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Supporting Information

Backbone-Functionalised Ruthenium Diphosphine Complexes for Catalytic Upgrading of Ethanol and Methanol to *iso*-Butanol

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Contents:

Experimental

1. General Experimental Information

All reactions were carried out under an inert atmosphere of N_2 using conventional Schlenk glassware or glovebox techniques under an Ar atmosphere. The reagents anhydrous ethanol and methanol were purchased from Sigma-Aldrich and used as received. Pentane and deuterated solvents were dried using established procedures and further degassed under nitrogen. Other reagents were purified using an Anhydrous Engineering Grubbs-type solvent system. Complexes **1**-**7** were synthesised according to literature methods and(or) modified procedures. NMR spectra were recorded using Jeol ECS 300-400, Varian 400 or Bruker 400-500 NMR spectrometers. Proton and carbon chemical shifts (δ) are reported in ppm relative to the residual solvent resonances in the deuterated solvent. Data is reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet), coupling constant (Hz) and assignment. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard. Mass spectra (ESI) were recorded on a Bruker Daltonics micrOTOF II. All liquid products of catalysis were analysed by GC-FID using an Agilent 7820A GC, fitted with a DB-WAX column (30m x 320µm, I.D. 0.25 µm). Method: column oven temperature programme starts at 60 °C for 5 minutes, heat to 220 °C at 40 °C min^{-1} then hold at 220 °C for 5 minutes; helium carrier gas (flow rate of 2.5 mL min^{-1}); 1 µL injection volume; 1:100 split ratio.

2. Synthesis of Complexes

Synthesis of $[RuCl_2\{(PPh_2)_2CH=CH_2\}_2]$ (Pre-Cat)

The **Pre-Cat** was synthesised using a modified literature method.[1,2] dppen (0.82 g, 2.07 mmol) in 10 mL DCM was added to a solution of $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) in 10 mL DCM under a flow of nitrogen. The resulting blackish brown mixture was left to stir for 16 h at room temperature. On the following day, a red coloured solution was observed. The product mixture was filtered, washed with DCM (2 x 10 mL) and Et_2O (2 x 10 mL). The red powder product was left to dry overnight under vacuum. Additional product was obtained by reducing the DCM filtrate under vacuum and thereafter precipitated with Et_2O. The product mixture was kept in the freezer overnight, then filtered, washed with Et_2O (3 x 10 mL) and dried overnight under vacuum. Total product yield 87% (0.84 g). ESI-MS: *m/z* calc. 987 $[M + Na]^+$; 964 $[M]^+$; 929 $[M - Cl]^+$, 447 $[M - 2Cl]^{2+}$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.08 (m, 40H, ***Ph***), 6.14 (p, $^3J_{HP}$ = 12.6 Hz, 4H, ***C=CH₂***). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 15.35 (s) $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 134.73 – 134.51 (m, ***o*-Ph**), 132.42 (s, *C=**CH₂***), 132.09 – 131.59 (m, ***C**=CH₂*), 129.43 (s, ***p*-Ph**), 127.62 – 127.30 (m, ***m*-Ph**). See Figures S1-S2 for spectra.

Synthesis of Complexes 1-7

(a) Synthesis of $[RuCl_2\{(Ph_2P)_2CHCH_2NH(CH_2)_2NH_2\}_2]$ (1)

Complex **1** was synthesised by adapting a literature procedure.[1,2] Ethylenediamine (1.0 mL, 14.96 mmol) was added to a solution of **Pre-Cat** (0.10 g, 0.10 mmol) in toluene (10 mL) and the resulting mixture was stirred for 2 h during which the colour changed to yellow. The solvent was reduced under vacuum to ca. 4 mL and the product was crystallised with pentane (10 mL). The yellow crystals obtained were washed with pentane and dried under vacuum. Single crystals suitable for X-ray diffraction studies were obtained from a fluorobenzene/pentane mixture. Yield, 47% (0.053 g). ESI-MS: *m/z* calc. 1085 $[M + H]^+$; 1048 $[M - Cl]^+$; 593 $[M – Cl - L]^+$; 457 $[L + H]^+$ (L = $(Ph_2P)_2CHCH_2NH(CH_2)_2NH_2$); 385 $[(Ph_2P)_2CH_2 + H]^+$. ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 8H, ***o*-Ph**), 7.54 – 7.48 (m, 8H, ***o*-Ph**), 7.29 – 7.23 (m, 12H, ***m, p*-Ph**), 7.10 (t, J_{HH} = 7.8, 1.8 Hz, 16H, ***m, p*-Ph**), 5.46 (sept, J_{PH} = 6.5 Hz, 2H, P_2CHCH_2), 3.10 – 3.00 (m, 4H, P_2CHCH_2), 2.61 (t, *J* = 5.7 Hz, 4H, $NHCH_2CH_2NH_2$), 2.52 – 2.45 (m, 4H, $NHCH_2CH_2NH_2$), 0.93 (s, br, 6H, ***NH***). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 10.82 (s). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.22 (s, ***C*$_i$-Ph**), 134.59 – 134.18 (m, ***o*-Ph**), 129.90 (s, ***p*-**

Ph), 129.44 (s, ***p*-Ph**), 127.61 (s, ***m*-Ph**), 61.34 – 60.75 (m, NH***C***$H_2$$CH_2$$NH_2$), 52.68 (s, P_2CH***C***H_2NH), 51.09 (s, P_2***C***HCH_2), 42.07 (s, $NHCH_2$***C***$H_2$$NH_2$). See Figures S3-S4 for spectra.

(b) Synthesis of [$RuCl_2${$(Ph_2P)_2CHCH_2NH(CH_2)_3NH_2$}$_2$] (2)

Complex **2** was synthesised using a literature procedure.[1,2] 1,3-diaminopropane (0.4 mL, 4.79 mmol) was added to a suspension of **Pre-Cat** (0.20 g, 0.2 mmol) in toluene (10 mL) under a nitrogen flow with continuous stirring. The colour of the solution changed from red to cloudy yellow after 4 h. The solution mixture was left to stir overnight. The product mixture was filtered, and the resulting yellow residue was triturated with MeOH (3 x 10 mL). After filtration, the yellow product was dried under vacuum. Yield, 46% (0.106 g,). ESI-MS: *m/z* calc. 1113 $[M + H]^+$; 557 $[M + 2H]^{2+}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 7H, **Ph**), 7.54 – 7.47 (m, 7H, **Ph**), 7.29 – 7.22 (m, 11H, **Ph**), 7.14 – 7.05 (m, 15H, **Ph**), 5.45 (p, $^1J_{PH}$ = 6.5 Hz, 2H, P_2***CH***CH_2), 3.07 – 2.97 (m, 4H, P_2CH***C***H_2), 2.60 (t, J_{HH} = 6.8 Hz, 4H, -NH***C***$H_2$$CH_2$$CH_2$$NH_2$), 2.48 (t, J_{HH} = 6.7 Hz, 4H, -$NHCH_2CH_2$***C***$H_2$$NH_2$), 1.46 (p, J_{HH} = 6.7 Hz, 4H, -$NHCH_2$***C***$H_2$$CH_2$$NH_2$), 0.95 (br, s, 6H, amine H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 11.35 (s)**.** ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 135.96 (s, ***C*$_i$-Ph**), 134.31 – 133.99 (m, ***o*-Ph**), 131.62 – 131.19 (m, P_2***CH***CH_2), 129.62-129.16 (s, ***p*-Ph**), 127.36 (d, *J* = 3.0 Hz, ***m*-Ph**), 61.03-60.52 (m, P_2***CH***CH_2), 51.15 (s, P_2CH***C*H_2***NH**), 47.74 (s, -NH***C*$H_2$$CH_2CH_2NH_2$), 40.72 (s, -$NHCH_2CH_2$***C*$H_2$***NH**$_2$), 33.77 (s, -$NHCH_2$***C*$H_2$***CH**$_2$$NH_2$). See Figures S5-S6 for spectra.

(c) Synthesis of [$RuCl_2${$(Ph_2P)_2CHCH_2NH(CH_2)_3Si(OEt)_3$}$_2$] (3)

Complex **3** was synthesised using a literature procedure.[1,2] 3-(Aminopropyl)triethoxysilane (1.0 mL, 4.27 mmol) was added under a nitrogen flow to a suspension of **Pre-Cat** (0.2 g, 0.2 mmol) in toluene (10 mL). The mixture was left to stir overnight. The red suspension dissolved gradually to give a yellow solution. The next day, the mixture was filtered to remove any solid impurities. The filtrate was reduced under vacuum to ca. 4 mL and the product precipitated with Et_2O. The product mixture was kept in the freezer overnight. Thereafter, the product was filtered, washed with Et_2O (3 x 10 mL) and dried under vacuum. Yield, 40% (0.117 g). ESI-MS: *m/z* calc. 1407 $[M + H]^+$, 705 $[M + 2H]^{2+}$. Selected ^{1}H NMR (400 MHz, $CDCl_3$): 5.49 – 5.39 (m, 2H, P_2***CH***CH_2), 3.74 (q, J_{HH} = 7.0 Hz, 12H, *Si(O*CH_2CH_3*)*$_3$), 3.48 (q, *J* = 7.0 Hz, 2H, -*NH*$CH_2CH_2CH_2Si$), 3.01 (br, s, 4H, P_2CH***C*H_2**), 1.42 (p, J_{HH} = 8.3 Hz, 4H, -*NHCH*$_2$***C*H_2***CH**$_2$*Si*), 1.17 (t, J_{HH} = 7.0 Hz, 18H, *Si(*OCH_2***C*H_3*)*$_3$), 0.85 (br, s, 4H, -***NH***$CH_2CH_2CH_2Si$), 0.51 – 0.43 (m, 4H, -*NHCH*$_2$$CH_2$***C*$H_2$***Si**). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 11.31 (s). Selected ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.99 (s, ***C*$_i$-Ph**), 134.31 – 134.03 (m, ***o*-Ph**), 129.57 (s, ***p*-Ph**), 129.09 (s, ***p*-Ph**), 127.32 (s, ***m*-Ph**), 60.85 (s, *PCH*CH_2***), 58.45 (s, -*$SiOCH_2$***C*H_3***), 52.32 (s, -*N*$CH_2CH_2CH_2Si$), 50.87 (s, P_2***CH***CH_2), 23.24 (s, -*NCH*$_2$***C*H_2***CH**$_2$*Si*), 18.45 (s, -*SiO*CH_2CH_3), 7.98 (s, -*NCH*$_2CH_2$***C*H_2***Si**). Et_2O impurity was present in the spectrum. See Figures S7-S8 for spectra.

(d) Synthesis of [$RuCl_2${$(Ph_2P)_2CHCH_2NH(CH_2)C_6H_5$}$_2$] (4)

Complex **4** was synthesised using a literature procedure.[1,2] To a suspension of **Pre-Cat** (0.20 g, 0.20 mmol) in toluene (10 mL) was added benzylamine (1.0 mL, 9.16 mmol) under nitrogen and left to stir overnight. The suspension dissolved to give a yellow precipitate. The product mixture was filtered and washed with toluene (10 mL). The yellow residue was triturated with MeOH (10 mL). The final product was washed with MeOH (2 x 10 mL) to obtain a yellow solid product which was dried under vacuum. Yield, 55% (0.135 g). ESI-MS: *m/z* calc. 1178 $[M]^+$, 1143 $[M - Cl]^+$, 590 $[M + 2H]^{2+}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 - 7.04 (m, 50H, **Ph**), 5.50 (p, *J* = 6.5 Hz, 2H, P_2***CH***CH_2), 3.62 (s, 4H, *NH*CH_2Ph), 3.09 (s, 4H, P_2CH***C*H_2***), 0.84 (br, s, 2H, ***NH***). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 11.52 (s). Selected ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 140.07 (s, ***C*$_i$-Bz**), 135.97 (s, ***C*$_i$-Ph**), 134.28 – 134.08 (m, ***o*-Ph**), 129.62 -129.15 (s, ***p*-Ph**), 128.45 (s, ***o*-Bz**), 128.03 (s, ***m*-Bz**), 127.37 (s, ***m*-Ph**), 127.02 (s, ***o*-Bz**), 53.57 – 53.32 (m, *NH*CH_2Bz), 50.46 (s, P_2CH***C*H_2***). See Figures S9-S10 for spectra.

(e) Synthesis of [RuCl$_2${(Ph$_2$P)$_2$CHCH$_2$NH(CH$_2$)PPh$_2$}$_2$] (5)

Complex **5** was synthesised by adapting a literature procedure.[1,2] 2-(Diphenylphosphino)ethylamine (3 mL) was added to a suspension of **Pre-Cat** (0.10 g, 0.10 mmol) in toluene (10 mL) under a nitrogen flow with continuous stirring overnight. No colour change was observed. A crude ^{31}P{^{1}H} NMR spectrum of the mixture was recorded with no traces of product formed. An additional 0.3 mL of the ligand was added and allowed to stir overnight. The solution changed from red to yellow. The solvent was removed in vacuo to give a yellow oily product. The oily product was triturated with MeOH to give a yellow product. The product was filtered, washed with MeOH (3 x 10 mL) and dried under vacuum. Yield, 47% (0.070 g,). ESI-MS: *m/z* calc. 1423 $[M + H]^+$; 712 $[M + 2H]^{2+}$. Selected ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.32 (m, 2H, *P$_2$**CH**CH$_2$*), 2.95 (d, *J* = 6.7 Hz, 4H, *P$_2$CH**CH$_2$***), 2.56 (q, *J* = 8.0 Hz, 4H, *NHCH$_2$**CH$_2$**PPh$_2$*), 2.12 – 2.02 (m, 4H, *NH**CH$_2$**CH$_2$PPh$_2$*), 0.88 (s, 2H, *NH*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 10.64 (s), -20.81 (s). Selected ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 131.42 (s, ***p*-Ph**), 128.48 (s, ***m*-Ph**, *(**PPh$_2$**)$_2$CH*), 127.20 (s, ***m*-Ph**, *NHCH$_2$CH$_2$**PPh$_2$***). See Figures S11-S12 for spectra.

(f) Synthesis of [RuCl$_2${(Ph$_2$P)$_2$CHCH$_2$NH(CH$_2$)SH}$_2$] (6)

Complex **6** was synthesised by adapting a literature procedure.[1,2] Cysteamine (0.016 g, 0.207 mmol) was dissolved in DCM (5 mL) overnight and was added to a suspension of **Pre-Cat** (0.10 g, 0.10 mmol) in DCM (10 mL) and left to stir overnight. The product mixture was concentrated under vacuum to ca. 4 mL and crystallised with pentane (10 mL) and kept in the freezer. The product was filtered, washed with pentane and dried under vacuum to obtain a yellow solid. Yield, 58% (0.067 g). ESI-MS: *m/z* calc. 1083 $[M - Cl]^+$, 1047 $[M - 2Cl]^+$, 542 $[M - Cl]^{2+}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.11 (m, 30H, **Ph**), 5.50 (p, *J* = 6.4 Hz, 2H, *P$_2$**CH**CH$_2$*), 2.96 (q, *J* = 5.9 Hz, 4H, *P$_2$CH**CH$_2$***), 2.70 (t, J_{HH} = 6.4 Hz, 4H, *HN**CH$_2$**CH$_2$SH*), 2.47 (t, J_{HH} = 6.4 Hz, 4H, *HNCH$_2$**CH$_2$**SH*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 15.95 (s). See Figures S13-S14 for spectra.

(g) Synthesis of [RuCl$_2${(Ph$_2$P)$_2$CHCH$_2$NH(CH$_2$)OH}$_2$] (7)

Complex **7** was synthesised by adapting a literature procedure.[1,2] To a suspension of **Pre-Cat** (0.20 g, 0.10 mmol) in DCM (15 mL) was added ethanolamine (2.0 mL, 33.14 mmol) under a flow of nitrogen. A yellow colour was observed within 1 h. The solution was concentrated under vacuum to ca. 4 mL and the resulting oil was triturated with MeOH (10 mL) to give a yellow precipitate. The mixture was kept in the freezer overnight. The product was filtered, washed with MeOH (3 x 10 mL) and dried under vacuum to give a yellow powder. Yield, 93% (0.101 g). ESI-MS: *m/z* calc. 1087 $[M + H]^+$, 630 $[M + H - L]^+$, 629 $[M - L]^+$, 458 $[L + H]^+$, 273 $[L + PPh_2]^+$, 385 $[(PPh_2)_2CH + H]^+$, (L = $(Ph_2P)_2CHCH_2NH(CH_2)_2OH$). Selected ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 (p, *J* = 6.6 Hz, 2H, *P$_2$**CH**CH$_2$*), 3.46 (t, *J* = 5.1 Hz, 4H, *HNCH$_2$**CH$_2$**OH*), 3.08 (q, *J* = 5.7 Hz, 4H, *P$_2$CH**CH$_2$***), 2.63 – 2.57 (m, 4H, *HN**CH$_2$**CH$_2$OH*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 10.93 (s). Selected ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 131.09 (s, ***p*-Ph**), 127.78 (s, ***m*-Ph**, *NHCH$_2$CH**PPh$_2$***). See Figures S15-S16 for spectra.

3. Catalysis

All catalytic reactions were carried out in a 100 mL Parr stainless steel autoclave using an aluminium heating mantle as heating source and magnetic stirring at (500 rpm). A typical procedure is outlined below.

Typical Catalytic procedure[3-5]

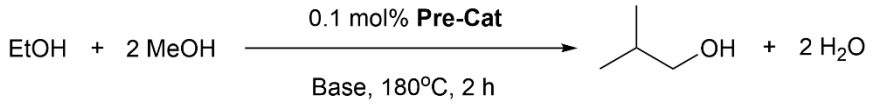
Pre-Cat, *trans*-$[RuCl_2(dppen)_2]$, (0.0165 g, 0.0171 mmol, 0.1 mol%), NaOMe (1.85 g, 34.26 mmol, 200 mol%) and a stirrer bar were added to a clean oven dried fitted PTFE insert inside a glove box. The insert was sealed within a 100 mL Parr stainless steel autoclave which was then transferred to a

nitrogen/vacuum manifold. Methanol (10 mL, 247.13 mmol) and ethanol (1 mL, 17.13 mmol) were injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed into a pre-heated (180°C) aluminium heating mantle and stirred at 500 rpm. After the reaction run time (2 h), the autoclave was cooled to room temperature in an ice-water bath. The autoclave was carefully vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of hexadecane standard, 1.7 mL diethyl ether – sample filtered through a glass filter paper to remove insoluble salts). For subsequent usage, the PTFE autoclave sleeve was cleaned with bleach (soak overnight), followed by washing with soap and water and finally with acetone and deionised water. In some cases, there was need to soak the sleeve in aqua regia to dissolve any residue metal catalysts.

Tables of Catalytic results

Complete catalytic results are shown in Tables S1 and S2 below.

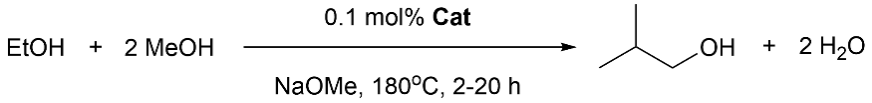
Table S1: Ruthenium catalysed conversion of ethanol and methanol to *iso*-butanol using different bases.



						TON[d](Yield)[e][Selectivity]%			
Run[a]	**Catalyst**	**Time(h)**	**Base**	**Conversion[b]**	**Total TON[c]**	***Iso*-butanol**	**1-propanol**	**2-methyl-1-butanol**	**1-hexanol**
1	**Pre-Cat**	2	NaOMe	48	480	460(46)[97]	10(1)[2]	0(0)[0]	10(1)[1]
2	**Pre-Cat**	2	NaOEt	33	330	270(27)[87]	30(3)[10]	10(1)[1]	20(2)[2]
3	**Pre-Cat**	2	KOEt	35	350	290(29)[88]	30(3)[10]	0(0)[0]	30(3)[3]
4	**Pre-Cat**	2	NaO^{t}Bu	56	560	520(52)[96]	20(2)[3]	0(0)[0]	20(2)[1]
5	**Pre-Cat**	2	KO^{t}Bu	42	420	400(40)[98]	10(1)[2]	0(0)[0]	10(1)[1]
6	**Pre-Cat**	2	NaOH	73	730	670(67)[93]	50(5)[7]	0(0)[0]	10(1)[*]
7	**Pre-Cat**	2	KOH	44	440	390(39)[89]	50(5)[10]	0(0)[0]	10(1)[1]
8	**Pre-Cat**	2	LiOH	13	130	110(11)[85]	20(2)[13]	0(0)[0]	10(1)[2]
9	**Pre-Cat**	2	NaH	39	390	370(37)[97]	10(1)[2]	0(0)[0]	<5(*)[*]
10	**Pre-Cat**	2	KH	61	610	580(58)[96]	20(2)[4]	0(0)[0]	10(1)[*]
11	**Pre-Cat**	2	LiH	3	30	30(3)[100]	0(0)[0]	0(0)[0]	0(0)[0]
12	**Pre-Cat**	2	Et_3N	0	0	0(0)[0]	0(0)[0]	0(0)[0]	0(0)[0]
13	**Pre-Cat**	2	DBU	0	0	0(0)[0]	0(0)[0]	0(0)[0]	0(0)[0]
14	**Pre-Cat**	2	MgO	0	0	0(0)[0]	0(0)[0]	0(0)[0]	0(0)[0]
15[f]	**Pre-Cat**	2	MgO	0	0	0(0)[0]	0(0)[0]	0(0)[0]	0(0)[0]

[a] Conditions: Ethanol (1 mL, 17.13 mmol), methanol (10 mL, 247.13 mmol), [Ru] catalyst (0.01713 mmol, 0.1 mol%), Base (34.26 mmol, 200 mol%), mol% is based on ethanol substrate, 180 °C. [b] Total conversion of ethanol to Guerbet products, *iso*-butanol, 1-propanol, 2-methyl-1-butanol, 1-hexanol. [c] Total TON based on mmol of total ethanol converted to products per mmol of [Ru] catalyst (ethanol equivalent relative to mmol of catalysts x conversion = 1000 x conversion). [d] TON based on mmol of any product formed per mmol [Ru] catalyst (ethanol equivalent relative to mmol of catalysts x product yield = 1000 x product yield). [e] Total yield and selectivity of alcohol products in the liquid fraction as determined by GC. [f] 40 bar H_2. *Yield or selectivity less than 0.5%.

Table S2: Ruthenium catalysed conversion of ethanol and methanol to *iso*-butanol.



							TON[d](yield)[e][selectivity]%		
Run[a]	**Catalyst**	**Time(h)**	**Base**	**Conversion[b]**	**Total TON[c]**	***Iso*-butanol**	**1-Propanol**	**2-methyl-1-butanol**	**Hexanol**
1	**1**	2	NaOMe	78	780	740(74)[94]	40(4)[5]	0(0)[0]	20(2)[1]
2	**2**	2	NaOMe	84	840	590(59)[97]	10(1)[2]	0(0)[0]	10(1)[1]
3	**2**	20	NaOMe	94	940	690(69)[94]	20(2)[2]	0(0)[0]	80(8)[4]
4	**3**	2	NaOMe	83	830	590(59)[97]	10(1)[2]	0(0)[0]	10(1)[1]
5	**3**	20	NaOMe	95	950	690(69)[96]	20(2)[2]	0(0)[0]	40(4)[2]
6	**4**	2	NaOMe	83	830	600(60)[98]	10(1)[2]	0(0)[0]	10(1)[1]
7	**4**	20	NaOMe	95	950	660(66)[96]	20(2)[2]	0(0)[0]	40(4)[2]
8	**5**	2	NaOMe	89	890	600(60)[94]	30(3)[5]	0(0)[0]	10(1)[1]
9	**5**	20	NaOMe	89	890	680(68)[94]	30(3)[4]	0(0)[0]	60(6)[3]
10	**6**	2	NaOMe	88	880	620(62)[100]	0(0)[0]	0(0)[0]	0(0)[0]
11	**6**	20	NaOMe	100	1000	790(79)[100]	0(0)[0]	0(0)[0]	0(0)[0]
12	**7**	2	NaOMe	79	790	520(52)[97]	20(2)[3]	0(0)[0]	10(1)[1]
13	**7**	20	NaOMe	94	940	720(72)[96]	20(2)[2]	0(0)[0]	40(4)[2]

[a] Conditions: Ethanol (1 mL, 17.13 mmol), methanol (10 mL, 247.13 mmol), [Ru] catalyst (0.01713 mmol, 0.1 mol%), Base (34.26 mmol, 200 mol%), mol% is based on ethanol substrate, 180 °C. [b] Total conversion of ethanol to liquid product as determined by GC analysis of the liquid phase. [c] Total TON based on mmol of total ethanol converted to products per mmol of [Ru] catalyst (ethanol equivalent relative to mmol of catalysts x conversion = 1000 x conversion). [d] TON based on mmol of any product formed per mmol [Ru] catalyst (ethanol equivalent relative to mmol of catalysts x product yield = 1000 x product yield). [e] Total yield and selectivity of alcohol products in the liquid fraction as determined by GC.

4. NMR Spectra

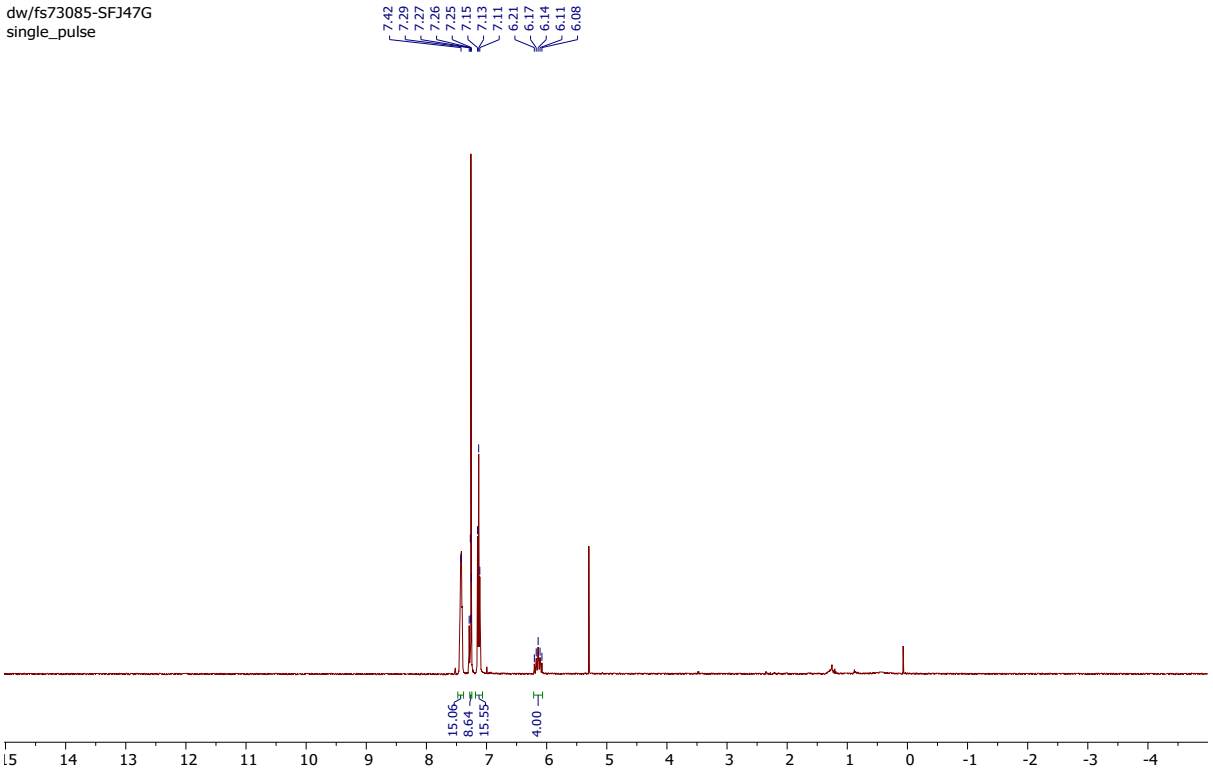


Figure S1: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **Pre-Cat**

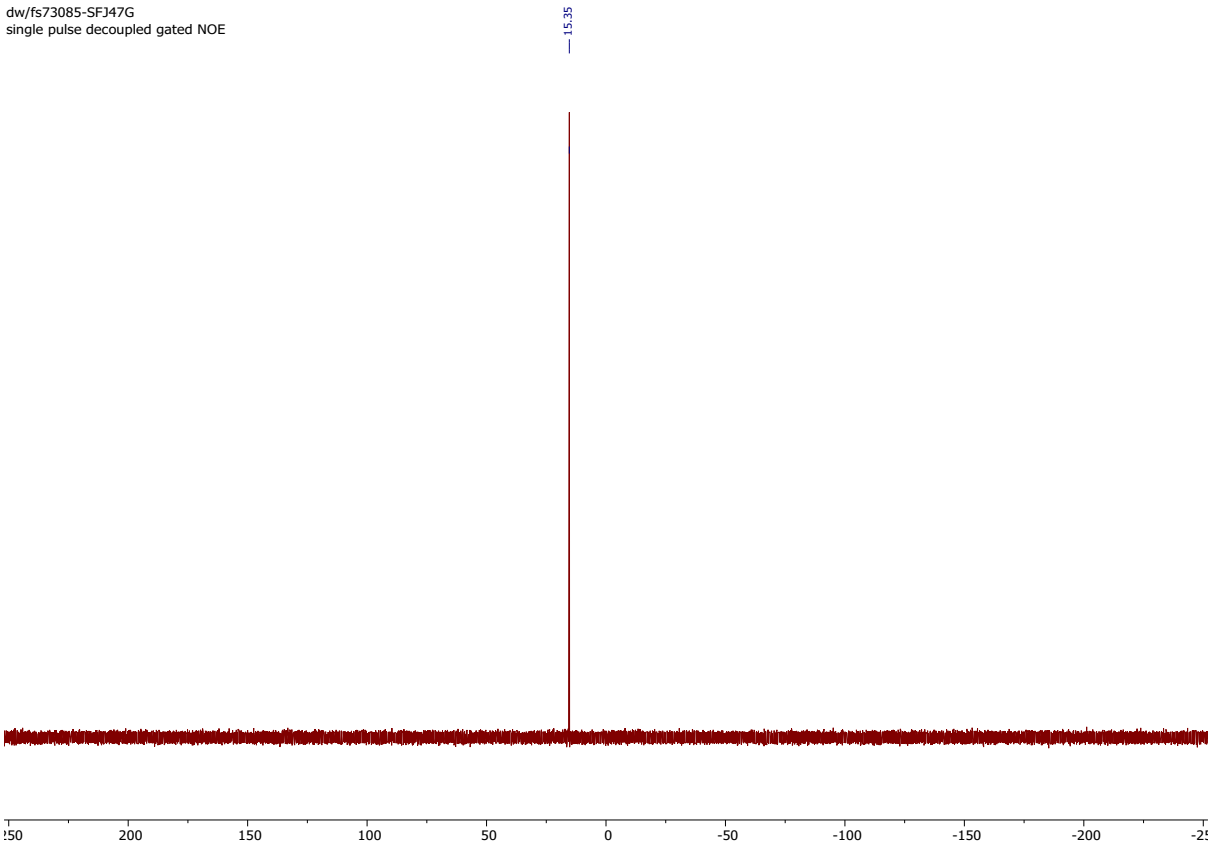


Figure S2: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **Pre-Cat**

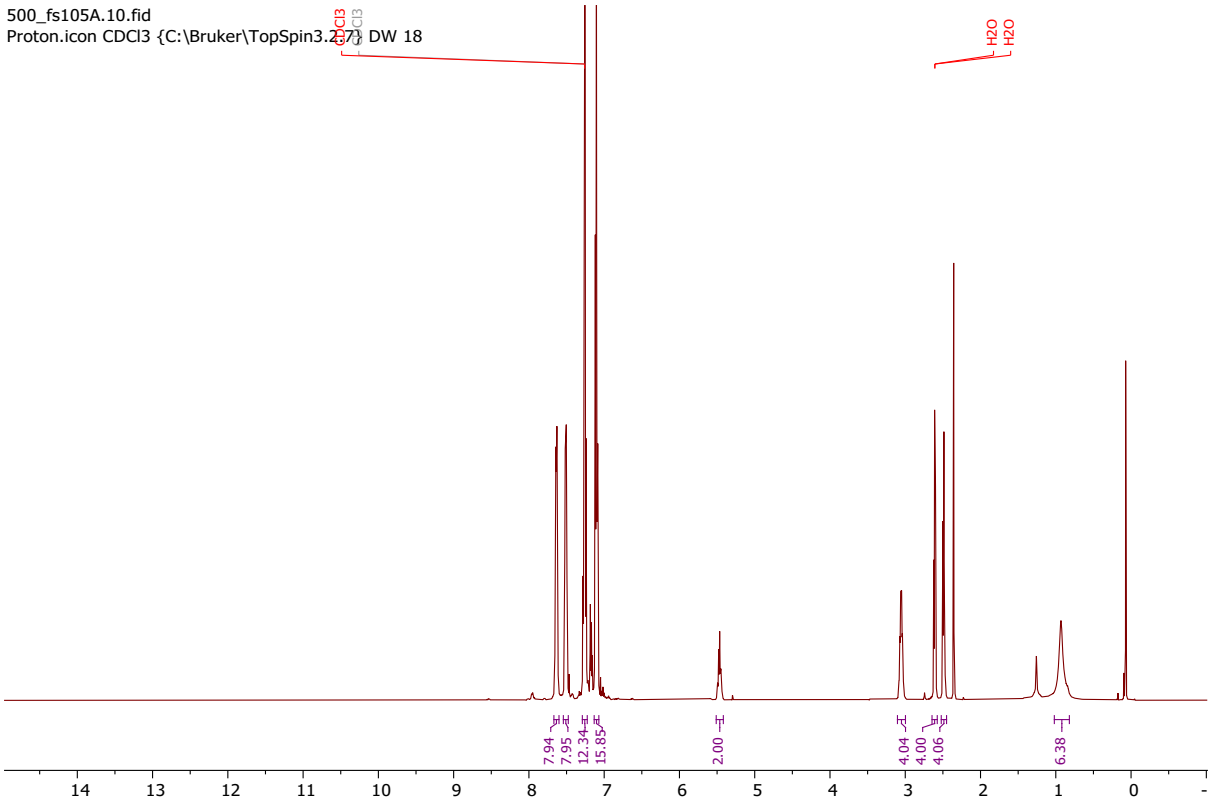


Figure S3: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **1**

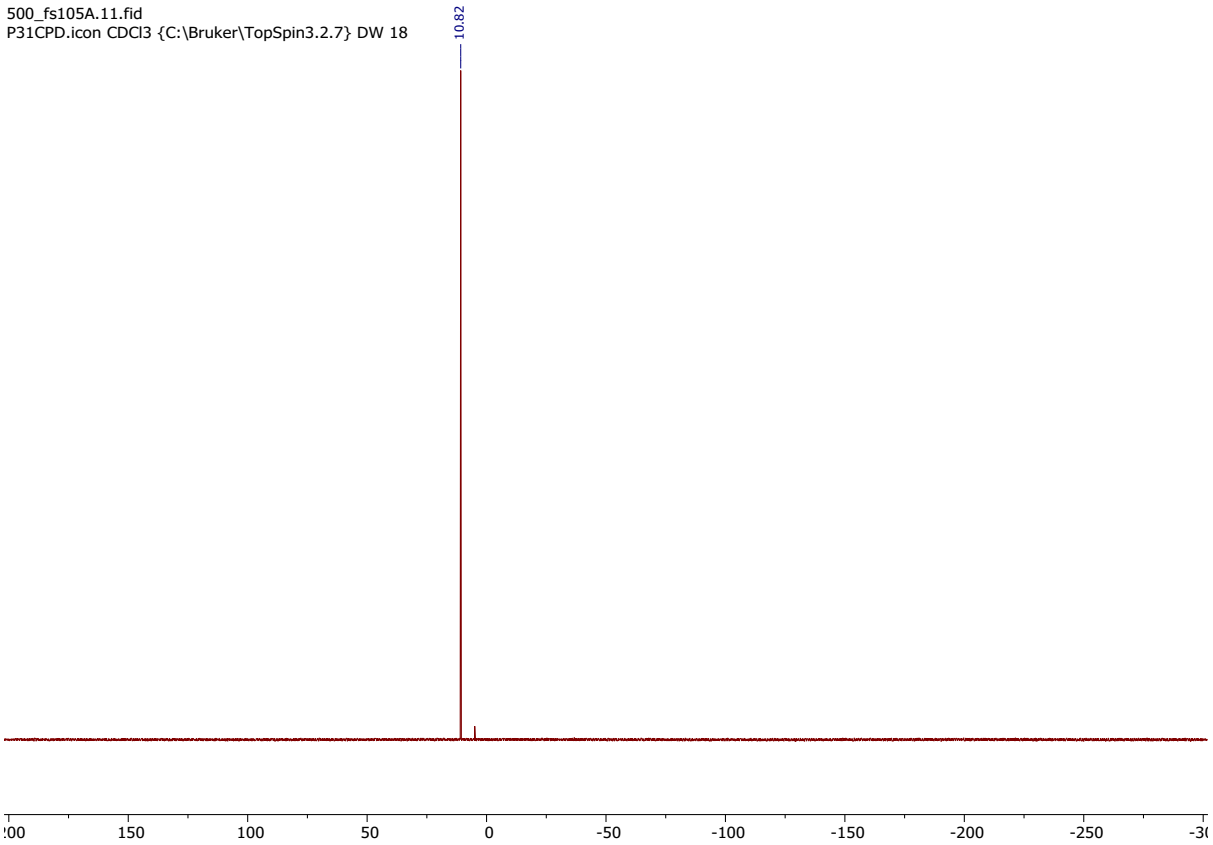


Figure S4: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum of **1**

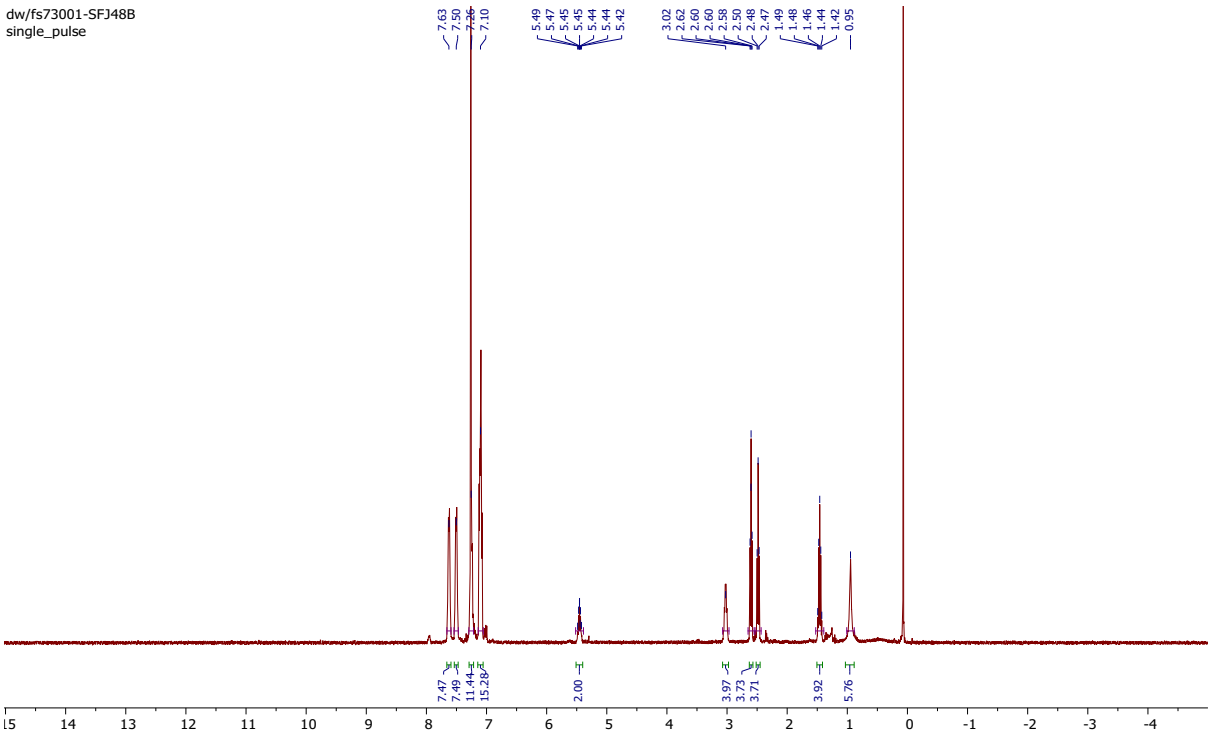


Figure S5: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2**

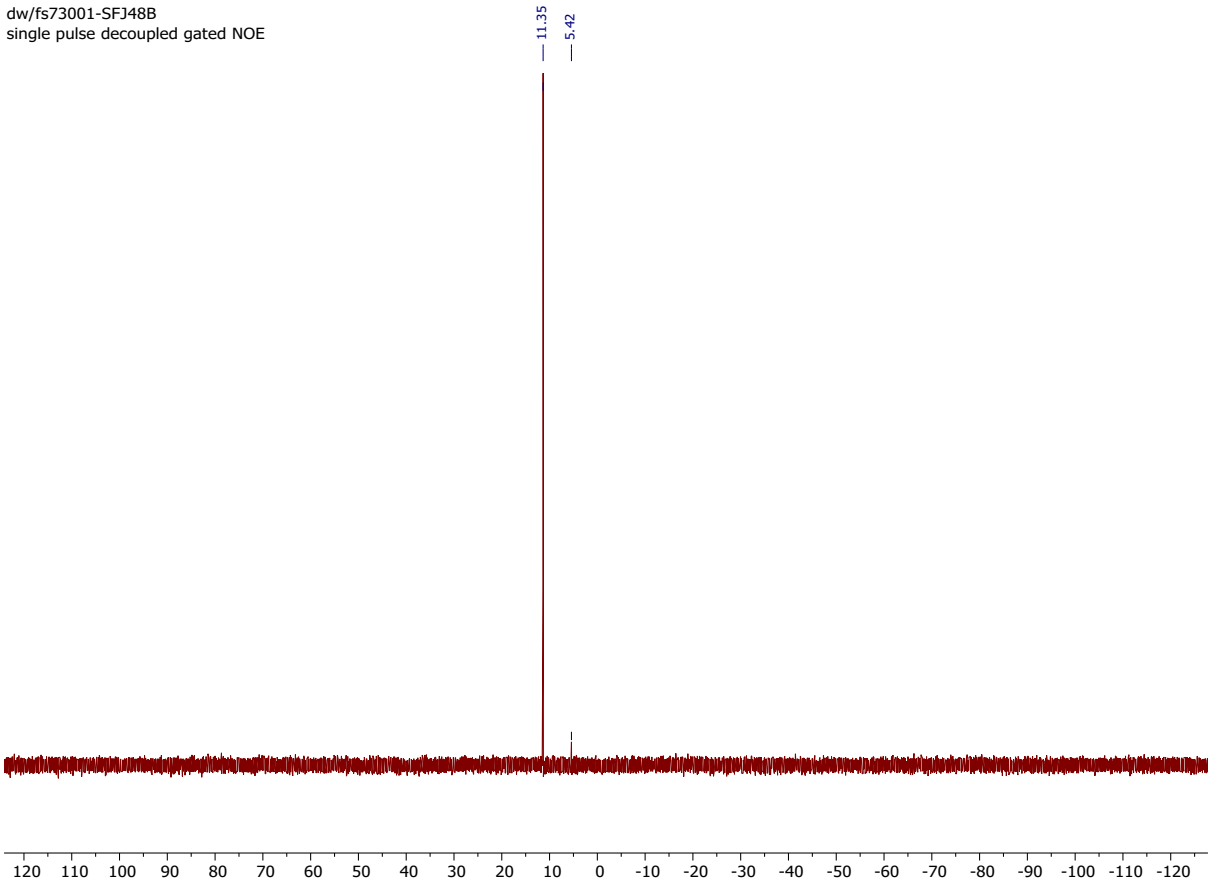


Figure S6: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **2**

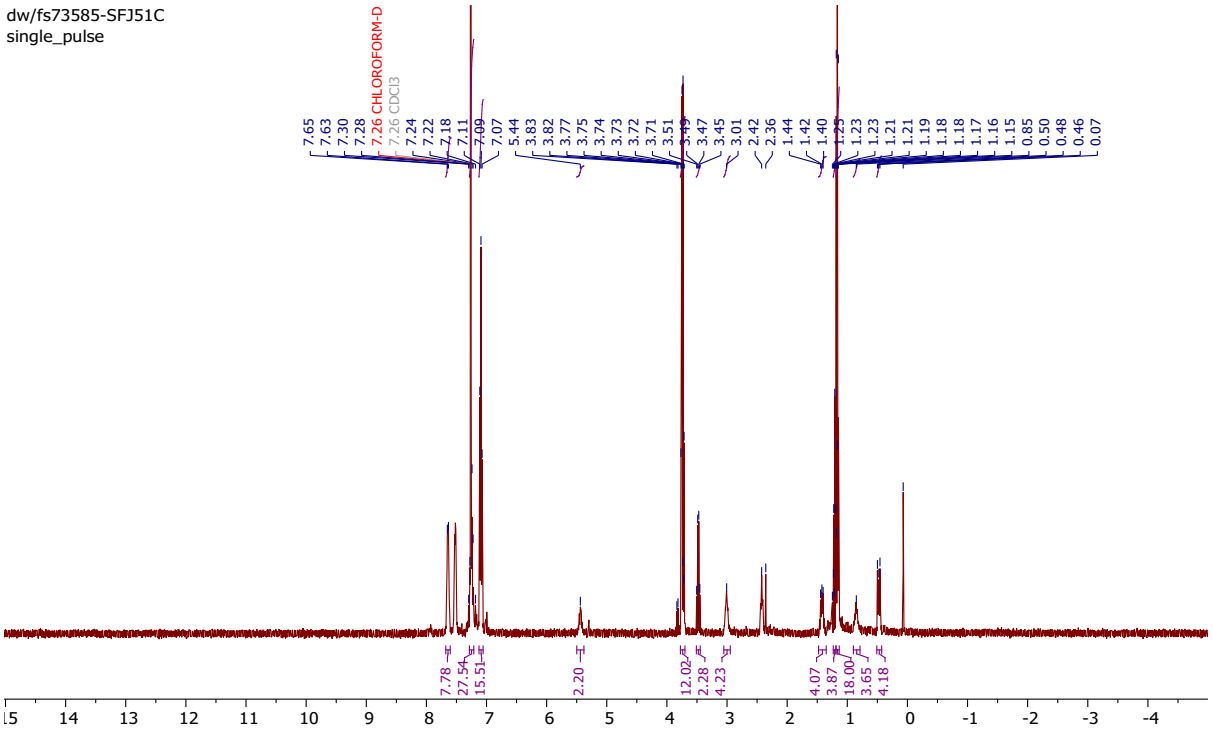


Figure S7: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3**

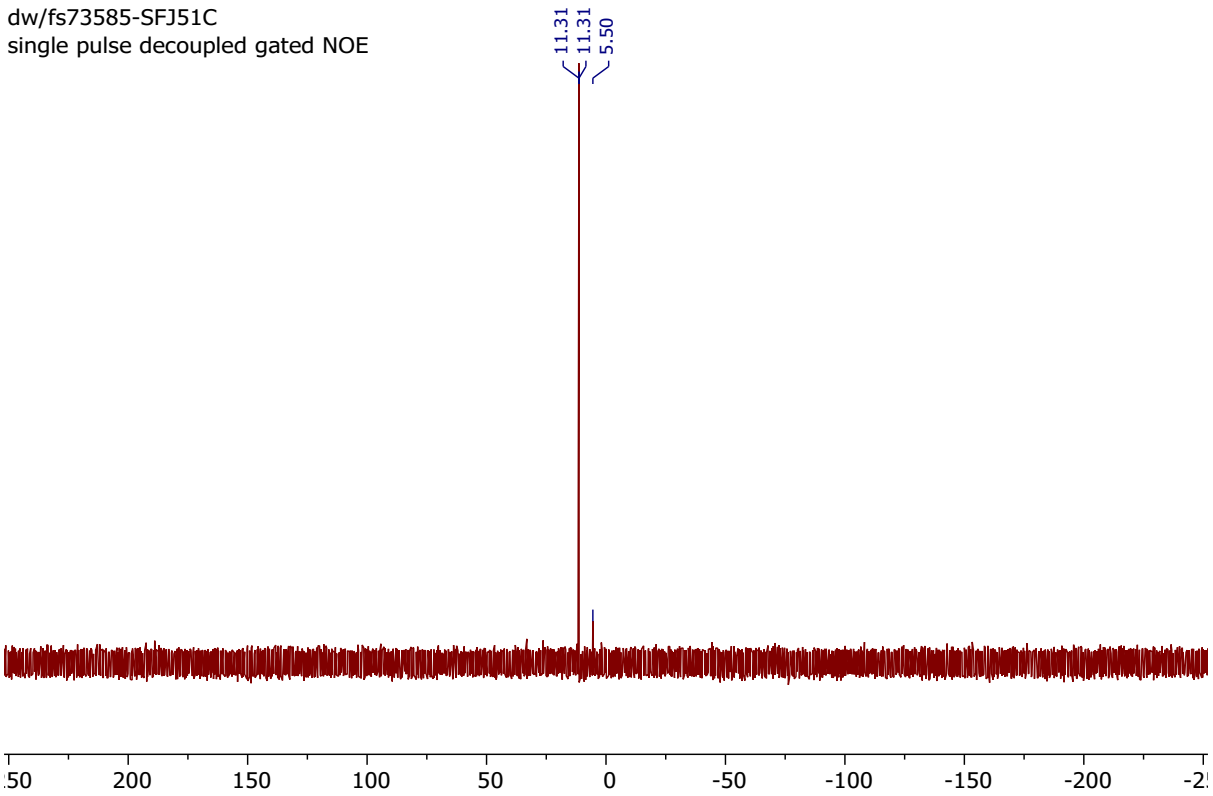


Figure S8: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **3**

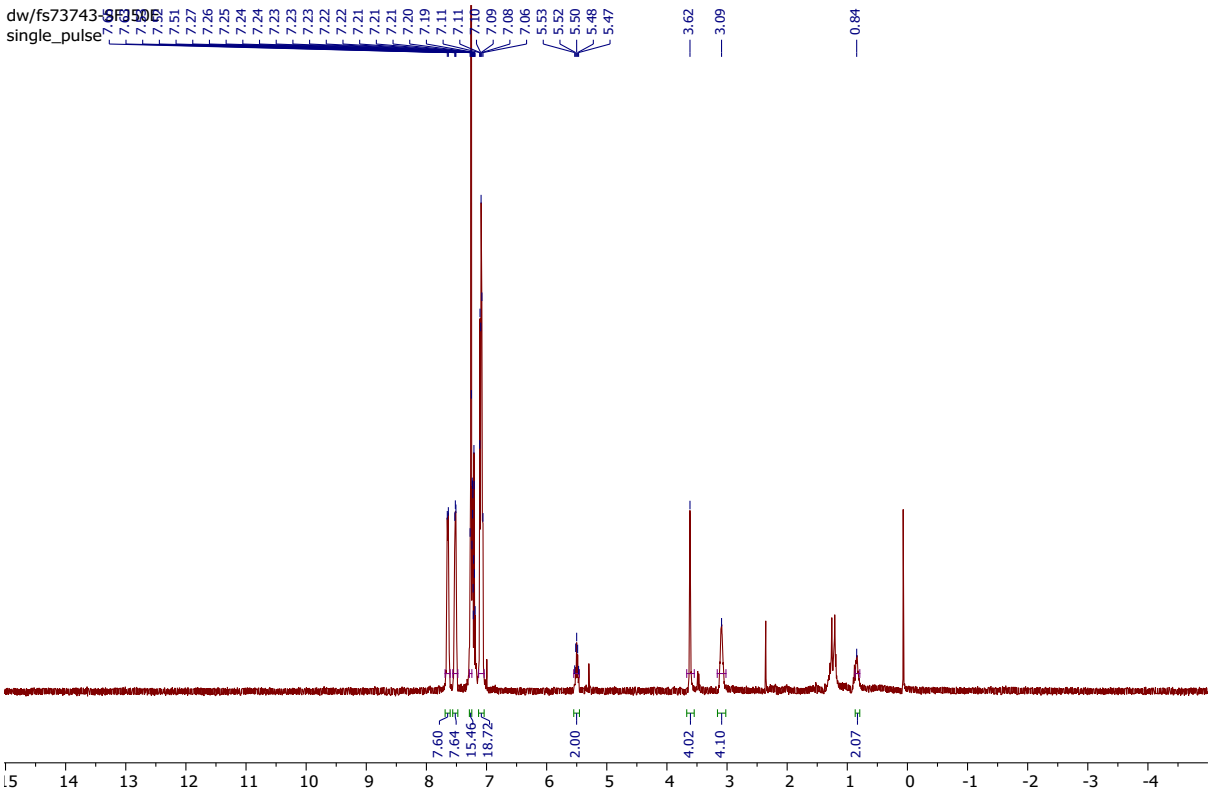


Figure S9: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**

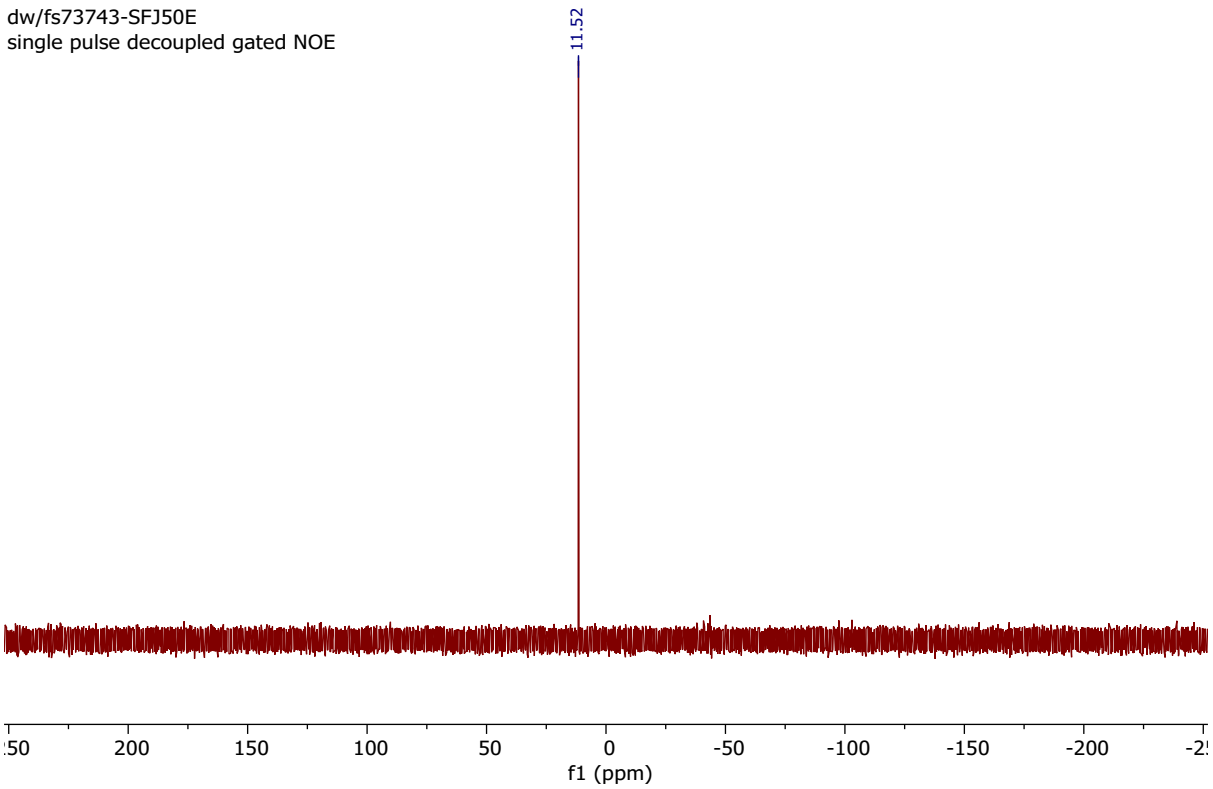


Figure S10: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **4**

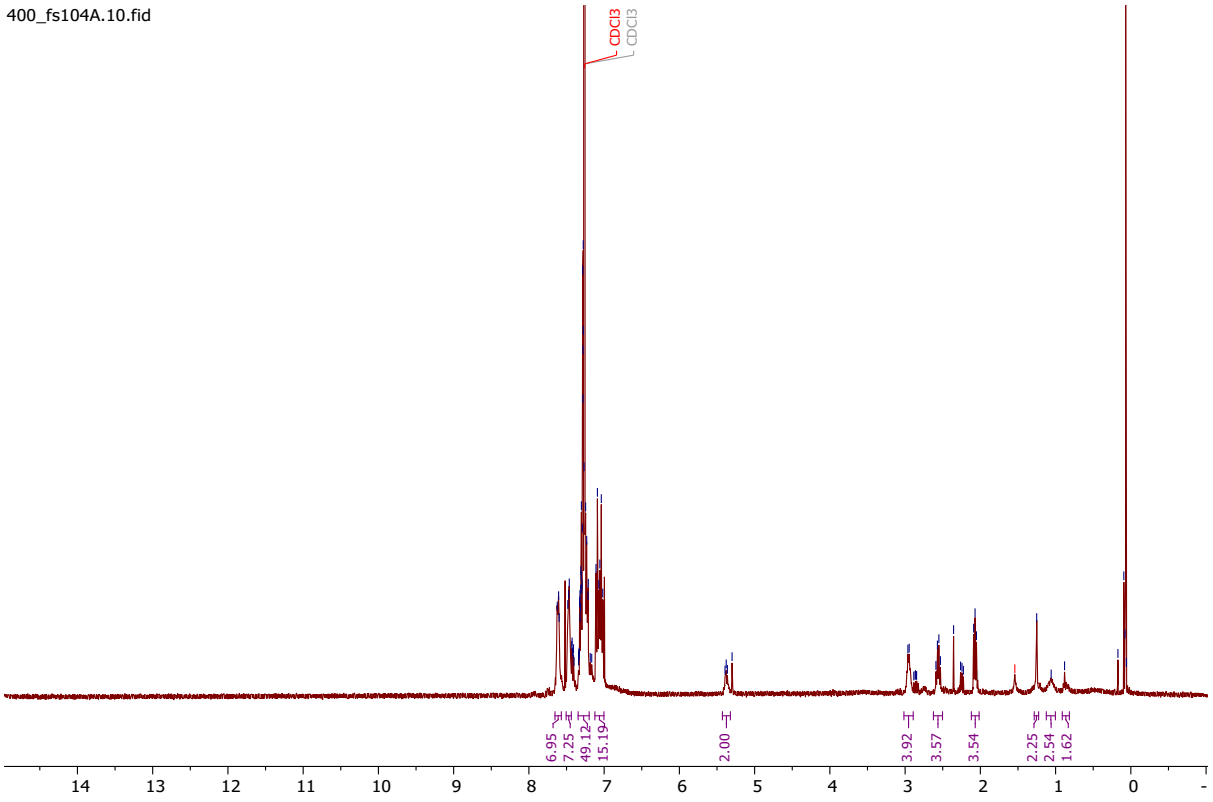


Figure S11: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**

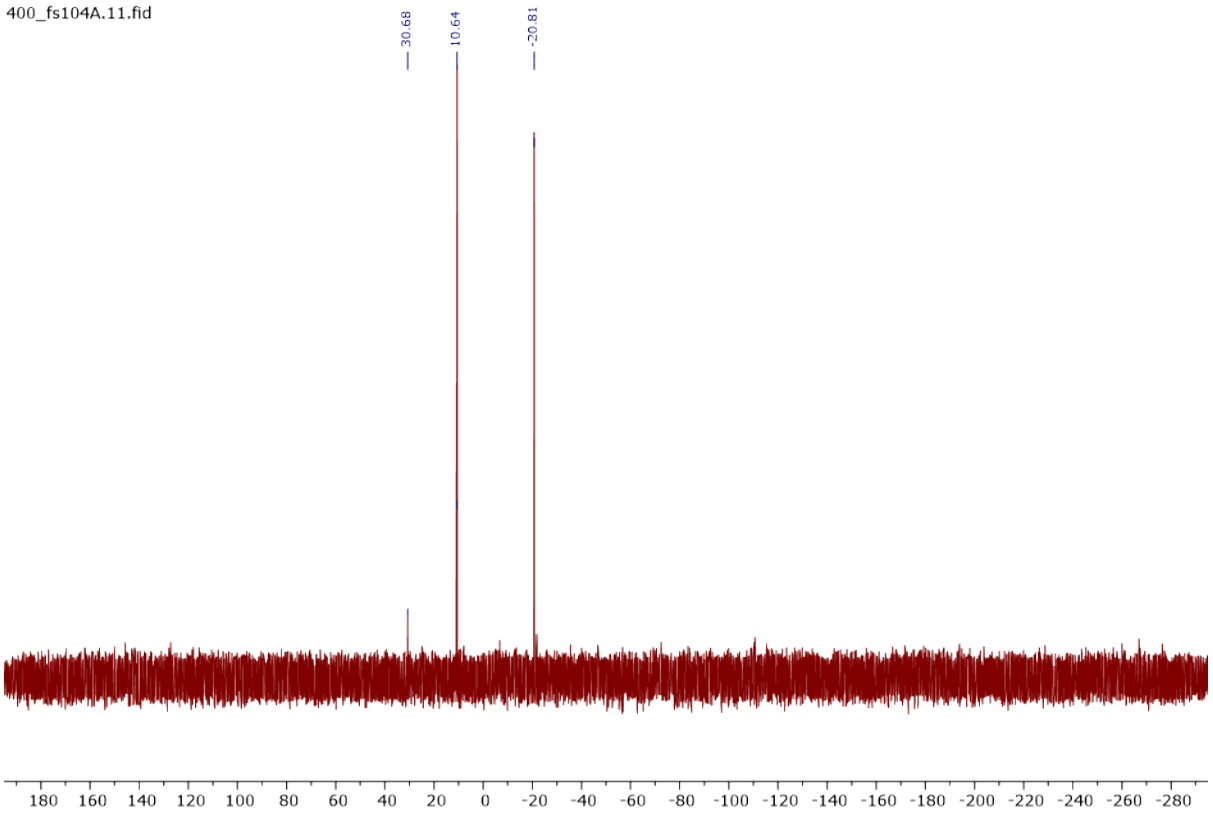


Figure S12: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **5**

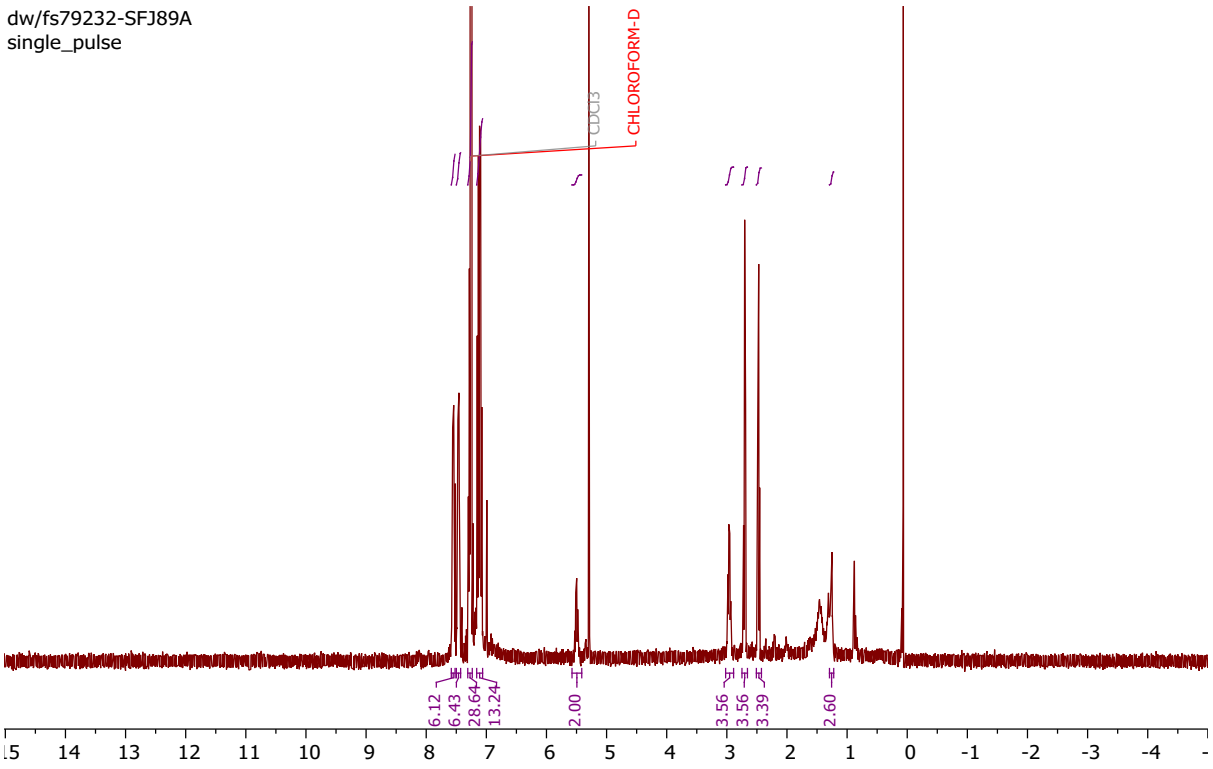


Figure S13: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **6**

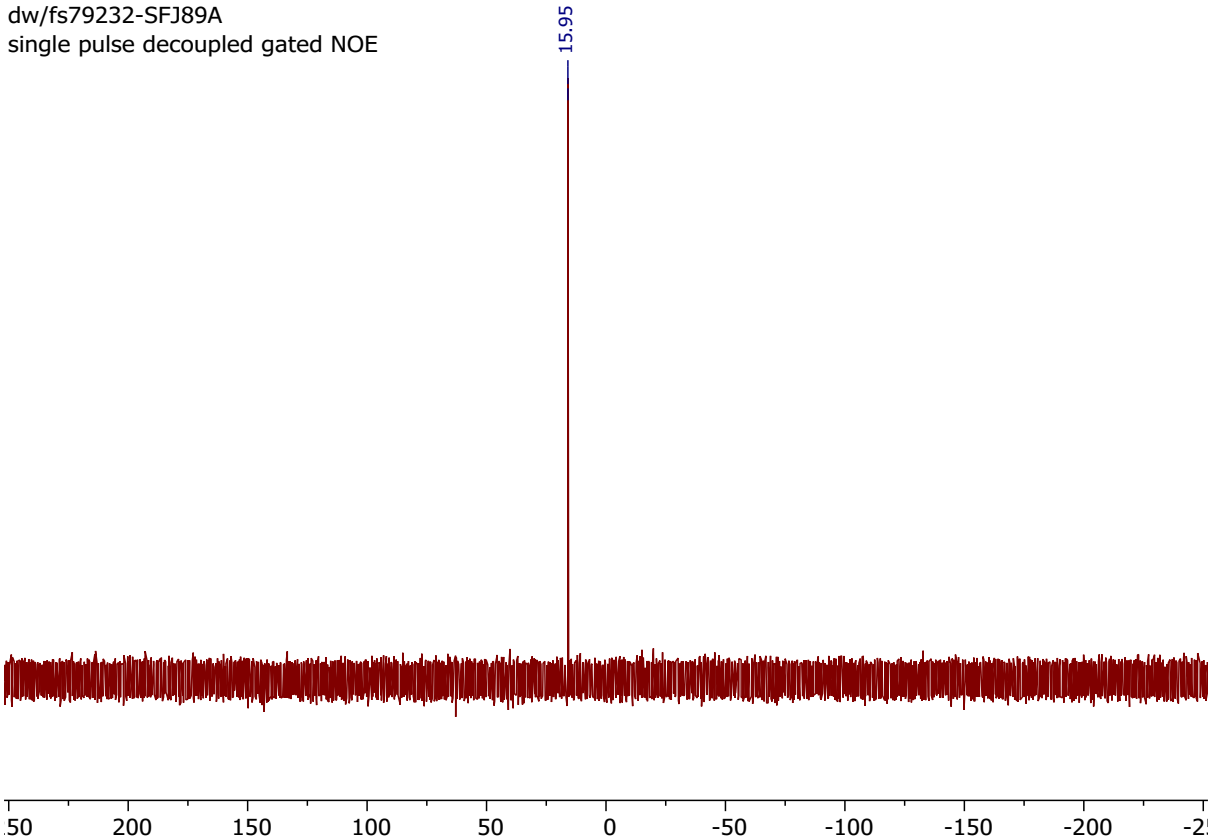


Figure S14: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **6**

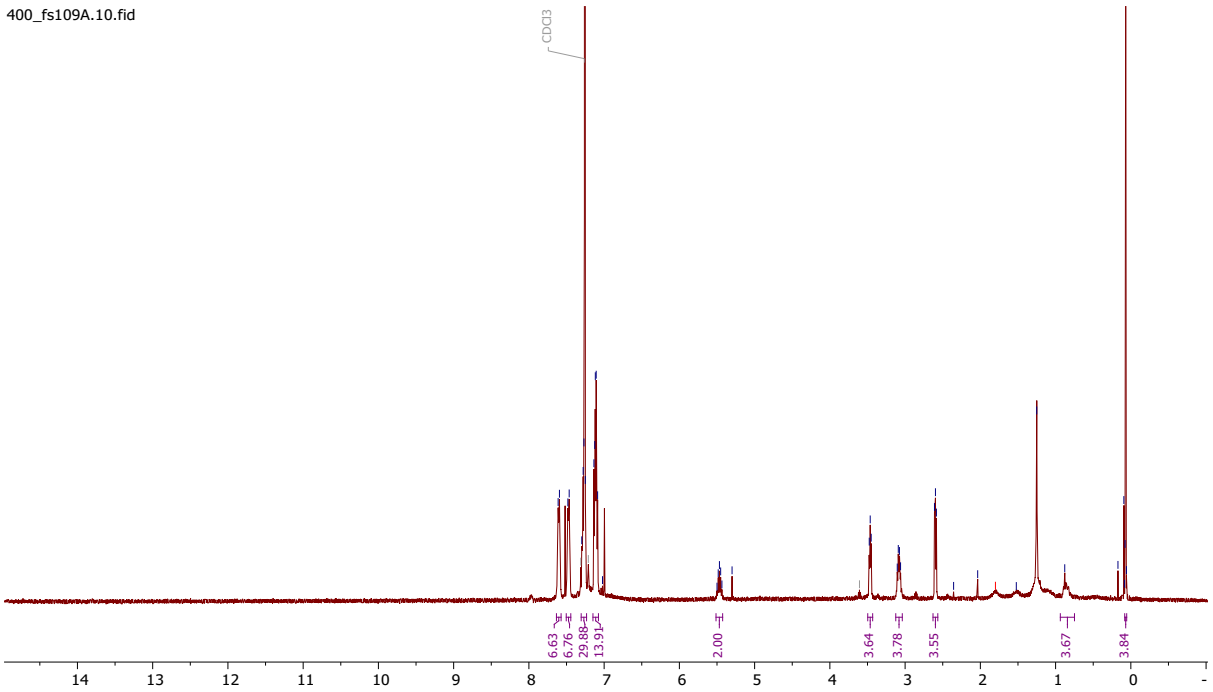


Figure S15: ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7**

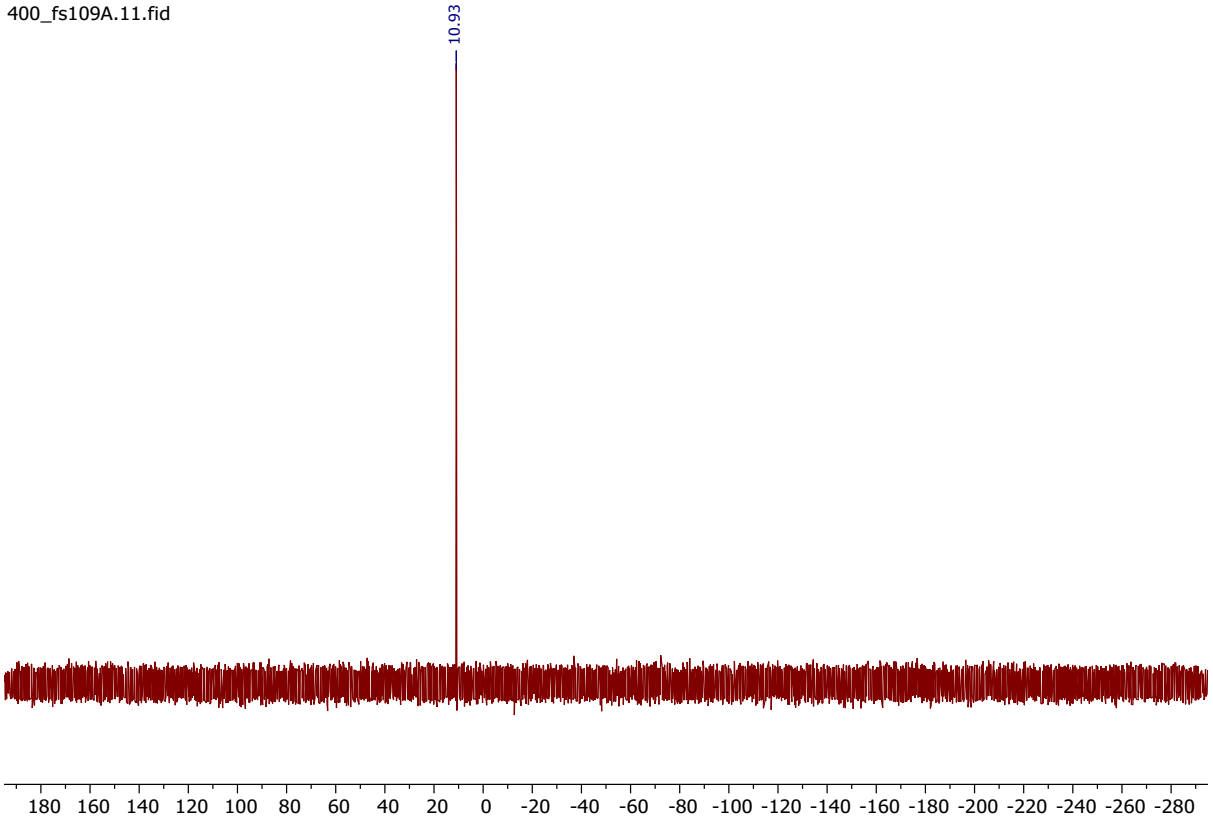


Figure S16: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **7**

5. Crystallography

X-ray diffraction experiments were carried out at 100(2) K on a Bruker APEX II diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å). Intensities were integrated in SAINT[6] and absorption corrections based on equivalent reflections were applied using SADABS.[7] Structures **3** was solved using Superflip[8, 9] while other structures were solved using ShelXT[10] all of the structures were refined by full matrix least squares against F^2 in ShelXL[11, 12] using Olex2.[13] All of the non-hydrogen atoms were refined anisotropically. While all of the hydrogen atoms were located geometrically and refined using a riding model, apart from the N-H protons in **3** and **4** which were located in the difference map. In the case of **3** the molecule displayed disorder in one of the ethyl chains and in **4** the solvent was a disordered mix of fluorobenzene and pentane. In both cases the occupancies of the disordered fragments was determined by refining them against free variable with the sum of the sites set to equal 1, restraints and constraints were applied to maintain sensible thermal and geometric parameters. Crystal structure and refinement data are given in Table S3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2334885-2334886. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Table S3: Crystallographic data and structure refinement for complexes **1**, **3**, **4** and **7**.

Crystal data	**1**	**3**	**4**	**7**
Identification code	fs1902c_1 (2)	SFJ51	SFJ50	dw1903d_1
Empirical formula	$C_{63}H_{66}Cl_2N_4P_4Ru$	$C_{70}H_{90}Cl_2N_2O_6P_4RuSi_2$	$C_{74.03}H_{73.39}Cl_2F_{0.84}N_2P_4Ru$	$C_{58.5}H_{63}Cl_7N_2O_2P_4Ru$
Formula weight	1175.04	1407.46	1302.90	1299.21
Temperature/K	200(2)	100	100(2)	200(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	$P2_1/c$	P-1	P-1
a/Å	10.4353(3)	13.1386(3)	10.3517(3)	10.6436(3)
b/Å	16.5511(6)	10.9694(3)	11.7890(3)	11.7714(3)
c/Å	17.3827(6)	23.2017(6)	14.7461(4)	24.4707(8)
α/°	85.285(3)	90	86.830(2)	82.484(3)
β/°	86.600(2)	92.5001(15)	82.892(2)	88.161(3)
γ/°	77.255(3)	90	66.874(2)	75.155(3)
Volume/Å^3	2915.77(17)	3340.71(15)	1642.19(8)	2938.14(15)
Z	2	2	1	2
ρ_{calc} (g/cm^3)	1.338	1.399	1.317	1.469
μ/mm^{-1}	0.513	0.500	0.464	0.738
F(000)	1220	1476.0	677.0	1334.0
Crystal size/mm^3	0.277 x 0.237 x 0.033	0.499 × 0.419 × 0.204	0.277 × 0.179 × 0.168	0.380 × 0.120 × 0.056
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	1.176 to 29.861	3.102 to 60.228	3.756 to 52.734	1.678 to 59.44
Index ranges	-13<=h<=12, -20<=k<=21, -22<=l<=20	-18 ≤ h ≤ 18, -15 ≤ k ≤ 15, -32 ≤ l ≤ 32	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-12 ≤ h ≤ 14, -15 ≤ k ≤ 16, -28 ≤ l ≤ 33
Reflections collected	25358	73176	27125	27259
Independent reflections	13851 [R_{int} = 0.0386, R_{sigma} = 0.0822]	9837 [R_{int} = 0.0382, R_{sigma} = 0.0223]	6706 [R_{int} = 0.0738, R_{sigma} = 0.0666]	13872 [R_{int} = 0.0291, R_{sigma} = 0.0544]
Data/restraints/parameters	13851/461/756	9837/2/406	6706/339/476	13872/21/686
Goodness-of-fit on F^2	1.049	1.036	1.003	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0663, wR_2 = 0.1590	R_1 = 0.0289, wR_2 = 0.0653	R_1 = 0.0452, wR_2 = 0.1082	R_1 = 0.0532, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.1177, wR_2 = 0.1980	R_1 = 0.0371, wR_2 = 0.0687	R_1 = 0.0668, wR_2 = 0.1190	R_1 = 0.0747, wR_2 = 0.1284
Largest diff. peak/hole/e Å^{-3}	1.131/-1.053	0.85/-0.43	0.79/-0.83	1.17/-1.11

Table S4. Bond lengths (Å) and angles (°) for complexes **1**, **3**, **4** and **7**.

Complex	**Bond lengths** (Å)		**Bond angles** (°)	
1	Ru(1)-Cl(1)	2.4266(12)	Cl(1)-Ru(1)-Cl(2)	176.35(4)
	Ru(1)-Cl(2)	2.4263(11)	P(1)-Ru(1)-P(2)	71.81(4)
	Ru(1)-P(1)	2.3351(12)	P(3)-Ru(1)-P(4)	72.08(4)
	Ru(1)-P(2)	2.3722(12)	P(2)-Ru(1)-P(4)	109.04(4)
	Ru(1)-P(3)	2.3296(12)	P(3)-Ru(1)-P(1)	107.08(4)
	Ru(1)-P(4)	2.3887(12)	P(1)-C(25)-P(2)	95.5(2)
	P(1)-C(25)	1.861(5)	P(3)-C(53)-P(4)	96.0(2)
	P(2)-C(25)	1.869(5)		
3	Ru(1)-Cl(1) = Ru(1)-Cl(1)'	2.4272(3)	Cl(1)-Ru(1)-Cl(1)'	180.000(14)
	Ru(1)-P(1) = Ru(1)-P(1)'	2.3409(3)	P(1)-Ru(1)-P(2) = P(1)'-Ru(1)-P(2)'	71.745(12)
	Ru(1)-P(2) = Ru(1)-P(2)'	2.3604(3)	P(1)'-Ru(1)-P(2) = P(1)-Ru(1)-P(2)'	108.256(12)
	P(1)-C(1)	1.8642(14)	P(1)-C(1)-P(2) = P(1)'-C(1)'-P(2)'	94.90(6)
	P(2)-C(1)	1.8752(13)		
4	Ru(1)-Cl(1) = Ru(1)-Cl(1)'	2.4271(8)	Cl(1)-Ru(1)-Cl(1)'	180.0
	Ru(1)-P(1) = Ru(1)-P(1)'	2.3731(8)	P(1)-Ru(1)-P(2) = P(1)'-Ru(1)-P(2)'	71.06(3)
	Ru(1)-P(2) = Ru(1)-P(2)'	2.3350(8)	P(1)'-Ru(1)-P(2) = P(1)-Ru(1)-P(2)'	108.94(3)
	P(1)-C(13)	1.866(3)	P(1)-C(13)-P(2) = P(1)'-C(13)'-P(2)'	94.44(15)
	P(2)-C(13)	1.862(3)		
7	Ru(1)-Cl(1)	2.4232(8)	Cl(1)-Ru(1)-Cl(2)	176.51(3)
	Ru(1)-Cl(2)	2.4290(8)	P(1)-Ru(1)-P(2)	72.02(3)
	Ru(1)-P(1)	2.3504(9)	P(3)-Ru(1)-P(4)	71.48(3)
	Ru(1)-P(2)	2.3654(9)	P(2)-Ru(1)-P(4)	108.92(3)
	Ru(1)-P(3)	2.3445(9)	P(3)-Ru(1)-P(1)	107.70(3)
	Ru(1)-P(4)	2.3717(9)	P(1)-C(25)-P(2)	95.25(15)
	P(1)-C(25)	1.880(3)	P(3)-C(53)-P(4)	94.74(15)
	P(2)-C(25)	1.873(3)		

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