

# A Bridging Bis-Phosphanido-Phosphinidene Complex of Lanthanum Supported by a Sterically Encumbering PN Ligand

## Supporting Information

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## General Considerations

Unless otherwise stated, all operations were performed in a GS glovebox under an atmosphere of purified argon or using high-vacuum standard Schlenk techniques under an argon atmosphere. Solvents were purchased from Aldrich in Sure-Seal reservoirs (18L) and were dried using an MBraun SPS and stored over 3 Å molecular sieves at least 3 days prior to use. THF and DME was distilled, under argon, from purple sodium benzophenone ketyl and stored with 3 Å molecular sieves. Celite® and 3 Å molecular sieves were activated under vacuum overnight at 250 °C. 4,4"-di-tert-butyl-2'-iodo-1,1':3',1"-terphenyl was synthesized following a previously reported procedure.<sup>1</sup> Compound **O** was synthesized through slightly modified procedure to the literature.<sup>2</sup> All other chemicals were used as received unless otherwise stated. CDCl<sub>3</sub> was used as received. Toluene-d<sub>8</sub> and C<sub>6</sub>D<sub>6</sub> was stored over 3 Å molecular sieves. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on 400 MHz Bruker Avance 4 Neo spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks. <sup>31</sup>P NMR chemical shifts are reported with respect to external H<sub>3</sub>PO<sub>4</sub> (aqueous solution, delta 0.0 ppm). IR spectra were measured neat on an IR Bruker Alpha ATR spectrometer. All UV/Vis/NIR spectra were collected on an Avantes spectrometer equipped with a deuterium and halogen light source and a CMOS detector. Elemental analysis was performed using an Elementar vario microcube instrument at the University of Innsbruck.

Single crystal X-ray diffraction were collected on a Bruker D8 Quest diffractometer under a stream of N<sub>2</sub>(g) at low temperatures. Data was collected using the ApexIV software package. Structures were solved using SHELXT<sup>3</sup> and refined using the OLEX 2 software package.<sup>4</sup> All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model. In case of heavily disordered solvents, the SQUEEZE algorithm was applied.<sup>5</sup> 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.

## Experimental Section

### *Preparation of O.*

In a 100 mL Schlenk flask 4,4"-di-tert-butyl-2'-iodo-1,1':3',1"-terphenyl **N** (1.0 equiv., 36.00 mmol, 16.86 g), sodium *tert*-butoxide (1.2 equiv., 43.20 mmol, 4.15 g), Pd(OAc)<sub>2</sub> (6 mol%) and dppf (12 mol%) were combined and suspended in toluene (50 mL). The reaction vessel was brought outside of the glovebox and 2-bromo-4-methylaniline **M** (1.5 equiv., 53.99 mmol, 10.05 g) was added *via* syringe. Afterwards the reaction heated to 120 °C and stirred for 96 hours. The reaction was allowed to cool down to room temperature and filtered through Celite®. All volatile components were removed under reduced pressure. The residue was redissolved in diethyl ether (100 mL) and washed twice with water (50 mL) and once with brine (50 mL). The organic phase dried over anhydrous sodium sulfate, filtered through a medium porosity frit and all volatile components were removed under reduced pressure. Finally, the residue redissolved in hexane and filtered through a tall silica pad. The crude product was recrystallized from 2-propanol. 5.59 g (29.5 %) of colorless crystals. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.47 (d, *J* = 8.4 Hz, 4H, CH<sub>Ar</sub>), 7.41 (d, *J* = 7.6 Hz, 2H, CH<sub>Ar</sub>), 7.20 (d, *J* = 8.4 Hz, 4H, CH<sub>Ar</sub>), 6.91 (s, 1H, CH<sub>Ar</sub>), 6.45 (s, 1H, CH<sub>Ar</sub>), 6.44 (s, 1H, CH<sub>Ar</sub>), 5.94 (s, 1H, NH), 1.74 (s, 3H, CH<sub>3</sub>), 1.14 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 150.1 (C<sub>Ar</sub>), 140.6 (C<sub>Ar</sub>), 138.8 (C<sub>Ar</sub>), 137.4 (C<sub>Ar</sub>), 136.8 (C<sub>Ar</sub>), 132.7 (CH<sub>Ar</sub>), 130.8 (CH<sub>Ar</sub>), 129.2 (CH<sub>Ar</sub>), 128.9 (CH<sub>Ar</sub>), 125.7 (CH<sub>Ar</sub>), 125.6 (C<sub>Ar</sub>), 115.5 (CH<sub>Ar</sub>), 111.4 (C<sub>Ar</sub>), 34.5 (C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 19.9 (CH<sub>3</sub>). Hi – Res Mass (ESI<sup>+</sup>) *calc'd* for [C<sub>33</sub>H<sub>37</sub>BrN]<sup>+</sup>: 526.2104; found: 526.2099. Elemental analysis (%) *calc'd* for C<sub>33</sub>H<sub>36</sub>BrN: C, 75.27; H, 6.89; N, 2.66; found: C, 75.42; H, 6.90; N, 2.60. UV/VIS/NIR: λ = 324 (ε = 18960 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 3400, 2967, 2950, 2903, 2865, 1499, 1460, 1441, 1392, 1360, 1292, 1270, 1198, 1145, 1119, 1102, 1076, 1037, 1019, 1006, 841, 829, 790, 747, 733, 686, 672, 653, 606, 596, 578, 557, 433.

### *Preparation of HPN<sup>Terph</sup>.*

In a 100 mL Schlenk flask compound **O** (1.0 equiv., 10.62 mmol, 5.59 g) was dissolved in diethyl ether (50 mL) and cooled down to – 114 °C using an ethanol/liquid nitrogen bath. Afterwards a 2.5 M solution of <sup>n</sup>BuLi in hexane (2.1 equiv., 22.29 mmol, 8.92 mL) was added *via* syringe. The reaction vessel was allowed to warm up to room temperature and stirred over night. At the next day the reaction mixture cooled to – 114 °C and chlorodiisopropylphosphine (1.05 equiv., 11.15 mmol, 1.70 g) was added *via* syringe. After reaching room temperature a yellow suspension was observed and stirred for 48 hours. The reaction mixture was quenched with carefully degassed water (5 mL) and stirred for further 30 min. Afterwards diethyl ether (100 mL) was added to the mixture and washed twice with water (50 mL) and once with brine (50 mL). All volatile components were removed under reduced pressure, redissolved in hexane (70 mL) and filtered through a silica pad. Finally, the crude product crystallized from hexane at room temperature. 4.84 g (80.9 %) of a white solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.44 (d, *J* = 8.4 Hz, 4H, CH<sub>Ar</sub>), 7.39 (d, *J* = 7.6 Hz, 2H, CH<sub>Ar</sub>), 7.17 (d, *J* = 8.6 Hz, 4H, CH<sub>Ar</sub>), 7.04 (d, *J* = 9.8 Hz, 1H, NH), 6.93 – 6.85 (m, 1H, CH<sub>Ar</sub>), 6.66 (dd, *J* = 8.3, 1.8 Hz, 1H, CH<sub>Ar</sub>), 6.49 (dd, *J* = 8.4, 5.1 Hz, 1H, CH<sub>Ar</sub>),

1.96 (s, 3H, CH<sub>3</sub>), 1.87 (ddt, *J* = 10.9, 6.9, 3.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.00 (dd, *J* = 15.4, 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.86 (dd, *J* = 11.9, 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 149.4 (C<sub>Ar</sub>), 140.1 (C<sub>Ar</sub>), 138.1 (C<sub>Ar</sub>), 137.3 (C<sub>Ar</sub>), 132.8 (CH<sub>Ar</sub>), 132.8 (C<sub>Ar</sub>), 130.9 (CH<sub>Ar</sub>), 130.5 (CH<sub>Ar</sub>), 129.1 (CH<sub>Ar</sub>), 126.3 (C<sub>Ar</sub>), 125.4 (CH<sub>Ar</sub>), 118.0 (C<sub>Ar</sub>), 113.3 (CH<sub>Ar</sub>), 34.4 (C<sub>Ar</sub>), 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 24.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.8 (CH<sub>3</sub>), 20.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.8 (CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -17.30 (s, 1P); <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -17.31 (s, 1P). Hi – Res Mass (ESI<sup>+</sup>) *calc'd* for [C<sub>39</sub>H<sub>51</sub>NP]<sup>+</sup>: 564.3754; found: 564.3737. Elemental analysis (%) *calc'd* for C<sub>39</sub>H<sub>50</sub>NP: C, 83.08; H, 8.94; N, 2.48; found: C, 82.81; H, 9.03; N, 2.35. UV/VIS/NIR: λ = 327 (ε = 29560 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2963, 2865, 1605, 1497, 1445, 1392, 1362, 1296, 1264, 1200, 1145, 1115, 1100, 1017, 880, 827, 806, 788, 745, 731, 686, 655, 608, 596, 578, 559, 492.

#### Preparation of **LiPN<sup>Terph</sup>**.

In a 10 mL Schlenk flask, compound **HPN<sup>Terph</sup>** (1.0 equiv., 206 μmol, 116 mg) was dissolved in pentane (8 mL) and a 2.5 M solution of <sup>n</sup>BuLi (0.98 equiv., 202 μmol, 80.7 μL) was added to the reaction mixture. The reaction mixture stirred for 48 hours at room temperature and a yellow suspension was observed. Afterwards the suspension was centrifuged and washed twice with a small amount of pentane (2x5 mL). The solid residue was dried *in vacuo*. 70.4 mg (60.1 %) of a yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.55 (m, 6H, CH<sub>Ar</sub>), 7.13 (d, *J* = 8.3 Hz, 5H, CH<sub>Ar</sub>), 6.70 (d, *J* = 8.5 Hz, 1H, CH<sub>Ar</sub>), 6.67 (d, *J* = 5.6 Hz, 1H, CH<sub>Ar</sub>), 6.34 (dd, *J* = 8.4, 6.1 Hz, 1H, CH<sub>Ar</sub>), 2.07 (s, 3H, CH<sub>3</sub>), 1.68 (dq, *J* = 13.5, 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.83 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 163.9 (C<sub>Ar</sub>), 152.6 (C<sub>Ar</sub>), 149.4 (C<sub>Ar</sub>), 148.3 (C<sub>Ar</sub>), 140.7 (C<sub>Ar</sub>), 138.6 (C<sub>Ar</sub>), 132.8 (C<sub>Ar</sub>), 129.6 (CH<sub>Ar</sub>), 129.1 (CH<sub>Ar</sub>), 124.9 (CH<sub>Ar</sub>), 120.6 (CH<sub>Ar</sub>), 117.5 (CH<sub>Ar</sub>), 114.1 (CH<sub>Ar</sub>), 110.4 (CH<sub>Ar</sub>), 110.3 (CH<sub>Ar</sub>), 34.4 (C<sub>Ar</sub>), 31.6 (C(CH<sub>3</sub>)<sub>3</sub>), 23.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.6 (CH<sub>3</sub>), 19.9 (CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -10.32 (s, 1P); <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -10.41 (s, 1P); <sup>7</sup>Li{<sup>1</sup>H} NMR (156 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -0.62 (s, 1Li); <sup>7</sup>Li NMR (156 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -0.63 (s, 1Li). Elemental analysis (%) *calc'd* for C<sub>39</sub>H<sub>49</sub>LiNP: C, 82.22; H, 8.67; N, 2.46; found: C, 82.51; H, 9.16; N, 2.21. UV/VIS/NIR: λ = 311 (ε = 48980 L mol<sup>-1</sup> cm<sup>-1</sup>), 378 (ε = 40680 L mol<sup>-1</sup> cm<sup>-1</sup>), 422 (ε = 32230 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2952, 2865, 1601, 1511, 1464, 1421, 1386, 1362, 1321, 1268, 1147, 1019, 831, 780, 745, 686, 606, 584, 557, 476.

#### Preparation of **KPN<sup>Terph</sup>**.

In a 20 mL scintillation vial, compound **HPN<sup>Terph</sup>** (1.0 equiv., 0.89 mmol, 500 mg) was dissolved in hexane (10 mL) and a suspension of KHMDs (0.98 equiv., 0.87 mmol, 173 mg) in hexane (10 mL) was added to the reaction mixture. A color change to intense orange and later a thick suspension was observed. The solid was washed with hexane (2x10 mL) and dried *in vacuo*. 473 mg (88.6 %) of a yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.52 (d, *J* = 8.3 Hz, 4H, CH<sub>Ar</sub>), 7.47 (d, *J* = 7.4 Hz, 2H, CH<sub>Ar</sub>), 7.10 (d, *J* = 8.4 Hz, 4H, CH<sub>Ar</sub>), 6.94 (t, *J* = 7.4 Hz, 1H, CH<sub>Ar</sub>), 6.92 – 6.87 (m, 1H, CH<sub>Ar</sub>), 6.79 (dd, *J* = 8.4, 1.9 Hz, 1H, CH<sub>Ar</sub>), 6.41 (dd, *J* = 8.4, 6.1 Hz, 1H, CH<sub>Ar</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 1.97 (pd, *J* = 6.8, 2.5 Hz,

2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.07 – 0.91 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 163.9 (C<sub>Ar</sub>), 163.7 (C<sub>Ar</sub>), 155.6 (C<sub>Ar</sub>), 148.7 (C(CH<sub>3</sub>)<sub>3</sub>), 141.5 (C<sub>Ar</sub>), 140.7 (C<sub>Ar</sub>), 137.4 (C<sub>Ar</sub>), 133.6 (CH<sub>Ar</sub>), 132.2 (CH<sub>Ar</sub>), 131.6 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ar</sub>), 125.3 (CH<sub>Ar</sub>), 118.1 (CH<sub>Ar</sub>), 116.7 (CH<sub>Ar</sub>), 115.5 (CH<sub>Ar</sub>), 111.9 (C<sub>Ar</sub>), 34.4 (C<sub>Ar</sub>), 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.2 (CH<sub>3</sub>), 20.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.2 (CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -12.19 (s, 1P); <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = -12.23 (s, 1P). Elemental analysis (%) *calc'd* for C<sub>39</sub>H<sub>49</sub>KNP · C<sub>4</sub>H<sub>10</sub>O: C, 76.40; H, 8.80; N, 2.07; found: C, 76.07; H, 8.44; N, 2.05. UV/VIS/NIR: λ = 318 (ε = 51950 L mol<sup>-1</sup> cm<sup>-1</sup>), 405 (ε = 54650 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2952, 2863, 1590, 1511, 1466, 1419, 1384, 1343, 1278, 1239, 1211, 1143, 835, 817, 776, 768, 602, 557, 502.

### Preparation of 1.

Compound **KPN<sup>Terph</sup>** (2.0 equiv., 0.42 mmol, 250 mg) and LaCl<sub>3</sub>(thf)<sub>1.2</sub> (1.0 equiv., 0.42 mmol, 63 mg) were combined and toluene (10 mL) was added. The resulting suspension was heated to 120 °C and stirred for 12 hours. Afterwards the suspension was filtered and all volatile components were removed *in vacuo* and redissolved in hexane and filtered through a glass fibre filter. Finally, all volatile components were removed under reduced pressure. 254 mg (94.1 %) of a yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.58 (d, *J* = 8.4 Hz, 8H, CH<sub>Ar</sub>), 7.57 (d, *J* = 7.8 Hz, 4H, CH<sub>Ar</sub>), 7.25 (t, *J* = 7.7 Hz, 2H, CH<sub>Ar</sub>), 7.07 (d, *J* = 8.3 Hz, 8H, CH<sub>Ar</sub>), 6.93 – 6.85 (m, 2H, CH<sub>Ar</sub>), 6.57 (dd, *J* = 8.5, 1.8 Hz, 2H, CH<sub>Ar</sub>), 6.01 (dd, *J* = 8.5, 5.1 Hz, 2H, CH<sub>Ar</sub>), 2.44 – 2.28 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.93 (s, 6H, CH<sub>3</sub>), 1.25 – 1.17 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 162.5 – 161.6 (m, C<sub>Ar</sub>), 150.3 (C(CH<sub>3</sub>)<sub>3</sub>), 141.5 (C<sub>Ar</sub>), 141.2 (C<sub>Ar</sub>), 136.4 (C<sub>Ar</sub>), 133.0 (CH<sub>Ar</sub>), 132.8 (CH<sub>Ar</sub>), 132.7 (C<sub>Ar</sub>), 129.5 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ar</sub>), 126.6 (CH<sub>Ar</sub>), 125.9 (CH<sub>Ar</sub>), 123.2 (C<sub>Ar</sub>), 116.4 (CH<sub>Ar</sub>), 115.2 (C<sub>Ar</sub>), 34.4 (C<sub>Ar</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.4 (CH<sub>3</sub>), 18.5 (CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 0.36 (s, 1P); <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 0.37 (s, 1P). Elemental analysis (%) *calc'd* for C<sub>78</sub>H<sub>98</sub>ClLaN<sub>2</sub>P<sub>2</sub>: C, 72.07; H, 7.60; N, 2.15; found: C, 71.90; H, 7.92; N, 1.99. UV/VIS/NIR: λ = 323 (ε = 60690 L mol<sup>-1</sup> cm<sup>-1</sup>), 370 (ε = 61310 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2959, 2903, 2869, 1603, 1513, 1470, 1423, 1386, 1364, 1280, 1262, 1215, 1202, 1151, 1117, 1098, 1019, 933, 882, 857, 827, 808, 784, 741, 731, 686, 665, 649, 608, 596, 559, 504, 467, 455.

### Preparation of 3.

Compound **HPN<sup>Terph</sup>** (1.0 equiv., 0.33 mmol, 200 mg) and LaCl<sub>3</sub>(thf)<sub>1.2</sub> (1.0 equiv., 0.33 mmol, 100 mg) were combined and 1,2-dimethoxyethane (10 mL) was added. The resulting suspension stirred for 12 hours. Afterwards the suspension was filtered and all volatile components were removed *in vacuo*. The resulting oily residue was solved in hexane and stirred at room temperature over night. On the next day the suspension was filtered, washed with a small amount of hexane (2x5 mL) and dried *in vacuo*. 203 mg (75.5 %) of a yellow solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 8.05 – 7.42 (m, 12H, CH<sub>Ar</sub>), 7.41 – 7.21 (m, 10H, CH<sub>Ar</sub>), 6.84 (d, *J* = 5.3 Hz, 2H, CH<sub>Ar</sub>), 6.68 (d, *J* = 8.0 Hz, 2H, CH<sub>Ar</sub>), 6.30 (dd, *J* = 8.2, 5.0 Hz, 2H, CH<sub>Ar</sub>), 3.23 (s, 4H, dme – CH<sub>2</sub>), 3.10 (s, 6H, dme – CH<sub>3</sub>), 2.35 – 2.20 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>),

2.11 (s, 6H, CH<sub>3</sub>), 1.29 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 – 1.13 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 161.0 (C<sub>Ar</sub>), 148.83 (C<sub>Ar</sub>), 141.53 (C<sub>Ar</sub>), 132.83 (CH<sub>Ar</sub>), 132.00 (CH<sub>Ar</sub>), 130.08 (CH<sub>Ar</sub>), 125.29 (CH<sub>Ar</sub>), 123.85 (C<sub>Ar</sub>), 123.82 (C<sub>Ar</sub>), 116.96 (C<sub>Ar</sub>), 116.27 (CH<sub>Ar</sub>), 72.03 (CH<sub>2</sub> – dme), 58.77 (CH<sub>Ar</sub> – dme), 31.49 (C(CH<sub>3</sub>)<sub>3</sub>), 23.58 (CH(CH<sub>3</sub>)<sub>3</sub>), 20.59 (CH<sub>3</sub>), 19.43 (CH(CH<sub>3</sub>)<sub>3</sub>), 18.55 (CH(CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 8.96; <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 8.92. Elemental analysis (%) *calc'd* for C<sub>82</sub>H<sub>108</sub>Cl<sub>5</sub>La<sub>2</sub>N<sub>2</sub>OP<sub>2</sub>: C, 58.14; H, 6.43; N, 1.65; found: C, 57.99; H, 6.75; N, 1.52. UV/VIS/NIR: λ = 324 (ε = 69070 L mol<sup>-1</sup> cm<sup>-1</sup>), 349 (ε = 61540 L mol<sup>-1</sup> cm<sup>-1</sup>), 399 (ε = 47680 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2955, 2869, 1601, 1501, 1468, 1423, 1386, 1364, 1315, 1272, 1247, 1196, 1145, 1127, 1100, 1082, 1060, 1033, 859, 833, 782, 751, 733, 686, 608, 592, 563, 504, 465, 422.

### Preparation of 2.

Compound **3** (1.0 equiv., 117 μmol, 200 mg) was solved in toluene (10 mL) and solid potassium mesitylphosphanide (8.2 equiv., 506 μmol, 96.3 mg) was added to the reaction mixture. The suspension stirred overnight and a color change from yellow to red was observed. On the next day the reaction mixture was filtered through a glass fibre filter and all volatile components were removed *in vacuo*. The residue was washed twice with hexane and dried *in vacuo*. 112 mg (48.9 %) of an orange powder. *Alternative preparation of 2*: Compound **1** (1.0 equiv., 38 μmol, 50 mg) was solved in toluene (5 mL) and solid potassium mesitylphosphanide (1.1 equiv., 42 μmol, 8.1 mg) was added to the reaction mixture. The suspension stirred for 48 hours. The reaction mixture was filtered through a glass fibre filter and all volatile components were removed under reduced pressure. The residue was washed with hexane and dried *in vacuo*. The solid was redissolved in diethyl ether and was concentrated to yield the product in single crystalline quantities. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 7.40 (br. s, 4H, CH<sub>Ar</sub>), 7.38 (d, *J* = 8.1 Hz, 8H, CH<sub>Ar</sub>), 7.20 (t, *J* = 7.6 Hz, 2H, CH<sub>Ar</sub>), 7.02 (br. s, 4H, CH<sub>Ar</sub>), 6.95 (br. s, 2H, CH<sub>Ar</sub>), 6.83 (d, *J* = 8.3 Hz, 8H, CH<sub>Ar</sub>), 6.77 – 6.72 (m, 4H, CH<sub>Ar</sub>), 6.19 (dd, *J* = 8.5, 4.9 Hz, 2H, CH<sub>Ar</sub>), 2.59 (s, 6H, CH<sub>3</sub>), 2.56 (s, 12H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 2.36 (s, 6H, CH<sub>3</sub>), 1.98 (br. s, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.92 (s, 6H, CH<sub>3</sub>), 1.14 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 0.79 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, in ppm) δ = 161.7 (C<sub>Ar</sub>), 150.1 (C<sub>Ar</sub>), 149.7 (C<sub>Ar</sub>), 141.5 (C<sub>Ar</sub>), 138.4 (C<sub>Ar</sub>), 136.5 (C<sub>Ar</sub>), 133.3 (CH<sub>Ar</sub>), 133.2 (CH<sub>Ar</sub>), 132.7 (CH<sub>Ar</sub>), 131.9 (C<sub>Ar</sub>), 129.8 (CH<sub>Ar</sub>), 129.3 (C<sub>Ar</sub>), 128.2 (CH<sub>Ar</sub>), 127.3 (CH<sub>Ar</sub>), 126.8 (CH<sub>Ar</sub>), 125.7 (CH<sub>Ar</sub>), 123.8 (C<sub>Ar</sub>), 116.5 (C<sub>Ar</sub>), 116.4 (C<sub>Ar</sub>), 115.2 (CH<sub>Ar</sub>), 34.4 (C<sub>Ar</sub>), 31.3 C(CH<sub>3</sub>)<sub>3</sub>, 28.0 (CH<sub>3</sub>), 24.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.4 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 18.8 (CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, toluene-*d*<sub>8</sub>, 288K, in ppm) δ = 333.98 (s, 1P), 13.44 (s, 2P), -51.69 (m, 1P), -64.06 (s, 1P). <sup>31</sup>P NMR (162 MHz, toluene-*d*<sub>8</sub>, 288K, in ppm) δ = 333.95 (s, 1P), 13.50 (s, 2P), -51.91 (br. s, 1P), -63.73 (br. s, 1P). Despite numerous attempts, due to the high reactivity of complex **2** towards moisture and air, no useful elemental analysis could be obtained. UV/VIS/NIR: λ = 327 (ε = 97980 L mol<sup>-1</sup> cm<sup>-1</sup>), 358 (ε = 99520 L mol<sup>-1</sup> cm<sup>-1</sup>), 399 (ε = 94590 L mol<sup>-1</sup> cm<sup>-1</sup>). IR (cm<sup>-1</sup>): 2961, 1599, 1468, 1419, 1392, 1290, 1270, 1147, 1027, 896, 859, 847, 833, 815, 790, 600, 584, 559, 422.

# NMR spectra

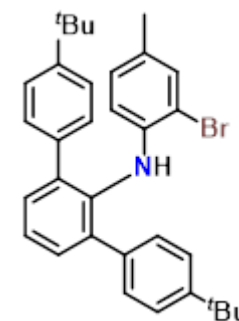
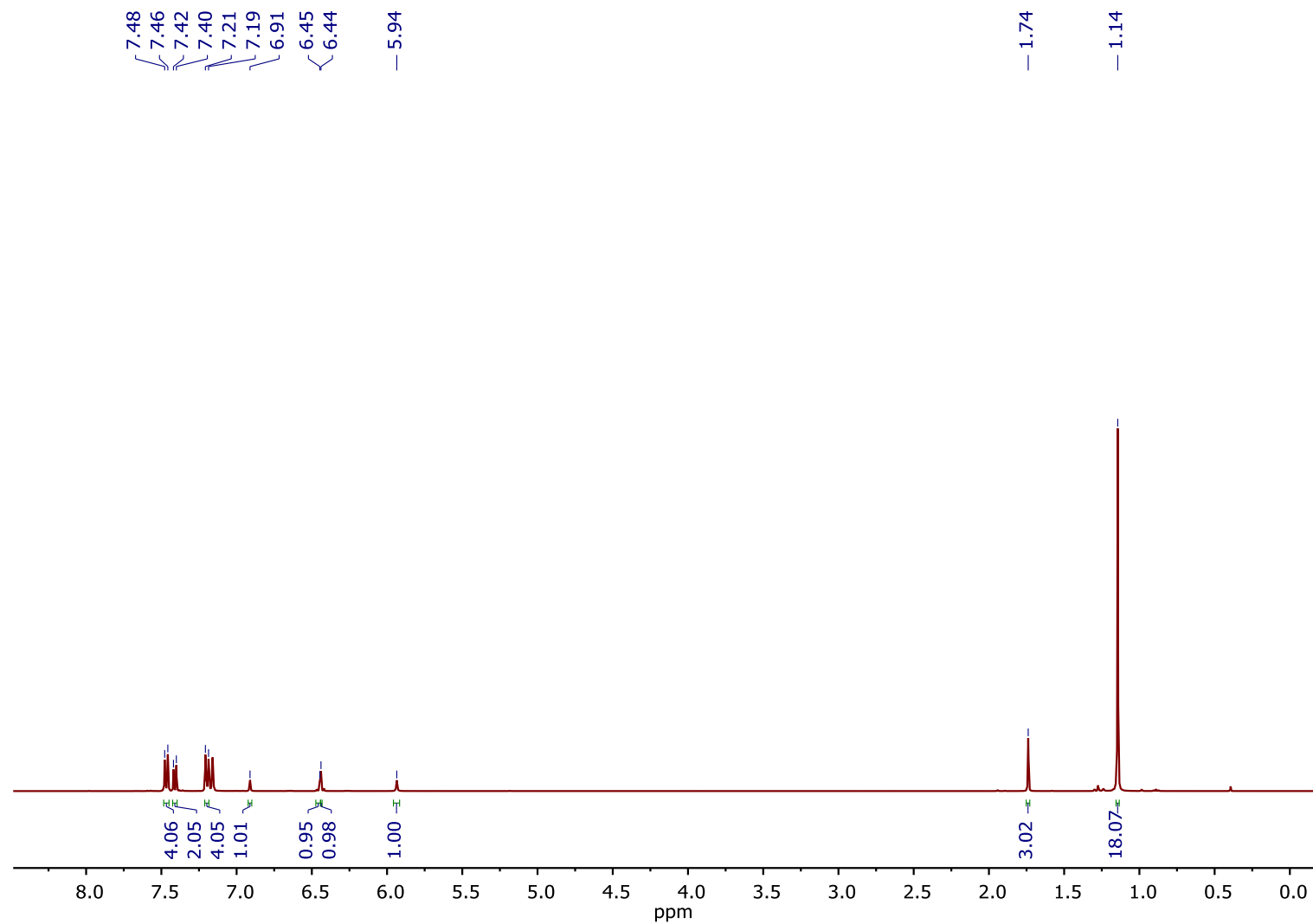


Figure S 1:  $^1\text{H}$  NMR spectrum of **O** in  $\text{C}_6\text{D}_6$  at 298 K.

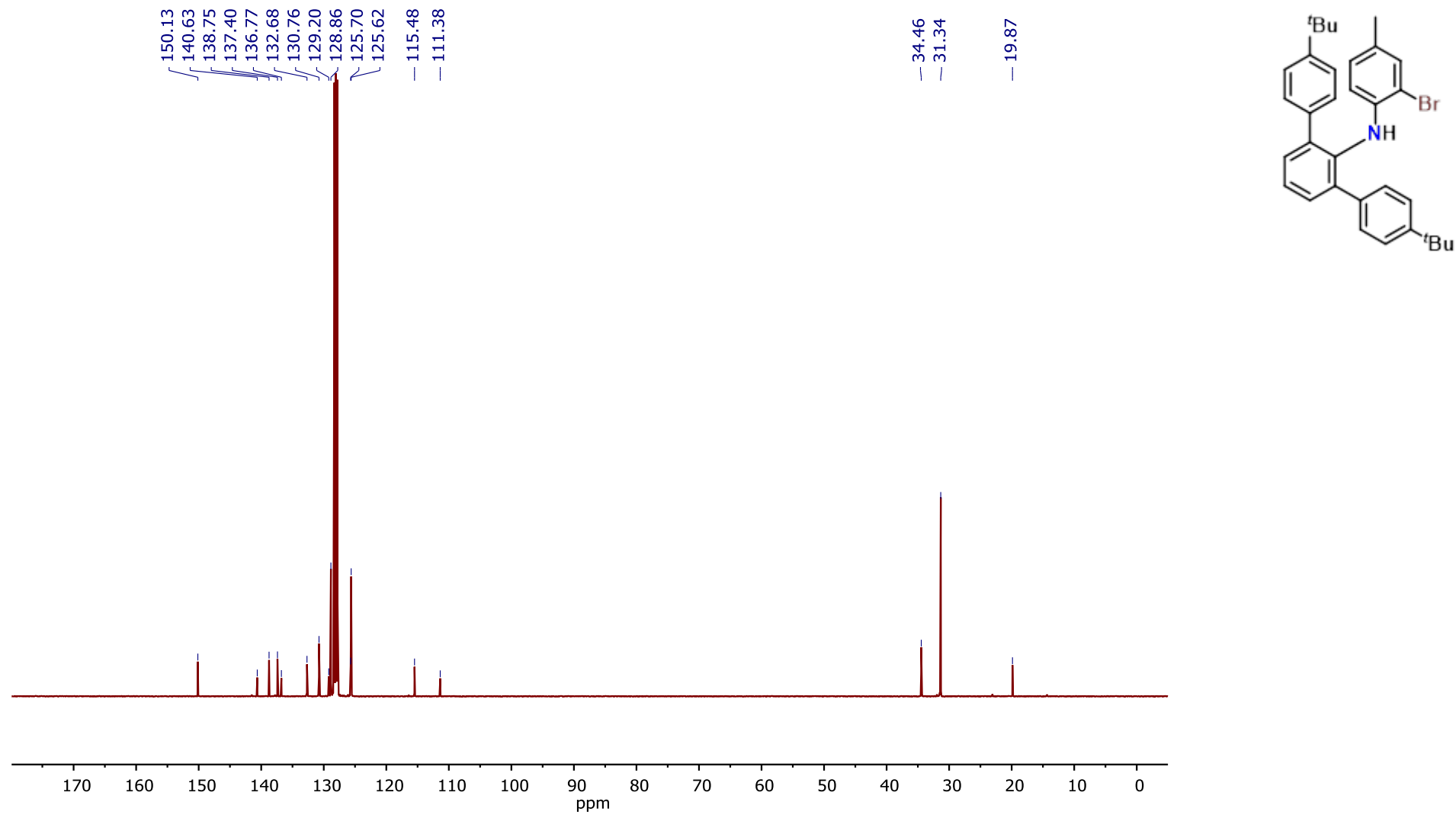


Figure S 2:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **O** in  $\text{C}_6\text{D}_6$  at 298 K.



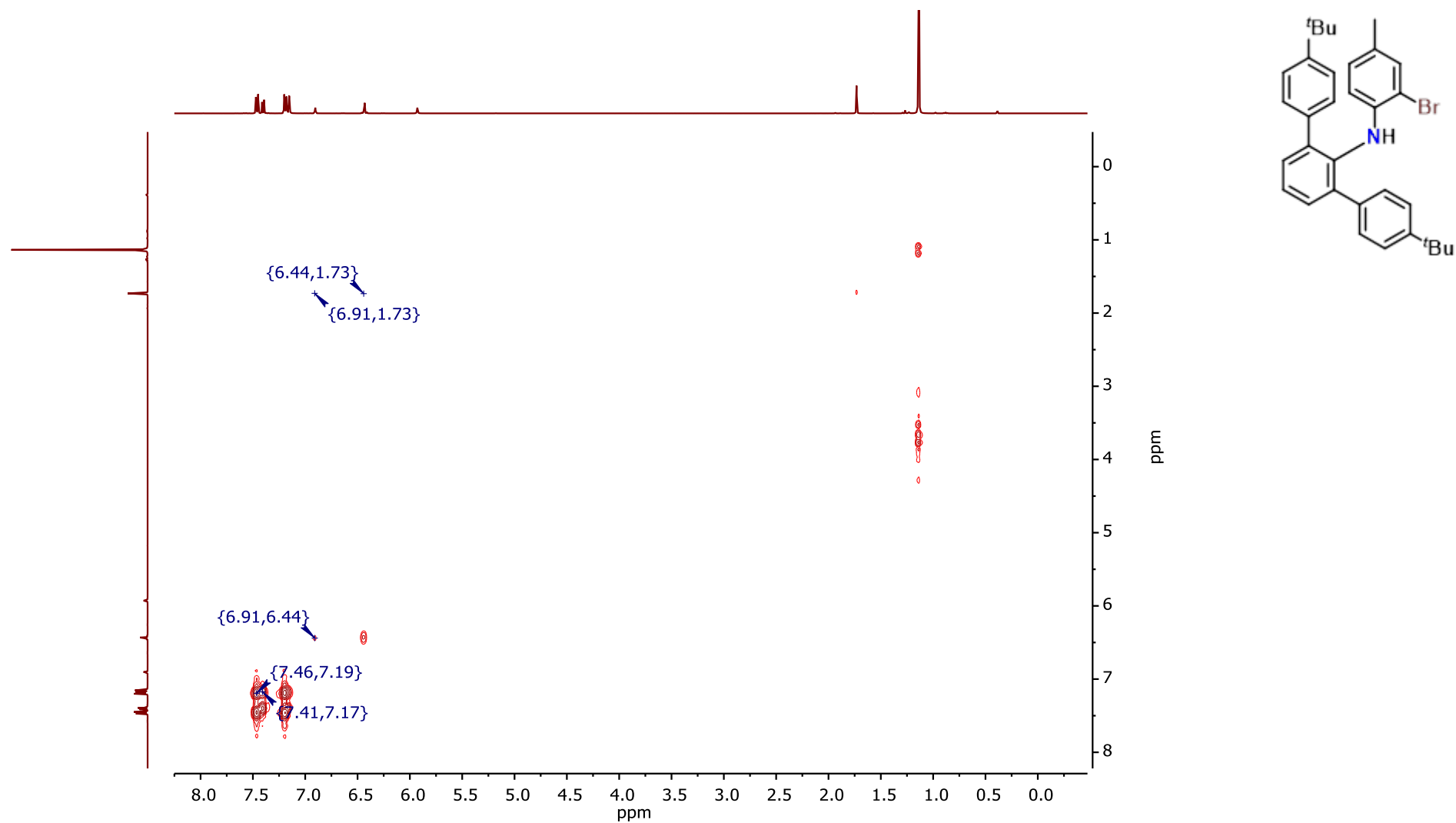


Figure S 3:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

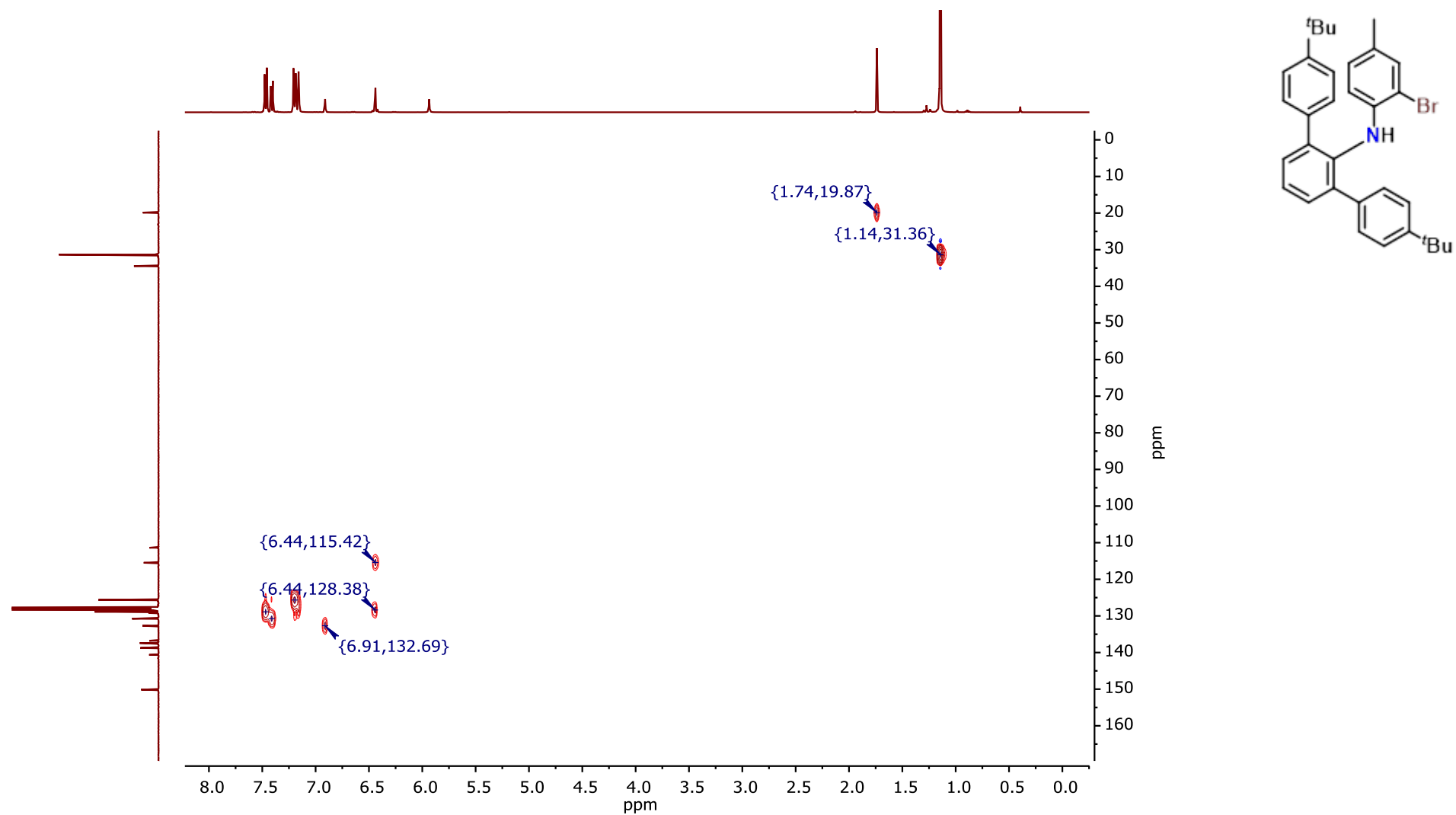


Figure S 4:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **O** in  $\text{C}_6\text{D}_6$  at 298 K.

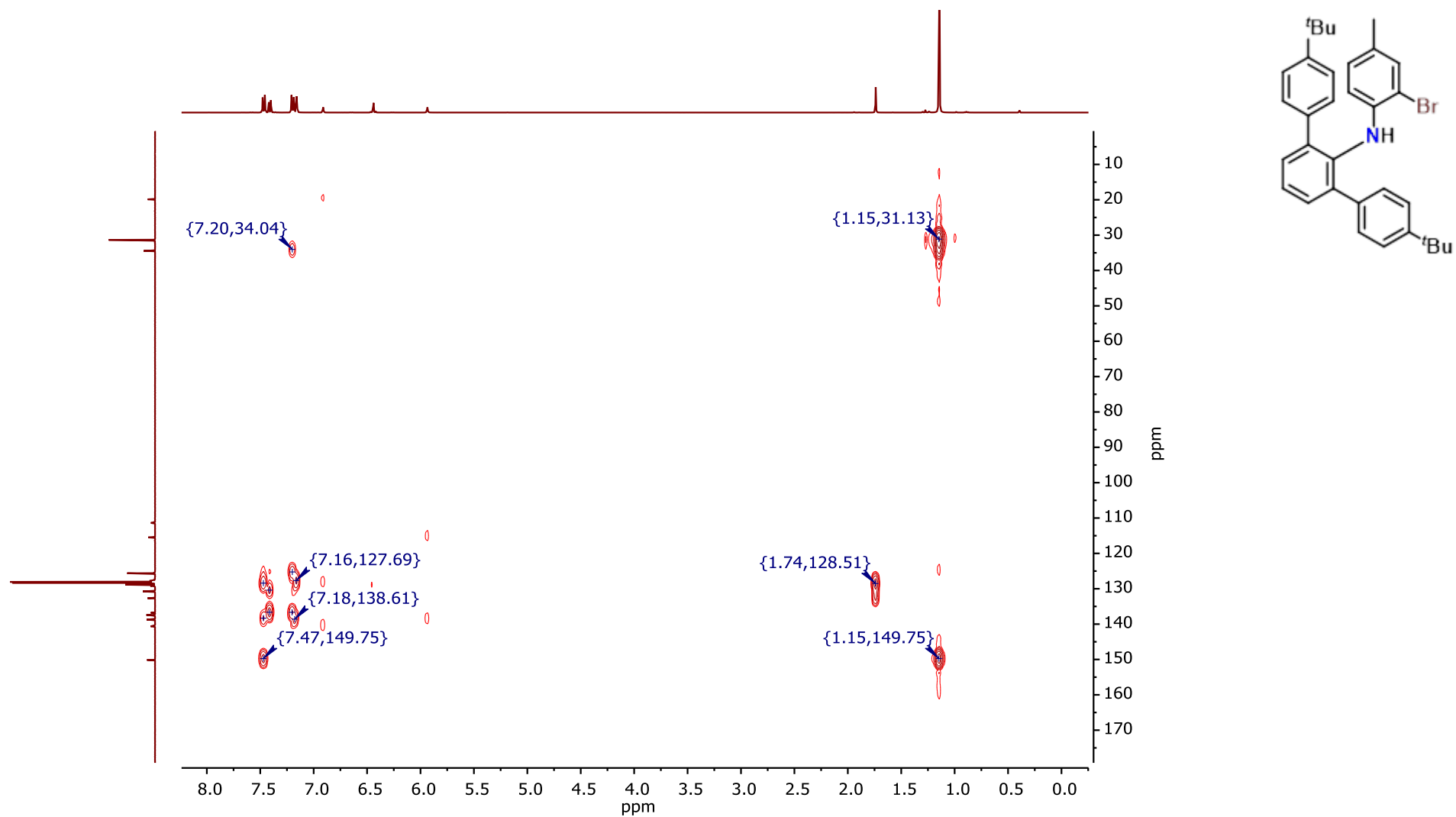


Figure S 5:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **O** in  $\text{C}_6\text{D}_6$  at 298 K.

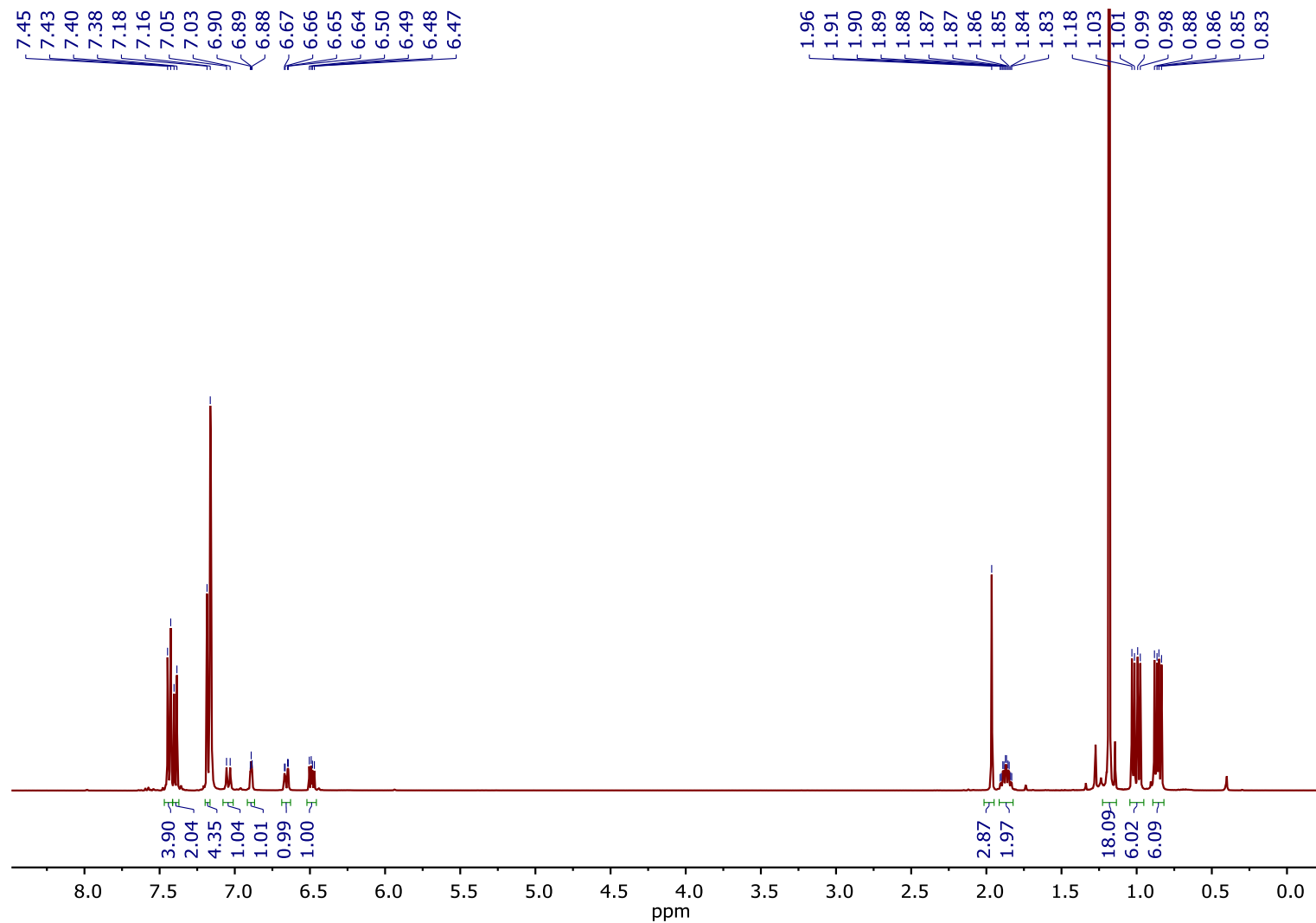


Figure S 6:  $^1H$  NMR spectrum of  $HPN^{Terph}$  in  $C_6D_6$  at 298 K.

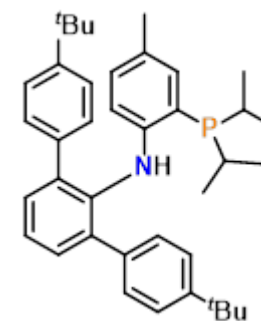
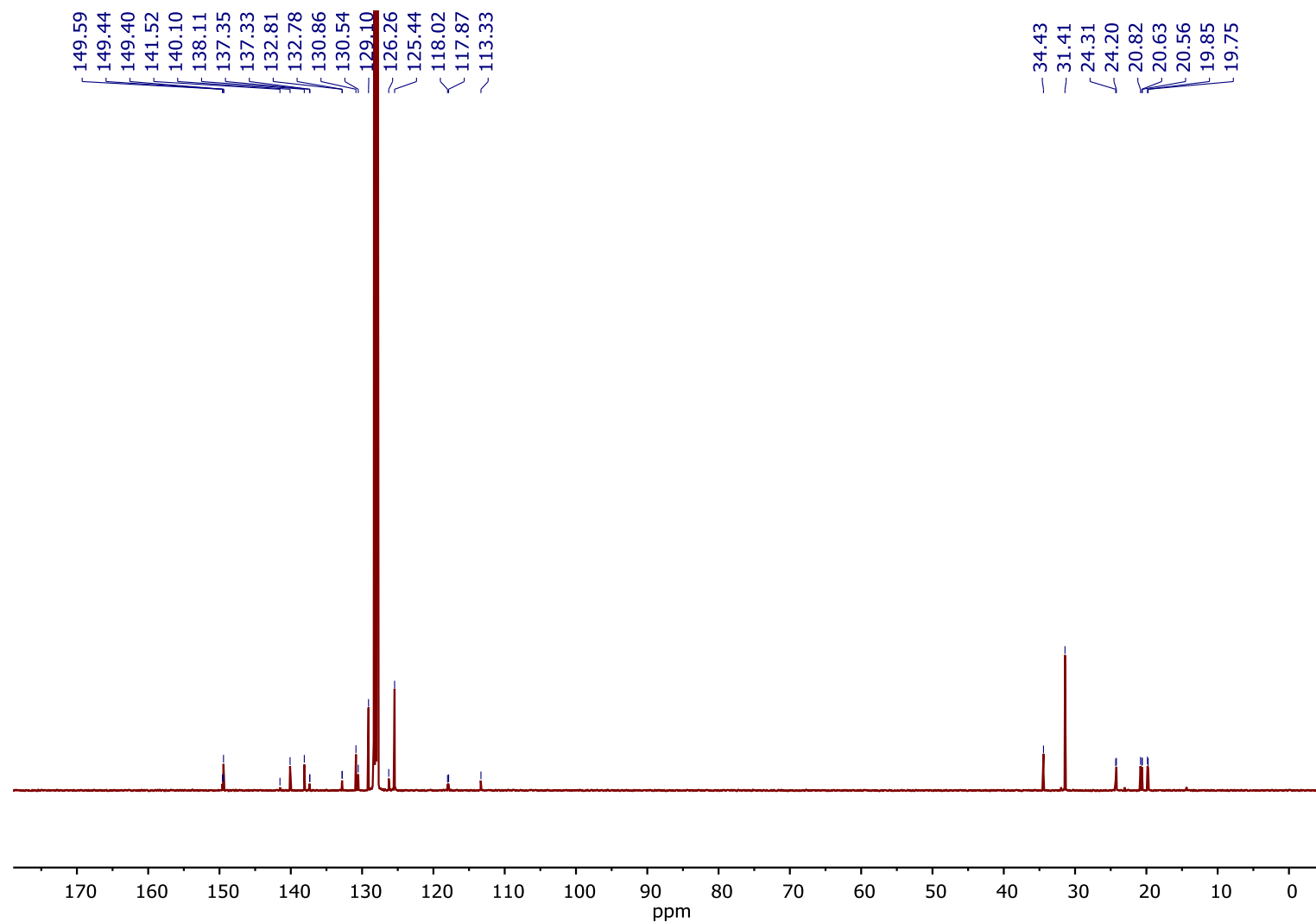


Figure S 7:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{HPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

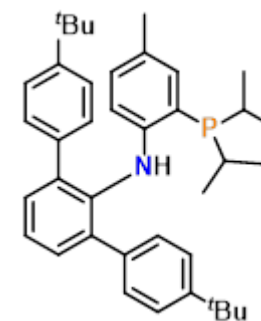
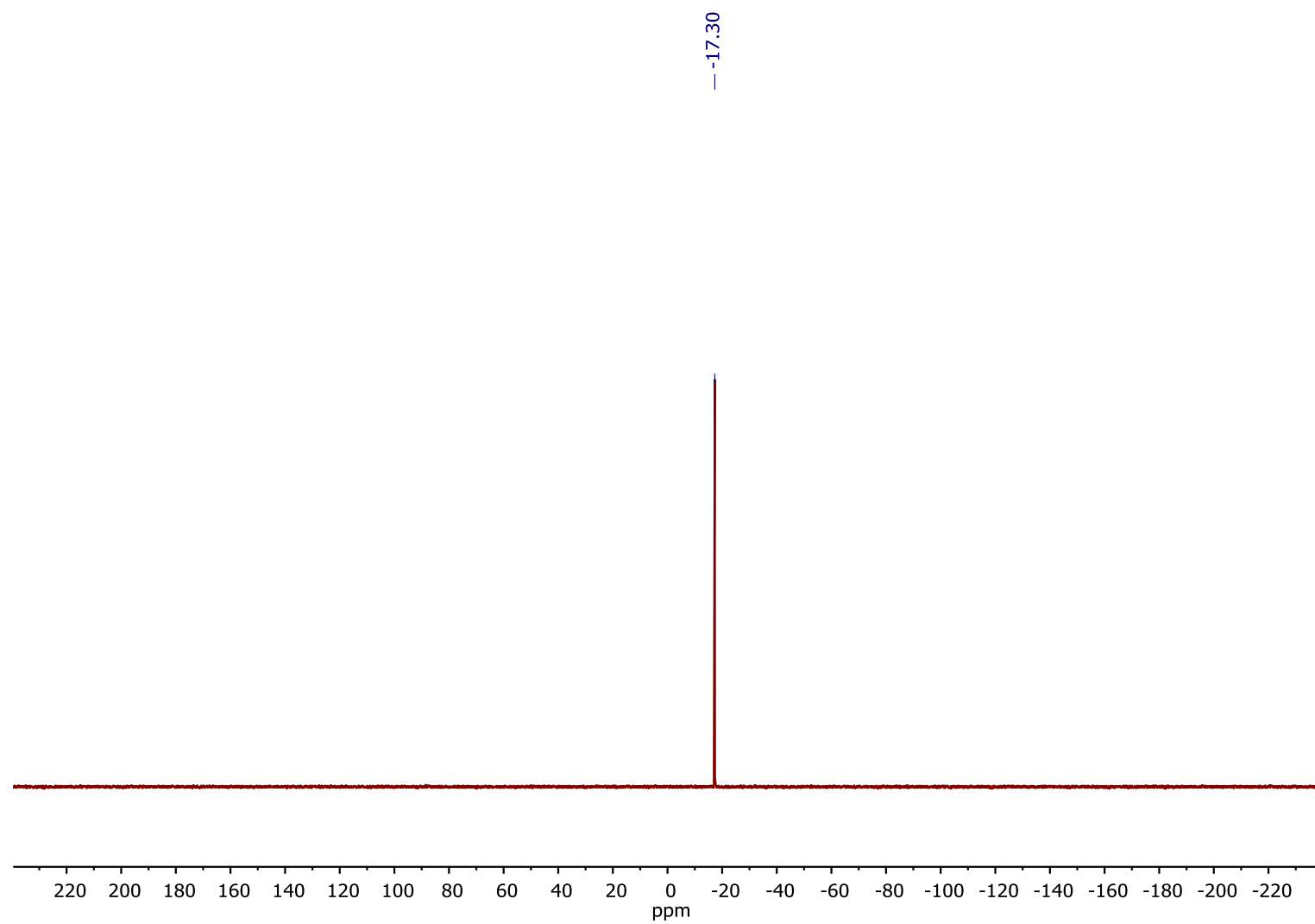


Figure S 8:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{HPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

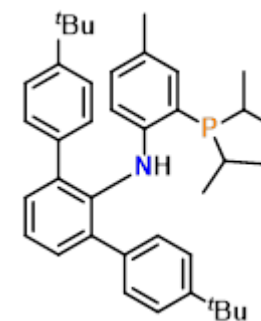
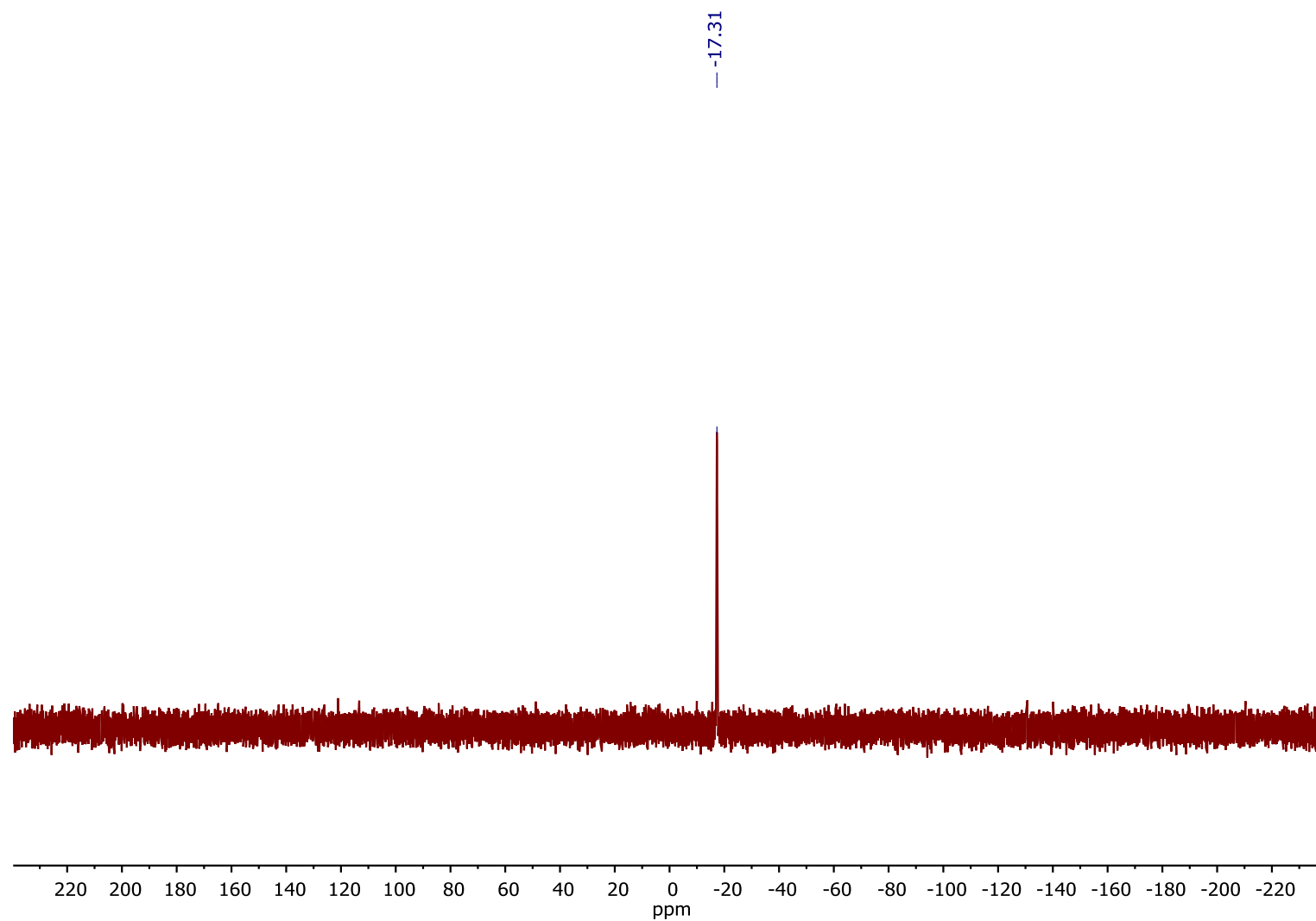


Figure S 9:  $^{31}P$  NMR spectrum of  $HPN^{Terph}$  in  $C_6D_6$  at 298 K.

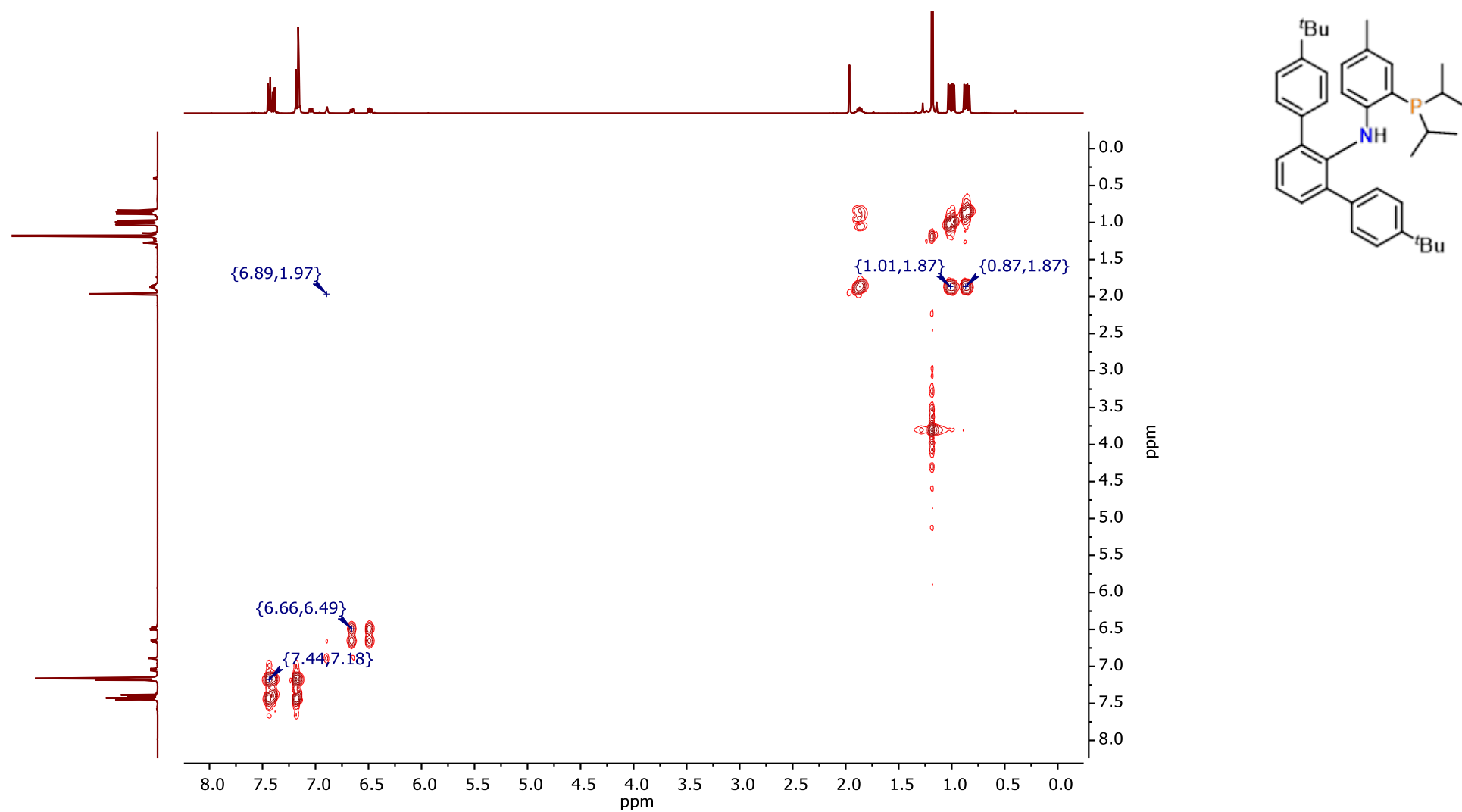


Figure S 10:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of  $\text{HPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.



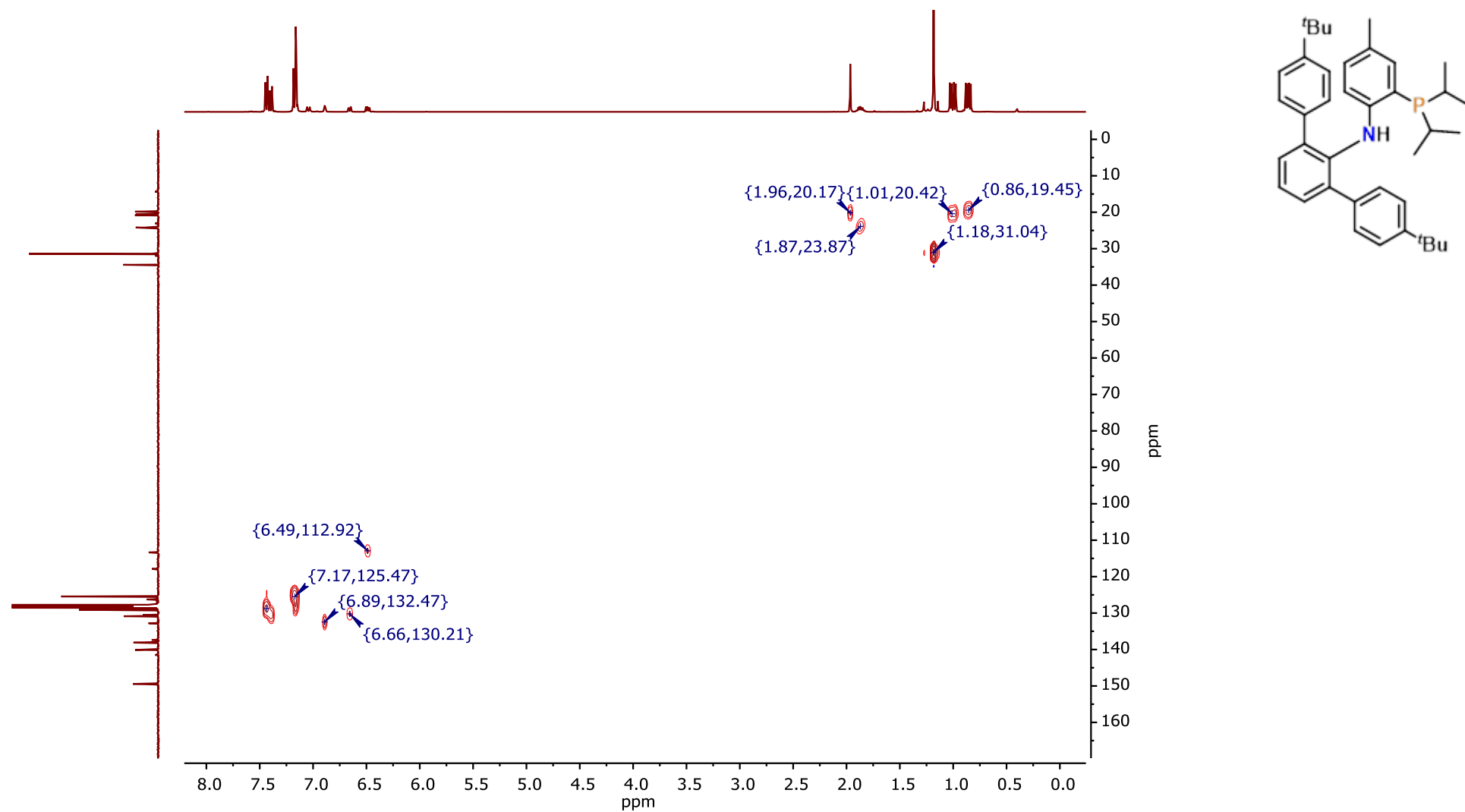


Figure S 11:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of  $\text{HPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

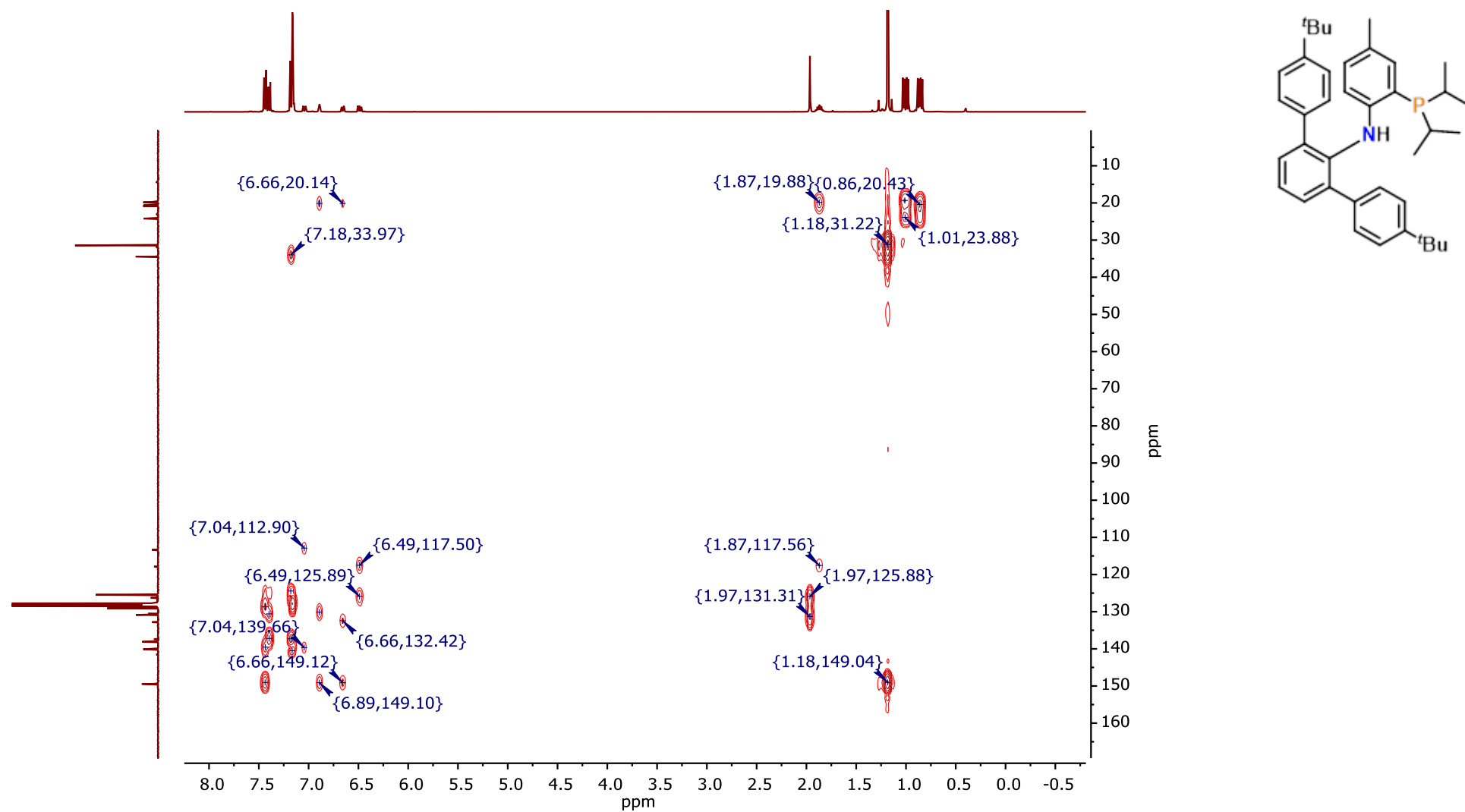


Figure S 12:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of  $\text{HPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

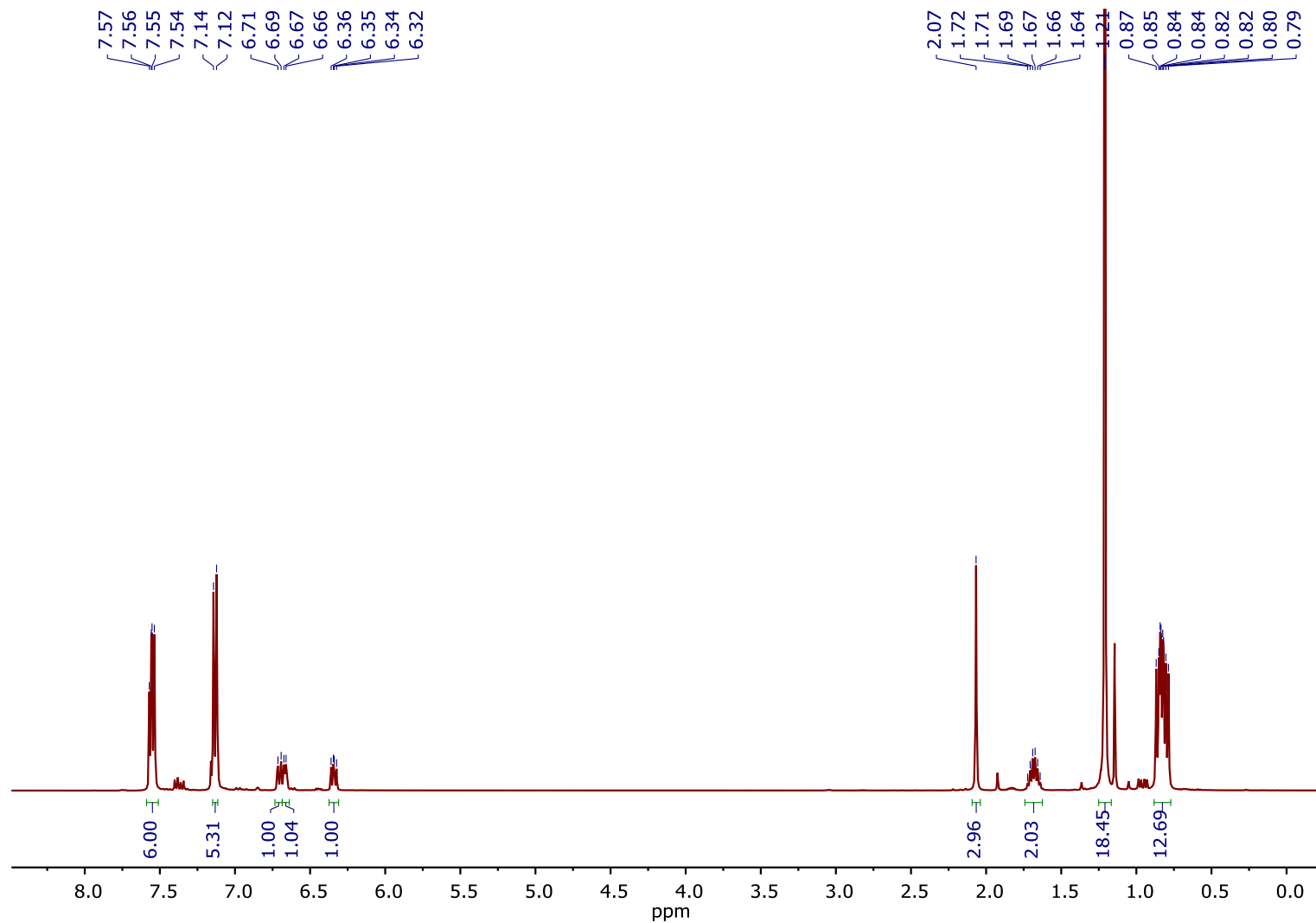
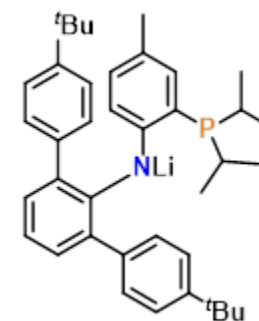


Figure S 13:  $^1\text{H}$  NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.



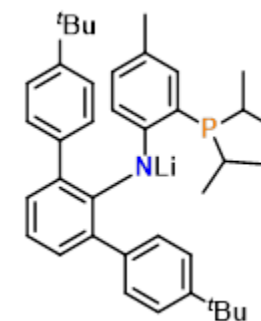
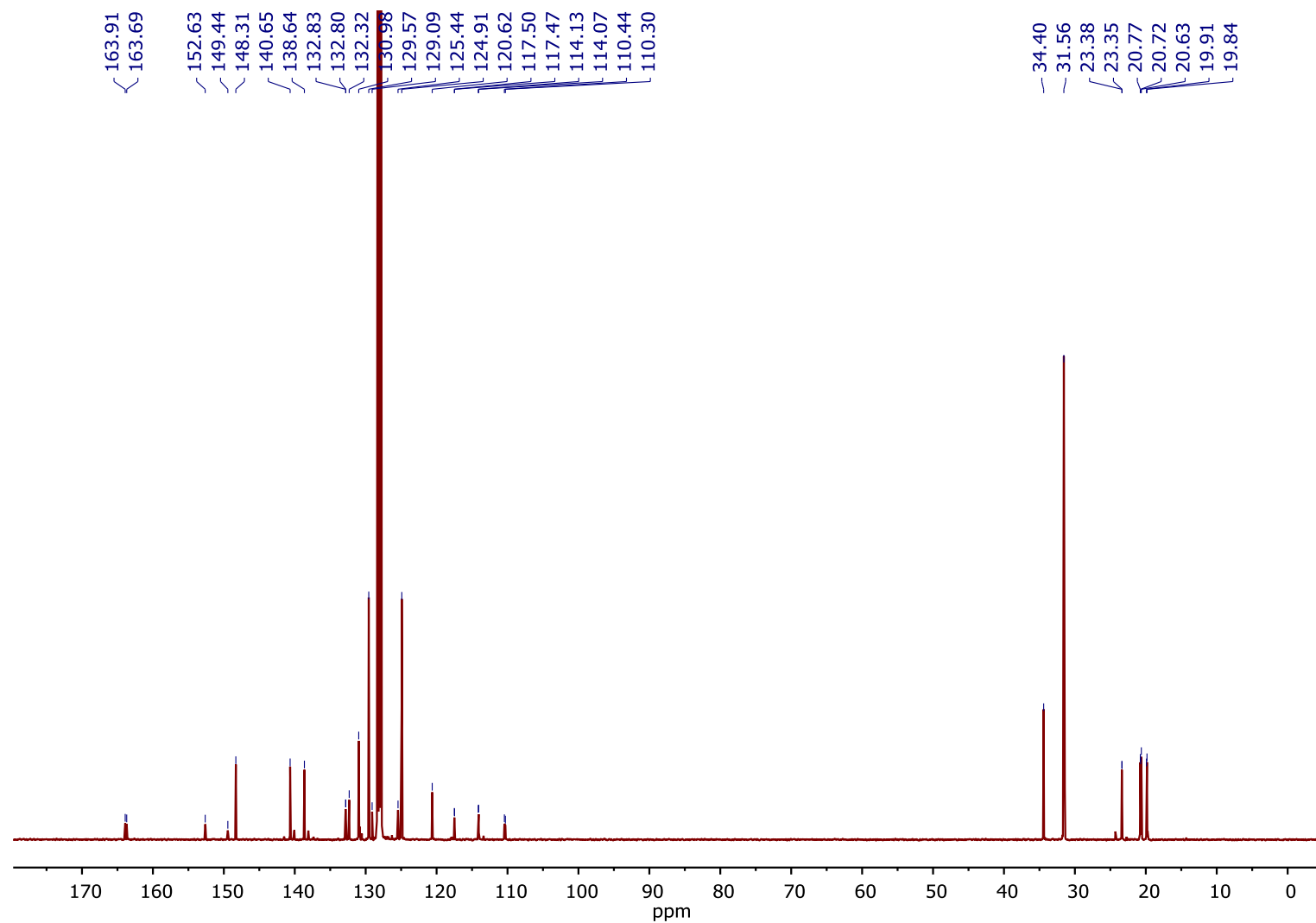


Figure S 14:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

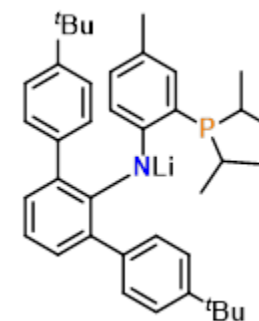
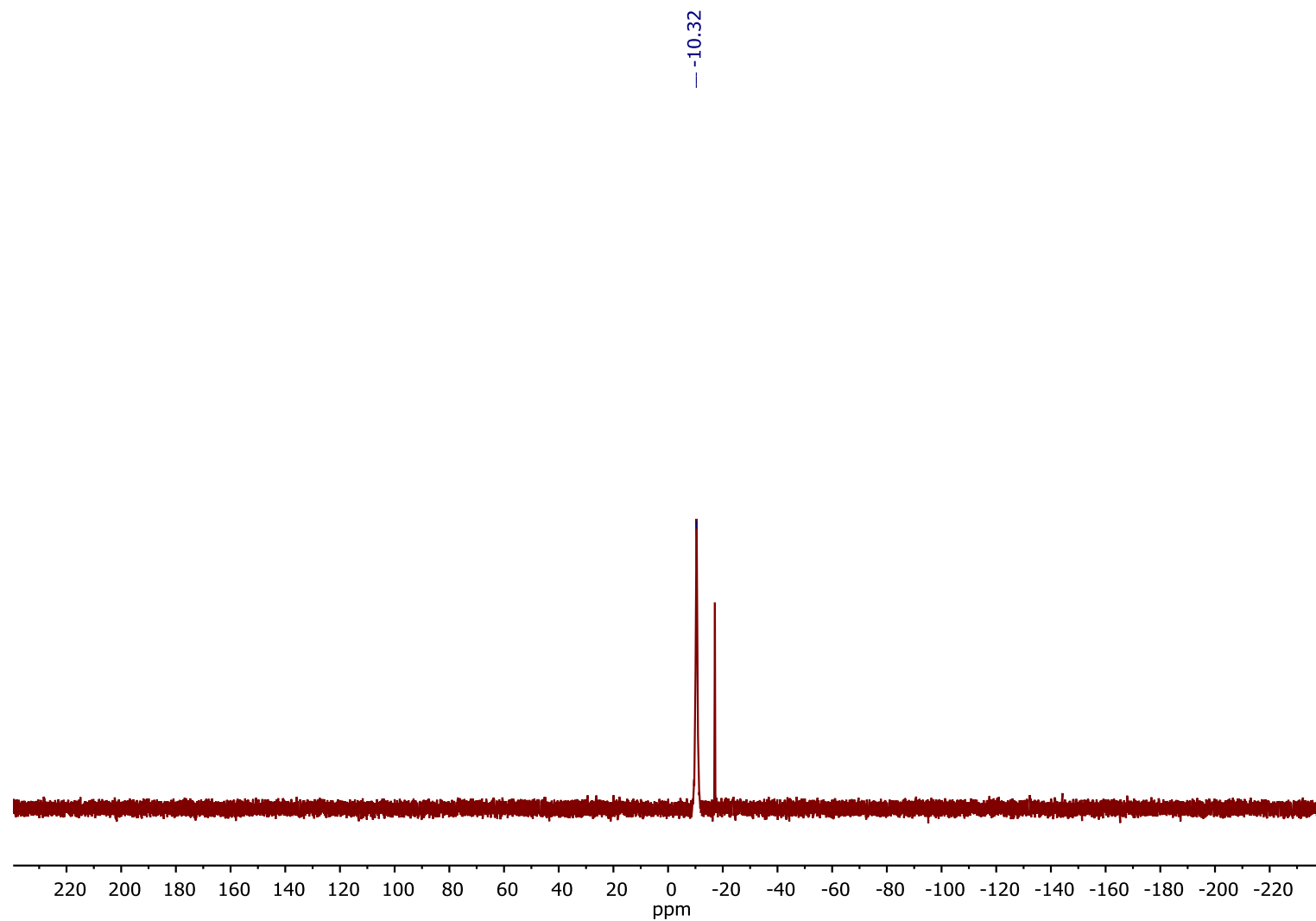


Figure S 15:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **LiPN<sup>Terph</sup>** in  $\text{C}_6\text{D}_6$  at 298 K. The signal at  $-17$  ppm belongs to an impurity of free HPN, which integrates to roughly 6% impurity as the LiPN signal is reasonably broad.

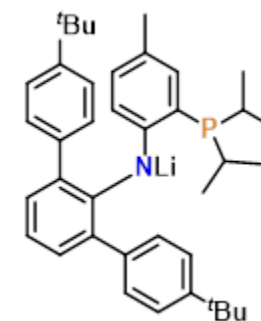
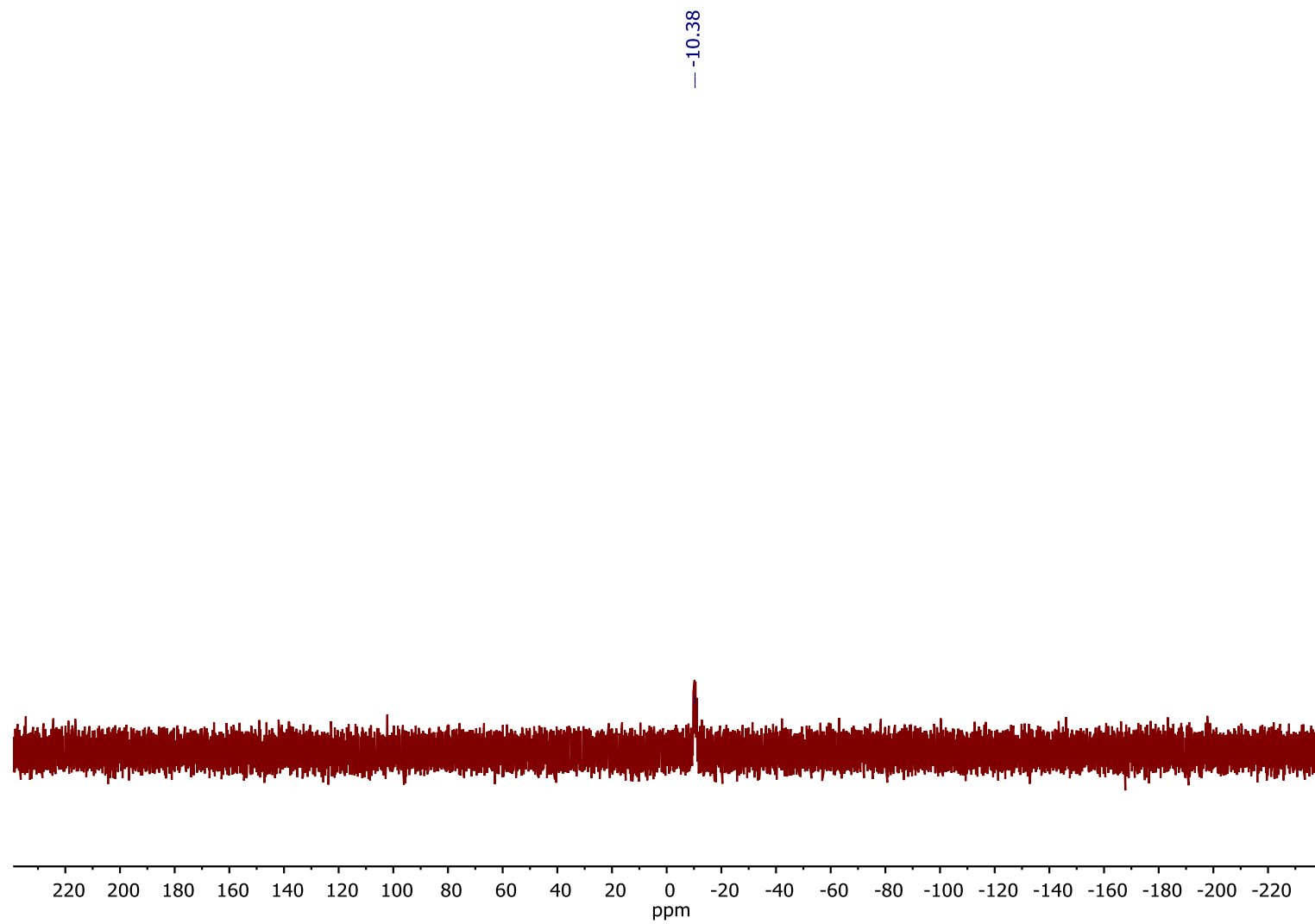


Figure S 16:  $^{31}\text{P}$  NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

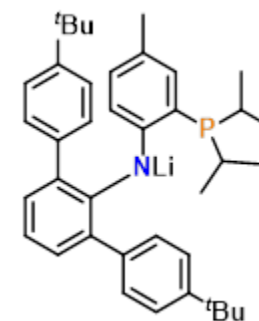
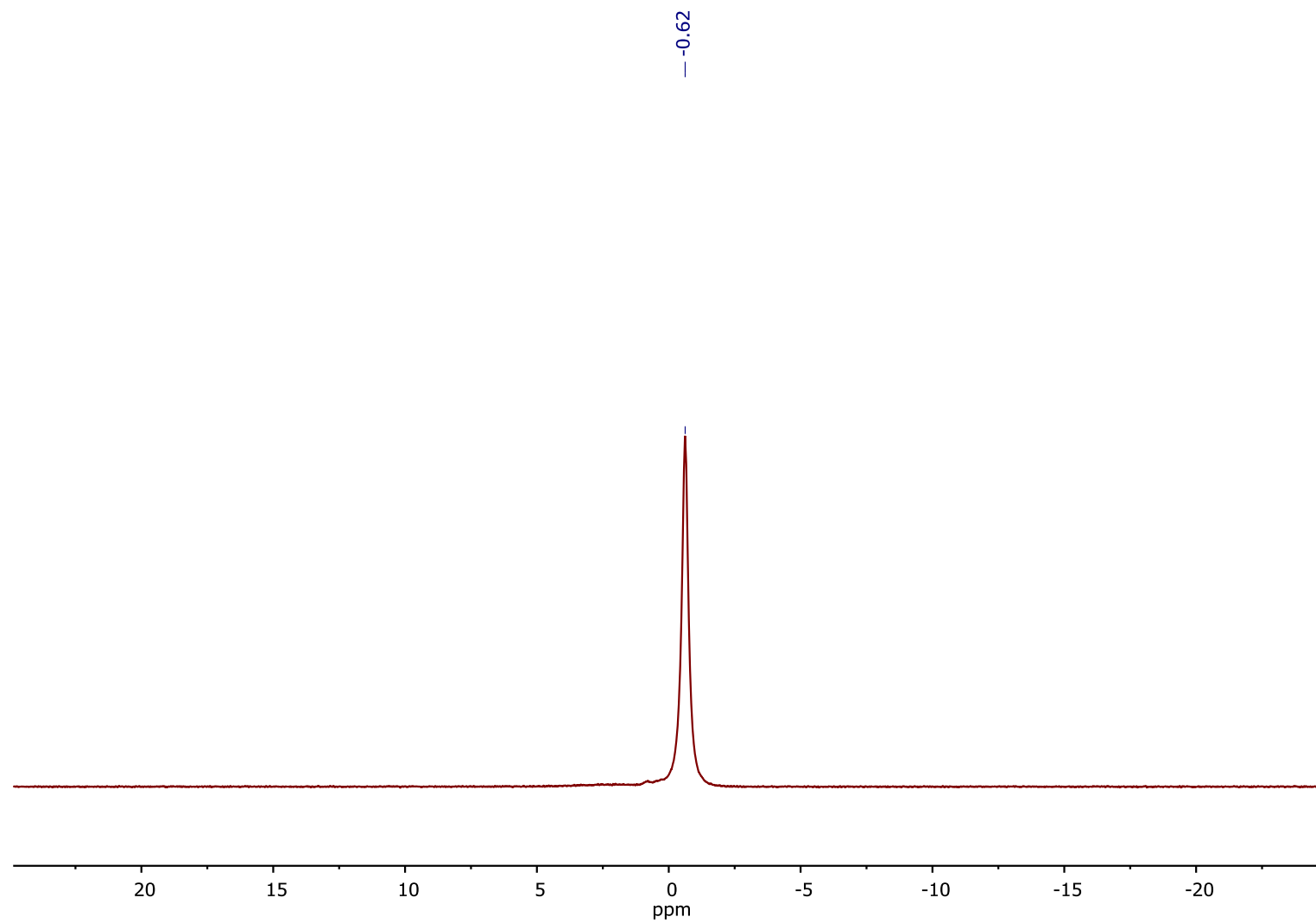


Figure S 17:  ${}^7\text{Li}\{^1\text{H}\}$  NMR spectrum of **LiPN<sup>Terph</sup>** in  $\text{C}_6\text{D}_6$  at 298 K.

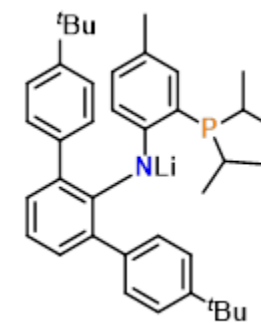
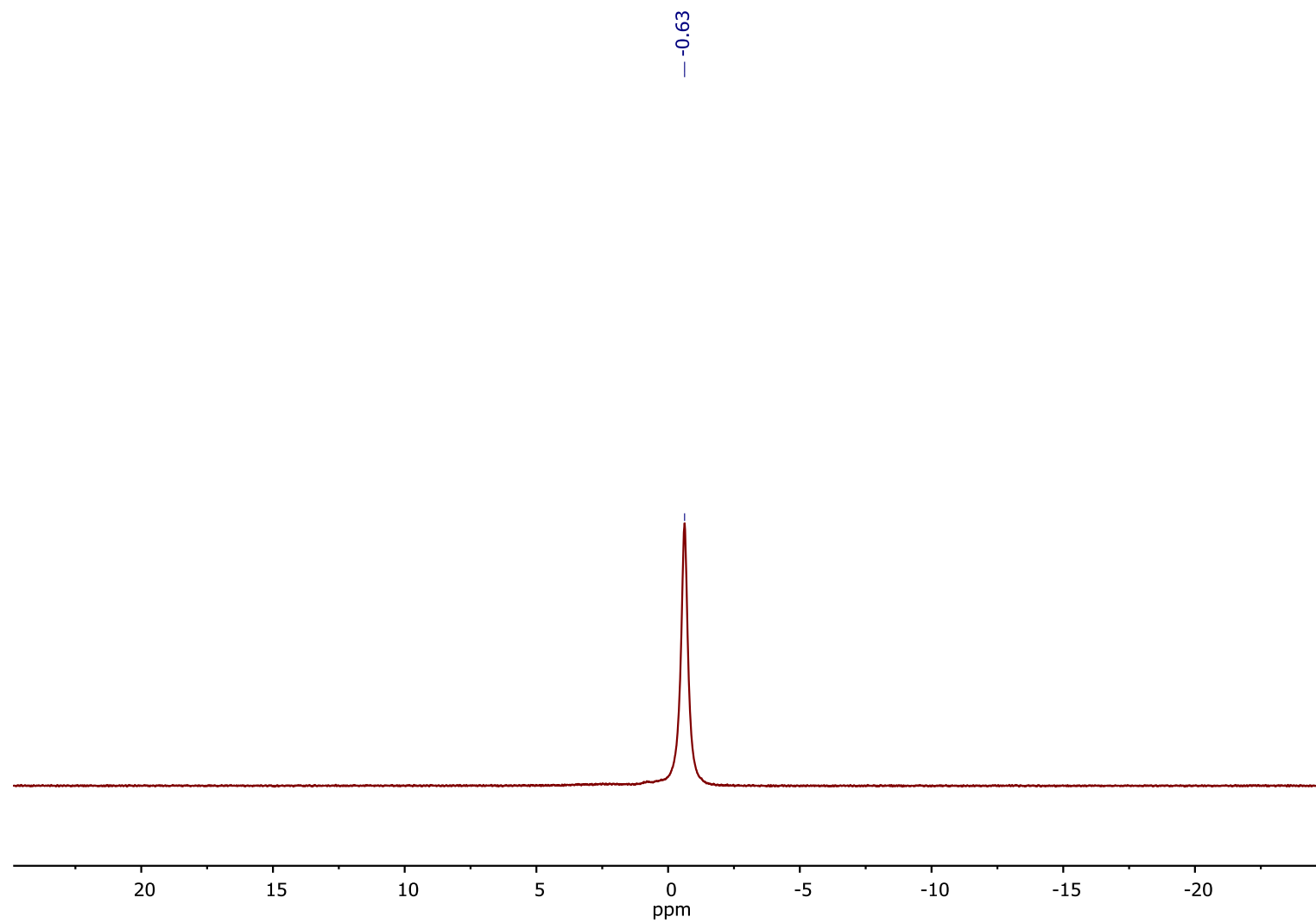
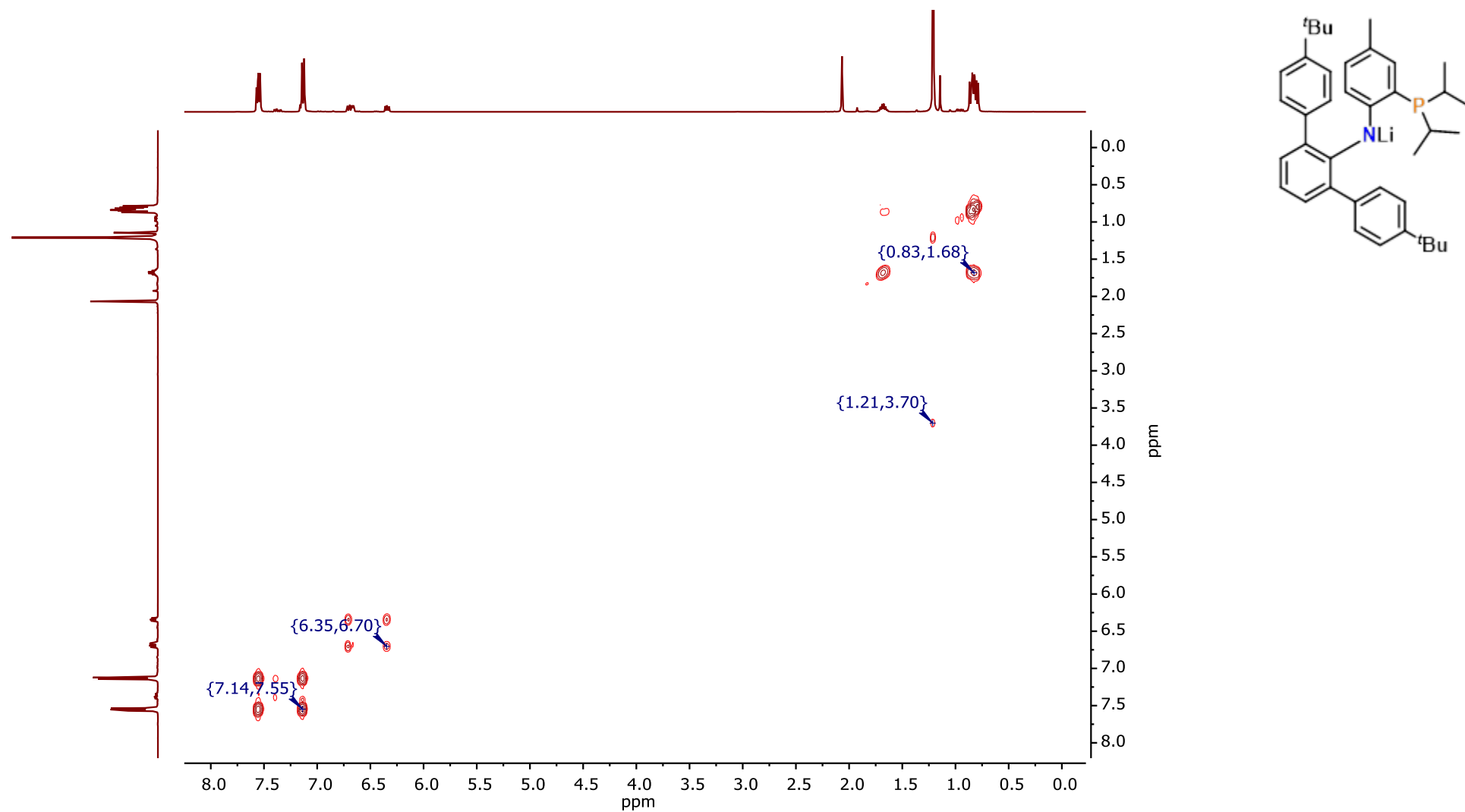


Figure S 18:  ${}^7\text{Li}$  NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.





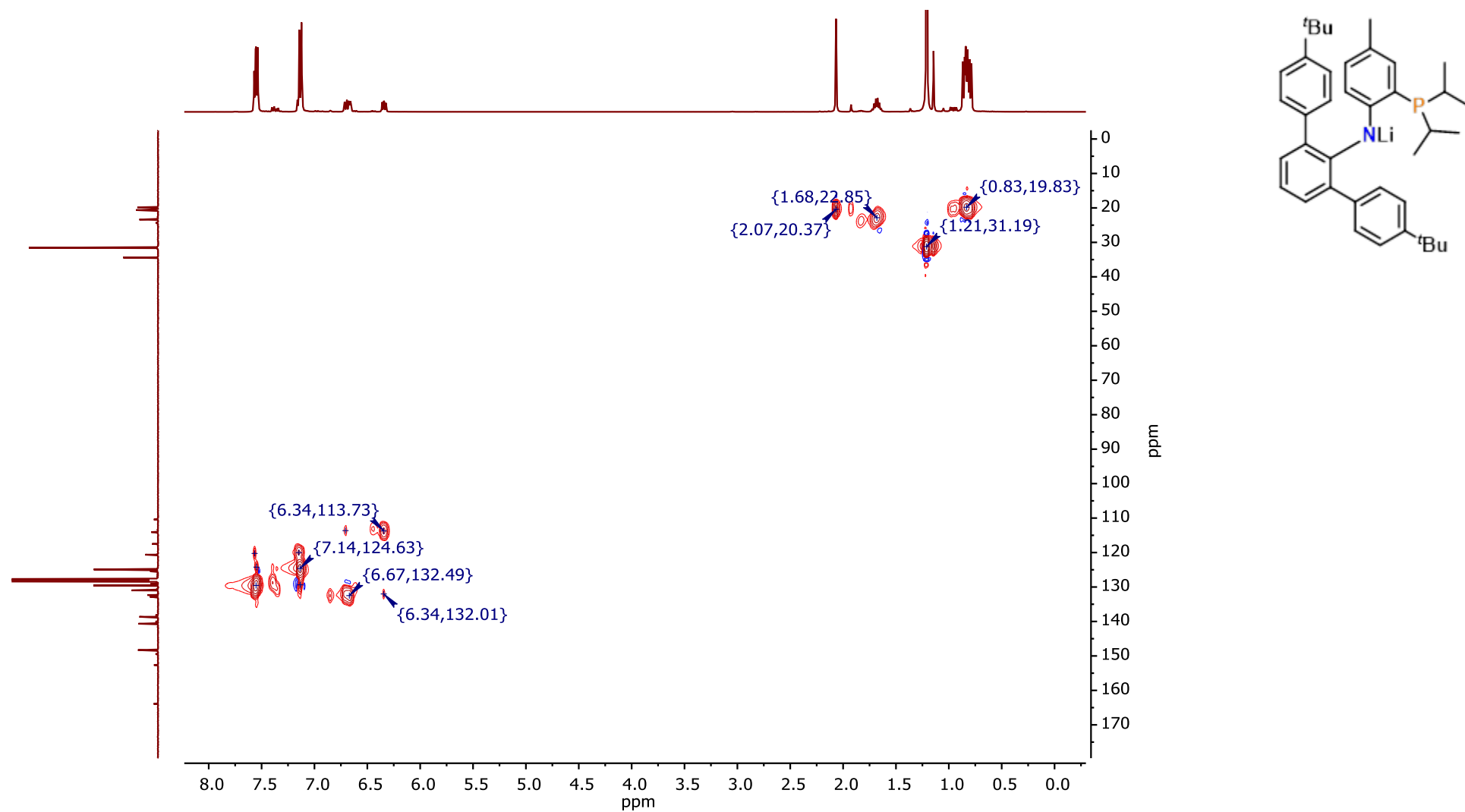


Figure S 20:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

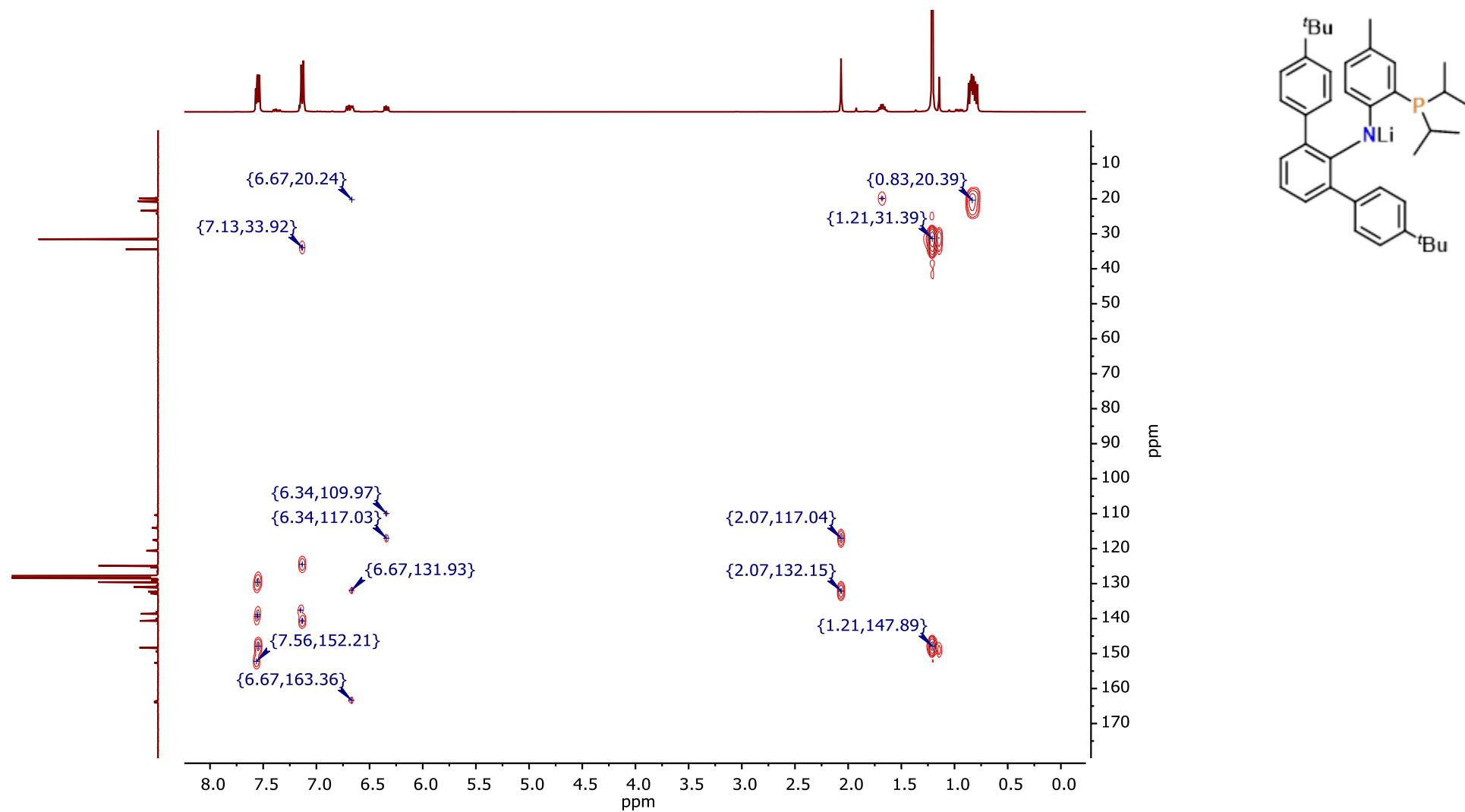


Figure S 21:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of  $\text{LiPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

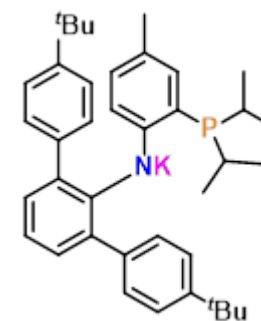
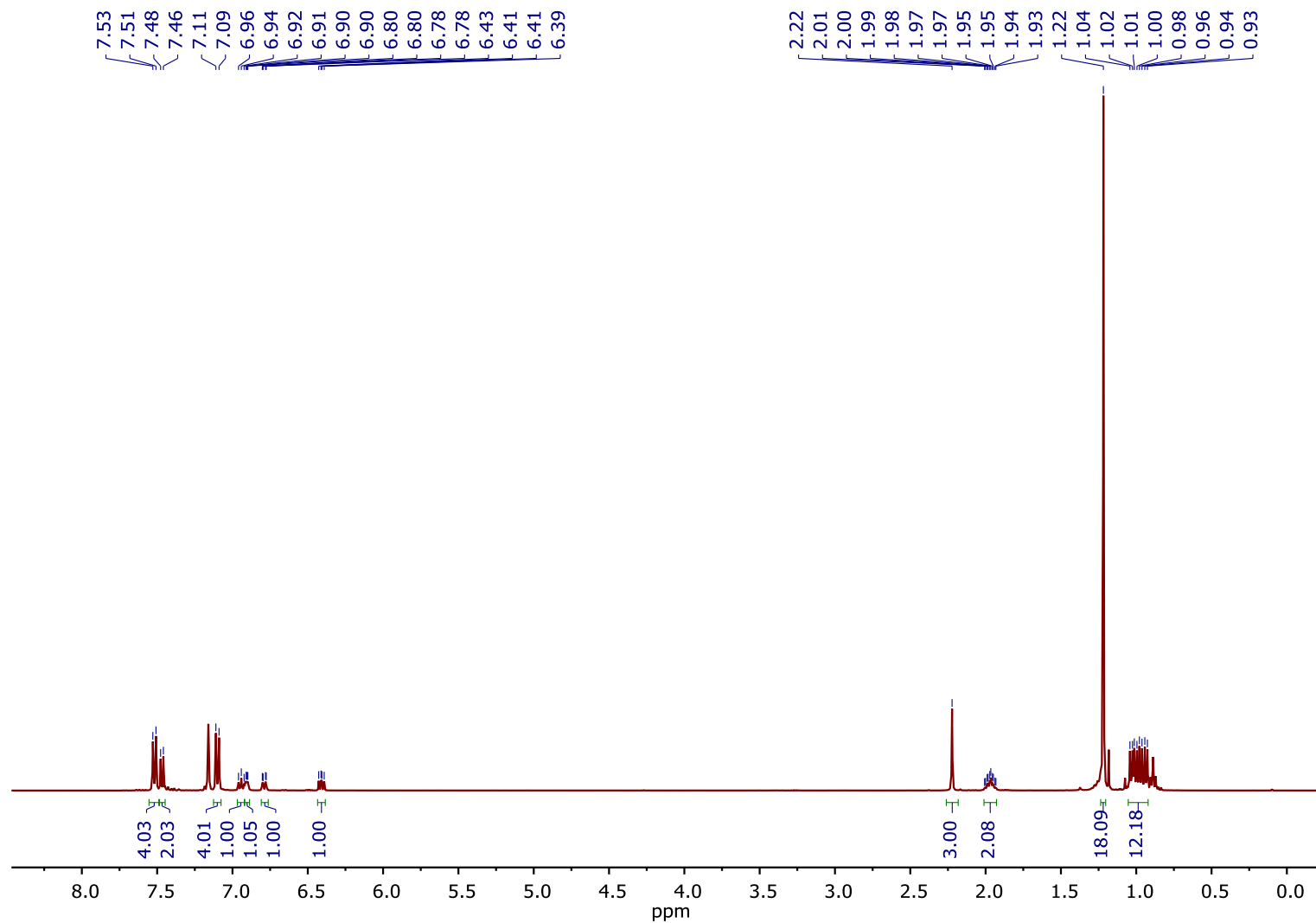


Figure S 22:  $^1\text{H}$  NMR spectrum of  $\text{KPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

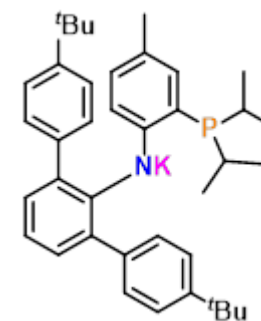
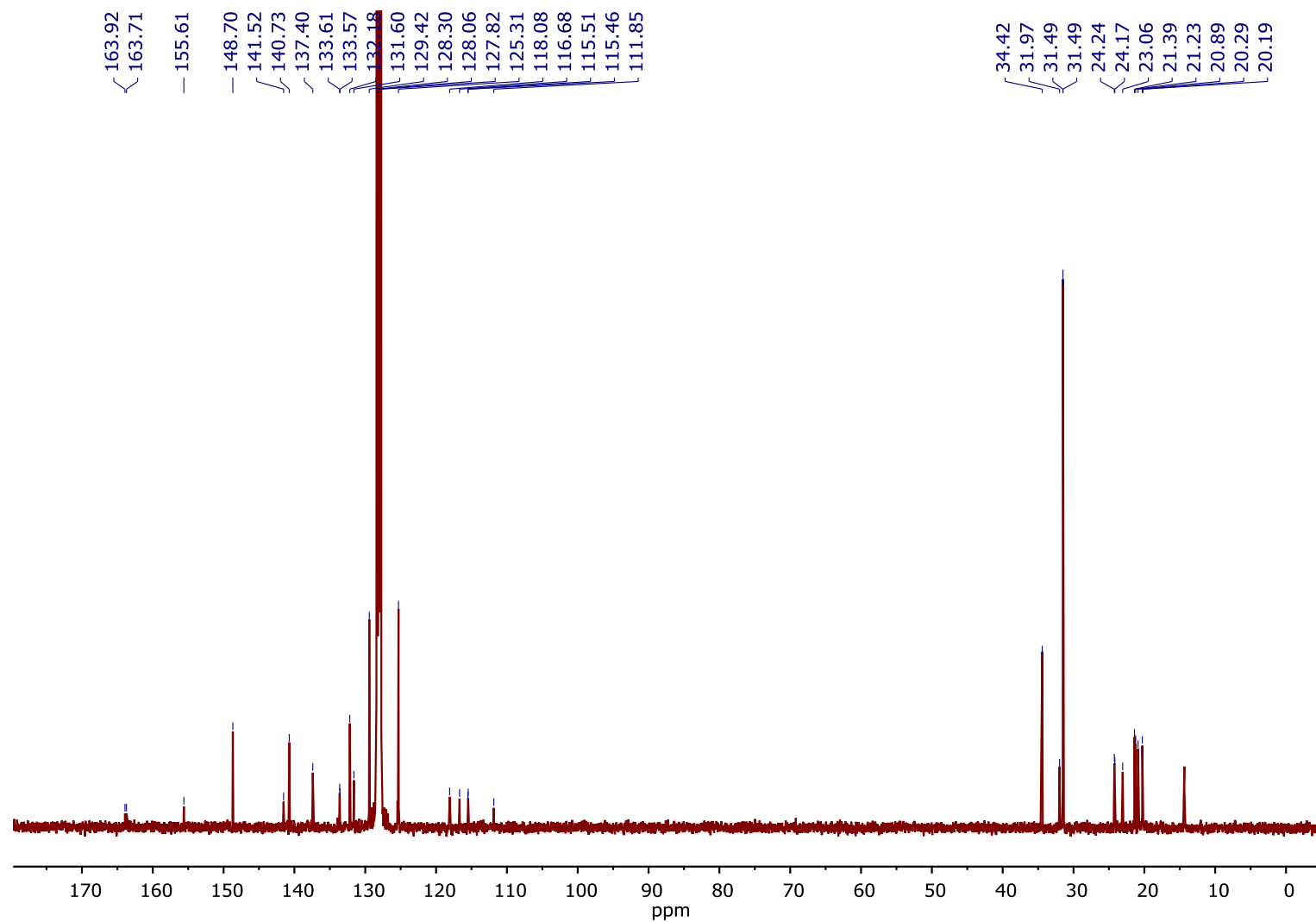


Figure S 23:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{KPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

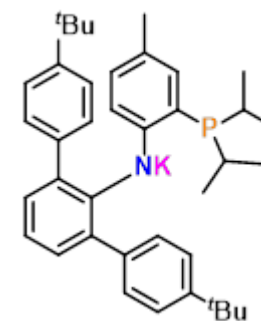
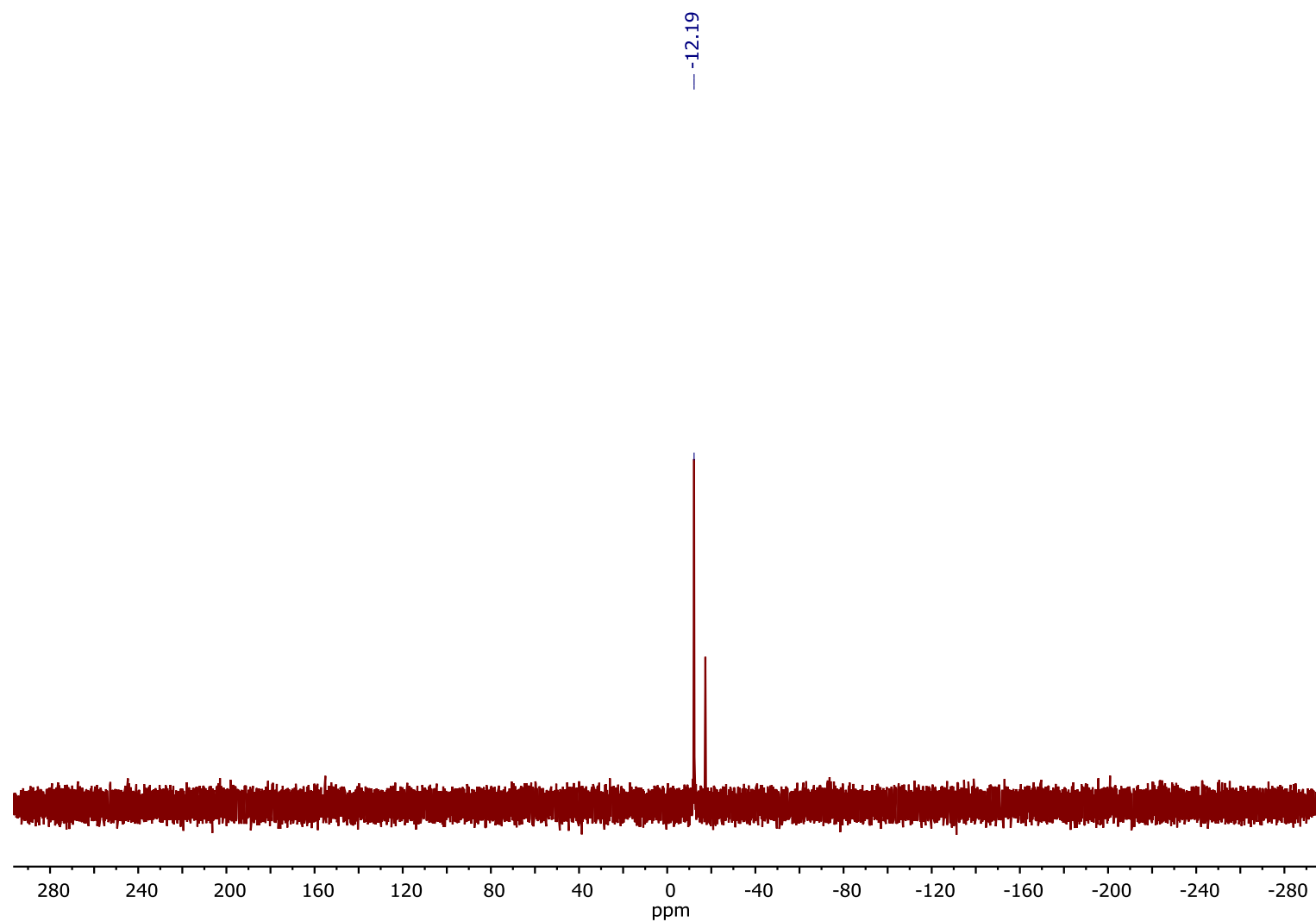


Figure S 24:  $^{31}P\{^1H\}$  NMR spectrum of  $KPN^{Terph}$  in  $C_6D_6$  at 298 K. The impurity at -17 ppm belongs to free HPN, and corresponds to an approx. amount of 5 %.

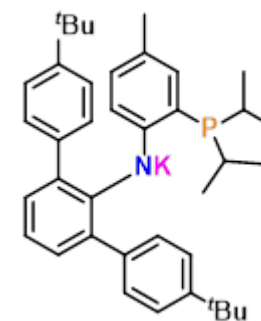
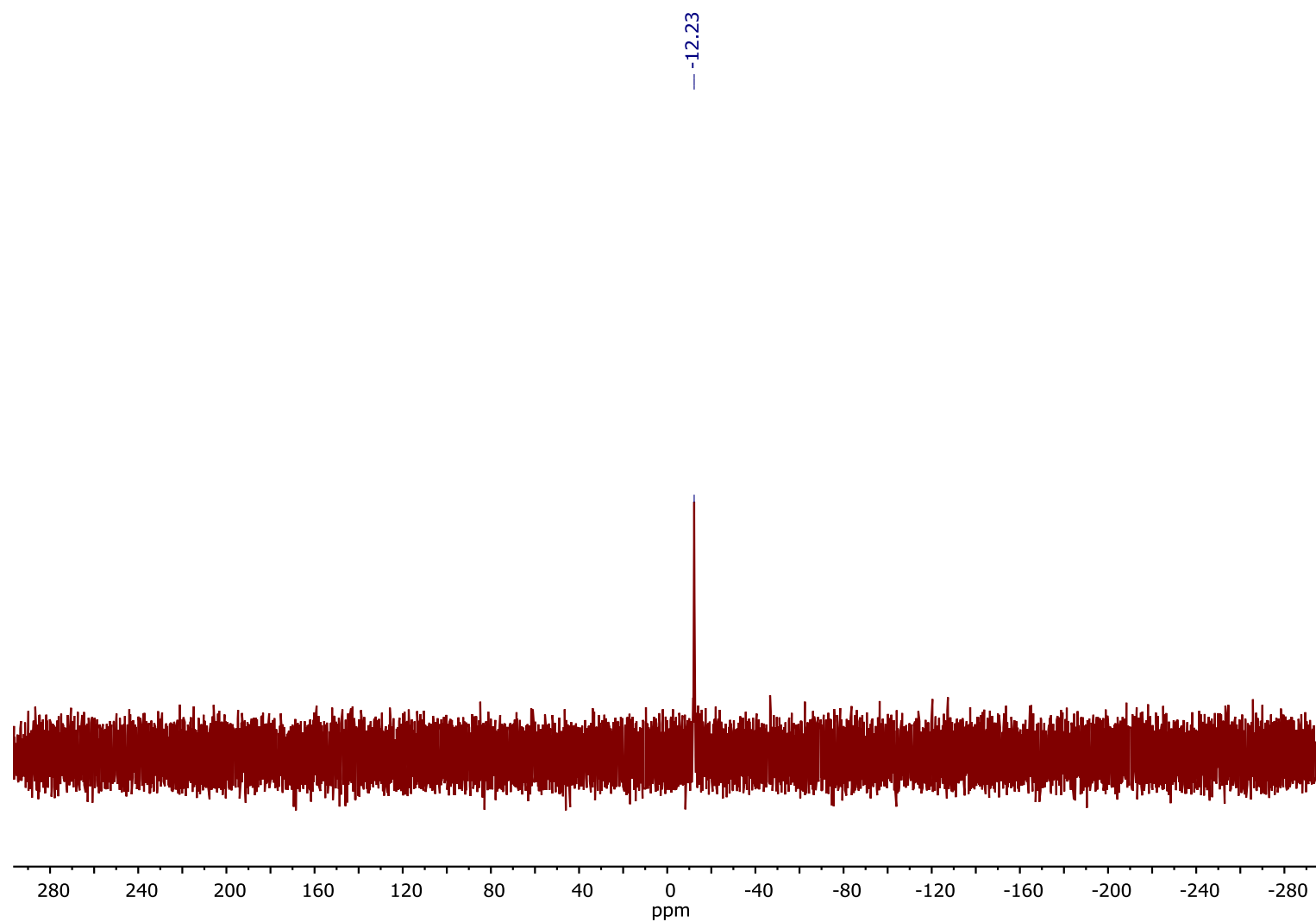


Figure S 25:  $^{31}P$  NMR spectrum of  $KPN^{Terph}$  in  $C_6D_6$  at 298 K.

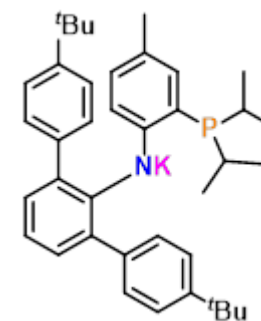
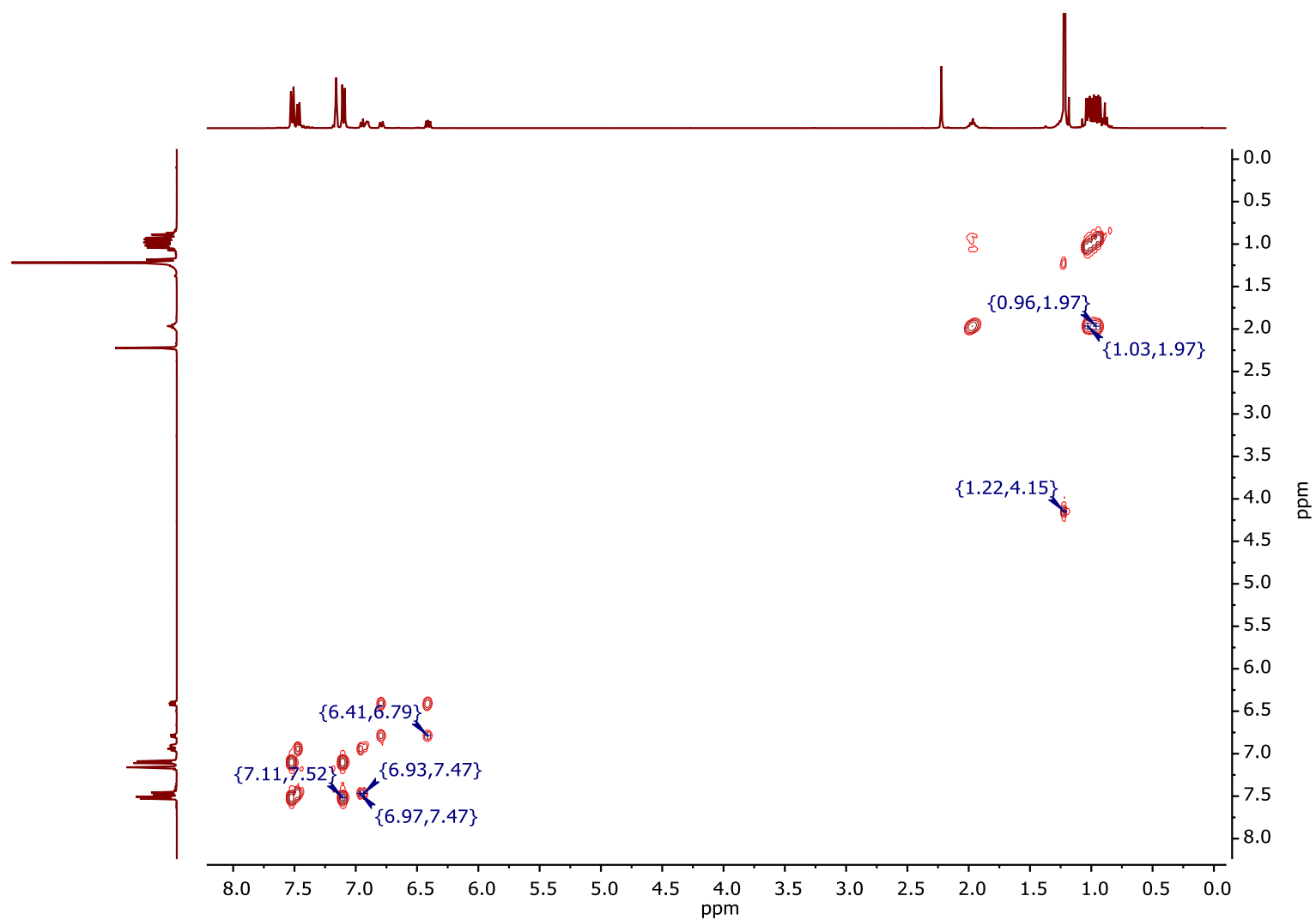


Figure S 26:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of  $\text{KPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.



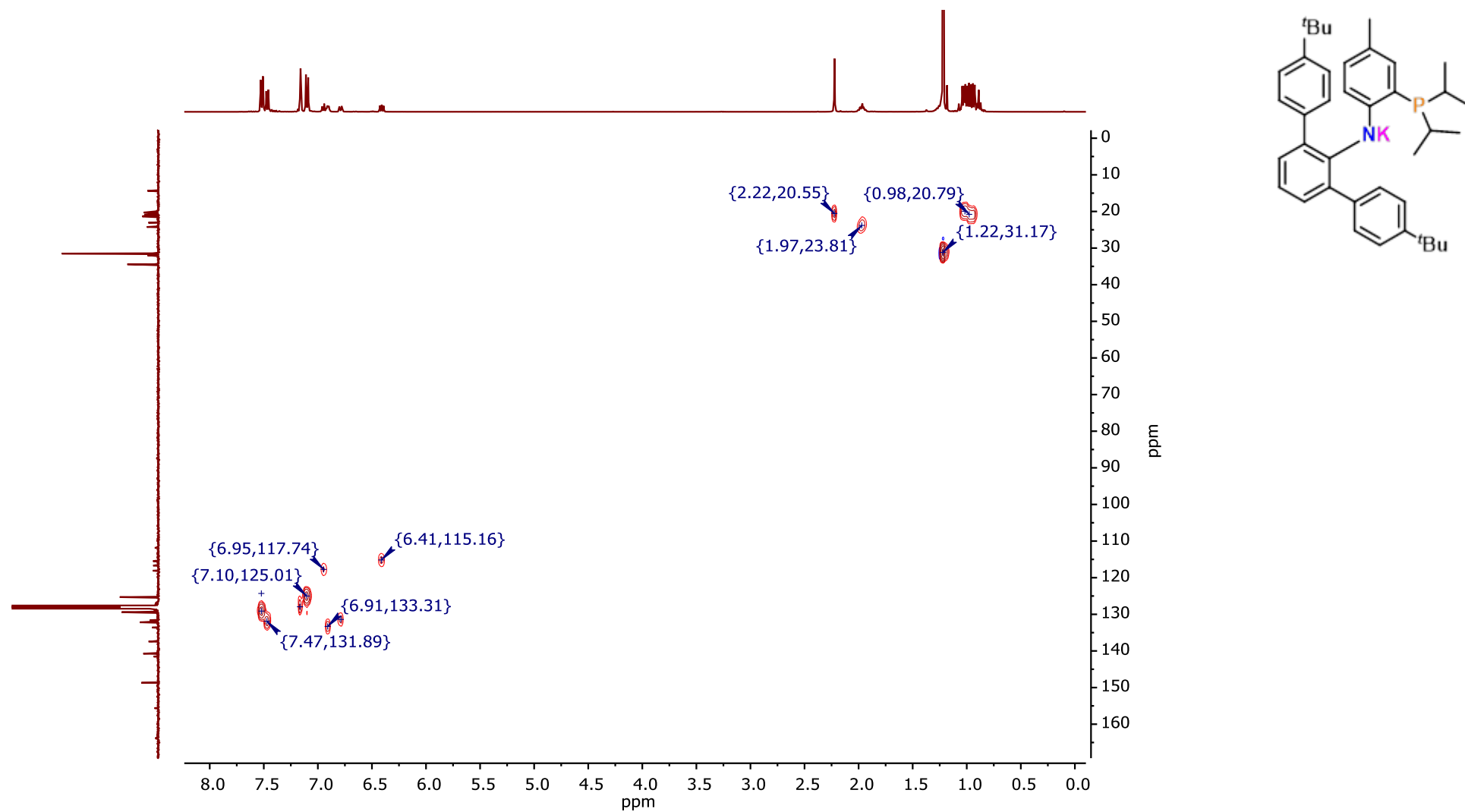


Figure S 27:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of  $\text{KPN}^{\text{Terph}}$  in  $\text{C}_6\text{D}_6$  at 298 K.

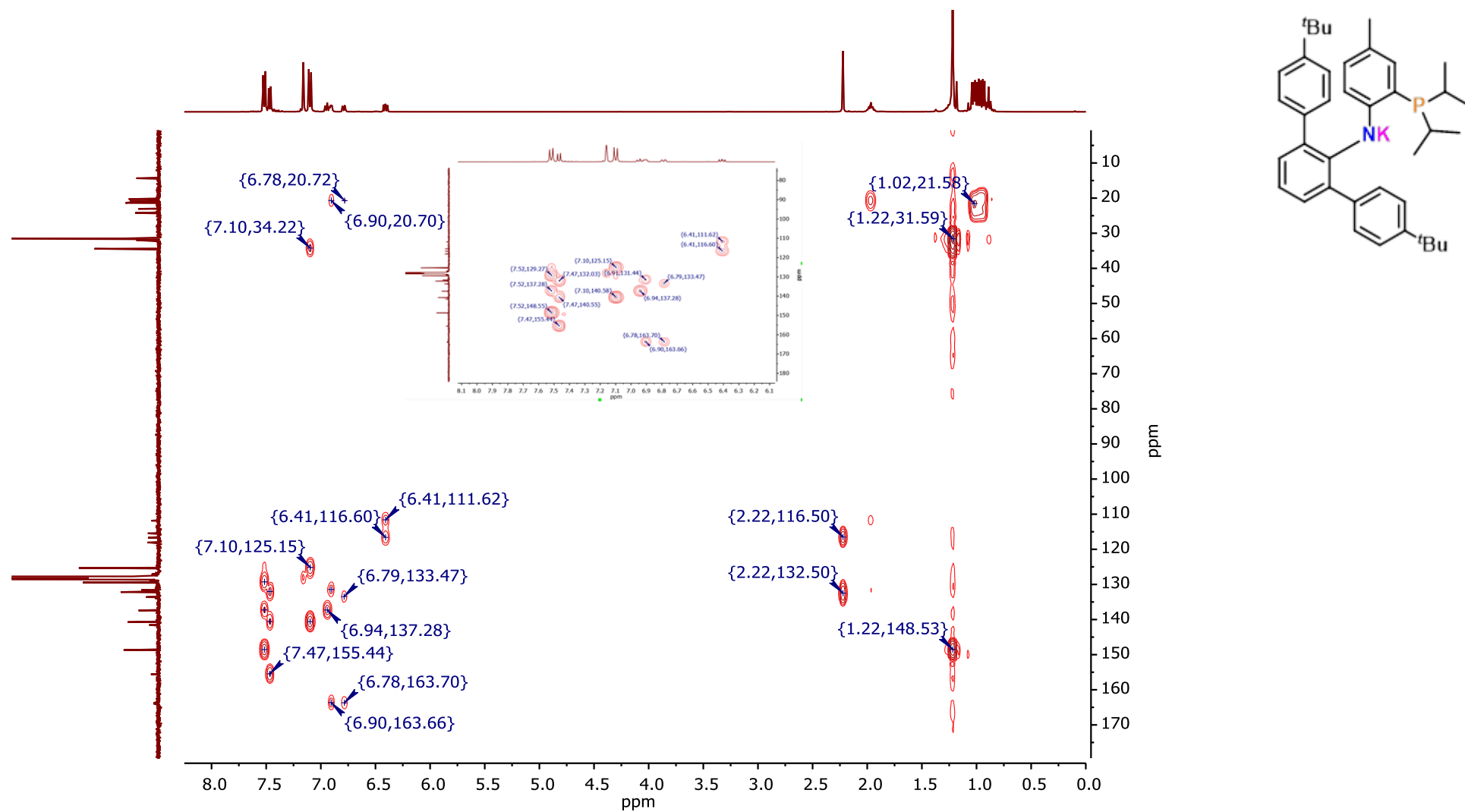


Figure S 28:  $^1H$ - $^{13}C$  HMBC NMR spectrum of  $KPN^{Terph}$  in  $C_6D_6$  at 298 K.

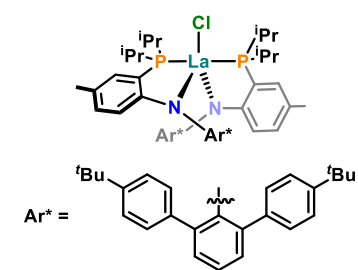
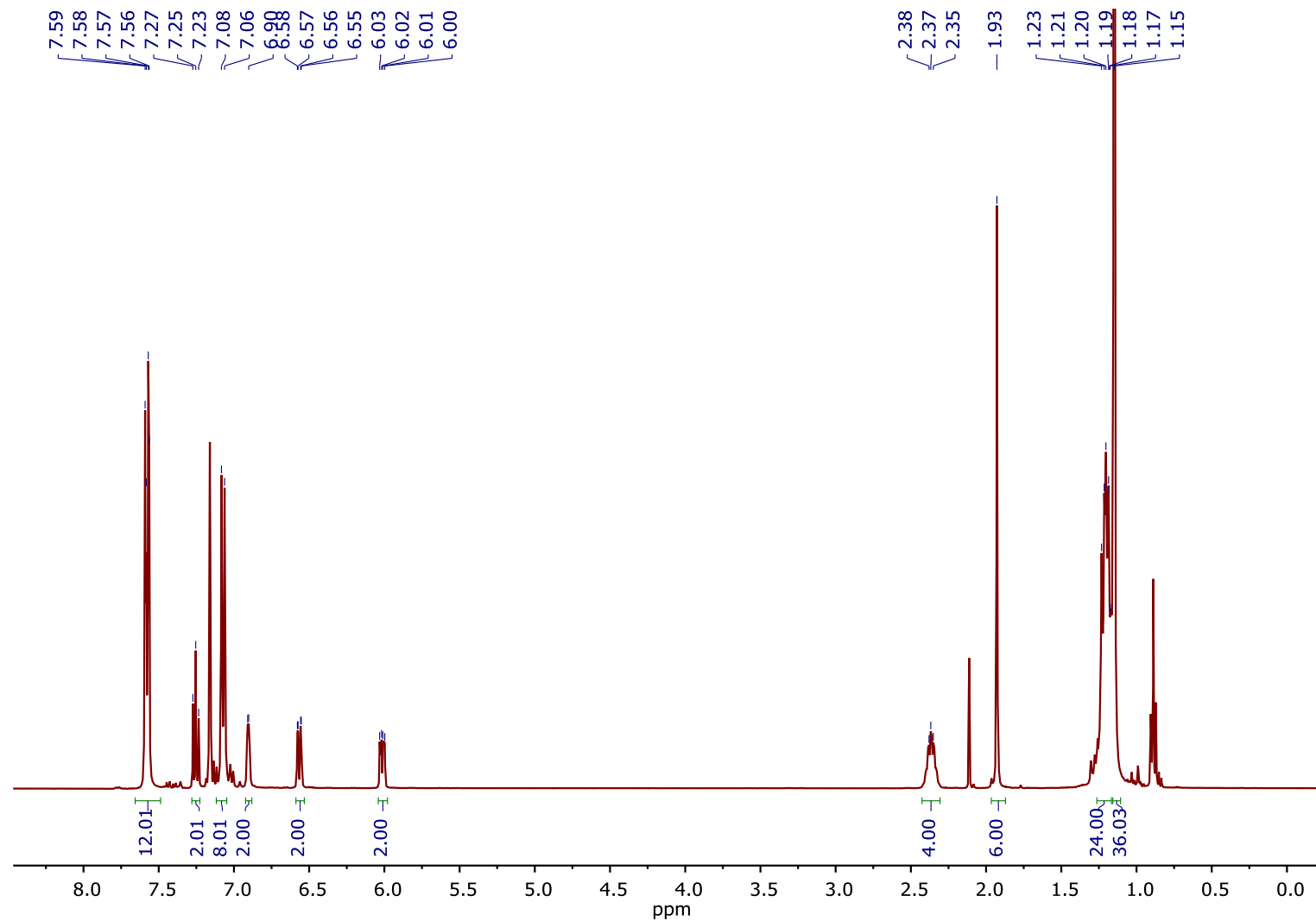


Figure S 29:  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

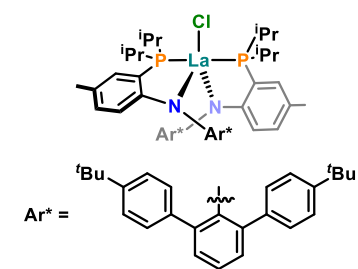
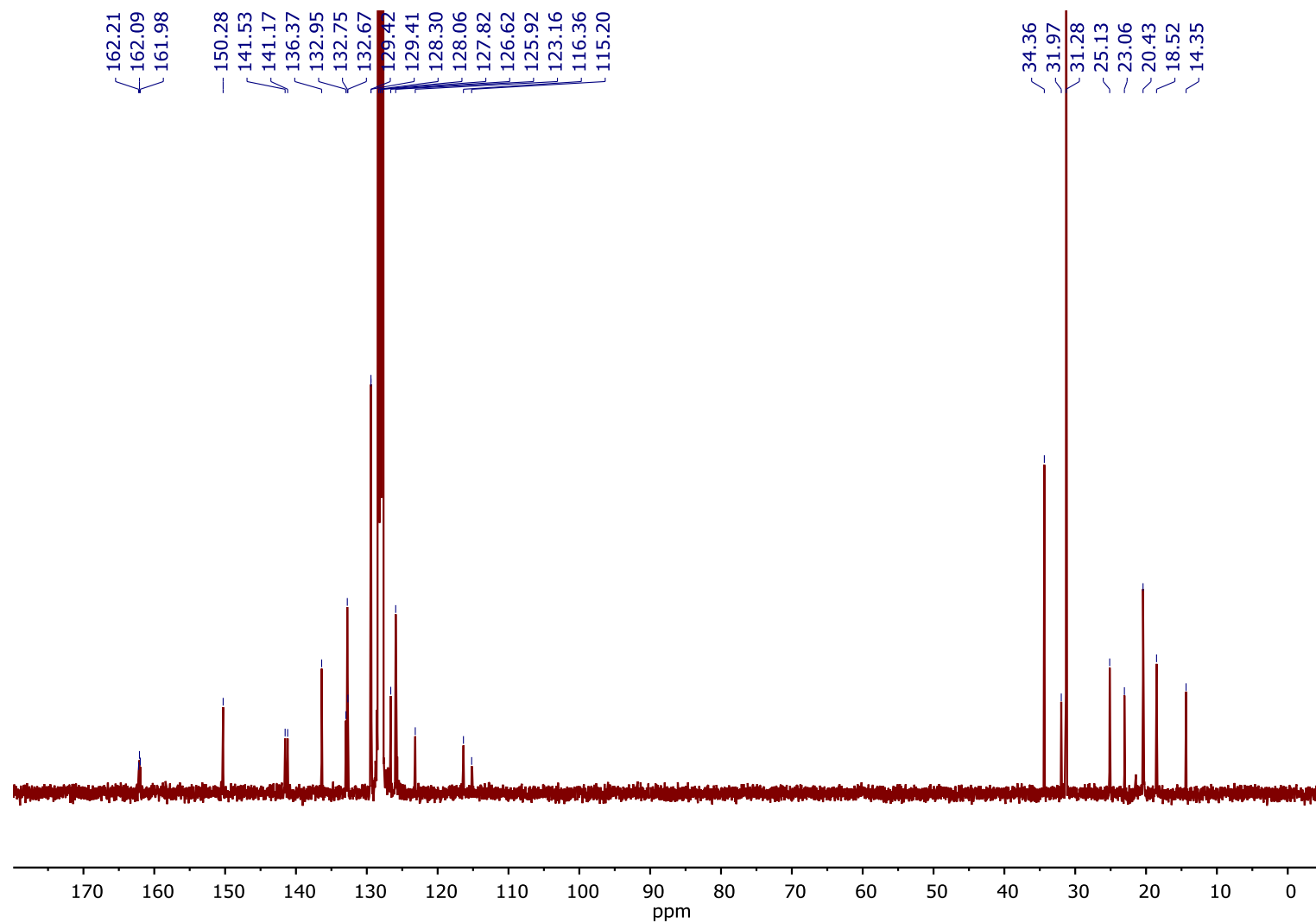


Figure S 30:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

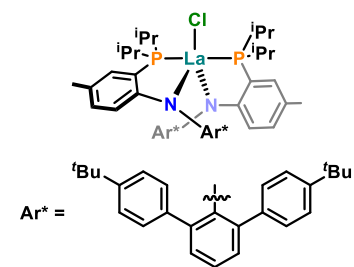
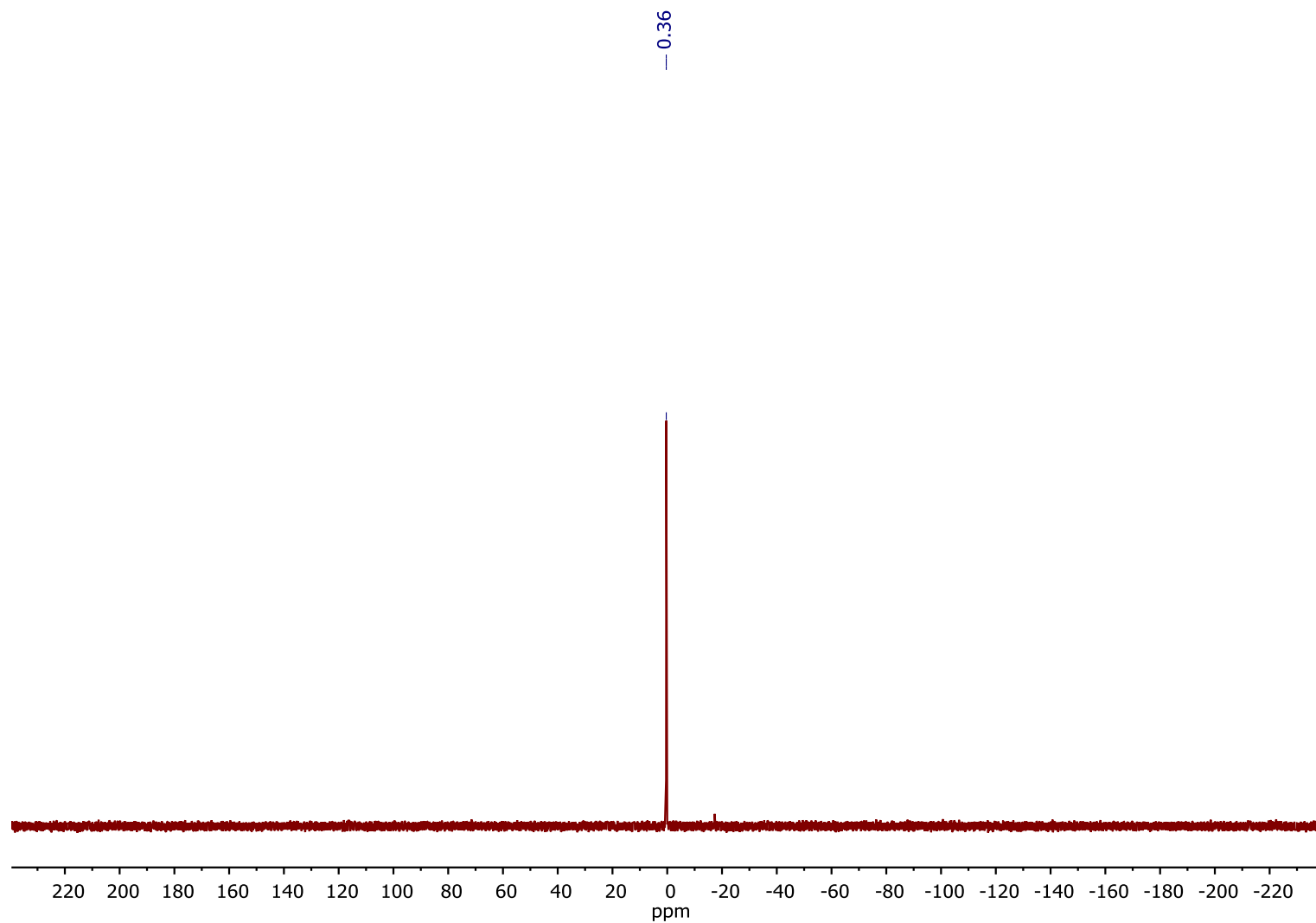


Figure S 31:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

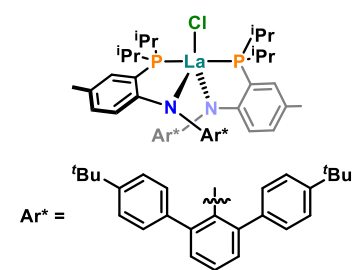
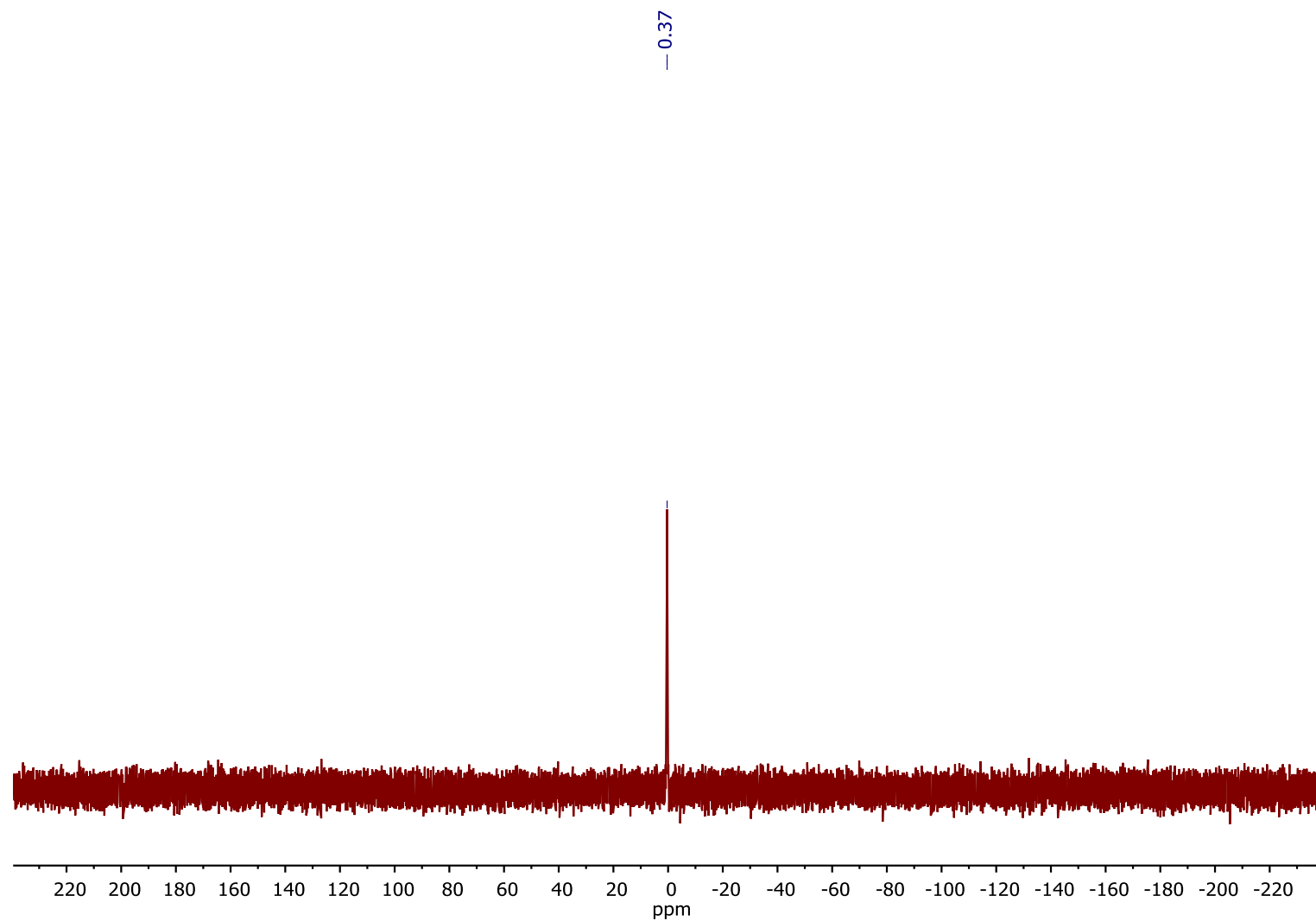


Figure S 32:  $^{31}\text{P}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

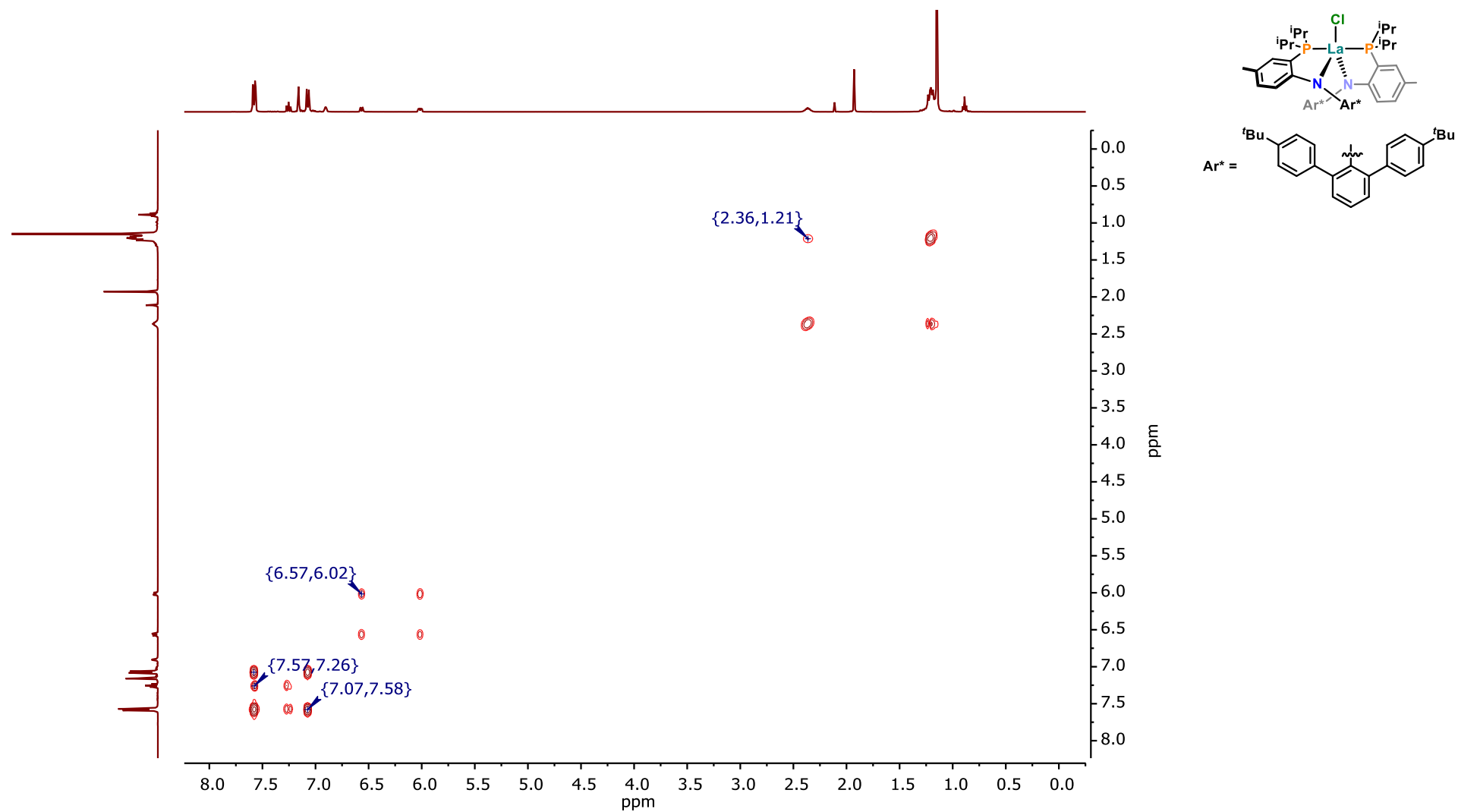


Figure S 33:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

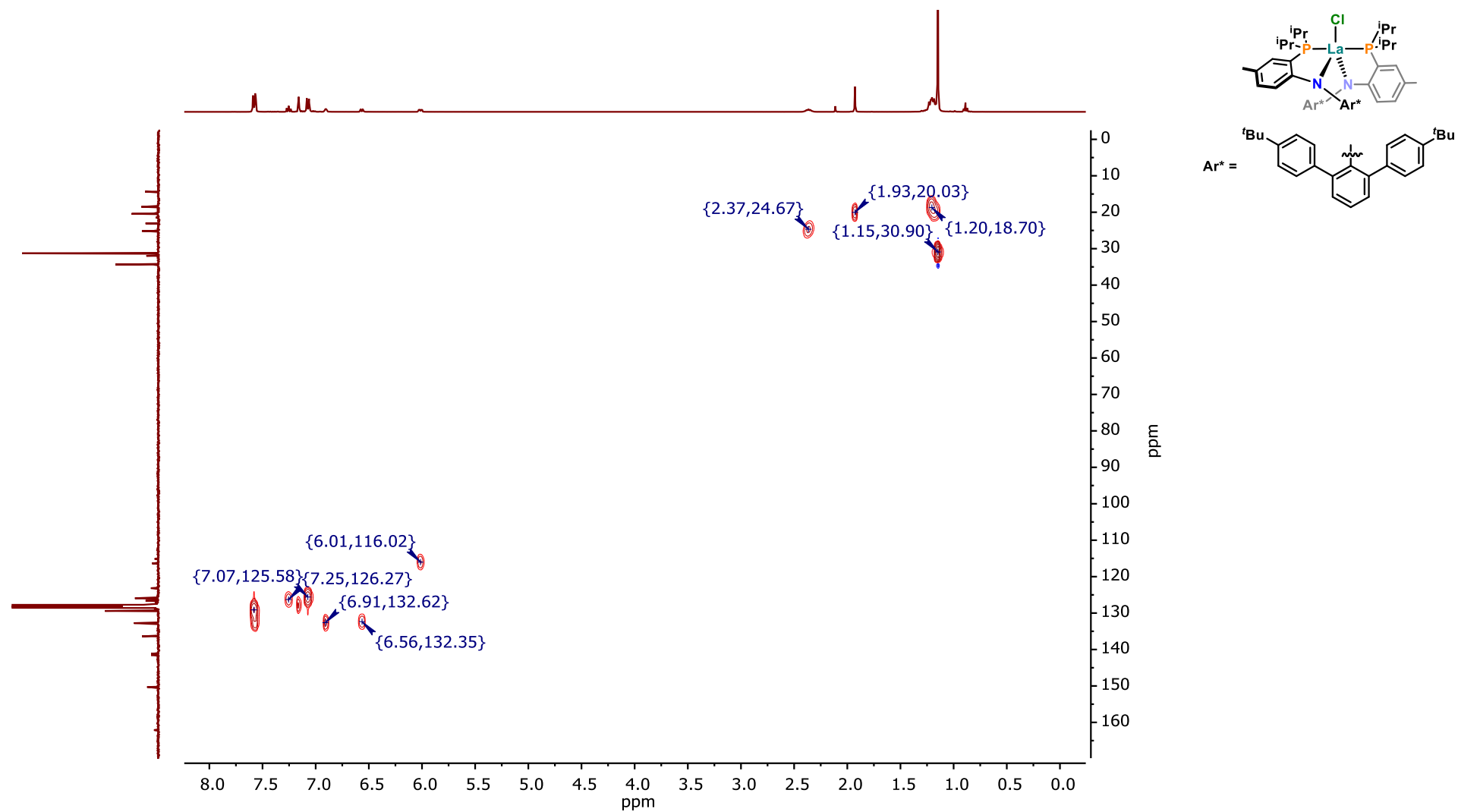


Figure S 34:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.



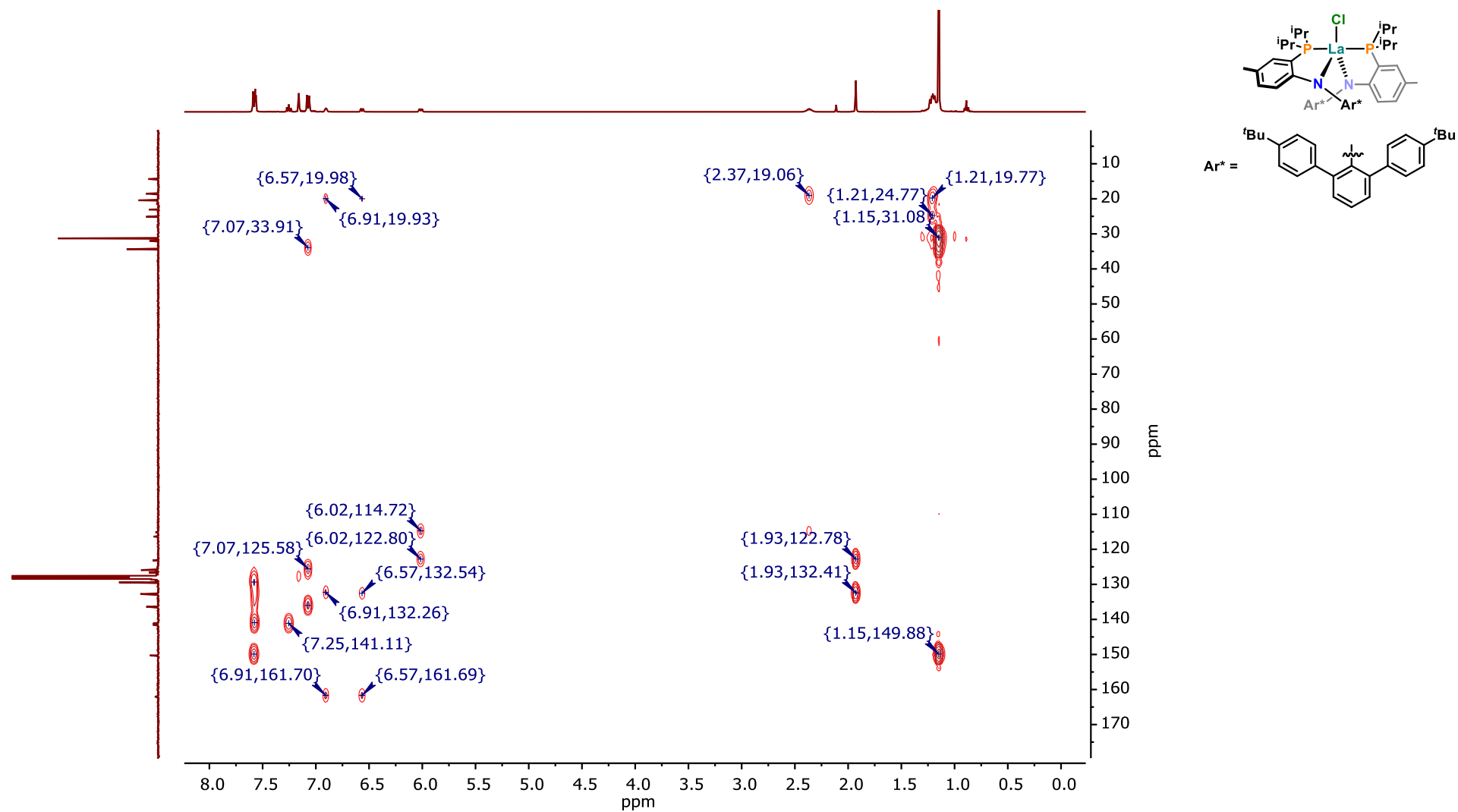


Figure S 35:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

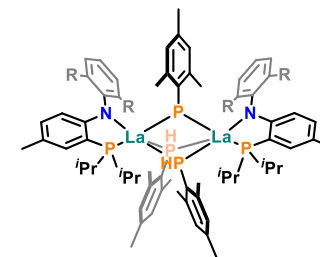
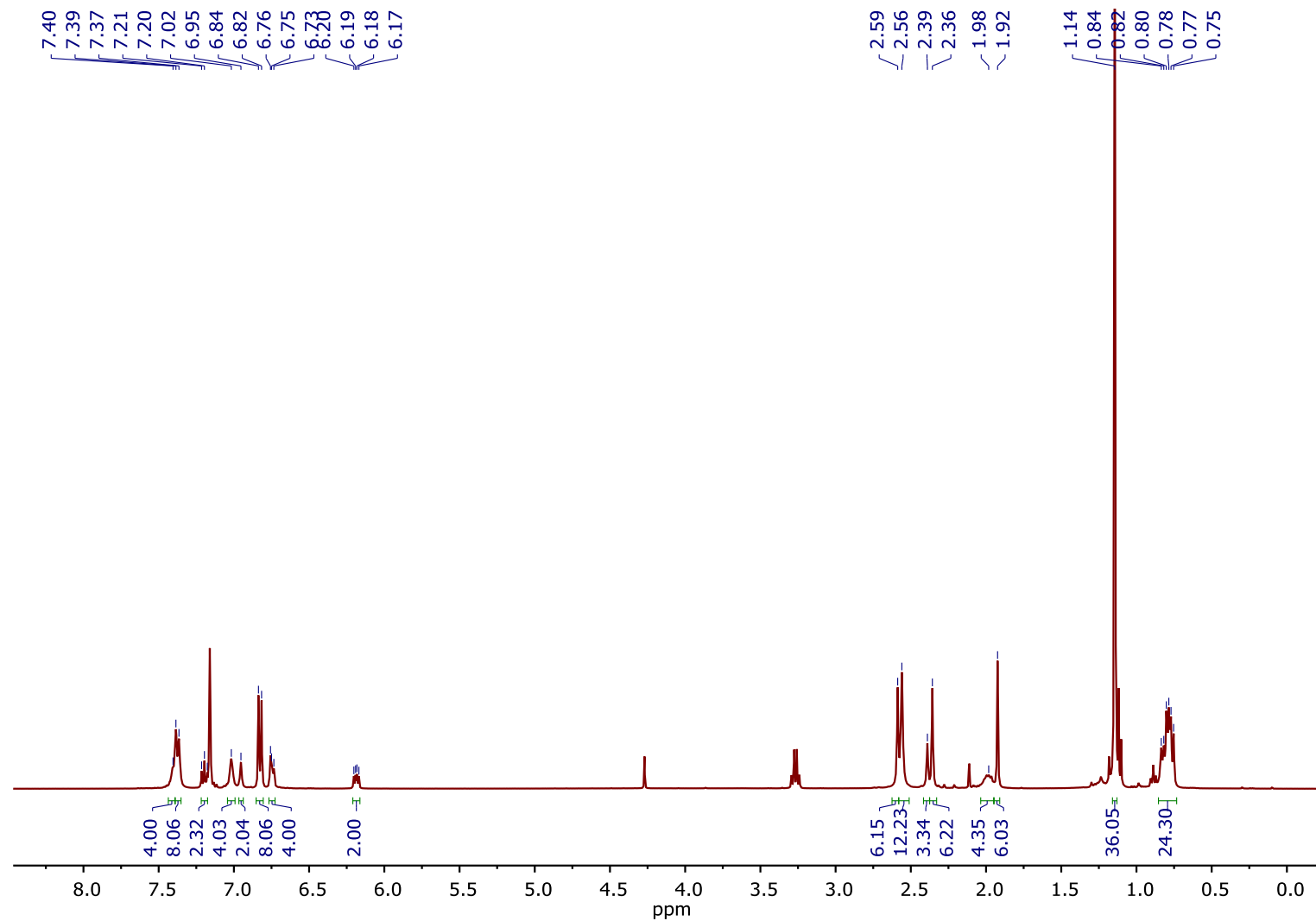


Figure S 36:  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

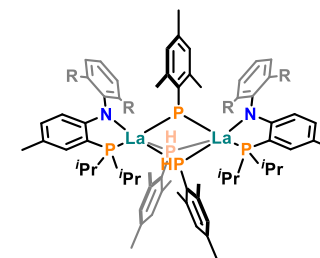
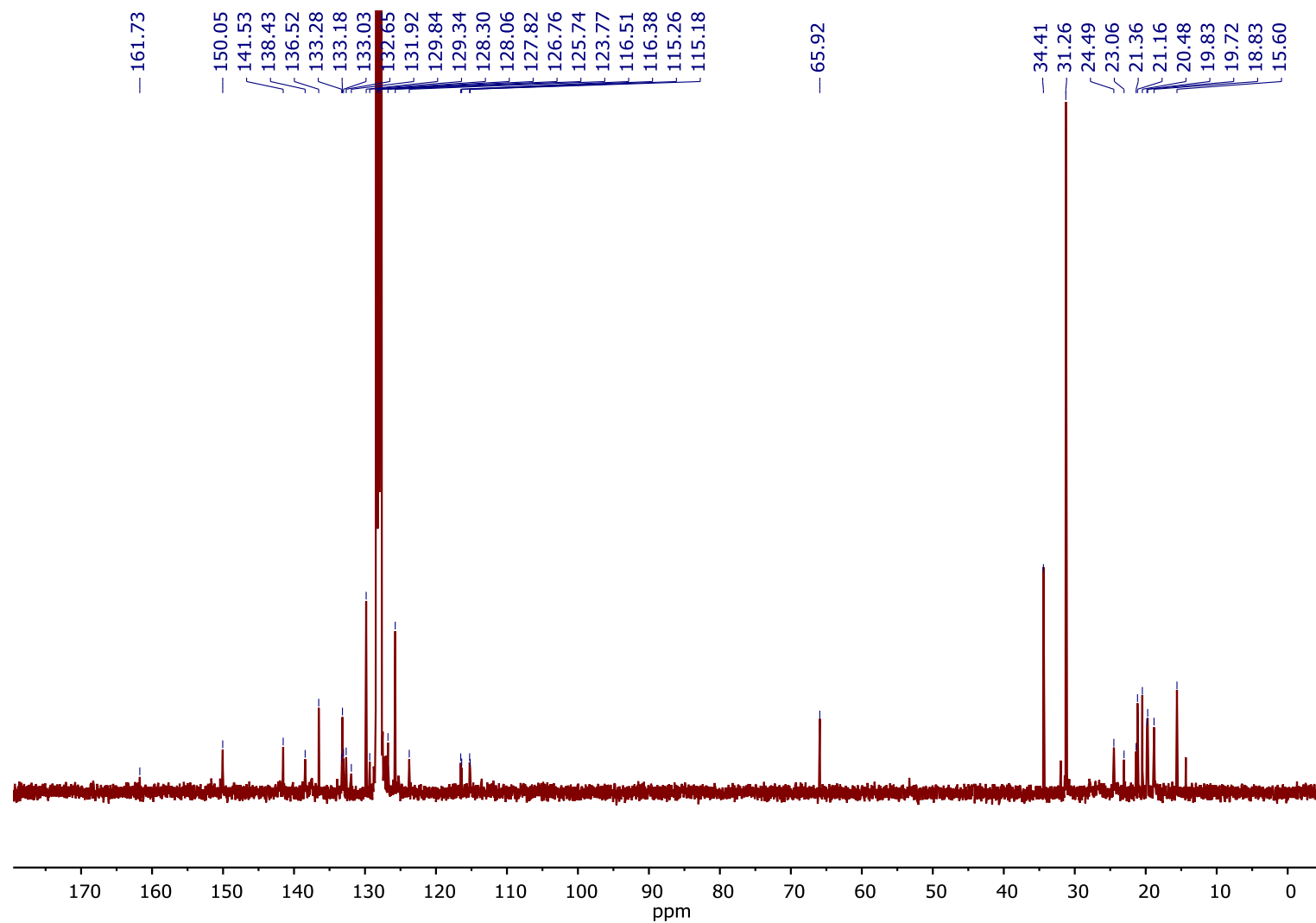


Figure S 37:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

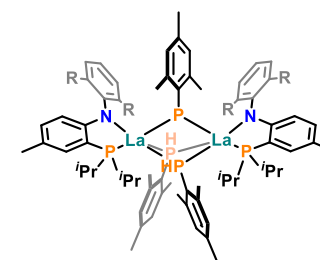
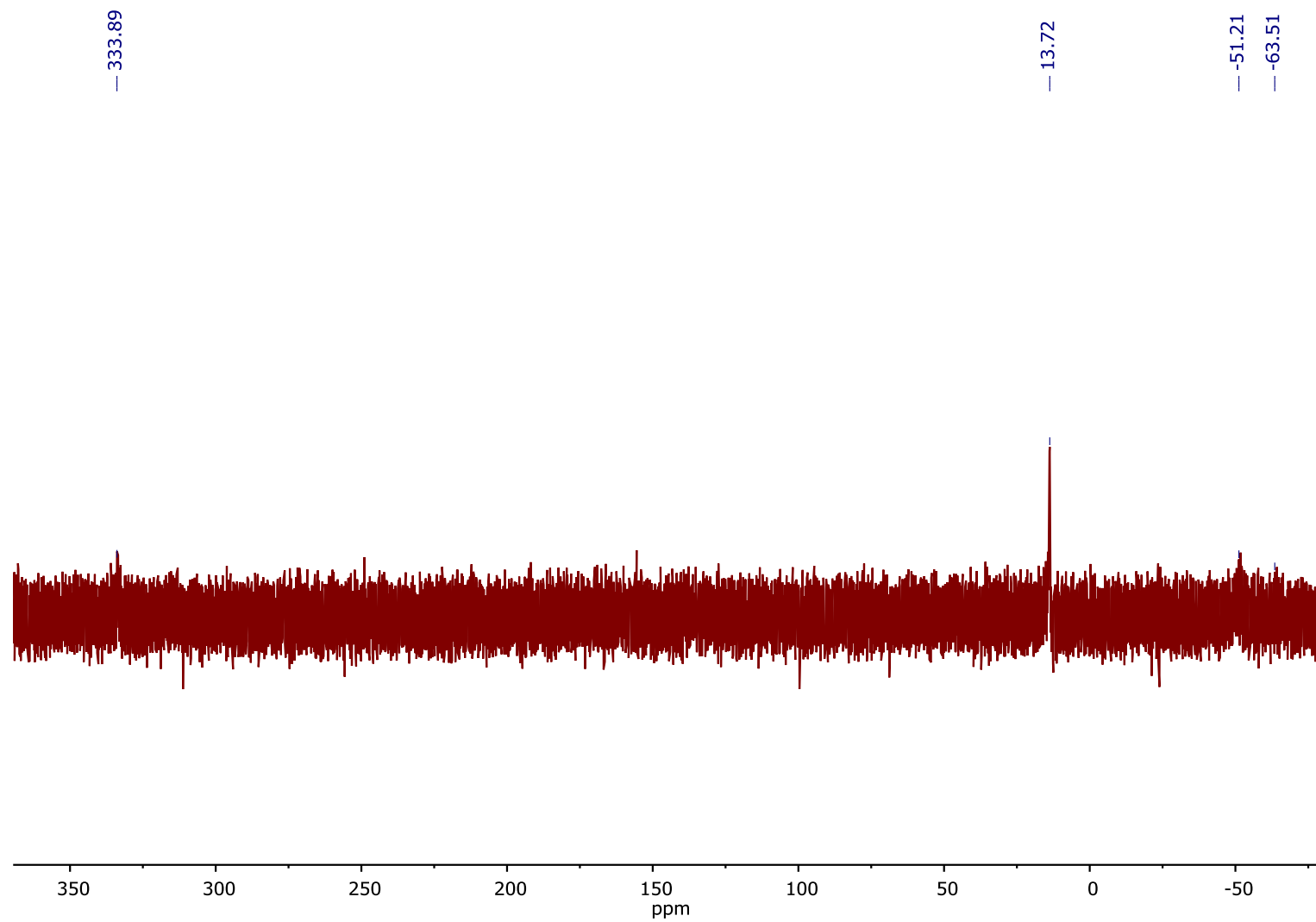


Figure S 38:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

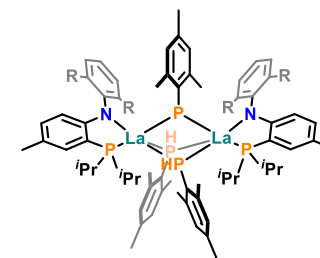
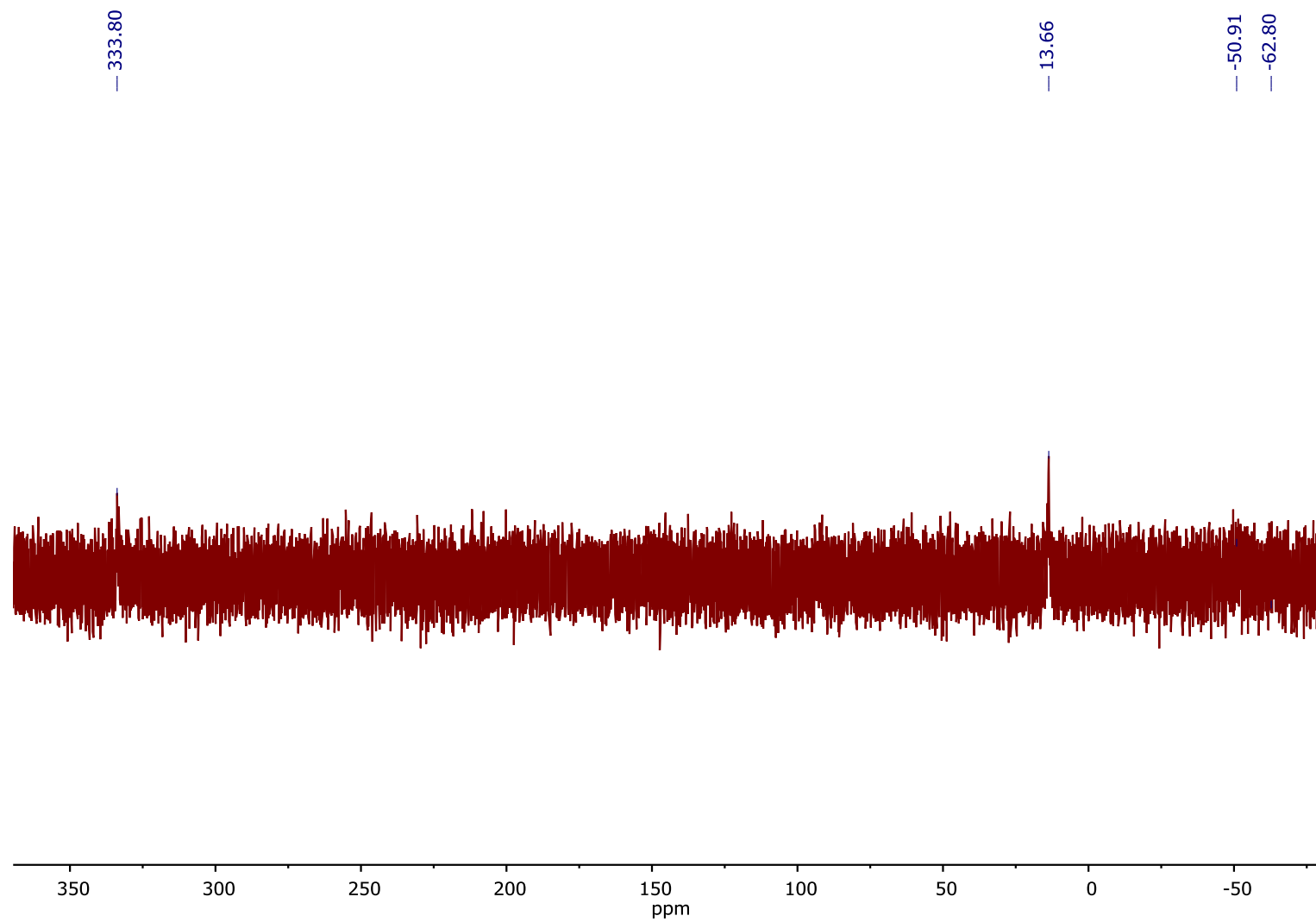


Figure S 39:  $^{31}\text{P}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

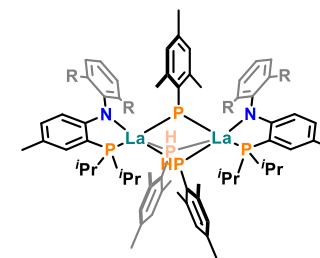
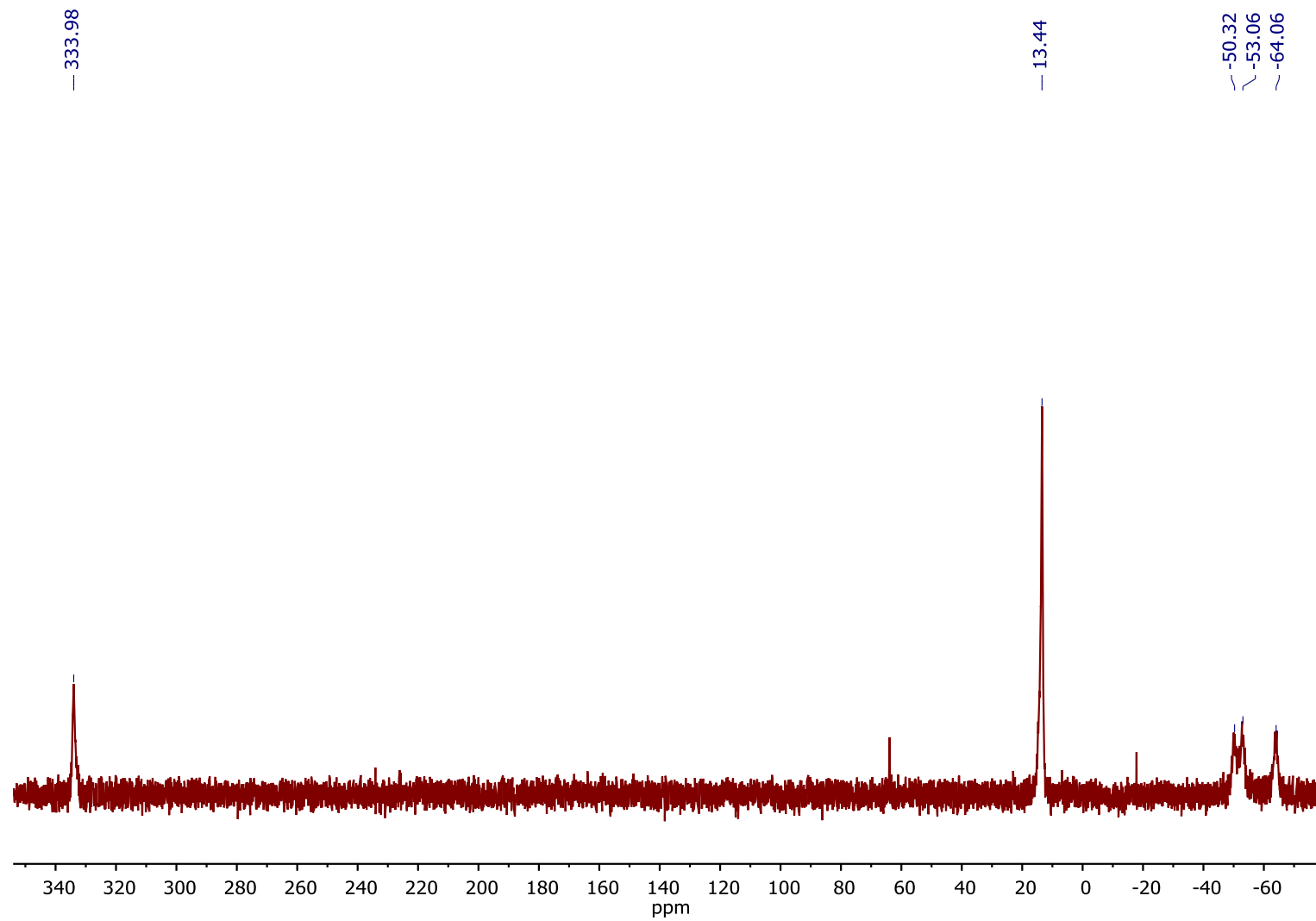


Figure S 40:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in toluene- $d_8$  at 288 K.

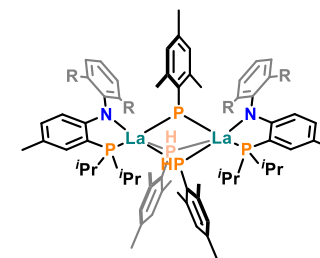
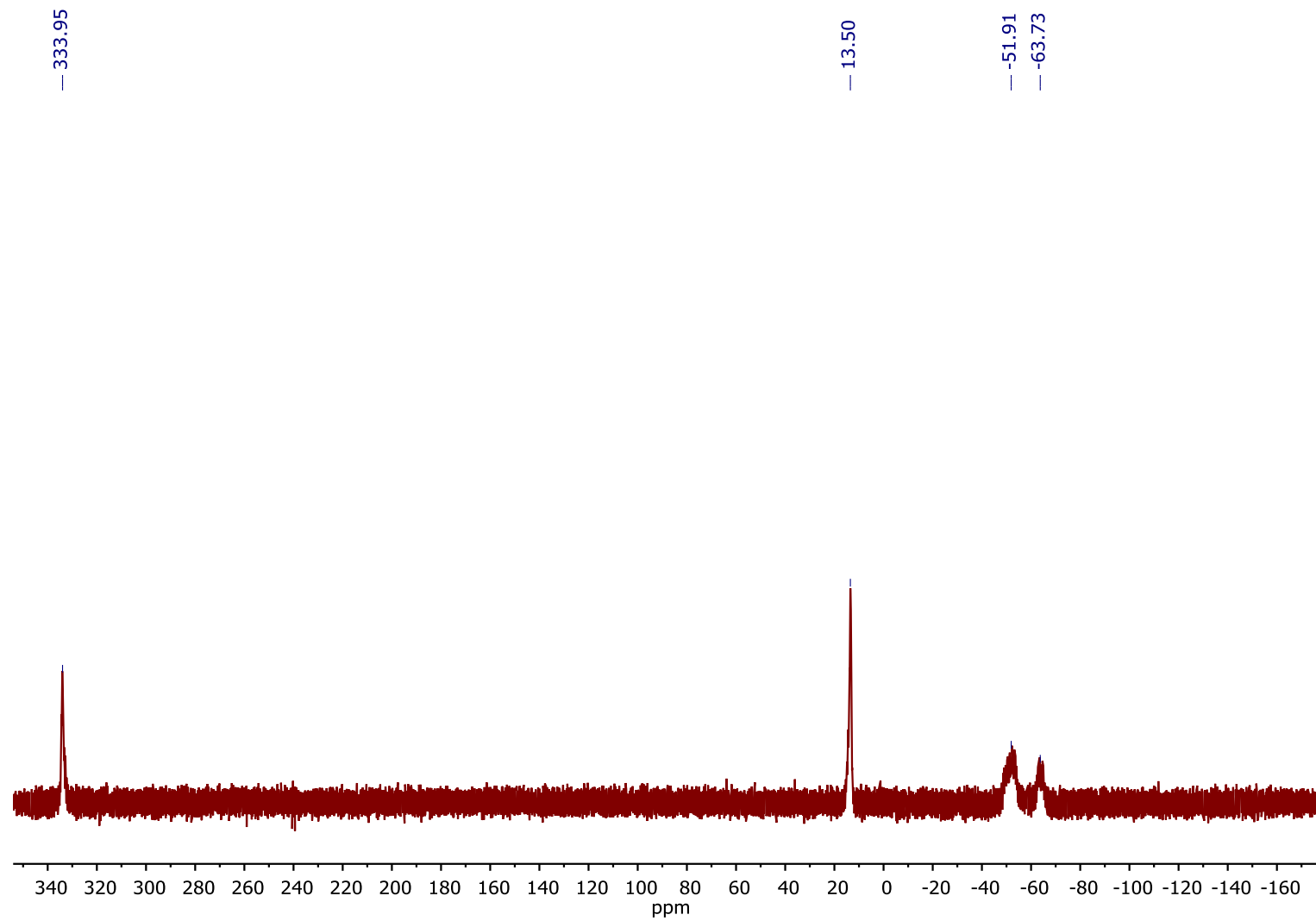


Figure S 41:  $^{31}\text{P}$  NMR spectrum of **2** in toluene- $d_8$  at 288 K.

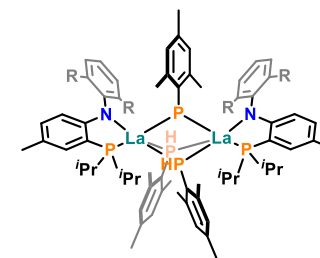
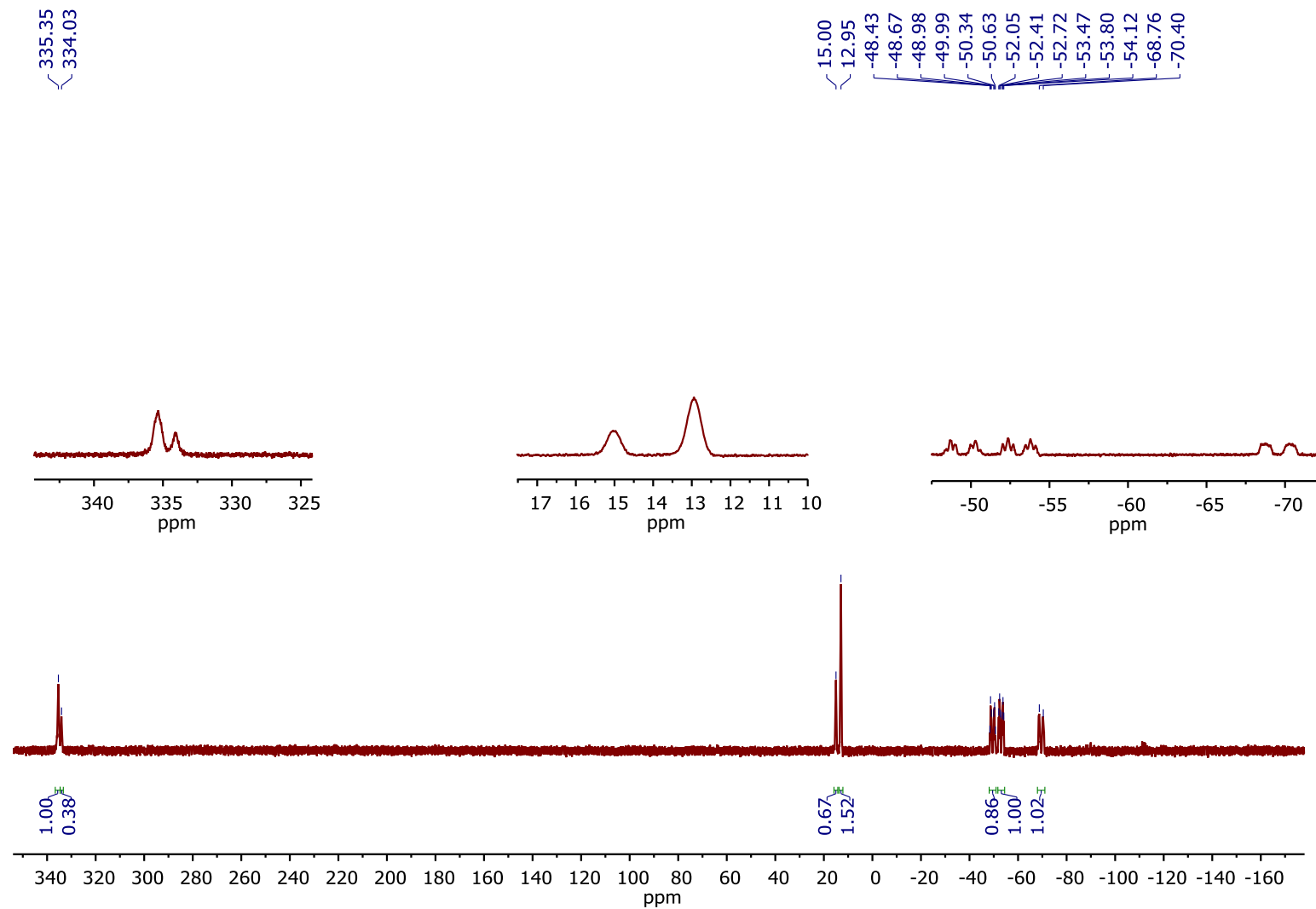


Figure S 42:  $^{31}\text{P}$  NMR spectrum of **2** in toluene- $d_8$  at 233 K. The signals at 335.3, 12.9, -53.0 and -69.5 ppm belong to the anti-isomer, while the signals at 334.0, 15.0, -49.5 belong to the syn-isomer.



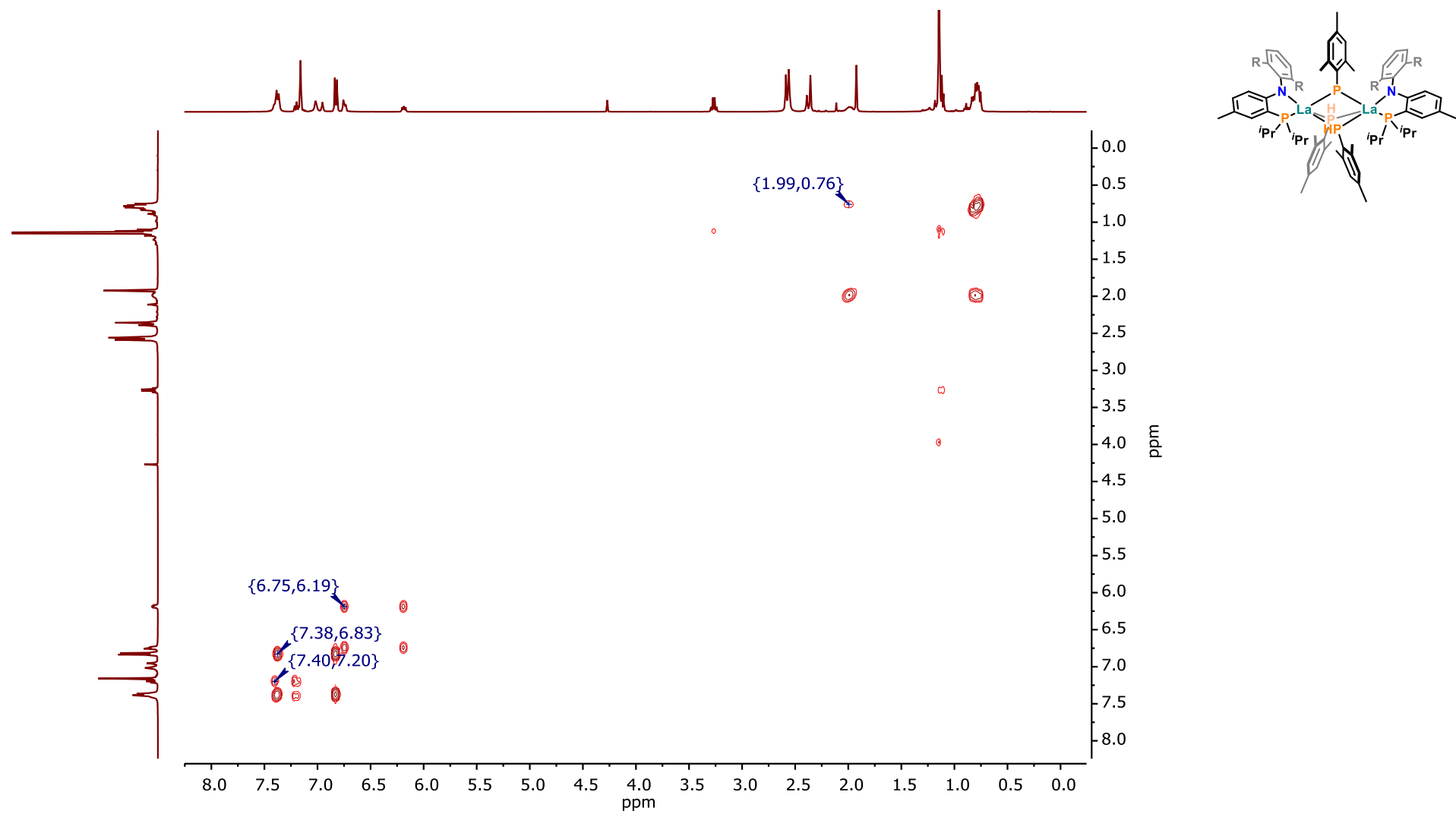


Figure S 43:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

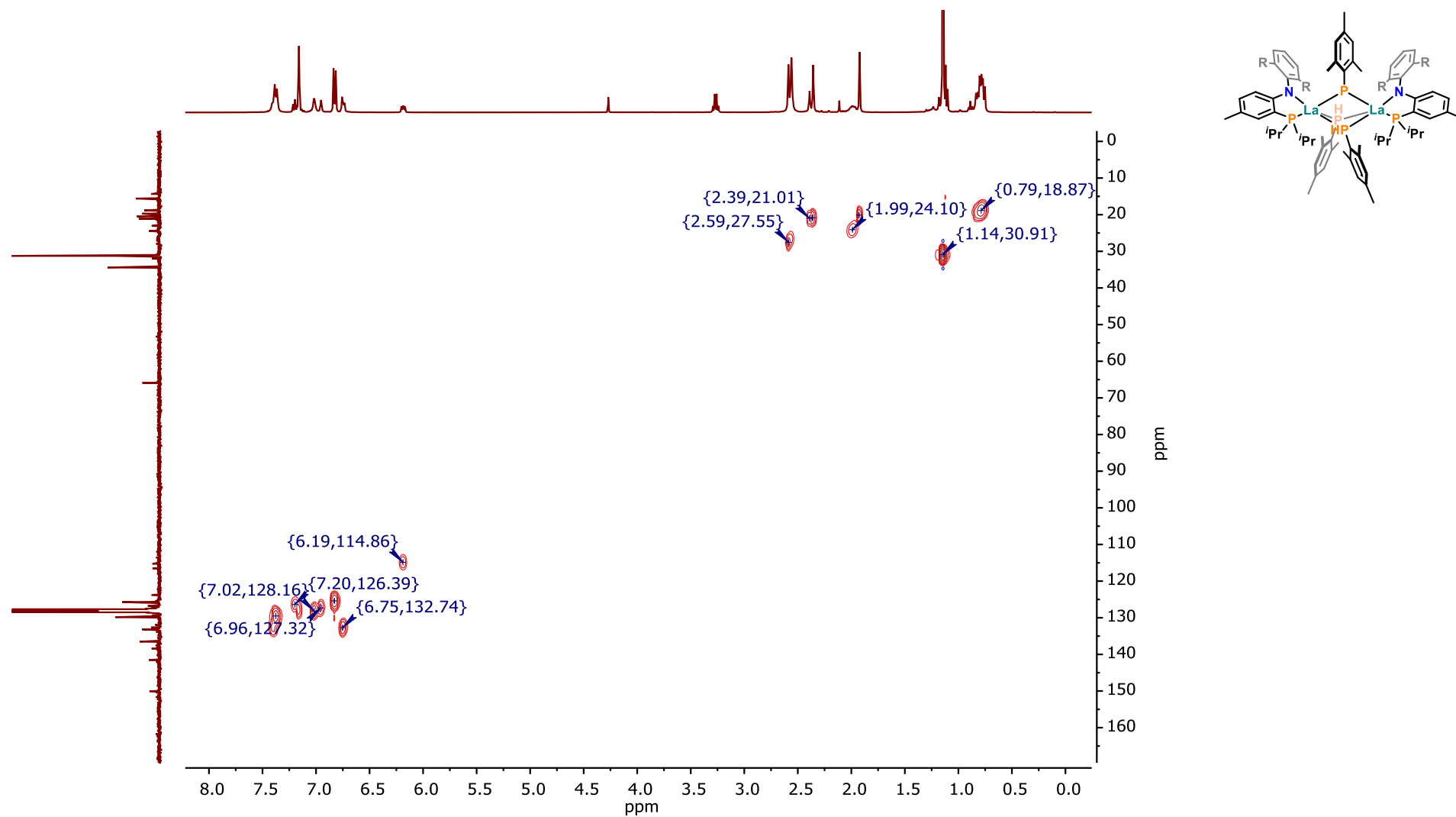


Figure S 44:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

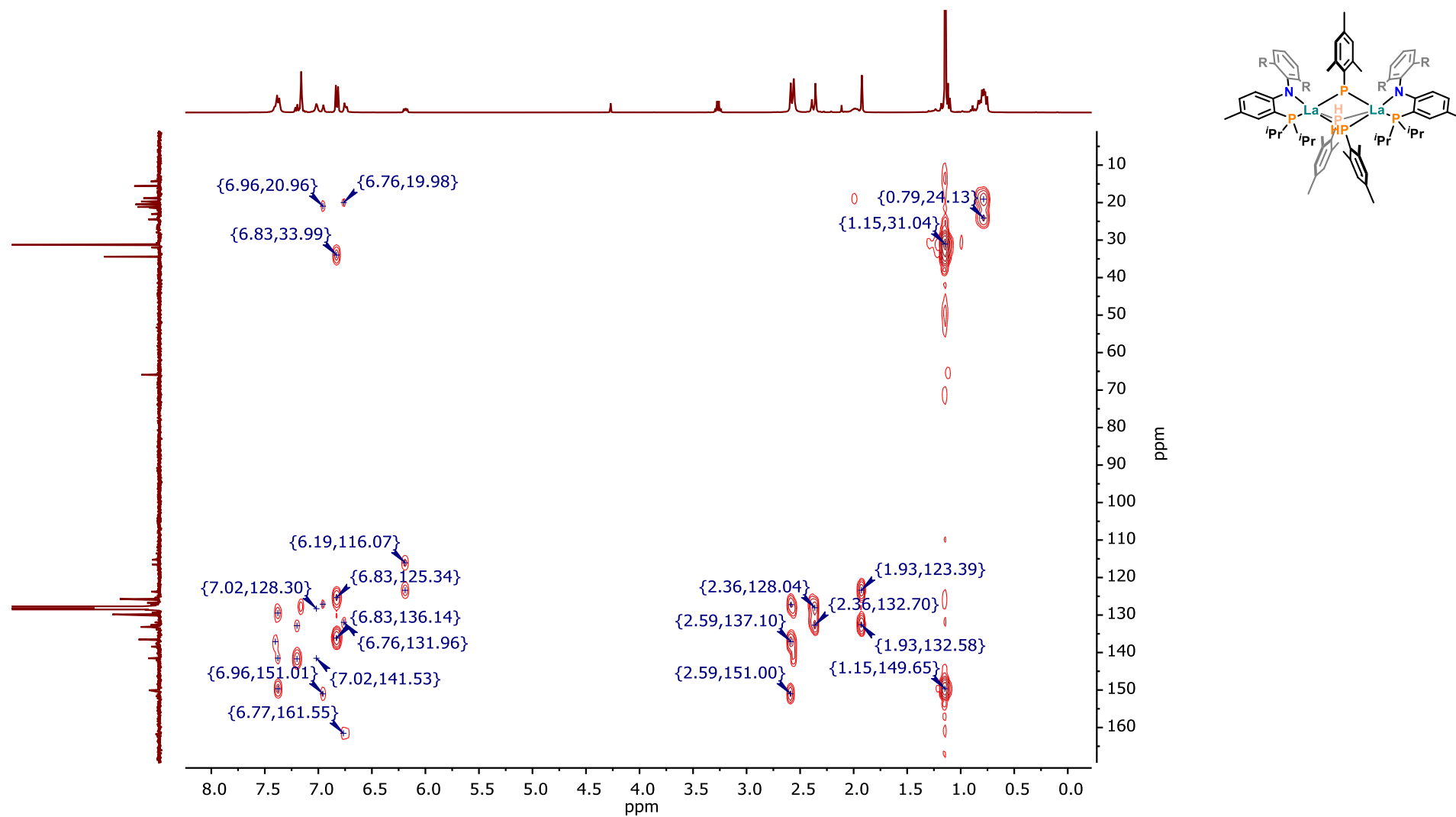


Figure S 45:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  at 298 K.

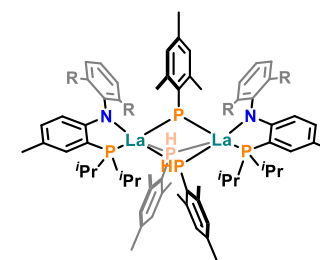
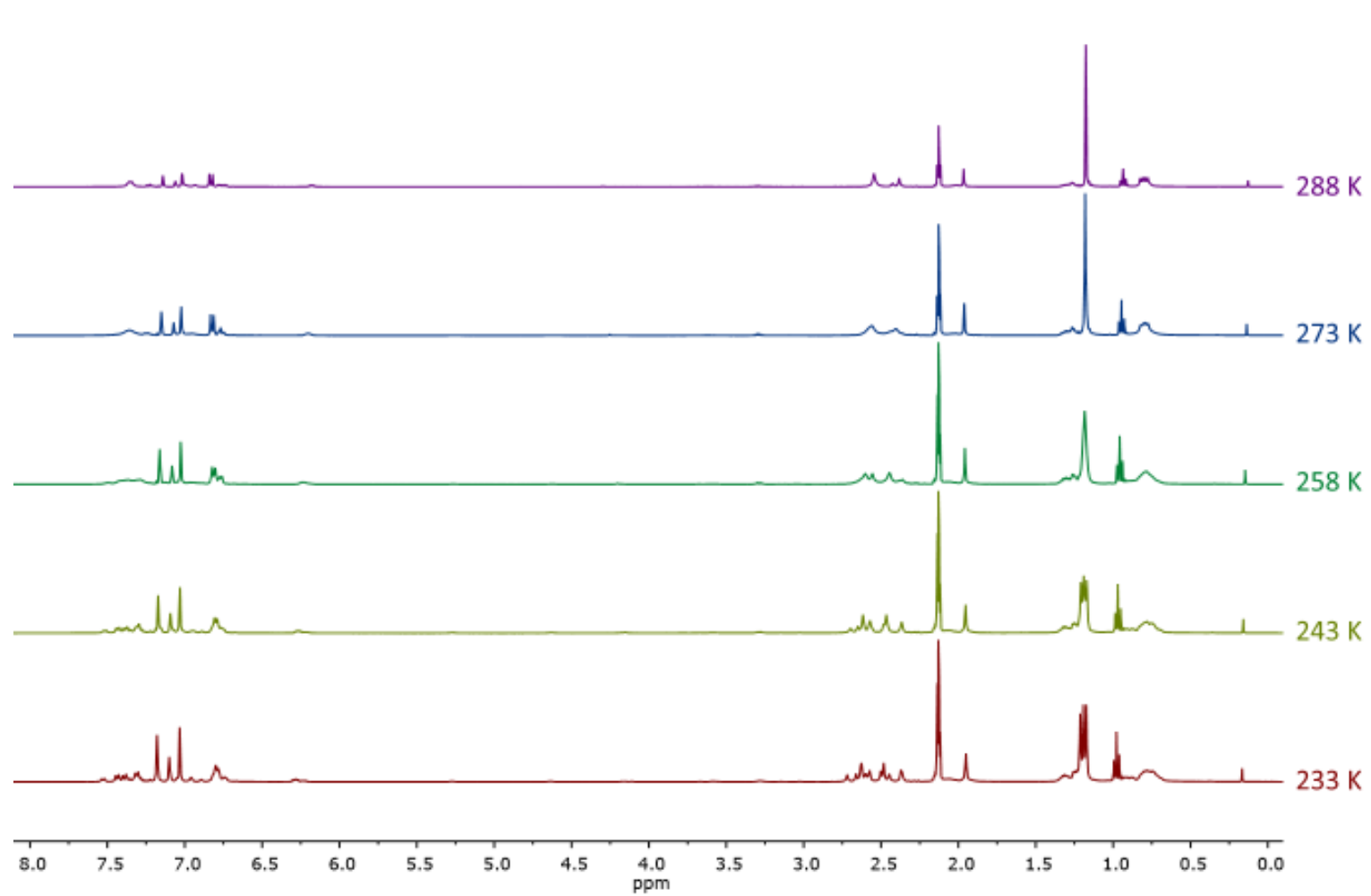


Figure S 46: VT  $^1\text{H}$  NMR of **2** in toluene- $d_8$  at 233 K (red), 243 K (yellow), 258 K (green), 273 K (blue) and 288 K (purple).

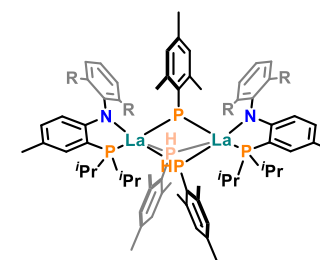
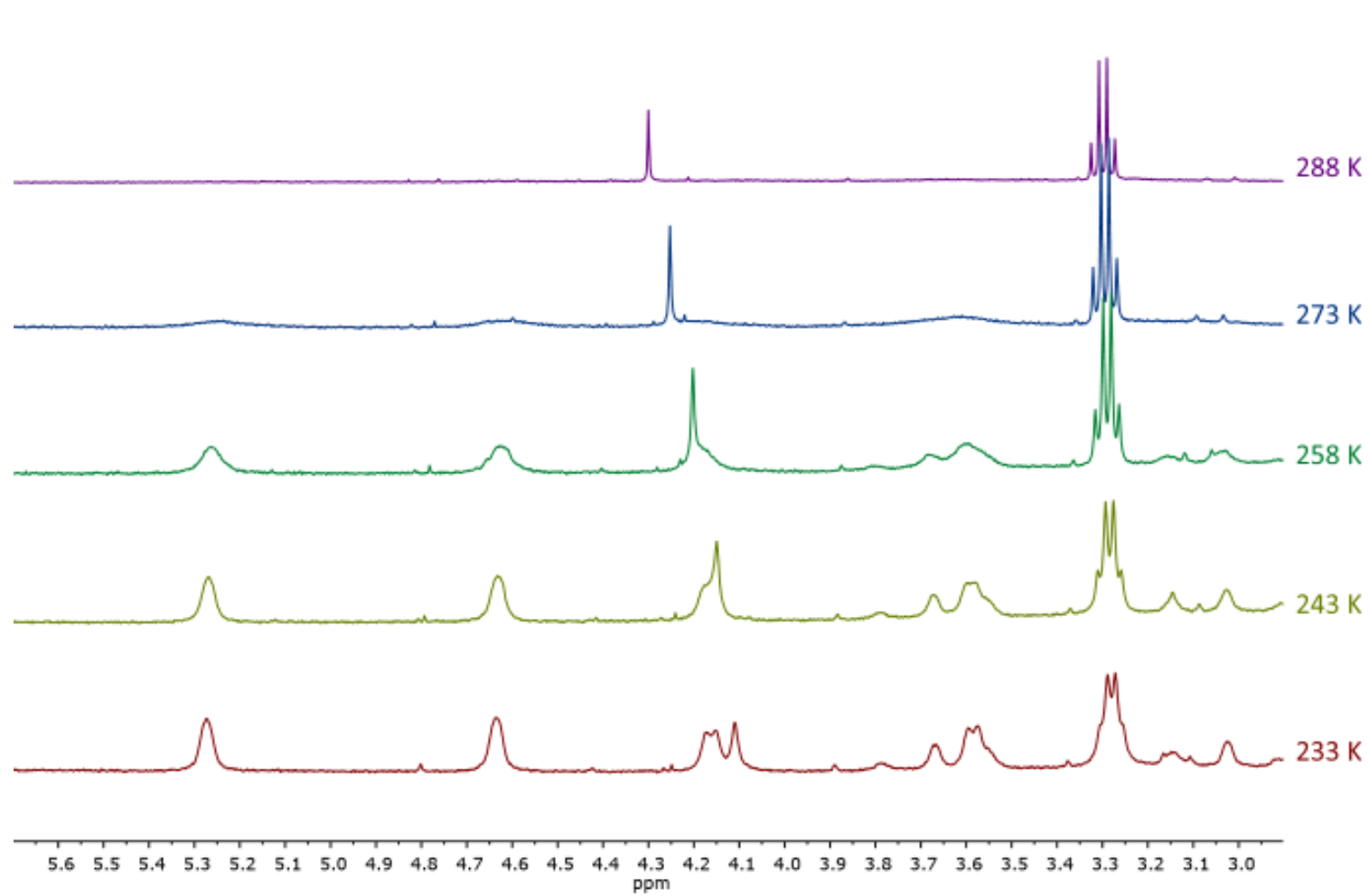


Figure S 47: Section of VT  $^1\text{H}$  NMR of **2** in  $\text{toluene-d}_8$  at 233 K (red), 243 K (yellow), 258 K (green), 273 K (blue) and 288 K (purple).

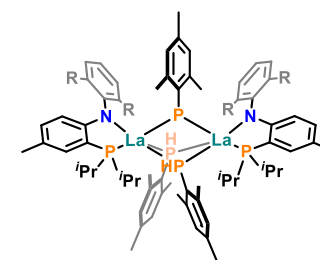
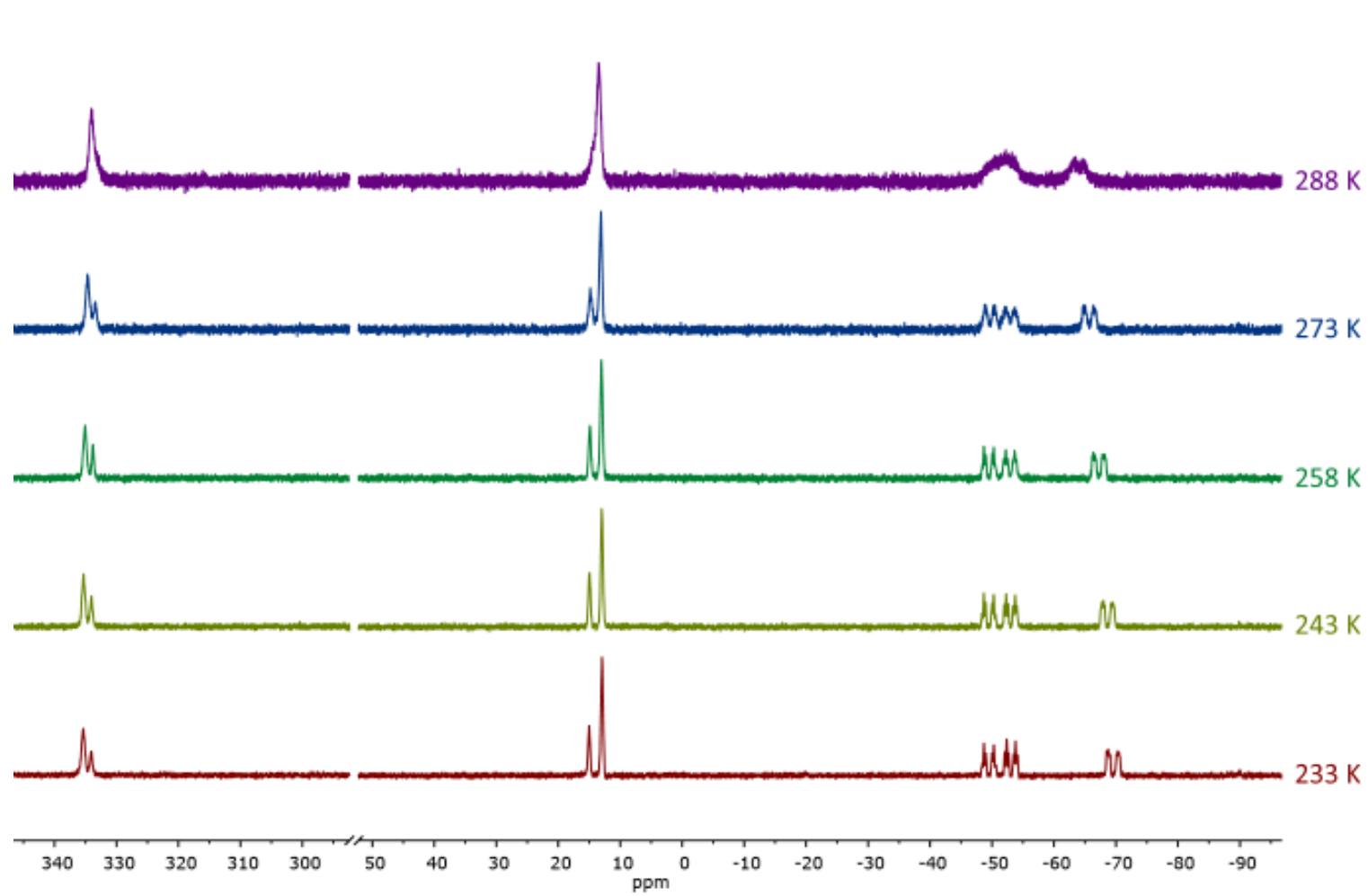


Figure S 48: VT  $^{31}\text{P}$  NMR of **2** in toluene- $d_8$  at 233 K (red), 243 K (yellow), 258 K (green), 273 K (blue) and 288 K (purple).

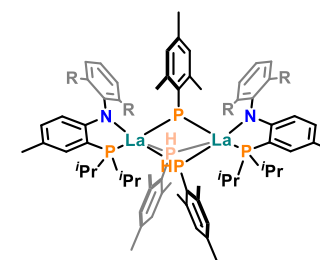
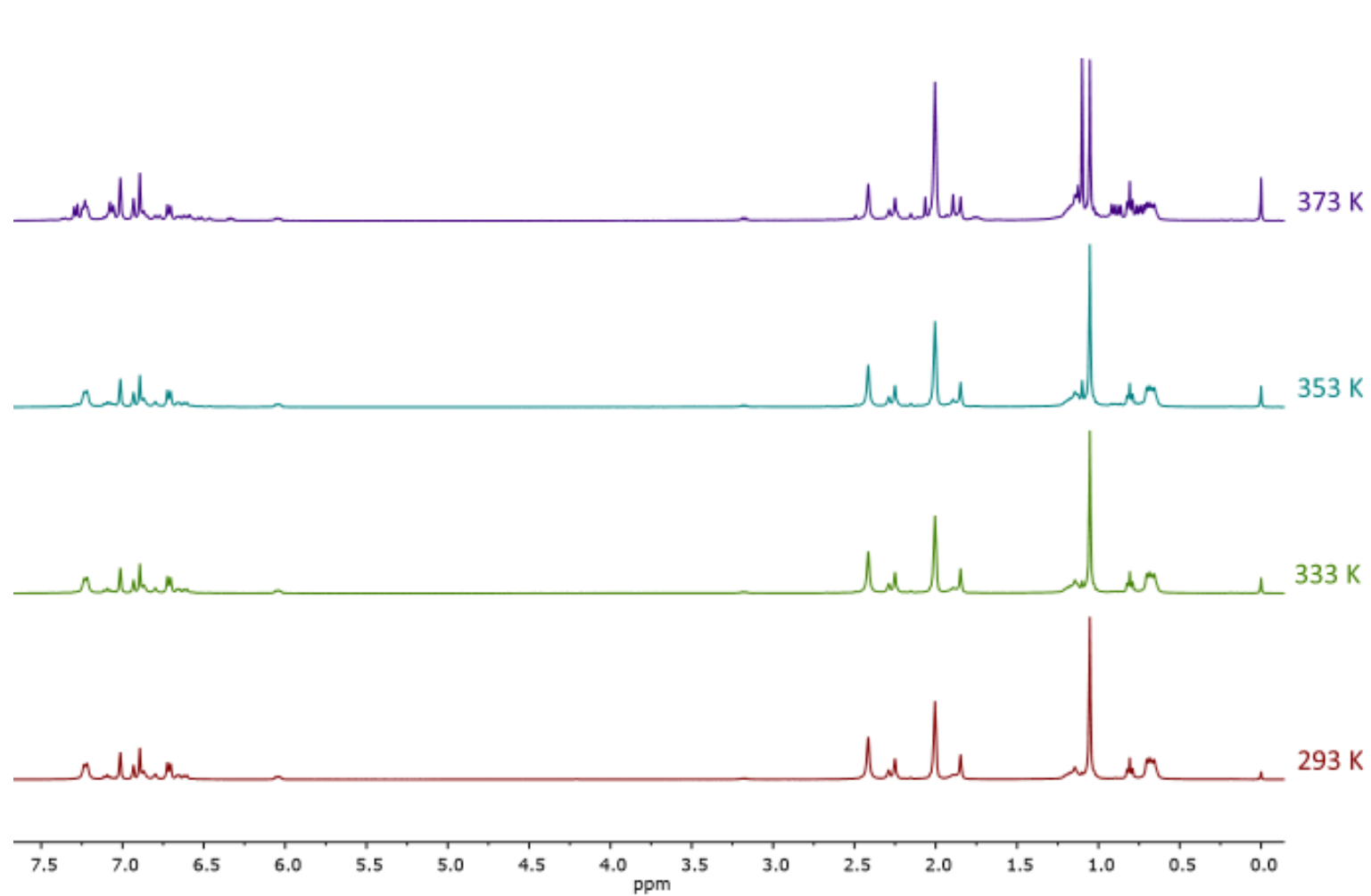


Figure S 49:  $^1\text{H}$  NMR of decomposition of **2** in toluene- $d_8$  at 293 K (red), 333 K (green), 353 K (blue) and 373 K (purple). (Complex **2** was heated in a J. Young NMR tube at the different temperatures for 24 h before measuring.)

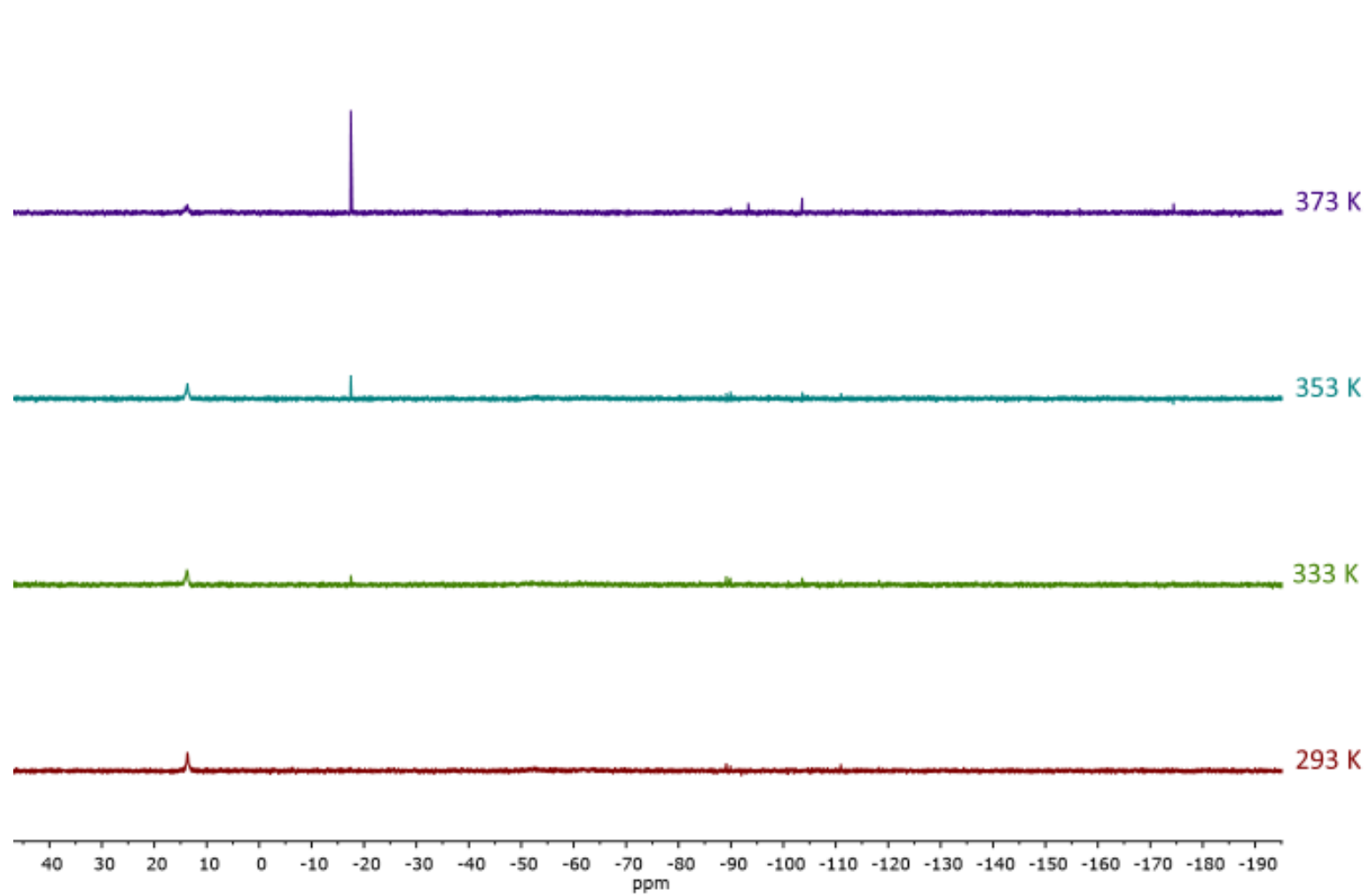


Figure S 50:  $^{31}\text{P}$  NMR of decomposition of **2** in  $\text{toluene-d}_8$  at 293 K (red), 333 K (green), 353 K (blue) and 373 K (purple). (Complex **2** was heated in a J. Young NMR tube at the different temperatures for 24 h before measuring.)



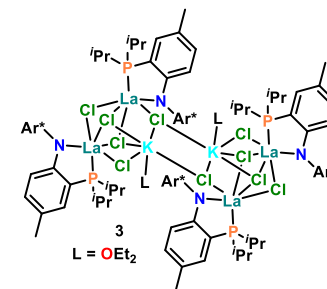
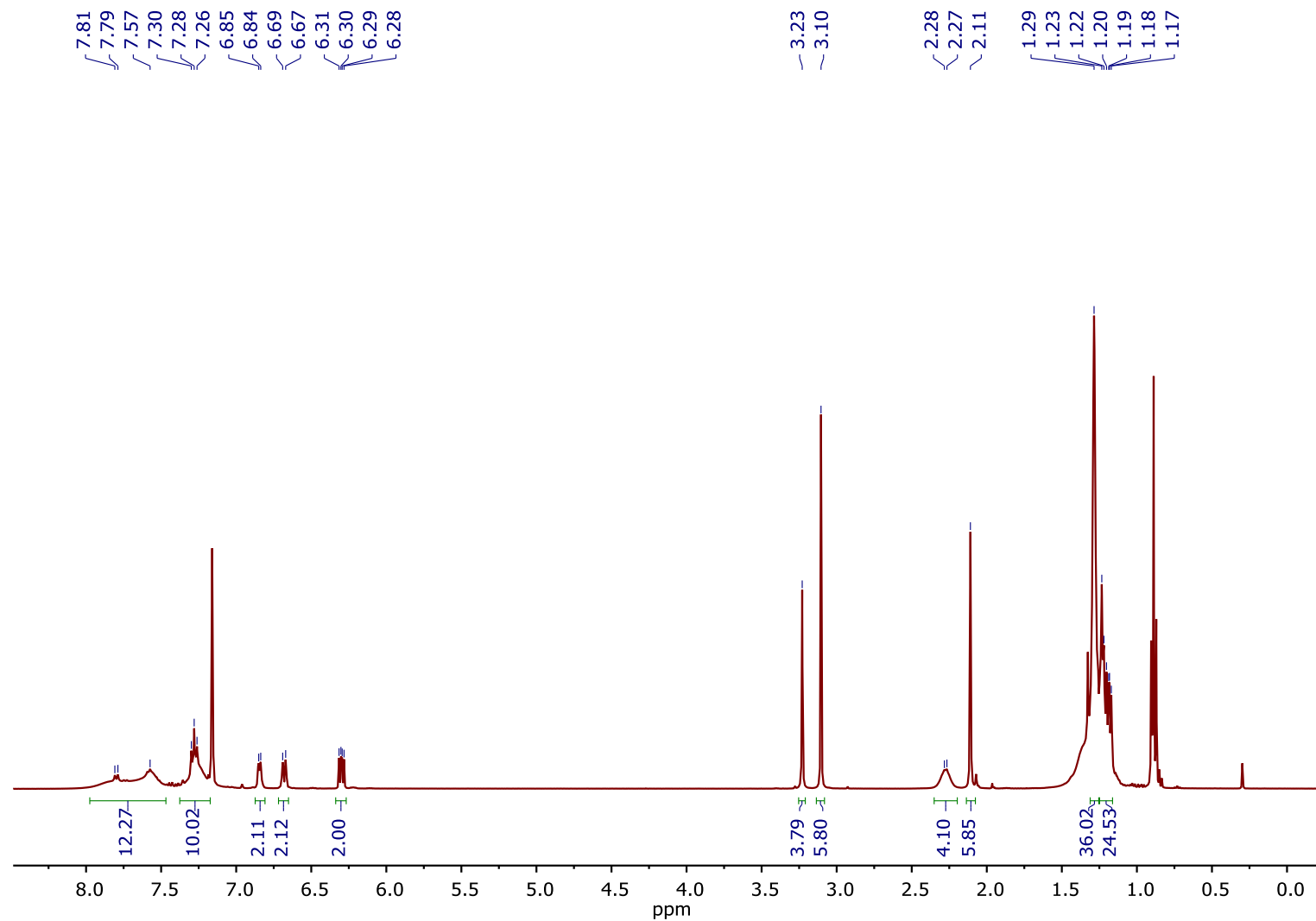


Figure S 51: <sup>1</sup>H NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> at 298 K.

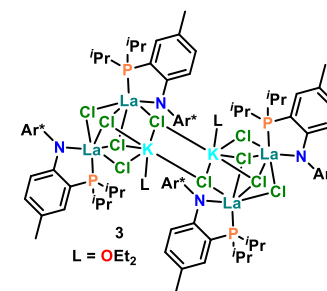
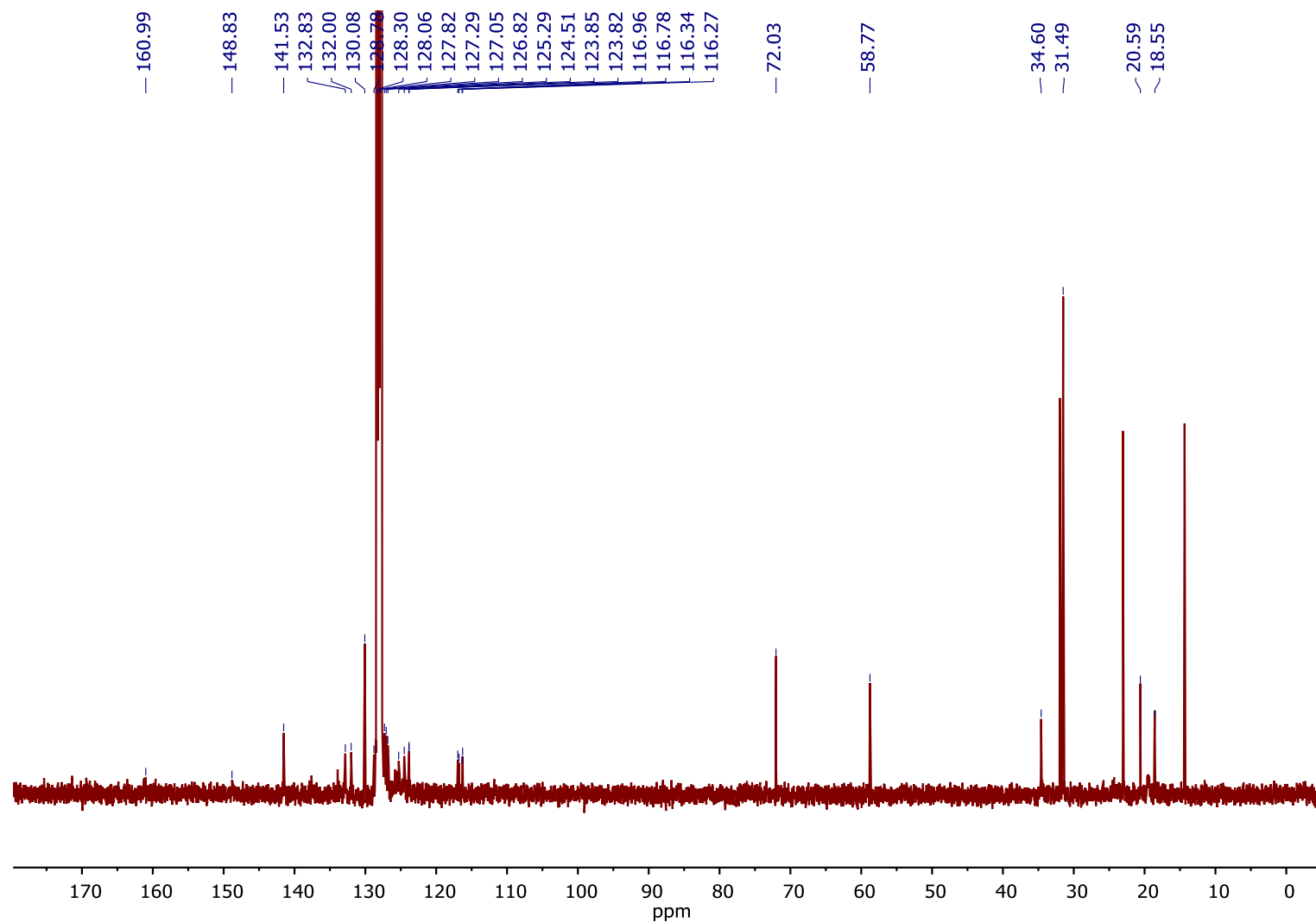


Figure S 52:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K.

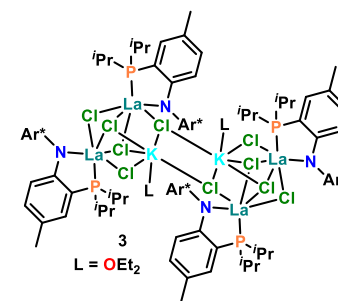
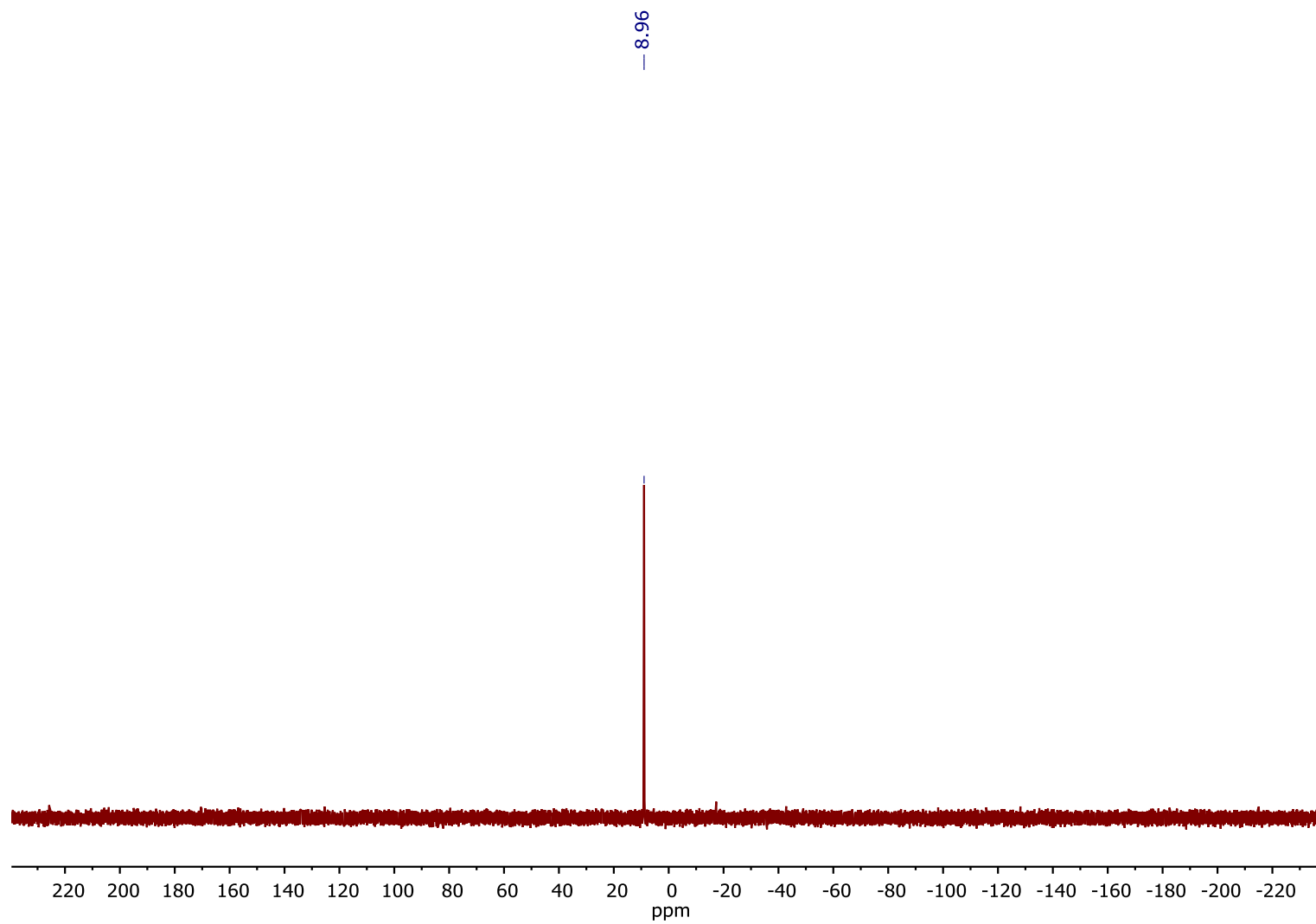


Figure S 53:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K.

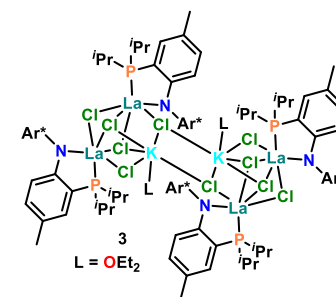
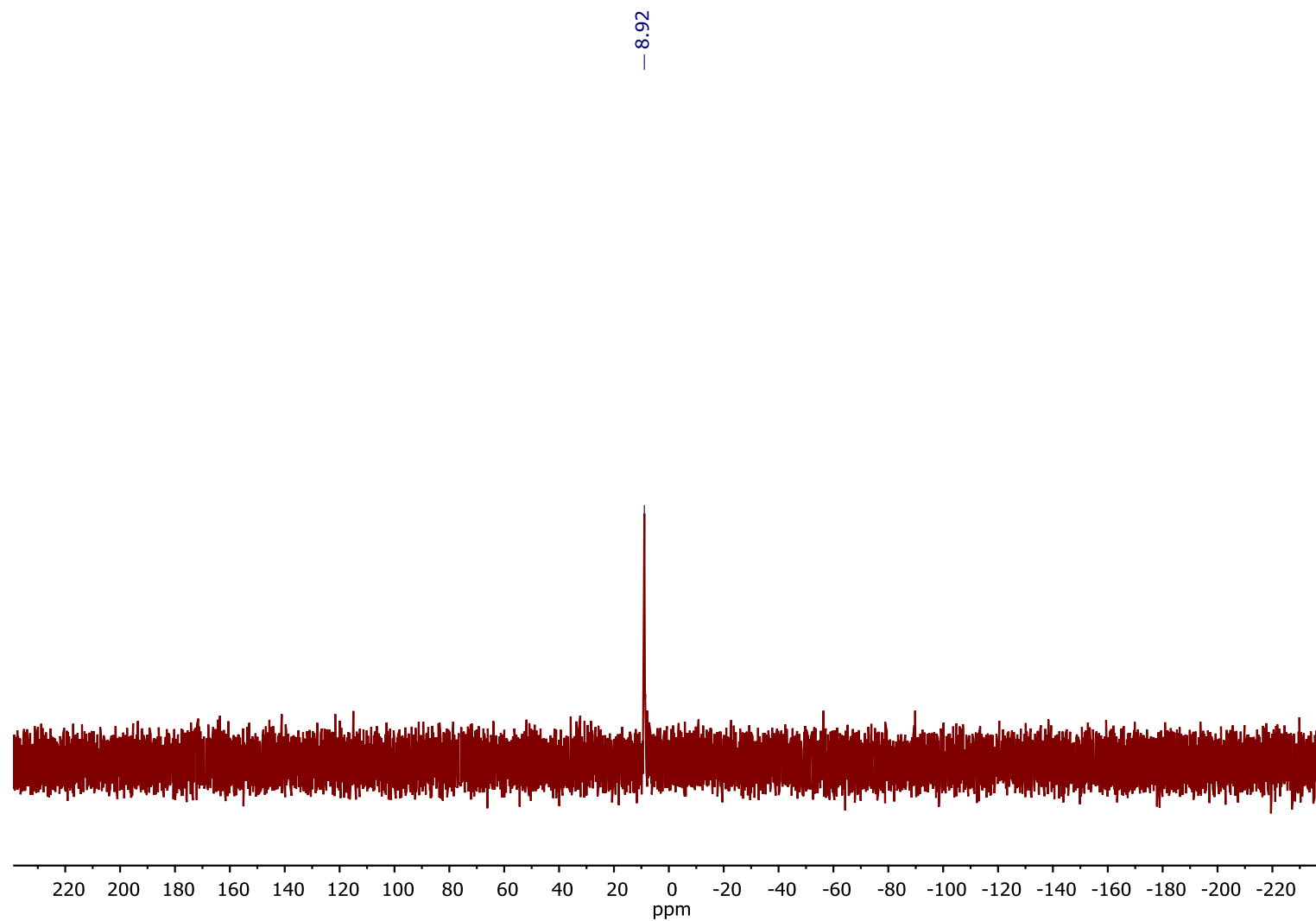


Figure S 54: <sup>31</sup>P NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> at 298 K.

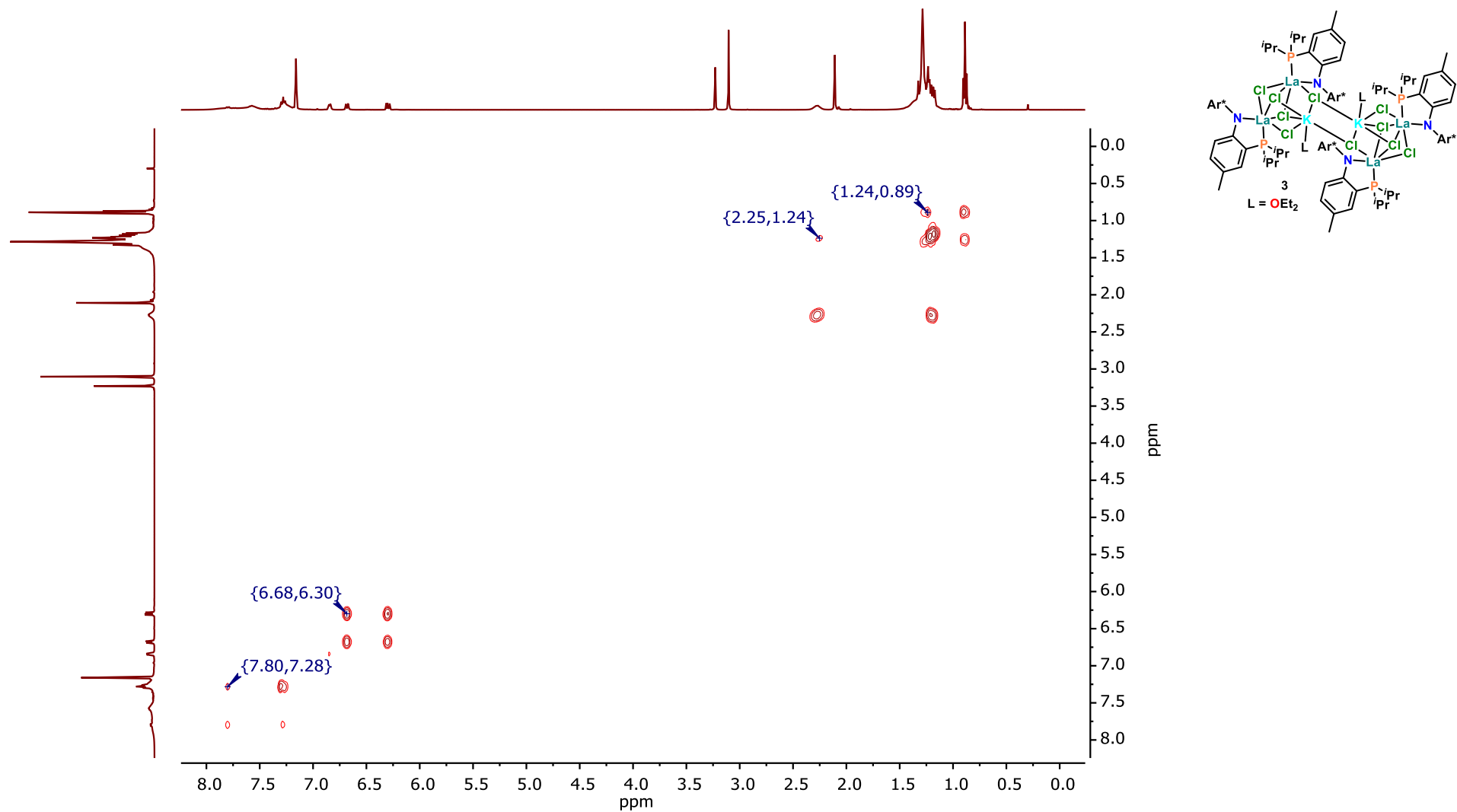


Figure S 55:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K.

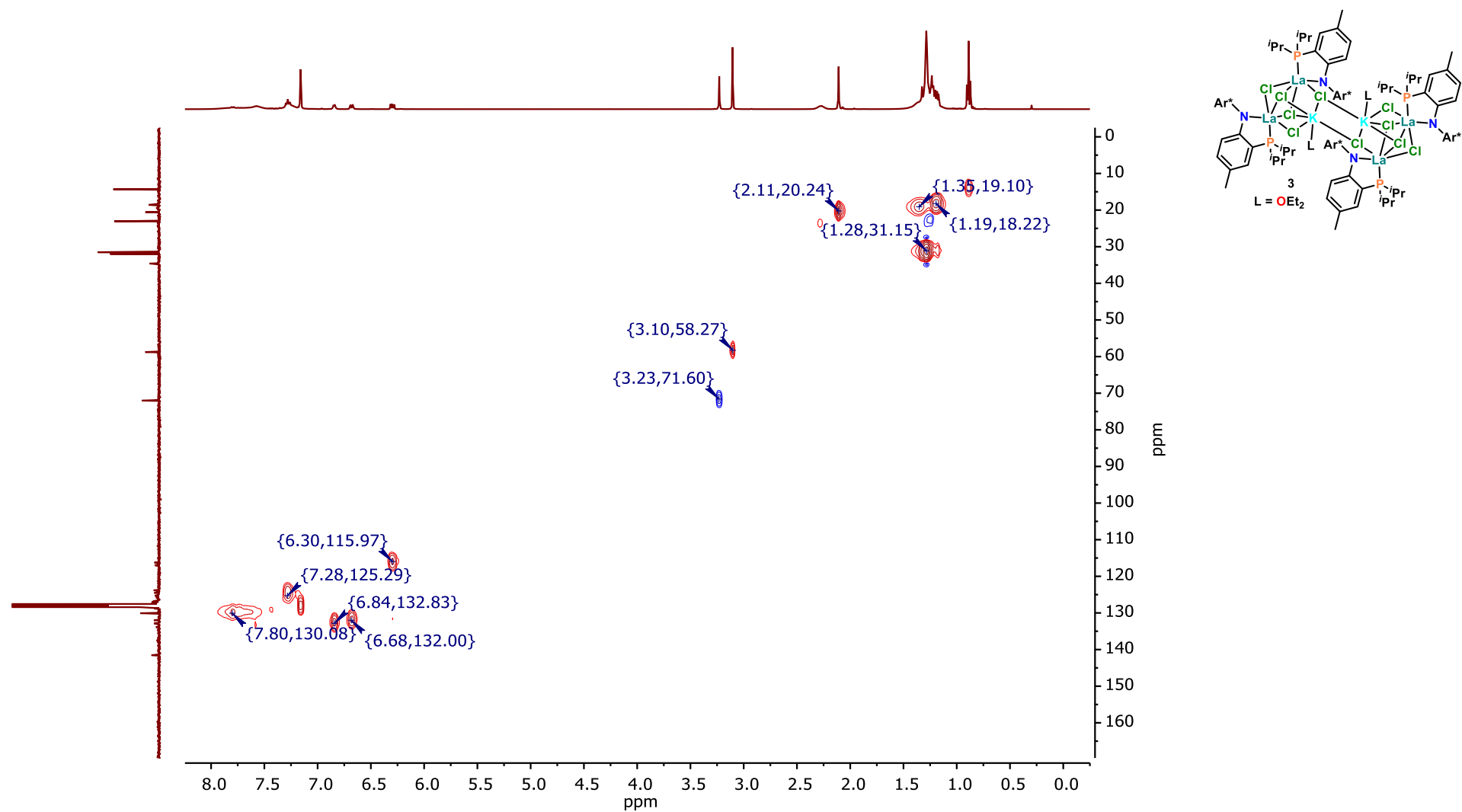


Figure S 56:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K.

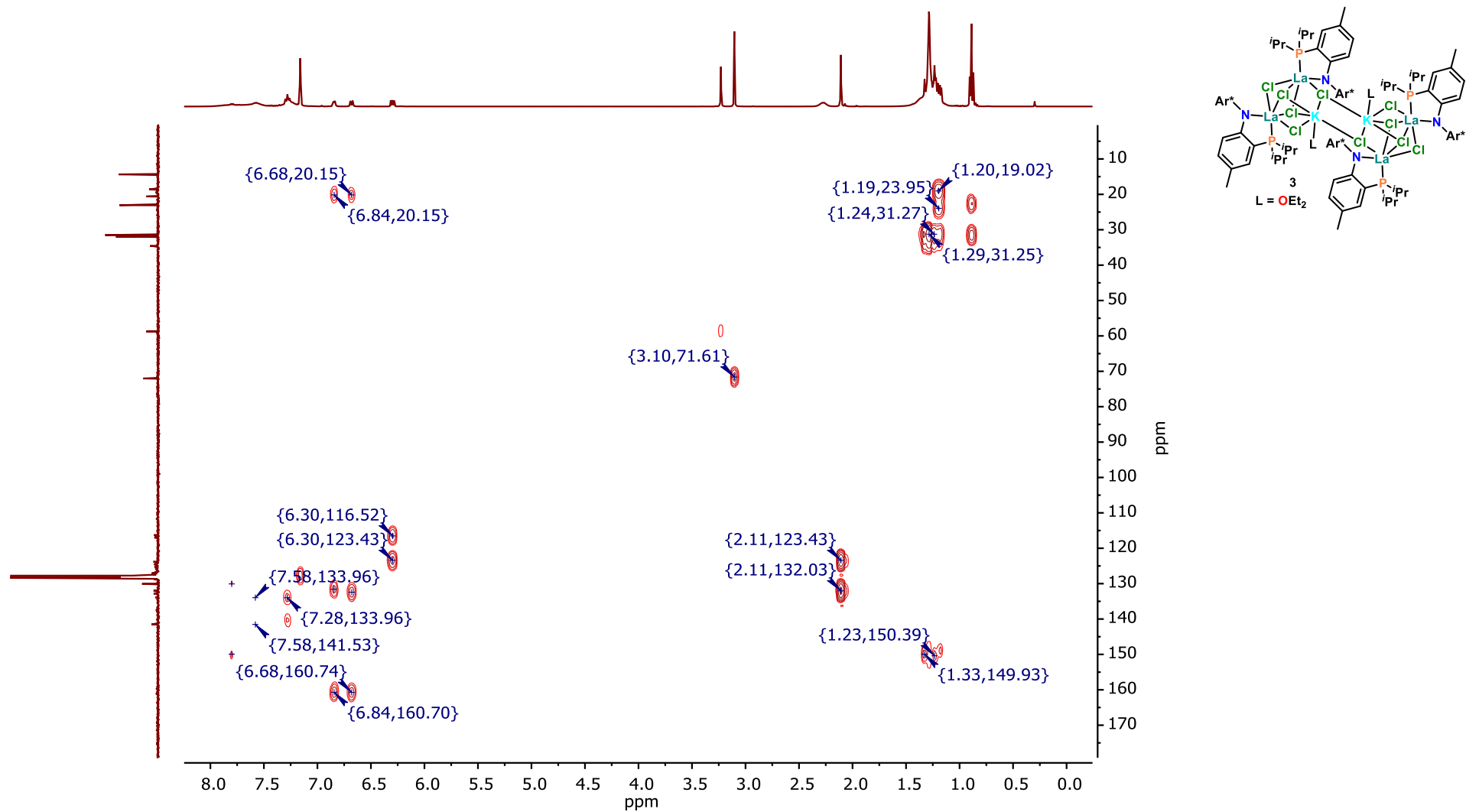


Figure S 57:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K.

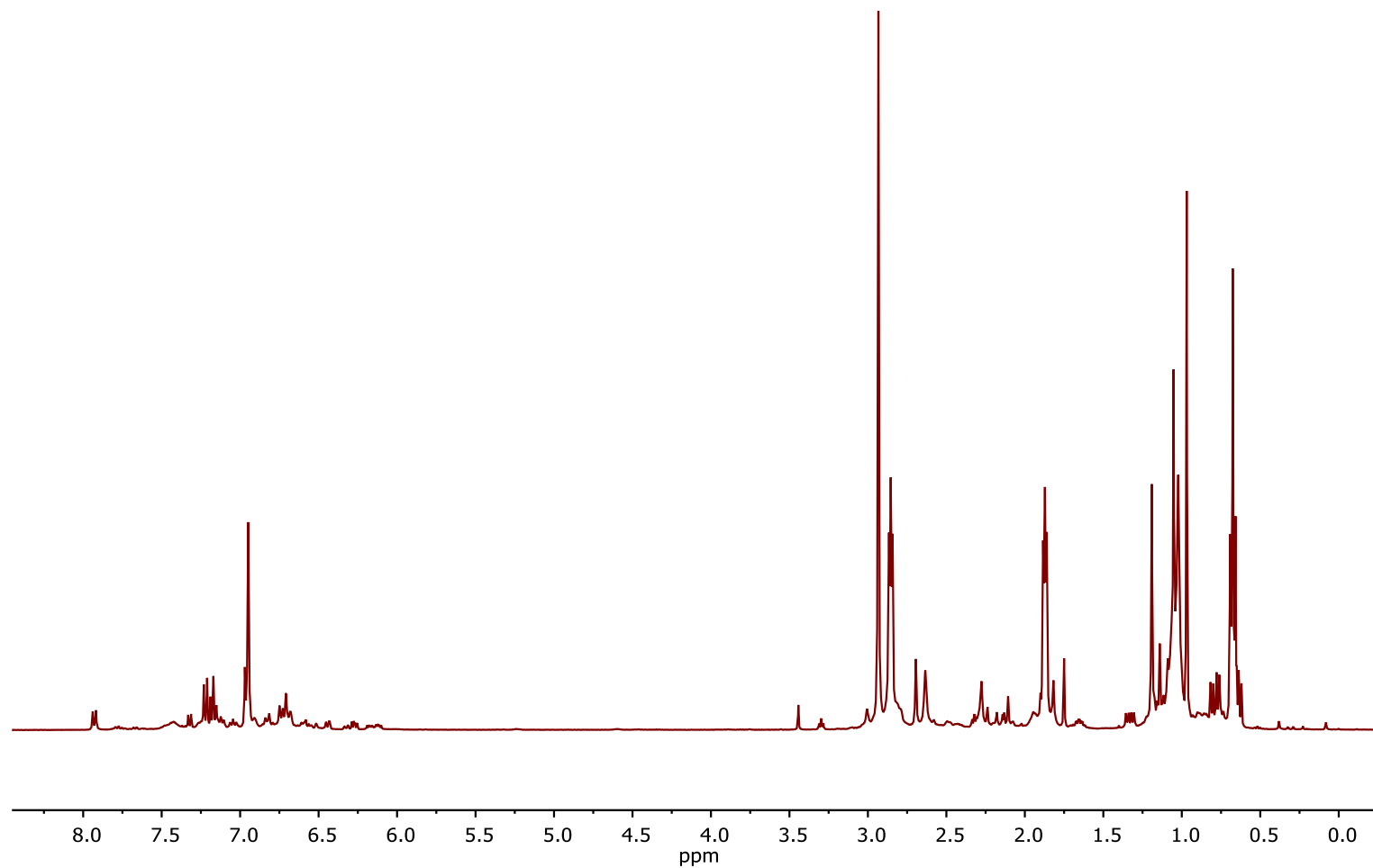


Figure S 58:  $^1\text{H}$  NMR of deprotonation experiment of complex **2** using BnK in presence of [2.2.2]Cryptand.



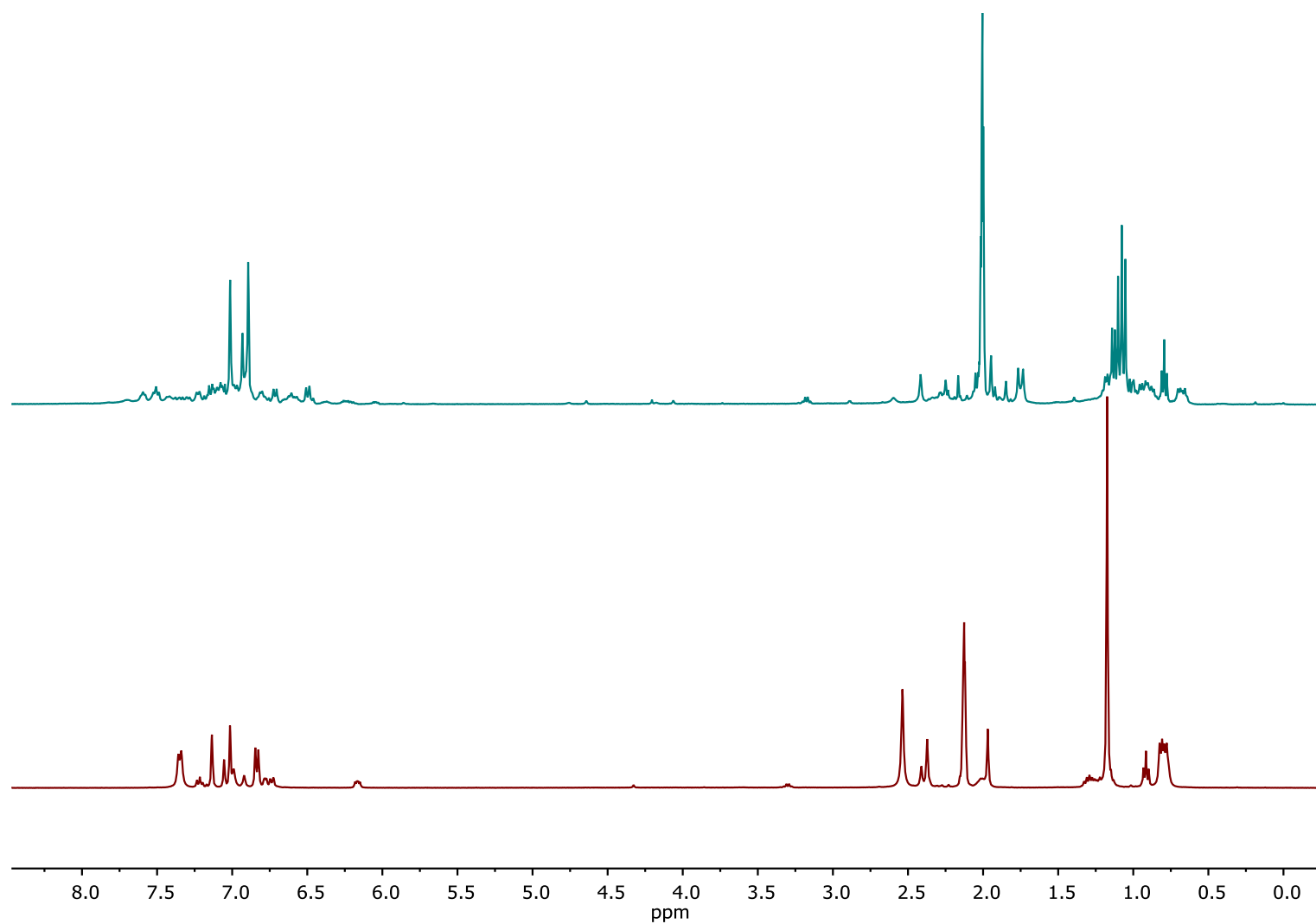


Figure S 59: <sup>1</sup>H NMR spectra of the Phospha-Wittig type reaction between **2** and benzophenone. Before the addition of benzophenone (red) and after the addition of benzophenone (blue).

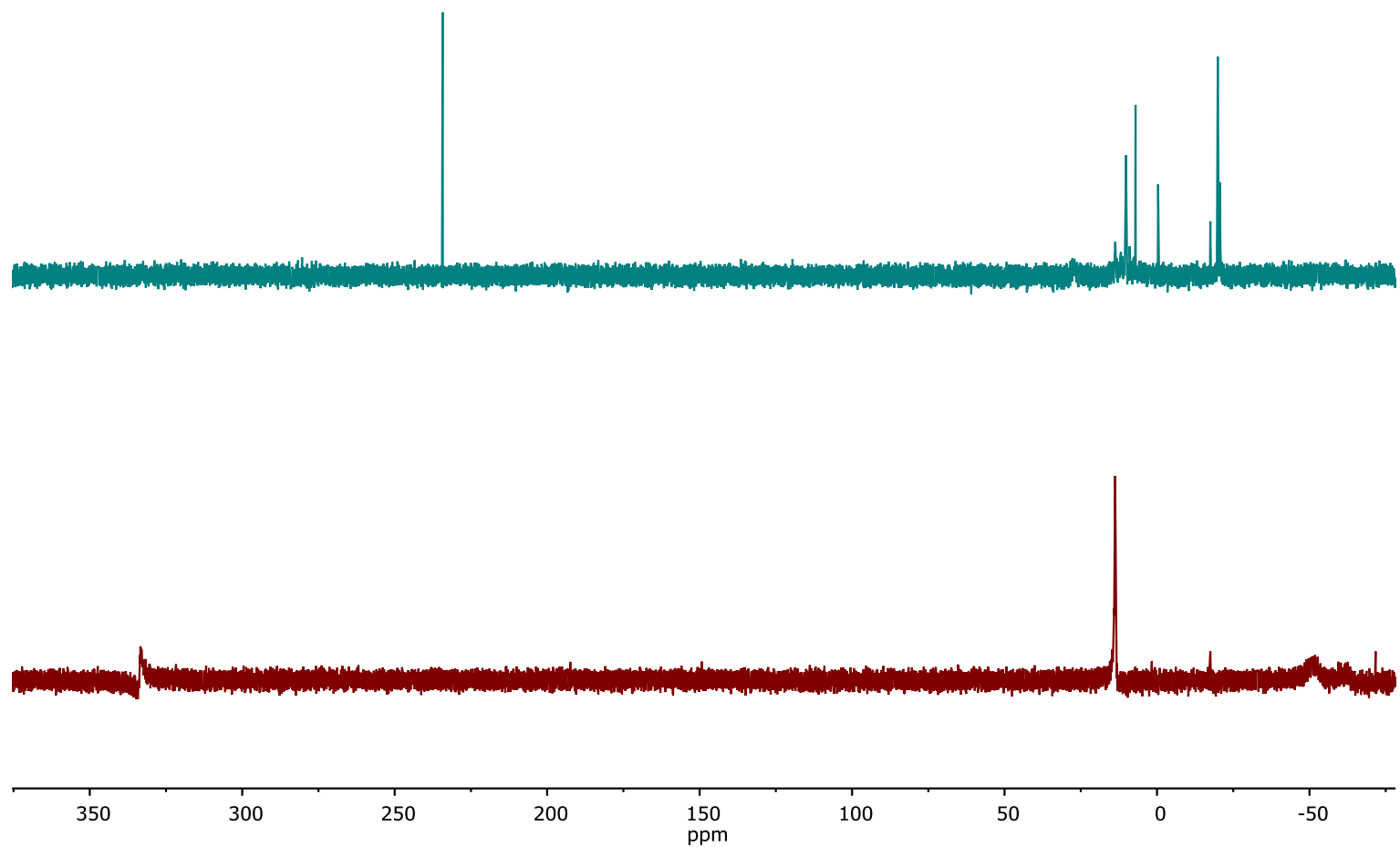


Figure S 60:  $^{31}\text{P}$  NMR spectra of the Phospha-Wittig type reaction between **2** and benzophenone. Before the addition of benzophenone (red) and after the addition of benzophenone (blue).

## UV-Vis spectra

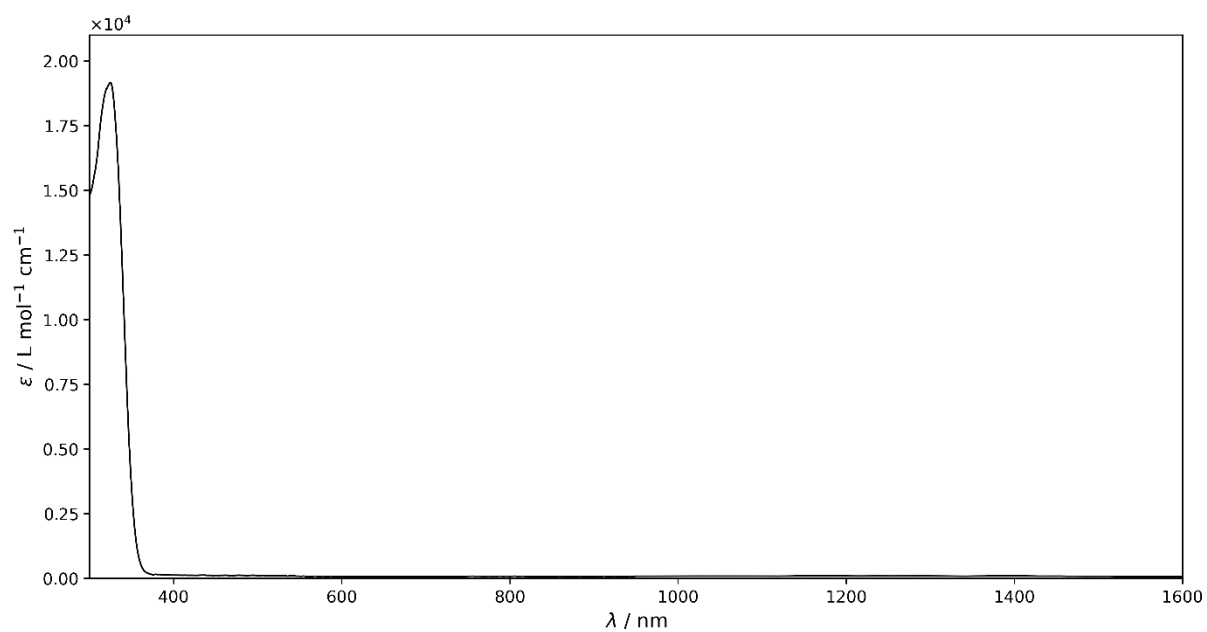


Figure S 61: UV-Vis-NIR spectrum of **O** in toluene at 298 K.

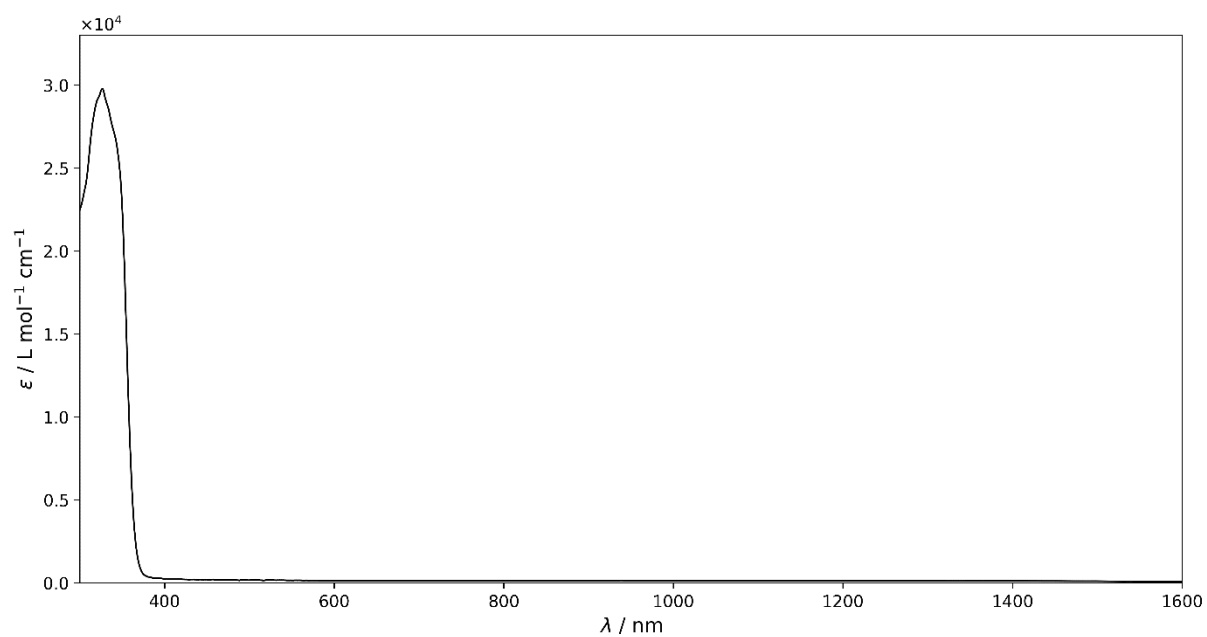


Figure S 62: UV-Vis-NIR spectrum of **HPN<sup>Terph</sup>** in toluene at 298 K.

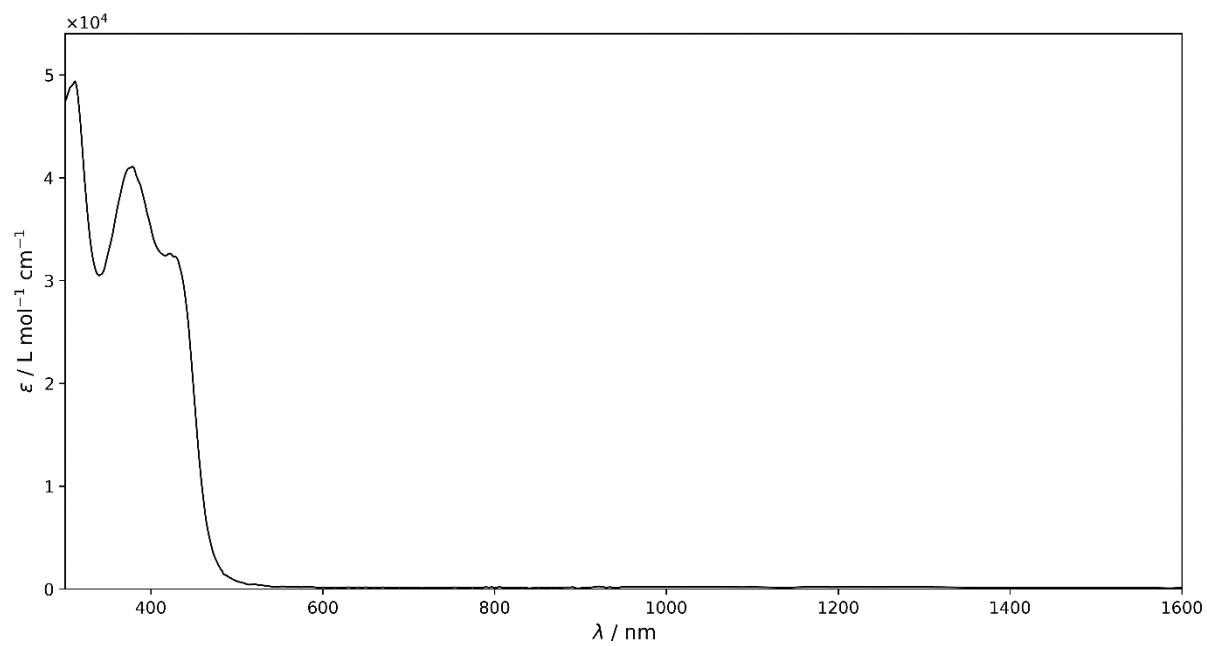


Figure S 63: UV-Vis-NIR spectrum of  $\text{LiPN}^{\text{Terph}}$  in toluene at 298 K.

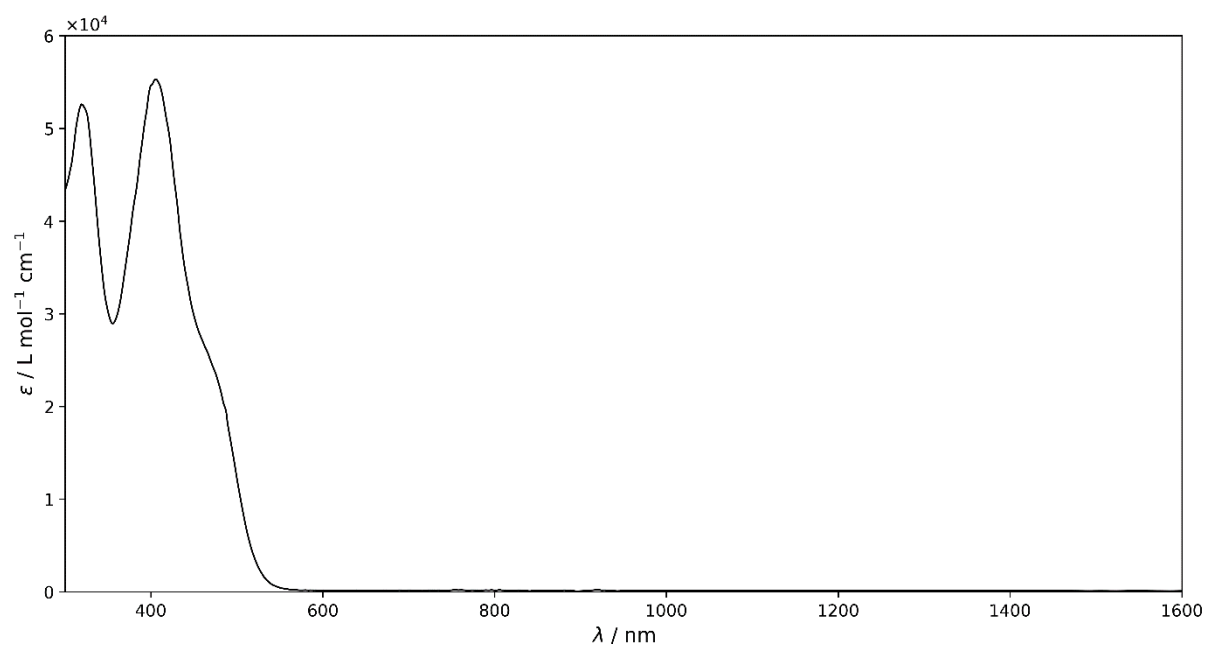


Figure S 64: UV-Vis-NIR spectrum of  $\text{KPN}^{\text{Terph}}$  in toluene at 298 K.

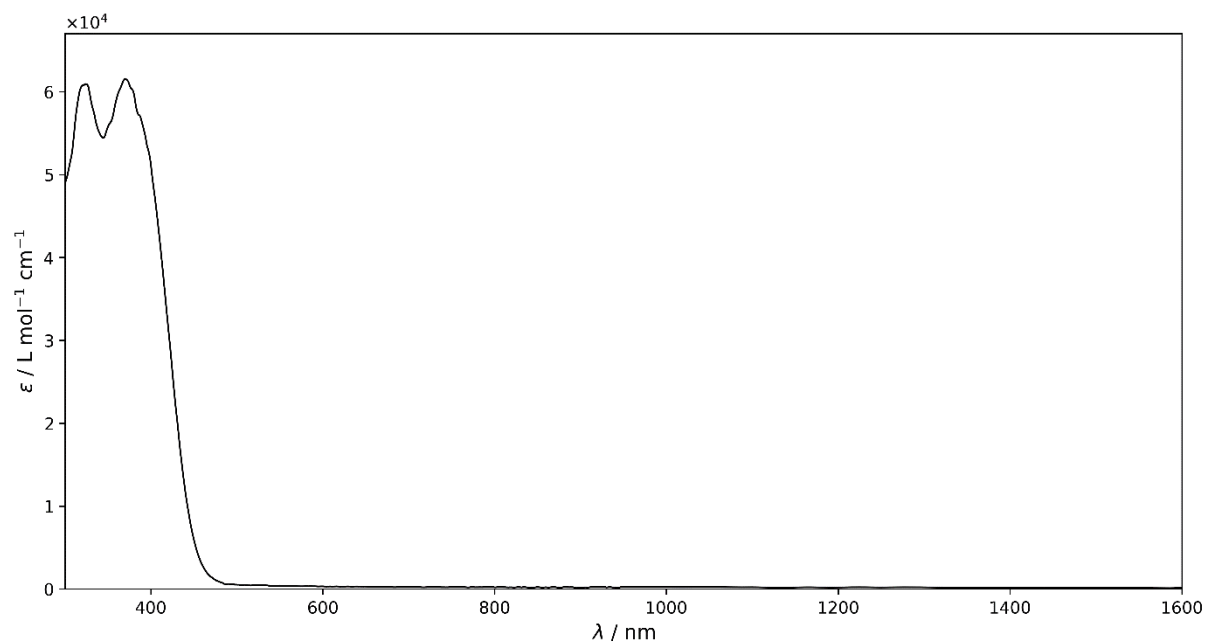


Figure S 65: UV-Vis-NIR spectrum of **1** in toluene at 298 K.

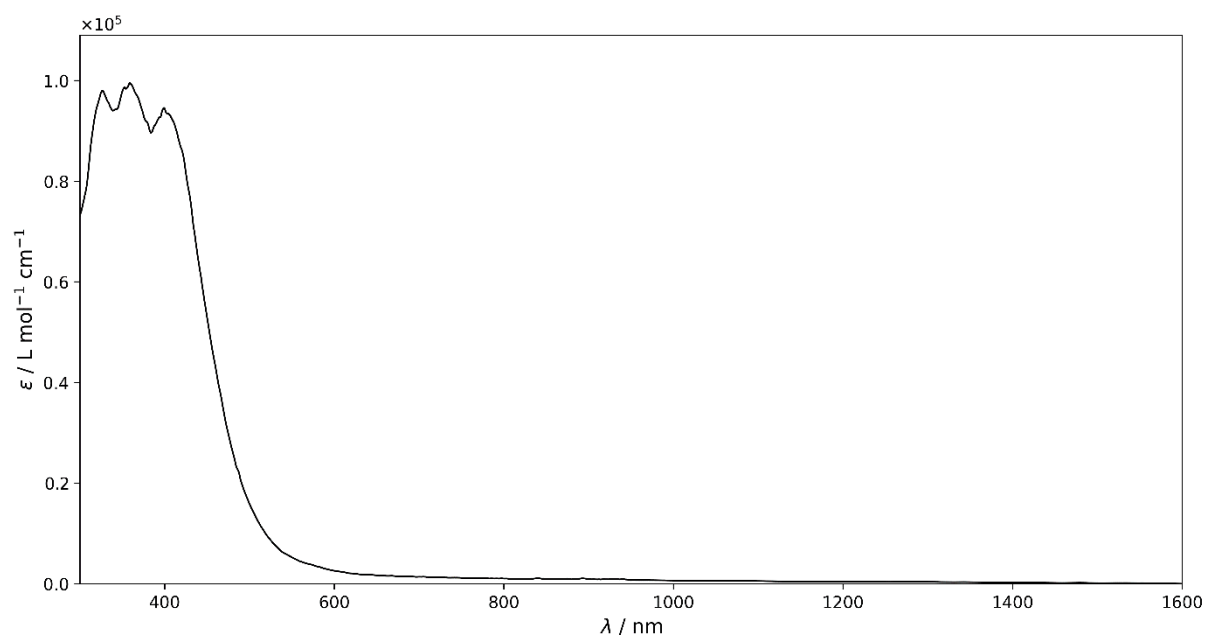


Figure S 66: UV-Vis-NIR spectrum of **2** in toluene at 298 K.

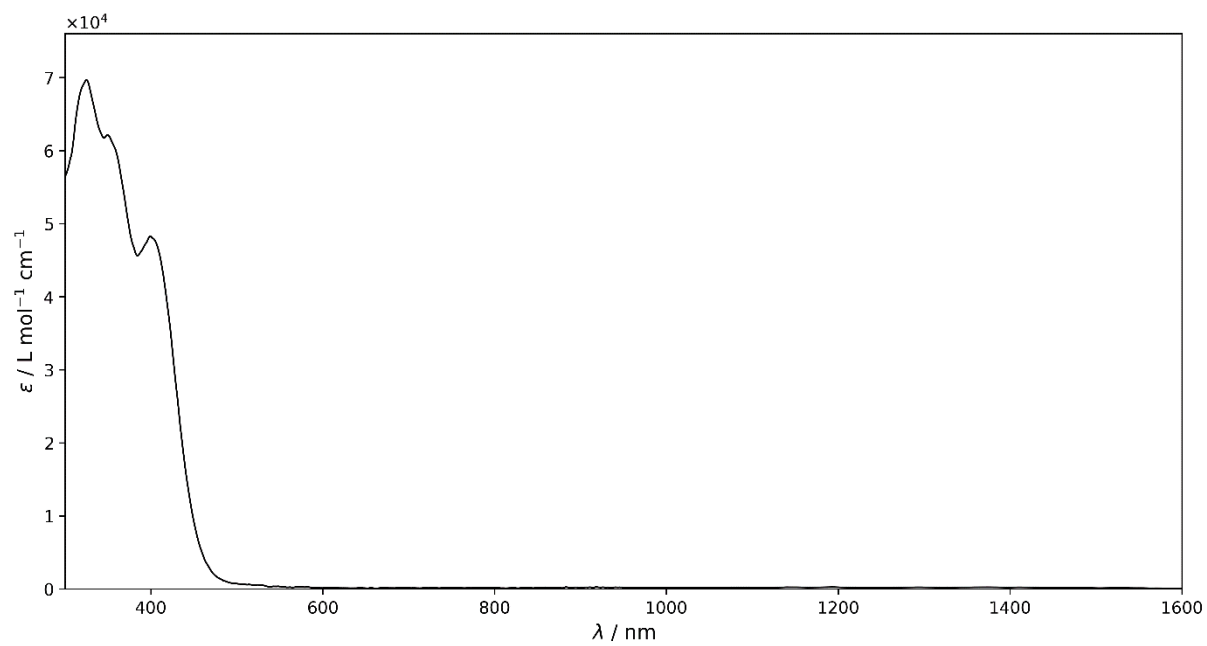


Figure S 67: UV-Vis-NIR spectrum of **3** in toluene at 298 K.

## IR spectra

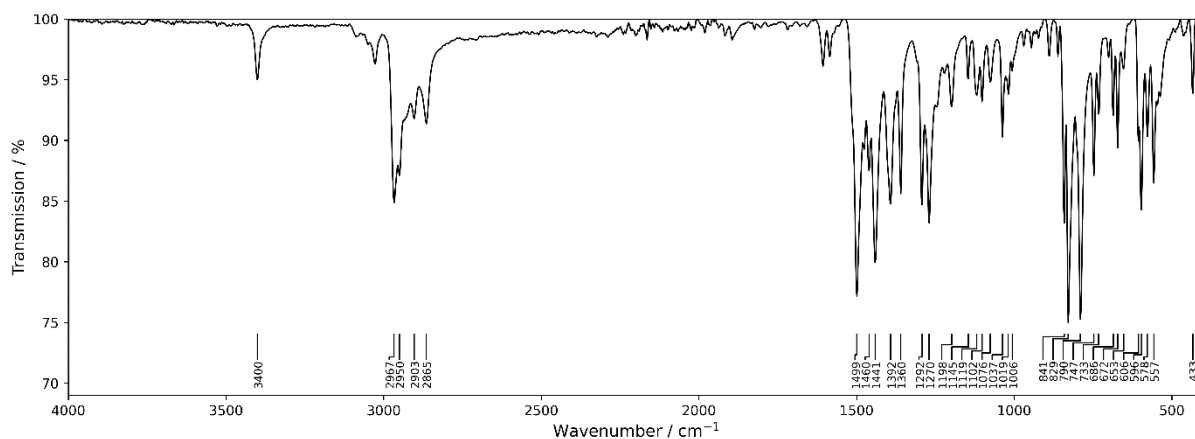


Figure S 68: ATR-IR spectrum of **O**.

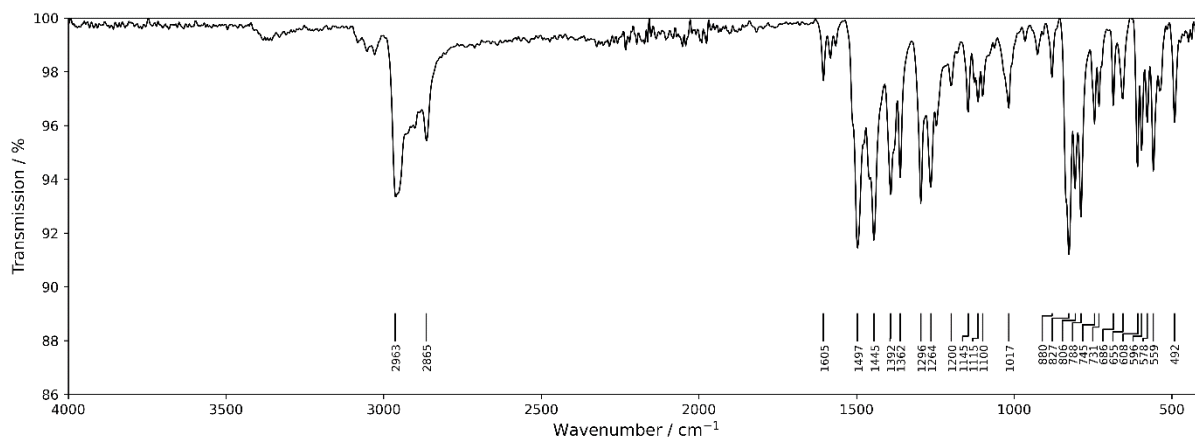


Figure S 69: ATR-IR spectrum of **HPN<sup>Terph</sup>**.

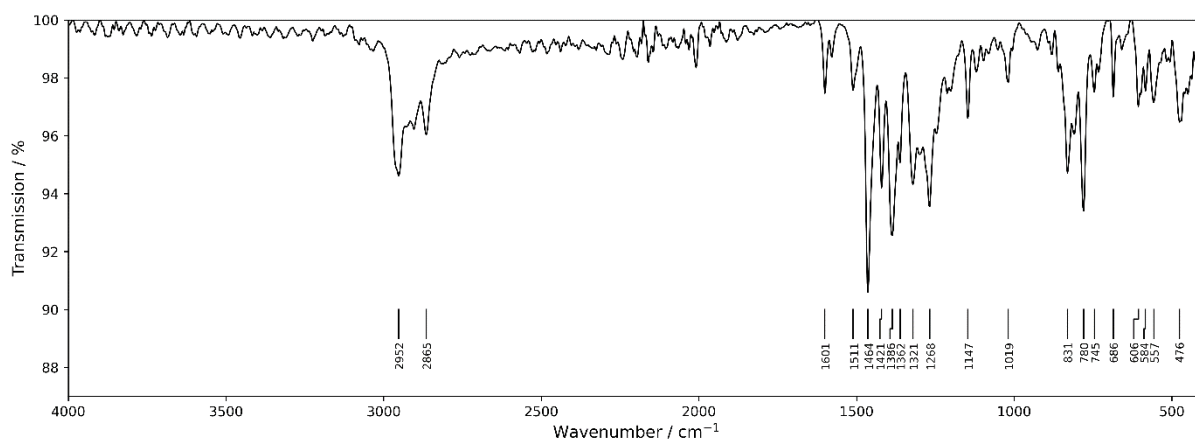


Figure S 70: ATR-IR spectrum of **LiPN<sup>Terph</sup>**.

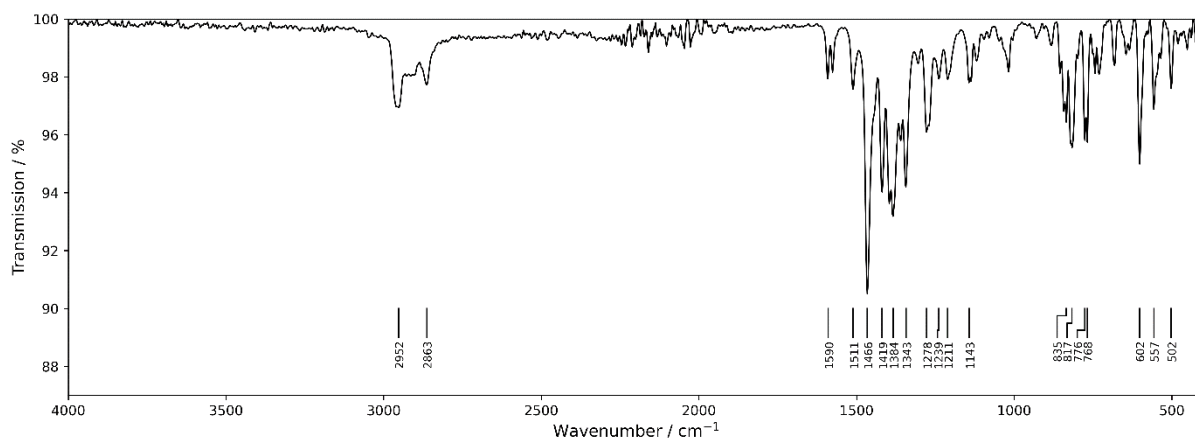


Figure S 71: ATR-IR spectrum of **KPN<sup>Terph</sup>**.

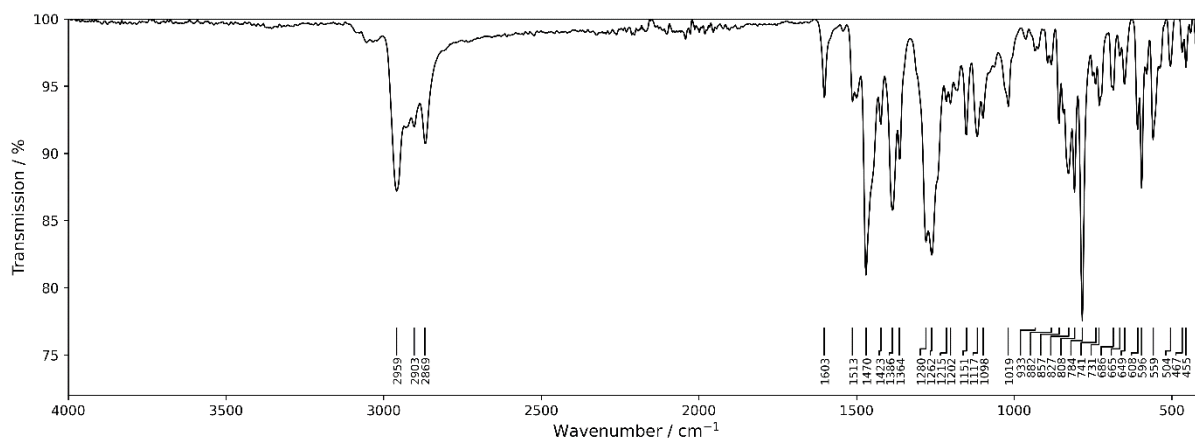


Figure S 72: ATR-IR spectrum of **1**.

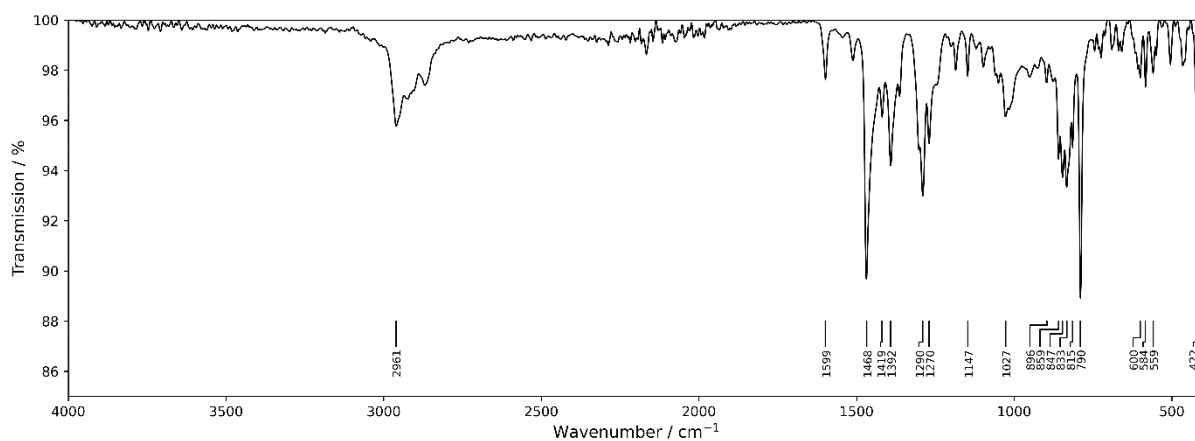


Figure S 73: ATR-IR spectrum of **2**.



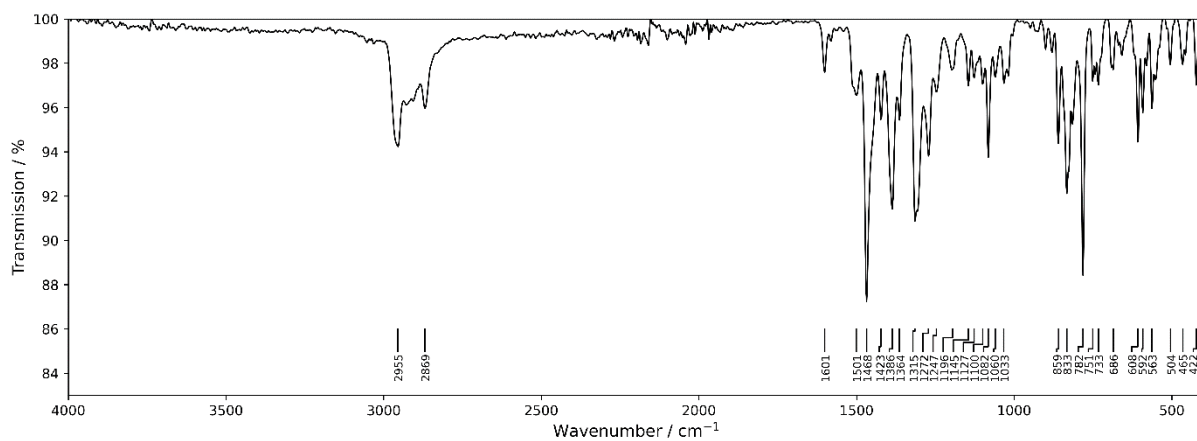


Figure S 74: ATR-IR spectrum of 3.

## Mass spectra

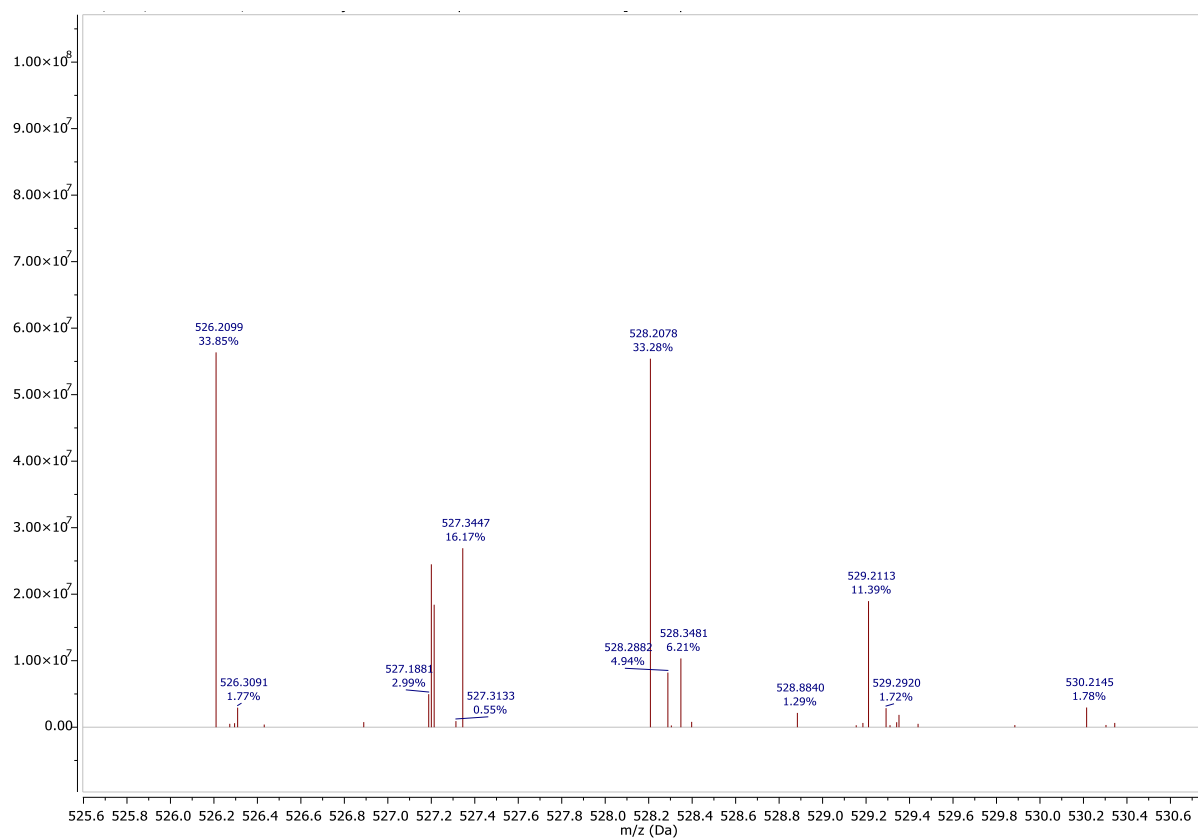


Figure S 75: Hi – Res Mass (ESI<sup>+</sup>) of O.

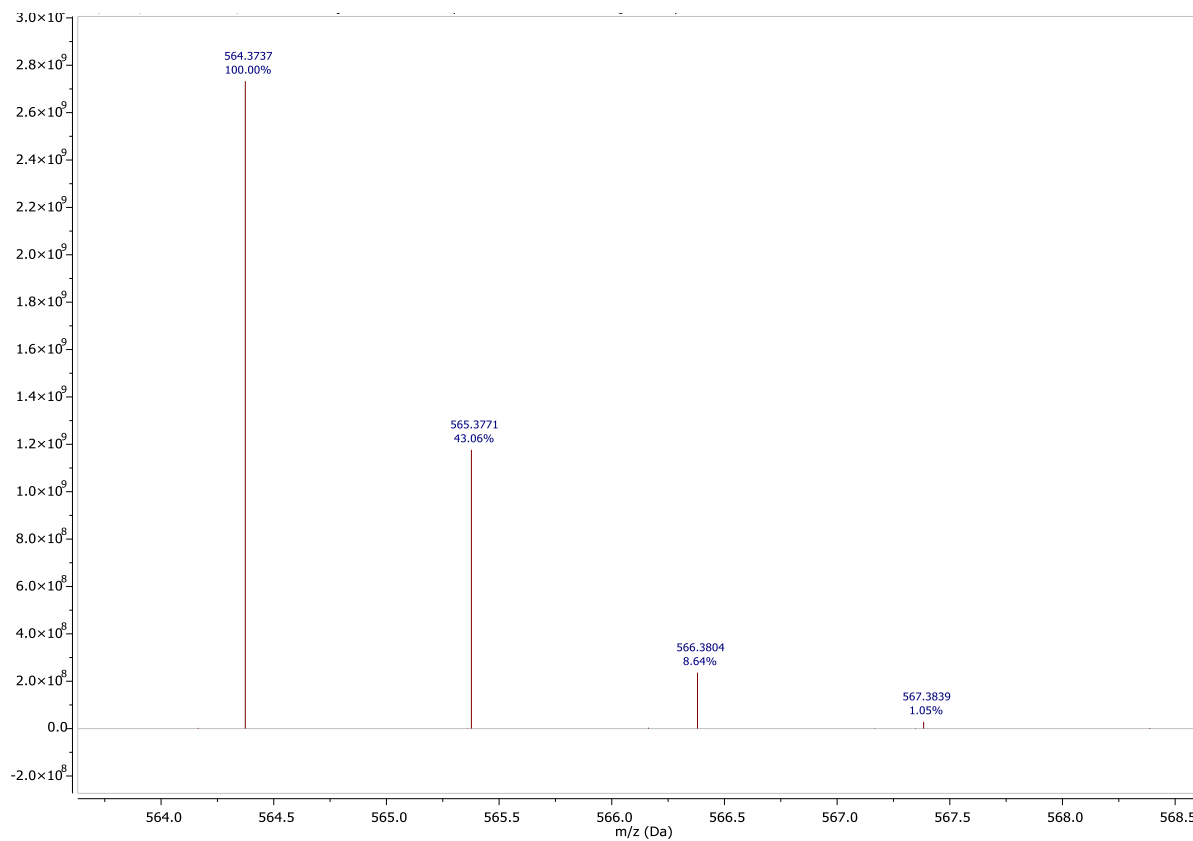


Figure S 76: Hi – Res Mass (ESI<sup>+</sup>) of HPN<sup>Terph</sup>.

## Crystallographic details

Table S 1: Crystallographic data for compounds **N**, **HPN<sup>Terph</sup>**, **KPN<sup>Terph</sup>**, **1**, **2** and **3**.

	<b>N</b>	<b>HPN<sup>Terph</sup></b>	<b>KPN<sup>Terph</sup></b>	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	C <sub>33</sub> H <sub>36</sub> N <sub>1</sub> Br <sub>1</sub>	C <sub>39</sub> H <sub>50</sub> N <sub>1</sub> P <sub>1</sub>	C <sub>47</sub> H <sub>59</sub> N <sub>1</sub> O <sub>2</sub> P <sub>1</sub> K <sub>1</sub>	C <sub>78</sub> H <sub>98</sub> N <sub>2</sub> P <sub>2</sub> Cl <sub>1</sub> La <sub>1</sub> 1.9 C <sub>4</sub> H <sub>10</sub> O	C <sub>105</sub> H <sub>133</sub> N <sub>2</sub> P <sub>5</sub> La <sub>2</sub> C <sub>4</sub> H <sub>10</sub> O	C <sub>164</sub> H <sub>216</sub> N <sub>4</sub> O <sub>2</sub> P <sub>4</sub> Cl <sub>10</sub> K <sub>2</sub> La <sub>4</sub>
<i>M<sub>r</sub></i>	526.54	563.77	750.10	1440.70	1929.92	3387.61
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P-1</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>P-1</i>	<i>P-1</i>
a (Å)	10.4197(3)	10.7562(12)	11.4630(4)	20.5986(13)	15.498(3)	12.8330(13)
b (Å)	14.0561(4)	13.4826(16)	16.2623(5)	24.7411(15)	16.566(4)	16.6810(17)
c (Å)	18.9616(6)	14.1323(17)	24.9920(10)	32.569(2)	22.288(4)	21.1112(18)
α (°)	90	115.435(4)	90	90	76.309(6)	98.117(3)
β (°)	100.3630(10)	107.508(4)	97.3740(10)	95.767(2)	70.924(6)	100.137(3)
γ (°)	90	96.665(5)	90	90	69.957(7)	108.631(4)
V (Å <sup>3</sup> )	2731.82(14)	1692.0(3)	4620.3(3)	16514.1(19)	5030.0(19)	4120.0(7)
Z	4	2	4	8	2	1
Density (g cm <sup>-3</sup> )	1.280	1.107	1.078	1.159	9815	1.365
F(000)	1104	612	1632	6110	2016	1740
Radiation Type	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
μ (mm <sup>-1</sup> )	1.526	0.107	0.184	0.632	0.965	1.318
Crystal size (mm)	0.45x0.40x0.38	0.35x0.25x0.15	0.50x0.45x0.20	0.45x0.42x0.37	0.13x0.04x0.015	0.24x0.13x0.05
Meas. Refl.	60778	32936	113957	412057	147923	179841
Indep. Refl.	6298	6950	8187	29081	18709	16929
Obsvd. [ <i>I</i> > 2σ( <i>I</i> )]	5491	5734	7511	22960	14825	13006
R <sub>int</sub>	0.0390	0.0517	0.0556	0.1221	0.0645	0.1310
R <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0377	0.0522	0.0450	0.0519	0.0346	0.0465
wR <sub>2</sub> (F <sup>2</sup> )	0.1074	0.1350	0.1303	0.1299	0.0869	0.1278
Goof	1.024	1.069	1.039	1.073	1.040	1.049
Δρ <sub>max</sub> (e Å <sup>-3</sup> )	0.879	0.497	0.649	0.768	1.204	0.968
Δρ <sub>min</sub> (e Å <sup>-3</sup> )	-1.399	-0.322	-0.268	-0.607	-0.709	-0.839
CCDC	2341843	2341842	2341850	2341846	2341844	2341845

Table S 2: Selected bond lengths and angles for compounds **N**, **HPN<sup>Terph</sup>**, **KPN<sup>Terph</sup>**, **1**, **2** and **3**.

	<b>N</b>	<b>HPN<sup>Terph</sup></b>	<b>KPN<sup>Terph</sup></b>	<b>1</b>	<b>2</b>	<b>3</b>
M1 – M2	-	-	-	-	4.2281(7)	4.1379(6)
M1 – P1	-	-	3.3347(6)	3.2253(12)	3.0998(10)	3.1113(13)
M2 – P2	-	-	-	-	3.1510(10)	3.1007(14)
M1 – P2	-	-	-	3.1981(11)	-	-
M1 – N1	-	-	2.6923(13)	2.427(3)	2.386(2)	2.409(4)
M2 – N2	-	-	-	-	2.383(2)	2.407(4)
M1 – N2	-	-	-	2.445(3)	-	-
M1 – C11	-	-	-	2.6728(12)	-	2.8775(12)
M1 – C12	-	-	-	-	-	2.9763(12)
M1 – C13	-	-	-	-	-	2.8427(13)
M1 – C14	-	-	-	-	-	2.7648(13)
M2 – C11	-	-	-	-	-	2.9005(13)
M2 – C12	-	-	-	-	-	2.8849(12)
M2 – C13	-	-	-	-	-	2.9316(12)
M2 – C15	-	-	-	-	-	2.7240(13)
M1 – P3	-	-	-	-	3.0465(10)	-
M1 – P4	-	-	-	-	3.0687(10)	-
M1 – P5	-	-	-	-	2.8471(11)	-
M2 – P3	-	-	-	-	3.1130(10)	-
M2 – P4	-	-	-	-	3.0268(11)	-
M2 – P5	-	-	-	-	2.8207(10)	-
$\tau_5 / \tau_4^i$			0.72	0.17	0.24 / 0.06	
N1 – C10	1.407(2)	1.399(2)	1.3637(16)	1.391(5)	1.391(4)	1.398(6)
C10 – C11	1.397(3)	1.409(2)	1.427(2)	1.407(6)	1.416(4)	1.412(7)
C11 – P1	-	1.8386(17)	1.8255(16)	1.822(4)	1.816(3)	1.809(5)
C11 – Br1	1.901(2)	-	-	-	-	-

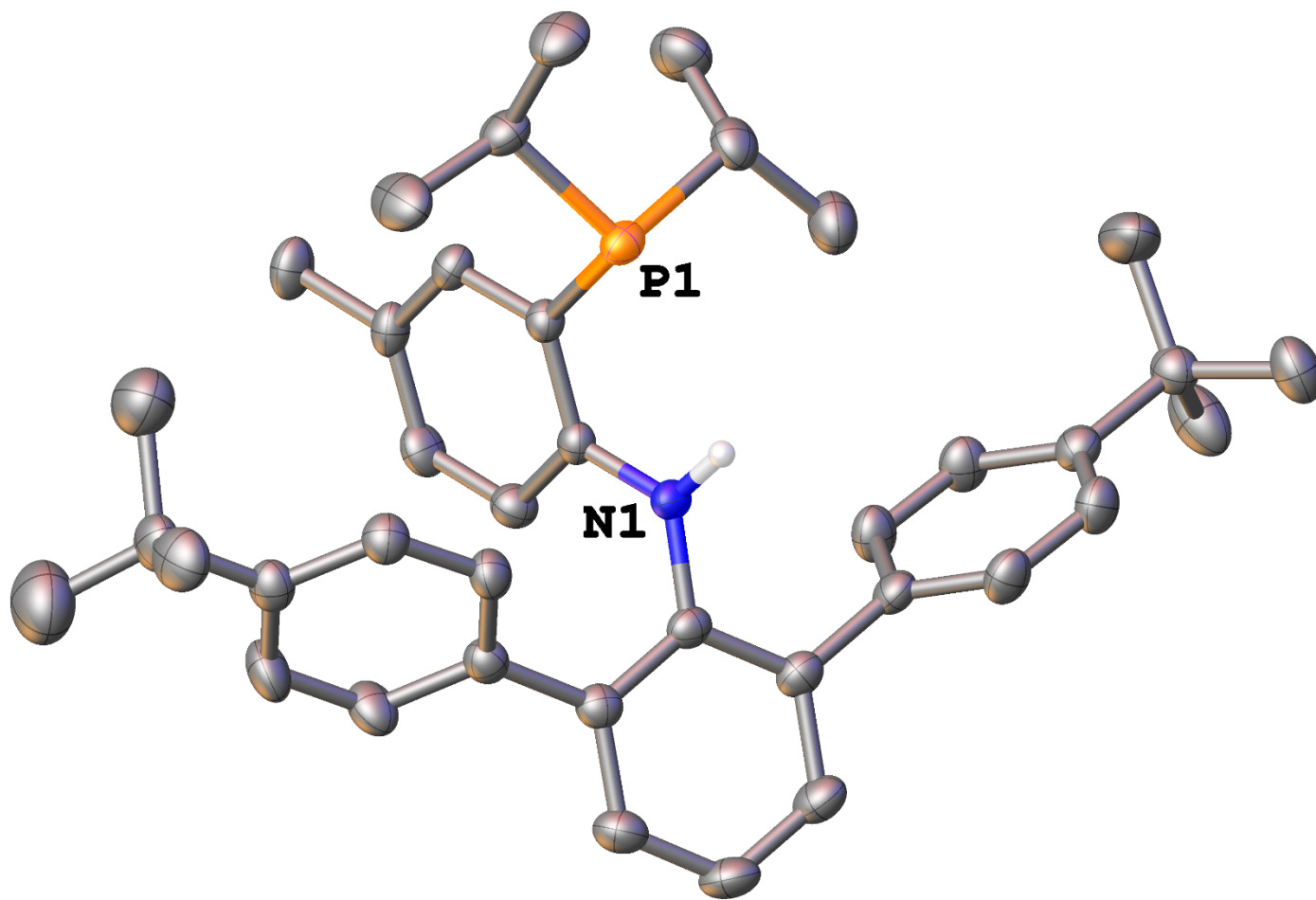


Figure S 77: Molecular structure **HPN<sup>Teph</sup>**. Ellipsoids are shown at a probability level of 50%. Hydrogen atoms except for the amine proton at N1 have been omitted for clarity.

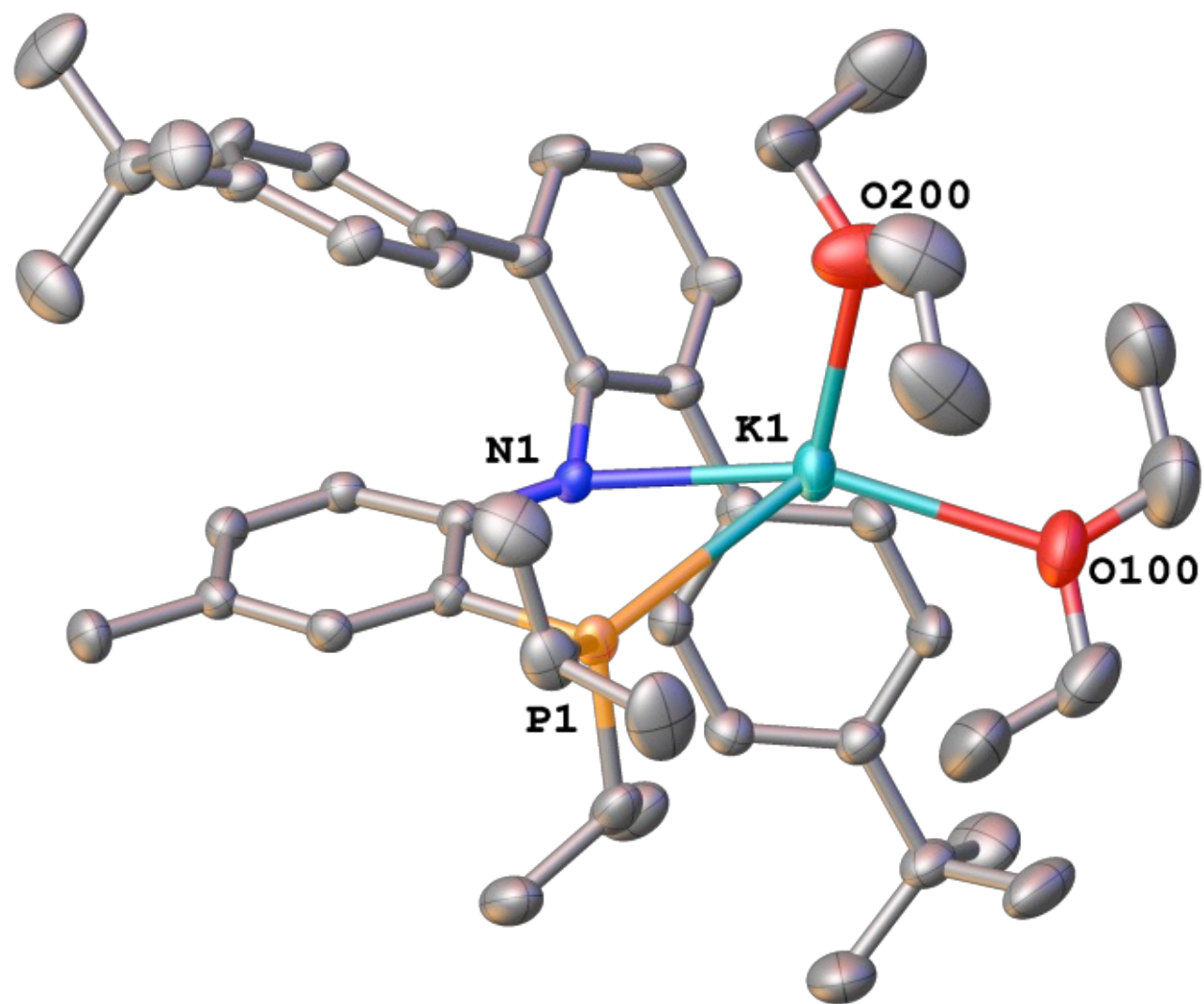


Figure S 78: Molecular structure  $KPN^{Tep^h}$ . Ellipsoids are shown at a probability level of 50%. Hydrogen atoms have been omitted for clarity.

Table S 3: %V buried for complex **I** (left) and complex **1** (right)

%V Free	%V Buried	% V Tot/V Ex
52.5	47.5	99.9

%V Free	%V Buried	% V Tot/V Ex
30.1	69.9	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	22.4	22.4	44.9	50.0	50.0
NW	28.1	16.8	44.9	62.5	37.5
NE	17.4	27.4	44.9	38.8	61.2
SE	26.3	18.5	44.9	58.7	41.3

Quadrant	V f	V b	V t	%V f	%V b
SW	15.7	29.2	44.9	34.9	65.1
NW	10.8	34.0	44.9	24.1	75.9
NE	16.3	28.6	44.9	36.3	63.7
SE	11.3	33.6	44.9	25.1	74.9

## Literature

- 1 B. Schiemenz and P. P. Power, *Organometallics*, 1996, **15**, 958;
- 2 B. L. Tran, M. Pink and D.J. Mindiola, *Organometallics* 2009, **28**, 7, 2234–2243;
- 3 G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, **71**, 3–8;
- 4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Appl. Crystallogr.*, **2009**, **42**, 339–341.
- 5 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **2015**, **71**, 9–18.