Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 2409–2413

Incorporation of an allene unit into 1,4-dihydronaphthalene: generation of 1,2-benzo-1,4,5-cycloheptatriene and its dimerization

Akin Azizoglu,[a,*] Onur Demirkol,[b] Turgut Kilic[a] and Y. Kemal Yildiz[b,*]

[a]*Department of Chemistry, Balikesir University, Balikesir TR-10145, Turkey*
[b]*Department of Chemistry, Nigde University, Nigde TR-51200, Turkey*

Received 20 October 2006; revised 4 January 2007; accepted 11 January 2007
Available online 14 January 2007

Abstract—1-Bromo-1-fluoro-[1a,2,7,7a]-tetrahydro-1*H*-cyclopropa[*b*]naphthalene (**19**) has been prepared by the addition of bromofluorocarbene to 1,4-dihydronaphthalene (**18**). Treatment of a solution of **19** in dry ether with MeLi afforded the tricyclic hydrocarbon **17**, resulting from the intramolecular C–H insertion of carbene **16**, and two dimerization products, the head-to-head **20** and head-to-tail **21** allene dimers, confirming the formation of title cycloallene **15** as a reactive intermediate. B3LYP/6-31G(d) calculation predicts the activation barriers for insertion product **17** and allene product **15** as 3.70 and 9.52 kcal/mol, respectively. This prediction was in good agreement with our experimental results.

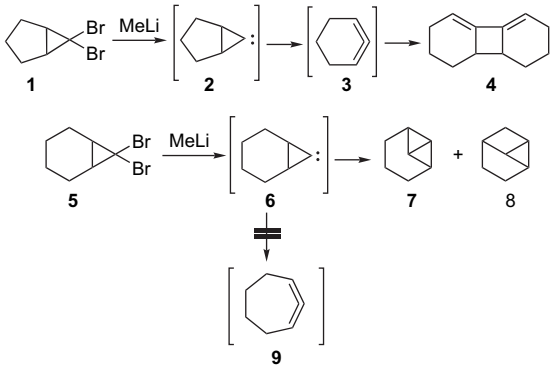
1. Introduction

Cyclic strained-allenes are of considerable interest in organic and computational chemistries because of their enhanced reactivity and their unusual physical properties.[1–9] They are non-planar chiral allenes rather than planar zwitterionic or carbene-like species, even in the case of the highly strained cyclohexa-1,2-diene and cyclohepta-1,2-diene.[3]

Over the years the Doering–Moore–Skattebol method,[4] briefly the treatment of 1,1-dihalocyclopropanes with alkyllithium reagents, has been used to prepare a range of cyclic allenes.[5] Although this method is the most efficient for the generation of cyclohexa-1,2-diene[6] **3**, paradoxically, it was not successful for the higher homologue **9**. A mixture of hydrocarbons **7** and **8** was isolated from the reaction of **5** with methyllithium[7] (Scheme 1).

Recently, Scheleyer et al. have elucidated the ring opening of carbenes **2** and **6** to the corresponding cyclic allenes using density functional theory computations.[8] For the cyclopropylidene **2**, the barrier to ring opening leading to allene **3** was found to be 0.2 kcal/mol. However, the activation barrier of **6** for the isomerization to cyclohepta-1,2-diene **9** was found to be 14.6 kcal/mol. The half-chair conformation of the cyclohexane ring in **6** is not suitable for the ring-opening reaction, and the needed change to the chair conformation during the reaction is responsible for this high activation barrier. On the other hand, the activation barriers for intramolecular CH-insertions to yield **7** and **8** were found to be 6.4 and 9.1 kcal/mol, respectively (Scheme 1).

Due to the inexplicability of Doering–Moore–Skattebol approach for the synthesis of a seven-membered ring allene, Balci et al.[9] applied the base-catalyzed elimination method using the appropriate vinylcycloalkenes, **10** and **13**, to generate the benzene-annulated six-membered ring allenes **11** and **15**. Although they succeeded in isolating the dimer **12**,

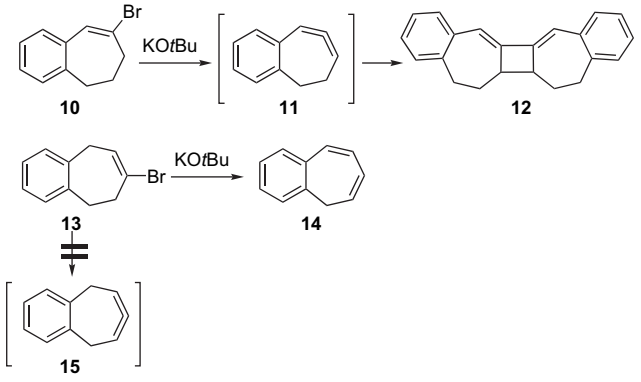


Scheme 1.

Keywords: Cyclic allenes; Carbenes; Rearrangements; DFT calculations.
* Corresponding authors. Tel.: +90 266 612100; fax: +90 266 6121215; e-mail addresses: azizoglu@balikesir.edu.tr; ykemal@nigde.edu.tr

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.01.017

confirming the formation of cycloallene **11**, the reaction of **13** with base gave the hydrocarbon **14**, instead of the expected allene **15** (Scheme 2). Some of the derivatives of **11** were also reported in the literature.[10] However, the synthesis of **15** has not been achieved before.



Scheme 2.

Hence, we have performed density functional theory (DFT) calculations to answer the question that '*does the Doering–Moore–Skattebol approach fail really to provide the symmetrical strained allene **15**?*' at the start of our study.

2. Computational methods

Density functional theory (DFT)[11] has been applied to optimize all of the structures and to predict harmonic vibrational frequencies. Becke's three-parameter non-local exchange functional along with the Lee–Yang–Parr non-local correlation function (B3LYP)[12] was employed. The 6-31G (d) basis set was used throughout. Stationary points were characterized as minima or transition structures by analytical evaluation of harmonic vibrational frequencies at the level of geometry optimization. All these calculations were performed using the Gaussian 03W program package.[13]

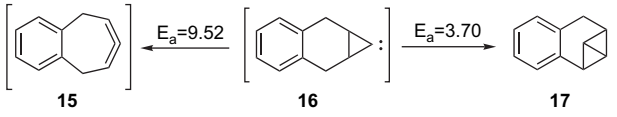
3. Results and discussions

The chosen computational level, B3LYP/6-31G(d), has been very successful in modeling the ring opening of cyclopropylidenes.[2f,8] The computational results for the ring opening of **6** were also compared with their literature values[8] to analyze the reliability of the 6-31G(d) basis set with respect to the TZP basis set. Single-point energies were evaluated at this level. As can be seen from Table 1, our results were found to be consistent with the reported literature values.

Table 1. Energies relative to the corresponding carbene ground state including zero-point corrections (in kcal/mol) for the corresponding insertion and allene product and related transition states

	Relative energy values	
	B3LYP/6-31G(d)	B3LYP/TZP[8]
TS1 (6→7)	6.2	6.4
TS2 (6→8)	9.6	9.1
TS3 (6→9)	15.1	14.6

Then, we turned our attention to elucidate the possible reaction products of **16**. One is the insertion product **17** and the other is the ring opening of **16** resulting from the cyclic allene **15** (Scheme 3). The computed activation barrier for the intramolecular CH-insertion reaction of **16** is predicted to be 3.70 kcal/mol (**TS4** for **16→17**), which is almost half of that for the CH-insertion reaction of **6** (**TS1**) (Tables 1 and 2). On the other hand, the activation barrier for the disrotatory ring-opening reaction of **16** forming allene, **16→15**, is found to be 9.52 kcal/mol (**TS5**), which is much lower than that for the ring opening of **6** (**TS3**) (Tables 1 and 2). Hence, the benzo-annulation decreases drastically the activation barriers for the possible allene product **15** and insertion product **17** (Fig. 1). This explains that both of them can be isolated when the Doering–Moore–Skattebol route is carried out for this purpose.



Scheme 3.

Therefore, we have decided to generate the seven-membered ring allene **15** after the explicability of the Doering–Moore–Skattebol approach shown by computational methods. The starting compound, 1,4-dihydronaphthalene **18**, was first prepared by the literature procedure.[14] Then, addition of fluorobromocarbene, generated from $CHBr_2F$[15] and NaOH under phase-transfer conditions,[5] to 1,4-dihydronaphthalene **18** afforded the expected addition product, fluorobromocyclopropane **19** in a total yield of 36%. Structural assignments were made on the basis of the spectral data. In particular, the observation of six signals in the ^{13}C NMR spectrum, as required by the symmetry in molecule **19**, is in good agreement with the structure (Scheme 4).

The obtained fluorobromocyclopropane **19** was reacted with MeLi in dry ether at room temperature. After careful aqueous workup, the residue was analyzed by ^{1}H and ^{13}C NMR spectroscopies, and GC–MS measurements, which showed the formation of one insertion product, **17**, and two dimeric products, **20** and **21**, with a total yield of 49% (Scheme 4).

Column chromatography on SiO_2 and subsequent recrystallization from hexane afforded the insertion product **17** as colorless crystals, whose ^{1}H and ^{13}C NMR spectra showed no peak relating to olefinic protons and carbon atoms except for aromatic ones. The molecular peak of 142 (M^+) also indicates the existence of an insertion product.

Table 2. Absolute energies (*E*, in hartree/particle), number of imaginary frequencies [in brackets], zero-point vibrational energies (ZPVE, in kcal/mol), and energies relative to the corresponding carbene ground state including zero-point corrections (in kcal/mol) for the corresponding insertion and allene product and related transition states at the level of B3LYP/6-31G(d)

	E	*ZPVE*	Δ*E*
16	−425.02569 [0]	108.30	0.00
17	−425.11921 [0]	110.28	−56.7
15	−425.10311 [0]	109.53	−47.36
TS4 (16→17)	−425.01835 [1]	107.39	3.70
TS5 (16→15)	−425.01031 [1]	108.17	9.52

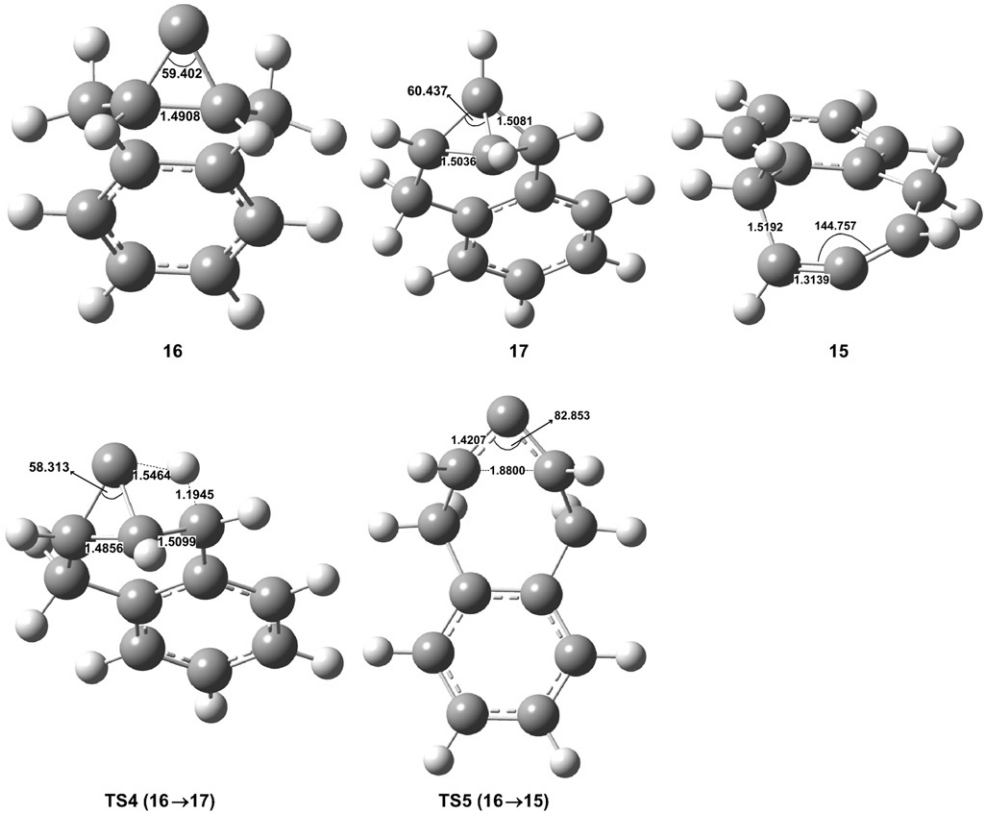
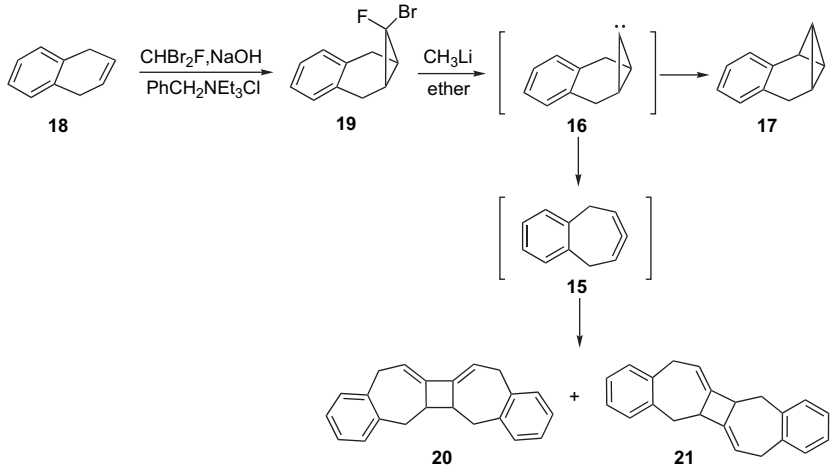


Figure 1. Optimized structures of **15**, **16**, **17**, and transition structures for the CH-insertion **TS4** and ring opening **TS5** at B3LYP/6-31G (d) (bond lengths are in angstrom and bond angles are in degree).

All efforts with column chromatography, crystallization, and distillation to separate two allene dimers consisting of head-to-head allene dimer **20** and head-to-tail allene dimer **21** in a ratio of 2:1 (determined by ^{1}H NMR spectroscopy) failed. The 24 lines in the ^{13}C NMR spectrum indicate two dimerization products differing from each other. The mass spectrum of the mixture showed a single peak at 284 (M^{+}), which is equal to the molecular weight of the allene dimer. The elemental analysis of the mixture was also in agreement with that of the expected structures.

In summary, we have illustrated that the title compound **15**, the symmetrical strained cyclic allene, can be generated from the bromofluorocyclopropane **19** by α-elimination of Br and F with MeLi, briefly named as Doering–Moore–Skattebol method. However, HBr elimination from 1-bromo-4,5-benzo-1,4-cycloheptadiene **13** with KO^{t}Bu results in the formation of the hydrocarbon **14** instead of the allene **15**.[9] Furthermore, these results are in good agreement with our computational results at B3LYP/6-31G(d).



Scheme 4.

4. Experimental

4.1. General

Melting points were taken on a capillary tube apparatus and are uncorrected. NMR spectra were recorded on 400 MHz instruments. IR spectra of liquids were obtained as films on NaCl plates, and spectra of solids were obtained from solutions in 0.1-mm cells or KBr films on a Jasco model 300 FT-IR spectrometer. Mass spectra (electron impact) were recorded at 70 eV. All solvents used were purified and dried by standard methods wherever needed. Other commercially available reagents were of reagent-grade quality and used as received. TLC was done on aluminum sheets with precoated silica gel 60 F_{254} (40×80 mm). Purification by column chromatography was carried out with neutral silica gel 60 (70–230 mesh ASTM) from Merck Company. 1,4-Dihydronaphthalene was prepared by the literature procedure.[14]

4.2. Addition of bromofluorocarbene to 1,4-dihydronaphthalene (18)

A solution of NaOH (9.6 g, 0.24 mol) in water (9.6 mL) was added dropwise to a magnetically stirred solution of 1,4-dihydronaphthalene **18** (3.5 g, 26.9 mmol), benzyltriethylammonium chloride (0.34 g, 1.47 mmol), and dibromofluoromethane[15] (7.08 g, 36.9 mmol) in methylene chloride (25 mL) cooled to −15 °C during 2 h. After the addition was completed, the mixture was stirred at room temperature for 2 h and then hydrolyzed through the addition of water (100 mL). The organic layer was separated and the water layer was extracted with methylene chloride (3×50 mL). Combined organic layers were dried over $MgSO_4$, and then solvents removed under reduced pressure. The oily residue was purified by column chromatography. The first fraction consisted of unreacted 1,4-dihydronaphthalene. The latter is the cyclopropane adduct **19**, *1-bromo-1-fluoro-[1a,2,7,7a]-tetrahydro-1H-cyclopropa[b]naphthalene*, and was crystallized from hexane (2.34 g, 36%): colorless crystals; mp 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (dd, J=10.6, 6.3 Hz, 2H), 2.78 (d, J=6.8 Hz, 2H), 3.29 (d, J=9.7 Hz, 2H), 7.14 (m, aromatic, 3H), 7.28 (s, aromatic, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 39.2 (d, J=11.8 Hz), 77.3 (d, J=217 Hz), 126.4, 128.8, 133.9; IR (KBr, cm^{-1}) 3052, 2983, 1431, 750, 723; MS (70 eV) *m/z* 241/243 (M^+, 21%), 161 (100), 141 (53), 115 (100). Anal. Calcd for $C_{11}H_{10}BrF$: C, 54.80; H, 4.18. Found: C, 54.91; H, 4.03.

4.3. Reaction of 1-bromo-1-fluoro-[1a,2,7,7a]-tetrahydro-1*H*-cyclopropa[*b*]naphthalene (19) with MeLi

To a magnetically stirred solution of **19** (0.61 g, 2.53 mmol) in dry ether (20 mL) under nitrogen atmosphere was added dropwise a solution of 1.6 M MeLi in ether (4.8 mmol, 3 mL) over 10 min at room temperature. After the resulting solution was stirred for 2 h, it was quenched *carefully* with water. The reaction mixture was extracted with ether, and the organic layer was washed with saturated NaCl and dried over $MgSO_4$. After the removal of solvent under the reduced pressure, the oily residue was chromatographed over silica gel (100 g). Elution with *n*-hexane afforded insertion product **17** (1.02 g, 28%): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89–1.48 (m, 3H), 2.78 (dd, J=4.2, 0.7 Hz, 1H), 3.28 (d, J=0.5 Hz, 2H), 6.98–7.25 (m, aromatic, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 20.2, 24.8, 39.1, 41.8, 125.7, 126.5, 126.7, 131.3, 137.6, 138.8; IR (NaCl, cm^{-1}) 3026, 2994, 2890, 1485, 1368, 1207, 1109, 883; MS (70 eV) *m/z* 142 (M^+, 25%), 129 (100), 128 (26), 115(52), 91 (25). Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 93.04; H, 6.98.

The second fraction was the oil of a mixture of head-to-head allene dimer **20** and head-to-tail allene dimer **21** (1.48 g, 21%): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98–3.15 (m, 12H), 3.48 (m, 4H), 3.65 (m, 4H), 6.82 (m, 4H), 7.10 (m, aromatic, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.40, 29.43, 29.70, 29.74, 30.37, 31.97, 63.48, 78.22, 117.84, 118.63, 125.31, 125.68, 125.74, 126.05, 126.07, 128.06, 128.53, 128.69, 128.94, 129.08, 134.99, 135.01, 135.27, 135.62; IR (NaCl, cm^{-1}) 3017, 2921, 1492, 1043, 841, 729; MS (70 eV) *m/z* 284 (M^+, 18%), 269 (10), 255 (10), 240 (8), 128 (34), 115 (61). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.83; H, 7.02.

Acknowledgements

The authors are indebted to the Scientific and Technical Research Council of Turkey (Grants: TUBITAK-TBAG103T129 and TUBITAK-TBAG104T371) for their financial support. We thank a reviewer for helpful comments.

Supplementary data

The Cartesian coordinates of the optimized stationary point structures **15**, **16**, and **17** and transition structures **TS4** and **TS5** at the B3LYP/6-31G(d) level. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.01.017.

References and notes

1. For reviews, see: (a) Christl, M. *Modern Allene Chemistry*; Krause, N., Hashmi, S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 1, pp 242–357; (b) Balci, M.; Taskesenligil, Y. *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI: Stamford, CT, 2000; Vol. 8, pp 43–81.
2. For recent examples, see: (a) Daoust, K. J.; Hernandez, S. M.; Konrad, K. M.; Mackie, I. D.; Winstanley, J., Jr.; Johnson, R. P. *J. Org. Chem.* **2006**, *71*, 5708–5714; (b) Kilbas, B.; Azizoglu, A.; Balci, M. *Helv. Chim. Acta* **2006**, *89*, 1449–1456; (c) Mieusset, J. L.; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572–10575; (d) Kassaee, M. Z.; Koohi, M. *J. Mol. Struct. (THEOCHEM)* **2005**, *755*, 91–98; (e) Nikitina, A. F.; Sheridan, R. S. *Org. Lett.* **2005**, *7*, 4467–4470; (f) Azizoglu, A.; Ozen, R.; Hokelek, T.; Balci, M. *J. Org. Chem.* **2004**, *69*, 1202–1206; (g) Algi, F.; Ozen, R.; Balci, M. *Tetrahedron Lett.* **2002**, *43*, 3129–3131.
3. (a) Schmidt, M. W.; Angus, R. O.; Johnson, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6838–6839; (b) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1981**, *103*, 2874–2876; (c) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607–7608.

4. (a) Doering, W. v. E.; LaFlamme, P. M. *Tetrahedron* **1958**, *2*, 75–79; (b) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1960**, *25*, 2073; (c) Skattebol, L. *Tetrahedron Lett.* **1961**, *2*, 167–172.
5. (a) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133–1150; (b) Fedorynski, M. *Chem. Rev.* **2003**, *103*, 1099–1132.
6. Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469–5474.
7. Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019–2020.
8. Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F. *J. Org. Chem.* **1997**, *62*, 9267–9275.
9. Yildiz, Y. K.; Secen, H.; Krawiec, M.; Watson, W. H.; Balci, M. *J. Org. Chem.* **1993**, *58*, 5355–5359.
10. Fink, H. J.; Christl, M.; Peters, E. M.; Peters, K.; Schnering, H. v. G. *Chem. Ber.* **1991**, *124*, 2569–2575.
11. *Modern Density Functional Theory: A Tool for Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.
12. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, 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 03W, Revision C.2*; Gaussian: Wallingford, CT, 2004.
14. Wittig, G.; Eggers, H.; Duffner, P. *Liebigs Ann. Chem.* **1958**, *619*, 10–27.
15. Schlosser, M.; Heinz, G. *Chem. Ber.* **1971**, *104*, 1934–1941.