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Electronic Supporting Information for:

A Ruthenium *cis*-Dihydride with 2-Phosphinophosphinine Ligands Catalyses the Acceptorless Dehydrogenation of Benzyl Alcohol

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Contents

Experimental

General Considerations. All reactions and product isolations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNIlab Plus glovebox, unless otherwise stated. Xylene was dried over 4 Å molecular sieves and degassed. All anhydrous solvents were degassed before use and stored over activated molecular sieves. Non-dry solvents were used as received from Fisher Scientific. NMR spectra were recorded at 25°C, on Bruker AVIII400 and AVHD400, spectrometers using the internal standard, 1,3,5-trimethoxybenzene ~30mg, as an internal reference for integrations. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4 as 0ppm. Mass spectrometry analysis for complex **2**, *cis*-$[RuH_2(PP')_2]$, was performed at the UK National Mass Spectrometry Facility at Swansea University, using an Atmospheric Solids Analysis Probe (ASAP) interfaced to a Water Xevo G2-S instrument. Molecular ion peaks for esters were obtained from an ASAP Shimadzu LCMS 2020 instrument. X-ray diffraction experiments were performed on single crystals of **2** placed under a cold stream (100 K) of a Bruker X8 APEXII four-circle diffractometer (Heriot-Watt University). Structures were solved using direct methods (SHELXT) and refined using SHELXL.

1. Synthesis of $[Ru(H)_2(dppm)_2]$

cis-$[Ru(Cl)_2(dppm)_2]$[1] and *cis*-$[Ru(Cl)_2(PP')_2]$[2] were prepared according to literature procedures:

$[Ru(Cl)_2(dmso)_4]$. $RuCl_3.xH_2O$ (2 g) and degassed ethanol (50 mL) were added to a Schlenk along with DMSO and the reaction was heated under reflux for 3 hours. The ethanol was then removed, and the reaction mixture was refluxed at 140°C for 2 hours forming a caramel colour. On addition of acetone (60 mL), a yellow micro-crystalline solid formed. The solid was filtered and washed with 3 x 5 mL acetone.

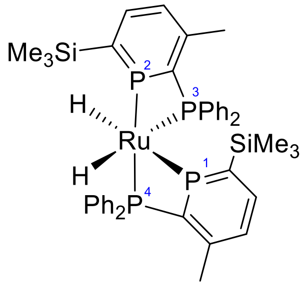
Ruthenium dichloride bis(diphenylphosphino)methane $[Ru(Cl)_2(dppm)_2]$. Ruthenium trichloride hydrate (0.316g, 1.52 mmol), bis(diphenylphosphino)methane (1.22g, 3.17 mmol), triphenyl phosphine (1.12g, 4.27 mmol) and pentanol (55 mL) were added to a round bottom flask. This mixture was heated under reflux (138°C) for 3 hours. The yellow precipitate was filtered and washed with amyl alcohol (5 mL), methanol/ether (3 x 5 mL) and ether (3 x 5 mL), then dried on Buchner funnel. A yellow powder was formed (0.6049g, 42 %).[3]

^1H NMR (400 MHz, 25°C, $CDCl_3$): δ(ppm) 8.26 (s), 7.97 (s), 7.4 (s), 7.29 (septet, J = 2.16), 7.02 (s), 6.9 (s), 6.8 (s), 6.6 (s), 4.9 (s), 4.7 (s), 1.58 (septet, J=2.18) **$^{31}P\{^1H\}$ NMR (162 MHz, 25°C, $CDCl_3$):** δ(ppm) -0.86 (t), -26.9 (t)

Ruthenium dihydride bis(diphenylphosphino)methane $[RuH_2(dppm)_2]$. A 100 mL Schlenk flask was charged with NaOH (0.3526g, 8mmol), $[RuCl_2(dppm)_2]$ (0.3925 g, 0.42 mmol), and degassed methanol (30 mL) (ethanol or iso-propanol worked similarly) was added via cannula. This solution was heated under reflux overnight. The solution was then cooled to room temperature, and degassed water was added to dissolve the excess NaOH. The resulting suspension was then transferred via a cannula onto a medium porosity frit, and the yellow solid obtained was washed with degassed MeOH (20 mL) and finally dried in vacuo to yield a pale yellow solid (0.275 g, 60 – 80%). [4]

^1H NMR (400 MHz, 25°C, $CDCl_3$): δ(ppm) -5 (quintet) and -7.5 (doublet of quartets) **$^{31}P\{^1H\}$ NMR (162 MHz, 25°C, $CDCl_3$):** δ(ppm) 14.7 (t), 10 (s), 1.3 (t).

2. Synthesis and crystal structure of **2**



To a Schlenk flask containing **1** (*cis*-[Ru(Cl)$_2$(PP')$_2$], 100 mg, 0.11 mmol, 1 equiv.) and toluene (2 cm^3), Na[HBEt$_3$] in THF (0.22 cm^3, 1 M, 2 equiv.) was added. On addition of Na[HBEt$_3$] the solution turned red instantly. The reaction was stirred for 1 h and subsequently filtered under N$_2$ to remove NaCl. The solvent was reduced in volume to *ca.* 1 cm^3 under a flow of N$_2$ (decomposition occurred under vacuum). On addition of petroleum ether (5 cm^3), a bright orange precipitate formed, which was then isolated by cannula filtration. Both the precipitate and filtrate were dried under a flow of N$_2$ and shown by ^{1}H/^{31}P NMR spectroscopy to be **2** (25 mg, 0.03 mmol, 25 %).

^{1}H-NMR (400 MHz, C$_6$D$_6$, 298 K): δ = 8.26 (m, 2H, C$H_{\text{arom.}}$), 7.78 (m, 2H, C$H_{\text{arom.}}$), 7.57 (ddd, 1H, C$H_{\text{arom.}}$), 7.48 (m, 3H, C$H_{\text{arom.}}$), 7.16 (m overlapping with C$_6$D$_5$H), 7.05-6.89 (m, 7H, C$H_{\text{arom.}}$), 6.87 (m, 3H, C$H_{\text{arom.}}$), 6.77 (m, 2H, C$H_{\text{arom.}}$), 6.37 (dd, 2H, CH$_{arom}$), 1.64 (s, 3H, CH$_3$), 1.61 (s, 3H, CH$_3$), 0.62 (s, 9H, SiMe$_3$), 0.27 (s, 9H, SiMe$_3$), -6.55 (m, 1H, H$_{\text{hydride}}$), -7.04 (m, 1H, H$_{\text{hydride}}$) ppm; **^{31}P{^{1}H}-NMR (162 MHz, C$_6$D$_6$, 298 K):** δ = 253.3 (ddd, $^2J_{\text{P2-P4}}$ = 291 Hz, *P$_2$*), 250.4 (m, *P$_1$*), 31.6 (ddd, $^2J_{\text{P4-P2}}$ = 291 Hz, *P$_4$*), 15.7 (m, *P$_3$*) ppm; **HRMS** (APCI/QTof) m/z: calcd for [C$_{42}$H$_{49}$P$_4$^{96}RuSi$_2$]$^+$ 829.1400 [M-H]$^+$, found 829.1404; calcd for [C$_{30}$H$_{40}$P$_3$RuSi$_2$]$^+$ 651.0919 [M – HPPh$_2$]$^+$, found 651.0930.

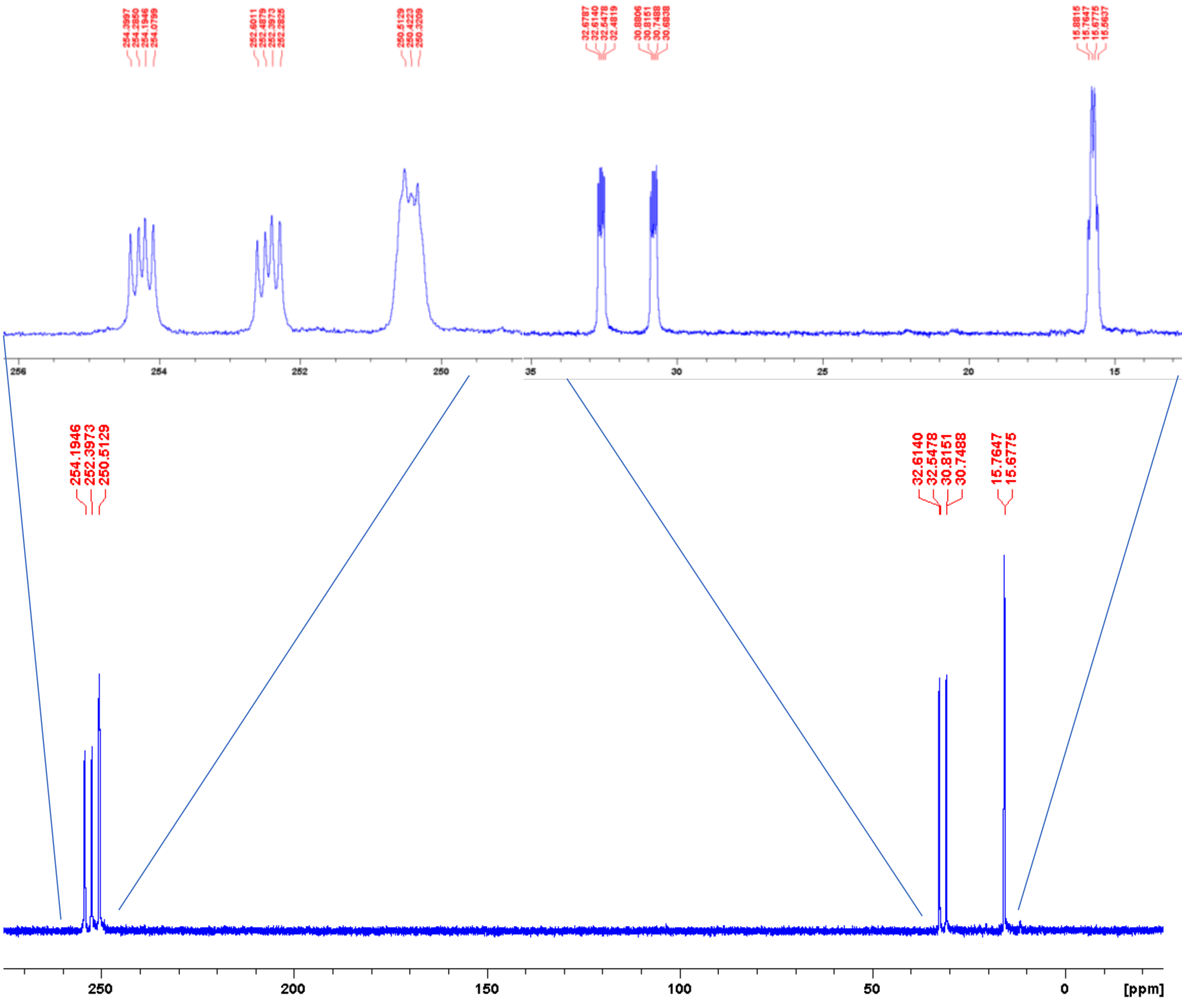


Figure S1. $^{31}P\{^1H\}$ NMR spectrum of *cis*-[RuH$_2$(PP')$_2$] (**2**) dried under N$_2$ (298K, C$_6$D$_6$).

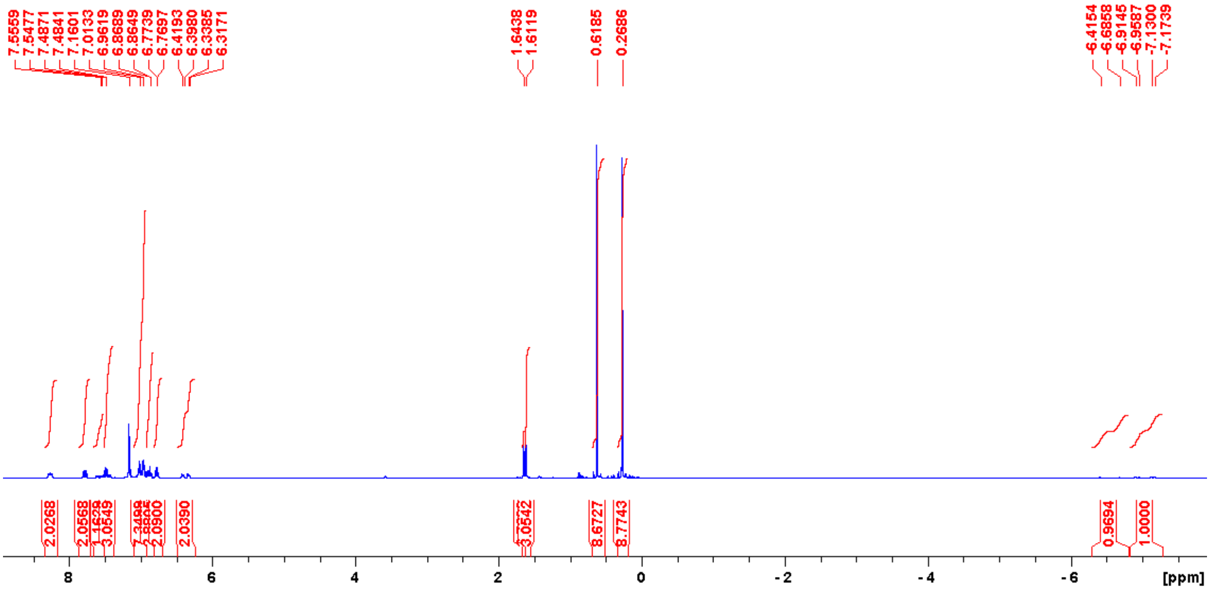


Figure S2. ^1H NMR spectrum of *cis*-[RuH$_2$(PP')$_2$] (**2**) dried under N$_2$ (400 MHz, 298 K, C$_6$D$_6$).

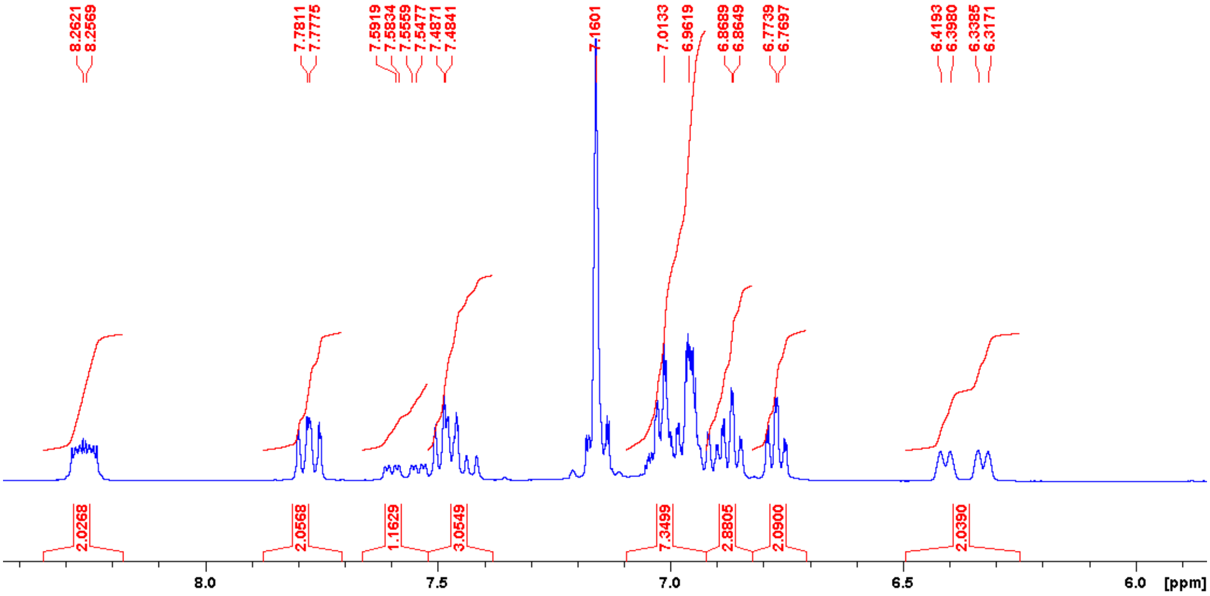


Figure S3. Expansion of ^{1}H aromatic region for **2**.

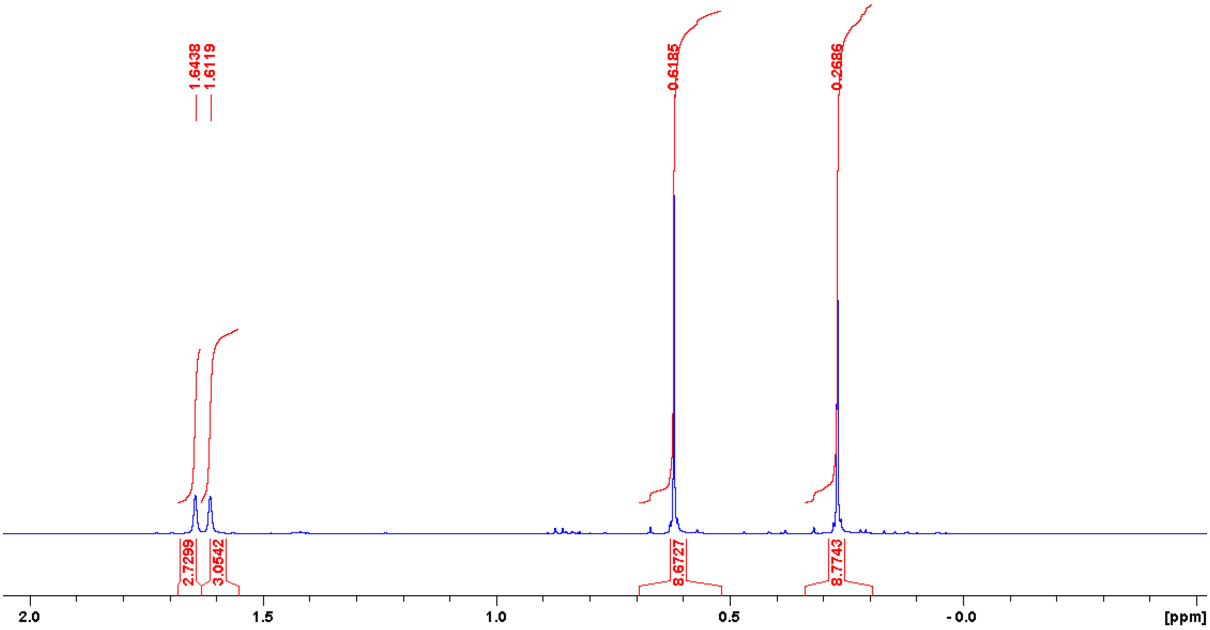


Figure S4. Expansion of ^{1}H alkyl region for **2**.

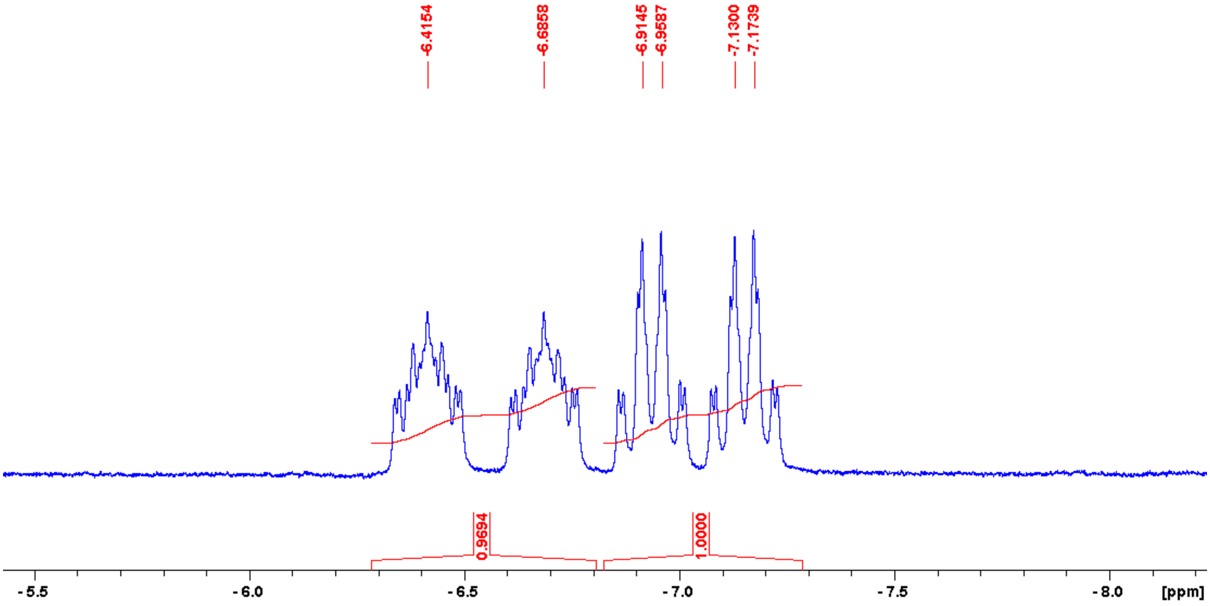


Figure S5. Expansion of ^{1}H hydride region for **2**.

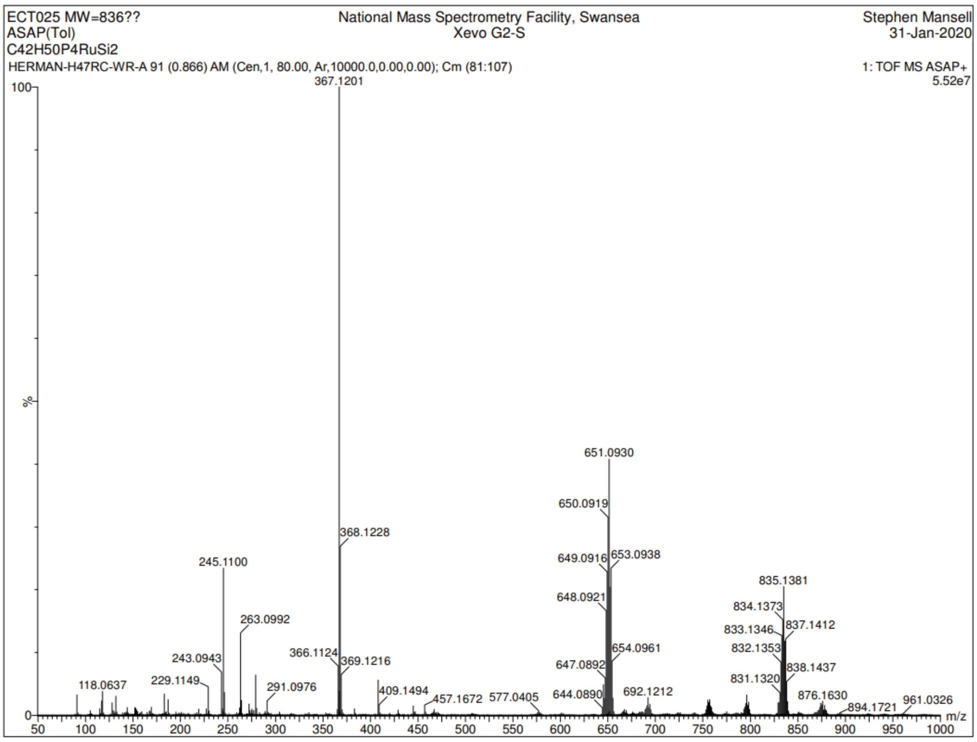


Figure S6. Mass spectrometry (m/z) of **2** dried under nitrogen.

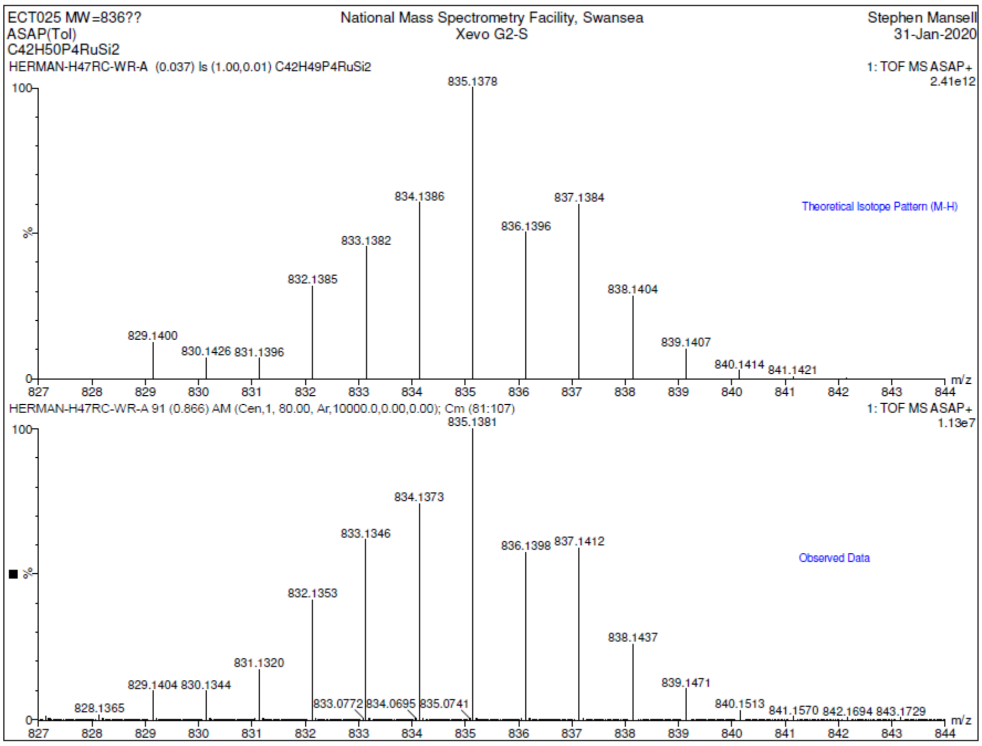


Figure S7. Accurate mass determination (m/z) of **2** dried under nitrogen.

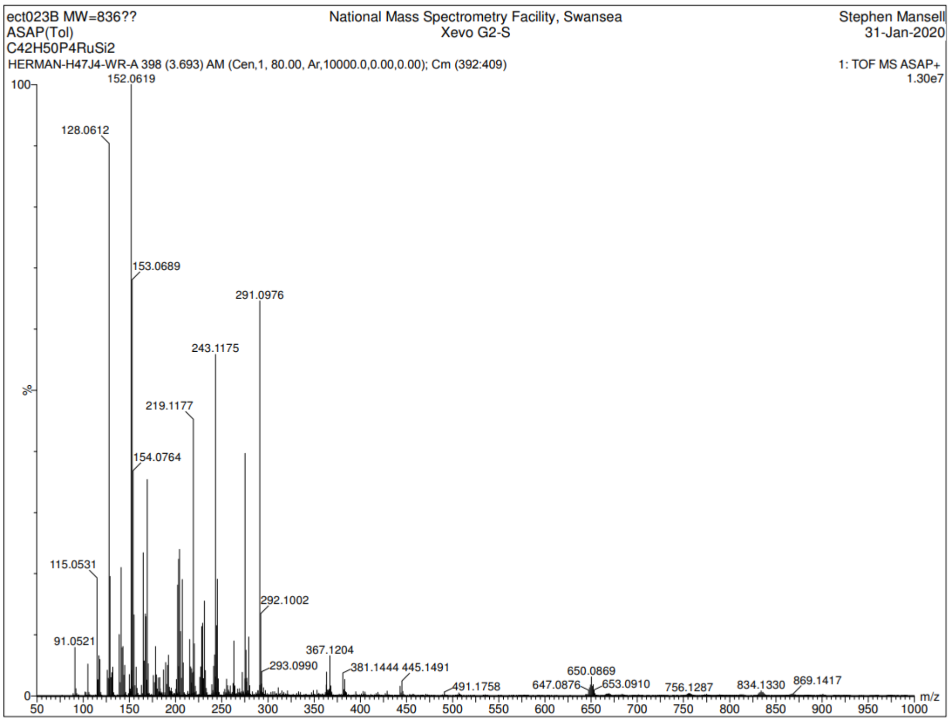
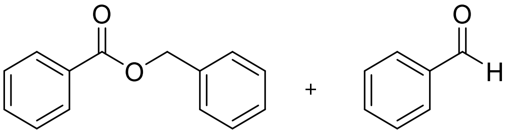


Figure S8. Mass spectrum (m/z) of **2** dried under vacuum

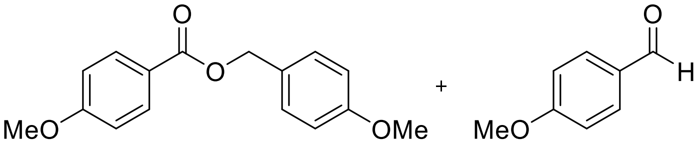
3. Benzyl alcohol analysis

General Procedure for Acceptorless Dehydrogenation Reactions: In a dry nitrogen-filled glovebox, a Schlenk flask along with a PTFE-coated magnetic stirrer bar, was charged with [Ru] complex **1** or **3** (1 mol% or 2 mol%) and ~ 30 mg of the internal standard 1,3,5-trimethoxy benzene. The flask was removed from the glove box and attached to the nitrogen Schlenk line. The solid was dissolved in xylene (~ 7 mL) and then for **1** Na[HBEt$_3$] was added (2 equivalents). Finally, benzyl alcohol (1.5 mmol) was added. The flask was equipped with a waterless condenser. The solution was heated in an oil bath to reflux under nitrogen while stirring at 140°C. Xylene was removed under vacuum and a ^{1}H NMR spectrum could be taken in air of the concentrated sample. Yields calculated using the internal standard. ^{1}H and ^{13}C resonances match the literature.

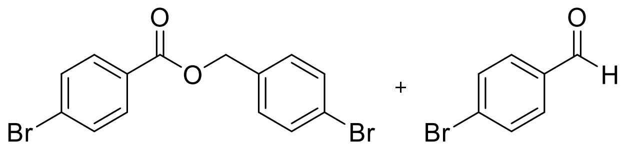
Entry	Cat.	Substrate R=	Temp (°C)	Na[HBEt$_3$] (mol%)	Time (h)	Yield (%) ester	Yield (%) aldehyde
0	none	H	140	4	50	0	0.5



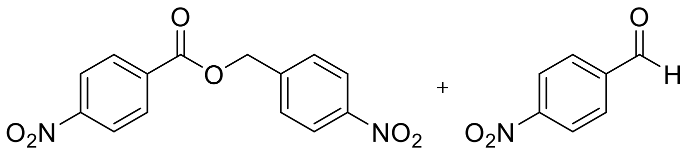
Benzyl benzoate.[5] **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.0 – 7.96 (m, 2H), 7.46 – 7.40 (m, 1H), 7.36-7.25 (m, 7H), 5.26 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 166.5, 161.6, 136.1, 133.0, 129.7, 128.5, 127.6, 127.0, 128.1, 66.7. **Shimadzu LCMS 2020, ASAP with APCI ionisation** m/z: 212 (M+H, 213). **IR:** 1718 cm^{-1}, 1271 cm^{-1}.



4-Methoxybenzyl 4-methoxybenzoate.[5] **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.06 -7.98 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 6.94 – 6.89 (m, 4H), 5.27 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 164, 162, 159, 130, 130.0, 128.4, 122.9, 114.0, 113.9, 65.2, 55.6, 55.5. **Shimadzu LCMS 2020, ASAP with APCI ionisation** m/z: 272.



4-Bromobenzyl 4-bromobenzoate.[6] **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.92 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.316 – 7.310 (m, 2H), 5.43 (s, CH_2); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.5, 134.7, 131.78, 131.75, 131.2, 129.9, 128.7, 128.3, 122.4, 66.1.



4-Nitrobenzyl 4-nitrobenzoate.[6] **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.3 (d, J = 8.8, 2H), 8.27 - 8.20 (m, 4H), 7.86 (d, J = 8.4 Hz, 2H), 5.54 (s, CH_2); **^{13}C NMR (400 MHz, $CDCl_3$)**: δ 164.5, 150.9, 147.8, 143.8, 135.2, 131.4, 129.3, 124.4, 124.2, 66.3.

i) **3** - RuH$_2$(dppm)$_2$ – Benzyl benzoate

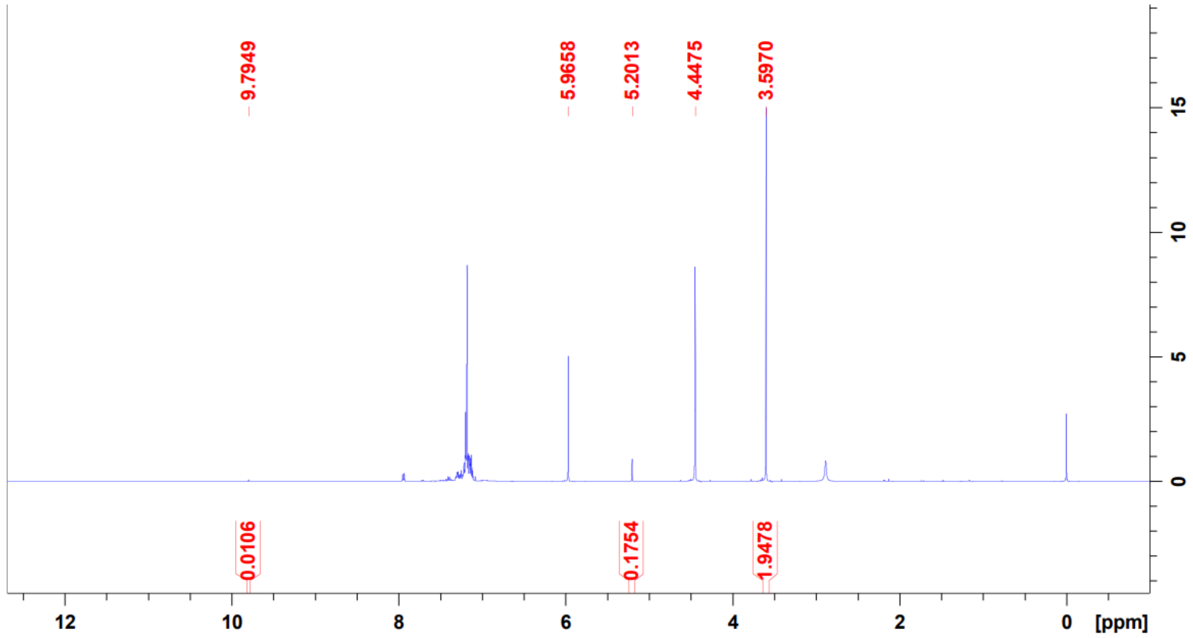


Figure S9: 1 mol%, 45 hours. Benzaldehyde: δ 9.8 ppm, 1,3,5-trimethoxybenzene: (CH) δ 6.0 ppm (CH$_3$) δ 4.4, benzyl benzoate: (CH$_2$) δ 5.2, benzyl alcohol: (CH$_2$) δ 4.4.

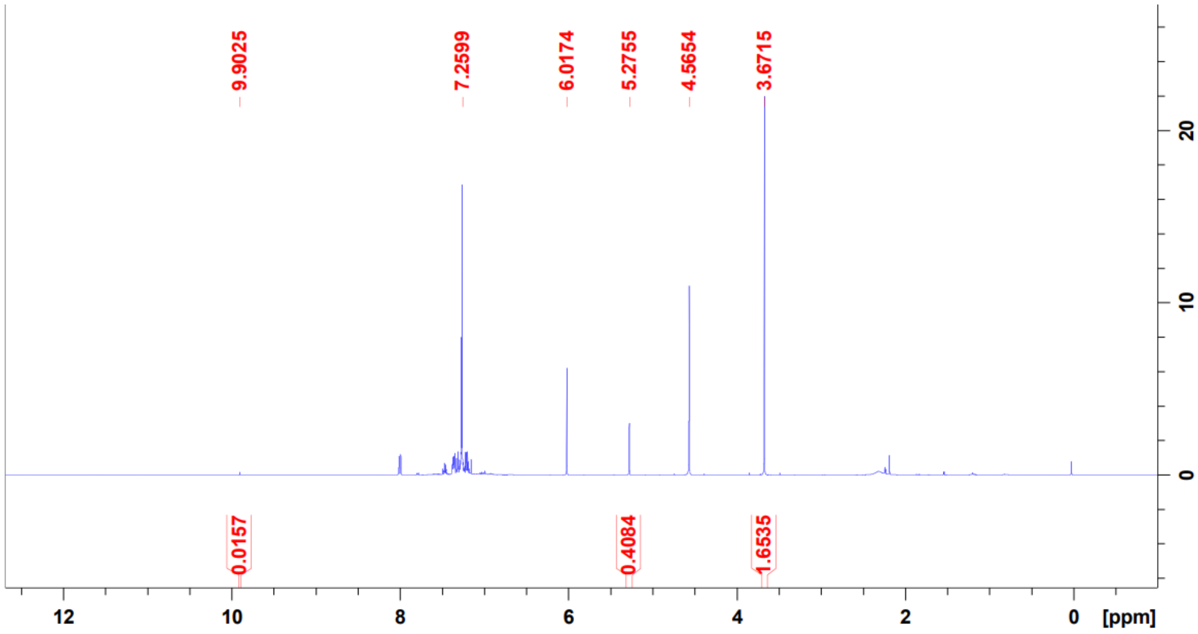


Figure S10: 2 mol%, 45 hours

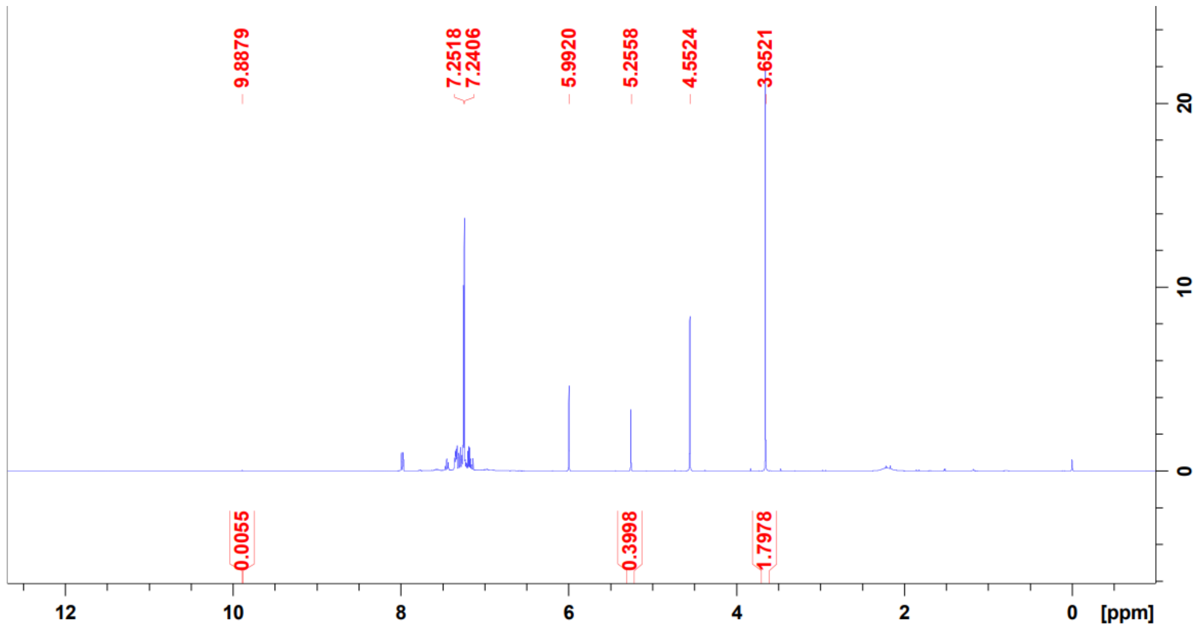


Figure S11. 2 mol%, 94 hours

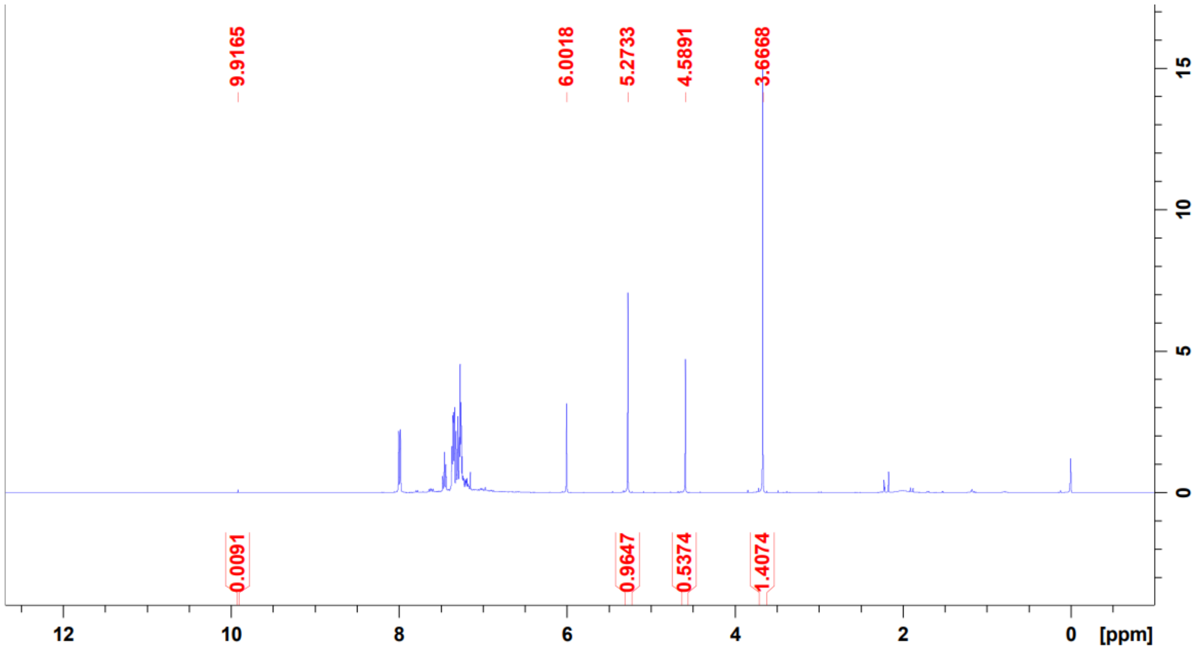


Figure S12. 2 mol%, 140 hrs

i) **3** - RuH$_2$(dppm)$_2$ 4-Methoxy benzyl 4-methoxy benzoate

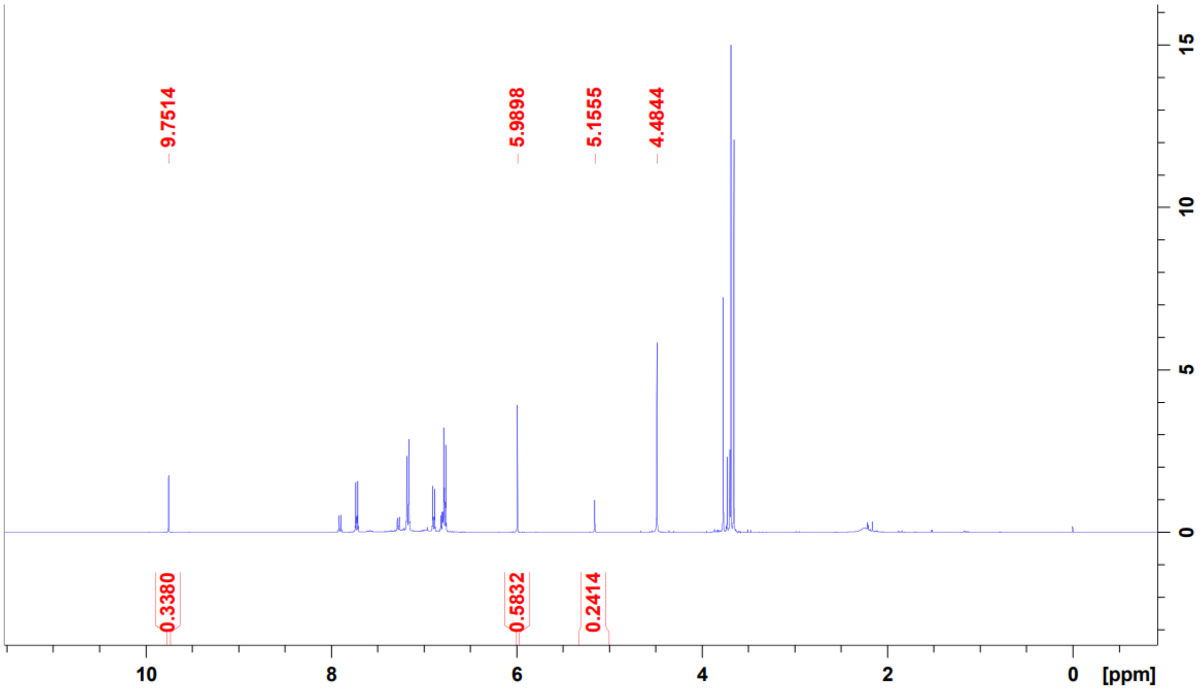


Figure S13. 2 mol%, 45 hrs

ii) **3** – RuH$_2$(dppm)$_2$ – 4-Bromo benzyl 4-bromo benzoate

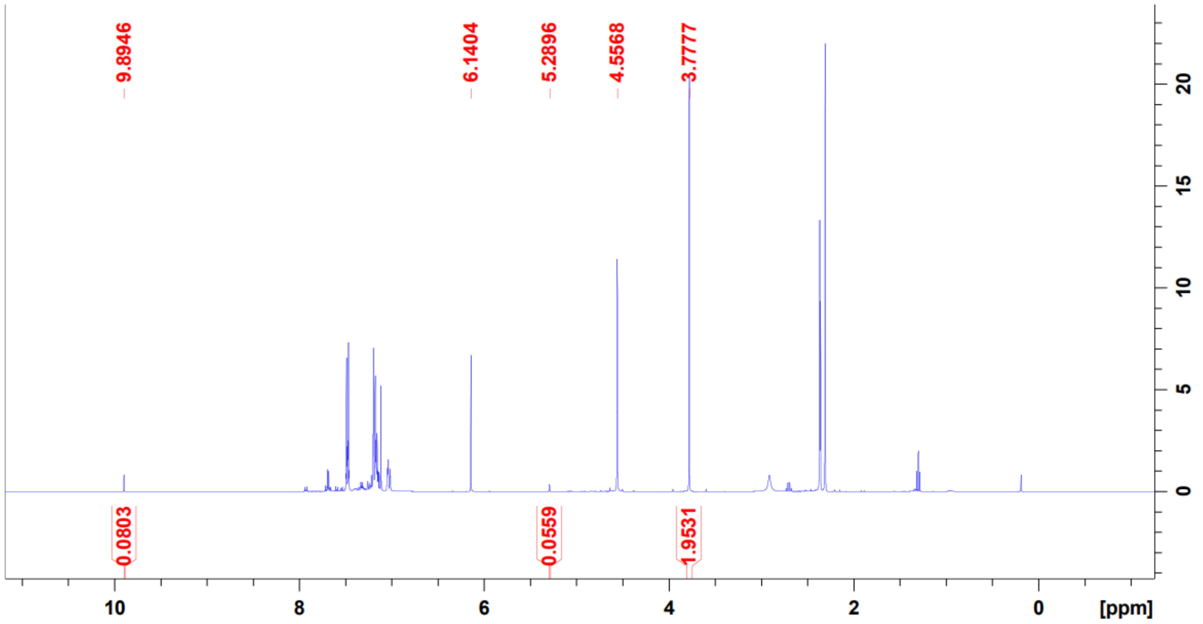


Figure S14. 2 mol%, 45 hrs

iii) **3** - RuH$_2$(dppm)$_2$ – 4-Nitro-benzyl 4-nitro-benzoate

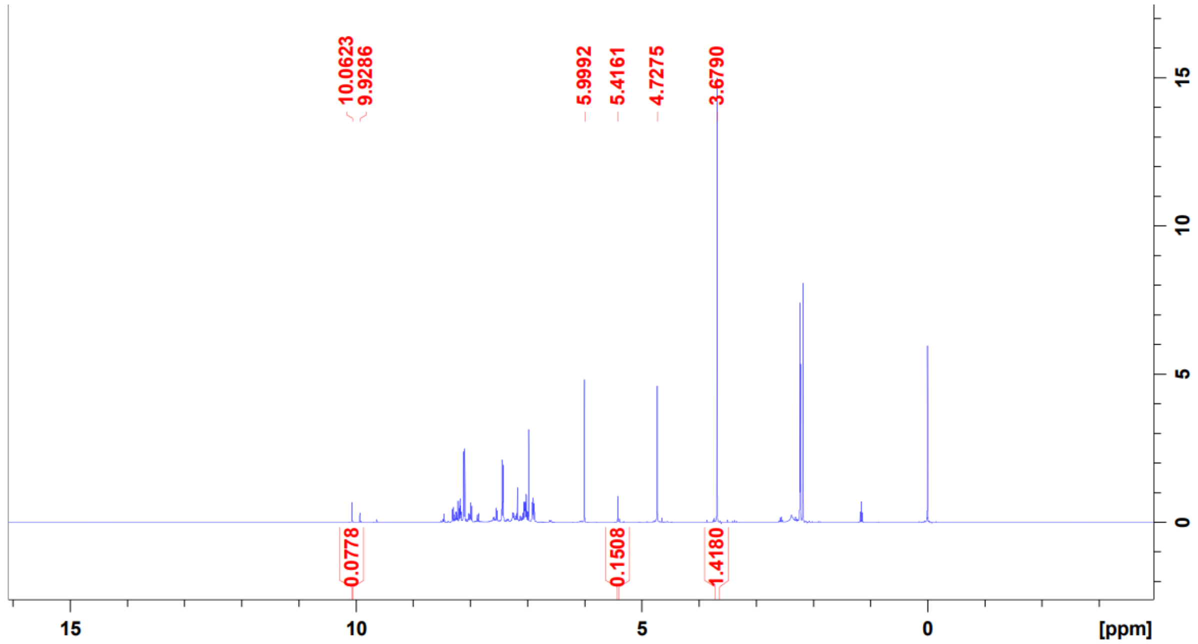


Figure S15. 2 mol%, 45 hrs

iv) **2** - RuH$_2$(PP')$_2$ – Benzyl benzoate [5]

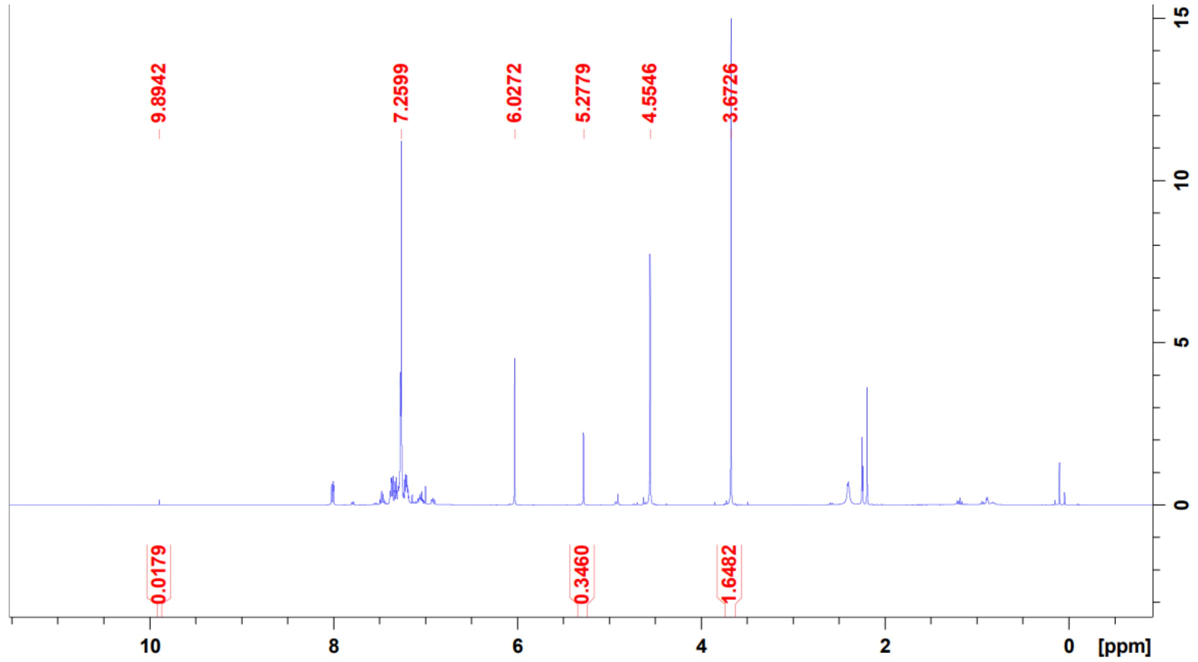


Figure S16. 1 mol %, 45 hrs

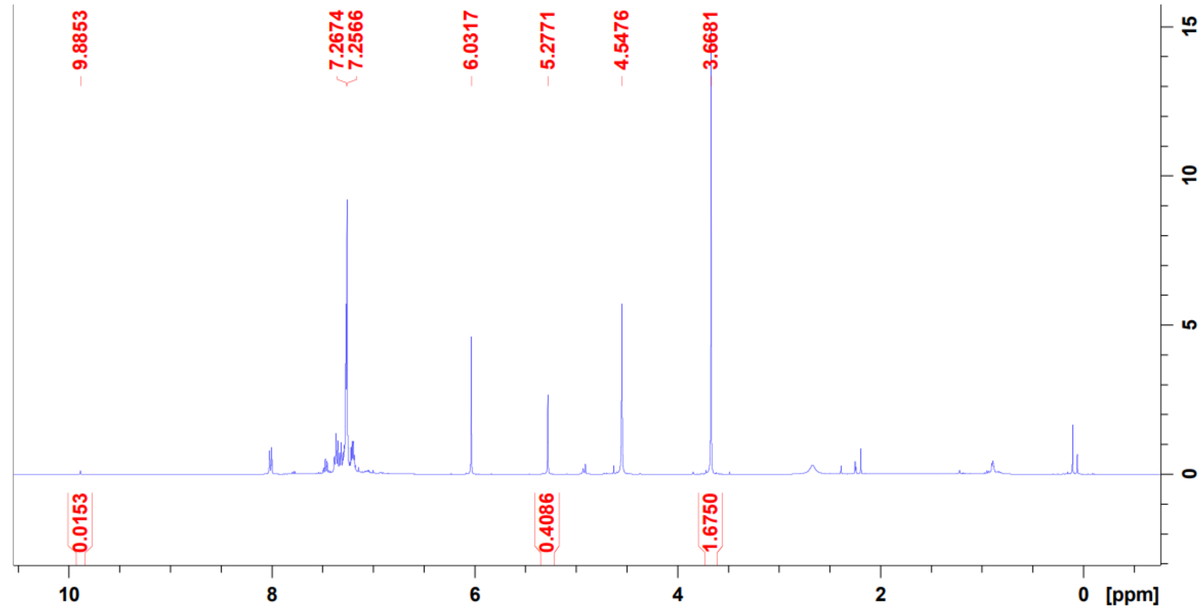


Figure S17. 2 mol%, 45 hrs

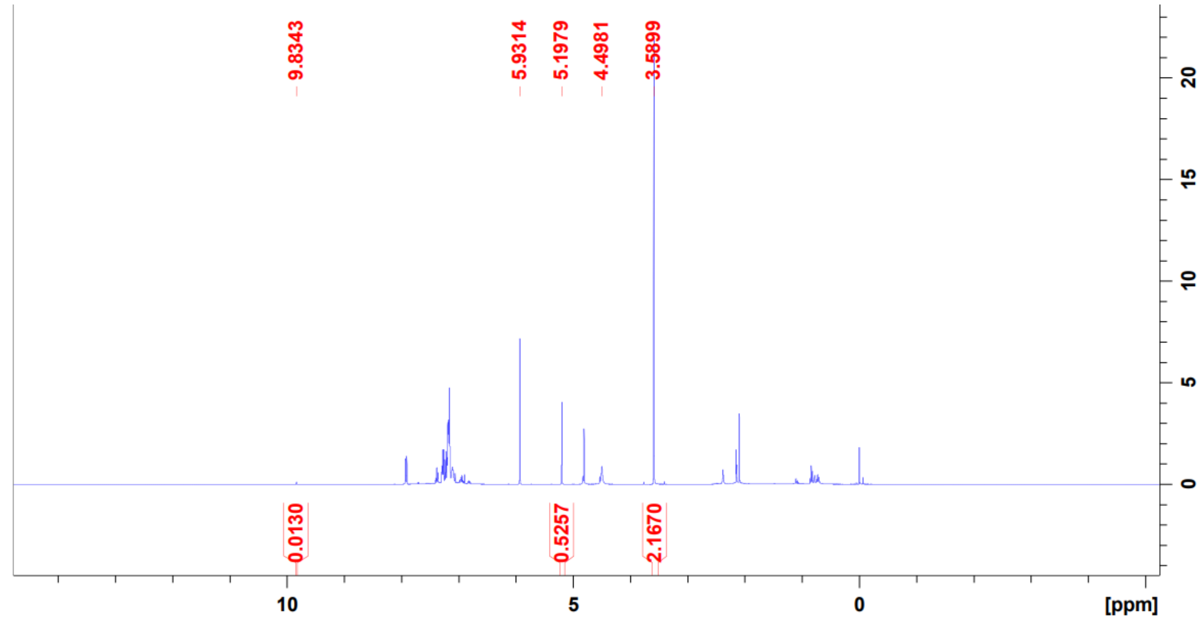


Figure S18. 5 mol%, 45 hrs

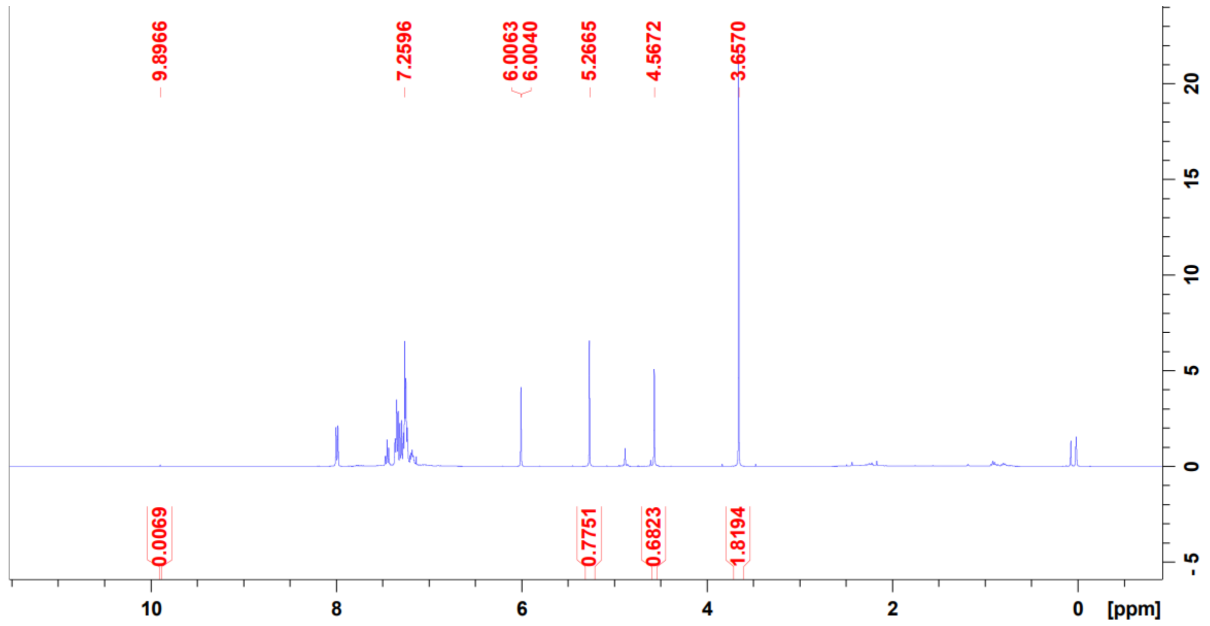


Figure S19. 2 mol%, 92 hr

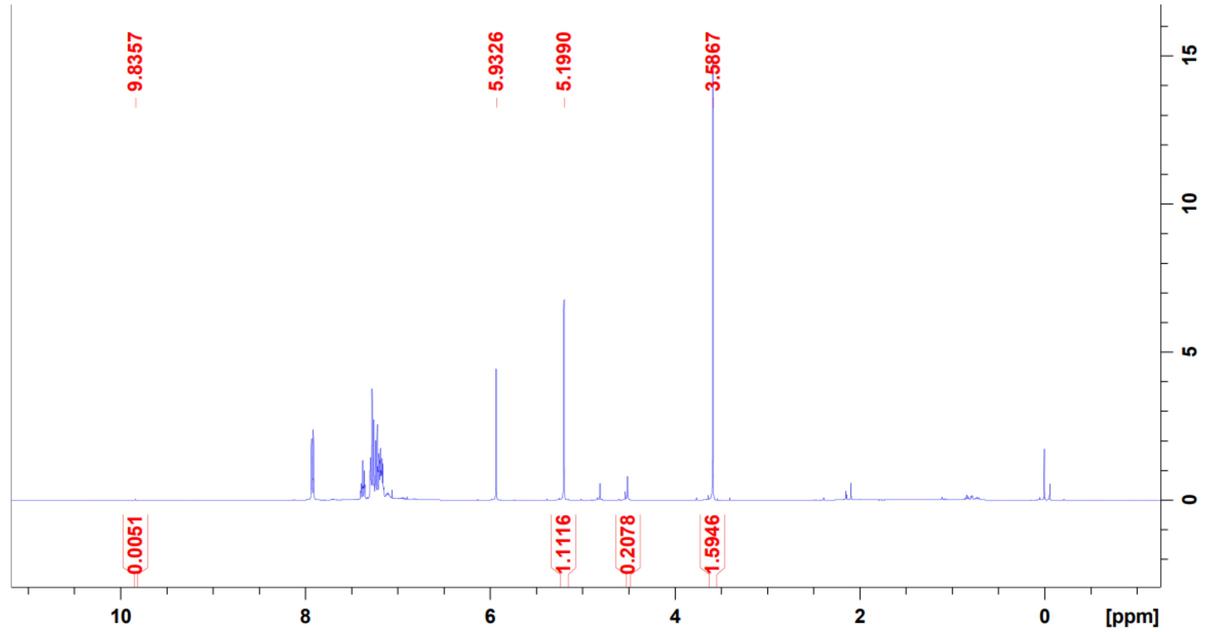


Figure S20. 2 mol%, 140 hrs

v) **2** - $RuH_2(PP')_2$ – 4-Methoxy benzyl 4-methoxy benzoate [5]

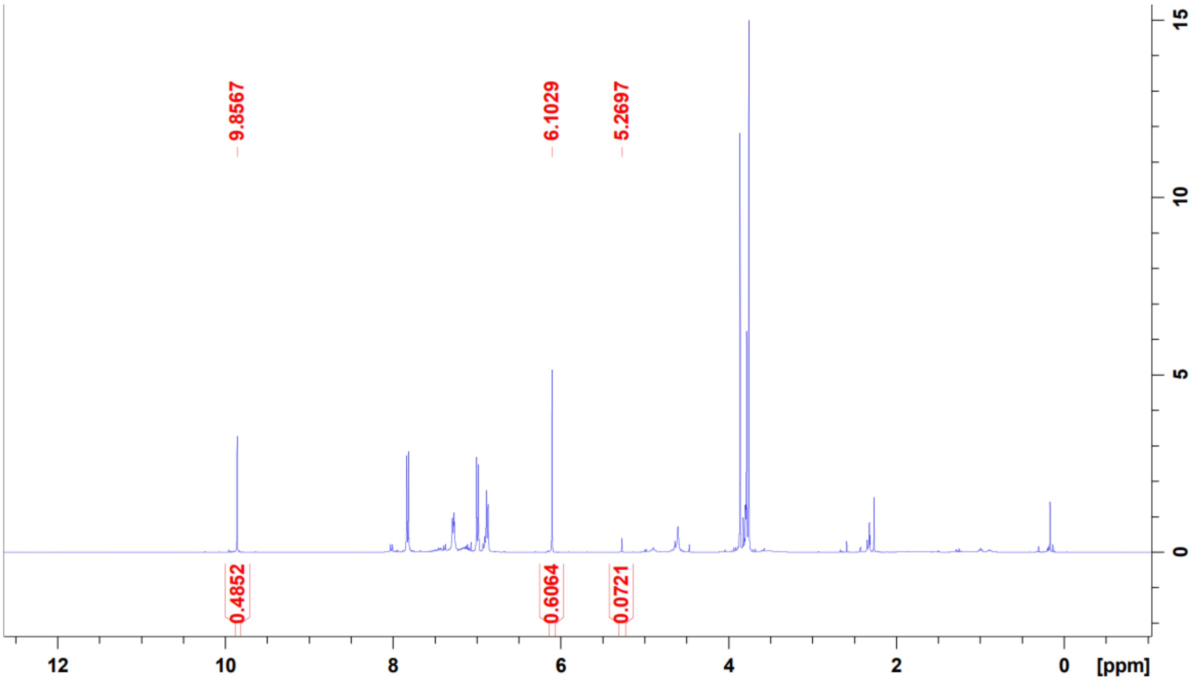


Figure S21. 2 mol%, 45 hrs

vi) **2** - $RuH_2(PP')_2$ – 4-Bromo benzyl 4-bromo benzoate [6]

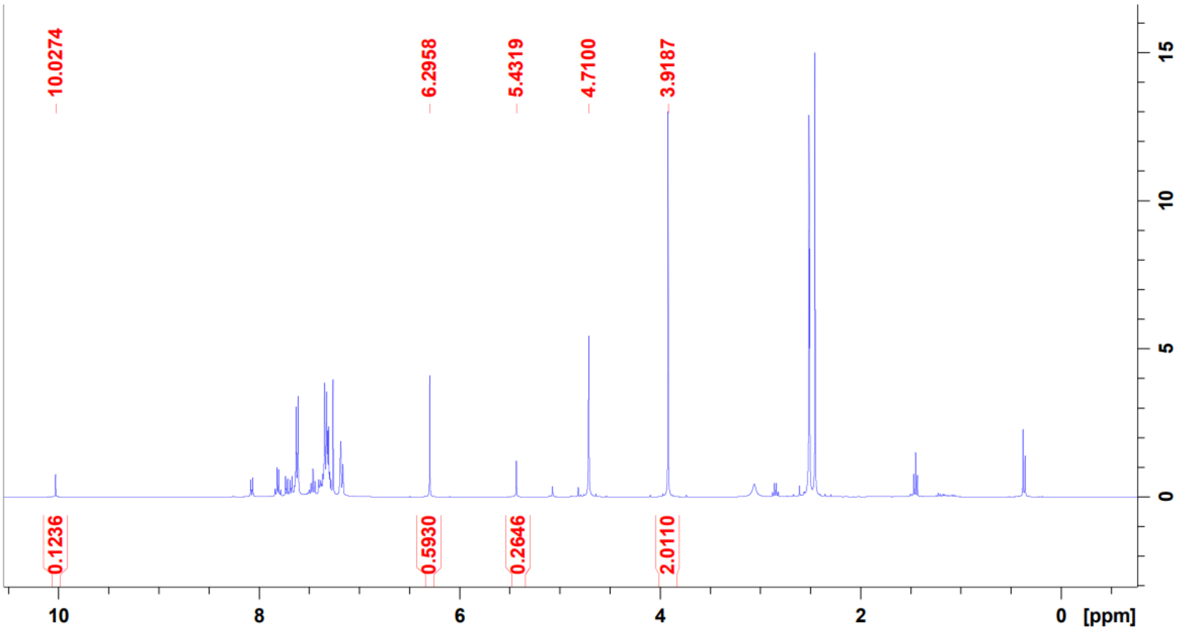


Figure S22. 2 mol%, 45 hrs

vii) **2** – $RuH_2(PP')_2$ – 4-Nitro benzyl 4-nitro benzoate [6]

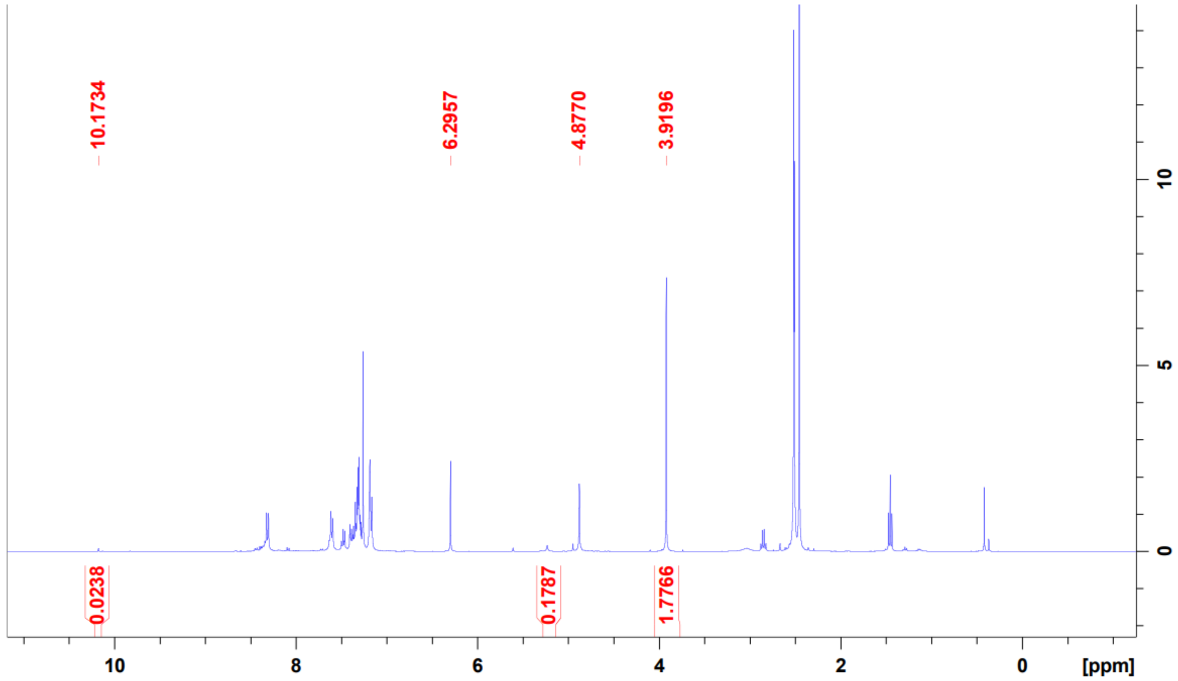


Figure S23. 2 mol%, 45 hrs

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