mixture was stirred for 3 h at −70 °C. After warming to room temperature, 10% NH_4Cl was added and the aqueous layer extracted 3 times with ether. The combined organic layers were washed with 5% HCl, 5% $NaHCO_3$, and water, then dried over $MgSO_4$. Filtration and evaporation yielded 0.31 g of yellow oil: NMR δ 1.75 (s, 3 H), 3.56 (s, 3 H), 3.6–3.7 (m, 1 H), 7.30, 7.52 (2m, 5 H); IR λ_{max} 5.77 μm.

The crude selenoester was dissolved in ethyl acetate (6 mL) and with ice-cooling, 30% H_2O_2 (0.6 mL, 5.3 mmol) was added cautiously. After stirring for 2 h at 0 °C, the reaction mixture was diluted with water (10 mL) and extracted twice with ether. The organic extracts were washed with 10% $NaHSO_3$, 5% $NaHCO_3$, and water. Drying ($MgSO_4$), filtration, and concentration afforded 0.11 g of an oil. Column chromatography (10 g silica gel, $CHCl_3$) was used to elute the desired product **5a** (55 mg, 30%) having R_f = 0.6 in $CHCl_3$: NMR δ 5.37 (d, 1 H, J = 2 Hz), 4.58 (d, 1 H, J = 2 Hz), 3.76 (s, 3 H), 3.8–4.05 (m, 1 H); IR λ_{max} 5.80, 6.16 μm. This material was identical in every respect with an authentic sample of **5a** prepared by the anionic condensation of methyl cyclohexyloxyacetate with formaldehyde, then dehydration.

Selenation of Methyl 2-(2-Cyclohexen-1-yl)oxypropionate. Preparation of 4b and Oxidation to 5b. A solution of LDA (1.8 mmol) was prepared as usual from diisopropylamine (0.252 mL) and n-BuLi (1.125 mL of a 1.6 M solution) in THF (6.5 mL), then cooled to −70 °C under N_2. A mixture of **3b** (0.276 g, 1.5 mmol) and HMPA (0.537 g, 3 mmol) in THF (1.5 mL) was added slowly and the colorless solution was stirred for 1 h at −70 °C. Then PhSeSePh (0.562 g, 1.8 mmol) in THF (1.5 mL) was introduced and after 1 h at −70 °C followed by 3 h at −40 °C, the reaction was terminated by adding 10% NH_4Cl (10 mL). Three ether extracts were combined and washed with 5% HCl, 5% $NaHCO_3$, and water. Drying ($MgSO_4$), filtration, and concentration afforded 0.60 g of yellow oil: NMR δ 1.80 (s, 3 H), 3.55 (s, 3 H), 4.4–4.5 (broad m, 1 H), 5.75 (broad s, 2 H), 7.33, 7.55 (2 m, 5 H); IR λ_{max} 5.77 μm.

The crude product was dissolved in ethyl acetate (9 mL) and cooled to 0 °C. Thirty percent H_2O_2 (0.8 ml, 7 mmol) was added slowly, the reaction mixture stirred 2 h at 0 °C, then worked up by diluting with water (10 mL) and extracting twice, with ether. The combined ether layers were washed with cold $NaHCO_3$ and water, then dried over $MgSO_4$. Filtration and evaporation furnished 0.199 g of oil. TLC showed a UV active spot having R_f = 0.5 in $CHCl_3$. The crude product was chromatographed on a column of silica gel (10 g) using $CHCl_3$ to afford 0.099 g of clear, colorless **5b** (36%): NMR δ 5.82 (broad s, 2 H), 5.38 (d, 1 H, J = 2 Hz), 4.63 (d, 2 H, J = 2 Hz), 4.50 (broad m, 1 H), 3.77 (s, 3 H); IR λ_{max} 5.79, 6.17 μm. This substance was identical in every respect with an authentic sample of **5b** prepared by the condensation of methyl cyclohexenyloxyacetate with formaldehyde, then dehydration.

Preparation of Acetoxyselenide 8. Oxidation of 8 to 9. A solution of methyl 2-phenylselenopropionate (0.30 g, 1.24 mmol) in THF (3 mL) was cooled to −22 °C under N_2 and treated with powdered m-chloroperoxybenzoic acid (85%; 0.251 g, 1.24 mmol). After 30 min, acetic anhydride (0.152 g, 1.49 mmol) was added by microsyringe followed by pyridine (0.216 g, 2.73 mmol). The contents of the flask were stirred for 1 h at −20 °C then 2 h at 0 °C. Ether was added and the organic layer separated, washed with 5% $NaHCO_3$ and water, and finally dried ($MgSO_4$). Filtration and concentration afforded 0.40 g of an oil. This crude product was chromatographed on a column of silica gel (15 g) eluting with $CHCl_3$. Two major fractions were collected. First, 0.050 g (11%) of oil having R_f = 0.65 in $CHCl_3$ was eluted whose structure was shown to be methyl 2-(m-chlorobenzoyloxy)-2-phenylselenopropionate. Continued elution afforded 0.120 g (32%) of **8** as a colorless oil: NMR δ 1.83 (s, 3 H), 2.03 (s, 3 H), 3.59 (s, 3 H), 7.32, 7.60 (2m, 5 H); IR λ_{max} 5.78 μm (broad).

The above sample of **8** was dissolved in ethyl acetate (2.5 mL) and oxidized at 0 °C for 2 h with 30% H_2O_2 (0.3 mL). Workup as described above afforded 0.025 g of pure acetoxyacrylic ester **9** (44%): NMR δ 6.05 (d, 1 H, J = 2 Hz), 5.46 (d, 1 H, J = 2 Hz), 3.82 (s, 3 H), 2.23 (s, 3 H); IR λ_{max} 5.65, 5.78, 6.09 μm. These values are essentially identical with those reported[6] for an authentic sample of **9**.

Preparation of Chloroselenide 11. Oxidation of 11 to 12. A THF (30 mL) solution of LDA was prepared as usual from diisopropylamine (1.54 mL) and n-BuLi (6.9 mL of a 1.6 M solution) and cooled to −78 °C under N_2. To it was added a solution of methyl α-chloropropionate (1.225 g, 10 mmol) in THF (10 mL) with stirring over 1 h. Meanwhile PhSeBr was prepared from PhSeSePh (1.72 g, 5.5 mmol) and Br_2 (.88 g, 5.5 mmol) in THF (10 mL) at 0 °C. The selenating agent was then taken up in a syringe and added rapidly dropwise to the −70 °C enolate solution. After an additional hour at −70 °C the reaction mixture warmed slowly to room temperature and was poured into cold 10% NH_4Cl. Three ether extractions were performed and the combined organic layers were washed with 5% HCl, H_2O, 5% $NaHCO_3$, and saturated NaCl solution. Drying ($MgSO_4$), filtration, and concentration afforded 2.9 g of yellow oil. Using silica gel column chromatography, the major product **11** (R_f 0.6 in $CHCl_3$) was isolated (0.69 g, 69%) as a very pale yellow oil: NMR δ 2.05 (s, 3 H), 3.65 (s, 3 H), 7.35, 7.65 (2m, 5 H); IR λ_{max} 5.76 μm.

A portion of this sample (0.15 g, .54 mmol) was dissolved in ethyl acetate (3 mL) and treated with 30% H_2O_2 (0.31 mL) at 0 °C for 2 h. Workup in the standard fashion with precautions to prevent loss of the low-boiling product gave a concentrate of **12** containing some diethyl ether solvent: NMR δ 6.47 (d, 1 H, J = 2 Hz), 5.97 (d, 1 H, J = 2 Hz), 3.74 (s, 3 H), 1.97 (s, 3 H). These spectral data were identical with an authentic sample of **12** prepared according to Nield.[10]

Acknowledgment. We thank the National Institutes of Health and Eli Lilly & Company for partial support of this research.

Registry No.—**3a,** 65275-60-7; **3b,** 65275-61-8; **4a,** 65275-62-9; **4b,** 65275-63-0; **5a,** 65275-64-1; **5b,** 65275-65-2; **6,** 65275-66-3; **7,** 686-46-4; **8,** 65275-67-4; **10,** 17639-93-9; **11,** 65275-68-5; **12,** 80-63-7; PhSeBr, 34837-55-3; PhSeSePh, 1666-13-3; methyl 2-(m-chlorobenzoyloxy)-2-phenylselenopropionate, 65275-69-6.

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(9) Tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) were distilled from $LiAlH_4$. NMR spectra are of deuteriochloroform solutions and were measured on a Varian A-60A or EM-390 spectrometer relative to an internal tetramethylsilane standard. IR spectra were determined as neat films on a Perkin-Elmer 137 spectrophotometer. Diphenyl diselenide, methyl α-chloropropionate, m-chloroperoxybenzoic acid, and diisopropylamine were purchased from Aldrich Chemical Co. Except for the last substance, which was redistilled from BaO, all other commercial products were used directly.
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Nitration of *N*-Alkylphthalimides

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The nitration of N-methylphthalimide (**1a**) and N-ethylphthalimide (**1b**) has been reported to give "almost exclusively" the 4-nitro derivative, **2.**[1] However, no details of reaction conditions, actual isomer distributions, or the yields of nitrated products were presented. We recently investigated this reaction in an effort to develop a high-yield synthesis of 4-nitro-N-alkylphthalimides,[2] and we wish at this time to report our results.

We initially nitrated **1a,** slightly modifying the conditions described for the nitration of phthalimide,[3] to give an 85–90% yield of pure **2a.** If the reaction time was reduced from 16 to 2 h, similar results were obtained (see Table I), but a small amount of 3-nitro isomer, **3a,** was obtained. Although the re-

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Table I. The Nitration of *N*-Methylphthalimide (1, R = CH_3)

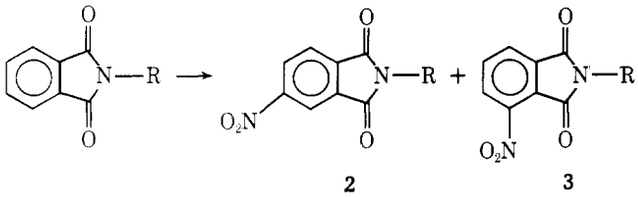
HNO_3 (equiv)[a]	H_2SO_4 (mL)[b]	Temp (°C), time (h)	% unreacted 1	% 2[c]	% 3[c]	Ratio 2/3
90 (3.5)	96 (6)	15–25, 16	0	90[i]	0	100/0
90 (3.5)	96 (6)	15–25, 5	0	92	3	97/3
90 (3.5)	96 (6)	15–25, 2	1	81	5	94/6
			0	91	0	100/0
90 (1.2)	96 (1.8)	70, 2	36	43	3	93/7[d]
90 (1.2)	96 (1.8)	90, 2	24	40	1	98/2
90 (1.5)	96 (1.8)	70, 2	18	57	4	93/7
90 (2.0)	96 (1.8)	70, 2	0	77[j]	7	92/8[e]
90 (3.0)	96 (1.8)	70, 2	0	80	5	94/6[f]
90 (1.5)	100 (1.8)	70, 2	0.5	72	7	91/9[g]
90 (2.0)	100 (1.8)	70, 1	0	82	6	93/7
90 (3.0)	100 (1.8)	70, 1	0	80	6	93/7[h]
98 (2.0)	100 (1.8)	70, 1	0	79	7	92/8

[a] The first number is the percentage of the nitric acid solution used. The second number is the molar equivalent of nitric acid used per 1 mol of 1. [b] The first number is the percentage of the sulfuric acid solution used. The second number is the mL of sulfuric acid solution used per mL of nitric acid solution. [c] The percent yield of this compound in the isolated mixture of products. [d] Stirring 1 g of this material with 4 mL of methanol resulted in a 72% recovery of material containing 71% of **2** and 29% of **1**. [e] Extraction of the filtrate with a combination of methylene chloride and diethyl ether gave 0.58 g of material consisting of 3% phthalic anhydride, 41% 4-nitrophthalic anhydride, 4% 3-nitrophthalic anhydride, 15% of **1a**, 9% of **2a**, and 28% of **3a** by VPC analysis. [f] Ratio from ^{13}C NMR was 95/5. [g] Stirring 1 g of this material with 4 mL of methanol resulted in an 89% recovery of material containing 100% of **2a**. [h] Ratio from ^{13}C NMR was 97/3. [i] The reaction was repeated on 10X this scale (50 g of **1a**) and the crude product was treated with methanol to give an 88% yield of pure **2a**. [j] The reaction was repeated on 10X this scale (50 g of **1a**) and the crude product was treated with methanol to give an 81% yield of pure **2a**.

Table II. *N*-Alkylphthalimide Nitrations

R	HNO_3 (equiv)[a]	H_2SO_4 (mL)[b]	Temp (°C), time (h)	% unreacted 1	% 2[c]	% 3[c]	Ratio 2/3
CH_3CH_2	90 (2.0)	96 (1.8)	70, 2	3	84[i]	5	94/6
CH_3CH_2	90 (3.5)	96 (6.0)	15–25, 5	0	86[g]	0	100/0
$CH_3(CH_2)_3$	90 (2.0)	96 (1.8)	70, 2	1	76[j]	4	95/5
$CH_3(CH_2)_3$	90 (3.5)	96 (6.0)	15–25, 5	0	78[k]	5	94/6
$CH_3(CH_2)_5$[a]	90 (2.0)	96 (1.8)	70, 2	40	21	2	91/9
$CH_3(CH_2)_5$[a]	90 (3.5)	96 (6.0)	15–25, 5	14	13	0.6	96/4
$CH_3(CH_2)_7$[a,e]	90 (2.0)	96 (1.8)	70, 2	65	6	1	90/10
$CH_3(CH_2)_7$[a,e]	90 (3.5)	96 (6.0)	15–25,[f] 5	33	4	0	100/0

[a] The first number is the percentage of the nitric acid solution used. The second number is the molar equivalents of nitric acid used per 1 mol of 1. [b] The first number is the percentage of the sulfuric acid solution used. The second number is the mL of sulfuric acid solution used per mL of nitric acid solution. [c] The percent yield of this compound in the isolated mixture of products. [d] Large amount of bubbling took place during the reaction. [e] Isolated product contained unidentified side products. [f] Extremely exothermic reaction; reaction temperature rose to 140 °C in 10 s even with ice bath cooling. [g] Mp 113–114 °C (lit.[h] 114–115 °C). [h] J. H. Billman and R. V. Cash, *J. Am. Chem. Soc.*, **75**, 2499 (1953). [i] Mp of material after MeOH treatment (63% recovery) 114–115 °C (lit.[h] 114–115 °C). [j] Mp of material after MeOH treatment (70% recovery) 94–95 °C (lit.[h] 95–96 °C). [k] Mp of material after MeOH treatment (65% recovery) 94–95 °C (lit.[h] 95–96 °C).



2 **3**

a, R = CH_3
b, R = CH_2CH_3
c, R = $(CH_2)_3CH_3$
d, R = $(CH_2)_5CH_3$
e, R = $(CH_2)_7CH_3$

action did produce a high yield of pure **2a**, we felt it suffered from several disadvantages. Foremost was the potential danger of a delayed exotherm during the nitration at these low temperatures. We wished to develop a procedure in which such an exotherm could be controlled and in which the large excess of nitric and sulfuric acid could be avoided.

Reactions were carried out in which a mixture of *N*-methylphthalimide and sulfuric acid was heated to 70 °C and, after removal of the heat, nitric acid was added at such a rate to maintain the temperature at 70–75 °C. The mixture was then stirred at the indicated temperature for the desired time and added to ice to precipitate the product. As shown in Table I, under these reaction conditions, the molar equivalents of nitric acid could be reduced from 3.5 to 2.0 and the volume of sulfuric acid could also be greatly reduced. The use of 90% nitric acid and 96% sulfuric acid was adequate for carrying out the nitrations; the only exception to this was when only 1.5 molar equivalents of nitric acid was used. In this case the use of 100% sulfuric acid gave much less unreacted starting material.

Using this procedure the nitric acid was consumed as soon as it was added and the danger of delayed exotherm was removed. However, by carrying out these reactions at elevated temperatures, we did produce small amounts of the isomer **3a**. Fortunately we found that if the isolated mixture was simply stirred with methanol, the 3-nitro isomer, **3a**, and the starting imide, **1a**, could be removed and pure **2a** could be obtained.

As shown in Table II, we also investigated the nitration of *N*-ethyl-, *N*-butyl-, *N*-hexyl-, and *N*-octylphthalimide using both sets of nitrating conditions. The *N*-ethyl system gave results very similar to the *N*-methyl system; however, as the size of the R group was further increased, the yield of nitrated products greatly decreased although the ratio of 4-nitro/3-nitro product remained relatively constant. By stirring the mixture of products obtained from the nitration of **1b** and **1c** with methanol, pure **2b** and **2c** could be obtained although the percent recovery of pure **2** was lower in each case than for the *N*-methyl system. Nitration of the *N*-hexyl and *N*-octyl system resulted in severe bubbling which was thought to arise

from oxidation of the alkyl chain by the nitric acid.[4] In the *N*-octyl system this side reaction is especially critical and when the reaction is carried out at room temperature, an extremely rapid and dangerous exothermic reaction takes place.

In summary, high yields of pure 4-nitro-*N*-methylphthalimide can be obtained from the nitration of *N*-methylphthalimide. Although the nitration of **1a** at 15–25 °C gives excellent yields of pure **2a**, we feel that it is much safer to carry out these reactions under conditions which provide for a controlled exotherm. The small amount of 3-nitro isomer which is isolated in the product under these conditions can easily be separated by methanol treatment to give pure **2a**. The nitration of *N*-ethyl- and *N*-butylphthalimide gives reaction mixtures containing primarily the corresponding 4-nitro compounds which can also be isolated by a methanol treatment although the yields of the recovered products **2** are lower than for the *N*-methyl system. The nitro group of these compounds is extremely labile to nucleophilic displacement which makes these nitro imides useful starting materials for the synthesis of a variety of new phthalimide derivatives.[5]

Experimental Section

All ^1H spectra were recorded with a Varian Associates T-60 NMR spectrometer using tetramethylsilane as an internal standard and deuteriochloroform or Me_2SO-d_6 as a solvent. All ^{13}C NMR spectra were recorded with a Varian Associates CFT-20 NMR spectrometer using complete ^1H decoupling at 79.5 MHz with simultaneous ^{13}C observation at 20.0 MHz. Chemical shifts were measured from internal tetramethylsilane or calibrated to this standard using known chemical shifts of solvent peaks. Mass spectra were determined on a CEC 21-104 analytical mass spectrometer at 70 eV. Vapor phase chromatography (VPC) was carried out on a Hewlett Packard 5750 instrument using a 6 ft 10% UC-W98 on 80/100 Chromosorb W column with temperature programming between 150 and 300 °C at 8 °C/min. Melting points were determined on a Thomas-Hoover instrument and are uncorrected.

All N-substituted phthalimides were prepared by reacting the appropriate alkylamine with either phthalic anhydride, 3-nitrophthalic anhydride, or 4-nitrophthalic anhydride in refluxing acetic acid. The structures of these imides were confirmed by ^{13}C NMR (see Supplemental Material Available paragraph), mass spectral analysis, and by a comparison of the melting points with literature values. The nitric and sulfuric acid solutions were purchased commercially and were used as received.

Analysis of the *N*-methyl system was done by both ^{13}C NMR and VPC. All other systems were analyzed only by VPC. VPC yields were obtained using an internal standard and correcting for detector response differences. Integrations were done on a Spectra Physics SP4000. The ^{13}C NMR analyses were done in Me_2SO-d_6 with the ratios of the products being determined from the average relative peak heights of the carbons for the 4 isomer at 129.4, 124.5, and 117.6 and for the 3 isomer at 136.1, 128.0, and 126.6 ppm.

Typical Nitration Procedure. The Nitration of *N*-methylphthalimide (1a). A. At Lower Temperature. A mixture of 30.8 mL of 96% sulfuric acid and 5.13 mL of 90% nitric acid was cooled to 15 °C. To this well-stirred solution was added 5.00 g of **1a** at such a rate to maintain the reaction temperature between 15 and 20 °C. When addition was complete, a clear bright yellow-orange solution was obtained. The mixture was allowed to slowly warm to room temperature and then to stand overnight at room temperature. The reaction mixture was then poured into ca. 600 mL of ice and the resulting precipitate was filtered, washed with cold water, and dried to give 5.80 g (90%) of **2a** which was pure by VPC analysis.

This reaction was repeated using 50 g of **1a** to give a crude product containing 98.5% of **2a** and 1.5% of **3a**. This material was stirred with 250 mL of methanol and filtered to give 56.53 g (88%) of pure **2a**, mp 175–176 °C (lit.[1] 177–178 °C).

B. At Elevated Temperature. A mixture of 5.0 g of **1a** and 5.28 mL of 96% sulfuric acid was heated at 70 °C with an oil bath. The bath was removed and 2.93 mL of 90% nitric acid was added at such a rate as to maintain the internal temperature at 70 °C (ca. 20 to 30 min). The reaction mixture was then heated at 70 °C for an additional 1.5 h, cooled to room temperature, and added to 200 mL of ice. The resulting precipitate was collected by filtration and dried to give 5.39 g of material. Analysis of this material by VPC showed it to consist of 92% of **2a** and 8% of **3a** for an isolated yield of 77% **2a** and 7% **3a**.

The reaction was repeated using 50 g of **1a**. The nitric acid was added over a period of ca. 100 min. Workup gave a crude product which contained 1% of **1a**, 88% of **2a**, and 11% of **3a**. This crude product was stirred with 250 mL of methanol to give 51.5 g (80.5%) of **2a** which was pure by VPC analysis, mp 175–177 °C (lit.[1] 177–178 °C).

Acknowledgments. We would like to thank N. C. Cook, G. C. Davis, and J. M. Gasaway for their many helpful suggestions and interesting discussions concerning this work.

Registry No.—**1a**, 550-44-7; **1b**, 5022-29-7; **1c**, 1515-72-6; **1d**, 20320-48-3; **1e**, 59333-62-9; **2a**, 41663-84-7; **2b**, 55080-56-3; **2c**, 54395-37-8; **2d**, 65311-53-7; **2e**, 65311-54-8; **3a**, 2593-81-9; **3b**, 2778-84-9; **3c**, 54395-36-7; **3d**, 2593-84-2; **3e**, 2593-54-6.

Supplementary Material Available: Tabulated ^{13}C NMR chemical shifts for all the *N*-alkylphthalimides studied (1 page). Ordering information is given on any current masthead page.

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(2) Both 3- and 4-nitro-substituted phthalimides can easily be prepared from the reaction of the appropriate alkyl amine with either 3- or 4-nitrophthalic anhydride. Unfortunately, the nitration of phthalic anhydride results in an ca. 50/50 mixture of 3- and 4-nitro isomers which are very difficult to separate.
(3) E. H. Huntress and R. L. Shriner report that the nitration of phthalimide at 10–25 °C gives a 52% yield of the pure 4-nitro isomer ("Organic Syntheses", Collect. Vol. 2, John Wiley, New York, N.Y., 1943, p 459). L. F. Levy and H. Stephen (*J. Chem. Soc.*, 79 (1931)) report that if the nitration mixture is allowed to warm to 80 °C for 30 min, 78% of the pure 4-nitro isomer could be obtained.
(4) N. C. Cook and G. C. Davis have shown that some oxidation of the alkyl group takes place even when R = CH_3 (private communication, General Electric Co., Corporate Research and Development).
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Convenient Synthesis of a Highly Efficient and Recyclable Chiral Director for Asymmetric Induction

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Asymmetric syntheses utilizing the menthyloxy group as a chirality director have been reported frequently; however, optical yields are generally too low to be really useful.[2] Although Lewis-acid catalyzed Diels–Alder reactions of menthyl acrylate are unusually efficient (optical yields approach 80%[3]), the menthyloxy group is still far from ideal.

As a result of a study directed toward the enantioselective synthesis of intermediates useful for the preparation of naturally occurring prostaglandins we introduced the use of (1*S*,2*R*,5*S*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexanol, (+)-**1**, which proved to be an exceptionally efficient chirality director.[4]

The reaction of the acrylate ester of (−)-**1** with cyclopentadiene afforded the *endo*-norbornenecarboxylic ester **2** in 82% yield with 99% enantiselectivity.[5] Similarly, the acrylate ester of (+)-**1**, on reaction with 5-benzyloxymethylcyclopentadiene, resulted in the formation of **3** in 89% yield and 97% enantioselectivity.[4]

The preparation of (−)-**1** in 71% yield from (*R*)-(+)-pule-

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