Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rh-Catalyzed Direct Arylation of a Polyhedral Oligomeric Silsesquioxane

Hiroaki Imoto, Wada Satoshi and Kensuke Naka*

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.

Contents:

1. Materials

p-Bromobenzonitrile, tetrabutylammonium iodide, bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate ([Rh(cod)(MeCN)$_2$]BF$_4$), and trimethoxyphenylsilane (PhTMOS) were purchased from Sigma Aldrich. Toluene, hexane, ethyl acetate (EtOAc), methanol (MeOH), triethylamine (Et$_3$N), diisopropylethylamine (*i*Pr$_2$EtN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), iodobenzene, and *p*-bromoanisole were purchased from Nacalai Tesque, Inc. Tetrahydrofuran (THF, super dehydrated grade) and *N*,*N*-dimethylformamide (DMF, super dehydrated grade) were purchased from Wako Pure Chemical Industry, Ltd. Trichlorosilane, *p*-iodotoluene, *p*-iodoanisole, *o*-iodoanisole, and *p*-iodobenzonitrile were purchased from Tokyo Chemical Industry Co., Ltd. Heptaisobutyl-trisilanol-POSS was purchased from Hybrid Plastics.

Heptaisobutyl-POSS (**1**) was prepared from heptaisobutyl-trisilanol-POSS in reference to the previous literature.[1]

2. Measurement

^{1}H- (400 MHz), ^{13}C- (100 MHz), and ^{29}Si- (80 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer. The samples were analyzed in CDCl$_3$ using Me$_4$Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, dd: doubledoublet, t: triplet, m: multiplet. The UV−vis spectra were recorded on a Jasco spectrophotometer (V-670 KKN).

3. Synthesis

*General procedure of direct arylation of heptaisobutyl-POSS (**1**) with aryl halides.*

A solution (2 mL) of **1** (245 mg, 0.3 mmol), aryl halide (0.45 mmol), [Rh(cod)(MeCN)$_2$]BF$_4$ (6 mg, 0.015 mmol), and amine (2.3 mmol) was stirred for 1.5 h under nitrogen atmosphere. After the reaction, toluene (75 mL) was added to the reaction mixture, and the organic layer was washed with water. The volatile were removed under reduced pressure, and the residue was subjected to short column chromatography on silica gel (eluent: hexane/EtOAc = 9/1). The product including small amounts of impurities was recrystallized from CH$_2$Cl$_2$, EtOAc, and MeOH to obtain colorless crystals.

3a: ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 7.60 (d, 2H, J = 8.7 Hz), 6.91 (d, 2H, J = 8.7 Hz), 3.82 (s, 3H), 1.91-1.83 (m, 7H), 0.98-0.94 (m, 42H), 0.64-0.61 (m, 14H) ppm; ^{29}Si-NMR (CDCl$_3$, 80 MHz) δ -67.3, -67.8, -78.7 ppm. The data of ^{1}H-NMR spectrum were corresponding to the previous paper.[2]

3b: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, 2H, J = 7.9 Hz), 7.19 (d, 2H, J = 7.6 Hz), 2.36 (s, 3H), 1.92-1.81 (m, 7H), 0.98-0.95 (m, 42H), 0.64-0.61 (m, 14H) ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz) δ -67.2 -67.8 -80.0 ppm. The data of ^{1}H-NMR spectrum were corresponding to the previous paper.[2]

3c: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67 (dd, 2H, J = 1.4, 7.9 Hz), 7.44-7.40 (m, 1H), 7.37-7.34 (m, 2H), 1.91-1.84 (m, 7H), 0.98-0.94 (m, 42H) 0.65-0.62 (m, 14H) ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz) δ -67.2 -67.8 -80.5 ppm. The data of ^{1}H-NMR spectrum were corresponding to the previous paper.[2]

3d: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59 (dd, 1H, J = 1.7, 7.2 Hz), 7.42-7.37 (m, 1H), 6.96 (t, 1H, J = 7.3 Hz), 6.83 (d, 1H, J = 8.3 Hz), 3.75 (s, 3H), 1.91-1.83 (m, 7H), 0.98-0.93 (m, 42H), 0.63-0.61 (m, 14H) ppm; ^{13}C-NMR($CDCl_3$, 100 MHz) δ 164.6 136.5 132.2 120.0 119.9 109.5 54.9 25.8 25.7 24.0 23.9 23.8 22.6 22.5 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz) δ -67.5 -67.8 -80.8 ppm. HR-FAB-MS (m/z): calcd for $C_{80}H_{96}O_{12}N_8Si_8$ $[M+H]^+$, 923.3049; obs, 923.3061.

4. NMR spectra

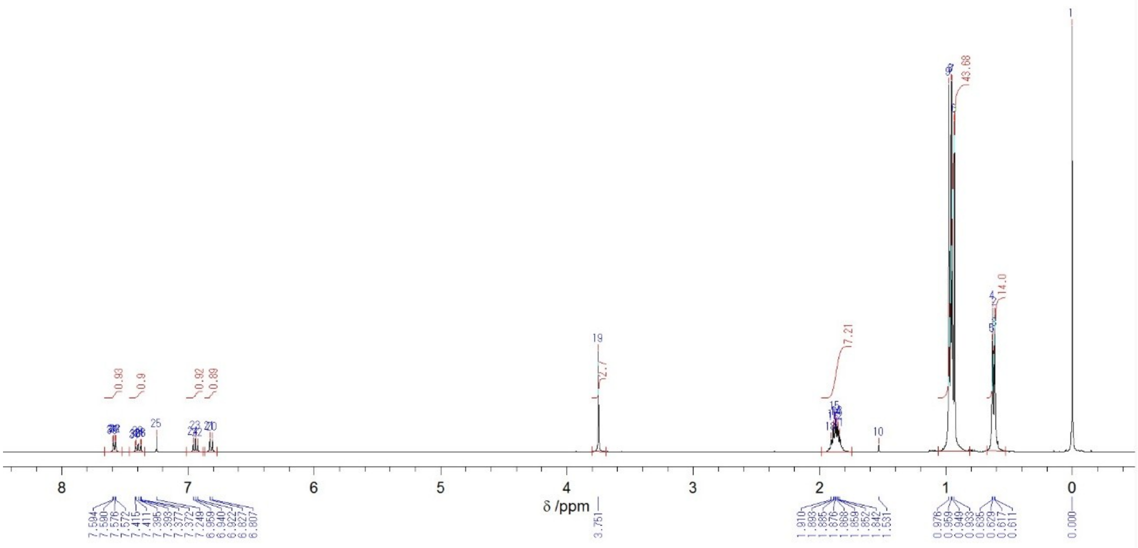


Figure S1. ^{1}H-NMR spectrum (400 MHz) of **3d** in CDCl$_3$.

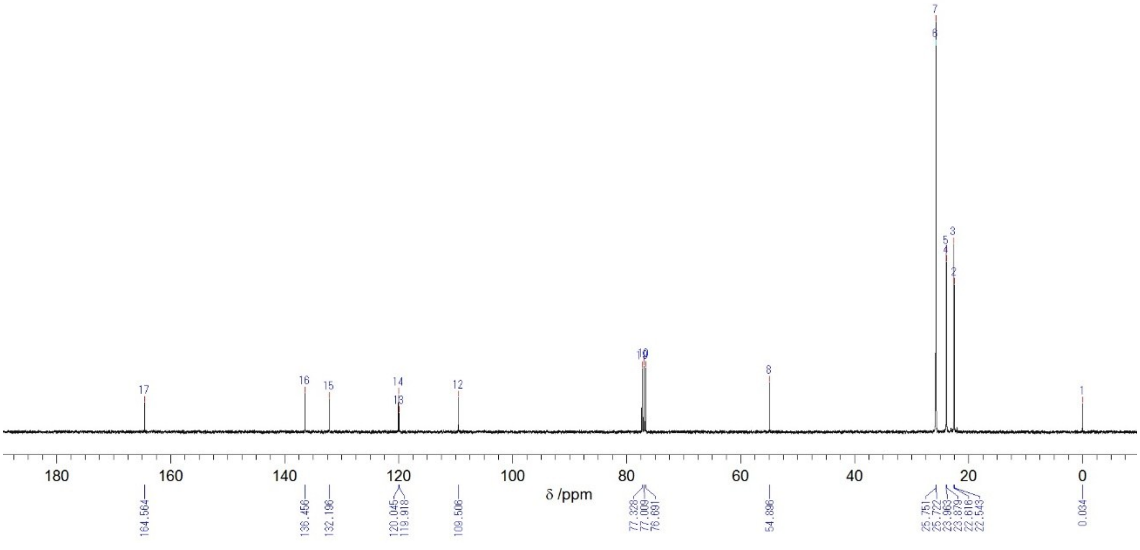


Figure S2. ^{13}C-NMR spectrum (100 MHz) of **3d** in CDCl$_3$.

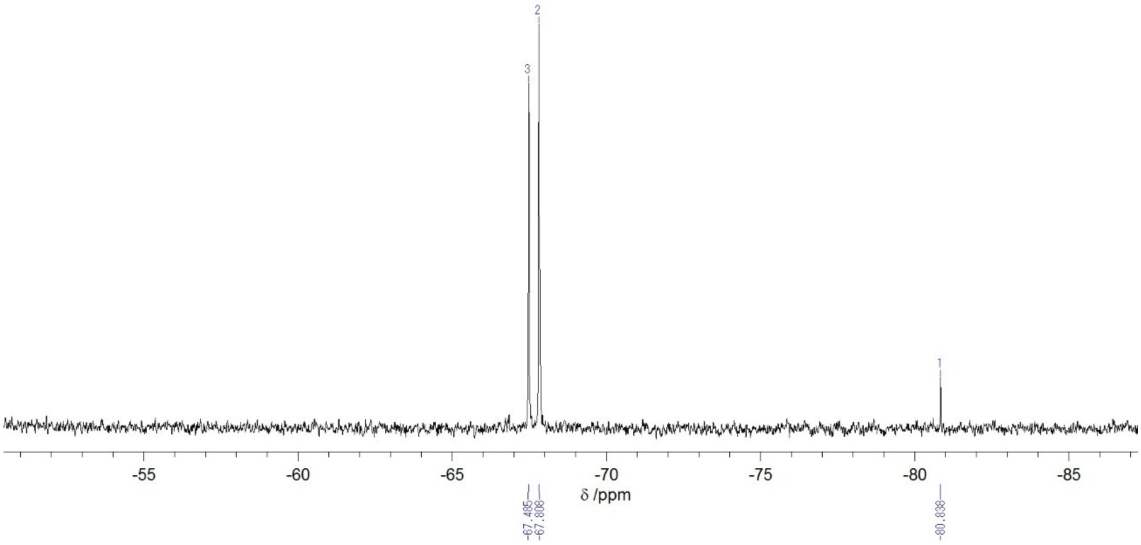
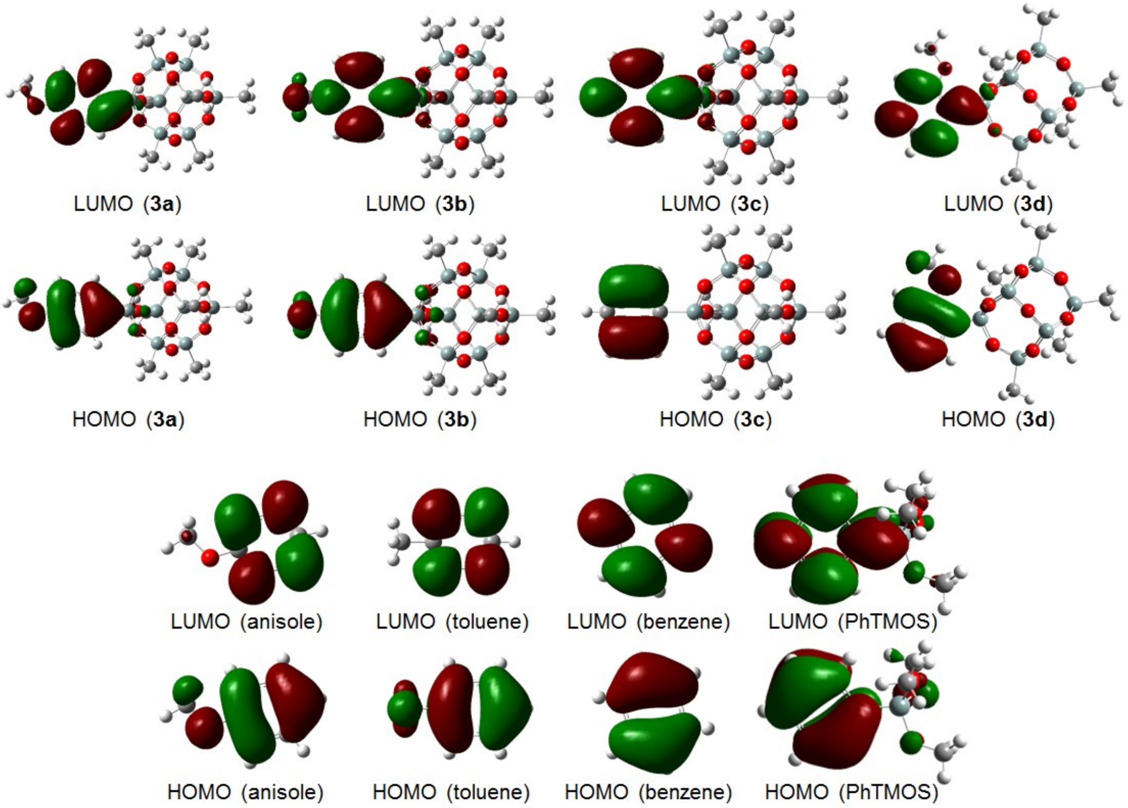


Figure S3. ^{29}Si-NMR spectrum (80 MHz) of **3d** in $CDCl_3$.

5. Theoretical calculation

DFT calculation was performed at the B3LYP/6-31G+(d,p) level of theory with the Gaussian 09 suit program.[3] 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 to reduce the calculation cost. The structures of anisole, toluene, benzene, and PhTMOS were optimized by DFT calculation at the B3LYP/6-31G+(d,p) level of theory.


LUMO (**3a**) LUMO (**3b**) LUMO (**3c**) LUMO (**3d**)

HOMO (**3a**) HOMO (**3b**) HOMO (**3c**) HOMO (**3d**)

LUMO (anisole) LUMO (toluene) LUMO (benzene) LUMO (PhTMOS)

HOMO (anisole) HOMO (toluene) HOMO (benzene) HOMO (PhTMOS)

Figure S4. Frontier orbitals of **3a-d**, anisole, toluene, benzene, and PhTMOS.

6. References

1. C.-H. Lu, C.-H. Tsai, F.-C. Chang, K.-U. Jeong, S.-W. Kuo, *J. Colloid Interface Sci.* **2011**, *358*, 93.
2. I. Blanco, L. Abate, F. A. Bottino, P. Bottino, *J. Therm. Anal. Calorim.* **2012**, *108*, 807.
3. 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.