Supporting Information

Catalytic, Oxidant Free, Direct Olefination of Alcohols using Wittig Reagents

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General Specifications

All catalytic experiments with metal complexes were carried out via a general procedure specified in the main manuscript. Identity and distribution of the products were established on an 7820A GC System containing an HP-5MS column, coupled with a 5975 Series MSD, all manufactured by Agilent. Reported distributions and yields of products were confirmed via an HP6890 series GC/FID system containing a Supelco SPB-5 column, with cyclooctene internal standard in ambiguous cases and/or NMR confirmation. Inert atmosphere experiments were carried out under an atmosphere of purified nitrogen in Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier. Deuterated solvents used in the study: CDCl₃, DMSO-d₆, and D₂O were used as received from Cambridge Isotope Laboratories. The complex bipyP-RuH(Cl)(CO) **1** was synthesized according to published procedure.¹

¹H, ¹³C and ³¹P NMR spectra were recorded at 300 or 400, 75 and 100 MHz respectively, using a Bruker AMX-250 and AMX-400 NMR spectrometers. In order to verify the identity of some isomers (entry 8 and 18, Table 1), some ¹H spectra were recorded on a Bruker AMX-500 spectrometer at 500MHz and simulated. ¹H and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane. Some of the products were found on the SDBS online database which was used to confirm their identity, while similar compounds could be used to confirm the structural isomerism.²

Experimental Procedures

General procedure for synthesis of Wittig salts

The Wittig salts were prepared from the corresponding halides and triphenylphosphine by well established procedures: usually a halide was mixed together with a slight (1.1 eq) excess of PPh3: an amount of methanol or xylenes was added to dissolve the reactants and ensure a good reflux, and the solution was refluxed under ambient atmosphere overnight. Cooling the solution allowed for precipitation of the salt, which was washed with ether and hexanes, and subsequently dried under vacuum. NMR in dmso-d6 was used to confirm the identity of the salt. If the salt did not precipitate (only when MeOH was used as a solvent), the solvent was evaporated by rotary evaporation and hexanes were added to the remaining sludge in order to precipitate the desired salt, which was subsequently washed with hexanes and ether to remove the excess PPh₃.

General procedure for determining product identity, yields and stereochemistry

After a typical reaction, 5 drops of the reaction mixture were added to a vial containing several mls of conc. NH₄Cl or conc. NaHCO₃ (for amines) and several mls of diethyl ether. After vigorous shaking, the ether layer was sampled by chromatography. The identity of most products could be determined via the GC/MS system by considering elution times against a stilbene standard, by the mass fragmentation spectrum which often included the molecular ion peak, and checking which structural isomer (cis or trans) has a higher boiling point. Since the HP-5 and SPB-5 are non-polar columns, this can often give definitive information. In addition, many of the compounds synthesized could be compared to samples present in the Agilent MSD software database, which served to confirm identity, but often did not provide good stereo-assignment.

Yields were determined by GC/FID, using cyclooctene, added after the reaction, as internal standard. In addition crude reaction mixtures after workup in entries 8, 9, and 10 (Table 1) also had 10% cyclooctene standard added to them and an NMR spectrum was obtained, confirming the quantitative yield assignments and isomer distribution.

For some of the substrates, column chromatography was carried out after workup in order to remove the phosphine byproducts and determine isolated yields by weighing, giving strong support for the GC/FID method. NMR of products in these cases are reproduced below. In the case where PPh₃ was common isolated yields were lower as products tended to elute with some overlap with PPh₃ and these fractions were discarded. Isolated yields can often be optimized and in general, large scale reactions (more than 1mmol which was not the case in the current initial report) lead to larger isolated yields while techniques such as prep-HPLC (not available in the current study) lead to large isolated yields on a small scale. Thus, isolated yields in a methods development study are a support of crude/NMR yields, but they are not indicative of reaction efficacy.

Structural isomer determination that was ambiguous via GC/MS and boiling point differences, was always determined by NMR of the isolated product and simulation of the coupling constants where required. In case of overlapping NMR signals, stereoisomer distribution information was taken from GC/FID, and could not be obtained only in the case of entry 1, where ¹³C integration of olefinic peaks was used to determine isomer ratio instead (Table 1).

Specific Information on Table 1 entries as well as selected NMR spectra where applicable (including all isolated products)

Entry 1: Yield was determined by GC/FID integration against a cyclooctene standard added after reaction completion. In a separate reaction without standard, the reaction mixture was extracted with 2x50 ml of ether, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the ether extracts were collected, dried over MgSO₄, filtered and concentrated to get a crude reaction mixture. A part of the crude mixture was dissolved in CDCl₃, based on which the tentative assignement of the *cis* isomer as the major product was made. The isomers could not be separated by GC. Due to the volatility (high vapor pressure) of the product, it was difficult to get good isolated yields, with the best yield obtained from a reaction of 100uL of hexanol at 37% isolated yield. The olefinic envelope appeared representative of earlier reactions and its spectrum is reproduced below. Based on integration of olefinic carbon NMR signals, stereochemistry is assigned as 72%Z to 28%E. The product is well known and is commercially available. A good reference that includes ¹³C spectral data of both isomers is available.³

Z72%/E28% mixture

Figure S1: ¹HNMR of Entry 1 Table 1 olefin region



Entry 2: Reaction of the Wittig salt occurred according to ¹HNMR and ¹⁹FNMR spectra, however olefin products were not isolated from the complex mixture.

Entry 3: Yield was determined via GC/FID integration against a cyclooctene standard added after reaction completion. In a separate reaction without standard, the reaction mixture was extracted with 2x50ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the hexane extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was separated via column chromatography with the product eluting in the first hexanes fractions. The three other isomers are assigned as the *cis* isomer and products of isomerization to give 1-phenyl-2-heptenes. Olefinic peaks for the non-benzylic olefin products are seen in the ~5.5-5.8ppm range in the ¹HNMR. NMR spectrum is reported for the major isomer.⁴ ¹H (300 MHz, CDCl₃) δ : 0.96 (t, 3H, *J*_{HH} = 7.1Hz), 1.31-1.44 (m, 4H), 1.48-1.58 (m, 2H), 2.26 (q, 2H, *J*_{HH} = 7.1Hz), 6.28 (dt, 1H, *J*_{HH} = 15.9Hz; 6.8Hz), 6.43 (d, 1H, *J*_{HH} = 15.9Hz), 7.23 (vt, 1H), 7.34 (t, 2H, *J*_{HH} = 7.6Hz), 7.38 (t, 2H, *J*_{HH} = 7.6Hz). ¹³C{¹H}</sup> NMR (75 MHz, CDCl₃): 14.2, 22.7, 29.2, 31.6, 33.2, 126.0 (2C), 126.9, 128.5, 128.6, 129.8, 131.4, 138.1.



Figure S2: ¹HNMR of extracted products Entry 3 Table 1





Figure S3: ¹HNMR of extracted products Entry 3 Table 10lefin region

Entry 4: Yield was determined via GC/FID integration against a cyclooctene standard added after reaction completion. In a separate reaction without standard, the reaction mixture was extracted with 2x50ml n-hexane, washed with NH₄Cl, NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was extracted via column chromatography with the product eluting in the first hexanes fractions. Latter hexanes fractions which also contained the product were not collected, due to the presence of large amount of PPh₃ formed due to decomposition of the ylide and/or Wittig salt. When this reaction was repeated with 1.7 eq. of base instead of 1.2 eq., an addition product of hexanol to the double bond of the product olefin was seen in large amounts, while with 1.2 eq. of base, the amount of this product was minimized. Olefinic peaks for the non-benzylic olefin products are seen in the ~5.5-5.8ppm range in the ¹HNMR. The trans (E) isomer peaks are observed at ~7.3ppm. The NMR spectrum helped assign the major isomer as Z; some 13 C peaks could not be found/assigned due to fluorine coupling. NMR spectra are reported for the major isomer. ¹H (300 MHz, CDCl₃) δ: 0.92 (m, 3H), 1.21-1.39 (m, 4H), 1.44-1.56 (m, 2H), 2.25 (q, 2H, J_{HH} = 6.9Hz), 6.28 (dt, 1H, $J_{\rm HH}$ = 15.9Hz; 6.8Hz), 6.43 (m, 2H), 7.62 (bs, 1H), 7.68 (bs, 1H), 7.39 (bs, 1H). ¹³C{¹H} NMR (75 MHz, CDCl₃): 14.2, 22.7, 28.8, 31.6, 33.2, 120.3 (2C), 125.6 (2C), 127.4, 135.8, 140.1.



Figure S5: ¹HNMR of extracted products Entry 4 Table 1



Figure S6: ¹HNMR of extracted products Entry 4 Table 10lefin region





Figure S7: ${}^{13}C{}^{1}H$ NMR of extracted products Entry 4 Table 1

Entry 5. Yield was determined via GC/FID integration. Although all starting alcohol was consumed, hexyl hexanoate ester was detected in this reaction and it contained 7.6% of the alcohol moieties with the rest being 82.1% E-1phenyl-1-octene product of rearrangement and the others being the cis isomer and 1phenyl-2-octene in 5.8 and 4.7 percent ratios, respectively. Olefinic peaks for the non-benzylic olefin products are seen in the ~5.2-5.8ppm range in the ¹HNMR. Despite trace peaks at 3.3 ppm which may correspond to hydrogenated products, there were no detectable products of double bond hydrogenation by GC/MS. The reaction mixture was extracted with 2x50 ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine. The extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude reaction mixture was purified by column chromatography, with the product eluting in the first hexanes fractions, to get an isolated yield of 33%. Latter hexanes fractions which also contained the product were not collected, due to the presence of large amount of PPh₃ formed due to decomposition of the ylide and/or Wittig salt. The NMR spectra are derivative of entry 4, with one extra CH₂ group in the alkyl chain as can be seen in the Figures below.⁴



Figure S8: ¹HNMR of extracted products Entry 5 Table 1



Figure S9: ¹HNMR of extracted products Entry 5 Table 1 olefin region



Figure S10: ${}^{13}C{}^{1}H$ NMR of extracted products Entry 5 Table 1



Entry 6: Yield was determined via GC/FID integration. Reaction did not go to completion with 10% alcohol and aldehyde remaining; however, no ester byproduct was observed. Both mono and dialkylated salts were obtained, with the latter obtained as a slightly major product. Unreacted alcohol and aldehyde elute together on the GC/FID instrument and are 10% of total. The mono products were obtained as a mixture of four isomers, with trans being determined as major (0.4/2.1/2.1/33.7)%. Two of the minor isomers are assumed to be 1-methylphenyl-2heptenes and the other *cis*. The di-products gave three major peaks, with the major isomer being the di-trans 4-(1-heptene)-phenyl-1-heptene (6.7/5.0/40.0)%. Each di-product contains 2 molecules of the alcohol moiety and this is taken into account in the percentages as they are calculated with regards to the starting alcohol. There were no detectable products of double bond hydrogenation. The reaction mixture was extracted with 2x50 ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was purified via column chromatography with the product eluting in the first hexanes fractions to get a tentative isolated yield of 32%. Latter hexanes fractions which also contained the product were not collected, due to the presence of large amount of PPh₃ formed due to decomposition of the ylide and/or Wittig salt. The isolated yield refers both to the mono and di-product. The NMR spectrum was useful for confirming the identity of the major products as *trans* isomers. However, due to significant overlap between the two products present in roughly equal amounts, the peaks are not assigned to a specific product, but are reproduced below. The peak at 2.35 ppm is likely 1,4- xylene from decomposition of excess Wittig salt and the mono product(s).



Figure S11: ¹HNMR of extracted products Entry 6 Table 1





Figure S12: ¹HNMR of extracted products Entry 6 Table 1 olefin region

Figure S13: ¹³C{¹H}NMR of extracted products Entry 6 Table 1



Entry 7: Yield was determined via GC/FID integration and subsequent isolation of the product. Reaction did not go to completion with 1% alcohol remaining; however, no ester byproduct was observed. The reaction mixture was extracted with 2x50 ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was purified by column chromatography, with the product eluting in the first hexanes fractions, to get an isolated yield of 84%. The inner olefin assignment as 87% cis (Z) was determined on the basis of GC/MS integration data (The isomers could not be cleanly isolated via GC/FID) and ¹HNMR coupling constant evidence. 1H NMR (300 MHz, CDCl₃) δ 5.83 (ddt, J_{HH} = 16.9, 10.1, 6.7 Hz, 1H), 5.64 – 5.27 (m, 2H), 5.01 (dd, J_{HH} = 16.9, 1.4 Hz, 1H), 4.95 (dd, J_{HH} = 10.1, 1.4 Hz, 1H), 2.17 – 1.69 (m, 6H), 1.55 – 1.13 (m, 14H), 0.92 (t, J_{HH} = 7.3 Hz, 3H). 13C NMR (75 MHz, CDCl₃) δ : 139.40, 130.24, 129.79, 114.24, 33.97, 32.77, 29.92, 29.81, 29.63, 29.45, 29.30, 29.10, 27.37, 23.06, 13.96.





Figure S14: ¹HNMR of extracted products Entry 7 Table 1



Figure S15: ¹HNMR of extracted products Entry 7 Table 1 olefin region

Figure S16: ¹³C{¹H}NMR of extracted products Entry 7 Table 1



Entries 8-10: These are well known compounds and their yields and relative stereochemistry (only two isomers possible and hydrogenated product), are easily determined via the GC/MS spectral library (except entry 10) and GC/FID. Therefore, these compounds were not isolated. The reactions to produce these stilbenes were clean and proceeded with quantitative yields under the standard reaction conditions. The stereochemistry in the case of all three products (E major product), and yields (with 10% cyclooctene internal standard) were confirmed by NMR spectra of the crude mixture. The olefin section of the NMR spectrum of the crude mixture in the case of entry 10 is reproduced below as an example. Entry 9 showed considerable (~14%) hydrogenation of the olefin. However, when reaction time was only 1hr (Table 2 entry 1) or the catalyst loading was only 0.02 mol% (Table 2, entry 4), only 4% and 1% respectively of the hydrogenated product were obtained

Entry9:

Entry10:

Entry11: ⁵



Figure S17: Crude ¹HNMR Entry 10 Table 1 olefin and aromatic region



Entry 11: The reaction mixture was extracted with 2x50ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was separated by column chromatography with the product eluting in the first hexanes fractions. The NMR helped assign the major isomer as *trans* (E). Olefinic peaks for the non-benzylic olefin products are seen in the ~5.5-5.8ppm range in the ¹HNMR. The percentages of isomers were determined by GC/FID as 91% E, with the Z and 2-pentene accounting for 5 and 4% respectively. NMR spectrum is reported for the major isomer.⁴ ¹H (300 MHz, CDCl₃) δ : 1.00 (t, 3H, *J*_{HH} = 7.2Hz), 1.54 (sext, 2H, *J*_{HH} = 7.2Hz), 2.23(q, 2H, *J*_{HH} = 7.2Hz), 6.26 (dt, 1H, *J*_{HH} = 15.9Hz), 7.22 (bt, 1H, *J*_{HH} = 7.4Hz) 7.30 (bt, 2H, *J*_{HH} = 7.4Hz), 7.37 (bt, 2H, *J*_{HH} = 7.4Hz). ¹³C {¹H}</sup> NMR (75 MHz, CDCl₃): 13.9, 22.7, 35.3, 125.0 (2C), 125.9, 128.6 (2C), 130.0, 131.1, 138.1.



Figure S18: ¹HNMR of extracted products Entry 11 Table 1





Figure S19: ¹HNMR of extracted products Entry 11 Table 1 olefin region



Entry 12: Decomposition of the Wittig salt/ylide is a significant problem with this substrate (see also entry 5) under the reaction conditions. 23% of the alcohol units remain as alcohol/aldehyde during the reaction. Significantly however, no benzyl benzoate ester was detected in this reaction. Yield was determined by GC/FID. NMR of the crude product confirmed the stereochemistry assignment (95% E/5% Z).⁶



Entry 13: As is generally known, ketones react slowly with Wittig reagents. A significant amount of the alcohol moieties, 32%, was conserved as alcohol or ketone, with the GC/MS able to distinguish between the two. Yield was obtained via GC/FID. A good isolated yield could not be obtained due to the volatility of the product under the extraction conditions, however, ¹HNMR characterization that was used to confirm the stereochemical assignment is presented here. The reaction mixture was extracted with 2x50 ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude mixture. The crude mixture was purified by column chromatography, with the product eluting in the first hexanes fractions. No hydrogenated product was detected ¹HNMR⁷ (400 MHz, CDCl₃) δ 5.13 (tt, 1H, J_{HH} = 7.3Hz, 1.0Hz), 2.26 – 2.14 (m, 4H), 1.94 (q, J_{HH} = 7.3Hz, 2H), 1.70 – 1.40 (m, 6H), 1.36 (dq, J_{HH} = 14.6Hz, 7.3Hz, 2H), 1.28 (bs, 2H), 0.90 (t, J_{HH} = 7.3 Hz, 3H).



Figure S21: ¹HNMR of extracted products Entry 13 Table 1



<u>Entry 14:</u> Conversion was lower (55%) as compared to entry 13 and is likely due to the greater sterically demanding nature of the ylide intermediate. The two other minor isomers obtained are likely cycloheptenes with a benzyl group in the 1 position, and are formed due to the activated nature of the benzyl double bond, which contrasts with only one isomer being obtained in entry 13 (see entries 4-6 for similar chemistry). No hydrogenated product was detected.⁸ Yield was determined via GC/FID.



Entry 15: Although all of the alcohol was converted, 26% remained as unreacted aldehyde. Based on the mass spectra and retention times of previously isolated products (entries 3,5,6 and 11), the major product was identified as the product of rearrangement, E-1-phenyl-1-hexene (88% of total hydrocarbon products). The other minor isomers are the Z-1-phenyl-1-hexene (7%) and 1-phenyl-2-hexene (5%). No hydrogenated product was found.⁴ Yield was determined by GC/FID.



<u>Entry 16</u>: This highly stereo-demanding secondary alcohol was fully converted to acetophenone (75%) and two stereoisomeric hydrocarbon products (25%) in 60%/40% ratio, that were assigned as E/Z respectively.⁹ Identity of the products was determined by GC/MS and yield by GC/FID.



Entry 17: Samples for GC/FID and GC/MS were prepared by utilizing 3 ml of conc. NaHCO₃ solution as the aqueous layer and 3 ml of ether as an organic layer with a few drops of the reaction mixture serving as the sample. During the extraction, the reaction was acidified with 1M HCl solution and washed 3x with CH₂Cl₂. Afterwards, the remaining water layer was made basic with NaOH and was washed 3x with CH₂Cl₂. The organic washings were collected, dried over MgSO₄, filtered and concentrated to get the product relatively pure, albeit in an isolated yield of only 32%, which is a function of the acid/base isolation procedure; quantitative yield was obtained via GC/FID with cyclooctene as internal standard. NMR assignment of the product as Z was made after simulating the olefin peaks, with the biggest coupling constant found to be ~11Hz.¹⁰ ¹HNMR (300MHz, CDCl₃) δ 5.39 (m, 2H), 2.15 – 2.35 (m, 2H), 2.23 (s, 6H), 1.92 – 2.06 (m, 2H), 1.31-1.44 (m, 2H), 1.28 (bs, 2H), 0.90 (t, *J*_{HH} = 7.2 Hz, 3H). ¹³C{¹H} NMR (75MHz, CDCl₃): 13.9, 23.0, 25.9, 29.9, 45.5 (2C), 59.7, 127.3, 131.2.





Figure S22: ¹HNMR of extracted products Entry 17 Table 1

Figure S23: ¹HNMR of extracted products Entry 17 Table 1 olefin region





Figure S24: ¹³C{¹H}NMR of extracted products Entry 17 Table 1

Entry 18: A significant amount of debrominated products was obtained under the reaction conditions, however no ester byproduct was observed. The amounts of each isomer, cis/trans and brominated/debrominated, or four in total, were determined by GC/FID and confirmed by NMR of the isolated mixture. A high amount of isolated material was obtained, but the 37% isolated yield in Table 1 refers only to the brominated products, which are minor. The reaction was performed on a 0.4 mmol scale (75 mg of 4-bromobenzyl alcohol), giving 75 mg of products. The reaction mixture was extracted with 2x50 ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was purified by column chromatography with the product eluting in 1/50 diethylether/hexanes mixture. All isomers have significant boiling point and slight polarity differences, which should make it possible to separate them by preparative HPLC or GC. An NMR spectrum of the isolated mixture which includes the olefin and aromatic regions is reproduced below.¹¹





Figure S25: ¹HNMR of extracted products Entry 18 Table 1

Entry 19: This compound was chosen to check for an amidation side-reaction. Although the desired product was the main product, two high-boiling products were obtained that could not be integrated correctly and made NMR assignment difficult. They were tentatively assigned as an amide and a compound with two amide units, both terminated by a stilbene moiety. The assignment of the major isomer as trans (E) was confirmed by NMR (consistent with literature) after extraction which was done according to the following procedure: The reaction was acidified with 1M HCl solution and washed 3x with 50 ml of CH₂Cl₂. Afterwards, the remaining aqueous layer was made basic with NaOH to a pH of ~12 and was washed 3x with 50 ml of CH₂Cl₂. The organic washings were collected, dried over MgSO₄, filtered and concentrated. The resulting crude mixture was purified by column chromatography on a neutral alumina column and eluted with MeOH, not resulting in significant separation from the amide byproducts. Yields of the main amino stilbene E/Z units (and hydrogenated byproduct) were determined by GC/FID integration against a cyclooctene internal standard added to the mixture after the column isolation procedure and were determined as 60%, with the breakdown being 87/8% E/Z and hydrogenated byproduct being 7%.¹².



Entry 20: Cinnamic alcohol gave a significant amount of product, with the starting material all being consumed. However, the product was exclusively hydrogenated in the benzyl double bond

position and was found to be >95% of total cinnamyl alcohol containing moieties. The hydrogenation may have occurred before the addition of the ylide to the aldehyde, as 4% of 3-phenyl-propanal were found after the reaction. Traces of 1-phenyl-1pentene were also observed, suggesting that some retro-Michael addition also took place. The reaction mixture was extracted with 2x50ml of n-hexane, washed with conc. NH₄Cl, conc. NaHCO₃, and brine, the extracts were collected, dried over MgSO₄, filtered and concentrated to get a reaction crude. The crude mixture was purified by column chromatography, with the product eluting in the first hexanes fractions. Simulation of the olefin region helped assign the major isomer as Z with the largest coupling being 11Hz. It was difficult to determine the ratio of Z/E isomers as they eluted together even on the GC/MS, but the NMR spectrum suggests that Z is by far the major product. ¹³C integration information gave conflicting information for different peaks, but a ratio of ~9/1 Z/E is an average.¹³ ¹H (300 MHz, CDCl₃) δ : 0.91 (t, 3H, *J*_{HH} = 7.0Hz), 1.31-1.40 (m, 2H), 2.01(q, 2H, *J*_{HH} = 7.0Hz), 2.39 (m, 2H), 2.70 (t, 2H, *J*_{HH} = 7.0Hz), 5.35-5.51 (m, 2H), 7.18-7.26 (m, 3H), 7.27-7.35 (m, 2H). ¹³C {¹H} NMR (75 MHz, CDCl₃): 13.9, 22.9, 29.3, 29.4, 36.2, 125.9, 128.4 (2C), 128.6 (2C), 129.0, 130.6, 142.3 .



Figure S26: ¹HNMR of extracted products Entry 20 Table 1



Figure S27: ¹HNMR of extracted products Entry 20 Table 1 olefin region

Figure S28: ¹³C{¹H}NMR of extracted products Entry 20 Table 1



Entry 21: Cyclooctene standard was added to the reaction mixture and integrating the products by GC/FID showed quantitative yield when considering all possible products. The product was sampled by dissolving a few drops of the reaction mixture in a mix of concentrated NaHCO₃ and diethylether. A significant oxygenated mass ion peak (that grew over time) was observed, meaning that the product was not stable towards extraction conditions; its isolation was thus not attempted. 4 olefin isomers were observed with two of them designated as 1-(orthopyridil)-2pentene and the major isomers as the expected products 1-(orthopyridil)-1-pentene based on the mass fragment pattern. A peak of the hydrogenated product 2-pentylpyridine was also found overlapping with one of the minor isomers. The oxygenated product appeared to be a ketone with an extra mass of 16 units in the M⁺¹ ion peak. The breakdown of the products (out of a total of 100) is as follows: 4% is the overlapping peak of hydrogenated and minor isomer; 4% is the cis (Z) product; 2% is the other minor isomer; 75% is the major expected trans (E) product; 15% is the oxygenated product.¹⁴



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