

**VILNIUS UNIVERSITY**

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**SYNTHESIS, STRUCTURAL AND ASSOCIATION STUDIES OF CHIRAL  
SUPRAMOLECULAR TECTONES BASED ON BICYCLO[3.3.1]NONANE  
FRAMEWORK**

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**VILNIAUS UNIVERSITETAS**

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**CHIRALINIŲ SUPRAMOLEKULINIŲ TEKTONŲ, TURINČIŲ  
BICIKLO[3.3.1]NONANO FRAGMENTĄ, SINTEZĖ, STRUKTŪROS IR  
ASOCIACIJOS TYRIMAI**

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## LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
CD	Circular Dichroism spectroscopy
CE	Cotton effect
DIAD	Diisopropyl azodicarboxylate
DIPEA	<i>N,N</i> -diisopropylethylamine (Hünig's base)
DLS	Dynamic light scattering method
DMAP	<i>N,N</i> -dimethylpyridin-4-amine
Dppp	1,3-Bis(diphenylphosphino)propane
ESI MS	Electrospray ionization mass spectrometry
Eu(TFC) <sub>3</sub>	Europium <i>d</i> -3-trifluoroacetylcamphorate
HMDSLi	Lithium bis(trimethylsilyl)amide
LED	Light-emitting diode
NMR	Nuclear magnetic resonance spectroscopy
Py	Pyridine
SEM	Scanning electron microscope
TD-DFT	Time-dependent density functional theory
TEA	Triethylamine
TEBA	Benzyltriethylammonium chloride
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine

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## INTRODUCTION

Supramolecular chemistry is a rapidly developing research area. The molecular structures composed of a limited or infinite number of the molecules that interact with each other *via* noncovalent interactions are investigated. Supramolecular chemistry is like a game with Lego bricks. The molecular building blocks are called tectons (*lot.* tectonicus – construction). Supramolecular tectons can assemble to larger aggregates *via* a process called self-association. In the course of evolution the nature has created complex biological molecules like DNA/RNA, enzymes and cell membranes as supramolecules.

An object or a system is chiral if it cannot be superimposed with its mirror image. The most obvious chiral object is our hands – they are each other's mirror image. Living organisms possess chirality in proteins and genes which are composed of *L*-amino acids and contain *D*-sugars, respectively. RNA nucleotides of definite chirality recognize and bind to each other to form one type helical supramolecular RNA molecules<sup>1</sup>. Thus the chirality is one of the factors in molecular recognition.

The enantiomerically pure bicyclo[3.3.1]nonan-2,6-dione is a convenient V-shaped synthon for the formation of supramolecular structures. Molecules containing the latter fragments with complementary hydrogen bonded moieties were obtained in our laboratory and were shown to form helices<sup>2</sup> and cyclic<sup>3</sup> associates in solution.

The supramolecular chemistry of assemblies composed of a limited or infinite number of the molecular tectons interacting with each other *via* noncovalent interactions was investigated with a special emphasize on the chirality of the building blocks. Understanding the molecular electronic structure and supramolecular interactions could lead to a construction of organic LEDs, solar cells and other new functional materials as well.

### The novelty and significance of the work

Chiral polycyclic compounds containing carbonyl, 1,2-methylenedioxybenzene and indole chromophores were obtained and their chiroptical properties were investigated. The empirical charge transfer and octant rule for determination of the absolute configuration can be applied by comparison of the CD spectra and *ab initio* calculations. The exciton coupling between the benzoate chromophores in substituted

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<sup>1</sup> (a) Joyce, G. F.; Visser, G. M.; van Boeckel, C. A. A.; van Boom, J. H.; Orgel, L. E.; van Westrenen, J. *Nature* **1984**, *310*, 602–604. (b) Joyce, G. F.; Schwartz, A. W.; Miller, S. L.; Orgel, L. E. *PNAS* **1987**, *84*, 4398–4402. (c) Avetisov, V. A.; Kuz'min, V. V.; Goldanskii, V. I. *Phys. Today* **1991**, *44*, 33–41.

<sup>2</sup> Stončius, S.; Orentas, E.; Butkus, E.; Öhrström, L.; Wendt, O. F.; Wärnmark, K. *J. Am. Chem. Soc.* **2006**, *128*, 8272–8285.

<sup>3</sup> Orentas, E.; Wallentin, C.-J.; Bergquist, K.-E.; Lund, M.; Butkus, E.; Wärnmark, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 2071–2074.

bicyclo[3.3.1]nonane-2,6-diol was demonstrated experimentally and by theoretical methods. Computations proved that interaction between benzoates was possible only if the distance is equal to approximately 12 Å. The calculations show the orbital overlap in chiral bicyclo[3.3.1]nonane  $\alpha,\beta$ -unsaturated acids and nitrile due to a small interchromophoric distance between the two chromophores. Nevertheless, the distance is appropriate for interchromophoric  $\pi$  orbital interaction, which in turn creates a charge circulation between the unsaturated bicyclic fragments though the exciton interaction has not been observed.

New chiral  $C_3$  symmetry ketones and alcohols with different size central aromatic and external bicyclo[3.3.1]nonane fragments were synthesized. These compounds form nanoparticles on the surface and probably supramolecular structures exist in solution. The correlation of structure and association constants has shown that Van der Waals forces of bicyclic parts and hydrogen bond between hydroxyl groups give the largest contribution to the association in solution. It should be noted that in all cases  $\pi$ - $\pi$  interaction does not have a significant impact on the association. The synthesized V-shaped ligands having coordinating pyridine and bicyclo[3.3.1]nonanyl substituent form rhomb-shaped palladicycle forming [2]catenanes and nanoparticles with regular structure.

**The following objectives were pursued in this work:** 1) to determine electronic structure of the chiral conformationally rigid and labile bicyclo[3.3.1]nonane compounds, and the effect of origin, mutual orientation and distance of the chromophores to chiroptical properties, 2) to study the influence of chirality, structure of trisubstituted compounds containing external bicyclo[3.3.1]nonanyl- and different size aromatic fragments and palladicycle on the formation of various supramolecular structures.

**In order to achieve the objectives of the work, the following aims have been set:**

1. To synthesize chiral and conformationally strained bicyclo[3.3.1]nonane compounds with different electronic nature of chromophores; to characterize electronic transitions from the data obtained by circular dichroism spectroscopy and *ab initio* calculations and investigate the exciton interaction and charge transfer phenomena.
2. To synthesize chiral conformationally labile bicyclo[3.3.1]nonane benzoates and explore the exciton interaction between aromatic chromophores; to determine the solvent effect on the distribution of conformers.
3. To synthesize chiral bicyclo[3.3.1]nonane  $\alpha,\beta$ -unsaturated carboxylic acid and nitrile to investigate the electronic structure of these molecules by CD and UV spectroscopy; to formulate rules for the determination the absolute configurations of similar compounds.
4. To find the optimal conditions for synthesis of trisubstituted compounds containing external bicyclo[3.3.1]nonanyl- and different size aromatic fragments; to



investigate influence of chirality and structure of these compounds to supramolecular association in solution and on surface.

5. To synthesize V-shaped ligand and their rhombic palladium complex and explore the influence of the ligand chirality to the formation and further association of the complex.

## RESULTS AND DISCUSSION

### 1.1 The synthesis and chiroptical properties of chiral polycyclic compounds

Circular dichroism (CD) spectroscopy is a well-established technique in stereochemistry studies<sup>4</sup>. The most common application of CD related spectra is the assignment of the absolute configuration *via* the sector and helicity rules. Different chromophores have been investigated extensively both experimentally and theoretically<sup>5</sup>. Thus CD spectroscopy is not only a tool for studying the absolute configuration of organic molecules but also is a mean to examine interactions between functional groups, i.e. chromophores. Chiral molecules having two chromophores with strong electric-dipole allowed transitions couple to each other through space (exciton coupling). This phenomenon was intensively studied over the years by the circular dichroism (CD) spectroscopy, and many examples are available in the literature demonstrating employment of the exciton chirality method for stereochemical studies<sup>6</sup>. To study such phenomena, relevant dichromophoric molecular structures are required. Because of a proper molecular geometry bridged bicyclic compounds are suitable model structures for studying chiroptical properties and interaction between the nonconjugated chromophores<sup>7</sup>.

#### 1.1.1 A study of planar chromophores in dichromophoric molecules by circular dichroism spectroscopy

For an experimental study of chiroptical properties and application of rules relating to the sign of the Cotton effect (CE) to the absolute configuration the enantiomerically pure compounds of the bicyclo[3.3.1]nonane framework containing carbonyl and planar aromatic 1,2-methylenedioxybenzene, indole chromophores have been synthesized. Natural compounds with indole fragment are widespread among alkaloids<sup>8</sup>. In turn, the

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<sup>4</sup> Berova, N.; Bari, L. D.; Pescitelli, G. *Chem. Soc. Rev.* **2007**, *36*, 914–931.

<sup>5</sup> Crawford, T. *Theor. Chem. Acc.* **2006**, *115*, 227–245.

<sup>6</sup> (a) Ko, J.; Morinaka, B. I.; Molinski, T. F. *J. Org. Chem.* **2011**, *76*, 894–901. (b) Pescitelli, G.; Bari, L. D.; Berova, N. *Chem. Soc. Rev.* **2011**, *40*, 4603–4625. (c) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2007**, *108*, 1–73

<sup>7</sup> (a) Butkus, E.; Berg, U.; Žilinskas, A.; Kubilius, R.; Stončius, S. *Tetrahedron: Asymm.* **2000**, *11*, 3053–3057. (b) Butkus, E.; Stončius, S.; Žilinskas, A. *Chirality* **2001**, *13*, 694–698. (c) Orentas, E.; Bagdžiūnas, G.; Berg, U.; Žilinskas, A.; Butkus, E. *Eur. J. Org. Chem.* **2007**, 4251–4256.

<sup>8</sup> Finefield, J. M.; Frisvad, J. C.; Sherman, D. H.; Williams, R. M. *J. Nat. Prod.* **2012**, *75*, 812–833.

alkaloids with 1,2-methylenedioxybenzene fragment (podophyllotoxin and lycorine) are cytotoxic and were tested as potential anticancer drugs<sup>9</sup>.

The (+)-(*1S,5S*)-bicyclo[3.3.1]nonane-2,6-dione **1** was obtained in an enantiomerically pure form by kinetic resolution of the corresponding racemic diketone by using Baker's yeast.<sup>10</sup> Monoprotected acetal derivative **5** and pyrocatechol acetals **2** and **3** were obtained by acetalization reactions. Reaction of **1** with an equimolar amount of benzene-1,2-diol (pyrocatechol) in toluene exclusively afforded monoacetal **2** in excellent yield. Treatment of **1** with an excess of benzene-1,2-diol afforded the bisacetal derivative **3**. Eleven distinct signals in the <sup>13</sup>C NMR spectrum are consistent with the C<sub>2</sub> molecular symmetry of **3**. The compound **7** with the 1,2-methylenedioxybenzene reference chromophore was synthesized *via* the protected monothioacetal derivative **6** obtained from **2** and subsequent reduction of the protective group with Raney nickel. It should be noted that the direct Wolff–Kishner reduction of carbonyl group in **2** gave a mixture of compounds which could not be purified. The reaction of the mono pyrocatechol acetal **2** with phenylhydrazine in the presence of a catalytic amount of hydrochloric acid under Fischer indolization reaction conditions afforded the indole derivative **4** in excellent yield. CD data for compounds **8**<sup>11</sup>, **9**<sup>12</sup> and **10**<sup>13</sup> reported earlier were used for comparison (**Scheme 1**).

The application of the CD spectral data to analyze the sign of the CE and relating it with the absolute configuration is achieved when the chiral compound possesses a rigid skeleton or is in a predictable geometry. We performed a lowest energy conformational search of **2–5** and **7** with Spartan program<sup>14</sup> using the Monte–Carlo method and MMFF94 force field. For all the investigated compounds **2–5** and **7**, the double chair (*chair-chair*) conformation was found to be the most stable and prevailed over other conformations. The conformational analysis revealed that for all the compounds investigated a single conformer, i.e. *chair-chair* is prevailing in the gas phase at room temperature.

The CD spectra of compounds **2–5** and **7** in ethanol were analyzed in order to study input of the chromophores into the Cotton effect (CE) and to relate the latter to the absolute configuration of the enantiomers. Compounds **5** and **7** are regarded as molecules having the reference chromophores, the carbonyl and the 1,2-methylenedioxybenzene, respectively.

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<sup>9</sup> Chen, G. L.; Yang, L.; Rowe, T. C.; Halligan, B. D.; Tewey, K. M.; Liu, L. F. *J. Biol. Chem.* **1984**, *259*, 13560–13566.

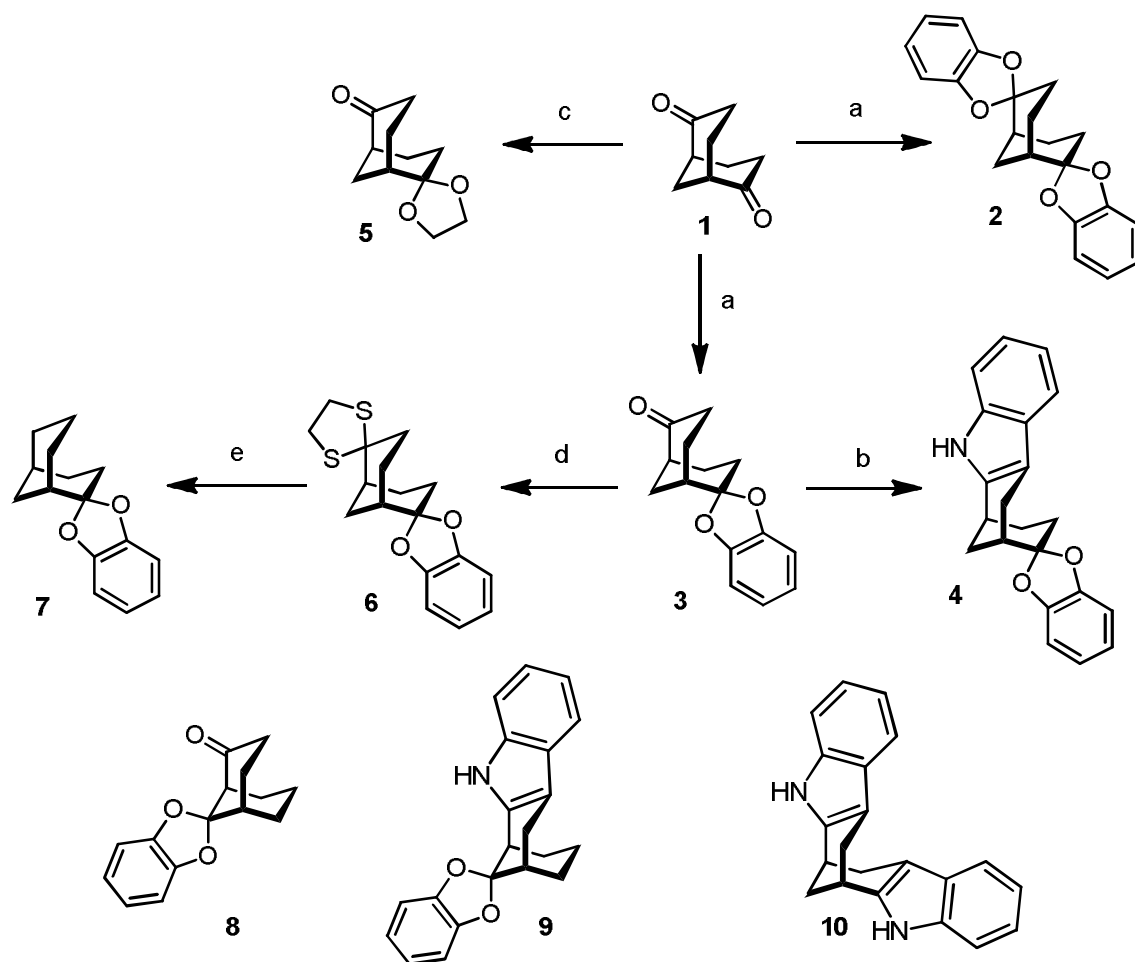
<sup>10</sup> Wallentin, C. J.; Orentas, E.; Butkus, E.; Warnmark, K. *Synthesis* **2009**, 864–867.

<sup>11</sup> Butkus, E.; Berg, U.; Stončius, A.; Rimkus, A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2547–2552.

<sup>12</sup> Butkus, E.; Malinauskienė, J.; Stončius, S. *Org. Biomol. Chem.* **2003**, *1*, 391–394.

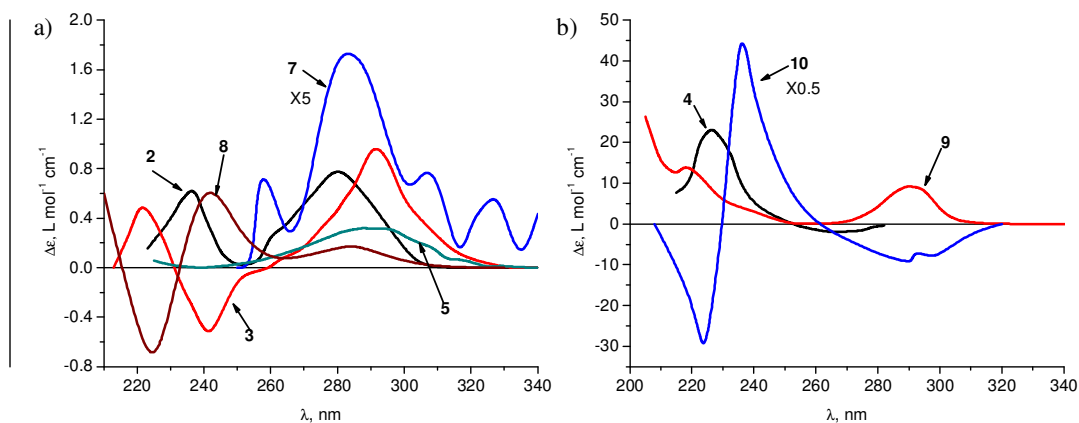
<sup>13</sup> Butkus, E.; Berg, U.; Malinauskienė, J.; Sandström, J. *J. Org. Chem.* **2000**, *65*, 1353–1358.

<sup>14</sup> Spartan'10 for Windows Version 1.0.1. 1840 Von Karman Avenue, Suite 370, Irvine, CA 92612: Wavefunction, Inc.; **2010**.



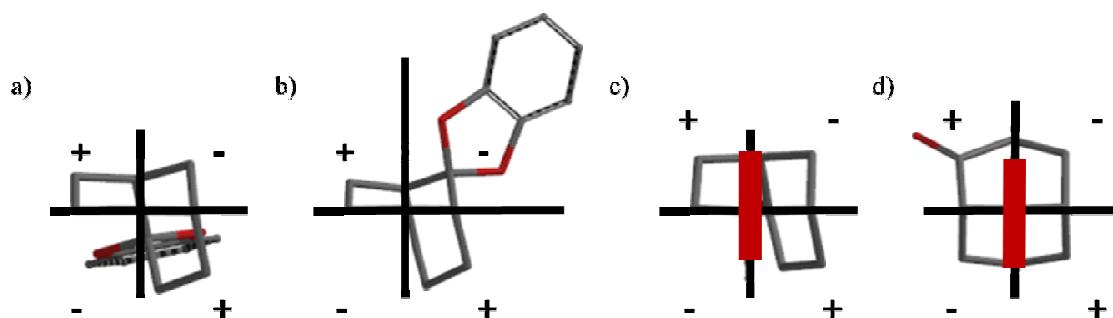
**Scheme 1.** Reagents and conditions: a) Benzene-1,2-diol, PhMe,  $\Delta$ ; b) PhNHNH<sub>2</sub>, EtOH, HCl (cat.),  $\Delta$ ; c) 1) 1,2- ethanediol, TsOH (cat.), PhMe, 3 Å MS,  $\Delta$ ; 2) TsOH (cat.), acetone, 40°C.; d) 1,2- ethanedithiol, BF<sub>3</sub>·OEt<sub>2</sub> (cat.), PhH, RT; e) Ra-Ni, EtOH,  $\Delta$ .

The  $n \rightarrow \pi^*$  transition of the carbonyl chromophore or catechol  $^1L_b$  transition in the CD spectrum of **3** appears around 290 nm giving a positive CE and the intensity is typical for such a chromophore. The CD spectrum of enantiomer **7** exhibited positive fine structure of band at around 280 nm. Dipyrocatechol acetal **2** with  $C_2$  symmetry contains two 1,2-methylenedioxybenzene chromophores, however no exciton coupling was observed in the CD spectrum. The  $^1L_b$  transition is either electrically or magnetically forbidden for this chromophore; however the rotational strength is still generated by a chiral environment. The UV absorption of **3** as well as the CD bands is analogous to compound **7** containing a single 1,2-methylenedioxybenzene chromophore (**Figure 1**).



**Figure 1.** CD spectra of compounds **2-10**: a) dipyrocatechol acetal **2** (black), 2,6-ketocatechol **3** (red), **5** (green), monocatechol **7** (blue), 2,9-ketocatechol **8** (brown); b) 2,6-katecholindole **4** (black), 2,9-katecholindole **9** (red), diindole **10** (blue).

Two bands at 270 and 230 nm in CD spectrum of compound **4** were observed. However, the interpretation of the experimental CD spectrum and the assignment of observed CE's to particular electronic transitions are rather complicated due to the fact that both indole and 1,2-methylenedioxybenzene (catechol) chromophores exhibit transitions at the same wavelength. For the indole chromophore bands are observed at about 300 nm ( $^1L_b$  transition), 290 nm ( $^1L_a$ ) and 230 nm ( $^1B_b$ ) and below 210 nm ( $^1B_a$ ), whereas the 1,2-methylenedioxybenzene chromophore exhibits bands at about 280 nm ( $^1L_b$ ) and 240 nm ( $^1L_a$ ). The superimposition of the above mentioned bands of the same or opposite signs give resultant positions and magnitudes of the CEs in the CD spectrum of **4** (Figure 1).



**Figure 2.** Location of carbonyl (a, b) and catechol (c, d) chromophore of ketoacetals **3, 8** (red line – catechol chromophore) into octants.

To interpret the CD spectra of ketocatechols **3, 8** and the acetal **7** we applied the sector and octant rules, developed for the 1,2-dioxophenylene and carbonyl chromophore; in the case of **3**, the two rules predicts the positive CE sign (Figure 2 a, c). Herewith, the *ab initio* calculations of the CD spectrum of **3** with TD-DFT B3LYP/aug-cc-PVDZ method shown that CD spectrum band at around 290 nm can be assigned to

carbonyl group  $n \rightarrow \pi^*$  transition. Thus, for the compounds **3**, **8** only the octant rule can be applied to relate the absolute configuration with the sign of CE at 290 nm (**Figure 2** a, b). Accordingly, the exciton coupling in CD spectrum of dichromophoric compound **2** is not observed since the angle between  $^1L_a$  transitions is nearly parallel. Location of any of chromophores in sectors gives the positive CE in contrary to compound **7** and the sector rule for 1,2-methylenedioxybenzene chromophore is applicable for this compound (**Figure 2** c). The transitions of indol chromophores of compound **10** are not parallel consequently exciton interaction between indoles is observed<sup>13</sup>.

Calculations of the CD spectrum of compound **4** by TD-DFT/CAM-B3LYP/6-311G++(dp) method showed that CD spectrum band at 290 nm can be assigned to charge transfer from catechol to indole chromophore. Therefore, we believe that it is possible to apply a charge transfer rule, postulated for chiral metal complexes: charge transferred clockwise induces a negative CE (compound **4**), whereas anticlockwise transition induces positive CE (compound **9**)<sup>15</sup>.

### 1.1.2 Synthesis of diastereomeric bicyclo[3.3.1]nonane dibenzoyl esters and study of their chiroptical properties

Herein, we present the synthesis of chiral diastereomeric bicyclo[3.3.1]nonane dibenzoyl esters **12**, **13**, and **17** and the respective monoesters **15** and **16** (**Scheme 2**), and a study of their CD spectra. The benzoate chromophores with an intense  $\pi \rightarrow \pi^*$  absorptions are classical excitons that give rise to a characteristic pair of CD bands with opposite signs originating from the  $^1L_a$  transitions<sup>16</sup>. The conformational analysis of the diastereomeric dibenzoates **12**, **13**, and **17** was performed, and dependence of the CD spectra on the conformational ambiguity was studied by using TD-DFT methodology.

The reduction of carbonyl groups in **1** as well as in **5** with sodium borohydride afforded exclusively *endo*-isomer as was proved for the racemic compound<sup>17</sup>, leading to *endo*, *endo*-2,6-diol **11**. *Endo,endo*-dibenzoate **12** was obtained by a standard benzylation procedure (**Scheme 2**). The inversion of the *endo* configuration of substituents in the bicyclo[3.3.1]nonane molecule has not been described previously to our knowledge. The *exo,exo*-dibenzoate **13** was synthesized from diol **11** by a Mitsunobu reaction with diisopropyl azodicarboxylate via adducts with triphenylphosphine and inversion of the configuration.

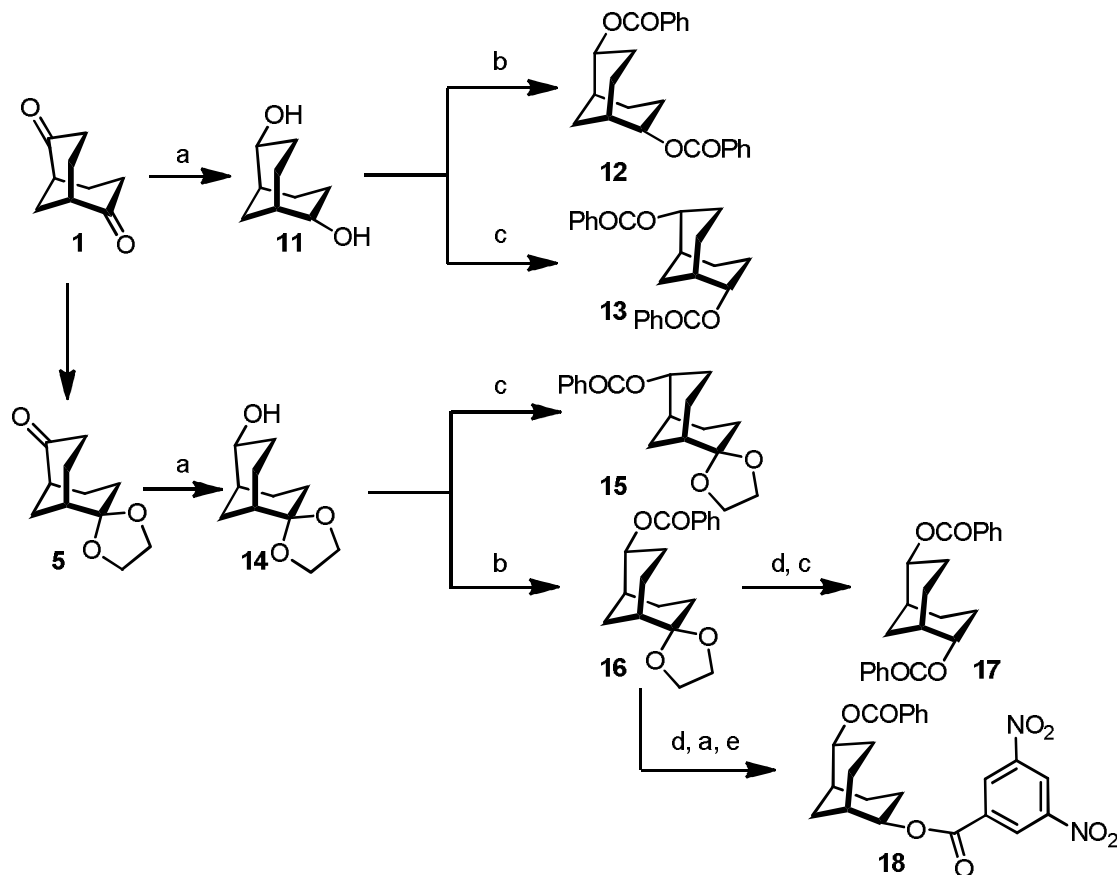
Synthesis of the *endo,exo*-diester **17** involved the reduction of monoacetal **5** with  $\text{NaBH}_4$ , followed by selective benzylation of the intermediate *endo*-alcohol **14** under Mitsunobu or standard conditions to give the corresponding *exo*-monobenzoates and *endo*-monobenzoates **15** and **16**, respectively. Subsequent deprotection of the *endo*-monobenzoate **16** with *p*-TsOH in acetone afforded the corresponding carbonyl

<sup>15</sup> Ziegler, M.; von Zelewsky, A. *Coordin. Chem. Rev.* **1998**, *177*, 257–300.

<sup>16</sup> Grajewski, J.; Gawronska, K.; Gawronski, J. *Monatsh. Chem.* **2005**, *136*, 447–459.

<sup>17</sup> Butkus, E.; Malinauskiene, J.; Kadziauskas, P. *Z. Chem.* **1980**, *20*, 103–103.

derivative, the reduction of which followed by Mitsunobu reaction or benzylation with 3,5-dinitrobenzoyl chloride yielded *endo,exo*-dibenzoate **17** or dibenzoate **18** (Scheme 2).



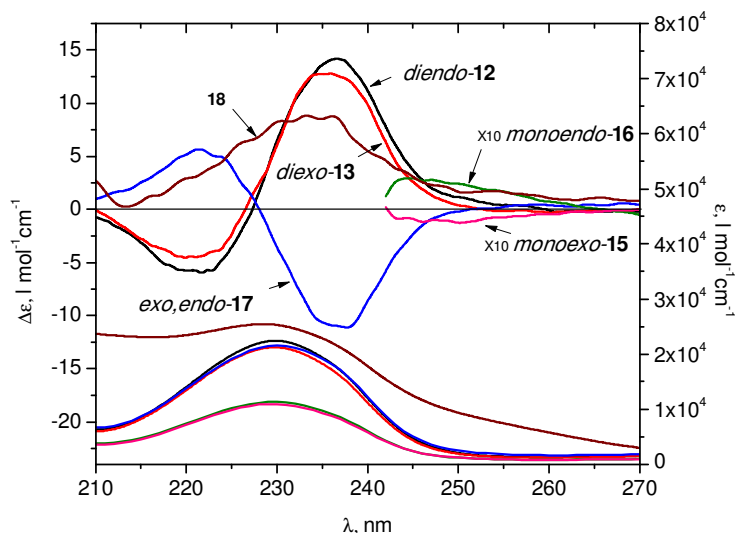
**Scheme 2.** Reagents and conditions: a) NaBH<sub>4</sub>, MeOH, 0°C; b) PhCOCl, DIPEA, DMAP (cat.), CH<sub>2</sub>Cl<sub>2</sub>, 0°C → 40°C; c) PhCO<sub>2</sub>H, Ph<sub>3</sub>P, DIAD, THF, 0 → 60°C; d) *p*-TsOH·H<sub>2</sub>O (cat.), acetone, 40°C; e) 3,5-dinitrobenzoyl chloride, DIPEA, DMAP (cat.), CH<sub>2</sub>Cl<sub>2</sub>, 0°C → 40°C.

In general, for all diastereomeric dibenzoates MMFF94 calculations predict three (four in the case of **17** and **18**) stable chair-chair conformations. The benzoate moieties adopt conformation typical for alkyl benzoates<sup>18</sup>, that is, *trans* conformation around the benzoate O=C–O bond with the ester carbonyl group *syn* with respect to bicyclic methine H – C 2,6 hydrogens.

In the experimental CD spectra of the dibenzoates **12**, **13**, and **17**, the exciton couplet located at the chromophore <sup>1</sup>L<sub>a</sub> transition wavelength near 230 nm was observed, but the exciton couplet in benzoate with different chromophores **18** has not been observed. In concordance with the exciton-type coupling, the strong absorption maxima at the same wavelength are observed in the UV spectra. For *diendo* and *diexo* benzoates **12** and **13**, the positive intense exciton couplet due to coupling between the two <sup>1</sup>L<sub>a</sub> transitions was observed, whereas the *endo,exo*-benzoate **17** exhibited couplet of the

<sup>18</sup> Pescitelli, G.; Bari, L. D.; Berova, N. *Chem. Soc. Rev.* **2011**, *40*, 4603–4625.

opposite sign and virtually the same intensity. Unequivocally, the exciton through-space coupling was confirmed by a comparison with the respective mono congeners **15** and **16**, the CD spectra of which were of a very low intensity. We believe that positive CD spectrum band at 230 nm of **18** creates anticlockwise charge transfer from benzoate to dinitrobenzoyl chromophore (**Figure 3**).



**Figure 3.** CD and UV spectra of **12** (black), **13** (red), **15** (pink), **16** (green), **17** (blue), **18** (brown).

The solvent effect (solvatochromism) on the CD spectra of the dibenzoates **12**, **13**, and **17** was also studied. The CD spectra were recorded in solvents of different polarity — ethanol, dichloromethane, cyclohexane, 2,2,2-trifluoroethanol, however, no significant effect on the intensity and position of the respective CEs was observed. This indicates that the dielectric constant of media has no major effect on the conformational distribution or conformers exhibit very similar CD spectra in terms of intensity and position.

The CD spectra were calculated using Gaussian software<sup>19</sup>. The predicted spectra for the individual conformers of diesters **12** and **13** using TD-DFT with the 6-31G (d) basis set and the B3LYP model were very similar regarding the pattern, absolute and relative intensity of the Cotton effects. In each case, a strong positive couplet due to exciton coupling between <sup>1</sup>L<sub>a</sub> transitions was predicted. Theoretical calculations have shown that the intensity of the split Cotton effect for the vicinal dibenzoates is maximal at a dihedral angle of ca. 70° and is inversely proportional to the square of the interchromophoric distance. From the obtained data, it was estimated that the exciton coupling between the benzoates are only up to about 12 Å.

<sup>19</sup> Gaussian 03, Revision C.02. Wallingford CT: Gaussian, Inc.; **2004**.



### 1.1.3 Synthesis of chiral bicyclo[3.3.1]nonane $\alpha,\beta$ -unsaturated carboxylic acids and nitrile derivatives

The synthesis of  $\alpha,\beta$ -unsaturated carboxylic acids has gained attention because of their occurrence in natural products such as shikimic acid<sup>20</sup> and heteroyohimbine alkaloids<sup>21</sup>. The  $\alpha,\beta$ -unsaturated carbonyl compounds are also important models for studying chiroptical properties<sup>22</sup>.

Using the classical way, conjugated acids were prepared from ketone or aldehyde cyanohydrins by sequential dehydration using phosphorous oxychloride/pyridine or thionyl chloride followed by acidic or alkaline hydrolysis of the resulting conjugated nitriles. Quast et al. used this method for synthesis a bicyclo[3.3.1]nona-2,6-diene-2,6-dicarbonitrile and 2,6-dicyanobarbaralanes from racemic bicyclo[3.3.1]nonane-2,6-dione **1**<sup>23</sup>. We have improved this method for synthesis enantiomeric pure dinitrile **20** intermediate.

We used other catalyst for nucleophilic addition of TMSCN to diketone **1**. The catalyst Cu(OTf)<sub>2</sub> in this case is more effective than ZnI<sub>2</sub><sup>24</sup>. The cyanohydrins **19** were dehydrated using phosphorous oxychloride and pyridine and the obtained dinitrile **20** was hydrolyzed with concentrated HCl in acetic acid. Also, we tried another way to get diacid **21** via an addition of bromoform to ketone **1** in alkaline conditions. Unfortunately, only keto unsaturated carboxylic acid **23** was isolated. It is likely that this reaction takes place through oxatricyclic intermediate **22**. The similar compound was isolated and identified by Quast<sup>25</sup>. The oxatricyclic intermediate **22** was easily hydrolyzed in acidic conditions (Scheme 3).

We performed a lowest energy conformational search of dinitrile **20**, diacid **21** and monoacid **23** using the Monte–Carlo method and MMFF94 force field. For all the investigated compounds **20**, **21** and **23**, the double chair (*c-c*) conformation was found to be the most stable and prevailed over other conformations. However, in compounds **21** and **23** the carboxyl substituent can be either *cis* or *trans* about the C=C-C=O bond. All of the three possible conformers of **21** and **23** were optimized at the DFT/B3LYP/6-31G(d) level to give the lowest energy for the *trans-trans* and *trans* respectively. We

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<sup>20</sup> Rapoport, H.; Windgassen, R. J.; Hughes, N. A.; Onak, T. P. *J. Am. Chem. Soc.* **1960**, *82*, 4404–4414.

<sup>21</sup> Finch, N.; Taylor, W. I.; Emerson, T. R.; Klyne, W.; Swan, R. J. *Tetrahedron* **1966**, *22*, 1327–1333.

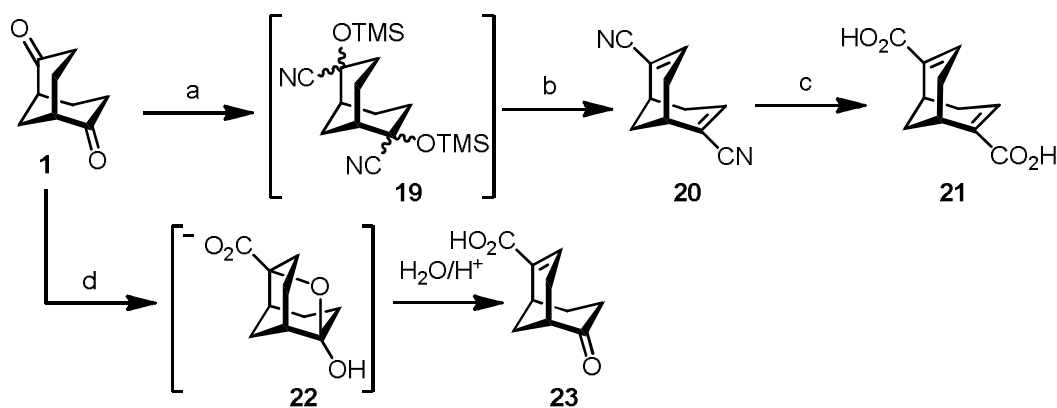
<sup>22</sup> Orentas, E.; Bagdžiūnas, G.; Berg, U.; Žilinskas, A.; Butkus, E. *Eur. J. Org. Chem.* **2007**, 4251–4256.

<sup>23</sup> Quast, H.; Görlach, Y.; Stawitz, J.; Peters, E.-M.; Peters, K.; Schnering, H. G. V. *Chem. Berichte* **1984**, *117*, 2745–2760.

<sup>24</sup> Saravanan, P.; Anand, R. V.; Singh, V. K. *Tetrahedron Lett.* **1998**, *39*, 3823–3824.

<sup>25</sup> Quast, H.; Becker, C.; Witzel, M.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Lieb. Ann.* **1996**, 985–997.

conducted conformational analysis of dinitrile **20**, which gave only one conformer which nitrile  $\pi$  orbitals are conjugated with C=C bond.



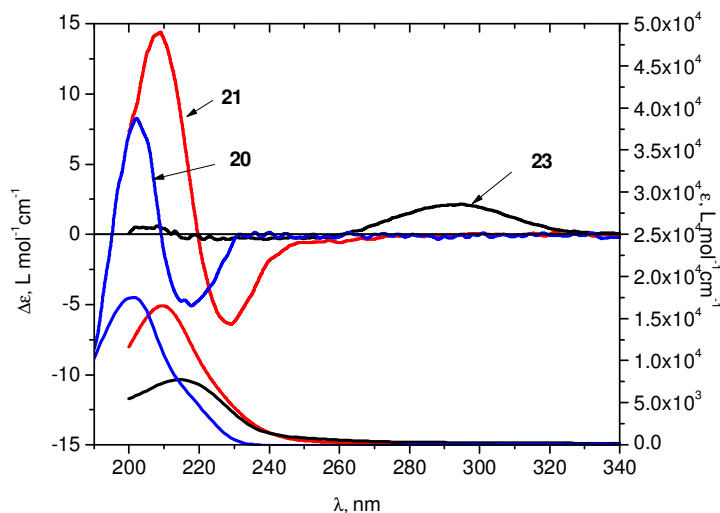
**Scheme 3.** Reagents and conditions: a) TMSCN, Cu(OTf)<sub>2</sub> (cat.), CH<sub>3</sub>CN, 80°C, Ar, 3 h.; b) POCl<sub>3</sub>, Py, Ar,  $\Delta$ ; c) conc. HCl, AcOH,  $\Delta$ ; d) CHBr<sub>3</sub>, LiOH·H<sub>2</sub>O, TEBA (cat.), *t*-BuOH/H<sub>2</sub>O, Ar, RT.

The positive CE around 290 nm in the CD spectrum of **23** is assigned to  $n \rightarrow \pi^*$  transition of the carbonyl group and the intensity is typical for such a chromophore (**Figure 4**). The sign of this CE can be accurately predicted using the octant rule for carbonyl chromophore (**Figure 5a**). However, the interpretation of the experimental CD spectra of **20**, **21** and the assignment of observed CE's to particular electronic transitions are rather complicated because the strong absorption bands are not the exciton-type coupling. Linhard et al assigned the CD spectra bands around 230 nm of  $\alpha$ ,  $\beta$ -unsaturated acid esters to  $\pi \rightarrow \pi^*$  transition and related the sign of CE's with the intrinsic chirality of the unsaturated moiety, reflected by the twist of carbonyl group of carboxylate in relation to C=C bond.<sup>26</sup> However, the carboxyl and C=C chromophore in diacid **21** is twisted by very small angle around 4.1° and nitrile **20** substituent is not twisted, but negative CE's bands at 229 and 217 nm were observed (**Figure 4**).

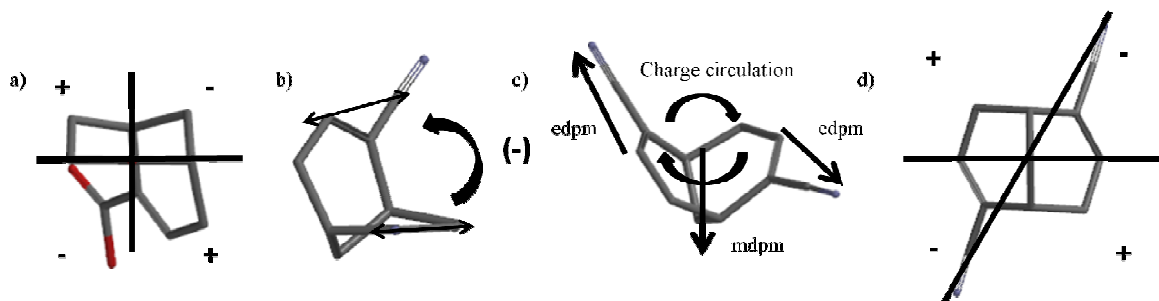
Moreover, calculations of the CD spectrum of compound **20** with DT-DFT/B3LYP/6-31G(dp)) method and analysis of molecular orbitals has shown that CD spectrum negative band at 217 nm can be assigned to  $\pi \rightarrow \pi^*$  transition and to charge transfer within acrylonitrile (C=C-CN) chromophores. In this case a negative CE is created due to twisted intrachromophoric  $\pi$  orbitals like *syn*-dienes (**Figure 5b**)<sup>27</sup>.

<sup>26</sup> Vlahov, I. R.; Bazin, H. G.; Linhardt, R. J. *Chem. Commun.* **1998**, 1819–1820.

<sup>27</sup> Snatzke, G. *Angew. Chem. Int. Ed.* **1979**, *18*, 363–377.



**Figure 4.** CD and UV spectra of dinitrile **20** (blue) in MeCN, diacid **21** (red) and ketoacid **23** (black) in EtOH.



**Figure 5.** a) Projection of monoacid **23** into octants; b) twist of acrylonitrile chromophores for **20**; c) inductions of charge circulations within acrylonitrile for **20** and d) sectors rule of imaginary aromatic system for **20**.

Also calculations for compounds **20** and **21** has shown the orbital overlap between acrylonitrile chromophores C=C molecular orbitals due to a very small interchromophoric distance between the two chromophores (3.1 Å). Therefore exciton interaction was not observed, but that distance creates an opportunity to interact interchromophoric  $\pi$  orbitals, which in turn creates a charge circulation between the unsaturated bicyclic fragments (**Figure 5c**). For these unsaturated fragments sectors rule could be applied and positive CE's was predicted (**Figure 5d**).

## 1.2 Synthesis of chiral supramolecular polycyclic tectons and investigations of their association

Various  $C_3$  symmetric planar multifunctional compounds are widely tested for their capability to form strong non-covalent associates. Variation of the peripheral flexible chains and of the aromatic core is decisive for the tuning of self-assembly in solution and in bulk. Supramolecular organization of discotic molecules can be effectively controlled by the choice of the aromatic and periphery functional groups<sup>28</sup>.

On the other hand, metallo-supramolecular complexes have attracted attention of synthetic chemists because of their pre-programmed self-assembly into supramolecular systems and their application in host-guest chemistry, cavity controlled reactions and photophysical properties<sup>29</sup>.

### 1.2.1 Synthesis of chiral bicyclo[3.3.1]nonane mono- and trifunctional aromatic derivatives and their supramolecular association

Mono-**25**, **26** and trifunctional compounds **27-33** with the lateral bicyclo[3.3.1]nonene substituent were synthesized (**Scheme 4**). The tris-**27**, **29**, **32** and corresponding monofunctional ketones **25** and **26** were obtained from (*S,S*)-6-oxobicyclo[3.3.1]non-2-en-2-yl triflate **24** via palladium catalyzed Suzuki and Sonogashira reactions in good yields. We have shown that the optimum conditions of Suzuki reactions are Pd(Ph<sub>3</sub>P)<sub>4</sub> (3 mol%), PhB(OH)<sub>2</sub> (150 mol%), CsF (200 mol%), THF, Ar, 60°C and Sonogashira - Pd(Ph<sub>3</sub>P)<sub>4</sub> (3 mol%), PhC≡CH (150 mol%), TEA (150 mol%), AgOTf (15 mol%), THF, Ar, 60°C, respectively. We would like to highlight that under these Sonogashira reaction conditions dimerization of terminal alkyne does not occur.

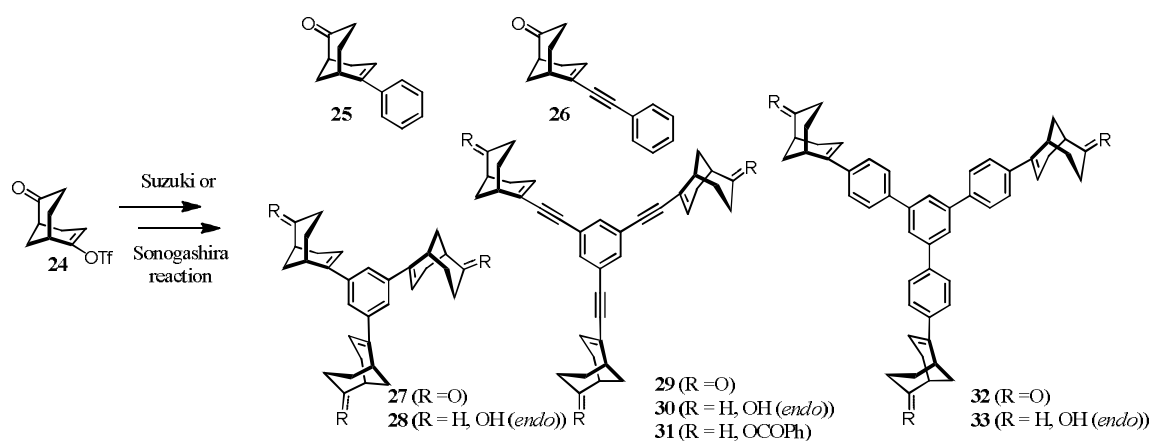
Treatment of **27**, **29** and **32** with an excess of sodium borohydride afforded the *triendo*- alcohols **28**, **30** and **33**. The triester **31** was obtained from *triendo* alcohol **30** via standard esterification reaction with benzoyl chloride, triethylamine and catalytic amount of 4-dimethylaminopyridine (**Scheme 4**).

The structure of the compounds has been confirmed by <sup>1</sup>H and <sup>13</sup>C NMR data. We conclude from <sup>13</sup>C NMR spectra that all the compounds **27-33** exist in  $C_3$  symmetry. The conformational analysis was performed using Monte-Carlo method and molecular mechanics MMFF94 force field. All of the possible conformers were optimized by the B3LYP/6-311G(d) (for **25-30**) and semi-empirical/PM6 (**31**, **32** and **33**) methods in vacuum. The calculations predicted two stable conformers for compound **25**, with phenyl ring turned at different angles (42 and -27°, respectively). Calculations of **26** structure predicted only one conformer in which the phenyl chromophore is parallel to C=C bond of bicyclic fragment. These observations apply to tris functional compounds **27-30**, **32**

<sup>28</sup> Sergeev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902-1929.

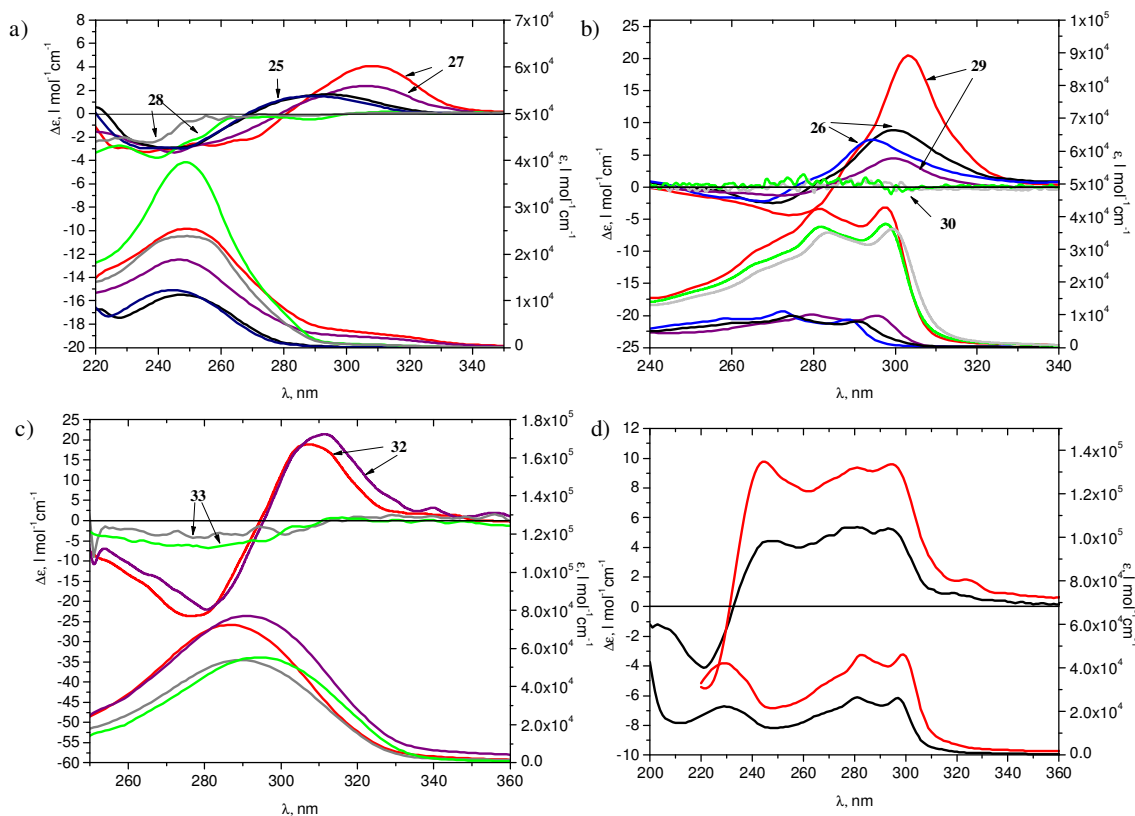
<sup>29</sup> Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810-6918.

and **33**. The molecular mechanics, DFT or semi-empirical calculations forecasted two very similarly distributed conformers, which are in  $C_3$  or  $C_1$  symmetry, respectively. In the triester **31**, four conformers have been predicted because they contribute additional rotomers of benzoate. We noted that for all compounds bicyclo moiety adopts the most stable *chair-chair* conformations. The conformational energy differences for conformers of all compounds are smaller than  $kT_{N_A}$  (0.6 kcal/mol), indicating they are in dynamic equilibrium at room temperature in vacuum.

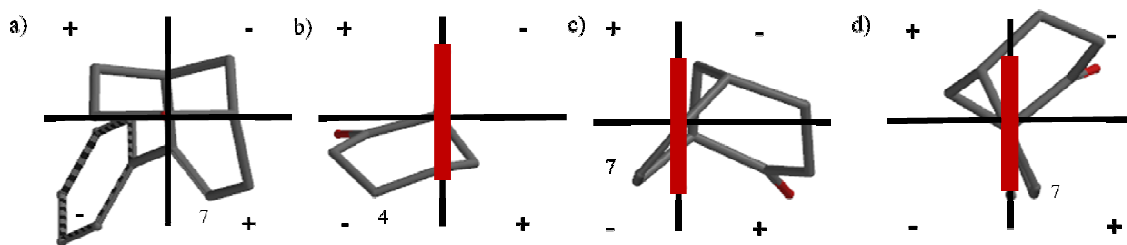


**Scheme 4.** The synthesized tris-**27-33** and monofunctional **25, 26** derivatives.

In the experimental CD spectra of all mono **25, 26** and tris functional ketones **27, 29, 32** positive CE around 290-300 nm was assigned to  $n \rightarrow \pi^*$  transition of a carbonyl group (**Figure 6**). Accordingly, such bands in CD spectra of alcohols **28, 30** and **33** were not monitored. However, small intensity negative CE band in the CD spectra of alcohols and ketones around 240-280 nm can be assigned to phenyl chromophore  $^1L_b$  transition. TD-DFT calculations of the CD spectra for the individual conformers of **25** and **26** using the 6-31G(dp) basis set and the B3LYP model confirmed these observations. Thus, the positive and negative signs of CE's can be accurately predicted using the octant rule for carbonyl and sector rule for phenyl chromophores, respectively (**Figure 7**).



**Figure 6.** CD and UV spectra of **25-33**: a) **25** (black), **27** (red), **28** (grey) in  $\text{CH}_2\text{Cl}_2$  and **25** (blue), **27** (purple) **28** (green) in EtOH; b) **26** (black), **29** (red), **30** (grey) in  $\text{CH}_2\text{Cl}_2$  and **26** (blue), **29** (purple), **30** (green) in EtOH; c) **32** (red), **33** (grey) in  $\text{CH}_2\text{Cl}_2$  and **32** (purple), **33** (green) in EtOH; d) **31** (red) in  $\text{CH}_2\text{Cl}_2$  and **31** (black) in EtOH.



**Figure 7.** a) Octant rule for ketone **25**; sector rule for phenyl chromophore of b) **26** and c-d) **25** different conformers (red line – Ph or  $\text{C}\equiv\text{C}$ -Ph chromophore)

In the CD spectra of the tribenzoate **31**, the exciton couplet located at wavelength near 230 nm ( $^1\text{L}_a$  transition) was observed. In concordance with the exciton-type coupling, the strong absorption maximum at the same wavelength is observed in the UV spectrum (**Figure 6** d). However, the calculations show that the distance between benzoates in **31** is 18.6 Å. We previously have shown that exciton-type coupling between benzoate chromophores exist only up to 12 Å. So it suggests that this interaction can only

occur in supramolecular sandwich type associates of **31**. In the CD spectra of compounds **27** and **29**, the intensity of CD spectral bands around 300 nm increases in CH<sub>2</sub>Cl<sub>2</sub> compared to EtOH solutions and type of bands in the CD spectrum of tribenzoate **31** suggests the supramolecular association in solution.

Dynamic light scattering (DLS) was used to measure the hydrodynamic size of the particles in diluted (*ca.* 10<sup>-4</sup> M) solutions of **27**, **29**, **31** and **32**. This measurement indicated formation of discrete aggregates in CH<sub>2</sub>Cl<sub>2</sub> solutions of **27**, **29** and **32** with a diameter of 160, 90 and 70 nm, respectively. However, in solution of **31** smaller aggregates with diameter of 4 nm were observed. Consequently, it clearly shows that the compounds are associated to the nanoparticles, but this method does not give any information about the structure and geometry of supramolecular aggregates.

The concentration-dependent UV spectra were utilized for an analysis of the association behavior of **29** (as well as for **27-33**) in CH<sub>2</sub>Cl<sub>2</sub> and DMSO by plotting the experimental absorption data against the total concentrations as shown in **Figure 8**. We used the dimerisation (eq. 1) and isodesmic (eq. 2) models for determination of association constants<sup>30</sup>:

$$\varepsilon(c) = \frac{1}{2} \varepsilon_d + (\varepsilon_m - \frac{1}{2} \varepsilon_d) \cdot \frac{\sqrt{8Kc+1}-1}{4Kc} \quad (1)$$

$$\varepsilon(c) = \varepsilon_p + (\varepsilon_m - \varepsilon_p) \cdot \frac{2Kc+1-\sqrt{4Kc+1}}{2K^2c^2} \quad (2)$$

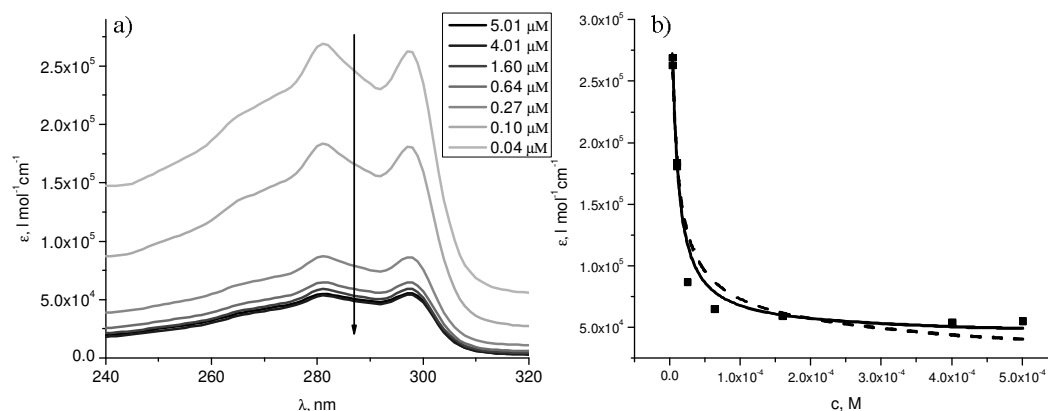
where *c* is the concentration of all species,  $\varepsilon_m$ ,  $\varepsilon_d$  and  $\varepsilon_p$  – extinction coefficient of monomer, dimer and polymer, *K* - association constant.

The obtained data were analyzed using both models and values were calculated employing the model which gave the largest estimated value of the square of the correlation coefficient (*r*<sup>2</sup>). In all cases, the calculated results using isodesmic model provided the best fit to the experimental data and obtained constants are presented in **Table 1**.

We can see some trends from the obtained constants. The association constants of trialcohols are several orders of magnitude higher in CH<sub>2</sub>Cl<sub>2</sub> than in DMSO solutions. This trend is less noticeable in case of triketones. In addition, association constants of trialcohols are higher than of triketones in CH<sub>2</sub>Cl<sub>2</sub> and, respectively, *vice versa* in DMSO. This indicates that the associations are affected by the intermolecular dipole – dipole forces between the alcohol and carbonyl functional groups.

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<sup>30</sup> Chen, Z.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, 38, 564–584.



**Figure 8.** a) Concentration-dependent UV/Vis absorption spectra of **29** in CH<sub>2</sub>Cl<sub>2</sub> at 20°C; b) Dependence of the absorption coefficients at 290 and 300 nm on concentration and fitted plots using dimerisation (---) and isodesmic (—) models.

**Table 1.** Calculated constants of compounds **27-33**

Compound	Solvent	K <sub>a</sub> , M <sup>-1</sup>	r <sup>2</sup>
Triketone <b>27</b>	CH <sub>2</sub> Cl <sub>2</sub>	1.3·10 <sup>4</sup>	0.995
Triketone <b>27</b>	DMSO	1.1·10 <sup>4</sup>	0.988
TriOH <b>30</b>	CH <sub>2</sub> Cl <sub>2</sub>	4.9·10 <sup>4</sup>	0.997
TriOH <b>30</b>	DMSO	1.4·10 <sup>3</sup>	0.968
Trialkynketone <b>29</b>	CH <sub>2</sub> Cl <sub>2</sub>	2.3·10 <sup>5</sup>	0.983
Trialkynketone <b>29</b>	DMSO	5.0·10 <sup>4</sup>	0.997
TrialkynOH <b>30</b>	CH <sub>2</sub> Cl <sub>2</sub>	2.1·10 <sup>6</sup>	0.991
TrialkynOH <b>30</b>	DMSO	5.9·10 <sup>3</sup>	0.984
Triester <b>31</b>	CH <sub>2</sub> Cl <sub>2</sub>	1.9·10 <sup>4</sup>	0.999
Triester <b>31</b>	DMSO	3.5·10 <sup>4</sup>	0.994
Triphenylketone <b>32</b>	CH <sub>2</sub> Cl <sub>2</sub>	1.5·10 <sup>6</sup>	0.977
Triphenylketone <b>32</b>	DMSO	1.3·10 <sup>6</sup>	0.981
TriphenylOH <b>32</b>	CH <sub>2</sub> Cl <sub>2</sub>	1.9·10 <sup>6</sup>	0.995
TriphenylOH <b>32</b>	DMSO	1.7·10 <sup>5</sup>	0.990

Knowing that the association constants were obtained under the same conditions, we can make the correlation analysis of structure and association constants. Assuming that the van der Waals and  $\pi$  -  $\pi$  interaction forces are proportional to the molecular area<sup>31</sup>, and the association between the alcohols and carbonyl functional groups are proportional to the their binding energy, respectively, we can write the formula of correlation (eq. 3):

<sup>31</sup> (a) Eisenberg, D.; McLachlan, A. D. *Nature* **1986**, *319*, 199–203. (b) Ooi, T.; Oobatake, M.; Némethy, G.; Scheraga, H. A. *PNAS* **1987**, *84*, 3086–3090. (c) Still, W. C.; Tempczyk, A.; Hawley, R. C.; Hendrickson, T. *J. Am. Chem. Soc.* **1990**, *112*, 6127–6129.

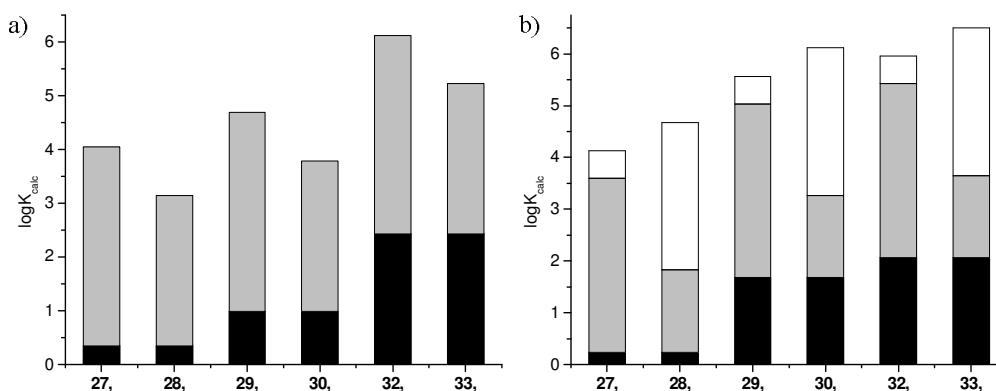


$$\log K = a \cdot S_{\pi} + b \cdot S_{\text{bicyclo}} + c \cdot E \quad (3)$$

where  $S_{\pi}$ ,  $S_{\text{bicyclo}}$  – area of aromatic and bicyclic moiety,  $E$  - binding energy of alcohols and carbonyl functional groups,  $a$ ,  $b$ ,  $c$  – descriptors.

It is known that the calculated hydrogen bonding energy of alcohol is about 5 kcal/mol<sup>32</sup> and energy of dipole – dipole interaction between carbonyls is 2 kcal/mol<sup>33</sup>. In turn, the calculated (DFT/B3LYP/6-31G(d)) area of benzene, 1,3,5-trialkylbenzene and 1,3,5-triphenylbenzene is 115, 208 and 355 Å<sup>2</sup>, respectively, and area of bicyclic moieties (bicyclo[3.3.1]non-6-en-one and bicyclo[3.3.1]non-6-en-ol) is 163 and 169 Å<sup>2</sup>.

Calculations were performed with Solver program<sup>34</sup>. The  $a \cdot S_{\pi}$  component reflects the association due to  $\pi$  -  $\pi$  stacking of the aromatic parts,  $b \cdot S_{\text{bicyclo}}$  – reflects the van der Waals interaction of bicyclic parts and  $c \cdot E$  – part of dipole – dipole interaction between carbonyls and alcohols. We can say that descriptors  $a$ ,  $b$ ,  $c$  are equal for the compounds with the same aromatic, bicyclic moiety and carbonyl or alcohol groups, respectively. For calculation of constants in DMSO solution the dipole – dipole interaction was not taken into account ( $c=0$ ) (**Figure 9**).



**Figure 9.** Correlation of structure and association constants of **27**, **28**, **29**, **30**, **32** and **33** a) in DMSO ( $r^2 = 0.999$ ); b) in CH<sub>2</sub>Cl<sub>2</sub> ( $r^2 = 0,957$ ): the contribution of aromatic (**black**), bicyclic (**grey**) and carbonyl or alcohol (**white**) part to calculated logarithm of association constant.

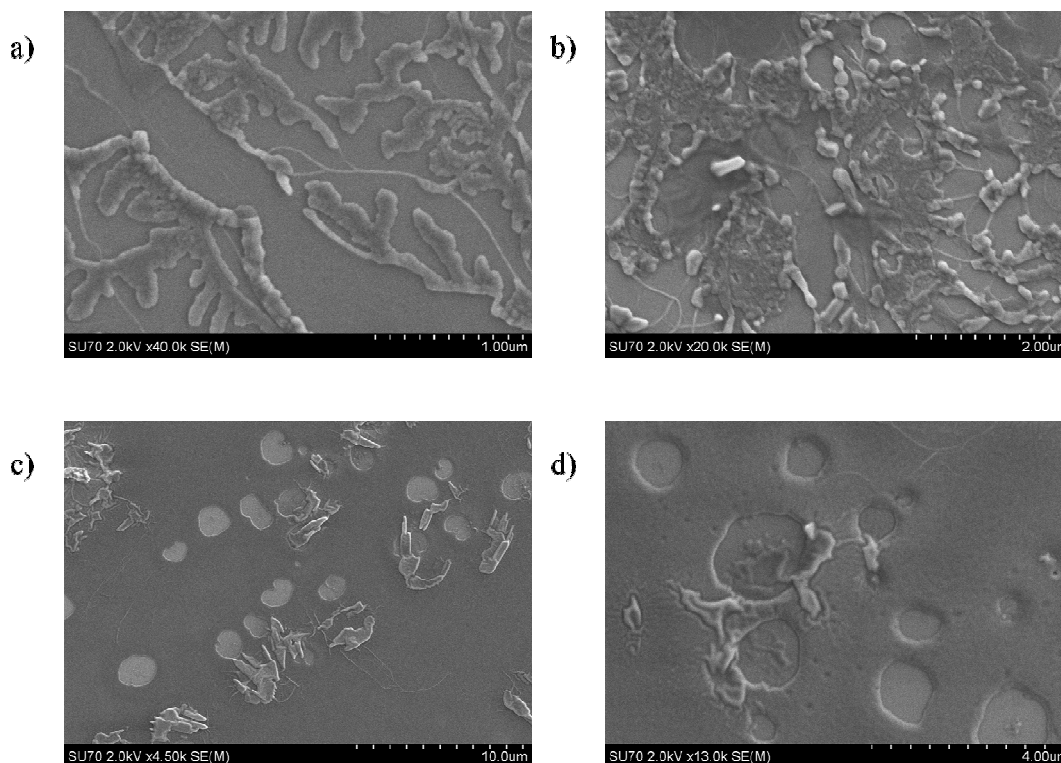
Thus, van der Waals forces of bicyclic parts and hydrogen bond between alcohol groups give the largest contribution to association in DMSO and CH<sub>2</sub>Cl<sub>2</sub>, respectively. It should be noted that in all cases,  $\pi$ - $\pi$  interaction does not have a significant impact on association constants.

<sup>32</sup> (a) Fileti, E. E.; Chaudhuri, P.; Canuto, S. *Chem. Phys. Lett.* **2004**, *400*, 494–499. (b) Bondesson, L.; Mikkelsen, K. V.; Luo, Y.; Garberg, P.; Ågren, H. *J. Mol. Struct.* **2006**, *776*, 61–68.

<sup>33</sup> Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319–4325.

<sup>34</sup> Kemmer, G.; Keller, S. *Nat. Protoc.* **2010**, *5*, 267–281.

It is known from DLS experiments that compounds **27** and **29** in solution exist in the form of nanoparticles. SEM images shown that nanoparticles of **29** and **27** on surface are aggregate in the form of dendrites and nano-plates, respectively (**Figure 10**). This indicates that the compound **27** exists in solution in the form of nano-plates and, furthermore, the particles are sticking together into larger units in order to reduce its surface tension.



**Figure 10.** SEM images of **29** (a, b) and **27** (c, d) from diluted (*ca.*  $10^{-4}$  M)  $\text{CH}_2\text{Cl}_2$  solution on Si(100) surface.

Assembled structures of **29** on surface were examined by X-ray diffraction analysis, which shown a broad pattern with the d-spacing of 20.86, 13.87, 12.17, 7.03, 6.09, 5.06, 4.55, 4.11, 3.71 and 3.03 Å, which were indexed to (100), (110), (001), (300), (002), (400), (420), (430), (440) and (004), respectively. In literature it is known that this type of compounds commonly associate on the surface to hexagonal columnar mesophases<sup>35</sup>. However, the best fit of experimental and calculated d-spacing with the modified hexagonal crystalline lattice parameters  $a = 27.97$  Å,  $c = 18.78$  Å,  $\alpha = 48.7^\circ$ ,  $\beta = 131.3^\circ$  and  $\gamma = 120^\circ$  was obtained. Thus, the 3.03 Å distance between the planes (004) is equal to the distance between the planes of molecules **29** in the lattice. Furthermore, this indicates

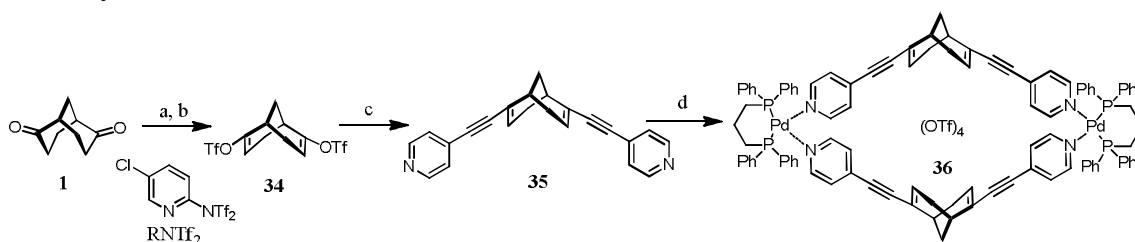
<sup>35</sup> Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887.

that the particles on the surface and probably in solution form regular supramolecular structures.

### 1.2.2 Synthesis of chiral supramolecular palladium complexes and their association

Many research groups prepared ligands with pyridine or nitrile and Troger's base moieties.<sup>36</sup> In the most approaches, chiral ligands are employed to achieve enantio- or diastereoselective assembly, but these processes are non-trivial in predicting when racemic ligands are used. We synthesized chiral and racemic ligand with bipyridyl and bicyclo[3.3.1]nonane moiety and studied self-association into palladium complexes.

Two-step synthesis starting from (*1S,5S*)- or racemic bicyclo[3.3.1]nonane-2,6-dione **1** yielded ligands (*S,S*)-**35** and (*rac*)-**35**. Formation of bisenolate from diketone **1** and trapping with a triflating agent gave ditriflate **34**, which was used as a coupling partner in Sonogashira cross coupling reaction with 4-ethynylpyridine. Mixing equimolar amounts of ligand **35** and Pd(dppp)(OTf)<sub>2</sub> in CDCl<sub>3</sub> resulted in formation of the palladacycle **36** (Scheme 5).



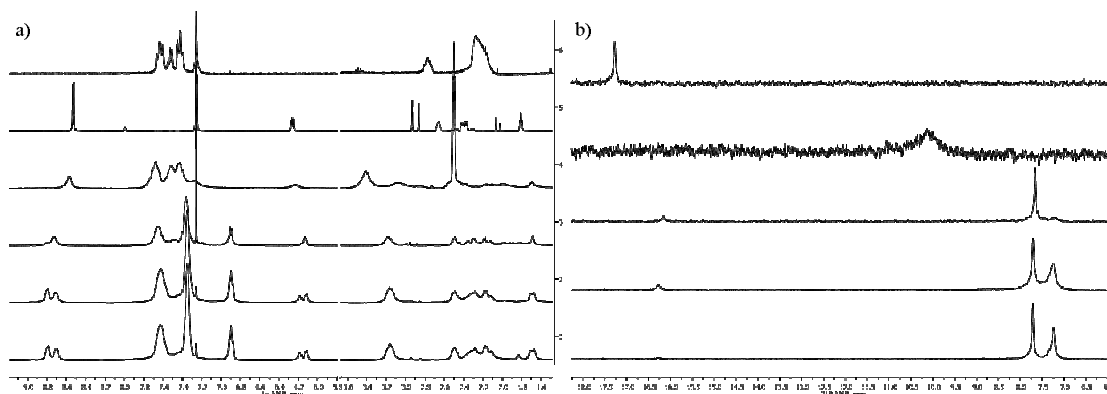
**Scheme 5.** Reagents: a) HMDSLi, TMEDA, THF, -40°C; b) RNTf<sub>2</sub>, THF, -70°C → RT; c) 4-PyC≡CH·HCl, Pd(PPh<sub>3</sub>)<sub>4</sub> (cat.), AgOTf (cat.), TEA, THF, Ar, 50°C, 24 h; d) Pd(dppp)(OTf)<sub>2</sub>, CDCl<sub>3</sub>, RT.

Spontaneous formation of supramolecular coordination complexes was evidenced by distinctive changes of chemical shifts in the NMR spectra (**Figure 11**). Signals corresponding to 2-proton of pyridine ring and phosphorus atom in dppp ligand are shielded and thus are shifted upfield relative to the signal of free ligand **35** and free Pd(dppp)(OTf)<sub>2</sub>. The palladium is *cis*-protected so the right angle is provided for the formation of macrocyclic ring. It is noted that the (*rac*)- and (*S,S*)-**36** complexes in chloroform exist in two forms of rhombs and [2]catenane, as very similar signals are observed in the <sup>1</sup>H and <sup>31</sup>P NMR spectra (*vide infra*). Accordingly, the complex **36** in DMSO solution exists in the polymer form as indicated by the broad signals in the <sup>1</sup>H and <sup>31</sup>P NMR spectra.

<sup>36</sup> (a) Weilandt, T.; Kiehne, U.; Schnakenburg, G.; Lützen, A. *Chem. Commun.* **2009**, 2320-2322. (b) Weilandt, T.; Kiehne, U.; Bunzen, J.; Schnakenburg, G.; Lützen, A. *Chem.-Eur. J.* **2010**, *16*, 2418-2426. (c) Arribas, C. S.; Wendt, O. F.; Sundin, A. P.; Carling, C.-J.; Wang, R.; Lemieux, R. P.; Wärnmark, K. *Chem. Commun.* **2010**, *46*, 4381-4383.

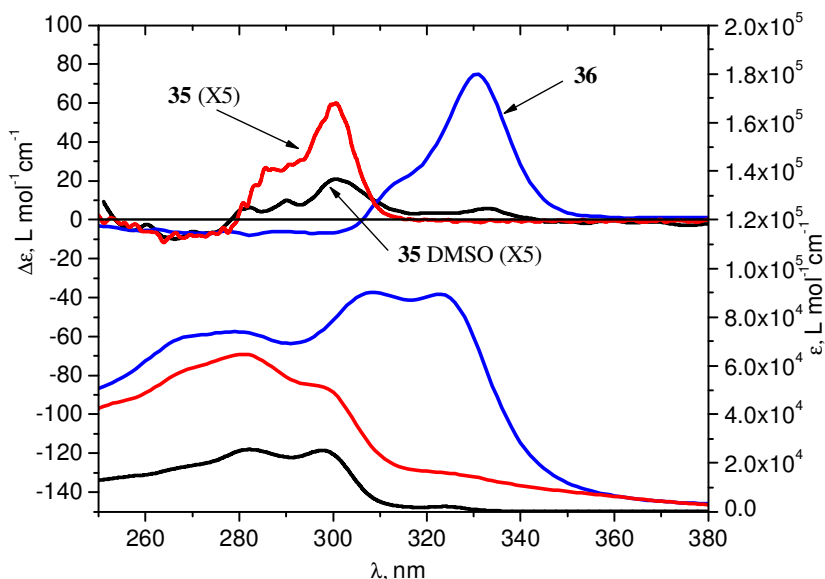
Interestingly,  $^1\text{H}$  NMR spectrum of racemic sample is consistent with that of enantiomerically pure sample, what could be attributed to self-recognition process operating during self-assembly, i.e. each enantiomer of **35** recognizes itself to give a heterochiral complex in the case of the racemic ligand. This was confirmed by performing an additional experiment with a  $\text{Eu}(\text{TFC})_3$  as a chiral shift reagent. No splitting of the signals could be observed in either the  $^1\text{H}$  or  $^{31}\text{P}$  NMR spectra even upon addition of a larger excess of the chiral shift reagent into (*rac*)-**36** solution.

Further information about supramolecular complexes in solution was gained from the MS data. ESI MS spectrum of Pd complex in diluted MeCN solution confirmed the formation of macrocyclic ring  $\text{M}_2\text{L}_2$  and their dimer  $\text{M}_4\text{L}_4$ . The positively charged molecular ions  $m/z$  2129, 1720, 1369, 989, 581 and 420 were observed that correspond to the species  $\text{M}_2\text{L}_2^+$  and  $\text{M}_4\text{L}_4^{2+}$ ,  $\text{M}_3\text{L}_4^{2+}$ ,  $\text{M}_4\text{L}_4^{3+}$ ,  $\text{ML}^+$ ,  $\text{ML}_2^{2+}$ ,  $\text{ML}^{2+}$ , respectively.  $\text{M}_4\text{L}_4^{2+}$  and  $\text{M}_4\text{L}_4^{3+}$  support [2]catenane formation as well.



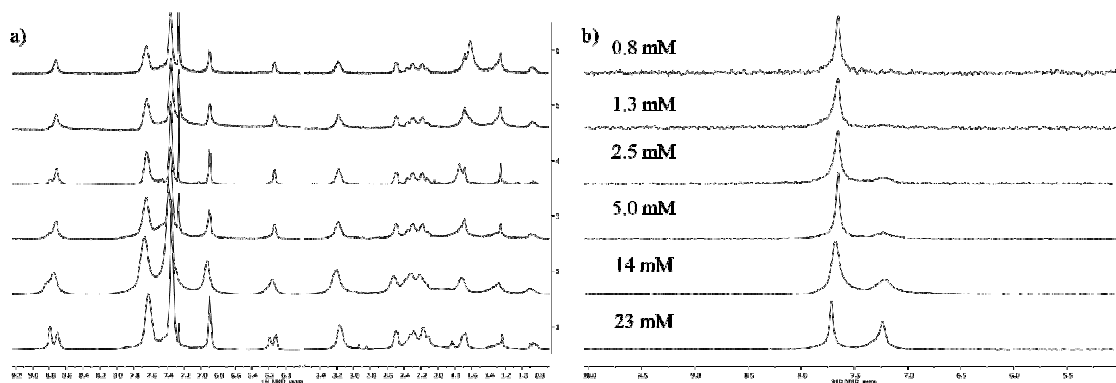
**Figure 11.** a)  $^1\text{H}$  NMR: 1) (*S,S*)-complex **36** (23 mM), 2) *rac*-**36** (30 mM), 3) *rac*- and (*S,S*)- **36** (1:1) (1.8 mM), 4) *rac*-**36** in  $d_6$ -DMSO (4.4 mM), 5) ligand **35**, 6)  $\text{Pd}(\text{dppp})(\text{OTf})_2$  in  $\text{CDCl}_3$ ; b)  $^{31}\text{P}$  NMR: 1) (*S,S*)-**36**, 2) *rac*-**36**, 3) *rac*- and (*S,S*)-**36** 1:1, 4) *rac*- **36** in  $d_6$ -DMSO, 5)  $\text{Pd}(\text{dppp})(\text{OTf})_2$  in  $\text{CDCl}_3$ .

In the CD spectrum of palladacycle rhombs **36**, the positions of the CD bands attributable to the pyridine chromophore are shifted to longer wavelengths as compared to that of free ligand. This observation clearly indicates coordination of the ligand to the Pd(II) centers.



**Figure 12.** CD and UV spectra of ligand **35** (red) and complex **36** (blue in CH<sub>2</sub>Cl<sub>2</sub>, black in DMSO).

A concentration dependent <sup>1</sup>H NMR titration from 23 mM to 0.8 mM range revealed that two supramolecular species are in dynamic equilibrium with each other. The set of proton signals belonging to coordination [2]catenane eventually disappears when concentration of (*S,S*)-complex is decreased. <sup>31</sup>P NMR titration provides complementary results (**Figure 13**).



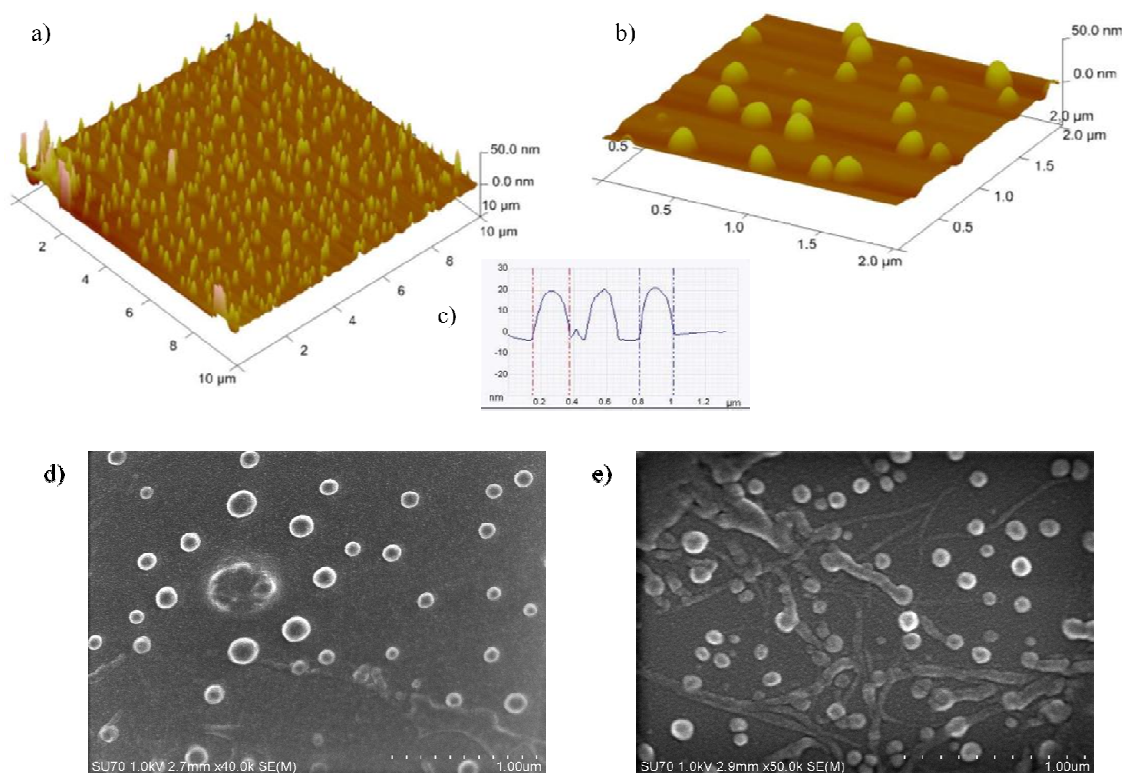
**Figure 13.** <sup>1</sup>H NMR and <sup>31</sup>P NMR titration of **36** in CDCl<sub>3</sub> (conc. decreasing from 23 mM to 0.8 mM from the bottom to the top).

The equilibrium constant ( $K_{\text{cat}} = [\text{Catenane}]/[\text{Rhomb}]^2$ ) was calculated from these titration results using formula 4 and was estimated to be 27 M<sup>-1</sup>.

$$K_{\text{kat}} = \frac{\frac{[\text{Catenane}]}{[\text{Rhomb}]} (2 \frac{[\text{Catenane}]}{[\text{Rhomb}]} + 1)}{c} \quad (4)$$

where  $c$  is the concentration of all species,  $[\text{Catenane}]$ ,  $[\text{Rhomb}]$  – equilibrium concentration of [2]catenane and rhombs.

The DLS experiment of a freshly prepared dilute solution of complex **36** in  $\text{CH}_2\text{Cl}_2$  indicates the coexistence of two species with hydrodynamic radius of approximately 3 nm and 90 nm. The smaller species can be assigned to monomer of **36** and the larger ones are to be the higher order assemblies. The concentration-dependent UV absorption spectra were utilized for an analysis of the aggregation behavior for complex **36**. By using the isodesmic (eq 1) model for aggregation, the association constants of (*rac*)- and (*S,S*)-**36** were estimated to be  $1.2 \cdot 10^5 \text{ M}^{-1}$  and  $1.0 \cdot 10^5 \text{ M}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , indicating that chirality does not affect to association. UV peaks of higher order associates of **36** were shifted to a longer wavelength, indicating the formation of *J*-type associates.



**Figure 14.** AFM (a, b) and SEM (d, e) images of diluted complex **36** solution ( $\text{CH}_2\text{Cl}_2$ ), c) height profiles of the assemblies from AFM.

When diluted complex **36** in  $\text{CH}_2\text{Cl}_2$  solution (*ca.*  $10^{-5} \text{ M}$ ) was applied to Si(100) surface, a formation of spherical objects was observed in AFM and SEM images (**Figure 14**). Particles formed on surface are homogeneous in size (*ca.* 200 nm height and 20 nm width) as estimated with the aid of AFM. Interestingly, the same particles and polymeric aggregates were obtained, when the complex **36** was dissolved in DMSO and then precipitated with  $\text{Et}_2\text{O}$ . In addition, the complex **36** was found to be surface-active

material that reduces surface tension by 2.0%. This property of the molecule may prevent nanoparticles from sticking together.

In literature there are very few examples than the metal complexes exist in stable nanoparticles, however, these particles are amorphous<sup>37</sup>. Nevertheless, X-ray diffraction analysis of nanoparticles has shown that supramolecular rhomb **36** forms regular higher order structure and have triclinic unit cell with parameters:  $a = 21.29 \text{ \AA}$ ,  $b = 16.64 \text{ \AA}$  and  $c = 19.16 \text{ \AA}$ ,  $\alpha = 43.1^\circ$ ,  $\beta = 136.9^\circ$  and  $\gamma = 125.4^\circ$ . Particle/crystallite size as calculated using the Scherrer formula<sup>38</sup> is *ca.* 100 nm which is in good agreement to SEM and AFM results.

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<sup>37</sup> (a) Baytekin, H. T.; Baytekin, B.; Schulz, A.; Springer, A.; Gross, T.; Unger, W.; Artamonova, M.; Schlecht, S.; Lentz, D.; Schalley, C. A. *Chem. Mater.* **2009**, *21*, 2980–2992. (b) Baytekin, H. T.; Baytekin, B.; Schulz, A.; Schalley, C. A. *Small* **2009**, *5*, 194–197. (c) Kaminker, R.; Popovitz-Biro, R.; van der Boom, M. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 3224–3226.

<sup>38</sup> Patterson, A. L. *Phys. Rev.* **1939**, *56*, 978–982.

## CONCLUSIONS

1. Chiroptical properties of bicyclo[3.3.1]nonane derivatives containing carbonyl, 1,2-methylenedioxybenzene and indole chromophore were investigated. In the CD spectra positive Cotton effect at 270-300 nm range accounts for the carbonyl  $n \rightarrow \pi^*$  and not 1,2-methylenedioxybenzene  $^1L_b$  transition, in contrast, the charge transfer band in compounds with 1,2-methylenedioxybenzene and indole chromophores was observed.
2. The exciton interaction in chiral *diendo*, *diexo* and *exo,endo* bicyclo[3.3.1]nonane benzoates was demonstrated experimentally and theoretically. It was estimated that interaction between benzoates is possible only if the distance is only up about 12 Å. Exciton coupling was not observed changing one benzoate chromophore to 3,5-dinitrobenzoate, suggesting that this interaction is resonance by its nature.
3. The chromophores of bicyclo[3.3.1]nonane  $\alpha,\beta$ -unsaturated acids and dinitrile in space are close to each other what results in the molecular orbital overlap.
4. The optimal condition for the Suzuki cross coupling reaction between vinyl triflates and phenylboronic is catalyzed using  $\text{Pd}(\text{Ph}_3\text{P})_4$  and CsF in dry tetrahydrofuran. It was shown that the Sonogashira cross coupling reaction between the vinyl triflates and terminal alkyne instead of CuI catalyst needed to use Ag(I) salts for preventing alkyne dimerization. Using these conditions of new chiral  $C_3$  symmetry bicyclo[3.3.1]nonanones and alcohols with different size central aromatic fragments were obtained.
5. The exciton couplet between benzoate chromophores in  $C_3$  symmetry tribenzoate due to supramolecular sandwich type associates was observed.
6. The trisubstituted ketones containing external bicyclo[3.3.1]nonanyl- and different size aromatic fragments in solution exist in the form of nanoparticles. The X-ray diffraction analysis showed that nanoparticles of regular structure on the surface and, probably, in solution are formed. Analysis of structures and associations constants was performed and van der Waals forces of bicyclic parts and hydrogen bond between alcohol groups give the largest contribution to the association was obtained.
7. The V-shaped chiral and racemic dialkynbicyclo[3.3.1]nonenyl- ligands having coordinating pyridine substituent were obtained. It was shown that these ligands consist of rhomb-shaped palladicycle. It was found that the racemic and chiral complexes exist in solution in the form of [2]catenanes and nanoparticles of diameter about 100 nm. The association constants of formation of [2]catenane ( $27 \text{ M}^{-1}$ ) and nanoparticles ( $1.2 \cdot 10^{-5} \text{ M}^{-1}$ ) were calculated. The X-ray diffraction analysis showed that the nanoparticles of regular structure on the surface and, probably, in solution are formed.



## LIST OF PUBLICATIONS

1. Stončius, S.; **Bagdžiūnas, G.**; Malinauskienė, J.; Butkus, E. A Study of Planar Chromophores in Dichromophoric Molecules by Circular Dichroism Spectroscopy, *Chirality* **2008**, *20*, 3-4, 337-343.
2. **Bagdžiūnas, G.**; Butkus, E.; Stončius, S. Synthesis of Diastereomeric Bicyclo[3.3.1]nonane Dibenzoyl Esters and Study of Their Chiroptical Properties, *Chirality*, **2012**, *24*, 810-816.

### Conference materials on the subject of dissertation

1. Orentas, E.; **Bagdžiūnas, G.**; Butkus, E. Facile synthesis of unsaturated bicyclic carbonyl derivatives. In: *International conference on Organic Synthesis "BOS 2008"*, Program and Abstracts, Vilnius, Lithuania, **2008**, June 29 – July 2, PO95. (Poster presentation)
2. Orentas, E.; **Bagdžiūnas, G.**; Butkus, E.; Stončius, S. Synthesis of molecules containing planar chromophores and study by circular dichroism spectroscopy. In: *20<sup>th</sup> International Symposium on Chirality "Chirality 2008"*, Abstracts, Geneva, Switzerland, **2008**, July 6-9, P-211, pp. 246. (Poster presentation)
3. Butkus, E.; Orentas, E.; **Bagdžiūnas, G.**; Jurgelėnas, M. Chiral bicyclic molecules en route to supramolecules. *XXII Conference on Advances in Organic Synthesis*, Poland, Karpacz. 8-12 July **2009**. Book of Abstracts, IL14. (Oral presentation)
4. **Bagdžiūnas, G.**; Račkauskaitė, D.; Butkus, E. The Suzuki-Miyaura coupling reactions with 6-oxobicyclo[3.3.1]non-2-en-yl triflate, tosylate and phosphate. *Organic Chemistry*, Proceedings of Scientific Conference, Kaunas, Technologija, **2010**, p. 41. (Poster presentation)
5. Račkauskaitė, D.; **Bagdžiūnas, G.**; Butkus, E. Synthesis of pyridyl ligands based on bicyclo[3.3.1]nonane framework. *International conference of students "Chemistry and technology"*, Abstracts, Vilnius, **2010**. (Poster presentation)
6. **Bagdžiūnas, G.**; Račkauskaitė, D.; Jurgelėnas, M.; Butkus, E. Towards the synthesis and crystal engineering of ligands with bicyclo[3.3.1]nonane framework. In: *International conference on Organic Synthesis "BOS 2010"*, Program and Abstracts, Riga, Latvia, **2010**, June 27 – 30, PO8. (Poster presentation)
7. **Bagdžiūnas, G.**; Račkauskaitė, D.; Butkus, E. Towards synthesis of chiral C<sub>3</sub> symmetric tris(bicyclo[3.3.1]noneno)benzenes. *2<sup>nd</sup> Summer School of Synthetic Chemistry*, Book of abstracts, Jyväskylä, Finland, **2010**, August 16-17, p. 20. (Oral presentation)
8. **Bagdžiūnas, G.**; Račkauskaitė, D.; Butkus, E. The synthesis of chiral Pd(II) metallocycles and cages based on bicyclo[3.3.1]nonane framework. *Organic*

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9. **Bagdžiūnas, G.**; Stončius, S.; Butkus, E. The Synthesis of chiral heteroleptic molecular complexes and their chiroprical properties. *Paul Walden 7<sup>th</sup> Symposium in Organic Chemistry*, Riga, September 12-13, **2011**, D3. (*J. Latv. chem*, **2012**, 1, 53.) (Poster presentation)
  10. **Bagdžiūnas, G.**; E. Butkus. Synthesis of diastereomeric bicyclo[3.3.1]nonane dibenzoyl esters and their chiroptical properties. *Internation Conference of Lithuanian Chemists "Chemistry 2011"*. Abstracts, Vilnius, October 14-15, **2011**, 27. (Poster presentation)
  11. **Bagdžiūnas, G.**; Stončius, S.; Butkus, E. Synthesis of chiral star-like molecules with bicyclo[3.3.1]nonene moiety and their aggregation into supramolecules. *Organic Chemistry*, Proceedings of Scientific Conference, Kaunas, Technologija, **2012**, p. 10. (Oral presentation)
  12. **Bagdžiūnas, G.**; Račkauskaitė, D.; Stončius, S.; Butkus, E. Synthesis of chiral metallo-supramolecular rhombs and their aggregation into nanoparticles. In: *International conference on Organic Synthesis "BOS 2012"*, Program and Abstracts, Tallinn, Estonia, **2012**, July 1 - 4, PO7, p. 54. (Poster presentation)

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## SANTRAUKA

Nustatyta, kad chiralinių biciklo[3.3.1]nonano darinių, turinčių karbonilo ir 1,2-metilendioksibenzono chromoforus, apskritiminio dichroizmo spektruose stebimą teigiamo Cotton'o ženklą juostą 270-300 nm bangų intervale nulemia karbonilo  $n \rightarrow \pi^*$ , bet ne 1,2-metilendioksibenzono  ${}^1L_b$  šuolis; junginių, turinčių 1,2-metilendioksibenzono ir indolo chromoforus – krūvio pernaša. Eksperimentiškai ir teoriškai įrodyta, kad tarp susintetintų chiralinių *diendo*-, *diegzo*- ir *egzo,endo*-biciklo[3.3.1]nonandiolio dibenzoatų chromoforų yra eksitoninė sąveika. Apskaičiuota, kad tarp benzoatų ši sąveika galima tik esant atstumui nedidesniam nei 12 Å. Pakeitus vieną benzoato chromoforą į 3,5-dinitrobenzoatą eksitoninė sąveika nestebima, tai rodo, kad ši sąveika yra rezonansinio pobūdžio. Susintetintose chiralinėse biciklo[3.3.1]nonano  $\alpha,\beta$ -nesočiojoje rūgštyje ir nitrile chromoforai erdvėje yra arti vienas kito ir tarp jų galima orbitalių sąveika.

Nustatytos optimalios sąlygos Suzuki kryžminio jungimo reakcijai tarp 6-oksobiciklo[3.3.1]nona-2-en-2-iltriflato ir fenilboronio rūgšties naudojant katalizinį  $\text{Pd}(\text{Ph}_3\text{P})_4$  ir CsF tetrahidrofurane. Parodyta, kad Sonogashira kryžminio jungimo reakcijoje tarp šio viniltriflato ir terminalinių alkinų, išvengiant jų dimerizacijos, vietoj Cu(I) katalizatoriaus reikia naudoti Ag(I) druskas. Šiomis sąlygomis susintetinti nauji chiraliniai  $C_3$  simetrijos tripakeisti biciklo[3.3.1]nonenilketonai ir alkoholiai, turintys įvairius centrinius aromatinis pakaitus.  $C_3$  simetrijos trifenilbiciklo[3.3.1]noneniltribenzoate tarp chromoforų stebima eksitoninė sąveika tik susidarant asociatams, nes monomere tarp chromoforų yra daug didesni atstumai nei 12 Å, todėl eksitoninė sąveika negalima. Parodyta, kad tripakeisti aromatiniai biciklo[3.3.1]nonenilketonai ir alkoholiai tirpale asocijuojasi į nanodaleles ir nustatytos asociacijos konstantos. Struktūros – asociacijos konstantų sąsajos analizė parodė, kad asociaciją lemia tarp biciklo fragmentų esanti van der Waals'o sąveika ir vandenilinis ryšys tarp alkoholių, o  $\pi$  sistemos įtaka yra maža. Rentgeno spindulių difrakcijos metodu nustatyta, kad aromatinis biciklo[3.3.1]nonenilketonas asocijuojasi į tvarkingus nanokristalitus. Susintetinti V formos chiralinis ir raceminis dialkinbiciklo[3.3.1]nonenil-ligandai, turintys koordinuojantį piridino pakaitą, sudaro rombo formos kompleksus, kurių stochiometrija patvirtinta masių spektrometrijos metodu. Komplexas gali egzistuoti [2]katenanų ir apie 100 nm diametro nanodalelių pavidalu. Nustatytos kompleksų asociacijos konstantos į [2]katenanus ( $27 \text{ M}^{-1}$ ) ir nanodaleles ( $1,2 \cdot 10^{-5} \text{ M}^{-1}$ ). Rentgeno spindulių difrakcijos metodu parodyta, kad nanodalelės yra tvarkios struktūros.