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[10] Abbreviations: 9-BBN = 9-borabicyclo[3.3.1]nonane; DDQ = 2,3-dichloro-5,6-dicyanoquinone; DIBAL-H = diisobutylaluminum hydride; DMAP = 4-dimethylaminopyridine; DMPM = 3,4-dimethoxybenzyl; DMS = dimethyl sulfide; DMSO = dimethyl sulfoxide; HMDS = hexamethyldisilazane; NMO = 4-methylmorpholine *N*-oxide; PMB = *para*-methoxybenzyl; TAS-F = tris(dimethylamino)sulfonium difluorotrimethylsilicate; TBAF = tetrabutylammonium fluoride; TBS = *tert*-butyldimethylsilyl; TES = triethylsilyl; TFA = trifluoroacetic acid; TMS = trimethylsilyl.
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Selective Hydrovinylation of Styrene in a Membrane Reactor: Use of Carbosilane Dendrimers with Hemilabile P,O Ligands**

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Despite the numerous advantages of homogeneous catalysis, a major drawback remains in the need for efficient catalyst recovery. For many catalytic applications seen today, the finding of an elegant and convenient solution to this problem had been crucial for their commercialization. Catalyst recovery also becomes increasingly important in fine chemicals production when sophisticated ligands are used, whose cost often exceeds that of the noble metal used.

The use of dendritic materials is currently generating enormous attention in a number of areas in science and

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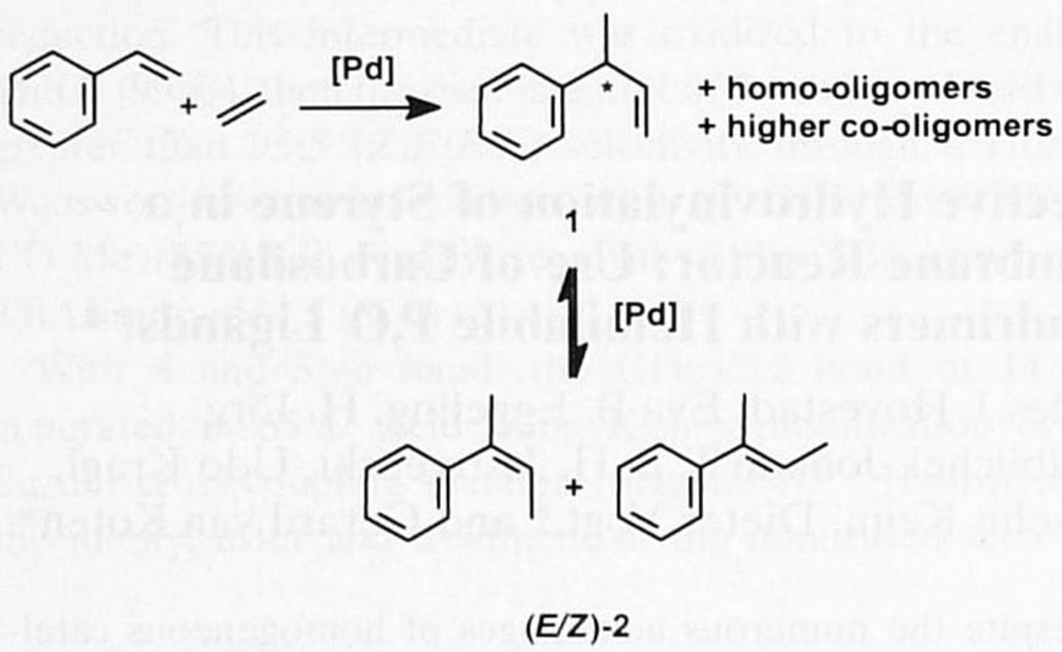
technology.[1–4] This includes transition metal containing dendrimers[3] and their use in catalysis.[5] Earlier we presented a carbosilane dendrimer decorated with 12 organonickel groupings as an active catalyst for the Kharash addition of CCl_4 to alkenes.[4] Both the well defined structure and the possibility of attaching a large number of active sites with respect to the total molecular weight make these dendritic materials especially interesting for catalyst immobilization.

Hydrovinylation of olefins[6] provides an easy access to building blocks for fine chemicals.[7] Recently we reported the first asymmetric hydrovinylation with a ligand bearing a stereogenic phosphorus atom. Enantioselectivities of up to 86% *ee* at room temperature were achieved.[8] In the hydrovinylation of styrene (Scheme 1) high activity and selectivity

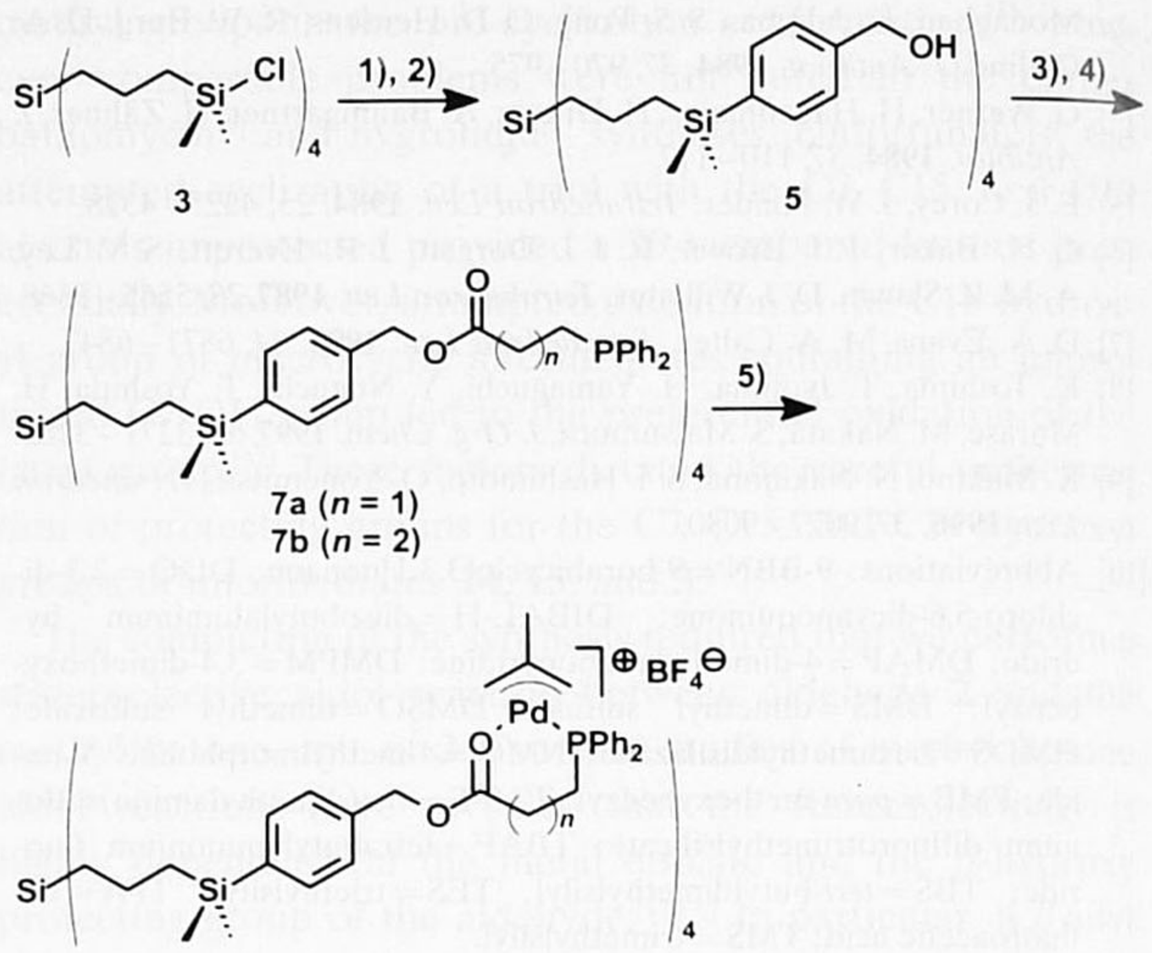


Scheme 1. Hydrovinylation of styrene and side reactions.

was observed with phosphanylcarboxylic acid derivatives.[9] However, isomerization of the chiral product 3-phenylbut-1-ene (**1**) to internal achiral olefins (*E*/*Z*)-**2** takes place at higher conversions. Therefore, it would be useful to run the reaction continuously at lower conversion.

Herein we report on the synthesis of dendritic carbosilanes functionalized with various ω-diphenylphosphanylcarboxylic acid ester end groups. These dendritic hemilabile ligands were applied successfully in the palladium-catalyzed hydrovinylation of styrene. The new dendritic Pd-catalysts derived from hemilabile P,O ligands are stable under the reaction conditions, whereas similar complexes of monodentate ligands are susceptible to decomposition, namely to the formation of palladium black. For the first time the hydrovinylation was carried out continuously in a pressure membrane reactor using a nanofiltration membrane, which gave rise to the selective formation of the desired, chiral 3-phenylbut-1-ene (**1**).

In order to obtain a functionalized dendrimer suitable for catalysis in the hydrovinylation of styrene we coupled the chlorosilane G_0-$SiMe_2Cl$ **3** with a protected linker group, 4-bromobenzyl-*tert*-butyldimethylsilyl ether (Scheme 2). Lithiation with *t*BuLi followed by reaction with **3** afforded **4** in 89% yield. Desilylation of **4** afforded the dendritic polyol **5** in 74% yield. Coupling of **5** with the phosphanoxycarboxylic acid chlorides $ClC(O)(CH_2)_nCH_2P(O)Ph_2$ ($n=1,2$) afforded compounds **6a** and **6b**. The model compounds $PhCH_2O$-$C(O)(CH_2)_nCH_2P(O)Ph_2$ **8a** ($n=1$) and **8b** ($n=2$) were prepared in high yields in an analogous manner by coupling the corresponding acid chlorides with benzylic alcohol.[10] The



Scheme 2. Synthesis of the functionalized carbosilane dendrimers. 1) $LiC_6H_4CH_2OSiMe_2(t\mathrm{Bu})$, Et_2O, $-20\,^\circ C$; 2) $Et_3N\cdot 3HF$, THF, 17 h; 3) $Ph_2P(O)CH_2(CH_2)_nC(O)Cl$, 4-dimethylaminopyridine (DMAP), DMF, RT; 4) $HSiCl_3$, NEt_3, benzene, reflux, 17 h; 5) $[(\eta^3\text{-}C_4H_7)Pd(cod)]BF_4$, CH_2Cl_2, $0\,^\circ C$, 1 h.

dendritic phosphane oxides **6a** and **6b** and the model compounds **8a** and **8b** were converted into the phosphane compounds **7a** and **7b** and **9a** and **9b**, respectively by reduction with trichlorosilane.[11] The catalysts were prepared in situ by treatment of the ligands with equimolar amounts of $[(\eta^3\text{-}C_4H_7)Pd(cod)]BF_4$ (cod = 1,5-cyclooctadiene).

High selectivity to the codimers was observed when the resulting catalysts were applied in batch reactions (Table 1).

Table 1. Hydrovinylation of styrene: comparison of dendritic ligands and model compounds.[a]

Entry	Ligand	Conv. [%][b]	Yield [%][c]	$S_{(1+2)}$ [%][d]	$S_{(1)}$ [%][e]
1	G_0-$(CH_2)_2PPh_2$ (**7a**)	68.1	56.8	97.1	85.8
2	$C_6H_5CH_2OCO(CH_2)_2PPh_2$ (**9a**)	96.9	49.5	90.7	56.4
3	G_0-$(CH_2)_3PPh_2$ (**7b**)	99.9	0.2	91.5	4.7
4	G_0-$(CH_2)_3PPh_2$ (**7b**)	3.4[f]	3.2	95.0	99.9
5	$C_6H_5CH_2OCO(CH_2)_3PPh_2$ (**9b**)	99.9[f]	4.4	93.4	0.2
6	G_0-$(CH_2)_3PPh_2$ (**7b**)[g]	8.1	7.6	96.3	98.3

[a] Conditions: T = room temperature; reaction time = 17 h; initial pressure 30 bar; P/Pd = 1; styrene/Pd = 500–1000, CH_2Cl_2 (20 mL), styrene (4 mL; 34.8 mmol). [b] Conversion of styrene. [c] Yield of **1**. [d] $S_{(1+2)}$ = [(yield (**1**) + yield (**2**))/conv.] × 100. [e] $S_{(1)}$ = [(yield (**1**)/(yield (**1**) + yield (**2**))] × 100. [f] t = 3 h. [g] Continuous run for t = 9h, for the conditions see Figure 1.

The model compounds $PhCH_2OC(O)(CH_2)_nCH_2PPh_2$ **9a** ($n=1$) and **9b** ($n=2$) showed higher activity than the corresponding G_0 dendritic phosphanyl esters **7a** ($n=1$) and **7b** ($n=2$) (entries 2 and 5 versus entries 1 and 4). The catalysts become more active as the Pd-P,O chelate ring increases in size from the six-membered ($n=1$) to the seven-membered ring ($n=2$), as a consequence of the decreased stability of the hemilabile chelate.

Complete conversion and almost complete isomerization of 3-phenylbut-1-ene (**1**) into the *E*/*Z* mixture of achiral

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2-phenylbut-2-ene ((*E*/*Z*)-**2**) was observed within 17 h for the ligands derived from diphenylphosphanylbutyric acid **7b** and **9b** ($n=2$) (entries 3 and 5 in Table 1). However, as the isomerization is a consecutive reaction that occurs only at considerably high conversion with the phosphanylcarboxylic acid ester type of ligands, it can be suppressed efficiently by limiting the conversion (entry 4 in Table 1).

Therefore the next step was to run the catalysis in a continuous high-pressure membrane reactor with the new dendritic phosphane – Pd catalysts derived from **7a** and **7b**. In preceding experiments the retention of the dendritic model compound G_0-Si(Me)$_2$(*t*Bu) **4** in the membrane reactor was determined to be 85 %. Although this retention is still far from being sufficient for practical purposes, the results under catalytic conditions with the dendritic Pd-catalyst derived from ligand G_0-$(CH_2)_3PPh_2$ **7b** look very promising (entry 6 in Table 1, Figure 1). It should be noted also that this catalyst is already much larger ($M_W = 2867.97\ g\,mol^{-1}$) than **4** ($M_W = 1314.62\ g\,mol^{-1}$).

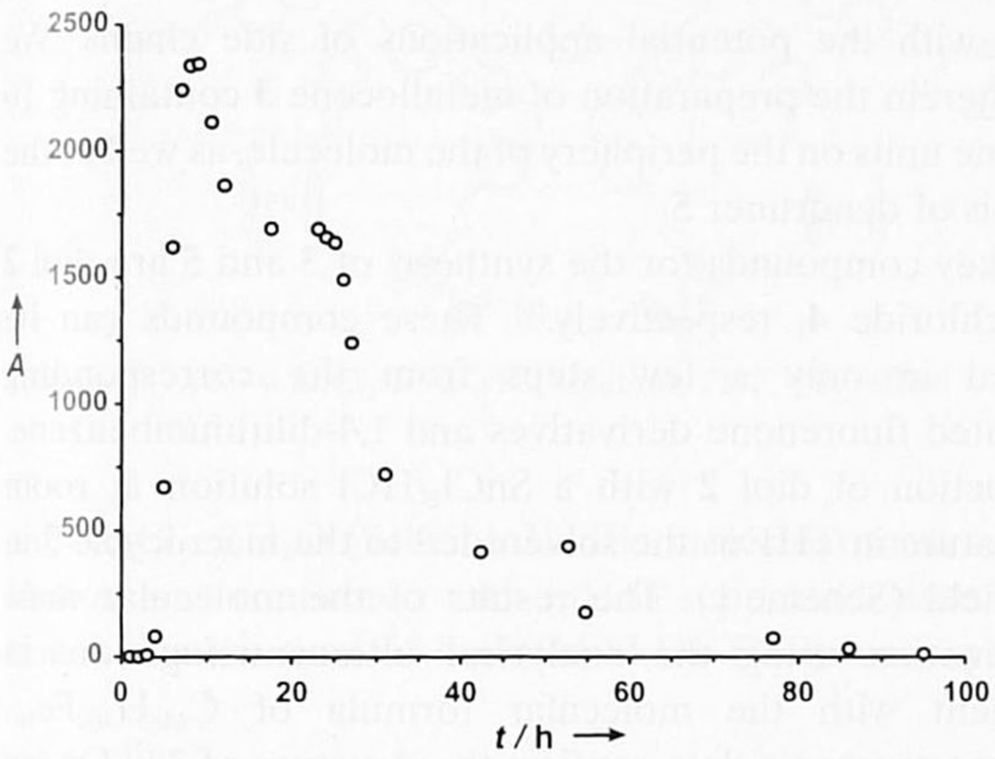

Figure 1. Continuous hydrovinylation of styrene in a membrane reactor using dendrimer **7b**. Conditions: $T = 23\,^{\circ}C$, $p = 30$ bar, 0.05 mmol Pd, P/Pd = 1, flow rates: ethene solution 2.5 mL h^{-1} (10 M), styrene solution 2.5 mL h^{-1} (1.8 M), $\tau = 4$ h, MPF-60 NF membrane (Koch Int., Düsseldorf, Germany). A = space time yield [mg L^{-1}h^{-1}].

It takes about 9 h before the system reaches its maximum productivity of 2.3 g L^{-1} h^{-1}.[12] It can clearly be seen that the catalyst is washed out of the reactor, assuming that the decreased activity correlates with a lower concentration of the dendritic G_0-Pd_4 catalyst. This decrease is accelerated most probably by the formation of small amounts of Pd (black) on the membrane surface, which can be seen after reaction.

Though the retention of the G_0 dendrimer is modest, the desired 3-phenylbut-1-ene (**1**) was produced over a period of 80 h. Most important is the observation that hardly any isomerization or other side products could be detected in the product solution (entry 6 in Table 1). Under these conditions a highly selective conversion is achieved by using a dendritic G_0–Pd_4 catalyst and a continuous reaction mode, though the yields are quite low so far. It can be expected that the dendritic G_1–Pd_{12} catalyst derived from the next generation of ligands (G_1-$(CH_2)_3PPh_2)_{12}$ will already allow sufficient hold back by a nanofiltration membrane to give efficient catalyst immobilization.

Experimental Section

Preparation of the cationic allyl-Pd-phosphane complexes: A solution of 1.00 equivalent of the phosphorus P,O ligand (0.05 mmol) in CH_2Cl_2 was added to a solution of 0.05 mmol of [(η^3-C_4H_7)Pd(cod)]BF_4[13] in CH_2Cl_2. After stirring the mixture for 60 min at 0 °C the resulting solution was used for catalysis.

Hydrovinylation

Batch reaction: The cold catalyst solution (0.05 mmol of [(η^3-C_4H_7)Pd(P,O)]BF_4 in 20 mL of CH_2Cl_2) was transferred into a 75-mL stainless steel autoclave by a syringe with a stainless steal cannula. The autoclave was cooled in an ice bath. Chilled styrene (4 mL, 34.8 mmol) was added and the autoclave was pressurized with ethylene (30 bar). After the reaction the autoclave was slowly vented, the reaction mixture was separated from the catalyst, and higher oligomers were purified by flash chromatography on basic alumina. The products were analyzed by gas chromatography.

Continuous catalysis: The membrane (MPF-60 NF membrane, Koch Int., Düsseldorf, Germany), stored in ethanol, was rinsed with acetone and carefully transferred into the membrane reactor. After the membrane had been thoroughly flushed by several 100 mL portions of CH_2Cl_2, the reactants (ethylene solution 1.8 M in CH_2Cl_2, flow rate 2.5 mL h^{-1}; styrene solution 10 M in CH_2Cl_2, flow rate 2.5 mL h^{-1}) were pumped through the reactor. The catalyst solution (0.05 mmol of [(η^3-C_4H_7)Pd(P,O)]BF_4 in 2 mL of CH_2Cl_2) was injected through an HPLC injection valve. Samples of the outcoming product solution were taken continuously and analyzed by gas chromatography.

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[10] The structure of the novel functionalized dendrimers were confirmed by elemental microanalysis, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, and FAB-MS.

[11] The compounds were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, FAB-MS, and elemental microanalysis. Elemental microanalysis of **7a** did not give satisfying results because of its air sensitivity.

[12] There is also a significant induction period in the batch reactions, but this is much shorter than that obtained here. As the catalyst is fed into the reactor together with the styrene, complexes other than that initially present in the batch reactions could be formed. This is presently under investigation.

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Self-Assembly of Quinodimethanes through Covalent Bonds: A Novel Principle for the Synthesis of Functional Macrocycles**

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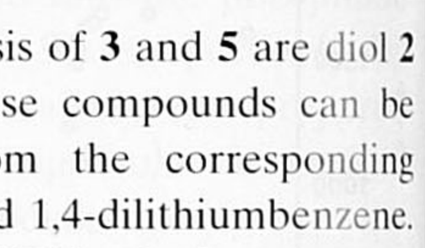
Dedicated to Professor Fritz Vögtle on the occasion of his 60th birthday

The development of methods for the synthesis of very large molecules such as dendrimers, supramolecules, and nanostructures with specific functions has increasingly become the center of attention in recent years.[1, 2] We have developed a synthetic strategy which is based on a directed tetramerization of basic building blocks in the final synthetic step.[3] With this method it is possible to obtain large and uniform molecular structures in one step from small molecules.

We could recently demonstrate that the quinodimethane derivative **1** assembles itself to a spherical cyclic tetramer in high yield.[3, 4] This spontaneous self-assembly process is driven by the four weak C_{sp^3}–C_{sp^3} bonds between the fluorene units that are formed during the tetramerization, and also by the *gauche* arrangement of these units to one another.[3, 5] Furthermore, these products have a remarkable property: Upon addition of energy they undergo a reversible color change to blue-violet as the reverse reaction to form the quinodimethane units occurs to a certain extent.[3]


1

We have tested this synthetic strategy towards the construction of highly branched systems as well as multifunctional metallocenes, which combine the reversible color change with the potential applications of side chains. We report herein the preparation of metallocene **3** containing 16 ferrocene units on the periphery of the molecule, as well as the synthesis of dendrimer **5**.

The key compounds for the synthesis of **3** and **5** are diol **2** and dichloride **4**, respectively.[6] These compounds can be obtained in only a few steps from the corresponding substituted fluorenone derivatives and 1,4-dilithiumbenzene.

Reduction of diol **2** with a $SnCl_2$/HCl solution at room temperature in THF as the solvent led to the macrocycle **3** in 82% yield (Scheme 1). The results of the molecular mass determination using the analytical ultracentrifuge are in agreement with the molecular formula of $C_{448}H_{400}Fe_{16}$. NMR spectroscopic data confirm the structure of **3**.[7] Owing to the S_4 symmetry of the molecular conformation, the ^{13}C NMR spectrum of **3** shows two characteristic signals at $\delta = 65.45$ and 65.24 for the C9 atoms of the fluorene units. Important information about the constitution of the macrocycle can be obtained from the ^{1}H NMR spectrum, which shows two signals for the protons of the inner phenyl rings at $\delta = 8.70$ and 8.26 (broad doublets) and two singlets each at $\delta = 5.93/5.90$ and 7.85/7.72.[8] Because of the S_4 symmetry of the molecule, the protons on the unsubstituted Cp ring of the ferrocenyl groups show up as four singlets at $\delta = 4.09$, 4.07, 3.98, and 3.97.

It was determined by cyclovoltammetry that all ferrocene units of **3** are reversibly oxidized at $E_{1/2} = 0.49$ V.[9] A redox splitting of consecutive electron transfer processes was not observed. The number of electrons transferred per molecule of **3** was determined by addition of $[(\eta^6\text{-}C_6H_6)_2Cr]$ in a ratio of 1:16 and comparison of the respective peak currents, which showed an approximate ratio of 1:1. The deviation in the peak currents is caused by the different diffusion coefficients of the two molecules, which result from the differences in size.

The principle of the synthesis of **3** was applied towards the preparation of **5**. In this case, the synthesis started from dichloride **4**, which afforded **5** in 63% yield upon reaction

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