Supporting Information for

Highly Efficient Ir-Catalyst for the Solventless Dehydrogenation of Formic Acid: The Key Role of an *N*-heterocyclic Olefin

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Table of Contents:

Experimental procedure

General:

All experiments were carried out under an inert atmosphere using standard Schlenk techniques. The solvents were dried by known procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). All other commercially available starting materials were purchased from Sigma-Aldrich, Merck and J. T. Baker and were used without further purification. H_2 gas (>99.5 %) was obtained from Infra. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{19}F spectra were recorded either on a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^{1}H\}$). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C APT and ^{1}H-^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC-MS spectra were recorded on a Hewlett-Packard GC-MS system.

General procedure for the dehydrogenation of formic acid.

All the reactions were performed in a Man on the Moon series X102 kit micro-reactor with a total volume of 19 ml. Formic acid and water were degassed prior to use.

- *Formic acid (neat) dehydrogenation.*

500 μL (13 mmol) of formic acid was added to 44 mg (5 mol%, 0.65 mmol) of sodium formate at 0ºC under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 353K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (2 mg, 0.016 mol%, 0.002 mmol) in 20 μL of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases (CO_2 + H_2) produced during the reaction was calculated using the Ideal Gas Law.

- *Formic acid dehydrogenation in H_2O.*

A solution of 3 mg (10 mol%, 0.04 mmol) of sodium formate in water (2 mL) was prepared under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 353K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (4 mg, 1 mol%, 0.004 mmol) in 20 μL (0.4 mmol) of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases (CO_2 + H_2) produced during the reaction was calculated using the Ideal Gas Law.

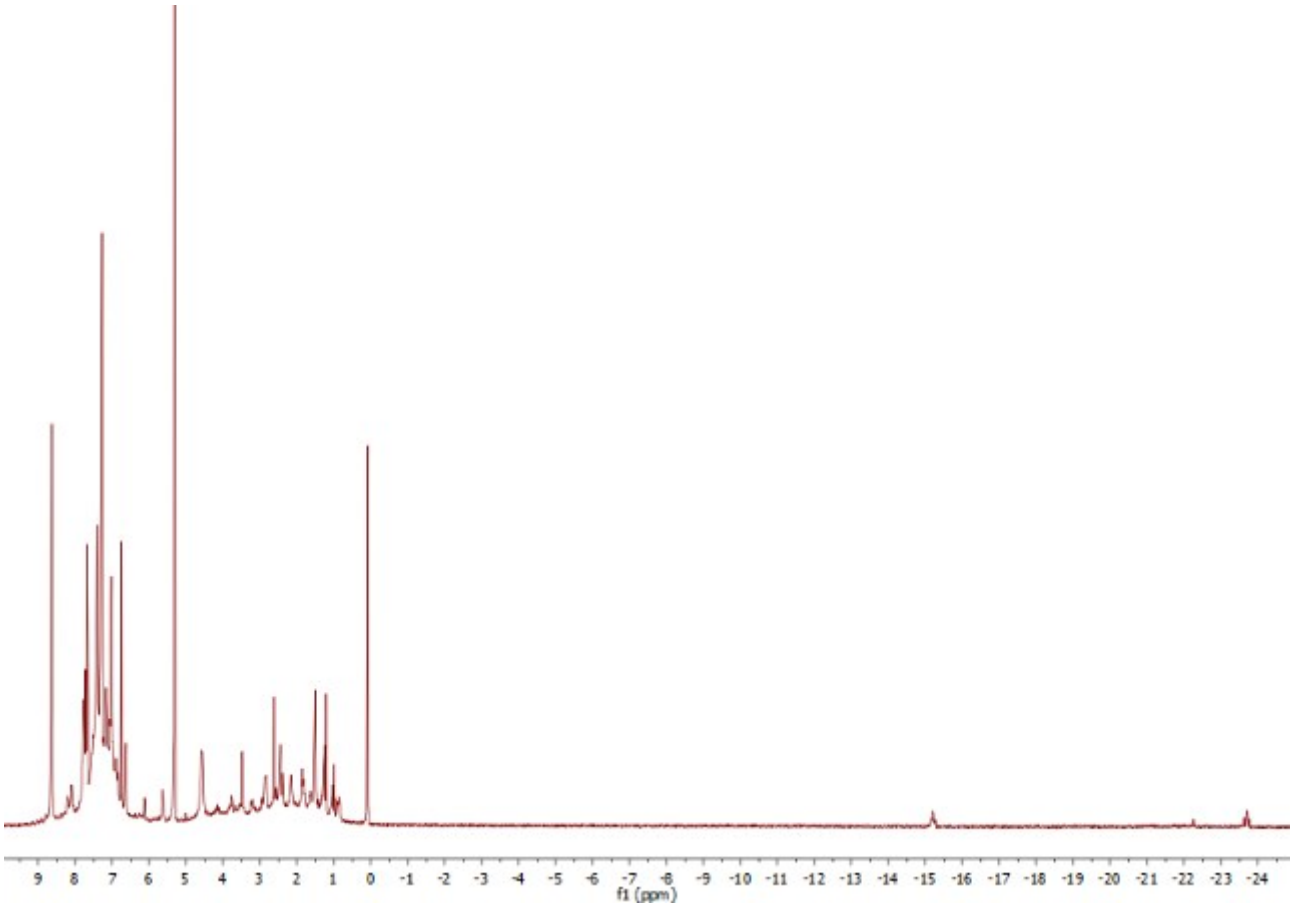
- *Formic acid dehydrogenation under optimized conditions (100 mol% of H_2O).*

500 μL (13 mmol) of formic acid was added to 264 mg (30 mol%, 3.9 mmol) of sodium formate and 235 μL (100 mol% 13 mmol) of water at 0ºC under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 363 K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (2 mg, 0.016 mol%, 0.002 mmol) in 20 μL of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases ($CO_2 + H_2$) produced during the reaction was calculated using the Ideal Gas Law.

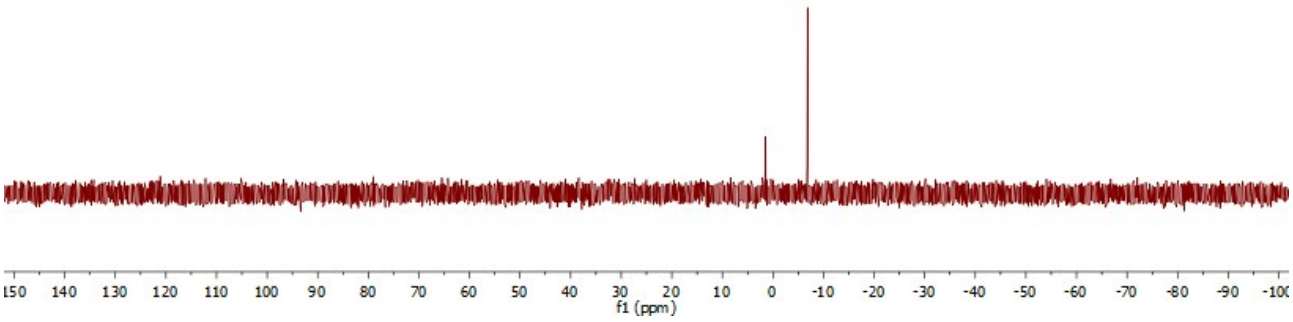
Reactivity of [Ir(PCP)(COD)]BF_4 (1) with HCOOH in CD_2Cl_2 (preparation of 5).

HCOOH (13 μL, 0.35mmol) and an excess of pyridine (50 μL, 0.60 mmol) were added to a solution of **1** (80 mg, 0.087 mmol) in 5 mL of dichloromethane. The resulting mixture was stirred for 18 h at 50 ^oC. After this time the solvent was removed under vacuum. Crystals of [Ir$(H)_2$(PCP)(py)]BF_4 (**5**) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the crude. HRMS (ESI) m/z calcd. for $C_{37}H_{39}IrN_3P_2BF_4$ (M - pyridine - BF_4) 701.1822, found 701.1828.

^{1}H NMR



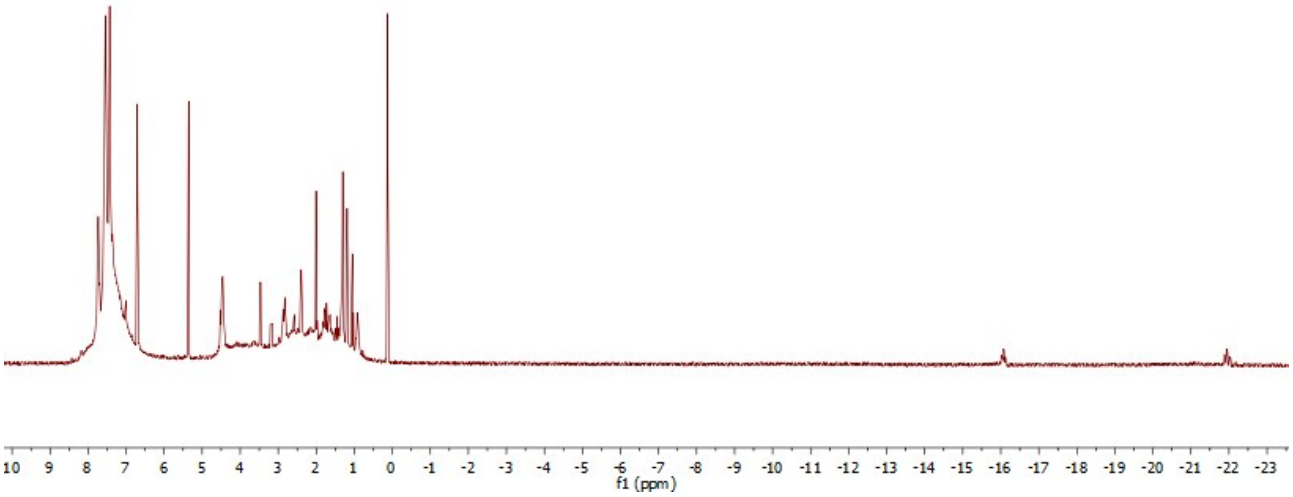
^{31} P NMR



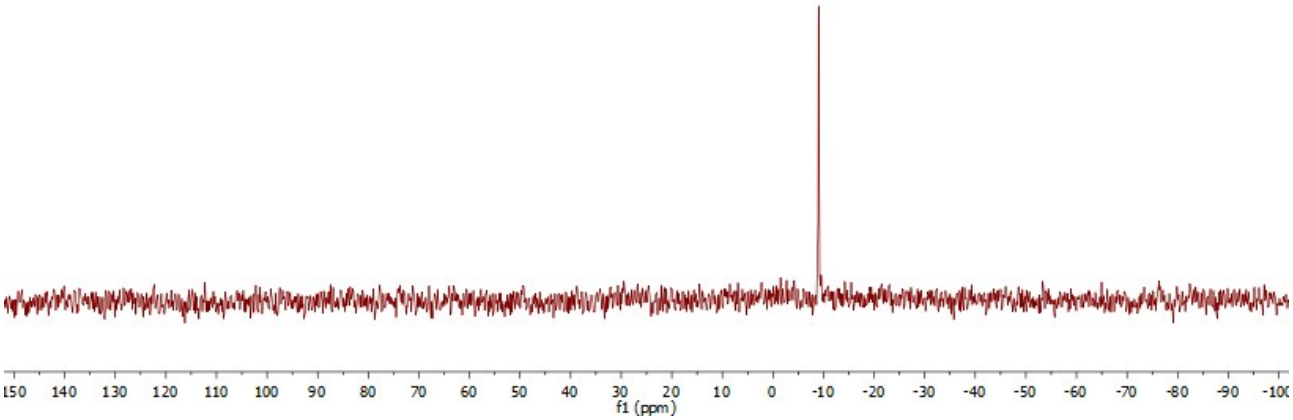
Reactivity of [Ir(PCP)(COD)]BF_4 (1) with HCOOH/HCOONa in CD_3CN.

An excess of HCOOH (6 µL, 0.15 mmol) and an excess of sodium formate (10 mg, 0.15 mmol) were added to a solution of **1** (30 mg, 0.037 mmol) in 3 mL of acetonitrile. The resulting mixture was stirred for 18 h at 80 ºC. After this time the solvent was removed under vacuum and the solid (compound **5**) was washed with diethyl ether.

^{1}H NMR



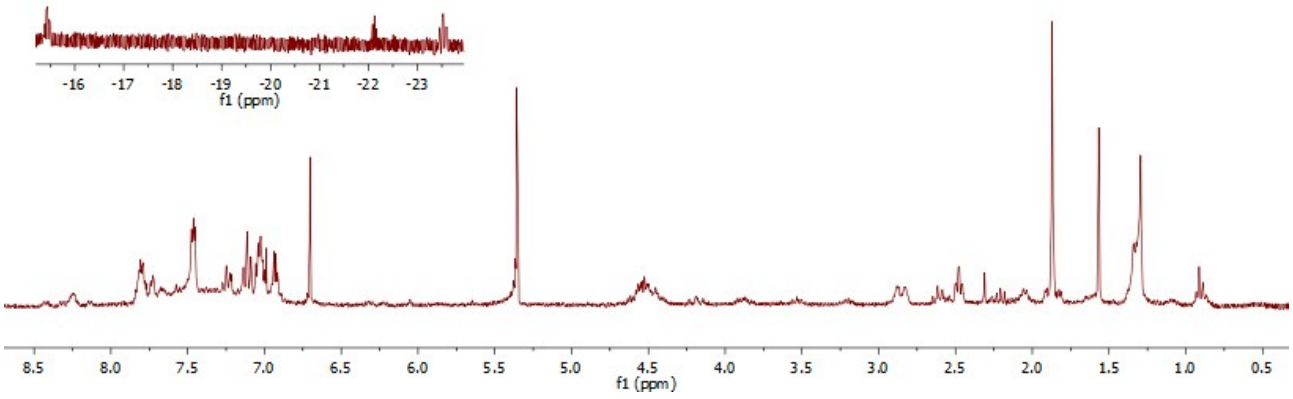
^{31}P NMR



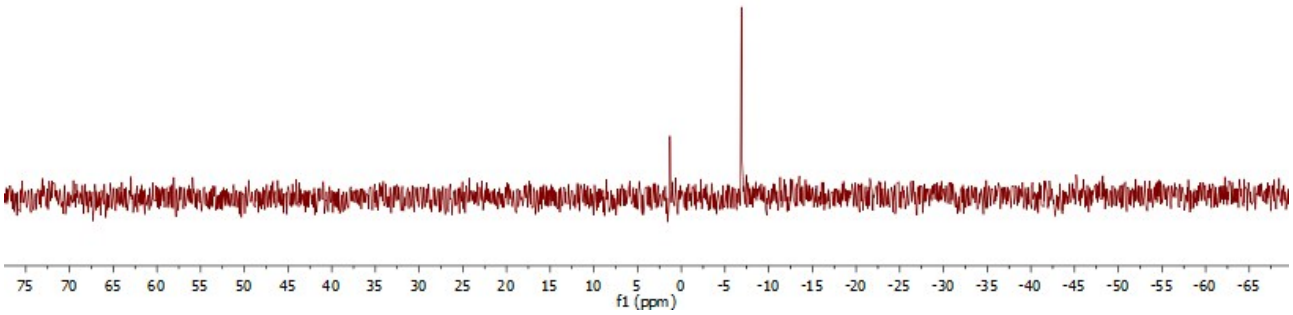
Reactivity of $[Ir(H)_2(PCP)(py)]BF_4$ (5) with 3,5-dimethylpyridine in CD_2Cl_2 (preparation of 6)

To a solution of **5** in CH_2Cl_2, prepared as described above, an excess of 3,5-dimethylpyridine was added at room temperature, resulting in the formation of a mixture of a monohydride and a dihydride complex. Crystals of $[Ir(H)_2(PCP)(Me_2py)]BF_4$ (**6**) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the crude mixture.

^{1}H NMR



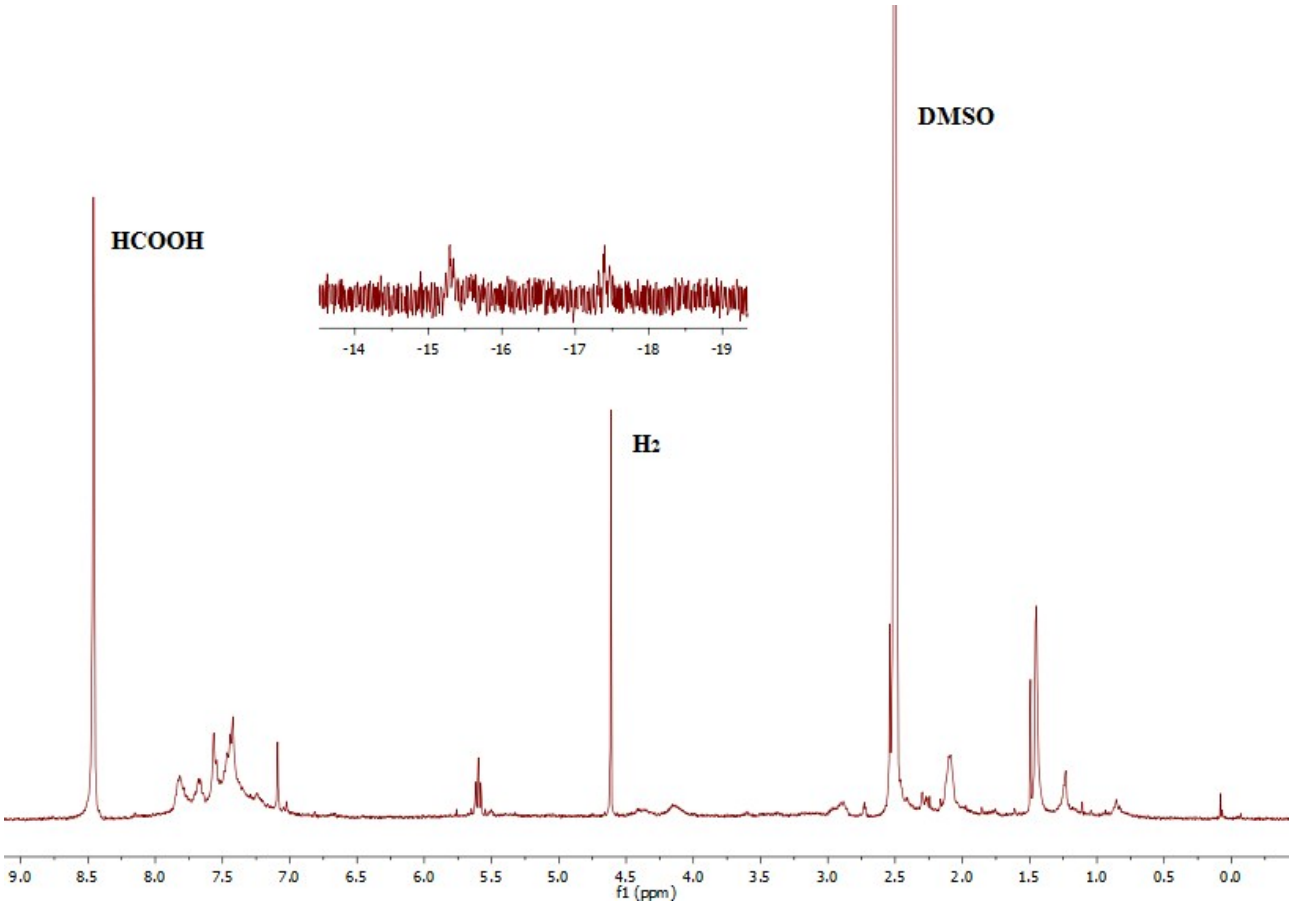
^{31} P NMR



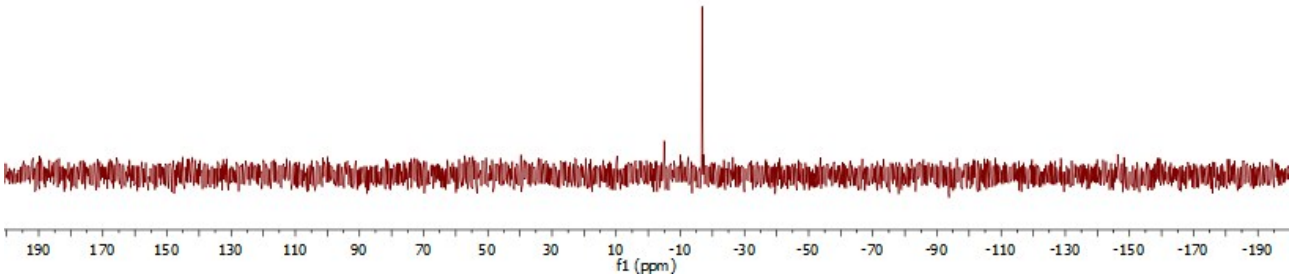
Dehydrogenation HCOOH in DMSO-d_6 using 1 as catalyst.

Formic acid (10 µL, 0.25 mmol), sodium formate (1.5 mg, 10 mol%, 0.025 mmol), complex **1** (2.2 mg, 1 mol%, 0.0023 mmol) and 0.3 mL of DMSO-d^6 were placed in a Young NMR tube under an argon atmosphere. The resulting solution was placed in a thermostated oil bath at 353K and monitored by NMR.

^{1}H NMR after 150 min:



^{31} P NMR after 150 min:



IR Spectrum of the mixture of gases obtained from catalysis

The region between 2200 and 2050 cm^{-1}, where the bands of gaseous CO would be expected, shows no traces of the by-product.

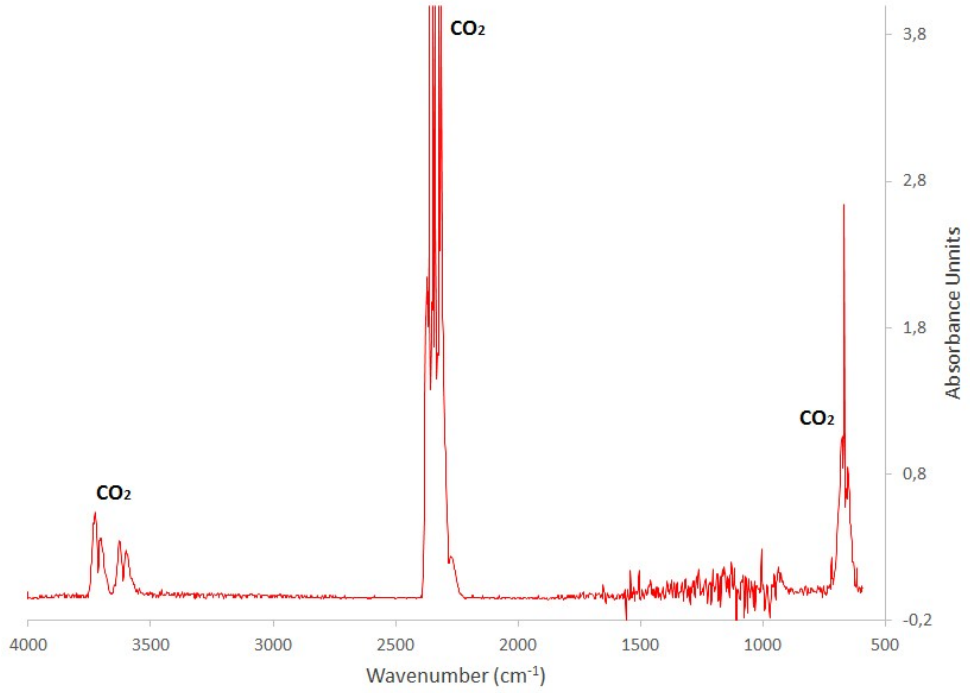


Figure S1. IR Spectrum of the gaseous products obtained under optimized reaction conditions (100 mol% of H_2O and 30 mol% of HCOONa and 0.016 mol% **1**).

Reaction profiles

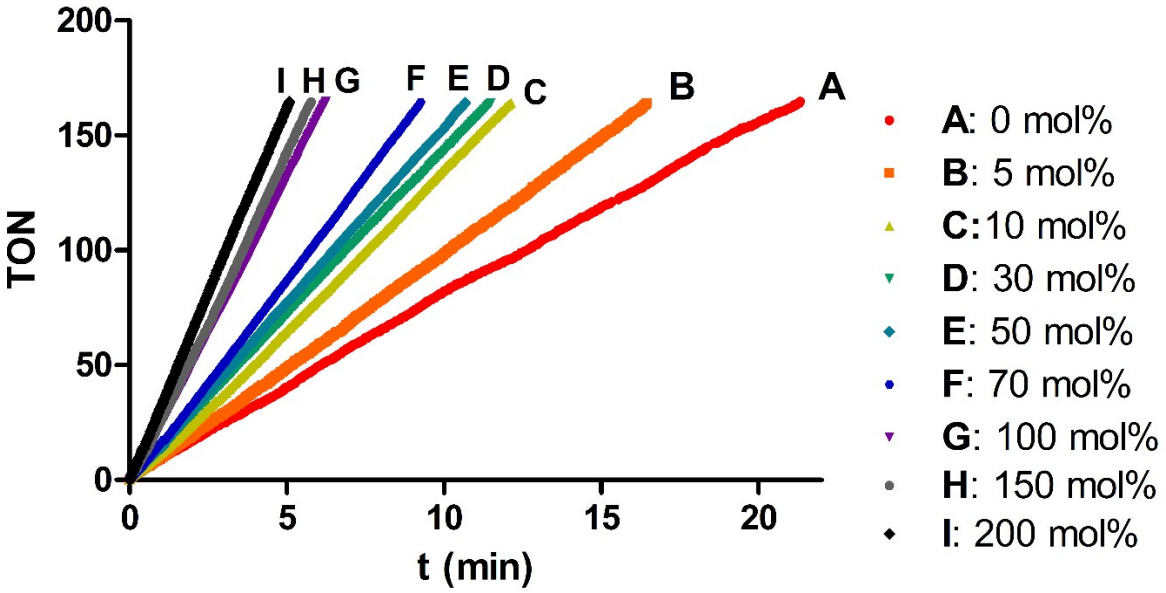


Figure S2. Optimization of H_2O mol%

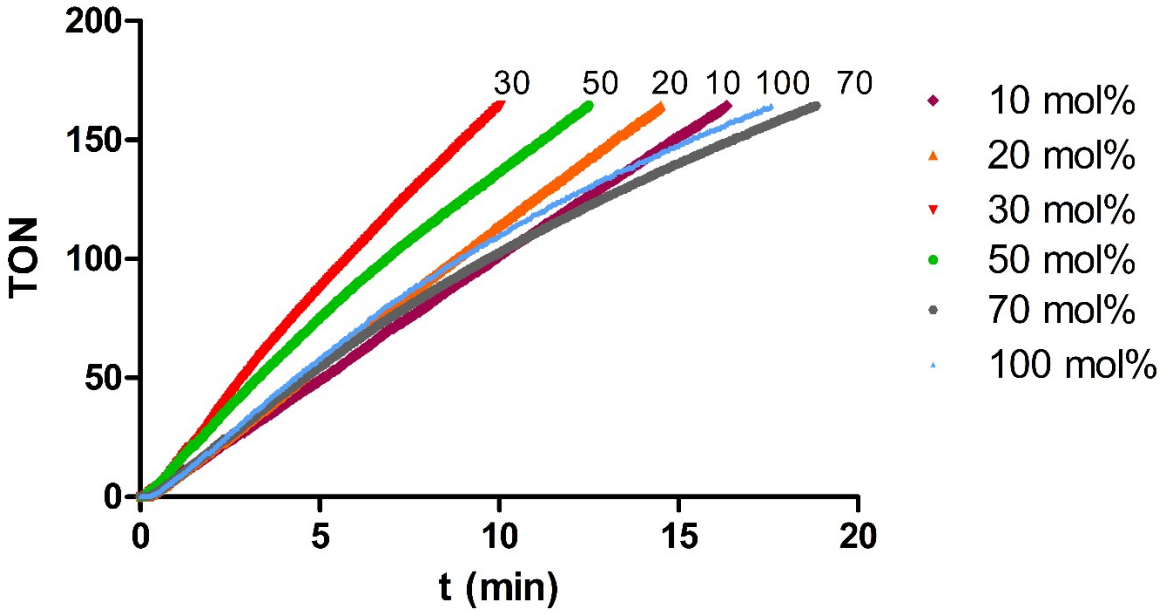


Figure S3. Optimization of HCOONa mol% (at 5 mol% H_2O loading)

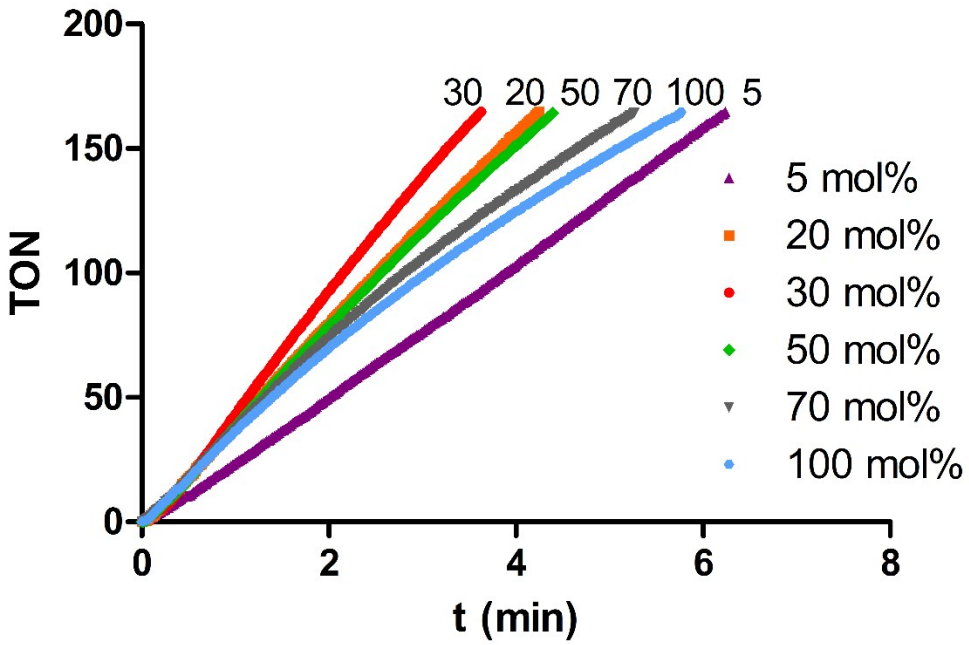


Figure S4. Optimization of HCOONa mol% (at 100 mol% H_2O loading)

Arrhenius plots

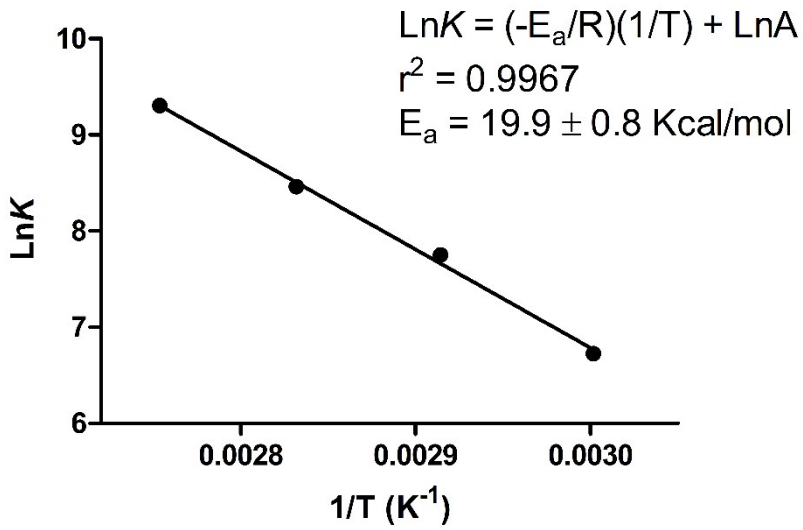


Figure S5. Arrhenius plot for the dehydrogenation of FA using complex **1** (conditions: 100 mol% of H_2O and 30 mol% of HCOONa and 0.016 mol% **1**).

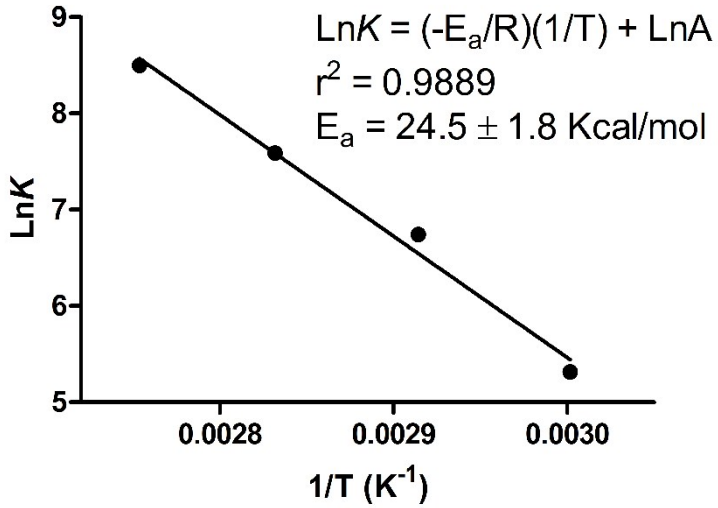


Figure S7. Arrhenius plot for the dehydrogenation of FA using complex **1** in the absence of H_2O (conditions: 30 mol% of HCOONa and 0.016 mol% **1**).

Recycling experiments

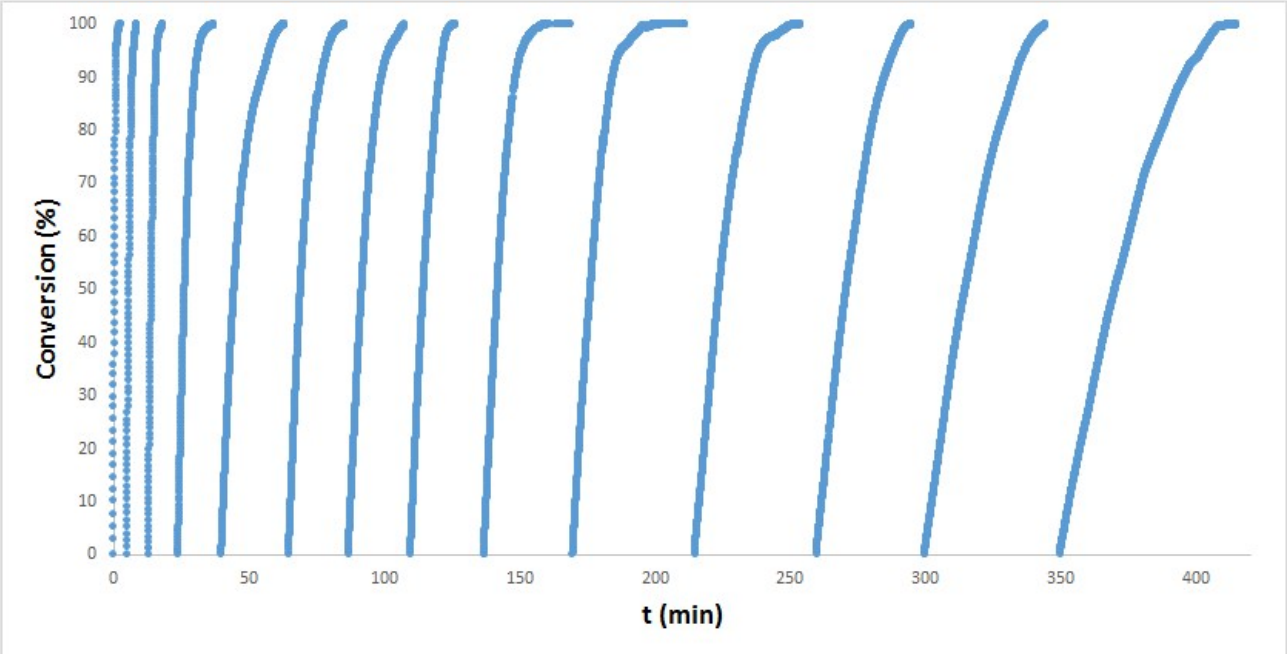


Figure S8. Recycling experiments for the dehydrogenation of FA (20 μL) using complex **1** in H_2O (2 mL). Conditions: 10 mol% of HCOONa, 1 mol% **1**, 80 ºC.

Crystal structure determination. X–ray diffraction data were collected at 100.0(2) K on an APEX SMART Bruker diffractometer with graphite–monochromated Mo–Kα radiation (λ = 0.71073 Å) using narrow ω rotations (0.3–0.6°). Intensities were integrated and corrected for absorption effects with SAINT-PLUS,[1] and SADABS[2] programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-2013[3] and refined by full matrix least–squares on F^2 with SHELXL-2014[4] under WinGX.[5]

Crystal data and structure refinement for 5. $C_{38}H_{41}BCl_2F_4IrN_3P_2$, M = 951.59 g mol^{-1}, monoclinic, $P2_1/n$, a = 15.5008(17) Å, b = 11.5673(13) Å, c = 21.116(2) Å, β = 97.5830(10)°, V = 3753.1(7) Å^3, Z = 4, D_{calc} = 1.684 g cm3, μ = 3.838 mm^{-1}, F(000) = 1888, 0.260 x 0.060 x 0.040 mm, θ_{min}/ θ_{max} 2.061/26.371°, 1.537/25.027°, limiting indexes –18≤h≤18, –13≤h≤13, –25≤h≤25, reflections collected/unique 32133/6587 [R(int) = 0.0854], data/restraints/parameters 6587/0/466, GOF = 1.194, R_1 = 0.0788, wR^2 = 0.1577, largest diff. peak/hole 2.959/-2.104 e A^{-3}. CCDC deposit number 1858260.

Crystal data and structure refinement for 6. $C_{40}H_{45}BCl_2F_4IrN_3P_2$, M = 979.64 g mol^{-1}, triclinic, P–1,

a = 11.0544(15) Å, b = 13.3742(18) Å, c = 14.3388(19) Å, α = 84.204(2)°, β = 84.669(2)°, γ = 72.812(2)°, V = 2010.4(5) Å^3, Z = 2, D_{calc} = 1.618 g cm^{-3}, μ = 3.585 mm^{-1}, F(000) = 976, 0.280 x 0.120 x 0.120 mm^3, θ_{min}/ θ_{max} 2.061/26.371°, limiting indexes –13≤h≤13, -16≤k≤16, -17≤l≤17, reflections collected/unique 20667/8144 [R(int) = 0.0448], data/restraints/parameters 8144/9/482, GOF = 1.058, R_1 = 0.0463 [I>2σ(I)], wR^2 = 0.1174 (all data), largest diff. peak/hole 2.262/–2.004 e Å^{-3}. CCDC deposit number 1858261.

[1] SAINT-PLUS: Area-Detector Integration Software, version 6.01; Bruker AXS: Madison, WI, 2001.
[2] SADABS program; University of Göttingen: Göttingen, Germany, 1999.
[3] G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr*., *Sect. A: Fundam. Crystallogr*. **2008**, *64*, 112–122.
[4] G. M. Sheldrick, Crystal structure refinement with SHELXL. .*Acta Crystallogr*., *Sect. C: Cryst. Struct. Commun*. **2015**, *71*, 3–8.
[5] L. J. Farrugia, WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr*. **2012**, *45*, 849–854.