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Synthesis and X-ray characterization of alkali metals 2-acyl-1,1,3,3-tetracyanopropenides

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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 methylketones, malononitrile, bromine and alkali metals acetates is reported. The starting aryl(heteroaryl)methylketones were oxidized to corresponding α-ketoaldehydes by new 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 caesium 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, a salts containing tetracyanoallyl (TCA) anion (Figure 1) have received considerable attention. This is due to the TCA anions have a variable denticity and might be used as bridging ligands for construction of various 1D, 2D and 3D coordination polymeric frameworks.[1]

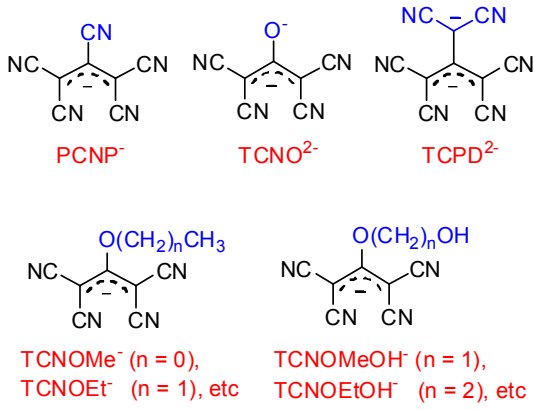


Figure 1. TCA ligands family portrait

TCA salts can be applied for creating materials with potentially useful properties, such as magnetic,[2] thermo- and photochromic,[3] semiconducting[4] and photomagnetic.[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 a some chemical properties of new 2-acyl-1,1,3,3-tetracyanopropenides (ATCN) salts **1** containing a carbonyl group in position 2 of TCA anion.[10] The carbonyl oxygen can form an additional coordination bonds with cation. Moreover, ATCN 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 design of coordination polymers and as precursors for heterocyclic synthesis.

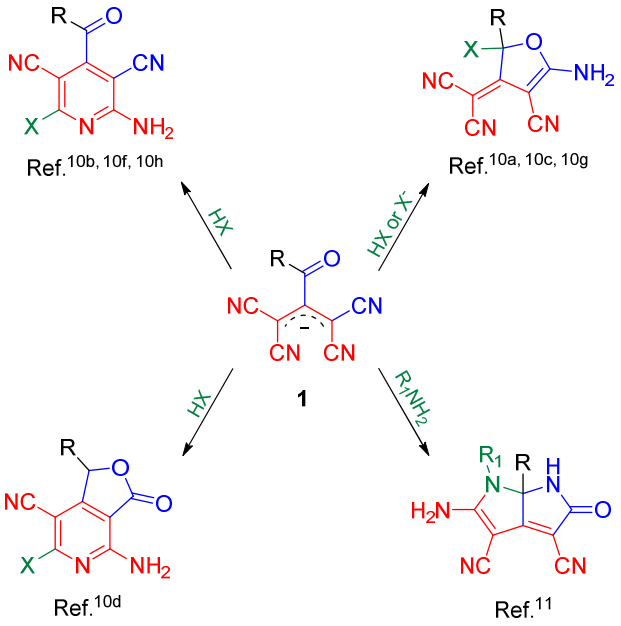
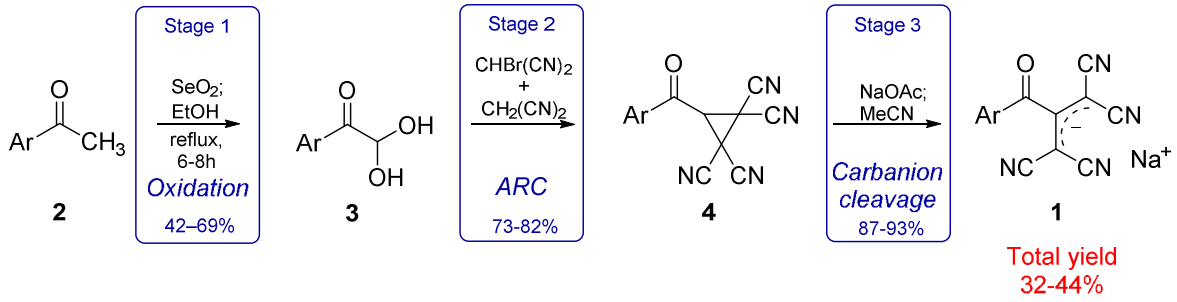


Figure 2. A described routes for heterocyclization of $ATCN^-$

Scheme 1. The first synthesis of ATCN[12]



The ATCN salts were first obtained by Bardasov et al. *via* a three-step synthesis using acetophenones, selenium dioxide, malonodinitrile and brommalonodinitrile 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 mixture of equal amounts of malonodinitrile and brommalonodinitrile with formation of the corresponding cyclopropanes **4** *via* Adduction and Ring Closure (ARC) process.

At the final stage of the ATCN salts synthesis, cyclopropanes **4** were being reacted with equal amount of sodium acetate in acetonitrile followed by solvent removing by rotary evaporation. The total yield of ATCN (based on starting acetophenones) does not exceed 44%. In addition, this method of ATCN preparation has a number of significant disadvantages such as: a necessity of long refluxing and the formation of fine particulate selenium which have polluted the product at oxidation stage; a necessity a preliminary synthesis of unstable irritant brommalonodinitrile at stage 2 as well as a necessity of toxic acetonitrile using as solvent at final stage.

Herein, we report a novel process version for ATCN salts preparation based on the oxidation of aryl(heteroaryl)methylketones to aryl(heteroaryl)glyoxals by new DMSO - NaBr - H_2SO_4 system and subsequent ARC reaction with malonodinitrile and bromine in water. At the final stage, the corresponding cyclopropylketones **4** were being undergo 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 ATCN salts total yields up to 80% and decrease total synthesis time to less than 3 hours. Also, this method is not required 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 caesium 2-benzoyl-1,1,3,3-tetracyanopropenides were characterized by X-ray diffraction analysis.

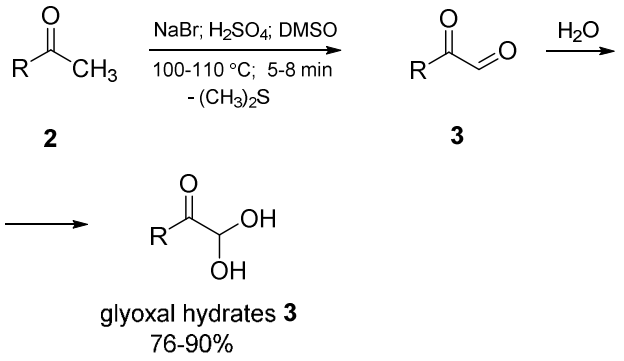
RESULTS AND DISCUSSION

Stage 1. Oxidation of aryl(heteroaryl)methylketones to glyoxales by the NaBr - DMSO - H_2SO_4 oxidizing system.

Currently, a variety of methods for the oxidation of methylketones to α-ketoaldehydes are described. One of the most applied methods involves using of CrO_3, diphenylselenoxide or selenium dioxide.[13,14] More safe and accessible reagent is DMSO-HBr mixture, but this method also have a disadvantages such as a long reaction time (1-24h) and medium yields (low to 50% on average).[14b]

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

Scheme 2. Reaction of aryl(heteroaryl)methylketones with DMSO - NaBr - H_2SO_4 mixture



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

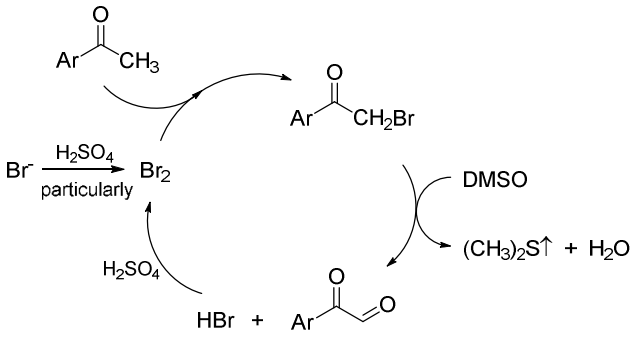
Table 1. The substituents and yields of isolated glyoxal hydrates 3

Entry	R	Yield (%)
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

Using KBr instead of NaBr leads to decreased glyoxals **3** yields of about 10-20%.

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

Scheme 3. A proposed mechanism for oxidation of aryl(heteroaryl)methylketones



Stage 2. Adduction and Ring Closure (ARC) reaction

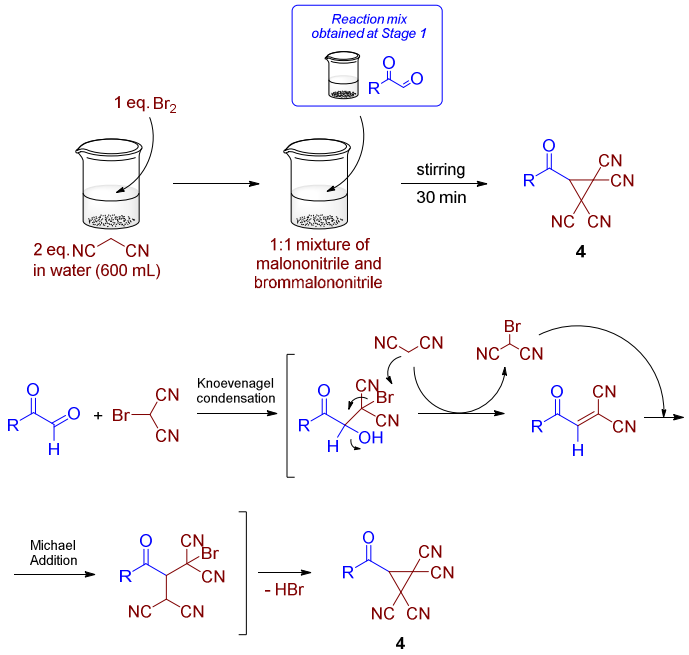
At the second stage, the resulting glyoxals were being undergo the ARC reaction under the action of a mixture of equal amounts of malonodinitrile and brommalonodinitrile.

The outdated version[12] of this synthesis requires a preliminary preparation of pure crystalline monobrommalonodinitrile *via* bromination of malonodinitrile. Subsequent ARC reaction with glyoxals was realized in acetonitrile in quite good yields of resulting tetracyanocyclopropylketones (73-82%). Our approach to reaction optimization comprises preparation of malonodinitrile and brommalonodinitrile equimolar mixture in water and subsequent cyclopropanation under "one-pot" reaction conditions (Scheme 4). This method allows obtaining the tetracyanocyclopropylketones **4** in good yields (Table 2) and quite purities.

Table 2. The 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

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



*Stage 3. Synthesis of ATCN salts **1** via carbanion cleavege of tetracyanocyclopropylketones **4**.*

At the third stage, the resulting tetracyanocyclopropylketones **4** were reacted with alkali acetates in ethanol (Scheme 5). We have found, that ATCN salts solubility in saturated corresponding metal chloride solutions is drastically reduced. This allowed to isolate ATCN salts **1** in high yields (Table 3) by salting out without usage of rotary evaporator. According to ^{1}H NMR data, the purity of the crude products (after drying in vacuo) is 97-99%.

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

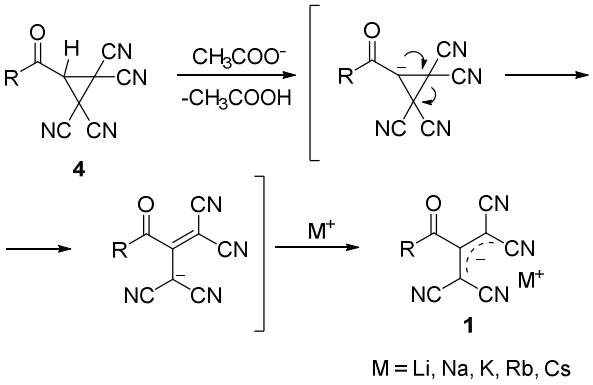


Table 3. The substituents and yields of ATCN salts 1

Entry[a]	R	Yield (%)	Total yield[b] (%)
1a	Ph	89 (**1a$_{Li}$**) 91 (**1a$_{Na}$**) 94 (**1a$_{K}$**) 95 (**1a$_{Rb}$**) 96 (**1a$_{Cs}$**)	57 (**1a$_{Li}$**) 59 (**1a$_{Na}$**) 60 (**1a$_{K}$**) 60 (**1a$_{Rb}$**) 61 (**1a$_{Cs}$**)
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 metals ATCN salts.

Further, we have investigated the crystal structure of alkali metals 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 caesium salts was carried out analogously to potassium salts preparation *via* using appropriate metal acetates and chlorides. CCDC 1452031-1452035 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 $\mathbf{1a_{(Li\text{-}Cs)}}$ showing the atom labelling scheme one can see on the Figures S1-S5 in Supporting Information. The crystal parameters and refinement metrics, to accompany the thermal ellipsoid plot are also provided in the SI (Tables: S1 for $\mathbf{1a_{Li}}$, S3 for $\mathbf{1a_{Na}}$, S5 for $\mathbf{1a_{K}}$, S7 for $\mathbf{1a_{Rb}}$ and S9 for $\mathbf{1a_{Cs}}$). Selected bond lengths and angles for $\mathbf{1a_{(Li,Na,K,Rb,Cs)}}$ are in the tables (SI): S2, S4, S6, S8 and S10 correspondingly.

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*-1. The coordination environment of Li, shown in Figure S1 (a), 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 a oxygen O2 from coordinated water in a slightly distorted tetrahedral geometry. Each lithium cation connect the N1 and N2 nitrogens belonging to different $ATCN^-$ anions to form a 1D chain. The carbonyl groups of $ATCN^-$ connects the neighboring 1D chains to generate a 1D ribbons (Figure S1 (b)). 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 S1 (c)).

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 *P* 21/*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). 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 on Figures S2 (b) and S3 (b). Each ATCN anion connects three sodium atom pairs to form 2D mesh structure. The 3D supramolecular structure is formed by stacking 2D layers. Potassium salt $\mathbf{1a_{K}}$ displays similar topological structure to $\mathbf{1a_{Na}}$.

Rubidium ($\mathbf{1a_{Rb}}$) and caesium ($\mathbf{1a_{Cs}}$) 2-benzoyl-1,1,3,3-tetracyanopropenides crystallize in monoclinic symmetry with space group *P* 21/*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).

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 benzene ring with minimum distances 3.882 Å ($Cs^{\cdots}C4^{iv}$) and 3.821 Å ($Cs^{\cdots}C5^{vi}$) (Figure S5 (a)).

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 reveals an intense yellow-green luminescence in solid state under UV lamp irradiation and have no luminescence properties in any solutions.

In summary, we have developed the new fast, simple and efficient route for ATCN salts synthesis. All ATCN salts for the first time were characterized by ^1H and ^{13}C NMR. X-ray diffraction analysis reveals that $ATCN^-$ anion has the ability to form multiple coordination bonds that makes them candidates 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 500 and 121 MHz respectively, solvent DMSO-*d6*, internal reference TMS. HRMS data were acquired with a QTOF mass spectrometer. The X-ray data was collected by using STOE diffractometer Pilatus 100K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, 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 (multi-scan method). The structures were solved and refined with SHELX[15a] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square 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)methylketones by DMSO - NaBr - H_2SO_4 system (general procedure).*

Aryl(heteroaryl)methylketone (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 ºC under stirring and then a ~5 mL of concentrated sulfuric acid was quickly added to the reaction. The reaction mass was foaming 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 ºC. When the reaction is finished (5-7 min), the formation of dimethyl sulphide bubbles have sharply reduced and the reacting mixture becomes viscous. After cooling, the yellow-orange oil which formed was dissolved in 50 mL of ethanol, the resulting solution was then used at the second stage of ATCN synthesis.

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

Notes: 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 irritant. 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 under stirring. Malonodinitrile (13.2 g, 0.2 mol) was dissolved in 50 ml of EtOH and the resulting mixture was poured into bromine solution. A mixture obtained at previous stage and containing aryl(heteroaryl)glyoxal was added dropwise to the resulting solution under vigorous stirring. After the mixture had been 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, cyclopropylketones **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) then stirred at 45-50 ºC until the solids had dissolved. The resulting dark-yellow solution was filtered, the filtrate allowed to cool then poured into 10% corresponding alkali metal chloride solution (75 ml) and left for 30 min at 5-10 ºC. The resulting precipitate was filtered, washed with diethyl ester and dryed in air.

*3-Benzoylcyclopropane-1,1,2,2-tetracarbonitrile (**4a**)*

White solid **4a** (19.43 g, 79% yield), m.p. 214-215 °C (Lit.[12] 211-212 °C) (decomp.); ^{1}H NMR (500.13 MHz, DMSO-d_6), δ: 8.26 (d, ^{3}J *(H,H)* = 7.3 Hz, 2H), 7.80 (t, ^{3}J *(H,H)* = 7.3 Hz, 1H), 7.65 (t, ^{3}J *(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**)*

White solid **4b** (21.6 g, 83% yield), m.p. 209-210 °C (decomp.); ^{1}H NMR (500.13 MHz, DMSO-d_6), δ: 8.17 (d, ^{3}J *(H,H)* = 7.93 Hz, 2H), 7.47 (d, ^{3}J *(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**)*

White solid **4c** (24.37 g, 75% yield), m.p. 215-217 °C (Lit.[12] 214-215 °C) (decomp.); ^{1}H NMR (500.13 MHz, DMSO-d_6), δ: 8.18 (d, ^{3}J *(H,H)* = 9.16 Hz, 2H), 7.88 (d, ^{3}J *(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, 325.9626, found 323.9649, 325.9625.

*3-(4'-Nitrobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (**4d**)*

Pale-yellow solid **4d** (20.7 g, 71% yield), m.p. 253-254 °C (decomp.); ^{1}H NMR (500.13 MHz, Acetone-d_6), δ: 8.63 (d, ^{3}J *(H,H)* = 8.54 Hz, 2H), 8.50 (d, ^{3}J *(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**)*

White solid **4e** (23.7 g, 86% yield), m.p. 205-206°C (Lit.[12] 204-205 °C) (decomp.); ^{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)***

Pale-yellow solid **4f** (21.7 g, 69% yield), m.p. 228-229 °C (decomp.); ^{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, 315.9735, found 313.9762, 315.9734.

3-(3'-Chlorobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile ***(4g)***

White solid **4g** (20.4 g, 73% yield), m.p. 221-222 °C (decomp.); ^{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)***

White solid **4h** (27.5 g, 90% yield), m.p. 184-185 °C (Lit.[12] 186-187°C) (decomp.); ^{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)***

White solid **4i** (19.24 g, 65% yield), m.p. 208-209 °C (decomp.); ^{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)***

White solid **4j** (23.44 g, 93% yield), m.p. 204-205 °C (Lit.[12] 201-202°C) (decomp.); ^{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)***

White solid **4k** (21.0 g, 89% yield), m.p. 215-216 °C (decomp.); ^{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.

3-[(5'-Bromo-2'-thienyl)carbonyl]cyclopropane-1,1,2,2-tetracarbonitrile ***(4l)***

White solid **4l** (29.79 g, 90% yield), m.p. 227-228 °C (decomp.); ^{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 $C_{12}H_3BrN4OS$ 329.9211, 331.9190, found 329.9213, 331.9191.

Potassium 2-benzoyl-1,1,3,3-tetracyanopropenide ***(1a$_K$)***

Yellow crystalline powder **1a$_K$** (13.35 g, 94% yield), m.p. 272-273 °C (decomp.); ^{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. The HRMS, ^{1}H NMR and ^{13}C NMR data for lithium, sodium, rubidium and caesium salts **1a** are completely analogously for **1a$_K$**.

Yellow crystalline powder **1a$_{Li}$** (11.2 g, 89% yield), m.p. 172-173 °C (decomp.);

Yellow crystalline powder **1a$_{Na}$** (12.19 g, 91% yield), m.p. 303-304 °C (Lit.[12] 228-229 °C) (decomp.);

Yellow crystalline powder **1a$_{Rb}$** (15.67 g, 95% yield), m.p. 275-276 °C (decomp.);

Yellow crystalline powder **1a$_{Cs}$** (18.2 g, 96% yield), m.p. 269-270 °C (decomp.).

Potassium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide ***(1b)***

Lemon-yellow crystalline powder **1b** (13.3 g, 94% yield), m.p. 277-278 °C (decomp.); ^{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)***

Yellow crystalline powder **1c** (16.65 g, 90% yield), m.p. 260-261 °C (decomp.); ^{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, 324.9554, found 322.9576, 324.9555.

Potassium 2-(4'-nitrobenzoyl)-1,1,3,3-tetracyanopropenide ***(1d)***

Orange-yellow crystalline powder **1d** (14.2 g, 86% yield), m.p. 253-254 °C (decomp.); ^{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**)*

Pale-yellow crystalline powder **1e** (15.0 g, 96% yield), m.p. 306-308 °C (decomp.); ^{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**)*

Yellow crystalline powder **1f** (14.65 g, 83% yield), m.p. 299-300 °C (decomp.); ^{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, 314.9660, found 312.9694, 314.9661.

*Potassium 2-(3'-chlorobenzoyl)-1,1,3,3-tetracyanopropenide (**1g**)*

Yellow crystalline powder **1g** (13.87 g, 87% yield), m.p. 320-321 °C (decomp.); ^{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, 281.0050, found 279.0081, 281.0052.

*Potassium 2-(3',4'-dimethoxybenzoyl)-1,1,3,3-tetracyanopropenide (**1h**)*

White crystalline powder **1h** (15.99 g, 93% yield), m.p. 331-332 °C (decomp.); ^{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**)*

Brown-yellow crystalline powder **1i** (14.69 g, 88% yield), m.p. 218-220 °C (decomp.); ^{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**)*

Green-yellow crystalline powder **1j** (13.77 g, 96% yield), m.p. 256-257 °C (decomp.); ^{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**)*

Green-yellow crystalline powder **1k** (13.15 g, 96% yield), m.p. 292-923 °C (decomp.); ^{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**)*

Green-yellow crystalline powder **1l** (17.16 g, 93% yield), m.p. 276-278 °C (decomp.); ^{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, 330.9118, found 328.9140, 330.9119.

ASSOCIATED CONTENT

Supporting Information

Supporting Information contains ^{1}H and ^{13}C NMR spectra graphics for all synthesized compounds and X-ray characterization data for compounds $\mathbf{1a_{(Li-Cs)}}$. This material is available free of charge *via* the Internet on the ACS Publications website. CCDC 1452031-1452035 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.

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Notes

The authors declare no competing financial interest.

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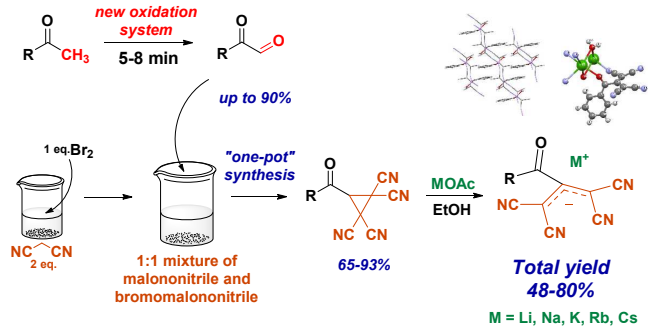
new oxidation system
5-8 min
up to 90%
1 eq. Br2
"one-pot" synthesis
2 eq.
1:1 mixture of malononitrile and bromomalononitrile
65-93%
MOAc
EtOH
Total yield 48-80%
M = Li, Na, K, Rb, Cs