Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Iridium-(κ^2-NSi) Catalyzed Dehydrogenation of Formic Acid: Effect of Auxiliary Ligands on the Catalytic Performance

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1. Experimental Details

1. 1. Selected spectra of complexes 2 y 3

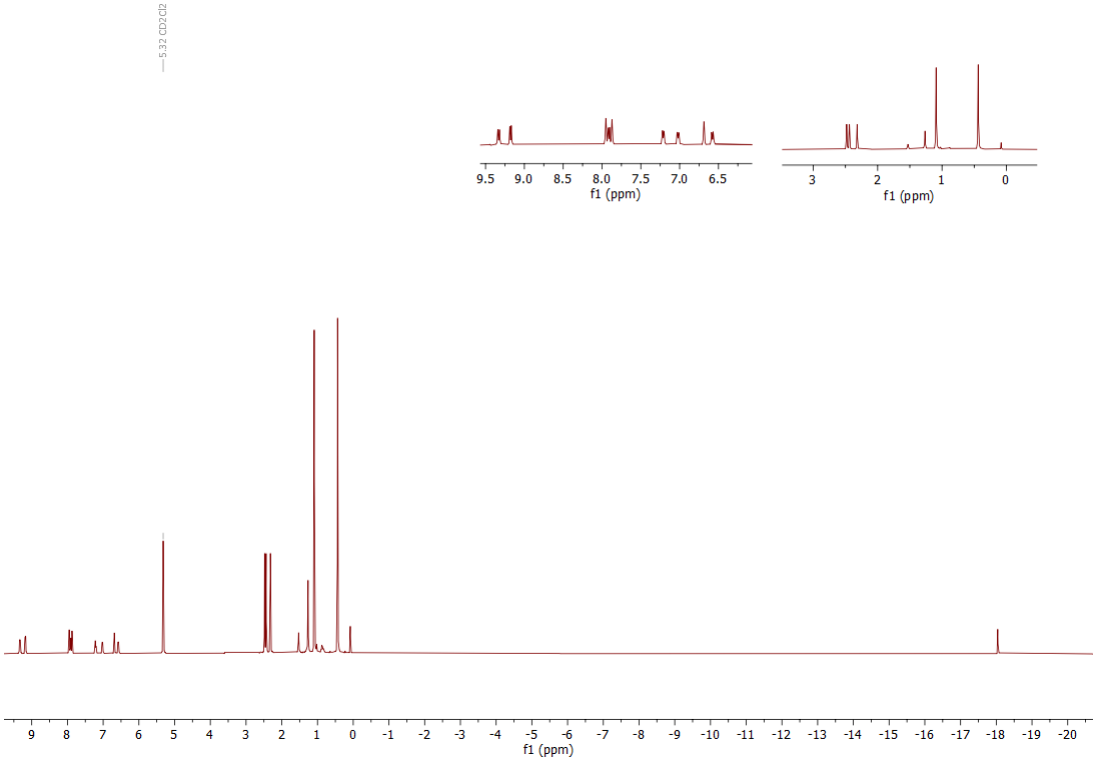

Figure S1. ^{1}H NMR spectrum of **2** in CD_2Cl_2 (300 MHz, 298K).

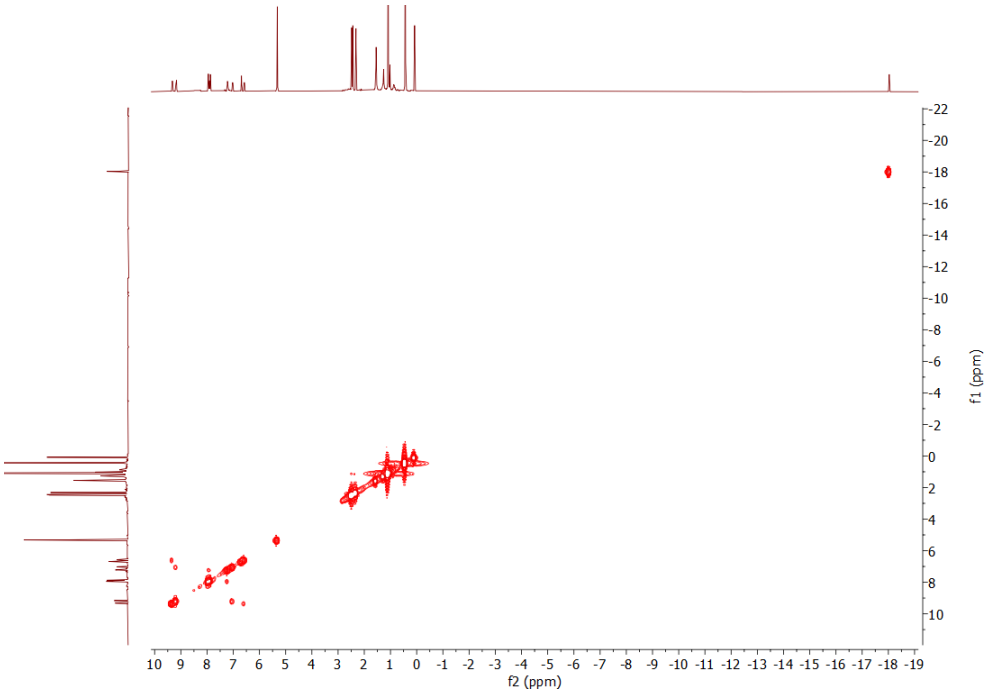

Figure S2. ^{1}H-^{1}H COSY NMR spectrum of **2** in CD_2Cl_2 (300 MHz, 298K).

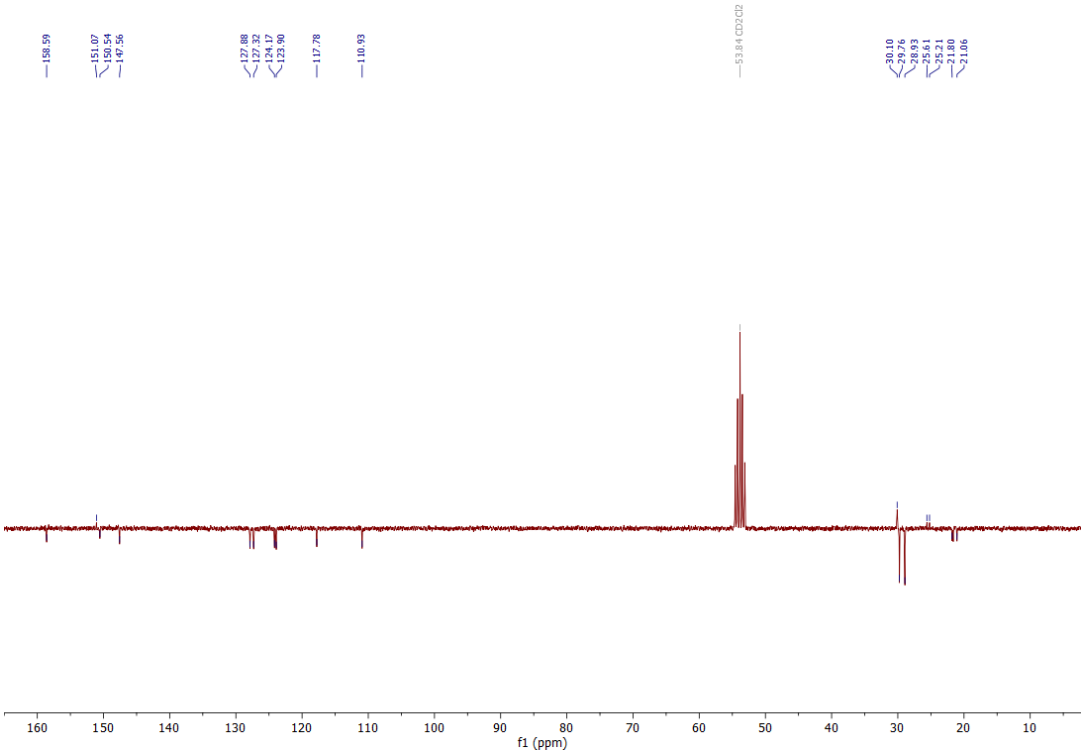

Figure S3. ^{13}C APT NMR spectrum of **2** in CD_2Cl_2 (75 MHz, 298K).

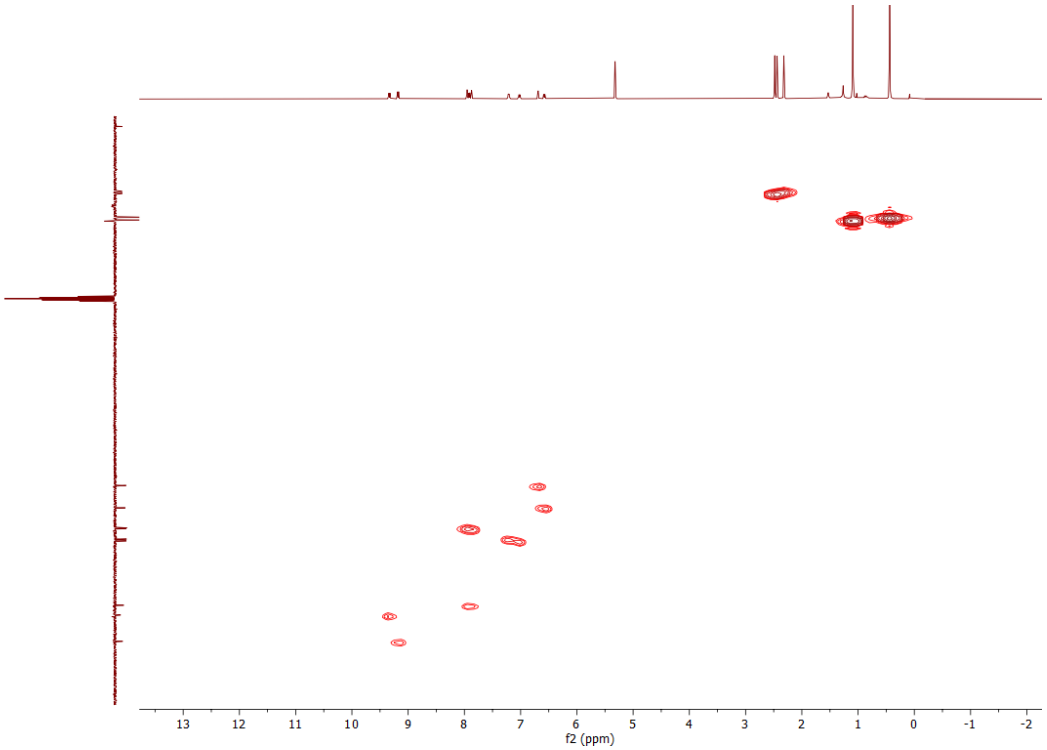

Figure S4. $^{1}H–^{13}C$ HSQC NMR spectrum of **2** in CD_2Cl_2 (298K).

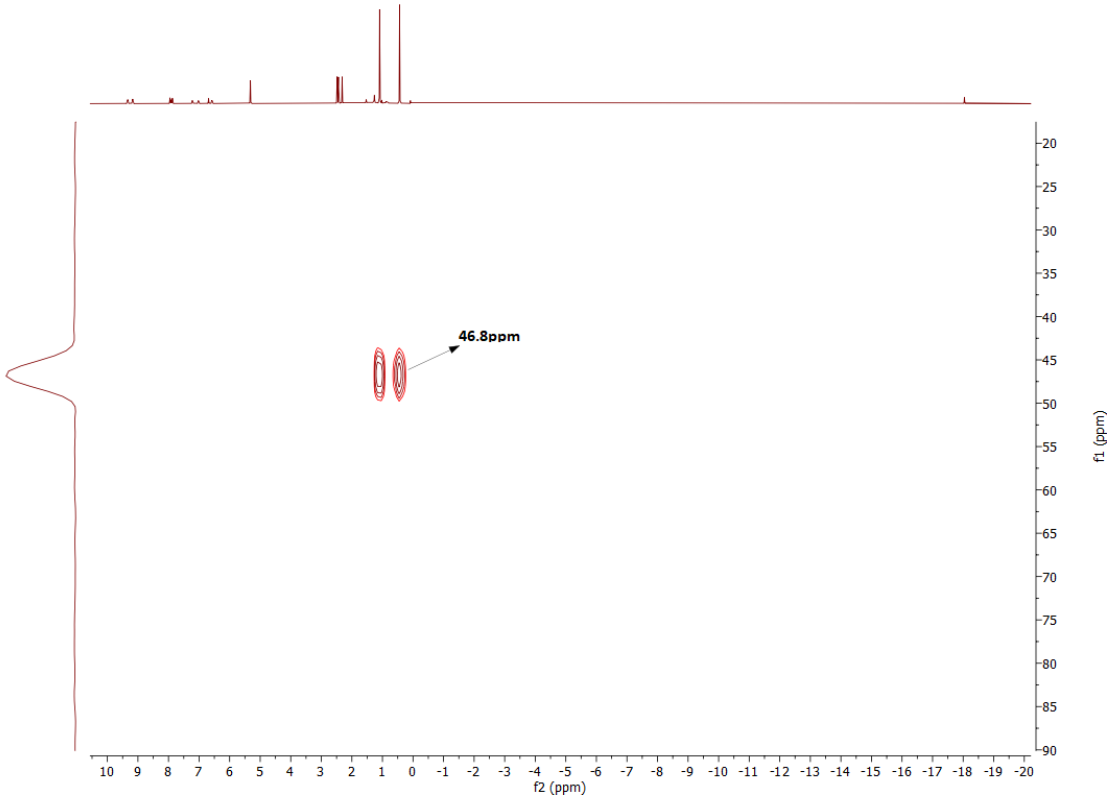

Figure S5. $^{1}H–^{29}Si$ HMBC spectrum of **2** in CD_2Cl_2 (60 MHz, 298K).

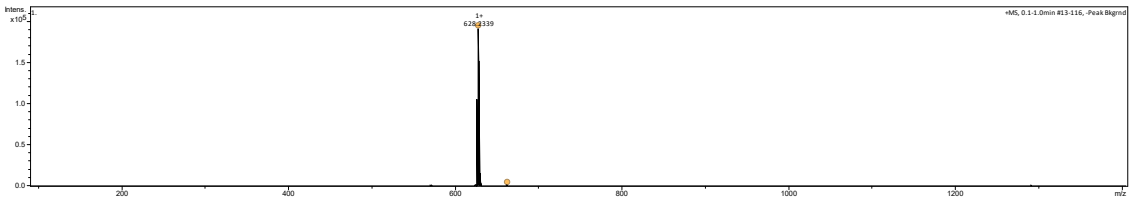

Figure S6. HR-MS of complex **2.**

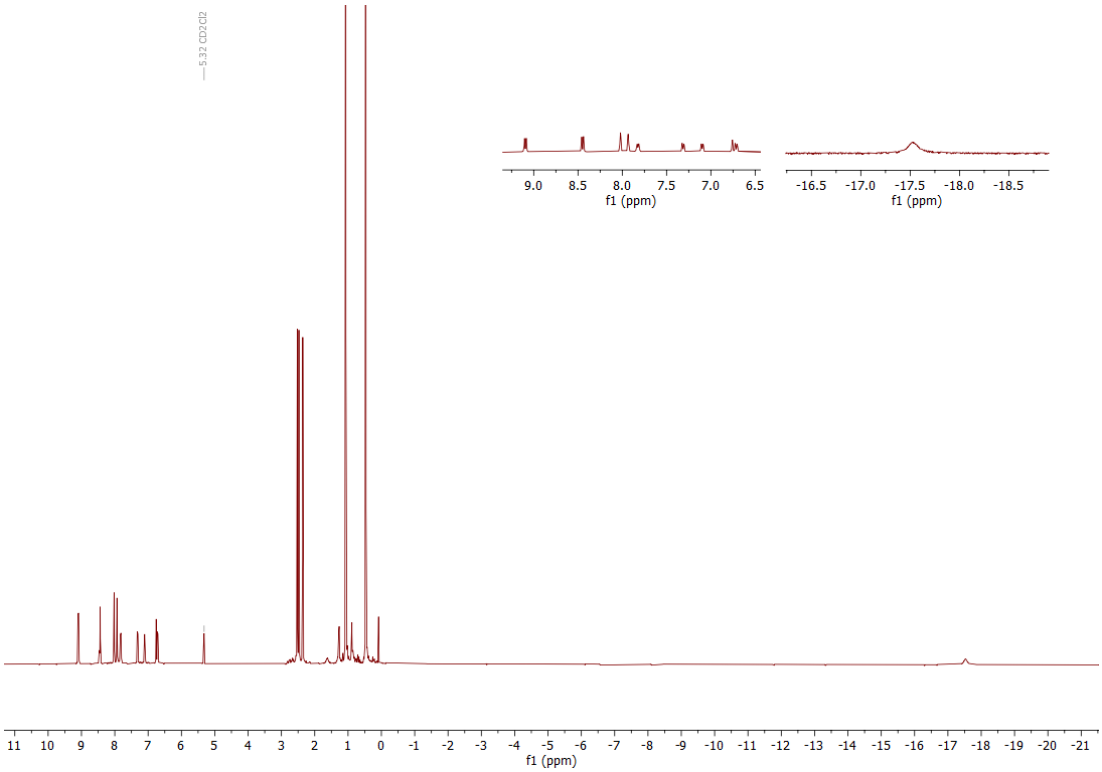

Figure S7. ^{1}H NMR spectrum of **3** in CD_2Cl_2 (300 MHz, 298K).

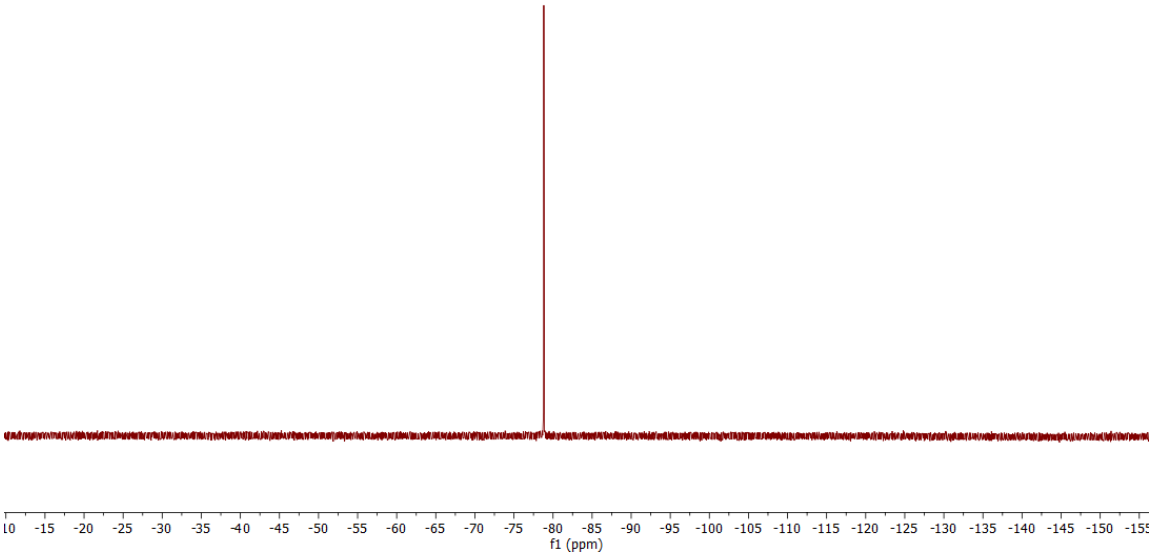

Figure S8. $^{19}F\{^{1}H\}$ NMR spectrum of **3** in CD_2Cl_2 (282 MHz, 298K)

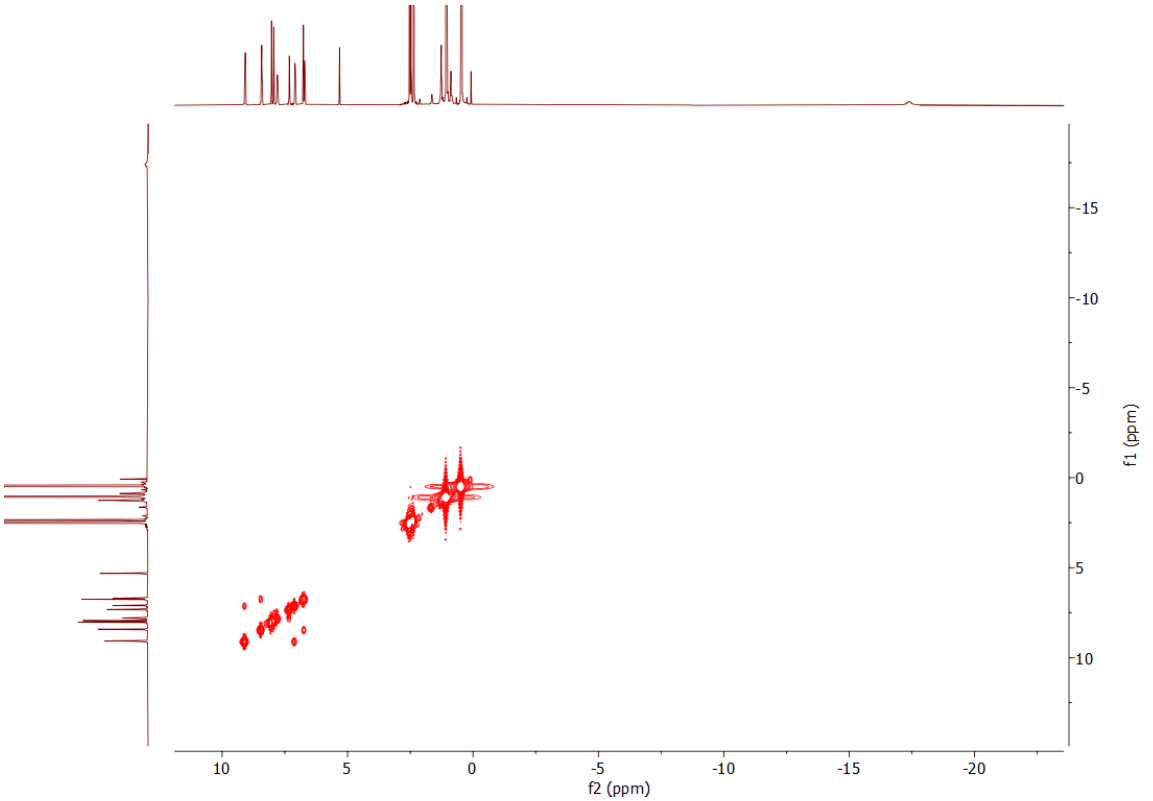

Figure S9. ^{1}H-^{1}H COSY NMR spectrum of **3** in CD_2Cl_2 (300 MHz, 298K).

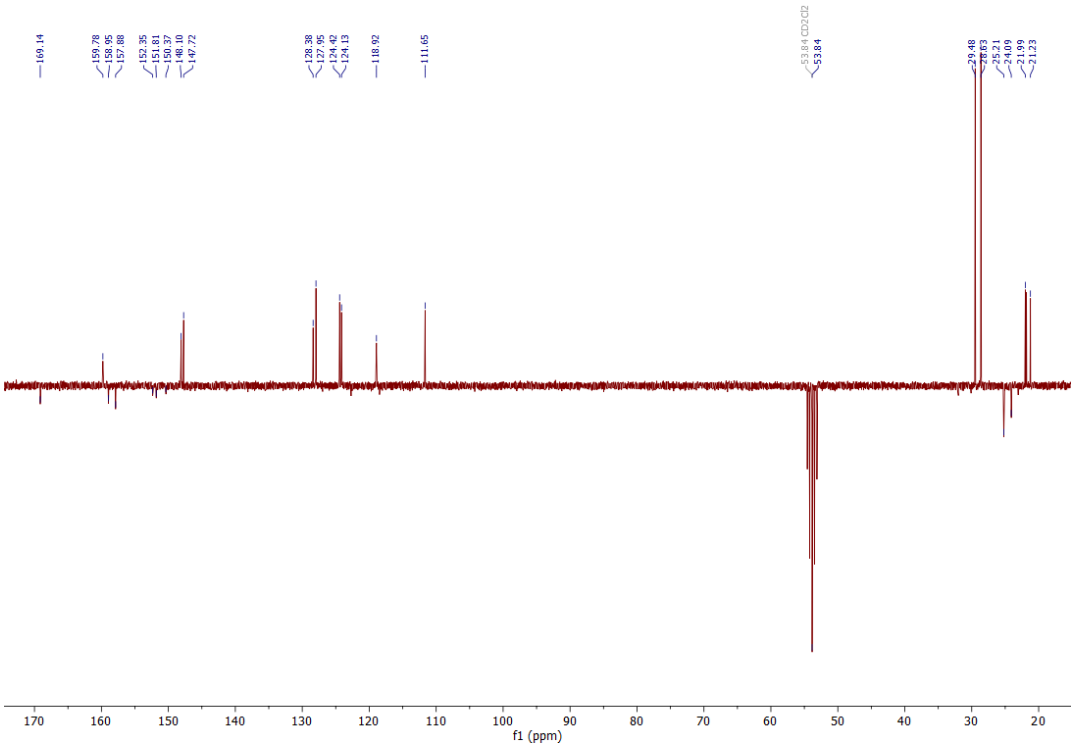

Figure S10. ^{13}C APT NMR spectrum of **3** in CD_2Cl_2 (75 MHz, 298K).

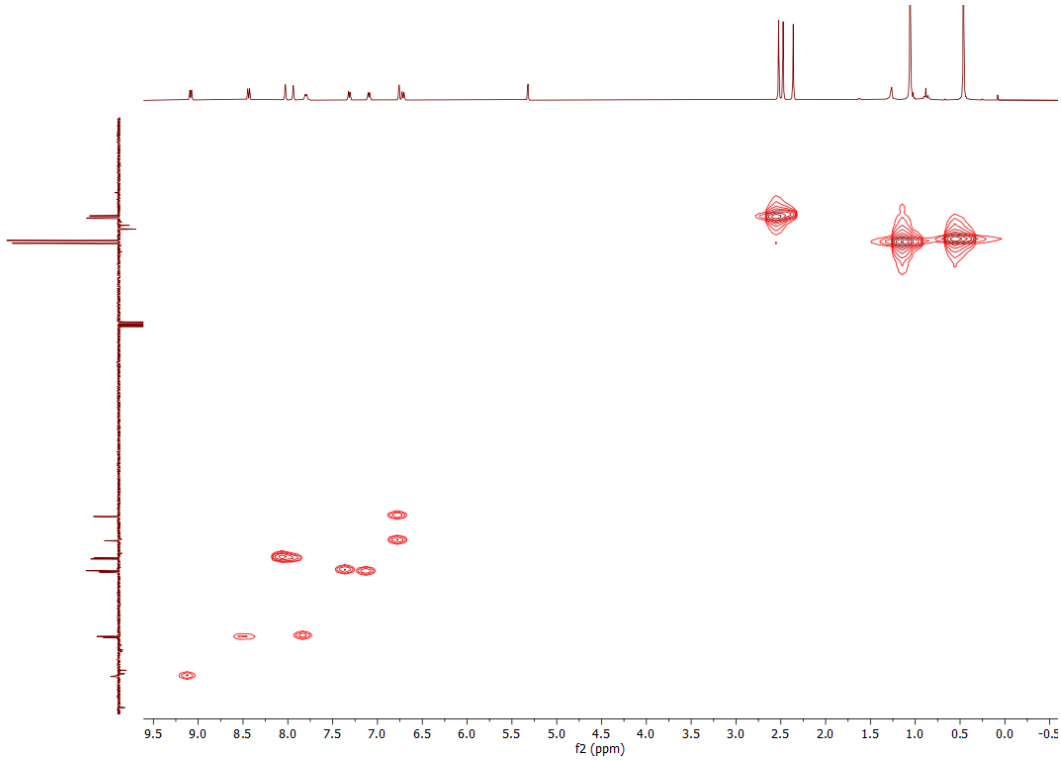

Figure S11. $^{1}H-^{13}C$ HSQC NMR spectrum of **3** in CD_2Cl_2 (298K).

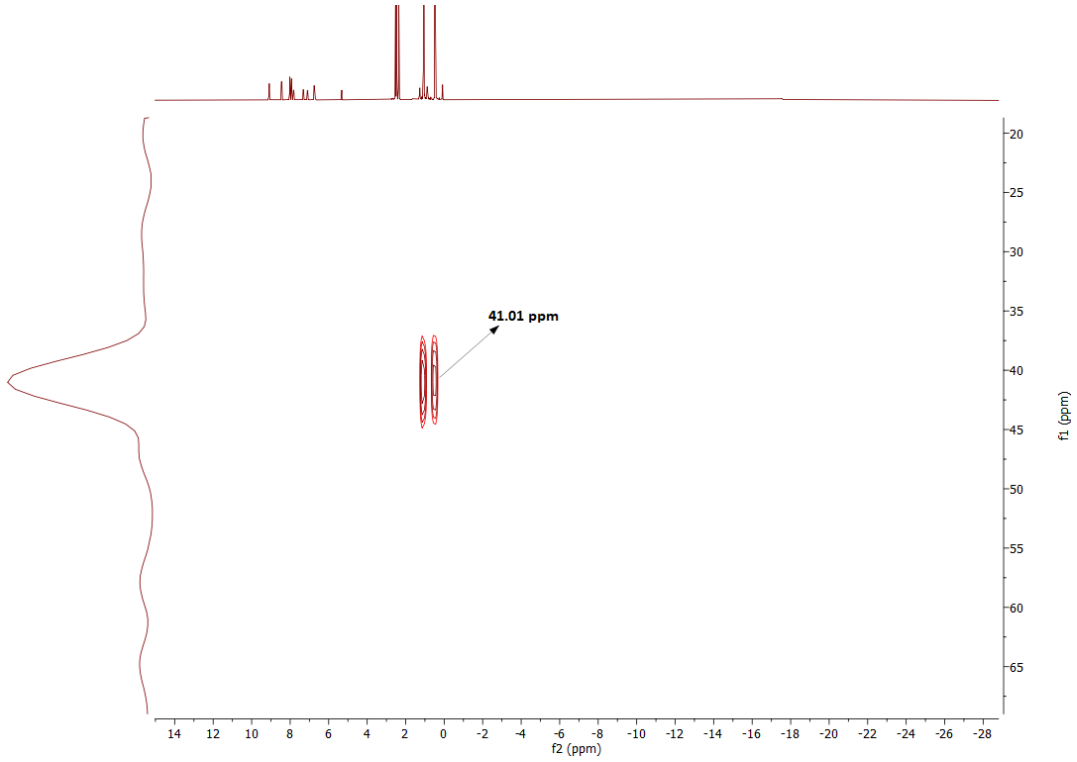

Figure S12. $^{1}H-^{29}Si$ HMBC spectrum of **3** in CD_2Cl_2 (60 MHz, 298K).

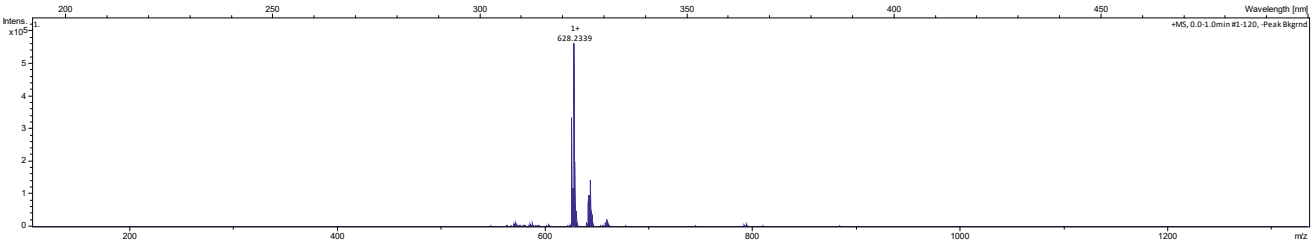

Figure S13. HR-MS of complex **3.**

2. TON and TOF determination

H_2 pressure: $P_{H2} = \frac{P_{measured}}{2}$

Amount of H_2 formed calculated with the Ideal Gas Law: $n_{H2} = \frac{P_{H2}V}{RT}$

Total Volume = 0.0162 L; R constant= 0.08205 atm L mol^{-1} K^{-1}

$$TON = \frac{n_{H2}}{n_{cat}}$$

$$TOF = \frac{TON}{t}$$

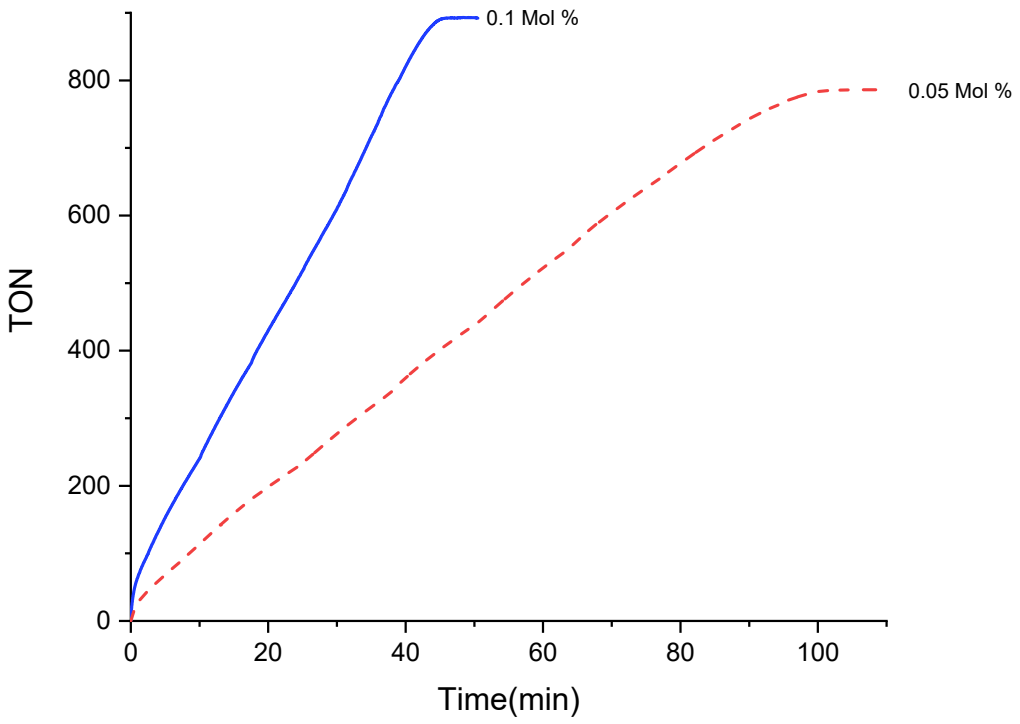

Figure S14. TON vs time representation of the **3**-catalyzed (0.1 and 0.05 mol%) FA solvent-less dehydrogenation with NEt_3 (40 mol %) at 353 K

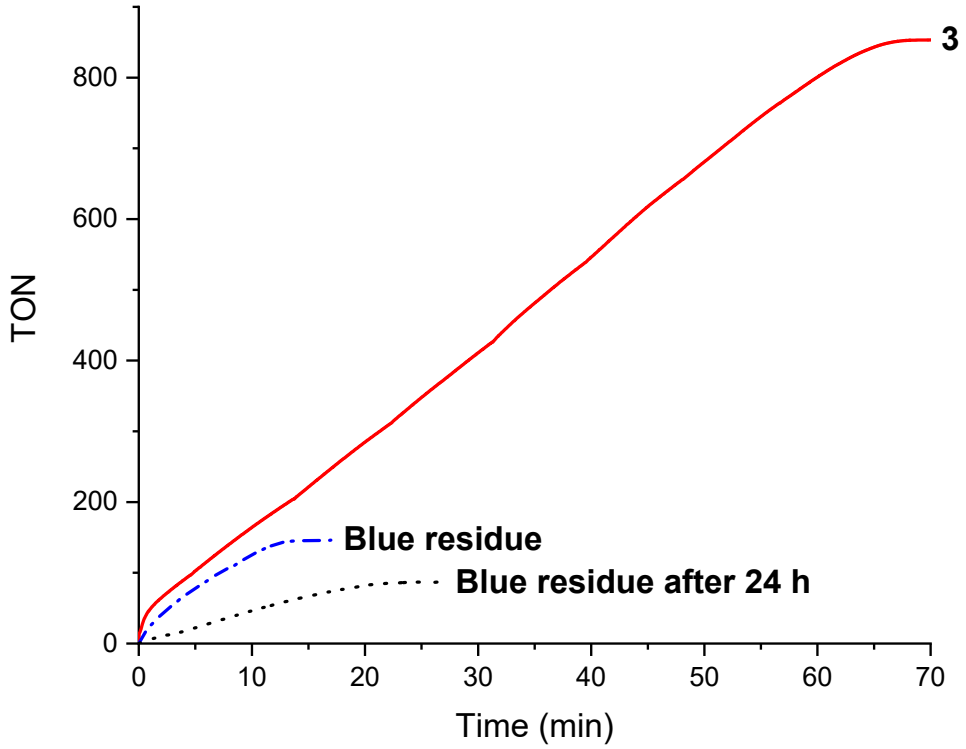

Figure S15. TON vs time (min) from the **3**-catalyzed (0.1 mol %) in presence of Et_3N (40 mol %) and the blue-residue catalyzed solventless dehydrogenation of HCOOH at 353 K until 24 hours later.

Entry	Temperature (K)	TOF (5 min)
1	**323**	86
2	**333**	205
3	**343**	778
4	**353**	1210
5	**363**	1500
6	**373**	3260

Table S16. TOF_{5min} for the **3**-catalyzed (0.1 mol%) FA solvent-less dehydrogenation with NEt_3 (40 mol %) from 323 K to 373 K.

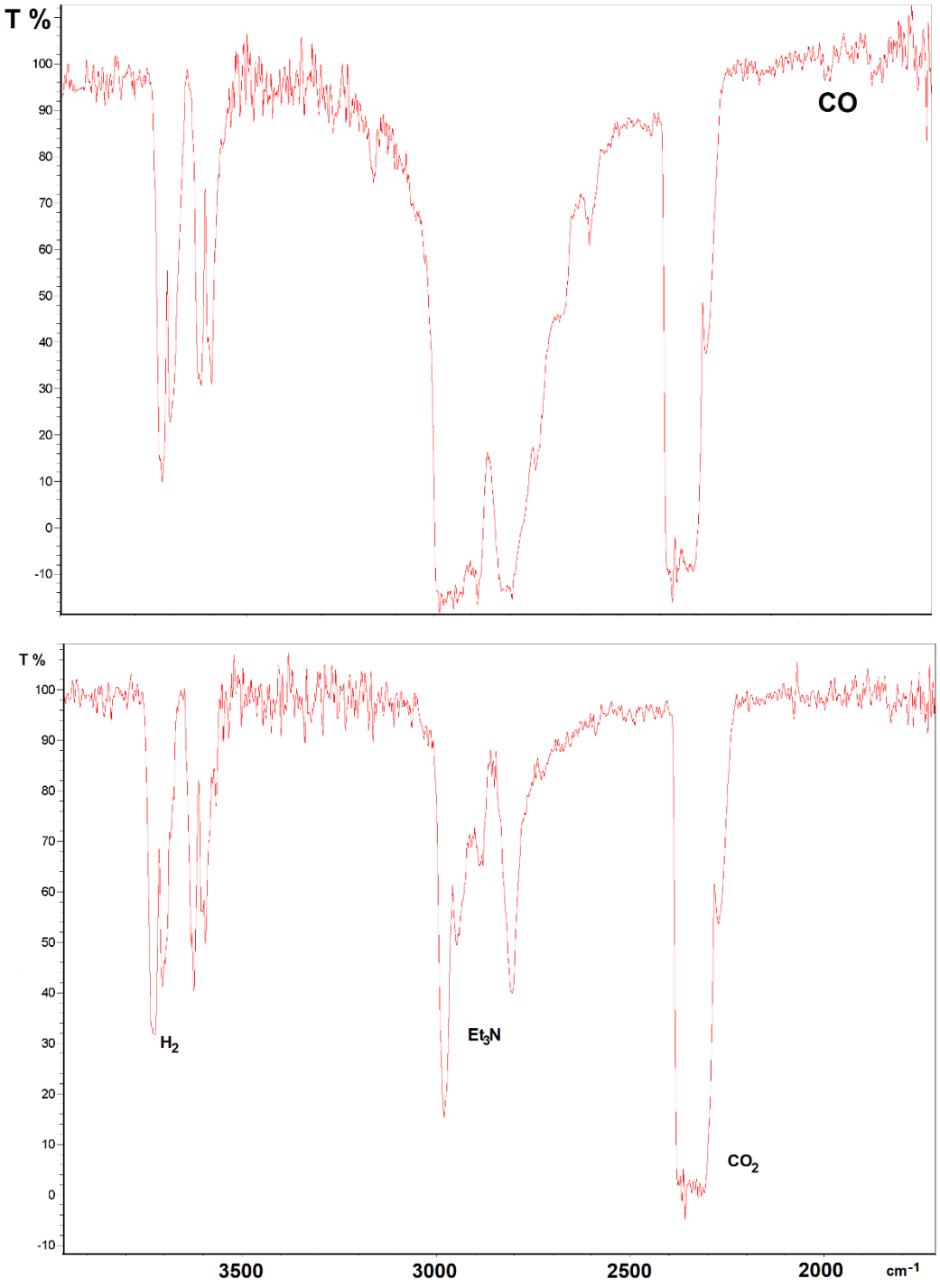

Figure S17. FT-IR spectrum of the gaseous product from the catalytic reaction. Up: reaction at 373 K. Down: reaction at 353 K.

3. NMR study of the blue residue from the catalytic reactions

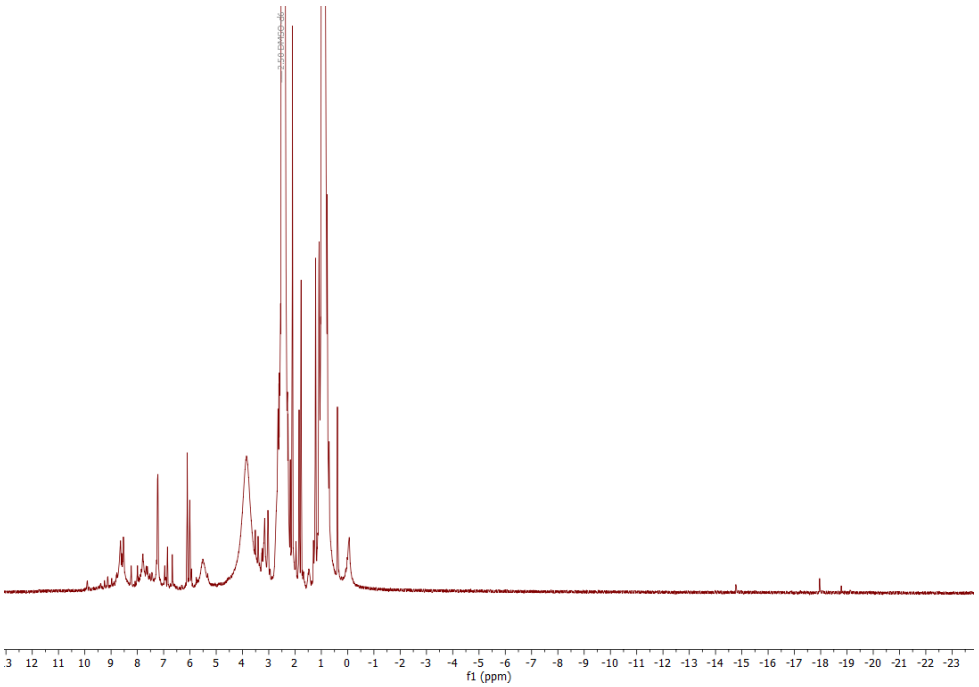

Figure S18. ^{1}H NMR spectrum of the blue-residue from the solvent-free FA dehydrogenation using **3** in DMSO (400 MHz, 298K).

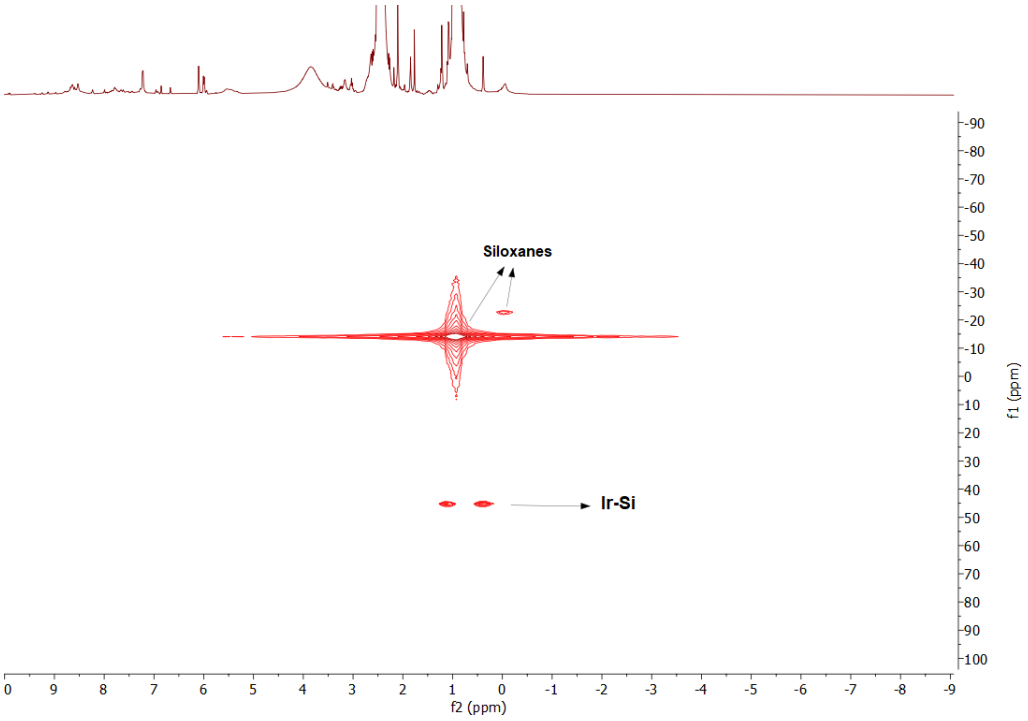

Figure S19. $^{1}H–^{29}Si$ HMBC spectrum of the blue-residue from the solvent-free FA dehydrogenation using **3** in DMSO (400 MHz, 298K).