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The Synthesis and Evaluation of New α-Hydrogen Nitroxides for "Living" Free Radical Polymerization

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Dedication: in honor of the illustrious career of Professor Bernd Giese and his influence on the chemical community

Abstract: Three *N*-alkoxyamines were synthesized for use in Nitroxide Mediated Radical Polymerization. Upon thermolysis, they generate new acyclic α-hydrogen nitroxides: one adamantyl substituted and two diol-containing nitroxides. The initiators were tested in polymerization reactions in direct comparison with the initiator derived from the nitroxide TIPNO.

Key words: nitroxide, nitrone, free radicals, polymers, Grignard reaction

Nitroxide-mediated "living" free radical polymerization (NMRP) has become a very attractive method for the controlled polymerization of olefins, as monomers bearing a wide variety of functionality can be tolerated under the polymerization conditions. The resulting polymers generally display good control over both molecular weight and polydispersity, and the "living" nitroxide endcap allows for the preparation of nanoscopic materials with highly designed architecture.[1] Other "living" radical techniques such as Atom Transfer Radical Polymerization (ATRP) mediated by a metal complex,[2] and Reversible Addition Fragmentation Transfer (RAFT) mediated by a thiocarbonyl intermediate[3] have also been developed. ATRP has the advantage that it can be run at lower temperatures, and it functions well with methacrylates, but amine containing monomers sometimes coordinate to the metal catalyst, interfering with the polymerization process. Polymers made by ATRP contain traces of metal, derived from the metal catalyst. RAFT polymerization is effective with a wider range of monomers, including electron rich vinyl acetates, which are not good substrates for NMRP and ATRP. However sulfur-containing impurities may lead to undesirable colored polymers prepared by the RAFT process. Thus all three methods constitute valuable options in the methodologies available for producing designed polymers using free radical intermediates, yet there is room for improvement. With NMRP, an important achievement would be developing a system that would allow polymerizations to be carried out at temperatures lower than the 105-125° C that are typically employed. The ability to polymerize electron rich olefins in a controlled manner would further extend the versatility of NMRP. For all of these goals, the characteristics of the nitroxide end-cap are key to improving the polymerization profile. Previously, we[4] and the group of Tordo[5] have introduced α-hydrogen nitroxides TIPNO **1** and SG-1 **2**, which are effective in the polymerization of styrenes and a variety of electron poor olefin monomers. Very recently a number of cyclic[6] and acyclic[7] new nitroxides have been introduced for improved efficacy in NMRP. Herein we present work on initiators based on several new acyclic α-hydrogen nitroxides for NMRP, in which the *N*-*t*-butyl has been modified.

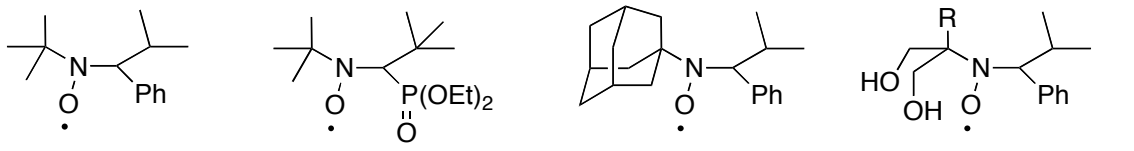
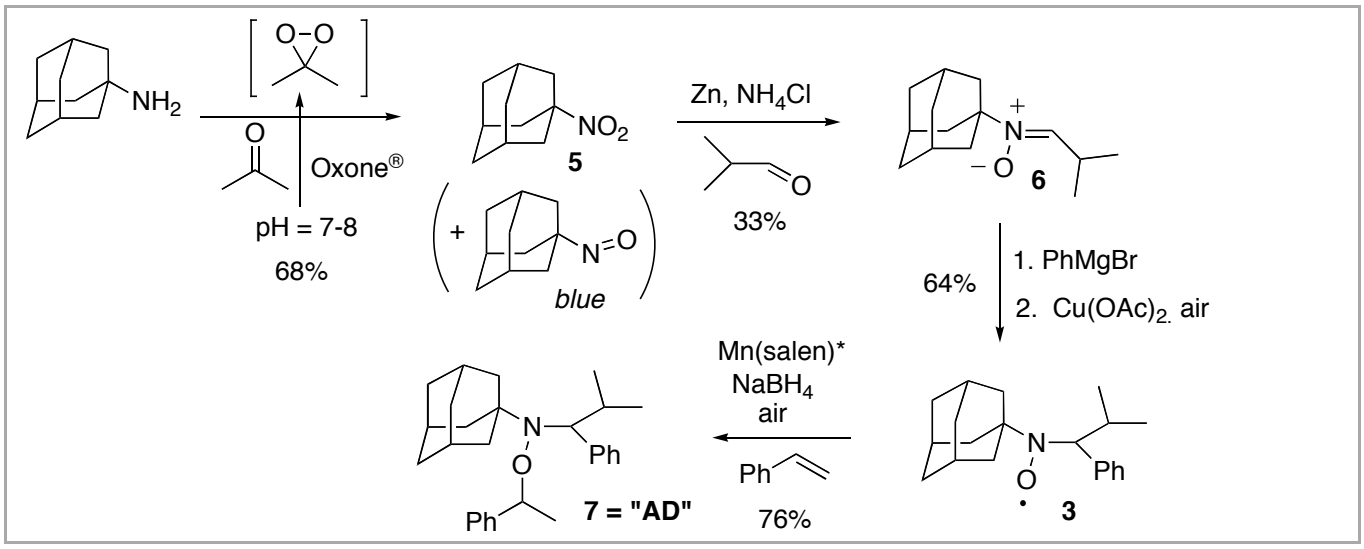


Figure 1

The synthesis of the adamantyl-based nitroxide[8] was initially approached using the methodology previously developed in this laboratory for the preparation of TIPNO **1**.[4] To prepare the starting nitro compound nitroadamantane **5**, oxidation of adamantylamine was carried out by preparing dimethyldioxirane *in situ* from Oxone® and acetone under buffered conditions.[9] This reaction appeared to proceed in reasonable yield, however the product apparently contained the nitroso compound as a contaminate, as indicated by a pale blue tint to the solid product. As the next step involves *in situ* reduction of the nitro compound to the hydroxylamine, it seemed unimportant to remove the nitroso impurity, which is already one oxidation state closer to hydroxylamine than the nitro compound. Thus the crude nitroadamantane was treated with zinc and ammonium chloride in the presence of isobutyraldehyde to give the nitrone **6** in a disappointing 33% yield.



Scheme 1

It is likely that the low yield of nitrone is due to inefficient reduction of nitroadamantane due to the presence of residual oxidizing species derived from Oxone® and

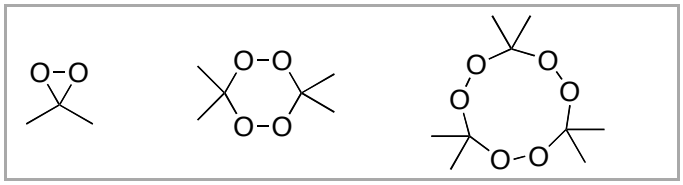
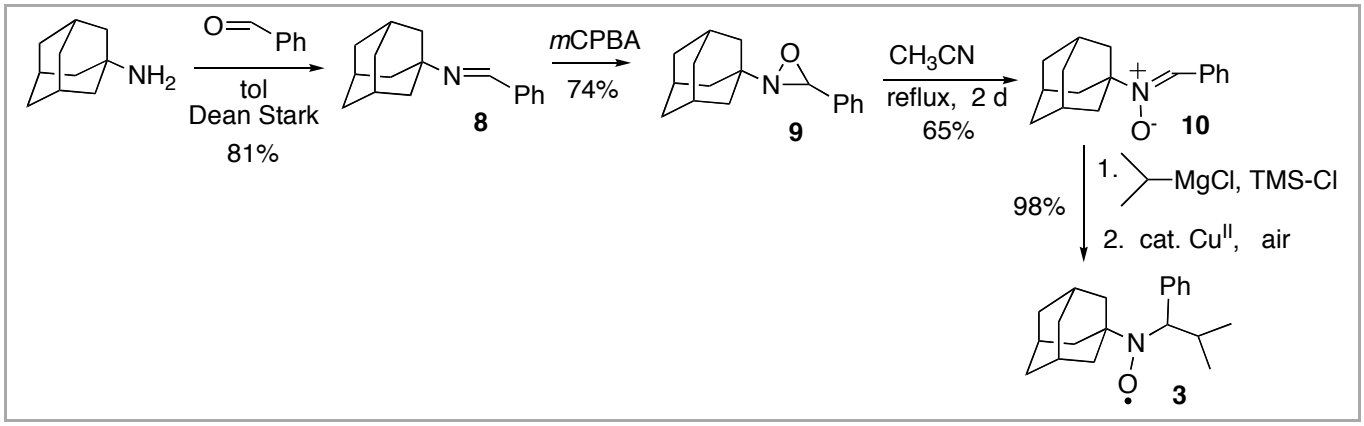


Figure 2

acetone used in the previous step. This is supported by the ^{13}C-NMR spectrum of the nitro compound, which shows three peaks: δ 38.6, 36.0 and 30.2 ppm corresponding to the three contaminants dimethyldioxirane, di-dimethyldioxirane, and tri-dimethyldioxirane.[9] Addition of phenyl Grignard to the nitrone, followed by $Cu^{(II)}$ catalyzed oxidation of the resulting hydroxylamine gave the adamantyl nitroxide **3** in 64% yield. Use of Hawker's manganese catalyzed *N*-alkoxyamine preparation using Jacobsen's catalyst[10] afforded the adamantyl initiator **7,** "**AD"**.

Unsatisfied with the low yields obtained at the beginning of this sequence, an alternative route to the nitrone was developed. Thus the imine **8** produced from the condensation of adamantyl amine and benzaldehyde was oxidized with *m*-chloroperbenzoic acid to prepare the oxaziridine **9**. The nitrone **10** was formed by thermal rearrangement in refluxing acetonitrile.[11a] Rearrangement induced by treatment with Lewis Acid[11b-d] was also examined, however the mild conditions of acetonitrile thermolysis give superior results. Addition of isopropyl Grignard in conjunction with trimethylsilyl chloride followed by copper catalyzed oxidation provided the same adamantyl nitroxide **3** in good yields.



Scheme 2

Polymerizations using this adamantyl initiator **AD 7** were run side-by side with polymerizations using TIPNO derived initiator for direct comparison. The results can be seen in Table 1. Polymerizations with and without added free nitroxide were examined. Addition of free nitroxide did not enhance the polymerization of styrene (St), consistent

with previous observations.[4] In polymerizations using dimethyl acrylamide (DMA), *t*-butyl acrylate (TBA) and *n*-butyl acrylate (NBA), polydispersities were slightly improved by addition of 5% free nitroxide using either initiator. In comparing the two initiators, the results of the polymerization of styrene showed no significant difference, whereas with all three of the other monomers, the new adamantyl initiator generally displayed slightly lower polydispersities and concurrently higher molecular weights of the resulting polymers.

Table 1 Polymerization using Adamantyl Initiator **7** vs. TIPNO-based initiator at 125 °C

Entry	Monomer	Initiator	Added Nitroxide	Equiv. of Monomer	Time (h)	M_w (GPC)	PD (GPC)
1	St	TIPNO	5% BV	1000	20	61,000	1.19
2	St	TIPNO	None	1000	20	69,000	1.20
3	St	AD	5% AD	1000	20	85,000	1.22
4	St	AD	None	1000	20	122,000	1.19
5	DMA	TIPNO	5% TIPNO	1000	19	55,000	1.27
6	DMA	TIPNO	None	1000	19	25,000	1.30
7	DMA	TIPNO	5% TIPNO	200	24	24,000	1.48
8	DMA	AD	5% AD	1000	19	51,000	1.25
9	DMA	AD	None	1000	19	36,000	1.31
10	DMA	AD	5% AD	200	24	27,000	1.19
11	TBA	TIPNO	5% TIPNO	1000	39	46,000	1.18
12	TBA	TIPNO	None	1000	39	53,000	1.22
13	TBA	AD	5% AD	1000	39	84,000	1.17
14	TBA	AD	None	1000	39	111,000	1.17
15	NBA	TIPNO	5% TIPNO	1000	92	115,000	1.36
16	NBA	TIPNO	None	1000	92	115,000	1.42
17	NBA	TIPNO	5% TIPNO	200	16	71,000	1.45
18	NBA	AD	5% AD	1000	92	123,000	1.31
19	NBA	AD	None	1000	92	109,000	1.35
20	NBA	AD	5%AD	200	16	78,000	1.46

St = styrene, DMA = *N,N*-dimethyl acrylamide, TBA = *t*-butyl acrylate, NBA = *n*-butyl acrylate
AD = adamantyl initiator **7**, TIPNO = *N*-*t*-butyl isopropylphenyl nitroxide-based initiator
Note: in some cases, a portion of the monomer was lost during the freeze/pump/thaw procedure.

As TIPNO functions nicely at 125 °C, the real advantage of a new nitroxide-based initiator would be in the ability to conduct polymerizations at milder temperatures. Thus polymerizations at 105 °C were conducted with both TIPNO and the adamantyl initiators (Table 2). At this lower temperature, polymerizations were run for 120 h (5 days). With acrylate monomers, the adamantyl initiator was clearly superior to TIPNO-based initiator, whereas with dimethyl acrylamide, both initiators demonstrated poor control. However, neither initiator showed good control at 105 °C.

Table 2 Polymerization using Adamantyl Initiator **7** vs. TIPNO initiator at 105 °C

Entry	Monomer	Initiator	Added Nitroxide	Time (h)	M_w (NMR)	M_w (GPC)	PD (GPC)
1	DMA	AD	5% AD	120	97,200	13,000	1.99
2	DMA	TIPNO	5% TIPNO	120	95,800	10,300	1.76
3	NBA	AD	5% AD	120	52,600	96,000	1.29
4	NBA	TIPNO	5% TIPNO	120	26,200	28,300	1.15
5	TBA	AD	5% AD	120	119,400	140,000	1.48
6	TBA	TIPNO	5% TIPNO	120	115,500	91,000	1.97

DMA = *N,N*-dimethyl acrylamide, TBA = *t*-butyl acrylate, NBA = *n*-butyl acrylate.
Note: All of these polymerizations were carried out with 1000 equivalents of monomer.

In 1999, we introduced the monohydroxy analogue of TIPNO **11**.[4] It functions slightly better than TIPNO, but the synthesis is not as straightforward, as it requires protection of the hydroxy group by trimethylsilyl or THP[12] during the entire reaction sequence. During polymerization, it is believed that hydrogen bonding between the hydroxy group and the nitroxide oxygen[13] in a six-membered ring **12** stabilizes the nitroxide. This is reflected in a lower BDE of the key carbon-oxygen bond and an associated faster K_d of the *N*-alkoxyamine growing chain-end. There is also a weak contribution by polar ground state effects that destabilize the *N*-alkoxyamine with the addition of hydroxy substituents.[14] Recently Studer[7b] and Hawker[7c] have developed the triol-substituted analogue of TIPNO **13**, with the idea that three hydrogen bonds should be better than one in stabilizing the nitroxide intermediate. This triol initiator does have a lower BDE and faster K_d at 120 °C (BDE = 125.1 kJ/mol, $K_d = 5.6 \times 10^{-3}$ sec^{-1})[14,15] than the TIPNO based initiator (BDE = 129.6 kJ/mol, $K_d = 3.3 \times 10^{-3}$ sec^{-1}),[16,15] and it does indeed function effectively in effecting polymerization at lower temperatures than TIPNO. However, the synthesis requires the use of an ortho ester as a triol protection group, and is somewhat challenging. We felt that the diol analogue would be easier to protect and

deprotect, and would likely afford a similar hydrogen-bonding advantage in lowering the BDE of the *N*-alkoxyamine initiator and macroinitiators during polymerization. Thus we prepared *N*-alkoxyamine initiators based on nitroxide diols **4a** and **4b**. In the latter, the extra steric bulk of the neopentyl phenyl group might also help to lower the BDE to allow for polymerization to proceed at lower temperatures.

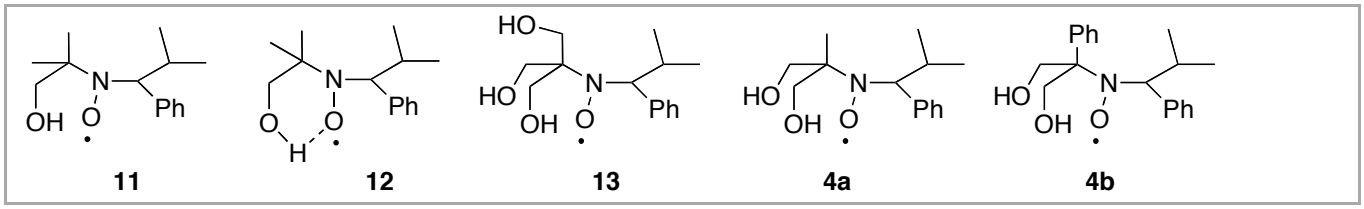
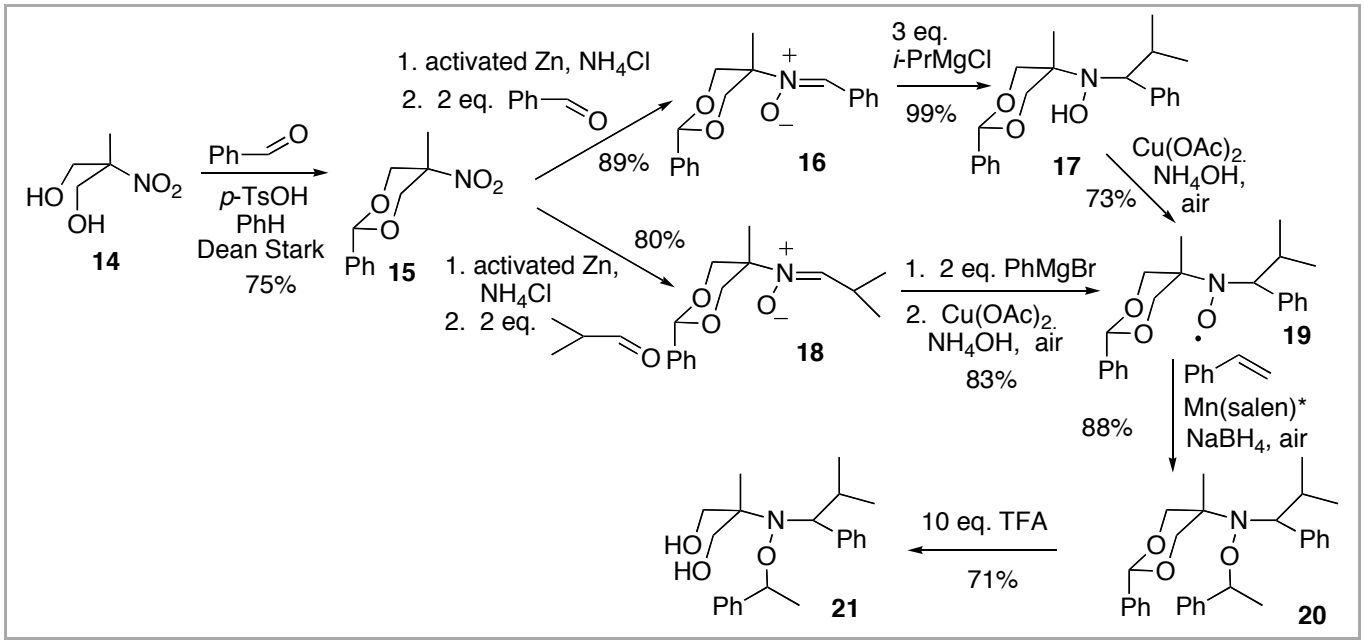


Figure 3

To prepare an initiator based on methyl substituted nitroxide diol **4a**, the hydroxy groups of 2-nitro-2-methyl-1,3-propanediol **14** were protected as acetal **15** using benzaldehyde following the procedure of Piotrowska et al.[17] Although our general procedure for nitrone formation usually involves a one-pot reaction involving reduction of the nitro compound to the hydroxylamine, followed by *in situ* condensation with an aldehyde, with this substrate, a two-step procedure gave superior results. Both benzaldehyde and isobutyroaldehyde were utilized to prepare nitrones **16** and **18**, respectively. Grignard addition followed by Cu^{II} catalyzed air oxidation gave protected diol nitroxide **19**. Conversion to the *N*-alkoxyamine **20**, followed by deprotection with 10 equivalents of trifluoroacetic acid (TFA) gave the diol-Me initiator **21** in 71%. Use of fewer equivalents of TFA resulted in significantly lower yields.



Scheme 3

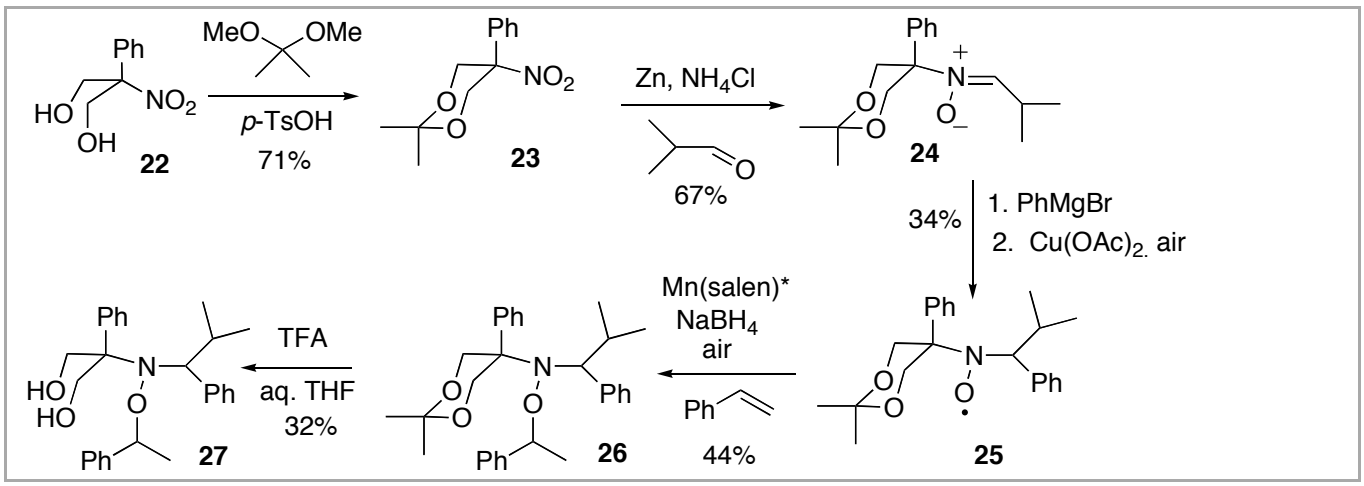
In initial polymerization screens (Table 3), Me-diol initiator **21** showed slightly less control than the TIPNO-based initiator. Since the free nitroxide Me-diol **4a** could not be obtained, 2.5% of the nitroxide TIPNO was added in the *n*-butyl acrylate polymerizations. Although it is clear that nitroxides are free to exchange during the polymerization reaction,[18] any significant excess of free α-hydrogen nitroxide is expected to decompose[19] at 124 °C. Thus incorporation of TIPNO into the growing polymer chains would at most be 2.5%, but is likely significantly less. The role of the added nitroxide is to prevent undesired radical chain termination reactions from occurring at the onset of the polymerization before the Persistent Radical Effect[20] can establish a steady state concentration of free nitroxide. By spiking the polymerization with a small amount of nitroxide, the system is forced to "livingness" and thus to control in the early moments of the polymerization.[21]

Table 3 Polymerizations using Diol Initiator **21** vs. TIPNO-based Initiator

Entry	Initiator	Monomer	Temp. (°C)	Time (h)	M_w (NMR)	M_w (GPC)	PD (GPC)
1	TIPNO	St	124	8	71,000	63,900	1.24
2	21	St	124	8	71,100	62,600	1.27
3	TIPNO	St	90	72	53,400	63,500	1.19
4	21	St	90	72	49,200	69,300	1.25
5	TIPNO*	NBA	124	120	97,600	97,600	1.39
6	21*	NBA	124	8	Not determined	184,000	1.57
7	TIPNO*	NBA	90	140	27,200	25,100	1.42
8	21*	NBA	90	17	95,100	96,600	5.03

NBA = *n*-butyl acrylate, St = styrene
1000 equivalents of Monomer were used.
*In all NBA polymerizations, 2.5% of the nitroxide TIPNO was added.

The second diol starting material, phenyl substituted **22**, was protected as the acetonide, which was then converted to the *N*-alkoxyamine **26** following a similar procedure. Final deprotection using trifluoroacetic acid provided the phenyl substituted *N*-alkoxyamine diol **27**.



Scheme 4

Polymerizations using the diol-Ph initiator **27** (Table 4) showed significantly poorer control than those using the TIPNO-derived *N*-alkoxyamine, particularly with *t*-butyl acrylate and dimethyl acrylamide monomers. This was surprising, as the increased steric bulk of the phenyl group in diol-Ph **4b** compared to the methyl group in diol-Me **4a** was expected to help destabilized the parent *N*-alkoxyamine, and thus lower the BDE.

Table 4 Polymerizations using Diol **27** vs. TIPNO-based Initiator at 124 °C

Entry	Initiator	Monomer	M_w (GPC)	PD (GPC)
1	TIPNO	ST	108,700	1.18
2	27	ST	143,100	1.22
3	TIPNO	NBA	105.100	1.39
4	27	NBA	54,100	1.44
5	TIPNO	TBA	55,200	1.20
6	27	TBA	44,400	2.37
7	TIPNO	DMA	36,800	1.19
8	27	DMA	19,400	1.53

St = styrene, NBA = *n*-butyl acrylate, TBA = *t*-butyl acrylate, DMA = *N,N*-dimethyl acrylamide Note: All of these polymerizations were carried out with 1000 equivalents of monomer for 24 h. No free nitroxide was added.

A clue to the poor behavior of **4b** in polymerizations might be provided by MOPAC calculations of the conformation of nitroxides **4a** and **4b.** Energy minimization predicts the diols to be proximal to the nitroxide oxygen in **4a**, but distal to the nitroxide oxygen in **4b**, preventing H-bonding (Fig. 4).

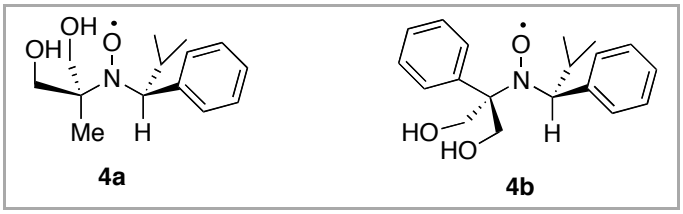


Figure 4

In summary, three novel nitroxides for use in Nitroxide Mediated Radical Polymerization were synthesized. Compared to TIPNO, each contains a modified *t*-butyl group. For adamantyl nitroxide **3**, thermally induced rearrangement of oxaziridine **9** provided a much more efficient route to the requisite nitrone intermediate than our conventional route. The corresponding *N*-alkoxyamines were screened against TIPNO in free radi-

cal polymerizations: **AD 7** performed slightly better than the well-established TIPNO initiator, whereas both diol initiators **21** and **27** were not as effective at controlling free radical polymerization.

Tetrahydrofuran was distilled from sodium/benzophenone. All other reagents were used as received. Flash chromatography was performed using EM Science Silica Gel 60. FTIR spectra were recorded in deuterochloroform solution unless otherwise noted. NMR spectra were recorded at 250-MHz or 500 MHz as specified with tetramethylsilane as internal standard for proton and the $CDCl_3$ triplet as an internal standard for carbon. Mass spectra were obtained on an Electrospray Ionization Time of Flight (ESITOF) mass spectrometer. Melting points are uncorrected.

1-Nitro-adamantane[22] **(5):** Following the general procedure of Murray and Jeyaraman,[9] a suspension of 1-amino-adamantane (5.00 g, 33.1 mmol), acetone (10.3 g, 179 mmol), and 131 ml of a pH=8 phosphate buffer was cooled to 8° C. A solution of Oxone® (48.79 g, 79.4 mmol) in 260 ml H_2O was added dropwise with vigorous stirring while maintaining the pH between 7-8 by careful addition of 6 M aq. KOH. Following the addition of Oxone,® the pH was monitored until stable at ~8, then the reaction was allowed to slowly return to room temperature, and stirred for an additional 20 h. The reaction mixture was then extracted with 4x200 ml of CH_2Cl_2, and the combined extracts were washed with 300 ml saturated NaCl, dried over solid $MgSO_4$, filtered and concentrated under vacuum to give the crude product as a pale blue solid (5.19 g, 87%). This material was used without purification in the next step. The blue color is from a small amount of nitrosoadamantane by-product. If desired, the nitroso compound can be removed chromatographically by elution with hexanes, and the nitro compound can then be obtained by elution with 5:1 hexanes:acetone. M.P. 157-162 °C. TLC: EtOAc, visible by UV, brown with I_2, R_f=0.89.

IR (nujol)**:** 1540, 1342, 1250 cm.$^{-1}$

^{13}C-NMR (63 MHz, $CDCl_3$) δ 84.5, 40.6, 29.5, 35.3 ppm.

***N*-Adamantyl-α-propylnitro n e** (**6**): Crude 1-nitroadamantane **5** (1.3204 g, 7.99 mmol), ammonium chloride (427.9 mg, 8.0 mmol), and isobutyraldehyde (0.38 mL, 7.3 mmol) were suspended in 15 mL of water. Diethyl ether (7.3 mL) was added to dissolve all solids. The solution was cooled to 0° C in an ice bath, and zinc powder (1.9036 g, 29.12 mmol) was added in multiple small portions over the period of 30 min. After stirring for 24 h, the mixture was filtered through Celite, and the filter cake was washed 3 times with 20 mL of diethyl ether. The two-phase filtrate was extracted four times with 50 mL of diethyl ether. The combined organic layers were washed with 100 mL of brine, dried over magnesium sulfate, filtered, and concentrated to give 845.5 mg of crude nitrone. The nitrone was then purified by flash column chromatography (hexanes, 5:1 hexanes: EtOAc, and 5:1 hexanes: acetone) to afford 527.7 mg (32.7%) of **6** as a white solid at room temperature. M.P. 226-235 °C (decomp). TLC: 10:1 EtOAc: methanol, UV detection, R_f = 0.23.

IR (neat): 1583, 1181 cm^{-1}.

^{1}H-NMR (250 MHz, $CDCl_3$) δ = 6.55-6.52 (d, 1H, J = 7.6 Hz), 3.21-3.18 (m, 1H), 2.19 (s, broad, 3H), 2.1 (m, 6H), 1.74-1.69 (m, 6H), 1.07 (d, 6H, J = 7.0 Hz).

^{13}C-NMR (63 MHz, $CDCl_3$) δ = 139.36, 99.29, 68.78, 40.75, 36.06, 29.63, 25.72, 19.10.

1-Adamantyl-3-methyl-2-phenyl-azabutane-1-nitroxide (**3**): Under an atmosphere of nitrogen, *N*-adamantyl-α-propylnitrone **6** (500 mg, 2.26 mmol) was dissolved in 4 mL of anhydrous THF and cooled to 0°; then 1.51 mL of phenylmagnesium bromide (3 M in diethyl ether, 4.52 mmol) was added dropwise over five minutes. The reaction was allowed to stir for 3 h and then quenched with 1.5 mL saturated ammonium chloride solution followed by addition of 10 mL of water to dissolve all solids. The organic layer was separated and the aqueous layer extracted four times with 12.5 mL of diethyl ether. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated, and the residue was treated with a mixture of 11 mL of methanol, 0.90 mL concentrated ammonium hydroxide, and 23.04 mg (0.08 mmol) of copper acetate, producing a yellow solution. A stream of air was bubbled through the mixture until the color changed to dark blue (approximately 20 min). The mixture was dissolved in 15 mL of chloroform, 3 mL concentrated sodium hydrogen sulfate, and 15 mL of water. The organic layer was separated and the aqueous layer extracted with 30 mL chloroform. The organic layers were combined and washed with 20 mL saturated sodium bicarbonate solution, dried over magnesium sulfate, filtered, and concentrated to give 637.7 mg of crude nitroxide. The nitroxide was then purified by flash column chromatography (hexanes to 5:1 hexanes: EtOAc) to afford 432.4 mg (64%) of **3** as an orange oil. TLC 5:1 hexanes: EtOAc, UV detection, R_f = 0.38.

IR (neat): 2906, 2851, 1453, 1306, 1095, 701 cm^{-1}.

HRMS**:** M+ $C_{20}H_{28}NO$ 298.217 calculated; 298.218 observed.

For purposes of characterization, the nitroxide was reduced with phenyl hydrazine in the NMR tube to form the corresponding *N*-hydroxylamine:

^{1}H-NMR (250 MHz, $CDCl_3$ after addition of phenyl hydrazine) δ = 7.25-7.46 (m, 5 H, partially obscured by phenylhydrazine), 3.45 (d, 1H, J=10 Hz), 2.25 (m, 1H), 1.99 (m, 3H), 1.68 (m, 6H), 1.56 (m, 6H), 1.15 (d, 3H, J=6.5 Hz), 0.61 (d, 3H, J=6.5 Hz).

^{13}C-NMR (63 MHz, $CDCl_3$ after addition of phenyl hydrazine) δ = 129.6, 127.3, 126.2, 73.4, 69.6, 39.0, 36.4, 31.0, 29.2, 21.3, 20.2.

***N*-Adamantyl phenyl imine**[23] **(8).** 1-Adamantylamine (2.00 g, 13.23 mmol) was dissolved in 25 mL of toluene and refluxed for a period of 2 h with a Dean-Stark trap to remove residual water. Benzaldehyde (14.04 g, 132.30 mmol) was added and the mixture was refluxed with a Dean-Stark trap for 18 h. The reaction was allowed to cool to room temperature and magnesium sulfate was added to remove any residual water. The mixture was filtered and most of the excess benzaldehyde was removed under vacuum. The product was obtained as 3.35 g of a slightly yellow wet solid contaminated with 24% benzaldehyde as indicated by ^{1}H-NMR (81% yield). TLC: CH_2Cl_2, visible in UV, no stain with I_2, R_f = 0.60.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 8.29 (s, 1H), 7.73-7.77 (m, 2H), 7.38-7.41 (m, 3H), 2.17 (broad s, 3H), 1.82 (d, 6H, J = 2.8 Hz), 1.74 (broad s, 6H).

***N*-Adamantyl-phenyl-oxaziradine (9).** *N*-Adamantyl phenyl imine **8** (3.00 g, 12.53 mmol) was dissolved in a minimum amount of chloroform and chilled in an ice bath. A solution of *m*-chloroperbenzoic acid (3.71 g of 70% mCPBA, 15.04 mmol) in 120 mL chloroform was dried over magnesium sulfate, and then added drop-wise with vigorous stirring over a period of 1.5 h. The reaction mixture was stirred at 0 °C for 3 h and then filtered through a plug of basic alumina. The filtrate was washed with a 50 mL portion of a saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo* to give 2.61 g of a light orange wet solid. ^{1}H-NMR indicated that the product was contaminated with 9 % benzaldehyde, resulting in a final yield of 74%. A very pure sample was obtained by recrystallization from pentane. M.P. 62-66 °C. TLC: CH_2Cl_2, visible in UV, R_f = 0.80.

IR: ($CDCl_3$) 3156, 2906, 1794, 1456, 1396, 1308, 1256, 1084 cm.$^{-1}$

^{1}H-NMR ($CDCl_3$, 500 MHz): δ =7.34-7.50 (m, 5H), 4.93 (s, 1H), 2.15 (broad s, 3H), 1.79 (broad s, 6H), 1.70 (broad s, 6H) ppm.

^{13}C-NMR (CDCl3, 63 MHz): δ = 135.8, 129.6, 128.4, 127.4, 72.3, 58.4, 38.7, 36.5, 29.1 ppm.

***N*-Adamantyl-α-phenylnitrone**[8b] **(10).** *N*-Adamantyl-α-phenyl-oxaziridine **9** (0.114 g, 0.45 mmol) was dissolved in 10 mL acetonitrile. The mixture was refluxed for 48 hours. It was concentrated in vacuo, and the crude product was purified by flash column chromatography using 16:1 (hexanes/ EtOAc) to give 0.074 g (65% yield) of an amber colored solid. TLC: 1:1 hexanes:EtOAc, UV, R_f = 0.59.

^{1}H-NMR (250 MHz, $CDCl_3$) δ = 8.24 (m, 2H), 7.43 (s, 1H), 7.37-7.40 (m, 3H), 2.25 (s, 3H), 2.20 (s, 6H), 1.73 (s, 6H).

^{13}C-NMR (125 MHz): δ = 131.2, 130.1, 129.6, 129.0, 128.5, 70.9, 40.1, 36.1, 29.9.

HRMS: (M + 1) $C_{17}H_{21}NO$ calcd: 256.16959; observed: 256.16791.

1-Adamantyl-3-methyl-2-phenyl-azabutane-1-nitroxide (3). *N*-adamantyl-α-phenylnitrone **10** (0.2 g, 0.78 mmol) was dissolved in 5 mL THF and the mixture was cooled to 0° C in an ice-bath. Distilled trimethylsilyl chloride (0.2 mL, 1.56 mmol) was added, and the mixture was allowed to stir for 5 minutes. *Iso*-propyl magnesium chloride (1.18 mL, 2.35 mmol) was then added, and the mixture was stirred at room temperature for 2 hours. To decompose the excess Grignard reagent, 5 mL of concentrated ammonium chloride was added, followed 15 mL of deionized water. The organic layer was separated and extracted with 25 mL diethyl ether. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo to give an orange oil. This product was purified by flash column chromatography using 16:1 hexanes/ EtOAc to yield 0.1523 g of product. This was collected was dissolved in 5 mL of THF and $Cu(OAc)_2$ (3.64 mg, 0.02 mmol), and 2 drops concentrated ammonium hydroxide were added to give a pale yellow-green solution. Methanol was added drop wise until the copper compound dissolved. Air was bubbled through the solution for about 30 minutes, but only a slight color change was observed: from pale yellow-green to a pale forest green. The reaction was concentrated, 5 mL chloroform and 5 mL of aqueous potassium hydrogen sulfate and 3 mL of deionized water were added. The organic layer was separated, washed with 5 mL concentrated sodium bicarbonate solution, dried over magnesium sulfate, filtered, and concentrated in vacuo to give 0.117 g (98% yield) of an orange oil. Treatment of a small sample with phenylhydrazine in an NMR tube gave a sample identical to that formed by the alternative method above.

1-Adamantyl-3-methyl-1-(1´-phenylethoxy)-2-phenyl-1-azabutane "AD" (7): To a solution of styrene (302.04 mg, 2.90 mmol) and 1-adamantyl-3-methyl-2-phenyl-azabutane-1-nitroxide, **3**, (432.4 mg, 1.45 mmol) in 1:1 toluene: ethanol (11 mL) was added [*N, N*-bis- (3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato] manganese(II) chloride (184.21 mg, 0.29 mmol) followed by sodium borohydride (164.56 mg, 4.35 mmol). The reaction mixture was stirred for 48 h, evaporated to dryness, and partitioned between dichloromethane (11 mL) and water (15 mL). The aqueous layer was extracted three times with 10 mL of dichloromethane and the organic layers were combined and evaporated to dryness to provide 493.2 mg of crude product, which was purified twice by flash column chromatography (hexanes followed by 16:1 hexanes: EtOAc) to give 421.1 mg (76.5%) of **7** as a thick, colorless oil, as a mixture of two diastereomers. TLC: 16:1 hexanes: EtOAc, UV detection, R_f = 0.81.

IR ($CDCl_3$): 2852, 1453, 1383, 1061 cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$) Major Diastereomer: δ = 7.53-7.02 (m, 10H), 4.93 (m, 1H), 3.55 (d, 1H, J=11.0 Hz), 2.37 (m, 1H), 2.05 (m, 3H), 1.83 (m, 6H), 1.61 (m, 6H), 1.61 (d, 3H, J= 7.0 Hz), 1.33 (d, 3H, J=6.0 Hz), 0.58 (d, 3H, J=6.0Hz); Minor Diastereomer: δ 7.53-7.02 (m, 10H), 4.93 (m, 1H), 3.44 (d, 1H, J=10.5 Hz), 2.05 (m, 3H), 1.83 (m, 6H), 1.68 (d, 3H, J= 7.0 Hz), 1.61 (m, 6H), approx. 1.4 (m, 1H [note: this $CH_{isopropyl}$ is buried]), 0.95 (d, 3H, J=6.5 Hz), 0.22 (d, 3H, J=6.0 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$) (major + minor diastereomers) δ = 146.0, 145.2, 143.2, 143.0, 131.2, 131.1, 128.22, 128.18, 127.5, 127.4, 127.3, 127.2, 126.8, 126.5, 126.4, 126.2, 83.8, 83.1, 70.65, 70.60, 61.4, 61.3, 40.9, 40.6, 37.0, 36.8, 32.3, 31.9, 30.1, 29.9, 24.8, 23.4, 22.4, 22.2, 21.4, 21.3.

HRMS**:** M+1 ($C_{28}H_{38}NO$) 404.295 calcd; 404.294 observed.

5-Methyl-5-nitro-2-phenyl-1,3-dioxane (15). Following the procedure of Piotrowska,[17] benzaldehyde (0.2124 g, 2.0 mmol), 2-methyl-2-nitro-propane-1,3-diol (0.2702 g, 2.0 mmol) and *p*-toluenesulphonic acid were heated in benzene (5 mL) with a Dean Stark trap until no further water was produced. After cooling, the reaction mixture was washed with saturated sodium bicarbonate solution (3x10 mL), dried over magnesium sulfate and filtered. After the product was concentrated *in vacuo*, the crude product was recrystallized with cold EtOH to give 0.3337 g (75%) of the product **15** as a white solid. M.P. 119-120 °C (recryst. from EtOH, Literature m.p.121-122 °C). TLC: 3:10 EtOAc:hexanes, UV, *p*-anisealdhyde, R_f = 0.52.

IR ($CDCl_3$): 3006, 2944, 2902, 1554 (NO_2), 1226 (C-O), 1111 (C-O) cm^{-1}.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.50-7.30 (m, 10H, Ar*H*), 5.52 (s, 1H, N-C*H*Ph), 4.99 (d, *J* = 12.0, Hz, 2H, CH_2O), 3.94 (d, *J* = 12.0, Hz, 2H, CH_2O), 1.44 (s, 3H, CH_3).

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 136.7 (C_q of Ar), 129.4 (*C*H of Ar), 128.3 (2x*C*H of Ar), 126.1 (2x*C*H of Ar), 101.7 (*C*HPh), 82.8 (*C*($CH_2O)_2$), 71.6 (2x*C*H_2O), 19.4 (*C*H_3).

***N*-(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-phenylnitrone (16).** Zinc powder was activated by washing sequentially with 5% HCl x 3, H_20 x 3, MeOH x 3, and Et_2O x 3 in a Büchner funnel, and then dried under vacuum. To a flask containing 5-methyl-5-nitro-2-phenyl-1,3-dioxane 15 (0.4465 g, 2.0 mmol) in EtOH (15 mL) was added a solution of NH_4Cl (0.1177 g, 2.2 mmol) in H_2O (5.0 mL) and then 15 mL of THF was added until all solids dissolved. Activated zinc powder (0.5230 g, 8.0 mmol) was added over a period of 15 min. with stirring. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h. The zinc salts were filtered off and washed with hot 95% EtOH (20 mL) and hot $CHCl_3$ (20 mL). The filtrate was concentrated to 5 mL *in vacuo* and used directly in next step. Benzaldehyde (0.4248 g, 4.0 mmol)) was added, and the reaction mixture was refluxed for 2 h. After concentration by rotary evaporation, the residue was extracted with CH_2Cl_2 (3x20 mL). The combined organic layers was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (hexane → 7:10 EtOAc/hexane as eluent) gave 0.4662 g (89%) of product 16 as a white solid. M.P. (recryst. from EtOH) 149-150 °C (Literature[24] m.p. = 150-152 °C). TLC: 4:5 EtOAc:hexanes, UV, *p*-anisealdhyde, R_f = 0.22.

IR ($CDCl_3$): 2964, 2905, 2867, 1643, 1563 (C=N), 1266 (C-O), 1223 (C-O) cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.37-8.34 (m, 2H, Ar*H*), 8.07 (s, 1H, N=C*H*), 7.46-7.26 (m, 8H, Ar*H*), 5.61 (s, 1H, C*H*Ph), 4.82 (d, *J* = 12.8, Hz, 2H, CH_2O), 4.02 (d, *J* = 12.8, Hz, 2H, CH_2O), 1.45 (s, 3H, CH_3).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 137.3 (C_q of Ar), 134.9 (N=*C*H), 131.0 (C_q of Ar), 130.6 (*C*H of Ar), 129.5 (3x*C*H of Ar), 128.6 (2x*C*H of Ar), 128.5 (2x*C*H of Ar), 126.3 (2x*C*H of Ar), 102.5 (*C*HPh), 72.4 (2x*C*H_2O), 68.5 ($CH_3C(CH_2O)_2$), 19.5 (*C*H_3).

***N*-(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-*N*-(2-methyl-1-phenyl-propyl)-nitroxide (19).** *N*-(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-phenylnitrone 16 (0.5048, 1.92 mmol) was dissolved in THF (20 mL) and the solution cooled to 0 °C. A 2.0 M solution of *iso*-propylmagnesium chloride (2.9 mL, 5.76 mmol) in THF was added by syringe over 5 min. The mixture was allowed to warm to room temperature. After 16 h, excess Grignard reagent was decomposed by the addition of concentrated NH_4Cl solution (5 mL) followed by water (10 mL) until all solids had dissolved. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3x10 mL). The organic layers were combined, dried over magnesium sulfate, and filtered. Removal of solvent *in vacuo* gave hydroxylamine 17 in 0.6528 g (99%). This hydroxylamine 17 was treated with a mixture of MeOH (10 mL), concentrated NH_4OH (0.3 mL) and $Cu(OAc)_2H_2O$ (0.0192 g, 0.10 mmol) to give a pale yellow solution. A steam of air was bubbled through the yellow solution until it became dark blue (5-10 min). This mixture was concentrated and the residue dissolved in a mixture of $CHCl_3$ (10 mL), concentrated $NaHSO_4$ solution (5 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3x10 mL). The organic layers were combined, washed with saturated sodium bicarbonate solution (10 mL), dried over magnesium sulfate and filtered. The filtrate was concentrated *in vacuo* to give the crude product. Purification by flash column chromatography (hexane → 1:10 EtOAc/hexane eluent) provided nitroxide 19 in 0.0.4769 g (73%) as an orange solid. M.P. 116-117 °C. TLC: 3:10 EtOAc:Hexanes, UV, *p*-anisealdhyde, R_f= 0.41.

IR ($CDCl_3$): 2984, 2902, 1561 (N-O), 1469 (N-O), 1366 (N-O), 1225 (C-O), 1093 (N-O) cm^{-1}.

LRMS: m/z (%relative intensity) 364 (M^+ +Na +H, 25), 364 (M^+ + Na, 100), 341 (M^++H, 65), 310 (25), 298 (20), 235 (38).

^{1}H-NMR (250 MHz, $CDCl_3$, in the presence of phenylhydrazine): δ = 7.60-7.20 (m, 10H, 2xAr*H*), 5.51 (s, 1H, C*H*Ph), 4.90 (br s, 1H, O*H*), 4.45 (d, *J* = 12.5 Hz, 1H, C*H*$_2$O), 4.35 (d, *J* = 12.5 Hz, 1H, C*H*$_2$O), 3.64 (d, *J* = 12.5 Hz, 1H, C*H*$_2$O), 3.60 (d, *J* = 12.5 Hz, 1H, C*H*$_2$O), 3.36 (d, *J* = 11.8 Hz, 1H, N-C*H*Ph), 2.50-2.30 (m, 1H, C*H*$(CH_3)_2$), 1.34 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.65 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.32 (s, 3H, C*H*$_3$).

^{13}C-NMR (63 MHz, $CDCl_3$, in the presence of phenylhydrazine): δ = 142.2 (C_q of Ar), 138.3 (C_q of Ar), 129.7 (*C*H of Ar), 129.1 (2x*C*H of Ar), 127.9 (2x*C*H of Ar), 126.9 (*C*H of Ar), 126.4 (2x*C*H of Ar), 102.2 (*C*HPh), 74.2 (N-*C*HPh), 72.8 (*C*H$_2$O), 70.6 (*C*H$_2$O), 58.3 ($CH_3C(CH_2O)_2$), 31.9 *C*H$(CH_3)_2$), 21.5 (*C*H$_3$), 20.6 (CH(*C*H$_3$)$_2$), 14.0 (CH(*C*H$_3$)$_2$).

HRMS (after treatment with phenylhydrazine): Molecular ion calcd for $C_{21}H_{26}NO_3$ (M^++H): 342.20637; found: 342.20825.

5-Methyl-2-phenyl-*N*-(*iso*-propylen)-1,3-dioxan-5-amin-*N*-oxide (18). Following the procedure outline above for the formation of the nitrone 16, 2-phenyl-5-methyl-5-nitro-1,3-dioxane 15 (0.1756 g, 0.8 mmol), activated zinc (0.2057 g, 3.2 mmol), NH_4Cl (0.0463 g, 0.9 mmol) and isobutyraldehyde (0.1134 g, 1.6 mmol) were employed. The reaction mixture was stirred at room temperature overnight (16 h). Purification with flash column chromatography (hexane → EtOAc → 1:5 MeOH/EtOAc as eluent) gave product 18 in 0.1657 g (80%) as a white solid. M.P. 115-116 °C. TLC: 1:5 MeOH:EtOAc, UV, *p*-anisealdhyde, R_f= 0.29.

IR ($CDCl_3$): 2977, 2902, 2869, 1563 (C=N), 1468 (N-O), 1364 (N-O), 1266 (C-O), 1223 (C-O) 1101 (C-O) cm^{-1}.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 5H, Ar*H*), 7.14 (d, *J* = 7.3 Hz, 1H, N=C*H*), 5.52 (s, 1H, C*H*Ph), 4.67 (d, *J* = 12.5 Hz, 2H, C*H*$_2$O), 3.90 (d, *J* = 12.5 Hz, 2H, C*H*$_2$O), 3.35-3.27 (m, 1H, C*H*$(CH_3)_2$), 1.43 (s, 3H, C*H*$_3$), 1.16 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$).

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 145.3 (N=*C*H), 137.3 (C_q of Ar), 129.4 (*C*H of Ar), 128.4 (2x*C*H of Ar), 126.2 (2x*C*H of Ar), 102.2 (*C*HPh), 71.9 (2x*C*H$_2$O), 66.7 ($CH_3C(CH_2O)_2$), 26.3 *C*H$(CH_3)_2$), 19.13 (*C*H$_3$), 19.10 (CH(*C*H$_3$)$_2$).

LRMS: m/z (%relative intensity) 286 (M^+ + Na, 40), 264 (M^+ + H, 70), 158 (20), 102(100).

HRMS: Molecular ion calcd for $C_{15}H_{21}NO_3$ (M^++H): 264.15942; found: 264.15799.

Alternate Procedure for *N*-(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-*N*-(2-methyl-1-phenyl-propyl)-nitroxide (19). According to the procedure described above, 5-methyl-2-phenyl-*N*-(*iso*-propylene)-1,3-dioxan-5-amin-*N*-oxide 18 (0.0511 g, 0.19 mmol), phenylmagnesium bromide (3.0 M in Et_2O, 0.13 mL, 0.38 mmol), $Cu(OAc)_2H_2O$ (0.0020 g, 0.0097 mmol), THF (2 mL), MeOH (3 mL) and concentrated NH_4OH (0.1 mL) were employed. Purification by flash column chromatography (hexane → 1:10 EtOAc/hexane as eluent) yielded the same nitroxide 19 in 0.0545 g (83%) as an orange solid.

***N*-(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine (20).** To a solution of styrene (0.2916 g, 2.8 mmol) and *N*-(5-methyl-2-phenyl-[1,3]dioxan-5-yl)-*N*-(2-methyl-1-

phenyl-propyl)-nitroxide 19 (0.4769 g, 1.4 mmol) in 1:1 toluene/EtOH (15 mL) was added (R,R)-Jacobsen's catalyst (0.1779 g, 0.28 mmol) and $NaBH_4$ (0.1589 g, 4.2 mmol). The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated *in vacuo* to dryness and filtered through a plug of silica gel using EtOAc as the eluent. The filtrate was concentrated and the residue was purified by flash column chromatography (hexane → 2:5 CH_2Cl_2/hexane as eluent) to give desired product 20 in 0.3009 g (88%) as a colorless oil as a 1:1 mixture of diastereomers. TLC: 1:10 EtOAc:Hexanes, UV, *p*-anisealdhyde, R_f= 0.36.

IR ($CDCl_3$): 3025, 2931, 2959, 2869, 1602, 1560 (N-O), 1469 (N-O), 1281 (C-O), 1100 (C-N) cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$, two diastereomers 1:1): δ = 7.70-7.05 (m, 30H, Ar*H*), 5.60 (s, 1H, C*H*Ph), 5.42 (s, 1H, C*H*Ph), 5.21 (q, *J* = 6.5 Hz, 1H, CH_3C*H*Ph), 5.17 (q, *J* = 6.5 Hz, 1H, CH_3C*H*Ph), 4.56-4.39 (m, 4H, CH_2O), 3.72-3.49 (m, 4H, CH_2O), 3.45 (d, *J* = 11.5 Hz, 1H, N-C*H*Ph), 2.98 (d, *J* = 12.5 Hz, 1H, N-C*H*Ph), 2.26-2.24 (m, 1H, C*H*(CH_3)$_2$), 1.68 (d, *J* = 6.5 Hz, 3H, CH_3CHPh), 1.61 (d, *J* = 6.5 Hz, 3H, CH_3CHPh), 1.50 (d, *J* = 6.0 Hz, CH(CH_3)$_2$), 1.14 (d, *J* = 6.0 Hz, CH(CH_3)$_2$), 0.60 (d, *J* = 6.5 Hz, 3H, CH(CH_3)$_2$), 0.60 (d, *J* = 6.5 Hz, 3H, CH(CH_3)$_2$), 0.45 (s, 3H, CH_3), 0.29 (d, *J* = 6.5 Hz, 3H, CH(CH_3)$_2$).

^{13}C-NMR (125 MHz, $CDCl_3$, two diastereomers 1:1): δ = 144.8 (C_q of Ar), 144.2 (C_q of Ar), 142.5 (C_q of Ar), 142.2 (C_q of Ar), 139.0 (C_q of Ar), 138.7 (C_q of Ar), 129.1 (*C*H of Ar), 128.8 (*C*H of Ar), 128.5 (2x*C*H of Ar), 128.4 (5x*C*H of Ar), 128.2 (2x*C*H of Ar), 127.8 (2x*C*H of Ar), 127.7 (2x*C*H of Ar), 127.4 (*C*H of Ar), 127.0 (2x*C*H of Ar), 126.9 (3x*C*H of Ar), 126.8 (5x*C*H of Ar), 126.6 (*C*H of Ar), 126.1 (2x*C*H of Ar), 102.7 (*C*HPh), 102.6 (*C*HPh), 83.7 (O-*C*HPh), 82.8 (O-*C*HPh), 74.8 (*C*H_2O), 74.6 (*C*H_2O), 74.3 (*C*H_2O), 71.9 (N-*C*HPh), 71.7 (N-*C*HPh), 59.6 (CH_3C(CH_2O)$_2$), 59.3 (CH_3C(CH_2O)$_2$), 32.5 *C*H(CH_3)$_2$), 31.9 *C*H(CH_3)$_2$), 24.9 (*C*H_3), 23.5 (*C*H_3), 22.2 (*C*H_3), 22.0 (*C*H_3), 21.2 (2x*C*H_3), 15.1 (CH_3), 15.0 (CH_3).

LRMS: m/z (%relative intensity) 468 (M^+ + Na, 14), 446 (M^+ + H, 23), 365 (20), 337 (16), 314 (22), 102 (100).

HRMS: Molecular ion calcd for $C_{29}H_{35}NO_3$ (M^++H): 446.26897; found: 446.26389.

2-Methyl-2-[(2-methyl-1-phenyl-propyl)-(1-phenyl-ethoxy)-amino]-propane-1,3-diol (21). To a solution of *N*-(5-methyl-2-phenyl-[1,3]dioxan-5-yl)-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine 20 (0.5661 g, 1.27 mmol) in THF (8 mL) and H_2O (2 mL) was added trifluoroacetic acid (0.94 mL, 12.7 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and then refluxed (66 °C) overnight. After quenching with saturated sodium bicarbonate solution (10 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x10 mL). The organic layers were combined, washed with saturated sodium bicarbonate solution (3x5 mL), dried with magnesium sulfate and filtered. Removal of volatiles *in vacuo* followed by flash column chromatography (hexane → 3:10 EtOAc/hexane eluent) gave 0.3238g (71%) of product 21 as colorless oil as a mixture of two diastereomers. The proton NMR spectrum was complex: D_2O exchange removed the coupling from the hydroxy protons, giving a somewhat simplified spectrum. TLC: 2:5 EtOAc:Hexanes, UV, *p*-anisealdhyde, R_f= 0.29.

IR ($CDCl_3$): 3539 (O-H), 2982, 2902, 1602, 1561 (N-O), 1469 (N-O), 1223 (C-O), 1094 (C-N), 1052 (C-O) cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$, with addition of D_2O, two diastereomers): δ = 7.60-7.10 (m, 20H, Ar*H*), 4.97 (q, *J* = 6.5 Hz, 1H, O-C*H*Ph major isomer), 4.93 (q, *J* = 6.5 Hz, 1H, O-C*H*Ph minor isomer), 3.86 (d, AB-system, *J* = 11.5 Hz, 2H, CH_2OH minor isomer), 3.70 (d, AB-system, *J* = 11.5 Hz, 2H, CH_2OH minor isomer), 3.57 (d, AB-system, *J* = 12.0 Hz, 2H, CH_2OH minor isomer), 3.55 (d, AB-system, *J* = 12.0 Hz, 2H, CH_2OH minor isomer), 3.48 (d, AB-system, *J* = 11.5 Hz, 1H, CH_2OH major isomer), 3.40 (d, AB-system, *J* = 11.5 Hz, 1H, CH_2OH major isomer), 3.31 (d, AB-system, *J* = 11.5 Hz, 1H, N-C*H*Ph minor isomer), 3.30 (d, *J* = 10.0 Hz, 1H, N-C*H*Ph major isomer), 3.02 (d, AB-system, *J* = 11.5 Hz, 1H, CH_2OH major isomer), 2.92 (d, AB-system, *J* = 11.5 Hz, 1H, CH_2OH major isomer), 2.50-2.38 (m, 1H, C*H*(CH_3)$_2$ major isomer), 1.69 (d, *J* = 6.5 Hz, 3H, CH_3CHPh major isomer), 1.61 (d, *J* = 6.5 Hz, 3H, CH_3CHPh minor isomer), 1.56-1.43 (m, 1H, C*H*(CH_3)$_2$ minor isomer), 1.40 (d, *J* = 6.5 Hz, CH(CH_3)$_2$ major isomer), 0.90 (d, *J* = 6.5 Hz, CH(CH_3)$_2$ minor isomer), 0.89 (s, 3H, CH_3 major isomer), 0.60 (d, *J* = 6.5 Hz, 3H, CH(CH_3)$_2$ major isomer), 0.52 (s, 3H, CH_3 minor isomer), 0.25 (d, *J* = 6.5 Hz, 3H, CH(CH_3)$_2$ minor isomer).

^{13}C-NMR (125 MHz, $CDCl_3$, two diastereomers): δ = 143.7 (C_q of Ar), 143.6 (C_q of Ar), 141.5 (C_q of Ar), 141.0 (C_q of Ar), 130.5 (*C*H of Ar), 128.8 (3x*C*H of Ar), 128.5 (2x*C*H of Ar), 128.3 (2x*C*H of Ar), 128.0 (2x*C*H of Ar), 127.9 (3x*C*H of Ar), 127.2 (2x*C*H of Ar), 127.0 (2x*C*H of Ar), 126.6 (3x*C*H of Ar), 84.0 (O-*C*HPh), 83.7 (O-*C*HPh), 72.8 (N-*C*HPh), 72.4 (N-*C*HPh), 68.7 (*C*H_2O), 68.4 (*C*H_2O), 67.7 (*C*H_2O), 67.4 (*C*H_2O), 66.9 (CH_3C(CH_2O)$_2$), 66.0 (CH_3C(CH_2O)$_2$), 32.1 *C*H(CH_3)$_2$), 31.5 *C*H(CH_3)$_2$), 23.7 (*C*H_3), 23.2 (*C*H_3), 22.1 (*C*H_3), 22.0 (*C*H_3), 21.4 (*C*H_3), 21.0 (CH_3), 18.7 (CH_3), 17.0 (CH_3).

LRMS: m/z (%relative intensity) 380 (M^+ + Na, 48), 359 (M^+ + 2H, 24), 358 (M^++H, 100), 275 (13), 254 (5), 226 (14), 133 (27), 102 (56).

HRMS: Molecular ion calcd for $C_{22}H_{31}NO_3$ (M^++H): 358.23766; found: 358.23438.

2,2-Dimethyl-5-nitro-5-phenyl-[1,3]-dioxane (23). To a solution of 2-nitro-2-phenylpropane-1,3-diol 22 (5.21 g, 26.4 mmol) and *para*-toluenesulfonic acid monohydrate (5.02 g, 26.4 mmol) in THF (25 ml) with 4 Å activated molecular sieves (5 g), was added 2,2-dimethoxypropane (11.0 g, 106 mmol) over 10 minutes with stirring. The reaction mixture was refluxed for 12 h, quenched with 100 ml of water and extracted with dichloromethane (3 x 100 ml). The combined organic layers were dried with magnesium sulfate, filtered and concentrated *in vacuo* to give a white resin. Flash chromatography (1:1 hexanes/EtOAc) afforded 4.45 g of a white solid (71% yield). M.P. 95 °C. TLC: 1:1 hexanes:EtOAc, UV, R_f = 0.42.

IR (CDCl3): 2902, 1557, 1450, 1376, 1348, 1136, 1093 cm^{-1}.

^{1}H-NMR (250 MHz, CDCl3): δ = 7.4-7.3 (m, 5H), 5.0 (d, *J* = 14.4 Hz, 2H), 4.3 (d, *J* =14.4 Hz, 2H), 1.5 (s, 3H), 1.4 (s, 3H) ppm.

^{13}C-NMR (63 MHz, CDCl3): δ = 133.1, 130.2, 129.4, 125.1, 98.8, 87.1, 64.5, 28.2, 18.8 ppm.

2,2-Dimethyl-5-nitrone-*N*-(2-methyl-1-propene)-5-phenyl-[1,3]-dioxane (24). To 2,2-dimethyl-5-nitro-5-phenyl-[1,3]-dioxane 23 (5.339 g, 22.5 mmol) was added isobutyraldehyde (3.245 g, 4.09 mL, 45.0 mmol) and ammonium chloride (1.324 g, 24.75 mmol) in H_2O (40 mL) and ether (13 mL). Zn powder (5.88 g, 90.0 mmol) was added batchwise over 20-25 min at 0 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The solution was filtered and the zinc residues were washed with CH_2Cl_2. The solution was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product nitrone 24 was purified by flash chromatography (1:2 hexanes:EtOAc) yielding 4.1903 g (67%) of oil. TLC: 1:1hexanes: EtOAc, UV, R_f = 0.16.

IR (CDCl3): 2942, 1698, 1556, 1450, 1375, 1308, 1151, 1091, 972 cm^{-1}.

^{1}H -NMR (250 MHz, CDCl3): δ = 7.5-7.2 (m, 5H), 7.0 (d, *J* = 7.5 Hz, 1H), 4.5 (AB system, *J*=13.5 Hz, 2H), 3.9 (AB system, *J*=13.5 Hz, 2H), 3.3 (m, 1H), 1.5 (s, 3H), 1.4 (s, 3H) 1.2 (d, *J* = 6.8 Hz, 6H) ppm.

^{13}C-NMR (63 MHz, CDCl3): δ = 147.2, 140.0, 128.8, 128.0, 125.6, 99.2, 98.4, 69.6, 28.8, 19.2, 18.4 ppm.

LRMS: 486.4, 485.4, 292.3, 278.2, 264.2, 209.2, 208.2, 150.16 amu.

2,2-Dimethyl-5-nitroxide-*N*-(2-methyl-1-phenyl-propyl)-5-phenyl-[1,3]-dioxane (25). To 2,2-dimethyl-5-nitrone-*N*-(2-methyl-1-propene)-5-phenyl-[1,3]-dioxane 24 (1.40 g, 5.05 mmol) and 5 mL THF was added phenylmagnesium bromide ((3.4 ml, 10.1 mmol)) dropwise over 5 minutes at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. Excess Grignard was quenched with 7 mL of saturated NH_4Cl solution. To this was added 5 mL H_2O and the aqueous layer was extracted with $CHCl_3$ (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was dissolved in 20 mL of MeOH and 0.7 mL of concentrated NH_4OH, and copper acetate monohydrate (51 mg, 0.253 mmol) was added with stirring. Air was bubbled into the solution for 30-40 minutes, and then the solution was concentrated *in vacuo*. To this was added 35 mL of 2M NH_4OH and 35 mL of $CHCl_3$ and the aqueous layer was extracted with $CHCl_3$ (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography (hexanes, 16:1 hexanes:EtOAc) to afford 610 mg of the product as a dark orange oil (34% yield). TLC: 6% EtOAc in hexanes, UV, R_f = 0.22.

IR (CDCl3): 2960, 2874, 1682, 1554, 1450, 1385, 1090 cm^{-1}.

^{1}H-NMR (250 MHz, CDCl3, isomers, with addition of phenyl hydrazine): δ = 7.6-6.8 (m, 10H), 4.4-3.4 2.3 (m, 4H), 2.97 (d, *J* = 7.4 Hz, 1H), 2.23 (m, 1H), 1.50 (d, *J* = 7 Hz, 6H), 1.39 (s, 3H), 1.22 (s, 3H), 1.20 (d, *J* = 7 Hz, 3H), 0.92 (d, *J* = 7 Hz, 3H), 0.41 (d, *J* = 7 Hz, 3H) ppm.

LRMS: 356.4, 341.4, 340.4, 284.2, 208.1, 150.2, 134.1, 133.1 amu.

***N*-(2,2-Dimethyl-5-phenyl-[1,3]-dioxan-5-yl)-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl)-hydroxylamine (26).** To 2,2-dimethyl-5-nitroxide-*N*-(2-methyl-1-phenyl-propyl)-5-phenyl-[1,3]-dioxane 25 (611 mg, 1.72 mmol) was added [*N*, *N*'-bis(3,5-di-*t*butylsalicylidene)-1,2-cyclohexanediaminato] manganese(III) chloride (Jacobsen's catalyst) (164 mg, 0.258 mmol), styrene (215 mg, 2.06 mmol), and $NaBH_4$ (130 mg, 3.44 mmol) in 11 mL of 1:1 toluene:EtOH. The

reaction mixture was stirred overnight at room temperature. The product was concentrated *in vacuo* and 55 mL of H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography (32:1 hexanes:EtOAc) yielding 350 mg of the product as a white opaque oil (44% yield). TLC: 6% EtOAc in hexanes, UV, $R_f = 0.62$.

IR (CDCl3): 2957, 1683, 1494, 1453, 1373, 1086 cm^{-1}.

^{1}H-NMR (500 MHz, CDCl3, two isomers): δ = 7.7-7.1 (m, 15H), 5.06 (q, *J* = 6.6 Hz, 1H), 5.00 (q, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 10.5 Hz, 1H), 3.85 (d, *J* = 10.5 Hz, 1H), 3.65 (d, *J* = 10.5 Hz, 1H), 3.50 (d, *J* = 10.5 Hz, 1H), 2,99 (dd, *J* = 10.5 Hz, 1H), 2.30 (m, 1H), 1.75 (2d, *J* = 6.6 Hz, 6H), 1.45 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 6H), 1.20 (s, 3H), 1.00 (s, 3H), 0.91 (d, *J* = 7.0 Hz, 6H), 0.86 (s, 3H), 0.33 (d, *J* = 7.0 Hz, 6H), 0.30 (d, *J* = 7.0 Hz, 6H) ppm.

^{13}C-NMR (125 MHz, CDCl3): δ = 144.2, 141.9, 141.6, 128.5, 128.3, 128.1, 127.9, 127.7, 127.5, 127.1, 126.8, 126.6, 97.6, 84.4, 71.8, 68.8 61.3, 31.8, 28.2, 27.3, 23.7, 22.9, 21.8, 21.7, 21.0, 20.5, 19.1 ppm.

HRMS: Molecular ion calcd for $C_{30}H_{38}NO_3$ (M^++H): 460.28243; found: 460.28462.

2-[(2-Methyl-1-phenyl-propyl)-(1-phenyl-ethoxy)-amino]-2-phenyl-propane-1,3-diol (27). To a solution of *N*-(2,2-dimethyl-5-phenyl-[1,3]-dioxan-5-yl)-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenylethyl)-hydroxylamine 26 (180 mg, 0.39 mmol) in 4:1 tetrahydrofuran/water (1 ml), was added trifluoroacetic acid (107 mg, 0.94 mmol). The reaction mixture was refluxed overnight, neutralized to pH=7 with ammonium hydroxide, and concentrated *in vacuo*. The residue was resuspended in water (50 ml) and extracted with dichloromethane (2 x 50 ml). The combined organic layers were washed with brine (10 ml), dried with magnesium sulfate, filtered and concentrated *in vacuo*. Flash chromatography (8:1 hexanes/EtOAc) afforded 53 mg of a gold oil (32% yield). TLC: 6% EtOAc in hexanes, UV, R_f = 0.39.

IR (CDCl3): 2956, 1683, 1453, 1384, 1306, 1140, 1072 cm-1.

^{1}H -NMR (250 MHz, CDCl3): δ = 7.5-7.1 (m, 15H), 5.03 (q, *J* = 6.6 Hz, 1H), 4.46 (d, *J* = 10.5 Hz, 1H), 4.09 (d, *J* = 10.5 Hz, 1H), 3.84 (d, *J* = 10.5 Hz, 1H), 3.75 (d, *J* = 10.5 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.47 (d, *J* = 10.5 Hz, 1H), 3.09 (d, *J* = 10.5 Hz, 1H), 3.03 (d, *J* = 10.5 Hz, 1H), 2.52 (br s, 2H), 2.32 (m, 1H), 1.72 (d, *J* = 7 Hz, 3H), 1.59 (d, *J* = 7 Hz, 3H), 1.25 (d, *J* = 7 Hz, 6H), 0.94 (d, *J* = 7 Hz, 6H), 0.37 (d, *J* = 7 Hz, 6H), 0.13 (d, *J* = 7 Hz, 6H) ppm.

^{13}C-NMR (63 MHz, CDCl3): δ = 143.0, 141.3, 140.2, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.0, 126.7, 84.2, 72.8, 67.8, 63.7, 32.2, 23.1, 22.5, 22.0, 21.8, 21.1, 21.0 ppm.

HRMS: Molecular ion calcd for $C_{27}H_{34}NO_3$ (M^++H): 420.25658; found: 420.25332.

General Polymerization Procedure. A mixture of *N*-alkoxyamine initiator (0.0192 mmol, 1 equivalent) olefin monomer (19.2 mmol, 1000 mole equivalents unless otherwise specified) and nitroxide (if added: 0.00096 mmol, 0.05 mole equivalent) was degassed in an ampoule by three consecutive freeze pump/thaw cycles and sealed under argon. The mixture was heated to the specified temperature in an oil bath for the amount of time indicated. After cooling to room temperature, a small sample of the crude polymer was collected for ^{1}H-NMR analysis, and the remaining product was dissolved in 6-10 ml of CH_2Cl_2 and poured into 300 ml of the specified precipitation solvent at 0 °C. The precipitated polymer was separated by decantation, re-dissolved in approximately 6 ml of CH_2Cl_2 and mixed with another 300 ml of the specified solvent. The precipitated polymer was separated by decantation, allowed to air dry, and analyzed by ^{1}H-NMR and GPC. Polymers were precipitated as follows: St with methanol, DMA with hexanes, TBA with 50% aq. methanol, and NBA with 70% aq. methanol.

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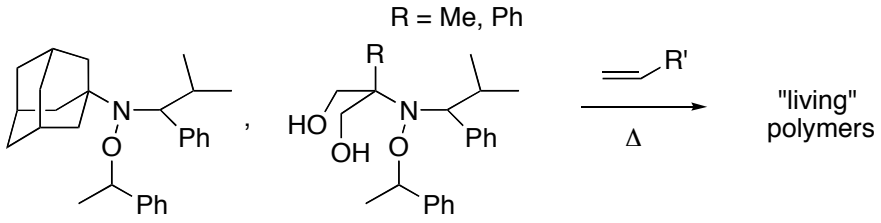

α-Hydrogen Nitroxides for NMRP