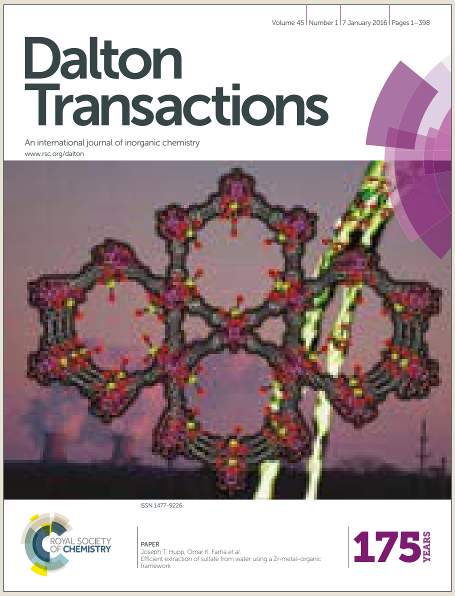
Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Imoto, S. Wada and K. Naka, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT01106G.



Volume 45 | Number 1 | 7 January 2016 | Pages 1–398

Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

ISSN 1477-9226

ROYAL SOCIETY OF CHEMISTRY

PAPER
Joseph T. Hupp, Omar K. Farha et al.
Efficient extraction of sulfate from water using a Zr-metal–organic framework

175 YEARS

View Article Online
DOI: 10.1039/C7DT01106G

Journal Name

COMMUNICATION

Rh-Catalyzed Direct Arylation of a Polyhedral Oligomeric Silsesquioxane

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hiroaki Imoto,[a] Satoshi Wada,[a] and Kensuke Naka[a*]

Electronic properties of polyhedral oligomeric silsesquioxane (POSS) have recently been subjected to study. Although theoretical calculations have predicted that POSS can work as an acceptor for π-conjugated organic units, an effective reaction to incorporate aryl groups into a POSS backbone remains to be established. In this work, Rh-catalyzed direct arylation has been developed. Heptaisobutyl-POSS with a Si−H group was reacted with various aryl halides to be aryl-substitued POSSs.

Increasing attention has been given to polyhedral oligomeric silsesquioxane (POSS).[1] POSS has advantages in designability and material properties due to organic substituents and inorganic core, respectively. Because of these aspects, numerous kinds of materials have been developed utilizing POSSs for improvement of conventional organic materials: cross-linkers,[2] side-chain substituents,[3] and fillers.[4] More recently, POSS-based materials such as main-chain polymers[5] and single-molecular films[6] have been reported. The characteristic natures in the applications of POSSs are mainly transparency and thermal stability. The caged silsesquioxane moieties have been usually regarded as a non-conjugated unit with π-electrons of the functional organic substituents. On the other hand, some researches have proposed that POSS is a potential candidate as optoelectronic materials.[7-10] In 1989, Feher and Budzichowski reported experimental results showing an electron-accepting behaviour of a POSS framework.[7] Theoretical calculations by Kieffer and coworkers revealed that the HOMO-LUMO gap can be effectively lowered via functionalization by aryl groups.[8] However, in spite of these pioneering findings, the experimental knowledge on the properties of aryl-substituted POSSs remains to be accumulated. This is because there is few synthetic routes for access to aryl-substituted POSSs.

Conventionally, aryl-substituted POSSs are produced by condensation reaction of incompletely condensed POSS with silane coupling agents (Scheme 1a),[11,12] which must be separately prepared with each aryl group. These silane coupling agents such as trichlorosilanes[11] and trialkoxysilanes[12] require special care after the syntheses because they are highly reactive; decomposition and/or self-condensation could occur. Meanwhile, the seminal works on functionalization of POSSs have been carried out by Laine's group.[9,13] Heck reaction and olefin metathesis of octavinylPOSS offer various kinds of POSS derivatives with π-conjugated systems.[9a] Moreover, they also synthesized octa(*p*-iodophenyl)POSS, which can be applied to traditional coupling chemistries.[9b,13] These works motivated us to develop facile synthetic routes for the functionalization of POSS with aryl groups.

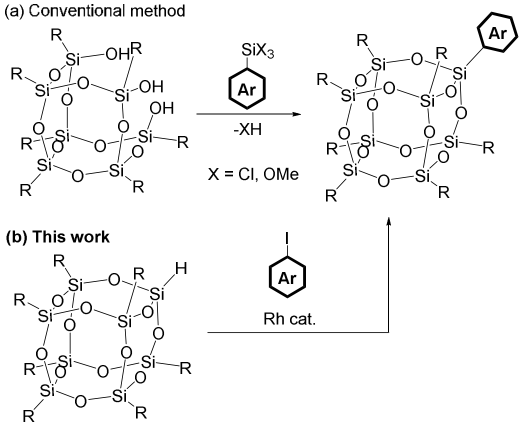
We envisioned that direct arylation, in which a Si−H group on the corner of POSS is converted to a Si−aryl group, should be a powerful tool for the incorporation of a POSS into π-conjugated systems. Although there is no report on the direct arylation of POSSs, we got an idea from Rh-catalyzed silylation of aryl halides with triethoxysilane.[14] In the presence of Rh(I) species with tertiary amine, the Si−H bond is activated, and Si−C bonds are formed with aryl halides. Inspired by this synthetic protocol, we herein investigated Rh-catalyzed direct arylation of a POSS. We have selected heptaisobutyl-POSS (**1**)[15] as a reaction substrate because mono-functional simple structure is constructed. Additionally, **1** has advantages in availability and solubility. In this work, the reaction condition was optimised, and several aryl halides with electron-donating and withdrawing groups were examined. This is the first example of transition metal-catalyzed direct arylation of a POSS.

---

[a] *Faculty of Molecular Chemistry and Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. E-mail: kenaka@kit.ac.jp*

†Electronic Supplementary Information (ESI) available: experimental detail, spectra, and theoretical calculation. For ESI see DOI: 10.1039/c000000x/

View Article Online
DOI: 10.1039/C7DT01106G



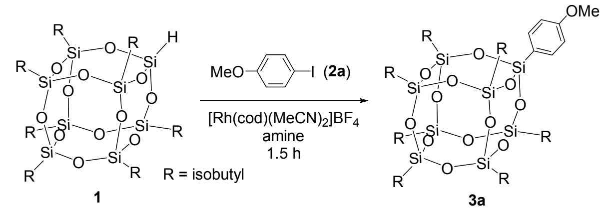
Scheme 1. Synthetic routes of aryl-substituted POSSs: (a) traditional condensation, and (b) direct arylation.

Heptaisobutyl-POSS (**1**)[15] was readily prepared by condensation of commercially-available incompletely condensed POSS[16] with trichlorosilane. As a rhodium catalyst, $[Rh(cod)(MeCN)_2]BF_4$ was selected because this catalyst has been used for silylation of aryl halides with triethoxysilane to obtain silane coupling agents.[14,17] Firstly, we chose the direct arylation of **1** with *p*-iodoanisole **2a** to screen the reaction parameters. A solution of **1**, **2a** (1.5 eq.), $[Rh(cod)(MeCN)_2]BF_4$ (5 mol%), and amine (7.5 eq.) was stirred for 1.5 h under nitrogen (N_2) atmosphere. In reference to the reported ^{1}H-NMR spectrum of (*p*-anisyl)-heptaisobutyl-POSS (**3a**),[12] the NMR yields were estimated. The reaction conditions and results are summarized in Table 1.

In run 1-4, triethylamine (Et_3N), diisopropylethylamine ($i Pr_2EtN$), diazabicycloundecene (DBU), and diisopropylamine ($i Pr_2NH$) were examined as an amine. After the reaction under the condition of run 1-3, the ^{1}H-NMR spectrum of the crude product showed no signal due to the Si−H group of **1**, but small amounts of oligomeric by-products were included. Additionally, in the case of run 4, decomposition of POSS cage was observed. These results implied that the caged structure of POSS was hydrolysed and condensed under the basic condition. Sterically hindered amine, $i Pr_2EtN$ (run 2, 87%), was the most suitable for the present reaction thanks to its weak nucleophilicity. In order to attempt for suppression of the side-reactions, the reaction temperature was lowered to 50 °C (run 5). However, the reaction hardly proceeded even in the presence of $i Pr_2EtN$ (16%), suggesting that the higher temperature (80 °C) was necessary for this reaction.[18] The solvents besides *N*,*N*-dimethylformamide (DMF) were investigated, but little amounts of the desired product **3a** were obtained when toluene (run 6) and THF (run 7) were employed. More polar solvents such as dimethyl sulfoxide and methanol cannot be used due to their poor solubility of **1**.

We investigated the scope of the aryl halides with the optimal reaction condition in hand (run 2 in Table 1). The substrates and yields are summarized in Table 2. Aryl halides with electron-donating groups (**2a** and **2b**) were more reactive than iodobenzene **2c**. This trend is corresponding to the results in the previous literature on transition-metal catalyzed aryl silylation.[14a,19] A sterically hindered substrate, *o*-anisyl iodide **2d** was applicable to the present reaction as well. However, *p*-iodobenzonitrile **2e** did not react. It is reported that aryl

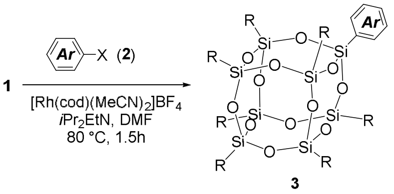
Table 1. Optimization of the reaction conditions[a]

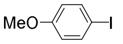
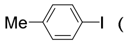
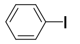
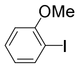
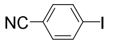
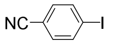
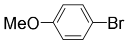
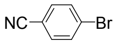


Run	base	solvent	temperature [°C]	yield[b] [%]
1	Et_3N	DMF	80	80
2	$i Pr_2EtN$	DMF	80	87
3	$i Pr_2NH$	DMF	80	75
4	DBU	DMF	80	n.d.
5	$i Pr_2EtN$	DMF	50	16
6	$i Pr_2EtN$	toluene	80	3
7	$i Pr_2EtN$	THF	reflux	5

[a] [POSS] = 0.15 M, [*p*-iodoanisole] = 0.225 M, [Rh] = 7.5 mM, [amine] = 1.25 M. [b] NMR yield.

Table 2. Direct arylation of **1** with arylhalides[a]



Run	Aryl halide	Product	yield of **3**[b] [%]
1	 (**2a**)	**3a**	87 (78)
2	 (**2b**)	**3b**	87 (62)
3	 (**2c**)	**3c**	81 (74)
4	 (**2d**)	**3d**	78 (71)
5	 (**2e**)	**3e**	n.d.
6[c]	 (**2e**)	**3e**	n.d.
7	 (**2a'**)	**3a**	54
8[c]	 (**2e'**)	**3e**	n.d.

[a] Reaction condition of run 2 in Table 1. [b] NMR yield (bare) and isolated yield (in a parenthesis).
[c] Tetrabutylammonium iodide (1.0 eq.) was added.

View Article Online
DOI: 10.1039/C7DT01106G

silylation of substrates with electron-withdrawing groups is a challenging matter.[19] Addition of tetrabutylammonium iodide did not work (run 6 and 8), in spite of the reported effect of iodide ion.[14] The reaction system should be modified to be utilized for substrates with an electron-withdrawing group. Aryl bromide can also be used in this reaction, though the reaction yield is significantly lowered (run 7) in comparison to aryl iodide (run 1).

Finally, the effect of POSS on the electronic properties of aryl groups was investigated. The UV-vis absorption spectra of **3a**-**d** were measured in hexane solutions ($c = 1 \times 10^{-4}$ M, Figure 1a). The offsets of the absorption spectra of **3a**-**d** (**3a**: 283 nm, **3b**: 280 nm, **3c**: 274 nm, **3d**: 291 nm) were red-shifted from those of their corresponding aryl moieties, *i.e.*, anisole (281 nm), toluene (273 nm), and benzene (264 nm). To understand the narrower HOMO-LUMO gaps, density functional theory (DFT) calculation was carried out. The results of the calculation showed that the LUMO levels of the aryl moieties were significantly lowered by the incorporation of POSS in general (Figure 1b). For example, the LUMO level of **3c** (-0.74 eV) was much lower than that of benzene (-0.42 eV), whereas the HOMO levels of **3c** (-7.02 eV) and benzene (-7.01 eV) were similar. Therefore, the red-shifts of the absorption spectra were caused by lowering the LUMO levels due to the electron-acceptance of the POSS. This result is well corresponding to the previously reported experimental and theoretical researches.[7-10] However, the absorption spectrum and calculated frontier orbital energies of trimethoxyphenylsilane (PhTMOS) showed no significant difference from **3c**, suggesting that the π-conjugation of the phenyl group was not expanded to whole of the POSS moiety. To understand the effect of the closed-cage structure of POSS, further investigation should be carried out. Here, it has been demonstrated that the present reaction strongly contributes the systematic studies on aryl-substituted POSSs.

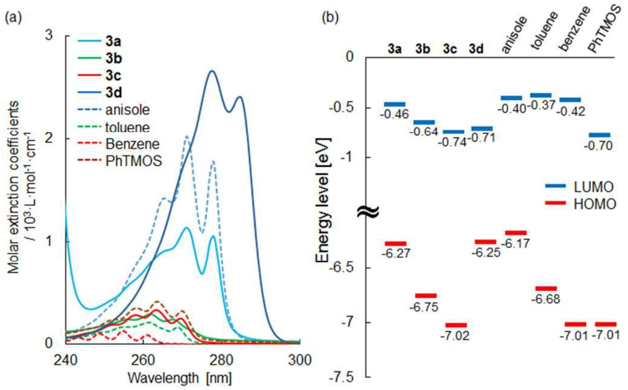


Fig. 1 (a) UV-vis absorption spectra and (b) frontier orbital energies of **3a**-**d** and their aryl moieties. The energy levels were estimated by DFT calculations at the B3LYP/6-31G+(d,p) level of theory with the Gaussian 09 suit program.[20,21]

Conclusions

In conclusion, Rh-catalyzed direct arylation of heptaisobutyl-POSS **1** has been developed. The reaction with aryl halides readily proceeded to produce aryl POSSs. Electron-donating groups improved the reaction yields. Sterically hindered substrate and aryl bromide were also applicable in the present reaction, though a substrate with an electron-withdrawing group cannot react. This reaction has opened the avenue towards experimental studies on electronic contributions of POSSs to π-electrons of functional organic units. Further improvement of the reaction system, incorporation of various π-conjugated systems, and introduction of substituents other than isobutyl group are under investigation.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No.2401)” (JSPS KAKENHI Grant Number JP24102003) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Notes and references

1 For reviews, see: (a) R. M. Laine, C. Zhang, A. Sellinger and L. Viculis, *Appl. Organometal. Chem.*, 1998, **12**, 715; (b) R. M. Laine, *J. Mater. Chem.*, 2005, **15**, 3725; (c) D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chem. Rev.*, 2010, **110**, 2081; (d) K. Tanaka and Y. Chujo, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 1231; (e) Y. Chujo and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 633; (f) Q. Ye, H. Zhou and J. Xu, *Chem. Asian J.*, 2016, **11**, 1322; (g) K. Naka and Y. Irie, *Polym. Int.*, 2017, **66**, 187.

2 For recent papers, see: (a) S. Neyertz, D. Brown, M. J. T. Raaijmakers and N. E. Benes, *Phys. Chem. Chem. Phys.*, 2016, **18**, 28688; (b) P. Yang, G. Zhu, X. Shen, X. Yan and J. Nie, *RSC Adv.*, 2016, **6**, 90212; (c) S. Banerjee, S. Kataoka, T. Takahashi, Y. Kamimura, K. Suzuki, K. Sato and A. Endo, *Dalton Trans.*, 2016, **45**, 17082; (d) X. Zhou, X. Fan and C. He, *Macromolecules*, 2016, **49**, 4236.

3 (a) R. Goseki, A. Hirao, M. Kakimoto, and T. Hayakawa, *ACS Macro Lett.*, 2013, **2**, 625; (b) L. Hong, Z. Zhang and W. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 10673; (c) T. Suzuki, A. Yoshida, S. Ando and K. Nagai, *Polym. Int.*, 2015, **64**, 1209; (d) F. Kato, A. Chandra, S. Horiuchi and T. Hayakawa, *RSC Adv.*, 2016, **6**, 62172; (e) T. Seshimo, Y. Utsumi, T. Dazai, T. Maehashi, T. Matsumiya, Y. Suzuki, C. Hirano, R. Maeda, K. Ohmori and T. Hayakawa, *Polym. J.*, 2016, **48**, 407.

4 (a) K. Tanaka, S. Adachi and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5690; (b) K. Tanaka, S. Adachi and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5712; (c) J.-H. Jeon, K. Tanaka and Y. Chujo, *RSC Adv.*, 2013, **3**, 2422; (d) J.-H. Jeon, K. Tanaka and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 3583; (e) J.-H. Jeon, K. Tanaka and Y. Chujo, *J. Mater. Chem. A*, 2014, **2**, 624; (f) K. Ueda, K. Tanaka and Y. Chujo, *Polym. J.*, 2016, **48**, 1133.

5 (a) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe and H. Oikawa, *Macromolecules*, 2006, **39**, 3473; (b) S. Wu, T. Hayakawa, R. Kikuchi, S. J. Grunzinger, M. Kakimoto and H. Oikawa, *Macromolecules*, 2007, **40**, 5698; (c) S. Wu, T. Hayakawa, M. Kakimoto and H. Oikawa, *Macromolecules*, 2008, **41**, 3481; (d) Md. A. Hoque, Y. Kakihana, S. Shinke and Y. Kawakami, *Macromolecules*, 2009, **42**, 3309; (e) M. Yoshimatsu, K. Komori, Y. Ohnagamitsu, N. Sueyoshi, N. Kawashima, S. Chinen, Y. Murakami, J. Izumi, D.

DOI: 10.1039/C7DT01106G

Inoki, K. Sakai, T. Matsuo, K. Watanabe and M. Kunitake, *Chem. Lett.*, 2012, **41**, 622; (f) T. Maegawa, Y. Irie, H. Fueno, K. Tanaka and K. Naka, *Chem. Lett.*, 2014, **43**, 1532; (g) T. Maegawa, Y. Irie, H. Imoto, H. Fueno, K. Tanaka and K. Naka, *Polym. Chem.*, 2015, **6**, 7500; (h) T. Maegawa, O. Miyashita, Y. Irie, H. Imoto and K. Naka, *RSC Adv.*, 2016, **6**, 31751.

6 (a) H. Araki and K. Naka, *Macromolecules*, 2011, **44**, 6039; (b) H. Araki and K. Naka, *Polym. J.*, 2012, **44**, 340; (c) H. Araki and K. Naka, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4170; (d) Y. Yasumoto, T. Yamanaka, S. Sakurai, H. Imoto and K. Naka, *Polym. J.*, 2016, **48**, 281.

7 F. J. Feher and T. A. Budzichowski, *J. Organomet. Chem.*, 1989, **379**, 33.

8 C.-G. Zhen, U. Becker and J. Kieffer, *J. Phys. Chem. A*, 2009, **113**, 9707.

9 (a) S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III and R. M. Laine, *Chem. Mater.*, 2008, **20**, 5563; (b) R. M. Laine, S. Sulaiman, C. Brick, M. Roll, R. Tamaki, M. Z. Asuncion, M. Neurock, J.-S. Filhol, C.-Y. Lee, J. Zhang, T. Goodson III, M. Ronchi, M. Pizzotti, S. C. Rand and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 3708.

10 (a) A. F.-Ugalde, E. J. J.-Pérez, F. Teixidor, C. Viñas and R. Núñez, *Chem. Eur. J.*, 2013, **19**, 17021; (b) Y. Xia, H. Yao, M. Cui, Y. Ma, Z. Kong, B. Wu, Z. Qi and Y. Sun, *RSC Adv.*, 2015, **5**, 80339.

11 (a) C.-M. Leu, G. M. Reddy, K.-H. Wei and C.-F. Shu, *Chem. Mater.*, 2003, **15**, 2261; (b) H. Liu, S. Kondo, N. Takeda and M. Unno, *Eur. J. Inorg. Chem.*, 2009, 1317; (c) D. J. Clarke, J. G. Matisons, G. P. Simon, M. Samoc and A. Samoc, *Appl. Organometal. Chem.*, 2010, **24**, 184; (d) B. M. Moore, S. M. Ramirez, G. R. Yandek, T. S. Haddad and J. M. Mabry, *J. Organomet. Chem.*, 2011, **696**, 2676; (e) D. Gnanasekaran, K. Madrhavan, J. Tsibouklis and B. Reddy, *Polym. Int.*, 2013, **62**, 190.

12 I. Blanco, L. Abate, F. A. Bottino and P. Bottino, *J. Therm. Anal. Calorim.*, 2012, **108**, 807.

13 (a) M. F. Roll, M. Z. Asuncion, J. Kampf and R. M. Laine, *ACS Nano*, 2008, **2**, 320; (b) M. Z. Asuncion, M. F. Roll and Richard M. Laine, *Macromolecules*, 2008, **41**, 8047.

14 (a) M. Murata, M. Ishikura, M. Nagata, S. Watanabe and Y. Masuda, *Org. Lett.*, 2002, **4**, 1843; (b) M. Murata, H. Yamasaki, T. Ueta, M. Nagata, M. Ishikura, S. Watanabe and Y. Masuda, *Tetrahedron*, 2007, **63**, 4087.

15 C.-H. Lu, C.-H. Tsai, F.-C. Chang, K.-U. Jeong and S.-W. Kuo, *J. Colloid Interface Sci.*, 2011, **358**, 93.

16 J. Zhou, Y. Zhao, K. Yu, X. Zhou and X. Xie, *New J. Chem.*, 2011, **35**, 2781.

17 (a) N. Mizoshita, M. Ikai, T. Tani and S. Inagaki, *J. Am. Chem. Soc.*, 2009, **131**, 14225; (b) H. Yang, X. Han, G. Li, Z. Ma and Y. Hao, *J. Phys. Chem. C*, 2010, **114**, 22221, (c) T. Seki, K. McEleney and C. M. Crudden, *Chem. Commun.*, 2012, **48**, 6369; (d) M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W.-J. Chun, S. Muratsugu, M. Tada, A. Fukuoka and S. Inagaki, *J. Am. Chem. Soc.*, 2014, **136**, 4003.

18 Even under the optimized condition (run 2, in Table 1), the hydrolysis and condensation of the POSS skeleton slightly proceeded, resulting in oligomeric by-products. Therefore, column chromatography on silica gel and recrystallization were necessary to remove the impurities. For the detail, see ESI.

19 (a) M. Murata, K. Suzuki, S. Watanabe and Y. Masuda, *J. Org. Chem.*, 1997, **62**, 8569; (b) A. S. Manoso and P. DeShong, *J. Org. Chem.*, 2001, **66**, 7449.

20 In order to reduce the calculation cost, the structures of **3a**-**d** were simplified by replacement of the isobutyl groups to methyl groups, and optimized by DFT calculation at the B3LYP/6-31G(d) level of theory. For the detail of the calculation, see ESI.

21 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

View Article Online
DOI: 10.1039/C7DT01106G

Graphical Abstract
Dalton Transactions

Rh-Catalyzed Direct Arylation of a Polyhedral Oligomeric Silsesquioxane

Hiroaki Imoto, Satoshi Wada and Kensuke Naka*

Conjugation of a polyhedral oligomeric silsesquioxane (POSS) with π-electrons of functional organic units has recently attracted much attention. This is the first example of catalytic direct arylation of a POSS.