

The synthesis of new functionalized 1,3,5-triazine-based stable bi- and trinitroxides of the 2,5-dihydroimidazole series

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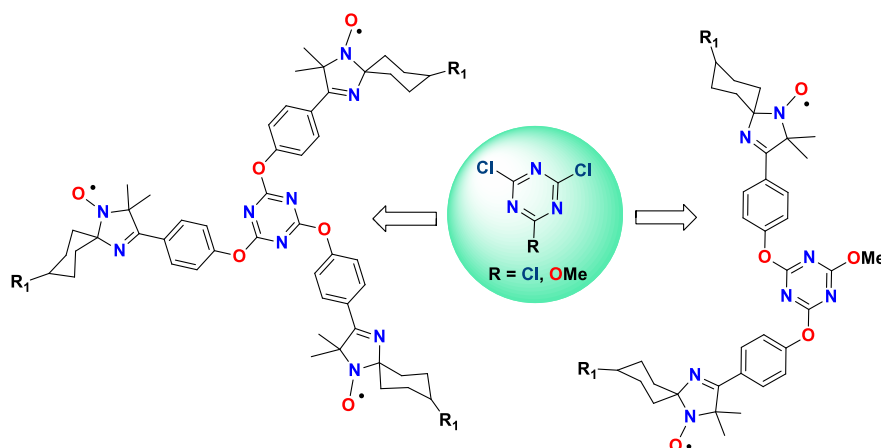
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Abstract

New non-conjugated functionalized 2,5-dihydroimidazole-type bi- and trinitroxyl radicals are described. The synthesis of which was based on a nucleophilic substitution reaction between 2,4,6-trichloro-1,3,5-triazine or 2,4-dichloro-6-methoxy-1,3,5-triazine and spiro-fused 2,5-dihydroimidazole-type monoradicals bearing both a *p*-hydroxyaryl moiety at the C-4 atom of the heterocycle and a residue at the fourth position of the cyclohexane ring. The model tris-nitroxide with an unsubstituted cyclohexane unit was structurally characterized in the solid state.



Keywords: 1,3,5-Triazine-based nitroxides, biradicals, triradicals, *organic* free radicals, 2,5-dihydroimidazoles

Introduction

Trisubstituted 1,3,5-triazines represent a rapidly developing class of organic compounds. Due to their symmetrical structure and self-organized ability to form ordered media as well as good thermal stability, *s*-triazines are useful in materials science and manifest a wide range of practical characteristics such as nonlinear optical^{1,2} and liquid crystalline³⁻⁸ properties including photoluminescence.⁹ In addition, triazine derivatives were recently proved to be stable molecular glasses highly resistant to crystallization,¹⁰ promising inhibitors of organic corrosion of steel in acids,¹¹ and unique scaffolds in the synthesis of highly efficient covalent organic frameworks (COFs) applied to photocatalytic hydrogen production.¹²

Magnetic liquid crystals (LCs) attract a great deal of attention because they may engage in unique magnetic interactions and have unconventional magneto-electric and magneto-optical properties.¹³ Over the last decade, stable organic radicals such as pyrrolidine-type nitroxides (PROXYLs),^{14,15} trityls,¹⁶ verdazyls, and benzo[*e*][1,2,4]triazinyls (Blatter's radicals)¹⁷⁻²⁰ were used to designing all-organic paramagnetic calamitic, discotic, and bent-core LCs. Unique magnetic, optical, and electronic phenomena have been discovered during research into these types of LCs, *e.g.*, i) unusual anisotropic and inhomogeneous ferromagnetic interactions arising in smectic and nematic LC phases of PROXYL-type rod-like mono-^{21,22} and biradicals¹⁵ as well as in the hexagonal columnar LC phase of an achiral π -delocalized hexa-*peri*-hexabenzocoronene derivative carrying a conjugated *tert*-butyl nitroxide moiety²³ induced in a weak magnetic field (the positive magneto-LC effect); ii) existence of two magnetic bistable states in the ferroelectric LC phase of a chiral rod-like PROXYL radical in an applied electric field (magneto-electric effect)²⁴; and iii) charge photogeneration and photoinduced ambipolar charge transport in discotic and bent-core conjugated verdazyls and benzo[*e*][1,2,4]triazinyls.¹⁷⁻²⁰

In this regard, the synthesis of new paramagnetic all-organic liquid crystalline bi- and triradicals containing nitroxide moieties inside the lateral heterocyclic 2,5-dihydroimidazole skeleton as spin sources and a central 1,3,5-triazine core as a robust linker seems to be promising. Besides, an *s*-triazine core may be a useful template for elaborating synthetic approaches to various disjoint hetero- di- and triradicals containing paramagnetic nuclei of different structural types.

It is worth noting that only a limited number of paramagnetic derivatives—mainly nitroxides, nitronyl nitroxides, and phenoxyls linked with a triazine central core—have been successfully prepared. Three strategies have been implemented to introduce various radical fragments into the 2nd, 4th, and 6th positions of the heterocyclic nucleus: a) nucleophilic substitution of 1–3 chlorine atoms in cyanuric chloride with alkoxy, phenoxy, or amino groups in a reaction with the corresponding paramagnetic alcohols,²⁵⁻²⁸ phenols,^{29,30} or amines³¹; b) organometallic reactions of a radical-protected derivative of arylboronic acid or an organolithium derivative with 2,4,6-trichlorotriazine³²; c) initial formation of the 1,3,5-triazine nucleus by the trimerization reaction of a functionalized benzonitrile followed by transformation of the functional group into a stable radical.³³

The present report continues our research on the synthesis of functional derivatives of spirocyclic mono- and oligoradicals of the azole series.³⁴⁻³⁶ The present paper describes the synthesis as well as structural characterization of new paramagnetic derivatives of 2,4,6-tris(aryloxy)-1,3,5-triazine (**1a–c**) and of 2,4-bis(aryloxy)-6-methoxy-1,3,5-triazine (**2a–c**; Figure 1).

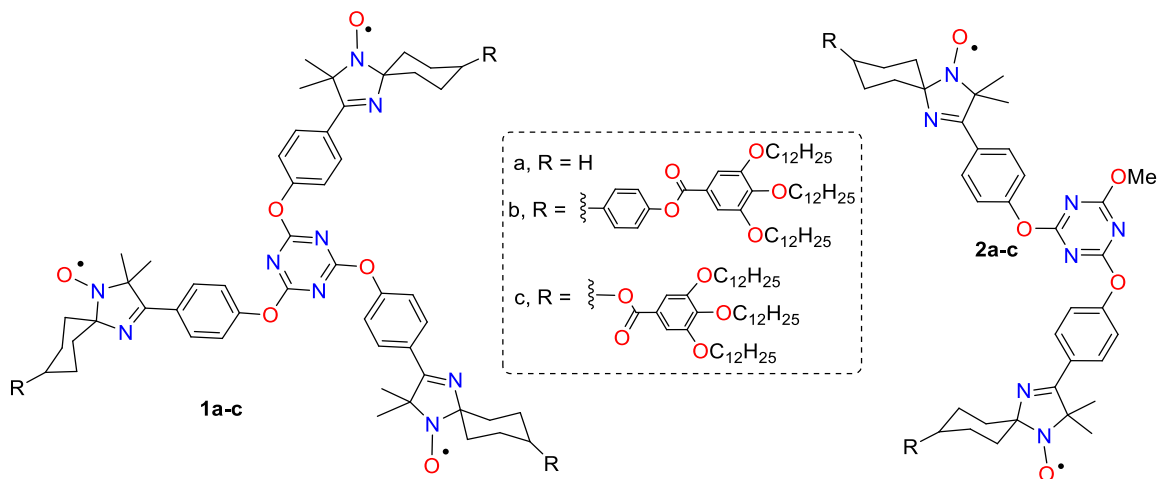


Figure 1. Chemical structures of the desired paramagnetic derivatives of 2,4,6-tris(aryloxy)-1,3,5-triazine (**1a–c**) and of bis(aryloxy)-6-methoxy-1,3,5-triazine (**2a–c**).

Results and Discussion

To synthesize paramagnetic compounds **1a–c** and **2a–c**, we applied a nucleophilic substitution reaction of cyanuric chloride or 2,4-dichloro-6-methoxy-1,3,5-triazine and the corresponding derivatives of spirocyclic 2,5-dihydroimidazole-type monoradicals **3**,³⁴ **4**, and **5** containing a 4-hydroxyaryl residue in the presence of a base (Figure 2). In this regard, first, we describe the preparation and structural characterization of novel nitroxides **4** and **5**.

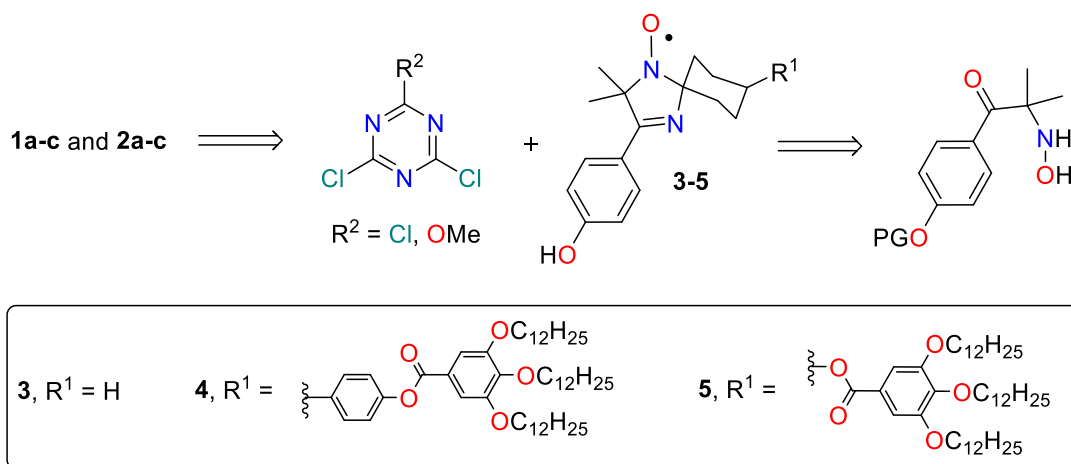
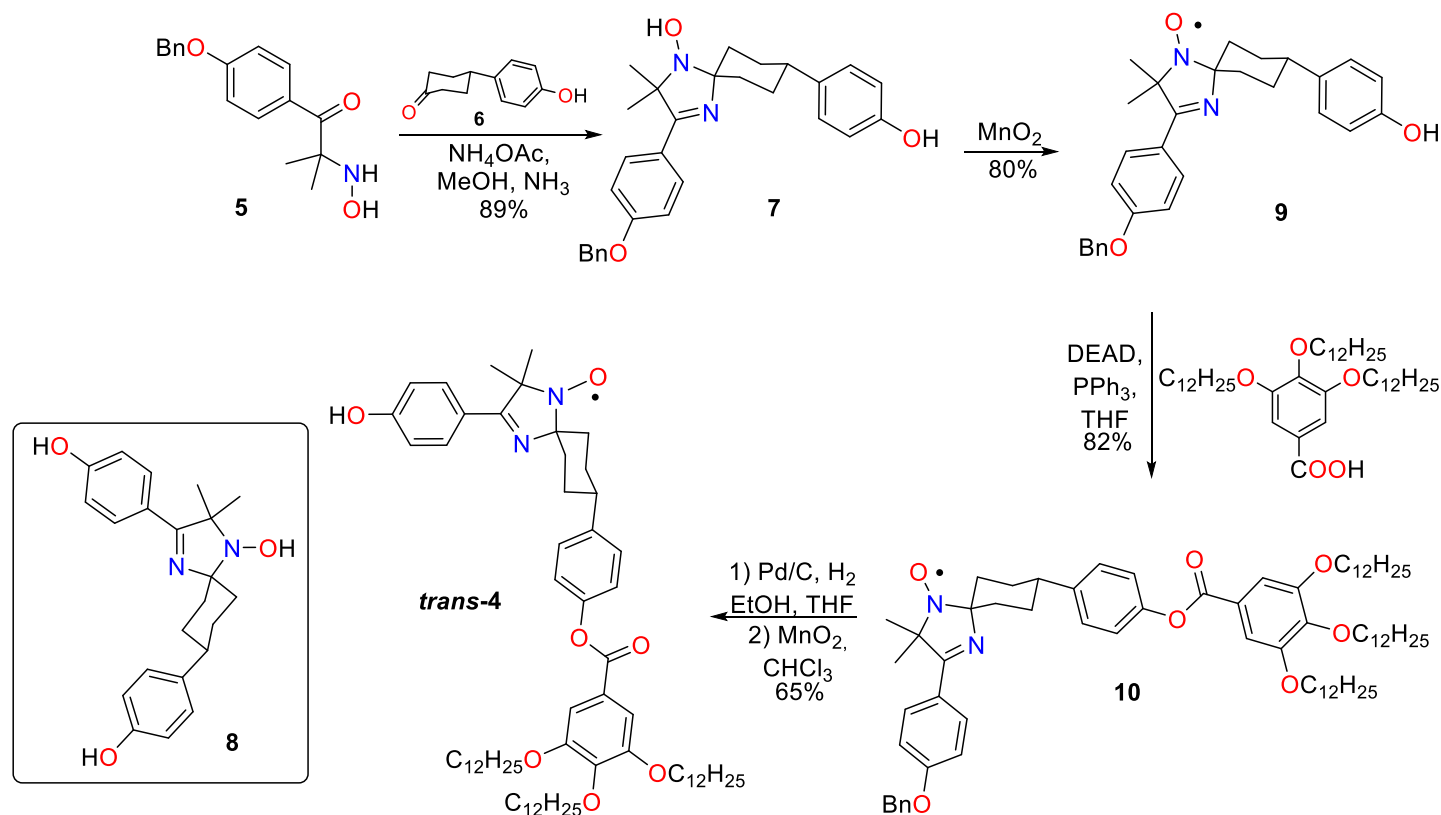


Figure 2. Retrosynthetic disconnection of target bi- and triradicals **1a–c** and **2a–c**.

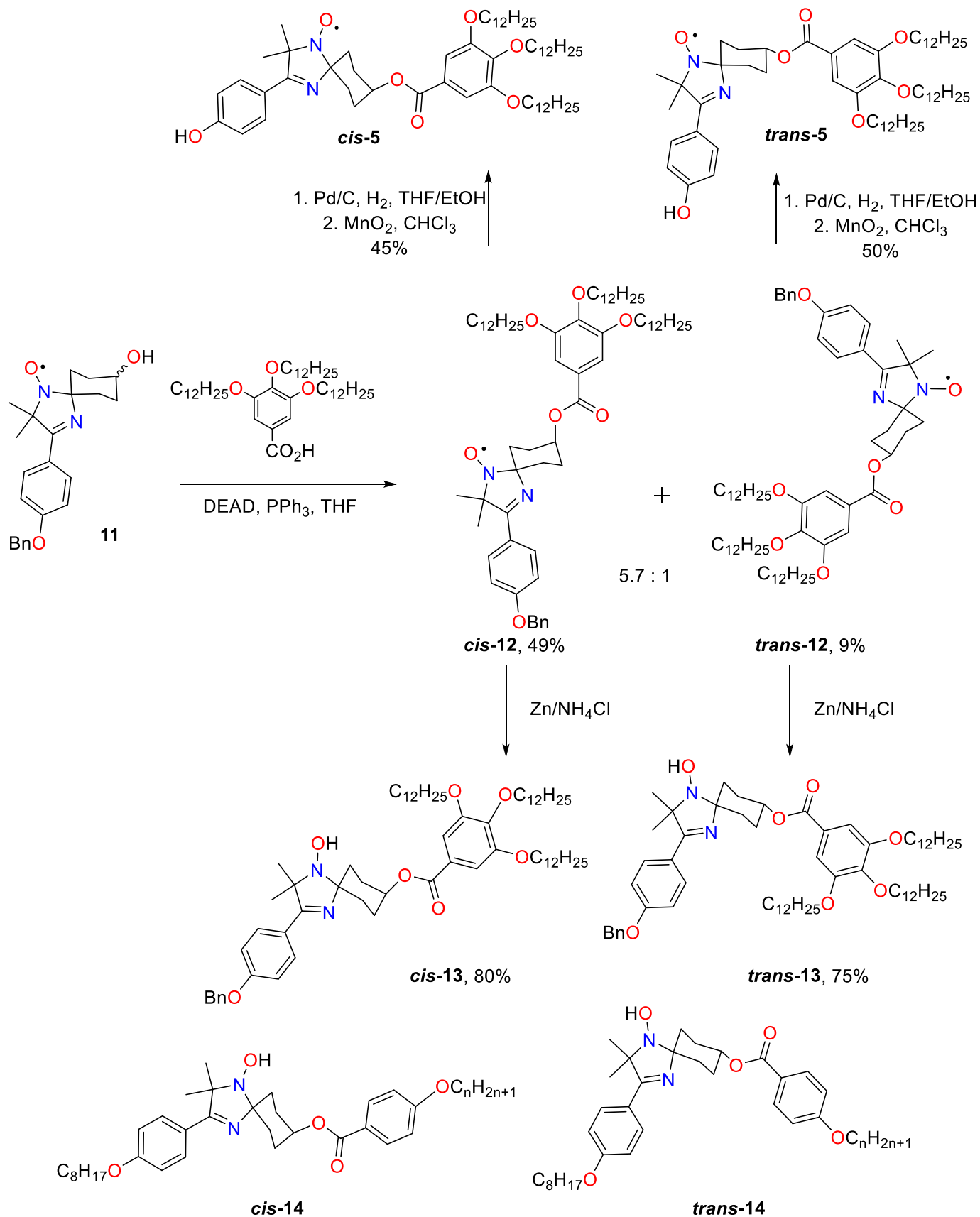
Condensation of commercially available 4-(4-hydroxyphenyl)cyclohexanone (**6**) with 1-(4-benzyloxyphenyl)-2-(hydroxylamino)-2-methylpropan-1-one (**5**)³⁵ possessing a protected phenolic group proceeded with high stereoselectivity and quantitatively led to a single isomer of **7**. The stereochemistry of **7** was determined by comparing its ¹H and ¹³C NMR spectra with those recorded for compound **8**. In our previous publication, **8** was found to have a *trans-ee*-configuration.³⁶ Because the corresponding chemical shifts and coupling constants (see the Experimental section) of **7** were identical to those obtained for debenzylated analogue **8**,

we assigned the structure of a *trans-ee*-isomer to **7**. Oxidation of hydroxylamine **7** with manganese dioxide in chloroform gave nitroxide **9** with an 80% yield. As already mentioned, tris(alkyloxy)benzoic acid derivatives can have LC properties and show columnar mesophases,⁶ as such, we added this mesogenic residue to our nitroxide radicals. Thus, acylation of nitroxide **9** by 3,4,5-tris(dodecyloxy)benzoic acid under Mitsunobu reaction³⁷ conditions allowed us to obtain the desired acylated derivative **10** with a high yield. Debenzylation of ester **10** by hydrogenation on a palladium catalyst was always accompanied by a side reaction of reduction of the nitroxyl function to a cyclic hydroxylamine. Oxidation of the intermediate imidazoline by MnO₂ in CHCl₃ produced target nitroxide *trans*-**4** containing a phenolic group with a moderate yield (Scheme 1).

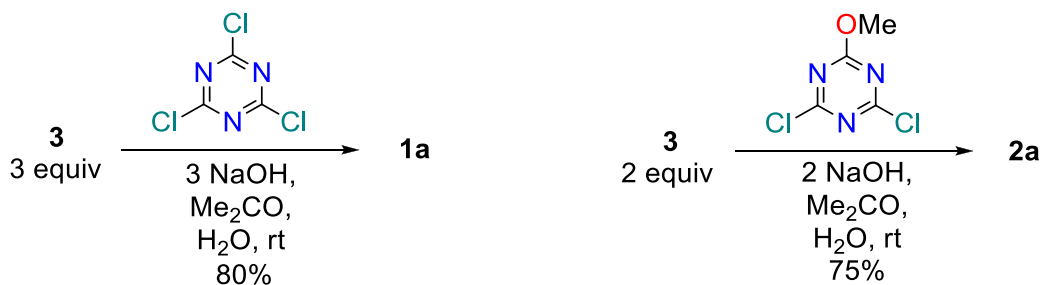


Scheme 1. The synthesis of phenolic-group-containing nitroxide *trans*-**4**.

The synthesis of the next paramagnetic phenol **5** was started from spiro-fused derivative **11** prepared as a diastereomeric mixture by a previously described synthetic procedure.³⁵ The subsequent Mitsunobu acylation reaction with 3,4,5-tris(dodecyloxy)benzoic acid and separation of obtained isomers *cis*-**12** and *trans*-**12** by preparative thin-layer chromatography (TLC) on silica gel afforded the individual compounds *cis*-**12** and *trans*-**12** in the ratio 5.7:1.0. To confirm the spatial structure of the obtained isomers, they were reduced in aqueous tetrahydrofuran (THF) to the corresponding diamagnetic *N*-hydroxy derivatives *cis*-**13** and *trans*-**13** by means of a Zn/NH₄Cl system. A comparison of ¹H and ¹³C NMR spectra of *cis*-**13** and *trans*-**13** (see the Experimental section and Supporting Information) with those of previously described analogues *cis*-**14** and *trans*-**14**³⁵ allowed us to identify their stereochemistry, as depicted in Scheme 2. Subsequent hydrogenation of both isomers on the palladium catalyst followed by oxidation with MnO₂ in CHCl₃ led to the desired 4,5-dihydroimidazole derivatives *cis*-**5** and *trans*-**5** in moderate yields. Given that the overall yield of minor isomer *trans*-**5** was very low, we did not subject this compound to further transformations; only isomer *cis*-**5** was used in the next synthetic step.

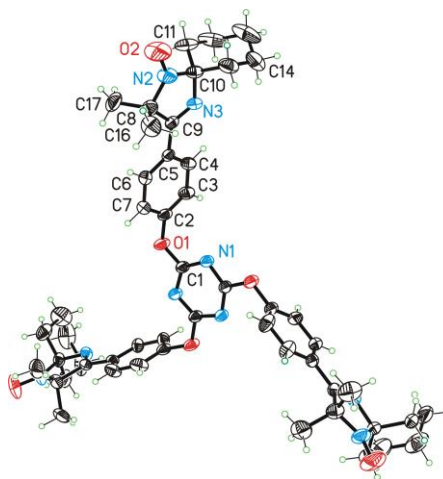
Scheme 2. The synthesis of phenolic-group-containing nitroxides *cis-5* and *trans-5*.

The final step of our synthesis was the nucleophilic substitution of chlorides from cyanuric chloride and 2,4-dichloro-6-methoxy-1,3,5-triazine, respectively via a reaction with the synthesized paramagnetic phenols. At first, we tried to carry out this reaction with compound **3**, which has no substituents at position 4 of the cyclohexane ring. Because radical **3** does not contain lipophilic groups (long alkyl chains), it was possible to generate its phenolate anion in an alkaline aqueous solution. The interaction of **3** or 2 molar equivalents of this anion with 1,3,5-trichlorotriazine or 2,4-dichloro-6-methoxy-1,3,5-triazine successfully produced the corresponding tri- and biradicals **1a** and **2a** in 80 and 75% yields, respectively (Scheme 3).

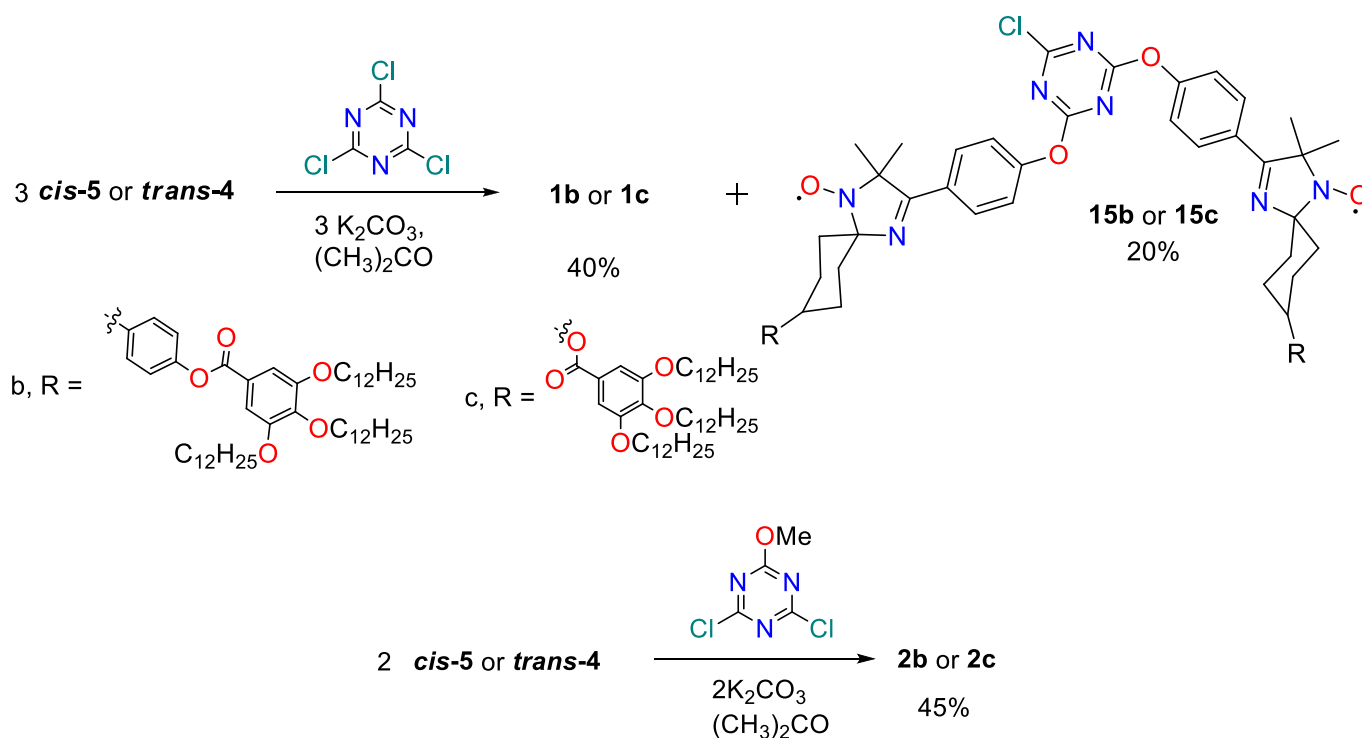


Scheme 3. The synthesis of target tri- and biradicals **1a** and **2a**.

The crystal structure of triradical **1a** was determined by the X-ray diffraction method (Figure 3). The molecules of **1a** are located on threefold rotational axes and have Δ -conformations inside the crystal.³⁸ At the same time, phenoxy moieties of each molecule are almost perpendicular to the plane of the triazine core [torsion angle C1-O1-C2-C3: 83.4(2)°]. An analogous orientation of phenoxy groups is observed, for example, in a solvate of 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine with hexamethylbenzene.³⁹ The geometry of the 3-phenyl-1,4-diazaspiro[4.5]dec-3-ene 1-oxyl moiety is almost similar to that in 2,2-dimethyl-3-[4-(decyloxy)-phenyl]-1,4-diazaspiro[4.5]dec-3-ene 1-oxyl.³⁴ The dihedral angle between the phenyl and 2,5-dihydroimidazole planes is 4.2(2)°. It is worth noting that the formed layers are parallel to the *ab* plane owing to the C6-H...O2 interaction (the H...O distance: 2.38, the C-H...O angle: 140°) in the crystal packing of triradical **1a**. Moreover, inside and between the layers, there are some voids, which are filled with highly disordered solvent molecules (see the Experimental section).



Because we could successfully realize the coupling between unsubstituted paramagnetic derivative **3** and 1,3,5-trichlorotriazine as well as 2,4-dichloro-6-methoxy-1,3,5-triazine, we tried to conduct the same reaction with more complex and encumbered nucleophiles, such as radicals **trans-4** and **cis-5**. Given that these compounds contain lipophilic groups, it was impossible to obtain their phenolate anions in an alkaline aqueous solution. For this reason, we chose potassium carbonate in acetone as a base medium. Because of the relatively weak basicity of the medium, boiling the mixture containing cyanuric chloride, **trans-4**, or **cis-5** and potassium carbonate in acetone within 5 h gave the mixture of target triradicals **1b** or **1c**, respectively along with disubstitution products: diradicals **15b** and **15c** in the ratio 2:1 with an overall yield of ~60%. On the other hand, such reaction incompleteness makes it in principle possible to obtain mono- and disubstitution products under the experimental conditions. The interaction between 2,4-dichloro-6-methoxy-1,3,5-triazine and nitroxides **trans-4** and **cis-5** enabled obtaining desired biradicals **2b** and **2c**, respectively with a 45% yield.



Scheme 4. The synthesis of target tri- and biradicals **1b,c** and **2b,c**.

Mono-,bi- and trinitroxides **1b,c**, **2b,c**, **trans-4**, **trans-5**, **cis-5**, and **15b,c** containing mesogenic groups were investigated for LC properties by means differential scanning calorimetry (DSC) and optical polarizing microscope. The phase transition data determined by DSC is presented in the Table S1 (see the Supporting Information). None of the compounds possesses liquid crystalline properties. **Trans-4**, **trans-5** and **cis-5** represent pale-yellow amorphous solids and showed only crystal-to-crystal and crystal-to-isotropic liquid phase transitions. **1b,c**, **2b,c** and **15b,c** are pale yellow waxy solids and showed no peaks in differential scanning calorimetry (DSC) curves in the temperature interval from 25 to 140 °C. When the starting temperature was decreased to -10 °C the corresponding melting peaks appeared at the temperatures lower than 25 °C (see Table S1). No birefringent texture was observed for all the compounds by optical polarizing microscope if the temperature was higher than their melting point in the heating and in the cooling runs. It was assumed that they do not possess liquid crystalline properties as a consequence of low space fill factors of such bulky molecules.

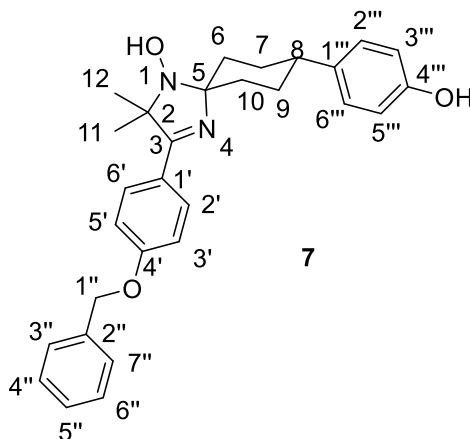
Conclusions

We developed a convenient approach to the synthesis of stable 1,3,5-triazine-based bi- and triradicals of the 2,5-dihydroimidazole series. Six new bi- and tris(nitroxides) were obtained, and symmetrical nature of the model tris(nitroxide) was confirmed by single crystal X-ray diffraction analysis. Investigation of the bi- and tris(nitroxides) containing mesogenic groups by means DSC and optical polarizing microscope revealed that none of synthesized radicals possess LC properties. Nevertheless, the proposed conditions for the nucleophilic substitution of chloride from cyanuric chloride with paramagnetic phenols allow us to expect successful syntheses of new hetero bi- and triradicals containing various structural types of paramagnetic units.

Experimental Section

General. Analytical and spectroscopic studies were performed in the Multi-Access Chemical Research Center SB RAS for spectral and analytical measurements. Melting points and DSC thermograms were obtained on an FP 81 HT METTLER TOLEDO device. Infrared (IR) spectra were acquired on a Vector-22 Bruker spectrometer in KBr. ^1H and ^{13}C NMR spectra were recorded by means of Bruker AV-400 and AV-500 spectrometers for solutions of compounds in CDCl_3 or $\text{DMSO}-d_6$, and chemical shifts were recorded in parts per million (ppm or δ) relative to internal standard residual solvent signals: CDCl_3 (δ_{H} 7.26, δ_{C} 77.16) and $\text{DMSO}-d_6$ (δ_{H} 2.50, δ_{C} 39.52). Electron spin resonance (ESR) spectra of the radicals were obtained on a Bruker 300 spectrometer for 10^{-4} M solutions in chloroform. The reactions were monitored by TLC in silica gel on Sorbfil UV-254 plates. Column chromatography (CC) was performed in silica gel (ACROS, 0.060-0.200 mm). All the chemicals and solvents were of commercial reagent quality and used without further purification unless stated otherwise. Dry THF was obtained by distillation over a LiH/CaH₂ (50:50) mixture. 4-(4-Hydroxyphenyl)cyclohexanone (**6**) was purchased from Aldrich. 3-(4-Hydroxyphenyl)-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-ene-1-oxyl (**3**),³⁴ 1-(4-benzyloxyphenyl)-2-(hydroxylamino)-2-methyl-1-propanone hydrochloride (**5**),³⁵ 3-(4-benzyloxyphenyl)-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-ene-8-ol 1-oxyl (**11**),³⁶ 3,4,5-tris(dodecyloxy)benzoic acid,⁴⁰ and 1-methoxy-3,5-dichloro-1,3,5-triazine⁴¹ were obtained by the procedures described in the literature.

2,2-Dimethyl-3-(4-benzyloxy)phenyl-1-hydroxy-8-(4-hydroxyphenyl)-1,4-diazaspiro[4,5]-deca-3-ene (7). A mixture of 4-(4-hydroxyphenyl)cyclohexanone (**6**) (1.605 g, 5.0 mmol), 1-(4-benzyloxyphenyl)-2-(hydroxylamino)-2-methylpropan-1-one hydrochloride (**5**) (0.950 g, 5.0 mmol), and ammonium acetate (1.560 g, 20 mmol) in MeOH (50 mL) saturated with ammonia was stirred at room temperature for 5 h. The precipitate formed was filtered out and washed with water and MeOH to give **7** as a colorless solid (2.03 g, 89%), which was used for the next step without further purification. An analytical sample was purified by recrystallization from EtOH to obtain **7** as a colorless powder; mp 118–120 °C (EtOH). IR (solid, KBr, ν_{max} , cm^{-1}): 3458 (OH), 1598, 1571 (C=N). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ_{H} 1.37 (6H, s, Me-11 and Me-12), 1.48–1.55 (2H, m, H-6e,10e), 1.68–1.75 (2H, m, H-7e,9e), 1.87–2.06 (4H, m, H-6a,7a,9a,10a), 2.42–2.51 (1H, m, H-8a), 5.16 (2H, s, CH_2-1''), 6.68 (2H, d, 3J 8.2Hz, H-3''',5'''), 6.99–7.08 (4H, m, H-2''',6''',3',5'), 7.32–7.50 (5H, m, H-3'',4'',5'',6'',7''), 7.62 (1H, s, NOH), 7.84 (2H, d, 3J 8.6Hz, H-2',6'), 9.13 (1H, s, OH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ_{C} 24.7 (C-11, C-12), 31.7 (C-7, C-9), 36.0 (C-6, C-10), 42.6 (C-8), 69.4 (C-2), 69.6 (C-1'), 88.7 (C-5), 114.8 (C-3',C-5'), 115.1 (C-3''',C-5'''), 126.1 (C-1'), 127.6 (C-2''',C-6'''), 127.9 (C-3'',C-7''), 128.1 (C-5''), 129.1 (C-4'',C-6''), 129.4 (C-2',C-6'), 137.0 (C-2''), 137.6 (C-1'''), 155.6 (C-4'''), 160.0 (C-4'), 171.7 (C-3). Anal. calcd for $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_3$ (456.58): C, 76.29; H, 7.06; N, 6.14. Found: C, 76.01; H, 7.01; N, 6.14%.



2,2-Dimethyl-3-(4-benzyloxy)phenyl-8-(4-hydroxyphenyl)-1,4-diazaspiro[4.5]deca-3-ene 1-oxyl (9). A suspension of 2,2-dimethyl-3-(4-benzyloxy)phenyl-1-hydroxy-8-(4-hydroxyphenyl)-1,4-diazaspiro[4.5]-deca-3-ene(7) (1.824 g, 4.0 mmol) and MnO_2 (1.720 g, 20 mmol) in a $\text{CHCl}_3/\text{MeOH}$ (75:25) mixture (50 mL) at room temperature was stirred for 3 h. An excess of the oxidant was filtered out, and the solvent was evaporated. The residue was purified by CC (hexane/EtOAc, 2:1) to obtain the *title compound* 9 as a pale yellow powder (1.456 g, 80%); mp 220–222 °C (hexane). IR (solid, KBr, ν_{max} , cm^{-1}): 3197 (OH), 1608, 1591 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_3$ (455.57): C, 76.46; H, 6.86; N, 6.15. Found: C, 76.40; H, 6.75; N, 6.14%.

4-[(5*r*,8*r*)-3-(4-Benzyloxyphenyl)-2,2-dimethyl-1-oxido-1,4-diazaspiro[4.5]dec-1-en-8-yl]phenyl 3,4,5-tris(dodecyloxy)benzoate (10). A round-bottom flask was filled with argon, then charged with compound 8 (455 mg, 1 mmol), Ph_3P (576 mg, 2.2 mmol), 3,4,5-tris(dodecyloxy)benzoic acid (1.350 g, 2.0 mmol), and dry THF (10 mL). Diethyl azodicarboxylate (DEAD) (348 mg, 2.0 mmol) was added to the resulting solution followed by stirring at room temperature for 24 h. The mixture was concentrated in vacuum, the residue was triturated with Et_2O , cooled to 0 °C, and the precipitate was filtered off. Evaporation of the solvent gave a solid, which was purified by preparative TLC on silica gel with hexane/EtOAc (80:20) to give the *title compound* 10 as a pale yellow solid (911 mg, 82%), which was used for the next step without further purification. An analytical sample was prepared by recrystallization from EtOH to obtain ester 10 as a pale yellow amorphous solid mp 38–40 °C (EtOH). IR (solid, KBr, ν_{max} , cm^{-1}): 1747 (C=O), 1587 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for $\text{C}_{72}\text{H}_{107}\text{N}_2\text{O}_7$ (1112.63): C, 77.72; H, 9.69; N, 2.52. Found: C, 77.42; H, 9.63; N, 2.50%.

4-[(5*r*,8*r*)-3-(4-Hydroxyphenyl)-2,2-dimethyl-1-oxido-1,4-diazaspiro[4.5]dec-1-en-8-yl]phenyl 3,4,5-tris(dodecyloxy)benzoate (*trans*-4). A catalyst (4% Pd/C) (300 mg) was added to a solution of nitroxide 9 (889 mg, 0.8 mmol) in a mixture of EtOH (8 mL) and THF (16 mL). The flask was purged with Ar in an Ar atmosphere, then once with H_2 , and the reaction mixture was hydrogenated under 1-bar pressure at 20 °C for 3.5 h with stirring. The catalyst was filtered off and washed with THF/EtOH (2:1). The filtrate and washings were combined, and the solvent was evaporated. The residue was dissolved in chloroform (20 mL), and the solution was mixed with MnO_2 (344 mg, 4 mmol) and stirred for 3 h at 20 °C. The excess oxidant was filtered out, the solvent was removed in vacuum, and the residue was purified by CC (hexane/EtOAc, 80:20) to obtain the *title compound trans*-4 as a pale yellow amorphous solid (531 mg, 65%). There are two peaks in the DSC curve on the heating run: at 78 and 96 °C. IR (solid, KBr, ν_{max} , cm^{-1}): 1745 (C=O), 1587 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for $\text{C}_{76}\text{H}_{101}\text{N}_2\text{O}_7$ (1022.51): C, 76.35; H, 9.96; N, 2.74. Found: C, 76.51; H, 9.90; N, 2.78%.

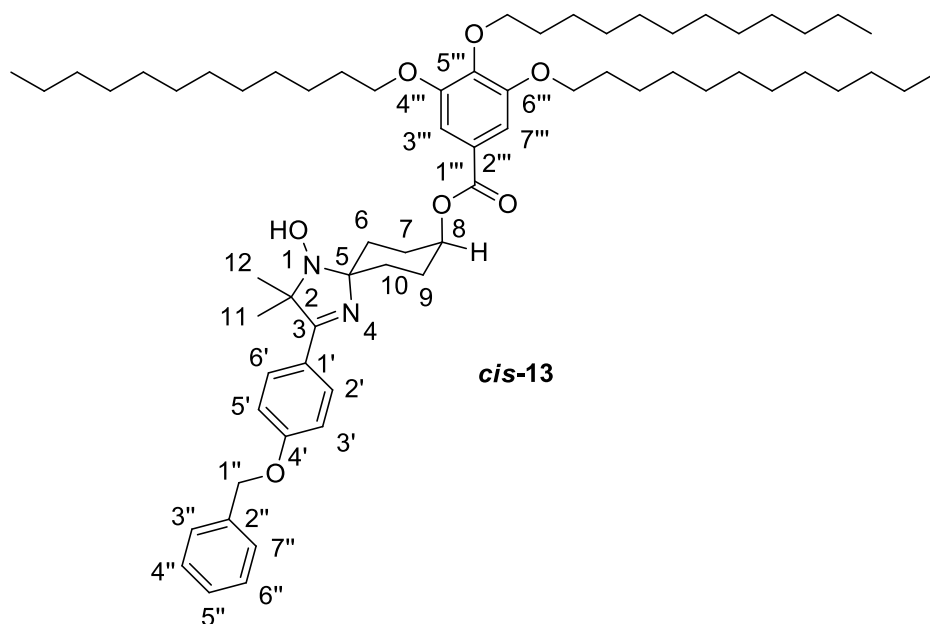
Cis- and trans- 2-(4-Benzyloxyphenyl)-3,3-dimethyl-4-oxido-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)benzoate (12). A round-bottom flask was purged with Ar, then charged with 3-(4-benzyloxyphenyl)-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-ene-8-ol 1-oxyl (11) (378 mg, 1.0 mmol), Ph_3P (576 mg, 2.2 mmol),

3,4,5-tris(dodecyloxy)benzoic acid (1.350 g, 2.0 mmol), and THF (10 mL). DEAD (348 mg, 2.0 mmol) was added to the resultant solution followed by stirring at room temperature for 24 h. The mixture was concentrated in vacuum, and the residue was triturated with Et₂O and cooled to 0 °C. The precipitate was filtered off. The solvent was removed, and the residue was subjected to chromatography (preparative TLC) on silica gel (hexane/EtOAc, 5:1), with collection of the fractions with *R_f* 0.30 (*cis* isomer) and *R_f* 0.35 (*trans* isomer). The total yield was 58%.

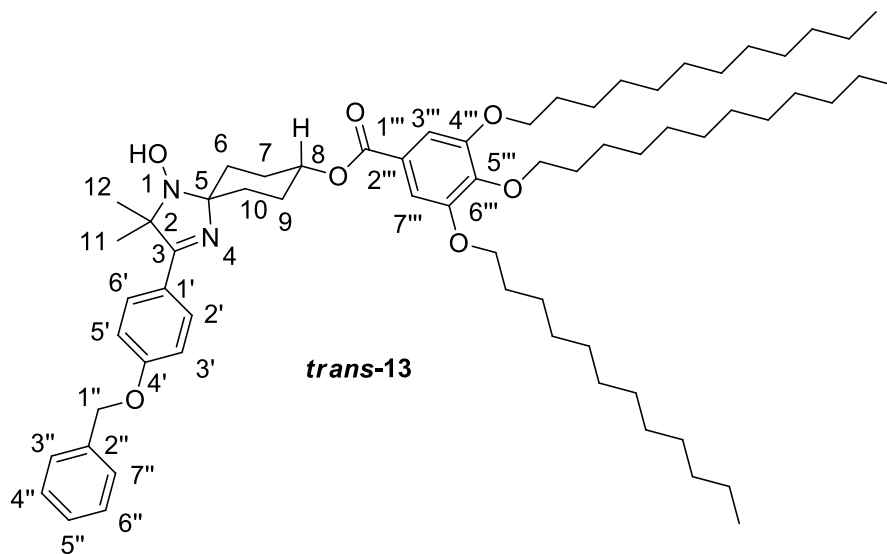
(5*s*,8*s*)-2-(4-Benzyloxyphenyl)-4-oxido-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)-benzoate (*cis*-12). Pale yellow amorphous solid (507 mg, 49%); mp 66–68 °C (EtOH). IR (solid, KBr, ν_{\max} , cm⁻¹): 1705 (C=O), 1608, 1591 (C=N). ESR: *t*, *A_N* 1.45 mT, *g_{iso}* 2.0058. Anal. calcd for C₆₆H₁₀₃N₂O₇ (1036.53): C, 76.48; H, 10.02; N, 2.70. Found: C, 76.56; H, 9.95; N, 2.78%.

(5*s*,8*s*)-2-(4-Benzyloxyphenyl)-4-oxido-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)-benzoate (*trans*-12). Pale yellow amorphous solid (93 mg, 9%); mp 50–52 °C (EtOH). IR (solid, KBr, ν_{\max} , cm⁻¹): 1751 (C=O), 1607, 1591 (C=N). ESR: *t*, *A_N* 1.45 mT, *g_{iso}* 2.0058. Anal. calcd for C₆₆H₁₀₃N₂O₇ (1036.53): C, 76.48; H, 10.02; N, 2.70. Found: C, 76.45; H, 9.95; N, 2.80%.

(5*s*,8*s*)-2-(4-Benzyloxyphenyl)-4-hydroxy-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)benzoate (*cis*-13). A solution of nitroxide *cis*-12 (52 mg, 0.05 mmol) in THF (1 mL) was treated with zinc dust (5 mg, 0.075 mmol), then a solution of NH₄Cl (5 mg, 0.1 mmol) in H₂O (20 μ L) was added to the resulting suspension, and the reaction mixture was stirred for 1 h at 20 °C under Ar. The Zn/ZnO cake was removed by filtration, the filtrate was concentrated, and the residue was triturated with EtOH. The precipitate that formed was filtered off and washed with EtOH to obtain *cis*-13 as a colorless powder (41 mg, 80%); mp 78–80 °C (EtOH). IR (solid, KBr, ν_{\max} , cm⁻¹): 1706 (C=O), 1607, 1591 (C=N). ¹H NMR (400 MHz, DMSO-*d*₆+CDCl₃): δ_{H} 0.81–0.86 (9H, m, 3CH₃), 1.16–1.35 (48H, m, 24CH₂), 1.39 (6H, s, Me-11 and Me-12), 1.40–1.42 (2H, m, H-6*e*,10*e*), 1.41–1.49 (6H, m, 3CH₂), 1.60–1.68 (2H, m, OCH₂CH₂), 1.70–1.78 (4H, m, 2OCH₂CH₂), 1.88–1.98 (2H, m, H-7*e*,9*e*), 2.02–2.12 (2H, m, H-7*a*,9*a*), 2.24–2.34 (2H, m, H-6*a*,10*a*), 3.89–3.93 (2H, m, OCH₂CH₂), 3.93–4.20 (4H, m, 2OCH₂CH₂), 5.11 (2H, s, CH₂-1''), 5.15–5.19 (1H, m, H-8*e*), 7.00 (2H, d, ³*J* 8.3 Hz, H-3',5'), 7.22 (2H, s, H-3''',7'''), 7.25–7.40 (5H, m, H-3'',4'',5'',6'',7''), 7.78 (2H, d, ³*J* 8.3 Hz, H-2',6'), 8.11 (1H, s, NOH). ¹³C NMR (100 MHz, DMSO-*d*₆+CDCl₃): δ_{C} spiro system and aryl carbon signals: 25.1 (C-11, C-12), 27.8 (C-7, C-9), 30.3 (C-6, C-10), 69.8 (C-1''), 70.0 (C-8), 70.3 (C-2), 89.0 (C-5), 107.7 (C-3''',7'''), 114.8 (C-3',5'), 125.8 (C-2'''), 126.4 (C-1'), 127.8 (C-3'',7''), 128.1 (C-5''), 128.7 (C-2',6'), 129.5 (C-4'', C-6''), 137.0 (C-2''), 141.8 (C-5'''), 152.8 (C-4''', 6'''), 160.1 (C-4'), 165.0 (C-1'''), 172.4 (C-3); lateral alkyl chain carbon signals: 14.4 (3CH₃), 22.6, 26.1, 26.2, 29.2, 29.3, 29.51, 29.55, 29.61, 29.63, 29.65, 29.7, 30.9, 31.8, 68.9 (OCH₂CH₂), 73.1(OCH₂CH₂). Anal. calcd for C₆₆H₁₀₄N₂O₇ (1037.54): C, 76.40; H, 10.10; N, 2.70. Found: C, 76.50; H, 9.98; N, 2.71%.



(5*r*,8*r*)-2-(4-Benzyloxyphenyl)-4-hydroxy-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyl-oxy)benzoate (*trans*-13) was obtained analogously to *cis*-isomer **13** via reduction of compound *trans*-12.



A colorless powder (38 mg, 75%); mp 58–60 °C (EtOH). IR (solid, KBr, ν_{max} , cm^{-1}): 1748 (C=O), 1608, 1591 (C=N). ^1H NMR (400 MHz, $\text{DMSO-}d_6 + \text{CDCl}_3$): δ_{H} 0.80–0.86 (9H, m, 3CH₃), 1.16–1.35 (48H, m, 24CH₂), 1.38 (6H, s, Me-11 and Me-12), 1.40–1.50 (6H, m, 3CH₂), 1.52–1.58 (2H, m, H-6*e*,10*e*), 1.59–1.68 (2H, m, OCH₂CH₂), 1.68–1.79 (4H, m, 2OCH₂CH₂), 1.97–2.07 (6H, m, H-7*e*, 9*e*, 7*a*, 9*a*, 6*a*, 10*a*), 3.87–3.94 (2H, m, OCH₂CH₂), 3.94–4.30 (4H, m, 2OCH₂CH₂), 4.84–4.95 (1H, m, H-8*a*), 5.12 (2H, s, CH₂-1''), 7.00 (2H, d, 3J 7.5 Hz, H-3',5'), 7.17 (2H, s, H-3''',7'''), 7.25–7.49 (5H, m, H-3'',4'',5'',6'',7''), 7.58 (1H, s, NOH), 7.80 (2H, d, 3J 7.5 Hz, H-2',6'). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6 + \text{CDCl}_3$): δ_{C} spiro system and aryl carbon signals: 24.5 (C-11, C-12), 28.5 (C-7, C-9), 33.2 (C-6, C-10), 69.5 (C-2), 70.0 (C-1''), 73.1 (C-8), 88.1 (C-5), 107.4 (C-3''',7'''), 114.5 (C-3',5'), 125.1 (C-2'''), 125.9 (C-1'), 127.5 (C-3'',7''), 127.8 (C-5''), 128.4 (C-2',6'), 129.2 (C-4'', C-6''), 136.7 (C-2''), 141.5 (C-5'''), 152.4 (C-4''', 6'''), 159.8 (C-4'), 164.9 (C-1'''), 172.1 (C-3); lateral alkyl chain carbon signals: 13.9 (3CH₃), 22.2, 25.6, 25.7, 28.85, 28.91, 29.10, 29.17, 29.20, 29.25, 29.3, 29.9, 31.4, 31.8, 68.6 (OCH₂CH₂), 72.7 (OCH₂CH₂). Anal. calcd for C₆₆H₁₀₄N₂O₇ (1037.54): C, 76.40; H, 10.10; N, 2.70. Found: C, 76.52; H, 9.95; N, 2.72%.

(5s,8s)-2-(4-Hydroxyphenyl)-4-oxido-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)-benzoate (cis-5). The catalyst (4% Pd/C) (100 mg) was added to a solution of nitroxide **cis-12** (316 mg, 0.3 mmol) in a mixture of EtOH (7 mL) and THF (7 mL), the flask was purged with Ar in an Ar atmosphere, then once with H₂, and the reaction mixture was hydrogenated under 1-bar pressure at 20 °C for 3 h with stirring. The catalyst was filtered off and washed with THF/EtOH (50:50). The filtrate and washings were combined, and the solvent was evaporated. The residue was dissolved in chloroform (15 mL), and the solution was mixed with MnO₂ (129 mg, 1.5 mmol) and stirred for 3 h at 20 °C. The excess oxidant was filtered out, the solvent was removed in vacuum, and the residue was purified by CC (hexane/EtOAc, 75:25) to obtain nitroxide **cis-5** as a pale yellow amorphous solid (128 mg, 45%); mp 62–64 °C (EtOH). IR (solid, KBr, ν_{\max} , cm⁻¹): 3437 (OH), 1703 (C=O), 1612, 1598 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₅₉H₉₇N₂O₇ (946.41): C, 74.88; H, 10.33; N, 2.96. Found: C, 74.73; H, 10.30; N, 3.02%.

(5r,8r)-2-(4-Hydroxyphenyl)-4-oxido-3,3-dimethyl-1,4-diazaspiro[4.5]dec-1-en-8-yl 3,4,5-tris(dodecyloxy)-benzoate (trans-5) was obtained similarly to nitroxide **cis-5** from compound **trans-12**. A pale amorphous solid (141 mg, 50%); mp 80–82 °C (EtOH). IR (solid, KBr, ν_{\max} , cm⁻¹): 3388 (OH), 1697 (C=O), 1608, 1587 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₅₉H₉₇N₂O₇ (946.41): C, 74.88; H, 10.33; N, 2.96. Found: C, 74.75; H, 10.25; N, 2.95%.

4,4',4''-[4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tris(oxy)tris(benzene-4,1-diyl)]tris(5,5-dimethyl-2,2-pentamethylen-1-oxido-2,5-dihydro-1H-imidazole) (1a). The solution of sodium phenoxide obtained by dissolving 3-(4-hydroxyphenyl)-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-oxyl (**3**) (84 mg, 0.31 mmol) in 1 mL of aqueous 0.3N NaOH was gradually added to the mixture of 18 mg (0.1 mmol) of cyanuric chloride and 2 mL of acetone during vigorous stirring. After stirring for 3 h at room temperature, acetone was evaporated, and the crystal precipitate was filtered off, washed with water, and air dried. The crude product was purified by CC (hexane/EtOAc, 2:1) to prepare trinitroxide **1a** as a yellow powder (71 mg, 80%); mp 146–148 °C (hexane). Single crystals for X-ray analysis were obtained by recrystallization of compound **1a** from hexane/EtOAc (75:25). IR (solid, KBr, ν_{\max} , cm⁻¹): 1606, 1566 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₅₁H₆₀N₉O₆ (895.08): C, 68.43; H, 6.76; N, 14.08. Found: C, 68.33; H, 6.81; N, 13.98%.

4,4'-[4,4'-(6-Methoxy-1,3,5-triazine-2,4-diyl)bis(oxy)bis(4,1-phenylene)]bis(5,5-dimethyl-2,2-pentamethylen-1-oxido-2,5-dihydro-1H-imidazole) (2a) was obtained similarly to nitroxide **1a** from 18 mg (0.1 mmol) of 2,4-dichloro-6-methoxy-1,3,5-triazine, 57 mg (0.21 mmol) of phenol **3**, and 8 mg (0.21 mmol) of sodium hydroxide in a solution in water/acetone (1:2). The crude solid was recrystallized from hexane/EtOAc to obtain **2a** as a yellow powder (48 mg, 75%); mp 73–75 °C. IR (solid, KBr, ν_{\max} , cm⁻¹): 1606, 1570 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₃₆H₄₃N₇O₅ (653.77): C, 66.14; H, 6.63; N, 15.00. Found: C, 66.00; H, 6.53; N, 14.90%.

Trinitroxide (1b) and binitroxide (15b). A mixture of 168 mg (0.165 mmol) 4-[(5r,8r)-3-(4-hydroxyphenyl)-2,2-dimethyl-1-oxido-1,4-diazaspiro[4.5]dec-1-en-8-yl]phenyl 3,4,5-tris(dodecyloxy)benzoate (**trans-4**), 9 mg (0.05 mmol) cyanuric chloride, and 22 mg (0.165 mmol) of potassium carbonate in 2 mL of dry acetone was refluxed for 5 h. The solvent was evaporated, and the residue was mixed with water (4 mL) and chloroform (10 mL). The organic layer was separated, washed with water, and dried over magnesium sulfate. The organic filtrate was condensed in vacuum, and the residue was separated into individual compounds by CC (hexane/EtOAc, 75:25) to obtain compound **1b** (R_f 0.50) and compound **15b** (R_f 0.20) in that order.

Trinitroxide (1b). A yellow waxy solid. Yield: 62 mg (40%). There are no peaks in the DSC curve on the heating run. IR (solid, KBr, ν_{\max} , cm⁻¹): 1762, 1733 (C=O), 1585, 1558 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₉₈H₃₀₀N₉O₂₁ (3142.65): C, 75.67; H, 9.62; N, 4.01. Found: C, 75.50; H, 9.80; N, 4.10%.

Binitroxide (15b). A yellow waxy solid. Yield: 21 mg (20%). There are no peaks in the DSC curve on the heating run. IR (solid, KBr, ν_{\max} , cm⁻¹): 1762, 1733 (C=O), 1585, 1558 (C=N). ESR: t, A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₃₃H₂₀₀ClN₇O₁₄ (2156.50): C, 74.07; H, 9.35; N, 4.55; Cl 1.64. Found: C, 74.20; H, 9.45; N, 4.53; Cl 1.63%.

Binitroxide (2b). A mixture of 112 mg (0.11 mmol) of 4-[(5*r*,8*r*)-3-(4-hydroxyphenyl)-2,2-dimethyl-1-oxido-1,4-diazaspiro[4.5]dec-1-en-8-yl]phenyl 3,4,5-tris(dodecyloxy)benzoate (*trans*-4), 9 mg (0.05 mmol) of 2,4-dichloro-6-methoxy-1,3,5-triazine, and 15 mg (0.11 mmol) of potassium carbonate in 2 mL of dry acetone was refluxed for 5 h. The solvent was evaporated, and the residue was mixed with water (4 mL) and chloroform (10 mL). The organic layer was separated, washed with water, and dried over MgSO₄. The filtrate was condensed in vacuum, and the residue was mixed with 5 mL of EtOH and cooled to 0 °C. The formed precipitate was immediately filtered off, washed with EtOH, and air dried to obtain **2b** as a yellow waxy solid (31 mg, 45%). There are no peaks in the DSC curve on the heating run. IR (solid, KBr, ν_{\max} , cm⁻¹): 1762, 1732 (C=O), 1581, 1560 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₃₄H₂₀₃N₇O₁₅ (2152.08): C, 74.78; H, 9.51; N, 4.56. Found: C, 74.30; H, 9.45; N, 4.53%.

Trinitroxide (1c) and binitroxide (15c) were obtained analogously to compounds **1b** and **15b** from compound *cis*-5.

Trinitroxide (1c). A yellow waxy solid (61 mg, 42%). There are no peaks in the DSC curve on the heating run. IR (solid, KBr, ν_{\max} , cm⁻¹): 1703 (C=O), 1585, 1546 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₈₀H₂₈₈N₉O₂₁ (2914.26): C, 74.18; H, 9.96; N, 4.33. Found: C, 74.24; H, 9.97; N, 4.40%.

Binitroxide (15c). A yellow waxy solid (20 mg, 20%). There are no peaks in the DSC curve on the heating run. IR (solid, KBr, ν_{\max} , cm⁻¹): 1712 (C=O), 1604, 1568 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₂₁H₁₉₂ClN₇O₁₄ (2004.31): C, 72.51; H, 9.66; N, 4.89; Cl, 1.77. Found: C, 72.86; H, 9.60; N, 4.82; Cl, 1.76%.

Binitroxide (2c) was prepared similarly to compound **2b** from *cis*-5. A yellow waxy solid (46 mg, 46%); mp 72–74 °C. IR (solid, KBr, ν_{\max} , cm⁻¹): 1708 (C=O), 1585, 1560 (C=N). ESR: t , A_N 1.45 mT, g_{iso} 2.0058. Anal. calcd for C₁₂₂H₁₉₅N₇O₁₅ (1999.89): C, 73.27; H, 9.83; N, 4.90. Found: C, 73.01; H, 9.60; N, 4.85%.

X-Ray crystallography

The X-ray single-crystal diffraction data for triradical **1a** were collected at 200 K on a Bruker Kappa APEX II instrument with MoK α radiation (λ = 0.71073 Å) and a CCD area detector. The structures were solved by direct methods in the SHELXS software and refined on F^2 using all the data by full-matrix least-square procedures in SHELXL-97. Multiscan absorption corrections were performed in the SADABS software. The positions of nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in the calculated positions with isotropic displacement parameters at 1.2 times the isotropic equivalent of their carrier atoms. The guest molecules of hexane and EtOAc are strongly disordered and located next to the threefold and rotoinversion threefold axes. Therefore, the SQUEEZE function in PLATON was employed to calculate the potential solvent-accessible area in the unit cell; 3×396 and 3×140 Å³ were calculated containing approximately 3×106 and 3×37 electrons. Accordingly, the first three voids may contain six solvent molecules (hexane/EtOAc), and the next three voids may contain water or be empty.

Crystal data on **1a** (without guest solvents): C₅₁H₆₀N₉O₆, FW 895.08, rhombohedral, space group R-3, a = b = 20.6189(6), c = 22.8065(8) Å, α = β = 90, γ = 120°, V = 8396.9(5) Å³, Z = 6, $\mu(\text{MoK}\alpha)$ = 0.071 mm⁻¹, ρ_{calc} = 1.062 g·cm⁻³, $2\theta_{\max}$ = 52°, GOF = 1.09, $wR(F^2)$ = 0.2217 (all 3675 data), R = 0.0607 [2866 data with $I > 2\sigma(I)$], CCDC 1578986.

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Supplementary Material

IR, ^1H and ^{13}C NMR spectra and phase transition data of new compounds.

References

1. Wolff, J. J.; Siegler, F.; Matschiner, R.; Wortmann, R. *Angew. Chem. Int. Ed.* **2000**, *39*, 1436.
[http://dx.doi.org/10.1002/\(SICI\)1521-3773\(20000417\)39:8<1436::AID-ANIE1436>3.0.CO;2-U](http://dx.doi.org/10.1002/(SICI)1521-3773(20000417)39:8<1436::AID-ANIE1436>3.0.CO;2-U)
2. Cherioux, F.; Maillotte, H.; Audebert, P.; Zyss, J. *Chem. Commun.* **1999**, 2083.
<http://dx.doi.org/10.1039/A905899K>
3. Wöhrle, T.; Wurzbach, I.; Kirres, J.; Kostidou, A.; Kapernaum, N.; Litterscheidt, J.; Haenle, J. C.; Staffeld, P.; Baro, A.; Giesselmann, F.; Laschat, S. *Chem. Rev.* **2016**, *116*, 1139.
<http://dx.doi.org/10.1021/acs.chemrev.5b00190>
4. Yang, F.; Xie, J.; Guoa, H.; Xua, B.; Lia, C. *Liq. Cryst.* **2012**, *39*, 1368.
<http://dx.doi.org/10.1080/02678292.2012.717112>
5. Majumdera, K. C.; De, N.; Roy, B.; Bhaumik, A. *Liq. Cryst.* **2010**, *37*, 1459.
<http://dx.doi.org/10.1080/02678292.2010.520750>
6. Goldmann, D.; Janietz, D.; Festag, R.; Schmidt, C.; Wendorff, J. H. *Liq. Cryst.* **1996**, *21*, 619.
<http://dx.doi.org/10.1080/02678299608032873>
7. Holst, H. G.; Pakulab, T.; Meier, H. *Tetrahedron* **2004**, *60*, 6765.
<http://dx.doi.org/10.1016/j.tet.2004.06.031>
8. Lee, C.; Yamamoto, T. *Tetrahedron Lett.* **2001**, *42*, 3993.
[http://dx.doi.org/10.1016/S0040-4039\(01\)00640-2](http://dx.doi.org/10.1016/S0040-4039(01)00640-2)
9. Veerabhadraswamy, B. N.; Dambal, H. K.; ShankarRao, D. S.; Yelamaggad, C. V. *ChemPhysChem* **2016**, *17*, 2225.
<http://dx.doi.org/10.1002/cphc.201600280>
10. Laventure, A.; De Grandpre, G.; Soldera, A.; Lebel, O.; Pellerin, C. *Phys. Chem. Chem. Phys.* **2016**, *18*, 1681.
<http://dx.doi.org/10.1039/c5cp06630a>
11. El-Faham, A.; Dahlous, K.; AL Othman, Z. A.; Al-Lohedan, H. A.; El-Mahdy, G. A. *Molecules* **2016**, *21*, 436.
<http://dx.doi.org/10.3390/molecules21040436>
12. Stegbauer, L.; Schwinghammer, K.; Lotsch, B. V. *Chem. Sci.* **2014**, *5*, 2789.
<http://dx.doi.org/10.1039/c4sc00016a>
13. Tamura, R.; Uchida, Y.; Suzuki, K. In *Handbook of Liquid Crystals* (2nd Ed.); Goodby, J. W.; Collings, P. J.; Kato, T.; Tschierske, C.; Gleeson, H. F.; Raynes, P. Eds.; Wiley-VCH: Weinheim, 2014; Vol. 8, pp. 837-864.
14. Tamura, R.; Uchida, Y.; Ikuma, N. *J. Mater. Chem.* **2008**, *18*, 2872.
<http://dx.doi.org/10.1039/B802407C>
15. Suzuki, K.; Takemoto, Y.; Takaoka, S.; Taguchi, K.; Uchida, Y.; Mazhukin, D. G.; Grigor'ev, I. A.; Tamura, R. *Chem. Commun.* **2016**, 52, 3935.
<http://dx.doi.org/10.1039/c5cc09202g>
16. Castellanos, S.; Lopez-Calahorra, F.; Brillas, E.; Julia, L.; Velasco, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 6516.
<http://dx.doi.org/10.1002/anie.200902641>
17. Jankowiak, A.; Pocięcha, D.; Monobe, H.; Szczytko, J.; Kaszynski, P. *Chem. Commun.* **2012**, 48, 7064.
<http://dx.doi.org/10.1039/c2cc33051b>

18. Jankowiak, A.; Pocięcha, D.; Szczytko, J.; Monobe, H.; Kaszynski, P. *J. Am. Chem. Soc.* **2012**, *134*, 2465.
<http://dx.doi.org/10.1021/ja209467h>
19. Jasinski, M.; Pocięcha, D.; Monobe, H.; Szczytko, J.; Kaszynski, P. *J. Am. Chem. Soc.* **2014**, *136*, 14658.
<http://dx.doi.org/10.1021/ja507594h>
20. Jasinski, M.; Szczytko, J.; Pocięcha, D.; Monobe, H.; Kaszynski, P. *J. Am. Chem. Soc.* **2016**, *138*, 9421.
<http://dx.doi.org/10.1021/jacs.6b06444>
21. Uchida, Y.; Suzuki, K.; Tamura, R.; Ikuma, N.; Shimono, S.; Noda, Y.; Yamauchi, J. *J. Am. Chem. Soc.* **2010**, *132*, 9746.
<http://dx.doi.org/10.1021/ja101930d>
22. Suzuki, K.; Uchida, Y.; Tamura, R.; Shimono, S.; Yamauchi, J. *J. Mater. Chem.* **2012**, *22*, 6799.
<http://dx.doi.org/10.1039/c2jm16278d>
23. Ravat, P.; Marszalek, T.; Pisula, W.; Müllen, K.; Baumgarten, M. *J. Am. Chem. Soc.* **2014**, *136*, 12860.
<http://dx.doi.org/10.1021/ja507421x>
24. Suzuki, K.; Uchida, Y.; Tamura, R.; Noda, Y.; Ikuma, N.; Shimono, S.; Yamauchi, J. *Soft Matter* **2013**, *9*, 4687.
<http://dx.doi.org/10.1039/C3SM27295H>
25. Rozenberg, A. N.; Povoroznik, O. M.; Golubev, V. A.; Sen, V. D.; Bogdanov, G. N. *Izv. Akad. NaukSSSR, Ser. Khim.* 1977, 875; *Chem. Abstr.* **1977**, *87*, 68294a.
26. Chalmers, A. M.; Jack, J.; Cook, B. U.S. Pat. 4 028 334, 1977; *Chem. Abstr.* **1977**, *87*, P 202584a.
27. Sommerlade, R.; Grutzmacher, H.; Boulmaaz, S. Eur. Pat. Appl. 1103537, 2001; *Chem. Abstr.* **2001**, *135*, P 5246a.
28. Li, J.; Zhang, Z.; Zhu, X.; Zhu, J.; Cheng, Z. *e-Polymers* **2010**, *10*, no. 145.
<http://dx.doi.org/10.1515/epoly.2010.10.1.1622>
29. Peng, L.; Chen, C.; Gonzalez, C. R.; Balogh-Nair, V. *Int. J. Mol. Sci.* **2002**, *3*, 1145.
<http://dx.doi.org/10.3390/i3111145>
30. Wang, H.; Wang, J.; Yang, Q.; Zhang, X.; Gao, P.; Xu, S.; Sun, X.-L.; Wang, Y. K. *Neurochem. Res.* **2015**, *40*, 1526.
<http://dx.doi.org/10.1007/s11064-015-1602-5>
31. Nesvadba, P.; Bugnon, L. PCT Int. Appl. 107468, 2007; *Chem. Abstr.* **2007**, *147*, P 409765a.
32. Lahti, P. M.; Liao, Y.; Julier, M.; Palacio, F. *Synth. Met.* **2001**, *122*, 485.
[http://dx.doi.org/10.1016/S0379-6779\(01\)00340-X](http://dx.doi.org/10.1016/S0379-6779(01)00340-X)
33. Hayami, S.; Inoue, K. *Chem. Lett.* **1999**, *28*, 545.
<http://dx.doi.org/10.1246/cl.1999.545>
34. Zaytseva, E. V.; Gatilov, Yu. V.; Amitina, S. A.; Tamura, R.; Grigor'ev, I. A.; Mazhukin, D. G. *Russ. J. Org. Chem. (Engl. Transl.)* **2014**, *50*, 72.
<http://dx.doi.org/10.1134/S107042801401014X>
35. Zaitseva, E. V.; Shernyukov, A. V.; Amitina, S. A.; Tamura, R.; Grigor'ev, I. A.; Mazhukin, D. G. *Chem. Heterocycl. Compd. (Engl. Transl.)* **2014**, *50*, 1113.
<http://dx.doi.org/10.1007/s10593-014-1571-7>
36. Zaytseva, E. V.; Shernyukov, A. V.; Genaev, A. M.; Tamura, R.; Grigor'ev, I. A.; Mazhukin, D. G. *Arkivoc* **2014**, (vi), 10.
<http://dx.doi.org/10.3998/ark.5550190.p008.808>
37. Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. *Chem. Rev.* **2009**, *109*, 2551.
<http://dx.doi.org/10.1021/cr800278z>
38. Aakeroy, C. B.; Desper, J.; Urbina, J. F. *Cryst. Eng. Comm.* **2005**, *7*, 193.
<http://dx.doi.org/10.1039/b419029g>

39. Saraswatula, V. G.; Bhat, M. A.; Bhattacharya, S.; Saha B. K. *J. Chem. Sci.* **2014**, 126, 1265.
<http://dx.doi.org//10.1007/s12039-014-0690-0>
40. Hersmis, M. C.; Spiering, A. J. H.; Waterval, R. J. M.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof L. A. *Org. Process. Res. Dev.* **2001**, 5, 54.
<http://dx.doi.org//10.1021/op000066e>
41. Naseer, M. M.; Wang, D. X.; Zhao, L.; Huang, Z. T., Wang, M. X. *J. Org. Chem.* **2011**, 76, 1804.
<http://dx.doi.org//10.1021/jo102483x>