Electronic Supplementary Material (ESI) for ChemComm.

Biomimetic oxidation of pyrene and related aromatic hydrocarbons. Unexpected electron accepting abilities of pyrenequinones.

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Experiment Section

General Consideration: NMR spectra were recorded with BRUKER AVANCE III-HD NANOBAY 300MHz and BRUKER DRX 500MHz. Mass spectra were measured with ULTRAFLEX III (MALDI-TOF/TOF). Electrochemistry was measured with Potentiostat Autolab PGSTAT 30.

All materials used for synthesis were obtained from Sigma-Aldrich or Alfa Aesar. All organic solvents for synthesis were of analytical grade and were obtained commercially. They were used without further purification. All reactions were monitored by thin-layer chromatography (TLC) with Merck silica gel plates (60F-254) under irradiation by UV-lamp (254 nm). Scharlau silica gel (230-400 mesh) was used in the column-chromatography purification.

EXPERIMENTAL PROCEDURE (5% OF CATALYST)

A 100 mL round bottom flask was charged with 0.5 mL of CH_2Cl_2, 1.5 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)$(OTf)_2$ (9 mg, 0.016 mmol, 1.6 mol %) and pyrene (200 mg, 1 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A solution of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M) was added dropwise via syringe. After stirring for 10 min, 1 mL of a 0.5

M AcOH solution in CH_3CN and Fe(bpmen)$(OTf)_2$ (9 mg, 0.016 mmol, 1.6 mol %) were added. This was followed by the dropwise addition of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M). A third addition was performed for a total of 5 mol % Fe(bpmen)$(OTf)_2$, 1.5 equiv of AcOH, and 3.6 equivalents of H_2O_2. After the last 10 min of stirring, a $NaHCO_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Mg_2SO4, evaporated under reduced pressure and purified by chromatographic column (H:AcOEt 7:3) to obtain 121 mg of pyrene, 32 mg (14%) of 1,6-pyrenedione and 18.2 mg (8%) of 1,8-pyrendione.

EXPERIMENTAL PROCEDURE (10% OF CATALYST)

A 100 mL round bottom flask was charged with 0.5 mL of CH_2Cl_2, 1.5 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)$(OTf)_2$ (20 mg, 0.033 mmol, 3.3 mol %)~~,~~ and pyrene (200 mg, 1 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A solution of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M) was added dropwise via syringe. After stirring for 10 min, 1 mL of a 0.5 M AcOH solution in CH_3CN and Fe(bpmen)$(OTf)_2$ (20 mg, 0.033 mmol, 3.3 mol %) were added. This was followed by the dropwise addition of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M). A third addition was performed for a total of 10 mol % Fe(bpmen)$(OTf)_2$, 1.5 equiv of AcOH and 3.6 equiv of H_2O_2. After the last 10 min of stirring, a $NaHCO_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Mg_2SO4, evaporated under reduced pressure and purified by chromatographic column (H:AcOEt 7:3) to obtain 98 mg of pyrene, 40 mg (17%) of 1,6-pyrenedione and 20 mg (9%) of 1,8-pyrendione.

EXPERIMENTAL PROCEDURE (15% OF CATALYST)

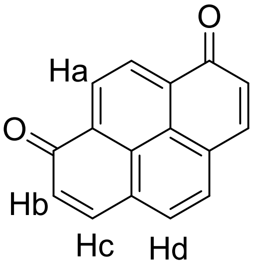
A 100 mL round bottom flask was charged with 0.5 mL of CH_2Cl_2, 1.5 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)$(OTf)_2$ (31.2 mg, 0.05 mmol, 5 mol %) and pyrene (200 mg, 1 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A solution of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN

(8 mL, 0.13 M) was added dropwise via syringe. After stirring for 10 min, 1 mL of a 0.5 M AcOH solution in CH_3CN and Fe(bpmen)$(OTf)_2$ (31.2 mg,0.05 mmol, 5 mol %) were added. This was followed by the dropwise addition of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M). A third addition was performed for a total of 15 mol % Fe(bpmen)(OTf)2, 1.5 equiv of AcOH and 3.6 equiv of H_2O_2. After the last 10 min of stirring, a $NaHCO_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Mg_2SO4, evaporated under reduced pressure and purified by chromatographic column (H:AcOEt 7:3) to obtain 62 mg of pyrene, 68 mg (29%) of 1,6-pyrenedione, 36.5 mg (16%) of 1,8-pyrenedione and 11 mg (5%) of 4,5-pyrenedione.

EXPERIMENTAL PROCEDURE (20% OF CATALYST)

A 100 mL round bottom flask was charged with 0.5 mL of CH_2Cl_2, 1.5 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)$(OTf)_2$ (42 mg, 0.067 mmol, 6.7 mol %)~~,~~ and pyrene (200 mg, 1 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A solution of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M) was added dropwise via syringe. After stirring for 10 min, 1 mL of a 0.5 M AcOH solution in CH_3CN and Fe(bpmen)$(OTf)_2$ (42 mg,0.067 mmol, 6.7 mol %) were added. This was followed by the dropwise addition of H_2O_2 (30 wt %, 0.136 mL, 1.2 mmol, 1.2 equiv) in CH_3CN (8 mL, 0.13 M). A third addition was performed for a total of 20 mol % Fe(bpmen)(OTf)2, 1.5 equiv of AcOH and 3.6 equiv of H_2O_2. After the last 10 min of stirring, a $NaHCO_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Mg_2SO4, evaporated under reduced pressure and purified by chromatographic column (H:AcOEt 7:3) to obtain 43 mg of pyrene, 34 mg (15%) of 1,6-pyrenedione and 20.2 mg (9%) of 1,8-pyrendione.

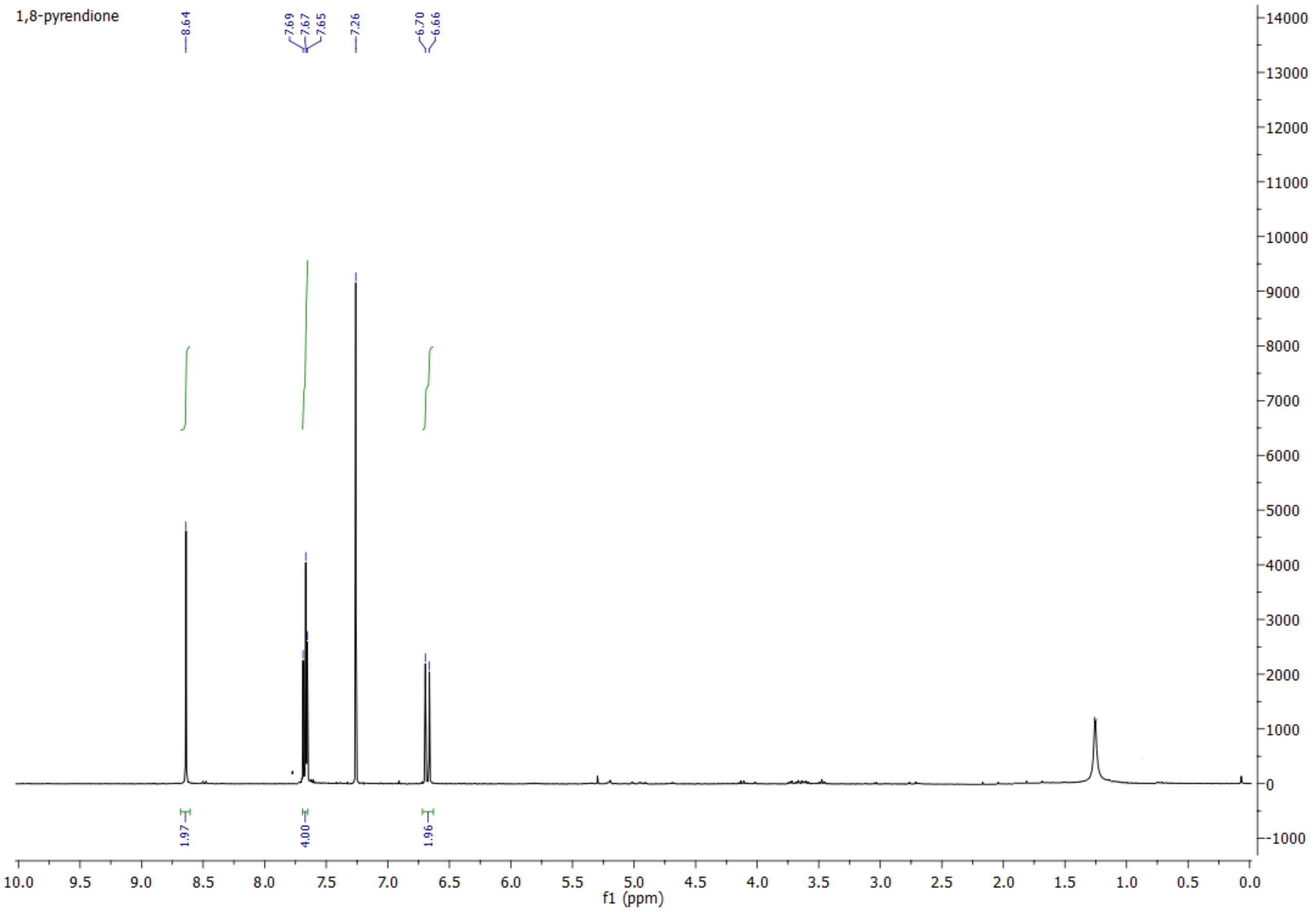
The reactions of anthracene, naphtlene, phenantrene, and benzene were carried out using the 15% of catalyst procedure.

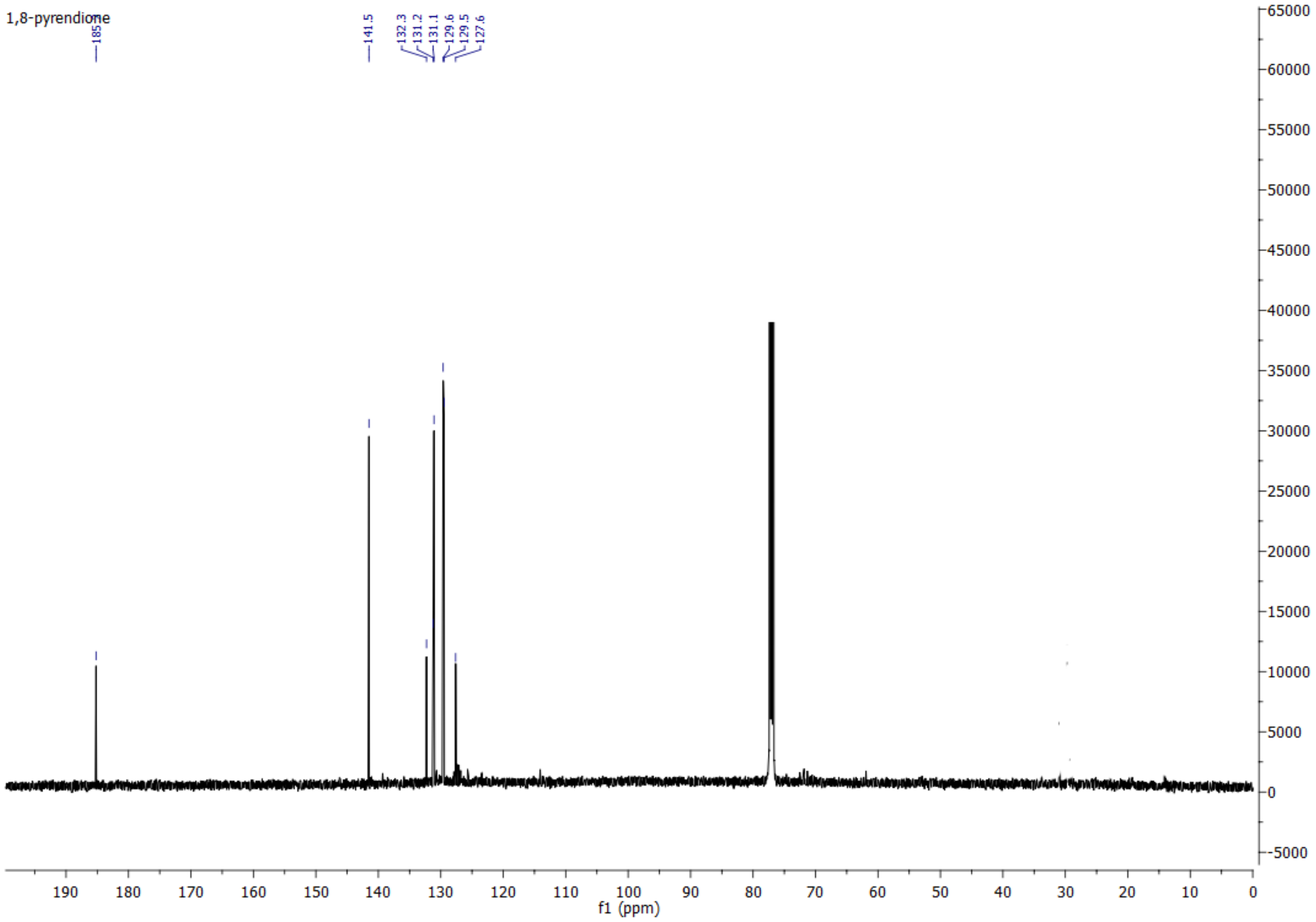


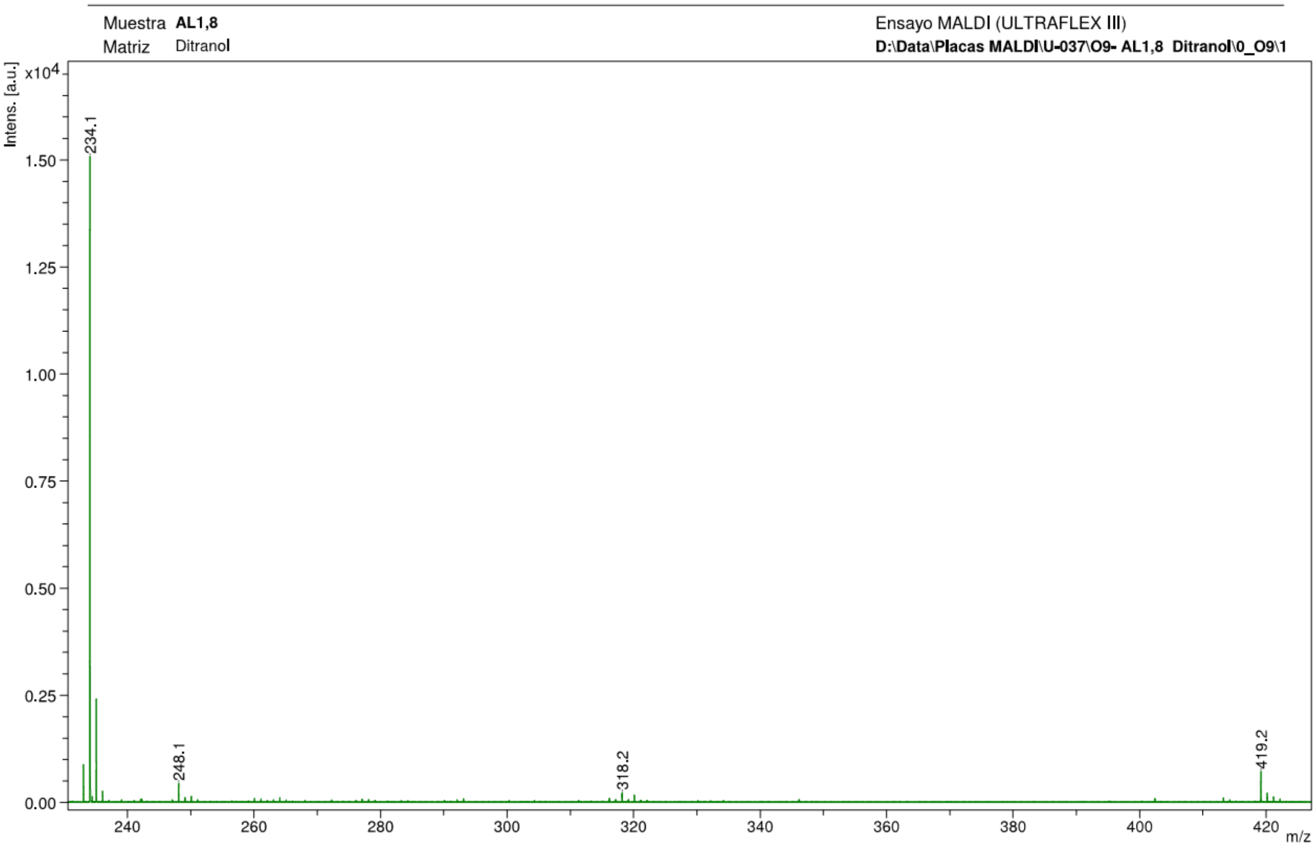
^{1}H NMR (300 MHz, CDCl$_3$) δ 8.64 (s, 2H, Ha), 7.67 (d, 2H, J = 9.8 Hz, Hc), 7.67 (s, 2H, Hd), 6.68 (d, 2H, J = 9.8 Hz, Hb).

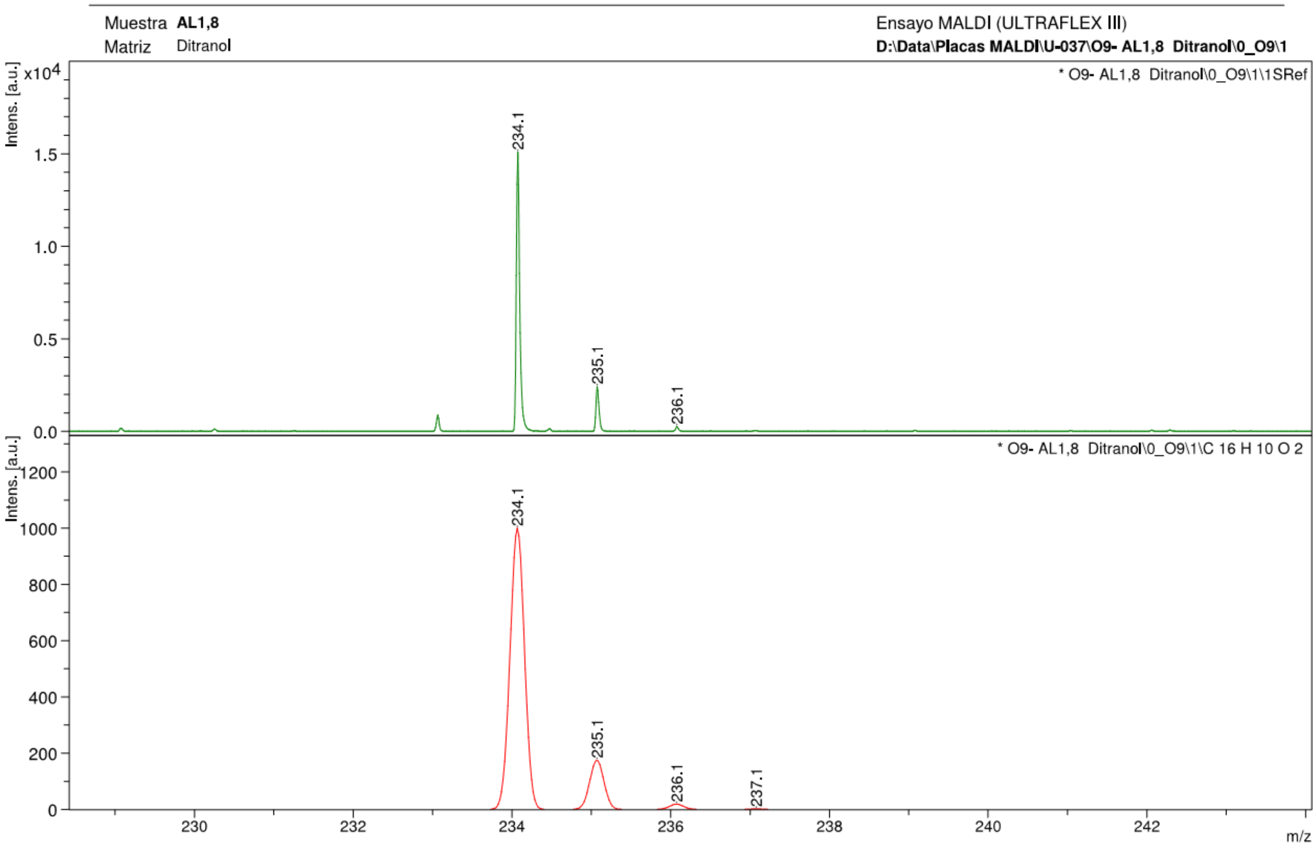
^{13}C NMR (125 MHz, CDCl$_3$) δ 185.2, 141.5, 132.3, 131.2, 131.1, 129.6, 129.5, 127.6.

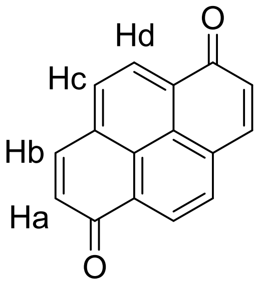
MS m/z: calcd. for $C_{16}H_8O_2$ [M+2H+] 234.06, found MALDI-TOF 234.1




1,8-pyrendione
185
141.5
132.3
131.2
131.1
129.6
129.5
127.6
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Muestra AL1,8
Matriz Ditranol
Ensayo MALDI (ULTRAFLEX III)
D:\Data\Placas MALDI\U-037\O9- AL1,8 Ditranol\0_O9\1
Intens. [a.u.]
x10^4
1.50
1.25
1.00
0.75
0.50
0.25
0.00
234.1
248.1
318.2
419.2
240 260 280 300 320 340 360 380 400 420
m/z

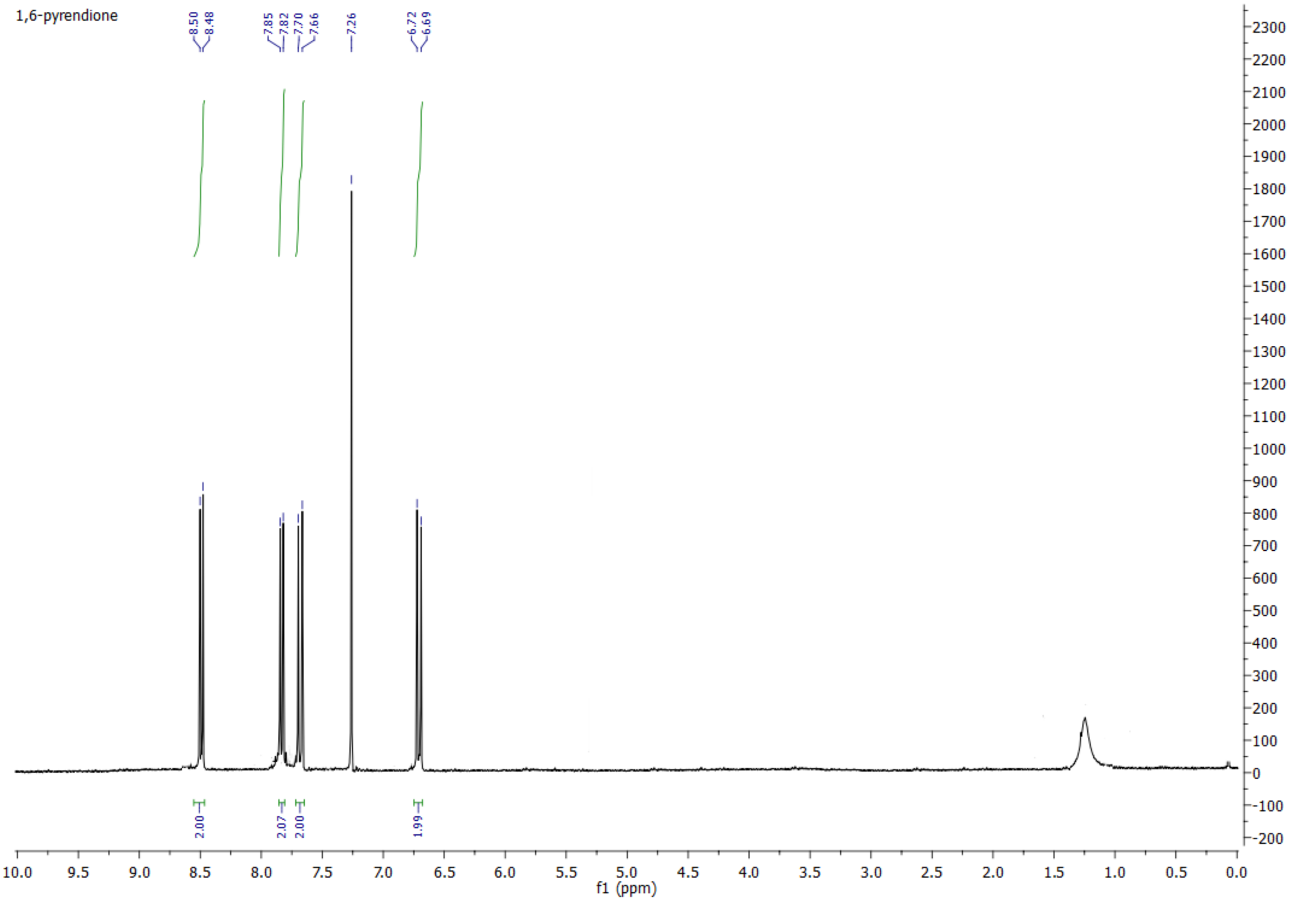


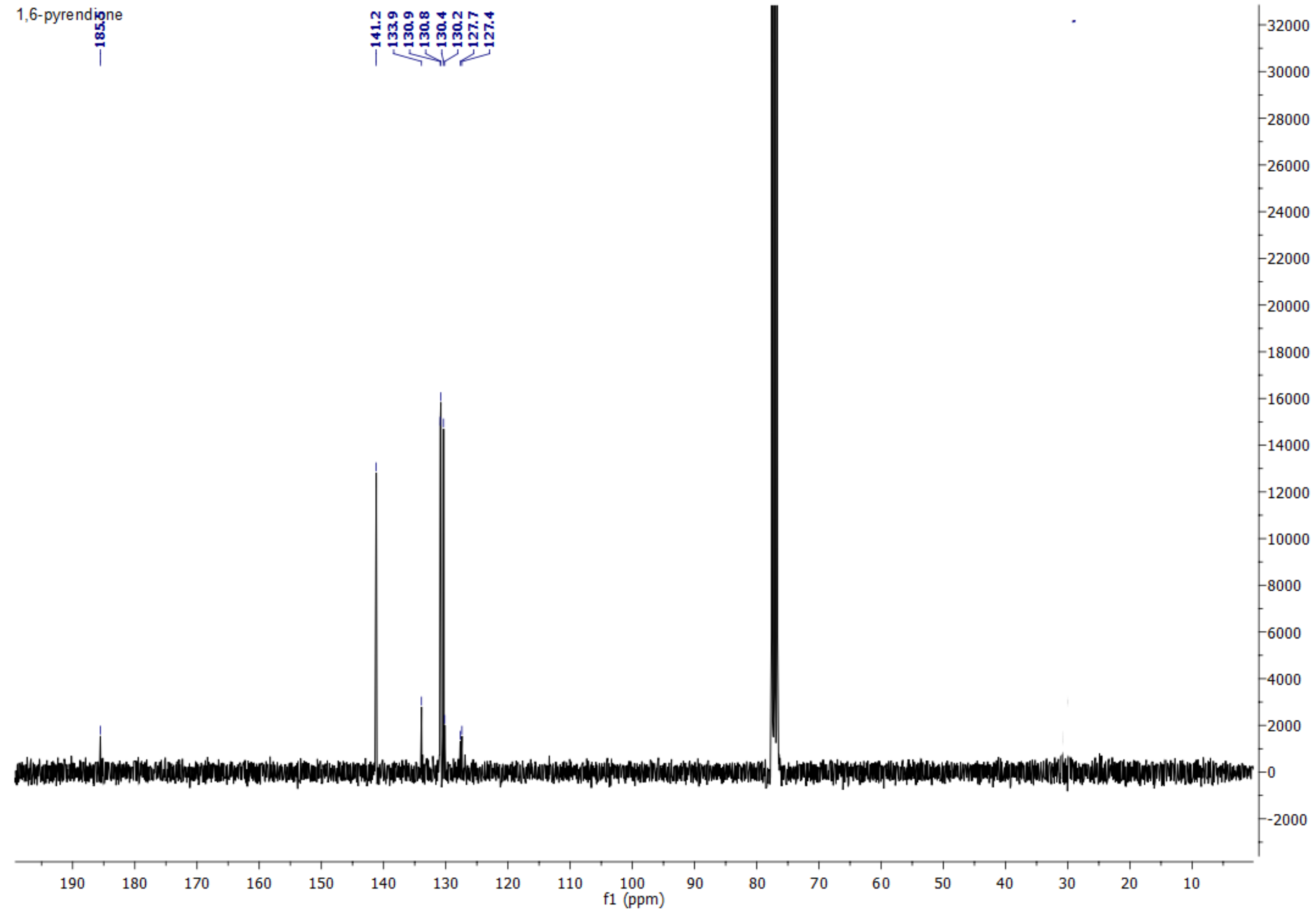


^{1}H NMR (300 MHz, CDCl$_3$) δ 8.49 (d, J = 7.5 Hz, 2H, Hd), 7.83 (d, J = 7.5 Hz, 2H, Hc), 7.68 (d, J = 9.8 Hz, 2H, Hb), 6.71 (d, J = 9.8 Hz, 2H, Ha).

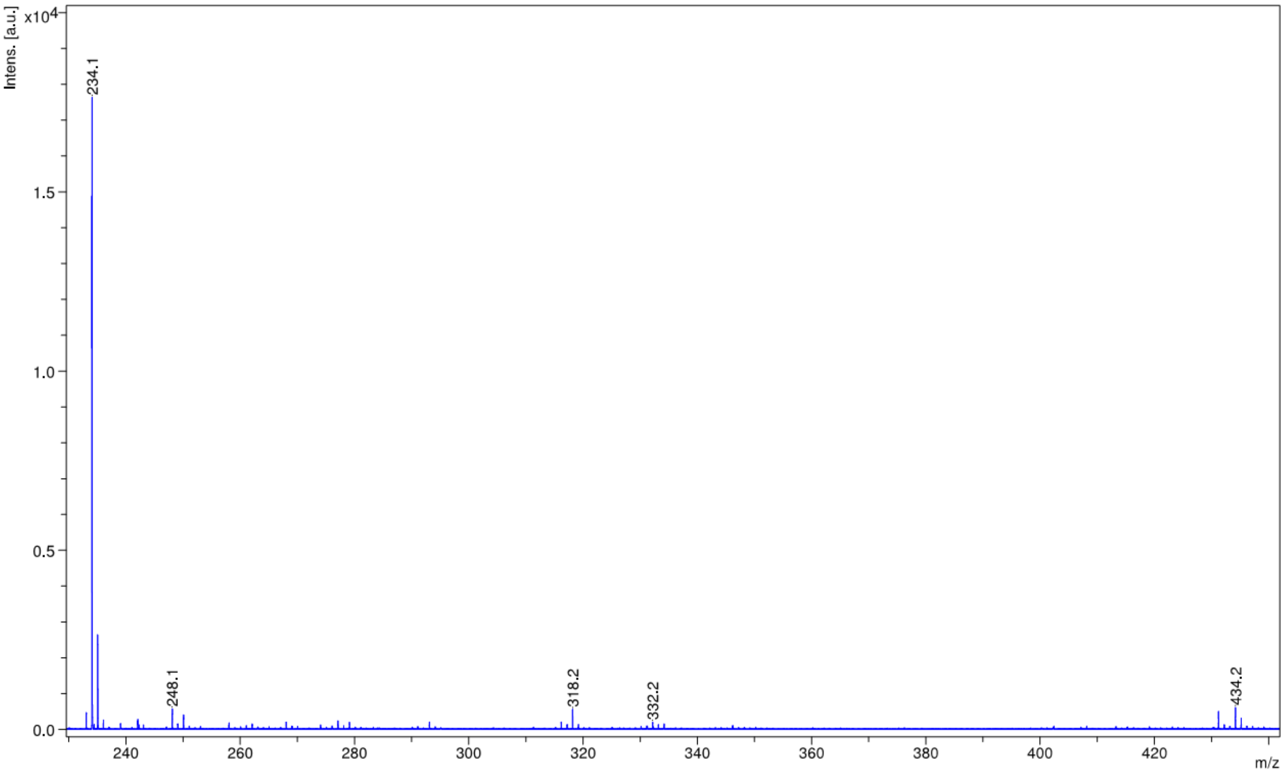
^{13}C NMR (75 MHz, CDCl$_3$) δ 185.5, 141.2, 133.9, 130.9, 130.8, 130.4, 130.2, 127.7.

MS m/z: calcd. for $C_{16}H_8O_2$ [M+2H+] 234.06 found MALDI-TOF 234.1

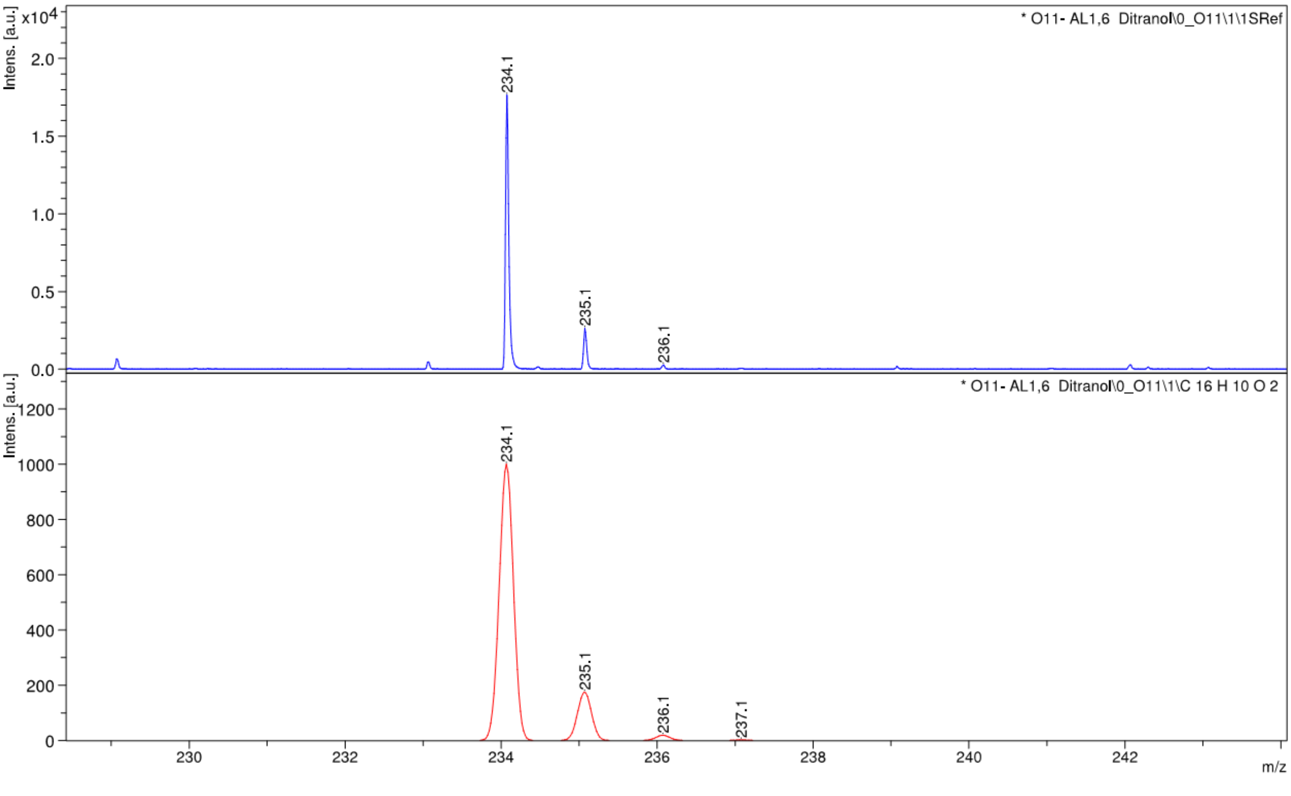

1,6-pyrendione
8.50
8.48
7.85
7.82
7.70
7.66
7.26
6.72
6.69
2.00
2.07
2.00
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

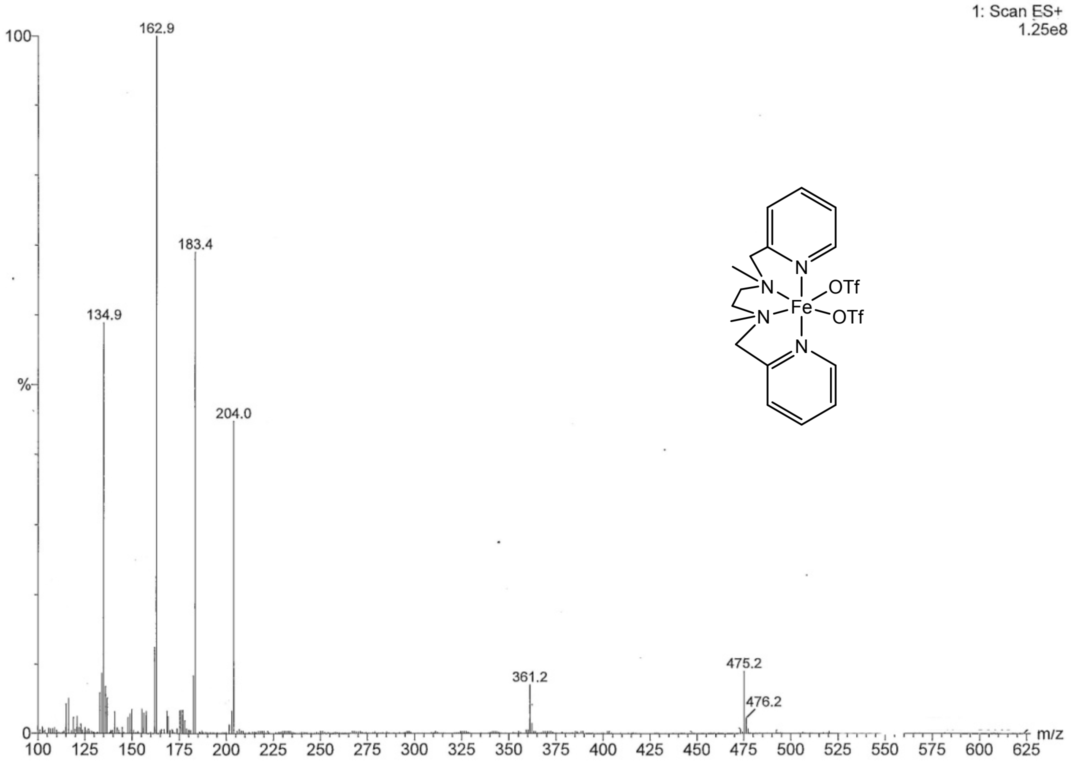

1,6-pyrendione
185.5
141.2
133.9
130.9
130.8
130.4
130.2
127.7
127.4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

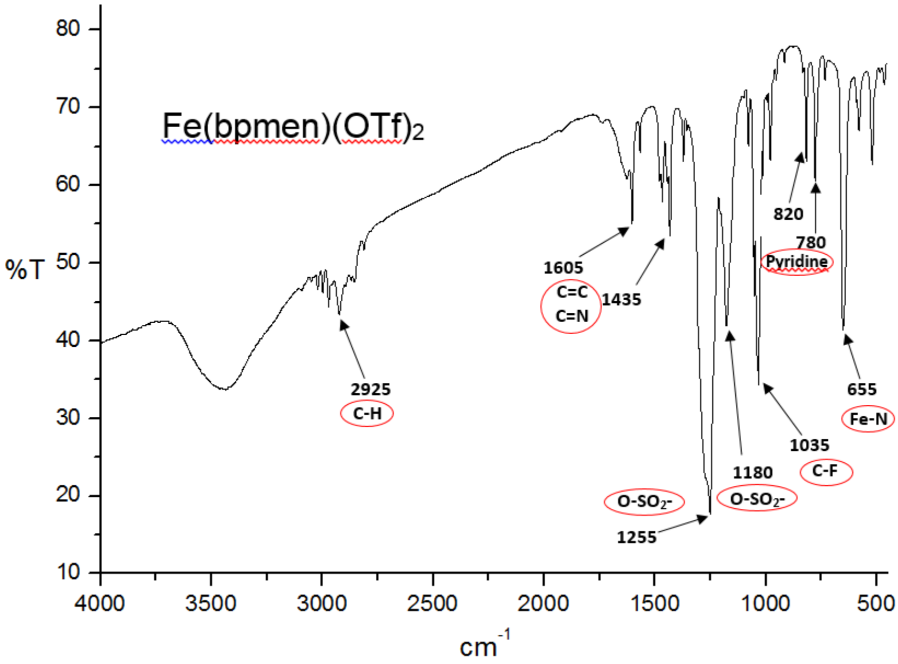
Muestra **AL1,6** Ensayo MALDI (ULTRAFLEX III)
Matriz Ditranol **D:\Data\Placas MALDI\U-037\O11- AL1,6 Ditranol\0_O11\1**

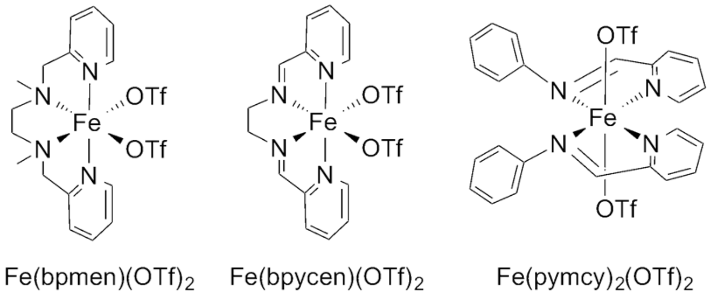


Muestra **AL1,6** Ensayo MALDI (ULTRAFLEX III)
Matriz Ditranol **D:\Data\Placas MALDI\U-037\O11- AL1,6 Ditranol\0_O11\1**




1: Scan ES+
1.25e8
100
%
0
162.9
183.4
134.9
204.0
361.2
475.2
476.2
m/z
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
600
625
N
N
N
N
Fe
OTf
OTf


Fe(bpmen)(OTf)2
%T
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
cm-1
2925
C-H
1605
C=C
C=N
1435
1255
O-SO2-
1180
O-SO2-
1035
C-F
820
780
Pyridine
655
Fe-N



bpmen = N,N'-bis-(2-pyridylmethyl)-N,N'-dimethyl-1,2-ethylenediamine

bpycen = N,N'-bis(pyridin-2-ylmethylene)ethane-1,2-diimine

pymcy = N-(pyridin-2-ylmethylene)cyclohexanamine

Figure S1. Iron Catalysts. Fe(bpmen)(OTf)$_2$ was synthetized following previous work.[1] Fe(bpycen)(OTf)$_2$ and Fe(pymcy)$_2$(OTf)$_2$ were synthetized following previous work.[2]

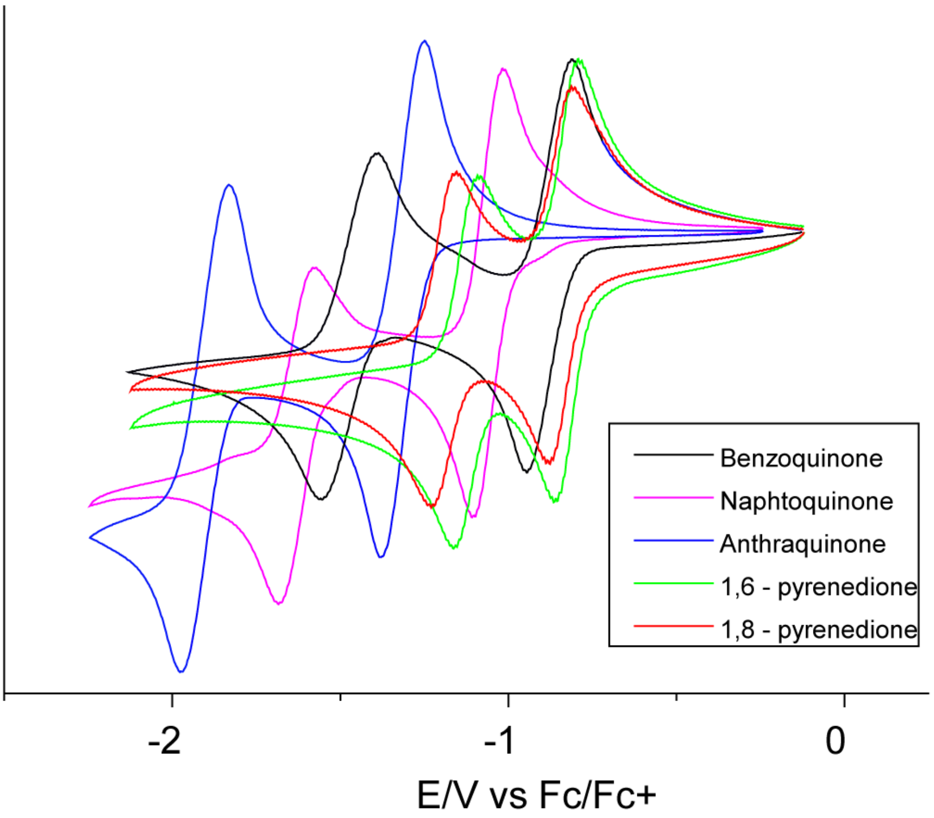


Figure S2. Cyclic voltammograms of benzoquinone, naphtoquinone, anthraquinone and pyrenequinones.

Computational details

All the calculations were carried out using the Gaussian 09 (version D01) program package.[3] Full-geometry optimization of both neutral and anion species of parent *p*-benzoquinone (*p*-BQ) and pyrenediones **1** and **2** was performed with the Becke's three parameter B3LYP exchange-correlation functional[4, 5] and the cc-pVTZ Dunning's basis set.[6] The anions were calculated as open-shell doublet systems using the unrestricted UB3LYP approach. Even though no special symmetry restriction was imposed during the optimization process, minimum-energy conformations of C_{2h} and C_{2v} symmetry were obtained for **1** and **2**, respectively, in both neutral and reduced states. To calculate the free energy of solvation ($\Delta\Delta G_{\mathrm{solv}}$) of the one-electron attachment $\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^-$ reaction, single-point B3LYP/cc-pVTZ energy calculations were performed for *p*-BQ and the two pyrenediones in the presence of the solvent (acetonitrile, $\varepsilon = 35.688$) within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM).[7, 8] The PCM model considers the solvent as a continuous medium with a dielectric constant ε, and represents the solute by means of a cavity built with a number of interlaced spheres. Other continuum solvation models such as the conductor-like PCM (CPCM)[9, 10] and SMD[11] were used to compare the effect of the solvation model on the free energy of solvation.

Table S1 presents the thermochemical and electrochemical data calculated for the one-electron attachment $\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^-$ process depicted in Figure S3, where A stands for *p*-BQ and pyrenediones **1** and **2**. Thermodynamic data were computed both at the B3LYP/cc-pVTZ level and by means of the more accurate Gaussian-3 theory using reduced Moller-Plesset order (G3(MP2)).[12] The G3(MP2) theory is based on MP2(full)/6-31G(d)-optimized geometries using all electrons and a series of single-point energy calculations at higher levels of theory. An accurate estimation of the total energy is performed by a QCISD(T)/6-31G(d) calculation followed by a series of corrections according to the formula:

$$E_0[\mathrm{G3(MP2)}] = \mathrm{QCISD(T)/6\text{-}31G(d)} + \Delta E_{\mathrm{MP2}} + \Delta E(\mathrm{SO}) + E(\mathrm{ZPE}) + E(\mathrm{HLC})$$

where the correction at the second-order Moller-Plesset level is given by

$$\Delta E_{\mathrm{MP2}} = [E(\mathrm{MP2/G3MP2large})] - [E(\mathrm{MP2/6\text{-}31G(d)})],$$

the spin-orbit correction, ΔE(SO), is included for atomic species only and the zero-point correction, E(ZPE), is obtained from scaled (0.8929) HF/6-31G(d) frequencies. Finally, a higher level correction, E(HLC), is added to take into account remaining deficiencies in the energy calculations.

Table S2 compares the solvation free energy differences ($\Delta\Delta G_{solv}$) between the neutral and the anion species of *p*-BQ, **1** and **2** computed at the B3LYP/cc-pVTZ level using different solvation models. The three models employed lead to identical trends with similar relative values.

Table S1. Thermochemical (in eV) and electrochemical (in V) data calculated for the one-electron attachment A + e$^-$ → A$^-$ process depicted in Figure S3.

	B3LYP/cc-pVTZ			G3(MP2)		
	BQ	**1**	**2**	BQ	**1**	**2**
EA[a]	1.943	2.312	2.302	1.852	2.230	2.254
EA + ZPE[b]	1.993	2.374	2.366	1.916	2.322	2.341
EA + ZPE + 298K[c]	1.999	2.376	2.368	1.923	2.324	2.344
$\Delta H_{g,298K}$[d]	–1.999	–2.376	–2.368	–1.923	–2.324	–2.344
$\Delta S_{g,298K}$[e]	0.017	0.693	0.715	–0.347	0.453	0.322
$\Delta G_{g,298K}$[f]	–2.000	–2.385	–2.377	–1.919	–2.330	–2.348
$\Delta G_{g,corrected}$[g]	–2.146	–2.531	–2.523	–2.065	–2.476	–2.494
ΔG_{solv} (A)[h]	–0.223	–0.323	–0.331			
ΔG_{solv} (A$^-$)[h]	–2.245	–1.940	–1.954			
$\Delta\Delta G_{solv}$[i]	–2.023	–1.617	–1.623	–2.023	–1.617	–1.623
ΔG_{red}[j]	–4.169	–4.148	–4.146	–4.088	–4.093	–4.117
$E_{1/2,absolute}$[k]	4.169	4.148	4.146	4.088	4.093	4.117
$E_{1/2,relative}$[l]	–0.819	–0.840	–0.842	–0.900	–0.895	–0.871

[a] Adiabatic electron affinities calculated as the energy difference between the total energies computed for the neutral and the anion species at their respective fully-optimized geometries.

[b] Adiabatic electron affinities including the zero-point energy (ZPE).

[c] Adiabatic electron affinities including the ZPE and the correction at 298 K to the internal thermal energy ($E_{tot} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$).

[d] Enthalpy difference between the anion and the neutral species for the one-electron attachment reaction depicted in Figure S4.

[e] Entropy difference for the one-electron attachment reaction. Values expressed in cal/K·mol.

[f] Free energy difference for the one-electron attachment reaction in gas phase. $\Delta G_{g,298K} = \Delta H_{g,298K} - T\Delta S_{g,298K}$

[g] Corrected values taking into account the free electron as an ideal monoatomic gas, 5/2 RT,[13] and the correction for the change in standard state from 1 atm to 1 mol·L^{-1},[14] according to the following formula:[15] $\Delta G_{g,corrected} = \Delta G_{g,298K} - 5/2\ RT + RT \ln 24.46$.

[h] Free energy of solvation for the neutral (A) and the anion (A^-) species (see Figure S1). Values are calculated at the B3LYP/cc-pVTZ level using the polarized continuum model (PCM) with acetonitrile as solvent. Minimum-energy geometries in gas phase at the same level of theory are employed.

[i] Free energy of solvation for the one-electron attachment reaction defined as follows: $\Delta\Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{solv}}(A^-) - \Delta G_{\mathrm{solv}}(A)$.

[j] Free energy difference in solution for the thermodynamic cycle shown in Figure S1. $\Delta G_{\mathrm{red}} = \Delta G_{\mathrm{g,298K}} + \Delta\Delta G_{\mathrm{solv}}$

[k] Absolute first half-wave reduction potentials. $E_{1/2} = \Delta G_{\mathrm{red}}/(-1 \times F)$

[l] First half-wave reduction potentials with respect to ferrocene/ferricenium. $E_{\mathrm{ref}} = -4.99$ V (reduction potential of $\mathrm{Fc/Fc^+}$).[16]

$$\begin{tikzcd}
A_{(g)} + e^-_{(g)} \arrow[r, "\Delta G_{gas}"] \arrow[d, "\Delta G_{solv}(A)"'] & A^-_{(g)} \arrow[d, "\Delta G_{solv}(A^-)"] \\
A_{(solv)} + e^-_{(g)} \arrow[r, "\Delta G_{red}"] & A^-_{(solv)}
\end{tikzcd}$$

$$\Delta\Delta G_{solv} = \Delta G_{solv}(A^-) - \Delta G_{solv}(A)$$

Figure S4. Thermodynamic cycle for the analysis of solution effects on the one-electron attachment $A + e^- \rightarrow A^-$ reaction.

Table S2. Solvation free energy differences ($\Delta\Delta G_{\mathrm{solv}}$) in eV between the neutral and the anion species of *p*-BQ, **1** and **2** computed at the B3LYP/cc-pVTZ level using different solvation models and the B3LYP/cc-pVTZ minimum-energy geometries.

	p-BQ	**1**	**2**
PCM	–2.023	–1.617	–1.623
CPCM	–2.022	–1.618	–1.625
SMD	–1.823	–1.447	–1.455

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