ORGANIC LETTERS

2013
Vol. 15, No. 14
3558–3561

Synthesis of Substituted Picenes through Pd-Catalyzed Cross-Coupling Reaction/Annulation Sequences and Their Physicochemical Properties

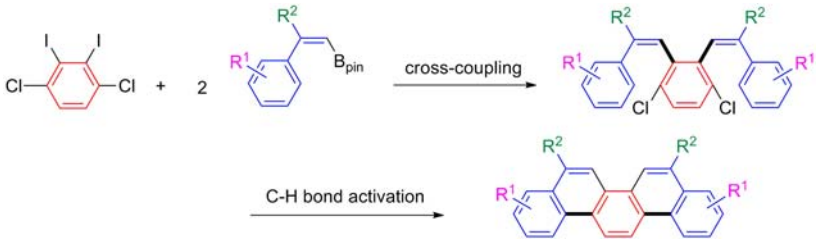
Ning-hui Chang,[†] Xi-chao Chen,[†] Hikaru Nonobe,[†] Yasuhiro Okuda,[†] Hiroki Mori,[†] Kiyohiko Nakajima,[‡] and Yasushi Nishihara*[,†,§]

Division of Earth, Life, and Molecular Sciences, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan, Japan Science and Technology Agency, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan, and Department of Chemistry, Aichi University of Education, 1 Hirosawa, Igaya-cho, Kariya, Aichi 448-8542, Japan

ynishiha@okayama-u.ac.jp

Received May 16, 2013

ABSTRACT



A novel and versatile synthetic method for picene derivatives is developed using the Pd-catalyzed intramolecular double cyclization of the corresponding 2,3-bis[(1*Z*)-2-phenylethenyl]-1,4-dichlorobenzenes, which are readily prepared by Suzuki–Miyaura cross-coupling reactions of polyhalobenzenes with (*Z*)-arylethenylboronates. The physical properties of the obtained picenes can be modified via introducing a variety of functional groups to the picene framework. All compounds are investigated by UV–vis and fluorescence spectroscopic measurements, CV, and DFT calculations as well as X-ray diffraction analysis.

Among the fused polycyclic compounds, [*n*]phenacenes, arm-chair edged benzenoid compounds possessing extended π-conjugation, have attracted a great deal of attention as an active layer in organic field-effect transistors (OFETs)[1] because of their mechanical flexibility, lightweight, large-area coverage, ambipolar property, and low-cost/low-temperature fabrication process. Picene ([5]phenacene; Figure 1) represents a novel and promising class of materials for organic electronics.[2] However, the systematic modification of a picene core has rarely been reported,[3] although the development of methods to prepare various picene derivatives is of great interest because it may adjust their optical and electronic properties as well as their solubility and packing structures in the crystals.[4] In addition, there are several critical drawbacks for the

[†] Okayama University.
[‡] Japan Science and Technology Agency.
[§] Aichi University of Education.

(1) (a) Sugawara, Y.; Kaji, Y.; Ogawa, K.; Eguchi, R.; Oikawa, S.; Gohda, H.; Fujiwara, A.; Kubozono, Y. *Appl. Phys. Lett.* **2011**, *98*, 013303. (b) Komura, N.; Goto, H.; He, X.; Mitamura, H.; Eguchi, R.; Kaji, Y.; Okamoto, H.; Sugawara, Y.; Gohda, S.; Sato, K.; Kubozono, Y. *Appl. Phys. Lett.* **2012**, *101*, 083301.

(2) (a) Okamoto, H.; Kawasaki, N.; Kaji, Y.; Kubozono, Y.; Fujiwara, A.; Yamaji, M. *J. Am. Chem. Soc.* **2008**, *130*, 10470. (b) Kawasaki, N.; Kubozono, Y.; Okamoto, H.; Fujiwara, A.; Yamaji, M. *Appl. Phys. Lett.* **2009**, *94*, 043310. (c) Mitsuhashi, R.; Suzuki, Y.; Yamanari, Y.; Mitamura, H.; Kambe, T.; Ikeda, N.; Okamoto, H.; Fujiwara, A.; Yamaji, M.; Kawasaki, N.; Maniwa, Y.; Kubozono, Y. *Nature* **2010**, *464*, 76. (d) Wang, Y.; Motta, S. D.; Negri, F.; Friedlein, R. *J. Am. Chem. Soc.* **2011**, *133*, 10054. (e) Kawai, N.; Eguchi, R.; Goto, H.; Akaike, K.; Kaji, Y.; Kambe, T.; Fujiwara, A.; Kubozono, Y. *J. Phys. Chem. C* **2012**, *116*, 7983.

(3) (a) Okamoto, H.; Yamaji, M.; Gohda, S.; Kubozono, Y.; Komura, N.; Sato, K.; Sugino, H.; Satake, K. *Org. Lett.* **2011**, *13*, 2758. (b) Kitazawa, K.; Kochi, T.; Nitani, M.; Ie, Y.; Aso, Y.; Kakiuchi, F. *Chem. Lett.* **2011**, *40*, 300. (c) Xia, Y.; Liu, Z.; Xiao, Q.; Qu, P.; Ge, R.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 5714. (d) Mallory, F. B.; Mallory, C. W.; Regan, C. K.; Aspden, R. J.; Ricks, A. B.; Racowski, J. M.; Nash, A. I.; Gibbons, A. V.; Carroll, P. J.; Bohen, J. M. *J. Org. Chem.* **2013**, *78*, 2040.

(4) For examples of pentacene, see: (a) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986.

10.1021/ol401375n
Published on Web 07/01/2013

established synthetic methods for picenes, such as limitation of irradiation for large scale,[3a,d] multiple steps for their preparation,[3b,d] and a requirement of unstable precursors.[3c] Therefore, a simple and convenient strategy for the synthesis of various substituted picene derivatives is highly desirable in order to promote further investigations into its use in organic electronics. Herein we report the synthesis, characterization, and physicochemical properties of a series of novel substituted picenes.

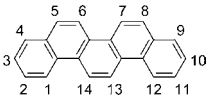
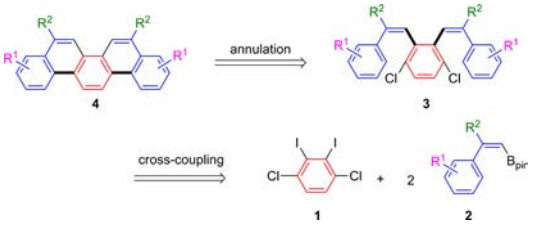


Figure 1. Structure of picene.

An outline for the synthesis of the substituted picene derivatives **4** is shown in Scheme 1. Although there have been no examples of the application of Pd-catalyzed C−H arylation to the picene synthesis, to the best of our knowledge, it would be a powerful method for the construction of the desired framework.[5] In order to obtain picene precursors **3**, Suzuki−Miyaura coupling reaction of 1,4-dichloro-2,3-diiodobenzene (**1**) with the stereodefined (*Z*)-alkenylboronates **2** bearing various substituents was designed.

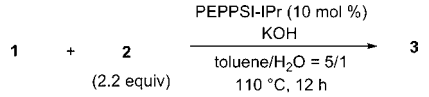
A series of (*Z*)-alkenylboronates **2a**−**e** were successfully prepared by Rh-catalyzed stereoselective hydroboration of terminal alkynes[6] or the zirconium-mediated synthesis from alkynylboronate.[7] Suzuki−Miyaura coupling reactions of **1** with **2a**−**e** catalyzed by PEPPSI-IPr[8] gave the corresponding **3a**−**e** in moderate to high yields (Table 1).

Scheme 1. Retrosynthetic Route to Picene Derivatives **4**



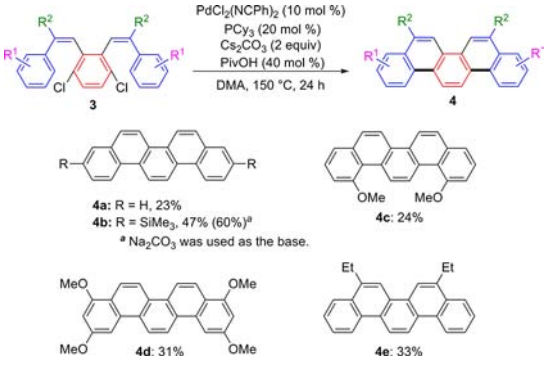
Next, we investigated the Pd-catalyzed double cyclization of **3a** through the C−H functionalization toward the synthesis of picene (**4a**). Among the different catalyst systems, the in situ generated $PdCl_2(PCy_3)_2$ from $PdCl_2(NCPh)_2$ and PCy_3 and pivalic acid as the additive was found to be the best. Encouraged by an identical ^1H NMR spectrum of the isolated **4a** to that of the commercial source, a series of picene derivatives **4b**−**e** were synthesized in moderate yields under optimized reaction conditions (Scheme 2).[9]

Table 1. Synthesis of the Picene Precursors **3** through Suzuki−Miyaura Coupling Reactions of **1** with **2**



entry	**2**		**3**	yield (%)
1	**2a**	(R^1 = R^2 = H)	**3a**	57
2	**2b**	(R^1 = 3-$SiMe_3$, R^2 = H)	**3b**	68
3	**2c**	(R^1 = 3-OMe, R^2 = H)	**3c**	67
4	**2d**	(R^1 = 2,4-OMe, R^2 = H)	**3d**	38
5	**2e**	(R^1 = H, R^2 = Et)	**3e**	67

Scheme 2. Synthesis of Picenes **4a**−**e**



It is noteworthy that the structure of compound **4c** is different from our initial expectation that two methoxy groups would locate in the 3,10-positions by the C−H bond functionalization to avoid a steric congestion. However, as shown in Figure 2, X-ray structural analysis successfully clarified the structure of **4c**, in which two OMe groups are situated at the 1,12-positions.[10] Moreover, the ^1H NMR measurement of **4c** showed a characteristic singlet at δ 9.92 ppm.

The optical properties of **4a**−**e** were studied by UV−vis and steady-state fluorescence spectroscopy. The observed optical properties are listed in Table 2. As shown in Figure 3(A), the wavelengths of maximum absorptions (λ_{max}^{abs}) of **4a**−**e** are ca. 290 nm. The substituted picenes **4b**−**e** exhibited absorption peaks at longer wavelengths, but their molar

(5) For reviews, see: (a) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; Frutos, Ó. D. *Synlett* **2003**, 585. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

(6) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990.

(7) Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 12634.

(8) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem.—Eur. J.* **2006**, *12*, 4743.

(9) Although the picene precursor **3** from a (*Z*)-arylethenylboronate bearing an electron-withdrawing CF_3 group in the 3-position was successfully synthesized, Pd-catalyzed double cyclization resulted in the formation of a mixture of structural isomers in a ratio of 46:54.

(10) CCDC-932531 (**4c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 2. ORTEP drawing of **4c** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. Hydrogen atoms are omitted for simplicity.

extinction coefficient ε values are smaller compared to that of **4a**. These results indicate that an introduction of the substituents into a picene framework can affect the physical properties, since no concentration influence was observed when UV−vis spectra of **4a**−**e** in different concentrations were measured.[3,11] The absorption spectra of the either edged- (as **4b**) or side- (as **4c** and **4e**) substituents are similar in shape, possessing the main transition around 290 nm and at higher wavelengths the other transitions appeared as a shoulder.

Table 2. UV−vis[a] and Fluorescence[b] Data of Picenes **4a**−**e**

picenes	λ_{max}^{abs} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max}^{emc} (nm)	Stokes shift (cm^{-1})	Φ_f[d]
4a	285	94300	378	212	0.07
4b	293	56800	384	274	0.10
4c	290	49700	388	201	0.06
4d	290	55100	391	331	0.18
4e	290	43700	385	273	0.13

[a] 1×10^{-5} M in CH_2Cl_2. [b] 5×10^{-7} M in CH_2Cl_2. [c] Wavelength of maximum fluorescence emission. [d] *p*-Terphenyl was used as a standard sample.

Since all the compounds **4a**−**e** are fluorescent, we performed the fluorescence spectral measurements by using the diluted CH_2Cl_2 solution (5×10^{-7} M), as shown in Figure 3(B). The results are also summarized in Table 2. Using the λ_{max}^{abs} values of picenes as the 0−0 transition wavelength, the emission maxima (λ_{max}^{em}) displayed Stokes shifts by approximately 4 nm.[12] The relative fluorescence quantum yields (Φ_f) of **4a**−**e** were estimated with Williams' relative method.[13]

The substituents in the picene framework can significantly affect the Φ_f values. The Φ_f values of **4d** and **4e** were 0.18 and 0.13, respectively. An introduction of the methoxy group decreased the Φ_f values for **4c**. It is uncertain at present why the Φ_f value was changed by an introduction of these substituents.

The absorption band edges (λ_{onset}) of picenes **4a**−**e** and the corresponding optical band gaps (E_g^{opt}) calculated

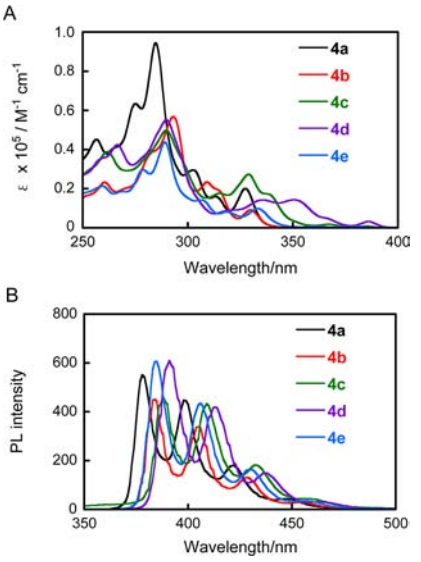


Figure 3. (A) Absorption spectra (1×10^{-5} M) and (B) fluorescence emission spectra with excitation wavelength at λ_{max}^{abs} (5×10^{-7} M) of **4a**−**e** in CH_2Cl_2.

from $1240/\lambda_{onset}$ are summarized in Table 3. The electrochemical properties of **4a**−**e** were also investigated by cyclic voltammetry (CV). The CV curves were recorded versus the potential of the Ag/Ag^+, which was calibrated by the ferrocene−ferrocenium (Fc/Fc^+) redox couple (−4.8 eV below the vacuum level).[14] The electrochemical data are also summarized in Table 3. The highest occupied molecular orbital (HOMO) energy levels were calculated from the CV data and the corresponding LUMO levels were estimated from formula $E_{LUMO} = E_{HOMO} + E_g^{opt}$. The observed oxidation waves and no reduction waves in the CV measurement suggest that all compounds are p-type semiconductors, which have potent applications in organic electronics. Moreover, all picene derivatives exhibited quasi-reversible oxidation wave,[15] reflecting that they possess an excellent electrochemical stability.

Picene derivative **4b** bearing the substituents in the 3,10-positions have the similar HOMO energy levels and slightly narrow optical band gaps than that of a parent picene **4a**. These results indicate that a substitution effect of a picene core in the 3,10-positions is rather small. In sharp contrast, other substituted picenes, **4c**, **4d**, and **4e**, have lower HOMO energy levels and smaller optical band gaps than that of **4a**. Furthermore, their HOMO levels significantly elevate with increasing the number of the substituents. In these cases, alkyl and methoxy groups introduced into the picene framework in the 1,12-, 2,11-, and 4,9-positions act as strong electron-donating groups. New five picenes **4b**−**e** could show better electron transfer capability in electronic devices since they showed relatively smaller the band gaps of than picene (3.23 eV).[16] Thus we calculated

(11) Kato, S.; Noguchi, H.; Kobayashi, A.; Yoshihara, T.; Tobita, S.; Nakamura, Y. *J. Org. Chem.* **2012**, *77*, 9120.
(12) Okamoto, H.; Yamaji, M.; Gohda, S.; Sato, K.; Sugino, H.; Satake, K. *Res. Chem. Intermed.* **2013**, *39*, 147.
(13) (a) Fery-Forgues, S.; Lavabre, D. *J. Chem. Educ.* **1999**, *76*, 1260. (b) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.
(14) Liu, S.-Y.; Shi, M.-M.; Huang, J.-C.; Jin, Z.-N.; Hu, X.-L.; Pan, J.-Y.; Li, H.-Y.; Jen, A. K.-Y.; Chen, H.-Z. *J. Mater. Chem. A* **2013**, *1*, 2795.
(15) See the Supporting Information.

Table 3. Physicochemical Properties of Picenes **4a**–**e**

compd	E_{onset}[a] (V)	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]	$E_g^{opt}/\lambda_{onset}$[(eV)[d]/nm]	E_{HOMO} (eV)[e]	E_{LUMO} (eV)[e]	E_g (eV)[e]
4a	+0.88	−5.80	−2.57	3.23/384	−5.48	−1.27	4.21
4b	+0.86	−5.78	−2.60	3.18/390	−5.45	−1.25	4.20
4c	+0.59	−5.51	−2.38	3.13/396	−5.12	−1.02	4.10
4d	+0.37	−5.29	−2.21	3.08/402	−4.80	−0.84	3.96
4e	+0.74	−5.67	−2.52	3.15/393	−5.33	−1.19	4.14

[a] Obtained from cyclic voltammograms in CH_2Cl_2. Reference electrode: Ag/Ag^+. [b] All of the potentials were calibrated with the Fc/Fc^+ ($E^{1/2} = -0.12$ V measured under identical conditions). Estimated with the following equation: E_{HOMO} (eV) = $-4.92 - E_{onset}$. [c] Calculated according to the formula $E_{LUMO} = E_{HOMO} + E_g^{opt}$. [d] Optical band gap, $E_g^{opt} = 1240/\lambda_{onset}$. [e] Obtained from theoretical calculations.

molecular reorganization energy (λ), which may potentially affect the transport properties.[17] From the results of λ^h, **4c** should be advantageous for efficient carrier transport. However, the calculated transfer integrals (t_{HOMO}s) of **4c** were found to be fairly small, because packing structure of **4c** is less effective for carrier transport, which was quite different from **4a** with high field-effect mobility.[18]

Electronic structures of novel picenes **4a**–**e** are theoretically investigated through calculation. The molecular geometries of **4a**–**e** were optimized using density functional theory (DFT) at the B3LYP/6-31G(d) level using Gaussian 09, Revision A. 02.[19] The results are also listed in Table 3. The frontier molecular orbitals of the optimized molecules were also calculated, as shown in Figure 4. The theoretically calculated HOMO–LUMO gaps are higher than those obtained in the UV–vis spectroscopic measurements (E_g^{opt}) by ca. 1.0 eV. All the HOMOs and LUMOs of picenes **4a**–**e** are evenly delocalized over the entire molecular π-frameworks. In addition, coefficients of picenes **4c**–**e** reside on the 1,12-, 2,11-, and 4,9-methoxy and 5,8-alkyl groups in the HOMO. On the other hand, the carbon atoms in the 3,10-position in **4b** have nodal planes in the HOMO. These results clearly support the similarity/difference of the energy levels of the frontier orbitals as well as the molecular electronic structures among **4a**–**e**.

In summary, we have developed a novel and versatile synthetic method for the synthesis of various picene derivatives by sequential Suzuki–Miyaura coupling and cyclization via intramolecular C–H bond functionalization. This methodology might also be used for the synthesis of other picene analogues, for instance, heteroatom-containing picenes and unsymmetric fused aromatic compounds such as [6]-phenacene. On the basis of this study, the effects of the structural variations of substituents on their electronic and electrochemical properties have emerged. A further elucidation of their physical properties involving the FET characters is underway in our laboratories.

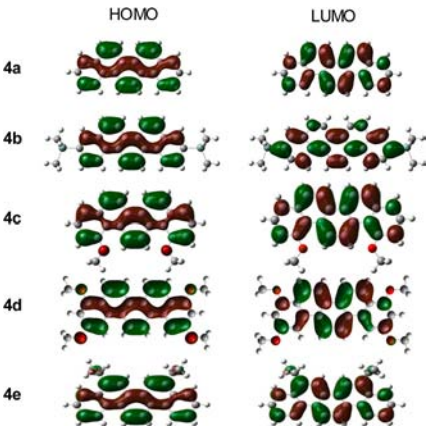


Figure 4. Wave functions for the HOMO and LUMO of **4a**–**e**.

Acknowledgment. We gratefully thank Profs. Koichi Mitsudo and Seiji Suga (Okayama University) for the measurements of CV and Ms. M. Kosaka and Mr. M. Kobayashi at the Department of Instrumental Analysis, Advanced Science Research Center, Okayama University, for the measurements of elemental analyses, respectively. The SC-NMR Laboratory of Okayama University for the NMR spectral measurements is gratefully acknowledged.

Supporting Information Available. Copies of ^1H NMR and $^{13}C\{^1H\}$ NMR spectra for all the new compounds, as well as details on experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(16) Li, G.; Wu, Y.; Gao, J.; Wang, C.; Li, J.; Zhang, H.; Zhao, Y.; Zhao, Y.; Zhang, Q. *J. Am. Chem. Soc.* **2012**, *134*, 20298.

(17) (a) Bredas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971. (b) Sakanoue, K.; Motoda, M.; Sugimoto, M.; Sakaki, S. *J. Phys. Chem. A* **1999**, *103*, 5551.

(18) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347.

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