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1. Synthesis of Compounds (IL_1, IL_2, IL_1-$OPPh_2$, IL_2-$OPPh_2$, 1-6) [1,2]

1.1. (IL_1, IL_2, IL_1-$OPPh_2$, IL_2-$OPPh_2$, 1-6) were prepared according to the literature procedures.

1.1.1. Synthesis of 3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride, (IL_1): IR (cm^{-1}): υ 3369 (O-H), 3116, 3041 (aromatic C-H), 2989, 2888 (aliphatic C-H), 1575 (C=N), 1162 (C-N) cm^{-1}; Anal. for $C_8H_{12}Cl_2N_2O$ (223.10 g/mol): calcd. C 43.07, H 5.42, N 12.56; found C 42.98, H 5.36, N 12.51; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 9.46 (s, 1H, –NC<u>H</u>N^+–), 8.19 and 7.85 (2xs, 2H, –NC<u>H</u>C<u>H</u>N–), 7.35-7.29 (m, 1H –C<u>H</u>=CH_2), 6.05 (bs, 1H, –CHO<u>H</u>), 5.98-5.94 (m, 1H, –CH=C<u>H</u>$_2$ (a)), 5.44-5.41 (m, 1H, –CH=C<u>H</u>$_2$ (b)), 4.42-4.39 (m, 1H, –N^+C<u>H</u>$_2$ (a)), 4.20-4.15 (m, 1H, –N^+C<u>H</u>$_2$ (b)), 4.10 (br, 1H –CHOH), 3.45 (m, 2H,–C<u>H</u>$_2$Cl); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ 136.43 (–N<u>C</u>HN^+–), 129.22 (–N<u>C</u>H=CH_2), 124.46, 119.20 (–N<u>C</u>H<u>C</u>HN^+–), 109.21 (–NCH=<u>C</u>H_2), 68.86 (–<u>C</u>HOH), 52.99 (–N^+<u>C</u>H_2CH(OH)), 46.91 (–<u>C</u>H_2Cl).

1.1.2. Synthesis of 3-(3-chloro-2-hydroxypropyl)-1-butyl-1H-imidazol-3-ium chloride, (IL_2): IR (cm^{-1}): υ 3372 (O-H), 3134, 3067 (aromatic C-H), 2959, 2870 (aliphatic C-H), 1561 (C=N), 1162 (C-N) cm^{-1}; Anal. for $C_{10}H_{18}Cl_2N_2O$ (253.17g/mol): calcd. C 47.44, H 7.17, N 11.07; found C 47.40, H 7.12, N 11.02; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 9.33 (s, 1H, –NC<u>H</u>N^+–), 7.84 and 7.80 (2xs, 2H, –NC<u>H</u>C<u>H</u>N^+–), 6.23 (bs, 1H, –CHO<u>H</u>), 4.50-4.39 (m, 1H, –N^+C<u>H</u>$_2$ (a)), 4.22-4.18 (m, 3H, –N^+C<u>H</u>$_2$ (b) + –NC<u>H</u>$_2$$CH_2$$CH_2$$CH_3$), 4.08-4.01 (m, 1H –C<u>H</u>OH), 3.65 (d, 2H, J = 5.2 Hz, –C<u>H</u>$_2$Cl), 1.81-1.74 (m, 2H, –NCH_2C<u>H</u>$_2$$CH_2$$CH_3$), 1.30-1.21 (m, 2H, –$NCH_2CH_2$C<u>H</u>$_2$$CH_3$), 0.90 (t, 3H, J = 7.4 Hz, –$NCH_2CH_2CH_2$C<u>H</u>$_3$); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ: 137.23 (–N<u>C</u>HN^+–), 123.65, 122.57 (–N<u>C</u>H<u>C</u>HN^+–), 69.02 (–<u>C</u>HOH), 52.34 (–N^+<u>C</u>H_2CH(OH)), 48.95 (–N<u>C</u>$H_2$$CH_2$$CH_2$$CH_3$), 46.93 (–<u>C</u>$H_2$Cl), 31.80 (–$NCH_2$<u>C</u>$H_2$$CH_2$$CH_3$), 19.23 (–$NCH_2CH_2$<u>C</u>$H_2$$CH_3$), 13.77 (–$NCH_2CH_2CH_2$<u>C</u>$H_3$).

1.1.3.Synthesis of 3-(3-chloro-2-((diphenylphosphaneyl)oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride (IL_1-$OPPh_2$) and 3-(3-chloro-2-((diphenylphosphaneyl)oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride (IL_2-$OPPh_2$): A dry and degassed CH_2Cl_2 (20 mL) solution of 3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride, IL_1 (0.105 g, 0.47 mmol) or 3-(3-chloro-2-hydroxypropyl)-1-butyl-1H-imidazol-3-ium chloride, IL_2 (0.119 g, 0.47 mmol) under argon atmosphere was cooled to −78 °C in acetone and dry ice bath. To the cooled solution was added dropwise a hexane solution of *n*-BuLi (0.293 mL, 0.47 mmol). After the addition, the mixture was stirred at −78 °C for 1 h and additional 45 minutes at room temperature. The reaction solution was cooled to −78 °C again and a solution of diphenylchlorophosphine (0.106 g, 0.47 mmol) in CH_2Cl_2 (10 mL) was added dropwise to the reaction medium. Stirring was continued for a further 1 h at −78 °C. Then the cooling bath was removed and the mixture was stirred for 3 h at room temperature. The reaction was followed by ^{31}P NMR spectroscopy. After ligand formation was observed, the precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated in vacuo to leave a viscous oil phosphinite ligand, **IL_1-$OPPh_2$** and **IL_2-$OPPh_2$**. ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm): δ 119.20 (s, O<u>P</u>Ph_2) and 119.17 (s, O<u>P</u>Ph_2), respectively.

1.1.4.General procedure for the synthesis of (IL-$OPPh_2$-Metal) complexes (1-6)

Metal precursor (0.20 mmol) and **IL_1-$OPPh_2$** or **IL_2-$OPPh_2$** (0.40 mmol) were dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere. The reaction mixture was allowed to proceed under stirring at room temperature for 1 h. After the reaction, the solvent of the solution was reduced to 1-2 mL under vacuum, and the addition of petroleum ether (15 mL) caused precipitation of the corresponding metal complexes as microcrystalline solid. The solid was collected by filtration and dried in vacuo.

1.1.4.1. [3-(3-chloro-2-({[dichloro(η^6-benzene)ruthenium]diphenylphosphanyl}oxy) propyl)- 1-vinyl-1H-imidazol-3-ium chloride], (1); Clear red solid product (245 mg, 93.2%). M.p.:135-136 °C decomposition; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 9.97 (br, 1H, –NC<u>H</u>N$^+$–), 8.00-7.53 (m, 13H, –P(C_6H_5)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$– + –C<u>H</u>=CH$_2$), 5.93 (br, 1H, CH=C<u>H</u>$_2$ (a)), 5.49 (s, 6H, aromatic protons of benzene), 5.36 (br, 1H, CH=C<u>H</u>$_2$(b)), 5.13 (br, 1H, –C<u>H</u>OP), 4.62 (br, 2H, –N$^+$C<u>H</u>$_2$), 3.49 (br, 2H, –C<u>H</u>$_2$Cl); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ:139.48 (–N<u>C</u>HN$^+$–), 137.23 (d, *J_{P-C}=52.2 Hz, i*-P(<u>C</u>$_6$H$_5$)$_2$), 133.78 (d, *J_{P-C}=20.1 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 131.45 (–N<u>C</u>H=CH$_2$), 128.88 (d, *J_{P-C}=3.2 Hz, p*-P(<u>C</u>$_6$H$_5$)$_2$), 128.75 (d, *J_{P-C}=9.2 Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 123.97, 122.63 (–N<u>C</u>H<u>C</u>HN$^+$–), 109.98 (–NCH=<u>C</u>H$_2$), 90.40 (aromatic carbons of benzene), 73.84 (–<u>C</u>HOP), 53.56 (–N$^+$<u>C</u>H$_2$CH(OP)), 44.81 (–<u>C</u>H$_2$Cl), ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) *δ*: 123.91 (s, O<u>P</u>Ph$_2$); IR (cm^{-1}); υ 3052 (aromatic C-H), 2959, 2872 (aliphatic C–H), 1435 (P-Ph), 1043 (O-P), 529 (Ru-P); Anal. for $C_{26}H_{27}Cl_4N_2OPRu$ (657.36 g/mol): calcd. C 47.51, H 4.14, N 4.26; found C 47.43, H 4.07, N 4.19 %.

1.1.4.2. [3-(3-chloro-2-({[dichloro(η^6-p-cymene)ruthenium]diphenylphosphanyl}oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride], (2); Clear red solid product (260 mg, 91.1%). M.p.:136-138 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 10.63 (s, 1H, –NC<u>H</u>N$^+$–), 7.97-7.52 (m, 13H, –P(C_6H_5)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$– + –C<u>H</u>=CH$_2$), 5.89 (d, 1H, *J=15.6 Hz*, CH=C<u>H</u>$_2$ (a)), 5.52 (dd, 2H, *J=13.6 Hz, J=6.4 Hz*, aromatic protons of *p*-cymene), 5.37 (d, 1H, *J =6.0 Hz*, CH=C<u>H</u>$_2$ (b)), 5.19 (d, 1H, *J=5.2 Hz*, aromatic proton of *p*-cymene), 4.94 (d, 1H, *J=5.6 Hz*, aromatic proton of *p*-cymene), 4.82-4.67 (m, 3H, –N$^+$C<u>H</u>$_2$ + –C<u>H</u>OP), 3.47-3.39 (m, 2H,–C<u>H</u>$_2$Cl), 2.50 (m, 1H, C<u>H</u>(CH$_3$)$_2$ of *p*-cymene); 1.92 (s, 3H, C<u>H</u>$_3$Ph of *p*-cymene), 1.07 (d, 3H, *J=6.8 Hz*, (C<u>H</u>$_3$)$_2$CH Ph of *p*-cymene), 0.74 (d, 3H, *J=6.8 Hz*, (C<u>H</u>$_3$)$_2$CH Ph of *p*-cymene); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ: 138.08 (–N<u>C</u>HN$^+$–), 137.54 (d, *J_{P-C}=52.3 Hz, i*-P(<u>C</u>$_6$H$_5$)$_2$), 134.41 (d, *J_{P-C}=12.3 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 133.41 (d, *J_{P-C}=6.2 Hz, p*-P(<u>C</u>$_6$H$_5$)$_2$), 131.63 (d, *J_{P-C}=10.2 Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 128.80 (–N<u>C</u>H=CH$_2$), 128.39, 124.63 (–N<u>C</u>H<u>C</u>HN$^+$–), 109.59 (–NCH=<u>C</u>H$_2$), 110.60, 96.54 (quaternary carbons of *p*-cymene), 94.11 (d, *J_{P-C}=7.0 Hz*, aromatic carbons of *p*-cymene), 89.77 (d, *J_{P-C}=9.1 Hz*, aromatic carbons of *p*-cymene), 88.55 (s, aromatic carbon of *p*-cymene), 85.68 (s, aromatic carbon of *p*-cymene), 74.29 (d, *J_{P-C}=9.1 Hz*, (–<u>C</u>HOP)), 53.47 (–N$^+$<u>C</u>H$_2$CH(OP)), 43.68 (–<u>C</u>H$_2$Cl), 30.06 (–<u>C</u>H(CH$_3$) of *p*-cymene), 22.32, 22.49 (–CH(<u>C</u>H$_3$)$_2$ of *p*-cymene), 17.27 (–<u>C</u>H$_3$ of *p*-cymene), ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) *δ*: 126.20 (s, O<u>P</u>Ph$_2$); IR (cm^{-1}); υ 3049 (aromatic C-H), 2955, 2866 (aliphatic C–H), 1435 (P-Ph), 1043 (O-P), 533 (Ru-P); Anal. for $C_{30}H_{35}Cl_4N_2OPRu$ (713.47 g/mol): calcd. C 50.50, H 4.94, N 3.93; found C 50.41, H 4.82, N 3.86 %.

1.1.4.3. [3-(3-chloro-2-({[dichloro(η^5-pentamethylcyclopentadienyl)iridium]diphenyl phosphanyl}oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride], (3); Orange microcrystalline solid product (290 mg, 90.0 %) M.p.: 158–160 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 9.40 (s, 1H, –NC<u>H</u>N$^+$–), 7.82-7.31 (m, 13H, –P(C_6H_5)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$– + –C<u>H</u>=CH$_2$), 5.96 (d, 1H, *J = 16 Hz*, CH=C<u>H</u>$_2$ (a)), 5.35 (d, 1H, *J = 6 Hz*, CH=C<u>H</u>$_2$ (b)), 4.77-4.63 (m, 3H, –N$^+$C<u>H</u>$_2$ + –C<u>H</u>OP), 3.34 (br, 2H, –C<u>H</u>$_2$Cl), 1.25 (s, 15H, C_5Me_5); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ:136.91 (–N<u>C</u>HN$^+$–), 135.47 (s, *i*-P(<u>C</u>$_6$H$_5$)$_2$), 134.78 (d, *J_{P-C}=12.1 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 133.17 (d, *J_{P-C}=3.7 Hz, p*-P(<u>C</u>$_6$H$_5$)$_2$), 131.97 (d, *J_{P-C}=9.2 Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 128.56 (–N<u>C</u>H=CH$_2$), 124.49, 124.10 (–N<u>C</u>H<u>C</u>HN$^+$–), 109.66 (–NCH=<u>C</u>H$_2$), 94.24 (s, <u>C</u>$_5$Me$_5$), 74.36 (–<u>C</u>HOP), 51.08 (–N$^+$<u>C</u>H$_2$CH(OP)), 43.54 (–<u>C</u>H$_2$Cl), 8.20 (C$_5$<u>Me</u>$_5$) *assignment was based on the ^{1}H-^{13}C HETCOR, DEPT, and ^{1}H-^{1}H COSY spectra.* ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) *δ*: 96.24 (s, O<u>P</u>Ph$_2$); IR (cm^{-1}); υ 3052 (aromatic C-H), 2947, 2915 (aliphatic C–H), 1435 (P-Ph), 1043 (O-P); Anal. for $C_{30}H_{36}Cl_4N_2OPIr$ (805,62 g/mol): calcd.: C 44.73, H 4.50, N 3.48; found C 44.64, H 4.44, N 3.39 %.

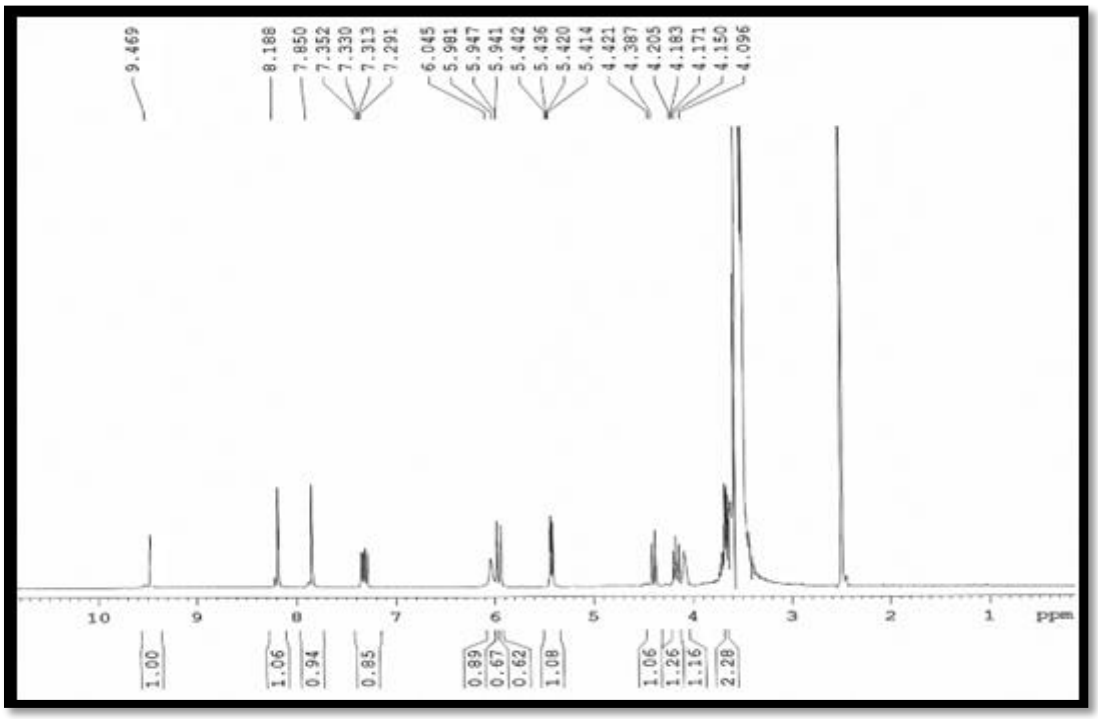
1.1.4.4. [3-(3-chloro-2-({[dichloro(η^6-benzene)ruthenium]diphenyl phosphanyl}oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride], (4); Clear red solid product (310 mg, 95.9%). M.p.:124-126 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 9.10 (s, 1H, –NC<u>H</u>N$^+$–), 7.88-7.22 (m, 12H, –P(C$_6$<u>H</u>$_5$)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$–), 5.56 (s, 6H, aromatic protons of benzene), 5.11 (br, 1H, –C<u>H</u>OP) 4.40 (m, 2H, –N$^+$C<u>H</u>$_2$CH), 4.15 (m, 2H, –NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.37 (d, 2H, *J=6.8 Hz*, –C<u>H</u>$_2$Cl), 1.79-1.74 (m, 2H, –NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.29-1.23 (m, 2H, –NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.91 (t, 3H, *J=7.0 Hz*, –NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ: 138.51 (*i*-P(<u>C</u>$_6$H$_5$)$_2$), 137.29 (–N<u>C</u>HN$^+$–), 133.67 (d, $J_{P\text{-}C}$*=12.1 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 131.77 (br, *p*-P(<u>C</u>$_6$H$_5$)$_2$), 128.82 (d, $J_{P\text{-}C}$=8.0 *Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 123.69, 122.78 (–N<u>C</u>H<u>C</u>HN$^+$–), 90.59 (aromatic carbons of benzene), 74.91 (–<u>C</u>HOP), 50.93 (–N$^+$<u>C</u>H$_2$CH(OP)), 48.99 (–NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$) 44.89 (–<u>C</u>H$_2$Cl), 31.80 (–NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 19.27 (–NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 13.78 (–NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$), ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$, ppm) *δ*: 122.57 (s, O<u>P</u>Ph$_2$);IR (cm^{-1}); υ 3056 (aromatic C-H), 2959, 2870 (aliphatic C–H), 1435 (P-Ph), 1043 (O-P), 529 (Ru-P); Anal. for C$_{28}$H$_{33}$Cl$_4$N$_2$OPRu (687.43 g/mol): calcd. C 48.92, H 4.84, N 4.08; found C 48.83, H 4.81, N 4.03 %.

1.1.4.5. [3-(3-chloro-2-({[dichloro(η^6-p-cymene)ruthenium]diphenylphosphanyl}oxy)-propyl)-1-butyl-1H-imidazol-3-ium chloride], (5); Dark red solid product (330 mg, 94.4 %). M.p.:125-127 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 10.14 (s, 1H, –NC<u>H</u>N$^+$–), 8.02-7.13 (m, 12H, –P(C$_6$<u>H</u>$_5$)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$–), 5.51 (m, 2H, aromatic protons of *p*-cymene), 5.23 (d, 1H, *J=4.0 Hz*, aromatic proton of *p*-cymene), 5.02 (d, 1H, *J=5.2 Hz*, aromatic proton of *p*-cymene), 4.91 (br, –C<u>H</u>OP), 4.64 (br, 2H, –N$^+$C<u>H</u>$_2$CH), 4.25 (br, 2H, –NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.45 (br, 2H, –C<u>H</u>$_2$Cl), 2.52 (m, 1H, C<u>H</u>(CH$_3$)$_2$ of *p*-cymene), 1.93 (m, 5H, C<u>H</u>$_3$Ph of *p*-cymene + –NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.44-1.35 (m, 2H, –NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 1.09 (d, 3H, *J=6.8 Hz*, (C<u>H</u>$_3$)$_2$CH Ph of *p*-cymene), 0.97 (t, 3H, *J=7.2 Hz*, –NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), 0.82 (d, 3H, *J=7.2 Hz*, (C<u>H</u>$_3$)$_2$CH Ph of *p*-cymene); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ: 138.15, 137.61 (–N<u>C</u>HN$^+$– + *i*-P(<u>C</u>$_6$H$_5$)$_2$), 134.15 (d, $J_{P\text{-}C}$*=12.1 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 131.51 (d, $J_{P\text{-}C}$*=11.1 Hz, p*-P(<u>C</u>$_6$H$_5$)$_2$), 128.74 (d, $J_{P\text{-}C}$*=10.1 Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 124.89, 122.56 (–N<u>C</u>H<u>C</u>HN$^+$–), 110.84, 96.92 (quaternary carbons of *p*-cymene), 93.63 (d, $J_{P\text{-}C}$*=5.0 Hz*, aromatic carbons of *p*-cymene), 89.57 (d, $J_{P\text{-}C}$*=7.0 Hz*, aromatic carbons of *p*-cymene) 88.85 (s, aromatic carbon of *p*-cymene), 86.14 (br, aromatic carbons of *p*-cymene), 74.64 (d, $J_{P\text{-}C}$*=8.0 Hz*, (–<u>C</u>HOP)), 51.55, 52.27 (–N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$ + –N$^+$<u>C</u>H$_2$CH(OP)), 44.75 (–<u>C</u>H$_2$Cl), 32.34 (–NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 30.07 (–<u>C</u>H(CH$_3$)$_2$ of *p*-cymene), 22.28, 22.41 (–CH(<u>C</u>H$_3$)$_2$ of *p*-cymene + –NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 20.65 (–CH(<u>C</u>H$_3$) of *p*-cymene), 17.39 (–<u>C</u>H$_3$ of *p*-cymene), 13.57 (–NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$), ^{31}P-{^{1}H} NMR (162.0 MHz, CDCl$_3$, ppm) *δ*: 124.87 (s, O<u>P</u>Ph$_2$); IR (cm^{-1}); υ 3056 (aromatic C-H), 2959, 2870 (aliphatic C–H), 1435 (P-Ph), 1047 (O-P), 536 (Ru-P); Anal. for C$_{32}$H$_{41}$Cl$_4$N$_2$OPRu (743.54 g/mol): calcd. C 51.69, H 5.56, N 3.77; found C 51.61, H 5.52, N 3.86 %.

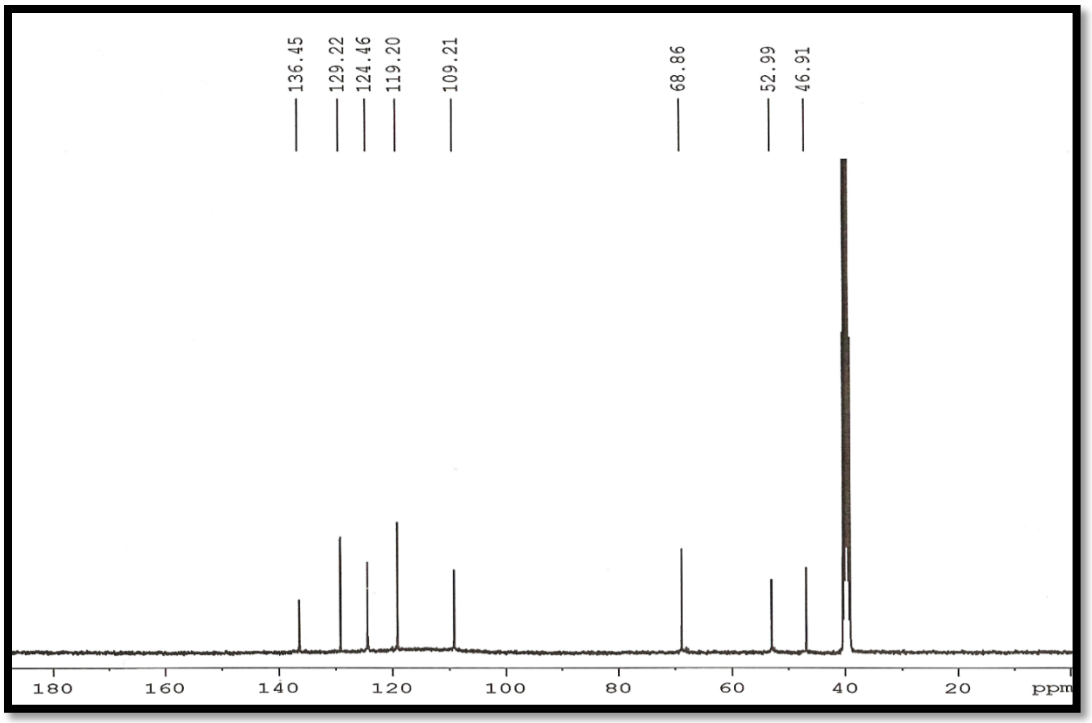
1.1.4.6. [3-(3-chloro-2-({[dichloro(η^5-pentamethylcyclopentadienyl)iridium]diphenyl phosphanyl}oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride], (6); Yellow microcrystalline solid (350 mg, 89.1 %). M.p.: 130–132 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm): δ: 10.10 (s, 1H, –NC<u>H</u>N$^+$–), 7.91-7.46 (m, 12H, –P(C$_6$<u>H</u>$_5$)$_2$ + –NC<u>H</u>C<u>H</u>N$^+$–), 5.27 (br, 1H, –C<u>H</u>OP), 4.75-4.70 (m, 1H, –N$^+$C<u>H</u>$_2$CH (a)), 4.61-4.58 (m, 1H, –N$^+$C<u>H</u>$_2$CH (b)), 4.33 (m, 2H, –NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.33 (br, 2H –C<u>H</u>$_2$Cl), 1.88-1.84 (m, 2H, –NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.35 (m, 17H, –NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$ + CH$_3$ of Cp*(C$_5$<u>Me</u>$_5$)), 0.95 (t, 3H, *J=7.2 Hz*, –NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm): δ: 137.94 (–N<u>C</u>HN$^+$–), (not observed *i*-P(<u>C</u>$_6$H$_5$)$_2$), 132.35 (d, $J_{P\text{-}C}$*=13.1 Hz, o*-P(<u>C</u>$_6$H$_5$)$_2$), 131.92 (*p*-P(<u>C</u>$_6$H$_5$)$_2$), 128.53 (d, $J_{P\text{-}C}$*=10.1 Hz, m*-P(<u>C</u>$_6$H$_5$)$_2$), 123.58, 121.62 (–N<u>C</u>H<u>C</u>HN$^+$–), 94.20 (s, <u>C</u>$_5$Me$_5$), 74.54 (–<u>C</u>HOP), 50.72, 49.97 (–N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$ + –N$^+$<u>C</u>H$_2$CH(OP)), 44.61 (–<u>C</u>H$_2$Cl), 32.11 (–NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 19.49 (–NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 17.47 (–

$NCH_2CH_2CH_2\underline{C}H_3$), 8.19 ($C_5\underline{Me}_5$), ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 96.15 (s, $O\underline{P}Ph_2$); IR (cm^{-1}); υ 3052 (aromatic C-H), 2959, 2866 (aliphatic C–H), 1435 (P-Ph), 1042 (O-P); Anal. for $C_{32}H_{42}Cl_4N_2OPIr$ (835.69 g/mol): calcd.: C 45.99, H 5.07, N 3.35; found C 45.94, H 5.04, N 3.31 %.

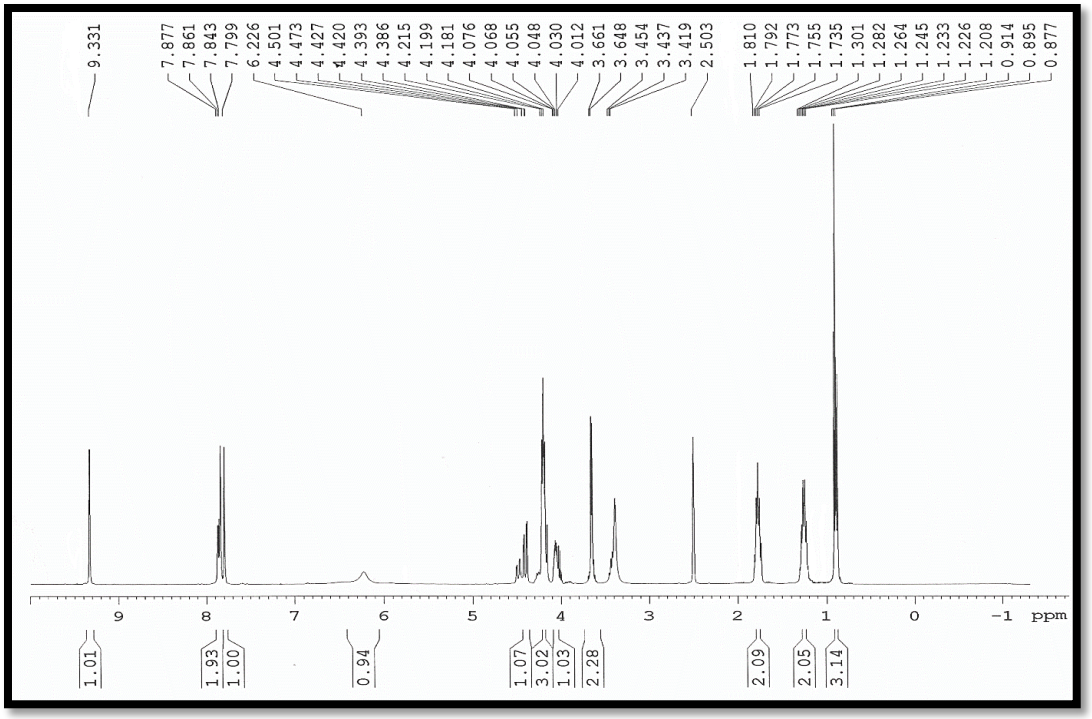
SPECTRA



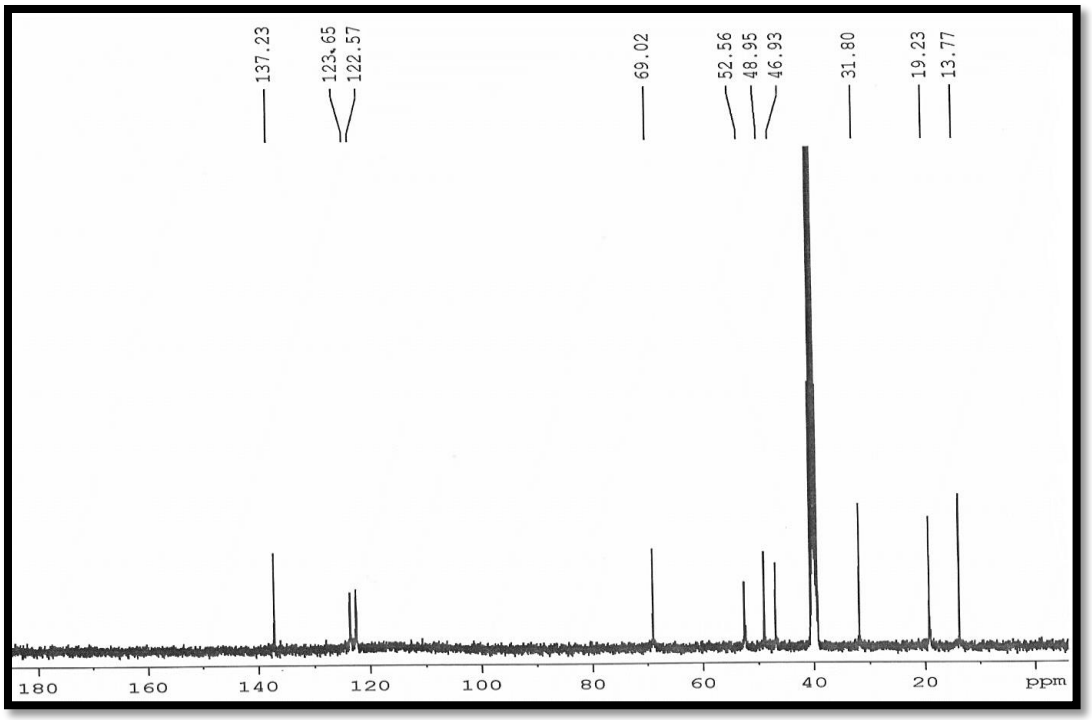
Spectrum 1. [1]H NMR spectrum of *3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride,* ***(IL$_1$)***



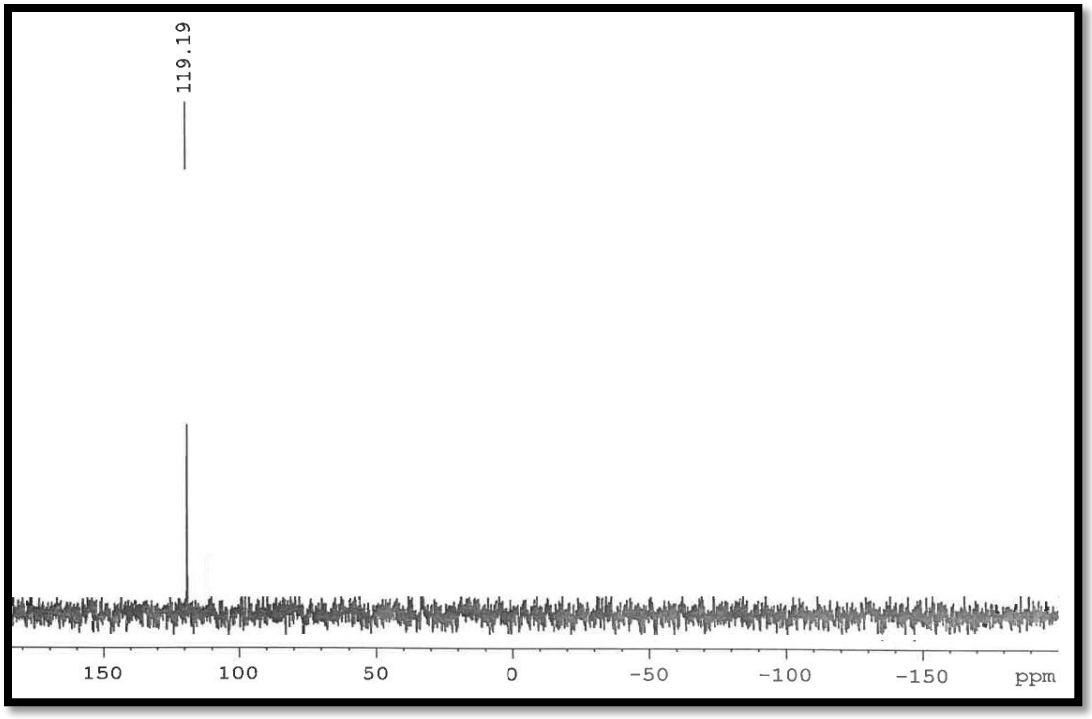
Spectrum 2. [13]C NMR spectrum of *3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride,* ***(IL$_1$).***



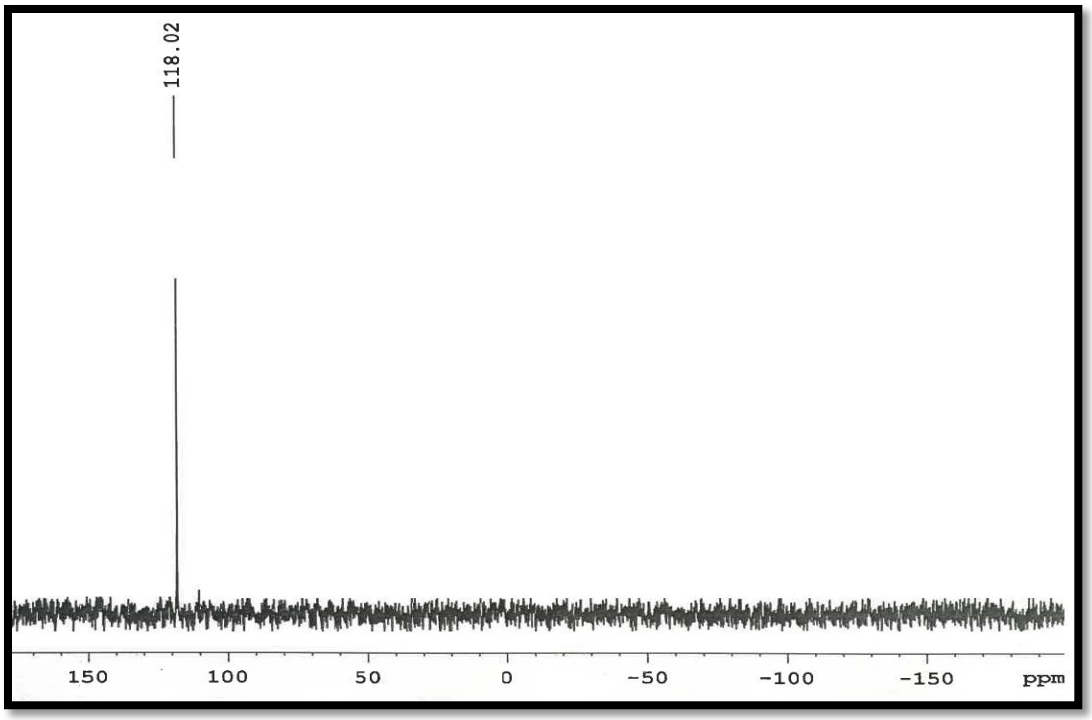
Spectrum 3. [1]H NMR spectrum of *3-(3-chloro-2-hydroxypropyl)-1-butyl-1H-imidazol-3-ium chloride,* ***(IL₂)*****.**



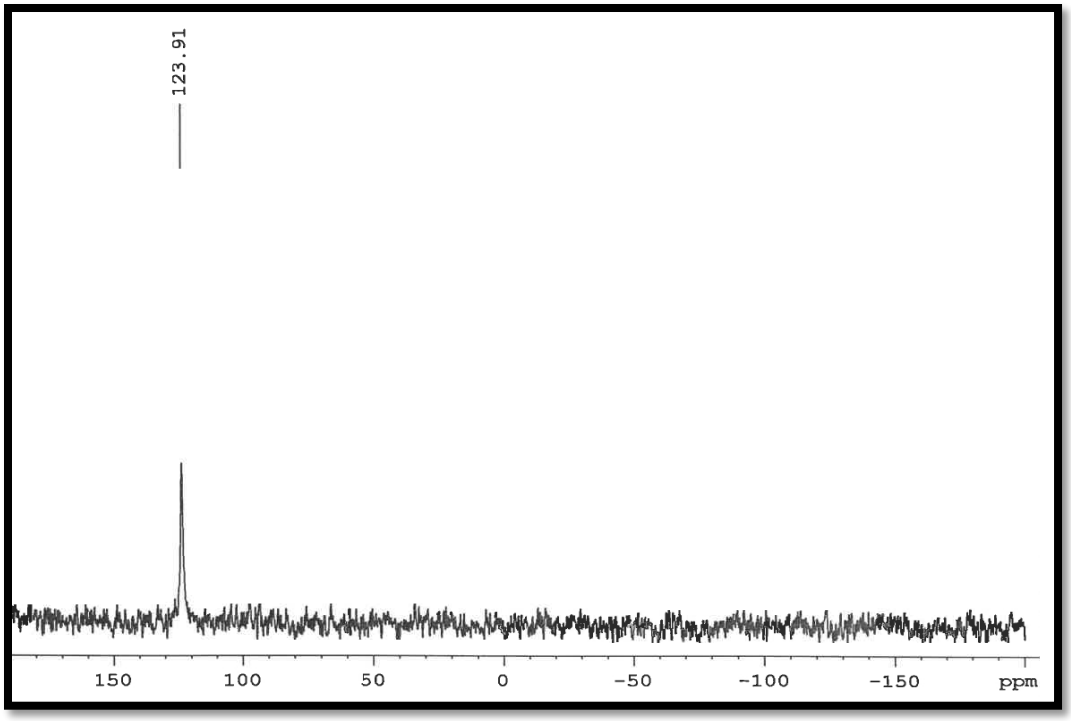
Spectrum 4. [13]C NMR spectrum of *3-(3-chloro-2-hydroxypropyl)-1-butyl-1H-imidazol-3-ium chloride,* ***(IL₂)*****.**



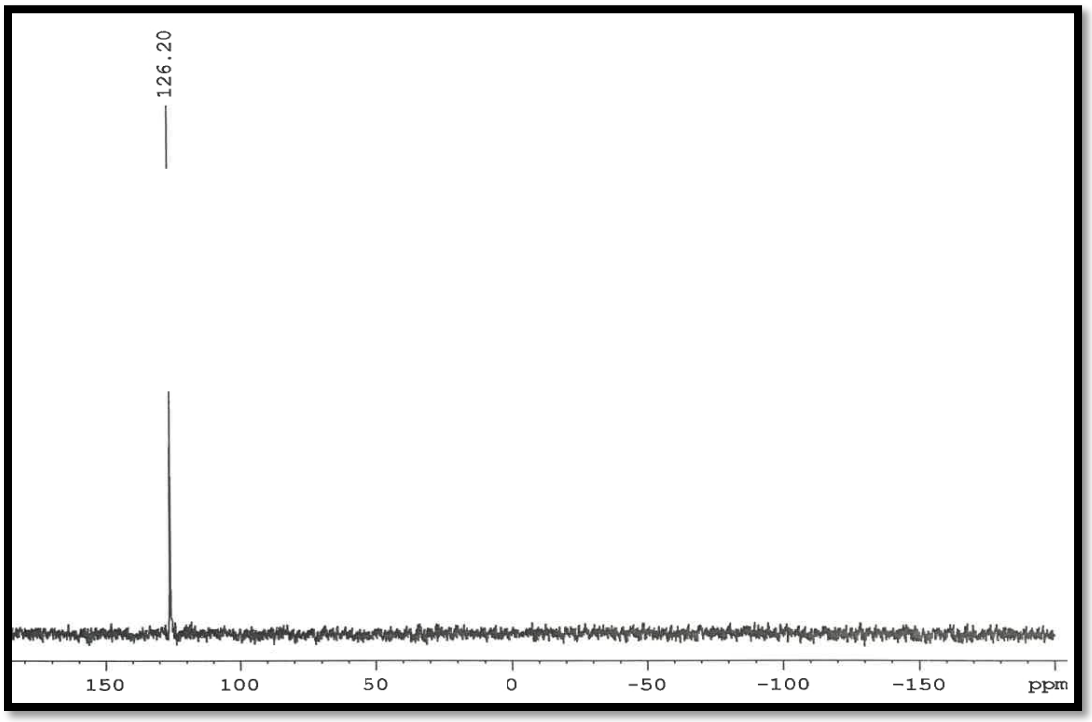
Spectrum 5. ^{31}P NMR spectrum of *3-(3-chloro-2-((diphenylphosphaneyl)oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride* ***(IL$_1$-OPPh$_2$).***



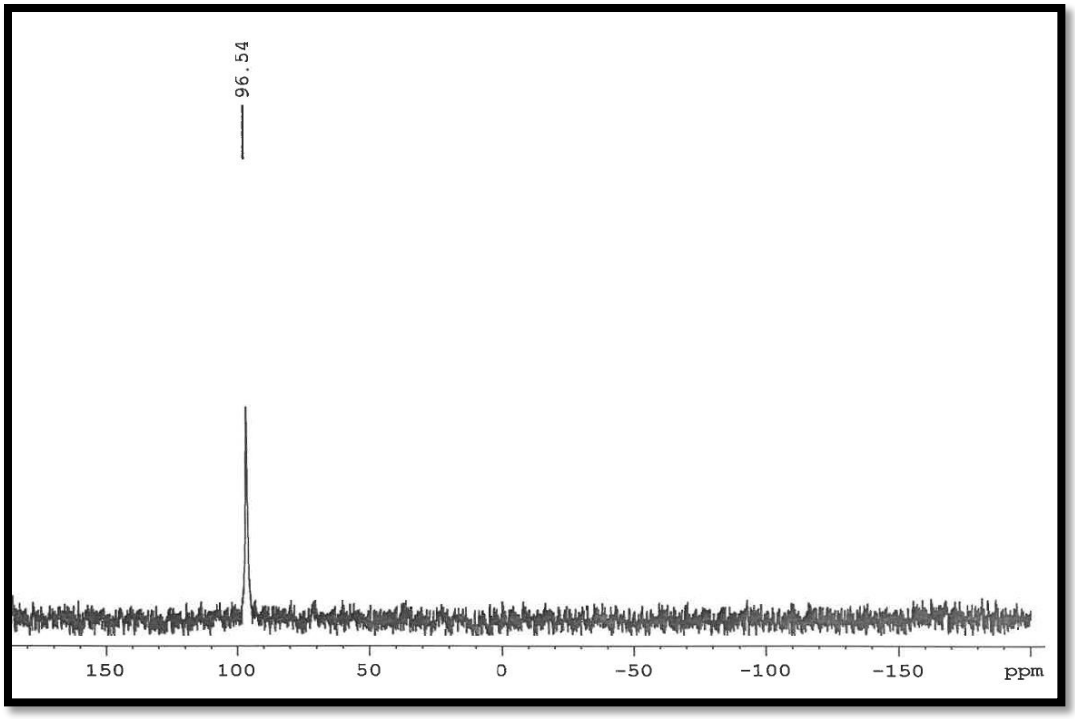
Spectrum 6. ^{31}P NMR spectrum of *3-(3-chloro-2-((diphenylphosphaneyl)oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride* ***(IL$_2$-OPPh$_2$).***



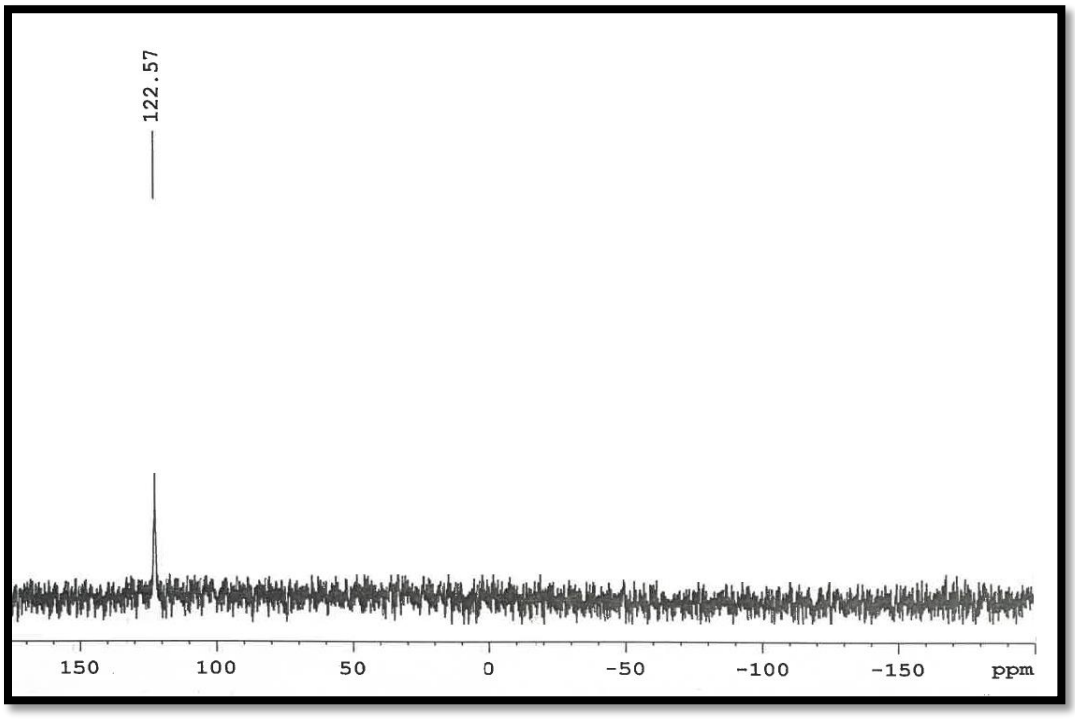
Spectrum 7. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^6-benzene)-ruthenium]diphenylphosphanyl}oxy) propyl)- 1-vinyl-1H-imidazol-3-ium chloride],* ***(1).***



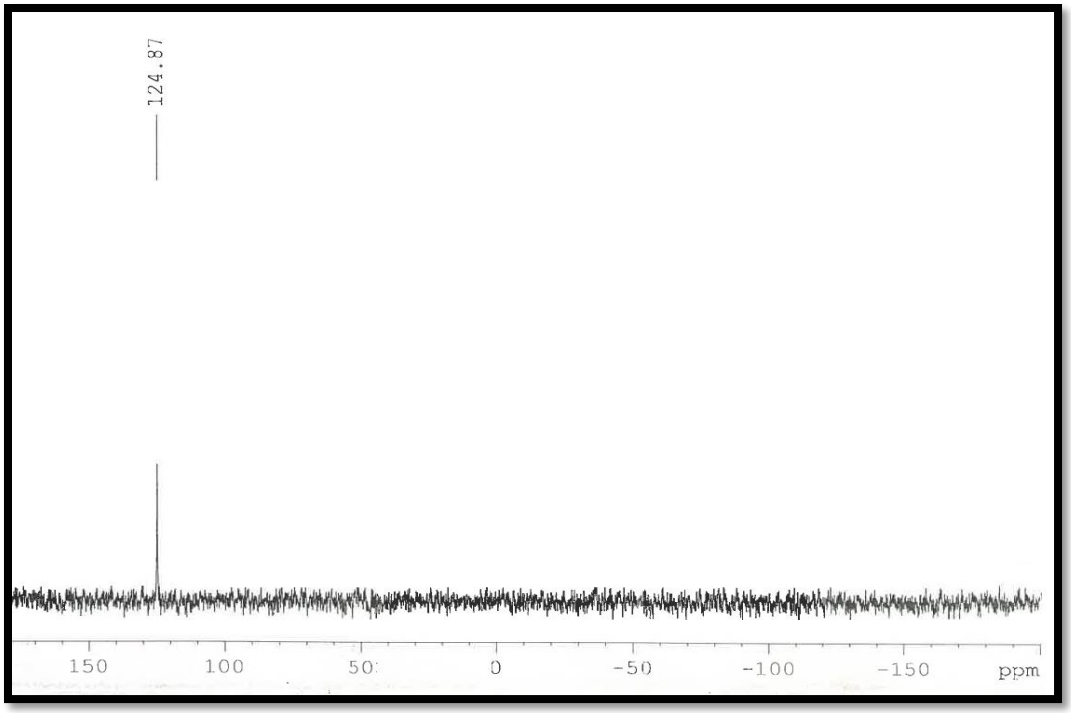
Spectrum 8. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^6-p-cymene)-ruthenium]diphenylphosphanyl}oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride],* ***(2).***



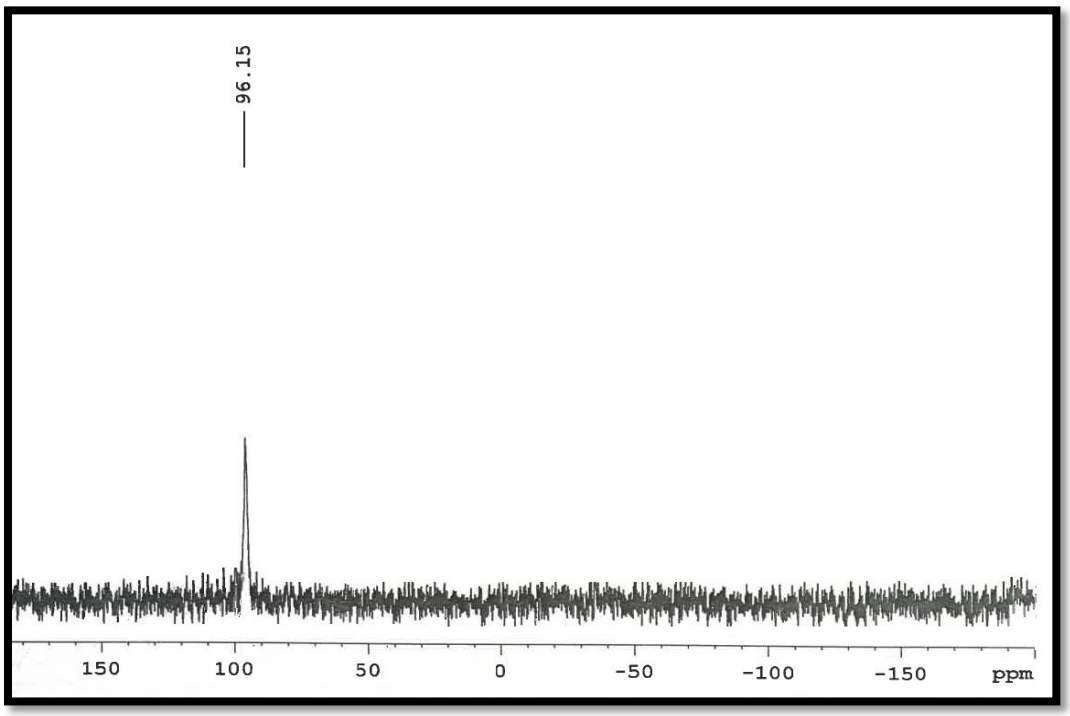
Spectrum 9. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^5-pentamethylcyclopentadienyl)iridium]diphenyl phosphanyl}oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride],* ***(3).***



Spectrum 10. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^6-benzene)ruthenium]diphenyl phosphanyl}oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride],* ***(4).***



Spectrum 11. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^6-p-cymene)-ruthenium]diphenylphosphanyl}oxy)-propyl)-1-butyl-1H-imidazol-3-ium chloride],* ***(5).***



Spectrum 12. ^{31}P NMR spectrum of *[3-(3-chloro-2-({[dichloro(η^5-pentamethylcyclopentadienyl)iridium]diphenyl phosphanyl}oxy)propyl)-1-butyl-1H-imidazol-3-ium chloride],* ***(6).***

References

[1] U. Işık, N. Meriç, M. Aydemir, Novel Mononuclear Metal-Phosphinite Compounds and Their Catalytic Performance in Transfer Hydrogenation of Ketones, Middle East J. Sci. 2022, 8(1), 1-15. https://doi.org/10.51477/mejs.1077805.

[2] U. Işık, N. Meriç, C. Kayan, A. Kılıç, Y. Belyankova, A. Zazybin, M. Aydemir, Synthesis of half-sandwich ruthenium(II) and iridium(III) complexes containing imidazole-based phosphinite ligands and their use in catalytic transfer hydrogenation of acetophenone with isopropanol, J. Organomet. Chem. 2023, 998, 122800. https://doi.org/10.1016/j.jorganchem.2023.122800