Appendix. Supporting Information

New o-substituted diphenylphosphinic amides ligands: synthesis, characterization and complexation with Zn$^{2+}$, Cu$^{2+}$ and Y$^{3+}$

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1

White solid. Yield: 80%. Empirical formula: C_{18}H_{24}NOP. MW: 301.36 g/mol. Mp: 115 °C. $^1$H-NMR (499.84 MHz, CDCl$_3$, ppm): $\delta$ 1.15 (d, 12 H, $^3$J$_{HH} = 6.8$ Hz, H-1) 3.39 (dhep, 2H, $^3$J$_{HH} = 6.7$ Hz and $^3$J$_{PH} = 5.9$ Hz, H-2), 7.32-7.44 (m, 6H, H-5, H-6), 7.73-7.81 (m, 4 H, H-4). $^{31}$P-NMR (202.34 MHz, CDCl$_3$, ppm): $\delta$ 30.44. IR: 2970 cm$^{-1}$ ($\nu$C-H), 1435 ($\nu$P-Ph), 1173 ($\nu$P=O), 1021 ($\nu$P N-C).

2

White solid. Yield: 88%. Empirical formula: C$_{19}$H$_{24}$NO$_2$P. MW: 329.37 g/mol. Mp = 116-117 °C. $^1$H-NMR (299.95 MHz, CDCl$_3$, ppm): $\delta$ 1.31 and 1.22 (2d, 12H, $^3$J$_{HH} = 6.0$ Hz, H-1), 3.48 (dhep, 2H, $^3$J$_{HH} = 6.5$ Hz and $^3$J$_{PH} = 7.5$ Hz, H-2), 7.54 to 7.44 (m, 3H), 7.70 to 7.58 (m, 3H), 7.76-7.72 (m, 2H, H-4), 8.11 to 8.09 (m, 1H, H-8), 10.95 (s, 1H,
H-13). $^{31}$P-NMR (202.34 MHz, CDCl$_3$, ppm): $\delta$ 32.49. IR: 2970 cm$^{-1}$ (vC-H), 1689 (vC=O), 1404 (vP-Ph), 1190 (vP=O), 984 (vP N-C).

Yellow solid. Yield: 65%. Empirical formula: C$_{20}$H$_{24}$NO$_3$P. MW: 357.38 g/mol. Mp = 123 °C. $^1$H-NMR (299.95 MHz, CDCl$_3$, ppm): $\delta$ 1.24 (12H, H-1), 3.45 (2H, H-2), 7.64 to 7.37 (m, 6H, H-5, H-6, H-7), 8.10-8.05 (m, 2H, H-4), 10.94 (s, 2H, H-9). $^{13}$C-NMR (75.43 MHz, CDCl$_3$, ppm): $\delta$ 23.67 and 23.45 (C-1), 48.28 (C-2), 129.12 (C-4), 132.48 (C-5), 132.72 (C-6), 132.89 (C-7), 136.95 (d, $^1J_{PC} = 116.9$ Hz, C-3), 139.84 (C-8), 192.49 (C-9). $^{31}$P-NMR (121.42 MHz, CDCl$_3$, ppm): $\delta$ 34.94. IR: 2969 (vC-H), 1688 (vC=O), 1398 (vP-Ph), 1190 (vP=O), 976 (vP-N-C). HRMS (ESI) $m/z$, calc. for C$_{20}$H$_{24}$NO$_3$P: 358.1572 [M+H]$^+$; found: 358.1561.

White solid. Yield: 65%. Empirical Formula: C$_{12}$H$_{11}$ClN$_2$O$_2$. MW: 250.68 g/mol. Mp = 291 °C. $^1$H-NMR (500 MHz, DMSO-$d_6$, ppm): $\delta$ 1.36 (t, 3H, $^3J_{HH} = 7.1$ Hz, CH$_3$), 4.35
\( q, 2H, ^3J_{HH} = 7.1 \text{ Hz, CH}_2 \), 7.48 (t, 1H, \(^3J_{HH} = 7.1 \text{ Hz, H-6}\)), 7.91 (d, 1H, \(^3J_{HH} = 6.5 \text{ Hz, H-7}\)), 8.36 (d, 1H, \(^3J_{HH} = 8.4 \text{ Hz, H-5}\)), 8.42 (s, 2H, NH\(_2\)), 8.98 (s, 1H, H-2). \(^{13}\)C-NMR (125.69 MHz, DMSO-\(d_6\), ppm): \( \delta 14.61 \) (CH\(_3\)), 61.09 (CH\(_2\)), 100.89 (C-3), 120.12 (C-4a), 122.77 (C-5), 125.84 (C-6), 132.22 (C-7), 132.98 (C-4), 145.16 (C-8), 152.30 (C-2), 154.73 (C-8a), 167.74 (C=O). IR: 3374 (\(\nu\)N-H), 3159 (\(\nu\)C-H), 1687 (\(\nu\)C=O), 753 (\(\nu\)C-Cl).

**5b**

White solid. Yield: 62%. Empirical Formula: C\(_{12}\)H\(_{11}\)BrN\(_2\)O\(_2\). MW: 295.13 g/mol. Mp = 265 °C. \(^1\)H-NMR (500 MHz, DMSO-\(d_6\), ppm): \( \delta 1.36 \) (t, 3H, \(^3J_{HH} = 7.1 \text{ Hz, CH}_3\)), 4.36 (q, 2H, \(^3J_{HH} = 7.1 \text{ Hz, CH}_2\)), 7.41 (t, 1H, \(^3J_{HH} = 7.1 \text{ Hz, H-6}\)), 8.10 (d, 1H, \(^3J_{HH} = 10.0 \text{ Hz, H-7}\)), 8.37 (s, 2H, NH\(_2\)), 8.39 (m, 1H, H-5), 8.98 (s, 1H, H-2). \(^{13}\)C-NMR (125.69 MHz, DMSO-\(d_6\), ppm): \( \delta 14.46 \) (CH\(_3\)), 62.34 (CH\(_2\)), 101.13 (C-3), 101.37 (C-4), 119.23 (C-8), 125.08 (C-5), 128.05 (C-6), 138.16 (C-7), 148.24 (C-2), 165.83 (C=O). IR: 3368 (\(\nu\)N-H), 3139 (\(\nu\)C-H), 1688 (\(\nu\)C=O), 558 (\(\nu\)C-Br).
White solid. Yield: 70%. Empirical Formula: C_{12}H_{11}FN_{2}O_{2}. MW: 234.23 g/mol. Mp = 289 °C. ^1H-NMR (300 MHz, DMSO-d$_6$, ppm): $\delta$ 1.28 (t, 3H, $^3J_{HH} = 7.1$ Hz, CH$_3$), 4.22 (q, 2H, $^3J_{HH} = 7.1$ Hz, CH$_2$), 7.25 (1H, H-6), 7.37 (1H, H-7), 8.22 (m, 1H, H-5), 8.55 (s, 1H, H-2). ^13C-NMR (75.43 MHz, DMSO-d$_6$, ppm): $\delta$ 14.11 (CH$_3$), 59.47 (CH$_2$), 104.04 (C-6), 110.33 (C-4), 113.00 (C-7), 124.10 (C-8), 128.81 (C-5), 140.38 (C-8a), 145.19 (C-2), 162.27 (C-4a), 164.44 (C-3), 165.58 (C=O). IR: 3106 (vN-H), 2988 (vC-H), 1692 (vC=O), 1194 (vC-F).

White solid. Yield: 62%. Empirical formula: C$_{31}$H$_{35}$ClN$_3$O$_3$P. MW: 564.05 g/mol. Mp = 211 °C. ^1H-NMR (499.84 MHz, CDCl$_3$, ppm): $\delta$ 1.15 and 1.22 (12H, H-22), 1.36 (t, 3H, $^3J_{HH} = 7.1$ Hz, OCH$_2$CH$_3$), 3.45 (2H, H-21), 4.35 (q, 2H, $^3J_{HH} = 7.1$ Hz, OCH$_2$), 4.45 (d, 1H, $^2J_{HH} = 9.9$ Hz, H-10), 4.71 (d, 1H, $^2J_{HH} = 9.9$ Hz, H-10'), 6.05 (s, 1H, H-9), 7.23-7.27 (m, 1H, H-6), 7.31-7.46 (m, 7H), 7.66-7.78 (m, 4H), 9.17 (s, 1H, H-2). ^13C-NMR (125.69 MHz, CDCl$_3$, ppm): $\delta$ 14.61 (s, OCH$_3$CH$_3$), 23.41-23.43 (C-22), 47.63 (d, $^2J_{PC}$
= 5.0 Hz, C-21), 60.80 (OCH₂CH₃), 64.69 (d, 3J_PC = 5.0 Hz, C-10), 101.68 (C-3), 119.44 (C-4a), 119.84 (C-5), 125.06 (C-6), 126.96 (d, 3J_PC = 12.5 Hz, C-19 or C-14), 128.24 (d, 3J_PC = 12.5 Hz, C-19 or C-14), 131.46 (C-13), 131.63 (C-18 or C-16), 133.46, 133.47 (C-17 or C-16), 134.50, 152.43 (C-2), 153.74 (C-8), 167.99 (C=O). 31P-NMR (202.34 MHz, CDCl₃, ppm): δ 35.77. IR: 3378 (vNH), 3165 (vCH), 1687 (vC=O), 1626 (vC=N), 1495 (vP-Ph), 1254 (vC-O), 1167 (vP=O), 781 (vC-Cl).

6b

White solid. Yield: 59%. Empirical formula: C₃₃H₳₃BrN₳O₳P. MW: 608.51 g/mol. Mp = 249 °C. 1H-NMR (499.84 MHz, DMSO-d₆, ppm): δ 1.12 and 1.22 (12H, H-22), 1.36 (t, 3H, 3J_HH = 7.1 Hz, OCH₂CH₃), 3.45 (2H, H-21), 4.36 (q, 2H, 3J_HH = 7.1 Hz, OCH₂), 4.61 (d, 1H, 3J_HH = 9.9 Hz, H-10), 4.63 (d, 1H, 3J_HH = 9.9 Hz, H-10'), 5.52 (1H, H-9), 7.40-7.66 (m, 9H), 8.10 (H-7 or H-5), 8.11 (H-7 or H-5), 8.40 to 8.43 (m, 2H), 8.98 (s, 1H, H-2). 13C-NMR (125.69 MHz, DMSO-d₆, ppm): δ 14.32 (OCH₂CH₃), 23.09 and 23.14 (C-22), 46.97 (C-21), 60.67 (OCH₂CH₃), 61.95 (d, 3J_PC = 5.0 Hz, C-10), 100.57 (C-3), 119.82 (C-4a), 123.30 (C-5), 124.53 (C-4), 125.96 (C-6), 126.58 (d, 2J_PC = 12.5 Hz, C-18), 128.56 (d, 2J_PC = 11.3 Hz, C-15), 128.85 (C-12), 130.92 (C-11), 131.62 (C-19 or C-14), 131.79 (C-19 or C-14), 132.03 (C-18 or C-15), 132.66 (C-18 or C-15), 134.91 (d, 1J_PC = 120.6 Hz, C-17 or C-16), 135.32 (C-7), 146.27 (d, 1J_PC = 118.1 Hz, C-
17 or C-16), 152.19 (C-2), 154.43 (C-8), 167.41 (C=O). $^{31}$P-NMR (202.34 MHz, DMSO-$_d_6$, ppm): $\delta$ 34.18. IR: 3370 ($\nu$NH), 2961 ($\nu$CH), 1687 ($\nu$C=O), 1628 ($\nu$C=N), 1442 ($\nu$P-Ph), 1258 ($\nu$C-O), 1175 ($\nu$P=O), 980 ($\nu$P-N-C), 760 ($\nu$C-Br).

White solid. Yield: 69%. Empirical formula: C$_{31}$H$_{35}$FN$_3$O$_3$P. MW: 547.60 g/mol. Mp = 228 °C. $^1$H-NMR (499.84 MHz, DMSO-$_d_6$, ppm): $\delta$ 1.16 and 1.22 (12H, $^3$J$_{HH}$ = 4.9 Hz, H-22), 1.55 (m, 3H, OCH$_2$CH$_3$) 3.44 (2H, $^3$J$_{HH}$ = 4.9 Hz and $^3$J$_{PH}$ = 9.9 Hz, H-21), 4.05 (q, 2H, $^3$J$_{HH}$ = 7.1 Hz, OCH$_2$), 4.45 (d, 1H, $^2$J$_{HH}$ = 9.9 Hz, H-10), 4.71 (d, 1H, $^2$J$_{HH}$ = 9.9 Hz, H-10$'$), 6.05 (1H, H-9), 6.72 (H-5), 7.02 (m, 1H, H-7), 7.23-7.27 (m, 1H, H-6), 7.33-7.46 (m, 6H), 7.55 (m, 1H), 7.66-7.70 (m, 2H), 8.29 (s, 1H, H-2). $^{13}$C-NMR (125.69 MHz, DMSO-$_d_6$, ppm): $\delta$ 14.47 (OCH$_2$CH$_3$), 23.18 and 23.21 (C-22), 47.08 (C-21), 60.12 (OCH$_2$CH$_3$), 62.01 (d, $^3$J$_{PC}$ = 3.8 Hz, C-10), 126.68 (d, $^2$J$_{PC}$ = 12.6 Hz, C-18), 128.65 (d, $^2$J$_{PC}$ = 12.6 Hz, C-15), 128.93 (d, $^3$J$_{PC}$ = 11.3 Hz, C-12), 130.94 (C-11), 131.72 (C-19 or C-14), 131.90 (C-19 or C-14), 132.14 (C-6), 132.77 (d, $^2$J$_{FC}$ = 11.3 Hz, C-7), 134.91 (d, $^1$J$_{PC}$ = 122.2 Hz, C-17 or C-16), 146,73 (C-8), 162.02 (C=O). $^{31}$P-NMR (202.34 MHz, DMSO-$_d_6$, ppm): $\delta$ 34.20. IR: 3380 (vNH), 2960 (vCH), 1683 (vC=O), 1627 (vC=N), 1435 (vP-Ph), 1180 (vP=O), 980 (vP-N-C), 1181 (vCF).
Yellow oil. Yield: 71%. Empirical formula: C_{25}H_{32}N_3OP. MW: 421.51 g/mol. \(^1\)H-NMR (499.84 MHz, CDCl\(_3\), ppm): \(\delta\) 1.15 and 1.22 (H-21), 3.44 (2H, H-20), 3.78-4.07 (m, 2H, H-7), 4.45 (d, 1H, \(^2\)J\(_{HH}\) = 9.9 Hz, H-9), 4.71 (d, 1H, \(^2\)J\(_{HH}\) = 9.9 Hz, H-9'), 5.73 (1H, H-8), 7.23-7.27 (m, 1H, H-4), 7.33-7.46 (m, 6H), 7.48-7.64 (m, 1H), 7.64-7.70 (m, 2H, H-17), 7.74-7.86 (m, 1H), 8.01-8.04 (m, 1H, H-6). \(^{31}\)P-NMR (202.34 MHz, CDCl\(_3\), ppm): \(\delta\) 33.69. IR: 3298 (\(\nu\)N-H), 2968 (\(\nu\)C-H), 1591 (\(\nu\)C=N), 1435 (\(\nu\)P -Ph), 1176 (\(\nu\)P=O), 978 (\(\nu\)P-N-C).

Yellow oil. Yield: 69%. Empirical formula: C_{26}H_{34}N_3OP. MW: 435.54 g/mol. \(^1\)H-NMR (499.84 MHz, CDCl\(_3\), ppm): \(\delta\) 1.10 and 1.22 (2d, 12H, H-22), 2.82-2.92 (m, 4H, H-7, H-8), 3.38 (2H, H-21), 3.79 (d, 1H, \(^2\)J\(_{HH}\) = 14.9 Hz, H-10), 4.03 (d, 1H, \(^2\)J\(_{HH}\) = 14.9 Hz, H-10'), 7.00 (1H, H-5), 7.08 (d, 1H, \(^3\)J\(_{HH}\) = 9.9 Hz, H-3), 7.19-7.22 (m, 1H, H-4), 7.50-7.31 (m, 6H), 7.62 (d, 2H, \(^3\)J\(_{HH}\) = 9.9 Hz, H-18), 8.41 (d, 1H, \(^3\)J\(_{HH}\) = 9.9 Hz, H-6). \(^{31}\)P-
NMR (202.34 MHz, CDCl\textsubscript{3}, ppm): δ 34.20. IR: 3298 (vN-H), 2968 (vC-H), 1591 (vC=N), 1435 (vP-Ph), 1176 (vP=O), 978 (vP-N-C).

11a

Yellow oil. Yield: 68%. Empirical formula: C\textsubscript{27}H\textsubscript{45}N\textsubscript{3}O\textsubscript{4}P\textsubscript{2} MW: 537.61 g/mol. \textsuperscript{1}H-NMR (299.95 MHz, CDCl\textsubscript{3}, ppm): δ 1.21-1.31 (m, 24H, H-1, H-19), 2.51 (1H, H-14), 2.64 (m, 2H, H-15), 2.89-3.03 (m, 2H, H-16), 3.46 (dhep, 2H, \textsuperscript{3}J_{HH} = 5.9 Hz, \textsuperscript{3}J_{PH} = 8.9 Hz, H-2), 3.70 (d, 1H, \textsuperscript{3}J_{HH} = 11.9 Hz, H-13b), 3.91 (d, 1H, \textsuperscript{3}J_{HH} = 11.9 Hz, H-13a), 4.48-4.62 (m, 2H, H-18), 6.12 (1H, H-17), 7.36-7.53 (m, 7H, H-5, H-6, H-9, H-10, H-11), 7.63-7.77 (m, 3H, H-4, H-12). \textsuperscript{31}P-NMR (121.42 MHz, CDCl\textsubscript{3}, ppm): δ 8.83 (Pb), 34.29 (Pa). IR: 3361 and 3254 (vN-H), 2978 (vC-H), 1214 (vP=O phosphoramidate), 1178 (vP=O phosphinic amide) 979 (vP-O).
Yellow oil. Yield: 65%. Empirical formula: C$_{29}$H$_{49}$N$_3$O$_4$P$_2$ MW: 565.66 g/mol. $^1$H-NMR (499.84 MHz, CDCl$_3$, ppm): $\delta$ 1.15-1.25 (m, 24H, H-1, H-21), 1.44 (m, 4H, H-16, H-17), 2.48 (m, 2H, H-15), 2.79 (m, 2H, H-18), 3.17 (1H, H-14), 3.41 (2H, H-2), 3.68 (d, 1H, $^2$J$_{HH}$ = 14.9 Hz, H-13b), 4.02 (d, 1H, $^2$J$_{HH}$ = 14.9 Hz, H-13a), 4.43-4.54 (m, 2H, H-20), 7.33-7.47 (m, 7H, H-5, H-6, H-9, H-10, H-11, H-12), 7.61-7.69 (m, 2H, H-4). $^{13}$C-NMR (125.69 MHz, CDCl$_3$, ppm): $\delta$ 23.23 (d, $^3$J$_{PC}$ = 8.8 Hz, C-1), 23.64 (d, $^3$J$_{PC}$ = 8.8 Hz, C-2), 26.40 (C-16), 29.13 (d, $^3$J$_{PC}$ = 11.3 Hz, C-17), 41.05 (C-18), 47.28 (d, $^2$J$_{PC}$ = 7.5 Hz, C-2) 48.17 (C-15), 52.15 (d, $^3$J$_{PC}$ = 6.3 Hz, C-13), 70.27 (d, $^2$J$_{PC}$ = 8.8 Hz, C-20), 126.51, 128.05 (C-5), 131.69, 131.99 (C-4), 132.88 (C-9), 133.67 (d, $^1$J$_{PC}$ = 109.3 Hz, C-3), 135.31 (d, $^1$J$_{PC}$ = 101.8 Hz, C-7). $^{31}$P-NMR (202.34 MHz, CDCl$_3$, ppm): $\delta$ 8.11 (Pb), 34.46 (Pa). IR: 3340 and 3227 ($\nu$N-H), 2976 ($\nu$C-H), 1228 ($\nu$P=O phosphoramidate), 1176 ($\nu$P=O phosphinic amide) 976 ($\nu$P-O). HRMS (ESI) m/z, calc. for C$_{29}$H$_{49}$N$_3$O$_4$P$_2$: 566.3263 [M+H]$^+$; found: 566.3276.
Yellow oil. Yield: 68%. Empirical formula: C\textsubscript{30}H\textsubscript{51}N\textsubscript{3}O\textsubscript{4}P\textsubscript{2} MW: 579.69 g/mol. \textsuperscript{1}H NMR (499.84 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 0.82 (m, 2H, H-17), 1.11-1.25 (m, 24H, H-1, H-22), 1.34-1.48 (m, 4H, H-16, H-18), 2.47 (H-15), 2.75-2.84 (m, 2H, H-19), 3.35-3.45 (m, 3H, H-2, H-14), 3.70 (d, 1H, \(^2\text{J}_{\text{HH}} = 14.9\) Hz, H-13b), 4.04 (d, 1H, \(^2\text{J}_{\text{HH}} = 14.9\) Hz, H-13a), 4.45-4.54 (m, 2H, H-21), 7.36-7.47 (m, 7H, H-5 H-6, H-9, H-10, H-11, H-12), 7.60-7.65 (m, 2H, H-4). \textsuperscript{13}C-NMR (125.69 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 23.25 (C-1), 23.67 (C-22), 24.09 (C-17), 28.75 (C-16), 31.24 (C-18), 41.20 (C-19), 47.34 (C-2), 48.50 (C-15), 52.23 (d, \(^3\text{J}_{\text{PC}} = 5.0\) Hz, C-13), 70.36 (d, \(^2\text{J}_{\text{PC}} = 6.3\) Hz, C-21), 126.63, 128.10 (C-5), 131.36, 131.73 (C-4), 132.92 (C-9), 132.55 (d, \(^1\text{J}_{\text{PC}} = 123.2\) Hz, C-3), 134.72 (d, \(^1\text{J}_{\text{PC}} = 121.9\) Hz, C-7), 134.88 (C-8). \textsuperscript{31}P-NMR (202.34 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 7.66 (Pb) and 34.82 (Pa). IR: 3371 and 3203 (\(\nu\text{N-H}\)), 2927 (\(\nu\text{C-H}\)), 1205 (\(\nu\text{P=O phosphoramidate}\)), 1177 (\(\nu\text{P=O phosphinic amide}\)) 978 (\(\nu\text{P-O}\)). HRMS (ESI) \(m/z\), calc. for C\textsubscript{30}H\textsubscript{51}N\textsubscript{3}O\textsubscript{4}P\textsubscript{2}: 580.3433 [M+H]\textsuperscript{+}; found: 580.3428.
Yellow oil. Yield: 69%. Empirical formula: C_{31}H_{53}N_{3}O_{4}P_{2} MW: 593.72 g/mol. \(^1\)H-NMR (299.95 MHz, CDCl\(_3\), ppm): \(\delta 1.11-1.13\) (m, 4H, H-17, H-18), \(1.23-1.25\) (m, 24H, H-1, H-23), \(1.33-1.43\) (m, 4H, H-16, H-19), \(2.32-2.44\) (m, 3H, H-14, H-15), \(2.76-2.84\) (m, 2H, H-20), \(3.33-3.48\) (m, 2H, H-2), \(3.69\) (d, 1H, \(^2\)J\(_{HH}\) = 11.9 Hz, H-13b), \(4.03\) (d, 1H, \(^2\)J\(_{HH}\) = 11.9 Hz, H-13a), \(4.46-4.57\) (m, 2H, H-22), \(7.34-7.49\) (m, 7H, H-5, H-6, H-9, H-10, H 11, H-12), \(7.61-7.68\) (m, 2H, H-4). \(^{13}\)C-NMR (75.43 MHz, CDCl\(_3\), ppm): \(\delta 23.13\) (C-1), \(23.57\) (C-23), \(26.17\) (C-18), \(26.58\) (C-17), \(28.88\) (C-16), \(31.27\) (\(^3\)J\(_{PC}\) = 6.8 Hz, C-19), \(41.13\) (C-20), \(47.22\) (C-2), \(48.38\) (C-15), \(51.99\) (d, \(^3\)J\(_{PC}\) = 3.8 Hz, C-13), \(70.25\) (d, \(^2\)J\(_{PC}\) = 6.0 Hz, C-22), \(126.54\), \(127.99\) (C-5), \(131.26\), \(131.60\) (C-4), \(132.50\) (C-9), \(132.83\), \(134.70\) (d, \(^1\)J\(_{PC}\) = 121.4 Hz, C-3), \(132.21\) (d, \(^1\)J\(_{PC}\) = 123.7 Hz, C-7), \(142.54\) (C-8). \(^{31}\)P-NMR (121.42 MHz, CDCl\(_3\), ppm): \(\delta 7.66\) (Pb), \(34.87\) (Pa). IR: 3405 and 3251 (vN-H), 2931 (vC-H), 1205 (vP=O phosphoramidate), 1176 (vP=O phosphinic amide) 976 (vP-O). HRMS (ESI) \(m/z\), calc. for C_{31}H_{53}N_{3}O_{4}P_{2}: 594.3589 [M+H]^+; found: 594.3584.
Yellow oil. Yield: 68%. Empirical formula: C_{36}H_{66}N_{5}O_{7}P_{3} MW: 773.85 g/mol. \(^1H\)-NMR (299.95 MHz, CDCl\(_3\), ppm): \(\delta\) 0.84 (m, 4H, H-12), 1.12-1.22 (m, 36H, H-1, H-15), 1.49-1.98 (m, 4H, H-11), 2.73-2.79 (2H, H-10), 3.42-3.51 (m, 2H, H-9/9'), 3.64 (1H, H-9), 3.92 (1H, H-9'), 4.38 (dhep, 4H, \(^3J_{HH}= 5.9\), \(^3J_{PH}= 8.9\) Hz, H-14), 4.70-4.79 (2H, H-13), 7.51-7.80 (m, 8H, H-4, H-5, H-6, H-7). \(^13C\)-NMR (75.43 MHz, CDCl\(_3\), ppm): \(\delta\) 23.69 (C-15), 29.36 (C-1), 39.33 (C-11), 42.59 (d, \(^3J_{PC}= 5.3\) Hz, C-9), 47.73 (d, \(^2J_{PC}= 5.3\) Hz, C-12), 70.76 (d, \(^2J_{PC}= 5.3\) Hz, C-14), 70.43 (C-2), 127.21-133.54 (C-3, C-4, C-5, C-6, C-7, C-8). \(^{31}P\)-NMR (121.42 MHz, CDCl\(_3\), ppm): \(\delta\) 8.62 (2P, Pb), 28.90 (1P, Pa). IR: 3386 and 3233 (\(\nu\)N-H), 2976 (\(\nu\)C-H), 1205 (\(\nu\)P=O phosphoramidate), 1177 (\(\nu\)P=O phosphinic amide) 979 (\(\nu\)P-O).

**13b**

Yellow oil. Yield: 58%. Empirical formula: C_{40}H_{74}N_{5}O_{7}P_{3} MW: 829.96 g/mol. \(^1H\)-NMR (299.95 MHz, CDCl\(_3\), ppm): \(\delta\) 1.14-1.27 (m, 36H, H-1, H-17), 1.41-1.49 (m, 4H, H-13), 2.43-2.57 (m, 4H, H-12), 2.72-2.87 (m, 4H, H-14), 3.13-3.22 (2H, H-10), 3.39
(dhep, 2H, 3JHH = 5.9 Hz, 3JPH = 8.9 Hz, H-2), 3.70 (d, 2H, 2JHH = 14.9 Hz, H-9/9’), 4.09 (d, 2H, 2JHH = 14.9 Hz, H-9/9’), 4.49 (4H, H-16), 7.19-7.20 (m, 2H, H-6), 7.23 (m, 4H, H-4, H-5), 7.73-7.80 (m, 1H, H-7). 13C-NMR (75.43 MHz, CDCl3, ppm): δ 22.82 and 22.88 (C-17), 25.64 (C-12), 28.38 (C-1), 40.21 (C-13), 46.07 (d, 3JPC = 4.5 Hz, C-9), 46.67 (d, 2JPC = 5.3 Hz, C-14), 47.23 (C-11), 69.39 (d, 2JPC = 5.3 Hz, C-2), 69.64 (d, 2JPC = 5.3 Hz, C-16), 125.62-132.90 (C-3, C-4, C-5, C-6, C-7, C-8). 31P-NMR (121.42 MHz, CDCl3, ppm): δ 8.23 (2P, Pb), 38.84 (1P, Pa). IR: 3409 and 3265 (νN-H), 2918 (νC-H), 1229 (νP=O phosphoramidate), 1179 (νP=O phosphinic amide), 979 (νP-O). HRMS (ESI) m/z, calc. for C40H74N5O7P3: 830.4879 [M+H]+; found: 830.4883.

Yellow oil. Yield: 62%. Empirical formula: C42H78N5O7P3 MW: 858.01 g/mol. 1H-NMR (499.84 MHz, CDCl3, ppm): δ 1.12-1.26 (m, 36H, H-1, H-18), 1.30-1.61 (m, 12H, H-12, H-13, H-14), 2.41-2.55 (m, 4H, H-11), 2.74-2.84 (m, 4H, H-15), 3.35-3.43 (m, 2H, H-2), 3.72 (d, 2H, 3JHH = 14.9 Hz, H-9/9’), 4.10 (d, 2H, 2JHH = 14.9 Hz, H-9/9’), 4.43-4.56 (m, 4H, H-17), 7.20 (m, 2H, H-6), 7.34-7.76 (m, 6H, H-4, H-5, H-7). 13C-NMR (125.69 MHz, CDCl3, ppm): δ 15.08 (C-13), 23.66 and 23.67 (C-18), 24.17 (C-13), 28.91 (C-12), 31.18 (d, 3JPC = 6.3 Hz, C-14), 41.15 (d, 3JPC = 1.3 Hz, C-9), 47.54 (C-11), 48.50 (C-15), 70.26 (d, 2JPC = 5.0 Hz, C-2), 70.41 (d, 2JPC = 5.0 Hz, C-17), 126.60-133.33 (C-3, C-4, C-5, C-6, C-7, C-8). 31P-NMR (202.34 MHz, CDCl3, ppm): δ 8.15 (2P, Pb), 38.62 (1P, Pa). IR: 3420 and 3251 (νN-H), 2930 (νC-H), 1205 (νP=O).
phosphoramide), 1177 (vP=O phosphinic amide), 978 (vP-O). HRMS (ESI) m/z, calc.
for \( \text{C}_{42}\text{H}_{78}\text{N}_{5}\text{O}_{7}\text{P}_{3} \): 858.5192 \([\text{M}+\text{H}]^+\); found: 858.5159.

13d

Yellow. Yield: 69%. Empirical formula: \( \text{C}_{44}\text{H}_{82}\text{N}_{5}\text{O}_{7}\text{P}_{3} \) MW: 886.07 g/mol. \( ^1\text{H}-\text{NMR} \)
(299.95 MHz, CDCl\(_3\), ppm): \( \delta \) 0.91-1.12 (m, 4H, H-14), 1.14-1.27 (m, 36H, H-1, H-19),
1.28-1.61 (m, 8H, H-1, 13), 2.51 (m, 4H, H-15 or H-16), 2.72-2.85 (m, 4H, H-11),
3.32-3.46 (m, 2H, H-2), 3.73 (d, 2H, \( ^2J_{\text{HH}} = 11.9 \) Hz, H-9/9’), 4.10 (d, 2H, \( ^2J_{\text{HH}} = 11.9 \)
Hz, H-9,9’), 4.45-4.57 (m, 4H, H-18), 7.19 (m, 2H, H-6), 7.24-7.77 (m, 6H, H-4, H-5,
H-7). \( ^{13}\text{C}-\text{NMR} \) (75.43 MHz, CDCl\(_3\), ppm): \( \delta \) 23.45-23.68 (C-19), 26.17 (C-14), 26.79
(C-13), 31.48 (d, \( ^3J_{\text{PC}} = 6.8 \) Hz, C-15), 41.23 (C-12), 47.55 (C-11), 48.67 (C-16), 51.97
(d, \( ^3J_{\text{PC}} = 4.5 \) Hz, C-9), 70.33 (d, \( ^2J_{\text{PC}} = 5.3 \) Hz, C-2), 70.41 (d, \( ^2J_{\text{PC}} = 6.0 \) Hz, C-18),
126.66-133.59 (C-3, C-4, C-5, C-6, C-7, C-8). \( ^{31}\text{P}-\text{NMR} \) (121.42 MHz, CDCl\(_3\), ppm): \( \delta \)
4.75 (2P, Pb), 5.76 (1P, Pa). IR: 3409 and 3244 (vN-H), 2928 (vC-H), 1205 (vP=O
phosphoramide), 1182 (vP=O phosphinic amide), 979 (vP-O). HRMS (ESI) m/z, calc.
for \( \text{C}_{44}\text{H}_{82}\text{N}_{5}\text{O}_{7}\text{P}_{3} \): 886.5505 \([\text{M}+\text{H}]^+\); found: 886.5535.
$^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, IR and HRMS (ESI) spectra

IR spectrum of 1

$^1$H NMR spectrum of 2
$^{31}\text{P}$ NMR spectrum of \(2\)

IR spectrum of \(2\)
\(^1\)H NMR spectrum of 3


APT \(^{13}\)C NMR spectrum of 3


$^{31}$P NMR spectrum of 3

[Image of a $^{31}$P NMR spectrum]

IR spectrum of 3

[Image of an IR spectrum]
HRMS (ESI) spectrum of 3

\[ \text{HRMS (ESI) spectrum of 3} \]

\[ \text{1H NMR spectrum of 5a} \]
APT $^{13}$C NMR spectrum of 5a

IR spectrum of 5a
$^1$H NMR spectrum of 5b

APT $^{13}$C NMR spectrum of 5b
IR spectrum of 5b

$^{1}$H NMR spectrum of 5c
APT $^{13}$C NMR spectrum of 5c

IR spectrum of 5c
$^1$H NMR spectrum of 6a

APT $^{13}$C NMR spectrum of 6a
$^3$P NMR spectrum of 6a

$^1$H NMR spectrum of 6b
APT $^{13}$C NMR spectrum of 6b

$^{31}$P NMR spectrum of 6b
$^1$H NMR spectrum of 6c

APT $^{13}$C NMR spectrum of 6c
$^{31}$P NMR spectrum of 6c

$^1$H NMR spectrum of 8a
$^{31}$P NMR spectrum of 8a

$^1$H NMR spectrum of 8b
\(^{31}\)P NMR spectrum of 8b

\(^{1}\)H NMR spectrum of 11a
$^{31}$P NMR spectrum of 11a

$^1$H NMR spectrum of 11b
\(^{31}\)P NMR spectrum of \(11b\)

APT \(^{13}\)C NMR spectrum of \(11b\)
HRMS (ESI) spectrum of 11b

1H NMR spectrum of 11c
APT $^{13}$C NMR spectrum of 11c

$^{31}$P NMR spectrum of 11c
HRMS (ESI) spectrum of 11c
$^1$H NMR spectrum of 11d

APT $^{13}$C NMR spectrum of 11d
$^{31}$P NMR spectrum of 11d

HRMS (ESI) spectrum of 11d
$^1$H NMR spectrum of 13a

$^{13}$C NMR spectrum of 13a
$^{31}$P NMR spectrum of 13a

$^1$H NMR spectrum of 13b
$^{13}$C NMR spectrum of 13b

$^{31}$P NMR spectrum of 13b
HRMS (ESI) spectrum of 13b
$^{1}$H NMR spectrum of 13c

$^{13}$C NMR spectrum of 13c
$^{31}$P NMR spectrum of 13c
HRMS (ESI) spectrum of 13c

m8cm62
03-17-07 (0.030) C42H79N5O7P3
859.5225
03-17-07 435 (1.651) Cm (435-271:262)
1: TOF MS ES+
6.00e12

m8cm62
03-17-07 435 (1.651) Cm (435-271:292)
1: TOF MS ES+
1.60e3

03-17-07 435 (1.651) Cm (435-271:292)
1: TOF MS ES+
2.60e3
$^1$H NMR spectrum of 13d

$^{13}$C NMR spectrum of 13d
$^{31}$P NMR spectrum of 13d
HRMS (ESI) spectrum of 13d
Complexation data

1) $^1$H NMR spectra of 11b and 11b/ZnCl$_2$

*from methanol*
2) IR spectra

IR spectrum of 6a

IR spectrum of 6a in the presence of ZnCl₂
IR spectrum of 6a in the presence of CuSO₄

IR spectrum of 6a in the presence of Y(NO₃)₃
IR spectrum of 6b

IR spectrum of 6b in the presence of ZnCl₂
IR spectrum of 6b in the presence of CuSO₄

IR spectrum of 6b in the presence of Y(NO₃)₃
IR spectrum of 6c

IR spectrum of 6c in the presence of ZnCl₂
IR spectrum of 6c in the presence of CuSO$_4$

IR spectrum of 6c in the presence of Y(NO$_3$)$_3$
IR spectrum of 8a

IR spectrum of 8a in the presence of ZnCl$_2$
IR spectrum of 8a in the presence of CuSO₄

IR spectrum of 8a in the presence of Y(NO₃)₃
IR spectrum of 8b

IR spectrum of 8b in the presence of ZnCl₂
IR spectrum of 8b in the presence of CuSO₄

IR spectrum of 8b in the presence of Y(NO₃)₃
IR spectrum of 11a

IR spectrum of 11a in the presence of ZnCl₂
IR spectrum of **11a** in the presence of CuSO$_4$

IR spectrum of **11a** in the presence of Y(NO$_3$)$_3$
IR spectrum of 11b

IR spectrum of 11b in the presence of ZnCl₂
IR spectrum of 11b in the presence of CuSO$_4$

IR spectrum of 11b in the presence of Y(NO$_3$)$_3$
IR spectrum of **11c**

IR spectrum of **11c** in the presence of ZnCl₂
IR spectrum of 11c in the presence of CuSO₄

IR spectrum of 11c in the presence of Y(NO₃)₃
IR spectrum of 11d

IR spectrum of 11d in the presence of ZnCl₂
IR spectrum of 11d in the presence of CuSO₄

IR spectrum of 11d in the presence of Y(NO₃)₃
IR spectrum of 13a

![IR spectrum of 13a](image)

IR spectrum of 13a in the presence of ZnCl₂

![IR spectrum of 13a in the presence of ZnCl₂](image)
IR spectrum of 13a in the presence of CuSO₄

IR spectrum of 13a in the presence of Y(NO₃)₃
IR spectrum of 13b

IR spectrum of 13b in the presence of ZnCl₂
IR spectrum of 13b in the presence of CuSO₄

IR spectrum of 13b in the presence of Y(NO₃)₃
IR spectrum of 13c

IR spectrum of 13c in the presence of ZnCl₂
IR spectrum of 13c in the presence of CuSO$_4$

IR spectrum of 13c in the presence of Y(NO$_3$)$_3$
IR spectrum of 13d

IR spectrum of 13d in the presence of ZnCl₂
IR spectrum of **13d** in the presence of CuSO₄

![IR spectrum of 13d in the presence of CuSO₄](image)

IR spectrum of **13d** in the presence of Y(NO₃)₃

![IR spectrum of 13d in the presence of Y(NO₃)₃](image)
3) Spectrofluorimetric spectra

6a in the presence of ZnCl$_2$

6a in the presence of CuSO$_4$

6a in the presence of Y(NO$_3$)$_3$
6b in the presence of ZnCl$_2$

6b in the presence of CuSO$_4$

6b in the presence of Y(NO$_3$)$_3$
6c in the presence of ZnCl$_2$

6c in the presence of CuSO$_4$

6c in the presence of Y(NO$_3$)$_3$
8a in the presence of ZnCl₂
**8b** in the presence of ZnCl$_2$

![Graph showing emission spectra in the presence of ZnCl$_2$.]

**8b** in the presence of CuSO$_4$

![Graph showing emission spectra in the presence of CuSO$_4$.]

**8b** in the presence of Y(NO$_3$)$_3$

![Graph showing emission spectra in the presence of Y(NO$_3$)$_3$.]
**11a in the presence of ZnCl₂**

![Graph 1](image1)

**11a in the presence of CuSO₄**

![Graph 2](image2)

**11a in the presence of Y(NO₃)₃**

![Graph 3](image3)
**11b in the presence of ZnCl$_2$**

![Graph 1](image1)

**11b in the presence of CuSO$_4$**

![Graph 2](image2)

**11b in the presence of Y(NO$_3$)$_3$**

![Graph 3](image3)
**11c** in the presence of ZnCl$_2$
11d in the presence of ZnCl$_2$

11d in the presence of CuSO$_4$

11d in the presence of Y(NO$_3$)$_3$
13a in the presence of ZnCl$_2$

13a in the presence of CuSO$_4$

13a in the presence of Y(NO$_3$)$_3$
13b in the presence of CuSO₄

In situ (a.u.)

13b in the presence of Y(NO₃)₃

In situ (a.u.)
**13c** in the presence of ZnCl$_2$

![Graph showing the intensity of light at different wavelengths for 13c in the presence of ZnCl$_2$.](image1)

**13c** in the presence of CuSO$_4$

![Graph showing the intensity of light at different wavelengths for 13c in the presence of CuSO$_4$.](image2)

**13c** in the presence of Y(NO$_3$)$_3$

![Graph showing the intensity of light at different wavelengths for 13c in the presence of Y(NO$_3$)$_3$.](image3)
13d in the presence of CuSO₄

13d in the presence of Y(NO₃)₃
4) Titration curves

Titration curves of ligands 6a-c and 8a-b with Zn$^{2+}$.

Titration curves of ligands 6a-c and 8a-b with Cu$^{2+}$.

Titration curves of ligands 6a-c and 8a-b with Y$^{3+}$. 

90
Titration curves of ligands 11a-d and 13a-c with Zn$^{2+}$.

Titration curves of ligands 11a-d and 13a-d with Cu$^{2+}$.

Titration curves of ligands 11a-d and 13a-d with Y$^{3+}$.