

A concise synthesis of multiply fused phenanthroline diamide (fused-PTDA) by palladium-catalyzed intramolecular C–H arylation. Highly efficient and selective extraction performance of fused-PTDA toward early lanthanidesⁱ

Towa Asano,^a Yuki Nakanishi,^a Shoichi Sugita,^b Kentaro Okano,^a Hirokazu Narita,^c Tohru Kobayashi,^d Tsuyoshi Yaita,^{de*} Atsunori Mori^{ab*}

^a Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

^b Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

^c Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), Onogawa 16-1, Tsukuba, Ibaraki, Japan

^d Actinide Sciences Research Group, Materials Sciences Research Center, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

^e Synchrotron Radiation Research Center, National Institute for Quantum Science and Technology(QST), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

Abstract

The reaction of phenanthroline diamide bearing a bromoaryl moiety on the amide substituent in the presence of palladium catalyst proceeded efficiently to afford multiply-fused phenanthroline derivatives through intramolecular C–H arylation. The obtained diamide derivatives was found to extract lanthanide remarkably highly efficiently with distribution ratio (*D*: up to ca. 500) and it was also found show the metal-selective extraction (separation factor *SF* = up to 4.4).

ⁱ A part of this work was preliminary reported in the 41st Symposium on Solvent Extraction on November 25, 2022 (Tokyo).

Introduction

Recycle of rare metals has attracted increasing interest recently in connection with the utilization of resources. Much efforts have been devoted to the efficient recovery of metal resources. Solvent extraction has been an effective tool for the recovery of metals and the development of metal-specific extracting agent has been our major concern. Recovery of rare-earth elements is particularly important due to the use of those as a wide range of electronic devices, which remarkably increase the demand recently.¹ Because of the difficulty in the metal-selective separation of rare-earth due to the similarity of there chemical properties, currently used extraction process employing phosphorous acid derivatives^{2,3} requires multiple stages to guarantee the metal purity. Phenanthroline derivatives has recently attracted remarks as a selective and highly efficient extractant for rare-earth metals.⁴⁻¹⁴

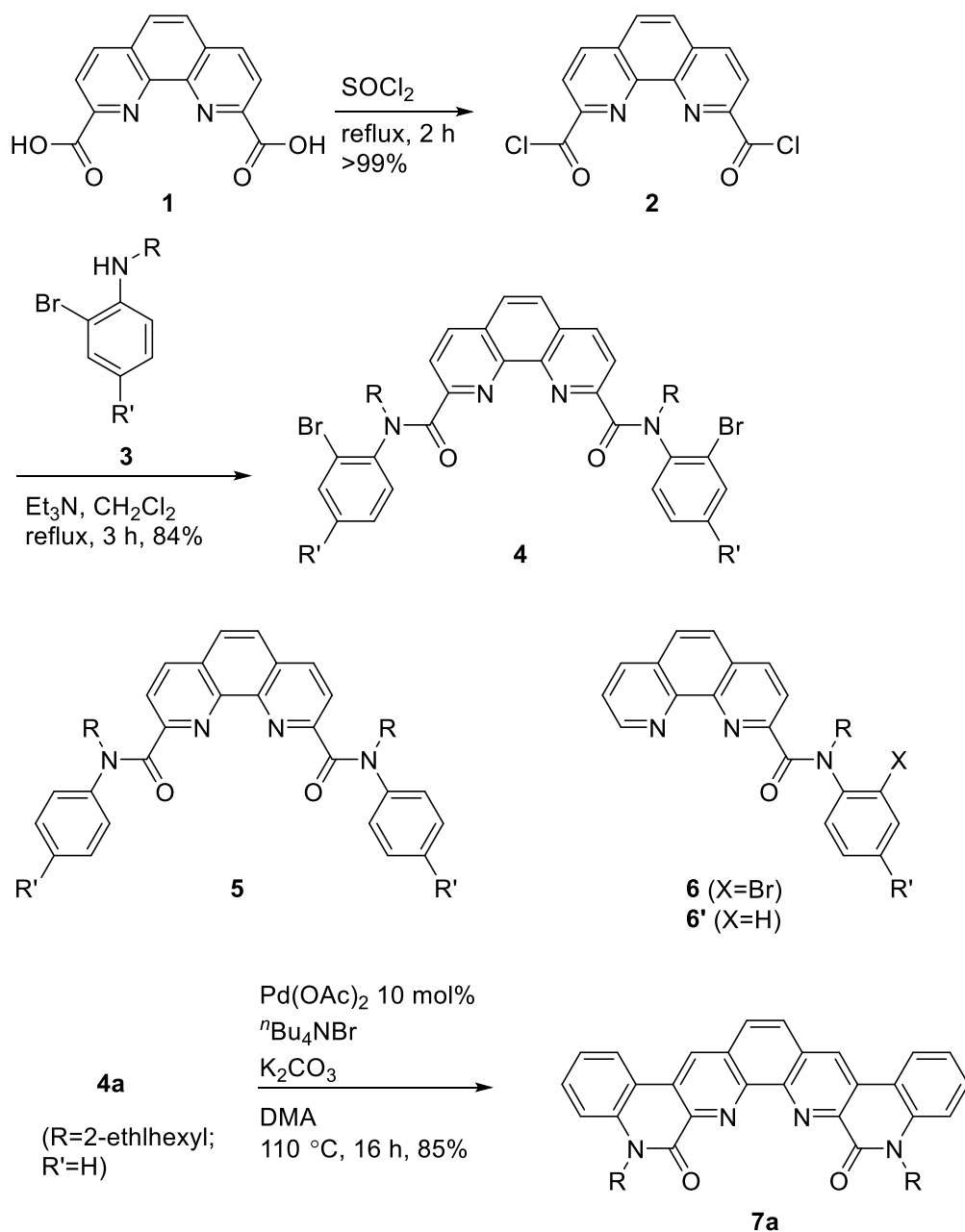
Construction of organic skeleton of complex structures is of great concern in synthetic chemistry. Transition metal catalysis plays a key role in the formation carbon-carbon and carbon-heteroatom bonds.¹⁵⁻¹⁷ In particular, such bond-forming reactions utilizing a C–H bond has attracted major concern recently in conjunction with the point of atom efficiency and step efficiency, etc.¹⁸⁻²⁰ When the reaction was designed to be performed in a intramolecular manner,^{21,22} the protocol is considered to be a powerful tool for the formation of fused ring structures.

Accordingly, our concern has centered to the concise preparation of heteroaromatic ring structure employing transition metal catalysis and we have been engaged in the application of C–H bond functionalization for the purpose of the construction of a variety of heteroaromatic compounds.²³⁻²⁵ Intramolecular application of such a C–H bond functionalization has been an attractive issue in organic synthesis to build a ring structure in a facile manner and the application to several heteroaromatic molecules including pyridines and their more fused analogs would also be a significant challenge to form a fused heteroaromatic skeleton. Recent publication on the extraction of lanthanides with fused phenanthroline amide derivatives by Popova and coworkers²⁶ prompted us to report our continuing separate researches. We herein describes palladium-catalyzed annulative formation of fused phenanthroline through the C–H functionalization reaction and our preliminary studies on several metal extraction with thus obtained fused phenanthrolines.

Results and discussion

Synthesis of phenanthroline 2,9-dicalboxamide **4** was performed by the reaction of the acid chloride **2** of phenanthroline-2,9-dicarboxylic acid **1**, which was subjected to the reaction with thionyl chloride, with *N*-alkylated 2-bromoaniline derivative **3**. The reaction was found to proceed smoothly to afford **4** in good to excellent yields.²⁷ Phenanthroline diamide bearing no bromo group at the 2-position of the benzene ring **5** was prepared in a similar manner. The related mono amide **6** (X = Br) and **6'** (X = H) were also synthesized. The obtained amide **4** was then subjected to the intramolecular C–H coupling reaction at the 3-position of phenanthroline and at the C–Br bond of the aniline moiety.¹⁸ We first examined the reaction with **4a** under similar conditions shown in previous C–H arylation with pyridine derivatives.^{28,29} When the reaction was carried out in the presence of 10 mol% of palladium acetate, 2.0 equivalents of tetra-*n*-butylammonium bromide, and 2.0 equivalents of potassium carbonate in *N,N*-dimethylacetamide (DMA) as a solvent at 110 °C for 16 h, the C–H coupling reaction proceeded to afford the multiply fused diamide **7a** in 85% yield.

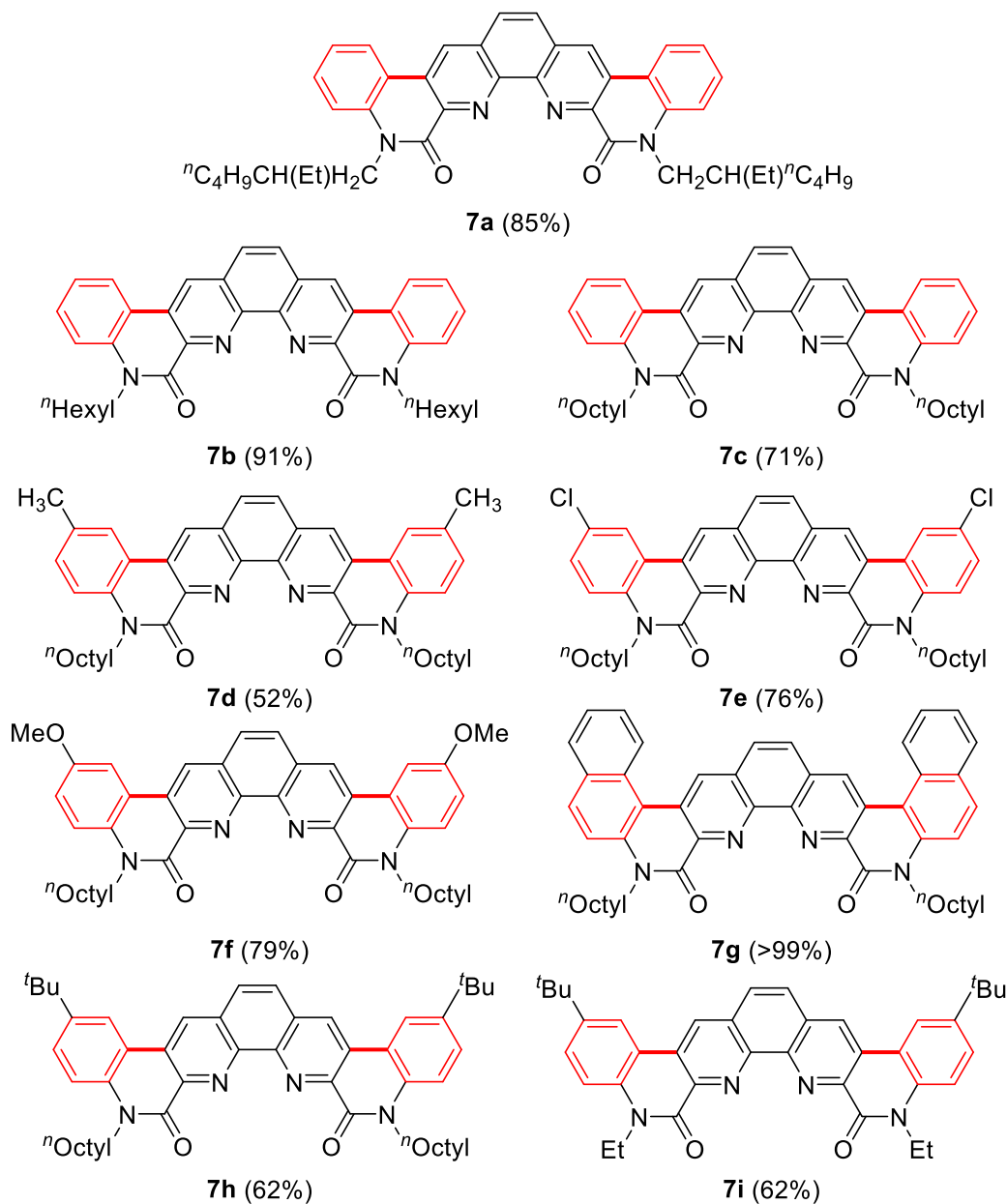
The measurement of ¹H NMR spectrum of **7a** showed the characteristic singlet signal at 8.96 ppm assigned as the hydrogen atom at the 4 and 7-positions of the phenanthroline ring suggesting that C–H coupling took place at the 3 and 8-positions.



Scheme 1. Synthesis of multiply fused phenanthroline diamide and the related compounds

Several amide derivatives **7** bearing different alkyl substituent and a substituent at the 4-position of aniline were also subjected to the C–H coupling reaction in a similar manner and found that the coupling reaction proceeded smoothly to afford a variety of multiply fused diamides. The result is summarized in Table 1. The coupling reaction proceeded smoothly in good to excellent yields irrespective of the effect of alkyl substituents and the substituent on the aniline moiety.

Table 1. Synthesis of multiply fused phenanthroline diamide derivatives by palladium-catalyzed C–H arylation ^a



^a Unless noted, the reaction was carried out with **4** (0.3 mmol), K₂CO₃ (2 equiv), *n*-Bu₄NBr (2 equiv), and 10 mol% of Pd(OAc)₂ at 110 °C for 18 h under an aerobic conditions. ^b The yield (isolated) was shown in the parenthesis.

We have attempted to carry out the C–H coupling reaction with a reduced amount of catalyst loading of palladium, however, the reaction was found to proceed much slower. The reaction was examined with diamide **4a** (R = 2-ethylhexyl; R' = H). When the amount of Pd(OAc)₂ was reduced to 5.0 mol%, the yield of **7a** decreased to 67% and no reaction took place with the use of 1.0 mol% of Pd(OAc)₂ with recovery of starting material **4a**. We thus studied the effect of the ligand of palladium. Among a variety of ligand examined, the use of Buchwald-type phosphines³⁰ (RuPhos, *t*-BuXPhos, BrettPhos, SPhos) in the presence of 2.5 mol% Pd(OAc)₂ was found ineffective to yield only <10% of the desired product **7a**.¹⁸ The yield of **7a** was slightly improved when JackiePhos was employed as a ligand (35%). Remarkably improved yields were observed in the use of CyJohnPhos (81%), PhDavePhos (97%), and tricyclohexylphosphine (85%).

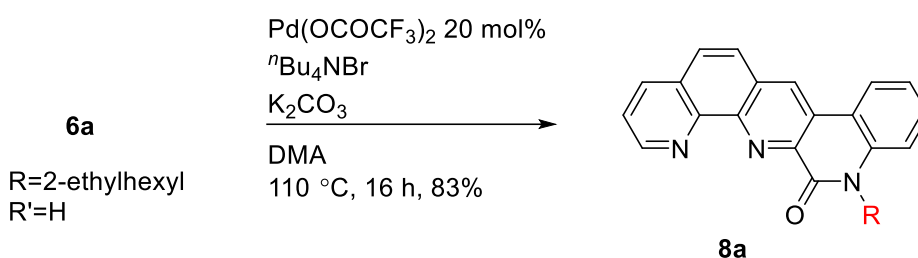
Table 2. The reaction of **4a** catalyzed by palladium in the presence of Buchwald-type phosphine ligands ^a

entry	Ligand ^b	Yield (%) ^c	
		4a	7a
1	RuPhos (L1)	74	trace
2	<i>t</i> -BuXPhos (L2)	58	4
3	SPhos (L3)	>99	1
4	BrettPhos (L4)	67	10
5	JackiePhos (L5)	22	35
6	CyJohnPhos (L6)	0	81
7	PhDavePhos (L7)	0	97
8	Cy ₃ P ^d	0	85

^a The reaction was carried out with cyclization precursor **4a** (0.16 mmol), Pd cat. (2.5 mol%), ligand (10 mol%), KOAc (0.32 mmol), and *n*-Bu₄NBr (0.32 mmol) in 5 mL of DMA at 110 °C for 18 h under an argon atmosphere. ^b Details on Buchwald-type ligand **L1**–**L7**: See Supporting Information. ^c The yield was determined by ¹H NMR analysis using C₂H₄Cl₂ as an internal standard. ^d Cy: tricyclohexyl

We then studied the reaction of the related phenanthroline monoamide **6a** under similar conditions. However, the coupling reaction was found to take place much less efficiently. When the reaction was carried out 10 mol% of Pd(OAc)₂ under similar conditions, the yield of the coupling product **8a** was found to decrease to 31% accompanied by the recovery of starting amide **6a** (31%). The reaction at the elevated temperatures (130 °C and 150 °C) resulted in little improvement. Although the addition of phosphine ligand was also examined, improvement of the yield of **8a** was hardly observed as found in the

case of the formation of diamide **7a** (See Supporting Information). The optimum yield was observed in the use of $\text{Pd}(\text{OCOCF}_3)_2$ as a catalyst³¹ to give 83% of **8a** whereas 20% of catalyst loading was the requirement.



Scheme 2. Cyclization reaction of phenanthroline monoamide **6** catalyzed by $\text{Pd}(\text{OCOCF}_3)_2$.

Employing thus obtained phenanthroline amide derivatives **7** we next performed the extraction studies of lanthanides. A mixture of 14 lanthanides(III) nitrate (La to Lu) where pH was arranged to 3.0. The resulting aqueous phase was extracted into the 1.0 mM organic solution of phenanthroline ligand **7** in 1,2-dichloroethane by shaking at 25°C for 90 min. The extraction performance was analyzed by ICP–MS with the remained aqueous solution of lanthanide and shown as distribution ratio D of each metal. The selectivity of lanthanides was expressed with separation factor SF , which was defined by the ratio of D of the corresponding metals.

Figure 1 shows the result of extraction with the multiply fused phenanthroline **7a–7c** for the comparison of the effect of alkyl substituent at the amide nitrogen. The result shows that phenanthroline diamide with the cyclized structure extracts early lanthanides ^{57}La to ^{62}Sm efficiently whereas extraction of ^{63}Eu to ^{71}Lu results in inferior. The distribution ratio for La of diamide **7c** bearing longer alkyl chain ($\text{R} = n\text{octyl}$) showed remarkably high $D_{\text{La}} = 131$, while D_{La} of **7b** and **7a** was slightly lower ($D_{\text{La}} = 41$ and 15, respectively). Since the D value of **7** decreased as the increase of the atomic number of lanthanide, the different D values between early lanthanides was observed and thus appeared marked separation factor in ^{59}Pr and ^{60}Nd ($SF_{\text{Pr/Nd}} = 2.3$).

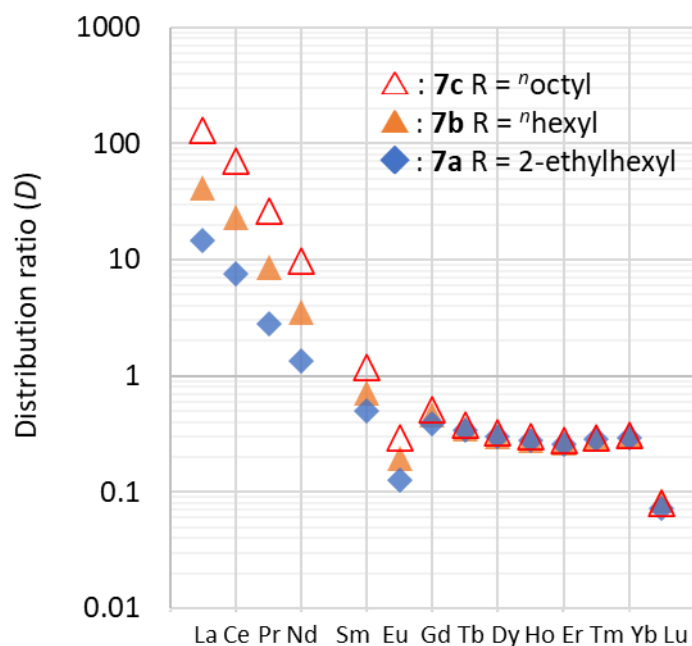


Figure 1. Extraction of lanthanides La–Lu with cyclized diamide **7**. The distribution ratio D was measured by ICP-MS analyses

Worthy of note is that the preferentially high extraction of the cyclized diamide **7c** for early lanthanides compared with that of acyclic diamide **5** ($R = {}^n\text{C}_8\text{H}_{17}$, $R' = \text{H}$) as shown in Figure 2. A high distribution ratio of early lanthanides was not observed in acyclic **5** only resulting in mostly equal extraction of all of lanthanides. The extraction performance of **5** were much inferior to those of cyclic diamide **7c** and the preferential extraction of early lanthanides was not observed.

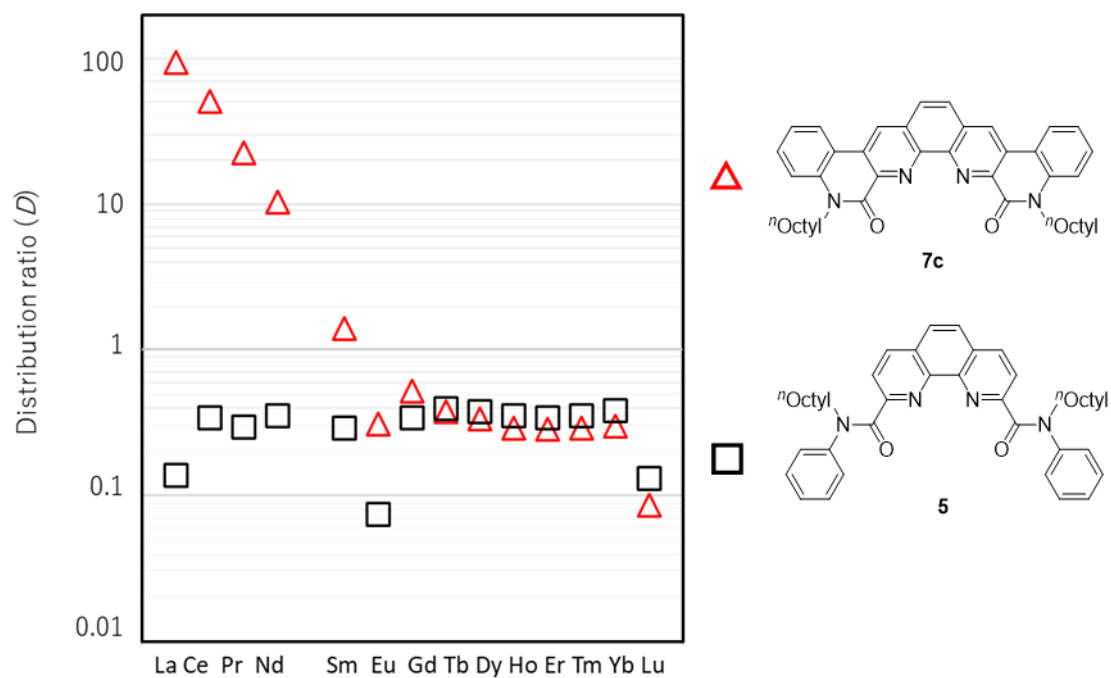


Figure 2. Extraction of lanthanides with phenanthroline diamide **7c** and the cyclization precursor **5**

Figure 3 shows the extraction of lanthanides in **7c** with that of the related monoamide of cyclized **8** ($R = {}^n\text{C}_8\text{H}_{17}$). The performance of **7c** was compared with that of cyclized monoamide analog **8** bearing the same alkyl and aryl substituents. The result suggested that specific extraction of early lanthanides in **7c** was only found in the diamide structure, while the cyclized monoamide **8** showed mostly equal extraction in 14 lanthanides ($SF_{\text{La/Lu}} = 1.3$).

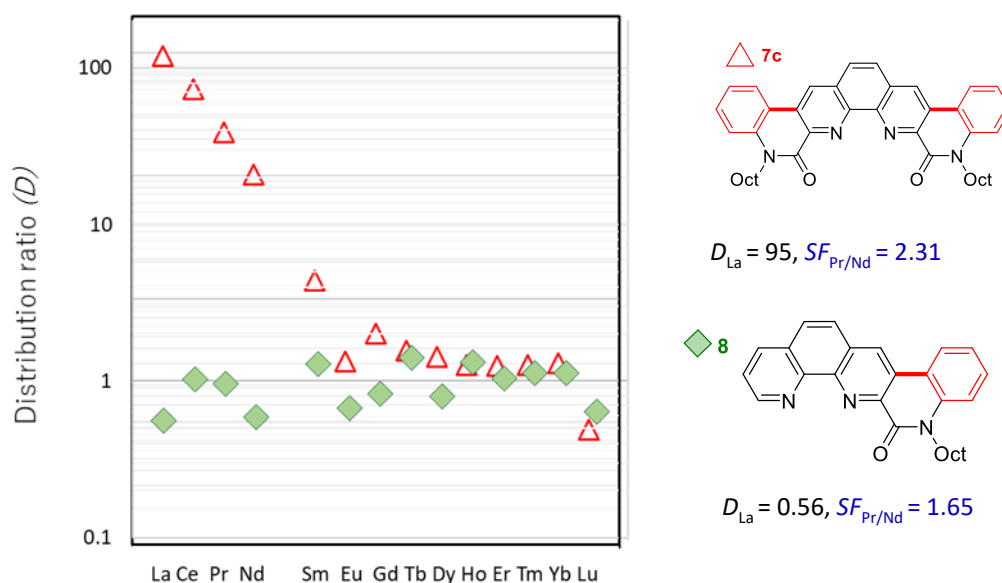
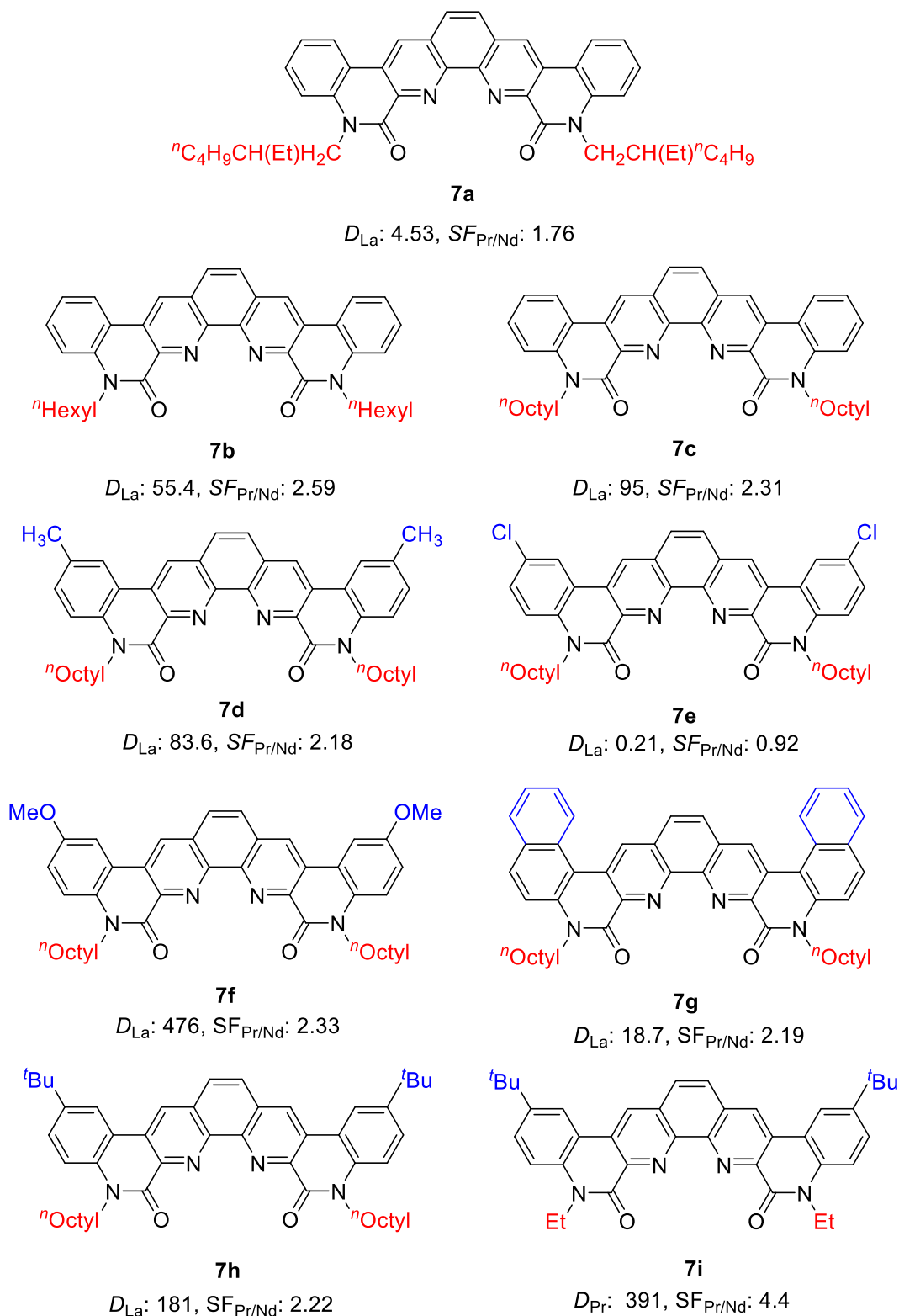


Figure 3. Difference of the extraction performance between cyclized diamide **7c** and the related monoamide **8**

Table 3 summarizes the results of the distribution ratio and the separation factor of **7** with various substituent at the benzene ring of the aniline moiety. The D value of La and SF of Pr/Nd was shown as a representative example. The performance was found to depend on the substituent structure on the anilide moiety. An electron donating group on the benzene ring suggested superior distribution ratio D , while an electron withdrawing chloro group showed a lower D value. Multiply fused diamide bearing a methoxy group **7f** and a *t*-butyl group **7h** showed rather high distribution ratio (D_{La} = 476 and 181, respectively).

Table 3. Extraction of lanthanides with phenanthroline diamide **7** bearing different substituent at the 4-position of the anilide moiety ^a



^a *D*: distribution ratio of Ln with cyclized diamide **7** and the separation factor (*SF*) between specific two metals shown in the subscript

We consider that such high extraction and selectivity to early lanthanides are attributed by the fused structure of phenanthroline ring, which limits rotation of the carbon–carbon single bond between pyridine rings. In addition, the formation of the cyclic structure of amide further improves the conformationally rigid structure of **7**. Since the further fused benzene also enhances the planarity, a remarkably superior extraction of a specific lanthanide ion would be achieved, accordingly.

Summary

We have shown facile synthesis of multiply fused phenanthroline diamides, which extract lanthanides highly efficiently. The fused diamide derivatives extracted early lanthanides more selectively and efficiently than the related monoamide. Such a simple and diversity-oriented synthetic protocol allowed the preparation of diamide derivatives with a wide range of structural analogs and thus the synthesis can lead to the tuning of the extraction performances.

Acknowledgment

This work is based on results obtained from a project, JPNP17001, subsidized by the New Energy and Industrial Technology Development Organization (NEDO).

References

- (1) Xie, F.; Zhang, T. A.; Dreisinger, D.; Doyle, F. A Critical Review on Solvent Extraction of Rare Earths from Aqueous Solutions. *Miner. Eng.* **2014**, *56*, 10–28. <https://doi.org/10.1016/j.mineng.2013.10.021>.
- (2) Li, D. Development Course of Separating Rare Earths with Acid Phosphorus Extractants: A Critical Review. *J. Rare Earths* **2019**, *37*, 468–486. <https://doi.org/10.1016/j.jre.2018.07.016>.
- (3) Tunsu, C.; Menard, Y.; Eriksen, D. Ø.; Ekberg, C.; Petranikova, M. Recovery of Critical Materials from Mine Tailings: A Comparative Study of the Solvent Extraction of Rare Earths Using Acidic, Solvating and Mixed Extractant Systems. *J. Clean. Prod.* **2019**, *218*, 425–437. <https://doi.org/10.1016/j.jclepro.2019.01.312>.
- (4) Simonnet, M.; Kobayashi, T.; Shimojo, K.; Yokoyama, K.; Yaita, T. Study on Phenanthroline Carboxamide for Lanthanide Separation: Influence of Amide Substituents. *Inorg. Chem.* **2021**, *60*, 13409–13418. <https://doi.org/10.1021/acs.inorgchem.1c01729>.
- (5) Kobayashi, T.; Suzuki, S.; Shiwaku, H.; Yaita, T. Lanthanides Complexation Properties of O, N-Hetero Donor Ligand PTA. *Prog. Nucl. Sci. Technol.* **2018**, *5*, 74–77. <https://doi.org/10.15669/pnst.5.74>.
- (6) Healy, M. R.; Ivanov, A. S.; Karslyan, Y.; Bryantsev, V. S.; Moyer, B. A.; Jansone-Popova, S. Efficient Separation of Light Lanthanides(III) by Using Bis-Lactam Phenanthroline Ligands. *Chem. – A Eur. J.* **2019**, *25*, 6326–6331. <https://doi.org/10.1002/chem.201806443>.
- (7) Nakase, M.; Kobayashi, T.; Shiwaku, H.; Suzuki, S.; Grimes, T. S.; Mincher, B. J.; Yaita, T. Relationship Between Structure and Coordination Strength of N and N,O -Hybrid Donor Ligands with Trivalent Lanthanides. *Solvent Extr. Ion Exch.* **2018**, *36*, 633–646. <https://doi.org/10.1080/07366299.2018.1532137>.
- (8) Simonnet, M.; Suzuki, S.; Miyazaki, Y.; Kobayashi, T.; Yokoyama, K.; Yaita, T. Lanthanide Intra-Series Separation by a 1,10-Phenanthroline Derivative: Counterion Effect. *Solvent Extr. Ion Exch.* **2020**, *38*, 430–440. <https://doi.org/10.1080/07366299.2020.1744806>.
- (9) Wang, S.; Yang, X.; Xu, L.; Miao, Y.; Yang, X.; Xiao, C. Selective Extraction of Uranium(VI) from Thorium(IV) Using New Unsymmetrical Acidic Phenanthroline Carboxamide Ligands. *Ind. Eng. Chem. Res.* **2023**, *62*, 15613–15624. <https://doi.org/10.1021/acs.iecr.3c02101>.
- (10) Wang, S.; Yang, X.; Xu, L.; Xiao, C. Separation and Complexation of

- Lanthanides with an Acidic Phenanthroline Carboxamide Ligand: Extraction, Spectroscopy, and Crystallography. *Ind. Eng. Chem. Res.* **2024**, *63*, 10773–10781. <https://doi.org/10.1021/acs.iecr.4c01205>.
- (11) Ustynyuk, Y. A.; Borisova, N. E.; Babain, V. A.; Gloriov, I. P.; Manuilov, A. Y.; Kalmykov, S. N.; Alyapyshev, M. Y.; Tkachenko, L. I.; Kenf, E. V.; Ustynyuk, N. A. N,N'-Dialkyl-N,N'-Diaryl-1,10-Phenanthroline-2,9-Dicarboxamides as Donor Ligands for Separation of Rare Earth Elements with a High and Unusual Selectivity. DFT Computational and Experimental Studies. *Chem. Commun.* **2015**, *51*, 7466–7469. <https://doi.org/10.1039/C5CC01620G>.
 - (12) Xiao, C.-L.; Wang, C.-Z.; Yuan, L.-Y.; Li, B.; He, H.; Wang, S.; Zhao, Y.-L.; Chai, Z.-F.; Shi, W.-Q. Excellent Selectivity for Actinides with a Tetradentate 2,9-Diamide-1,10-Phenanthroline Ligand in Highly Acidic Solution: A Hard–Soft Donor Combined Strategy. *Inorg. Chem.* **2014**, *53*, 1712–1720. <https://doi.org/10.1021/ic402784c>.
 - (13) Alyapyshev, M.; Ashina, J.; Dar'in, D.; Kenf, E.; Kirsanov, D.; Tkachenko, L.; Legin, A.; Starova, G.; Babain, V. 1,10-Phenanthroline-2,9-Dicarboxamides as Ligands for Separation and Sensing of Hazardous Metals. *RSC Adv.* **2016**, *6*, 68642–68652. <https://doi.org/10.1039/C6RA08946A>.
 - (14) Manna, D.; Mula, S.; Bhattacharyya, A.; Chattopadhyay, S.; Ghanty, T. K. Actinide Selectivity of 1,10-Phenanthroline-2,9-Dicarboxamide and Its Derivatives: A Theoretical Prediction Followed by Experimental Validation. *Dalt. Trans.* **2015**, *44*, 1332–1340. <https://doi.org/10.1039/C4DT02402H>.
 - (15) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998. <https://doi.org/10.1002/9783527612222>.
 - (16) DeMeire, A.; Bräse, S.; Oestreich, M. *Metal-Catalyzed Cross-Coupling Reactions and More*; de Meijere, A., Bräse, S., Oestreich, M., Eds.; Wiley: Weinheim, Germany, 2014. <https://doi.org/10.1002/9783527655588>.
 - (17) Hartwig, J. F. Approaches to Catalyst Discovery. New Carbon-Heteroatom and Carbon-Carbon Bond Formation. *Pure Appl. Chem.* **1999**, *71*, 1417–1423. <https://doi.org/10.1351/pac199971081417>.
 - (18) Campeau, L.-C.; Parisien, M.; Leblanc, M.; Fagnou, K. Biaryl Synthesis via Direct Arylation: Establishment of an Efficient Catalyst for Intramolecular Processes. *J. Am. Chem. Soc.* **2004**, *126*, 9186–9187. <https://doi.org/10.1021/ja049017y>.
 - (19) *C-H Bond Activation and Catalytic Functionalization I*, I.; Dixneuf, P. H.,

- Doucet, H., Eds.; Springer: Heidelberg, 2016.
- (20) Nakao, Y. Transition-Metal-Catalyzed C-H Functionalization for the Synthesis of Substituted Pyridines. *Synthesis* **2011**, 2011, 3209–3219.
<https://doi.org/10.1055/s-0030-1260212>.
 - (21) Chiusoli, G. P.; Catellani, M.; Costa, M.; Motti, E.; Della Ca', N.; Maestri, G. Catalytic C–C Coupling through C–H Arylation of Arenes or Heteroarenes. *Coord. Chem. Rev.* **2010**, 254, 456–469.
<https://doi.org/10.1016/j.ccr.2009.07.023>.
 - (22) Cuellar, M. A.; Heredia, M. D.; Brarda, G.; Barolo, S. M.; Vázquez, E. D. D.; Uberman, P. M.; Martín, S. E.; Budén, M. E. Visible-Light-Driven Synthesis of Phenanthridin-6(5 H)-one and N-Substituted Carbazole Derivatives through Intramolecular C-H Arylation. *Eur. J. Org. Chem.* **2023**, 26.
<https://doi.org/10.1002/ejoc.202300361>.
 - (23) Shibuya, Y.; Mori, A. Dehalogenative or Deprotonative? The Preparation Pathway to the Organometallic Monomer for Transition-Metal-Catalyzed Catalyst-Transfer-Type Polymerization of Thiophene Derivatives. *Chem. – A Eur. J.* **2020**, 26, 6976–6987. <https://doi.org/10.1002/chem.201905653>.
 - (24) Mori, A. Structure- and Functionality-Based Molecular Design of Azoles and Thiophenes. *Bull. Chem. Soc. Jpn.* **2020**, 93, 1200–1212.
<https://doi.org/10.1246/bcsj.20200169>.
 - (25) Mori, A. Transition Metal-Catalyzed Bond-Forming Reactions at the C-H Bond of Heteroaromatic Compounds. *J. Synth. Org. Chem. Jpn.* **2011**, 69, 1202–1211.
<https://doi.org/10.5059/yukigoseikyokaishi.69.1202>.
 - (26) Pramanik, S.; Li, B.; Driscoll, D. M.; Johnson, K. R.; Evans, B. R.; Damron, J. T.; Ivanov, A. S.; Jiang, D.; Einkauf, J.; Popovs, I.; Jansone-Popova, S. Tetradentate Ligand's Chameleon-Like Behavior Offers Recognition of Specific Lanthanides. *J. Am. Chem. Soc.* **2024**, 146, 25669–25679.
<https://doi.org/10.1021/jacs.4c07332>.
 - (27) Alyapyshev, M.; Ashina, J.; Dar'in, D.; Kenf, E.; Kirsanov, D.; Tkachenko, L.; Legin, A.; Starova, G.; Babain, V. 1,10-Phenanthroline-2,9-Dicarboxamides as Ligands for Separation and Sensing of Hazardous Metals. *RSC Adv.* **2016**, 6, 68642–68652. <https://doi.org/10.1039/C6RA08946A>.
 - (28) Majumdar, K. C.; De, N.; Chakravorty, S. Palladium-Mediated Bis-Arylation of Inactivated and Activated Arenes. *Synth. Commun.* **2010**, 41, 121–130.
<https://doi.org/10.1080/00397910903531870>.
 - (29) Lavrov, H. V.; Ustynyuk, N. A.; Matveev, P. I.; Gloriov, I. P.; Zhokhov, S. S.;

- Alyapyshev, M. Y.; Tkachenko, L. I.; Voronaev, I. G.; Babain, V. A.; Kalmykov, S. N.; Ustynyuk, Y. A. A Novel Highly Selective Ligand for Separation of Actinides and Lanthanides in the Nuclear Fuel Cycle. Experimental Verification of the Theoretical Prediction. *Dalt. Trans.* **2017**, 46, 10926–10934. <https://doi.org/10.1039/C7DT01009E>.
- (30) Surry, D. S.; Buchwald, S. L. Biaryl Phosphane Ligands in Palladium-Catalyzed Amination. *Angew. Chem. Int. Ed.* **2008**, 47, 6338–6361. <https://doi.org/10.1002/anie.200800497>.
- (31) Amatore, C.; Jutand, A.; Lemar[^]tre, F.; Luc Ricard, J.; Kozuch, S.; Shaik, S. Formation of Anionic Palladium(0) Complexes Ligated by the Trifluoroacetate Ion and Their Reactivity in Oxidative Addition. *J. Organomet. Chem.* **2004**, 689, 3728–3734. <https://doi.org/10.1016/j.jorganchem.2004.05.012>.