SUPPORTING INFORMATION

μ-Oxo-Bridged Iron(III) Complexes for Selective Reduction of Aromatic Ketones Catalyzed through Base Promoted *In-situ* Nanoparticles Formation

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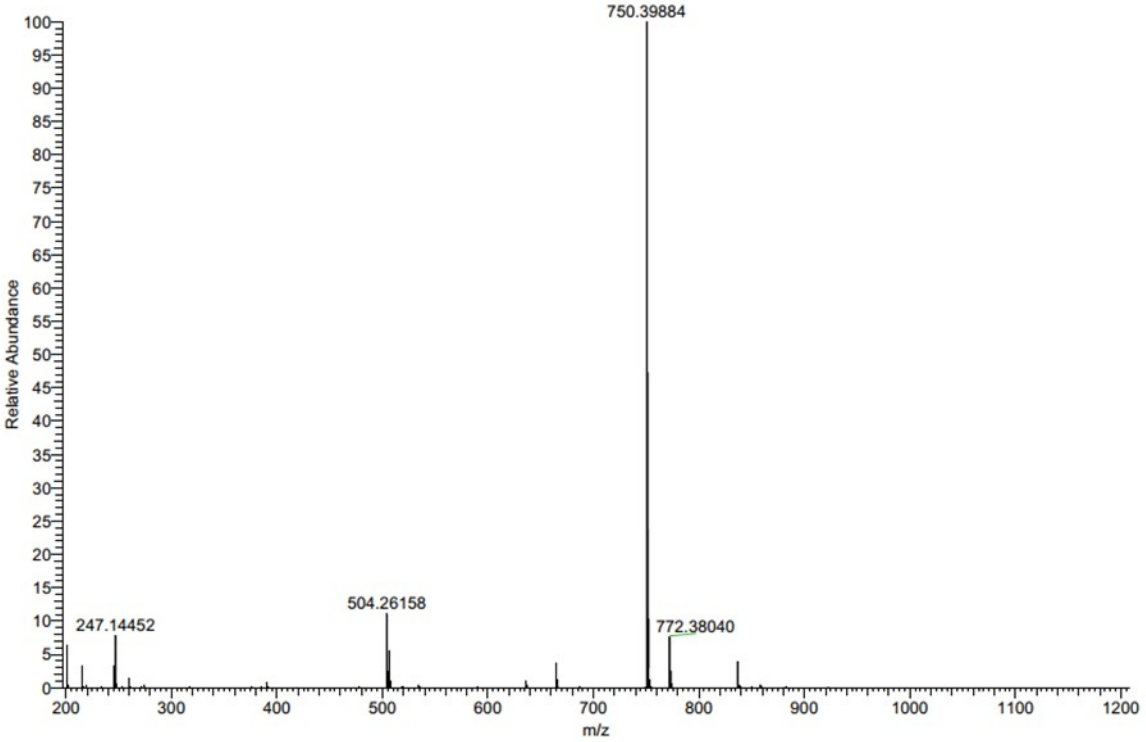
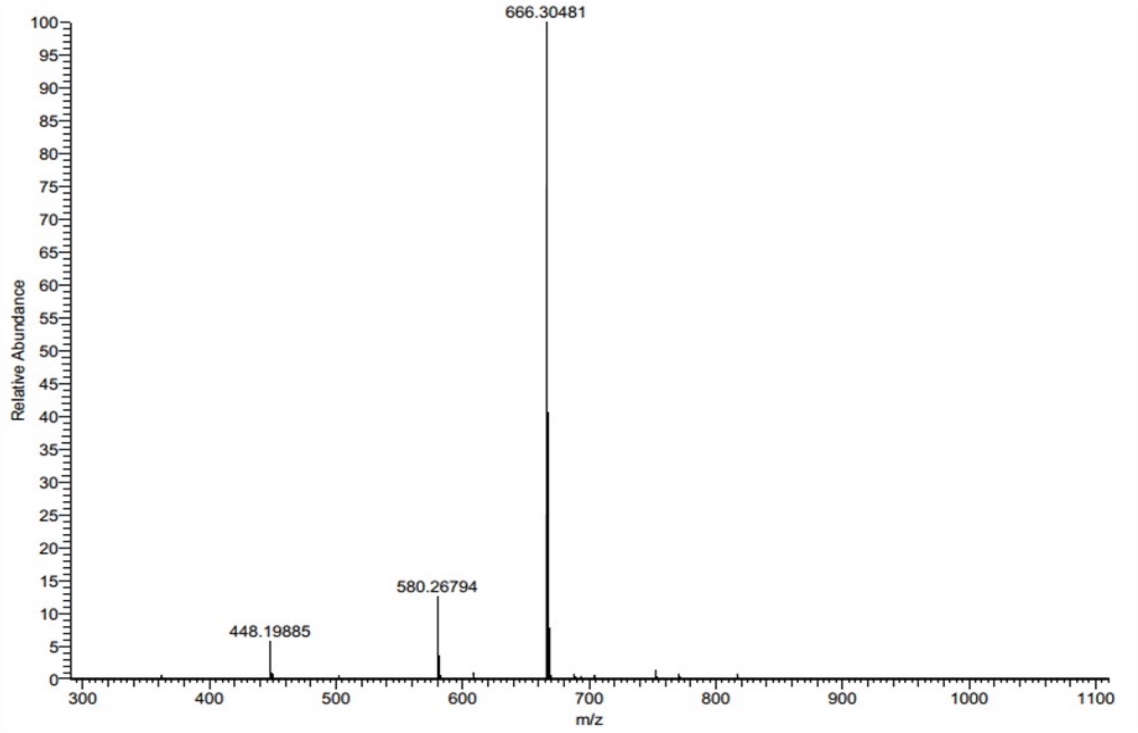


(A)



(B)

Figure S1. ESI-MS mass spectra of the ligands A) $\mathbf{L_1}$ and B) $\mathbf{L_2}$.

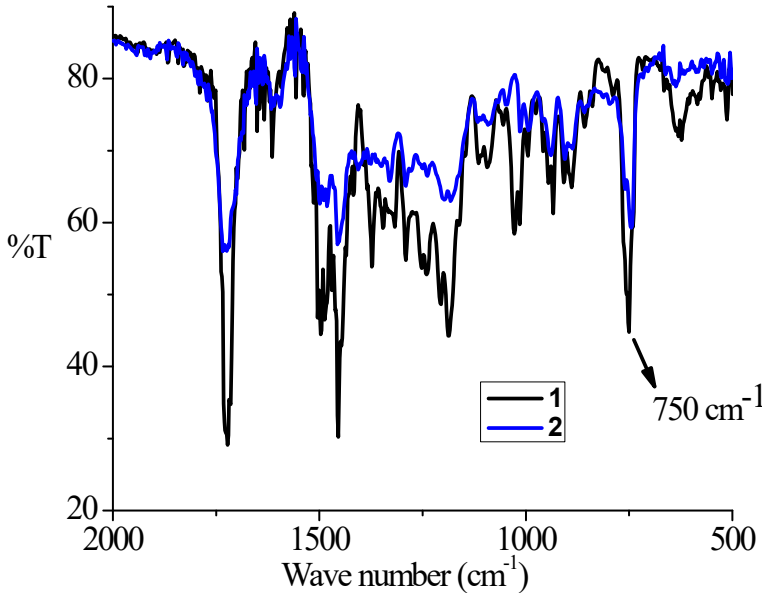


Figure S2. IR spectra of the complexes **1** and **2** were recorded using KBr pellet.

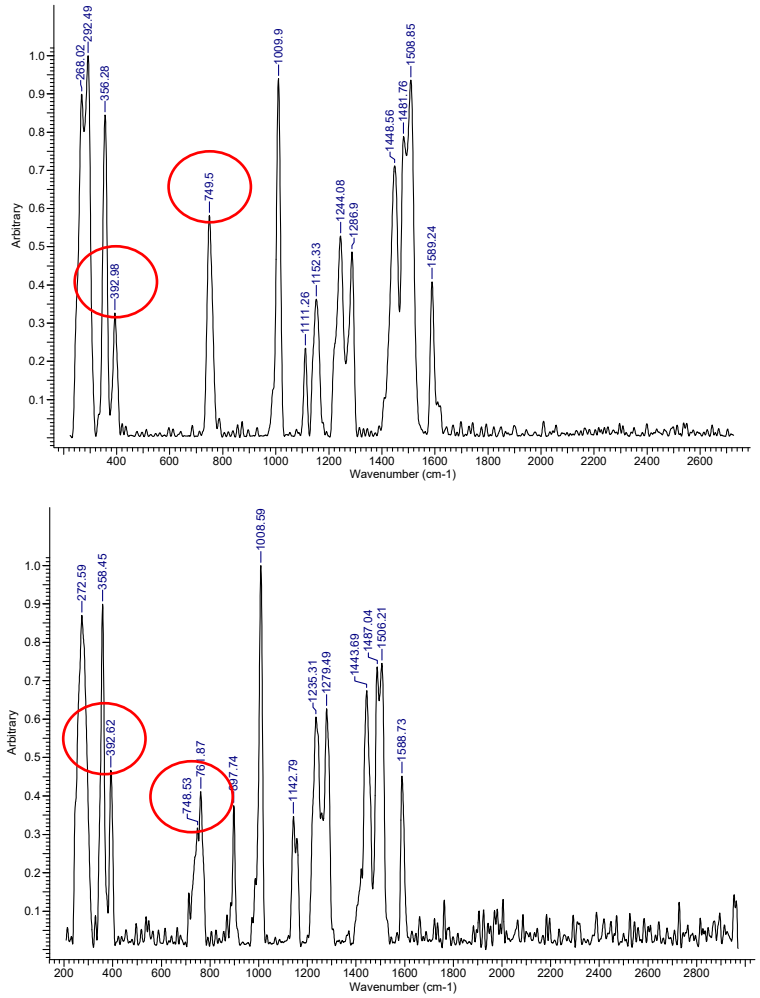
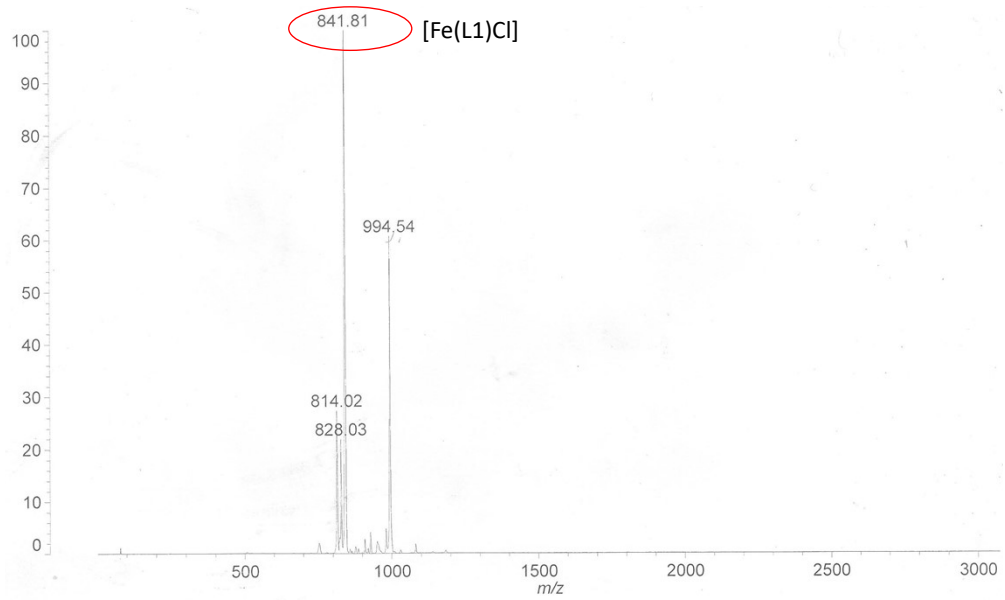


Figure S3. The Raman spectra of the complexes **1** (top) and **2** (bottom).

A)



B)

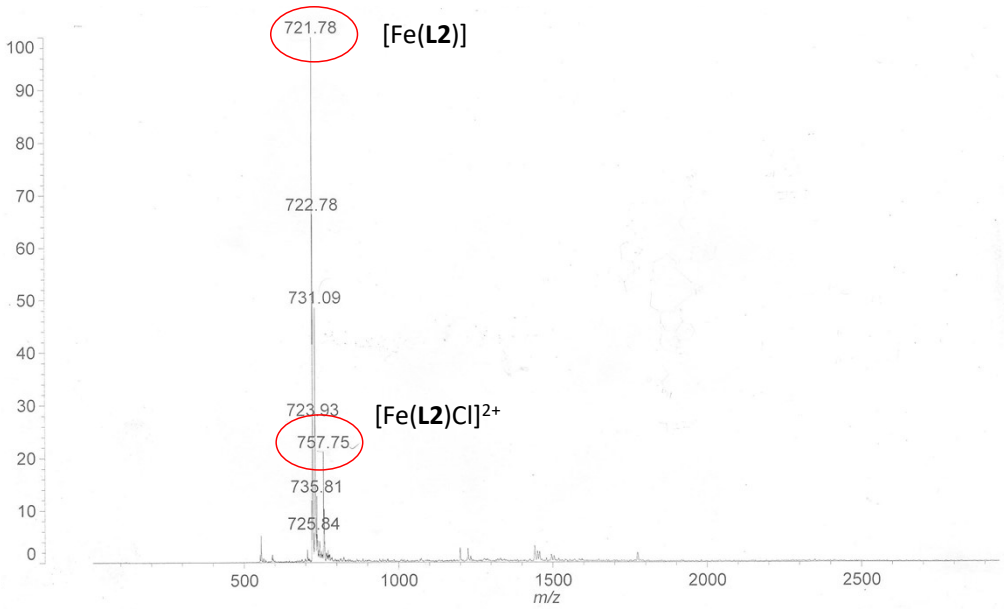


Figure S4. MALDI-TOF mass spectra of the complexes A) **1** and B) **2**.

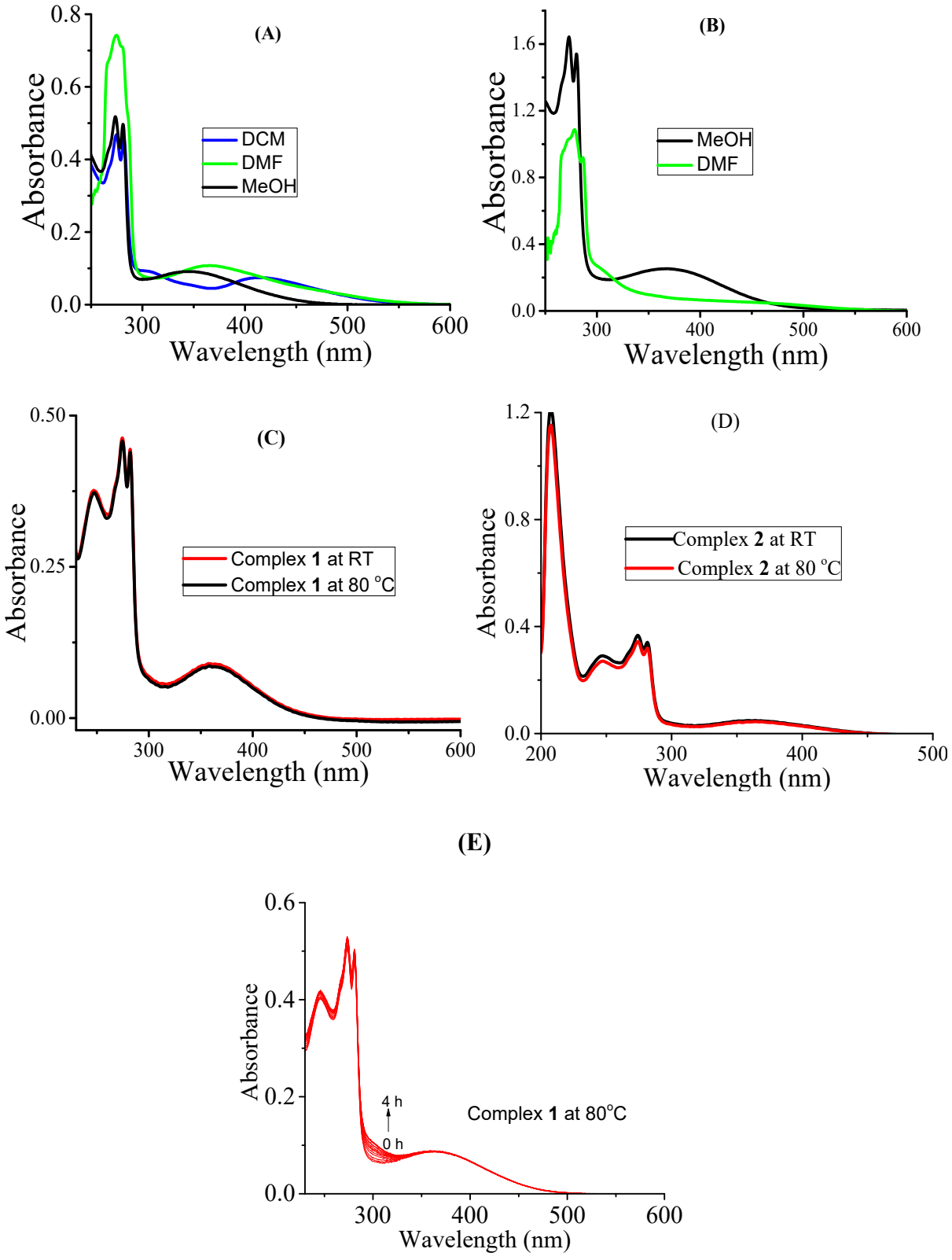


Figure S5. UV-visible spectra of the complexes **(A) 1**, ([c] = 1.7 x 10^{-5} M) and **(B) 2**, ([c] = 2.0 x 10^{-5}) in different solvents. **(C, D)** UV-Visible spectra of complexes **1** and **2** at temperature 25°C and 80 °C (in MeOH). **(E)** Time dependent UV-Visible study of complex **1** at 80 °C (in MeOH) monitored for 4 h with 15 min interval.

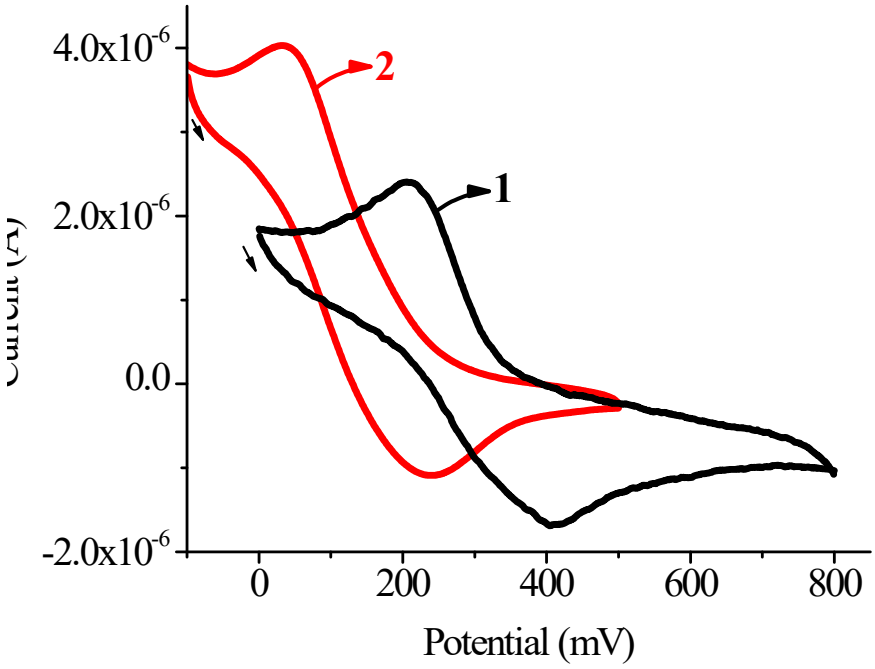
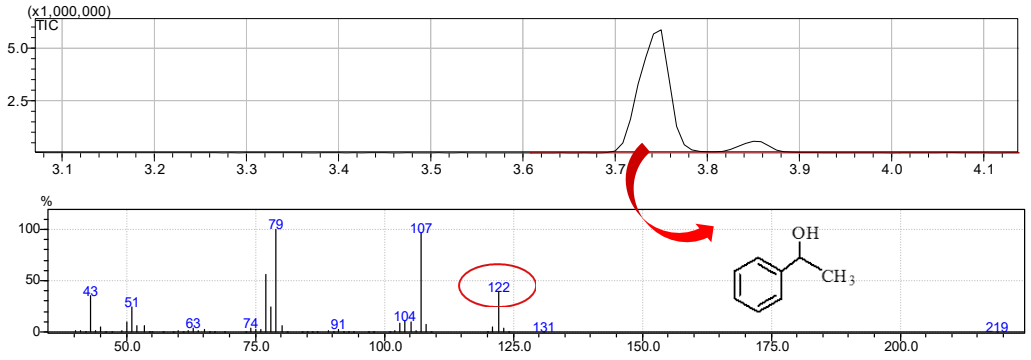
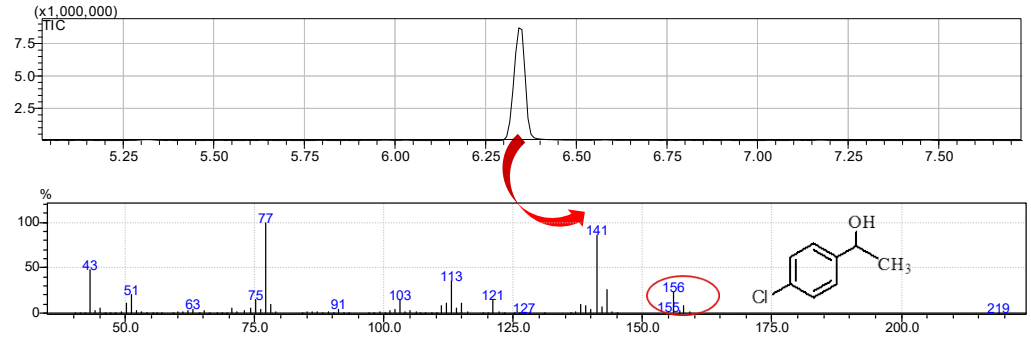


Figure S6. Cyclic voltammograms of a 10^{-3} M solution of **1** and **2** in DMF, in presence of 0.1 M tetrabutylammonium perchlorate (TBAP), using working electrode: glassy-carbon (0.07 cm^2); reference electrode: Ag/AgCl; auxiliary electrode: platinum wire, scan rate 75 mV/s.

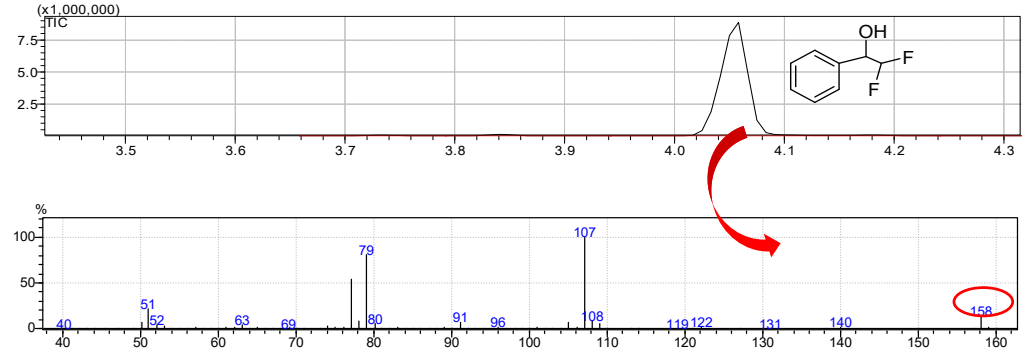
A)


(x1,000,000)
TIC
OH
CH3

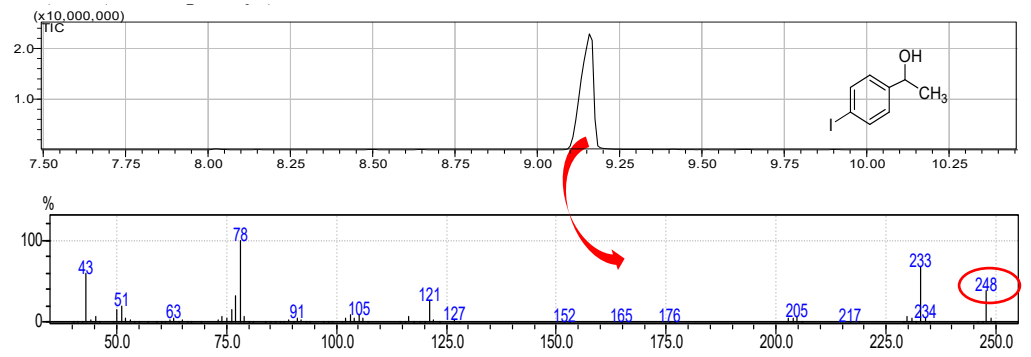
B)

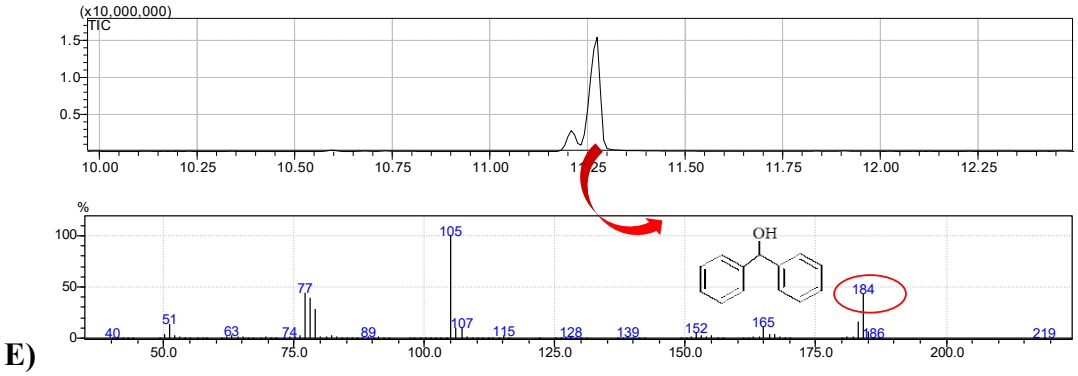

(x1,000,000)
TIC
OH
CH3
Cl

C)

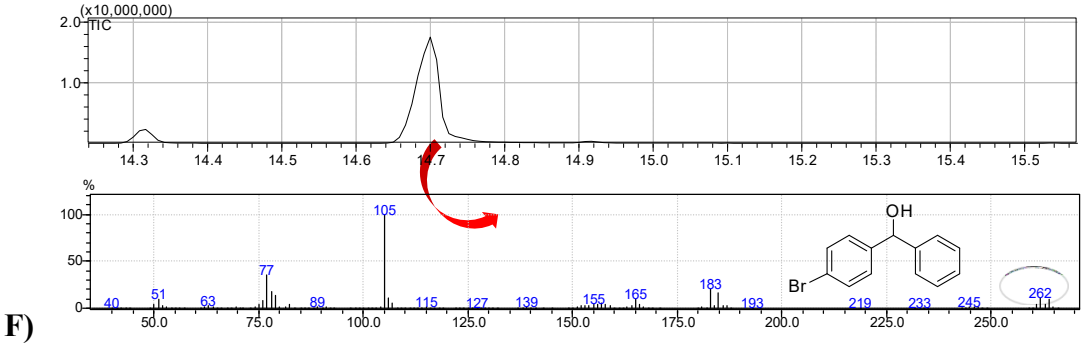

(x1,000,000)
TIC
OH
F
F

D)

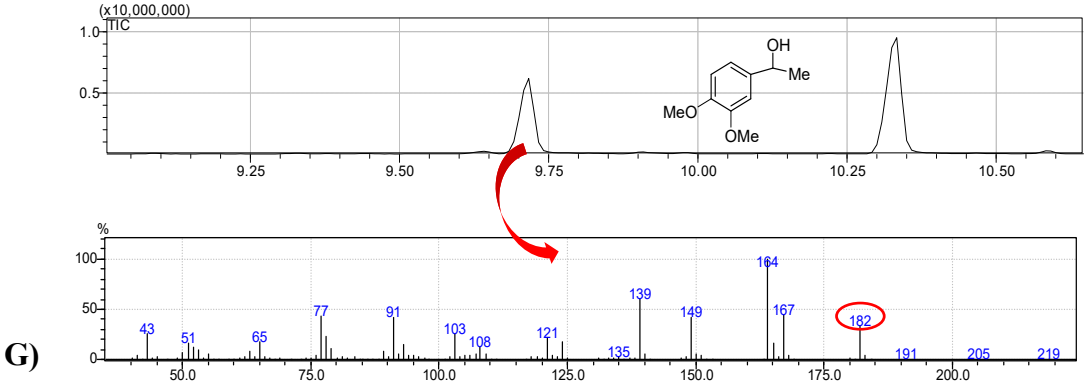

(x10,000,000)
TIC
OH
CH3
I



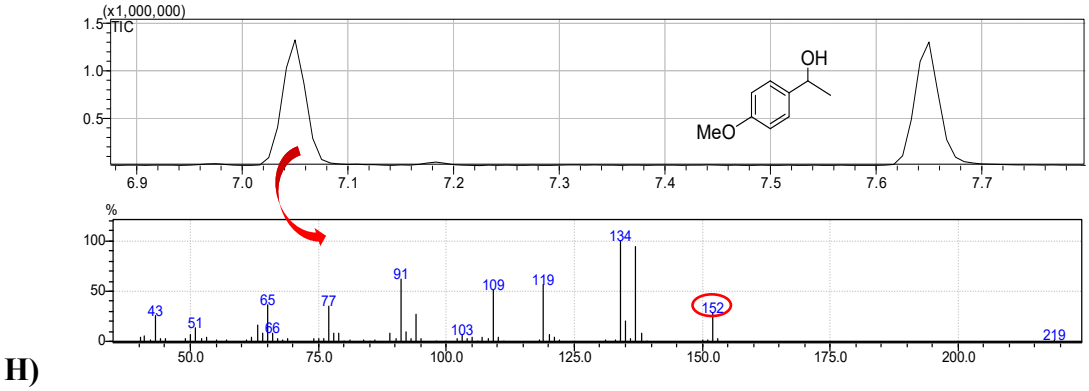
E)



F)



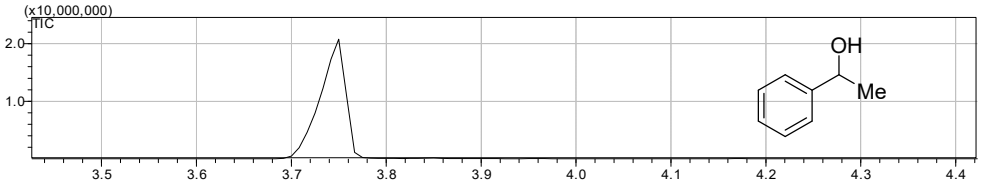
G)



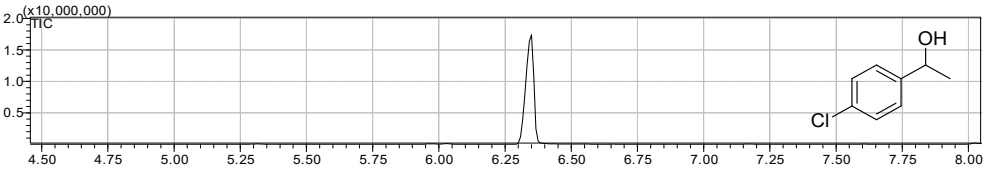
H)

Figure S7. GC-MS spectra (**A-H**) of selected alcohol products obtained from the transformation of the corresponding ketones in presence of the complex **1** (2 mol%) with KOH and *i*-PrOH.

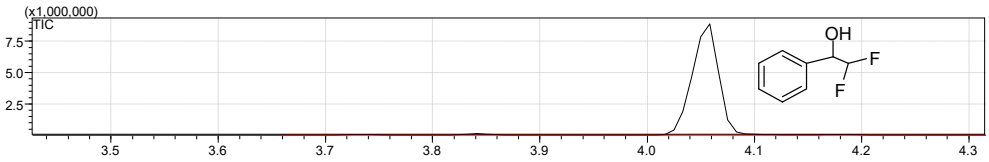
A)


(x10,000,000)
TIC
2.0
1.0
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
OH
Me

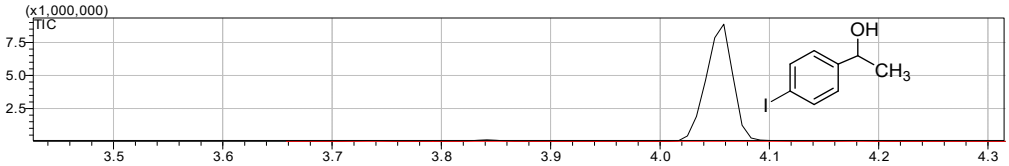
B)


(x10,000,000)
TIC
2.0
1.5
1.0
0.5
4.50
4.75
5.00
5.25
5.50
5.75
6.00
6.25
6.50
6.75
7.00
7.25
7.50
7.75
8.00
OH
Cl

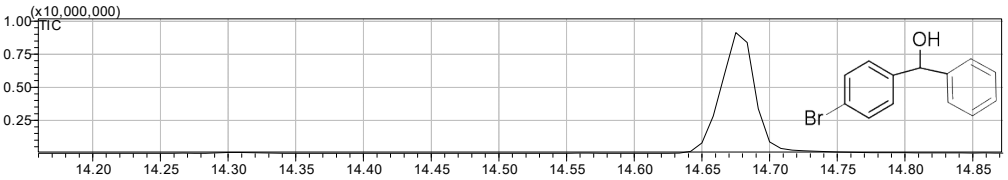
C)


(x1,000,000)
TIC
7.5
5.0
2.5
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
OH
F
F

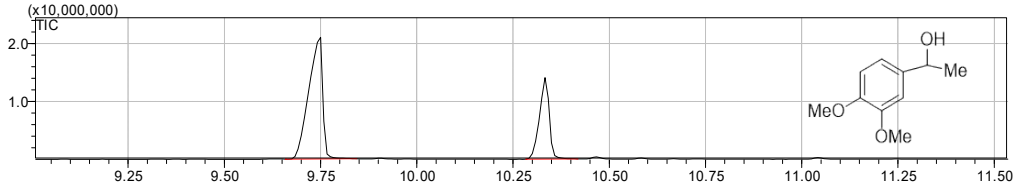
D)


(x1,000,000)
TIC
7.5
5.0
2.5
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
OH
CH3
I

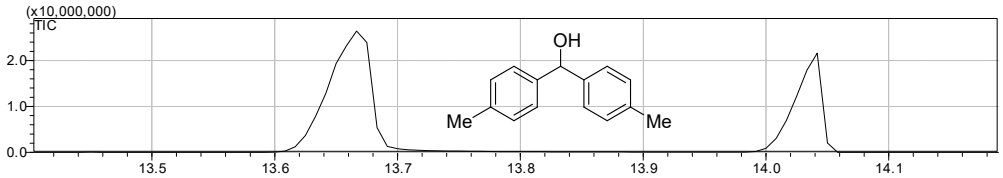
E)

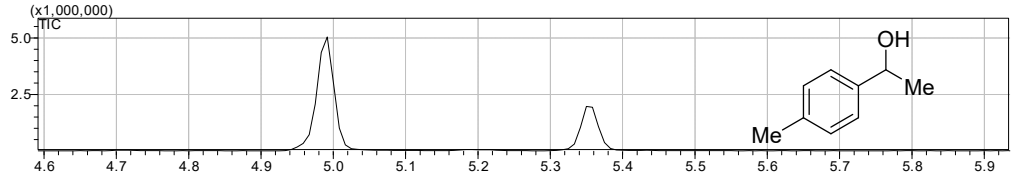

(x10,000,000)
TIC
1.00
0.75
0.50
0.25
14.20
14.25
14.30
14.35
14.40
14.45
14.50
14.55
14.60
14.65
14.70
14.75
14.80
14.85
OH
Br

F)


(x10,000,000)
TIC
2.0
1.0
9.25
9.50
9.75
10.00
10.25
10.50
10.75
11.00
11.25
11.50
OH
Me
MeO
OMe

G)

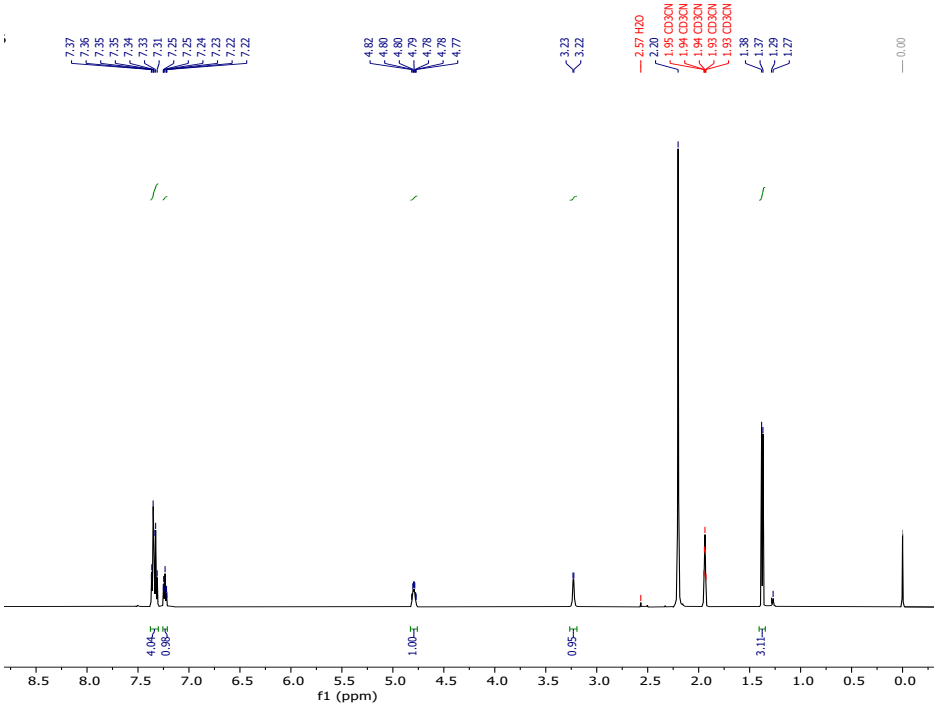

(x10,000,000)
TIC
2.0
1.0
0.0
13.5
13.6
13.7
13.8
13.9
14.0
14.1
OH
Me
Me

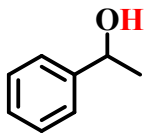


H)

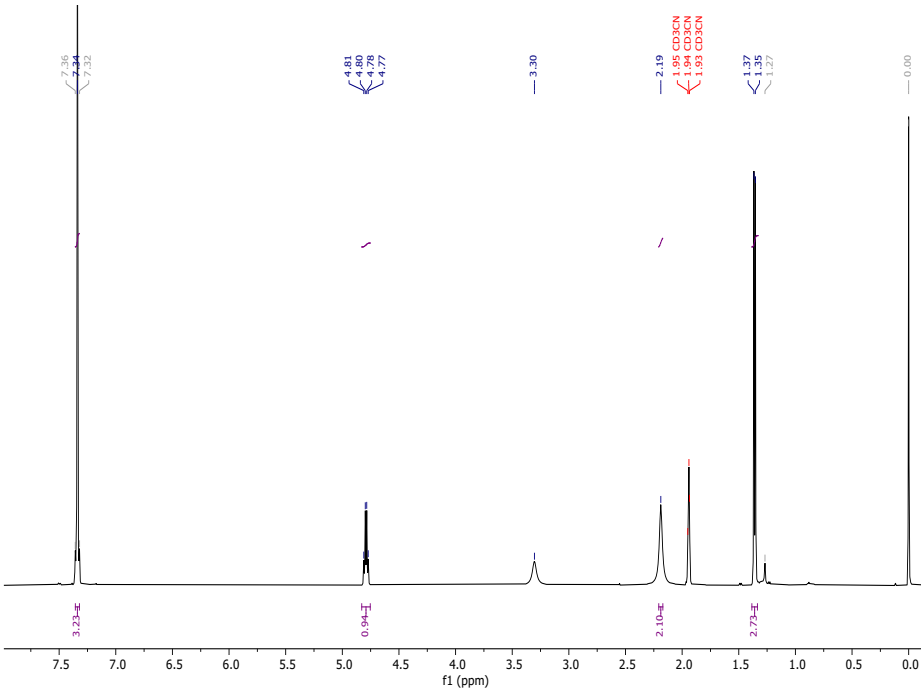
Figure S8. GC-MS spectra (**A**-**H**) of selected alcohol products obtained from the transformation of the corresponding ketones in presence of the complex **2** (2 mol%) with NaOH and *i*-PrOH.

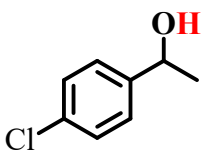
A)


7.37
7.36
7.35
7.35
7.34
7.33
7.31
7.25
7.25
7.24
7.23
7.22
7.22
4.82
4.80
4.80
4.79
4.78
4.78
4.77
3.23
3.22
2.57 H2O
2.20
1.95 CD3CN
1.94 CD3CN
1.94 CD3CN
1.93 CD3CN
1.93 CD3CN
1.38
1.37
1.29
1.27
0.00
4.04
0.98
1.00
0.95
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

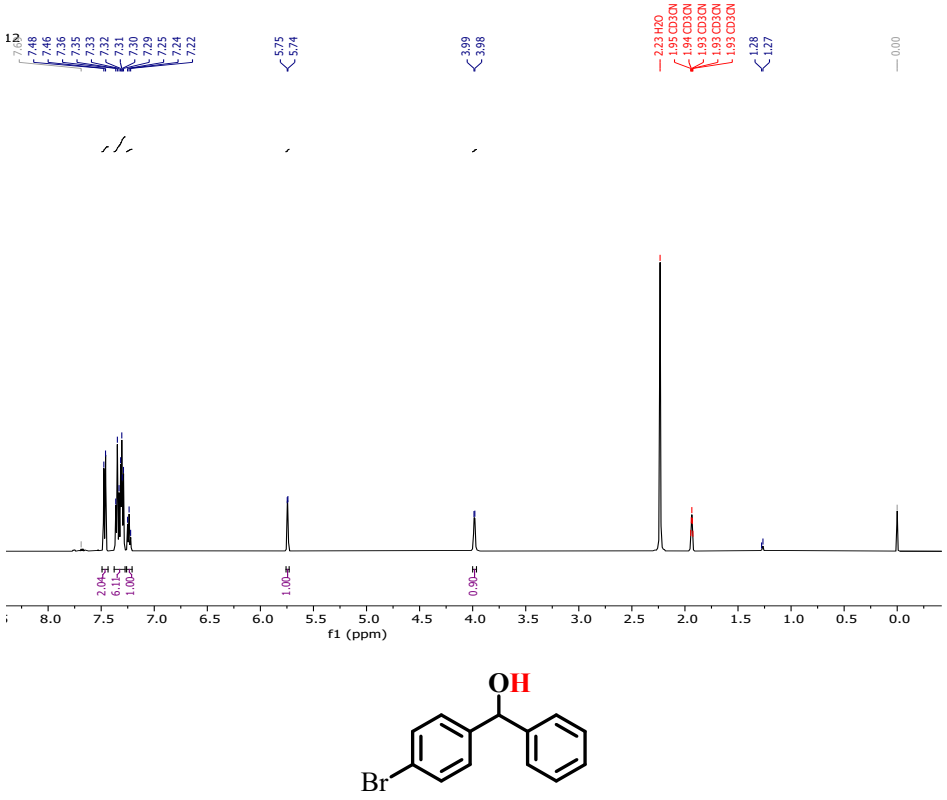

OH

B)


7.36
7.34
7.32
4.81
4.80
4.78
4.77
3.30
2.19
1.95 CD3CN
1.94 CD3CN
1.93 CD3CN
1.37
1.35
1.27
0.00
3.23
0.94
2.10
2.73
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
Cl

C)



D)

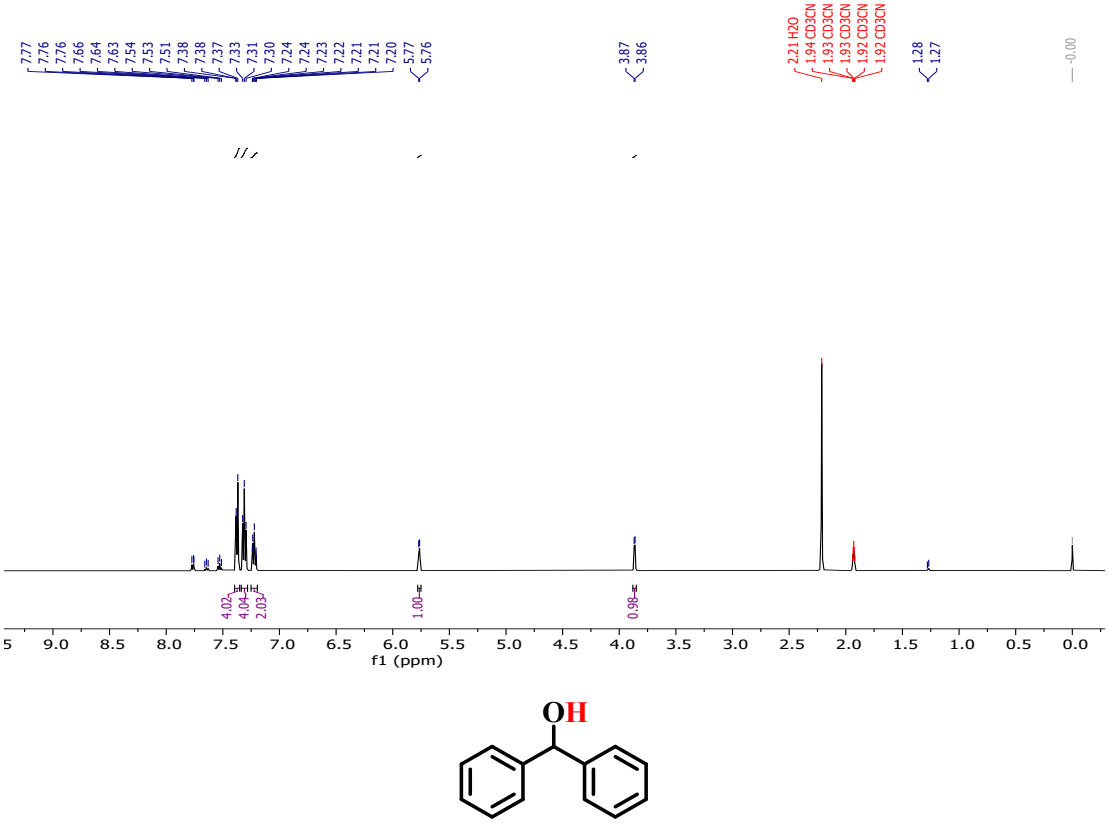
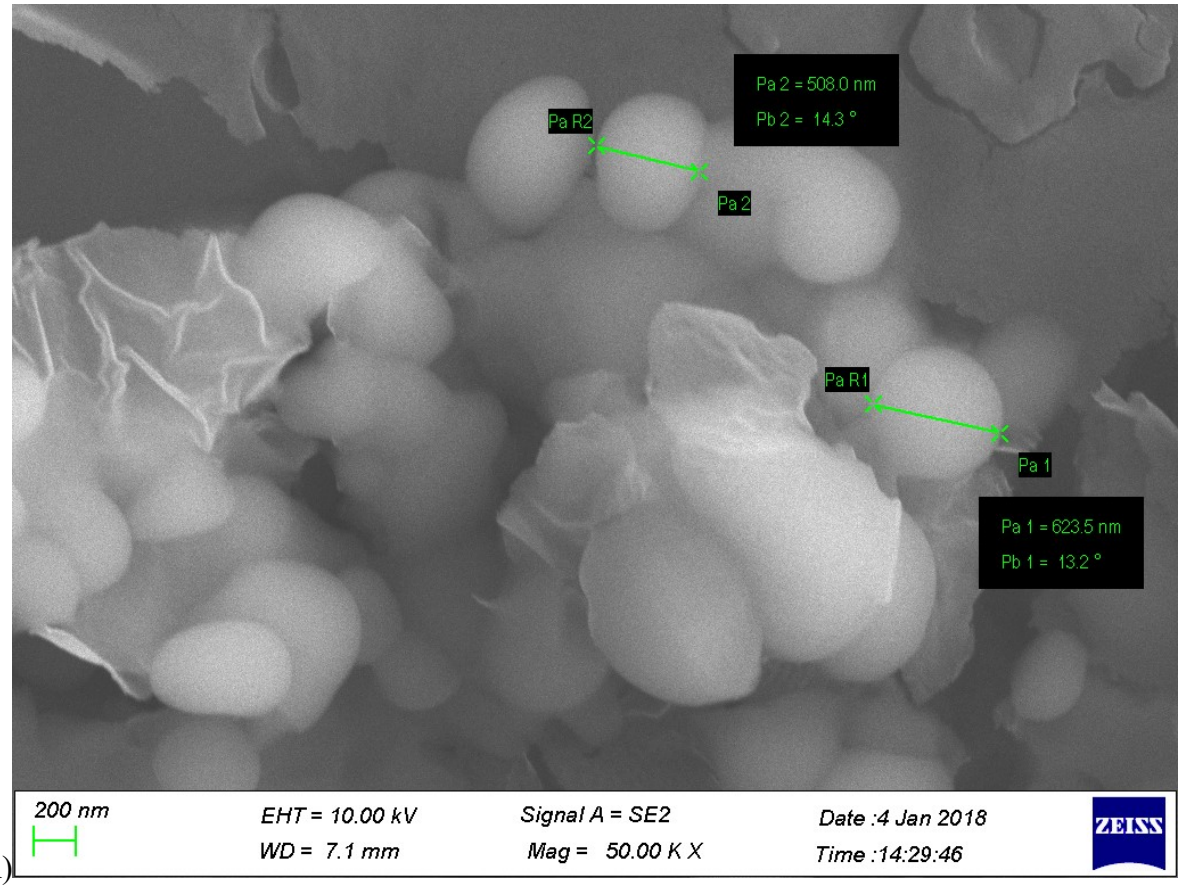
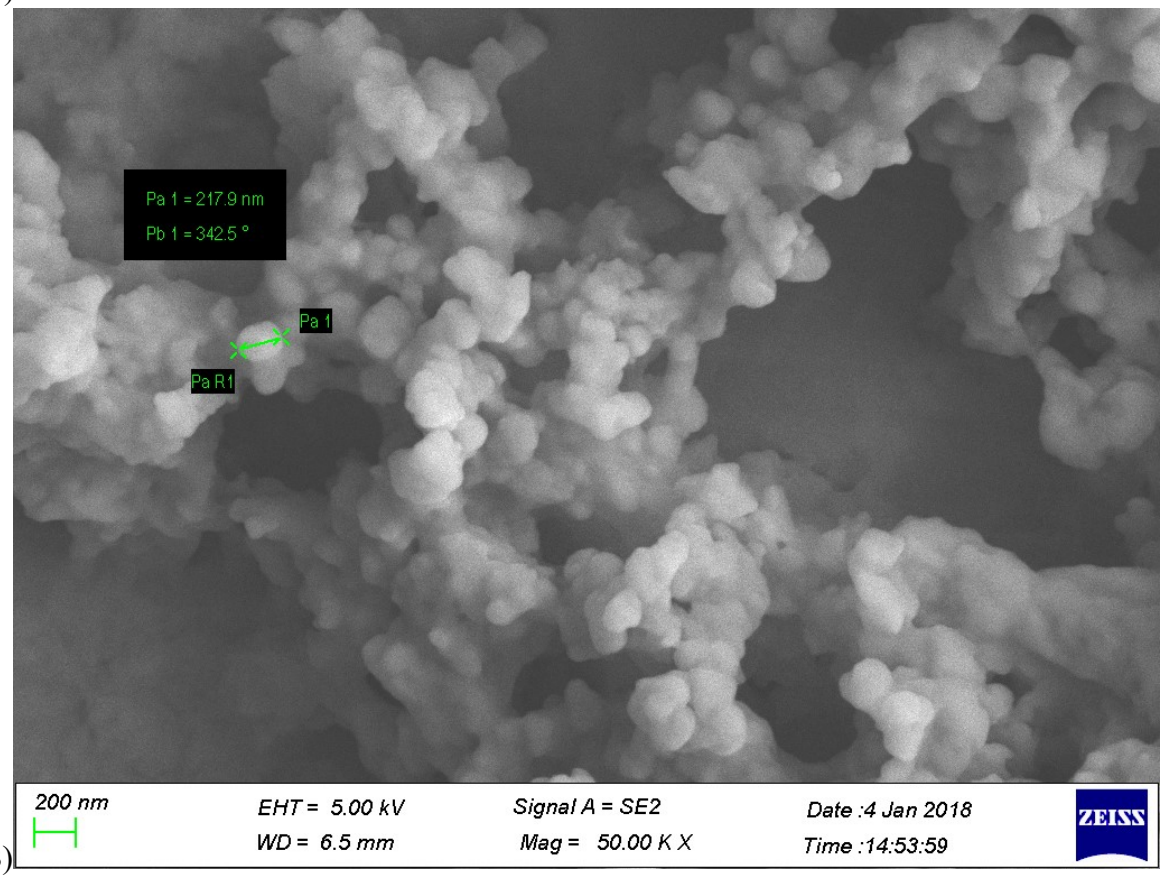


Figure S9. ^{1}H NMR spectra of few selected alcohols **A)** 1-phenylethanol **B)** 1-(4-chlorophenyl)ethanol **C)** (4-bromophenyl)(phenyl)methanol **D)** diphenylmethanol in CD_3CN.

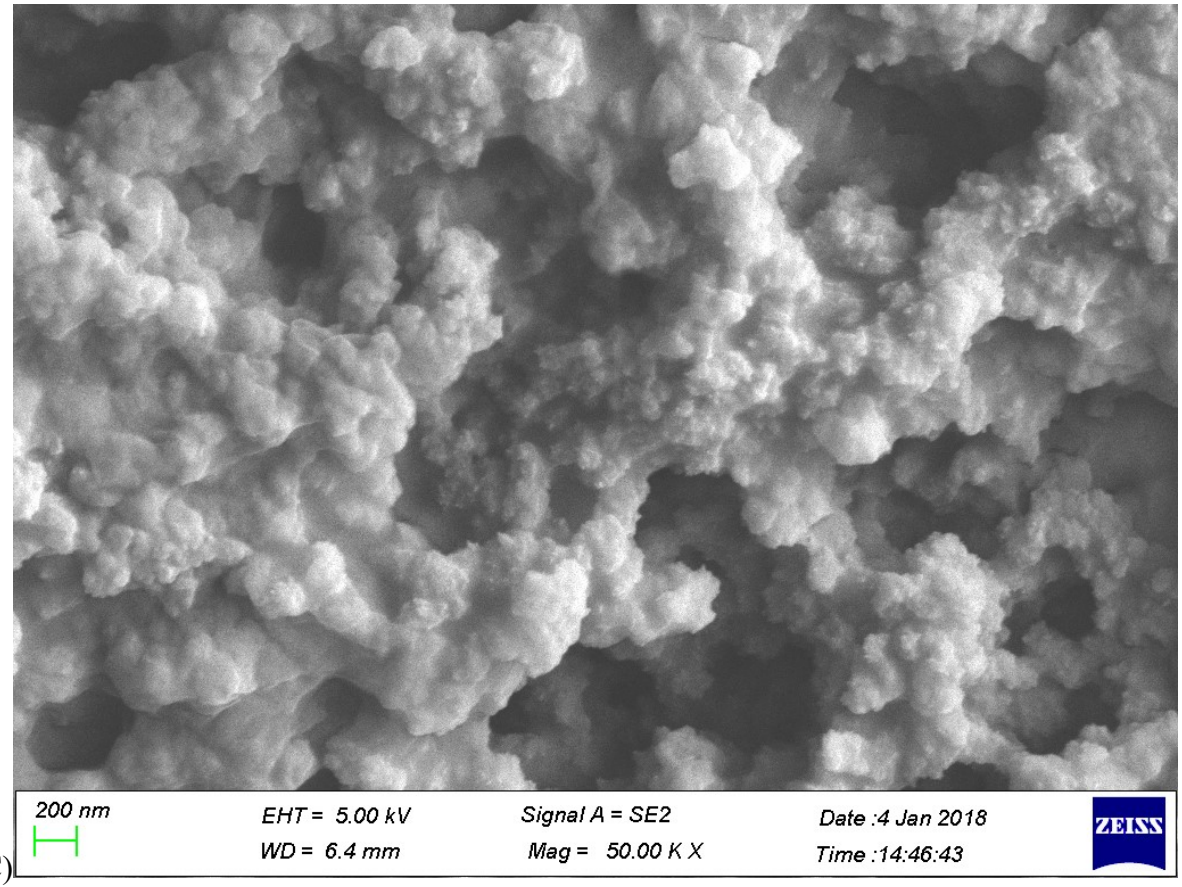
A)


Pa 2 = 508.0 nm
Pb 2 = 14.3 °
Pa R2
Pa 2
Pa R1
Pa 1
Pa 1 = 623.5 nm
Pb 1 = 13.2 °
200 nm
EHT = 10.00 kV
WD = 7.1 mm
Signal A = SE2
Mag = 50.00 K X
Date :4 Jan 2018
Time :14:29:46
ZEISS

B)


Pa 1 = 217.9 nm
Pb 1 = 342.5 °
Pa 1
Pa R1
200 nm
EHT = 5.00 kV
WD = 6.5 mm
Signal A = SE2
Mag = 50.00 K X
Date :4 Jan 2018
Time :14:53:59
ZEISS

C)



D)

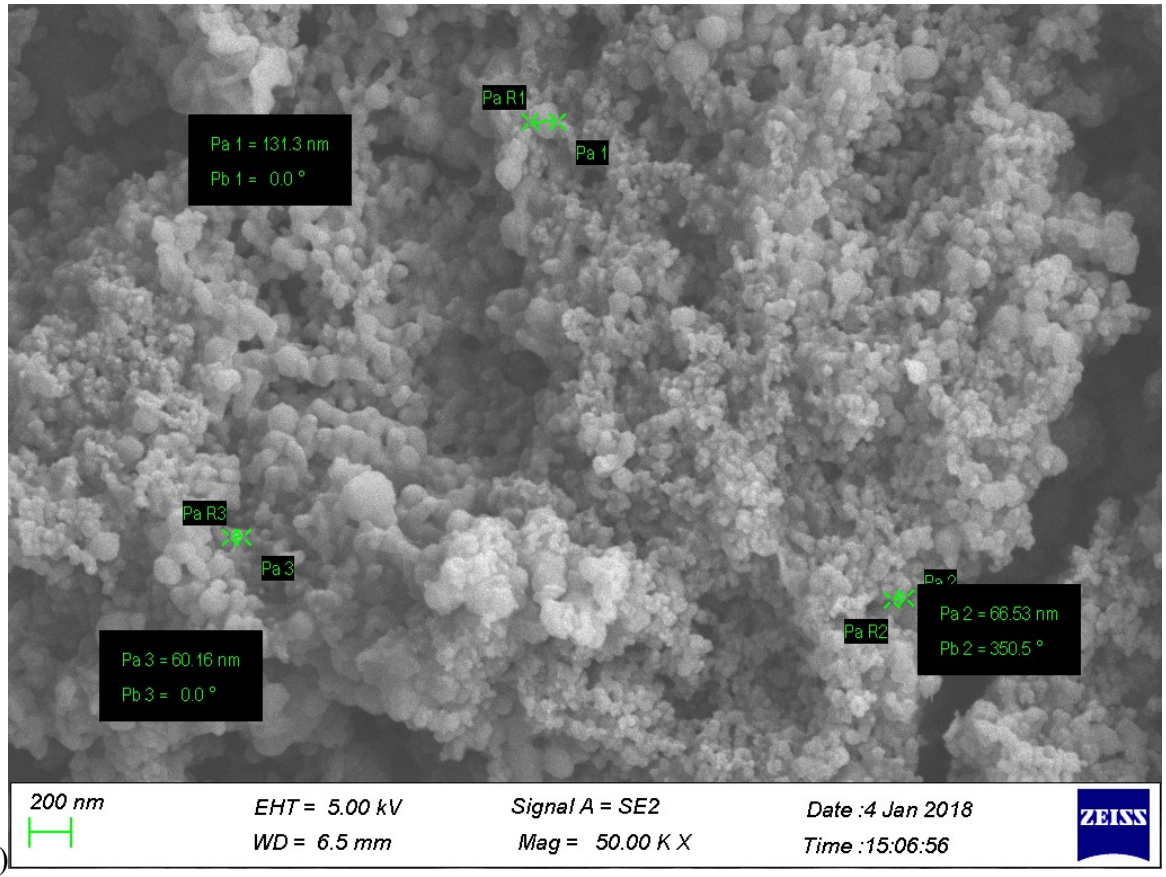


Figure S10. FESEM images of the A, B) complexes **1** and **2** in *i*-PrOH respectively. C, D) complex **1** and **2** + base in *i*-PrOH**.**

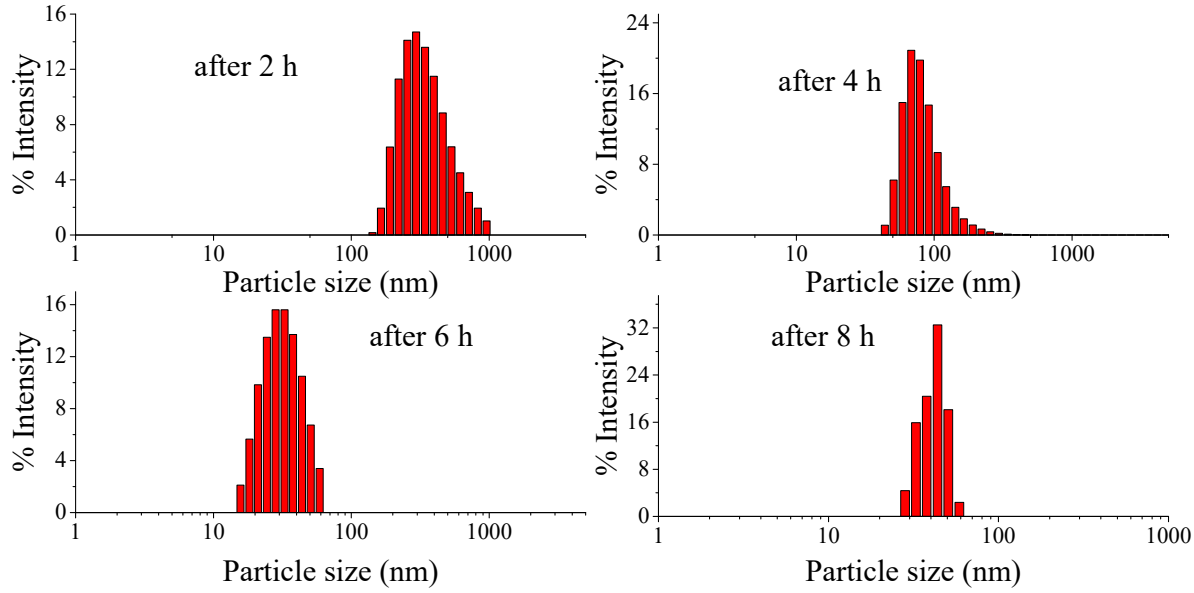


Figure S11. Time dependent DLS studies of catalytic mixture of complex **1** in *i*-PrOH after every 2 h interval.

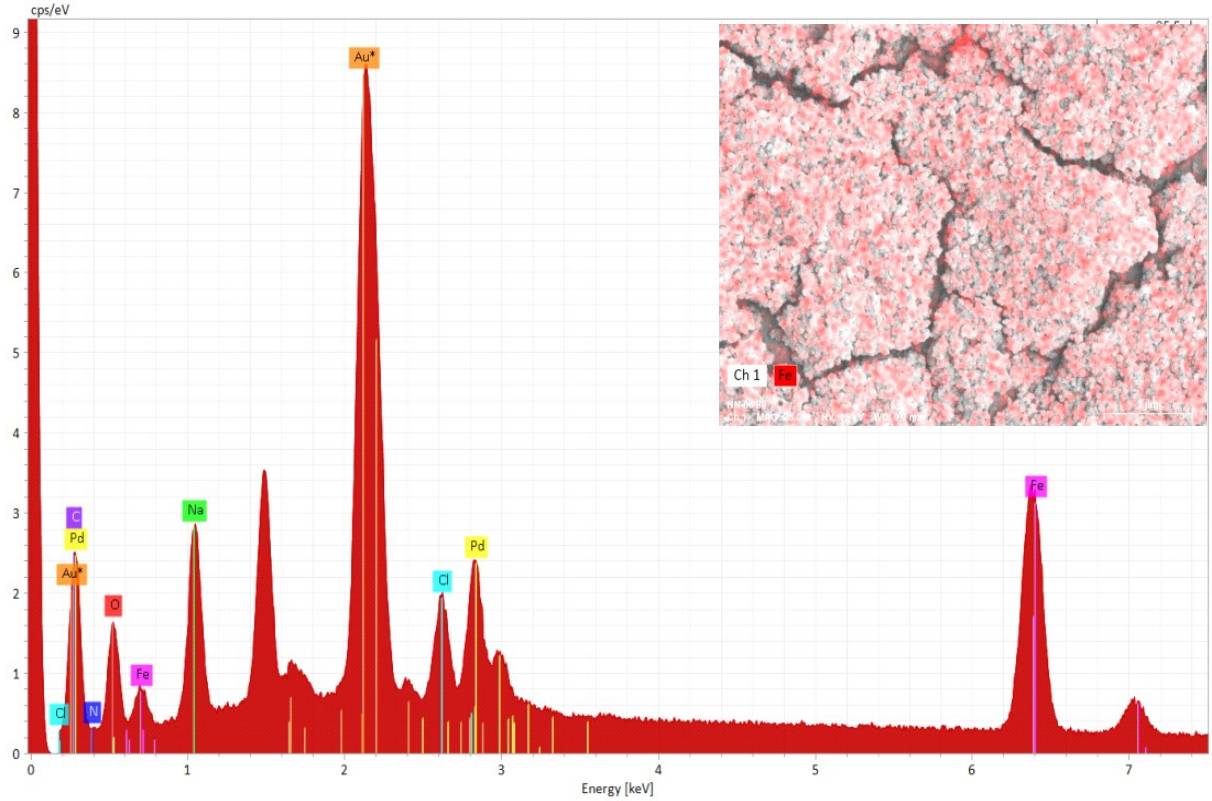


Figure S12. Energy dispersive X-ray (EDX) analysis showing the presence of iron and other elements (inset) in catalytic mixture, in presence of complex **2**. (Presence of gold and palladium is due to Au/Pd coating to sample using Quorum Q150T sputter unit)

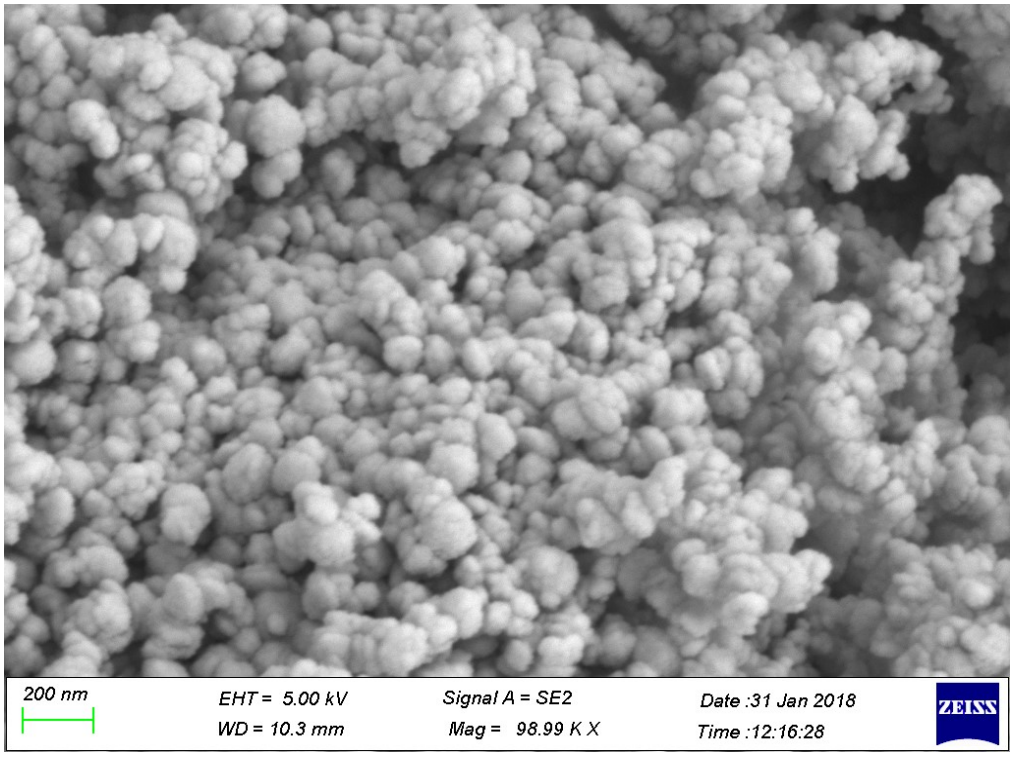


Figure S13. FESEM image of the iron oxide alone.

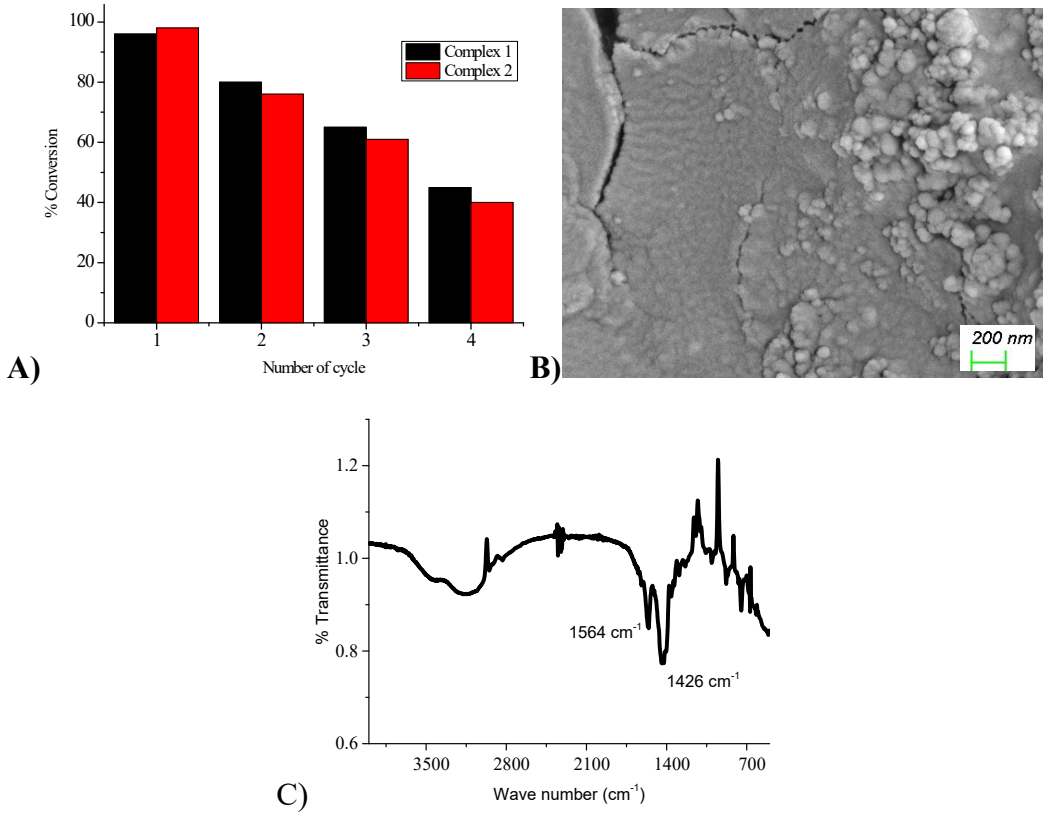


Figure S14. A) Recyclability of the catalysts **(1** and **2)** using acetophenone as a substrate. B, C) FESEM image and IR spectrum of catalytic mixture after 4th cycle, using complex **1**.

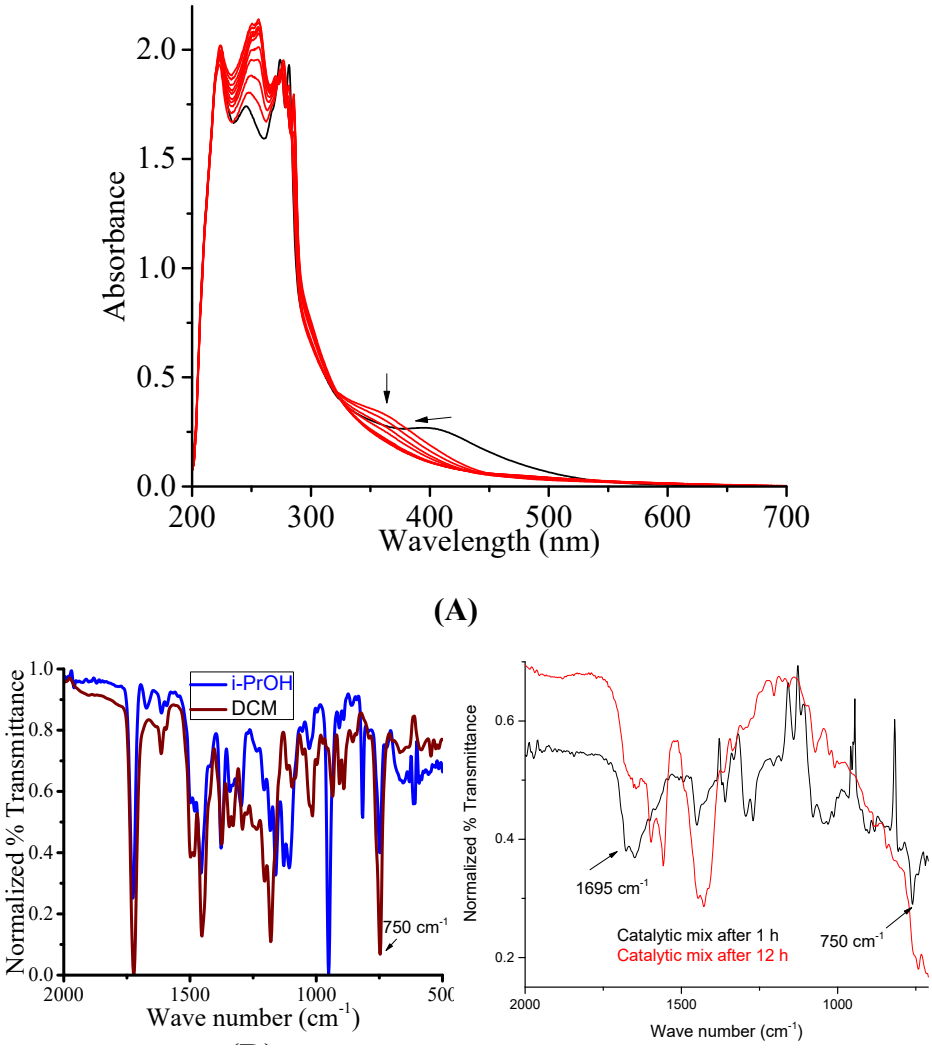


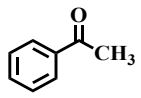
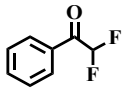
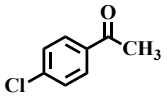
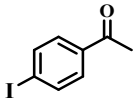
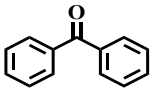
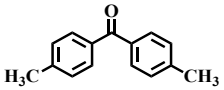
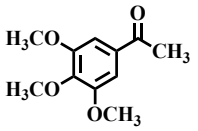
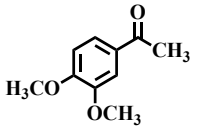
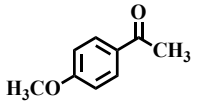
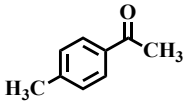
Figure S15. A) UV-Visible spectra of the complex **1** in *i*-PrOH (black, [$C_{\textbf{complex 1}}$ = 40 μM] in presence of base (red, [C_{base}]= 40 mM) B) ATR-IR spectra of complex **1** in DCM and *i*-PrOH, C) ATR-IR spectra of catalytic reaction mixture in presence of complex **1** at time t = 1 h and 12 h (benzophenone (0.1 mmol), base (0.2 mM) in 2-propanol (1 mL) and catalyst (2 mol%), respectively.

Table S1. X-ray crystal structure refinement data of the complex **1**.

Formula weight ($gmol^{-1}$)	1950.94	β (◦)	68.4270(10)
Crystal system	Triclinic	γ (◦)	66.3200(10)
Space group	$P\,\bar{1}$	V ($Å^3$)	2391.33(15)
λ (Å) (Mo-K_α)	0.71073	Z	1
Crystal size (mm)	0.25x0.15x0.10	θ range (deg)	1.4-26.5
a (Å)	13.4221(5)	F (000)	1025
b (Å)	13.5676(5)	R_1[a] [I >2σ(I)]	0.0469
c (Å)	15.5152(5)	wR_2[b] [I >2σ(I)]	0.1301
α (◦)	86.9640(10)	GOF	1.089

[a] $R_1=(\Sigma||F_o|-|F_c||)/(|F_o|)$, [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Complexes **1** and **2** catalyzed TH of various aromatic ketones using KOH.[a, b]

Si.No	Substrate	Complex **1** Conversion yield (%)[b] (TOF, h^{-1})	Complex **2** Conversion yield (%)[b] (TOF, h^{-1})
1		92 (3.83)	90 (3.75)
2		100 (4.16)	88 (3.67)
3		98 (4.08)	100 (4.16)
4		100 (4.16)	51 (2.13)
5		89 (3.71)	94 (3.92)
6		87 (3.63)	79 (3.29)
7		30 (1.25)	12 (50)
8		5 (0.21)	47 (1.95)
9		41 (1.70)	40 (1.66)
10		44 (1.83)	13 (0.54)
11		15 (0.63)	9 (0.38)

[a]Data represent the mean (SD ± 1%) of three independent experiments. Reaction conditions: acetophenone (0.1 mM), complexes **1** or **2** (2 mol%), base (KOH, 0.2 mM), solvent (*i*-PrOH, 1 mL), temperature (80-85 °C), time 12 h, argon atmosphere. [b]Conversions determined by GC-MS analysis. TOF = TON/time in h, and TON was calculated using moles of catalyst.