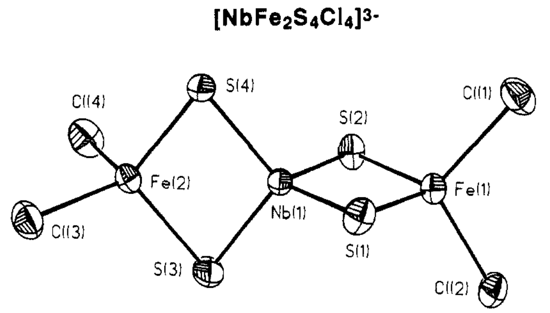

Figure 2. The structure of $[NbFe_2S_4Cl_4]^{3-}$, showing 50% thermal ellipsoids and the atom-labeling scheme. The following mean values are averaged over the two inequivalent anions. Bond distances (Å): Nb–S, 2.290 (4); Fe–S, 2.327 (5); Nb–Fe, 2.842 (8); Fe–Cl, 2.272 (3). Bond angles (deg): Fe–Nb–Fe, 176.16 (6); S(1)–Nb–S(2), 105.0 (2); Nb–S–Fe, 76.0 (2); S–Fe–S, 102.7 (3); Cl–Fe–Cl, 108.2 (6). $[TaFe_2S_4Cl_4]^{3-}$ is isostructural with this cluster.

of one $[MS_4]^{3-}$ anion and are chelated by one TMEDA molecule each. Relative to idealized T_d anion symmetry, Li^+ binding decreases S–M–S angles while the angle unbridged by Li^+ is considerably expanded. The unique Nb–S distance is slightly longer than those in K_3NbS_4 (2.241 (8)–2.258 (8) Å[5]). When compared to the shortest M–S bridge bonds in $[M_6S_{17}]^{4-}$ (M–μ_2S: mean 2.414 (4) Å (Nb), 2.405 (6) Å (Ta)[6]), it is clear that $[MS_4]^{3-}$ bond lengths correspond to multiple bonds,[10] a consistent property of all d^0 tetrathiometalates.

The compounds $Li_3[MS_4]\cdot 2TMEDA$ are freely soluble in strongly polar solvents such as DMF and Me_2SO, are somewhat soluble in THF and acetonitrile, and are very soluble in the latter two solvents in the presence of ca. 4 equiv of TMEDA/M. Anaerobic solutions lacking protic impurities are stable for days. Unlike other tetrathiometalates, $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are not intensely colored but form pale yellow solutions in solvents such as THF and acetonitrile with patterns of narrow absorption bands characteristic of $[MS_4]^{z-}$ chromophores. The two lowest-energy LMCT bands (ν_1, ν_2) occur in the UV region in the energy order Ta > Nb;[8] ν_1, likely $1t_1 \rightarrow 2e$,[12] is solvent dependent and is split in THF solution (335, 376 nm, Nb; 295, 329 nm, Ta). In comparison, the red-purple $[VS_4]^{3-}$ chromophore absorbs into the visible but also with a split ν_1 band (523, 560 (sh) nm, Me_2SO).[4] The spectra indicate retention of tetrahedral structures of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ in solution and define the optical electronegativity series V > Nb > Ta.

The different outcomes of reactions 2 and 3 are dependent on reactant X. In reaction 3, we propose that the stronger silyl nucleophile MeO^- reacts irreversibly and completely with $(Me_3Si)_2S$ to afford the silyl methyl ether and $Me_3SiS^-Li^+$,[13] which then attacks $M(OEt)_5$ to give the silyl ethyl ether and $[MS_4]^{3-}$. Inasmuch as Et_4NCl does not react with $(Me_3Si)_2S$ in acetonitrile over 1 week at room temperature, $[M_6S_{17}]^{4-}$ probably arises from direct reaction of the silyl sulfide with $M(OEt)_5$. That the cage product is sulfide poor with respect to initial mole ratios suggests incomplete reaction of the sulfiding agent and/or decomposition of initial products via sulfide loss. Also, Li^+ may have a stabilizing effect on $[MS_4]^{3-}$ by ion-pair interactions, as are quite apparent in the crystal structures of $Li_3[MS_4]\cdot 2TMEDA$.[14]

The potential of $[MS_4]^{3-}$ as precursors for cluster synthesis is evident from the reaction of these species (generated in situ) with 2 equiv of $FeCl_2$ or $[FeCl_4]^{2-}$. From orange-red acetonitrile solutions crystalline R_4N^+ salts (R = Me, Et) of $[MFe_2S_4Cl_4]^{3-}$ are readily isolated in moderate yields. The compound $(Me_4N)_3[NbFe_2S_4Cl_4]\cdot DMF$ crystallizes with two metrically similar anions in the asymmetric unit. $[NbFe_2S_4Cl_4]^{3-}$, shown in Figure 2, is a linear trinuclear cluster (Fe–Nb–Fe 176.16 (6)°) which approaches D_{2d} symmetry and is isostructural with $[TaFe_2S_4Cl_4]^{3-}$[9] and with previously reported $[VFe_2S_4Cl_4]^{3-}$[15] and $[MFe_2S_4Cl_4]^{2-}$ (M = Mo,[16] W,[16] Re[17]). Complexation results in only a small increase (0.02 Å) in the mean Nb–S bond length.

The ready accessibility of soluble forms of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ provides entry to what should be a diverse solution reaction chemistry of these ions. One manifestation of this is formation of the clusters $[MFe_2S_4Cl_4]^{3-}$ which, as was $[VFe_2S_4Cl_4]^{3-}$,[16] may themselves be precursors to the unknown heterometal MFe_3S_4 cubane-type clusters. We also anticipate that the synthetic methodology of reaction 3 may be applied to other transition metals to yield previously unknown $[MS_4]^{z-}$ species with as yet unexplored reactivities. These are areas of our continuing research.

Acknowledgment. This research was supported by NSF Grant CHE 89-03283. X-ray diffraction equipment was obtained by NIH Grant 1-S10-RR-02247.

Supplementary Material Available: Positional and thermal parameters of $Li_3[MS_4]\cdot 2TMEDA$ and $(Me_4N)_3[NbFe_2S_4Cl_4]\cdot DMF$ (17 pages). Ordering information is given on any current masthead page.

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(10) These M–S bond distances are as much as ca. 0.1–0.2 Å longer than those at Nb/Ta atoms with a single terminal sulfide,[6,11] a feature qualitatively rationalized in terms of 4 strongly π-bonding ligands in a tetrahedral arrangement vs one such ligand in other stereochemistries.

(11) (a) Do, Y.; Holm, R. H. *Inorg. Chim. Acta* **1985**, *104*, 33 and references therein. (b) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358.

(12) (a) Müller, A.; Diemann, E.; Ranade, A. C. *Chem. Phys. Lett.* **1969**, *88*, 1205. (b) El-Issa, B. D.; Ali, A. A. M.; Zanati, H. *Inorg. Chem.* **1989**, *28*, 3297.

(13) The sodium salt of Me_3SiS^- has been isolated: Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809.

(14) Li–S contact distances are entirely comparable to those in $[Cp^*TaS_3Li_2(THF)_2]_2$ where ion pair interactions also appear to play a stabilizing role: Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Van-Doorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782.

(15) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.

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(17) Müller, A.; Krickemeyer, E.; Bögge, H. *Z. Anorg. Allg. Chem.* **1987**, *554*, 61.

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Tailored Cationic Palladium(II) Compounds as Catalysts for Highly Selective Linear Dimerization of Styrene and Linear Polymerization of *p*-Divinylbenzene

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An important advantage in using transition-metal compounds as catalysts is the ability to tailor their activity and selectivity by a rational choice of ligands. We had earlier reported[1] that the palladium(II) species $[Pd(MeCN)_4](BF_4)_2$ (**1**) was an active catalyst for the polymerization of styrene (typical MW: 70 000) and the di- and trimerization of α-methylstyrene to the corresponding indan derivatives at room temperature. The usual cationic mechanism was invoked for these transformations.[1] Herein, we report that the replacement of the weakly coordinating MeCN ligands in **1** by more strongly ligating and bulkier pyridine and phosphine derivatives results in the formation of highly selective catalysts for selective linear dimerization of styrene and linear polymerization of *p*-divinylbenzene. The new catalyst systems differ from most existing systems[2] for the cationic oligomerization and polymerization of styrene derivatives in several important ways. Specifically, (a) no indan derivative or higher oligomers are formed from styrene;[2] (b) only styrene reacts when a mixture of styrene and α-methylstyrene is employed, although

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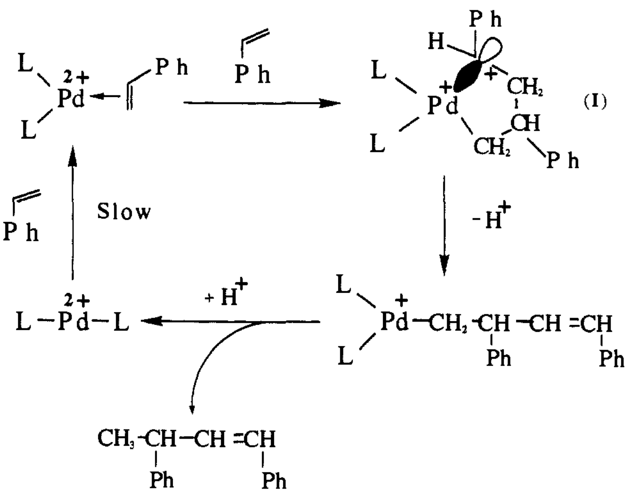
(1) (a) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421. (b) Sen, A.; Lai, T.-W.; Thomas, R. R. *J. Organomet. Chem.* **1988**, *358*, 567.

(2) Review: Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley: New York, 1982; p 196.

Scheme I



the latter is usually significantly more reactive in reactions involving the intermediacy of carbocations;[3] and (c) the ability to effect clean, linear dimerization of styrene allowed the formation of an unusual, soluble, linear polymer from *p*-divinylbenzene; no cross-linked material was observed.[4]

The catalysts are Pd(PPh$_3$)$_2$(BF$_4$)$_2$ (**2**), Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(BF$_4$)$_2$ (**3**), and Pd(2,6-^{t}Bu$_2$C$_5$H$_3$N)$_2$(MeNO$_2$)$_2$(BF$_4$)$_2$ (**4**). **2** was synthesized by the reaction of Pd(PPh$_3$)$_2$Cl$_2$ with 2 equiv of AgBF$_4$ in MeNO$_2$. **3** and **4** were formed through the reaction of **1** with the appropriate ligand in MeNO$_2$. All three compounds are air-stable solids that are soluble in polar organic solvents. The compounds gave satisfactory elemental analysis results, and ^{19}F NMR spectra of **2** and **3** support the presence of Pd–F–BF$_3$ bridges.

Compounds **2**–**4**, *both in solution and in the solid state*, were effective catalysts for the linear dimerization of styrene to 1,3-diphenyl-1-butene.[5] Solution-phase dimerization was usually carried out in MeNO$_2$ or a MeNO$_2$–CHCl$_3$ mixture. However, it was more convenient to omit the solvent and use the Pd(II) compound in the solid form. This allowed the removal of the catalyst simply by filtration at the end of the reaction. With either procedure, several hundred turnovers were observed in a 12-h period.[5] Neither indan nor higher oligomers were observed as side products.

Consistent with a cationic mechanism, no reaction was observed when *m*-nitrostyrene was employed instead of styrene. On the other hand, the use of *p*-methoxystyrene resulted in the formation of a polymer with MW as high as 1.4×10^6.

α-Methylstyrene was found not to undergo any reaction at room temperature in the presence of **2**–**4**. When any one of the above Pd(II) compounds was added to a 1:1 mixture of styrene and α-methylstyrene at room temperature, *only* styrene was dimerized. This selectivity is remarkable since α-methylstyrene is normally significantly more reactive than styrene in reactions involving carbocations.[3] Although α-methylstyrene was unreactive at room temperature, it was converted to linear and cyclic(1,3,3-trimethyl-1-phenylindan) dimers, as well as higher oligomers, at 45 °C. The product distribution was similar to that obtained with BF$_3$·Et$_2$O and further supports a cationic mechanism for these reactions.[6]

Scheme I outlines a possible mechanism for the linear dimerization of styrene. In the key intermediate, I, the propagated carbocation is stabilized by donation of electron density from a Pd(II) d orbital. The carbocation, thus stabilized, no longer participates in electrophilic attack on the γ-phenyl group or an olefin to form an indan or a higher oligomer (polymer), respectively.[1] Instead, a H$^+$ ion is lost to eventually form the linear dimer. β-Hydrogen abstraction apparently does not occur since 2,4-diphenyl-1-butene or its more stable isomer, 1,3-diphenyl-2-butene, was not observed (1,3-diphenyl-1-butene was observed to convert very slowly to 1,3-diphenyl-2-butene but only after all the styrene had been consumed). The ability of the Pd(II) center to donate electron density to the carbocation would, of course, depend on the ancillary ligands present, with strongly donating ligands aiding the process. Hence, it is understandable that the presence of strong donors like pyridine or tertiary phosphine leads to dimerization catalysts whereas **1**, which only possesses the weakly ligating MeCN ligand, is a catalyst for the polymerization of styrene.[1] In the latter case, no stabilization of the carbocation occurs and, therefore, its reactivity is not attenuated. Even when the carbocation is stabilized, it may participate in electrophilic attack if a highly electron rich olefin is present, and this would explain the formation of polymer when *p*-methoxystyrene was used as the substrate.[7] Thus, whether dimer or higher oligomers (polymer) are formed depends critically on both the ancillary ligands present on the metal and the nature of the olefin that is used as a substrate.

The reactivity difference between styrene and α-methylstyrene is ascribable to steric factors. α-Methylstyrene is expected to coordinate less strongly than styrene, and in addition, the intermediate I is expected to be more crowded in the case of α-methylstyrene. In support of this proposal we observed that selectivity for styrene was lost when [Pd(C$_5$H$_5$N)$_2$(MeNO$_2$)$_n$](BF$_4$)$_2$ (**5**), which lacks the bulky *tert*-butyl substituents at the ortho positions of the pyridine ligand (cf. **4**), was used as the catalyst. Thus, unlike **4**, **5** was found to catalyze the dimerization of *both* styrene and α-methylstyrene (the latter to mainly 1,3,3-trimethyl-1-phenylindan) at room temperature.

Finally, protonated species have been shown to be initiators in many systems for the cationic oligomerization and polymerization of olefins.[8] We were able to rule out this possibility for our systems since 2,6-di-*tert*-butylpyridinium tetrafluoroborate was found to be inactive under our reaction conditions.

The ability of compound **2** to effect clean, linear dimerization of styrene allowed us to use it as a catalyst for the linear polymerization of *p*-divinylbenzene (DVB). The polymerization of DVB by either cationic, anionic, or free-radical initiators usually leads to the formation of an insoluble cross-linked material.[4,7] Alternatively, under certain reaction conditions, "cyclopolymerization" occurs to incorporate cyclic units into the polymer backbone.[9] Only one procedure, involving AcClO$_4$ as initiator, has been previously described for the linear polymerization of DVB.[4] Such polymers are of interest due to the high degree of unsaturation present in the backbone and at the chain ends.[4,10]

Compound **2**, in MeNO$_2$–CHCl$_3$, was found to polymerize DVB at 40–70 °C to form soluble poly(DVB),[11] eq 1. Both head-to-tail and head-to-head arrangements were observed. The more con-

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[3] For a comparison of reactivity ratios, see ref 2, p 328.

[4] Hasegawa, H.; Higashimura, T. *Macromolecules* **1980**, *13*, 1350 and references therein.

[5] Typical procedure: 0.02 g of **4**, 5 mL of styrene, and 2 mL of MeNO$_2$ were stirred together at 45 °C for 12 h. After workup, 1.0 g of 1,3-diphenyl-1-butene was obtained (number of turnovers = 190). ^{1}H NMR (CDCl$_3$) (ppm): 7.29 (10 H, m), 6.39 (2 H, d, J = 4.5 Hz), 3.46 (1 H, m), 1.46 (3 H, d, J = 7.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$) (ppm): 145.6, 137.5, 135.2, 128.5, 127.3, 127.0, 126.2, 126.1, 42.5, 21.2. Mass spectrum *m/e* 208 (M).

[6] (a) Kawakami, Y.; Toyoshima, N.; Yamashita, Y. *Chem. Lett.* **1980**, 13. (b) Reference 2, p 89.

[7] For a discussion of a similar effect, see: Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49.

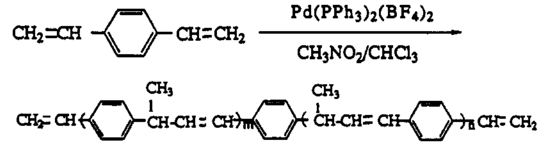
[8] Reference 2, p 81.

[9] Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley: New York, 1975; pp 275, 304.

[10] For derivatization of polyDVB, see: (a) Aoshima, S.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2443. (b) Higashimura, T.; Aoshima, S.; Hasegawa, H. *Macromolecules* **1982**, *15*, 1222.

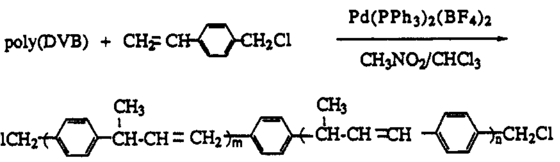
[11] Typical procedure: 0.005 g of **2** was dissolved in 2 mL of MeNO$_2$ and 5 mL of CHCl$_3$. To it was added 2 mL of a 0.439 M solution of DVB in CHCl$_3$. The resultant reaction mixture was stirred at 68 °C for 30 h. Following workup, 0.115 g (92% yield) of polyDVB (MW = 3900) was obtained. ^{1}H NMR (CDCl$_3$) (ppm): 7.30–7.15 (4 H, m), 6.34 (2 H, br), 3.59 (1 H, br), 1.44 (3 H, br). In addition, three small absorptions at 6.69, 5.73, and 5.23 ppm were observed due to the terminal vinyl groups. The chemical shifts of these were identical with those of DVB. Selected data for ^{13}C{^{1}H} NMR (CDCl$_3$) (ppm): 21.12 (*C*H$_3$CH=), 42.26 (CH$_3$*C*H=). The ^{1}H NMR spectrum was identical with that reported earlier.[4]

ventional addition polymerization process is not involved; rather, the polymer is formed through a step-growth mechanism involving the terminal vinyl groups. Consistent with this mechanism was the observation of an exponential increase in molecular weight with time (highest observed MW = 6000). For a given reaction time, the molecular weight of the poly(DVB) obtained increased markedly with both increasing temperature and increasing catalyst concentration. Thus, it was possible to control the molecular weight of poly(DVB) by an appropriate choice of reaction conditions. Our procedure for the linear polymerization of DVB appears to be superior to that described earlier in that the use of lower temperatures (<70 °C) and higher monomer concentrations (>0.1 M) does not result in side reactions.



(1)

Lastly, as shown in eq 2, it was possible to synthesize a telechelic (α,ω-difunctional) polymer from preformed poly(DVB) using the Pd(II) catalyst **2**. Indeed, a "one-pot" synthesis of the telechelic polymer was carried out by first adding DVB to the catalyst solution, waiting for poly(DVB) to form, and then adding *p*-(chloromethyl)styrene. The telechelic polymer opens up the possibility of forming block copolymers incorporating highly unsaturated poly(DVB) blocks.



(2)

Acknowledgment. Support of this research by the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295), is gratefully acknowledged. We also thank Johnson Matthey, Inc., for a generous loan of palladium metal.

Supplementary Material Available: The synthesis and characterization of the palladium complexes **2–4** (2 pages). Ordering information is given on any current masthead page.

Total Synthesis of the Anthelmintic Agent Hikizimycin

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Hikizimycin was isolated from the fermentation broth of *Streptomyces A-5*[1] and was determined to be identical with anthelmycin, which was isolated from *Streptomyces longissimus*.[2] Biochemical studies of hikizimycin revealed significant anthelmintic activity against a variety of common parasites.[3] Degradation studies[4] identified the presence of a cytosine base, a 3-amino-3-deoxyglucose sugar (kanosamine), and a 4-aminoundecose sugar (hikosamine). Eventually, the structure of hikizimycin was proposed as shown in Figure 1.[5] Herein, we report the first total synthesis of hikizimycin, the most structurally complex member of the long-chain carbohydrate class of natural products.[6]

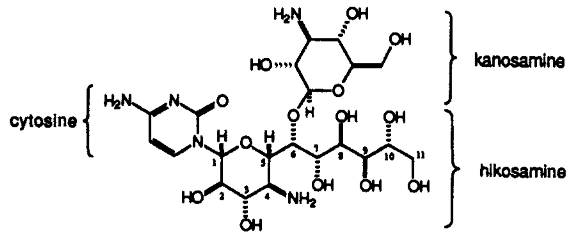
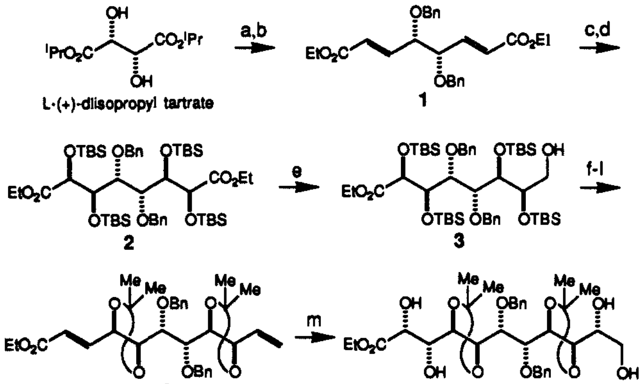


Figure 1. Hikizimycin (anthelmycin).

Scheme I[a]



[a] (a) NaH, BnBr (2.1 equiv), NBu_4NI, THF (53% product; 12% monobenzyl ether); (b) $(EtO)_2POCHLiCO_2Et$ (2.6 equiv), CH_2Cl_2, DIBAL-H (2.6 equiv) (53%); (c) OsO_4 (0.05 equiv), NMO (3 equiv), acetone–H_2O (8:1) (71%); (d) TBSOTf, 2,6-lutidine, CH_2Cl_2 (100%); (e) DIBAL-H (2.3 equiv), CH_2Cl_2, −78 °C (82%); (f) oxalyl chloride, DMSO, Et_3N (97%); (g) $Cp_2TiCH_2ClAlMe_2$, tol–THF–Py, −78 to −15 °C (82%); (h) DIBAL-H, CH_2Cl_2 (95%); (i) oxalyl chloride, DMSO, Et_3N (98%); (j) $(EtO)_2POCHLiCO_2Et$ (97%); (k) nBu_4NF, THF, 0 °C (86%); (l) acetone, H_2SO_4 (89%); (m) OsO_4 (0.05 equiv), NMO (3 equiv), acetone–H_2O (10:1) (88% yield; 75% of mixture is desired diastereomer).

The undecose fragment of hikizimycin[7] was prepared by a chain extension/osmylation strategy,[8] conducted efficiently by a two-directional chain synthesis.[9] L-(+)-Diisopropyl tartrate furnished the C6 and C7 stereocenters, which served as handles for introducing the remaining stereocenters (Scheme I). Bisbenzylation followed by a one-pot reduction/homologation procedure[10] furnished the α,β-unsaturated ester **1**. This was oxidized with catalytic osmium tetraoxide and excess *N*-methylmorpholine *N*-oxide (NMO)[11] to yield the tetraol as a pure crystalline solid (mp 113–115 °C).[12] The tetraol was protected as its tetrakis(*tert*-butyldimethylsilyl ether) **2**.[13]

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[4] (a) Das, B. C.; Defaye, J.; Uchida, K. *Carbohydr. Res.* **1972**, *22*, 293. (b) Uchida, K.; Das, B. *Biochimie* **1973**, *55*, 635. (c) Uchida, K. *Agric. Biol. Chem.* **1976**, *40*, 395.

[5] Vuilhorgne, M.; Ennifar, S.; Das, B. C.; Paschal, J. W.; Nagarajan, R.; Hagaman, E. W.; Wenkert, E. *J. Org. Chem.* **1977**, *42*, 3289.

[6] See: (a) Isono, K. *J. Antibiot.* **1988**, *41*, 1711. (b) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15.

[7] Syntheses of a protected form of hikosamine, methyl peracetyl-α-hikosaminide, have been reported: (a) Secrist, J. A., III; Barnes, K. D. *J. Org. Chem.* **1980**, *45*, 4526. (b) Danishefsky, S.; Maring, C. J. *J. Am. Chem. Soc.* **1989**, *111*, 2193; (c) **1985**, *107*, 7762.

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[11] VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

[12] The diastereofacial selectivity at each olefin was determined to be 12.9:1 based on HPLC ratios of the tetraacetates obtained from acetylation following osmylation of HPLC-purified **1**.

[13] The stereochemistry was confirmed by correlation with D-*threo*-L-*galacto*-octitol octaacetate. Reduction followed by deprotection and peracetylation afforded material possessing comparable melting point and optical rotation.