DOI: 10.1002/cssc.201100017

Solvent-Free Conversion of Linalool to Methylcyclopentadiene Dimers: A Route To Renewable High-Density Fuels

Heather A. Meylemans, Roxanne L. Quintana, Bryan R. Goldsmith, and Benjamin G. Harvey*^[a]

Dedicated to Professor Richard D. Ernst on the occasion of his 60th birthday

The development of techniques for the efficient synthesis of custom fuels and chemicals from sustainable natural feedstocks is of fundamental importance to society as the direct and indirect costs of petroleum use continue to increase.^[1] For general transportation fuels, complex mixtures of molecules that have somewhat lower utility than petroleum-based analogs may be sufficient; however, for specific applications, such as jet and missile propulsion, a more selective model that produces molecules with defined and specialized properties is required. Well-characterized, single-site catalysis is the basis of elegant synthetic strategies for the production of pure compounds. In particular, ruthenium-based olefin metathesis catalysts are known to catalyze a number of reactions, including self-metathesis, cross-metathesis, ring-closing metathesis (RCM), and ring-opening metathesis polymerization (ROMP).^[2] This family of catalysts is ubiquitous in the literature and has been applied in many fields of chemistry, ranging from natural product synthesis^[3] to polymer chemistry.^[4] The transition of these catalysts to large-scale industrial processes has in the past been hindered by their modest turnover numbers and high cost.^[5] To overcome these difficulties, catalytic systems that can efficiently yield pure products while maintaining low catalyst concentrations need to be developed. In this report, we detail a ruthenium-catalyzed method for the synthesis of dimethyldicyclopentadiene from linalool, a linear terpene alcohol.

Recent work in our laboratory has focused on the conversion of terpenes into high-density fuel surrogates.^[6] Although terpenes are naturally produced by pine trees and a variety of plants, a truly sustainable method may require the utilization of bioengineered microbes to produce specific molecules or families of molecules from waste cellulose.^[7] Within the terpene family, linalool is a particularly intriguing feedstock for fuels because of its molecular structure. Although RCM of linalool must proceed through a sterically hindered transition state, the reaction is facilitated by coordination of the allylic alcohol.^[8] This results in an efficient method for the synthesis of 1-methylcyclopent-2-enol (1) and isobutylene (Scheme 1). Both products are of significant interest as they can be converted to

 [a] Dr. H. A. Meylemans, R. L. Quintana, B. R. Goldsmith, Dr. B. G. Harvey Research Department, Chemistry Division US Navy, Naval Air Warfare Center Weapons Division (NAWCWD) 1900 N. Knox Rd Stop 6303 China Lake, CA 93555 (USA) Fax: (+1)760-939-1617 E-mail: benjamin.g.harvey@navy.mil
 Supporting Information for this article is available on the WWW under

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201100017.



Scheme 1. Catalytic conversion of linalool to well-defined, renewable fuels.

renewable fuel and polymer products. Isobutylene is a valuable side-product that can be selectively trimerized to produce jet fuel,^[9] dimerized or alkylated with C4 raffinate to produce high-octane gasoline,^[10] or polymerized to polyisobutylene.^[11] Meanwhile, **1** is a promising precursor for the synthesis of methylcyclopentadiene dimer, which can be hydrogenated and isomerized to produce the high-density missile fuel RJ-4^[12] (Scheme 1).

NMR-scale conversions of linalool to **1** under dilute conditions and at elevated temperatures have been reported in the literature. Catalysts used for this reaction (Figure 1) have included the first-generation Grubbs catalyst (**2**),^[8] both a second-generation Grubbs (**5**) and Grubbs–Hoveyda catalyst



Figure 1. Structures of selected ruthenium metathesis catalysts that have been studied for the RCM of linalool.

CHEMSUSCHEM

(4),^[13] as well as catalysts with electron-withdrawing alkoxides and labile pyridine ligands (**6**, **7**).^[14] More recently the RCM of linalool and several other substrates has been studied with ruthenium catalysts functionalized with N-napthyl-substituted heterocyclic carbene ligands.^[15] Among these examples, the alkoxide-functionalized catalysts are particularly notable as they were able to achieve 100% conversion in 15 min at 0.5 mol% loading and in some cases, full conversion in 1 h at 0.05 mol% loading in refluxing chloroform. This is in contrast to the other catalyst studies, which utilized relatively high catalyst loadings (1–5%) to achieve high conversion efficiencies (Table 1). Although these preliminary studies are intriguing, the

Table 1. Reaction conditions and yield of 1 for a series of ruthenium metathesis catalysts.							
Catalyst	Loading [mol %]	Temp [°C]	Time	Solvent	Yield [%]		
2	5	ambient	minutes	CDCl ₃	100 ^[a]		
2	0.1	ambient	16 h	neat	0		
2	0.1	45	1 h	neat	55		
3	0.1	60	30 min	neat	36		
3	0.01	ambient	16 h	neat	0		
3	0.01	60	30 min	neat	18		
4	0.1	ambient	45 min	neat	100		
4	0.01	ambient	1 h	neat	44		
5, 6, 7a, 7b, 7c	0.5	60	15 min	CDCl₃	100 ^[b]		
5, 6, 7a, 7b, 7c	0.05	60	1 h	CDCl ₃	24, 29, 100,		
					17, 34 ^[b]		
[a] Reference [8]. [b] Reference [14].							

work in our laboratory focused on maximizing the turnover number (TON) for the RCM of linalool while reducing the use of extraneous solvents and the energy footprint of the process (a key requirement for the synthesis of renewable fuels). To help accomplish this, all of the reactions were run neat, a condition that has been shown to be effective in promoting high TONs for certain substrates.^[16]

As the first step in the development of a large-scale synthesis of the high-density fuel RJ-4 from a renewable source, the solvent-free, preparative-scale RCM of linalool with three commercial catalysts was studied. The first-generation Grubbs catalyst 2, a second-generation Grubbs catalyst with a sterically open N-heterocyclic carbene ligand 3, and a second generation Grubbs-Hoveyda catalyst 4 were screened for activity. For catalyst 2, attempts to decrease the loading to 0.1 mol% resulted in incomplete conversion to the alcohol. No reaction was observed at room temperature, while reaction at 45 °C resulted in 55% conversion after 1 h. Increasing the reaction time did not lead to further reaction. Catalyst 3, which was chosen based on its well-established activity in the RCM of sterically hindered substrates, produced no discernible product after 16 h at ambient temperature with either 0.1 or 0.01 mol% loading, however at 60°C, yields of 36 and 18% were obtained, respectively. Unfortunately, catalyst 3 deactivated within 30 min at this temperature, a result that was not surprising given the reported modest thermal stability of this catalyst.^[17] To improve the conversion efficiency, the more stable catalyst **4** was evaluated at a loading of 0.1 mol%. At room temperature the reaction proceeded rapidly (Figure 2) with co-



Figure 2. Photograph of the room temperature, solvent-free reaction of linalool with catalyst **4** at five minutes after addition. Vigorous bubbling is due to production of isobutylene.

pious production of isobutylene. By this method linalool was converted quantitatively to 1 in 45 min at ambient temperature. At 0.01 mol% loading, a 44% conversion to the alcohol was achieved in 1 h, representing a remarkable TON of 4400. Reaction for longer periods of time resulted in no improvement in yield. Based on the catalyst screening, **4** was utilized in preparative-scale (30 g) syntheses of **1**. Isobutylene was either collected with a dry-ice condenser or allowed to escape through a bubbler. At the conclusion of the reaction, the product was isolated by vacuum distillation at room temperature; yields of > 95% were routinely achieved.

In an attempt to improve the TON for catalysts **2** and **4**, the effect of increasing the temperature was studied. Interestingly, when either **2** or **4** were used as the catalyst, a reaction temperature of 60 °C resulted in partial conversion of **1** to methyl-cyclopentadiene (MCPD). GC/MS analysis of the reaction mixture showed that linalool had been converted to a complex mixture of **1**, cyclopentenol ethers, MCPD, and methylcyclopentadiene dimers (Scheme 2). In effect, it appeared that **2**



Scheme 2. Mechanism for the acid catalyzed dehydration of 2-methyl-1-cyclopentenol.

and **4** were acting as dehydration catalysts.^[18] Interestingly, for **4**, this same effect was not observed when sufficient linalool was present in solution. As a control, a 0.01 mol% solution of catalyst **4** in linalool was prepared. After the reaction had proceeded to 44% conversion, the mixture was heated to 60 °C for 16 h. No dehydration of the product was observed. It is also important to note that catalyst decomposed through air exposure was not active for the dehydration of the alcohol. After complete conversion of linalool to **1**, rapid stirring of the reaction mixture in open air or, alternatively, active bubbling of air into the reaction flask resulted in a color change from green to brown–black. This oxidized mixture was much less prone to dehydration reactions.

Although the dehydration reaction appeared to be mediated by the ruthenium catalyst, another possibility is that the catalyst reacted with linalool, 1, or water to exchange alkoxide or hydroxide ligands with the chloride ligands. This process would release catalytic amounts of HCl, which could then lead to dehydration of the alcohol. To investigate the extent to which a Lewis acid would dehydrate 1, the alcohol was allowed to react with the Lewis acids PdCl₂(PhCN)₂ and [Ru- $(COD)Cl_2]_n$ at room temperature in CDCl₃. As a control, Pd⁰ (5%) Pd/C) was also evaluated as a catalyst for the dehydration of 1. Interestingly, all of the catalysts converted 1 to similar mixtures of dehydrated products comparable to those observed with the metathesis catalysts. Further observation revealed that although neat samples of 1 were stable indefinitely in closed flasks at room temperature, NMR samples in CDCl₃ slowly converted to dehydrated mixtures, albeit at a much slower rate than for the Lewis-acid-catalyzed reactions. Given the known decomposition of chloroform to produce HCl and phosgene, it seems likely that even this small amount of acid was sufficient to promote the dehydration of the alcohol.

Although the ruthenium catalysts showed some modest activity for the partial dehydration of 1, more efficient and selective methods were sought to convert 1 to MCPD. Given the rapid room-temperature conversion of MCPD to dimer, particularly in the presence of acid catalysts, two distinct routes to the dimer were conceived. In the first route, a solid acid catalyst would be employed and the dehydration and dimerization would occur in the same flask. In the second route, a dehydration catalyst of much lower acidity would be employed and the reaction carried out under reduced pressure allowing the volatile MCPD to be easily separated from the reaction mixture. For the first route, heterogeneous solid acid catalysts were employed to allow for easy isolation of the product. Montmorillonite K10 (MMT-K10), an acid clay, and Nafion SAC-13, a silica-supported perfluorinated cation exchange resin, were screened for activity. Although both catalysts resulted in high conversions (95% conversion in 1 h at ambient temperature), both yielded complex mixtures consisting of ether, dimer, significant amounts of trimer, and other heavier oligomers (Table 2). To try and trap MCPD prior to oligomerization, the reaction was conducted with Nafion SAC-13 at 40 $^\circ C$ under reduced pressure (40 torr). Although the isolated MCPD was >90% pure, the yield was low and the reaction mixture rapidly oligomerized to a thick orange oil composed of heavy oligo-

COMMUNICATIONS

Table 2. Catalysts for the dehydration of 1.						
Catalyst	Temp. [°C]	Time [h]	Products 1:ether:dimer:oligomer			
MMT-K10	25	1	5:41:22:32			
Nafion Sac-13	25	1	6:35:23:36			
Pd(COD)Cl ₂	25	16	< 1:14:66:23			
2м HCl	25	1	0:(86):13 ^[a]			
MgSO ₄	25	16	16:84:0:0			
Benzoic acid	25	16	8:66:21:4			
AIPO ₄	25	16	19:76:5:0 ^[b]			
[a] The number in parentheses is the mass% of ethers and dimers com- bined. [b] The use of a mixed AlPO ₄ /MgSO ₄ catalyst (60 °C, 5 h, 40 torr; 1 torr = 1.333×10^2 Pa) allowed for isolation of MCPD in 78% yield. The						

pot residue from this reaction consisted of 10% 1 and 90% ethers.

mers. From this result it was clear that in the case of strong heterogeneous acid catalysts, oligomerization occurred more rapidly than MCPD could be removed from the reaction flask.

To further investigate optimal dehydration conditions, a series of weak Bronsted- and Lewis-acid catalysts were screened to determine their activity in the selective dehydration of 1 (Table 2). Benzoic acid and dilute HCl were unselective and produced primarily ether, along with dimer and trimer. Surprisingly, Pd(COD)Cl₂ reacted almost quantitatively and produced 66% dimer along with significant amounts of trimer and tetramer. In the search for a milder dehydrating agent, magnesium sulfate was employed as a catalyst and produced only ethers. In contrast to the other dehydration catalysts that produced primarily one ether isomer, MgSO₄ produced the two distinguishable ether isomers in nearly equal amounts. This difference in isomer distribution is attributed to the lack of suitable acid sites on the catalyst. In the absence of these sites the reaction is driven by the coordination of water to magnesium cations and is dependent on the auto-ionization of the alcohol. Based on these initial screening results, an aluminum phosphate catalyst was prepared^[19] and evaluated as a dehydration catalyst. Under a variety of conditions, this catalyst was selective for the production of only ethers, MCPD, and dimers; no heavier oligomers were formed. Despite the favorable product distribution, the conversion efficiency of this catalyst was limited by the production of water in the dehydration reaction. To overcome this hurdle, mixtures of AIPO_4 with a suitable drying agent were employed. An AIPO₄/molecular sieve catalyst resulted in a low overall yield of MCPD with formation of an oligomeric mixture. In contrast, an AIPO₄/MgSO₄ catalyst permitted the direct conversion to MCPD. The optimized catalyst allowed for a 78% isolated yield of isomeric MCPD from 1.

The dimer product distribution resulting from the room temperature Diels–Alder cycloaddition of MCPD (Figure 3) is of significant interest and is in part controlled by the starting composition of MCPD isomers. Dehydration of the alcohol with AlPO₄ at 60 °C yields 84% 2-methylcyclopentadiene (8) and 16% 1-methylcyclopentadiene (9), while 5-methylcyclopentadiene was not observed. This preference for 8 results from the formation of a more stable tertiary carbocation compared to



Figure 3. GC chromatogram of MCPD dimers derived from dehydration of 1 with AlPO_4/MgSO_4 followed by ambient temperature dimerization.

the secondary carbocation intermediate required for **9** (Scheme 2). In commercial methylcyclopentadiene dimer, seven peaks are observed in the gas chromatogram.^[20] The distribution contains four major peaks representing various isomers resulting from the cycloaddition of 2-methyl and 1-methyl cyclopentadiene. The dimers are present almost exclusively as the endo isomers. In the current work, seven peaks are observed, however the distribution is significantly different than for the commercial product, with two peaks representing 88% of the dimers. The largest peak (56%) is observed for 3,9-dimethyl-*endo*-tricyclo[5.2.1.0^{2,6}] deca-3,8-diene (**10**), while the other main peak (33%) is observed for 4,9-dimethyl-*endo*-tricyclo[5.2.1.0^{2,6}] deca-3,8-diene (**11**) (Scheme 3). In comparison,



Scheme 3. Prominent *endo*-isomers produced from the thermal dimerization of MCPD isomers derived from 2-methyl-1-cyclopentenol. The first number of a pair represents the % composition produced in this work, while the numbers in brackets refer to % composition of the commercial product.

the commercial product is 36% 10 and 29% 11.^[21] Coupling of two molecules of 8 yields 10, while coupling of 8 and 9 yields 11. The distribution of isomers is also dependent on both the relative dimerization rates of 8 and 9 as well as concomittant monomer isomerization. Previous studies have shown that 2methylcyclopentadiene dimerizes faster than 1-methylcyclopentadiene ostensibly due to less steric crowding at the site of cycloaddition;^[22] this effect further influences the final distribution. Interestingly, dimer 12 which represents roughly 10% of commercial dimer is only 3% of the current mixture. This is likely the result of the known [3,3]-sigmatropic Woodward-Katz rearrangement to $\mathbf{11}^{[21]}$ being catalyzed by the dehydration conditions.

In order to convert the dimer mixture to RJ-4, it must first be hydrogenated. This was accomplished under mild conditions (40 psi, PtO₂ catalyst) and resulted in six distinguishable isomers. The four major peaks representing 91% of the product are the four sets of diasteriomers arising from the non-stereospecific hydrogenation of **10** and **11**.^[23] After hydrogenation, these mixtures can be isomerized with strong Lewis acid catalysts to fuels rich in *exo*-isomers. Although this final step improves the low temperature fluidity of the fuel, it was not explored in the current work.

In summary, a highly efficient and selective synthesis for the conversion of linalool to specialized fuel products has been developed. The optimized approach offers a high catalyst turnover number, solvent free conditions, low external energy demands, and an exceptionally well defined product distribution. Another key finding of this work is the unexpected capacity of ruthenium metathesis catalysts to dehydrate a tertiary alcohol. Further work to effectively reduce catalyst loadings and to establish how the distribution of dimers will affect the performance of high density fuel mixtures is ongoing.

Experimental Section

General Procedure for RCM reaction: Typically reactions were run with 0.1 mol% of the Grubbs-Hoveyda second-generation catalyst (4). The catalyst was transferred to a flask in a glove box, fitted with a septum, and then removed from the inert atmosphere. Freshly distilled linalool was then slowly added via a syringe through the septum. The flask was vented through an oil bubbler along with a slow flow of nitrogen. Within 30 s vigorous bubbling began while stirring at room temperature. The bubbling continued for 30-45 min and then ceased. Once bubbling had stopped air was bubbled into the reaction mixture for 15 min to oxidize the catalyst. ¹H NMR of the crude reaction mixture showed 100% conversion of starting linalool. The product was immediately vacuum distilled (1 torr) to a receiving flask cooled in a dry ice bath. After the transfer, the product was sealed under nitrogen and stored at room temperature. The product was analyzed via NMR.^[24] ¹H NMR (CDCl₃): $\delta = 1.29$ (s, 3 H), 1.84 (m, 2 H), 2.23 (m, 1 H), 2.37 (m, 1 H), 2.57 (broad s, 1 H), 5.65 ppm (m, 2 H).

Dehydration with AIPO₄/MgSO₄: Aluminum phosphate (1.34 g, 11 mmol) and magnesium sulfate (1.63 g, 13 mmol) were placed in a 50 mL round-bottom flask charged with a stirbar. To this flask 2-methylcyclopentenol (1) (13.01 g, 0.13 mol) from the RCM reaction was added, and the flask was fit with a small distillation head. The receiving flask was placed in a dry ice bath and the reaction was placed under vacuum (40 torr). The reaction flask was heated at 60 °C for 5 h. Total yield of the distillate was 78%. ¹H NMR for major product 2-methylcyclopentadiene^[25] (CDCl₃): δ = 2.06 (s, 3 H), 2.98 (s, 2 H), 6.04 (s, 1 H), 6.44 ppm (s, 2 H).

Acknowledgements

The authors would like to thank NAWCWD and the Office of Naval Research for funding this work. We thank Neal Barry for creating the Table of Contents image of this manuscript.

Keywords: green chemistry \cdot high density fuels \cdot methylcyclopentadiene \cdot renewable fuels \cdot ring closing metathesis

- a) A.-L. Marshall, P. J. Alaimo, *Chem. Eur. J.* 2010, *16*, 4970–4080; b) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallet, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* 2006, *311*, 484–489; c) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 2006, *106*, 4044–4098; d) J. Hill, in *Sustainability Agriculture Part* 1 (Eds.: E. Lichtfouse, M. Navarrete, P. Debaeke, V. Souche're, C. Alberola), Springer, Dordrecht, 2009, pp. 125–139..
- [2] See for example: a) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* 2010, 110, 1746–1787; b) A. H. Hoveyda, A. R. Zhugralin, *Nature* 2007, 450, 243–251; c) R. H. Grubbs, *Angew. Chem.* 2006, 118, 3845–3850; *Angew. Chem. Int. Ed.* 2006, 45, 3760–3765; d) R. H. Grubbs, *Tetrahedron* 2004, 60, 7117–7140; e) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* 2009, 109, 3708–3742.
- [3] a) D. E. White, I. C. Stewart, R. H. Grubbs, B. M. Stoltz, J. Am. Chem. Soc. 2008, 130, 810-811; b) M. Arisawa, A. Nishida, M. Nakagawa, J. Organomet. Chem. 2006, 691, 5109-5121.
- [4] a) G. O. Wilson, M. M. Caruso, N. T. Reimer, S. R. White, N. R. Sottos, J. S. Moore, *Chem. Mater.* **2008**, *20*, 3288–3297; b) R. M. Thomas, R. H. Grubbs, *Macromolecules* **2010**, *43*, 3705–3709.
- [5] a) M. Ulman, R. H. Grubbs, J. Org. Chem. 1999, 64, 7202-7207; b) J. C. Conrad, J. L. Snelgrove, M. D. Eeelman, S. Hall, D. E. Fogg, J. Mol. Catal. A: Chem. 2006, 254, 105-110.
- [6] B. G. Harvey, M. E. Wright, R. L. Quintana, *Energy Fuels* 2010, 24, 267– 273.
- [7] a) M. C. Y. Chang, J. D. Keasling, *Nat. Chem. Biol.* 2006, *2*, 674–681;
 b) F. M. Carrau, K. Medina, E. Boido, L. Farina, C. Gaggero, E. Dellacassa,
 G. Versini, P. A. Henschke, *FEMS Microbiol. Lett.* 2005, *243*, 107–115.
- [8] T. R. Hoye, H. Zhao, Org. Lett. 1999, 1, 1123-1125.
- [9] a) R. Alcántara, E. Alcántara, L. Canoira, M. J. Franco, M. Herrera, A. Navarro, *React. Funct. Polym.* 2000, 45, 19–27; b) J. W. Yoon, S. H. Jhung, T-

J. Kim, H-D. Lee, N. H. Jang, J.-S. Chang, Bull. Korean Chem. Soc. 2007, 28, 2075–2078.

- [10] a) D. M. Haskell, F. Floyd, US Patent No. 4301315, **1981**; b) T. I. Evans, L. J. Karas, R. Rameswaran, US Patent No. 5877372, **1999**.
- [11] a) Y. Li, Y. Wu, L. Liang, Y. Li, G. Wu, Chin. J. Polym. Sci. 2010, 28, 55–62;
 b) I. V. Vasilenko, A. N. Frolov, S. V. Kostjuk, Macromolecules 2010, 43, 5503–5507;
 c) Q. Liu, Yi-X. Wu, Y. Zhang, P-F. Yan, R-W. Xu, Polymer 2010, 51, 5960–5969.
- [12] a) G. W. Burdette, A. I. Schneider, US Patent No. 4398978, **1983**, b) J. S. Chickos, A. E. Wentz, D. Hillesheim-Cox, *Ind. Eng. Chem. Res.* **2003**, *42*, 2874–2877.
- [13] D. C. Braddock, A. Matsuno, Tetrahedron Lett. 2002, 43, 3305-3308.
- [14] J. C. Conrad, H. H. Parnas, J. L. Snelgrove, D. E. Fogg, J. Am. Chem. Soc. 2005, 127, 11882–11883.
- [15] L. Vieille-Petit, H. Clavier, A. Linden, S. Blumentritt, S. P. Nolan, R. Dorta, Organometallics 2010, 29, 775–788.
- [16] M. B. Dinger, J. C. Mol, Adv. Synth. Catal. 2002, 344, 671-677.
- [17] I. C. Stewart, T. Ung, A. A. Pletnev, J. M. Berlin, R. H. Grubbs, Y. Schrodi, Org. Lett. 2007, 9, 1589–1592.
- [18] Direct dehydradion of an RCM product by a first-generation Grubbs catalyst has recently been observed: D. L. J. Clive, M. P. Pham, J. Org. Chem. 2009, 74, 1685 – 1690.
- [19] See Supporting Information, adapted from: A. W. Wang, Final Report US Department of Energy, Contract No. DE-FC22–94PC93052, 2002.
- [20] M. A. Diez, M. D. Guillen, C. G. Blanco, J. Bermejo, J. Chromatography 1990, 508, 363-374.
- [21] W. Thommen, H. Pamingle, K. H. Schulte-Elte, *Helv. Chim. Acta* 1989, 72, 1346–1353.
- [22] S. M. Csicsery, J. Org. Chem. 1960, 25, 518-521.
- [23] See Supporting Information (Figure S7).
- [24] C. Morrill, PhD Thesis, California Institute of Technology, 2006.
- [25] V. I. Mstislavsky, V. A. Korenevsky, N. M. Sergeyev, V. N. Solkan, Org. Magn. Reson. 1976, 8, 368–374.

Received: January 13, 2011 Published online on February 23, 2011