Electronic Supplementary Information

Direct, Copper-Catalyzed Oxidation of Aromatic C-H Bonds with Hydrogen Peroxide under Acid-Free Conditions

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General methods and Experimental procedures

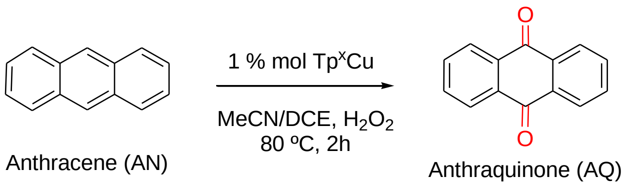
General Methods. All catalytic experiments were carried out under air. The chemicals were purchased from Aldrich and were used without purification. The Tp^{x} ligands[1] and the complexes [Tp^{x}Cu(NCMe)][2] were prepared according to the literature procedures. ^{1}H and ^{13}C spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts □□are reported relatively to tetramethylsilane as internal standard in ppm. GC data were collected with a Varian GC-3900 with a FID detector.

General Catalytic Procedure for Direct Oxidation of Benzene into Phenol Catalyzed by [Tp^{x}Cu(NCMe)]. The oxidation reactions were performed in a 25 mL round bottomed flask equipped with a reflux condenser and a magnetic stirrer bar. In a typical experiment, 0.005 mmol of catalyst were dissolved in 2 mL of acetonitrile and 1 mmol (88 μL) of benzene and 1.5 mmol (0.15 mL) of an aqueous commercial solution of hydrogen peroxide (30% v/v) were added in one portion. The mixture was stirred for 2 hours at 80 ºC. After cooling at room temperature, the phases were separated and the aqueous phase was extracted with CDCl$_3$ (1-2 mL). An exactly weighted amount of diethyl malonate was added as internal standard and the mass balance in the organic phase was then determined by ^{1}H NMR.

General Catalytic Procedure for Direct Oxidation of Anthracenes into Anthraquinones Catalyzed by [Tp^{x}Cu(NCMe)]. With the same experimental setup 1.5 mL (15 mmol) of an aqueous commercial solution of hydrogen peroxide (30% v/v) was added to a solution of 6 mg (0.01mmol) of Tp^{*,Br}Cu(NCCH$_3$) and 44.5 mg (0.25 mmol) of anthracene in 6 mL of a mixture dichloromethane:acetonitrile (1:1, v/v). The resulting solution was stirred for 2 hours at 80 ºC, and then cooled to room temperature. Extraction with dichloromethane (2 x 5 mL) followed by treatments of the organic phase with MgSO$_4$ gave, upon evaporation, pure anthraquinones as yellow solids. (purity assessed by NMR).

The influence of temperature, catalyst screening and reaction time were studied and the results are shown in Tables S1 and S2 for anthracene and ethylanthracene respectively. We have observed that the temperature has no appreciable influence on the selectivity, although it seems to have a certain effect in the yield of the reaction.

Table S1. Tp^{x}Cu-Catalyzed Selective Oxidation of Anthracene[a]



Entry[a]	Catalyst	Temp (°C)	*n* (H_2O_2)	Conv.(%) AN[b]	Selectivity (%) AQ
1	Tp^{*,Br}Cu(NCMe)	20	10	11	>95
2[c]	Tp^{*,Br}Cu(NCMe)	20	10	85	>95
3	Tp^{*,Br}Cu(NCMe)	40	10	34	>95
4	Tp^{*,Br}Cu(NCMe)	60	10	34	>95
5	Tp^{*,Br}Cu(NCMe)	80	10	>95	>98
6[d]	Tp^{*,Br}Cu(NCMe)	80	30	75	80
7[d,e]	Tp^{*,Br}Cu(NCMe)	80	30	>95	>98
8	Tp^{*,Br}Cu(NCMe)	80	15	>95	>98
9	Tp^{Ms}Cu(NCMe)	80	15	>95	>98
10	Tp^{Ph}Cu(NCMe)	80	15	>95	>98
11	Tp^{Br3}Cu(NCMe)	80	15	>95	>98

[a] Reaction conditions: 0.01 mmol of catalyst, 0.25 mmol of anthracene, 6 mL of dichloroethane/acetonitrile (3:3, v/v), reaction time 2h unless otherwise noted. [b] Isolated yield. [c] Reaction time = 24h. [d] 1 mmol of anthracene; reaction time= 4 h

Table S2. Tp^{x}Cu-Catalyzed Selective Oxidation of 2-Ethylanthracene[a]

Entry	Catalyst	Temp (°C)	Time (h)	Conv (%) 2EAN[b]	Selectivity (%) 2EAQ
1	Tp^{*,Br}Cu(NCMe)	20	24	95	>95
2	Tp^{*,Br}Cu(NCMe)	40	10	82	>95
3	Tp^{*,Br}Cu(NCMe)	60	4	>98	>98
4	Tp^{*,Br}Cu(NCMe)	80	2	>98	>98
5[c]	Tp^{*,Br}Cu(NCMe)	80	2	>98	>98
6[c]	Tp^{Ms}Cu(NCMe)	80	2	>98	>98
7[c]	Tp^{Ph}Cu(NCMe)	80	2	>98	>98
8[c]	Tp^{Br3}Cu(NCMe)	80	2	>98	>98

[a] Reaction conditions: 0.01 mmol of catalyst, 0.25 mmol of 2-ethylanthracene, 6 mL of dichloroethane/acetonitrile (3:3, v/v), 10 mmol of H_2O_2 unless otherwise note. [b] Isolated yield. [c] 15 mmol of H_2O_2

NMR Data of Compounds:

Commercial samples were used to identify by ^{1}H NMR reactants and products. These are the significative resonances for all of them:

Phenol

^{1}H NMR (400MHz, CDCl$_3$): δ 7.26 (t, 2H), 6.95 (t, 1H), 6.85 (d, 2H), 4.83 (bs,-OH).

Benzoquinone

^{1}H NMR (400MHz, CDCl$_3$): δ 6.79 (s, 4H).

Tetramethylene sulfone

^{1}H NMR (400MHz, CDCl$_3$): δ 2.99 (m, 4H), 2.19 (m, 4H).

Anthracene

^{1}H NMR (400MHz, CDCl$_3$): δ 8.44 (s, 2H), 8.02 (m, 4H), 8.48 (m, 4H).

Anthraquinone

^{1}H NMR (400MHz, CDCl$_3$): δ 8.32 (m, 4H), 7.81 (m, 4H).

2-Ethylanthracene

^{1}H NMR (400MHz, $CDCl_3$): δ 8.37(d, 2H), 7.99 (m, 2H), 7.94 (d, 1H), 7.76 (s, 1H), 7.44 (m, 2H), 7.35 (d, 1H), 2.86 (m, 2H), 1.37 (t, 3H).

2-Ethylanthraquinone

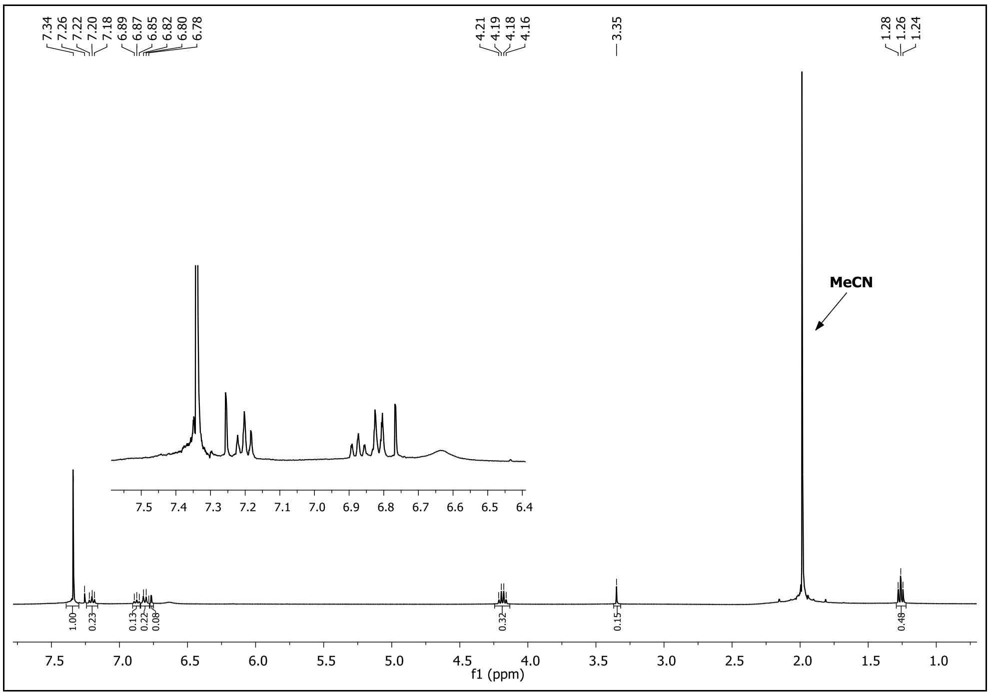
^{1}H NMR (400MHz, $CDCl_3$): δ 8.31(m, 2H), 8.23 (d, 1H), 8.14 (d, 1H), 7.79 (m, 2H), 7.83 (dd, 1H), 2.83 (m, 2H), 1.33 (t, 3H).

Diethyl Malonate (commercial product, internal standard)

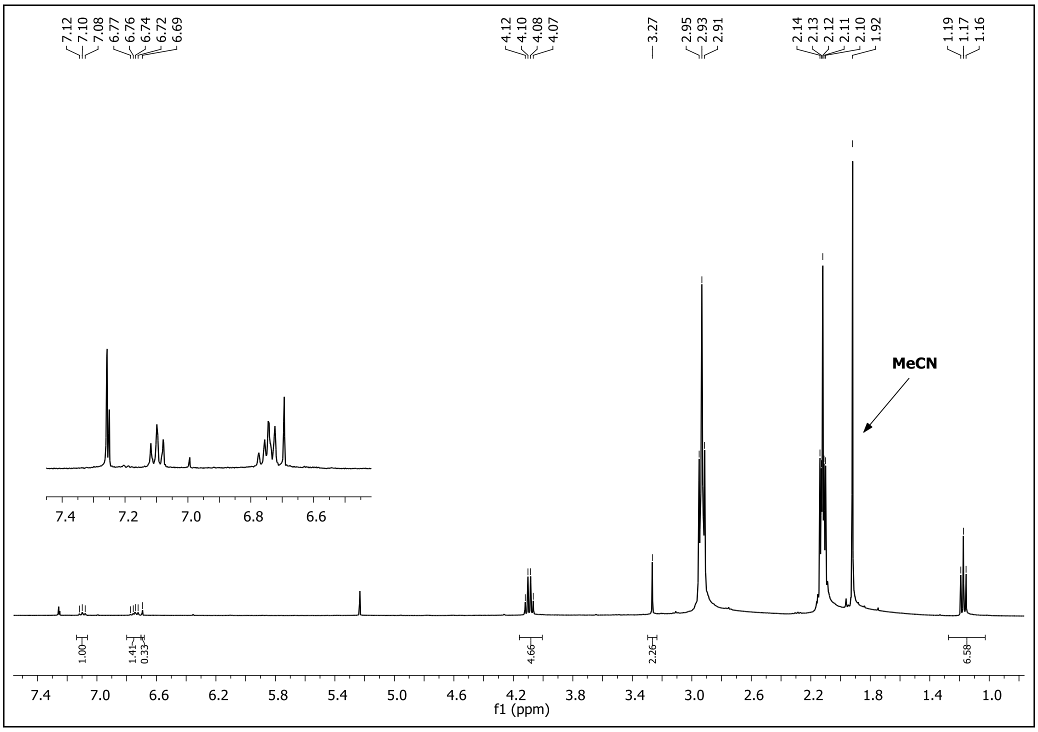
^{1}H NMR (400MHz, $CDCl_3$): δ 4.18 (m, 4H), 3.34 (s, 2H), 1.26 (t, 6H).

NMR Spectra

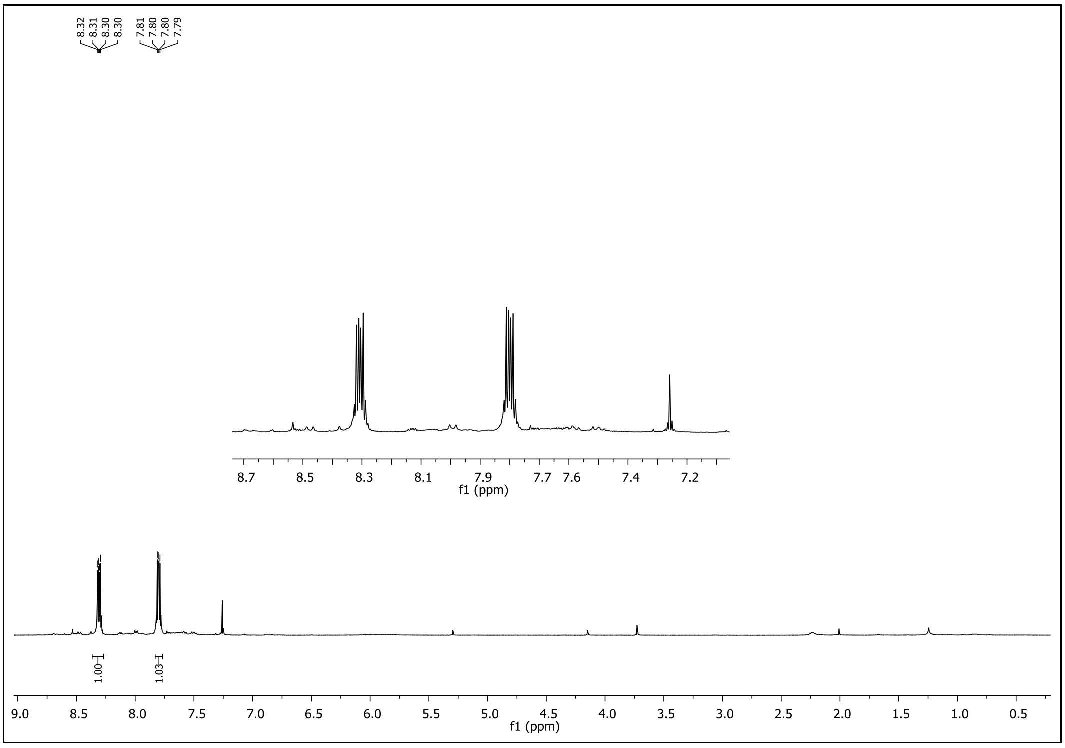
^{1}H NMR spectrum of the extract (organic phase) from the reaction of benzene with hydrogen peroxide in acetonitrile in the presence of [Tp^{x}Cu(NCMe)] as catalyst**.**



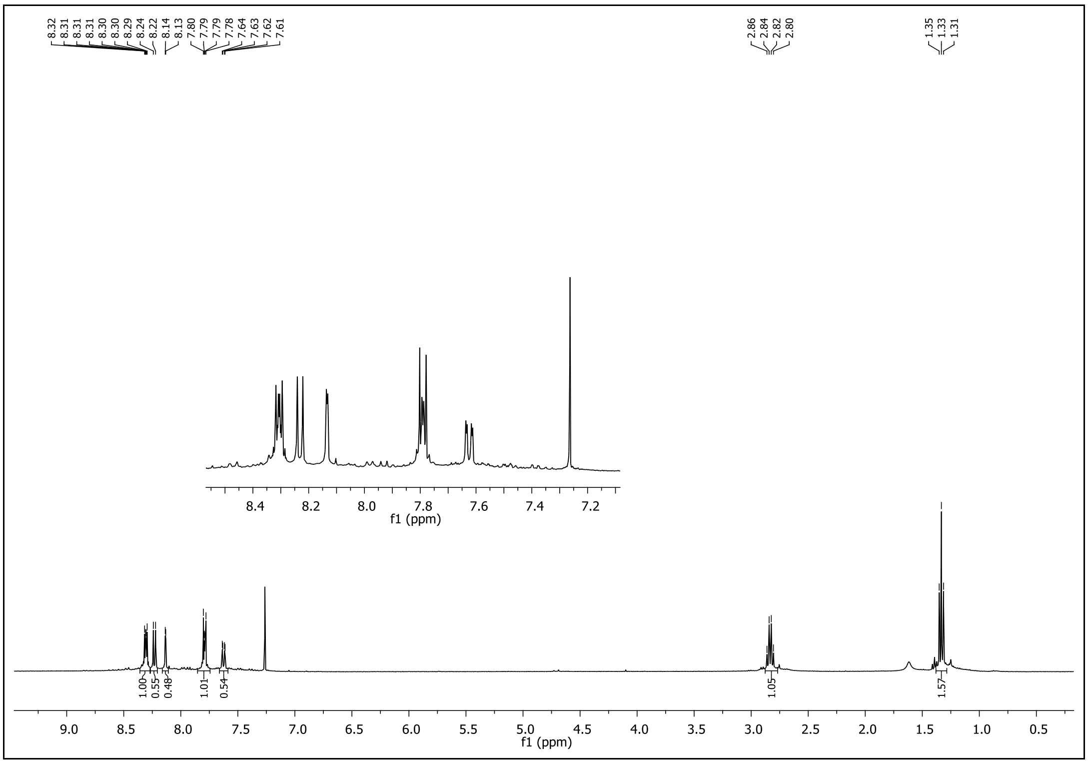
^{1}H NMR spectrum of the extract (organic phase) from the reaction of benzene with hydrogen peroxide in acetonitrile using sulfolane as co-solvent in the presence of [Tp^{x}Cu(NCMe)] as catalyst**.**



^{1}H NMR spectrum of the organic phase (after extraction) from the reaction of anthracene with hydrogen peroxide in mixture dichloromethane:acetonitrile in the presence of [Tp^{x}Cu(NCMe)] as catalyst**.**



^{1}H NMR spectrum of the organic phase (after extraction) from the reaction of 2-ehtylanthracene with hydrogen peroxide in the presence of [Tp^{x}Cu(NCMe)] as the catalyst**.**



References

1 (a) S. Trofimenko in *Scorpionates*, *The Coordination Chemistry of Polypyrazolylborate Ligands;* Imperial College Press: London, 1999. (b) C. Pettinari in *Scorpionates II: Chelating Borate Ligands*; Imperial College Press; River Edge NJ 2008.

2 (a) C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks, J. Ibers, A. *J. Am. Chem. Soc.* 1976, **98**, 711-718. (b) J. L. Schneider, S. M. Carrier, C. E. Ruggiero, V. G. Jr.Young, W. B. Tolman, *J. Am. Chem. Soc.* 1998, **120**, 11408-11418. (c) Mairena M. A., J. Urbano, J. Carbajo, J. J. Maraver, E. Alvarez, M. M. Díaz-Requejo, *Inorg. Chem.* 2007, **46**, 7428-7435.