Electronic Supplementary Information for

# Enhanced acyl radicals formation in the Au nanoparticlecatalysed aldehyde oxidation

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#### Chemicals

DMPO, PBN, TEMPO, and other chemicals were purchased from Aldrich and used without further purification.

### Preparation and characterization of Polymer-Incarcerated Gold Nanoparticles.

Polymer incarcerated gold nanoparticles<sup>1</sup> were prepared using a modified procedure reported for Pd<sup>2</sup> and Sc<sup>3</sup> catalysts. Styrene based copolymer (800.0 mg) and NaBH<sub>4</sub> (10.1 mg) were dissolved in diglyme (13 mL) at room temperature. To this solution was slowly added triphenylphosphine gold(I) chloride (31.1 mg) with 3 mL of diglyme. The solution turned wine red. The mixture was stirred for 3h at room temperature, and ethylether (30 mL) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethylether several times and dried at room temperature. Next, the catalyst capsules were heated at 150 °C for 5 h without solvent to prepare the wine red solid. The solid thus prepared was washed with dichloromethane and water, crushed, and dried to afford wine red powder. This powder was heated at 150 °C for 5 h without solvent to afford PI-Au. To determine Au composition, 20-30 mg of PI-Au were heated in a mixture of sulfuric acid and nitric acid at 200 °C for 3 h, the mixture was cooled to room temperature, and aqua regia was added. The amount of gold in the resulting solution was determined as  $0.083 \text{ mmol g}^{-1}$  by ICP analysis.

#### Synthesis of styrene based copolymer.

Synthesis of 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy



To sodium hydride (60% in mineral oil, 5.2 g) suspended in THF (150 mL), tetraethyleneglycol (25.4 g) was added at 0 °C. After the reaction mixture was stirred for 1 h at room temperature, 1-(chloromethyl)-4-vinylbenzene (13.3 g) was added and the mixture was further stirred for 12 h. The mixture was cooled to 0 °C and diluted

with diethyl ether. Saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed in vacuo. The residue was purified by flash chromatography to afford 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol ether (20.6 g, 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.55-2.59 (m, 1H), 3.59-3.73 (m, 16H), 4.55 (s, 2H), 5.25 (d, 1H, J = 6.4 Hz), 5.53 (d, 1H, J = 18 Hz), 6.71 (dd, 1H, J = 11.0, 17.9 Hz), 7.22-7.27 (m, 3H), 7.31-7.39 (m, 2H); <sup>13</sup>C NMR  $\delta$  61.8, 69.5, 70.5, 70.69, 70.74, 72.6, 73.0, 113.8, 126.3, 128.0, 136.0, 137.1, 138.0.

Preparation of styrene-based copolymer: Styrene (2.1 g), 4-vinylbenzyl glycidyl ether (4.0 g), 2-(2-(2-(2-(4-vinylbenzyloxy)eth



Scheme S1: x, y and z components of the styrene based copolymer. The x, y, z ratio was determined via <sup>1</sup>H-NMR spectroscopy as x: y: z = 29: 35: 36. (n=4).

## Spin trapping and EPR experiments

The samples were prepared by mixing the aldehyde (200  $\mu$ L) with a 0.1 M solution of DMPO, PBN or MNP in toluene (200  $\mu$ L) in a glass pipette closed with a septum and the sample was heated at 50 °C. For reactions in the presence of catalyst, 12 mg of PI-Au were added prior to mixing of the two solutions. Control tests confirmed that the catalyst cannot oxidize toluene and consequently this does not affect the spin trapping result.

Spin trapping measurements were carried out using a JEOL JES-RE1X ESR spectrometer. The instrumental parameters for the acquisition of the X-band EPR spectra were: frequency 9.13 GHz, power 5mW, sweep width 100G, centre field 3247 G, sweep time 60 s, time constant 30 ms, modulation frequency 100 kHz, modulation width 1 G.  $^4$ 

## Bulk Catalyst Activity Test and product characterization via <sup>1</sup>H-NMR.

In order to emulate the spin trapping reaction conditions, PI-Au (5 mg) was mixed with 1 mL of aldehydes at 50 °C for 5 h under vigorous stirring in a vial open to air. Tests were also carried out using 0.5 mL of aldehydes and 0.5 mL of toluene for the evaluation of TEMPO effect.

For the experiments carried out in the presence of TEMPO (0.5 mL solution in toluene at 100 ppm), the reaction was treated with phenyl hydrazine prior to recording of <sup>1</sup>H-NMR spectra in order to reduce unreacted paramagnetic TEMPO (which broadens NMR peaks).

The reaction mixture was dissolved in CD<sub>3</sub>OD, and the conversion of starting material was determined by <sup>1</sup>H-NMR using a Jeol ECX400 instrument operating at 400 MHz.



**Figure S1**: MNP in toluene containing di-tert-butyl aminoxyl (DTBA) radical  $(a_N=15.4 \text{ G})$ .<sup>5</sup> From top to bottom: (-) MNP in toluene in deoxygenated sample and (-) MNP in toluene in non deoxygenated sample.



**Figure S2**: spin adducts from the autoxidation of benzaldehyde in a sealed pipette at 50 °C. From top to bottom: (--) DMPO-COC<sub>6</sub>H<sub>5</sub> adduct<sup>6</sup> ( $a_N = 14.03$  G,  $a_H = 15.73$  G), (--) PBN-OOCR<sub>3</sub> adduct<sup>7</sup> ( $a_N = 13.4$ ,  $a_H = 1.72$  G) and (--) MNP-COC<sub>6</sub>H<sub>5</sub> adduct<sup>8</sup> ( $a_N = 8.1$  G). The latter includes di-tert-butyl aminoxyl radical (the most intense three lines on the spectra, with bigger coupling constants:  $a_N = 15.4$  G). In the case of PBN, it is impossible to distinguish between ·OOC and ·OOCO radicals, hence our general notation ·OOCR<sub>3</sub>



**Figure S3**: spin adducts from the autoxidation of benzaldehyde in a sealed pipette at 50 °C in presence of PBN spin trap. From bottom to top: (a) PBN-OOCR<sub>3</sub> adduct ( $a_N = 13.4$ , aH = 1.72 G); (b) PBN-OOCR<sub>3</sub> adduct after degassing the sample (a) with N<sub>2</sub>; (c) PBN-COR adduct ( $a_N = 14.3$ ,  $a_H = 4.57$  G)<sup>7</sup> from a benzaldehyde sample degassed with N<sub>2</sub>, prior to addition of spin trapping and sealing. In this case it is possible to observe the different affinity of PBN to different radicals under different conditions. This is further highlighted in figure S4.



**Figure S4**: spin adducts intensity evolution for the valeraldehyde autoxidation in toluene at 70  $^{\circ}$ C in presence of PBN. ( $\Box$ ) intensity (height) of the PBN-COR adduct and ( $\circ$ ) intensity (height) of the PBN-OOCR<sub>3</sub> adduct



**Figure S5**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h. Benzaldehyde:  $\delta$  7.30-7.53 (m, 3H), 7.44-7.77 (m, 2H), 9.84 (s, 1H); benzoic acid:  $\delta$  7.26-7.47 (m, 3H), 8.02-8.07 (m, 2H); toluene:  $\delta$  2.20 (s, 3H), 7.02-7.18 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.32 (q, 1H, J = 1.6 Hz); water  $\delta$  5.28



**Figure S6**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h in presence of PI-Au catalyst (5mg). Benzaldehyde:  $\delta$  7.34-7.67 (m, 3H), 7.86-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.26-7.60 (m, 3H), 7.98-8.02 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.06-7.22 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.29 (q, 1H, J = 1.6 Hz); water  $\delta$  4.91



**Figure S7**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of valeraldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h. Valeraldehyde:  $\delta$  0.87-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.60 (m, 2H), 2.36-2.43 (td, 2H, J = 7.4 Hz, J = 1.6Hz), 9.67 (t, 1H, J = 2 Hz); valeric acid:  $\delta$  0.87-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.60 (m, 2H), 2.23-2.28 (t, 2H, J = 7.6 Hz); toluene:  $\delta$  2.30 (s, 3H), 7.07-7.23 (m, 5H), methanol (CHD<sub>2</sub> peak)  $\delta$  3.28 (q, 1H, J = 1.6 Hz); water  $\delta$  4.93 hemiacetal:  $\delta$  4.46 (t, 1H, J = 5.6 Hz)



**Figure S8**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of valeraldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h in presence of PI-Au catalyst (5mg). Valeraldehyde: δ 0.86-0.95 (m, 3H), 1.27-1.38 (m, 4H), 1.49-1.63 (m, 2H), 2.34-2.42 (td, 2H, J = 7.4 Hz, J = 1.6Hz), 9.65 (t, 1H, J = 2 Hz); valeric acid: δ 0.86-0.95 (m, 3H), 1.27-1.38 (m, 4H), 1.49-1.63 (m, 2H), 2.22-2.28 (t, 2H, J = 7.6 Hz); toluene: δ 2.30 (s, 3H), 7.07-7.22 (m, 5H); methanol (CHD<sub>2</sub> peak) δ 3.31 (q, 1H, J = 1.6 Hz); water δ 5.06; hemiacetal: δ 4.47 (t, 1H, J = 5.6 Hz)



**Figure S9**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h, in presence of TEMPO (100 ppm in toluene solution, TEMPO was quenched with an equimolar amount of phenyl hydrazine after reaction). <sup>1</sup>H-NMR (CD<sub>3</sub>OD): Benzaldehyde:  $\delta$  7.40-7.64 (m, 3H), 7.83-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.35-7.58 (m, 3H), 8.09-8.12 (m, 2H); toluene:  $\delta$  2.31 (s, 3H), 7.12-7.27 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.39 (q, 1H, J = 1.6 Hz); water  $\delta$  4.92



**Figure S10**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h, in presence PI-Au catalyst (5mg) and TEMPO (100 ppm in toluene solution, TEMPO was quenched with an equimolar amount of phenyl hydrazine after reaction). <sup>1</sup>H-NMR (CD<sub>3</sub>OD): Benzaldehyde:  $\delta$ 7.48-7.65 (m, 3H), 7.82-7.88 (m, 2H), 9.95 (s, 1H); benzoic acid:  $\delta$  7.43-7.54 (m, 3H), 8.03-8.08 (m, 2H); toluene:  $\delta$  2.31 (s, 3H), 7.09-7.24 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.34 (q, 1H, J = 1.6 Hz); water  $\delta$  4.90



**Figure S11**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of valeraldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h, in presence of TEMPO (100 ppm in toluene solution). Valeraldehyde: δ 0.86-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.62 (m, 2H), 2.36-2.41 (td, 2H, J = 7.4 Hz, J = 1.6Hz ), 9.66 (t, 1H, J = 2 Hz); valeric acid: δ 0.86-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.62 (m, 2H), 2.22-2.27 (t, 2H, J = 7.6 Hz); toluene: δ 2.30 (s, 3H), 7.06-7.22 (m, 5H); methanol (CHD<sub>2</sub> peak) δ 3.30 (q, 1H, J = 1.6 Hz); water δ 4.86; hemiacetal: δ 4.46 (t, 1H, J = 5.6).



**Figure S12**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of valeraldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h, in presence of TEMPO (100 ppm in toluene solution) and PI-Au catalyst (5 mg). Valeraldehyde: δ 0.87-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.64 (m, 2H), 2.34-2.38 (td, 2H, J = 7.4 Hz, J = 1.6Hz), 9.65 (t, 1H, J = 2 Hz); valeric acid: δ 0.87-0.94 (m, 3H), 1.27-1.39 (m, 4H), 1.48-1.64 (m, 2H), 2.22-2.27 (t, 2H, J = 7.6 Hz); toluene: δ 2.30 (s, 3H), 7.06-7.22 (m, 5H); methanol (CHD<sub>2</sub> peak) δ 3.31 (q, 1H, J = 1.6 Hz); water δ 4.86; hemiacetal: δ 4.47 (t, 1H, J = 5.6 Hz)



**Figure S13**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h, in presence of PI-Au catalyst (5mg). No toluene oxidation is observed. Toluene:  $\delta$  2.32 (s, 3H), 7.12-7.28 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.38 (q, 1H, J = 1.6 Hz) traces ; water  $\delta$  4.97 traces



**Figure S14**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h in presence of a PI-Au catalyst (5mg) pretreated with TEMPO (100 ppm in 0.5 mL of toluene at 50 °C for 5h, the catalyst was washed several time with toluene, then dried at room temperature and re-used). Benzaldehyde:  $\delta$  7.35-7.67 (m, 3H), 7.84-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$ 7.26-7.58 (m, 3H), 7.97-8.02 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.06-7.21 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.29 (q, 1H, J = 1.6 Hz); water  $\delta$  4.92;

#### Oxygen consumption trends from EPR spectra.

EPR spectroscopy can be used to monitor oxygen consumption by measuring the peak intensity or width of TEMPO lines.<sup>9,10</sup> Reduction in oxygen concentration leads to progressive sharpening of the EPR lines due to the shortening of the electron relaxation times  $T_1$  and  $T_2$  of the nitroxide. Consequently, the square root of the peak intensity is inversely proportional to the oxygen concentration in the reaction mixture.<sup>11,12</sup>

In our case, the reactions were carried out using a suspension of 2 mg of PI-Au in 200  $\mu$ L of benzaldehyde, and 200  $\mu$ L of a 20 ppm TEMPO solution in toluene. The resulting suspension was sealed in a pipette and heated at 50 °C. EPR spectra were recorded every 78 s using a Jeol JES-RE1X spectrometer. The same procedure was applied to determine the oxygen consumption in absence of catalyst.



**Figure S15**: Inverse square root of the TEMPO intensity, versus time for benzaldehyde: ( $\bullet$ ) in the presence and ( $\bullet$ ) in the absence of catalyst PI-Au (2 mg) at 50 °C in a sealed pipette. From the slopes of the straight lines it is possible to estimate the oxygen consumption, which is *ca.* 2 times faster in the presence of catalyst.



**Figure S16**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of neat benzaldehyde (0.5 mL) after heating, under stirring in air, at 50 °C for 5 h in presence of ZnO (50mg). Benzaldehyde:  $\delta$  7.41-7.62 (m, 3H), 7.78-7.86 (m, 2H), 9.93 (s, 1H); benzoic acid:  $\delta$  7.24-7.53 (m, 3H), 8.13-8.16 (m, 2H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.33 (q, 1H, J = 1.9 Hz); water  $\delta$  4.85



**Figure S17**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of neat benzaldehyde (0.5 mL) after heating, under stirring in air, at 50 °C for 5 h. An higher autoxidation if compared with figure S13, thus proving the quenching effect of ZnO. <sup>1</sup>H-NMR (CD<sub>3</sub>OD): Benzaldehyde:  $\delta$  7.39-7.64 (m, 3H), 7.83-7.89 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.28-7.57 (m, 3H), 8.03-8.08 (m, 2H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.37 (q, 1H, J = 1.9 Hz); water  $\delta$  5.0



4.0 3.5 2.5 2.0 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 3.0

**Figure S18**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 5 h in presence of a PI-Au catalyst (5mg) in polyethylene bottles. A marked increasing in activity is observed, thus proving the effect of termination to the walls by glass surfaces. <sup>1</sup>H-NMR (CD<sub>3</sub>OD): benzaldehyde:  $\delta$  7.30-7.66 (m, 3H), 7.85-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$ 7.27-7.58 (m, 3H), 7.99-8.04 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.07-7.23 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.31 (q, 1H, J = 1.6 Hz); water  $\delta$  5.01;



**Figure S19**: EPR spectra of benzaldehyde (200  $\mu$ L) with base (NaOH, 5 mg) and DMPO (0.1 M solution in toluene, 200  $\mu$ L), in the presence (–) of PI-Au catalyst (5mg) spectrum on top), and absence (–) of catalyst. The mixture was in a sealed pipette heated at 50 °C. In the presence of catalyst a weak DMPO-H adduct<sup>10</sup> is detected, in the absence of catalyst no adduct is detected.



**Figure S20**: EPR spectra of valeraldehyde (200  $\mu$ L) with base (NaOH, 5 mg) and DMPO (0.1 M solution in toluene, 200  $\mu$ L), in the presence (–) of PI-Au catalyst (5mg) and absence (–) of catalyst. The mixture was in a sealed pipette heated at 50 °C. In the presence of catalyst (–) a DMPO-H adduct<sup>11</sup> is detected, in the absence of catalyst (–) a DMPO-CH<sub>2</sub>R adduct<sup>6</sup> is detected.



**Figure S21**: EPR spectra of perdeuteriated acetaldehyde (CD<sub>3</sub>COD, 200  $\mu$ L) with base (NaOH, 5 mg) and DMPO (0.1 M solution in toluene, 200  $\mu$ L), in the presence (–) of PI-Au catalyst (5mg), and absence (–) of catalyst. The mixture was in a sealed pipette heated at 50 °C. In the presence of catalyst (–) a DMPO-D adduct<sup>12</sup> is detected, in the absence of catalyst (–) a DMPO-CH<sub>2</sub>R adduct<sup>6</sup> is detected.

Entry <sup>(a)</sup>	Catalyst (b)	Reaction medium <sup>(c)</sup>	Conversion (%)	Benzoic acid selectivity (%)	Benzyl alcohol selectivity (%)
1	-	Toluene	21.1	89.2	10.8
2	PI-Au	Toluene	29.2	92.2	7.8
3	-	Toluene/TEMPO	6.2	72.2	27.8
4	PI-Au	Toluene/TEMPO	6.8	74.3	25.7

**Table S1:** conversion of benzaldehyde under different experimental conditions in the presence of base (NaOH, ground powder, 5mg). (a) Reaction conditions: substrate (0.5 ml), solvent (0.5 mL), T = 50 °C, P = 1 atm, reaction time 24 h. (b) catalyst (5mg); (c) TEMPO (100 ppm) in toluene; (d) Determined by <sup>1</sup>H-NMR.



11.0 10.5 10.0 9.5 9.0 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

**Figure S22**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 24 h in presence of base (NaOH, ground powder, 5mg). Benzaldehyde:  $\delta$  7.27-7.67 (m, 3H), 7.85-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.26-7.56 (m, 3H), 7.96-7.99 (m, 2H); toluene:  $\delta$  2.28 (s, 3H), 7.05-7.21 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.38 (q, 1H, J = 1.6 Hz); Water  $\delta$  4.88, benzyl alcohol:  $\delta$  4.57 (s, 2H), 7.20-7.35 (m, 5H)



11.0 10.5 10.0 9.5 9.0 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

**Figure S23**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 24 h in presence of a PI-Au catalyst (5mg) and base (NaOH, ground powder, 5mg). Benzaldehyde:  $\delta$  7.26-7.67 (m, 3H), 7.85-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.26-7.57 (m, 3H), 7.95-7.98 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.06-7.20 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.28 (q, 1H, J = 1.6 Hz); water  $\delta$  4.88; benzyl alcohol:  $\delta$  4.55 (s, 2H), 7.20-7.35 (m, 5H)



11.0 10.5 10.0 9.5 9.0 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

**Figure S24**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 24 h in presence of base (NaOH, ground powder, 5mg) and TEMPO (100 ppm solution in toluene). Benzaldehyde:  $\delta$  7.26-7.67 (m, 3H), 7.85-7.89 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$  7.27-7.56 (m, 3H), 7.93-7.96 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.06-7.21 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.29 (q, 1H, J = 1.6 Hz); water  $\delta$  4.88; benzyl alcohol:  $\delta$  4.57 (s, 2H), 7.20-7.35 (m, 5H)



# 11.0 10.5 10.0 9.5 9.0 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

**Figure S25**: <sup>1</sup>H-NMR (CD<sub>3</sub>OD) of benzaldehyde (0.5 mL) in toluene (0.5mL) after heating, under stirring in air, at 50 °C for 24 h in presence of catalyst PI-Au (5mg), base (NaOH, ground powder, 5mg) and TEMPO (100 ppm solution in toluene). Benzaldehyde:  $\delta$  7.27-7.67 (m, 3H), 7.86-7.90 (m, 2H), 9.96 (s, 1H); benzoic acid:  $\delta$ 7.25-7.56 (m, 3H), 7.93-7.96 (m, 2H); toluene:  $\delta$  2.29 (s, 3H), 7.05-7.21 (m, 5H); methanol (CHD<sub>2</sub> peak)  $\delta$  3.29 (q, 1H, J = 1.6 Hz), water  $\delta$  4.88; benzyl alcohol:  $\delta$  4.57 (s, 2H), 7.20-7.35 (m, 5H)

### References

- 1 (a) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, Angew. Chem., Int. Ed., 2007, 46, 4151.
- (a) K. Okamoto, R. Akiyama and S. Kobayashi, J. Org. Chem., 2004, 69, 2871; (b) K. Okamoto, R. Akiyama and S. Kobayashi, Org. Lett., 2004, 6, 1987. (c) H. Miyamura, R. Akiyama, T. Ishida, R. Matsubara, M. Takeuchi and S. Kobayashi, Tetrahedron 2005, 61, 12177. (d) H. Hagio, M. Sugiura and S. Kobayashi, Synlett 2005, 813. (e) R. Nishio, M. Sugiura and S. Kobayashi, Org. Lett., 2005, 7, 4831.
- M. Takeuchi, R. Akiyama and S. Kobayashi, J. Am. Chem. Soc., 2005, 127, 13096.
- 4 Simulation was carried out using WinSim software: <u>http://epr.niehs</u>. nih.gov/pest.html.
- 5 L.-B. Luo, D.-Y. Han, Y. Wu, X.-Y. Song and H.-L. Chen, *J. Chem. Soc.*, *Perkin Trans.* 2, 1998, 1709.
- 6 E. G. Janzen and J.-P. Liu, J. Magn. Reson., 1973, 9, 510.
- 7 E. G. Janzen, E. R. Davis and C. M. DuBoset, *Magn. Res. Chem.*, 1995,
  33, S166.
- 8 M. Novak and B. A. Brodeur, J. Org. Chem., 1984, 49, 1142.
- 9 (a) M. Conte, Y. Ma, C. Loyns, P. Price, D. Rippon, and V. Chechik, Org. Biomol. Chem., 2009, 7, 2685; (b) A. I. Smirnov, R. B. Clarkson and R. L. Belford, J. Magn. Reson. B, 1996, 111, 149; (c) G. F. Pedulli, M. Lucarini, P. Pedrielli, M. Sagrini and M. Cipollone, Res. Chem. Intermed., 1996, 22, 1.
- 10 T. I. Smirnova, A. I. Smirnov, R. B. Clarkson, R. L. Belford, *Magn. Reson.*, 1995, **33**, 801.
- P. Maillard, J. C. Massot and C. J. Giannotti, *Organomet. Chem.*, 1978, 159, 219.
- 12 P. Maillard and C. Giannotti, *Can. J. Chem.*, 1982, **60**, 1402.