Supporting Information

Synthesis and reactivity of rare-earth metal phosphaethynolates

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I. Characterization

General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2).

Nuclear Magnetic Resonance (NMR)

NMR samples were prepared inside an inert atmosphere glovebox in NMR tubes fitted with a gas-tight valve. ^{1}H, ^{11}B, ^{13}C{^{1}H}, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded on the following NMR instruments with appropriate resonance frequencies: a) Bruker Avance III HD nanobay NMR equipped with a 9.4 T magnet (^{1}H 400.2 MHz, ^{11}B 128.4 MHz, ^{13}C 100.6 MHz, ^{19}F 376.5 MHz, ^{31}P 162.0 MHz), b) Bruker Avance III NMR equipped with a 11.75 T magnet (^{1}H 499.9 MHz, ^{11}B 160.4 MHz, ^{13}C 125.7 MHz,^{19}F 470.4 MHz, ^{31}P 202.4 MHz), c) Bruker Avance NMR equipped with a 11.75 T magnet and a ^{13}C detect cryoprobe (^{1}H 500.3 MHz, ^{13}C 125.8 MHz). ^{89}Y{^{1}H} INEPT and ^{1}H-{^{89}Y} HMQC NMR spectra were recorded at 19.6 MHz and (400.2 MHz / 19.6 MHz), respectively, on the Bruker Avance III HD nanobay NMR. ^{1}H and ^{13}C{^{1}H} NMR spectra are reported relative to TMS and referenced to the most downfield residual solvent resonance where possible. ^{31}P{^{1}H} NMR spectra were externally referenced to an 85% solution of H_3PO_4 in H_2O ($\delta = 0$ ppm). ^{89}Y{^{1}H} NMR spectra were externally referenced to a 1M solution of $Y(NO_3)_3(H_2O)_6$ in D_2O.

Infrared (IR) Spectroscopy

IR spectra were obtained on a Bruker Tensor 37 as Nujol mulls.

Elemental Analysis (EA)

Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U. K.). Samples (approx. 10 mg) were submitted in sealed Pyrex ampoules.

II. Materials and general synthetic procedures

n-Pentane, *n*-hexane (hex; Sigma-Aldrich, HPLC grade), benzene and toluene (Sigma-Aldrich; HPLC grade) were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (thf; Sigma-Aldrich, HPLC grade) was distilled over sodium metal/benzophenone. All dry solvents were stored under argon in gas-tight ampoules. Additionally, *n*-pentane, *n*-hexane and thf were stored over activated 3 Å molecular sieves. thf-d_8 (Sigma-Aldrich, 99.5%) was dried over CaH_2 and vacuum distilled before use. C_6D_6 was stored over activated 3 Å molecular sieves and degassed prior to use. Potassium bis(trimethylsilyl)amide (KHMDS) was purchased from Sigma Aldrich (95 %) and used as received. Anhydrous YCl_3 and $NdCl_3$ were purchased from Strem chemicals and used as received. Sm metal was obtained from smart-elements® GmbH (Austria). $[Na(OCP)(dioxane)_x]$ (x = 3.42, 2 or 0.3) was prepared according to literature procedures.[1] The dioxane content was determined by $^{31}P\{^1H\}$ NMR spectroscopy using PPh_3 as internal standard. $B(C_6F_5)_3$ was prepared according to literature procedures.[2] *N*, *N'*-bis(2,6-diisopropylphenyl)formamidine (DippFormH),[3] $SmI_2(thf)_2$,[4] and $[(DippForm)_2Sm(thf)_2]$[5-6] were prepared according to literature procedures. DippFormK was reported previously using a slightly different procedure.[7]

III. Synthesis of metal complexes

Synthesis of [(DippForm)K]

To a mixture of *N*,*N'*-bis(2,6-diisopropylphenyl)formamidine (4.00 g, 10.97 mmol, 1.00 eq.) and KHMDS (2.410 g, 12.08 mmol, 1.10 eq.), toluene (50 ml) was added. The cloudy suspension was stirred at room temperature for 4 hours before the solvent was removed by filtration. The resulting solid residue was washed with toluene (30 ml) and dried thoroughly under vacuum for 2 hours to yield the product as colorless powder. The compound was used for subsequent reactions without further purification. Yield: 4.343 g (98 %).

^{1}H NMR (400.2 MHz, thf-d_8): δ [ppm] = 1.11 (d, $^3J_{H\text{–}H}$ = 6.9 Hz, 24H, CH*Me*$_2$), 3.62 (sept, $^3J_{H\text{–}H}$ = 6.9 Hz, overlapping with solvent peak, 4H, C*H*Me$_2$), 6.64 (t, $^3J_{H\text{–}H}$ = 7.6 Hz, 2H, *p*-C*H*), 6.87 (d, $^3J_{H\text{–}H}$ = 7.6 Hz, 4H, *m*-C*H*), 7.49 (s, 1H, NC*H*N).

^{13}C{^{1}H} NMR (125.8 MHz, thf-d_8): δ [ppm] = 24.9 (CH*Me*$_2$), 28.3 (*C*HMe$_2$), 119.9 (*p*-*C*), 122.7 (*m*-*C*), 142.5 (*o*-*C*), 154.0 (*ipso*-*C*), 163.2 (N*C*HN).

*Synthesis of [(DippForm)$_2$YCl(thf)] (**A**)*

[(DippForm)K] (1.275 g, 3.17 mmol, 2.00 eq.) and anhydrous YCl$_3$ (309 mg, 1.58 mmol, 1.00 eq.) were added to a Schlenk tube and dissolved in thf (20 mL). After stirring at 50 - 60 °C overnight, the solvent was removed under vacuum and the residue was extracted with toluene (2 x 10 mL). After filtration using a filter cannula, a clear colorless solution was obtained, which was concentrated until incipient precipitation occurred. Colorless crystals suitable for single crystal X-ray diffraction were obtained from a saturated toluene solution at room temperature. Yield: 765 mg (52 %, single crystals).

^{1}H NMR (500.3 MHz, C$_6$D$_6$): δ [ppm] = 0.75 (m, 4H, OCH$_2$C*H*$_2$ (thf)), 1.19 (d, $^3J_{H\text{–}H}$ = 6.8 Hz, 48H, CH*Me*$_2$), 3.66 (m, overlapping, 12H, C*H*Me$_2$ and OC*H*$_2$ (thf)), 7.02 - 7.10 (m, 12H, C*H*), 8.17 (d, $^3J_{H\text{–}Y}$ = 3.6 Hz, 2H, NC*H*N).

^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$): δ [ppm] = 23.4 (CH*Me*$_2$), 25.1 (OCH$_2$*C*H$_2$ (thf)), 26.8 (CH*Me*$_2$), 28.5 (*C*HMe$_2$), 71.4 (O*C*H$_2$ (thf)), 123.9 (*m*-*C*), 125.3 (*p*-*C*), 143.9 (*o*-*C*), 145.1 (*ipso*-*C*), 171.6 (d, $^2J_{C\text{-}Y}$ = 3.3 Hz, N*C*HN).

^{89}Y{^{1}H} INEPT NMR (19.6 MHz, C$_6$D$_6$): δ [ppm] = 412.7.

^{1}H-{^{89}Y} HMQC NMR ((400.2 MHz / 19.6 MHz), C$_6$D$_6$): δ [ppm] = 8.17 / 412.7.

IR (Nujol, cm^{-1}): 1668 (w), 1593 (w), 1525 (s), 1460 (s), 1378 (s), 1319 (w), 1276 (s), 1261 (m), 1194 (w), 1097 (m), 1057 (m), 1045 (m), 1017 (m), 945 (w), 862 (w), 801 (m), 775 (w), 758 (w), 722 (w), 672 (w).

*Synthesis of [(DippForm)$_2$NdCl(thf)] (**B**)*

[(DippForm)K] (1.56 g, 3.87 mmol, 2.00 eq.) and anhydrous $NdCl_3$ (486 mg, 1.93 mmol, 1.00 eq.) were added to a Schlenk tube and dissolved in thf (20 mL). After stirring at 50 - 60 °C overnight, the solvent was removed under vacuum and the residue was extracted with toluene (2 x 10 mL). After filtration using a filter cannula, a clear blueish solution was obtained, which was concentrated until incipient precipitation occurred. The suspension was heated until a clear solution was obtained. Overnight, a small amount of microcrystalline precipitate formed, which was separated from the mother liquor by filtration and discarded. Storing the so obtained solution at ambient temperature afforded large blueish-purple crystals within 48 hours, which were isolated and dried under vacuum. A second crop of crystals was obtained by further concentrating the mother liquor and storage for a week. Yield: 920 mg (50 %, single crystals).

^{1}H NMR (400.2 MHz, C_6D_6): δ [ppm] = –3.14, –1.34, 2.32, 7.66, 9.04, 25.64. Due to the paramagnetic nature of **B**, only broad and unstructured resonances were observed.

IR (Nujol, cm^{-1}): 1665 (m), 1592 (w), 1523 (s), 1362 (m), 1316 (m), 1279 (s), 1261 (m), 1234 (w), 1191 (m), 1177 (m), 1160 (w), 1108 (m), 1097 (m), 1056 (w), 1043 (w), 1016 (m), 942 (w), 934 (w), 863 (w), 800 (m), 775 (m), 757 (m), 757 (m), 722 (m).

Elemental analysis calcd (%) for [$C_{54}H_{78}ClN_4NdO$] (978.94 g/mol): C 66.25, H 8.03, N 5.72; found C 66.18, H 8.09, N 5.42.

*Synthesis of [(DippForm)$_2$Y(OCP)(thf)] (**1**)*

The complex [(DippForm)$_2$YCl(thf)] (**A**) (300 mg, 0.33 mmol, 1.00 eq.) and [Na(OCP)(dioxane)$_{3.42}$] (130 mg, 0.33 mmol, 1.00 eq.) were dissolved in thf (10 mL) and stirred overnight. The solvent was then removed under vacuum and the residue was extracted with toluene (10 mL) and filtered. Upon concentration of the organic phase, colorless crystals formed after 2 days and were separated from the mother liquor by decantation. Yield: 136 mg (44 %, single crystals).

^{1}H NMR (500.3 MHz, C_6D_6): δ [ppm] = 0.82 (m, 4H, OCH_2CH_2 (thf)), 1.21 (bs, 48H, CHMe_2), 3.46 (hept, $^3J_{H\text{-}H}$ = 6.9 Hz, 8H, CHMe$_2$), 3.74 (m, 4H, OCH_2 (thf)), 7.00 - 7.08 (m, 12H, CH), 8.12 (d, $^3J_{H\text{-}Y}$ = 3.9 Hz, 2H, NCHN).

$^{13}C\{^1H\}$ **NMR** (125.8 MHz, C_6D_6): δ [ppm] = 23.8 (CH*Me*$_2$), 25.1 (OCH$_2$*C*H$_2$ (thf)), 26.7 (CH*Me*$_2$), 28.9 (*C*HMe$_2$), 71.0 (O*C*H$_2$ (thf)), 123.8 (*m-C*), 125.5 (*p-C*), 143.6 (*o-C*), 144.5 (d, $^2J_{C-Y}$ = 1.3 Hz, *ipso-C*), 156.0 (dd, $^1J_{C-P}$ = 7.3 Hz, $^2J_{C-Y}$ = 4.4 Hz, O*C*P), 172.1 (d, $^2J_{C-Y}$ = 3.4 Hz, N*C*HN).

$^{31}P\{^1H\}$ **NMR** (162.0 MHz, C_6D_6): δ [ppm] = –346.9.

$^{89}Y\{^1H\}$ **INEPT NMR** (19.6 MHz, C_6D_6): δ [ppm] = 292.3 (s).

^1H-$\{^{89}Y\}$ **HMQC NMR** ((400.2 MHz / 19.6 MHz), C_6D_6): δ [ppm] = 8.12 / 292.3.

IR (Nujol, cm^{-1}): 1691 (OCP), 1668 (w), 1520 (m), 1461 (s), 1377 (s), 1316 (w), 1272 (m), 1191 (w), 1098 (m), 1056 (b), 923 (w), 865 (w), 801 (w), 757 (w), 721 (w), 667 (w).

Elemental analysis calcd (%) for [$C_{55}H_{78}N_4O_2PY$] (947.13 g/mol): C 69.75, H 8.30, N 5.92; found C 69.25, H 8.32, N 5.72.

*Synthesis of [(DippForm)$_2$Nd(OCP)((thf)] (**2**)*

The complex [(DippForm)$_2$NdCl(thf)] (**B**) (164 mg, 0.16 mmol, 1.00 eq.) and [Na(OCP)(dioxane)$_{3.42}$] (75 mg, 0.19 mmol, 1.20 eq.) were dissolved in thf (10 mL) and stirred overnight at 50 °C. The solvent was then removed under vacuum and the residue was extracted with toluene (10 mL) and filtered. Upon concentration of the organic phase, colorless crystals formed after 2 days and were separated from the mother liquor by decantation. Yield: 90 mg (57 %, single crystals).

^1H **NMR** (400.2 MHz, C_6D_6): δ [ppm] = –3.16, –2.37, 1.15, 1.78, 2.28, 6.08, 7.52, 8.88, 14.76, 24.32. Due to the paramagnetic nature of **2**, only broad and unstructured resonances were observed.

$^{31}P\{^1H\}$ **NMR** (162.0 MHz, C_6D_6): δ [ppm] = –292.2.

IR (Nujol, cm^{-1}): 1685 (w, OCP), 1667 (m), 1591 (w), 1363 (m), 1316 (w), 1278 (m), 1260 (s), 1234 (w), 1189 (w), 1095 (br), 1019 (br), 943 (w), 862 (w), 800 (s), 757 (m), 721 (w).

Elemental analysis calcd (%) for [$C_{55}H_{78}N_4NdO_2P$] (1002.47 g/mol): C 65.90, H 7.84, N 5.59; found C 65.84, H 7.81, N 5.33.

*Synthesis of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**)*

To a mixture of [(DippForm)$_2$YCl(thf)] (**A**) (400 mg, 0.43 mmol, 1.00 eq.) and [Na(OCP)(dioxane)$_{0.3}$] (95 mg, 0.86 mmol, 2.00 eq.), thf (10 ml) was added. The resulting light-yellow suspension was stirred at room temperature for two hours before all volatiles were removed under vacuum. 18-crown-6 (114 mg, 0.43 mmol, 1.00 eq.) was added to the solid residue followed by thf (10 ml). The cloudy suspension was stirred at room temperature overnight. The precipitate was separated from the solution by cannula filtration. Upon addition of *n*-hexane, the product precipitated from the thf solution as a colourless powder (343 mg, 55% crude yield). Because the powder slowly decomposed when it was dried under vacuum, an aliquot (150 mg) was redissolved in thf and layered with *n*-hexane for further purification. Colourless crystals suitable for single crystal X-ray diffraction were obtained within days.

^{1}H NMR (500.3 MHz, thf-d_8): δ [ppm] = 1.08 (d, $^3J_{H–H}$ = 6.8 Hz, 48H, CH*Me*$_2$), 1.77 (m, OCH$_2$*C*H$_2$ (thf)), 3.43 (m, fluxional, 4H, C*H*Me$_2$), 3.62 (m, overlapping, OC*H*$_2$ (thf)), 3.62 (m, overlapping, 24H, OC*H*$_2$C*H*$_2$O (18-crown-6)), 3.85 (m, fluxional, 4H, C*H*Me$_2$), 6.85 (m, fluxional, 12H, aromatic H), 7.81 (d, $^3J_{H–Y}$ = 3.0 Hz, 2H, NC*H*N).

VT ^{1}H NMR (400.2 MHz, thf-d_8, 333K): δ [ppm] = 1.09 (d, $^3J_{H–H}$ = 6.7 Hz, 24H, CH*Me*$_2$), 1.12 (d, $^3J_{H–H}$ = 6.7 Hz, 24H, CH*Me*$_2$), 1.77 (m, OCH$_2$*C*H$_2$ (thf)), 3.63 (m, overlapping, 8H, C*H*Me$_2$), 3.63 (m, overlapping, OC*H*$_2$ (thf)), 3.63 (m, overlapping, 24H, OC*H*$_2$C*H*$_2$O (18-crown-6)), 6.80 (t, $^3J_{H–H}$ = 7.6 Hz, 4H, *p*-C*H*), 6.90 (d, $^3J_{H–H}$ = 7.6 Hz, 8H, *m*-C*H*), 7.82 (d, $^3J_{H–Y}$ = 3.1 Hz, 2H, NC*H*N).

^{13}C{^{1}H} NMR (125.8 MHz, thf-d_8): δ [ppm] = 24.5 (br, fluxional, CH*Me*$_2$), 26.6 (OCH$_2$*C*H$_2$ (THF)), 28.5 (br, fluxional, *C*HMe$_2$), 68.4 (O*C*H$_2$ (thf)), 70.9 (O*C*H$_2$*C*H$_2$O (18-crown-6)), 123.5 (br, fluxional, aromatic C), 160.4 (dd, $^1J_{C–P}$ = 18.0 Hz, $^2J_{C–Y}$ = 3.7 Hz, O*C*P), 170.4 (d, $^2J_{C–Y}$ = 3.0 Hz, N*C*HN).

^{31}P{^{1}H} NMR (162.0 MHz, thf-d_8): δ [ppm] = –368.7.

^{89}Y{^{1}H} INEPT NMR (19.6 MHz, thf-d_8): δ [ppm] = 147.3 ppm.

^{1}H-{^{89}Y} HMQC NMR ((400.2 MHz / 19.6 MHz), thf-d_8): δ [ppm] = 7.81 / 147.3.

IR (Nujol, cm^{-1}): 1799 (w), 1771 (w, OCP), 1600 (b), 1463 (s), 1377 (s), 1300 (w), 1260 (w), 1238 (w), 1152 (w), 1093 (m), 1020 (w), 944 (w), 800 (w), 722 (w).

Elemental analysis calcd (%) for [$C_{76}H_{118}N_4NaO_{11}P_2Y$] (1437.64 g/mol): No satisfactory results could be obtained.

Synthesis of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Nd(OCP)$_2$(thf)] (4)

To a mixture of [(DippForm)$_2$NdCl(thf)] (**A**) (210 mg, 0.21 mmol, 1.00 eq.) and [Na(OCP)(dioxane)$_{0.3}$] (47 mg, 0.43 mmol, 2.05 eq.), thf (10 ml) was added. The resulting light-yellow suspension was stirred at room temperature for two hours before all volatiles were removed under vacuum. 18-crown-6 (57 mg, 0.21 mmol, 1.00 eq.) was added to the solid residue followed by thf (10 ml). The cloudy suspension was stirred at room temperature overnight and subsequently filtered. The thf solution was concentrated and layered with *n*-hexane, which ultimately led to the formation of colorless (light bluish) crystals, which partially decompose over time. The mother liquor was removed via decantation and the crystalline residue was shortly dried under vacuum. Yield: 180 mg (58 %). Fresh samples can be crystallized from crude product.

^{1}H NMR (400.2 MHz, thf-d_8): δ [ppm] = –2.86 (bs), –1.40 (bs), 0.90 (s), 4.16 (bs, crown, thf), 5.72 (bs), 7.66 (bs), 9.30 (bs), 12.93 (bs), 21.11 (bs). Due to the paramagnetic nature of **4**, only broad and unstructured resonances were observed.

^{31}P{^{1}H}NMR (162.0 MHz, thf-d_8): δ [ppm] = –289.7.

IR (Nujol, cm^{-1}): 1702 (s), 1683 (s, OCP), 1591 (w), 1525 (s), 1351 (m), 1317 (m), 1284 (m), 1247 (m), 1191 (m), 1109 (s), 1054 (w), 964 (m), 937 (w), 844 (m), 800 (w), 772 (w), 756 (w), 722 (w).

Elemental analysis calcd (%) for [$C_{76}H_{118}N_4NaNdO_{11}P_2$] (1492.98 g/mol): No satisfactory results could be obtained.

*Synthesis of [(DippForm)$_2$Nd(μ^2-OCP)]$_2$ (**5**)*

[(DippForm)$_2$Nd(OCP)((thf)] (**2**) (59 mg, 0.058 mmol, 1.00 eq.) and B(C_6F_5)$_3$ (30 mg, 0.058 mmol, 1.00 eq.) were added to an NMR or Schlenk tube and dissolved in benzene (1–2 ml). The pale blueish mixture was shaken until a clear solution was obtained and left standing for at two days. Light blue block-like crystals were obtained and separated from the mother liquor by decantation. The crystals were quickly washed with small amounts of benzene and dried under vacuum. Yield: 42 mg (78 %, single crystals).

^{1}H NMR (400.2 MHz, thf-d_8): δ [ppm] = –1.09 (bs), 1.19 (bs), 3.40 (bs), 7.10 (bs), 8.13 (bs), 29.14 (s). Due to the paramagnetic nature of **5**, only broad and unstructured resonances were observed.

^{31}P{^{1}H} NMR (162.0 MHz, thf-d_8): δ [ppm] = –278.1.

IR (Nujol, cm^{-1}): 1748 (m, OCP), 1363 (w), 1260 (m), 1156 (m), 1094 (br), 1021 (br), 800 (s), 720 (w).

Elemental analysis calcd (%) for [$C_{102}H_{140}N_8Nd_2O_2P_2$] (1860.73 g/mol): C 65.84, H 7.58, N 6.02; found 65.42, H 7.27, N 5.97.

*Synthesis of [(DippForm)Sm(18-crown-6)(thf)][DippForm] (**6**)*

[(DippForm)$_2$Sm(thf)$_2$] (50 mg, 0.04 mmol, 1.00 eq.) and 18-crown-6 (13 mg, 0.04 mmol, 1.00 eq.) were dissolved in thf (0.6 mL) in an J. Young NMR tube and shaken until a clear green solution was obtained. The mixture was concentrated to approximately 0.2 mL and layered with *n*-hexane. Dark green crystals were obtained within a few days, separated from the mother liquor by decantation and dried under vacuum. Yield: 35 mg (60 %, single crystals).

^{1}H NMR (400.2 MHz, thf-d_8): δ [ppm] = –9.58, 1.47, 3.62, 3.66, 5.32, 6.79, 7.43. Due to the paramagnetic nature of **6**, only broad and unstructured resonances were observed.

IR (Nujol, cm^{-1}): 2723 (w), 1591 (w), 1541 (m), 1342 (w), 1303 (m), 1236 (w), 1180 (w), 1154 (vw), 1085 (m), 1038 (w), 961 (w), 920 (vw), 896 (vw), 837 (vw), 777 (vw), 767 (vw), 757 (w), 721 (w).

Elemental analysis calcd (%) for [$C_{66}H_{102}N_4O_7Sm$] (1213.92 g/mol): C 65.30, H 8.47, N 4.62; found 64.76, H 8.44, N 4.39.

Synthesis of [(DippForm)Sm(OCP)(18-crown-6)] (7)

[(DippForm)$_2$Sm(thf)$_2$] (100 mg, 0.10 mmol, 1.00 eq.) and 18-crown-6 (26 mg, 0.10 mmol, 1.00 eq.) were dissolved in thf (2 mL) in an J. Young tube and stirred until a clear green solution was obtained (~ 1–2 hours). Subsequently, a solution of [Na(OCP)(dioxane)$_{0.3}$] (11 mg, 0.10 mmol, 1.00 eq.) in thf (1 mL) was added to the reaction mixture, which was stirred for another 4 hours. The clear dark green solution was layered with *n*-hexane (25 mL) and left standing until dark green crystals formed (4–7 days). The crystals were isolated by decantation from the mother liquor and dried under vacuum. Yield: 42 mg (50 %, single crystals). **Note:** After prolonged periods, the formation of colorless block-like crystals is also observed, which were found to be the oxidized species [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Sm(OCP)$_2$(thf)] (**7b**, See crystallographic section for the structure) .

^{1}H NMR (400.2 MHz, C_6D_6): δ [ppm] = –9.16 (bs; 2H, NC*H*N), 0.33 (bs, 12H, C*H*$_3$), 3.09 (bs, overlapping, 16H, C*H*$_3$ and C*H*(CH$_3$)$_2$), 4.91 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *m*-CH), 6.29 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, *p*-CH), 6.56 (bs, 12H, C*H*$_2$), 8.51 (bs, 12H, C*H*$_2$).

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ [ppm] = 22.9, 24.5, 35.6, 114.9, 115.8, 120.6, 124.5, 129.5.

^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ [ppm] = –391.7.

IR (Nujol, cm^{-1}): 1758 (m, OCP), 1666 (w), 1592 (vw), 1526 (m), 1326 (w), 1295 (m), 1258 (w), 1183 (w), 1099 (m), 1079 (m), 995 (vw), 965 (w), 876 (vw), 838 (w), 802 (w), 763 (w), 721 (w).

Elemental analysis calcd (%) for [$C_{38}H_{59}N_2O_7Sm$] (837.23 g/mol): C 54.52, H 7.10, N 3.35; found 53.92, H 7.22, N 3.21.

*Synthesis of [(DippForm)Sm(2,2,2-crypt)][DippForm] (**8**)*

[(DippForm)$_2$Sm(thf)$_2$] (45 mg, 0.04 mmol, 1.00 eq.) and 2,2,2-crypt (16 mg, 0.04 mmol, 1.00 eq.) were dissolved in thf (0.6 mL) in an J. Young NMR tube and shaken until a clear red solution was obtained. The mixture was concentrated to approximately 0.2 mL and left standing overnight. Large dark-red crystals formed which were separated from the mother liquor by decantation and subsequently washed with thf (2 × 0.5 mL) and dried under vacuum. Yield: 40 mg (80 %, single crystals).

^{1}H NMR (400.2 MHz, thf-d_8): δ [ppm] = –9.95, –2.50, –2.39, –1.80, –1.41, 0.00, 0.40, 0.60, 1.52, 2.92, 4.41, 6.12, 7.31, 8.30, 8.78, 11.41. 11.43. Due to the paramagnetic nature of **8**, only broad and unstructured resonances were observed.

IR (Nujol, cm^{-1}): 1592 (w), 1377 (w), 1311 (w), 1342 (w), 1259 (w), 1235 (w), 1180 (w), 1092 (w), 1063 (w), 1018 (w), 802 (w).

Elemental analysis calcd (%) for [$C_{68}H_{106}N_6O_6Sm$] (1253.99 g/mol): C 65.13, H 8.52, N 6.70; found C 65.01, H 8.49, N 6.41.

*Synthesis of [(2,2,2-crypt)Sm(OCP)$_2$](**9**)*

A mixture of [(DippForm)$_2$Sm(thf)$_2$] (100 mg, 0.10 mmol, 1.00 eq.) and 2,2,2-crypt (37 mg, 0.10 mmol, 1.00 eq.) was dissolved in thf (2 ml) inside the glovebox. The solution was left standing at room temperature for 2 hours and during this period, a colour change of the solution from green to red was observed. [Na(OCP)(dioxane)$_{0.3}$] (22 mg, 0.20 mmol, 2.00 eq.) was added to the solution as a solid, and red crystals suitable for single crystal X-ray diffraction rapidly formed. Yield: 30 mg (47 %, single crystals).

^{1}H NMR (500.3 MHz, d_5-pyridine): δ [ppm] = 1.46 (s, 12H, NCH_2), 3.26 (s, 12H, OCH_2CH_2O), 3.58 (s, 12H, NCH_2CH_2O).

^{13}C{^{1}H} NMR (125.8 MHz, d_5-pyridine): δ [ppm] = 92.4 (NCH_2), 99.4 (NCH_2CH_2O), 99.6 (OCH_2CH_2O), 183.9 (d, $^1J_{C–P}$ = 48.4 Hz, OCP).

^{31}P{^{1}H} NMR (162.0 MHz, d_5-pyridine): δ [ppm] = –374.0 (s).

IR (Nujol, cm^{-1}): 1782 (w), 1763 (PCO), 1749 (PCO), 1623 (b), 1463 (s), 1377 (s), 1351 (w), 1302 (w), 1261 (w), 1125 (m), 1090 (m), 1066 (m), 1030 (b), 957 (w), 800 (w), 722 (w), 668 (w).

Elemental analysis calcd (%) for [$C_{20}H_{36}N_2O_8P_2Sm$] (644.82 g/mol): C 37.25, H 5.63, N 4.34; found C 37.39, H 5.62, N 4.30.

IV. X-ray crystallography

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[8] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å; Oxford Diffraction Supernova). Data collected on the Oxford Diffraction Supernova diffractometer were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[9] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using direct methods and refined on F^2 using the ShelXL 2013 package and ShelXle.[10][11]

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication No. 1857886-1857895. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

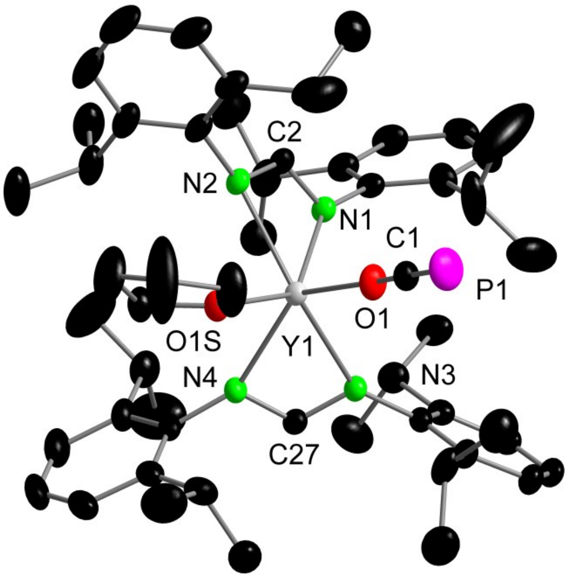

Figure S1: Molecular structure of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-O1 2.1562(12), Y1-N1 2.3503(13), Y1-N2 2.3818(14), Y1-N3 2.3858(13), Y1-N4 2.3426(13), Y1-O1S 2.3687(11), P1-C1 1.559(2), C1-O1 1.250(2); O1-C1-P1 178.5(2), N1-Y1-N2 57.31(5), O1-Y1-N4 134.31(5), O1-Y1-N1 107.44(5), O1-Y1-N2 105.65(5).

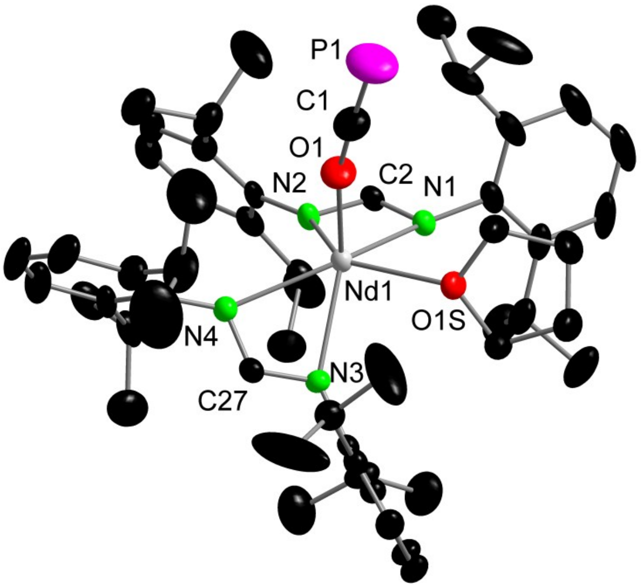

Figure S2: Molecular structure of [(DippForm)$_2$Nd(OCP)(thf)] (**2**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd1-N1 2.495(3), Nd1-N2 2.435(3), Nd1-N3 2.439(3), Nd1-N4 2.481(3), Nd1-O1 2.224(3), Nd1-O1S 2.471(3), P1-C1 1.557(6), C1-O1 1.252(6); O1-Nd1-N1 105.00(12), O1-Nd1-N3 125.40(13), O1-Nd1-N2 108.19(13), N1-Nd1-N2 54.84(10), N3-Nd1-N4 54.93(10), O1-C1-P1 177.3(5).

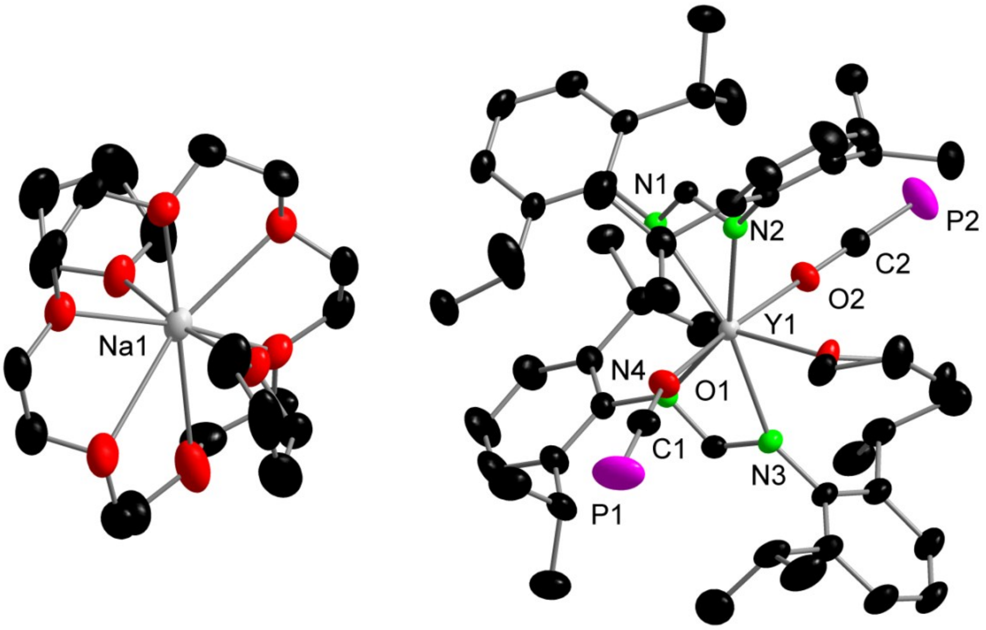

Figure S3: Molecular structure of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-O1 2.221(2), Y1-O2 2.225(2), Y1-N1 2.430(2), Y1-N2 2.439(2), Y1-N3 2.437(2), Y1-N4 2.400(2), O1-C1 1.227(3), C1-P1 1.570(3), O2-C2 1.229(3), C2-P2 1.570(3), O1-Y1-O2 173.06(7), C1-O1-Y1 164.2(2), O1-C1-P1 179.2(3), C2-O2-Y1 162.5(2), O2-C2-P2 179.2(2).

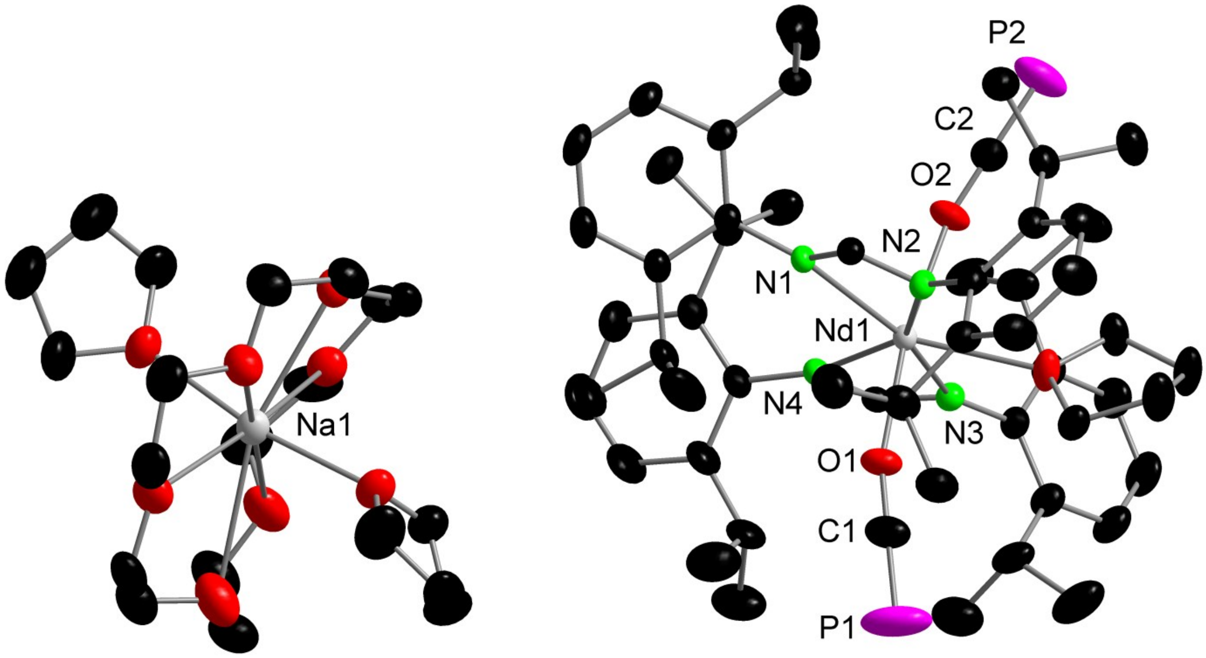

Figure S4: Molecular structure of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Nd(OCP)$_2$(thf)] (**4**) in the solid state. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd1-O1 2.3106(15), Nd1-O2 2.3263(15), Nd1-N1 2.501(2), Nd1-N2 2.508(2), Nd1-N3 2.510(2), Nd1-N4 2.468(2), O1-C1 1.234(3), C1-P1 1.562(3), O2-C2 1.214(3), C2-P2 1.562(2); O1-Nd1-O2 170.96(6), N1-Nd1-N2 54.25(5), N4-Nd1-N3 54.54(5), O1-C1-P1 178.9(2), O2-C2-P2 179.0(2).

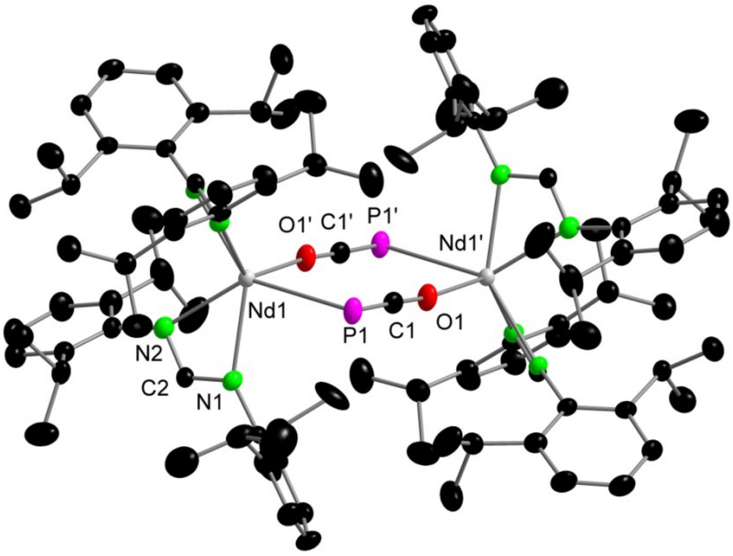

Figure S5: Molecular structure of [(DippForm)$_2$Nd(μ^2-OCP)]$_2$ (**5**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd1-O1 2.352(3), Nd1-N1 2.468(3), Nd1-N2 2.431(4), Nd1-N3 2.454(4), Nd1-N4 2.450(3), Nd1-P1 3.058(2), O1-C1 1.234(5), C1-P1 1.582(4); O1-C1-P1 176.0(4), N1-Nd1-N2 55.31(11), N3-Nd1-N4 55.55(10), O1-Nd1-N1 109.60(12), O1-Nd1-N2 109.72(12), O1-Nd1-N3 131.42(11), O1-Nd1-N4 95.03(11).

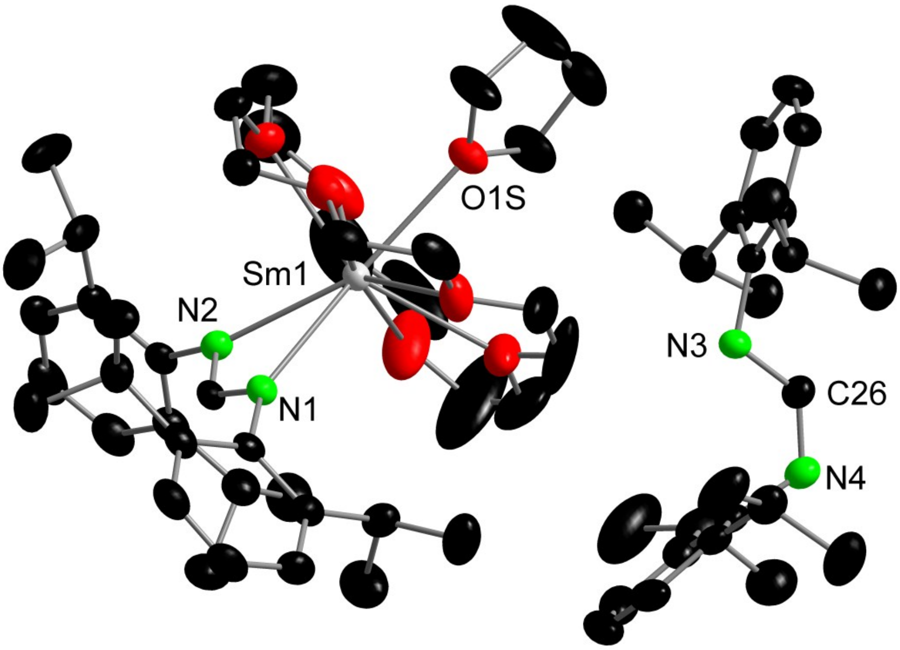

Figure S6: Molecular structure of [(DippForm)Sm(18-crown-6)(thf)][DippForm] (**6**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-N1 2.707(4), Sm1-N2 2.649(4), N3-C26 1.317(7), N4-C26 1.309(7); N2-Sm1-N1 51.07(13), O1S-Sm1-N1 152.92(14), N2-Sm1-O1S 152.39(14), N3-C26-N4 128.9(5).

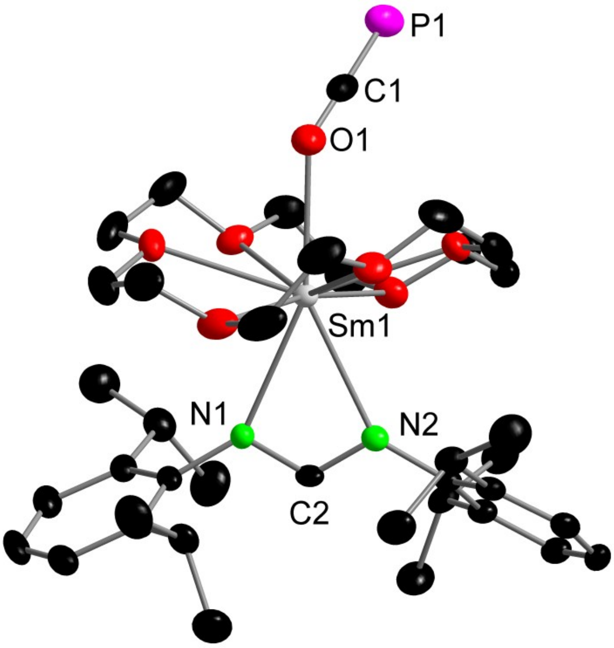

Figure S7: Molecular structure of [(DippForm)Sm(OCP)(18-crown-6)] (**7**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-O1 2.610(3), Sm1-N1 2.642(3), Sm1-N2 2.655(3), Sm1-O101 2.765(3), Sm1-O102 2.697(3), Sm1-O103 2.651(3), Sm1-O104 2.737(3), Sm1-O105 2.708(3), Sm1-O106 2.706(3), P1-C1 1.586(4), C1-O1 1.219(5); O1-Sm1-N1 155.20(9), O1-Sm1-N2 152.68(9), N1-Sm1-N2 51.32(8), O1-C1-P1 178.4(3).

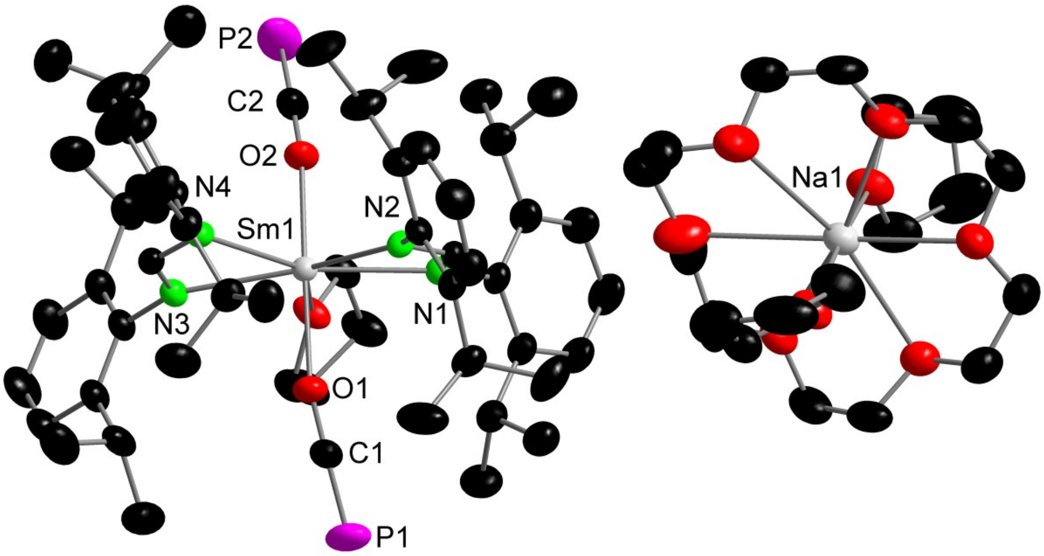

Figure S8: Molecular structure of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Sm(OCP)$_2$(thf)] (**7B**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-O1 2.299(2), Sm1-O2 2.286(2), Sm1-O3 2.432(2), Sm1-N1 2.499(2), Sm1-N2 2.486(2), Sm1-N3 2.497(2), Sm1-N4 2.458(2), P1-C1 1.576(3), C1-O1 1.218(4), P2-C2 1.563(4), C2-O2 1.234(4); O1-Sm1-O2 171.64(9), O1-Sm1-O3 87.39(8), O2-Sm1-O3 84.27(8), O1-Sm1-N1 89.49(8), N1-Sm1-N2 54.27(7), N4-Sm1-N3 54.71(7), O2-Sm1 -N3 92.47(8), O1-Sm1-N1 89.49(8).

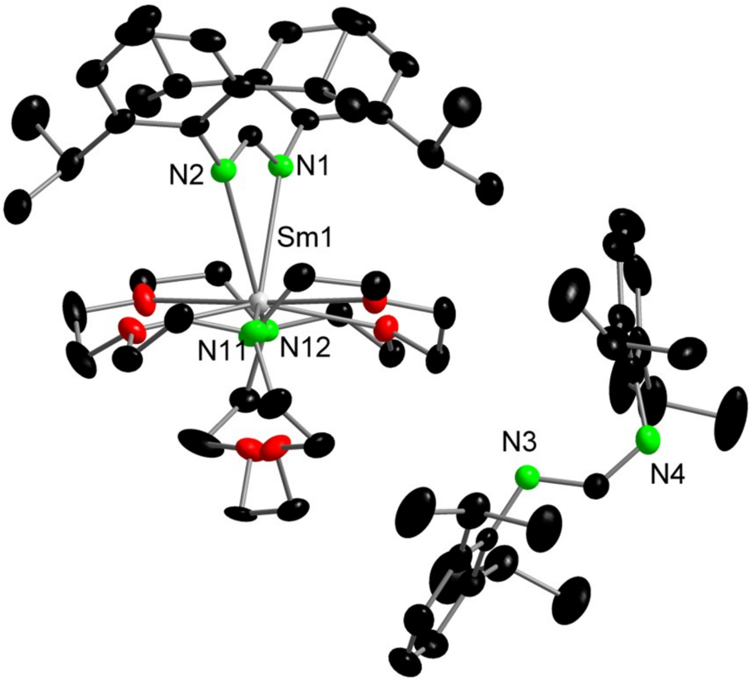

Figure S9: Molecular structure of [(DippForm)Sm(2,2,2-crypt)][DippForm] (**8**) in the solid state. The thermal ellipsoids are set at a 50% probability level.Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-N1 2.790(3), Sm1-N2 2.799(3), Sm1-N11 2.952(3), Sm1-N12 2.971(2), N3-C26 1.316(4), N4-C26 1.316(5); N1-Sm1-N2 49.19(7), N11-Sm1-N12 158.65(8), N3-C26-N4 129.9(3).

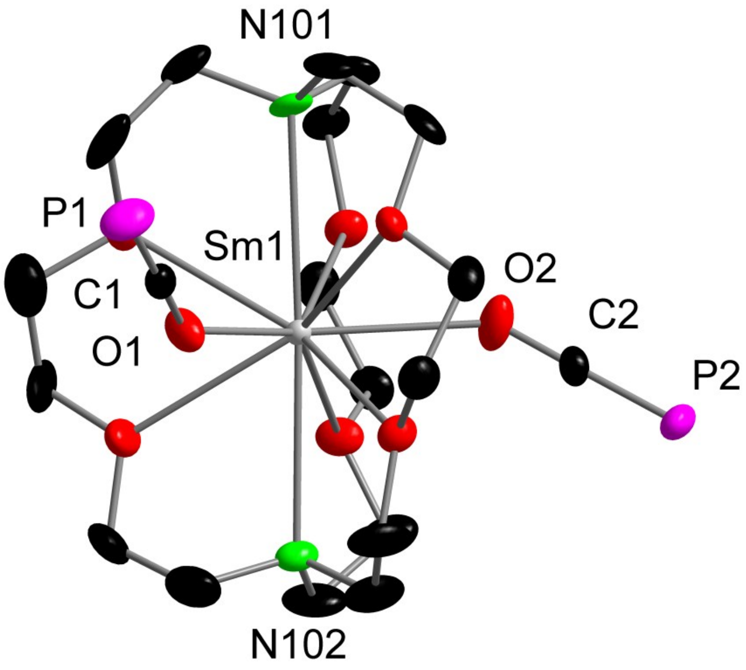

Figure S10: Molecular structure of [(2,2,2-crypt)Sm(OCP)$_2$] (**9**) in the solid state. The thermal ellipsoids are set at a 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-O1 2.568(6), Sm1-O2 2.613(6), P1-C1 1.580(8), C1-O1 1.212(10), P2-C2 1.591(9), C2-O2 1.205(11), Sm1-N101 2.972(6), Sm1-N102 2.919(7); O1-Sm1-O2 134.3(2), O1-C1-P1 178.8(7), C1-O1-Sm1 145.0(5), O2-C2-P2 179.2(8), C2-O2-Sm1 140.6(6).

Table S1: Crystallographic table.

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**7B**	**8**	**9**
CCDC	1857886	1857887	1857888	1857889	1857890	1857891	1857892	1857893	1857894	1857895
Empirical formula	$C_{55}H_{78}N_4O_2PY$	$C_{55}H_{78}N_4NdO_2P$	$C_{81}H_{128}N_4NaO_{11.5}P_2Y$	$C_{81}H_{128}N_4NaNdO_{11.5}P_2$	$C_{108}H_{146}N_8Nd_2O_2P_2$	$C_{66}H_{102}N_4O_7Sm$	$C_{38}H_{59}N_2O_7PSm$	$C_{80.7}H_{128.1}N_4NaO_{11.65}P_2Sm$	$C_{68}H_{106}N_6O_6Sm$	$C_{20}H_{36}N_2O_8P_2Sm$
Formula weight	947.09	1002.42	1515.71	1571.04	1938.74	1213.86	837.19	1576.04	1253.93	644.80
Temperature/K	150(2)	293(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P-1	P-1	$P2_1/n$	$P2_1/n$	P-1	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	Pc
a/Å	12.3914(5)	16.2099(3)	16.6407(2)	16.6407(2)	12.339(3)	11.01160(10)	11.151(2)	16.674(3)	11.036(2)	11.237(2)
b/Å	13.6795(6)	16.9858(3)	24.6511(3)	24.6511(3)	13.458(3)	20.7007(2)	27.883(6)	24.610(5)	21.134(4)	9.6634(19)
c/Å	15.9103(6)	29.5661(8)	20.6049(2)	20.6049(2)	16.372(3)	28.2458(3)	13.270(3)	20.762(4)	28.094(6)	24.483(5)
α/°	94.764(3)	80.844(2)	90	90	85.06(3)	90	90	90	90	90
β/°	91.951(3)	83.341(2)	93.0970(10)	93.0970(10)	89.92(3)	90	95.00(3)	92.84(3)	90	94.81(3)
γ/°	97.911(3)	86.754(2)	90	90	69.91(3)	90	90	90	90	90
Volume/Å^3	2659.20(19)	7976.7(3)	8440.02(17)	8440.02(17)	2542.6(10)	6438.57(11)	4110.5(14)	8509(3)	6552(2)	2649.2(9)
Z	2	6	4	4	1	4	4	4	4	4
ρ_{calc}g/cm^3	1,183	1,252	1,193	1,236	1,266	1,252	1,353	1,230	1,271	1,617
μ/mm^{-1}	2,142	8,047	1,837	5,557	8,383	7,258	11,464	6,040	7,145	18,173
F(000)	1012.0	3162.0	3256.0	3340.0	1016.0	2576.0	1736.0	3346.0	2664.0	1304.0
Crystal size/mm^3	0.530 × 0.320 × 0.310	0.140 × 0.090 × 0.090	0.220 × 0.140 × 0.090	0.220 × 0.140 × 0.090	0.050 × 0.040 × 0.030	0.200 × 0.120 × 0.080	0.270 × 0.090 × 0.060	0.200 × 0.200 × 0.080	0.240 × 0.220 × 0.150	0.200 × 0.140 × 0.140
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.978 to 152.818	7.42 to 152.774	7.172 to 152.602	7.172 to 157.082	7.022 to 153.19	7.578 to 153.026	7.4 to 152.488	7.184 to 152.352	7.556 to 152.568	7.246 to 153.79
Index ranges	-15 ≤ h ≤ 11, -17 ≤ k ≤ 17, -19 ≤ l ≤ 20	-16 ≤ h ≤ 20, -21 ≤ k ≤ 20, -36 ≤ l ≤ 37	-18 ≤ h ≤ 20, -30 ≤ k ≤ 25, -20 ≤ l ≤ 25	-20 ≤ h ≤ 20, -29 ≤ k ≤ 30, -26 ≤ l ≤ 26	-11 ≤ h ≤ 15, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20	-13 ≤ h ≤ 12, -16 ≤ k ≤ 25, -34 ≤ l ≤ 35	-10 ≤ h ≤ 13, -30 ≤ k ≤ 34, -16 ≤ l ≤ 16	-19 ≤ h ≤ 20, -30 ≤ k ≤ 30, -21 ≤ l ≤ 25	-13 ≤ h ≤ 12, -26 ≤ k ≤ 26, -34 ≤ l ≤ 35	-14 ≤ h ≤ 14, -12 ≤ k ≤ 11, -30 ≤ l ≤ 29
Reflections collected	28248	86069	59552	54103	25361	41724	23470	50089	78072	24920
Independent reflections	10988 [R_{int} = 0.0269, R_{sigma} = 0.0258]	32862 [R_{int} = 0.0345, R_{sigma} = 0.0408]	17464 [R_{int} = 0.0326, R_{sigma} = 0.0286]	17600 [R_{int} = 0.0300, R_{sigma} = 0.0287]	10500 [R_{int} = 0.0617, R_{sigma} = 0.0758]	13317 [R_{int} = 0.0501, R_{sigma} = 0.0521]	8501 [R_{int} = 0.0457, R_{sigma} = 0.0512]	17563 [R_{int} = 0.0442, R_{sigma} = 0.0485]	13630 [R_{int} = 0.0517, R_{sigma} = 0.0341]	9089 [R_{int} = 0.0414, R_{sigma} = 0.0436]
Data/restraints/parameters	10988/0/584	32862/0/1702	17464/19/971	17600/19/971	10500/0/566	13317/30/704	8501/0/450	17563/19/972	13630/48/759	9089/2/597
Goodness-of-fit on F^2	1,041	1,052	1,108	1,039	1,056	1,039	1,051	1,034	1,021	1,025
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0820	R_1 = 0.0439, wR_2 = 0.1166	R_1 = 0.0444, wR_2 = 0.1127	R_1 = 0.0308, wR_2 = 0.0781	R_1 = 0.0414, wR_2 = 0.0987	R_1 = 0.0418, wR_2 = 0.0999	R_1 = 0.0373, wR_2 = 0.0898	R_1 = 0.0369, wR_2 = 0.0888	R_1 = 0.0248, wR_2 = 0.0586	R_1 = 0.0409, wR_2 = 0.1028
Final R indexes [all data]	R_1 = 0.0335, wR_2 = 0.0831	R_1 = 0.0601, wR_2 = 0.1286	R_1 = 0.0508, wR_2 = 0.1169	R_1 = 0.0356, wR_2 = 0.0818	R_1 = 0.0519, wR_2 = 0.1066	R_1 = 0.0477, wR_2 = 0.1047	R_1 = 0.0444, wR_2 = 0.0953	R_1 = 0.0496, wR_2 = 0.0987	R_1 = 0.0260, wR_2 = 0.0593	R_1 = 0.0415, wR_2 = 0.1039
Largest diff. peak/hole / e Å^{-3}	0.54/-0.70	3.34/-1.31	0.83/-0.45	1.16/-0.65	1.10/-1.18	1.96/-0.72	0.70/-1.59	0.85/-0.76	0.38/-0.36	1.55/-1.41
Flack parameter	none	none	none	none	none	-0.033(3)	none	none	-0.0128(12)	0.070(4)

V. NMR Spectra

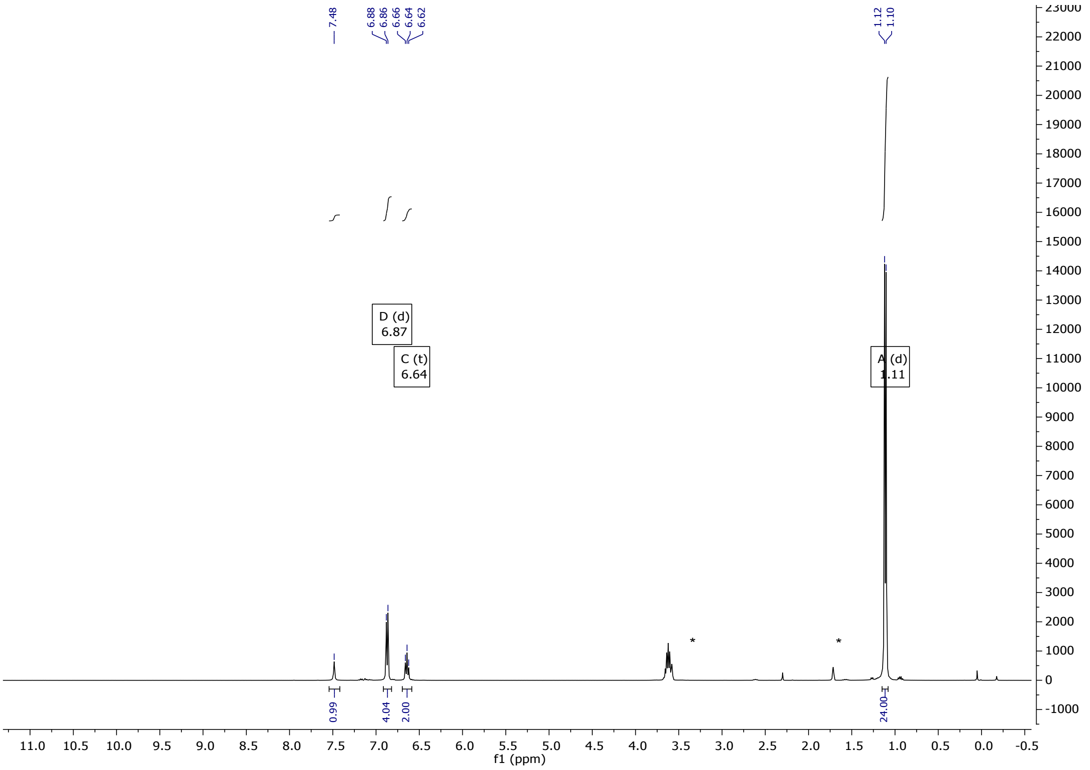

Figure S11: ^{1}H NMR spectrum of [K(DippForm)] in thf-d_8. Asterixes denote thf (solvent) peaks.

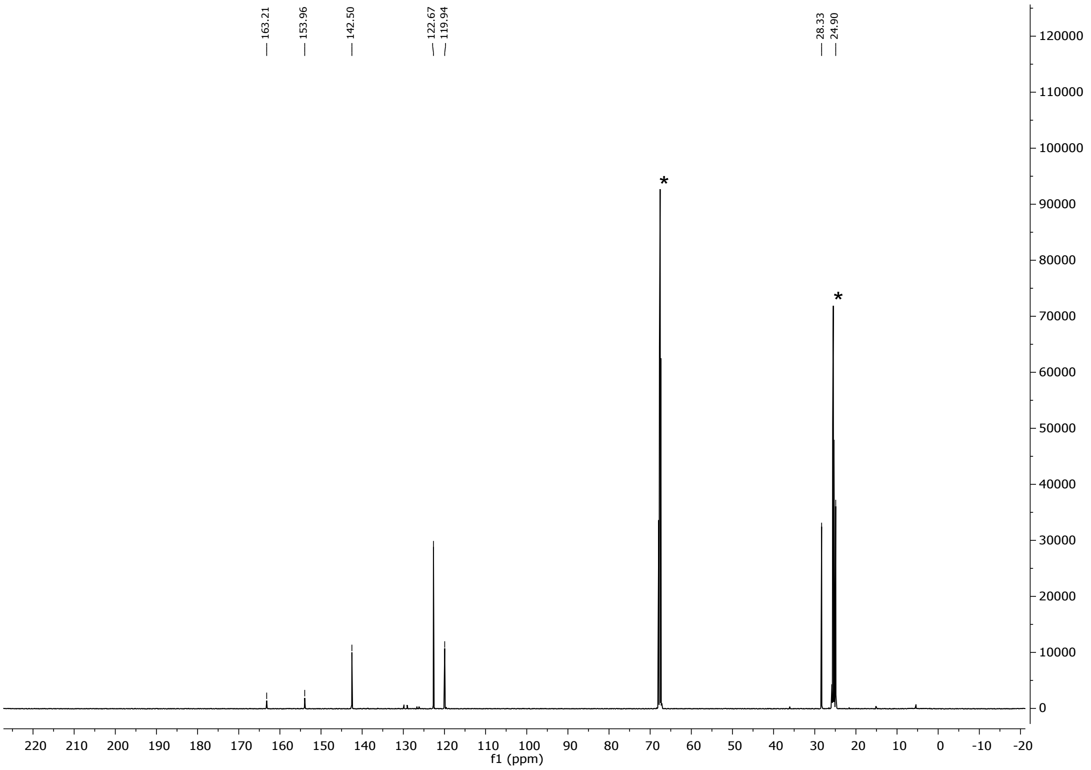

Figure S12: ^{13}C{^{1}H} NMR spectrum of [K(DippForm)] in thf-d_8. Asterixes denote residual thf (solvent) peaks.

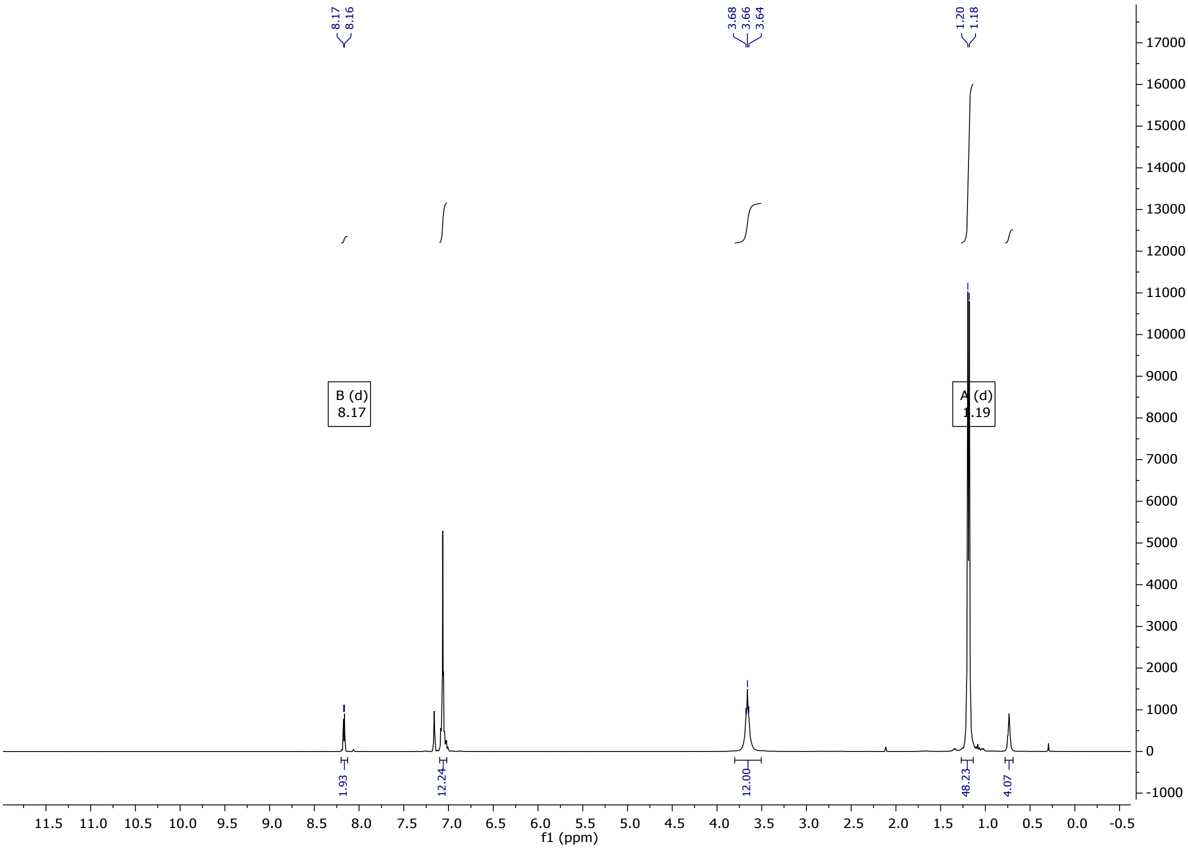

Figure S13: ^{1}H NMR spectrum of [(DippForm)$_2$YCl(thf)] (**A**) in C_6D_6.

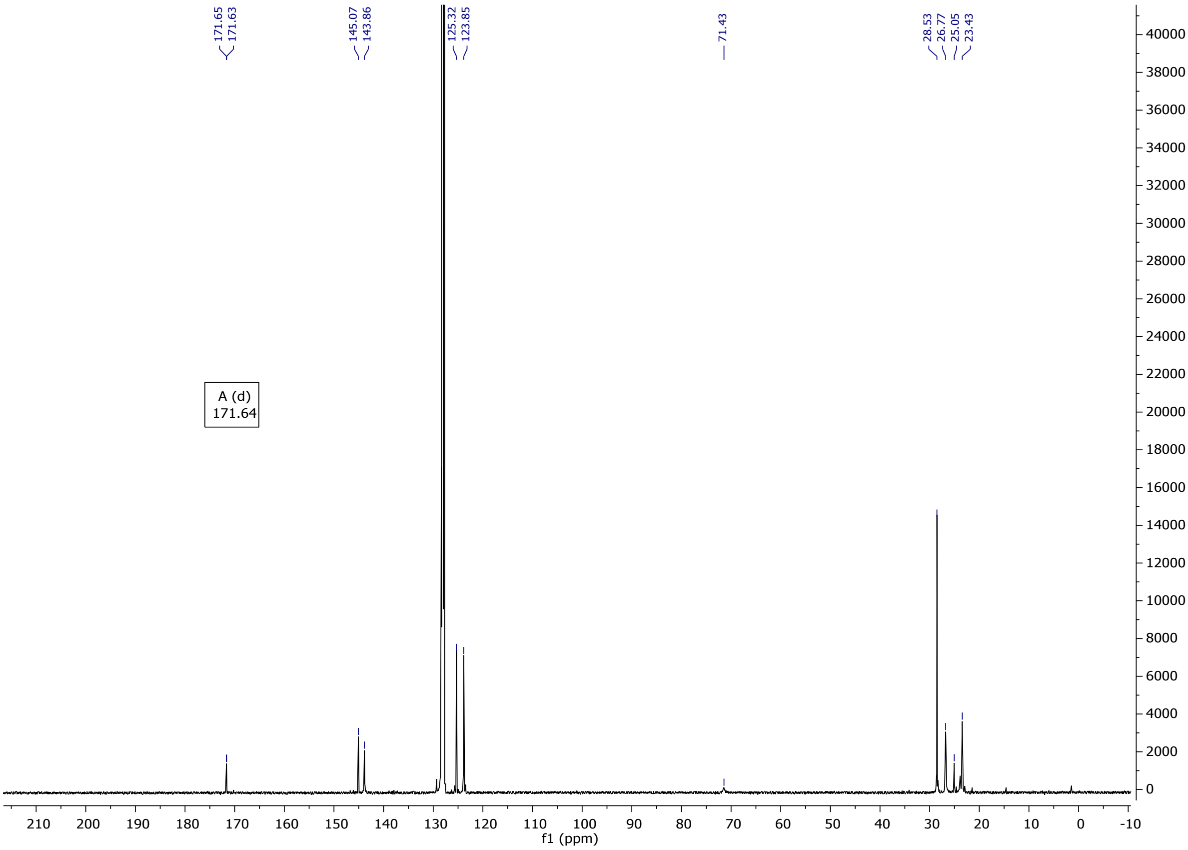

Figure S14: ^{13}C{^{1}H} NMR spectrum of [(DippForm)$_2$YCl(thf)] (**A**) in C_6D_6.

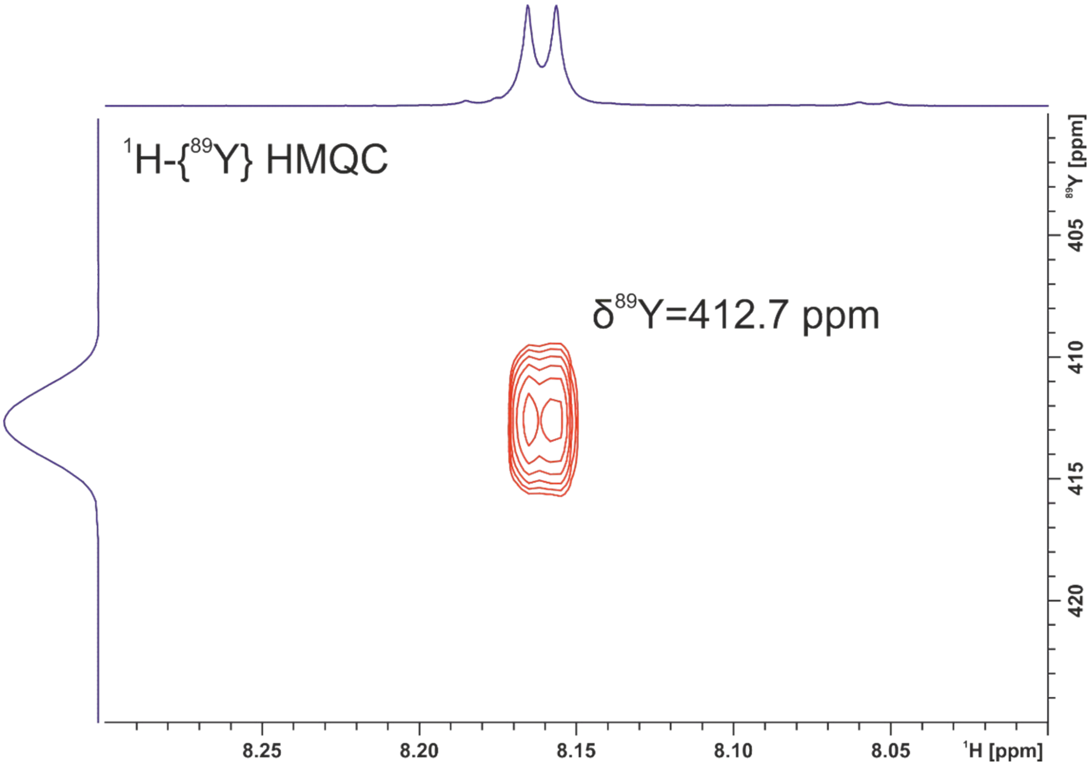

Figure S15: ^{1}H-{^{89}Y} HMQC NMR spectrum (C_6D_6) of [(DippForm)$_2$YCl(thf)] (**A**) in C_6D_6. The ^{89}Y NMR spectrum is on the vertical axis and the ^{1}H NMR spectrum is on the horizontal axis.

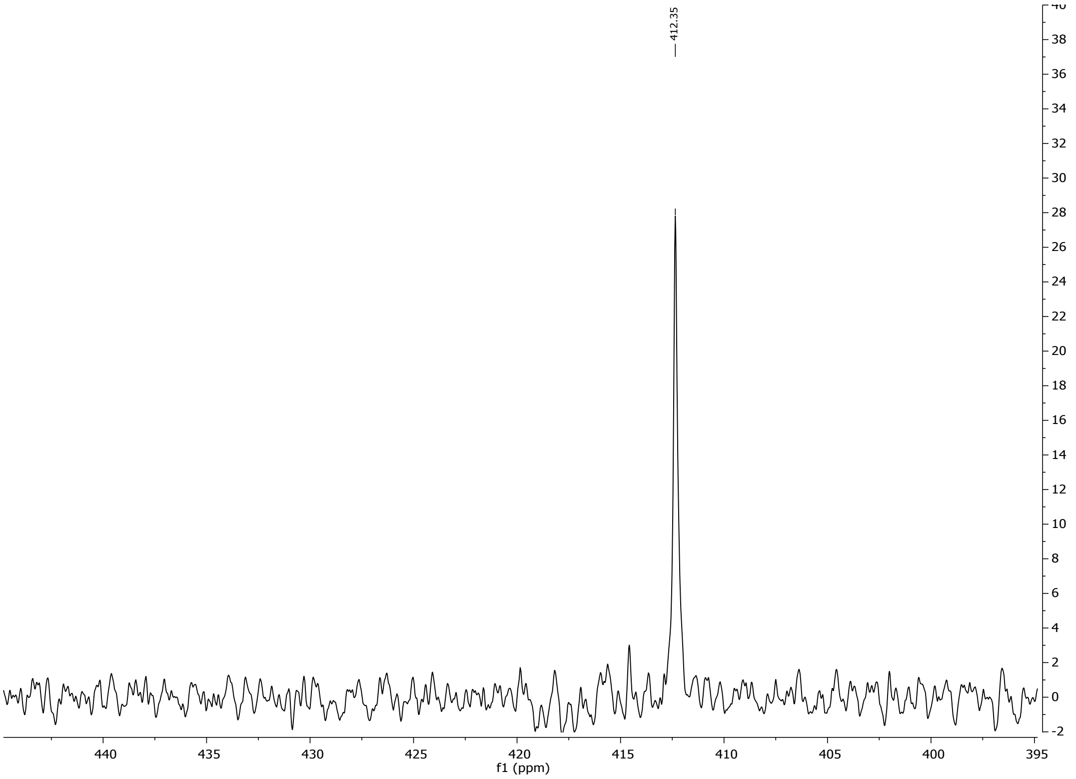

Figure S16: ^{89}Y{^{1}H} INEPT NMR spectrum (C_6D_6) of [(DippForm)$_2$YCl(thf)] (**A**) in C_6D_6.

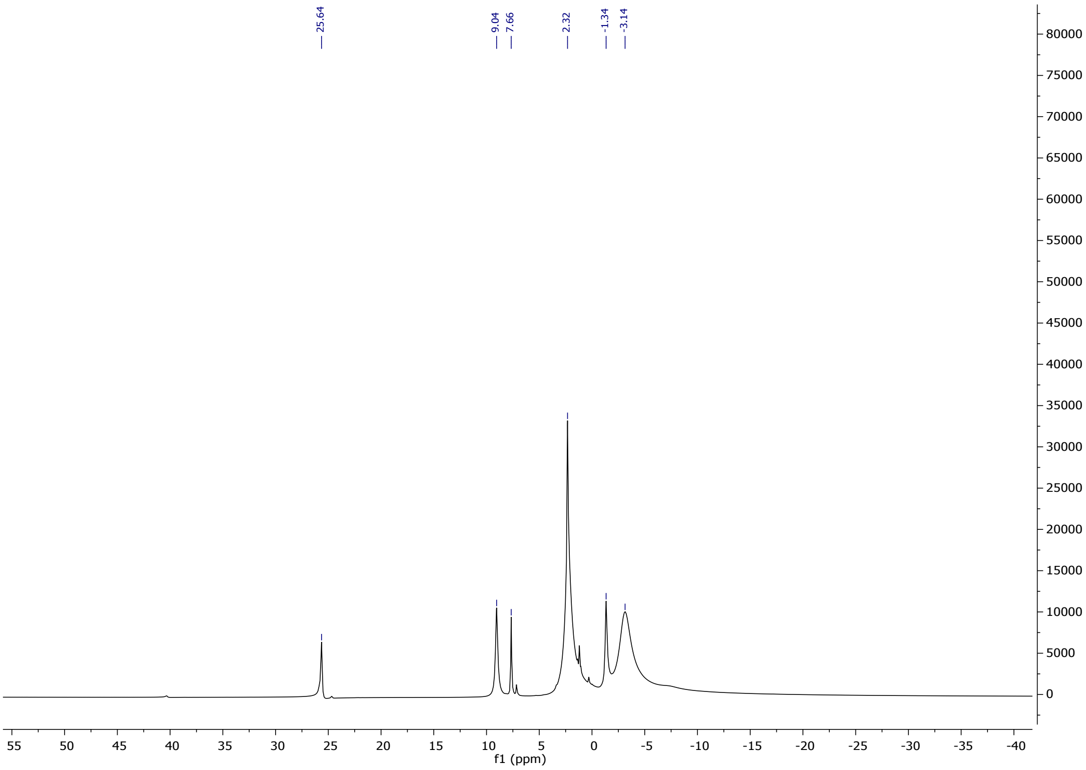

Figure S17: ^{1}H NMR spectrum of [(DippForm)$_2$NdCl(thf)] (**B**) in C_6D_6.

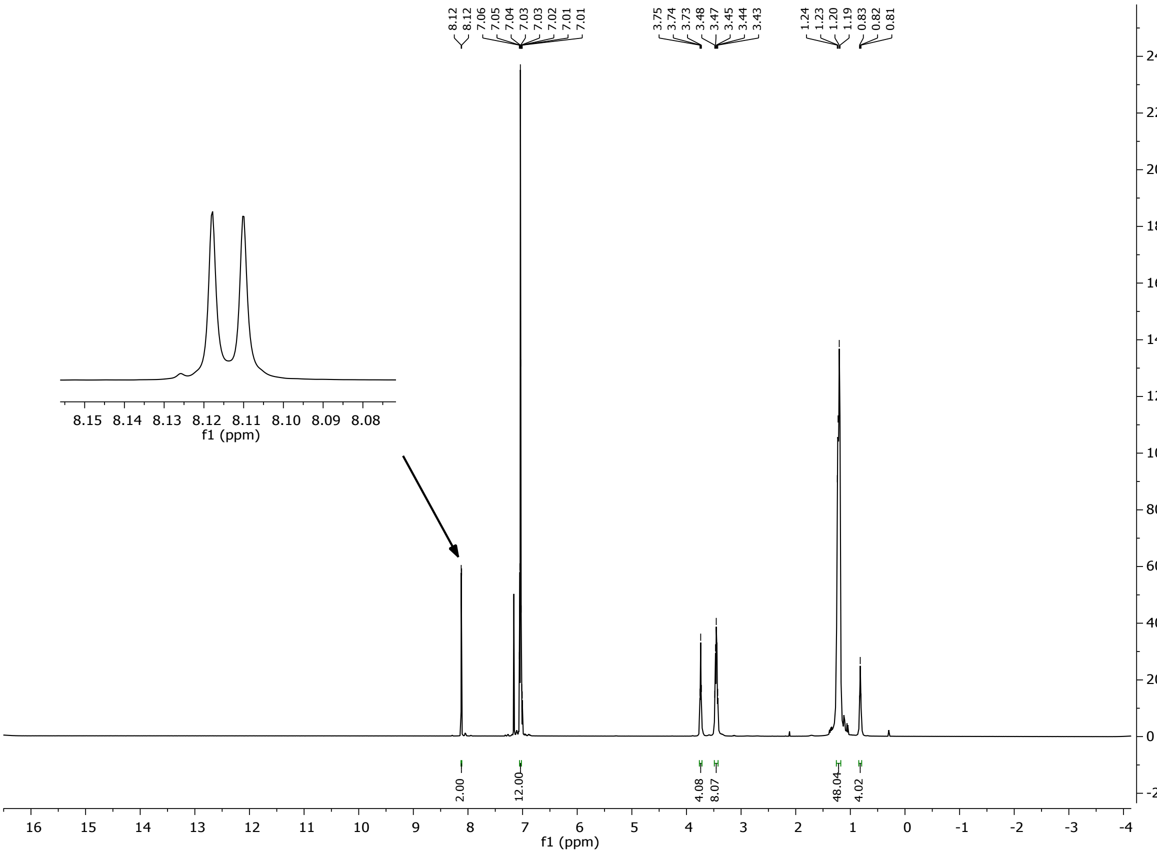

Figure S18: ^{1}H NMR spectrum of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in C_6D_6. The NMR solvent resonance is marked with *.

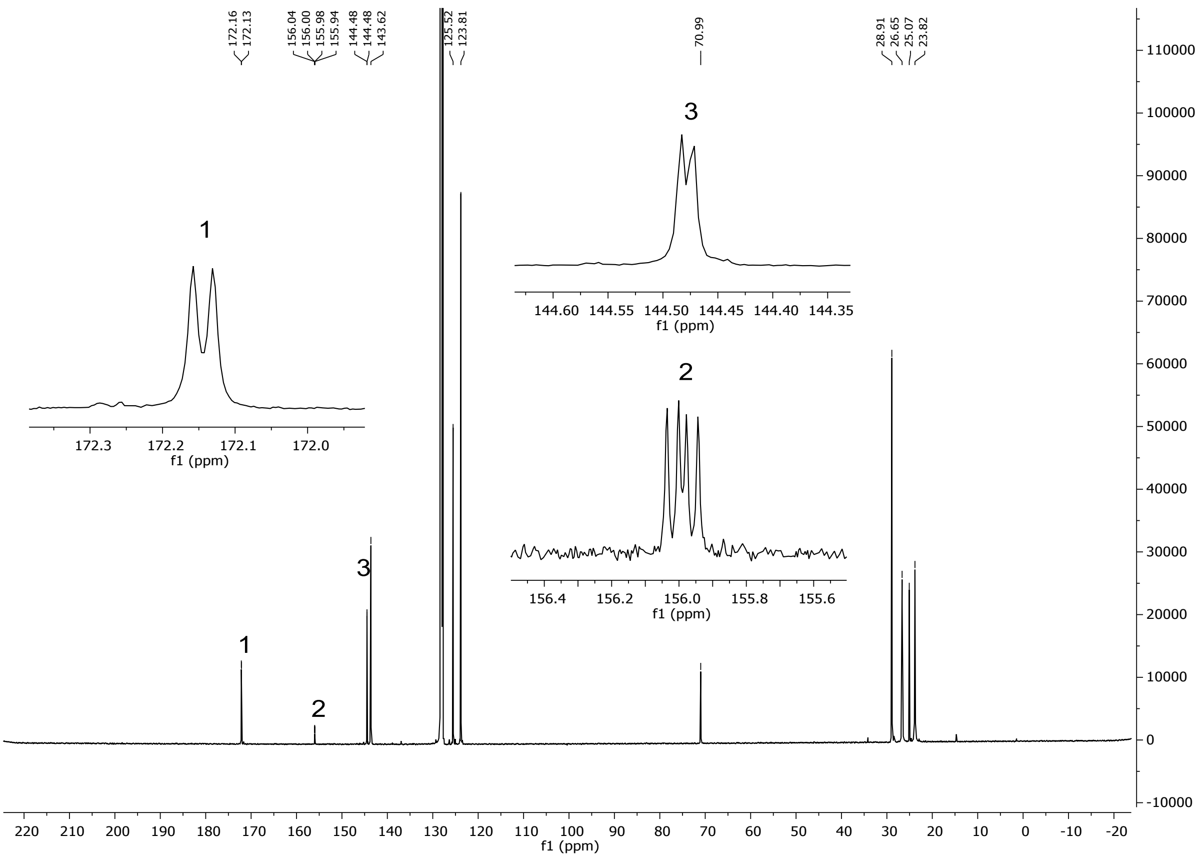

Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in C_6D_6. The NMR solvent resonance is marked with *.

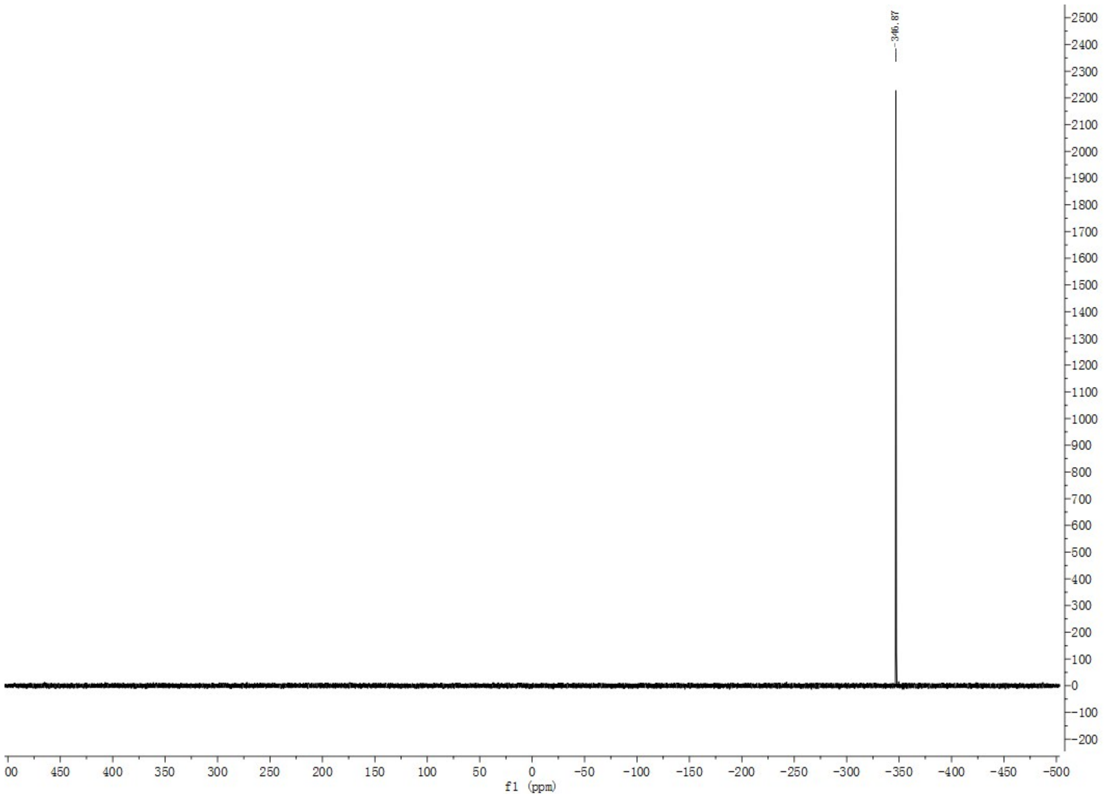

Figure S20: $^{31}P\{^{1}H\}$ NMR spectrum of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in C_6D_6.

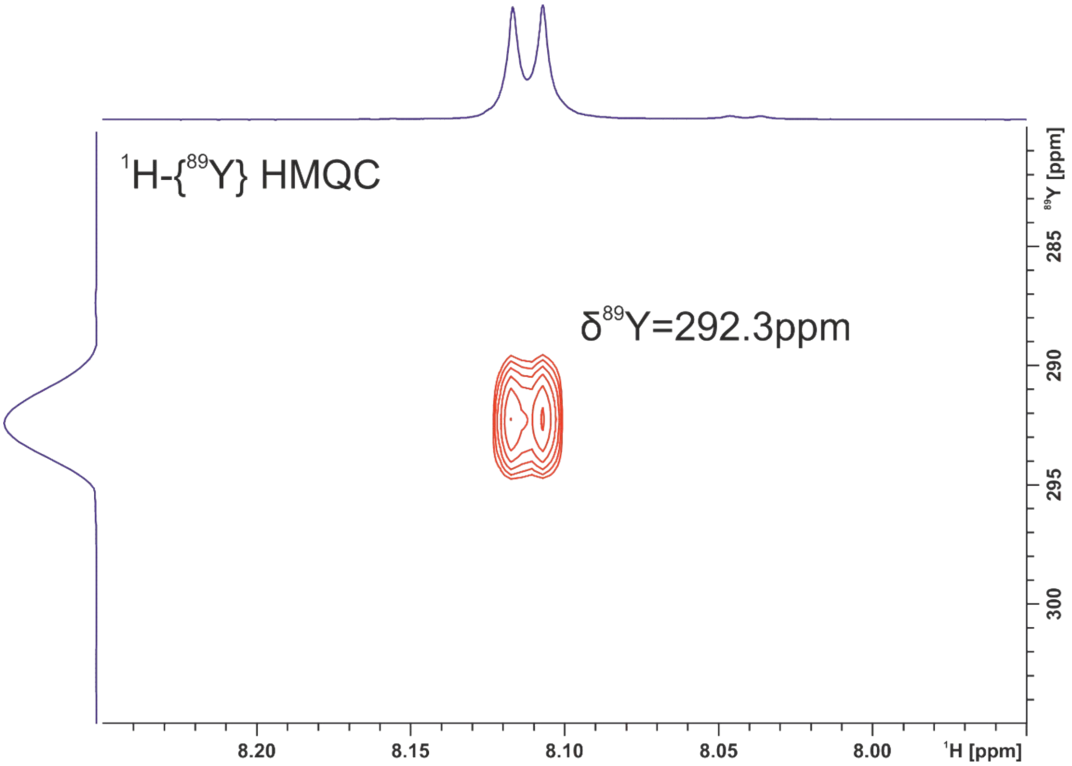

Figure S21: ^{1}H-{^{89}Y} HMQC NMR spectrum (C_6D_6) of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in C_6D_6. The ^{89}Y NMR spectrum is on the vertical axis and the ^{1}H NMR spectrum is on the horizontal axis.

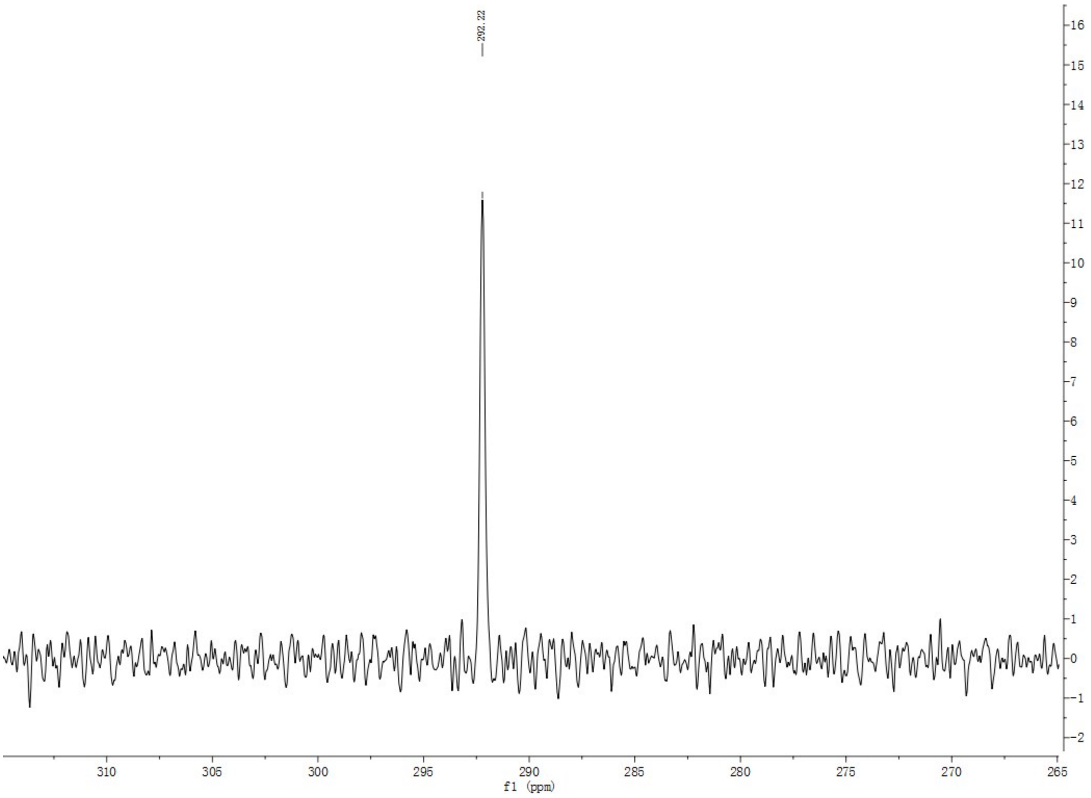

Figure S22: ^{89}Y{^{1}H} INEPT NMR spectrum of [(DippForm)$_2$Y(OCP)(thf)] (**1**) in C_6D_6.

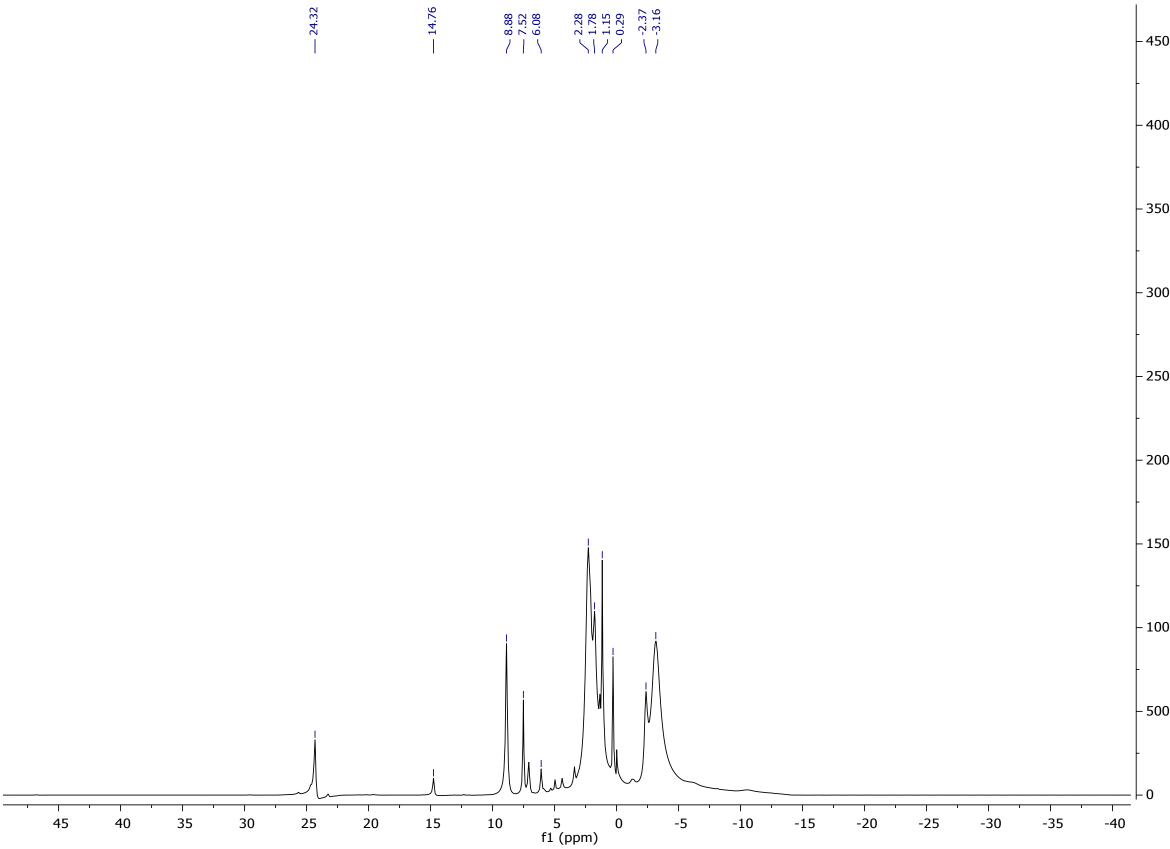

Figure S23: ^{1}H NMR spectrum of [(DippForm)$_2$Nd(OCP)((thf)] (**2**) in C_6D_6.

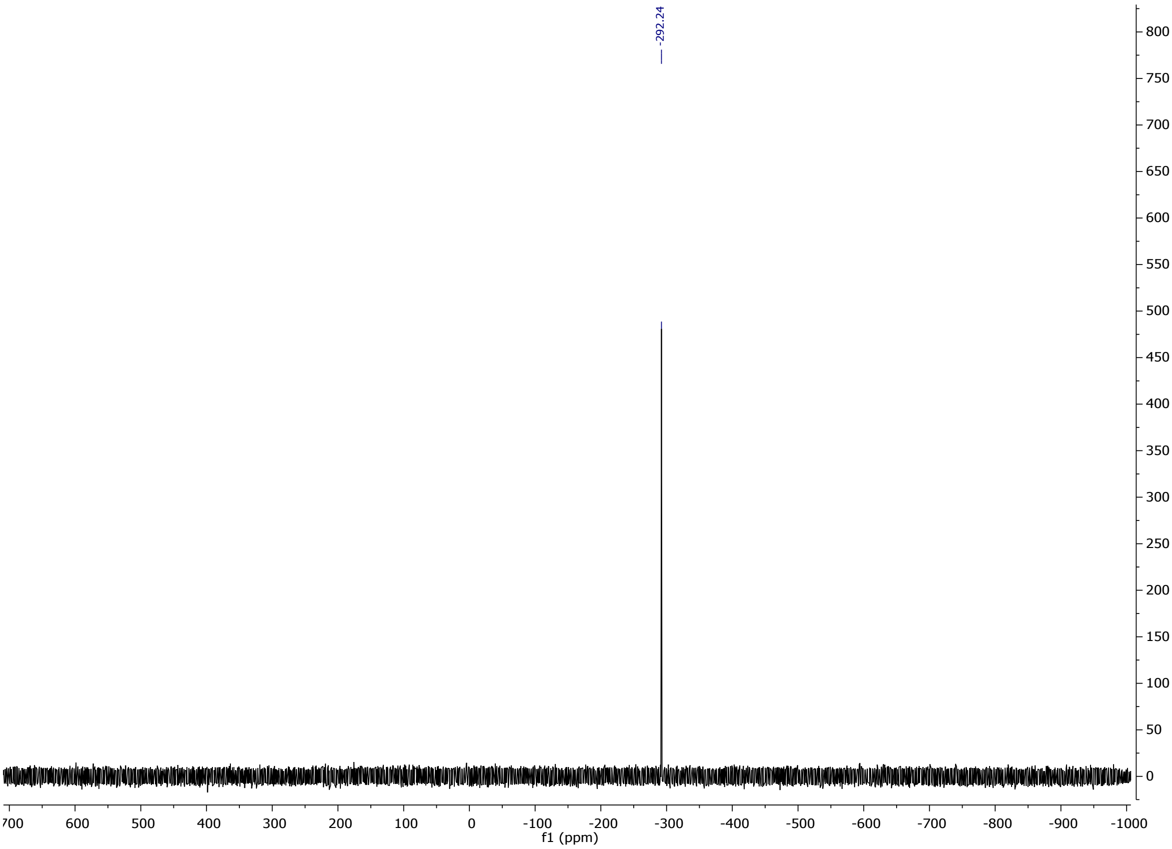

Figure S24: ^{31}P{^{1}H} NMR spectrum of [(DippForm)$_2$Nd(OCP)((thf)] (**2**) in C_6D_6.

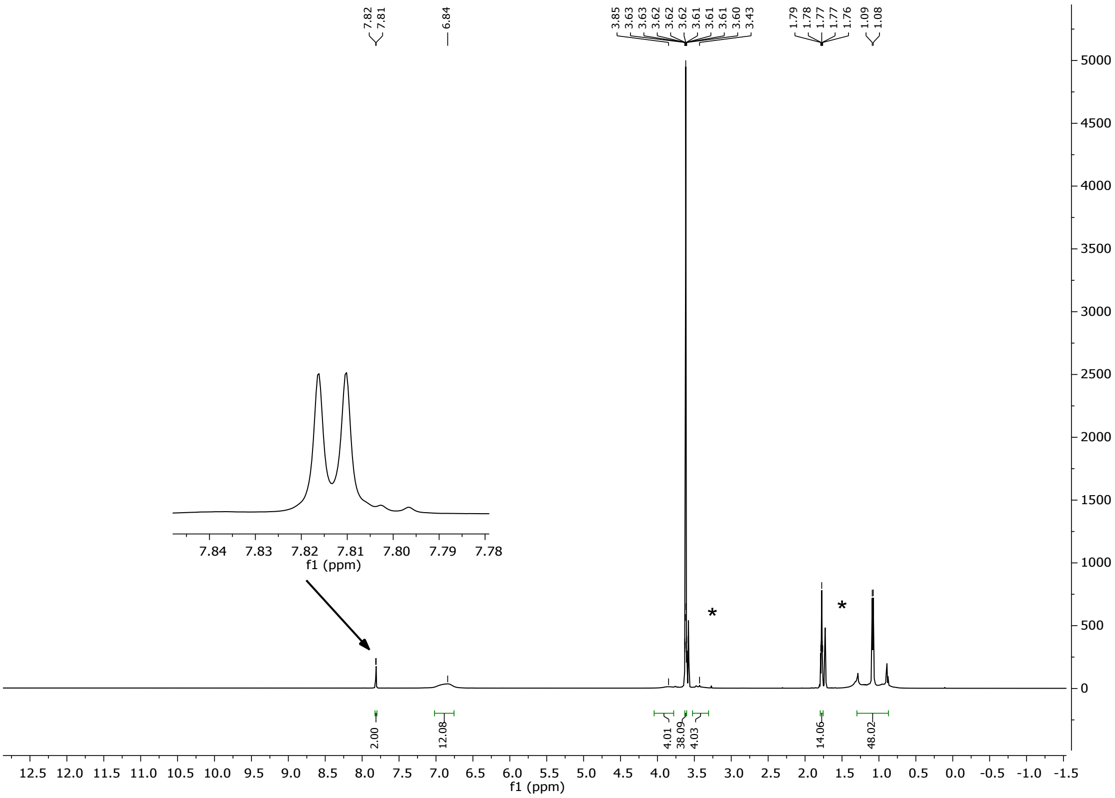

Figure S25: ^{1}H NMR spectrum of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**) in thf-d_8. The NMR solvent resonances are marked with *.

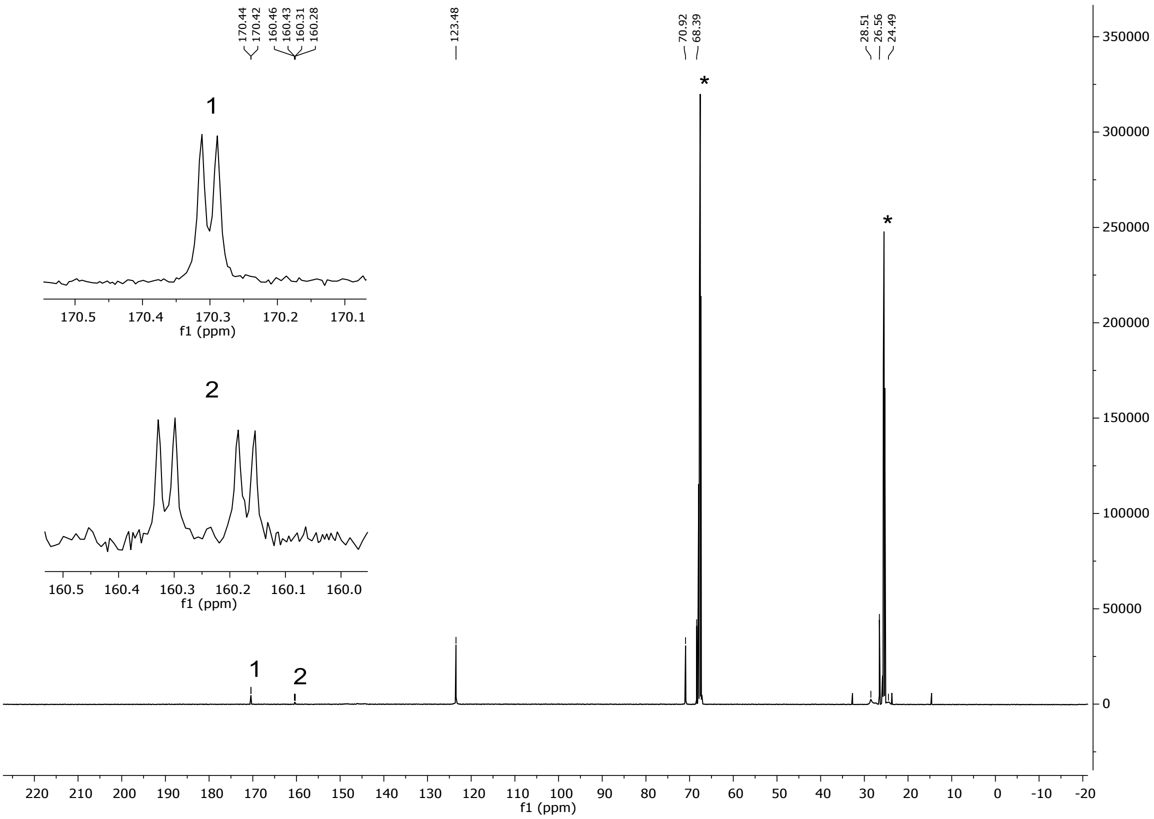

Figure S26: ^{13}C{^{1}H} NMR spectrum of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**) in thf-d_8. The NMR solvent resonances are marked with *.

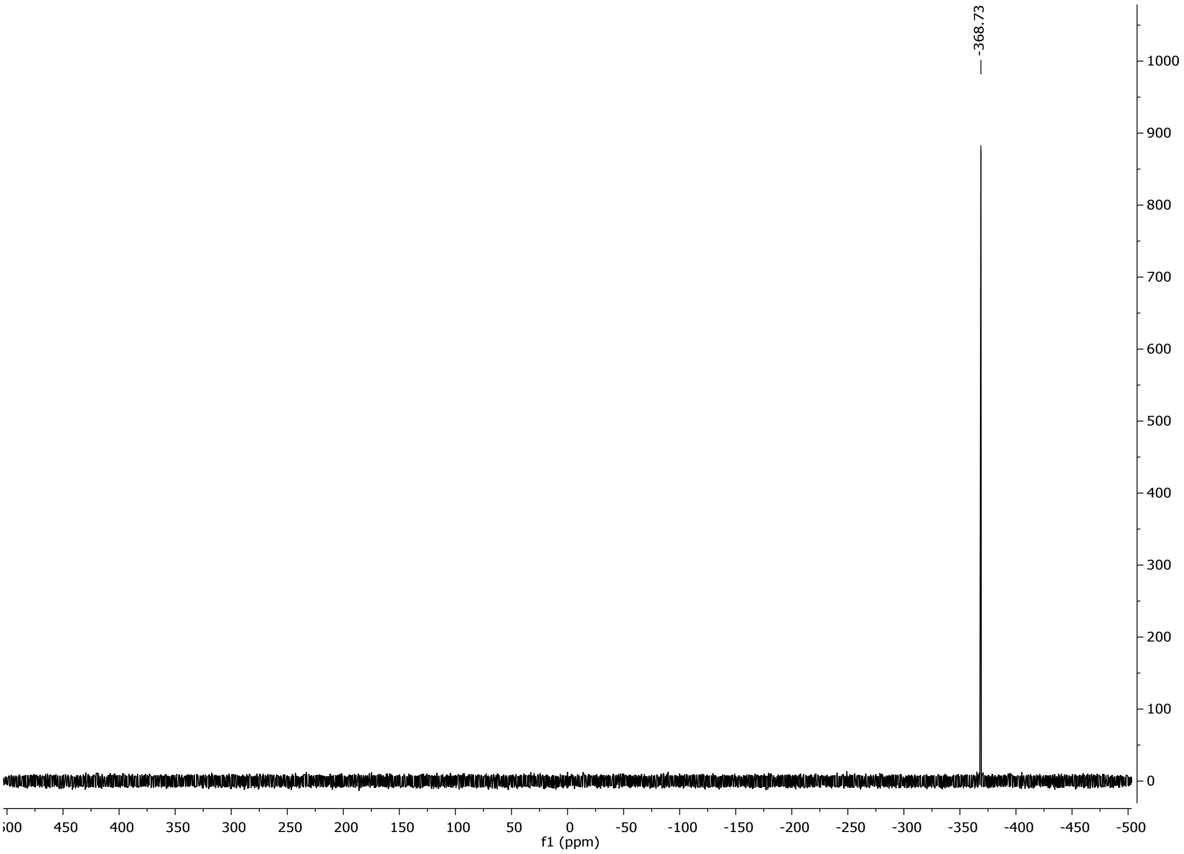

Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of $[Na(18\text{-crown-6})(thf)_2][(DippForm)_2Y(OCP)_2(thf)]$ (**3**) in thf-d_8.

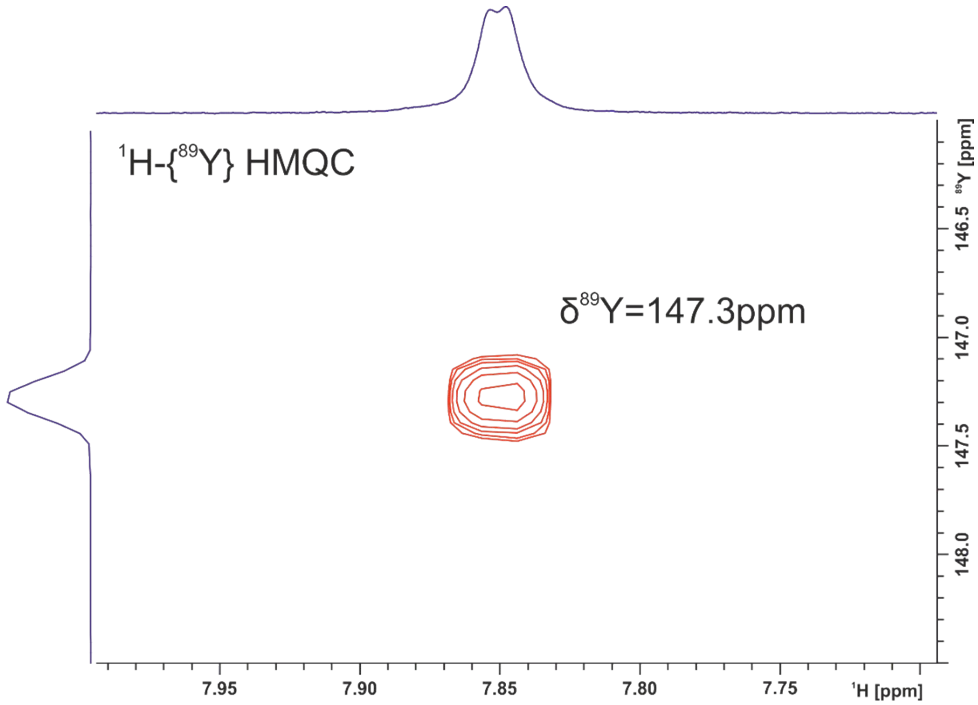

Figure S28: $^{1}H\text{-}\{^{89}Y\}$ HMQC NMR spectrum of $[Na(18\text{-crown-6})(thf)_2][(DippForm)_2Y(OCP)_2(thf)]$ (**3**) in thf-d_8. The ^{89}Y NMR spectrum is on the vertical axis and the ^{1}H NMR spectrum is on the horizontal axis.

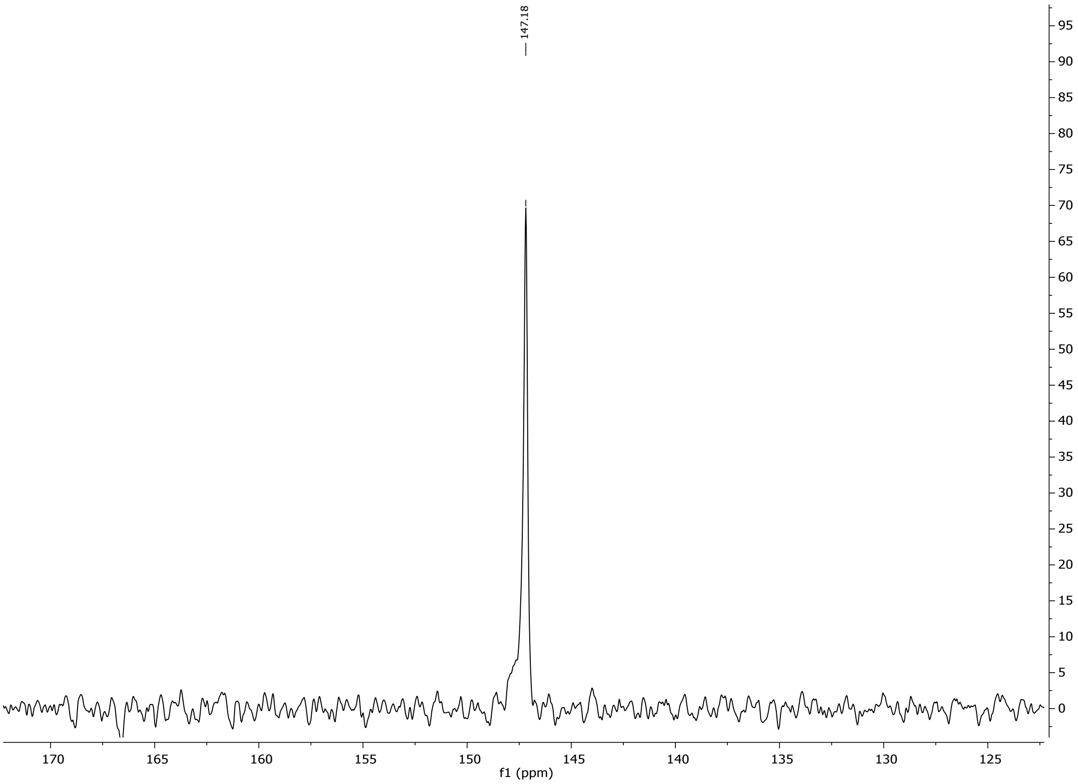

Figure S29: ^{89}Y{^{1}H} INEPT NMR spectrum of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**) in thf-d_8.

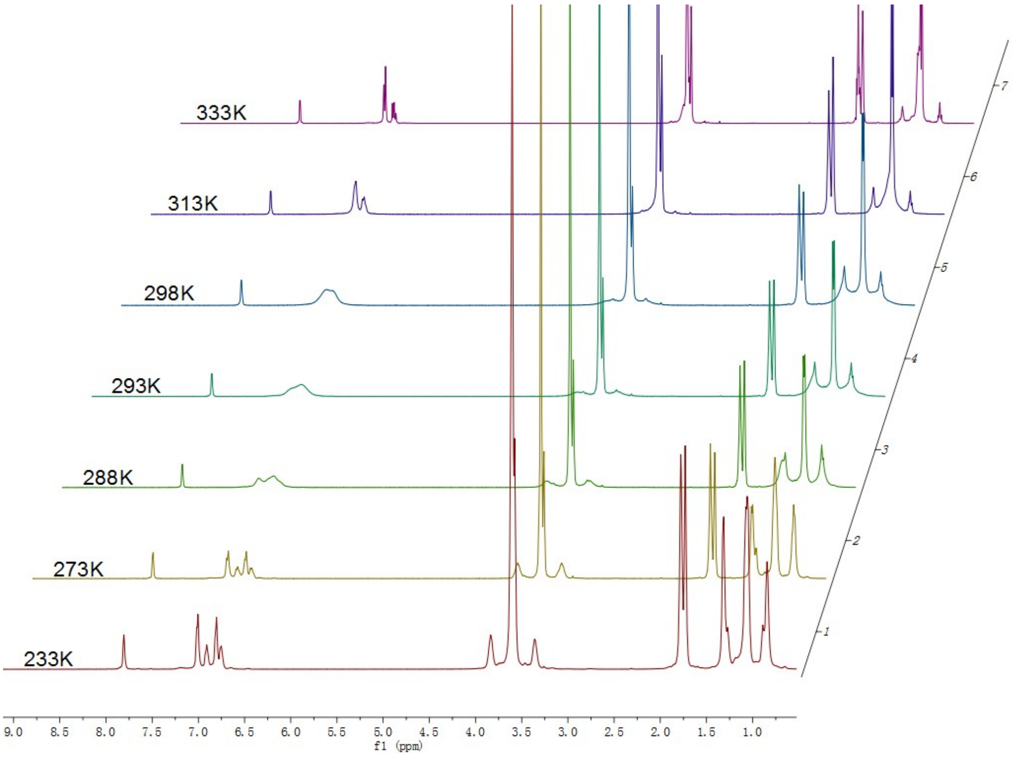

Figure S30: Variable temperature ^{1}H NMR spectra of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Y(OCP)$_2$(thf)] (**3**) in thf-d_8 in a range between 233 K and 333 K.

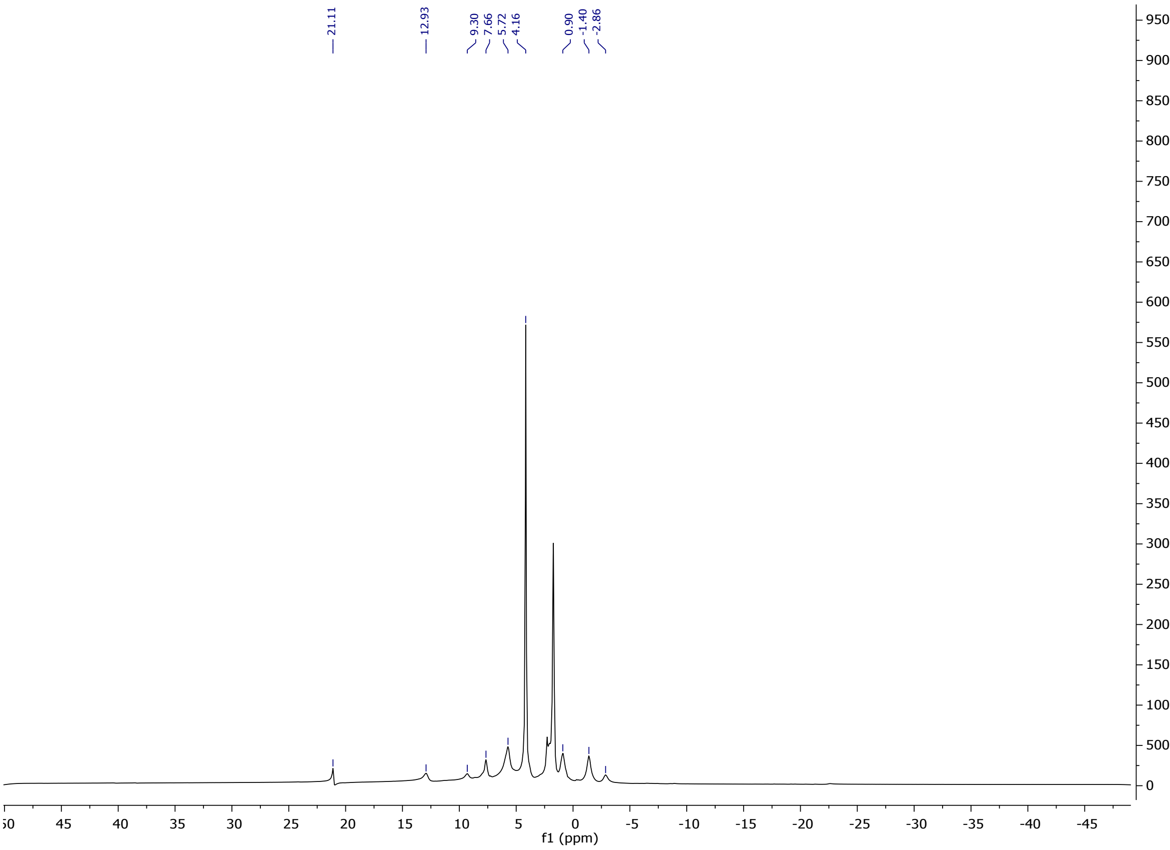

Figure S31: ^{1}H NMR spectrum of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Nd(OCP)$_2$(thf)] (**4**) in thf-d_8.

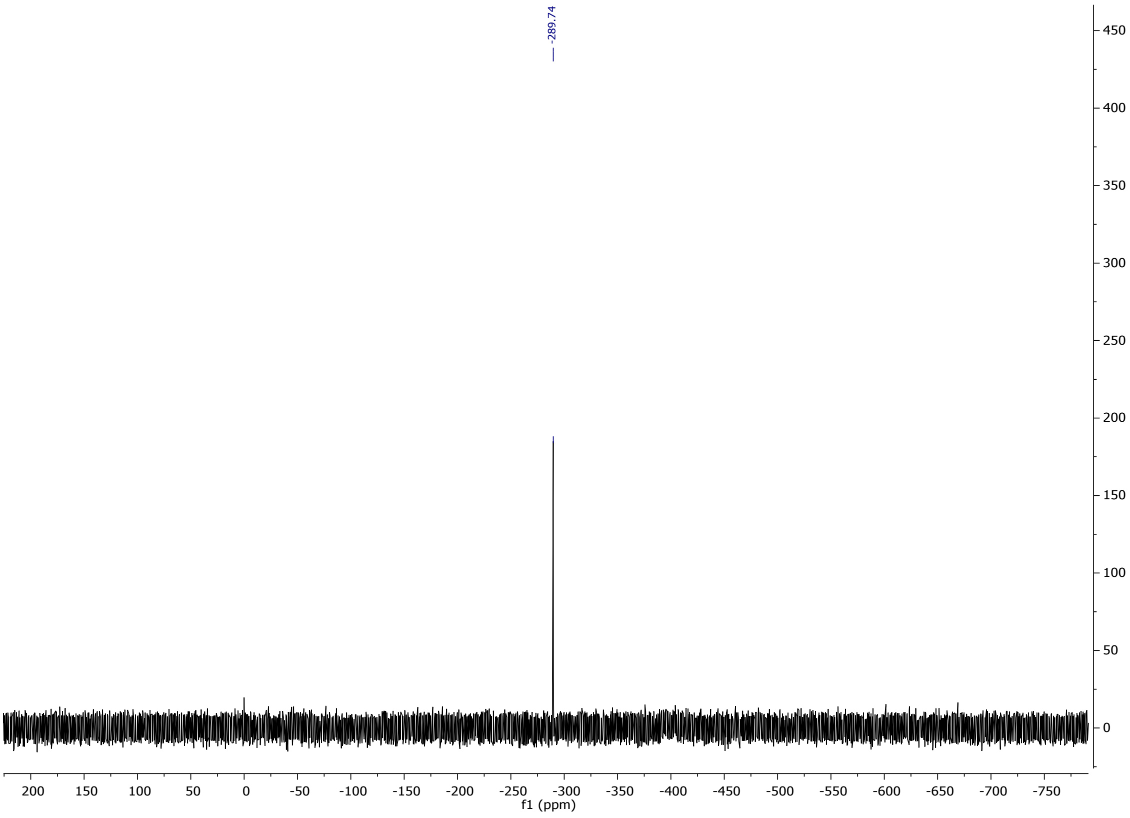

Figure S32: ^{31}P{^{1}H} NMR spectrum of [Na(18-crown-6)(thf)$_2$][(DippForm)$_2$Nd(OCP)$_2$(thf)] (**4**) in thf-d_8.

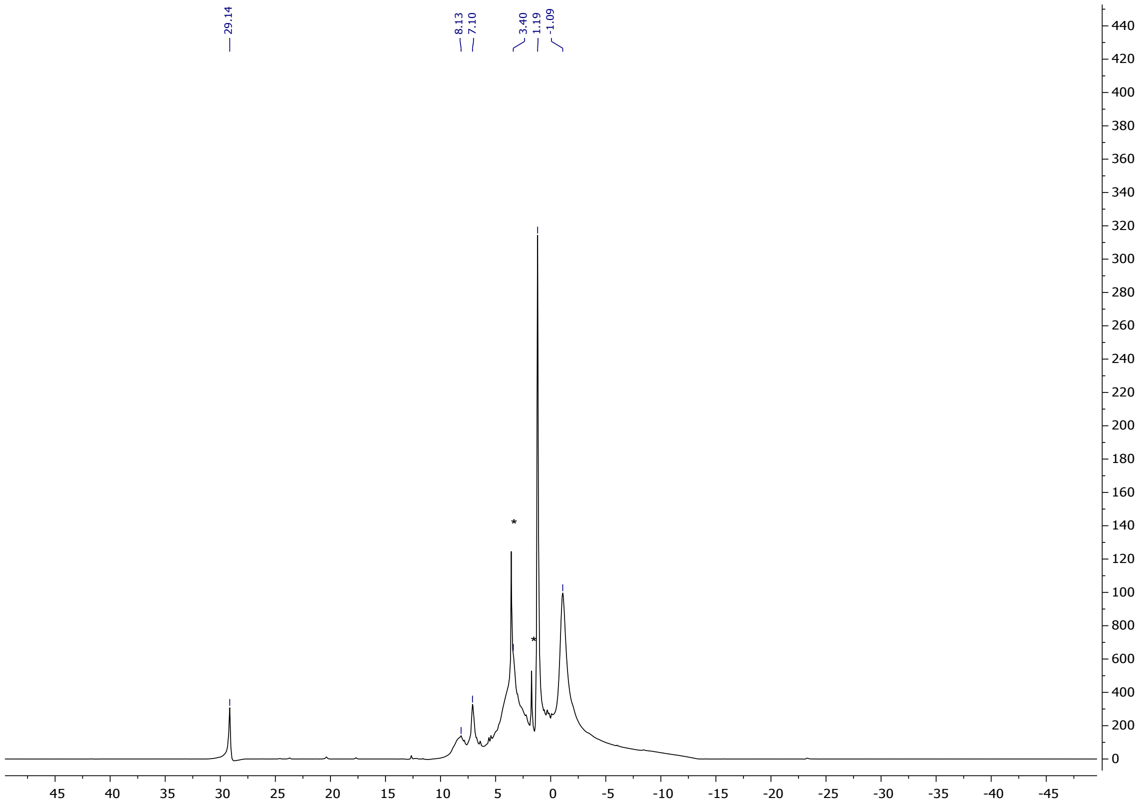

Figure S33: ^{1}H NMR spectrum of $[(DippForm)_2Nd(\mu^2\text{-}OCP)]_2$ (**5**) in thf-d_8. * denote residual solvent peaks from thf-d_8.

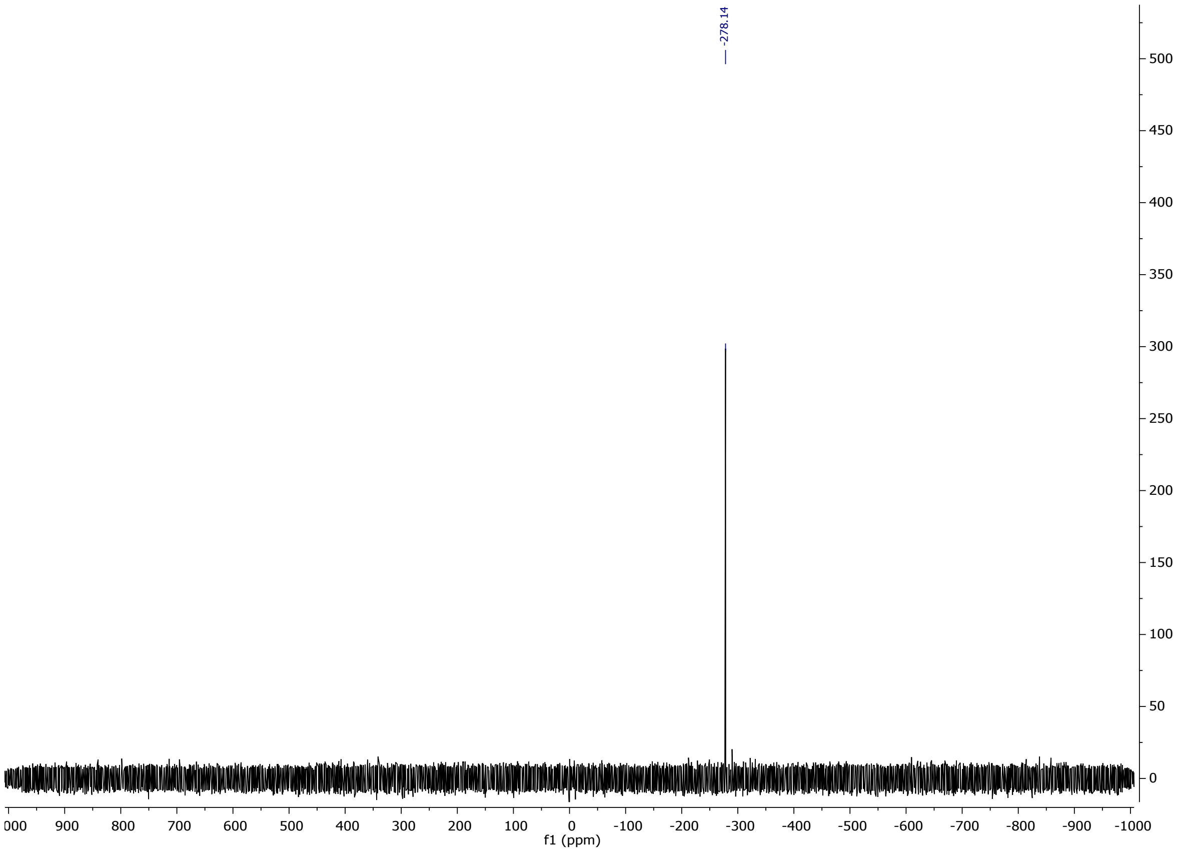

Figure S34: $^{31}P\{^{1}H\}$ NMR spectrum of $[(DippForm)_2Nd(\mu^2\text{-}OCP)]_2$ (**5**) in thf-d_8.

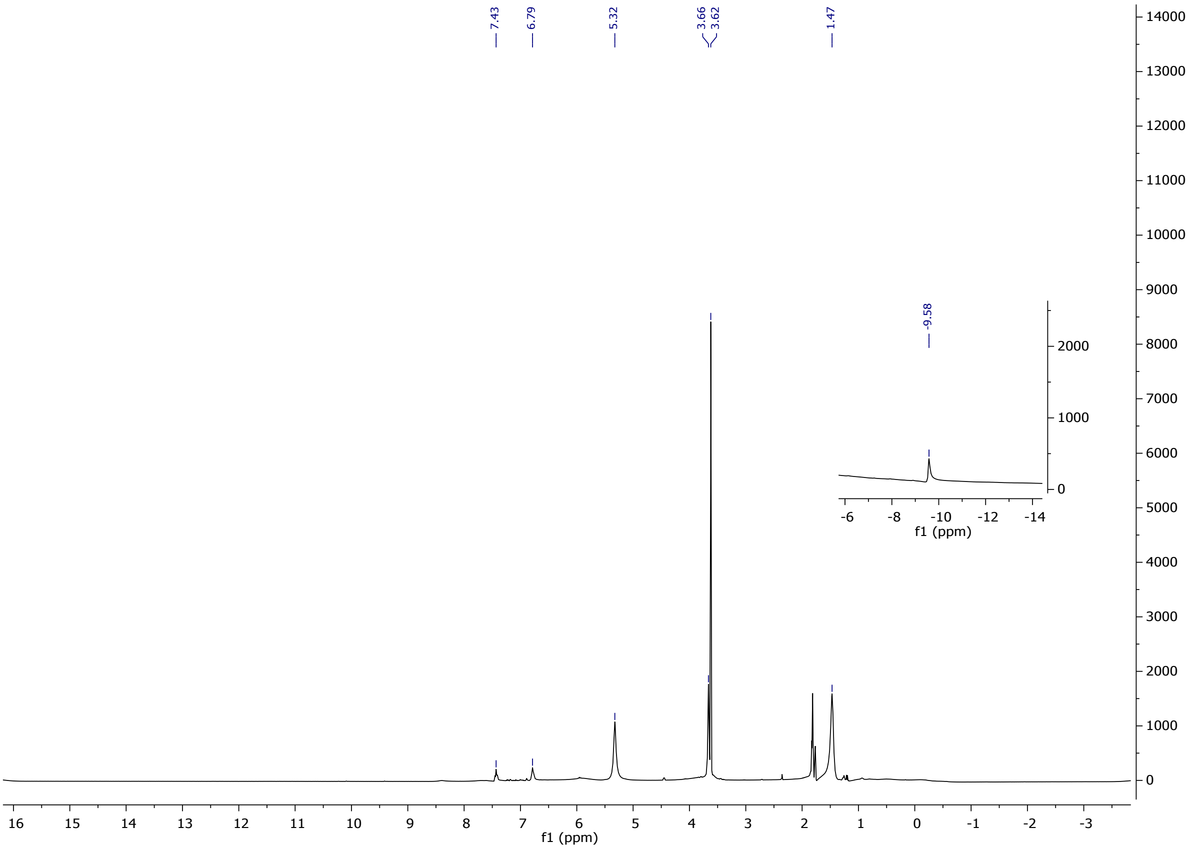

Figure S35: ^{1}H NMR spectrum of [(DippForm)Sm(18-crown-6)(thf)][DippForm] (**6**) in thf-d_8..

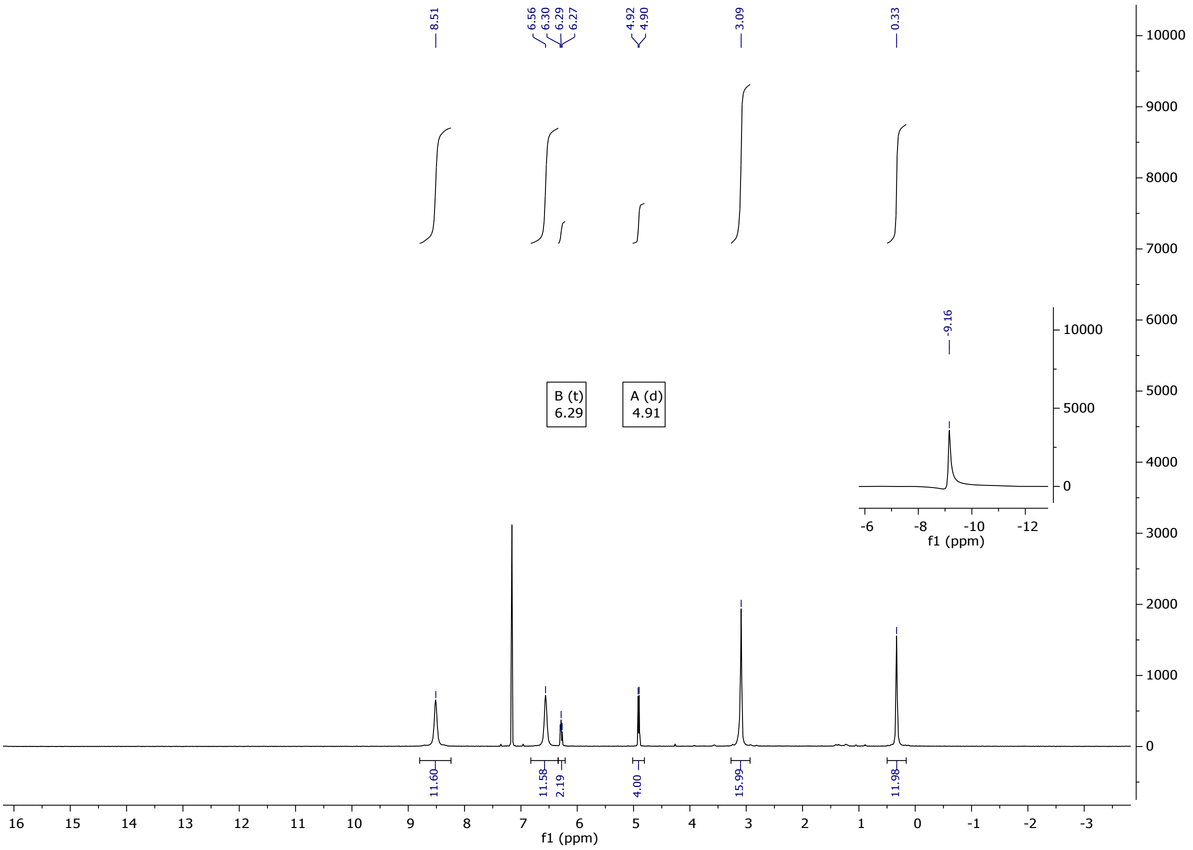

Figure S36: ^{1}H NMR spectrum of [(DippForm)Sm(OCP)(18-crown-6)] (**7**) in C_6D_6.

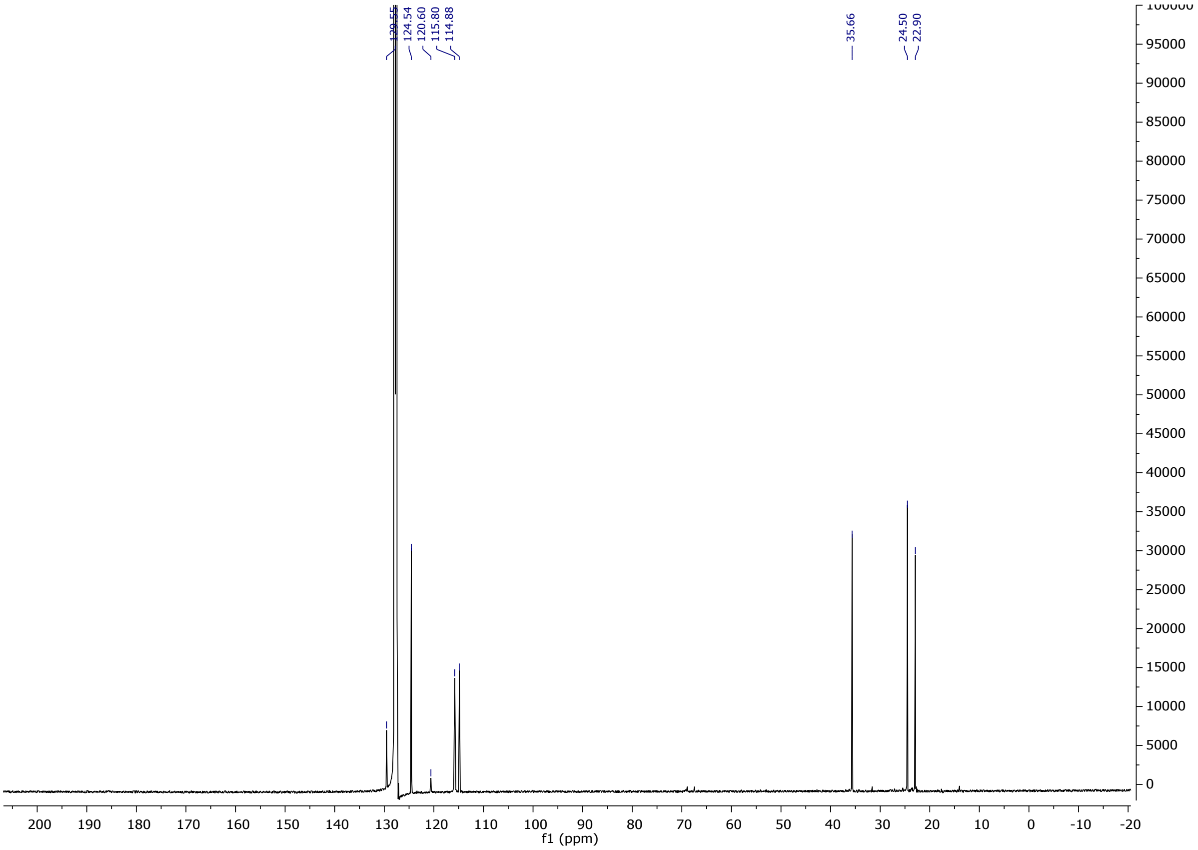

Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of [(DippForm)Sm(OCP)(18-crown-6)] (**7**) in C_6D_6.

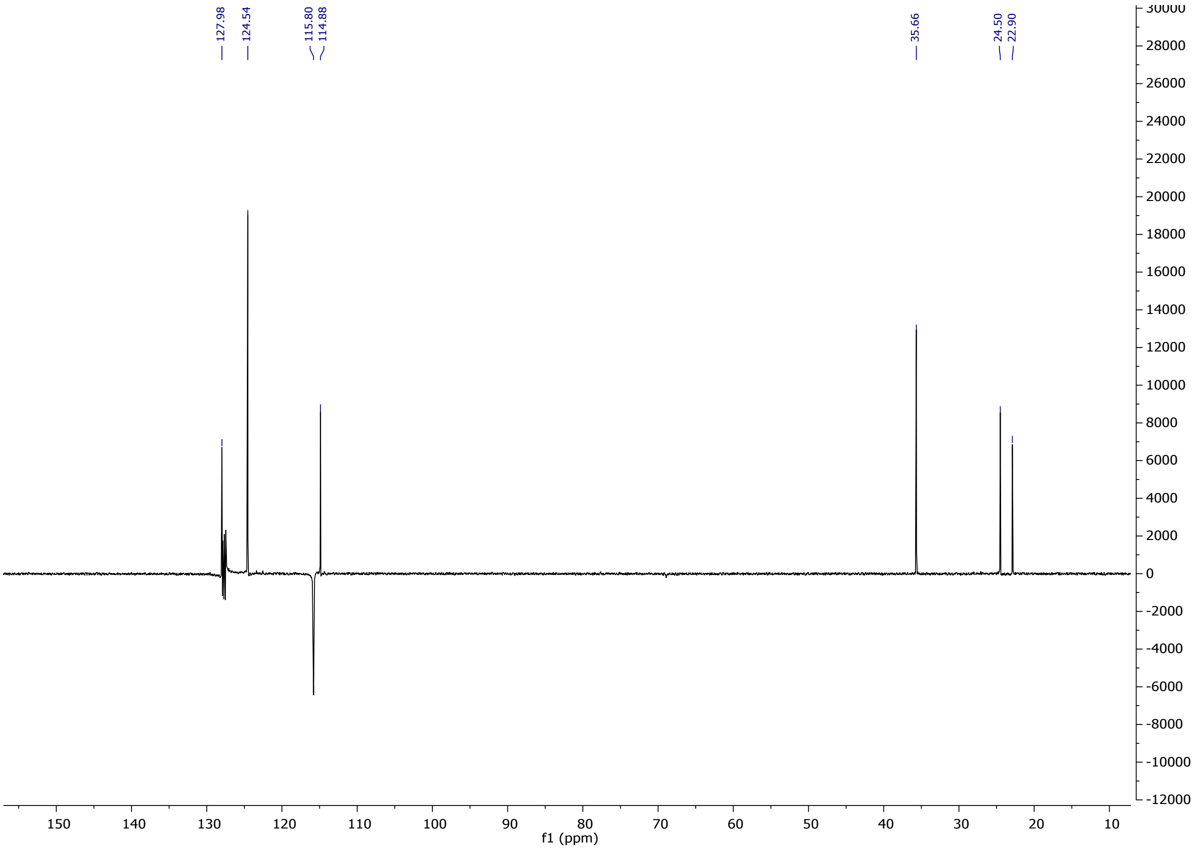

Figure S38: 135dept NMR spectrum of [(DippForm)Sm(OCP)(18-crown-6)] (**7**) in C_6D_6.

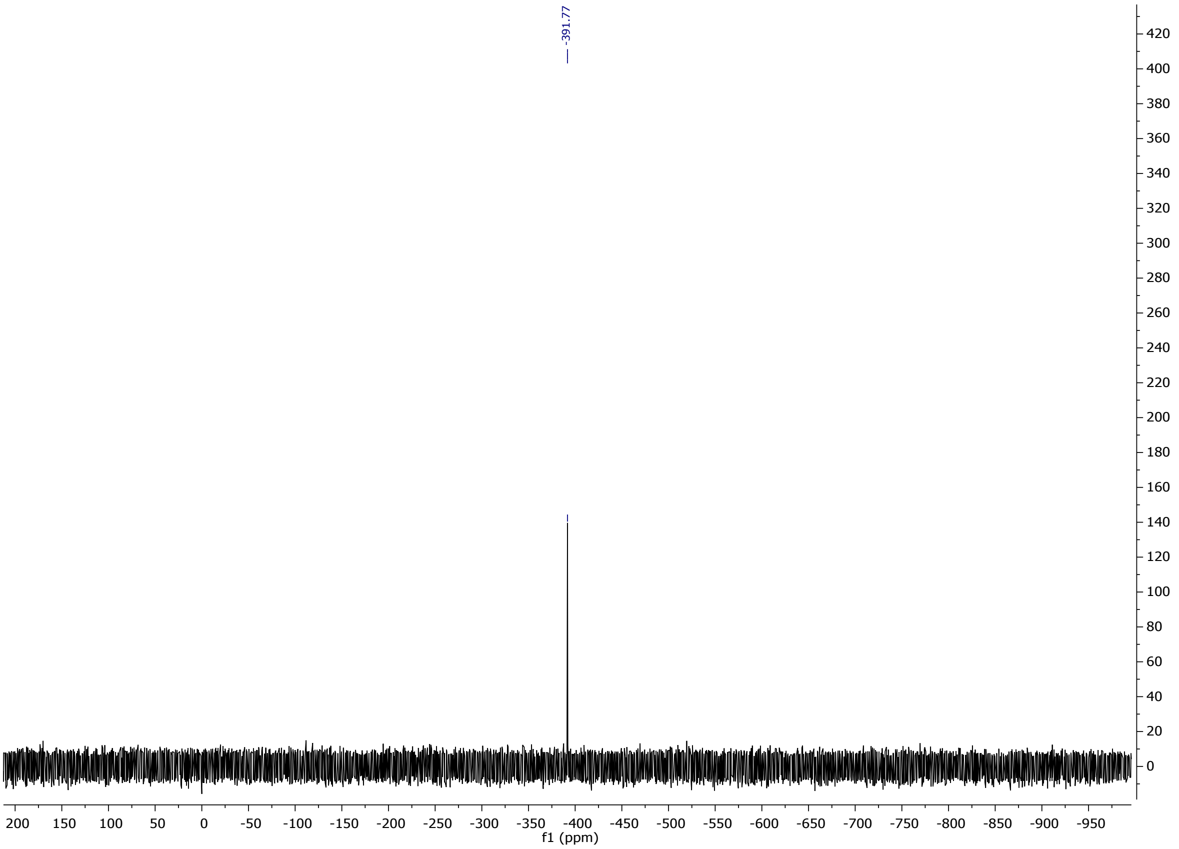

Figure S39: $^{31}P\{^{1}H\}$ NMR spectrum of [(DippForm)Sm(OCP)(18-crown-6)] (**7**) in C_6D_6.

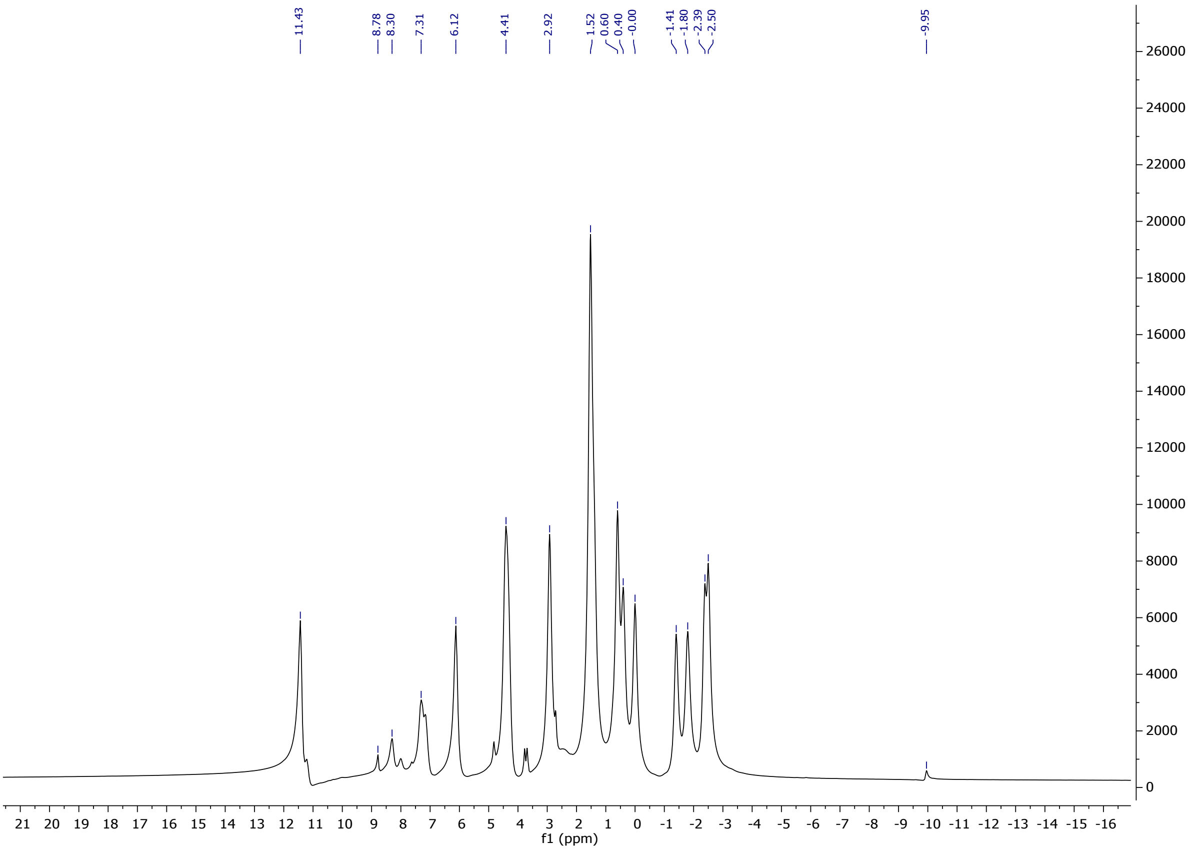

Figure S40: ^{1}H NMR spectrum of [(DippForm)Sm(2,2,2-crypt)][DippForm] (**8**) in pyridine-d_5.

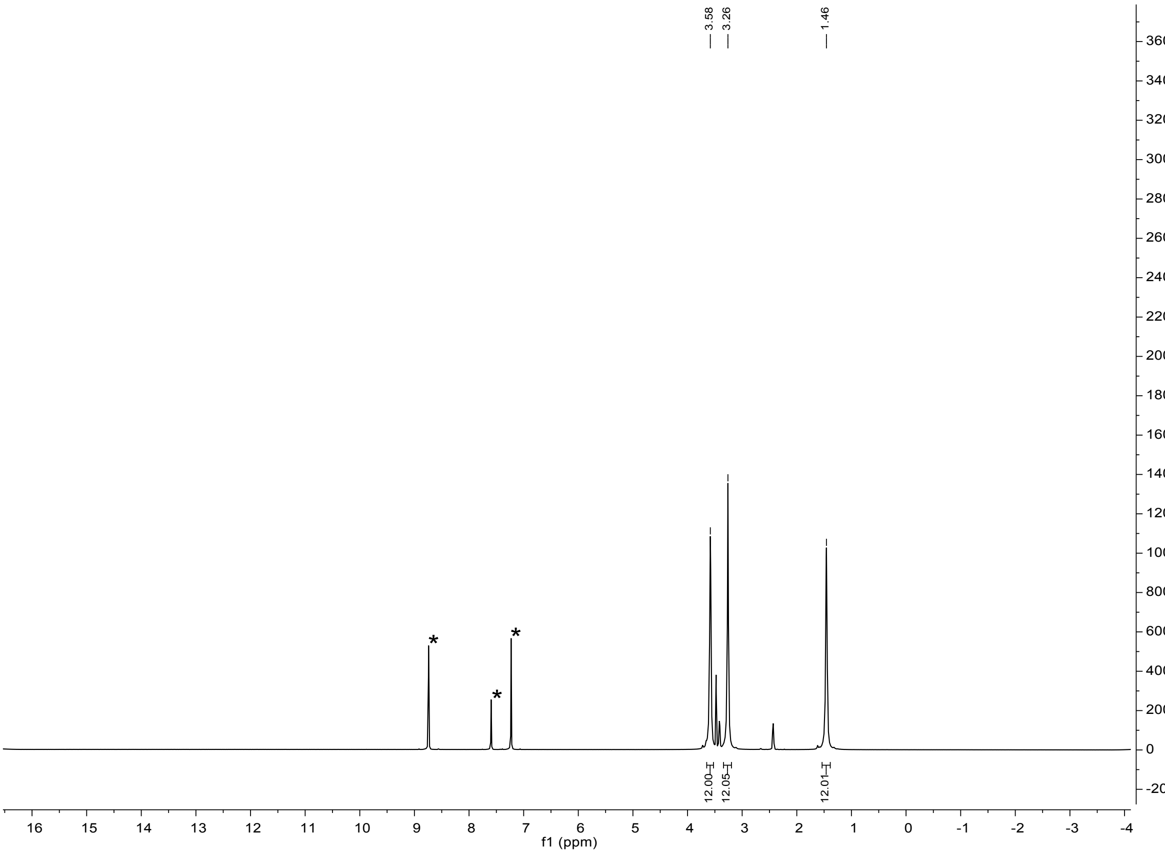

Figure S41: ^{1}H NMR spectrum of [(2,2,2-crypt)Sm(OCP)$_2$] (**9**) in pyridine-*d*$_5$. * denote residual solvent peaks from pyridine-*d*$_5$.

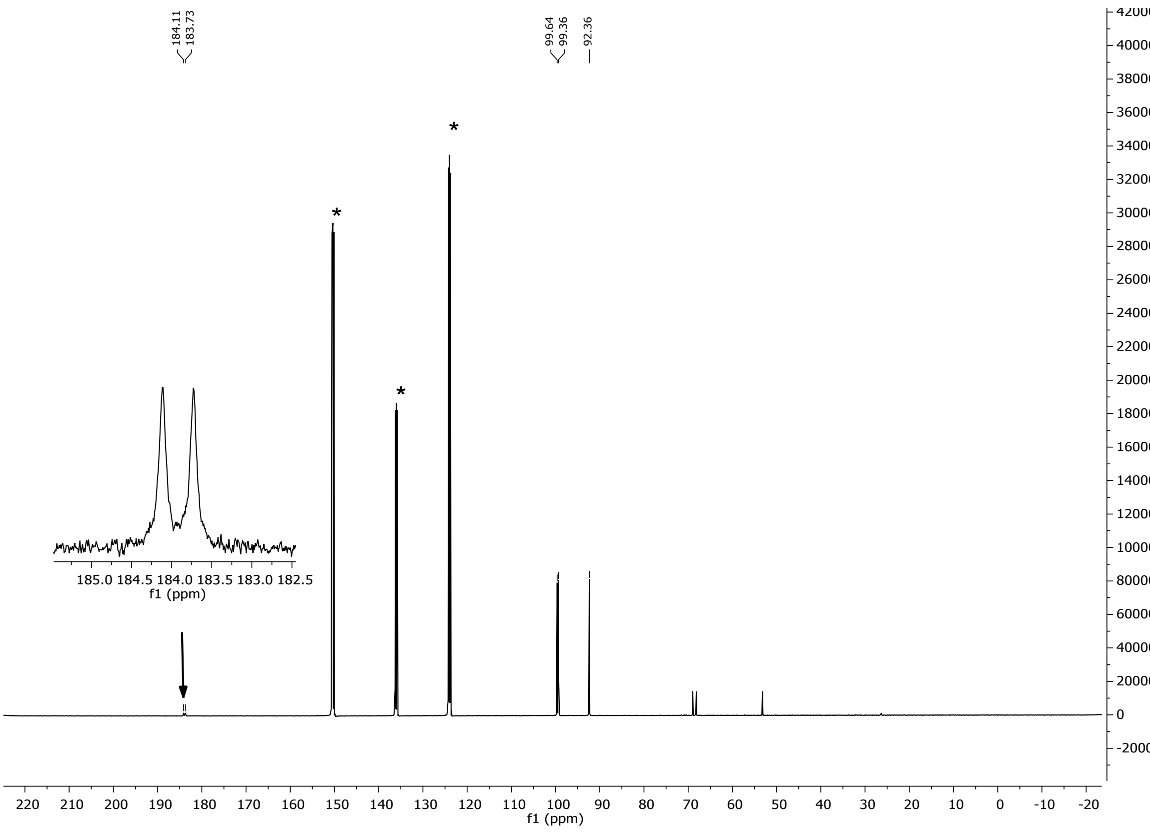

Figure S42: ^{13}C{^{1}H} NMR spectrum of [(2,2,2-crypt)Sm(OCP)$_2$] (**9**) in pyridine-*d*$_5$. * denote residual solvent peaks from pyridine-*d*$_5$.

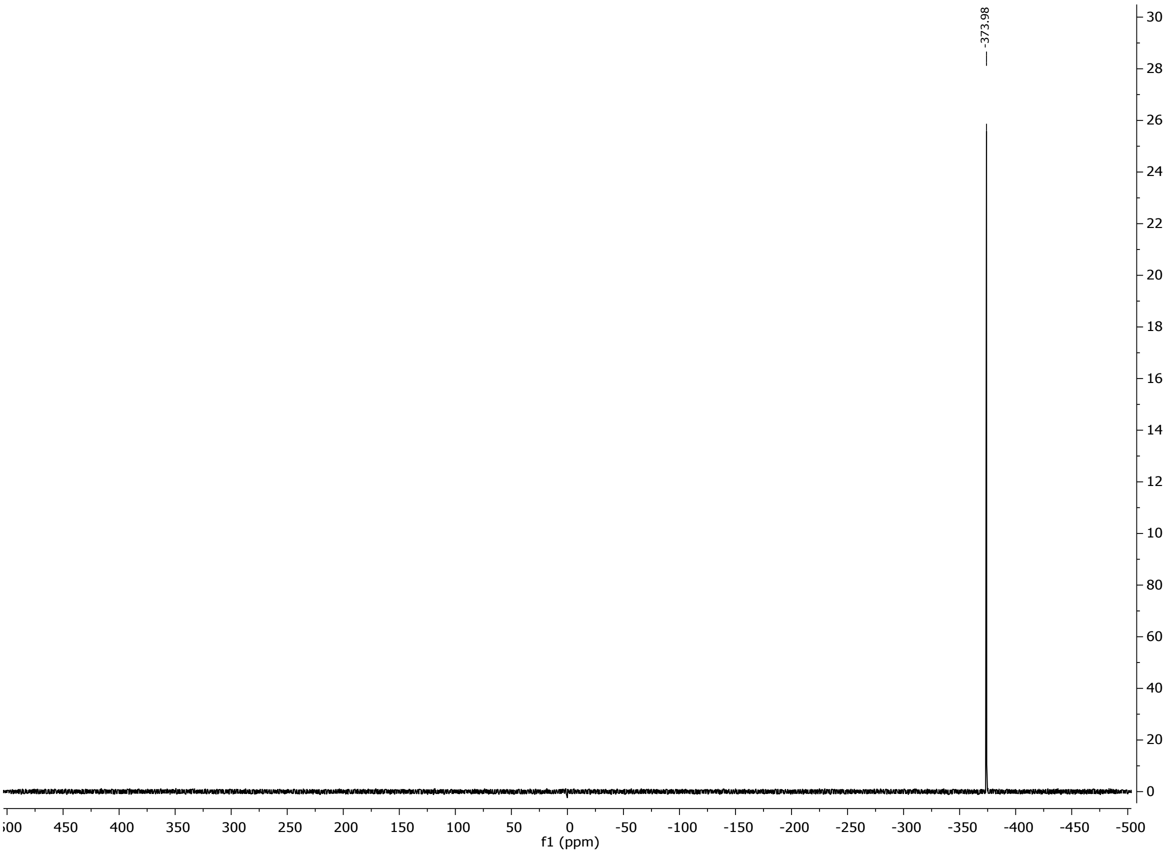

Figure S43: $^{31}P\{^{1}H\}$ NMR spectrum of [(2,2,2-crypt)Sm(OCP)$_2$] (**9**) in pyridine-*d*$_5$.

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