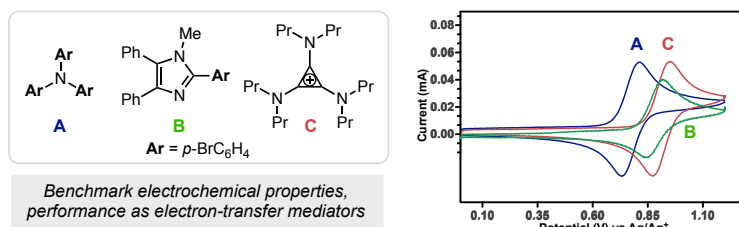


Benchmarking Trisaminocyclopropeniums as Mediators for Anodic Oxidation Reactions

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ABSTRACT: This report benchmarks a tris(amino)cyclopropenium (TAC) salt as an electron-transfer mediator for anodic oxidation reactions in comparison to two known mediators: a triarylamine and a triarylhydrazine derivative. The three mediators have similar redox potentials, diffusion coefficients, and heterogeneous electron transfer rates with glassy carbon electrodes in acetonitrile/KPF₆. However, they differ significantly in their performance in two electroorganic reactions: anodic fluorination of a dithiane and anodic oxidation of 4-methoxybenzyl alcohol. These differences are rationalized based on variable stability in the presence of reaction components (e.g., NEt₃•HF, lutidine, Cs₂CO₃) as well as very different rates of electron transfer with the organic substrate. Overall, this work highlights advantages and disadvantages of each mediator and provides a foundation for expanding the applications of TACs in electroorganic synthesis moving forward.

Introduction

Electrochemistry has emerged as a powerful modality in synthetic organic chemistry.¹ As such, there is increasing demand for tunable electron-transfer mediators that can effectively function as soluble electrodes during electro-organic redox reactions.² Mediated electrochemical transformations are highly desirable, as they often proceed at lower cell potentials, with higher yields and selectivities, and with less electrode passivation than the corresponding direct electrolysis pathways.² Several characteristics are required for an effective electron-transfer mediator, including (i) fast and reversible electron transfer with both solid electrodes and organic substrates, (ii) stability of all redox states to electro-organic reaction conditions, (iii) readily tunable redox potentials, and (iii) high solubility in all oxidation states. Oxidative mediators that meet most or all of these criteria while exhibiting relatively high redox potentials ($\geq +0.7$ V versus Ag/Ag⁺) remain rare. To date, the most widely used examples are polyaromatic molecules such as triarylamine³ or triarylhydrazine⁴ derivatives (for example, **A** and **B** in **Figure 1a**). While these have been successfully employed as electron-transfer mediators for a variety of anodic oxidation reactions,² they can be challenging to synthesize/derivatize in a modular fashion, suffer from modest solubility due to their propensity for aggregation and π -stacking, and have variable stability under some electroorganic reaction conditions. Overall, there is a need for new high redox potential mediators for anodic

oxidations that are readily synthetically tunable, are soluble in common organic media, and have complementary stability.

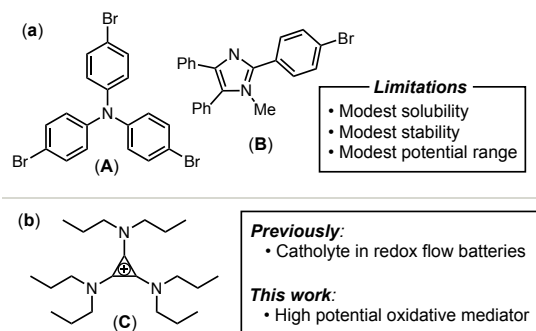


Figure 1. (a) Known high-potential oxidative mediators for electro-organic synthesis. (b) *This work*: Tris(amino)cyclopropeniums as mediators for electro-organic synthesis.

The Sanford group has recently developed cyclopropenium salts such as trisaminocyclopropenium (TAC) **C** (**Figure 1b**) as electrochemical energy storage materials in non-aqueous redox flow batteries (RFBs).⁵ We have disclosed a series of cyclopropenium derivatives that undergo oxidation at potentials ranging from +0.7 to 1.2 V vs Fc/Fc⁺ in acetonitrile (MeCN)/KPF₆.⁶ Many of the properties required for efficient energy storage (reversible redox events at high potentials accompanied by high stability and solubility) mirror those necessary for redox mediators.⁷ However, there are two key challenges for transitioning

from energy storage materials to mediators in electro-organic synthesis. First, electrochemical cycling in RFBs occurs under highly controlled conditions: under an inert atmosphere with rigorously purified and dried solvent and supporting electrolyte. In contrast, electro-organic reactions are often conducted on the benchtop and contain a mixture of organic reactants and additives (e.g., acids, bases, water, supporting salts). Second, in RFBs, the electron transfer reactions occur exclusively at the solution-electrode interface. In contrast, effective redox mediators must undergo fast electron transfer with both the solid electrode and the relevant organic substrate.

In this report, we evaluate and compare cyclopropenium **C** (a high-potential, soluble TAC derivative)⁸ with triarylamine **A** and triarylimidazole **B** as redox mediators in organic synthesis. **A-C** have similar redox potentials ($E_{1/2} \sim 0.8$ V vs Ag/AgBF₄) and should, thus, be effective mediators for comparable classes of organic substrates. We first compare their electrochemical properties ($E_{1/2}$, diffusion and electron transfer rates) under standard conditions and evaluate their compatibility with acidic and basic additives. Next, we assess their performance as mediators in two electroorganic reactions: the anodic fluorination of a dithiane⁹ and the anodic oxidation of 4-methoxybenzyl alcohol.^{4a} Overall, this work reveals advantages and disadvantages for each mediator and provides a foundation for expanding the applications of TACs in electroorganic synthesis moving forward.

Results and Discussion

We initiated these studies by using cyclic voltammetry (CV) to compare the redox potentials ($E_{1/2}$), diffusion rates (D), and heterogeneous electron transfer rates (k_{het}) of **A-C** (Table 1 and Figures S1-4). CVs were conducted with **A-C** (2 mM) in 0.5 M KPF₆ in MeCN, using a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgBF₄ reference electrode. KPF₆ was chosen as the supporting electrolyte because it has been used extensively with TACs in flow batteries.⁵ Under these conditions, the $E_{1/2}$ values of **A-C** are within 140 mV of one another, ranging from 0.77 V (**A**) to 0.88 V (**B**) to 0.91 V (**C**) versus Ag/AgBF₄. At 100 mV/s, we observe reversible redox peaks for **A** and **C** ($i_{pa}/i_{pc} \sim 1$), while **B** displays quasi-reversibility that is exacerbated at slower scan rates ($i_{pa}/i_{pc} = 2.23$ at 10 mV/s). This suggests that the oxidized species **A**⁺ and **C**⁺ are significantly longer-lived intermediates than **B**⁺.

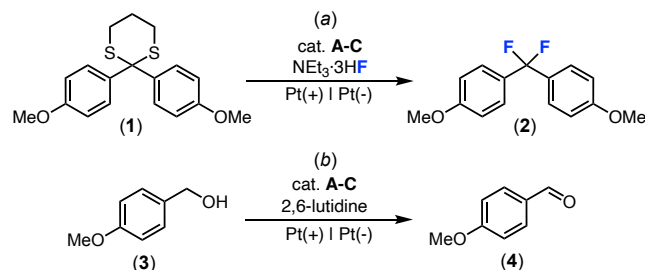
Table 1. Electrochemical properties of **A-C**

	A	B	C
$E_{1/2}$ (V)	0.77	0.89	0.91
i_{pa}/i_{pc} (10 mV/s)	1.00	2.23	1.14
i_{pa}/i_{pc} (100 mV/s)	1.08	1.43	1.17
D [cm ² /s]	1.42×10^{-5}	6.48×10^{-6}	1.46×10^{-5}
k_{het} [cm/s]	2.2×10^{-2}	1.88×10^{-2}	1.76×10^{-2}
k_{ET-1} [M ⁻¹ s ⁻¹]	22	6.3	140

The rates of heterogeneous electron transfer for **A-C** at glassy carbon are similar to one another ($\sim 2 \times 10^{-2}$ cm/s) as determined using the Nicholson method.¹⁰ Notably, the values for **A** and **B** are similar to those reported by Little in 0.1 M LiClO₄ in MeCN, 1.38×10^{-2} cm/s and 1.53×10^{-2} cm/s respectively.^{4c} The diffusion coefficients (D) for **A-C** were experimentally determined by applying the Randles-Sevcik equation (Figure

S4).¹¹ **A** and **C** have diffusion coefficients of 1.4×10^{-5} cm²/s while that for **B** is about 2-fold slower (6.58×10^{-6} cm²/s). Again, the values for **A** and **B** are similar to those determined by Little in 0.1 M LiClO₄ in MeCN.^{4c}

We next sought to benchmark **A-C** as mediators in two different electrooxidative reactions: (a) the anodic fluorination of dithiane **1** with NEt₃•HF to form **2** and (b) the anodic oxidation of 4-methoxybenzyl alcohol **3** to generate aldehyde **4** (Scheme 1). These transformations were selected for several reasons. First, substrates **1** and **3** have peak anodic potentials (E_{pa}) of 1.00 V and 1.23 V vs Ag/AgBF₄, respectively (Figure S1), which are well matched for mediation by **A-C**. Second, anodic fluorinations analogous to (a) have been studied with **A**,³ while benzyl alcohol oxidations analogous to (b) have been investigated with both **A** and **B**.² As such, these transformations offer an opportunity to compare the performance of **C** to the known mediators. Third, the conditions for these reactions are quite different, with (a) performed in mildly acidic (NEt₃•HF) and (b) conducted in basic (lutidine) media. We hypothesized that these conditions might thus highlight complementary compatibility/performance between **A-C**.³



Scheme 1. Electrochemical oxidation reactions used to benchmark mediators **A-C**

Table 2. Stability of **A-C** towards NEt₃•HF and lutidine as assessed by CV^a

entry	mediator	additive	% decrease of i_{pa}
1	A	none	2
2	A	NEt ₃ •HF	4
3	A	lutidine	2
4	B	none	7
5	B	NEt ₃ •HF	>19 ¹³
6	B	lutidine	8
7	C	none	9
8	C	NEt ₃ •HF	6
9	C	lutidine	14

^a CV conditions: mediator (2 mM) and additive (10 mM) in 0.5 M KPF₆ in MeCN with glassy carbon working electrode, platinum wire counter electrode, and Ag/AgBF₄ reference electrode. CVs acquired at 100 mV/s over 10 consecutive scans. %decrease in i_{pa} between cycle 2 to 10 is reported for each.

To test this latter point, we preliminarily examined the stability of **A-C** towards CV cycling in the absence and presence of NEt₃•HF and lutidine as additives. CVs were conducted with **A-C** (2 mM) and the additive (10 mM) in 0.5 M KPF₆ in MeCN under ambient conditions.¹² In each case, 10 sequential CVs of the mediator were acquired at 100 mV/s. We then determined the % change in anodic peak current from cycle 2 to cycle 10 (% decrease of i_{pa}) to estimate stability towards each additive.¹³ The CVs from these experiments are available in Figure S7,

and the data are summarized in **Table 2**. Overall, the % decrease of i_{pa} varied from 2 to >19%,¹³ and **A-C** exhibited complementary stability towards these additives. **A** and **B** showed the largest decrease in i_{pa} with $\text{NET}_3\cdot\text{HF}$ (4% and >19%, respectively), while **C** showed the largest decrease with lutidine (14%).

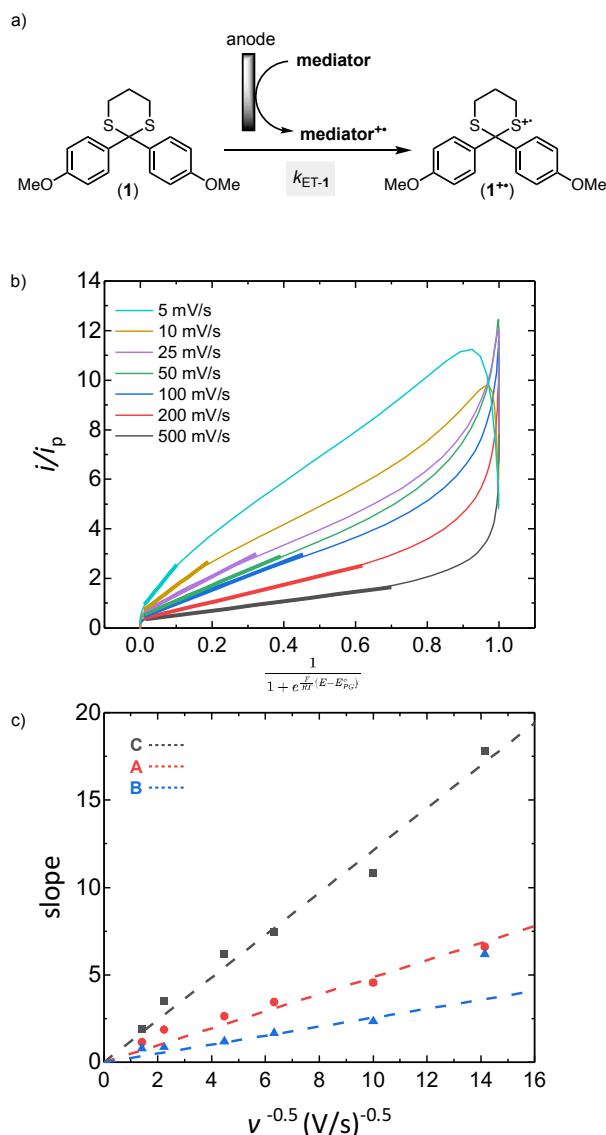


Figure 2. (a) Electron transfer between the oxidized mediator (mediator⁺⁺) and substrate **1**. (b) Foot of the wave analysis for mediator **C**. (c) Fitting to obtain k_{ET-1} for **A-C**.

The first step of the anodic fluorination of dithiane **1** involves electron transfer between the mediator and **1** to form radical cation **1**^{•+} (**Figure 2a**). We sought to compare the rate constant of this electron transfer reaction (k_{ET-1}) for each of the mediators. Rate constants were obtained via foot-of-the-wave analysis¹⁴ of the CVs of **A-C** (2 mM in 0.5 M KPF_6 in MeCN) in the presence of 40 mM of dithiane **1** at scan rates ranging from 5 to 500 mV/s. During the foot-of-the-wave analysis, the CV data were post-processed to generate the foot-of-the-wave analysis plots exemplified in **Figure 2b** for **C**. The y-axis is the ratio between the electrochemical current for **C** in the presence of substrate **1** (i) and the peak current for **C** in the absence of **1** (i_p^0) at the same scan rate. The x-axis is a function of electrode potential (E): $\frac{1}{1 + \exp\left[\frac{F}{RT}(E - E^0)\right]}$, where F is the Faraday constant (= 96480 C/mol), R is the gas constant, T is 298 K, and E^0 is the

standard reduction potential of the mediator. The slope of the linear fit of the initial stage of the curve (i.e., foot-of-the-wave, highlighted in thick lines in **Figure 2b**) provides the rate constant (k_{ET-1}) based on eq. 1, where C^0 is the concentration of substrate **1**, and v is the scan rate.

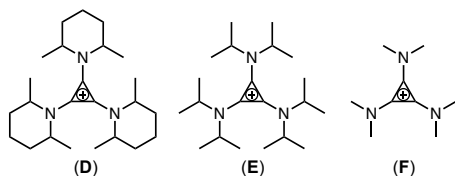
$$\frac{i}{i_p^0} = (2.24 \sqrt{\frac{RT}{Fv}} 2k_{ET-1}C^0) \frac{1}{1 + \exp\left[\frac{F}{RT}(E - E^0)\right]} \quad (1)$$

As shown in **Figure 2c**, the slopes at different scan rates obtained by linear fitting were proportional to $v^{-0.5}$, in excellent agreement with eq. 1. The k_{ET-1} values were calculated from the slopes of the dotted fit lines in **Figure 2c**. Large differences are observed between the three mediators, with k_{ET-1} varying from 6.3 (**B**) to 22 (**A**) to 140 (**C**) $\text{M}^{-1}\text{s}^{-1}$. Notably, these values do not directly track with differences in redox potential,^{4c} suggesting that a more complex set of factors impacts k_{ET-1} . Overall, the large value of k_{ET-1} with **C** is promising for the mediated electrolysis of dithiane **1** at the preparative scale.

The preparative scale **A-C**-catalyzed electrolysis reactions of **1** with $\text{NET}_3\cdot\text{HF}$ were next evaluated in a divided cell equipped with Pt foil electrodes, using 0.7 M $\text{NET}_3\cdot\text{HF}$ as both the electrolyte and fluorinating reagent in MeCN. The reactions were first performed at a constant potential of 1.1–1.2 V (vs Ag wire) using 10 mol % of **A**, **B**, or **C** (**Table 3**, entries 1–4). Under these conditions, the unmediated direct electrolysis reaction afforded low (<10%) conversion of **1** and only traces (4%) of product **2**, indicating that direct electrolysis is inefficient at this potential. In contrast, with 10 mol % of **A** or **C** under otherwise identical conditions, the yield of **2** was 68 and 83%, respectively, demonstrating effective mediation. A significantly lower yield (15%) was obtained using 10 mol % of **B**. The moderate performance of **B** likely reflects a combination of the relatively slow k_{ET} between **1** and **B** and the modest stability of **1** towards $\text{NET}_3\cdot\text{HF}$ (**Table 2**, entry 5).

Table 3. **A-F**-catalyzed anodic fluorination of dithiane **1** with $\text{NET}_3\cdot\text{HF}$

entry	conditions	mediator	mol %	yield 3 (%)
1	CPE, 1.2 V	none	--	4
2	CPE, 1.1 V	A	10	68
3	CPE, 1.2 V	B	10	15
4	CPE, 1.2 V	C	10	83
5	CCE, 3 mA	none	--	16
6	CCE, 3 mA	A	10	79
7	CCE, 3 mA	B	10	45
8	CCE, 3 mA	C	10	80
9	CCE, 3 mA	D	10	46
10	CCE, 3 mA	E	10	83
11	CCE, 3 mA	F	10	68
12	CCE, 3 mA	A	1	37
13	CCE, 3 mA	C	1	90
14	CCE, 3 mA	E	1	73



Controlled potential electrolysis (CPE) is limited by relatively low current densities and long reaction times. These are particularly problematic when using $\text{NEt}_3 \cdot \text{HF}$, which slowly dissolves glass components (e.g., the reference electrode and fritted separator). As such, we also examined the conversion of **1** to **2** using controlled current electrolysis (CCE), with a current density of 3 mA (**Table 3**, entries 5-8). Under these conditions, the direct electrolysis reaction afforded a low (16%) yield of **2**. Significantly higher yields were obtained in the presence of 10 mol % of the mediators, with **A** (79%) and **C** (80%) outperforming **B** (45%).

The modular synthesis of TAC derivatives allows for the facile installation of sterically diverse amino groups on the cyclopropenium core without significant modification of the redox potential.⁵ This enabled the exploration of several additional cyclopropenium mediators (**D-F**) under analogous conditions. As shown in **Table 3**, entries 9-11, the structure of the TAC significantly impacts catalytic performance, with yields ranging from 46-83%. Using the three top-performing mediators (**A**, **C**, and **E**), we dropped the loading to 1 mol %. The yield of **2** decreased substantially with **A** and **E** at this lower loading but remained high (90%) with **C**. This finding highlights the importance of high $k_{\text{ET-1}}$ for **C**, as it enables catalyst faster turnover and, thus, lower catalyst loading.

We next turned our focus to the **A-C**-catalyzed oxidation of 4-methoxybenzyl alcohol **3** to aldehyde **4**. Little and coworkers studied electron transfer rates between **3** and mediators **A** and **B** in the presence of lutidine, revealing $k_{\text{ET-3}}$ values of $6.11 \text{ M}^{-1} \text{ s}^{-1}$ and $74.76 \text{ M}^{-1} \text{ s}^{-1}$ for **A** and **B**, respectively.^{4c} However, when we attempted an analogous experiment with **C**, we observed a complete disappearance of the reversible redox couple. Under these conditions, the anodic scan no longer showed a diffusion-limited current response (**Figure S8**), implicating the decomposition of **C**. Consistent with these observations, preparative scale **C**-catalyzed oxidation of **3** under Little's conditions (2 equiv of lutidine in 0.2 M LiClO_4 in 1:4 CH_2Cl_2 :MeCN) showed no catalysis. Instead, the observed yield of **4** was within the error of that for direct electrolysis (38% versus 42%, respectively). These results are consistent with the CV studies showing poor stability of **C** in the presence of lutidine (**Table 2**, entry 9) and reflect a key limitation of **C** as a mediator relative to compared to **A** and **B**.

We hypothesized that this instability stems from the fast decomposition of the radical dication C^{++} in the presence of lutidine. This was confirmed by subjecting an isolated sample⁸ of C^{++} (5 mM in CH_3CN) to 1 equiv of lutidine, which resulted in a dissipation of the characteristic dark red color of C^{++} within 1 min at 25 °C (**Figure S9**). We reasoned that a less soluble base might exhibit improved compatibility with C^{++} . Indeed, upon screening a variety of inorganic bases, we found that subjecting C^{++} to 1 equiv of Cs_2CO_3 under otherwise analogous conditions resulted in minimal decay over 2 h at 25 °C (**Figure S9**).

The use of a heterogeneous base makes it challenging to determine $k_{\text{ET-3}}$ using CV. Thus, we moved directly to evaluate preparative-scale oxidations of **3** to **4** with Cs_2CO_3 as the base. These reactions were conducted in a divided cell equipped with

reticulated vitreous carbon (RVC) electrodes in 0.1 M KPF_6 in MeCN with 10 mol % of mediators **A-C**. Upon constant potential electrolysis (1.1 V vs Ag wire) over 5 h, the unmediated reaction passed 2.5 F/mol of charge and afforded a moderate 29% yield of **4**. In contrast, with 10 mol % of **A** or **C**, the reactions passed a total of 3.7 and 3.6 F/mol, respectively, and both afforded a 70% yield of **4**. Interestingly, while **B** outperforms **A** and **C** with lutidine as the base,⁴ under these Cs_2CO_3 conditions, **B** affords a very low yield (1%), with the corresponding current response never exceeding 1 mA. These results highlight the value of having different mediators with similar potentials, as even relatively small changes to the reaction conditions can have a dramatic impact on mediator performance and compatibility.¹⁵

Table 3. A-C-catalyzed benzylic oxidation of 4-methoxybenzyl alcohol

entry	mediator	yield 4 (%)
1	none	29
2	A	70
3	B	1
4	C	70

In conclusion, this report compares trisaminocyclopropeniums to two known redox mediators for several electro-organic transformations. We show that the TACs exhibit electrochemical properties (diffusion rates, electron transfer rates) and catalytic performance similar or superior to triarylamine and triarylimidazole derivatives with comparable redox potentials. We note that the TACs are poorly compatible with the soluble base lutidine; however, this issue can be mitigated by changing to a less soluble base such as Cs_2CO_3 . We anticipate that these studies will motivate the application of TACs and other readily accessible aminocyclopropenium derivatives to a wider variety of electro-organic transformations.

ASSOCIATED CONTENT

Supporting Information

Experimental details are available as Supporting Information for Publication. SI contains general procedures for cyclic voltammetry studies and preparative scale electrolyses.

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- ¹² CV cycling studies were conducted under ambient conditions on the benchtop, using a previously dried solution of electrolyte. Stock solutions of electrolyte were dried over activated molecular sieves for at least one day prior to use.
- ¹³ The % loss in peak height was calculated based on the ratio between the peak anodic current response at the tenth cycle and second cycle. This significantly underestimates the decomposition of mediator **B** because there is a large loss of current between cycles 1 and 2, particularly with $\text{NEt}_3 \cdot \text{HF}$, as shown in **Figure S7**.
- ¹⁴ Foot-of-the-wave analysis minimizes interfering phenomena, such as side reactions, at high current densities. Strategies for optimized preparative scale electrolysis may then be devised on this basis.

¹⁵ Using controlled current electrolysis (current density = 3 mA) under otherwise identical conditions, the mediated reactions proceeded to form **4** in yields between 45-64%. However, direct electrolysis in the absence of mediator afforded comparable yield of 40%, so the mediators offer minimal advantage under these CCE conditions.