Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

1. Experimental Part

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard Schlenk techniques or in an MBraun dry-box containing an atmosphere of purified dry argon. THF-d_8, C_6D_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratories, dried over molecular sieves (4 Å) and degassed prior to use. Solvents THF, toluene and *n*-hexane were degassed prior to filtration over alumina in the PureSolv-purification system by "inert". [Na(dioxane)$_x$][OCP],[S1] salen(*t*Bu)AlCl,[S2] salophen(*t*Bu)AlCl[S2] and salen(*t*Bu)GaCl[S3] were synthesized according to reported procedures. All other reagents were purchased from commercial resources and used without further purification.

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{31}P NMR spectra were recorded on a Bruker spectrometers operating at 200, 250, 300, 400 or 500 MHz at 298K unless stated otherwise. All chemical shifts are reported in ppm. ^{1}H and ^{13}C{^{1}H} MMR chemical shifts are relative to $SiMe_4$ using the ^{1}H (residual) and ^{13}C{^{1}H} chemical shifts of the solvent as secondary standard. And ^{31}P{^{1}H} and ^{31}P chemical shifts were referenced externally to an 85% solution of H_3PO_4 in H_2O.

Melting points were measured on samples in sealed capillaries under Argon and are uncorrected. Infrared spectra were collected on a Bruker-alpha FT-IR spectrometer with the ATR measuring device. Elemental analyses were performed by the micro analytical laboratory of ETH Zürich.

Syntheses and Characterizations

Compound **1**:
In a glovebox, the commercially available solution of diisobutyl aluminium chloride in *n*-hexane (0.2 mL, 1M) was evaporated to give a colourless oil. Subsequently, 0.6 mL C_6D_6 were added to give a colourless solution. Na[OCP](Dioxane)$_{2.5}$ (66 mg, 0.22 mmol, 1.1 equiv.) was added at room temperature to form a black mixture which was stirred for 10 min at room temperature and subsequently filtrated through celite. The filtrate was collected and analyzed using multinuclear NMR spectroscopy. The recorded ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra (presented below) indicated that the formation of **1** proceeded quantitatively. Evaporation of the volatiles resulted in a black oil which turned into a black metallic solid upon prolonged drying indicating decomposition of the product. The same was observed when the reactions were performed under the same conditions but using instead *n*-hexane, toluene or THF. Note that in all these solvents **1** is generated equally selective. For collecting the in situ IR data the filtrate obtained from the reaction mixture in *n*-hexane was used.
^{1}H NMR (C_6D_6, 500 MHz): δ = 1.95 (nonet, 2H, C*H*), 1.08 (d, 12H, CH_3), 0.04 (d, 4H, CH_2).
^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ = 152.6 (s, O*C*P), 28.2 (s, *C*H$_3$), 25.8 (s, *C*H), 19.8 (s, br, *C*H$_2$).
^{31}P{^{1}H} NMR (C_6D_6, 202.4 MHz): δ = –331.5 (s).
IR [cm^{-1}] *n*-hexane solution: 1676 (OCP).

Compound **2a**:
In a glovebox, solid Na[OCP](dioxane)$_{2.8}$ (263 mg, 0.80 mmol, 1.0 equiv.) was added in portions over the course of 10 min to a stirred suspension of salen(*t*Bu)AlCl (446 mg, 0.80 mmol, 1.0 equiv.) in toluene (8 mL) at room temperature. The resulting brown mixture was stirred for 30 min and then filtrated through celite. The residue was washed several times with toluene. The combined filtrate and wash solutions were concentrated to about 1 mL to give a sticky mixture. Layering the mixture with *n*-hexane (10 mL) resulted in the precipitation of a yellow solid within 1 h. The supernatant was decanted and the remaining solid was washed with *n*-hexane (3 x 2 mL) and subsequently dried *in vacuo* to afford yellow crystalline **2a** (312 mg, 0.54 mmol, 68%). Light yellow crystals suitable for X-ray diffraction were obtained from a toluene solution of **2a** layered with *n*-hexane at room temperature.
MP: 256 °C (decomp.).
^{1}H NMR (C_6D_6, 500 MHz): δ = 7.76 (d, 2H, Ph), 7.57 (s, 2H, NC*H*), 6.93 (d, 2H, Ph), 3.34-2.91 (br, 4H, CH_2), 1.77 (s, 18H, C(CH_3)$_3$), 1.35 (s, 18H, C(CH_3)$_3$).
^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ = 171.3 (s, N*C*H), 163.4 (s, *C*(O)), 155.1 (d, $^{1}J_{PC}$ = 4.7 Hz, O*C*P), 141.4 (s, *C*), 139.3 (s, *C*), 131.6 (s, *C*H), 128.0 (s, *C*H), 118.9 (s, *C*), 54.4 (s, *C*H$_2$), 36.0 (s, *C*(CH$_3$)$_3$), 34.3 (s, *C*(CH$_3$)$_3$), 31.7 (s, C(*C*H$_3$)$_3$), 30.2 (s, C(*C*H$_3$)$_3$).
^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = –336.8 (s).
IR [cm^{-1}] solid: 3029, 2948, 2903, 2866, 1973, 1692 (OCP), 1641, 1621, 1556, 1542, 1495, 1469, 1462, 1444, 1418, 1389, 1361, 1337, 1309, 1276, 1253, 1235, 1210, 1202, 1178, 1139, 1106, 1060, 1031, 994, 916, 886, 866, 844, 816, 785, 756, 729, 707, 640, 611, 579, 568, 554, 524, 498, 467, 441.
Anal. Calcd. for $C_{33}H_{46}N_2O_3PAl$: C 68.73, H 8.04, N 4.86. Found: C 68.94, H 8.17, N 4.80.

Compound **2a**-THF:
Light yellow crystals suitable for X-ray diffraction were obtained at –30 °C from a THF solution of **2a** layered with toluene/*n*-hexane mixture.
^{1}H NMR (THF-d_8, 300 MHz): δ = 8.55 (s, 2H, NC*H*), 7.50 (d, 2H, Ph), 7.20 (s, 2H, Ph), 4.00 (s, 4H, CH_2), 1.52 (s, 18H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$).
^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ = 170.3 (s, N*C*H), 163.6 (s, *C*(O)), 161.3 (d, $^{1}J_{PC}$ = 24.6 Hz, O*C*P), 140.6 (s, *C*), 138.0 (s, *C*), 130.7 (s, *C*H), 129.0 (s, *C*H), 119.9 (s, *C*), 54.6 (s, *C*H$_2$), 36.3 (s, *C*(CH$_3$)$_3$), 34.6 (s, *C*(CH$_3$)$_3$), 31.9 (s, C(*C*H$_3$)$_3$), 30.3 (s, C(*C*H$_3$)$_3$).
^{31}P{^{1}H} NMR (THF-d_8, 121.5 MHz): δ = -353.9 (s, br).

Variable temperature NMR spectroscopy of **2a** in THF:
A sample of **2a** in THF-d_8 was analyzed using ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy at temperatures of 298 K, 273 K, 253 K, 233K and 223K. The spectra are presented below. With descending temperature, the intensity of the ^{31}P NMR signal corresponding to **2a**-THF (δ = –349.6 ppm) decreased and that of a new species at δ = –385.9 ppm

increased. The identity of this new product could not be determined unambiguously, but could involve solvent separated ion pair of the type [salen(*t*Bu)Al(THF)$_2$][OCP] as the observed chemical shift is in close range to that of Na[OCP] (δ^{31}P at 298K in THF = –392.0 ppm). Its NMR data are given below.

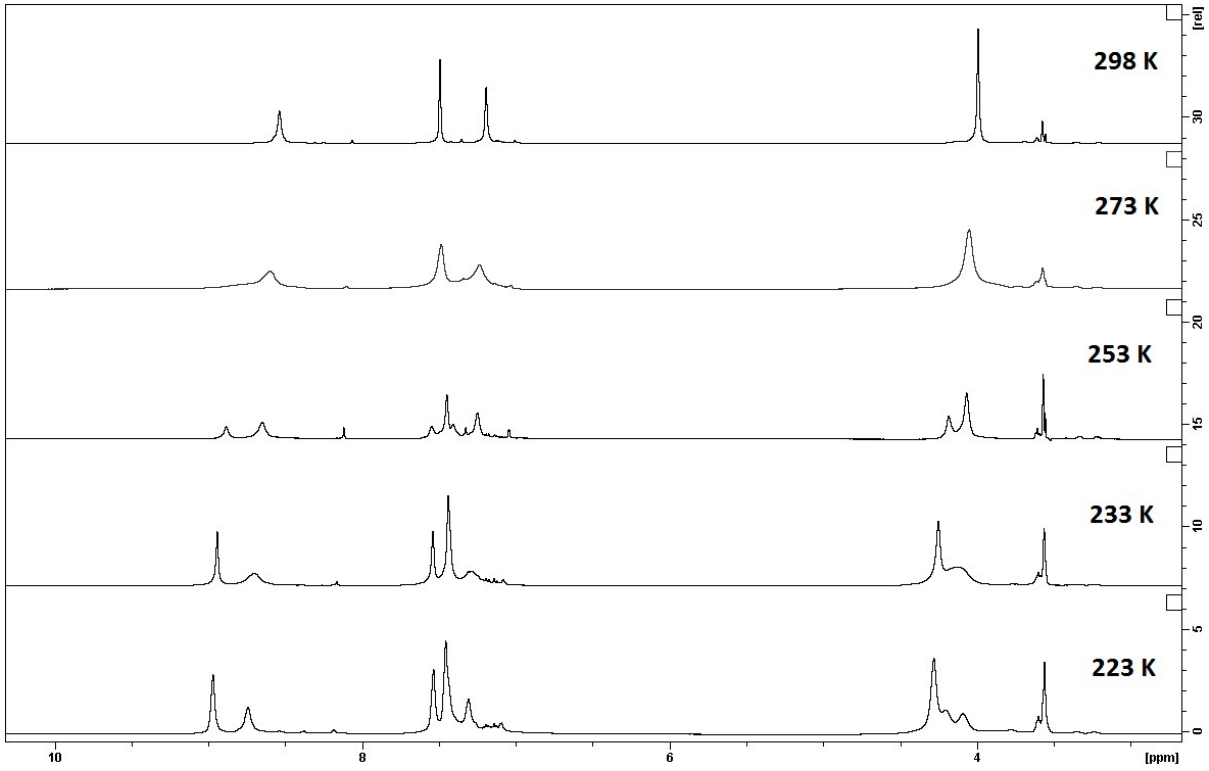
^{1}H-NMR (THF-d_8, 500 MHz, 223 K): δ (ppm) = 8.97 (s, 2H, NC*H*), 7.54 (s, 2H, Ph), 7.46 (s, 2H, Ph), 4.28 (s, 4H, CH_2), 1.53 (s, 18H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$).

^{13}C{^{1}H}-NMR (THF-d_8, 100.6 MHz, 233K): δ (ppm) = 172.1 (s, NC*H*), 162.6 (s, *C*(O)), 139.7 (s, *C*), 138.6 (s, *C*), 131.3 (s, *C*H), 129.8 (s, *C*H), 119.9 (s, *C*), 54.5 (s, *C*H$_2$), 36.2 (s, *C*(CH$_3$)$_3$), 34.8 (s, *C*(CH$_3$)$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 29.9 (s, C(*C*H$_3$)$_3$).

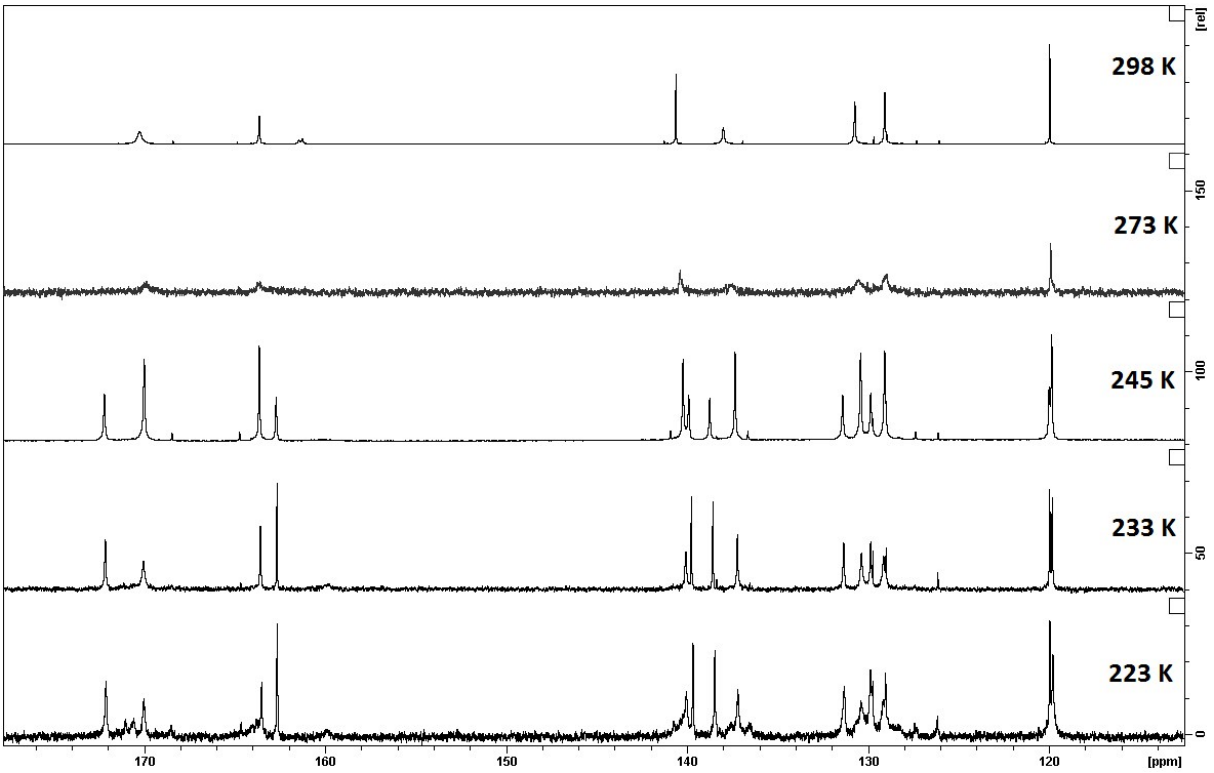
^{31}P{^{1}H}-NMR (THF-d_8, 202.5 MHz, 223 K): δ (ppm) = -385.9 (s).

Note: While cooling the sample from 245 K to 223 K, a precipitate was observed. The substance completely precipitated from the solution when the temperature reached 213K. Subsequently the sample was warmed to RT and the evaporation of the solvent yielded **2a** again. Attempts to grow crystals of the precipitate by storing a solution of **2a** in THF in a freezer at 243 K were unsuccessful.

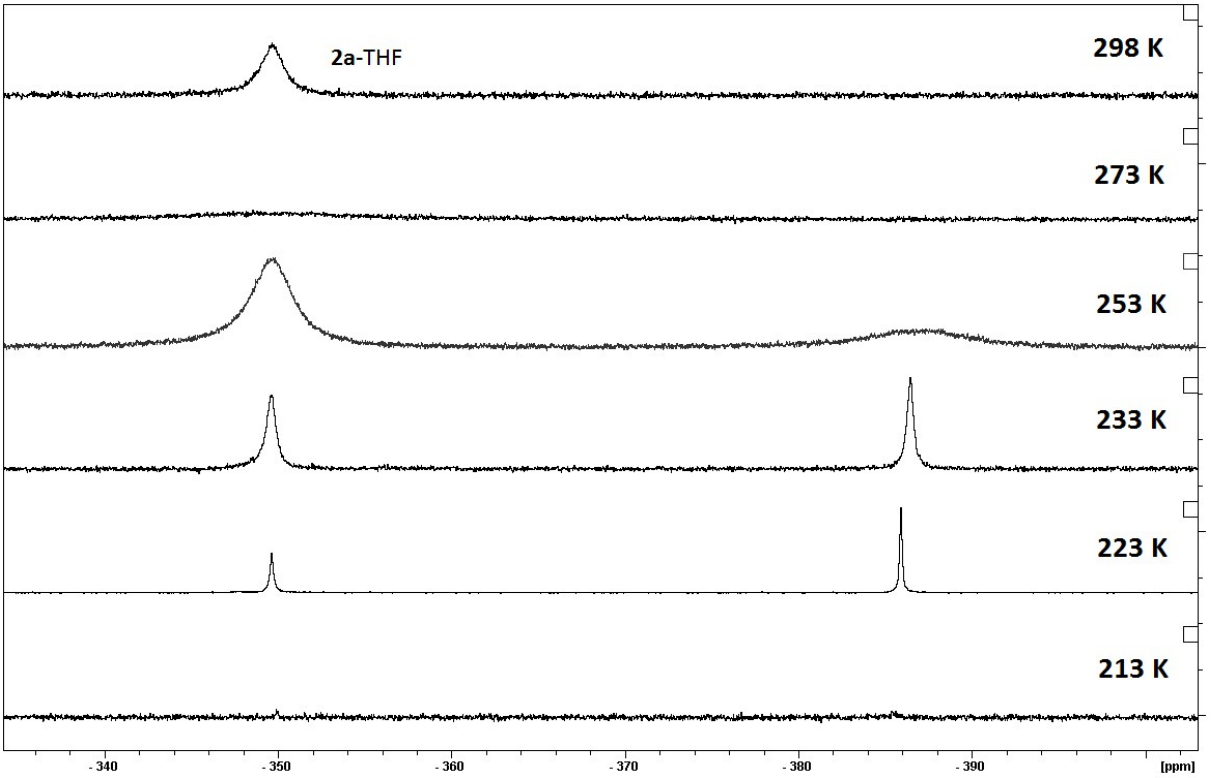
^{1}H NMR spectra of **2a** in THF-d_8 at variable temperatures:



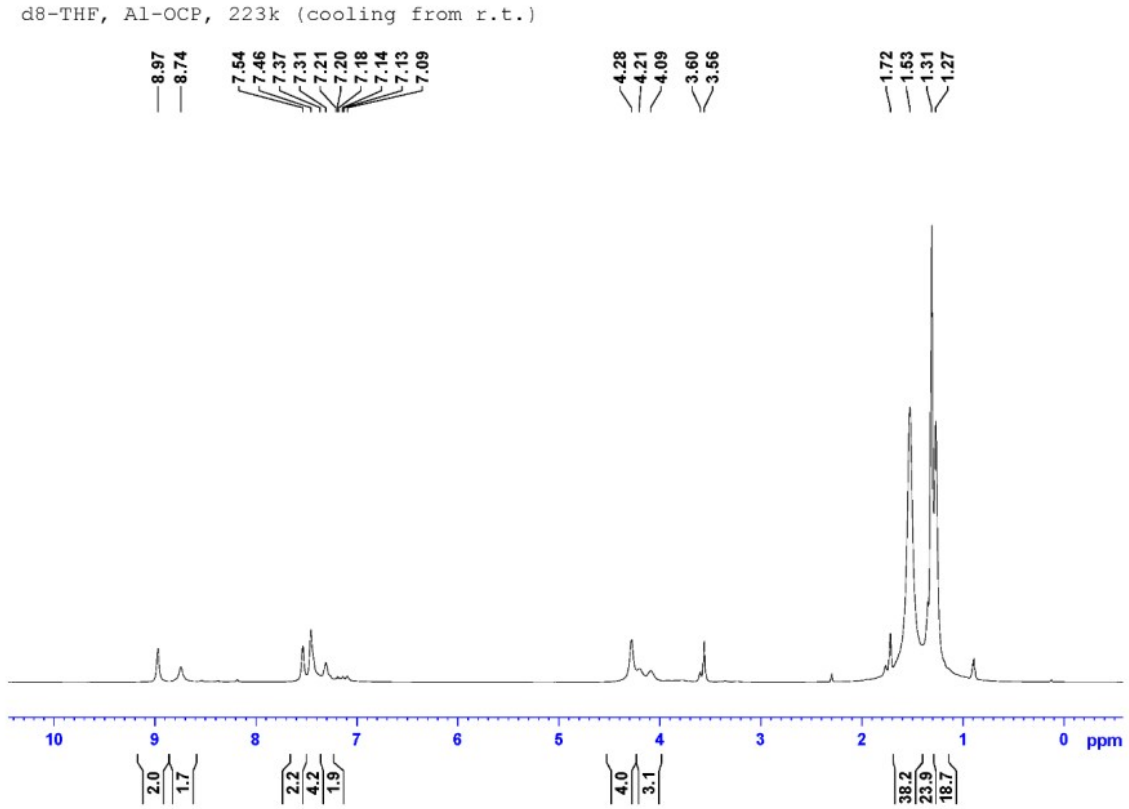
$^{13}C\{^{1}H\}$ NMR spectra of **2a** in THF-d_8 at variable temperatures:



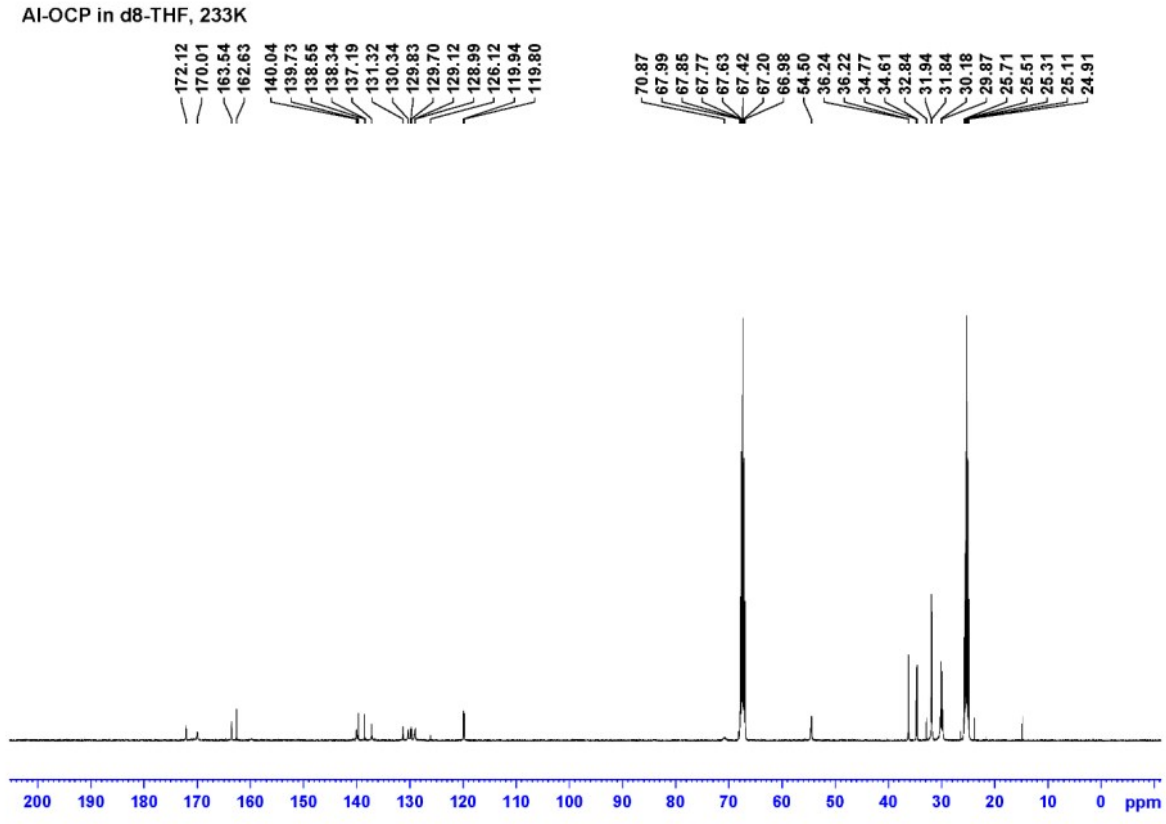
^{31}P NMR spectra of **2a** in THF-d_8 at variable temperatures:



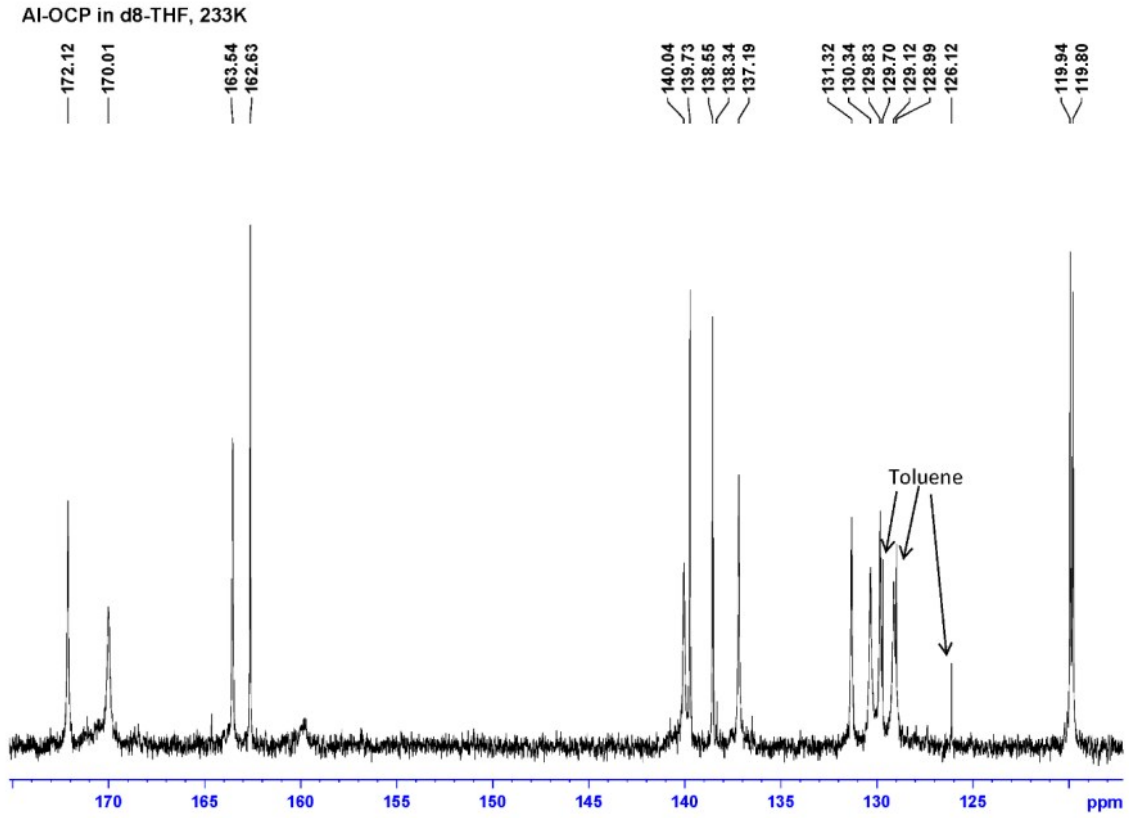
^{1}H NMR spectrum of **2a** in THF-d_8 at 223 K:



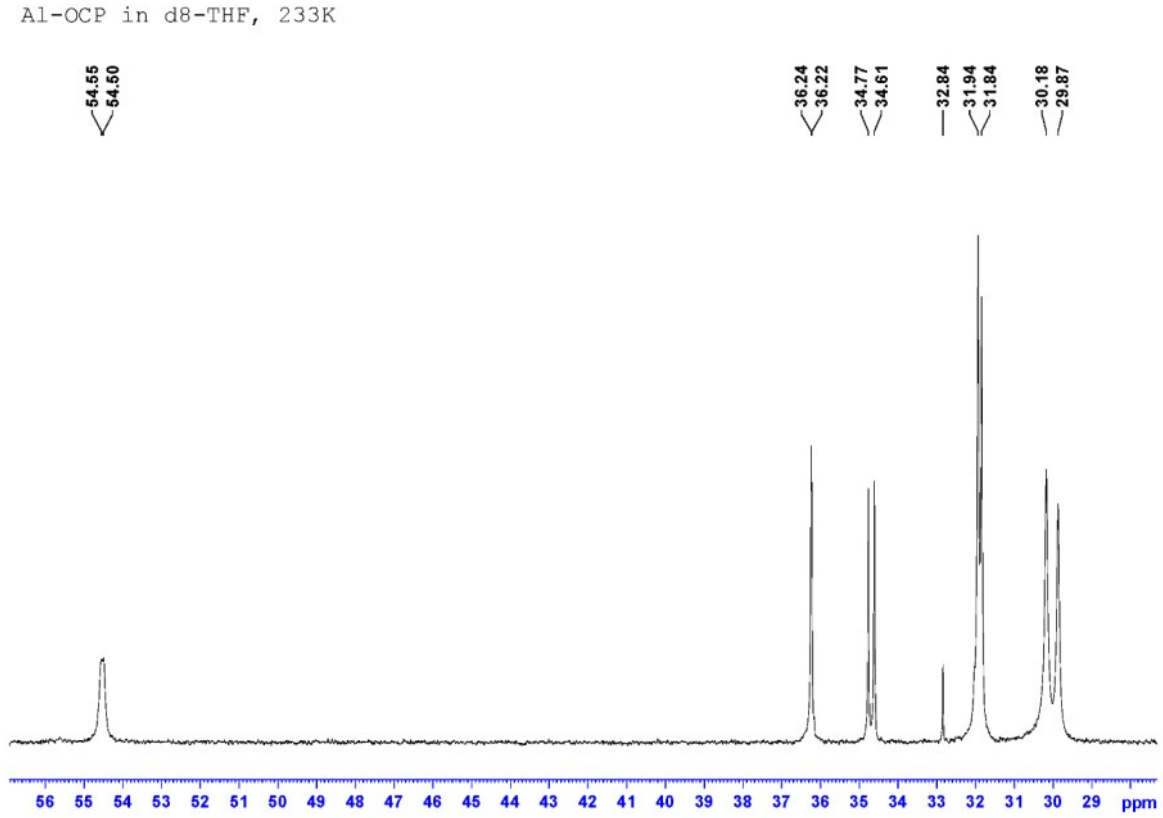
^{13}C{^{1}H} NMR spectrum of **2a** in THF-d_8 at 233 K:



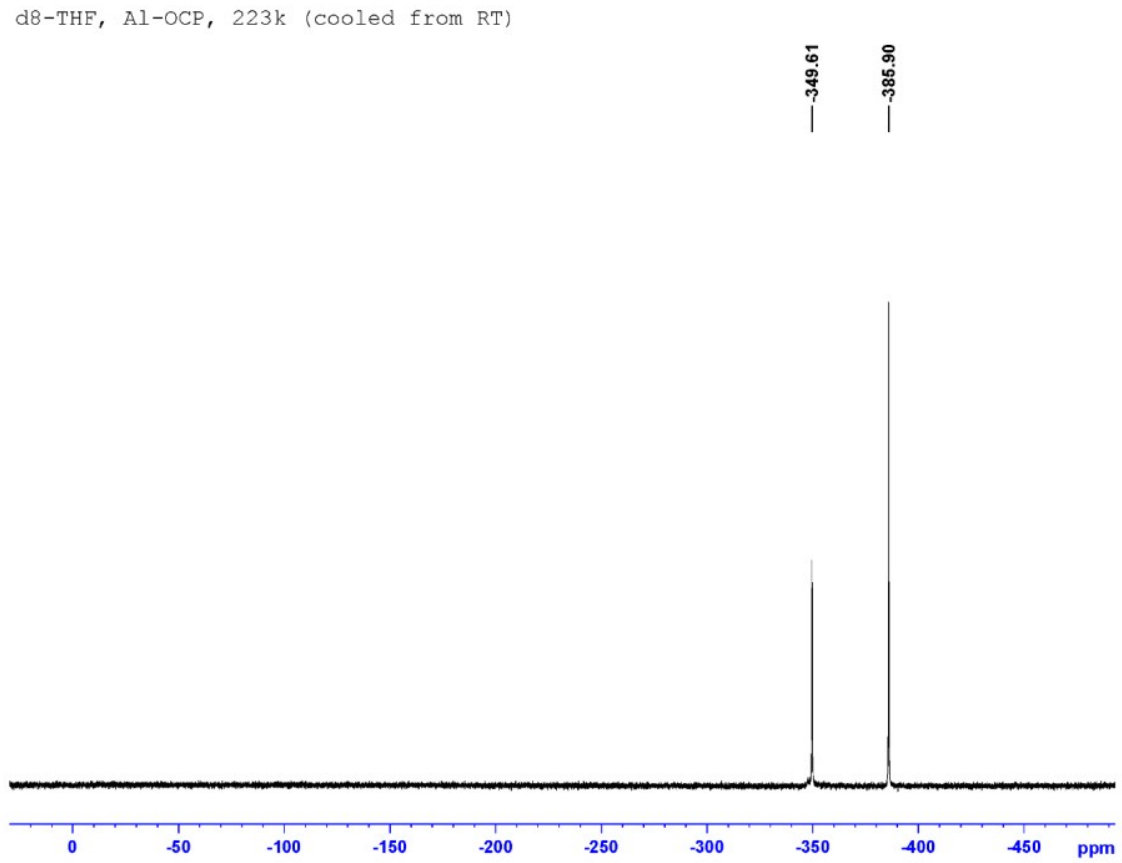
Zoomed section $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in THF-d_8 at 233K:



Zoomed section $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in THF-d_8 at 233K:



^{31}P NMR spectrum of **2a** in THF-d_8 at 223 K:

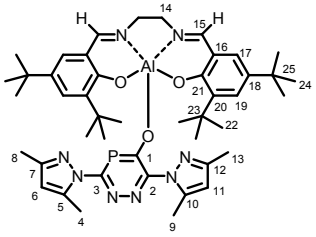


Compound **2b**:
In a glovebox, solid Na[OCP](dioxane)$_{2.8}$ (290 mg, 0.90 mmol, 1.0 equiv.) was added in portions over the course of 10 min to a stirred suspension of Salophen(*t*Bu)AlCl (540 mg, 0.90 mmol, 1.0 equiv.) in toluene (10 mL) at room temperature. The resulting orange mixture was stirred for 30 min and then filtrated through celite. The residue was washed several times with toluene and the combined filtrate and wash solutions were concentrated to about 1 mL to give a sticky mixture. Layering the mixture with *n*-hexane (10 mL) resulted in the precipitation of a yellow solid within 18 h. The supernatant was decanted and the remaining solid was washed with *n*-hexane (5 x 2 mL) and subsequently dried *in vacuo* to afford **2b** as a yellow powder (225 mg, 0.36 mmol, 40%). The product is insoluble in benzene, but soluble in toluene.
MP: 290 °C.
^{1}H NMR (THF-d_8, 500 MHz): δ = 9.18 (s, 2H, NC*H*), 7.97 (s, 2H, C*H*, C_6H_4), 7.60 (s, 2H, C*H*, C_6H_2), 7.40 (s, 2H, C*H*, C_6H_2), 7.32 (dd, 2H, C*H*, C_6H_4), 1.60 (s, 18H, C(CH_3)$_3$), 1.35 (s, 18H, C(CH_3)$_3$).
^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ = 165.2 (s, *C*(O), C_6H_2), 162.3 (s, N*C*H), 159.1 (s, br, O*C*P), 140.9 (s, *C*, C_6H_2), 139.2 (s, *C*, C_6H_4), 138.3 (s, *C*, C_6H_2), 132.2 (s, *C*H, C_6H_2), 130.0 (s, *C*H, C_6H_2), 128.5 (s, *C*H, C_6H_4), 120.0 (s, *C*, C_6H_2), 116.5 (s, *C*H, C_6H_4), 36.1 (s, *C*(CH$_3$)$_3$), 34.5 (s, *C*(CH$_3$)$_3$), 31.6 (s, C(*C*H$_3$)$_3$), 30.3 (s, C(*C*H$_3$)$_3$).
^{31}P{^{1}H} NMR (THF-d_8, 162.0 MHz): δ = −345.2 (s, br).
IR [cm^{-1}] solid: 3084, 3031, 2955, 2904, 2867, 2244-1977 (broad region with multiple weak peaks), 1690 (OCP), 1615, 1601, 1581, 1555, 1538, 1494, 1468, 1439, 1411, 1385, 1359, 1318, 1275, 1260, 1250, 1199, 1184, 1166, 1135, 1115, 1050, 1029, 1003, 985, 965, 921, 877, 847, 817, 795, 785, 772, 753, 732, 718, 708, 656, 608, 594, 577, 569, 551, 531, 501, 463, 438, 407.
Anal. Calcd. for $C_{33}H_{46}N_2O_3PAl$: C 71.13, H 7.42, N 4.48. Found: C 71.09, H 7.75, N 4.54.

Compound **3**:
In a glovebox, solid Na[OCP](dioxane)$_{2.8}$ (35.9 mg, 0.11 mmol, 1.1 equiv.) was added to a stirred suspension of salen(*t*Bu)GaCl (59.9 mg, 0.10 mmol, 1.0 equiv.) in toluene (3 mL) at room temperature. The resulting brown mixture was stirred for 1 h and then filtrated through celite. The residue was washed several times with toluene and the combined filtrate and wash solutions were concentrated to about 0.5 mL. Layering the solution with *n*-hexane (5 mL) gave cubic yellow crystals suitable for X-ray diffraction of the course of 2 days at room temperature. The crystals were collected by decantation, washed with *n*-hexane (3 x 0.5 mL) and dried in *vacuo* to give analytically pure **3** (50.3 mg, 0.081 mmol, 81%).
MP: 244 °C (decomp.).
^{1}H NMR (THF-d_8, 500 MHz): δ = 8.56 (s, 2H, NC*H*), 7.50 (d, 2H, Ph), 7.08 (d, 2H, Ph), 4.04 (s, 2H, CH_2), 3.86 (s, 2H, CH_2), 1.52 (s, 18H, C(CH_3)$_3$), 1.30 (s, 18H, C(CH_3)$_3$).
^{13}C{^{1}H} NMR (THF-d_8, 125.8 MHz): δ = 182.5 (d, $^{1}J_{PC}$ = 88.2 Hz, O*C*P), 171.8 (s, N*C*H), 166.4 (s, *C*(O)), 142.1 (s, *C*), 138.2 (s, *C*), 130.7 (s, *C*H), 128.7 (s, *C*H), 118.4 (s, *C*), 54.2 (s, *C*H$_2$), 36.2 (s, *C*(CH$_3$)$_3$), 34.4 (s, *C*(CH$_3$)$_3$), 31.5 (s, C(*C*H$_3$)$_3$), 30.2 (s, C(*C*H$_3$)$_3$).
^{31}P{^{1}H} NMR (THF-d_8, 202.5 MHz): δ = −376.9 (s).
IR [cm^{-1}] solid: 3005, 2952, 2905, 2866, 1927(PCO), 1910(PCO), 1637, 1611, 1555, 1536, 1463, 1439, 1411, 1384, 1359, 1333, 1320, 1299, 1270, 1249, 1234, 1200, 1173, 1135, 1099, 1076, 1055, 1027, 981, 964, 929, 913, 876, 844, 831, 810, 784, 744, 701, 640, 615, 589, 565, 550, 533, 502, 493, 465, 454, 419, 406.
Anal. Calcd. for $C_{33}H_{46}N_2O_3PGa$: C 63.99, H 7.49, N 4.52. Found: C 64.41, H 7.41, N 4.45.

Compound **6**:
In a glovebox, solid Na[OCP](dioxane)$_{2.8}$ (68.5 mg, 0.22 mmol, 1.1 equiv.) was added to a stirred suspension of salen(*t*Bu)AlCl (112.4 mg, 0.20 mmol, 1.0 equiv.) in toluene (3 mL) at room temperature. The resulting yellow mixture was stirred for 30 min and then filtrated through celite. The residue was washed several times with toluene and the combined filtrate and wash solutions were collected. To this solution 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (44.3 mg, 0.17 mmol, 0.85 equiv.) was added upon which gas evolution was observed and the color changed to brown. The reaction mixture was stirred for 1h and subsequently filtrated through celite. The solvents were removed under reduced pressure to give a yellow solid which was washed with *n*-hexane (3 x 1 mL) and dried *in vacuo* to afford analytically pure **6** (75.4 mg, 0.092 mmol, 46%). Colorless crystalssuitable for X-ray diffraction were obtained from a saturated toluene solution at room temperature (see section 3 for the structure determination).
MP: 258 °C (decomp.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.17 (s, 2H, 14-C*H*), 7.56 (s, 2H, 19-C*H*), 7.02 (s, 2H, 17-C*H*), 5.97 (s, 1H, C*H*), 5.55 (s, 1H, C*H*), 3.75 (d, 2H, CH_2), 3.55 (d, 2H, CH_2), 2.63 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.52 (s, 18H, C(CH_3)$_3$), 1.45(s, 3H, CH_3), 1.35 (s, 18H, C(CH_3)$_3$).



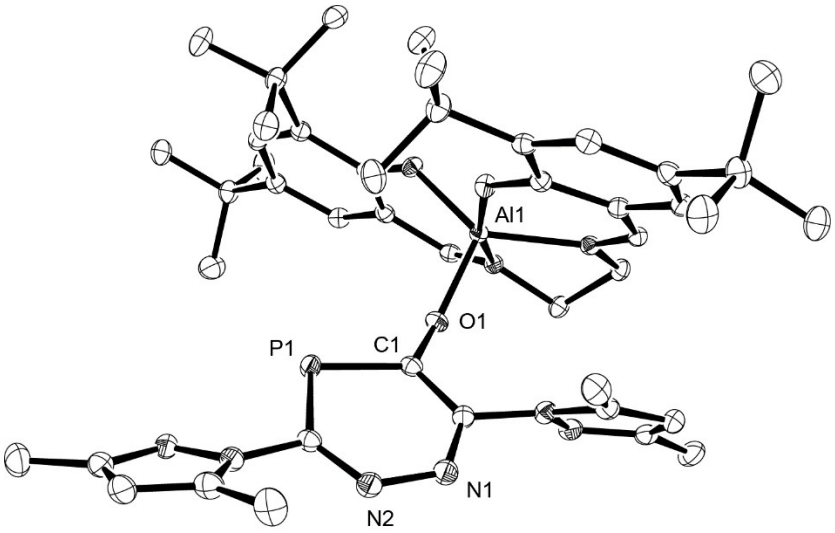
^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 192.1 (d, $^{1}J_{C,P}$ = 47.7 Hz, 1-*C*), 183.4 (d, $^{1}J_{C,P}$ = 66.2 Hz, 3-*C*), 170.5 (s, 15-*C*H), 162.9 (s, 21-*C*), 151.1 (s, *C*), 148.3 (s, *C*), 146.3 (d, $^{2}J_{PC}$ = 3.2 Hz, 2-*C*), 142.5 (s, *C*), 141.9 (s, *C*), 141.1 (s, 20-*C*), 139.1 (s, 18-*C*), 131.2 (s, 19-*C*H), 127.5 (s, 17-*C*H), 118.4 (s, 16-*C*), 110.2 (s, *C*H), 105.9 (s, *C*H), 55.1 (s, 14-*C*H_2), 35.7 (s, 23-*C*(CH$_3$)$_3$), 34.2 (s, 25-*C*(CH$_3$)$_3$), 31.5 (s, 24-C(*C*H$_3$)$_3$), 29.8 (s, 22-C(*C*H$_3$)$_3$), 15.2 (s, *C*H$_3$), 14.0 (s, *C*H$_3$), 13.7 (s, *C*H$_3$), 10.2 (s, *C*H$_3$).

^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ = 132.0 (s).

IR [cm^{-1}] solid: 3060, 3004, 2952, 2905, 2866, 1649, 1624, 1558, 1544, 1476, 1459, 1444, 1415, 1390, 1374, 1343, 1322, 1307, 1276, 1256, 1236, 1201, 1176, 1138, 1106, 1078, 1053, 1023, 979, 970, 952, 930, 917, 883, 865, 843, 816, 783, 771, 753, 732, 705, 696, 678, 643, 630, 609, 589, 576, 568, 536, 495, 477, 464, 435, 422.

Anal. Calcd. for $C_{45}H_{60}N_8O_3PAl$: C 66.00, H 7.38, N 13.68. Found: C 65.82, H 7.38, N 12.80.

Molecular structure of **6** in the crystal (ellipsoids are set at 50% probability):

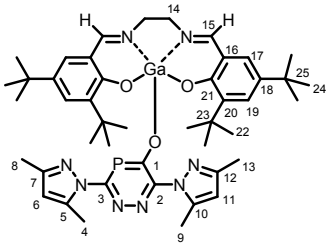


Compound **7**:

In a glovebox, toluene (1 mL) was added to a mixture of **3** (26.2 mg, 0.0423 mmol, 1.1 equiv.) and 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (10.5 mg, 0.0388 mmol, 1.0 equiv.) at room temperature. Immediate gas evolution was observed and the color gradually changed from red to brown over the course of 30 min. The solution was concentrated to 0.2 mL and subsequently layered with *n*-hexane (2 mL). Over the course of 1 h the product precipitated and was collected by decantation. The yellow solid was washed with *n*-hexane (3 x 1 mL) and dried *in vacuo* to afford analytically pure **7** (25.2 mg, 0.0282 mmol, 75%).

MP: 223 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.21 (s, 2H, 14-C*H*), 7.54 (d, 2H, 19-C*H*), 6.94 (s, 2H, 17-C*H*), 5.96 (s, 1H, C*H*), 5.57 (s, 1H, C*H*), 3.69 (d, 2H, CH_2), 3.60 (d, 2H, CH_2), 2.63 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.52 (s, 18H, C(CH_3)$_3$), 1.33 (s, 18H, C(CH_3)$_3$).

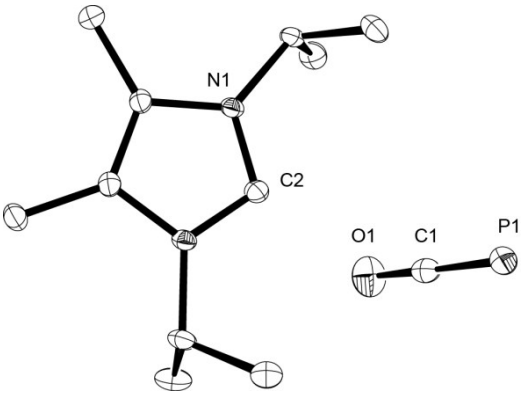


^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ = 194.5 (d, $^{1}J_{C,P}$ = 49.1 Hz, 1-*C*), 183.1 (d, $^{1}J_{C,P}$ = 66.7 Hz, 3-*C*), 171.2 (s, 15-*C*H), 165.9 (s, 21-*C*), 150.9 (s, *C*), 148.4 (s, *C*), 146.8 (d, $^{2}J_{PC}$ = 3.7 Hz, 2-*C*), 142.9 (s, *C*), 141.9 (s, *C*), 141.8 (s, 20-*C*), 138.8 (s, 18-*C*), 131.3 (s, 19-*C*H), 128.1 (s, 17-*C*H), 116.9 (s, 16-*C*), 110.1 (d, $J_{C,P}$ = 2.7 Hz, *C*H), 105.9 (s, *C*H), 53.7 (s, 14-*C*H_2), 35.8 (s, 23-*C*(CH$_3$)$_3$), 34.2 (s, 25-*C*(CH$_3$)$_3$), 31.5 (s, 24-C(*C*H$_3$)$_3$), 29.8 (s, 22-C(*C*H$_3$)$_3$), 15.2 (s, *C*H$_3$), 14.0 (s, *C*H$_3$), 13.7 (s, *C*H$_3$), 10.5 (s, *C*H$_3$).

^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ = 133.1 (s).

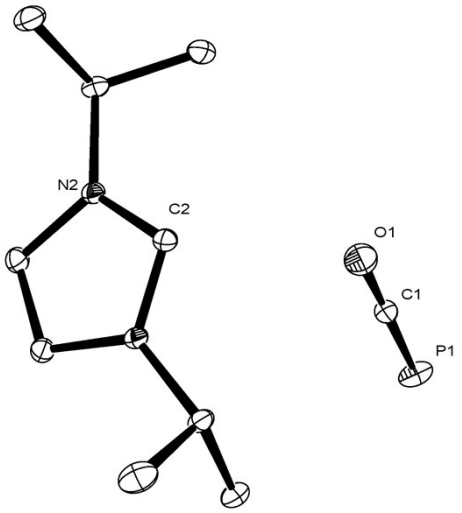
IR [cm^{-1}] solid: 2955, 2903, 2867, 1645, 1619, 1554, 1538, 1464, 1441, 1415, 1390, 1360, 1333, 1309, 1272, 1252, 1233, 1201, 1175, 1139, 1106, 1075, 1057, 1026, 981, 972, 952, 916, 893, 873, 851, 834, 811, 781, 747, 703, 657, 639, 621, 594, 568, 543, 506, 492, 467, 417.
Anal. Calcd. for $C_{45}H_{60}N_8O_3PGa$: C 62.72, H 7.02, N 13.00. Found: C 62.66, H 7.11, N 12.94.

Compound **4**:
Molecular structure of **4** in the crystal (ellipsoids are set at 50% probability):



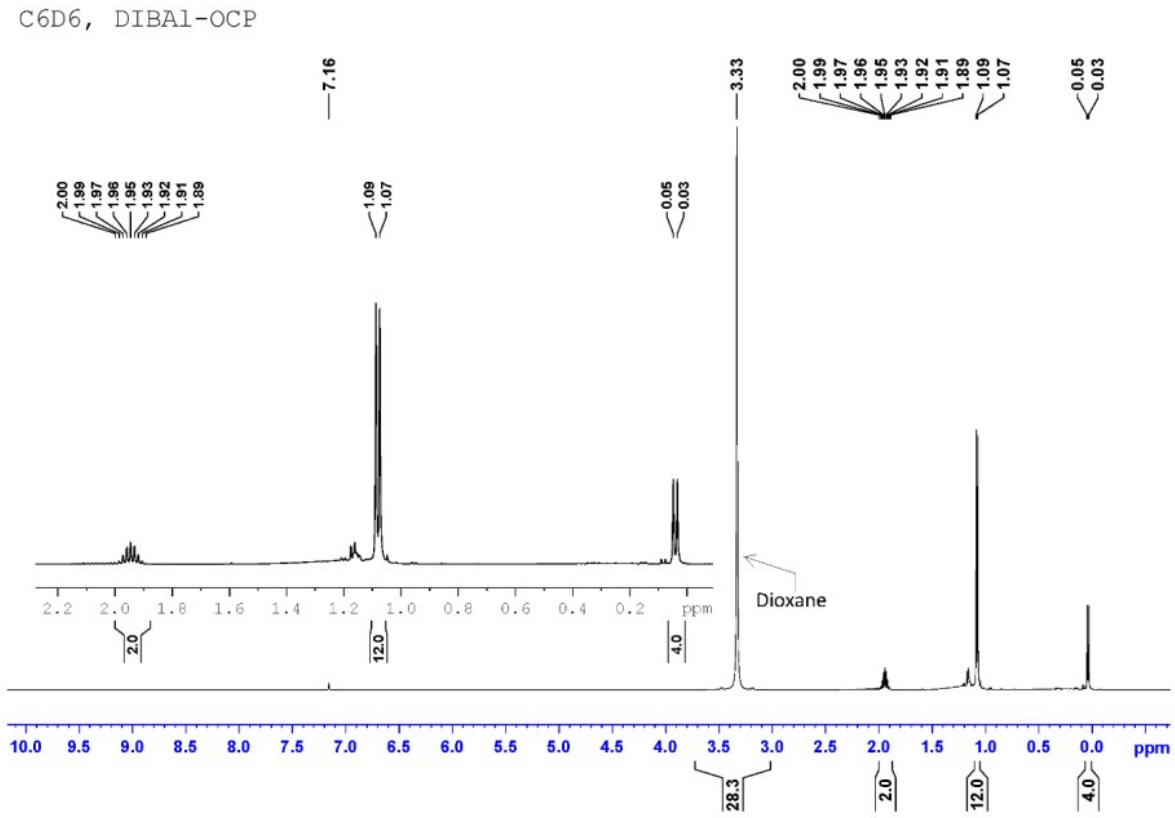
Reaction of Na[OCP] with 1,3-diisopropyl imidazolium chloride to give the [NHC-H][OCP] salt **4-H**:
A suspension of imidazolium chloride (114 mg, 0.6 mmol, 1.2 equiv.) and Na[OCP] (165 mg, 0.5 mmol, 1 equiv.) in THF (3 mL) was stirred overnight. The mixture was then filtrated through celite and the residue was washed several times with THF. The filtrate and wash solutions were combined and evaporated to dryness to give a brown oil. The oil was washed with a THF/toluene mixture (1:1, 3 x 2 mL) and subsequently dried *in vacuo* to afford **4-H** as a brown solid (74 mg, 0.35 mmol, 70%). Colorless crystals of **4-H** were obtained from a THF solution layered with toluene at room temperature. The product is stable in THF and slowly decomposes in $CHCl_3$ over the course of several hours.
^{1}H NMR (THF-d_8, 500 MHz): δ = 9.79 (s, 1H, C*H*), 7.95 (s, 2H, C*H*), 4.94 (sept., 2H, C*H*), 1.62 (d, 12H, CH_3).
^{13}C{^{1}H} NMR (THF-d_8, 125.8 MHz): δ = 170.6 (d, $^1J_{PC}$ = 62.1 Hz, O*C*P), 135.3 (s, *C*H), 121.5 (s, *C*H), 54.1 (s, *C*H), 23.2 (s, *C*H_3).
^{31}P{^{1}H} NMR (THF-d_8, 81.0 MHz): δ = −388.0 (s).
IR [cm^{-1}] solid: 3122, 3062, 2978, 2939, 2876, 2811, 1802, 1787, 1762 (OCP), 1600, 1586, 1552, 1462, 1430, 1392, 1375, 1333, 1282, 1261, 1235, 1181, 1148, 1134, 1104, 937, 884, 857, 824, 803, 754, 730, 693, 645, 549, 527, 495, 456, 444.

Molecular structure of **4-H** in the crystal (ellipsoids are set at 50% probability):

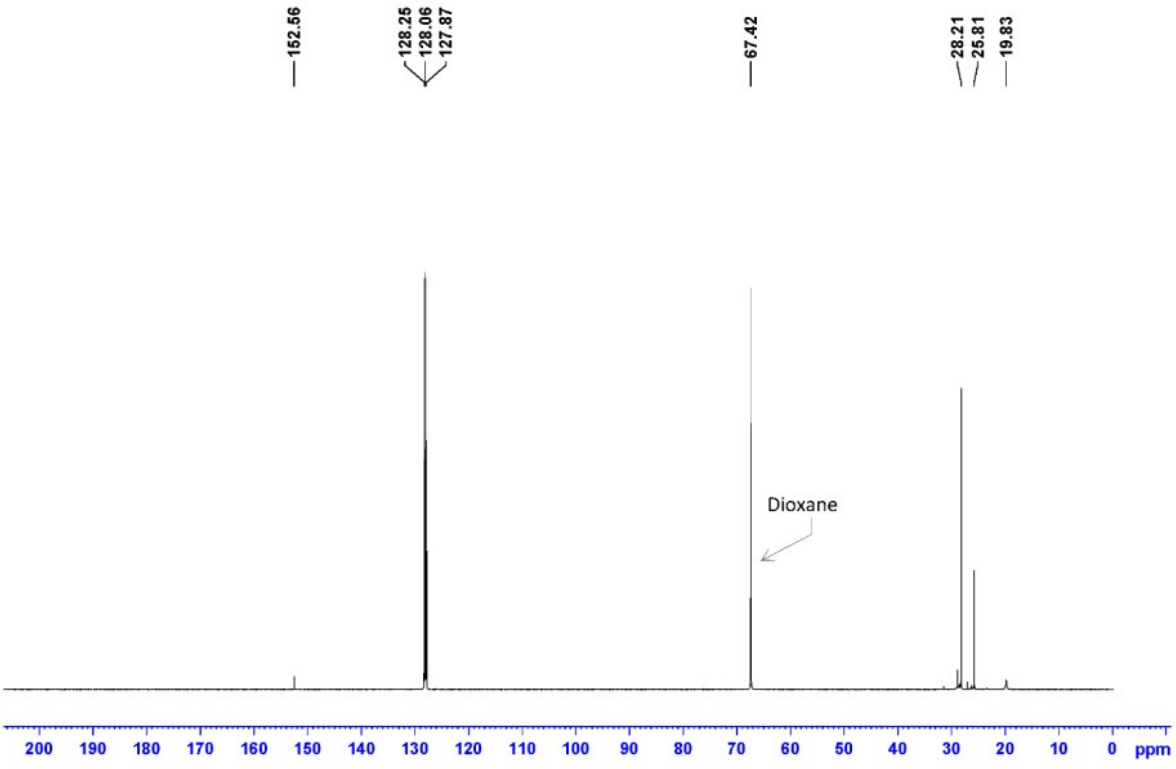


2. NMR and IR spectra

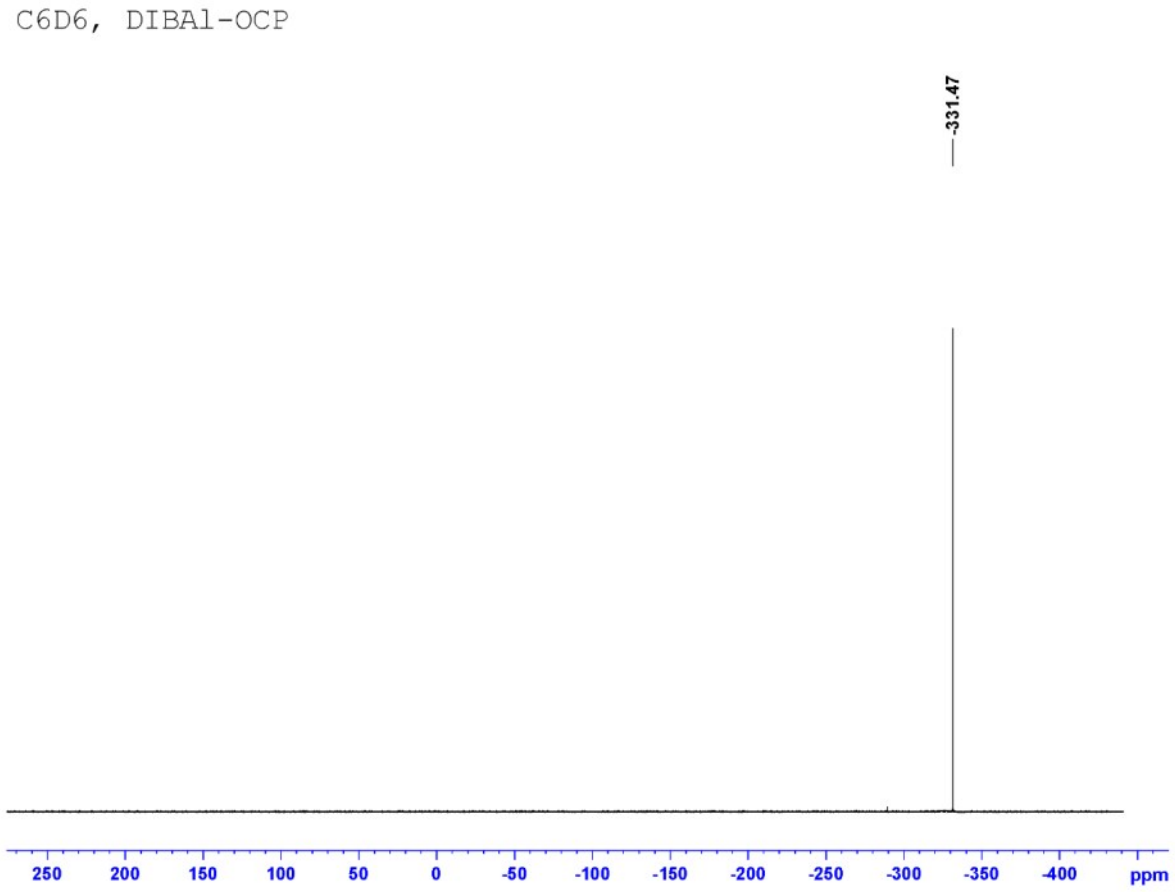
^{1}H NMR spectrum of **1** in C_6D_6:



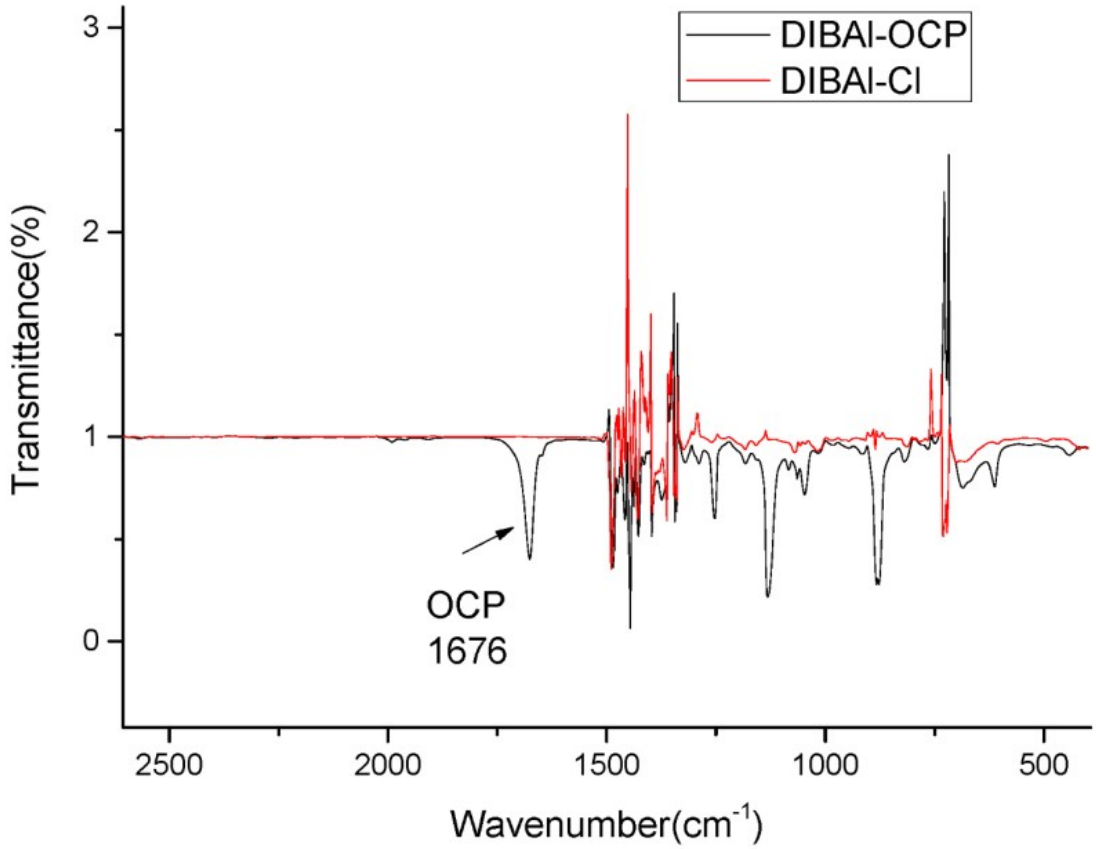
^{13}C{^{1}H} NMR spectrum of **1** in C_6D_6:



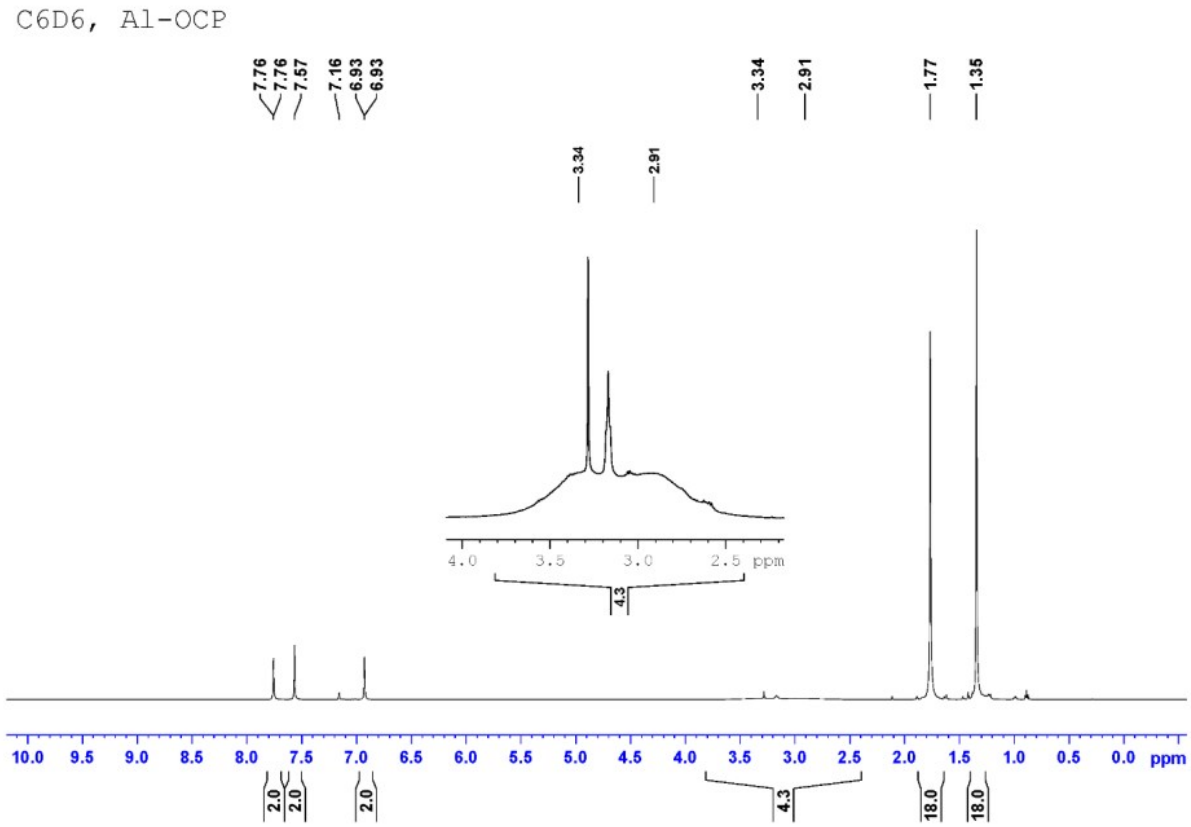
^{31}P NMR spectrum of **1** in C_6D_6:



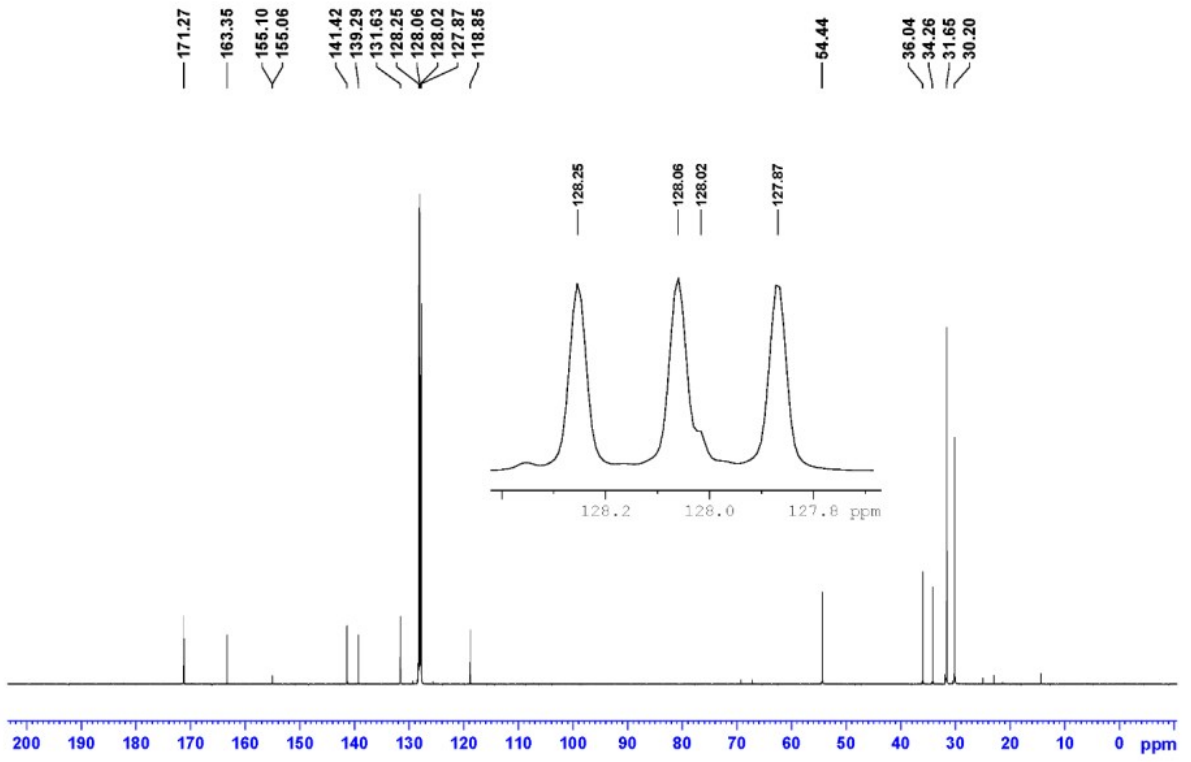
IR spectrum of **1 in** *n*-hexane solution:



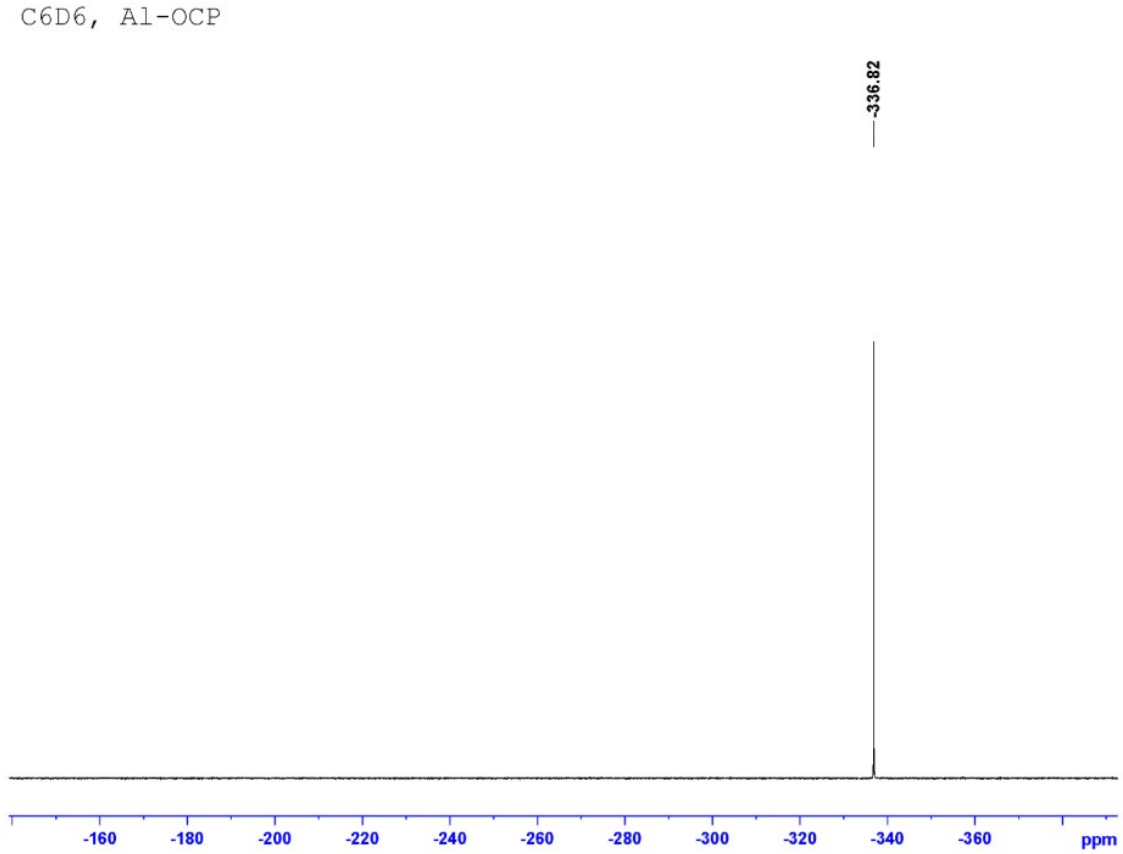
^{1}H NMR spectrum of **2a** in C_6D_6:



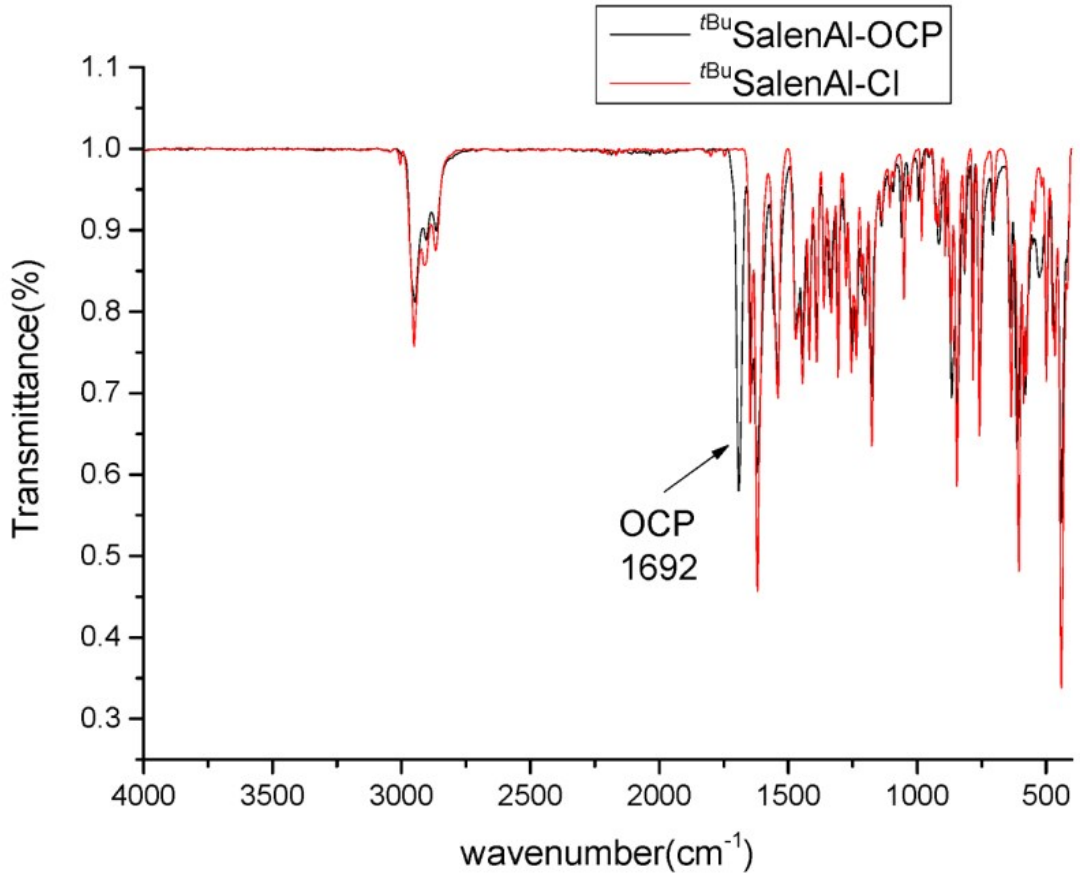
^{13}C{^{1}H} NMR spectrum of **2a** in C_6D_6:



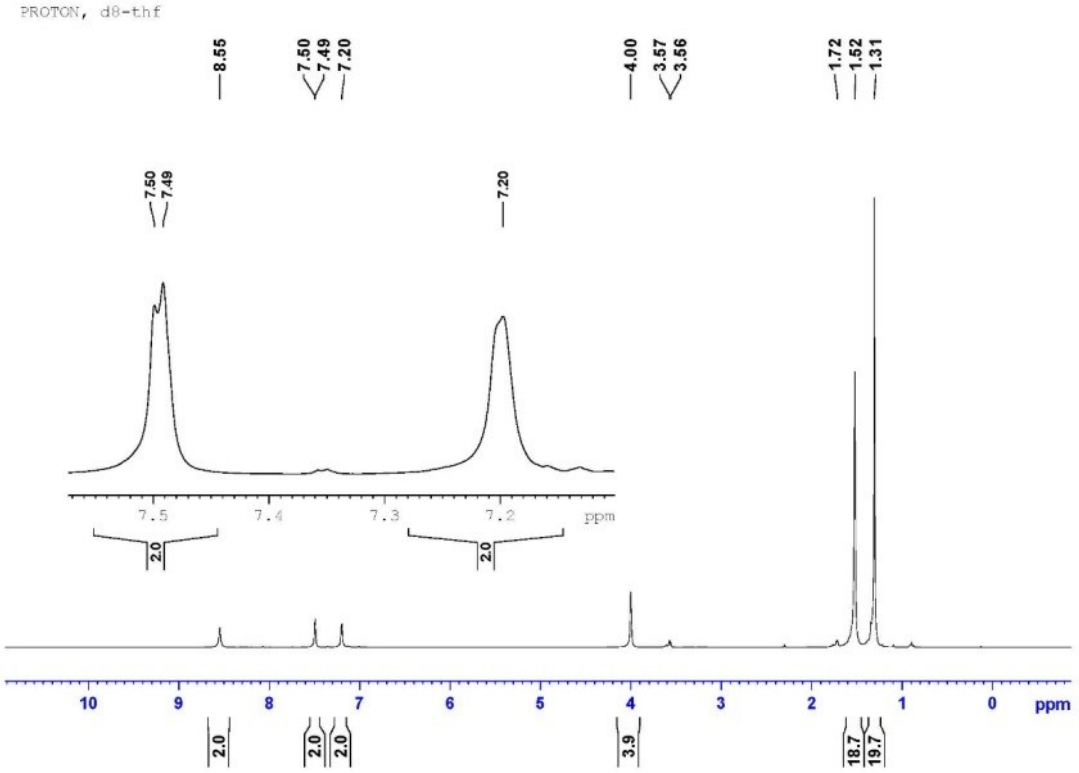
^{31}P NMR spectrum of **2a** in C_6D_6:



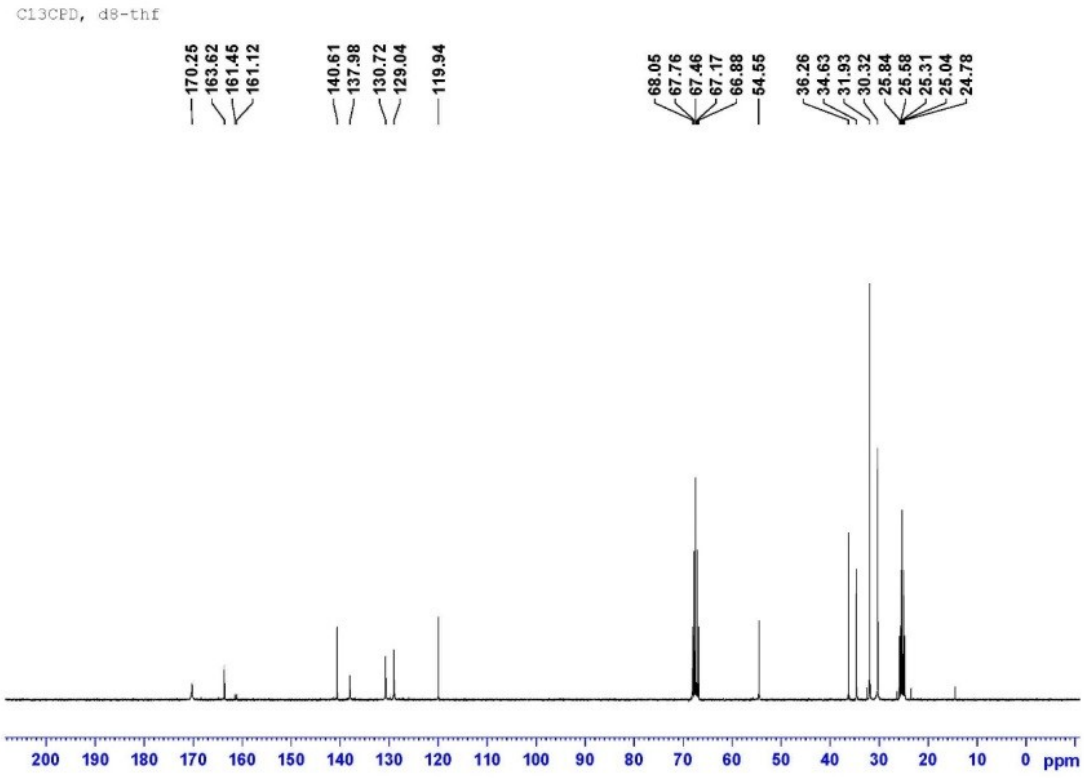
IR spectrum of **2a**:



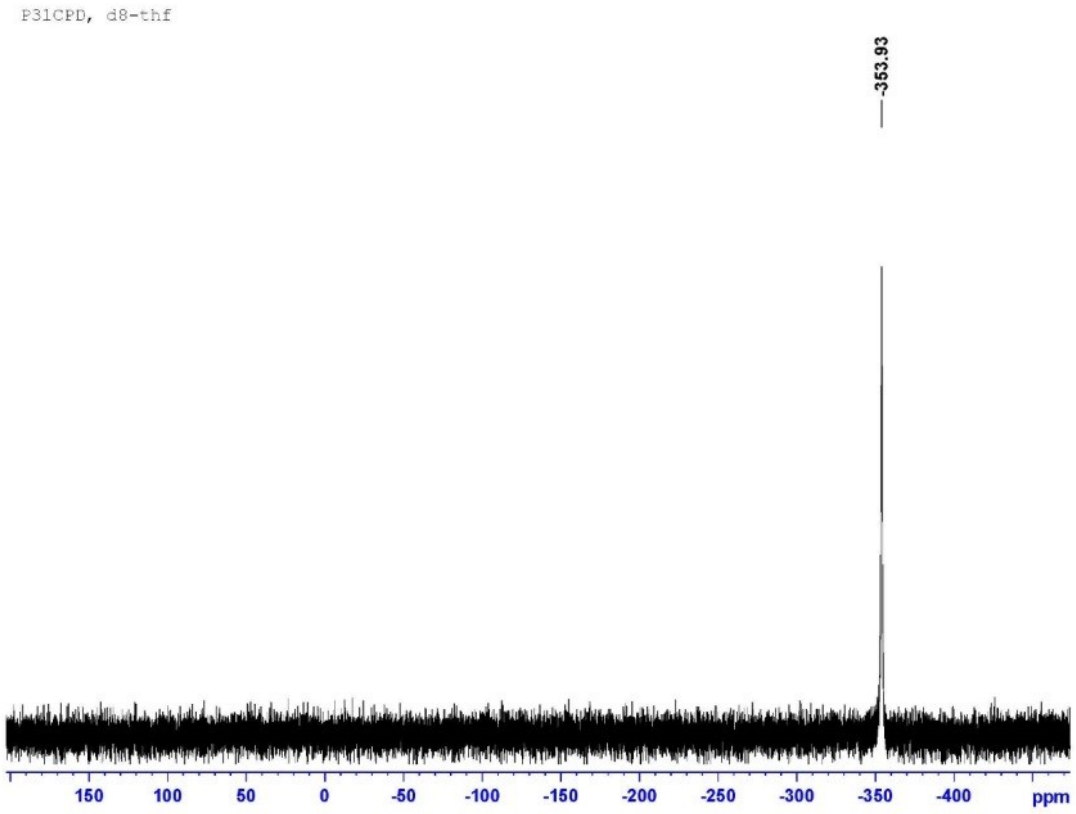
^{1}H NMR spectrum of **2a** in THF-d_8:



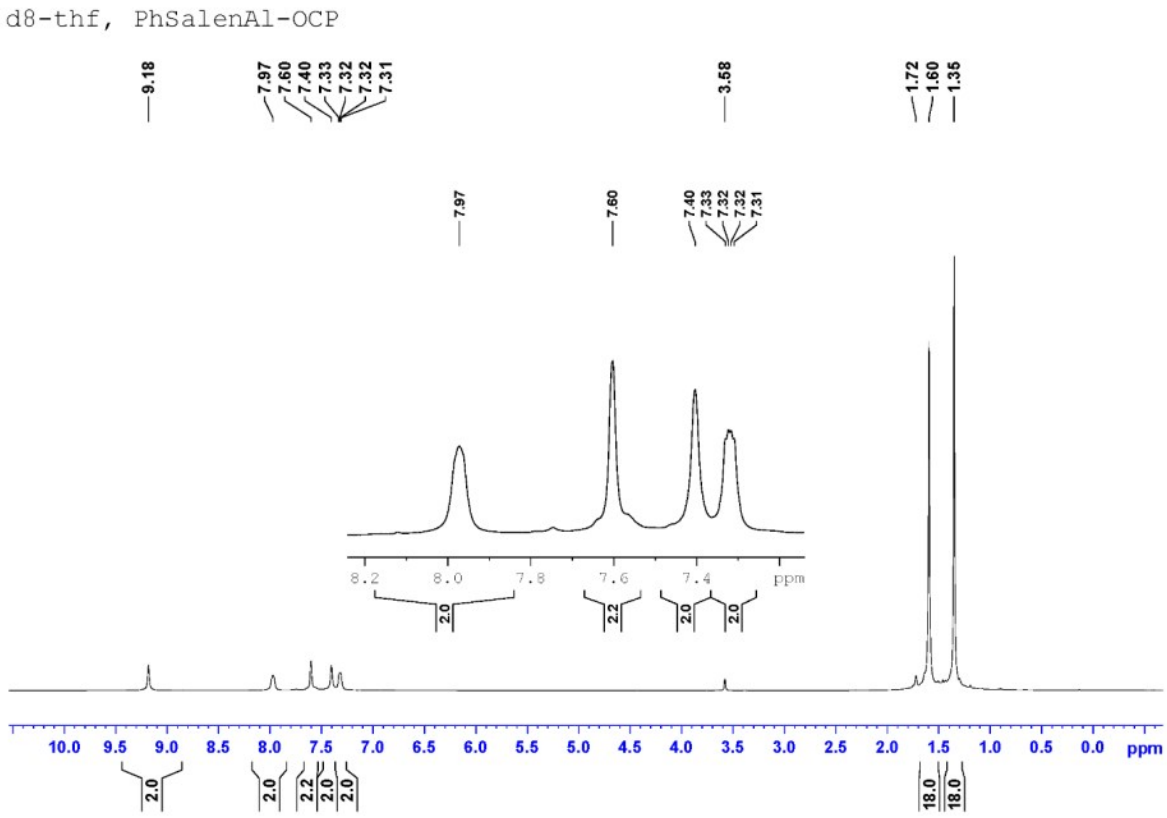
^{13}C{^{1}H} NMR spectrum of **2a** in THF-d_8:



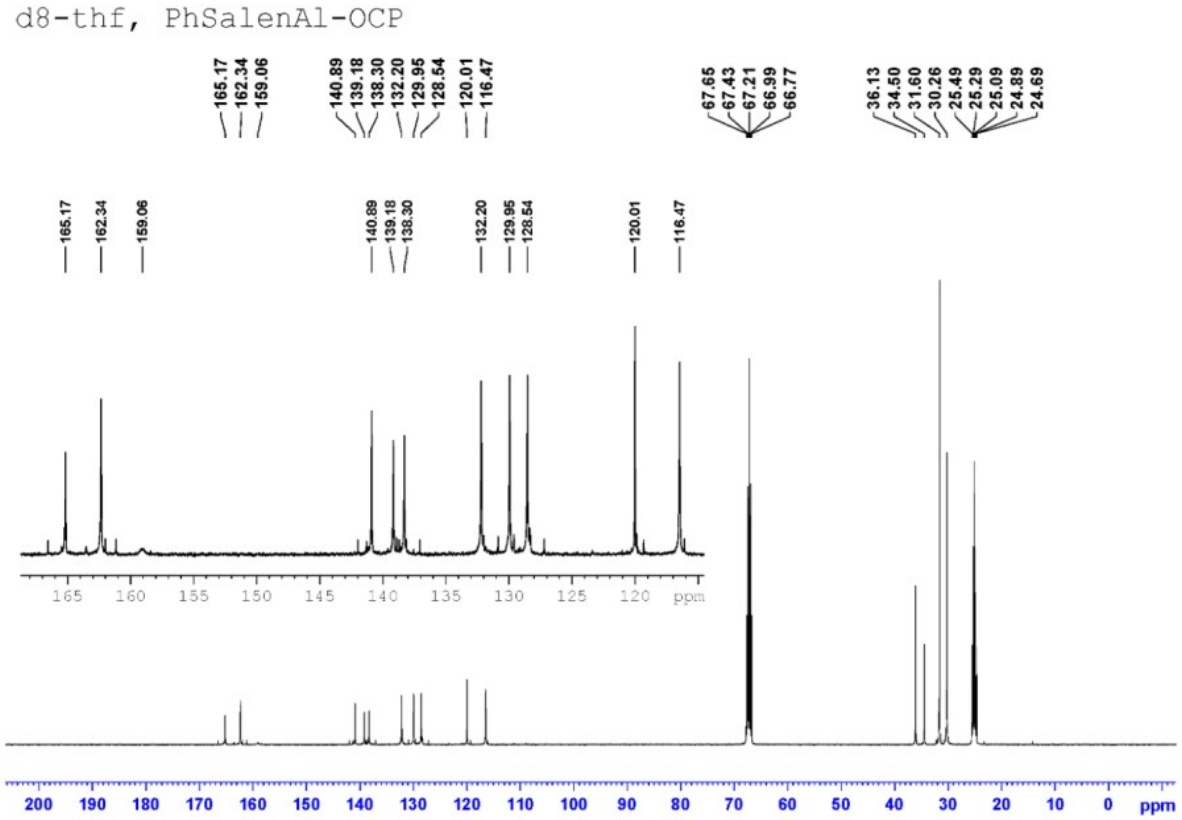
^{31}P NMR spectrum of **2a** in THF-d_8:



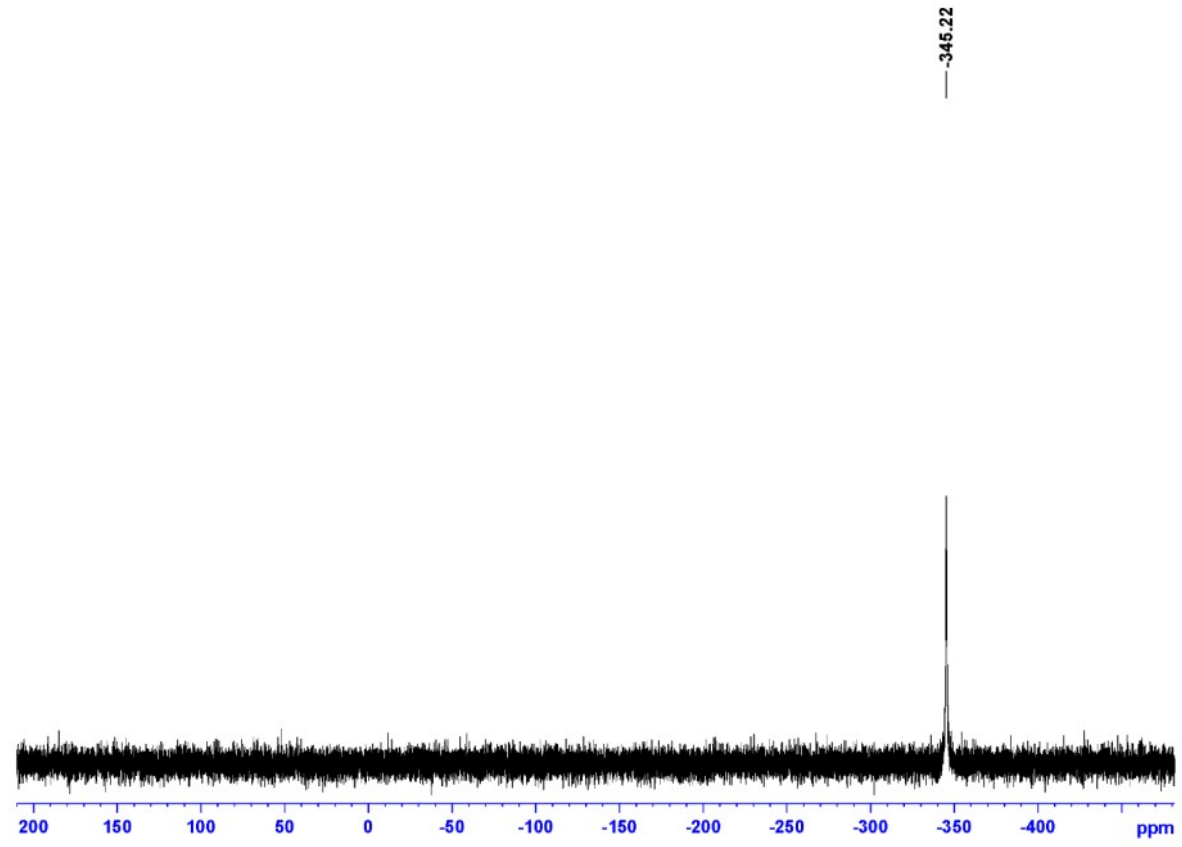
^{1}H NMR spectrum of **2b** in THF-d_8:



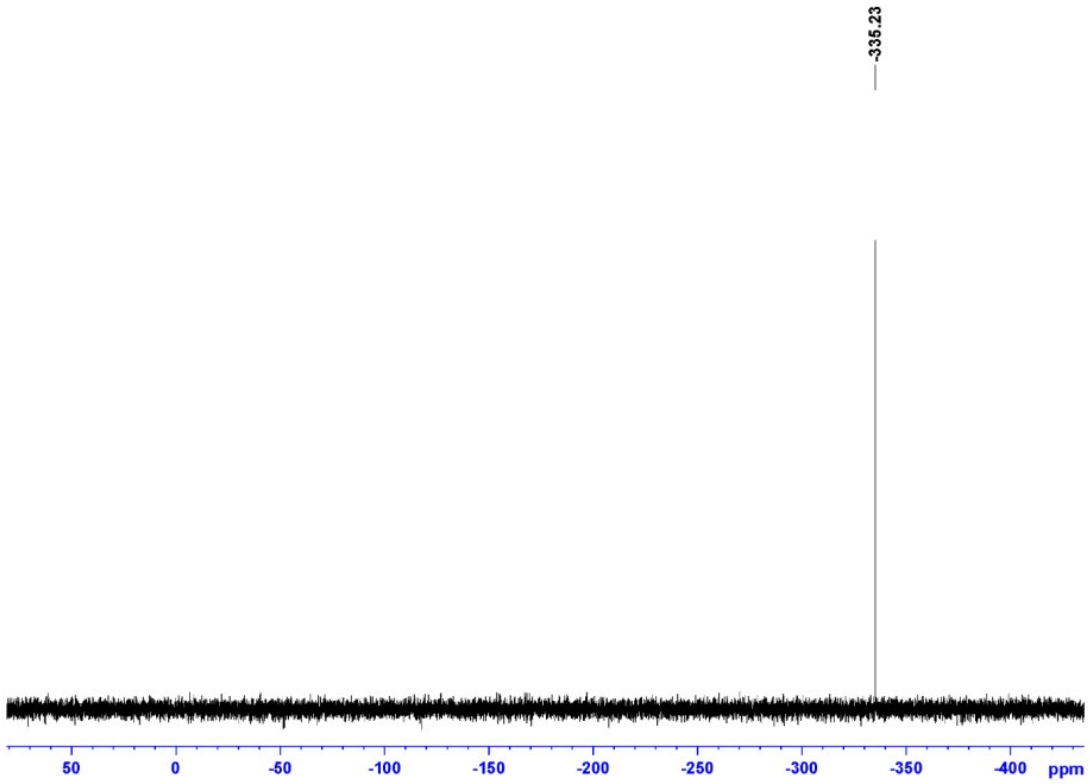
$^{13}C\{^{1}H\}$ NMR spectrum of **2b** in THF-d_8:



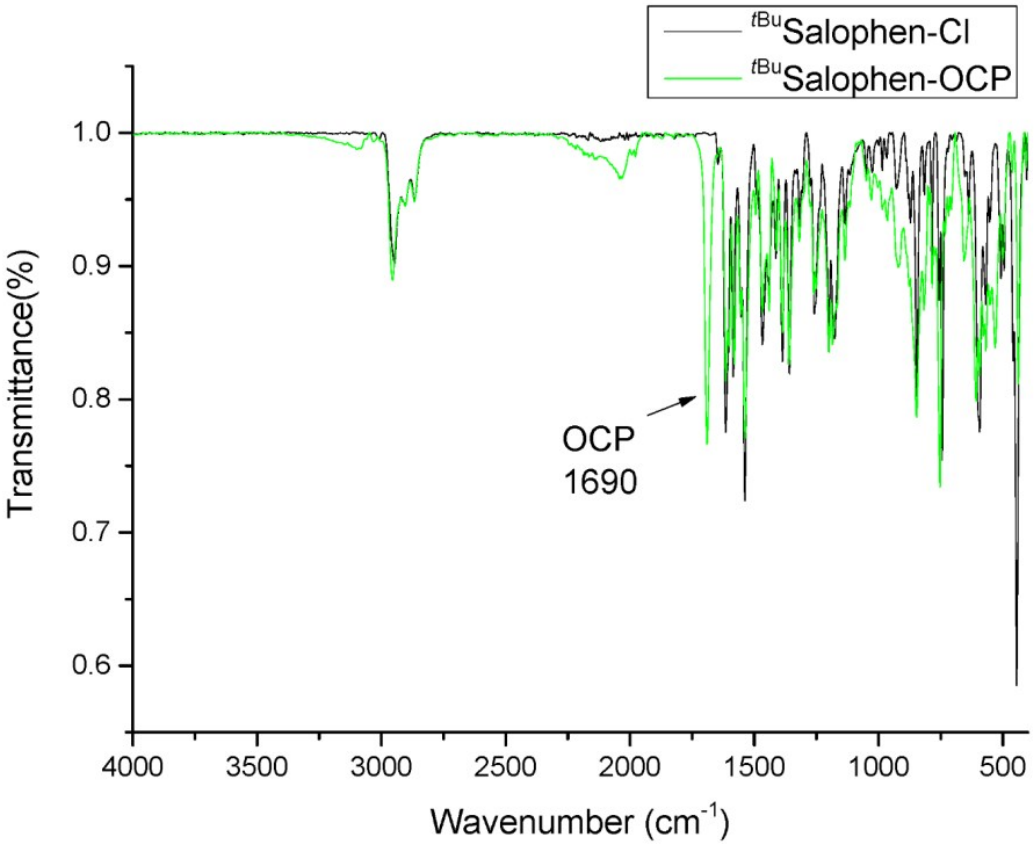
^{31}P NMR spectrum of **2b** in THF-d_8:



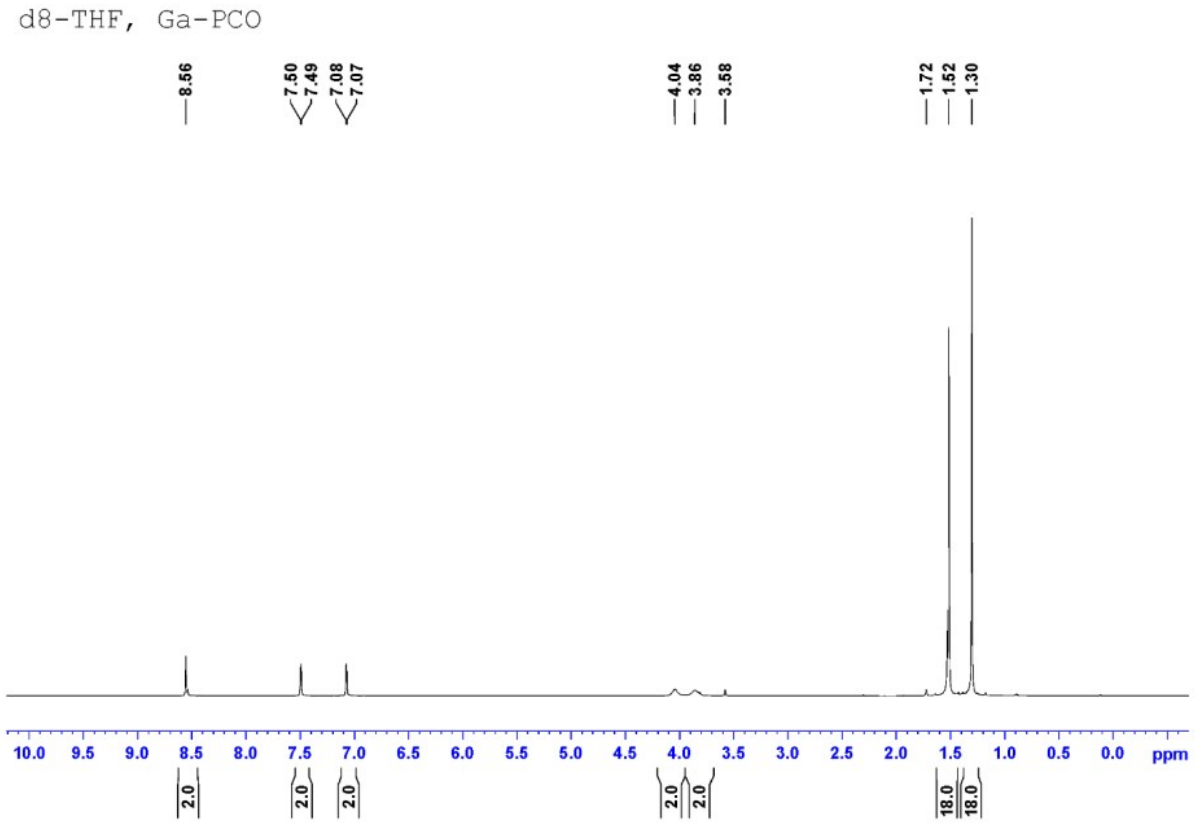
^{31}P NMR spectrum of **2b** in toluene:



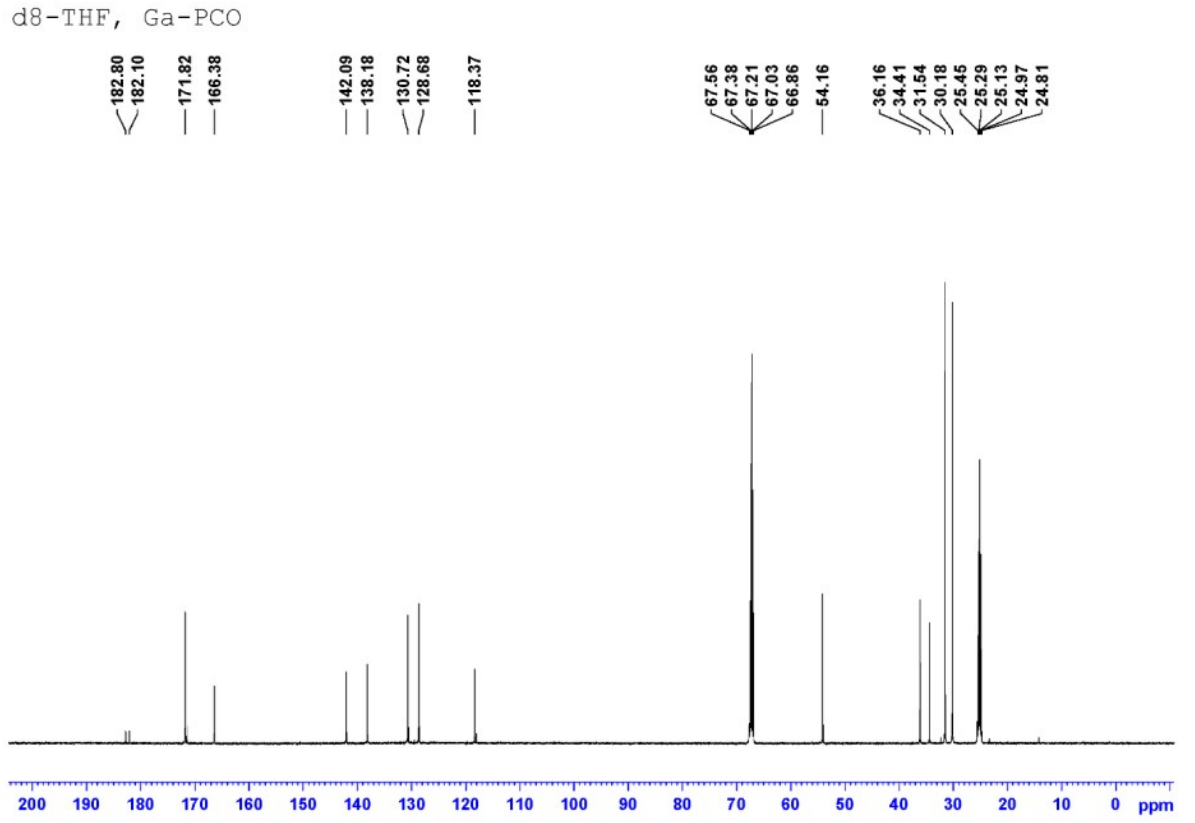
IR spectrum of **2b**:



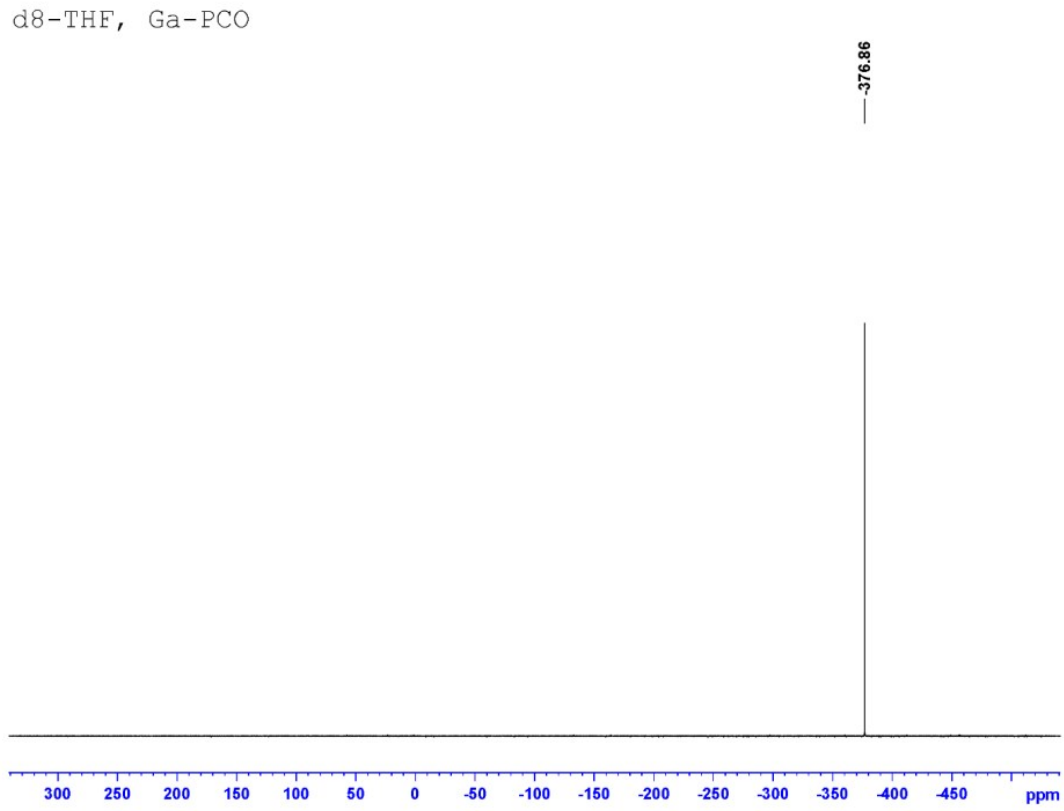
^{1}H NMR spectrum of **3** in THF-d_8:



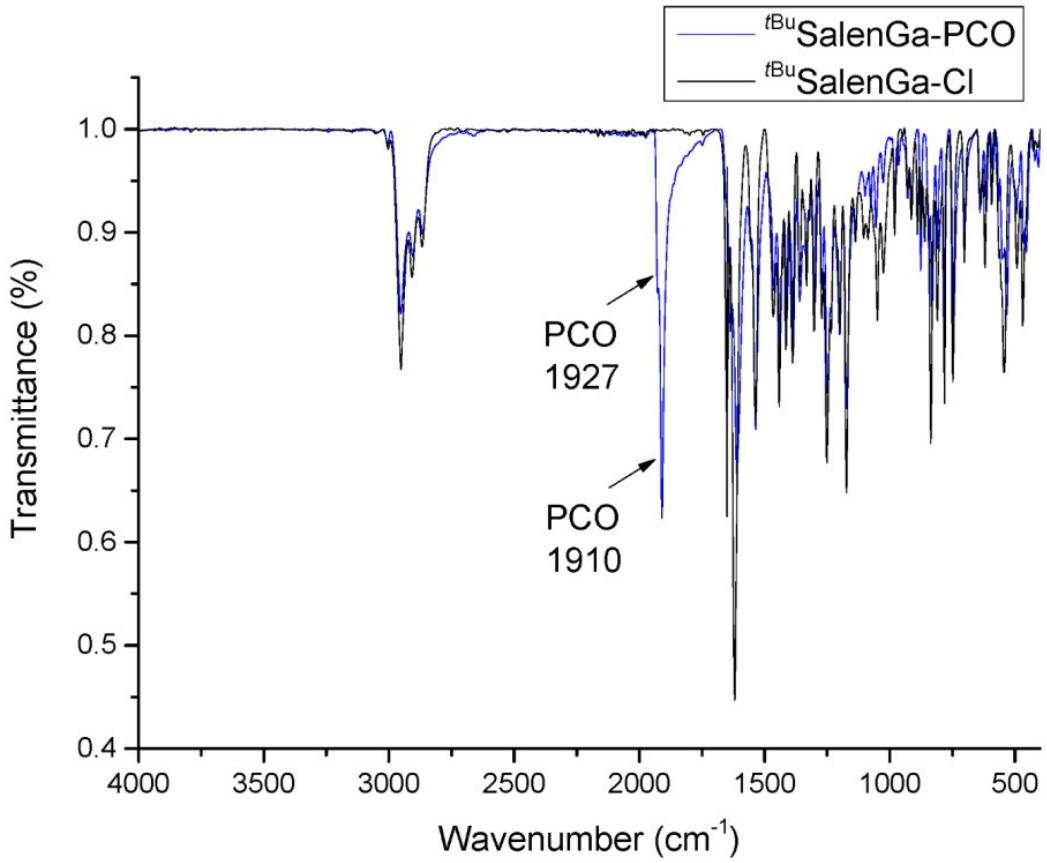
^{13}C{^{1}H} NMR spectrum of **3** in THF-d_8:



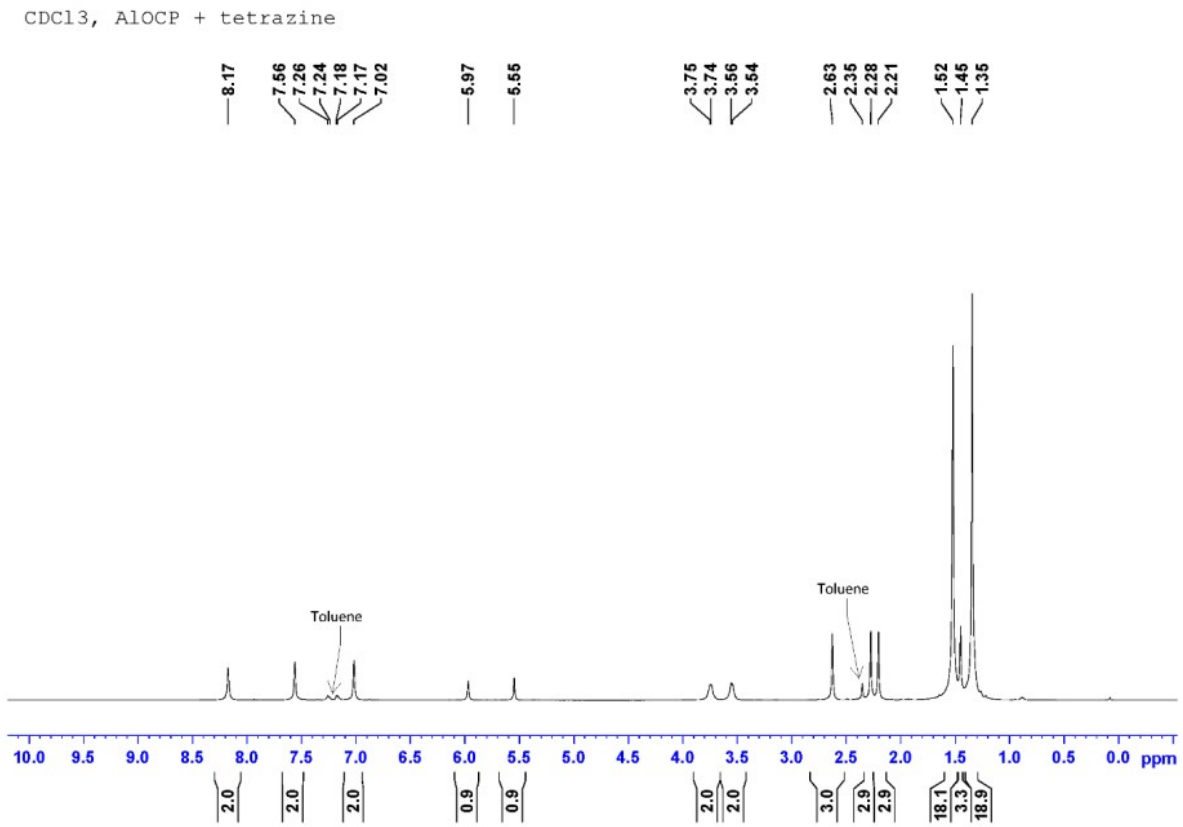
^{31}P NMR spectrum of **3** in THF-d_8:



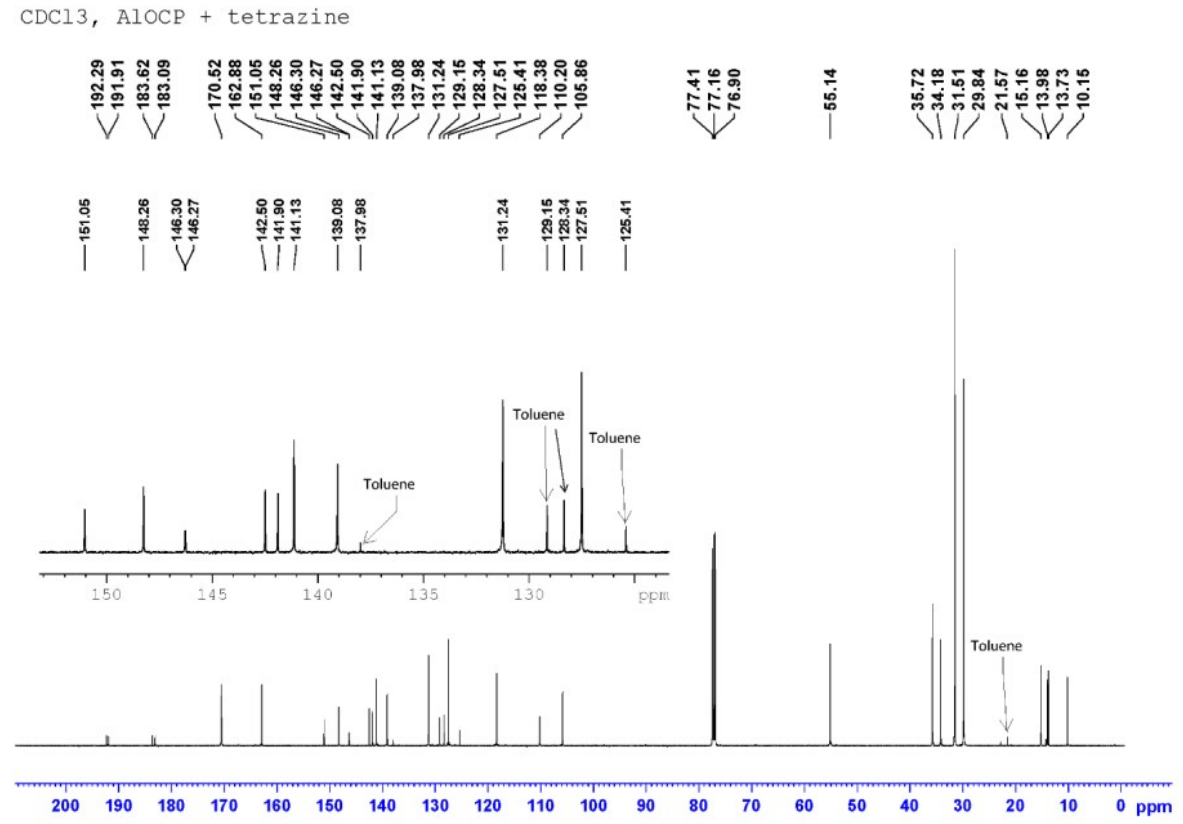
IR spectrum of **3**:



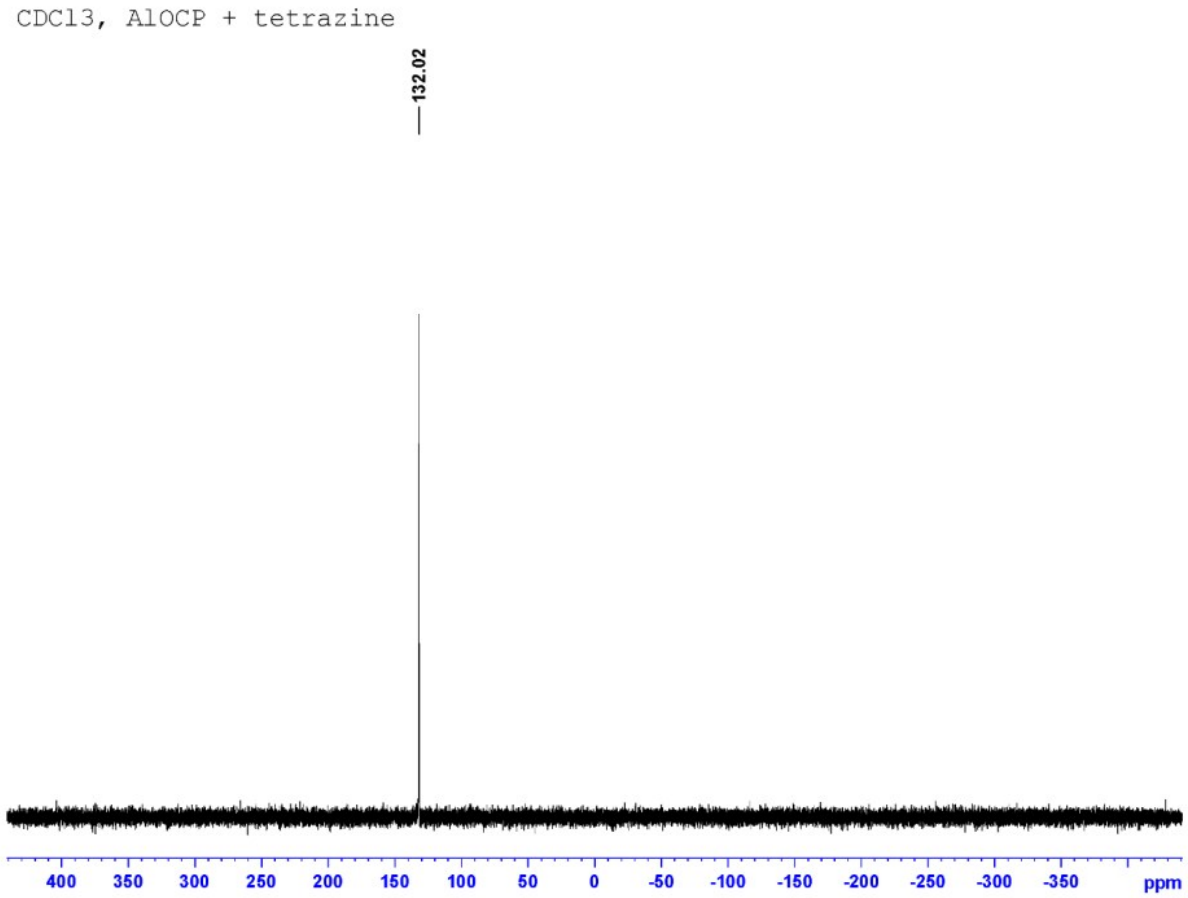
^{1}H NMR spectrum of **6** in $CDCl_3$:



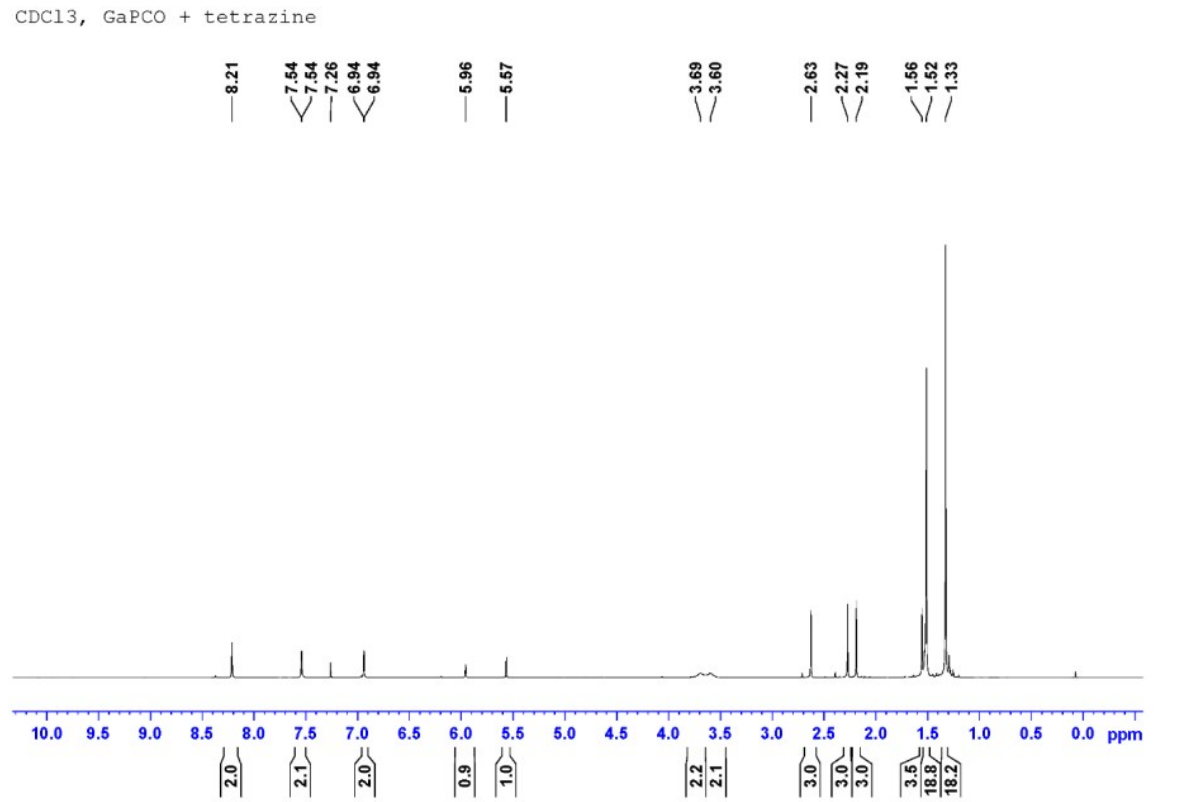
^{13}C{^{1}H} NMR spectrum of **6** in $CDCl_3$:



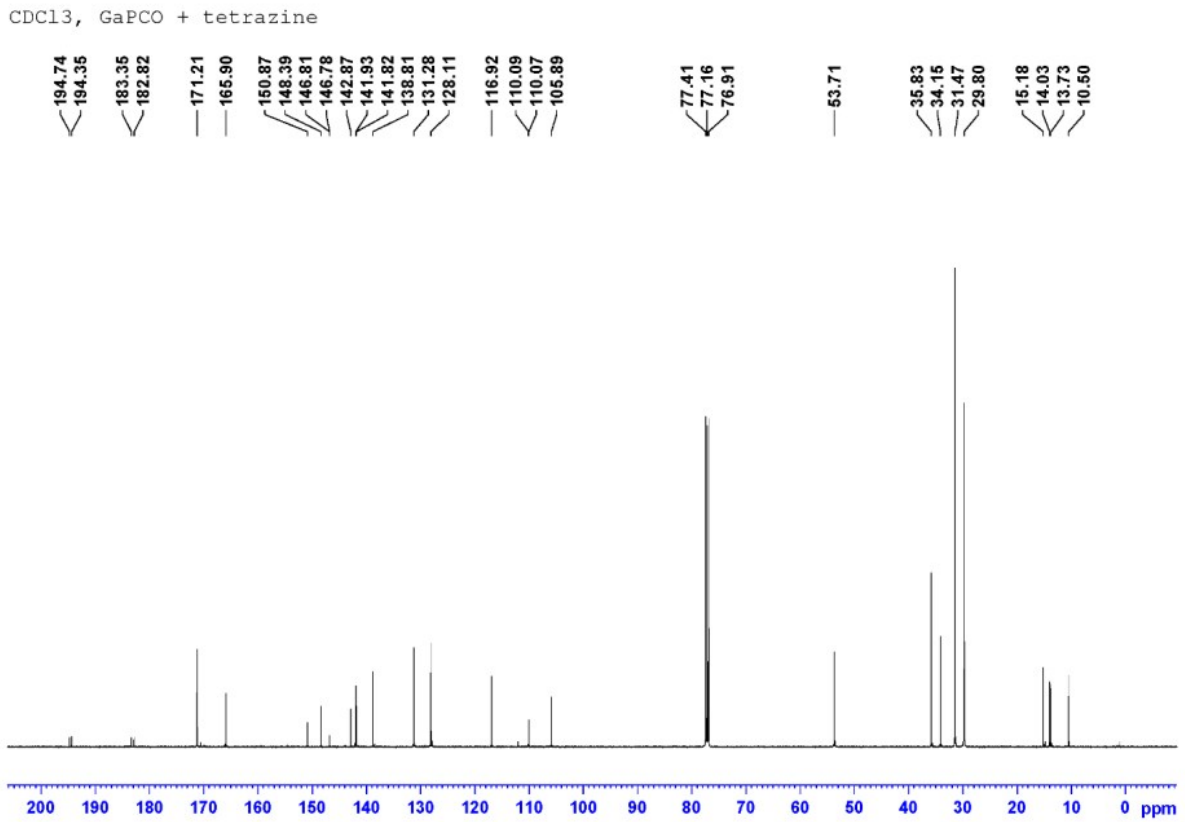
^{31}P NMR spectrum of **6** in $CDCl_3$:



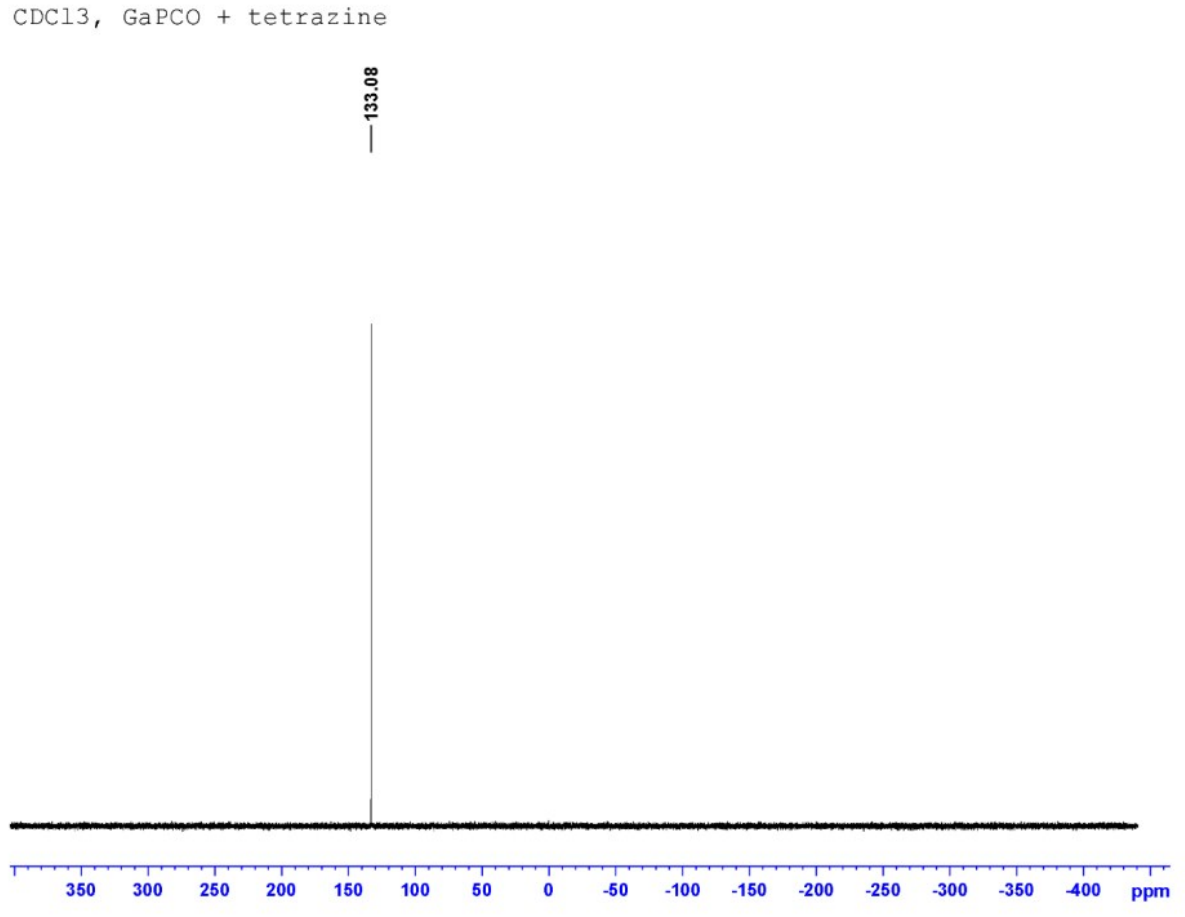
^{1}H NMR spectrum of **7** in $CDCl_3$:



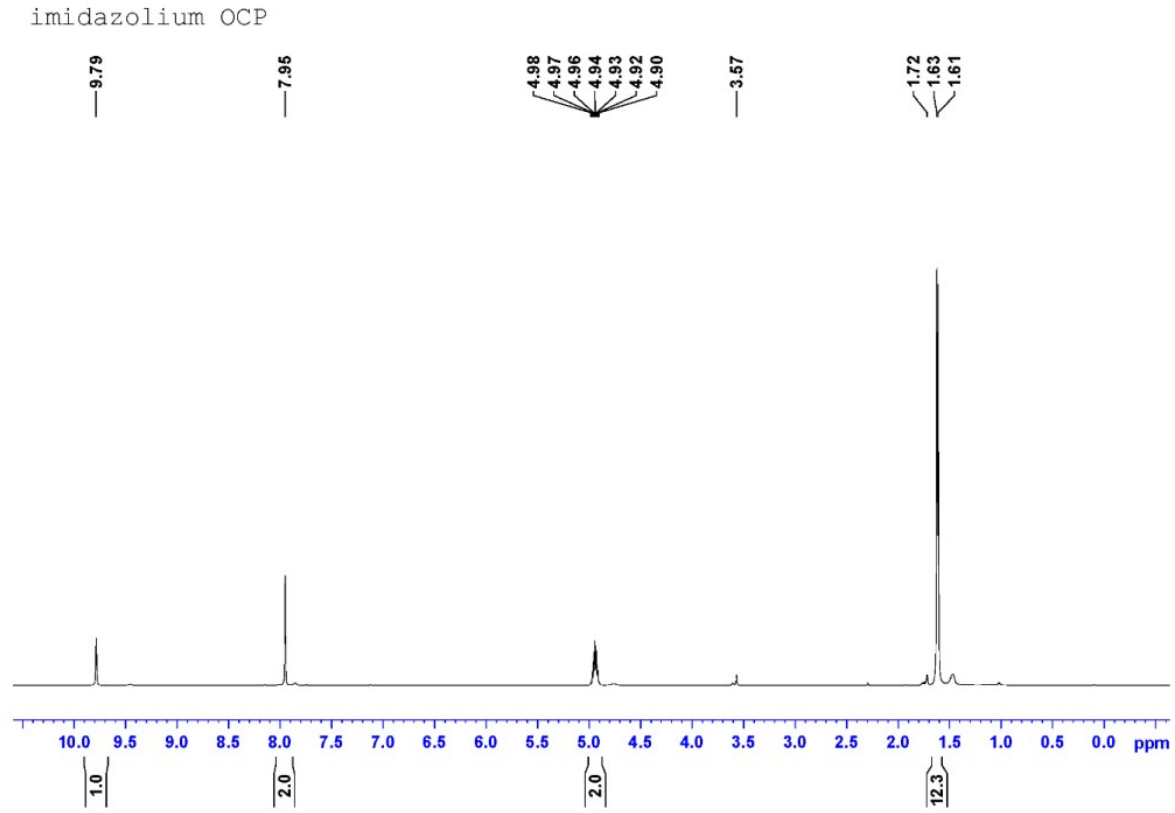
$^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$:



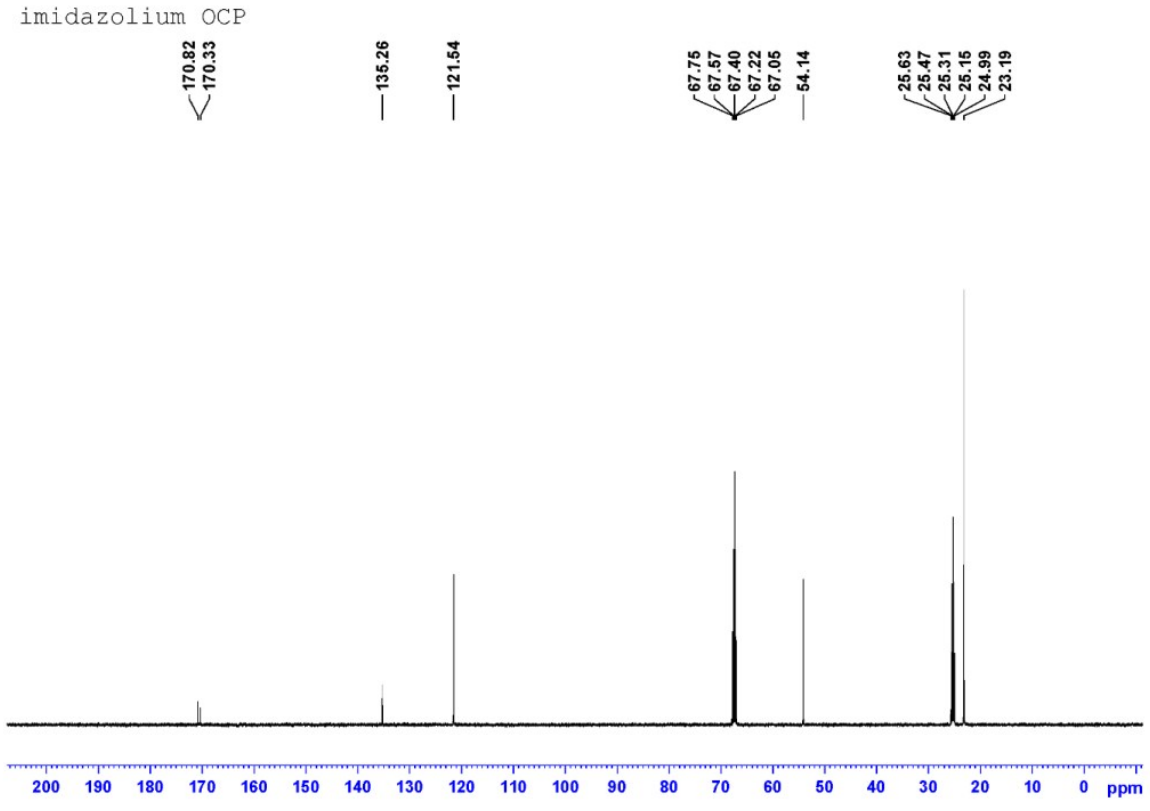
^{31}P NMR spectrum of **7** in $CDCl_3$:



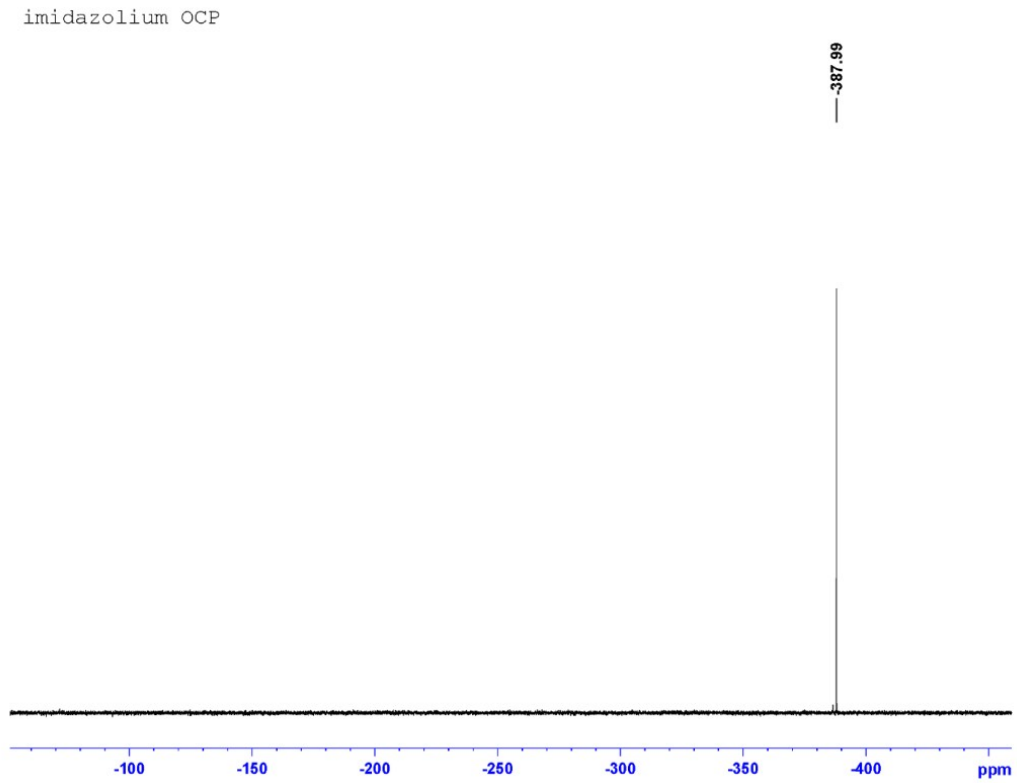
^{1}H NMR spectrum of **4-H** in THF-d_8:



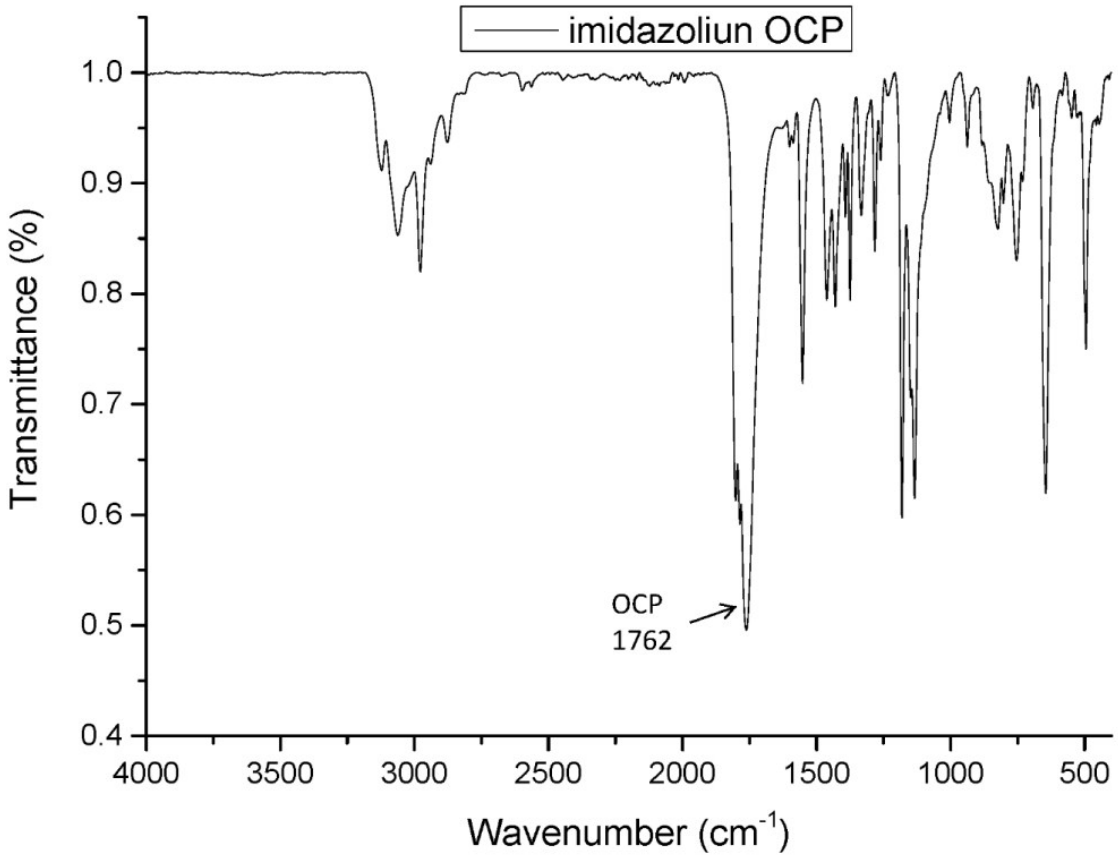
^{13}C{^{1}H} NMR spectrum of **4-H** in THF-d_8:



^{31}P NMR spectrum of **4-H** in THF-d_8:



IR spectrum of **4-H**:



2. Computational Section

Density functional calculations were performed using Gaussian09, revision D.01.[S4] Geometry optimizations and frequency calculations were performed using the B3LYP[S5] functional and the 6-311G(2d,p) basis set,[S6,S7] including diffuse function +[S8] in case of structures marked with an asterisk. Chemical shifts and coupling constants were derived using the GIAO method.[S9] The computed absolute shifts σ(S, calc) were referenced to the experimentally determined absolute shift of 85% H_3PO_4 in the gas phase (σ(ref1) = 328.35 ppm),[S10] using PH_3 as secondary standard (σ(ref2) = 594.45 ppm), according to the equation:[S11] δ(S, calc) = (σ(ref1) – σ(ref2)) – (σ(S, calc) – σ(PH_3, calc)) = σ(PH_3, calc) – σ(S, calc) – 266.1 ppm.

Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)

PH_3*

E: -343.176295575

P	0.000000000	0.000000000	0.128850000
H	0.000000000	1.190699000	-0.644250000
H	1.031176000	-0.595349000	-0.644250000
H	-1.031176000	-0.595349000	-0.644250000

$iBu_2Al–O–C≡P$*

E: -1013.02294140

Al	0.059704000	-0.078121000	-0.061635000
P	-1.356000000	3.961328000	-0.058744000
O	0.271150000	1.657244000	-0.306394000
C	-0.472854000	2.682006000	-0.189701000
C	-1.689052000	-0.663471000	0.590203000
H	-1.665543000	-0.589969000	1.686603000
H	-2.439993000	0.072968000	0.277144000
C	1.686393000	-1.069613000	-0.504447000
H	1.611741000	-2.081687000	-0.084588000
H	1.696199000	-1.215324000	-1.593569000
C	3.019461000	-0.424386000	-0.063911000
H	3.079845000	0.572629000	-0.514304000
C	4.223532000	-1.233568000	-0.562381000
H	4.210624000	-1.331604000	-1.650453000
H	5.166921000	-0.758304000	-0.279930000
H	4.216618000	-2.242172000	-0.137314000
C	3.079302000	-0.250340000	1.458118000
H	2.275815000	0.397373000	1.826726000
H	2.991531000	-1.215824000	1.966351000
H	4.022015000	0.204355000	1.771015000
C	-2.139959000	-2.080639000	0.176811000
H	-1.377497000	-2.798043000	0.505900000
C	-3.458495000	-2.469946000	0.857884000
H	-4.262402000	-1.790020000	0.560290000
H	-3.762052000	-3.485560000	0.589021000
H	-3.370311000	-2.422609000	1.945838000
C	-2.265169000	-2.202882000	-1.346694000
H	-2.997466000	-1.488515000	-1.734815000
H	-1.312461000	-2.009201000	-1.852818000
H	-2.587886000	-3.203760000	-1.642821000

$iBu_2Al–P=C=O$*

E: -1013.02989829

Al	0.023455000	0.216819000	-0.077974000
C	-0.996324000	2.880406000	-0.006042000
C	-1.737650000	-0.380287000	0.574331000

H	-1.681683000	-0.359989000	1.672491000
H	-2.508628000	0.356248000	0.319618000
C	1.530769000	-0.988596000	-0.492751000
H	1.295037000	-1.987440000	-0.101605000
H	1.548327000	-1.105783000	-1.585527000
C	2.932917000	-0.568149000	-0.004603000
H	3.150034000	0.433345000	-0.396722000
C	4.019985000	-1.511981000	-0.536201000
H	4.013690000	-1.546198000	-1.628307000
H	5.016340000	-1.194815000	-0.215698000
H	3.859671000	-2.531138000	-0.170959000
C	2.989610000	-0.489695000	1.525441000
H	2.277016000	0.241615000	1.921602000
H	2.754529000	-1.460867000	1.972379000
H	3.981973000	-0.194931000	1.875030000
C	-2.191443000	-1.781485000	0.112308000
H	-1.408528000	-2.504756000	0.372834000
C	-3.475664000	-2.219977000	0.829211000
H	-4.298359000	-1.535457000	0.601194000
H	-3.781678000	-3.224593000	0.523417000
H	-3.340559000	-2.225681000	1.913464000
C	-2.382146000	-1.832038000	-1.408295000
H	-3.141148000	-1.111496000	-1.727989000
H	-1.456226000	-1.596831000	-1.944290000
H	-2.703807000	-2.822627000	-1.738885000
P	0.567705000	2.476195000	-0.428465000
O	-2.067104000	3.220080000	0.277275000

[$iBu_2Al(OCP)Cl$]$^-$*

E: -1473.42372503

Al	-0.065886000	0.059535000	0.655440000
P	-3.979358000	1.072773000	-1.121210000
O	-1.844931000	-0.221311000	0.190325000
C	-2.772690000	0.366958000	-0.386172000
C	0.658552000	1.376191000	-0.656848000
H	0.226797000	1.109578000	-1.632615000
H	0.242106000	2.367673000	-0.428579000
C	0.684450000	-1.786866000	0.776975000
H	1.777153000	-1.727593000	0.901242000
H	0.316006000	-2.186789000	1.731817000
C	0.366025000	-2.801535000	-0.338202000
H	-0.721976000	-2.820386000	-0.479356000
C	0.800452000	-4.228090000	0.035697000
H	0.326344000	-4.550235000	0.966946000
H	0.539181000	-4.952778000	-0.744763000
H	1.885259000	-4.273332000	0.185147000
C	0.992800000	-2.401167000	-1.680070000
H	0.643115000	-1.421201000	-2.011690000
H	2.084428000	-2.351060000	-1.596646000
H	0.752576000	-3.124886000	-2.466187000
C	2.187046000	1.502984000	-0.812891000
H	2.604584000	0.498777000	-0.969029000
C	2.574938000	2.343584000	-2.040322000
H	2.188305000	3.364028000	-1.943729000
H	3.662830000	2.407103000	-2.164531000
H	2.154798000	1.918682000	-2.956244000
C	2.845334000	2.081511000	0.446422000
H	2.473016000	3.092741000	0.642063000
H	2.622487000	1.482799000	1.331901000
H	3.933945000	2.140443000	0.337177000
Cl	-0.142710000	0.894704000	2.706139000

[$iBu_2Al(PCO)Cl$]$^-$*

E: -1473.41836745

Al	-0.016902000	-0.366611000	0.512301000
C	-0.842861000	-2.790767000	-1.211391000
C	-1.396984000	0.545378000	-0.617919000
H	-1.075207000	0.403875000	-1.659483000
H	-2.343322000	-0.007956000	-0.538703000
C	1.770209000	0.509786000	0.795821000
H	1.591881000	1.504687000	1.234202000
H	2.240485000	-0.070579000	1.601634000
C	2.769281000	0.649354000	-0.366454000
H	2.891505000	-0.336710000	-0.832915000
C	4.159258000	1.098202000	0.114603000
H	4.560102000	0.402628000	0.857158000
H	4.877019000	1.160308000	-0.712431000
H	4.104222000	2.086496000	0.585132000
C	2.259705000	1.604374000	-1.453111000
H	1.307036000	1.267398000	-1.866253000
H	2.105552000	2.608782000	-1.042592000
H	2.973416000	1.689182000	-2.279809000
C	-1.679068000	2.045123000	-0.391313000
H	-0.720202000	2.580399000	-0.366104000
C	-2.499196000	2.654605000	-1.540671000
H	-3.473736000	2.160329000	-1.619971000
H	-2.677689000	3.726539000	-1.390770000
H	-1.987914000	2.528467000	-2.499303000
C	-2.383720000	2.303927000	0.946549000
H	-3.359354000	1.806219000	0.965791000
H	-1.809372000	1.914123000	1.788510000
H	-2.551307000	3.374885000	1.107449000
Cl	-0.803139000	-0.779096000	2.559759000
P	0.610824000	-2.566016000	-0.473065000
O	-1.860264000	-3.002269000	-1.758508000

THF

E: -232.520104650

C	1.166019000	0.429097000	0.130308000
O	-0.000027000	1.250958000	-0.000062000
C	-1.166060000	0.429039000	-0.130230000
C	-0.733445000	-0.995033000	0.223446000
C	0.733516000	-0.994971000	-0.223481000
H	1.942706000	0.818912000	-0.531691000
H	1.534797000	0.485925000	1.162126000
H	-1.942655000	0.818786000	0.531920000
H	-1.535018000	0.485895000	-1.161979000
H	-0.801820000	-1.158277000	1.302154000
H	-1.338352000	-1.754815000	-0.273280000
H	1.338470000	-1.754753000	0.273190000
H	0.801910000	-1.158121000	-1.302202000

2a'

E: -1575.71351634

Al	0.103349000	-0.043809000	0.043660000
P	-1.216395000	3.471866000	2.195942000
O	-1.076611000	-1.371458000	0.247729000
O	0.137491000	1.113017000	1.440696000
O	1.466545000	-1.106714000	0.551317000
N	1.281150000	0.799571000	-1.336420000
N	-1.262758000	0.974322000	-1.016854000
C	-2.376244000	-1.461556000	0.085655000
C	-3.144872000	-0.457335000	-0.568957000
C	-2.519921000	0.702918000	-1.119846000

H	-3.159391000	1.390771000	-1.678575000
C	-3.048112000	-2.605405000	0.556742000
C	-4.536848000	-0.625601000	-0.718195000
H	-5.102987000	0.152771000	-1.219215000
C	-4.412077000	-2.737068000	0.401101000
H	-4.904885000	-3.624619000	0.781819000
C	2.572776000	0.681728000	-1.388193000
H	3.113341000	1.280262000	-2.125802000
C	0.616843000	1.691442000	-2.295885000
H	0.402640000	1.128571000	-3.210588000
H	1.252920000	2.541177000	-2.555953000
C	-0.694456000	2.152060000	-1.660665000
H	-0.499932000	2.905970000	-0.891180000
H	-1.370492000	2.580536000	-2.405209000
C	-0.473474000	2.154258000	1.770141000
C	-5.173054000	-1.745975000	-0.237995000
C	3.362581000	-0.172907000	-0.571379000
C	2.755755000	-1.052894000	0.373689000
C	4.767116000	-0.169763000	-0.729006000
H	5.206875000	0.507070000	-1.454376000
C	4.964422000	-1.871648000	0.943099000
H	5.589664000	-2.531733000	1.533921000
C	3.599318000	-1.904233000	1.118799000
C	5.565608000	-1.001325000	0.015741000
H	-6.242818000	-1.864356000	-0.350547000
H	-2.457902000	-3.367185000	1.049696000
H	6.640690000	-0.991587000	-0.107073000
H	3.134358000	-2.572302000	1.832262000

2a‘-I

E: -1575.70550573

Al	-0.087331000	0.009000000	0.147012000
O	-1.423356000	-1.198453000	0.094928000
O	1.131181000	-1.334259000	0.103893000
N	1.123004000	1.090451000	-1.045771000
N	-1.386669000	1.393265000	-0.574590000
C	-2.725744000	-1.119312000	-0.020541000
C	-3.397188000	0.077201000	-0.403587000
C	-2.664501000	1.267918000	-0.697045000
H	-3.242449000	2.125245000	-1.053076000
C	-3.509060000	-2.266153000	0.217785000
C	-4.801441000	0.085529000	-0.528775000
H	-5.290601000	1.008302000	-0.823792000
C	-4.881841000	-2.222921000	0.095194000
H	-5.459124000	-3.119263000	0.292770000
C	2.393933000	0.876320000	-1.193600000
H	2.978123000	1.614718000	-1.748174000
C	0.535327000	2.266968000	-1.696427000
H	0.267660000	2.001671000	-2.724786000
H	1.242290000	3.099434000	-1.727024000
C	-0.728221000	2.645491000	-0.925496000
H	-0.455906000	3.167829000	-0.005189000
H	-1.375599000	3.297193000	-1.518426000
C	1.064775000	2.038306000	1.962896000
C	-5.545151000	-1.044011000	-0.279718000
C	3.105908000	-0.257306000	-0.712403000
C	2.419462000	-1.343864000	-0.093466000
C	4.502895000	-0.327435000	-0.909553000
H	5.003268000	0.511055000	-1.382962000
C	4.540381000	-2.502715000	0.088917000
H	5.100557000	-3.376204000	0.403748000
C	3.178155000	-2.470680000	0.288473000

C	5.220536000	-1.428230000	-0.511642000
H	-6.623276000	-1.027360000	-0.372019000
H	-2.994711000	-3.174451000	0.504546000
H	6.291630000	-1.473133000	-0.659263000
H	2.653243000	-3.295772000	0.752486000
O	1.773831000	2.915969000	1.646001000
P	0.052217000	0.828068000	2.443193000

2a'-THF

E: -1808.24317665

Al	-0.000522000	0.047948000	-0.087365000
P	-0.994662000	4.291151000	0.503362000
O	1.395525000	-0.300157000	-1.185808000
O	-0.317752000	1.821095000	-0.674005000
O	-1.279147000	-0.689353000	-1.142059000
N	-1.314055000	0.213552000	1.418735000
N	1.242645000	0.733609000	1.342439000
C	2.645271000	0.082225000	-1.155732000
C	3.243200000	0.706423000	-0.019063000
C	2.491046000	1.004014000	1.162969000
H	3.033427000	1.517667000	1.961528000
C	3.463056000	-0.148850000	-2.282101000
C	4.606248000	1.067738000	-0.056848000
H	5.037076000	1.549544000	0.815005000
C	4.792017000	0.217325000	-2.284296000
H	5.390902000	0.031684000	-3.169077000
C	-2.587558000	0.311925000	1.242451000
H	-3.215273000	0.592092000	2.092345000
C	-0.720252000	0.421814000	2.734084000
H	-0.483509000	-0.558039000	3.161467000
H	-1.405895000	0.938709000	3.411243000
C	0.564137000	1.229498000	2.544055000
H	0.301659000	2.278603000	2.373531000
H	1.207992000	1.162462000	3.425769000
C	-0.615576000	2.904501000	-0.154154000
C	5.381154000	0.830415000	-1.167766000
C	-3.262248000	0.049474000	0.006807000
C	-2.568957000	-0.461650000	-1.132821000
C	-4.656586000	0.251587000	-0.055250000
H	-5.160950000	0.646498000	0.820627000
C	-4.691594000	-0.547459000	-2.308960000
H	-5.245171000	-0.776197000	-3.212991000
C	-3.330074000	-0.762218000	-2.280918000
C	-5.371968000	-0.034169000	-1.194143000
H	6.424464000	1.117374000	-1.185534000
H	3.003855000	-0.614609000	-3.144901000
H	-6.440383000	0.133658000	-1.232378000
H	-2.801827000	-1.150076000	-3.142775000
O	0.314608000	-1.963829000	0.755069000
C	-0.701690000	-3.001774000	0.625798000
C	1.617623000	-2.571158000	0.977910000
C	-0.037472000	-4.276207000	1.128003000
H	-1.567576000	-2.693413000	1.209681000
H	-0.985974000	-3.065339000	-0.423954000
C	1.424677000	-4.060277000	0.720624000
H	2.330795000	-2.102121000	0.306429000
H	1.908062000	-2.372754000	2.013185000
H	-0.480925000	-5.167996000	0.684581000
H	-0.124600000	-4.358010000	2.214592000
H	1.560575000	-4.281752000	-0.340158000
H	2.127264000	-4.669802000	1.289417000

3‘-I (O-bound isomer)

E: -3258.02326076

O	-1.487051000	-1.361868000	0.239254000
O	1.190746000	-1.504889000	0.271465000
N	1.154525000	0.797991000	-1.299332000
N	-1.394140000	1.202217000	-0.842415000
C	-2.787901000	-1.193318000	0.155459000
C	-3.419073000	-0.022317000	-0.361422000
C	-2.677979000	1.092734000	-0.861699000
H	-3.260689000	1.907012000	-1.301929000
C	-3.617062000	-2.250978000	0.582252000
C	-4.828900000	0.040063000	-0.421615000
H	-5.287620000	0.939609000	-0.818951000
C	-4.989569000	-2.152834000	0.514936000
H	-5.596878000	-2.982401000	0.859229000
C	2.430653000	0.583874000	-1.359726000
H	3.027295000	1.240978000	-1.997661000
C	0.542915000	1.844730000	-2.118627000
H	0.255820000	1.410418000	-3.082216000
H	1.244510000	2.662012000	-2.303222000
C	-0.706586000	2.360197000	-1.396740000
H	-0.404242000	3.011839000	-0.571013000
H	-1.347447000	2.923282000	-2.080983000
C	0.590335000	1.999337000	1.819798000
C	-5.613670000	-1.000920000	0.011041000
C	3.141918000	-0.447807000	-0.684926000
C	2.484669000	-1.454099000	0.089090000
C	4.547987000	-0.490794000	-0.837007000
H	5.026030000	0.283979000	-1.427311000
C	4.650364000	-2.472848000	0.496313000
H	5.235971000	-3.259838000	0.958296000
C	3.284358000	-2.467164000	0.662082000
C	5.301015000	-1.479269000	-0.256598000
H	-6.692820000	-0.936572000	-0.036079000
H	-3.131774000	-3.137333000	0.970112000
H	6.376331000	-1.497749000	-0.375583000
H	2.780784000	-3.229223000	1.242753000
Ga	-0.087312000	-0.125030000	0.030113000
O	0.130900000	0.843906000	1.686753000
P	1.165406000	3.452650000	2.016522000

3‘

E: -3258.03683942

O	-1.474521000	-1.275274000	0.095524000
O	1.183726000	-1.437167000	0.020668000
N	1.147846000	1.109240000	-1.086306000
N	-1.408150000	1.413867000	-0.606691000
C	-2.769095000	-1.132253000	-0.035890000
C	-3.412802000	0.080769000	-0.430143000
C	-2.680753000	1.270054000	-0.736113000
H	-3.264154000	2.114808000	-1.116437000
C	-3.589349000	-2.258648000	0.197737000
C	-4.817891000	0.113926000	-0.566673000
H	-5.283136000	1.046189000	-0.870791000
C	-4.957956000	-2.186994000	0.063362000
H	-5.555802000	-3.070454000	0.258339000
C	2.415992000	0.894534000	-1.226238000
H	3.001836000	1.629825000	-1.785666000
C	0.529801000	2.255699000	-1.750138000
H	0.250174000	1.961483000	-2.767455000
H	1.221605000	3.100155000	-1.814336000
C	-0.733866000	2.646253000	-0.976836000

H	-0.453748000	3.181997000	-0.065608000
H	-1.373157000	3.298746000	-1.578853000
C	1.053827000	2.015696000	2.003989000
C	-5.591635000	-0.994278000	-0.321129000
C	3.133582000	-0.236540000	-0.740122000
C	2.472837000	-1.365680000	-0.160774000
C	4.536531000	-0.260049000	-0.916190000
H	5.014469000	0.606866000	-1.361046000
C	4.636788000	-2.458057000	0.019739000
H	5.220587000	-3.322013000	0.317855000
C	3.272639000	-2.475932000	0.197184000
C	5.288569000	-1.343715000	-0.538273000
H	-6.668041000	-0.951954000	-0.424216000
H	-3.097582000	-3.177447000	0.490673000
H	6.362480000	-1.346118000	-0.671485000
H	2.768991000	-3.332332000	0.626928000
O	1.703443000	2.937181000	1.698096000
P	0.124071000	0.735650000	2.494379000
Ga	-0.071224000	0.012165000	0.199423000

3. Single-Crystal X-ray Structure Determinations

Crystal data and structure refinement for 2a CCDC 1860668.	
Identification code	2a CCDC 1860668
Empirical formula	$C_{33}H_{46}AlN_2O_3P$
Formula weight	576.67
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.0738(7)
b/Å	10.0930(4)
c/Å	35.0786(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6753.0(4)
Z	8
ρ_{calc}g/cm^3	1.134
μ/mm^{-1}	0.140
F(000)	2480.0
Crystal size/mm^3	0.55 × 0.35 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.644 to 74.162
Index ranges	-32 ≤ h ≤ 28, -17 ≤ k ≤ 17, -58 ≤ l ≤ 59
Reflections collected	109152
Independent reflections	17240 [R_{int} = 0.0393, R_{sigma} = 0.0289]
Data/restraints/parameters	17240/0/373
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0472, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1232
Largest diff. peak/hole / e Å^{-3}	0.49/-0.56

Crystal data and structure refinement for 2a-THF CCDC 1860669.	
Identification code	2a-THF CCDC 1860669
Empirical formula	$C_{54.5}H_{74}AlN_2O_4P$
Formula weight	879.10
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9542(6)
b/Å	15.5877(11)
c/Å	17.6774(11)
α/°	80.140(6)
β/°	81.069(5)
γ/°	73.920(6)
Volume/Å^3	2579.7(3)
Z	2
ρ_{calc}g/cm^3	1.132
μ/mm^{-1}	0.115
F(000)	950.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.366 to 52.74
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -21 ≤ l ≤ 22
Reflections collected	21744
Independent reflections	10538 [R_{int} = 0.0683, R_{sigma} = 0.1448]
Data/restraints/parameters	10538/0/559
Goodness-of-fit on F^2	1.034

Final R indexes [I>=2σ (I)]	R_1 = 0.0854, wR_2 = 0.1831
Final R indexes [all data]	R_1 = 0.1577, wR_2 = 0.2318
Largest diff. peak/hole / e Å^{-3}	0.65/-0.48

Crystal data and structure refinement for 3 CCDC 1860673.	
Identification code	3 CCDC 1860673
Empirical formula	$C_{33}H_{46}GaN_2O_3P$
Formula weight	619.41
Temperature/K	100.01(18)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.4606(2)
b/Å	15.6198(3)
c/Å	18.0911(3)
α/°	90
β/°	102.324(2)
γ/°	90
Volume/Å^3	3163.90(10)
Z	4
ρ_{calc}g/cm^3	1.300
μ/mm^{-1}	0.955
F(000)	1312.0
Crystal size/mm^3	0.06 × 0.04 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.48 to 56.564
Index ranges	-15 ≤ h ≤ 13, -20 ≤ k ≤ 20, -24 ≤ l ≤ 23
Reflections collected	24123
Independent reflections	7848 [R_{int} = 0.0474, R_{sigma} = 0.0548]
Data/restraints/parameters	7848/0/373
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1079
Final R indexes [all data]	R_1 = 0.0597, wR_2 = 0.1161
Largest diff. peak/hole / e Å^{-3}	1.07/-0.47

Crystal data and structure refinement for 6 CCDC 1860732.	
Identification code	6 CCDC 1860732
Empirical formula	$C_{45}H_{60}AlN_8O_3P$
Formula weight	818.96
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	10.5943(2)
b/Å	14.5344(3)
c/Å	16.0916(3)
α/°	68.0520(10)
β/°	82.4710(10)
γ/°	74.7440(10)
Volume/Å^3	2215.76(8)
Z	2
ρ_{calc}g/cm^3	1.227
μ/mm^{-1}	1.127
F(000)	876.0
Crystal size/mm^3	0.15 × 0.07 × 0.07
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.926 to 144.424
Index ranges	-12 ≤ h ≤ 13, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	32836
Independent reflections	8663 [R_{int} = 0.0463, R_{sigma} = 0.0388]
Data/restraints/parameters	8663/0/539

Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1234
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.31

Crystal data and structure refinement for 4 CCDC 1860759.	
Identification code	imidazolium OCP CCDC 1860759
Empirical formula	$C_{12}H_{21}N_2OP$
Formula weight	240.28
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.2221(4)
b/Å	7.4477(4)
c/Å	22.3476(12)
α/°	90
β/°	92.833(2)
γ/°	90
Volume/$Å^3$	1366.80(12)
Z	4
$\rho_{calc}g/cm^3$	1.168
μ/mm^{-1}	0.185
F(000)	520.0
Crystal size/mm^3	0.32 × 0.22 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.2 to 56.556
Index ranges	-10 ≤ h ≤ 10, -9 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	10929
Independent reflections	3343 [R_{int} = 0.0417, R_{sigma} = 0.0470]
Data/restraints/parameters	3343/0/155
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0861
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.0926
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.26

Crystal data and structure refinement for 4H CCDC 1876471.	
Identification code	imidazolium OCP CCDC 1876471
Empirical formula	$C_{10}H_{17}N_2OP$
Formula weight	212.22
Temperature/K	104(6)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.2080(2)
b/Å	14.4448(3)
c/Å	11.7071(3)
α/°	90
β/°	100.729(3)
γ/°	90
Volume/$Å^3$	1197.61(5)
Z	4
$\rho_{calc}g/cm^3$	1.177
μ/mm^{-1}	0.203
F(000)	456.0
Crystal size/mm^3	0.55 × 0.25 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.526 to 56.556
Index ranges	-9 ≤ h ≤ 9, -19 ≤ k ≤ 19, -15 ≤ l ≤ 15
Reflections collected	17624
Independent reflections	2978 [R_{int} = 0.0420, R_{sigma} = 0.0246]
Data/restraints/parameters	2978/0/131
Goodness-of-fit on F^2	1.096

Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1002
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.1032
Largest diff. peak/hole / e Å^{-3}	0.34/-0.23

4. References

S1 D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.*, 2013, **43**, 831–840.

S2 D. Rutherford, D. A. Atwood, *Organometallics*, 1996, **15**, 4417–4422.

S3 D. J. Darensbourg, D. R. Billodeaux, *C. R. Chimie,* 2004, **7**, 755–761.

S4 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

S5 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.

S6 a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650–654; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* 1980, **72**, 5639–5648; c) R. C. Binning and L. A. Curtiss, *J. Comput. Chem.*, 1990, **11**, 1206–1216; d) L. A. Curtiss, M. P. McGrath, J. Blaudeau, N. E. Davis, R. C. Binning and L. Radom, *J. Chem. Phys.*, 1995, **103**, 6104–6113.

S7 For the polarization functions, see: M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* 1984, **80**, 3265–3269.

S8 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.

S9 a) F. London, *J. Phys. Radium*, 1937, **8**, 397–409; b) R. McWeeny, *Phys. Rev.*, 1962, **126**, 1028–1034; c) R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789–807; d) J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys.*, 1996, **104**, 5497–5509; e) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.

S10 C. J. Jameson, A. De Dios and A. Keith Jameson, *Chem. Phys. Lett.*, 1990, **167**, 575–582.

S11 C. van Wüllen, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2137–2144.