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Rational synthetic methods in creating promising (hetero)aromatic molecules and materials

Grigory V. Zyryanov,*[a,b] Dmitry S. Kopchuk,[a,b] Igor S. Kovalev,[a] Sougata Santra,[a] Matiur Rahman,[a] Albert F. Khasanov,[a,b] Alexey P. Krinochkin,[a,b] Olga S. Taniya,[a,b] Oleg N. Chupakhin[a,b] and Valery N. Charushin[a,b]

[a] *Ural Federal University, 620002 Ekaterinburg, Russian Federation. E-mail: gvzyryanov@gmail.com*

[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620219 Ekaterinburg, Russian Federation*

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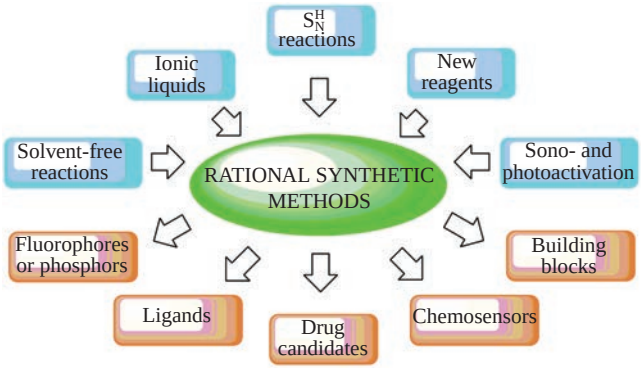
In this focus article, the recent syntheses of various (hetero)-aromatic/macrocyclic molecules/scaffolds such as (thia)-calixarenes, iptycenes, [poly](aza)arenes, 2,2′-bipyridines, 1,2,4-triazines, (ox)azoles and aziri(di)nes are reviewed. The employed rational synthetic schemes and green chemistry principles such as solvent-free reactions, reactions in ionic liquids, aryne-mediated reactions, domino and multi-component reactions, sono-, photo- and mechanoactivated processes, and direct C–H functionalization are described. The obtained compounds exhibited promising photophysical and coordination properties, intriguing supramolecular properties as well as biological activities. The possible application of these compounds as fluorophores, luminophores, organic phosphors, chemosensors, ligands and drug candidates is discussed.



Keywords: macrocycles, (hetero)arenes, transition metal-free methods, C–H functionalization, chemosensors, ligands, fluorophores, drug candidates.

Introduction

(Hetero)aromatic/macrocyclic molecules/scaffolds have found wide application in area of functional materials, including those for gas and energy transport and storage, fluorophores, photoluminescent sensors/probes, biologically, pharmaceutically potent compounds and many others. PASE (Pot, Atom, Step, Economy), green and sustainable chemistry-based approaches in the synthesis of the above mentioned organic molecules are the key terms of recent two decades and generally they mean the rational synthesis with environmentally friendly characteristics of reactions that give a minimum or no destructive effect on the environment,[1–5] including lower E-factors.[6,7] The most of wastes is produced not only from the starting reagents but the reaction medium also plays a significant role. In terms of green chemistry, solvent-less/solvent-free chemical transformations are more desirable than reactions in any kind of solvents.[2,8–10] One-pot procedures, including multistep ones, can be beneficial for the synthetic organic chemistry to ensure minimizing amount of waste, reaction time, and simplifying the synthetic procedures. Application of green chemistry methodologies to traditional organic synthetic processes offers highly appropriate alternatives. Among them is the replacement of some conventional approaches with more environmentally friendly ones, such as direct nucleophilic C–H functionalization, new methods of activation or chemical interactions. These include the use of water-based reaction media, ionic liquids, microwave, electrochemical synthesis, sono- or mechano-activated syntheses, photoactivation, heterogeneous, solid- supported or bio-based catalysts, *etc*. All of the above approaches/methods play a significant role in the development of the basic principles of green chemistry in the field of organic synthesis in both laboratory and industry, reducing the risks of adverse effects on health and the environment.[11–13]

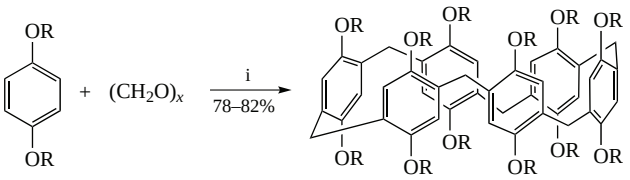
In this review, we would briefly state some of our efforts made on the development of greener and/or more rational synthetic approaches towards various (hetero)aromatic molecules/scaffolds of different uses, as well as highlight some challenging problems that have to be or may be solved in the near future.

1. Rational synthesis of some important macro(hetero)cycles

Macro(hetero)cycles are of interest for various fields of chemistry since they, on the one hand, can be constructed using various methods of organic chemistry, and on the other hand, are capable of selective interacting (molecular recognition) with other charged and neutral molecules and particles *via* dipole–dipole, ion–dipole, hydrogen bonds and their combinations.[11–13] Macro(hetero)cycles mimic the work of natural receptors and

enzymes,[14,15] which makes them practically useful.[16–18] The most popular macro(hetero)cycles are crown ethers[19,20] and, lately, calixarenes, which are used for recognition/supramolecular extraction of inorganic[21] and organic cations,[22] and some neutral molecules.[23] Thiocalixarenes[24] and resorcinarenes,[25,26] including carcerands[27] and hemicarcerands,[28] also found application in supramolecular chemistry. In 2008, Ogoshi and co-authors discovered new prospective supramolecular hosts, pillar[5]-arenes.[29,30] Later, pillar[6]-[31,32] and higher pillararenes[33] were discovered. For the synthesis of most macro(hetero)cycles, solvation/supramolecular effects play a significant role.[34,35] For example, to obtain pillar[*n*]arenes, the template effect of the solvent used determines the nature of the formed pillararene,[29–35] such as the thermodynamically stable pillar[5]arenes or kinetic products of pillar[*n*]arenes ($n > 5$).

Taking the abovementioned into account, we proposed a solvent-free synthesis of pillar[6]arenes[36] **1** (Scheme 1) by the reaction of paraformaldehyde with 1,4-dialkoxyhydroquinones (Alk ≠ Me) in the presence of catalytic amounts of H_2SO_4. The absence of any solvent, medium for interconversions, provides



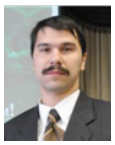
R = Et, Pr, Bu, BuCH(Et)CH_2, *n*-C_7H_{15} **1**

Scheme 1 *Reagents and conditions*: i, H_2SO_4 (10 mol%), 25 °C, solvent-free, 10 min.

the formation of kinetic products, pillar[6]arenes, in up to 83% yields.

In a similar manner, a solvent-free preparation of thiacalix[4]-arene **2** by reacting *p-tert*-butylphenol and S_8 at 150–170 °C followed by heating to 230 °C (Scheme 2) was elaborated.[37] When carrying out the reaction at lower temperature, kinetic products are formed, namely (poly)thiacalix[*n*]arenes **3**–**6** containing phenolic units connected by di- and trisulfide bridges. The (poly)sulfide bond chemistry in organic solutions is reported

Grigory V. Zyryanov, Professor of the RAS, earned his PhD (Organic Chemistry) in 2000, and Dr. Sci. (Organic Chemistry) in 2012 from the Ural Federal University. In 2001–2003 he worked as a post-doc with Professor D. Rudkevich (UT Arlington, TX, USA) on supramolecular chemistry of gases, and, in 2004–2010 with Professor P. Anzenbacher, Jr. (Bowling Green State University, OH, USA) on photochemistry and molecular recognition. His current research interests include the development of novel approaches and PASE-methods in synthetic organic chemistry, green chemistry, coordination chemistry, photochemistry, and chemosensors.



Dmitry S. Kopchuk earned his PhD (Organic Chemistry) in 2010 and Dr. Sci. (Organic Chemistry) in 2019 from the Ural Federal University. His current research interests include the development of novel synthetic approaches to (hetero)aromatic compounds, including new bi- and terpyridine ligands, substituted 1,2,4-triazines, chemosensors for the metal cations, and explosive detection.

Igor S. Kovalev earned his PhD (Organic Chemistry) in 2003 from the Ural Federal University. His current research interests include the development of novel approaches to new (hetero)aromatic compounds exhibiting biological activity and/or luminescent properties, mass spectrometry, and green chemistry processes.

Sougata Santra obtained his PhD (Organic Chemistry) from Visva-Bharatti University under the supervision of Dr. Adinath Majee in 2014. In January 2015, he joined the research group of Professor Grigory V. Zyryanov at Ural Federal University as post-doctoral fellow. In July 2015 he was promoted for the Senior Research Scientist position. His research interests include new synthetic methodologies and green chemistry.

Matiur Rahman obtained his PhD degree (Organic Chemistry) from Visva-Bharatti University under the joint supervision of Dr. Adinath Majee and Dr. Alakananda Hajra in 2013. In 2013–2015, he worked as HIR post-doctoral research fellow with Professor Rauzah Hashim at University of Malaya, Kualalumpur. Currently, he is working as Senior Research Scientist at Ural Federal University with Professor Grigory V. Zyryanov. His research interests include the synthesis of functionalized heterocyclic and bioactive compounds using environmentally friendly methods. Currently, he is working on supramolecular chemistry and aryne chemistry.

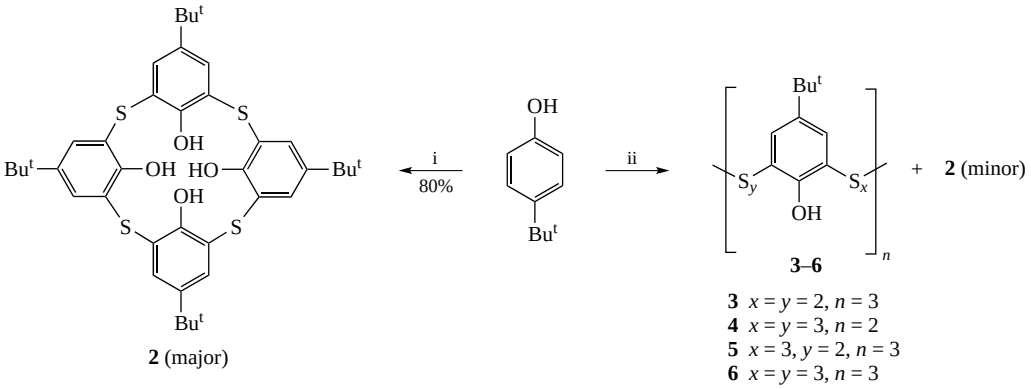
Albert F. Khasanov earned his PhD (Organic Chemistry) in 2018 from the Ural Federal University. His scientific interests are represented by chemistry of heterocyclic compounds, supramolecular chemistry, molecular recognition and photochemistry.

Alexey P. Krinochkin earned his PhD (Organic Chemistry) in 2019 from the Ural Federal University. His scientific interests are represented by chemistry of heterocyclic compounds, supramolecular chemistry, molecular recognition and photochemistry.

Olga S. Taniya earned her PhD (Organic Chemistry) in 2018 from the Ural Federal University. Her scientific interests include the synthesis and study of the photophysical properties of poly(aza)aromatic chemosensors/fluorophores, supramolecular chemistry and molecular recognition.

Oleg N. Chupakhin, Academician of the RAS, Principal Research Scientist at the Institute of Organic Synthesis of Ural Branch of the RAS, earned his PhD (Organic Chemistry) in 1962 and Dr. Sci. (Organic Chemistry) in 1976 from the Ural Federal University. His current research interests include the development of new green methodologies in organic synthesis, medicinal chemistry, mechanisms of organic reactions, fluorine chemistry, coordination chemistry, photochemistry, chemosensors, molecular recognition and supramolecular chemistry.

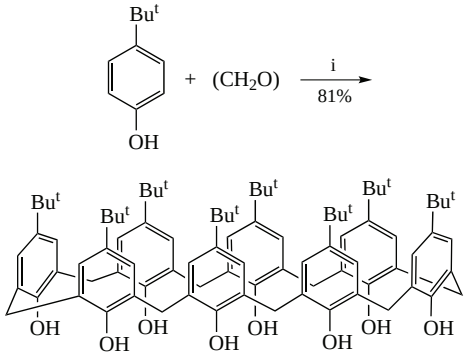
Valery N. Charushin, Academician of the RAS, Director of the Institute of Organic Synthesis of Ural Branch of the RAS, earned his PhD (Organic Chemistry) in 1976 and Dr. Sci. (Organic Chemistry) in 1987 from the Ural Federal University. His current research interests include novel methods in organic synthesis, heterocyclic chemistry, fluorine chemistry, green chemistry, coordination chemistry, photochemistry, chemosensors, molecular recognition and medicinal chemistry.



Scheme 2 *Reagents and conditions*: i, *p-tert*-butylphenol (1 equiv.), S_8 (2 equiv.), NaOH (0.5 equiv.), Ar, 150–170 °C, 3 h, then 230 °C, 24 h; ii, *p-tert*-butylphenol (1 equiv.), S_8 (2 equiv.), NaOH (0.5 equiv.), Ar, 150–170 °C, 3 h, then 200 °C, 3 h.

with regard to dynamic combinatorial chemistry.[38–43] The kinetic nature of the formation of thiomacrocycles **3**–**6** was confirmed by their conversion to thermodynamically stable compound **2** upon heating.

Finally, we reported[44] on a rational synthesis of calix[8]arene **7** in 81% yield by condensation of *p-tert*-butylphenol with 40% aqueous formaldehyde in the presence of NaOH (Scheme 3). Compared to common synthesis of calix[8]arene, the current approach requires less solvent and has E-factors as low as 1.83, which is 25 to 50 times lower compared to other reported methods.[45]



Scheme 3 *Reagents and conditions*: i, CH_2O (40% aq.), NaOH, Ar, 150 °C, then 250 °C.

In our opinion, the key advantage of all the above processes is the low reaction E-factors, as well as, in most cases, the possibility of obtaining kinetic reaction products, which is difficult to achieve using traditional synthesis methods.

2. Fluorescent chemosensors for the detection of some important analytes

Fluorescence detection methods are based on a change in the fluorescent signal of the fluorophore in the presence of target compounds (analytes). The advantage of such methods is the simplicity of instrumentation, fast response time and the real time detection on the spot.

2.1. Fluorescent chemosensors for the detection of nitro-containing compounds (explosives)

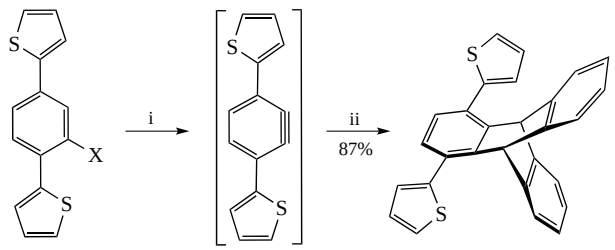
The creation of new materials for the detection of nitro-containing explosives is relevant in connection with the high risk of terrorist attacks on civilian objects using improvised explosive devices. The most typical components for creating such devices are nitro-explosives, namely 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).[46] Due to the fact that nitro compounds are fluorescence quenchers, the 'turn-off' fluorescence methods for the detection of nitro-explosives by using various (hetero)aromatic fluorescent chemosensors are most widely developed.[47]

2.1.1. Iptycenes for the detection of nitroaromatic compounds and RDX

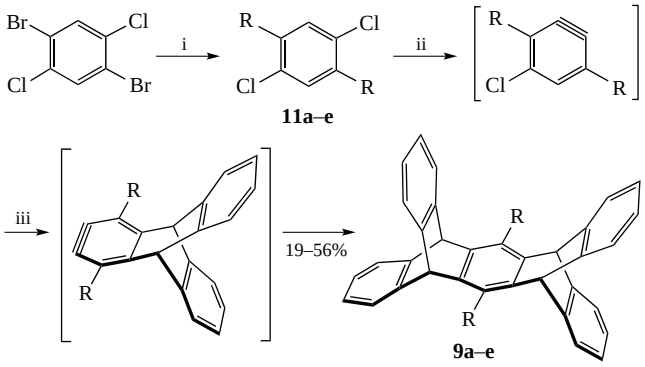
Iptycenes are aromatic compounds composed of varying number of arene subunits bound to a bridged bicyclooctatriene core structure. The first iptycene was prepared by E. Clar *et al.*,[48] and the first triptycene was prepared by P. Bertlett's research group.[49] Due to their unique 3D architecture with a large 'free volume', iptycenes have found application in materials science[50,51] including hydrogen[52] and other gases transport, storage and separation.[53–57] In 1998, T. Swager and J. Yang published a pioneering work on the synthesis of pentiptycene-containing polymers as materials for the fluorescence detection of nitroaromatic compounds in a gas phase.[58,59] Among the ways of constructing iptycene core, one can distinguish the 'aryne-based method' *via* the Diels–Alder reaction between *in situ* generated arynes and anthracene. Depending on the method of aryne generation, the target iptycenes were obtained in 3.7[60] to 94%[61] yields.

In development of the 'aryne approach' to iptycenes, we proposed a method[62] for the obtaining of iptycenes **8**, **9** substituted with various (het)arene moieties (Schemes 4, 5). The starting arynes were generated *in situ* by means of dehydrohalogenation in the corresponding halogen(het) arenes **10**, **11** under the action of Bu^{t}OK in toluene in a pressure vessel at 135–140 °C. The following Diels–Alder cycloaddition of arynes to anthracene afforded products **8**, **9** in 19–87% yields.

Iptycenes **9** allow one to visually detect nitroaromatic compounds in solutions with quenching constants $K_{sv} = (1.1–3.5) \times 10^3$ dm^3 mol^{-1}. The possibility of detecting



Scheme 4 *Reagents and conditions*: i, Bu^{t}OK, PhMe, 135 °C, pressure vessel; ii, anthracene (5 equiv.), PhMe, 135 °C, pressure vessel, 12 h.



a R = Ph
b R = benzo[*b*]thiophen-2-yl
c R = 2-thienyl
d R = 2,2′-bithiophen-5-yl
e R = 9,9-dialkyl-9*H*-fluoren-2-yl

Scheme 5 *Reagents and conditions*: i, R–B(OH)$_2$ or Ar–SnAlk$_3$, Pd(PPh$_3$)$_4$, PhMe, 80–135 °C, 4–48 h; ii, Bu^{t}OK, PhMe, 135 °C, pressure vessel; iii, anthracene (10 equiv.), PhMe, 135 °C, pressure vessel, 24–48 h.

nitroaromatic compounds in the gas phase is confirmed by the formation of 'pentiptycene–nitrobenzene' 1 : 1 inclusion complexes in the 'face-to-edge' geometry according to X-ray diffraction data[63] [Figure 1(*a*)], as well as by fluorescence quenching in polyurethane (PU) matrices doped with iptycenes **9** [see Figure 1(*f*),(*i*)]. An increase in the efficiency of the obtained materials for the detection of nitroaromatic compounds in the gas phase is achieved by using the electrospinning technique, and as a result, nanofiber materials (from 200 nm in thickness) were obtained [see Figure 1(*d*),(*g*)].[64]

We managed to synthesize iptycenes **12** with larger cavities by the reaction of anthracene with pyrene-based arynes, generated from 1,3,6,8-tetrabromopyrene **13** (Scheme 6).[65] The advantage of thus obtained iptycenes is an expanded cavity with an integrated fluorophore system enabling to fit nitroaromatic

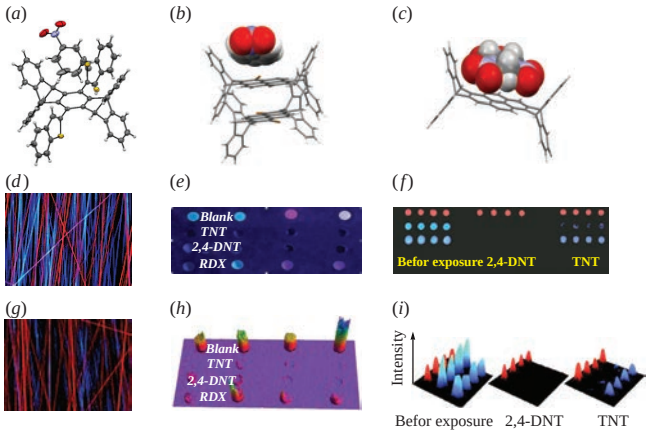
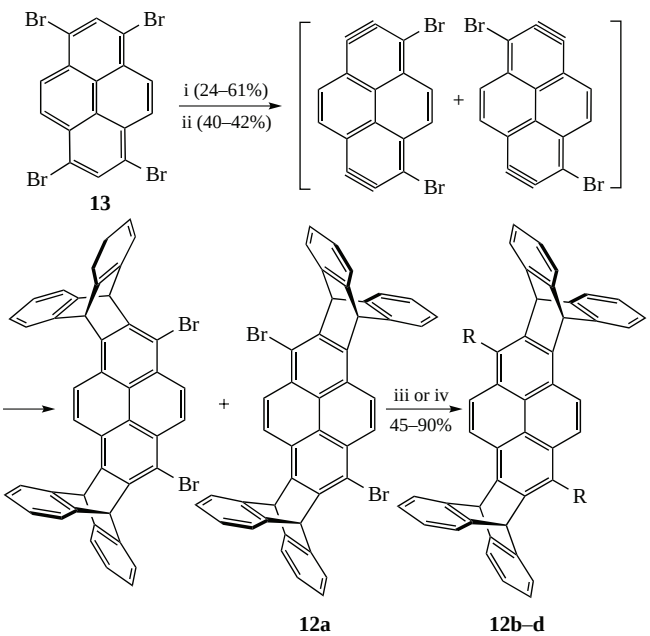


Figure 1 Application of aryne-derived iptycenes **9**, **12**: (*a*) structure of the iptycene **9b** : nitrobenzene (1 : 1) inclusion complex (reproduced with permission from ref. 63. © 2012 American Chemical Society); (*b*) the same for iptycene **12a** : nitrobenzene complex (reproduced from ref. 48 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry); (*c*) DFT-simulated structure of the iptycene **12b** : RDX complex (reproduced from ref. 65 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry); (*d*), (*g*) quenching of iptycene **9d** doped electrospuned PU fibers in the presence of TNT (adapted with permission from ref. 64. © 2012 Wiley-VCH, Weinheim); (*e*), (*h*) quenching of iptycene **12a**–**d** doped PU films in the presence of nitro-explosives vapors (reproduced from ref. 65 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry); (*f*), (*i*) quenching of ipycene **9c**–**d** doped PU in the presence of nitro-explosives vapors (reproduced with permission from ref. 62. © 2008 American Chemical Society).



b R = H
c R = Ph
d R = 5-dodecyl-2-thienyl

Scheme 6 *Reagents and conditions*: i, NaNH$_2$/Bu^{t}ONa, anthracene (10 equiv.), xylenes, 140 °C, 48 h; ii, Bu^{t}OK, anthracene (10 equiv.), melt, 210 °C, 22 h; iii, BuLi, THF, −78 °C, 1 h, then MeOH or H$_2$O, −78 to 25 °C, overnight; iv, R–SnBu$_3$, PhMe, PPh$_3$/PdCl$_2$(PPh$_3$)$_2$, reflux, 24 h.

compounds *via* the formation of iptycene–nitroaromate complexes in a 'face-to-face' geometry.

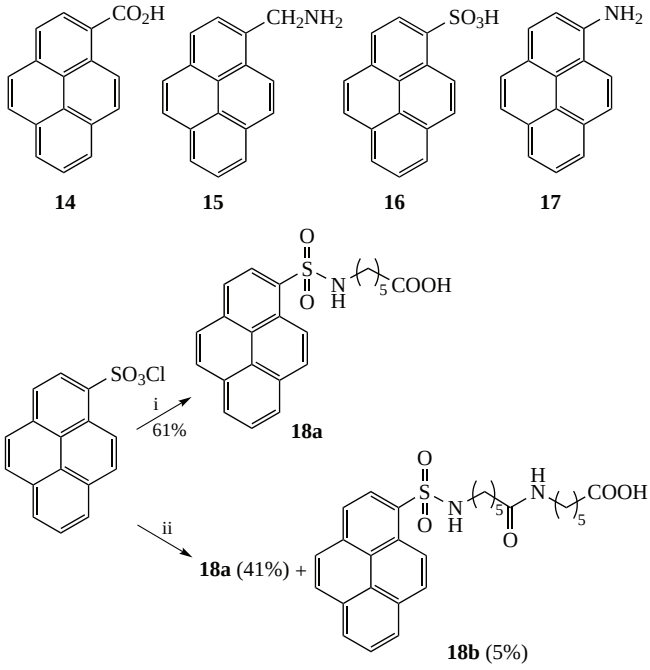
In addition, low LUMO energy of ipycenes **12** allows them to form non-fluorescent molecular complexes with aliphatic nitro compounds, such as RDX [see Figure 1(*b*),(*c*)]. The applicability of the obtained iptycenes **12** for the detection of nitro compounds was confirmed by fluorescence quenching experiment in solution in the presence of nitroaromatic compounds with quenching constants $K_{sv} = (0.4–8.0) \times 10^3$ dm^3 mol^{-1}, as well as in the presence of RDX ($K_{sv} = 1.54 \times 10^3$ dm^3 mol^{-1}), and by experiments in a gas phase (50–90% of fluorescence quenching) with sensors **12** impregnated in polyurethane matrices [see Figure 1(*e*),(*h*)].[65]

2.1.2. Micellar sensors for the detection of nitro-explosives

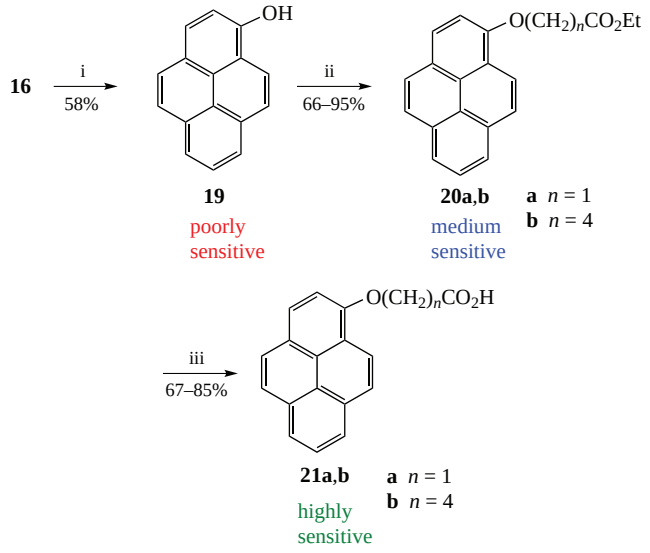
Fluorescence detection of nitro compounds in aqueous media is relevant primarily for environmental monitoring.[66–68] Most of (hetero)aromatic chemosensors (for nitro compounds) are slightly or non-soluble in (semi)aqueous media. An effective solution is that where the formation of micelles through the use of polyaromatic chemosensors, usually pyrene, integrated with external surfactants would occur.[69–72]

However, the use of most of these sensory systems was limited by poor encapsulation of (bis)pyrenes in the surfactant and, therefore, low micelle stability, low fluorescence intensity and, as a result, low efficiency of this sensory system. We were the first to obtain new micellar chemosensors **18**[73] (Scheme 7) and **20**, **21**[74] (Scheme 8) by covalent functionalization of pyrene derivatives with surface-active fragments. To prove the effectiveness of micellar sensors, some simple water soluble pyrenes **14**–**17** and **19** (see Schemes 7, 8) were also used.

The formation of fluorescent micelles in aqueous solutions was confirmed by the Tyndall experiments, dynamic light scattering experiments, as well as DFT calculations (Figures 2–4). In aqueous solutions, quenching of the fluorescence of sensors **14**–**18** in the presence of 2,4-DNT and TNT is observed with quenching constants $K_{sv} = (3.3–7.5) \times 10^5$ dm^3 mol^{-1} [see Figure 3(*a*)], as



Scheme 7 *Reagents and conditions*: i, $NaOOC(CH_2)_5NH_2$ (1.5 equiv.), Bu_4NBr, THF (dry); ii, $NaOOC(CH_2)_5NH_2$ (3.0 equiv.), Bu_4NBr, THF (dry), room temperature, 72 h.



Scheme 8 *Reagents and conditions*: i, NaOH/KOH (40 : 56, w/w), melt, 12 h, then H_3O^+; ii, $Hal(CH_2)_nCO_2Et$, K_2CO_3, MeCN, 60 °C, 48 h; iii, H_2O/EtOH, KOH, reflux, 1 h, then H_3O^+.

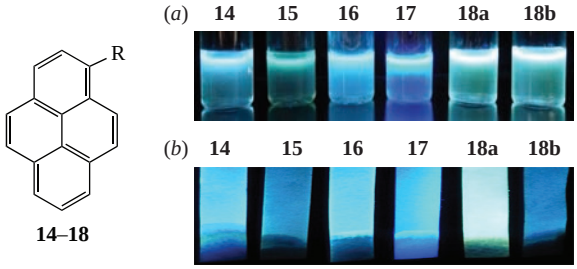


Figure 2 Application of water-soluble pyrenes **14**–**18** (for R, see Scheme 7): (*a*) aqueous solutions of pyrenes **14**–**18** (1×10^{-5} M) under UV-light; (*b*) contact quenching of paper strips, impregnated with aqueous solutions of **14**–**18** in a solution of TNT in water (50 ppb) (reproduced and adapted with permission from ref. 73. © 2016 Wiley-VCH, Weinheim).

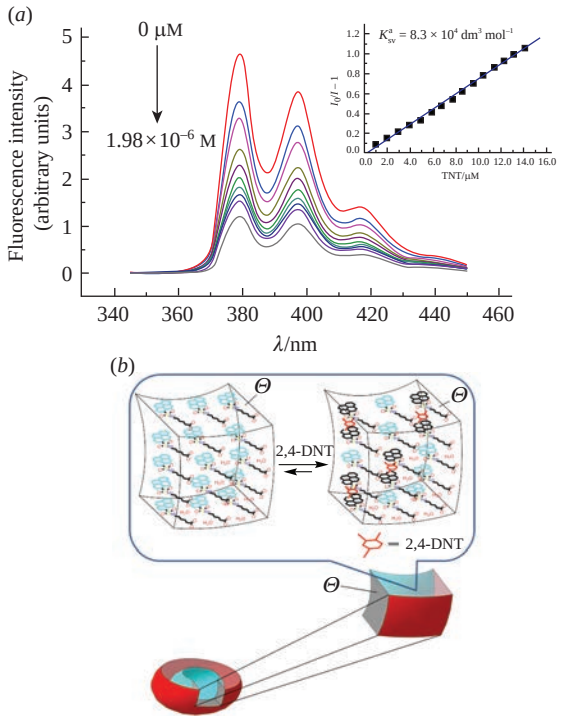


Figure 3 Application of water-soluble pyrenes **15**, **18a**: (*a*) fluorescence titration in aqueous solution of chemosensor **15** (10^{-5} M) with a TNT solution (10^{-3} M), insert shows the Stern–Volmer plot for the fluorescence quenching; (*b*) proposed model for the formation of a micelle of a chemosensor **18a** and quenching its fluorescence (reproduced and adapted with permission from ref. 73. © 2016 Wiley-VCH, Weinheim).

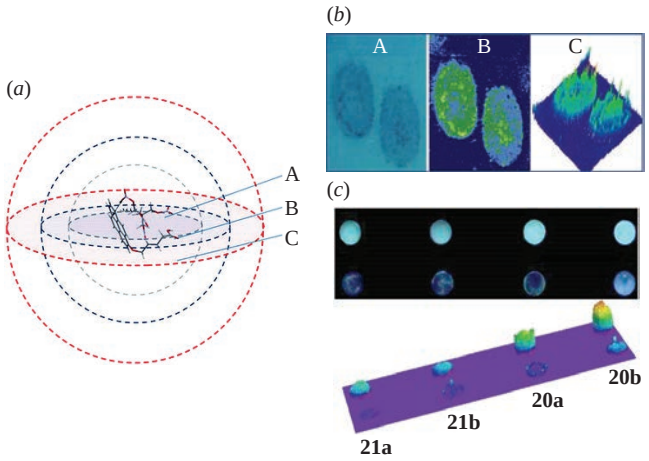


Figure 4 (*a*) DFT optimized model for static **21b** in the presence of PETN (quenching radii 0.35 nm, 3.5 Å); (*b*) contact detection of 2,3-dimethyl-2,3-dinitrobutane (DMDNB) using silica gel impregnated with chemosensor **21b**; (*c*) quenching of silica gel impregnated with chemosensors **20**, **21** in the presence of DMDNB vapors (reproduced from ref. 74 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry).

well as fluorescence of sensors **20**, **21** in the presence of RDX and nitro esters with quenching constants K_{sv} up to 6.5×10^5 dm^3 mol^{-1} according to the so-called pseudostatic mechanism (sphere of action quenching)[75] [see Figure 4(*a*)]. The practical applicability of the obtained sensors was proved by experiments on contact detection, as well as experiments using the paper strips impregnated with chemosensors **11**–**16** [see Figure 2(*c*)] or silica gel impregnated with chemosensors **20**, **21** [see Figure 4(*c*)].

2.2. 'Turn-on' chemosensors for anions and nerve agents

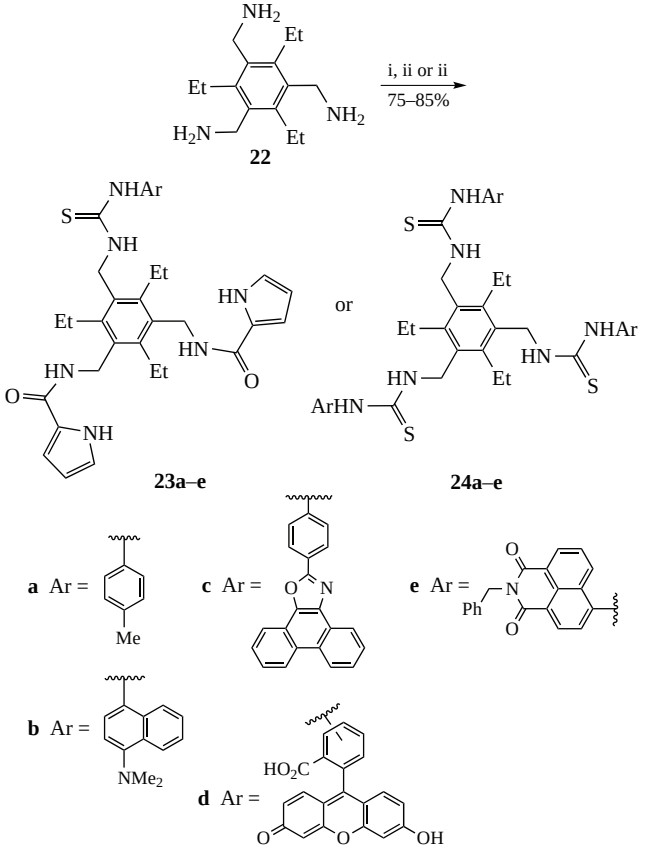
Anions are common components of food additives, medications, and synthetic detergents. Exceeding the level of anions in human

blood can be associated with the occurrence of pathological processes. For example, excess phosphate anion is a marker of cardiovascular disease or renal failure.[76–78]

Phosphate anion has a tetrahedral structure with three negative charges, acceptors of hydrogen bonds distributed between four oxygen atoms. To selectively bind this anion, we developed a group of 3D chemosensors with three pairs of hydrogen bond donors through the reaction of (2,4,6-triethylbenzene-1,3,5-triyl) trimethanamine **22** with 2-trichloroacetylpyrrole and/or (het)-arylisothiocyanates. The reaction can be effectively controlled by stoichiometry of the reagents and, along with trisubstituted pyrrolcarboxamide and tris(het)arylureas **26**, hybrid molecules **23** were obtained containing two pyrrolcarboxamide units and one (het)arylurea unit (Scheme 9). [79]

In the absence of anions in DMSO–H_2O solutions, the chemosensors **23**, **24** are locked in a '2-up-1-down' conformation [Figure 5(*a*)], whereas in the presence of anions, chemosensors adapt their structure to encapsulate the anion in the chemosensor cavity [Figure 5(*b*)]. Along with 'turn-on' fluorescent detection of spherical anions [Figure 5(*c*)], the obtained chemosensors can be used for selective ratiometric fluorescent 'turn-on' detection of phosphate anions in aqueous media [Figure 5(*d*)]. The structure of phosphate complexes was established by the single crystal X-ray diffraction [see Figure 5(*b*)] and the DFT methods. The applicability of the obtained chemosensors for 'turn-on' detection of biotic phosphates such as AMP and ATP in blood serum was also revealed [Figure 5(*e*)], which can be used to create effective sensory devices for early rapid diagnosis of cardiovascular diseases.

The possibility of practical application of these chemosensors for effective 'turn-on' detection of the products of hydrolysis of sarin, such as isopropyl methylphosphonate (IMP) and methylphosphonate (MP) was also demonstrated [Figure 5(*f*)],



Scheme 9 *Reagents and conditions*: i, 2,2,2-trichloro-1-(pyrrol-2-yl)-ethanone, DMSO, stirring at room temperature for 24 h; ii, ArNCS, DMSO, room temperature, 24 h.

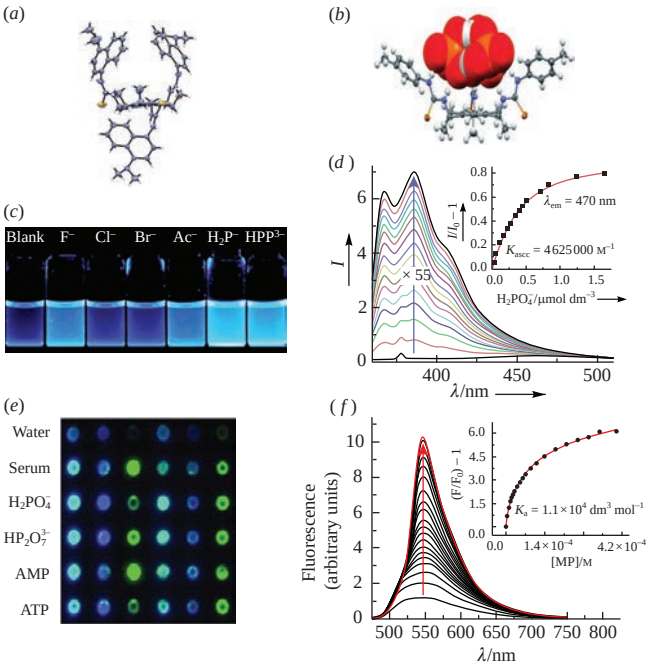


Figure 5 Crystal structures of (*a*) chemosensor **24b** in the absence of anions (reproduced with permission from ref. 80. © 2013 The Royal Society of Chemistry); (*b*) complex **24a** · 3 $H_2PO_4^-$ (reproduced with permission from ref. 79. © 2007 Wiley-VCH, Weinheim); (*c*) change in the fluorescence of chemosensor **24b** in the presence of anions in aqueous DMSO solutions; (*d*) fluorescence titration of **24b** (0.4 μM) in the presence of $H_2PO_4^-$ (reproduced with permission from ref. 79. © 2007 Wiley-VCH, Weinheim); (*e*) qualitative changes in the fluorescence of PU doped with the chemosensors **24** after adding human serum and serum with added anions (reproduced with permission from ref. 79. © 2007 Wiley-VCH, Weinheim); (*f*) enhancement of the fluorescence of **24d** in the presence of methylphosphonate (MP) (reproduced with permission from ref. 80. © 2013 The Royal Society of Chemistry).

which can be used to create systems for the rapid detection of phosphorus-containing nerve agents.[80]

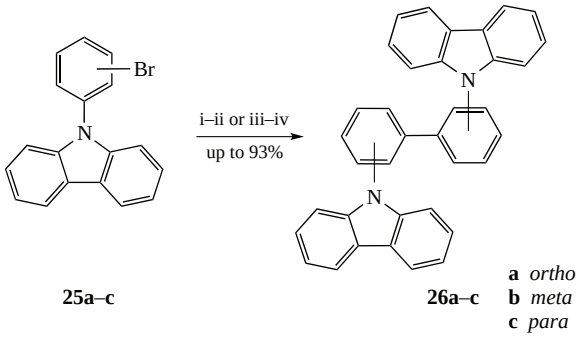
3. Rational synthetic approaches to organic materials

3.1. Palladium-free synthesis of isomeric *N*-arylcarbazoles, materials for molecular electronics

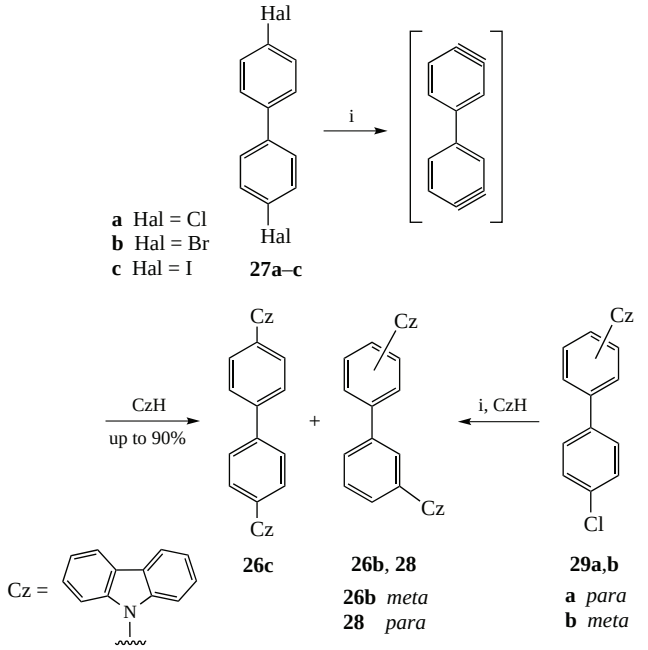
N-Arylcarbazoles have promising electroluminescent properties and subsequently find application as hole-transporting as well as a host or luminescent material in phosphorescent OLEDs (PhOLEDs).[81–86] The most typical method for constructing *N*-arylcarbazoles are Pd-catalyzed N-arylation reactions.[87] Palladium-free methods for the preparation of components of PhOLEDs[88] are prospective and often free from the disadvantages of Pd-catalyzed methods such as reagent cost, toxicity, and purification problems.[89–92]

Isomeric 2,2′- and 3,3′-di(9*H*-carbazol-9-yl)biphenyls are more promising materials for PhOLEDs due to the higher energy of the triplet state[93] because of the lower degree of the conjugation of (hetero)aromatic rings. The use of traditional methods that are well established for the synthesis of 4,4′-di(9*H*-carbazol-9-yl) biphenyls, namely, the Ulmann or Buchwald cross-coupling of 3,3′- and 2,2′-dihalobiphenyls **25** with carbazole, is significantly limited by low product yields due to the significant steric hindrances. We developed Pd-free one-pot procedures for the preparation of symmetric 2,2′-, 3,3′- and 4,4′-di(9*H*-carbazol-9-yl)biphenyls **26a–c** (Scheme 10) using *in situ* generated Lipshutz organocuprates Ar_2Cu (in case of CuCN) or Gilman cuprates Ar–Cu–Li (in case of $CuCl_2$). [94] The target products were obtained in up to 93% yields.

Isomeric symmetric 3,3′- and 4,4′-di(9*H*-carbazol-9-yl)-biphenyls **26b**,**c** as well as 3,4′-di(9*H*-carbazol-9-yl)biphenyl **28**



Scheme 10 *Reagents and conditions*: i, Bu^{t}Li, THF, –78 °C; ii, $CuCl_2$; iii, CuCN; iv, **25** (with the corresponding **a**–**c**), THF, –78 → 25 °C, benzoquinone.



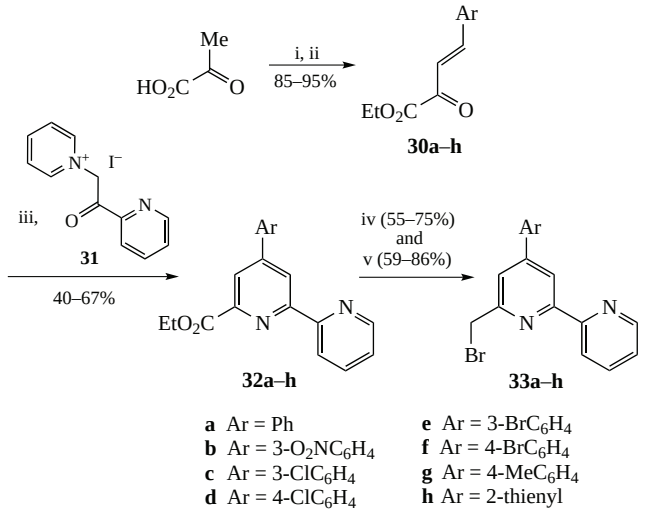
Scheme 11 *Reagents and conditions*: i, 9*H*-carbazole, Bu^{t}OK, PhMe, 140 °C, 12–24 h.

were also synthesized *via* the reaction of the corresponding biarynes generated *in situ* from 4,4′-dihalogenobiphenyls (Scheme 11).[95] Depending on the nature of the halogen atoms, the yield of the main product, 4,4′-di(9*H*-carbazol-9-yl)biphenyl **26c** reached up to 90%. It worth mentioning that partially substituted with carbazole chloro-biphenyls **29** also afforded products **26b**, **28** *via* reaction of *in situ* generated mono-arynes with carbazole.

3.2. Prospective 2,2′-bipyridine ligands, chemosensors and fluorophores, their aza and annulated derivatives

2,2′-Bipyridine ligands are among the oldest one (discovered in 1888)[96] and perhaps the most widely used organic ligands for various metal cations,[97] including lanthanide ones. The latter are widely employed as they have intense long-lived luminescence in the long-wavelength region. Intense luminescence of the lanthanide cation is achieved by the targeted design of the ligand structure in order to create the condition sites, which are enough for the saturation of all coordination bonds (usually 9) of the chelated lanthanide cation to ensure the absence of water molecules in the first coordination sphere. In most cases, this is achieved by introducing hard chelating units, for example, iminodiacetic acid fragments[98,99] or various polyamino carboxylic acids such as DTTA or DO3A,[100,101] through aliphatic spacers into the 2,2′-bipyridine ring. An additional modification of the ligand structure can lead to more efficient sensitization of the chelated lanthanide cation.

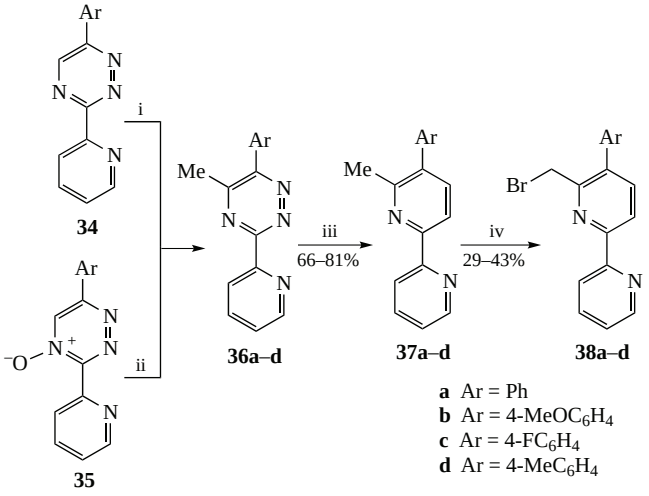
We have effectively constructed new 2,2′-bipyridine ligands using simple and efficient procedure from accessible arylidenepyruvates **30a**–**h** (Scheme 12), for example, the Kröhnke method to prepare ligands **33a**–**h**.[102,103]



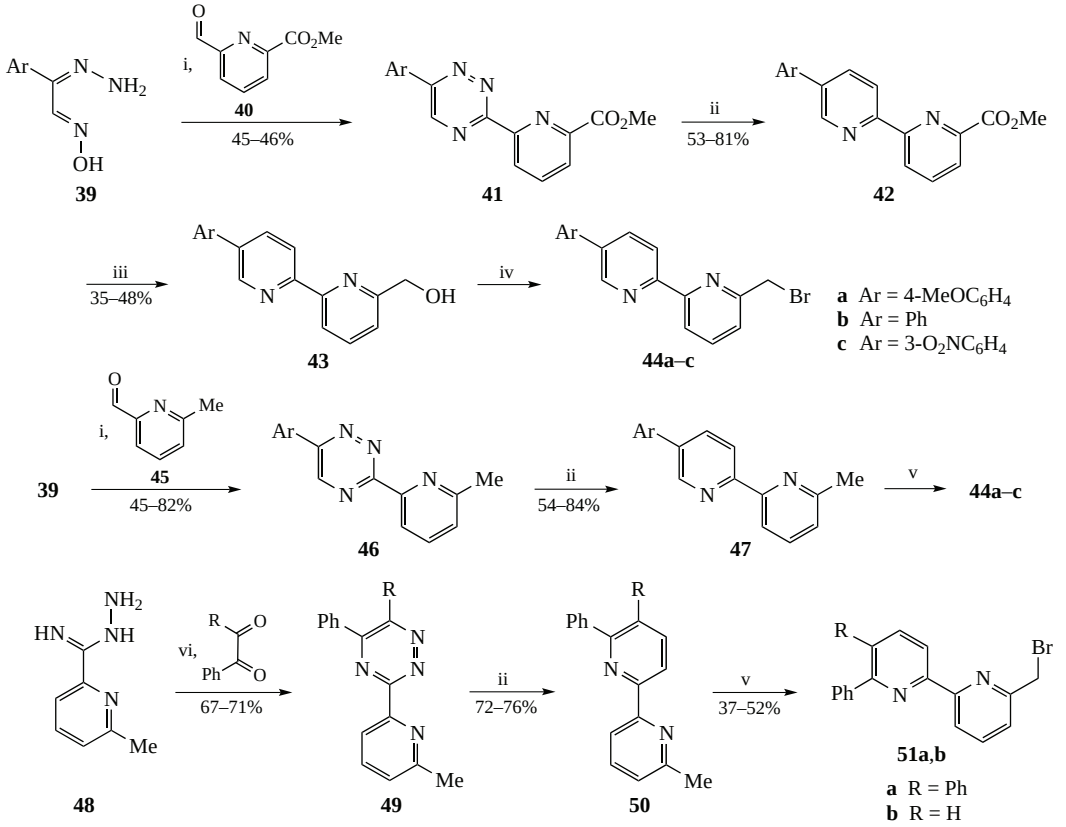
Scheme 12 *Reagents and conditions*: i, ArCHO, KOH, 35–40 °C, 3–6 h, then HCl; ii, EtOH, H_2SO_4, room temperature, overnight; iii, NH_4OAc, EtOH, reflux, 8 h; iv, $NaBH_4$, EtOH, reflux, 4 h; v, $PBr_3/C_2H_4Cl_2$, 50 °C, 2 h.

The effectiveness of so-called '1,2,4-triazine methodology' for the construction of multisubstituted bipyridines was also demonstrated. For example, the sequence of nucleophilic substitution of hydrogen (S_N^H) in 1,2,4-triazines **34** or their 4-oxides **35** for the direct introduction of methyl fragments into 1,2,4-triazines, followed by the aza-Diels–Alder reaction of thus obtained 1,2,4-triazines **36** with 2,5-norbornadiene (to afford bipyridine **37**), and bromination reaction resulted in 6-bromomethyl-2,2′-bipyridines **38a**–**d** (Scheme 13).[104–106]

The sequence of heterocyclization reaction to afford 1,2,4-triazines **41**, **46** and **49** followed by the aza-Diels–Alder reaction was also effective for the preparation of isomeric bipyridines **43**, **47** and **50** (Scheme 14). The bromination reaction of thus obtained 2,2′-bipyridines afforded bromometyl bipyridines **44** and **51**.[107]



Scheme 13 *Reagents and conditions*: i, MeLi, THF, –78 °C, then DDQ; ii, PhC(O)Me, NaH/THF, –20 °C, 3 h, then KOH; iii, 2,5-norbornadiene, *o*-xylene, reflux, 18 h; iv, NBS, Bz_2O_2, CCl_4, reflux, 7 h.

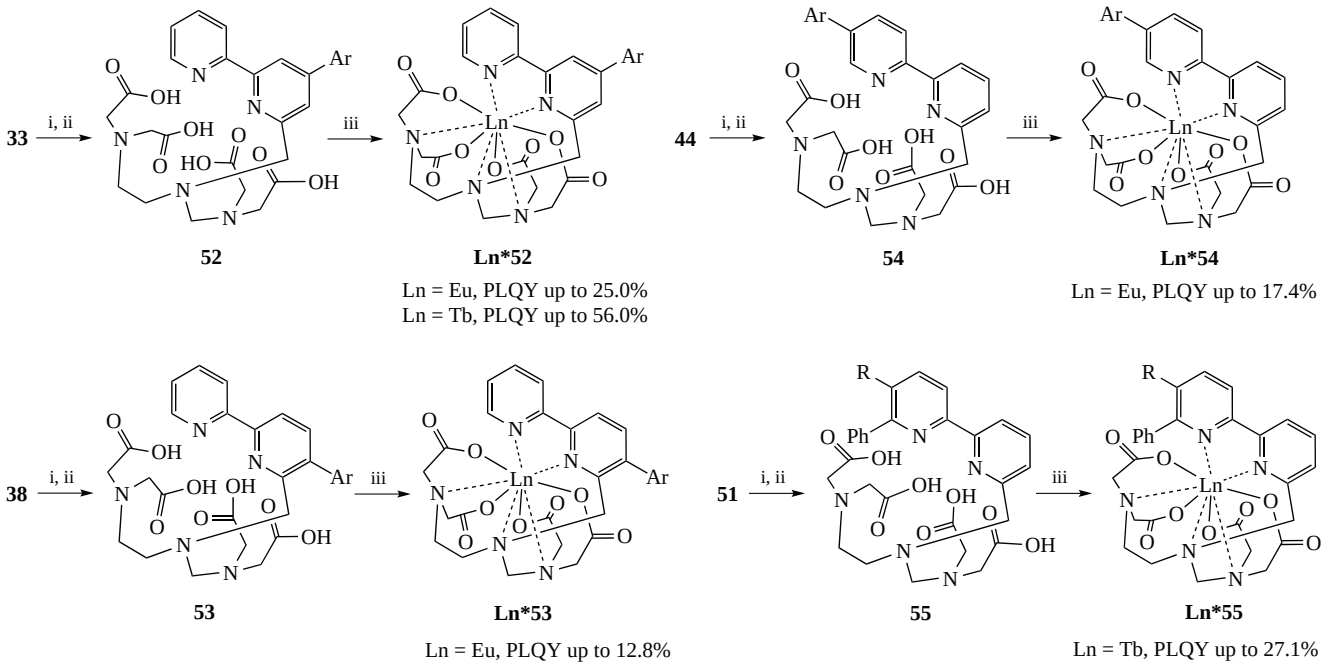


Scheme 14 *Reagents and conditions*: i, AcOH; ii, 2,5-norbornadiene, *o*-xylene, reflux, 24 h; iii, $NaBH_4$, EtOH, 20–78 °C, 4 h; iv, PBr_3, CH_2Cl_2, 40 °C, 5 h; v, NBS, benzoyl peroxide, CCl_4, 77 °C, 7 h; vi, EtOH, reflux, 12 h.

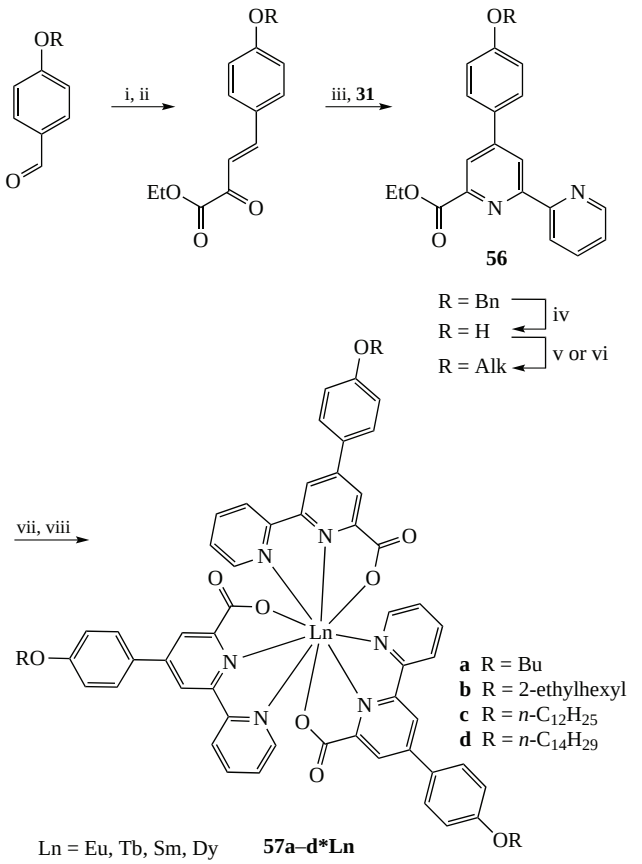
As the last stage, based on the obtained 2,2′-bipyridines **33**, **38**, **44**, **51** DTTA-modified ligands **52**–**55** and the corresponding water-soluble lanthanide complexes **Ln*52**–**55** were prepared through a three-step reaction sequence (Scheme 15).

The efficiency of the synthesized ligands for the chelation/sensitization of lanthanide cations is confirmed by the promising photophysical characteristics of the obtained complexes. For example, in the case of complexes **Ln*52**, **Ln*54** the photoluminescence quantum yield (PLQY) for terbium complexes up to 56% was observed, and for europium complexes **Ln*52** and **Ln*54** the quantum yields were 25 and 17%, respectively, which was close or exceeded such values for known complexes.[102–108]

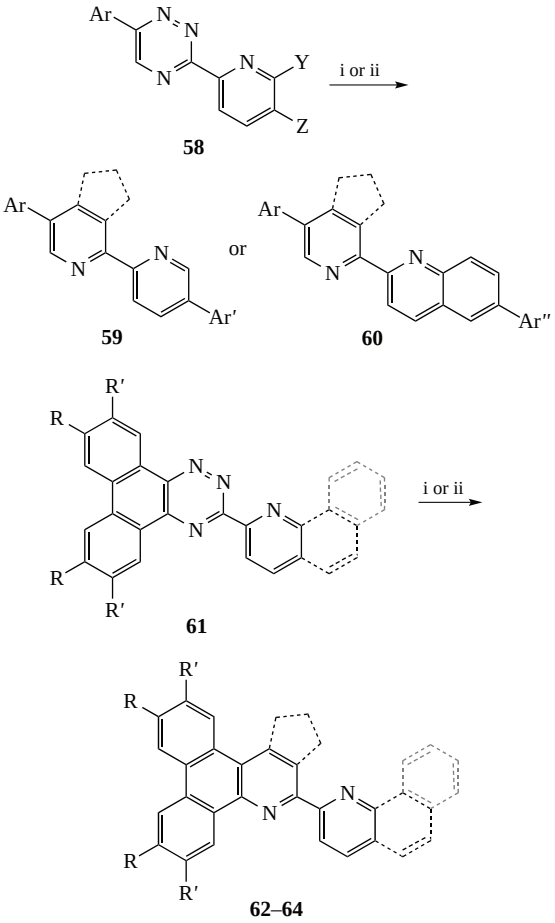
In addition to water-soluble lanthanide complexes 2,2′-bipyridines substituted with carboxylate moiety at C^6 were used for the preparation of neutral lanthanide complexes $[Ln(L)_3]$ (L = bipyridinecarboxylate). To achieve good photophysical properties and acceptable solubility in organic solvents, the



Scheme 15 *Reagents and conditions*: i, DTTA *tert*-butyl ester, K_2CO_3, MeCN, reflux; ii, 5 N HCl, room temperature, 12 h; iii, NaOH, H_2O, room temperature, then $LnCl_3 \cdot 6H_2O$, room temperature, overnight.



Scheme 16 *Reagents and conditions*: i, pyruvic acid, KOH, EtOH, 40 °C, 2 h, then HCl, water, room temperature, 5 min; ii, EtOH, H_2SO_4, room temperature, overnight; iii, NH_4OAc, EtOH, reflux, 10 h; iv, $HCOONH_4$, Pd/C, MeOH–THF (10 : 1), reflux, 1 h; v, AlkBr, K_2CO_3, KI, DMF, 130 °C, 8 h; vi, tetradecan-1-ol, PPh_3, DEAD, THF, room temperature, overnight, then MeOH, room temperature, 5 min; vii, NaOH, EtOH, reflux, 1 h, then HCl, room temperature, 5 min; vi, KOH, MeOH, reflux, 20 min, then $LnCl_3$, room temperature, 2 h.



Scheme 17 *Reagents and conditions*: i, 2,5-norbornadiene, *o*-xylene, reflux, 18–48 h; ii, 1-morpholinocyclopentene, neat, 200 °C, 12 h.

modification of the ligand molecules should be considered, for instance *via* the introduction of long aliphatic chains. Thus, soluble in organic solvents ligands **56a–d** were prepared and their neutral lanthanide complexes **Ln*57** (Ln = Eu, Tb, Sm, Dy) were constructed (Scheme 16). The obtained europium complexes **Eu*57** exhibited high luminescence of the europium cation with quantum yields varying from 24.1% (**Eu*57a**) to 27.3% (**Eu*57b**), the highest luminescence lifetime of the europium cation of 1.75 ms having been detected for complex **Eu*57c**. Additionally, we observed the residual fluorescence of 4-aryl-2,2′-bipyridine chromophore around 6.5% for complex **Eu*57d**, and almost the same values were found for other Eu^{III}

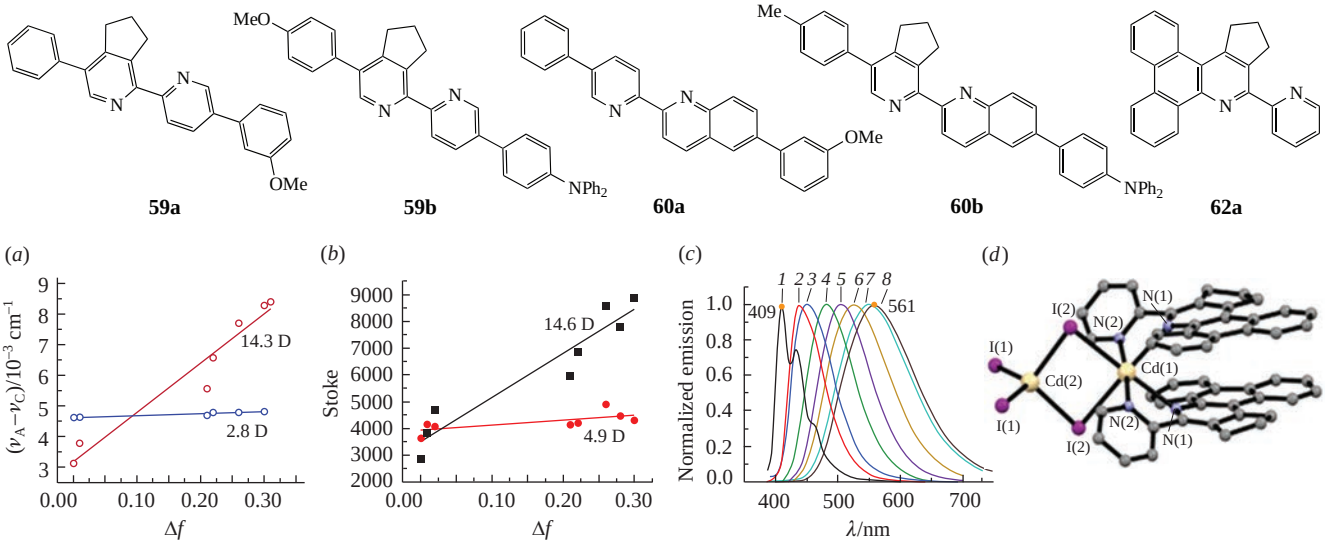


Figure 6 Lippert–Mattag plots for (*a*) fluorophores **59a (**2.8 D**)**, **59b (**14.3 D**)** (reproduced with permission from ref. 111. © 2018 Elsevier. All rights reserved); (*b*) fluorophores **60a (**4.9 D**)**, **60b (**14.6 D**)** (reproduced with permission from ref. 116. © 2019 Elsevier. All rights reserved); (*c*) dependence of the fluorescence of fluorophore **60b** on the solvent polarity: *1* – hexane, *2* – toluene, *3* – dioxane, *4* – THF, *5* – CH_2Cl_2, *6* – acetone, *7* – MeCN, *8* – DMSO (reproduced with permission from ref. 116. © 2019 Elsevier. All rights reserved); (*d*) single crystal structure of Cd^{II} complex with ligand **62a** (reproduced with permission from ref. 113. © 2016 Elsevier. All rights reserved).

complexes. For complexes **Tb*57** very low luminescence was observed with a highest value of 0.8% for complex **Tb*57a** and the highest lifetime value of 0.184 ms for complex **Tb*57c**. No detectable luminescence was exhibited by complexes **Sm*57** and **Dy*57**.[109]

The '1,2,4-triazine methodology' proved to be efficient for the preparation of new push-pull fluorophores based on aryl-functionalized 2,2′-bipyridines **59**, **60**,[110,111] as well as their areno-annulated monoaza triphenylenes **61**[112–114] and (benzo)-quinolones **62**, **63** (Scheme 17, Figure 6).[115,116] At the first step, the heterocyclization leads to 1,2,4-triazines **58**, **61**, and their subsequent aza-Diels–Alder reaction with 2,5-norbornadiene or cyclic enamines leads to 2,2′-bipyridines.

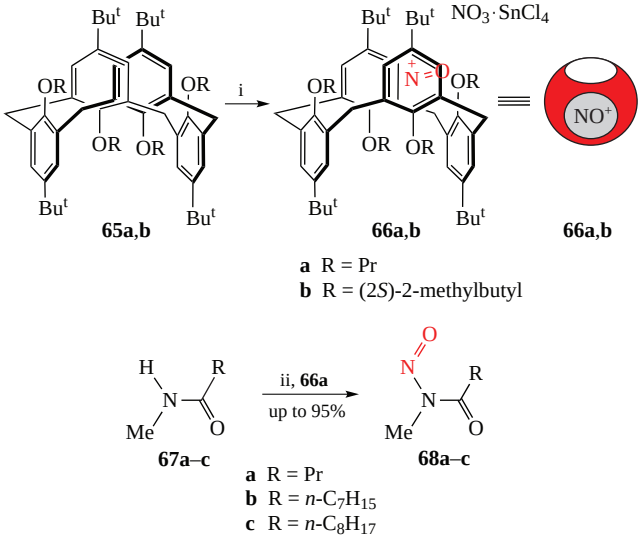
4. Promising organic reagents, synthons and solvents

In recent years, more effective synthetic strategies have been developed using new organic reagents, synthons and solvents as prerequisites for more environmentally friendly laboratory and industrial processes. Some examples are presented below.

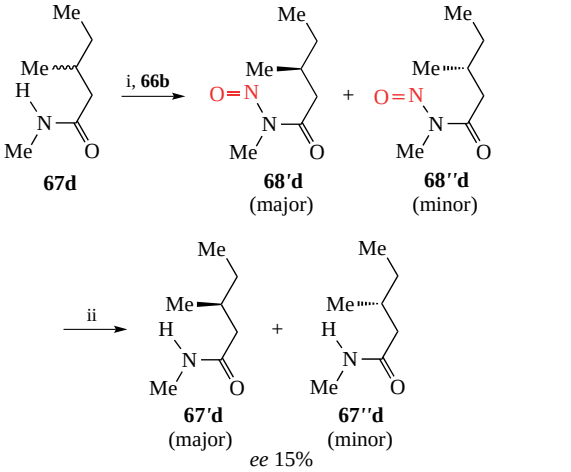
4.1. Encapsulated nitrosating reagents

N-Nitrosation processes play a key role in synthetic organic chemistry.[117] Alkyl nitrites, nitrosoamines/amides, and nitrosoureas are used in medicine as, *e.g.*, NO-releasing agents,[118–121] and cytotoxic drugs.[122] In organic synthesis, the N=O fragment serves as an important activating group that promotes efficient conversion of amides to carboxylic acids and derivatives.[123–138]

Nitrogen oxides NO_2/N_2O_4 and other NO_x gases are effective reagents for organic synthesis, however, reaction selectivity with their application is usually low.[139] The effectiveness of using simple calix[4]arenes for the chemical conversion of $NO/NO_2/N_2O_4$ through the formation of stable complexes 'calixarene-NO^+' was also demonstrated.[140–142] We have shown that these complexes can be successfully used as encapsulated nitrosating reagents, while the calixarene cavity geometry successfully controls the reactivity and selectivity of the process.[141,143] Complexes **66** were effectively used for nitrosation of secondary amides (Scheme 18). At the same time, unique size and shape of such complexes allowed for exclusive nitrosation of less sterically hindered *NH*–Me amides providing up to 95% yields of *N*-nitrosoamides. More bulky *NH*–Alk (Alk > Me) amides did not react with **66**.



Scheme 18 *Reagents and conditions*: i, NO_2/N_2O_4, $SnCl_4$, $CHCl_3$, room temperature, 5–10 min; ii, $CHCl_3$, room temperature, 1 h (adapted with permission from ref. 143. © 2005 Wiley-VCH, Weinheim, and from refs. 141 and 142. © 2003 American Chemical Society).



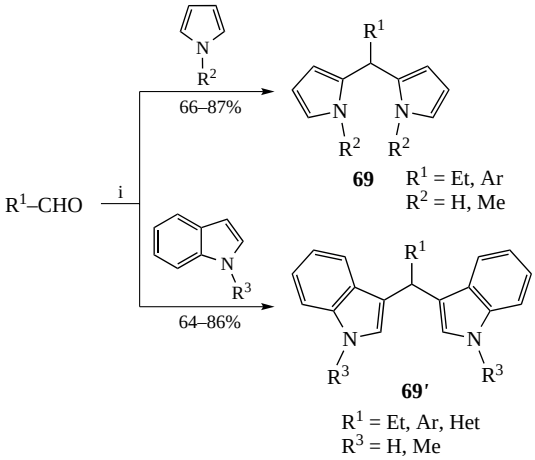
Scheme 19 *Reagents and conditions*: i, $CHCl_3$, room temperature; ii, CF_3CO_2H, room temperature, 12 h.

Chiral tetrakis-*O*-[(2*S*)-2-methylbutyl]-containing calixarene **66b** under similar conditions gave a chiral encapsulating reagent **66b** (see Scheme 18). In reaction with racemic (±)-3-methylvaleric acid *N*-methylamide **67d**, this chiral encapsulating reagent provides partial chiral discrimination with the preferred formation of (*S*)-3,*N*-dimethyl-*N*-nitroso enantiomer **67′d** *vs.* (*R*)-enantiomer **67′′d** with an enantiomeric excess of ~15% (Scheme 19).[143]

4.2. Ionic liquids for some key organic transformations

Ionic liquids (ILs) are known as low melting point salts containing organic cations (dialkylimidazolium, alkylpyridinium, alkylammonium, alkylphosphonium), as well as inorganic (Br^-, BF_4^-, PF_6^-, *etc.*) or organic ($CF_3CO_2^-$, $CF_3SO_3^-$ and other) anions.[144–147] ILs are traditionally used as electrolytes in electrochemical processes or as a medium in chemical and separation processes. Due to the low toxicity, non-volatility, non-combustibility, and stability at wide temperature ranges, as well as chemical inertness with respect to various chemicals, ILs are considered as promising 'green solvents' for organic synthesis.[148]

We have carried out some key reactions in ILs. In particular, by reactions of pyrroles with aldehydes in imidazole-based zwitterionic salt, 4-(3-methylimidazol-1-ium-1-yl)butanesulfonate, bis-pyrrolylmethanes **69** were synthesized. Regardless of the nature of the substituents, the target products were obtained in high yields within 1 h at room temperature (Scheme 20, Figure 7).[149] Similarly, bis-indolylmethanes **69′** were prepared. The resulting compounds are promising for the creation of BODIPY fluorophores.[150]



Scheme 20 *Reagents and conditions*: i, 4-(3-methylimidazol-1-ium-1-yl)-butanesulfonate (10 mol%), neat, room temperature, 1 h.

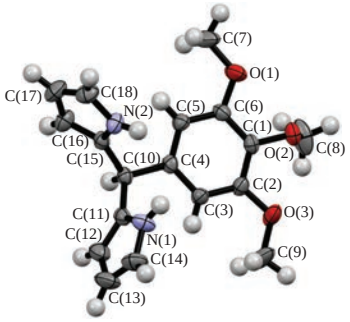
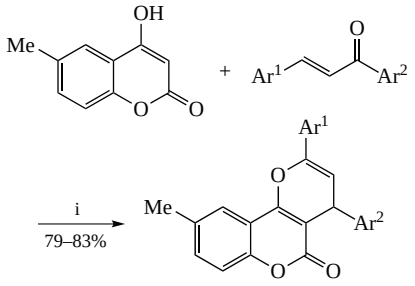


Figure 7 Single crystal structure of one representative of type **69** (reproduced with permission from ref. 149. © 2018 Wiley-VCH, Weinheim).

The possibility of one-step synthesis of biologically important pyrano[3,2-*c*]coumarins **70**[151–154] in ionic liquids has been demonstrated (Scheme 21).[155] Thus, 3-methyl-1-(4-sulfobutyl)-imidazolium tosylate, [BSMIM]OTs, was used as the medium to carry out a tandem cyclization between 4-hydroxycoumarin with multisubstituted chalcones.



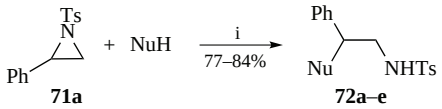
a $Ar^1 = Ar^2 = Ph$ **70a–d**
b $Ar^1 = Ph$, $Ar^2 = 4\text{-}MeC_6H_4$
c $Ar^1 = 4\text{-}ClC_6H_4$, $Ar^2 = Ph$
d $Ar^1 = 4\text{-}ClC_6H_4$, $Ar^2 = 4\text{-}MeOC_6H_4$

Scheme 21 *Reagents and conditions*: i, [BSMIM]OTs (5 mol%), neat, 100 °C, 3 h.

4.3. Aziridine transformations

Aziridines and epoxides are valuable synthones and building blocks in synthetic organic chemistry.[156] We have demonstrated the effectiveness of using aziridines for some key transformations in organic synthesis.

The regioselective ring-opening in aziridine **71a** under the action of various nucleophiles such as indoles, pyrroles, methanol, ethanol, acetic acid and diisopropylamine proceeded in the presence of zwitterionic IL, 4-(3-methylimidazol-1-ium-1-yl)butanesulfonate (MBS), as an organocatalyst (Scheme 22).[157] An advantage of this procedure is high regioselectivity providing azirinide ring opening products **72** as a result of a nucleophilic attack on a benzylic carbon atom. The procedure is applicable to gram scale syntheses.

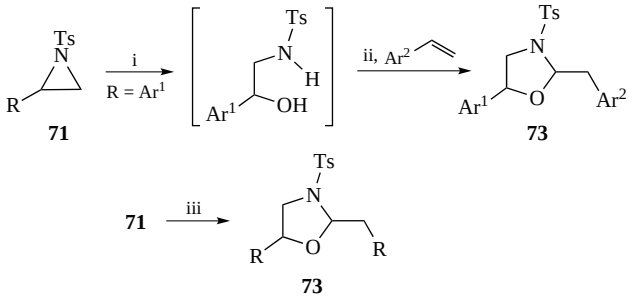


71a **72a–e**

a Nu = AlkO **d** Nu = pyrrol-3-yl
b Nu = AcO **e** Nu = indol-3-yl
c Nu = Pr^i_2N

Scheme 22 *Reagents and conditions*: i, MBS (10 mol%), neat, 85 °C, 3 h.

A one-pot synthesis of 1,3-oxazolidines **73** was developed using the ring-opening reactions of aziridines **71** *via* two different routes (Scheme 23).[158] In the first case, aziridines **71** were used as synthetic equivalents of amino alcohols. When implementing

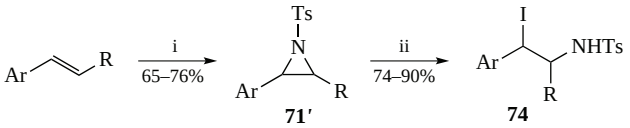


R = Et, CH_2Br, $(CH_2)_2OH$, Ar

Scheme 23 *Reagents and conditions*: i, AgOTf (1.4 equiv.), H_2O (1 equiv.), CH_2Cl_2, room temperature, 4 h; ii, NBS (1.2 equiv.); iii, AgOTf (1.4 equiv.), H_2O (1 equiv.), CH_2Cl_2, room temperature, 2 h.

the second approach, we observed a reaction so far unparalleled, in which one aziridine molecule reacted with the *in situ* formed ring opening product of the same aziridine (see Scheme 23, case iii). Nothing for this type of cyclization, to the best of our knowledge, was documented.

We also developed a new method for the synthesis of disubstituted aziridines **71′** using a multicomponent reaction between styrenes and chloramine-T (sodium tosylchloramide) as an effective reagent[159,160] in the presence of hydroxylamine hydrochloride and $NaIO_4$ (Scheme 24). We found that the combination $NH_2OH \cdot HCl/NaIO_4$ system is also very effective for nucleophilic ring opening of the thus obtained aziridines **71′** with the formation of *N*-(2-iodo-2-arylethyl)tosylamides **74**.[161,162]



Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}FC_6H_4$
R = H, C(O)Ph

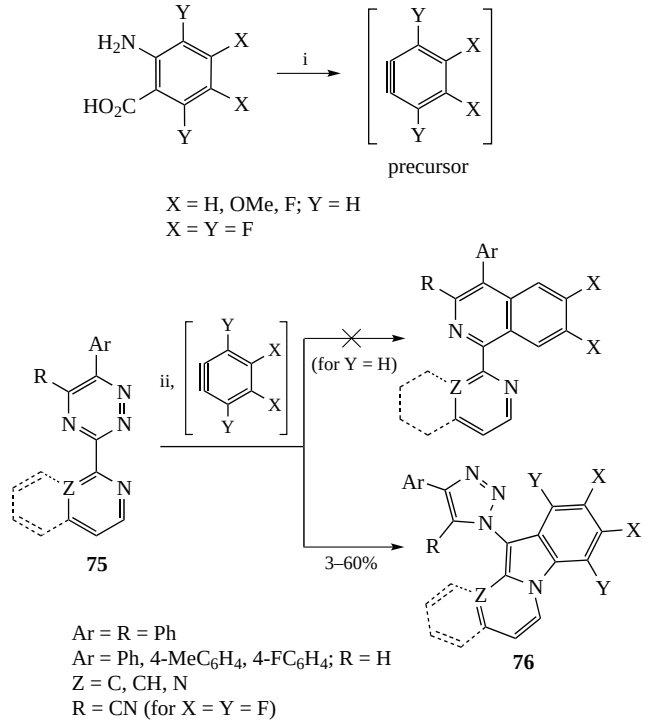
Scheme 24 *Reagents and conditions*: i, $NaIO_4$ (1 equiv.), $NH_2OH \cdot HCl$ (1.5 equiv.), TsN(Cl)Na (1 equiv.), K_2CO_3 (1 equiv.), CH_2Cl_2/MeCN, room temperature, 14 h; ii, $NaIO_4$ (1 equiv.), $NH_2OH \cdot HCl$ (1.5 equiv.), MeCN, room temperature, 8–12 h.

4.4. New aryne-induced transformations of cyclic azines

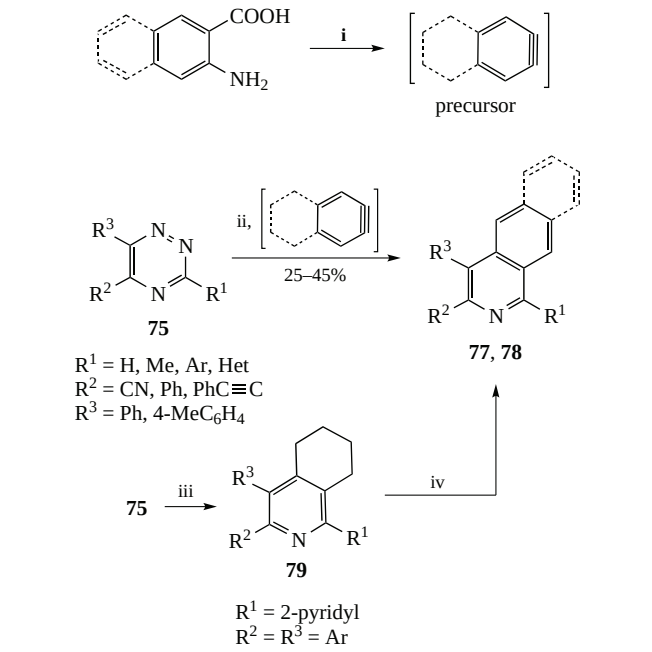
Arynes, in particular *ortho*-arynes, compounds with a hypothetical triple bond, formally formed from aromatic precursors by abstraction of two *ortho*-substituents in a benzene ring are the subject of study of synthetic organic chemistry for more than 100 years.[163] In the last two decades, a renaissance of aryne chemistry has been observed when arynes were used for the synthesis of, *e.g.*, heterocycles,[164,165] natural and synthetic drug candidates[166–169] and polyaromatic systems.[170,171]

We have studied in detail the transformations of multi-substituted 1,2,4-triazines and their annulated derivatives in reactions with *in situ* generated arynes. It was found that 3-(pyrid-2-yl)-, 3-(pyrimidin-2-yl)- and 3-(isoquinolin-2-yl)-1,2,4-triazines **75** react with substituted 1,2-dehydrobenzenes, including (per)fluorinated and dimethoxy derivatives, to afford the products of new domino transformation of the 1,2,4-triazine ring, namely 1,2,3-triazole-substituted pyrido[1,2-*a*]indoles **76**, including perfluorinated and annulated derivatives (Scheme 25).[172–176]

It should be noted that 5-cyano-3-(2-pyridyl)-1,2,4-triazines **75** reacted with benzyne and 2,3-dehydronaphthalene with the formation of the aza-Diels–Alder adducts, namely, pyridyl-substituted isoquinolines[177] of type **76** (see Scheme 25) and 2-azaanthracenes of type **77**[178–180] (Scheme 26) being



Scheme 25 *Reagents and conditions*: i, $Pr^i(CH_2)_2ONO$, 1,4-dioxane; ii, PhMe, reflux, 1.5 h.



Scheme 26 *Reagents and conditions*: i, $Pr^i(CH_2)_2ONO$, 1,4-dioxane; ii, PhMe, reflux, 1 h; iii, 1-morpholinocyclohexene, neat, 200 °C, 4 h; iv, DDQ, *o*-xylene, 143 °C, 10 h.

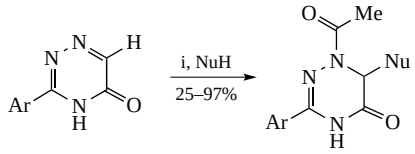
promising push-pull fluorophores and materials for the molecular electronics. Isoquinolines **76** were also formed in reactions of 1,2,4-triazines bearing 3-positioned substituent other than pyridyl with benzyne or 4,5-dimethoxybenzyne.[181,182] An alternative approach to 1-(2-pyridyl)isoquinolines *via* the neat reaction of some **75** (R^1 = 2-pyridyl) with 1-morpholinocyclohexene and the following aromatization of tetrahydroisoquinoline **79** with DDQ (see Scheme 26) was also reported.[183]

The thus obtained domino transformations products, pyrido[1,2-*a*]indoles, are of interest as push-pull fluorophores with green fluorescence.[184]

5. Direct C–H functionalization in cyclic azines (S_N^H processes)

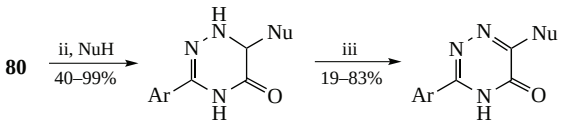
Direct C–H functionalization in (het)arenes is a progressive direction in modern chemistry, since in this case there is no stage of pre-functionalization of the initial reactants, and the leaving group is hydrogen atom.[185–187]

Using direct C–H functionalization methodology, we have developed methods for introducing fragments of natural alcohols, π-excessive heterocycles and CH-active compounds, aliphatic amines, *etc*., into 1,2,4-triazines **80** and **85**, as well as pyrimidines **84** with the formation of stable σ-adducts **81**, **82** and **86** or S_N^H products **83** and **87** (Schemes 27, 28).[188–191]



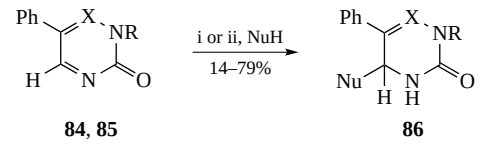
a Ar = Ph
b Ar = 4-MeC_6H_4
c Ar = 4-ClC_6H_4

NuH: indole, 1(2)-methylindoles, 1-methylpyrrole, 1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one, *N*-(4-phenylthiazol-2-yl)acetamide, *N*-(thiazol-2-yl)acetamide, borneol, isoborneol, cholesterol



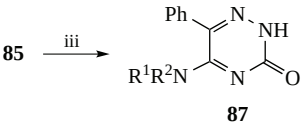
NuH: indole, 1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one

Scheme 27 *Reagents and conditions*: i, Ac_2O, neat, 25 °C, 2–24 h; ii, AcOH, reflux, 2–4 h; iii, DMF, air, reflux, 8–10 h.



84 X = CH, R = Me
85 X = N, R = H

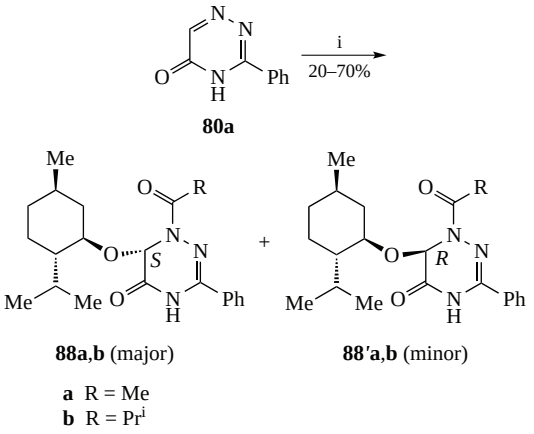
NuH: indole, 1(2)-methylindoles, 1-methylpyrrole, thiophene, 1-(thiophen-2-yl)ethan-1-one, acetophenone



R^1R^2NH = pyrrolidine, morpholine, piperidine, $PhCH_2NH_2$, $H_2N(CH_2)_6NH_2$

Scheme 28 *Reagents and conditions*: i, $BF_3 \cdot OEt_2$, AcOH, neat, reflux, 1–3 h; ii, CF_3CO_2H, $CHCl_3$, room temperature, 18–24 h; iii, S_8, R^1R^2NH, neat, reflux, 12–24 h.

In S_N^H reactions, a nucleophilic attack is directed towards a prochiral unsubstituted carbon atom, and the adducts always form as mixtures of two stereoisomers. However, the production of enantiomerically pure σ^H adducts is preferable in terms of drug design. We were the first to demonstrate the possibility of obtaining σ^H adducts with a high degree of diastereoselectivity in the reactions of achiral 1,2,4-triazin-5(4*H*)-one **80a** with *l*-menthol.[192,193] With an increase in the size of acyl substituent next to the reaction center, the reaction gives predominantly (*S*)-1-acyl-6-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]-3-phenyl-1,6-dihydro-1,2,4-triazin-5(4*H*)-ones **88a**,**b** (Scheme 29).



Scheme 29 *Reagents and conditions*: i, *l*-menthol, $(RCO)_2O$, neat, room temperature, 12–24 h.

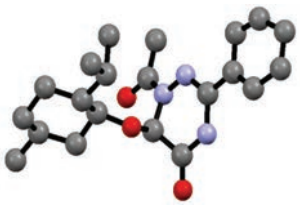
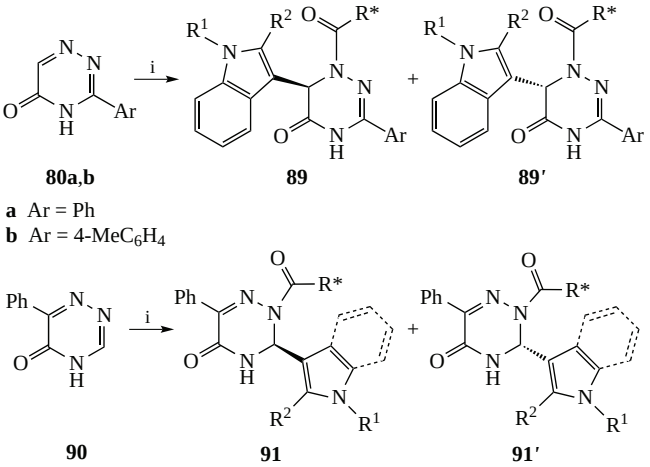


Figure 8 Single crystal structure of minor diastereoisomer **88′a** (adapted with permission from ref. 192. © 2001, Elsevier Science Ltd. All rights reserved).

The single crystal structure of (6*S*)-diastereoisomer **88a** was confirmed by XRD analysis (Figure 8).

In a similar manner, in the presence of a chiral acylating agent, for example (*S*)-2-(6-methoxynaphthalen-2-yl)propionic acid (*S*-Naproxen) or amino acids, the diastereoselectivity depends strongly on the size of the substituent near the reaction center, for example R* in chiral acylating agent and/or R^1, R^2 in indole or pyrrole (Scheme 30). However, the yields of products in the most cases were moderate (Table 1).[194]

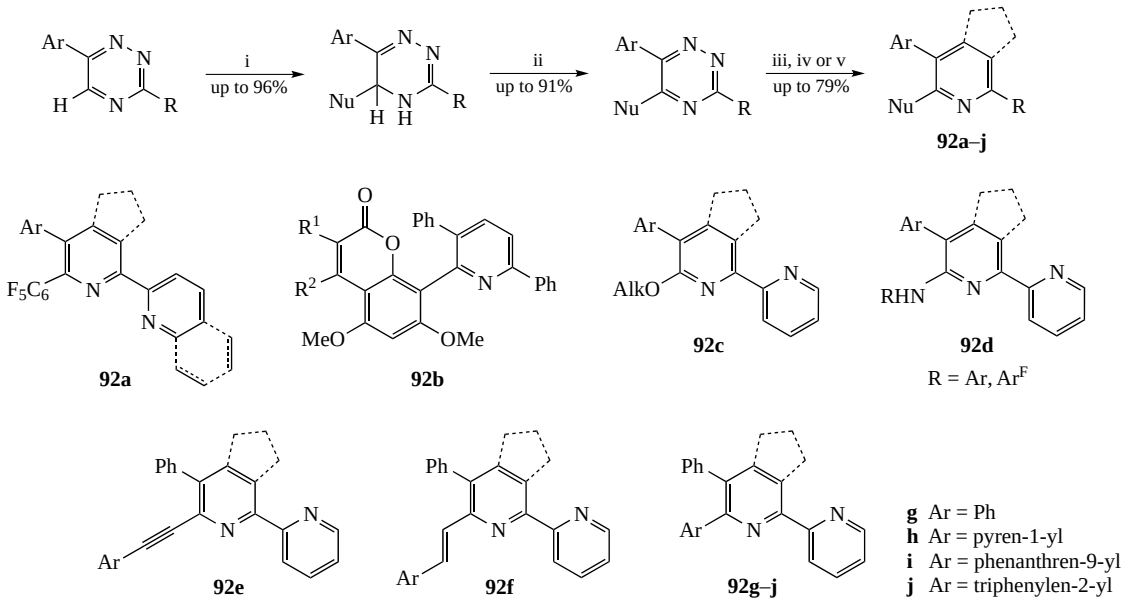


Scheme 30 *Reagents and conditions*: i, NuH, R*-CO_2H, THF, room temperature, 24 h.

The applied nature of S_N^H reactions is expressed in the possibility of obtaining push-pull fluorophores and ligands based on multisubstituted 2,2′-bipyridines **92** through a combination of S_N^H processes in 1,2,4-triazines by reaction with activated (organolithium compounds) or unactivated nucleophiles and the subsequent Diels–Alder reaction as a possible transition metal (TM)-free alternative to known cross-coupling processes (Scheme 31). In this way, we synthesized family of multisubstituted 2,2′-bipyridines.[173,195–197] Along with the use of the S_N^H and Diels–Alder reaction sequence, for introducing fragments of low-reactive N-nucleophiles, anilines, including fluoroanilines, as well as some alcohols the S_N^H, S_N^{ipso} and Diels–Alder reaction sequence proved to be well established. Thus, the sequence of S_N^H reaction for the introduction the cyano group in the C(5) position of the 1,2,4-triazines, S_N^{ipso} reaction for the replacement of the C(5)-cyano group by the residues of anilines, as N-nucleophiles, or alcohols, and the Diels–Alder reaction for the preparation of difficult-to-access α-aniline- or α-alkoxy-2,2′-bipyridine fluorophores was used.[198–200]

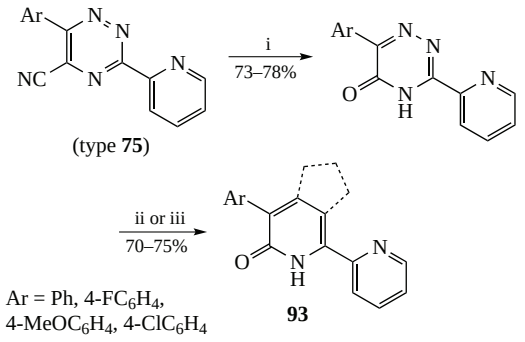
Table 1 Reactions of 1,2,4-triazines **80a**,**b** and **90** with indoles or pyrroles in the presence of chiral acylating agents (for the structures, see Scheme 30).

Entry	Substrate	NuH	R*-CO_2H	Product type	Yield (%)	Stereoconfiguration	*dr* (%)
1	**80a**	indole	*N*-Boc-Gly	**89**	48	–	–
2	**80a**	indole	*N*-Bz-D,L-Leu	**89**	34	*SS*,*RR*	>95:5
3	**80a**	indole	*N*-formyl-D-Ala	**89**	28	*RR*	>95:5
4	**80a**	indole	*N*-Ac-L-Trp	**89**	21	*SS*	>95:5
5	**80a**	indole	*N*-Ac-D,L-Phe	**89**	22	*SS*,*RR*	>95:5
6	**80b**	indole	*N*-Ac-L-Val	**89**	24	*SS*	95:5
7	**80b**	indole	*N*-Ac-D-Ala	**89**	15	*RR*	95:5
8	**80b**	indole	*N*-Ac-D,L-Phe	**89**	22	*SS*,*RR*	95:5
9	**80b**	indole	*N*-Ac-L-Trp	**89**	18	*SS*	>95:5
10	**80b**	indole	*N*-Ac-D-Trp	**89**	16	*RR*	>95:5
11	**80b**	indole	*N*-Ac-D,L-Trp	**89**	25	*SS*,*RR*	95:5
12	**80a**	2-methylindole	*N*-Bz-D,L-Leu	**89**	36	*SS*,*RR*	>95:5
13	**80a**	2-methylindole	*N*-Ac-L-Trp	**89**	25	*SS*	>95:5
14	**80b**	2-methylindole	*N*-Ac-L-Val	**89**	22	*SS*	>95:5
15	**80b**	1-methylindole	*N*-Bz-D,L-Leu	**89**	30	*SS*,*RR*	>95:5
16	**80b**	1-methylpyrrole	*N*-Bz-D,L-Leu	**89**	14	*SS*,*RR*	>95:5
17	**90**	indole	*N*-Ac-L-Leu	**91**	49	*SS*,*RR*	95:5
18	**90**	indole	*N*-Ac-L-Val	**91**	76	*SS*,*RR*	95:5
19	**90**	indole	*N*-Ac-L-Trp	**91**	32	*SS*,*RR*	95:5
20	**90**	1-methylindole	*N*-Ac-L-Val	**91**	40	*SS*,*RR*	95:5
21	**90**	pyrrole	*N*-Ac-L-Val	**91**	30	*SS*,*RR*	95:5
22	**90**	indole	(*S*)-Naproxen	**91**	33	*SS*	98:2



Scheme 31 *Reagents and conditions*: i, NuH, MsOH, CH_2Cl_2, room temperature, 24 h or NuLi, dry THF–toluene (1:1), –78 → 20 °C, overnight; ii, DDQ, CH_2Cl_2, room temperature, 0.5–24 h; iii, 2,5-norbornadiene, *o*-xylene, 143 °C, 10–18 h; iv, 1-morpholinocyclopentene, neat, 200 °C, 12 h; v, (if Nu = CN): AlkOH or $ArNH_2$, neat, 150 °C, 10–12 h, then iii or iv.

Along with fluorophores and ligands, the sequence of S_N^H/S_N^{ipso} processes in 1,2,4-triazines of type **75** and the subsequent Diels–Alder reaction can be used for obtaining modified derivatives of some potential drug candidates, for example, 2-pyridones **93**, whose derivatives exhibit a wide range biological activity,[201–204] including antitumor activity[205] (Scheme 32).[206]

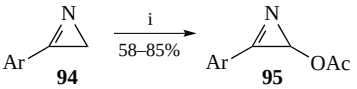


Scheme 32 *Reagents and conditions*: i, NaOH, CH_2Cl_2/H_2O (1:2 w/w), room temperature, 3 h, then H_3O^+; ii, 2,5-norbornadiene, 1,2-dichlorobenzene, reflux, 20 h, autoclave; iii, 1-morpholinocyclopentene, 200 °C, 10 h.

Finally, the S_N^H methodology was successfully employed for the direct introduction of 2-lithio-25,26,27,28-tetramethoxycalix[4]arenes into 1,2,4-triazines to afford calix[4]arenes substituted with 1,2,4-triazine moiety at the *meso*-position.[207]

6. Green activation methods and catalysts

The direct functionalization of the C–H bond under the irradiation with visible light in the presence of organic photo-redox catalysts mimics the photosynthesis process and thereby attracts considerable interest.[208–212] Ideally, these reactions catalyzed by organic photo-redox catalysts, for example, commercially available organic dyes, are an excellent 'green' alternative to TM-catalyzed processes.[213–216] In the development of such studies, we carried out direct O-acetylation at the C(sp^3)–H atom in aryl-2*H*-azirines **94** under photoactivation conditions using



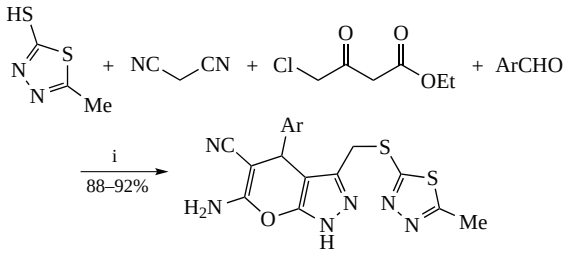
Ar = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$Bu^tC_6H_4$, 4-PhC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 2-ClC_6H_4, 4-BrC_6H_4, 3-BrC_6H_4, 3-FC_6H_4, 4-$CF_3C_6H_4$

Scheme 33 *Reagents and conditions*: i, $PhI(OAc)_2$, Rose Bengal, 34 W blue LED irradiation, PhMe, room temperature, 24 h.

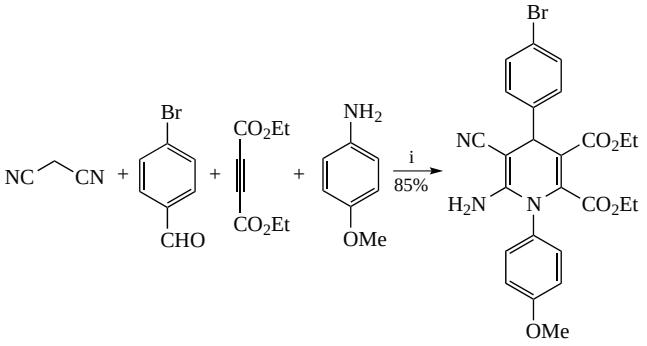
Rose Bengal dye (see Scheme 25). The advantage of the process is its high regioselectivity and the possibility to carry out the reaction under aerobic conditions at room temperature with the formation of *O*-acetylazirines **95** in yields of 58–85% (Scheme 33). The protocol is also applicable to a gram scale synthesis.[217]

In development of 'green catalysis', we have shown the possibility of obtaining bis-indolylmethanes (see Scheme 19) using melgumine, (2*R*,3*R*,4*R*,5*S*)-6-(methylamino)hexane-1,2,3,4,5-pentaol, as a catalyst. The reaction proceeds at room temperature with the formation of products of type **70** up to 96% yields. The obtained compounds showed promising antioxidant activity.[218]

Using a natural catalyst montmorillonite (K 10), we carried out multicomponent syntheses of biologically active heterocycles, such as multisubstituted pyranopyrazoles **96**, which showed promising antimicrobial activity[219] (Scheme 34), as well as multisubstituted 1,4-dihydropyridines[220] **97** (Scheme 35).



Scheme 34 *Reagents and conditions*: i, $N_2H_4 \cdot H_2O$, montmorillonite (K 10), $EtOH/H_2O$, 65–70 °C, 5 h.



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Scheme 35 *Reagents and conditions*: i, montmorillonite (K 10), EtOH/H_2O, 60 °C, 6 h.

Conclusions

In summary, we have reviewed herein our recent synthetic approaches and methods for the obtaining some prospective (hetero)aromatic/macrocyclic molecules/scaffolds.

These approaches can be helpful in solving some frequently encountered problems of synthetic organic chemistry, such as low solubility of reagents/products, low reaction yields, prolonged reaction times, especially for multistep reactions, and stereo-, regio- and chemoselective formation of chemical bonds. In terms of green and sustainable chemistry prospects, our results would be beneficial for the development of energy/resource saving and environmentally benign/safe synthetic methodologies, such as atom-economic and atom-efficient reactions, domino reactions, including multicomponent ones, 'green' catalyst-promoted transformations, photoactivated transformations, reactions in water/supercritical fluids or solvent-free reactions.

As for future challenges, many greener synthetic processes still remain largely unexplored, such as mechanoactivated organic synthesis, including asymmetric one,[221] laser-driven reactions at room temperature,[222] reactions in new media/carriers (gas-phase organic chemistry,[223,224] or continuous flow reactions[225]), encapsulated reagent chemistry,[226–228] nanoreactor chemistry,[229,230] electrochemistry[231,232] and related innovative protocols. All the mentioned above is at the core of some scientific and technological advances expected in years to come.

Another future challenge lies in a highly confident targeted computer-assisted prediction of molecular structures, which can be able to pursue a specific task, such as to discover (hetero)aromatic hosts/scaffolds capable of recognition specific analytes, or drug candidates to fit into specific biological targets and modulate their biological functions, or novel chemical reagents or catalysts for the organic synthesis. Usually the synthesis and subsequent testing of the effectiveness of new chemosensors, catalysts, novel reagents or drug candidates remains expensive as it requires extensive experimental base and human resources. Therefore, it is highly expected that the predicted computer simulation would allow with a high degree of reliability the creation of new molecular candidates, such as selective chemosensors, or drugs with a well predictable biological properties, or reagents with a certain chemical functions, or novel catalyst with an expected catalytic activity.

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