JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Synthesis and X-ray Characterization of Alkali Metal 2-Acyl-1,1,3,3-tetracyanopropenides

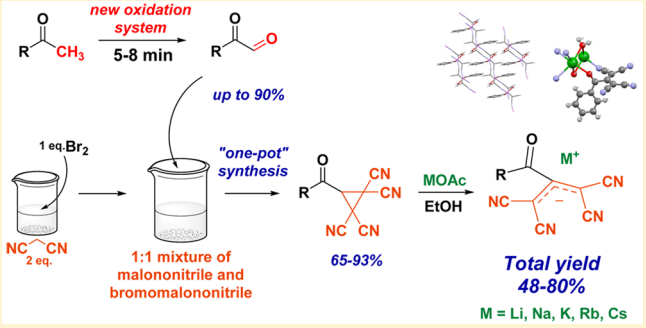
Sergey V. Karpov,*[,†] Arthur A. Grigor'ev,[†] Yakov S. Kayukov,[†] Irina V. Karpova,[†] Oleg E. Nasakin,[†] and Victor A. Tafeenko[‡]

[†]I. N. Ul'yanov Chuvash State University, Moskovskii Prospekt 15, Cheboksary, 428015, Russia

[‡]Lomonosov Moscow State University, Leninskiye Gory 1-3, Moscow, 119991, Russia

Supporting Information

ABSTRACT: A novel route for synthesis of 2-acyl-1,1,3,3-tetracyanopropenides (ATCN) salts in high yields and excellent purities starting from readily available methyl ketones, malononitrile, bromine, and alkali metal acetates is reported. The starting aryl(heteroaryl) methyl ketones were oxidized to the corresponding α-ketoaldehydes by new a DMSO−NaBr−H_2SO_4 oxidation system in yields up to 90% within a short reaction time of 8−10 min. The subsequent stages of ATCN preparation are realized in aqueous media without use of any toxic solvents, in accordance with principle 5 of "green chemistry". Lithium, sodium, potassium, rubidium, and cesium 2-benzoyl-1,1,3,3-tetracyanopropenides were characterized by X-ray diffraction analysis. These salts show a good potential for synthesis of five- and six-membered heterocycles and may serve as potentially useful ligands in coordination and supramolecular chemistry.



INTRODUCTION

Currently, salts containing tetracyanoallyl (TCA) anion (Figure 1) have received considerable attention. This is because TCA

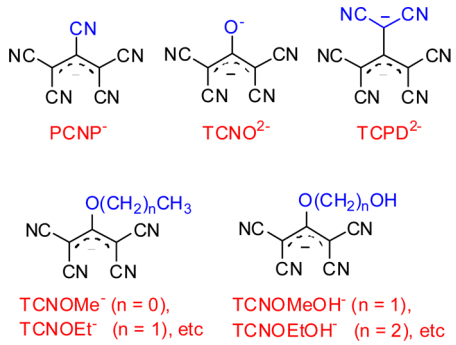


Figure 1. Family portrait of TCA ligands.

anions have a variable denticity and might be used as bridging ligands for construction of various 1D, 2D, and 3D coordination polymeric frameworks.[1]

TCA salts can be applied to create materials with potentially useful properties, such as magnetic,[2] thermo- and photochromic,[3] semiconducting,[4] and photomagnetic ones.[5] The spin-crossover (SCO) materials based on TCA ligands are also described.[6] Moreover, these salts have received interest as components of new propellants,[7] ionic liquids,[8] and burning-rate catalysts.[9]

We previously described some chemical properties of new 2-acyl-1,1,3,3-tetracyanopropenide (ATCN) salts **1** containing a carbonyl group in position 2 of the TCA anion.[10,11] The carbonyl oxygen can form an additional coordination bonds with cation. Moreover, ATCNs are prospective precursors for synthesis of five- and six-membered heterocycles (Figure 2). Consequently, these compounds might be of interest as new building blocks in the design of coordination polymers and as precursors for heterocyclic synthesis.

The ATCN salts were first obtained by Bardasov et al. via a three-step synthesis using acetophenones, selenium dioxide, malonodinitrile, and bromomalonodinitrile as starting compounds[12] (Scheme 1). At the first stage, glyoxal hydrates **3** were obtained by a well-known method[13] via oxidation of acetophenones **2** with selenium dioxide in 42−69% yields. At the second stage, the resulting glyoxal hydrates were reacted with a mixture of equal amounts of malonodinitrile and bromomalonodinitrile with formation of the corresponding cyclopropanes **4** via an adduction and ring closure (ARC) process.

At the final stage of the synthesis of ATCN salts, cyclopropanes **4** were reacted with an equal amount of sodium acetate in acetonitrile followed by solvent removal by rotary evaporation. The total yield of ATCN (based on starting acetophenones) did not exceed 44%. In addition, this method of ATCN preparation has a number of significant disadvan-

Received: May 4, 2016
Published: July 6, 2016

DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408

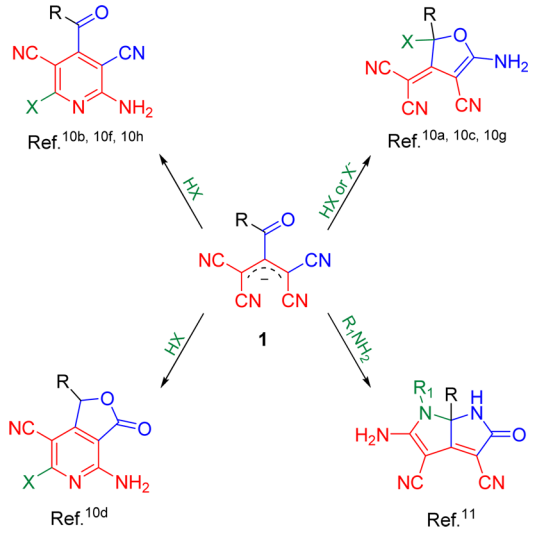


Figure 2. Described routes for heterocyclization of $ATCN^-$.

tages, such as the necessity for a long period of refluxing and the formation of fine particulate selenium, which polluted the product at the oxidation stage; the necessity for a preliminary synthesis of unstable irritant bromomalonodinitrile at stage 2; and the necessity for toxic acetonitrile to be used as solvent at the final stage.

Herein, we report a novel process version for the preparation of ATCN salts based on the oxidation of aryl(heteroaryl) methyl ketones to aryl(heteroaryl)glyoxals by a new DMSO–NaBr–H_2SO_4 system and subsequent ARC reaction with malonodinitrile and bromine in water. At the final stage, the corresponding cyclopropyl ketones **4** undergo the ring-opening reaction under the action of potassium acetate in ethanol. The resulting potassium ACTN salts were precipitated by saturated aqueous KCl.

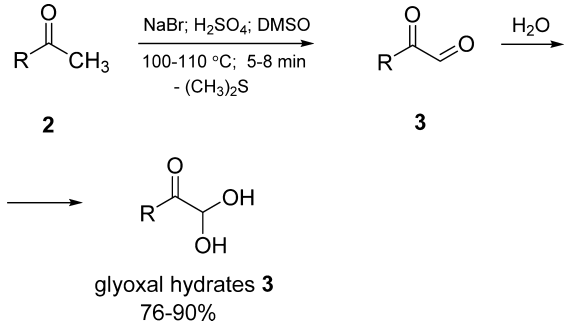
The application of this method allowed us to increase the total yields of ATCN salts up to 80% and decrease the total synthesis time to less than 3 h. Also, this method does not require toxic and expensive reagents, such as selenium dioxide and acetonitrile, in accordance with principle 5 of "green chemistry". In addition, lithium, sodium, potassium, rubidium, and cesium 2-benzoyl-1,1,3,3-tetracyanopropenides were characterized by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Stage 1. Oxidation of Aryl(heteroaryl) Methyl Ketones to Glyoxales by the NaBr–DMSO–H_2SO_4 Oxidizing System. Currently, a variety of methods for the oxidation of methyl ketones to α-ketoaldehydes have been described. One of the most applied methods involves use of CrO_3, diphenylselenoxide, or selenium dioxide.[13,14] A more safe and accessible reagent is a DMSO–HBr mixture, but this method also has disadvantages, such as a long reaction time (1–24 h) and medium yields (low to 50% on average).[14b]

We have developed an alternative method of oxidation of aryl(heteroaryl) methyl ketones **2** to the corresponding aryl(heteroaryl)glyoxals **3** based on readily available reagents such as DMSO, NaBr, and concentrated sulfuric acid (Scheme 2).

Scheme 2. Reaction of Aryl(heteroaryl) Methyl Ketones with DMSO–NaBr–H_2SO_4 Mixture



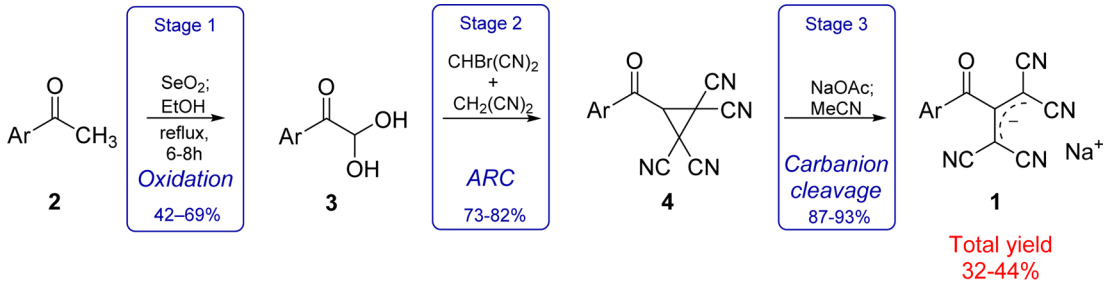
This method allows one to obtain glyoxal hydrates **3** significantly faster and in higher yields. The reaction process comprises heating at 100–110 °C a mixture of ketone **2**, DMSO, and sodium bromide in the presence of sulfuric acid. When the reaction is finished, the formation of dimethyl sulfide bubbles is sharply reduced, which is a convenient visual indication of the completion of the process. The isolation of glyoxals is not required for further ARC reaction, but it can be readily carried out if necessary (see Table 1 and the Experimental Section for details).

A proposed mechanism for this "one-pot" reaction comprises initial particular oxidation of bromide ion to bromine by sulfuric acid. Subsequent bromination of aryl(heteroaryl) methyl ketones leads to α-bromo ketone, which immediately oxidized with DMSO. The forming hydrogen bromide is then particularly oxidized to bromine by sulfuric acid (Scheme 3).

Stage 2. Adduction and Ring Closure Reaction. At the second stage, the resulting glyoxals undergo the ARC reaction under the action of a mixture of equal amounts of malonodinitrile and bromomalonodinitrile.

The outdated version[12] of this synthesis requires a preliminary preparation of pure crystalline monobromomalonodinitrile via bromination of malonodinitrile. Subsequent ARC reaction with glyoxals was realized in acetonitrile in quite

Scheme 1. First Synthesis of ATCN[12]



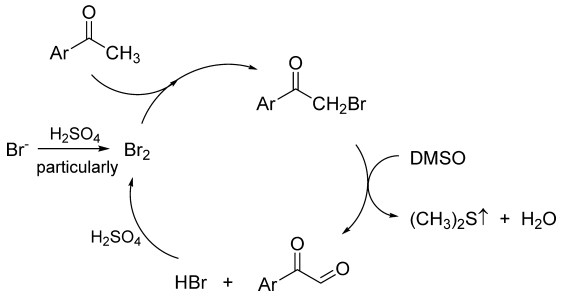
DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402–6408

Table 1. Substituents and Yields of Isolated Glyoxal Hydrates 3

entry	R	yield (%)[a]
3a	Ph	87
3b	4-$CH_3C_6H_4$	90
3c	4-BrC_6H_4	81
3d	4-$NO_2C_6H_4$	76
3e	4-$CH_3OC_6H_4$	89
3f	2,4-$Cl_2C_6H_3$	78
3g	3-ClC_6H_4	86
3h	3,4-$(OCH_3)_2C_6H_3$	90
3i	2-naphthyl	77
3j	2-thienyl	81
3k	2-furyl	80
3l	5-Br-2-thienyl	83

[a]Using KBr instead of NaBr leads to decreased glyoxals **3** yields of about 10−20%.

Scheme 3. A Proposed Mechanism for Oxidation of Aryl(heteroaryl) Methyl Ketones



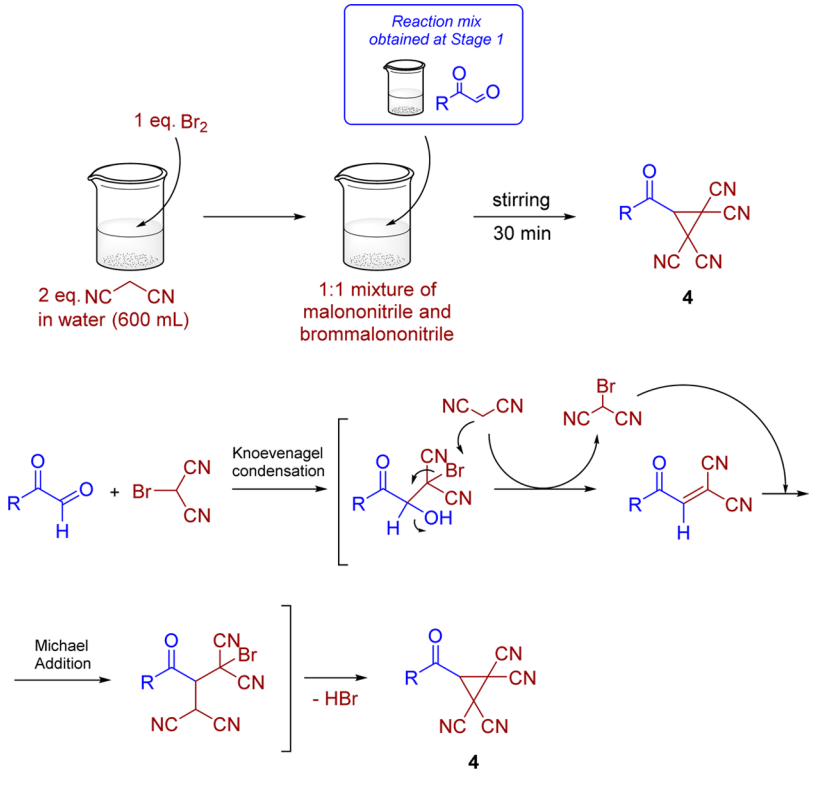
good yields of the resulting tetracyanocyclopropyl ketones (73−82%). Our approach to reaction optimization comprises preparation of an equimolar mixture of malonodinitrile and bromomalonodinitrile in water and subsequent cyclopropanation under "one-pot" reaction conditions (Scheme 4). This method allows one to obtain the tetracyanocyclopropyl ketones **4** in good yields (Table 2) with high purities.

Table 2. Substituents and Yields of 3-Aroyl(heteroaroyl)cyclopropane-1,1,2,2-tetracarbonitriles 4

entry	R	yield (%)
4a	Ph	79
4b	4-$CH_3C_6H_4$	83
4c	4-BrC_6H_4	75
4d	4-$NO_2C_6H_4$	71
4e	4-$CH_3OC_6H_4$	86
4f	2,4-$Cl_2C_6H_3$	69
4g	3-ClC_6H_4	73
4h	3,4-$(OCH_3)_2C_6H_3$	90
4i	2-naphthyl	65
4j	2-thienyl	93
4k	2-furyl	89
4l	5-Br-2-thienyl	90

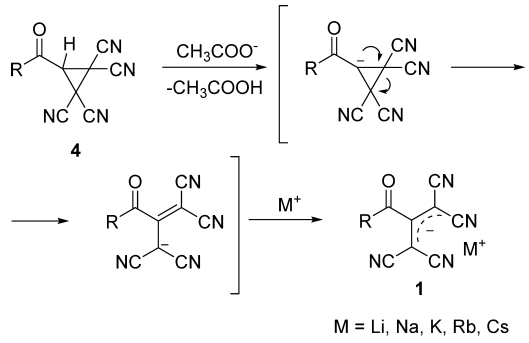
Stage 3. Synthesis of ATCN Salts 1 via Carbanion Cleavege of Tetracyanocyclopropyl Ketones 4. At the third stage, the resulting tetracyanocyclopropyl ketones **4** were reacted with alkali acetates in ethanol (Scheme 5). We have found that the solubility of ATCN salts in saturated solutions of the corresponding metal chloride is drastically reduced. This allowed one to isolate ATCN salts **1** in high yields (Table 3) by salting out without usage of a rotary evaporator. According to

Scheme 4. Synthesis of 3-Aroyl(heteroaroyl)cyclopropane-1,1,2,2-tetracarbonitriles 4



DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408

Scheme 5. Synthesis of 2-Acyl-1,1,3,3-tetracyanopropenides (ATCN) 1



4 1

^{1}H NMR data, the purity of the crude products (after drying in vacuo) is 97−99%.

Table 3. Substituents and Yields of ATCN Salts 1

entry[a]	R	yield (%)	total yield[b] (%)
$\mathbf{1a_{Li}}$	Ph	89	57
$\mathbf{1a_{Na}}$	Ph	91	59
$\mathbf{1a_{K}}$	Ph	94	60
$\mathbf{1a_{Rb}}$	Ph	95	60
$\mathbf{1a_{Cs}}$	Ph	96	61
1b	4-$CH_3C_6H_4$	95	69
1c	4-BrC_6H_4	90	58
1d	4-$NO_2C_6H_4$	86	49
1e	4-$CH_3OC_6H_4$	96	75
1f	2,4-$Cl_2C_6H_3$	83	48
1g	3-ClC_6H_4	87	51
1h	3,4-$(OCH_3)_2C_6H_3$	93	80
1i	2-naphthyl	88	55
1j	2-thienyl	95	73
1k	2-furyl	96	74
1l	5-Br-2-thienyl	93	77

[a]Compounds **1b**−**l** are potassium salts. [b]Total yield is based on the starting acetophenones without intermediate isolation of glyoxals **3** and purification of cyclopropanes **4**

X-ray Characterization of Alkali Metal ATCN Salts. Further, we have investigated the crystal structure of the alkali metal 2-benzoyl-1,1,3,3-tetracyanopropenide salts **1a** by X-ray diffraction analysis, because these compounds might be of considerable interest as new ligands in coordination chemistry. The synthesis of lithium, sodium, rubidium, and cesium salts was carried out analogously to potassium salt preparation by using the appropriate metal acetates and chlorides. CCDC 1452031, 1452032, 1452033, 1452034, and 1452035 for $\mathbf{1a_{Cs}}$, $\mathbf{1a_{K}}$, $\mathbf{1a_{Li}}$, $\mathbf{1a_{Na}}$ and $\mathbf{1a_{Rb}}$ respectively contain the supplementary crystallographic data for this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The molecular structures of salts **1a** showing the atom labeling scheme can be see in Figures S1−S5 of the Supporting Information (SI). The crystal parameters and refinement metrics to accompany the thermal ellipsoid plot are also provided in the SI (Table S1 for $\mathbf{1a_{Li}}$, Table S3 for $\mathbf{1a_{Na}}$, Table S5 for $\mathbf{1a_{K}}$, Table S7 for $\mathbf{1a_{Rb}}$, and Table S9 for $\mathbf{1a_{Cs}}$). Selected bond lengths and angles for $\mathbf{1a_{Li}}$, $\mathbf{1a_{Na}}$, $\mathbf{1a_{K}}$, $\mathbf{1a_{Rb}}$, and $\mathbf{1a_{Cs}}$ are correspondingly in Tables S2, S4, S6, S8, and S10 of the SI.

Single-crystal X-ray diffraction analysis reveals that lithium 2-benzoyl-1,1,3,3-tetracyanopropenide ($\mathbf{1a_{Li}}$) is a monohydrate and crystallizes in the triclinic system with space group $P\bar{1}$. The coordination environment of Li, shown in Figure S1a (SI), is four-coordinate with two nitrogens (N1^{i} and N4^{i}) belonging to the two $ATCN^-$ ligands, a carbonyl oxygen (O1) from the third $ATCN^-$, and an oxygen (O2) from coordinated water in a slightly distorted tetrahedral geometry. Each lithium cation connects the N1 and N2 nitrogens belonging to different $ATCN^-$ anions to form a 1D chain. The carbonyl groups of $ATCN^-$ connect the neighboring 1D chains to generate a 1D ribbon (Figure S1b, SI). Moreover, the neighboring 1D ribbons are further connected through dipole−dipole interactions between cyano groups as well as hydrogen bonds between coordinated water molecules and N2 nitrogen atoms (Figure S1c).

Sodium ($\mathbf{1a_{Na}}$) and potassium ($\mathbf{1a_{K}}$) 2-benzoyl-1,1,3,3-tetracyanopropenides crystallize as monohydrates in monoclinic symmetry with space group $P21/n$. X-ray diffraction analysis demonstrates that $\mathbf{1a_{Na}}$ and $\mathbf{1a_{K}}$ crystals are isostructural and show only minor differences in bond lengths and bond angles (Figures S2 and S3, SI). The coordination environment of Na is six-coordinate with three cyano group nitrogens (N1^{iii}, N2^{i}, and N3^{ii}) belonging to the three $ATCN^-$ ligands, a carbonyl oxygen (O1) from the fourth $ATCN^-$, and a two oxygens (O2 and O2^{i}) from coordinated water in a slightly distorted octahedral geometry. The two neighboring sodium or potassium cations are combined into pair through two water molecules, as shown in Figures S2b and S3b (SI). Each ATCN anion connects three sodium atom pairs to form a 2D mesh structure. The 3D supramolecular structure is formed by stacking 2D layers. The potassium salt $\mathbf{1a_{K}}$ displays a topological structure similar to that of $\mathbf{1a_{Na}}$.

Rubidium ($\mathbf{1a_{Rb}}$) and cesium ($\mathbf{1a_{Cs}}$) 2-benzoyl-1,1,3,3-tetracyanopropenides crystallize in monoclinic symmetry with space group $P21/c$. X-ray diffraction analysis demonstrates that $\mathbf{1a_{Rb}}$ and $\mathbf{1a_{Cs}}$ crystals are isostructural and show minor differences in bond lengths and bond angles (Figures S4 and S5, SI).

The coordination environment of Cs comprises five cyano group nitrogens (N1^{iii}, N2^{i}, N3^{vi}, N4^{ii}, N4^{iii}) belonging to the four ATCN ligands, a carbonyl oxygen (O1) from the fifth $ATCN^-$, and a benzene ring with minimum distances 3.882 Å (Cs···C4^{iv}) and 3.821 Å (Cs···C5^{vi}) (Figure S5a, SI).

All salts **1a** are yellow or yellow-green crystalline powders and have a good solubility in water and polar organic solvents. $\mathbf{1a_{Li}}$ and $\mathbf{1a_{Na}}$ also reveal an intense yellow-green luminescence in the solid state under UV-lamp irradiation and have no luminescence properties in any solutions.

In summary, we have developed a new fast, simple, and efficient route for ATCN salts synthesis. All ATCN salts for the first time were characterized by ^{1}H and ^{13}C NMR. X-ray diffraction analysis reveals that $ATCN^-$ anion has the ability to form multiple coordination bonds that make it a candidate for creation of various 1D, 2D, and 3D supramolecular structures and potential functional materials.

EXPERIMENTAL SECTION

General. All starting materials and solvents were obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were registered at operating frequencies of 500 and 121 MHz, respectively, with DMSO-d_6 as solvent and TMS as internal reference. HRMS data were acquired with a QTOF mass

DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408

spectrometer. The X-ray data were collected by using an STOE diffractometer with Pilatus 100 K detector, focusing mirror collimation, Cu Kα (1.54086 Å) radiation, and rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multiscan method). The structures were solved and refined with the SHELX[15a] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-squares procedure. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND[15b] and Mercury[15c] software.

Preparation of Aryl(heteroaryl)glyoxals 3 via Oxidation of Aryl(heteroaryl) Methyl Ketones by the DMSO−NaBr−H_2SO_4 System (General Procedure). Aryl(heteroaryl) methyl ketone (0.1 mol) and sodium bromide (5.0 g, 0.048 mol) were dissolved in DMSO (50 mL) in a 150 mL tall-form beaker. The mixture was heated strictly to 85 °C with stirring and then ∼5 mL of concentrated sulfuric acid was quickly added to the reaction. The reaction mass foamed due to dimethyl sulfide gas formation and the reaction temperature began to rise. It is important to maintain the temperature of the reaction mass within the range between 100 and 115 °C. When the reaction is finished (5−7 min), the formation of dimethyl sulfide bubbles will be sharply reduced and the reacting mixture will become viscous. After cooling, the yellow-orange oil which formed was dissolved in 50 mL of ethanol, and the resulting solution was then used at the second stage of ATCN synthesis.

If necessary, aryl(heteroaryl)glyoxals might be isolated (as the hydrated form). For this purpose, 50 mL of distilled water was added to the resulting yellow-orange oil, and the resulting mixture was refluxed for 5 min under stirring. The aqueous phase was separated, cooled to 0−5 °C, and left for 3 h or overnight. The formed white precipitate was filtered and dried in air.

Note that using KBr instead of NaBr leads to decreased yields of glyoxale hydrates of about 10−20% due to gelling of the reaction mass, dimethyl sulfide is an irritant, and this reaction should be carried out in a well-ventilated fume hood.

Stage 2. Synthesis of 3-Aroyl(heteroaroyl)cyclopropane-1,1,2,2-tetracarbonitriles 4 (General Procedure). Bromine (16.0 g, 0.1 mol) was dissolved in 600 mL of distilled water with stirring. Malonodinitrile (13.2 g, 0.2 mol) was dissolved in 50 mL of EtOH and the resulting mixture was poured into bromine solution. The mixture obtained during the previous stage containing aryl(heteroaryl)glyoxal was added dropwise to the resulting solution with vigorous stirring. After the mixture was stirred for 30 min, the white precipitate was filtered off, washed with ice-cold ethanol, and used at next stage without additional purification. If necessary, cyclopropyl ketones **4** might be recrystallized from acetone or acetic acid.

Stage 3. Synthesis of 2-Aroyl(heteroaroyl)-1,1,3,3-tetracyanopropenides 1 (General Procedure). 3-Aroyl(heteroaroyl)-cyclopropane-1,1,2,2-tetracarbonitrile **4** (0.05 mol) was added to a mixture of alkali metal acetate (0.07 mol) and ethanol (20 mL) and then stirred at 45−50 °C until the solids had dissolved. The resulting dark-yellow solution was filtered, the filtrate was allowed to cool and then was poured into a 10% solution of the corresponding alkali metal chloride (75 mL), and the mixture was left for 30 min at 5−10 °C. The resulting precipitate was filtered, washed with diethyl ester, and dried in air.

*3-Benzoylcyclopropane-1,1,2,2-tetracarbonitrile (**4a**).* Yield: white solid, 19.43 g, 79%. Mp: 214−215 °C (lit.[12] 211−212 °C) (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.26 (d, $^3J_{H,H}$ = 7.3 Hz, 2H), 7.80 (t, $^3J_{H,H}$ = 7.3 Hz, 1H), 7.65 (t, $^3J_{H,H}$ = 7.9 Hz, 2H), 5.67 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 186.7, 136.4, 135.7, 130.5, 129.6, 111.7, 109.7, 38.2, 23.9. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_6N_4O$ 246.0542, found 246.0543.

*3-(4′-Methylbenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4b**).* Yield: white solid, 21.6 g, 83%. Mp: 209−210 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.17 (d, $^3J_{H,H}$ = 7.93 Hz, 2H), 7.47 (d, $^3J_{H,H}$ = 7.93 Hz, 2H), 5.64 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 186.0, 133.7, 130.6, 130.5, 130.2, 111.7, 109.7, 38.2, 23.7, 22.3. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{15}H_8N_4O$ 260.0698, found 260.0699.

*3-(4′-Bromobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4c**).* Yield: white solid, 24.37 g, 75% yield. Mp: 215−217 °C (lit.[12] 214−215 °C) (dec.); ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.18 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 7.88 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 5.65 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 186.2, 165.0, 135.4, 133.7, 132.6, 130.9, 111.7, 109.6, 38.0, 24.0. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_5BrN_4O$ 323.9647 and 325.9626, found 323.9649 and 325.9625.

*3-(4′-Nitrobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4d**).* Yield: pale-yellow solid, 20.7 g, 71% yield. Mp: 253−254 °C (dec.). ^{1}H NMR (500.13 MHz, acetone-d_6) δ: 8.63 (d, $^3J_{H,H}$ = 8.54 Hz, 2H), 8.50 (d, $^3J_{H,H}$ = 8.54 Hz, 2H), 5.78 (s, 1H). ^{13}C NMR (125.77 MHz, acetone-d_6) δ: 185.6, 151.7, 140.5, 131.2, 124.2, 110.7, 108.3, 38.5, 23.4. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_5N_5O_3$ 291.0392, found 291.0391.

*3-(4′-Methoxybenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4e**).* Yield: white solid, 23.7 g, 86%. Mp: 205−206 °C (lit.[12] 204−205 °C) (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.25 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 7.18 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 5.63 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 184.6, 165.6, 133.1, 129.0, 115.0, 111.7, 109.7, 56.8, 38.3, 23.5. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{15}H_8N_4O_2$ 276.0647, found 276.0649.

*3-(2′,4′-Dichlorobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4f**).* Yield: pale-yellow solid, 21.7 g, 69%. Mp: 228−229 °C (dec.). ^{1}H NMR (500.13 MHz, acetone-d_6) δ: 8.23 (d, $^3J_{H,H}$ = 8.55 Hz, 1H), 7.79 (d, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.69 (dd, $^3J_{H,H}$ = 6.71 Hz, $^4J_{H,H}$ = 1.83 Hz, 1H), 5.48 (s, 1H). ^{13}C NMR (125.77 MHz, acetone-d_6) δ: 185.4, 140.0, 134.4, 134.2, 133.7, 131.2, 128.1, 110.5, 108.1, 41.0, 23.2. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_4Cl_2N_4O$ 313.9762 and 315.9735, found 313.9762 and 315.9734.

*3-(3′-Chlorobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4g**).* Yield: white solid, 20.4 g, 73%. Mp: 221−222 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.43 (s, 1H), 8.12 (d, $^3J_{H,H}$ = 7.93 Hz, 1H), 7.86 (d, $^3J_{H,H}$ = 7.93 Hz, 1H), 7.66 (t, $^3J_{H,H}$ = 7.93 Hz, 1H), 5.71 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 186.0, 138.1, 135.0, 134.5, 131.4, 130.7, 128.5, 111.7, 109.6, 38.0, 24.1. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_5ClN_4O$ 280.0152, 282.0122, found 280.0154, 282.0123.

*3-(3′,4′-Dimethoxybenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4h**).* Yield: white solid, 27.5 g, 90%. Mp: 184−185 °C (lit.[12] 186−187 °C) (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.00 (dd, $^3J_{H,H}$ = 6.71 Hz, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.69 (d, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.21 (d, $^3J_{H,H}$ = 9.16 Hz, 1H), 5.70 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 184.5, 155.6, 149.5, 128.9, 126.1, 112.2, 111.8, 111.7, 109.7, 57.0, 56.7, 38.1, 23.5. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{16}H_{10}N_4O_3$ 306.0753, found 306.0755.

*3-(1′-Naphthoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4i**).* Yield: white solid, 19.24 g, 65%. Mp: 208−209 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.69 (d, $^3J_{H,H}$ = 8.54 Hz, 1H), 8.60 (d, $^3J_{H,H}$ = 7.32 Hz, 1H), 8.33 (d, $^3J_{H,H}$ = 8.54 Hz, 1H), 8.33 (d, $^3J_{H,H}$ = 8.54 Hz, 1H), 8.10 (d, $^3J_{H,H}$ = 8.55 Hz, 1H), 7.8−7.73 (m, 3H); 5.71 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 188.3, 136.0, 134.1, 133.7, 132.9, 129.9, 129.6, 128.0, 127.7, 126.3, 125.4, 111.7, 109.7, 24.0. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{18}H_8N_4O$ 296.0698, found 296.0697.

*3-(2′-Thienylcarbonyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4j**).* Yield: white solid, 23.44 g, 93%. Mp: 204−205 °C (lit.[12] 201−202 °C) (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.58 (d, $^3J_{H,H}$ = 3.66 Hz, 1H.), 8.29 (d, $^3J_{H,H}$ = 4.88 Hz, 1H), 7.42 (t, $^3J_{H,H}$ = 4.27 Hz, 1H), 5.57 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 178.9, 143.4, 139.3, 138.7, 130.2, 111.6, 109.5, 38.7, 23.5. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_4N_4OS$ 252.0106, found 252.0105.

*3-(2′-Furoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4k**).* Yield: white solid, 21.0 g, 89%. Mp: 215−216 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.25 (s, 1H), 8.12 (br. s, 1H), 6.90−6.93 (m, 1H), 5.32 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 173.1, 151.9, 151.2, 115.4, 114.7, 111.6, 109.3, 38.7, 23.3. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_4N_4O_2$ 236.0334, found 236.0333.

DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408

*3-[(5′-Bromo-2′-thienyl)carbonyl]cyclopropane-1,1,2,2-tetracarbonitrile (**4l**).* Yield: white solid, 29.79 g, 90%. Mp: 227−228 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.39 (d, $^3J_{H,H}$ = 4.27 Hz, 1H), 7.60 (d, $^3J_{H,H}$ = 4.27 Hz, 1H), 5.52 (s, 1H). ^{13}C NMR (125.77 MHz, DMSO- d_6) δ: 178.2, 144.9, 141.7, 139.2, 133.8, 126.2, 111.6, 109.4, 38.2, 23.7. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_3BrN_4OS$ 329.9211 and 331.9190, found 329.9213 and 331.9191.

*Potassium 2-Benzoyl-1,1,3,3-tetracyanopropenide (**1a$_K$**).* Yield: yellow crystalline powder, 13.35 g, 94%. Mp: 272−273 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.96 (d, $^3J_{H,H}$ = 7.32 Hz, 2H), 7.81 (t, $^3J_{H,H}$ = 7.32 Hz, 1H), 7.66 (t, $^3J_{H,H}$ = 7.93 Hz, 2H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 193.1, 165.7, 136.4, 133.6, 130.4, 130.4, 117.9, 115.3, 51.2. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_5N_4O$ 245.0469, found 245.0470.

1a$_{Li}$. Yield: yellow crystalline powder, 11.2 g, 89%. Mp: 172−173 °C (dec.)

1a$_{Na}$. Yield: yellow crystalline powder, 12.19 g, 91%. Mp: 303−304 °C (lit.[12] 228−229 °C) (dec.).

1a$_{Rb}$. Yield: yellow crystalline powder, 15.67 g, 95%. Mp: 275−276 °C (dec.).

1a$_{Cs}$. Yield: Yellow crystalline powder , 18.2 g, 96%. Mp: 269−270 °C (dec.).

The HRMS, ^{1}H NMR, and ^{13}C NMR data for lithium, sodium, rubidium, and cesium salts **1a** are completely analogous to that of **1a$_K$**.

*Potassium 2-(4′-Methylbenzoyl)-1,1,3,3-tetracyanopropenide (**1b**).* Yield: lemon-yellow crystalline powder, 13.3 g, 94%. Mp: 277−278 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.85 (d, $^3J_{H,H}$ = 7.32 Hz, 2H), 7.46 (d, $^3J_{H,H}$ = 7.93 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 192.5, 166.0, 147.4, 131.2, 131.0, 130.5, 117.9, 115.4, 51.1, 22.3. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{15}H_7N_4O$ 259.0625, found 259.0626.

*Potassium 2-(4′-Bromobenzoyl)-1,1,3,3-tetracyanopropenide (**1c**).* Yield: yellow crystalline powder, 16.65 g, 90%. Mp: 260−261 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.85−7.93 (m, 4H); ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 192.3, 165.0, 133.7, 132.6, 132.2, 130.9, 117.8, 115.1, 51.2. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_4BrN_4O$ 322.9574 and 324.9554, found 322.9576 and 324.9555.

*Potassium 2-(4′-Nitrobenzoyl)-1,1,3,3-tetracyanopropenide (**1d**).* Yield: orange-yellow crystalline powder, 14.2 g, 86%. Mp: 253−254 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.45 (d, $^3J_{H,H}$ = 8.54 Hz, 2H), 8.25 (d, $^3J_{H,H}$ = 8.54 Hz, 2H); ^{13}C NMR (125.77 MHz, DMSO- d_6) δ: 192.2, 164.4, 152.1, 137.8, 131.9, 125.7, 117.7, 115.0, 51.4. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_4N_5O_3$ 290.0320, found 290.0321.

*Potassium 2-(4′-Methoxybenzoyl)-1,1,3,3-tetracyanopropenide (**1e**).* Yield: pale-yellow crystalline powder, 15.0 g, 96% yield. Mp: 306−308 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.91 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 7.17 (d, $^3J_{H,H}$ = 9.16 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125.77 MHz, DMSO- d_6) δ: 191.2, 166.2, 165.7, 133.0, 126.6, 118.0, 115.8, 115.5, 56.7, 51.0. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{15}H_7N_4O_2$ 275.0574, found 275.0576.

*Potassium 2-(2′,4′-Dichlorobenzoyl)-1,1,3,3-tetracyanopropenide (**1f**).* Yield: yellow crystalline powder, 14.65 g, 83%. Mp: 299−300 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.96 (d, $^3J_{H,H}$ = 8.54 Hz, 1H), 7.90 (d, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.69 (dd, $^3J_{H,H}$ = 6.12 Hz, $^4J_{H,H}$ = 1.83 Hz, 2H); ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 190.5, 165.0, 140.7, 135.5, 135.4, 132.5, 131.2, 129.2, 117.7, 115.3, 51.8. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_3Cl_2N_4O$ 312.9689 and 314.9660, found 312.9694 and 314.9661.

*Potassium 2-(3′-Chlorobenzoyl)-1,1,3,3-tetracyanopropenide (**1g**).* Yield: yellow crystalline powder, 13.87 g, 87%. Mp: 320−321 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.95 (d, $^3J_{H,H}$ = 6.71 Hz, 2H), 7.90 (d, $^3J_{H,H}$ = 8.55 Hz, 1H), 7.71 (t, $^3J_{H,H}$ = 7.93 Hz, 1H); ^{13}C NMR (125.77 MHz, DMSO- d_6) δ: 192.1, 164.7, 136.2, 135.4, 135.3, 132.7, 129.5, 129.1, 117.8, 115.1, 51.4. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{14}H_4ClN_4O$ 279.0079 and 281.0050, found 279.0081 and 281.0052.

*Potassium 2-(3′,4′-Dimethoxybenzoyl)-1,1,3,3-tetracyanopropenide (**1h**).* Yield: white crystalline powder, 15.99 g, 93%. Mp: 331−332 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.56 (dd, $^3J_{H,H}$ = 8.54 Hz, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.42 (d, $^4J_{H,H}$ = 1.83 Hz, 1H), 7.20 (d, $^3J_{H,H}$ = 8.54 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 191.1, 166.2, 155.8, 150.2, 127.1, 126.5, 118.1, 115.5, 112.3, 110.4, 56.9, 56.5, 51.2. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{16}H_9N_4O_3$ 305.0680, found 305.0681.

*Potassium 2-(1′-Naphthoyl)-1,1,3,3-tetracyanopropenide (**1i**).* Yield: brown-yellow crystalline powder, 14.69 g, 88%. Mp: 218−220 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 9.00 (d, $^3J_{H,H}$ = 8.55 Hz, 1H), 8.38 (d, $^3J_{H,H}$ = 7.93 Hz, 1H), 8.24 (d, $^3J_{H,H}$ = 6.71 Hz, 1H), 8.13 (d, $^3J_{H,H}$ = 7.93 Hz, 1H), 7.74−7.82 (m, 2H), 7.70 (t, $^3J_{H,H}$ = 7.93 Hz, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 194.5, 166.9, 137.4, 135.8, 134.6, 131.0, 130.4, 129.9, 129.2, 128.0, 126.2, 126.1, 118.1, 115.5, 51.9. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{18}H_7N_4O$ 295.0625, found 295.0623.

*Potassium 2-(2′-Thienylcarbonyl)-1,1,3,3-tetracyanopropenide (**1j**).* Yield: green-yellow crystalline powder, 13.77 g, 96%. Mp: 256−257 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.27 (d, $^3J_{H,H}$ = 5.87 Hz, 1H), 7.96 (d, $^3J_{H,H}$ = 5.14 Hz, 1H), 7.35 (t, $^3J_{H,H}$ = 5.14 Hz, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 184.9, 165.1, 140.3, 139.8, 138.5, 130.6, 117.9, 115.4, 51.4. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_3N_4OS$ 251.0033, found 251.0032.

*Potassium 2-(2′-Furoyl)-1,1,3,3-tetracyanopropenide (**1k**).* Yield: green-yellow crystalline powder, 13.15 g, 96%. Mp: 292−923 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 8.23 (s, 1H), 7.71 (d, $^3J_{H,H}$ = 3.66 Hz, 1H), 6.87 (dd, $^3J_{H,H}$ = 3.66 Hz, $^4J_{H,H}$ = 1.22 Hz, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 179.3, 164.1, 151.9, 149.8, 125.1, 117.9, 115.4, 114.7, 51.5. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_3N_4O_2$ 235.0261, found 235.0260.

*Potassium 2-[(5′-Bromo-2′-thienyl)carbonyl]-1,1,3,3-tetracyanopropenide (**1l**).* Yield: green-yellow crystalline powder, 17.16 g, 93%. Mp: 276−278 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 7.88 (d, $^3J_{H,H}$ = 4.27 Hz, 1H), 7.53 (d, $^3J_{H,H}$ = 4.26 Hz, 1H). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ: 184.0, 163.9, 141.7, 139.5, 134.4, 127.0, 117.8, 115.2, 51.6. HRMS-ESI (m/z) [M]$^+$ calcd for $C_{12}H_2BrN_4OS$ 328.9138 and 330.9118, found 328.9140 and 330.9119.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01040.

Crystallographic data in CIF format for **1a$_{Li}$** (CIF)
Crystallographic data in CIF format for **1a$_{Na}$** (CIF)
Crystallographic data in CIF format for **1a$_K$** (CIF)
Crystallographic data in CIF format for **1a$_{Rb}$** (CIF)
Crystallographic data in CIF format for **1a$_{Cs}$** (CIF)
^{1}H and ^{13}C NMR spectra graphics for all synthesized compounds and X-ray characterization data for compounds **1a$_{Li}$**, **1a$_{Na}$**, **1a$_K$**, **1a$_{Rb}$**, and **1a$_{Ca}$** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: serg31.chem@mail.ru

Notes

The authors declare no competing financial interest.

CCDC 1452031, 1452032, 1452033, 1452034, and 1452035 respectively contain the supplementary crystallographic data for **1a$_{Cs}$**, **1a$_K$**, **1a$_{Li}$**, **1a$_{Na}$**, and **1a$_{Rb}$** of this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ACKNOWLEDGMENTS

This work was supported by RFBR, research project 16-33-49360135 mol_a_dk. The X-ray study was supported in part by

DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408

M. V. Lomonosov Moscow State University Program of Development.

REFERENCES

(1) (a) Klimova, E. I.; Garcia, M. M.; Flores-Alamo, M.; Churakov, A. V.; Cortez Maya, S.; Beletskaya, I. P. *Polyhedron* **2014**, *68*, 272−278. (b) Duclos, S.; Conan, F.; Triki, S.; Le Mest, Y.; Liu-Gonzalez, M.; Sala-Pala, J. *Polyhedron* **1999**, *18*, 1935−1939. (c) Thetiot, F.; Triki, S.; Sala-Pala, J.; Golhen, S. *Inorg. Chim. Acta* **2005**, *358*, 3277−3282. (d) Funasako, Yu.; Abe, K.-I.; Mochida, T. *Thermochim. Acta* **2012**, *532*, 78−82. (e) Setifi, Z.; Setifi, F.; El Ammari, L.; El-Ghozzi, M.; Sopková-de Oliveira Santos, J.; Merazig, H.; Glidewell, C. *Acta Crystallogr., Sect. C: Struct. Chem.* **2014**, *70*, 19−22. (f) Asrial; Olbrich, F.; Spoida, M.; Fischer, A.; Edelmann, F. T. *Anorg. Allg. Chem.* **2011**, *637*, 190−194.

(2) (a) Triki, S.; Sala-Pala, J.; Decoster, M.; Molinie, P.; Toupet, L. *Angew. Chem., Int. Ed.* **1999**, *38*, 113−115. (b) Triki, S.; Thetiot, F.; Vandevelde, F.; Sala-Pala, J.; Gomez-Garcia, C.-J. *Inorg. Chem.* **2005**, *44*, 4086−4093. (c) Lefebvre, E.; Conan, F.; Cosquer, N.; Kerbaol, J.-M.; Marchivie, M.; Sala-Pala, J.; Kubicki, M.; Vigier, E.; Gomez-Garcia, C.-J. *New J. Chem.* **2006**, *30*, 1197−1206. (d) Yates, M. L.; Ari, A. M.; Manson, J. L.; Kalm, B. A.; Burkhart, B. B.; Miller, J. S. *Inorg. Chem.* **1998**, *37*, 840−841. (e) Addala, A.; Setifi, F.; Kottrup, K. G.; Glidewell, C.; Setifi, Z.; Smith, G.; Reedijk, J. *Polyhedron* **2015**, *87*, 307−310.

(3) Dupouy, G.; Triki, S.; Marchivie, M.; Cosquer, N.; Gomez-Garcia, C.-J.; Pillet, S.; Bendeif, E.-E.; Lecomte, C.; Asthana, S.; Letard, J.-F. *Inorg. Chem.* **2010**, *49*, 9358−9368.

(4) Sekizaki, S.; Tada, C.; Yamochi, H.; Saito, G. *J. Mater. Chem.* **2001**, *11*, 2293−2302.

(5) (a) Dupouy, G.; Marchivie, M.; Triki, S.; Sala-Pala, J.; Gomez-Garcia, C. J.; Pillet, S.; Lecomte, C.; Letard, J. F. *Chem. Commun.* **2009**, 3404−3406. (b) Dupouy, G.; Triki, S.; Marchivie, M.; Cosquer, N.; Gómez-García, C. J.; Pillet, S.; Bendeif, E.-E.; Lecomte, C.; Asthana, S.; Létard, J.-F. *Inorg. Chem.* **2010**, *49*, 9358−9368.

(6) (a) Dupouy, G.; Marchivie, M.; Triki, S.; Sala-Pala, J.; Salaün, J.-Y.; Gómez-García, C. J.; Guionneau, P. *Inorg. Chem.* **2008**, *47*, 8921−8931. (b) Dupouy, G.; Marchivie, M.; Triki, S.; Sala-Pala, J.; Gómez-García, C. J.; Pillet, S.; Lecomte, C.; Letard, J.-F. *Chem. Commun.* **2009**, 3404−3406. (c) Benmansour, S.; Atmani, C.; Setifi, F.; Triki, S.; Marchivie, M.; Gómez-García, C. J. *Coord. Chem. Rev.* **2010**, *254*, 1468−1478.

(7) Gao, H.; Zeng, Z.; Twamley, B.; Shreeve, J. M. *Chem. - Eur. J.* **2008**, *14*, 1282−1290.

(8) Yoshida, Y.; Kondo, M.; Saito, G. *J. Phys. Chem. B* **2009**, *113*, 8960−8966.

(9) Liu, X.; Li, J.; Bi, F.; Zhang, W.; Zhang, G.; Gao, Z. *Eur. J. Inorg. Chem.* **2015**, *2015*, 1496−1504.

(10) (a) Karpov, S. V.; Kayukov, Ya. S.; Bardasov, I. N.; Kayukova, O. V.; Ershov, O. V.; Nasakin, O. E. *Russ. J. Org. Chem.* **2011**, *47*, 405−407. (b) Karpov, S. V.; Kayukov, Ya. S.; Bardasov, I. N.; Ershov, O. V.; Nasakin, O. E.; Kayukova, O. V. *Russ. J. Org. Chem.* **2011**, *47*, 1161−1164. (c) Karpov, S. V.; Kayukov, Ya. S.; Bardasov, I. N.; Kayukova, O. V.; Lipin, K. V.; Nasakin, O. E. *Russ. J. Org. Chem.* **2011**, *47*, 1492−1497. (d) Kayukov, Ya. S.; Karpov, S. V.; Bardasov, I. N.; Ershov, O. V.; Nasakin, O. E.; Kayukova, O. V. *Russ. J. Org. Chem.* **2012**, *48*, 1107−1110. (e) Kayukov, Ya. S.; Karpov, S. V.; Bardasov, I. N.; Ershov, O. V.; Nasakin, O. E.; Rizatdinov, M. M.; Tafeenko, V. A. *Russ. J. Org. Chem.* **2013**, *49*, 707−711. (f) Kayukov, Ya. S.; Karpov, S. V.; Kayukova, O. V.; Ershov, O. V.; Nasakin, O. E. *Russ. J. Org. Chem.* **2014**, *50*, 1097−1106. (g) Grigor'ev, A.; Karpov, S.; Kayukov, S. Y.; Nasakin, O.; Tafeenko, V. *Synlett* **2015**, *26*, 2313−2317. (h) Grigor'ev, A.; Karpov, S. V.; Kayukov, Y. S.; Belikov, M. Y.; Nasakin, O. E. *Tetrahedron Lett.* **2015**, *56*, 6279−6281.

(11) Kayukov, Ya. S.; Karpov, S. V.; Bardasov, I. N.; Ershov, O. V.; Nasakin, M.; Belikov, M. Yu.; Kayukova, O. V. *Russ. J. Org. Chem.* **2012**, *48*, 491−493.

(12) (a) Bardasov, I. N.; Kayukova, O. V.; Kayukov, Ya. S.; Ershov, O. V.; Nasakin, O. E. *Russ. J. Appl. Chem.* **2009**, *82*, 1431−1434. (b) Bardasov, I. N.; Kayukova, O. V.; Kayukov, Ya. S.; Ershov, O. V.; Nasakin, O. E.; Tafeenko, V. A. *Russ. J. Org. Chem.* **2009**, *45*, 1325−1335.

(13) Rabjohn, N. *Org. React. (N. Y.).* **1976**, *24*, 261.

(14) (a) Rubin, M. B. *Chem. Rev.* **1975**, *75*, 177. (b) Filimonov, V. D.; Yusubov, M. S.; Chi, K.-V. *Russ. Chem. Rev.* **1998**, *67*, 725−747.

(15) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122. (b) Brandenburg, K. *DIAMOND, Release 2.1d*; Crystal Impact GbR: Bonn, Germany, 2000. (c) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466−470.

DOI: 10.1021/acs.joc.6b01040
J. Org. Chem. 2016, 81, 6402−6408