Chemoselective Hydrogenation of Carbonyl Compounds and Acceptorless Dehydrogenative Coupling of Alcohols.

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Supporting Information

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Deposited crystallographic data

CCDC 877565 (complex **1b**), CCDC 877564 (complex **1c**)

Experimental

Unless mentioned otherwise, all manipulations were performed under argon. NMR spectra were recorded on an Agilent DD2 400 MHz spectrometer. All ^{31}P chemical shifts were measured indirectly, relative to 85% H_3PO_4. ^{1}H and ^{13}C chemical shifts were measured relative to the solvent peaks, but are reported relative to TMS. OsO_4 and $OsCl_3·nH_2O$ (54.98% Os) were purchased from Heraeus South Africa. 2-Aminoethyl-diisopropylphosphine, 3-aminopropyl-diisopropylphosphine, Ru-MACHO, the Milstein and Firmenich catalysts **I**, **II**, and **IV** were purchased from Strem. All other chemicals and anhydrous grade solvents were obtained from Aldrich, Alfa Aesar, and TCI. All commercial esters, ketones, amines, and alcohols substrates of Tables 2 and 3 were purified by passing them through activated basic alumina. $(NEt_4)_2OsCl_6$, $OsHCl(CO)(AsPh_3)_3$, and di(1-adamantyl)chlorophosphine were prepared according to previously reported methods[1,2, 3]

Syntheses

$PyCH_2NH(CH_2)_2NH_2$. *Method A.* Picolinaldehyde (22 g, 0.205 mol) is pipetted into a 100 mL flask containing ethylenediamine (25 g, 0.416 mol or 37 g, 0.616 mol) with stirring. The flask becomes hot but does not require external cooling or a condenser. After 10 min, the mixture is transferred into a 300 mL steel Parr reactor containing 1 g of 5% Pd/C (0.23 mol%) and a stirbar. The reactor is charged with 50 bar H_2 and placed into an oil bath preheated to 100 °C. After 4 - 5 h of stirring at 500 rpm, the pressure decreases to 36 - 37 bar, when the reaction is finished and no further pressure change is observed. The reactor is allowed to cool to r.t. (p = ca. 30 bar), then it is vented and opened. The product is filtered through a medium-porosity frit; the steel bottle and the solids are washed with 3 × 3 ml of toluene. The product is isolated by vacuum distillation using a short-path distillation apparatus. First, the volatiles are evaporated and condensed into a cold (ice or liq. N_2 bath) trap under vacuum at r.t., then with heating at 50 °C. The distillation apparatus is fitted with a cow type receiver and the bath temperature is increased to 135 °C. After collecting a small forerun (6-7 drops), the light-yellow product boiling above 80 °C is collected (most product distills between 95 and 98 °C under 0.05 torr). Yield: 21.59 g (69.5%) when using 25 g of ethylenediamine and 24.31 g (78.3%) when using 37 g of the diamine. ^{1}H NMR (C_6D_6) δ 8.48 (m, 1H, Py), 7.13 (overlapped m, 2H, Py), 6.69 (m, 1H, Py), 3.85 (s, 2H, CH_2), 2.57 (m, 2H, CH_2), 2.47 (m, 2H, CH_2), 1.13 (br, 3H, NH). $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ 161.78 (s, Py), 149.79 (s, Py), 136.26 (s, Py), 122.26 (s, Py), 121.96 (s, Py), 55.99 (s, CH_2), 53.16 (s, CH_2), 42.75 (s, CH_2).

Method B. Picolinaldehyde (38.0 g, 0.355 mol) in 100 mL of methanol was slowly (over 2 h) added to 1,2-ethanediamine (42.6 g, 0.710 mol) in 100 ml of methanol and the mixture was stirred for 1 h.

During the next 2 h, the reaction mixture was treated portionwise with $NaBH_4$ (20.2 g, 0.533 mol). It was stirred for additional 1 h, then refluxed overnight for 16 h, then evaporated under vacuum. The remaining semisolid was treated with aqueous NaOH (100 mL, 20 wt%) and the product was extracted with 3×70 mL of toluene. The combined extract was again washed with aqueous NaOH (100 mL, 10 wt%), then passed through a short plug (2×1 cm) of alumina and evaporated. The product was distilled to give a colorless liquid (30.5 g, 57 %).

$PyCH_2NH(CH_2)_2OH$. All manipulations were carried in air. 2-Picolyl aldehyde (49.3 g, 0.461 mol) in 150 mL of methanol was slowly added to 2-ethanolamine (28.1 g, 0.461 mol) in 50 ml of methanol and the mixture was stirred for 1 h. The obtained Schiff base was treated portionwise with $NaBH_4$ (17.5 g, 0.461 mol) during 1 h and the reaction mixture was left to stir for an additional 1 h. After that time, methanol was removed *in vacuo* and remaining semisolid was treated with 100 mL of NaOH (20 w%) and the product was extracted with 3×50 mL of *i*PrOH. Extract was combined and *i*PrOH was removed *in vacuo*. The obtained oil was purified by vacuum distillation while collecting a fraction at 130-132 °C (0.1 mmHg). The product was obtained as a colorless liquid (28.1 g, 40 %). ^1H NMR (C_6D_6) δ 8.42 (d, *J* = 4.5, 1H, Py), 7.06 (td, *J* = 7.6, 1.7, 1H, Py), 6.94 (d, *J* = 7.7, 1H, Py), 6.62 (dd, *J* = 7.0, *J* = 5.4, 1H, Py), 3.77 (s, 2H, CH_2), 3.67 – 3.52 (m, 2H, CH_2), 3.13 (br, 2H, OH, NH), 2.71 – 2.48 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 169.52 (s, Py), 149.76 (s, Py), 136.88 (s, Py), 122.73 (s, Py), 121.42 (s, Py), 61.56 (s, CH_2), 55.18 (s, CH_2), 51.86 (s, CH_2).

$PyCH_2NH(CH_2)_2P(iPr)_2$. Picolinaldehyde (3.66 g, 34.17 mmol) was pipetted into a 100 mL flask containing 50 g of 2-aminoethyl diisopropylphosphine in THF (10%, 31.01 mmol) with stirring. The mixture was transferred into a 300 mL steel Parr reactor containing 0.5 g of 5% Pd/C (0.76 mol%) and a stirbar. The reactor was charged with 50 bar H_2 and placed into an oil bath preheated to 100 °C. After 3 h of stirring at 500 rpm the reactor was placed in a cold water bath, then it was vented and opened. The product was filtered through a medium-porosity frit; the steel bottle and the solids were washed with 3 × 3 ml of toluene. After evaporating the volatiles under vacuum and drying the residue under vacuum at 70 °C for 1.5 h, the product is isolated using a short-path distillation apparatus fitted with a cow-type receiver. After collecting a small forerun (5-6 drops), the product boiling between 115 and 130 °C is collected (under 10^{-3} torr, bath at 170 °C). Yield: 6.11 g (78%) of a pale-yellow liquid. ^1H NMR (C_6D_6) δ = 8.49 (dt, *J*=4.7, 1.8, 1H, Py), 7.15 (d, *J* = 8.3, 1H, Py), 7.11 (td, *J*=7.8, *J*=1.8, 1H, Py), 6.65 (ddd, *J*=7.0, 4.9, 1.7, 1H, Py), 3.92 (s, 2H, $PyCH_2$), 2.80 (m, 2H, NCH_2), 1.82 (br. s, 1H, NH), 1.55 (dq, *J* = 2.1, 7.0, 2H, CH), 1.49 (m, 1H, CH_2), 1.01 (dd, *J*=13.8, 7.1, 6H, CH_3), 0.96 (dd, *J*=10.8, 7.0, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ = 161.66 (s, Py), 149.78 (s, Py), 136.17 (s, Py), 122.23 (s, Py), 121.91 (s, Py), 56.02 (s, NCH_2), 49.42 (d, *J*(CP)=24.9, NCH_2), 24.04 (d, J(CP)=13.5, PCH), 23.69 (d, J(CP)=19.3, PCH_2), 20.61 (d, J(CP)=16.5, CH_3), 19.25 (d, J(CP)=9.9, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ = -1.0 (s).

$PyCH_2NH(CH_2)_3P(iPr)_2$. 3-Aminopropyl-diisopropylphosphine (25.0 g, 10 % solution in THF, 0.0143 mmol) was added to a freshly distilled 2-picolyl aldehyde (1.53 g, 0.0143 mmol) in 10 mL of THF and the mixture was stirred for 1 h. After that time, THF was removed under reduced pressure and the remaining oil was dried for 1 h. The oil was dissolved in 40 mL of toluene and diisobutyl aluminum hydride (22.7 mL, 1.5 M, 0.0341 mmol) was added during 1 h (Caution!!! Exothermic reaction!). The mixture was left to stir for an additional one hour. After that time, the solution was quenched dropwise with 1 mL of water (Caution!!! Exothermic reaction!) and the obtained suspension was filtered through a short plug (3 × 2 cm) of basic alumina. The alumina was washed with toluene (3 × 10 mL) and the collected filtrate was evaporated and dried under vacuum for 3 h. The product was obtained as a yellow oil (3.32 g, 87 %). $^1H\{^{31}P\}$ NMR (C_6D_6) δ 8.55 (dt, J = 4.8, 1.2, 1H, Py), 7.30 – 7.02 (m, 2H, Py), 6.82 – 6.57 (m, 1H, Py), 3.95 (s, 2H, $PyCH_2$), 2.69 (t, J = 6.8, 2H, CH_2), 1.87 – 1.53 (m, 5H), 1.51 – 1.30 (m, 2H, CH_2), 1.10 (d, J = 7.1, 6H, CH_3), 1.06 (d, J = 7.0, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 161.45 (s, Py), 149.50 (s, Py), 135.83 (s, Py), 121.97 (s, Py), 121.59 (s, Py), 55.86 (s, CH_2), 51.31 (d, J(CP) = 12.0, CH_2), 29.32 (d, J(CP) = 18.9, CH_2), 23.82 (d, J(CP) = 14.2, CH), 20.38 (d, J(CP) = 16.2, CH_3), 19.84 (d, J(CP) = 19.0, CH_2), 19.10 (d, J(CP) = 10.0, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 4.1 (s).

$PyCH_2NH(CH_2)_2OP(iPr)_2$. To a solution of $PyCH_2NH(CH_2)_2OH$ (2.00 g, 13.2 mmol) and triethylamine (1.60 g, 15.8 mmol) in THF (25 mL) was added chlorodiisopropyl phosphine (96% assay, 2.09 g, 13.2 mmol). The resulting mixture was stirred for 2 h, and the solvent was evaporated under vacuum to give an oily residue. The product was extracted with hexanes (3×25 mL) filtered through a glass frit, and hexanes were removed *in vacuo* to give a colorless oil (3.31 g, 94%). ^1H NMR (C_6D_6) δ 8.62 – 8.30 (m, 1H, Py), 7.13 – 7.06 (m, 2H, Py), 6.73 – 6.52 (m, 1H, Py), 3.89 (s, 2H, CH_2), 3.87 – 3.73 (m, 2H, CH_2), 2.72 (t, J = 5.5, 2H, CH_2), 2.05 (br, 1H, NH), 1.71 – 1.49 (m, 2H, CH), 1.12 (dd, J = 10.2, 7.0, 6H, CH_3), 1.00 (dd, J = 15.3, 7.2, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 161.56 (s, Py), 149.83 (s, Py), 136.17 (s, Py), 122.16 (s, Py), 121.93(s, Py), 72.68 (d, J(CP) = 19.2, CH_2), 55.97 (s, CH_2), 51.25 (d, J(CP) = 6.9, CH_2), 28.81 (d, J(CP) = 17.8, CH), 18.51 (d, J(CP) = 20.8, CH_3), 17.53 (d, J(CP) = 8.6, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 152.1 (s).

$PyCH_2NH(CH_2)_2NHP(iPr)_2$. $i$$Pr_2PCl$ (95% assay, 12 g, ca. 78.6 mmol) was added to a solution of $PyCH_2NH(CH_2)_2NH_2$ (12 g, 79.4 mmol) and triethylamine (10 g, 98.8 mmol) in THF (100 mL). A solid formed quickly, and the resulting thick mixture was stirred for 24 hours (note: the use of a powerful, e.g. rare-earth, stirbar and ^{31}P NMR control of the reaction are recommended to ensure the complete conversion of *i*Pr_2PCl). The reaction mixture was filtered, and the filtrate was evaporated under vacuum. The product was isolated using a short-path distillation apparatus fitted with a cow type receiver. After collecting a small forerun (12 drops), the product boiling between 100 and 130 °C was collected (under 0.001 torr, bath at 170 °C). Yield: 18.03 g (86%) of a pale-yellow liquid containing 93-94% of the product by ^{31}P NMR. ^{1}H NMR (C_6D_6) δ 8.48 (dm, *J* = 4.8, 1H, Py), 7.10, 7.06 (overlapped, 2H, Py), 6.65 (m, 1H, Py), 3.86 (s, 2H, CH_2), 2.98 (dq, *J* = 6.4, 8.4, 2H, CH_2), 2.57 (t, *J* = 5.9, 2H, CH_2), 1.79 (br, 1H, NH), 1.46 (sept, *J* =7.0, 2H, CH), 1.19 (br, 1H, NH), 1.05 (d, *J* = 7.1, 3H, CH_3), 1.01 (d, *J* = 7.0, 6H, CH_3), 0.99 (d, *J* = 6.9, 3H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ 161.56 (s, Py), 149.81 (s, Py), 136.16 (s, Py), 122.25 (s, Py), 121.94 (s, Py), 55.87 (s, CH_2), 52.77 (d, *J*(CP) = 6.3, CH_2), 49.17 (d, *J*(CP) = 23.7, CH_2), 27.26 (d, *J*(CP) = 13.1, CH), 19.80 (d, *J*(CP) = 20.8, CH_3), 17.97 (d, *J*(CP) = 8.3, CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ 64.5 (s).

$PyCH_2NH(CH_2)_2NHP$(*t*Bu)$_2$. *t*Bu_2PCl (96% assay, 12.42 g, ca. 66 mmol) was added to a solution of $PyCH_2NH(CH_2)_2NH_2$ (10.0 g, 66.0 mmol) and triethylamine (8 g, 79 mmol) in THF (100 mL). The resulting mixture was rapidly stirred for 24 hours (note: the reaction is fast until it reaches ca. 50% conversion, then it becomes slow because the remaining $PyCH_2NH(CH_2)_2NH_2$ precipitates as a hydrochloride; ^{31}P NMR control of the reaction is recommended to ensure the complete conversion of *t*Bu_2PCl). The reaction mixture was filtered, and the filtrate was evaporated under vacuum. The resulting solid was dissolved in a hexane/Et_2O solvent mixture (3:1, 40 mL) and filtered through a 1 cm layer of activated basic alumina on a glass frit. Further 3 × 6 mL of the hexane/Et_2O mixture was used to wash the alumina. The filtrate was evaporated and dried under vacuum to give a white solid (18.2 g, 93%). ^{1}H NMR (C_6D_6) δ 8.48 (d, *J* = 4.9, 1H, Py), 7.20 – 6.97 (m, 2H, Py), 6.64 (ddd, *J* = 6.5, 4.9, 1.7, 1H, Py), 3.87 (s, 2H, CH_2), 3.05 (m, 2H, CH_2), 2.62 (t, *J* = 5.9, 2H, CH_2), 1.88 (br, 1H, NH), 1.49 (br, 1H, NH), 1.08 (d, *J*(HP) = 11.1, 18H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ 161.27 (s, Py), 149.54 (s, Py), 135.84 (s, Py), 121.97 (s, Py), 121.63 (s, Py), 55.54 (s, *J*(CP) = 3.0, CH_2), 52.33 (d, *J*(CP) = 7.2, CH_2), 50.66 (d, *J*(CP) = 29.0, CH_2), 34.12 (d, *J*(CP) = 21.6, C{*t*Bu}), 28.59 (d, *J*(CP) = 15.3, CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ 79.4 (s).

$PyCH_2NH(CH_2)_2NHPAd_2$. $PyCH_2NH(CH_2)_2NH_2$ (3.3 g, 21.8 mmol) was pipetted into a stirring THF (50 mL) solution of triethylamine (2.6 g, 25.7 mmol) and Ad_2PCl (7.14 g, ca. 19.6 mmol, 92.4%, containing an impurity resonating at δ(^{31}P, C_6D_6) 83.5 of presumably $Ad_2ClP{=}O$). The resulting mixture was stirred for 5 days (note: ^{31}P NMR control of this slow reaction is recommended to ensure >99% conversion of Ad_2PCl). The reaction mixture was filtered, and the filtrate was evaporated under vacuum. The resulting very viscous material was dissolved in hexane (20 mL) and vacuum-filtered through a 1 cm layer of activated basic alumina in a 30 mL glass frit. Further 10 mL of hexane was used to wash the alumina. An attempt to crystallize the product from this solution at -30 °C overnight produced no solid. Thereafter, the hexane was evaporated and the residue was dried under vacuum at 80 °C for 1h to give a glass-like, extremely viscous material (7.58 g) containing ca. 90% of PyNNP-Ad. Among the prominent impurities in the $^{31}P\{^{1}H\}$ NMR spectrum was Ad_2PCl (0.8%), and two species at δ 83.4 (5.5%) and 55.7 (1.4%). According to the ^{1}H NMR, no impurity contained the $PyCH_2NHCH_2CH_2NH$- group. This product was used 'as is' in the preparation of **1c** as no further purification deemed practical. ^{1}H NMR (C_6D_6) δ 8.50 (dt, *J* = 4.8, 1.3, 1H, Py), 7.13-7.08 (m, 2H, Py), 6.65 (m, 1H, Py), 3.91 (s, 2H, CH_2), 3.09 (m, 2H, CH_2), 2.70 (t, *J* = 5.8, 2H, CH_2), 2.17 (dd, *J*=3.6, 5.2, 1H NH), 1.93, 1.72, 1.51 (br, 31H, Ad+NH). $^{13}C\{^{1}H\}$(C_6D_6) δ 161.68 (s, Py), 149.88 (s, Py), 136.17 (s, Py), 122.30 (s, Py), 121.96 (s, Py), 56.00 (s, CH_2), 52.70 (d, *J*=6.9, CH_2), 51.56 (d, *J*=29.2, CH_2), 40.41 (d, *J* = 12.7, CH_2), 39.08 (d, *J* = 21.5, C), 37.98 (d, *J*(CP)=0.8, CH_2), 29.43 (d, *J* = 8.3, CH). $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 75.8 (s).

OsHCl(CO)[PyCH₂NH(CH₂)₂NHP(*i*Pr)₂] (1a). A flask containing a mixture of $OsHCl(CO)(AsPh_3)_3$ (1.74 g, 1.49 mmol) and $PyCH_2NH(CH_2)_2NHP$(*i*Pr)$_2$ (400 mg, 1.49 mmol) in 15 mL of *m*-xylene was placed in a preheated to 150 °C oil bath and stirred for 1 h, affording a dark-red suspension. After cooling to room temperature, the mixture was placed in a freezer at -13 °C for 2 h. The precipitated product was filtered off, washed with diethyl ether (3 × 2 mL), and dried under vacuum for 1 h to give a brown-grey solid. Yield: 660 mg (85 %).

A preparation of **1a** from $[OsCl_2$(*p*-cymene)$]_2$ (5.3 g, 13.41 mmol [Os]), following the method described below for **1b**, using $PyCH_2NH(CH_2)_2NHP$(*i*Pr)$_2$ (3.85, ca. 14.40 mmol) and Li (94.2 mg, 13.57 mmol) in 100 mL of anhydrous ethanol (5 h at 175 °C) yielded only 1.2 g (17%) of the product that crystallized from the reaction solution at -30 °C after 1 d. The poor yield in this case could be due to the difficulty of displacing *p*-cymene by the sterically less demanding $PyCH_2NH(CH_2)_2NHP$(*i*Pr)$_2$ ligand and the relatively good solubility of **1a** compared to **1b**.

^{1}H NMR (CD_2Cl_2) δ 8.97 (dm, *J* = 5.6, 1H, Py), 7.70 (td, *J* = 1.5, 7.7, 1H, Py), 7.35 (d, *J* = 7.7, 1H, Py), 7.24 (t, *J* = 6.8, 1H, Py), 4.49 (d, 1H, CH_2), 3.92 (t, *J* = 12.1, 1H, CH_2), 3.89 (br, 1H, NH), 3.32 (m, 1H, CH_2), 3.23-3.18 (overlapped m, 2H, CH_2), 2.71 (m, 1H, CH_2), 2.38 (ds, *J* = 7.2, 9.7, 1H, CH), 1.92 (ds, *J* = 6.9, 9.6 1H, CH), 1.75 (br, 1H, NH), 1.31 (dd, *J* = 7.3, 14.6, 3H, CH_3), 1.26 (d, *J* = 7.1, 14.7, 3H, CH_3), 1.11 (dd, *J* = 6.9, 6.9, 3H, CH_3), 1.07 (dd, *J* = 7.0, 9.0, 3H, CH_3), -16.40 (d, *J*(HP) = 19.7, *J*(HOs) = 92.4, 1H, OsH). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ 187.74 (d, *J* = 11.0, CO), 157.34 (s, Py), 153.28 (d, *J* = 1.8, Py), 136.57 (s, Py), 125.14 (d, *J* = 2.1, Py), 121.27 (d, *J* = 2.2, Py), 62.91 (d, *J* = 2.7, CH_2), 57.77 (d, *J* = 1.3, CH_2), 44.91 (d, *J* = 4.4, CH_2), 33.28 (d, *J* = 30.0, CH), 31.23 (d, *J*

= 46.0, CH), 19.01 (d, *J* = 3.7, CH_3), 18.83 (d, *J* = 1.3, CH_3), 18.66 (d, *J* = 0.9, CH_3), 17.97 (d, *J* = 1.0, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 71.8 (s). IR (Nujol): ν_{CO} =1883. Anal. Calcd for $C_{15}H_{27}ClN_3OOsP$: C, 34.51; H, 5.21; N, 8.05. Found: C, 35.01; H, 5.20; N, 7.87.

[$OsCl_2$(*p*-cymene)]$_2$. This preparation is based on a reported procedure;[4] all manipulations have been performed under argon, although the product may not be air-sensitive and can probably be filtered in air. A mixture of α-terpinene (60 mL, ≥89%, Aldrich W355801) and anhydrous 2-propanol (240 mL) was added to 20 g of Os(III) chloride (54.98% Os, 57.8 mmol) in a 0.5 L flask to form a dark solution upon stirring. The flask was fitted with a condenser, and the reaction mixture was refluxed while stirring for 16 h. After cooling to r.t., the flask was left for 1 h at -15 °C, then the product was filtered, washed with 4 × 50 mL of 2-propanol, and dried under vacuum for 3 h. Yield: 20.77g (90.9%) of an orange powdery solid.

Note: When a sample of the product is taken in CD_2Cl_2, it gives an orange solution, yet a small amount of a grey solid is visible when the NMR tube is examined under a microscope. This insoluble material does not look like osmium black. In the original preparation of [$OsCl_2$(*p*-cymene)]$_2$, performed on a 3 g scale,[4] the product was recrystallized from 120 mL of hot 2-propanol. This is not practical on a large scale, since the osmium dimer is sparingly soluble in 2-propanol (and in most organic solvents except dichloromethane). However, [$OsCl_2$(*p*-cymene)]$_2$ dissolves in ethanol upon stirring with $PyCH_2NHC_2H_4NHPR_2$ and lithium in the preparations of complexes **1** (*vide infra*), and these solutions can be filtered, if necessary. In our experience, the reaction solutions were homogeneous, and thus, it appears that the 'grey solid' mentioned above dissolves in the reaction together with [$OsCl_2$(*p*-cymene)]$_2$.

OsHCl(CO)[(*t*Bu)$_2$PNH(CH_2)$_2$NHCH$_2$Py] (1b).

Method 1. Anhydrous ethanol (100 mL) was poured into a 300 mL flask equipped with a magnetic stir bar and containing $PyCH_2NHC_2H_4NHP$*t*Bu_2 (5.6 g, 18.96 mmol) and [$OsCl_2$(*p*-cymene)]$_2$ (7.2 g, 9.11 mmol). Stirring this mixture gave a dark brown solution. Then 136 mg (19.59 mmol) of lithium was added and stirring continued until all lithium dissolved. The resulting dark-red solution was filtered through a layer of Celite (3 g) in a 60 mL fritted funnel, and the filter material was washed with 4 × 10 mL of anhydrous ethanol. The filtered solution was poured into a 300 mL steel autoclave equipped with a magnetic stir bar, and more ethanol was used to wash the glassware, to bring the total solvent volume to 150 mL. The autoclave was closed, tightened, and placed into an oil bath preheated to 175 °C on a hotplate stirrer. This temperature was maintained for 3.5 h, while stirring at 600 rpm. During this time, the pressure increased to 350 psi. Then, the autoclave was removed from the oil bath, and it was transferred into a cold water bath. After 1 h, the autoclave was vented, opened in air, and the crystalline product was isolated by vacuum filtration. The autoclave and the filtered solid were liberally washed with denatured ethanol under air, and the product was dried under vacuum of an oil pump (0.01 mmHg) overnight. Yield: 7.75 g (77.5%). Complex **1b** is insoluble in most organic solvents; the solubility in dichloromethane is ca. 4 mg/mL and that in dimethylformamide is ca. 12 mg/mL.

The above procedure was further tested with slightly different amounts of lithium and the aminophosphine: 137 mg (19.74 mmol of Li) with 5.5 g (18.62 mmol of NNNP-*t*Bu), and 139 mg (20.03 mmol of Li) with 5.65 g (19.13 mmol of NNNP-*t*Bu). These reactions afforded 7.68 g (76.7% yield) and 7.95 g (79.4% yield) of **1b**, respectively. Allowing the autoclave to cool down to room temperature slowly, together with the oil bath, gave **1b** as a large-crystalline material, where the larger crystals take a brown color, while the smaller crystals appear yellow or lemon-yellow (see Figure S1).

Figure S1. The isolated 7.68 g of **1b** in a 60 mL fritted funnel.

Method 2. A flask containing a mixture of $OsHCl(CO)(AsPh_3)_3$ (3.48 g, 2.98 mmol) and $PyCH_2NH(CH_2)_2NP(tBu)_2$ (880 mg, 2.48 mmol) in 15 mL of *m*-xylene was placed in a preheated to 140 °C oil bath and stirred for 2 h, affording a brown suspension. After cooling to room temperature, the mixture was placed in a freezer at -15 °C for 2 h. The precipitated product was filtered off, washed with diethyl ether (3 × 2 mL), and dried under vacuum for 1 h to give a lemon-yellow microcrystalline solid. Yield: 1.51 g (92%).

^{1}H NMR (CD_2Cl_2) δ 8.99 (d, J = 5.3, 1H, Py), 7.71 (td, J = 1.5, 7.7, 1H, Py), 7.35 (d, J = 7.7, 1H, Py), 7.25 (t, J = 6.5, 1H, Py), 4.48 (d J = 10.8, 1H, CH_2), 3.93 (overlapped, 2H, CH_2 + NH), 3.29

(overlapped, 3H, CH_2), 2.77 (m, 1H, CH_2), 2.05 (br, 1H, NH), 1.39 (d, *J* = 13.1, 9H, CH_3), 1.29 (d, *J* = 12.9, 9H, CH_3), -16.83 (d, *J*(HP) = 19.2, *J*(HOs) = 92.6, 1H, OsH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 180.35 (d, *J*(CP) = 10.5, CO), 157.43 (s, Py), 153.44 (s, Py), 136.58 (s, Py), 125.31 (s, Py), 121.17 (s, Py), 62.98 (s, CH_2), 57.22 (s, CH_2), 46.30 (d, *J*(CP) = 3.7, CH_2), 43.79 (d, *J*(CP) = 22.0, C{*t*Bu}), 39.72 (d, *J*(CP) = 39.2, C{*t*Bu}), 30.10 (d, *J*(CP) = 4.6, CH_3), 29.71 (d, *J*(CP) = 2.4, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 80.7 (s). Anal. Calcd for $C_{17}H_{31}ClN_3OOsP$: C, 37.12; H, 5.68; N, 7.64. Found: C, 37.20; H, 5.56; N, 7.42.

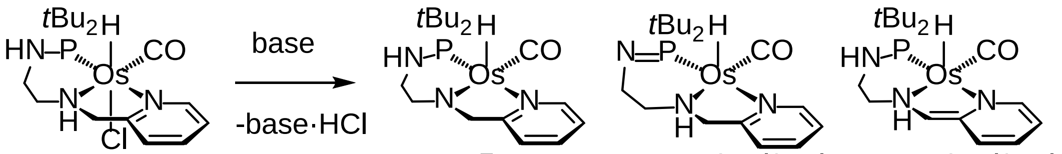
OsHCl(CO)[PyCH$_2$NH(CH$_2$)$_2$NHPAd$_2$] (1c). Anhydrous ethanol (40 mL) was poured into a 100 mL flask equipped with a magnetic stir bar and containing [OsCl$_2$(p-cymene)]$_2$ (3 g, 7.59 mmol Os) and PyCH$_2$NH(CH$_2$)$_2$NHPAd$_2$ (3.77 g, 8.35 mmol). After stirring the mixture for 10 min, lithium (52.9 mg, 7.62 mmol) was added and stirring continued for 2 h (until all lithium was reacted). The dark red solution was filtered through a layer of Celpure P300 filter aid (1 g) in a 30 mL fritted funnel, and the filter material was washed with 18 mL of anhydrous ethanol. The filtered solution was transferred into a 300 mL steel autoclave equipped with a magnetic stir bar, and more ethanol was used to wash the glassware, to bring the total solvent volume to 60 mL. The autoclave was closed, tightened, and placed into an oil bath preheated to 175 °C on a hotplate stirrer. This temperature was maintained for 4 h, while stirring at 500 rpm. Then, the hotplate was turned off and the autoclave was left in the oil bath overnight. Next morning, the autoclave was vented (slight positive pressure), opened in air, and the crystalline product was isolated by vacuum filtration. The autoclave and the filtered solid were washed with 4 × 25 mL of denatured ethanol (in air), and the product was dried under vacuum of an oil pump (0.01 mmHg) for 2 h. Yield: 3.33 g (62%) of a green crystalline solid of the spectroscopically pure product containing a trace amount (2.6 mol%) of ethanol. Complex **1c** is well-soluble in dichloromethane. ^1H NMR (CD_2Cl_2) δ 8.97 (d, *J* = 5.6, 1H, Py), 7.65 (t, *J* = 7.6, 1H, Py), 7.27 (d, *J* = 7.6, 1H, Py), 7.22 (unresolved dd, average *J* = 6.6, 1H, Py), 4.44 (dd, *J* = 14.4, 2.3, 1H, CH_2), 4.07 (br t, 1H, NH), 3.85 (dd, *J*=12.0, 14.4, 1H, CH_2), 3.27 (overlapped m, 3H, CH_2), 2.69 (dt, *J* = 10.2, 9.2, 1H, CH_2), 2.36-2.07 (m, 12H, CH_2), 1.98 (br s, 6H, CH), 1.8-1.67 (m, 12H, CH_2), -16.99 (d, *J*(HP)=18.9, *J*(HOs)=92.1, 1H, OsH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 188.03 (d, *J*(CP)=11.3, CO), 157.63 (s, Py), 153.24 (d, *J*(CP)=1.6, Py), 136.35 (s, Py), 125.10 (d, *J*(CP)=1.9, Py), 121.05 (d, *J*(CP)=2.1, Py), 62.84 (d, *J*(CP)=2.6, NCH_2), 57.25 (s, NCH_2), 47.65 (d, *J*(CP)=20.9, C), 46.42 (d, *J*(CP)=3.0, NCH_2), 43.60 (d, *J*(CP) = 37.3, C), 40.08 (d, *J*(CP)=1.3, CH_2), 39.72 (br, CH_2), 37.57 (d, *J*(CP)=19.3, CH_2), 37.55 (d, *J*(CP)=19.5, CH_2), 29.67 (d, *J*(CP)=8.7, CH), 29.65 (d, *J*(CP)=8.7, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 78.4 (s, *J*(OsP)=261.1 Hz). Anal. Calcd for $C_{29}H_{44}ClN_3OOsP$: C, 49.31; H, 6.14; N, 5.95. Found: C, 49.34; H, 6.34; N, 5.89.

$OsHCl(CO)[PyCH_2NH(CH_2)_3P(\textit{i}Pr)_2]$ (2). A flask containing a mixture of $OsHCl(CO)(AsPh_3)_3$ (1.74 g, 1.49 mmol) and $PyCH_2NH(CH_2)_2NHP(\textit{i}Pr)_2$ (400 mg, 1.49 mmol) in 15 mL of *m*-xylene was placed in a preheated to 140 °C oil bath and stirred for 1 h, affording a dark-red suspension. After cooling to room temperature, the mixture was placed in a freezer at -15 °C for 2 h. The precipitated product was filtered off, washed with diethyl ether (3 × 2 mL), and dried under vacuum for 1 h to give a brown-yellow solid. Yield: 437 mg (57 %). $^{1}H\{^{31}P\}$ NMR (CD_2Cl_2) δ 8.98 (d, *J* = 5.6, 1H, Py), 7.69 (td, *J* = 7.7, 1.5, 1H, Py), 7.33 (d, *J* = 7.3, 1H, Py), 7.22 (t, *J* = 6.6, 1H, Py), 4.49 (dd, *J* = 13.9, 3.3, 1H, CH_2), 3.87 (dd, *J* = 27.8, 14.2, 1H, CH_2 overlapped with NH), 3.80 (br, 1H, NH), 3.58 – 3.29 (m, 1H), 2.61 (q, *J* = 11.4, 1H), 2.47 (sept, *J* = 14.2, 7.1, 1H, CH), 2.21 – 2.06 (m, 1H), 2.06 – 1.92 (m, 2H), 1.75 (dd, *J* = 26.3, 13.2, 1H CH_2), 1.46 (td, *J* =2.72, 13.82, 1H, CH_2), 1.39 (d, *J* = 7.2, 3H, CH_3), 1.29 (d, *J* = 7.1, 3H, CH_3), 1.17 (d, *J* = 7.1, 3H, CH_3), 1.12 (d, *J* = 7.0, 3H, CH_3), -16.47 (s, 1H, OsH) $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ 187.21 (d, *J* = 10.8, CO), 157.55 (s, Py), 153.33 (s, Py), 136.48 (s, Py), 125.10 (s, Py), 121.10 (s, Py), 63.35 (s, CH_2), 56.64 (s, CH_2), 28.97 (d, *J* = 29.7, CH), 28.28 (d, *J* = 37.7, CH), 26.25 (s, CH_2), 20.54 (s, CH_3), 20.00 (d, *J* = 26.2, CH_2), 19.20 (s, CH_3), 19.07 (s, CH_3), 18.61 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ 22.2 (s). Anal. Calcd for $C_{16}H_{28}ClN_2OOsP$: C, 36.88; H, 5.42; N, 5.38. Found: C, 36.91; H, 5.19; N, 5.04.

$OsHCl(CO)[PyCH_2NH(CH_2)_2OP(\textit{i}Pr)_2]$ (3). A flask containing a mixture of $OsHCl(CO)(AsPh_3)_3$ (1.74 g, 1.49 mmol) and $PyCH_2NH(CH_2)_2OP(\textit{i}Pr)_2$ (400 mg, 1.49 mmol) in 23 mL of *m*-xylene was placed in a preheated to 150 °C oil bath and stirred for 1 h, affording a dark-red suspension. After cooling to room temperature, the mixture was placed in a freezer at -14 °C for 2 h. The precipitated product was filtered off, washed with diethyl ether (3 × 2 mL), and dried under vacuum for 1 h to give a brown-grey solid. Yield: 530 mg (68 %). ^{1}H NMR (CD_2Cl_2) δ 8.94 (d, *J* = 5.4, 1H, Py), 7.72 (td, *J* = 7.7, 1.1, 1H, Py), 7.37 (d, *J* = 7.8, 2H, Py), 7.32 – 7.22 (m, 1H, Py), 4.54 (dd, *J* = 13.5, 2.9, 1H, CH_2), 4.13 – 3.72 (m, 4H), 3.37 (dt, *J* = 12.7, *J*(HP) =3.7, 1H, CH_2), 2.87 (dd, *J* = 21.6, 10.8, 1H, CH_2), 2.77 – 2.52 (m, 1H, CH), 2.26 – 2.04 (m, 1H, CH), 1.32 (dd, *J* = 15.7, 7.4, 3H), 1.23 (dd, *J* = 13.7, 7.2, 3H), 1.09 (dd, *J* = 11.9, *J*(HH) = 3.9, 3H), 1.02 (dd, *J* = 14.5, *J*(HH) = 4.3, 3H), -16.08 (d, *J* = 20.4, 1H, OsH). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ 187.94 (d, *J* = 10.0, CO), 157.14 (s, Py), 153.31 (s, Py), 136.96 (s, Py), 125.28 (d, *J* = 1.8, Py), 121.48 (d, *J* = 2.1, Py), 66.92 (s, CH_2), 62.80 (s, CH_2), 56.13 (s, CH_2), 33.28 (d, *J* = 29.1, CH), 32.40 (d, *J* = 46.2, CH), 18.82 (s, CH_3), 18.27 (d, *J* = 3.0, CH_3), 18.15 (d, *J* = 5.8, CH_3), 17.16 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ 136.4 (s, 1P). Anal. Calcd for $C_{15}H_{27}ClN_2O_2OsP$: C, 34.38; H, 5.19; N, 5.35. Found: C, 34.51; H, 4.83; N, 5.35.

$OsH(CO)[PyCH_2N(CH_2)_2NHP(\textit{t}Bu)_2]$ (5). Complex **1b** (20.6 mg, 0.037 mmol) and *t*BuOK (4.2 mg, 0.037 mmol) were reacted in THF-d_8 (0.64 g) in a NMR tube to cleanly give a solution of **5**, characterized by NMR. $^{31}P\{^1H\}$ NMR (THF-d_8) δ 86.0 (s). ^1H NMR (THF-d_8) δ 9.09 (d, *J* = 5.6, 1H, Py), 7.69 (t, *J* = 7.8, 1H, Py), 7.53 (d, *J* = 7.6, 1H, Py), 7.05 (t, *J* = 6.6, 1H, Py), 4.22 (d, *J* = 21.7, 1H, CH_2), 3.83 (d, *J* = 21.7, 1H, CH_2), 3.28 – 3.17 (overlapped, 3H, CH_2), 2.96 (m, 1H, CH_2), 2.69 (br, 1H, NH), 1.30 (d, *J* = 12.3, 9H, CH_3), 1.27 (d, *J* = 12.4, 9H, CH_3), −21.07 (d, *J* = 16.0, 1H, OsH); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 196.87 (d, *J*(CP) = 8.2, CO), 167.08 (s, C, Py), 155.06 (s, CH, Py), 135.54 (s, CH, Py), 122.93 (d, *J* = 2.3, CH, Py), 120.20 (d, *J* = 1.9, CH, Py), 75.82 (d, *J* = 3.2, $PyCH_2$), 61.59 (d, *J* = 2.0, CH_2), 52.76 (d, *J*(CP) = 6.8, CH_2), 41.07 (d, *J*(CP) = 30.5, C), 40.76 (d, *J*(CP) = 32.5, C), 29.78 (d, *J*(CP) = 4.6, CH_3), 28.77 (d, *J*(CP) = 4.3, CH_3).

A NMR tube reaction of **1b** with NaOMe also produced **5**, at a slow rate. Formation of **5** from **1b** and NaOEt in THF was also evident by ESI-MS. Disappearance of peaks due to **1b** (manifested as [**1b** - Cl]$^+$ and [**1b** + Na]$^+$ cations) concomitant with formation of **5** (manifested as [**5** - H]$^+$, Figure S4c) was observed. M06L calculations of **5** found the $OsH(CO)(PyCH_2NC_2H_4NHP$*t*$Bu_2]$ structure to be more stable than the alternative formulations:



$OsH_2(CO)[PyCH_2NH(CH_2)_2NHP($*t*$Bu)_2]$ (6). 1 M solution of $Li[Et_3BH]$ in THF (6.49 g, 7.27 mmol) was added into a 20 mL vial containing 2 g (3.64 mmol) of complex **1b** and a 1.3 × 0.95 cm (½ × ⅜") rare-earth (samarium-cobalt) spinbar. The mixture was stirred for 1 h. Most of **1b** dissolved in the first 10 – 15 min affording an orange solution. Then, the product precipitated and the mixture became thick and somewhat difficult to stir. The product was isolated by vacuum filtration, washed with 3 × 2 mL of THF, and dried under vacuum for 16 h. Yield: 1.30 g (69%) of a bright-yellow thermally stable powdery solid. NMR spectra of **6** in DMSO-d_6 revealed complex **6** and residual THF, with **6** as a mixture of two isomers: *mer*-, *trans*- (**6a**, 86%) and *fac*-, *cis*- (**6b**, 14%), see Scheme 3. In THF-d_8, the *trans*/*cis* isomer ratio is close to 4:1 at room temperature. M06L calculations (vide infra) of the isomers of **6** in THF gave a ΔG value of 0.3 kcal/mol, in agreement with the experimental ΔG = 0.8 kcal/mol. $^{31}P\{^1H\}$ NMR ([D6]DMSO) δ 93.2 (s, **6a**), 80.1 (s, **6b**). ^1H NMR of **6a** (DMSO-d_6) δ 9.01 (d, *J* = 5.2, 1H, Py), 7.63 (t, *J* = 7.4, 1H, Py), 7.40 (d, *J* = 7.6, 1H, Py), 7.12 (t, *J* = 6.6, 1H, Py), 5.49 (br. t, 1H, NH), 4.34 (dd, *J* = 3.6, 13.8, 1H, CH_2), 3.33 (t, *J* = 12.6, 1H, CH_2), 3.18 (m, 1H, CH), 3.07 (2H, NH+CH), 2.77 (m, 1H, CH_2), 2.39 (q, *J* = 10.3, 1H, CH_2), 1.28 (d, *J* = 12.4, 18H, CH_3), −4.74 (dd, *J* = 5.8, 14.1, 1H, OsH), −5.17 (dd, *J* = 5.8, 13.4, 1H, OsH). ^1H NMR of **6b** (DMSO-d_6), the hydride resonances: δ −4.69 (dd, *J* = 6.7, 91.2, 1H, OsH), −13.97

(dd, *J* = 6.7, 16.9, 1H, OsH). $^{13}C\{^1H\}$ NMR (DMSO-d$_6$) δ 193.72 (d, *J*(CP) = 11, CO), 157.91 (s, C, Py), 151.70 (s, CH, Py), 133.59 (s, CH, Py), 123.29 (s, CH, Py), 120.56 (s, CH, Py), 63.91 (d, *J* = 2.5, PyCH$_2$), 57.08 (s, CH$_2$), 46.15 (d, *J*(CP) = 3.7, CH$_2$), 41.01 (d, *J*(CP) = 24.8, C), 37.18 (d, *J*(CP) = 35.4, C), 29.69 (d, *J*(CP) = 4.3, CH$_3$), 29.07 (d, *J*(CP) = 4.6, CH$_3$). Anal. Calcd for $C_{17}H_{32}N_3OOsP$·0.075 THF: C, 39.88; H, 6.31; N, 8.06. Found: C, 39.89; H, 6.33; N, 8.02. The ESI mass spectrum of **6** displays peaks due to [**6** - H]$^+$ and [**6** + Na]$^+$. The collision induced dissociation (CID) mass spectrum of [**6** + Na]$^+$ exhibits formation of [**5** + Na]$^+$ (Figures S5-6), indicating a tendency of the dihydride to lose H_2.

Although good-quality NMR spectra of **6** were obtained in DMSO-d$_6$, even a freshly prepared and sealed under H_2 solution of **6** in THF-d$_8$ exhibited broad resonances at δ -20.8 (^{1}H) and 85.6 (^{31}P) due to **5** (17% of the dissolved material). Formation of *trans*-**6** from **5** under 1 atm of H_2 in THF is favourable by calculated ΔG = -2.6 kcal/mol (M06L calculations, vide infra). Thus, the equilibrium constant is ca. 80 at r.t., being qualitatively consistent with the formation of **5** from **6** in THF. Two unidentified minor species appear in solutions of **6** in THF-d$_8$ under H_2 upon standing: ^{1}H δ -11.4 (dd, *J* = 3.2, 24.4 Hz), -18.66 (dd, *J* = 3.2, 18.8 Hz). These also form with time in THF solutions of **5**.

An NMR tube reaction of **6** (0.033 M, THF-d$_8$) with ca. 1.1 equiv. of methylformate produced an equivalent of MeOH with ca. 0.6 equiv. of unreacted HCO_2Me, wherein **6** was converted to **5**. No methoxide, OsH(OMe)(CO)(NNNP-*t*Bu) was observed. If, based on [**5**], there was ≤ 1 mol% of the methoxide in the sample, and assuming [**5**] ≈ [MeOH] ≈ 0.033 M, the equilibrium constant, [methoxide]·[**5**]$^{-1}$·[MeOH]$^{-1}$ < 1 and ΔG > 0 at r.t. A NMR tube reaction of **1b** with NaOMe also gave **5**. We thus conclude that the methoxide OsH(OMe)(CO)(NNNP-*t*Bu) must be unstable.

Details of the Catalytic Studies

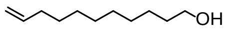
All ester hydrogenation experiments of Table 2 with 20 mmoles of the substrates were performed in a 70 mL stainless-steel Parr reactor, and those with 40 – 100 mmoles of the substrates were performed in a 300 mL stainless-steel Parr reactor fitted with a glass liner. Teflon tape was wrapped around the glass liner, around the rim, to seal the narrow gap between the steel body of the reactor and the glass liner. This way, the liner fitted tightly into the reactor that mostly prevented the volatiles from collecting outside the liner.

*The typical procedure of ester hydrogenation catalyzed by **1b**.* In an argon glovebox, the required amounts of the catalyst (typically between 4.4 to 11.0 mg) and the base were weighted into a 20 mL vial on a calibrated analytical balance accurate to 0.1 mg. This vial was emptied into the reactor (that resulted in a transfer of ca. 97% of the solids) and subsequently it was used to collect the substrate (0.04 moles), followed (when required) by 2-propanol (14 mL). After stirring in the vial, the liquids were poured into the reactor (typical residual amounts of the liquids left behind in the vial were about 50 mg; therefore the substrate and the solvent were weighted to include extra 50 mg quantities, to compensate for the incomplete transfer). Afterwards, the reactor was closed, taken out of the glovebox, tightened, connected to a tank of UHP H_2, and pressurized to 725 psi (50 Bar). Then the reactor was disconnected from the hydrogen tank and placed in an oil bath preheated to 100 $^{\circ}$C. At the end of the reaction time, the reactor was moved into a cold tap water bath for 20 – 30 min and depressurized. All reaction mixtures were analyzed within 10 – 20 min by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, using ca. 0.2 g samples taken from the reactor and dissolved in ca. 0.5 mL of anhydrous CD_2Cl_2. All ^{1}H NMR spectra were collected with a 5 s acquisition time and a 30 s relaxation delay between 0.5 μs pulses, to ensure accurate integration.

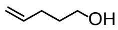
The typical procedure of acceptroless dehydrogenative coupling. In an argon glovebox, the required amounts of **1b** or **6** (typically between 6 and 22 mg) and the base (when used) were weighted into two 50 mL reaction tubes on a calibrated analytical balance accurate to 0.1 mg. Next, the required amounts of the substrates (typical total volume: 10 to 12 mL) were weighted into the reaction tubes on a balance accurate to 1 mg. After taking the tubes out of the box, they were connected to a vacuum/Ar manifold. Under argon, the stoppers were replaced by finger condensers connected to a circulating refrigerated bath. When the temperature in the bath reached -5 °C, the flasks were placed in an oil bath, the argon tank was closed, and H_2 produced as the bath temperature increased to 90 °C was allowed to pass freely through a mineral oil bubbler (independently from each reaction flask). Throughout the reaction, the temperature in the cold fingers was maintained between -10 and -15 °C. The experimental setup is pictured in Figure S2.

Figure S2. The ADC reactions of methanol with butylamine and benzylamine (see entries 5-6, Table 3).

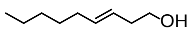
Identification of the products of catalytic hydrogenaton.



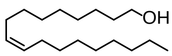
The product is identified by ^{1}H NMR by the diagnostic vinyl proton resonances at 5.80, 4.97, and 4.90 ppm in combination with the resonance of CH_2O at 3.53 (t, J=6.8 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 139.82, 114.54, 62.78, 34.51, 33.43, 30.31, 30.20, 30.16, 29.84, 29.67, 26.56. Hydrogenation of the C=C bond gives rise to ^{1}H and ^{13}C methyl resonances at δ 0.79 and 14.1 ppm, respectively, whereas the 9-enes exhibit the distinct ^{13}C shifts at δ 12.6, 123.7, 131.0 (*Z*) and 17.8, 124.8, 131.9 (*E*).



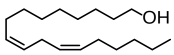
The product is identified by ^{1}H NMR by the diagnostic vinyl proton resonances at 5.82, 5.01, and 4.93 ppm in combination with the resonance of CH_2O at 3.55 (t, J=6.6 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 139.12, 114.91, 62.14, 32.47, 30.70.



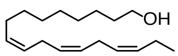
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances at 5.50 and 5.38 ppm in combination with the resonance of CH_2O at 3.54 (t, J=6.8 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 133.83, 126.73, 62.58, 36.68, 33.29, 32.06, 29.85, 23.17, 14.44.



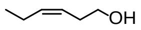
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonance at 5.35 ppm in combination with the resonance of CH_2O at 3.57 (t, J=6.7 Hz). ^{13}C NMR (C_6D_6): δ 130.55, 130.52, 62.97, 33.56, 32.71, 30.64, 30.62, 30.44, 30.38, 30.34, 30.17, 30.14, 30.12, 28.08, 28.07, 26.67, 23.49, 14.74.



The product is identified by ^{1}H NMR by the diagnostic CH=CH resonance at 5.28 ppm in combination with the resonances of CH_2O at 3.49 (t, J=6.8 Hz) and =$CHC\underline{H}_2CH$= at 2.71 ppm (t, J=6.5). ^{13}C NMR (CD_2Cl_2): δ 130.68, 130.64, 128.55, 128.52, 63.15, 33.43, 32.20, 30.35, 30.22, 30.14, 30.03, 29.95, 27.86, 27.82, 26.47, 26.22, 23.23, 14.50.

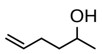


The product is identified by ^{1}H NMR by the diagnostic CH=CH resonance at 5.36 ppm in combination with the resonances of CH_2O at 3.57 (t, J=6.7 Hz) and =$CHC\underline{H}_2CH$= at 2.82 ppm (t, *J*=6.1). ^{13}C NMR (CD_2Cl_2): δ 132.42, 130.85, 128.81, 128.78, 128.23, 127.71, 63.10, 33.41, 30.32, 30.20, 30.13, 29.93, 27.86, 26.46, 26.20, 26.10, 21.15, 14.70.



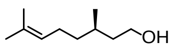
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances at 5.46 and 5.32 ppm in combination with the resonance of CH_2O at 3.53 (t, *J*=7.0 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 134.42, 125.52, 62.44, 31.36, 21.23, 14.70.

The product (like the corresponding ester) is a mixture of *cis*- (34%) and *trans*- (66%) isomers identified by ^{1}H NMR by the diagnostic =CH resonances at 4.96 and 4.89 ppm in combination with the resonances of CH_2O of the *trans*- isomer at 3.71 (dd, *J*=6.4, 11.4 Hz) and 3.50 (dd, *J*=8.3, 11.4 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): *cis*- δ 135.30, 119.95, 60.35, 31.37, 29.24, 26.78, 26.04, 22.82, 18.80, 18.72. *trans*- δ 133.35, 124.40, 63.46, 35.71, 29.24, 25.94, 23.14, 21.69, 18.72, 18.60.

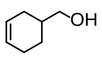


The product is identified by ^{1}H NMR by the diagnostic vinyl proton resonances at 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz), 5.03, and 4.95 ppm in combination with the resonance of CHO at 3.76 (m). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 139.33, 114.83, 67.74, 38.97, 30.76, 23.81.

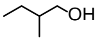
The product is a mixture of *trans*- (6%) and *cis*- (94%) isomers identified by ^{1}H NMR by the diagnostic =CH resonances at 5.52 and 5.44 ppm, respectively, in combination with the resonances of CHO overlapped between 3.88 and 3.94 ppm. ^{13}C NMR (2-propanol/CD_2Cl_2): *cis*- δ 140.08, 122.57, 66.93, 49.53, 33.07, 29.20, 26.93, 25.95, 24.31, 23.76, 23.32, 20.53.



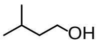
The product is identified by ^{1}H NMR by the diagnostic =CH resonance at 5.13 (m) in combination with the resonance of CH_2O at 3.62 – 3.75 (m). ^{13}C NMR ($CDCl_3$): δ 131.3, 124.7, 61.2, 39.9, 37.2, 29.2, 25.7, 25.4, 19.5, 17.6.



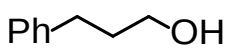
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances overlapped at 5.67 (m) in combination with the resonances of CH_2O at 3.48 – 3.55 (m). ^{13}C NMR (THF): δ 127.2, 126.0, 67.9, 36.4, 28.2, 25.3, 24.7.



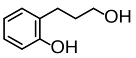
The product is identified by ^{1}H NMR by the diagnostic resonances of $CHC\underline{H}_2O$ at 3.39 (dd, *J*=6.0, 10.4 Hz) and 3.29 ppm (t, *J*=6.8, 10.4 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): 67.84, 38.09, 26.58, 16.67, 11.79.



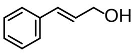
The product is identified by ^{1}H NMR by the diagnostic resonances of $C\underline{H}_2C\underline{H}_2O$ at 1.40 (q, *J*=6.8 Hz) and 3.56 ppm (t, *J*=6.8 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 61.0, 42.33, 25.50, 23.20.



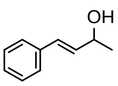
The product is identified by ^{1}H NMR by the diagnostic $PhC\underline{H}_2C\underline{H}_2$- resonances at 2.69 (t, *J*=7.8 Hz) and 1.86 (m) ppm in combination with the resonance of CH_2O at 3.61 (t, *J*=6.6 Hz). ^{13}C NMR (2-propanol/CD_2Cl_2): δ 142.926, 129.035, 128.895, 126.298, 62.10, 35.02, 32.75.



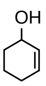
The product is identified by ^{1}H NMR by the diagnostic resonances of $C\underline{H}_2C\underline{H}_2C\underline{H}_2O$ at 2.77 (t, *J*=7.4 Hz), 1.89 (m), and 3.64 ppm (t, *J*=6.2 Hz) together with four CH resonances in the 6.8 to 7.2 ppm range. ^{13}C NMR (2-propanol/CD_2Cl_2): δ 155.67, 130.99, 128.88, 127.69, 120.61, 116.30, 61.62, 33.33, 26.56.



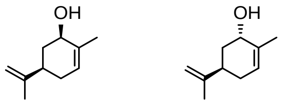
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances at 6.57 (d, *J*=15.9 Hz) and 6.36 (dt, *J*=5.0, 15.9 Hz) ppm in combination with the resonance of CHO at 4.30 (d, *J*=5.0 Hz). ^{13}C NMR ($CDCl_3$): δ 136.76, 130.77, 128.60, 128.53, 127.53, 126.44, 63.21.



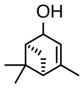
The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances at 6.57 (d, *J*=15.9 Hz) and 6.30 (dd, *J*=5.8, 15.9 Hz) ppm in combination with the resonance of CHO at 4.49 (qui, *J*=6.1 Hz).



The product is identified by ^{1}H NMR by the diagnostic CH=CH resonances (all m) at 5.75 and 5.69 ppm in combination with the resonance of CHO at 4.13. ^{13}C NMR (2-propanol/CD_2Cl_2): δ 131.20, 130.07, 65.84, 32.62, 25.65, 19.96.



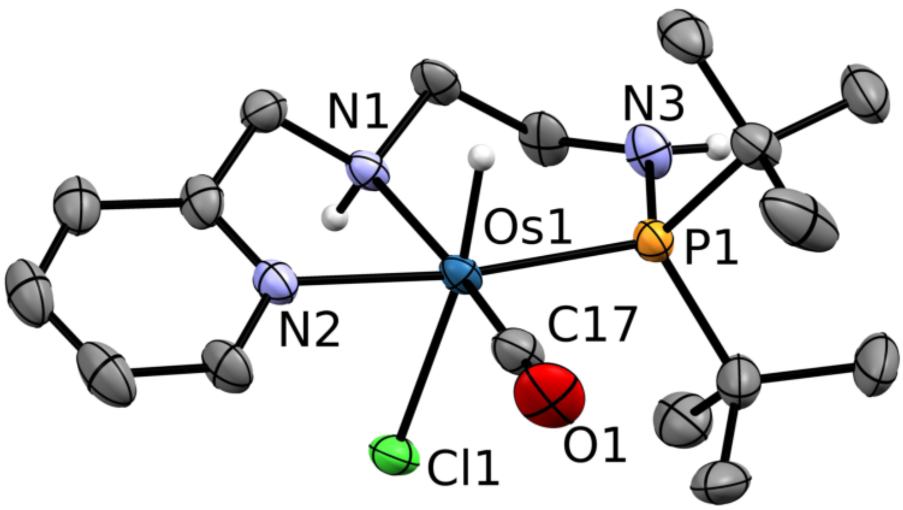
The product is a mixture of *cis*- (92%) and *trans*- (8%) isomers identified by ^{1}H NMR by the diagnostic =CH resonances (all m) at 5.44 and 5.53 ppm, respectively, in combination with the =CH_2 resonances at 4.71 and 4.67, and that of CHO at 4.13 ppm. ^{13}C NMR (2-propanol/CD_2Cl_2): *cis*- δ 149.84, 137.42, 123.93, 109.12, 71.08, 41.51, 38.61, 31.75, 20.63, 19.17.



The product is identified by ^{1}H NMR by the diagnostic =CH resonance at 5.41 in combination with the resonance of CHO at 4.53. ^{13}C NMR (THF): δ 145.55, 120.20, 72.42, 48.12, 48.06, 39.09, 35.16, 27.11, 22.82, 22.53.

Crystal Structure Determination.

Single crystals of complexes **1b** and **1c** were grown by slow diffusion of hexanes into their saturated solutions in dichloromethane. Diffraction data for **1b** and **1c** were collected with Cu Kα radiation on a Bruker Microstar/Proteum equipped with Helios MX mirror optics and rotating anode source (**1b**), or on a Bruker Microsource/APEX2 (**1c**) systems. Cell refinement and data reduction were done using SAINT.[5] An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[6] The space group was confirmed by XPREP routine[7] of SHELXTL.[8] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-2013[9] as a part of LinXTL[10] tool box. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter, except those of the NH, OH moieties and hydrides, which were positioned from residual peaks in the difference Fourier map. All publication materials (cif files validation and ORTEP drawings) were prepared using LinXTL and Platon[11] programs.



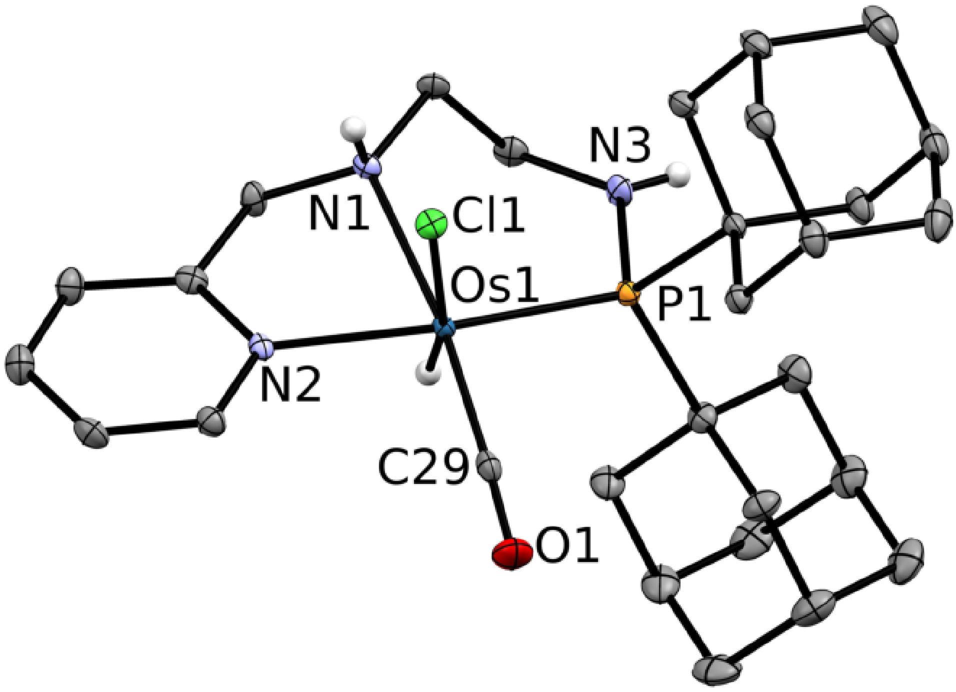


Figure S3. ORTEP diagrams for complexes **1b** and **1c**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystal Data Collection and Refinement Parameters for Complexes **1b** and **1c**.

	1b	**1c**
chemical formula	$C_{17}H_{27}N_3OPClOs$	$C_{29}H_{43}N_3OPClOs$
crystal colour	Yellow	Yellow
Fw; *F*(000)	550.07; 1080	706.28; 2832
T (K)	150	100
wavelength (Å)	1.54178	1.54178
space group	P21/c	C2/c
a (Å)	12.8403(4)	29.5260(3)
b (Å)	10.7117(3)	13.6981(2)
c (Å)	15.9847(5)	13.5978(2)
α (deg)	90	90
β (deg)	110.275(1)	90.42
γ (deg)	90	90
Z	4	8
V ($Å^3$)	2062.3(1)	5499.5(1)
ρ_{calcd} ($g{\cdot}cm^{-3}$)	1.772	1.706
μ (mm^{-1})	13.672	10.412

θ range (deg); completeness	3.670 − 70.056; 0.988	2.993 − 71.248; 0.989
collected reflections; R_σ	66993; 0.0201	35741; 0.0200
unique reflections; R_{int}	66993; 0.0622	35741; 0.0339
R1[a]; wR2[b] [I > 2σ(I)]	0.0426; 0.1371	0.0197; 0.0503
R1; wR2 [all data]	0.0435; 0.1374	0.0198; 0.0503
GOF	1.174	1.181
largest diff peak and hole	3.542 and -1.428	0.716 and -0.584

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1b** and **1c**.

1b			**1c**	
C17-Os1	1.85(1)		C29-Os1	1.843(3)
Cl1-Os1	2.531(2)		Cl1-Os1	2.5409(5)
N1-Os1	2.191(8)		N1-Os1	2.187(2)
N2-Os1	2.133(8)		N2-Os1	2.127(2)
Os1-P1	2.311(3)		Os1-P1	2.2943(6)
C17-Os1-N1	172.27(9)		C29-Os1-N1	172.27(9)
N2-Os1-N1	76.2(3)		N2-Os1-N1	75.49(8)
C17-Os1-P1	92.1(4)		C29-Os1-P1	91.97(8)
N1-Os1-P1	95.75(6)		N1-Os1-P1	95.75(6)
C17-Os1-N2	95.4(4)		C29-Os1-N2	93.78(7)

Electrospray Ionization Mass Spectrometry (ESI-MS) and Collision Induced Dissociation (CID) experiments.

ESI-MS studies were conducted on a QTOF Premier instrument with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK) operating in the W-mode at a resolution of ca. 15000 (FWHM). The drying and cone gas was nitrogen set to flow rates of 300 and 30 L/h, respectively. A capillary voltage of 3.5 kV was used in the positive ESI(+) scan mode. The cone voltage was adjusted to a low value (typically Uc = 5−15 V) to control the extent of fragmentation in the source region. Chemical identification of the Os-containing species was facilitated by the characteristic isotopic pattern at natural abundance of Os and it was carried out by comparison of the isotope experimental and theoretical patterns using the MassLynx 4.1. For CID experiments, the cations of interest were mass-selected using the first quadrupole (Q1) and interacted with argon in the T-wave collision cell at variable collision energies ($E_{laboratory}$ = 3 -15 eV). The ionic products of fragmentation were analyzed with the time-of-flight analyzer. The isolation width was 1Da and the most abundant isotopomer was mass-selected in the first quadrupole analyzer.

ESI-MS characterization of compounds 1b, 5 and 6.

Compound 1b. For ESI-MS characterization of **1b**, ethanol sample solutions were introduced through a fused-silica capillary to the ESI source via syringe pump at a flow rate of 10 μL/min. The most favorable ionization mechanism for **1b** in neat ethanol was Os-Cl bond breaking to yield the [**1b** – Cl]$^+$ (m/z 516.2) cation. A minor signal due the intact compound as sodium adduct, namely [**1b** + Na]$^+$ (m/z 574.2) was also observed. Because of the interest of finding out the chemical environment at the Os site (both for characterization purposes and during catalysis) by ESI-MS, we modified the mobile phase in order to maximize the visualization of the intact **1b** species via sodium adduct formation. For this purpose, ethanol solutions of compound **1b** and $NaBF_4$ were mixed using a micro reactor directly coupled to the ESI source, increasing the ion abundances of the [**1b** + Na]$^+$ cation, the [**1b** – Cl]$^+$ still being the base peak (see Figure S4a).[12]

Compound 5. Analogous procedure to that described above for **1b** was applicable for the ESI-MS characterization of **5**; however, the use of ethanol as the mobile phase resulted in formation of a new species formulated as OsH(OEt)(CO)(NNNP-*t*Bu) (MS**1**) corresponding to the addition of EtOH to compound **5** (see Figure S4b). We believe that MS**1** results from the large excess of EtOH with respect to **5** used for the ESI-MS analysis, which shifts the **5** + EtOH equilibrium towards MS**1**. Support to this hypothesis (and in agreement with NMR characterization of **5**) is given by inspection of the ESI mass spectrum of **5** in THF where the [**5** – H]$^+$ cation was observed and species MS**1** was not detected (see Figure S4c).

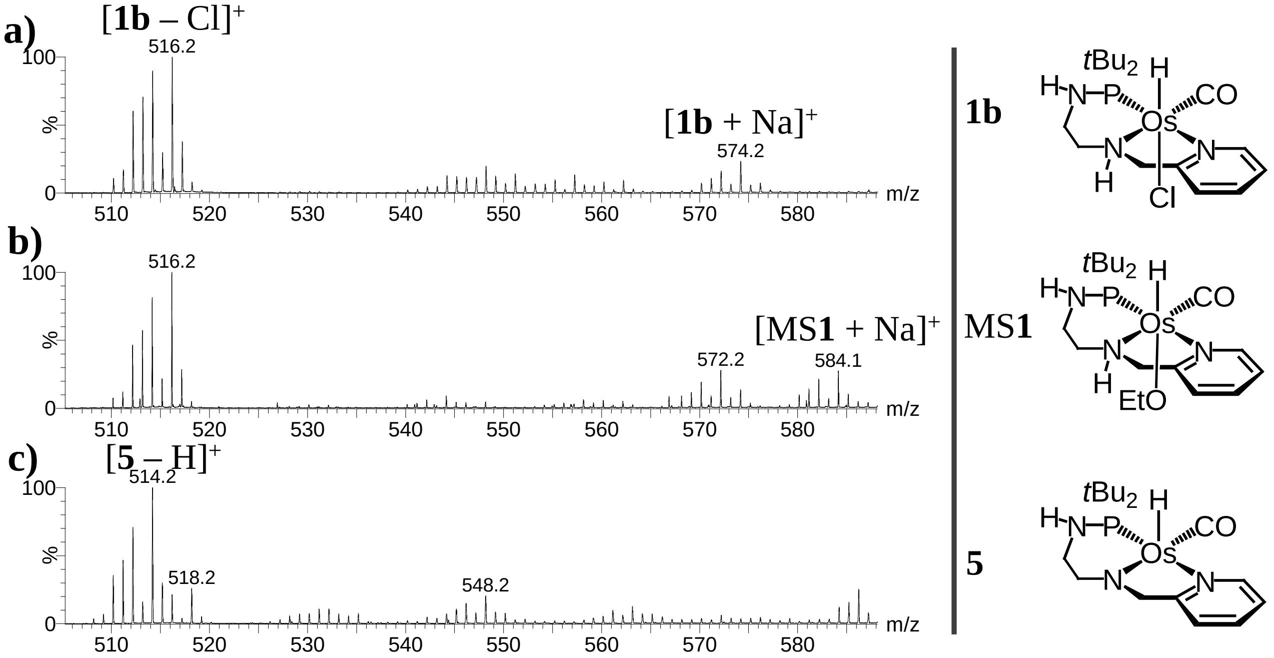


Figure S4. a) ESI mass spectrum of ca. 1 × 10^{-5} ethanol solution of **1b** and ethanol solution of $NaBF_4$ mixed using a micro reactor directly coupled to the ESI source (the peaks at m/z 516.2 and 574.2 correspond to [**1b** - Cl]$^+$ and [**1b** + Na]$^+$, respectively; b) ESI mass spectrum of a reaction of **1b** with NaOEt in ethanol, further diluted to ca. 1 × 10^{-5} M with ethanol; c) ESI mass spectrum of the reaction of **1b** with NaOEt in THF, further diluted to ca. 1 × 10^{-5} M with THF.

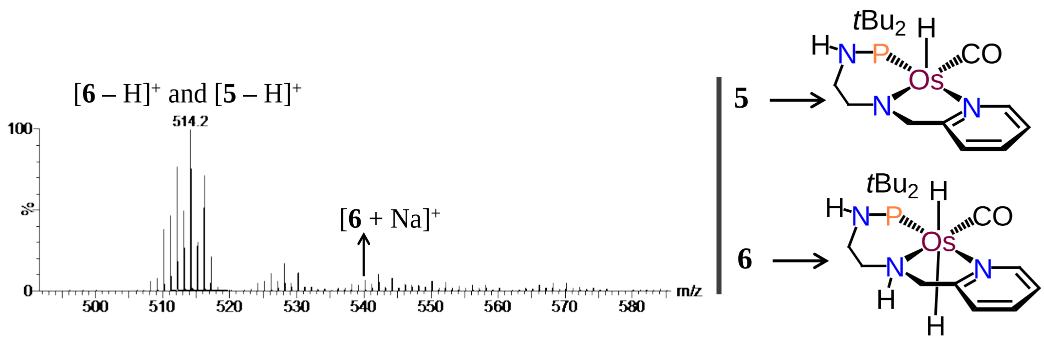


Figure S5. a) ESI mass spectrum of ca. 1 × 10^{-5} M THF solutions of **6**. Note the coexistence of species [**6** – H]$^+$ and [**5** – H]+ in the m/z 510-516 region. The [**6** + Na]$^+$ cation was barely detected at m/z 540.2.

Compound 6. All attempts to detect the intact compound **6** in ethanol were unsuccessful due its intrinsic instability in this solvent. For this particular case, ESI-MS was performed in THF solutions of **6** and coexistence of compounds **5** and **6** was evidenced. This is clearly seen in Figure S5 where partially overlapped peaks due to [**6** – H]$^+$ (m/z 516.1) and [**5** – H]$^+$ (m/z 514.1) were observed in agreement with the NMR characterization of **6** in THF. Low-intensity peaks assigned to [**6** + Na]$^+$ were also detected. The CID mass spectrum of the [**6** + Na]$^+$ adduct (mass selection at m/z 540.2) illustrates the propensity of compound **6** to expel H_2 in the gas-phase, leading to compound **5** (see Figure S6).

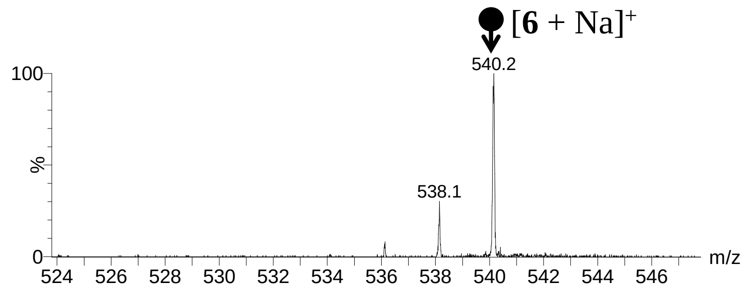


Figure S6. CID mass spectrum of a mass-selected [**6** + Na]$^+$cation at m/z 540.2 ($CE_{Elaboratory}$ = 10 eV).

Pressurized sample introduction and ESI-MS studies of 1b under catalytic conditions. Figure S7a illustrates the detection of reaction intermediates by ESI-MS using the pressurized sample infusion technique.[13] This technique has proved to be ideal for *in situ* analyzing complex mixtures during catalysis. Note that in the system depicted in Figure S7b i) the NaOEt base in the catalytic system produces significant ion abundances of sodium adducts of the ESI-MS detected species, so that neat ethanol was used as the diluting solvent (instead of $NaBF_4$ solutions in ethanol, used for the characterization of **1b**, **5**, and **6** above) and ii) obtaining the temporal profile of this particular catalytic reaction was not possible because of the continuous delivery of NaOEt into the ESI source which dramatically reduces the sensitivity of the experiment.

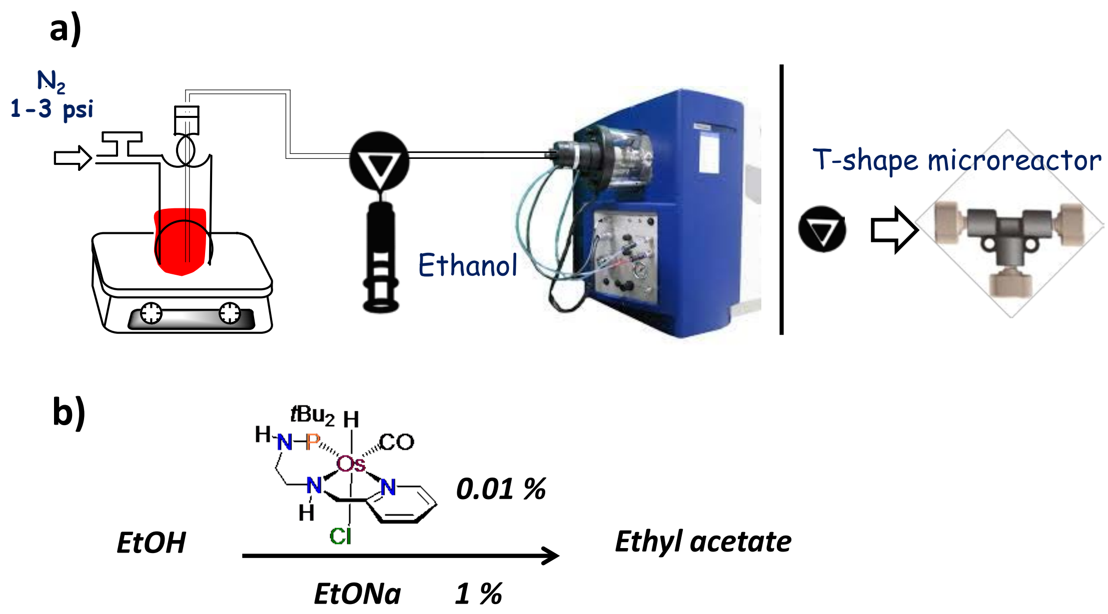


Figure S7 a) Experimental setup for the pressurized sample infusion technique using compound **1b**; b) The catalytic reaction.

The ESI mass spectra were recorded at different time intervals by introducing the sample solutions under N_2 pressure (1-3 psi) according to Figure S7a. Further dilution with ethanol was carried out prior to the delivery of the samples into the mass spectrometer. Figure S8 shows the typical ESI mass spectra, recorded after 30 minutes and 1 hour. The base peak in all ESI mass spectra along the reaction is that at m/z 516.2, corresponding to $[OsH(CO)(PyCH_2NHC_2H_4NHP\mathit{t}Bu_2)]^+$. This cation forms by Os-X bond breaking of the OsHX(CO)(NNNP-*t*Bu) reaction intermediates, yielding $[M - X]^+$ where X could be Cl, OEt, 1-ethoxyethanolate or acetate and, consequently, it is not a diagnostic peak. We use the observation of sodium $[M + Na]^+$ adducts as the identification criterion of the intermediates.

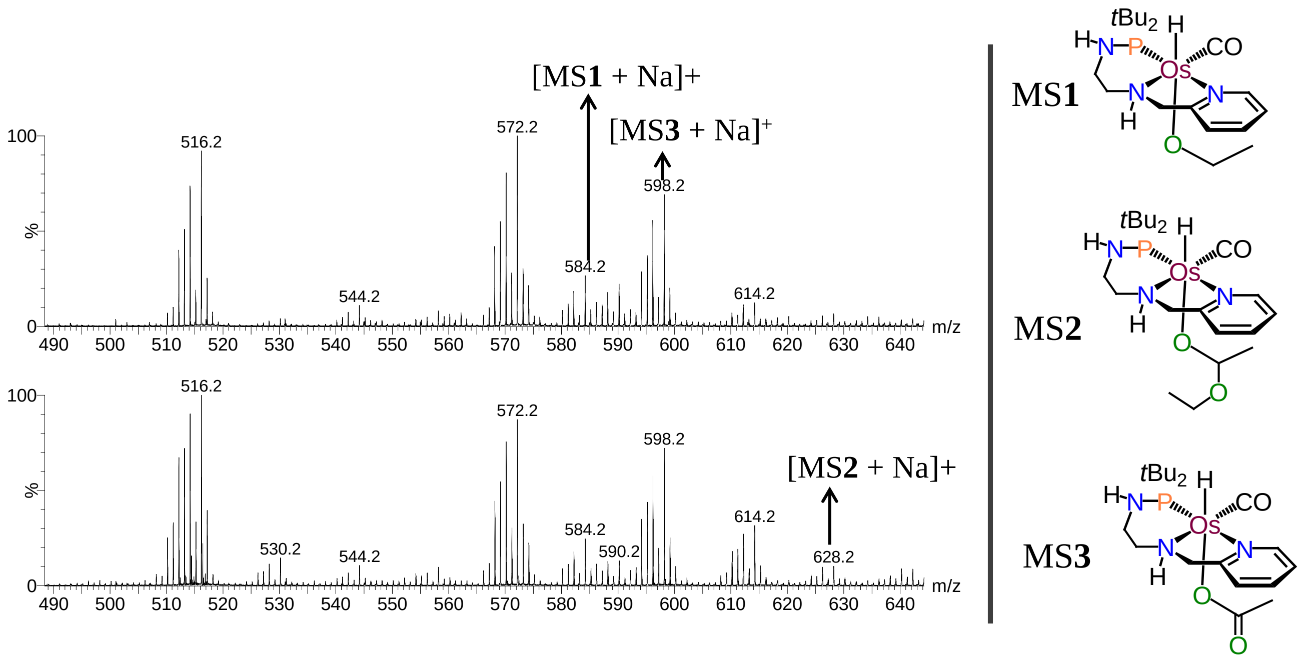


Figure S8. ESI mass spectrum ethanol (2 mL) in the presence of 0.01 % of **1b** and 1 % EtONa under reflux after 30 (top) and 60 (bottom) minutes using the pressurized sample infusion technique.

We observed disappearance of peaks due to **1b** and formation of new species in the early stages of the reaction. One of these was intermediate MS**1** identified as the $[MS\mathbf{1} + Na]^+$ cation at m/z 584.2. The ESI-MS studies described above suggest that MS**1** is in equilibrium with **5** and EtOH. and its structural form depicted in Figure S8 has precedent.[14] Intermediate MS**2** is formed as the reaction proceeds and it is manifested as the sodium $[MS\mathbf{2} + Na]^+$ adduct at m/z 628.2. The CID mass spectra (Figure 1 and S9) suggest that it is a 1-ethoxyethanolate complex as depicted in Figure S8. Another prominent peak was observed at m/z 598.2 whose m/z value and CID fragmentation suggest formation of an acetate MS**3** (Figures S8, S11), based on the observed elimination of sodium acetate upon the CID conditions. After repeating the experiments in triplicate, this species was invariably observed. We hypothesize that this acetate species is a side product formed as a consequence of traces of water during sample preparation or most likely during the ESI-MS analysis. Formation of acetate ligands in related ethanol dehydrogenative processes in the presence of water has been recently reported and is proposed to occur via water addition to the putative acetaldehyde bound metal complex.[15] Other prominent species at m/z 572.2 and 614.2 were also observed, although we cannot propose precise structures; according to the m/z values and CID experiments both species possess an acetate ligand and are probably not involved in the catalytic cycle of ADC of ethanol to yield ethylacetate. Species at m/z 572.2 and 614.2 could tentatively be assigned to [(MS**3**-2H) – H]$^+$ and [MS**3** + O + Na]$^+$ cations, respectively.

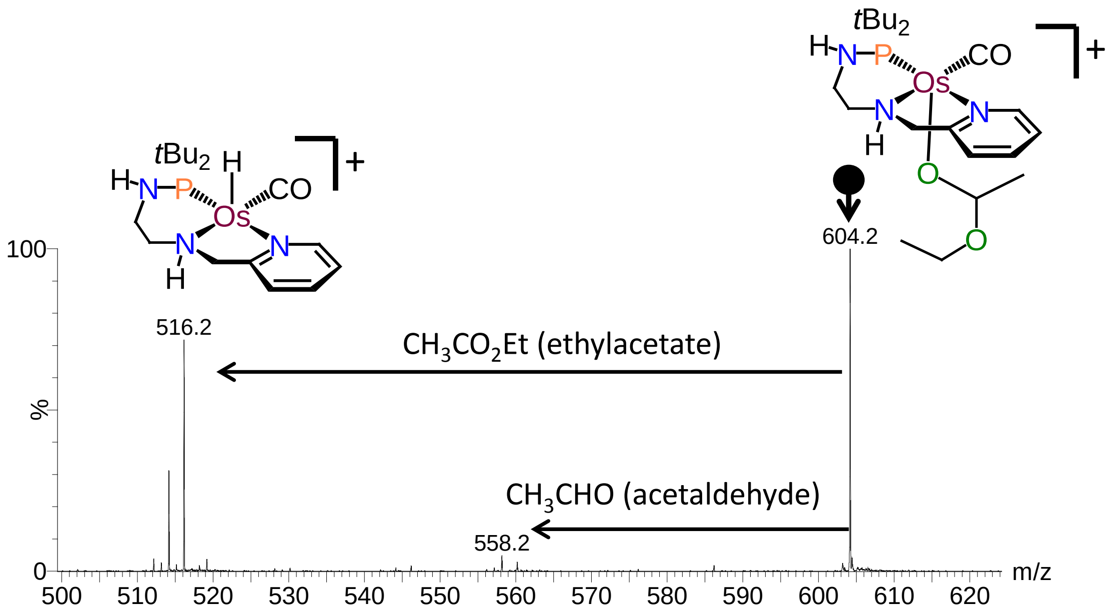


Figure S9. CID mass spectrum of mass-selected [MS**2** – H]$^+$ at m/z 604.2 ($CE_{Elaboratory}$ = 10 eV).

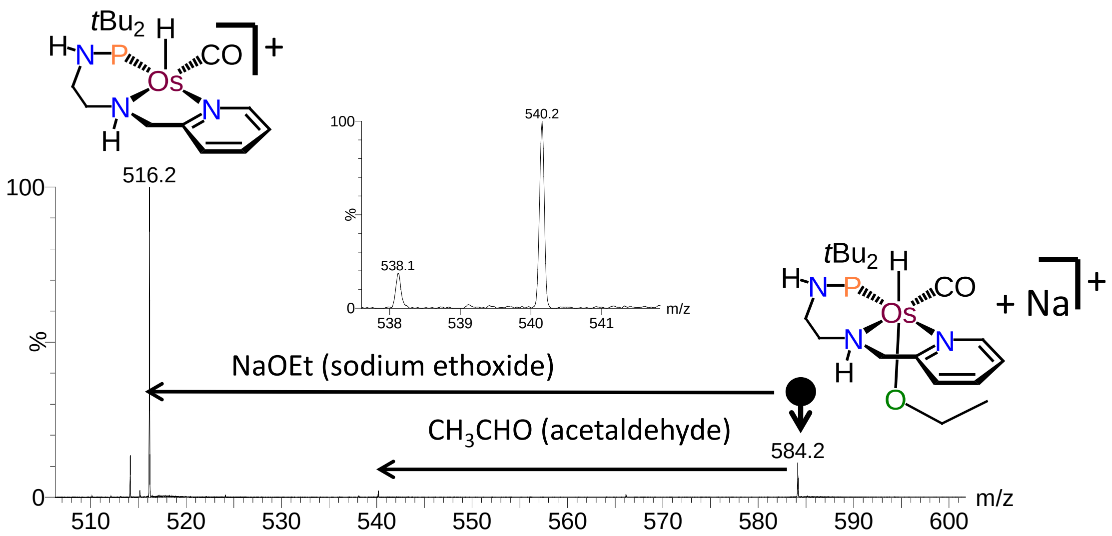


Figure S10. CID mass spectrum of mass-selected [MS**1** + Na]$^+$ at m/z 584.2 ($CE_{Elaboratory}$ = 15 eV). The inset shows the expanded region in the m/z 538 to 540 range to illustrate that a secondary H_2 liberation step is also observed.

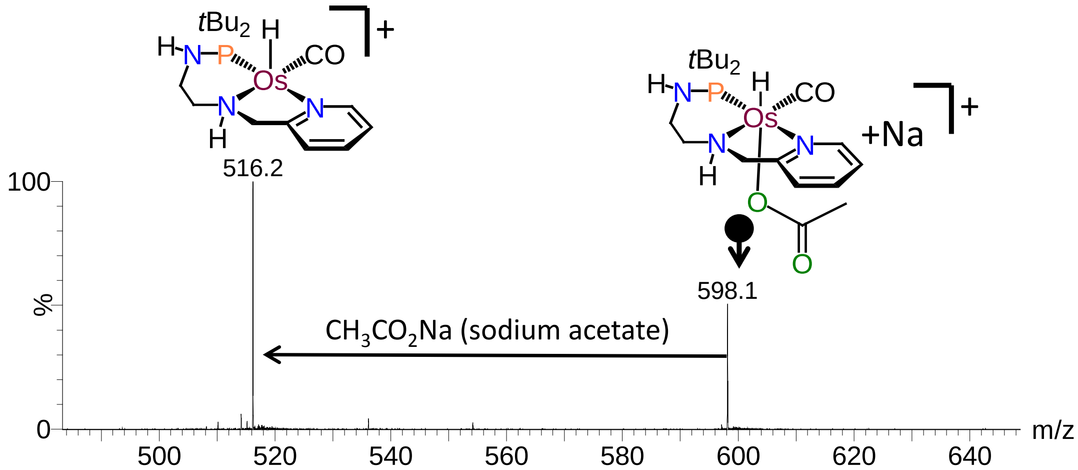


Figure S11. CID mass spectrum of mass-selected [MS**3** + Na]$^+$ at m/z 598.1 ($CE_{Elaboratory}$ = 10 eV).

Calculated data.

For M06L computational details and relevant references, see D.G. Gusev, *Organometallics* **2013**, *32*, 4239.

Table S3. M06L energies and enthalpies (Hartree) of structures fully optimized in the indicated solvents; the free energies were calculated under the corresponding pressure.

Compound	Solvent	Pressure, atm	E	H	G
H_2	None	50	-1.171737	-1.158548	-1.169650
MeOH	MeOH	605	-115.753000	-115.697454	-115.718402
MeOH…OHMe	MeOH	605	-231.513656	-231.400014	-231.432862
EtOH…OHEt	EtOH	419	-310.166911	-309.994162	-310.033884
Trans-OsH_2(CO)(NNNP-*t*Bu)	MeOH	605	-1338.981509	-1338.482409	-1338.556639
Trans-OsH_2(CO)(NNNP-*t*Bu)	THF	302	-1338.977826	-1338.478603	-1338.553526
Cis-OsH_2(CO)(NNNP-*t*Bu)	THF	302	-1338.978120	-1338.477711	-1338.552999
Complex **5**	MeOH	605	-1337.778788	-1337.301872	-1337.377422
Complex **5**	EtOH	419	-1337.779279	-1337.302331	-1337.378145
OsH(OMe)(CO)(NNNP-*t*Bu), **Int1**	MeOH	605	-1453.559039	-1453.022170	-1453.102883
Int2	MeOH	605	-1453.536231	-1452.999428	-1453.085388
Int3	MeOH	605	-1453.523285	-1452.986607	-1453.070459
Int4	MeOH	605	-1453.503036	-1452.970124	-1453.054090
Int5	MeOH	605	-1569.267329	-1568.676854	-1568.772665
Int6	MeOH	605	-1569.272179	-1568.682084	-1568.774393
Int7	MeOH	605	-1568.092913	-1567.520946	-1567.613442
Int7 with η^2-methoxymethoxide	MeOH	605	-1568.097198	-1567.525819	-1567.615467
Int8	MeOH	605	-1568.120695	-1567.548601	-1567.634635
Int9	MeOH	605	-1568.111387	-1567.540223	-1567.626029
Int10, OsH_2(CO)(NNNP-*t*Bu) with methyl formate	MeOH	605	-1568.111185	-1567.542735	-1567.631738
TS1, MeOH elimination from **Int1**	MeOH	605	-1453.535805	-1453.004861	-1453.085676
TS2, between **Int5** and **Int6**	MeOH	605	-1569.252151	-1568.665803	-1568.756262
TS3, between **Int8** and **Int9**	MeOH	605	-1568.101907	-1567.531283	-1567.617367
TS4, between **Int9** and **Int10**	MeOH	605	-1568.102300	-1567.535578	-1567.620326
Rate-limiting **TS** of ADC of EtOH	EtOH	419	-1647.909527	-1647.263964	-1647.361159

Optimized geometries

Cis-$OsH_2(CO)$(NNNP-*t*Bu) in THF

0 1

Os	2.44543200	12.48275600	-1.00235400
P	4.54388700	13.31881700	-1.86077900
C	3.13834800	12.11287800	0.64087700
N	2.22482400	10.41242000	-1.76223300
H	0.85359300	12.24193600	-0.46450400
H	2.18658700	14.05658500	-0.57433400
N	1.40638000	12.68276300	-3.02906400
C	6.04745000	12.14490000	-2.04045700
C	5.13402800	14.92230100	-0.97559800
N	4.41879800	13.82003700	-3.51528000
O	3.54968700	11.81688000	1.70371800
C	1.33539200	10.24435600	-2.76692700
C	2.79210200	9.30852000	-1.23873600
C	2.23077900	12.92142800	-4.23109800
C	0.58695200	11.46835900	-3.18234100
H	0.77012600	13.46902300	-2.93429600
C	7.16938200	12.65020500	-2.94564500
C	6.59411400	11.79431300	-0.66205500
C	5.48131300	10.88131800	-2.68364300
C	4.18877400	16.04495300	-1.40557200
C	5.04396600	14.75618500	0.53837000
C	6.55032700	15.35206700	-1.34213600
H	5.10701400	14.52187500	-3.76293700
C	3.11841500	14.13950600	-4.09313400
C	1.05411700	8.99684200	-3.29902100
H	3.48311100	9.47778600	-0.42209100
C	2.52782400	8.03472800	-1.69729600
H	1.56978100	13.03161400	-5.09740300
H	2.84529900	12.03269500	-4.39607400
H	0.20697900	11.36442900	-4.20337100
H	-0.27275400	11.57517400	-2.51439100
H	6.79344200	12.98018700	-3.91527500
H	7.86054400	11.82474600	-3.13912500
H	7.75454900	13.45443100	-2.51016900
H	5.80474100	11.45287400	0.01183700
H	7.10121500	12.63632500	-0.18928400
H	7.32440800	10.98431800	-0.74546400
H	4.77745200	10.38092000	-2.02509900
H	4.97047400	11.09584100	-3.62567800
H	6.29395600	10.18221600	-2.89893600
H	4.30632600	16.29757400	-2.46115500
H	4.41914000	16.94575600	-0.83033400
H	3.14355800	15.79509900	-1.22440700
H	5.63936400	13.92028600	0.90702900
H	4.01609500	14.60501800	0.86420000
H	5.41868900	15.66203300	1.02395500
H	7.30879000	14.68560400	-0.93306800
H	6.70652000	15.43298600	-2.41999200
H	6.73755500	16.34418400	-0.92095900
H	3.30417400	14.54282000	-5.08958000
H	2.56982500	14.91802800	-3.54098500
H	0.35039800	8.92021400	-4.11812200
C	1.65560000	7.87078400	-2.76271200
H	3.01317300	7.18945800	-1.22866200
H	1.44166300	6.88749100	-3.16081700

Trans-$OsH_2(CO)$(NNNP-*t*Bu) in THF

0 1

Os	2.52406400	12.51595300	-0.81644900
P	4.56832800	13.14027800	-1.72432200
C	3.30727400	12.12305600	0.78665800
H	2.61391600	10.92738800	-1.49098000
H	2.16246100	14.14883700	-0.38281100
N	1.33044100	12.89699000	-2.70280100
N	0.47950100	12.03959400	-0.28081500
C	6.01494700	11.88274300	-1.68960200
C	5.24816100	14.83523100	-1.11382900
N	4.42673300	13.33438200	-3.43807800
O	3.75769000	11.85476100	1.84098600
C	2.05526900	12.79767100	-3.98365600
H	0.96280800	13.84385900	-2.63462700
C	0.19257000	11.96158100	-2.66639800
C	-0.39670200	11.89289900	-1.29941300
C	0.01653800	11.93122000	0.97752500
C	6.68802000	11.87846200	-0.32027200
C	5.43214900	10.49305000	-1.93796000
C	7.05248600	12.13262600	-2.78453600
C	5.19542400	14.90072500	0.40999400
C	6.65709700	15.16597100	-1.59473500
C	4.32020500	15.91064800	-1.68020000
C	3.19269000	13.79102700	-4.07131100
H	5.23041500	13.80443000	-3.83942300
H	2.43191700	11.77580900	-4.06788000
H	1.35635400	12.97182700	-4.80914600
H	0.59504500	10.97521700	-2.92257000
H	-0.56677300	12.21468300	-3.41175900
C	-1.74060100	11.64463400	-1.07625600
H	0.74742300	12.06880500	1.76278000
C	-1.30565300	11.66640200	1.26455200
H	7.25389300	12.78805400	-0.12275400
H	7.39398400	11.04488300	-0.26996500
H	5.96980100	11.73986500	0.48890000
H	4.83734300	10.45500300	-2.85307000
H	4.79766400	10.16556200	-1.11653100
H	6.25435200	9.77956900	-2.04265300
H	7.83005900	11.36758900	-2.70779400
H	7.54892500	13.09661200	-2.71379100
H	6.61614600	12.04106300	-3.77949300
H	4.17556800	14.78236800	0.77649100
H	5.55797400	15.87803200	0.74188200
H	5.81593800	14.14421000	0.88995800
H	6.74792500	15.11192800	-2.68195900
H	7.42381600	14.53127200	-1.15354300
H	6.89423600	16.19575400	-1.31126900
H	3.27259500	15.71016300	-1.45391200
H	4.43275000	16.01456200	-2.76074900
H	4.57769400	16.87526500	-1.23450700
H	2.83636200	14.76050300	-3.69338000
H	3.42230400	13.94217700	-5.12694100
H	-2.40664400	11.54498500	-1.92344500
C	-2.20706600	11.52257500	0.22087000
H	-1.61859400	11.58519800	2.29641400

H	-3.25317300	11.32423800	0.41410200

OsH(CO)($PyCH_2NC_2H_4NHP\mathit{t}Bu_2$) (**5**) in MeOH
0 1

Os	-0.91332600	12.57694700	-2.28049700
P	-1.56029300	14.81508200	-2.09574200
C	0.30824000	12.78387900	-3.60627000
H	-2.01108700	12.43007600	-3.50386800
N	-0.88218500	12.29772600	-0.27086200
N	-0.63269500	10.44871400	-2.10923600
C	-3.44064500	15.07436400	-2.29782200
C	-0.60498800	16.12026100	-3.10463500
N	-1.39325300	15.31466000	-0.45451700
O	1.22836200	12.85174700	-4.35571700
C	-0.87000900	13.25743800	0.81744500
C	-0.83863900	10.94373600	0.23465300
C	-0.66396300	9.94979400	-0.85573500
C	-0.44708300	9.60087900	-3.14261100
C	-3.83196800	15.09159000	-3.76981500
C	-4.09819700	13.87605300	-1.61007300
C	-3.95829700	16.33649300	-1.61128800
C	-0.63131700	15.81227600	-4.59903400
C	-1.12768300	17.53589300	-2.88683800
C	0.83657600	16.05463900	-2.59605800
H	-1.37392900	16.31960500	-0.33024300
C	-0.41919000	14.63640900	0.39771300
H	-1.85723100	13.32895200	1.30239600
H	-0.17799900	12.90900400	1.59813500
H	-1.75051300	10.68946700	0.80004300
H	-0.02113300	10.81252300	0.96180700
C	-0.52301500	8.58905900	-0.61784400
H	-0.43069100	10.05276300	-4.12556200
C	-0.29033900	8.24610500	-2.96645700
H	-3.53923100	16.02195500	-4.25751500
H	-4.91833800	15.00840100	-3.86174500
H	-3.39188000	14.25982800	-4.32448700
H	-3.79184500	13.79471300	-0.56442700
H	-3.85971900	12.93401800	-2.10586900
H	-5.18454400	14.00010300	-1.62662500
H	-5.04854300	16.35919100	-1.69578300
H	-3.58531900	17.25588300	-2.05623000
H	-3.71859700	16.34693100	-0.54793100
H	-0.34495800	14.78730200	-4.82562400
H	0.07748900	16.46937400	-5.11070100
H	-1.60978100	15.99049000	-5.04116400
H	-1.21318900	17.80102900	-1.83061900
H	-2.09499900	17.69325800	-3.36295200
H	-0.42913200	18.24793600	-3.33535900
H	0.91012900	16.34913900	-1.54768000
H	1.45325300	16.74882000	-3.17283300
H	1.27230500	15.05999000	-2.70031900
H	0.57153000	14.54969600	-0.07222600
H	-0.29392600	15.24708900	1.29346000
H	-0.55727500	8.22677400	0.40173400
C	-0.33297600	7.72598400	-1.67812500
H	-0.13983400	7.60977600	-3.82759900
H	-0.21583200	6.66347000	-1.50757400

OsH(OMe)(CO)(NNNP-*t*Bu), **Int1**
0 1

Os	2.56887100	12.54349500	-0.78842900
P	4.62314700	13.13121400	-1.74211800
C	3.37688900	12.14650600	0.79035300
N	1.37830500	12.97462900	-2.62758500
H	2.79463600	11.01451400	-1.35605000
N	0.55487500	11.99413900	-0.22795900
O	1.83533600	14.61695200	-0.43819100
C	6.02280800	11.82575600	-1.70297400
C	5.34838300	14.80535800	-1.14715500
N	4.44277800	13.29050300	-3.45161800
O	3.84923100	11.87477600	1.84096800
C	2.02557300	12.90463700	-3.95139100
H	1.12780200	13.94876600	-2.43493500
C	0.14790300	12.16503000	-2.60007300
C	-0.36942300	11.99335500	-1.21274100
C	0.15386400	11.74231000	1.03175900
C	1.14020300	14.89111600	0.72896000
C	6.70702000	11.81333000	-0.33900700
C	5.41247700	10.44564600	-1.94267200
C	7.05774300	12.05037700	-2.80646800
C	5.24956000	14.88312300	0.37474700
C	6.77811600	15.09405400	-1.59094300
C	4.46423800	15.89495300	-1.75773200
C	3.22159500	13.82042800	-4.06029700
H	5.26124000	13.71101300	-3.87869900
H	2.31459800	11.86589400	-4.12659900
H	1.29771000	13.18069800	-4.72155900
H	0.40517300	11.17672600	-2.99553100
H	-0.62091000	12.57961700	-3.25718900
C	-1.71094600	11.76914300	-0.94721000
H	0.92664800	11.75577800	1.78935200
C	-1.16098800	11.48626000	1.35492300
H	0.10826200	14.49188300	0.74794600
H	1.63134600	14.50216500	1.64055600
H	7.28830900	12.71379900	-0.14649800
H	7.40050200	10.96903600	-0.29557400
H	5.99546500	11.68588500	0.47755000
H	4.78921000	10.41759100	-2.83905400
H	4.80871000	10.11069500	-1.10145200
H	6.22293600	9.72487500	-2.08212200
H	7.83127700	11.28288100	-2.71751100
H	7.55716600	13.01360000	-2.75497900
H	6.61895300	11.94349100	-3.79886800
H	4.21286800	14.82247000	0.71025000
H	5.65119600	15.84192600	0.71526400
H	5.81361200	14.09754500	0.87875100
H	6.89024600	15.03349900	-2.67537000
H	7.51963400	14.44319500	-1.13034000
H	7.03113000	16.11964100	-1.30498000
H	3.40537500	15.72888000	-1.55715400
H	4.61626800	15.97643900	-2.83524500
H	4.73943200	16.85913500	-1.32021400
H	2.93740500	14.81134300	-3.68291400
H	3.43763500	13.95112200	-5.12129900

H	-2.42183100	11.79343200	-1.76284800
C	-2.11662600	11.51181600	0.34997400
H	-1.42730400	11.28690500	2.38376600
H	-3.16012500	11.33092900	0.57336600
H	1.03850100	15.97917400	0.88100100

Int2

0 1

Os	2.64463800	12.82986300	-0.84266400
P	4.71583600	13.11203800	-1.78221600
C	3.41633300	12.49906700	0.76266700
N	1.50850600	12.98900200	-2.81838700
H	2.98454400	11.32972900	-1.32275700
N	-0.74141600	13.96582800	-4.09056600
O	0.91499500	13.74533000	-0.24340600
C	6.12589300	11.84520200	-1.53075300
C	5.36217800	14.85991600	-1.31815500
N	4.65144400	13.11189800	-3.50621800
O	3.87917200	12.23067600	1.81797100
C	2.26163300	12.64420000	-4.04461700
H	1.21693800	13.96460900	-2.91780500
C	0.25466000	12.21308200	-2.75878300
C	-0.77078600	12.66921600	-3.76130600
C	-1.66742500	14.41706500	-4.93974400
C	0.57218500	13.95103500	1.10146300
C	6.79664600	12.02405300	-0.17200000
C	5.50749400	10.44949600	-1.58489400
C	7.18132800	11.92642600	-2.63381200
C	5.32271200	15.07505100	0.19327500
C	6.75587700	15.17202300	-1.84987400
C	4.38072900	15.84312600	-1.95935500
C	3.46776900	13.52487100	-4.25834700
H	5.48994000	13.50284600	-3.92228800
H	2.55638600	11.59510600	-3.97076300
H	1.60037400	12.74080200	-4.91208500
H	-0.15641200	12.32364800	-1.75286200
H	0.48979700	11.15711100	-2.89629300
C	-1.72116600	11.79146300	-4.27145800
H	-1.61244500	15.47268700	-5.18818900
C	-2.65405200	13.61795300	-5.49072300
H	0.30278500	13.01393100	1.60777400
H	1.38057200	14.41357200	1.68475700
H	7.38628500	12.93812700	-0.11003200
H	7.48323600	11.18970800	-0.00354600
H	6.08070500	12.02145700	0.64977300
H	4.91711100	10.29553400	-2.49076100
H	4.86638400	10.25129700	-0.72599800
H	6.30848000	9.70503900	-1.58270500
H	7.97827000	11.21309900	-2.40710900
H	7.64565400	12.90666100	-2.72020700
H	6.77282400	11.65503300	-3.60707600
H	4.30330200	15.01310600	0.57873900
H	5.69906400	16.07635100	0.42162500
H	5.93376900	14.36448300	0.74838600
H	6.83852600	15.00160600	-2.92540400
H	7.53895500	14.60189500	-1.35135800
H	6.97399200	16.23068100	-1.68018200
H	3.34155000	15.60285600	-1.71238800
H	4.48010700	15.87098400	-3.04500900
H	4.58375200	16.85164700	-1.58940300
H	3.17337500	14.56827700	-4.08100700
H	3.73945300	13.46521200	-5.31319800
H	-1.70189900	10.74715700	-3.98426100
C	-2.67737400	12.27468200	-5.14711600
H	-3.37900800	14.03796800	-6.17545800
H	-3.42761600	11.61163600	-5.56061500
H	-0.29860100	14.61619900	1.17514700

Int3

0 1

Os	2.77031800	12.66645700	-1.25260400
P	4.91425300	12.96070700	-1.90395800
C	3.28854100	12.56553900	0.48162700
H	3.05251100	11.05655900	-1.47318600
H	-0.34695300	14.14185500	-1.39392700
N	1.91523000	12.70323700	-3.39050500
N	-0.43159000	13.26849000	-4.72343600
C	6.29663300	11.94542800	-1.04810900
C	5.39589600	14.81135900	-1.90948900
N	5.11571000	12.50820900	-3.54942500
O	3.58514800	12.48733800	1.62275800
C	2.82683900	12.72642700	-4.55904100
H	1.40122900	13.58633900	-3.38816300
C	0.90306300	11.63934500	-3.53276000
C	-0.16740400	11.97042900	-4.53895600
C	-1.41019900	13.59296600	-5.57184500
C	6.73840000	12.56567600	0.27371400
C	5.76302900	10.53943700	-0.78140900
C	7.50981100	11.80835200	-1.96873100
C	5.08533200	15.41157400	-0.53820000
C	6.84576800	15.09595600	-2.28780900
C	4.48508200	15.48567000	-2.93683100
C	4.06184600	11.87662700	-4.33262900
H	5.60541900	13.20920300	-4.09220200
H	0.43544800	11.47321400	-2.55721800
H	1.40410000	10.70561100	-3.79132000
C	-0.86872200	10.96473400	-5.19535000
H	-1.59622400	14.65492400	-5.70091900
C	-2.16358100	12.66029600	-6.26307400
H	7.28082800	13.50023200	0.13332700
H	7.42048400	11.87372200	0.77542400
H	5.90900600	12.74901000	0.95507800
H	5.36534600	10.07298700	-1.68512400
H	4.97987700	10.52867600	-0.02418100
H	6.58496700	9.91398000	-0.42257700
H	8.28847700	11.25701100	-1.43475200
H	7.93825000	12.76246700	-2.26753400
H	7.26924000	11.25042200	-2.87227800
H	4.02663900	15.31460100	-0.29225100
H	5.32480600	16.47812100	-0.55411800
H	5.66189400	14.96191900	0.26842900
H	7.12286800	14.66236800	-3.25110800
H	7.55557800	14.74760700	-1.53856300
H	6.98065000	16.17767500	-2.37751600

H	3.43318900	15.24447500	-2.76965200
H	4.74417700	15.21748200	-3.96217700
H	4.59385800	16.56980100	-2.85043700
H	-0.61583200	9.92588100	-5.02119100
C	-1.88280800	11.31631900	-6.06854000
H	-2.94532800	12.98132000	-6.93878600
H	-2.44323500	10.55292400	-6.59435700
O	1.68832500	14.57017200	-1.24940100
C	0.54133500	13.96293100	-0.76683400
H	0.29559600	14.23789000	0.27129900
H	0.59747100	12.83045800	-0.72900700
H	3.11980800	13.76022200	-4.74255000
H	2.28841400	12.38248000	-5.44802800
H	4.49364800	11.61400300	-5.29981500
H	3.77601700	10.93529500	-3.85519300

Int4

0 1

Os	2.28950300	12.65391900	-1.21819300
P	4.56136100	13.01168900	-1.98010100
C	2.73715100	12.74516200	0.53327300
H	2.61198600	11.05809400	-1.25516500
H	0.69181300	16.53527900	-1.13314600
N	1.62127400	12.60710200	-3.40949500
N	0.16623500	13.88188300	-5.41553700
C	5.93211800	12.01188200	-1.10277900
C	5.09076400	14.85371300	-2.01997600
N	4.79821100	12.42102000	-3.58198300
O	2.99886700	12.82391600	1.68608200
C	2.48126000	11.80634100	-4.31712800
H	1.70864000	13.57724700	-3.72189000
C	0.19576000	12.27952700	-3.61292600
C	-0.31859400	12.72022300	-4.95685000
C	-0.29460500	14.33335700	-6.58349100
C	6.30456100	12.66596500	0.22387100
C	5.38748500	10.61310500	-0.81799700
C	7.18425000	11.84910200	-1.96534000
C	4.75547300	15.50125400	-0.67747800
C	6.55038100	15.11271100	-2.36987800
C	4.23219000	15.48825600	-3.11707000
C	3.78851400	12.48914800	-4.63400700
H	5.71115800	12.65850900	-3.95428900
H	2.64063700	10.82554900	-3.86481700
H	1.95800300	11.64959600	-5.26615000
H	-0.37412300	12.78333900	-2.82932500
H	0.05432900	11.20825700	-3.46814700
C	-1.26915100	11.98240400	-5.65167800
H	0.12071900	15.27557600	-6.92823400
C	-1.24583900	13.66849200	-7.33929900
H	6.86161800	13.59266200	0.09133500
H	6.94503600	11.98549800	0.79156300
H	5.43101000	12.87688700	0.84189100
H	4.98249200	10.13865300	-1.71448700
H	4.60644200	10.62410100	-0.05871300
H	6.20227900	9.98296000	-0.45049700
H	7.94485400	11.32392400	-1.38138900
H	7.62106900	12.79240500	-2.28524600
H	6.99040100	11.24386500	-2.85124700
H	3.75210900	15.24232900	-0.33893200
H	4.80686100	16.59003000	-0.76949700
H	5.44919400	15.21081100	0.11045500
H	6.84244800	14.62347900	-3.30191000
H	7.23768500	14.79718800	-1.58561600
H	6.70207900	16.18685900	-2.51499100
H	3.17735300	15.21962300	-3.03947400
H	4.58331500	15.20466900	-4.11013200
H	4.29907600	16.57761100	-3.04855600
H	3.56515100	13.51535100	-4.96037200
H	4.21529200	11.98519100	-5.50327200
H	-1.62486300	11.04234600	-5.24790800
C	-1.74072500	12.46582300	-6.86042900
H	-1.58232700	14.08208900	-8.28087300
H	-2.47956900	11.90902500	-7.42386900
O	1.46546600	14.71768300	-1.50780500
C	1.21173900	15.64551400	-0.75392700
H	1.47760100	15.61858400	0.31293100
H	0.69759200	12.18930500	-0.83017900

Int5

0 1

Os	2.25962300	12.73547300	-1.22727400
P	4.54201100	13.03609300	-1.96408200
C	2.68931800	12.84894400	0.52817000
H	2.54369000	11.13435500	-1.21926600
H	0.56893300	16.57002600	-1.14467900
N	1.61771000	12.67805700	-3.42455800
N	0.27085000	13.96471900	-5.48780300
C	5.87910300	12.02715200	-1.04531200
C	5.10923500	14.86413200	-2.04209000
N	4.78337700	12.39828200	-3.54710400
O	2.94030900	12.94081000	1.68247300
C	2.45975600	11.82771900	-4.30327300
H	1.75085300	13.63786100	-3.75192000
C	0.18265700	12.41039900	-3.64355800
C	-0.29317300	12.85112000	-5.00189700
C	-0.15422600	14.41590400	-6.66952700
C	6.24957500	12.70100000	0.27191300
C	5.30023000	10.64701300	-0.73714100
C	7.13856000	11.81741500	-1.88693300
C	4.75874700	15.55390600	-0.72520600
C	6.58090300	15.08261100	-2.36825300
C	4.28589100	15.48926500	-3.17071800
C	3.79248400	12.46107000	-4.61777200
H	5.70661000	12.60517900	-3.91215800
H	2.58109700	10.85274900	-3.82725600
H	1.94328700	11.66738800	-5.25534400
H	-0.37668700	12.95237900	-2.87703200
H	-0.00949300	11.34915300	-3.48347600
C	-1.28956900	12.16172400	-5.68219900
H	0.32626700	15.31790300	-7.03647800
C	-1.14653600	13.79831700	-7.41222800
H	6.82482200	13.61472100	0.12747700
H	6.87186000	12.02019900	0.85919300
H	5.37372600	12.93862800	0.87660800

H	4.89479400	10.16223700	-1.62782500
H	4.51118400	10.69075400	0.01294000
H	6.09695200	10.00753700	-0.34686700
H	7.87895800	11.28879800	-1.28061300
H	7.60114300	12.74315400	-2.22142200
H	6.94315800	11.19665200	-2.76170100
H	3.72746200	15.36114600	-0.42878300
H	4.87840700	16.63569500	-0.83355900
H	5.39978200	15.23921000	0.09732000
H	6.88085000	14.56353900	-3.28142100
H	7.24546300	14.77301600	-1.56234200
H	6.75823200	16.14934800	-2.53695700
H	3.22182000	15.25715000	-3.09732500
H	4.63989900	15.16447400	-4.14999500
H	4.38666900	16.57755300	-3.13488800
H	3.60652500	13.48263700	-4.98019000
H	4.21834900	11.91698900	-5.46300700
H	-1.71024400	11.25918500	-5.25596600
C	-1.72375900	12.64489600	-6.90480400
H	-1.45144100	14.20933000	-8.36561900
H	-2.49758000	12.12574900	-7.45710300
O	1.45255400	14.81785800	-1.58826900
C	1.15101300	15.70348500	-0.80248900
O	-0.83966200	14.16839500	0.27896900
H	1.46605100	15.68388700	0.25076900
C	-0.56579800	14.00766700	1.66184200
H	0.37337200	14.48852900	1.95769700
H	-1.37560400	14.47679700	2.22008800
H	-0.51714700	12.95275700	1.94825100
H	0.64969200	12.29184800	-0.86587600
H	-0.24113500	13.55704400	-0.19915700

Int6

0 1

Os	2.40879300	12.53165800	-1.21955800
P	4.62377200	13.00262900	-1.95647300
C	2.91746600	12.54091800	0.53026600
H	2.89125000	10.97567200	-1.42264100
H	0.56901600	16.12293300	-0.52361000
N	1.68878300	12.59020000	-3.36715600
N	0.18407100	13.91184600	-5.29271400
C	6.01621300	12.00379000	-1.10812800
C	5.09487200	14.85064300	-1.94812900
N	4.82936000	12.43514800	-3.56458400
O	3.19774000	12.55960900	1.67349800
C	2.51906000	11.84778700	-4.34537400
H	1.75965100	13.58211200	-3.60840200
C	0.25552700	12.27120100	-3.52430800
C	-0.31351100	12.75839100	-4.82930200
C	-0.32566500	14.40092800	-6.42477900
C	6.41526400	12.63990000	0.22051100
C	5.51895000	10.58585200	-0.83377500
C	7.25071000	11.88171900	-2.00528200
C	4.73467200	15.46348400	-0.59585600
C	6.55556800	15.13233700	-2.28093000
C	4.24423600	15.50093300	-3.04257400
C	3.82751600	12.54128000	-4.62452500
H	5.74792000	12.66388200	-3.92841400
H	2.67157100	10.83501400	-3.96823000
H	1.98174300	11.77045600	-5.29564200
H	-0.28106000	12.75778600	-2.70499100
H	0.11517500	11.19595000	-3.41051400
C	-1.32523000	12.06486400	-5.48215000
H	0.10199800	15.33528800	-6.77555300
C	-1.33990800	13.78300700	-7.13697800
H	6.94203900	13.58439100	0.09437300
H	7.09543900	11.96188600	0.74235500
H	5.56242800	12.80780900	0.87734600
H	5.11938300	10.10812900	-1.73005200
H	4.75090500	10.55893400	-0.06257700
H	6.36322800	9.98429800	-0.48643200
H	8.03441200	11.37028600	-1.44105300
H	7.65948800	12.83672100	-2.32618800
H	7.05169200	11.27676200	-2.88995000
H	3.68045000	15.31863800	-0.35889000
H	4.92231100	16.54046500	-0.62873300
H	5.32655900	15.05759700	0.22319800
H	6.85671000	14.67259900	-3.22480400
H	7.24573400	14.80925400	-1.50313000
H	6.68749900	16.21194900	-2.39764100
H	3.18566600	15.25267000	-2.95718600
H	4.59602500	15.22382300	-4.03687400
H	4.33164300	16.58783700	-2.96086400
H	3.60838500	13.57822700	-4.91235300
H	4.26536100	12.06886100	-5.50520200
H	-1.68910700	11.12912200	-5.07560000
C	-1.84747400	12.58767800	-6.65281000
H	-1.71457000	14.22643100	-8.05011400
H	-2.63561100	12.06698300	-7.18294500
O	1.59733500	14.61682900	-1.40715900
C	0.85557500	15.06242800	-0.38247400
O	-0.39123800	14.30707500	-0.28527400
H	1.34741500	14.97555100	0.61024800
C	-0.90460600	14.27048700	1.02698400
H	-0.19201300	13.80999900	1.72533900
H	-1.15355200	15.27008200	1.40473400
H	-1.81704000	13.67465600	1.01499600
H	0.98169500	11.55442400	-0.82582300
H	0.68161500	12.34896000	-0.69694100

Int7

0 1

Os	2.44882700	12.74978400	-0.73483000
P	4.48130600	13.04217000	-1.73005100
C	3.26195200	12.25336000	0.81109300
N	1.22241200	13.10233700	-2.60879800
H	2.68607700	11.28015600	-1.33010200
N	-1.09192800	14.25861900	-3.55791500
O	0.71925000	13.62703900	0.06566200
C	5.83355800	11.69336800	-1.68494700
C	5.23074100	14.69804800	-1.11108100
N	4.33222900	13.23366600	-3.43756800
O	3.73195100	11.87044500	1.82543300
C	1.90668200	12.89748400	-3.90515300

H	0.92782800	14.08263000	-2.58615600
C	-0.03315300	12.32503900	-2.57187000
C	-1.11635200	12.92738200	-3.42544800
C	-2.06392500	14.83566400	-4.26820100
C	0.47647400	13.56050400	1.40285900
C	6.56138000	11.68875900	-0.34408500
C	5.14180200	10.34364200	-1.86590500
C	6.84826000	11.85115500	-2.81747000
C	5.25582500	14.75499900	0.41509400
C	6.61876000	14.99816800	-1.66368100
C	4.27610500	15.78702700	-1.60421900
C	3.12757100	13.76892700	-4.07055400
H	5.16396600	13.63745900	-3.85486500
H	2.17483400	11.84115900	-3.97583700
H	1.20651800	13.11562300	-4.71856200
H	-0.37433300	12.28757300	-1.53461000
H	0.17948300	11.30003200	-2.87698400
C	-2.10743100	12.13897400	-3.99937500
H	-2.01128800	15.91643200	-4.35841500
C	-3.09329000	14.13109700	-4.86766800
H	1.31115600	13.94733400	2.02230800
H	-0.43190300	14.13473200	1.66598900
H	7.19608200	12.56372500	-0.20830800
H	7.21106100	10.81057400	-0.29475700
H	5.87571000	11.62762600	0.50124200
H	4.50744300	10.32069300	-2.75495200
H	4.52736700	10.08017600	-1.00492900
H	5.90151600	9.56605800	-1.98377700
H	7.60692300	11.07003400	-2.71853000
H	7.36890000	12.80633800	-2.80515900
H	6.38638300	11.72560300	-3.79664800
H	4.24755500	14.71843800	0.83186800
H	5.70539300	15.70157600	0.72834000
H	5.83621700	13.95354200	0.87054300
H	6.65416200	14.93622900	-2.75342500
H	7.38834700	14.34292100	-1.25685600
H	6.89663700	16.02199500	-1.39586300
H	3.23589800	15.56365600	-1.34563000
H	4.34085500	15.93155800	-2.68329100
H	4.53615100	16.73856800	-1.13284700
H	2.87533200	14.78932800	-3.75136300
H	3.34553500	13.83333600	-5.13746100
H	-2.08308700	11.06341200	-3.87360500
C	-3.11094500	12.75143800	-4.72919400
H	-3.85553200	14.65110700	-5.43279500
H	-3.89385300	12.16066200	-5.18898100
O	0.25996700	12.19053100	1.77398400
C	0.16311500	12.04086600	3.17564000
H	0.00427300	10.98467800	3.38586400
H	-0.67780900	12.61001800	3.59024900
H	1.08142200	12.36848200	3.67913500

Int7 with η^2-methoxymethoxide

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Os	2.67307000	12.68161700	-1.34074500
P	4.85660500	12.99667400	-1.93816600
C	3.12716700	12.61726900	0.41222400
H	2.99013200	11.08878300	-1.51011900
H	-0.47356200	14.66734800	-1.06818900
N	1.87948600	12.64888600	-3.48346500
N	-0.54843500	12.97459400	-4.77519700
C	6.22427600	11.98726600	-1.05340400
C	5.33059600	14.84943200	-1.89858100
N	5.11987600	12.56687200	-3.58277300
O	3.37289600	12.55169400	1.56675600
C	2.82539200	12.81929900	-4.61120300
H	1.25565400	13.45890500	-3.47779800
C	1.01398700	11.47335600	-3.70750000
C	-0.06361900	11.72813200	-4.72581600
C	-1.53827800	13.22663900	-5.63465500
C	6.60418400	12.59052400	0.29536800
C	5.68764200	10.57528400	-0.82407100
C	7.47398300	11.86825900	-1.92484500
C	4.96117800	15.43456800	-0.53529400
C	6.79269000	15.14662600	-2.21200800
C	4.46294200	15.53384300	-2.95561700
C	4.08146200	11.98661200	-4.42369200
H	5.68485500	13.23560600	-4.09094200
H	0.54740400	11.20331200	-2.75738100
H	1.63350100	10.62617700	-4.00211100
C	-0.55188300	10.70492000	-5.53073100
H	-1.90512500	14.24839500	-5.65249900
C	-2.09002200	12.26911800	-6.46828700
H	7.14398100	13.53165000	0.19415800
H	7.26783200	11.89679700	0.81918000
H	5.74243500	12.75788800	0.94049700
H	5.32221700	10.11889100	-1.74662100
H	4.87780900	10.55425400	-0.09498300
H	6.49694000	9.94589100	-0.44368300
H	8.22917300	11.29849600	-1.37639200
H	7.91788800	12.82808500	-2.17984700
H	7.26919500	11.33584900	-2.85266800
H	3.89450400	15.32666200	-0.33180800
H	5.19215300	16.50331300	-0.53118000
H	5.50903500	14.98170300	0.28943900
H	7.11246600	14.72520500	-3.16731400
H	7.47329500	14.79422600	-1.43807200
H	6.92558900	16.23003000	-2.28466500
H	3.40591000	15.29127000	-2.83236200
H	4.76269100	15.27018400	-3.97104000
H	4.56745900	16.61751000	-2.85738100
H	-0.12309500	9.71247500	-5.46311900
C	-1.58194800	10.98030200	-6.41301900
H	-2.89222300	12.53071900	-7.14565000
H	-1.97901200	10.20207600	-7.05340600
O	1.55803400	14.66112200	-1.41013900
C	0.48943200	14.24560100	-0.72720100
O	0.42506600	12.76888500	-0.97457900
H	0.55718300	14.34577400	0.37646000
C	-0.20258400	12.01460700	0.05433100
H	0.25348400	12.21828000	1.02836500
H	-1.26879000	12.25018400	0.10121300
H	-0.07800200	10.96023000	-0.18622500
H	3.08325900	13.87520700	-4.68448600

H	2.32763600	12.54269600	-5.54690400
H	4.53083500	11.80030700	-5.40006800
H	3.80612600	11.00512700	-4.02480100

Int8

0 1

Os	2.63402600	12.52022700	-0.74129000
P	4.66615600	13.11602900	-1.73649000
C	3.48012500	12.10249300	0.81185500
N	1.39213300	12.95971800	-2.54597100
H	2.85561500	11.00639500	-1.32477600
N	0.63677500	11.96678700	-0.13186600
O	1.91667100	14.61229500	-0.30583000
C	6.06362000	11.80921400	-1.73965700
C	5.40215200	14.78487100	-1.14137300
N	4.44416800	13.29095100	-3.43847700
O	3.97397300	11.81941100	1.84807700
C	2.01790800	12.89418700	-3.88188700
H	1.11609400	13.92856100	-2.36882000
C	0.17966600	12.12176500	-2.49353700
C	-0.30926500	11.95533200	-1.09564500
C	0.26200000	11.73943400	1.13967800
C	1.26667300	14.88016400	0.83138200
C	6.78182100	11.78698600	-0.39339100
C	5.44438500	10.43217900	-1.97373700
C	7.07073200	12.04147800	-2.86693700
C	5.34372000	14.84788900	0.38369600
C	6.81970700	15.07953900	-1.61961300
C	4.50123500	15.87823400	-1.72018300
C	3.20533900	13.81877000	-4.01247500
H	5.25063100	13.71490700	-3.88430500
H	2.31188100	11.85741300	-4.05974600
H	1.27381400	13.16280800	-4.63878500
H	0.45438100	11.13690800	-2.88544100
H	-0.60797200	12.51482100	-3.14101700
C	-1.64467700	11.73881500	-0.79924300
H	1.05082500	11.75437100	1.88054200
C	-1.04794000	11.49805600	1.49560800
H	1.47694300	14.16899100	1.66168000
H	1.48515600	15.90098600	1.21781800
H	7.36873300	12.68578200	-0.21049500
H	7.47554100	10.94206400	-0.37310000
H	6.09124200	11.65482600	0.44027200
H	4.79947300	10.41171100	-2.85484800
H	4.86038200	10.09302300	-1.12020000
H	6.24922100	9.71041100	-2.13806500
H	7.84521500	11.27246600	-2.80365200
H	7.57221800	13.00394400	-2.81974000
H	6.60688600	11.94356200	-3.84874900
H	4.31853000	14.76928300	0.75023400
H	5.74152100	15.80948500	0.72081400
H	5.93425300	14.06679100	0.86370500
H	6.90324200	15.02732100	-2.70709100
H	7.57319200	14.42580100	-1.18319900
H	7.07916600	16.10305900	-1.33221800
H	3.44743800	15.70948400	-1.49811200
H	4.62746700	15.97012700	-2.80013500
H	4.78419200	16.83885000	-1.28006300
H	2.92474300	14.80485400	-3.61991800
H	3.39470500	13.95968800	-5.07719800
H	-2.37240000	11.75271700	-1.60008800
C	-2.02432700	11.50976200	0.51151400
H	-1.29303200	11.32139800	2.53399600
H	-3.06376300	11.33877600	0.76048300
O	-0.17637700	14.83871900	0.61173000
C	-0.88086900	15.11400100	1.80040600
H	-1.94718600	15.03842400	1.58942600
H	-0.66973100	16.12458400	2.17566200
H	-0.63159000	14.40102900	2.59872800

Int9

0 1

Os	2.61963000	12.46546100	-0.83935200
P	4.67355700	13.07640700	-1.77154700
C	3.40109300	12.06259200	0.76283100
H	2.85106100	10.96809300	-1.37486000
N	1.44646800	12.92921600	-2.66174400
N	0.58849900	11.98540000	-0.27505900
C	6.09187100	11.80590000	-1.69632800
C	5.30553000	14.77038000	-1.14307700
N	4.51839000	13.24194900	-3.47898700
O	3.84243700	11.79084800	1.82113400
C	2.10382800	12.82982500	-3.98021700
H	1.14148300	13.91552400	-2.50875300
C	0.21122400	12.12268900	-2.64549000
C	-0.33173400	12.00461200	-1.26489000
C	0.16971200	11.78986200	0.98934500
C	6.73530600	11.79918900	-0.31304700
C	5.49440700	10.42377800	-1.95896000
C	7.15621200	12.05517900	-2.76457300
C	5.15343500	14.84013400	0.37466100
C	6.73545300	15.11024500	-1.54375400
C	4.39170000	15.81915800	-1.77866000
C	3.29786200	13.74291100	-4.11550600
H	5.33613900	13.67777900	-3.89204600
H	2.39190700	11.78792200	-4.13964100
H	1.37757200	13.09264300	-4.75670400
H	0.46115100	11.12060500	-3.00981800
H	-0.53772600	12.53512000	-3.32687500
C	-1.68351200	11.85800500	-1.00100900
H	0.93907400	11.77310400	1.75001400
C	-1.15897200	11.62200900	1.31239600
H	7.28796300	12.71301600	-0.09809500
H	7.44850500	10.97251000	-0.25702100
H	6.00505400	11.64662900	0.48202800
H	4.90787400	10.39501000	-2.87981300
H	4.85837600	10.09100600	-1.13990800
H	6.30843500	9.70165400	-2.06396100
H	7.92807200	11.28682900	-2.67027500
H	7.65150600	13.01835900	-2.67197000
H	6.74824200	11.97245200	-3.77224500
H	4.10530200	14.76549600	0.67562600
H	5.52986600	15.80251600	0.73242200
H	5.70617500	14.05788000	0.89625200

H	6.88497300	15.04157000	-2.62308400
H	7.48156500	14.48820900	-1.05153600
H	6.94384800	16.14612100	-1.26019900
H	3.33558200	15.56069000	-1.69671000
H	4.62082700	15.96450300	-2.83519700
H	4.53728400	16.77941800	-1.27684400
H	3.00934000	14.74810300	-3.78306500
H	3.52185300	13.82863400	-5.17955500
H	-2.38825400	11.89489100	-1.82124500
C	-2.10740500	11.66752800	0.30164200
H	-1.43974100	11.46937500	2.34543200
H	-3.16023700	11.55368500	0.52542200
H	1.89776100	14.45292000	-0.42821300
C	1.09962900	15.29989000	-0.51936800
O	0.50559900	15.35893300	-1.67350800
O	0.18286600	15.02137100	0.56686800
H	1.68718800	16.20062100	-0.21679300
C	0.86034600	14.92636500	1.80038800
H	0.12927100	14.69659800	2.57384000
H	1.61924200	14.12940400	1.78127300
H	1.36521100	15.86567500	2.06044000

Int10, *trans*-OsH_2(CO)(NNNP-tBu) with methylformate
0 1

Os	2.61159800	12.50038500	-0.81602300
P	4.67076200	13.09748700	-1.73888300
C	3.39712900	12.05765700	0.76371300
H	2.63332900	10.93266400	-1.55800100
N	1.43003900	13.01445100	-2.66769200
N	0.55408000	12.11465200	-0.25332100
C	6.10139400	11.82290900	-1.68341900
C	5.35958500	14.78798800	-1.13231400
N	4.52388700	13.26979600	-3.45070000
O	3.85692800	11.77569100	1.81790700
C	2.11219300	12.86681600	-3.96818400
H	1.14875400	13.99202900	-2.58145600
C	0.19529100	12.20923500	-2.63071600
C	-0.35871600	12.13550000	-1.24991500
C	0.11602500	11.96544900	1.01051300
C	6.79185800	11.84274800	-0.32256100
C	5.50563000	10.43157500	-1.88947200
C	7.12993200	12.03990900	-2.79356200
C	5.32429300	14.86089000	0.39265800
C	6.76723600	15.10651100	-1.62707200
C	4.43634000	15.86840600	-1.69958700
C	3.31197900	13.77558600	-4.09486900
H	5.34591000	13.70077400	-3.86008400
H	2.40340700	11.81929400	-4.07514500
H	1.40553300	13.10207700	-4.77114700
H	0.46474000	11.19651900	-2.95147900
H	-0.55091100	12.58852000	-3.33399000
C	-1.71650500	12.03309800	-0.99596400
H	0.87700400	11.95523100	1.78010700
C	-1.21970800	11.83504200	1.32487100
H	7.37192800	12.74863500	-0.15333400
H	7.48786800	11.00138400	-0.26469200
H	6.08431900	11.73008800	0.49984700
H	4.90089000	10.37033400	-2.79683000
H	4.88208800	10.12579200	-1.05004700
H	6.32159100	9.70987600	-1.98450700
H	7.91320200	11.28348500	-2.69381500
H	7.61806800	13.01018500	-2.75953000
H	6.68991000	11.91175600	-3.78277400
H	4.30798900	14.76779400	0.77729600
H	5.71026400	15.83256900	0.71408500
H	5.93546000	14.09548300	0.87061700
H	6.84792000	15.04025400	-2.71405800
H	7.53411700	14.47269300	-1.18490100
H	7.01072800	16.13796000	-1.35542400
H	3.38236300	15.66930200	-1.49909600
H	4.56789400	15.98490700	-2.77627800
H	4.68512900	16.82803100	-1.23826200
H	3.02288600	14.78168900	-3.76071300
H	3.54401400	13.86595300	-5.15685800
H	-2.41178000	12.07207600	-1.82447100
C	-2.15914900	11.87997800	0.30588800
H	-1.51212400	11.71554200	2.35927700
H	-3.21647400	11.79754500	0.52199900
H	2.32589800	14.12172300	-0.32934700
C	0.26445200	15.60782000	-0.59651300
O	-0.11933800	15.41604400	-1.72932700
O	-0.34759300	15.05082900	0.44225400
H	1.09452800	16.28218300	-0.33485300
C	0.26871600	15.26975900	1.72711100
H	-0.44366700	14.92313600	2.46878000
H	1.19410700	14.69437900	1.79500400
H	0.47338100	16.32897600	1.87878200

TS1, MeOH elimination from **Int1**
0 1

Os	2.59884700	12.61811000	-0.72547100
P	4.64784900	13.17264400	-1.70799900
C	3.36283000	12.47620100	0.93274100
N	1.42051500	12.94397800	-2.52823700
H	2.94317700	11.06726200	-0.99010300
N	0.58782200	12.03973400	-0.16616200
O	1.55868000	14.79375100	-0.92711300
C	5.97957900	11.80178800	-1.75853900
C	5.45720700	14.79612700	-1.06984700
N	4.42359300	13.41406800	-3.39953200
O	3.80431400	12.36375800	2.02425400
C	1.99649900	13.04531200	-3.85940800
H	1.27162800	14.12610400	-1.83140800
C	0.24289200	12.09383100	-2.54913900
C	-0.29879400	11.89519700	-1.17611800
C	0.16068000	11.86614300	1.09942600
C	0.46958100	15.13392600	-0.09616500
C	6.62420300	11.65339800	-0.38472600
C	5.29739300	10.48196400	-2.12269000
C	7.04860900	12.04839000	-2.82388200
C	5.39313500	14.84828400	0.45360900
C	6.89205800	15.02372400	-1.52980300
C	4.61299000	15.94358800	-1.62497700
C	3.17868300	13.98652600	-3.92487100

H	5.22989600	13.85161900	-3.83207200
H	2.29827400	12.05334300	-4.23129300
H	1.23406000	13.41504600	-4.56126100
H	0.48752000	11.10218300	-2.96710700
H	-0.54433200	12.49789100	-3.20097700
C	-1.62518900	11.57450300	-0.92918400
H	0.90312800	12.00002500	1.87538000
C	-1.14249100	11.54148500	1.40504600
H	-0.44536400	14.58942200	-0.35956700
H	0.69627900	14.91885600	0.95356700
H	7.24312900	12.50889900	-0.11440500
H	7.27238700	10.77270500	-0.38002200
H	5.87988000	11.50837200	0.40135800
H	4.66352200	10.57527300	-3.00728700
H	4.68911200	10.09308800	-1.30909100
H	6.06752200	9.73906300	-2.34673100
H	7.74147800	11.20264300	-2.82024600
H	7.63976100	12.94340300	-2.65918100
H	6.61797100	12.09976700	-3.82464700
H	4.36124900	14.87054400	0.80791200
H	5.87997900	15.76372800	0.80194300
H	5.89698100	14.00857700	0.93346800
H	6.99059900	14.97417300	-2.61586400
H	7.60206800	14.32783600	-1.08452500
H	7.19964300	16.02989200	-1.22931400
H	3.55378700	15.82767400	-1.39383300
H	4.72459000	16.04382700	-2.70577600
H	4.95233700	16.88156300	-1.17636100
H	2.90138300	14.93291200	-3.44274500
H	3.36851500	14.22066400	-4.97337900
H	-2.30688600	11.47746200	-1.76428100
C	-2.05698200	11.39426200	0.37160700
H	-1.43213400	11.41648000	2.43935000
H	-3.09029600	11.14698000	0.57888200
H	0.24541500	16.20416600	-0.17377700

TS2, between **Int5** and **Int6**

0 1

Os	2.37170300	12.62163600	-1.20446600
P	4.59094500	13.00816600	-1.95149200
C	2.87121200	12.64336300	0.53871400
H	2.67892900	11.01951800	-1.32506900
H	0.22452800	16.03029900	-0.52744000
N	1.66475700	12.62900600	-3.37217800
N	0.17398500	13.92383600	-5.33930100
C	5.97743200	11.99378700	-1.10781200
C	5.10931700	14.85013900	-1.95626700
N	4.82060900	12.44974600	-3.56669800
O	3.15699900	12.66954400	1.68743900
C	2.50519100	11.85361600	-4.31677900
H	1.74666300	13.60958500	-3.65122000
C	0.23412500	12.30993200	-3.54711800
C	-0.31032000	12.76469200	-4.87453300
C	-0.31417300	14.38720700	-6.49135400
C	6.37674800	12.61748600	0.22625200
C	5.44591300	10.58606600	-0.84313500
C	7.21676500	11.85050600	-1.99333000
C	4.74804900	15.48063600	-0.61252800
C	6.57431100	15.11360500	-2.28165200
C	4.26859900	15.50425600	-3.05559100
C	3.81275900	12.54080100	-4.61919900
H	5.73254300	12.70063400	-3.93277800
H	2.66222100	10.85710400	-3.89941900
H	1.97164700	11.73431000	-5.26530100
H	-0.31657400	12.81429100	-2.74989200
H	0.08949400	11.23830500	-3.40772900
C	-1.28749500	12.04093200	-5.54688600
H	0.10160500	15.32706300	-6.84190400
C	-1.29341800	13.73737200	-7.22412600
H	6.91951200	13.55428500	0.10674900
H	7.04103700	11.92862600	0.75522200
H	5.51941100	12.79879200	0.87408900
H	5.03391500	10.12600200	-1.74378200
H	4.67415200	10.57514100	-0.07466200
H	6.27087600	9.95635000	-0.49834600
H	7.98649900	11.31717200	-1.42920200
H	7.64801400	12.79957800	-2.30291800
H	7.01179800	11.25946100	-2.88611300
H	3.68619300	15.36609000	-0.39105600
H	4.96605900	16.55228200	-0.64412000
H	5.31310300	15.06029200	0.21866400
H	6.87681700	14.64328800	-3.21999400
H	7.25464500	14.78485400	-1.49715000
H	6.72524400	16.19053100	-2.40460500
H	3.20990500	15.25150900	-2.97997100
H	4.62430300	15.22597600	-4.04850300
H	4.35128100	16.59186300	-2.97531200
H	3.59021500	13.57371600	-4.92296300
H	4.24030300	12.05470100	-5.49817900
H	-1.64186800	11.10225600	-5.13867500
C	-1.78761400	12.53697600	-6.73891100
H	-1.65172700	14.16067500	-8.15324900
H	-2.54836900	11.99184600	-7.28434000
O	1.54168500	14.75268100	-1.41137100
C	0.82530200	15.11824600	-0.39012500
O	-0.32271100	14.02865300	-0.17710100
H	1.31726000	15.11924900	0.60103700
C	-0.73431900	13.88267900	1.18821500
H	0.10843000	13.58758400	1.81806100
H	-1.14128600	14.83046700	1.53586200
H	-1.50793000	13.11869300	1.22288600
H	0.74377000	12.10704200	-0.77253200
H	0.26653100	13.07672100	-0.49915700

TS3 between **Int8** and **Int9**

0 1

Os	2.68348600	12.52274000	-0.82074100
P	4.72276600	13.08936200	-1.80124300
C	3.49547500	12.16399000	0.77281900
H	2.94146100	11.01608800	-1.25090000
N	1.47287900	12.85670700	-2.65199200
N	0.65188300	12.06972000	-0.21366600
C	6.10309900	11.77408700	-1.80206500
C	5.43102200	14.74651700	-1.15681200

N	4.51132600	13.28956200	-3.49760700
O	3.96380800	11.88919500	1.81902600
C	2.10512900	12.82388800	-3.97957100
H	1.18143300	13.81855800	-2.42001000
C	0.27236400	12.00865000	-2.59032300
C	-0.26688700	11.97631200	-1.20060600
C	0.23714300	11.99768400	1.06418700
C	6.81137100	11.73226200	-0.45182300
C	5.45267500	10.41346100	-2.05092200
C	7.12016200	12.00486800	-2.91954500
C	5.38769500	14.77118900	0.36925200
C	6.83641100	15.06688700	-1.65001700
C	4.49438200	15.83623600	-1.67657400
C	3.26420600	13.78980700	-4.07957700
H	5.31480300	13.72188400	-3.93996200
H	2.43440700	11.80101200	-4.17928800
H	1.35978700	13.08447300	-4.73858000
H	0.55940300	10.99459500	-2.88835500
H	-0.49171800	12.34645800	-3.29572300
C	-1.61391200	11.81717900	-0.92172000
H	1.00624100	12.08008700	1.82127400
C	-1.08793300	11.82656100	1.40449000
H	7.41143000	12.62143100	-0.26254400
H	7.49074400	10.87596200	-0.43124900
H	6.11325200	11.60795000	0.37699700
H	4.80881000	10.41737000	-2.93320000
H	4.86148000	10.08082800	-1.19876200
H	6.23784400	9.67193900	-2.22081800
H	7.88369600	11.22477400	-2.86072300
H	7.63357200	12.96074400	-2.85391700
H	6.66203600	11.92764700	-3.90568600
H	4.36181600	14.70750200	0.73903100
H	5.80371900	15.71807300	0.72450700
H	5.96219200	13.96862300	0.83165300
H	6.90658000	15.03058100	-2.73913800
H	7.59921600	14.41086700	-1.23279000
H	7.09182700	16.08737000	-1.34971500
H	3.44879400	15.63672200	-1.43080100
H	4.57703400	15.96412700	-2.75687700
H	4.76558300	16.78978300	-1.21519300
H	2.94717100	14.75792500	-3.66892100
H	3.46481600	13.95954000	-5.13771700
H	-2.31978400	11.75972700	-1.73975900
C	-2.03394300	11.74309000	0.39484300
H	-1.36735600	11.77880600	2.44808600
H	-3.08370600	11.62229100	0.62947500
O	1.04293600	15.15977600	-1.14191200
C	0.96197400	15.28871700	0.17194300
H	1.48881200	14.49240500	0.76317700
H	1.33606700	16.26627900	0.56997400
O	-0.44343000	15.20290100	0.60699800
C	-0.55861800	15.34514000	2.00261100
H	-1.60155000	15.19153600	2.27979100
H	-0.25185400	16.34454400	2.34069200
H	0.05471900	14.60884300	2.54197300

TS4 between **Int9** and **Int10**

0 1

Os	2.52364400	12.52927300	-0.84620800
P	4.59162400	13.13751700	-1.74966400
C	3.27740500	12.17186800	0.77460800
H	2.68632800	10.97023800	-1.46516700
N	1.38389200	12.96688200	-2.71486000
N	0.47916900	12.08513500	-0.30863700
C	6.03608100	11.89204300	-1.61028400
C	5.22050200	14.86057800	-1.18533000
N	4.47532500	13.24465400	-3.46805600
O	3.70844200	11.94500800	1.85193400
C	2.07389000	12.80505100	-4.01042600
H	1.10966900	13.95235900	-2.61894300
C	0.13913400	12.17569700	-2.68780900
C	-0.42641900	12.10880100	-1.31178600
C	0.03549000	11.92423400	0.95140700
C	6.67750700	11.96409400	-0.22739700
C	5.47146600	10.48489100	-1.79939400
C	7.09950400	12.10163000	-2.68840500
C	5.09765400	14.98917000	0.33114800
C	6.64352900	15.19599600	-1.61787400
C	4.29799300	15.88527000	-1.84879000
C	3.26944000	13.71607800	-4.15094000
H	5.29915700	13.67461900	-3.87517200
H	2.36829200	11.75748000	-4.10607900
H	1.36923100	13.02818400	-4.81843500
H	0.39278500	11.15949400	-3.00861500
H	-0.59517100	12.56557900	-3.39739700
C	-1.78573100	12.01028000	-1.06580300
H	0.79312200	11.89949800	1.72389300
C	-1.30250900	11.80078800	1.25799300
H	7.23036200	12.88779700	-0.06218500
H	7.39056600	11.14172700	-0.12335700
H	5.94538400	11.85567700	0.57351000
H	4.88917500	10.39265800	-2.71865500
H	4.83598700	10.18444900	-0.96727600
H	6.30304600	9.77746400	-1.86006400
H	7.89177100	11.36251600	-2.54236900
H	7.56865100	13.08142100	-2.65820900
H	6.69757400	11.94353000	-3.68954700
H	4.06088400	14.89910600	0.66019000
H	5.45738000	15.97476200	0.64020300
H	5.68485500	14.24538800	0.87029600
H	6.78197500	15.08766400	-2.69543900
H	7.40168900	14.60151700	-1.11056000
H	6.84583300	16.24405500	-1.37755700
H	3.24369500	15.62454000	-1.75632600
H	4.52486000	15.99944900	-2.90979400
H	4.44260200	16.86159900	-1.37828100
H	2.96922200	14.73189800	-3.86165100
H	3.51781900	13.76509800	-5.21192600
H	-2.47670500	12.05190200	-1.89758800
C	-2.23540000	11.85801100	0.23379900
H	-1.60157000	11.67428000	2.28954700
H	-3.29440300	11.78148600	0.44381300
H	2.06424300	14.21902900	-0.46305300
C	0.98175900	15.41771500	-0.48207000

O	0.46588900	15.47624400	-1.60855800
O	0.18205300	15.03910800	0.56621600
H	1.78815400	16.10223300	-0.16706400
C	0.85145800	14.99675000	1.82332200
H	0.09987800	14.78124900	2.57790900
H	1.61252400	14.20956100	1.82412700
H	1.32694600	15.95477500	2.04860700

Rate-limiting **TS** of ADC of EtOH
0 1

Os	2.55300700	12.46767700	-0.49616100
P	4.50523000	13.01489000	-1.72169200
C	3.49822800	12.19234000	1.02919000
N	1.30422400	12.85285700	-2.36919800
H	2.77175100	10.90981500	-0.95511400
N	-0.53221800	14.51899000	-3.61631700
O	1.75621100	14.56403600	-0.17790900
C	6.03637300	11.89606700	-1.46494800
C	5.05311600	14.83951000	-1.54841300
N	4.28511500	12.74586500	-3.41123100
O	4.08103500	12.01520300	2.04319100
C	1.83213900	12.26472100	-3.62311500
H	1.37032600	13.86869100	-2.47050400
C	-0.13893500	12.58948100	-2.21979100
C	-0.97667700	13.31283600	-3.24055100
C	-1.27015900	15.21452900	-4.48358000
C	1.27079400	14.81664700	1.00785500
C	6.78866700	12.28180400	-0.19464400
C	5.55269900	10.45384200	-1.32345300
C	6.99483300	11.93543700	-2.65689300
C	5.06944200	15.22189300	-0.06971500
C	6.39072500	15.18244000	-2.19234000
C	3.97276200	15.65666100	-2.26116400
C	3.04362200	13.00153900	-4.13676400
H	5.07728000	13.07470600	-3.95227200
H	2.04915400	11.20976200	-3.44437800
H	1.06501200	12.31722000	-4.40281100
H	-0.43814000	12.92671900	-1.22453700
H	-0.31251600	11.51360600	-2.25752300
C	-2.16387400	12.77265700	-3.72033600
H	-0.87928500	16.18606000	-4.77076600
C	-2.46834400	14.75857000	-5.00712500
H	1.97277500	14.68066500	1.85427700
H	7.30759400	13.23503900	-0.28692900
H	7.54908500	11.52361200	0.01200400
H	6.13732100	12.32924200	0.67775300
H	4.90084600	10.15728800	-2.14782400
H	5.01398900	10.28973800	-0.39149800
H	6.41988700	9.78746100	-1.33087300
H	7.86977900	11.32480000	-2.41875300
H	7.35678800	12.93205700	-2.89828100
H	6.54541800	11.50718400	-3.55307400
H	4.09810800	15.04868800	0.39532100
H	5.29864300	16.28739900	0.02674200
H	5.82091400	14.67691700	0.50109800
H	6.43052400	14.88470100	-3.24253400
H	7.24122100	14.73882100	-1.67617800
H	6.53125200	16.26747300	-2.16562200
H	2.96623200	15.38353000	-1.94028700
H	4.04023900	15.55108900	-3.34461400
H	4.11303500	16.71681400	-2.03122100
H	2.78953200	14.06911300	-4.20057000
H	3.21341800	12.67144100	-5.16349500
H	-2.48023500	11.78863800	-3.39618700
C	-2.92161000	13.50881800	-4.61502700
H	-3.02512500	15.36665500	-5.70786800
H	-3.85003400	13.11043200	-5.00576000
O	0.20079000	13.64485700	1.33582500
C	0.15697700	13.25724600	2.72408600
H	0.00841800	14.16605700	3.31138000
H	1.12837800	12.83286700	3.00317200
H	1.07277800	11.85430100	0.24439400
H	0.71864100	12.74127300	0.71924700
C	0.47135500	16.08289600	1.12386700
H	-0.01294400	16.17575400	2.09593100
H	1.13825700	16.93625000	0.99566300
H	-0.28660400	16.11853100	0.34029700
C	-0.95697100	12.27323900	2.93545000
H	-0.99934500	11.98175100	3.98472300
H	-1.92087600	12.70326400	2.66341400
H	-0.80428400	11.37023100	2.34371600

Hydrogen-bonded complex of methoxymethanol with MeOH (mPW1k/6-311++g(d,p), Pressure=605 Solvent=Methanol).
E/H/G = -345.995700 -345.842388 -345.882792
0 1

O	-1.35484000	2.47684200	-0.61240400
C	-1.35291300	1.19388700	-0.06348900
C	-0.06665900	2.99178100	-0.85915300
O	-0.85472400	1.15832100	1.23203200
H	-2.38757200	0.85917800	-0.09722500
H	-0.72672600	0.53299200	-0.66324300
H	0.48738300	3.14608000	0.06540100
H	0.50084700	2.32138400	-1.50694500
H	-0.19169700	3.94706400	-1.35889600
H	-1.50882400	1.55647700	1.82889100
O	-2.71089500	2.28319100	2.90410700
C	-3.88047100	1.53668300	3.17785100
H	-2.96000600	3.15388300	2.60135700
H	-4.49774800	1.42477900	2.28799900
H	-4.46767000	2.00554700	3.96554400
H	-3.56612100	0.55376600	3.51372300

TS for methanol–assisted splitting of methoxymethanol (mPW1k/6-311++g(d,p), Pressure=605, Solvent=Methanol).
E/H/G = -345.947513 -345.801560 -345.836759
0 1

C	-1.40999800	0.85719900	0.01701000
O	-0.95060900	0.44885400	1.18801400
O	-1.72687600	2.34891500	0.05563100
H	-2.38470800	0.45267700	-0.27157500
H	-1.68736300	1.30266600	2.13905600
H	-0.70756900	0.77057100	-0.81578800

C	-0.61228900	3.19331200	-0.22149700
H	-0.90724600	4.21114200	0.00827100
H	0.24194700	2.90923500	0.38776800
H	-0.36978600	3.11197000	-1.27581300
H	-2.07594400	2.46726800	1.15653700
O	-2.19645200	2.18334200	2.35006300
C	-3.51933100	1.95337200	2.81243600
H	-3.48366000	1.58151900	3.83203300
H	-4.05501800	2.89647200	2.79227600
H	-4.03231700	1.23177000	2.18027000

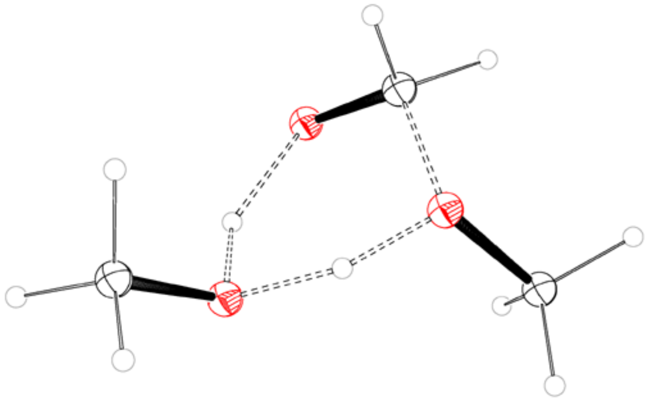


Figure S12. The **TS** structure of the methanol-assisted splitting of methoxymethanol to give formaldehyde + 2MeOH.

Hydrogen-bonded complex of 1-ethoxyethanol with EtOH
(mPW1k/6-311++g(d,p), Pressure=249 Solvent= EthylEthanoate).
E/H/G = -463.957721 -463.714617 -463.763988
0 1

C	-1.45703200	0.97365500	-0.02025200
O	-0.76305300	0.69162700	1.15021300
O	-1.61315000	2.35801700	-0.19788200
H	-1.26098600	1.07915400	1.87747100
H	-0.84108500	0.57894200	-0.82966400
C	-0.41762700	3.03645300	-0.53069500
H	0.31965600	2.89692400	0.26027900
H	-0.00791800	2.60513800	-1.44705900
H	-2.31342800	2.87129100	1.62473200
O	-2.41085400	2.56274300	2.52871200
C	-0.72386800	4.49467400	-0.72514100
H	0.18266900	5.03004500	-1.00006400
H	-1.45643200	4.63694700	-1.51668500
H	-1.11276300	4.94106400	0.18825900
C	-2.82852200	0.35422700	-0.04664800
H	-3.32108300	0.55687200	-0.99412900
H	-2.74508900	-0.72159300	0.08221300
H	-3.44276100	0.75273700	0.75857500
C	-2.08660800	3.60365900	3.42694800
H	-1.07032300	3.95860600	3.24187300
H	-2.76333600	4.44745100	3.27822300
C	-2.20466800	3.08779800	4.83356700
H	-1.96194900	3.87564100	5.54398000
H	-3.21760200	2.74612200	5.03664400
H	-1.52164700	2.25707500	5.00056500

TS for ethanol–assisted splitting of 1-ethoxyethanol (mPW1k/6-311++g(d,p), Pressure=249, Solvent= EthylEthanoate).
E/H/G = -463.908255 -463.673162 -463.718693
0 1

C	-1.56304800	1.03153200	0.26338000
O	-1.20809500	0.83788500	1.50347200
O	-1.84556600	2.59432200	0.05073500
H	-1.85768200	1.76256300	2.19859900
H	-0.76336500	0.87608100	-0.46799800
C	-0.71319700	3.33863000	-0.40045200
H	0.12352400	3.16061400	0.27416100
H	-0.45025600	2.95061900	-1.38104300
H	-2.14363400	2.87796300	1.10035700
O	-2.38102400	2.71379200	2.34653700
C	-1.05645300	4.79963500	-0.47984700
H	-0.19716400	5.35106700	-0.85561300
H	-1.89193300	4.96757600	-1.15531900
H	-1.31199300	5.20558800	0.49664700
C	-2.85534500	0.40374100	-0.18395800
H	-3.10280400	0.67384200	-1.20750100
H	-2.74247400	-0.67701200	-0.12512100
H	-3.67066700	0.69551800	0.47478300
C	-1.76114300	3.55973000	3.29393200
H	-0.68220300	3.58301400	3.12572300
H	-2.14040000	4.56793100	3.13617500
C	-2.05821200	3.10636200	4.69913400
H	-1.59147100	3.77823000	5.41768600
H	-3.13049600	3.09894200	4.88369900
H	-1.67273700	2.10374300	4.87483300

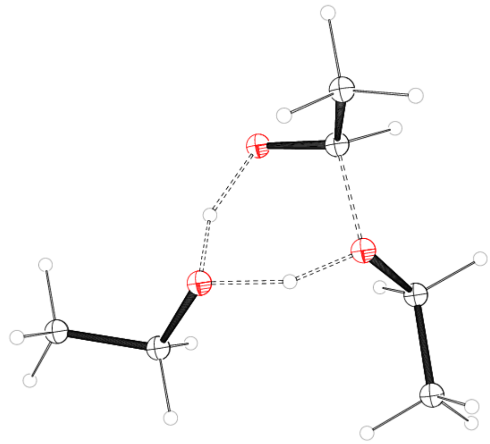


Figure S13. The **TS** structure of the ethanol-assisted splitting of 1-ethoxyethanol to give acetaldehyde + 2EtOH.

Results of additional experiments performed at the request of the reviewers

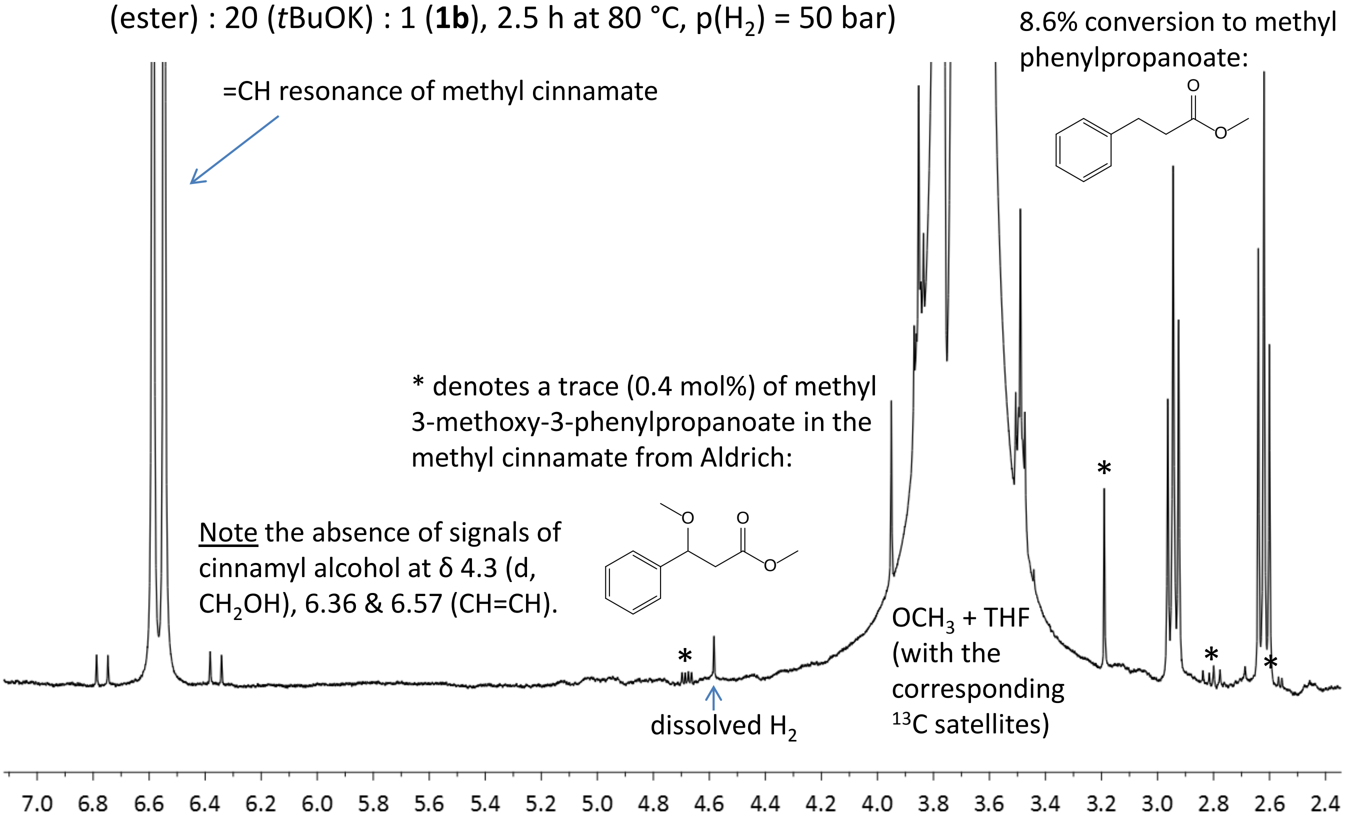
(a) The authors proposed "catalyst deactivation" by aldehydes at room temperature (paragraph above Figure 1). This is very interesting. I am wondering if ketones would also deactivate the catalyst. Would hydrogenation of a 1 : 1 mixture of ethyl acetate and **K4** at room temperature also fail?

Response: Ethyl acetate and **K4** (1:1, 0.04+0.04 moles) were hydrogenated in a 75 mL autoclave with **6** (S/C=1000:1000:1) at r.t., while maintaining p(H_2) = 50 bar for 1h. A rapid hydrogenation ensued and the autoclave became hot (ca. 45 °C). A sample of the neat reaction solution was analyzed by ^{1}H and ^{13}C NMR that established full conversion of **K4** to cyclohexanol (94.5%) and cyclohexenol (5.5%), and 56% conversion (TON = 560) of ethyl acetate to ethanol. The latter is similar to TON = 715 reported in the manuscript for r.t. hydrogenation of neat ethyl acetate with **6**.

No selectivity was observed for α,β-unsaturated esters (**E10-E13**, Table 2). In contrast, related α,β-unsaturated aldehydes and ketones (**A4**, **K3**, Table 2) show excellent selectivity for C=O hydrogenation (>99%). It is noteworthy, however, that *the experimental conditions for some of these reactions are vastly different*. For example, for **E12**: 0.02 mol% [Os], ester (40 mmol), *i*PrOH (solvent), K_2CO_3 (0.2 mol%), 100 °C and for **A4**: 0.05 mol% [Os], aldehyde (20 mmol), THF (solvent), K_2CO_3 (1 mol%), 80 °C. These differences might affect the rate and therefore selectivity of these reactions and therefore should not be compared directly.
(b) Authors should run these two substrates under identical conditions and then compare the selectivity. It will be helpful if these results are included in Table 2.

Response: **E12** was hydrogenated under the exact conditions for **A4** in Table 2. Selective hydrogenation of **E12** to give methyl 3-phenylpropanoate was observed. The results are summarized in the following figure. An entry was added in Table 2.

Partial ^{1}H NMR spectrum of the product of hydrogenation of 0.02 moles of methyl cinnamate in 7 ml THF (2000 (ester) : 20 (*t*BuOK) : 1 (**1b**), 2.5 h at 80 °C, p(H_2) = 50 bar)



(c) In addition, as complex **6** ($Os(H)_2$) can also efficiently catalyze the hydrogenation process at room temperature (at least for some esters), it is possibly worth studying **E12** under this condition to check if there is any selectivity at all.

Response: **E12** (0.02 moles) was hydrogenated in 7 ml THF with 0.05 mol% **6**. No significant pressure change was observed at r.t., and, after 40 min, the autoclave was placed into an oil bath pre-heated to 80 °C. After 30 min, the reaction was stopped. Selective hydrogenation of **E12** to give methyl 3-phenylpropanoate (4.1% conversion) was observed in the ^{1}H and ^{13}C NMR spectra of the reaction mixture.

(d) Is the catalyst (**1b**) still active after the 1st hydrogenation run? A sequential ester addition experiment is suggested. Please report the conversion/selectivity for the 2nd run.

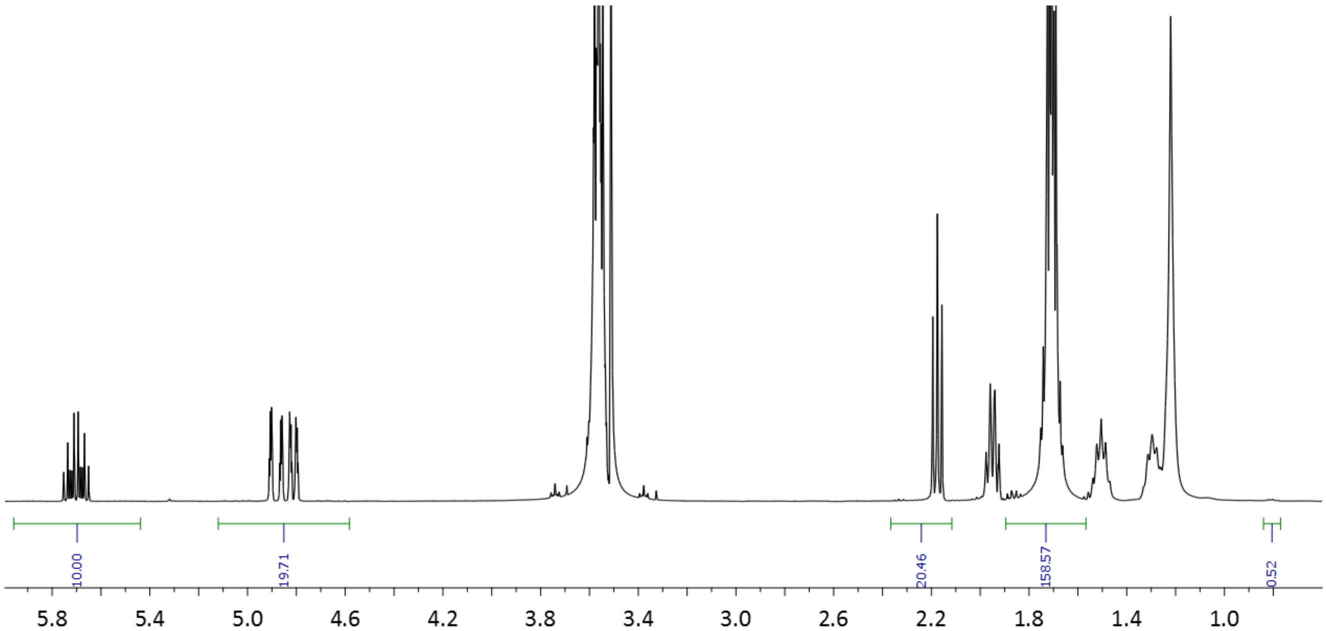
Response: We performed this experiment in a 75 ml autoclave, using 0.02 moles of methyl 10-undecenoate in 7 mL THF, 1 mol% *t*BuOK, 0.05 mol% **1b**, 2.5 h reaction time at 100 °C, under 50 bar H_2. After cooling to 6 °C, the autoclave was taken in and opened in an Ar glovebox. A ca. 0.8 mL sample of the reaction solution (clear yellow liquid) was analyzed by ^{1}H and ^{13}C NMR that established 95±1% conversion to 10-undecenol and 98±0.5% selectivity (retention of the C=C bond). This sample was returned into the autoclave, and further 0.02 moles of methyl 10-undecenoate was added. The autoclave was pressurized to 50 bar H_2 and returned into an oil bath at 100 °C for 2.5 h. The final product (clear yellow solution) showed 92±1% conversion to 10-undecenol with retained 98±0.5% selectivity. The slightly reduced conversion can be due to reduced catalyst and substrate molar concentrations when the volume of the reaction mixture increased in the second step.

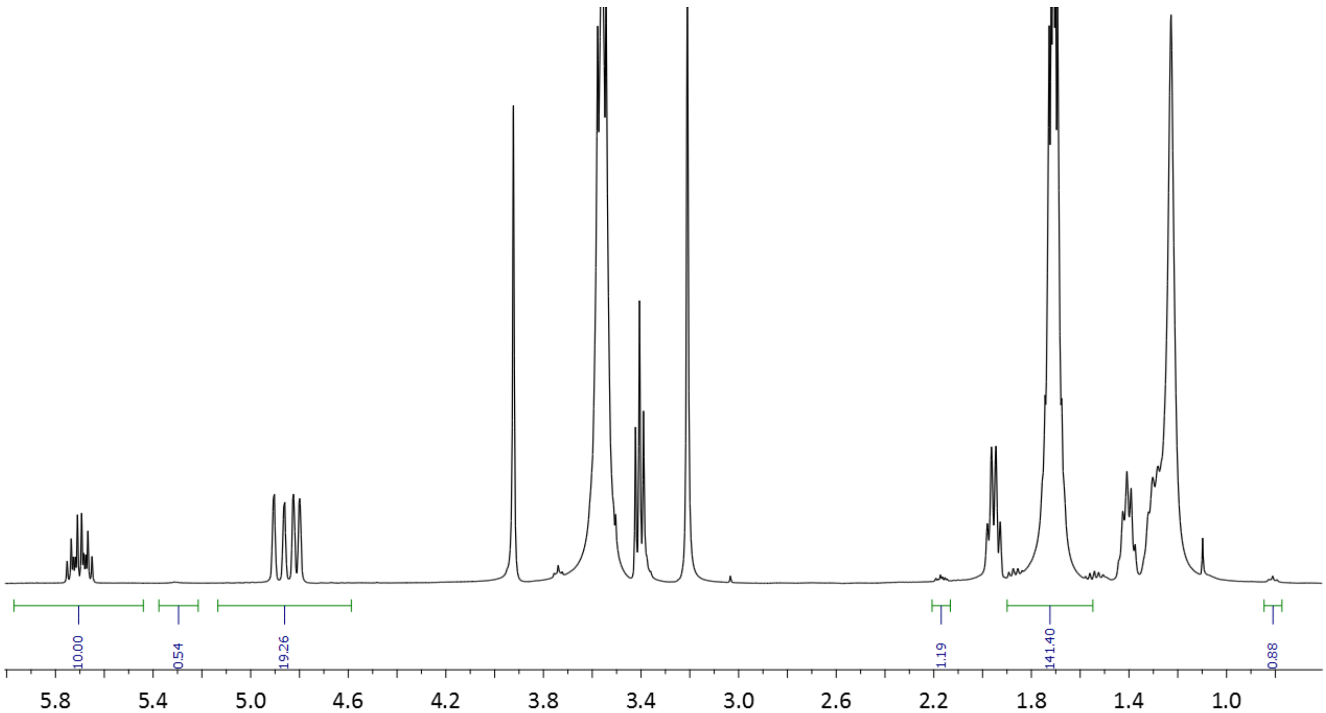
The following ^{1}H NMR spectra are of

1) a sample of a solution of 0.02 moles of methyl 10-undecenoate in 7 ml THF (with a small amount of CD_2Cl_2 used as a reference),

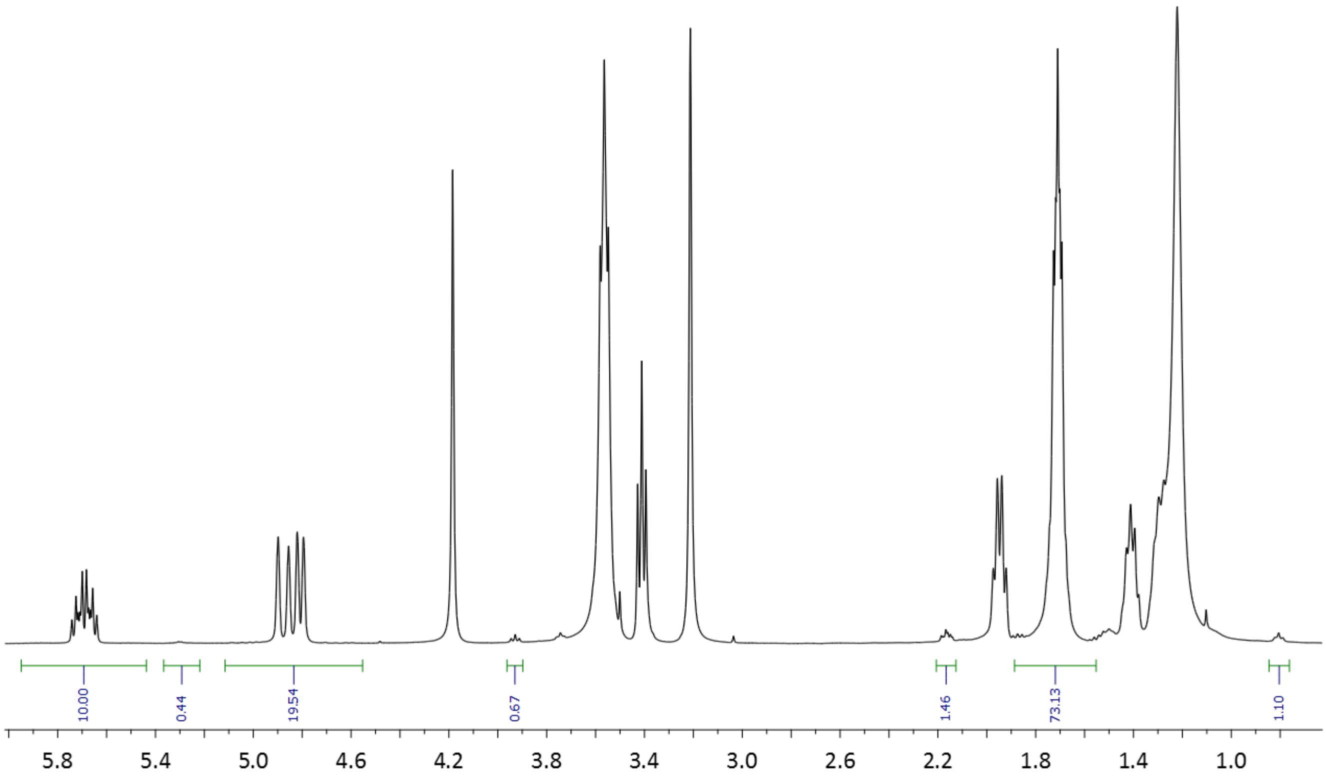
2) a sample of the reaction solution (neat) after the 1st hydrogenation,

3) a sample of the reaction solution (neat) after the 2nd hydrogenation (note a low intensity resonance of the trans-esterification product, 10-undecenyl 10-undecenoate, at 3.93 ppm).





10.00
0.54
19.26
1.19
141.40
0.88
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0



10.00
0.44
19.54
0.67
1.46
73.13
1.10
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0

References

[1] Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2001**, *20*, 1001.

[2] Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem.* **2012,** *51*, 2772–2775.

[3] a) Köllhofer, A.; Plenio, H. *Chem. Eur. J.* **2003**, *9*, 1416–1425; b) Goerlich, *J*. R.; Schmutzler, R. *Phosphorus Sulfur und Silicon.* **1995**, *102*, 211–215.

[4] Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343-4346.

[5] SAINT (**1999**) Release 6.06; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, Wisconsin, USA.

[6] Sheldrick, G.M. (**1999**). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, Wisconsin, USA.

[7] XPREP (**1997**) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program.Bruker AXS Inc., Madison, Wisconsin, USA.

[8] SHELXTL (**1997**) Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, Wisconsin, USA.

[9] a) Sheldrick, G.M. (**1997**). SHELXS97, Program for the Solution of Crystal Structures. Univ. of Gottingen, Germany; b) Sheldrick, G.M. (**1997**). SHELXL97, Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

[10] LinXTL is a local program; available free of charge from http://sourceforge.net/projects/linxtl/.

[11] Spek, A. L. *Acta Cryst*. **2009**, *D65*, 148-155.

[12] Wang, H. Y.; Yin, W. L.; Klüner, T.; Metzger, J. O. *Chem. Eur. J.* **2009**, *15*, 10948-10959.

[13] a) Vikse, K. L.; Ahmadi, Z.; Luo, J.; van der Wal, N.; Daze, K.; Taylor, N.; McIndoe, J. S. *Int. J. Mass Spectrom.* **2012**, *323*, 8-13; b) Yunker, L. P. E.; Stoddard, R. L.; McIndoe, J. S. *J. Mass Spectrom.* **2014**, *49*, 1-8.

[14]Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem. Int. Ed.* **2013**, *52*, 2538-2542.

[15]Balaraman, E.; Khaskin, E.; Leitus, G.; Milstein, D. *Nat. Chem.* **2013**, *5*, 122-125.