Received: 3 April 2018 | Revised: 8 October 2018 | Accepted: 5 December 2018

DOI: 10.1002/poc.3930

RESEARCH ARTICLE

WILEY Journal of Physical Organic Chemistry

Triarylpyridinium salts: Synthesis and electrochemical properties

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Funding information
Russian Foundation for Basic Research, Grant/Award Number: 18-03-00211; Ministry of Education and Science of the Russian Federation within the framework of government task in the field of scientific activities, Grant/Award Number: 4.4566.2017/8.9

Abstract

The electrochemical properties of the triarylpyridinium salts were studied. The effect of functional substituents on redox properties has been investigated in detail. Electrochemical reduction of salts to the anion in acetonitrile is the result of two one-electron-transfer steps through the stage of the radical formation and its subsequent reduction (EE electrochemical mechanism). A correlation between the reduction potentials and the structure of the salts was established.

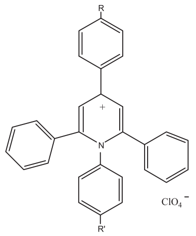
KEYWORDS

electrochemical reduction, metal-free electrocatalyst, redox property, triarylpyridinium salt

1 | INTRODUCTION

Despite the significant progress made in recent years in the field of hydrogen energy, the practical use of the developed technologies is still very limited due to the low efficiency of synthetic catalysts.[1,2] Work in this area aimed to obtaining of catalysts based on transition metals such as cobalt, iron, or copper, as well as biomimetic models of hydrogenases.[3–5] In present, many complexes of transition metals have a high activity in the electrocatalytic generation of hydrogen including those that exceed the hydrogenases by catalytic activity and the magnitude of the overpotential.[6–11] Despite this, none of the large variety of molecular complexes has combined low overpotential with availability, high activity, and stability, which are a prerequisite for an economically viable catalyst.[12] Although the hydrogenases possess high catalytic activity, in the absence of overpotential, their use on an industrial scale is not possible due to the complexity of their production in large quantities and their extremely high sensitivity to environmental conditions (temperature, pH, and oxygen availability).[6] Thus, the development of new-generation catalysts for the electrochemical process of obtaining molecular hydrogen is an important and actual task.

Previously, we first described a new type metal-free electrocatalyst for the hydrogen evolution reaction on base of the 9-phenyl-*N*-phenylacridinium iodide (PhAcrI).[13,14] The proposed catalytic system equally effectively catalyzed the process of electrochemical hydrogen production from both aprotic solvents in the presence of perchloric acid and from water at different pH values. Here, we report the synthesis and electrochemical properties of new heterocyclic salts based on 2,4,6-triaryl pyridinyl derivatives, close analogues of acridine derivatives (Scheme 1). The presence of substituents in the 2-, 4-, and 6- positions is necessary for shielding the reactive intermediates formed during the electrocatalytic process. When reducing unsubstituted pyridium salts, the radicals formed in the first stage have high chemical activity and rapidly are reacted, particular are easily dimerized.[15] Thus, the absence of substituents in the presented



SCHEME 1 General view heterocyclic salts based on 2,4,6-triaryl pyridinyl perchloroate

positions leads to a rapid loss of catalytic activity of the catalyst due to the occurrence of side chemical processes.

2 | MATERIAL AND METHODS

2.1 | Materials

Reagents and solvents were purchased from Aldrich and used as received unless otherwise noted.

2.2 | Synthetic procedures

2.2.1 | *N*-Phenyl-2,6-diphenyl-4-arylpyridinium perchlorates (2a-d)

A mixture of 2.4 mmol of 2,6-diphenyl-4-arylpyridium perchlorate (**1a-d**), 2.4 mmol of arylamine, 0.33 mL (2.4 mmol) of triethylamine, and 10 mL of chloroform was kept at room temperature and with constant stirring for 10 to 15 minutes then 0.4 M (7.5 mmol) of glacial acetic acid and stirring was continued for an additional 40 to 60 minutes during which time the discoloration of the solution was observed. After that, approximately 10 to 15 mL of ethanol was added to the reaction mixture. The precipitate that formed was filtered off. We dried it in the air.

2.2.2 | *N* -Phenyl-2,4,6-triphenylpyridinium perchlorate (2a)

Yield 0.82 g (70.7%). ^{1}H NMR (CD_2Cl_2): 6.97, 7.3, 7.44, 7.66 m (20H); 8.33 d (2H); 8.61 s (2H). ^{13}C NMR (CD_2Cl_2): δ 21.06, 125.76, 128.62, 130.23, 130.46, 133.78, 134.04, 139.98, 155.99, 156.96.

2.2.3 | *N*-Phenyl(*p*-methoxyphenyl)-2,4,6-triphenylpyridinium perchlorate (2b)

Yield 0.84 g (61.6%). ^{1}H NMR (CD_2Cl_2): δ 3.57 s (3H); 6.69, 6.71, 7.3, 7.46, 7.66 m (15H); 8.31, 8.60 d (4H). ^{13}C NMR (CD_2Cl_2): δ 55.92, 114.06, 125.72, 128.66, 130.23, 130.48, 133.87, 155.96, 157.24, 159.96.

2.2.4 | *N*-Phenyl(*p*-bromophenyl)-2,4,6-triphenylpyridinium perchlorate (2c)

Yield 0.6 (43.5%). ^{1}H NMR (CD_2Cl_2): δ 7.37-7.66 (17H); 8.32-8.34 m (2H); 8.65 s (2H). ^{13}C NMR (CD_2Cl_2): δ 125.52, 127.47, 128.90, 132.35, 133.96, 155.86, 128.91.

2.2.5 | *N*-Phenyl(*p*-tolyl)-2,4,6-triphenylpyridinium perchlorate (2d)

Yield 0.78 g (65.53%). ^{1}H NMR (CD_2Cl_2): δ 2.08 s (3H); 6.97, 7.3, 7.44, 7.66 m (17H); 8.33 d (2H); 8.61 s (2H). ^{13}C NMR (CD_2Cl_2): δ 21.06, 125.76, 128.62, 130.23, 130.46, 133.78, 134.04, 139.98, 155.99, 156.96.

2.2.6 | *N*-Aryl-2,6-diphenyl-4-(*p*-methoxyphenyl)pyridinium perchlorates (3a-d)

_N_-Phenyl-2,6-diphenyl-4-(_p_-methoxyphenyl) pyridinium perchlorate (3a)

A mixture of 0.44 g (1 mmol) of 2,6-diphenyl-4-(*p*-methoxyphenyl)pyrilium perchlorate (**1a**) and 7 mL of ethanol was boiled for 20 minutes, and then a solution of 0.19 g (2 mmol) of aniline in 3 mL of ethanol was added. The reaction mixture was boiled for 1 hour; 0.4 mL of triethylamine was added, and the mixture was boiled for an additional 3 hours until complete dissolution (**1a**). At the end of the reaction, the mixture was cooled to room temperature. The precipitate that formed was filtered off, dried in air, and purified by recrystallization from isobutanol. We obtained shiny crystals (**3a**) of white color. Yield: 0.38 g (74%). ^{1}H NMR (CD_2Cl_2): δ 3.49 s (3H); 6.76-7.04 m (17H); 7.96-8.00 d (2H); 8.18 s (2H). ^{13}C NMR (CD_2Cl_2): δ 55.91, 115.41, 123.88, 125.43, 128.19, 129.84, 131.05, 133.42, 139.18, 155.01, 156.05, 163.32.

_N_-(_p_-Methoxyphenyl-2,6-diphenyl-4-(_p_-methoxyphenyl)pyridinium perchlorate (3b)

A mixture of 0.44 g (1 mmol) of 2,6-diphenyl-4-(*p*-methoxyphenyl)pyrilium perchlorate and 7 mL of ethanol was boiled for 20 minutes, and then a solution of 0.12 g (1 mmol) of *p*-anisidine in 3 mL of ethanol was added. The reaction mixture was boiled for 1 hour; 0.4 mL of triethylamine was added, and the mixture was boiled for another 2 hours until complete dissolution (**1a**). After completion of the reaction, the mixture was cooled to room temperature. The precipitate was filtered off, dried in air, and purified by recrystallization from isobutanol, crystals (**3b**) green color. Yield: 0.35 g (64%). ^{1}H NMR (CD_2Cl_2): δ 3.17 (3H), 3.48 s (3H), 6.27-6.29 d (2H), 6.76-7.04 m (14H), 7.94-7.97 m (2H), 8.14 s (2H). ^{13}C NMR (CD_2Cl_2): δ 55.50, 55.88, 113.61, 115.38, 123.87, 125.48, 128.22, 129.79, 130.99, 133.59, 154.82, 156.45, 159.48, 163.25.

N-(*p*-Bromophenyl-2,6-diphenyl-4-(*p*-methoxyphenyl) pyridinium perchlorate (3c)

A mixture of 0.44 g (1 mmol) of 2,6-diphenyl-4-(*p*-methoxyphenyl)pyrylium perchlorate and 7 mL of ethanol was boiled for 20 minutes, and then a solution of 0.17 g (1 mmol) of *p*-bromoaniline in 5 mL of ethanol was added. The reaction mixture was boiled for 1 hour; 0.4 mL of triethylamine was added, and the mixture was boiled for a further 2 hours before the complete dissolution (**1b**). After the reaction was completed, the mixture was cooled to room temperature. The precipitate was filtered off, dried in air, and purified by recrystallization from isobutanol, crystals (**3c**). Yield: 0.34 g (57%). ^{13}C ^{1}H NMR (CD_2Cl_2): δ 123.71, 125.77, 128.78, 130.28, 132.14, 133.48, 133.98, 156.43, 156.73.

N-(*p*-Tolyl-2,6-diphenyl-4-(*p*-methoxyphenyl) pyridinium perchlorate (3d)

A mixture of 0.44 g (1 mmol) of 2,6-diphenyl-4-(*p*-methoxyphenyl)pyrylium perchlorate and 7 mL of ethanol was boiled for 20 minutes, and then a solution of 0.1 g (1 mmol) of *p*-methylaniline in 3 mL of ethanol was added. The reaction mixture was boiled for 1 hour; 0.4 mL of triethylamine was added, and the mixture was boiled for another 2 hours until complete dissolution (**1b**). After the reaction was completed, the mixture was cooled to room temperature. The precipitate was filtered off, dried in air, and purified by recrystallization from isobutanol. Yield: 0.39 g (74%). ^{1}H NMR (CD_2Cl_2): δ 3.39, 4.47, 6.58, 7.13, 7.18, 7.29, 7.63, 7.66, 7.67. ^{13}C NMR (CD_2Cl_2): δ 55.48, 114.24, 120.67, 126.22, 128.85, 133.31, 136.98, 138.94, 152.37, 160.74, 190.07, 196.23.

2.3 | Cyclic voltammetry

The CV experiments were carried out in acetonitrile with 0.1M [*n*-Bu4N][BF4] as a supporting electrolyte using a Gamry Instruments Reference 3000 (10 mL of solution). Glass carbon electrode ($S = 0.125\ cm^2$) was used as a working electrode. The sweep rate of the potential was 200 mV/s. The electrode was carefully polished and washed before and between measurements. A platinum counter electrode and a standard Ag/AgCl reference electrode were used. Ferrocene was used as an internal standard: the $E^0(Fc^+/Fc) = 0.31$ V versus Ag/AgCl in acetonitrile.

2.4 | Spectroscopy

NMR spectrums ^{1}H and ^{13}C solutions of bonds in $CDCl_3$-d_6 and DMSO-d_6 are written down on spectrometer JNM-ECX400 of firm JEOL (400 MHz). Intrinsic standard hexamethyldisiloxane (GMDS). Conditions of thin-layer chromatography : adsorbent - Silufol UV-254, eluent - ethyl ether and ethyl acetate (1:1).

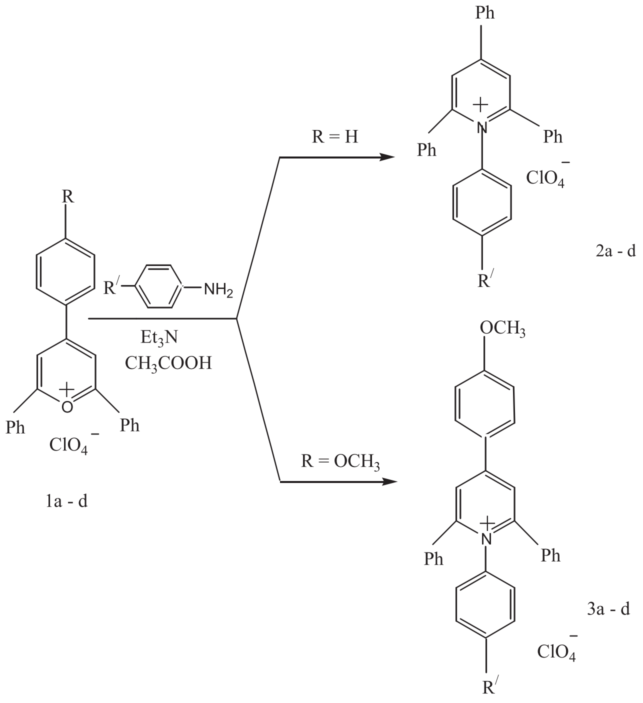
3 | RESULTS AND DISCUSSION

Synthesis of 2,4,6-triarylpyridinyl salts was carried out according to the following scheme. Triarylpyridinium salt (**2a-d** and **2a-d**) was obtained from the corresponding pyrilium salts (**1a** and **1b**) (Scheme 2).

The resulting pyridinium salts **2a-d** and **3a-d** in contrast to the intensely stained pyridium salts **1a-d** are usually colorless (**2a-d**, **3d**, **3d**) or slightly colored (**3b**, **3c**) crystalline compounds melting at high temperature (approximately 250°C) with decomposition. Compared with the initial pyrilium salts, the salts **2a-d** and **3a-d** are better soluble in organic solvents.

All the compounds obtained are capable of oxidation and a reduction in a wide range of potentials (Table 1).

All the waves observed on voltammograms correspond to processes with diffusion limitation in the sweep



R′ = H (a), OCH_3 (b), CH_3 (c), Br (d)

SCHEME 2 General route of synthesis of 2,4,6-triarylpyridinyl salts

TABLE 1 Electrochemical characteristics (mV) for the triarylpyridinium salt (CH3CN, GC electrode, 200 mV/s, rel. Ag/AgCl/KCl)

Compound	Reduction, E_{1red}		ΔE	Reduction, E_{2red}		ΔE
2a	−0.91	−0.80	0.11	−1.01	−0.94	0.07
2b	−0.91	−0.78	0.13	−1.06	−0.98	0.08
2c	−0.90	−0.81	0.11	−1.07	−0.97	0.1
2d	−0.92	−0.78	0.12	−1.03	−0.92	0.09
3a	−0.93	−0.86	0.17	−1.15	−1.06	0.09
3b	−0.93	−0.8	0.13	−1.27	−1.18	0.09
3c	−0.90	−0.80	0.1	−1.20	−1.12	0.09
3d	−0.92	−0.82	0.1	−1.18	−1.10	0.08

speed range from 50 to 1000 mV/s. The method of the reference additive (Fc) was used to determine the number of electrons participating in each stage of the electrochemical processes.

As can be seen from Table 1, the electrochemical properties strongly depend on the nature of the substituents located both at the nitrogen atom and on the fourth carbon atom. The cyclic voltammograms (cva) for the pyrilium salts **2a-d** and **3a-d** on the anodic region have similar shapes and contain only one irreversible wave to oxidation of the perchlorate-ion (E = 1.85 V): The typical cyclic voltammogram obtained for the compound **2a** is shown in Figure 1.

In the cathode region, two quasi-reversible one-electron waves are observed for the **2a-3d** compounds in the CV in the corresponding sequential electrochemical reduction of the salts to the anion through the radical formation stage (Scheme 3), which corresponds to the EE mechanism[16] (Figure 2).

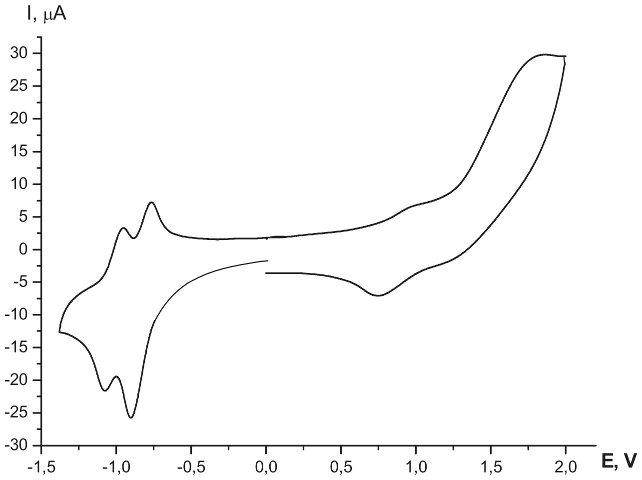
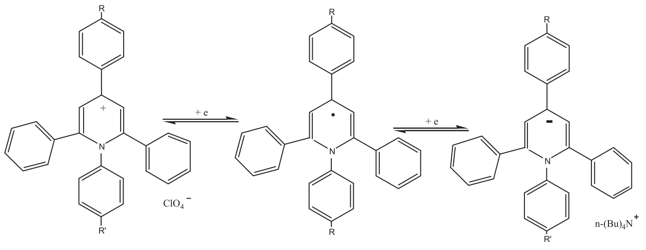
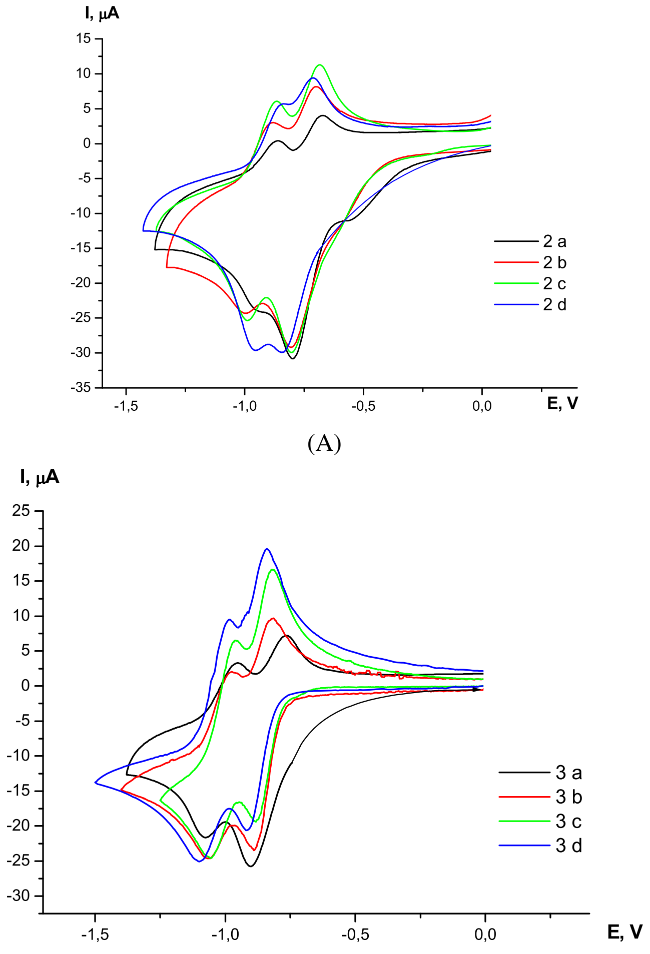


FIGURE 1 Cyclic voltammogram for 1mM acetonitrile solutions of pyridinium salt **2a** on a glassy carbon electrode



SCHEME 3 EE mechanism reduction triarylpyridinium salts



(B)

FIGURE 2 Cyclic voltammograms for 1mM acetonitrile solutions of (A) **2a-d** and of (B) **3a-d** on a glassy carbon electrode

As was shown earlier, in the case of one-electron electrochemical reduction of the pyridinium ion PyH$^+$, a radical (PyH$^\cdot$) is formed, and the nature of which is confirmed by EPR spectroscopy.[17] By analogous mechanism (EE), an electrochemical reduction of 9-phenyl-*N*-phenylacridinium chloride occurs.[18]

As can be seen from Table 1 and Figure 1, the substituents located both in the phenyl ring at the nitrogen atom and in the phenyl ring at fourth position have a slight effect on the values of the first potentials of the reduction waves. It should be noted that the recovery potentials for the eight compounds are very slightly different. Such unusual electrochemical behavior of salts containing fragments with various electromeric effects is difficult to explain within the framework of classical concepts of the effect of substituents on oxidation-reduction properties.[16,19] Compounds containing groups with strong electron-donating properties (—OCH_3) should be more difficult to reduce compared with compounds containing substituents Br— and —CH_3.[19] One of the reasons for this unusual electrochemical behavior of salts may be the absence of conjugation between substituents and the redox active center. Earlier, the same fact was established in the study of the electrochemical reduction of *N*-substituted pyridines.[20] The conjugation can be disrupted by the steric repulsion of the phenyl substituent located at the nitrogen atom and by the substituents at positions 2 and 6. The plane of the phenyl substituent at position 4 is broken due to interaction with hydrogen atoms at positions 3 and 5 (Scheme 4).

It is important to note that the values of ΔE ($\Delta E = E_{\text{red}} - E_{\text{reox}}$) characterize the reversibility of the redox process, in all cases, significantly more than 60 mV (Table 1)[21] that may indicate the quasi-reversible character of the reduction process. Indeed, it turned out that the high values of ΔE are associated with the quasi-reversibility of the reduction process, as evidenced by the CV data obtained at different scan rates (Figure 3).

As can be seen from Figure 3, the parameter ΔE for both reduction waves increases with increasing the sweep rate of the potential, which unambiguously (diagnostic criteria) indicates the quasi-reversible character of the reduction process.[15,21] It should be noted that a similar shape of CV curve is observed for all compounds of the series. As can be seen from Figure 3, the difference between direct and backward redox processes increases with an increase in the scanning rate of the potential. This fact indicates the occurrence of a quasi-reversible process. It should be noted that a similar shape of CV curve is observed for all compounds of the series. It can be assumed that the quasi-reversibility of the reduction process is associated with small structural deformations of molecules that occur after one-electron transfer, for example, with partial inversion of substituents at the nitrogen atom and at the fourth carbon atom. As can be seen from Table 1, the value of the second reduction potential, opposite, strongly depends on the nature of the substituents: In the case of a series of compounds **2**, the difference between the first and second reduction potential lies in the region of 100 to 150 mV, whereas for the series of compounds **3**, the difference is 220 to 340 mV. The two-electron triarylpyridinium reduction product can be considered as a very high-energy species, which becomes obvious when the anti-aromatic (8n) character of such anion is recognized. Therefore, the reduction potentials ($E_{2\text{red}}$) are so strongly shifted to the cathode region. A similar electrochemical behavior was observed with two electronic reduction of the unsubstituted pyridinium ion PyH^+. The difference between the reduction potentials was 350 mV.[15] It is important to note that when a radical is reduced to an anion, the nature of the substituents on the nitrogen atom is already beginning to play an important role in electrochemical behavior. In our opinion, this is due to the destabilizing effect of the methoxy group on the anion formed during the electrochemical reduction of the radical.

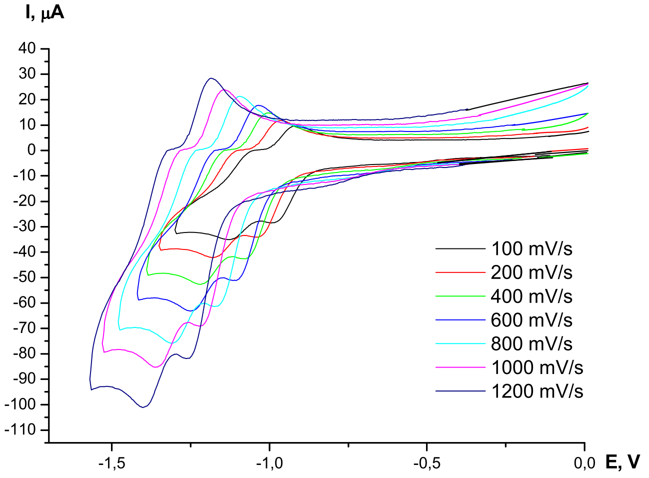
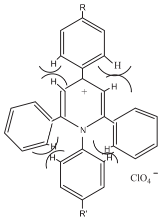


FIGURE 3 Cyclic voltammograms for 1mM acetonitrile solutions of **2a** at different potential scan rate



SCHEME 4 Steric interaction of substituents in the cation triarylpyridinium

4 | CONCLUSIONS

In summary, we have studied the electrochemical properties of a number of heterocyclic salts based on pyridine. The main factors influencing the oxidation-reduction properties of salts are determined. The potential of the first reduction wave is mainly influenced by steric factors and by $E_{2\text{red}}$ the electrical factors of the methoxy group.

ACKNOWLEDGEMENT

This work was supported by the Russian Foundation for Basic Research (18-03-00211) and Ministry of Education and Science of the Russian Federation within the framework of government task in the field of scientific activities (project No. 4.4566.2017/8.9).

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How to cite this article: Dolganov AV, Tanaseichuk BS, Pryanichnikova MK, et al. Triarylpyridinium salts: Synthesis and electrochemical properties. *J Phys Org Chem*. 2019; e3930. https://doi.org/10.1002/poc.3930