**Electronic Supplementary Information**

**for**

# Hydrocarbon Oxidation Catalyzed by a Cheap Nonheme Imine-based Iron(II) Complex

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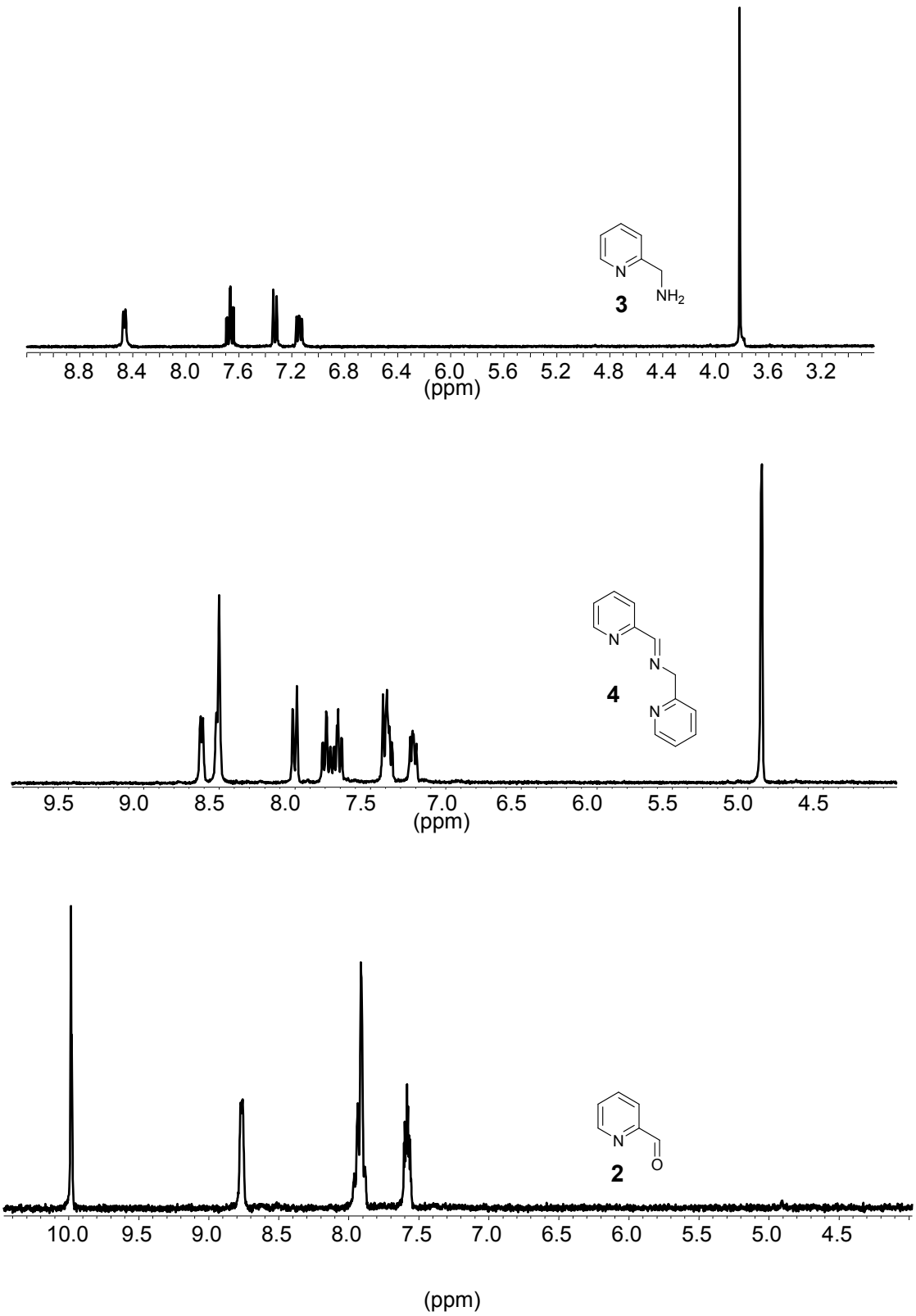



The $^{1}H$ NMR spectrum of **4** in $C_6D_6$ is identical to that previously reported in the literature.[S1]

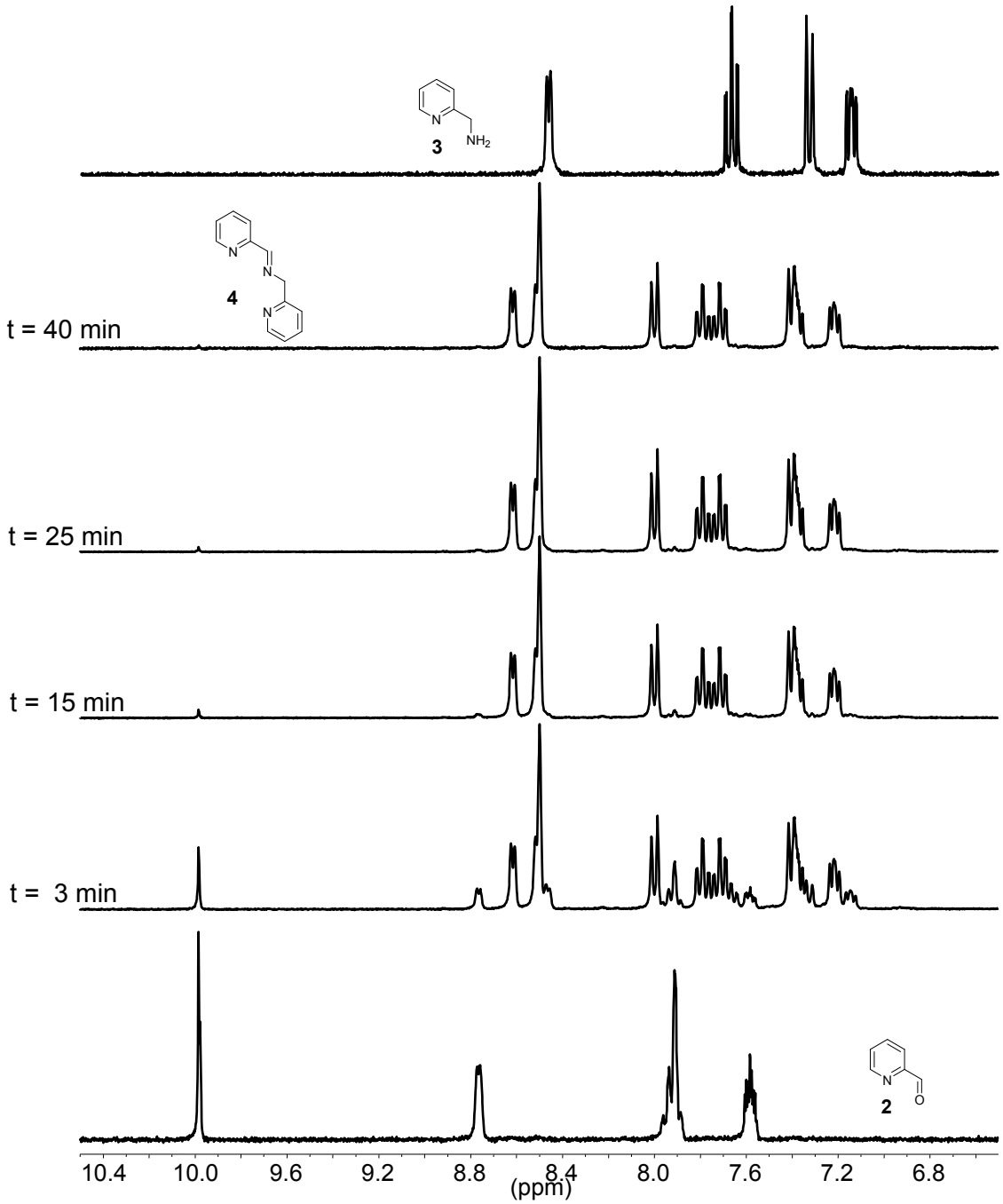



**Figure S1**. NMR spectra (aromatic region) of 33 mM **2** at increasing time after the addition of 33 mM **3** in $CD_3CN$ at 25 °C. Formation of **4** is complete within 40 min. The spectrum of **3** is reported on the top for the sake of comparison.

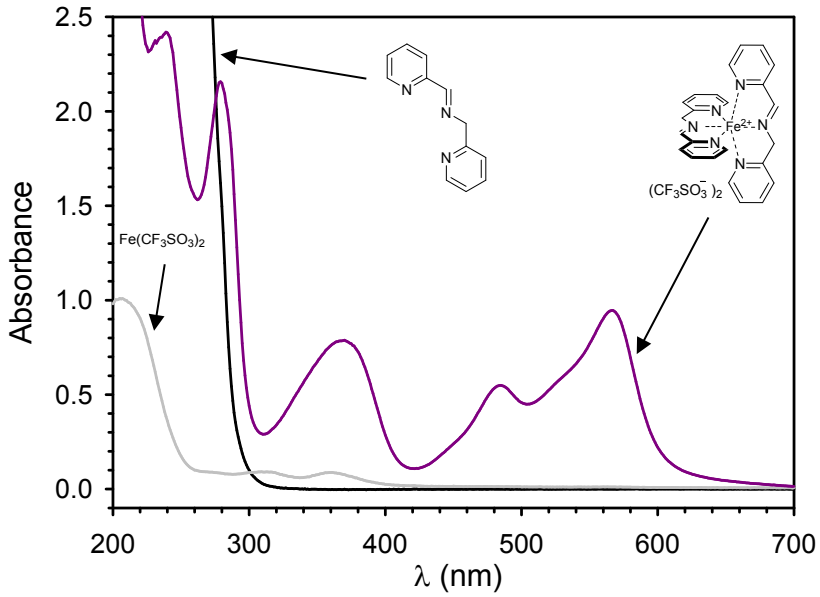



**Figure S2**. UV-Vis spectra of 0.5 mM **4** (black), 0.25 mM $Fe(CF_3CO_3)_2$ (gray) and 0.25 mM **1** (dark purple) in $CH_3CN$ at 25 °C.

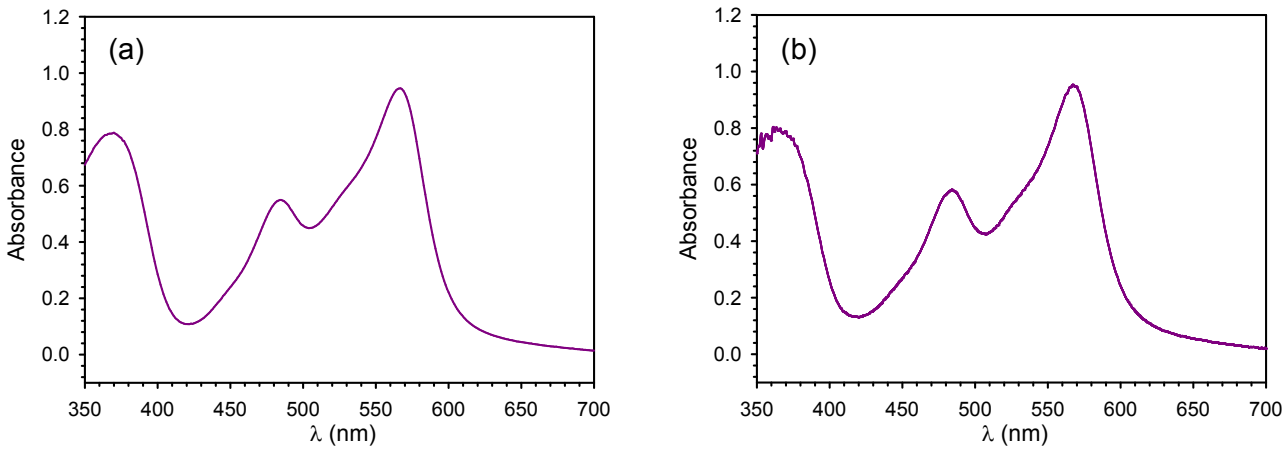



**Figure S3**. UV-Vis spectra of the solutions obtained by: (a) addition of 0.50 mM preformed **4** to 0.25 mM $Fe(CF_3CO_3)_2$, and (b) addition of 0.50 mM **2** and 0.50 mM **3** to 0.25 mM $Fe(CF_3CO_3)_2$ in $CH_3CN$ at 25 °C. In both cases spectra were scanned immediately after the addition of components in solution.

*Instruments and General Methods*

NMR spectra were recorded on either a 300 MHz spectrometer. The spectra were internally referenced to the residual proton solvent signal. UV-Vis spectra were registered by a double-ray spectrophotometer. GC analyses were carried out on a gas chromatograph equipped with a capillary methylsilicone column (30 m x 0.25 mm x 25 μm) Chrompack CP-Sil 5 CB. GC-MS analyses were performed with a mass detector (EI at 70eV) coupled with a gas chromatograph equipped with a melted silica capillary column (30 m x 0.2 mm x 25 μm) covered with a methylsilicone film (5% phenylsilicone, OV5).

*Materials*

All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise stated. (*d*)-Menthyl acetate was prepared following a literature procedure.[S2]

*Oxidation Procedure*

In all oxidation reactions performed at 1% catalyst loading complex **1** was prepared *in situ* treating 1.80 mg (5.08 μmol) of iron (II) triflate with 50 μL (10.2 μmol) of a 0.207 M acetonitrile solution of aldehyde **2** and 50 μL (10.2 μmol) of a 0.202 M acetonitrile solution of amine **3**. The solution immediately turned dark purple. At this point, to the reaction vessel were added:

i) 250 μL of acetonitrile, 14 μL of AcOH (254 μmol, 50 mol%) and 54 μL of cyclohexane (508 μmol, 100 mol%); or

ii) 200 μL of acetonitrile, 14 μL of AcOH (254 μmol, 50 mol%), and 110 μL of (*d*)-menthyl-acetate (508 μmol, 100 mol%).

After the addition of the above reagents, 310 μL of a 2.50 M solution of $H_2O_2$ in acetonitrile were added by a syringe pump over a period of 15 minutes, and the reaction mixture was left under stirring for a total time of 90 minutes. After addition of the internal standard and 1.0 mL of a saturated $NaHCO_3$ solution the mixture was extracted with $Et_2O$. The organic layer was dried over $Na_2SO_4$, filtered and analyzed by GC chromatography. In the case of (*d*)-menthyl acetate oxidation the yield was determined by $^1$H-NMR spectroscopy.

In oxidation reactions performed at 2.5% catalyst loading complex **1** was prepared *in situ* treating 4.50 mg (12.7 μmol) of iron (II) triflate with 125 μL (25.4 μmol) of a 0.207 M acetonitrile solution of aldehyde **2** and 125 μL (25.4 μmol) of a 0.202 M acetonitrile solution of amine **3**. The solution immediately turned dark purple. At this point to the reaction vessel were added:

i) 240 μL of acetonitrile, 14 μL of AcOH (254 μmol, 50 mol%), 63 μL of tetrahydronaphtalene (508 μmol, 100 mol%); or

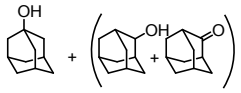
ii) 240 μL of acetonitrile, 14 μL of AcOH (254 μmol, 50 mol%), 68 μL of α-tetralone (508 μmol, 100 mol%).

Then 310 μL of a 2.50 M solution of $H_2O_2$ in acetonitrile were added by a syringe pump over a period of 15 minutes, and the mixture reaction was left under stirring for a total time of 90 minutes. After addition of the internal standard and 1.0 mL of a saturated $NaHCO_3$ solution the mixture was extracted with $Et_2O$; the organic layer was dried over $Na_2SO_4$, filtered and analyzed by GC chromatography.

In the case of adamantane oxidation, complex **1** was prepared *in situ* treating 0.53 mg of iron (II) trifluoromethanesulfonate (1.50 μmol) with 14 μL (3.0 μmol) of a 0.207 M acetonitrile solution of aldehyde **2** and 15 μL (3.0 μmol) of a 0.202 M acetonitrile solution of amine **3**. To the resulting solutions were added: 4.0 μL of AcOH (75 μmol, 50 mol%) and 5.0 mL of a 0.030 M acetonitrile solution of adamantane (150 μmol, 100 mol%). After the addition of the above reagents, 900 μL (180 μmol) of a 0.20 M solution of $H_2O_2$ in acetonitrile were added by a syringe pump over a period of 15 minutes, and the mixture reaction was stirred for 75 minutes. After addition of the internal standard and 1.0 mL of a saturated $NaHCO_3$ solution the mixture was extracted with $Et_2O$. The organic layer was dried over $Na_2SO_4$, filtered and analyzed by GC chromatography.

*Oxidation reactions in the absence of ligand **4**.*

**Table S1**. Oxidation of some hydrocarbons by $H_2O_2$ catalyzed by $Fe(CF_3SO_3)_2$ in $CH_3CN$ at 30 °C. Yields are average of two or three runs. TON are reported in brackets.

| Entry | Substrate | Products | Total yield |
|---|---|---|---|
| 1[a,b] |  |  3.5 ±0.5 2.5±0.5 | 6 (6) |
| 2[c,d] |  | no products detected | - |
| 3[b,e] |  |  5.5±0.5 11±1 | 16 (11) |
| 4[b,e] |  |  3±1 | 3 (2.4) |

[a] Conditions: $Fe(CF_3SO_3)_2$ (1.5 µmol, 1 mol%), adamantane (150 µmol), $H_2O_2$ (180 µmol, 120 mol%), AcOH (75 µmol, 50 mol%). [b] GC yields. [c] Conditions: $Fe(CF_3SO_3)_2$ (5.1 µmol, 1 mol%), (*d*)-menthyl acetate (508 µmol), AcOH (254 µmol, 50 mol%), $H_2O_2$ (610 µmol, 120 mol%). [d] $^1$H-NMR yield. [e] Conditions: $Fe(CF_3SO_3)_2$ (13 µmol, 2.5 mol%), substrate (508 µmol), $H_2O_2$ (1.16 mmol, 200 mol%), AcOH (254 µmol, 50 mol%).

**References**

S1 C. Incarvito, M. Lam, B. Rhatigan, A. L. Rheingold, C. J. Qin, A. L. Gavrilova, B. Bosnich, *J. Chem. Soc., Dalton Trans.*, 2001, 3478.

S2 S. Hata, M. Iguchi, T. Iwasawa, K. Tomioka, K.-I. Yamada, *Org. Letters* 2004, **6**, 1721.