# Synthesis and structures of heterasumanenes having different heteroatom functionalities

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## ARTICLE INFO

## ABSTRACT

After the protection of two α-carbons of the dibenzothiophene moiety in triphenylenothiophene **1** by trimethylsilyl groups, the resulting compound **4** reacted with butyllithium followed by dichlorodimethylsilane to afford 10H-silolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-*bcd*]thiophene **8**, which reacted with butyllithium followed by dichlorodimethylsilane to afford novel heterasumanene **11**. Using dichlorodimethylstannane instead of dichlorodimethylsilane afforded heterasumanene **12**, which is the first example of a heterasumanene having three different heteroatom functionalities.

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Corannulene has received considerable attention even for a long time before the discovery of C$_{60}$, because it is a beautiful bowl-shaped molecule and a fascinating extended π-delocalized system.[1] On the other hand, quite recently, sumanene, which is another type of partial-C$_{60}$ structure, has been reported.[2] Sumanene[3] itself is a very attractive molecule because it has three fluorene units in the molecule, each of which has an *sp*$^3$-hybridized carbon atom. Fluorene has long intensively been investigated from the viewpoint of its fluorescent nature,[4] synthetic utility as a ligand and a spacer of transition metal complexes,[5] and aromaticity of its anionic species.[6] On the other hand, 9-heterafluorenes have also received considerable attention in terms of their unique electronic properties dependent on the central heteroatoms on the 9-position,[7] applied in the synthesis of such intelligent materials as fluorescent polymers[8] and chemical sensors.[9] Being inspired by the first synthesis of sumanene, we became interested in substituting the *sp*$^3$ benzyl carbons in sumanene by heteroatoms to perturb the electronic and structural properties of sumanene. The molecules whose heteroatom functionalities are introduced into these positions can be called heterasumanenes. When we undertook our project of the synthesis of heterasumanenes, the sole example of heterasumanenes was the trithiasumanene, which has three dibenzothiophene units in the molecule.[10] However, during the synthetic process, the severe reaction conditions of flash vacuum pyrolysis are needed, and we can only access heterasumanenes having three identical heteroatoms. Therefore, development of methods for the simpler synthesis of heterasumanenes remains a goal.[11] We chose the known triphenyleno[1,12-*bcd*]thiophene (**1**) as a starting compound, because it can be easily prepared from triphenylene.[12] We report herein the

synthesis of novel heterasumanenes, having different heteroatom functionalities, and their structures and properties.

To functionalize the starting triphenyleno[1,12-*bcd*]thiophene (**1**), direct abstraction of the bay protons of **1** was first attempted. After treatment of **1** with 4 equiv of butyllithium in hexane–TMEDA at 60 °C for 3 h, the reaction was quenched with D$_2$O to afford 3,5-dideuteriated compound **2** in 80% yield (Scheme 1). Protons on the α-carbons of the dibenzothiophene moiety were abstracted more easily than bay protons to afford dilithio derivative **3**. For further functionalization of a bay area of **1**, the α-carbons of the dibenzothiophene moiety were protected by trimethylsilyl
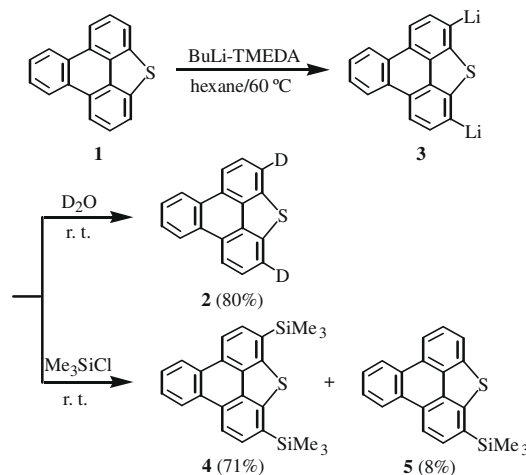


**Scheme 1.** Lithiation and silylation of **1**.

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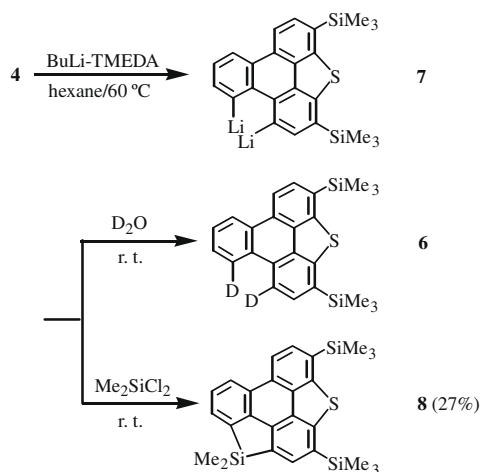  E-mail address: masaichi@chem.saitama-u.ac.jp (M. Saito).

groups to give bis(trimethylsilyl) derivative **4** in 71% yield[13] together with mono-substituted **5** in 8% yield (Scheme 1).[14]

For further functionalization of **4**, first, lithiation of **4** was examined. After treatment of **4** with 4 equiv of butyllithium in hexane–TMEDA at 60 °C for 3 h, the reaction was quenched with $D_2O$. A ^{1}H NMR spectrum of the crude mixture revealed the formation of dideuteriated compound **6**, the yield of which was estimated to be about 20% (Scheme 2). Although the generation efficiency of lithiated compound **7** was not very good,[15] arching of a bay area of **4** with a heteroatom functionality was carried out. Treatment of a solution of **7**, generated by the reaction of **4** with 4 equiv of butyllithium, with dichlorodimethylsilane afforded novel 10,10-dimethyl-10*H*-silolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-*bcd*]thiophene **8** in 27% yield, the structure of which was established by X-ray crystallographic analysis (Scheme 2).[14,16,17]
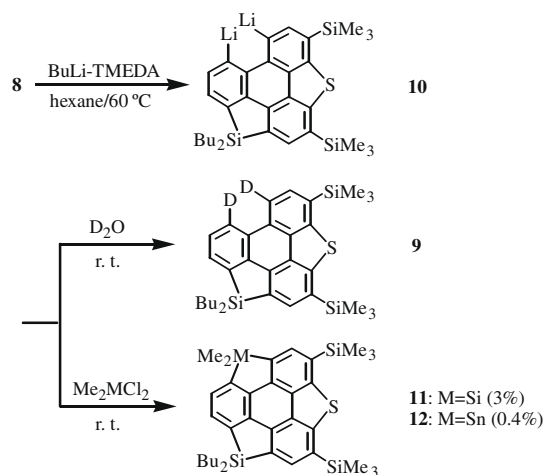
The final step for the synthesis of a heterasumanene from compound **8** was to arch the remaining bay area by a heteroatom functionality. Lithiation of compound **8** was therefore examined. After treatment of silolotriphenylenothiophene **8** with butyllithium, the reaction was quenched with deuterium oxide to afford dideuterio derivative **9** in which two butyl groups were introduced onto the silicon atom, as shown by MASS spectrometry. Hence, we assigned an intermediate to dibutyl-substituted dilithio species **10** (Scheme 3). Since 9,9-dimethyl-9-silafluorene reacted with butyllithium to give 9,9-dibutyl-9-silafluorene,[18] the introduction of butyl groups onto the silicon atom of **8** through this reaction is quite reasonable. The dilithio species **10** thus obtained reacted with dichlorodimethylsilane to afford novel heterasumanene **11** in 3% yield (Scheme 3),[19] the structure of which was established by X-ray crystallographic analysis (Fig. 1).[20] Treatment of dilithio species **10** with dichlorodimethylstannane to afford heterasumanene **12** in 0.4% yield,[14] which is the first example of a heterasumanene having three different heteroatom functionalities.

The *ORTEP* drawings of heterasumanene **11** are shown in Figure 1. The C–C bonds in the central six-membered ring slightly alter from 1.367 Å to 1.450 Å, and the degree of alternation in **11** is larger than those found in the parent triphenylene (1.411–1.470 Å)[21] and sumanene (1.381–1.431 Å).[22] The π-framework slightly deviates from planarity. The bowl depth of 0.23 Å is shallower than those of sumanene (1.11 Å)[22] and trithiasumanene (0.79 Å).[10] In contrast, trisilasumanene was predicted to be planar by theoretical calculations.[23] To understand the slightly bent structure of **11**, theoretical calculations were carried out.

Based on the X-ray structure, optimization of the structure of **11** was carried out with hybrid density functional theory at the M05-

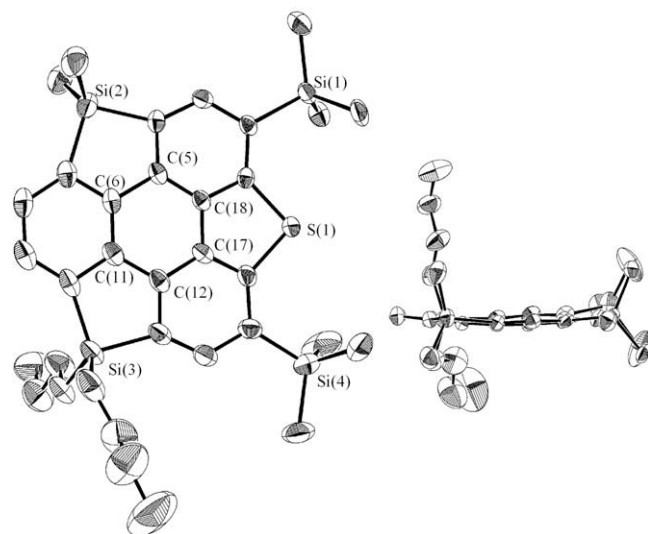**Scheme 3.** Synthesis of heterasumanenes **11** and **12**.

**Figure 1.** *ORTEP* drawings of **11** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). Top view (left) and side view (right). All hydrogen atoms and a disordered minor moiety were omitted for clarity. Selected bond lengths (Å), C(5)–C(6), 1.450(5); C(6)–C(11), 1.407(6); C(11)–C(12), 1.428(6); C(12)–C(17), 1.384(6); C(17)–C(18), 1.408(5); C(18)–C(5), 1.367(6).

2X[24] level using the GAUSSIAN 03 program.[25] However, the optimized structure was not bent but planar, inconsistent with the X-ray structure. To elucidate the geometric feature of the X-ray structure, a dimeric unit of **11** (Fig. 2) where three $CH_3$ groups of part A directly point toward the aromatic ring of the part B was also optimized. In this unit, the similar $CH_3$ groups that point to the ring of part A in the X-ray structure were neglected (Fig. 3). The optimization of the dimer unit produced a pair of a bent and a planar structures with the average distance of 2.771 Å between the $CH_3$ groups and the ring (Table 1), comparable to 2.917 Å in the X-ray structure (Fig. 3). Details of the calculated data are shown in the Supplementary data. The stabilization energy in comparison of a dimeric structure with two planar structures was calculated to be 9.8 kcal/mol. It is noteworthy that the energy of the bent part in the dimeric unit is higher by only 0.7 kcal/mol than that of the optimized planar structure of **11**. The similar dimeric structure was also found in the calculations for the simplified model system with methyl groups instead of butyl groups on the silicon atom that showed a stabilization energy of 8.5 kcal/mol, suggesting that

**Scheme 2.** Synthesis of silolotriphenylenothiophene **8**.
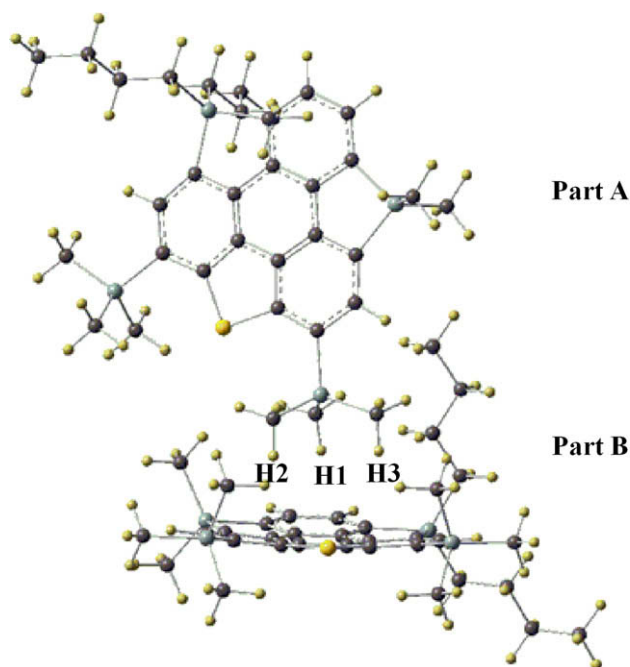
**Figure 2.** Optimized structure of the dimeric unit of **11**. One is planar and the other is bent. The three dot lines show CH–π interactions between the CH$_3$ groups on the silicon atom and the aromatic ring.
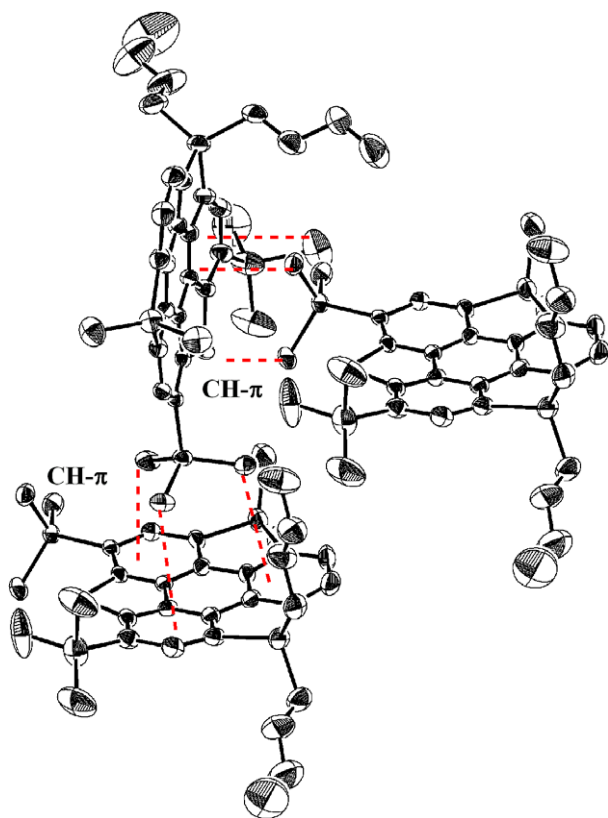


**Figure 3.** CH–π interactions in **11** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogens and a disordered minor moiety were omitted for clarity. The dot lines show CH–π interactions between the CH$_3$ groups on the silicon atom and the aromatic ring.

the butyl groups have no significant effect on the structural feature. Therefore, it is concluded that intermolecular CH–π interac-

**Table 1**
CH distances (Å) related with CH–π interactions in **11**
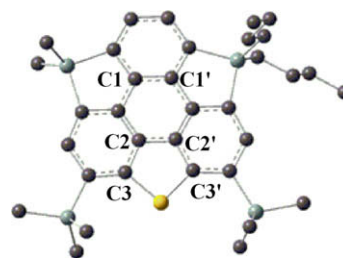


| | C–H distances (Å) | |
| --- | --- | --- |
| | Calculated | Experimental |
| H1–C1 | 2.614 | 2.895 |
| H1–C1′ | 2.629 | 3.042 |
| H2–C2 | 2.852 | 2.772 |
| H2–C2′ | 2.652 | 2.777 |
| H3–C3 | 3.008 | 2.980 |
| H3–C3′ | 2.870 | 3.038 |
| av | 2.771 | 2.917 |

tions strongly affect the deviation of planarity of **11** in the solid state (Fig. 3). This conclusion, furthermore, is demonstrated by the planar ring of part A in the dimeric unit without the effects of the CH$_3$ groups, because this part is also bent in the solid state, being affected by CH–π interactions of another molecule (Fig. 3).

In summary, we succeeded in the synthesis of novel heterasumanenes **11** and **12** from triphenylenothiophene **1**. The preparation of **12** is worthy of note from the standpoint of the first heterasumanene having three different heteroatom functionalities. Although the yields of **11** and **12** were not high, the present method will enable us to synthesize heterasumanenes with three different functionalities, leading to the development of the less-explored chemistry of heterasumanenes. Further investigation on the properties of **11** and **12**, and the synthesis of other types of heterasumanenes is currently in progress.

### Acknowledgments

### Supplementary data

Supplementary data (details for experiments and theoretical calculations) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.102.

### References and notes

1. (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380; (b) Lawton, R. G.; Barth, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 1730.
2. Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.
3. Mehta, G.; Shah, S. R.; Ravikumarc, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1006.
4. For examples of recent reviews, see: (a) Monkman, A.; Rothe, C.; King, S.; Dias, F. *Adv. Polym. Sci.* **2008**, *212*, 187; (b) DaComo, E.; Becker, K.; Lupton, J. M. *Adv. Polym. Sci.* **2008**, *212*, 293; (c) Belfield, K. D.; Yao, S.; Bondar, M. V. *Adv. Polym. Sci.* **2008**, *213*, 97.
5. For recent examples, see: (a) Gentil, S.; Dietz, M.; Pirio, N.; Meunier, P.; Gallucci, J. C.; Gallou, F.; Paquette, L. A. *Organometallics* **2002**, *21*, 5162; (b) Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 943.
6. Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075.

7. Chen, R.-F.; Zheng, C.; Fan, Q.-L.; Huang, W. *J. Comput. Chem.* **2007**, *28*, 2091.
8. For recent examples, see: (a) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Macromolecules* **2008**, *41*, 1237; (b) Tamura, K.; Shiotsuki, M.; Kobayashi, N.; Masuda, T.; Sanda, F. *J. Polym. Sci., Part A Polym. Chem.* **2009**, *47*, 3506; (c) King, S. M.; Perepichka, I. I.; Perepichka, I. F.; Dias, F. B.; Bryce, M. R.; Monkman, A. P. *Adv. Funct. Mater.* **2009**, *19*, 586.
9. For recent examples, see: (a) You, J.; Yan, T.; Zhao, H.; Sun, Z.; Xia, L.; Suo, Y.; Li, Y. *Anal. Chim. Acta* **2009**, *636*, 95; (b) Sanchez, J. C.; Di Pasquale, A. G.; Mrse, A. A.; Trogler, W. C. *Anal. Bioanal. Chem.* **2009**, *395*, 387.
10. Imamura, K.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1999**, 1859.
11. Very recently, trisilasumanene has been synthesized and characterized, see: Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 14192.
12. (a) Klemm, L. H.; Lawrence, R. F. *J. Heterocycl. Chem.* **1979**, *16*, 599; (b) Ashe, A. J., III; Kampf, J. W.; Savla, P. M. *J. Org. Chem.* **1990**, *55*, 5558.
13. Saito, M.; Tanikawa, T.; Tajima, T. *Acta Crystallogr., Sect. E* **2007**, *63*, o2923.
14. Experimental details, see Supplementary data.
15. When 10 equiv of butyllithium were used for lithiation of **4**, the reaction became complicated, probably because lithiation at more than two bay areas occurred.
16. The structural details and the properties of **8** will appear elsewhere. CCDC 745674 contains the Supplementary data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).
17. Although the yield of **8** was slightly higher than that of **6**, we think that the difference is within errors in integrations of the NMR spectroscopic analysis.
18. Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1983**, *250*, 109.
19. *Preparation of heterasumanene* **11**: To a hexane (10 mL) solution of silolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-*bcd*]thiophene **8** (193.1 mg, 0.35 mmol) were added TMEDA (0.53 mL, 3.56 mmol) and butyllithium (2.64 M in hexane; 1.34 mL, 3.56 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After being cooled to 0 °C, the mixture was treated with dichlorodimethylsilane (0.23 mL, 1.92 mmol). After being stirred for 12 h at room temperature, the mixture was concentrated and materials insoluble in chloroform were removed by filtration. After removal of volatile substances, the residue (422.9 mg) was subjected to gel permeation chromatography followed by preparative thin layer chromatography to afford 2,9-bis(trimethylsilyl)-4,4-dibutyl-7,7-dimethyl-4,7-dihydrobissilolo[2′,3′,4′,5; 2″,3″,4″,5″:8,9]triphenyleno[1,12-*bcd*]thiophene (**11**) (6.7 mg, 3%). Hetera-sumanene **11**: $^1$H NMR(CDCl$_3$, 400 MHz) $\delta$ 0.567 (s, 9H), 0.569 (s, 9H), 0.66 (s, 6H), 0.83 (t, *J* = 7 Hz, 6H), 1.12–1.16 (m, 4H), 1.34 (q, *J* = 7, 7 Hz, 4H), 1.43–1.50 (m, 4H), 7.90 (s, 2H), 8.10 (s, 1H), 8.13 (s, 1H); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ −1.87(q), −0.80(q), −0.77(q), 13.00(t), 13.69(q), 26.34(t), 26.39(t), 127.62(s), 129.46(s), 130.31(s), 131.39(d), 132.12(s), 132.25(s), 135.44(d), 136.07(d), 138.34(s), 138.91(s), 138.99(s), 139.65(s), 141.13(s), 141.58(s), 148.09(s), 148.18(s). HRMS (EI/70 eV): Calcd for C$_{34}$H$_{46}$SSi$_4$: 598.2397. Found: 598.2396.
20. Crystals suitable for X-ray diffraction were obtained by recrystallization in chloroform solution of **11** at −20 °C. The intensity data were collected at −170 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo–K$_\alpha$ radiation ($\gamma$ = 0.71073 Å) and graphite monochromator. Formula C$_{34}$H$_{46}$SSi$_4$, FW = 599.13, crystal dimension 0.20 × 0.15 × 0.08 mm, monoclinic, space group $P2_1/n$, $Z$ = 4, $a$ = 12.167(3) Å, $b$ = 12.252(3) Å, $c$ = 24.285(6) Å, $\beta$ = 95.753(7)°, $V$ = 3601.8(16) Å$^3$, $D_{calcd}$ = 1.105 g cm$^{-3}$, $R_1$ = 0.085 ($I > 2\sigma(I)$, 4184 reflections), $wR_2$ = 0.249 (for all reflections) for 8667 reflections and 393 parameters, GOF = 1.021. CCDC 745675 contains the Supplementary data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc. cam.ac.uk).
21. Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.
22. Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580.
23. Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2001**, *66*, 6523.
24. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.
25. GAUSSIAN 03, Revision E.01; Gaussian: Wallingford, CT, 2004.