Supporting Information

Exploring the electrochemistry in the renewable solvent Dihydrolevoglucosenone (Cyrene^{TM})

José Manuel Ramos-Villaseñor,[a,b] Jessica Sotelo-Gil,[b] Maricarmen Paola Flores-Morales,[b] Rubén César Vásquez Medrano[c] and Bernardo Antonio Frontana-Uribe*[a,b]

[a]Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Toluca, 50200, Estado de México, México.

[b]Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, Ciudad de México, México.

[c]Depto. Ing. y. C. Químicas, Universidad Iberoamericana, Prol. Reforma 880, 01219, Ciudad de México, México.

*Corresponding author: bafrontu@unam.mx

Content

General

Dihydrolevoglucosenone (DLG or Cyrene^{TM}) was purchased from Sigma-Aldrich (98.5%). Prior to use in electrochemistry, a purification process is required. Briefly, it was filtered in silica gel (230-400 mesh) combined with activated carbon, then dried over magnesium sulphate and distilled under vacuum at 60°C at 4 mmHg, stored under a nitrogen atmosphere. 3-*tert*-butyl-4-hydroxyanisole (Sigma Aldrich 98%), 3,4-Ethylenedioxythiophene (Sigma Aldrich 97%), Indole (Sigma Aldrich 97%), 4-Ethylmorpholine (Sigma Aldrich 99%) and were used without any treatment. Bu_4NBF_4 (Sigma-Aldrich 99%), Bu_4NPF_6 (Sigma-Aldrich 98%), Bu_4NClO_4 (Sigma Aldrich 95%), Et_4NBF_4 (Sigma-Aldrich 99%), Et_4NPF_6 (Sigma-Aldrich 99%) were recrystallised three times prior to use according to the literature[1]. *N*-(aminobenzyliden)phthalimide was synthesised according to the procedure reported[2]

Electrochemistry

Cyclic voltammetry (CV) and chronoamperometry (CA) experiments were carried out using a Metrohm Autolab PGSTAT101 potentiostat connected to a PC and controlled using the NOVA 2.1 software package. A three-electrode set-up consisting of a 1.5 mm diameter glassy carbon working electrode and a Pt counter electrode was used. The reference used was an $Ag/AgNO_3$ reference electrode containing 10 mM of $AgNO_3$, 0.1 M of Bu_4NClO_4 in acetonitrile separated from the bulk solution using a ceramic frit. Prior to each experiment, the working electrode was polished using alumina paste (0.03 µm), a wet polishing cloth, followed by rinsing with distilled water and drying. The ohmic was compensated at 90% using a positive feedback method with a resistance value of 2000 Ω. The first cycle was read out, and the cut-off current density for the electrochemical windows was taken at least50 times the capacitive current density.

Conductivity measurements

Conductivity measurements were carried out with a Mettler Toledo EasyPlus P30 conductimeter using an INLAB760 model dip probe with a cell constant of 0.805 cm^{-1}. Typically, 10 mL of solution was added to the conductivity cell and then stirred, and the temperature of the solution was controlled with a thermostatic bath (25 °C ± 0.3 °C) throughout the experiment. The dip probe contains a thermistor, and the temperature of the solution was recorded during each experiment.

Table S1.- Molar Conductivity (Λ) and the corresponding concentration (c) of supporting electrolytes in dihydrolevoglucosenone at T = 298.15 K.

C	Λ	C	Λ	C	Λ	C	Λ	C	Λ	C	Λ	C	Λ
Bu_4NBF_4		Bu_4NPF_6		Bu_4ClO_4		Bu_4NBPh_4		Et_4NBF_4		Et_4NPF_6		$MeEt_3NBF_4$	
0.004	7.225	0.004	6.675	0.004	6.75	0.003	5.072	0.004	8.7	0.004	8.437	0.004	9.227
0.006	6.97	0.006	6.62	0.006	6.56	0.004	4.755	0.006	8.5	0.006	8.36	0.006	9.045
0.008	6.864	0.008	6.67	0.008	6.46	0.005	4.485	0.008	8.2	0.008	8.288	0.008	8.863
0.01	6.5	0.01	6.571	0.01	6.36	0.006	4.259	0.01	8.098	0.01	8.188	0.01	8.73
0.02	6.33	0.02	6.5	0.02	5.78	0.007	4.080	0.02	7.87	0.02	7.69	0.02	8.202
0.03	5.7968	0.03	6.325	0.03	5.33	0.008	3.962	0.03	7.638	0.03	7.35	0.03	7.69
0.05	5.5025	0.05	5.649	0.05	5.07	-	-	0.05	7.397	0.05	6.827	0.05	7.374
0.08	5.055	0.08	5.187	0.08	5	-	-	0.08	7.076	0.08	6.149	0.08	6.969
0.1	7.225	0.1	4.828	0.1	6.75	-	-	0.1	6.923	0.1	5.842	0.1	6.545

Considering a symmetrical electrolyte MX; at infinite dilution it is assumed the complete dissociation of the solute into the species M^+ and X^-. the corresponding association equilibrium can be represented by equation (1):

$$MX \leftrightarrow M^+ + X^- \#(1)$$

$$\Lambda = \gamma\Lambda_0\left[1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3\right] - \frac{(\rho\kappa)}{(1+\kappa R)}\left[1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \frac{\kappa R}{12}\right]\#(2)$$

$$\rho = \frac{Fe}{3\pi\eta_0}\#(3)$$

$$q = \frac{e^2}{8\pi\varepsilon kT}\#(4)$$

$$\kappa^2 = 16\pi N_A q\#(5)$$

$$K_A = \frac{1-\gamma}{c\gamma^2 f_\pm^2}\#(6)$$

$$f_\pm^2 = exp[-(\kappa\beta)/2(1+\kappa R]\#(7)$$

$$\gamma = -1 + \left(1 + 4K_A c f_{\pm}^{2}\right)^{1/2} / 2K_A c f_{\pm}^{2} \#(8)$$

Where C_1-C_5 are functions of t and ln t (t =κR)

$$C_1 = -0.09753 + 0.08185t - 0.04144t^2 + 0.01114t^3 \#(9)$$

$$C_2 = 0.11798 - 0.18737t + 0.09052t^2 - 0.02393t^3 + 0.08358\ln t \#(10)$$

$$C_3 = -0.19454 + 0.39764t - 0.37557t^2 + 0.25118t^3 - 0.07843t^4 - 0.10296\ln t \#(11)$$

$$C_4 = -0.04724 + 0.06445t - 0.07419t^2 + 0.01784t^3 + 0.12428\ln t + 0.09863t\ln t \#(12)$$

$$C_5 = 0.84185 - 0.90051t + 0.07809t^2 - 0.05333t^3 + 0.50097\ln t + 0.45252t\ln t \#(13)$$

R is the distance centre to centre between ions in the ion-pair formed, κ is the Debye parameter, $\beta = 2q$ (where q is the Bjerrum critical distance), e is the proton charge, ε is the dielectric constant of the solvent; F is the Faraday´s constant, η is the viscosity of the solvent, K_A is the association constant. In these expressions, γ is the degree of dissociation, the mean activity coefficient of free ions, $f^2_{\pm}$. The values of the Λ° and K_A were adjusted, minimising the standard deviation (σ) (Eq. 8) for a sequence of R values.

$$\sigma = \left[\sum (\Lambda_{m,j(Calc)} - \Lambda_{m,j(Exp)})^2 / (n-2)\right]^{1/2} \#(14)$$

Where the best fit of the R value corresponds to the minimum in σ *vs.* R curves and the R values were varying from Bjerrum distance until the $R = a + d$, where a is the sum of crystallographic radii of anion and cation, and d is the solvent space obtained from the relation

$$d = 1.183(M/\rho_0)^{1/3} \#(15)$$

Where M is the molecular weight of the solvent and ρ_0 its density.

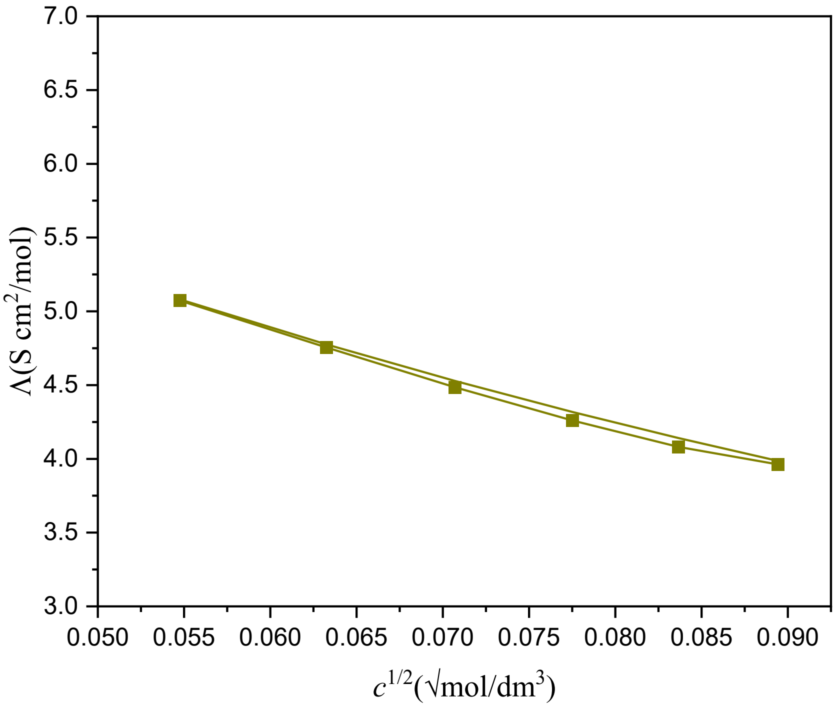

Figure S1.- Molar conductivities of tetrabutyl ammonium tetraphenylborate *vs*. square root of the concentration in DLG at 298.15 K. Symbols denote the experimental data and line denote the LWPT calculations.

Viscosity behaviour of pure DLG

The viscosity was measured using a Brookfield DV-III viscosimeter with a spindle size of S62, and the temperature was maintained at 25 °C with a thermostatic bath throughout the experiment.

Table S2- Summary of the viscosity values of DLG at different temperatures and the corresponding data calculated for constructing the VTF plot. The B_{VTF} coefficient was obtained from the following equation.

$$\ln \eta(T) = A_{VTF} + \frac{B_{VTF}}{T - T_0} \#(16)$$

Table S2.- Summary of the viscosity values of DLG at different temperatures.

T(°C)	T (K)	1/T-T$_0$	Viscosity	ln(η)
-8	265.1500	0.038240918	0.038240918	4.119037175
0	273.1500	0.029282577	0.029282577	3.453157121

5	278.1500	0.025542784	0.025542784	3.212186837
10	283.1500	0.022650057	0.022650057	2.989043285
15	288.1500	0.02034588	0.02034588	2.803360381
20	293.1500	0.018467221	0.018467221	2.671847152
25	298.1500	0.016906171	0.016906171	2.595254707
30	303.1500	0.015588465	0.015588465	2.602689685
35	308.1500	0.014461316	0.014461316	2.512846018
40	313.1500	0.013486177	0.013486177	2.437115986
45	318.1500	0.012634239	0.012634239	2.326952449
50	323.1500	0.011883541	0.011883541	2.215391881
55	328.1500	0.01121705	0.01121705	2.111424588
60	333.1500	0.010621349	0.010621349	2.061786606

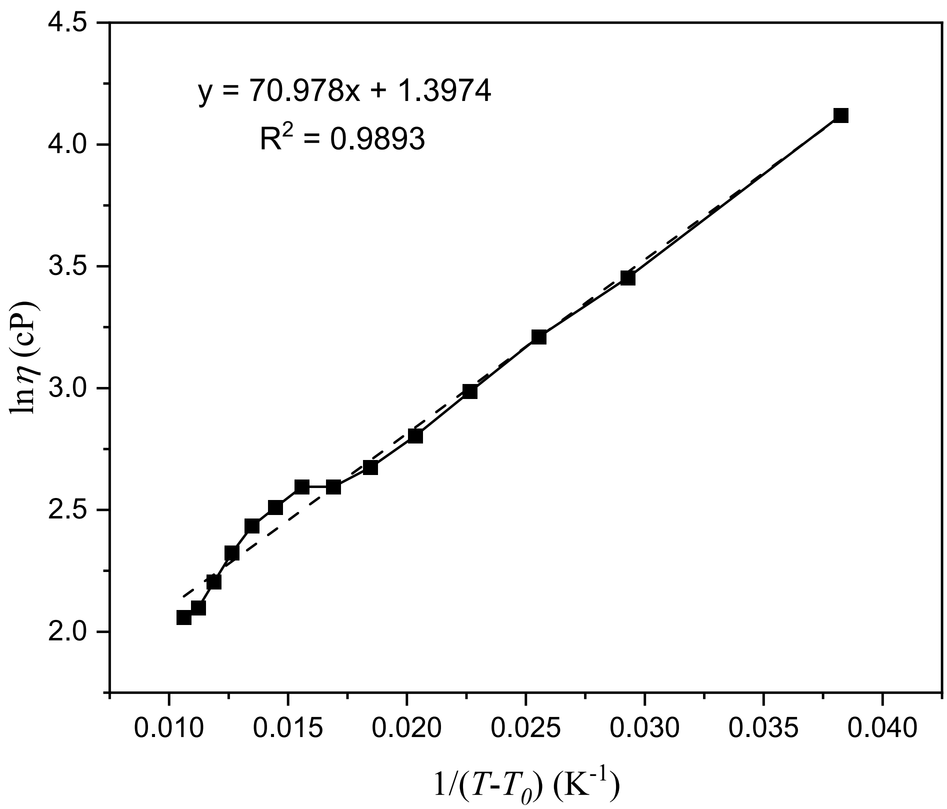

Figure S2. Experimental adjustment of DLG using Vogel-Tamman-Fulcher equation.

IR (ATR) spectroscopy of DLG electrolytes

The IR(ATR) spectroscopy measurements were performed with Bruker TENSOR 27 spectrometer equipped with Platinum ATF.

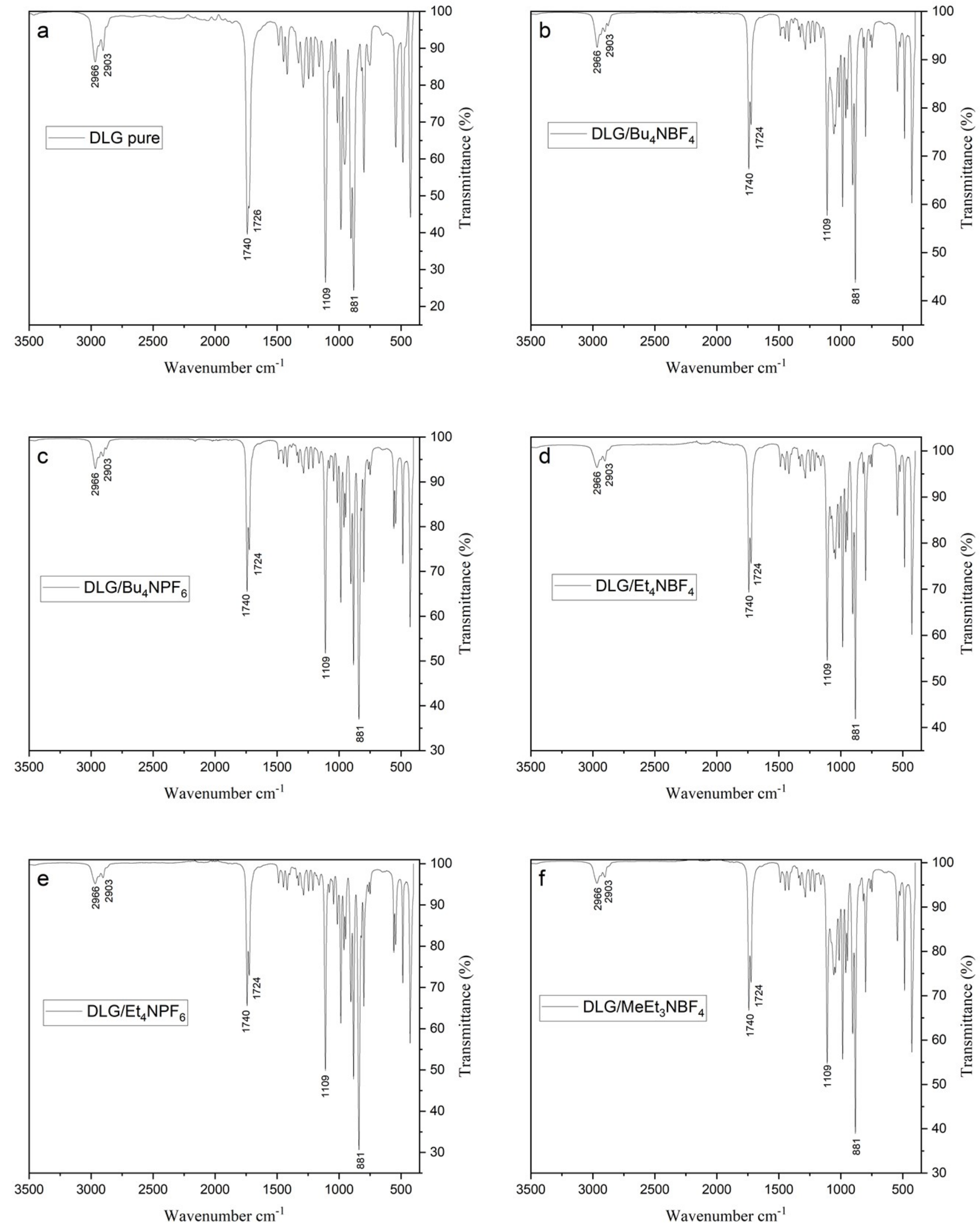

Figure S3.- IR (ATR) spectroscopy of solutions of tetraalkylammonium salts in DLG.

As shown in Figure S3. The double absorption band at 1740 cm^{-1} and 1724 cm^{-1}, corresponding to the carbonyl group, and the absorption bands corresponding to the internal ketal C-O-C bond at 1109 cm-1 remain in all IR spectra without any shift; only the intensity of the absorption band decreases. Therefore, the solvation of tetraalkylammonium salts could occur by the interaction of cations with the internal ketal instead of the carbonyl group. This leads to the possibility that DLG forms a structural aggregation. However, more studies are required to confirm that hypothesis.

Measurement of diffusion coefficients of ferrocene in DLG.

Chronoamperometry experiments were conducted using a Metrohm Autolab PGSTAT101 potentiostat, connected to a PC and controlled with the NOVA 2.1 software package. A three-electrode set-up consisting of a 1.5 mm diameter glassy carbon working electrode and a Pt counter electrode was used. The reference used was an $Ag/AgNO_3$ reference electrode separated from the bulk solution using a porosity frit. Prior to each experiment, the working electrode was polished using alumina paste (0.03 µm), a wet polishing cloth, followed by rinsing with distilled water and drying. The electroactive area of the glassy carbon electrode was calculated using chronoamperometry experiments in acetonitrile, taking into account the diffusion coefficient of ferrocene in this medium. Under these electrochemical conditions, the experimental data had been extensively simulated on a reliable calculation reported by Shoup and Szabo, which has been found well-suited for the analysis of experimental data with the following equation

Current Shoup and Szabo equation[3]

$$I = 4FDr_e[A]_{bulk}f(\tau)\#(17)$$

Where the dimensionless time is defined as

$$\tau = 4FDr_e^{-2}\#(18)$$

For short dimensionless times (τ <1) f(τ) can be approximated as

$$f(\tau) = \left(\frac{\pi}{4\tau}\right)^{0.5} + \frac{\pi}{4} + 0.094\tau^{0.5}\#(19)$$

And for long times (τ >1)

$$f(\tau) = 1 + 0.71835\tau^{-0.5} + 0.0562\tau^{-1.5} - 0.0064\tau^{-2.5}\#(20)$$

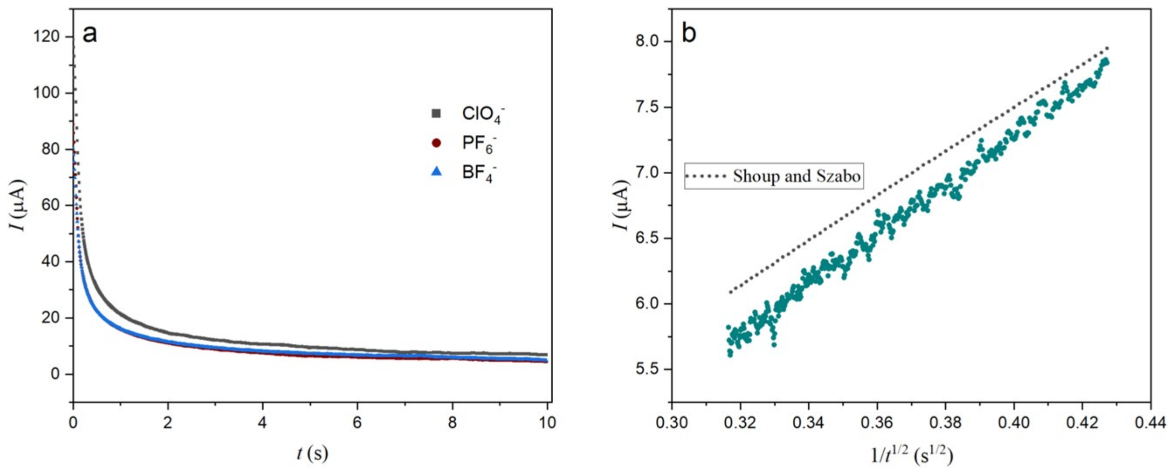

Figure S4.- a) Chronoamperometric responses of 5 mM of ferrocene in DLG with different supporting electrolytes at glassy carbon electrode. b) *I vs.* $1/t^{1/2}$ experimental data (green dotted line) and predicted (gray dotted line)

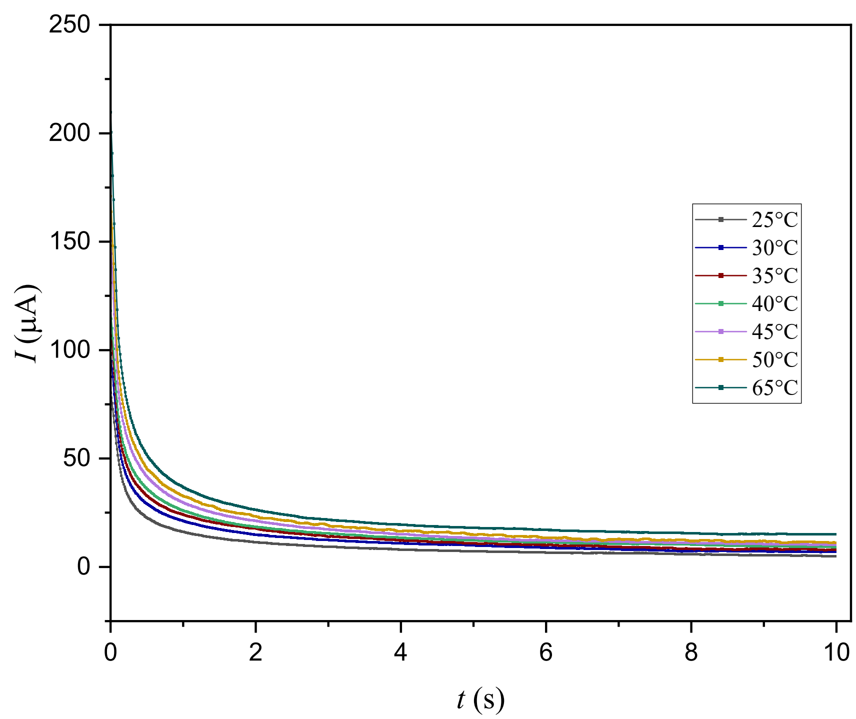

Figure S5.- Chronoamperometric responses of 5 mM of ferrocene in DLG/Bu_4NPF_6 with different supporting electrolytes at different temperatures at glassy carbon electrode.

The values of the diffusion coefficient at different temperatures are summarised in Table S3.

Table S3.- Diffusion coefficients of ferrocene (5 mM) in DLG with different supporting electrolytes (0.15 M) at different temperatures from 25 °C to 60 °C.

	Diffusion coefficient of ferrocene (cm^2/s)		
Temperature (K)	Bu_4NBF_4	Bu_4NPF_6	Bu_4ClO_4
298.15	$9.055x10^{-7}$	$6.105x10^{-7}$	$1.07601x10^{-6}$
303.15	$1.22x10^{-6}$	$1.18393x10^{-6}$	$1.27145x10^{-6}$
308.15	$1.46466x10^{-6}$	$1.41776x10^{-6}$	$1.46453x10^{-6}$
313.15	$1.63428x10^{-6}$	$1.6506x10^{-6}$	$1.57516x10^{-6}$
318.15	$1.8x10^{-6}$	$2.09524x10^{-6}$	$1.9393x10^{-6}$
323.15	$2.17485x10^{-6}$	$2.57303x10^{-6}$	$1.97521x10^{-6}$
328.15	$2.331x10^{-6}$		$2.56941x10^{-6}$
333.15	$2.79565x10^{-6}$		$2.60251x10^{-6}$

Cyclic voltammetry data of ferrocene in DLG

Table S4.- Scan rate (υ), anodic (E_{ap}) and cathodic (E_{cp}) peak potentials, anodic and cathodic current ratio (i_{ap}/i_{pc}), anodic and cathodic peak separation (ΔE) and half wave potential ($E_{1/2}$) for ferrocene in DLG at 293.15 K at GC electrode

υ / (V s^{-1})	E_{pa} / (V)	E_{pc} / (V)	i_{ap}/i_{pc}	ΔE_p / (V)	$E_{1/2}$ / (V)
0.05	0.134	0.056	0.99	0.078	0.10005
0.1	0.136	0.063	0.98	0.073	0.10005
0.15	0.136	0.063	0.99	0.073	0.10005
0.2	0.139	0.061	0.99	0.078	0.10005
0.25	0.141	0.058	0.98	0.083	0.0988
0.3	0.139	0.058	0.98	0.080	0.0976
0.35	0.139	0.056	0.97	0.083	0.10005
0.4	0.141	0.058	0.97	0.083	0.10005
0.45	0.141	0.056	0.97	0.085	0.09885
0.5	0.141	0.056	0.97	0.090	0.09885
0.6	0.144	0.053	0.96	0.090	0.09885
0.65	0.144	0.053	0.96	0.090	0.09885
0.7	0.144	0.053	0.96	0.090	0.09885
0.75	0.146	0.053	0.96	0.092	0.1005
0.8	0.144	0.053	0.96	0.090	0.09885
0.85	0.146	0.051	0.95	0.095	0.0988
0.9	0.146	0.051	0.95	0.095	0.0988
0.95	0.146	0.048	0.95	0.097	0.097
1	0.148	0.051	0.95	0.097	0.1001

Impurities in DLG solvent and their effects on cyclic voltammetry responses

Due to the DLG being a biodegradable solvent under environmental conditions, it is probable that it contains some impurities. The Figure S6 shows a cyclic voltammetry of anodic region of dihydrolevoglucosenone direct from the bottle commercially available with 98.5% (Cyrene^{TM}) without any treatment showing a oxidation peak at E = 1.16 V *vs* Ag/ $AgNO_3$ followed by a second oxidation peak at E = 1.53 V *vs* Ag/$AgNO_3$ at glassy carbon electrode, both oxidations peaks are irreversible which could interfere with the oxidation peak of other functional groups and could be a trouble that may causes some confusions about its anodic potential window.

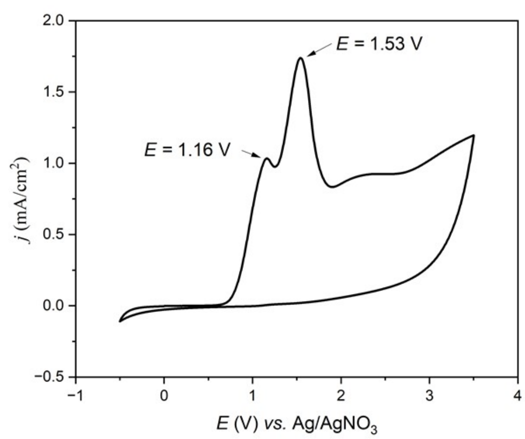

Figure S6.- Cyclic voltammetry of anodic region of commercially available DLG without any treatment.

The DLG appearance from the bottle is a clear, light-yellow liquid, as can be seen in Figure S8 (left), which contains impurities responsible for its appearance. Part of these impurities are eliminated by distillation under reduced pressure, although the yellow colour diminishes, it is not enough to obtain a clean DLG, even with a double distillation pathway. The CV still shows the irreversible oxidation peak at a E = 1.43 V, as shown in Figure S7.

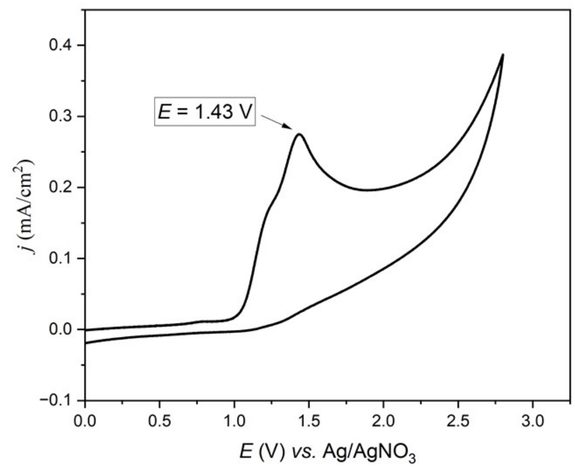

Figure S7.- Cyclic voltammetry of DLG after a second distillation.

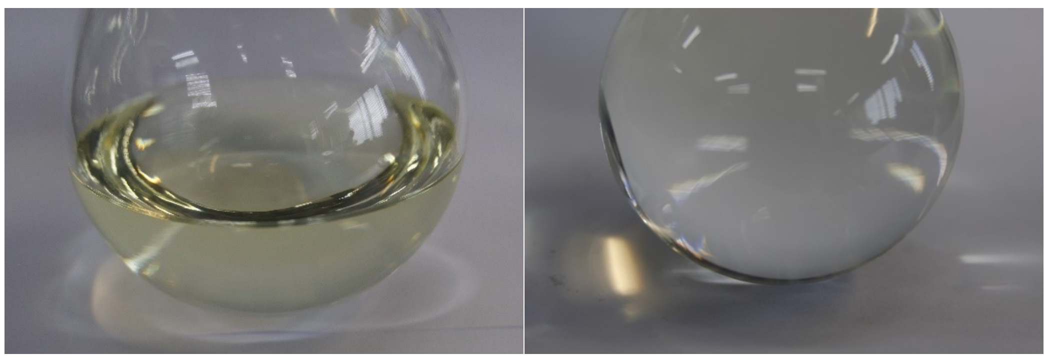

Figure S8.- The appearance of DLG from bottle (left) and after a filtration step over chromatography column (right)

To successfully purify DLG it is first eluted over a chromatography column with silica gel 230-400 mesh intercalated with activated carbon, the yellow-orange impurities are almost entirely retained in the stationary phase, enhancing the appearance of DLG as shown in Figure S8 (right), where a slightly yellow colour remains in the solvent. Following this step, DLG is stirred with dry magnesium sulphate, followed by reduced pressure distillation at 50-65 °C and 4 mmHg. It is important not to exceed this temperature due to impurities can be carried over during distillation. It is then kept under N_2 or Ar in the dark to prevent environmental degradation. This procedure removes the electroactive impurities contained in DLG, yielding clean cyclic voltammograms, where the previously mentioned anodic signals are eliminated, resulting in a transparent and colourless DLG (Figure S9).

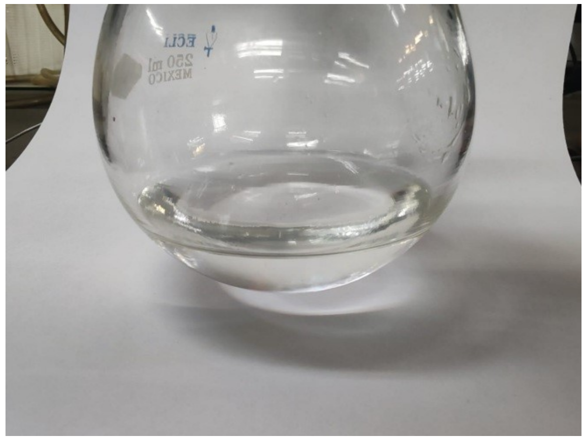

Figure S9.- The appearance of DLG after a filtration step over a chromatography column, followed by low-pressure distillation

If purified DLG is exposed to the environment for some days, the anodic signals appear again after some days, indicating the presence of degradation products (Figure S10). Additionally, if the solvent is left in an open flask, after two weeks fungi start to grow (See Figure S11), which is in accordance with its biodegradable nature.

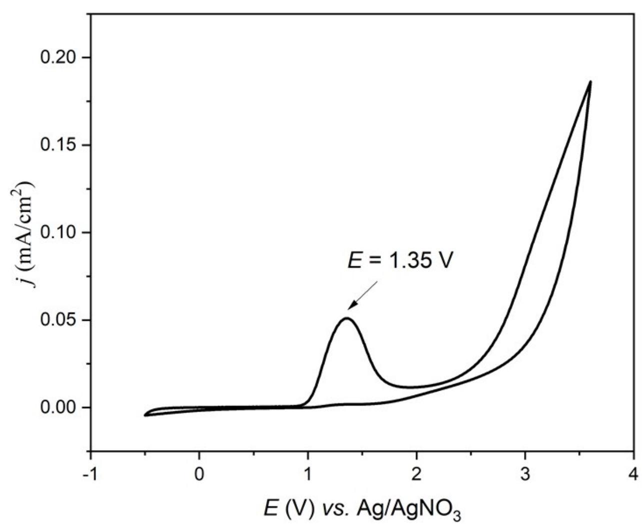

Figure S10.- Cyclic voltammetry of anodic region of DLG at glassy carbon electrode after two days of purification step.

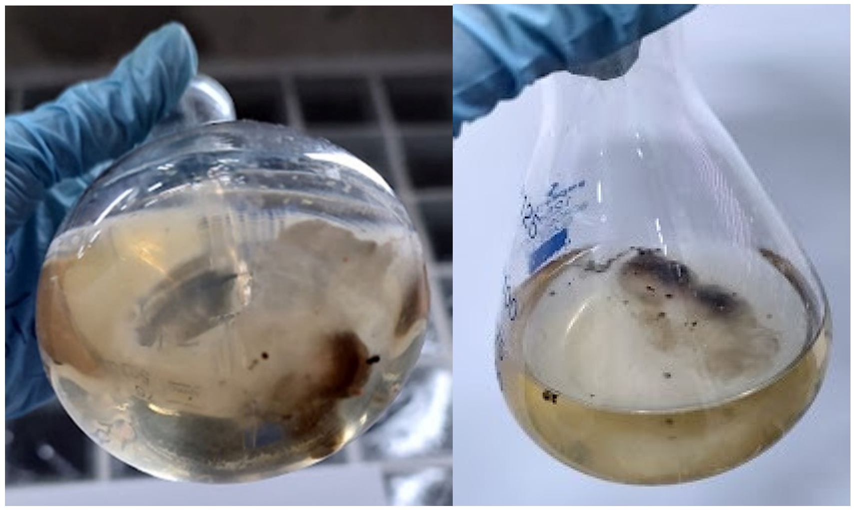

Figure S11.- Fungi grew after two weeks in DLG contained in an open flask

Our recommendation is to use freshly purified DLG to perform electrochemical experiments. It is important to store it in the dark under an inert atmosphere because the combination of oxygen and light promotes its degradation.

Comparison of cyclic voltammetry of selected organic compounds in acetonitrile and DLG

The cyclic voltammetry of the organic compounds was carried out in acetonitrile at a concentration of 5 mM, using Bu_4NBF_4 (0.1 M) and compared with those recorded in DLG.

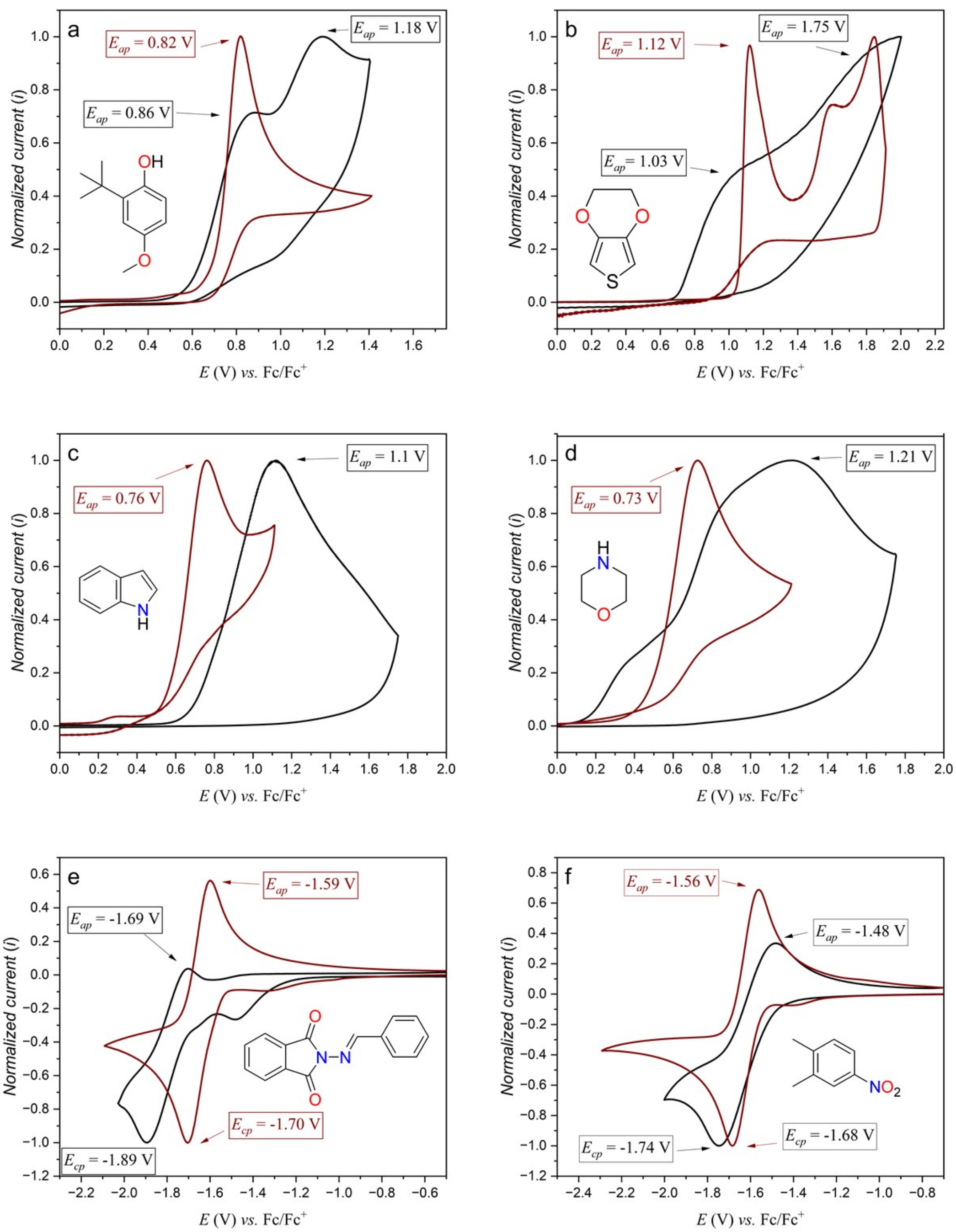

Figure S12.- Normalized cyclic voltammograms of organic compounds in DLG (black line) in comparison with acetonitrile (red line) at glassy carbon electrode

The cyclic voltammograms of Figure S12 show the behavior of the organic molecules in both media. It can be observed that there are some differences in their electrochemical response. The electrochemical behavior of 3-tert-butyl-4-hydroxianisole in DLG (Figure S12a black line) shows two oxidation peaks, one at E = 0.86 V, followed by a second at E = 1.18 V, while in acetonitrile (red line), only one oxidation peak is observed at E = 0.82 V, similar to that in DLG. This fact implies that oxidized species generated are rapidly transformed into their products in ACN. In DLG, this process is slower, allowing for the observation of a second corresponding to the second electron transfer. In the case of the electrochemical response of 3,4-ethylendialkoxythiophene (EDOT) (Figure S12b), it presents an oxidation peak at E = 1.03 V in DLG (black line), followed by a second oxidation peak that appears at E = 1.75 V. In ACN (red line), a well-defined oxidation peak appears at E = 1.12 V, similar to that in DLG, and followed by two more oxidation peaks. The solvation of EDOT in DLG promotes its oxidation at lower potential values than in ACN. The cyclic voltammograms of indole and 4-ethylmorpholine (Figure S12c, 12d) present one irreversible oxidation peak in both media, being in acetonitrile (red line) where the oxidation of both molecules occurs at a lower potential than in DLG (black line). In Figure S12e, the cathodic reduction of N-N imino-phthalimide exhibits a reversible system with a $E_{1/2}$ = -1.64 V in ACN (red line), while in DLG presents a quasi-reversible system at $E_{1/2}$ = -1.79 V corresponding to the generation of the radical anion. Additionally, the electrochemical response of nitrobenzene derivative (Figure S12f) is compared in both solvents. In ACN (red line), the classical reversible system shows $E_{1/2}$ = -1.65 V, while in DLG, a quasi-reversible system has an $E_{1/2}$ = -1.61 V, corresponding to the Ar-NO2$^{\bullet-}$ radical anion system. The presence of quasi-reversible systems indicates the formation of stable radical anions in DLG, despite DLG being a potentially protic solvent. Consequently, this behavior suggests that protonation of these reactive species is very slow.

Green Score assessment of DLG in the electrochemical reduction of benzophenone.

For the Green Score assessment, in the Solvent score stage the corresponding value of DLG or Cyrene™ is 22 which is based on the GSK's solvent selection guide.[4] For the evaluation of the item "Waste" are considered the calculation of PMI (Process mass intensity), which is the total mass of all chemical inputs, the RME (reaction mass efficiency), the yield of the reaction and the stoichiometry of the reagents. The calculation of PMI and RME are carried out using the following equations

$$PMI = \frac{\sum mass\ of\ all\ inputs}{mass\ of\ desired\ product} \#(21)$$

$$= \frac{m_{reactants} + m_{reagents} + m_{catalyst}}{m_{product}} + \frac{m_{solvent}}{m_{product}} \#(22)$$

$$= PMI_{RRC} + PMI_{solv} \#(23)$$

$$RME = \frac{mass\ of\ desired\ product}{\sum mass\ of\ reactants} x\ 100 \#(24)$$

Table S5.- Summary of the calculation of PMI, PMI_{solv} and PMI_{RRC} values for electrochemical ketone reduction

Metric	DLG/EtOH	DMF
PMI	57.3	114.2
PMI_{solv}	51.55	108.8
PMI_{RRC}	5.8	5.4
RME	17.26	17.15

Table S6.- Summary of the data used for calculation of PMI, PMI_{RRC} and PMI_{solv} values for electrochemical ketone reduction in DLG/EtOH.

	Starting materials			Product	Solvents	
Compound	Benzophenone	DABCO	Bu_4NBF_4	$(Ph)_2CHOH$	DLG	EtOH
MW (g/mol)	182.22	112.17	329.27	184.24		
V (mL)	-	-	-	-	4	4
ρ (g/mL)	-	-	-	-	1.25	0.78
n (mmol)	1	3	-	-	-	-
m (g)	0.1822	0.3399	0.39	0.1575	5	3.12

Table S7.- Summary of the data used for calculation of PMI, PMIRRC and PMIsolv values forelectrochemical ketone reduction in DMF.

	Starting materials			Product	Solvent
Compound	Benzophenone	DABCO	Bu_4NBF_4	$(Ph)_2CHOH$	DMF
MW (g/mol)	182.22	112.17	329.27	184.24	
V (mL)	-	-	-	-	5.0
ρ (g/mL)	-	-	-	-	0.95
n (mmol)	0.3	0.9	0.25	-	-
m (g)	0.055	0.101	0.082	0.044	4.75

$$Waste\ Score = \frac{\sum scores\ (PMI, RME, Yield, Stoichiometry)}{12} x\ 100 \#(25)$$

For each item, points are added and expresses as a percentage of the maximum possible number of points.

$$Item\ Score = \frac{\sum points\ obtained}{Maximun\ score}\ x\ 100\#(26)$$

To obtain the Green Score of the electrochemical process, the sum of the scores of each item are divided by 5, which is the total number of the categories.

$$Green\ Score = \frac{\sum Item\ scores}{5}\#(27)$$

Table S8.- Summary of the score obtained for electrochemical ketone reduction. In DLG/EtOH and DMF.

Item	**Answer**	**Score**	**DMF**		**DLG/EtOH**	
Waste Scoring			Answer	Score	Answer	Score
What is the yield of the reaction?	yield ≥ 85%	3	79%	2	85%	3
	70% ≤ yield <85%	2				
	60% ≤ yield <70%	1				
	yield <60%	0				
What is the PMI of the reaction?	PMI ≤ 25	3	114.2	0	51.55	1
	25 < PMI ≤ 40	2				
	40 < PMI ≤ 75	1				
	PMI > 75	0				
What is the RME of the reaction?	RME ≥ 75%	3	17.15	0	17	0
	50% ≤ RME < 75%	2				
	25% ≤ RME < 50%	1				
	RME < 25%	0				
What is the stoichiometry of the reaction (only reagents)?	stoichio ≤ 1,1 equiv or catalytic	3	3,0 equiv	1	3,0 equiv	1
	1,1 < stoichio ≤ 2,0 equiv	2				
	2,0 < stoichio ≤ 3,0 equiv	1				
	>3,0 equiv	0				
Sustainability Scoring			Answer	Score	Answer	Score
Does the reaction involve scarce elements?	No critical stock	3	Pt, growing threat	2	Pt, growing threat	2
	Future risk	2				
	Growing threat	1				
	Critical stock	0				
If an organometallic catalyst is used, is the metal recycled?	Yes	3	-			
	No	1				
	N/A	-				
Does the reaction use renewable material?	Yes	1	No	0	yes	1
	No	0				
Solvent Scoring			Answer	Score	Answer	Score
Number of solvents used in the reaction	1		1		2	
Solvent 1	≤18	3	DMF	0	DLG,22	2
	18 to 22	2				
	23 to 24	1				
	≥25	0				
Solvent 2	≤18	3	-	-	EtOH, 12	3

	18 to 22	2				
	23 to 24	1				
	≥25	0				
Number of solvents used in the workup/isolation	2					
Solvent 1	≤18	3	Petroleum ether	1	Hexane	1
	18 to 22	2				
	23 to 24	1				
	≥25	0				
Solvent 2	≤18	3	Ethyl acetate	2	Ethyl acetate	2
	18 to 22	2				
	23 to 24	1				
	≥25	0				
Is the solvent recycled?	Yes	1	No	0	No	0
	No	0				
Energy Scoring			Answer	Score	Answer	Score
What is the temperature of the reaction?	15 °C ≤ T °C ≤ 25 °C	3	r.t.	3	r.t.	3
	0 °C ≤ T °C < 15 or 25 °C < T °C ≤ 70 °C	2				
	−20 °C ≤ T °C < 0 or 70 °C< T °C ≤ 140 °C	1				
	<-20 °C or >140 °C	0				
Does the reaction operate at reflux?	Yes	0	No	2	No	2
	No	2				
Does the reaction operate at continuous manufacturing?	Yes	1	Yes	1	Yes	1
	No	0				
Workup and isolation?	no workup and no isolation	3	chromatography	0	chromatography	
	filtration extractions liq/liq (≤2) distillation (≤50 °C)	2				
	concentration until dryness extractions liq/liq (>2) solvent switch recrystallization distillation (50 to 90 °C)	1				
	chromatography distillation (>90 °C) multirecrystallization	0				
HSE Scoring			Answer	Score	Answer	Score
What are the hazards of the reagents used?	harmful, irritating	3	DABCO: Flammable, health hazard, corrosive (2) DMF: Flammable, acute toxicity (1)	1	DABCO: Flammable, health hazard, corrosive (2)	2
	corrosive, flammable, oxidizing	2				
	explosive, CMR2, acute toxicity, ecotoxicity	1				
	CMR1A/B, fatal toxicity	0				
Are we carrying out a dangerous chemical reaction (with high energy potential)?	Yes	-2	No	0	No	0
	No	0				

References.

1 K. Izutsu, *Electrochemistry in Nonaqueous Solutions,* Wiley-VCH Verlag GmbH, 2002.
2 E. S. Patiño-Alonzo, J. Barroso-Flores and B. A. Frontana-Uribe, *ChemCatChem*, 2023, **15**, e202300489.
3 D. Shoup and A. Szabo, *J. Electroanal. Chem. Interf. Electrochem.*, 1982, **140**, 237–245.

4 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.