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Synthesis and Structural Characterization of Isomeric Bis[3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl]dimethoxysilanes

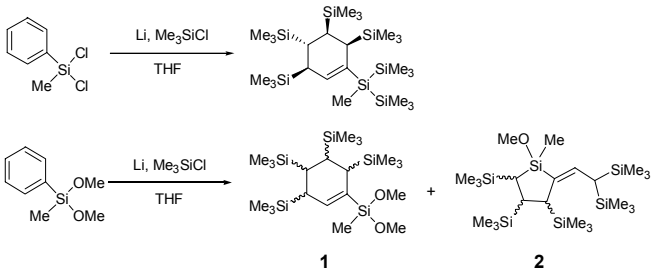
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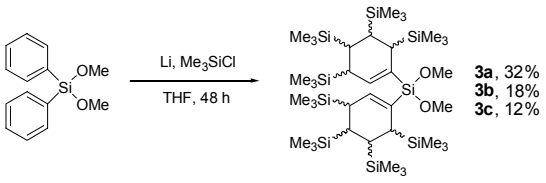
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The syntheses of polysilylated cycles from aromatic precursors have been accomplished by Birch type reductive silylation[1-14] and electrochemical silylation.[15-19] Although the strategy of Birch type reductive silylation has several drawbacks *vs* electrochemical silylation such as using metal reducing agents, and irregular yields, it has been well developed as one of useful methods for the formation of carbon-silicon bonds in both carbon and organosilicon chemistry.[20-25] Reductive polysilylations of $PhSiCl_3$ and $PhMeSiCl_2$ were reported to occur with excess lithium and Me_3SiCl in THF to yield tetrasilylated cyclohexene (Ttc = tetrakis(trimethylsilyl)cyclohex-1-ene) derivatives.[7,8,11] However, to our knowledge, no investigation for the synthesis of a compound having two Ttc substituents on the same silicon atom has been appeared. Recently, we reported the Birch-type reductive polysilylation of dimethoxymethylphenylsilane with excess Li and chlorotrimethylsilane in THF solvent, which gave not only tetrasilylated cyclohexenyl derivatives, **1**, but interesting five-membered ring contracted compounds, **2**.[26] These results indicated that substituents on silicon atom other than phenyl groups play an important role in the reductive polysilylation process (Scheme 1).

In this paper we report the synthesis and structural characterizations of three diastereomeric isomers of bis[Ttc]dimethoxysilanes, synthesized by Birch type polysilylation of dimethoxydiphenylsilane with excess lithium and Me_3SiCl in THF.



Scheme 1



Scheme 2. Synthesis of diastereomeric isomers, **3**.

The reaction of dimethoxydiphenylsilane with excess Li metal and chlorotrimethylsilane was carried out in THF solvent at −30 °C and monitored by gas chromatography. After stirring for 48 h at that temperature, the color of the solution turned from colorless to dark-brown and all the starting material was consumed indicating that the reaction was complete. The two phenyl groups were readily reduced to give bis[Ttc]dimethoxysilanes, **3**; ring contracted five-membered silacyclic products were not observed. In this reductive silylation, one can expect that there are many diastereomeric isomers due to the position of trimethylsilyl substituents in the cyclohexene ring. Theoretically, the number of the expected isomers for one Ttc substitiuent having 4 chiral centers is 16. Experimentally, only three diastereomeric isomers, **3a**, **3b**, and **3c** of bis[Ttc]dimethoxysilanes were isolated by filtration and column chromatography. The isolated isomers were recrystallized in hexane solvent giving colorless

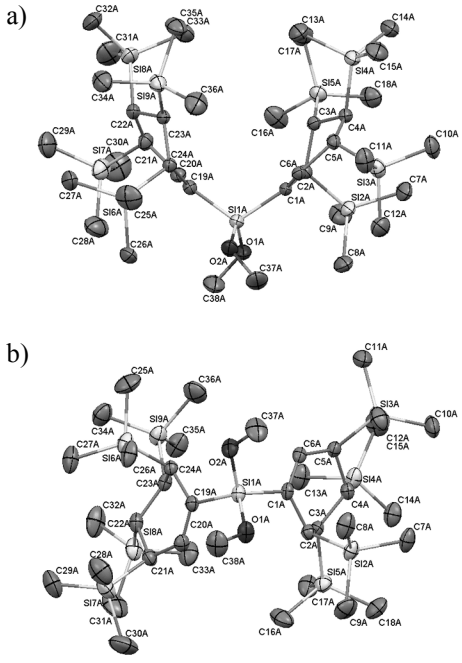


Figure 1. X-ray structure of **3a**, shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. a) side view, b) bottom view.

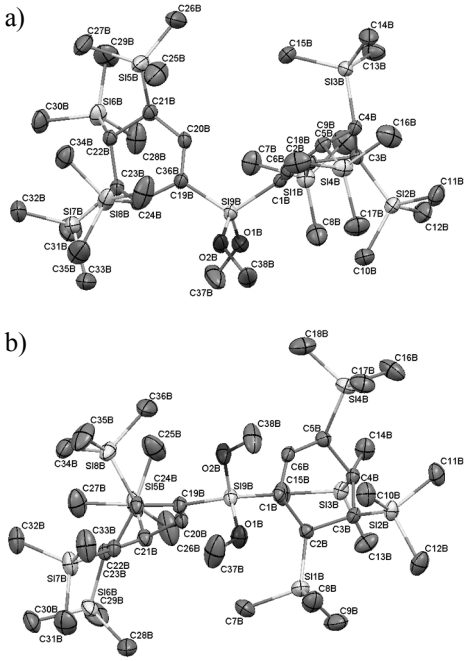


Figure 2. X-ray structure of **3b**, shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. a) side view, b) bottom view.

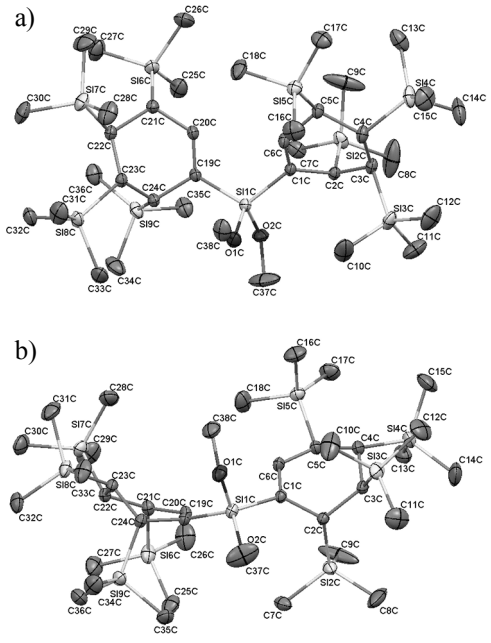


Figure 3. X-ray structure of **3c**, shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. a) side view, b) bottom view.

crystals (Scheme 2).The structure of diastereomers **3a**, **3b** and **3c** were characterized by X-ray crystallography (Figure 1, 2 and 3). The average Si-O bond length of **3a**, **3b** and **3c** is 1.636 Å, similar to the known average value of Si-O bond lengths (1.629 Å).[27] Simplified models of **3a**, **3b** and **3c** show the characteristic stereochemistry of isomers due to the different positions of trimethylsilyl substituents in the Ttc groups (Fig. 4).

Figure 5 shows the structure of Ch1 of **3a** which indicates that the cyclohexene back-bone adopts a half-boat conformation.

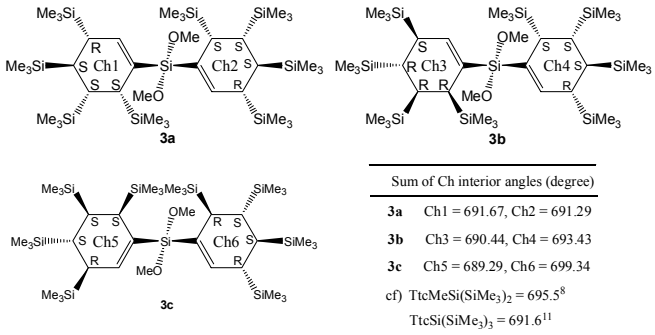


Figure 4. Simplified models for the **3a**, **3b** and **3c** (Ch = cyclohex-1-enyl).

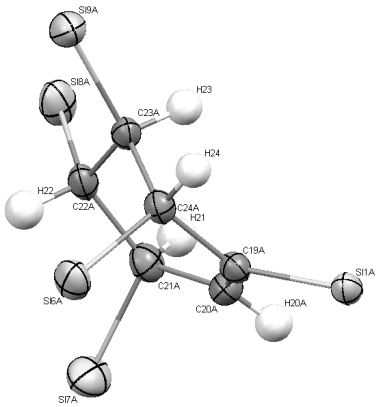


Figure 5. The structure of Ch1 of **3a**. All methyl groups are omitted for clarity.

Table 1. The calculated energy of **3a**, **3b** and **3c**.

	Calculated zero point energy (A.U.)	
	HF/6-31G	B3LYP/6-31G
3a	−4238.2734	−4255.2363
3b	−4238.2657	−4255.2231
3c	−4238.2696	−4255.2263

The torsion angle C19A, C20A, C21A, and C24A was 2.71°, nearly coplanar. From C21A to C24A, trimethylsilyl groups have a trans-trans-cis orientation about the cyclohexene ring. The sum of the interior angles of Ch1 of **3a** was 691.67. The bond lengths of silicon-sp^3 carbon atom span the range between 1.907 and 1.935 Å, somewhat longer than the usual bond length of 1.865 - 1.879 Å.[28] The endocyclic carbon-carbon bonds of cyclohexene ring range from 1.566 to 1.574, longer than the normal value of 1.53 Å.[29] The structure of other cyclohexene rings shows a similar pattern to Ch1 of **3a**.

To understand the thermo-chemical stabilities of **3a**, **3b**, and **3c**, some preliminary quantum chemical calculations by HF/6-31G and B3LYP/6-31G were carried out.[30] The calculated zero point energies of compounds **3a**, **3b**, and **3c** are shown in Table 1, which show that **3a** is the most stable structure. These calculated results are in accordance with experimental results on relative yields. Among the various isomers, the most stable structure of **3a** was favored during the Birch type silylation reaction.

In summary, the reaction of dimethoxydiphenylsilane with

Table 2. Crystallographic data and structural refinement details for **3a**, **3b** and **3c**.

	3a	**3b**	**3c**
formula	$C_{38}H_{88}O_2Si_9$	$C_{38}H_{88}O_2Si_9$	$C_{38}H_{88}O_2Si_9$
M_r [gmol^{-1}]	829.89	829.89	829.89
crystal size	0.65 × 0.50 × 0.30	0.60 × 0.40 × 0.35	0.65 × 0.60 × 0.55
crystal color habit	colourless	colourless	colourless
crystal system	orthorhombic	monoclinic	triclinic
space group	Pbca (no. 61)	c2/c (no. 15)	p-1 (no. 2)
a [Å]	19.038(3)	56.053(6)	9.8062(8)
b [Å]	22.433(5)	10.008(2)	15.340(1)
c [Å]	25.846(3)	19.534(3)	19.413(2)
α [°]	90.00	90.00	99.808(1)
β [°]	90.00	99.01(1)	101.415(1)
γ [°]	90.00	90.00	105.039(1)
V (Å^3)	11038(3)	10823(3)	2687.6(4)
Z	8	8	2
ρ_{calcd} [gcm^{-3}]	0.999	1.019	1.026
μ [mm^{-1}]	0.243	0.247	0.249
F (000)	3664	3664	916
T [K]	298(2)	298(2)	293(2)
λ [Å]	0.71069	0.71069	0.71073
2θ range [°]	1.58-25.00	2.07-27.48	2.20-27.00
reflections collected	9724	12360	11518
data/parameters	9724/442	12360/442	11518/468
goodness-of-fit on F^2	1.179	1.112	1.019
final *R* indices [$I > 2\sigma(I)$]	R_1[a] = 0.0911, wR_2[b] = 0.1410	R_1[a] = 0.0787, wR_2[b] = 0.1442	R_1[a] = 0.0477, wR_2[b] = 0.1242
largest different peak/hole [e Å^{-3}]	−0.30, 1.20 Å from Si4A	---	---

excess Li metal and Me_3SiCl in THF gave three diastereomeric products of bis[Ttc]dimethoxysilanes, **3a**, **3b,** and **3c**. Their structures were fully characterized by X-ray crystallography.

Experimental Section

General Comments. In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. THF was distilled from Na/Ph_2CO. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance II$^+$ BBO 400 MHz S1 spectrometer in $CDCl_3$ with tetramethylsilane (TMS). Analyses of product mixtures were accomplished using an HP 5890 II Plus instrument with FID (HP-5, 30 m column) with dried decane as an internal standard. Mass spectra were recorded on a high-resolution Autospec M363 series instrument.

Syntheses of Bis[3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl]dimethoxysilane, 3a, 3b and 3c. A solution of dimethoxydiphenylsilane (12.9 g, 0.05 mol) in THF (20 mL) was added to a mixture of chlorotrimethylsilane (50.8 mL, 0.4 mol) and lithium (3.47 g, 0.5 mol) at −30 °C in THF (250 mL). The reaction mixture was stirred for about 48 h at −30 °C. The color of the solution turned from colorless to dark-brown. The reaction mixture was slowly warmed to room temperature and then kept at that temperature for 12 h and treated with saturated aqueous ammonium chloride. The organic layer was separated and dried over sodium bicarbonate and low boilers were removed by vacuum evaporation. After addition of *n*-hexane into the reaction mixture, recrystallization in *n*-hexane yield two kinds of products; colorless crystals of **3a** in 32% (13.3 g) yield, and a white powder. After separation of the two products manually using tweezers, the white powder was recrystallized in *n*-hexane to give **3b** in 18% (7.5 g) yield as colorless crystals. After the separation of the residual mixture by flash column chromatography (hexane eluent), **3c** was obtained in 12% (5.0 g) yield as colorless crystals.

Ttc$_2$Si(OMe)$_2$, 3a: Colorless crystals, mp 193 ~ 197 °C. ^{1}H-NMR (400 MHz, chloroform-*d*) : δ 0.00 (s, 9H), 0.05 (s, 18H), 0.07 (s, 18H), 0.12 (s, 9H), 0.15 (s, 9H), 0.16 (s, 9H), 1.04, 1.31, 1.62, 1.85, 2.24 (m, 8H, cyclohexenyl-H), 3.45, 3.49 (s, 6H, OCH_3), 5.83, 6.38 (s, 2H, vinyl-H). ^{13}C-NMR (100 MHz, chloroform-*d*) : δ -1.05, -0.64, 0.50, 1.38, 1.73, 1.99, 2.68, 3.49 ($SiMe_3$ × 8), 23.0, 23.4, 23.7, 27.0, 29.4, 30.6, 30.8, 31.6 (cyclohexenyl-C), 50.37, 50.48 (OCH_3), 134.2, 139.4 (*ipso*-C), 145.1, 145.6 (vinyl-CH). HRMS: $C_{38}H_{88}O_2Si_9$ 828.4708 (calcd), 828.4705 (found).

Ttc$_2$Si(OMe)$_2$, 3b: Colorless crystals, mp 152 ~ 154 °C. ^{1}H-NMR (400 MHz, chloroform-*d*) : δ 0.00 (s, 9H), 0.06 (s, 9H),

0.07 (s, 18H), 0.12 (s, 9H), 0.16 (s, 9H), 0.17 (s, 18H), 0.16 (s, 9H), 1.04, 1.08, 1.32, 1.52, 1.63, 1.85, 2.25 (m, 8H, cyclohexenyl-H), 3.46, 3.52 (s, 6H, OCH3), 6.10, 6.40 (s, 2H, vinyl-H). ^{13}C-NMR (100 MHz, chloroform-*d*): δ -1.46, -1.03, 0.11, 0.99, 1.34, 1.68, 2.29, 3.10 ($SiMe_3$ × 8), 22.7, 23.0, 23.3, 26.6, 29.1, 30.3, 30.5, 31.3 (cyclohexenyl-C), 50.08 (OCH_3), 133.9, 139.1 (*ipso*-C), 142.7, 145.30 (vinyl-CH).

$Ttc_2Si(OMe)_2$, 3c: Colorless crystals, mp 162 ~ 170 °C. ^{1}H-NMR (400 MHz, chloroform-*d*): δ - 0.02 (s, 9H), 0.00 (s, 9H), 0.06 (s, 9H), 0.10 (s, 9H), 0.12 (s, 9H), 0.13 (s, 18H), 0.16 (s, 9H), 1.00, 1.01, 1.02, 1.04, 1.39, 1.40, 2.00, 2.29 (m, 8H, cyclohexenyl-H), 3.46, 3.52 (s, 6H, OCH_3), 6.10, 6.40 (s, 2H, vinyl-H). ^{13}C-NMR (100 MHz, chloroform-*d*): δ -2.68, -1.84, -1.55, -0.75, 0.00, 1.21, 1.96 ($SiMe_3$ × 8), 16.7, 19.5, 21.6, 23.9, 25.6, 28.0, 28.7, 29.0 (cyclohexenyl-C), 48.96, 49.36 (OCH_3), 134.4, 134.7 (*ipso*-C), 141.0 (vinyl-CH).

X-ray Crystallography. The crystallographic data and the results of refinement for compounds **3a**, **3b** and **3c** were listed in Table 2. A single crystal was used for data collections on a STOE STADI4 four-circles-diffractometer[31a](**3a** and **3b**) and Brucker Smart CCD[31b](**3c**) with graphite monochromatic Mo-K radiation at room temperature. Unit cell parameters were determined by least-squares refinement, using the 31 (**3a**), 48 (**3b**) and 6534 (**3c**) having θ values in the ranges of 19.2 - 20.8 (**3a**), 19.0 - 21.0 (**3b**) 2.22 - 28.24 (**3c**), respectively. Intensities were collected ω-2θ (**3a** and **3b**) and φ- ω (**3c**) scan technique. During data collection three standard reflections were measured every hour and showed no significant difference (**3a** and **3b**). The intensity data were collected for Lorentz and polarization effect, and absorption correction were applied (**3a** and **3b**: X-SHAPE,[31a] **3c**: SADABS[31c]). The structure was solved by direct method (SHELXS-97[32]) and refined by full-matrix least-squares methods (SHELXL-97[32]). All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically and refined using a riding model, with C-H = 0.98 Å for the methine, 0.93 Å A for the aryl and 0.96 Å for the methyl H atoms. Uiso (H) = 1.2 Ueq (C) for the methine, the methane, and 1.5 for the methyl H atoms.

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Supplementary Materials. CCDC-747712 (**3a**), 747713 (**3b**) and 747714 (**3c**) contain 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.

References

1. Weyenberg, D. R.; Toporcer, L. H. *J. Am. Chem. Soc.* **1962**, *84*, 2843.
2. Weyenberg, D. R.; Toporcer, L. H. *J. Org. Chem.* **1965**, *30*, 943.
3. Laguerre, M. ; Félix, G.; Dunoguès, J.; Calas, R. *J. Org. Chem.* **1979**, *44*, 4275.
4. Laguerre, M.; Dunogues, J.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* **1976**, *112*, 49.
5. Laguerre, M.; Dunogues, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1976**, *120*, 319.
6. Tsuji, H.; Toshimitsu, A.; Tamao, K. *Chem. Heterocycl. Compd.* **2001**, *37*, 1369.
7. Gilman, H.; Harrel, R. L.; Smith, C. L.; Shiina, K. *J. Organomet. Chem.* **1966**, *5*, 387.
8. Beineke, T. A.; Martin, L. L. *J. Organomet. Chem.* **1969**, *20*, 65.
9. Dunoguès, J.; N'Gabe, D.; Laguerre, M.; Duffaut, N.; Calas, R. *Organometallics* **1982**, *1*, 1525.
10. Laguerre, M.; Léger, J. M.; N'Gabé, D. Y.; Biran, C.; Dunoguès, J. *Tetrahedron* **1986**, *42*, 669.
11. Puranik, D. B.; Fink, M. J. *J. Chem. Cryst.* **1994**, *24*, 293.
12. Reyx, D.; Martins, J. M.; Campistron, I.; Huet, F. *Bull. Soc. Chim. Fr.* **1994**, *131*, 1007.
13. Reyx, D.; Martins, J. M. N.; Campistron, I. *Macromol. Chem. Phys.* **1995**, *196*, 149.
14. Harloff, J.; Popowski, E.; Fuhrmann, H. *J. Organomet. Chem.* **1999**, *592*, 136.
15. Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans.1* **1974**, 2055.
16. Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans.1* **1975**, 470.
17. Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans.1* **1975**, 475.
18. Bordeau, M.; Biran, C.; Pons, P.; Léger-Lambert, M.; Dunoguès, J. *J. Org. Chem.* **1992**, *57*, 4705.
19. Deffieux, D.; Bordeau, M.; Biran, C.; Dunoguès, J. *Organometallics* **1994**, *13*, 2415.
20. Birch, A. J.; Smith, H. *Quart. Rev.* **1958**, *12*, 17.
21. Schultz, A. G.; Guzi, T. J.; Larsson, E.; Rahm, R.; Thakkar, K.; Bidlack, J. M. *J. Org. Chem.* **1998**, *63*, 7795.
22. Studer, A.; Amrein, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 3080.
23. Donophoe, T. J.; Guillermin, J.; Calabrese, A. A.; Walter, D. S. *Tetrahedron Lett.* **2001**, *42*, 5841.
24. Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 1556.
25. Marcinow, Z.; Clawson, D. K.; Rabideau, P. W. *Tetrahedron* **1989**, *45*, 5441.
26. Lim, Y. M.; Lee, M. E. *Organometallics* **2008**, *27*, 1000.
27. Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*, Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U. K., 1998; Vol. 2, p 218.
28. Armitage, D. A. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, U.S.A., 1982; Vol. 2.
29. Smith, M. B.; March, J. *March's Advanced Organic Chemistry*: *Reactions*, *Mechanisms*, *and Structure*, 5th ed, Wiley: New York, U. S. A., 2001; p 20.
30. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., Gaussian 03, Revision C.01, *Gaussian, Inc.*, Walling ford CT, 2004.
31. (a) STOE STADI 4 (Revision 1.09), X-RED (Revision 1.09) and X-SHAPE (Revision 1.06). STOE-Cie Gmbh, Hilpertstrasse 10, D64295 Darmstadt, Germany. (1996). (b) Bruker SMART. Bruker AXS Inc., Madison,Wisconsin, USA. (2001). (c) Sheldrick, G. M. SADABS. University of Göttingen, Germany. 2000.
32. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.