Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Content

1. Experimental Section

General procedure. All experiments and manipulations were carried out under a dry argon atmosphere using either standard Schlenk or glovebox techniques. Toluene and *n*-hexane were dried using an MBraun solvent drying system (SPS), degassed and stored over molecular sieve (4Å). Deuterated solvents (C_6D_6) were dried by refluxing over NaK alloy, distilled prior to use and stored over molecular sieve (4Å). XylOH (Xyl = 2,6-Me_2-C_6H_3), PhSH, and PhSeH were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. H_2O was degassed twice and NH_3 was dried over potassium metal prior to use. L(Cl)GaPGaL **1** (L = HC[C(Me)N(Dipp)]$_2$, Dipp = 2,6-*i*Pr_2-C_6H_3) was prepared by literature method.[1] NMR spectra (δ in ppm) were recorded using a Bruker Avance II 500 (^{1}H 500 MHz, ^{13}C{^{1}H} 126 MHz, ^{31}P{^{1}H} 202 MHz) spectrometer and were referenced to internal C_6D_5H (^{1}H $\delta = 7.16$; ^{13}C $\delta = 128.06$). ^{31}P NMR spectra are referenced to internal C_6D_5H (^{1}H $\delta = 7.16$) or C_7D_7H (^{1}H $\delta = 2.08$, 6.97, 7.01, 7.09) using chi-values (χ).[2] Elemental analyses were performed at the *Elementaranalyse Labor* der Universität Duisburg-Essen. IR spectra were recorded in a glovebox with a Bruker ALPHA-T FT-IR spectrometer equipped with a single-reflection ATR sampling module. Melting points were measured in sealed glass capillaries.

Synthesis of LGa(Cl)PH(NH$_2$)LGa (2): NH_3 (1 bar) was added to a toluene solution (10 mL) of **1** (300 mg, 0.29 mmol) at ambient temperature, immediately giving a colorless solution. All volatiles were removed in vacuo to yield a colorless crystalline solid, which was washed with *n*-hexane (1 mL) and dried. Yield: 92% (280 mg). Single crystals suitable for sc-XRD were grown by cooling a toluene solution of **2** at –30 °C overnight. M.p. 161 °C (dec.). Anal. calcd. (%) for $C_{58}H_{85}ClGa_2N_5P$ (1055.47): C, 65.83; H, 8.10; N, 6.62. Found: C, 65.93; H, 8.15; N, 6.71. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) $\delta = -0.84$ (d, $^1J_{PH} = 174.6$ Hz, 1H, P*H*), 0.48 (bs, 2H, N*H*$_2$), 0.98 (d, $^3J_{HH} = 6.8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, $^3J_{HH} = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH} = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{HH} = 6.7$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH} = 6.8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, $^3J_{HH} = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{HH} = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.46 (s, 12H, CC*H*$_3$), 3.14 (sept, $^3J_{HH} = 6.8$ Hz, 2H, C*H*(CH$_3$)$_2$), 3.23 (sept, $^3J_{HH} = 6.8$ Hz, 2H, C*H*(CH$_3$)$_2$), 3.39 (sept, $^3J_{HH} = 6.8$ Hz, 2H, C*H*(CH$_3$)$_2$), 3.58 (sept, $^3J_{HH} = 6.7$ Hz, 2H, C*H*(CH$_3$)$_2$), 4.66 (s, 1H, C*H*), 4.79 (s, 1H, C*H*), 6.96–7.00 (m, 4H, C_6*H*$_3$), 7.05–7.07 (m, 4H, C_6*H*$_3$), 7.14 (d, $^3J_{HH} = 6.7$ Hz, 4H, C_6*H*$_3$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) $\delta = 24.0$, 24.1, 24.2, 24.5, 24.6, 25.3, 25.4 (CH(*C*H$_3$)$_2$), 28.0, 28.4, 29.5, 29.9 (*C*H(CH$_3$)$_2$), 95.9, 97.7 (*C*H), 124.0, 124.1, 125.2, 125.5, 127.0, 127.5, 141.4, 142.4, 142.9, 145.2, 145.7 (*C*$_6$H$_3$), 168.1, 168.8 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) $\delta = -314.6$. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) $\delta = -314.6$ (d, $^1J_{PH} = 174.6$ Hz). **ATR-IR**: *v* 2948, 2919, 2855, 2260, 1521, 1431, 1380, 1311, 1250, 1173, 1093, 1016, 933, 860, 793, 755, 619, 529 cm^{-1}.

Synthesis of LGa(Cl)PH(NH*i*-Pr)LGa (3): *i*-PrNH$_2$ (16 µL, 0.19 mmol) was added to a toluene solution (10 mL) of **1** (200 mg, 0.19 mmol) at ambient temperature, and the reaction mixture immediately turned colorless. Removal of all volatiles in vacuo yielded a colorless crystalline solid, which was washed with *n*-hexane (1 mL) and dried. Yield: 97% (200 mg). Single crystals suitable for sc-XRD were grown by cooling a toluene solution of **3** at –30 °C for 2 days. M.p. 167 °C (dec.). Anal. calcd. (%) for $C_{61}H_{91}ClGa_2N_5P$ (1097.52): C, 66.59; H, 8.34; N, 6.37. Found: C, 66.65; H, 8.43; N, 6.45. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) δ = –0.88 (d, $^1J_{PH}$ = 175.6 Hz, 1H, P*H*), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.19 (t, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (s, 6H, CC*H*$_3$), 1.44 (s, 6H, CC*H*$_3$), 1.46 (bs, 1H, N*H*), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.16 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.64 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 3.67 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.78 (s, 1H, C*H*), 4.81 (s, 1H, C*H*), 6.97–7.00 (m, 4H, C$_6$*H*$_3$), 7.06–7.09 (m, 4H, C$_6$*H*$_3$), 7.13–7.15 (m, 4H, C$_6$*H*$_3$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) δ = 24.1, 24.7, 25.1, 25.2 (CH(*C*H$_3$)$_2$), 27.1, 27.4, 28.3, 28.9 (*C*H(CH$_3$)$_2$), 46.4 (N*C*H(CH$_3$)$_2$), 97.4, 97.9 (*C*H), 124.0, 124.2, 125.1, 125.2, 125.7, 126.9 127.4, 128.6, 129.3, 141.4, 143.3, 145.2, 145.7 (*C*$_6$H$_3$), 168.6, 168.7 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) δ = –313.7. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) δ = –313.9 (d, $^1J_{PH}$ = 175.6 Hz). **ATR-IR**: ν 2948, 2912, 2855, 2261, 1520, 1431, 1380, 1311, 1293, 1252, 1170, 1093, 1014, 934, 860, 792, 755, 725, 691, 619, 531 cm^{-1}.

Synthesis of LGa(Cl)PH(NHPh)LGa (4): $PhNH_2$ (18 µL, 0.19 mmol) was added to a toluene solution (10 mL) of **1** (200 mg, 0.19 mmol) at ambient temperature, immediately giving a colorless solution. All volatiles were removed in vacuo to yield a colorless crystalline solid, which was washed with *n*-hexane (1 mL) and dried. Yield: 95% (206 mg). Single crystals suitable for sc-XRD were grown by cooling a toluene solution of **4** at –30 °C for overnight. M.p. 166 °C (dec.). Anal. calcd. (%) for $C_{64}H_{89}ClGa_2N_5P$ (1131.51): C, 67.77; H, 7.91; N, 6.17. Found: C, 67.81; H, 7.95; N, 6.21. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) δ = –0.58 (d, $^1J_{PH}$ = 177.0 Hz, 1H, P*H*), 1.12 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.40 (t, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.65 (s, 6H, CC*H*$_3$), 1.68 (s, 6H, CC*H*$_3$), 3.27 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.31 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.36 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.71 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 5.02 (s, 1H, C*H*), 5.04 (bs, 1H, N*H*), 5.23 (s, 1H, C*H*), 6.93 (t, $^3J_{HH}$ = 6.8 Hz, 2H, C$_6$*H*$_5$), 7.15 (d, $^3J_{HH}$ = 6.7 Hz, 6H, C$_6$*H*$_3$), 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C$_6$*H*$_5$), 7.24 (d, $^3J_{HH}$ = 6.2 Hz, 2H, C$_6$*H*$_3$), 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 4H, C$_6$*H*$_3$), 7.47 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C$_6$*H*$_5$), 7.54 (t, $^3J_{HH}$ = 6.8 Hz, 2H, C$_6$*H*$_5$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) δ = 23.9, 24.1, 24.2, 24.4, 24.6, 24.7, 25.1, 26.3 (CH(*C*H$_3$)$_2$), 27.3, 27.8, 28.6, 29.3, 29.5, 29.6 (*C*H(CH$_3$)$_2$), 97.0, 97.8 (*C*H), 114.4, 124.0, 124.1, 125.4, 125.5, 127.2, 127.4, 140.9, 141.8, 142.4, 142.6, 145.5, 145.6 (*C*$_6$H$_3$, *C*$_6$H$_5$), 168.9, 169.0 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) δ = –315.0. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) δ = –315.0 (d, $^1J_{PH}$ = 177.0 Hz). **ATR-IR**: ν 2955, 2925, 2865, 2262, 1587, 1522, 1454, 1431, 1378, 1312, 1291, 1254, 1173, 1094, 1020, 934, 850, 794, 755, 691, 639, 531 cm^{-1}.

Synthesis of LGa(Cl)PH(OH)LGa (5): H_2O (5 µL, 0.28 mmol) was added to a toluene solution (10 mL) of **1** (300 mg, 0.29 mmol), immediately giving a colorless solution. All volatiles were removed in vacuo to yield a colorless crystalline solid, which was washed with *n*-hexane (1 mL) and dried. Yield: 95% (290 mg). M.p. 170 °C (dec.). Anal. calcd. (%) for $C_{58}H_{84}ClGa_2N_4OP$ (1056.46): C, 65.77; H, 7.99; N, 5.29. Found: C, 65.80; H, 8.05; N, 5.31. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) $\delta = -0.71$ (d, $^1J_{PH}$ = 174.3 Hz, 1H, P*H*), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (s, 1H, O*H*), 1.44 (s, 6H, CC*H*$_3$), 1.46 (s, 6H, CC*H*$_3$), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.44 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.63 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.75 (s, 1H, C*H*), 4.77 (s, 1H, C*H*), 6.95–6.98 (m, 4H, C$_6$*H*$_3$), 7.05–7.07 (m, 4H, C$_6$*H*$_3$), 7.13–7.15 (m, 4H, C$_6$*H*$_3$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) δ = 21.4, 23.8, 24.0, 24.1, 24.3, 24.4, 25.1 (CH(*C*H$_3$)$_2$), 27.4, 27.5, 27.8, 28.3, 29.3, 29.4, 29.6 (*C*H(CH$_3$)$_2$), 96.5, 97.5 (*C*H), 124.0, 125.2, 125.5, 127.1, 127.5, 128.6, 129.6, 140.0, 141.9, 142.6, 145.5, 145.6 (*C*$_6$H$_3$), 168.6, 168.9 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) $\delta = -312.9$. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) $\delta = -312.9$ (d, $^1J_{PH}$ = 173.7 Hz). **ATR-IR**: v 2961, 2922, 2865, 2265, 1528, 1436, 1374, 1317, 1260, 1179, 1017, 939, 884, 757, 732, 695, 617, 530 cm^{-1}.

Synthesis of LGa(Cl)PH(O(2,6-CH$_3$)$_2$C$_6$H$_3$)LGa (6): A toluene solution (2 mL) of 2,6-Dimethylphenol (23 mg, 0.19 mmol) was added to a toluene solution (10 mL) of **1** (200 mg, 0.19 mmol) at ambient temperature. The reaction mixture immediately turned colorless. All volatiles were then removed in vacuo to yield a colorless crystalline solid, which was washed with *n*-hexane (1 mL) and dried. Yield: 96% (215 mg). Single crystals suitable for sc-XRD were grown by diffusing *n*-hexane to a saturated toluene solution of **6** at ambient temperature. M.p. 179 °C (dec.). Anal. calcd. (%) for $C_{66}H_{92}ClGa_2N_4OP$ (1160.52): C, 68.14; H, 7.97; N, 4.82. Found: C, 68.17; H, 7.87; N, 4.89. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) $\delta = -0.21$ (d, $^1J_{PH}$ = 188.9 Hz, 1H, P*H*), 0.91 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.02 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.08–1.10 (m, 18H, CH(C*H*$_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.44 (s, 6H, CC*H*$_3$), 1.45 (s, 6H, CC*H*$_3$), 1.81 (s, 3H, C*H*$_3$), 2.45 (s, 3H, C*H*$_3$), 2.92 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.38 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.87 (s, 1H, C*H*), 4.99 (s, 1H, C*H*), 6.82 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C$_6$*H*$_3$), 6.98–7.01 (m, 4H, C$_6$*H*$_3$), 7.04 (d, $^3J_{HH}$ = 6.3 Hz, 1H, C$_6$*H*$_3$), 7.07–7.09 (m, 4H, C$_6$*H*$_3$), 7.11–7.14 (m, 5H, C$_6$*H*$_3$). **^{13}C{^{1}H}** NMR (126 MHz, C_6D_6, 298 K) δ = 18.6, 20.9, 22.3, 22.8, 23.1, 24.2, 24.4, 24.8, 24.9, 25.1, 25.6, 26.4 (CH(*C*H$_3$)$_2$), 27.5, 28.0, 28.6, 29.3, 32.0 (*C*H(CH$_3$)$_2$), 98.6, 99.9 (*C*H), 117.7, 124.4, 125.0, 125.5, 127.2, 127.5, 141.9, 142.4, 145.3, 145.7, 159.0 (*C*$_6$H$_3$), 169.1, 169.5 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) $\delta = -281.3$. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) $\delta = -281.6$ (d, $^1J_{PH}$ = 189.7 Hz). **ATR-IR**: v 2958, 2922, 2865, 2263, 1732, 1532, 1459, 1437, 1384, 1317, 1261, 1222, 1180, 1100, 1021, 936, 887, 797, 756, 640, 588, 534 cm^{-1}.

Synthesis of LGa(Cl)PH(SPh)LGa (7): Addition of PhSH (30 µL, 0.29 mmol) to a toluene solution (10 mL) of **1** (300 mg, 0.29 mmol) at ambient temperature immediately gave a colorless solution. All volatiles were removed in vacuo to yield a colorless crystalline solid, which was washed with *n*-

hexane (1 mL) and dried. Yield: 95% (315 mg). Single crystals suitable for sc-XRD were grown by cooling a toluene solution of **7** at –30 °C for overnight. M.p. 179 °C (dec.). Anal. calcd. (%) for $C_{64}H_{88}ClGa_2N_4PS$ (1148.47): C, 66.76; H, 7.70; N, 4.87. Found: C, 66.81; H, 7.73; N, 4.91. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) δ = –0.54 (d, $^1J_{PH}$ = 177.3 Hz, 1H, P*H*), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.99 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (s, 6H, CC*H*$_3$), 1.50 (s, 6H, CC*H*$_3$), 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.14 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.22 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.62 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.84 (s, 1H, C*H*), 4.94 (s, 1H, C*H*), 6.94 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C$_6$*H*$_5$), 6.94–7.02 (m, 4H, C$_6$*H*$_3$), 7.04 (d, $^3J_{HH}$ = 6.3 Hz, 1H, C$_6$*H*$_5$), 7.06 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C$_6$*H*$_3$), 7.13–7.15 (m, 4H, C$_6$*H*$_3$), 7.16–7.17 (m, 3H, C$_6$*H*$_3$, C$_6$*H*$_5$), 7.59 (t, $^3J_{HH}$ = 8.3 Hz, 2H, C$_6$*H*$_5$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) δ = 21.4, 24.1, 24.2, 24.5, 24.6, 24.9, 25.0, 25.2, 25.3, 26.9 (CH(*C*H$_3$)$_2$), 27.8, 28.0, 28.1, 29.3, 29.4 (*C*H(CH$_3$)$_2$), 97.6, 98.1 (*C*H), 123.9, 124.1, 125.3, 125.4, 125.7, 127.3, 127.5, 128.6, 129.3, 132.3, 141.6, 142.7, 145.9 (*C*$_6$H$_3$, *C*$_6$H$_5$), 168.7, 169.9 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) δ = –297.0. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) δ = –297.0 (d, $^1J_{PH}$ = 177.0 Hz). **ATR-IR**: *ν* 2958, 2921, 2862, 2270, 1523, 1460, 1435, 1381, 1314, 1256, 1175, 1085, 1019, 937, 864, 794, 728, 694, 637, 531 cm^{-1}.

Synthesis of LGa(Cl)PH(SePh)LGa (8): PhSeH (30 µL, 0.29 mmol) was added to a toluene solution (10 mL) of **1** (300 mg, 0.29 mmol) at ambient temperature, immediately gave a colorless solution. After removal of all volatiles in vacuo, a colorless crystalline solid was obtained, which was washed with *n*-hexane (1 mL) and dried. Yield: 97% (335 mg). Single crystals suitable for sc-XRD were grown by cooling a toluene solution of **8** at –30 °C for overnight. M.p. 173 °C (dec.). Anal. calcd. (%) for $C_{64}H_{88}ClGa_2N_4PSe$ (1196.41): C, 64.15; H, 7.40; N, 4.68. Found: C, 64.20; H, 7.45; N, 4.72. **^{1}H NMR** (500 MHz, C_6D_6, 298 K) δ = –0.45 (d, $^1J_{PH}$ = 176.4 Hz, 1H, P*H*), 1.00 (dd, $^3J_{HH}$ = 6.8, 4.15 Hz, 12H, CH(C*H*$_3$)$_2$), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (s, 6H, CC*H*$_3$), 1.50 (s, 6H, CC*H*$_3$), 3.11 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.19 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.46 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.61 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.83 (s, 1H, C*H*), 4.85 (s, 1H, C*H*), 6.99–7.01 (m, 5H, C$_6$*H*$_5$, C$_6$*H*$_3$), 7.05–7.10 (m, 4H, C$_6$*H*$_5$,C$_6$*H*$_3$), 7.15–7.18 (m, 6H, C$_6$*H*$_5$,C$_6$*H*$_3$), 7.82 (d, $^3J_{HH}$ = 7.1 Hz, 2H, C$_6$*H*$_5$). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K) δ = 24.1, 24.2, 24.5, 24.6, 24.9, 25.2, 25.3 (CH(*C*H$_3$)$_2$), 27.8, 27.9, 28.0, 28.2, 29.3, 29.4 (*C*H(CH$_3$)$_2$), 97.7, 98.9 (*C*H), 123.9, 124.2, 125.4, 125.6, 127.4, 128.6, 141.6, 142.7, 143.2, 146.0 (*C*$_6$H$_3$, *C*$_6$H$_5$), 168.8, 169.7 (*C*$_6$H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6, 298 K) δ = –294.0. **^{31}P NMR** (202 MHz, C_6D_6, 298 K) δ = –294.0 (d, $^1J_{PH}$ = 177.2 Hz). **ATR-IR**: *ν* 2948, 2912, 2853, 2265, 1587, 1522, 1434, 1378, 1312, 1292, 1173, 1094, 1016, 934, 850, 794, 755, 690, 635, 531 cm^{-1}.

Table S1. Selected ^{1}H, ^{31}P NMR, and IR data of compounds **1–8**.

Compound	^{1}H NMR (ppm), **P-*H*** unit	^{1}H NMR (ppm), **X-*H*** unit	^{31}P{^{1}H} NMR (ppm)	^{31}P NMR (ppm)	IR (cm^{-1}), **P-H** unit
1	—	–245.8	—	—	—
2	–0.84 ($^1J_{PH}$ = 174.5 Hz)	0.48 (X = N*H*$_2$)	–314.6 ($^1J_{PH}$ = 174.5 Hz)	–314.6	2260
3	–0.88 ($^1J_{PH}$ = 175.6 Hz)	1.46 (X = N*H*^{i}Pr)	–313.9 ($^1J_{PH}$ = 175.6 Hz)	–313.7	2261
4	–0.58 ($^1J_{PH}$ = 177.0 Hz)	5.04 (X = N*H*Ph)	–315.0 ($^1J_{PH}$ = 177.0 Hz)	–315.0	2262
5	–0.71 ($^1J_{PH}$ = 174.3 Hz)	1.41 (X = O*H*)	–312.9 ($^1J_{PH}$ = 173.7 Hz)	–312.9	2265
6	–0.21 ($^1J_{PH}$ = 188.9 Hz)	—	–281.6 ($^1J_{PH}$ = 189.7 Hz)	–281.3	2263
7	–0.54 ($^1J_{PH}$ = 177.3 Hz)	—	–297.0 ($^1J_{PH}$ = 177.0 Hz)	–297.0	2270
8	–0.45 ($^1J_{PH}$ = 176.4 Hz)	—	–294.0 ($^1J_{PH}$ = 177.2 Hz)	–294.0	2265

2. Spectroscopic Characterization

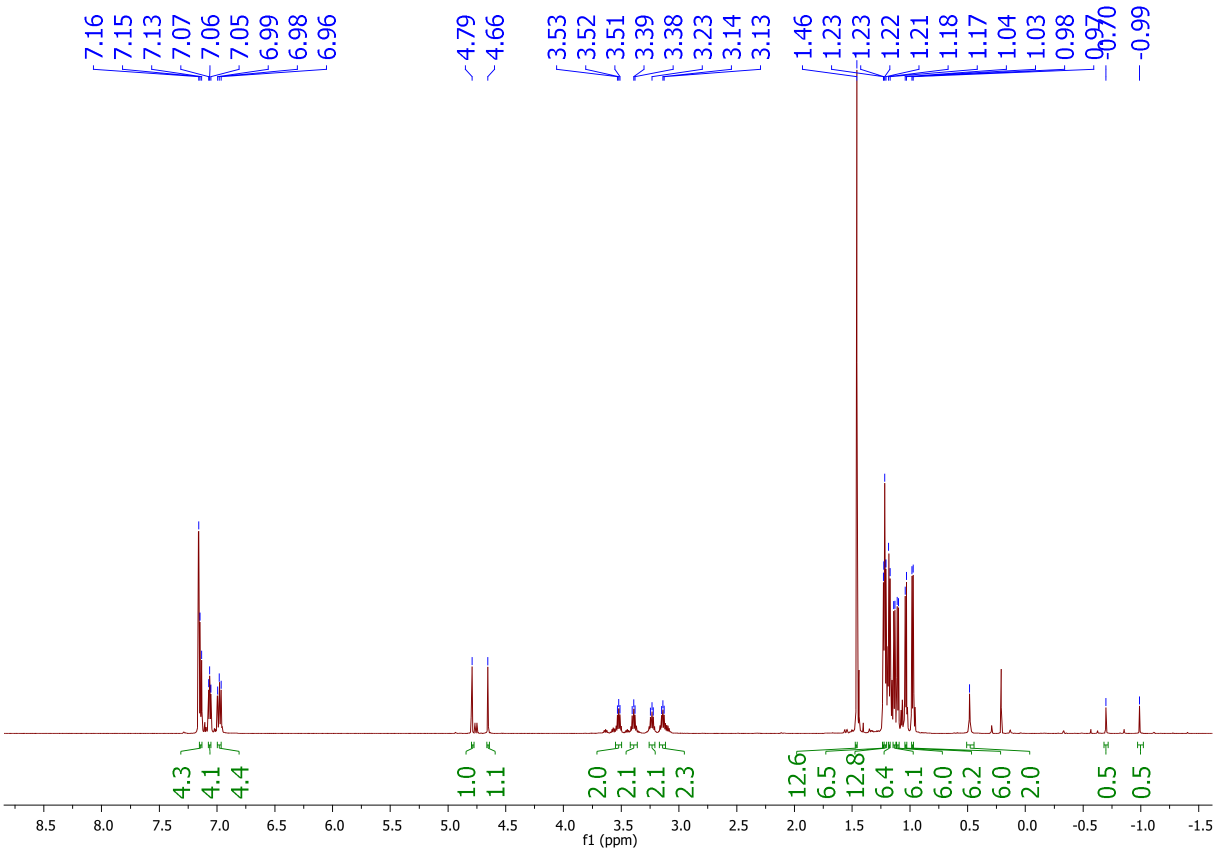

Figure S1. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **2**.

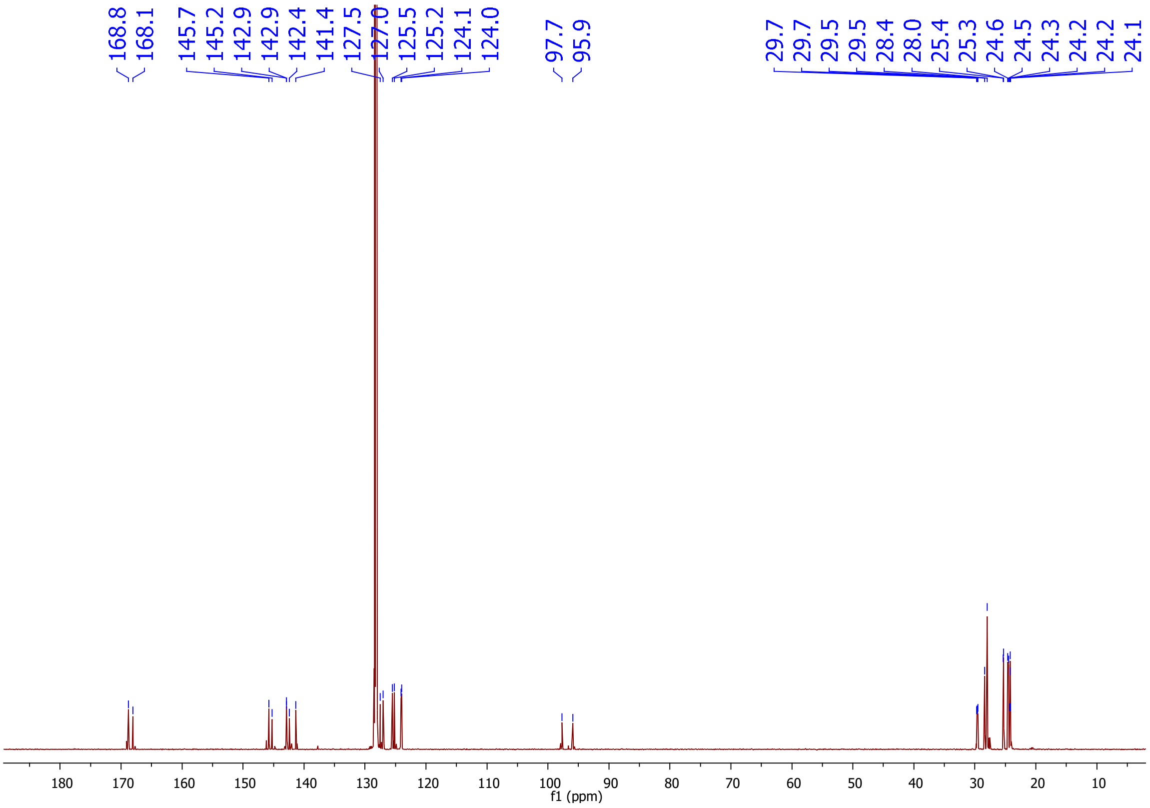

Figure S2. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **2**.

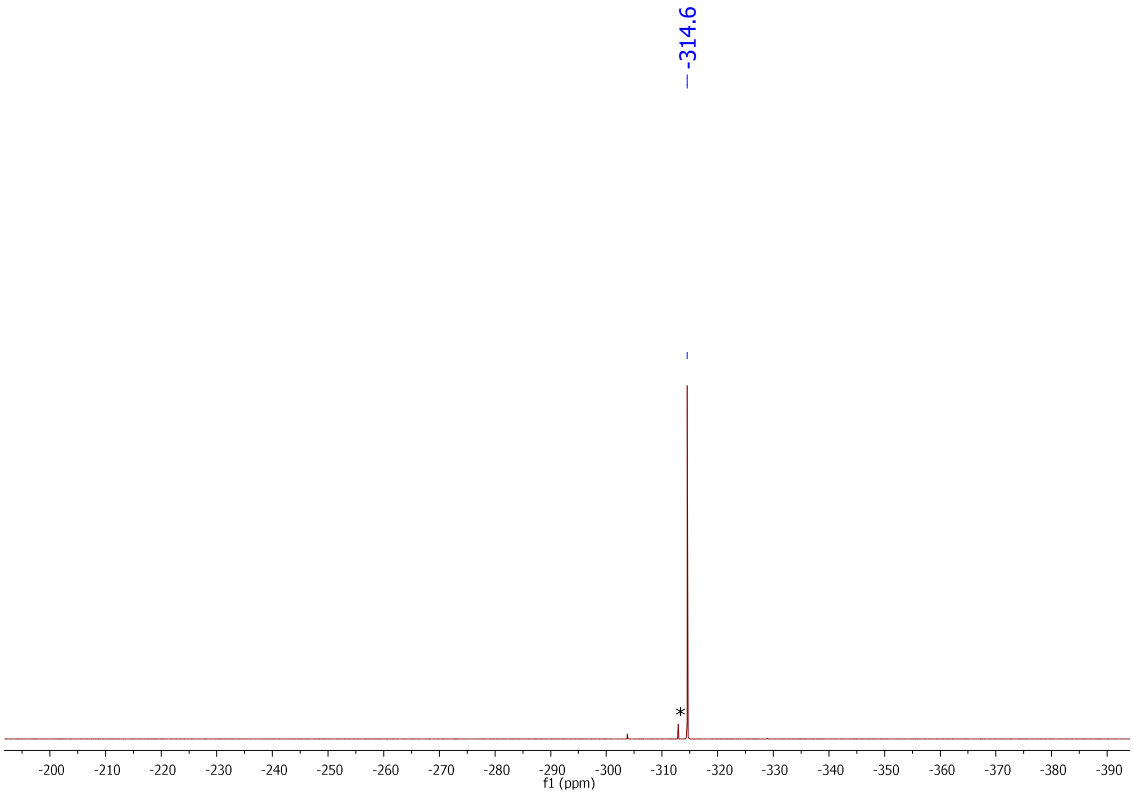

Figure S3. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **2**. (*Hydrolyzed species, #unknown species)

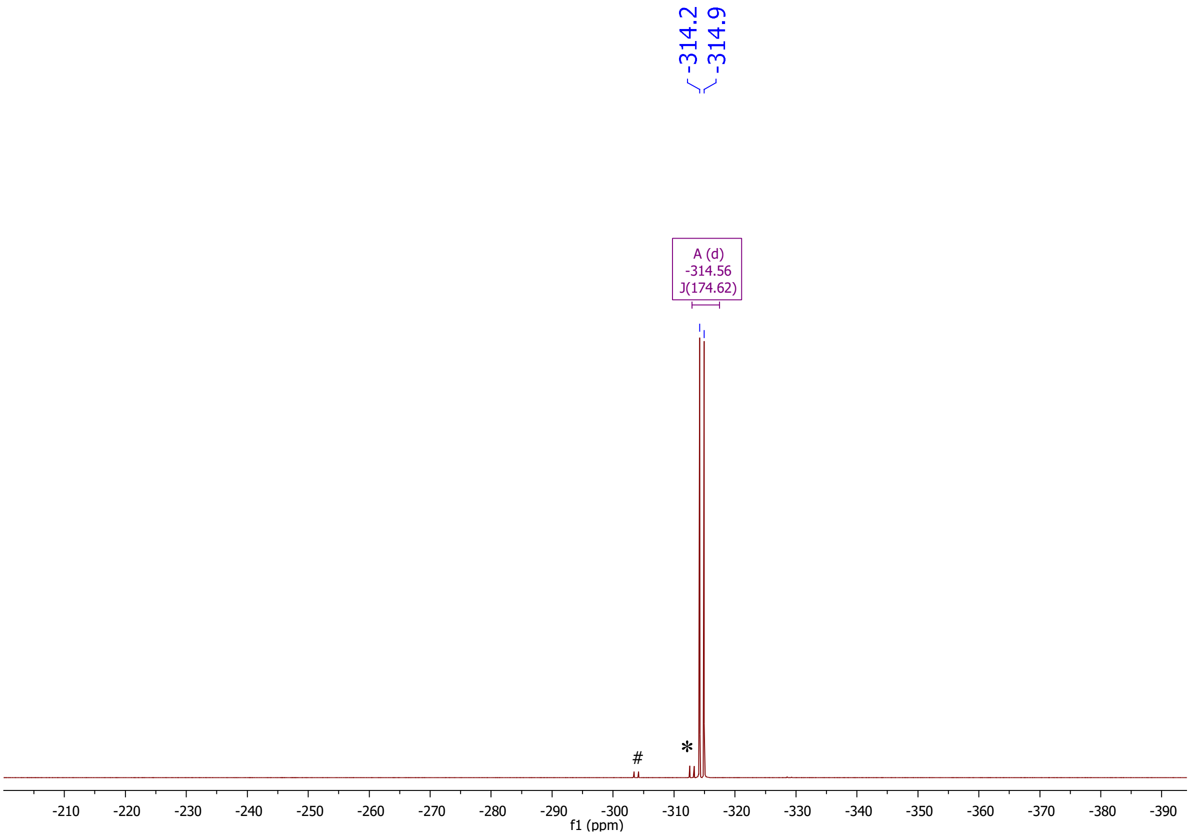

Figure S4. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **2**. (*hydrolyzed species, #unknown species)

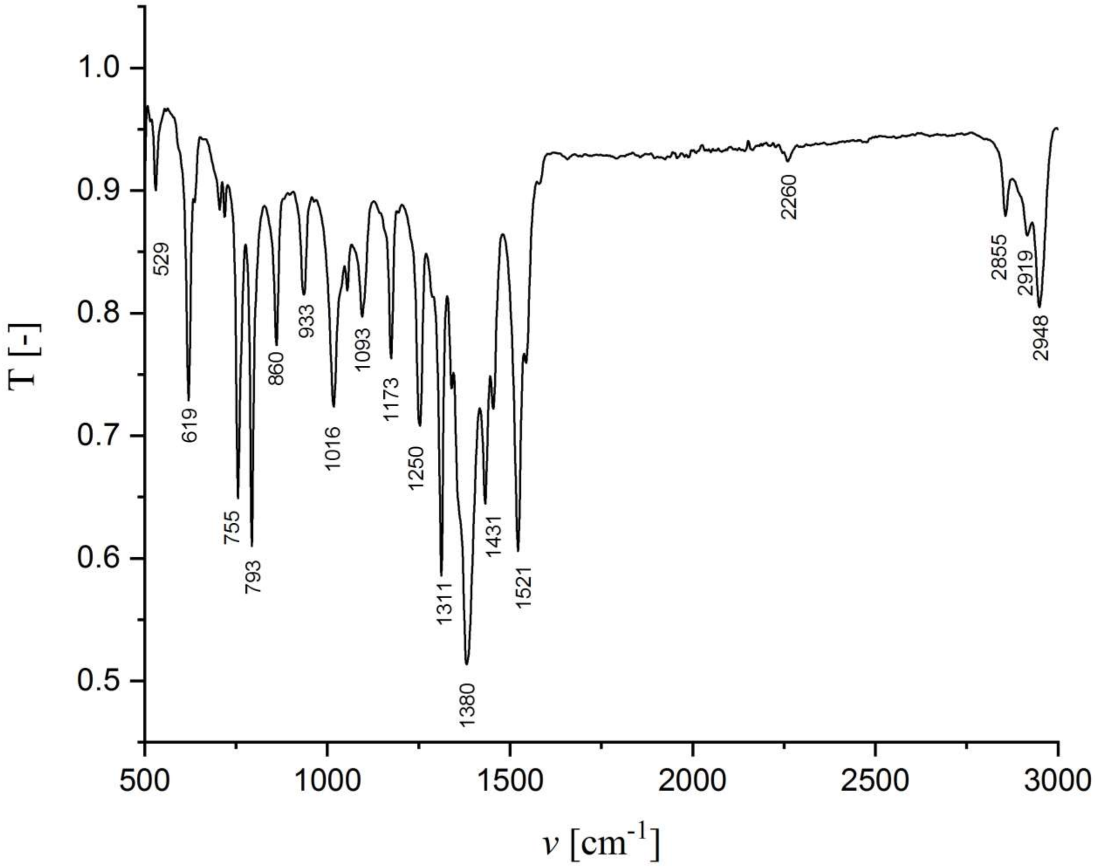

Figure S5. ATR-IR spectrum of **2**.

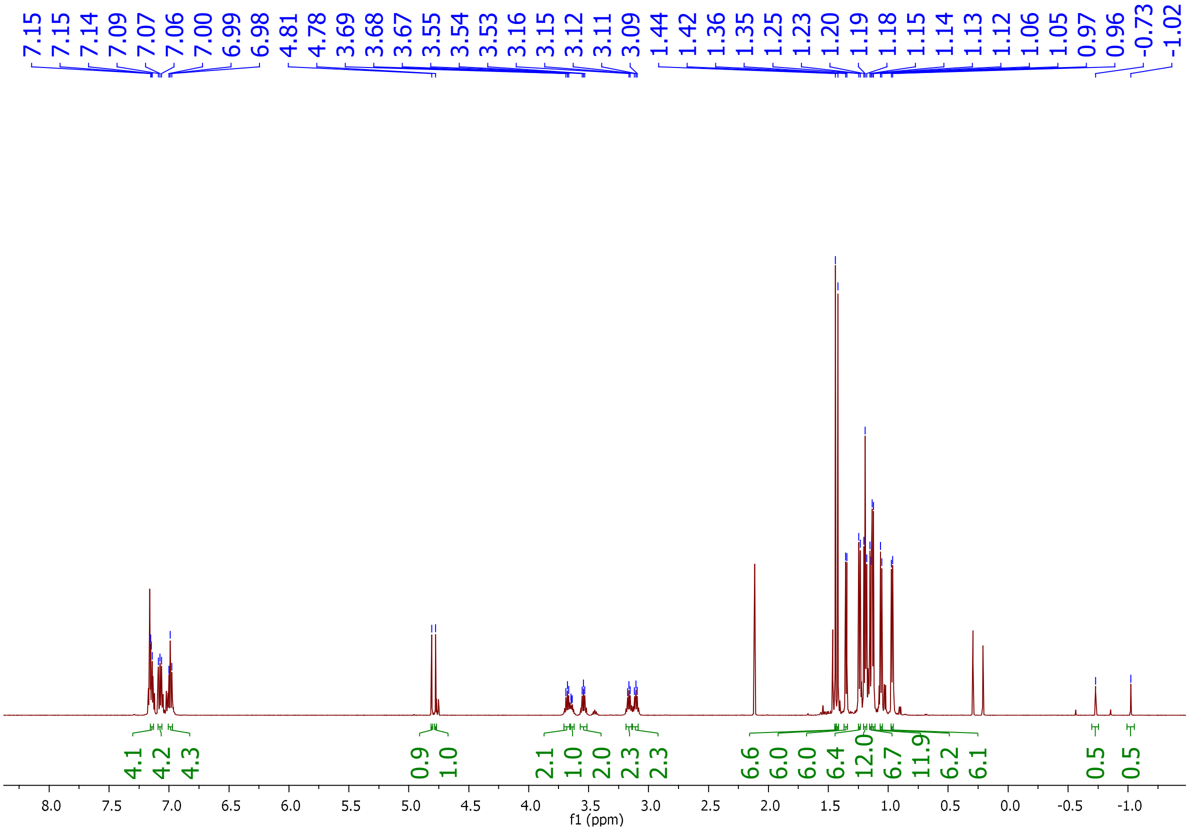

Figure S6. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **3**.

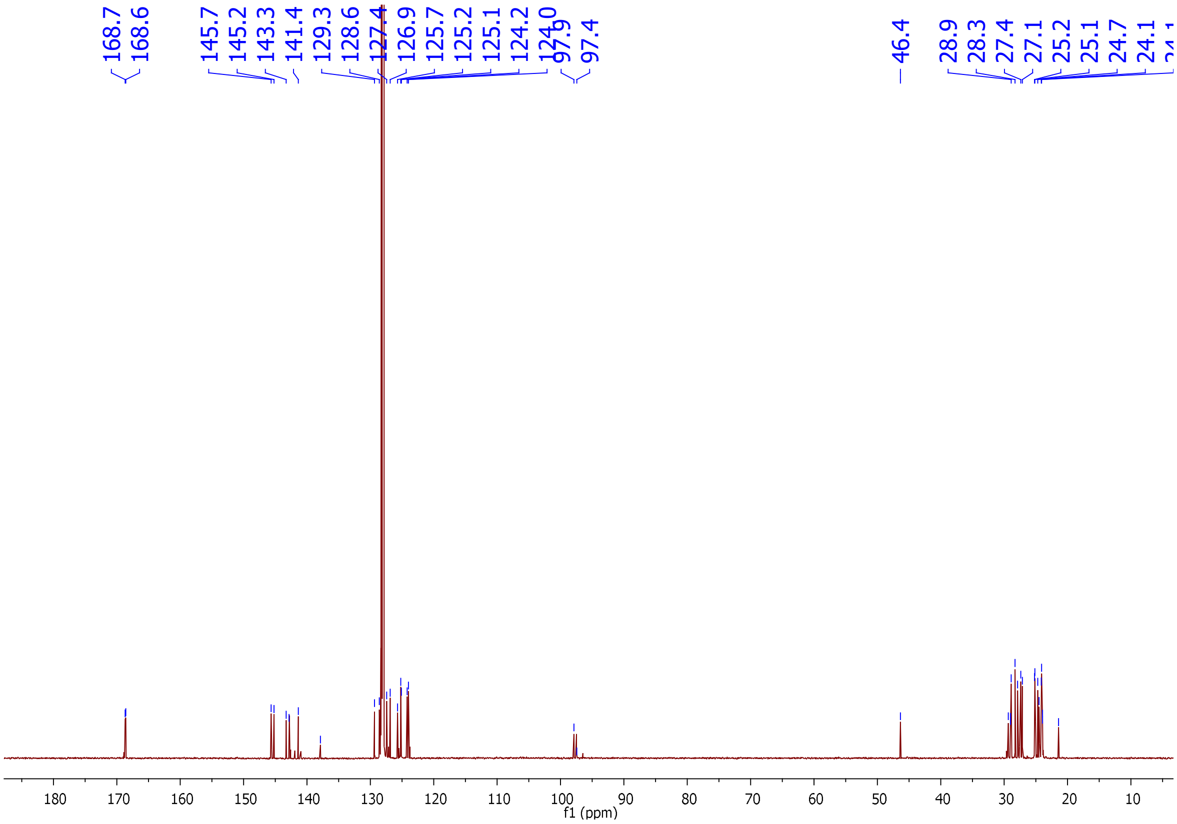

Figure S7. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **3**.

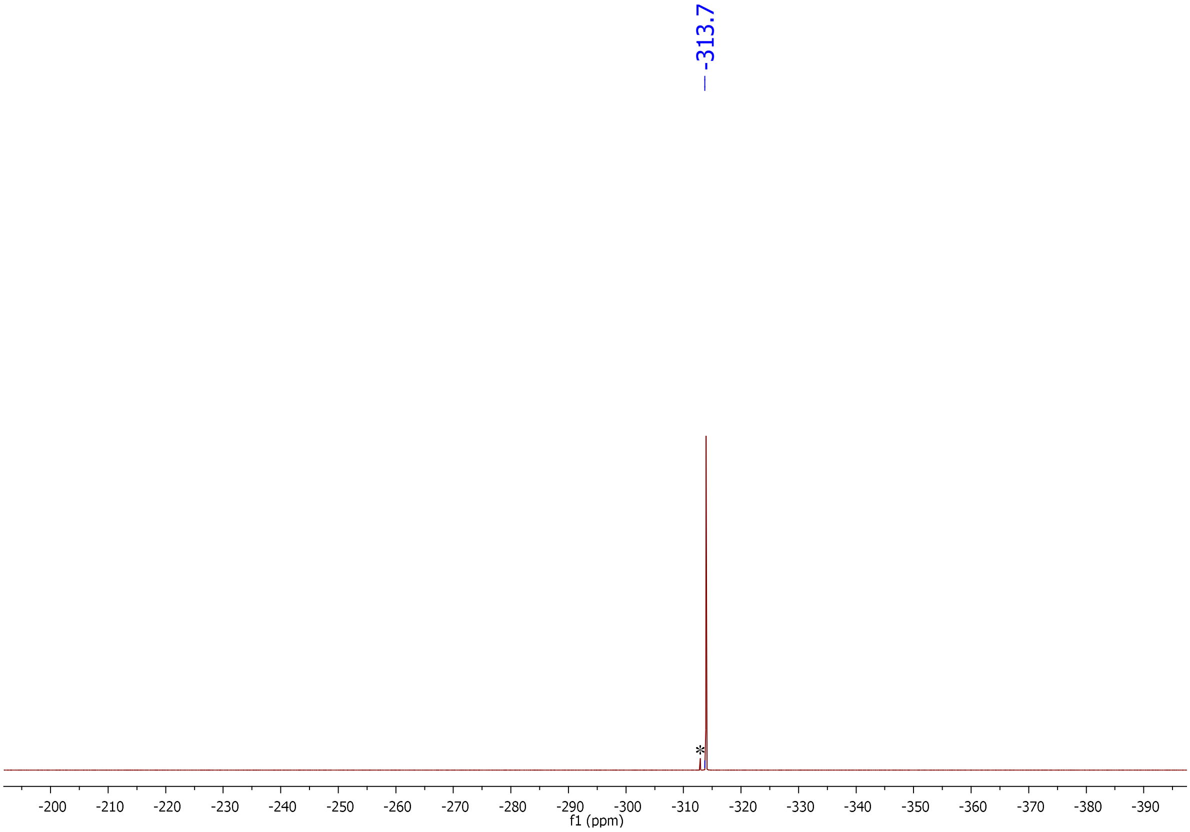

Figure S8. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **3**. (*hydrolyzed species)

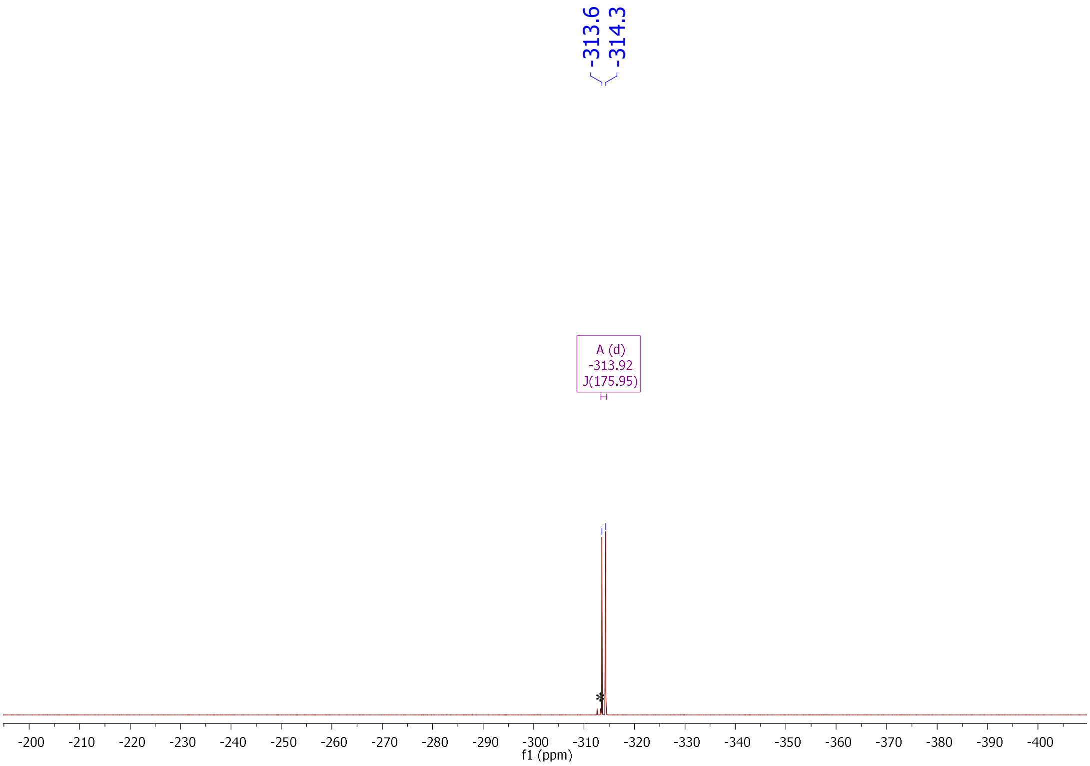

Figure S9. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **3**. (*hydrolyzed species)

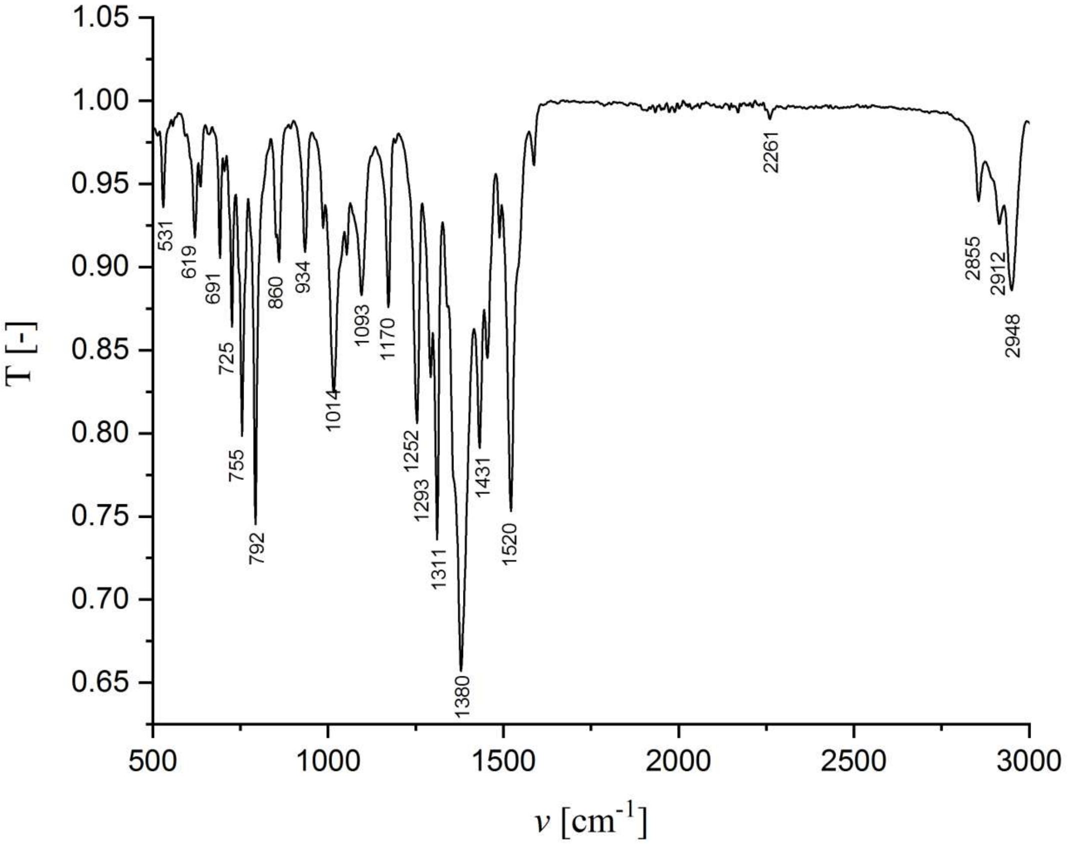

Figure S10. ATR-IR spectrum of **3**.

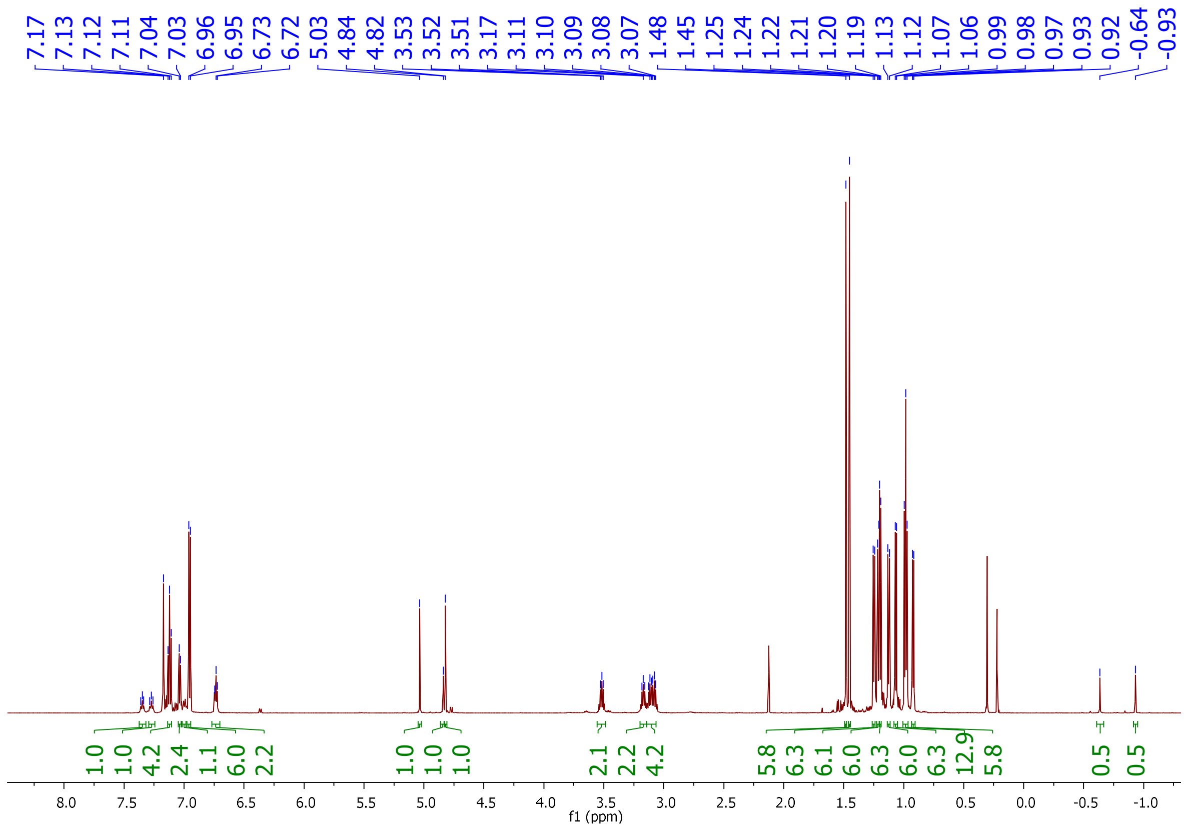

Figure S11. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **4**.

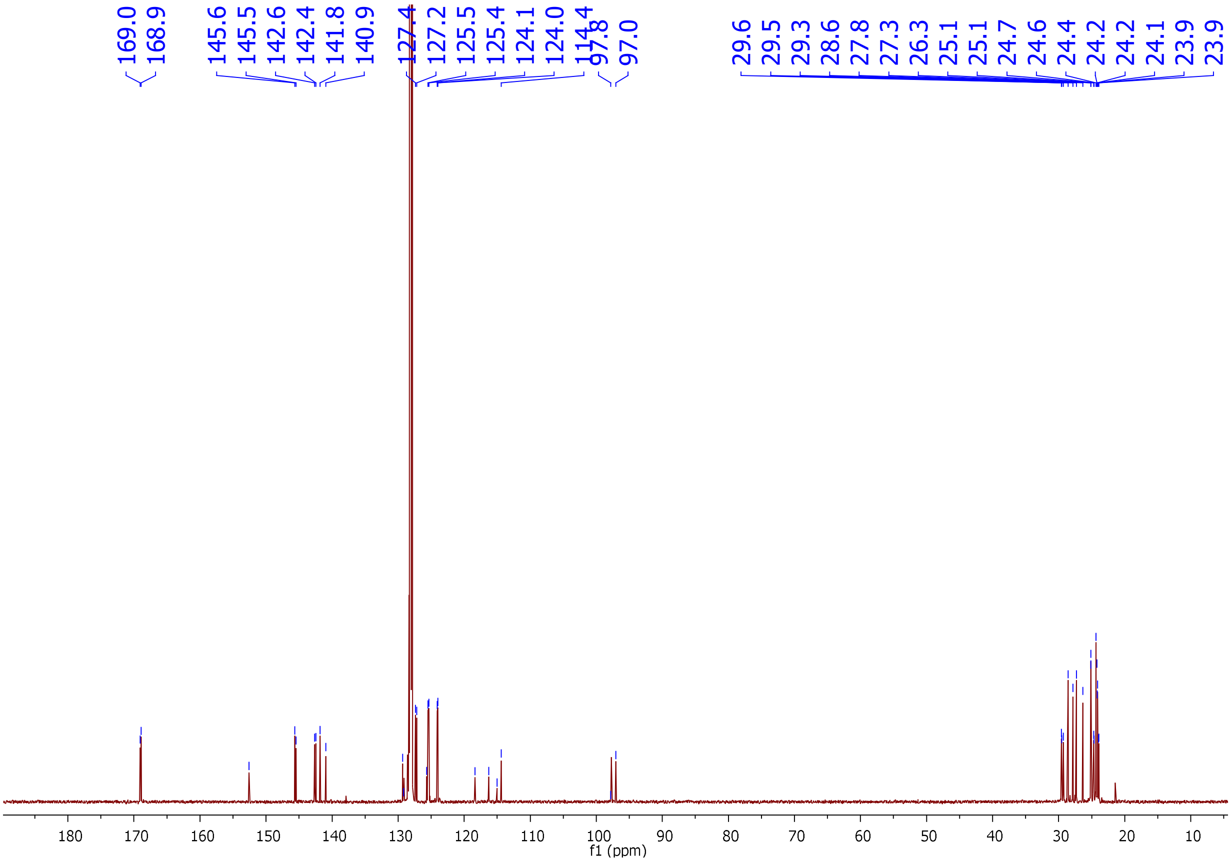

Figure S12. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **4**.

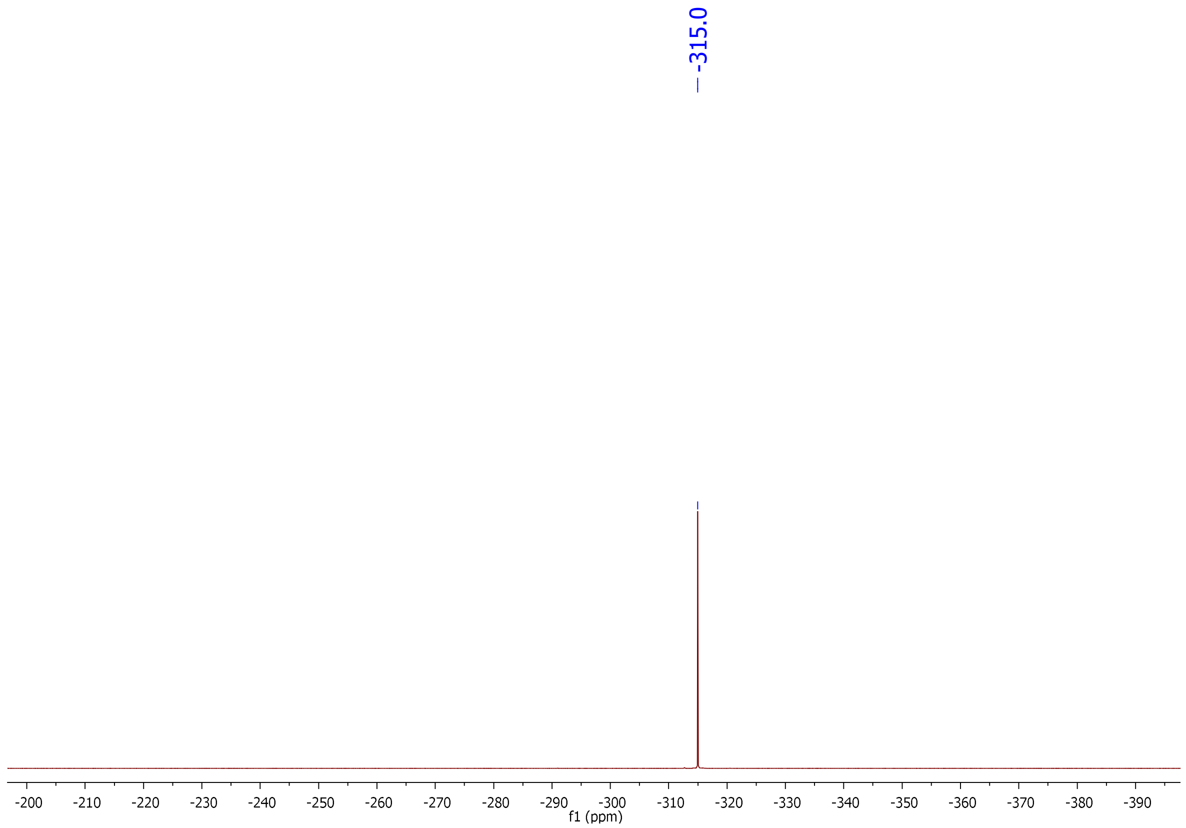

Figure S13. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **4**.

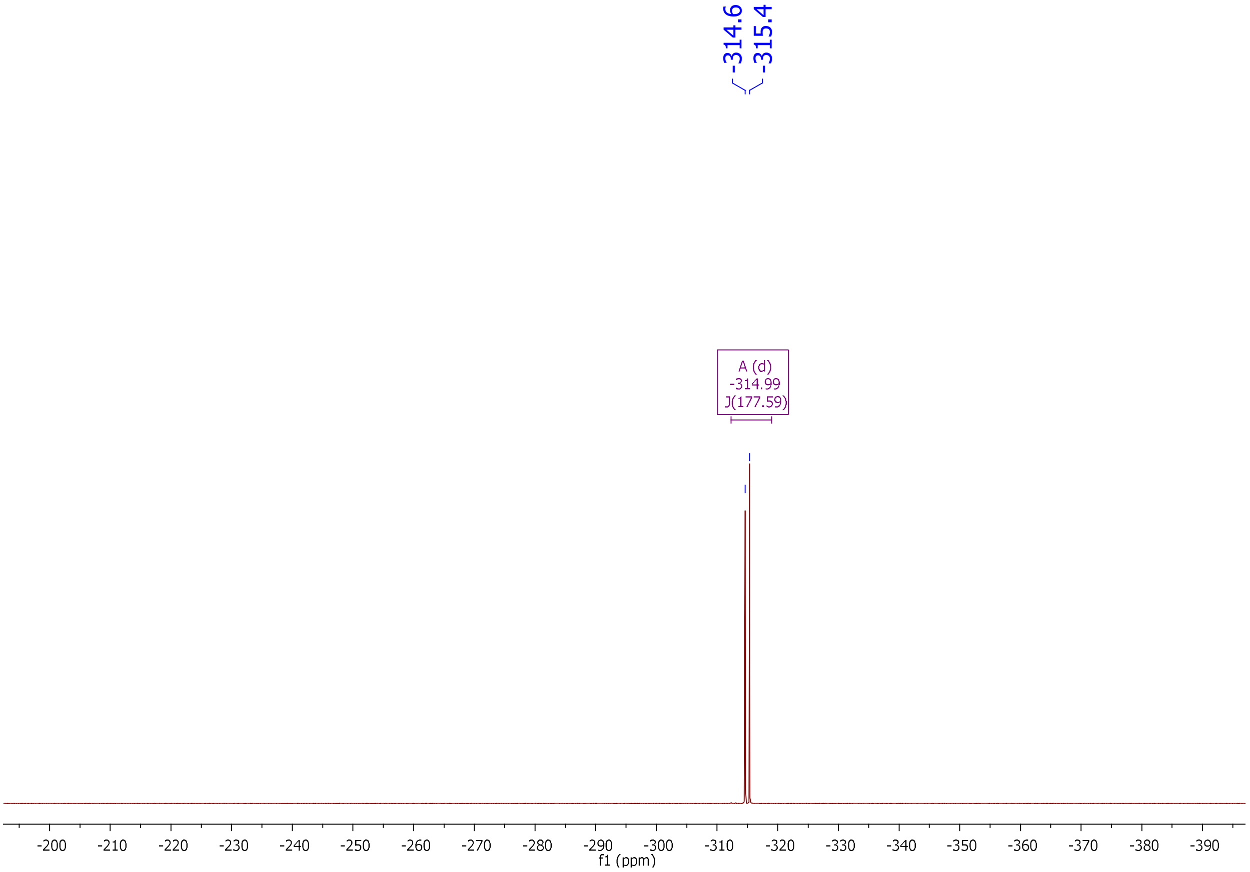

Figure S14. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **4**.

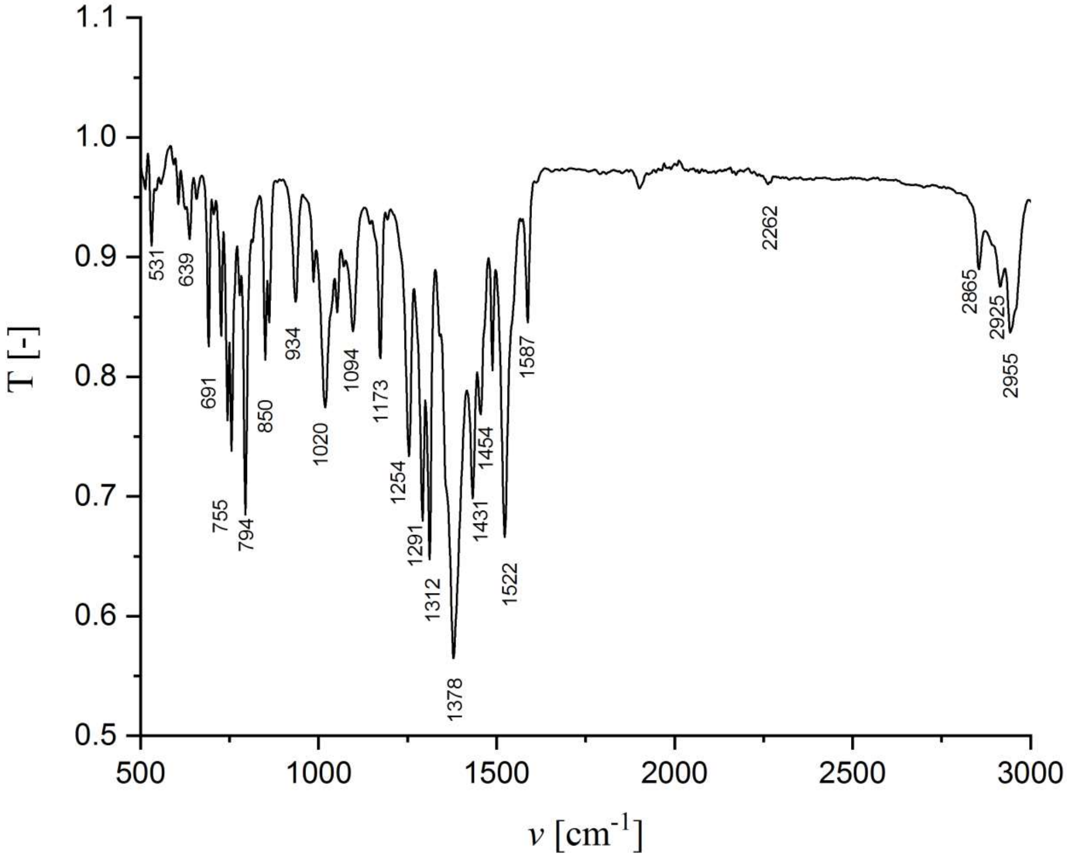

Figure S15. ATR-IR spectrum of **4**.

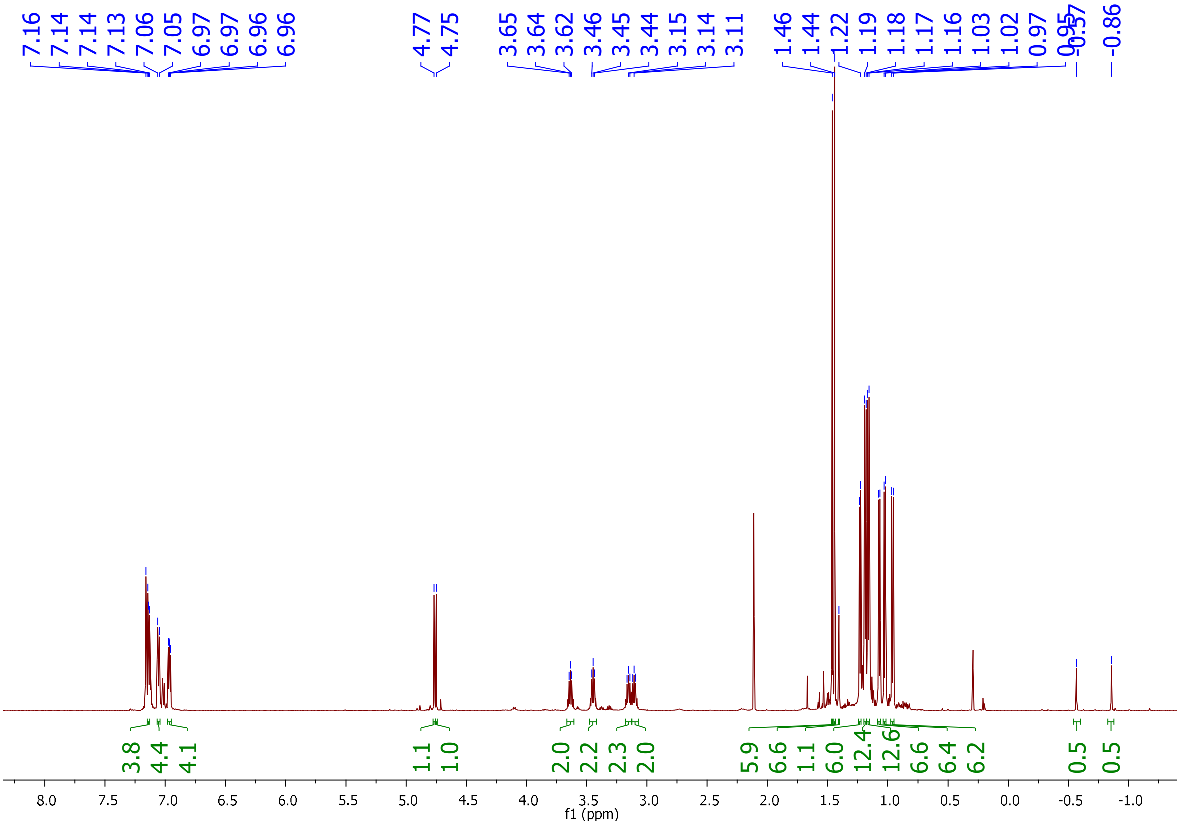

Figure S16. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **5**.

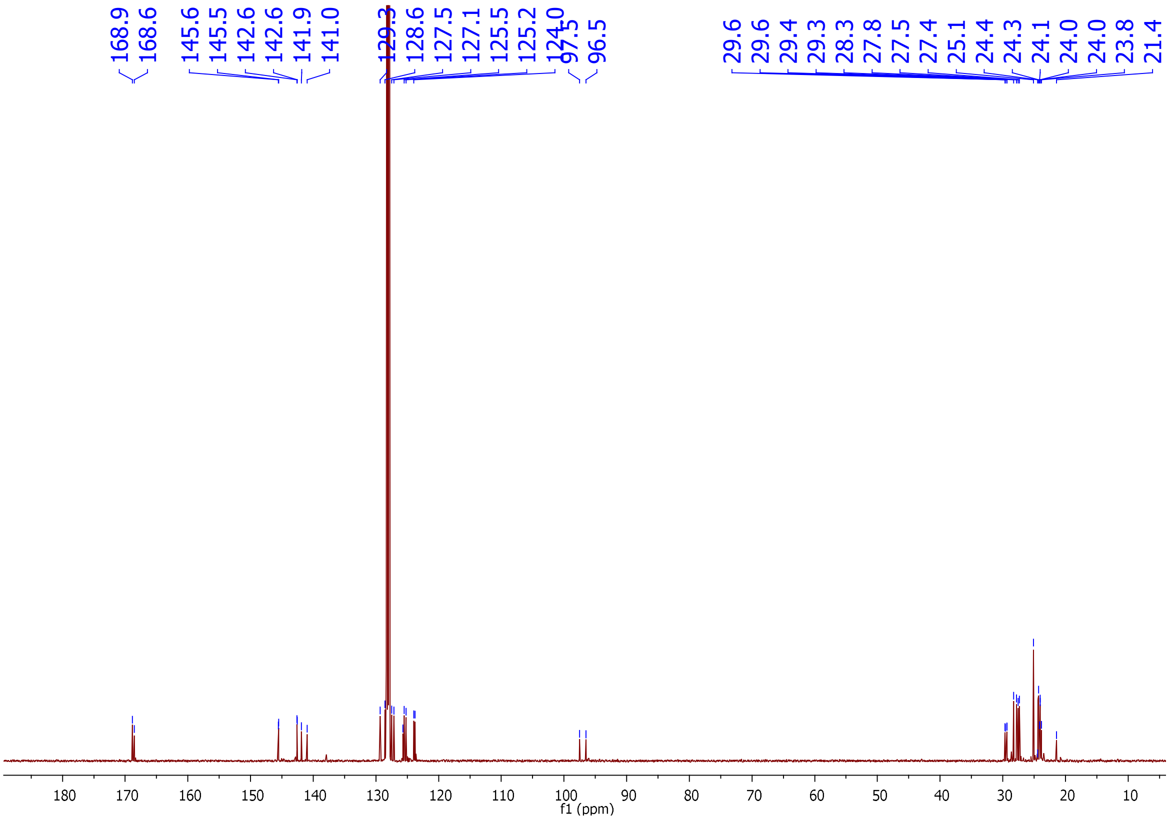

Figure S17. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **5**.

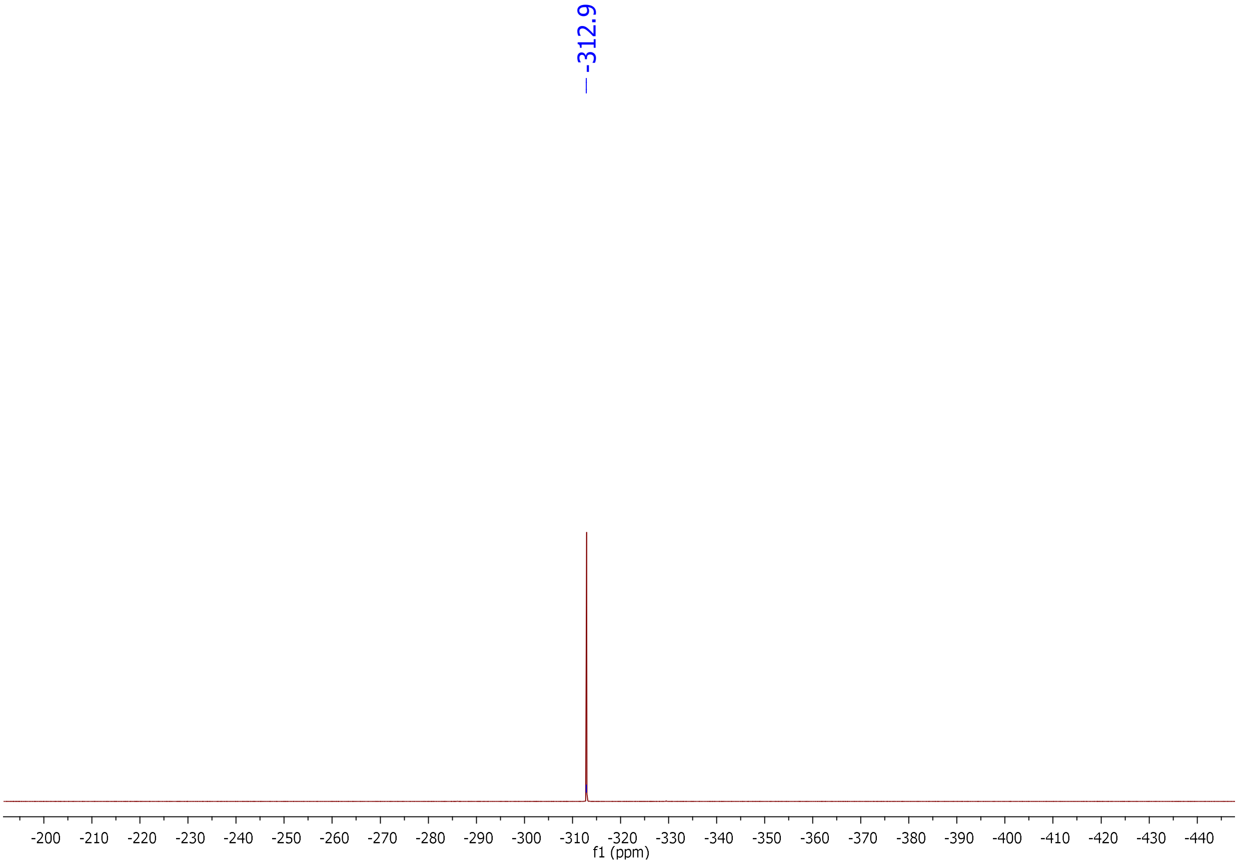

Figure S18. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **5**.

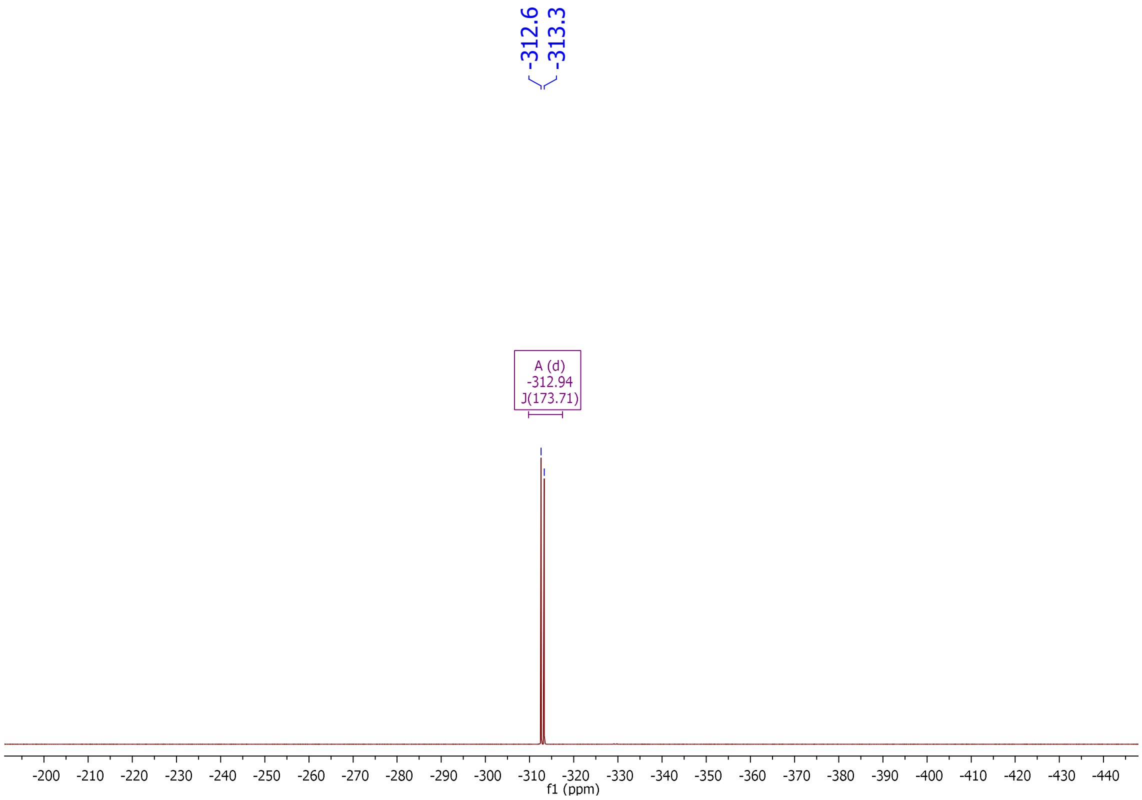

Figure S19. ^{31}P NMR (202 MHz, toluene-d_8, 298 K) spectrum of compound **5**.

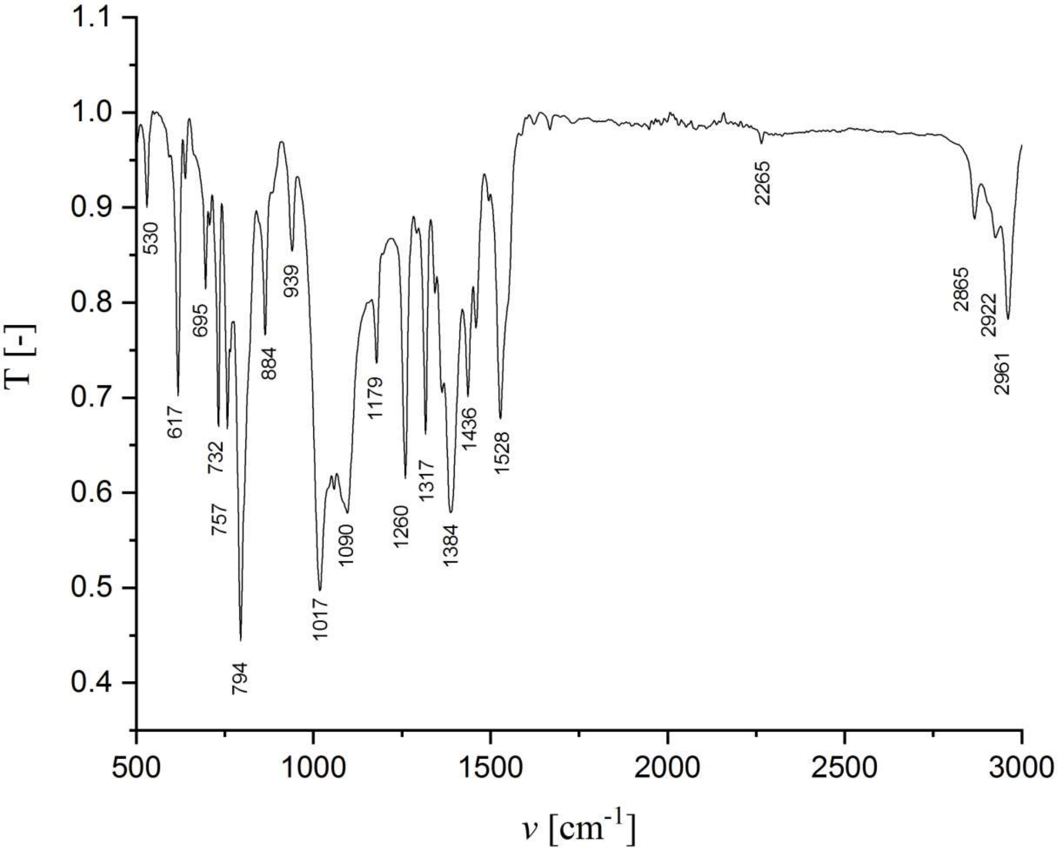

Figure S20. ATR-IR spectrum of **5**.

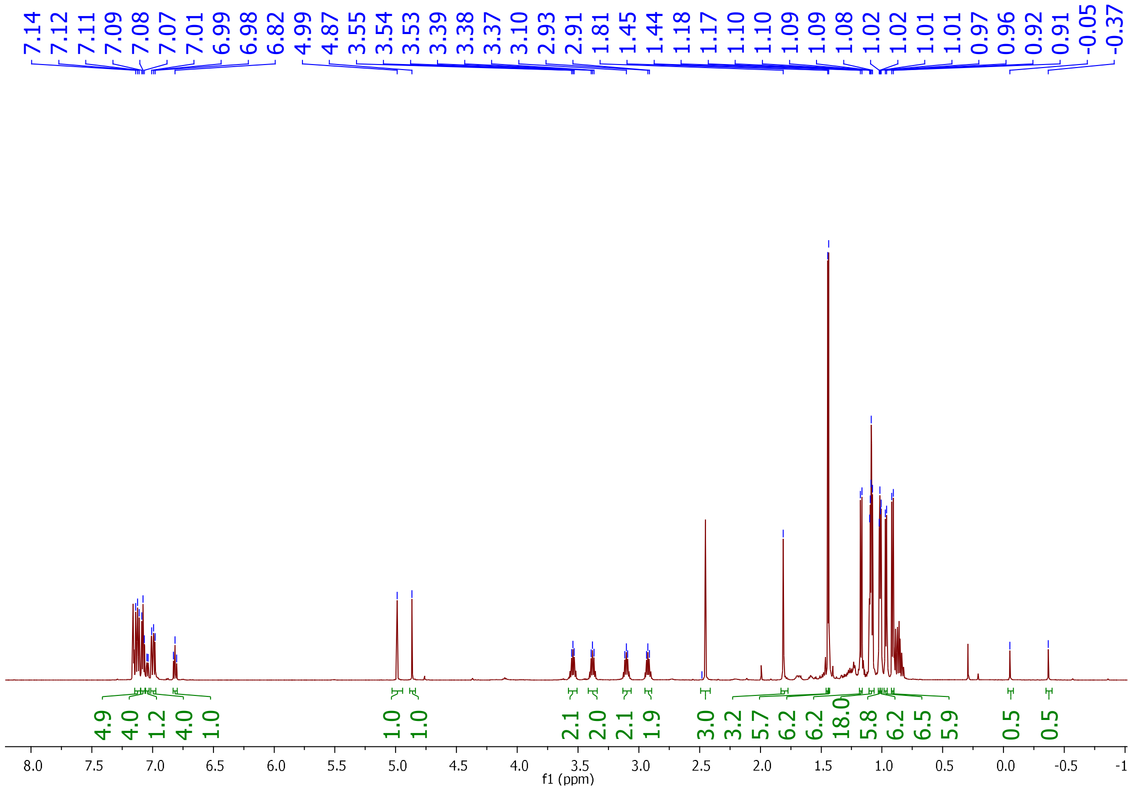

Figure S21. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **6**.

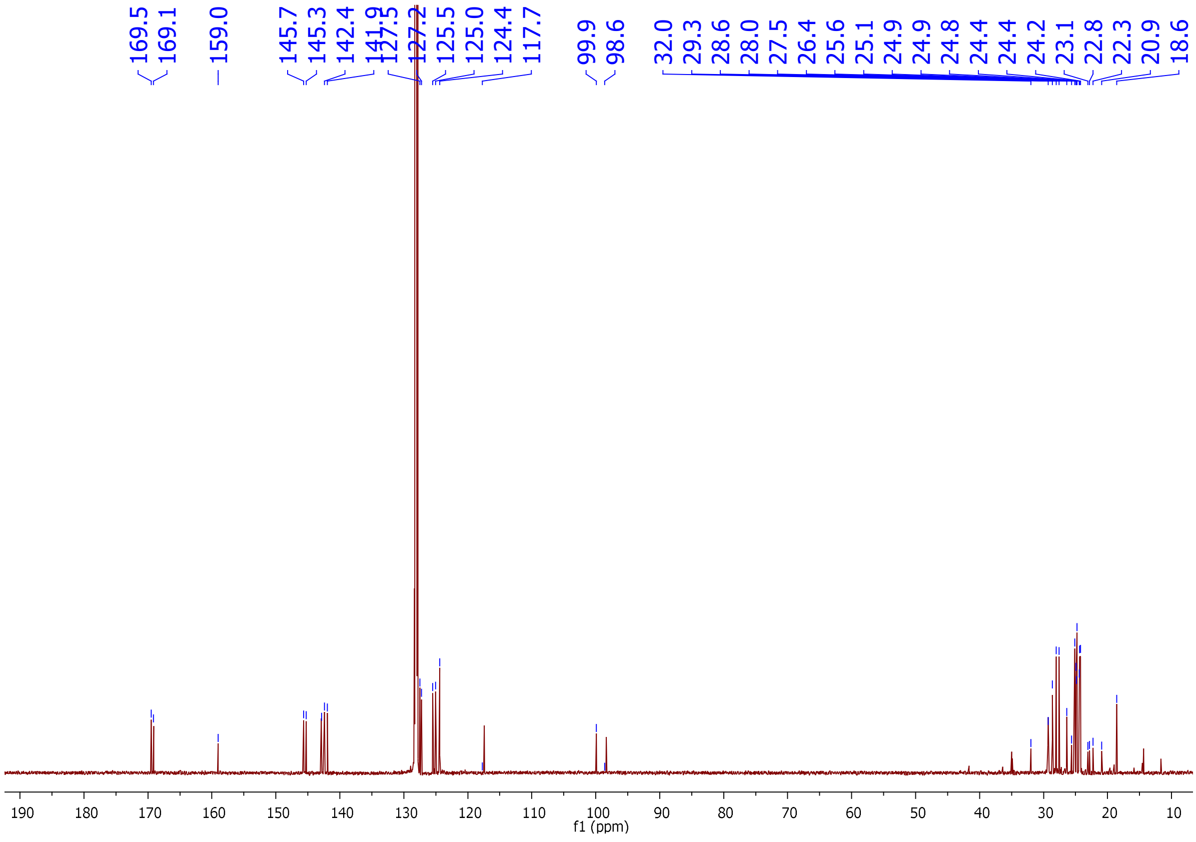

Figure S22. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **6**.

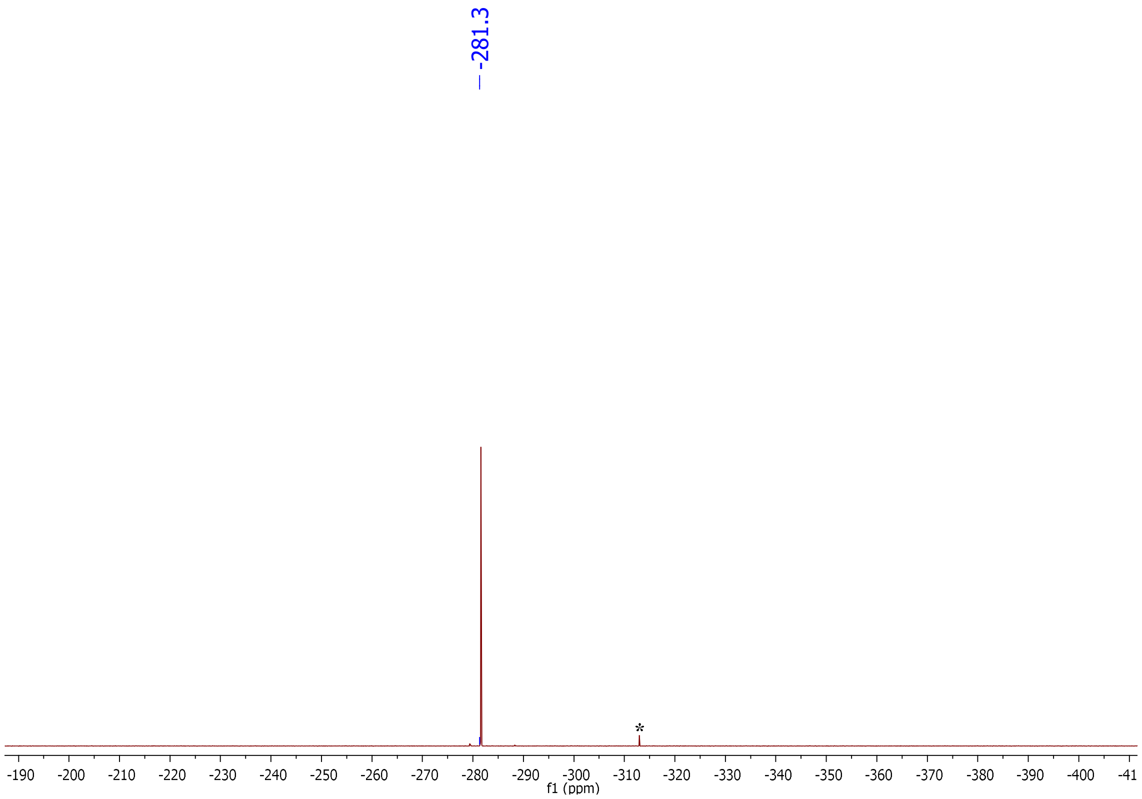

Figure S23. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **6**. (*hydrolyzed species)

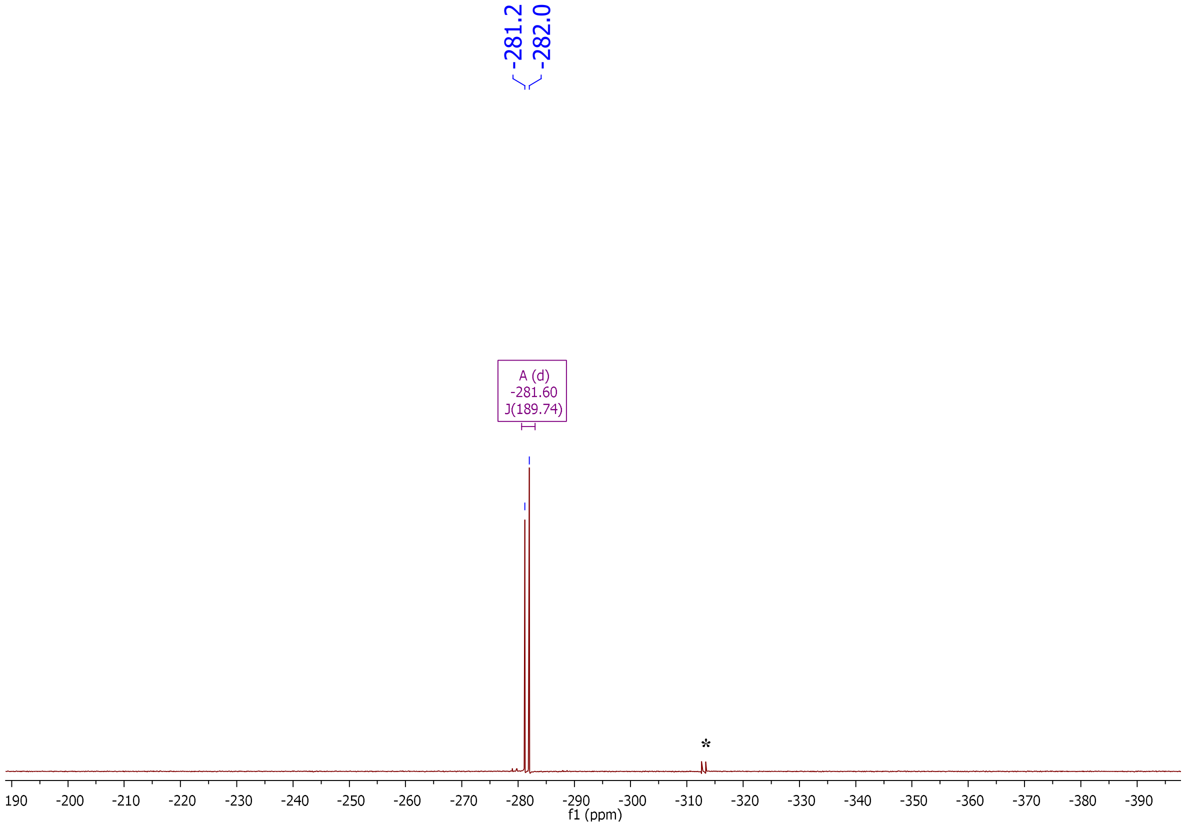

Figure S24. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **6**. (*hydrolyzed species)

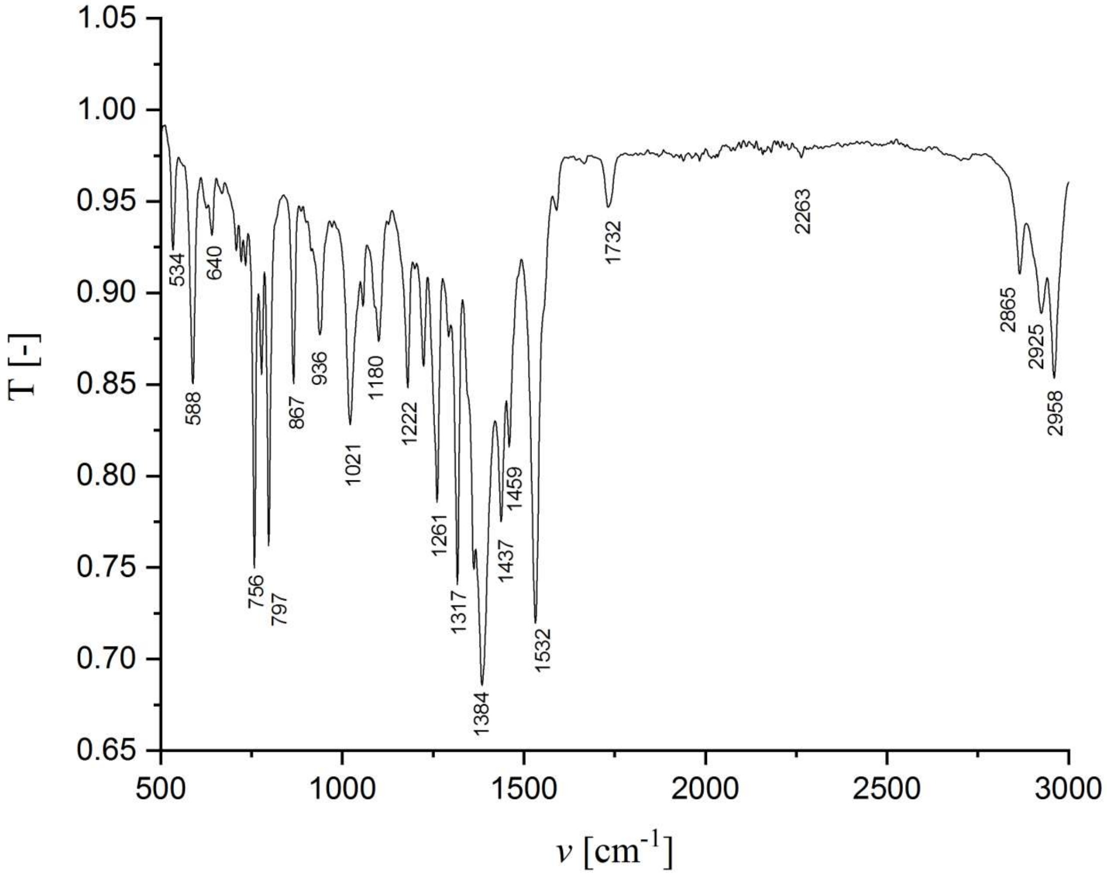

Figure S25. ATR-IR spectrum of **6**.

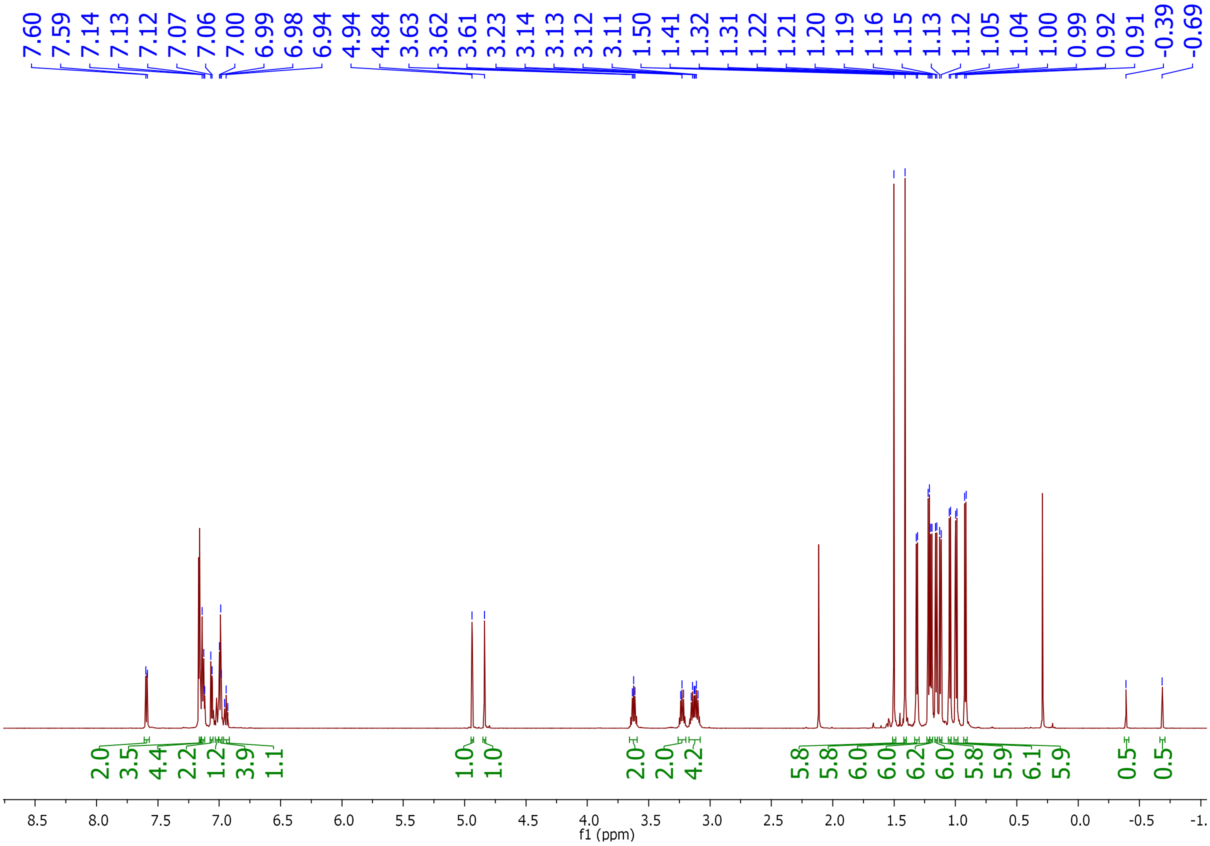

Figure S26. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **7**.

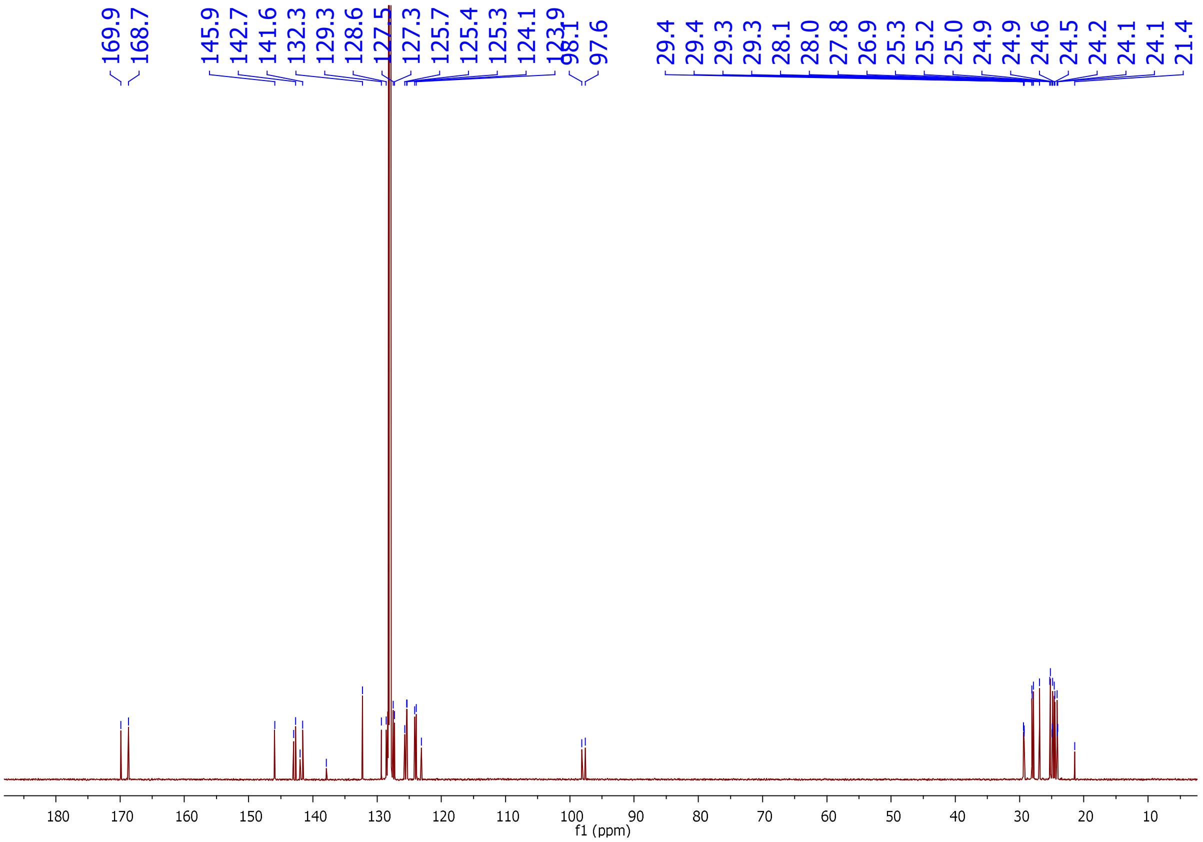

Figure S27. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **7**.

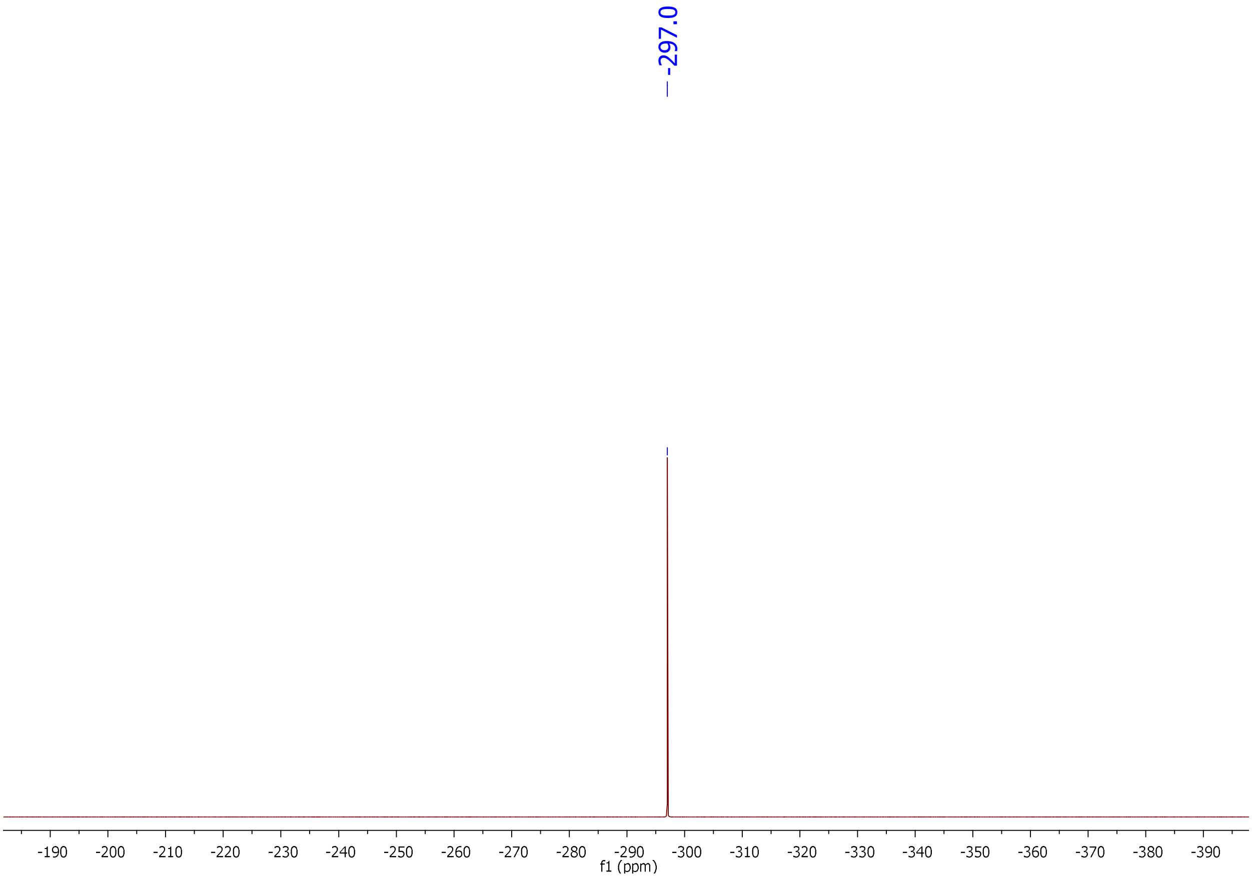

Figure S28. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **7**.

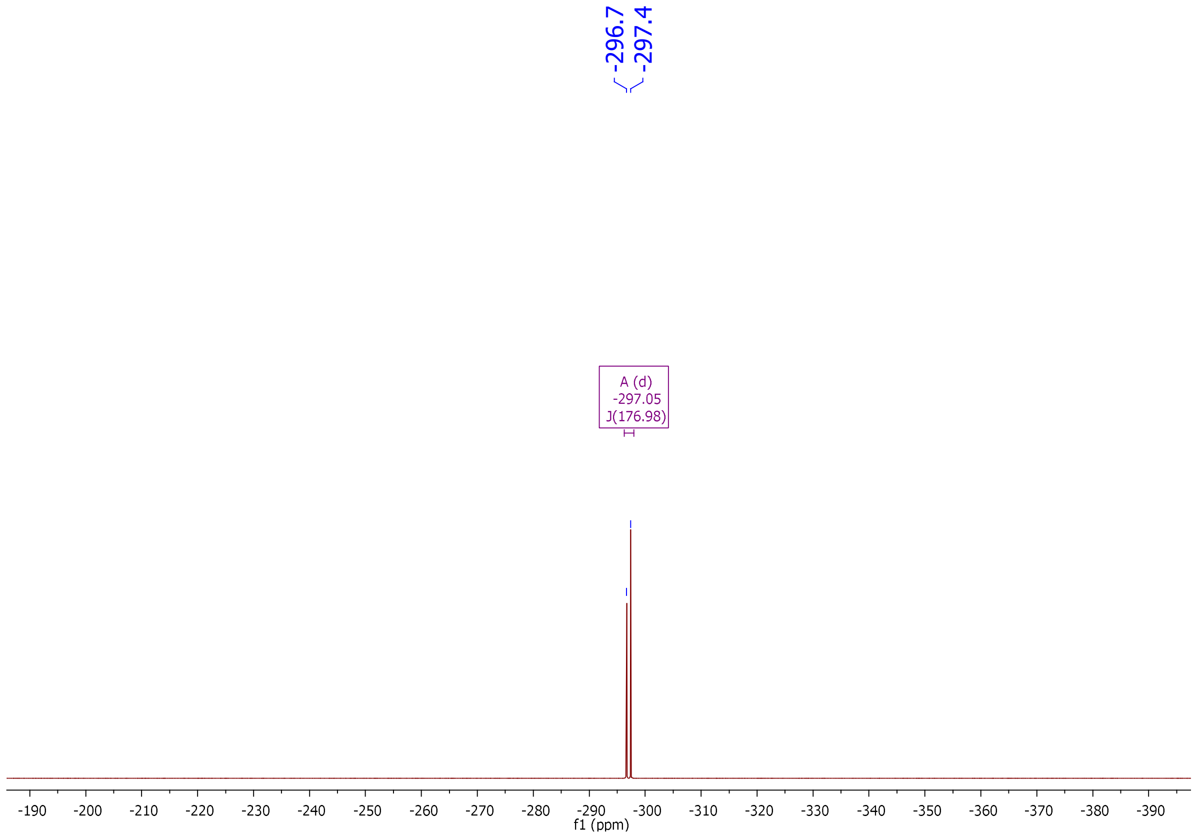

Figure S29. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **7**.

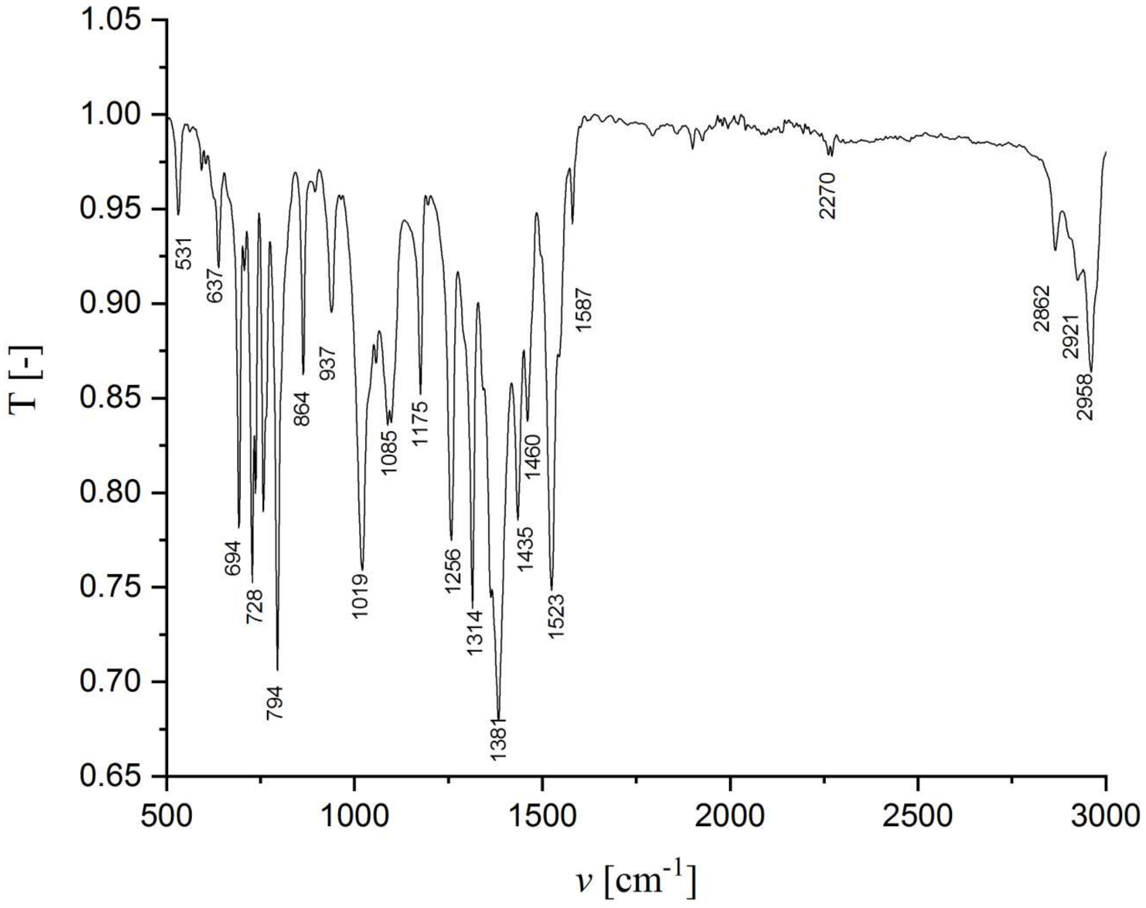

Figure S30. ATR-IR spectrum of **7**.

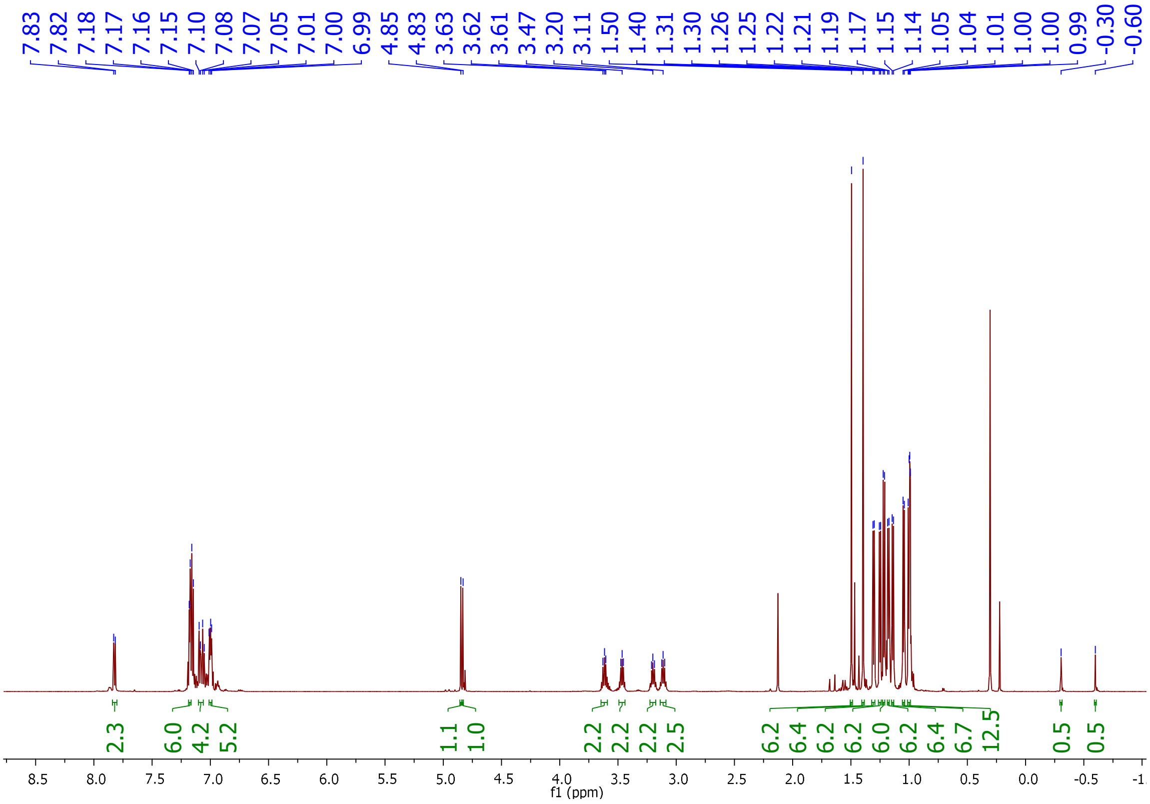

Figure S31. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **8**.

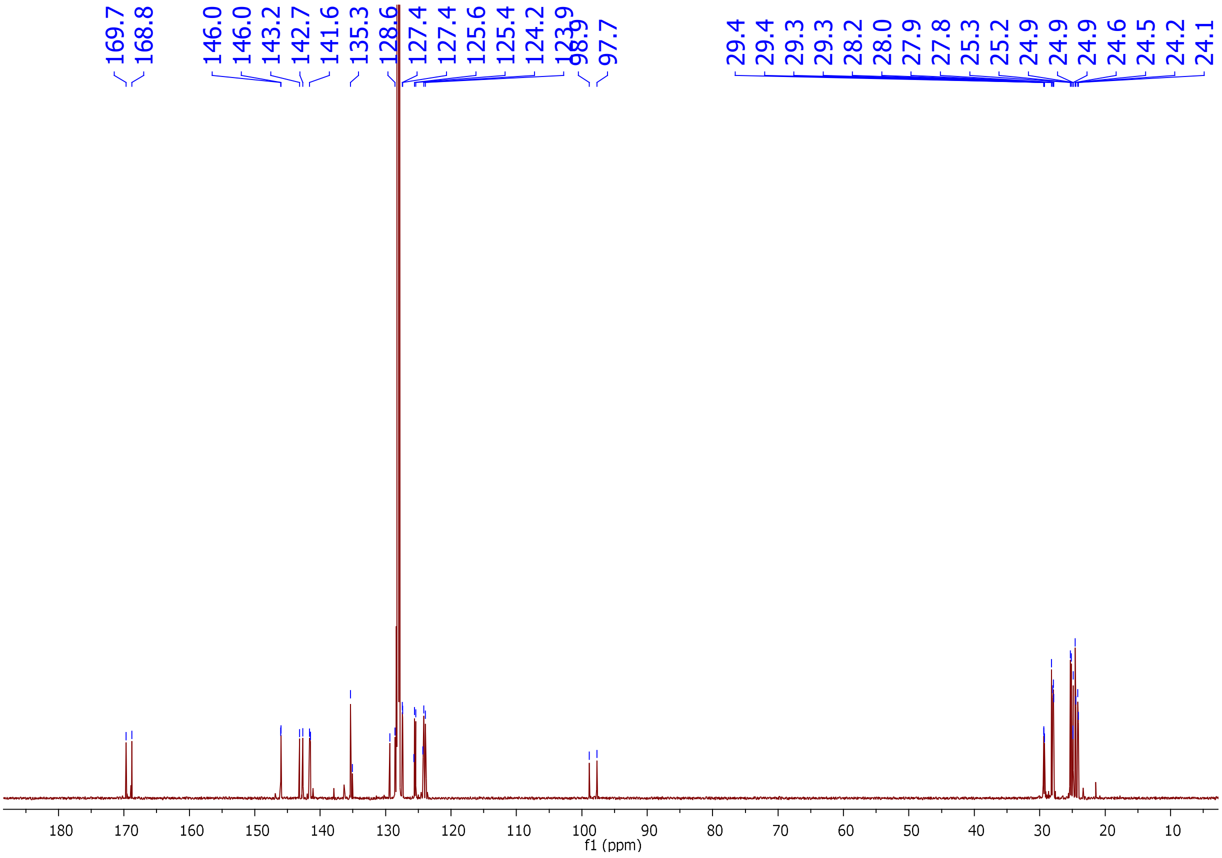

Figure S32. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **8**.

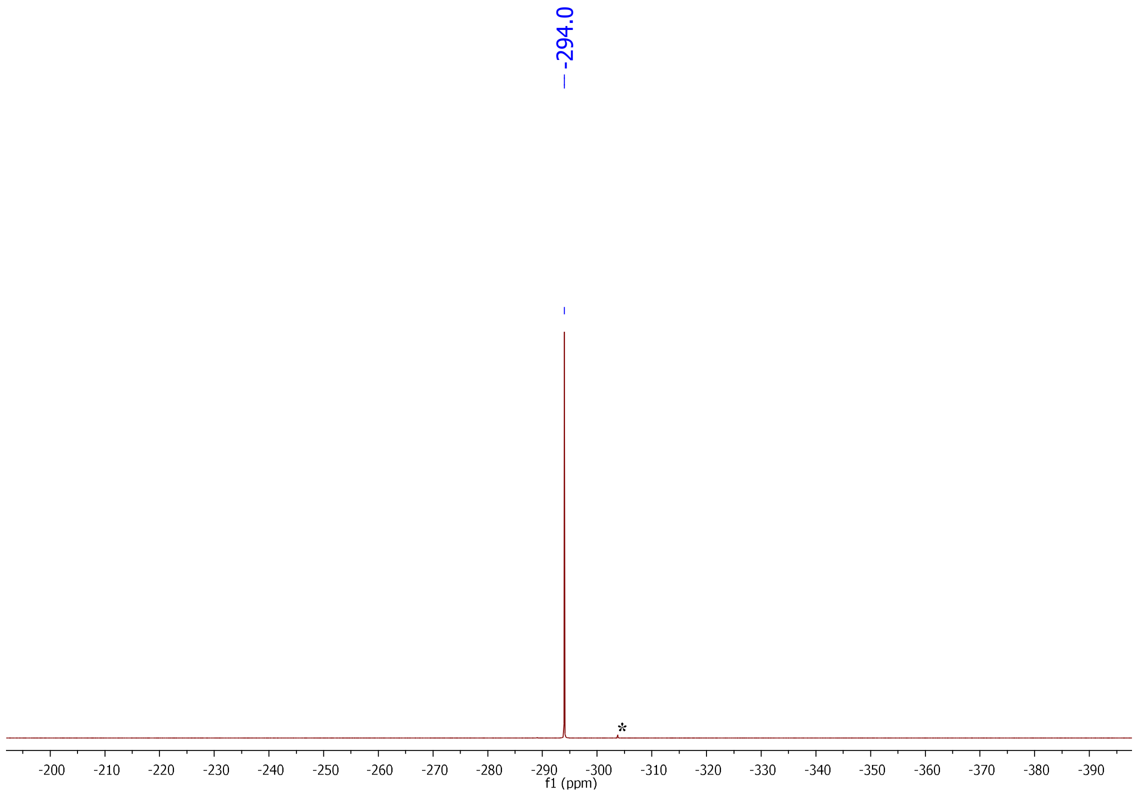

Figure S33. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **8**. (*hydrolyzed species)

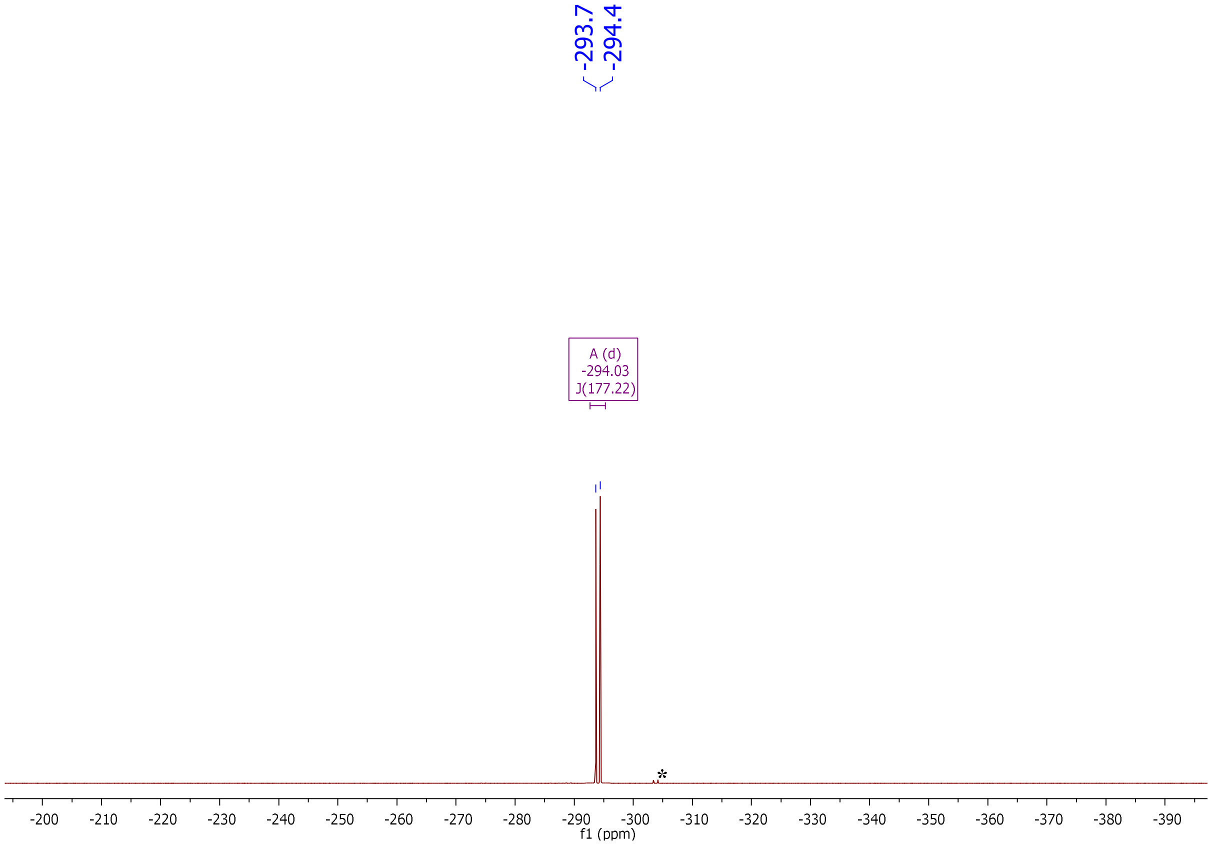

Figure S34. ^{31}P NMR (202 MHz, C_6D_6, 298 K) spectrum of compound **8**. (*hydrolyzed species)

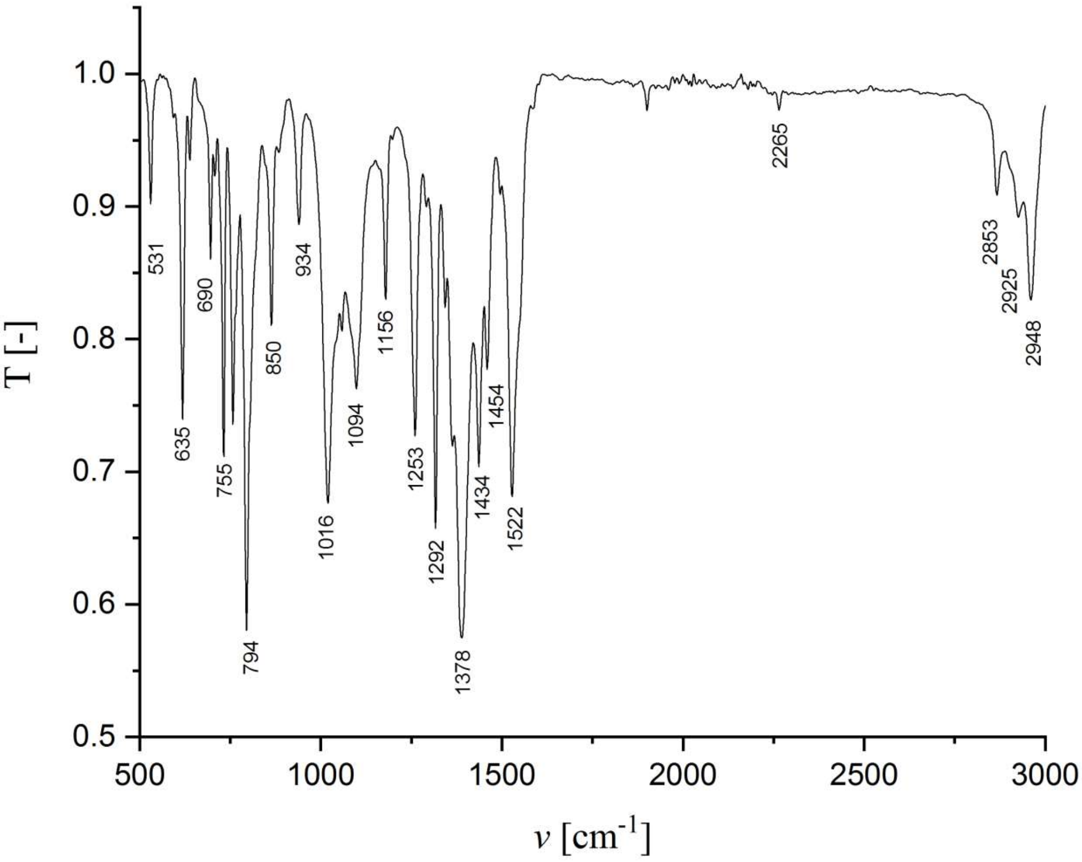

Figure S35. ATR-IR spectrum of **8**.

3. X-Ray Crystallographic Analysis

The crystals were mounted on nylon loops in inert oil. Data were collected either on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) or on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated Cu$_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, micro-focus source) at low temperature. The structures were solved by Direct Methods (SHELXS-97)[3] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2017).[4-6] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). The NH_2 group, Cl atom and the PH hydrogen atom in **2** are disordered over two positions. The corresponding bond lengths were restrained to be equal (SADI) and the neighbouring N and Cl atoms were refined with common sets of displacement parameters (EADP). The solvent molecule is disordered over a centre of inversion. Its corresponding bond lengths and angles were restrained to be equal with SADI restraints and RIGU restraints were applied to its displacement parameters. In addition, the structure contains another highly disordered toluene molecule. The final refinement was done with dataset from a PLATON/SQUEEZE[7] run removing this molecule. The molecule was included in the sum formula for completeness. In **4** one of the toluene molecules is disordered over two positions. The bond lengths and angles of its phenyl ring were restrained to equal (SADI) and its displacement parameters were refined with RIGU restraints. The crystal was a non-merohedral twin of two components and the model was refined against de-twinned hklf4 data. The crystal of **6** contained highly disordered solvent molecules – most likely *n*-hexane mixed with benzene. The final refinement was done with a solvent free dataset from a PLATON/SQUEEZE run.[7] Since the exact nature and amount of the solvent mixture is not clear it was not included in the sum formula. The toluene molecule in **7** is disordered and was modelled with two alternate positions. The anisotropic displacement parameters suggest that this is just a crude description however no further alternate positions could be identified. All corresponding bond length and angle were restrained to be equal (SADI) and RIGU and SIMU restraints were applied to the anisotropic displacement parameters. In **8** one toluene molecule is disordered over two sites the other over three. The bond lengths and angles of their phenyl rings were constrained to be equal (SADI) and RIGU and SIMU restraints were applied to the anisotropic displacement parameters.

CCDC-**2** (2115706), **3** (2115707), **4** (2115708), **6** (2115709), **7** (2115710), **8** (2115711) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement of **2**, **3**, and **4**.

Compound	**2**	**3**	**4**
Emp. formula	$C_{65}H_{93}ClGa_2N_5P$	$C_{68}H_{99}ClGa_2N_5P$	$C_{78}H_{105}ClGa_2N_5P$
Formula weight	1150.30	1192.38	1318.52
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	Monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$	*Pbca*	*P*-1
a [Å]	23.6153(16)	18.4348(8)	14.0881(15)
b [Å]	12.3232(8)	16.8780(8)	14.8425(16)
c [Å]	24.0156(17)	41.2991(18)	17.753(2)
α [°]	90	90	88.012(5)
β [°]	117.754(3)	90	85.678(5)
γ [°]	90	90	78.942(5)
V [Å^3]	6184.9(7)	12849.9(10)	3632.2(7)
Z	4	8	2
ρ [Mgm^{-3}]	1.235	1.233	1.206
μ [mm^{-1}]	2.022	1.964	1.787
F (000)	2448	5088	1404
Crystal size [mm]	0.237 × 0.197 × 0.086	0.416 × 0.254 × 0.250	0.329 × 0.197 × 0.042
θmax [°]	79.645	79.629	79.609
Index ranges	$-29 \leq h \leq 29$ $-15 \leq k \leq 15$ $-30 \leq l \leq 30$	$-23 \leq h \leq 19$ $-21 \leq k \leq 21$ $-52 \leq l \leq 51$	$-17 \leq h \leq 17$ $-18 \leq k \leq 18$ $0 \leq l \leq 22$
No. of reflect. collected	298081	270798	15678
Unique reflect.	13413	13946	15678
R_{int}	0.0712	0.0384	0.1191
Data / restraints / params.	13413 / 79 / 706	13676/0/725	14115/ 441/879
Goodness-of-fit on F^2	1.044	1.061	1.073
*R*1 [I>2σ(I)]	0.0304	0.0305	0.0392
*wR*2 [I>2σ(I)]	0.0826	0.0804	0.1045
*R*1 [all data]	0.0331	0.0311	0.0440
*wR*2 [all data]	0.0853	0.0808	0.1082
Largest diff. peak and hole max./min.[e·Å^{-3}]	0.829 and -0.471	0.570/-0.538	0.973/-0.666

Table S3. Crystal data and structure refinement of **6**, **7**, and **8**.

Compound	**6**	**7**	**8**
Emp. formula	$C_{66}H_{92}ClGa_2N_4OP$	$C_{71}H_{96}ClGa_2N_4PS$	$C_{78}H_{104}ClGa_2N_4PSe$
Formula weight	1163.29	1243.43	1382.47
Temperature [K]	120(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Iba*2	*Pbcn*	$P2_1/c$
a [Å]	21.415(2)	42.1677(8)	23.424(3)
b [Å]	39.087(4)	18.8932(4)	17.838(2)
c [Å]	16.2869(17)	16.6565(3)	17.2400(19)
α [°]	90	90	90
β [°]	90	90	97.743(3)
γ [°]	90	90	90
V [Å^3]	13633(2)	13269.9(4)	7137.9(14)
Z	8	8	4
ρ [Mgm^{-3}]	1.134	1.245	1.286
μ [mm^{-1}]	0.893	0.951	1.369
F (000)	4944	5280	2912
Crystal size [mm]	0.435 × 0.261 × 0.198	0.176 × 0.173 × 0.158	0.386 × 0.268 × 0.252
θ max [°]	30.726	33.170	33.264
Index ranges	$-30 \leq h \leq 30$ $-55 \leq k \leq 54$ $-23 \leq l \leq 23$	$-64 \leq h \leq 64$ $-27 \leq k \leq 29$ $-25 \leq l \leq 25$	$-36 \leq h \leq 36$ $-27 \leq k \leq 27$ $-26 \leq l \leq 26$
No. of reflect. collected	158409	467617	258395
Unique reflect.	21039	25352	27441
R_{int}	0.0426	0.0637	0.0624
Data / restraints / params.	21039/1/ 698	25352/313/ 811	20513/1306/1006
Goodness-of-fit on F^2	1.036	1.132	1.042
$R1$ [$I>2\sigma(I)$]	0.0316	0.0392	0.0367
$wR2$ [$I>2\sigma(I)$]	0.0878	0.0827	0.0778
$R1$ [all data]	0.0400	0.0581	0.0627
$wR2$ [all data]	0.0920	0.0896	0.0868
x(Flack)	0.000(2)	-	-
Largest diff. peak and hole max./min.[e·Å^{-3}]	0.807/-0.305	0.512/-0.427	0.657/-0.683

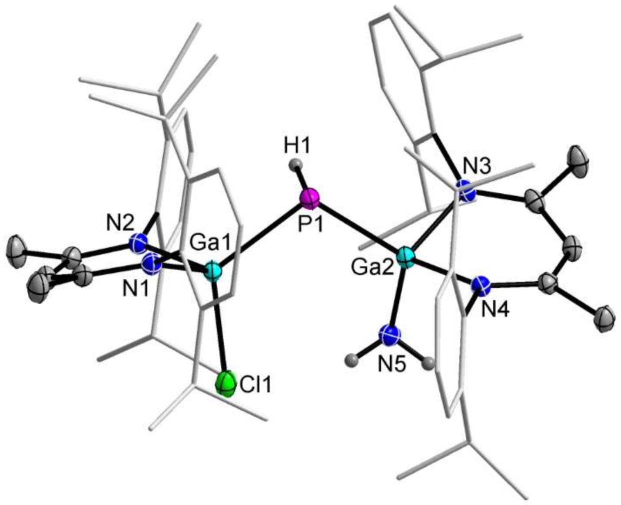

Figure S36. Molecular structure of **2** with thermal ellipsoids at 50% probability level. The hydrogen atoms, minor disordered part, and a solvent molecule (toluene) are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-N(2) 1.9647(11), Ga(1)-N(1) 1.9718(11), Ga(1)-Cl(1) 2.1913(14), Ga(1)-P(1) 2.3125(4), Ga(2)-N(5) 1.970(7), Ga(2)-N(3) 1.9748(11), Ga(2)-N(4) 1.9769(10), Ga(2)-P(1) 2.3187(4); N(2)-Ga(1)-N(1) 94.91(5), N(2)-Ga(1)-Cl(1) 103.21(4), N(1)-Ga(1)-Cl(1) 106.38(5), N(2)-Ga(1)-P(1) 118.07(3), N(1)-Ga(1)-P(1) 110.28(3), Cl(1)-Ga(1)-P(1) 120.54(4), N(5)-Ga(2)-N(3) 104.1(3), N(5)-Ga(2)-N(4) 108.4(2), N(3)-Ga(2)-N(4) 94.94(4), N(5)-Ga(2)-P(1) 119.1(3), N(3)-Ga(2)-P(1) 109.85(3), N(4)-Ga(2)-P(1) 116.90(3), Ga(1)-P(1)-Ga(2) 107.594(14).

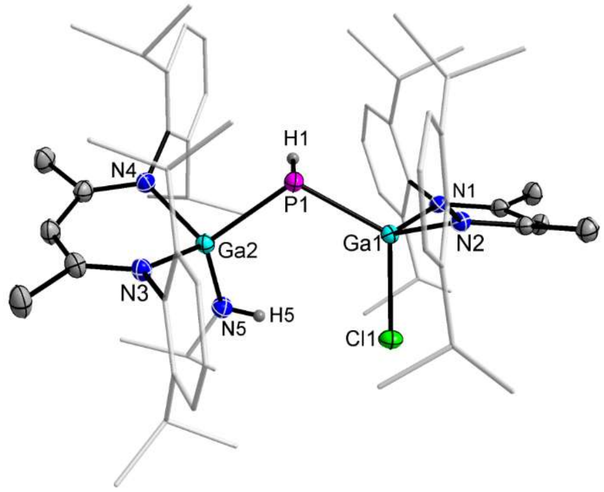

Figure S37. Molecular structure of **3** with thermal ellipsoids at 50% probability level. The hydrogen atoms and a solvent molecule (toluene) are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-N(2) 1.9652(11), Ga(1)-N(1) 1.9704(11), Ga(1)-Cl(1) 2.2361(4), Ga(1)-P(1) 2.3080(4), Ga(2)-N(5) 1.8606(12), Ga(2)-N(3) 1.9948(11), Ga(2)-N(4) 1.9955(11), Ga(2)-P(1) 2.3445(4); N(2)-Ga(1)-N(1) 96.12(5), N(2)-Ga(1)-Cl(1) 102.94(3), N(1)-Ga(1)-Cl(1) 102.67(3), N(2)-Ga(1)-P(1) 112.01(3), N(1)-Ga(1)-P(1) 119.18(3), Cl(1)-Ga(1)-P(1) 120.233(14), N(5)-Ga(2)-N(3) 113.47(5), N(5)-Ga(2)-N(4) 112.52(5), N(3)-Ga(2)-N(4) 93.09(5), N(5)-Ga(2)-P(1) 116.86(4), N(3)-Ga(2)-P(1) 112.93(3), N(4)-Ga(2)-P(1) 105.15(3), Ga(1)-P(1)-Ga(2) 112.955(15).

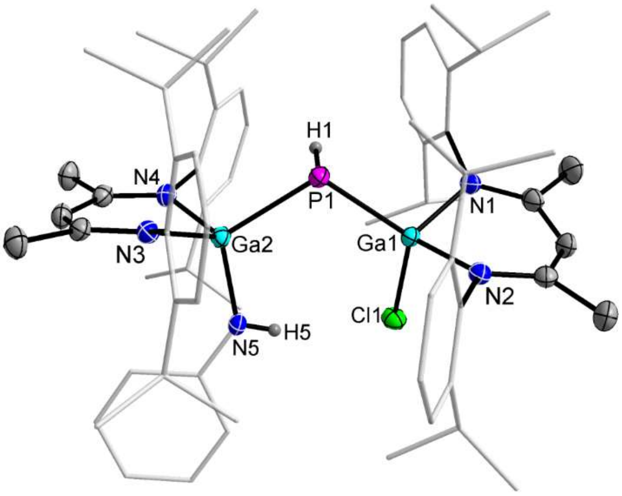

Figure S38. Molecular structure of **4** with thermal ellipsoids at 50% probability level. The hydrogen atoms and solvent molecules (toluene) are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-N(1) 1.9576(14), Ga(1)-N(2) 1.9628(15), Ga(1)-Cl(1) 2.2322(5), Ga(1)-P(1) 2.3132(5), Ga(2)-N(5) 1.8762(14), Ga(2)-N(3) 1.9740(14), Ga(2)-N(4) 1.9758(14), Ga(2)-P(1) 2.3395(5); N(1)-Ga(1)-N(2) 95.81(6), N(1)-Ga(1)-Cl(1) 104.10(4), N(2)-Ga(1)-Cl(1) 102.50(4), N(1)-Ga(1)-P(1) 113.11(4), N(2)-Ga(1)-P(1) 117.93(4), Cl(1)-Ga(1)-P(1) 119.932(18), N(5)-Ga(2)-N(3) 110.75(6), N(5)-Ga(2)-N(4) 110.94(6), N(3)-Ga(2)-N(4) 93.75(6), N(5)-Ga(2)-P(1) 113.26(5), N(3)-Ga(2)-P(1) 111.86(4), N(4)-Ga(2)-P(1) 114.73(4), Ga(1)-P(1)-Ga(2) 111.071(18).

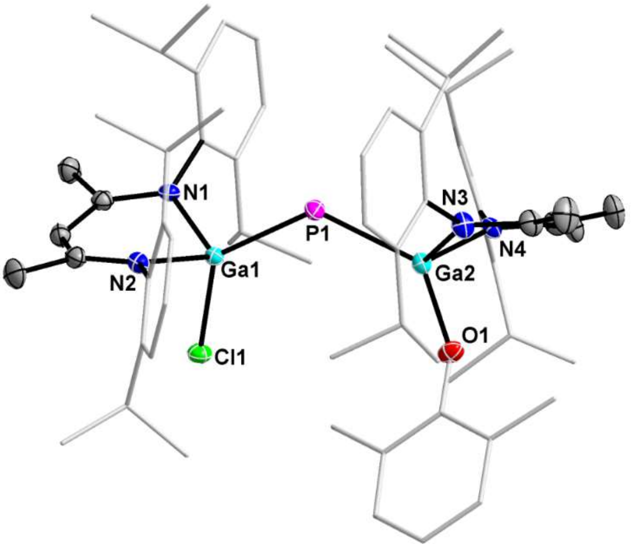

Figure S39. Molecular structure of **6** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-N(1) 1.955(2), Ga(1)-N(2) 1.972(2), Ga(1)-Cl(1) 2.2191(8), Ga(1)-P(1) 2.3235(8), Ga(2)-O(1) 1.842(2), Ga(2)-N(3) 1.962(2), Ga(2)-N(4) 1.968(2), Ga(2)-P(1) 2.3461(8); Ga(1)-P(1)-Ga(2) 127.49(3), N(1)-Ga(1)-N(2) 95.55(9), N(1)-Ga(1)-Cl(1) 100.95(6), N(2)-Ga(1)-Cl(1) 99.55(6), N(1)-Ga(1)-P(1) 110.79(6), N(2)-Ga(1)-P(1) 115.79(7), Cl(1)-Ga(1)-P(1) 128.58(3), O(1)-Ga(2)-N(3) 105.78(10), O(1)-Ga(2)-N(4) 94.90(9), N(3)-Ga(2)-N(4) 95.37(9), O(1)-Ga(2)-P(1) 134.25(7), N(3)-Ga(2)-P(1) 104.75(7), N(4)-Ga(2)-P(1) 115.22(6).

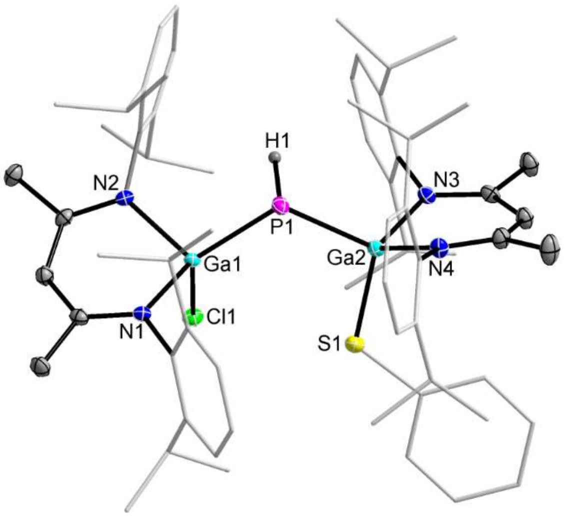

Figure S40. Molecular structure of **7** with thermal ellipsoids at 50% probability level. The hydrogen atoms and a solvent molecule (toluene) are omitted for clarity. Selected bond length (Å) and angels (°):Ga(1)-N(2) 1.9585(11), Ga(1)-N(1) 1.9640(11), Ga(1)-Cl(1) 2.2098(3), Ga(1)-P(1) 2.3144(4), Ga(2)-N(3) 1.9669(11), Ga(2)-N(4) 1.9723(12), Ga(2)-S(1) 2.2551(4), Ga(2)-P(1) 2.3304(4); Ga(1)-P(1)-Ga(2) 112.152(15), N(2)-Ga(1)-N(1) 95.83(5), N(2)-Ga(1)-Cl(1) 102.52(3), N(1)-Ga(1)-Cl(1) 102.19(3), N(2)-Ga(1)-P(1) 108.18(3), N(1)-Ga(1)-P(1) 119.75(3), Cl(1)-Ga(1)-P(1) 123.687(14), N(3)-Ga(2)-N(4) 94.85(5), N(3)-Ga(2)-S(1) 110.65(4), N(4)-Ga(2)-S(1) 116.31(4), N(3)-Ga(2)-P(1) 117.43(4), N(4)-Ga(2)-P(1) 109.01(4), S(1)-Ga(2)-P(1) 108.411(14).

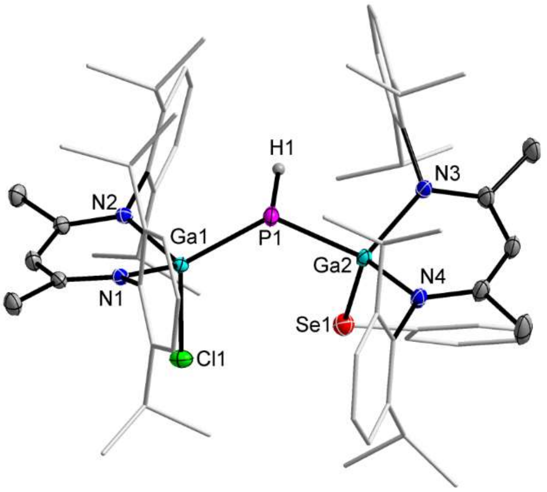

Figure S41. Molecular structure of **8** with thermal ellipsoids at 50% probability level. The hydrogen atoms and solvent molecules (toluene) are omitted for clarity. Selected bond length (Å) and angels (°): Se(1)-C(59) 1.9171(16), Se(1)-Ga(2) 2.3898(3), Ga(1)-N(1) 1.9555(12), Ga(1)-N(2) 1.9573(12), Ga(1)-Cl(1) 2.2143(4), Ga(1)-P(1) 2.3132(4), Ga(2)-N(3) 1.9655(12), Ga(2)-N(4) 1.9757(12), Ga(2)-P(1) 2.3319(5); C(59)-Se(1)-Ga(2) 109.65(5), N(1)-Ga(1)-N(2) 96.19(5), N(1)-Ga(1)-Cl(1) 102.83(3), N(2)-Ga(1)-Cl(1) 102.88(4), N(1)-Ga(1)-P(1) 110.27(4), N(2)-Ga(1)-P(1) 117.79(4), Cl(1)-Ga(1)-P(1) 122.808(17), N(3)-Ga(2)-N(4)94.66(5), N(3)-Ga(2)-P(1) 110.09(4), N(4)-Ga(2)-P(1) 113.37(4), N(3)-Ga(2)-Se(1) 113.23(4), N(4)-Ga(2)-Se(1) 112.83(4), P(1)-Ga(2)-Se(1) 111.623(12), Ga(1)-P(1)-Ga(2) 113.864(18).

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