

Supporting Information

Light-induced splitting of P-C bonds in a lanthanum(III) hemiphosphinal complex

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1. Experimental Section

General Remarks. If not otherwise mentioned, all transformations were carried out under inert conditions using an argon filled glovebox. All glassware (including glass-fibre filters) was stored in an oven at 150 °C for at least 12 h prior to use. Solvents were dried by a MBraun SPS system, degassed and stored over activated molecular sieves (3 Å) for at least 24 h prior to use. C₆D₆ was degassed by three freeze-pump-thaw cycles and then dried by storage over activated molecular sieves (3 Å) for at least 24 h. IR spectra were recorded at room temperature under inert conditions using a Bruker Vertex 70 with ATR equipment. If not otherwise stated, the NMR spectra were collected at 303 K on a Bruker AV-500 or an Ascent 700 spectrometer using a J-Young NMR tube. All chemical shifts (δ) are reported in ppm and coupling constants are given in Hz. ¹H and ¹³C chemical shifts were calibrated to residual solvent peaks. ³¹P chemical shifts were calibrated externally to phosphoric acid (H₃PO₄, 85% in water). EPR spectra were recorded on a Bruker Magnetech ESR5000 X-band EPR spectrometer using a temperature control unit and 3 mm o.d. J-Young fused silica tubes. For in-situ irradiation experiments a Hamamatsu LightningCure lamp (L9566-06A, 200W Mercury Xenon 365 nm wide band) was used. Analysis was performed using the EasySpin package for MatLab®. Values were obtained by least-squares fitting to the experimental spectra using the garlic function. Elemental analyses were performed using an Elementar vario microcube instrument at the University of Innsbruck. **KPH^tBu** was synthesized by adding KHMDs to commercially available PH₂^tBu (10 weight% in hexane) and filtering off the faint yellow solid. Starting materials **(PN)₂LaCl** and **1a** were synthesized following literature known procedures.¹ 9H-Fluoren-9-one and PPh₃ was used as received.

Synthetic Procedures

Preparation of **(PN)₂LaPPh** (**1b**).

Solid **(PN)₂LaCl** (342 mg, 400 μ mol, 1 eq.) and **KPPh** (71 mg, 480 μ mol, 1.2 eq.) were combined and toluene (6 mL) was added to this mixture. The resulting yellow suspension was stirred for 12 h at room temperature. After centrifugation the supernatant was filtered through a glass-fibre filter and all volatiles were removed *in vacuo* to yield the crude product. This solid was resuspended in *n*-pentane (4 mL) and stirred for 3 h at room temperature. The suspension was then centrifuged and the supernatant was separated from the solid with a pipette. The yellow solid was washed with additional *n*-pentane (3 x 2 mL) and dried *in vacuo*. (*Caution: The product complex and the phosphanide starting material are very malodorous as well as potentially pyrophoric and should therefore be quenched carefully and only in small quantities with sodium hypochlorite solution before disposal.*) Single crystals suitable for X-ray structure determination were obtained as thin, pale yellow plates by storing a concentrated *n*-hexane solution of **1b** at -40 °C for five weeks. Yield: 224 mg (240 μ mol, 60%). ¹H NMR (C₆D₆, 700 MHz, in ppm) δ = 7.44–7.39 (m, CH_{Ar}, 2 H), 7.00–6.96 (m, CH_{Ar}, 2 H), 6.89–6.86 (m, CH_{Ar}, 2 H), 6.85–6.79 (s at 6.85 & m, CH_{Ar}, 7 H), 5.69–5.64 (m, CH_{Ar}, 2 H), 4.06 (d, ¹J_{PH} = 194.8 Hz, PPh, 1 H), 2.27–2.22 (br. s, CH_{3Ar}, 12 H), 2.16 (s, CH_{3Ar}, 6 H), 2.11 (s, CH_{3Ar}, 6 H), 1.80–1.67 (br. s, CH_{iPr}, 4 H), 1.21–1.15 (br. m, CH_{3iPr}, 12 H), 0.94–0.85 (br. m, CH_{3iPr}, 12 H); ¹³C{¹H} NMR (C₆D₆, 176 MHz, in ppm) δ = 160.3 (*pseudo-t*, J_{CP} = 11.7 Hz, C_{qAr}), 148.6 (s, J_{CP} = 26.8 Hz, C_{qAr}), 138.3 (br. s, C_{qAr}), 138.0 (s, C_{qAr}), 135.3 (s, C_{qAr}), 133.8 (s, CH_{Ar}), 133.5 (s, CH_{Ar}), 131.8 (s, CH_{Ar}), 130.54 (s, C_{qAr}), 130.47 (s, CH_{Ar}), 127.9 (resonance obscured by C₆D₆ peak, only identifiable by ¹H–¹³C HSQC NMR spectroscopy, s, CH_{Ar}), 123.5 (s, C_{qAr}), 121.9 (s, CH_{Ar}), 113.9 (d, J_{CP} = 6.8 Hz, C_{qAr}), 113.8 (d, J_{CP} = 6.4 Hz, C_{qAr}), 112.7 (*pseudo-t*, J_{CP} = 3.8 Hz, CH_{Ar}), 22.4 (s, CH_{iPr}), 20.9 (s, CH_{3Ar}), 20.6 (s, CH_{3Ar}), 19.9 (*pseudo-t*, J_{CP} = 5.4 Hz, CH_{3iPr}), 19.7 (d, J_{CP} = 3.6 Hz, CH_{3Ar}), 17.7 (br. s, CH_{3iPr}); ³¹P{¹H} NMR (C₆D₆, 283 MHz, in ppm): δ = 10.3 (s, PN⁻, 2 P), -10.2 (s, PPh, 1 P); ³¹P NMR (C₆D₆, 283 MHz, in ppm): δ = 10.3 (s, PN⁻, 2 P), -10.2 (d, ¹J_{PH} = 194.8 Hz, PPh, 1 P). Elemental analysis *calc'd* for C₅₀H₆₈N₂P₃La₁ (%) C 64.65 H 7.38 N 3.02 found C 63.35 H 7.43 N 2.84. (Despite numerous attempts, this was the best elemental analysis that could be obtained for the complex). UV/VIS/NIR: λ_{max} = 327 (ϵ = 47370 L mol⁻¹ cm⁻¹), 339 (ϵ = 44560 L mol⁻¹ cm⁻¹), 388 (ϵ = 36360 L mol⁻¹ cm⁻¹). IR (cm⁻¹): 2957, 2918, 2865, 1599, 1576, 1464, 1394, 1382, 1303, 1280, 1268, 1249, 1215, 1194, 1156, 1098, 1076, 1025, 996, 931, 882, 861, 817, 733, 708, 696, 663, 616, 584, 545, 488, 467, 433.

Preparation of **(PN)₂LaPH^tBu** (**1c**).

In a 20 mL scintillation vial, **(PN)₂LaCl** (500 mg, 0.59 mmol, 1 eq.) dissolved in toluene (12 mL) and cooled down to -40 °C. A suspension of **potassium tert-butylhydrophosphanide (KPH^tBu)** (89.9 mg, 0.70 mmol, 1.2 eq.) in toluene (2 mL) was added slowly. After complete addition, the reaction mixture was allowed to warm up to room

temperature and stirred overnight. The resulting orange solution was centrifuged and the supernatant was filtered through a glass-fibre filter. Afterwards the filtrate dried *in vacuo* and the solid was redissolved in *n*-hexane, filtered again and concentrated to 2 mL under reduced pressure. The concentrated solution stored at $-40\text{ }^{\circ}\text{C}$ for crystallization. The crystals were washed with a small amount of $-40\text{ }^{\circ}\text{C}$ cold *n*-hexane to observe a yellow powder. Single crystals suitable for X-ray structure determination were obtained of a concentrated solution of **(PN)₂LaPH^tBu** in *n*-pentane at room temperature. Yield: 435 mg (0.48 mmol, 82 %). ¹H NMR (C₆D₆, 400 MHz, in ppm) δ = 6.89 (m, CH_{Ar}, 6 H), 6.81 (m, CH_{Ar}, 2 H), 5.78 – 5.55 (m, CH_{Ar}, 2 H), 3.47 (d, ¹J_{PH} = 200.7 Hz, PH^tBu, 1 H), 2.31 (s, CH_{3Ar}, 12 H), 2.17 (s, CH_{3Ar}, 6 H), 2.15 (s, CH_{3Ar}, 6 H), 1.72 (br. s, 4 H), 1.53 (d, *J* = 12.0 Hz, PHC(CH₃)₃, 9 H), 1.26 (s, CH_{3iPr}, 12 H), 1.03 (s, CH_{3iPr}, 12 H); ¹³C{¹H} NMR (C₆D₆, 101 MHz, in ppm) δ = 160.7 (*pseudo-t*, *J* = 11.5 Hz, C_{qAr}), 139.4 (s, C_{qAr}), 138.4 (br. s, CH_{qAr}), 134.5 (s, CH_{Ar}), 133.7 (s, CH_{Ar}), 133.4 (s, C_{qAr}), 131.5 (s, CH_{Ar}), 122.8 (s, C_{qAr}), 113.8 (t, *J* = 6.6 Hz, (s, CH_{Ar}), 112.6 (t, *J* = 4.0 Hz, (CH_{Ar}), 36.7 (d, *J* = 6.8 Hz, PHC(CH₃)₃), 32.0 (d, *J* = 6.8 Hz, PHC(CH₃)₃), 22.0 (br. s, CH(CH₃)_{2iPr}), 20.9 (s, CH(CH₂)_{3iPr}), 20.6 (br. s, CH(CH₂)_{3iPr}), 20.2 (br. s, CH_{3Ar}), 19.2 (s, CH(CH₃)_{2iPr}), 17.9 (br. s, CH(CH₃)_{2iPr}); ³¹P NMR (C₆D₆, 162 MHz, in ppm) δ = 97.45 (d, ¹J_{PH} = 199.3 Hz, PH^tBu, 1 P), 12.30 (s, PN⁻, 2 P); ³¹P{¹H} NMR (C₆D₆, 162 MHz, in ppm) δ = 97.44 (s, PH^tBu, 1 P), 12.30 (s, PN⁻, 2 P). Elemental analysis *calc'd* for C₄₈H₇₂N₂P₃La₁ · 0.25 KCl (%) C 62.15 H 7.82 N 3.02 found C 61.74 H 8.08 N 3.00. UV/VIS/NIR: λ_{max} = 327 (ϵ = 41220 L mol⁻¹ cm⁻¹), 368 (ϵ = 45130 L mol⁻¹ cm⁻¹), 397 (ϵ = 46070 L mol⁻¹ cm⁻¹). IR (cm⁻¹): 2959, 2920, 2865, 1599, 1537, 1464, 1390, 1303, 1278, 1266, 1249, 1215, 1192, 1156, 1098, 1033, 929, 882, 857, 821, 810, 731, 710, 690, 661, 616, 543, 490, 467, 433.

Preparation of **(PN)₂La{OFluoren(PHMes)}** (**2a**).

(Note: The product is light-sensitive, therefore the reaction is performed in a brown glass vial) In a 20 mL scintillation vial, **(PN)₂LaPHMes** (200 mg, 0.2 mmol, 1.0 eq.) was dissolved in toluene (8 mL) and cooled down to $-40\text{ }^{\circ}\text{C}$. A solution of **9H-fluoren-9-one** (37.1 mg, 0.2 mmol, 1.0 eq.) in toluene (2 mL) was added to the reaction mixture. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. On the next day the red solution was filtered through a glass-fibre filter and dried *in vacuo*. Afterwards the solid was washed twice with $-40\text{ }^{\circ}\text{C}$ *n*-hexane (2 mL). The solid was dried under reduced pressure to give a grey solid. Single crystals suitable for X-ray structure determination were obtained from a concentrated solution of **(PN)₂La{OFluoren(PHMes)}** in *n*-hexane at $-40\text{ }^{\circ}\text{C}$. Yield: 162 mg (0.14 mmol, 68 %). ¹H NMR (C₆D₆, 400 MHz, in ppm) δ = 7.74 (dd, *J* = 11.3, 7.8 Hz, CH_{Fl}, 2 H), 7.09 – 6.98 (m, CH_{Ar}, 6 H), 6.92 – 6.81 (m, CH_{Ar}, 8 H), 6.43 (s, CH_{Fl}, 2 H), 5.91 – 5.74 (m, CH_{Ar}, 2 H), 5.17 (d, ¹J_{PH} = 210.6 Hz, PHMes, 1 H), 2.40 (br. s, CH_{3Ar}, 6 H), 2.19 (s, CH_{3Ar}, 12 H), 2.11 (s, CH_{3Ar}, 6 H), 1.99 (s, CH_{3Ar}, 6 H), 1.83 (s, CH_{3Ar}, 3 H), 1.29 – 1.17 (m, CH_{iPr}, 4 H), 1.04 – 0.91 (m, CH_{3iPr}, 24 H); ¹³C{¹H} NMR (C₆D₆, 101 MHz, in ppm) δ = 161.3 (m, C_{qAr}), 143.1 (s, C_{qAr}), 143.0 (s, C_{qAr}), 141.6 (s, CH_{Ar}), 137.7 (s, C_{qFl}), 137.5 (s, C_{qAr}), 133.7 (s, CH_{Ar}), 133.5 (s, CH_{Ar}), 133.3 (s, CH_{Ar}), 131.5 (s, CH_{Ar}), 129.3 (C_{qAr}), 128.8 (s, CH_{Ar}), 126.9 (s, C_{qFl}), 122.0 (s, C_{qAr}), 113.1 (s, C_{qAr}), 95.3 (s, C_{qFl}), 23.1 (s, CH_{3Ar}), 20.9 (s, C_{qAr}), 20.7 (s, CH_{3Ar}), 20.6 (s, CH_{3Ar}); ³¹P NMR (C₆D₆, 162 MHz, in ppm) δ = 9.78 (s, PN⁻, 2 P), -32.02 (br. s, PHMes, 1 P); ³¹P{¹H} NMR (C₆D₆, 162 MHz, in ppm) δ = 9.78 (s, PN⁻, 2 P), -32.09 (br. s, PHMes, 1 P). Elemental analysis *calc'd* for C₆₆H₈₂N₂O₁P₃La₁ (%) C 68.86 H 7.18 N 2.43 found C 68.37 H 7.26 N 2.18. UV/VIS/NIR: λ_{max} = 326 (ϵ = 60890 L mol⁻¹ cm⁻¹), 366 (ϵ = 53740 L mol⁻¹ cm⁻¹), 379 (ϵ = 44950 L mol⁻¹ cm⁻¹), 441 (ϵ = 5710 L mol⁻¹ cm⁻¹). IR (cm⁻¹): 2952, 2918, 2865, 2336, 1691, 1599, 1537, 1497, 1462, 1392, 1303, 1280, 1268, 1196, 1156, 1135, 1109, 1080, 1045, 923, 880, 859, 821, 810, 782, 759, 733, 712, 692, 661, 606, 584, 541, 490, 463, 431.

Preparation of **(PN)₂La{OFluoren(PHPh)}** (**2b**).

(Note: The product is light-sensitive, therefore the reaction is performed in a brown glass vial) In a 20 mL scintillation vial, **(PN)₂LaPHPh** (136 mg, 0.15 mmol, 1.0 eq.) was dissolved in toluene (5 mL) and cooled down to $-40\text{ }^{\circ}\text{C}$. A solution of **9H-fluoren-9-one** (26.4 mg, 0.15 mmol, 1.0 eq.) in toluene (1 mL) was added dropwise. After complete addition, the reaction mixture was allowed to warm up to room temperature and stirred overnight. On the next day the red solution was filtered and dried under reduced pressure. The solid was washed twice with *n*-hexane (2 mL) and dried *in vacuo* to give a grey powder. Yield: 139 mg (0.13 mmol, 86 %). ¹H NMR (C₆D₆, 400 MHz, in ppm) δ = 7.84 (d, *J* = 8.0 Hz, CH_{Fl}, 1 H), 7.65 (d, *J* = 8.4 Hz, CH_{Fl}, 1 H), 7.11 – 6.92 (m, CH_{Ar}, 4 H), 6.92 – 6.80 (m, CH_{Ar}, 8 H), 6.72 (m, CH_{Ar}, 1 H), 5.81 (dd, *J* = 8.3, 5.1 Hz, CH_{Ar}, 1 H), 4.85 (d, ¹J_{PH} = 196.7 Hz, PHPh, 1 H), 2.39 (s, CH_{3Ar}, 12 H), 2.17 (br. s, CH_{3Ar}, 12 H), 1.33 – 1.17 (m, CH_{iPr}, 4 H), 0.96 (s, CH_{3iPr}, 24 H); ¹³C{¹H} NMR (C₆D₆, 101 MHz, in ppm) δ = 161.4

(*pseudo-t*, $J = 11.1$ Hz, C_{qAr}), 141.5 (s, C_{qAr}), 138.8 (s, C_{qFl}), 138.0 (s, C_{qFl}), 134.6 (s, CH_{Ar}), 134.1 (s, CH_{Ar}), 133.9 (s, C_{qAr}), 133.7 (s, CH_{Ar}), 133.5 (s, C_{qAr}), 133.4 (s, CH_{Ar}), 131.4 (s, CH_{Ar}), 127.2 (s, CH_{Ar}), 127.2 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 125.4 (s, CH_{Fl}), 124.3 (s, CH_{Fl}), 122.0 (s, CH_{3Ar}), 119.2 (s, C_{qAr}), 119.1 (s, CH_{Ar}), 113.2 (s, C_{qAr}), 113.0 (s, CH_{Ar}), 93.7 (d, $J = 6.8$ Hz, C_{qFl}), 22.7 (s, CH_{3Ar}), 20.9 (s, CH_{3Ar}), 20.7 (s, CH_{Ar}), 20.4 (br. s, CH_{iPr}); ^{31}P NMR (C_6D_6 , 162 MHz, in ppm) $\delta = 9.99$ (s, PN^- , 2 P), 5.46 (d, $J = 196.9$ Hz, $PHPh$, 1 P); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, in ppm) $\delta = 9.98$ (s, PN^- , 2 P), 5.46 (s, $PHPh$, 1 P). Elemental analysis *calc'd* for $C_{63}H_{76}N_2O_1P_3La_1 \cdot 0.20$ KCl (%) C 67.32 H 6.82 N 2.49 found C 66.99 H 6.86 N 2.53. UV/VIS/NIR: $\lambda_{max} = 330$ ($\epsilon = 55620$ L mol $^{-1}$ cm $^{-1}$), 367 ($\epsilon = 57870$ L mol $^{-1}$ cm $^{-1}$), 379 ($\epsilon = 55760$ L mol $^{-1}$ cm $^{-1}$), 392 ($\epsilon = 57580$ L mol $^{-1}$ cm $^{-1}$). IR (cm $^{-1}$): 2957, 2918, 2865, 2291, 1597, 1537, 1462, 1392, 1303, 1280, 1268, 1217, 1196, 1153, 1111, 1051, 927, 880, 857, 815, 794, 782, 739, 729, 710, 694, 663, 621, 543, 486, 467, 433, 414.

Preparation of $(PN)_2La\{OFluoren(PH^tBu)\}$ (2c).

(Note: The product is light-sensitive, therefore the reaction is performed in a brown glass vial) In a 20 mL scintillation vial, $(PN)_2LaPH^tBu$ (200 mg, 220 μ mol, 1 eq.) was dissolved in toluene (8 mL) and cooled down to -40 °C. A solution of **9H-fluoren-9-one** (39.7 mg, 220 μ mol, 1 eq.) in toluene (1 mL) was added and the reaction mixture was allowed to warm up to room temperature and stirred overnight. On the next day the red solution was filtered and all volatile components were removed under reduced pressure. The residue solid was solved in *n*-hexane and filtered again. The solution was concentrated and cooled down to -40 °C for crystallization. Afterwards the solution was removed and the residue was washed with -40 °C cold *n*-hexane to observe a green/grey powder. Single crystals for X-ray determination was obtained from a concentrated solution of $(PN)_2La\{OFluoren(PH^tBu)\}$ in *n*-hexane. Yield: 162 mg (0.15 mmol, 68 %). 1H NMR NMR (C_6D_6 , 400 MHz, in ppm) $\delta = 7.74$ (d, $J = 7.5$ Hz, CH_{Fl} , 1 H), 7.57 (d, $J = 7.6$ Hz, CH_{Fl} , 1 H), 7.44 (dd, $J = 7.5, 3.5$ Hz, CH_{Fl} , 2 H), 7.08 (t, $J = 7.4$ Hz, CH_{Fl} , 2 H), 6.92 – 6.83 (m, CH_{3Ar} , 6 H), 6.81 (s, CH_{Ar} , 2 H), 5.78 (m, CH_{Ar} , 2 H), 4.12 (d, $^1J_{PH} = 190.9$ Hz, $PHC(CH_3)_3$, 1 H), 2.34 (br. s, CH_3 , 12 H), 2.17 (s, CH_3 , 6 H), 2.16 (s, CH_3 , 6 H), 1.24 (s, $CH(CH_3)_2$, 4H), 0.98 (s, $CH(CH_3)_2$, 24 H), 0.53 (d, $^3J_{HP} = 10.9$ Hz, $PHC(CH_3)_3$, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6 , 101 MHz, in ppm) $\delta = 161.4$ (*pseudo-t*, $J = 11.2$ Hz, C_{qAr}), 141.7 (s, C_{qAr}), 138.8 (s, C_{qFl}), 138.6 (s, C_{qFl}), 133.5 (s, CH_{Ar}), 131.3 (s, CH_{Ar}), 127.4 (s, CH_{Fl}), 125.5 (s, CH_{Fl}), 121.9 (s, C_{qAr}), 119.7 (s, CH_{Fl}), 113.0 (*pseudo-t*, $J = 3.9$ Hz, C_{qAr}), 90.7 (d, $J = 12.6$ Hz, C_{qFl}), 30.2 (d, $J = 2.1$ Hz, $PHC(CH_3)_3$, 30.0 (s, CH_{3Ar}), 20.9 (s, CH_{3Ar}), 20.6 (s, CH_{3Ar}), 20.5 (s, CH_{3Ar}); ^{31}P NMR (C_6D_6 , 162 MHz, in ppm) $\delta = 23.58$ (d, $^1J_{PH} = 191.6$ Hz, PH^tBu , 1 P), 9.49 (s, PN^- , 2 P); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, in ppm) $\delta = 23.59$ (s, PH^tBu , 1 P), 9.49 (s, PN^- , 2 P). Elemental analysis *calc'd* for $C_{61}H_{80}N_2O_1P_3La_1 \cdot 0.1$ KCl (%) C 66.81 H 7.35 N 2.55 found C 66.78 H 7.86 N 2.35. UV/VIS/NIR: $\lambda_{max} = 326$ ($\epsilon = 46260$ L mol $^{-1}$ cm $^{-1}$), 379 ($\epsilon = 41880$ L mol $^{-1}$ cm $^{-1}$), 392 ($\epsilon = 43660$ L mol $^{-1}$ cm $^{-1}$). IR (cm $^{-1}$): 2955, 2920, 2865, 2297, 1691, 1599, 1537, 1462, 1390, 1303, 1280, 1252, 1213, 1194, 1156, 1104, 1031, 929, 886, 859, 812, 780, 747, 733, 710, 688, 661, 621, 584, 541, 488, 433, 414.

Preparation of $(PN)_2LaOFluorenyl$ -radical (3).

Complex $(PN)_2La\{OFluoren(PHMes)\}$ (15.6 mg, 13.6 μ mol) was solved in C_6D_6 and was irradiated in a photoreactor (5000k cold white LED) for 2 min, to ensure that the temperature inside the reaction vessel does rise to much (10 °C max). After the NMR cooled to room temperature the irradiation step was repeated. After 36 min almost no educts was left and compound **3** was crystallized from C_6D_6 layered with hexane to observe small black crystals. Yield: 3.4 mg (3.4 μ mol, 25.1 %). μ_{eff} (Evans method, 25 °C, Benzene-*d*₆) = 1.42 μ_B . UV/VIS/NIR: $\lambda_{max} = 321$ ($\epsilon = 26460$ L mol $^{-1}$ cm $^{-1}$), 366 ($\epsilon = 20260$ L mol $^{-1}$ cm $^{-1}$), 443 ($\epsilon = 9420$ L mol $^{-1}$ cm $^{-1}$). IR (cm $^{-1}$): 2950, 2920, 2865, 2272, 1601, 1566, 1494, 1464, 1443, 1401, 1341, 1319, 1305, 1282, 1198, 1153, 1135, 1111, 1080, 1045, 980, 929, 906, 880, 855, 845, 812, 774, 743, 712, 667, 629, 621, 606, 586, 537, 490, 465, 431.

Preparation of $(PN)_2LaOFluorenid$ (4).

In a 20 mL scintillation vial, $(PN)_2LaCl$ (120 mg, 0.14 mmol, 1.0 eq.) was dissolved in toluene (10 mL) and stirred at room temperature. A solution of **lithium 9H-fluoren-9-olate** (26.4 mg, 0.14 mmol, 1.0 eq.) in toluene (2 mL) was added to the mixture. After complete addition the reaction mixture was stirred overnight. On the next day the suspension was filtered through a glass-fibre filter and the filtrate dried under reduced pressure. Afterwards all

volatile components were removed *in vacuo*. The residue was washed twice with – 40 °C cold *n*-hexane (1 mL) and dried *in vacuo* to give **(PN)₂LaOFluorenid** as white solid. Single crystals suitable for X-ray structure determination were obtained from a concentrated solution of **(PN)₂LaOFluorenid** in diethyl ether at – 40 °C. Yield: 107 mg (0.11 mmol, 76 %). ¹H NMR (C₆D₆, 400 MHz, in ppm) δ = 7.58 (br. s, CH_{Fl}, 2 H), 7.50 (d, *J* = 7.5 Hz, CH_{Fl}, 2 H), 7.13 (m, CH_{Ar}, 2 H), (t, ¹J_{HH} = 7.4 Hz, CH_{Ar}, 2 H), 6.91 (s, CH_{Ar}, 4 H), 6.82 (m, CH_{Ar}, 2 H), 6.10 (s, OCH_{Fl}, 1 H), 5.76 (m, CH_{Ar}, 2 H), 2.48 (br.s, CH_{3Ar}, 6 H), 2.18 (s, CH_{3Ar}, 9 H), 2.14 (s, CH_{3Ar}, 9 H), 1.50 – 1.20 (m, 4 H), 0.92-0.69 (br. s, 24 H); ¹³C{¹H} NMR (C₆D₆, 101 MHz, in ppm) δ = 161.3 (t, *J* = 11.3 Hz, C_{qAr}), 140.7 (s, C_{qAr}), 140.1 (s, C_{qAr}), 133.8 (s, CH_{Ar}), 133.6 (s, C_{qAr}), 133.4 (s, C_{qAr}), 131.9 (s, CH_{Ar}), 131.4 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 121.8 (s, C_{qAr}), 119.6 (s, C_{Ar(Fl)}), 113.4 – 113.1 (m, CH_{Ar}), 112.6 (m, CH_{Ar}), 83.9 (s, OCH_{Fl}), 23.8 (s, CH(CH₃)₂), 21.0 (s, CH_{3Ar}), 20.6 (s, CH_{3Ar}), 20.0 (s, CH_{3Ar}), 19.5 (s, CH_{3Ar}), 19.2 (s, CH_{3Pr}); ³¹P NMR (C₆D₆, 162 MHz, in ppm) δ = 9.17 (s, PN[–], 2 P); ³¹P{¹H} NMR (C₆D₆, 162 MHz, in ppm) δ = 9.17 (s, PN[–], 2 P). Elemental analysis *calc'd* for C₅₇H₇₁LaN₂OP₂ · LiCl · Et₂O (%) C 65.56, H 7.31, N 2.51; found: C 65.51, H 7.70, N 2.35. UV/VIS/NIR: λ_{max} = 311 (ϵ = 31960 L mol^{–1} cm^{–1}), 328 (ϵ = 22560 L mol^{–1} cm^{–1}). IR (cm^{–1}): 2950, 2922, 2865, 1605, 1494, 1466, 1452, 1392, 1305, 1266, 1188, 1156, 1100, 1033, 943, 880, 855, 815, 770, 739, 659, 623, 606, 580, 514, 449, 410.

Irradiation experiments:

In a J. Young NMR tube, **2a-c** (1 eq.) was dissolved in C₆D₆ (600 μ L) and triphenylphosphine (1 eq.) was added as an internal standard. The reaction was then irradiated in a photoreactor equipped with 5000 K cold-white LEDs for 2 min followed by measuring ¹H, ³¹P and ³¹P{¹H} NMR. This step was repeated as long as reactants were still present (time depending on substrate).

X-ray Crystallography

Single crystals for X-ray diffraction experiments were measured at the analytical facility of the University of Innsbruck using a Bruker D8 Quest instrument. All crystals were kept at 153(2) K throughout data collection. Data collection was performed using the APEXIV software package. Data refinement and reduction were performed with Bruker Saint (V8.34A). All structures were solved with SHELXT^{2,3} and refined using the OLEX 2 software package.⁴ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model. All structures have been submitted to the CCDC and can be obtained under the numbers presented in Table S1. For further crystallographic details regarding crystal measurements, please check Tables S1 and S2.

2. NMR Spectra

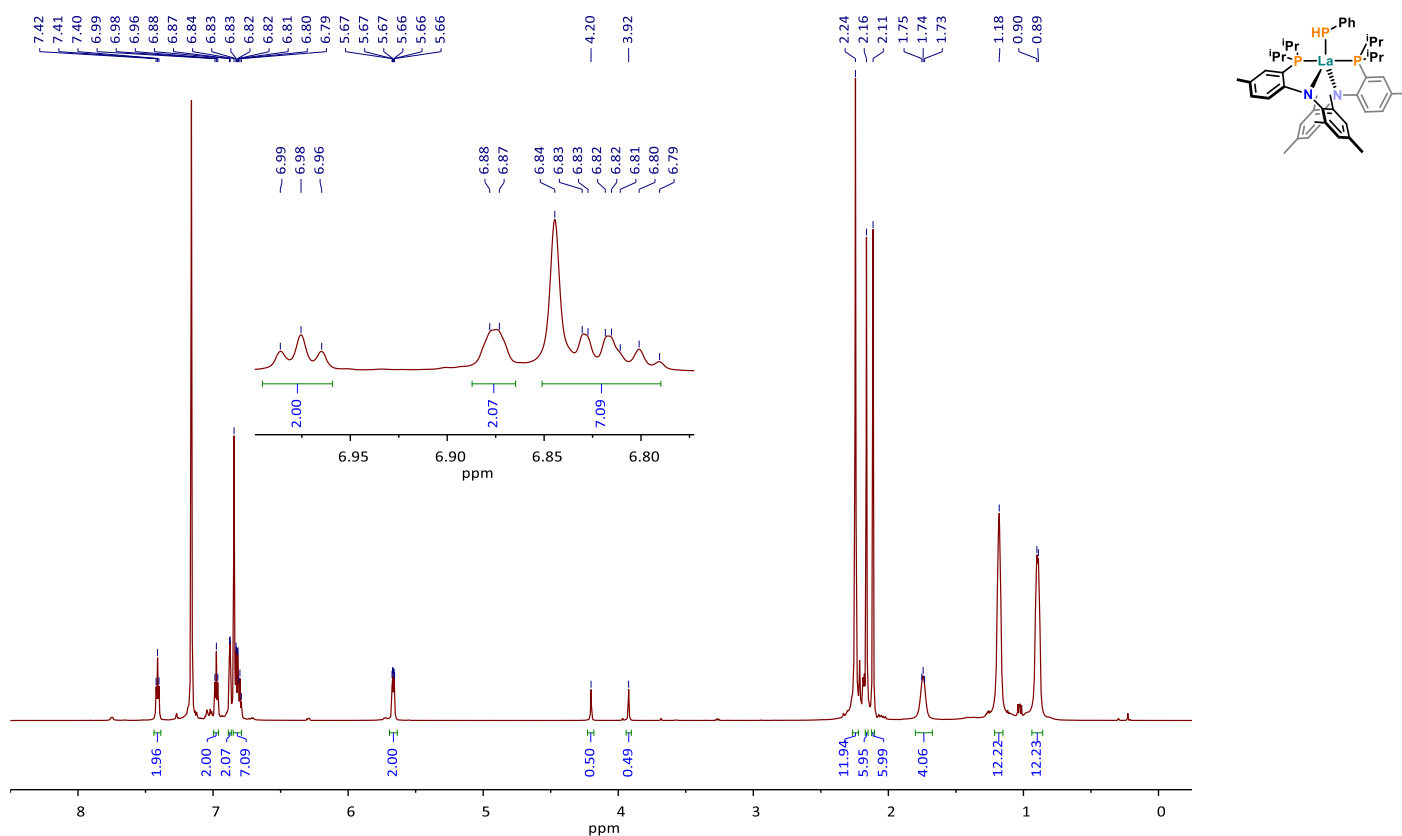


Figure S 1: ^1H NMR spectrum of **1b** in C_6D_6 (303 K). The enlargement shows the crowded resonances in the aromatic region. Traces of toluene from work-up are marked by *.

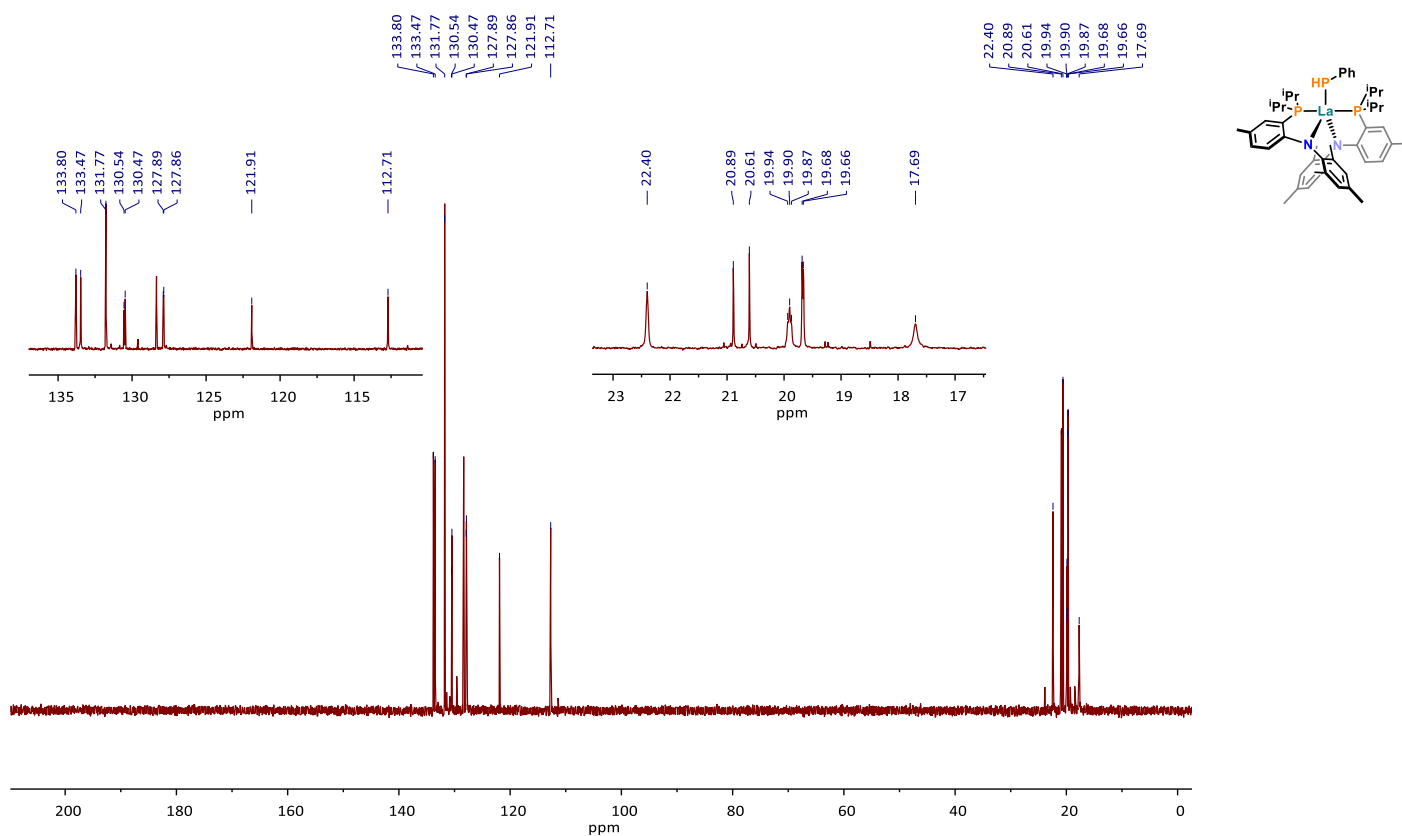


Figure S 2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1b** in C_6D_6 (303 K). The peak listing is given in the three enlargements of the relevant aromatic and aliphatic regions of the spectrum.

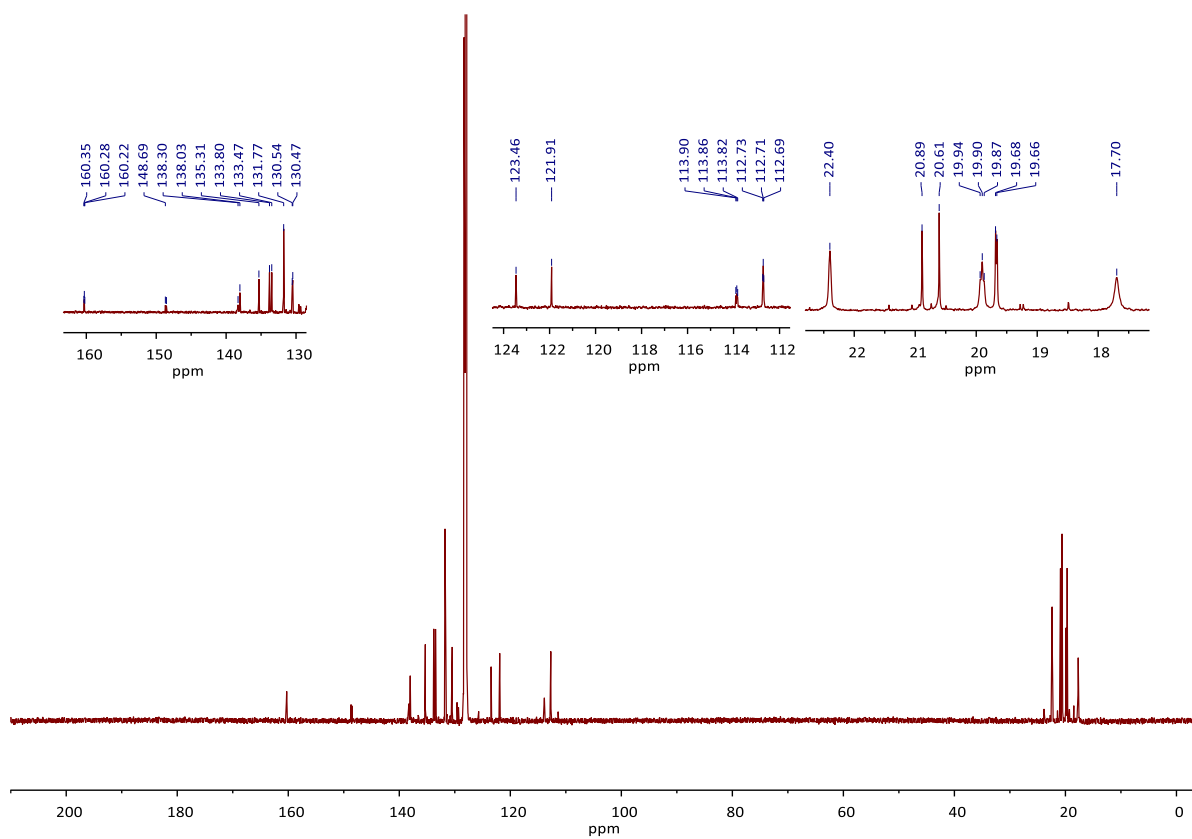


Figure S 3: $^{13}\text{C}\{^1\text{H}\}$ DEPT135 NMR spectrum of **1b** in C₆D₆ (303 K). The two enlargements show the resonances in the aromatic and aliphatic region.

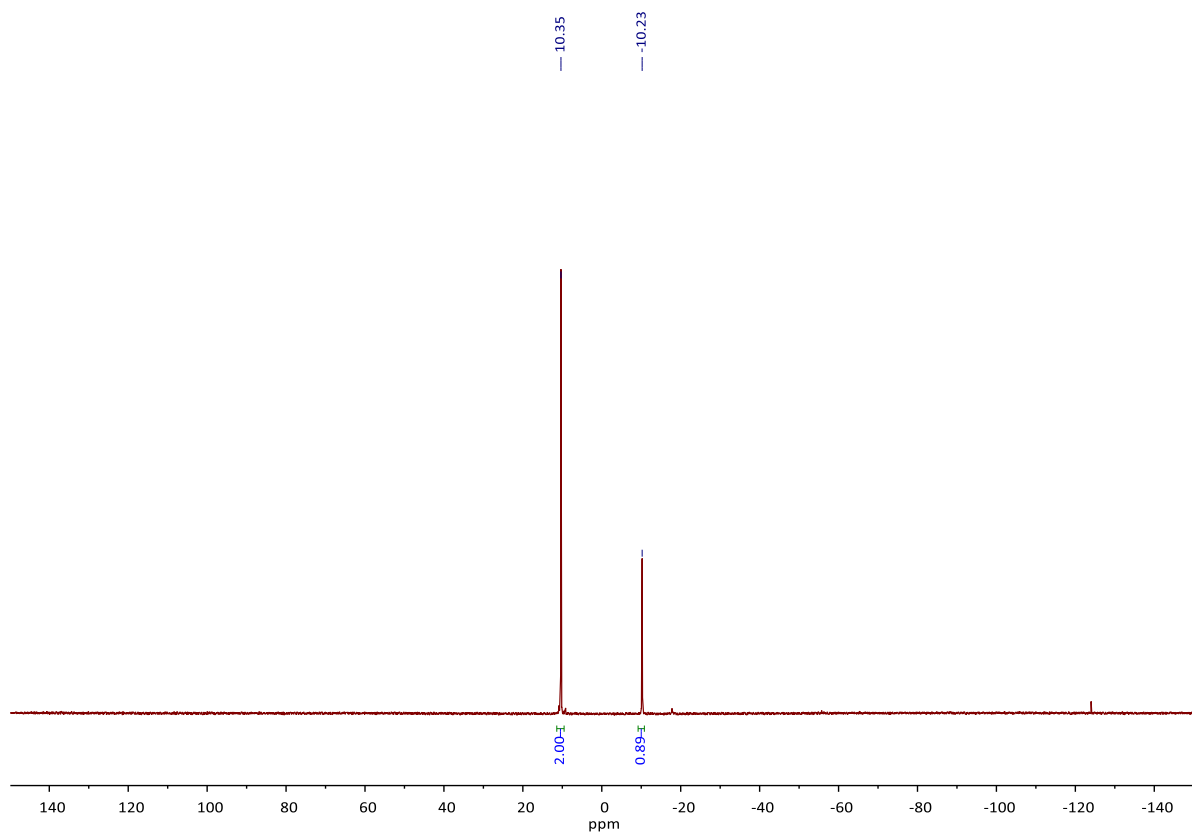


Figure S 4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1b** in C₆D₆ (303 K).

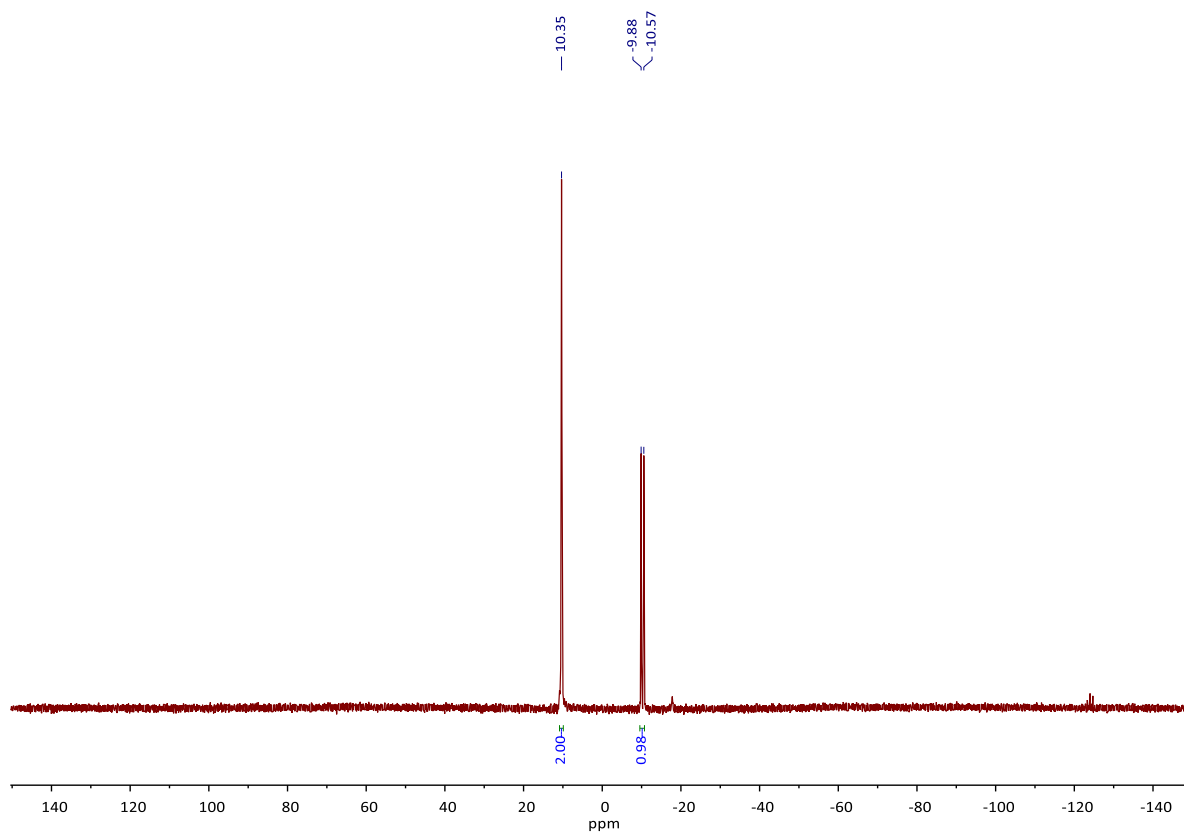


Figure S 5: ^{31}P NMR spectrum of **1b** in C_6D_6 (303 K).

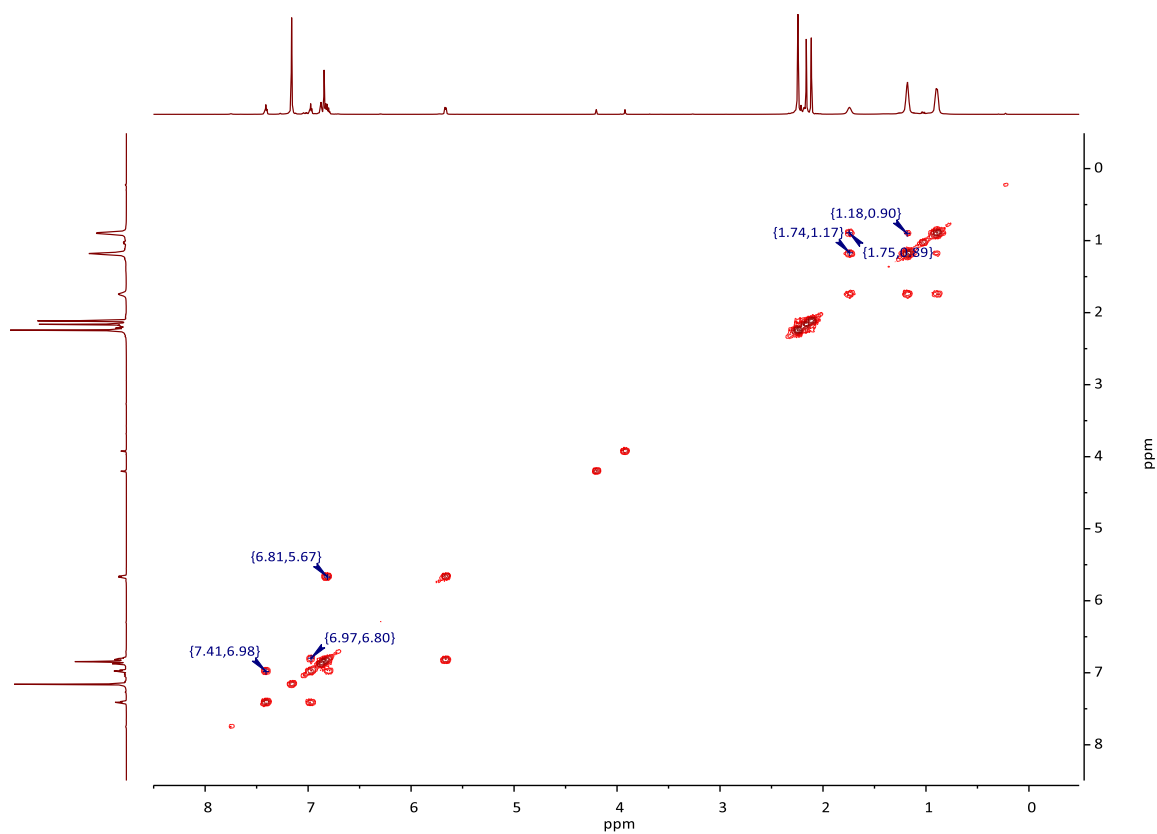


Figure S 6: ^1H - ^1H COSY NMR spectrum of **1b** in C_6D_6 (303 K).

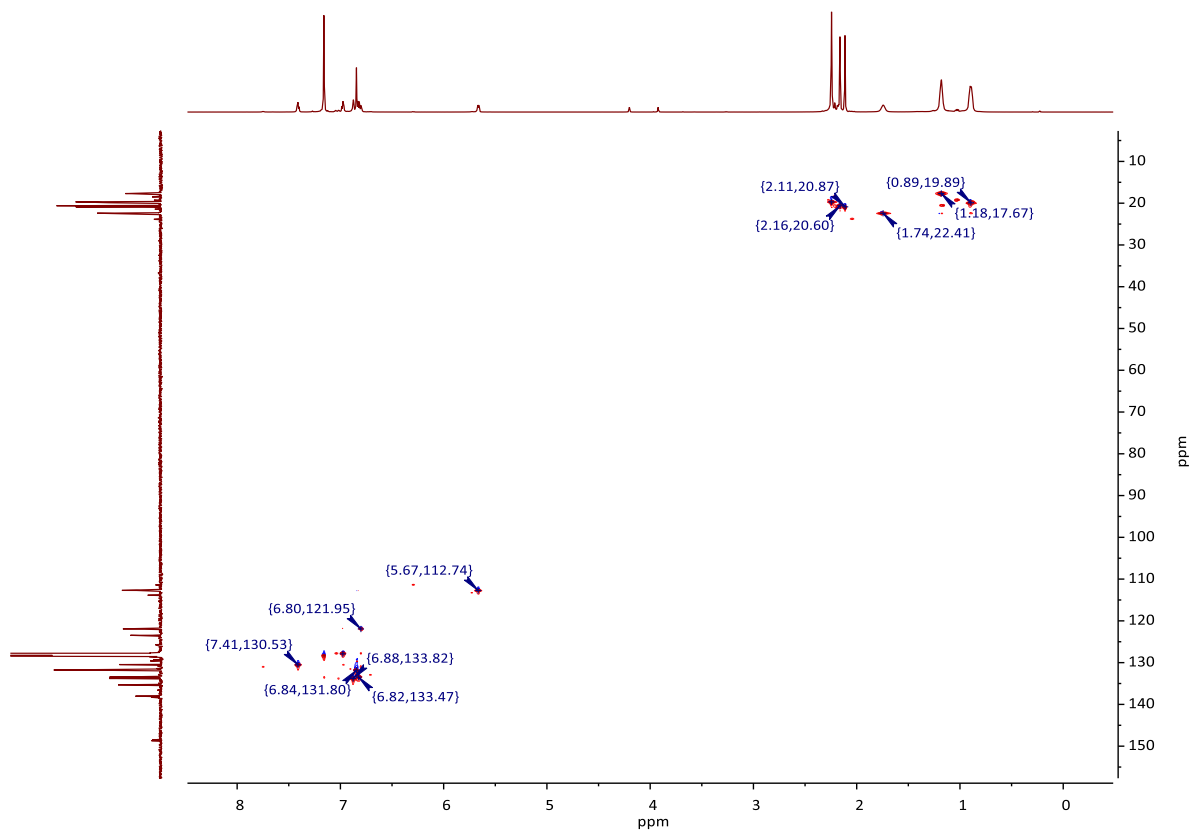


Figure S 7: ^1H - ^{13}C HSQC NMR spectrum of **1b** in C_6D_6 (303 K).

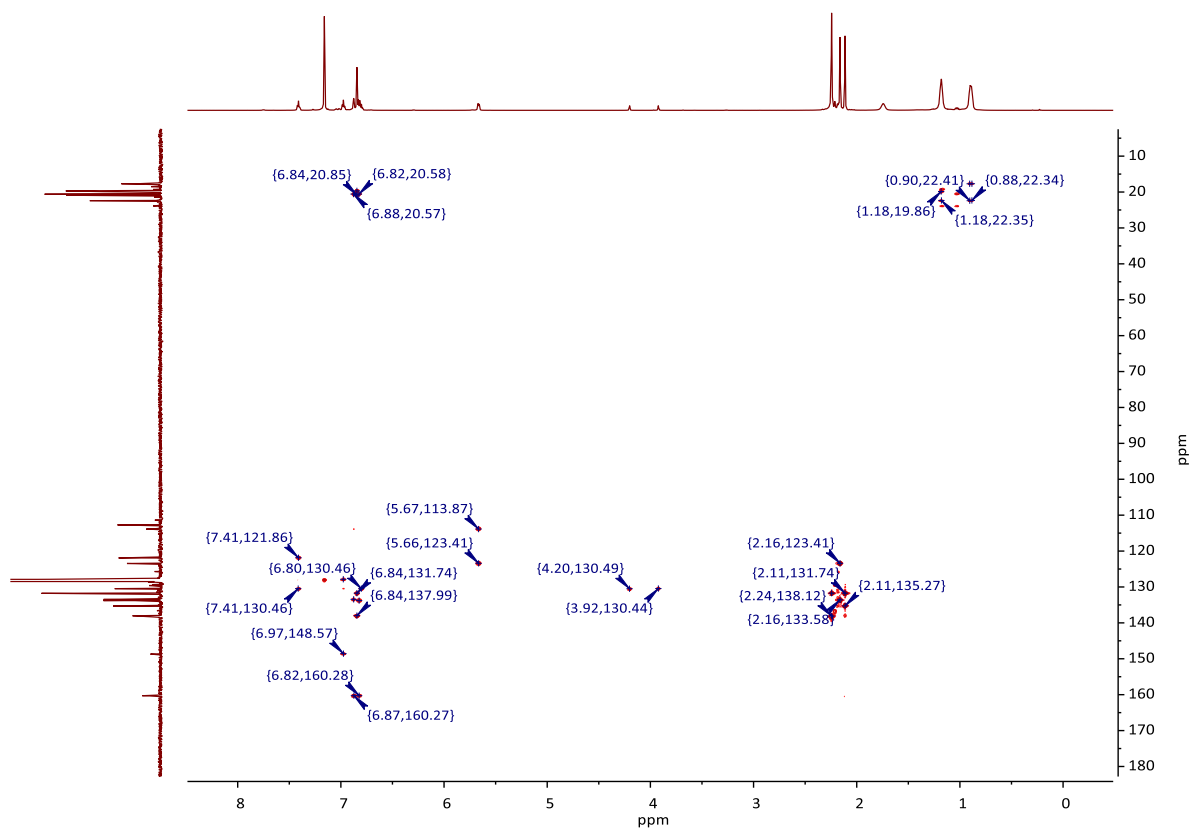


Figure S 8: ^1H - ^{13}C HMBC NMR spectrum of **1b** in C_6D_6 (303 K).

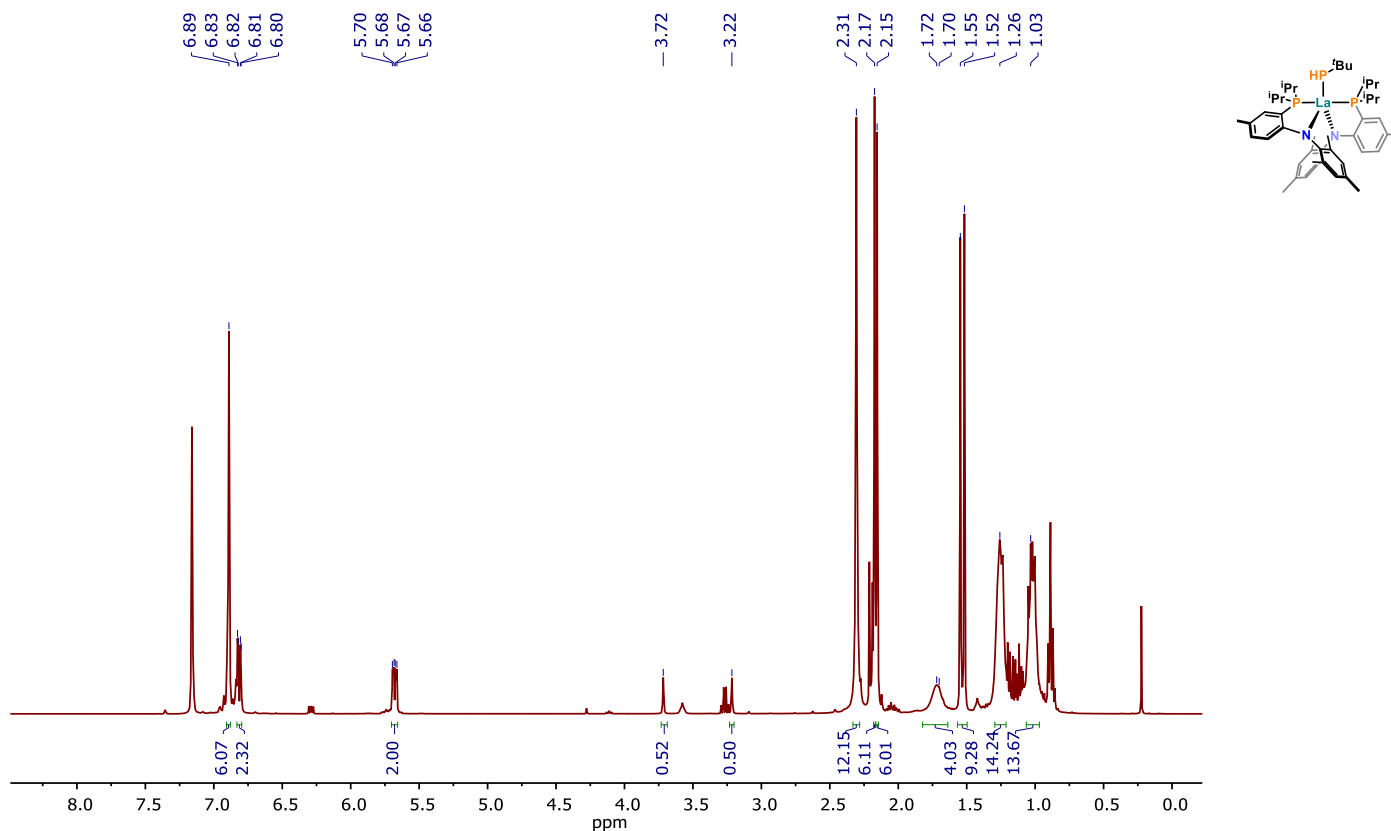


Figure S 9: ¹H NMR spectrum of 1c in C₆D₆ (303 K).

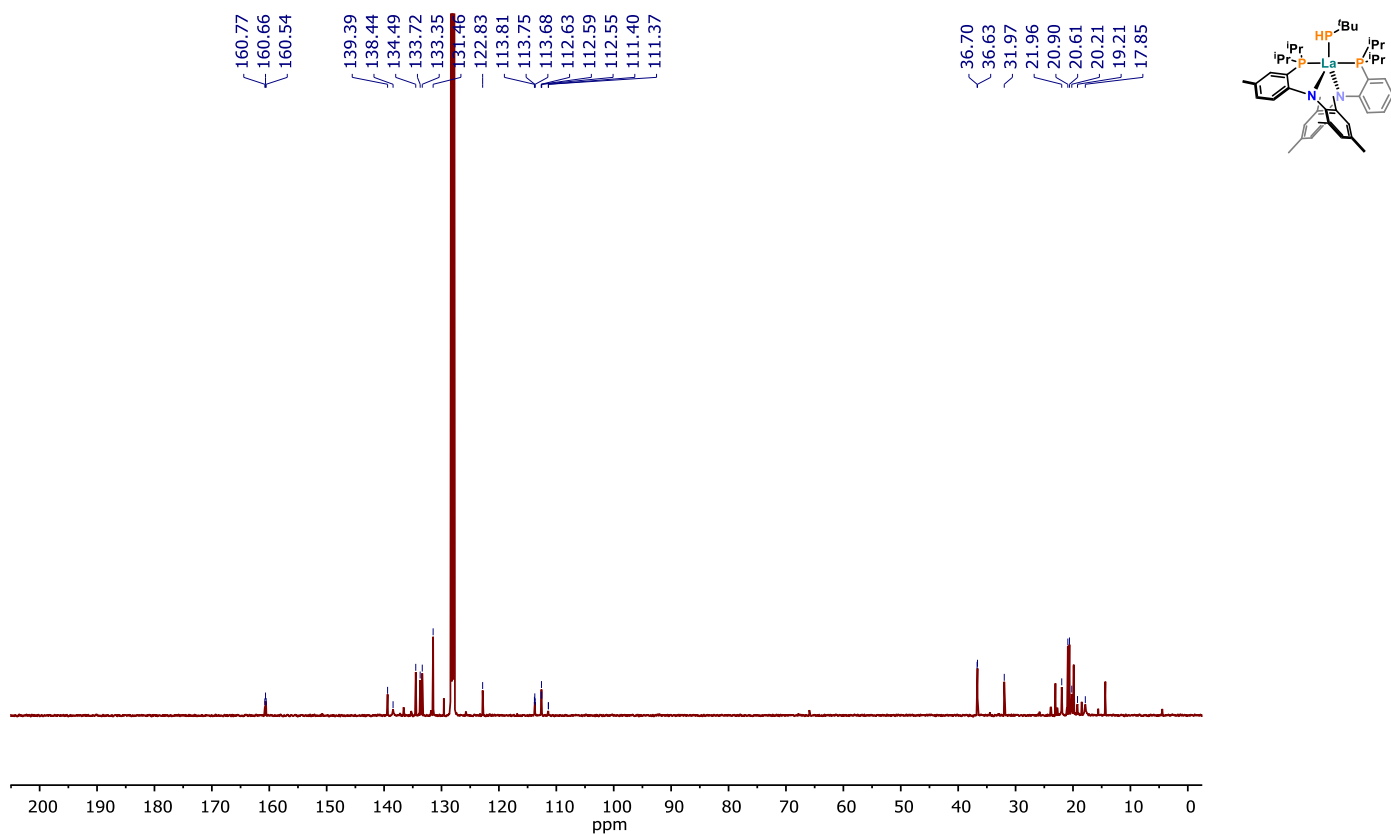


Figure S 10: ¹³C{¹H} NMR spectrum of 1c in C₆D₆ (303 K).

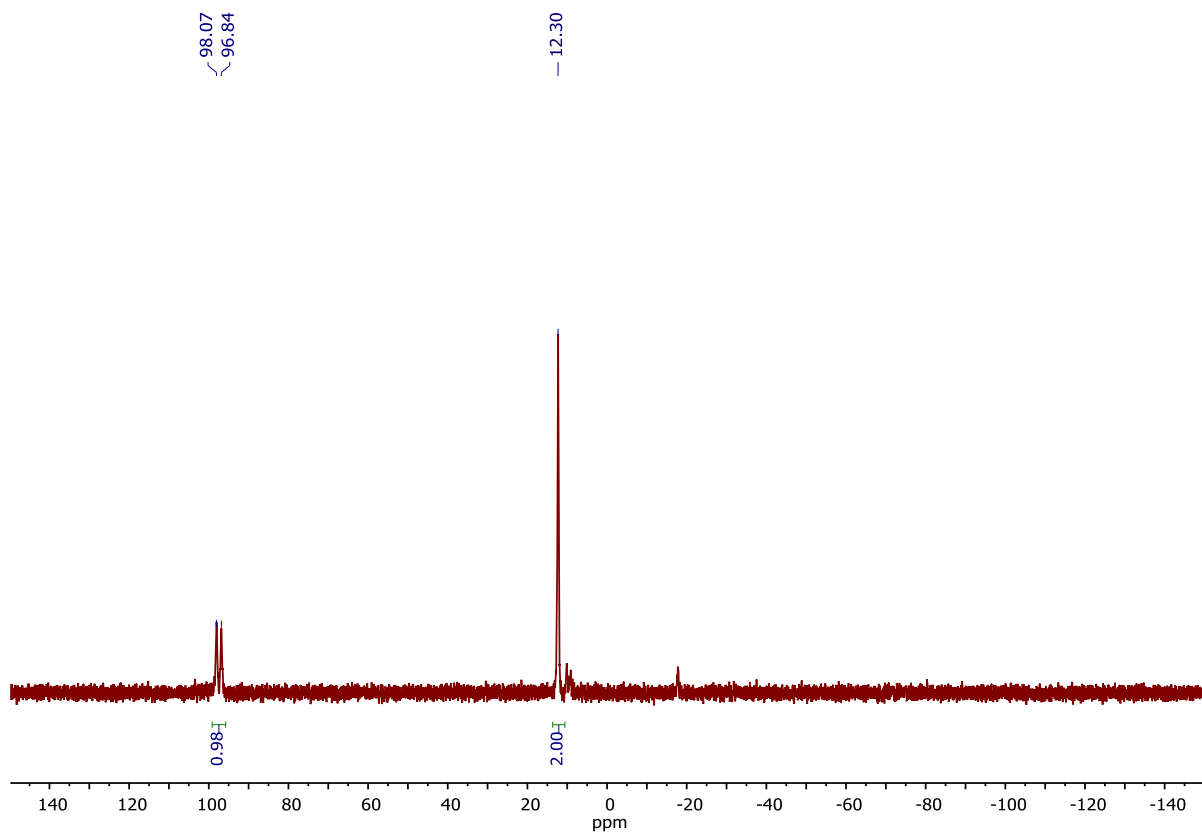


Figure S 11: ³¹P NMR of **1c** in C₆D₆ (303 K).

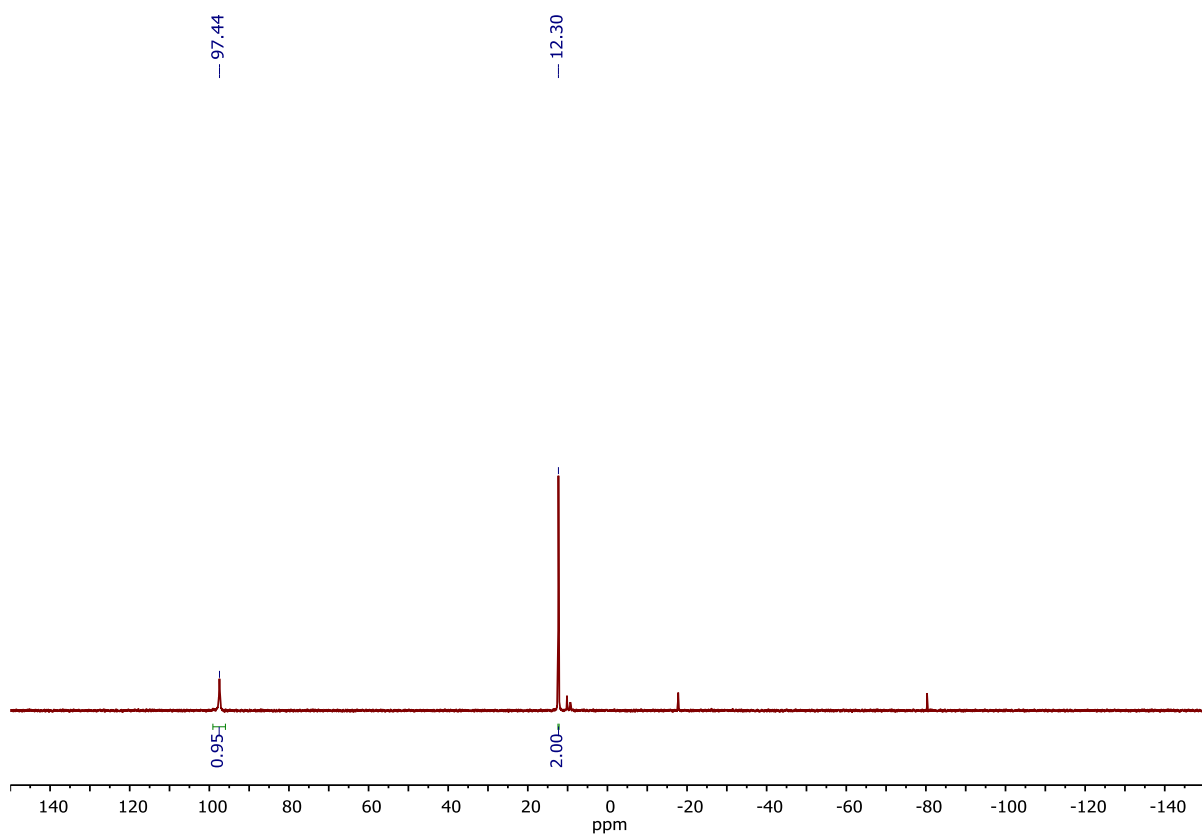


Figure S 12: ³¹P{¹H} NMR of **1c** in C₆D₆ (303 K).

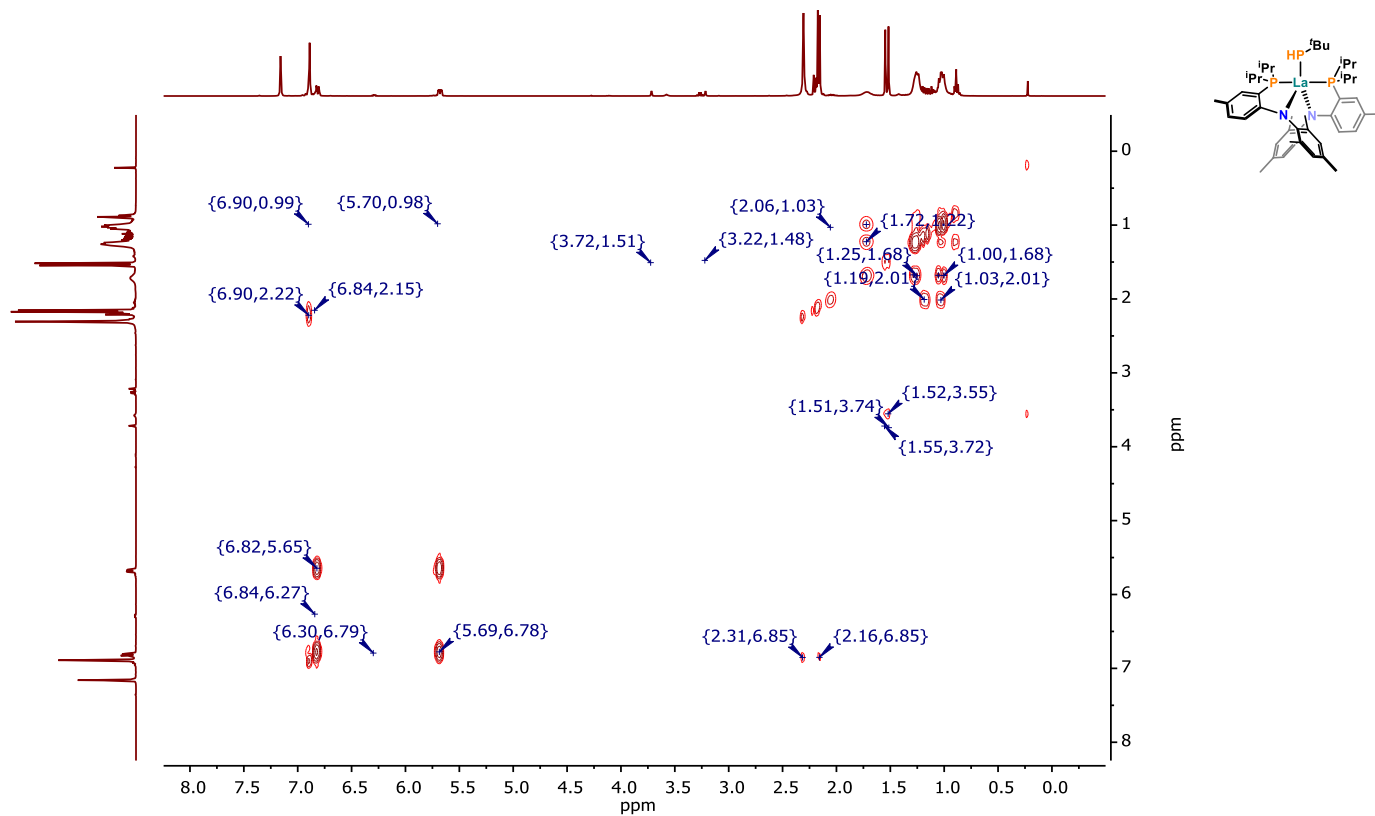


Figure S 13: ^1H - ^1H COSY NMR spectrum of **1c** in C_6D_6 (303 K).

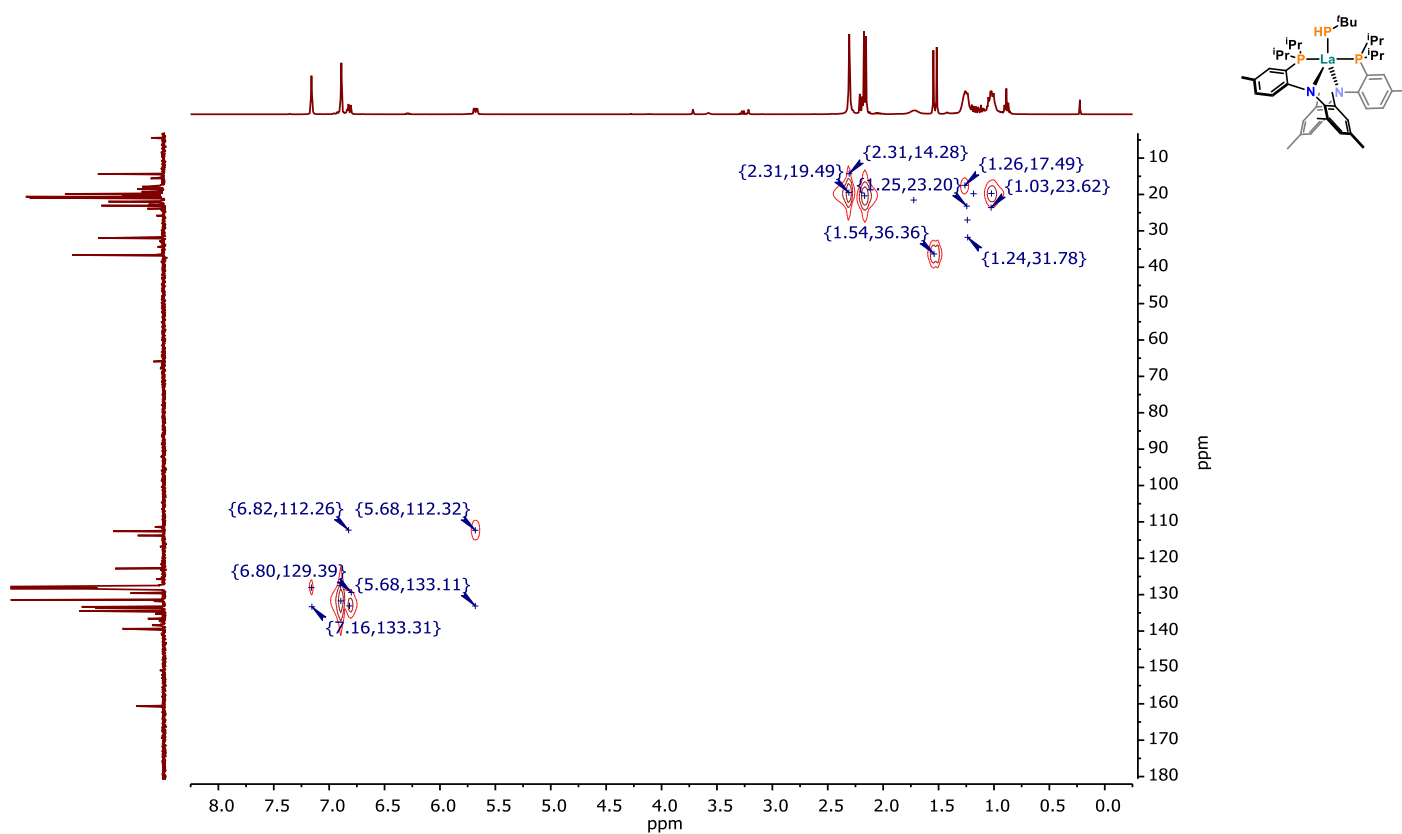


Figure S 14: ^1H - ^{13}C HMBC NMR spectrum of **1c** in C_6D_6 (303 K).

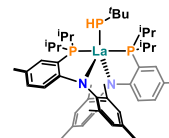
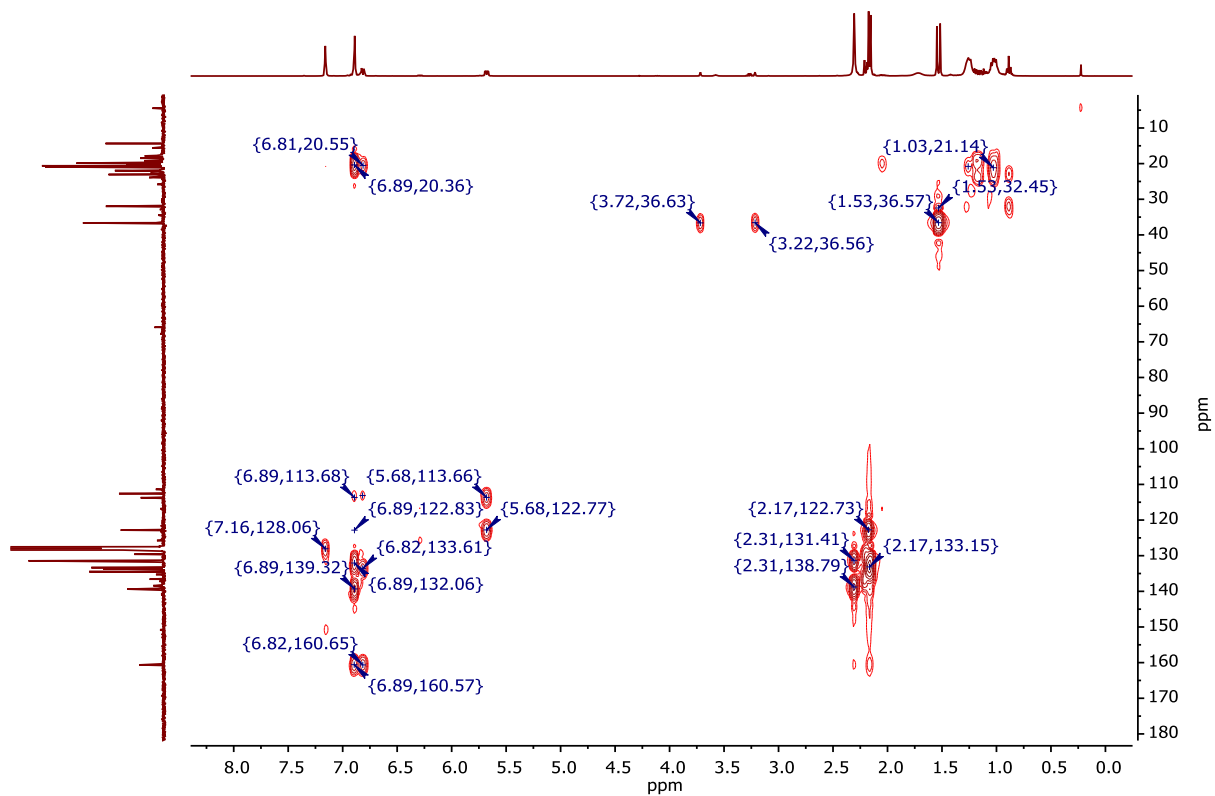


Figure S 15: ^1H - ^{13}C HMBC NMR spectrum of **1c** in C_6D_6 (303 K).

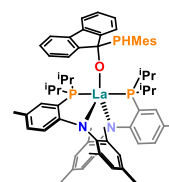
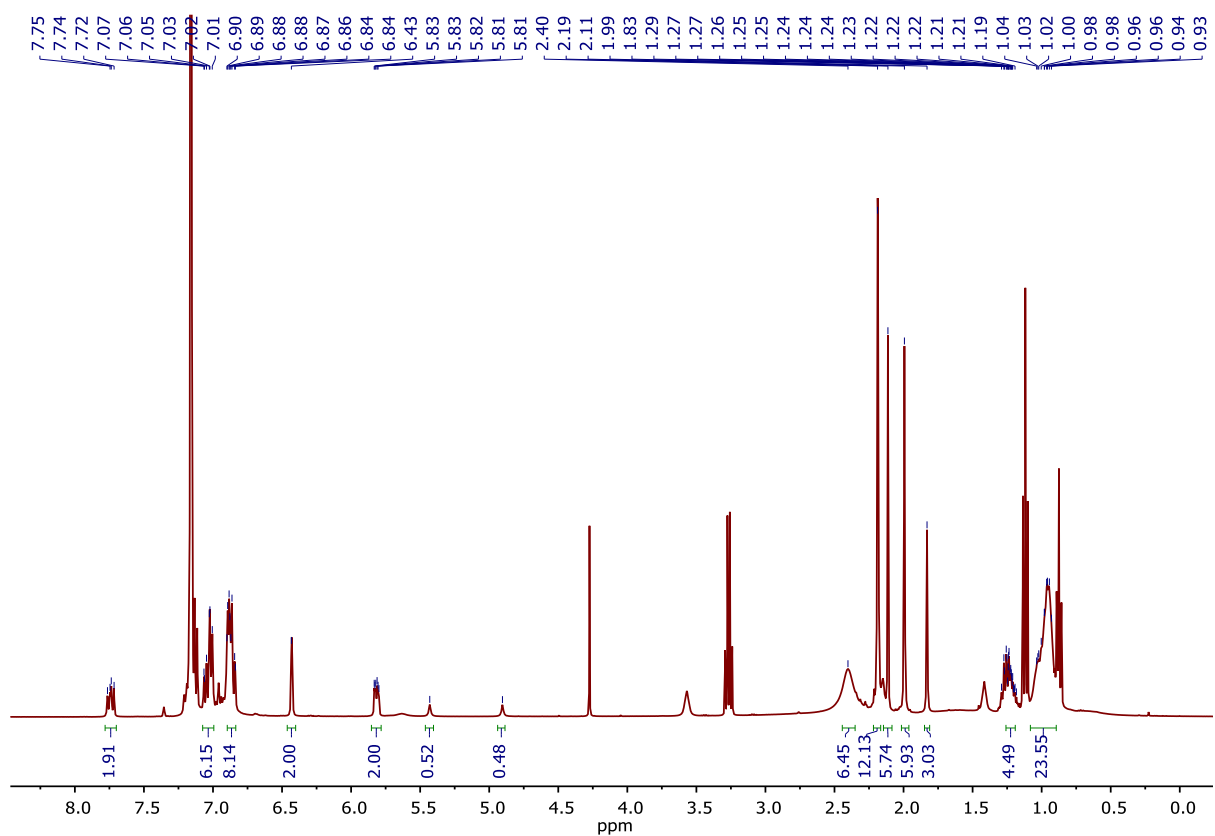


Figure S 16: ^1H NMR spectrum of **2a** in C_6D_6 (303 K).

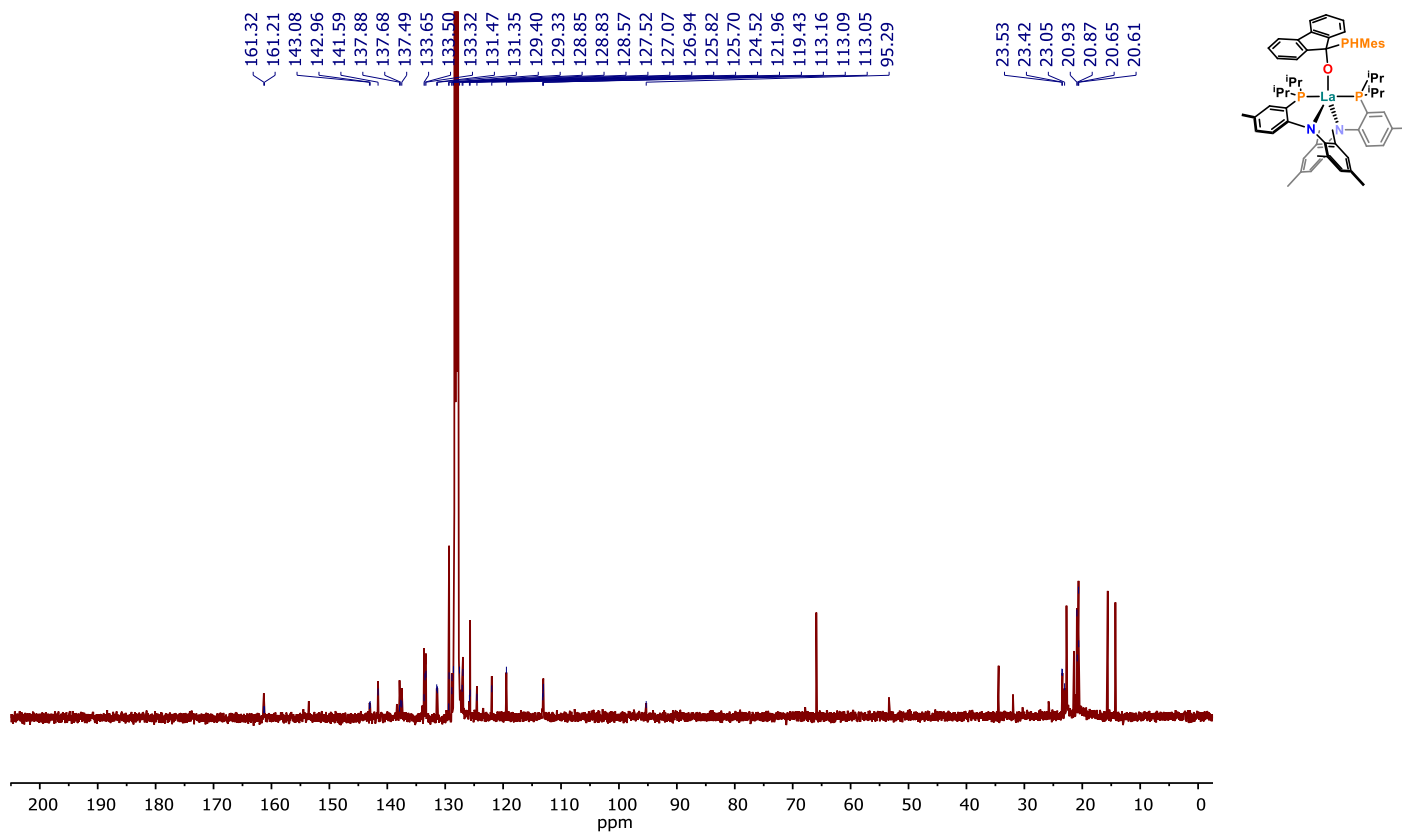


Figure S 17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** in C_6D_6 (303K).

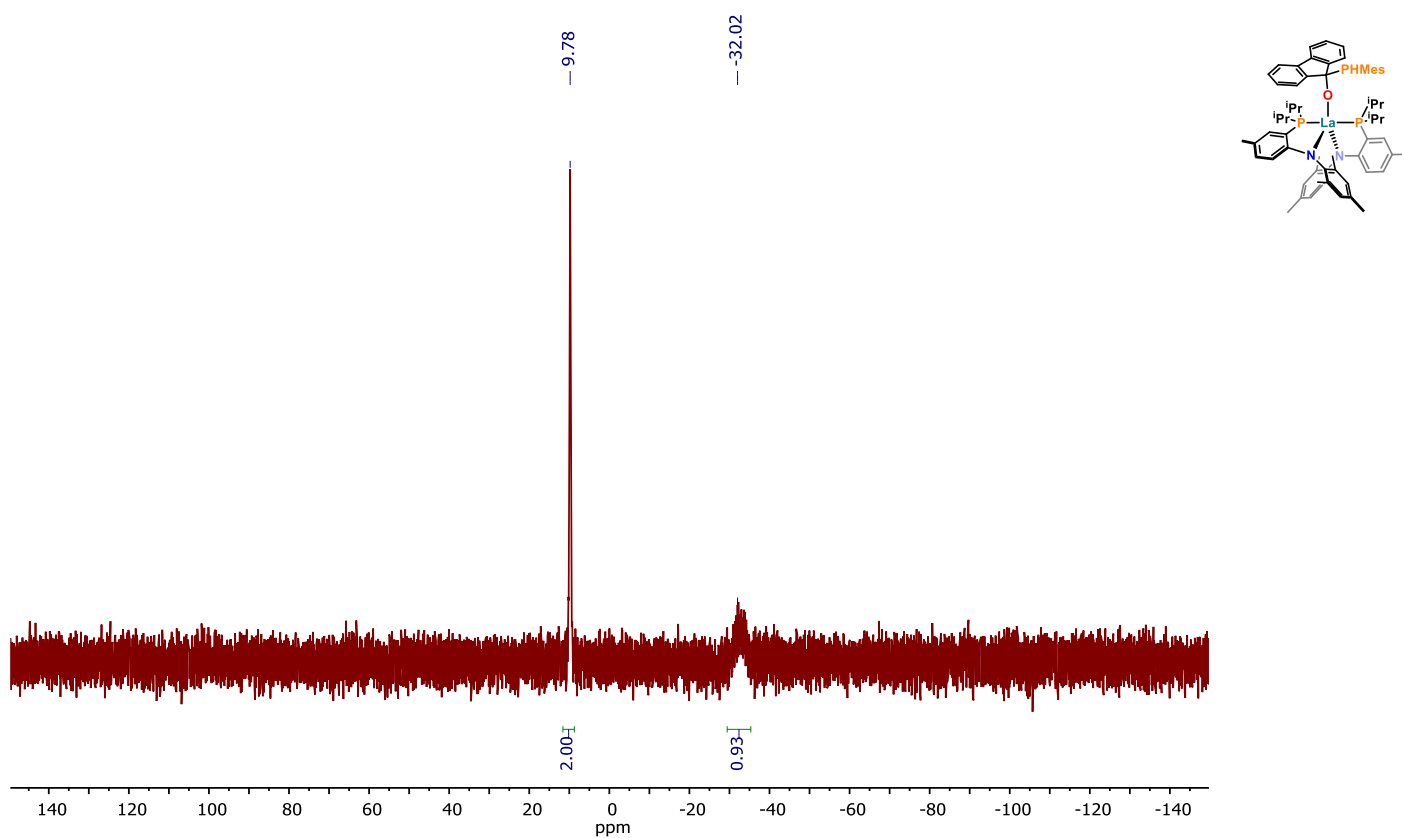


Figure S 18: ^{31}P NMR spectrum of **2a** in C_6D_6 (303 K).

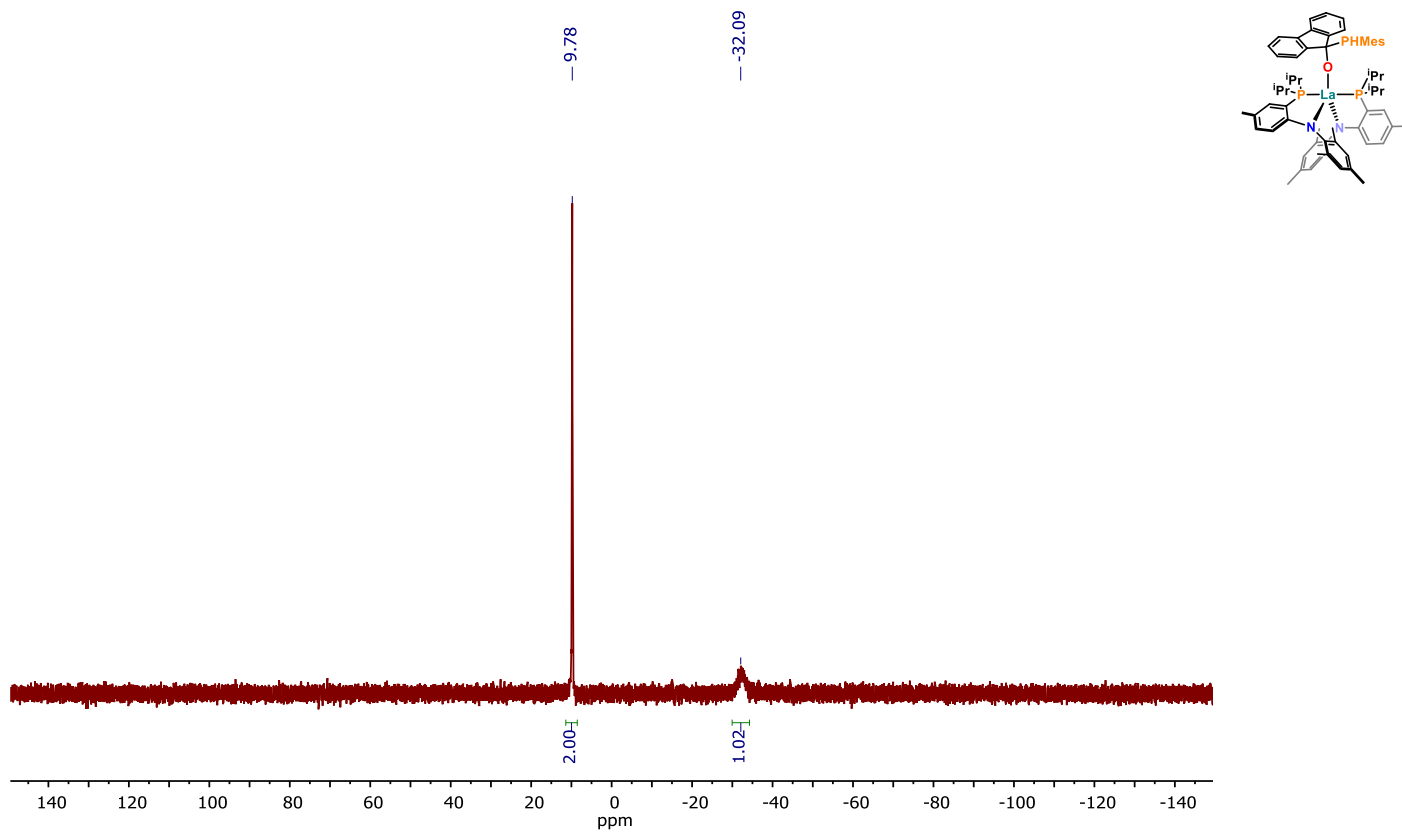


Figure S 19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** in C_6D_6 (303 K).

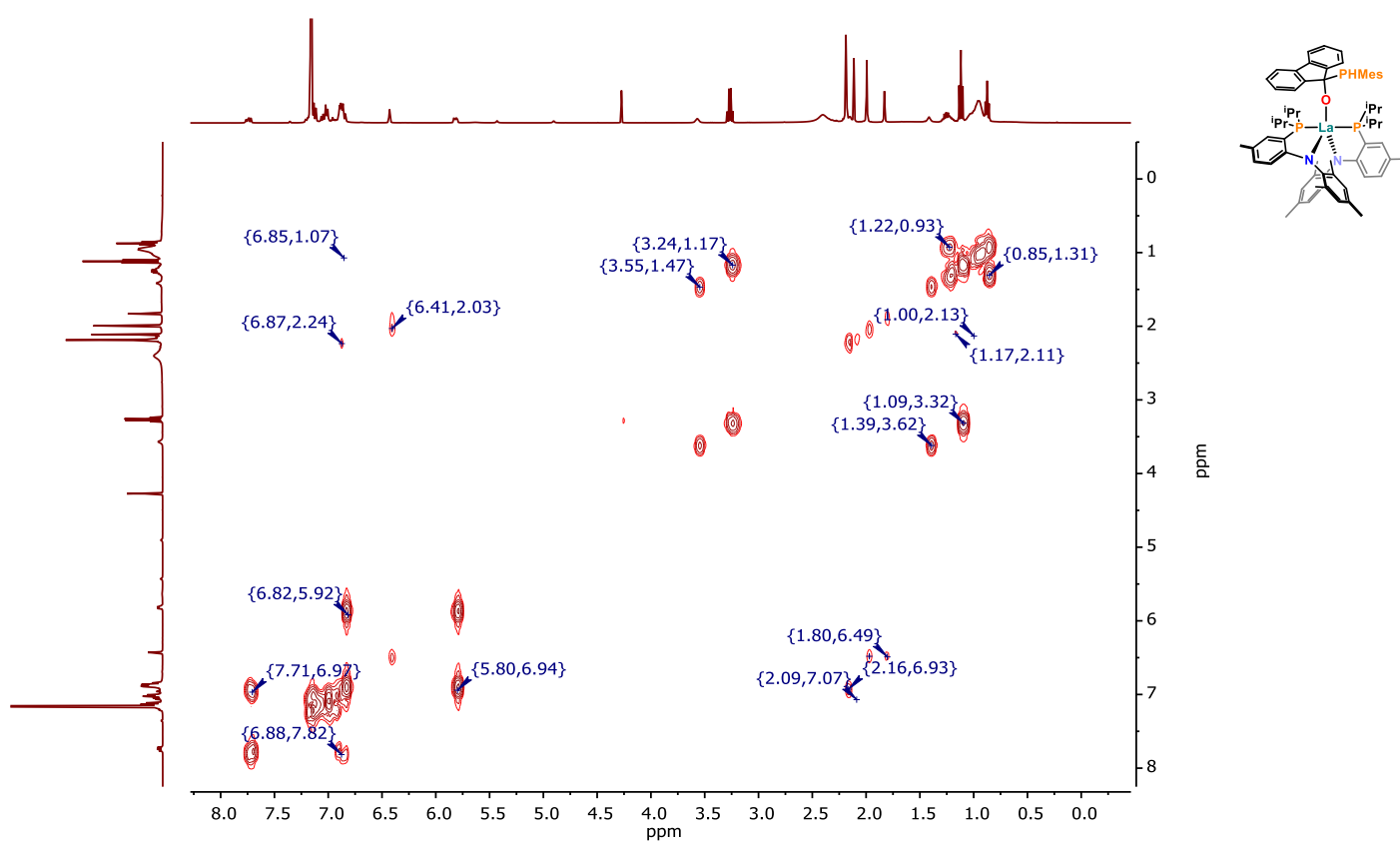


Figure S 20: $^1\text{H}-^1\text{H}$ COSY NMR spectrum of **2a** in C_6D_6 (303 K).

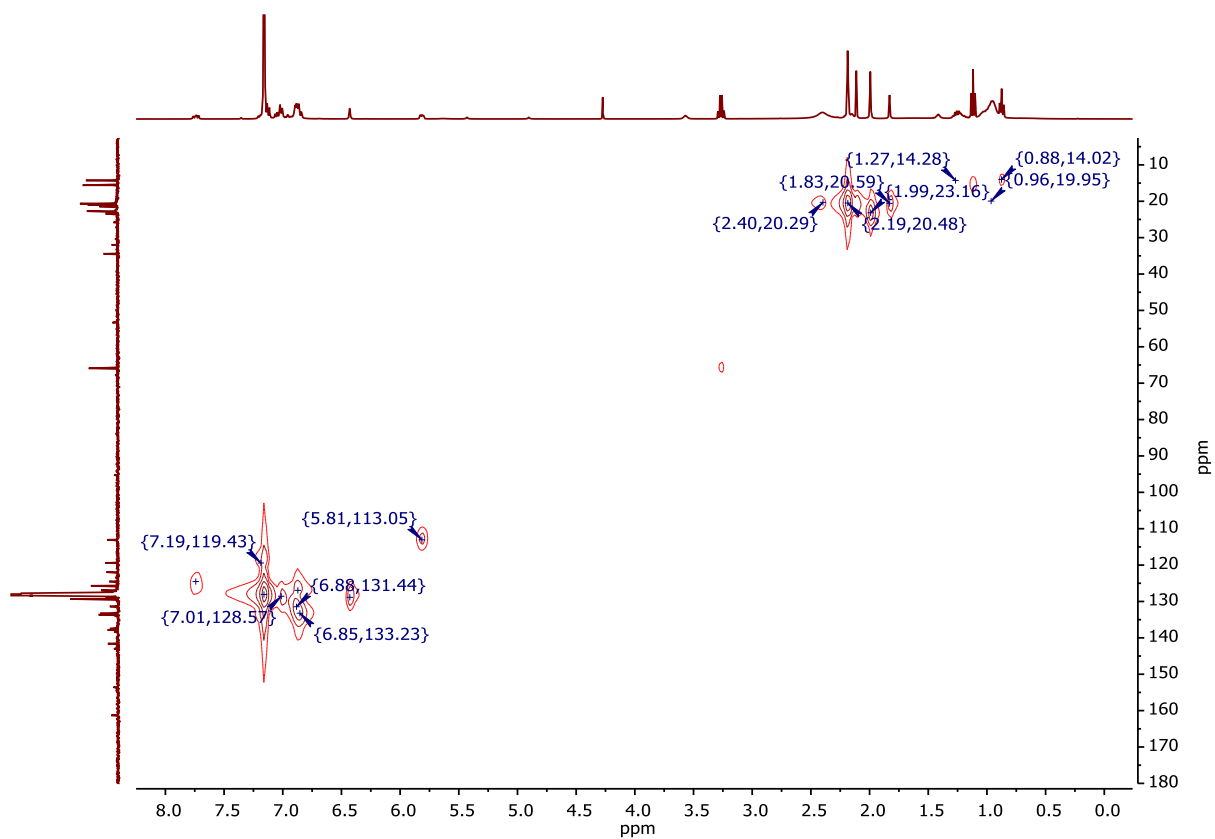


Figure S 21: ^1H - ^{13}C HSQC NMR spectrum of **2a** in C_6D_6 (303 K).

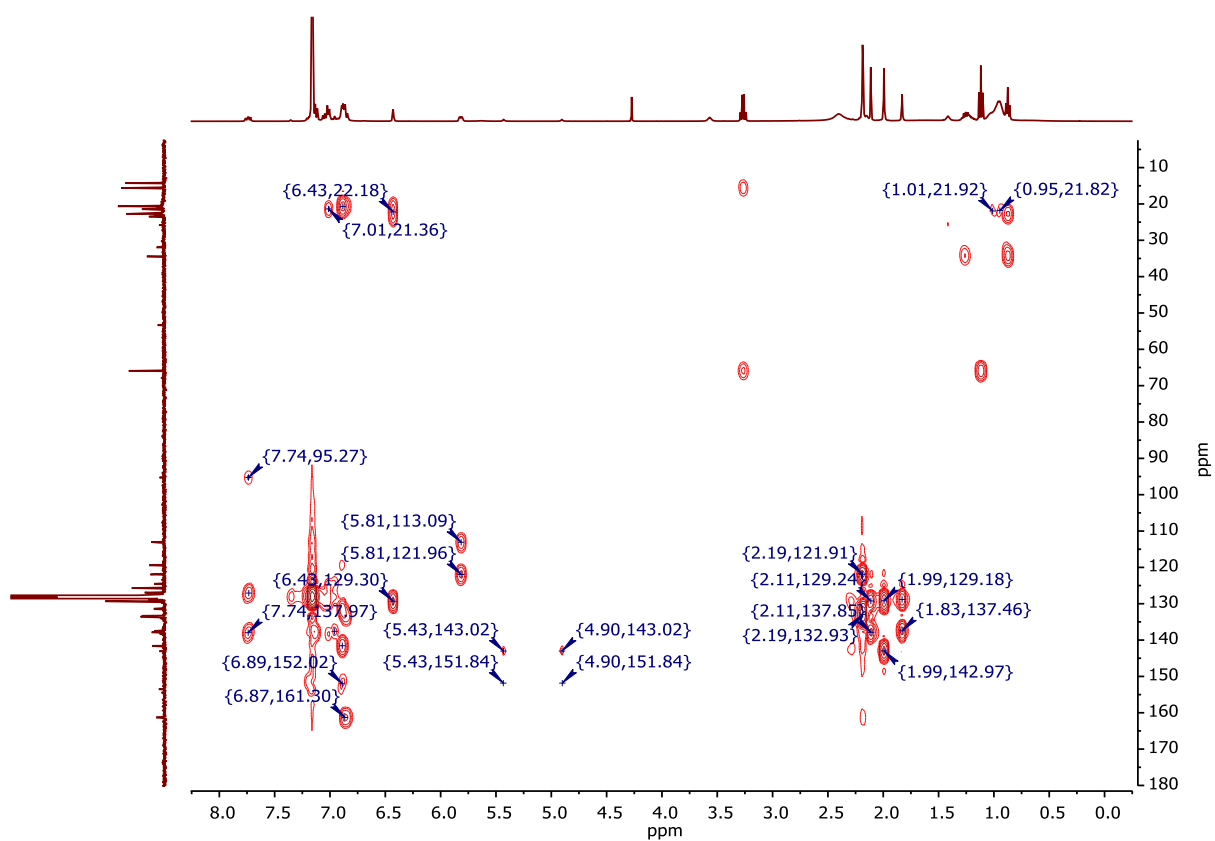
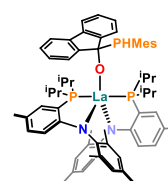
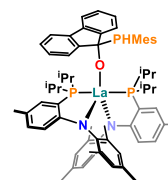


Figure S 22: ^1H - ^{13}C HMBC NMR spectrum of **2a** in C_6D_6 (303 K).



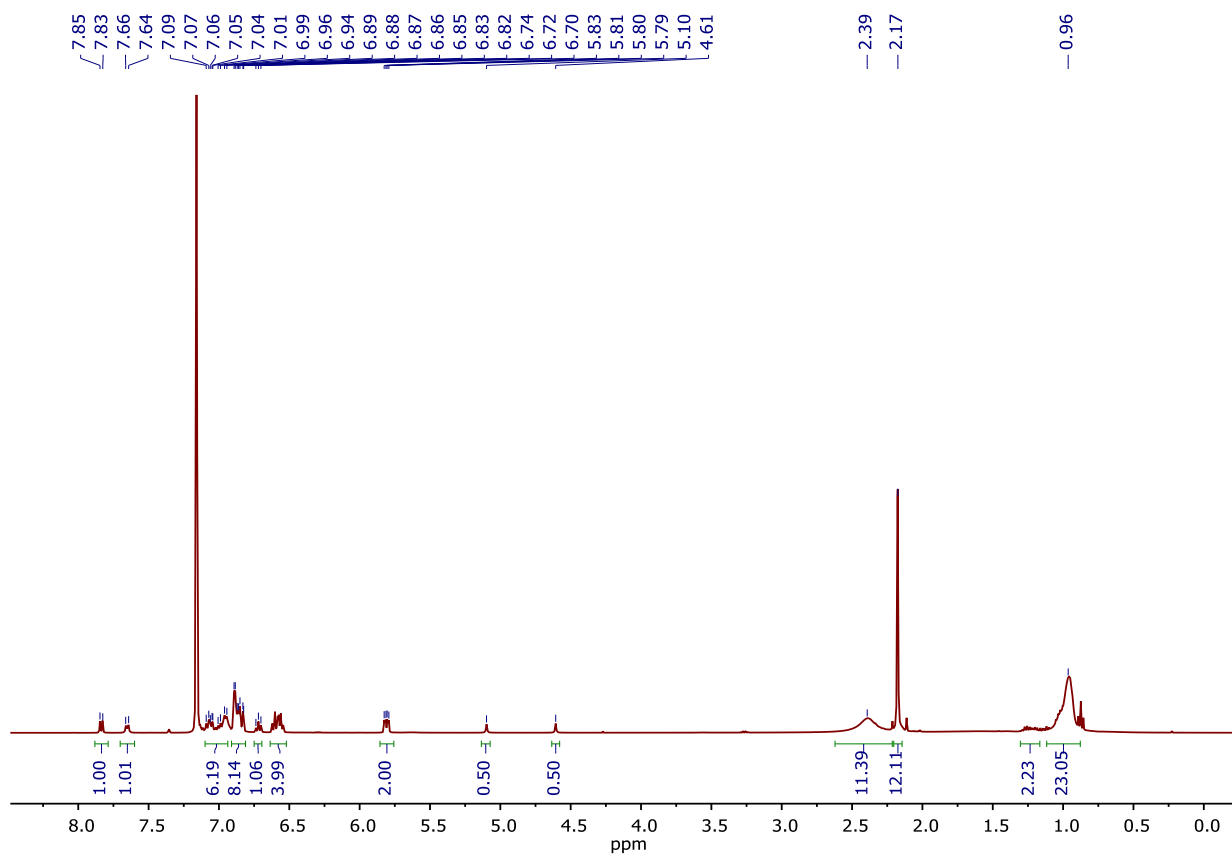


Figure S 23: ^1H NMR of **2b** in C_6D_6 (303 K).

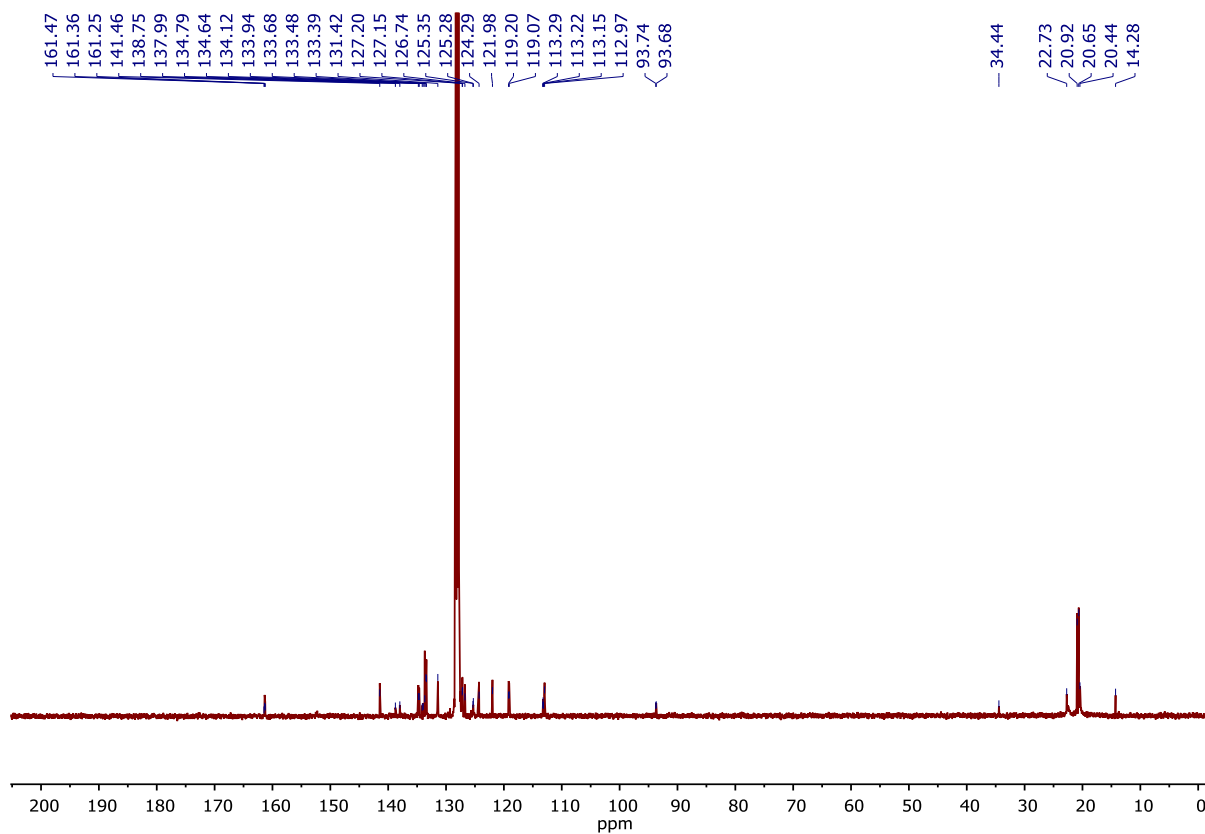


Figure S 24: $^{13}\text{C}\{^1\text{H}\}$ NMR of **2b** in C_6D_6 (303 K).

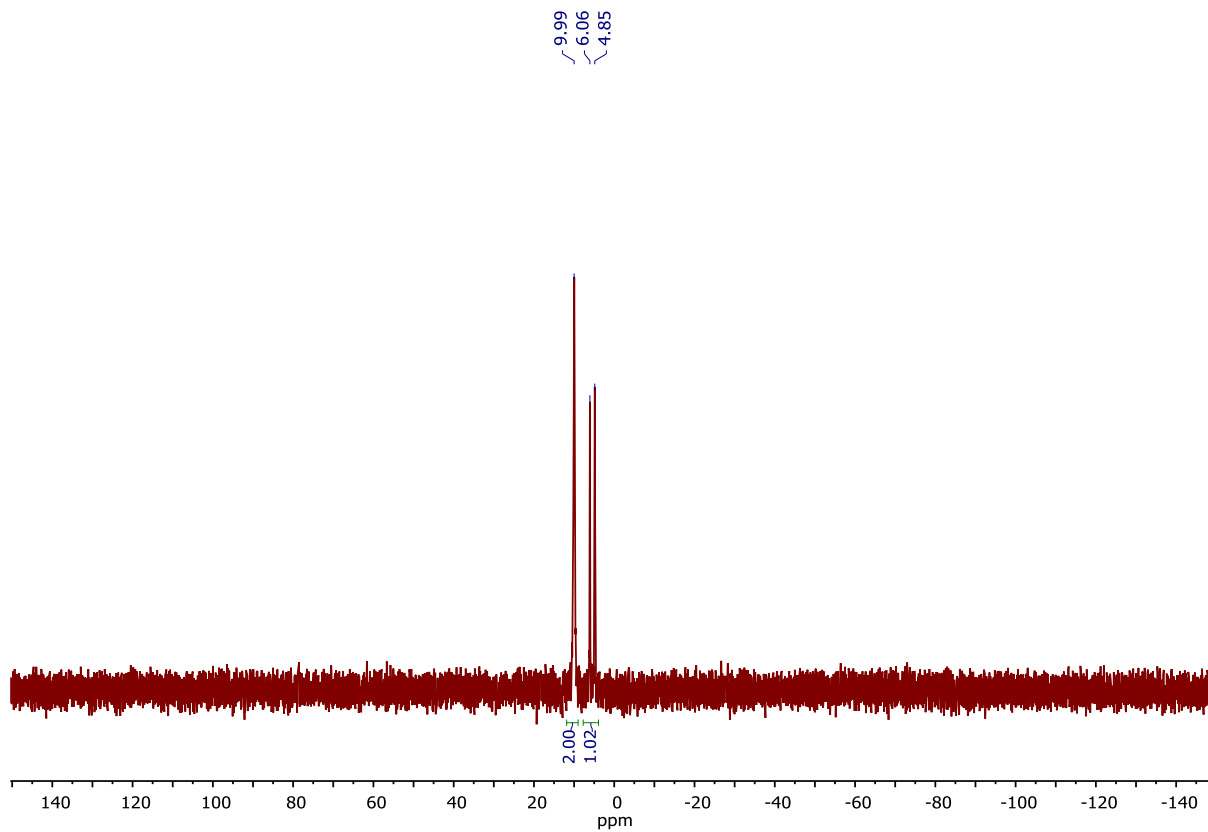


Figure S 25: ^{31}P NMR of **2b** in C_6D_6 (303 K).

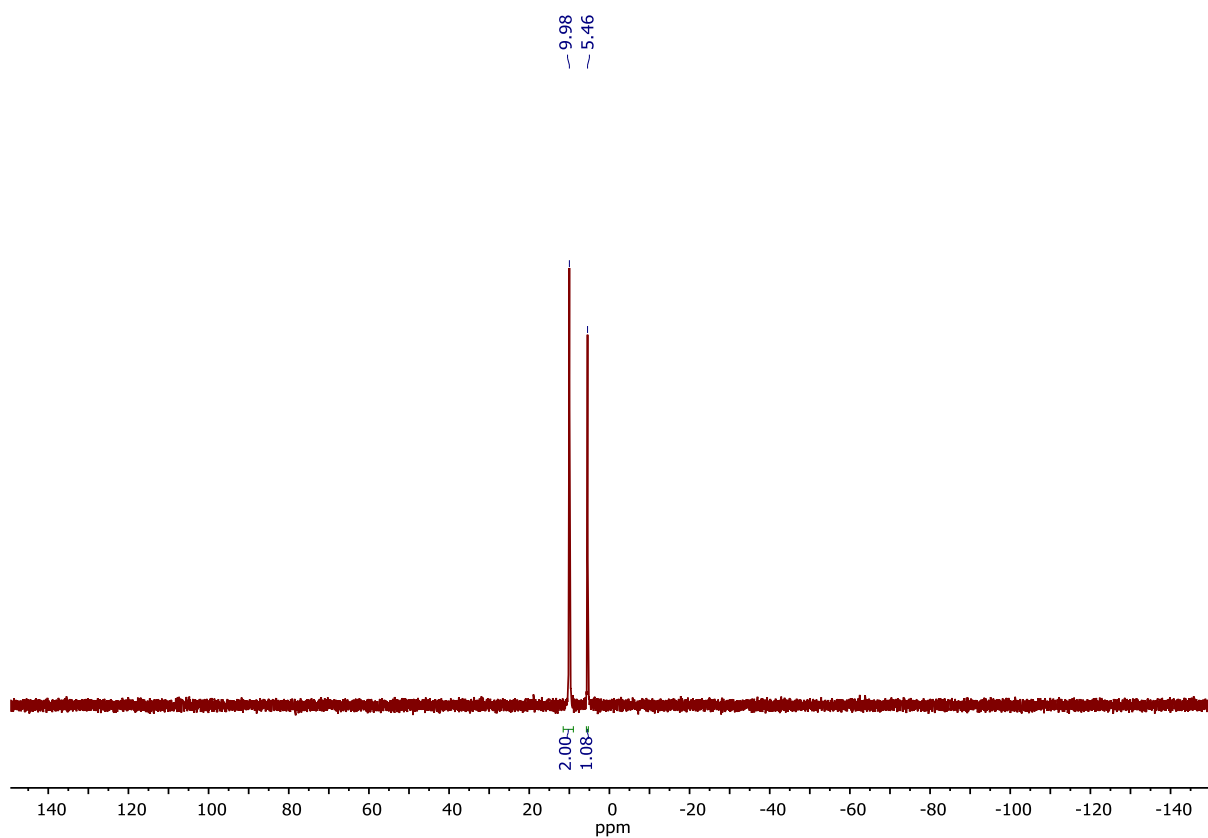


Figure S 26: $^{31}\text{P}\{^1\text{H}\}$ NMR of **2b** in C_6D_6 (303 K).

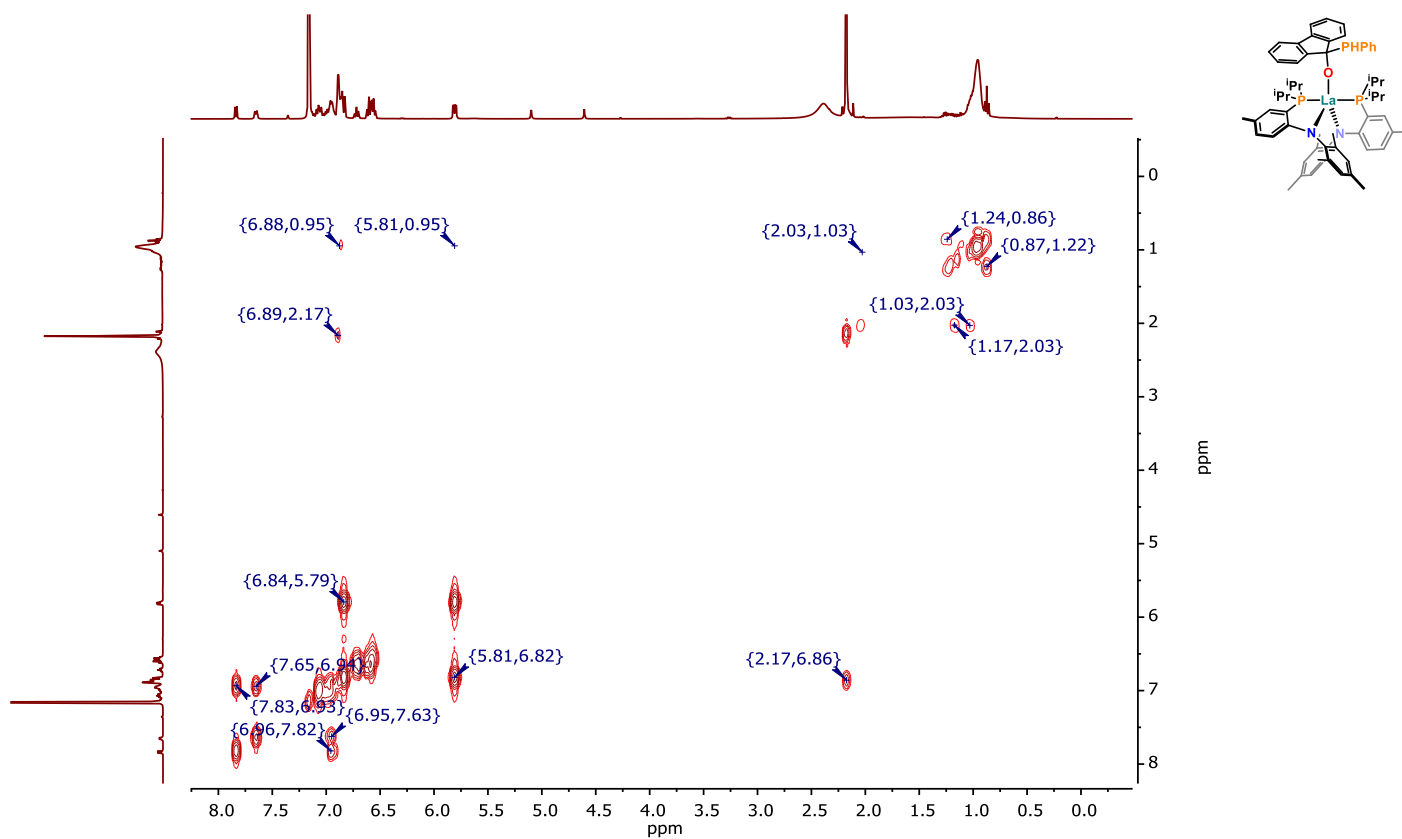


Figure S 27: ^1H - ^1H COSY NMR spectrum of **2b** in C_6D_6 (303 K).

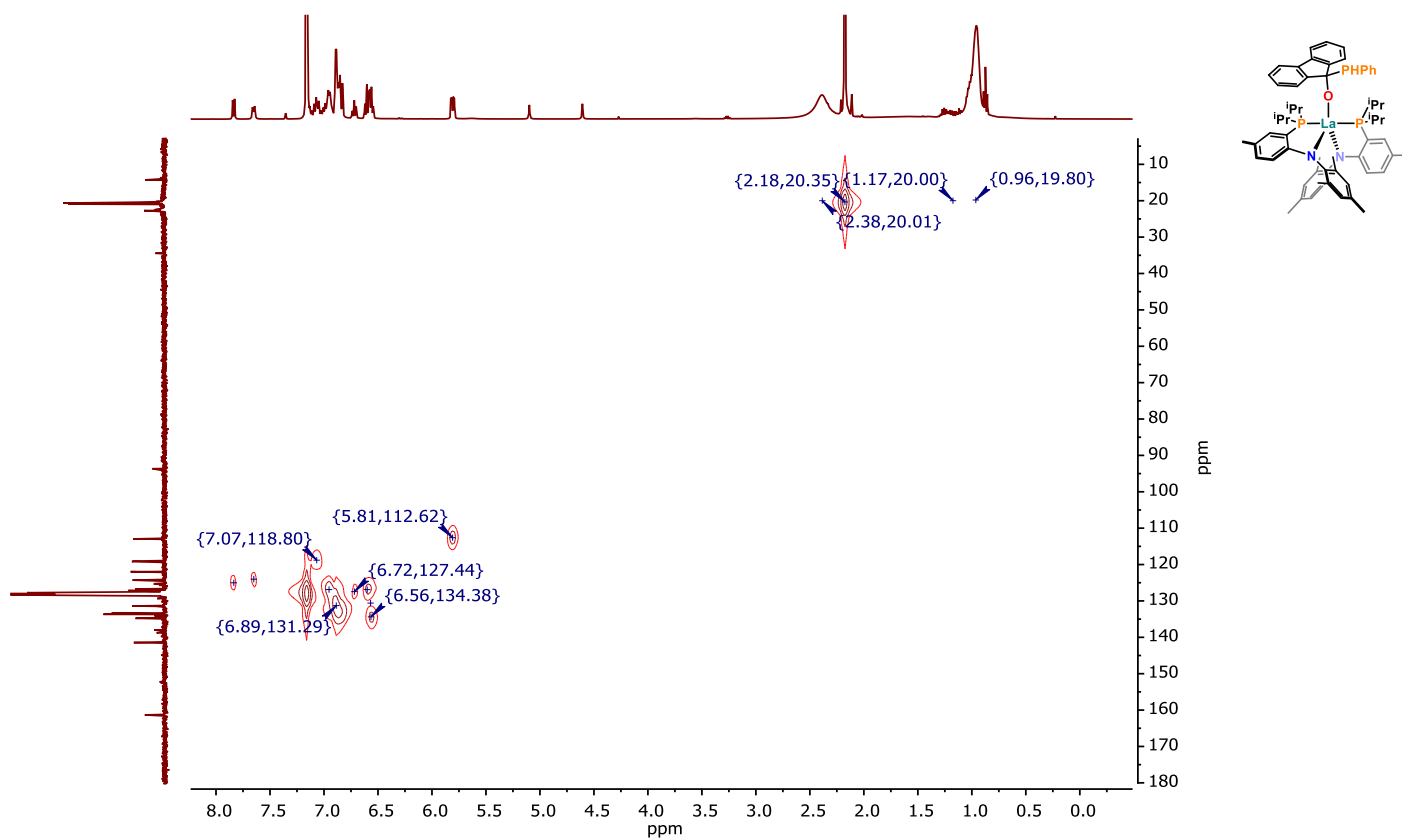


Figure S 28: ^1H - ^{13}C HSQC NMR spectrum of **2b** in C_6D_6 (303 K).

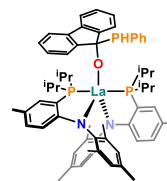
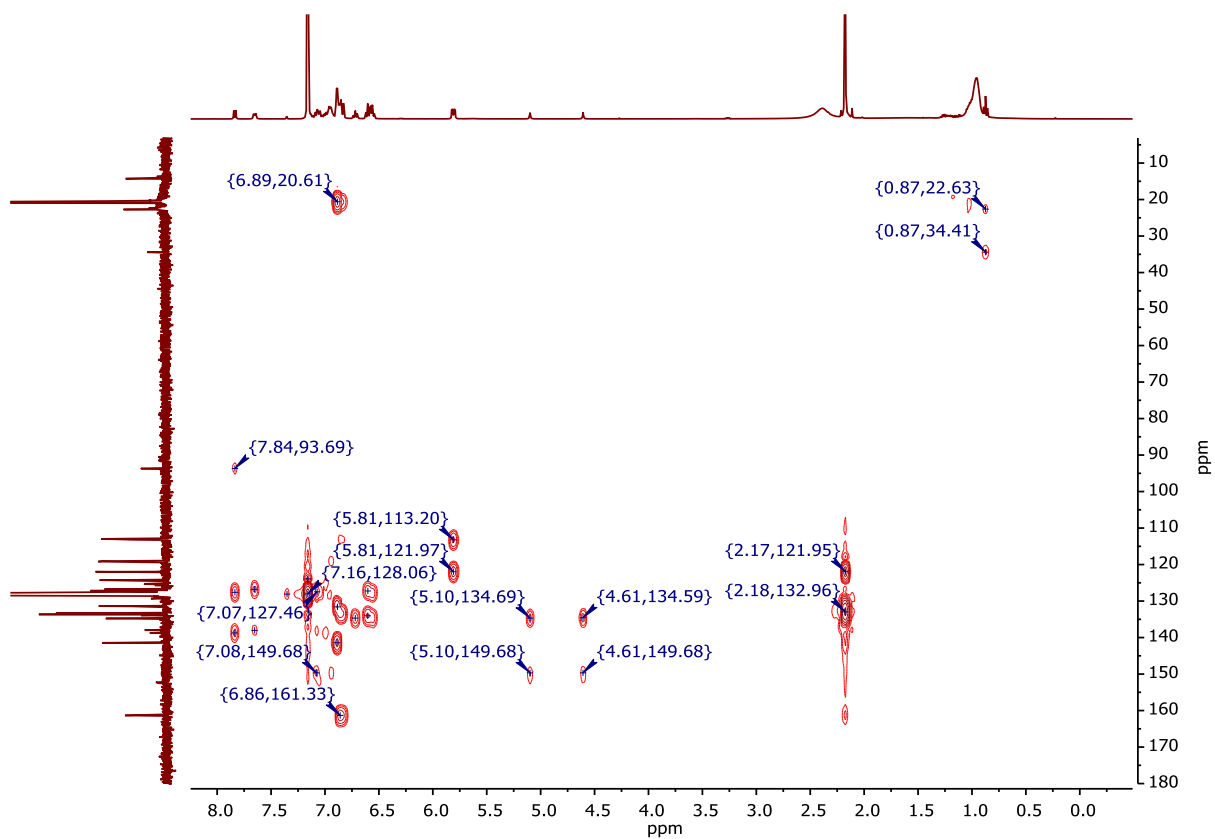


Figure S 29: ^1H - ^{13}C HMBC NMR spectrum of **2b** in C_6D_6 (303 K).

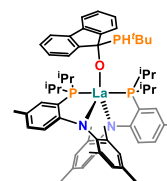
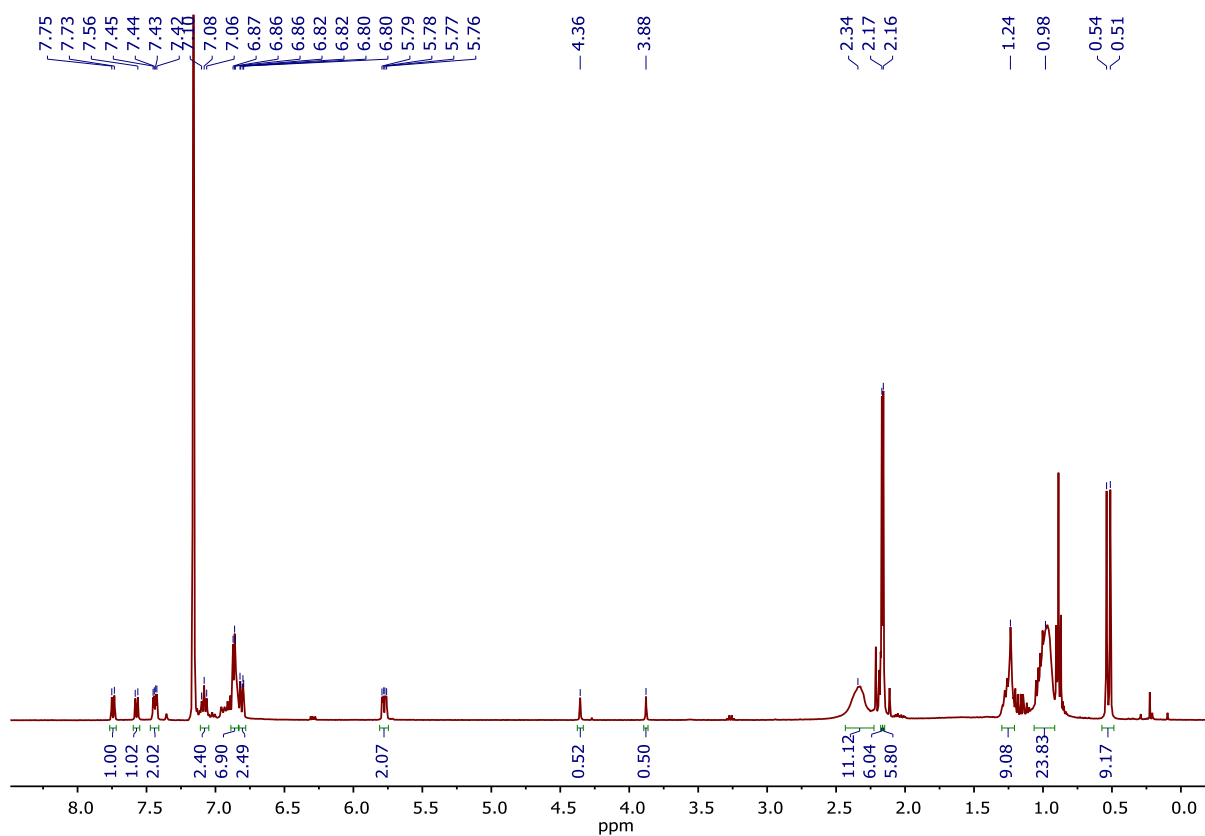


Figure S 30: ^1H NMR spectrum of **2c** in C_6D_6 (303 K).

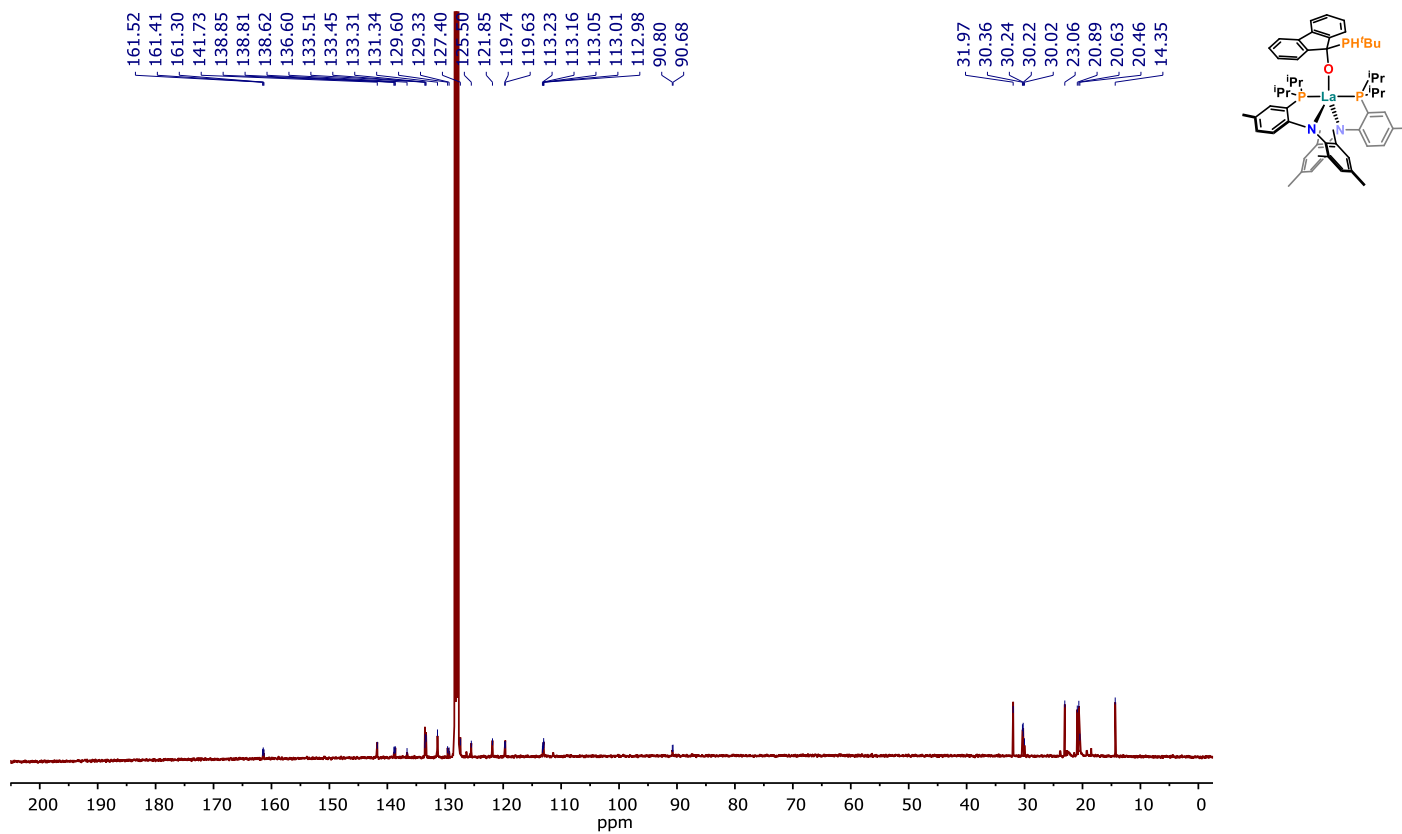


Figure S 31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2c** in C_6D_6 (303 K).

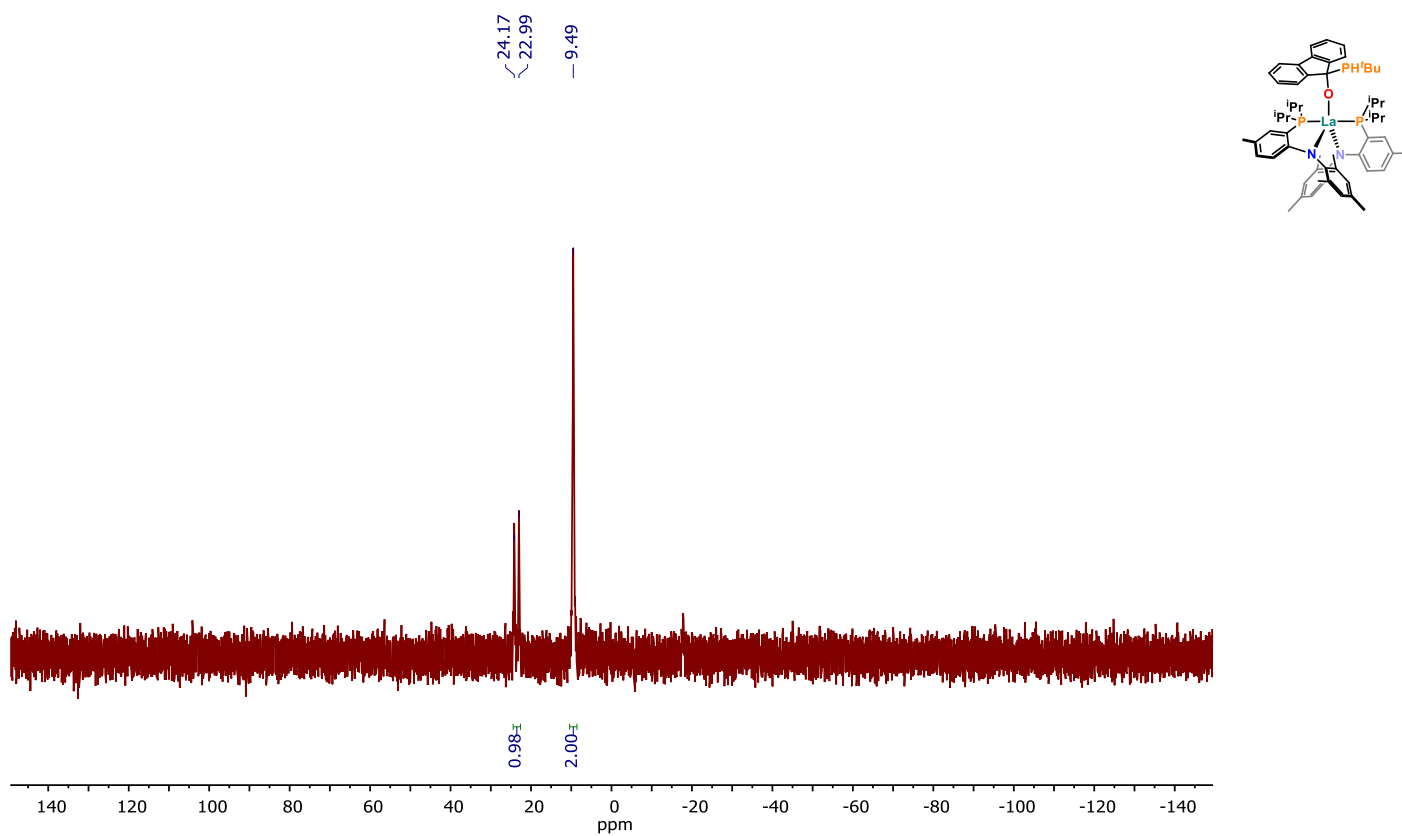


Figure S 32: ^{31}P NMR spectrum of **2c** in C_6D_6 (303 K). The peak at -17 ppm results from a small impurity of HPN.

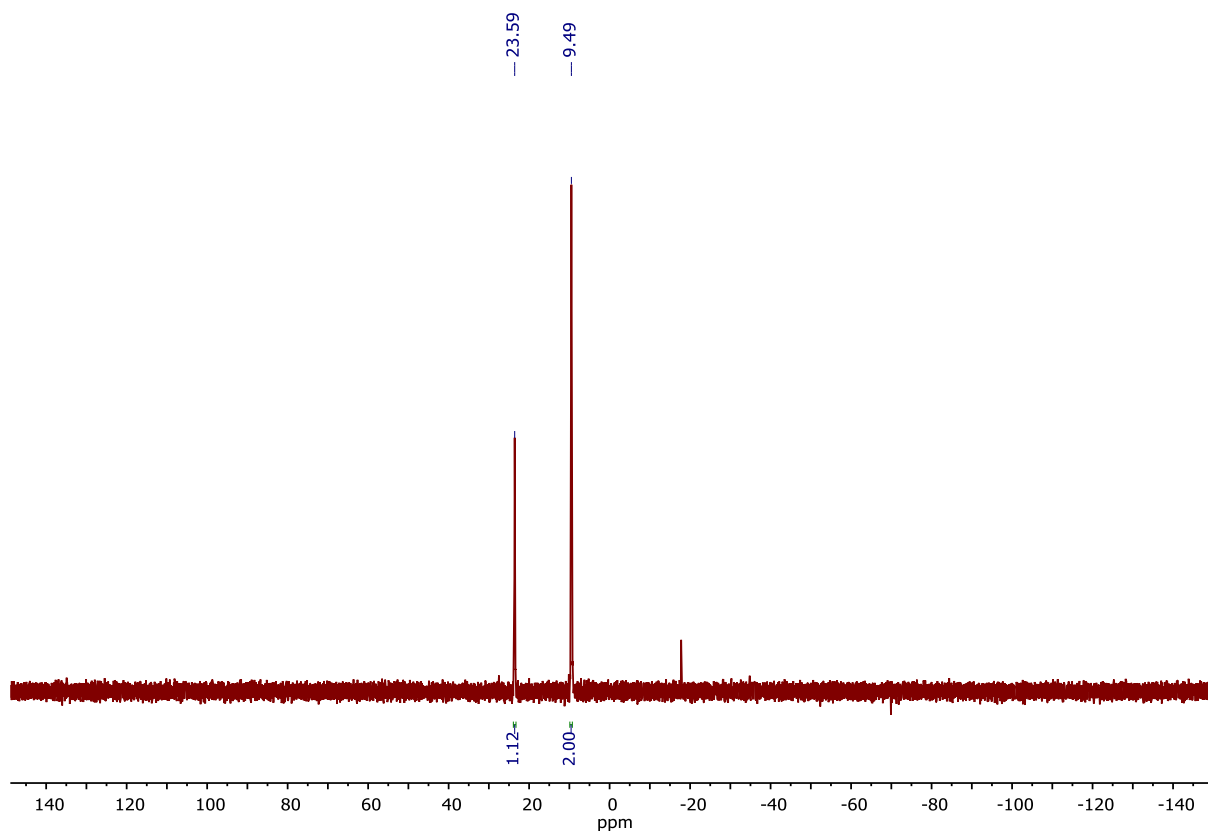


Figure S 33: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2c** in C_6D_6 (303 K). The peak at -17 ppm results from a small impurity of HPN.

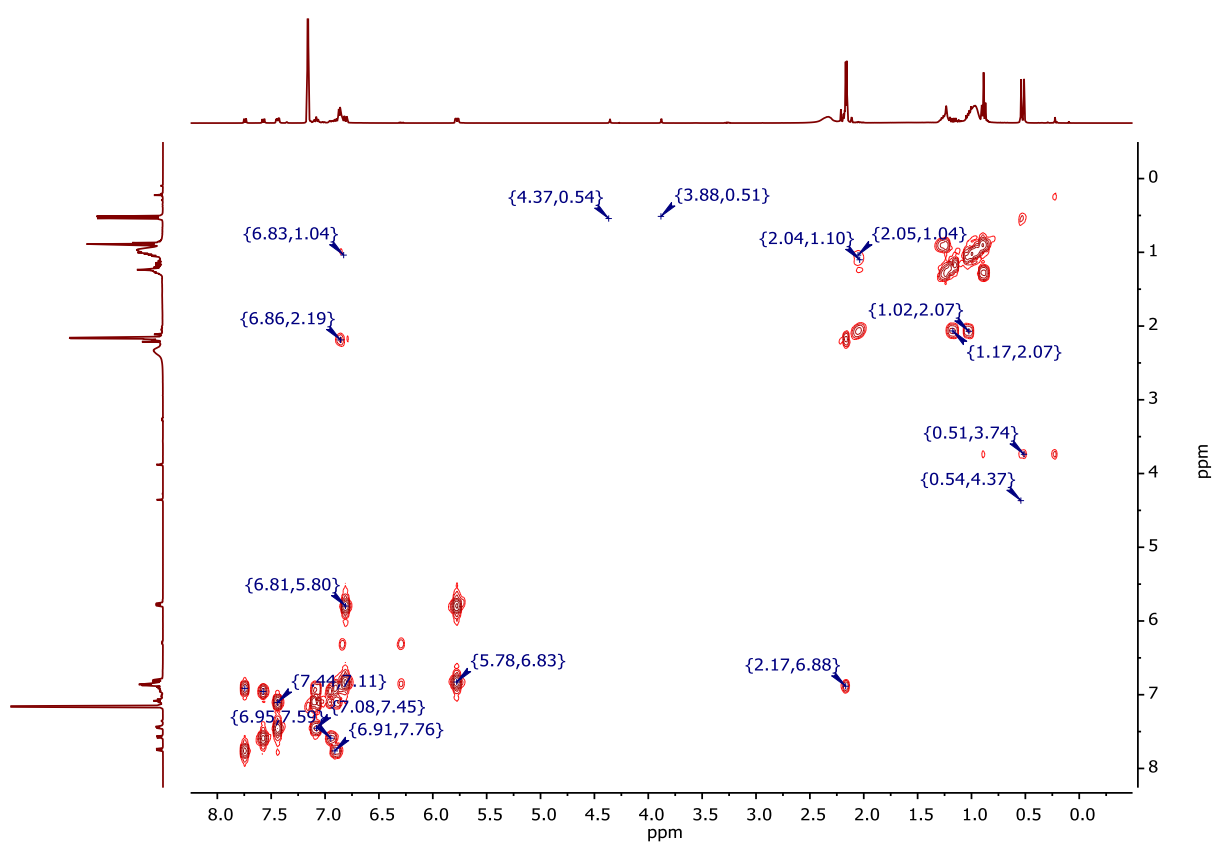


Figure S 34: $^1\text{H}-^1\text{H}$ COSY NMR spectrum of **2c** in C_6D_6 (303 K).

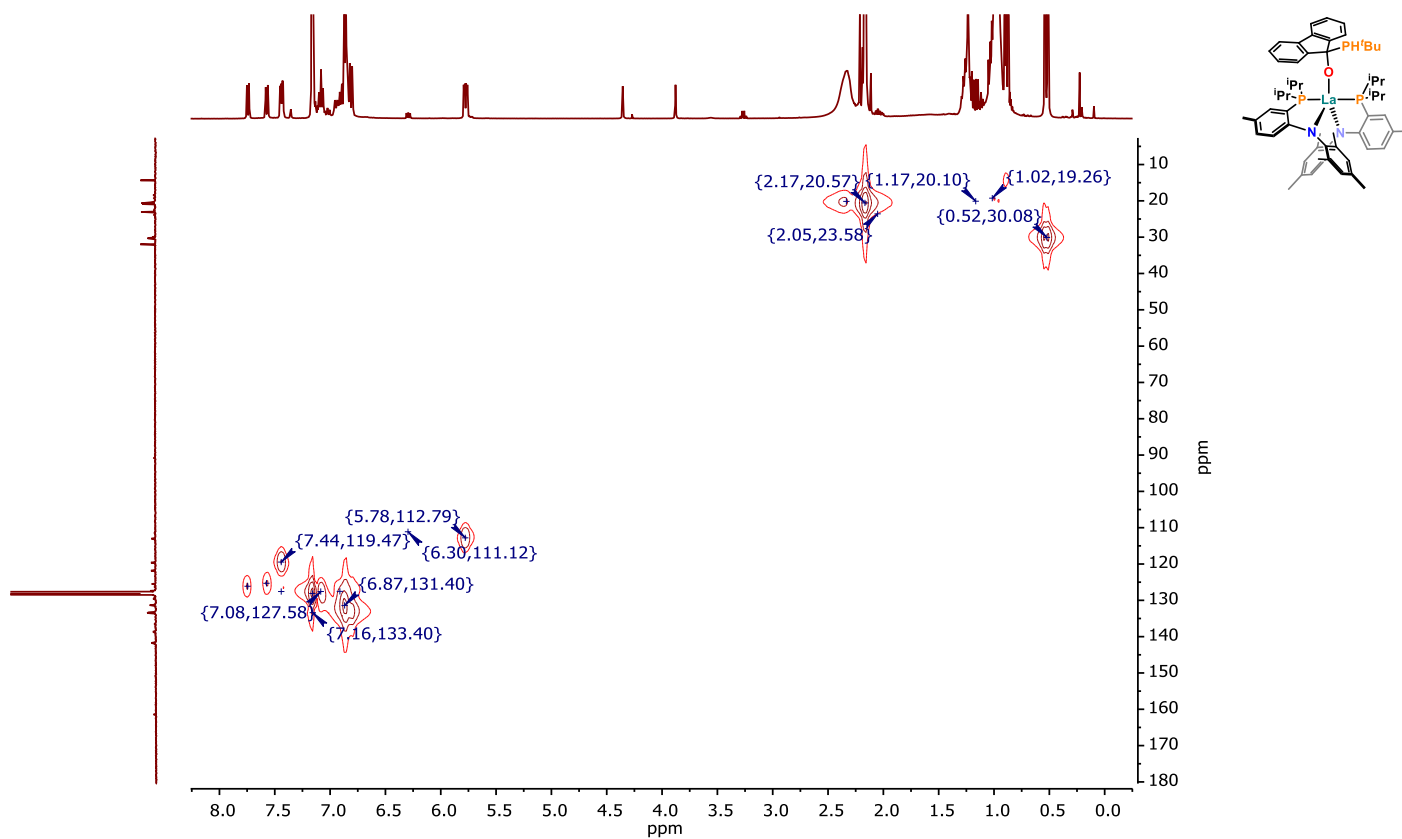


Figure S 35: ^1H - ^{13}C HSQC NMR spectrum of **2c** in C_6D_6 (303 K).

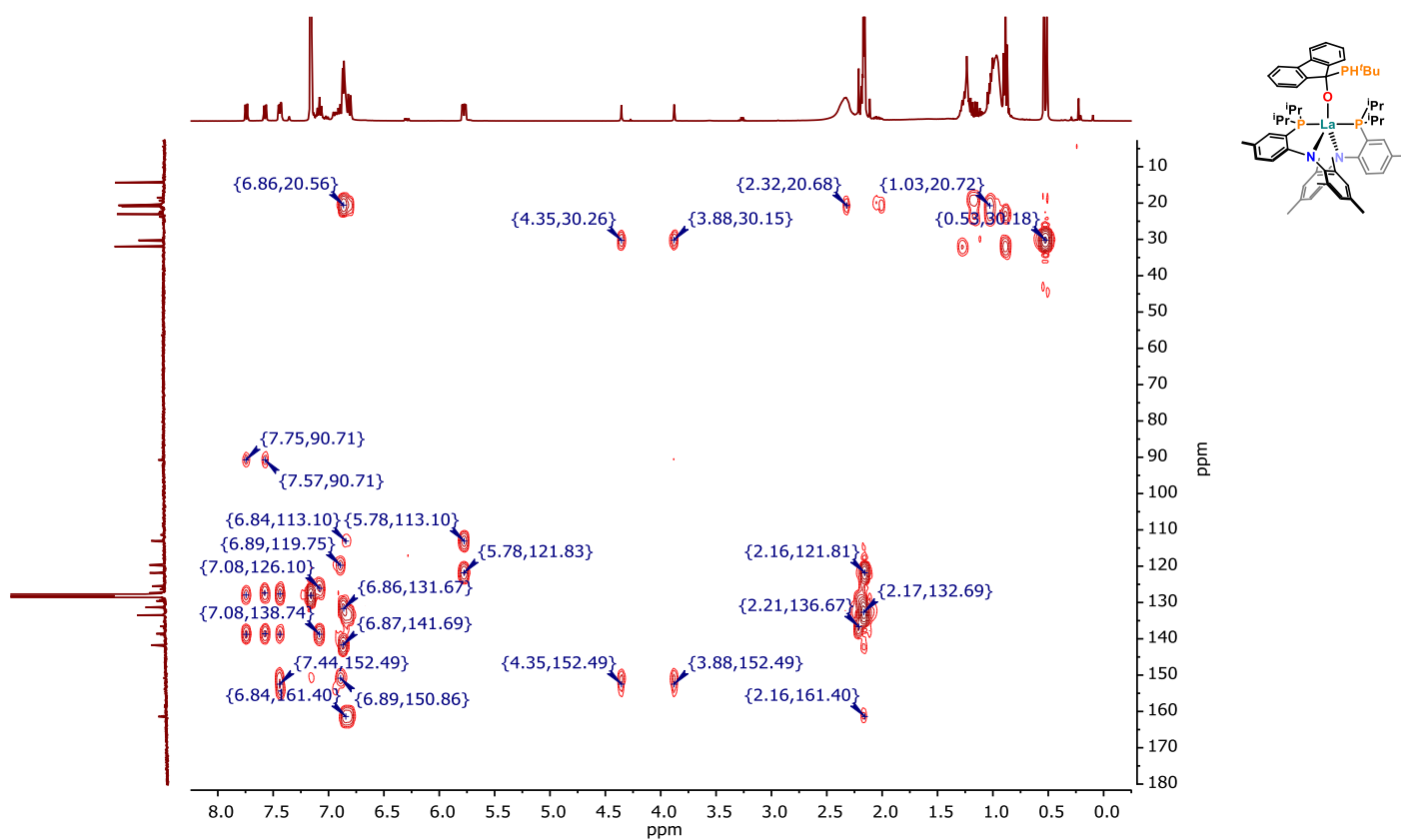


Figure S 36: ^1H - ^{13}C HMBC NMR spectrum of **2c** in C_6D_6 (303 K).

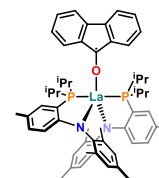
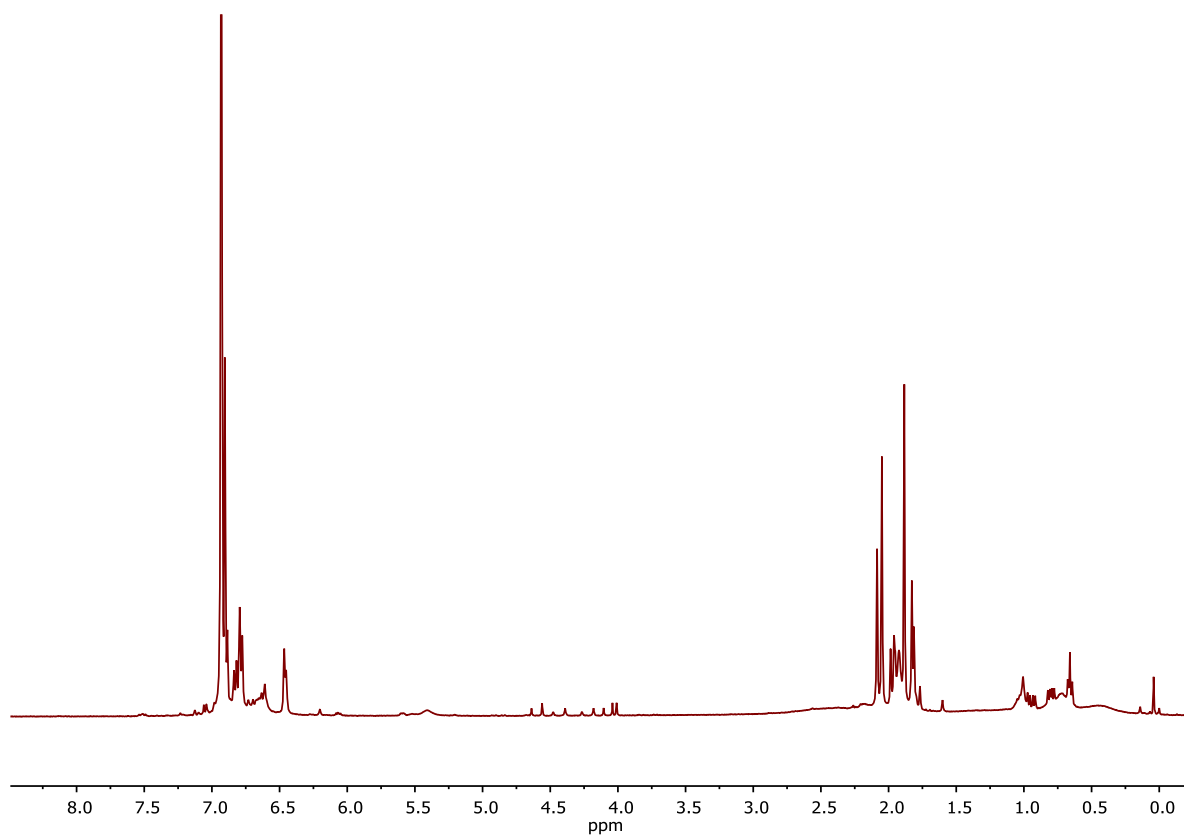


Figure S 37: ¹H NMR spectrum of **3** in C₆D₆ (303 K).

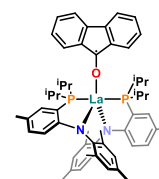
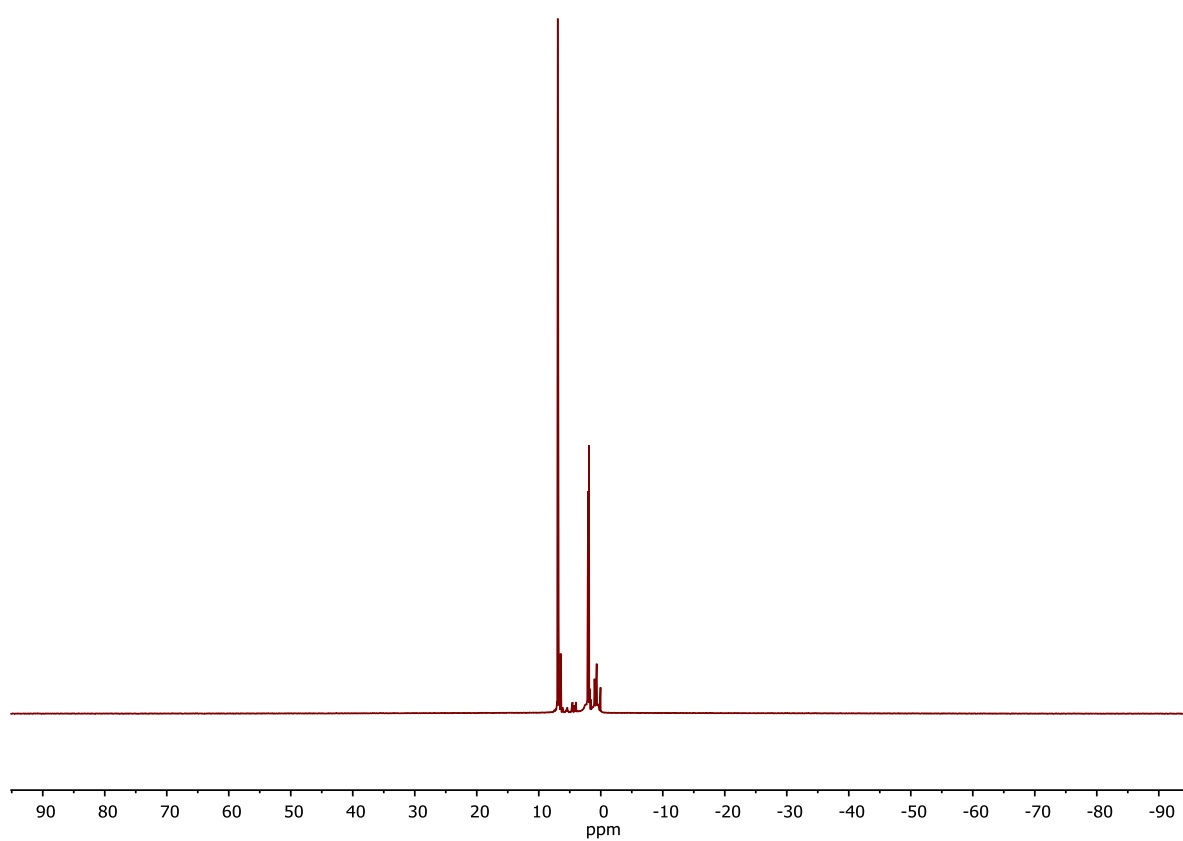


Figure S 38: ¹H NMR spectrum of **3** in C₆D₆ (303 K).

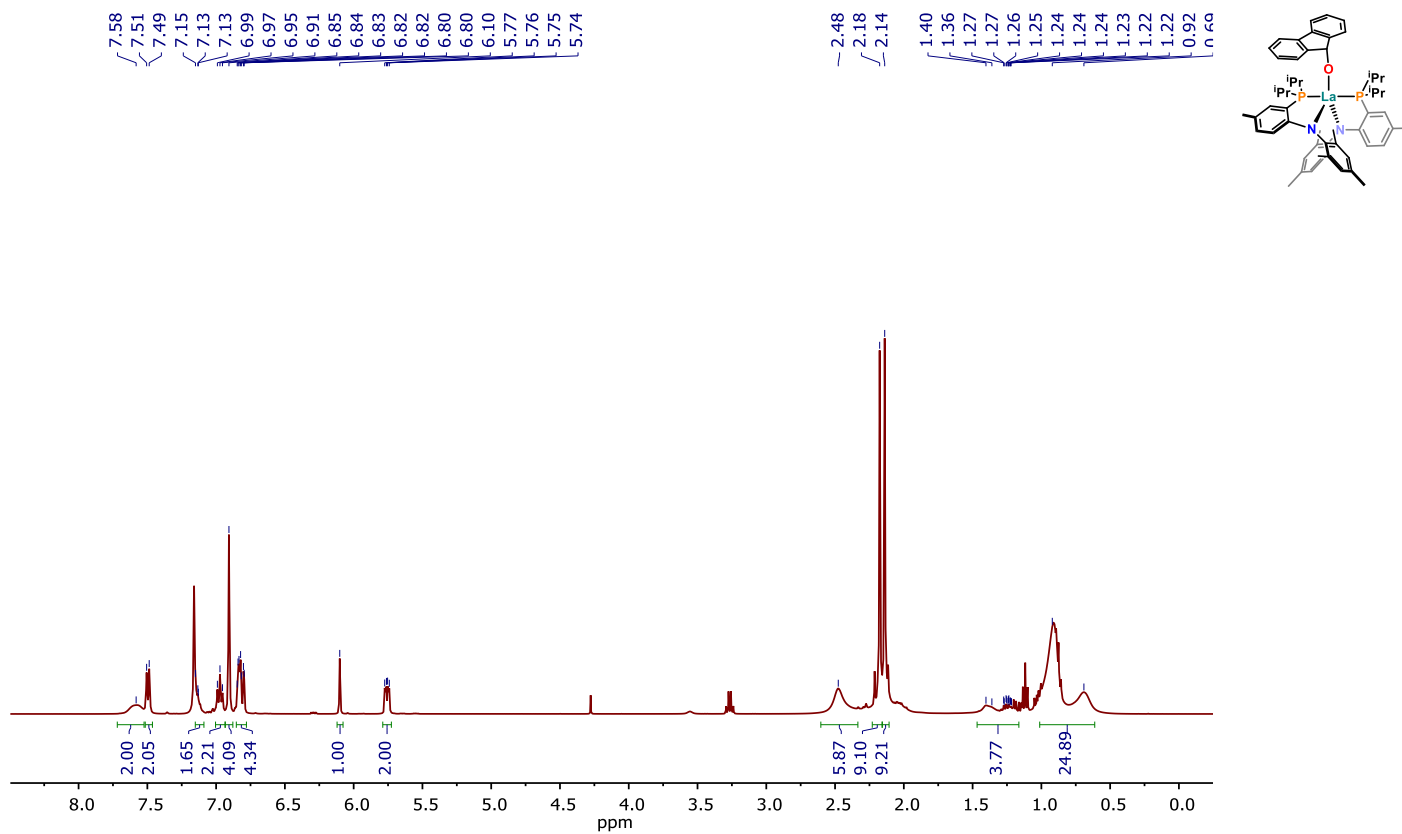


Figure S 39: ¹H NMR spectrum of 4 in C₆D₆ (303 K).

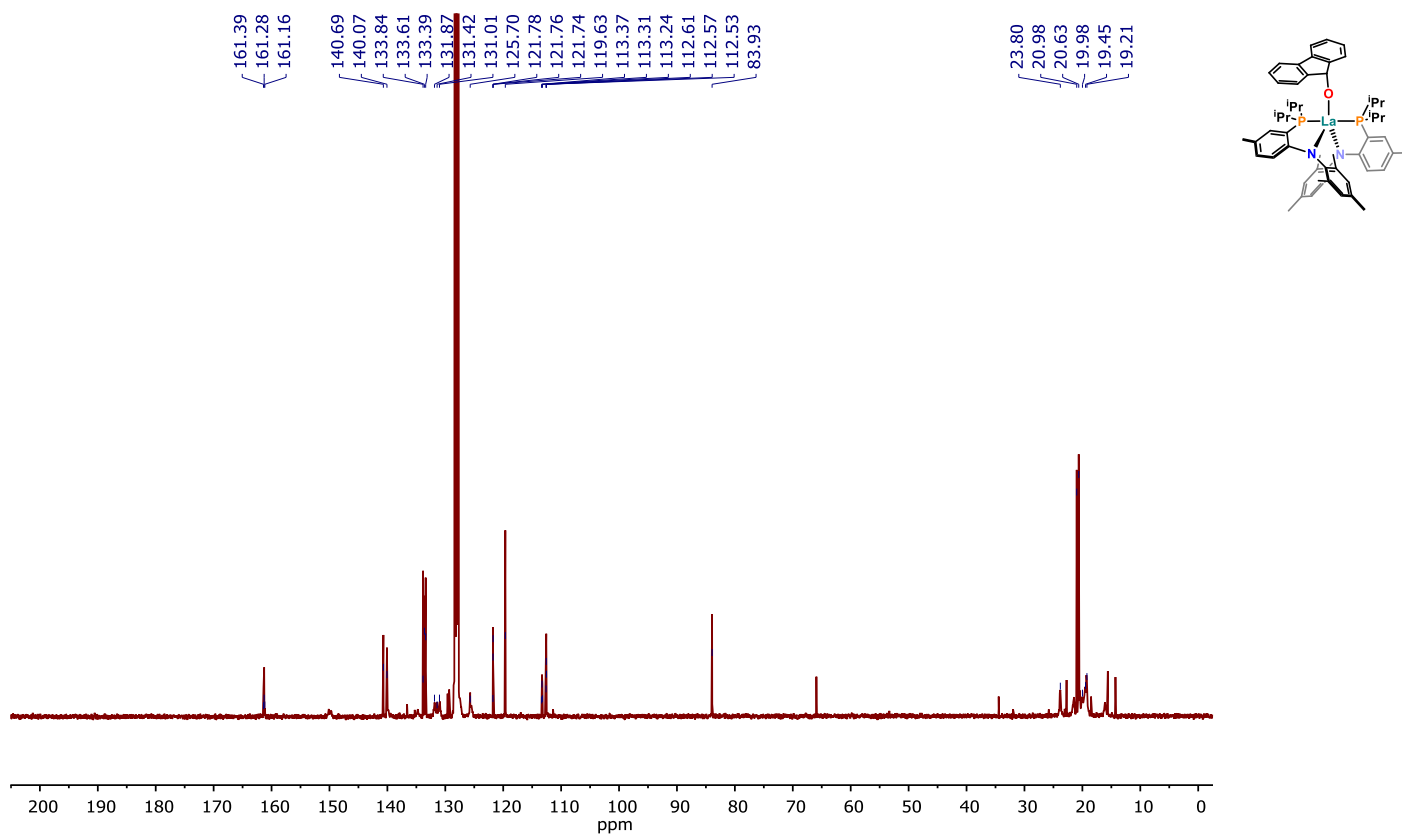


Figure S 40: ¹³C NMR spectrum of 4 in C₆D₆ (303 K).

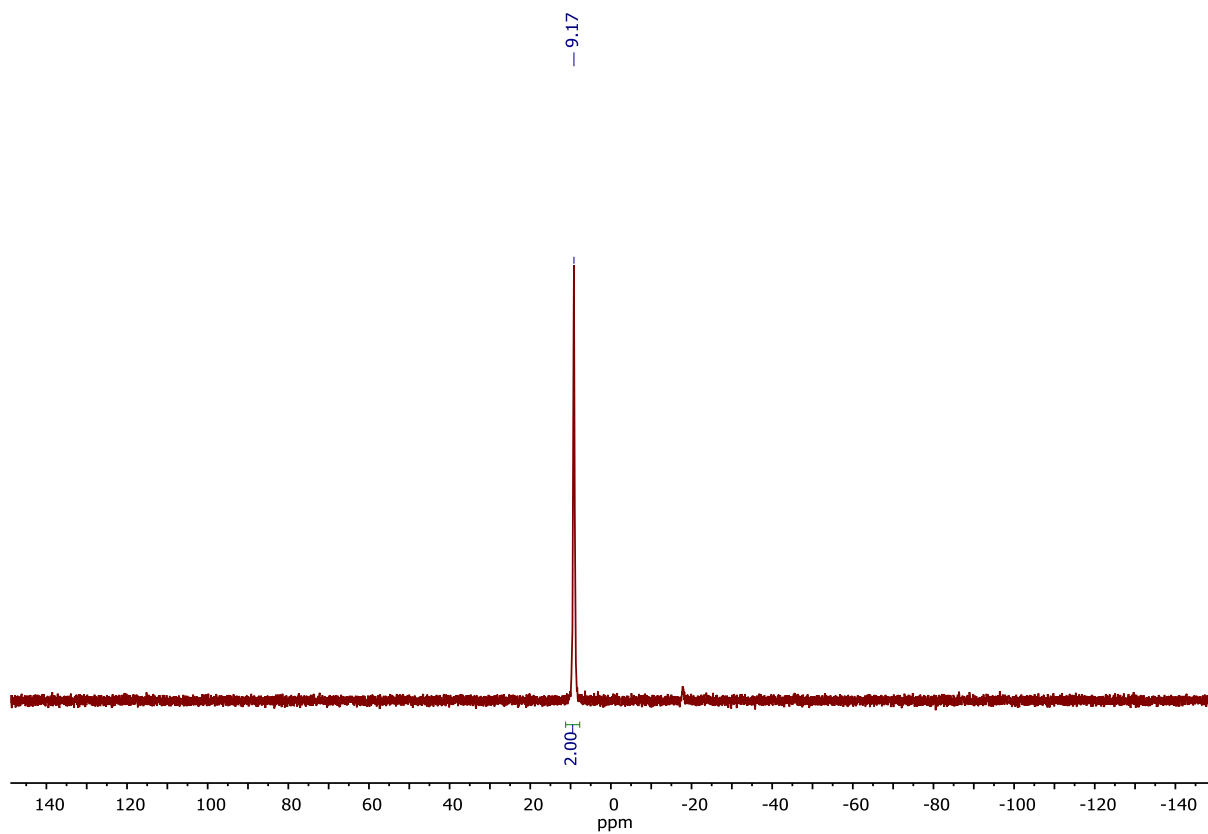


Figure S 41: ^{31}P NMR spectrum of **4** in C_6D_6 (303 K).

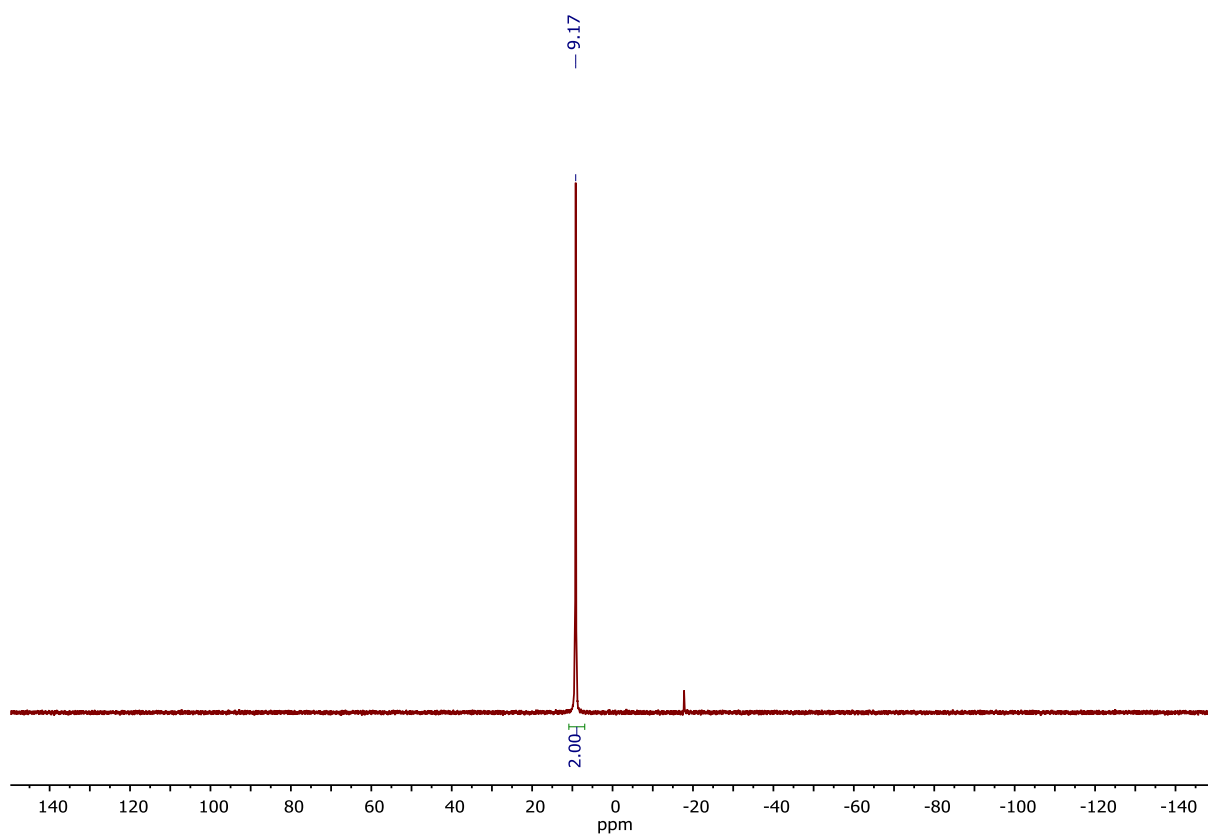


Figure S 42: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6 (303 K). Peak at -17 ppm results from a small impurity of HPN.

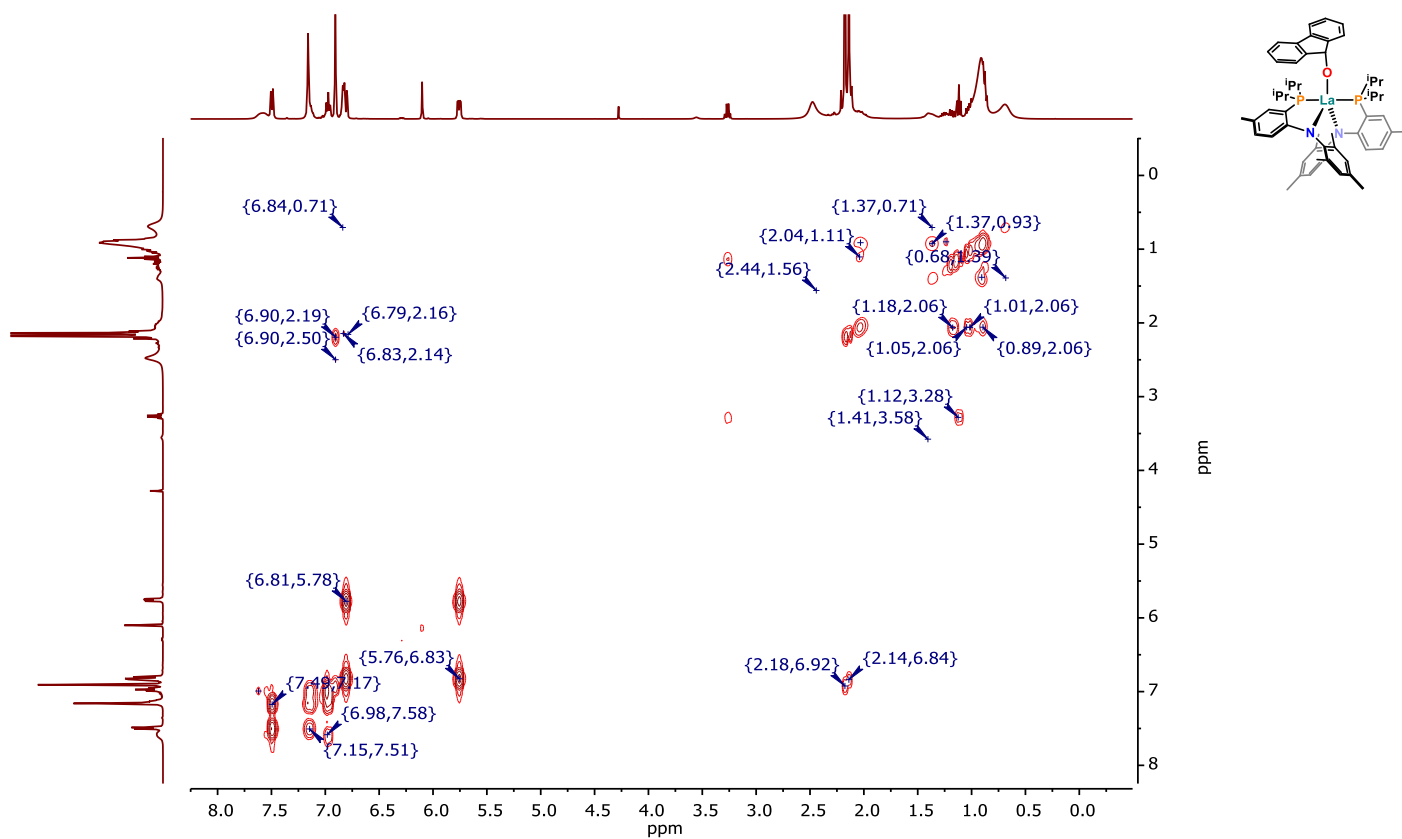


Figure S 43: ^1H - ^1H COSY NMR spectrum of **4** in C_6D_6 (303 K).

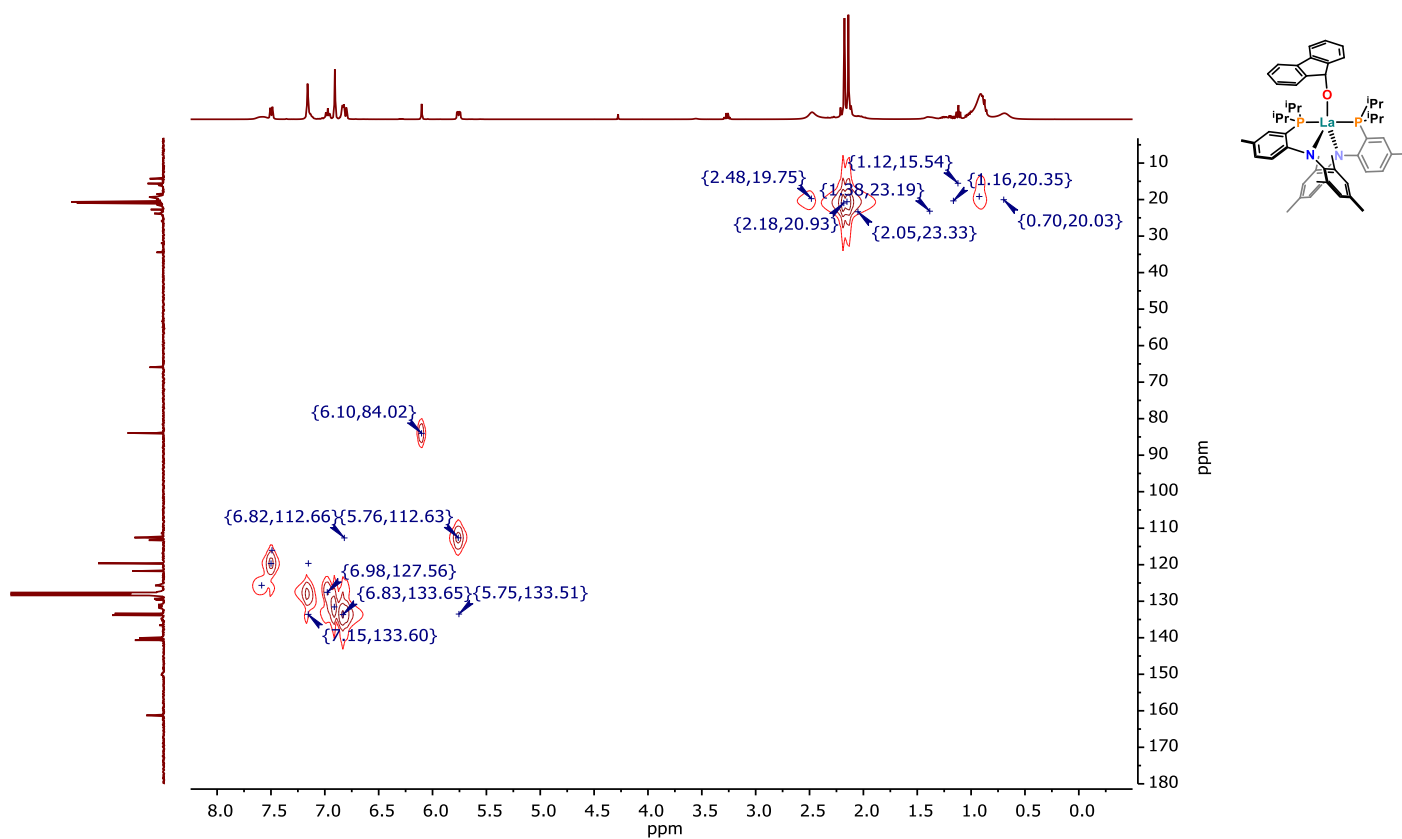


Figure S 44: ^1H - ^{13}C HSQC NMR spectrum of **4** in C_6D_6 (303 K).

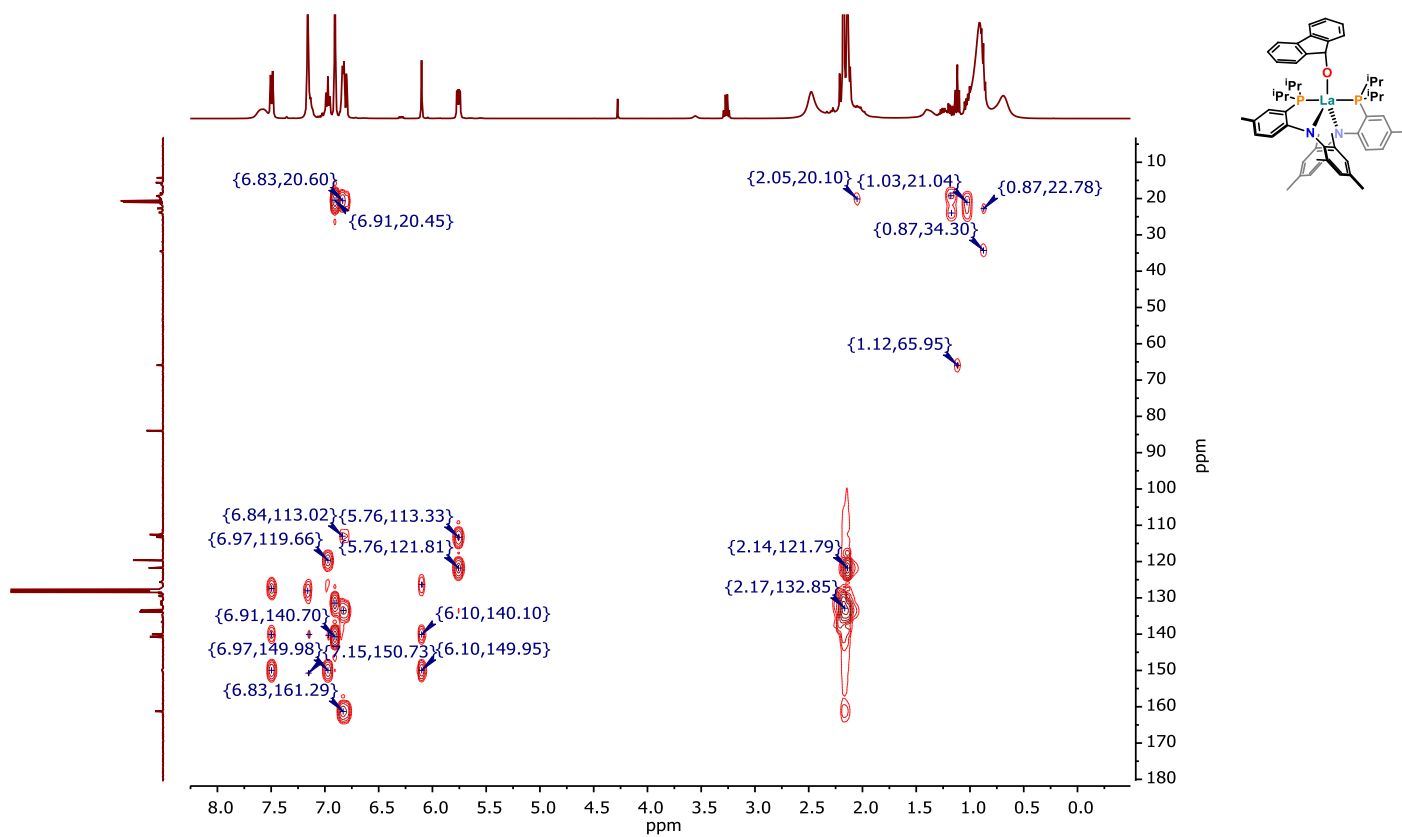


Figure S 45: ^1H - ^{13}C HMBC NMR spectrum of **4** in C_6D_6 (303 K).

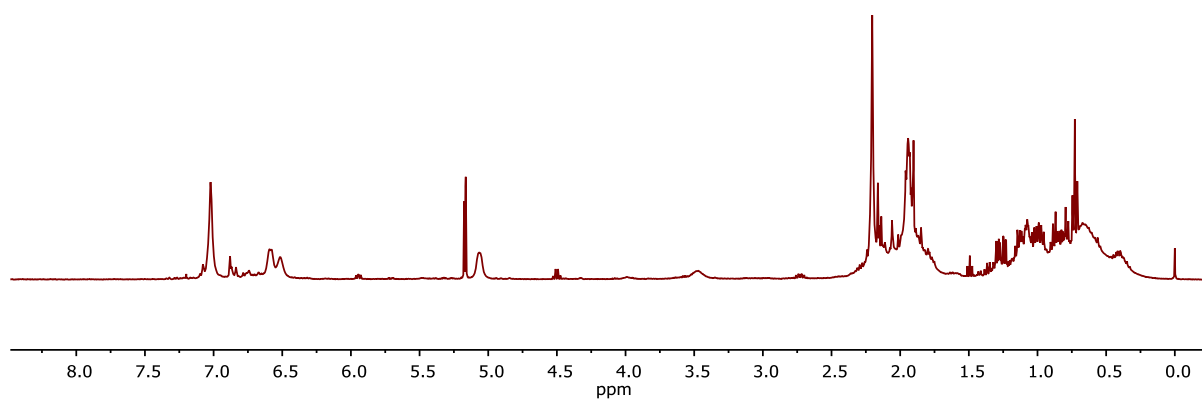


Figure S 46: Crude ^1H NMR of the reaction to synthesize the cationic fluorenone complex **5**.

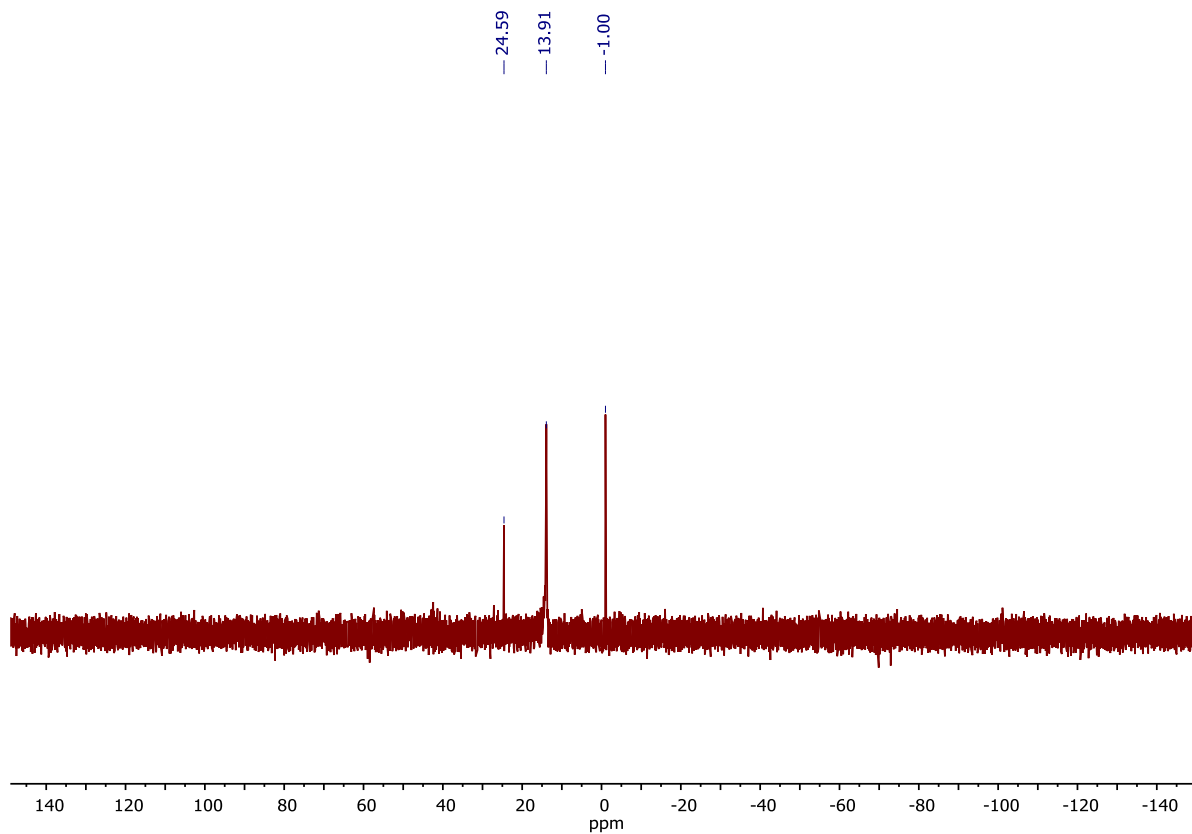


Figure S 47: Crude ^{31}P NMR of the reaction to synthesize the cationic fluorenone complex **5**.

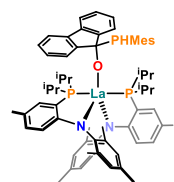
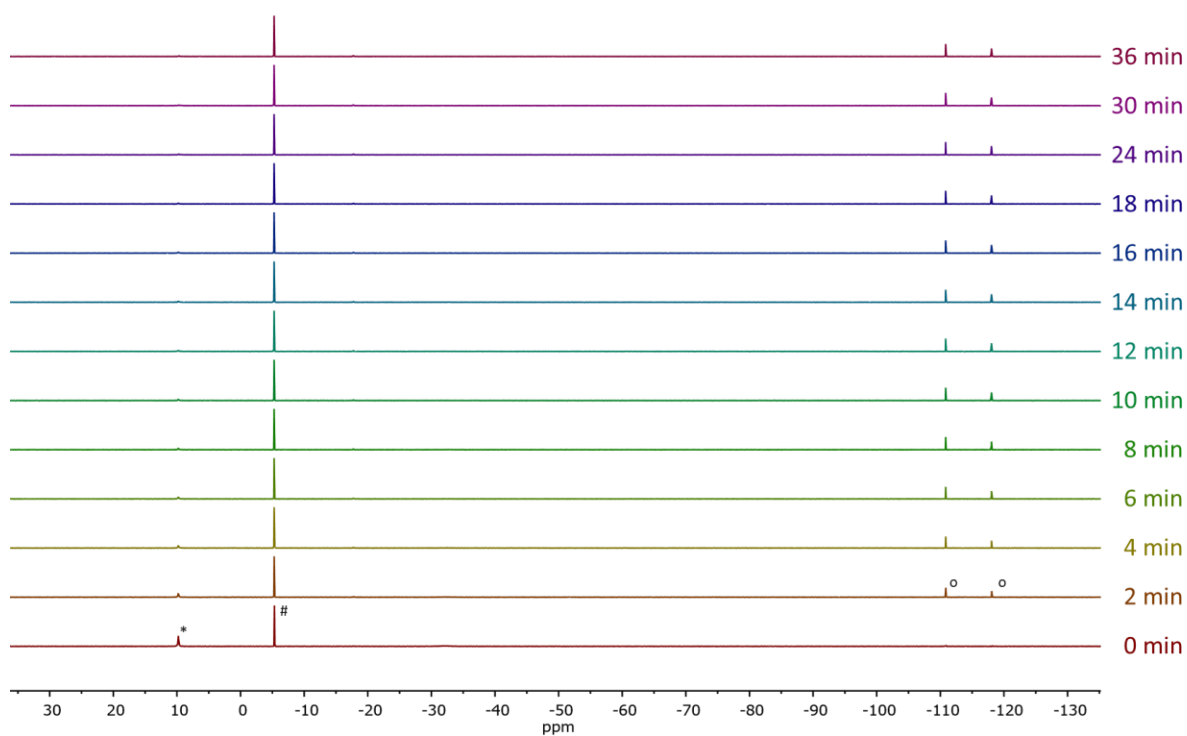


Figure S 48: $^{31}\text{P}\{^1\text{H}\}$ NMR of the light induced decomposition reaction of **2a** followed over time. # marks the signal of the internal standard (PPh_3), * corresponds to the PN ligand signal. Please note that the PH signal is there, but due to its broadening not observed / shown.

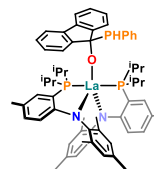
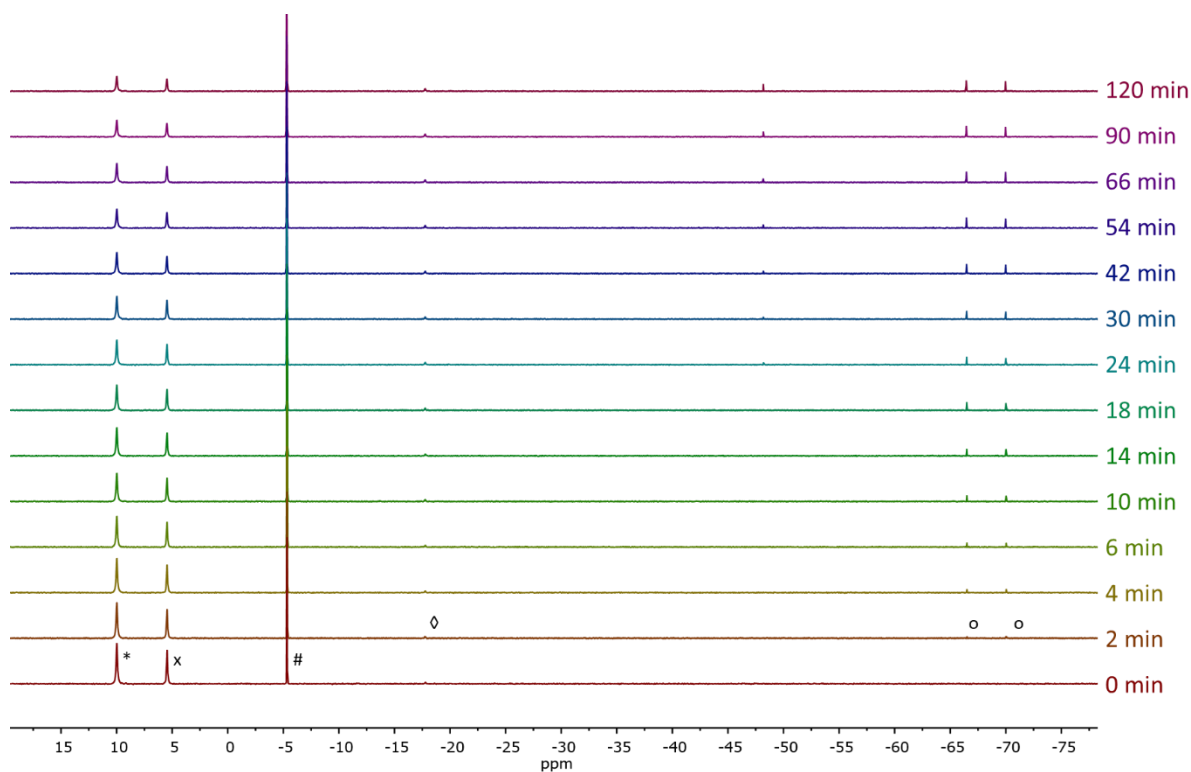


Figure S 49: $^{31}\text{P}\{^1\text{H}\}$ NMR of the light induced decomposition reaction of **2b** followed over time. # marks the signal of the internal standard (PPh_3), * corresponds to the PN ligand signal. x marks the PH resonance while \diamond shows minor impurities of protonated HPN being formed.

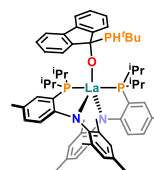
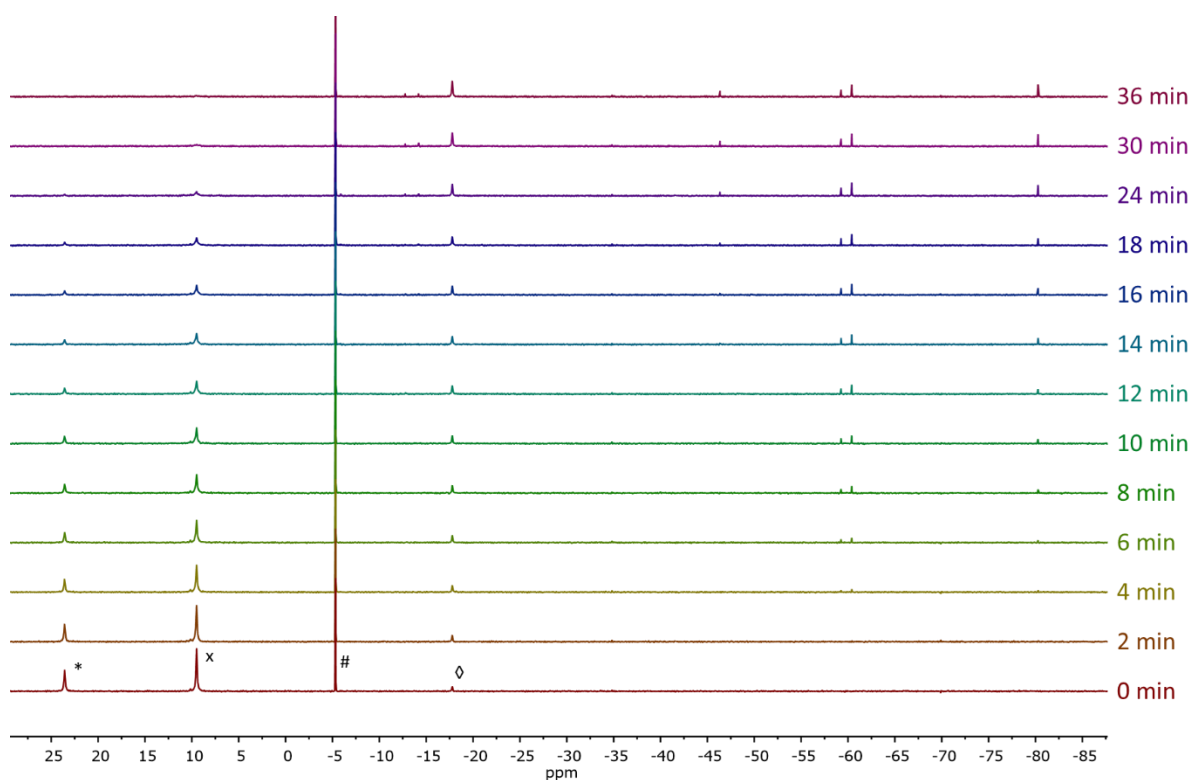


Figure S 50: $^{31}\text{P}\{^1\text{H}\}$ NMR of the light induced decomposition reaction of **2c** followed over time. # marks the signal of the internal standard (PPh_3), * corresponds to the PN ligand signal. x marks the PH resonance while \diamond shows minor impurities of protonated HPN being formed. Two unknown species are also formed after the reaction.

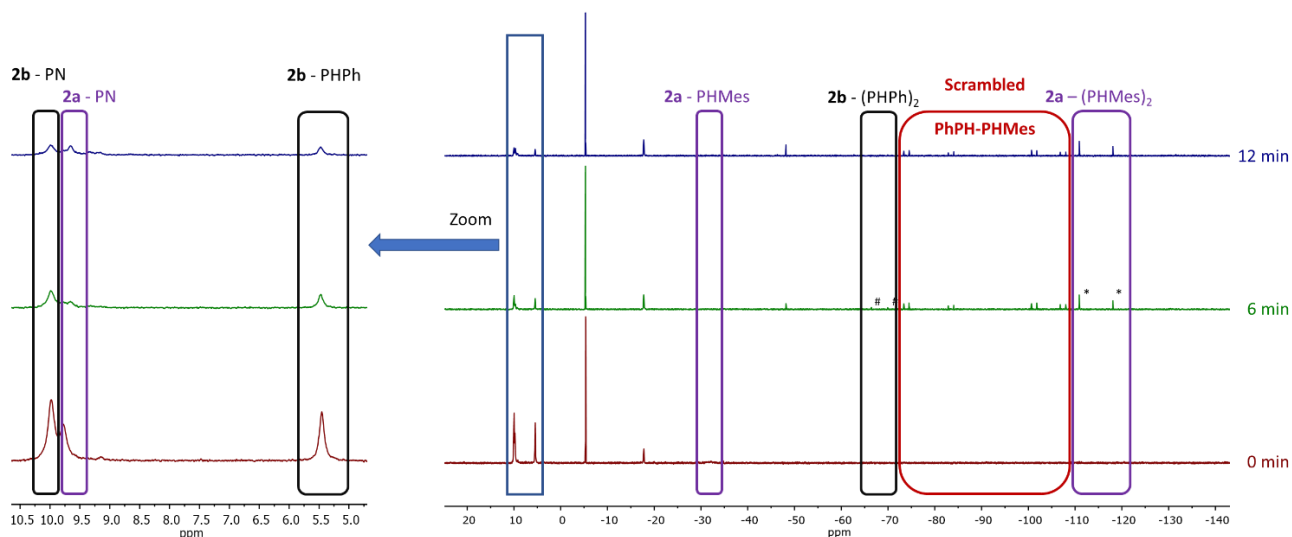


Figure S 51: Scrambling experiments from an equimolar mixture of **2a** and **2b**.

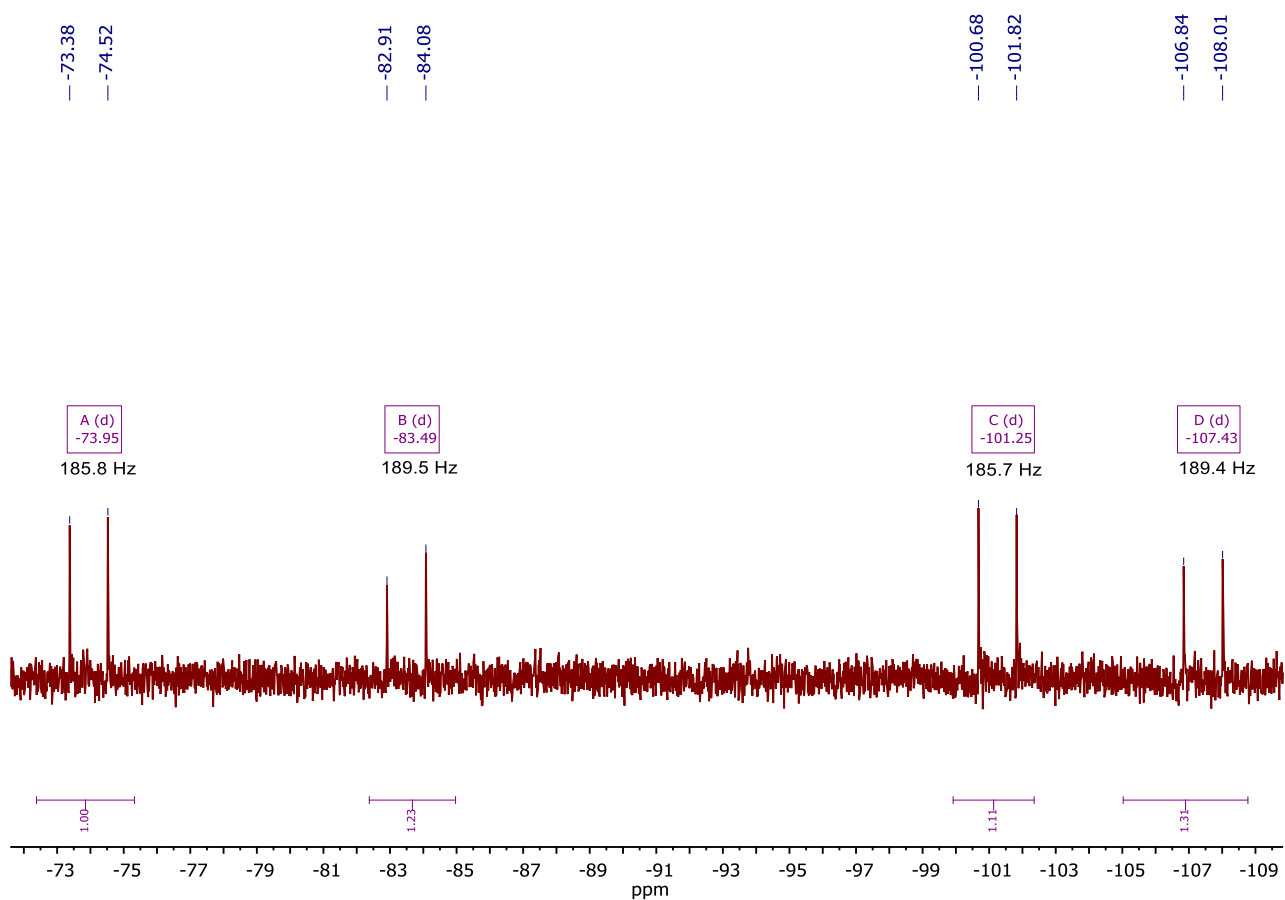


Figure S 52: Snippet from the ^{31}P NMR spectra of the scrambling experiment from Figure S 51 after 12 minutes. The coupling constants clearly display, that signal A and C as well as B and D belong to the same species, namely PhPH-PHMeS. The observation of overall 4 doublets is in line with the possible meso and d, l isomers of diphosphines.⁵

3. UV Vis

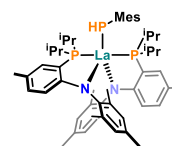
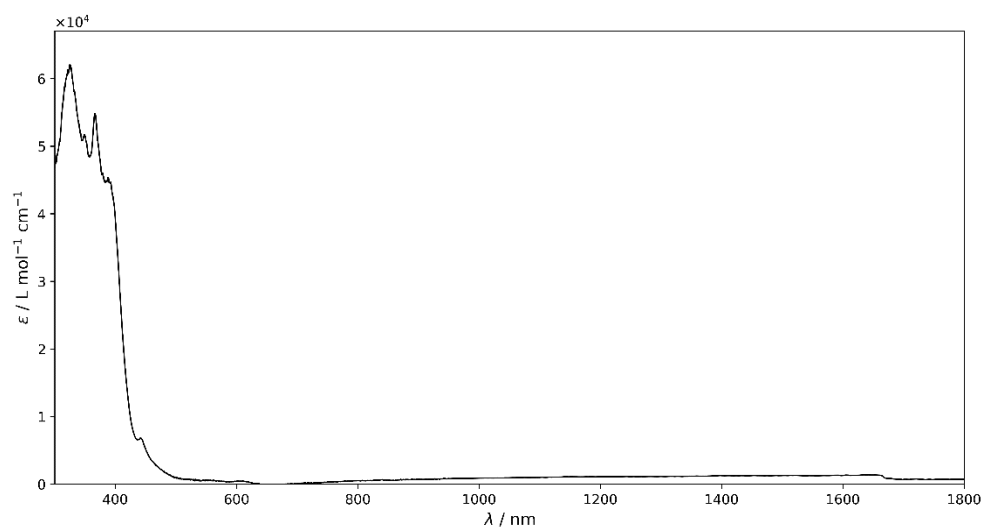


Figure S 53: UV-Vis of **1a** in toluene at 303K.

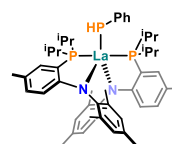
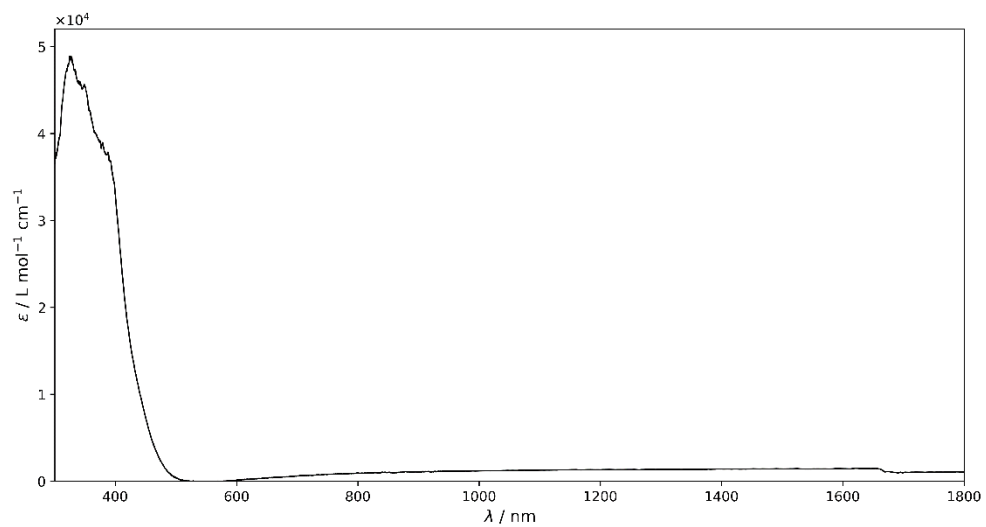


Figure S 54: UV-Vis of **1b** in toluene at 303K.

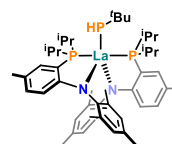
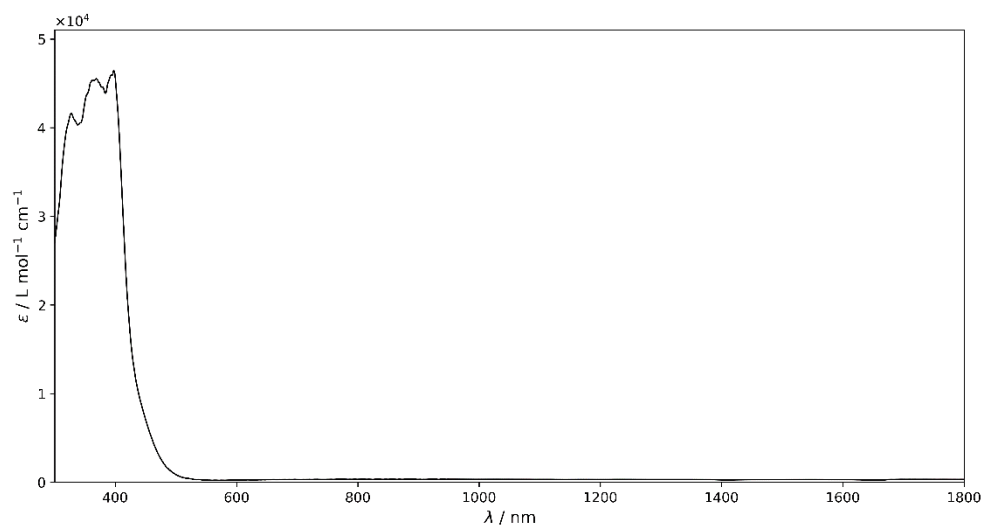


Figure S 55: UV-Vis of **1c** in toluene at 303K.

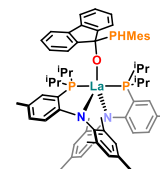
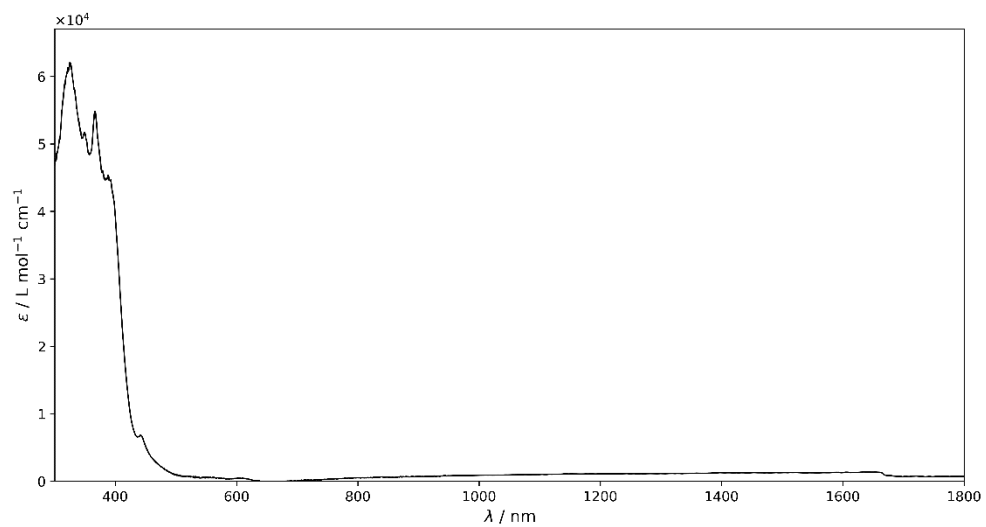


Figure S 56: UV-Vis of **2a** in toluene at 303K.

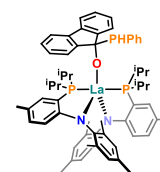
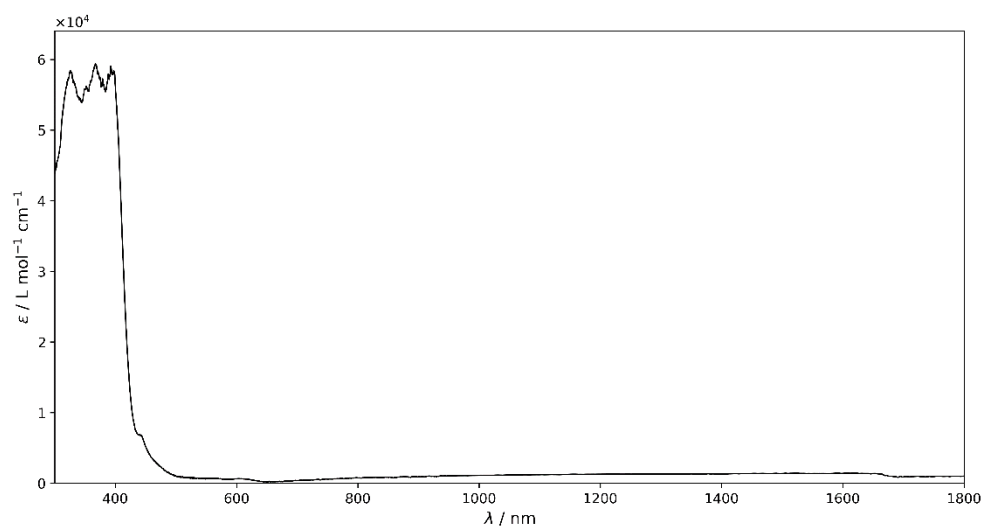


Figure S 57: UV-Vis of **2b** in toluene at 303K.

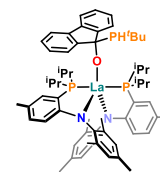
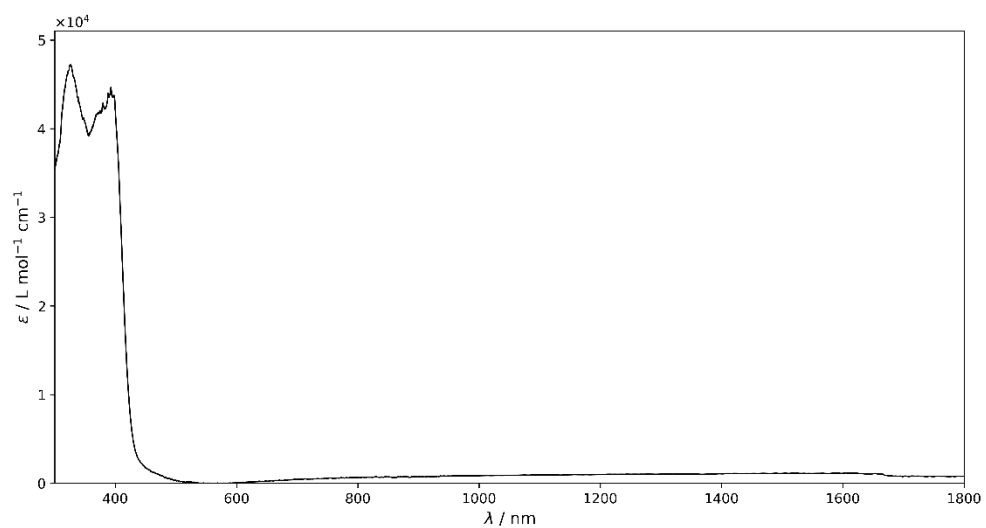


Figure S 58: UV-Vis of **2c** in toluene at 303K.

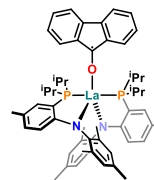
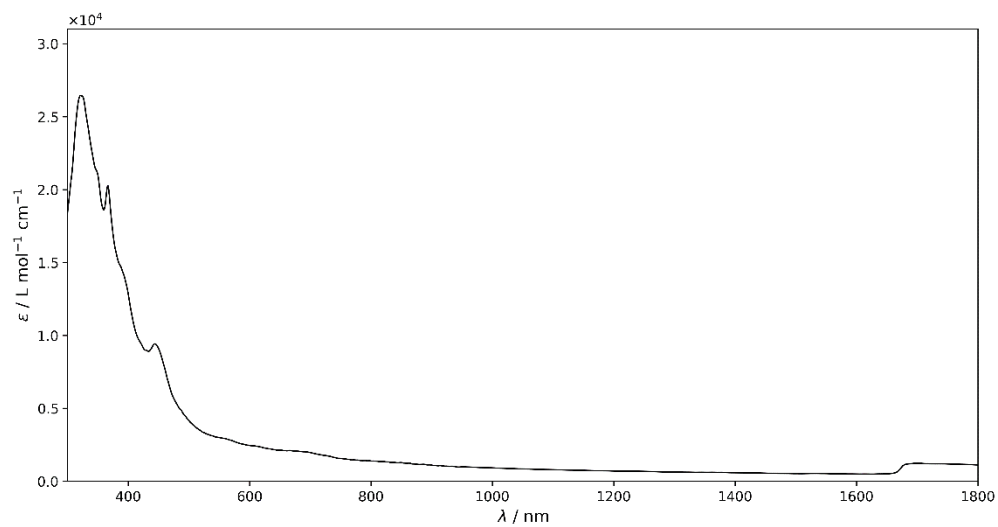


Figure S 59: UV-Vis of **3** in toluene at 303K.

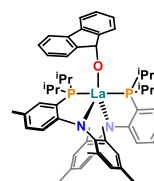
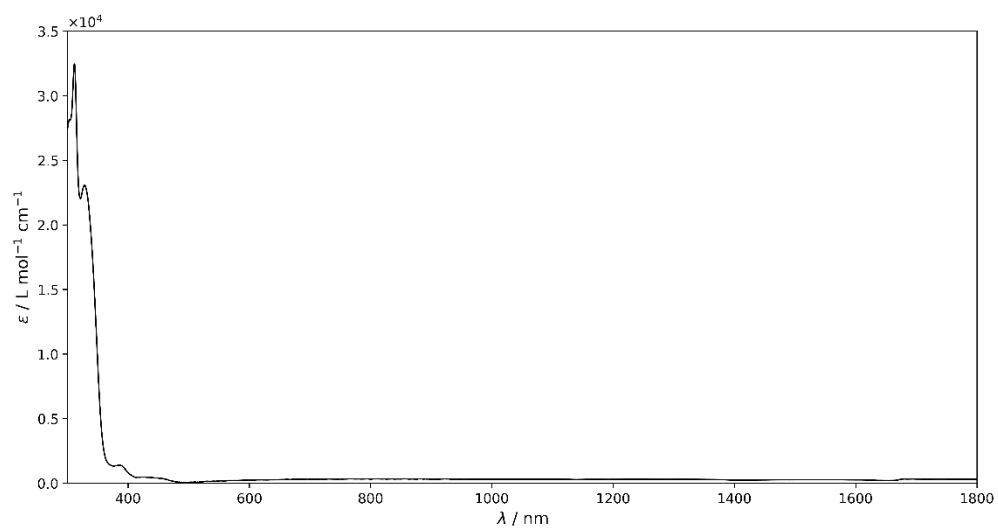


Figure S 60: UV-Vis of **4** in toluene at 303K.

4. IR

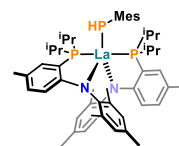
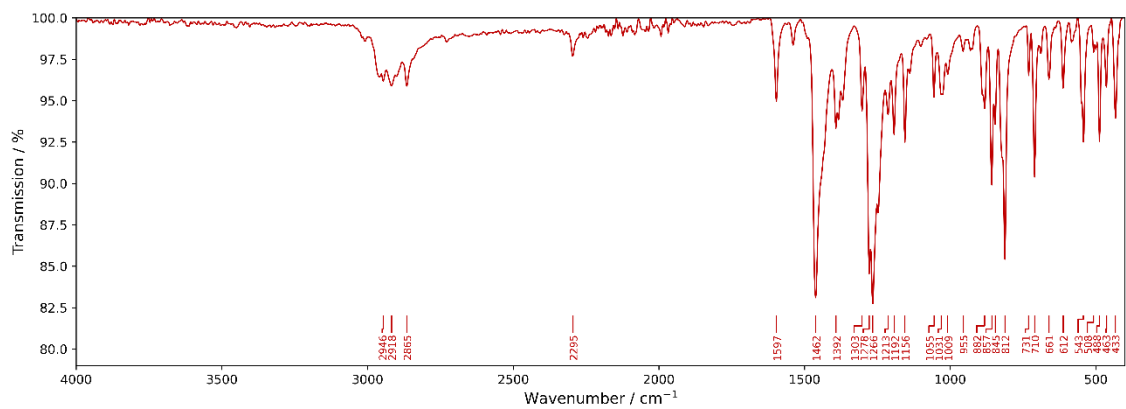


Figure S 61: ATR-IR spectrum of **1a**.

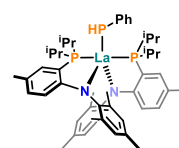
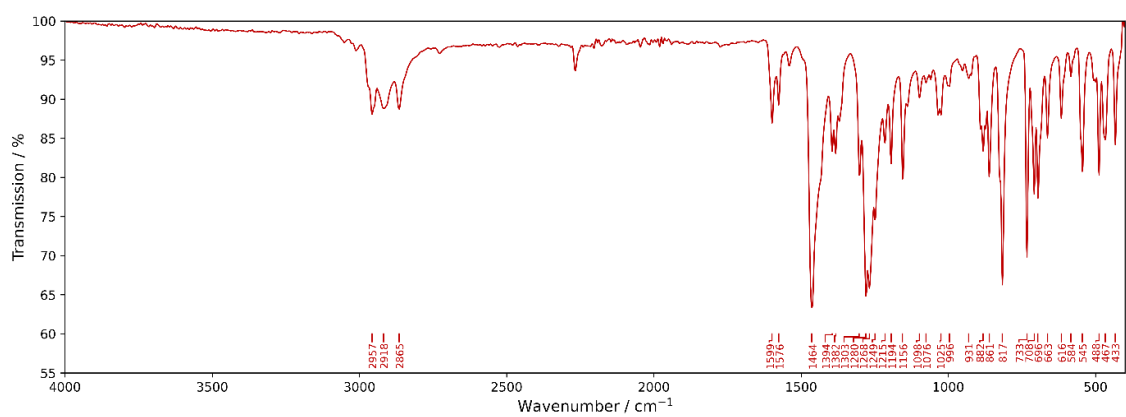


Figure S 62: ATR-IR spectrum of **1b**.

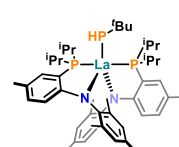
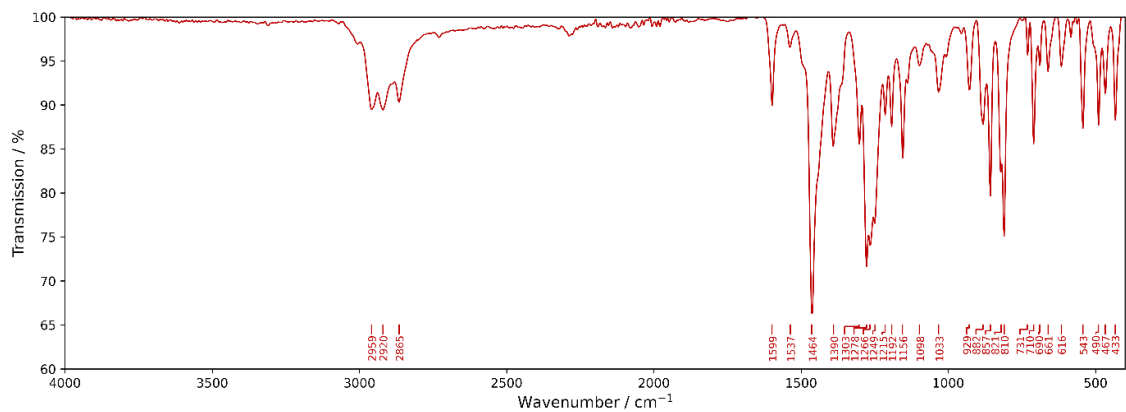


Figure S 63: ATR-IR spectrum of **1c**.

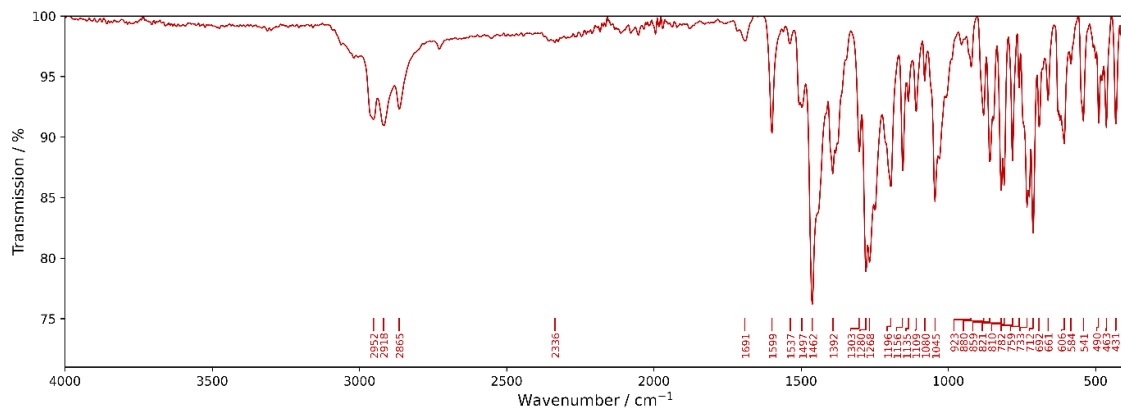


Figure S 64: ATR-IR spectrum of **2a**.

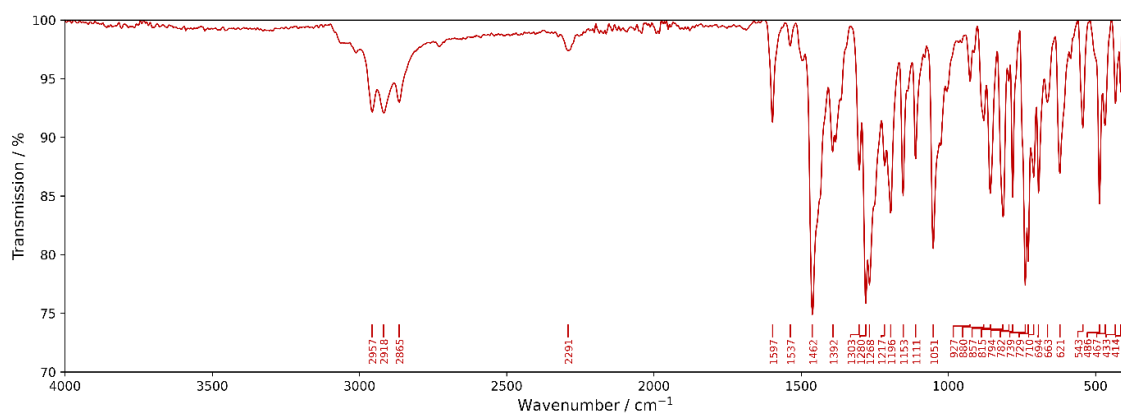


Figure S 65: ATR-IR spectrum of **2b**.

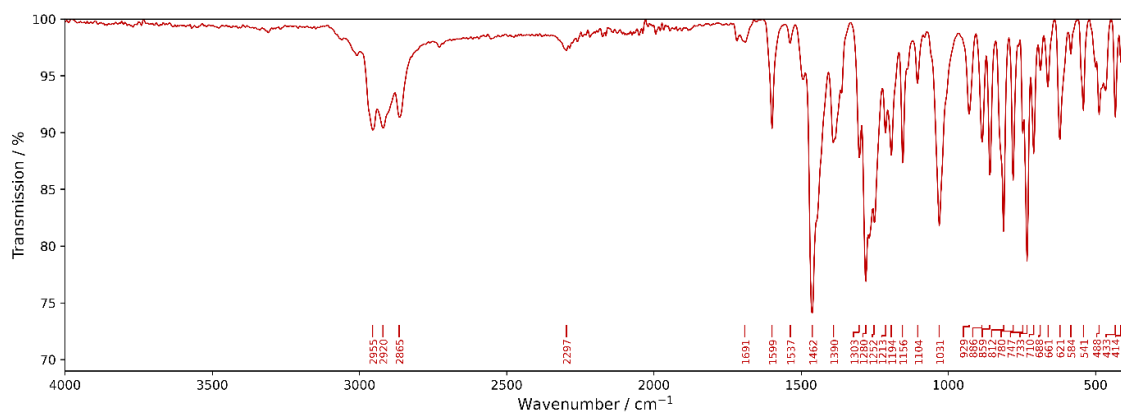


Figure S 66: ATR-IR spectrum of **2c**.

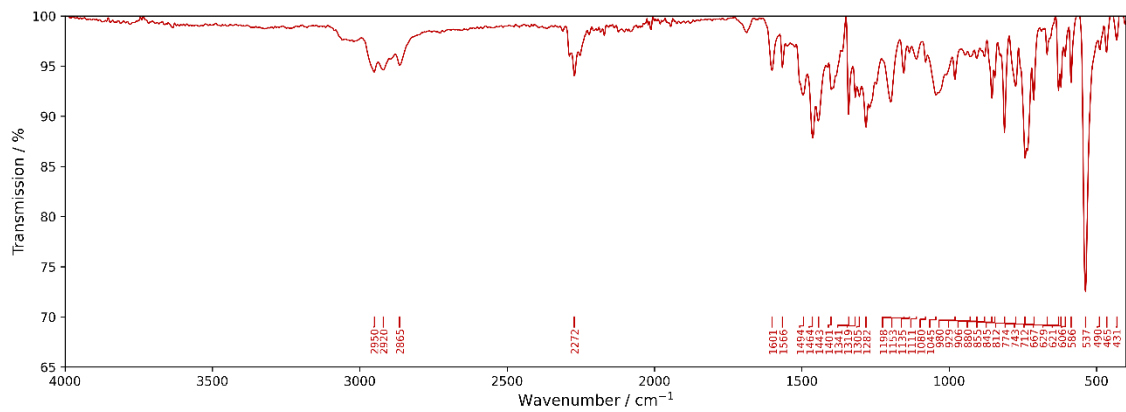


Figure S 67: ATR-IR spectrum of 3.

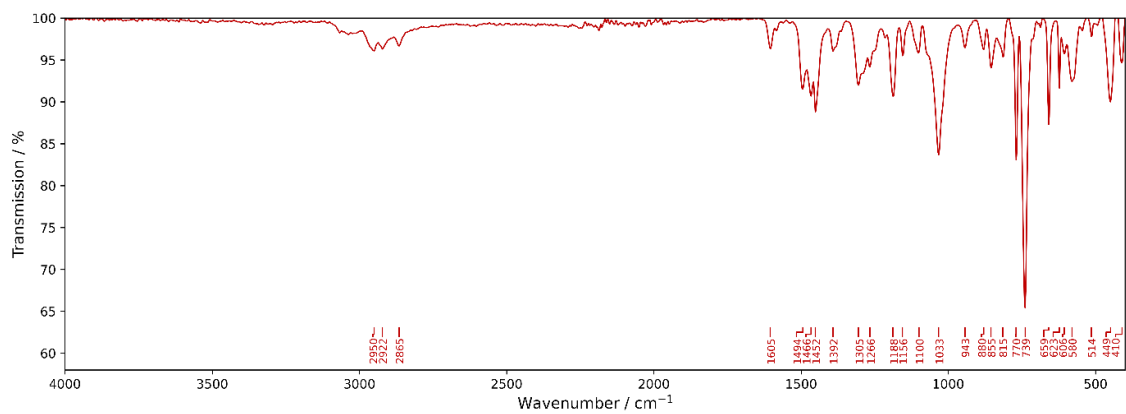


Figure S 68: ATR-IR spectrum of 4.

5. Crystallographic Details

Table S1: Crystallographic details on complexes **1b**, **1c**, **2a-c**, **3**, **4** and **5'**.

	1b	1c	1d	2a	2a' *	2b	2c	3	4	5'
Chemical formula	C ₅₀ H ₆₈ N ₂ P ₃ La C ₆ H ₁₄	C ₄₈ H ₇₂ N ₂ P ₃ La	C ₆₂ H ₈₄ N ₂ P ₃ La	C ₆₆ H ₈₂ N ₂ O ₁ P ₃ La 2.3 [C ₇ H ₈]	C ₆₆ H ₈₂ N ₂ O ₁ P ₂ La 1 [C ₇ H ₈]	C ₆₅ H ₇₆ N ₂ O ₁ P ₃ La	C ₆₁ H ₈₀ N ₂ O ₁ P ₃ La1 2(C ₆ H ₁₄)	C ₅₇ H ₇₀ N ₂ O ₁ P ₂ La	C ₅₇ H ₇₁ N ₂ O ₁ P ₂ La	C ₁₁₂ H ₁₁₀ N ₂ O ₆ P ₂ Cl ₅ La 2(B ₁ C ₂₄ F ₂₀) 4.11(CH ₂ Cl ₂) 1.25 C ₅ H ₁₂
<i>M_r</i>	1015.05	908.89	1089.13	1409.63	1242.78	1109.07	1261.43	1000.00	1001.00	4153.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>Pc</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	17.744(2)	13.2662(5)	15.214(3)	11.2622(5)	11.2398(5)	19.2050(11)	19.7451(12)	22.8982(12)	14.6738(8)	21.6976(11)
<i>b</i> (Å)	11.872(1)	16.5766(6)	20.568(3)	12.9391(6)	12.9575(5)	21.1858(12)	14.8165(8)	18.2040(11)	16.8989(7)	23.1126(12)
<i>c</i> (Å)	25.871(3)	23.4434(8)	19.803(4)	24.8329(12)	24.8031(11)	15.0967(7)	22.0097(16)	14.9403(9)	22.1725(1)	23.6214(12)
α (°)	90	90	90	84.844(2)	85.005(2)	90	90	90	87.752(2)	116.781(2)
β (°)	100.603(2)	106.2670(10)	108.256(3)	87.632(2)	87.618(2)	108.506(2)	93.176(2)	124.754(2)	78.029(2)	90.201(2)
γ (°)	90	90	90	67.020(3)	66.917(2)	90	90	90	75.074(2)	116.275(2)
<i>V</i> (Å ³)	5356.9(9)	4949.0(3)	5885.0(18)	3318.0(3)	3310.4(2)	5824.8(5)	6429.1(7)	5116.7(5)	5196.5(4)	972.7(8)
<i>Z</i>	4	4	4	2	2	4	4	4	4	2
Density (g cm ⁻³)	1.259	1.220	1.229	1.411	1.247	1.265	1.303	1.298	1.279	1.504
<i>F</i> (000)	2136	1904	2288	1485	1303	2312	2680	2084	2088	4146
Radiation Type	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
μ (mm ⁻¹)	0.923	0.991	0.845	0.769	0.761	0.857	0.784	0.937	0.923	0.991
Crystal size	0.45x0.38x0.01	0.10x0.09x0.08	0.10x0.08x0.07	0.20x0.19x0.07	0x20x0.19x0.07	0.38x0.32x0.30	0.45x0.40x0.35	0.05x0.04x0.02	0.15x0.14x0.10	0.21x0.18x0.15
Meas. Refl.	51208	119090	19415	168394	118106	172927	117564	56087	174927	37781
Indep. Refl.	11410	11399	5473	15305	11780	28386	14784	4763	19335	37781
Obsvd. [<i>I</i> > 2σ(<i>I</i>)]	8701	10596	4338	14278	9283	24611	12436	3804	13350	27796
<i>R</i> _{int}	0.0701	0.0391	0.0662	0.0385	0.1365	0.0597	0.0564	0.1188	0.1382	0.0861
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0414	0.0291	0.0403	0.0273	0.0405	0.0305	0.0296	0.0406	0.0475	0.0878
w <i>R</i> (<i>F</i> ²)	0.1327	0.0687	0.0894	0.0690	0.0946	0.0617	0.0834	0.1057	0.1299	0.2174
<i>S</i>	0.887	1.073	1.016	1.097	1.017	1.008	1.019	1.014	1.035	1.111
Δρ _{max}	1.891	0.880	0.799	0.657	0.436	0.430	0.329	0.456	2.787	1.980
Δρ _{min}	-0.835	-0.710	-1.006	-0.708	-0.890	-0.520	-0.653	-1.013	-0.938	-1.197
CCDC	2125273	2214931	2125577	2214933	2300656	2214999	2214932	2214929	2214934	2214930

*data after irradiation for 20 h with broad band light source used for photolysis experiments inside the EPR tube/instrument.

Table S2: Selected bond lengths in Å and angles in ° of complexes **1b**, **2a**, **2b**, **3a**, **3b**.

	1b	1c	1d	2a	2a[*]	2b	2c	3	4	5[#]
La1 – P1	3.126(1)	3.1164(5)	3.1142(9)	3.1364(5)	3.1359(9)	3.1334(11)	3.1520(6)	3.1444(10)	3.1718(13)	-
La1 – P2	3.1400(9)	3.1195(5)	-	3.1609(5)	3.1576(96)	3.1659(12)	3.1394(5)	-	3.11757(13)	-
La1 – N1	2.414(3)	2.4230(17)	2.404(3)	2.4463(14)	2.444(3)	2.453(3)	2.4452(16)	2.395(3)	2.419(4)	-
La1 – N2	2.392(3)	2.4131(16)	-	2.4421(15)	2.2437(3)	2.443(3)	2.4572(16)	-	2.422(4)	-
La1 – P70	3.009(1)	2.8364(6)	2.9216(14)	-	-	-	-	-	-	-
La1 – O1	-	-	-	2.1867(13)	2.182(2)	2.191(3)	2.1776(14)	2.261(4)	2.193(3)	2.469(9)
O1 – C80	-	-	-	1.401(2)	1.400(4)	1.402(5)	1.413(2)	1.303(6)	1.395(6)	1.228(16)
P70 – C70	1.763(5)	1.843(3)	1.851(3)	-	-	-	-	-	-	-
C80 – P70	-	-	-	1.9163(19)	1.918(4)	1.924(4)	1.895(2)	-	-	-
P70 – H70	1.32(2)	1.37(4)	-	1.32(4)	1.34(5)	1.39(3)	1.39(5)	-	-	-
P1–La1–P2/P1	157.86(3)	162.302(15)	158.77(4)	158.119(13)	158.02(3)	162.73(3)	158.087(14)	172.44(4)	177.58(4)	-
N1–La1–N2/N1	124.2(1)	125.11(6)	116.97(13)	124.17(5)	124.15(10)	122.55(11)	123.65(6)	115.08(15)	115.89(14)	-
N1–La1–O1/P70	112.23(8)	114.12(4)	121.51(7)	117.28(5)	117.60(9)	120.93(11)	117.22(6)	122.46(8)	120.45(13)	-
N2–La1–O1/P70	121.67(7)	120.77(4)	-	118.54(5)	118.25(10)	116.38(11)	118.91(6)	-	123.66(13)	-
P1–La1–O1/P70	85.14(3)	97.480(19)	100.617(18)	100.09(4)	100.12(47)	98.67(8)	100.44(5)	86.22(18)	87.38(9)	-
P2–La1–O1/P70	117.01(3)	100.17(2)	-	101.77(4)	101.85(7)	98.13(8)	101.00(5)	-	90.20(9)	-
La1–P70–C70	101.3(1)	144.59(9)	126.65(10)	-	-	-	-	-	-	-
La1–O1–C80	-	-	-	177.79(12)	178.0(2)	167.8(3)	176.90(15)	180.0	176.2(3)	170.2(11)
O1–C80–P70	-	-	-	103.22(12)	103.5(2)	107.4(3)	103.35(14)	-	-	-

[#] Only the La1-O1 and the O1-C80 distances, as well as the PN bound La1-O1-C80 angles are given since all other structural parameters are merely comparable to the body structures of the manuscript. The values given are averages over all La1-O1 (range 2.457(9) – 2.484(11) Å) and O1-C80 (range 1.223(15) – 1.243(15) Å) distances.

*data after irradiation for 20 h with broad band light source used for photolysis experiments inside the EPR tube/instrument.

6. Computational Details

All DFT calculations were performed with Gaussian 09.⁶ Geometries were fully optimized in gas phase without symmetry constraints, employing the B3PW91 functional.^{7,8} La atom was treated with a Stuttgart effective core potential⁹ augmented with a polarization function ($\zeta_f = 1.000$ for La).¹⁰ For P, N, C and H atoms, Pople's double- ζ basis set 6-31G(d,p) was used.^{11,12} Calculations of vibrational frequencies were systematically done in order to characterize the nature of stationary points. Analytical frequency calculations at 298.15 K and 1 atm were systematically done in order to characterize the nature of stationary points. IRC calculations were carried out in order to confirm the connectivity between reactant(s), transition state and product(s). TDDFT calculations were also carried out using Gaussian09.

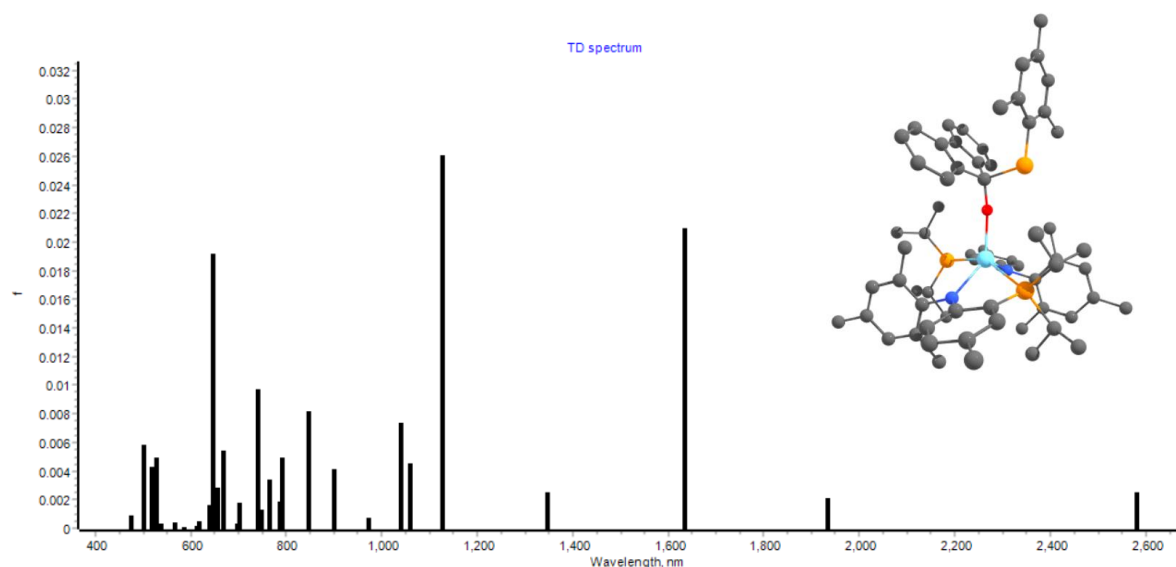


Figure S 69: TD-DFT spectra of complex **2a**.

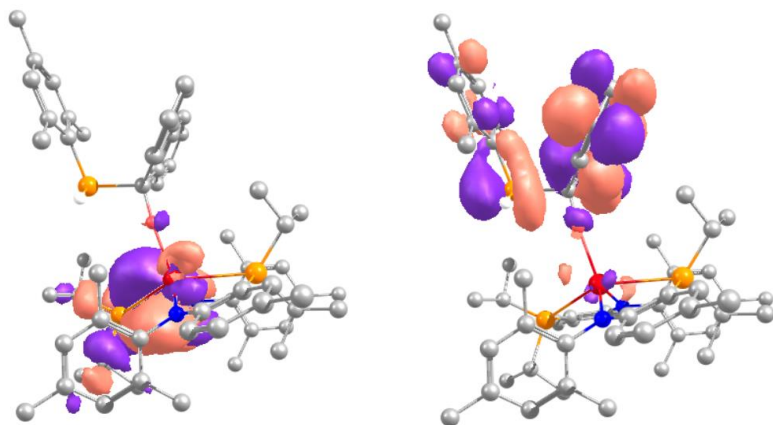


Figure S 70: Calculated HOMO (right) and LUMO (left) of complex **2a**. The LUMO corresponds to the antibonding P-C orbital.

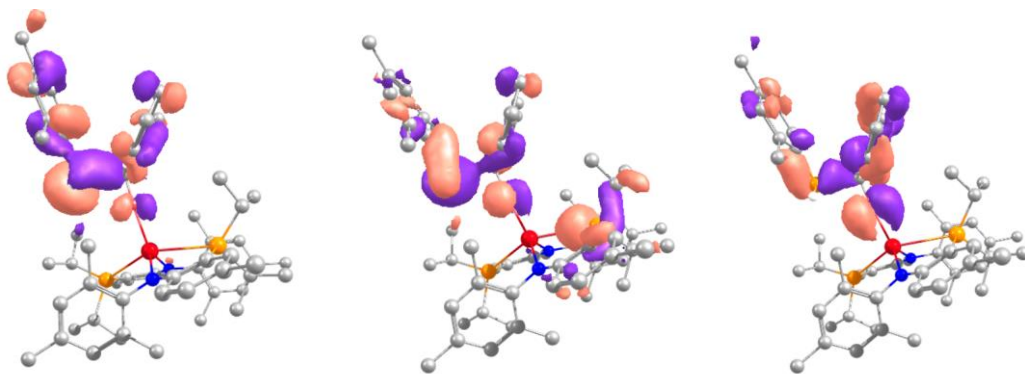


Figure S 71: Calculated HOMO-3, HOMO-15 and HOMO-17 involving the P-C bond.

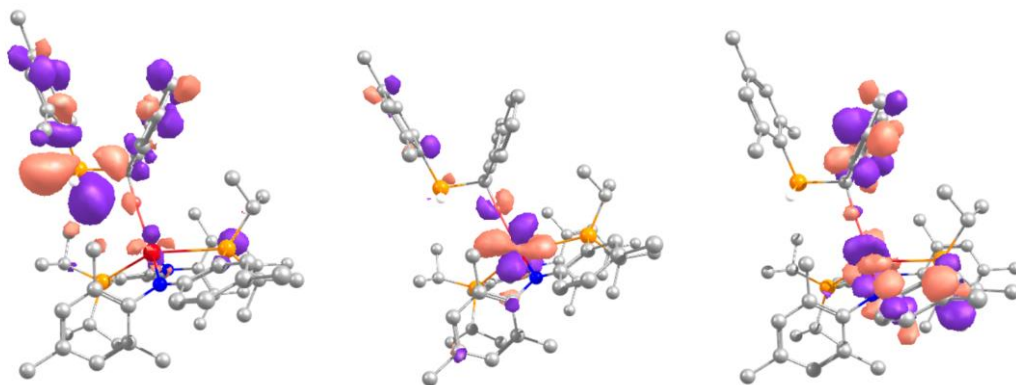


Figure S 72: MOs energies that equate to transitions of $\sim 600\text{nm}$ and $\sim 1000\text{nm}$ (LUMO+24, LUMO+21 and LUMO + 22; from left to right).

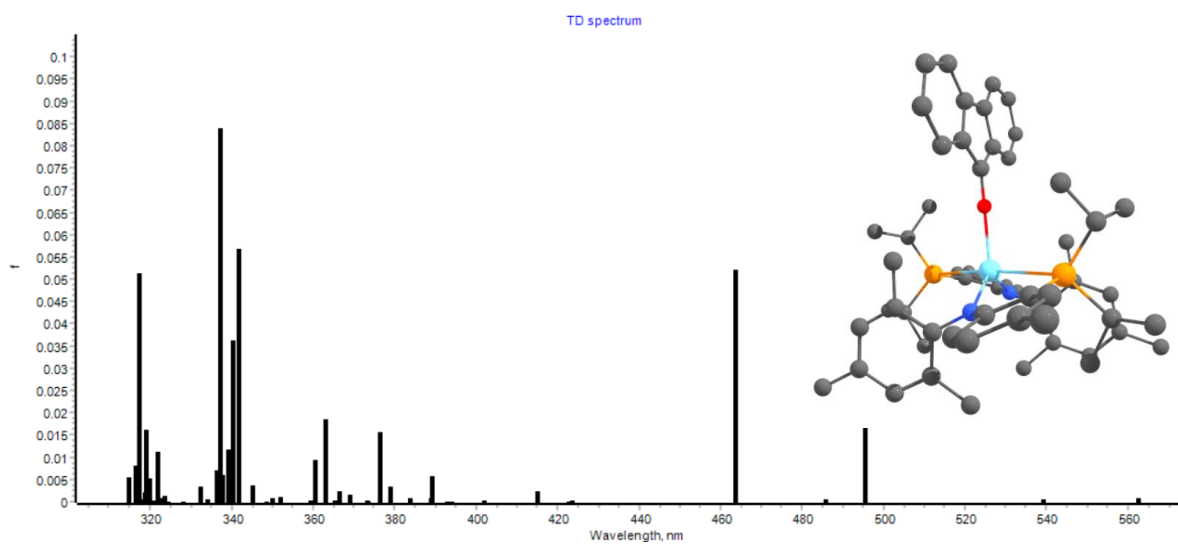


Figure S 73: TD-DFT spectrum of fluorenyl radical complex **3**.

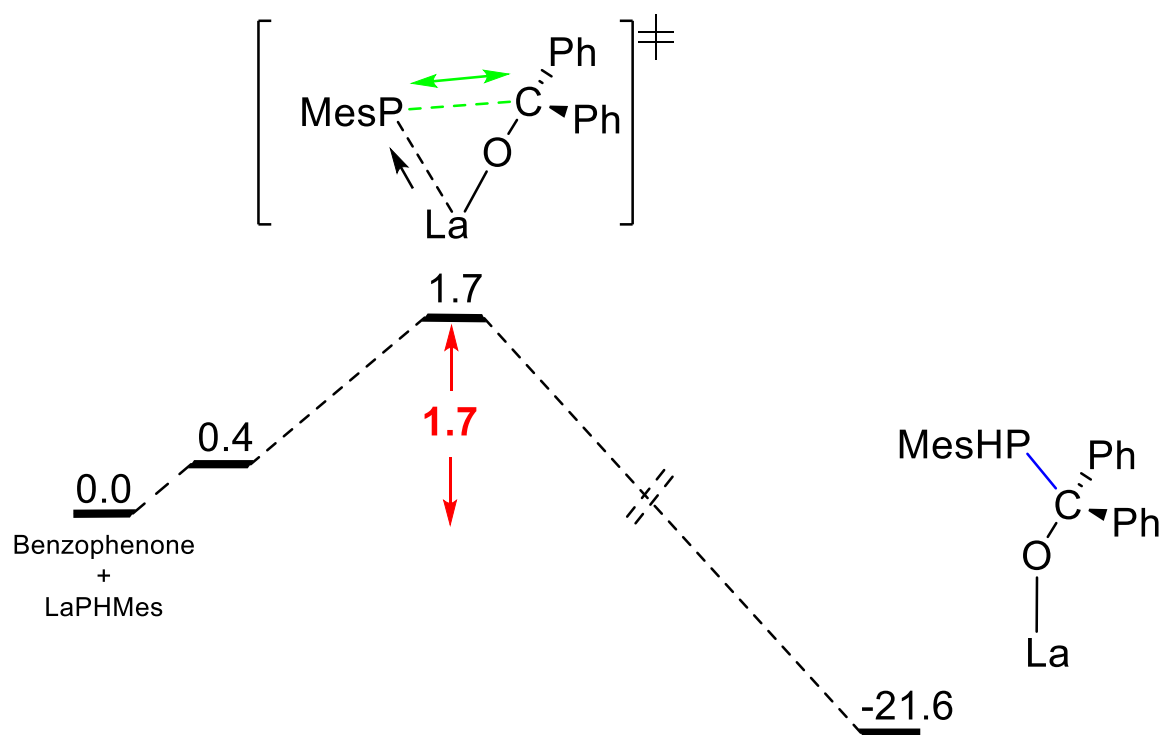


Figure S 74: Calculated insertion mechanism of benzophenone into the La-P bond.

Geometries							
				C	12.791023000	3.739322000	22.625568000
Complex 2a:				C	14.912259000	9.125963000	15.868242000
La	11.201164000	5.327251000	19.263369000	C	14.407955000	10.192923000	15.088996000
P	10.761487000	7.554692000	21.370879000	C	10.747406000	8.345888000	24.217623000
P	10.803173000	2.388315000	17.986607000	H	11.466392000	9.156241000	24.067769000
P	13.824178000	8.449082000	17.224819000	H	10.859737000	8.005837000	25.255682000
O	12.227108000	6.332051000	17.609430000	H	9.738138000	8.759478000	24.120312000
N	12.564882000	3.546100000	20.177610000	C	14.892330000	5.252347000	19.811923000
N	8.683343000	5.875518000	19.830662000	H	15.234129000	4.313489000	19.361621000
C	7.777188000	4.930062000	19.270181000	H	15.750346000	5.925303000	19.891615000
C	8.128687000	6.990380000	20.372540000	H	14.191495000	5.702352000	19.100116000
C	9.018405000	7.936793000	21.076695000	C	11.339001000	9.950753000	19.948895000
C	13.008777000	2.316280000	19.725004000	H	11.756669000	9.391606000	19.105788000
C	12.344584000	1.633135000	18.666412000	H	11.809907000	10.941778000	19.940539000
C	13.445491000	6.180203000	15.472824000	H	10.265797000	10.084131000	19.787044000
C	11.628007000	9.249862000	21.273067000	C	6.206419000	8.467709000	20.777628000
H	11.219049000	9.859792000	22.086736000	H	5.149965000	8.684570000	20.659691000
C	14.294001000	4.993350000	21.170448000	C	6.704651000	3.962198000	17.329673000
C	12.686442000	7.005304000	16.489659000	H	6.556819000	3.952197000	16.251624000
C	12.848643000	0.415256000	18.191659000	C	14.611046000	0.460360000	19.787708000
H	12.341599000	-0.078370000	17.365659000	H	15.494961000	0.017482000	20.244139000
C	8.413237000	9.120570000	21.587154000	C	16.256825000	8.715371000	15.673386000
H	9.028924000	9.846821000	22.109298000	C	10.962180000	7.174046000	23.261846000
C	13.210359000	4.092658000	21.319470000	H	11.999834000	6.823269000	23.337433000
C	14.147039000	1.672159000	20.274008000	C	10.853737000	1.963749000	16.144999000
H	14.672997000	2.152903000	21.093459000	H	10.952074000	0.873858000	16.073719000
C	12.986691000	6.465021000	14.172063000	C	7.058150000	9.393967000	21.450421000
C	7.056952000	4.044226000	20.101436000	C	7.182407000	4.103804000	21.599064000
C	13.130760000	9.077663000	21.500087000	H	8.216921000	4.268715000	21.911326000
H	13.359197000	8.602221000	22.458952000	H	6.821792000	3.179651000	22.058532000
H	13.632878000	10.052528000	21.482581000	H	6.597546000	4.936254000	22.006778000
H	13.578936000	8.466909000	20.708848000	C	11.618673000	7.656807000	15.634633000
C	7.600679000	4.887924000	17.872899000	C	10.037649000	6.014866000	23.618282000

H	8.986688000	6.316185000	23.550234000	C	14.602498000	4.936560000	13.267051000
H	10.226521000	5.670619000	24.642205000	H	15.068142000	4.450907000	12.413875000
H	10.187482000	5.161646000	22.949700000	C	14.503697000	-1.506317000	18.187871000
C	6.755648000	7.296276000	20.255701000	H	13.871323000	-1.885228000	17.379236000
H	6.121148000	6.602213000	19.713961000	H	14.541703000	-2.278839000	18.965453000
C	13.573435000	5.855904000	13.063785000	H	15.520508000	-1.404922000	17.789017000
H	13.229745000	6.080737000	12.057492000	C	14.452683000	5.244707000	15.671156000
C	5.983197000	3.073152000	18.127383000	H	14.775819000	4.986433000	16.675606000
C	14.877967000	5.565132000	22.304208000	C	9.434023000	1.288426000	20.175111000
H	15.711822000	6.252510000	22.172084000	H	10.347447000	0.821766000	20.556728000
C	13.413366000	4.324129000	23.729607000	H	8.576750000	0.732624000	20.572142000
H	13.083241000	4.038707000	24.726912000	H	9.378848000	2.304651000	20.574308000
C	13.981705000	-0.199643000	18.724510000	C	15.029384000	4.622903000	14.560456000
C	9.408177000	1.275589000	18.647826000	H	15.814825000	3.885976000	14.704309000
H	8.496967000	1.788444000	18.315942000	C	10.543762000	8.440691000	16.032356000
C	13.027048000	10.765555000	15.279196000	H	10.371364000	8.649120000	17.084893000
H	12.288208000	10.254184000	14.653958000	C	16.944302000	7.678632000	16.527017000
H	13.014392000	11.824599000	15.003505000	H	16.986301000	7.980765000	17.579660000
H	12.687253000	10.681379000	16.315637000	H	17.973983000	7.533160000	16.188736000
C	6.184442000	3.128886000	19.509723000	H	16.440257000	6.710044000	16.480391000
H	5.633742000	2.446821000	20.155294000	C	6.472309000	10.656809000	22.006432000
C	11.845438000	7.380769000	14.273757000	H	5.676350000	10.430549000	22.727224000
C	14.449083000	5.252638000	23.595734000	H	6.008237000	11.250367000	21.208333000
C	15.210951000	10.767035000	14.097411000	H	7.222466000	11.276834000	22.503867000
H	14.801695000	11.583591000	13.504981000	C	9.399496000	-0.159500000	18.124228000
C	8.309955000	5.872424000	16.983145000	H	9.301386000	-0.216303000	17.036263000
H	8.211248000	6.893952000	17.360782000	H	8.548361000	-0.701628000	18.554541000
H	7.904794000	5.847587000	15.968339000	H	10.308248000	-0.694779000	18.417006000
H	9.386122000	5.670218000	16.880591000	C	12.065065000	2.610181000	15.479143000
C	11.727477000	2.697165000	22.826294000	H	12.017203000	3.701771000	15.533073000
H	10.803873000	2.951472000	22.297579000	H	12.104919000	2.336025000	14.418552000
H	11.492798000	2.573998000	23.886942000	H	13.001858000	2.293723000	15.944085000
H	12.051747000	1.727988000	22.431380000	C	17.017962000	9.323383000	14.673655000

H	18.047162000	8.998036000	14.533298000	N	11.023040000	9.159719000	20.436616000
C	4.993924000	2.108477000	17.527615000	C	9.746080000	8.578610000	20.643612000
H	3.964083000	2.457409000	17.672120000	C	11.110894000	10.540723000	20.462037000
H	5.065380000	1.118908000	17.990673000	C	12.368486000	11.200394000	20.351805000
H	5.150996000	1.989692000	16.451828000	C	13.284443000	4.113422000	20.595606000
C	9.552934000	2.379171000	15.456951000	C	12.262458000	3.512498000	19.806522000
H	8.670002000	1.914068000	15.904687000	C	14.300497000	6.773017000	15.477840000
H	9.582369000	2.091553000	14.399268000	C	15.024334000	11.048960000	19.067686000
H	9.415832000	3.464553000	15.497424000	H	15.154472000	12.072807000	19.438545000
C	15.094419000	5.884874000	24.801128000	C	15.548129000	6.466172000	21.151540000
H	16.187062000	5.860994000	24.728385000	C	13.342180000	7.611188000	16.161348000
H	14.807836000	5.371216000	25.723132000	C	12.279890000	2.132399000	19.567816000
H	14.803264000	6.936981000	24.906463000	H	11.505894000	1.697399000	18.939494000
C	11.007971000	7.920395000	13.297716000	C	12.425898000	12.599295000	20.312612000
H	11.178593000	7.721174000	12.243003000	H	13.393332000	13.083120000	20.199002000
C	9.931710000	8.714263000	13.698887000	C	14.317050000	5.993725000	21.666450000
H	9.267357000	9.136942000	12.949942000	C	14.257919000	3.238704000	21.140751000
C	16.512184000	10.337311000	13.857966000	H	15.048458000	3.656675000	21.756989000
C	9.694049000	8.964745000	15.053883000	C	14.374984000	7.192157000	14.116063000
H	8.846872000	9.578453000	15.347435000	C	9.267766000	8.328476000	21.955800000
C	17.348476000	10.940795000	12.761704000	C	16.393570000	10.367658000	19.023914000
H	17.301964000	10.331245000	11.850532000	H	16.885196000	10.347503000	20.001585000
H	18.401972000	11.008437000	13.051009000	H	17.055464000	10.900727000	18.331607000
H	17.002710000	11.945196000	12.500090000	H	16.309813000	9.336059000	18.665691000
H	14.765946000	7.523680000	17.763571000	C	8.934008000	8.227182000	19.540109000
				C	14.092410000	6.047746000	23.065058000
				C	15.222913000	11.842419000	22.238084000
				H	15.945994000	12.189941000	21.494150000
				H	15.720460000	11.877587000	23.215234000
				H	14.392425000	12.554389000	22.269727000
				C	15.879126000	6.303226000	19.689410000
				H	15.683137000	5.278190000	19.360401000
				H	16.933471000	6.526335000	19.504892000
Complex 3							
La	12.437235000	7.387199000	19.587345000				
P	13.886627000	10.152582000	20.280964000				
P	10.931660000	4.606672000	19.145028000				
O	13.002938000	7.529405000	17.427225000				
N	13.324419000	5.482832000	20.791233000				

H	15.308804000	6.966523000	19.024547000	H	14.893577000	6.609755000	24.970909000
C	14.383139000	11.106687000	17.682075000	C	13.253014000	1.282080000	20.093472000
H	14.219323000	10.104790000	17.274521000	C	9.394070000	4.148600000	20.167635000
H	15.038627000	11.641590000	16.985042000	H	8.637106000	4.862583000	19.819256000
H	13.420604000	11.624436000	17.702222000	C	8.021284000	7.729261000	22.128908000
C	10.063683000	12.755640000	20.545473000	H	7.664195000	7.548551000	23.141599000
H	9.151326000	13.344465000	20.626896000	C	13.446916000	8.306566000	13.940497000
C	7.690836000	7.621700000	19.762033000	C	16.287648000	7.071552000	23.400912000
H	7.069959000	7.370866000	18.903688000	C	9.348593000	8.590437000	18.136162000
C	14.236418000	1.874516000	20.896018000	H	9.649310000	9.641295000	18.082143000
H	15.014377000	1.251897000	21.335187000	H	8.522246000	8.434076000	17.437413000
C	14.725098000	10.424059000	21.967013000	H	10.188713000	7.998066000	17.747957000
H	15.581565000	9.738666000	21.935440000	C	12.828170000	5.485199000	23.651915000
C	10.551944000	3.911187000	17.430076000	H	11.937934000	5.915384000	23.183879000
H	10.293278000	2.853039000	17.557019000	H	12.777761000	5.670540000	24.728256000
C	11.294047000	13.409891000	20.404031000	H	12.769952000	4.403302000	23.487928000
C	10.078726000	8.749558000	23.149180000	C	16.013987000	5.483997000	13.696358000
H	11.090515000	8.334587000	23.118239000	H	16.687002000	4.973567000	13.012774000
H	9.602075000	8.431874000	24.080455000	C	13.252207000	-0.197165000	19.811196000
H	10.193484000	9.838872000	23.177446000	H	12.381535000	-0.487973000	19.215729000
C	12.822939000	8.555568000	15.199118000	H	13.231293000	-0.786501000	20.735673000
C	13.782600000	9.956115000	23.075417000	H	14.146735000	-0.505049000	19.255915000
H	12.873020000	10.564629000	23.098952000	C	15.083454000	5.704344000	15.930416000
H	14.273708000	10.045707000	24.051354000	H	15.017901000	5.372007000	16.961946000
H	13.498003000	8.908138000	22.949191000	C	9.671162000	4.432699000	21.643341000
C	9.968561000	11.372985000	20.572920000	H	10.475865000	3.794091000	22.021162000
H	8.991571000	10.908486000	20.668447000	H	8.773843000	4.233595000	22.240665000
C	15.232078000	6.546487000	13.232647000	H	9.948460000	5.477043000	21.809519000
H	15.297558000	6.858498000	12.193117000	C	15.937015000	5.067567000	15.032967000
C	7.213027000	7.364655000	21.046102000	H	16.549607000	4.235801000	15.370775000
C	16.502706000	7.000074000	22.024188000	C	11.881806000	9.584300000	15.328068000
H	17.452205000	7.341934000	21.615505000	H	11.416389000	9.787088000	16.287851000
C	15.075806000	6.582253000	23.897877000	C	11.386500000	14.912108000	20.352278000

H	10.976257000	15.375603000	21.257589000
H	10.829537000	15.323826000	19.501833000
H	12.424740000	15.243423000	20.254960000
C	8.872710000	2.725768000	19.975752000
H	8.608052000	2.505207000	18.937361000
H	7.967952000	2.580756000	20.578986000
H	9.607777000	1.986266000	20.308183000
C	11.783397000	4.011549000	16.531373000
H	12.089017000	5.052027000	16.386445000
H	11.563657000	3.592891000	15.542390000
H	12.633921000	3.464490000	16.946238000
C	5.857537000	6.747144000	21.269966000
H	5.151898000	7.478959000	21.681321000
H	5.907270000	5.915869000	21.981496000
H	5.431128000	6.366894000	20.337514000
C	9.352560000	4.638623000	16.818889000
H	8.449529000	4.550311000	17.430973000
H	9.125027000	4.221788000	15.830945000
H	9.565473000	5.704299000	16.682155000
C	17.324818000	7.658609000	24.321894000
H	18.336770000	7.504695000	23.934835000
H	17.272884000	7.210562000	25.318864000
H	17.185018000	8.739751000	24.444727000
C	13.118801000	9.079597000	12.832976000
H	13.588250000	8.898239000	11.869126000
C	12.173957000	10.100994000	12.971579000
H	11.911260000	10.710384000	12.111153000
C	11.564074000	10.350153000	14.209267000
H	10.836103000	11.152581000	14.295512000

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