Electronic Supplementary Material (ESI) for Dalton Transactions.

CO_2 as hydrogen vector - Transition metal diamine catalysts for selective HCOOH dehydrogenation

Supporting Information

Cornel Fink and Gabor Laurenczy

École Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCOM
CH-1015 Lausanne

E-Mail : cornel.fink@epfl.ch; gabor.laurenczy@epfl.ch

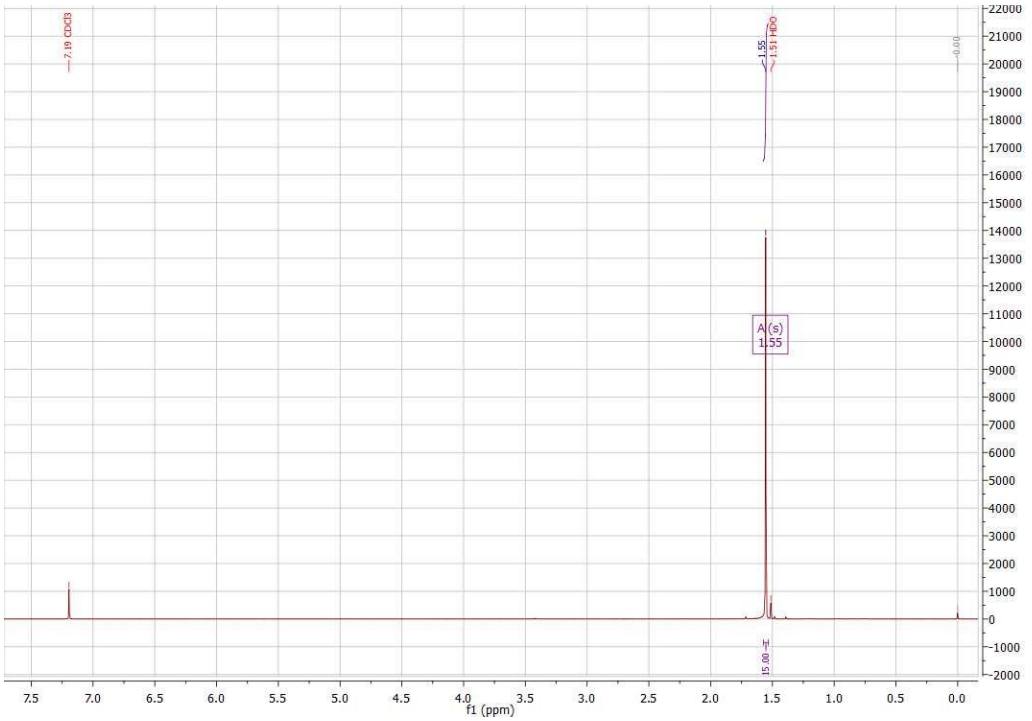

Fig. 1 $[Cp^*RhCl_2]_2$ in $CDCl_3$
^{1}H NMR (400 MHz, Chloroform-d) δ 1.55 (s, 15H)

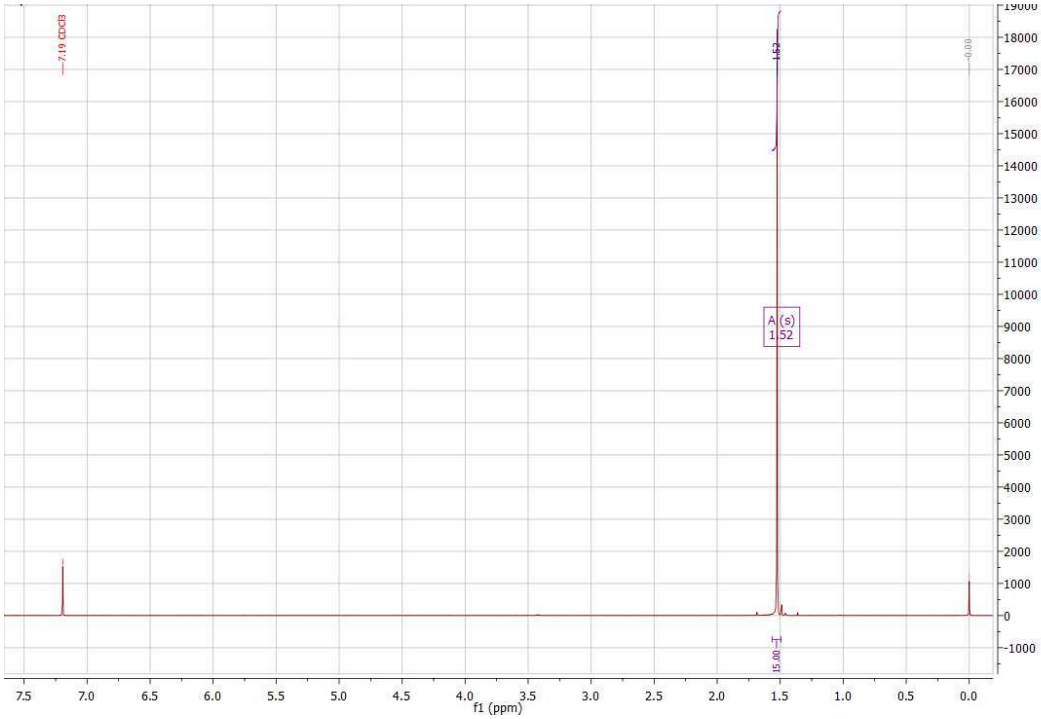

Fig. 2 $[Cp^*IrCl_2]_2$ in $CDCl_3$
^{1}H NMR (400 MHz, Chloroform-d) δ 1.52 (s, 15H).

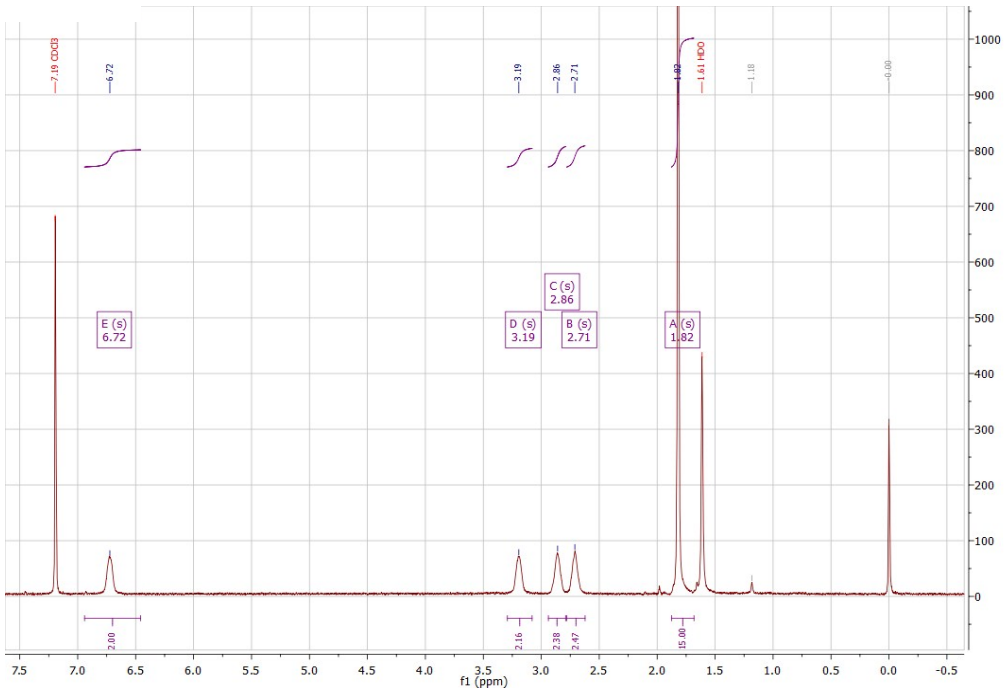

*Fig. 3 Complex **1** in $CDCl_3$*

*^1H NMR (400 MHz, Chloroform-*d*) δ 6.72 (s, 2H), 3.19 (s, 2H), 2.86 (s, 2H), 2.71 (s, 2H), 1.82 (s, 15H).*

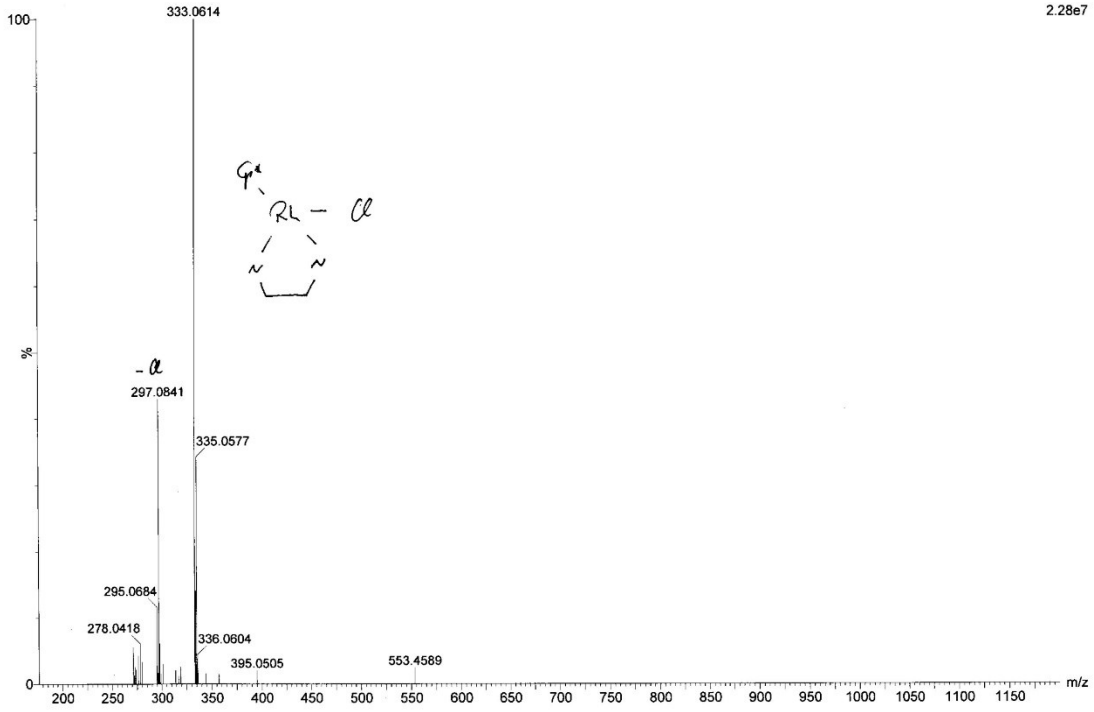

Fig. 4 Complex **2** *ESI (positive mode); exact mass: 333,69*

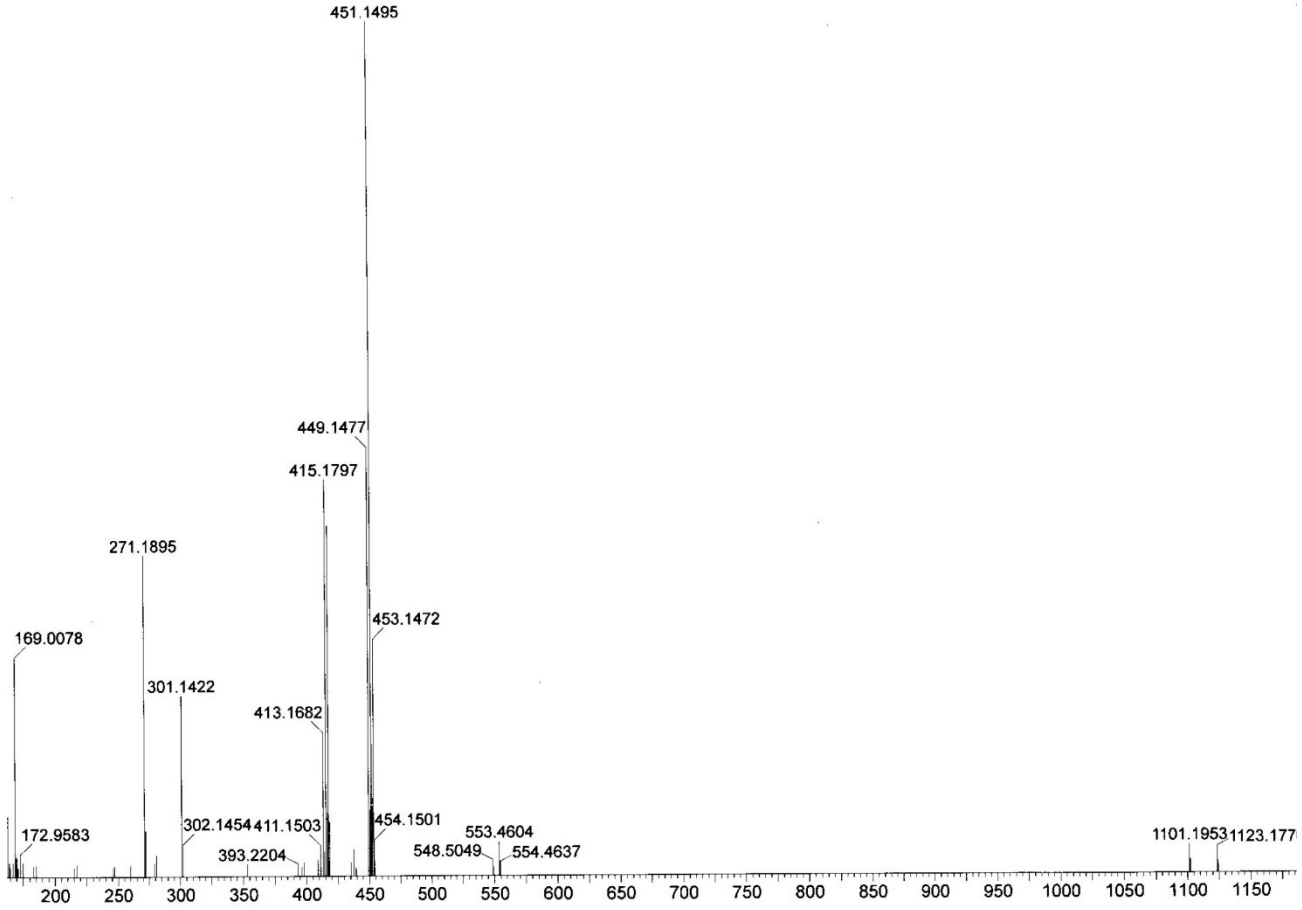

Fig. 5 Complex **3**; *ESI (positive mode); exact mass: 451,15*

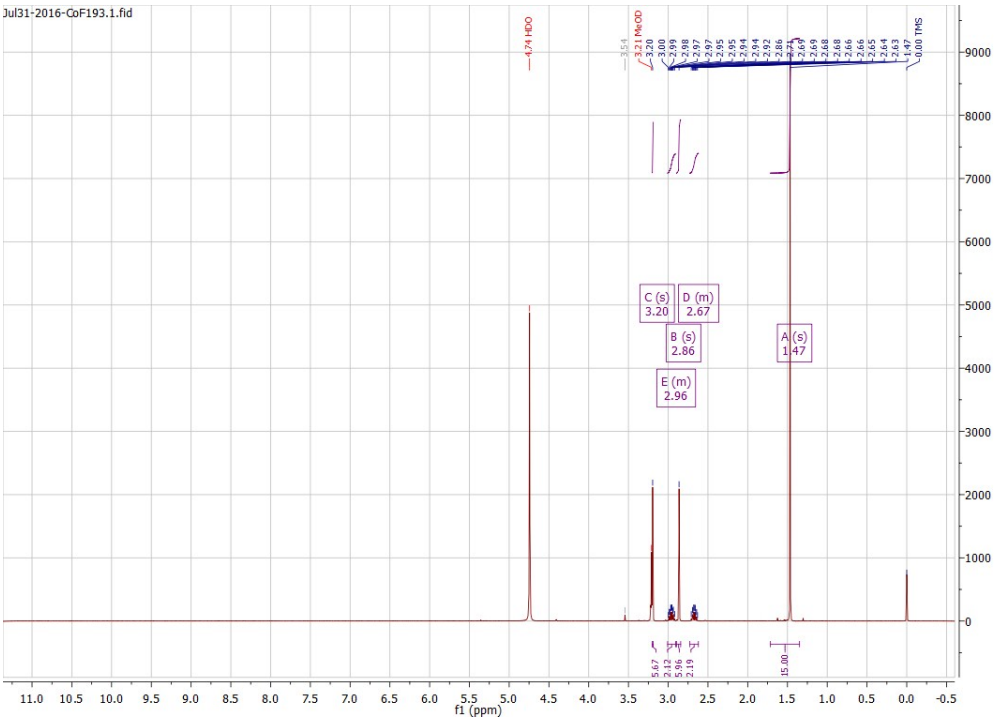

*Fig. 6 Complex **4** in MeOD[1]*

^{1}H NMR (400 MHz, Methanol-d_4) δ 3.20 (s, 6H), 3.01 – 2.91 (m, 2H), 2.86 (s, 6H), 2.73 – 2.62 (m, 2H), 1.47 (s, 15H).

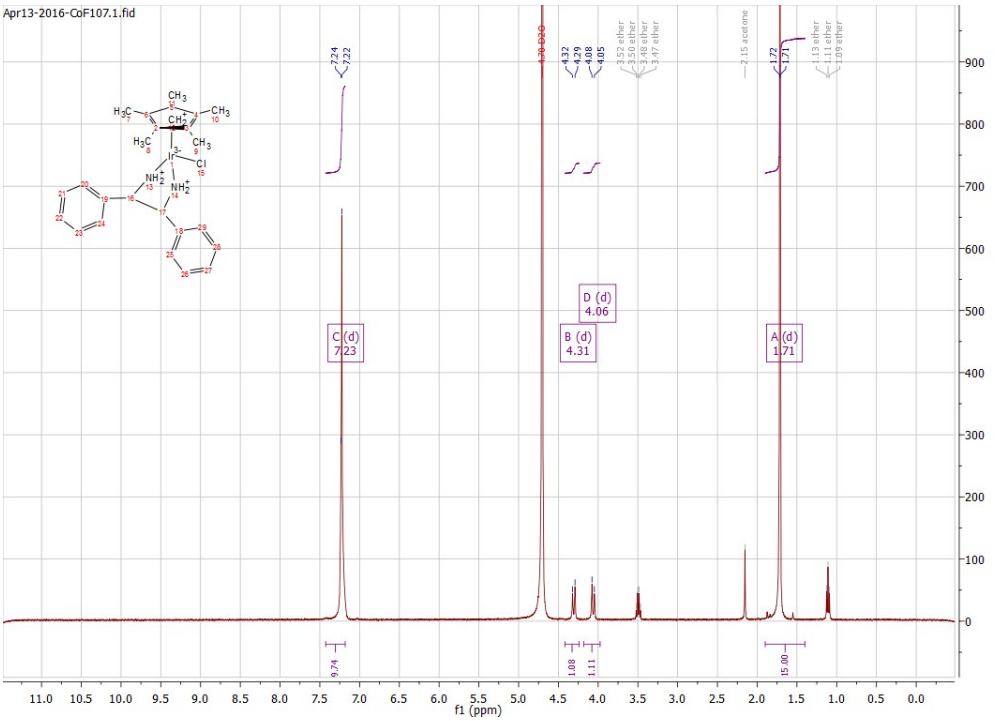

*Fig. 7 Complex **5** in D_2O*

^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.23 (d, J = 4.7 Hz, 10H), 4.31 (d, J = 12.3 Hz, 1H), 4.06 (d, J = 12.3 Hz, 1H), 1.71 (d, J = 1.4 Hz, 15H).

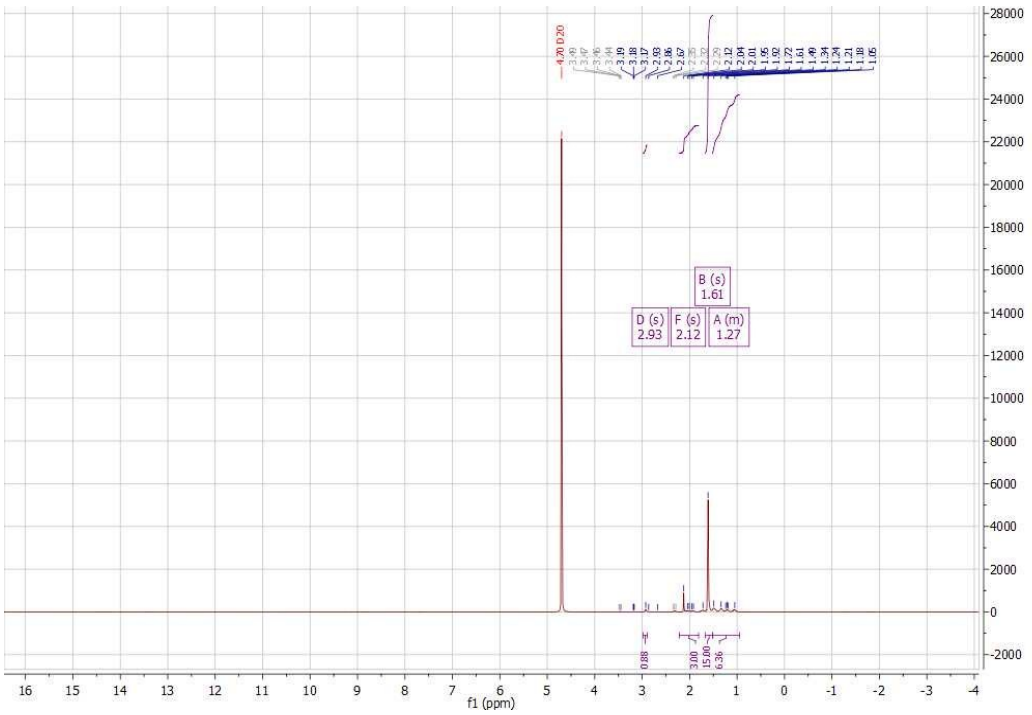

*Fig. 8 Complex **6** in D_2O*
δ 2.93 (s, 1H), 2.12 (s, 3H), 1.61 (s, 15H), 1.51 – 0.95 (m, 6H).

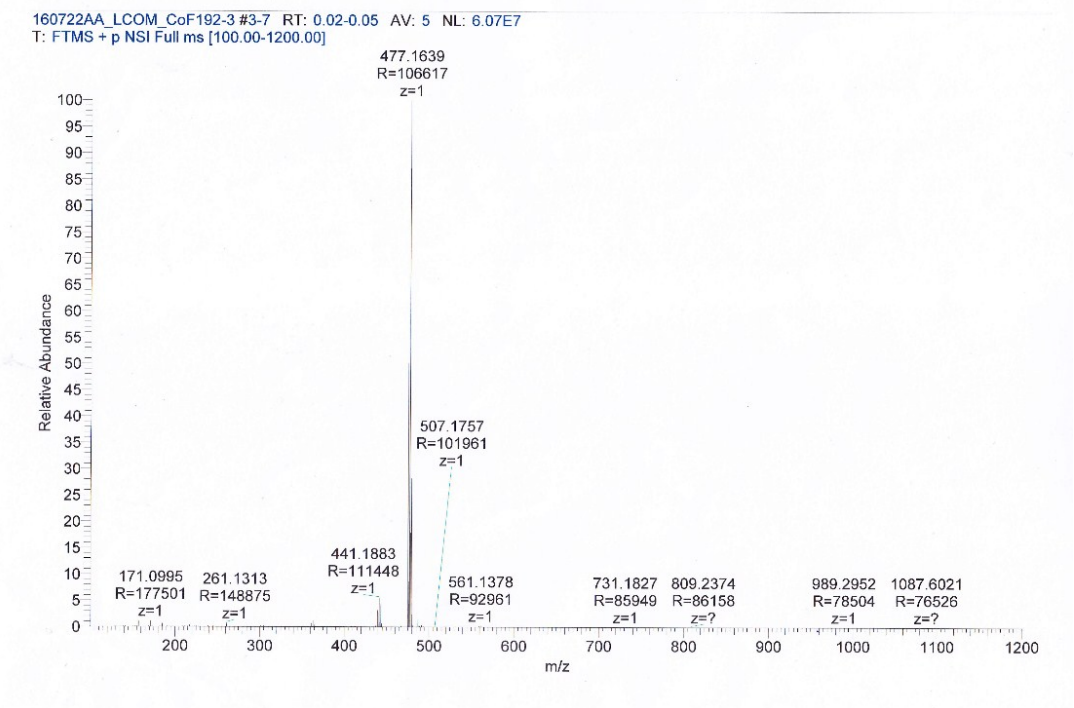

*Fig. 9 Complex **6** mass spectrum; ESI (positive mode); exact mass: 477.16*

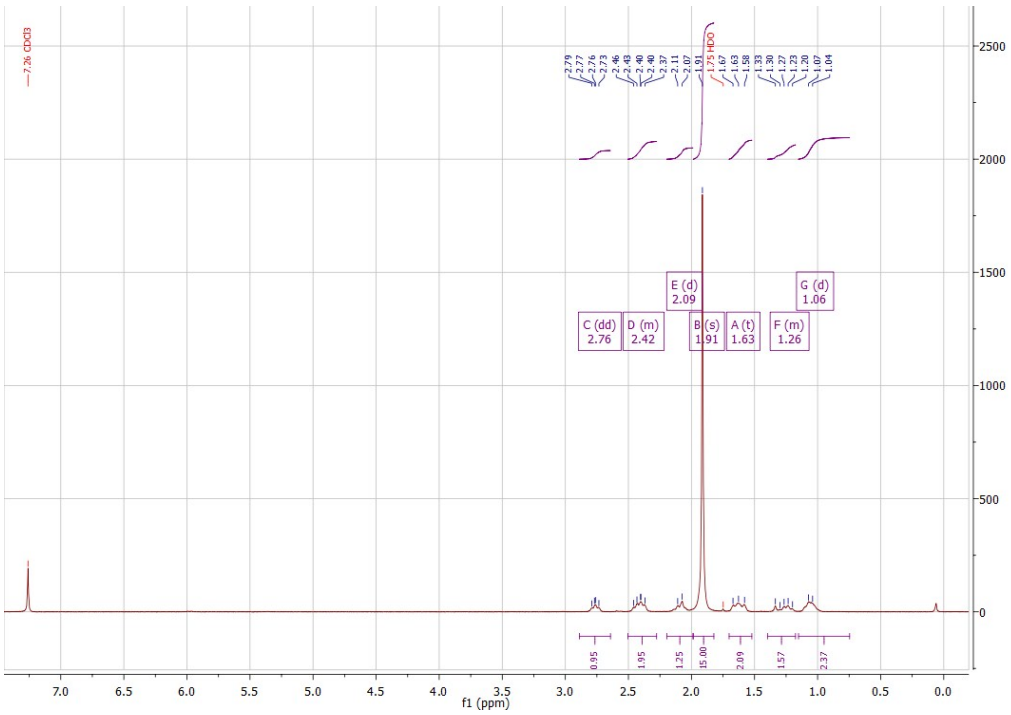

Fig. 10 Complex **7** in $CDCl_3$

^{1}H NMR (400 MHz, Chloroform-d) δ 2.76 (dd, J = 13.2, 9.1 Hz, 1H), 2.50 – 2.28 (m, 2H), 2.09 (d, J = 14.3 Hz, 1H), 1.91 (s, 15H), 1.63 (t, J = 18.3 Hz, 2H), 1.40 – 1.18 (m, 2H), 1.06 (d, J = 13.1 Hz, 2H)

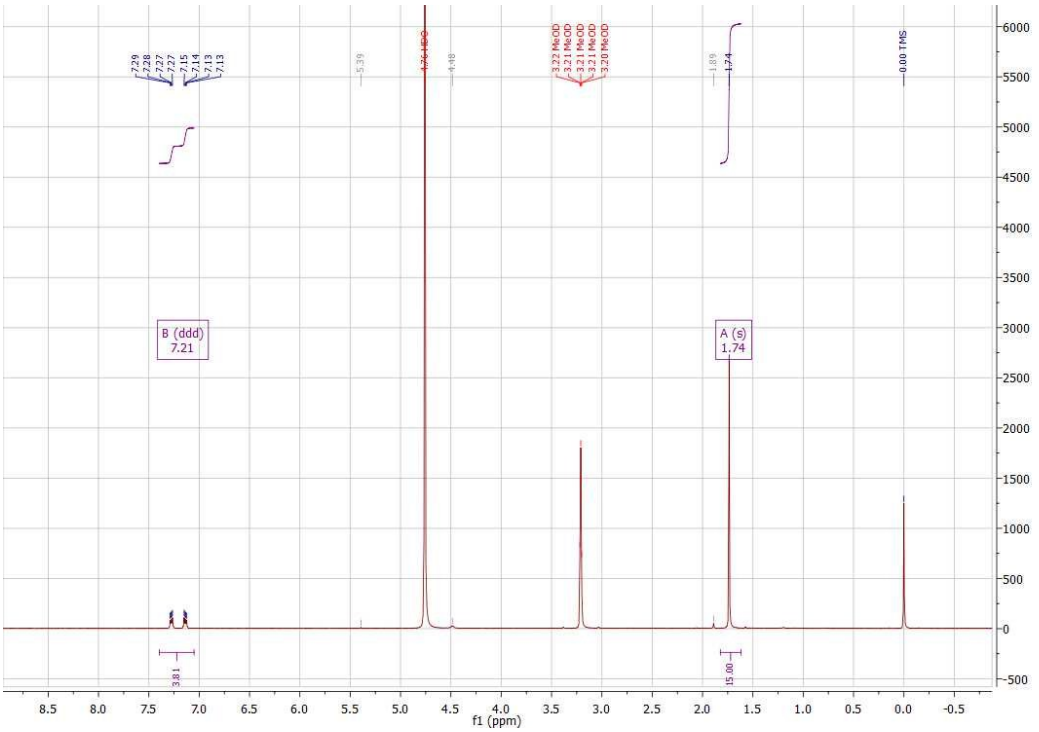

Fig. 11 Complex **8** in MeOH

1H NMR (400 MHz, Methanol-d4) δ 7.21 (ddd, J = 55.7, 6.0, 3.5 Hz, 4H), 1.74 (s, 15H).

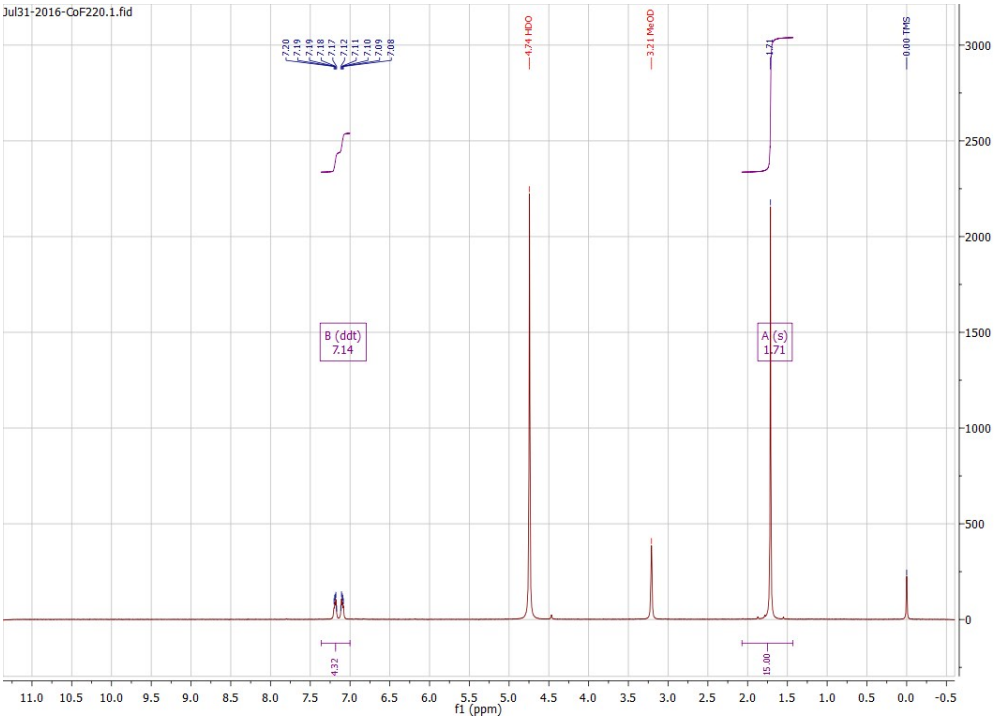

*Fig. 12 Complex **9** in MeOD*

1H NMR (400 MHz, Methanol-d4) δ 7.14 (ddd, J = 37.7, 6.0, 3.5 Hz, 4H), 1.71 (s, 15H).

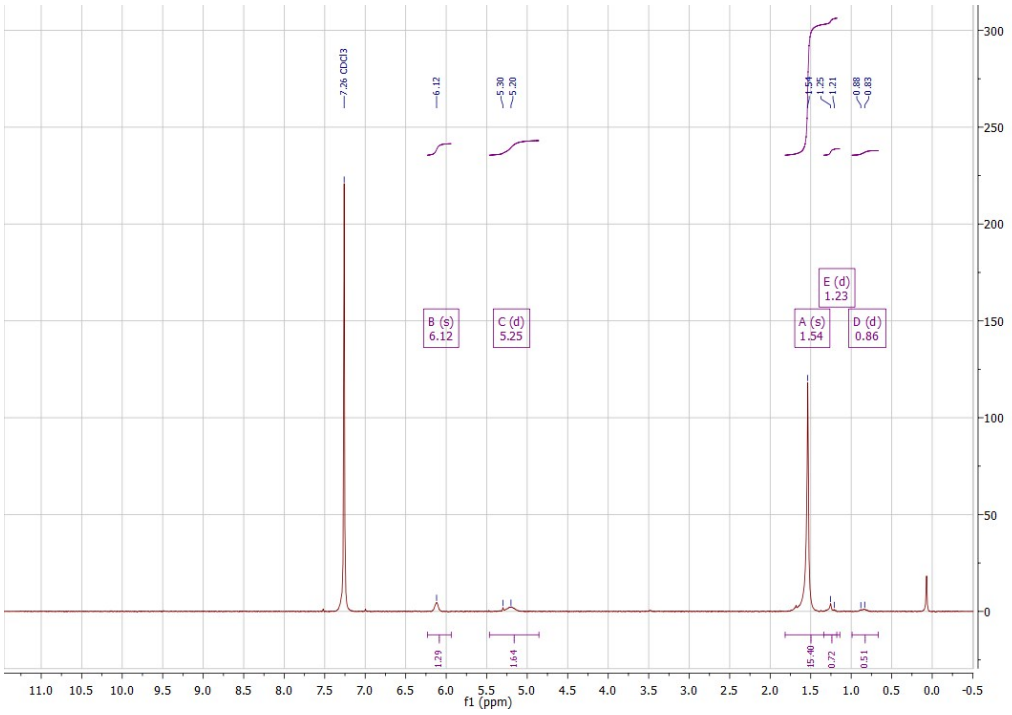

Fig. 13 Complex **10** in $CDCl_3$

^{1}H NMR (400 MHz, Chloroform-d) δ 6.12 (s, 1H), 5.25 (d, J = 39.7 Hz, 2H), 1.54 (s, 15H), 1.23 (d, J = 18.9 Hz, 1H), 0.86 (d, J = 19.3 Hz, 1H).

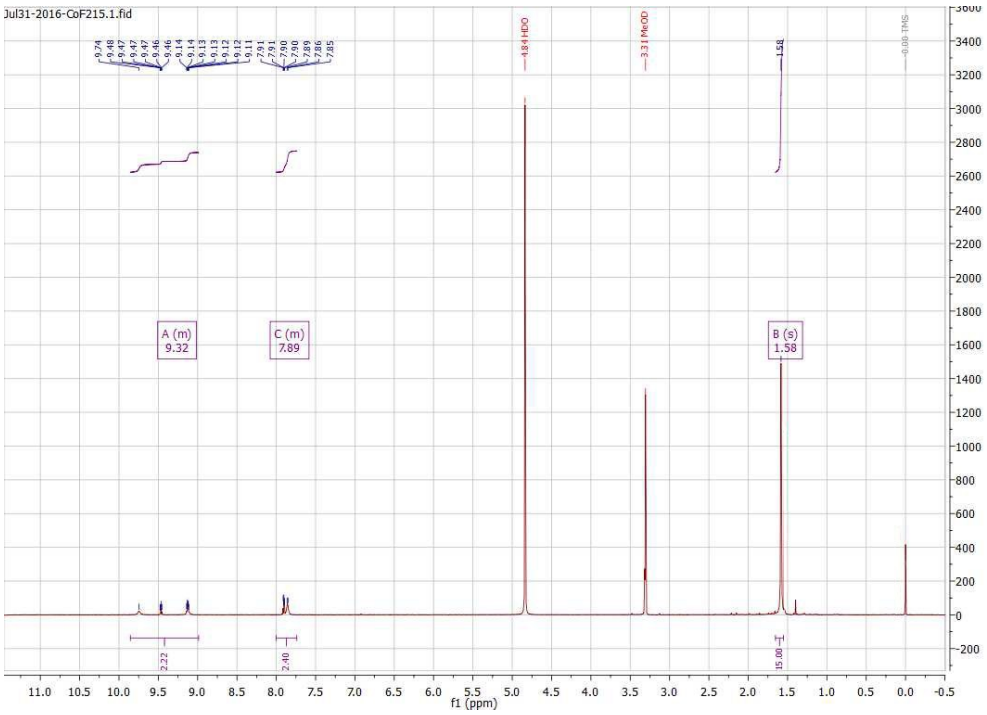

Fig. 14 Complex **11** in MeOD

^{1}H NMR (400 MHz, Methanol-d_4) δ 9.85 – 8.99 (m, 2H), 8.00 – 7.74 (m, 2H), 1.58 (s, 15H).

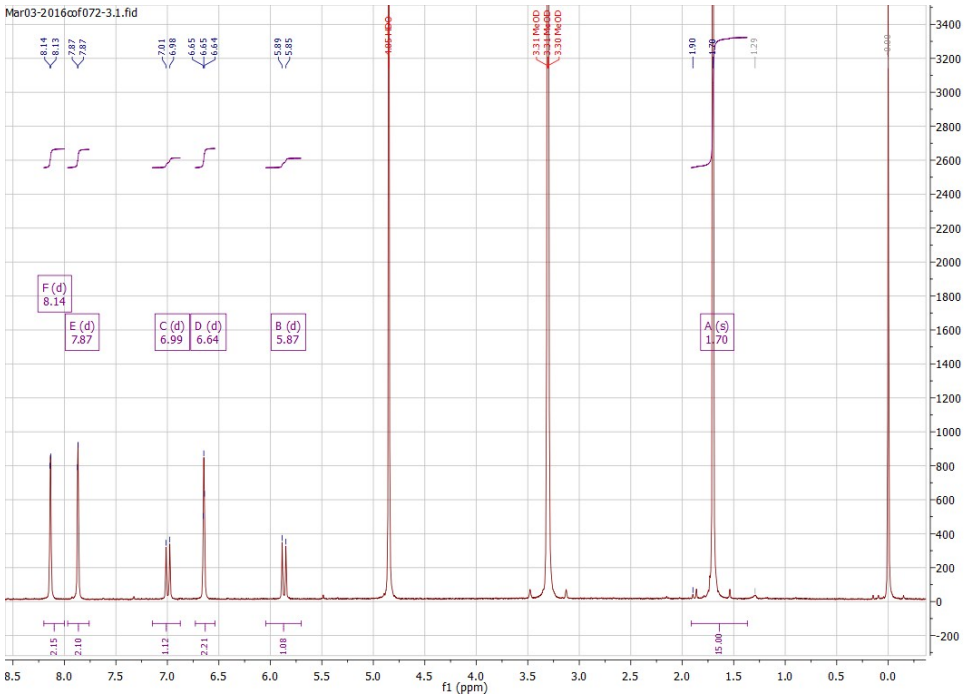

*Fig. 15 Complex **12** in MeOD*

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.14 (d, J = 2.8 Hz, 2H), 7.87 (d, J = 2.4 Hz, 2H), 6.99 (d, J = 14.5 Hz, 1H), 6.64 (d, J = 2.6 Hz, 2H), 5.87 (d, J = 14.5 Hz, 1H), 1.70 (s, 15H).

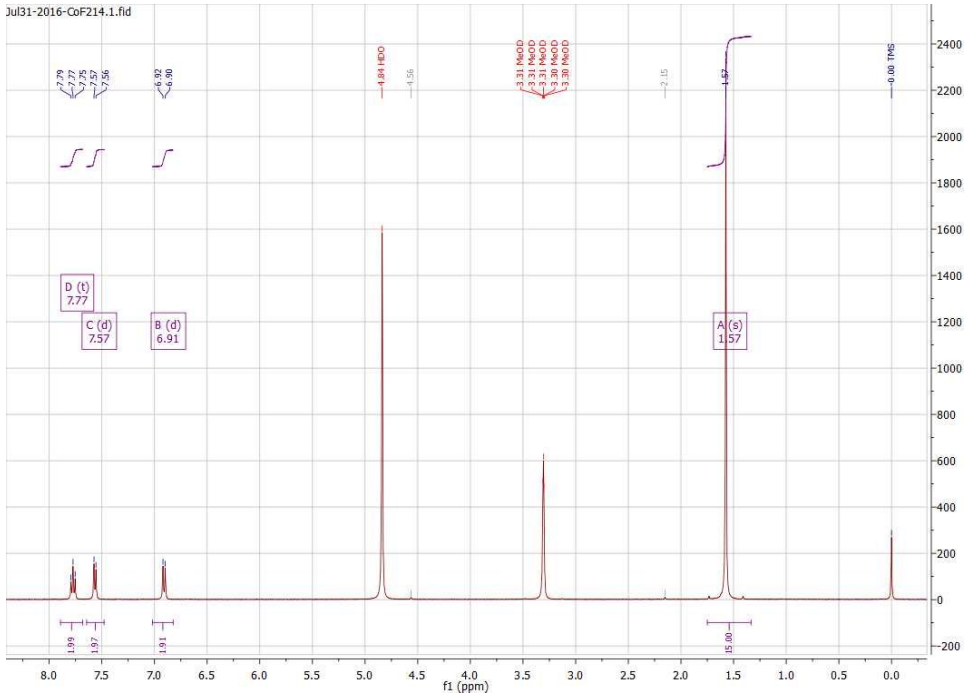

Fig. 16 Complex **13** in MeOH

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.77 (t, J = 8.0 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 1.57 (s, 15H).

Activation Energy for compound 6 [Cp*Ir(III)(N,N')Cl]Cl_2

ln(rate init) temp (°C)

-1.24034071 50
-0.105027238 60
0.421732081 70
1.55520561 80
1.912811366 90

delta H(*) = + 77.94 +/- 3.16 kJ/mol

slope = - 9374.8
inter. = +27.875

experiment\T°C	50	60	70	80	90
1	118,23	57,5	35,08	18,889	9,2
2	123,56	58,93	34,84	18,45	8,56
3	121,79	55,54	36,51	17,7	8,99
mean value	121,19	57,32	35,48	18,35	8,92
standard deviation	2,22	1,39	0,74	0,49	0,27

Table 1 Time in minutes for total decomposition of FA; values in table obtained by pressure measurements (constant pressure = total conversion); verified by NMR for one sample/temperature

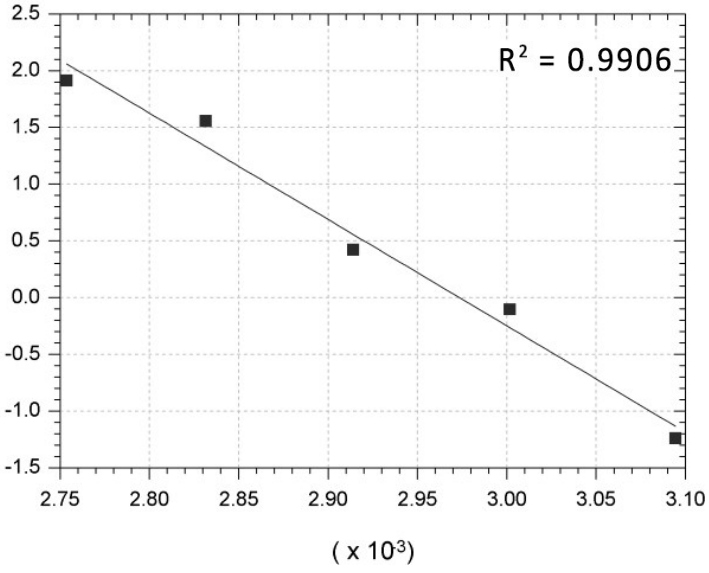

Fig. 17 Arrhenius plot; obtained from mentioned dataset above

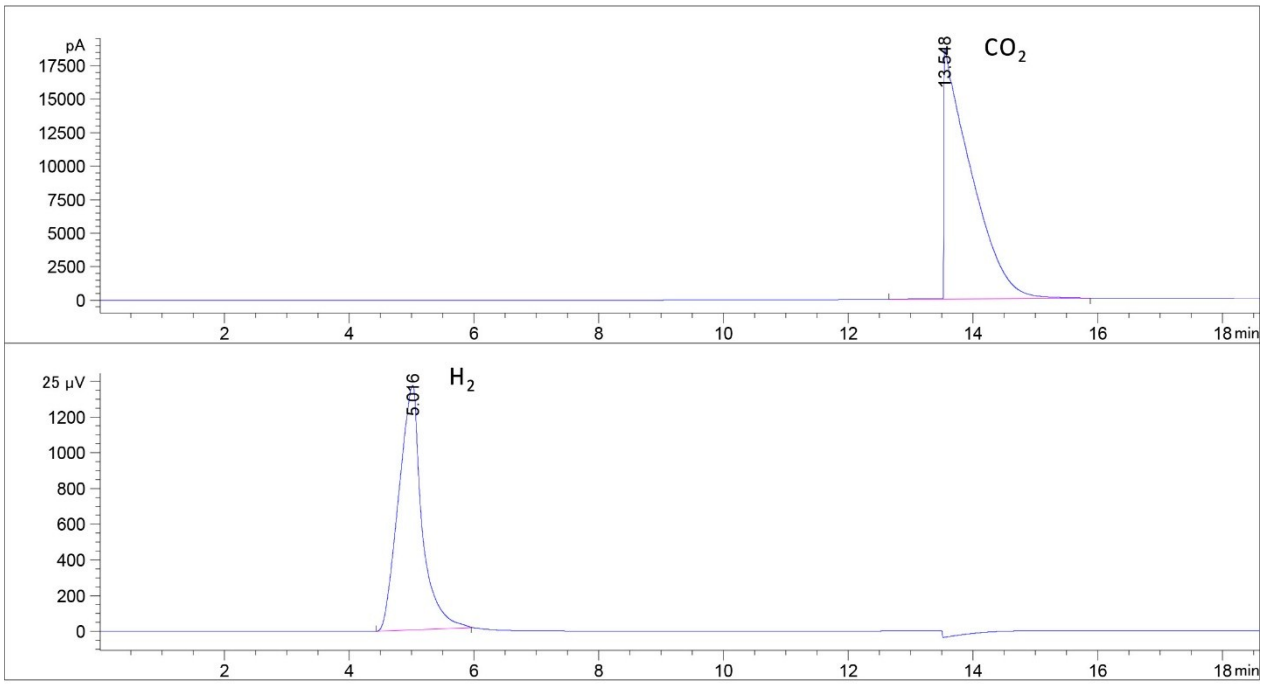

*Table 2 GC chromatogram for compound **6** (Table 1); reaction conditions: 65℃, 4 M FA in water; catalyst (12 µmol) was incubated for 3 h at 65℃; then gas collection was performed over 3 h; detection limit for CO: 15 ppm*

Referneces:

1. J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. D. Incarvito, O. Eisenstein, G. W. Brudvig and R. H. Crabtree, *J. Am. Chem. Soc.*, 2010, **132**, 16017-16029.
2. G. W. Karpin, D. M. Morris, M. T. Ngo, J. S. Merola and J. O. Falkinham Iii, *MedChemComm*, 2015, **6**, 1471-1478.