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A stilbene dendrimer with caltrop-shaped dendrons: synthesis and photophysical studies

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Abstract—A topologically new stilbene dendrimer is prepared using rigid caltrop-shaped dendrons derived from tetraphenylmethane. The dendrimer by virtue of its highly branched periphery, showed a strong emissive property with little excimer formation, even at the first generation.

Since 1990, when Holmes and co-workers first reported that poly(*p*-phenylenevinylene)s (PPVs) can be used as the emitting layer in light emitting diodes (LEDs),[1] interest in the synthesis and optical properties of stilbenoid compounds has increased considerably.[2,3] While most of the early studies dealt with linear oligophenylenevinylenes,[3] recently, much attention has been paid to branched stilbenoid architectures, especially the stilbene dendrimers.[4] Linear PPVs, owing to their highly crystalline nature, suffer from strong intermolecular associations in the solid phase resulting in diminished fluorescence intensities.[5] Stilbene dendrimers, in view of their three-dimensional structures, are expected to be free from such intermolecular associations and hence, promised to show superior emission properties.[6]

In 1998, Bazan and co-workers reported that tetrastilbenoid compounds built on a rigid tetrahedral core such as tetraphenylmethane (TPM) were free from intermolecular as well as intramolecular associations.[7a] Such caltrop-shaped molecules retained the strong emission properties of the individual stilbene units.[7a,c] Since then, we and others have shown that dendritic stilbenoid architectures based on a tetraphenylmethane core display properties that are strikingly different from those of the linear analogs.[7b,d–i] In an extension to these studies, we sought to prepare dendrimers with TPM based stilbenoid dendrons at the periphery. We reasoned that: (a) TPM can easily give rise to a tritopic dendron, which would ensure a high concentration of peripheral stilbene units; (b) since TPM is pivoted on a central sp^3 hybridized carbon, the latter will disrupt any through-bond interactions between the stilbene chromophores in the dendrons, that is, all the stilbene units in the dendrimer would behave as isolated chromophores, and (c) the topologically rigid caltrop-shaped dendrons would prevent intermolecular or intramolecular associations between the individual chromophores leading to a strong emissive property for the dendrimer. In this paper, we now describe the synthesis of a stilbene dendrimer having three such caltrop-shaped tri-stilbenoid dendrons and report on its steady state absorption and emission properties.

The caltrop-shaped dendrons **4** were prepared from the cheap commercial dye New Fuchsin **1** as shown in Scheme 1. Thus, threefold diazotization of **1** ($NaNO_2$, dil H_2SO_4, 0 °C) followed by an iodo-dediazoniation reaction with KI (H_2O, rt) produced the triiodoaryl carbinol **2** in 40% overall yield.[8] Acid catalyzed reaction of **2** with phenol then gave the key TPM based AB_3 synthon **3** (85%), exclusively as the *para*-isomer.[9] Finally, threefold Heck reactions of **3** with styrene or 4-*tert*-butyl styrene under Jeffery's PTC conditions (10% $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100 °C)[10] produced the desired dendrons **4a** and **4b** in 83% and 75% yields, respectively.[11] The ^1H NMR spectra of **4a**,**b** showed large coupling constants (∼16 Hz) for their vinylic protons indicating a *trans*-configuration for the newly constructed stilbene units. However, the dendron **4a** was insoluble in THF and alcohols and only sparingly soluble in CH_2Cl_2. Hence, the more soluble dendron **4b**

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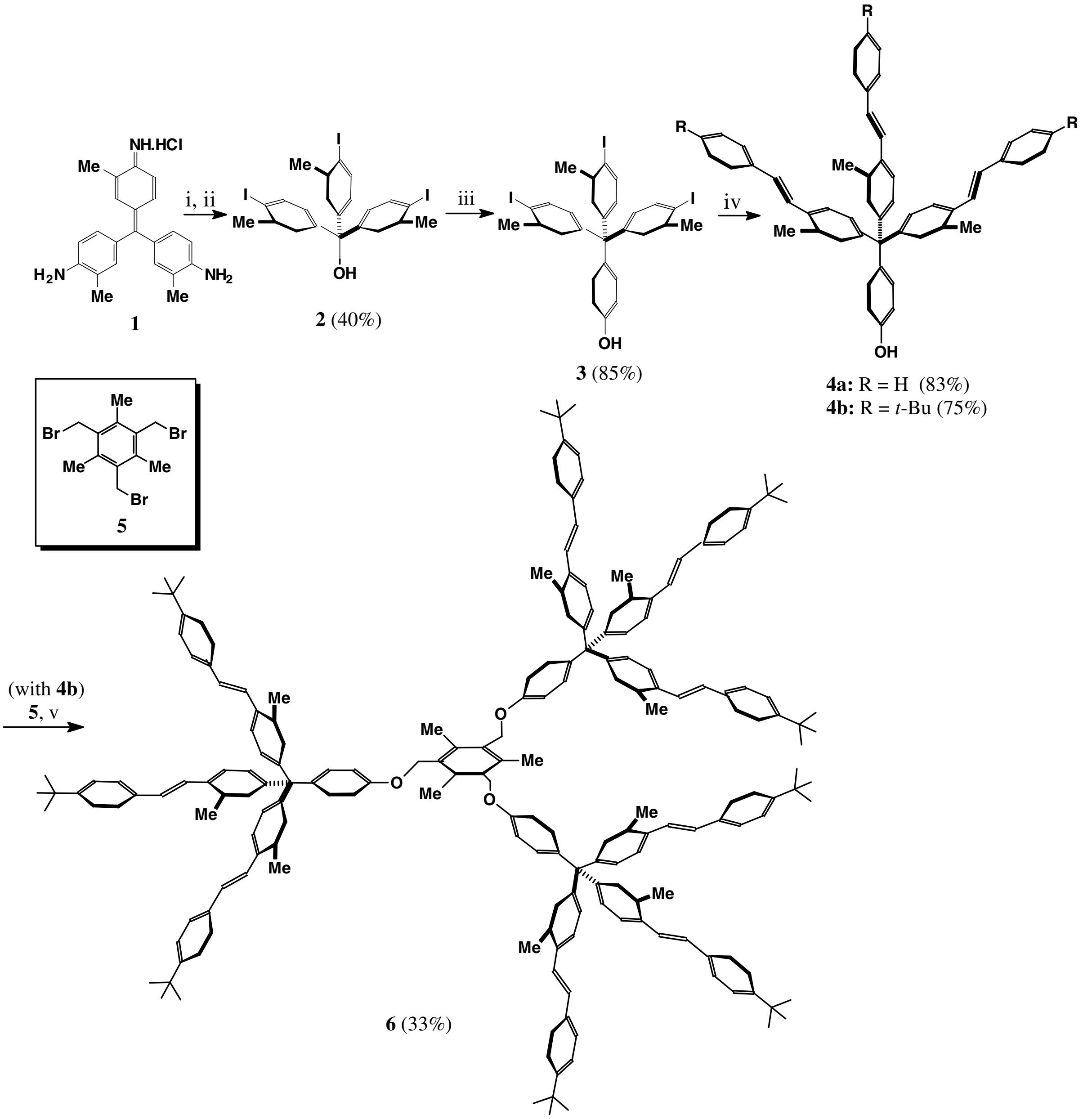
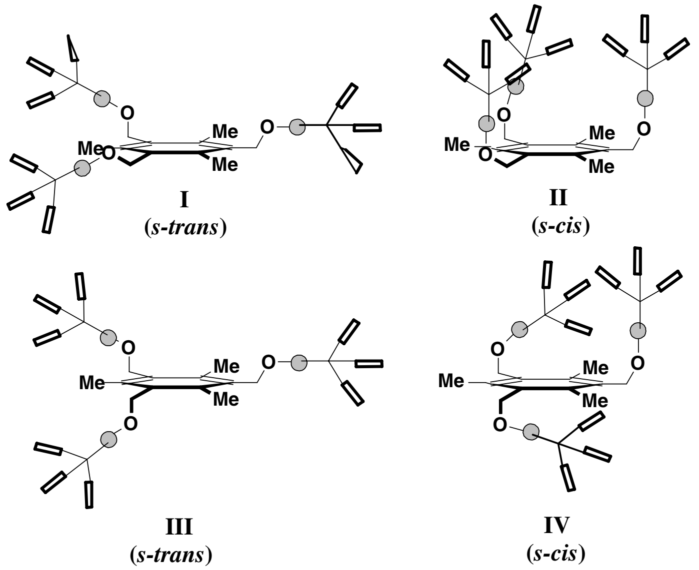


Scheme 1. Reagents and conditions: (i) $NaNO_2$, dil H_2SO_4, 0 °C; (ii) KI, H_2O, rt; (iii) phenol, cat. concd H_2SO_4, 80 °C; (iv) styrene or 4-*tert*-butyl styrene, 10% $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100 °C; (v) NaH, DMF, rt.

was used for dendrimer synthesis. Toward this end, threefold alkylation of 2,4,6-tris(bromomethyl)mesitylene core **5** was carried out with **4b** (NaH, DMF, rt) to produce the first generation dendrimer **6** in 33% yield after chromatographic purification on silica gel (5% EtOAc in light petroleum).[11] The ^1H NMR spectrum of **6** was diagnostic of the dendrimer structure. As expected, the aromatic region was virtually identical with that of dendron **4b**, except for minor changes in the chemical shift values. The signals for the *tert*-butyl and the tolyl methyl groups in **6** were slightly shielded compared to those in the free dendron. In addition, two new singlets appeared at δ 5.18 (benzylic methylene) and 2.39 (tolyl methyl), attributed to the hexasubstituted aromatic core. Finally, the MALDI-TOF mass spectrum of **6** showed a dominant M+1 peak at m/z 2713.

It should be noted that the dendrimer core in **6** is a hexasubstituted benzene nucleus. Therefore, in analogy to other hexasubstituted benzene derivatives,[12] **6** is expected to adopt a conformation in which the three stilbenoid dendrons (alternate substituents) would remain on the same side of the benzene plane, that is, conformation **I** or **III** (Fig. 1). Of these, conformation **I** having an all *s-trans* orientation of the caltrops is believed to be the preferred one because **II** and **IV**, having a *s-cis* orientation of the ether linkages, would suffer from severe steric interactions between the stilbenoid caltrops (as in **II**) or between the stilbenoid caltrops and the *ortho*-methyl groups of the central benzene ring (as in **IV**). However, at this moment, we cannot entirely rule out the presence of the conformer **III** having an 'up down' *s-trans* arrangement of the dendrons. It should



I
(*s-trans*)

II
(*s-cis*)

III
(*s-trans*)

IV
(*s-cis*)

Figure 1. Conformational analysis of the dendrimer **6**.

also be noted that conformations **II** and **IV** can lead to pre-organization of the stilbene chromophores toward association. However, since **II** and **IV** are the less stable conformations, it may be concluded that, irrespective of whether **6** prefers conformation **I** or **III**, excimer formation in the dendrimer via pre-organization of the stilbene chromophores would be highly disfavored.

The dendron **4b** showed an absorption maximum at λ 318 nm in CH_2Cl_2 due to its stilbene units. The $\lambda_{\max}$ value is slightly red-shifted from that of *trans*-stilbene ($\Delta\lambda \approx 20$ nm)[2a] and may be due to a small degree of homoconjugation operating through the central sp^3 hybridized carbon in **4b**. Bazan and co-workers have also reported similar red shifts in tetrastilbenylmethane derivatives and attributed them to homoconjugative effects.[7a,c] Notably, the 318 nm peak is associated with a large molar extinction coefficient ($\varepsilon_{\max} = 11.0 \times 10^4\ M^{-1}\ cm^{-1}$). This was as expected since **4b** consists of three *trans*-stilbene units held in a rigid tetrahedral arrangement.[13] The dendron **4b** produced a strong fluorescence with a maximum at λ 387 nm (λ_{exc} 318 nm), which is also red-shifted from stilbene fluorescence by ca. 20 nm.

The absorption maximum of the dendrimer **6** was found at λ 319 nm with a high molar extinction coefficient [$\varepsilon_{\max}(CH_2Cl_2)=21.7\times10^4\ M^{-1}\ cm^{-1}$]. As expected, the $\varepsilon_{\max}$ value is nearly nine times that of *trans*-stilbene. Excitation of **6** at 319 nm, caused a strong broad emission peak centered at λ 387 nm. Therefore, as far as the peak positions are concerned, the absorption and emission spectra of **6** virtually mimic those of the dendron **4b**. Thus, all nine stilbene units in **6** behave as isolated chromophores. This was possible due to the choice of tetraphenylmethane for dendron construction so that the stilbene units in the dendrons were held in a highly branched but rigid tetrahedral arrangement. As a result, no through-bond or through-space interactions were allowed between the individual stilbene units in **6**. Notably, the emission peak of **6** showed little red tailing indicating that excimer formation is retarded in the dendrimer. This vindicated our prognosis that dendrimers having caltrop-shaped stilbenoid dendrons would be less associated and hence, would provide a superior emission property. It may be mentioned that most of the stilbene dendrimers reported to date have been based on planar dendrons such as 3,5-distyryl styrenes.[4] Dendrimers prepared from such planar dendrons invariably led to strong intermolecular associations or excimer formation via π-stacking interactions, especially at a low dendrimer generation, as was evident by the extended red tailings reported in their emission spectra (up to ~650 nm).[4d,i,l] In contrast, we have shown that by using a highly branched caltrop-shaped dendron, association-free emission can be obtained even in a first generation stilbene dendrimer. Therefore, caltrop-shaped tri-chromophoric dendrons can be effectively used as light harvesting antennae. The synthesis and photophysical studies of higher generation dendrimers of this class are currently under investigation in our laboratories.

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References and notes

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
2. (a) Meier, H. *Angew. Chem., Int. Ed.* **1992**, *31*, 1399; (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402; (c) Mitschke, U.; Bäurele, P. *J. Mater. Chem.* **2000**, *10*, 1471.

3. (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350; (b) Segura, J. L.; Martín, N. *J. Mater. Chem.* **2000**, *10*, 2403; (c) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11.
4. (a) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079; (b) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643; (c) Meier, H.; Lehmann, M.; Kolb, U. *Chem. Eur. J.* **2000**, *6*, 2462; (d) Díez-Barra, E.; García-Martínez, J. C.; Rodríguez-López, J.; Gómez, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 3651; (e) Spangler, C. W.; Elandaloussi, E. H.; Reeves, B. *Polym. Prepr.* **2000**, *41*, 789; (f) Segura, J. L.; Gómez, R.; Martín, N.; Guldi, D. M. *Org. Lett.* **2001**, *3*, 2645; (g) Segura, J. L.; Gómez, R.; Martín, N.; Luo, C.; Swartz, A.; Guldi, M. *Chem. Commun.* **2001**, 707; (h) Langa, F.; Gómez-Escalonilla, M. J.; Díez-Barra, E.; García-Martínez, J. C.; de la Hoz, A.; Rodríguez-López, J.; Gonzáles-Cortés, A.; López-Arza, V. *Tetrahedron Lett.* **2001**, *42*, 3435; (i) Díez-Barra, E.; García-Martínez, J. C.; Merino, S.; del Rey, R.; Rodríguez-López, J.; Sánchez-Verdú, P.; Tejeda, J. *J. Org. Chem.* **2001**, *66*, 5664; (j) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bässler, H. *Synth. Met.* **2001**, *116*, 357; (k) Meskers, S. C. J.; Bender, M.; Hubner, J.; Romanovskii, Y. V.; Oestereich, M.; Schenning, A. P. H. J.; Meijer, E. W.; Bässler, H. *J. Phys. Chem. A* **2001**, *105*, 10220; (l) Sengupta, S.; Sadhukhan, S. K.; Singh, R. S.; Pal, N. *Tetrahedron Lett.* **2002**, *43*, 1117.
5. (a) Conwell, E. *Trends Polym. Sci.* **1997**, *5*, 218; (b) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J.-L. *J. Am. Chem. Soc.* **1998**, *120*, 1289; (c) Nguyen, T.-C.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J. Phys. Chem.* **2000**, *104*, 237; (d) Catalán, J.; Zimányi, L.; Saltiel, J. *J. Am. Chem. Soc.* **2000**, *122*, 2377.
6. (a) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371; (b) Pillow, J. N. G.; Burn, P. L.; Samuel, I. D. W.; Halim, M. *Synth. Met.* **1999**, *102*, 1468; (c) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985; (d) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bässler, H. *Adv. Mater.* **2001**, *13*, 258.
7. (a) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987; (b) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1998**, *39*, 1237; (c) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695; (d) Robinson, M. R.; Wang, S.; Bazan, G. C. *Adv. Mater.* **2000**, *12*, 1701; (e) Summers, M. A.; Robinson, M. R.; Bazan, G. C.; Buratto, S. K. *Chem. Phys. Lett.* **2002**, *364*, 542; (f) Varnavski, O. P.; Ostrowski, J. C.; Sukhomlinova, L.; Twieg, R. J.; Bazan, G. C.; Goodson, T., III. *J. Am. Chem. Soc.* **2002**, *124*, 1736; (g) Zimmermann, T. J.; Müller, T. J. J. *Eur. J. Org. Chem.* **2002**, 2269; (h) Sengupta, S.; Sadhukhan, S. K.; Muhuri, S. *Tetrahedron Lett.* **2002**, *43*, 3521; (i) Sengupta, S.; Sadhukhan, S. K. *Indian J. Chem.* **2003**, *42B*, 858.
8. (a) Sengupta, S.; Sadhukhan, S. K. *J. Mater. Chem.* **2000**, 1997; (b) Sengupta, S.; Sadhukhan, S. K. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4332.
9. **3**: mp 206–207 °C; IR (KBr, cm^{-1}) 3400, 1605, 1500, 1460, 1370; ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 2.33 (s, 9H), 6.65 (dd, 3H, $J = 8.4$, 2.1 Hz), 6.70 (d, 2H, $J = 6.6$ Hz), 6.99 (d, 2H, $J = 6.6$ Hz), 7.02 (d, 3H, $J = 2.1$ Hz), 7.65 (d, 3H, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 28.2, 63.3, 98.7, 114.5, 130.1, 131.9, 138.0, 140.5, 146.5, 153.6.
10. Jeffery, T. *Tetrahedron* **1996**, *52*, 10113.
11. **4a**: mp 201–202 °C; IR (KBr, cm^{-1}) 3290, 1595, 1500, 1445, 1260; ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 2.35 (s, 9H), 6.73 (d, 2H, $J = 8.7$ Hz), 7.00 (d, 3H, $J = 16.2$ Hz), 7.05–7.11 (m, 6H), 7.14 (d, 2H, $J = 8.7$ Hz), 7.20–7.31 (m, 6H), 7.34 (d, 3H, $J = 5.4$ Hz), 7.35 (d, 3H, $J = 16.2$ Hz), 7.45–7.54 (m, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.2, 63.7, 114.3, 124.4, 126.1, 126.5, 127.4, 128.6, 129.1, 129.7, 132.2, 132.7, 133.7, 134.7, 137.8, 139.2, 146.3, 153.4. **4b**: mp 220–224 °C; IR (KBr, cm^{-1}) 3300, 1600, 1510, 1440, 1280; ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 1.33 (s, 27H), 2.34 (s, 9H), 4.67 (br s, 1H), 6.72 (d, 2H, $J = 8.5$ Hz), 6.98 (d, 3H, $J = 16$ Hz), 7.04–7.11 (m, 6H), 7.14 (d, 2H, $J = 8.3$ Hz), 7.26 (d, 3H, $J = 16$ Hz), 7.37 (d, 6H, $J = 8.2$ Hz), 7.45 (d, 6H, $J = 8.8$ Hz), 7.48 (d, 3H, $J = 9.2$ Hz). **6**: mp >250 °C; calcd for $C_{204}H_{216}O_3$ (MW 2712): C, 90.26; H, 7.96. Found: C, 90.42; H, 7.77; IR (KBr, cm^{-1}) 2870, 1624, 1605, 1500, 1445, 1280; ^{1}H NMR (300 MHz, CDCl$_3$/TMS) δ 1.25 (s, 81H), 2.27 (s, 27H), 2.39 (s, 9H), 5.18 (s, 6H), 6.85 (d, 6H, $J = 8.5$ Hz), 6.90 (d, 9H, $J = 16.2$ Hz), 7.02–7.11 (m, 18H), 7.15 (d, 6H, $J = 8.4$ Hz), 7.19 (d, 9H, $J = 16$ Hz), 7.29 (d, 18H, $J = 8.4$ Hz), 7.37 (d, 18H, $J = 8.4$ Hz), 7.41 (d, 9H, $J = 9$ Hz); MS (MALDI-TOF) m/z 2713 (M+1).
12. (a) Hennrich, G.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2219; (b) Kumar, S.; Kaur, S.; Singh, G. *Supramol. Chem.* **2003**, *15*, 65; (c) Simaan, S.; Siegel, J. S.; Bali, S. E. *J. Org. Chem.* **2003**, *68*, 3699.
13. (a) Eldin, S.; Liebman, J. F.; Reynolds, L. D.; Dowd, P. *Tetrahedron Lett.* **1992**, *33*, 4525; (b) Langhals, H.; Wagner, C.; Ismael, R. *New J. Chem.* **2001**, *25*, 1047.