were unique (R_{int}=0.098). The structures were solved with SHELXS-2013[S5] by using direct methods and refined with SHELXL-2013[S6] 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 with 1 restraint. R_1=0.055 for 2997 reflections with $I>2\sigma(I)$ and wR_2=0.127 for 5136 reflections, S=0.944, residual electron density was between -1.29 and 0.96 $eÅ^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[S3]

Density Functional Theory (DFT) calculations

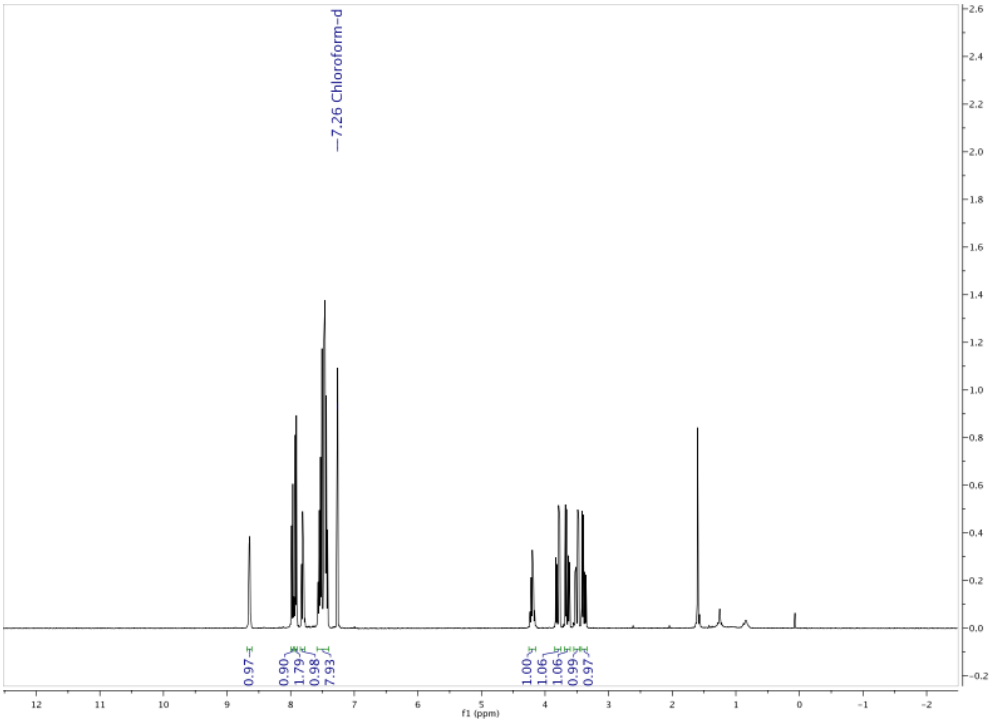
All calculations were carried out at the B3LYP/6-311+G(d,p) level of theory with the Gaussian 09 program.[S7] Full geometry optimization without any symmetry constraints was performed prior to the analysis of the electronic structure of the different phosphinine ligands. The nature of the stationary 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.

NMR Spectra:

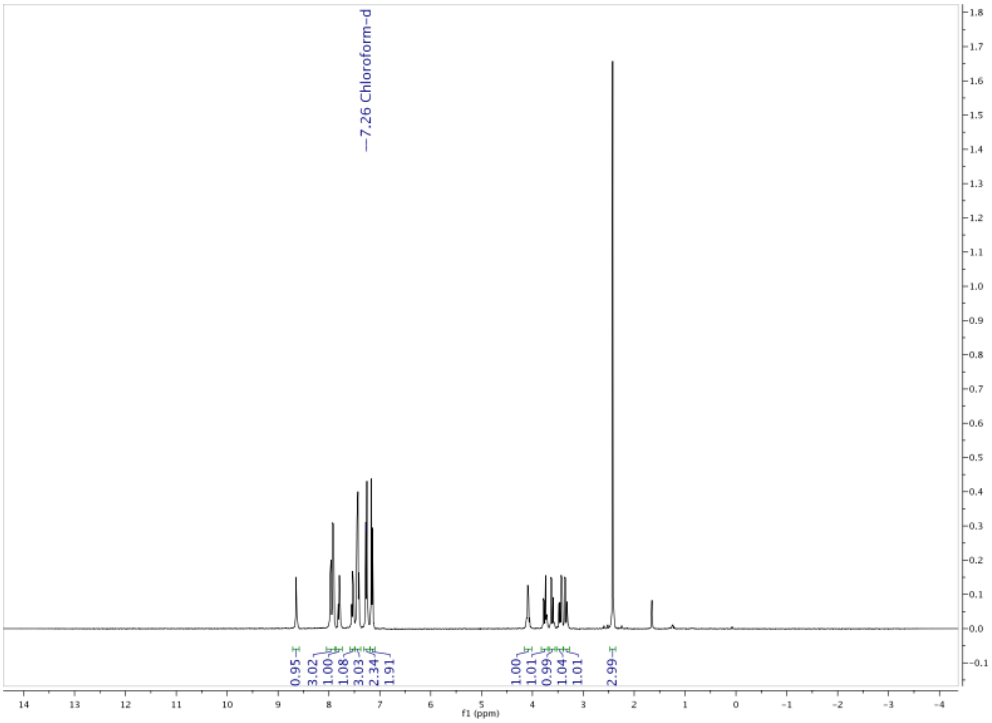
3-(4-Fluorophenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1b); (^{1}H)



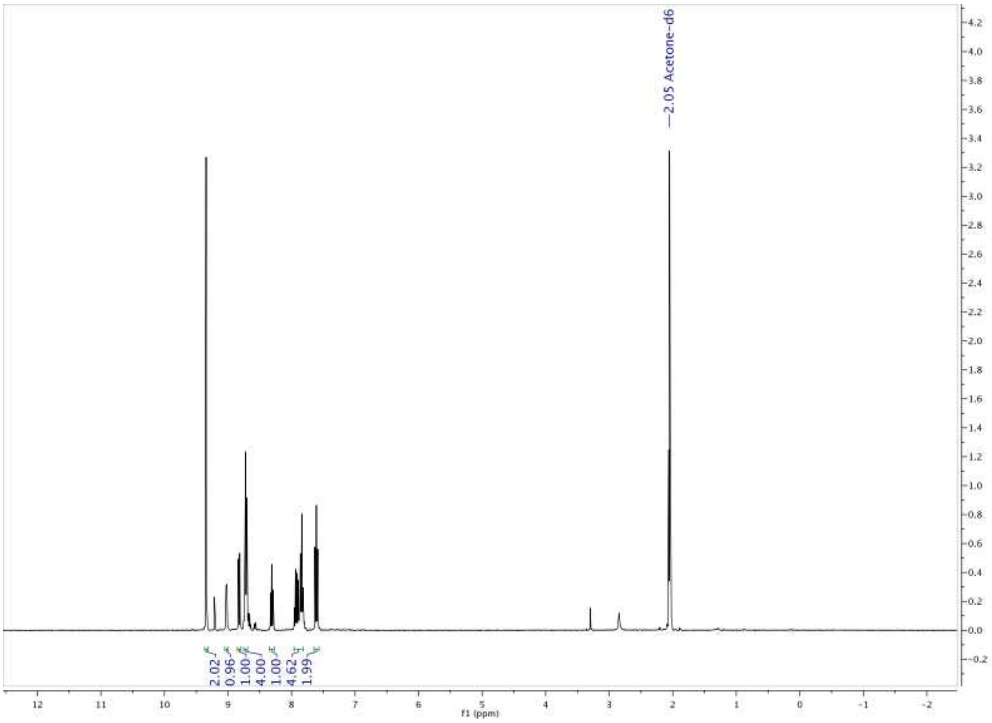
3-(4-Trifluoromethylphenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1c); (^{1}H)



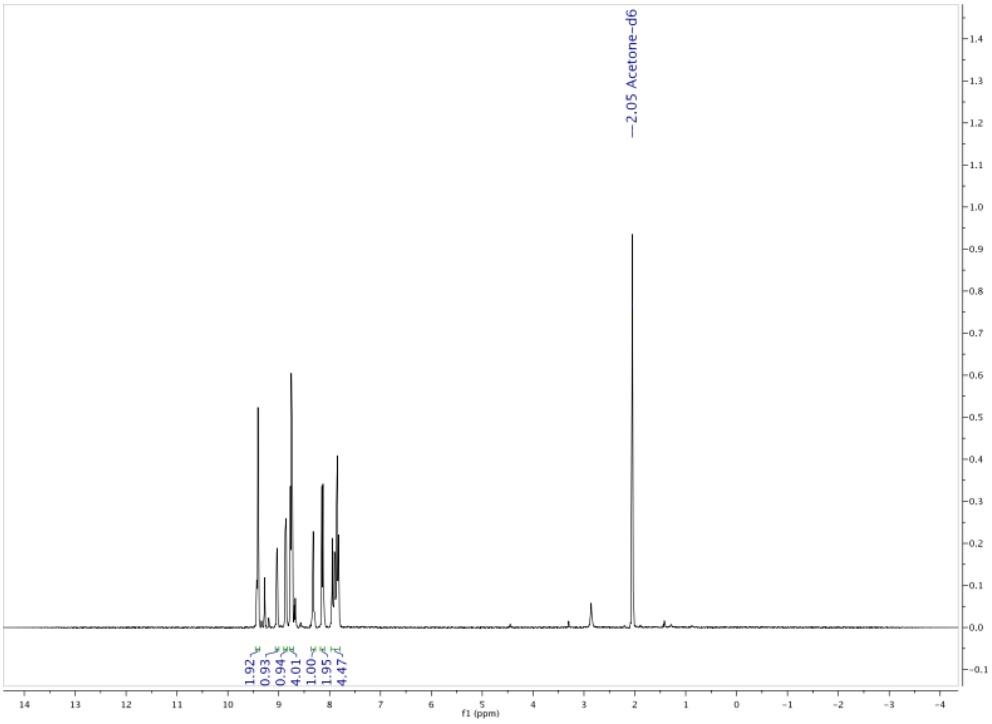
3-(4-Methylthiophenyl)-1-phenyl-5-(2-pyridyl)pentane-1,5-dione (1d); (^{1}H)



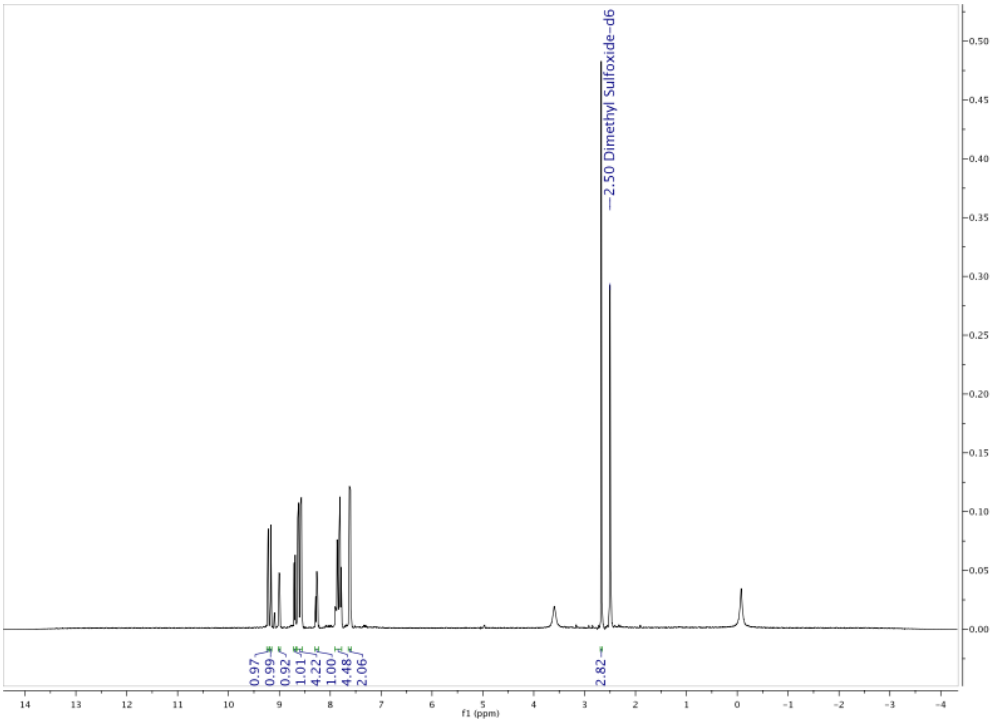
2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylpyrylium tetrafluoroborate (2b); (^{1}H)



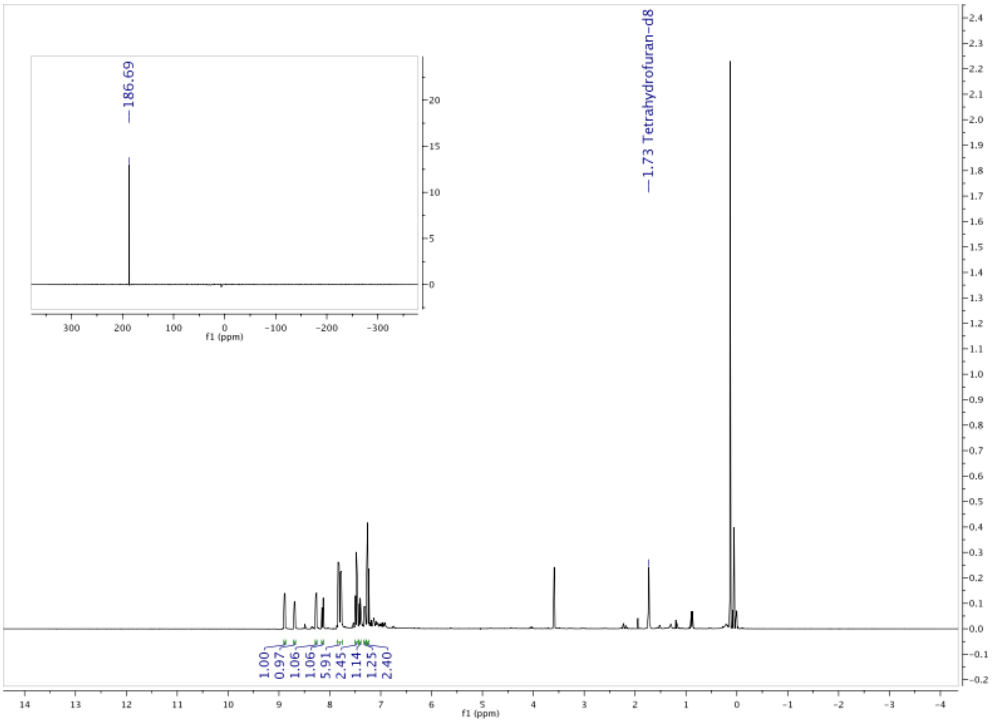
2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylpyrylium tetrafluoroborate (2c); (^{1}H)



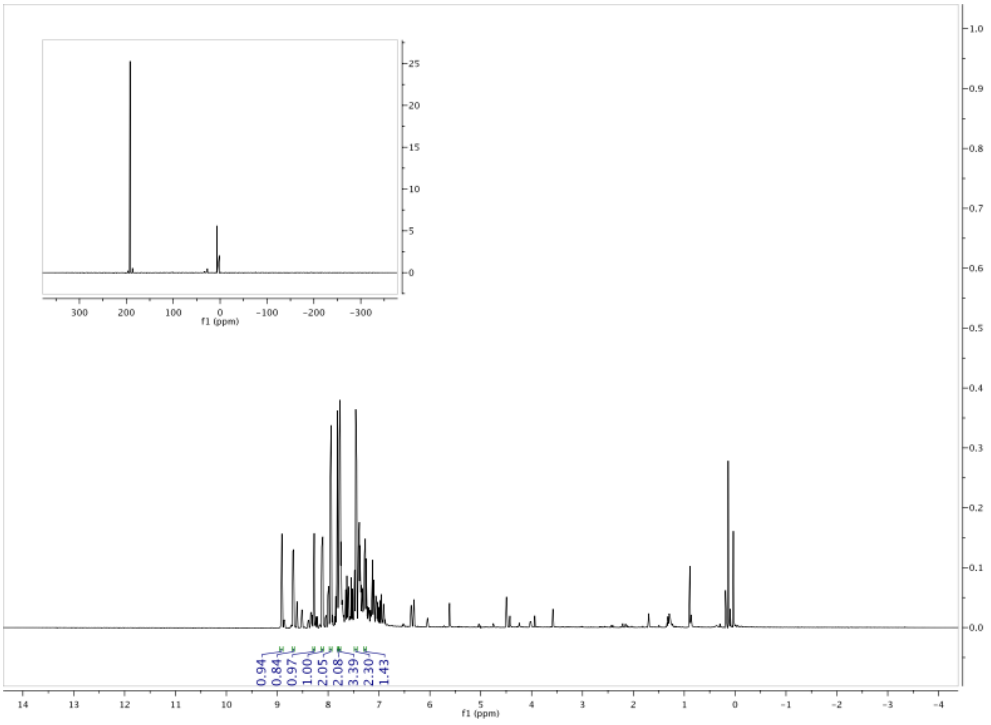
2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylpyrylium tetrafluoroborate (2d); (^{1}H)



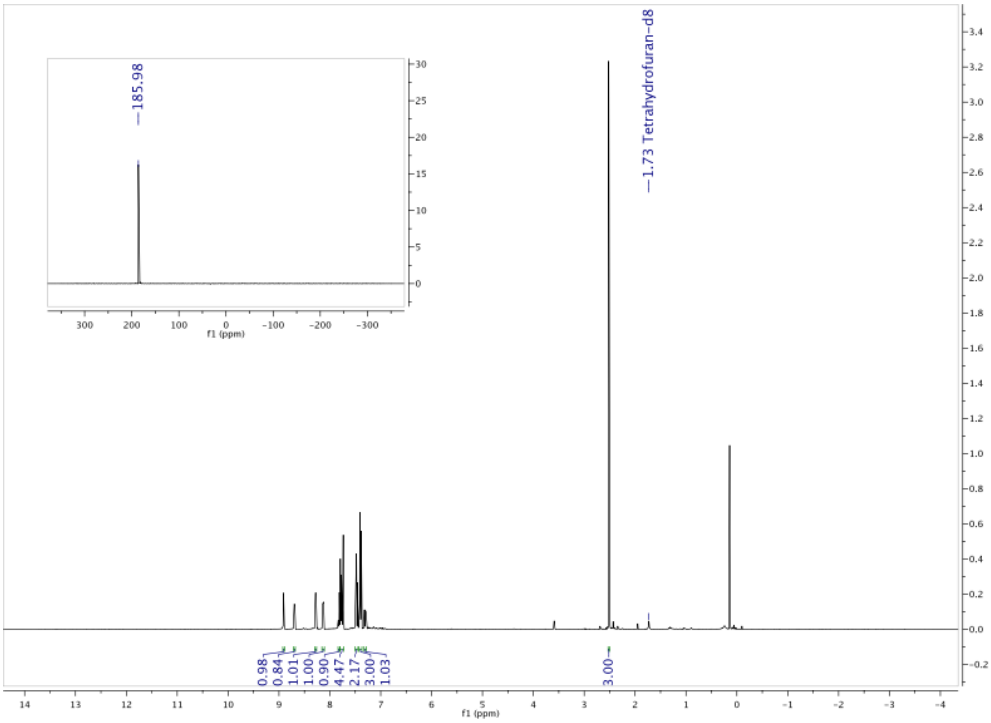
2-(2-Pyridyl)-4-(4-fluorophenyl)-6-phenylphosphinine (3b); (^{1}H, ^{31}P (inset))



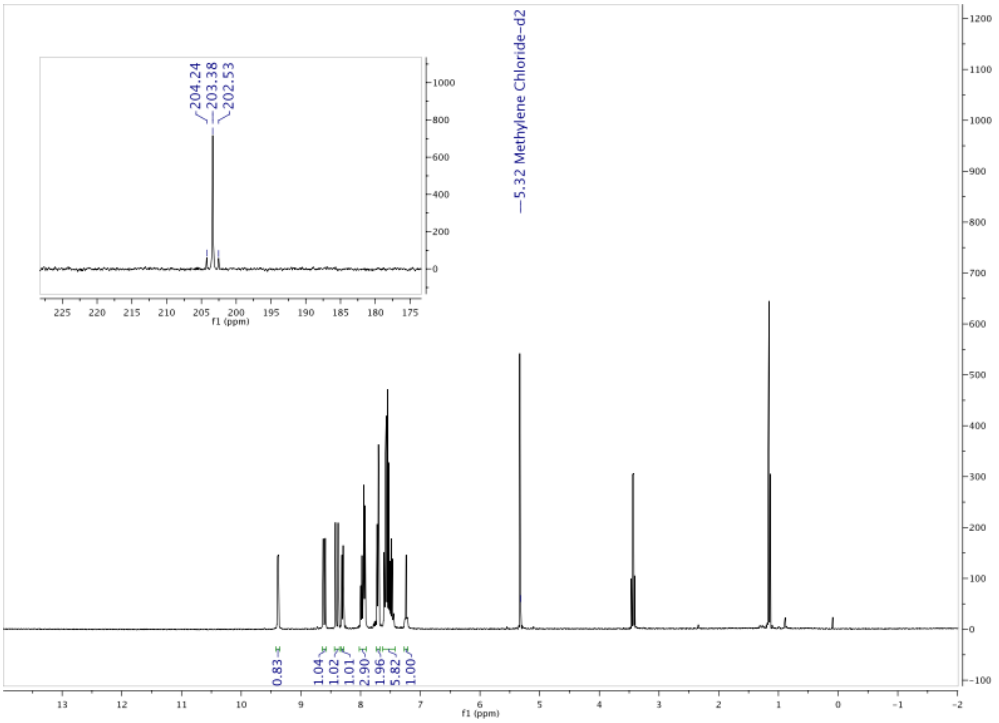
2-(2-Pyridyl)-4-(4-trifluoromethylphenyl)-6-phenylphosphinine (3c) (^{1}H, ^{31}P (inset))



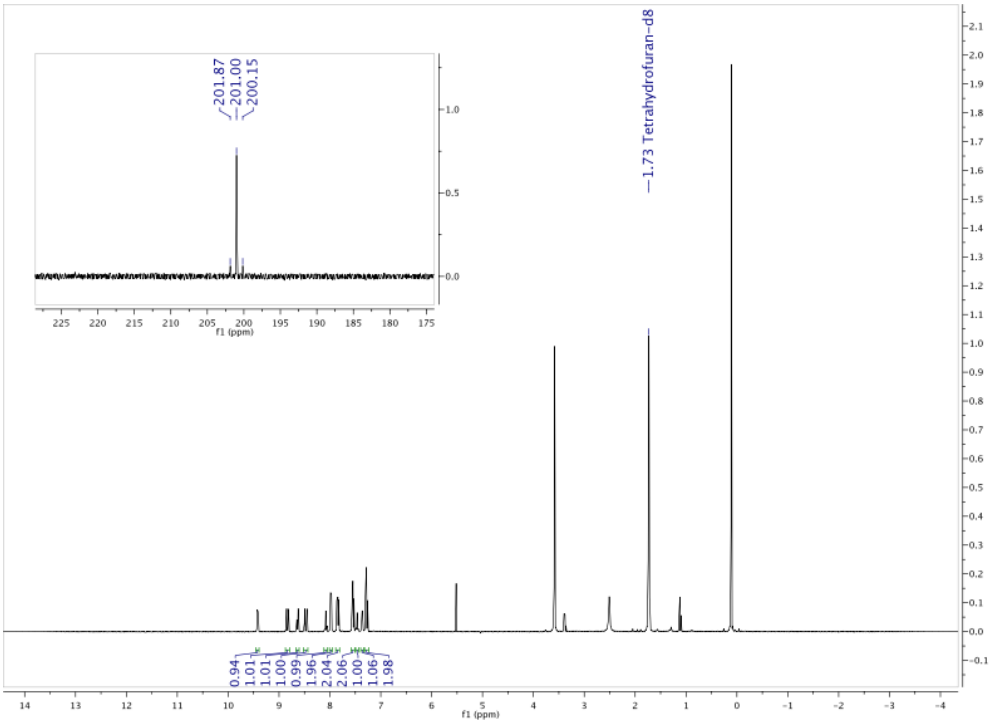
2-(2-Pyridyl)-4-(4-methylthiophenyl)-6-phenylphosphinine (3d); (^{1}H, ^{31}P (inset))



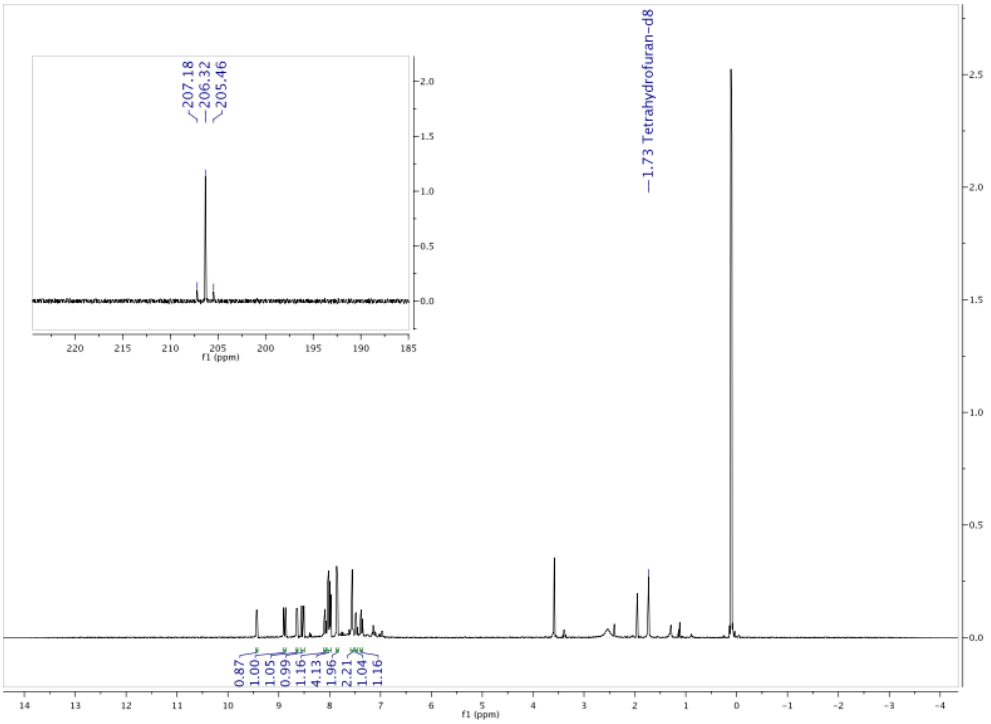
2-(2-Pyridyl)-4,6-diphenylphosphinine-P,N-tungsten tetracarbonyl (5a); (^{1}H, ^{31}P (inset))



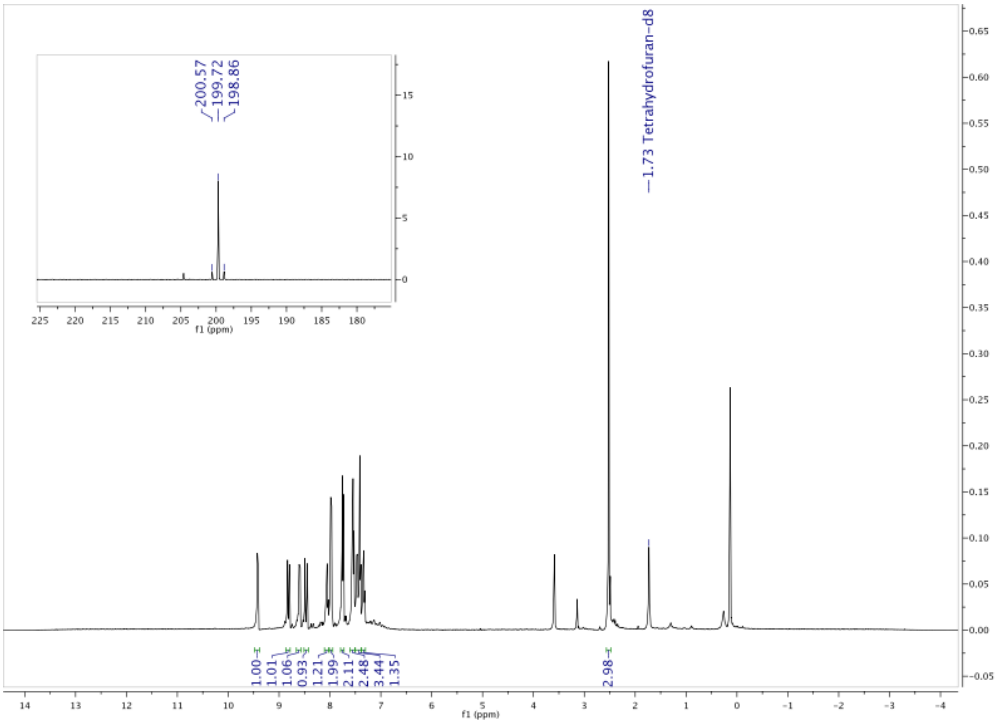
2-(2-Pyridyl)-4-phenyl-6-(4-fluorophenyl)phosphinine-P,N-tungsten tetracarbonyl (5b); (^{1}H, ^{31}P (inset))



2-(2-Pyridyl)-4-phenyl-6-(4-trifluoromethylphenyl)phosphinine-P,N-tungsten tetracarbonyl (5c); (^{1}H, ^{31}P (inset))



2-(2-Pyridyl)-4-phenyl-6-(4-methylthiophenyl)phosphinine-P,N-tungsten tetracarbonyl (5d); (^{1}H, ^{31}P (inset))



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