Supplementary Information

Catalytic Hydrogenation of Functionalized Amides Under Basic and Neutral Conditions

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General Information

All pressurized reactions were carried out in a steel pressure reactor (50 atm H_2) equipped with a magnetic stir bar. Deuterated solvents were obtained from Aldrich and Cambridge Isotope Laboratories. Common laboratory solvents were dried over appropriate drying agents before each experiment. For example CH_2Cl_2, THF and 2-PrOH were distilled over CaH_2, Na/benzophenone and anhydrous Mg, respectively. 2-oxazolidinone, 4*S*-(–)-isopropyl-2-oxazolidinone, 4-chlorobenzoyl chloride, 4-fluorobenzoyl chloride, 2-furoyl chloride and 1-phenyl-pyrrolidin-2-one (**4**) were obtained from Alfa Aesar. Acetyl chloride, benzoyl chloride, 4-fluoroaniline, 4-chloroaniline, aniline, potassium bis(trimethylsilyl)amide, lithium bis(trimethylsilyl)amide, (4*S*,5*R*)-(–)-4-methyl-5-phenyl-2-oxazolidinone, morpholine, propionyl chloride, 2-piperazin-1-yl-1-piperidin-1-yl-ethanone, tris(triphenylphosphine)ruthenium(II) dichloride and *N*-phenylbenzamide (**8f**) were obtained from Aldrich. *N*,*N*-diphenylacetamide (**8a**), *N*-methylacetanilide (**8b**) and *N*,*N*-dimethylacetamide (**8e**), were obtained from TCI America. 2-(diphenylphosphino)ethylamine and sodium borohydride were obtained from Strem and BDH Chemicals, respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using 400 and 600 MHz Varian Inova, and 500 MHz Varian DirectDrive spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (δ) relative to TMS with the deuterated solvent as the internal reference. ^{31}P chemical shifts are reported in parts per million (δ) relative to 85% H_3PO_4 as the external references. NMR peak assignments were made using ^{1}H–^{1}H gCOSY, ^{1}H–^{13}C gHSQC, ^{1}H–^{15}N gHSQC and TOSCY NMR experiments. Abbreviations used for NMR spectra are s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), tt (triplet of triplet), q (quartet), m (multiplet) and br (broad). High-resolution mass spectra were recorded using an Agilent 6220 oa TOF Mass Spectrometer. Elemental analysis data were obtained using a Carlo Erba CHNS-O EA1108 elemental analyzer.

General procedures used to synthesize amides

The amine (76.0 mmol) was dissolved in 150 mL of CH_2Cl_2 and cooled to 0 °C using an ice bath. NEt_3 (83.6 mmol, 1.10 equiv) was added to the amine solution followed by the corresponding acid chloride (76.0 mmol, 1.00 equiv) drop-wise over 30 min. Then the mixture was stirred for 3.0-24 h at rt. The mixture was then poured into a separatory funnel and washed with 3 x 40.0 mL of saturated $NaHCO_3$(aq) followed by washing with 50.0 mL of saturated NaCl (aq). The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude amide was obtained in 90-98% yield. The product suitable for hydrogenation was obtained from distillation (liquid amides), trituration in *n*-hexanes or from recrystallization using EtOH as a recrystallization solvent (solid amides).

Spectroscopic identification of amides

All amide substrates are known. The ^{1}H NMR chemical shift information is reproduced here for convenience.

1-phenyl-pyrrolidin-2-one (**4**): White powder: ^{1}H NMR (499.815 MHz, $CDCl_3$, 27 °C): δ 2.15 (2H, p, J = 7.2 Hz, CH_2), 2.60 (2H, t, J = 8.0 Hz, CH_2), 3.86 (2H, t, J = 7.0 Hz, CH_2), 7.13 (1H, t, J = 7.5 Hz, aromatic CH), 7.36 (2H, t, J = 7.5 Hz, 2 aromatic CH), 7.60 (2H, d, J = 8.0 Hz, 2 aromatic CH).

N,*N*-diphenylacetamide (**8a**): White powder: ^{1}H NMR (499.815 MHz, $CDCl_3$, 27 °C): δ 2.09 (3H, s, CH_3), 7.29 (4H, d, J = 8.0 Hz, 4 aromatic CH), 7.10-7.50 (6H, m, 6 aromatic CH).

N-methylacetanilide (**8b**): Colorless crystals: ^{1}H NMR (498.122 MHz, $CDCl_3$, 27 °C): δ 1.86 (3H, s, CH_3), 3.26 (3H, s, CH_3), 7.18 (2H, d, J = 7.8 Hz, 2 aromatic CH), 7.33 (1H, t, J = 7.5 Hz, aromatic CH), 7.42 (2H, t, J = 7.2 Hz, 2 aromatic CH).

acetanilide (**8c**): Colorless crystals: ^{1}H NMR (499. 815 MHz, $CDCl_3$, 27 °C): δ 2.18 (3H, s, CH_3), 7.10 (1H, t, J = 7.5 Hz, aromatic CH), 7.15 (1H, brs, NH), 7.32 (2H, t, J = 8.0 Hz, 2 aromatic CH), 7.49 (2H, d, J = 7.5 Hz, 2 aromatic CH).

1-morpholinoethanone (**8d**): Colorless oil: ^{1}H NMR (399.794 MHz, $CDCl_3$, 27 °C): δ 3.3-3.8 (8H, m, 4 CH_2), 7.43 (5H, m, 5 aromatic CH).

N,*N*-dimethylacetamide (**8e**): Colorless liquid: ^{1}H NMR (498.122 MHz, $CDCl_3$, 27 °C): δ 2.05 (3H, s, CH_3), 2.91 (3H, s, CH_3), 2.98 (3H, s, CH_3).

benzanilide (**8f**): Off-white powder: ^{1}H NMR (499.815 MHz, $CDCl_3$, 27 °C): δ 7.16 (1H, t, J = 7.2 Hz, aromatic CH), 7.38 (2H, t, J = 7.8 Hz, 2 aromatic CH), 7.49 (2H, t, J = 7.5 Hz, 2 aromatic CH), 7.55 (1H, t, J = 7.5 Hz, aromatic CH), 7.64 (2H, d, J = 8.2 Hz, 2 aromatic CH), 7.82 (1H, brs, NH), 7.86 (2H, d, J = 7.0 Hz, 2 aromatic CH).

4-fluorobenzanilide (**8g**): White powder: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 7.19 (3H, t, J = 8.5 Hz, 3 aromatic CH), 7.40 (2H, t, J =7.6 Hz, 2 aromatic CH), 7.64 (2H, d, J = 7.6 Hz, 2 aromatic CH), 7.77 (1H, br, NH), 7.89-7.92 (2H, m, aromatic 2 CH).

4-chloro-*N*-methyl-*N*-phenylbenzamide (**8h**): White powder ^{1}H NMR (399.794 MHz, $CDCl_3$, 27 °C): δ 3.50 (3H, s, CH_3), 7.04 (2H, d, *J* = 7.3 Hz, aromatic CH), 7.13-7.19 (3H, m, aromatic CH), 7.23-7.28 (4H, m, 4 aromatic CH).

N-(4-fluorophenyl)benzamide (**8i**): White powder: ^{1}H NMR (399.984 MHz, $CDCl_3$, 27 °C): δ 7.07 (2H, t, *J* = 8.6 Hz, 2 aromatic CH), 7.49 (2H, t, *J* = 7.1 Hz, 2 aromatic CH), 7.55-7.62 (3H, m, 3 aromatic CH), 7.79 (1H, br, NH), 7.87 (2H, d, *J* = 8.6 Hz, 2 aromatic CH).

N-(4-bromophenyl)benzamide (**8j**): Colorless crystals: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 7.49-7.53 (4H, m, 4 aromatic CH), 7.56-7.61 (3H, m, 3 aromatic CH), 7.80 (1H, br, NH), 7.88 (2H, d, *J* = 7.9 Hz, 2 aromatic CH).

N-phenyl-2-furancarboxamide (**8k**): Colorless crystals: ^{1}H NMR (499.118 MHz, $CDCl_3$, 27 °C): δ 6.58 (1H, dd, *J* = 3.5, 1.7 Hz, furan CH), 7.17 (1H, t, *J* = 7.4 Hz, aromatic CH), 7.27 (1H, d, *J* = 3.5 Hz, furan CH), 7.39 (2H, t, *J* = 7.4 Hz, 2 aromatic CH), 7.54 (1H, d, *J* = 1.7 Hz, furan CH), 7.67 (2H, d, *J* = 7.5 Hz, aromatic CH).

furan-2-yl(piperidin-1-yl)methanone (**8l**): Colorless crystals: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 1.62-1.72 (6H, m, CH_2 and CH_3 overlapping), 3.71 (4H, brs, CH_2), 6.47 (1H, dd, *J* = 3.5, 1.7 Hz, furan CH), 6.93 (1H, d, *J* = 3.5 Hz, furan CH), 7.47 (1H, d, *J* = 1.7 Hz, furan CH).

2-piperazin-1-yl-1-piperidin-1-yl-ethanone (**8m**): White powder: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 1.50-1.67 (7H, m, CH_2, CH_3 and NH overlapping), 2.48 (4H, brs, CH_2), 2.91 (4H, t, *J* = 4.7 Hz, CH_2), 3.16 (2H, s, CH_2), 3.52-3.57 (4H, m, CH_2).

General procedures used to synthesize *N*-acyloxazolidinones

The chiral *N*-acyloxazolidinones (**9a**) and (**9b**) were prepared according to a procedure reported by Evans and coworkers.[1]

Spectroscopic identification of *N*-acyloxazolidinones

9a: Viscous oil: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 0.62 (3H, d, *J* = 6.8 Hz, CH_3), 0.85 (3H, d, *J* = 7.0 Hz, CH_3), 1.18 (3H, d, *J* = 6.8 Hz, CH_3), 2.18 (1H, m, CH), 2.65 (1H, dd, *J* = 7.6 Hz, CH), 3.14 (1H, dd, *J* = 7.5 Hz, CH), 4.12-4.27 (1H, m, CH), 4.45 (1H, m, CH), 7.2 (1H, m, aromatic CH), 7.27 (4H, m, 4 aromatic CH).

9b: Viscous oil: ^{1}H NMR (498.118 MHz, $CDCl_3$, 27 °C): δ 0.75 (3H, d, *J* = 6.5 Hz, CH_3), 1.21 (3H, d, *J* = 6.5 Hz, CH_3), 2.68 (1H, dd, *J* = 8.0 Hz, CH), 3.14 (1H, dd, *J* = 7.0 Hz, CH), 4.17 (1H, m, CH), 4.78 (1H, m, CH), 5.65 (1H, d, *J* = 7.0 Hz, CH), 7.18-7.44 (10H, m, 10 aromatic CH).

Control Experiments

Nanoparticle mediated hydrogenation[2]

14.5 mg of ruthenium black (10.0 μmol assuming 7% of ruthenium atoms are on the surface) and 100 μmol (10.0 equiv) of **4** were added to a stainless steel autoclave equipped with a magnetic stir bar. The autoclave was then purged with H_2 for 10 min at room temperature. 8.0 mL of THF was then added to the autoclave using a gas tight syringe. The autoclave was then pressurized to 50 atm H_2. The reaction mixture was stirred at 100 °C for 17 h. The autoclave was then allowed to cool over the course of 1 h before venting at room temperature. The percent conversion was determined by ^{1}H NMR spectroscopy. Compound **4** was converted into *N*-cyclohexylpyrrolidin-2-one with TON = 1.

NMR study of the reaction between [Ru(η3-C_3H_5)($Ph_2P(CH_2)_2NH_2)_2$]BF_4 (2), $NaBH_4$, and H_2.

[Ru(η3-C_3H_5)($Ph_2P(CH_2)_2NH_2)_2$]BF_4 (**2**) (0.02 mmol, 13.5 mg) and $NaBH_4$ (0.04 mmol, 1.6 mg) were weighed into two separate NMR tubes inside the glove box. Distilled THF-d_8 (0.7 ml) added to **2** by cannula under argon and ^{1}H NMR and ^{31}P {^{1}H} NMR were recorded. Then the solution containing **2** was transferred to the tube containing $NaBH_4$ under H_2 (~ 2 atm). The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at room temperature. Then the resulting solution was heated at 60 ^{o}C for 30 minutes inside the NMR probe. The ^{1}H and ^{31}P{^{1}H} NMR spectra showed the reaction was complete, generating *trans*-Ru(H)(BH_4)($Ph_2CH_2CH_2NH_2)_2$ as the major product (95% spectroscopic yield). The product was identified using ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H},^{11}B{^{1}H} ^{1}H-^{15}N HSQC, gTOCSY, gCOSY and ^{1}H {^{31}P} NMR experiments in THF-d_8. ^{1}H NMR (399. 949 MHz, THF-d_8, 27 °C): δ -15.67 (1H, t, J = 25.0 Hz, Ru-H), -2.63—1.56 (4H, bs, HBH_3), 2.19-2.30 (2H, m, CH_2), 2.35-2.45 (2H, m, CH_2), 2.52-2.66 (2H, m, CH_2), 3.03-3.20 (2H, m, CH_2), 3.65-3.75 (2H, bs, NH), 4.00-4.10 (2H, bs, NH), 6.93-7.02 (8H, m, aromatic CH), 7.03-7.12 (4H, m, aromatic CH), 7.23-7.28 (4H, m, aromatic CH), 7.30-7.38 (4H, m, aromatic CH). ^{13}C{^{1}H} NMR (125.691 MHz, THF-d_8, 27 °C): δ 41.3 (CH$_2$), 48.45 (CH$_2$), 132.2 (aromatic), 133.3 (aromatic), 138.3 (m, aromatic), 145.6 (m, aromatic), 147.2 (m, aromatic), ^{31}P{^{1}H} NMR - (161.902 MHz, THF-d_8, 27 °C): δ 29.1 (*minor*, s), 80.3 (*major*, s), ^{11}B{^{1}H} NMR - (128.319 MHz, THF-d_8, 27 °C): δ -30.54 - -27.10 (bs, BH_4)

Figure S1 *^{31}P{^{1}H} NMR of trans-Ru(H)(BH_4)($Ph_2CH_2CH_2NH_2$).The top spectrum shows the product formed after 30 minutes at 60 ^{o}C. The bottom spectrum was recorded just after mixing at room temperature. Peak assigned to trans-[Ru(H)(BH_4)($Ph_2CH_2CH_2NH_2)_2$] are labeled*. The peaks assigned to **2** are labeled.*

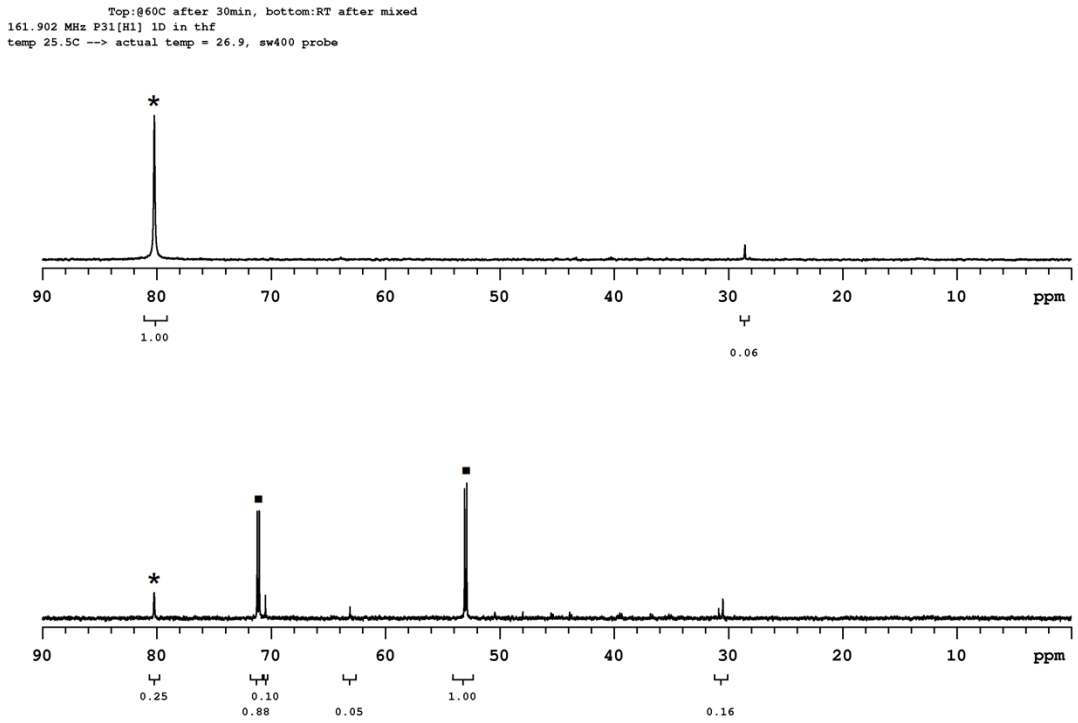


Figure S2. *^{1}H NMR spectrum (δ 6 to 0.4 ppm) of trans-Ru(H)(BH_4)($Ph_2CH_2CH_2NH_2$) formed by the reaction of **2** and $NaBH_4$ in ~2 atm H_2 in THF-d_8. Residual solvent, δ; 2-(diphenylphosphino)ethylamine ligand, NH=l*, CH=l* ; propylene, ϕ; Free hydrogen gas, H.*

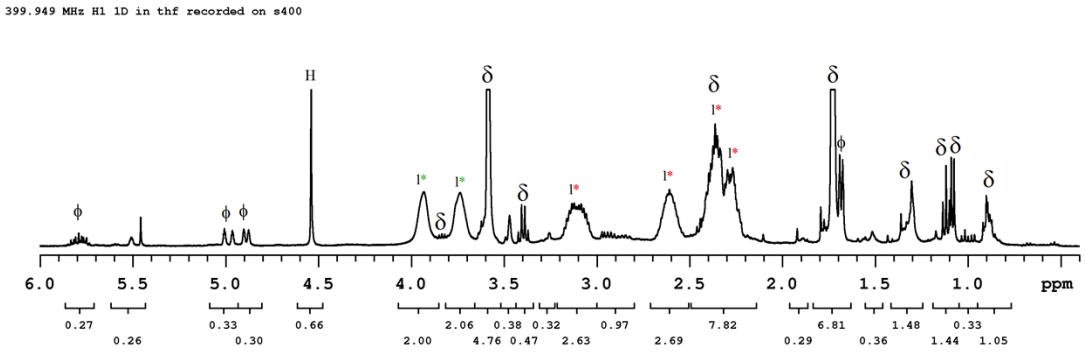
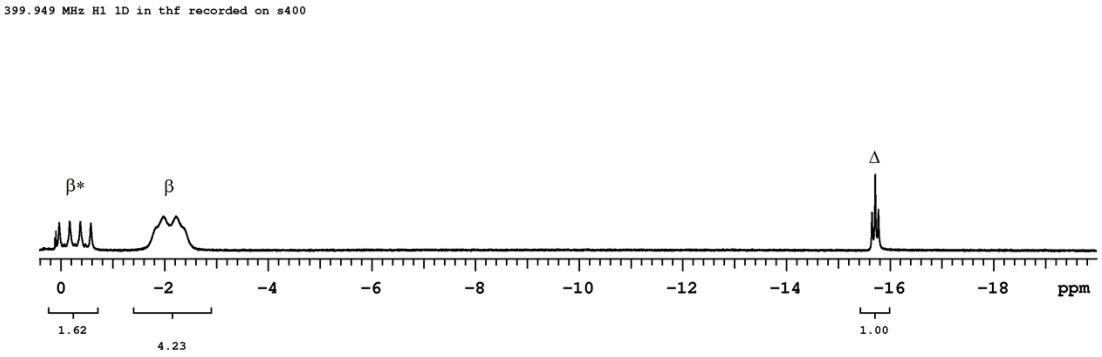


Figure S3. *^{1}H NMR spectrum (δ 0.4 to -20 ppm) of trans-Ru(H)(BH_4)($Ph_2CH_2CH_2NH_2$) formed by the reaction of **2** and $NaBH_4$ in ~2 atm H_2 in THF-d_8. Ruthenium hydride, Δ; BH_4 bonded to ruthenium, β; free BH_4^-, β*.*



Spectroscopic identification of hydrogenation products.

^{1}H NMR spectra for the base-free hydrogenation of **4.** Percent conversions and reaction times are listed on Table 1.

Figure S4 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of N-phenylpyrrolidin-2-one catalyzed by **2** and 2 equiv $NaBH_4$.*

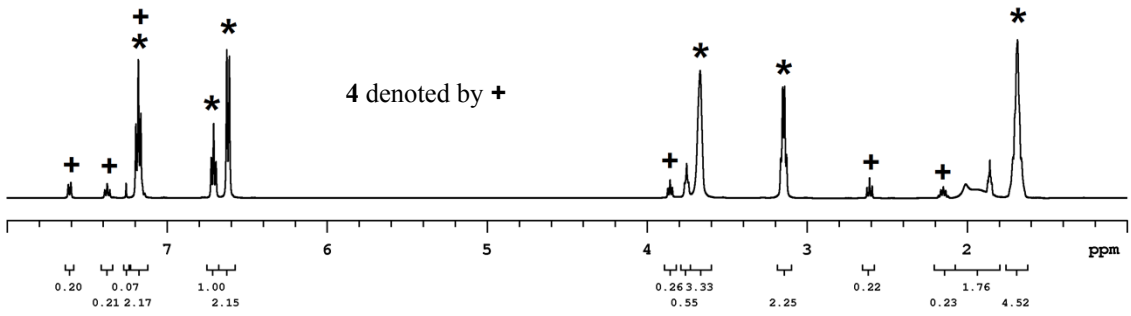


Figure S5 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of N-phenylpyrrolidin-2-one catalyzed by an in situ generated catalyst formed by the reaction of* ***5****, 2 equiv $Ph_2P(CH_2)_2NH_2$ and 5 equiv $NaBH_4$.*

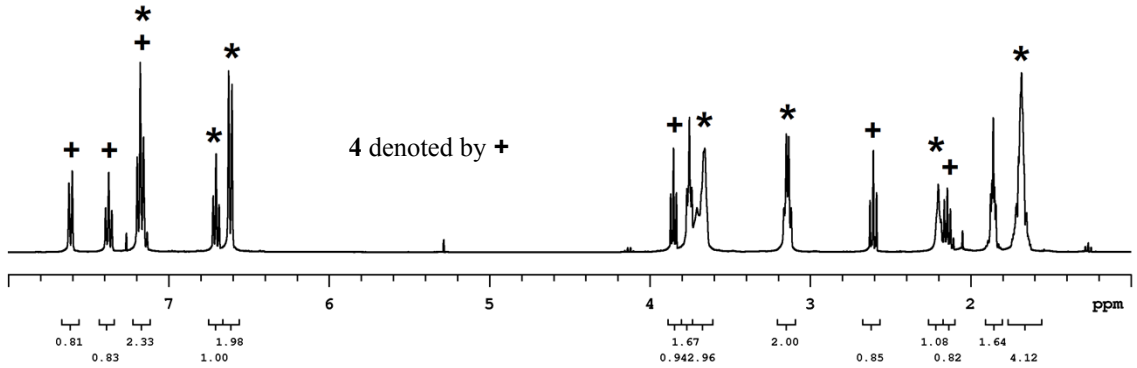


Figure S6 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of N-phenylpyrrolidin-2-one catalyzed by an in situ generated catalyst formed by the reaction of* ***6****, 2 equiv $Ph_2P(CH_2)_2NH_2$ and 5 equiv $NaBH_4$.*

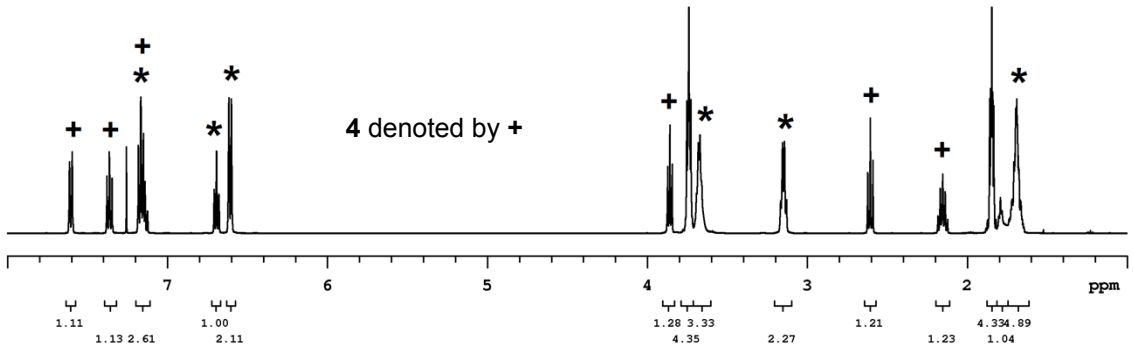
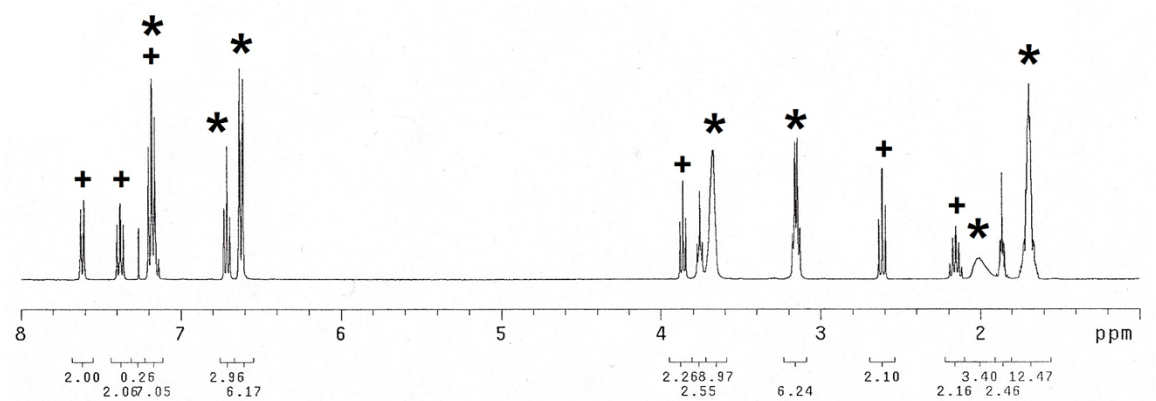


Figure S7 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of N-phenylpyrrolidin-2-one catalyzed by* ***3*** *and 5 equiv $NaBH_4$.*



^{1}H NMR spectra for the base-free hydrogenation of **8** using 0.1 mol% **2** and 0.2 mol% $NaBH_4$ under 50 atm H_2 at 100 °C in 24 h. Percent conversions and reaction times are listed on Table 2.

alcohol product denoted by (*)
amine product denoted by (■)
starting material denoted by (+)
internal standard denoted by (IS)
C–O cleavage product denoted by (X)

Figure S8 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of diphenylamine and ethanol resulting from the hydrogenation of N,N-diphenylacetamide (**8a**).*

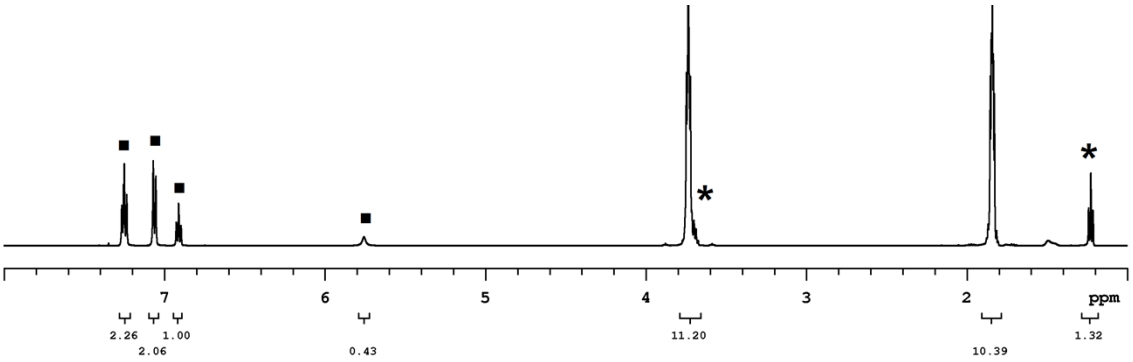


Figure S9 *The δ 8 to 1 ppm ^{1}H NMR spectrum showing the formation of N-methylaniline and ethanol resulting from the hydrogenation of N-methylacetanilide (**8b**).*

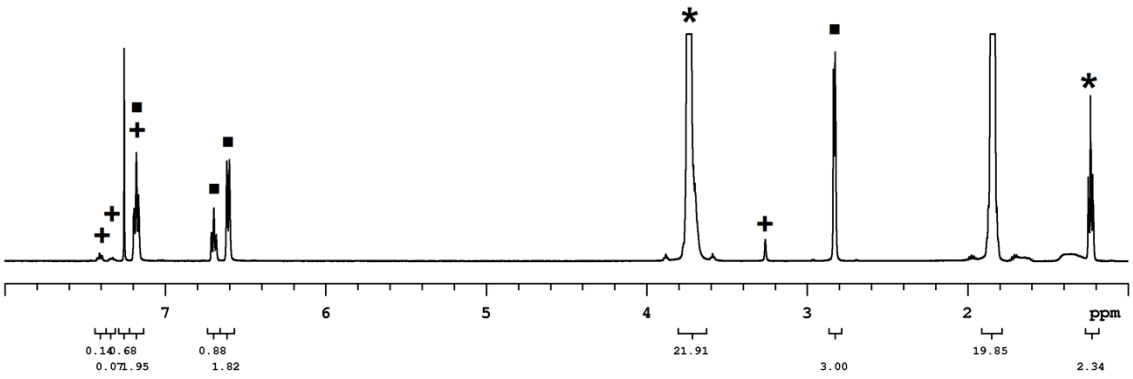


Figure S10 *The δ 8 to 1 ppm [1]H NMR spectrum showing the formation of aniline and ethanol resulting from the hydrogenation of acetanilide (**8c**).*

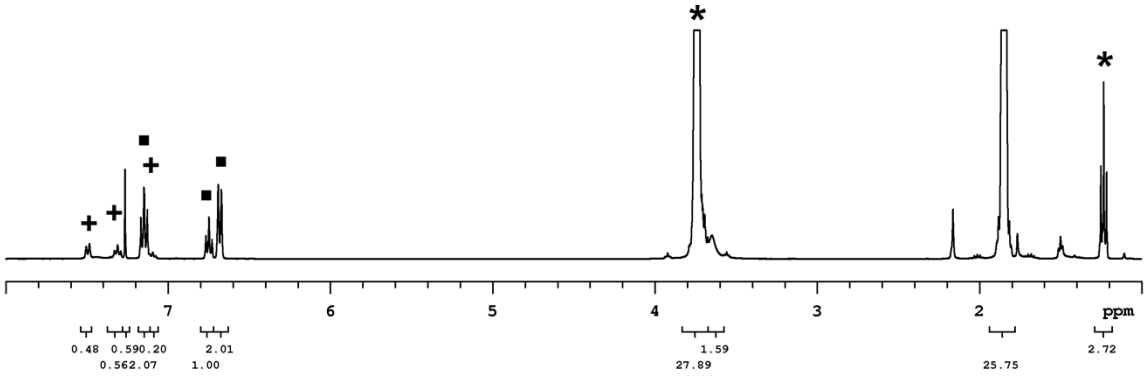


Figure S11 *The δ 5 to 1 ppm [1]H NMR spectrum showing the formation of morpholine and ethanol resulting from the hydrogenation of 1-morpholinoethanone (**8d**).*

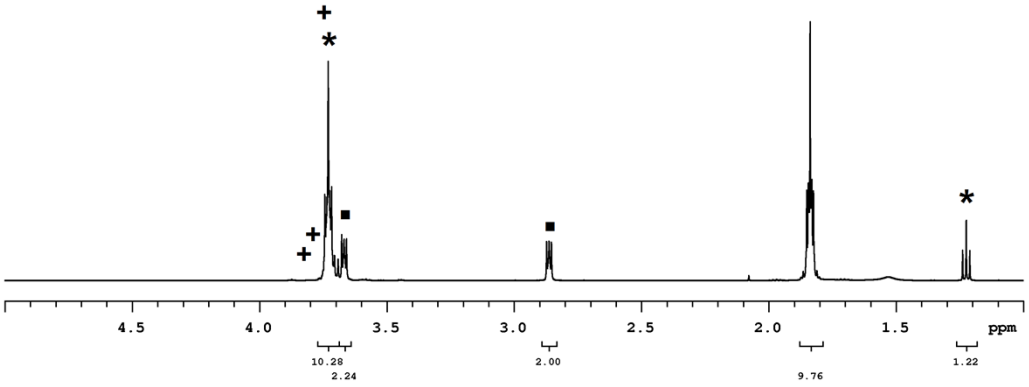


Figure S12 *The δ 9 to 1 ppm [1]H NMR spectrum showing the formation of dimethylamine and ethanol resulting from the hydrogenation of N,N-dimethylacetamide (**8e**).*

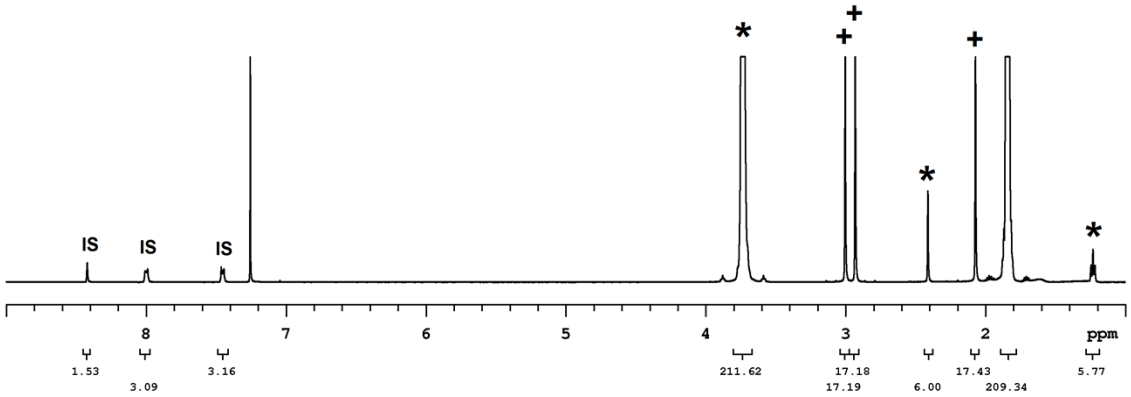
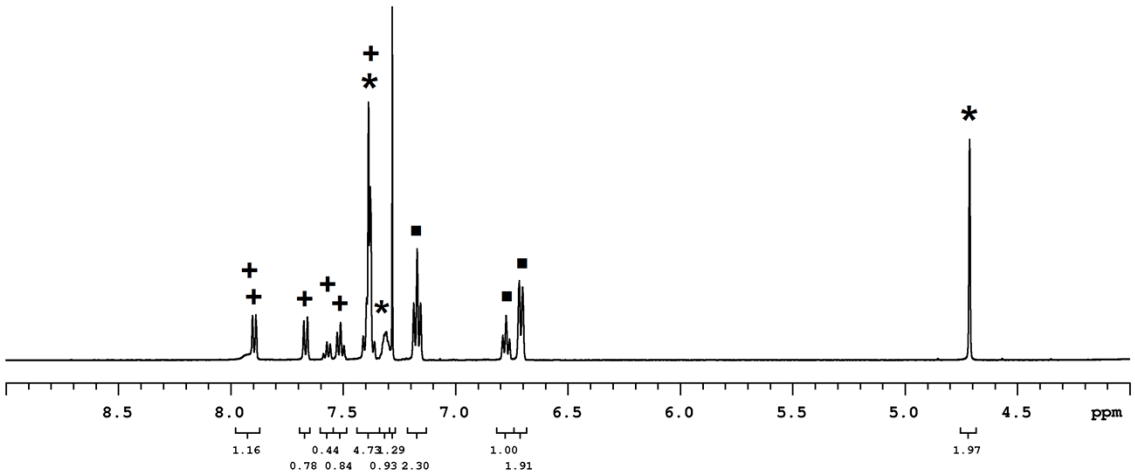


Figure S13 *The δ 5 to 1 ppm [1]H NMR spectrum showing the formation of aniline and benzyl alcohol resulting from the hydrogenation of benzanilide (**8f**).*



[1]H NMR spectra for the assisted and base-free hydrogenation of **8g-n** (*functionalized amides*). Percent conversions and reaction times are listed on Table 3.

Figure S14 *The δ 8 to 4 ppm [1]H NMR spectrum showing the formation of aniline and 4-fluorobenzyl alcohol resulting from the hydrogenation of* 4-fluorobenzanilide ***(8g)*** *under base-free conditions.*

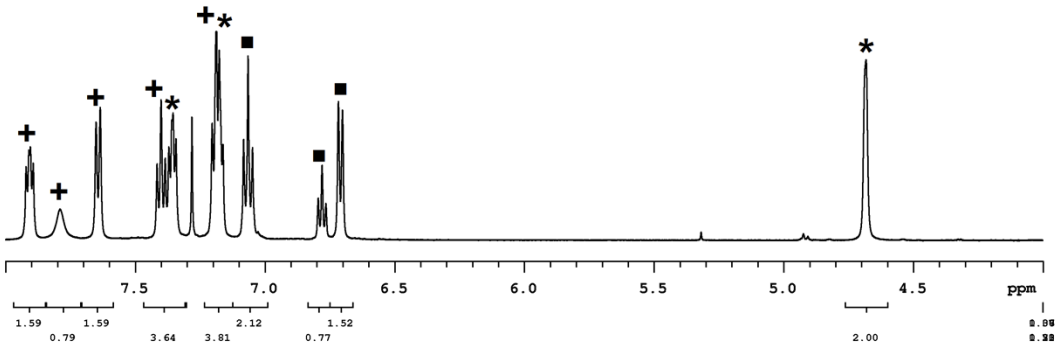


Figure S15 *The δ 8 to 4 ppm [1]H NMR spectrum showing the formation of aniline and 4-fluorobenzyl alcohol resulting from the hydrogenation of 4-fluorobenzanilide (**8g**) under base-assisted conditions.*

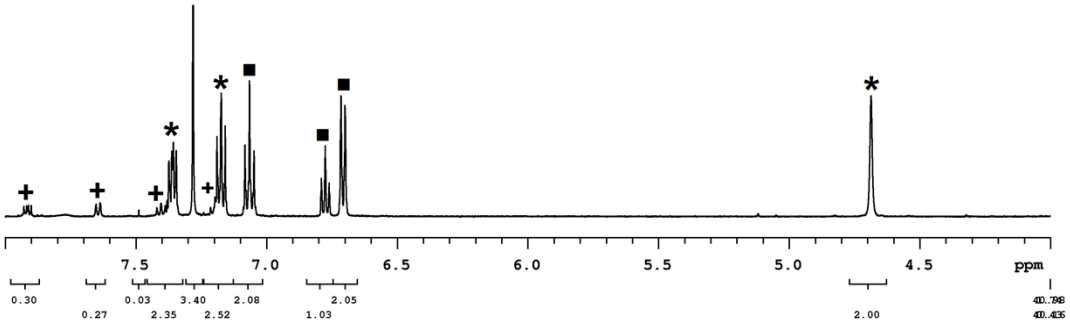


Figure S16 *The δ 7.5 to 3.0 ppm [1]H NMR spectrum showing the formation of N-methylaniline and 4-chlorobenzyl alcohol resulting from the hydrogenation of 4-chloro-N-methyl-N-phenylbenzamide (**8h**) under base-free conditions.*

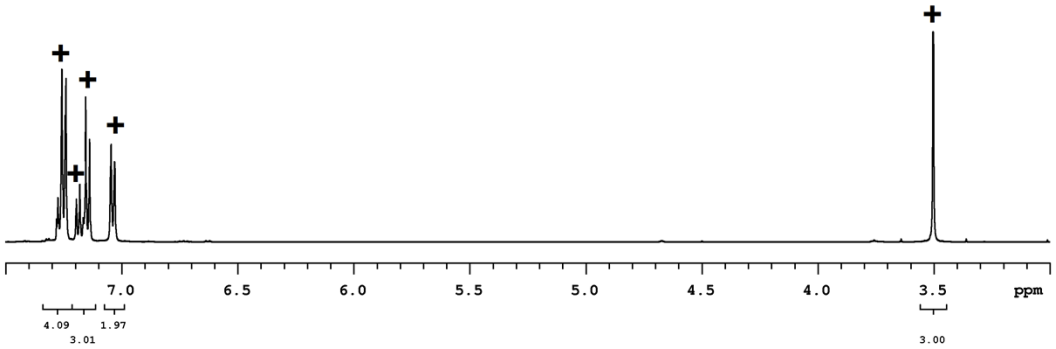


Figure S17 *The δ 7.5 to 3.0 ppm [1]H NMR spectrum showing the formation of N-methylaniline and 4-chlorobenzyl alcohol resulting from the hydrogenation of 4-chloro-N-methyl-N-phenylbenzamide (**8h**) under base-assisted conditions.*

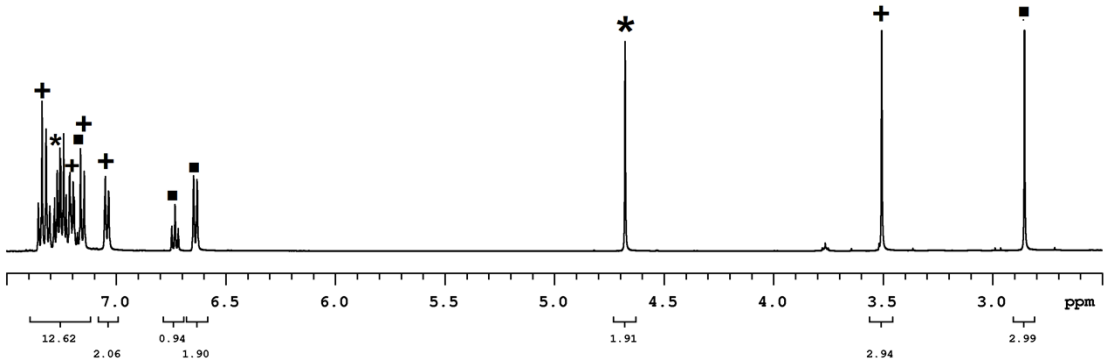


Figure S18 *The δ 8 to 4 ppm [1]H NMR spectrum showing the formation of 4-fluoroaniline and benzyl alcohol resulting from the hydrogenation of N-(4-fluorophenyl)benzamide (**8i**) under base-free conditions.*

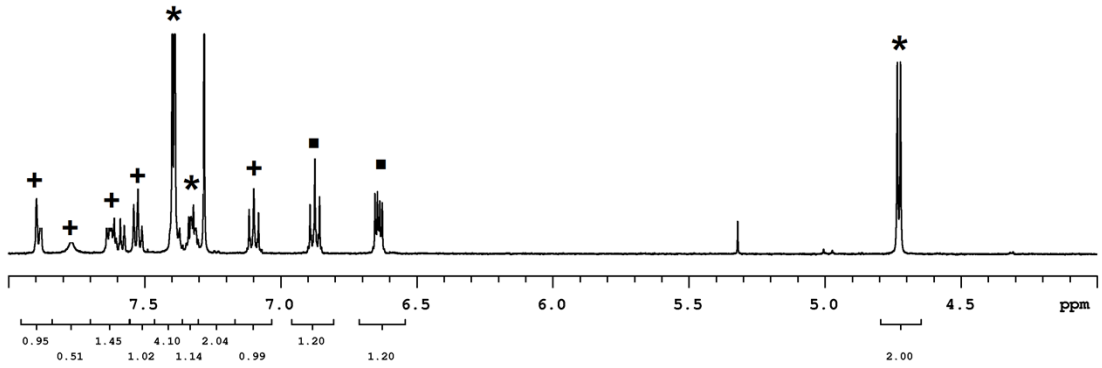


Figure S19 *The δ 8 to 4 ppm [1]H NMR spectrum showing the formation of 4-fluoroaniline and benzyl alcohol resulting from the hydrogenation of N-(4-fluorophenyl)benzamide (**8i**) under base-assisted conditions.*

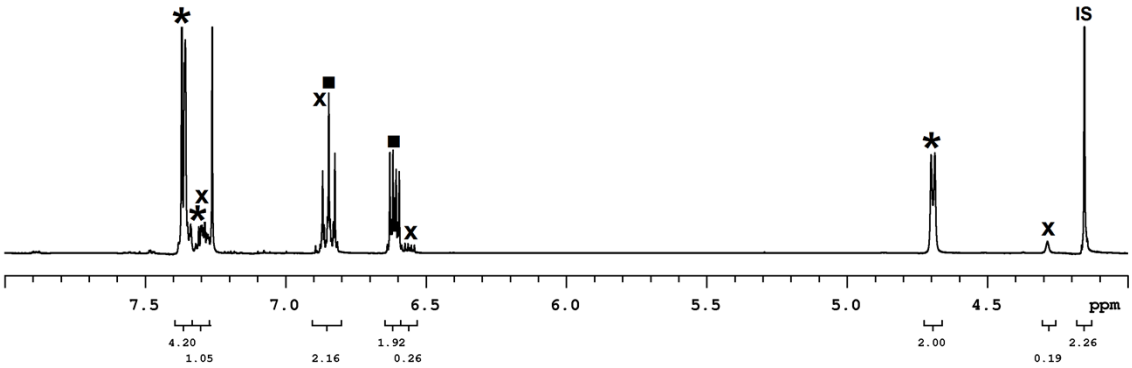


Figure S20 *The* HRMS (ESI+) *spectrum showing the product mixture resulting from the hydrogenation of N-(4-fluorophenyl)benzamide (**8i**) under base-assisted conditions.*[3]

Figure S21 *The δ 8 to 4 ppm [1]H NMR spectrum showing the formation of 4-bromoaniline and benzyl alcohol resulting from the hydrogenation of N-(4-bromophenyl)benzamide (**8j**) under base-assisted conditions.*

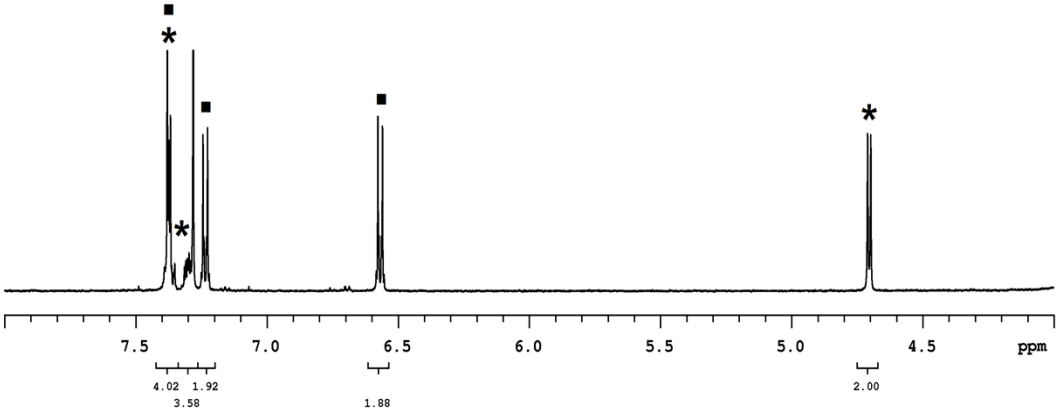


Figure S22 *The δ 9 to 2 ppm [1]H NMR spectrum showing the formation of aniline and furfuryl alcohol resulting from the hydrogenation of N-phenyl-2-furancarboxamide (**8k**) under base-free conditions.*

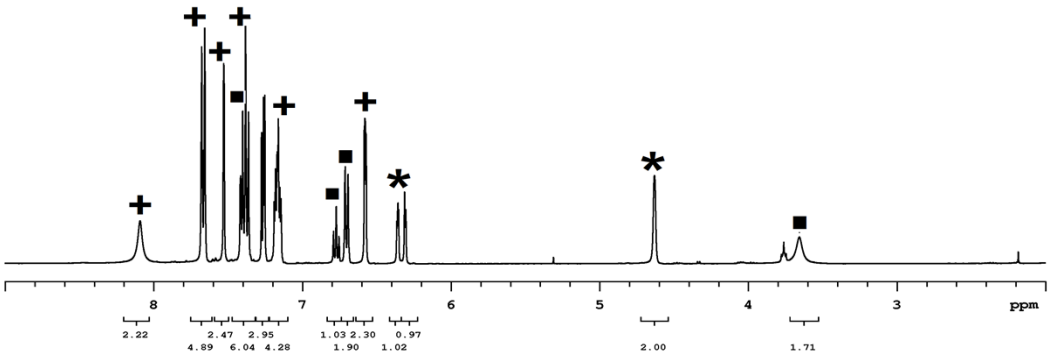


Figure S23 *The δ 8 to 1 ppm [1]H NMR spectrum showing the formation of aniline and furfuryl alcohol resulting from the hydrogenation of N-phenyl-2-furancarboxamide (**8k**) under base-free conditions.*

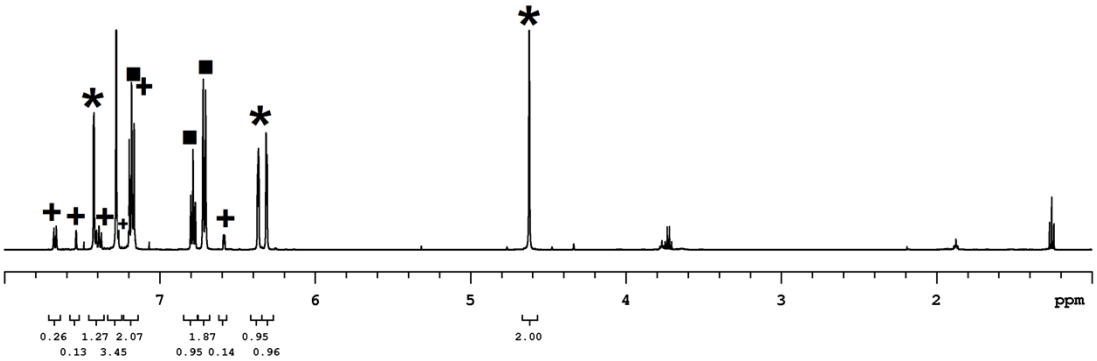


Figure S24 *The δ 8 to 1 ppm [1]H NMR spectrum showing the formation of piperidine and furfuryl alcohol resulting from the hydrogenation of furan-2-yl(piperidin-1-yl)methanone (**8l**) under base-assisted conditions.*

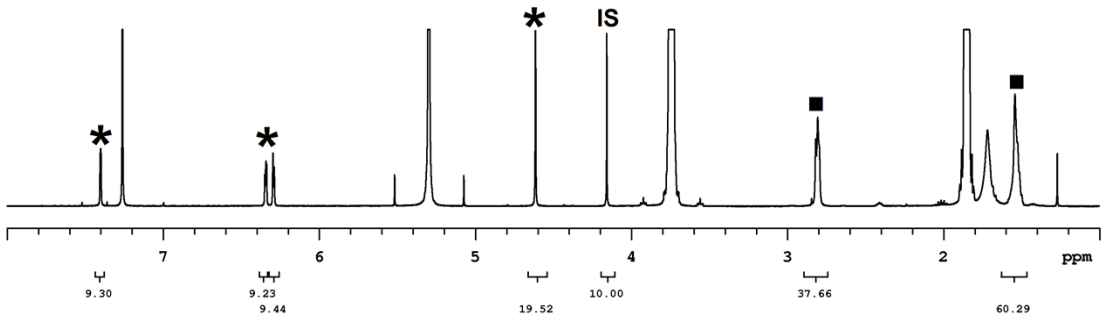


Figure S25 *The δ 4.5 to 1.0 ppm [1]H NMR spectrum showing the formation of piperidine and 1-(2-hydroxyethyl)piperazine resulting from the hydrogenation of 2-piperazin-1-yl-1-piperidin-1-yl-ethanone (**8m**) under base-free conditions.*

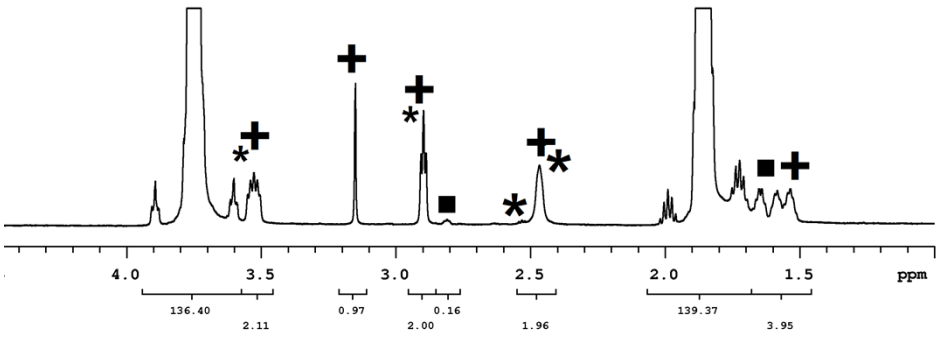


Figure S26 *The δ 4.5 to 1.0 ppm [1]H NMR spectrum showing the formation of piperidine and 1-(2-hydroxyethyl)piperazine resulting from the hydrogenation of 2-piperazin-1-yl-1-piperidin-1-yl-ethanone (**8m**) under base-assisted conditions.*

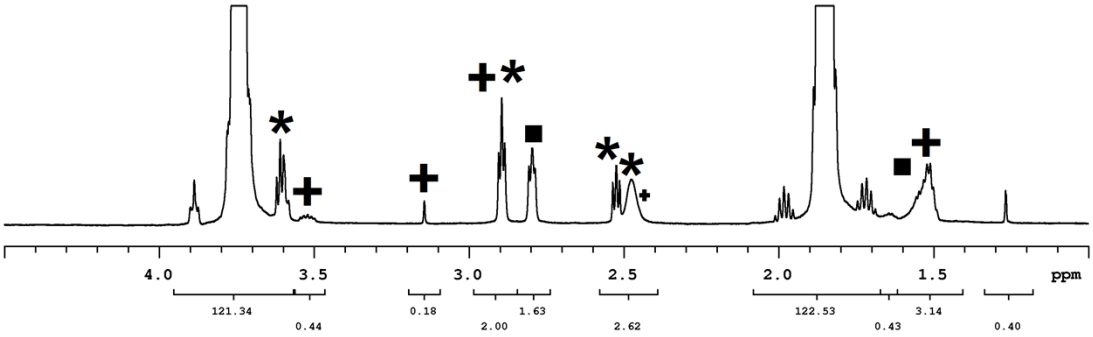
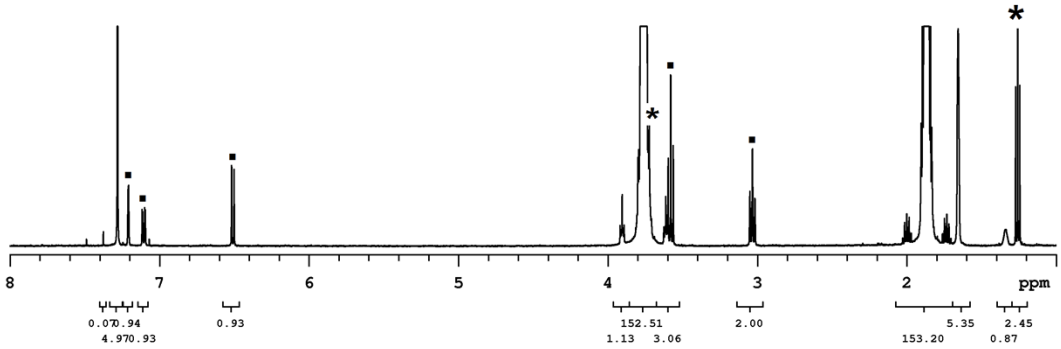


Figure S27 *The δ 8 to 1.0 ppm [1]H NMR spectrum showing the formation of 5-bromoindoline and Ethanol resulting from the hydrogenation of 1-acetyl-5-bromoindoline (**8n**) under base-free conditions.*



[1]H NMR spectra for the base-free hydrogenation of *N*-acyloxazolidinones (9a-b)

^{1}H NMR spectra for the base-free hydrogenation of **9a** and **9b** using 10 mol% **2** and 20 mol% $NaBH_4$ under 50 atm H_2 at 50 °C in 48 h. Percent conversions and reaction times are listed on Table 4. The hydroxyl-amides are denoted by *

Figure S28 *The δ 8 to 0 ppm ^{1}H NMR spectrum showing the hydroxyl amide product resulting from the hydrogenation of* ***9a.***

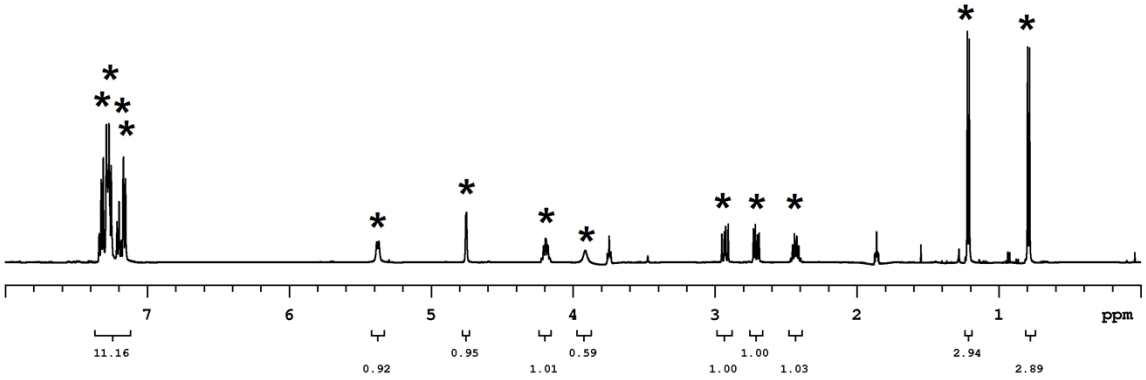


Figure S29 *The δ 8 to 0 ppm ^{1}H NMR spectrum showing the hydroxyl amide product resulting from the hydrogenation of* ***9b.***

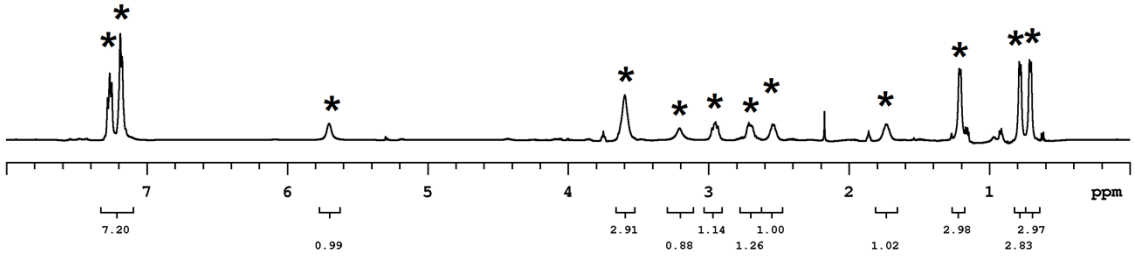
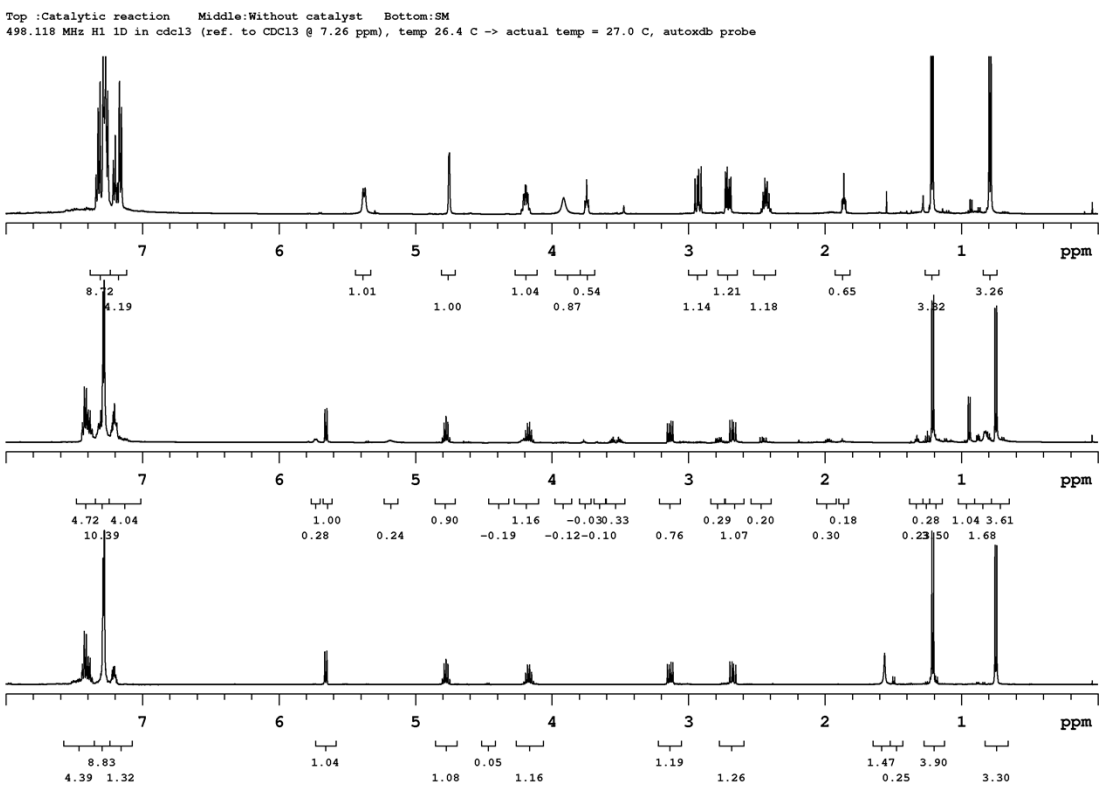


Figure S30 *The δ 8 to 0 ppm ^{1}H NMR spectrum showing the comparison of the result for substrate 9a with and without Ru catalyst in the presence of 20% $NaBH_4$. Top : Hydrogenation product using the condition given in table 4 (entry 1). Middle : Trace amount of unknown product formed at 50 °C without catalyst in the presence of 20 mol% $NaBH_4$. Bottom: Starting material.*



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[2] J. M. John, S. H. Bergens, *Angew. Chem., Int. Ed.* **2011***, 50*, 10377-10380.

[3] Q. Lei, Y. Wei, D. Talwar, C. Wang, C.; D. Xue, J. Xiao, *Chem. Eur. J.* **2013,** 19, 4021-4029.