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Enol Cation Radicals in Solution. 4 [1] An Improved Synthesis of 4,6,7-Trimethylbenzofurans by Oxidation of β-Mesityl Substituted Enols

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Abstract. An improved synthetic access for the construction of 4,6,7-trimethylbenzofurans (**B1–B8**) through the one-electron oxidation of mesityl-substituted enols (**E1–E8**) is presented. The transformation can be accomplished in good to excellent yields by using various oxidants; i.e. tris(1,10-phenanthroline)iron(III) hexafluorophosphate, $FeCl_3$, $Ce(NH_4)_2(NO_3)_6$, $Cu(OTf)_2/Cu_2O$ or anodic oxidation.

Natural and synthetic benzo[*b*]furans exhibit a variety of physiological, pharmacological and toxic properties [2]. For example, they have found interest as β-blockers [3], A_1-selective adenosine antagonists [4] and as antioxidants [5]. In addition, they play an important role as photosensitizers, optical brighteners, fluorescence dyes and light protectors [6]. This ample significance has spurred the development of a wide spectrum of synthetic routes to benzofurans among which are the catalytic dehydrocyclization of alkyl phenols, the cyclodehydration of aryloxyketones, the reaction of copper acetylides with *o*-halophenols and many others [2].

Through our interest in the one-electron oxidation chemistry of enols we have recently become aware of a new, efficient synthetic access to 4,6,7-trimethylbenzofurans. When the stable simple enols [7] of the Fuson type **E1–E4** were treated with 2 equivalents of the well known one-electron oxidant, tris(*p*-bromophenyl)aminium hexachloroantimonate ($E_{1/2}^{red}$ = 0.67 V vs $FeCp_2$) (**TBPA**$^{+\cdot}$), the color of the reagent was discharged *within seconds* and the benzofurans **B1–B4** were obtained in good yields [1, 8]. From a synthetic point of view, however, this route to benzofurans proved to be less valuable, since the separation of the pure products from the triarylamine was only possible by elaborative chromatography (Scheme 1).

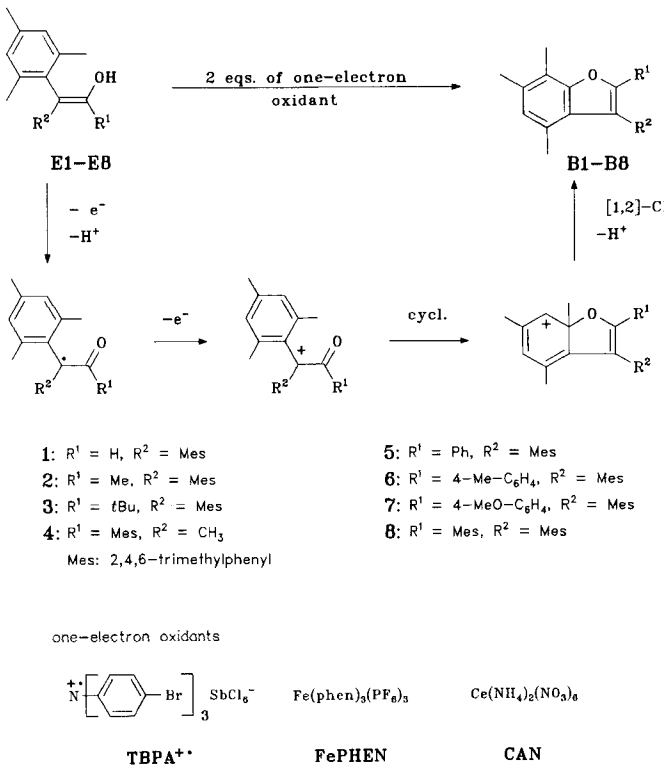
While our previous work [1, 8] has focused on understanding the reactivity of enol cation radicals in solution, we now wish to report how the use of mechanistic results has helped to develop a general preparative route to 4,6,7-trimethylbenzofurans. Thus, various other one-electron oxidants were tested for their potential in effecting the enol oxidation and in simplifying the work-up procedure. In addition, we have extended this methodology to the synthesis of the 2,3-diaryl-substituted benzofurans **B5–B8** from the corresponding enols **E5–E8**, which were prepared after procedures given by Fuson [9] and Rappoport [10–13]. Both the reactant and product oxidation potentials were determined by cyclic voltammetry in acetonitrile vs the ferrocene/ferrocenium couple ($FeCp_2$).

Table 1 Oxidation potentials of enols **E1–E8** and of benzofurans **B1–B8** determined by cyclic voltammetry at 100 $mV \cdot s^{-1}$ (vs $FeCp_2$).

	R^1	R^2	E_p^{ox} (**E**) [V]	$E_{1/2}^{ox}$ (**B**) [V]
1	H	Mes	0.67[a]	1.02[b]
2	CH_3	Mes	0.68[a]	0.99[a]
3	*t*Bu	Mes	0.64[a]	0.93[a]
4	Mes	CH_3	0.94[a]	0.89
5	Ph	Mes	0.61	0.87
6	*p*Tol	Mes	0.57	0.81
7	*p*An	Mes	0.51	0.69
8	Mes	Mes	0.76	0.94

[a] taken from reference [1] and [8].
[b] The reversible potential was determined at $v = 1000\ V \cdot s^{-1}$ at a 25 μm Au ultramicroelectrode.

Our recent mechanistic investigations have led to a detailed understanding of the above oxidative transformation (Scheme 1): After a one-electron oxidation of enols **E1–E8** (their oxidation potentials are provided in Table 1) the corresponding enol cation radicals undergo a rapid deprotonation. The resulting α-carbonyl radicals are oxidized (at potentials of ca. 300–500 mV lower than those of the enols [14]) to the α-carbonyl cation intermediates that cyclize intramolecularly and after a [1,2]-



Scheme 1

methyl shift the 4,6,7-trimethylbenzofurans are formed [1, 8]. This mechanistic scheme readily explains why two equivalents of a sufficiently strong one-electron oxidant ($E_{1/2}^{red} > 0.6$ V vs $FeCp_2$) are needed. In most cases the benzofurans **B1–B8** are more difficult to oxidize than the enols. **E1–E8** (s. Table 1) and their cation radicals are stable for seconds (except for **B1**$^{+\cdot}$). Hence, follow-up oxidation reactions can largely be avoided.

Tris(1,10-phenanthroline)iron(III) hexafluorophosphate (**FePHEN**), a well known outer-sphere oxidant ($E_{1/2}^{red} = 0.70$ V vs $FeCp_2$) [15], worked extremely well in the benzofuran synthesis providing yields ranging up to 99 %. The reaction could be accomplished either in acetonitrile or methylene chloride. A minor problem with this oxidant is the difficulty to detect the end point of the reaction by merely following the color change, since the red iron(II) salt exhibits a much higher extinction coefficient than the blue iron(III) salt. Hence, usually a fixed reaction time of 5 min was used. In most cases no chromatographic work-up was necessary, because sufficiently pure benzofurans (purity $\simeq$ 90–93 %) could be readily extracted in diethyl ether leaving behind the insoluble iron(II) salts, which can be readily recycled.

The other oxidants used in this study most likely do not operate via an outer-sphere mechanism [16], but they are readily available and easy to use. For example, the commercial oxidant, $FeCl_3$ ($E_{1/2}^{red} = 0.71$ V vs $FeCp_2$) [17], worked equally well in the oxidative benzofuran formation when methylene chloride was used as solvent (table 2). In acetonitrile the oxidation strength of the salt is largely diminished, most likely by complexation to the solvent. Similarly, in the reaction with other appropriately strong oxidants [18], like $Ce(NH_4)_2(NO_3)_6$ (**CAN**) and $Cu(OTf)_2$, the benzofurans were afforded in high yield. Again, recrystallization or chromatography of the benzofurans proved only necessary when a purity of >93 % was desired.

Electrooxidation is a viable alternative to using chemical oxidants in this transformation. In the anodic oxidation of enols **E1–E3, E5, E6** and **E8** in a triply-divided cell at a platinum electrode (current density: 0.1 A/cm^2) we obtained yields of 52–78 % benzofurans within 5 min in acetonitrile[1]. The yields are lower than with the chemical oxidants, because of partial diffusion of the product into other compartments of the cell. Thus, an undivided cell would be the optimum choice. For the work-up the

[1] Formation of 3 % of **B8** by ozonation of **E8** was described by Bailey about 20 years ago. It is important to note that he was unable to obtain **B8** by electrochemical oxidation of **E8**, s. ref. [21].

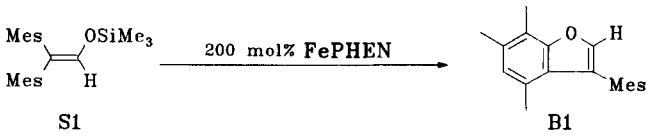
Table 2 Yields of benzofurans **B1–B8** in the oxidative cyclization of enols **E1–E8**.

	enols[a]		yield (%) of **B1–B8** with various oxidants						
	R^1	R^2	**TBPA**$^+$	**FePHEN** in CH_3CN	**FePHEN** in CH_2Cl_2	$FeCl_3$	**CAN**	$Cu(OTf)_2$/Cu_2O	anodic oxidation
E1	H	Mes	85[b]	84	76	83	76	83	75
E2	CH_3	Mes	84[b]	75[b]	89	64			78
E3	*t*Bu	Mes	82[b]	87	82	70	82		56
E4	Mes	CH_3	70[b][c]	70[c]	47[c]	60[c]			
E5	Ph	Mes		99	95	70			72
E6	*p*Tol	Mes		85	76	88	89		69
E7	*p*An	Mes		47[d]	48[d]	10[d]			
E8	Mes	Mes		99	91	78	88	94	52

[a] Mes: 2,4,6-trimethylphenyl, *p*Tol: 4-methylphenyl, *p*An: 4-methoxyphenyl.
[b] taken from reference [1] and [8].
[c] the other product is 1-mesitylvinyl mesityl ketone, s. ref. [1].
[d] several side products were detected but not identified.

solvent was switched from acetonitrile to cyclohexane and the electrolyte could readily be separated by filtration through silica gel.

At present, we probe this enol oxidation route for the synthesis of 3-formyl and 3-nitrobenzofurans starting from the corresponding β-dicarbonyl or α-nitroketone derived enols. Importantly, this new benzofuran synthesis is not necessarily restricted to stable enols, since enol cation radical chemistry is accessible through the selective oxidation of the enol tautomer starting from the corresponding ketones [19]. In addition, trialkylsilyl enol ethers can equally be used instead of enols in this oxidative cyclization [20], as demonstrated by the transformation of **S1** to **B1**.



S1 B1

Scheme 2

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Experimental

NMR spectra were recorded at 250 MHz (or 100 MHz for ^{13}C NMR) in $CDCl_3$. Chemical shifts are reported in δ and coupling constants in Hz. Two singlets within less than 0.01 ppm are denoted as 2 s. IR spectra are reported in cm^{-1}. The enols were synthesized by procedures given by Fuson [9] and Rappoport [10–13]. All enols were stable to oxygen, except for **E4**, which was stored and handled under nitrogen in a glovebox. As one-electron oxidants, we used tris(1,10-phenanthroline)iron(III) hexafluorophosphate [22], anhydrous ferric chloride (BASF), cupric triflate (Aldrich)/cuprous oxide (Aldrich) and ceric ammonium nitrate (Fluka). Acetonitrile (Rathburn Chemicals LTD, HPLC grade E) was distilled from CaH_2 under nitrogen atmosphere and methylene chloride (Roth, >99.5 % p.a.) from P_2O_5 under nitrogen. Yields are provided in table 2. Oxidation potentials were measured by cyclic voltammetry (CV), using an electrochemical cell equipped with a platinum disc (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a Ag wire as reference electrode (potentiostat: Princeton Applied Research Modell 362). The potential measurements were made on a 1 mM solution of the benzofuran in acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 0.1 $V \cdot s^{-1}$. All potentials were referenced against ferrocene ($E_{1/2}$ = 0.390 V_{SCE} [23]).

*General Procedure for the Synthesis of Benzofurans (**B1–B8**) using $Fe(phen)_3(PF_6)_3$*

Under nitrogen the enol (50 μmol) and $Fe(phen)_3(PF_6)_3$ (100 μmol) were weighed in a test tube that was closed by a rubber septum. The solvent (CH_3CN or CH_2Cl_2, 2.0 ml) was added by syringe. The solution was stirred at 25 °C for about 5 min although the blue colour (**FePHEN**) changed to red (Fe^{2+}-phenanthroline complex) within seconds. Thereafter the reaction mixture was quenched by addition of a saturated $NaHCO_3$ solution (1.0 ml), poured into CH_2Cl_2 (25 ml) and washed with saturated NaCl solution. The organic layer was concentrated in vacuo and the residue was extracted in diethylether. The insoluble Fe(II) complex was filtered off, the ether layer was dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by chromatography on silica gel (cyclohexene/CH_2Cl_2 = 2/1). Using the same procedure **B1** was obtained from **S1** in 67 % yield (without optimization [20]).

*General Procedure for the Synthesis of Benzofurans (**B1–B8**) using $FeCl_3$*

A test tube was loaded with the enol (50 μmol) and $FeCl_3$ (100 μmol), closed by a rubber septum, and 2.0 ml of CH_2Cl_2 was added by syringe. The solution was stirred at 25 °C until the color changed from green to yellow (5 min). The mixture was poured into water (25 ml) and extracted with diethyl ether. The ether layer was washed with saturated NaCl solution, dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by chromatography on silica gel (cyclohexane/CH_2Cl_2 = 2/1).

*General Procedure for the Synthesis of Benzofurans (**B1, B8**) using Cupric Triflate/Cuprous Oxide*

Via syringe a solution of the enol (50 μmol) in 1.0 ml of CH_3CN was added over 5 min to a solution of cupric triflate (100 μmol) and cuprous oxide (100 μmol) in CH_3CN (1.0 ml) at 25 °C. The resulting solution was stirred at 25 °C for 10 min, diluted with diethylether (20 ml), acidified with 5 % HCl solution and washed with saturated NaCl solution. The organic layer was dried (Na_2SO_4) and concentrated in vacuo.

*General Procedure for the Synthesis of Benzofurans (**B1, B3, B6, B8**) using Ceric Ammonium Nitrate (**CAN**)*

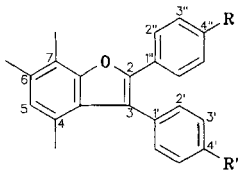
A solution of the enol (50 μmol) and **CAN** (100 μmol) in CH_3CN (2.0 ml) was stirred at 25 °C until the color changed (about 10 s). The solution was diluted with diethyl ether (10 ml), acidified with 5 % HCl, and washed with saturated NaCl solution. Thereafter it was dried (Na_2SO_4) and concentrated in vacuo.

*Synthesis of the Benzofurans (**B1–B3, B5, B6, B8**) by Electrolysis*

A solution of 0.1 M tetra-n-butylammonium hexafluorophosphate (25 ml) in CH_3CN and the enol (100 μmol) was electrolyzed in a three compartment cell, using a platinum net as anode, a graphite rod as cathode and a silver wire as reference electrode. After about 5 min at a potential of +1.0 $V_{Ag/AgCl}$ (potentiostat: Fa. Princeton Applied Research Modell 362) the current dropped down and the reaction was completed. The solution in the anodic compartment of the cell was removed, washed with saturated NaCl solution, dried over Na_2SO_4, and concentrated in vacuo. The solid remainder was dissolved in cyclohexane and filtered through silica gel to remove the electrolyte. The filtrate was evaporated in vacuo to provide the crude benzofuran.

Data of the benzofurans

Data of benzofurans **B1–B4** have been published in earlier articles [1, 8].



Scheme 3

B5: m.p.: 135–136 °C. – DC: R_f = 0.80 on silica gel M 60 using cyclohexane/methylene chloride = 2/1. – IR (neat) ν = 3000 cm^{-1} (m, C=CH), 2900 (s, CH), 1590 (s, C=C-Arom), 1580 (m), 1480 (s), 1430 (ss), 1370 (s), 1110 (s), 1060 (m), 920 (m), 845 (s), 770 (m), 755 (s), 730 (ss), 690 (s), 680 (s), 670 (m). – ^{1}H NMR ($CDCl_3$/250 MHz): δ = 1.86 (s, 3 H, *p*-CH_3-Mes); 2.02 (s, 6 H, *o*-CH_3-Mes), 2.37 (2 s, 6 H, 4,6-CH_3-Bf), 2.53 (s, 3 H, 7-CH_3-Bf), 6.76 (s, 1 H, 5-H-Bf); 6.99 (s, 2 H, H-Mes), 7.22-7.30 (m_c, 3 H, H-Ph), 7.51-7.57 (m, 2 H, H-Ph). – ^{13}C NMR ($CDCl_3$/100 MHz): δ = 11.53 (C-7-Me), 17.26 (C-4-Me), 19.16 (C-6-Me), 20.45 (C-2′a), 21.35 (C-4′a), 116.52 (C-3a); 117.17 (C-7), 124.94 (C-3″), 125.37 (C-5), 126.31 (C-1″), 127.51 (C-4″), 128.43 (C-3′), 128.58 (C-2″), 128.66 (C-4), 130.65 (C-3), 131.78 (C-6), 132.86 (C-1′), 137.45 (C-4′, 137.53 (C-2′), 148.11 (C-2), 153.72 (C-7a). – MS (70 eV): m/z (%) = 355 (28), 354 (100) [M$^+$], 339 (8), 219 (8), 138 (7), 105 (12), 88 (8), 86 (53), 81 (10), 49 (16), 47 (37). – HRMS (70 eV) $C_{26}H_{26}O$ calcd. 354.1984, found 354.1986

$C_{26}H_{26}O$	calcd.	C 88.09	H 7.39
(354.51)	found	C 87.99	H 7.46

B6: m.p.: 190–192. – DC: R_f = 0.77 on silicagel M 60 with cyclohexane/methylene chloride = 1/1. – IR (neat) ν = 3000 cm^{-1} (m, C=C-H), 2900 (m, CH), 1600 (m, C=C), 1490 (m), 1425 (m), 1100 (m), 920 (m), 900 (m), 840 (m), 810 (s), 720 (m). – ^{1}H NMR ($CDCl_3$/250 MHz): δ = 1.88 (s, 3 H, *p*-CH_3-Mes), 2.02 (s, 6 H, *o*-CH_3-Mes), 2.31 (2 s, 3 H, *p*-CH_3-Tol), 2.39 (2 s, 6 H, 4,6-CH_3-Bf), 2.52 (s, 3 H, 7-CH_3-Bf), 6.74 (s, 1 H, 5-H-Bf), 6.98 (s, 2 H, H-Mes), 7.07 (d, ^{3}J = 8.7 Hz, 2 H, H-Tol), 7.42 (d, ^{3}J = 8.7 Hz, 2 H, H-Tol). – ^{13}C NMR ($CDCl_3$/100 MHz): δ = 11.54 (C-7-Me), 17.26 (C-4-Me), 19.15 (C-6-Me), 20.46 (C-2′a), 21.34 (C-4′a + C-4″a), 115.70 (C-3a), 117.10 (C-7), 124.89 (C-3″), 125.44 (C-5), 126.19 (C-1″), 128.37 (C-3′), 128.49 (C-4″), 129.03 (C-4), 129.31 (C-2″), 130.77 (C-3), 132.58 (C-6), 137.36 (C-1′), 137.40 (C-4′), 137.59 (C-2′), 148.37 (C-2), 155.72 (C-7a). – MS (70 eV): m/z (%) = 370 (5), 369 (35), 368 (100) [M$^+$], 354 (11), 353 (7), 233 (7), 184 (6), 138 (6), 91 (5), 86 (19), 84 (31), 49 (6), 47 (7). – HRMS (70 eV) $C_{27}H_{28}O$ calcd. 368.2140, found 368.2139

$C_{27}H_{28}O$	calcd.	C 88.00	H 7.66
(368.53)	found	C 87.49	H 7.78

B7: m.p.: 138 °C. – DC R_f = 0.58 on silicagel M 60 cyclohexane/methylene chloride = 1/1. IR (neat) ν = 3000 (w, C=C-H), 2890 (s, CH), 2820 (m), 1600 (m, C=C), 1580 (m), 1550 (m), 1500 (ss), 1430 (s), 1240 (ss), 1160 (ss), 1020 (s), 900 (ss), 820 (s), 720 (ss). – ^{1}H NMR ($CDCl_3$/250 MHz): δ = 1.85 (s, 3 H, *p*-CH_3-Mes), 2.02 (s, 6 H, *o*-CH_3-Mes), 2.37 (2 s, 6 H, 4,6-CH_3-Bf), 2.51 (s, 3 H, 7-CH_3-Bf), 3.78 (s, 3 H, CH_3O-Ph), 6.72 (s, 1 H, 5-H-Bf), 6.79 (d, ^{3}J = 10 Hz, 2 H, H-An), 6.96 (s, 2 H, H-Mes), 7.43 (d, ^{3}J = 10 Hz, 2 H, H-An). – ^{13}C NMR ($CDCl_3$/100 MHz): δ = 11.54 (C-7-Me), 17.25 (C-4-Me), 19.13 (C-6-Me), 20.46 (C-2′a), 21.36 (C-4′a), 55.28 (OMe), 113.28 (C-3a), 114.09 (C-7), 124.67 (C-5), 126.17 (C-3″), 126.25 (C-1″), 126.39 (C-3′), 127.79 (C-4″), 128.32 (C-4), 128.38 (C-2″), 130.80 (C-3), 132.27 (C-6), 132.33 (C-1′), 133.01 (C-4′), 137.35 (C-2), 137.70 (C-2′), 159.13 (C-7a). – MS (70 eV): m/z (%) = 385 (10), 384 (33) [M$^+$], 369 (8), 291 (9), 121 (5), 119 (7), 88 (22), 86 (100), 85 (7), 84 (100), 83 (7), 71 (11), 69 (8), 57 (21), 55 (11), 49 (41), 47 (54), 43 (12). – HRMS (70 eV) $C_{27}H_{28}O_2$ calcd. 384.2089, found 384.2083

$C_{27}H_{28}O_2$	calcd.	C 84.34	H 7.34
(384.53)	found	C 83.92	H 7.52

B8: m.p.: 142 °C (colorless crystals). – DC: R_f = 0.76 on silica gel M 60 using cyclohexane/methylene chloride = 2/1. – IR (KBr): ν = 2910 cm^{-1} (ss, CH), 1600 (m, C=C), 1440 (s), 1370 (m), 1360 (m), 1290 (w), 1110 (s), 1030 (m), 920 (s), 850 (s). – ^{1}H NMR ($CDCl_3$/250 MHz): δ = 1.94 (s, 3 H, *p*-CH_3-Mes), 1.98 (s, 6 H, *o*-CH_3-Mes), 2.05 (s, 6 H, *o*-CH_3-Mes), 2.25 (s, 6 H, *p*-CH_3-Mes, 4-CH_3-Bf), 2.38 (s, 3 H, 6-CH_3-Bf), 2.43 (s, 3 H, 7-CH_3-Bf), 6.80 (s, 1 H, 5-H-Bf), 6.83 (s, 4 H, H-Mes). – ^{13}C NMR ($CDCl_3$/100 MHz): δ = 11.41 (C-7-Me), 17.36 (C-4-Me), 19.08 (C-6-Me), 20.73 (C-2″a), 20.81 (C-2′a), 21.15 (C-4′a and C-4″a), 117.29 (C-3a), 125.37 (C-7), 126.28 (C-5), 128.13 (C-4″), 128.37 (C-3″), 128.49 (C-1″), 128.66 (C-3′), 129.61 (C-1′), 132.09 (C-3), 136.78 (C-6), 137.76 (C-2″), 138.45 (C-4′), 138.57 (C-2′), 150.47 (C-2), 153.98 (C-7a). – MS (70 eV): m/z (%) = 397 (30), 396 (90) [M$^+$], 276 (18), 261 (10), 120 (16), 119 (15), 105 (20), 91 (12), 77 (8), 43 (10), 41 (14). – HRMS (70 eV) $C_{29}H_{32}O$ calcd. 396.2453, found 396.2448

$C_{29}H_{32}O$	calcd.	C 87.83	H 8.13
(396.59)	found	C 88.21	H 8.30

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[23] A value of $E_{1/2}$ = 0.390 V for ferrocene was measured in 0.1 M Bu_4NPF_6 (acetonitrile) vs. SCE (KCl).

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