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# Clean Ar–Me conversion to Ar–aldehyde with the aid of carefully designed metallocorrole photocatalysts

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#### **Experimental Procedures**

Materials: Experimental reagents (Aldrich) and solvents were used without further purification.

Spectroscopy: The electronic spectra were obtained via use of an Agilent Cary 8454 UV-VIS spectrometer.

#### Electrochemistry

Cyclic voltammetry measurements were carried out in acetonitrile (HPLC grade) containing 0.5 mM of those phosphorus (V) complexes and 0.1 M TBAP (Fluka, for electrochemical analysis) as the electrolyte under an argon atmosphere. A conventional three electrode system consisting of a glassy carbon working electrode, a platinum wire as counter electrode and silver wire separated from the bulk solution by a sample holder with a porous glass frit in 0.1 M TBAP / 0.01 M AgNO<sub>3</sub> solution. Electrochemical measurements were recorded with an EmStat<sup>3+</sup> electrochemical system with a scan rate of 100 mVs<sup>-1</sup>. All potentials are referenced vs the Fc<sup>+</sup>/0 redox potential added as an internal standard ( $E_{1/2} = 0.092$  V vs. Ag/Ag<sup>+</sup> in 0.1 M TBAP / 0.01 M AgNO<sub>3</sub> solution).

## **Photocatalysis**

#### Toluene + TFA $\rightarrow$ benzaldehyde

An acetonitrile solution (5 mL, with catalyst concentration of 15  $\mu$ M) was charged with toluene (54  $\mu$ L, 0.1 M) and TFA (78  $\mu$ L, 0.2 M) and placed in a 5 mL vial made of Pyrex. The stirred solution was irradiated by an LED lamp with (200 mW,  $\lambda_{max} = 400$  nm, placed 15 cm from the vial) for 20 h, at 36 °C (the internal temperature in the reaction solution). Prior to injection to the GC for product determination, the mixture was treated with solid K<sub>2</sub>CO<sub>3</sub> as to neutralize the acid and to dry the solution and nitrobenzene (5  $\mu$ L, 49  $\mu$ mol) was added as external reference. Identification of reaction products that were either purchased or independently prepared. The GC retention times for acetonitrile, toluene, nitrobenzene and benzaldehyde were determined at *ca*. 1.3 min, 1.8 min, 6.5 min and 3.5 min.

# $P\text{-xylene} + TFA \rightarrow p\text{-tolualdehyde}$

An acetonitrile solution (5 mL, with catalyst concentration of 15  $\mu$ M) was charged with p-xylene (62  $\mu$ L, 0.1 M) and TFA (78  $\mu$ L, 0.2 M) and placed in a 5 mL vial made of Pyrex. The stirred solution was irradiated by an LED lamp with (200 mW,  $\lambda_{max}$  = 400 nm, placed 15 cm from the vial) for 20 h, at 36 °C (the internal temperature in the reaction solution). Prior to injection to the GC for product determination, the mixture was treated with solid K<sub>2</sub>CO<sub>3</sub> as to neutralize the acid and to dry the solution and nitrobenzene (5  $\mu$ L, 49  $\mu$ mol) was added as external reference. Identification of reaction products that were either purchased or independently prepared. The retention times checked by the GC for acetonitrile, p-xylene, nitrobenzene and p-tolualdehyde were determined around 1.3 min, 2.4 min, 6.5 min and 6.3 min.

## Mesitylene + TFA $\rightarrow$ 3,5-dimethylbenzaldehyde

An acetonitrile solution (5 mL, with catalyst concentration of 15  $\mu$ M) was charged with mesitylene (68  $\mu$ L, 0.1 M) and TFA (78  $\mu$ L, 0.2 M) and placed in a 5 mL vial made of Pyrex. The stirred solution was irradiated by a LED lamp with (200 mW,  $\lambda_{max}$  = 400 nm, placed 15 cm from the vial) for 20 h, at 36 °C (the internal temperature in the reaction solution). Prior to injection to the GC for product determination, the mixture was treated with solid K<sub>2</sub>CO<sub>3</sub> as to neutralize the acid and to dry the solution and nitrobenzene (5  $\mu$ L, 49  $\mu$ mol) was added as external reference. Identification of reaction products that were either purchased or independently prepared. The retention times checked by GC for acetonitrile, mestiylene, nitrobenzene and 3,5-dimethylbenzaldehyde were determined around 1.3 min, 3.6 min, 6.5 min and 8.3 min.



**Fig S1.** The GC trace example of one reaction mixture in toluene assay (the peak around 1.5 min is assigned to solvent previous injections).



Fig S2. The GC trace example of one reaction mixture for the p-xylene assay.



Fig S3. The GC trace example of one reaction mixture in mesitylene assay (the peaks around 4 min and 6 min were assigned to residues from previous injections).



Fig S4. The <sup>1</sup>H-NMR of one reaction mixture using 4-P as a catalyst in the toluene assay.



**Fig S5.** The <sup>1</sup>H-NMR of one reaction mixture using **4-P** as catalyst in a p-xylene assay.



Fig S6. The <sup>1</sup>H-NMR of one reaction mixture using 4-P as catalyst in a mesitylene assay.



**Fig S7.** The UV-vis spectra of **3-Ga**, **3-Al**, **3-P**, **3-Co** and **3-Au** in MeCN with the concentration of  $5 \times 10^{-6}$  M (*left*); The UV-vis spectra of **4-Ga**, **4-Al**, **4-P** and **4-Au** in MeCN with the concentration of  $5 \times 10^{-6}$  M (*right*).



**Fig S8.** CV traces of **3-Ga**, **3-Al**, **3-P** and **3-Au** in MeCN in the oxidation region (*left*); CV traces of **4-Ga**, **4-Al**, **4-P** and **4-Au** in MeCN in the oxidation region (*right*). glassy carbon working electrode, a platinum wire as counter electrode, Ag/AgNO<sub>3</sub> as reference electrode, in acetonitrile with TBAP, scan rate of 100 mV/s was applied.



Fig S9. UV-vis spectra of reaction mixture of  $4CF_3$ -P with toluene and TFA before and after 24 hours of irradiation (LED,  $\lambda_{max} = 400$  nm).

Entry <sup>[a]</sup>	Photocatalyst	$E_{OX},$ (V) <sup>[b]</sup>	1 <sup>st</sup>	A <sub>400</sub> [c]	Substrate	Yield (%) [d]	TON <sup>[e]</sup>
1	3-Co	0.70		0.40	toluene	0.05	5
2	3-Ga	0.76		0.28	toluene	0.4	27
3	3-Al	0.62		0.30	toluene	0.7	43
4	3-Au	1.19		0.73	toluene	0.5	30
5	3-P	1.34		1.10	toluene	0.8	50
6	4-Ga	0.83		0.41	toluene	1.1	70
7	<b>4-Al</b>	0.73		0.29	toluene	0.7	43
8	4-Au	1.33		0.49	toluene	0.6	38
9	4-P	1.47		1.16	toluene	3.9	248
10	3-Co	0.70		0.40	p-xylene	0.1	9
11	3-Ga	0.76		0.28	p-xylene	0.7	47
12	3-Al	0.62		0.30	p-xylene	1.5	117
13	3-Au	1.19		0.73	p-xylene	4.4	286
14	3-P	1.34		1.10	p-xylene	3.0	198
15	4-Ga	0.83		0.41	p-xylene	1.1	72
16	<b>4-Al</b>	0.73		0.29	p-xylene	1.5	99
17	4-Au	1.33		0.49	p-xylene	4.1	266
18	4-P	1.47		1.16	p-xylene	8.2	536
19	3-Co	0.70		0.40	mesitylene	0.1	6
20	3-Ga	0.76		0.28	mesitylene	4.0	247
21	3-Al	0.62		0.30	mesitylene	1.4	84
22	3-Au	1.19		0.73	mesitylene	9.7	606
23	3-P	1.34		1.10	mesitylene	6.4	397
24	4-Ga	0.83		0.41	mesitylene	6.2	388
25	4-Al	0.73		0.29	mesitylene	1.3	80

**Table S1.** Representation of metallocorrole-catalyzed oxygenation of toluene and the related benzene derivatives and their conversion yields and TON into corresponding aldehydes.

26	4-Au	1.33	0.49	mesitylene	8.8	549
27	4-P	1.47	1.16	mesitylene	17.2	1072

([a] General procedure: a 5 mL-acetonitrile solution charged with photocatalyst (15  $\mu$ M), substrate (0.1 M), TFA (78  $\mu$ L, 0.2 M)) under LED irradiation ( $\lambda_{max}$  = 400 nm) for 20 h. [b] the 1<sup>st</sup> oxidation potential for all the corrole photocatalysts recorded here: glassy carbon working electrode, a platinum wire as counterelectrode, Ag/AgNO<sub>3</sub> as the reference electrode, in acetonitrile with TBAP, scan rate of 100 MV s<sup>-1</sup> was applied.[c] The absorbance of all corrole photocatalysts at 400 nm at 5 × 10<sup>-6</sup> M; [d] The yield of target aldehydes were determined by GC (nitrobenzene as the inner standard); [e] The TON (turnover number = the sum moles of product divided by the moles of photocatalyst used. All values of TON and yield were measured three times and the average value was adopted.)

Entry <sup>[a]</sup>	Catalyst	Substrate <sup>[b]</sup>	LED irradiation	Yield (%) <sup>[c]</sup>
1	4-P	toluene	dark	N.R
2	No cat	toluene	Yes (16 hours)	N.R
3	4-P	toluene (N <sub>2</sub> atmosphere)	Yes (16 hours)	0.01
4	4-P	p-xylene	dark	N.R
5	No cat	p-xylene	Yes (16 hours)	0.02
6	4-P	p-xylene (N <sub>2</sub> atmosphere)	Yes (16 hours)	0.03
7	4-P	mesitylene	dark	N.R
8	No cat	mesitylene	Yes (16 hours)	0.06
9	4-P	mesitylene (N <sub>2</sub> atmosphere)	Yes (16 hours)	0.04
10	4-P	mesitylene (no TFA)	Yes (16 hours)	0.12
11	4-Au	mesitylene	dark	N.R
12	4-Au	mesitylene (N <sub>2</sub> atmosphere)	Yes (16 hours)	0.08
13	4-Au	mesitylene (no TFA)	Yes (16 hours)	N.R
14 <sup>d</sup>	4-P	mesitylene (NaN3 added)	Yes (20 hours)	9.3
15	4-Ga	mesitylene (NaN3 added)	Yes (20 hours)	1.2
16	4-Al	mesitylene (NaN3 added)	Yes (20 hours)	0.3
17	4-Au	mesitylene (NaN <sub>3</sub> added)	Yes (20 hours)	6.1
18 <sup>e</sup>	4-P	mesitylene (Tiron added)	Yes (20 hours)	14.7
19	4-Ga	mesitylene (Tiron added)	Yes (20 hours)	5.2
20	4-Al	mesitylene (Tiron added)	Yes (20 hours)	1.0
21	4-Au	mesitylene (Tiron added)	Yes (20 hours)	3.8
22 <sup>f</sup>	4-P	mesitylene (tmtu added)	Yes (20 hours)	16.4
23	4-Ga	mesitylene (tmtu added)	Yes (20 hours)	6.0
24	4-Al	mesitylene (tmtu added)	Yes (20 hours)	1.2
25	4-Au	mesitylene (tmtu added)	Yes (20 hours)	4.3

 Table S2 Control experiments conducted to check the factors of catalyst, oxygen, TFA and light.

26	No cat	p-xylene (H <sub>2</sub> O <sub>2</sub> added)	Yes (2 hours)	3.6
27	No cat	p-xylene (H <sub>2</sub> O <sub>2</sub> added)	dark	N.R

([a] The general experimental procedure is : one 5mL-vial charged with 5 mL acetonitrile with cat 4-P (15  $\mu$ M, if present), TFA (78  $\mu$ L, 0.2 M), substrate (0.1 M, if present), LED light ( $\lambda_{max}$  = 400 nm), irradiation for 16 hours; [b] the substrate in N<sub>2</sub> atmosphere means the reaction solution was prepared in N<sub>2</sub> atmosphere and sealed tightly by parafilm; [c] the yield means the yields of generated aldehydes here which was determined by GC (nitrobenzene as the inner standard). [d] adding 0.1 M (33 mg) NaN<sub>3</sub> before irradiation, other reaction conditions remained the same except the choice of catalyst, for 4-P, 4-Ga ,4-Al and 4-Au, respectively; [e] adding 0.1 M (157 mg) Tiron (disodium 4,5-dihroxy-1,3-benzenedisulnate) added before irradiation, other conditions remained the same except the choice of catalysts, for 4-P, 4-Ga, 4-Al and 4-Au, respectively; [f] adding 0.1 M (66 mg) *tmtu* (tetramethylthiourea) before irradiation reaction, other conditions remained the same except the choice of catalysts, for 4-P, 4-Ga, 4-Al and 4-Au; the amount of added H<sub>2</sub>O<sub>2</sub> (30 %) in entries 26 & 27 was 39 µL (0.1 M in 5 mL acetonitrile solution) ).

		$ \begin{array}{c}                                     $	acid/air cat/LED (400 nm)	но		
		Substrate Toluene P-xylene Mesitylene	Prod Benz P-tolo 3,5-d	<b>uct</b> aldehyde aaldehyde imethylbenzaldehyde		
Entry <sup>a</sup>	Catalyst	Acid	Substrate	Irradiation time (h)	TON	Yield (%)
1	<b>4-P</b>	acetic	Toluene	16	8	0.1
2	<b>4-P</b>	acetic	P-xylene	16	5	0.1
3	<b>4-P</b>	acetic	Mesitylene	16	N.R	N.R
4	<b>4-P</b>	sulfuric	Toluene	16	32	0.5
5	<b>4-P</b>	sulfuric	P-xylene	16	49	0.7
6	<b>4-P</b>	sulfuric	Mesitylene	16	43	0.6

**Table S3.** Use of acetic acid or sulfuric acid for the oxygenation of toluene and derivatives.

(ageneral procedure: a 5mL-acetonitrile solution charged with catalyst 4-P (15  $\mu$ M), substrate (0.1 M), acetic acid (58 µL, 0.2 M) or sulfuric acid (54 µL, 0.2 M)) was under LED (400 nm) irradiation for 16 h and the yield of target aldehydes were determined by GC.

# END OF SUPPORTING INFORMATION