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Supporting Information

69451 Weinheim, Germany

Synthesis and Reactivity of Metal Complexes with Acyclic (Amino)-(Ylide)Carbene Ligands**

*Elisa González-Fernández, Jörg Rust, and Manuel Alcarazo**

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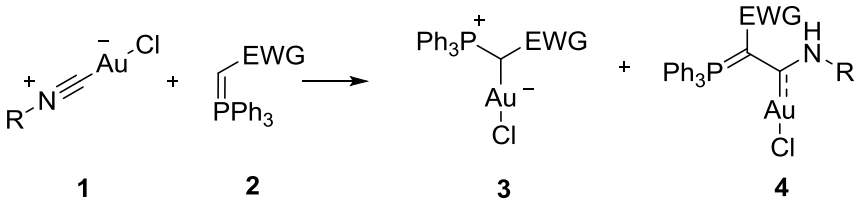
Table of Contents

Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropriate drying agents and were transferred under Ar. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR Spectra were recorded on a Bruker AV 500, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale.

All commercially available compounds (Acros, Aldrich) were used as received. The ylides **2d**[1], **2f**[2], **2e**[3] **5**[4], **7** and **9**[5] were prepared according to literature procedures. Gold (I) isonitriles **1a** and **1b** were prepared using the method described by Hashmi *et. al.* in quantitative yields[6]. Phenylisocyanide was prepared by the method of Weber *et. al.* from aniline[7].

General procedure for AAYC-gold complexes bearing phosphorus ylides:



1 **2** **3** **4**

In a typical procedure, Gold (I) isonitrile **1** is suspended in toluene (0.024M) followed by addition of ylide **2** at the indicated temperature**.** After stirring the reaction for the referred time, the mixture was allowed to reach room temperature and the solvents filtered out. The remaining white solid thus obtained was then washed with small portions of pentane and dried under vacuum.

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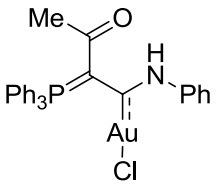
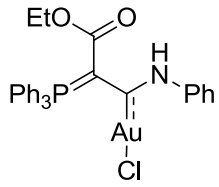
[6] A. S. K. Hashmi, T. Hengst, C. Lothschütz, F. Rominger *Adv. Synth. Catal.* **2010**, *352*, 1315.
[7] W. P. Weber, G. W. Gokel *Tetrahedron Lett.* **1972**, *17*, 1637



4a

Compound 4a: Following the general procedure described above, a mixture of phenylisocyanide gold (I) chloride **1a** (40 mg, 0.12 mmol) and 1-(Triphenylphosphoranylidene)-2-propanone **2a** (38 mg, 0.12 mmol) afforded pure **4a** (66 mg. 85%) after a reaction time of 3 d at room temperature.

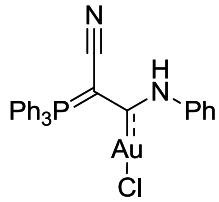
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 14.54 (s, 1 H), 7.97-7.92 (m, 6 H), 7.72-7.69 (m, 3 H), 7.65-7.59 (m, 8 H), 7.34-7.31 (m, 2 H), 7.24-7.21 (m, 1 H), 1.47 (s, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 200.9 (d, $J_{C\text{-}P}$ = 36.0 Hz), 195.3 (d, $J_{C\text{-}P}$ = 24.0 Hz), 144.1, 134.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 133.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 12.3 Hz), 129.1, 126.6, 125.8 (d, $J_{C\text{-}P}$ = 91.6 Hz), 123.7, 93.0 (d, $J_{C\text{-}P}$ = 124.9 Hz), 31.7 (d, $J_{C\text{-}P}$ = 2.3 Hz) ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 19.6 ppm. HRMS *calcd.* for $C_{28}H_{24}NOAuClPNa$: 676.084174; *found* 676.084426. IR (neat) $\tilde{\nu}$ = 680, 690, 706, 721, 736, 749, 756, 875, 901, 983, 998, 1024, 1052, 1095, 1133, 1182, 1227, 1253, 1365, 1415, 1438, 1482, 1506, 1506, 1567, 1587, 3052 cm^{-1}.



4b

Compound 4b: Following the general procedure described above, a mixture of phenylisocyanide gold (I) chloride **1a** (41 mg, 0.12 mmol) and the phosphorus ylide **2b** (45 mg, 0.12 mmol) afforded pure **4b** (62 mg, 74%) after a reaction time of 1 d at 35 °C.

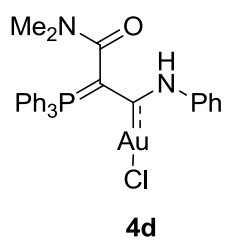
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 12.67 (s, 1 H), 7.89-7.84 (m, 6 H), 7.67-7.63 (m, 5 H), 7.58-7.53 (m, 6 H), 7.34-7.30 (m, 2 H), 7.23-7.19 (m, 1 H), 3.73 (q, *J* = 7.2 Hz, 2 H), 0.59 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 200.6 (d, $J_{C\text{-}P}$ = 35.9 Hz), 168.8 (d, $J_{C\text{-}P}$ = 17.2 Hz), 144.4, 134.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.4 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.1, 126.3, 126.2(d, $J_{C\text{-}P}$ = 94.0 Hz), 123.4, 79.4 (d, $J_{C\text{-}P}$ = 134.4 Hz), 60.0, 13.6 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 22.0 ppm. HRMS *calcd.* for $C_{29}H_{26}NO_2AuClPNa$: 706.094742; *found* 706.095558. IR (neat) $\tilde{\nu}$ = 688, 681, 698, 710, 748, 760, 799, 819, 849, 905, 937, 997, 1024, 1071, 1081, 1103,1156, 1164, 1185, 1197, 1233, 1292, 1336, 1368, 1392, 1436, 1479, 1517, 1588, 1629, 2907, 2976, 3054 cm^{-1}.



4c

Compound 4c: Following the general procedure described above, a mixture of phenylisocyanide gold (I) chloride **1a** (23 mg, 0.07 mmol) and the phosphous ylide **2c** (21 mg, 0.07 mmol) afforded pure **4c** (38 mg, 88%) after a reaction time of 3 d at 35 °C.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 8.89 (s, 1 H), 7.83-7.75 (m, 9 H), 7.71-7.69 (m, 2 H), 7.69-7.61 (m, 6 H), 7.38-7.34 (m, 2 H), 7.28-7.24 (m, 1 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 201.9 (d, $J_{C\text{-}P}$ = 35.9 Hz), 143.0, 134.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 134.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 129.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.3, 126.8, 123.1, 122.9 (d, $J_{C\text{-}P}$ = 94.1 Hz), 117.8 (d, $J_{C\text{-}P}$ = 22.1 Hz), 60.1 (d, $J_{C\text{-}P}$ = 154.6 Hz) ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 21.8 ppm. HRMS *calcd.* for $C_{27}H_{21}N_2AuClPNa$: 659.068858; *found* 659.069049. IR (neat) $\tilde{\nu}$ = 687, 715, 727, 748, 758, 788, 850, 900, 923, 996, 1026, 1073, 1102, 1120, 1190, 1225, 1284, 1300, 1319, 1343, 1436, 1491, 1529, 1594, 2175, 3242 cm^{-1}.



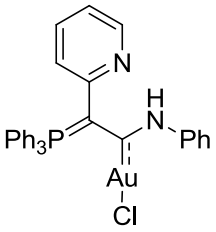
4d

Compound 4d: Following the general procedure described above, a mixture of phenylisocyanide gold (I) chloride **1a** (23 mg, 0.07 mmol) and phosphorus ylide **2d** (24 mg, 0.07 mmol) afforded pure **4d** (38 mg, 81%) after a reaction time of 6 h at 35 °C.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.98 (s, 1 H), 7.85-7.80 (m, 6 H), 7.69-7.65 (m, 3 H), 7.61-7.53 (m, 8 H), 7.29-7.25 (m, 2 H), 7.14-7.06 (m, 1 H), 2.88 (s, 6 H) ppm. ^{13}C-NMR (101 MHz,

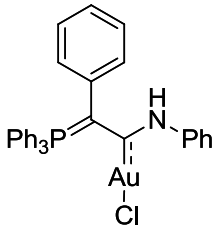
CD_2Cl_2) δ = 188.9 (d, J_{C-P} = 32.0 Hz), 167.8 (d, J_{C-P} = 19.1 Hz), 144.4, 134.6 (d, J_{C-P} = 9.3 Hz), 133.4 (d, J_{C-P} = 2.9 Hz), 129.3 (d, J_{C-P} = 12.4 Hz), 129.0, 125.1 (d, J_{C-P} = 92.0 Hz), 125.0, 122.4, 86.1 (d, J_{C-P} = 132.3 Hz), 37.0 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ =18.1 ppm. HRMS *calcd.* for $C_{29}H_{27}N_2OAuClPNa$: 705.110727; *found* 705.110773. IR (neat) $\tilde{\nu}$ = 691, 729, 144, 756, 841, 900, 937, 998, 1027, 1048, 1070, 1098, 1158, 1188, 1215, 1271, 1304, 1384, 1435, 1446, 1481, 1496, 1542, 1597, 3042, 3275 cm^{-1}.

Compound 4e: Following the general procedure described above, a mixture of phenylisocyanide gold (I) chloride **1a** (89 mg, 0.26 mmol) and phosphorus ylide **2e** (94 mg, 0.26 mmol) afforded pure **4e** (180 mg, 98%) after a reaction time of 6 h at 35 °C.



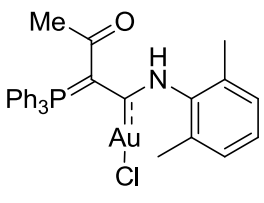
4e

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 9.77 (s, 1 H), 8.45 (d, *J* = 4.6 Hz, 1H), 7.82 (dd, *J* = 12.1, 8.1 Hz, 6 H), 7.62-7.58 (m, 5 H), 7.52-7.47 (m, 6 H), 7.30-7.22 (m, 3 H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.93-6.90 (m, 1 H), 6.81 (d, *J* = 7.9 Hz, 1 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 189.6 (d, J_{C-P} = 35.7 Hz), 156.4 (d, J_{C-P} = 20.1 Hz), 149.6, 144.5, 136.3, 134.7 (d, J_{C-P} = 9.1 Hz), 133.0 (d, J_{C-P} = 2.6 Hz), 129.2 (d, J_{C-P} = 12.1 Hz), 128.8, 126.8 (d, J_{C-P} = 3.0 Hz), 126.2 (d, J_{C-P} = 91.8 Hz), 124.4, 121.7, 120.8, 87.9 (d, J_{C-P} = 134.4 Hz) ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 20.0 ppm. HRMS *calcd.* for $C_{31}H_{25}N_2AuClPNa$: 711.100164; *found* 711.100454. IR (neat) $\tilde{\nu}$ = 688, 711, 742, 793, 862, 900, 997, 1017, 1051, 1098, 1154, 1183, 1263, 1312, 1379, 1425, 1435, 1460, 1494, 1514, 1557, 1582, 3056 cm^{-1}.



4f

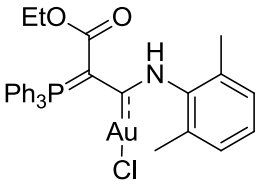
Compound 4f: Phenylisocyanide gold (I) chloride **1a** (44 mg, 0.12 mmol) is added to a cooled solution of the phosphorus ylide **2f** (43 mg, 0.12 mmol) at -78 °C. After 2 h, it was allowed to warm up to room temperature overnight. Filtration of the obtained suspension afforded a white solid, which contains both **4f** and the side product **3f**. Consecutive crystallizations (3 times) in DCM/pentane allowed the isolation of pure **4f** (4 mg) in 5 % yield. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.71-7.66 (m, 5 H), 7.64-7.59 (m, 3 H), 7.52-7.45 (m, 9 H), 7.30 (s, 1 H), 7.22-7.13 (m,5 H), 7.06-6.70 (m, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 187.1 (d, J_{C-P} = 37.7 Hz), 144.5, 134.8 (d, J_{C-P} = 9.0 Hz), 134.0 (d, J_{C-P} = 3.8 Hz), 133.1 (d, J_{C-P} = 2.8 Hz), 133.1 (d, J_{C-P} = 2.8 Hz), 132.3 (d, J_{C-P} = 9.9 Hz), 129.6 (d, J_{C-P} = 1.7 Hz), 129.1 (d, J_{C-P} = 12.3 Hz), 129.0 (d, J_{C-P} = 12.1 Hz), 128.9, 127.9 (d, J_{C-P} = 2.3 Hz), 125.8 (d, J_{C-P} = 91.1 Hz), 124.0, 121.2, 88.9 (d, J_{C-P} = 132.1 Hz) ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 21.0 ppm. HRMS *calcd.* for $C_{31}H_{31}N_2OAuClPNa$: 710.104912; *found* 710.105881. IR (neat) $\tilde{\nu}$ = 689, 704, 716,l 744, 784, 800, 853, 887, 913, 996, 1009, 1027, 1071, 1098, 1159, 1220, 1261, 1305, 1326, 1372, 1433, 1444, 1480, 1493, 1508, 1590, 2851, 2922, 2961, 3051, 3331, 3494, 3551 cm^{-1}.



4g

Compound 4g: Following the general procedure described above, a mixture of 2,6-dimethyl-phenylisocyanide gold (I) chloride **1b** (100 mg, 0.28 mmol) and phosphorus ylide **2a** (88 mg, 0.28 mmol) afforded pure **4g** (54 mg, 30%) after a reaction time of 3 d at 50 °C. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 13.70 (s, 1 H), 7.97-7.92 (m, 6 H), 7.73-7.68 (m, 3 H), 7.64-7.58 (m, 6 H), 7.13-7.06 (m, 3 H), 2.26 (s, 6 H), 1.48 (s, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 206.6 (d, J_{C-P} = 34.8 Hz), 195.0 (d, J_{C-P} = 28.0 Hz), 142.6, 135.0, 134.6 (d, J_{C-P} = 8.6 Hz), 133.6 (d, J_{C-P} = 2.9 Hz), 129.7 (d, J_{C-P} = 12.4 Hz), 128.4, 127.6, 125.9 (d, J_{C-P} = 92.0 Hz), 91.1

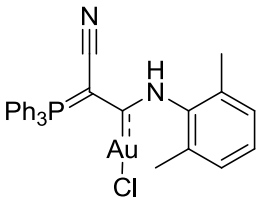
(d, $J_{C\text{-}P}$ = 124.3 Hz), 31.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 19.1 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 20.5 ppm. HRMS *calcd.* for $C_{30}H_{28}NOAuClPNa$: 704.115849; *found* 704.115049. IR (neat) $\tilde{\nu}$ = 682, 693, 709, 720, 734, 755, m768, 781, 842, 873, 920, 982, 998, 1018, 1046, 1098, 1142, 1213, 1250, 1268, 1342, 1360, 1418, 1435, 1500, 1572, 2975 cm^{-1}.



4h

Compound 4h: Following the general procedure described above, a mixture of 2,6-dimethyl-phenylisocyanide gold (I) chloride **1b** (46 mg, 0.13 mmol) and phosphorus ylide **2c** (47 mg, 0.13 mmol) afforded after 4 d at 50 °C a white solid that was further purified by crystallization from DCM : pentane. Thus, **4h** was obtained in 37% yield (33 mg).

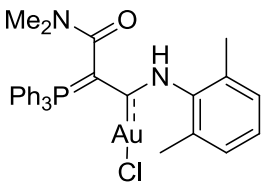
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 11.89 (s, 1 H), 7.89-7.83 (m, 6 H), 7.67-7.63 (m, 3 H), 7.57-7.53 (m, 6 H), 7.14-7.07 (m, 3 H), 3.75 (q, *J* = 7.1 Hz, 2 H), 2.20 (s, 6H), 0.59 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 206.1 (d, $J_{C\text{-}P}$ = 34.8 Hz), 168.8 (d, $J_{C\text{-}P}$ = 16.9 Hz), 142.9, 135.5, 134.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.4, 127.5, 126.2 (d, $J_{C\text{-}P}$ = 93.6 Hz), 76.9 (d, $J_{C\text{-}P}$ = 135.0 Hz), 59.6, 19.0, 13.6 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 22.4 ppm. HRMS *calcd.* for $C_{31}H_{30}NO_2AuClPNa$: 734.126042; *found* 734.125744. IR (neat) $\tilde{\nu}$ = 683, 698, 709, 722, 748, 776, 802, 938, 997, 1025, 1078, 1103, 1162, 1182, 1216, 1258, 1300, 1339, 1368, 1390, 1436, 1480, 1521, 1635, 2982, 3063 cm^{-1}.



4i

Compound 4i: Following the general procedure described above, a mixture of 2,6-dimethyl-phenylisocyanide gold (I) chloride **1b** (86 mg, 0.24 mmol) and phosphorus ylide **2c** (71 mg, 0.24 mmol) afforded after 4 d at 50 °C a white solid that was further purified by 3 consecutive crystallizations from DCM : pentane. Thus, **4i** was obtained in 25% yield (40 mg).

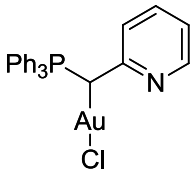
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 8.29 (s, 1 H), 7.82-7.75 (m, 9 H), 7.65-7.61 (m, 6 H), 7.20-7.17 (m, 1 H), 7.12-7.11 (m, 2 H), 2.36 (s, 6 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 207.0 (d, $J_{C\text{-}P}$ = 29.5 Hz), 141.2, 136.1, 134.7 (d, $J_{C\text{-}P}$ = 9.9 Hz), 134.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.6 (d, $J_{C\text{-}P}$ = 13.1 Hz), 128.7, 128.4, 123.1 (d, $J_{C\text{-}P}$ = 95.0 Hz), 117.8 (d, $J_{C\text{-}P}$ = 22.2 Hz), 57.3 (d, $J_{C\text{-}P}$ = 154.6 Hz), 19.0 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 22.1 ppm. HRMS *calcd.* for $C_{29}H_{25}N_2AuClPNa$: 687.100159; *found* 687.100556. IR (neat) $\tilde{\nu}$ = 687, 697, 716, 749, 780, 804, 907, 927, 952, 997, 1025, 1105, 1123, 1165, 1186, 1217, 1260, 1312, 1328, 1375, 1436, 1482, 1505, 2180, 2962, 3282 cm^{-1}.



4j

Compound 4j: 2,6-dimethyl-phenylisocyanide gold (I) chloride **1b** (94 mg, 0.26 mmol) was added to a cooled solution of the phosphorus ylide **2d** (90 mg, 0.26 mmol) in toluene (11 ml) at -78 °C. After 2 h at this temperature, the reaction mixtures was allowed to reach room temperature overnight. Filtration of the obtained suspension afforded a white solid which was purified by recrystallization (3 times from DCM : pentane). Thus, **4j** was obtained as colourless crystals (21 mg, 12%). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.86-7.81 (m, 6 H), 7.70-7.65 (m, 3 H), 7.58-7.54 (m, 6 H), 7.24 (s, 1 H), 7.14-7.07 (m,3 H), 2.95 (s, 6 H), 2.33 (s, 6 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 194.3 (d, $J_{C\text{-}P}$ = 31.0 Hz), 168.0 (d, $J_{C\text{-}P}$ = 19.2 Hz), 142.4, 136.6, 134.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 133.3 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.5, 127.6, 125.5 (d, $J_{C\text{-}P}$ = 92.7 Hz), 82.1 (d, $J_{C\text{-}P}$ = 134.1 Hz), 37.0, 19.3 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 18.8 ppm. HRMS *calcd.* for $C_{31}H_{31}N_2OAuClPNa$:

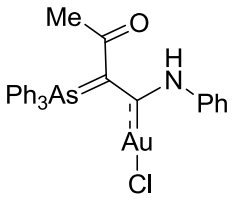
733.142026; *found* 733.142583. IR (neat) $\tilde{\nu}$ = 694, 712, 743, 755, 767, 854, 918, 946, 997, 1028, 1051, 1102, 1160, 1192, 1212, 1263, 1293, 1357, 1384, 1436, 1488, 1586, 1606, 2848, 2915, 2951, 3007, 3059, 3269 cm^{-1}.



3e

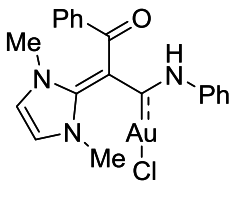
Compound 3e: Phenylisocyanide gold (I) chloride **1a** (230 mg, 0.63 mmol) was added to a cooled solution of phosphorus ylide **2e** (224 mg, 0.63 mmol) in toluene (26 ml) at -78 °C. After 2 h at this temperature, the reaction mixture was allowed to reach room temperature overnight. Filtration of the obtained suspension afforded a white solid (306 mg, 83 %) which corresponds to **3e**.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.64 (ddd, *J* = 0.9, 1.8, 5.0 Hz, 1 H), 7.90-7.85 (m, 6 H), 7.66-7.61 (m. 3H), 7.52-7.45 (m, 7 H), 7.23-7.21 (m, 1 H), 6.82-6.79 (m, 1 H), 4.5 (d, $J_{H\text{-}P}$ = 7.9 Hz, 1 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 161.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 147.9, 136.5, 134.5 (d, $J_{C\text{-}P}$ = 9.2 Hz), 133.3 (d, $J_{C\text{-}P}$ = 12.1), 125.9 (d, $J_{C\text{-}P}$ = 87.9), 122.7 (d, $J_{C\text{-}P}$ = 13.1 Hz), 119.3, 29.6 (d, $J_{C\text{-}P}$ = 49.1 Hz) ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 28.3 ppm. HRMS *calcd.* for $C_{31}H_{31}N_2OAuClPNa$: 733.142026; *found* 733.142583. IR (neat) $\tilde{\nu}$ = 694, 712, 743, 755, 767, 854, 918, 946, 997, 1028, 1051, 1102, 1160, 1192, 1212, 1263, 1293, 1357, 1384, 1436, 1488, 1586, 1606, 2848, 2915, 2951, 3007, 3059, 3269 cm^{-1}.



6

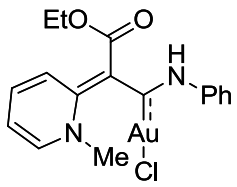
Compound 6: A suspension of Phenylisocyanide gold (I) chloride **1a** (38 mg, 0.11 mmol) in toluene (4.7 ml) was cooled at -10 °C and then the arsenic ylide **5** (41 mg, 0.11 mmol) was added. After stirring the obtained suspension for 1 d, the reaction mixture was allowed to reach room temperature. The solvents were then filtered out and the remaining a white solid washed with small portions of toluene and dried under vacuum. Thus, **6** was obtained as a white solid (32 mg, 40%). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 14.45 (s, 1 H), 7.85 (d, *J* = 7.2 Hz, 6 H), 7.70-7.60 (m, 11H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1 H), 1.61 (br, 3H) ppm. ^{13}C-NMR (75 MHz, CD_2Cl_2) δ = 198.0, 144.1, 133.3, 133.1, 130.5, 129.1, 129.0, 126.4, 123.4, 31.3 ppm HRMS *calcd.* for $C_{28}H_{24}AsAuClNONa$: 720.032365; *found* 720.033071. IR (neat) $\tilde{\nu}$ = 691, 741, 756, 793, 865, 1014, 1078, 1259, 1371, 1441, 1459, 1509, 1565, 1589, 2853, 2922, 2955 cm^{-1}.



9

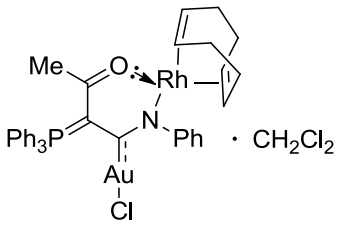
Compound 9: A mixture of phenylisocyanide gold (I) chloride **1a** (25 mg, 0.08 mmol) and diaminoalkene **7** (16 mg, 0.08 mmol) was suspended in toluene (3 ml) and warmed to 35 ºC. After 8 h the mixture was allowed to reach room temperature. Elimination of the solvents by filtration afforded pure **9** as a yellow solid (40 mg, 95 % yield). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 14.73 (s, 1 H), 7.86 (d, *J* = 7.8 Hz, 2 H), 7.43-7.40 (m, 2 H), 7.35-7.32 (m, 1 H), 7.29-7.25 (m,3 H), 7.06 (s, 2 H), 7.05-7.03 (m, 2 H) 3.63 (s, 6 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 194.6, 187.4, 151.5, 143.7, 142.3, 130.2, 129.3, 128.9, 126.2, 125.9, 122.7, 121.3, 98.4, 36.0 ppm. HRMS *calcd.* for $C_{20}H_{19}N_3OAuClNa$: 572.077435; *found* 572.078099.IR (neat) $\tilde{\nu}$ = 691, 704, 728, 760, 792, 906, 1025, 1071, 1155, 1173, 1235, 1278, 1384, 1446, 1488, 1519, 1595, 3125 cm^{-1}.

Compound 10: A mixture of phenylisocyanide gold (I) chloride **1a** (26 mg, 0.08 mmol) and diaminoalkene **9** (14 mg, 0.08 mmol) was suspended in toluene (3.3 ml) and warmed to 35 ºC. After 18 h the mixture was allowed to reach room temperature. Elimination of the solvents by filtration afforded pure **10** as a yellow solid (35 mg, 87 % yield).



10

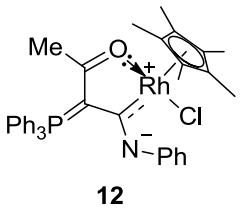
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 12.09 (s, 1 H), 8.32 (d, *J* = 6.2 Hz, 1H), 8.22 (t, *J* = 7.9 Hz, 1 H), 8.16 (d, *J* = 7.9 Hz, 1 H), 7.78-7.76 (m, 2H), 7.66-7.63 (m, 1H), 7.35-7.32 (m, 2H), 7.18-7.14 (m, 1 H), 4.17 (s, 3 H), 4.13-4.04 (m, 2 H), 1.15 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 189.6, 165.9, 162.2, 144.2, 143.1, 142.8, 135.3, 129.2, 125.0, 124.4, 122.0, 98.4, 59.5, 46.2, 14.8 ppm. HRMS *calcd.* for $C_{17}H_{18}N_2O_2AuClNa$: 537.061450; *found* 537.061877. IR (neat) $\tilde{\nu}$ = 680, 694, 749, 759, 788, 893, 931, 954, 1028, 1074, 1091, 1175, 1218, 1256, 1299, 1336, 1373, 1447, 1493, 1527, 1588, 1622, 1640, 2975, 3055 cm^{-1}.



11

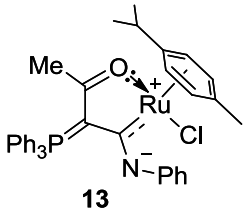
Compound 11 : KOMe (5.5 mg, 0.078 mmol) and $[Rh(COD)Cl]_2$ (19.3 mg, 0.039 mmol) were suspended in THF (2 ml) and stirred for 10 min, at 5 °C. Then, **4a** was added and the mixture stirred for 36h. Along this time a light yellow precipitate was slowly formed. The reaction was then allowed to reach room temperature and the solvent evaporated *in vacuo.* The yellow solid thus obtained was washed with small portions of DCM to afford **11** (54 mg, 72 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.06-8.01 (m, 6 H), 7.67-7.57 (m, 9 H), 7.13-7.09 (m, 2 H), 6.97 (t, *J* = 7.4 Hz, 1 H), 6.82 (d, *J* = 7.2 Hz, 2 H), 4.18 (br, 2 H), 3.33 (br, 2 H), 2.44-2.35 (m, 4 H), 1.83-1.72 (m, 4 H) 1.49 (s, 3 H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$) δ = 197.6 (d, $J_{C\text{-}P}$ = 35.0 Hz), 180.7 (d, $J_{C\text{-}P}$ = 24.1 Hz), 155.5, 134.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 133.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.4 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.2, 125.5 (d, $J_{C\text{-}P}$ = 91.6 Hz), 124.8, 124.6, 95.3 (d, $J_{C\text{-}P}$ = 126.6 Hz), 82.7 (d, $J_{C\text{-}Rh}$ = 11.8 Hz), 75.1 (d, $J_{C\text{-}Rh}$ = 11.8 Hz), 53.6, 31.6, 29.6, 28.7 ppm. ^{31}P-NMR (162 MHz, $CDCl_3$) δ = 19.9 ppm. IR (neat) $\tilde{\nu}$ = 687, 708, 725, 741, 759, 776, 800, 869, 911, 964, 998, 1023, 1070, 1096, 1142, 1187, 1218, 1262, 1350, 1362, 1404, 1440, 1483, 1494, 1591, 2228, 2838, 2858, 2942, 2994, 3052 cm^{-1}. HRMS *calcd.* for $C_{36}H_{35}AuClNOPRhNa^{+}$: 886.075756; *found* 886.076414.



12

Compound 12: $[RhCp^*Cl_2]_2$ (5.0 mg, 0.009 mmol) and **4a** (10.2 mg, 0.016 mmol) were disolved in DCE (0.2 ml) and NEt_3 (0.04 ml, 0.272 mmol) was dropwise added. This solution was heated at 50 °C and stirred at this temperature for 4 d. Then, the reaction mixture was allowed to cool down to room temperature and filtered in order to remove the formed precipitate. The bright red solution thus obtained was evaporated *in vacuo* affording a red solid that was redissolved in a small amount of toluene and filtrated again. Evaporation of the toluene produced an orange solid that could be further purified by consecutive crystallizations (2 times from DCM : pentane). Thus **11** was obtained as an orange solid (9.0 mg, 83 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.75-7.66 (m, 6 H), 7.53-7.50 (m, 3 H), 7.47-7.43 (m, 6 H), 6.96-6.92 (m, 2 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.54 (br, 2 H), 1.36 (s, 3 H), 1.34 (s, 15 H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 200.5 (dd, $J_{C\text{-}Rh}$ = 3.3 Hz, $J_{C\text{-}P}$ = 35.0 Hz), 192.8 (d, $J_{C\text{-}P}$ = 27.7 Hz), 149.2, 132.6 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.1 (d, $J_{C\text{-}P}$ = 3.3 Hz), 127.6 (d, $J_{C\text{-}P}$ = 12.4 Hz), 126.6, 126.2 (d, $J_{C\text{-}P}$ = 93.5 Hz), 121.1, 119.6, 93.6 (d, $J_{C\text{-}Rh}$ = 6.7 Hz), 92.8 (d, $J_{C\text{-}P}$ = 95.8 Hz), 22.1, 8.4 ppm. ^{31}P-NMR (162 MHz, $CDCl_3$) δ = 11.4 (d, $J_{P\text{-}Rh}$ = 2.9 Hz) ppm. IR (neat) $\tilde{\nu}$ = 695, 708, 722, 742, 756, 768, 843, 905, 984, 994, 1021, 1062, 1105, 1119, 1154, 1187, 1225, 1278, 1309, 1353, 1392, 1435, 1473, 1554, 1588, 2911, 3044 cm^{-1}. HRMS *calcd.* for $C_{38}H_{39}ClNOPRh$: 694.150034; *found* 694.150324.

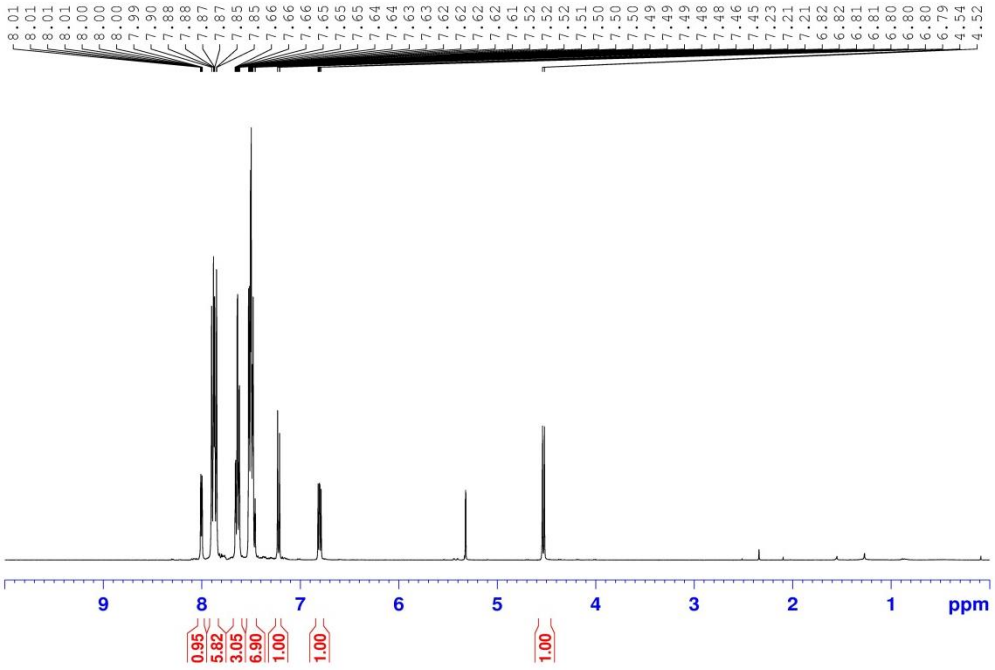


13

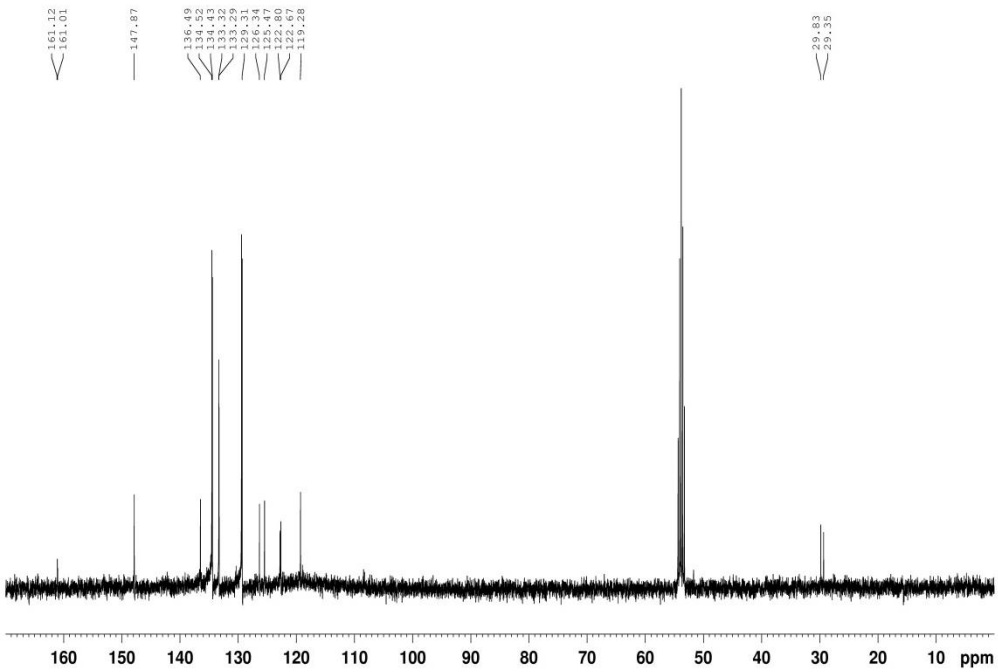
Compound 13: $[Ru(cym)Cl_2]_2$ (10.6 mg, 0.017 mmol) and **4a** (22.6 mg, 0.035 mmol) were dissolved in DCE (0.7 ml) and then NEt_3 (0.08 ml, 0.595 mmol) was added drop wise. The reaction mixture was heated at 50 °C and stirred for 1 d. Then, the mixture was allowed to cool down to room temperature and filtered. The bright red solution was evaporated *in vacuo* and the remaining orange solids purified by consecutive crystallizations (two times from DCM : pentane) to afford **13** (10.0 mg, 41 %) as an orange solid. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.72 (dd, *J* = 7.9, 12.3 Hz, 6 H), 7.56-7.55 (m, 3 H), 7.49-7.47 (m, 6 H), 7.00 (t, *J* = 7.4 Hz, 2 H), 6.78 (t, *J* = 7.4 Hz, 1 H), 6.40 (br, 2 H), 5.42 (d, *J* = 5.9 Hz, 1 H), 4.96 (d, *J* = 5.9 Hz, 1 H), 4.70 (d, *J* = 5.4 Hz, 1 H), 3.77 (d, *J* = 5.4 Hz, 1 H), 2.42 (quint. *J* = 6.8 Hz, 1 H), 1.94 (s, 3 H), 1.28 (s, 3 H), 1.08 (d, *J* = 6.8 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C-NMR (101 MHz, CD_2Cl_2) δ = 208.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 194.9 (d, $J_{C\text{-}P}$ = 28.1 Hz), 155.5, 134.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.1, 127.3 (d, $J_{C\text{-}P}$ = 93.0 Hz), 122.0, 120.8, 102.5, 98.0, 93.2 (d, $J_{C\text{-}P}$ = 97.3 Hz), 91.0, 84.2, 82.1, 76.6, 31.4, 23.2, 22.5, 22.2, 19.0 ppm. ^{31}P-NMR (162 MHz, CD_2Cl_2) δ = 11.6 ppm. IR (neat) $\tilde{\nu}$ = 692, 710, 726, 743, 801, 844, 864, 983, 1025, 1103, 1160, 1191, 1260, 1384, 1436, 1472, 1556, 1589, 1738, 2849, 1917, 2958, 3057 cm^{-1}. HRMS *calcd.* for $C_{38}H_{38}ClNOPRu$: 692.141123; *found* 692.141970.

Selected NMR spectra:

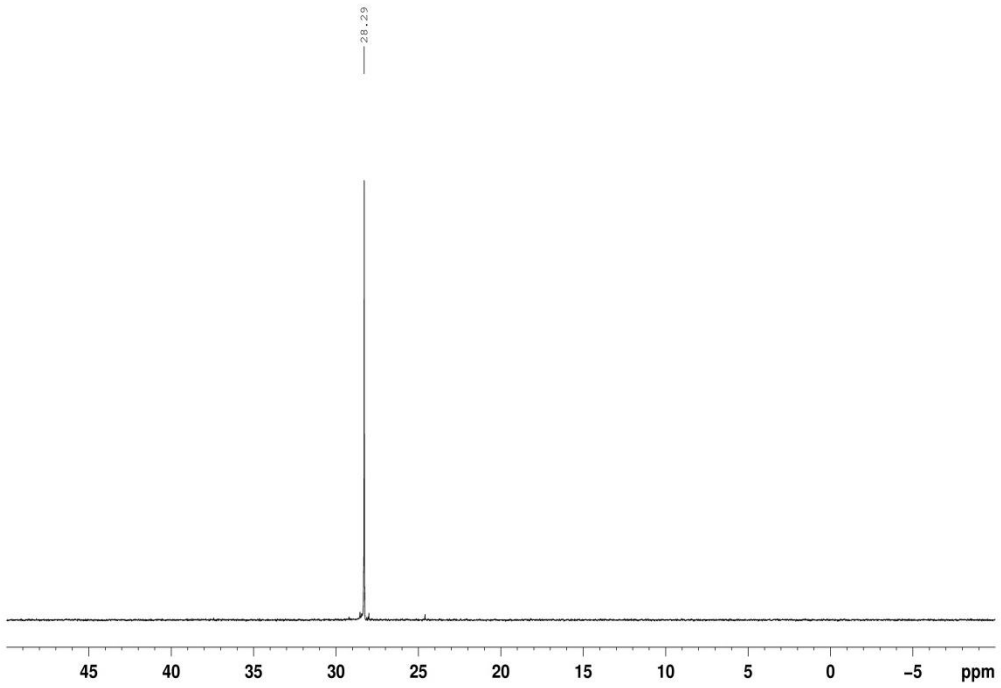
^{1}H-NMR (400 MHz, CD_2Cl_2) **3e**



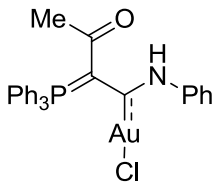
^{13}C-NMR (101 MHz, CD_2Cl_2) **3e**



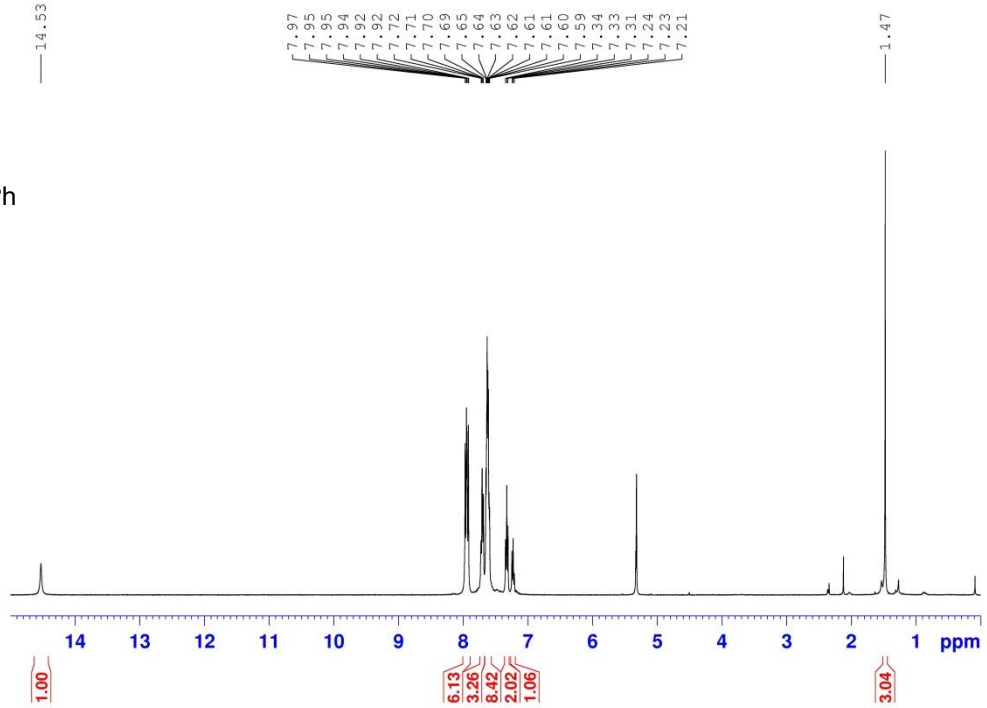
^{31}P-NMR (162 MHz, CD_2Cl_2) **3e**



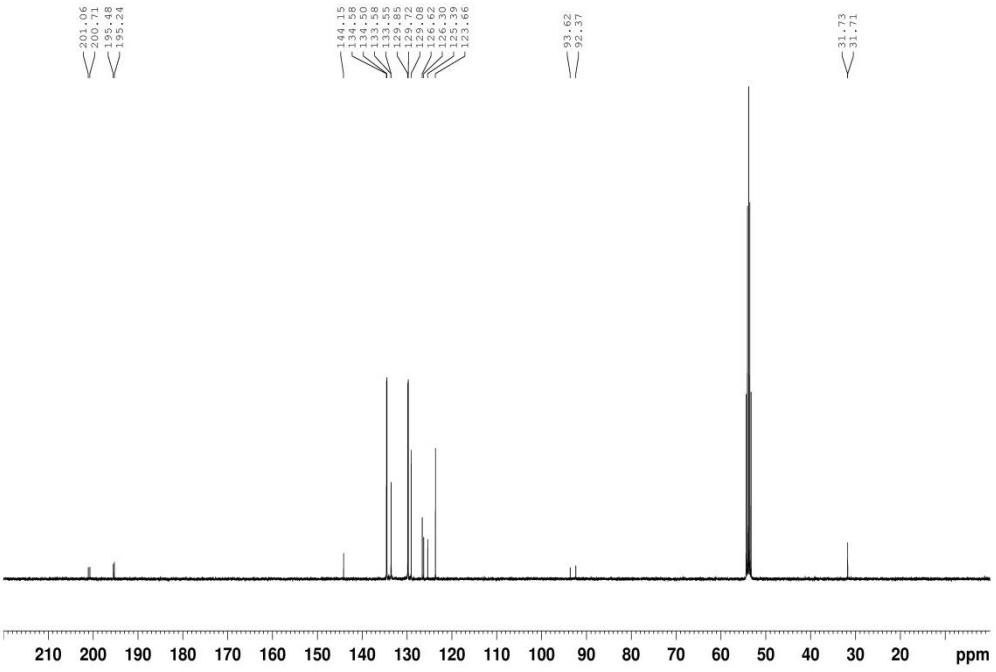
^{1}H-NMR (400 MHz, CD_2Cl_2) **4a**



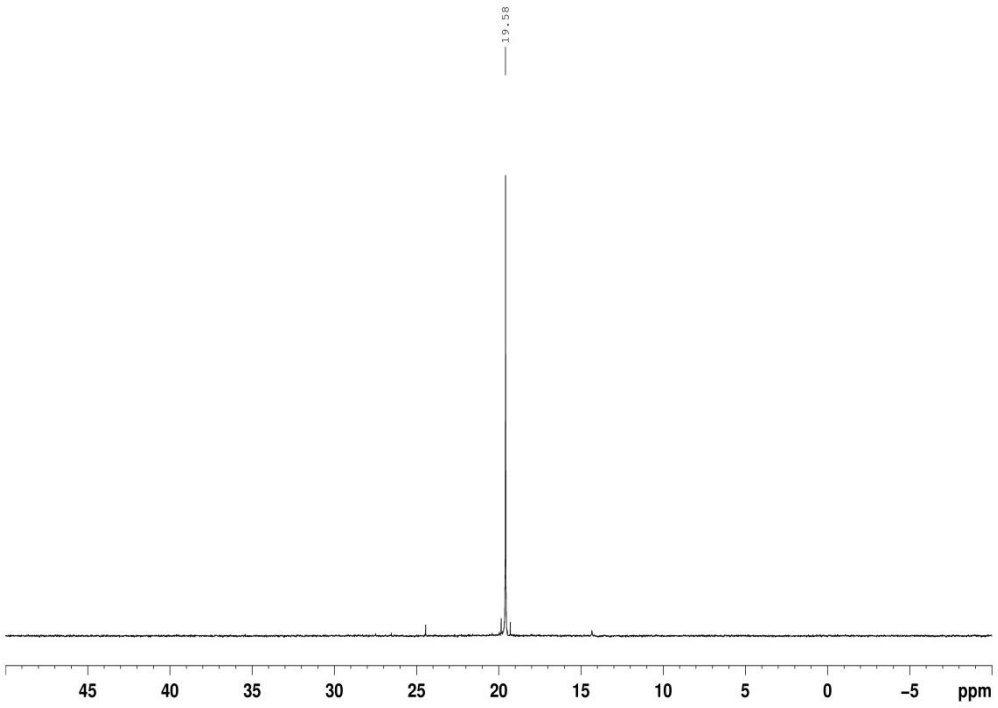
4a



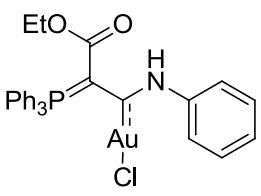
^{13}C-NMR (101 MHz, CD_2Cl_2) **4a**



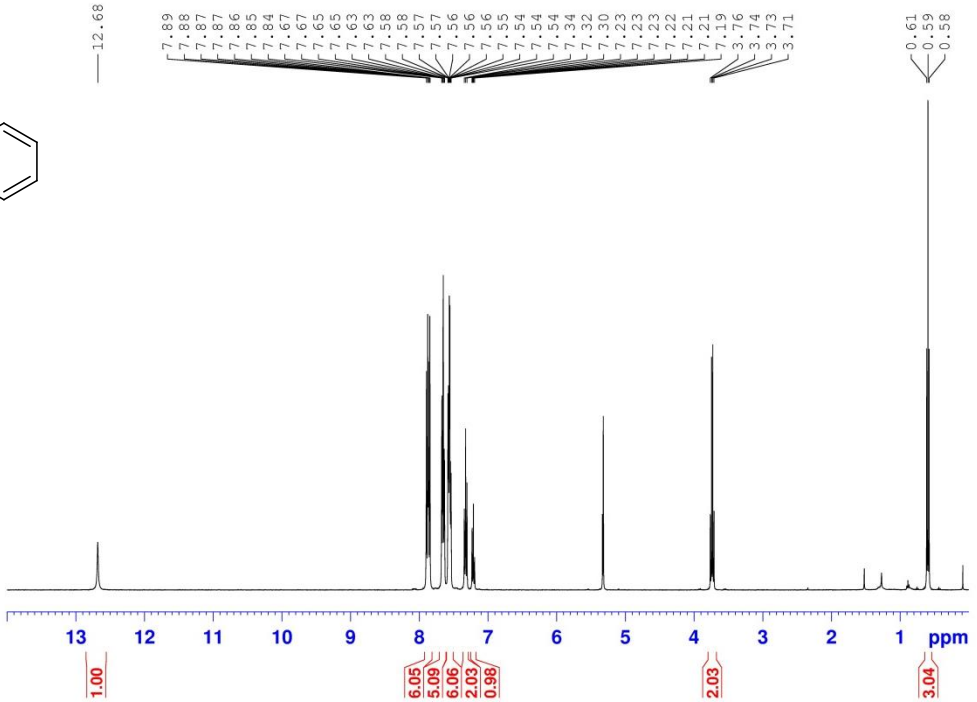
^{31}P-NMR (162 MHz, CD_2Cl_2) **4a**



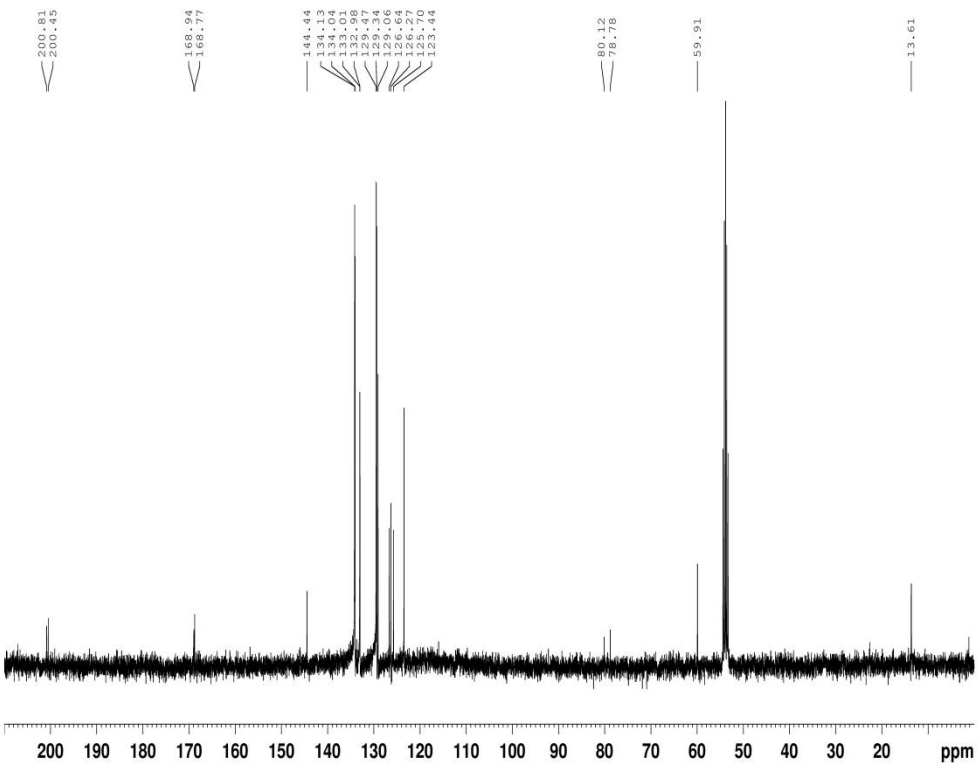
^{1}H-NMR (400 MHz, CD_2Cl_2) **4b**



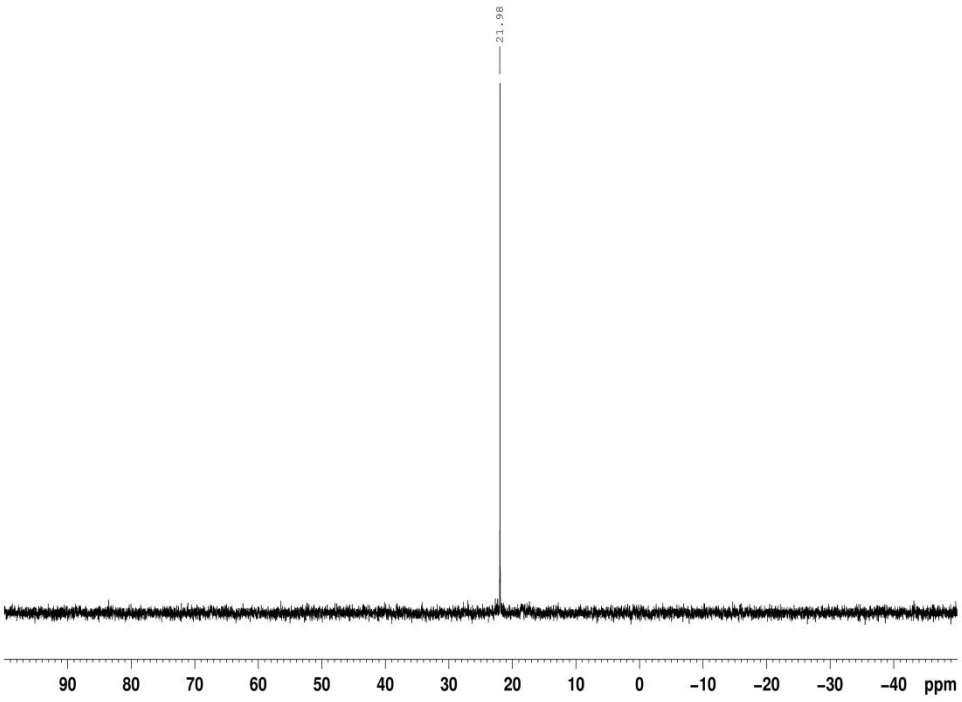
4b



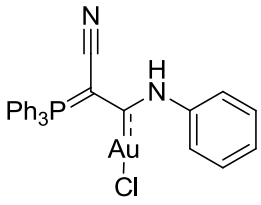
^{13}C-NMR (101 MHz, CD_2Cl_2) **4b**



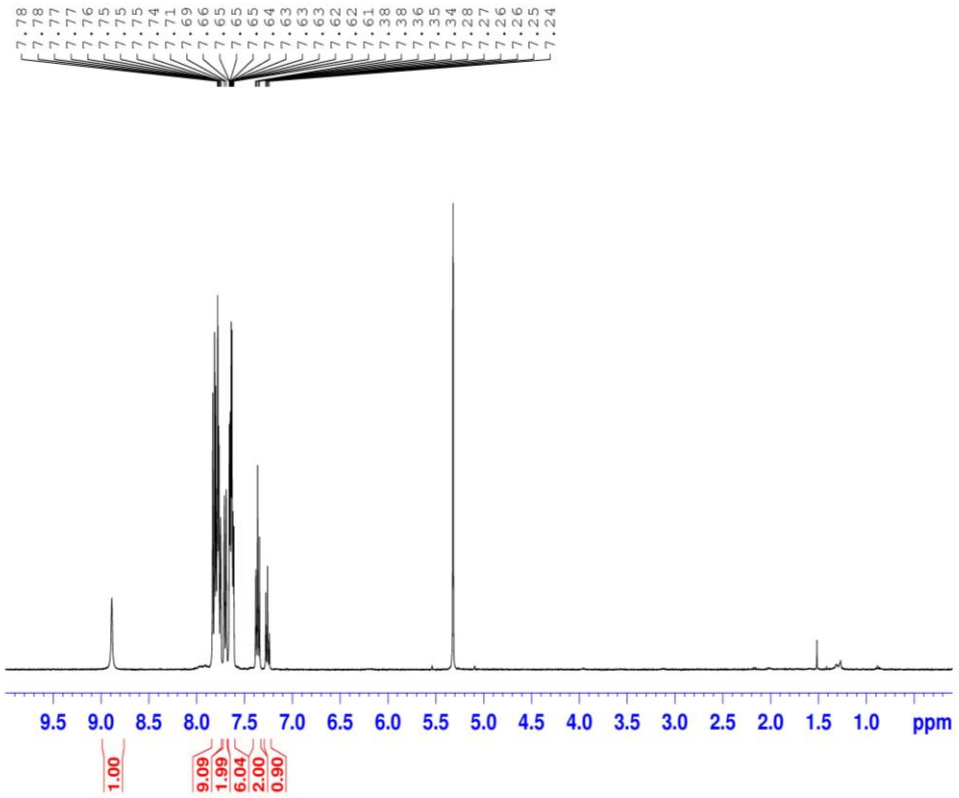
^{31}P-NMR (162 MHz, CD_2Cl_2) **4b**



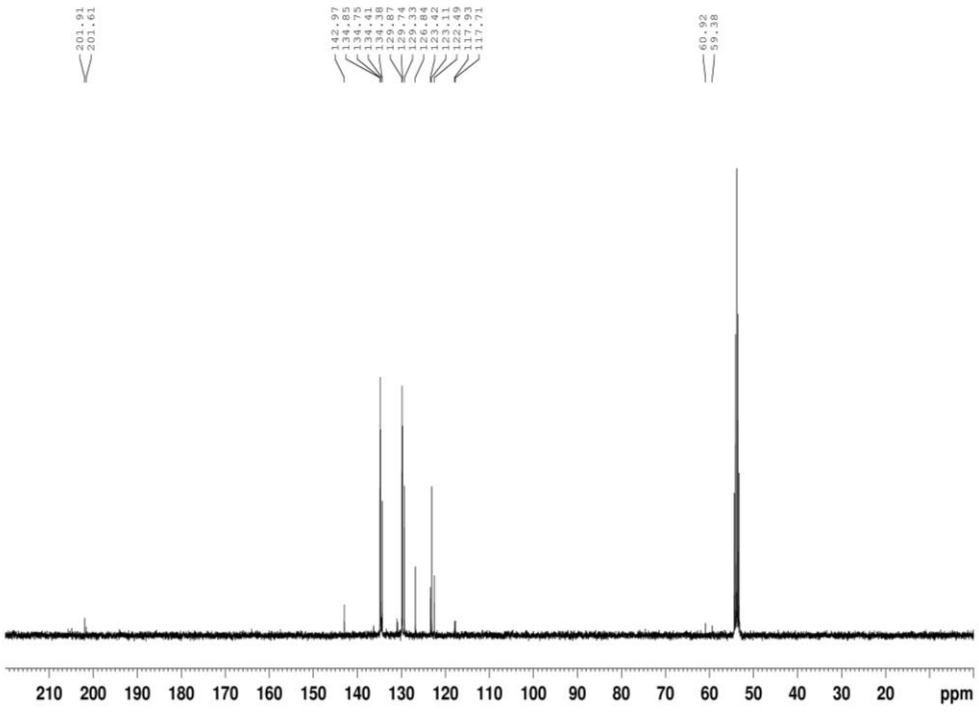
^{1}H-NMR (400 MHz, CD_2Cl_2) **4c**



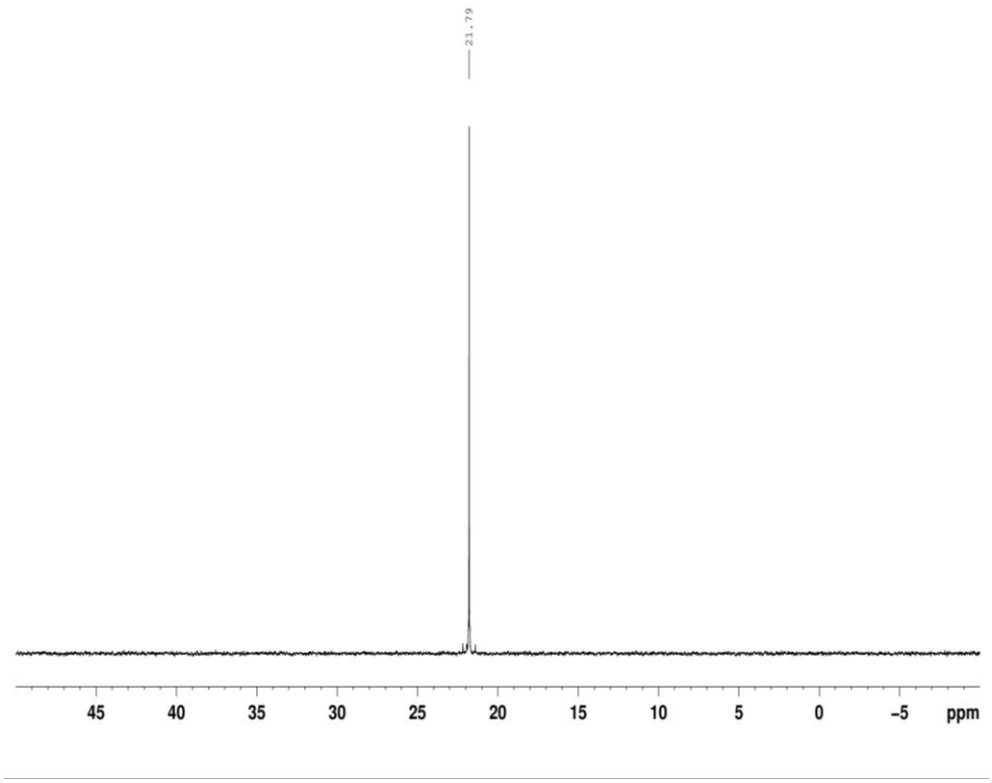
4c



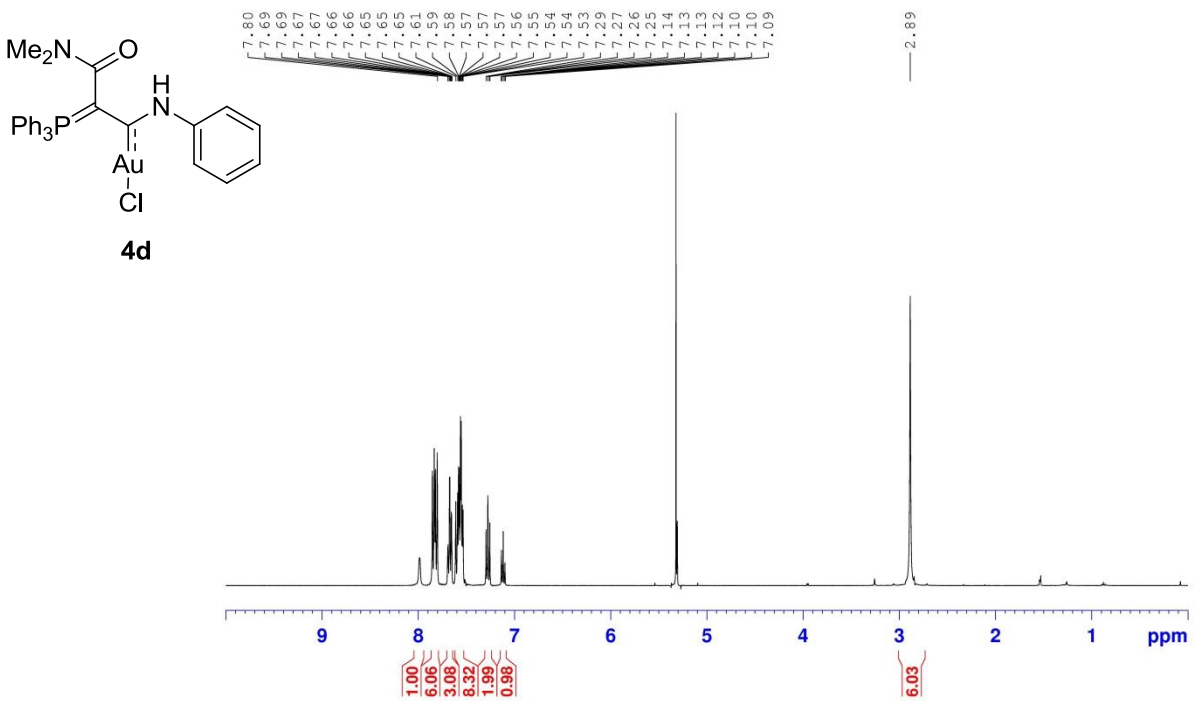
^{13}C-NMR (101 MHz, CD_2Cl_2) **4c**



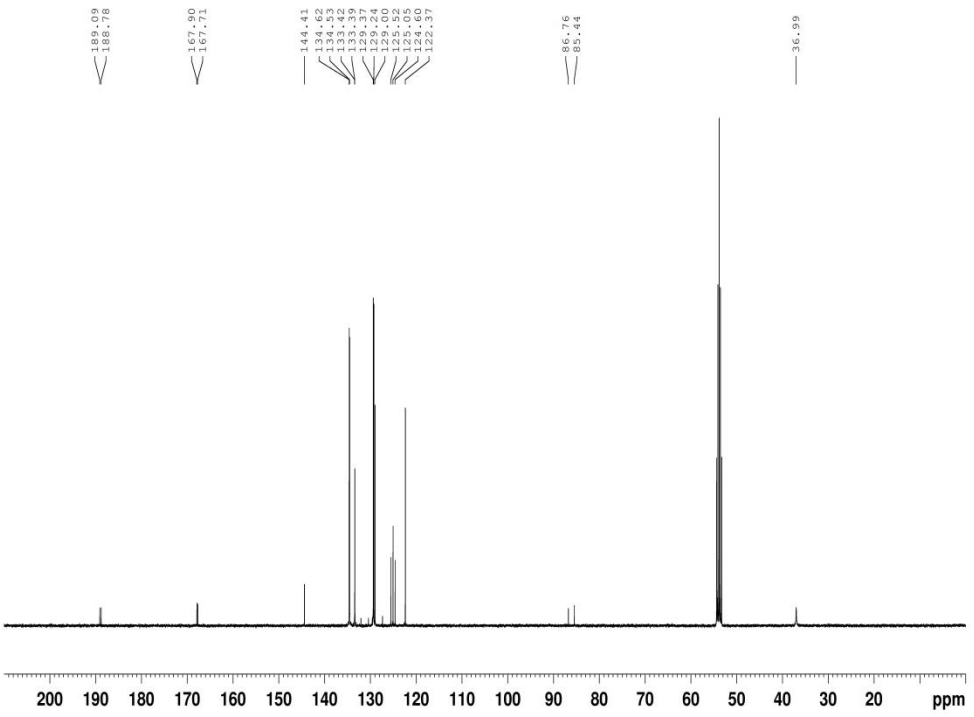
^{31}P-NMR (162 MHz, CD_2Cl_2) **4c**



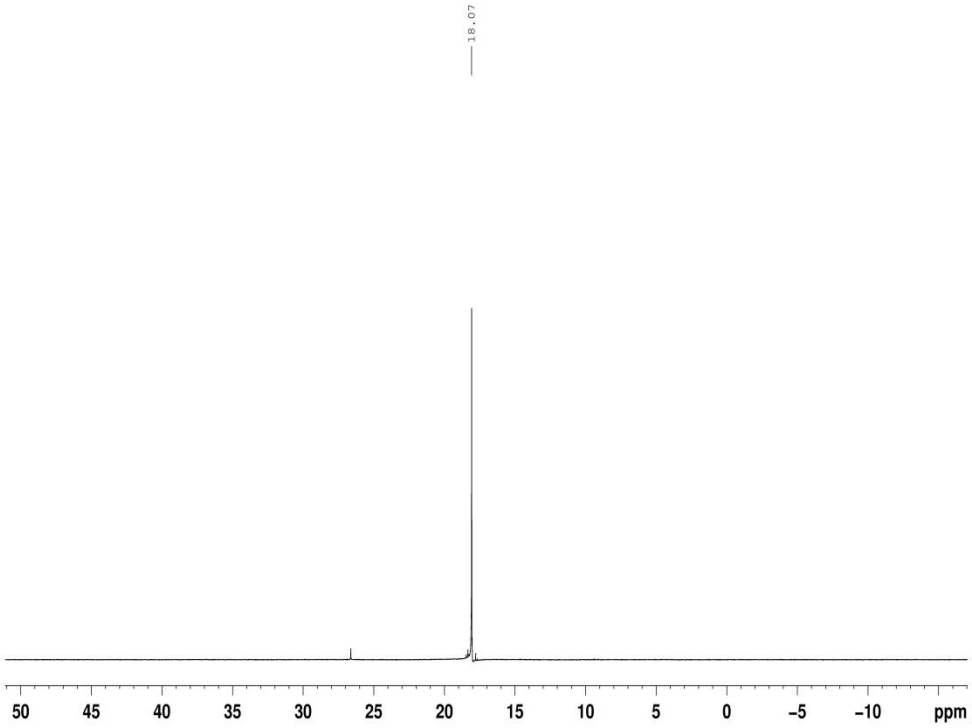
^{1}H-NMR (400 MHz, CD_2Cl_2) **4d**



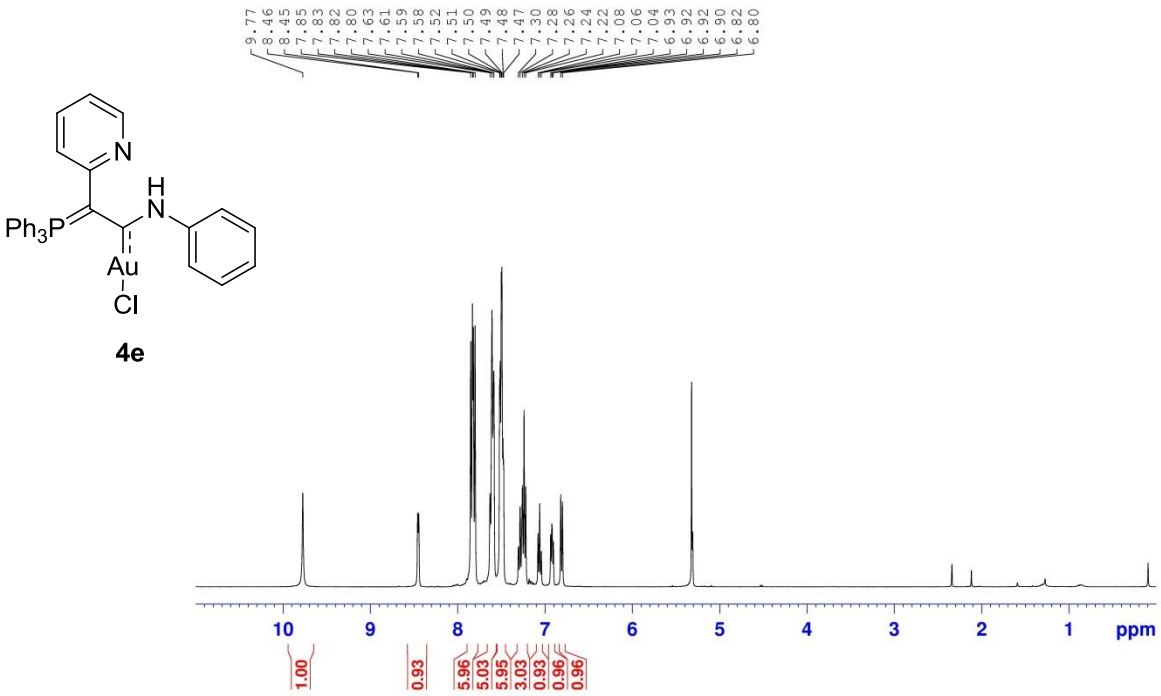
^{13}C-NMR (101 MHz, CD_2Cl_2) **4d**



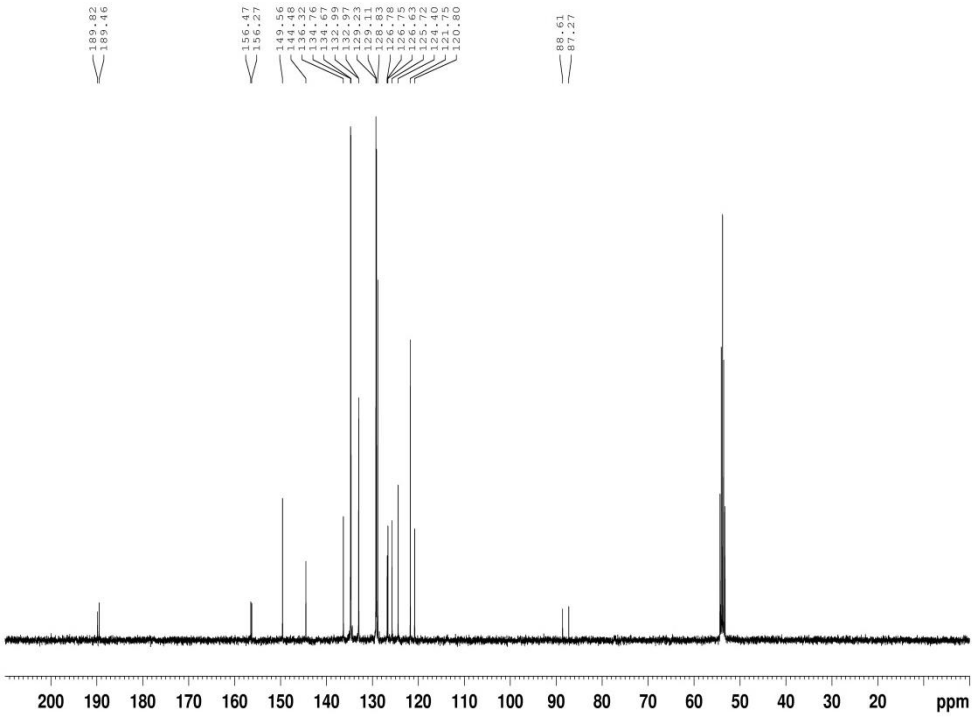
^{31}P-NMR (162 MHz, CD_2Cl_2) **4d**



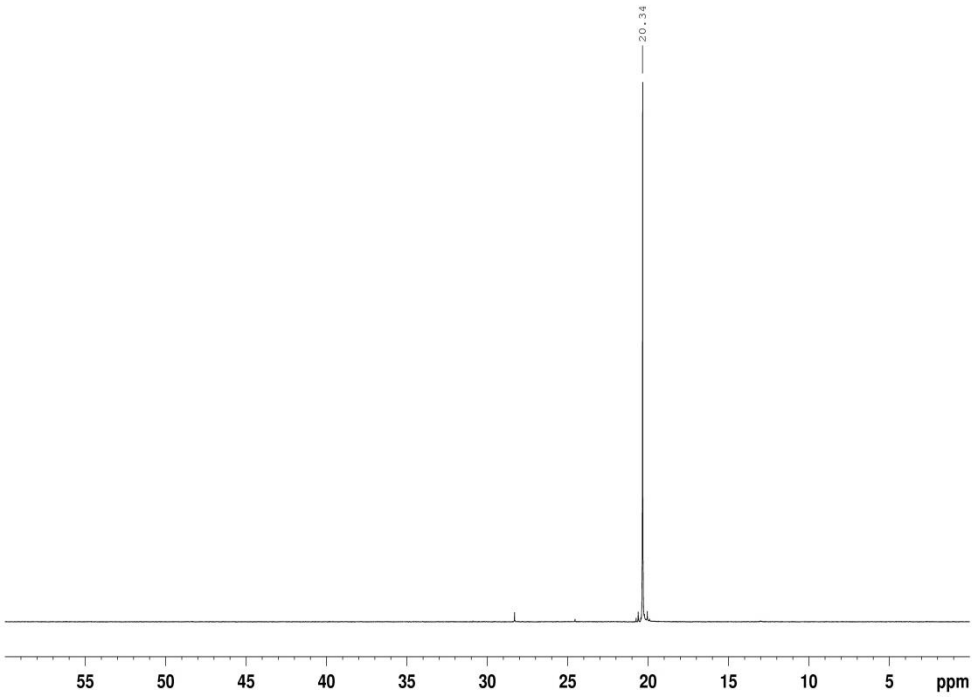
^{1}H-NMR (400 MHz, CD_2Cl_2) **4e**



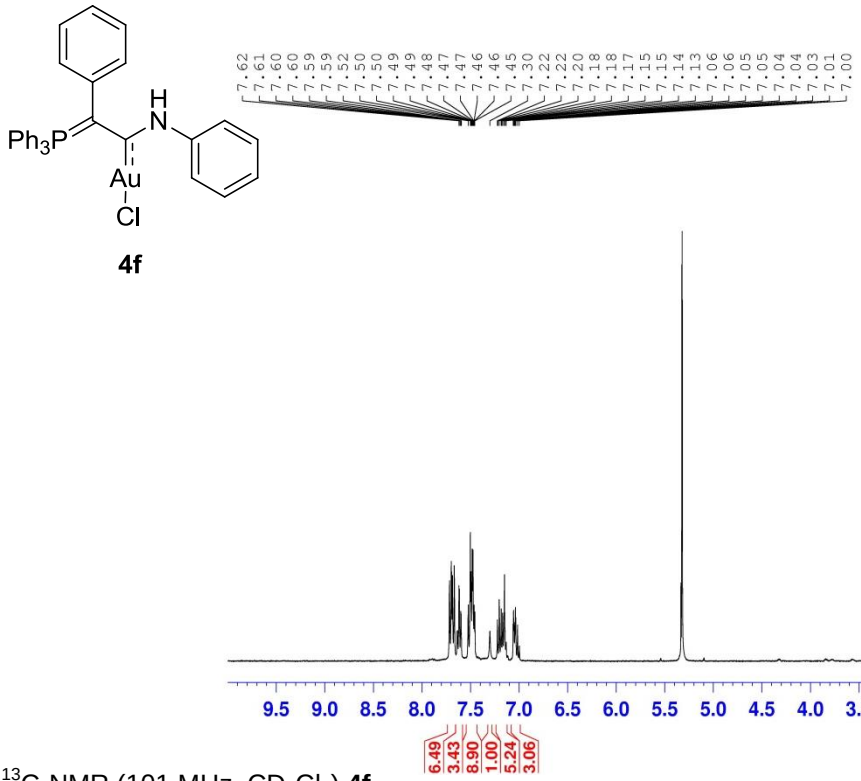
^{13}C-NMR (101 MHz, CD_2Cl_2) **4e**



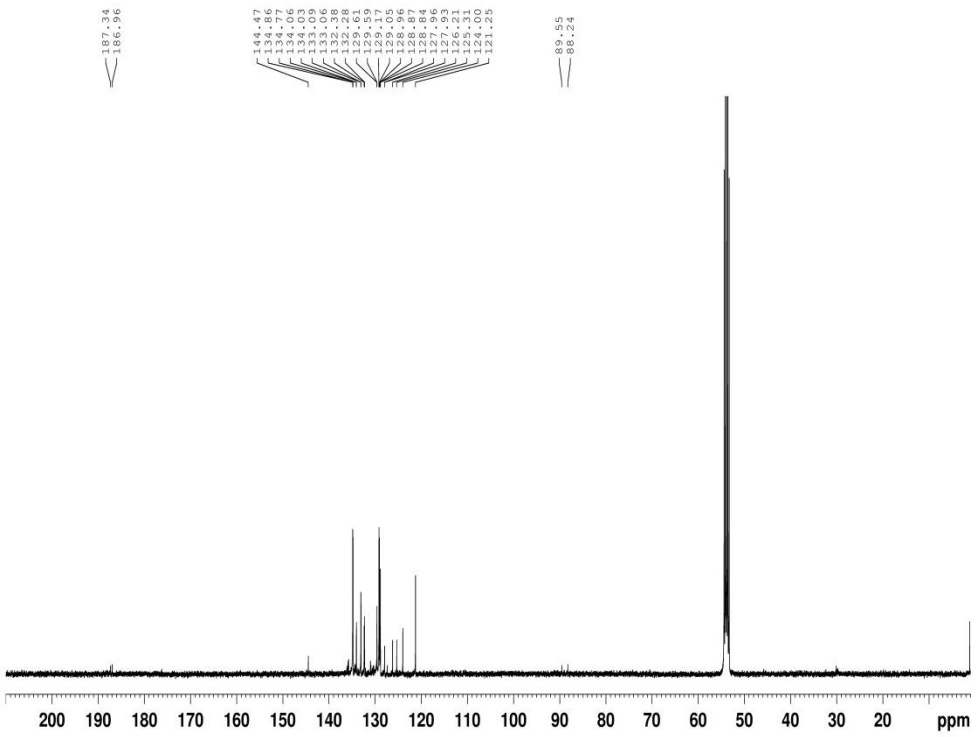
^{31}P-NMR (162 MHz, CD_2Cl_2) **4e**



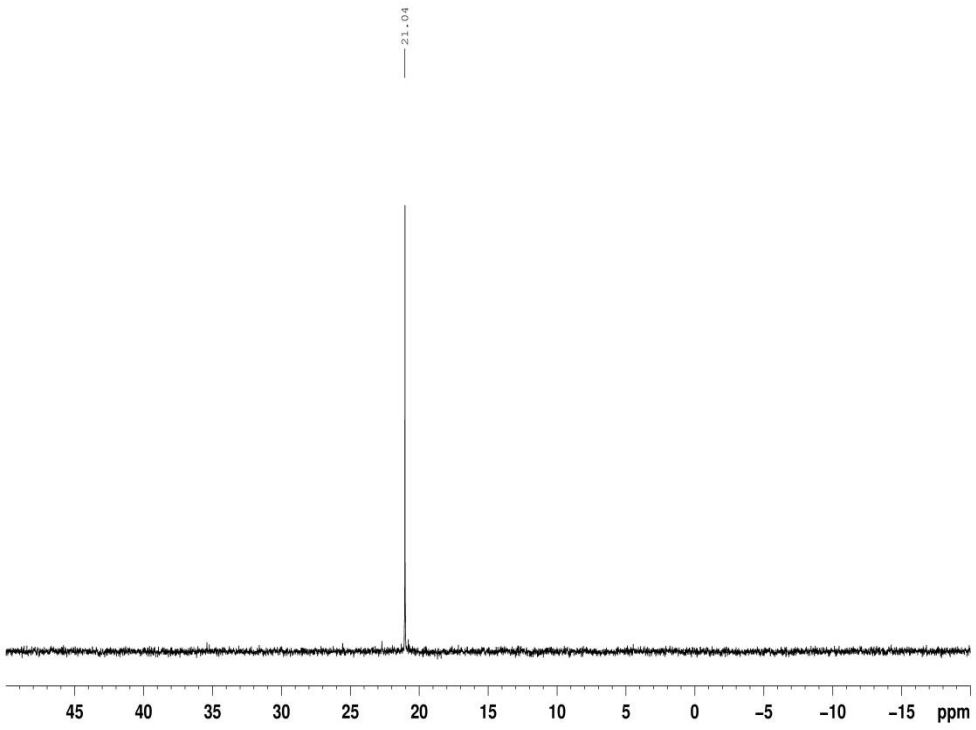
^{1}H-NMR (400 MHz, CD_2Cl_2) **4f**



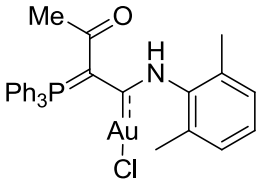
^{13}C-NMR (101 MHz, CD_2Cl_2) **4f**



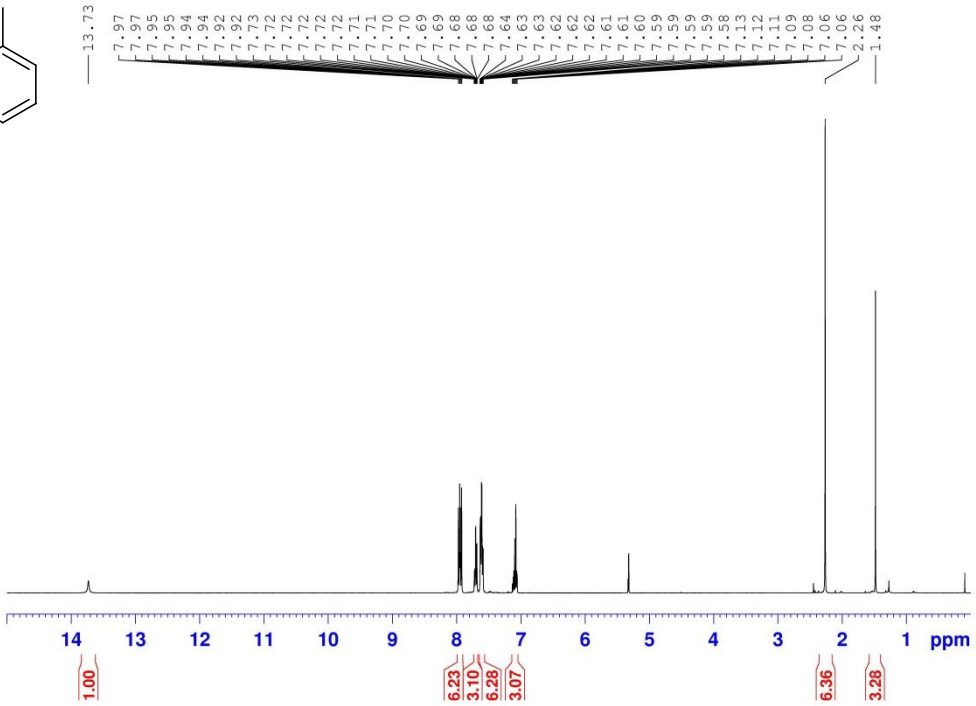
^{31}P-NMR (162 MHz, CD_2Cl_2) **4f**



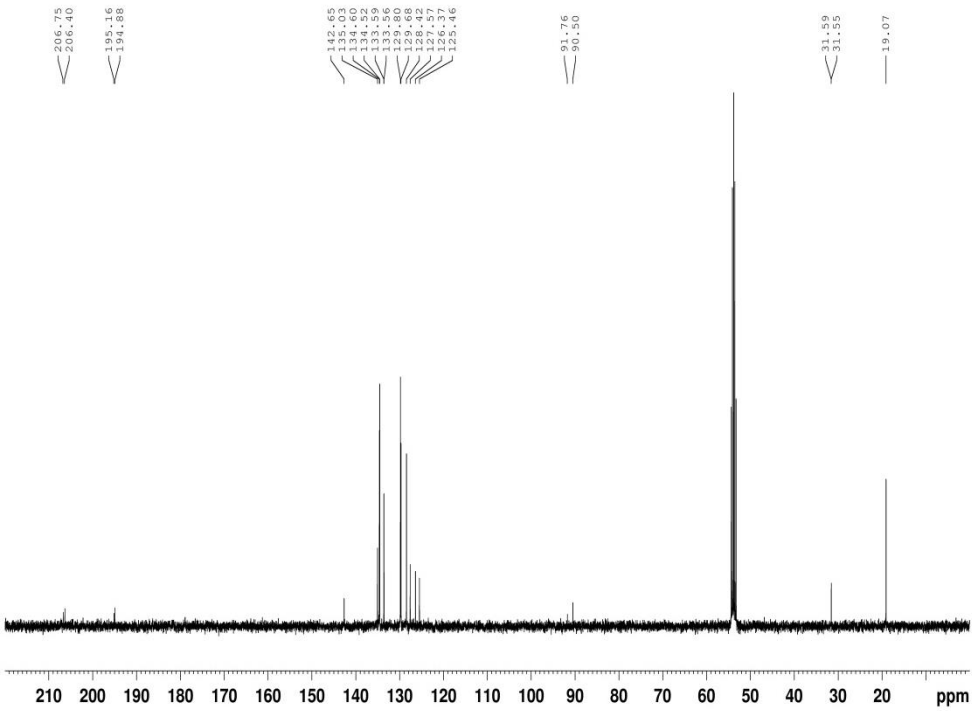
^{1}H-NMR (400 MHz, CD_2Cl_2) **4g**



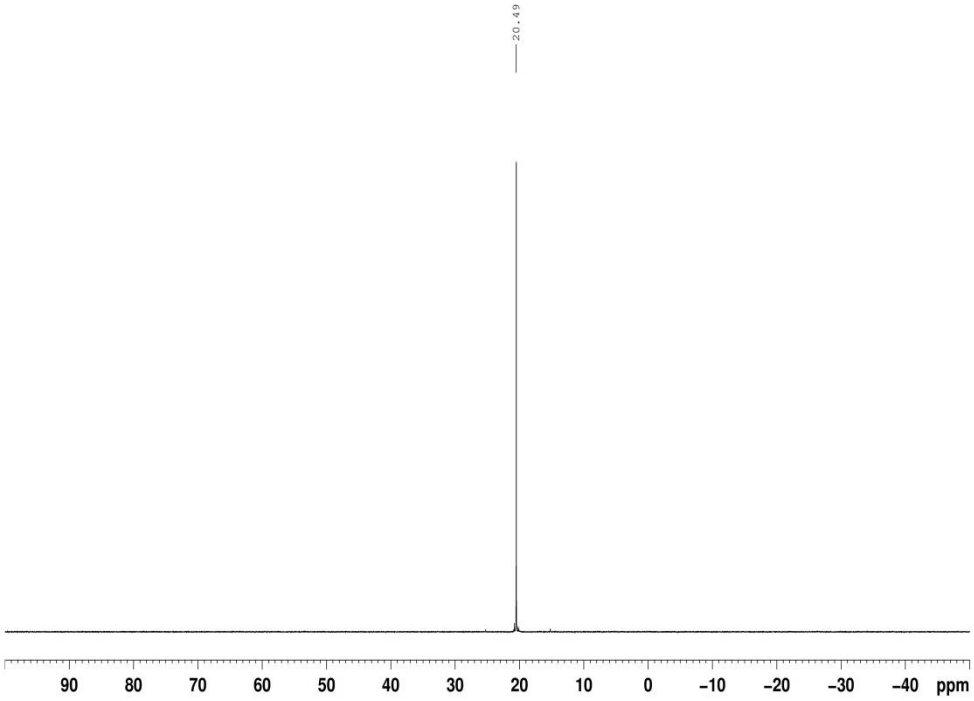
4g



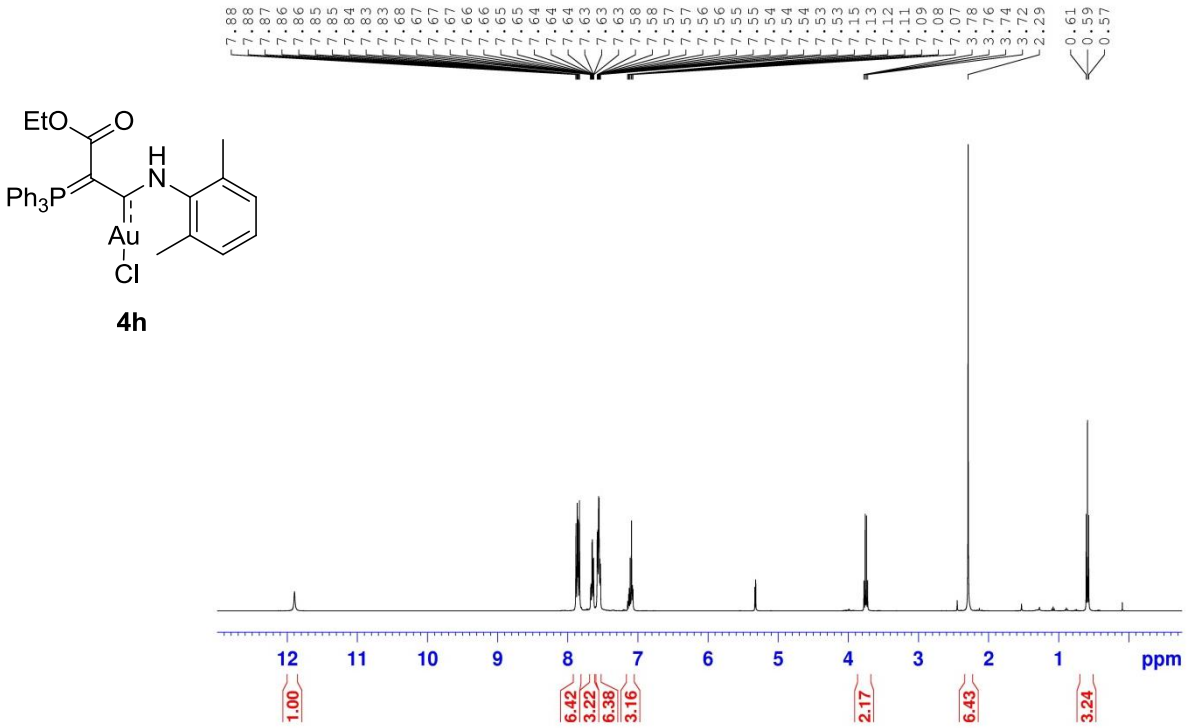
^{13}C-NMR (101 MHz, CD_2Cl_2) **4g**



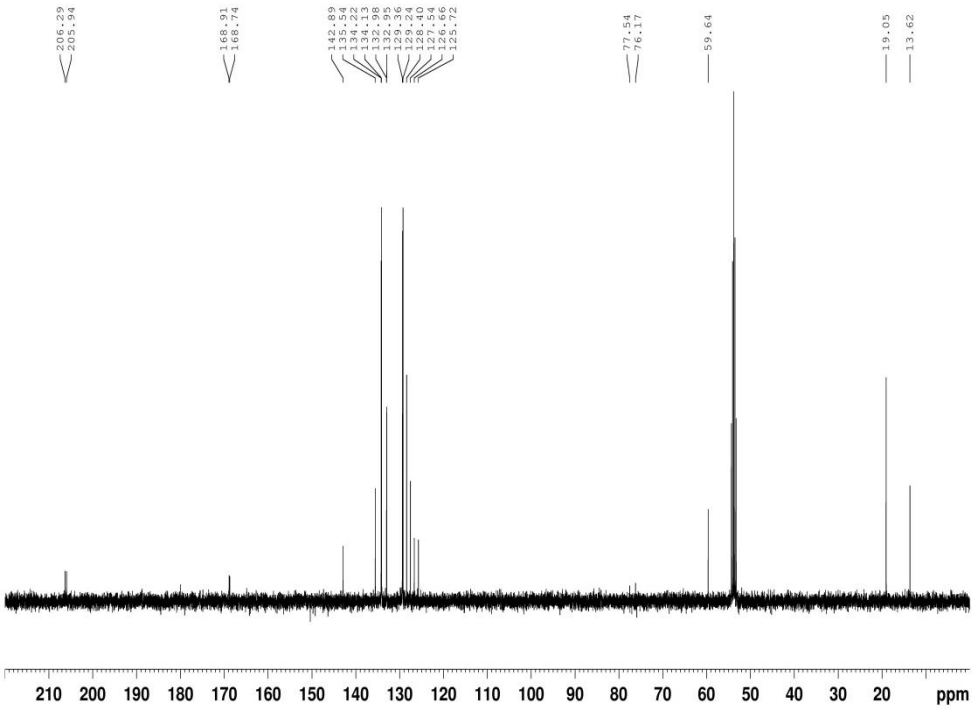
^{31}P-NMR (162 MHz, CD_2Cl_2) **4g**



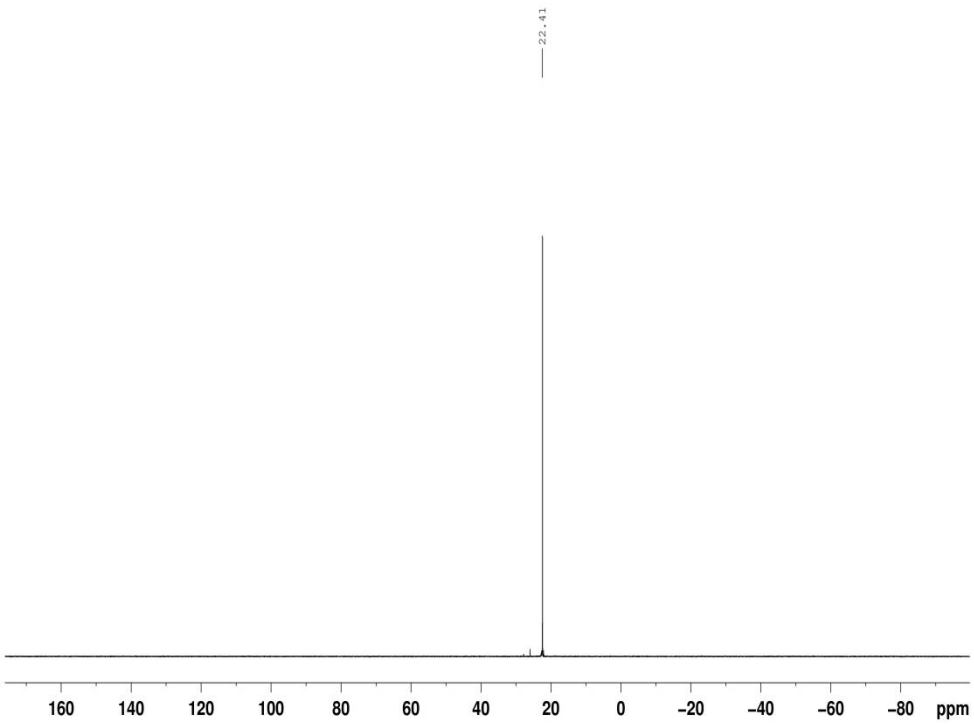
^{1}H-NMR (400 MHz, CD_2Cl_2) **4h**



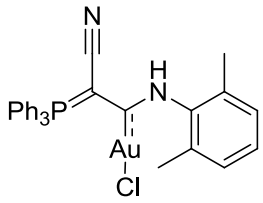
^{13}C-NMR (101 MHz, CD_2Cl_2) **4h**



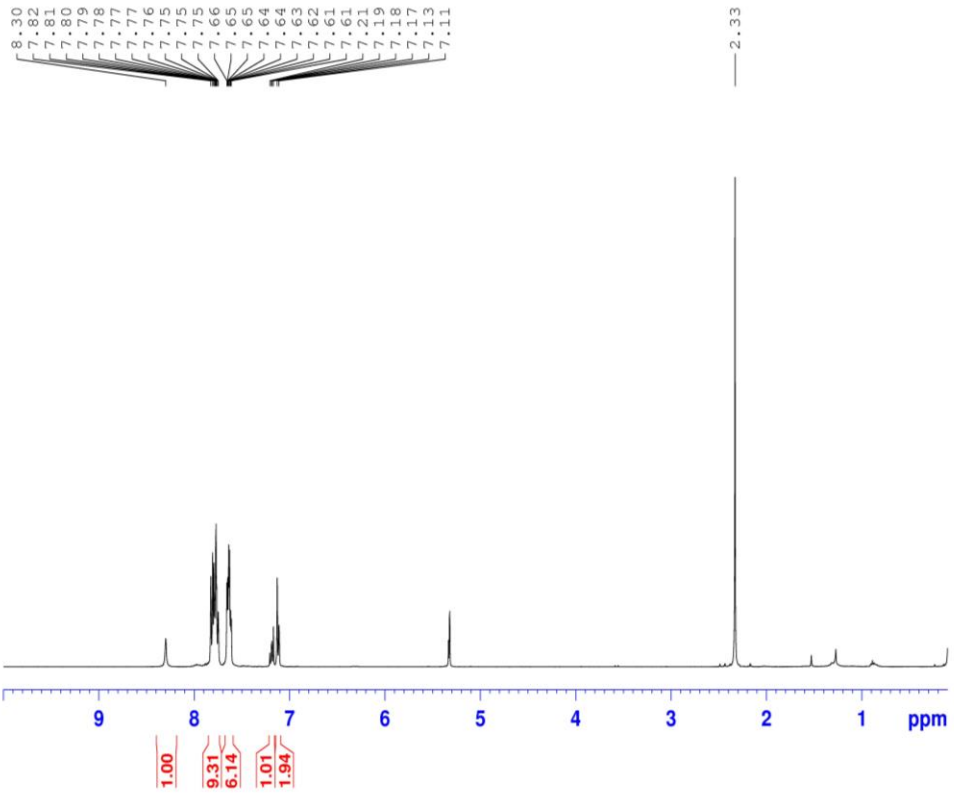
^{31}P-NMR (162 MHz, CD_2Cl_2) **4h**



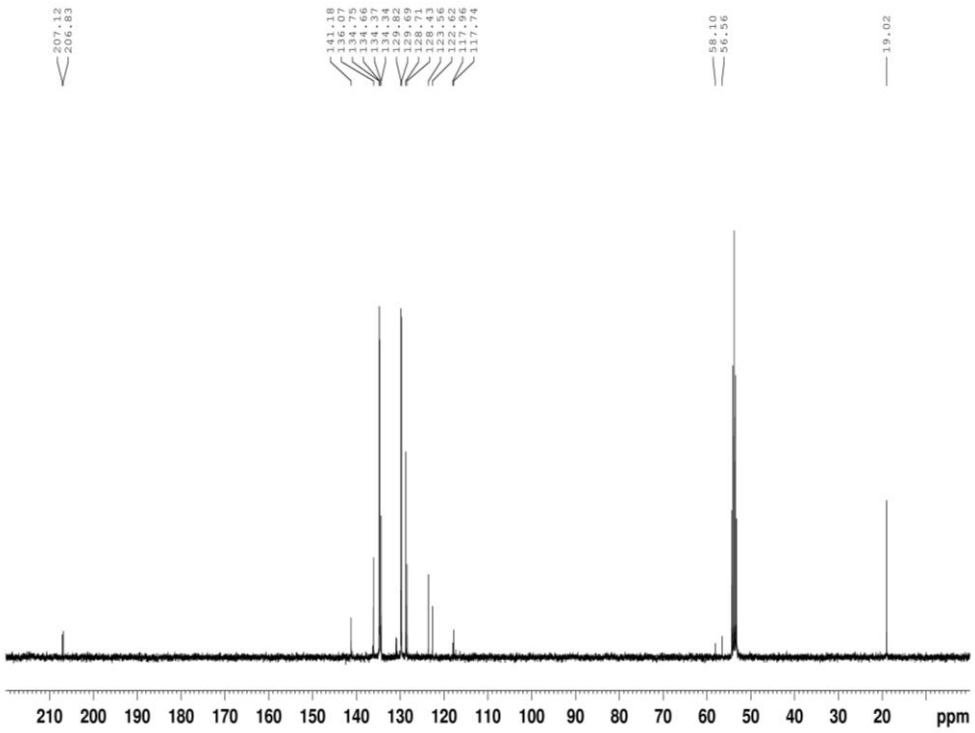
^{1}H-NMR (400 MHz, CD_2Cl_2) **4i**



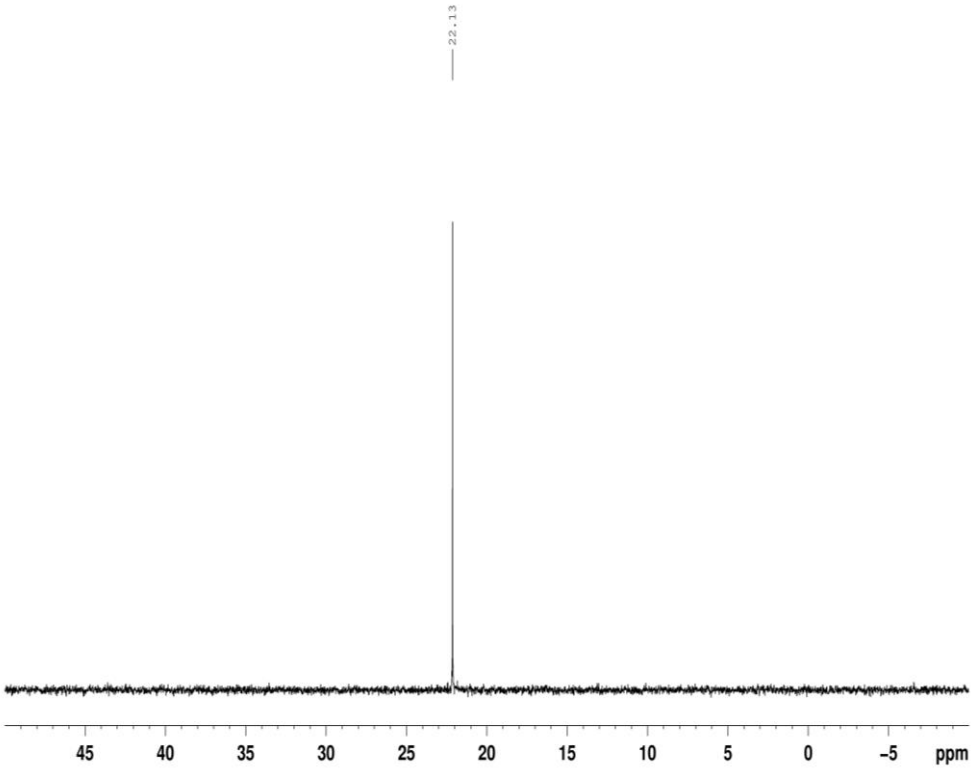
4i



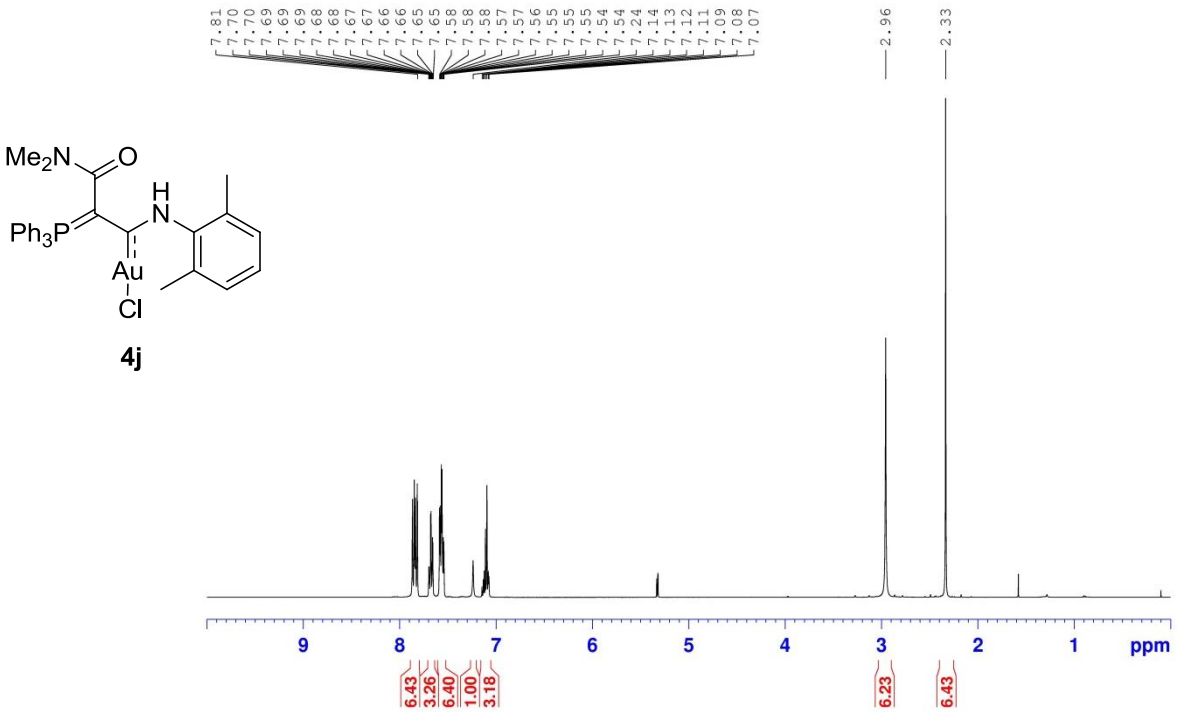
^{13}C-NMR (101 MHz, CD_2Cl_2) **4i**



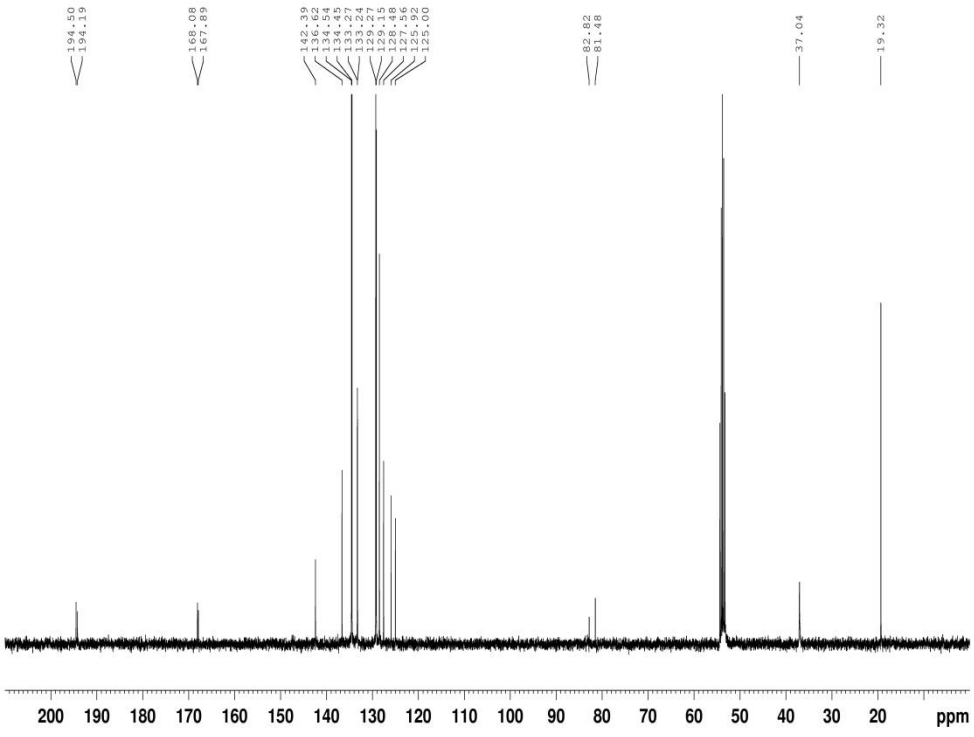
^{31}P-NMR (162 MHz, CD_2Cl_2) **4i**



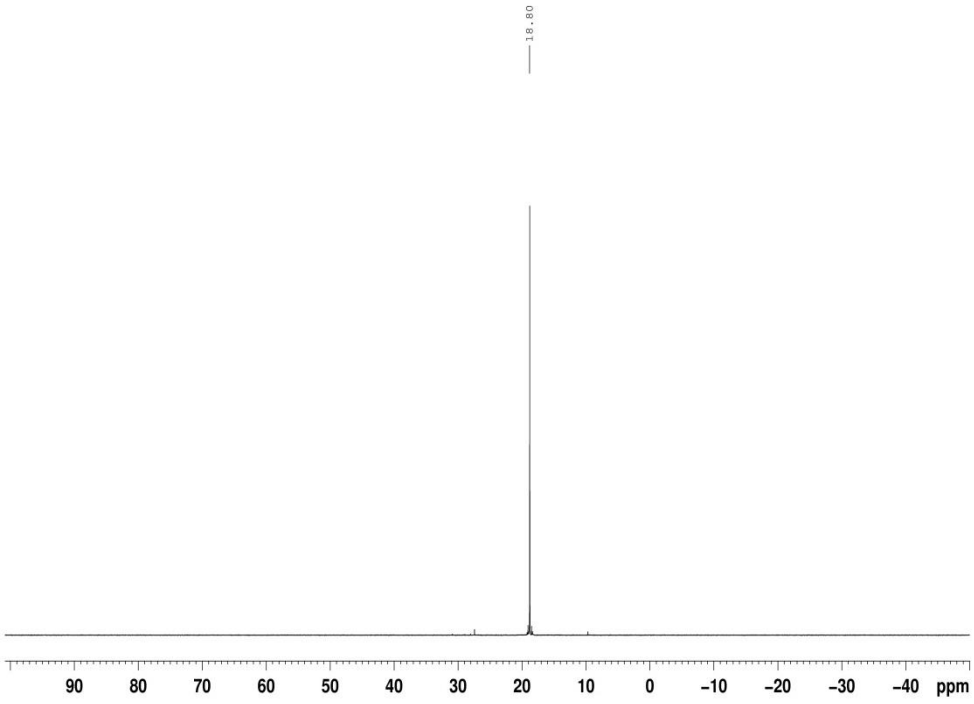
^{1}H-NMR (400 MHz, CD_2Cl_2) **4j**



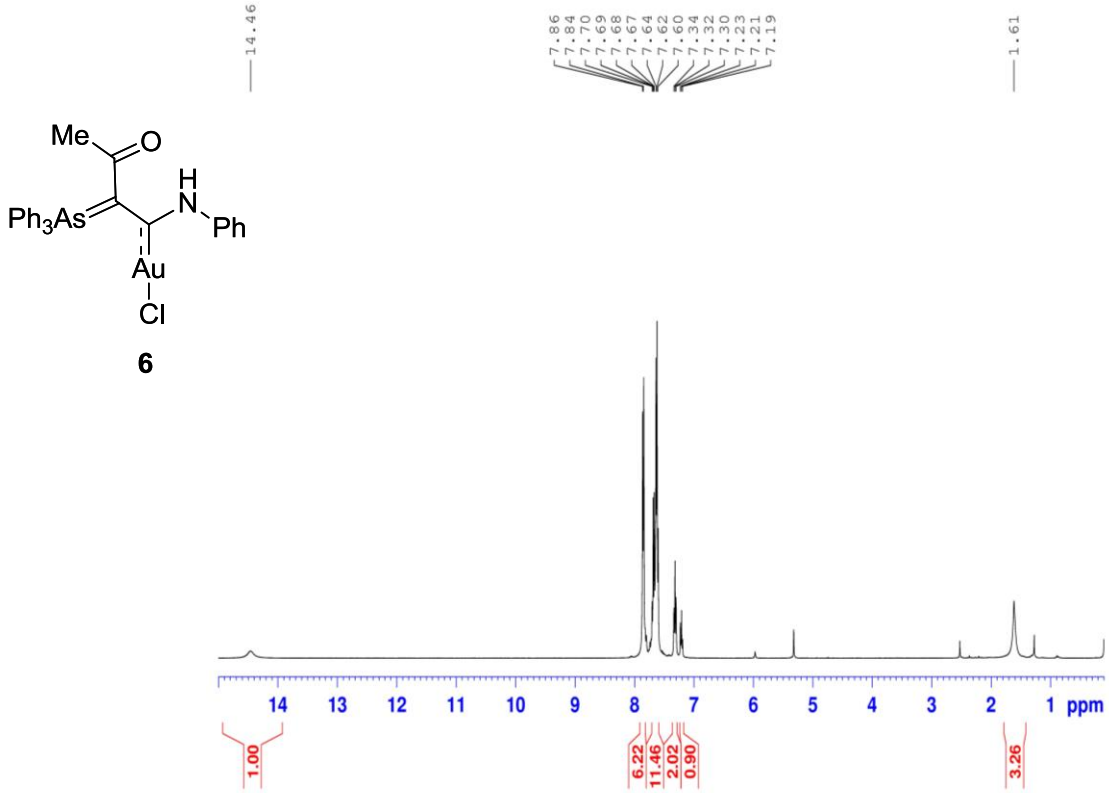
^{13}C-NMR (101 MHz, CD_2Cl_2) **4j**



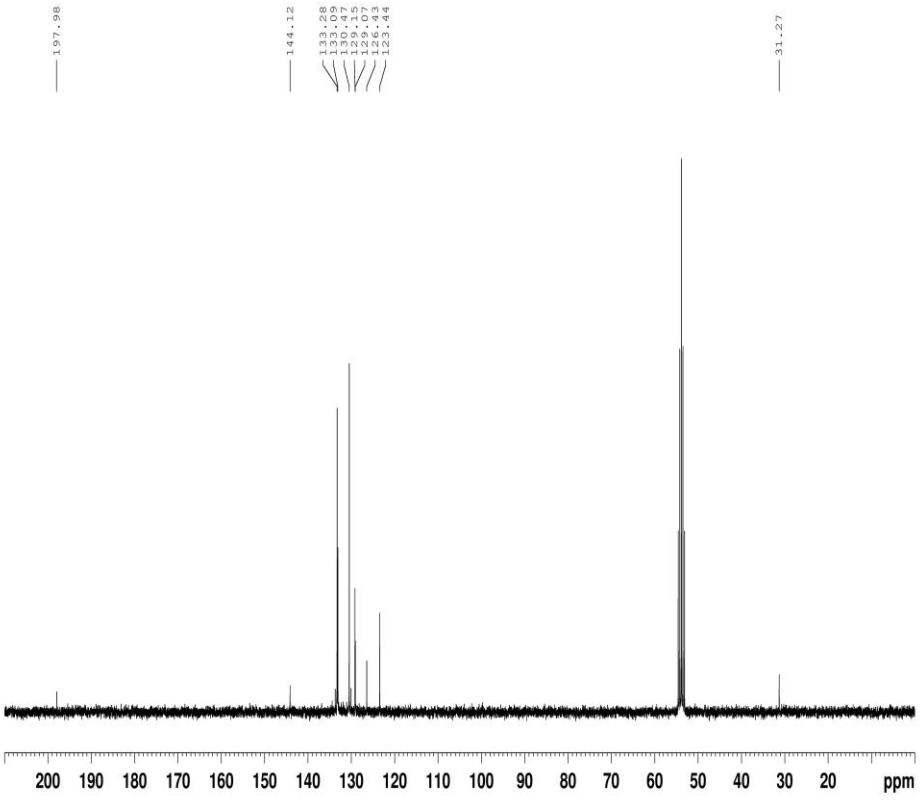
^{31}P-NMR (162 MHz, CD_2Cl_2) **4j**



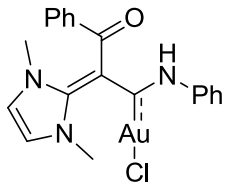
^{1}H-NMR (400 MHz, CD_2Cl_2) **6**



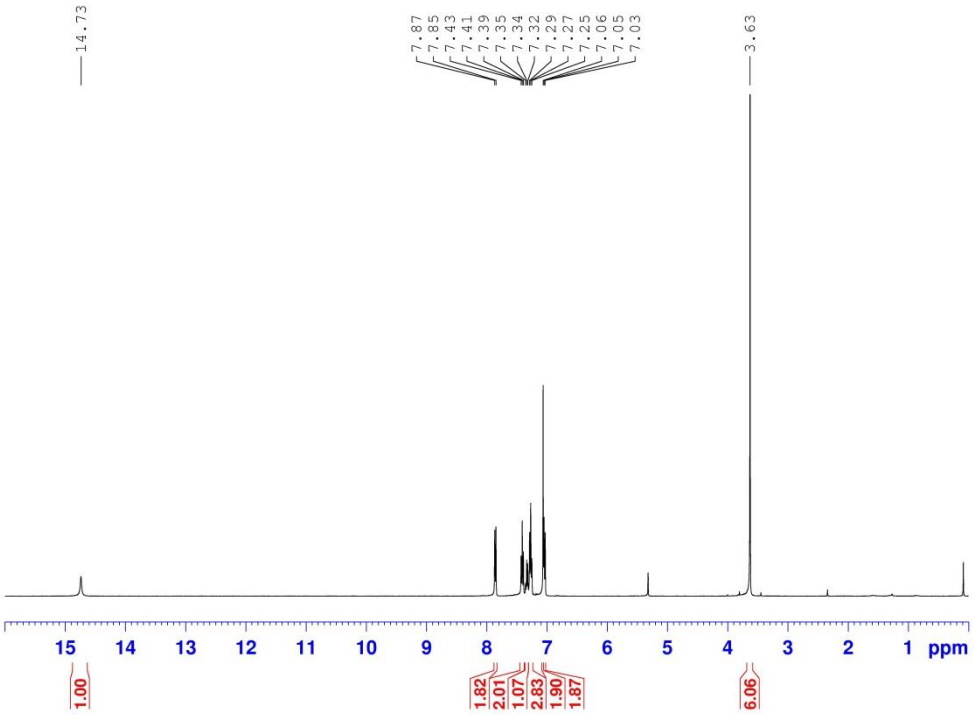
^{13}C-NMR (75 MHz, CD_2Cl_2) **6**



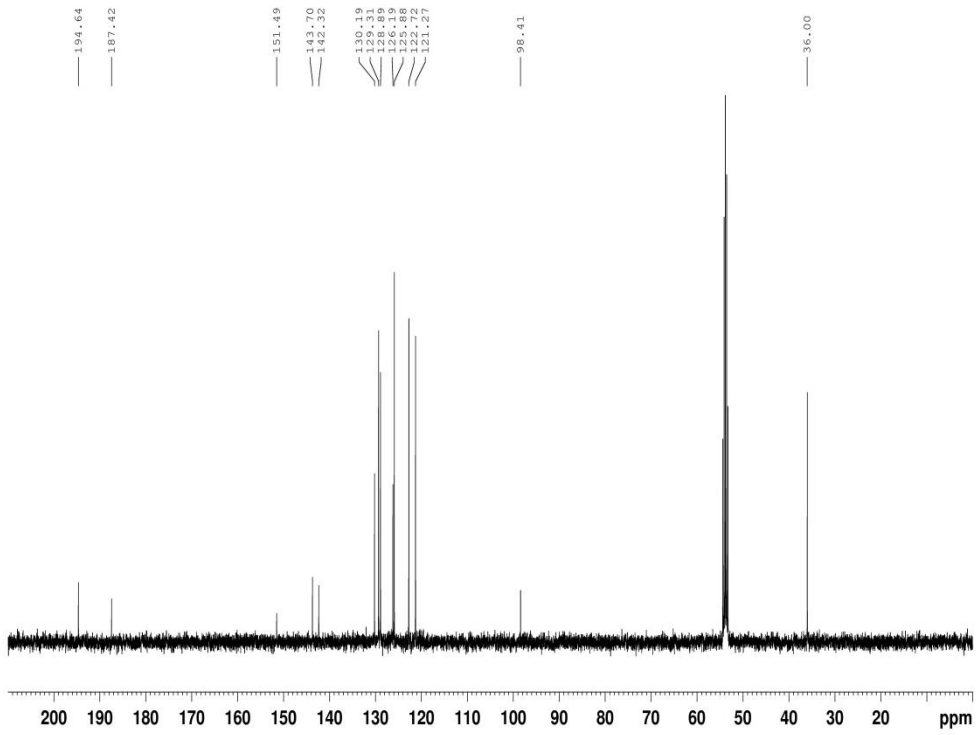
^{1}H-NMR (400 MHz, CD_2Cl_2) **8**



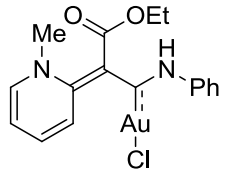
8



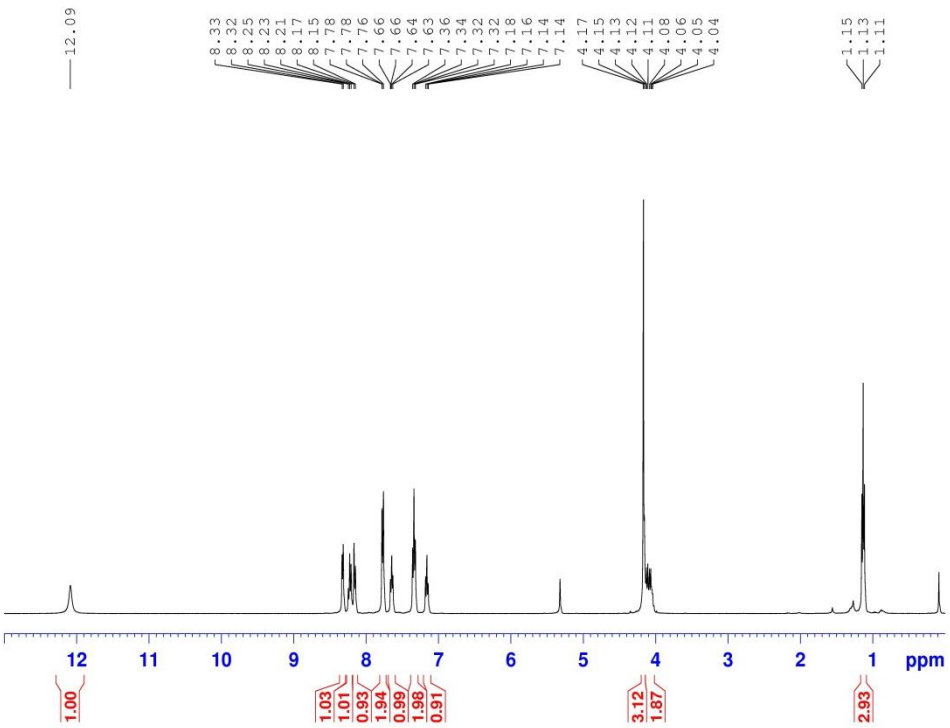
^{13}C-NMR (101 MHz, CD_2Cl_2) **8**



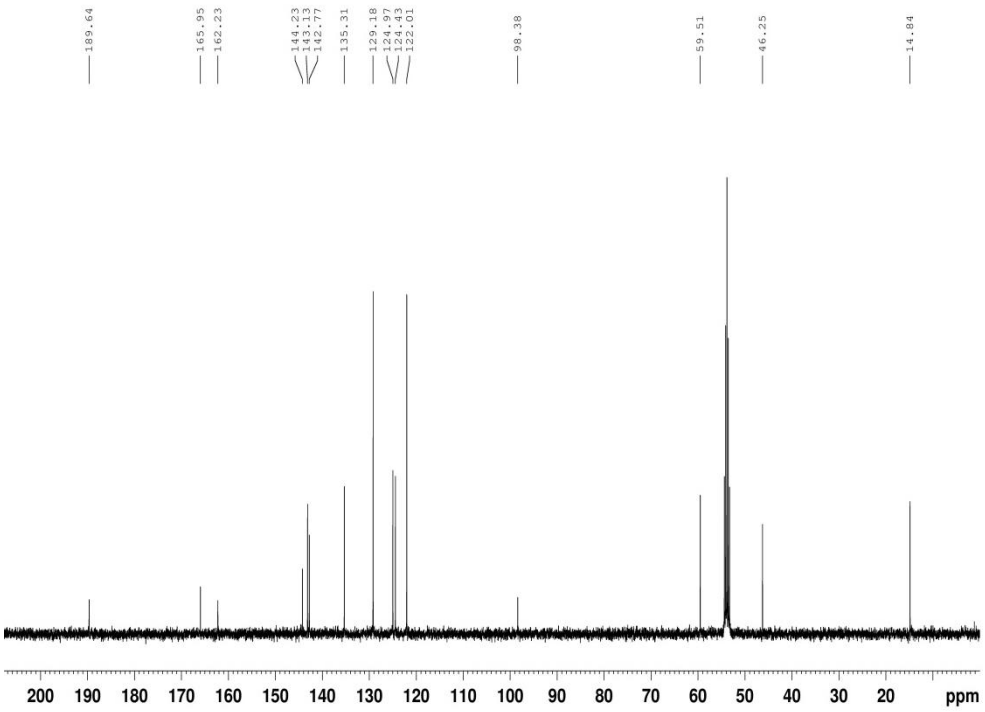
^{1}H-NMR (400 MHz, CD_2Cl_2) **10**



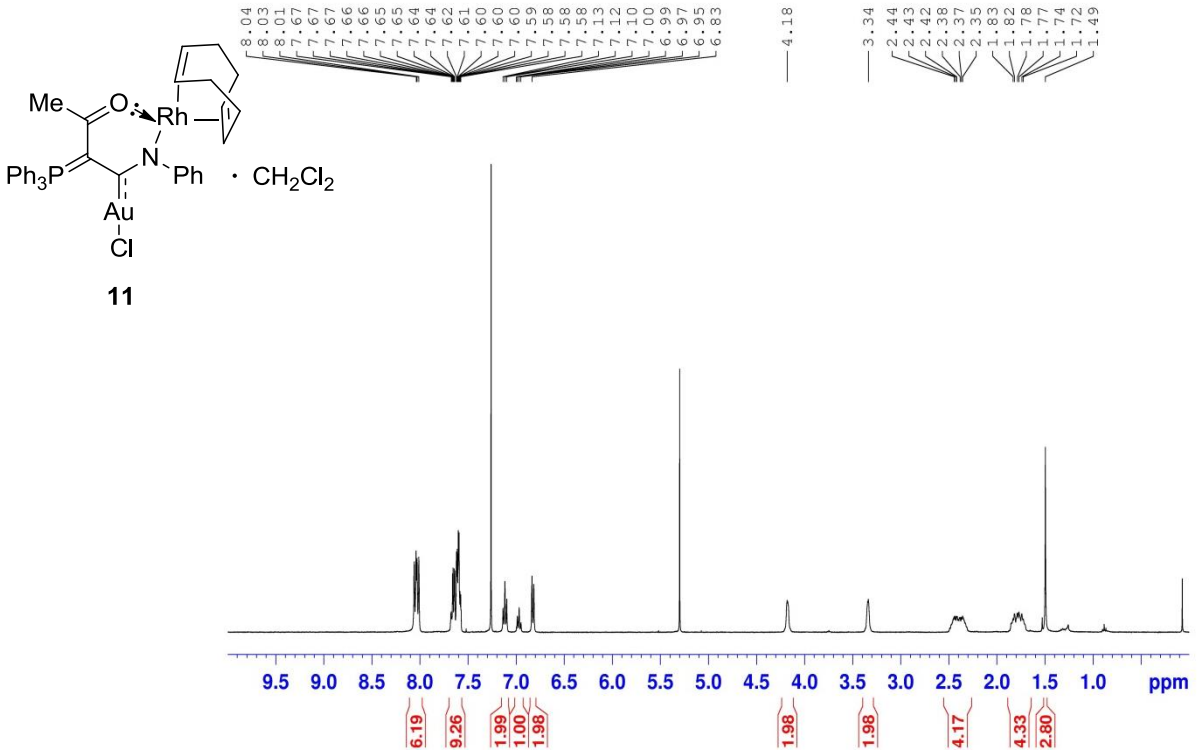
10



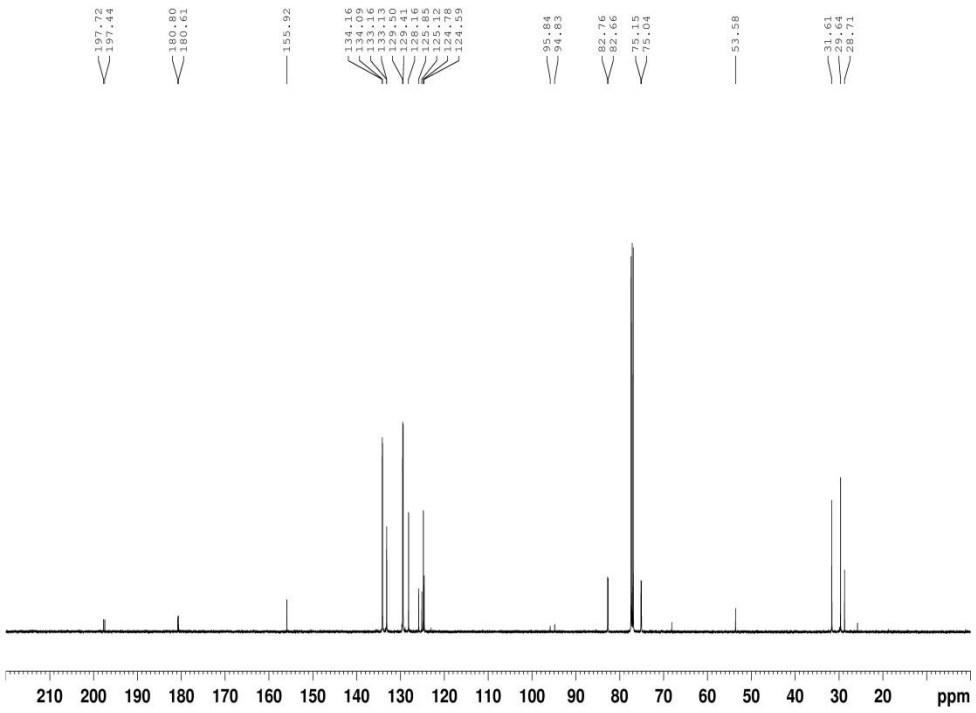
^{13}C-NMR (101 MHz, CD_2Cl_2) **10**



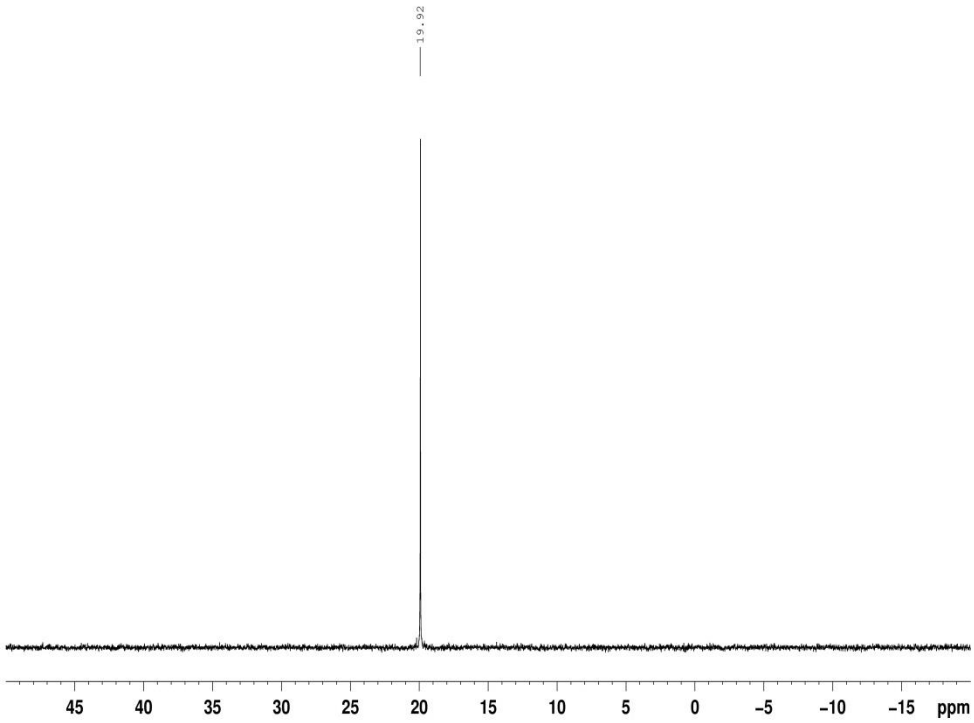
^{1}H-NMR (400 MHz, CD_2Cl_2) **11**



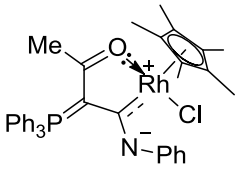
^{13}C-NMR (101 MHz, CD_2Cl_2) **11**



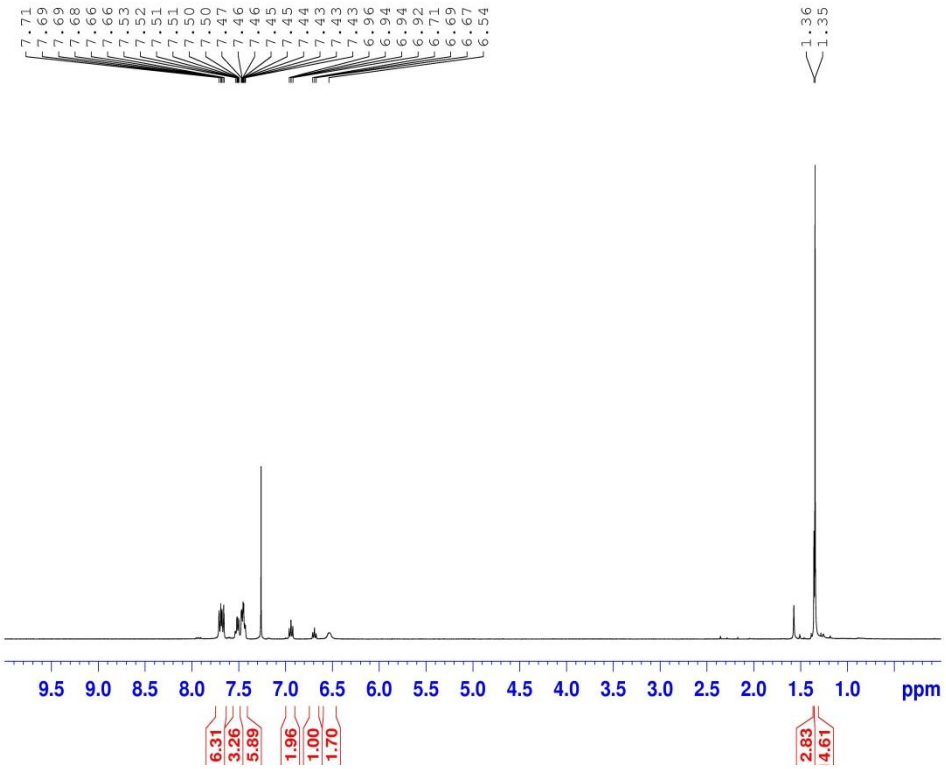
^{31}P-NMR (162 MHz, CD_2Cl_2) **11**



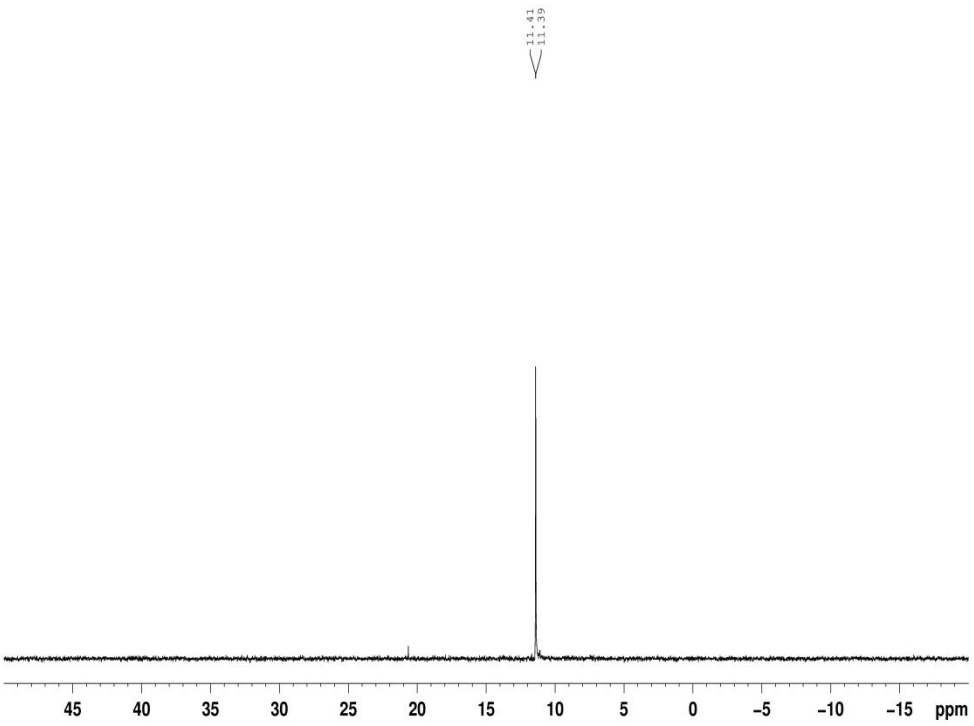
^{1}H-NMR (400 MHz, CD_2Cl_2) **12**



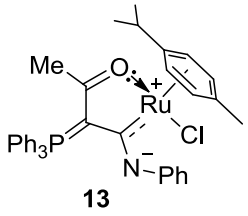
12



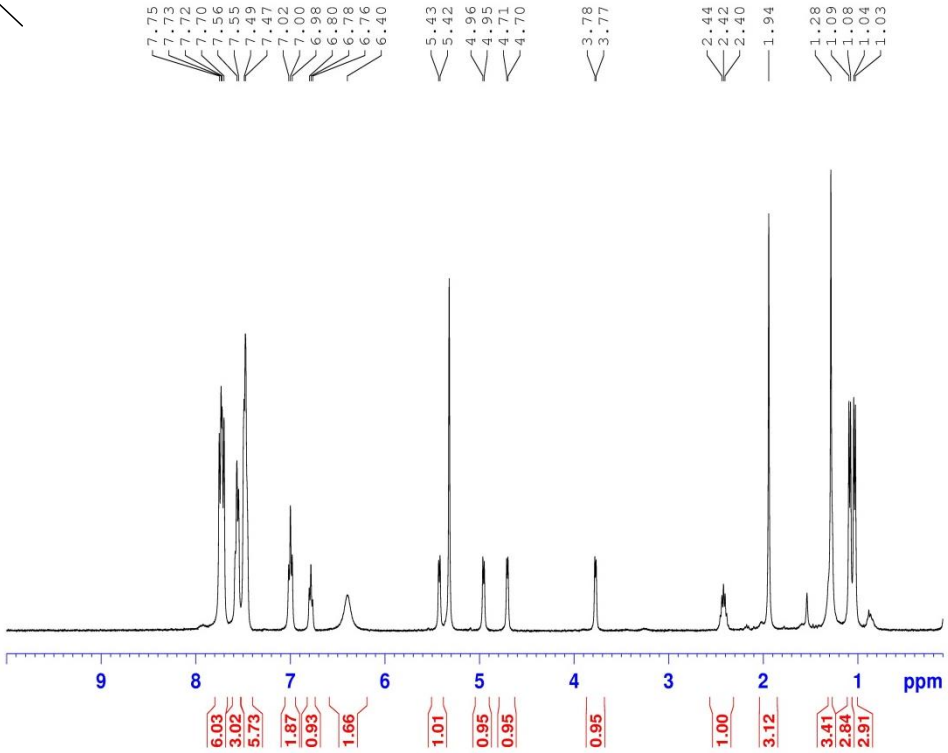
^{31}P-NMR (162 MHz, CD_2Cl_2) **12**



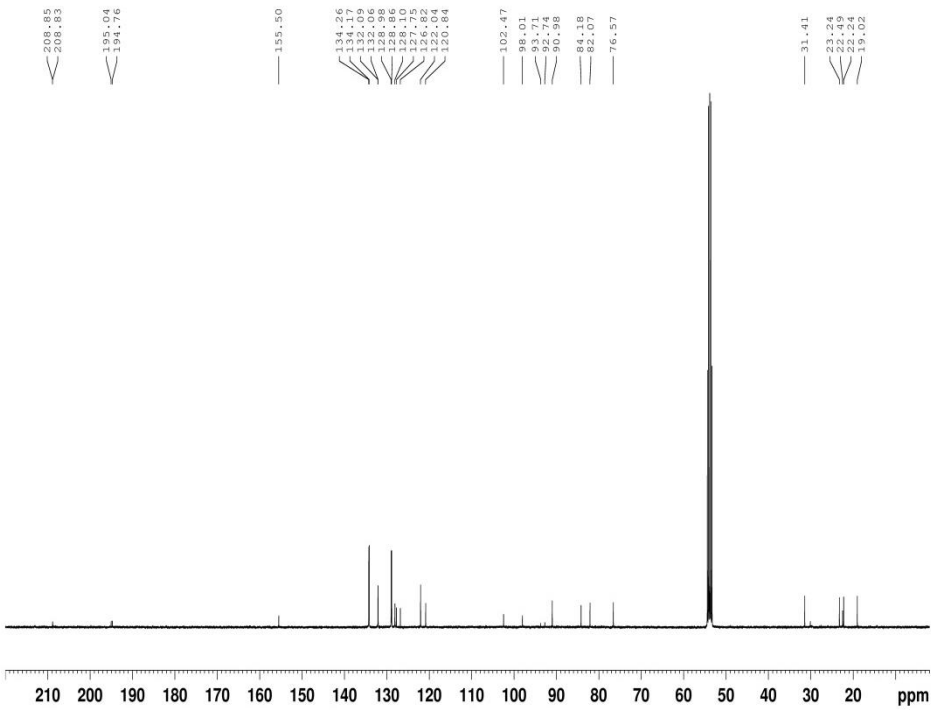
^{1}H-NMR (400 MHz, CD_2Cl_2) **13**



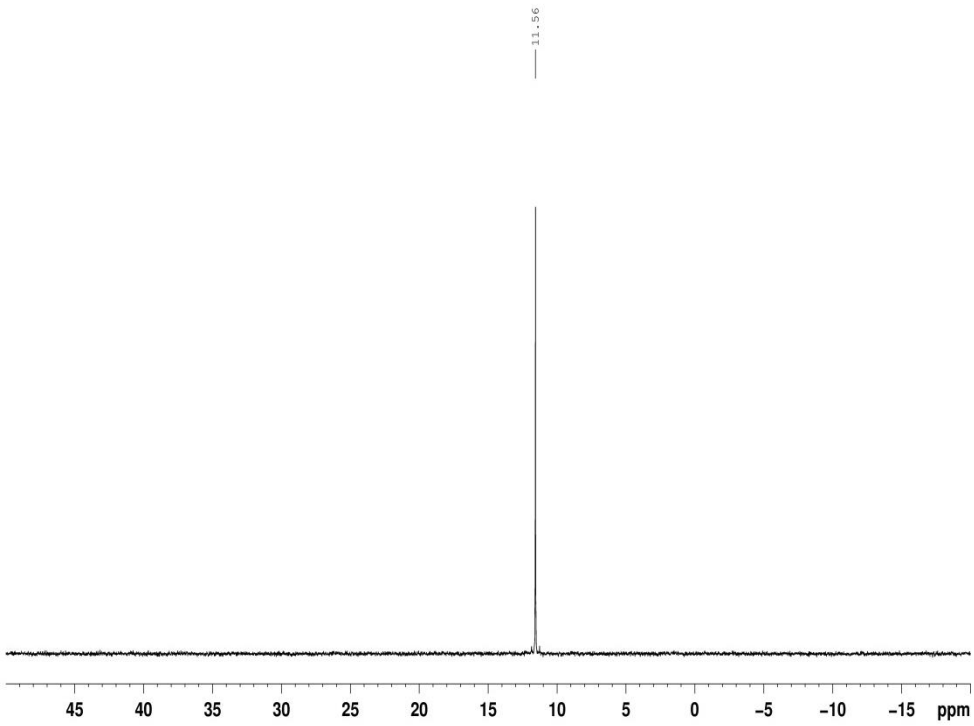
13



^{13}C-NMR (101 MHz, CD_2Cl_2) **13**

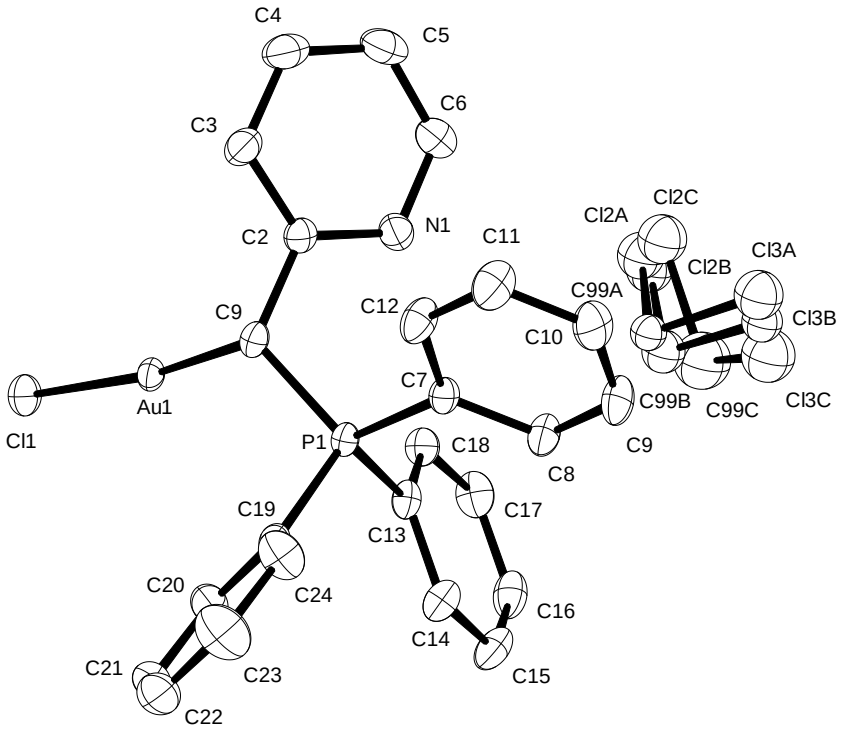


^{31}P-NMR (162 MHz, CD_2Cl_2) **13**



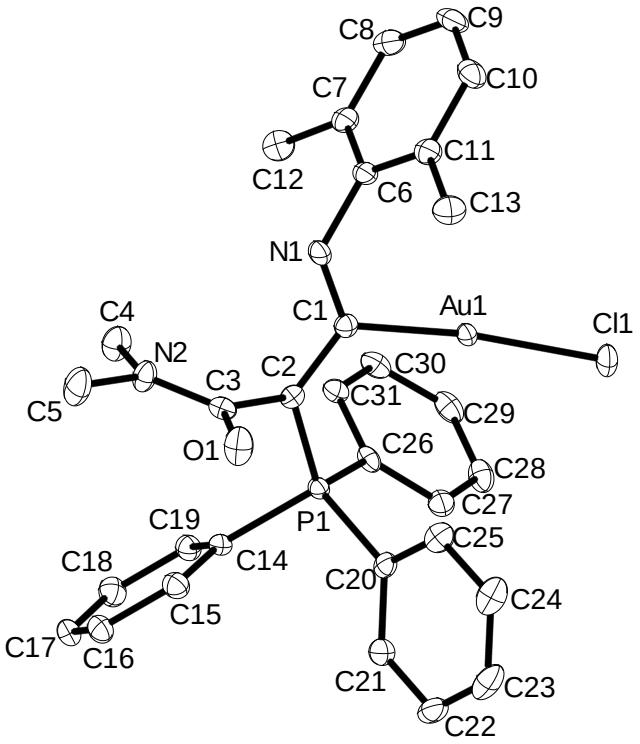
X-Ray Analyses

Compound 3e



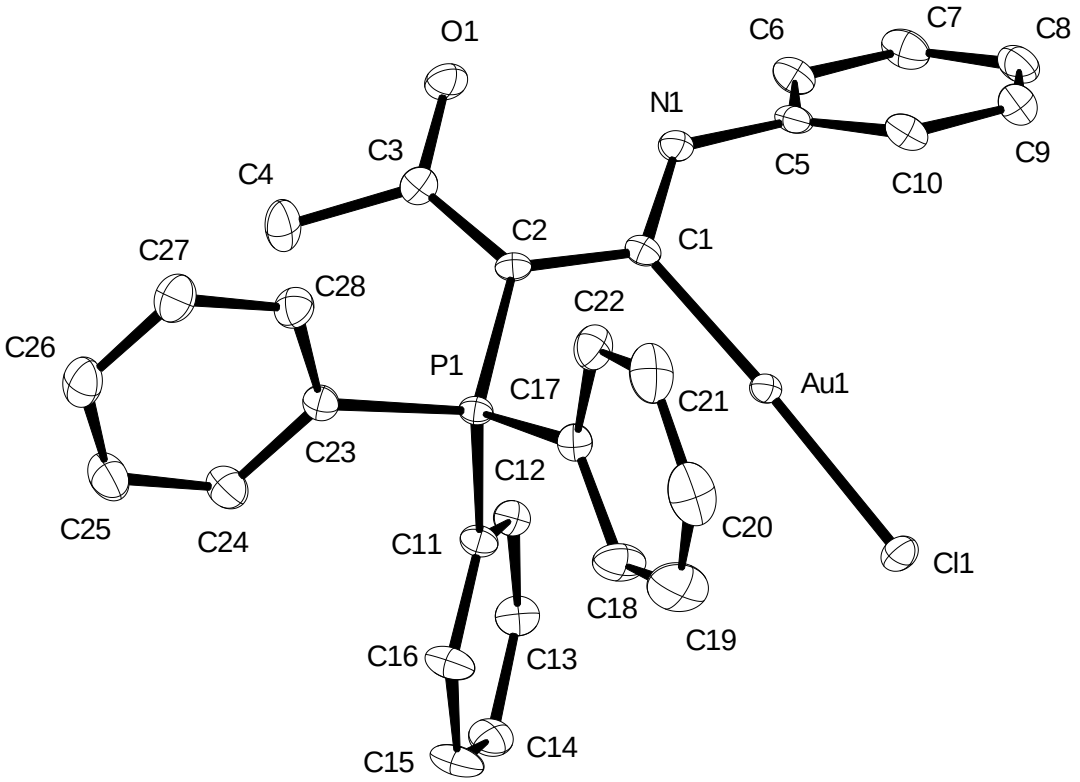
Empirical formula	$C_{25}H_{22}AuCl_3NP$	
Color	colourless	
Formula weight	670.72 $g \cdot mol^{-1}$	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**C2/c, (no. 15)**	
Unit cell dimensions	a = 24.4111(6) Å	α= 90°.
	b = 8.577(2) Å	β= 93.067(5)°.
	c = 23.0774(16) Å	γ = 90°.
Volume	4824.8(12) $Å^3$	
Z	8	
Density (calculated)	1.847 $Mg \cdot m^{-3}$	
Absorption coefficient	6.511 mm^{-1}	
F(000)	2592 e	
Crystal size	0.30 x 0.12 x 0.07 mm^3	
θ range for data collection	3.05 to 33.10°.	
Index ranges	$-37 \le h \le 37$, $-13 \le k \le 13$, $-35 \le l \le 35$	
Reflections collected	67463	
Independent reflections	9159 [R_{int} = 0.0532]	
Reflections with I>2σ(I)	7901	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.81 and 0.39	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9159 / 0 / 289	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2σ(I)]	R_1 = 0.0288	wR^2 = 0.0665
R indices (all data)	R_1 = 0.0378	wR^2 = 0.0704
Largest diff. peak and hole	1.327 and -2.047 e · $Å^{-3}$	

Compound 4j



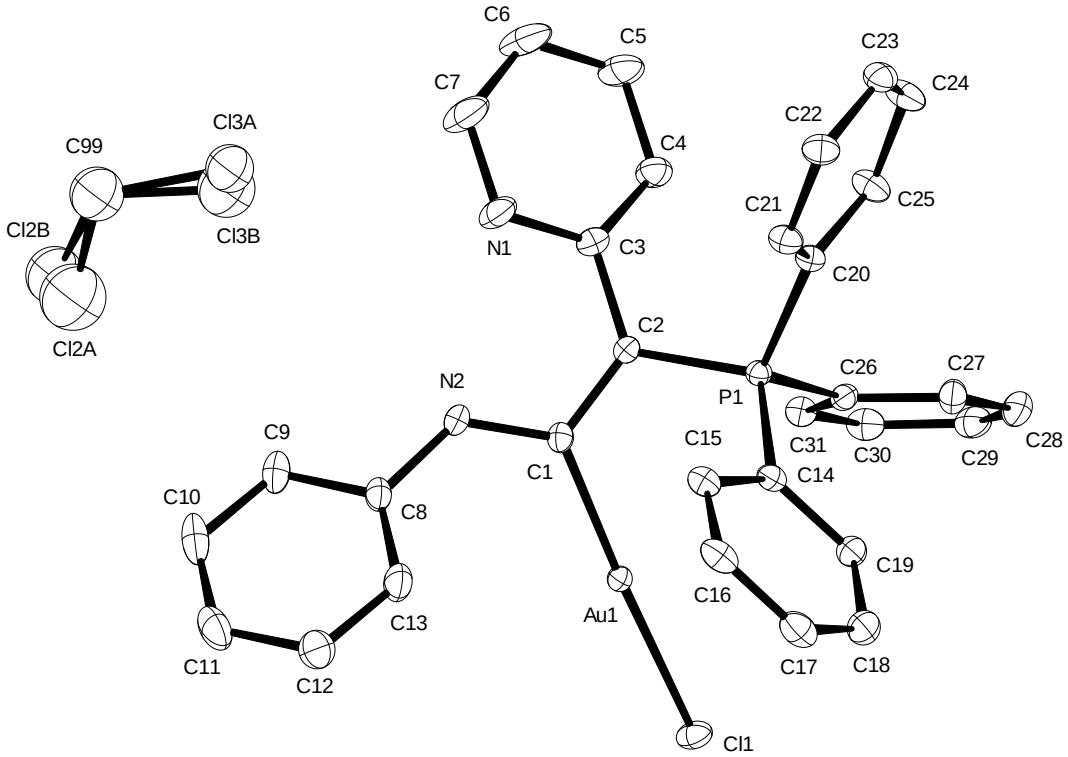
Empirical formula	$C_{31}H_{31}AuClN_2OP$	
Color	colourless	
Formula weight	710.96 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 16.8854(7) Å	α= 90°.
	b = 10.9240(5) Å	β= 111.3890(10)°.
	c = 16.4234(7) Å	γ = 90°.
Volume	2820.7(2) $Å^3$	
Z	4	
Density (calculated)	1.674 $Mg \cdot m^{-3}$	
Absorption coefficient	11.412 mm^{-1}	
F(000)	1400 e	
Crystal size	0.14 x 0.13 x 0.10 mm^3	
θ range for data collection	2.81 to 67.16°.	
Index ranges	$-18 \le h \le 20$, $-12 \le k \le 13$, $-19 \le l \le 19$	
Reflections collected	67770	
Independent reflections	4988 [R_{int} = 0.0481]	
Reflections with I>2σ(I)	4859	
Completeness to θ = 67.16°	99.2 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.54295 and 0.22715	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4988 / 0 / 338	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2σ(I)]	R_1 = 0.0186	wR^2 = 0.0442
R indices (all data)	R_1 = 0.0193	wR^2 = 0.0445
Largest diff. peak and hole	0.496 and -0.717 $e \cdot Å^{-3}$	

Compound 4a



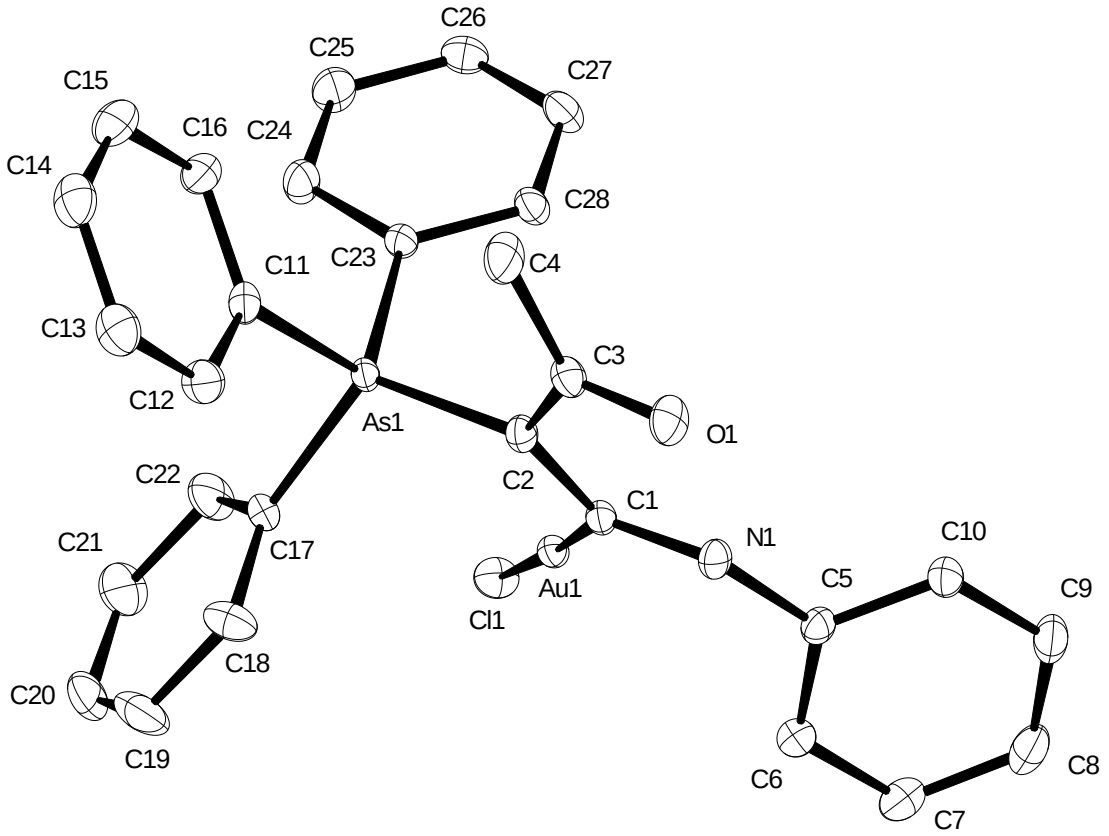
Empirical formula	$C_{28}H_{24}AuClNOP$	
Color	colourless	
Formula weight	653.87 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 14.7905(9) Å	α= 90°.
	b = 11.9586(10) Å	β= 115.796(4)°.
	c = 15.2551(7) Å	γ = 90°.
Volume	2429.3(3) Å^3	
Z	4	
Density (calculated)	1.788 Mg · m^{-3}	
Absorption coefficient	6.253 mm^{-1}	
F(000)	1272 e	
Crystal size	0.27 x 0.21 x 0.10 mm^3	
θ range for data collection	2.68 to 37.00°.	
Index ranges	-24 ≤ h ≤ 25, -20≤ k ≤ 20, -25 ≤ l ≤ 25	
Reflections collected	60767	
Independent reflections	12321 [R_{int} = 0.0518]	
Reflections with I>2σ(I)	9429	
Completeness to θ = 37.00°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.55184 and 0.21375	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12321 / 0 / 299	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R_1 = 0.0329	wR^2 = 0.0548
R indices (all data)	R_1 = 0.0580	wR^2 = 0.0605
Largest diff. peak and hole	1.425 and -2.498 e · Å^{-3}	

Compound 4e:



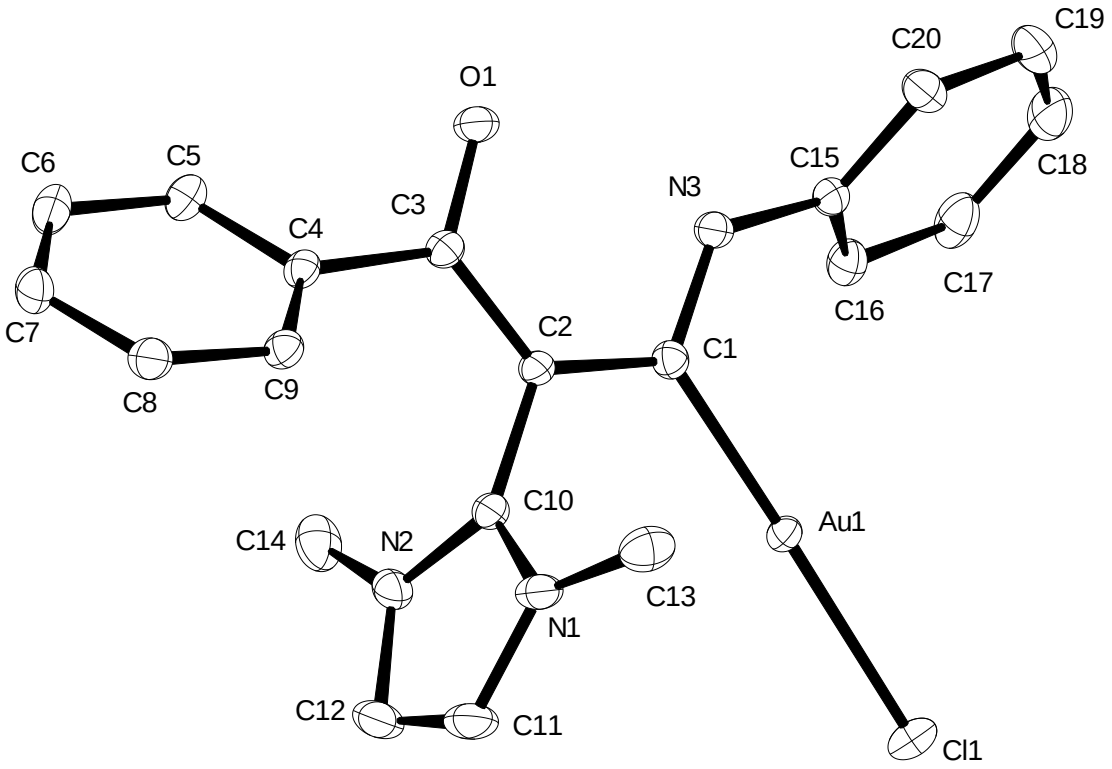
Empirical formula	$C_{31}H_{25}AuClN_2P \cdot 0.5\ CH_2Cl_2$	
Color	yellow	
Formula weight	731.38 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 8.7003(3) Å	α= 90°.
	b = 19.0210(12) Å	β= 90.348(4)°.
	c = 17.8177(14) Å	γ = 90°.
Volume	2948.6(3) $Å^3$	
Z	4	
Density (calculated)	1.648 $Mg \cdot m^{-3}$	
Absorption coefficient	5.248 mm^{-1}	
F(000)	1428 e	
Crystal size	0.17 x 0.10 x 0.09 mm^3	
θ range for data collection	3.17 to 34.94°.	
Index ranges	$-14 \le h \le 13, -28 \le k \le 30, -28 \le l \le 28$	
Reflections collected	95323	
Independent reflections	12890 [R_{int} = 0.0388]	
Reflections with I>2σ(I)	11231	
Completeness to θ = 27.50°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.66 and 0.49	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12890 / 0 / 345	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2σ(I)]	R_1 = 0.0244	wR^2 = 0.0570
R indices (all data)	R_1 = 0.0326	wR^2 = 0.0605
Largest diff. peak and hole	2.411 and -1.792 e $\cdot Å^{-3}$	

Compound 6:



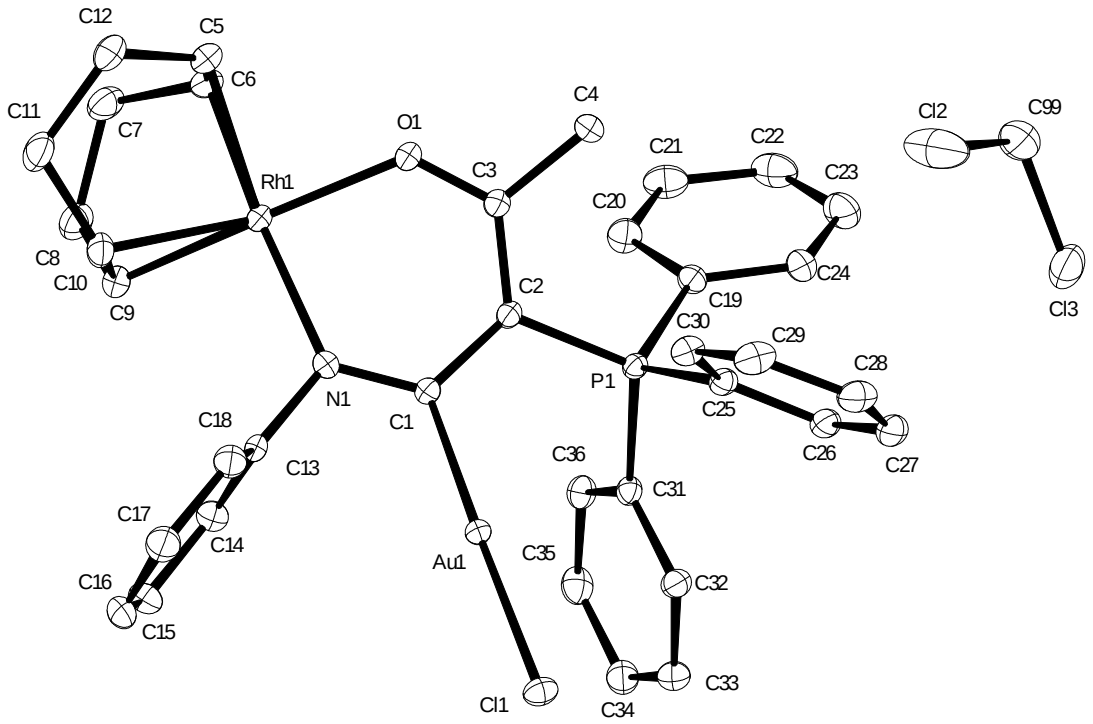
Empirical formula	$C_{28}H_{24}AsAuClNO$	
Color	colourless	
Formula weight	697.82 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 14.9063(15) Å	α= 90°.
	b = 12.0478(12) Å	β= 115.743(3)°.
	c = 15.3302(3) Å	γ = 90°.
Volume	2479.9(4) $Å^3$	
Z	4	
Density (calculated)	1.869 $Mg \cdot m^{-3}$	
Absorption coefficient	7.385 mm^{-1}	
F(000)	1344 e	
Crystal size	0.20 x 0.17 x 0.07 mm^3	
θ range for data collection	2.67 to 36.00°.	
Index ranges	$-24 \le h \le 24$, $-19 \le k \le 19$, $-25 \le l \le 25$	
Reflections collected	62465	
Independent reflections	11702 [R_{int} = 0.0491]	
Reflections with I>2σ(I)	10436	
Completeness to θ = 27.50°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.62 and 0.27	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11702 / 0 / 299	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2σ(I)]	R_1 = 0.0294	wR^2 = 0.0693
R indices (all data)	R_1 = 0.0357	wR^2 = 0.0723
Largest diff. peak and hole	1.897 and -4.624 e $\cdot Å^{-3}$	

Compound 9



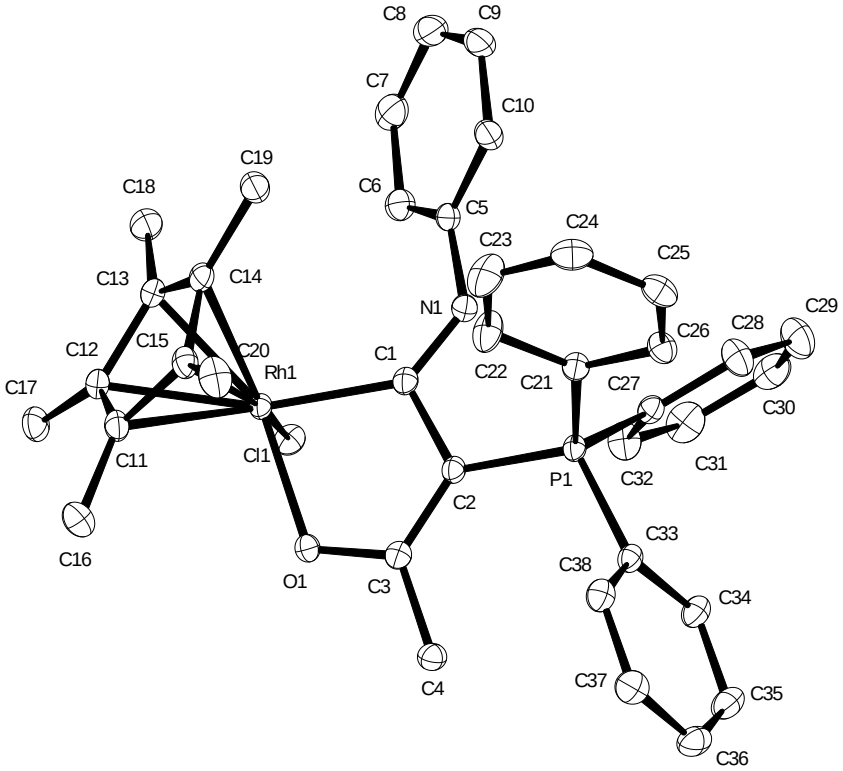
Empirical formula	$C_{20}H_{19}AuClN_3O$	
Color	yellow	
Formula weight	549.80 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 12.3447(8) Å	α= 90°.
	b = 11.9732(8) Å	β= 110.926(5)°.
	c = 13.8197(9) Å	γ = 90°.
Volume	1907.9(2) Å^3	
Z	4	
Density (calculated)	1.914 Mg · m^{-3}	
Absorption coefficient	7.864 mm^{-1}	
F(000)	1056 e	
Crystal size	0.27 x 0.26 x 0.05 mm^3	
θ range for data collection	2.76 to 34.99°.	
Index ranges	-19 ≤ h ≤ 19, -19≤ k ≤ 19, -22 ≤ l ≤ 22	
Reflections collected	55520	
Independent reflections	8346 [R_{int} = 0.0311]	
Reflections with I>2σ(I)	7679	
Completeness to θ = 34.99°	99.4 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.69 and 0.14	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8346 / 0 / 237	
Goodness-of-fit on F^2	1.172	
Final R indices [I>2σ(I)]	R_1 = 0.0157	wR^2 = 0.0432
R indices (all data)	R_1 = 0.0192	wR^2 = 0.0450
Largest diff. peak and hole	0.668 and -1.638 e · Å^{-3}	

Compound 11:



Empirical formula	$C_{37} H_{37} Au Cl_3 N O P Rh$	
Color	orange	
Formula weight	948.87 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 15.2528(12) Å	α= 90°.
	b = 12.7151(19) Å	β= 101.855(11)°.
	c = 17.885(4) Å	γ = 90°.
Volume	3394.7(10) $Å^3$	
Z	4	
Density (calculated)	1.857 $Mg \cdot m^{-3}$	
Absorption coefficient	5.118 mm^{-1}	
F(000)	1856 e	
Crystal size	0.14 x 0.12 x 0.06 mm^3	
θ range for data collection	2.729 to 33.218°.	
Index ranges	$-23 \le h \le 23$, $-19 \le k \le 19$, $-25 \le l \le 27$	
Reflections collected	58509	
Independent reflections	12950 [R_{int} = 0.0360]	
Reflections with I>2σ(I)	11849	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.75 and 0.51	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12950 / 0 / 407	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2σ(I)]	R_1 = 0.0294	wR^2 = 0.0676
R indices (all data)	R_1 = 0.0342	wR^2 = 0.0698
Extinction coefficient	n/a	
Largest diff. peak and hole	1.7 and -3.4 e $\cdot Å^{-3}$	

Compound 13:



Empirical formula	$C_{38}H_{38}Cl_1N_1O_1P_1Rh_1$	
Color	orange	
Formula weight	694.02 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 10.7983(10) Å	α= 90°.
	b = 13.1084(12) Å	β= 100.263(2)°.
	c = 23.391(2) Å	γ = 90°.
Volume	3258.0(5) $Å^3$	
Z	4	
Density (calculated)	1.415 $Mg \cdot m^{-3}$	
Absorption coefficient	0.686 mm^{-1}	
F(000)	1432 e	
Crystal size	0.15 x 0.12 x 0.08 mm^3	
θ range for data collection	1.77 to 33.31°.	
Index ranges	$-16 \le h \le 16$, $-20 \le k \le 20$, $-35 \le l \le 36$	
Reflections collected	107131	
Independent reflections	12543 [R_{int} = 0.0424]	
Reflections with I>2σ(I)	10641	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.77 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12543 / 0 / 394	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2σ(I)]	R_1 = 0.0233	wR^2 = 0.0596
R indices (all data)	R_1 = 0.0333	wR^2 = 0.0684
Largest diff. peak and hole	0.535 and -0.498 e $\cdot Å^{-3}$	