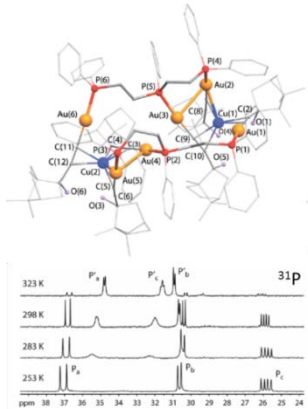
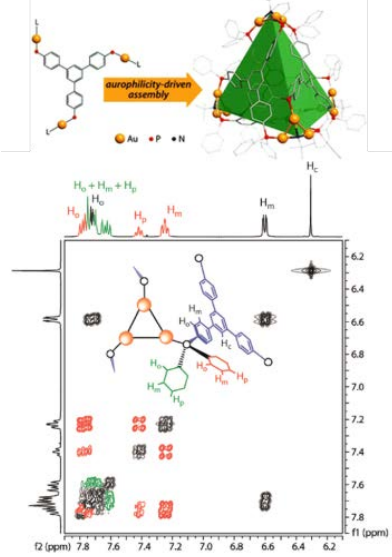
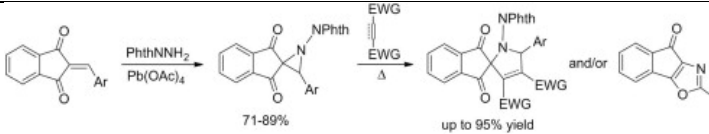
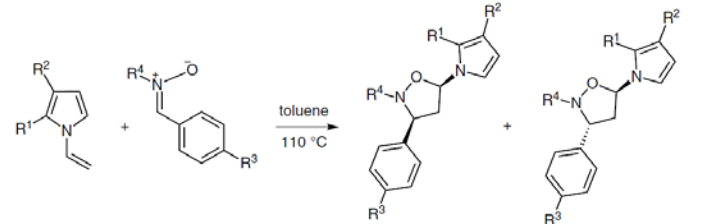
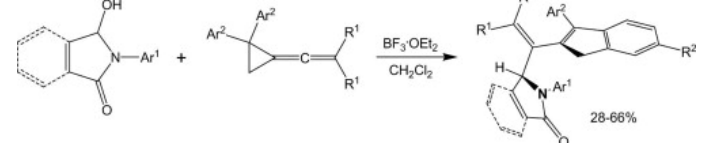
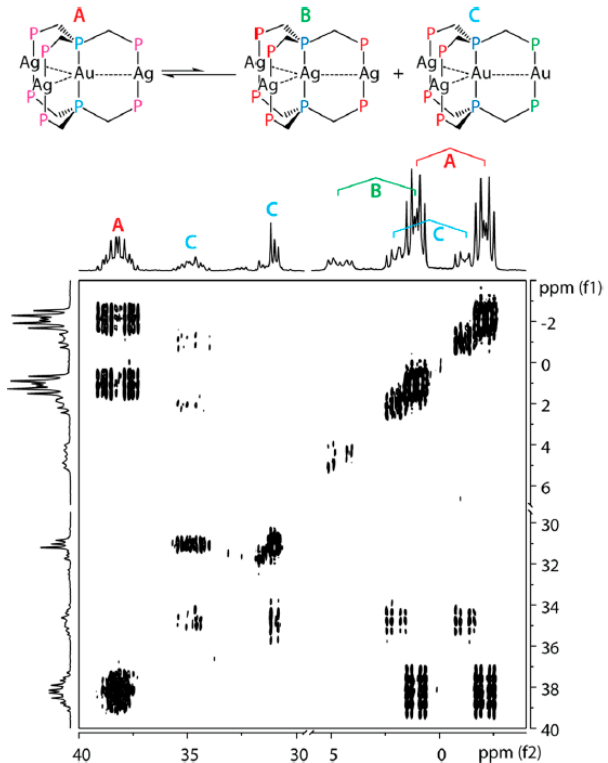
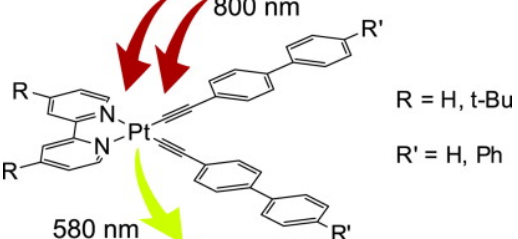
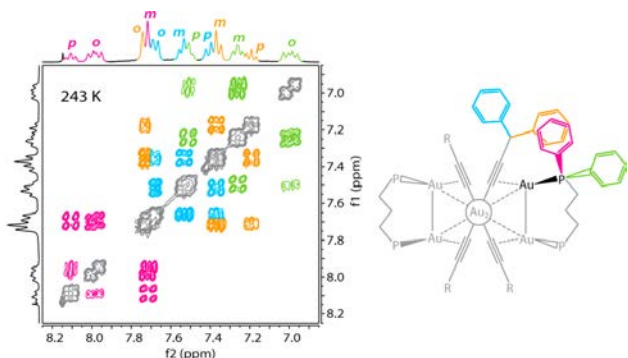
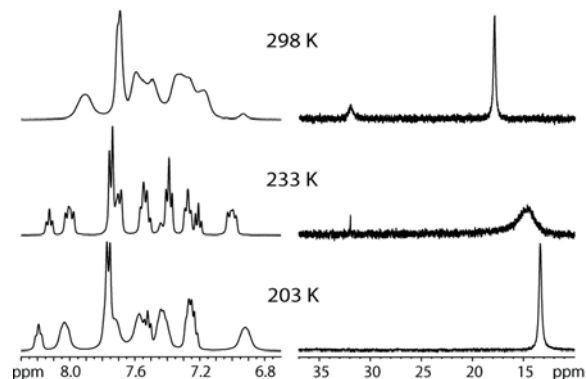


№	Иллюстрация, выходные данные	Краткое описание основной идеи	Использованное оборудование РЦ и краткое описание результатов, полученных по данным МР
1	 <p data-bbox="203 624 853 751">I.S. Krytchankou, D.V. Krupenya, A.J. Karttunen, S.P. Tunik, T.A. Pakkanen, P.-T. Choud, I.O. Koshevoy, "Triphosphine-supported bimetallic AuI-MI (M = Ag, Cu) alkyne clusters" Dalton Trans., 2014, 43, 3383-3394. DOI:10.1039/C3DT52658E</p>	<p data-bbox="936 204 1568 448">The reactions of gold acetylides (AuC₂R)_n with triphosphine ligands PPh₂-(CH₂)_n-PPh-(CH₂)₂-PPh₂ (n = 1, dpmp; 2, dpep) in the presence of M⁺ ions (M = Cu, Ag) lead to an assembly of the heterometallic clusters, the composition of which is determined by the steric bulkiness of the alkynyl groups and the flexibility of the phosphine motifs. All the title complexes exhibit room temperature luminescence in the solid state, showing a dependence of emission energy on the structure and composition of the metal core.</p>	<p data-bbox="1597 204 1962 252">Bruker Avance 400, Bruker DPX 300 spectrometers.</p> <p data-bbox="1597 284 2096 392">The NMR spectroscopic investigations showed that some complexes are stereochemically non-rigid in solution and reversibly undergo possible dissociation or isomerization processes.</p> <p data-bbox="1597 424 2085 533">The chemical structures of the studied compounds and complexes were confirmed by the solution 1D (¹H, ³¹P, ¹³C) and 2D (COSY, HMQC, HSQC, HMBC) NMR.</p>
2	 <p data-bbox="203 1337 853 1469">J.R. Shakirova, E.V. Grachova, A.J. Karttunen, V.V. Gurzhiy, S.P. Tunik, I.O. Koshevoy, "Metallophilicity-assisted assembly of phosphinebased cage molecules" Dalton Trans., 2014, 43, 6236-6243. DOI:10.1039/c3dt53645a</p>	<p data-bbox="936 762 1568 1007">A family of supramolecular cage molecules has been obtained via self-assembly of the phosphine-gold coordination complexes following an aurophilicity-driven aggregation approach. Use of the di- (PP) or tridentate (PPP) phosphine ligands P_n (n = 2, 3) with rigid polyaromatic backbones leads to clean formation of the coordination P_n(Au(tht))_nⁿ⁺ species, sequential treatment of which with H₂O/NEt₃ and excess of H₂NBu^t gives the finite 3D structures of two major types: the cylindrical-like hexametallic cages and tetrahedral dodecagold complexes.</p>	<p data-bbox="1597 762 1917 786">Bruker Avance 400 spectrometer.</p> <p data-bbox="1597 818 2096 978">The NMR spectroscopic investigations showed that cylindrical complexes undergo twisting-like interconversion of the helical P↔M isomers in solution, while some other complexes are stereochemically rigid and retain their axially chiral architecture.</p> <p data-bbox="1597 1010 2085 1090">The chemical structures of the studied compounds and complexes were confirmed by the solution 1D (¹H, ³¹P) and 2D COSY NMR.</p>

<p>3</p>	 <p>A.S. Pankova, M.A. Kuznetsov, "Synthesis and thermal transformations of spiro-fused N-phthalimidooziridines" <i>Tetrahedron Lett.</i>, 2014, 55, 2499-2503. DOI:10.1016/j.tetlet.2014.03.014</p>	<p>Oxidation of N-aminophthalimide in the presence of 2-arylideneinden-1,3-diones with electron-withdrawing substituents gives the corresponding 3-aryl-1-phthalimidospiro[aziridine-2,20-indene]-10,30-diones in good yields. Heating these aziridines with standard dipolarophiles (N-phenylmaleimide, dimethyl acetylenedicarboxylate, maleate, and fumarate) leads, in most cases, to spiro[inden-2,20-pyrrole] derivatives as products of 1,3-dipolar cycloaddition of the intermediate azomethine ylides with up to 70–95% yields in the case of N-phenylmaleimide.</p>	<p>Bruker DPX-300, Bruker Avance 400 spectrometers.</p> <p>Optimal reaction conditions were found and the chemical structures (including special configuration) of the studied compounds were confirmed by the solution ¹H and 2D ¹H NOESY NMR.</p>
<p>4</p>	 <p>A.P. Molchanov, R.S. Savinkov, A.V. Stepanov, G.L. Starova, R.R. Kostikov, V.S. Barnakova, A.V. Ivanov, "A Highly Efficient and Stereoselective Cycloaddition of Nitrones to N-Vinylpyrroles" <i>Synthesis</i> 2014, 46, 771-780. DOI:10.1055/s-0033-1340479</p>	<p>1,3-Dipolar cycloadditions of a number of C-aryl, C-carbamoyl-, and C,C-bis(methoxycarbonyl)nitrones and substituted N-vinylpyrroles proceed with high efficiency and regioselectivity with the formation of only one isomeric substituted 5-(1H-pyrrol-1-yl)isoxazolidine cycloadduct.</p>	<p>Bruker DPX-300, Bruker Avance 400 spectrometers.</p> <p>The chemical structures of the reaction products were confirmed with the help of NMR spectroscopy. The ratio of <i>cis/trans</i> isomers in products was measured using ¹H NMR.</p>
<p>5</p>	 <p>A.V. Stepanov, A.G. Larina, V.M. Boitsov, V.V. Gurzhiy, A.P. Molchanov, R.R. Kostikov, "Synthesis of indene derivatives via reactions of vinylidenecyclopropanes with the N-acyliminium cations generated from hydroxylactams" <i>Tetrahedron Lett.</i>, 2014, 55, 2022-2026. DOI:10.1016/j.tetlet.2014.02.039</p>	<p>A novel route for the synthesis of 1H-indene derivatives via the reactions of vinylidenecyclopropanes (VCPs) with the N-acyliminium cations generated from hydroxylactams is described.</p>	<p>Bruker DPX-300, Bruker Avance 400 spectrometers.</p> <p>The existence of some of the compounds as a mixture of rotamers was established by temperature-dependent NMR spectra (coalescence of exchanging signals upon heating).</p>

6	 <p>M.T. Dau, J.R. Shakirova, A.J. Karttunen, E.V. Grachova, S.P. Tunik, A.S. Melnikov, T.A. Pakkanen, I.O. Koshevoy, "Coinage Metal Complexes Supported by the Tri- and Tetraphosphine Ligands" <i>Inorg. Chem.</i>, 2014, 53, 4705-4715. DOI:10.1021/ic500402m</p>	<p>A series of tri- and tetranuclear phosphine complexes of d^{10} metal ions supported by the polydentate ligands, bis(diphenylphosphinomethyl) phenylphosphine (<i>PPP</i>) and tris(diphenylphosphinomethyl) phosphine (<i>PPPP</i>), were synthesized. The trinuclear clusters contain a linear metal core, while in the isostructural tetranuclear complexes the metal framework has a plane star-shaped arrangement. One cluster adopts a structural motif that involves a digold unit bridged by two arms of the <i>PPPP</i> phosphines and decorated two spatially separated Cu^I ions chelated by the remaining P donors.</p>	<p>Bruker Avance 400 spectrometer.</p> <p>The 1H, ^{31}P and COSY NMR spectroscopic investigation in DMSO solution revealed that some heterometallic clusters are stereochemically nonrigid and undergo reversible metal ions redistribution between several species, accompanied by their solvation-desolvation.</p>
7	 <p>R = H, t-Bu R' = H, Ph</p> <p>A.A. Melekhova, D.V. Krupenya, V.V. Gurzhiy, A.S. Melnikov, P.Yu. Serdobintsev, S.I. Selivanov, S.P. Tunik, "Synthesis, characterization, luminescence and non-linear optical properties of diimine platinum(II) complexes with arylacetylene ligands" <i>J. Organomet. Chem.</i>, 2014, 763-764, 1-5. DOI:10.1016/j.jorganchem.2014.04.002</p>	<p>A series of platinum(II) diimine-polyphenylacetylide complexes, which display appreciable nonlinear optical properties (TPA 9-22 GM) were synthesized and characterized. All complexes under study exhibit two-photon luminescence and their double quantum absorption cross-section was found to be in the 9-22 GM range</p>	<p>Bruker DPX-300 spectrometer.</p> <p>The structure, stoichiometry and symmetry of the complexes were confirmed by 1H and 1H COSY NMR. 1H NMR spectroscopic data indicate that in solution the complexes retain the structures found for some of them in solid state.</p>

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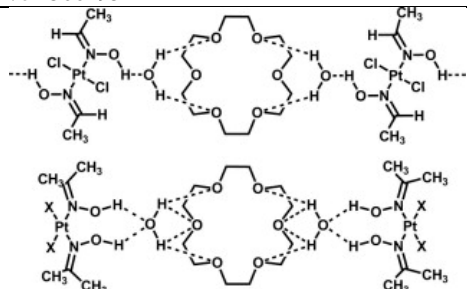
I.O. Koshevoy, Y.-C. Chang, Y.-A. Chen, A.J. Karttunen, E.V. Grachova, S.P. Tunik, J.Janis, T.A. Pakkanen, P.-T. Chou, "Luminescent Gold(I) Alkynyl Clusters Stabilized by Flexible Diphosphine Ligands" *Organometallics*, 2014, 33, 2363-2371.
DOI:10.1021/om5002952

Treatment of the homoleptic decanuclear compounds $(AuC_2R)_{10}$ with the cationic gold diphosphine complexes $[Au_2(PR'_2X-PR'_2)_2]_{2+}$ results in high-yield formation of the new family of hexanuclear clusters. All of these complexes are intensely emissive in the solid state at room temperature and demonstrate very high quantum yields from 0.61 to 1.0 with weak influence of the alkynyl substituents R' and the diphosphine backbones on luminescence energies.

Bruker Avance 400 spectrometer.

Studied compounds were characterized by 1H , ^{31}P and 1H COSY NMR. Variable-temperature NMR spectroscopic investigations showed that all but two compounds are fluxional in solution and demonstrate dissociative chemical equilibria between major and a few minor forms.

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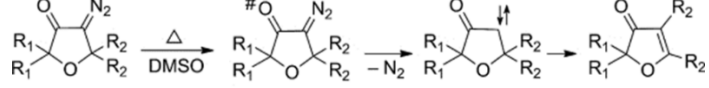


E.Yu. Bulatov, T.G. Chulkova, I.A. Boyarskaya, V.V. Kondratiev, M. Haukka, V.Yu. Kukushkin, "Triple associates based on (oxime)Pt(II) species, 18-crown-6, and water: Synthesis, structural characterization, and DFT study" *J. Molec. Struct.* 2014, 1068, 176-181.
DOI:10.1016/j.molstruc.2014.04.010

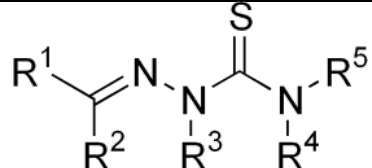

The associates $2(cis-[PtCl_2(acetoxime)_2]) \cdot 18\text{-crown-6} \cdot 2H_2O$, $2(cis-[PtBr_2(acetoxime)_2]) \cdot 18\text{-crown-6} \cdot 2H_2O$, and $trans-[PtCl_2(acetaldoxime)_2] \cdot (18\text{-crown-6}) \cdot 2H_2O$ were synthesized by co-crystallization of free corresponding platinum species. The (oxime)Pt(II) species are assembled with 18-crown-6 and water by hydrogen bonding between the hydroxylic hydrogen atoms of the oxime ligands and the oxygen atom of water and between the hydrogen atoms of water and the oxygen atoms of 18-crown-6. and were characterized by 1H NMR and by IR spectroscopies, high-resolution mass-spectrometry (ESI), TG/DTA, and X-ray crystallography.

Bruker DPX-300 spectrometer.

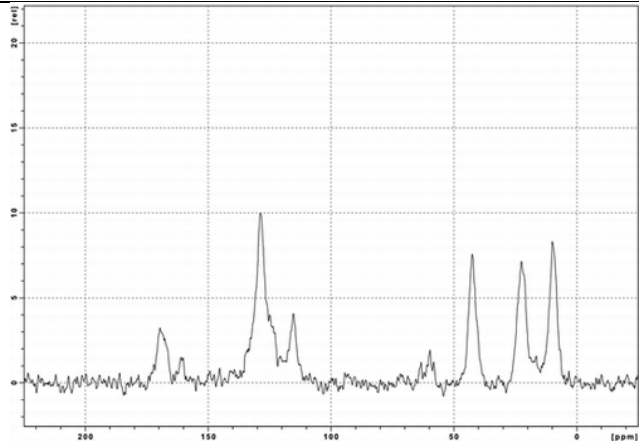
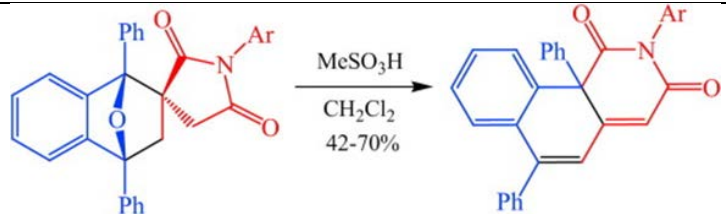
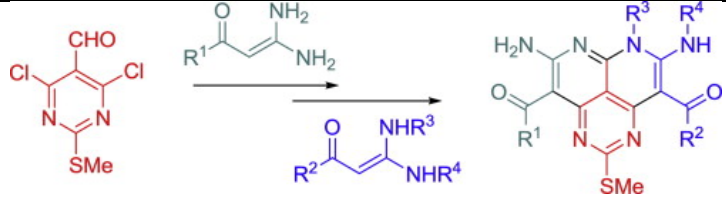
Studied associates were characterized by 1H NMR spectroscopy.

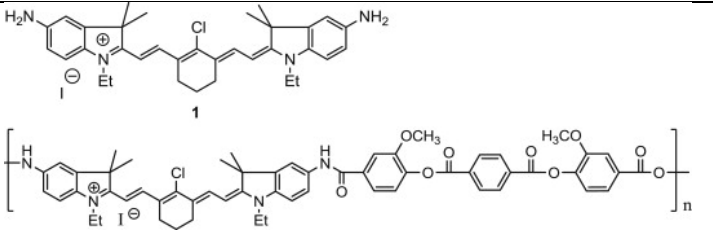
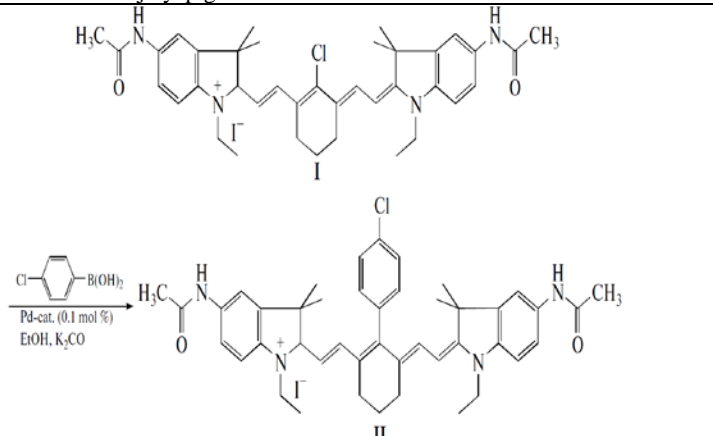
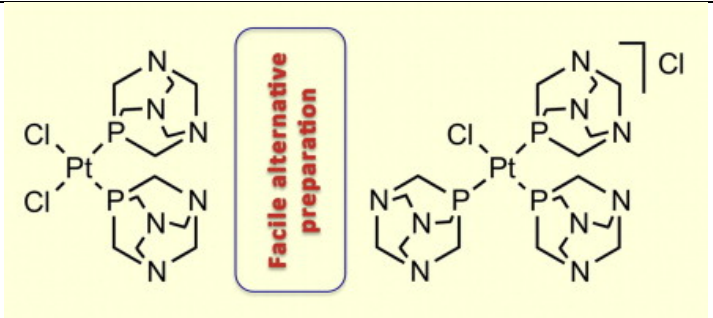
10	 <p>$R_1, R_2 = \text{Me or Ar}; 7 \text{ examples}$ L.L. Rodina, J.J. Medvedev, O.S. Galkina, V.A. Nikolaev, "Thermolysis of 4-Diazotetrahydrofuran-3-ones: Total Change of Reaction Course Compared to Photolysis" Eur. J. Org. Chem. 2014, 14, 2993-3000. DOI:10.1002/ejoc.201400161</p>	<p>Thermolysis of 2,2,5,5-tetrasubstituted 4-diazodihydrofuran-3-ones in protic (BnOH) and aprotic (DMSO) media, in contrast to photolysis, gives rise to the formation of 2,2,4,5-substituted 3(2H)-furanones as a result of 1,2-alkyl (aryl) shift. This is a first-order reaction that furnishes higher yields of furanones than thermolysis in BnOH. The reaction can serve as a preparative method for the synthesis of tetrasubstituted-3(2H)-furanones.</p>	<p>Bruker DPX-300, Bruker Avance 400 spectrometers.</p> <p>The chemical structures of the studied compounds in DMSO solution, kinetics of thermolysis and yields of products were determined by ^1H and ^{13}C NMR.</p>
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Продолжение таблицы (сделано 04.06.15)

№	Иллюстрация, выходные данные	Краткое описание основной идеи	Использованное оборудование РЦ и краткое описание результатов, полученных по данным МР
15	 <p>M.A. Kuznetsov, A.Ya. Bupalov, "One-pot, Three-component Synthesis of [1,3]thiazolo[4,3-b][1,3,4]thiadiazoles: Correct Structure of the Products" Chem. Heterocycl. Compd. 2014, 49, 1458-1463. DOI:10.1007/s10593-014-1396-4</p>	<p>The products of the one-pot, three-component synthesis of [1,3]thiazolo-[4,3-b][1,3,4]thiadiazoles from aromatic aldehydes, thioglycolic acid, and compounds containing a C(=S)-N-NH2 fragment (thiosemicarbazide or 4-amino-2,4-dihydro-3H-1,2,4-triazole-3-thiones) are not condensed heterocycles (as reported by several researchers), but are thiosemicarbazones or triazolylimines of the aldehydes used.</p>	<p>Bruker Avance 400 spectrometer.</p> <p>^1H and ^{13}C NMR spectra clearly contradict the condensed heterocyclic structure, proposed earlier in the literature, but are consistent with the thiosemicarbazones or triazolylimines of the aldehydes used.</p>
16	 <p>V.A. Rassadin, E. Nicolas, Y. Six, "Ti(OiPr)₄/nBuLi: an attractive reagent system for [2+2+2] cyclotrimerisation reactions" Chem. Commun. 2014, 50, 7666-7779. DOI:10.1039/C4CC02698E</p>	<p>A convenient method for the [2+2+2] cyclotrimerisation of alkynes using Ti(OiPr)₄/nBuLi is presented. Homotrimerisation of arylacetylenes proceeds within minutes with excellent regioselectivity. Moreover, the intermolecular construction of ABB heterotrimers can be achieved selectively from two different alkynes with similar electronic properties. The method is also suitable for the synthesis of pyridines.</p>	<p>Bruker Avance 400 spectrometer.</p> <p>The structures of the studied compounds and especially the presence and the fractions of their regioisomers was confirmed by NMR.</p>

<p>17</p>	<p>V.V. Sokolov, A.Yu. Ivanov, M.S. Avdontseva, A.A. Zolotarev, "Stereochemistry and NMR Spectra of Some Tricyclic Condensed Thiazolidine Derivatives with a Bridgehead Nitrogen Atom" Chem. Heterocycl. Compd. 2014, 50, 550-556. DOI:10.1007/s10593-014-1506-3</p>	<p>The configuration of a series of tricyclic condensed thiazolidines with a bridgehead nitrogen atom, for which erroneous data had been published, was determined by X-ray structural analysis and NMR spectroscopy.</p>	<p>Bruker DPX-300, Bruker Avance 400, Bruker Avance 500 spectrometers.</p> <p>The spacial structures of studied compounds were established reliably using an array of liquid-state NMR methods: ^1H, ^{13}C, 1D TOCSY, 1D NOESY, 2D HSQC etc.</p>
<p>18</p>	<p>P.B. Davidovich, D.S. Novikova, V.G. Tribulovich, S.N. Smirnov, V.V. Gurzhiy, G. Melino, A.V. Garabadzhiu, "First X-ray Structural Characterization of Isatin Schiff-Base Derivative. NMR and Theoretical Conformational Studies" J. Molec. Struct. 2014, 1075, 450-455. DOI:10.1016/j.molstruc.2014.07.008</p>	<p>Isatin (1H-indole-2,3-dione) is an endogenous natural compound under intense development in medicinal chemistry. In this paper isatin Schiff base derivative is characterized by X-ray, NMR, FT-IR, UV-Vis spectroscopy and by quantum chemistry calculations.</p>	<p>Bruker Avance 400, Bruker Avance 500 spectrometers.</p> <p>All NMR assignments and stereochemistry of the studied compounds were made on the basis of 1D (^1H, ^{13}C) and 2D NMR experiments (geCOSY, geNOESY, geHSQC, geHMBC). NMR data show that E-conformer interconverts to the Z-conformer when dissolved, this equilibrium weakly depends on the solvent type.</p>
<p>19</p>	<p>A. Miroslovov, Y. Polotskii, V. Gurzhiy, A. Ivanov, A. Lumpov, M. Tyupina, G. Sidorenko, P. Tolstoy, D. Maltsev, D. Suglobov, «Technetium and Rhenium Pentacarbonyl Complexes with C2 and C11 ω-Isocyanocarboxylic Acid Esters» Inorg. Chem. 2014, 53(15), 7861-7869. DOI:10.1021/ic500327s</p>	<p>Technetium(I) and rhenium(I) pentacarbonyl complexes with ethyl 2-isocynoacetate and methyl 11-isocyanoundecanoate, were prepared and characterized by IR, ^1H NMR, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.</p>	<p>The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance III 400. NMR characterized technetium(I) and rhenium(I) pentacarbonyl complexes.</p>

<p>20</p>  <p>Dz.N. Konshina, A.V. Furina, Z.A. Temerdashev, A.A. Gurinov, V.V. Konshin, "Immobilization of Guanazyl Functional Groups on Silica for Solid-Phase Extraction of Metal Ions" <i>Analytical Lett.</i> 2014, 47(16), 2665-2681. DOI:10.1080/00032719.2014.917421</p>	<p>Guanazyl groups were grafted on silica gel by 4-nitrobenzoyl chloride acylation, sodium dithionite reduction, diazotation, and reaction with 2-benzylidenehydrazinecarboximidamide. The applicability of pseudosecond order kinetic equations for metal sorption kinetics description was investigated. The method was employed for the determination of Cu(II) in water with a low limit of detection, high accuracy, and good precision.</p>	<p>¹³C NMR spectra were measured using a 400 MHz Bruker WB Avance III spectrometer. Cross-polarization magic angle spinning have made for {¹H}-¹³C. The two dimensional heteronuclear correlation experiment confirmed the presence of the carboxamide and guanyl carbons and showed cross-peaks between carbon and hydrogen atoms in the methylene and phenyl groups.</p>
<p>21</p>  <p>A.V. Stepanov, V.M. Boitsov, A.G. Larina, A.P. Molchanov, "Acid-induced rearrangement of cycloadducts from N-aryl itaconimides and 1,3-diphenylisobenzofuran"; <i>Tetrahedron Lett.</i> 2014, 55, 4895-4897 DOI:10.1016/j.tetlet.2014.06.107</p>	<p>Treatment of several Diels–Alder adducts of N-aryl itaconimides and 1,3-diphenylisobenzofuran with a strong acid triggers a skeletal rearrangement resulting in 2-aryl-6,10b-diphenylbenzo[h]isoquinoline-1,3(2H,10bH)-diones.</p>	<p>The ¹H and ¹³C NMR spectra were measured on a Bruker DPX-300.</p>
<p>22</p>  <p>O.Yu. Bakulina, A.Yu. Ivanov, P.S. Lobanov, D.V. Dar'in, "Synthesis of novel peri-fused heterocyclic systemsdpyrimido [4,5,6-de][1,8]naphthyridines, based on interaction of 4,6-dichloro-2-methylthiopyrimidine-5-carbaldehyde with geminal enediamines"; <i>Tetrahedron</i> 2014, 70, 7900-7905 DOI:10.1016/j.tet.2014.08.066</p>	<p>The synthetic approach to novel peri-fused heterocyclic systemsdpyrimido[4,5,6-de][1,8]naphthyridines, has been developed. It consists of successive treatment of 4,6-dichloro-2-methylthiopyrimidine-5-carbaldehyde with 2 mol of geminal b-(acyl)enediamines and includes substitution of a chlorine atom with the nucleophilic carbon atom of the enediamine and cyclization of the corresponding intermediate. The possibility of synthesis of both symmetrically and nonsymmetrically substituted pyrimidonaphthyridines was demonstrated.</p>	<p>The NMR spectra were recorded on a Bruker Avance III 400 spectrometer. The significant broadening of the ring carbon atoms signals in the ¹³C NMR spectrum demonstrates the tautomeric equilibrium in pyrimidonaphthyridines.</p>

23	 <p>S. Miltsov, V. Karavan, M. Goikhman, I. Podeshvo, S. Gómez-de Pedro, M. Puyol, J. Alonso-Chamarro, "Synthesis of bis-aminosubstituted indocyanine dyes for their use in polymeric compositions"; <i>Dyes and Pigments</i>, 2014, 109, 34-41 DOI:10.1016/j.dyepig.2014.05.002</p>	<p>The synthesis of a set of open-chain bis-aminosubstituted cyanine dyes as well as others with cyclic fragments in the polymethine chain is presented. These dyes are suitable for the development of polymeric compositions with variable optical characteristics as they can be covalently incorporated into the polymer. Bis-aminosubstituted cyanine dyes with cyclic fragments in the polymethine chain as well as open-chained were synthesized. All them are potential chromophores to be employed in the development of chromophore-containing polymeric systems by their covalently incorporation into the main or the side chains of the polymer. In this way, problems related to solubility, heterogeneous distribution, stability or low optical quality present in typical "guest"e"host" systems could be avoided.</p>	<p>¹H NMR spectra have been measured in a Bruker DPX-300 at 300 MHz to characterize bis-aminosubstituted cyanine dyes with cyclic fragments in the polymethine chain as well as open-chained.</p>
24	 <p>M.Ya. Goikhmana, N.P. Yevlampieva, I.V. Podeshvo, S.A. Mil'tsov, V.S. Karavan, I.V. Gofman, A.P. Khurchak, A.V. Yakimansky, "Polymers with Cyanine Chromophore Groups in the Main Chain: Synthesis and Properties"; <i>Polymer Science B</i>, 2014, 56, 352-359 DOI:10.1134/S1560090414030051</p>	<p>Polyamides containing fragments of two cyanine chromophores in the main chain are synthesized, and their viscometric and electrooptical properties in solutions, as well as their stress-strain properties in films, are investigated. It is shown that the molecular characteristics of the copolyamides are substantially affected by chromophore fragments at a content of 10 mol %, while the mechanical properties of the films are independent of the chemical structures of chromophores incorporated into polyamide chains.</p>	<p>¹H NMR spectra were recorded on a Bruker DPX 300 spectrophotometer at room temperature with the use of DMSO d₆ as a solvent to characterize cyanine chromophores.</p>
25	 <p>M.Ya. Demakova, K.V. Luzyanin, G.L. Starova, V.Yu. Kukushkin, "Facile alternative route to cis-[PtCl₂(PTA)₂] and [PtCl(PTA)₃]Cl (PTA = 1,3,5-triaza-7-phosphaadamantane)"; <i>Inorg. Chem. Commun.</i>, 2014,</p>	<p>The reaction of trans-[PtCl₂(Me₂SO)₂] with 2 equivs of 1,3,5-triaza-7-phosphaadamantane (PTA) in MeNO₂ at RT furnished cis-[PtCl₂(PTA)₂] in 87% isolated yield. Corresponding reaction of K₂[PtCl₄] with 1 equiv. of PTA in aqueous EtOH at RT led to [PtCl(PTA)₃]Cl in 84% isolated yield. Complexes were characterized by elemental analyses (C, H, N), HR-ESI+/-MS, IR, ¹H and ³¹P{¹H} NMR spectroscopic techniques, and by single-crystal X-ray diffraction for cis-[PtCl₂(PTA)₂].</p>	<p>¹H and ³¹P{¹H} NMR characterizes cis-[PtCl₂(PTA)₂] and [PtCl(PTA)₃]Cl.</p>

50, 17-18
DOI:10.1016/j.inoche.2014.10.002

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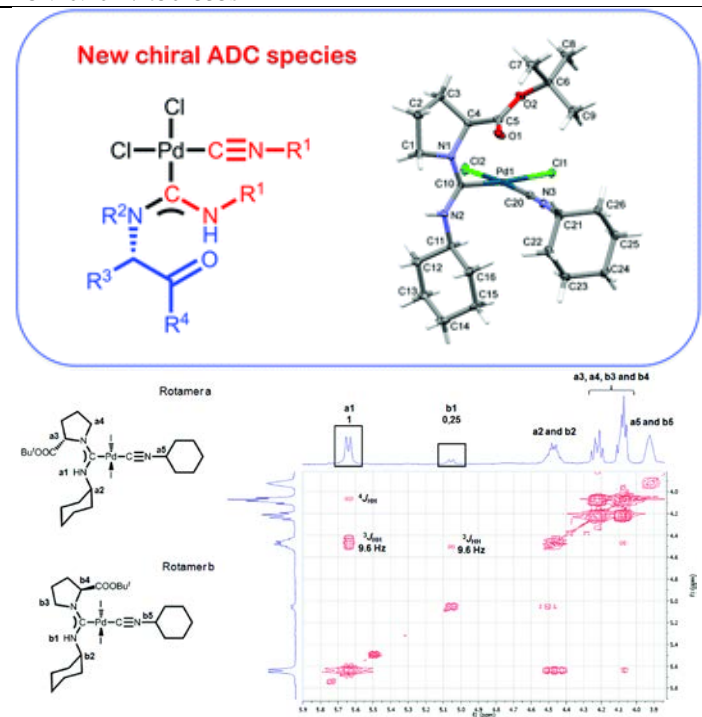


D.S. Bolotin, K.I. Kulish, N.A. Bokach, G.L. Starova, V.V. Gurzhiy, V.Yu. Kukushkin, "Zinc(II)-Mediated Nitrile–Amidoxime Coupling Gives New Insights into H⁺-Assisted Generation of 1,2,4-Oxadiazoles"; *Inorg. Chem.*, 2014, 53, 10312-10324
DOI:10.1021/ic501333s

The cyanamides Me₂NCN, OC₄H₈NCN, and PhC(=O)N(H)CN and the conventional nitriles PhCN and EtCN react with 1 equiv of each of the amidoximes R'C(=NOH)NH₂ (R' = Me, Ph) in the presence of 1 equiv of ZnCl₂ producing the complexes [ZnCl₂{HN=C(R)ON=C(R')NH₂}] (R/R' = NMe₂/Me, NMe₂/Ph, NC₄H₈O/Me, NC₄H₈O/Ph, N(H)C(=O)Ph/Me, N(H)C(=O)Ph/Ph, Ph/Me, Ph/Ph, Et/Ph) with the chelate ligands originating from the previously unreported zinc(II)-mediated nitrile–amidoxime coupling. All new obtained compounds were characterized by HRESI-MS, IR, ATR-FTIR, ¹H NMR, CP-MAS TOSS ¹³C NMR, elemental analyses (C, H, N), and single crystal X-ray diffraction. bbn

¹³C NMR spectra were measured on Bruker Avance III WB 400 with magic angle spinning. No reaction was observed between 1a–e and 2a,b (in all combinations) in ethyl acetate for 2 days at temperatures ranging from 20 to 80 °C either in the presence of 1 equiv of p- TolSO₃H or without the acid. Attempted reaction was monitored by ESI-MS and ¹H NMR spectroscopies by analyzing residues formed after evaporation of EtOAc and their redissolution in (CD₃)₂SO. All these blank experiments point out that the observed nitrile–amidoxime coupling is zinc(II)-mediated.

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T.B. Anisimova, M. Fátima C. Guedes da Silva, V.Yu. Kukushkin, A.J.

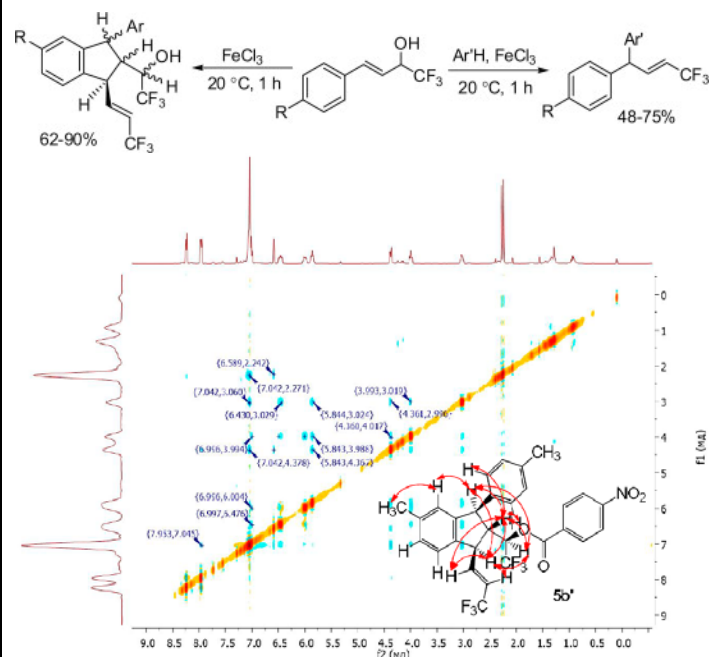
Metal-mediated coupling between equimolar amounts of cis-[PdCl₂(CNR¹)₂] and the amino acid esters L-HTyrOMe or L-HProOtBu proceeds at 40 °C in chloroform over ca. 6 h.

The subsequent workup affords the complexes cis-[PdCl₂(CNR¹){C(TyrOMe)[double bond, length as m-dash]NHR¹}] (R¹ = Xyl, 2-Cl-6-Me-C₆H₃) or cis-[PdCl₂(CNR¹){C(ProOtBu)[double bond, length as m-dash]NHR¹}] (R¹ = Xyl, 2-Cl-6-Me-C₆H₃, Cy, tBu, 2-naphthyl) in good to excellent isolated yields (75–94%). Some complexes were characterized by elemental analyses (C, H, N), ESI+/-MS, IR, 1D (¹H, ¹³C{H}) and 2D (¹H, ¹H-COSY, ¹H, ¹³C-HMQC/1H, ¹³C-HSQC, ¹H, ¹³C-HMBC) NMR spectroscopic techniques, and by single-crystal X-ray diffraction.

1D (¹H, ¹³C{H}) and 2D (¹H, ¹H-COSY, ¹H, ¹³C-HMQC/1H, ¹³C-HSQC, ¹H, ¹³C-HMBC) NMR technic were used for characterization of some complexes.

L. Pombeiro, K.V. Luzyanin, "Metal-mediated coupling of amino acid esters with isocyanides leading to new chiral acyclic aminocarbene complexes"; Dalton Trans., 2014, 43, 15861-15871
DOI:10.1039/c4dt01917b

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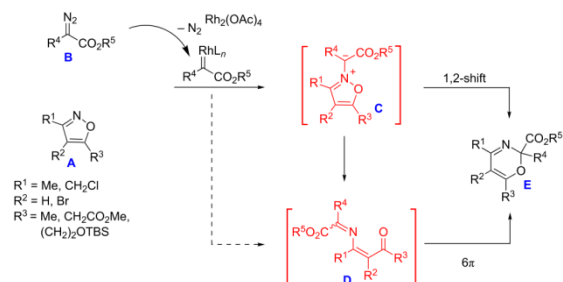


A.N. Kazakova, R.O. Iakovenko, V.M. Muzalevskiy, I.A. Boyarskaya, M.S. Avdontceva, G.L. Starova, A.V. Vasilyev, V.G. Nenajdenko, "Trifluoromethylated allyl alcohols: acid-promoted reactions with arenes and unusual 'dimerization'"; Tetrahedron Lett., 2014, 55, 6851-6855
DOI:10.1016/j.tetlet.2014.10.083

An unusual 'dimerization' of CF₃-allyl alcohols [ArCH=CH(OH)CF₃] under the action of anhydrous FeCl₃ was found to give fluorinated indanes in 62–90% yields via the formation of intermediate allyl cations. Reactions of CF₃-allyl alcohols with arenes (Ar'H) led to CF₃-alkenes [Ar(Ar')CH=CHCF₃] in 48–75% yields. The mechanisms of the transformations are discussed.

¹H NMR, ¹⁹F NMR, ¹³C NMR, NOESY H-H, NOESY H-F, DEPT spectrum. The proof of the structures of some compounds was obtained by NOESY experiments. The observed correlations clearly confirmed the stereochemistry of the compounds.

29



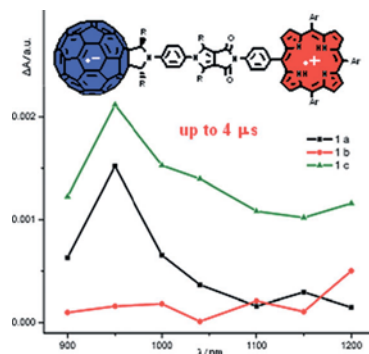
A.F. Khlebnikov, M.S. Novikov, Y.G. Gorbunova, E.E. Galenko, K.I. Mikhailov, V.V. Pakalnis, M.S. Avdontceva, "Isoxazolium N-ylides and 1-oxa-5-azahexa-1,3,5-trienes on the way from isoxazoles to 2H-1,3-

Theoretical and experimental studies of the reaction of isoxazoles with diazo compounds show that the formation of 2H-1,3-oxazines proceeds via the formation of (3Z)-1-oxa-5-azahexa-1,3,5-trienes which undergo a 6 π -cyclization. We found reaction conditions which allow for the preparation of aryl- and halogen-substituted 2H-1,3-oxazines as well as 1,4-di(alkoxycarbonyl)-2-azabuta-1,3-dienes starting from isoxazoles and diazo esters.

NMR spectra were determined in CDCl₃ with a Bruker DPX 300 and a Bruker AVANCE III 400 spectrometer. ¹H and ¹³C NMR have verified the structures of some compounds.

oxazines"; Beilstein J. Org. Chem. 2014, 10, 1896-1905
DOI:10.3762/bjoc.10.197

30



A.S. Konev, A.F. Khlebnikov, P.I. Prolubnikov, A.S. Mereshchenko, A.V. Povolotskiy, O.V. Levin, A. Hirsch, "Synthesis of New Porphyrin–Fullerene Dyads Capable of Forming Charge-Separated States on a Microsecond Lifetime Scale"; Chem. Eur. J. 2014, 20,1-15
DOI:10.1002/chem.201404435

A series of covalently linked axially symmetric porphyrin–fullerene dyads with a rigid pyrrolo[3,4-c]pyrrolic linker enabling a fixed and orthogonal arrangement of the chromophores has been synthesized and studied by means of transient absorption spectroscopy and cyclic voltammetry. The lifetime of the charge-separated state has been found to depend on the substituents on the porphyrin core, reaching up to 4 μs for a species with meso-(p-MeOC₆H₄) substituents. The ground and excited electronic states of model compounds have been calculated at the DFT and TD-DFT B3LYP(6-31G(d)) levels of theory and analyzed with regard to the effect of the substituent on the stabilization of the charge-separated state in the porphyrin–fullerene ensemble with a view to explaining the observed dependence.

¹H (300 or 400 MHz) and ¹³C (75 or 100 MHz) NMR spectra were determined in CDCl₃, [D₆]DMSO, or C⁶D⁶ on Bruker 400 Avance and Bruker DPX 300 spectrometers.
The structures were confirmed by NMR method.