The residues were then soluble in hexane. Small crystals were obtained by fractional crystallization from the hexane solution at 0 °C. IR (hexane, cm^{-1}): 3660 m (OH); 2510 w (BH); 2053 vs, 2034 s, 2023 s, 2000 m, 1992 m (sh) (CO). ^{11}B NMR (hexane, 20 °C, δ): 26.3 (br d, fwhm 360 Hz, $\{^1H\}$ 220 Hz; J_{B-H} = 140 Hz). ^1H NMR (C_6D_6, 20 °C, δ): 5.5 (br, BH), −26.72 (s, metal hydride). MS (EI, m/e): P^+ = 602 (−12 CO); $^{56}Fe_4{}^{12}C_{13}{}^{16}O_{13}{}^{11}B^1H_3{}^+$, 601.7054 (obsd), 601.7069 (calcd). ^1H NMR spectrum of $[HFe_4(CO)_{12}C]$-BHBr (THF-d_8, δ): 5.5 (br, BH), −26.38 (s, metal hydride).

Crystallographic Studies for $[HFe_4(CO)_{12}C]BHX$. The crystallographic data for $[HFe_4(CO)_{12}C]BXY$ (X = Y = H) have been published in the initial communication.[16] The data for X = H, Y = Cl, Br follow. Crystal data collection, and refinement parameters for X = Cl, Br are collected in Table III. Crystals were mounted on glass fibers with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of 25 reflections ($20° \leq 2\theta \leq 25°$). Preliminary photographic evidence showed $2/m$ Laue symmetry for both compounds. The systematic absences in diffraction data of both compounds established the 2_1 screw axis ($0k0$, $k = 2n + 1$). The centrosymmetric alternative, $P2_1/m$, was suggested by the E statistics of both, and this was confirmed by the chemically sensible results of refinement. Empirical absorption corrections were applied to both data sets (216 ψ-scan reflections, pseudoellipsoid model, T_{max}/T_{min} = 1.585 for X = Cl and 1.463 for X = Br). The structure for X = Cl was solved by direct methods and that for X = Br by isomorphous analogy to X = Cl. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The metal-bridging hydride atoms in both were not located and were not included in the refinement. The Cl atom is disordered over two sites, Cl and Cl′, in a 93:7 ratio. The atomic coordinates for the two compounds are given in Tables IV and V. All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (version 5.1 by G. Sheldrick, Nicolet Corp., Madison, WI).

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Supplementary Material Available: Tables containing refined temperature factors and bond distances and angles for $[HFe_4(CO)_{12}C]BHX$ (X = Cl, Br) and a structural drawing of $[HFe_4(CO)_{12}C]BHCl$ (7 pages); tables of calculated and observed structure factors for $[HFe_4(CO)_{12}C]BHX$ (X = Cl, Br) (20 pages). Ordering information is given on any current masthead page.

Synthesis of Large-Ring Keto Lactones by the Homogeneous and Polymer-Supported Palladium-Catalyzed Carbonylative Coupling of Esters Having Vinyl Triflate and Vinylstannane Termini

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Large-ring keto lactones having from 12 to 16 members were synthesized in fair yield by the palladium-catalyzed carbonylative coupling of long-chain esters having vinyl triflate and vinylstannane termini. A polystyrene-supported bis(diphenylphosphino)ferrocene ligand system was synthesized by the copolymerization of styrene, *p*-divinylbenzene, and bis(diphenylphosphino)vinylferrocene. Palladium catalysts supported on this polymer were more selective in these carbonylative cyclizations than were corresponding homogeneous catalyst systems.

Introduction

There is a broad spectrum of naturally occurring medium- and large-ring compounds, many of which display some biological activity. These macrocycles are of varying complexity and contain a range of functional groups. They represent an important group of compounds, and their synthesis in relatively high yield represents important methodology. However, there are relatively few *general* methods for the generation of medium-sized and macrocyclic rings in high yield.[1] The reactions that yield carbocycles are often effected under severe enough reaction conditions that the range of compatible functional groups is limited, and when present, extensive protection/deprotection sequences are often necessary.

There are, however, a number of examples of the synthesis of macrocycles via transition-metal-mediated coupling reactions[2-5] that occur under relatively mild conditions and tolerate a range of functional groups. Rings containing 9 to 27 members have been synthesized by this type of process.

The cross-coupling of an organic electrophile with an organometallic reagent is catalyzed by a number of group

† Deceased on July 19, 1989.

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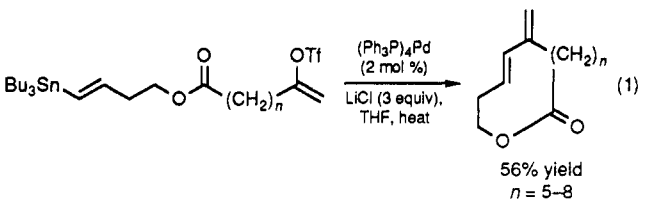
10 transition metals, particularly nickel and palladium,[6] and the mechanisms of most of these reactions are reasonably well understood.[7] One of the most versatile organometallic reagents is the organotin reagent. Organotins containing a variety of reactive functional groups can be prepared by a number of different reaction types.[8] These reagents are not particularly oxygen- or moisture-sensitive and can be purified by silica column chromatography, by distillation, or by crystallization without decomposition.

The palladium-catalyzed cross-coupling reaction of organotin reagents with a variety of organic electrophiles has been extensively studied in these laboratories.[9] Because this mild, versatile reaction is tolerant of a variety of organic functionalities on either coupling partner, is stereospecific, and gives high yields, it is ideal for use in the construction of complex organic molecules.

In this transformation, only one of the groups on tin enters into the coupling reaction. Fortunately, different types of groups transfer selectively from tin, the simple alkyl group having the slowest transfer rate. Thus, the necessary and important organotin reagent is an unsymmetrical one containing three alkyl groups such as methyl or butyl and a fourth group such as the acetylenic, vinylaryl, benzyl, or allyl group.

When the reaction is carried out under a moderate pressure (1–3 atm) of carbon monoxide, a ketone is obtained, resulting from cross-coupling accompanied by carbon monoxide insertion. We have previously reported the synthesis of large-ring lactones by the palladium-catalyzed cyclization of esters containing vinyl triflate and vinylstannane groups at the termini (eq 1).[10] Herein, we



(1)

report improved syntheses of the requisite starting materials, palladium-catalyzed carbonylative coupling reactions to macrocyclic keto lactones, and the synthesis and use of polymer-bound catalyst systems to suppress intermolecular reactions.

Results and Discussion

Synthesis of Acyclic Precursors. In order to evaluate the synthesis and cyclizations of aliphatic esters containing a terminal vinyl triflate on the carboxylic acid side of the molecule and a vinylstannane on the end of the alcohol unit, a series of such substrates was synthesized by conventional methods. The known keto esters[11] were obtained by the palladium-catalyzed reaction of the acid chloride of the half-ester with tetramethyltin.[12] The alcohol containing the vinyltin unit was obtained by the generation of (*E*)-(2-(tributylstannyl)vinyl)lithium[13] from the reaction of (*E*)-bis(tributylstannyl)ethene with butyllithium followed by its reaction with ethylene oxide. DCC coupling provided the keto ester (Scheme I).

When conventional methods[14,15] (LDA, −78 °C, *N*-phenyltriflimide) were used to generate the triflate, low yields (~30%) were usually obtained, but pure kinetic product could be isolated and purified by chromatography. Considerably higher yields were obtained with use of the Stork procedure for trapping the kinetic enolate.[16] Using

Scheme I

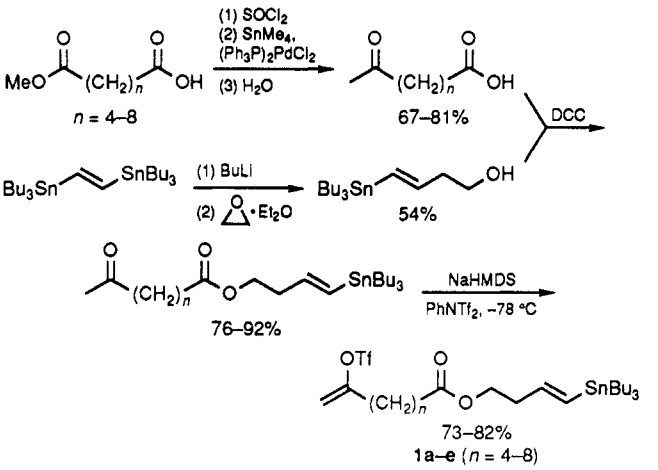
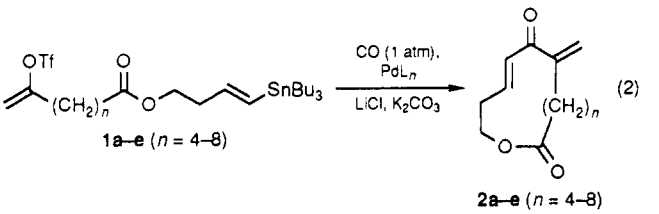


Table I



(2)

			isolated yield, %		
	n		$Pd(dba)_2$, 60 °C, THF or DMF	$Pd(Ph_3P)_4$, 90 °C, dioxane	$Pd(dppf)Cl_2$, THF, 65 °C
1a	4	**2a**	38–45		
1b	5	**2b**	33–46		47
1c	6	**2c**	35–45		60
1d	7	**2d**	44–52	59	55
1e	8	**2e**	34–39	60	

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sodium hexamethyldisilazide (NaHMDSA) and adding it rapidly to a diluted solution of keto ester and *N*-phenyl triflimide in excess (1.5–1.7 equiv) at −78 °C gave triflates containing only small amounts (<15%) of the thermodynamic enolate in yields of 73–82%.

Carbonylative Coupling Studies. Cyclization reactions with the above triflates were effected under 1 atm of carbon monoxide to give the corresponding macrocyclic keto ester (eq 2, Table I). When the reaction was run with bis(dibenzylideneacetone)palladium(0) as catalyst, in THF or DMF, only moderate yields of cyclized product were obtained. However, the use of tetrakis(triphenylphosphine)palladium(0) at 90 °C in dioxane or bis((diphenylphosphino)ferrocene)dichloropalladium at 65 °C in THF led to relatively higher yields of cyclized products. Several observations warrant comments.

The reactions were regiospecific, and neither positional nor cis–trans isomerization of the double bonds was observed. The reaction was relatively insensitive to the nature of the catalyst, although slightly higher yields were obtained with phosphine-containing complexes. The yield of cyclization was insensitive to ring size, as had been observed in the previous direct cyclization studies (eq 1). Under 1 atm of CO pressure *no* direct coupling was observed (CO insertion was fast) and the carbonylative coupling process required shorter overall reaction times than did the direct coupling (transmetalation to the acylpalladium intermediate was fast). The terminal (kinetic) triflates used were always contaminated with 10–15% of the related internal (thermodynamic) triflate, yet only the terminal triflate underwent carbonylative coupling, the internal triflate being recovered unchanged. In a separate experiment, pure internal triflate failed to cyclize under the above conditions but decomposed instead.

Polymer-Supported Catalysts. One of the major problems encountered in the synthesis of macrocyclic rings is the formation of linear oligomers,[17] and this process is one reason for the modest yields observed in Table I. One solution for this problem is the use of high-dilution techniques.[18] Another solution is "site isolation" of the catalytic sites on a polymer backbone.[19] If the catalytic sites are completely isolated from each other, then substrate molecules will not be able to react at more than one catalytic site. There are two major variables that affect site isolation: (a) the mobility of the polymer chain to which the catalyst is attached; (b) the loading density of catalyst on the support. When polystyrene is used as the polymeric support, 50% incorporation of divinylbenzene is necessary to sufficiently immobilize the polymer chains.[20] Site isolation has been achieved with catalyst loading densities of 0.14 mmol/g of polymer beads.[21]

The importance of site isolation in polymer-bound catalysts was confirmed in experiments with palladium catalysts bound to a commercial 20% cross-linked polystyrene polymer having 0.2 mmol of bound Ph_2P groups/g of polymer in the experiments listed in Table I. Virtually the same modest yields of cyclized products were obtained with the polymer-bound catalyst as with the homogeneous catalysts, indicating that site isolation had probably not been achieved. Because commercially available polymer-supported systems were ineffective, we decided to synthesize appropriate polymer-supported ligand systems.

There are available a number of methods of attaching phosphine ligands to polymers. Most of the methods require the attachment of phosphine to cross-linked polystyrene beads. We have used a different approach, in that we have synthesized monomers containing the phosphine ligand or a group readily replaced by a phosphine ligand.[22] These monomers were then copolymerized with a comonomer and a cross-linking monomer. This approach has several advantages. (1) The purity of the phosphine can be assured, just prior to its polymerization. (2) The nature of the polymer backbone (hydrophilic or hydrophobic) can be controlled by the appropriate choice of the monomer. (3) By adjustment of the ratio of the monomers, and with some knowledge of the reactivity ratios, the concentration of the phosphine-bearing monomer in the polymer can be controlled, thus assuring site isolation. (4) The degree of cross-linking can be adjusted, thereby reducing the mobility of the catalyst sites and reducing intermolecular reaction.

The ideal polymer-supported catalyst should incorporate a chelating phosphine ligand in order to minimize palladium loss through leaching. Either cross-linked polystyrene or poly(methylmethacrylate) beads are ideal supports, since the homopolymers are soluble in solvents such as tetrahydrofuran, and therefore the cross-linked beads will be compatible with these solvents, allowing access by the substrate to the catalyst site. The polymer should contain 50 mol % of a cross-linking monomer and about 2.5% of the monomer bearing the phosphine ligand, such that catalyst sites will achieve isolation. In order to optimize reactivity, it is important to maximize the surface area of the support. At the same time it is important to be able to easily separate the reaction product from the polymer support by filtration after the reaction is complete. Macroreticular beads in a size range of 50–100 μm are ideal. It is also important that the cyclization reaction is faster than the rate of diffusion of additional substrate molecules to the catalytic site.[19] The pore size must be large enough for substrate molecules to diffuse in, cyclize, and diffuse out.

Polymers containing chiral chelating phosphine prepared by copolymerization of styrene-like or acrylamide-like monomers with styrene/divinylbenzene under suspension polymerization conditions to yield 50-μm beads have been studied in these laboratories.[23] Because the palladium catalyst $(dppf)PdCl_2$ (dppf = 1,2-bis(diphenylphosphino)ferrocene) was demonstrated to be especially good for the carbonylative cyclizations, the synthesis of a vinyl monomer of dppf containing the chelating phosphine unit was examined. Vinylferrocene (r_1 = 0.1–0.2) undergoes copolymerization with styrene (r_2 = 2.5–4), the reactivity ratios ensuring isolation of the ferrocene units.[24]

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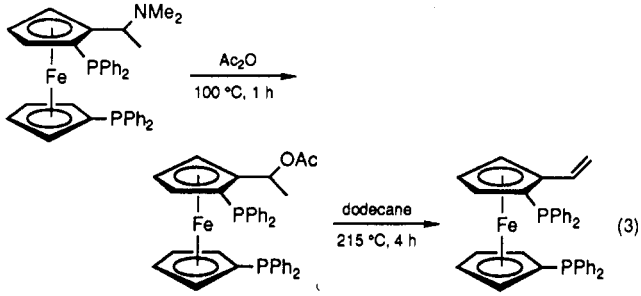
The vinyl-dppf derivative was synthesized according to literature procedures.[25-27] In a modified process, when 1-(1',2-bis(diphenylphosphino)ferrocenyl)ethyl acetate was heated in dodecane at the reflux temperature for 3.5 h, only the elimination product, vinyl-dppf, was detected by ^{31}P NMR spectroscopy. Isolation was achieved by chromatography on a silica column. Dodecane was removed by eluting the column with hexane. After the removal of dodecane was complete, vinyl-dppf was eluted with 1/10 ethyl acetate/hexane (eq 3).



(3)

The syntheses of macroreticular polymer beads in which the catalytic sites are isolated from each other requires a cross-linking density of >50%. In order to be able to accurately control the degree of cross-linking and to be able to obtain reproducible results, another copolymer, divinylbenzene (DVB), should ideally be just one isomer. However, commercial DVB consists of a mixture of about 55% of meta and para isomers of DVB, the remainder being ethylvinylbenzene. Thus, pure DVB was synthesized by following a literature procedure with use of the Wittig reaction.[28]

Macroreticular beads that incorporated a dppf group were synthesized by the terpolymerization of vinyl-dppf styrene and *p*-DVB. The synthesis of polymer beads with the desired physical characteristics is an empirical enterprise, since bead size is determined by a number of factors, including the shape of the reactor.[29] After considerable experimentation macroreticular beads having the desired particle and pore size were prepared as in eq 4. The key to proper bead size was the use of poly(vinylpyrrolidone)

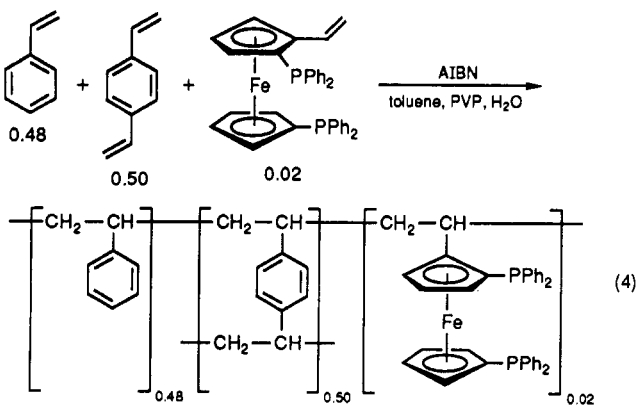


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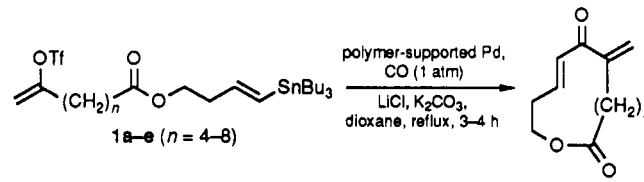
Table II



(5)

	n	ring size		isolated yield, %
1a	4	12	**2a**	0
1b	5	13	**2b**	28
1c	6	14	**2c**	78
1d	7	15	**2d**	76
1e	8	16	**2e**	70

(average molecular weight 40 000) as the suspension stabilizer.

This procedure gave 10–50-μm macromolecular beads (by microscopy) having a loading of 0.22 mmol of dppf/g of polymer by phosphorus elemental analysis.

Palladium(0) was incorporated into these polymer beads by heating together with 1 equiv of $Pd(PPh_3)_4$/equiv of polymer-bound dppf in toluene at reflux for 2 h, cooling, filtering, and washing with toluene until the washes were clear. After it was dried under vacuum (0.05 mmHg) for 20 h at room temperature, the polymer-bound catalyst was ready for use.

Carbonylative cyclization reactions of substrates **1a–e** with the polymer-bound dppf palladium catalyst (eq 5, Table II) were substantially different from those run under homogeneous conditions. While the homogeneous catalysts were insensitive to ring size, substrates **1a–e** cyclizing with roughly equivalent efficiency (40–60%), the polymer-bound catalyst failed to produce any of the 12-membered-ring compound **2a** (only decomposition products and recovered small amounts of **1a** were obtained) and gave only low yields of the 13-membered compound **2b**. In contrast the 14-, 15-, and 16-membered compounds **2c–2e** were formed in yields somewhat better (70–78%) than those obtained with the homogeneous system. In all cases, when consumption of starting material was complete, the polymer darkened, indicating a probable change in the constitution of the polymer-bound catalyst and making recycling of the catalyst unfeasible. The failure of **1a** and **1b** to undergo cyclization with the polymer-bound catalyst was unanticipated, and the reasons for this failure have not been experimentally explored. The somewhat better yields of the larger ring compounds *are* due to suppression of intermolecular reactions, as hoped. However, the multistep synthesis of the polymer-supported catalyst system will likely restrict its use to substrates for which homogeneous systems fail.

Experimental Section

Materials and Methods. Column chromatographic purifications were performed with silica gel 32-63 or 63-200. "Deactivated" silica gel was prepared by the following procedure. Silica gel was slowly added to a solution of hexane/triethylamine (1:1). The solution was stirred for several minutes and allowed to stand for 8 h. The silica gel was then isolated by filtration and air-dried (vacuum aspirator) on the filter for several minutes. The silica gel was then dried under reduced pressure as the temperature was slowly increased from 22 to 100 °C over 12 h in a vacuum oven. The temperature was maintained at 100 °C for 4 days.

NMR spectra were recorded with a Bruker AC 300P spectrometer or Bruker WP 270 spectrometer. The solvent was chloroform-*d*, except where otherwise stated. The chemical shifts

for ^1H NMR spectra (300.1 and 270 MHz) are reported in units of parts per million (δ, ppm) relative to tetramethylsilane (TMS) at 0.00 ppm by using, where possible, the residual protons in the solvent as an internal standard (benzene-d_6, 7.15; chloroform-d, 7.24) or TMS. The chemical shifts for ^{13}C NMR spectra (75.5 MHz) are reported in ppm (δ) relative to TMS at 0.0 ppm by using the chloroform signal (77.00 ppm) as an internal standard. The ^{13}C coupling assignments were determined by DEPT experiments. All ^{31}P (121.5 MHz) spectra are proton-decoupled and reported in ppm downfield from phosphoric acid (H_3PO_4, 85%) and referenced externally. High-resolution mass spectra (HRMS) were recorded at the Midwest Center for Mass Spectroscopy at the University of Nebraska. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Polymerization Procedure. Polymerization reactions were performed in a 1500-mL creased resin kettle. Stirring was maintained with use of a directed drive stirrer motor, which was a (Scientific Equipment Corp.) high-speed device bearing a stainless steel stir shaft with a Teflon cap on its end, and an Ace 8094 stainless steel agitator modified to have a 3.5-cm o.d. or an in-house-constructed agitator with three impeller blades pitched at a 45° angle. The bottom of the Ace impeller was set 3.5 cm from the bottom of the stir shaft. The Teflon cap on the stirrer shaft allowed reproducible setting of the stirrer blade height—i.e., the Teflon cap was placed resting on the bottom of the reactor flask.

Synthesis of Ferrocene Derivatives. Acetylferrocene[30] 1-ferrocenylethanol,[31] 1-ferrocenylethyl acetate,[32] *N,N*-dimethyl-1-ferrocenylethylamine,[25] *N,N*-dimethyl-1-(1′,2-bis(diphenylphosphino)ferrocenyl)ethylamine,[25] 1-(1′,2-bis(diphenylphosphino)ferrocenyl)ethyl acetate,[25] *N,N,N′,N′*-tetramethylethylenediamine,[33] and (dimethylamino)methylferrocene[25] were prepared according to literature methods. Acetylferrocene and 1-ferrocenylethanol were further purified by liquid chromatography (silica gel, 10% ethyl acetate/90% methylene chloride). 1-Ferrocenylethyl acetate was purified by recrystallization from tetrahydrofuran/pentane (1:1).

1′,2-Bis(diphenylphosphino)-1-vinylferrocene (vinyldppf). A 1000-mL round-bottomed flask was charged with 1-(1′,2-bis(diphenylphosphino)ferrocenyl)ethyl acetate (1.00 g, 1.56 mmol), dodecane (500 mL), and a large egg-shaped stirbar. A reflux condenser was attached with a gas inlet valve attached to the top. The gas inlet valve was connected to a manifold vacuum line. The solution was degassed by opening the gas inlet valve to the vacuum source (5×10^{-3} mmHg) for 20 min while the solution was rapidly stirred. The apparatus was then back-filled with argon. The portion of the flask that sat above the heating mantle was completely wrapped with glass wool. The solution was heated to the reflux temperature and maintained at a *vigorous* reflux for 2.5 h. Analysis of an aliquot by $^{31}P\{^1H\}$NMR spectroscopy indicated that all of the starting material had been consumed. The product was detected (-17.2 and 21.7 ppm, 97.1% conversion), and an unidentified resonance was also detected (-10.8 ppm, 2.9% conversion). The orange solution was cooled to room temperature with a water bath. The reaction solution was poured onto a column (7 × 17 cm) of "deactivated" silica gel/hexane. Dodecane was eluted, until the level reached the top of the silica, the elution was then continued with hexane (5000 mL). The elution solvent was then changed to hexane/triethylamine (10:1). Fractions were collected in test tubes. The volatiles were removed from the fractions containing (pure as detected by TLC) the product. A yellow crystalline powder (0.60 g, 65% yield) was obtained: R_f 0.35 (silica gel, 10:1 hexane/triethylamine); ^1H NMR δ 3.52 (br, 1 H), 3.65 (br m, 1 H), 4.12 (br m, 1 H), 4.21 (m, 2 H), 4.34 (br s, 1 H), 4.66 (br m, 1 H), 5.00 (dd, J = 11.2, 1.3 Hz, 1 H, *cis*-RC=CH_2), 5.32 (dd, J = 17.2, 1.3 Hz, 1 H, *trans*-RC=CH_2), 6.64 (ddd, J = 17.2, 11.2, and 2.1 Hz, 1 H, R-CH=C), 7.08-7.50 (m, 20 H, 20 Ar H); $^{31}P\{^1H\}$ NMR δ -17.7, -22.5. Anal. Calcd for $C_{36}H_{30}P_2Fe$: C, 74.49; H, 5.23. Found: C, 74.39; H, 5.23.

Terpolymerization of 1′,2-Bis(diphenylphosphino)-1-vinylferrocene, 1,4-Divinylbenzene (DVB), and Styrene (Typical Procedure). A solution of poly(vinylpyrrolidone) (5.14 g, average molecular weight 40 000) and water (420 mL) was degassed in the polymerization reactor by bubbling nitrogen through the stirred mixture (500 rpm) for 3 h. A degassed solution of 1′,2-bis(diphenylphosphino)-1-vinylferrocene (1.20 g, 2.06 mmol), *p*-divinylbenzene (2.68 g, 20.6 mmol), styrene (1.94 g, 18.6 mmol), and toluene (50 mL) was added to the reactor via syringe. After 10 min a solution of azobis(isobutyronitrile) (AIBN, 0.11 g) in toluene (2 mL) was added dropwise to the solution. After 5 min an oil bath at 80 °C was raised up so that the level of oil in the bath was higher than the level of the solution in the reactor. After 12 h the oil bath was lowered and stirring was stopped. Yellow polymer beads were collected by filtration. The beads were washed with water (500 mL), acetone (500 mL), tetrahydrofuran (500 mL), methanol (500 mL), and dichloromethane (500 mL) and rinsed with acetone until the rinse was clear. The beads were Soxhlet-extracted with acetone for 2.5 days and dried under reduced pressure (5×10^{-3} mmHg) at 40 °C for 24 h. A pale yellow powder (2.68 g, 46.1%) was obtained: bead size (determined by microscopy): 10–50 μm. Anal. Found: C, 89.19; H, 7.54; P, 1.35. This indicated that the loading density was 2.18×10^{-4} mol of dppf/g of polymer.

Loading of Palladium onto the Polymer-Supported DPPF. A 25-mL round-bottom flask fitted with a reflux condenser was charged with the polymer beads (400 mg, about 0.0872 mmol loading capacity) and tetrakis(triphenylphosphino)palladium (100 mg, 0.090 mmol) in toluene (7 mL). The suspension was heated at reflux for 2 h. The mixture was cooled to room temperature and filtered under argon. The polymer was washed with toluene until the rinse was clear. The beads were dried under reduced pressure (0.05 mmHg) at room temperature for 20 h. A dark yellow powder (454 mg, 98% yield) was obtained.

4-(Tri-*n*-butylstannyl)-but-3-en-1-ol. To a solution of *trans*-1,2-bis(tributylstannyl)ethene (9.79 mL, 12.37 mmol) in tetrahydrofuran (15 mL) was added *n*-butyllithium (1.6 M, 8.75 mL (hexane), 14 mmol) at -78 °C, under argon. The mixture was warmed to 0 °C and kept at that temperature for 30 min. Then it was cooled to -78 °C and an ethereal solution of ethylene oxide (9.8 mL, 1.3 M, 12.73 mmol) was added, followed by $BF_3{\cdot}OEt_2$ (1.81 g/1.56 mL, 12.73 mmol). The reaction mixture was stirred for a period of 15 min and then was allowed to reach -20 °C and was quenched with saturated sodium chloride. The two phases were separated. The aqueous phase was extracted with diethyl ether (3×). The combined organic phase was washed with saturated sodium chloride solution and dried over potassium carbonate. After removal of solvent, the residue was chromatographed (60 g of silica gel, eluent hexane/ethyl acetate (gradient, (19–2):1) which afforded a pale yellow oil (2.48 g, 54% yield): R_f 0.12 (hexane/EtOAc (9:1), silica gel); ^1H NMR δ 0.74–0.96 (m, 15 H, $(CH_2)_3$ and $(CH_3)_3$), 1.22–1.53 (m, 13 H), 2.40 (dt, J = 6.2, 6.1 Hz, 2 H, CH_2C=CSn), 3.66 (dt, J = 6.2, 6.1 Hz, 2 H, CH_2OH), 5.90 (dt, J = 18.9, 6.1 Hz, 1 H, CH=CSn), 6.05 (d, J = 19.6 Hz, 1 H, C=CHSn); ^{13}C NMR δ 8.7 (3 C, $Sn(CH_2)_3$), 13.7 (3 C, butyl $(CH_3)_3$), 27.4 (3 C, butyl $(CH_2)_3$), 29.3 (3 C, butyl $(CH_2)_3$), 41.2 (CH_2C=C), 61.5 (CH_2OH), 132.2 (Sn*C*=C), 144.8 (SnC=*C*); IR (film) ν_{max} 3330 (large), 2950 (s), 2915 (s), 2860 (s), 2840 (s), 1580 (m), 1455 (m), 1410 (w), 1370 (m), 1030 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.21; H, 9.49. Found: C, 53.17; H, 9.52.

10-Oxoundecanoic Acid (n = 8). Typical Preparation of the Keto Acid via Palladium-Catalyzed Tin Coupling Followed by Saponification. In a round-bottom flask (500 mL) fitted with a reflux condenser was charged methyl sebacoyl chloride (16.8 g, 71.6 mmol), tetramethylstannane (10.9 mL, 78.8 mmol), and bis(triphenylphosphine)palladium chloride (265 mg, 0.38 mmol) in dry dimethylformamide (200 mL). The solution was heated at reflux under argon for 24 h. The reaction mixture was poured into ice water (300 mL) and extracted with diethyl ether (300 mL × 3). The organic solution was washed with ammonium hydroxide (10%) and saturated sodium chloride solution and evaporated to dryness under reduced pressure. The residue was taken into a solution of potassium hydroxide in water/methanol (15%, 80 mL, 3:1 water/methanol) and the

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(32) Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052.
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mixture stirred at room temperature for 24 h. The solution was acidified with hydrochloric acid (10%) and extracted with ether. The ethereal fraction was washed with saturated sodium chloride solution and dried over magnesium sulfate. After removal of the solvent, the solid residue was recrystallized in benzene/hexane, which afforded white scaly crystals (11.6 g, 81.1% yield): ^{1}H NMR δ 1.27 (br s, 8 H, 4-CH_2), 1.55 (br m, 4 H, 2 CH_2), 2.11 (s, 3 H, $COCH_3$), 2.31 (t, J = 7.5 Hz, 2 H, CH_2COMe), 2.39 (t, J = 7.3 Hz, 2 H, CH_2COO), 10.8 (br, 1 H, COOH); ^{13}C NMR δ 23.7 (CH_2), 24.6 (CH_2), 28.93 (CH_2), 28.99 (CH_2), 29.03 (CH_2), 29.1 (CH_2), 29.8 ($COCH_3$), 33.9 (CH_2COO), 43.7 (CH_2COMe), 179.7 (COOH), 209.4 (COMe). These data are consistent with those reported in the literature.[11e]

6-Oxoheptanoic Acid (n = 4). This was synthesized by the procedure above with methyl adipoyl chloride and use of identical stoichiometry: ^{1}H NMR δ 1.56 (m, 4 H, 2 CH_2), 2.09 (s, 3 H, $COCH_3$), 2.31 (t, J = 7.4 Hz, 2 H, CH_2COMe), 2.41 (t, J = 7.4 Hz, 2 H, CH_2COO), 11.5 (br s, 1 H, COOH); ^{13}C NMR δ 22.97 (CH_2), 24.0 (CH_2), 29.8 ($COCH_3$), 33.7 (CH_2COOH), 43.1 (CH_2COMe), 179.4 (COOH), 208.8 (COMe). These data are consistent with those reported in the literature.[11a]

7-Oxooctanoic Acid (n = 5). This was synthesized by the procedure described above with methyl pimeloyl chloride and use of identical stoichiometry: ^{1}H NMR δ 1.35 (m, 2 H, CH_2), 1.61 (m, 4 H, 2 CH_2), 2.11 (s, 3 H, $COCH_3$), 2.30 (t, J = 7.4 Hz, 2 H, CH_2COMe), 2.40 (t, J = 7.4 Hz, 2 H, CH_2COO), 11.56 (br s, 1 H, COOH); ^{13}C NMR δ 23.3 (CH_2), 24.3 (CH_2), 24.3 (CH_2), 28.4 (CH_2), 29.9 ($COCH_3$), 33.8 (CH_2COOH), 43.3 (CH_2COMe), 179.8 (COOH), 209.2 (COMe). These data are consistent with those reported in the literature.[11b]

8-Oxononanoic Acid (n = 6). This was synthesized by the procedure described above with methyl suberoyl chloride and use of identical stoichiometry: ^{1}H NMR δ 1.29 (br m, 4 H, 2 CH_2), 1.56 (br m, 4 H, 2 CH_2), 2.09 (s, 3 H, $COCH_3$), 2.30 (t, J = 7.5 Hz, 2 H, CH_2COMe), 2.38 (t, J = 7.4 Hz, 2 H, CH_2COO), 11.2 (br s, 1 H, COOH); ^{13}C NMR δ 23.5 (CH_2), 24.4 (CH_2), 28.65 (CH_2), 28.68 (CH_2), 29.8 ($COCH_3$), 33.9 (CH_2COOH), 43.5 (CH_2COMe), 179.8 (COOH), 209.3 (COMe). These data are consistent with those reported in the literature.[11c]

9-Oxodecanoic Acid (n = 7). This was synthesized by the procedure described above with methyl azelaoyl chloride and use of identical stoichiometry: ^{1}H NMR δ 1.28 (br s, 6 H, 3 CH_2), 1.55 (m, 4 H, 2 CH_2), 2.11 (s, 3 H, $COCH_3$), 2.31 (t, J = 7.5 Hz, 2 H, CH_2COMe), 2.39 (t, J = 7.4 Hz, 2 H, CH_2COO), 10.8 (br s, 1 H, COOH); ^{13}C NMR δ 23.7 (CH_2), 24.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.8 ($COCH_3$), 33.9 (CH_2COO), 43.7 (CH_2COMe), 179.7 (COOH), 209.4 (COMe). These data are consistent with those reported in the literature.[11e]

Typical Procedure for Esterification: 4-(Tri-n-butylstannyl)-3(E)-butenyl 6-Oxoheptanoate (n = 4). To a solution of 4-(tri-n-butylstannyl)but-3-en-1-ol (1.01 g, 2.79 mmol), 6-oxoheptanoic acid (0.42 g, 2.91 mmol), and (dimethylamino)-pyridine (30 mg, 0.25 mmol, catalyst) in dry dichloromethane (20 mL) was added N,N'-dicyclohexylcarbodiimide (0.60 g, 2.91 mmol). Precipitation occurred immediately. The mixture was stirred at room temperature for 2 days. The precipitate was removed by filtration, and the filtrate was concentrated and purified by flash chromatography (silica gel, eluent hexane/ethyl acetate (10:1)), which afforded the product as a colorless oil (1.22 g, 89% yield): R_f 0.06 (silica gel, hexane/ethyl acetate (10:1)); ^{1}H NMR δ 0.72–0.95 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.21–1.60 (m, 16 H), 2.11 (s, 3 H, $COCH_3$), 2.28 (m, 2 H, CH_2COO), 2.40–2.26 (m, 4 H, CH_2C=C and CH_2COMe), 4.10 (dd, J = 6.9, 6.1 Hz, 2 H, $COOCH_2$), 5.87 (dt, J = 19.0, 6.1 Hz, 1 H, CH=CSn), 6.00 (d, J = 6.1 Hz, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.7 (3 C, butyl $(CH_3)_3$), 23.1 (CH_2), 24.4 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 29.1 (3 C, butyl $(CH_2)_3$), 29.9 ($COCH_3$), 34.0 (CH_2COO), 36.9 (CH_2CH=CH), 43.3 (CH_2COMe), 63.5 (OCH_2), 131.3 (SnC=C), 143.8 (SnC=C), 173.4 (OCO), 208.5 (CO); IR (film, KBr) ν_{max} 2955 (s), 2926 (s), 2871 (s), 2853 (s), 1736 (s, OCO), 1720 (s, CO), 1600 (m), 1463 (m), 1418 (w), 1376 (m), 1358 (m), 1173 (s), 1072 (w) cm^{-1}. Anal. Calcd for $C_{23}H_{44}O_3Sn$: C, 56.69; H, 9.10. Found: C, 56.78; H, 9.09.

4-(Tri-n-butylstannyl)-3(E)-butenyl 7-Oxooctanoate (n = 5). This compound was synthesized on the same scale as described above with use of the vinyltin alcohol and 7-oxooctanoic acid: colorless oil, 82% yield; R_f 0.089 (silica gel, hexane/ethyl acetate (10:1)); ^{1}H NMR δ 0.81–0.88 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.21–1.40 (m, 8 H), 1.40–1.65 (m, 10 H), 2.11 (s, 3 H, $COCH_3$), 2.27 (t, J = 7.5 Hz, 2 H, CH_2COO), 2.41 (m, 4 H, CH_2C=C and CH_2COMe), 4.10 (t, J = 6.9 Hz, 2 H, $COOCH_2$), 5.89 (dt, J = 19.0, 5.8 Hz, 1 H, CCH=C), 6.00 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.7 (3 C, butyl $(CH_3)_3$), 23.3 (CH_2), 24.7 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.6 (CH_2), 29.0 (3 C, butyl $(CH_2)_3$), 29.9 ($COCH_3$), 34.0 (CH_2COO), 36.9 (CH_2CH=CH), 43.4 (CH_2COMe), 63.4 ($COOCH_2$), 131.2 (SnC=C), 143.8 (SnC=C), 174.6 (OC=O), 208.8 (C=O); IR (film, KBr) ν_{max} 2955 (s), 2927 (s), 2871 (s), 2854 (s), 1736 (s, OCO), 1720 (s, CO), 1600 (w), 1463 (m), 1418 (w), 1376 (m), 1357 (m), 1170 (s), 1073 (w). Anal. Calcd for $C_{24}H_{46}O_3Sn$: C, 57.50; H, 9.25. Found: C, 57.28; H, 9.24.

4-(Tri-n-butylstannyl)-3(E)-butenyl 8-Oxononanoate (n = 6). This compound was synthesized on the same scale as described above with use of the vinyltin alcohol and 8-oxononanoic acid: colorless oil, 92% yield; R_f 0.12 (silica gel, hexane/ethyl acetate (10:1); ^{1}H NMR δ 0.78–0.95 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.23–1.35 (m, 10 H), 1.35–1.75 (m, 10 H), 2.11 (s, 3 H, $COCH_3$), 2.25 (t, J = 7.5 Hz, 2 H, CH_2COO), 2.37–2.44 (m, 4 H, CH_2C=C and CH_2COMe), 4.10 (t, J = 6.9 Hz, 2 H, $COOCH_2$), 5.87 (dt, J = 18.9, 5.7 Hz, 1 H, CH=CSn), 5.99 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.43 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 23.6 (CH_2), 24.7 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.8 (CH_2), 28.9 (CH_2), 29.0 (butyl $(CH_2)_3$), 29.8 ($COCH_3$), 34.2 (CH_2COO), 36.9 (CH_2CH=CH), 43.6 (CH_2COMe), 63.4 ($COOCH_2$), 131.2 (SnC=C), 143.8 (SnC=C), 173.6 (OC=O), 212.5 (COMe); IR (film, KBr) ν_{max} 2955 (s), 2927 (s), 2871 (s), 2854 (s), 1737 (s, OCO), 1720 (s, CO), 1600 (m), 1560 (w), 1463 (m), 1418 (w), 1376 (w), 1356 (w), 1169 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{48}O_3Sn$: C, 58.26; H, 9.32. Found: C, 58.32; H, 9.39.

4-(Tri-n-butylstannyl)-3(E)-butenyl 9-Oxodecanoate (n = 7). This compound was synthesized on the same scale as described above with use of the vinyltin alcohol and 9-oxodecanoic acid: colorless oil, 88% yield; R_f 0.68 (silica gel, hexane/ethyl acetate (3:1)); ^{1}H NMR δ 0.72–0.95 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.21–1.40 (m, 12 H), 1.40–1.62 (m, 10 H), 2.13 (s, 3 H, $COCH_3$), 2.28 (t, J = 7.5 Hz, 2 H, CH_2COO), 2.36–2.45 (m, 4 H, CH_2C=C and CH_2COMe), 4.12 (t, J = 7.0 Hz, 2 H, $COOCH_2$), 5.87 (dt, J = 18.9, 5.7 Hz, 1 H, CH=CSn), 5.99 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.7 (3 C, butyl $(CH_3)_3$), 23.7 (CH_2), 24.9 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.9 (CH_2), 29.0 (3 C, butyl $(CH_2)_3$), 29.2 (CH_2), 29.8 ($COCH_3$), 34.3 (CH_2COO), 36.9 (CH_2CH=CH), 43.7 (CH_2COMe), 63.4 ($COOCH_2$), 131.2 (C=CSn), 143.9 (C=CSn), 173.8 (OC=O), 209.2 (COMe); IR (film, KBr) ν_{max} 2960 (s), 2915 (s), 2840 (m), 1720 (s, OCO), 1700 (m, CO), 1580 (w), 1490 (w), 1140 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{50}O_3Sn$: C, 59.00; H, 9.52. Found: C, 59.13; H, 9.57.

4-(Tri-n-butylstannyl)-3(E)-butenyl 10-Oxoundecanoate (n = 8). This compound was synthesized on the same scale as described above with use of the vinyltin alcohol and 10-oxoundecanoic acid: colorless oil, 76% yield: R_f 0.248 (silica gel, hexane/ethyl acetate (10:1)); ^{1}H NMR δ 0.73–0.95 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.21–1.40 (m, 12 H), 1.40–1.62 (m, 12 H), 2.10 (s, 3 H, $COCH_3$), 2.26 (t, J = 7.6 Hz, 2 H, CH_2COO), 2.37–2.47 (m, 4 H, CH_2C=C and CH_2COMe), 4.12 (t, J = 7.0 Hz, 2 H, $COOCH_2$), 5.87 (dt, J = 18.8, 5.8 Hz, 1 H, CH=CSn), 6.00 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.3 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 22.6 (CH_2), 23.8 (CH_2), 24.9 (CH_2), 27.2 (3 C, butyl CH_2), 29.1 (3 C, butyl CH_2), 29.2 (CH_2), 29.8 ($COCH_3$), 31.6 (CH_2), 34.3 (CH_2COO), 36.9 (CH_2CH=CH), 43.3 (CH_2COMe), 43.7 (CH_2), 63.4 ($COOCH_2$), 131.2 (C=CSn), 143.9 (C=CSn), 173.7 (OC=O), 209.1 (COMe); IR (film, KBr) ν_{max} 2924 (s), 2854 (s), 1736 (s, OCO), 1720 (s, CO), 1600 (m), 1463 (w), 1418 (m), 1376 (m), 1356 (m), 1243 (s), 1168 (s), 1094 (m), 1071 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{52}O_3Sn$: C, 59.68; H, 9.65. Found: C, 59.60; H, 9.67.

Typical Triflating Procedure: 4-(Tri-n-butylstannyl)-3(E)-butenyl 9-(((Trifluoromethyl)sulfonyl)oxy)dec-9-enoate (1d, n = 7). In a flame-dried 50-mL round-bottom flask fitted with an argon inlet on a rubber septum was placed a solution of keto ester (225 mg, 0.425 mmol) and N-phenyltrifluoromethanesulfonimide (270 mg, 0.75 mmol) in tetrahydrofuran (40

mL). The mixture was cooled to −78 °C. To this solution was added sodium bis(trimethylsilyl)amide (0.45 mL, 1.0 M (THF), 0.45 mmol) by syringe. The resulting solution was stirred at −78 °C for a period of 20 min. Into the solution was introduced phosphate buffer (pH 7.0, 5%, 5 mL) to quench the reaction. The cold mixture was poured into hexane (200 mL) in a separation funnel and washed with saturated sodium chloride solution (2 × 50 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The excess of *N*-phenyltrifluoromethanesulfonimide was separated by crystallization in hexane at −20 °C. The residue was purified by flash chromatography (eluent hexane/ethyl acetate (50:1), silica gel 35 g, treated with 0.5% triethylamine in the eluent). After removal of solvent, the product (220 mg, 82% yield) was obtained as a pale yellow oil, which contained <15% of thermodynamic enolate: R_f 0.79 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 0.70–0.90 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$, 1.21–1.31 (m, 10 H, 5 CH_2), 1.38–1.57 (m, 12 H, 6 CH_2), 2.24 and 2.28 (t, J = 7.5 Hz, 2 H, CH_2COO; t, J = 7.4 Hz, 2 H, $CH_2C(OTf)$=C; overlapping), 2.42 (dt, J = 6.8, 6.1 Hz, 2 H, CH_2C=CSn), 4.08 (t, J = 6.8 Hz, 2 H, $COOCH_2$), 4.88 (d, J = 3.5 Hz, 1 H, *trans*-TfOC=CH), 5.04 (d, J = 3.5 Hz, 1 H, *cis*-TfOC=CH), 5.90 (dt, J = 19.0, 6.0 Hz, 1 H, CH=CSn), 5.97 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 24.8 (CH_2), 25.8 (CH_2), 27.2 (3 C, butyl CH_2), 28.4 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (3 C, butyl CH_2), 33.8 (CH_2), 34.2 (CH_2COO), 36.9 (CH_2CH=CH), 63.4 ($COOCH_2$), 104.0 (C=CH_2), 121.8 (O_3SCF_3), 131.2 (C=CSn), 143.9 (C=CSn), 156.9 (TfOC=C), 173.7 (OC=O); IR (film, KBr) ν_{max} 2950 (s), 2920 (s), 2860 (s), 2845 (s), 1730 (s, OCO), 1590 (m), 1460 (m), 1420 (m), 1370 (m), 1200 (m) cm^{-1}; EILRMS *m/e* (relative intensity) no molecular peak for M^+ = 661, 603 (M^+ − C_4H_9, 0.5), 455 (M^+ − Bu_4Sn, 44), 399 (36), 341 (17), 175 (32), 109 (29), 55 (100) 41 (75). Anal. Calcd for $C_{27}H_{49}F_3O_5SnS$: C, 49.02; H, 7.47. Found: C, 49.15; H, 7.49.

Minor isomer 4-(tri-*n*-butylstannyl)-3(*E*)-butenyl 9-(((trifluoromethyl)sulfonyl)oxy)-8(*Z*)-decenoate (thermodynamic triflate (minor):kinetic triflate (major) = 1:6, by ^{1}H NMR): ^{1}H NMR (200 MHz) δ 0.78–1.04 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.15–1.73 (m, 20 H), 2.02 (s, 3 H, $TfOCCH_3$), 2.08–2.20 (m, 2 H, CH_2C=COTf), 2.20–2.32 (m, 2 H, CH_2COO), 2.35–2.45 (m, 2 H, CH_2C=CSn), 4.10 (t, J = 6.9 Hz, 2 H, $COOCH_2$), 5.15 (br t, 1 H, TfOC=CH), 5.88–6.06 (d, J = 19 Hz, 1 H, CH=CSn; dt, J = 19.0, 6.0 Hz, 1 H, C=CHSn); IR (neat) ν_{max} 2950 (s), 2920 (s), 2850 (s), 1735 (s, OCO), 1600 (m), 1460 (m), 1410 (m), 1210 (s) cm^{-1}. The *Z* geometry was determined by an NOE NMR experiment.

This vinyltin triflate could be stored under argon in a refrigerator (<4 °C) without decomposition for several weeks.

4-(Tri-*n*-butylstannyl)-3(*E*)-butenyl 6-(((Trifluoromethyl)sulfonyl)oxy)hept-6-enoate (1a, *n* = 4). This compound was synthesized by the standard procedure described above with use of identical stoichiometry: pale yellow oil (73.3% yield); R_f 0.66 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 0.81–0.90 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.27 (br m, 6 H, $(CH_2)_3$), 1.30–1.70 (br m, 10 H), 2.26–2.38 (m, 4 H, $CH_2C(OTf)$=C and CH_2COO overlapping), 2.43 (dt, J = 6.3, 5.7 Hz, 2 H, CH_2C=CSn), 4.11 (t, J = 6.8 Hz, 2 H, $COOCH_2$), 4.93 (dt, J = 3.6, 1.0 Hz, 1 H, *cis*-TfOC=CH), 5.09 (d, J = 3.6 Hz, 1 H, *trans*-TfOC=CH), 5.87 (dt, J = 18.9, 5.7 Hz, 1 H, CH=CSn), 6.01 (d, J = 18.9 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 23.8 (CH_2), 25.4 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 29.0 (3 C, butyl $(CH_2)_3$), 33.5 (CH_2), 33.7 (CH_2COO), 36.9 (CH_2CH=CH), 63.6 ($CooCH_2$), 104.4 (C=CH_2), 120.8 (O_3SCF_3), 131.3 (C=CSn), 143.7 (C=CSn), 156.3 (TfOC=C), 173.1 (OC=O); IR (film, KBr) ν_{max} 2957 (s), 2927 (s), 1738 (s, OCO), 1671 (m), 1601 (m), 1471 (s), 1212 (s), 1144 (s), 1072 (m), 1018 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{43}F_3O_5SSn$: C, 46.54; H, 7.00. Found: C, 46.64; H, 7.00.

4-(Tri-*n*-butylstannyl)-3(*E*)-butenyl 7-(((Trifluoromethyl)sulfonyl)oxy)oct-7-enoate (1b, *n* = 5). This compound was synthesized by the standard procedure described above with use of identical stoichiometry: pale yellow oil(78% yield); R_f 0.64 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 0.81–0.92 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.21–1.65 (m, 18 H, CH_2), 2.28 and 2.32 (t, J = 7.5 Hz, 2 H, CH_2COO; t, J = 7.5 Hz, 2 H, CH_2C-(OTf)=C; overlapping), 2.43 (dt, J = 6.9, 5.7 Hz, 2 H, CH_2C=CSn), 4.10 (t, J = 6.9 Hz, 2 H, $COOCH_2$), 4.90 (d, J = 3.3 Hz, 1 H, *cis*-TfOC=CH), 5.06 (d, J = 3.5 Hz, 1 H, *trans*-TfOC=CH), 5.89 (dt, J = 18.9, 5.7 Hz, 1 H, CH=CSn), 6.00 (d, J = 18.9 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.7 (3 C, butyl $(CH_3)_3$), 24.5 (CH_2), 25.6 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.1 (CH_2), 29.0 (3 C, butyl CH_2), 33.6 (CH_2), 34.0 (CH_2COO), 36.8 (CH_2CH=CH), 63.5 ($COOCH_2$), 104.2 (C=CH_2), 121.3 (O_3SCF_3), 131.3 (C=CSn), 143.8 (C=CSn), 156.6 (TfOC=C), 173.4 (OC=O); IR (film, KBr) ν_{max} 2956 (s), 2927 (s), 2872 (s), 1738 (s, OCO), 1670 (m), 1600 (w), 1463 (m), 1417 (s), 1354 (w), 1247 (s), 1211 (s), 1143 (s), 1072 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{45}F_3O_5SSn$: C, 47.41; H, 7.16. Found: C, 47.58; H, 7.20.

4-(Tri-*n*-butylstannyl)-3(*E*)-butenyl 8-(((Trifluoromethyl)sulfonyl)oxy)non-8-enoate (1c, *n* = 6). This compound was synthesized by the standard procedure described above with use of identical stoichiometry: pale yellow oil (81% yield); R_f 0.62 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 0.79–0.96 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.20–1.34 (m, 12 H, 6 CH_2), 1.41–1.62 (m, 8 H, CH_2), 2.26 (t, J = 7.5 Hz, 2 H, CH_2COO), 2.31 (t, J = 7.4 Hz, 2 H, $CH_2C(OTf)$=C, overlapping with 2.26), 2.43 (dt, J = 6.8, 5.7 Hz, 2 H, CH_2C=CSn), 4.10 (t, J = 6.8 Hz, 2 H, $COOCH_2$), 4.90 (d, J = 3.5 Hz, 1 H, *cis*-TfOC=CH), 5.06 (d, J = 3.5 Hz, 1 H, *trans*-TfOC=CH), 5.82 (dt, J = 19.0, 5.7 Hz, 1 H, CH=CSn), 6.05 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 24.7 (CH_2), 25.8 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.3 (CH_2), 28.7 (CH_2), 29.0 (3 C, butyl $(CH_2)_3$), 33.7 (CH_2), 34.2 (CH_2COO), 36.9 (CH_2CH=CH), 63.5 ($COOCH_2$), 104.1 (C=CH_2), 121.6 (O_3SCF_3), 131.3 (C=CSn), 143.8 (C=CSn), 156.8 (TfOC=C), 173.6 (OC=O); IR (film, KBr) ν_{max} 2928 (s), 2855 (s), 1738 (s, C=O), 1670 (m), 1600 (w), 1464 (m), 1417 (s), 1340 (w), 1248 (s), 1211 (s), 1143 (s), 1072 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{47}F_3O_5SSn$: C, 48.23; H, 7.31. Found: C, 48.37; H, 7.35.

4-(Tri-*n*-butylstannyl)-3(*E*)-butenyl 10-(((Trifluoromethyl)sulfonyl)oxy)undec-10-enoate (1e, *n* = 8). This compound was synthesized by the standard procedure described above with use of identical stoichiometry: pale yellow oil (80% yield); R_f 0.80 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 0.74–0.92 (m, 15 H, $Sn(CH_2)_3$ and $(CH_3)_3$), 1.22–1.40 (m, 14 H, 7 CH_2), 2.26 and 2.33 (t, J = 7.5 Hz, 2 H, CH_2COO; t, J = 7.4 Hz, 2 H, $CH_2C(Otf)$=C; overlapping), 2.43 (dt, J = 6.5, 5.7 Hz, 2 H, CH_2C=CSn), 4.10 (t, J = 6.6 Hz, 2 H, $COOCH_2$), 4.90 (d, J = 3.5 Hz, 1 H, *cis*-TfOC=CH), 5.06 (d, J = 3.5 Hz, 1 H, *trans*-TfOC=CH), 5.82 (dt, J = 19.0, 5.7 Hz, 1 H, CH=CSn), 6.05 (d, J = 19.0 Hz, 1 H, C=CHSn); ^{13}C NMR δ 9.4 (3 C, $Sn(CH_2)_3$), 13.6 (3 C, butyl $(CH_3)_3$), 24.9 (CH_2), 25.9 (CH_2), 27.2 (3 C, butyl $(CH_2)_3$), 28.5 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 29.0 (3 C, butyl $(CH_2)_3$), 29.1 (CH_2), 33.8 (CH_2), 34.3 (CH_2COO), 36.9 (CH_2CH=CH), 63.4 ($COOCH_2$), 103.9 (C=CH_2), 122.1 (O_3SCF_3), 131.2 (C=CSn), 143.9 (C=CSn), 157.0 (TfOC=C), 173.7 (OC=O); IR (film, KBr) ν_{max} 2955 (s), 2928 (s), 2856 (s), 1739 (s, C=O), 1670 (w), 1600 (w), 1458 (m), 1418 (s), 1387 (m), 1340 (w), 1248 (s), 1211 (s), 1142 (s), 1072 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{51}F_3O_5SSn$: C, 49.79; H, 7.61. Found: C, 49.86; H, 7.64.

Typical Palladium-Catalyzed Ring-Closure Procedure (Homogenous Conditions). In a flame-dried, 25-mL two-necked round-bottom flask fitted with a reflux condenser, gas inlet tube, and rubber septum was placed the palladium catalyst (as indicated in the Results and Discussion, 5 mol %), lithium chloride (4 equiv relative to the starting material), and potassium carbonate (2 equiv relative to the starting material). The flask was evacuated twice and filled with argon. The vinyltin triflate (1 equiv) dissolved in an appropriate solvent (10^{-2} M concentration) was injected into the flask via a syringe. The resulting solution was saturated with carbon monoxide gas for 15 min. Then the reaction system was closed and fitted with a CO ballon (15 psi) and heated at the desired temperature for a period of 2–4 h. (The reaction was monitored by TLC and was run until the starting material had been consumed). After the mixture was cooled to room temperature, the catalyst was removed by filtration. The filtrate was concentrated by rotary evaporation under reduced pressure and taken into diethyl ether (100 mL); this solution was washed with ammonium hydroxide (10%, 2 × 25 mL) and saturated sodium chloride and dried over magnesium sulfate. After removal of solvent the residue was purified by chromatography (silica gel 15 g, eluent hexane/ethyl acetate varied from 6:1 to 10:1), which afforded the product. The characterizations of macrocyclic

compounds are in the following sections.

Typical Polymer-Supported Palladium-Catalyzed Ring-Closure Procedure (Heterogenous Conditions): (*E*)-10-Methylene-1-oxacyclopentadec-12-ene-2,11-dione (2d, *n* = 7). In a flame-dried, 25-mL, two-necked round-bottom flask fitted with a reflux condenser, gas inlet tube, and rubber septum was placed the polymer-supported palladium catalyst (80 mg), lithium chloride (35 mg, 0.82 mmol), and potassium carbonate (30 mg, 0.22 mmol). The flask was evacuated twice and filled with argon. The triflate **1d** (90.9 mg, 0.14 mmol) dissolved in dioxane (6 mL) was injected into the flask via a syringe. The resulting suspension was purged with carbon monoxide gas for 20 min. Then the reaction system was closed, fitted with a CO ballon, and heated at reflux for 3 h. The reaction was monitored by TLC. After it was cooled to room temperature, the suspension was filtered to remove the catalyst. The filtrate was concentrated under reduced pressure and taken into diethyl ether (100 mL); this solution was washed with ammonium hydroxide (10%, 2 × 25 mL) and saturated sodium chloride and dried over magnesium sulfate. After removal of solvent the residue was purified by chromatography (silica gel 15 g, eluent hexane/ethyl acetate (7:1)), which afforded the product as a colorless oil (26 mg, 76%): R_f 0.23 (silica gel, hexane/ethyl acetate (5:1)); ^{1}H NMR δ 1.14–1.40 (m, 8 H), 1.45–1.52 (m, 2 H), 2.25 (t, J = 6.6 Hz, 2 H, $CH_2C(CO)$=C), 2.38 (t, J = 6.1 Hz, 2 H, CH_2COO), 2.59 (dtd, J = 5.8, 5.6, 1.2 Hz, 2 H, CH_2C=CCO), 4.23 (t, J = 5.6 Hz, 2 H, $COOCH_2$), 5.44 (d, J = 1.0 Hz, 1 H, C=CH_2), 5.57 (d, J = 1.0 Hz, 1 H, C=CH_2), 6.46 (dt, J = 15.5, 1.2 Hz, 1 H, C=CHCO), 6.80 (dt, J = 15.5, 7.1 Hz, 1 H, CH=CCO); ^{13}C NMR δ 24.8 (CH_2), 26.6 (CH_2), 27.0 (CH_2), 27.4 (CH_2), 27.7 (CH_2), 31.8 (CH_2), 32.7 (CH_2), 34.5 (CH_2COO), 62.1 ($COOCH_2$), 121.1 (C=CH_2), 130.6 (C=CCO), 145.2 (*C*=CCO), 149.8 (O=*C*C=CH_2), 173.6 (OC=O), 194.9 (C=O); IR (neat) ν_{max} 3080 (w), 2955 (s), 2920 (s), 2840 (s), 1735 (s), 1670 (m), 1650 (m), 1620 (m), 1255 (m) cm^{-1}; HRMS m/e 250.1568 ($C_{15}H_{22}O_3$ requires 250.1563).

(*E*)-8-Methylene-1-oxacyclotridec-10-ene-2,9-dione (2b, *n* = 5). This compound was prepared by the procedure with use of the identical stoichiometry described above in 28% yield: colorless oil; R_f 0.21 (silica gel, hexane/ethyl acetate (5:1); ^{1}H NMR δ 1.22–1.35 (m, 4 H, CH_2), 1.60 (m, 2 H, CH_2), 2.28 (m, 2 H, $CH_2C(CO)$=C), 2.38 (t, J = 5.8 Hz, 2 H, CH_2COO), 2.62 (dtd, J = 6.0, 5.8, 1.3 Hz, 2 H, CH_2C=CCO), 4.36 (t, J = 5.8 Hz, 2 H, $COOCH_2$), 5.31 (dt, J = 1.2, 1.1 Hz, 1 H, C=CH_2), 5.39 (d, J = 1.2 Hz, 1 H, C=CH_2), 6.31 (dt, J = 15.7, 1.2 Hz, 1 H, C=CHCO), 6.73 (dt, J = 15.7, 6.9 Hz, 1 H, CH=CCO); ^{13}C NMR δ 24.4 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 31.9 (CH_2), 33.5 (CH_2), 33.7 (CH_2COO), 61.1 ($COOCH_2$), 119.1 (C=CH_2), 132.8 (C=CCO), 146.2 (*C*=CCO), 148.1 (O=*C*C=CH_2), 173.4 (OC=O), 196.8 (C=O); IR (neat) ν_{max} 2927 (s), 2856 (s), 1732 (s), 1681 (m), 1658 (s), 1633 (m), 1462 (m), 1247 (m), 1210 (s), 1145 (m) cm^{-1}; HRMS m/e 222.1264 ($C_{13}H_{18}O_3$ requires 222.1251).

(*E*)-9-Methylene-1-oxacyclotetradec-11-ene-2,10-dione (2c, *n* = 6). This compound was prepared by the procedure with use of the identical stoichiometry described above in 78% yield: colorless oil; R_f 0.31 (silica gel, hexane/ethyl acetate (5:1); ^{1}H NMR δ 1.10–1.30 (m, 4 H, 2 CH_2), 1.30–1.42 (m, 2 H, CH_2), 1.52–1.68 (m, 2 H, CH_2), 2.29 (ddd, J = 7.4, 5.2, 2.2 Hz, 2 H, $CH_2C(CO)$=C), 2.38 (t, J = 6.6 Hz, 2 H, CH32COO), 2.57 (dtd, J = 5.9, 5.4, 1.2 Hz, 2 H, CH_2C=CCO), 4.26 (t, J = 5.6 Hz, 2 H, $COOCH_2$), 5.40 (d, J = 1.2 Hz, 1 H, C=CH_2), 5.57 (d, J = 1.1 Hz, 1 H, C=CH_2), 6.41 (dt, J = 15.7, 1.2 Hz, 1 H, C=CHCO), 6.82 (dt, J = 15.7, 6.9 Hz, 1 H, CH=CCO); ^{13}C NMR δ 24.1 (CH_2), 26.8 (CH_2), 27.4 (CH_2), 27.9 (CH_2), 31.8 (CH_2), 32.6 (CH_2), 33.8 (CH_2COO), 61.6 ($COOCH_2$), 120.9 (C=CH_2), 130.5 (C=CCO), 145.2 (*C*=CCO), 149.3 (O=C*C*=CH_2), 173.4 (OC=O), 195.1 (C=O); IR (neat) ν_{max} 3082 (w), 2928 (s), 2857 (s), 1736 (s), 1676 (s), 1654 (s), 1624 (s), 1249 (s), 1152 (s) cm^{-1}; HRMS m/e 236.1407 ($C_{14}H_{20}O_3$ requires 236.1413).

(*E*)-11-Methylene-1-oxacyclohexadec-13-ene-2,12-dione (2e, *n* = 8). This compound was prepared by the procedure with use of the identical stoichiometry described above in 70% yield: colorless oil; R_f 0.20 (silica gel, hexane/ethyl acetate (5:1); ^{1}H NMR δ 1.07–1.59 (m, 12 H, 6 CH_2), 2.27 (t, J = 6.4 Hz, 2 H, $CH_2C(CO)$=C), 2.42 (t, J = 6.3 Hz, 2 H, CH_2COO), 2.60 (ddt, J = 6.4, 5.8, 1.3 Hz, 2 H, CH_2C=CCO), 4.24 (t, J = 5.4 Hz, 2 H, $COOCH_2$), 5.59 (d, J = 0.9 Hz, 1 H, C=CH_2), 5.67 (s, 1 H, C=CH_2), 6.47 (dt, J = 15.7, 1.3 Hz, 1 H, C=CHCO), 6.80 (dt, J = 15.7, 6.9 Hz, 1 H, CH=CCO); ^{13}C NMR δ 25.1 (CH_2), 26.5 (CH_2), 27.2 (CH_2), 27.5 (CH_2), 27.7 (CH_2), 27.8 (CH_2), 31.8 (2 C), 34.7 (CH_2COO), 62.4 ($COOCH_2$), 122.9 (C=CH_2), 129.8 (C=CCO), 144.9 (*C*=CCO), 149.7 (O=C*C*=CH_2), 173.9 (OC=O), 194.3 (C=O); IR (neat) ν_{max} 2929 (s), 2857 (s), 1736 (s), 1671 (m), 1619 (m), 1236 (m), 1211 (s) cm^{-1}; HRMS m/e 264.1726 ($C_{16}H_{24}O_3$ requires 264.1726).

(*E*)-7-Methylene-1-oxacyclotridec-9-ene-2,8-dione (2a, *n* = 4). This compound was prepared by the homogeneous catalytic procedure described above with use of $Pd(dba)_2$ (8 mg, 0.014 mmol), **1a** (190 mg, 0.307 mmol), and lithium chloride (70 mg, 1.65 mmol) in DMF (33 mL) heated at 60 °C for 1.5 h to give colorless needles as the product (27 mg, 42% yield): mp 56.2–57.5 °C; R_f 0.21 (silica gel, hexane/ethyl acetate (5:1); ^{1}H NMR δ 1.20–1.45 (m, 2 H, CH_2), 1.55–1.74 (m, 2 H, CH_2), 2.33–2.43 (m, 4 H, $CH_2C(CO)$=C and CH_2COO overlap), 2.48 (m, 2 H, CH_2C=CCO), 4.29 (t, J = 5.5 Hz, 2 H, $COOCH_2$), 5.23 (d, J = 1.6 Hz, 1 H, C=CH_2), 5.68 (d, J = 1.6 Hz, 1 H, C=CH_2), 6.51 (m, 2 H, C=CHCO and CH=CCO); ^{13}C NMR δ 24.2 (CH_2), 26.5 (CH_2), 31.9 (CH_2COO), 32.3 (CC=CH_2), 32.8 (CC=CCO), 60.8 ($COOCH_2$), 120.8 (C=CH_2), 134.1 (C=CCO), 140.4 (*C*=CCO), 148.3 (C=CH_2), 172.9 (OC=O), 195.1 (C=O); IR (KBr) ν_{max} 2937 (s), 2899 (m), 1731 (s), 1633 (m), 1378 (m), 1253 (m), 1146 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.12; H, 7.77.

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