Highly Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by Chiral Jacobsen's Catalyst Immobilized on Phenoxy-Modified Zirconium Poly(syrene-phenylvinylphosphonate)phosphate

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Abstract: Chiral Jacobsen's catalyst was axially immobilized onto phenoxy-modified zirconium poly(styrene-phenylvinylphosphonate)phosphate (ZPS-PVPA). The immobilized catalysts show comparable *ee* values for asymmetric epoxidation of styrene and much higher *ee* values for α -methylstyrene (73.7% *vs.* 54.0%) and indene (99.9% *vs.* 65.0%) than the homogeneous Jacobsen's catalyst. Moreover, the assynthesized catalysts are relatively stable and can be recycled at least five times without significant loss of activity and enantioselectivity. A point worth emphasizing is that the heterogeneous catalysts afforded remarkable increases of conversion and *ee* values in

the absence of expensive O-coordinating axial bases for the asymmetric epoxidation of olefins, especially for the epoxidation of α -methylstyrene (conversion: from 24.3% to 99.9%; *ee*: from 29.4% to 73.7%), which may overcome the last obstacle for the potential industry application of chiral Jacobsen's catalyst.

Keywords: asymmetric epoxidation of unfunctionalized olefins; axially coordinated immobilization; chiral Jacobsen's catalyst; phenoxy-modified support; zirconium poly(styrene-phenylvinylphosphonate)phosphate

Introduction

The importance of chiral building blocks, such as optically active epoxides, for pharmaceutics and agrochemical synthesis accounts for the impressive amount of papers published on homogeneous Jacobsen-type complexes in recent years.^[1] However, such catalysts are not easily recovered for reuse or recycle. Consequently, the last decades have witnessed an intense research effort to heterogenize chiral Jacobsentype salen Mn(III) complexes on supports^[2] in an attempt to make them recyclable and to enhance their stability, activity, and selectivity. Unfortunately, despite their excellent performance in easy separation, the heterogeneous catalysts often suffer from decreased catalytic efficiency, which is likely due to the leaching of salen Mn(III) complexes during reaction, and/or the inaccessibility of the reagents to the reactive centers^[3] as well as poor performance in recycles. Besides, almost all the asymmetric epoxidation reactions^[4] catalyzed by heterogeneous Mn(III) salen complexes were in need of excess and expensive additives as axial bases that made them insignificant for industry applications.

Inorganic-organic hybrid materials have been a topical object of a lot of studies because of their combining properties of the inorganic and organic components.^[5] These kinds of materials have the advantage of possessing a uniform distribution of functional organic groups within their framework, which allows us to tailor their density, chemical reactivity, and thermal stability. A large number of hybrid materials with various chemical compositions and organic groups have been well-documented, showing interesting properties,^[6] and their applications as catalysts and supports are emerging, especially in the application of catalyst



support for heterogenizing salen Mn(III) complexes. Our research has, for many years, been concerned with metal phosphonate chemistry for catalysts and catalyst supports.^[7] Recently, we have reported the chiral salen Mn(III) complex axially immobilized on diamine- or sulfonic groups-modified ZSPP and their catalytic epoxidation of styrene, which performed high conversion, enantioselectivity and reusability. We have also reported the chiral salen Mn(III) complex axially immobilized on diamine- or polyamine-modified ZPS-PVPA and their use in catalytic epoxidation, which exhibited great activity and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins. Especially, in the epoxidation of α -methylstyrene, both the conversion and enantiometric excess could exceed 99%. Furthermore, the immobilized catalyst could be reused at least ten times without significant loss of activity and enantioselectivity, but excess and expensive addititives as axial bases are still required to improve the catalytic activity of immobilized catalysts.

Herein, we extend our attempts to heterogenize chiral Jacobsen's catalyst which was axially immobilized on phenoxy-modified ZPS-PVPA in which inorganic/organic molar ratio and the framework of the organic-inorganic hybrid ZPS-PVPA can be easily designed and assembled to generate caves, holes, pores, micropores, channels and secondary channels with various sizes and shapes by appropriate modification process of the polystyrene part. In addition to these merits, the surface of the supports and the caves, holes, pores, micropores, channels in the supports may provide microenvironment effects different from either pure polystyrene or inorganic supports on catalytic performance for heterogeneous asymmetric epoxidation.

Results and Discussion

In conjunction with ongoing work in our laboratory on the heterogenization of salen Mn(III) complexes, in this work, chiral salen Mn(III) was axially immobilized onto phenoxy-modified zirconium poly(styrenephenylvinylphosphonate)phosphate by the phenoxy groups^[7b,8,9]. As illustrated in Scheme 1 and Scheme 2, the chiral homogeneous catalyst salen Mn(III) was



Scheme 1. Synthetic route for the support.

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Scheme 2. Synthetic route for the supported catalyst.

synthesized according to the standard literature procedures.^[1]

The immobilized catalysts were characterized by FT-IR, DR UV-Vis, AAS, XPS, SEM, and TEM, which evidenced the effective salen ligand and salen Mn heterogenization (see Supporting Information). FT-IR spectra and the DR UV-Vis spectra of catalysts of **1a-1d** matched well with the expected chemical structure of the salen Mn(III) complex. The presence of the characteristic imine band at 1630 cm⁻¹ in the FT-IR spectra and the broad bands at near 250, 320 and 420 nm in the diffusion reflection UV-Vis spectra confirmed the successful anchoring of the chiral Jacobsen catalyst axially coordinated onto ZPS-PVPA by phenoxy groups. The amount of salen Mn(III) complex was $0.36-0.60 \text{ mmol g}^{-1}$ as determined by AAS based on the element Mn. XPS of **1d** gave further evidence for the successful immobilization based on the fact that the characteristic peak at 642.3 eV of Mn $2p^{3/2}$ was clear. The SEM and TEM indicated that the diameter of the particles of the heterogeneous catalysts 1a-1d was in the submicron range. It also showed that the catalysts were loose and different shapes and sizes of caves, holes, pores and channels existed in every particle. Generally, one of the advantages of the layered zirconium phosphonate is that all the organic groups are located on the surfaces, interlamellar regions and interlayer surfaces no matter whether they are crystalline semi-crystalline or amorphous, which results from their self-assembled layered structure on the nanometer scale.^[7a] Actually for the micro-crystals of amorphous zirconium phosphonate, its layer structure followed the arrangement of "order in short range, but disorder in long distance", thus the possible structure of the heterogeneous catalysts was deduced as shown in Figure 1.

The catalytic activity and selectivity of catalysts 1a-1d were explored for the asymmetric epoxidation of unfunctionalzed olefins using *m*-CPBA as an oxidant system. Jacobsen's catalyst and corresponding homogeneous chiral Mn(salen)OPh (1e) were also exam-

Figure 1. Possible structure of the immobilized catalyst.

Entry	Substrate	Catalyst	Oxidant	Temperature [°C]	Conversion [% (h)] ^[b]	Selectivity [%] ^[c]	ee [%] ^[c]
1		Jacobsen	<i>m</i> -CPBA/NMO	0	99.9 (1)	99.1	52.0 ^[d]
2		1e	m-CPBA/NMO	0	98.0 (1)	99.5	49.5 ^[d]
3		1 a	m-CPBA	0	98.8 (1)	56.6	67.3 ^[d]
4		1b	m-CPBA	0	99.9 (1)	58.8	69.9 ^[d]
5		1c	<i>m</i> -CPBA	0	92.8 (1)	54.3	45.8 ^[d]
6		1d	m-CPBA	0	99.9 (1)	60.9	73.7 ^[d]
7		1d	<i>m</i> -CPBA/NMO	0	24.3 (1)	57.8	$29.4^{[d]}$
8		1d	<i>m</i> -CPBA	-78	74.3 (6)	62.1	$81.4^{[d]}$
9		Jacobsen	m-CPBA/NMO	0	99.9 (1)	98.7	47.0 ^[e]
10		1e	<i>m</i> -CPBA/NMO	0	98.9 (1)	99.1	45.8 ^[e]
11		1 a	m-CPBA	0	87.3 (1)	91.7	12.9 ^[e]
12		1b	<i>m</i> -CPBA	0	99.3 (1)	94.3	25.8 ^[e]
13		1c	<i>m</i> -CPBA	0	95.4 (1)	92.7	21.5 ^[e]
14		1d	<i>m</i> -CPBA	0	99.9 (1)	96.0	31.6 ^[e]
15		1d	<i>m</i> -CPBA/NMO	0	25.9 (1)	95.5	9.25 ^[e]
16		1d	<i>m</i> -CPBA	-78	76.9 (6)	96.6	43.4 ^[e]
17		Jacobsen	<i>m</i> -CPBA/NMO	0	99.9 (1)	99.8	65.0 ^[f]
18		1e	<i>m</i> -CPBA/NMO	0	99.2 (1)	98.1	63.5 ^[f]
19		1a	<i>m</i> -CPBA	0	98.9 (1)	98.8	56.6 ^[f]
20		1b	<i>m</i> -CPBA	0	98.5 (1)	99.2	95.5 ^[f]
21		1c	<i>m</i> -CPBA	0	96.0 (1)	97.6	82.3 ^[f]
22		1d	m-CPBA	0	99.9 (1)	>99.9	99.5 ^[f]
23		1d	<i>m</i> -CPBA/NMO	0	32.6 (1)	98.4	78.8 ^[f]

Table 1. Asymmetric epoxidation of alkenes catalyzed by 1a–1d with *m*-CPBA as oxidant.^[a]

^[a] Reactions were carried out at the desired temperature in CH₂Cl₂ (3.00 mL) with alkene (0.500 mmol), NMO (338 mg, 2.50 mmol, if necessary), nonane (internal standard, 56.0 mL, 0.500 mmol) and immobilized Mn(III)salen complexes (0.0250 mmol, 5.00 mol%).

^[b] Conversions were determined by GC, by integration of product peaks against an internal quantitative standard (nonane), correcting for response factors.

^[c] Determined by GC with a chiral capillary column (HP19091G-B233, $30 \text{ m} \times 25 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$).

^[d] Expoxide configuration *S*.^[2j]

^[e] Epoxide configuration *S*.^[4e]

^[f] Epoxide configuration 1*S*,2*R*.^[4e]

ined for comparison purposes. The results are summarized in Table 1. The racemic samples of the epoxides were independently prepared by the epoxidation of the corresponding alkenes with m-CPBA in CHC1₃ at 273 K^[2j] and detected by gas chromatography (GC). The conversions (with nonane as internal standard) and ee values of epoxidation reaction were determined by GC with a chiral capillary column (HP19091G-B233, $30 \text{ m} \times 25 \text{ } \mu \text{m} \times 0.25 \text{ } \text{m}$). All reactions proceeded smoothly, and the heterogeneous catalysts showed higher ee values at the same conversion level compared to the corresponding homogeneous Jacobsen's catalyst and **1e** under the same conditions with *m*-CPBA as oxidant system. Actually, when it comes to the Mn(salen)OPh, the classic Jacobsen's catalyst afforded somewhat higher ee values at equal conversions; this proved that the linker OPh plays a minor role to the same degree as in the homogeneous system.

When α -methylstyrene was used as substrate with immobilized catalysts **1a–1d**, there was a significant improvement in enantioselectivity (67.3–81.4% vs.

52.0%). And the increase in ee values was mainly attributed to the unique spatial environment constituted by the axially rigid bulky group and the special structure of ZPS-PVPA that is constituted by a large variety of polystyrene segments which are hydrophobic and easily modified, as well as the zirconium phosphate-phosphonate which is hydrophilic and has a self-assembled layered structure on the nanometer scale. Similar results were reported by Li,^[10] where salen Mn(III) axially immobilized on MCM-41 via rigid phenoxy groups presented a 72.0% ee value in the NaClO aqueous/organic biphasic system. The heterogenized catalysts also showed good catalytic activity and enantioselectivity for relatively bulkier olefins, like indene (conversion: 99.9%; ee: 99.5%). This indicated that the active sites in the caves, holes, pores, microporous, and channels of ZPS-PVPA also could be accessed readily by the bulkier reactant. However, in the case of styrene, the enantiomeric excess values (9.25-43.4%) were not encouraging.

It was also found that the conversions and the enantioselectivity increased with increasing linkage lengths. Similar results were obtained by Li^[11] so the results might be due to the active intermediates of salen Mn(V) immobilized salen Mn(III) complexes which may attack the substrate more expediently with increasing linkage lengths. Whereas, in the case of 1c, there was a slightly decrease in conversion and ee values (entries 5, 13, 21), The proper reason could be that the location between support and salen Mn(III) was so close that it led to a twist against each other, shielding and interfering with their active catalytic centers and lowering their catalytic performance. For all the substrates, enantiomeric excess values increased and conversions slightly decreased with decreasing temperature (entries 8, and 16). The reason should be attributed to both an increase in enantiofacial selectivity in the initial C-O bond-forming step and suppression of the trans-pathway in the second step at low temperature.[11]

In addition, it is interesting to find out here that remarkably increases of conversion and ee values were obtained in the absence of expensive O-coordinating axial bases for the asymmetric epoxidation with the heterogeneous catalyst 1d, especially for the epoxidation of α -methylstyene (conversion: from 24.3% to 99.9%; ee: from 29.4% to73.7%; entries 6 and 7), similar results were also obtained for styrene (entries 14 and 15) and indene (entries 22 and 23). These observations are not in agreement with other literature reported earlier for both homogeneous and heterogeneous systems, where O-coordinating axial bases are rather essential for catalyst stability and enantioselectivity.^[12] These observations are also not in accordance with heterogeneous salen Mn(III) catalysts axially coordinatively immobilized on diamine- or polyamine-modified organic-inorganic hybrid support ZPS-PVPA by our group.^[7b] Actually, the axial coordinating group for the immobilized catalysts **1a-1d** in this paper is the phenoxy linker group which has similar properties in electronic structure and coordination performance with O-coordinating axial bases such as NMO (N-methylmorpholine N-oxide). Therefore, it is deduced that these observations are caused by both organic-inorganic hybrid support ZPS-PVPA and the phenoxide axial coordinating group, for which, not a single one can be dispensed with. The O-coordinating axial bases additive may interfere with the well-defined molecular geometry and conformation of the chiral Mn(III) salen complex of the immobilized catalysts 1d, when it is added to the heterogeneous system, thus decreasing the conversion and chirality recognization. Further studies concerning the mechanism of this novel behaviour for these immobilized catalysts are currently in progress.

To study the recyclability of the heterogeneous catalyst and the leaching of the metal complex from the immobilized catalyst during the epoxidation of olefins, we applied catalyst **1d** in repeated epoxidation reactions with α -methylstyrene as a model substrate. At the end of each cycle, the catalyst was precipitated from the reaction system by adding hexane and subsequently used in the next runs without further purification. The filtrate showed no trace of the metal complex on UV-Vis and by AAS after the first run, which indicated that the salen Mn(III) complex was strongly bonded on the phenoxy-modified ZPS-PVPA supports. The data in Table 2 showed only a slightly decrease in activity and enantioselectivity for the first five runs (conversion: from 99.9% to 93.8%; *ee*: from

Entry	Cycle	Catalyst	Oxidant	Temperature [°C]	Conversion [% (h)] ^[b]	Selectivity [%] ^[c]	ee [%] ^[c,]
1	Fresh	1d	<i>m</i> -CPBA	0	99.9 (2)	60.9	73.7 ^[d]
2	2	1d	m-CPBA	0	99.9 (2)	61.2	72.1 ^[d]
3	3	1d	m-CPBA	0	98.5 (2)	59.5	73.1 ^[d]
4	4	1d	m-CPBA	0	95.5 (2)	57.6	69.5 ^[d]
5	5	1d	m-CPBA	0	93.8 (2)	57.3	67.5 ^[d]
6	6	1d	m-CPBA	0	88.8 (2)	53.2	65.2 ^[d]
7	7	1d	m-CPBA	0	85.8 (3)	52.8	63.7 ^[d]
8	8	1d	m-CPBA	0	77.8 (3)	50.2	60.5 ^[d]
9	9	1d	m-CPBA	0	70.1 (4)	50.0	55.8 ^[d]
10	10	1d	m-CPBA	0	67.8 (4)	43.7	54.2 ^[d]
11	11	1d	m-CPBA	0	43.6 (5)	39.9	53.4 ^[d]

Table 2. The recycling of immobilized catalyst in the asymmetric epoxidation of α -methylstyrene with *m*-CPBA as oxidant.^[a]

[a] Reactions were carried out at the desired temperature in CH₂Cl₂ (3.00 mL) with alkene (0.500 mmol), NMO (338 mg, 2.50 mmol, if necessary), nonane (internal standard, 56.0 mL, 0.500 mmol) and immobilized Mn(III)salen complexes (0.0250 mmol, 5.00 mol%).

^[b] Conversions were determined by GC, by integration of product peaks against an internal quantitative standard (nonane), correcting for response factors.

^[c] Determined by GC with a chiral capillary column (HP19091G-B233, $30 \text{ m} \times 25 \mu \text{m} \times 0.25 \mu \text{m}$).

^[d] Expoxide configuration *S*.^[2j]

73.7% to 67.5%). Further recycles of the heterogeneous catalyst resulted in poor conversions; however, still a higher enantioselectivity than that of the homogeneous counterpart was obtained even after eleven runs. The good performance of these heterogeneous catalysts with regard to ees maybe mainly due to their novel support, combining properties of the inorganic and organic components. The microenvironment^[13] of ZPS-PVPA for asymmetric epoxidation consisted of polystyrene parts which are hydrophobic and the hybrid zirconium phosphonate parts which are hydrophilic and their self-assembled layered structure on the nanometer scale. A large number of polystyrene segments exist in ZPS-PVPA, which are folding, have a curl assignment, parallel, crossing, coinciding, or even twining, combined with the layered zirconium phosphonate-phosphate all lead eventually to form different caves, holes, pores, micropores, channels and secondary channels with various sizes and shapes, and their threshold effect giving rise to their excellent catalytic properties. Generally, layered zirconium phosphonate is relatively stable, while the layered structure maybe destroyed under some extreme conditions such as base solutions. However, the virgin layered structure and channels, holes and caves could be roughly recovered in standing under aqueous phase conditions which is helpful to carry out self-assembly for layered zirconium phosphonate. Hence, these kinds of heterogeneous catalysts have the singular advantage of recyclability. The decrease in the activity for more cycles might be caused by a physical loss during the recovery process and/or by a gradual degradation of the catalysts under the epoxidation conditions and continuous stirring.

Conclusions

In summary, phenoxy-modified organic-inorganic hybrid support-zirconium poly(styrene-phenylvinylphosphonate)-phosphate has been synthesized and characterized for the first time, which was used for immobilization of chiral Jacobsen's homogeneous catalyst. Comparing the heterogeneous catalysts with the corresponding homogeneous catalyst and other heterogeneous catalysts known from the relevant literature, the as-synthesized heterogeneous catalysts showed comparable or even higher conversions and enantioselectivities, which was mainly attributed to the special structure of ZPS-PVPA. Moreover, the heterogeneous catalyst could be conveniently separated from the reaction system by simple precipitation in hexane and be recycled at least five times with insignificant loss of ee and activity. Especially, it was found here that the heterogeneous catalysts afforded remarkably increases of conversion and ee values in the absence of expensive O-coordinating axial bases for the asymmetric epoxidation of olefins, especially for the epoxidation of α -methylstyrene (conversion: from 24.3% to 99.9%; *ee*: from 29.4% to 73.7%). To the best of our knowledge, there are no other reports on the asymmetric epoxidation generating the products in very good conversions and excellent enantioselectivities under mild conditions without using any additives in the salen Mn(III) system, which may overcome the last obstacle for wide application in organic synthesis as well as in industry of chiral Jacobsen's catalyst.

Experimental Section

Preparation of Homogeneous Chiral Jacobsen's Catalyst

Chiral Jacobsen's catalyst were synthesized according to the standard literature procedures.^[1]

Preparation of Homogeneous Chiral Mn(salen)OPh Complex (1e)^[2j]

Mn(III) salenC1 (1.56 g, 2.56 mmol) and PhONa (0.359 g, 3.09 mmol, 1.2 equiv-) were added in ethanol (60.0 mL), and the mixture was refluxed for 5 h at 80 °C (Scheme 2). After cooling to room temperature, ethanol was removed, CH_2Cl_2 was added, and the organic phase was washed with distilled water. Then it was washed with saturated NaCl solution and dried over anhydrous Na₂SO₄. Removal of the CH_2Cl_2 gives the brown-dark solid Mn(III)salenOPh complex; yield: 80.0%.

Preparation of ZPS-PVPA

The synthesis and characterization of ZPS-PVPA have been reported early by our group. $^{\left[7b\right] }$

Preparation of ZHPS-PVPA (4a)

ZPS-PVPA (6.00 g, 8.55 mmol) was added to ethanol (80.0 mL) containing concentrated sulfuric acid (3.44 g, 35.0 mmol) and catalyst FeCl₃· $6H_2O$ (132 mg, 0.488 mmol) and this suspension was stirred for 30 min at 50 °C. Then H_2O_2 (13.2 mL) was added to the mixture and the mixture was stirred for an additional 20 h. The solid was filtered and washed with ethanol and deionized water until neutrality to give ZHPS-PVPA; yield: 86.0%.

Preparation of ZCMPS-PVPA (3)

Chloromethyl methyl ether (9.30 mL), anhydrous zinc chloride (1.92 g, 14.2 mmol) and ZSP-PVPA (6.00 g, 8.55 mmol) were mixed and stirred at 45 °C for 8 h. After cooling, a small amount of water and methanol was added into the mixture, which was filtered, washed with methanol and acetone and dried under vacuum to afford ZCMPS-PVPA; yield: 90.0.%.

Preparation of Phenoxy-Modified ZCMPS-PVPA (4b-4d)

The appropriate amount of hydroquinone or resorcin or bisphenol-A, respectively, was mixed with ZCMPS-PVPA (2.63 g, 3.45 mmol), K_2CO_3 (4.50 g, 30.0 mmol) and ethanol (20.0 mL) (the molar ratio of diphenol to chlorine element in ZCMPS-PVPA is 5:1), and the mixture was kept at 80 °C for 24 h under N₂. After the reaction, the resin-like product was filtered and washed with substantive amounts of deionized water and ethanol to remove superfluous diphenol and dried under vacuum. Yields: 93.0%, 86.0%, 95.0%, respectively.

Preparation of ZHPS-PVPA-[Mn(III)salen Complex] (1a)

A mixture of Mn(salen)Cl (2.73 g, 4.30 mmol), ZHPS-PVPA (0.50 g) and sodium hydroxide (0.150 g, 3.75 mmol) was added to tetrahydrofuran (80.0 mL) and this suspension was stirred for 20 h under reflux. The mixture was then filtered, washed thoroughly with ethanol, CH_2Cl_2 and deionized water, respectively, to produce **1a** as a dark brown powder that was dried under vacuum. The CH_2Cl_2 filtrate was examined by UV-Vis until no peaks could be detected (with CH_2Cl_2 as reference). Yield: 90.0%.

Preparation of Phenoxy-Modified ZCMPS-PVPA-[Mn(III)salen Complex] (1b–1d)

A solution of chiral salen Mn(III) (2.73 g, 4.30 mmol), phenoxy-modified ZCMPS-PVPA (**4b–4d**) (0.50 g) and an adequate amount of sodium hydroxide in tetrahydrofuran (50.0 mL) was vigorously stirred for 24 h under reflux. The dark brown powder was collected by filtration and washed thoroughly with ethanol, CH_2Cl_2 and deionized water, respectively, and dried under vacuum. The CH_2Cl_2 filtrate was examined by UV-Vis until no peaks could be detected (with CH_2Cl_2 as reference). Yields: 92.0%, 82.0%, 94.0%, respectively.

Asymmetric Epoxidation of Unfunctionalized Olefins

A solution of alkene (0.500 mmol), NMO (338 mg, 2.50 mmol, if necessary), nonane (internal standard, 56.0 mL, 0.500 mmol) and immobilized Mn(III)salen complexes (0.0250 mmol, 5%, based on the Mn amount in the catalyst) in CH₂Cl₂ (3 mL) was cooled to the desired temperature. Solid *m*-CPBA (138 mg, 0.800 mmol) was added in four portions over 2 min. After completion of the reaction as indicated by TLC, the mixture was washed with saturated sodium hydroxide and brine to remove *m*-CPBA and dried over anhydrous sodium sulfate. The conversion and *ee* values were determined by GC, with nonane as an internal standard. The catalyst was precipitated out from the solution by adding hexane and kept for subsequent use without further purification.

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