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# Ring-Opening Metathesis Polymer Sphere-Supported *seco*-Porphyrazines: Efficient and Recyclable Photooxygenation Catalysts

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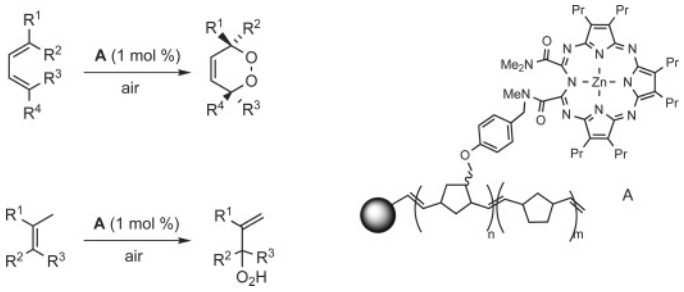
*Received October 16, 2005*




Crossover Linstead macrocyclization of norbornenyl-tagged diaminomaleonitrile with dipropylmaleonitrile gave the corresponding magnesium diaminohexapropylporphyrazine, which was subsequently converted into its zinc *seco*-derivative. Polymerization gave the corresponding ROMPgel and ROMPsphere (ROMP = ring-opening metathesis polymer) reagents, the latter of which proved efficient as an immobilized catalyst for the sensitized production of singlet oxygen for the purification-minimized parallel synthesis of endoperoxides and ene adducts.

## Introduction

Singlet oxygen is a versatile reagent for oxidation reactions including cycloaddition reactions to produce endoperoxides and ene reactions to provide allylic hydroperoxides.[1] Dye-sensitized photoexcitation of ground-state triplet oxygen is the preferred method for its generation.[2] Previously we demonstrated the high quantum yield for singlet oxygen production using *seco*-porphyrazines[3] and, furthermore, established their use as photooxygenation catalysts for the synthesis of endoperoxides from the corresponding dienes.[4] Indeed, the *seco*-porphyrazines proved themselves to be superior catalysts in several cases to traditional dyes such as Rose Bengal. However, the synthesis, purification, and recyclability of the macrocycles are not straightforward, and these limitations have hindered synthetic applications of these effective photooxygenation catalysts. We considered that the problem of catalyst recovery should be easily overcome by the use of solid-support reagents. Previously the Barrett group has been involved in extensive work on ring-opening metathesis (ROM) polymer-supported reagents, including reagents for the Horner−Emmons reaction,[5] immobilization of tosmic,[6] allylboronation reactions,[7] preparation of Mosher amides,[8] arene lithiation reductions,[9] immobilization of triphenylphosphine,[10] and selective rhodium-based hydrogenation catalysis,[11] an anhydride scavenger,[12] and reagents for parallel

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(2) (a) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. (b) For the use of MeO-PEG-supported porphyrin sensitizers for photooxidation reactions see: Benaglia, M.; Danelli, T.; Fabris, F.; Sperandio, D.; Pozzi, G. *Org. Lett.* **2002**, *4*, 4229.
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(7) Arnauld, T.; Barrett, A. G. M.; Seifried, R. *Tetrahedron Lett.* **2001**, *42*, 7899.
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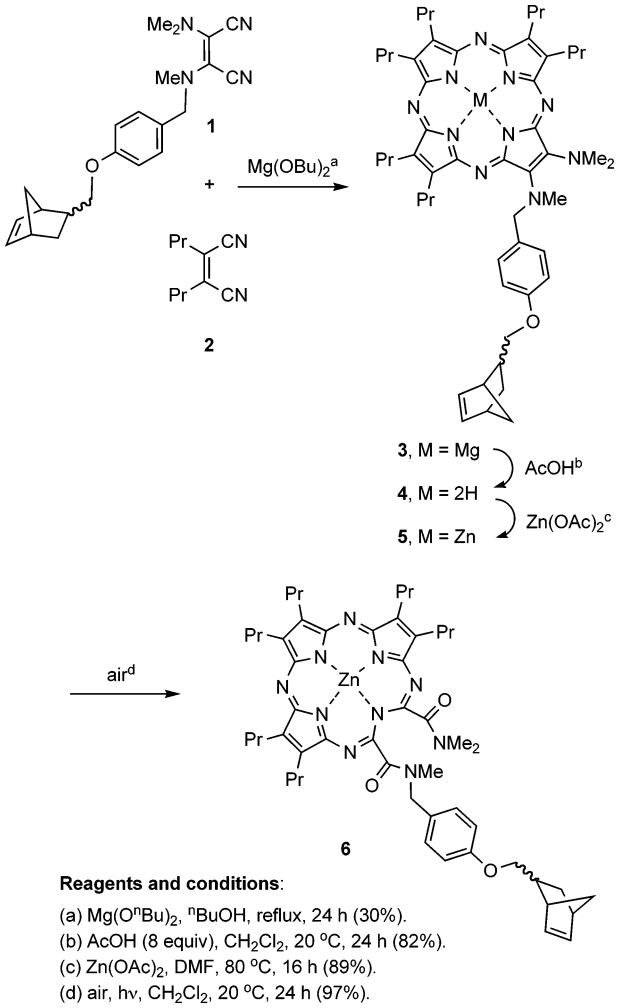
10.1021/jo052156t CCC: $33.50 
Published on Web 12/17/2005

**SCHEME 1. Synthesis of the *seco*-Porphyrazine Monomer**




alkyne synthesis[13] and Stetter reactions.[14] Other applications include polymerizable template-vanishing supports[15] and ROMPspheres[16] (ROMP = ring-opening metathesis polymer), and a detailed review on the applications of ROM polymers has been published.[17] Since porphyrazines display a wide tolerance to ROM[18] and recently we have prepared a norbornenyl-"tagged" maleonitrile for use in the ROM polymerization−capture−release strategy for the synthesis of porphyrazines,[19,20] it seemed feasible that a solid-supported *seco*-porphyrazine should be useful as an immobilized photooxygenation catalyst. There is,

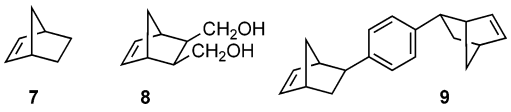
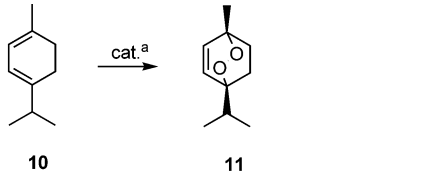



**FIGURE 1.** Comonomers and cross-linker for ROM polymerization studies.

**SCHEME 2. Photooxygenation of α-Terpinene**




of course, a significant potential problem with this proposal. Would the alkene backbone of the ROM polymer undergo competitive oxidative disassembly at such a rate so as to render substrate photooxygenation by singlet oxygen uncompetitive?

## Results and Discussion

Using the norbornenyl-tagged maleonitrile **1**, previously utilized in the ROM polymerization−release strategy for the chromatography-free synthesis of unsymmetrical porphyrazines,[19] a synthetic sequence toward a ROM polymer-supported *seco*-porphyrazine was developed. Mixed Linstead macrocyclization of maleonitrile **1** and dipropylmaleonitrile (**2**)[21] gave the unsymmetrical magnesium porphyrazine **3** (Scheme 1). Demetalation under mildly acidic conditions was necessary to avoid cleavage of the labile, norbornenyl linker. Remetalation using zinc acetate gave the zinc derivative **5**, which was subsequently converted to *seco*-porphyrazine **6** by aerobic oxidation.

In the initial attempts to produce a solid-supported photooxygenation catalyst, macrocycle **6** was copolymerized with two alternate monomers, either norbornene (**7**) or diol **8** (Figure 1), or a mixture of the two, in a ratio of 98.6:1.4 (comonomer: porphyrazine **6**) under previously established polymerization conditions.[19] It is important to note the chosen low ratio of porphyrazine **6** to comonomer had two functions. Previously this ratio had been shown to be optimal for ROM polymerization.[18] Additionally, the low loading of porphyrazine should minimize intramolecular triplet-state quenching of neighboring porphyrazine macrocycles in the polymer, which would have reduced photosensitization quantum yields. Norbornenedimethanol (**8**) was used in the polymer study due to the recent precedent that ROM polymers containing **8** display improved swelling in polar solvents.[13] The copolymerization of **6** with **7** and/or **8** produced ROM polymers, which were either partially or completely soluble in dichloromethane. Alternatively, insoluble copolymers were prepared by using additional cross-linker **9** (10 mol %).

The photooxygenation of α-terpinene (**10**) to give racemic ascaridole (**11**) (Scheme 2)[22] was chosen as a test reaction to screen the *seco*-porphyrazine polymers. The reactions were monitored by $^1$H NMR and conversions estimated by integration of the alkenyl protons. In general, the reactions were faster if

(11) Årstad, E.; Barrett, A. G. M.; Tedeschi, L. *Tetrahedron Lett.* **2003**, *44*, 2703.
(12) Arnauld, T.; Barrett, A. G. M.; Cramp, S. M.; Roberts, R. S.; Zécri, F. J. *Org. Lett.* **2000**, *2*, 2663.
(13) Barrett, A. G. M.; Hopkins, B. T.; Love, A. C.; Tedeschi, L. *Org. Lett.* **2004**, *6*, 835.
(14) Barrett, A. G. M.; Love, A. C.; Tedeschi, L. *Org. Lett.* **2004**, *6*, 3377.
(15) Ball, C. P.; Barrett, A. G. M.; Poitout, L. F.; Smith, M. L.; Thorn, Z. E. *Chem. Commun.* **1998**, 2453.
(16) Barrett, A. G. M.; Cramp, S. M.; Roberts, R. S. *Org. Lett.* **1999**, *1*, 1083.
(17) Barrett, A. G. M.; Hopkins, B. T.; Köbberling, J. *Chem. Rev.* **2002**, *102*, 3301.
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(19) Fuchter, M. J.; Vesper, B. J.; Murphy, K. A.; Collins, H. A.; Philips, D.; Hoffman, B. M.; Barrett, A. G. M. *J. Org. Chem.* **2005**, *70*, 2793.
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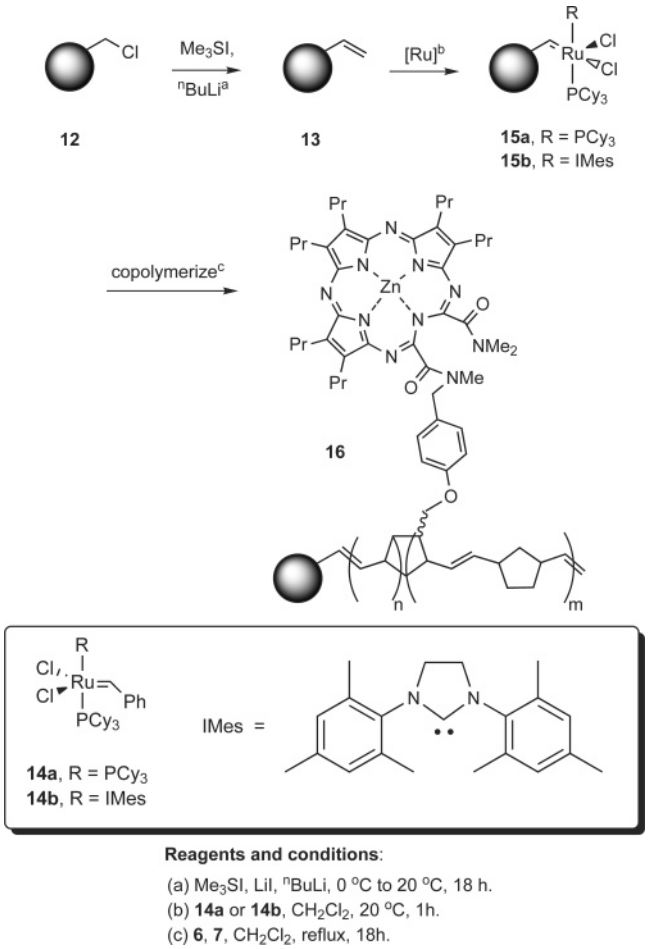
(21) Fitzgerald, J.; Taylor, W.; Owen, H. *Synthesis* **1991**, 686.
(22) Schenck, G. O. *Angew. Chem.* **1975**, *69*, 579.

illuminated with a simple 40 W desk lamp. All the polymers performed with a similar efficiency (approximately 30% conversion after 24 h). Since competitive degradation of the soluble polymers occurred after 8 h, whereas, slow, continuous conversion was observed for the insoluble, cross-linked polymers, the insoluble polymers became the focus of the study. In an effort to improve the proportion of endoperoxide product **11**, the reaction conditions were optimized. Out of the conditions surveyed, the largest effect was observed by decreasing the temperature to −20 °C. Presumably this was simply due to the increased solubility of oxygen at this temperature. Increasing the catalyst loading to 10 mol % increased conversion; however, it was hoped this higher loading could be avoided. Since no dramatic increase in conversion could be achieved, all the cross-linked polymers were examined for their swelling properties in a variety of solvents. Unfortunately, none of the polymers showed any significant swelling in methanol, acetonitrile, acetone, carbon tetrachloride, or dichloromethane. Presumably, the poor rate of singlet oxygen formation was the result of photosensitization by peripheral *seco*-porphyrazine units on the polymer particles only and not by bulk groups. Consistent with this, rates of conversion were improved using mechanically broken up polymer particles (76% conversion after 8 h with 1 mol % catalyst).

As a consequence of the limitations with ROM polymer *seco*-porphyrazines, we sought to examine the corresponding ROMPsphere reagents.[16,23,24] We considered that such graft copolymers should provide insoluble beads with a solvent-swellable ROM surface layer coated onto a polystyrene core, a system with potentially improved photosensitizing properties. Therefore, using the conditions of Miokowski and co-workers,[25] vinylpolystyrene (**13**) was prepared and subsequently converted to the catalysts **15a,b** (Scheme 3).[16] Initially, exposure of **15a** to a solution of porphyrazine **6** and **7** (1.4:98.6) in dichloromethane gave the ROMPsphere **16** with 41% monomer incorporation by weight. No dye was recovered from the reaction solution, indicating the porphyrazine had been fully incorporated into the polymer, giving a porphyrazine loading of 0.12 mmol $g^{-1}$ (Scheme 3). Interestingly, the copolymerization using diol **8** instead of **7** gave a polymer with 35% monomer incorporation by weight, but with virtually no porphyrazine incorporation.

Pleasingly, the photooxygenation of α-terpinene using 1 mol % catalyst **16** proceeded in >99% conversion after 4 h (Scheme 2). This result is comparable to those of other methods for the formation of endoperoxide **11**. For example, **11** has been previously synthesized using methylene blue (86%),[26] C60 (90%),[27] or a soluble porphyrazine (95%)[4] as the photocatalyst. Unfortunately, the preparation of subsequent samples of ROMPsphere catalyst **16** showed significant batch variability. To combat this issue, the reaction conditions for the synthesis of **16** were screened with focus on the solvent, concentration, temperature, ruthenium catalyst (i.e., **14a** or **14b**), ruthenium loading and vinyl loading on polystyrene **13**. The optimum conditions were shown to be the use of catalyst **15b** at reflux in dichloromethane (0.5 M monomer) using a low-loading

**SCHEME 3. Synthesis of the ROMPsphere *seco*-Porphyrazine**




vinylpolystyrene precursor (**13**) (0.5 mmol $g^{-1}$). These polymerization reaction conditions minimized release of ruthenium carbenes into solution with subsequent solution-phase ROMP, producing soluble polymers[18] rather than the required graft copolymers. Under these optimum conditions the ROMPsphere catalyst **16** was isolated with 69% monomer incorporation by weight (Scheme 3). The *seco*-porphyrazine loading of ROMPsphere **16** was determined by quantitative UV−vis spectra of the recovered filtrate to be 0.049 mmol $g^{-1}$. Alternatively, microanalysis of ROMPsphere **16** was consistent with a loading of 0.043 mmol $g^{-1}$.

ROMPsphere **16** was used to catalyze the conversion of 1,3-dienes into endoperoxides (Table 1). In all cases the starting material was smoothly converted to the product(s), with little or no decomposition observable by $^1$H NMR. For entries 1−4 the yields of photooxygenated products were comparable to those obtained with a soluble *seco*-porphyrazine.[4] Interestingly, however, significant amounts of hydroperoxide compounds were obtained for cyclohexadiene (entry 1) and α-phellandrene (entry 3), resulting from a singlet oxygen ene reaction.[28,29] In addition, the elimination product *p*-cymene was produced during the oxygenation of α-phellandrene (entry 3), a transformation

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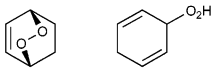
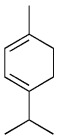
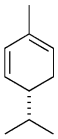
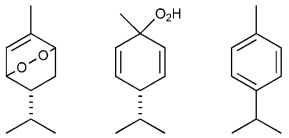
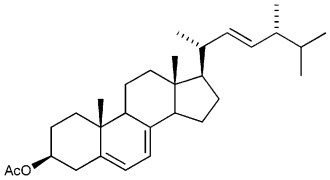
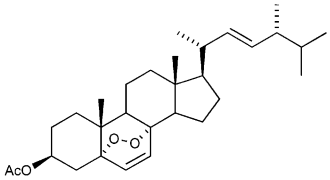
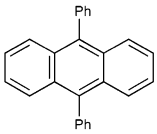
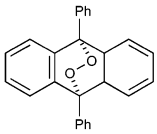
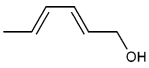
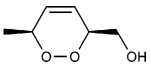
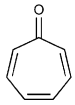
(29) Matusch, R.; Schmidt, G. *Helv. Chim. Acta* **1989**, *72*, 51.
(30) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.
(31) Atkins, R.; Carless, H. A. J. *Tetrahedron Lett.* **1987**, *28*, 6093.

**TABLE 1. [4+2] Cycloaddition of Singlet Oxygen to 1,3-Dienes Catalyzed by ROMPsphere 16**[b]

| Entry | Diene | t(h) | Product | Conversion[a] (Isolated yield) |
|---|---|---|---|---|
| 1 |  | 2.5 |  | 74 13 |
| 2 |  | 3 |  | >99 (97) |
| 3 |  | 3 |  (exo/endo) | 60 30 10 |
| 4 |  | 1 |  | >99 (98) |
| 5 |  | 48 |  | 50 |
| 6 |  | 7 |  | 93 7 |
| 7 |  | 36 |  | 62 |
| 8 |  | 48 | — | <1 |
| 9 |  | 48 | — | <3 |

[a] The yields were identified from $^1$H NMR of the crude reaction mixture. For references on known oxidation products, see entry 1,[28,30] entry 2,[26,27] entry 3,[29,31,32] entry 4,[33] entry 5,[34] entry 6,[35,36] and entry 7.[4] The yields in parentheses refer to isolated yields. [b] All reactions were carried out in $CDCl_3$ and $CCl_4$ (1:4) at 0.03 M and at −20 °C with 1 mol % ROMPsphere catalyst **16** and irradiation with a 40 W desk lamp.

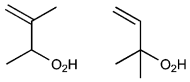
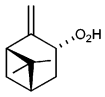
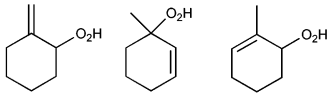
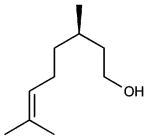
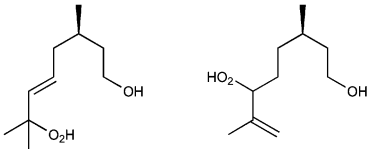
observed with other photosensitizers.[29] In the case of diphenylanthracene (entry 5), ROMPsphere **16** was more effective in providing the endoperoxide (50%) than the *seco*-porphyrazine in solution (20%).[4] In the case of cyclopentadiene (entry 6), the sensitive endoperoxide was observed in high yield along with a small amount of the rearrangement product.[4] Unfortunately, for the more difficult diene substrates (entries 8 and 9), virtually no product was observed even after prolonged reaction times. In general, for cases where the reaction goes to completion (entries 2−4 and 6) the pure oxygenated products can be isolated by a simple filtration of the supported catalyst and evaporation of the solvent. This makes this mild method particularity useful for the synthesis and isolation of delicate endoperoxides.

To investigate the reproducibility of the reaction, the photooxygenation of α-terpinene (Scheme 3) was repeated several times using the same batch of catalyst. No loss in activity was observed after four runs. It is therefore reasonable to assume it is stable to photooxygenation.

To further investigate the scope of the ROMPsphere catalyst **16**, several alkenes were screened for the ene reaction. The results are shown in Table 2. For simple substrates (entries 1 and 2) high yields of the hydroperoxide products were obtained,

(32) Matusch, R.; Schmidt, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 717.
(33) Ozer, G.; Saracoglu, N.; Balci, M. *J. Org. Chem.* **2003**, *68*, 7009.
(34) Rigaudy, J.; Scribe, P.; Breliere, C. *Tetrahedron* **1981**, *37*, 2585.
(35) Schenck, D. *Angew. Chem.* **1956**, *68*, 248.
(36) Adams, W. R.; Trecker, D. J. *Tetrahedron* **1971**, *27*, 2631.

**TABLE 2. Singlet Oxygen Ene Reaction Catalyzed by 16**[b]

| Entry | Starting material | t(h) | Product | Conversion (%)[a] |
|---|---|---|---|---|
| 1 |  | 20 |  | >99 |
| 2 |  | 20 |  | 43 57 |
| 3 |  | 44 |  | 68 |
| 4 |  | 16 |  | 30 28 8 |
| 5 |  | 20 |  | 37 19 |

[a] The conversions were identified from $^1$H NMR of the crude reaction mixture. For references on known products, see entry 1,[37] entry 2,[38] entry 3,[39] entry 4,[40] and entry 5.[41] [b] All reactions were carried out in $CDCl_3$ and $CCl_4$ (1:4) at 0.03 M and at −20 °C with 1 mol % ROMPsphere catalyst **16** and irradiated with a 40 W desk lamp.

whereas for more complex alkenes (for example, entry 3) extended reaction times were required. In general, for all the ene reactions slow discoloration and decomposition of the catalyst **16** was observed for prolonged reaction times presumably due to competitive degradation of the ROM alkene backbone.

## Conclusions

The development and application of a novel solid-supported *seco*-porphyrazine has been described. Although ROM polymerization of the norbornenyl-tagged *seco*-porphyrazine **6** gave polymers with poor swelling properties in solvents and low activity in the photooxygenation of **10**, application of our ROMPsphere methodology[16] gave polymers which efficiently catalyzed the production of singlet oxygen under mild conditions. For a range of substrates, both cycloaddition reactions and singlet oxygen ene reactions were demonstrated and the solid-supported catalyst proved an efficient, mild, and recyclable alternative to solution-phase photooxygenation catalysts. The oxidative disassembly of the ROM polymer backbone was not a significant problem in that polymer fragments did not significantly contaminate the endoperoxide products. In most cases, oxidative ene reactions with alkene substrates were less efficient probably due to substrate and polymer alkene backbone competition for the singlet oxygen.

## Experimental Section

**(7,8,12,13,17,18-Hexapropyl-2-(dimethylamino)-3-((4′-(bicyclo-[2.2.1]hept-5′-en-2′-ylmethoxy)benzyl)methylamino)porphyrazinato)magnesium(II) (3)**. Mg metal (0.26 g, 10.6 mmol) and $I_2$ (ca. two crystals) in 1-butanol (80 mL) were heated to reflux for 24 h under $N_2$. The mixture was allowed to cool, dinitrile **1**[19] (0.38 g, 1.06 mmol) and **2**[21] (1.20 g, 7.4 mmol) in 1-butanol (20 mL) were added, and the mixture was heated to reflux for a further 24 h. The mixture was filtered (Celite), and the solids were washed with $CH_2Cl_2$ and rotary evaporated. Chromatography (hexanes/EtOAc, 9:1) gave porphyrazine **3** (276 mg, 30%) as a blue solid: $R_f$ 0.60 (hexanes/EtOAc, 8:2); IR (neat) 1573, 1510, 1463, 1244, 1148, 1020, 968, 768, 721 cm$^{-1}$; UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 348 (4.66), 557 (4.09), 650 (4.34) nm; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.64 (m, 1H), 1.20−1.52 (m, 20H), 1.89 (m, 1H), 2.21−2.28 (m, 12H), 2.47 (m, 1H), 2.84 (m, 1H), 2.99 (m, 1H), 3.43 (m, 1H), 3.63−3.93 (m, 24H), 5.96 (m, 1H), 6.13 (m, 1H), 6.80 (m, 2H), 7.10 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 14.7, 14.8, 25.5, 25.6, 28.1, 29.0, 29.6, 38.3, 38.5, 41.5, 42.2, 43.6, 43.8, 44.3, 45.0, 49.4, 59.7, 71.4, 72.2, 114.3, 114.8, 129.9, 131.9, 132.3, 134.1, 136.4, 136.8, 137.4, 139.5, 141.7, 142.2, 142.4, 142.7, 143.0, 152.9, 158.1; MS (FAB) *m*/*z* 873 ($M^{\bullet+}$); HRMS (FAB) *m*/*z* calcd for $C_{52}H_{68}MgN_{10}O$ ($M^{\bullet+}$) 872.5428, found ($M^{\bullet+}$) 872.5430.

**7,8,12,13,17,18-Hexapropyl-2-(dimethylamino)-3-((4′-(bicyclo-[2.2.1]hept-5′-en-2′-ylmethoxy)benzyl)methylamino)porphyrazine (4)**. AcOH (4 $\mu$L, 0.069 mmol) was added to porphyrazine **3** (20 mg, 0.023 mmol) in degassed $CH_2Cl_2$ (1 mL) under $N_2$. Further AcOH (4 $\mu$L, 0.069 mmol; 2.6 $\mu$L, 0.046 mmol) was added after 18 and 24 h, respectively. After a further 2 h at ambient temperature, rotary evaporation and chromatography (hexanes/EtOAc, 95:5) gave porphyrazine **4** (16 mg, 82%) as a purple solid: $R_f$ 0.67 (hexanes/EtOAc, 95:5); IR (neat) 1583, 1510, 1455, 1241, 1143, 943, 756, 720 cm$^{-1}$; UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 338 (4.53), 555 (4.14), 638 (4.03) nm; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.55 (m, 1H), 1.20−1.29 (m, 19H), 1.43 (m, 1H), 1.85 (m, 1H), 2.20−2.32 (m, 12H), 2.50 (m, 1H), 2.80 (m, 1H), 2.99 (m, 1H), 3.47 (m, 1H), 3.63 (m, 1H), 3.71 (s, 2H), 3.80−3.93 (m, 21H),

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5.90 (m, 1H), 6.11 (m, 1H), 6.78 (m, 2H), 7.38 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 14.7, 14.8, 25.5, 25.6, 28.1, 29.0, 29.6, 38.3, 38.5, 41.5, 42.2, 43.6, 43.8, 44.3, 45.0, 49.4, 59.7, 71.4, 72.2, 114.3, 129.9, 131.9, 132.3, 134.1, 136.4, 136.8, 137.4, 139.5, 141.7, 142.2, 142.4, 142.7, 143.0, 152.9, 158.1; MS (FAB) *m*/*z* 851 ($M^{\bullet+}$); HRMS (FAB) *m*/*z* calcd for $C_{52}H_{71}N_{10}O$ [$(M + H)^+$] 851.5812, found [$(M + H)^+$] 851.5826. Demetalation of the magnesium porphyrazine **3** under more acidic conditions resulted in extensive decomposition.

**(7,8,12,13,17,18-Hexapropyl-2-(dimethylamino)-3-((4′-(bicyclo-[2.2.1]hept-5′-en-2′-ylmethoxy)benzyl)methylamino)porphyrazinato)zinc(II) (5)**. Porphyrazine **4** (9 mg, 0.01 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (3 mg, 0.014 mmol), and dry DMF (1 mL) were heated to 80 °C for 16 h under $N_2$. Rotary evaporation and chromatography (hexanes/EtOAc, 8:2) gave porphyrazine **5** (8.1 mg, 89%) as a deep blue solid: $R_f$ 0.55 (hexanes/EtOAc, 8:2); IR (neat) 1578, 1510, 1463, 1237, 1150, 1024, 954, 758, 720 cm$^{-1}$; UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 340 (4.80), 560 (4.34), 602 (4.43) nm; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.55 (m, 1H), 1.21−1.51 (m, 20H), 1.85 (m, 1H), 2.21 (m, 12H), 2.50 (m, 1H), 2.80 (m, 1H), 2.98 (m, 1H), 3.47 (m, 1H), 3.61−3.95 (m, 24H), 5.90 (m, 1H), 6.11 (m, 1H), 6.77 (m, 2H), 7.40 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 14.8, 25.5, 25.6, 28.2, 29.0, 29.6, 38.3, 38.4, 38.5, 41.6, 42.1, 42.2, 43.7, 43.9, 44.3, 45.0, 49.4, 59.9, 71.5, 71.9, 114.3, 114.8, 129.8, 131.9, 132.2, 132.4, 135.3, 136.5, 136.8, 137.4, 137.8, 140.4, 142.6, 143.0, 143.2, 143.8, 144.0, 153.8, 155.6, 155.7, 155.9, 156.3, 156.7, 156.8, 158.1; MS (FAB) *m*/*z* 913 [$(M + H)^+$]; HRMS (FAB) *m*/*z* calcd for $C_{52}H_{69}N_{10}O^{64}Zn$ [$(M + H)^+$] 913.4947, found [$(M + H)^+$] 913.4946.

**(7,8,12,13,17,18-Hexapropyl-2-(dimethylamino)-3-((4′-(bicyclo-[2.2.1]hept-5′-en-2′-ylmethoxy)benzyl)methylamino)-2-*seco*-2,3-dioxoporphyrazinato)zinc(II) (6)**. Porphyrazine **5** (8.1 mg, 0.0089 mmol) in $CH_2Cl_2$ (20 mL) was stirred in air for 24 h. Rotary evaporation and chromatography (hexanes/EtOAc, 7:3) gave **6** (8.2 mg, 97%) as a blue-purple solid: $R_f$ 0.29 (hexanes/EtOAc, 7:3); IR (neat) 1627, 1511, 1463, 1242, 1148, 1113, 1006, 955, 771, 720 cm$^{-1}$; UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 338 (4.53), 356 (4.53), 566 (4.30), 650 (4.40) nm; $^1$H NMR (400 MHz, $d_5$-pyridine) $\delta$ 0.64 (m, 1H), 1.14−1.37 (m, 19H), 1.44 (m, 1H), 1.88 (m, 1H), 2.17 (m, 4H), 2.43 (m, 8H), 2.60 (m, 1H), 2.71 (m, 1H), 3.07 (m, 1H), 3.39 (m, 2H), 3.53 (m, 4H), 3.69 (m, 4H), 3.80−3.97 (m, 9H), 4.07 (s, 3H), 4.14 (s, 3H), 6.01 (m, 1H), 6.16 (m, 1H), 7.21 and 7.31 (2 d, $J$ = 8 Hz, 2H), 7.87 and 7.97 (2 d, $J$ = 8 Hz, 2H); $^{13}$C NMR (100 MHz, $d_5$-pyridine) $\delta$ 14.3, 14.8, 14.9, 25.5, 25.7, 25.8, 26.0, 28.0, 28.2, 28.4, 28.5, 29.2, 29.9, 35.1, 38.0, 38.7, 39.7, 42.6, 44.3, 49.6, 50.2, 55.0, 71.8, 72.5, 115.3, 115.4, 129.6, 129.9, 130.0, 132.6, 137.8, 141.4, 145.0, 154.6, 155.9, 159.2, 159.3, 169.3, 169.5, 170.0; MS (FAB) *m*/*z* 947 [$(M + H)^+$]; HRMS (FAB) *m*/*z* calcd for $C_{52}H_{69}N_{10}O_3{}^{64}Zn$ [$(M + H)^+$] 945.4846, found [$(M + H)^+$] 945.4882.

**ROMPsphere-Supported (7,8,12,13,17,18-Hexapropyl-2-(dimethylamino)-3-((4-(bicyclo[2.2.1]hept-5-en-2-ylmethoxy)benzyl)-methylamino)-2-*seco*-2,3-dioxoporphyrazinato)zinc(II) (16)**. *seco*-Porphyrazine **6** (33 mg, 34 mmol) and **7** (225 mg, 2.4 mmol) in $CH_2Cl_2$ (2 mL) were added to a suspension of resin **15b**[23,24] (300 mg) in $CH_2Cl_2$ (2 mL) under $N_2$. The mixture was heated to 50 °C for 18 h, ethyl vinyl ether (3 drops) was added, and the mixture was heated for a further 30 min. The gel was filtered and washed sequentially with $CH_2Cl_2$ and MeOH (3 × 20 mL) and $CH_2Cl_2$ and $Et_2O$ (3 × 20 mL) to leave the ROMPsphere **16** (479 mg, 69% monomer incorporation by weight) as a blue solid: IR (drifts) 1576, 1490, 1197, 1143, 965, 749, 698 cm$^{-1}$; porphyrazine loading 0.049 mmol g$^{-1}$. Anal. Found: C, 86.09; H, 9.49; N, 0.60.

**General Method for Photooxidations.** The substrate (0.074 mmol) in $CDCl_3$ and $CCl_4$ (1:4, 2.5 mL) was cooled to −20 °C, catalyst **16** (15 mg, 0.74 $\mu$mol) was added, and the mixture was irradiated with a 40 W desk lamp for the allocated time. The products were identified from the $^1$H NMR spectra of the crude reaction mixture and comparisons with data for authentic materials. For several endoperoxides (Table 1, entries 2 and 4), filtration and rotary evaporation gave the products without the need for further purification.

**Acknowledgment.** We thank GlaxoSmithKline for a generous endowment (to A.G.M.B.), the Royal Society and the Wolfson Foundation for a Royal Society Wolfson Research Merit Award (to A.G.M.B.), the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Sciences at Imperial College, and the Engineering and Physical Sciences Research Council, the National Science Foundation, and Schering AG for generous support of our studies.

**Note added in proof.** Recently Janda and co-workers have reported the use of a cross-linked polyacrylamide hydrogel-supported hematoporphyrin for the preparation of the endoperoxide from anthracene. See Rogers, C. J.; Dickerson, T. J.; Wentworth, P., Jr.; Janda, K. D. *Tetrahedron*, **2005**, *61*, 12140.

**Supporting Information Available:** General experimental conditions, copies of $^1$H and $^{13}$C NMR spectra for **3**−**6**, and representative $^1$H NMR spectra for endoperoxides and allylic hydroperoxides. This material is available free of charge via the Internet via http://pubs.acs.org.

JO052156T