Supporting Information
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Synthesis, Structure, and Applications of Pyridiniophosphines**
Hendrik Tinnermann, Christian Wille, and Manuel Alcarazo*

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General procedures: All reactions were carried out in flame-dried glassware under Argon. All the solvents were purified by distillation over the drying agents indicated and were transferred under Argon. CH₂Cl₂ (CaH₂), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV). ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ¹H and ¹³C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. All commercially available compounds (Acros, Fluka, Lancaster, Alfa Aesar, Aldrich) were used as received unless stated otherwise. Compounds 7¹, 35² and 37³ were prepared accordingly to the procedure described in the literature.

¹ K. H. Müller, M. W. Drewes, P. Dahmen, D. Feucht, DE 100 24 938 A 1
General procedure for the Alkylation of 2-Chloropyridines. A solution of the corresponding 2-chloropyridine (1 equiv.) in DCM (0.05 M) was added to solid Me₃OBF₄ or Et₃OBF₄ (1 equiv.) and the suspension stirred overnight. Then, the solvent was filtered off and the remaining white solid washed twice with dichloromethane and dried in vacuum.

**Compound 6**: Prepared from 2-chloropyridine (2.0 g, 17.6 mmol) and Me₃OBF₄ (2.6 g, 17.6 mmol) following the general procedure. After washing with DCM (2 x 20 ml), 6 was obtained as a white solid (3.47 g, 91%).

\[ \text{1H NMR (300 MHz, CD₃CN) } \delta = 8.75 (d, J = 6.2 Hz, 1H), 8.47 (td, J = 8.2, 1.5 Hz, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.94 (t, J = 6.8 Hz, 1H), 4.30 (s, 3H); \]

**Compound 8**: Prepared from 2-chloro-5-fluoropyridine (1.0 g, 7.6 mmol) and Me₃OBF₄ (1.12 g, 7.6 mmol) following the general procedure. After washing with DCM (2 x 20 ml), 8 was obtained as a white solid (1.75 g, 99%).

\[ \text{1H NMR (300 MHz, CD₃CN) } \delta = 8.88 (t, J = 3.1 Hz, 1H), 8.36 (ddd, J = 9.4, 6.7, 2.9 Hz, 1H), 8.16 (dd, J = 9.3, 4.9 Hz, 1H), 4.31 (s, 3H); \]

**Compound 9**: Prepared from 2-chloro-5-(trifluoromethyl)pyridine (400 mg, 2.2 mmol) and Me₃OBF₄ (325 mg, 2.2 mmol) following the general procedure. After washing with DCM (2 x 2 ml), 9 was obtained as a white solid (620 mg, 99%).

\[ \text{1H NMR (300 MHz, CD₃CN) } \delta = 9.23 (s, 1H), 8.75 (dd, J = 8.7, 2.0 Hz, 1H), 8.34 (d, J = 8.7 Hz, 1H), 4.39 (s, 3H); \]

**HRMS calcd. for C₁₂H₁₄BCl₂F₄N₂**: 343.056684; **found**: 343.056646.

**HRMS calcd. for C₁₂H₁₂N₂BCl₂F₆**: 379.036928; **found**: 379.037035.

**HRMS calcd. for C₇H₆NClF₃**: 196.013540; **found**: 196.013563.
**Compound 11:** Prepared from 2-chloro-5-methoxypyridine (965 mg, 6.72 mmol) and Me$_3$OBF$_4$ (994 mg, 6.72 mmol) in DCM (20 ml) following the general procedure. After washing with DCM (2 x 20 ml), 11 was obtained as a white solid (1.47 g, 89%).

$^1$H NMR (300 MHz, CD$_3$CN) $\delta$ = 8.47 (d, $J$ = 2.7 Hz, 1H), 8.10 – 7.93 (m, 2H), 4.27 (s, 3H), 4.00 (s, 3H); $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta$ = 158.33, 140.00, 136.02, 134.07, 130.94, 58.76, 48.98; $^{19}$F NMR (282 MHz, CD$_3$CN) $\delta$ = -151.67, -151.72; IR (neat) $\tilde{\nu}$ = 697, 739, 847, 875, 936, 1013, 1037, 1099, 1159, 1177, 1197, 1271, 1308, 1391, 1425, 1445, 1469, 1513, 1590, 1622, 3101, 3156 cm$^{-1}$; HRMS calcd. for C$_{14}$H$_{18}$N$_2$BCl$_2$F$_4$O$_2$: 403.077864; found: 403.078070.

**Compound 10:** Prepared from 2-chloro-5-(trifluoromethyl)pyridine (1 g, 5.5 mmol) and Et$_3$OBF$_4$ (1.05 g, 5.5 mmol) in DCM (20 ml) following the general procedure and purified by filtration and washing with DCM (2 x 10 ml) to afford 10 as a white solid (1.6 g, 5.4 mmol, 99%).

$^1$H NMR (300 MHz, CD$_3$CN) $\delta$ = 9.24 (d, $J$ = 0.7 Hz, 1H), 8.74 (dd, $J$ = 8.7, 2.1 Hz, 1H), 8.34 (d, $J$ = 8.7 Hz, 1H), 4.82 (q, $J$ = 7.3 Hz, 2H), 1.62 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, CD$_3$CN) = 152.27, 146.25, 144.89 (q, $J_{C-F}$ = 3.0 Hz), 132.79, 129.92 (q, $J_{C-F}$ = 36.9 Hz), 122.21 (q, $J_{C-F}$ = 273.7 Hz); $^{19}$F NMR (282 MHz, CD$_3$CN) $\delta$ = -63.46, -151.88, -151.94; IR (neat) $\tilde{\nu}$ = 727, 740, 767, 809, 858, 939, 1023, 1056, 1095, 1110, 1146, 1183, 1193, 1233, 1299, 1328, 1395, 1413, 1453, 1473, 1509, 1586, 1639, 3089 cm$^{-1}$; HRMS calcd. for C$_8$H$_8$NClF$_3$: 210.029185; found: 210.028857.

**General procedure for the Preparation of Pyridiniophosphines.** To a solution of the corresponding 1-alkyl/aryl-2-chloropyridinium tetrafluoroborate (1 equiv.) in THF (2 ml) was added the desired secondary phosphine (2.5-3.0 equiv.) and the resulting suspension heated for 1 to 7 days. After cooling to rt, the solvents were evaporated and the crude reaction mixture washed with n-Pentan (2 x 2 ml), solved in DCM and washed with sat. NaBF$_4$ aqueous solution. The organic phase was dried over Na$_2$SO$_4$ and the solvent evaporated. If necessary, the resulting solid could be further purified by an additional wash with THF (1-2 ml).

**Compound 12:** Prepared by heating a THF suspension of 6 (400 mg, 1.8 mmol) and diphenylphosphine (1.1 ml, 5.6 mmol) at 65°C for 3 days. White solid (477 mg, 70%).
1H NMR (300 MHz, CDCl3) δ = 9.04 (d, J = 5.7 Hz, 1H), 8.25 (td, J = 7.9, 0.9 Hz, 1H), 8.03 – 7.95 (m, 1H), 7.57 – 7.43 (m, 6H), 7.39 – 7.27 (m, 5H), 4.30 (d, J = 1.1 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ = 161.02 (d, JCP = 33.4 Hz), 149.54, 144.04, 134.70 (d, JCP = 21.7 Hz), 132.63, 131.60, 130.20 (d, JCP = 21.0 Hz); 31P NMR (121 MHz, CDCl3) δ = -8.61; IR (neat) ν = 696, 724, 748, 798, 954, 1000, 1038, 1051, 1161, 1181, 1265, 1310, 1436, 1492, 1571, 1610, 3055, 3103, 3134 cm⁻¹; HRMS calcd. for C18H17NP: 278.109315; found: 278.109239.

Compound 13: Prepared by heating a THF suspension of 6 (500 mg, 2.3 mmol) and dicyclohexylphosphine (0.75 ml, 5.8 mmol) at 65°C for 3 days. White solid (699 mg, 80%).

1H NMR (400 MHz, CDCl3) δ = 9.11 (d, J = 5.2 Hz, 1H), 8.48 (t, J = 7.8 Hz, 1H), 8.05 (dd, J = 14.3, 7.5 Hz, 2H), 4.59 (s, 3H), 2.11 (t, J = 11.8 Hz, 2H), 1.91 (d, J = 12.0 Hz, 2H), 1.81 (d, J = 12.8 Hz, 2H), 1.69 (t, J = 11.9 Hz, 4H), 1.51 (d, J = 12.5 Hz, 2H), 1.41 – 1.01 (m, 10H); 13C NMR (101 MHz, CDCl3) δ = 160.33 (d, JCP = 42.5 Hz), 149.73, 143.58, 133.44 (d, JCP = 3.2 Hz), 128.24, 48.82 (d, JCP = 26.1 Hz), 34.36 (d, JCP = 15.1 Hz), 29.95 (d, JCP = 15.9 Hz), 29.44 (d, JCP = 8.6 Hz), 26.78 (d, JCP = 12.5 Hz), 26.65 (d, JCP = 8.8 Hz), 25.91; 31P NMR (162 MHz, CDCl3) δ = -3.52; IR (neat) ν = 728, 779, 851, 915, 1053, 1179, 1262, 1448, 1497, 1571, 1610, 2851, 2925 cm⁻¹; HRMS calcd. for C18H29NP: 290.203217; found: 290.203415.

Compound 14: Prepared by heating a THF suspension of 7 (650 mg, 2.3 mmol) and diphenylphosphine (1.2 ml, 6.9 mmol) at 130°C for 12 h in a microwave oven. White solid (715 mg, 71%).

1H NMR (300 MHz, CDCl3) δ = 8.76 (d, J = 5.1 Hz, 1H), 8.46 (dtd, J = 8.0 Hz, 1.3, 1H), 8.06 (t, J = 6.9 Hz, 1H), 7.66 – 7.50 (m, 4H), 7.50 – 7.37 (m, 6H), 7.32 – 7.21 (m, 6H); 13C NMR (75 MHz, CD3CN) δ = 149.53, 146.74, 135.83 (d, JCP = 22.5 Hz), 134.40, 132.53, 132.11, 131.40 (d, JCP = 8.2 Hz), 130.58 (d, JCP = 7.6 Hz), 128.25, 127.40 (d, JCP = 3.8 Hz); 19F NMR (282 MHz, CDCl3) δ = -151.82, -151.87; 31P NMR (121 MHz, CDCl3) δ = -7.74; IR (neat) ν = 692, 699, 734, 748, 757, 786, 841, 863, 901, 931, 979, 997, 1011, 1035, 1047, 1079, 1163, 1178, 1254, 1288, 1315, 1438, 1455, 1475, 1492, 1563, 1589, 1607, 3070, 3117 cm⁻¹; HRMS calcd. for C23H19NP: 340.124626; found: 360.124961.
**Compound 15:** Prepared by heating a THF suspension of 8 (500 mg, 2.14 mmol) and diphenylphosphine (0.92 ml, 5.35 mmol) at 65°C for 3 days. White solid (351 mg, 43%).

$^1$H NMR (300 MHz, CD$_3$CN) $\delta = 8.94 – 8.82$ (m, 1H), $8.18 – 8.07$ (m, 1H), $7.58$ (m, 6H), $7.42$ (m, 5H), $4.23$ (d, $J = 1.4$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCN) $\delta = 160.91$ (d, $J_{C-P} = 255.7$ Hz), $139.81$ (d, $J_{C-P} = 38.2$ Hz), $135.66$ (d, $J_{C-P} = 0.9$ Hz), $135.62$ (d, $J_{C-P} = 21.9$ Hz), $132.84$ (d, $J_{C-P} = 17.4$ Hz), $132.43$ (d, $J_{C-P} = 0.6$ Hz), $130.92$ (d, $J_{C-P} = 8.3$ Hz), $130.28$ (d, $J_{C-P} = 6.7$ Hz), $49.12$ (d, $J_{C-P} = 21.5$ Hz); $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = -9.34$; IR (neat) $\tilde{\nu} = 699, 715, 738, 753, 760, 858, 895, 931, 958, 998, 1024, 1143, 1165, 1181, 1273, 1314, 1384, 1436, 1479, 1500, 1583, 1623$ cm$^{-1}$; HRMS calcd. for C$_{18}$H$_{16}$NFP: 296.099965; found: 296.099889.

**Compound 16:** Prepared by heating a THF suspension of 9 (500 mg, 1.8 mmol) and diphenylphosphine (0.62 ml, 4.4 mmol) at 65°C for 1 day. White solid (451 mg, 60%).

$^1$H NMR (300 MHz, CD$_3$CN) $\delta = 9.18$ (s, 1H), $8.51$ (dd, $J = 8.4, 1.3$ Hz, 1H), $7.72 – 7.50$ (m, 7H), $7.50 – 7.38$ (m, 4H), $4.25$ (d, $J = 1.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta = 167.44$ (d, $J_{C-P} = 35.6$ Hz), $147.74$, $141.70$ (q, $J_{C-F} = 3.0$ Hz), $135.92$ (d, $J_{C-P} = 22.0$ Hz), $134.82$ (d, $J_{C-P} = 1.2$ Hz), $132.72$, $131.05$ (d, $J_{C-P} = 8.6$ Hz), $129.85$ (q, $J_{C-F} = 36.1$), $129.43$ (d, $J_{C-P} = 6.0$ Hz), $122.51$ (q, $J_{C-F} = 272.6$ Hz), $49.24$ (d, $J_{C-P} = 20.7$); $^{19}$F NMR (282 MHz, CD$_3$CN) $\delta = -63.67$, $-151.79$, $-151.84$; $^{31}$P NMR (121 MHz, CD$_3$CN) $\delta = -6.00$; IR (neat) $\tilde{\nu} = 693, 702, 727, 743, 752, 862, 892, 913, 996, 1048, 1090, 1115, 1148, 1174, 1267, 1342, 1435, 1504, 1579, 1639, 3103$ cm$^{-1}$; HRMS calcd. for C$_{19}$H$_{16}$NF$_3$P: 346.09727; found: 346.097027.

**Compound 17:** Prepared by heating a THF suspension of 8 (500 mg, 2.14 mmol) and dicyclohexylphosphine (1.08 ml, 5.35 mmol) at 65°C during 12 hours. White solid (648 mg, 77%).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 9.06$ (d, $J = 2.3$ Hz, 1H), $8.34 – 8.21$ (m, 1H), $8.21 – 8.08$ (m, 1H), $4.64$ (s, 3H), $2.12$ (t, $J = 11.5$ Hz, 2H), $1.98 – 1.61$ (m, 8H), $1.52$ (d, $J = 11.7$ Hz, 2H), $1.44 – 1.02$ (m, 10H); $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta = 160.88$ (d, $J_{C-F} = 255.9$ Hz), $158.18$ (dd, $J_{C-P} = 43.7$, $J_{C-F} = 4.2$ Hz), $140.06$ (d, $J_{C-P} = 36.1$ Hz), $136.29$ (dd, $J_{C-P} = 7.4$ Hz, $J_{C-F} = 3.4$ Hz), $131.93$ (d, $J_{C-P} = 17.2$ Hz), $50.13$ (d, $J_{C-P} = 26.4$ Hz), $34.72$ (d, $J_{C-P} = 14.3$ Hz), $30.48$ (d, $J_{C-P} = 16.2$ Hz), $30.01$ (d, $J_{C-P} = 8.7$ Hz), $27.42$ (d, $J_{C-P} = 10.9$ Hz), $27.28$ (d, $J_{C-P} = 10.9$ Hz), $26.61$; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta = -118.61$, $-151.62$, $-151.67$; $^{31}$P NMR (121 MHz, CD$_3$CN) $\delta = -4.49$; IR (neat) $\tilde{\nu} = 704, 738, 765, 817, 851, 889, 920, 958, 1004, 1025, 1040,$
Compound 18: Prepared by heating a THF suspension off 11 (500 mg, 2.05 mmol) and dicyclohexylphosphin (1.25 ml, 6.16 mmol) at 65°C during 12 hours. White solid (744 mg, 89%).

$^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.48 (d, $J = 2.1$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 1H), 7.94 (dd, $J = 9.0$, 2.6 Hz, 1H), 4.43 (s, 3H), 4.01 (s, 3H), 2.21 – 2.08 (m, 2H), 1.85 – 0.96 (m, 20H); $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta$ = 159.15, 138.13, 135.35, 135.31, 58.35, 49.85 (d, $J_{C,P} = 27.5$ Hz), 34.82 (d, $J_{C,P} = 13.5$ Hz), 30.76 (d, $J_{C,P} = 16.9$ Hz), 29.97 (d, $J_{C,P} = 8.1$ Hz), 27.48 (d, $J = 13.2$ Hz), 27.34 (d, $J_{C,P} = 8.8$ Hz), 26.73 (d, $J_{C,P} = 1.1$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ = -151.83, -151.85; $^{31}$P NMR (121 MHz, CDCN) $\delta$ = -7.27; IR (neat) $\tilde{\nu}$ = 704, 741, 816, 842, 884, 916, 1000, 1015, 1035, 1046, 1163, 1187, 1196, 1286, 1317, 1434, 1447, 1507, 1574, 1615, 2845, 2920 cm$^{-1}$; HRMS calcd. for C$_{18}$H$_{17}$NP: 308.193442; found: 308.193793.

Compound 19: To a suspension of KH (8.75 mg, 0.22 mmol) in THF (2 ml) was added bis(3,5-bis(trifluoromethyl)phenyl)phosphine (100 mg, 0.22 mmol) at -78 °C and the resulting deep red suspension stirred for 1 hour. Then, the suspension was transferred at the same temperature to a precooled suspension (-78 °C) of 10 (64.9 mg, 0.22 mmol) in THF (2 ml) and the mixture allowed to warm up to rt and stirred for 3 days. After evaporation of the solvent and washing with DCM (2x 2ml), compound 19 was obtained as an off white solid (48 mg, 30%).

$^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ = 9.32 (s, 1H), 8.62 (d, $J = 7.7$ Hz, 1H), 8.25 (s, 2H), 8.02 (d, $J = 7.2$ Hz, 4H), 7.92 (d, $J = 7.9$ Hz, 1H), 4.88 (m, 2H), 1.56 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta$ = 161.99 (d, $J_{C,P} = 33.4$ Hz), 147.95 – 146.40 (m), 143.99 – 142.39 (m), 137.44, 136.89 – 136.01 (m), 133.59 (qd, $J_{C,F} = 33.9$ Hz, $J_{C,P} = 7.7$ Hz), 133.19 (d, $J_{C,P} = 13.5$ Hz), 132.18 (d, $J_{C,P} = 36.9$ Hz), 124.10 (q, $J_{C,F} = 272.4$ Hz), 121.46 (q, $J_{C,F} = 273.0$ Hz), 58.60 (d, $J_{C,P} = 23.4$ Hz), 16.29 (d, $J_{C,P} = 3.5$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ = -63.52, -63.68, -151.80, -151.85; $^{31}$P NMR (121 MHz, CDCN) $\delta$ = -10.52; IR (neat) $\tilde{\nu}$ = 682, 700, 741, 767, 846, 862, 900, 913, 1051, 1095, 1120, 1279, 1331, 1356, 1405, 1459, 1502, 1588, 1634, 2001, 3090 cm$^{-1}$; HRMS calcd. for C$_{23}$H$_{14}$F$_{15}$NP: 632.062949; found: 632.061889.
General procedure for the preparation of pyridiniophosphine rhodium complexes:

[Rh(CO)2Cl]2 (0.25 equiv.) was added to a solution of the corresponding pyridiniophosphine ligand (1 equiv.) in DCM (2 ml). The resulting suspension was stirred for 1 hour at rt and after evaporation of the solvent, the solid was washed with n-pentan (2 x 2 ml) and dried in vacuum. These compounds can be crystallized from acetonitrile/ether mixtures.

**Compound 20:** Prepared from 12 (100 mg, 0.274 mmol) and [Rh(CO)Cl2]2 (26.6 mg, 0.063 mmol) following the general procedure. Yellow solid (121 mg, 99%).

\[ \begin{align*}
\text{F} & \quad \text{BF}_4^- \\
\text{N} & \quad \text{CO} \\
\text{Ph} & \quad \text{POH} \\
\text{Ph} & \quad \text{Cl} \\
\text{BF}_4^- & \\
\end{align*} \]

1H NMR (300 MHz, CDCN) \( \delta = 8.84 \) (d, \( J = 5.9 \) Hz, 2H), 8.38 (t, \( J = 7.7 \) Hz, 2H), 8.11 \( - 8.02 \) (m, 2H), 7.84 (s, 8H), 7.79 \( - 7.72 \) (m, 4H), 7.72 \( - 7.58 \) (m, 10H), 4.50 (s, 6H); 13C NMR (75 MHz, CDCN) \( \delta = 186.07 \) (dt, \( J_{C-Rh} = 31.9 \) Hz, \( J_{C-P} = 15.6 \) Hz), 153.59 (t, \( J_{C-P} = 18.1 \) Hz), 151.14, 145.60, 136.20, 134.99, 134.20, 131.14, 130.07, 126.58 (t, \( J_{C-P} = 24.3 \) Hz), 50.82; 31P NMR (121 MHz, CDCN) \( \delta = 37.82 \) (d, \( J_{P-Rh} = 130.7 \) Hz); IR (neat) \( \tilde{\nu} = 692, 707, 752, 773, 799, 900, 931, 998, 1056, 1165, 1182, 1274, 1314, 1411, 1438, 1481, 1499, 1576, 1610, 1996, 3093, 3138 \ cm\(^{-1}\)); HRMS calcd. for C\(_{37}\)H\(_{34}\)BClF\(_4\)N\(_2\)O\(_2\)P\(_2\)Rh: 809.092884; found: 809.093025.

**Compound 21:** Prepared from 15 (75 mg, 0.2 mmol) and [Rh(CO)2Cl]2 (19.3 mg, 0.05 mmol) following the general procedure. Yellow solid (121 mg, 69%).

\[ \begin{align*}
\text{F} & \quad \text{BF}_4^- \\
\text{N} & \quad \text{CO} \\
\text{Ph} & \quad \text{POH} \\
\text{Ph} & \quad \text{Cl} \\
\text{BF}_4^- & \\
\end{align*} \]

1H NMR (300 MHz, CDCN) \( \delta = 8.98 \) (s, 2H), 8.27 \( - 8.16 \) (m, 2H), 7.84 (s, 8H), 7.76 (t, \( J = 7.4 \) Hz, 4H), 7.68 (t, \( J = 7.6 \) Hz, 10H), 4.54 (s, 6H); 13C NMR (75 MHz, CDCN) \( \delta = 161.59 \) (d, \( J_{C-P} = 259.3 \) Hz), 150.65, 141.69 (d, \( J_{C-F} = 38.2 \) Hz), 136.72 (d, \( J_{C-P} = 8.5 \) Hz), 136.17, 134.35, 132.75 (d, \( J_{C-F} = 17.3 \) Hz), 131.22, 126.48, 51.51 (d, \( J_{C-P} = 1.6 \) Hz); 31P NMR (121 MHz, CDCN) \( \delta = 39.02 \) (d, \( J_{P-Rh} = 130.7 \) Hz); IR (neat) \( \tilde{\nu} = 694, 738, 754, 850, 962, 998, 1054, 1169, 1282, 1437, 1482, 1505, 1590, 1624, 1994, 3087 \ cm\(^{-1}\)); HRMS calcd. for C\(_{37}\)H\(_{32}\)BCIF\(_3\)N\(_2\)O\(_2\)P\(_2\)Rh: 845.074040; found: 845.073864.

**Compound 22:** Prepared from 16 (100 mg, 0.231 mmol) and [Rh(CO)2Cl]2 (22.5 mg, 0.058 mmol) following the general procedure. Yellow solid (68 mg, 57%).

\[ \begin{align*}
\text{F}_3\text{C} & \quad \text{BF}_4^- \\
\text{N} & \quad \text{CO} \\
\text{Ph} & \quad \text{POH} \\
\text{Ph} & \quad \text{Cl} \\
\text{BF}_4^- & \\
\end{align*} \]

1H NMR (300 MHz, CDCN) \( \delta = 9.28 \) (s, 2H), 8.65 (d, \( J = 8.2 \) Hz, 2H), 7.95 \( - 7.63 \) (m, 22H), 4.56 (s, 6H); 13C NMR (75 MHz, CDCN)
δ = 167.45 (d, J_C,P = 36.8 Hz), 147.80, 141.73, 136.46 (d, J_C,P = 22.1 Hz), 134.84, 132.76, 131.08 (d, J_C,P = 8.5 Hz), 129.81 (d, J_C,P = 36.7 Hz), 129.44 (d, J_C,P = 5.4 Hz), 122.54 (q, J_C,F = 272.8 Hz), 47.26 (d, J_C,P = 20.6 Hz); 31P NMR (121 MHz, CDCN) δ = 40.44 (d, J_Rh-P = 131.0 Hz); IR (neat) ṽ = 691, 705, 752, 858, 890, 932, 998, 1052, 1090, 1118, 1159, 1177, 1243, 1275, 1334, 1392, 1438, 1482, 1509, 1586, 1634, 1741, 2004, 3092 cm\(^{-1}\); HRMS calcd. for C_{39}H_{32}BClF_{10}N_{2}OP_{2}Rh: 945.067689; found: 945.067581.

**Compound 23:** Prepared from 14 (100 mg, 0.253 mmol) and [Rh(CO)₂Cl]₂ (24.6 mg, 0.063 mmol) following the general procedure. Yellow solid (94 mg, 78%).

\(^1H\) NMR (300 MHz, CDCl₃) δ =8.62 (d, J = 5.6 Hz, 2H), 8.49 (t, J = 7.9 Hz, 2H), 8.17 – 8.07 (m, 4H), 7.78 (dd, J = 12.7, 6.3 Hz, 8H), 7.54 (ddd, J =22.9, 14.9, 7.8 Hz, 16H), 7.33 (t, J = 7.5 Hz, 2H), 6.91 (t, J = 8.0 Hz, 4H); \(^13C\) NMR (101 MHz, CDCN) δ = 154.96, 151.72, 146.24, 142.28, 136.52 (t, J_C,P = 7.2 Hz), 136.12 – 135.26 (m), 133.73, 132.75, 130.74 (t, J_C,P = 5.5 Hz), 130.48, 129.97, 128.15, 127.91, 127.71; 31P NMR (121 MHz, CDCl₃) δ = 42.09 (d, J_Rh-P = 134.4 Hz); IR (neat) ṽ = 692, 749, 925, 998, 1034, 1048, 1182, 1254, 1286, 1318, 1437, 1457, 1479, 1587, 1603, 1891, 2350, 3060 cm\(^{-1}\); HRMS calcd. for C_{47}H_{38}BClF_{4}N_{2}OP_{2}Rh: 933.124354; found: 933.123835.

**Compound 24:** Prepared from 18 (75 mg, 0.184 mmol) and [Rh(CO)₂Cl]₂ (17.9 mg, 0.046 mmol) following the general procedure. Yellow solid (67 mg, 74%).

\(^1H\) NMR (300 MHz, DMSO) δ = 9.11 (s, 2H), 8.38 (d, J = 9.1 Hz, 2H), 8.20 (dd, J = 9.0, 2.3 Hz, 2H), 4.90 (s, 6H), 4.08 (s, 6H), 2.17 (s, 4H), 2.02 – 0.94 (m, 40H); \(^13C\) NMR (101 MHz, DMSO) δ = 185.13 (dt, J_C,Rh = 33.4 Hz, J_C,P = 16.4 Hz), 158.14, 140.35, 138.33 (t, J_C,P = 12.9 Hz), 134.89, 127.44, 57.59, 51.11 (t, J_C,P = 4.2 Hz), 36.04, 33.28, 29.39, 28.39, 27.61, 26.59, 25.77, 25.49; 31P NMR (121 MHz, DMSO) δ = 40.26 (d, J_Rh-P = 123.0 Hz); IR (neat) ṽ = 706, 739, 765, 815, 854, 888, 918, 940, 1018, 1050, 1098, 1172, 1180, 1207, 1269, 1317, 1415, 1450, 1475, 1515, 1614, 1974, 2850, 2928 cm\(^{-1}\); HRMS calcd. for C_{39}H_{62}BClF_{4}N_{2}O_{3}Rh: 893.301860; found: 893.302947.

**General procedure for the preparation of the phosphine platinum complexes.** Finely ground K₂PtCl₄ (1 equiv) was added to a solution of the pyridiniophosphine salt (1 equiv.)
in MeCN (2 ml) and the resulting suspension stirred overnight at rt. After evaporation of the solvent, the solid was washed with n-Pentan (2 x 2 ml), crystallized from DMSO/DCM and dried in vacuum to yield the desired platinum complexes.

**Compound 28:** Prepared from 12 (100 mg, 0.274 mmol) and K₂PtCl₄ (114 mg, 0.274 mmol) following the general procedure. White solid (127 mg, 80%).

¹H NMR (300 MHz, DMSO) δ = 9.18 (d, J = 5.7 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.20 (t, J = 6.9 Hz, 1H), 8.02 (dd, J = 12.3 Hz, J = 7.2 Hz, 4H), 7.79 – 7.57 (m, 6H), 7.39 (t, J = 7.0 Hz, 1H), 4.35 (s, 3H); ¹³C NMR (75 MHz, CD₃CN) δ = 150.13, 144.54 (d, J_C-P = 5.7 Hz), 135.32 (d, J_C-P = 11.6 Hz), 132.81 (d, J_C-P = 7.5 Hz), 132.63 (d, J_C-P = 2.5 Hz), 129.28 (d, J_C-P = 11.6 Hz), 128.78, 124.56, 123.71, 48.32 (d, J_C-P = 7.3 Hz); ³¹P NMR (121 MHz, DMSO) δ = 8.49 (J_C-Pt = 1954 Hz); IR (neat) v = 673, 822, 1003, 1023, 1051, 1659, 2126, 2253, 2342, 2383 cm⁻¹; HRMS for DMSO adduct calcd. for C₂₀H₂₃Cl₂NOPPtS: 621.024487; found: 621.024734.

**Compound 29:** Prepared from 16 (100 mg, 0.231 mmol) and K₂PtCl₄ (96 mg, 0.231 mmol) following the general procedure. White solid (59 mg, 40%).

¹H NMR (300 MHz, DMSO) δ = 9.85 (s, 1H), 8.98 (d, J = 8.2 Hz, 1H), 8.05 (dd, J = 12.4 Hz, J = 7.4 Hz, 4H), 7.81 – 7.60 (m, 6H), 7.55 (dd, J = 7.5 Hz, J = 7.1 Hz, 1H), 4.42 (s, 3H); ¹³C NMR (75 MHz, CD₃CN) δ = 155.07 (d, J_C-P = 46.9 Hz), 148.54, 141.59, 135.47 (d, J_C-P = 11.7 Hz), 133.48 (d, J_C-P = 7.7 Hz), 132.99, 129.46 (d, J_C-P = 11.6 Hz), 128.77 (d, J_C-P = 36.1 Hz), 123.54 (d, J_C-P = 64.0 Hz), 121.24 (q, J_C-P = 273.6 Hz), 49.19 (d, J_C-P = 6.8 Hz); ³¹P NMR (121 MHz, DMSO) δ = 10.63 (J_C-Pt = 1953 Hz); IR (neat) v = 692, 704, 725, 755, 872, 890, 1036, 1114, 1148, 1179, 1192, 1270, 1332, 1388, 1438, 1481, 1508, 1631, 3001, 3044 cm⁻¹; HRMS for DMSO adduct calcd. for C₂₁H₂₂Cl₂F₃NOPPtS: 689.013152; found: 689.014029.

**General procedure for the preparation of the phosphine gold complexes.** AuCl·SMe₂ (1 equiv.) was added to a solution of the desired pyridiniophosphine salt (1 equiv.) in DCM (2 ml) and the resulting suspension stirred for 1 hour at rt. After evaporation of the solvent, the resulting solid washed with n-Pentan (2 x 2 ml) and dried in vacuum to yield the desired gold complexes.
**Compound 30:** Prepared from 12 (100 mg, 0.274 mmol) and AuCl·SMe₂ (80.7 mg, 0.274 mmol) following the general procedure. White solid (159 mg, 99%).

$^1$H NMR (300 MHz, CDCl₃) $\delta = 9.06$ (d, $J = 0.5$ Hz, 1H), 8.44 (t, $J = 7.7$ Hz, 1H), 8.20 (t, $J = 6.4$ Hz, 1H), 7.86 – 7.53 (m, 10H), 7.38 (t, $J = 7.5$ Hz, 1H), 4.45 (s, 3H); $^{13}$C NMR (75 MHz, CDCl₃) $\delta = 151.71$, 147.12 (d, $J_{C-P} = 52.2$ Hz), 145.39 (d, $J_{C-P} = 5.6$ Hz), 134.83 (d, $J_{C-P} = 15.6$ Hz), 134.05 (d, $J_{C-P} = 2.0$ Hz), 133.77 (d, $J_{C-P} = 9.3$ Hz), 130.48 (d, $J_{C-P} = 12.8$ Hz), 122.55, 121.90, 48.64 (d, $J_{C-P} = 11.4$ Hz); $^{31}$P NMR (121 MHz, CDCl₃) $\delta = 30.88$; IR (neat) $\tilde{v} = 692, 729, 913, 998, 1055, 1097, 1162, 1185, 1438, 1482, 1500, 1609, 3061, 3138$ cm$^{-1}$; HRMS calcd. for C₁₈H₁₇NAuClP: 510.044722; found: 510.044585.

**Compound 31:** Prepared from 14 (50 mg, 0.12 mmol) and AuCl·SMe₂ (34.5 mg, 0.12 mmol) following the general procedure. White solid (53 mg, 68%).

$^1$H NMR (400 MHz, CD₃CN) $\delta = 8.94$ (s, 1H), 8.63 (t, $J = 8.0$ Hz, 1H), 8.29 (t, $J = 6.7$ Hz, 1H), 7.83 – 7.59 (m, 12H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.23 (d, $J = 7.9$ Hz, 2H); $^{13}$C NMR (101MHz, CD₃CN) $\delta = 152.22$, 148.28 (d, $J_{C-P} = 5.2$ Hz), 141.55 (d, $J_{C-P} = 4.5$ Hz), 136.26 (d, $J_{C-P} = 15.9$ Hz), 136.10 (d, $J_{C-P} = 8.2$ Hz), 134.89 (d, $J_{C-P} = 2.5$ Hz), 133.32, 131.31 (d, $J_{C-P} = 3.2$ Hz), 131.17, 131.01, 127.87, 125.84, 125.22; $^{31}$P NMR (162 MHz, CD₃CN) $\delta = 31.36$; IR (neat) $\tilde{v} = 668, 689, 712, 735, 753, 765, 786, 853, 926, 980, 997, 1030, 1044, 1099, 1144, 1162, 1189, 1256, 1283, 1433, 1442, 1458, 1483, 1587, 1603, 3060$ cm$^{-1}$; HRMS calcd. for C₂₃H₁₉NAuClP: 572.060365; found: 572.060083.

**Compound 32:** Prepared from 15 (100 mg, 0.26 mmol) and AuCl·SMe₂ (76.6 mg, 0.26 mmol) following the general procedure. White solid (166 mg, 97%).

$^1$H NMR (400 MHz, CD₃CN) $\delta = 9.02$ (dd, $J = 6.0$ Hz, 2.7, 1H), 8.27 (ddd, $J = 9.1, 6.6, 2.6$ Hz, 1H), 7.88 – 7.63 (m, 10H), 7.58 – 7.48 (m, 1H), 4.40 (s, 3H); $^{13}$C NMR (101MHz, CD₃CN) $\delta = 162.24$ (d, $J_{C-P} = 260.5$ Hz), 142.99 (d, $J_{C-P} = 37.3$ Hz), 137.51 (dd, $J_{C-F} = 10.0$ Hz, $J_{C-P} = 8.4$ Hz), 136.23 (d, $J_{C-P} = 15.9$ Hz), 135.36 (d, $J_{C-P} = 2.6$ Hz), 133.81 (d, $J_{C-P} = 6.2$ Hz), 133.58 (d, $J_{C-P} = 6.3$ Hz), 131.65 (d, $J_{C-P} = 12.8$ Hz), 123.98 (d, $J_{C-P} = 62.6$ Hz), 50.70 (d, $J_{C-P} = 11.9$ Hz); $^{31}$P NMR (162 MHz, CD₃CN) $\delta = 28.68$; IR (neat) $\tilde{v} = 690, 717, 737, 751, 852, 964, 996, 1034, 1048, 1170, 1279, 1437, 1478, 1505, 1594, 1615, 3055, 3079$ cm$^{-1}$; HRMS calcd. for C₁₈H₁₆NAuClF: 528.035295; found: 528.035127.
**Compound 33:** Prepared from 16 (100 mg, 0.23 mmol) and AuCl·SMe₂ (68 mg, 0.23 mmol) following the general procedure. White solid (151 mg, 99%).

$^1$H NMR (300 MHz, CD₂CN) δ = 9.38 (s, 1H), 8.80 – 8.71 (m, 1H), 7.90 – 7.67 (m, 11H), 4.47 (s, 3H); $^{13}$C NMR (75 MHz, CD₂CN) δ = 153.75 (d, $J_{C-P} = 46.8$ Hz), 150.38 (d, $J_{C-P} = 2.5$ Hz), 143.92 (td, $J_{C-P} = 6.1$, $J_{C-F} = 3.0$ Hz), 136.42 (d, $J_{C-P} = 15.7$ Hz), 136.41, 135.62 (d, $J_{C-P} = 2.7$ Hz), 133.42 – 131.99 (dq, $J_{C-P} = 37.1$ Hz, $J_{C-F} = 1.6$ Hz), 130.64 (d, $J_{C-P} = 10.9$ Hz), 130.07 (d, $J_{C-P} = 11.3$ Hz); $^{19}$F NMR (282 MHz, CDCl₃) δ= -63.71, -151.49, -151.54; $^{31}$P NMR (121 MHz, CD₂CN) δ = 31.54; IR (neat) $\tilde{\nu}$ = 691, 705, 715, 752, 873, 892, 996, 1053, 1118, 1162, 1200, 1280, 1334, 1393, 1440, 1481, 1510, 1590, 1634, 3092 cm$^{-1}$; HRMS calcd. for C$_{20}$H$_{18}$F$_{3}$NP: 578.032104; found: 578.032257.

**Compound 34:** Prepared from 19(SbF₆) (160 mg, 0.18 mmol) and AuCl·SMe₂ (54.3 mg, 0.18 mmol) following the general procedure to yield 34 as a white solid (104 mg, 51%).

$^1$H NMR (400 MHz, CD₂CN) δ = 9.42 (s, 1H), 8.77 (d, $J = 8.4$ Hz, 1H), 8.47 (s, 2H), 8.29 (d, $J = 13.8$ Hz, 4H), 7.89 (t, $J = 7.8$ Hz, 1H), 4.80 (qd, $J = 7.1$, 1.0 Hz, 2H), 1.64 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CD₂CN) δ = 149.19, 144.37 (dd, $J_{C-P} = 6.0$ Hz, $J_{C-F} = 3.1$ Hz), 138.51 (d, $J_{C-P} = 9.8$), 137.13 (d, $J_{C-P} = 3.1$), 136.96 (d, $J_{C-P} = 3.0$), 134.11 (qd, $J_{C-F} = 34.5$ Hz, 1H, $J_{C-P} = 13.3$ Hz), 134.00 (d, $J_{C-P} = 37.6$ Hz), 130.09 (d, $J_{C-P} = 2.9$ Hz), 126.33 (d, $J_{C-P} = 64.9$), 123.64 (q, $J_{C-P} = 272.5$), 121.94 (q, $J_{C-F} = 268.7$ Hz), 58.97 (d, $J_{C-P} = 12.4$), 16.47; $^{19}$F NMR (282 MHz, CDCl₃) δ = -63.49, -63.59, -124.01 (sext, $J_{F-121Sb} = 1940$ Hz), -124.01 (oct, $J_{F-123Sb} = 1060$ Hz); $^{31}$P NMR (121 MHz, CD₂CN) δ = 32.21; IR (neat) $\tilde{\nu}$ = 681, 699, 718, 731, 742, 764, 847, 866, 899, 927, 997, 1032, 1058, 1097, 1123, 1186, 1280, 1337, 1358, 1405, 1447, 1505, 1630, 3093 cm$^{-1}$; HRMS calcd. for C$_{24}$H$_{18}$NAuClF$_{15}$P: 863.997295; found: 863.997181.
Compound 6: $^1$H-NMR (300 MHz, CD$_3$CN)

Compound 6: $^{13}$C NMR (75 MHz, CD$_3$CN)
Compound 7: $^1$H NMR (300 MHz, CDCl$_3$)

Compound 8: $^1$H-NMR (300 MHz, CD$_3$CN)
Compound 8: $^{13}$C NMR (75 MHz, CD$_3$CN)

- 19F NMR (282 MHz, CD$_3$CN)
Compound 9: $^1$H-NMR (300 MHz, CD$_3$CN)

Compound 9: $^{13}$C NMR (75 MHz, CD$_3$CN)
**Compound 9:** $^{19}$F NMR (282 MHz, CD$_3$CN)

**Compound 10:** $^1$H NMR (300 MHz, CDCN)

**Compound 10:** $^{13}$C NMR (75 MHz, CDCN)
Compound 10: $^{19}$F NMR (282 MHz, CDCN)

Compound 11: $^1$H-NMR (300 MHz, CD$_3$CN)
Compound 11: $^{13}$C NMR (75 MHz, CD$_3$CN)

Compound 11: $^{19}$F NMR (282 MHz, CD$_3$CN)
Compound 12: $^1$H NMR (300 MHz, CD$_3$CN)
Compound 12: $^{13}$C NMR (75 MHz, CDCl$_3$)

Compound 12: $^{31}$P (121 MHz, CDCl$_3$):
Compound 13: $^1$H NMR (400 MHz, CDCl$_3$)

Compound 13: $^{31}$P NMR (162 MHz, CDCl$_3$)

Compound 13: $^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 14: $^1$H NMR (300 MHz, CDCN)

Compound 14: $^{13}$C NMR (75 MHz, CDCN)
Compound 14: $^{19}$F NMR (282 MHz, CDCN)

Compound 14: $^{31}$P NMR (121 MHz, CDCN)
Compound 15: $^1$H NMR (300 MHz, CD$_3$CN)

Compound 15: $^{13}$C NMR (282 MHz, CDCN)
Compound 15: $^{19}$F NMR (282 MHz, CDCN)

Compound 15: $^{31}$P NMR (75 MHz, CDCN)
Compound 16: $^1$H NMR (300 MHz, CDCN)

Compound 16: $^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 16: $^{19}$F NMR (282 MHz, CD$_3$CN)
Compound 16: $^{31}$P NMR (121 MHz, CD$_3$CN)

Compound 17: $^1$H NMR (300 MHz, CDCl$_3$)
**Compound 17**: $^{13}$C NMR (282 MHz, CDCN)

- 26.61 ppm
- 27.22 ppm
- 27.34 ppm
- 27.51 ppm
- 29.95 ppm
- 30.07 ppm
- 30.37 ppm
- 30.59 ppm
- 34.63 ppm
- 34.82 ppm
- 49.96 ppm
- 50.31 ppm
- 131.82 ppm
- 132.04 ppm
- 136.22 ppm
- 136.26 ppm
- 136.32 ppm
- 136.36 ppm
- 139.82 ppm
- 140.30 ppm
- 157.93 ppm
- 158.49 ppm
- 159.18 ppm
- 162.57 ppm

**Compound 17**: $^{19}$F NMR (282 MHz, CDCN)

- -151.67 ppm
- -151.62 ppm
- -118.61 ppm
**Compound 17:** $^{31}$P NMR (121 MHz, CDCN)

**Compound 18:** $^1$H NMR (300 MHz, CDCN)
Compound 18: $^{13}$C NMR (75 MHz, CDCl$_3$)

Compound 18: $^{19}$F NMR (282 MHz, CDCl$_3$)

Compound 18: $^{31}$P NMR (121 MHz, CDCl$_3$)
Compound 19: $^1$H NMR (300 MHz, CDCN)

Compound 19: $^{13}$C NMR (75 MHz, CDCN)
Compound 19: $^{19}$F NMR (282 MHz, CDCN)

Compound 19: $^{31}$P NMR (121 MHz, CDCN)
Compound 20: $^1$H NMR (300 MHz, CDCN)

Compound 20: $^{13}$C NMR (75 MHz, CDCN)
Compound 20: $^{31}$P NMR (121 MHz, CDCN)

Compound 21: $^1$H NMR (300 MHz, CDCN)
Compound 21: $^{13}$C NMR (75 MHz, CDCl$_3$)

Compound 21: $^{31}$P NMR (121 MHz, CDCl$_3$)
Compound 22: $^1$H NMR (300 MHz, CDCN)

Compound 22: $^{13}$C NMR (75 MHz, CDCN)
Compound 22: $^{31}$P NMR (121 MHz, CDCN)

Compound 23: $^1$H NMR (300 MHz, CDCl$_3$)
Compound 23: $^{13}$C NMR (75 MHz, CD$_3$CN)

Compound 23: $^{31}$P NMR (121 MHz, CDCl$_3$)
Compound 28: $^1$H NMR (300 MHz, d$_6$-DMSO/CD$_3$CN)

Compound 28: $^{13}$C NMR (75 MHz, DMSO)
Compound 28: $^{31}$P NMR (162 MHz, d$_6$-DMSO/CD$_3$CN)

Compound 29: $^1$H NMR (300 MHz, d$_6$-DMSO)
Compound 29: $^{13}$C NMR (75 MHz, DMSO)

Compound 29: $^{31}$P NMR (162 MHz, d$_6$-DMSO/CD$_3$CN)
Compound 30: $^1$H NMR (300 MHz, CDCl$_3$)

Compound 30: $^{13}$C NMR (75 MHz, CDCl$_3$)
**Compound 30:** $^{31}$P NMR (162 MHz, CDCl$_3$)

**Compound 31:** $^1$H NMR (400 MHz, CD$_3$CN)
Compound 31: $^{13}$C NMR (102 MHz, CD$_3$CN)

Compound 31: $^{31}$P NMR (162 MHz, CD$_3$CN)
Compound 32: $^1$H NMR (300 MHz, CD$_3$CN)

Compound 32: $^{13}$C NMR (75 MHz, CD$_3$CN)
Compound 32: $^{31}$P NMR (162 MHz, CD$_3$CN)

Compound 33: $^1$H NMR (300 MHz, CD$_3$CN)
Compound 33: $^{13}$C NMR (75 MHz, CD$_3$CN)

Compound 33: $^{19}$F NMR (282 MHz, CD$_3$CN)
Compound 33: $^{31}\text{P}$ NMR (162 MHz, CD$_3$CN)

Compound 34: $^1\text{H}$ NMR (400 MHz, CD$_3$CN)
Compound 34: $^{13}$C NMR (102 MHz, CD$_3$CN)

Compound 34: $^{19}$F NMR (282 MHz, CD$_3$CN)
**Compound 34:** $^{31}P$ NMR (162 MHz, CD$_3$CN)