

SYNTHESIS AND SPECTRAL STUDY OF LOW DIMENSIONAL POLY-YNE POLYMERS CONTAINING PHTHALOCYANINE SILICON AND DIMETHYL SILICON IN THE POLYMER BACKBONE

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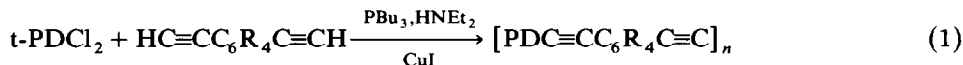
Summary

A pseudo-one-dimensional poly-yne polymer (I) in which phthalocyanine silicon (PcSi) moieties are bridged by *p*-diethynylbenzo groups has been obtained by a salt elimination reaction from dichlorophthalocyaninato silicon and the disodium salt of *p*-diethynylbenzene in tetrahydrofuran (THF) solution. A soluble mixture of short chain oligomers of this polymer was also obtained. For parallel study, an analogous low dimensional poly-yne polymer (III) was synthesized by reaction of dimethyldichlorosilicon with the disodium salt of diethynylbenzene in ether solution. Materials I and III were found to be stable in air and have good thermal stability. These two polymers were characterized by spectral and analytical data.

Introduction

One-dimensional organometallic polymers have received much attention recently because of their potential for having interesting optical and electronic properties, especially high electrical conductivity, and because they could exhibit interesting catalytic activity. In 1981, Hanack et al. [1] proposed a conceptual model for a new kind of one-dimensional conducting material which would include macrocycles such as phthalocyaninate (Pc^{2-}) or hemiporphyrinate (Hp^{2-}), a quadrivalent metal-like Si, Ge, Sn, and a linearly bridging bidentate species like C_2^{2-} , as shown in Fig. 1a. They suggested that this polymeric backbone structure with a face-to-face stacked macrocycle arrangement might give rise to efficient electronic charge transport. Recently, Hanack and coworkers have reported polymers of this type with Sn and Ge. However, no attempts to prepare poly-yne polymers with the PcSi moiety have been reported. The Sn and Ge polymers with $\text{C}\equiv\text{C}$ -bridges, were found to be decomposed readily by iodine [2]. We note, in addition, that the macrocyclic moiety has important visible light absorption properties that it can impart to a polymer in which it is incorporated.

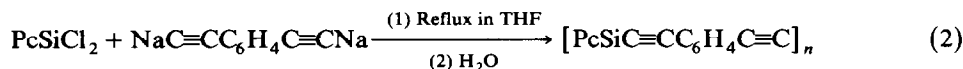
In 1982, Takahashi et al. [3] reported that a type of poly-yne polymer containing a transition metal and a conjugated acetylenic bridging unit could be obtained by polycondensation reactions. Thus, they obtained materials postulated as $[\text{PD}(\text{C}_2\text{C}_6\text{R}_4\text{C}_2)]_n$, where PD and R represent the $\text{Pd}(\text{PBU}_3)_2$ moiety and alkyl groups respectively, by reaction 1.



(R = H, CH_3 , CH_3CH_2 ; PD = $\text{Pd}(\text{PBU}_3)_2$)

They found that *p*-diethynylbenzene can function as a good linear bridging reagent under the proper conditions.

In order to realize a compound of the type shown in Fig. 1a, we have taken advantage of the ability of the $(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})$ moiety of *p*-diethynylbenzene to function as a linear bridge. We report the synthesis and characterization of the one-dimensional polymer I, containing phthalocyaninesilicon with a *p*-diethylbenzene as a bridging unit, by reaction 2. In place of a polycondensation reaction which does not proceed for these compounds, reaction 2 was designed and occurs as a salt-elimination in which PcSiCl_2 combines with the disodium salt of *p*-diethynylbenzene (DSS). Two products are obtained in addition to NaCl. One is an insoluble



polymer I and a THF soluble polymer II. In reaction 2, Pc is the phthalocyanine ring ($\text{C}_8\text{H}_4\text{N}_2$)₄.

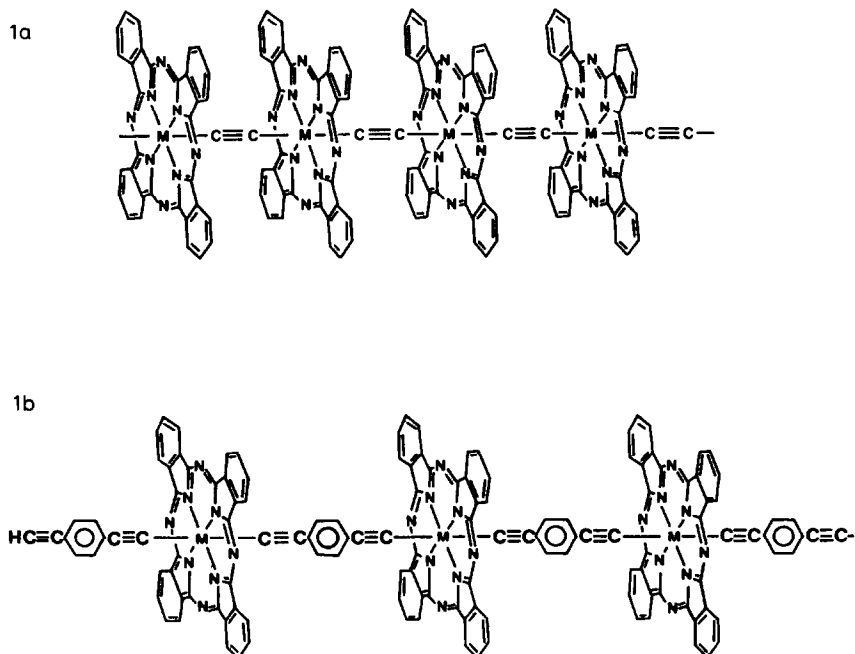
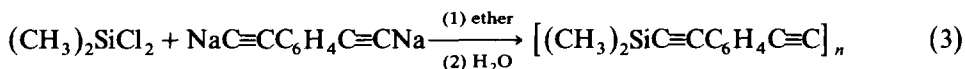


Fig. 1. Pseudo-one-dimensional polymers: (a) conceptual model suggested for synthesis by M. Hanack et al. [1], (b) the supposed structure of polymer product I in this work, where M is silicon.

To develop the reaction chemistry and to assist in the interpretation of the spectral data on the principal product, the analogous reaction 3 of $(\text{CH}_3)_2\text{SiCl}_2$ with DSS was also carried out.

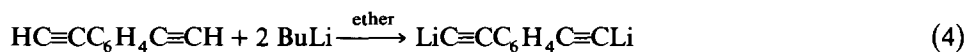


This results in product III, also polymeric, in addition to NaCl.

Results and discussion

The new materials synthesized, polymer I, II, and III, are thermally stable and inert to air. Only product II, a mixture of oligomers related to polymer I, is soluble in various organic solvents and it has an average molecular weight of 1683 ± 100 .

The synthetic route employed to make these low dimensional polymers was based on salt elimination during the reaction of dichlorosilicon compounds with organometallic compounds such as the lithium, sodium, or a magnesium derivative of a bridging reagent. Although this approach is straightforward in principle, in preliminary work, experimental difficulties were encountered in making pure dimetal salt, or di-Grignard reagents of *p*-diethynylbenzene, because the exact stoichiometric amount of *n*-BuLi, or RMgBr must be used.



Otherwise, either disproportionation occurs to yield monometallic derivatives (reaction 6) or unreacted *n*-BuLi, or RMgBr remains and can act as a terminator during

$$\text{XC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CX} + \text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH} \rightarrow 2\text{XC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH} \quad (6)$$

(X = Li, MgBr)

polymerization. In the case of sodium, however, it proved possible to make the pure dimetallic salt of diethynylbenzene and avoid these problems.

TABLE 1
IR SPECTRAL ^a DATA IN NUJOL MULL (cm^{-1})

Compounds	$\nu(\equiv\text{C}-\text{H})$	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}\equiv\text{CH})$	$\delta(\text{Ph}-\text{H})^b$	$\nu(\text{Si}-\text{C}\equiv)$	$\nu(\text{C}=\text{C})$
$\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$	3268(s) 3310(s)		2105(w) 2115(w)	837(s)		
<i>Polymers</i>						
I	3290(w)	2194(w)	2108(w)	838(s)	554(w)	
II	3290(w)	2135(w)	2108(w)	838(m)	554(w)	
III	3300(w)	2159(s)	2108(w)	841(s)	557(m)	
<i>Brominated polymers</i>						
I	-	-	-	838(m)	-	1680(m)
III	-	-	-	842(m)	-	1705(m)

^a Relative intensities: s, strong; m, medium; w, weak. ^b Characteristic C-H bending mode of 1,4-disubstituted benzene.

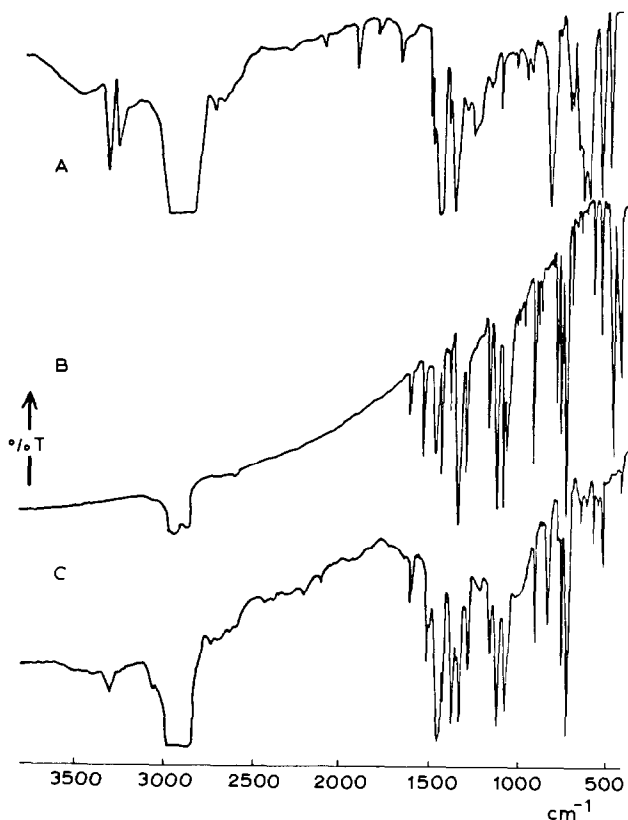


Fig. 2. Infrared spectra of (A) *p*-diethynylbenzene, (B) PcSiCl_2 , and (C) polymer I in Nujol mull.

Attempts to prepare these materials by polymerization of PcSiCl_2 and *p*-diethynylbenzene through a polycondensation reaction, using catalytic amounts of CuI and excess diphenylamine under reflux conditions, were unsuccessful.

The typical infrared spectral data for the polymers and *p*-diethynylbenzene are

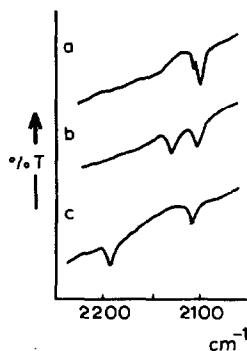


Fig. 3. Infrared spectra in $2100\text{--}2200\text{ cm}^{-1}$ region (a) *p*-diethynylbenzene, (b) polymer II, and (c) polymer I.

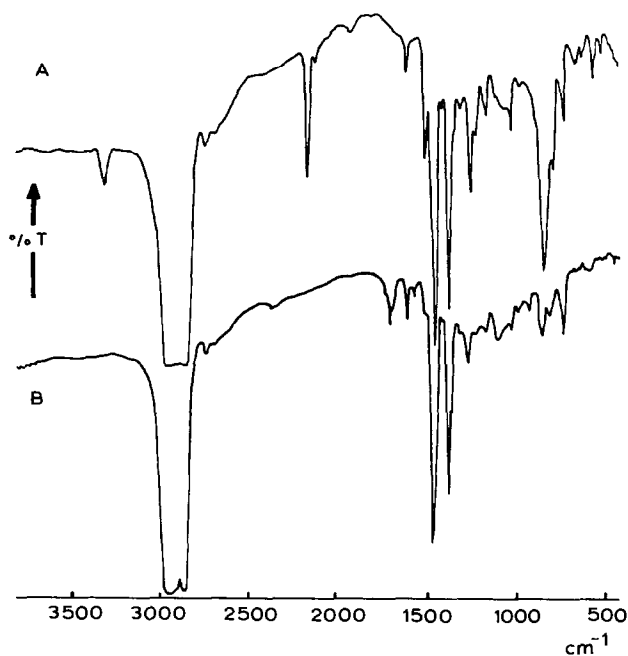


Fig. 4. Infrared spectra of (A) polymer III, and (B) brominated polymer III.

summarized in Table 1, and the spectra of *p*-diethynylbenzene, PcSiCl_2 polymer I, III, and the brominated polymer III are given in Fig. 2 and 4.

A. Polymers I and II from the reaction of PcSiCl_2 and DSS

The pseudo linear one-dimensional structure of the polymer I, and the progress of the reaction can be deduced from the infrared spectra. The strong antisymmetric Si-Cl stretching band at 468 cm^{-1} for PcSiCl_2 disappears completely during the polymerization reaction. The infrared spectrum of polymer I shows the characteristic bands of the macrocyclic silicon unit at 1611, 1427, 1334, 1290, 1165, 1123, 1081, 911, 760, 731, 575, 530 and 430 cm^{-1} . In addition, there are several bands which originate from the bridging unit ($\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$) and terminal unit ($\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$) of the polymer backbone at 3290 (acetylenic C-H stretching), 2194 (bridging triple bond stretching), 2108 (terminal triple bond stretching), 1518, 1506, 1220, 1019 (carbon-carbon double or single bond stretching), 837 (C-H bending of benzene), 648, 619 cm^{-1} (acetylenic C-H bending). (See Figs. 1b and 2.)

For the THF soluble polymer II, all of the infrared bands except those in the $2100\text{--}2200\text{ cm}^{-1}$ region are seen at the same positions, but with relatively weaker intensity, when compared to those of polymer I.

In the carbon-carbon triple bond stretching region, there are two bands at 2135 and 2108 cm^{-1} , which can be assigned to bridging and terminal triple bond stretching, respectively. Considering that polymer II has a short average chain length (M.W. 1683), the band at 2135 cm^{-1} is believed to come from the bridging carbon-carbon triple bond of short chain polymer backbone, and the band at 2194 cm^{-1} of polymer I from that of longer polymer backbone (see Fig. 3). The increase

in triple bond stretching frequencies from 2108 to 2134 to 2194 cm^{-1} is assumed to be related to the stronger interaction between the empty $3d$ orbitals of silicon atom and the conjugated π -orbitals of diethynylbenzene bridging unit.

As to the acetylenic carbon-silicon stretching assignment, there are only a few related reports. In 1979, Nakovich et al. reported the infrared spectral study of 1,4-bis(trimethylsilyl)-1,3-butadiyne, in which a band at 557 cm^{-1} could be assigned to an acetylenic carbon-silicon stretching band [4]. In the case of polymer I and II, there is a new band at 554 cm^{-1} and this band is assigned to the corresponding acetylenic carbon-silicon stretching mode.

Since it would be interesting to know the chain length (molecular weight) of the insoluble polymer I, it is tempting to estimate it from infrared band intensity ratios despite the realization that absolute absorptivities per vibrating unit are not known. However, if the absorptivity of the 911 cm^{-1} band, which is due to an internal Pc mode, is the same in I and II, and that of the 2108 cm^{-1} band due to terminal carbon-carbon triple bond vibration is the same for the two products, an estimate can be made since the molecular weight of each product is a unique function of the ratio of Pc to terminal carbon-carbon triple bond groups. Making these assumptions and using the ratio of the ratio of absorptivities of these two bands in the infrared spectra of I and II, we estimate the molecular weight of polymer I to be about 6×10^3 , suggesting the presence of an average of 9 repeat units.

Bromination of polymer I in ether solution occurred as a simple addition of bromine to carbon-carbon triple bonds. In the infrared spectrum, all of the bands that are related to the triple bond, such as 3290, 2194, 2108, 650, 617, 554 cm^{-1} disappear and a new band at 1680 cm^{-1} appears. It is characteristic of a carbon-carbon double bond stretching mode.

In the visible-ultraviolet absorption spectra, there are two significant changes upon polymerization. First, one of the two characteristic strong bands (670, 742 nm) of the phthalocyanine ring in the visible region is shifted from 670 to 648 nm. It is assumed that there is some interaction between the diethynylbenzene bridging unit and the macrocycle ring system-like charge transfer since there was no appreciable change in the visible spectrum when the *trans*-bis-*axial* chlorides of PcSiCl_2 were substituted by two phenyllithium acetylides [1]. The 742 nm band, however, is unshifted. Second, after the polymerization reaction there is an intense new absorption band at 368 nm, which is of the type expected for highly conjugated polymer systems. The strong electronic absorption bands in the 340–400 nm region have been observed in transition metal poly-yne polymers [3,5–8] and poly(xylylidene)s [9]. The UV-vis features of I and those of PcSiCl_2 and *p*-diethynylbenzene are listed in Table 2.

TABLE 2
UV/VIS SPECTRAL DATA IN NUJOL MULL

Compounds	λ_{max} (nm)
$\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$	208, 214, 258, 271, 291
PcSiCl_2	229, 276, 388, 670,, 742
Polymer I	207, 289, 368, 388(sh), 648, 742

B. Polymer III from the reaction of $(\text{CH}_3)_2\text{SiCl}_2$ and DSS

In a 1966 patent disclosure [10], the General Electric Co. reported an analogous light yellow polymer produced by the reaction of $(\text{Et})_2\text{SiCl}_2$ and the dilithium salt of diethylbenzene in ether solution followed by an oxidative coupling reaction, but no spectral data were reported. Our polymer III is formulated as $[(\text{CH}_3)_2\text{SiC}\equiv\text{C}-\text{C}_6\text{H}_4\text{C}\equiv\text{C}]_n$, and is assumed to have a zig-zag type structure, resulting from the retention of tetrahedral geometry around sp^3 hybridized silicon atom.

In the infrared spectrum of polymer III, there is a strong band at 2159 cm^{-1} and weak one at 2108 cm^{-1} which correspond to bridging and terminal carbon-carbon triple bond stretching modes, respectively. The band at 2159 cm^{-1} is very close to the bridged carbon-carbon triple bond stretching frequency (2158 cm^{-1}) of the related $p\text{-C}_6\text{H}_4(\text{C}\equiv\text{CSiMe}_3)_2$ compound [11]. (See Fig. 4).

In addition to these, there are several infrared bands which belong to the bridging and terminal diethynyl benzene units at 3300, 1915, 1601, 1504, 1407, 1223, 1159, 1105, 1020, 839, 665, 646 and 618 cm^{-1} . And the characteristic bands of the $(\text{CH}_3)_2\text{Si}$ moiety, namely Si-CH₃ bending and wagging bands, appear at 1253 and 788 cm^{-1} . In the infrared spectrum of polymer III taken in a KBr disk, the C-H stretching band of methyl groups was observed at 2960 cm^{-1} and that of 1,4-disubstituted benzene was found at 3025 cm^{-1} , as would be expected. As in the case of polymer I, a new band at 557 cm^{-1} appears and is assigned to the acetylenic carbon-silicon stretching bond. This band at 557 cm^{-1} disappeared after bromination of polymer III, as did all of the triple bond related bands (3300, 2159, 2108, 646, 618 cm^{-1}), while a new band appeared at 1705 cm^{-1} due to the resulting carbon-carbon double bond stretching mode. There was no evidence of breakage of the polymer backbone during the bromination reaction.

The conductivities of compressed pellets of products I and III and of brominated I were found to be less than $1 \times 10^{-8}\ \Omega^{-1}\text{ cm}^{-1}$.

Finally, we can conclude that the pseudo-one-dimensional polymer I as well as the low dimensional polymer III have been synthesized by salt elimination. Bromination of polymers I and III in ether solution under the conditions specified does not lead to doping-level interaction, but leads to simple addition of bromine to the carbon-carbon triple bonds and results in the formation of the brominated double bonds. The newly synthesized polymers I and III are thermally stable, inert in air, and have been characterized by spectral and analytical data.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen and all solvents were carefully dried and deoxygenated. The dichlorophthalocyaninosilicon (PcSiCl_2), and dimethyldichlorosilicon ($(\text{CH}_3)_2\text{SiCl}_2$) was obtained from Alfa Inorganics, and purified before reaction by washing with acetone, and distillation respectively.

The infrared spectra were measured on a Digilab FTS-15B Spectrometer and ultraviolet-visible absorption spectra were measured on a Perkin-Elmer 552A Spectrometer. Elemental analyses and the molecular weight measurement were conducted by the Galbraith Lab. Inc. and Schwartzkopf Microanalytical Laboratory.

The *p*-diethylbenzene was prepared as reported [12] and was identified by its infrared, and NMR spectra and its melting point (95°C).

Preparation of the disodium salt of p-diethynylbenzene (DDS)

This salt was prepared by the reaction of *p*-diethynylbenzene (5.04 g, 40 mmol) and sodium metal (1.84 g, 80 mmol) in dry ether solution (50 ml) under dry N₂. In a typical reaction, a mixture in these amounts was stirred for 48 h at room temperature in a 250 ml round bottom flask. The evolved H₂ gas was released frequently through the vacuum line. The dark grey DDS was filtered and washed with ether. To confirm that no terminal protons remained unreacted, a sample of the DDS product was deuterated by dissolving it in D₂O and its ¹H NMR spectrum was taken. In the NMR spectrum derived from each DDS sample used, no trace of unreacted terminal protons of *p*-diethynylbenzene, which would give a singlet at δ 3.19 ppm, was found.

The polymerization reaction of PcSiCl₂, and DDS

In a typical reaction 3 g of PcSiCl₂ (4.90 mmol) was added slowly to a dispersion of DDS (2.5 g, 14.70 mmol) in 60 ml of THF. The mixture was refluxed for 7 days and then the THF was removed under reduced pressure. To destroy unreacted excess DDS and to remove NaCl, water was added dropwise to the solid and removed by filtration. The NaCl produced was identified by the reaction with AgNO₃ and the formation of AgCl. The dark greenish blue polymer product was washed with ether and THF several times. The insoluble polymer product I was filtered and dried at 110°C in vacuum. ([PcSi≡CC₆H₄C≡C]_n, yield, 85% by weight). Anal. Found: C, 75.31; H, 3.95; Si, 4.32. C₄₂H₂₀N₈Si calcd.: C, 75.89; H, 3.03; Si, 4.22%. The THF-soluble polymer II was collected in 9% yield by evaporating the THF solution from the filtrate in the above washing procedure and by washing it with ethanol to remove *p*-diethynylbenzene. The measured molecular weight of the THF-soluble polymers II was 1683 (thermo-electric measurement by osmometry), which is the average for the soluble molecules. Both polymer product I and II were found to be stable in air until 320°C and seem to be quite thermally stable at higher temperature.

Polymerization reaction of (CH₃)₂SiCl₂ and DDS

Freshly distilled (CH₃)₂SiCl₂ (2 g, 15.50 mmol) was added slowly by syringe to a dispersion of DDS (7.91 g, 46.54 mmol) in 50 ml of ether in a 250 ml round bottom flask, and stirred for 4 days at room temperature. After reaction, the mixture was filtered under dry N₂ and ether (20 ml) was added again. Then water was added dropwise to the resulting ether solution and removed by filtration. This pale yellow polymer product III was washed with water and ether, and dried at 100°C in vacuum ([(CH₃)₂Si≡CC₆H₄C≡C]_n, yield, 97% by weight). Anal.: Found: C, 78.86; H, 5.93; Si, 15.19. C₁₂H₁₉Si calcd.: C, 79.06; H, 5.53; Si, 15.41%. This polymer III was stable in air and decomposed at 220°C.

Bromination of polymers I and III

Bromine was added dropwise to suspensions of each polymer in ether at room temperature until the bromine color persisted and the resulting solutions were stirred for 4 h. After reaction, the solvent was evaporated under reduced pressure. The resulting residue was washed with excess ether and dried at 100°C in vacuum.

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