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Supporting Information

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Supporting information for the paper

“Self-Supported and Clean One-Step Cathodic Coupling of Activated Olefins with Benzylbromides in a Flow Micro Reactor”

1. Experimental Details

1.1. Chemical Reagents

The reagents benzylbromide (Aldrich, 99%), 4-bromobenzylbromide (Aldrich, +98%), 4-iodobenzylbromide (Aldrich, +95%), 4-methylbenzylbromide (Aldrich, 97%), 4-methoxybenzylbromide (Aldrich, +98%), 1-phenylethylbromide (Aldrich, 97%), dimethylmaleate (Aldrich, 99%), dimethylfumarate (Aldrich, 99%), fumaronitrile (Aldrich, 98%), maleic anhydride (Aldrich, 98%), and 1,2-bis(bromomethyl)benzene (Fluka, +97%) were used without further purification. The solvent used was *N,N*-dimethylformamide (DMF, Fluka, 99%, stored over molecular sieve, H_2O ≤0.01%) and was further dried over molecular sieve 3A (Lancaster, 1-2 mm beads) for 72 h prior to use.[1] All solutions were degassed with nitrogen (BOC gases, UK) before cyclic voltammetric measurements.

1.2. Instrumentation

Cyclic voltammetric (CV) experiments were carried out with an Autolab PGSTAT30 system (Eco Chemie, The Netherland) in a conventional three electrode cell in the presence of supporting electrolyte (0.1 M n-Bu_4NBF_4). For conventional CV measurements, a Pt disc (diameter 0.5 mm) electrode was used as the working electrode. A Pt wire and silver wire (both diameter 0.1 mm) were used as the counter and the reference electrode, respectively. For microelectrode CV experiments a Pt micro-disc working electrode (diameter 25 µm) was used and a Pt wire and silver wire (both diameter 0.1 mm) were used as the counter and the reference electrode. Benzyl bromides and ferrocene (added as internal reference) with the same concentration were added to DMF containing 0.1 M n-Bu_4NBF_4.

A Harvard PHD 2000 syringe pump was used to pump the reaction solution without addition of electrolyte through the micro reactor cell system at controlled flow rate. The cell consisted of two glass plates (3 cm length, 2 cm width, 6 mm thickness) forming the bottom and top with two holes connecting PEEK tubes (I.D. 0.24 mm) which acted as the flow inlet and outlet. Two equally sized Pt foils (4 mm width and 15 mm length, 50 µm thickness, Goodfellow Cambridge Limited, purity 99.99%) were used as working and counter electrodes and PTFE spacers (Bohlender GmbH, Germany) with thicknesses of approximately 120 µm and 250 µm were used to produce a rectangular flow reacting zone (3 mm width and 15 mm length) with a working area of 45 mm^2 and inter-electrode distance of 160 µm and 320 µm, as described in the reference.[2]

A parallel cell (as shown in Figure 1) containing two equally sized cells was also evaluated using coupling reaction of dimethylfumarate with benzylbromide. The parallel cell was made from two equally sized Pt foils (8 mm width and 15 mm length, 50 µm thickness) and PTFE spacers with two equally sized paralleled rectangular windows to generate the parallel reaction cell. The parallel cells had a split inlet and individual outlet. Examination of flow indicated that each cell had an equal flow rate by measuring volume flow rate.

The electrochemical coupling of an activated olefin with benzyl bromide was carried out with controlled potential and in the absence of supporting electrolyte. During typical reaction runs, product samples were collected in a product vial for a duration of 5 minutes. Samples were analysed by GC/MS (Varian 2000) equipped with a capillary column (CP SIL 8, 30 m length, Phenomenex). The GC column temperature was held initially at 70 ^{o}C for 4 min, ramped at 20 ^{o}C/min to reach 240 ^{o}C which was then held for 12 min. The internal standard method was used for the quantitative determination of product yields with decane as an internal standard added to the reactant solution prior to reaction. The products were also identified using ^{1}H and ^{13}C NMR analysis.

1.3. Characterization of Products

All products produced by electrosynthesis have been purified and characterised by standard methods:

2-Benzyl-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.39-2.44 (1H, m, COCH), 2.64-2.78 (2H, m, $COCH_2$), 3.03-3.12 (2H, m, $PhCH_2$), 3.63 (3H, s, CO_2CH_3), 3.67 (3H, s, CO_2CH_3), 7.14-7.28 (5H, m, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=34.9, 37.8, 43.0, 51.8, 52.0, 126.8, 128.6 (2C), 129.0 (2C), 138.2, 172.2 (C=O), 174.2 (C=O). MS: *m/z* (%): 236 (12) [M^+], 205 (22) [$C_{12}H_{13}O_3^+$], 176 (100) [$C_{11}H_{12}O_2^+$], 163 (22) [$C_{10}H_{11}O_2^+$], 145 (24) [$C_{11}H_{13}^+$], 131 (56) [$C_{10}H_{11}^+$], 117 (42) [$C_9H_9^+$], 103 (10) [$C_8H_7^+$], 91 (28) [$C_7H_7^+$]. Retention time 12.4 min.

2-(4-Methyl-benzyl)-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.31 (3H, s, $PhCH_3$), 2.37-2.42 (1H, m, COCH), 2.63-2.73 (2H, m, $COCH_2$), 2.99-3.10 (2H, m, $PhCH_2$), 3.63 (3H, s, CO_2CH_3), 3.68 (3H, s, CO_2CH_3), 7.10 (4H, d, J 7.9 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=21.1, 34.9, 37.4, 43.1, 51.8, 52.0, 128.9 (2C), 129.3 (2C), 135.0, 136.3, 172.4 (C=O), 174.8 (C=O). MS: *m/z* (%): 250 (10) [M^+], 219 (20) [$C_{13}H_{15}O_3^+$], 191 (100) [$C_{12}H_{15}O_2^+$], 176 (22) [$C_{11}H_{12}O_2^+$], 160 (20) [$C_{11}H_{12}O^+$], 144 (40) [$C_{11}H_{12}^+$], 131 (35) [$C_{10}H_{11}^+$], 105 (25) [$C_8H_9^+$], 91 (10) [$C_7H_7^+$]. Retention time 12.9 min.

2-(4-Bromo-benzyl)-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.37-2.43 (1H, m, COCH), 2.64-2.77 (2H, m, $COCH_2$), 2.96-3.10 (2H, m, $PhCH_2$), 3.65 (3H, s, CO_2CH_3), 3.67 (3H, s, CO_2CH_3), 7.04 (2H, d, J 8.4 Hz, Ph), 7.42 (2H, d, J 8.4 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=35.0, 37.1, 42.9, 51.9, 52.0, 130.8 (2C), 131.7 (2C), 132.0, 137.2, 172.1 (C=O), 174.4 (C=O). MS: *m/z* (%): 315 (12) [M^+], 284 (12) [$C_{12}H_{12}BrO_3^+$], 256 (100) [$C_{11}H_{12}BrO_2^+$], 225 (12) [$C_{10}H_9BrO^+$], 209 (25) [$C_{10}H_9Br^+$], 197 (12) [$C_9H_9Br^+$], 170 (12) [$C_7H_6Br^+$], 89 (12) [$C_7H_6^+$]. Retention time 14.1 min.

2-(4-Iodo-benzyl)-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.37-2.42 (1H, m, COCH), 2.63-2.75 (2H, m, $COCH_2$), 2.95-3.00 (2H, m, $PhCH_2$), 3.65 (3H, s, CO_2CH_3), 3.67 (3H, s, CO_2CH_3), 6.92 (2H, d, J 8.4 Hz, Ph), 7.62 (2H, d, J 8.4 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=35.0, 37.2, 42.8, 51.9, 52.0, 130.9, 131.1 (2C), 137.6 (2C), 138.0, 172.1 (C=O), 174.4 (C=O). MS: *m/z* (%): 362 (12) [M+], 331 (8) [$C_{12}H_{12}IO_3^+$], 303 (100) [$C_{11}H_{12}IO_2^+$], 272 (12) [$C_{10}H_{19}IO^+$], 256 (12) [$C_{10}H_{19}I^+$], 217 (10) [$C_7H_6I^+$], 90 (10) [$C_7H_6^+$]. Retention time 15.6 min.

2-(4-Methoxy-benzyl)-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.36-2.44 (1H, m, COCH), 2.64-2.75 (2H, m, $COCH_2$), 3.01-3.06 (2H, m, $PhCH_2$), 3.64 (3H, s, CO_2CH_3), 3.68 (3H, s, CO_2CH_3), 3.79 (3H, s, $PhOCH_3$), 6.77 (2H, d, J 7.9 Hz, Ph), 7.23 (2H, d, J 7.9 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=34.9, 37.8, 42.9, 51.8, 52.5, 121.4 (2C), 129.6 (2C), 133.6, 139.7, 159.8, 172.3 (C=O), 174.7 (C=O). MS: *m/z* (%): 266 (87) [M+], 235 (30) [$C_{13}H_{15}O_4^+$], 207 (100) [$C_{12}H_{15}O_3^+$], 176 (50) [$C_{11}H_{12}O_2^+$], 148 (50) [$C_{10}H_{12}O^+$], 121 (20) [$C_8H_9O^+$], 103 (10) [$C_8H_7^+$], 91 (27) [$C_7H_7^+$]. Retention time 13.9 min.

2-(1-phenzyl-ethyl)-succinic acid dimethyl ester: ^{1}H-NMR (400 MHz, $CDCl_3$): d=1.27-1.29 (3H, m, $PhCHCH_3$), 2.55-2.62 (1H, m, COCH), 2.71-3.13 (3H, m, $COCH_2$, PhCH), 3.62 (3H, s, CO_2CH_3), 3.75 (3H, s, CO_2CH_3), 7.15-7.33 (5H, m, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): d=16.4, 32.3, 35.3, 42.4, 51.7, 51.8, 127.2, 127.5 (2C), 128.4 (2C), 128.8, 172.8 (C=O), 174.3 (C=O). MS: *m/z* (%): 250 (4) [M^+], 219 (30) [$C_{13}H_{15}O_3^+$], 190 (100) [$C_{12}H_{14}O_2^+$], 177 (28) [$C_{11}H_{13}O_2^+$], 159 (23) [$C_{11}H_{11}O^+$], 145 (54) [$C_{11}H_{13}^+$], 131 (34) [$C_{10}H_{11}^+$], 115 (15) [$C_9H_7^+$], 105 (72) [$C_8H_9^+$], 91 (12) [$C_7H_7^+$]. Retention time 12.7 min.

2-Benzyl succinonitrile: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.64-2.67 (2H, m, $CNCH_2$), 3.02-3.19 (3H, m, CNCH, $PhCH_2$), 7.26-7.39 (5H, m, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.1, 30.1, 37.0, 115.4 (CN), 118.5 (CN), 128.2, 129.1 (2C), 129.3 (2C), 134.4. MS: *m/z* (%): 170 (8) [M^+], 91 (100) [$C_7H_7^+$]. Retention time 12.3 min.

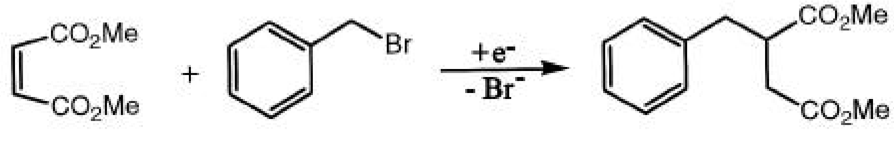
2-(4-Bromo-benzyl)-succinonitrile: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.66-2.68 (2H, m, $CNCH_2$), 3.03-3.10 (3H, m, CNCH, $PhCH_2$), 7.18 (2H, d, J 8.1 Hz, Ph), 7.53 (2H, d, J 8.1 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.2, 30.0, 36.4, 115.2 (CN), 118.1 (CN), 130.7, 131.0 (2C), 132.0 (2C), 133.3. MS: *m/z* (%): 249 (37) [M^+], 170 (100) [$C_7H_6Br^+$], 90 (27) [$C_7H_6^+$]. Retention time 14.7 min.

2-(4-Methyl-benzyl)-succinonitrile: ^{1}H-NMR (400 MHz, $CDCl_3$): d=2.35 (3H, s, $PhCH_3$), 2.63-2.77 (2H, m, $CNCH_2$), 3.03-3.12 (3H, m, CNCH, $PhCH_2$), 7.19 (2H, d, J 8.1 Hz, Ph), 7.28 (2H, d, J 8.1 Hz, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.0, 21.1, 30.2, 36.6, 115.2 (CN), 118.1 (CN), 129.0 (2C), 129.9 (2C), 131.2, 137.9. MS: *m/z* (%): 184 (25) [M+], 105 (100) [$C_8H_9^+$], 77 (12) [$C_6H_5^+$]. Retention time 13.1 min.

1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylic acid anhydride: ^{1}H-NMR (400 MHz, $CDCl_3$): 2.73-3.32 (4H, m, $PhCH_2$), 3.4-3.7 (2H, m, COCH), 7.21 (4H, m, Ph). MS: *m/z* (%): 202 (1) [M^+], 203 (16) [M+H], 175 (12) [$C_{11}H_{11}O_2^+$], 174 (100) [$C_{11}H_{10}O_2^+$], 130 (30) [$C_{10}H_{10}^+$], 129 (96) [$C_{10}H_9^+$], 128 (32) [$C_{10}H_8^+$], 115 (26) [$C_9H_7^+$]. Retention time 11.6 min.

1.4. Additional Electrochemical and Literature Information

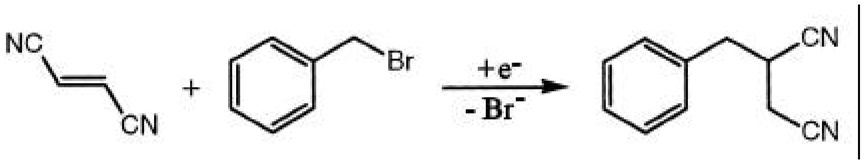
1.4.1. One-step micro reactor electrosynthesis of 2-benzyl dimethylsuccinate



(1)

The C-C coupling of benzylbromide with dimethylmaleate (see equation 1) has been described in the literature as a multi-step Grignard coupling reaction sequence.[3a] Alternatively, a photochemical procedure based on electron transfer to a photo-sensitizer has been proposed for the coupling of methylbenzene and dimethylsuccinate.[3b] but resulted in a complex mixture of reaction products. In contrast, the process described in this study is based on a clean one-step cathodic coupling process optimised for micro reactor flow through conditions (see equation 1). Dimethylmaleate and dimethylfumarate are known to be reduced in a one-electron processes, both leading to the dimethylfumarate radical anions as reactive intermediates followed by slow hydrodimerization.[4] Cyclic voltammetry at micro- and macroelectrodes confirms this behaviour.

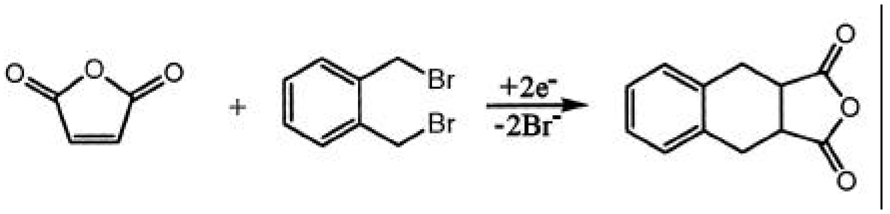
1.4.2. One-step micro reactor electrosynthesis of 2-benzylsuccinonitrile



(2)

The coupling of benzylbromide with fumaronitrile (equation 2) has been described in the literature using a photochemical process in the presence of organometallic catalysts.[6] It has been suggested[7] that substituents at the double bond in the olefin may have a significant effect on the competition between dimerization and hydrogenation in the electrochemical reduction process. Olefins with strong electron withdrawing groups are often more easily reduced and the resulting radical anions are more stable and inert towards H-abstraction processes, which lead to hydro-dimerization products. For fumaronitrile, cyclic voltammograms are chemically irreversible over a scan rate range of 0.1 to 10 V/s, suggesting rapid hydro-dimerization of the radical anion (see Figure 2). In the presence of benzylbromide, a shift of the irreversible reduction process to more positive potentials is observed consistent with a fast chemical follow-up reaction. In synthesis experiments the coupling product, 2-benzylsuccinonitrile, is isolated in good yield (see Table 1).

1.4.3. One-step micro reactor electrosynthesis of 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid anhydride



(3)

Maleic anhydride reduction processes were found to be chemically irreversible, even at scan rates of 10 V/s. This suggests that the dimerization of maleic anhydride occurs rapidly.[8] The electrochemical formation of 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid anhydride has been reported previously by Utley and coworkers[9] who obtained 44% yield in a cathodic process. With bromomaleic anhydride as the starting material and at a mercury pool electrode the same C-C coupling product could also be obtained.[10] This reaction has also been observed at a nickel contact without electrochemical potential control[11] and in the presence of sacrificial zinc[12]. A photochemical approach based on various starting materials has also been suggested.[13] Direct Diels-Alder coupling of the ortho-benzoquinodimethane generated as a short lived intermediate was also reported.[14] Here, it is shown that 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid anhydride can be obtained in high yield from a simple and versatile micro reactor electrosynthesis process (equation 3).

From cyclic voltammograms (see Figure 3), it can be seen that reduction of maleic anhydride occurs with a peak potential of -0.75 V vs. Ag (curve i) and the reduction of 1,2-bis(bromomethylbenzene) takes place at a much more negative peak potential of –1.65 V vs. Ag (curve ii). Both reduction responses are completely chemically irreversible over a scan rate range of 0.1 to 10 V/s. However, the addition of 1,2-bis(bromomethyl)benzene into a solution of maleic anhydride leads to a characteristic shift in the onset potential for reduction consistent with a new and fast chemical reaction between the maleic anhydride radical anion and 1,2-bis(bromomethyl)benzene. In the presence of increasing amounts of the 1,2-bis(bromomethyl)benzene, the cyclic voltammetric reduction current for maleic anhydride is found to be constant, indicating a one-electron transfer between maleic anhydride and 1,2-bis(bromomethyl)benzene. Micro reactor electrolysis of maleic anhydride in the presence of 1,2-bis(bromomethyl)benzene showed that 82% of maleic anhydride was converted to give the adduct product 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid anhydride[15] (equation 3). In this case, only a small amount of xylene, mono-substituted product and 2-methyl benzyl bromide were also detected (see Entry 16 in Table 1 in the paper). From the additional broad current response observed at *ca.* -1.0 V *vs.* Ag (See Figure 4) the occurrence of an overall (at least) two electron process is inferred. Further work will be required to study the mechanism of individual processes in more detail and to quantify important rate and process parameters.

1.4.4. Cyclic Voltammetry Data

Conventional cyclic voltammograms for each reactant were obtained at 0.5 mm diameter platinum disc electrode immersed in 0.1 M *n*-Bu_4NBF_4-DMF solution containing 3 mM reactant at scan rate of 1 V/s. The reduction halfwave potentials ($E_{1/2}$) obtained for each reactant are shown in Table 1. It should be mentioned that the number of electrons transferred for reduction of dimethylfumarate still remains one after addition of benzyl bromide.

Table 1 The reduction halfwave potentials ($E_{1/2}$) for each reactant

Reagent	$E_{1/2}$/V *vs.* Ag	Reagent	$E_{1/2}$/V *vs.* Ag
Maleic anhydride	-0.65	4-Bromobenzylbromide	-1.73
Dimethylfumarate	1.17	1-Phenylethylbromide	-1.77
Dimethylmaleate	-1.44	4-Methylbenzylbromide	-1.78
o-Xylylene dibromide	-1.55	4-Methoxybenzylbromide	-1.9
4-Iodobenzylbromide	-1.66	Ferrocene	0.75

In order to determine the overall number of electrons involved in the cathodic processes, CV experiments using a 25 μm diameter Pt micro-disc working electrode for dimethylfumarate, fumaronitrile and maleic anhydride were performed in DMF solution containing ferrocene (added as a standard) for each reagent with 0.1 M *n*-Bu_4NBF_4. In this case, the limiting current (I_{lim}) can be expressed using equation (4).

$$I_{\text{lim}} = 4nFDCr \quad (4)$$

In this expression, I_{lim} is the limiting current, n refers to the number of electrons transferred at the electrode, *F* is Faraday constant (96,485 C/mol), *D*, *C* and *r* refer to the diffusion coefficient, the concentration of reactant in the solution and the radius of the micro-disc electrode. The electrochemical oxidation of ferrocene (D = 1.0 × 10^{-9} m^2s^{-1})[2] serves as a "calibration" one electron transfer process. The calibrated value of the radius can then be employed for calculation of 'n' when using the measured limiting current of reactant. The calculated 'n' value (see Table 2) clearly confirms one electron processes in all cases.

Table 2. Cyclic voltammetry data obtained in 0.1 M *n*-Bu_4BNF_4-DMF for the reduction of olefins at a scan rate of 10 mV/s at a 25 µm diameter Pt micro-disc working electrode.

Reactant	**C_R[a]/molm^3**	**D[b]/ 10^{-9} m^2s^{-1}**	**$I_{lim\text{-}R}$[c]/ 10^{-9} A**	**n_{cal}[d]**
Dimethylfumarate	4.3	1.04[16]	19.5	0.9
Fumaronitrile	5.3	0.65[16]	16.9	1.0
Maleic anhydride	5.1	0.65[e]	14.0	0.86
Benzyl bromide	3.0	1.0[17]	26.0	1.8

[a] C_R is the concentration of the reactant. [b] D refers to the diffusion coefficient. [c] $I_{lim\text{-}R}$ is the limiting current of the reactant. [d] The n_{cal} is the calculated number of electrons transferred at the electrode, [e] Assumed to be similar to the value for fumaronitrile.

2.5 Bromine testing using 5% starch solution

0.75 g of sodium iodide was added to 1 ml of the product mixture. After sodium iodide completely dissolved, 1 ml of 5% starch solution was added to. No characteristic blue-black colour was observed. For comparison, a positive testing was also conducted in which 0.75 g of sodium iodide was added to 1 ml of 5 mM bromine (the same concentration as that to be obtained in the product mixture) in DMF solvent. After sodium iodide completely dissolved, 1 ml of 5% starch solution was added to, the characteristic blue-black colour was quickly observed because bromine oxidized the iodide to iodine which changed starch colour. A negative testing was also carried out under the same conditions by using sodium bromide replacing bromine. No blue-black colour was observed after adding starch solution.

References

[1] R.D. Burfield and R.H. Smithers, *J. Org. Chem.* **1978**, *43*, 3966.

[2] P. He, P. Watts, F. Marken and S.J. Haswell, *Electrochem. Comm.* **2005**, *7,* 918.

[3] a) S. Alder, *Justus Liebigs Ann. Chem.* **1949**, 565, 99; b) M. Mella, M. Fagnoni and A. Albini, *Eur. J. Org. Chem.* **1999**, *9*, 2137.

[4] a) A.J. Bard, V.J. Puglisi, J.V. Kenkel and A. Lomax, *Faraday Discuss.Chem. Soc.* **1973**, *56*, 353; b) J.P. Petrovich, M.M. Baizer and M.R. Ort, *J. Electrochem. Soc.* **1969**, *116*, 743; c) E. Lamy, L. Nadjo and J.M. Saveant, *J. Electroanal. Chem.* **1973**, *42*, 189; d) C. Degrand and H. Lund, Nouv. *J. Chim.* **1977**, *1*, 35; e) E.A. Casanova, M.C. Dutton, D.J. Kalota and J.H. Wagenknecht, *J. Electrochem. Soc.* **1993**, *140*, 2565.

[5] A.J. Bard and L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, pp. 496.

[6] B. Giese and G. Thoma, *Helv. Chim. Acta* **1991**, *74*, 1135.

[7] a) M. Fruianu, M. Marchetti, G. Melloni, G. Sanna and R. Seeber, *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 2039; b) V.J. Puglisi and A.J. Bard, *J. Electrochem. Soc.* **1972**, *119*, 829.

[8] I. Fussing, M. Gullu, O. Hammerich, A. Hussain, M.F. Nielsen and J.H.P Utley, *J. Chem. Soc. Perkin Trans. 2* **1996**, 649.

[9] A. Hussain, M. Motevalli, J.H.P. Utley, P.B. Wyatt and Y. Gao, *J. Org. Chem.* **1993**, *58*,

3578.

[10] E. Eru, G.E. Hawkes, J.H.P. Utley and P.B. Wyatt, *Tetrahedron* **1995**, *51*, 3033.

[11] S. Inaba, R.M. Wehmeyer, M.W. Forkner and R.D. Rieke, *J. Org. Chem.***1988**, *53*, 339.

[12] B.H. Han and B.P. Hee, *J. Org. Chem.* **1982**, *47*, 751.

[13] A. Ouchi and Y. Koga, *Chem. Commun.* **1996**, *17*, 2075.

[14] J.H.P. Utley, Y. Gao, J. Gruber and R. Lines, *J. Mater. Chem.* **1995**, *5*, 1297; (b) A. Ouchi, Z. Li, M. Sakuragi and T. Majima, *J. Am. Chem. Soc.* **2003**, *125*, 1104.

[15] P. Muller and M. Rey, *Helv. Chim. Acta* **1982**, *65*, 1157.

[16] F. Zhou, P.R. Unwin and A.J. Bard, *J. Phys. Chem.* **1992**, *96*, 4917.

[17] C.P. Andrieux, A.L. Georande and J.M. Savéant, *J. Am. Chem. Soc.* **1992**, *114*, 6892.

Figure 1

Schematic representation of the parallel electrochemical cell. The arrows show reagent flow direction.

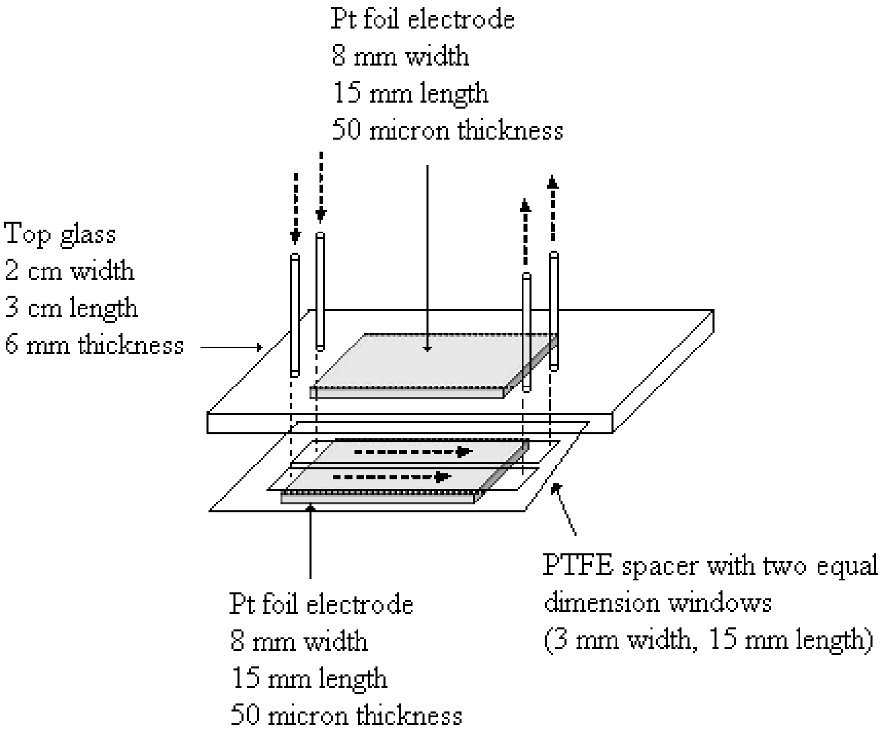


Figure 2

Cyclic voltammograms obtained at a 0.5 mm diameter platinum disc electrode immersed in 0.1 M *n*-Bu$_4$BNF$_4$-DMF: (i) 3 mM fumaronitrile at scan rate of 0.3 V/s, (ii) 3 mM fumaronitrile in the presence of 3 mM benzyl bromide at scan rate of 0.3 V/s.

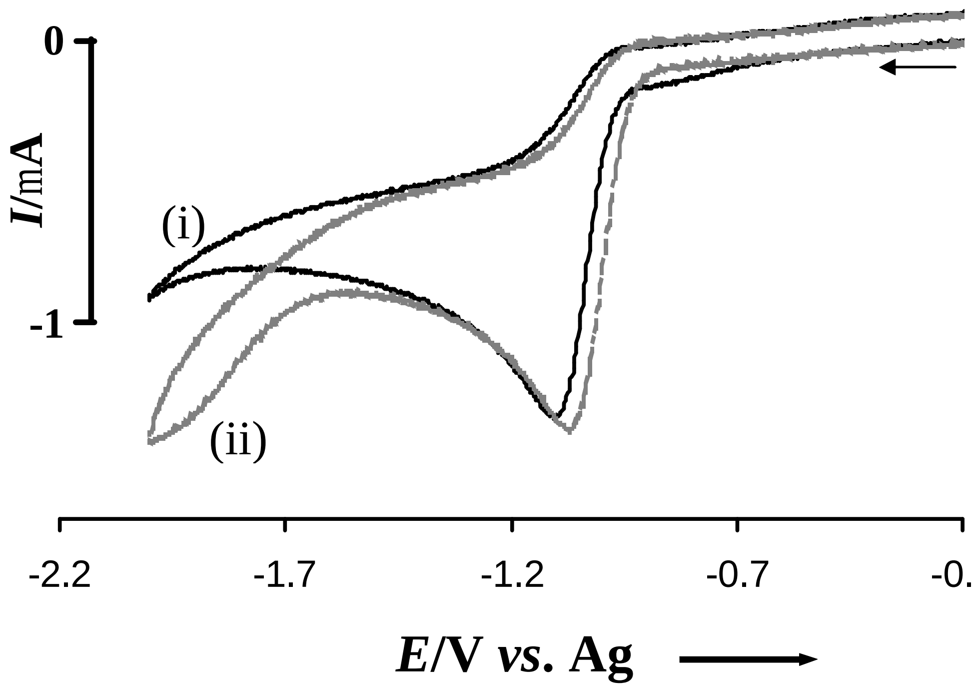


Figure 3

Cyclic voltammograms obtained at a 0.5 mm diameter platinum disc electrode immersed in 0.1 M *n*-Bu_4BNF_4-DMF: (i) 3 mM maleic anhydride at scan rate of 1 V/s, (ii) 2 mM 1,2-bisbromomethylbenzene at scan rate of 1 V/s, (iii) 3 mM maleic anhydride in the presence of 4.5 mM 1,2-bisbromomethylbenzene at scan rate of 0.3 V/s.