Electronic Supplementary Information for Dalton Transactions

Electronic Supporting Information:

Cu(I) complexes containing a multidentate and conformationally flexible dibenzylidene acetone ligand (dbathiophos): application in catalytic alkene cyclopropanation

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Contents

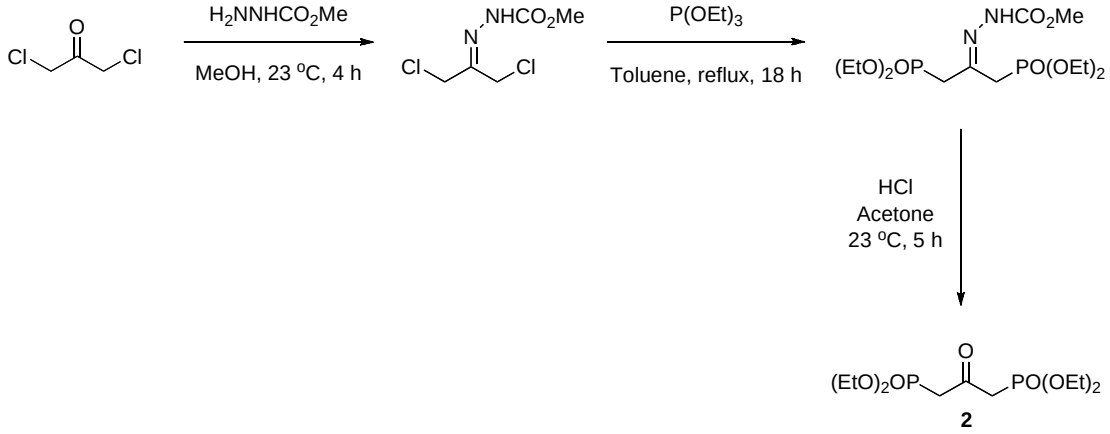
1. General information

NMR spectra were obtained in the solvent indicated, using a JEOL ECX400 or JEOL ECS400 spectrometer (400MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P respectively), a Bruker 500 (500 MHz, 126 MHz and 202 MHz for ^{1}H, ^{13}C and ^{31}P respectively) and low temperature NMR studies were carried out on a Bruker AV700 (700 MHz and 283 MHz for ^{1}H and ^{31}P respectively). Chemical shifts were referenced to the residual solvent of the deuterated solvent used ($CHCl_3$ δ = 7.26 and 77.16, $CDHCl_2$ δ = 5.31 and 53.80, ^{1}H and ^{13}C respectively). NMR spectra were processed using MestrNova software. Melting points were recorded using a Stuart digital SMP3 machine. TLC analysis was carried out on Merck TLC aluminium sheets (silica gel 60 F254) and flash chromatography run on silica gel 60. IR spectroscopy was undertaken using a Jasco/MIRacle FT/IR-4100 type A spectrometer on the neat compounds, or solution IR spectra were obtained on a Nicolet Avatar 370 FT-IR spectrometer in the solvent stated. MS spectra were measured using a Bruker Daltronics micrOTOF machine with electrospray ionisation (ESI) or on a Thermo LCQ using electrospray ionisation. UV-visible spectra were recorded using a JASCO V-560. Elemental

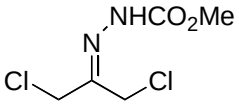
analysis was carried out on an Exeter Analytical CE-440 Elemental Analyser. Dry and degassed toluene, DCM and hexane were obtained from a Pure Solv MD-7 solvent purification system. THF and ether were either obtained from a Pure Solv MD-7 solvent purification system and degassed by the freeze-pump-thaw method, or dried over sodium-benzophenone ketyl and collected by distillation. Benzene was dried over sodium-benzophenone ketyl, and ethanol was dried and distilled from magnesium-iodine. Nitrogen gas was oxygen free and was dried immediately prior to use by passage through a column containing sodium hydroxide pellets and silica. Commercial chemicals were purchased from Sigma-Aldrich or Alfa Aesar.

2. Synthesis of the ligand

The synthetic route to compound **2** is shown below:

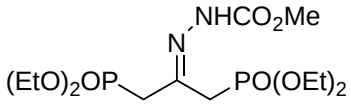


Methyl 2-[2-chloro-1-(chloromethyl)ethylidene]-1-hydrazinecarboxylate[1]



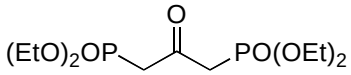
To a solution of methyl 1-hydrazinecarboxylate (4.90 g, 1 eq., 0.054 mol) in MeOH (100 mL) was added 1,3-dichloroacetone (6.97 g, 0.055 mol) in 2 parts. The reaction was stirred at 23 °C for 4 h and then left in the fridge overnight. The solvent was removed *in vacuo* until ~20 mL remained and the white product had precipitated. The product was isolated by filtration and washed with ether to afford a white powder (5.80 g, 54%). No further purification was carried out, before taking on in the following experiment. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 4.32 (s, 2H), 4.18 (s, 2H), 3.88 (s, 3H); HRMS (ESI) m/z 220.9854 $[M\text{Na}]^+$ (calculated for $C_5H_8Cl_2N_2NaO_2$ = 220.9854).

Methyl 2-2-(diethoxyphosphoryl)-1-[(diethoxyphosphoryl)methyl]ethylidene-1-hydrazinecarboxylate[1]



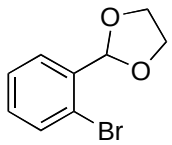
To a suspension of the hydrazinecarboxylate (5.8 g, 1 eq., 0.029 mol) in toluene (50 mL), triethylphosphite (11.15 mL, 2.2 eq., 0.064 mol) was added portion wise. The resulting mixture was refluxed for 18 h. The toluene was removed *in vacuo*, and the residue taken up in water (40 mL) and extracted with ethyl acetate (3x 20 mL). Solvent and excess triethylphosphite were removed *in vacuo* to give the crude product (12.8 g). No further purification was carried out. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 4.20-4.07 (m, 9H), 3.80 (s, 3H), 3.15 (dd, *J* = 22.5, 2.5 Hz, 2H), 3.00 (dd, *J* = 21.5, 2.5 Hz, 2H), 1.33 (td, *J* = 7.0, 3.0 Hz, 13H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.86–23.58 (m, br), 23.50 (d, *J* = 11.0 Hz); HRMS (ESI) m/z 425.1225 $[M\text{Na}]^+$ (calculated for $C_{13}H_{28}N_2NaO_8P_2$ = 425.1213).

[3-(Diethoxy-phosphoryl)-2-oxo-propyl]-phosphonic acid diethyl ester, (1,3-Bis(diethoxy-phosphonato)-acetone)[1] (2)



To a solution of the crude phosphoryl hydrazinecarboxylate (12.8 g) in acetone (20 mL) was added 3M HCl (20 mL). The reaction mixture was stirred at 23 °C for 5 h. Water (40 mL) was added and the acetone removed. Extraction with chloroform (3x 20 mL), followed by drying over Na_2SO_4, filtration and removal of the solvent *in vacuo*, gave the product as yellow oil (10.15 g, 94% purity by ^{1}H NMR, 99% yield). B.p. 200 °C, 1.5 mbar (*Lit.*[1] 185 °C, 0.03 mbar); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18-4.04 (m, 9H), 3.31 (dd, *J* = 23.0, 1.0 Hz, 4H), 1.31 (td, *J* = 7.0, 1.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 62.9-62.7 (m), 43.3 (d, *J* = 127 Hz), 16.5-16.2 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.48 (s); HRMS (ESI) m/z 331.1076 $[M\text{H}]^+$ (calculated for $C_{11}H_{25}O_7P_2$ = 331.1070).

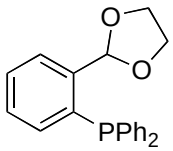
2-(*o*-Bromophenyl)-1,3-dioxolane[2]



2-Bromobenzaldehyde (15.0 g, 1 eq., 0.08 mol), ethylene glycol (6.7 ml, 1.33 eq., 0.12 mol) and *p*-toluenesulfonic acid (63 mg) were dissolved in toluene (100 mL) and refluxed while the evolved water was collected in a Dean-Stark trap. After water is no longer evolved (ca. 24 h) the solution is

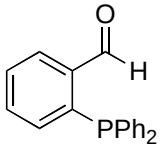
cooled and washed with a saturated solution of $NaHCO_3$ (40 mL), followed by a saturated solution of NaCl (20 mL). The solution is dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and distilled at 100 °C, 0.5 mmHg (*Lit.*[2] 135-137 °C, 4 mmHg), to give the title compound as a colourless oil (16.33 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.34 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.22 (ddd, *J* = 7.5, 8.0, 2.0 Hz, 1H), 6.10 (s, 1H), 4.20 – 4.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.7, 133.1, 130.7, 127.9, 127.5, 123.0, 102.7, 65.6; HRMS (ESI) m/z 228.9859 $[MH]^+$ (calculated for $C_9H_{10}BrO_2$ = 228.99); IR (neat, ν cm^{-1}): 2955 (w, br), 2886 (m, br), 1730 (w), 1592 (w), 1571 (w), 1472 (w), 1443 (w), 1387 (m), 1270 (w), 1211 (m), 1124 (m), 1084 (s, br), 1042 (m), 1021 (m), 969 (m), 941 (m), 754 (s).

2-(*o*-Diphenylphosphinophenyl)-1,3-dioxolane[3]



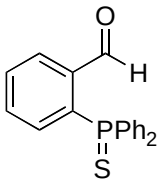
A solution of 2-(*o*-bromophenyl)-1,3-dioxolane (20.95 g, 1 eq., 91 mmol) in dry THF (220 mL) was cooled to -78 °C and kept under an inert atmosphere. *n*-BuLi in hexane (40 mL, 1.03eq, 93 mmol) was added by syringe pump at a rate of 30 cc/h. After stirring for 2 h at -78 °C, diphenylphosphine chloride (16.3 mL, 1 eq., 91 mmol) was added by syringe pump at a rate of 40 cc/h. The reaction was allowed to warm up to 24 °C overnight, before the addition of water (240 mL). The organic phase was extracted with Et_2O, dried over anhydrous Na_2SO_4, decanted and the solvent removed. The resulting oily liquid was purified by recrystallisation from hot ethanol and cooled to -25 °C, to afford the title compound as a waxy white solid (21.24 g, 70%). M.p. 94-95 °C, (*Lit.* 96 °C)[3]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 (dddd, *J* = 8.0, 4.0, 1.5, 0.5 Hz, 1H), 7.4 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 7.35-7.30 (m, 6H), 7.30-7.22 (m, 5H), 6.96 (ddd, *J* = 8.0, 4.5, 1.5 Hz, 1H), 6.43 (d, *J* = 5.0 Hz, 1H), 4.14-3.92 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 142.1 (d, *J* = 22 Hz), 137.1 (d, *J* = 10 Hz), 136.0 (d, *J* = 19 Hz), 134.2 (d, *J* = 1 Hz), 134.0, 133.8, 129.4 (d, *J* = 18 Hz), 128.7, 128.6 (d, *J* = 7 Hz), 126.6 (d, *J* = 6 Hz), 101.8 (d, *J* = 24 Hz), 65.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ -15.86 (s); LRMS (ESI) m/z (rel.%) 291.1 $[M\text{-}C_2H_4O]^+$ (100), 273.1 (26), 261.1 (3), 242.1 (5), 213.0 (8).

2-(Diphenylphosphino)benzaldehyde[2]



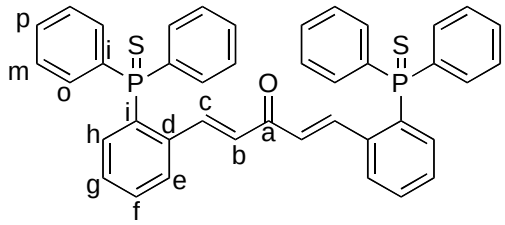
2-(*o*-Diphenylphosphinophenyl)-1,3-dioxolane (21.24 g, 1 eq., 64 mmol) and para-toluenesulfonic acid (0.45 g) were dissolved in acetone (450 mL) and refluxed for 8 h. Whilst still warm, water (100 mL) was added and the volume reduced to ~125 mL by solvent evaporation. The resulting mixture was cooled to -25 °C overnight, and the precipitate filtered and dried *in vacuo* to afford the title compound as a bright yellow powder (15.88g, 85%). M.p. 114-117 °C, (*Lit*. 118-119 °C)[2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (d, *J* = 5.5 Hz, 1H), 8.00 - 7.95 (m, 1H), 7.53 - 7.44 (m, 2H), 7.38 - 7.26 (m, 10H), 6.99-6.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9 (d, *J* = 19 Hz), 141.4, 136.2 (d, *J* = 10 Hz), 134.3, 134.1, 134.0, 133.8, 130.9 (d, *J* = 4 Hz), 129.3, 129.0, 128.9 (d, *J* = 7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.03 (s); HRMS (ESI) m/z $[M\text{H}]^+$ 291.0944, (calculated for $C_{19}H_{16}OP$: 291.1016); IR (solid, ν cm^{-1}): 3057 (w, br), 2851 (w), 1696 (m), 1672 (m), 1583 (w), 1432 (m), 1198 (m), 843 (m), 751 (s), 744 (s), 696 (s), 670 (s).

2-(Diphenylthiophosphino)benzaldehyde[4] (3)



The phosphine benzaldehyde (1.48 g, 1 eq., 5 mmol) and S_8 (1.31 g, 1 eq., 5 mmol) were stirred together in THF (60 mL) overnight. The resulting mixture was centrifuged (3000 rpm, 3 min) to remove the solid sulfur, and the solvent removed. Purification by column chromatography on silica gel eluting with petroleum ether to remove the remaining sulfur and then diethyl ether:pentane (1:4 to 3:7 v/v) afforded the title compound as a cream powder (1.31 g, 81%). M.p. 136-137 °C, (*Lit.*[5] 131-132 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.12 (ddd, *J* = 8.0, 4.0, 1.0 Hz, 1H), 7.85-7.77 (m, 4H), 7.66-7.61 (m, 1H), 7.60-7.44 (m, 7H), 7.03 (ddd, *J* = 14.5, 8.0, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3 (d, *J* = 8 Hz), 138.0 (d, *J* = 7 Hz), 137.9 (d, *J* = 79 Hz), 132.8 (d, *J* = 12 Hz), 132.7 (d, *J* = 10 Hz), 132.5 (d, *J* = 11 Hz), 132.3 (d, *J* = 3 Hz), 132.17 (d, *J* = 3 Hz), 132.13 (d, *J* = 85 Hz), 129.9 (d, *J* = 9 Hz), 129.0 (d, *J* = 13 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.74 (s); HRMS (ESI) m/z $[M\text{Na}]^+$ 345.0478 (calculated for $C_{19}H_{15}NaOPS$: 345.0473); IR (solid, ν cm^{-1}): 1685 (s), 1580 (w), 1435 (m), 1199 (m), 1099 (s), 822 (w), 749 (m), 711 (s), 691 (s), 640 (s), 633 (s), 613 (m).

(1E,4E)-1,5-bis(2-diphenylphosphorothioyl)phenyl)pentan-1,4-dien-3-one, Dbathiophos (1)



1,3-Bis(phosphonato)acetone (**2**) (256 mg, 1 eq., 0.776 mmol) was added to a stirring solution of compound **3** (500 mg, 2 eq., 1.56 mmol) in THF (3 mL). To this NaOH (124 mg, 4 eq., 3.11 mmol) dissolved in H_2O (0.5 mL) and THF (1 mL) was added dropwise. The mixture was refluxed for 48 h. After cooling, the solution was washed with saturated $NH_4Cl_{(aq)}$ (5 mL), extracted with ethyl acetate (5x 5 mL), dried over Na_2SO_3 and filtered. After removing the solvent *in vacuo* the product was recrystallised from DCM/Hexane (1:3 v/v) to afford the title compound as a yellow solid (435 mg, 84%). M.p. 133-138 °C_{dec}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.17 (d, *J* = 16.0 Hz, 2H, H_c), 7.84-7.69 (m, 10H, H_e and *o*-Ar), 7.64-7.57 (m, 2H, H_f), 7.56-7.49 (m, 4H, *p*-Ar), 7.49-7.41 (m, 8H, *m*-Ar), 7.34 (tdd, *J* = 7.5, 2.5, 1.5 Hz, 2H, H_g), 7.09 (ddd, *J* = 14.5, 8.0, 1.0 Hz, 2H, H_h), 6.48 (d, *J* = 16.0 Hz, 2H, H_b); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 188.6 (C=O), 141.5 (d, *J* = 8 Hz, C_c), 138.9 (d, *J* = 7 Hz, C_d), 133.9 (d, *J* = 83 Hz, *ipso*-C), 133.4 (d, *J* = 11 Hz, C_h), 132.7 (d, *J* = 11 Hz, *o*-Ar), 132.5 (d, *J* = 85, *ipso*-C), 132.4 (d, *J* = 3 Hz, C_f), 132.2 (d, *J* = 3 Hz, *p*-Ar), 129.6 (d, *J* = 12 Hz, C_g), 129.0 (d, *J* = 13 Hz, *m*-Ar), 128.8 (d, *J* = 10 Hz, C_e), 126.8 (C_b); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.07 (s); HRMS (ESI) m/z $[M\text{Na}]^+$ 689.1266 (calculated for $C_{41}H_{32}NaOP_2S_2$: 689.1262); LRMS (ESI) m/z (rel.%) 689.1 $[M\text{Na}]^+$ (100), 667.1 $[M\text{H}]^+$ (3); IR (solid, ν cm^{-1}): 3053 (w), 1656 (w), 1619 (w), 1602 (w), 1460 (w), 1436 (m), 1184 (w), 1098 (m), 753 (m), 711 (s), 692 (s), 636 (s), 614 (m), 575 (m); UV-vis (CH_2Cl_2) λ_{max} nm: 318 (ε = 19513 $mol^{-1}dm^3cm^{-1}$); Anal. Calcd. for $C_{41}H_{32}OP_2S_2.1/10CH_2Cl_2$ (675) C 73.10, H 4.81; Observed C 73.32, H 4.83. Elemental analysis conducted with crystals used for XRD analysis.

3. Synthesis of copper complexes 4 and 6

Tetrakis(acetonitrile)copper(I) hexafluorophosphate[6]

To a stirred suspension of Cu_2O (1g, 7 mmol) in MeCN (20 mL) was added 60 % HPF_6 (2.5 mL) in 0.5 mL portions. Heat is released, which helps dissolve the white solid formed. The hot solution was stirred for 3 min and filtered through a funnel with a sintered glass frit; any remaining white solid was washed through with a small amount of acetonitrile. The solution was cooled to -20 °C for 3 h and the resulting precipitate collected by filtration and washed with ether. The precipitate was then redissolved in acetonitrile (25 mL), filtered through a funnel with a sintered glass frit, ether (25 mL) added and cooled to -20 °C overnight. The white precipitate was filtered, washed with ether, dried *in vacuo* to afford the title compound as a white solid (4.17 g, 80%). The solid was stored in a glove-box. M.p. 147-152 °C (*Lit.*[7] 160 $°C_{(dec)}$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.18 (s); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 117.0, 2.53; IR (solid, ν cm^{-1}): 1419 (w, br), 1037 (w), 833 (s, br); Anal. Calcd. for $C_8H_{12}CuF_6N_4P$ (372.72) C 25.78, H 3.25, N 15.03; Observed C 25.77, H 3.20, N 14.80.

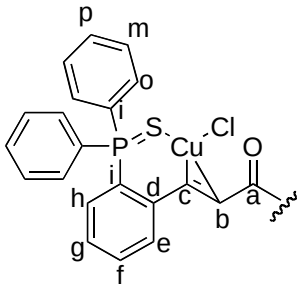
Cu(dbathiophos)PF_6.(solvent), complex 4

A solution of $Cu(MeCN)_4PF_6$ (168 mg, 1 eq., 0.45 mmol) in dry, degassed CH_2Cl_2 (5 mL) was added by cannula to a solution of dbathiophos, (**1**), (300 mg, 1 eq., 0.45 mmol) in dry, degassed CH_2Cl_2 (10 mL).* The resulting solution was stirred for 2 h at 20 °C. CH_2Cl_2 was removed *in vacuo* to give a concentrated solution (4 mL) and layered with dry, degassed toluene (5 mL) to afford yellow crystals (270 mg, 69 %) separated by filtration. M.p. 200 $°C_{(dec)}$; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.20-7.26 (br m, ~56H), 6.98 (dd, J = 15.0, 7.5 Hz, 4H), 6.52 (br s, 2H), 6.21 (br s, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 46.43 (br s), 40.59 (br s), -143.80 (hept, J_{PF} = 711 Hz); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.8 (d, J = 8 Hz), 136.4, 136.1, 134.8-134.3 (m), 134.0-132.1 (m), 131.1 (d, J = 14 Hz), 131.0-130.8 (m), 130.6-129.9 (m); HRMS (ESI) m/z 729.0708 (calculated for $C_{41}H_{32}OP_2S_2Cu$: 729.0660); IR (solid, ν cm^{-1}): 1652 (m), 1457 (m), 1438 (m), 1312 (w), 1170 (w), 1103 (m), 836 (s), 691 (s); UV-vis (CH_2Cl_2) λ_{max} nm: 320 (ε = 18345 $mol^{-1}dm^3cm^{-1}$); Anal. Calcd. for $C_{82}H_{64}Cu_4F_{12}P_6$ ($Cu_2(dbathiophos)_2PF_6$) C 56.26, H 3.69, N 0.00; Observed C 56.61, H 4.02, N 0.20.

* The reaction was also carried out in THF. The product precipitated overnight and the resulting yellow crystals were collected by filtration (48%).

Crystals of $(Cu(dbathiophos)PF_6.H_2O)_2$ (complex **4**) suitable for XRD were obtained by layering CH_2Cl_2 with Et_2O, along with crystals of $(Cu_2Cl(dbathiophos)PF_6)_2$ (complex **5**), presumably formed by halide abstraction from HCl or CH_2Cl_2.

Cu_2Cl_2(dbathiophos), complex 6



In a glovebox, dbathiophos, (**1**), (125 mg, 1 eq., 0.188 mmol) was dissolved in dry, degassed CH_2Cl_2 (7 mL) and CuCl (37 mg, 2 eq., 0.375 mmol) was added. After stirring for 1 h at 23 °C, more CH_2Cl_2 (2 mL) was added to dissolve the last traces of CuCl and the reaction stirred overnight, until no solid remained. Half the solvent was removed *in vacuo*, and the concentrated solution left overnight. The precipitate was filtered, washed with pentane (5 mL) and dried *in vacuo* to give a yellow crystalline product (119 mg, 73%). The solid was stored in a glove-box. M.p. 223 °$C_{(dec)}$; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83-7.79 (m, 2H, H_e), 7.79-7.67 (m, 12H, Ar), 7.66-7.54 (m, 10H, H_f and Ar), 7.37-7.31 (m, 2H, H_g), 6.92 (ddd, J = 14.5, 7.5, 1.0 Hz, 2H, H_h), 6.07 (d, J = 14.0 Hz, 2H, H_c), 5.83 (d (br), J = 14.0 Hz, 2H, H_b); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 184.2 (C=O), 139.8 (d, J = 8 Hz, C_d), 134.4 (d, J = 2 Hz, C_f), 133.9 (d, J = 3 Hz, *p*-Ar), 133.1 (d, J = 11 Hz, Ar), 132.9 (d, J = 11 Hz, C_h), 131.8 (d, J = 85 Hz, *ipso*-C), 131.6 (d, J = 9 Hz, C_e), 129.6 (d, J = 13 Hz, Ar), 128.6 (d, J = 13 Hz, C_g), 127.2 (d, J = 86 Hz, *ipso*-C), 95.3 (br, C=C), 94.4 (br, C=C); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 40.78 (s); LRMS (ESI) m/z (rel.%) 1397.2 $[Cu(dbathiophos)_2]^+$ (29), 829.0 $[M\text{-}Cl]^+$ (100), 729.1 $[M\text{-}CuCl_2]^+$ (87), 667.1 $[dbathiophos+H]^+$ (4); HRMS (ESI) m/z 826.9623 (calculated for $C_{41}H_{32}ClCu_2OP_2S_2$ = 826.9645); IR (solid, ν cm^{-1}): 1653 (w), 1537 (w), 1455 (w), 1433 (m), 1312 (m), 1247 (w), 1103 (m), 1084 (m), 1064 (m), 967 (m), 756 (s), 691 (s); IR (CH_2Cl_2, ν cm^{-1}): 3046 (w), 1653 (w), 1539 (w), 1457 (w), 1439 (m), 1314 (w), 1271 (m), 1265 (m), 1261 (m), 1106 (w); UV-vis (CH_2Cl_2) λ_{max} nm: 396 (ε = 12199 $mol^{-1}dm^3cm^{-1}$) shoulders at 326 (ε = 10213 $mol^{-1}dm^3cm^{-1}$) and 258 (ε = 34000 $mol^{-1}dm^3cm^{-1}$); Anal. Calcd. for $C_{41}Cl_2Cu_2H_{32}OP_2S_2.CH_2Cl_2$ (949) C 53.12, H 3.61; Observed C 53.17, H 3.58.

Crystals of Cu_2Cl_2(dbathiophos) suitable for XRD were obtained by from a solution of CH_2Cl_2 in an atmosphere of Et_2O.

4. NMR Spectra

4.i. Dbathiophos (1)

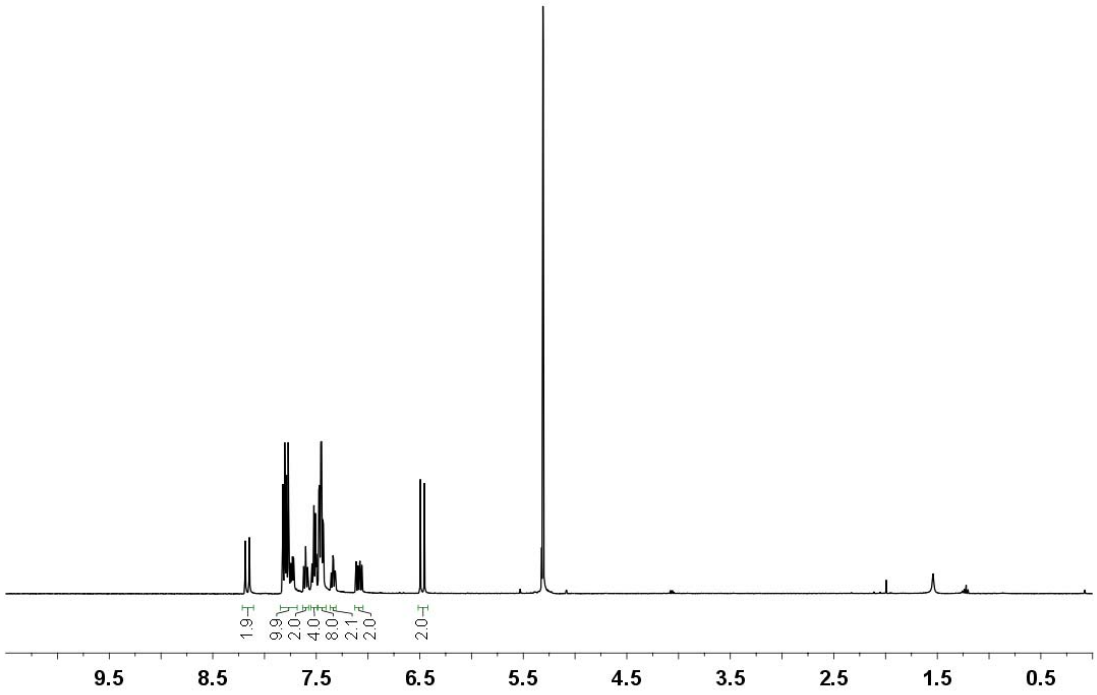


Figure 1: ^{1}H NMR spectrum of dbathiophos (1) (400 MHz, CD_2Cl_2, 298 K).

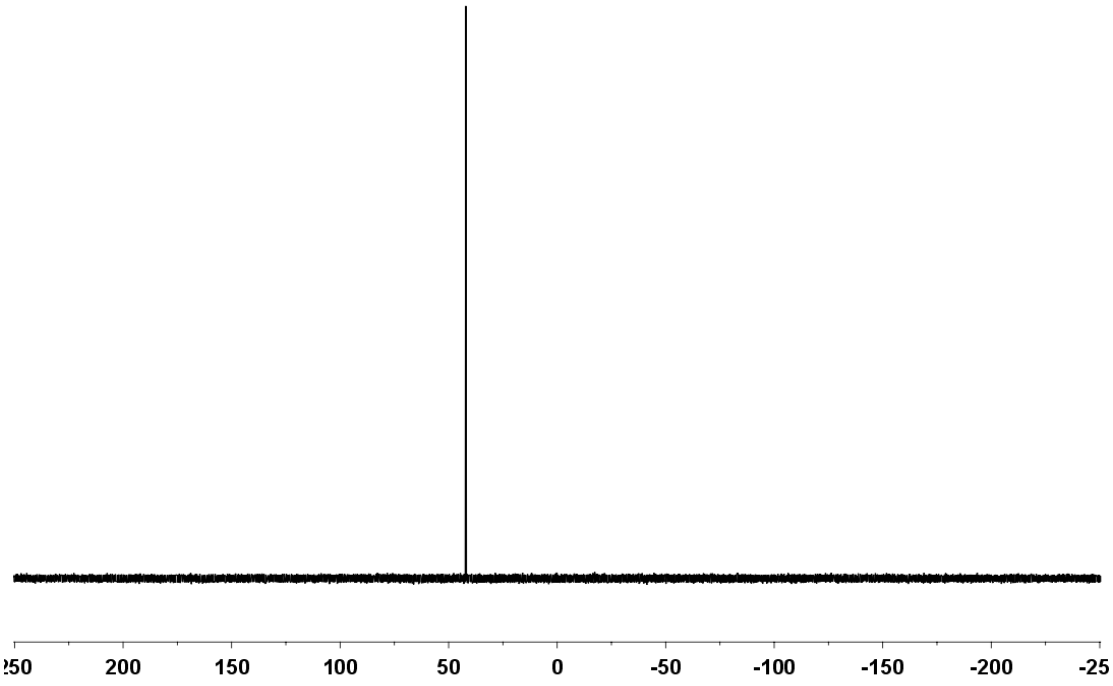


Figure 2: ^{31}P NMR spectrum of dbathiophos (1) (162 MHz, CD_2Cl_2, 298 K).

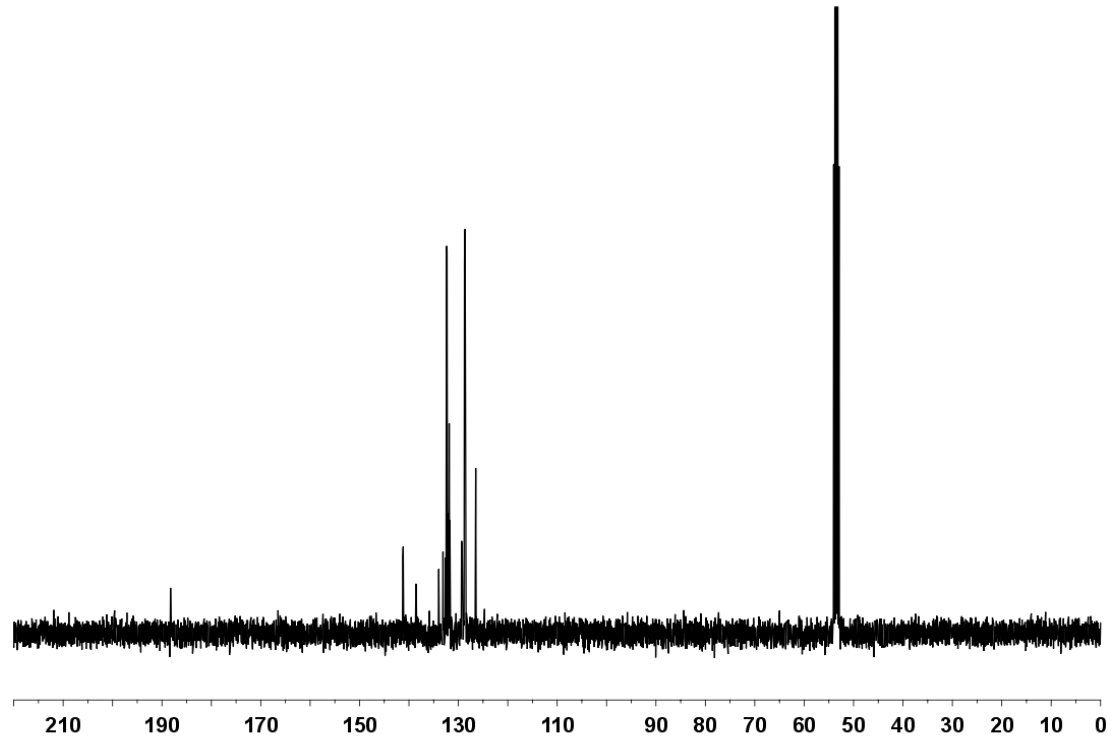


Figure 3: ^{13}C NMR spectrum of dbathiophos (1) (100 MHz, CD_2Cl_2, 298 K).

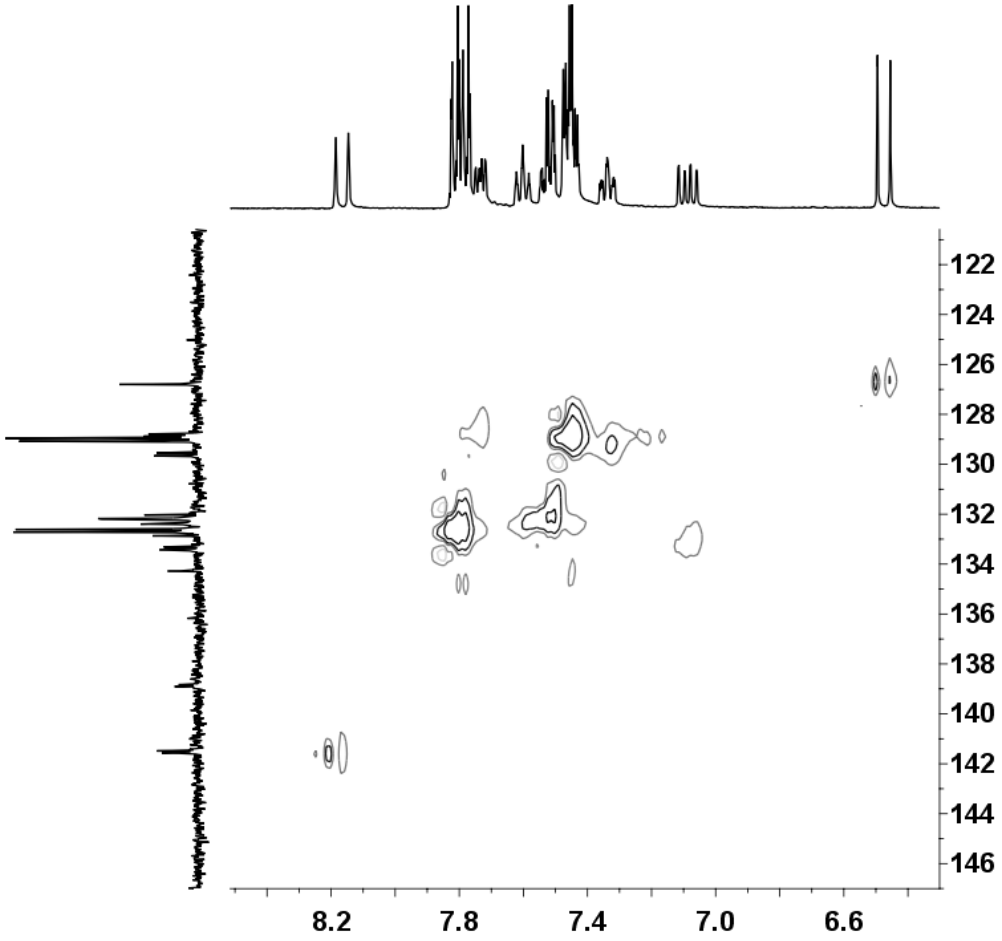


Figure 4: ^{1}H-^{13}C HSQC spectrum of dbathiophos (1) (400 MHz, CD_2Cl_2, 298 K).

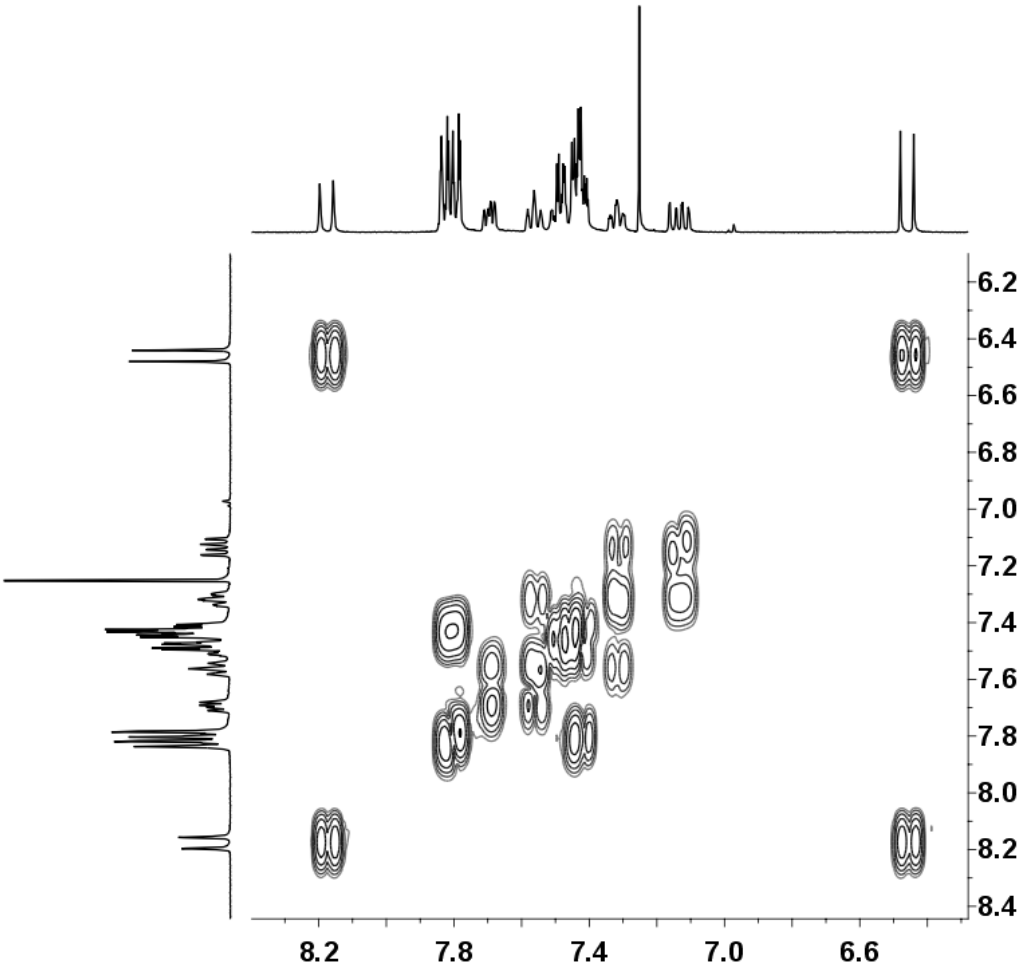


Figure 5: ^{1}H-^{1}H COSY spectrum of dbathiophos (1) (400 MHz, CD_2Cl_2, 298 K).

4.ii. Complex 4

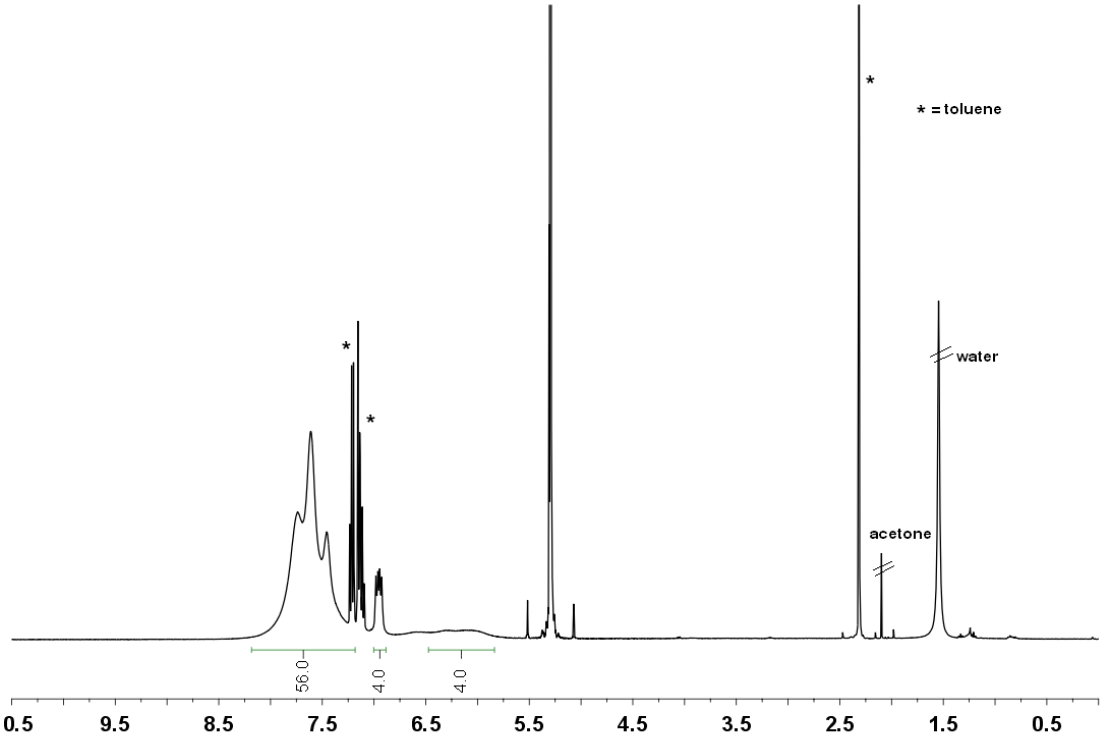


Figure 6: ^{1}H NMR spectrum of complex 4 at 298 K (400 MHz, CD_2Cl_2).

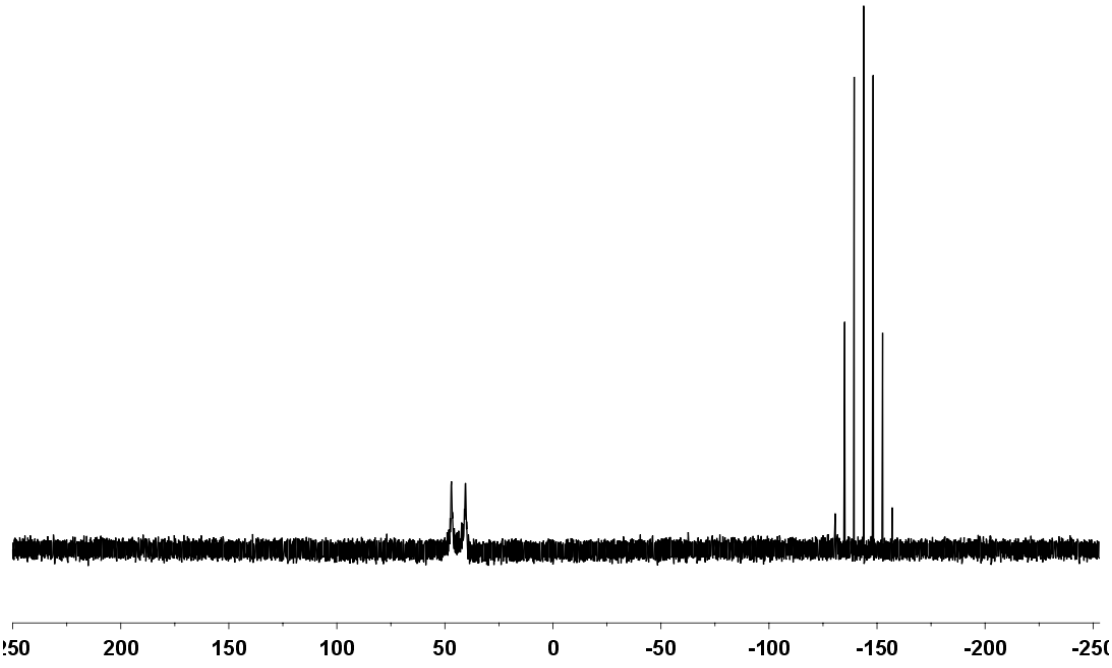


Figure 7: ^{31}P NMR spectrum of complex 4 at 298 K (162 MHz, CD_2Cl_2).

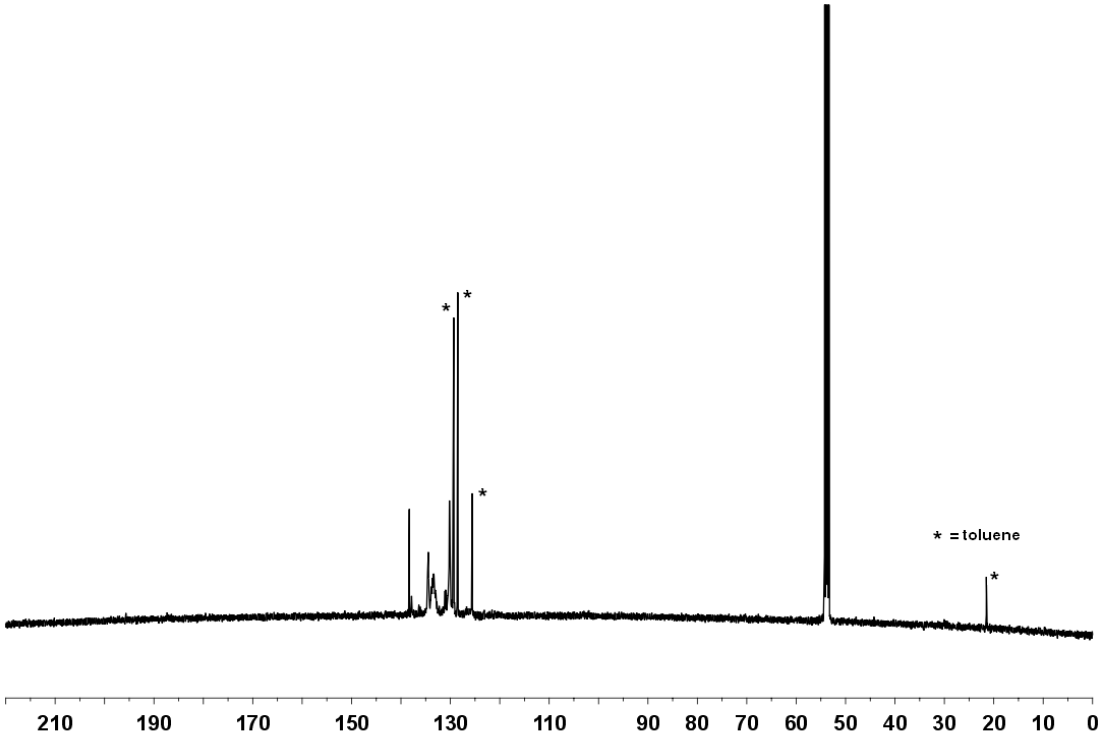


Figure 8: ^{13}C NMR spectrum of complex 4 at 298 K (126 MHz, CD_2Cl_2).

Shift, ppm	Mutiplicity	Coupling Constant, Hz	Assignment	Coupling to
5.94	d	13.7	**a**	**b**
5.99	d	13.7	**b**	**a**
6.60	d	16.4	**c**	**m**
6.95	dd	7.7, 15.2	**d**	**h**
7.01	dd	7.7,14.4	**e**	***i***
7.07-7.05	m	-	**f, Ar**	***o***
7.36-7.28	m	-	**Ar**	
7.48-7.38	m	-	**h, Ar**	**d, k**
7.60-7.49	m	-	**i, Ar**	***e, o***
7.67-7.60	m	-	**Ar**	
7.75-7.67	m	-	**k, Ar**	**h, l**
7.85-7.77	m	-	**l, Ar**	**k**
7.83	d	16.4	**m**	**c**
7.92-7.87	m	-	**Ar**	
7.93	d	7.3	**o**	***f, i***
7.96	d	9.2	**Ar**	
8.03	app. t	6.7	**Ar**	

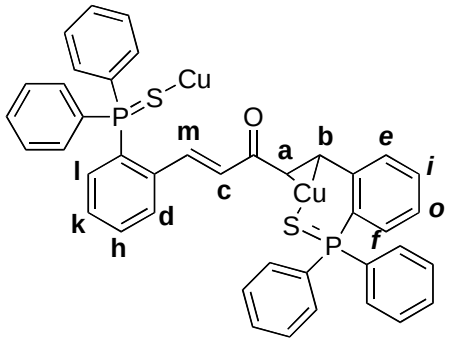


Figure 9: Assignment of peaks (Italicised means less certain; Only half the dimer shown for clarity).

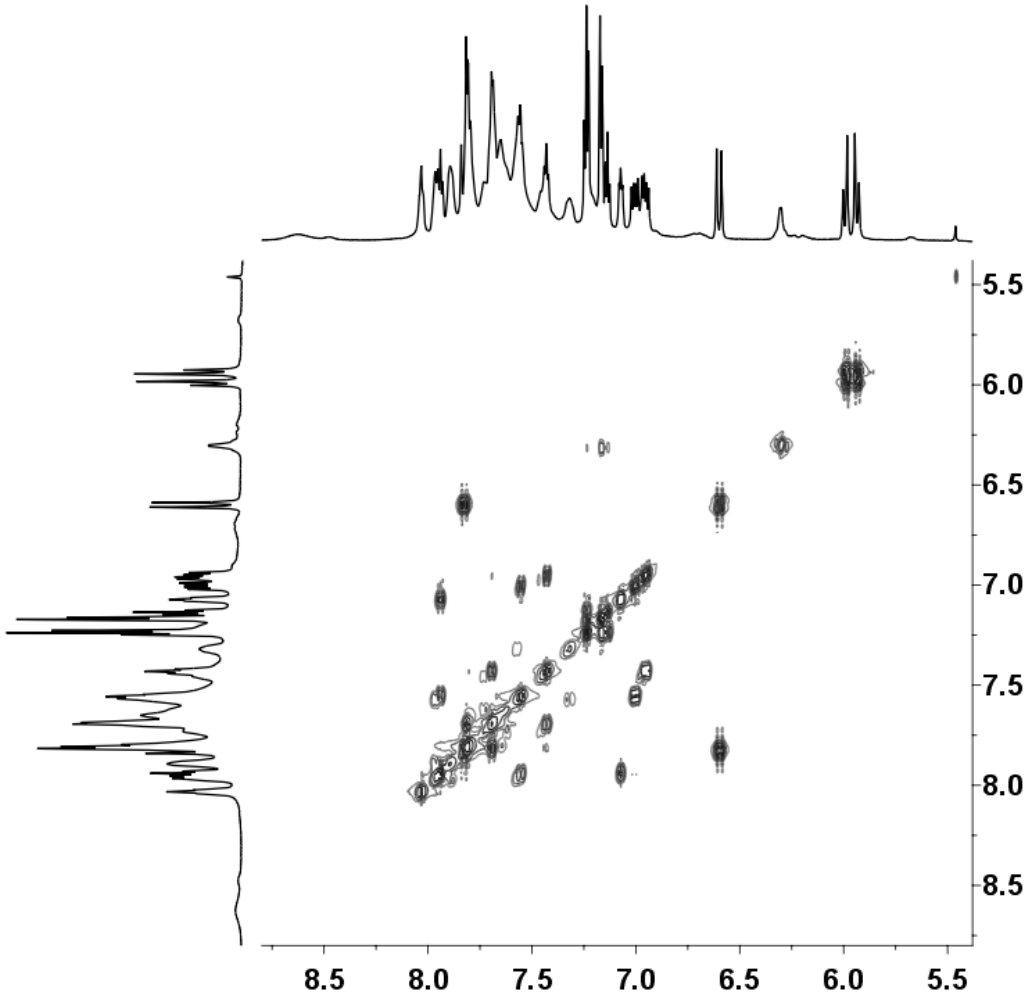


Figure 10: ^{1}H-^{1}H COSY spectrum of complex 4 at 230 K (700 MHz, CD_2Cl_2).

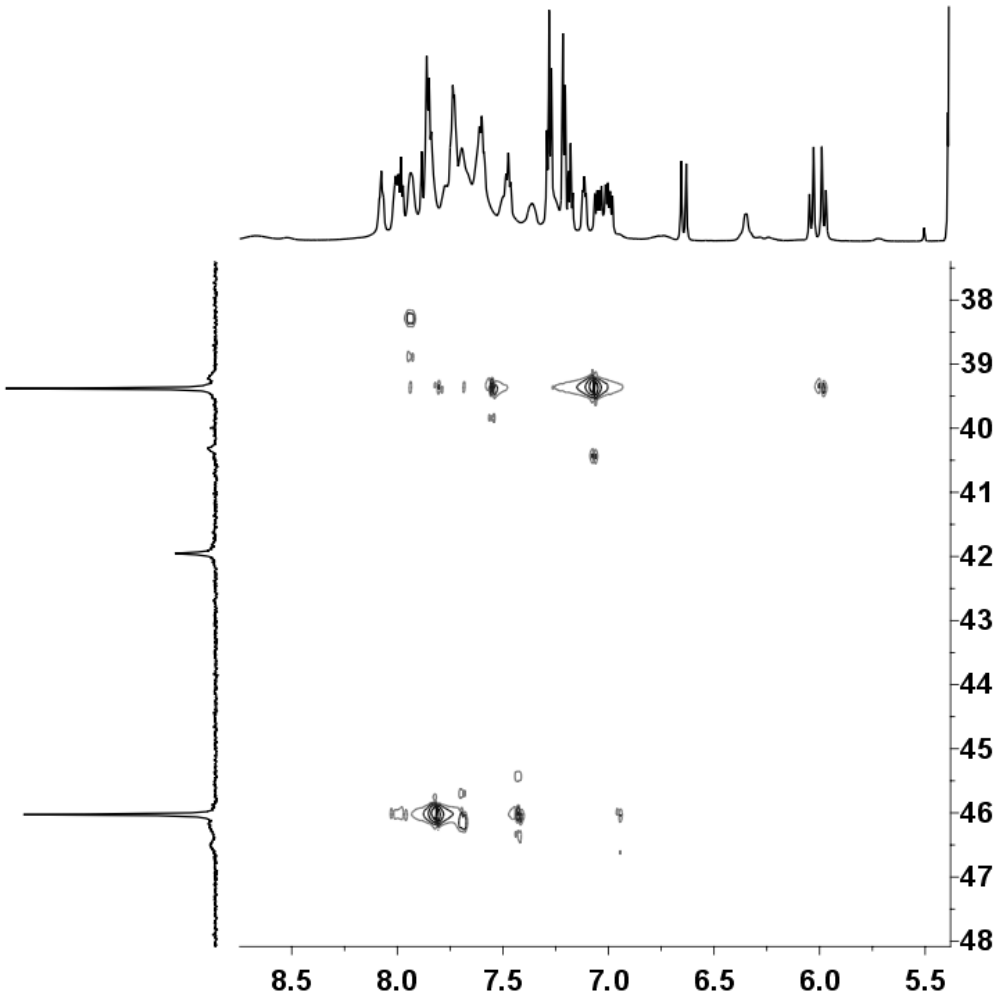


Figure 11: ^{1}H-^{31}P HMQC spectrum of complex 4 at 230 K (700 MHz, CD_2Cl_2).

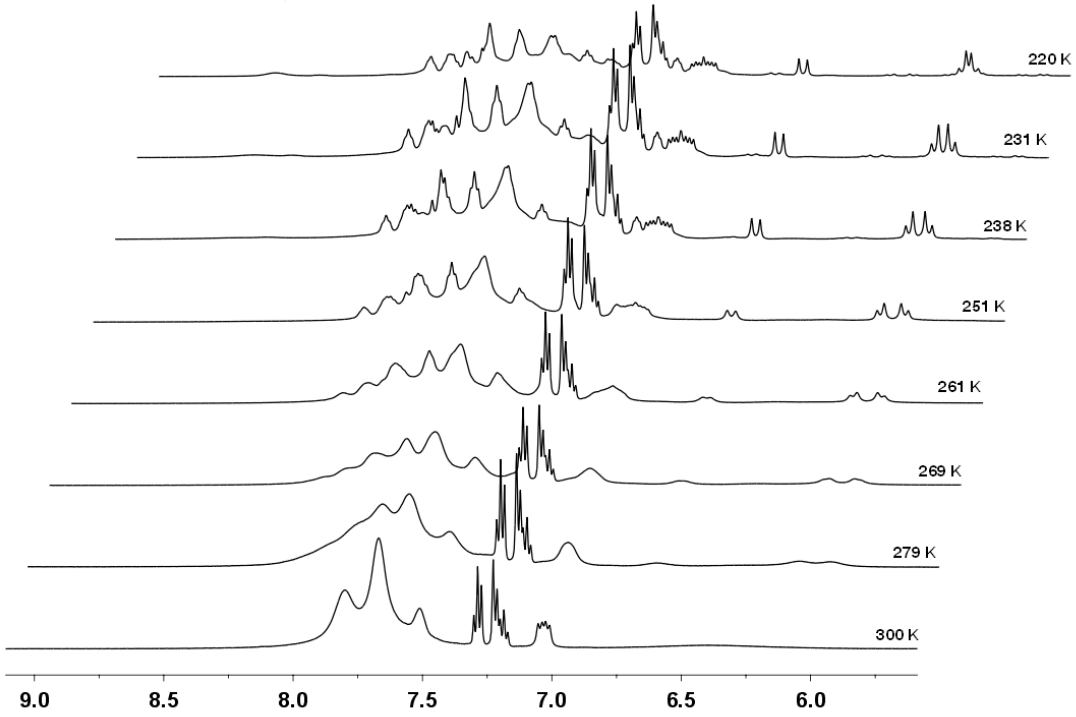


Figure 12: Variable temperature ^{1}H NMR spectra of complex 4 (500 MHz, CD_2Cl_2).

4.iii. Complex 6

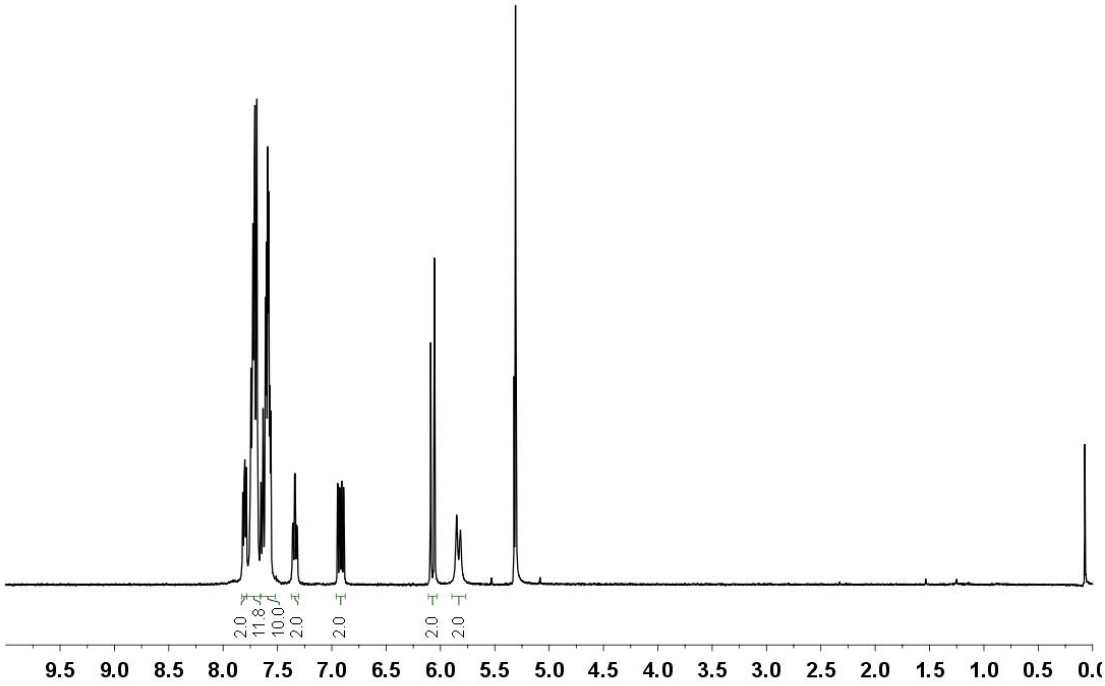


Figure 13: ^{1}H NMR spectrum of complex 6 at 298 K (400 MHz, CD_2Cl_2).

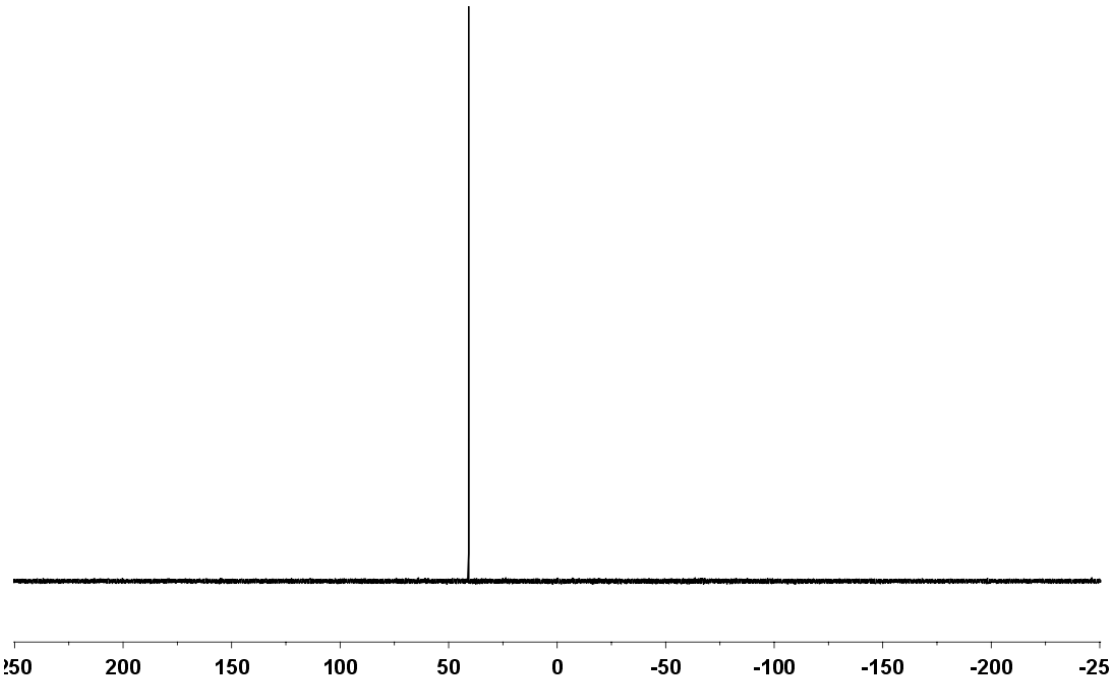


Figure 14: ^{31}P NMR spectrum of complex 6 at 298 K (162 MHz, CD_2Cl_2).

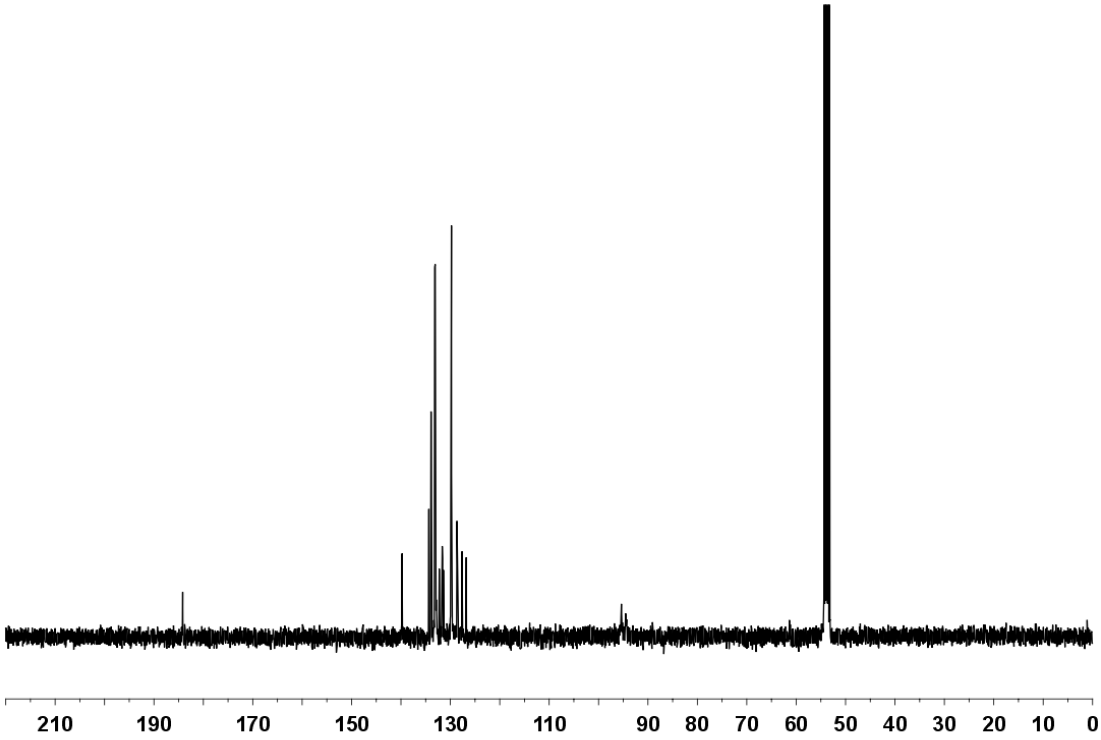


Figure 15: ^{13}C NMR spectrum of complex 6 at 298 K (100 MHz, CD_2Cl_2).

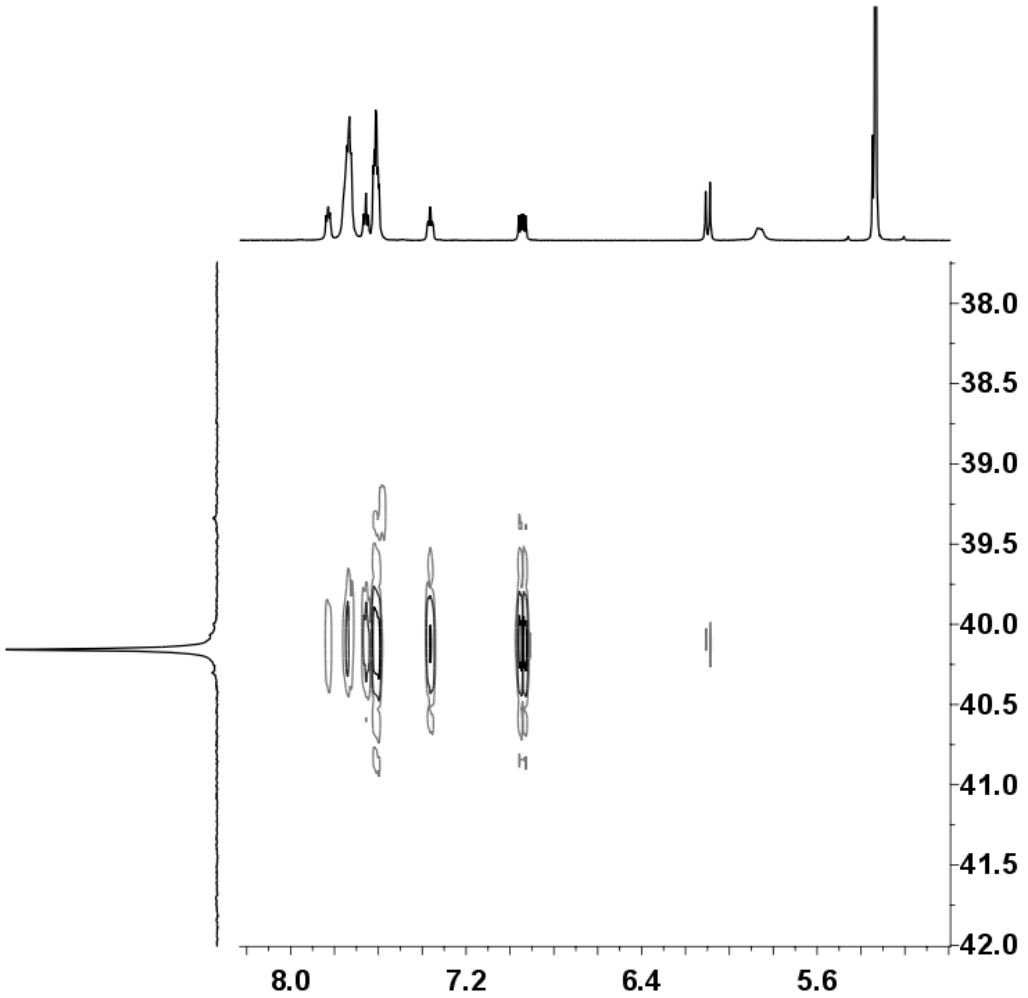


Figure 16: ^{1}H-^{31}P HMBC spectrum of complex 6 at 298 K (700 MHz, CD_2Cl_2).

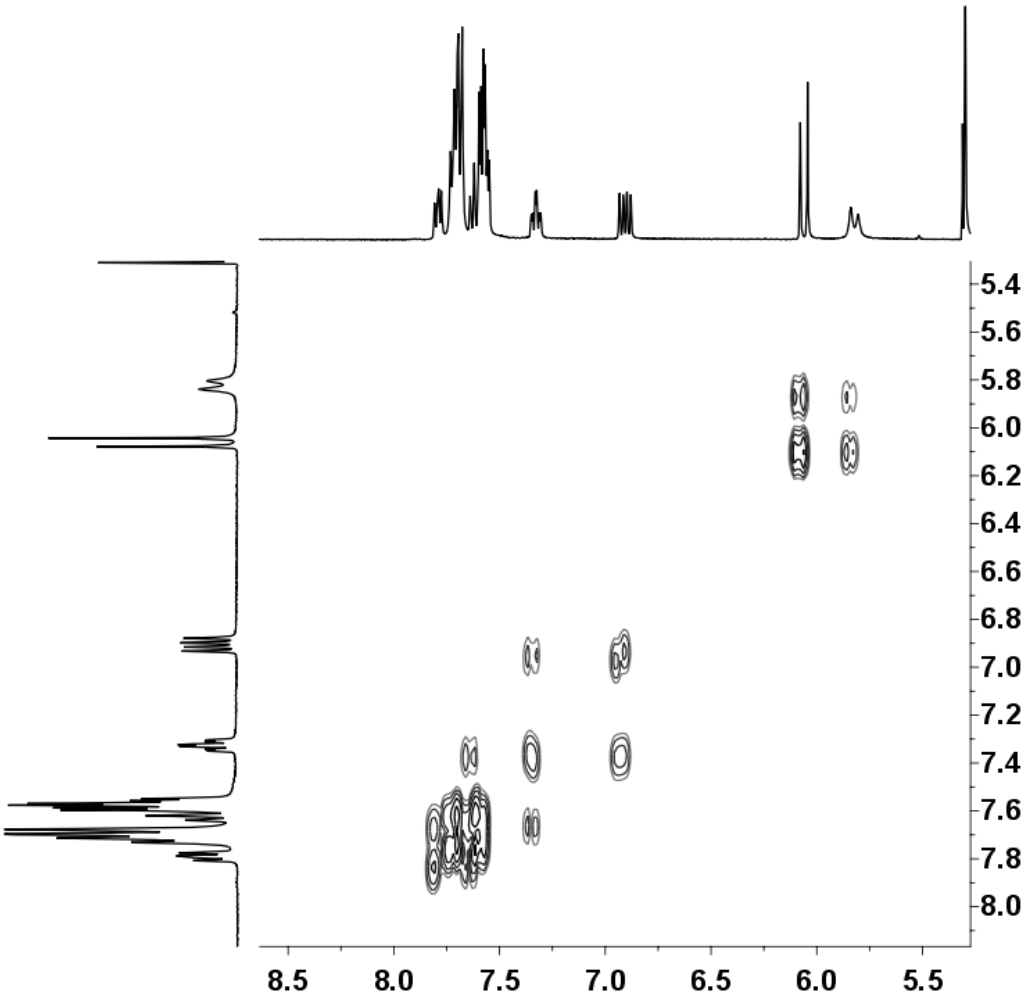


Figure 17: ^{1}H-^{1}H COSY spectrum of complex 6 at 298 K (400 MHz, CD_2Cl_2).

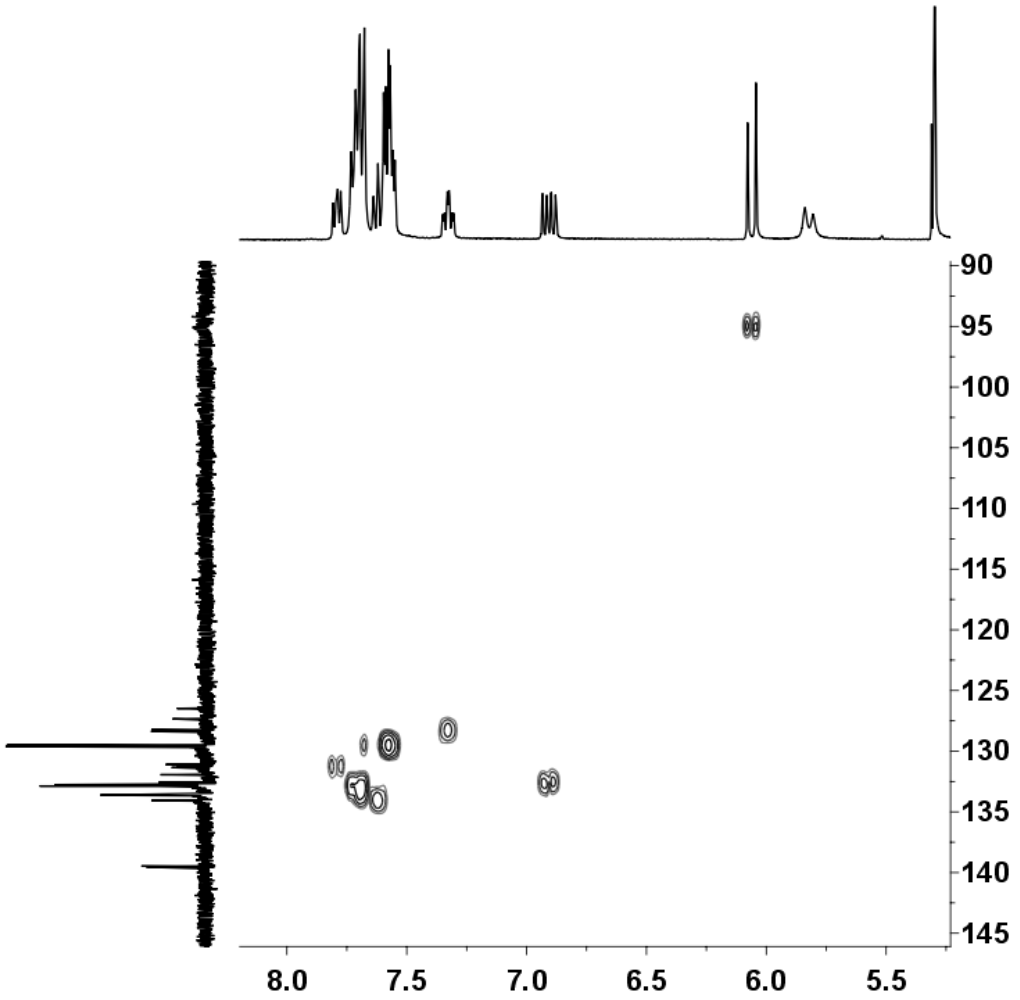


Figure 18: ^{1}H-^{13}C HSQC spectrum of complex 6 at 298 K (400 MHz, CD_2Cl_2).

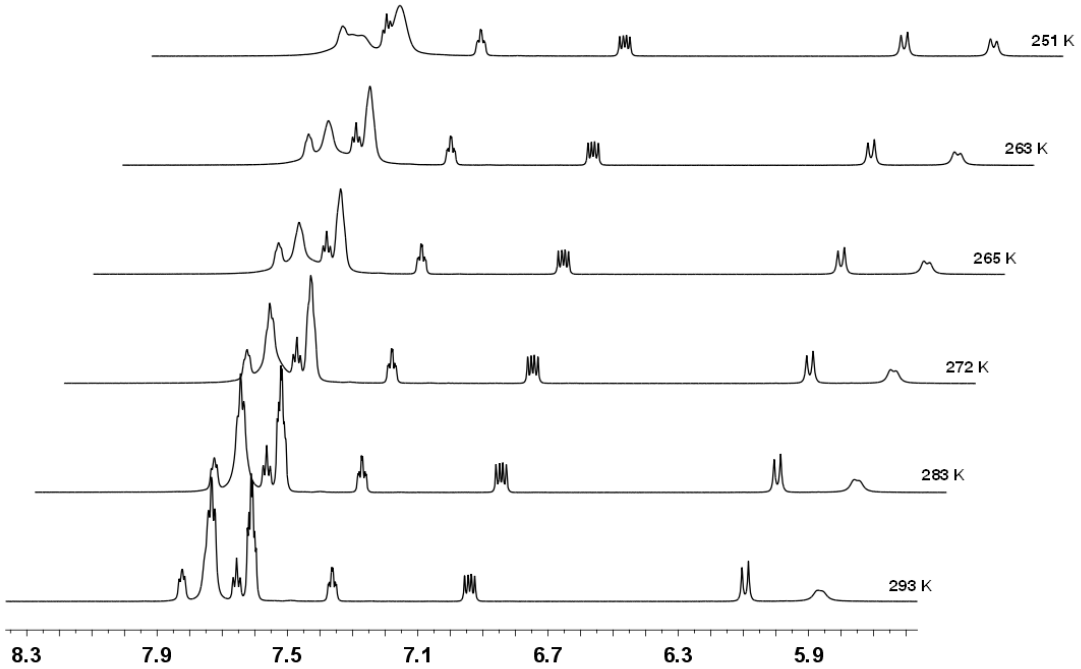


Figure 19: Variable temperature ^{1}H NMR spectrum of complex 6 (700 MHz, CD_2Cl_2).

5. NMR spectroscopic experiments

5.i. Chloride doping of complex 4:

To a solution of the complex **4** (15 mg, 0.01 mmol, 0.015 M) in CD_2Cl_2 was added aliquots of a solution of nBu$_4$NCl (0.01 ml, 0.25 eq., 0.25M) in CD_2Cl_2. The ^{1}H and ^{31}P NMR spectra were recorded after each aliquot was added.

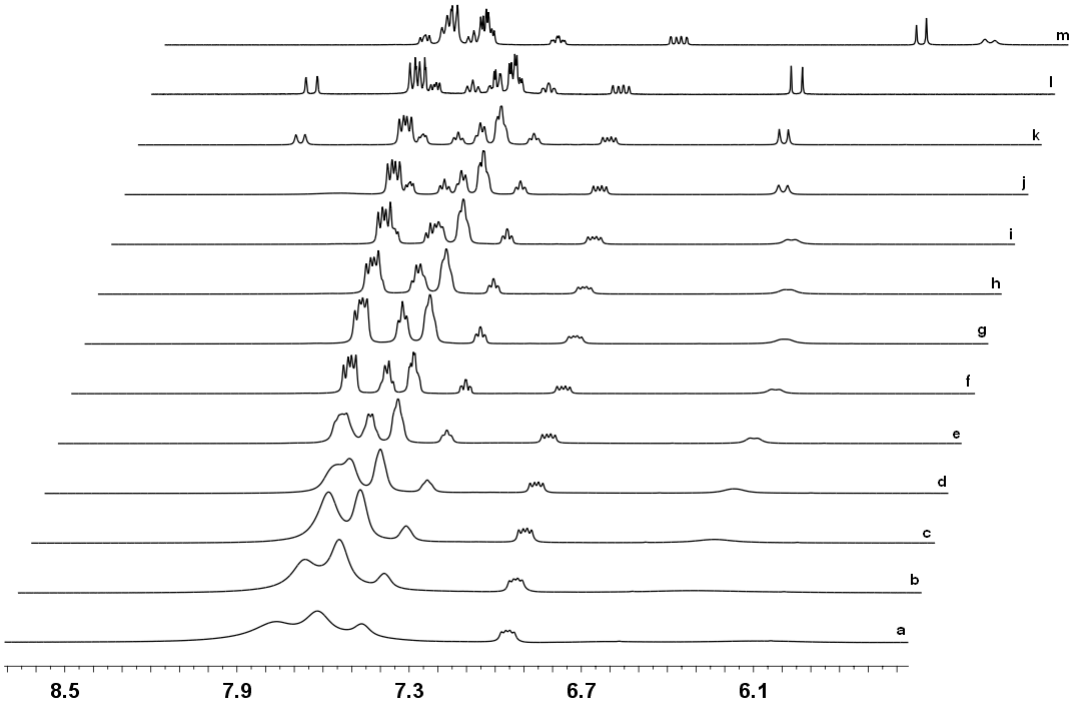


Figure 20: a) Complex 4; b) 0.3 eq. Cl^-; c) 0.6 eq.; d) 0.9 eq.; e) 1.2 eq.; f) 1.5 eq.; g) 1.8 eq.; h) 2.1 eq.; i) 2.4 eq.; j) 3 eq.; k) 3.6 eq.; l) dbathiophos (1); m) Complex 6.

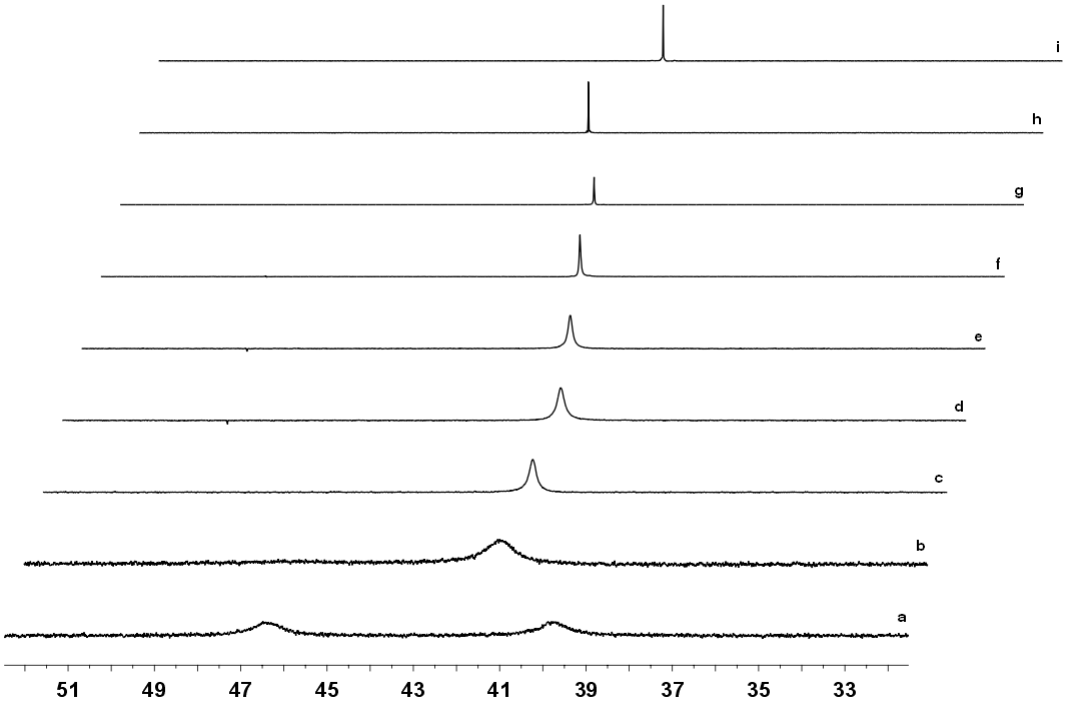


Figure 21: a) Complex 4; b) 0.6 eq. Cl^-; c) 1.2 eq.; d) 1.8 eq.; e) 2.4 eq.; f) 3 eq.; g) 3.6 eq.; h) dbathiophos (1); i) Complex 6.

5.ii. Addition of $AgPF_6$ to complex 6:

To solutions of complex **6** (9.5 mg, 0.011 mmol) in CD_2Cl_2 (0.8 ml) was added $AgPF_6$, (0.5 eq., 1 eq. and 2 eq. respectively). The ^{1}H and ^{31}P NMR spectra were recorded for each.

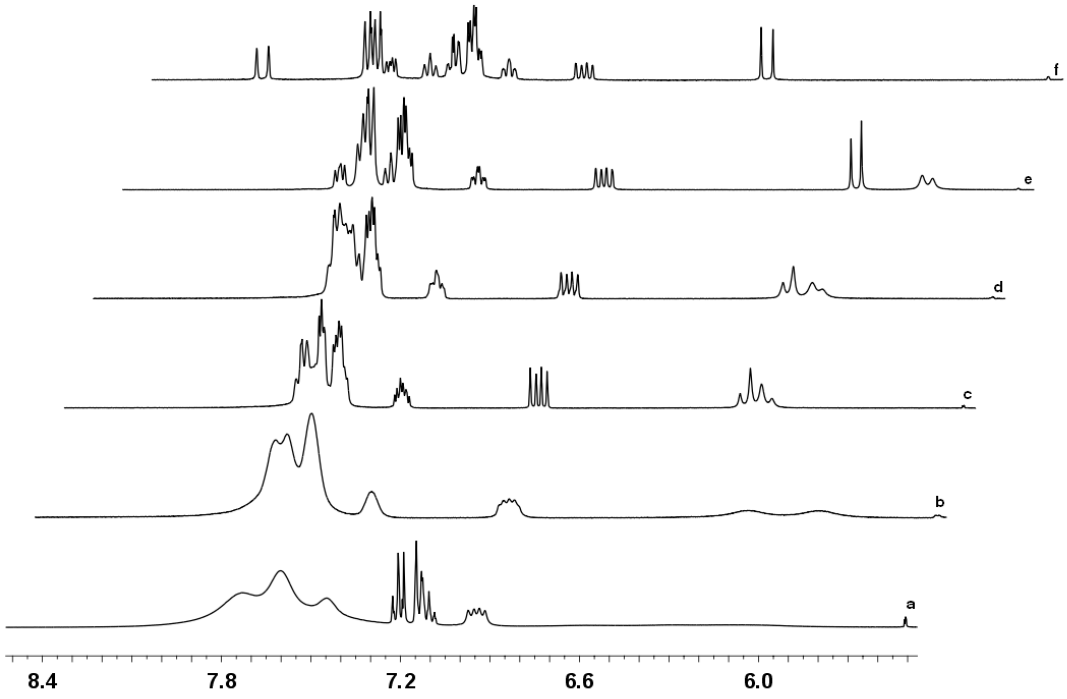


Figure 22: a) Complex 4 (contains trace toluene); b) 2 eq. $AgPF_6$; c) 1 eq. $AgPF_6$; d) 0.5 eq. $AgPF_6$; e) Complex 6; f) dbathiophos (1). (400 MHz, CD_2Cl_2).

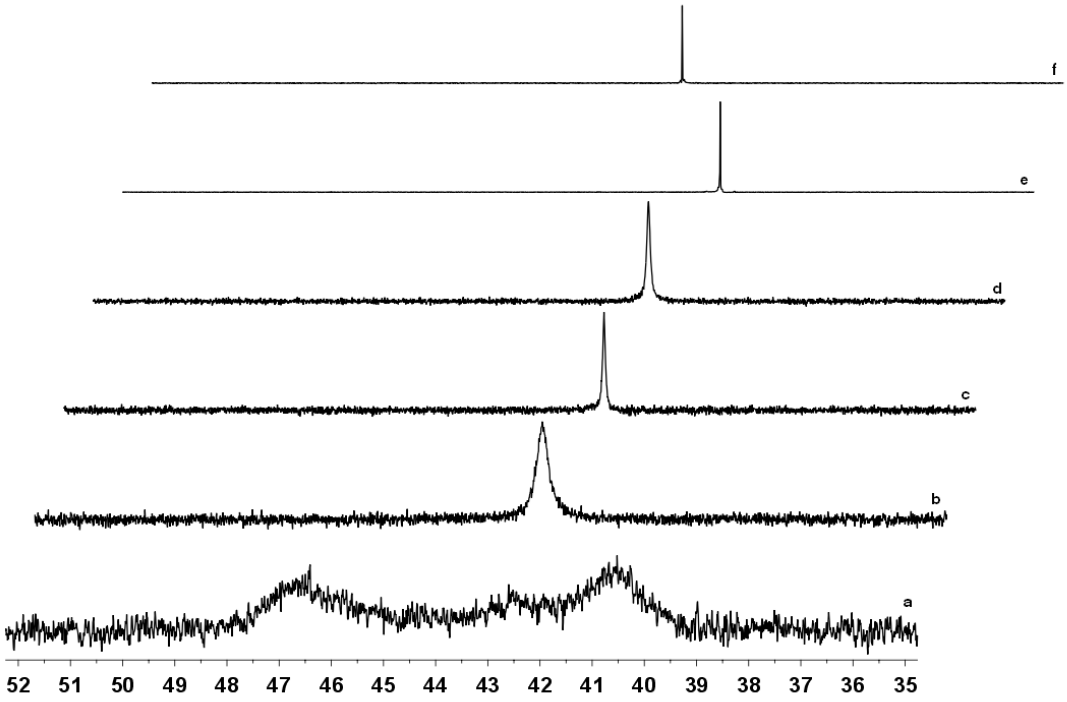
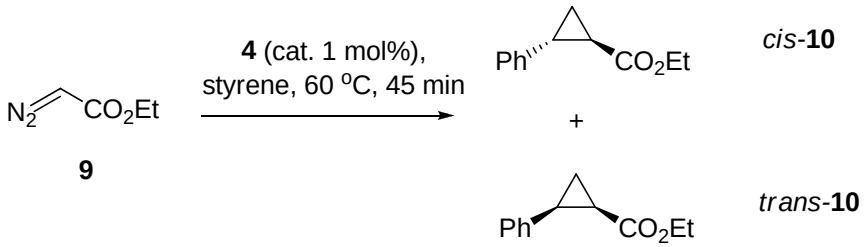


Figure 23: a) Complex 4; b) 2 eq. $AgPF_6$; c) 1 eq. $AgPF_6$; d) 0.5 eq. $AgPF_6$; e) Complex 6; f) dbathiophos (1). (400 MHz, CD_2Cl_2).

6. Catalysis

a. Cyclopropanation of styrene[8]



To a solution of Complex **4** (9.2 mg, 1 mol%, 0.0053 mmol) in distilled styrene (1 mL) at 60 °C was added ethyldiazoacetate **9**, EDA, (55 µl, 0.53 mmol) in three portions over 20 min. The reaction was stirred for a further 25 min at 60 °C. The reaction was left to cool and an aliquot (40 µl) measured into $CDCl_3$ (0.5 mL). ^{1}H NMR spectroscopic analysis determined that the product was formed in 85% conversion (not isolated) with a *cis:trans* ratio of 32:68 (*Figure 25*).

Control experiments were performed using CuBr and without the presence of Cu. When no Cu is present the reaction does not occur. When CuBr is used, after 45 min there is still EDA remaining, shown by the broad singlet at 4.7 ppm. ^{1}H NMR spectroscopy determined that the product was formed in 24% conversion (not isolated) with a *cis:trans* ratio of 40:60. In the case of complex **4**, a small amount of product (18% conversion) was observed by ^{1}H NMR spectroscopy after 90 min if the temperature was lowered to 40 °C with a *cis:trans* ratio of 50:50. See *Figure 24* for comparison by ^{1}H NMR spectroscopy.

The reaction was also carried out with complex **6** using the same procedure as above. ^{1}H NMR determined that the product was formed in 91% conversion (not isolated) with a *cis:trans* ratio of 30:70.

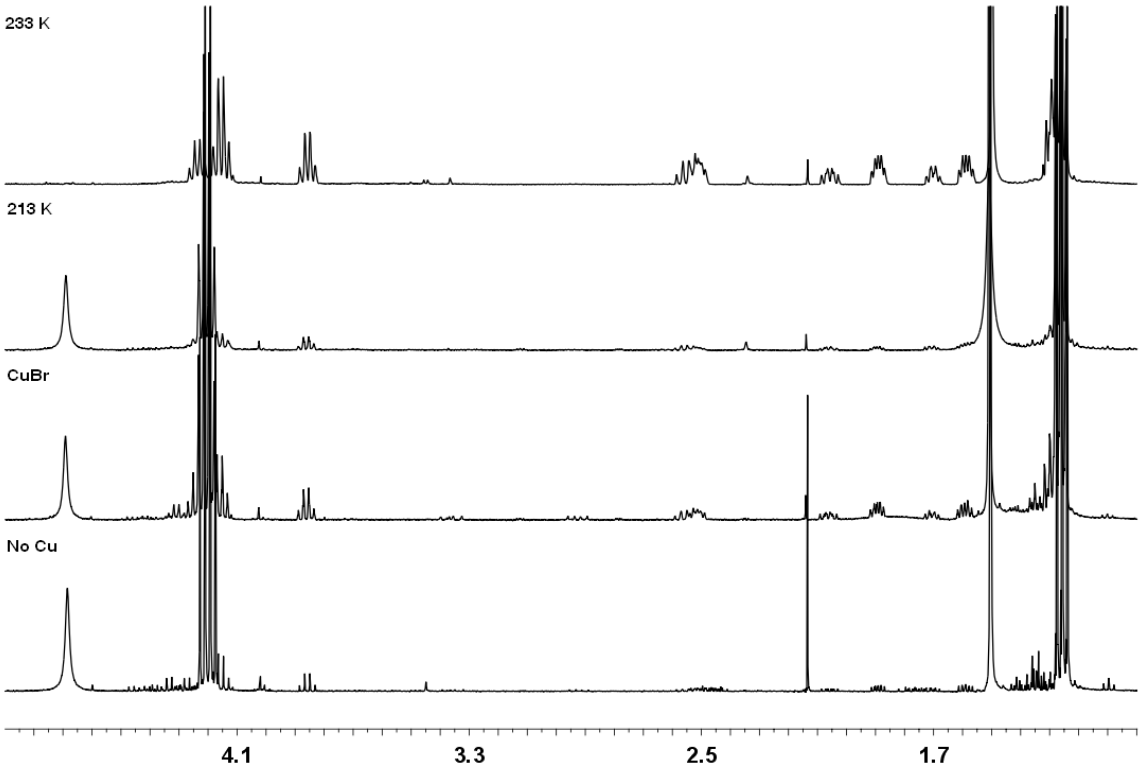


Figure 24: Comparison of catalysis with complex 4.

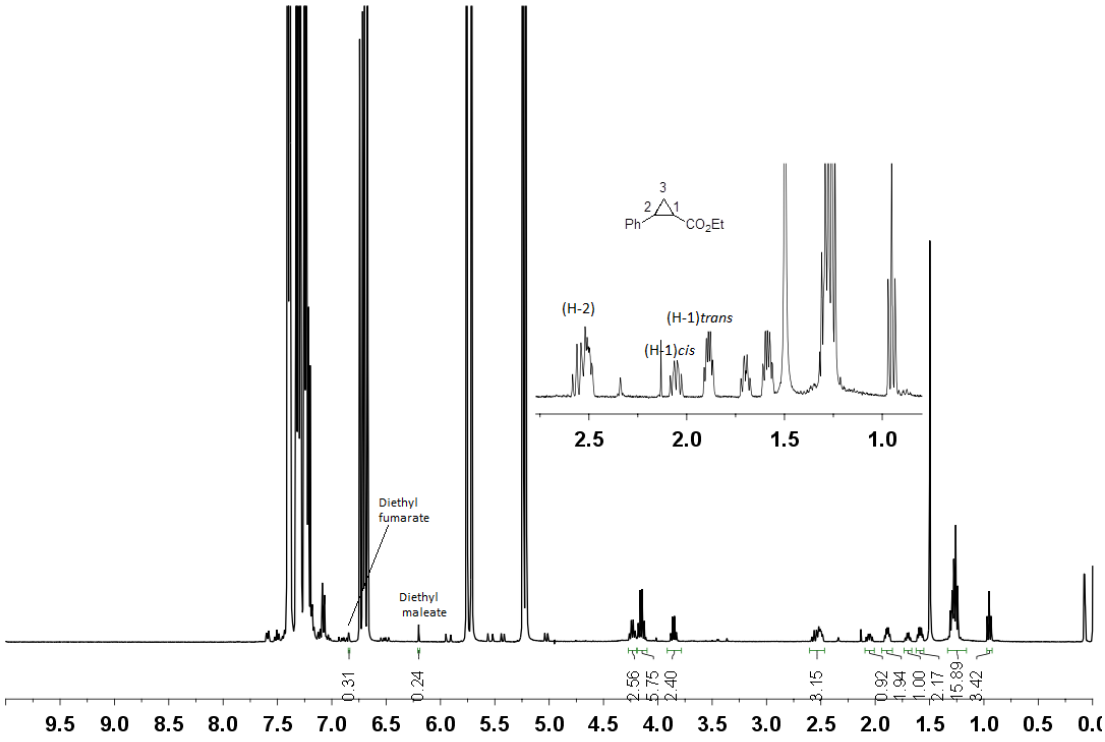


Figure 25: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, referenced to TMS) of the crude reaction mixture of the cyclopropanation with complex 4.

b. Reaction of complex 4 plus EDA (catalytic amounts of Cu)

Complex **4** (4.6 mg, 1 mol%, 0.0026 mmol) was dissolved in CD_2Cl_2 (0.5 mL). EDA (28 μL, 1 eq., 0.26 mmol) was added and the reaction monitored by ^1H NMR spectroscopy at room temperature. After ~1 h at room temperature over 80% conversion of the EDA to diethyl maleate and diethyl fumarate had occurred. After 24 h all the EDA had been converted.

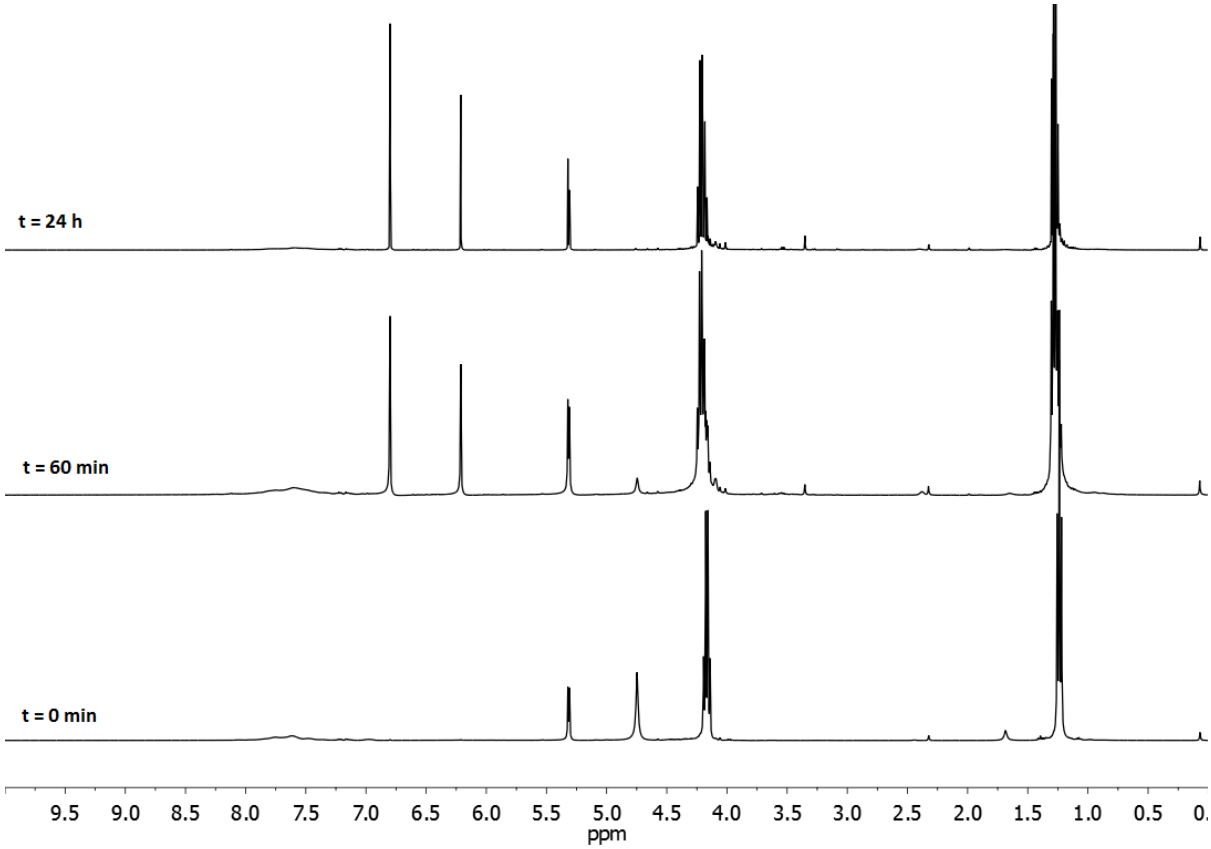


Figure 26: ^1H NMR spectrum (400 MHz, CD_2Cl_2) showing the conversion of EDA (δ 4.75 ppm) to diethyl maleate (δ 6.2 ppm) and diethyl fumarate (δ 6.8 ppm).

c. Reaction of complex 4 plus EDA (stoichiometric amounts of Cu)

Complex **4** (3.1 mg, 1 eq., 0.0017 mmol) was dissolved in CD_2Cl_2 (0.5 mL). EDA (3.7 μL, 2 eq., 0.0035 mmol) was added and the reaction followed by ^1H and ^{31}P NMR spectroscopy at room temperature. After 6 h no conversion to diethyl fumarate or diethyl maleate is observed. No changes are observed in the ^{31}P NMR spectrum and only very minor new peaks have appeared in the ^1H NMR spectrum. After 24 h two small peaks in the ^1H NMR have appeared at δ 6.2 and 6.8 ppm, diethyl maleate and diethyl fumarate, however most of the EDA remains. Two new phosphorous signals also appeared in the ^{31}P NMR spectrum at δ 42.21 and 41.55 ppm.

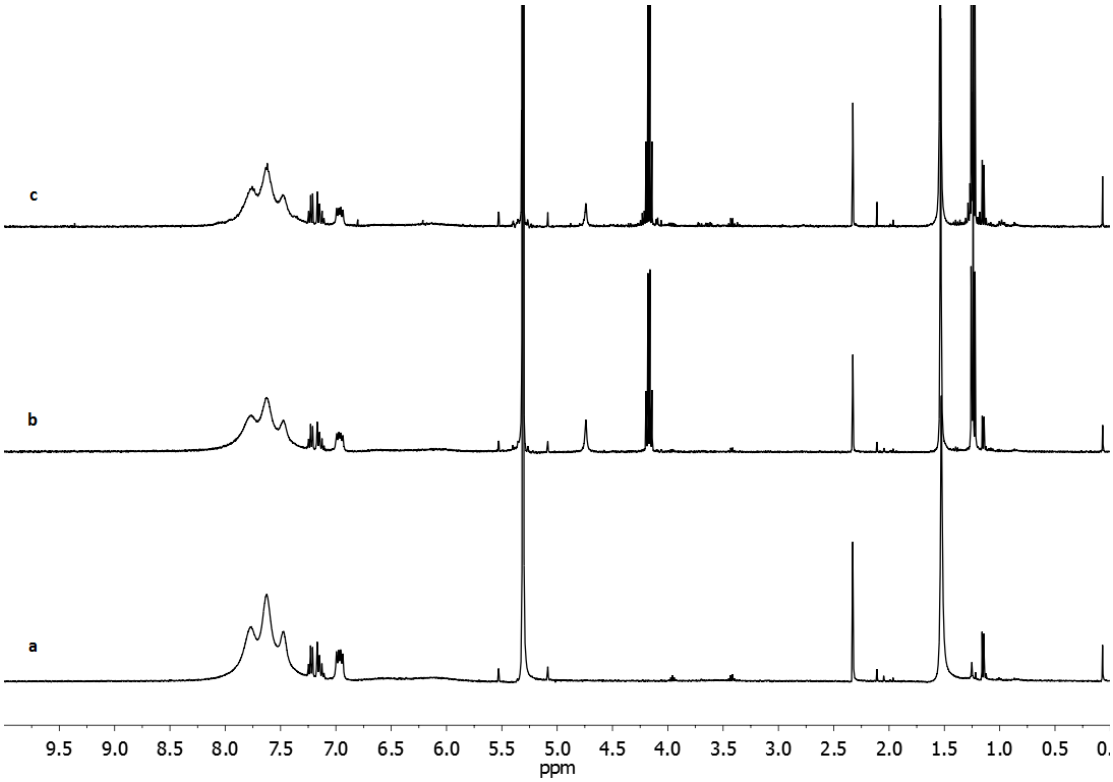


Figure 27: Reaction between EDA and stoichiometric amounts of complex 4: a) Complex 4; b) After addition of EDA and stirring for 1 h; c) After 24 h.

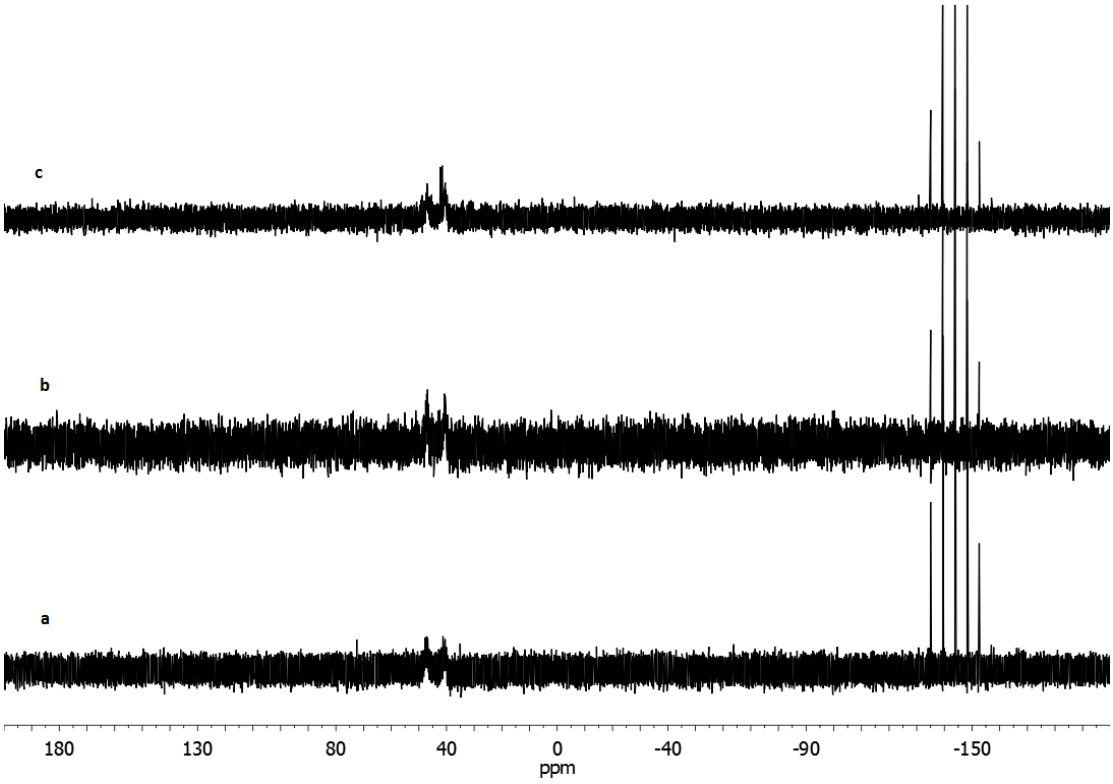


Figure 28: Reaction between EDA and stoichiometric amounts of complex 4: a) Complex 4; b) After addition of EDA and stirring for 1 h; c) After 24 h.

7. References

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