PhD STUDIES COURSE UNIT DESCRIPTION

Name of subject	Field of science, code	Faculty / Center	Department
Organometallic Chemistry	Chemistry N 003	Faculty of Geosciences and Chemistry/institute of Chemistry	Department of Organic Chemistry
Student's workload	**Credits**	**Student's workload**	**Credits**
Lectures	3	Consultations	1
Independent study	4	Seminars	1

Course annotation
Classification, nomenclature of organometallic compounds. Origin of bond "carbon-metal". π-complexes, stability of organometallic complexes. Ligands. Organomagnessium compounds, their structure, methods of synthesis, properties. Synthesis of polyfunctionalized Grignard reagents and application in organic synthesis. Organolithium compounds, their stucture, methods of synthesis and chemical properties, influence of aggregation, structure peculiarities and ligands on the reactivity of organolithium compounds. Ortho- and transmetallation reactions. Organotin compounds. Trialkyltin halogenides, stannanes: synthesis, properties, applications in organic synthesis. Radical halogen hydrogenolysis and alkylation of activated double bond by alkyl halogenides in the presence stannanes (formation of C-C bond). Organocopper compounds, their structure, synthesis and reactivity. Regio and stereoselectivity of reactions. Application of mixed organocuprates in synthesis of organic compounds. Organoboron compounds Boranes, their structure. Alkyl boranes (ThBH2, 9-BBN, Sia2BH and others), chiral boranes (Lgf_2BH, $IpcBH_2$, Ipc_2BH and others), organoboronic acids and esters. Regio- and stereoselectivity of hydroboration reaction and other chemical properties of organoboranes (protonolysis, halogenolysis, carbonylation cyanidation reactions, etc.), application in the synthesis of various classes of organic compounds. Organosilicon compounds. Comparison of carbon and silicon. Organic silanols and silicones. Silenes and polysilenes. Vinyl, aryl, alyl, acyl silanes: synthesis and reactions with electrophilic reagents. Brook rearrangement. Enolic silylethers, silylacetals: synthesis and properties. □-Hydroxysilanes. Peterson reaction. Transition metal catalysis reactions. C-C, C-O, C-N bonds formation reactions, their application for the synthesis of aryl and heteroaryl organic compounds. Palladium(0) catalyzed reactions. Steps of catalysis cycle, stereochemistry. Heck reaction, its regio- and stereochemistry. Cross-coupling reactions (Suzuki, Stille, Sonogashira, Negishi, Kumada reactions. Organonickel compounds. Structure. Formation. Ni catalysed cross-coupling reactions, C-C bond formation by Ni-catalyzed photoredox reactions. Advantages and disadvantages of organonickel compounds in organic synthesis.
Reading list
Scientific articles in international science journals such as J. Organomet. Chem.; Organometallics, Advanced Synthesis and Catalysis, JACS, J. Org. Chem, ACIE, Org. Letters, J. Materials chemistry C, Chem. Materials, etc. Sigitas Tumkevičius. Chemistry of Organometallics (in Lithuanian). – Vilnius: UAB TEV, 2012, 202 p. Gary O. Spessard, Gary L. Miessler. Organometallic Chemistry. 2nd Ed. Oxford University Press, 2009, 752p. Modern Organonickel Chemistry. Ed. Y. Tamaru. WILEY-VCH, 2005, 327 p. P. R. Jenkins. Organometallic Reagents in Synthesis. - New York: Oxford University Press, 2001. Metal-Catalyzed Cross-Coupling Reactions, Second, Completely Revised and Enlarged Edition, 2004 Eds: Armin de Meiejere, Francois Diederich. J. Tsuji. Palladium Reagents and Catalysts. Innovations in Organic Synthesis.-J.Wiley and Sons, 1999, 560 p.

The names of consulting teachers	Science degree	Main scientific works published in a scientific field in last 5 year period
Sigitas Tumkevičius Jelena Dodonova-Vaitkūnienė	Dr. Habil. Dr.	1. T. Serevicius, R. Skaisgiris, G. Kreiza, **J. Dodonova**, K. Kazlauskas, E. Orentas, **S. Tumkevicius,** S. Jursenas. TADF parameters in solid-state: an easy way to wrong conclusions. *Journal of physical Chemistry A*, **2021**, *125*, 7, 1637-1641; https://dx.doi.org/10.1021/acs.jpca.0c10391 2. T. Serevičius, R. Skaisgiris, I. Fiodorova, G. Kreiza, D. Banevičius, K. Kazlauskas, **S. Tumkevičius,** S. Juršėnas. Single-exponential solid-state delayed

		fluorescence decay in TADF compounds with minimized conformational disorder. *Journal of Materials Chemistry C,* **2021***, 9,* 836-861. https://doi.org/10.1039/D0TC05503D 3. J. Jovaisaite, D. Cīrule, A. Jeminejs, I. Novosjolova, M. Turks, P. Baronas, R. Komskis, **S. Tumkevicius**, G. Jonusauskas, S. Jursenas. Proof of principle of a purine D–A–D' ligand based ratiometric chemical sensor harnessing complexation induced intermolecular PET. *Physical Chemistry Chemical Physics*, **2020**, *22* (45), 26502-26508; https://dx.doi.org/10.1039/d0cp04091f 4. T. Serevičius, **J. Dodonova,** R. Skaisgiris, D. Banevičius, K. Kazlauskas, S. Juršėnas, **S. Tumkevičius**. Optimization of the carbazole–pyrimidine linking pattern for achieving efficient TADF. *Journal of Materials Chemistry C,* **2020***, 8,* 11192—11200; https://dx.doi.org/10.1039/d0tc02194f 5. T. Serevičius, R. Skaisgiris, **J. Dodonova,** L. Jagintavičius, D. Banevičius, K. Kazlauskas, **S. Tumkevičius**, S. Juršėnas. Achieving Submicrosecond TADF Lifetime and Highly Efficient Electroluminescence by Fine Tuning of Phenoxazine-Pyrimidine Structure. *ACS Applied Materials and Interfaces*, **2020**, *12*, 10727−10736. https://dx.doi.org/10.1021/acsami.9b21394 6. T, Serevicius, R. Skaisgiris, I. Fiodorova, V. Steckis, **J. Dodonova**, D. Banevicius, K. Kazlauskas, S. Jursenas, **S, Tumkevicius**. Achieving efficient deep-blue TADF in carbazole-pyrimidine compounds. *Organic Electronics,* **2020**, *82,* art.no. 105723; https://doi.org/10.1016/j.orgel.2020.105723 7. T. Serevičius, R. Skaisgiris, **J. Dodonova**, K. Kazlauskas, S. Juršėnas, **S. Tumkevičius**. Minimization of solid-state conformational disorder in donor–acceptor TADF compounds. *Physical Chemistry Chemical Physics*, **2020**, *22*, 265-272; DOI: 10.1039/C9CP05907E 8. S. Toliautas, **J. Dodonova**, A. Žvirblis, I. Čiplys, A. Polita, A. Devižis, **S. Tumkevičius**, J. Šulskus, A. Vyšniauskas. Enhancing the Viscosity-Sensitive Range of a BODIPY Molecular Rotor by Two Orders of Magnitude. *Chemistry – A European Journal*, **2019**, *25*(44), 10342-10349; doi: 10.1002/chem.201901315. 9. T. Serevičius, R. Skaisgiris, **J. Dodonova**, L. Jagintavičius, J. Bucevičius, K. Kazlauskas, S. Juršėnas, **S. Tumkevičius**. Emission wavelength dependence on the rISC rate in TADF compounds with large conformational disorder. *Chemical Communications,* **2019**, *55*, 1975-1978; DOI: 10.1039/c8cc08906j 10. A. Šišuļins, J. Bucevičius, Y.-T. Tseng, I. Novosjolova, K, Traskovskis, Ē. Bizdēna, H.-T. Chang, **S. Tumkevičius,** M. Turks. Synthesis and fluorescent properties of N(9)-alkylated 2-amino-6-triazolylpurines and 7-deazapurines. *Beilstein Journal of Organic Chemistry* **2019**, *15*, 474–489, doi:10.3762/bjoc.15.41

Certified during Doctoral Committee session on September 28th, 2021. Protocol No. 610000-KT-142.
Committee Chairman prof. habil. dr. Aivaras Kareiva