Electronic Supporting Information

for

Indolinic Nitroxides: Evaluation of their Potential as Universal Controlled Agent for Nitroxide Mediated Polymerization

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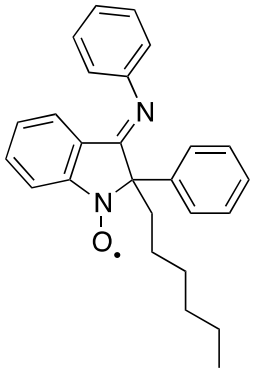
1. Nitroxides **1b,c**: spectroscopic data



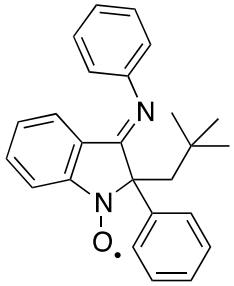
Nitroxide **1b**: 2,3-dihydro-2-hexyl-2-phenyl-(3-phenylimino)indole-1-oxyl

Yield 72%; red viscous oil.

ESI HRMS calcd for $C_{26}H_{27}N_2O$ = 383.2123; calcd. for $(M+H)^+$ = 384.2196; found 384.2206.

FT-IR, ν, cm^{-1}: 1659 (C=N); 1594 [PhN(O)-C(2)]. H.f.c.cs in $CHCl_3$:

a_N(NO) = 9.46; $a_{H\text{-}5}$ = 3.22; $a_{H\text{-}7}$ = 3.03; $a_{H\text{-}4/6}$ = 1.20(1H); $a_{H\text{-}4/6}$ = 0.96(1H), $a_{N\text{-}N=C}$ = 0.79; a_H = 0.41(1H-CH_2); a_H = 0.18(1H-CH_2) Gauss; g-factor 2.0055(4)



Nitroxide **1c**: 2,3-dihydro-2-neopentyl-2-phenyl-(3-phenylimino)indole-1-oxyl

Yields 70%;

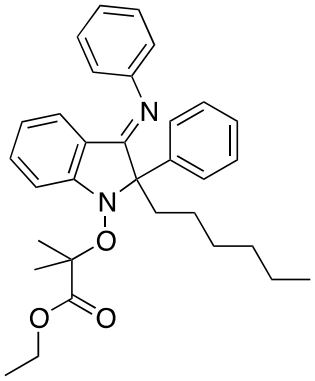
m.p. 164-5 °C from ethanol.

ESI HRMS calcd for $C_{25}H_{25}N_2O$ = 369.1967; Calcd. for $(M+H)^+$ = 370.2040; found 370.2039.

FT-IR, ν, cm^{-1}: 1664 (C=N); 1591 [PhN(O)-C(2)]. H.f.c.cs in $CHCl_3$:

a_N(NO) = 9.25; $a_{H\text{-}5}$ = 3.20; $a_{H\text{-}7}$ = 3.04; $a_{H\text{-}4/6}$ = 1.08(1H); $a_{H\text{-}4/6}$ = 1.03(1H), $a_{N\text{-}N=C}$ = 0.76; a_H= 0.4 (1H-CH_2); a_H= 0.1 (1H-CH_2) Gauss; g-factor 2.0057(1)

2. Alkoxyamines **2b-d,x-y**: spectroscopic data



Alcoxyamine **2b,x**: 2-Phenyl-2-hexyl-3-phenyimino-indoline-1-yloxy-O-ethyl-methylpropanoate

Yield 73%.

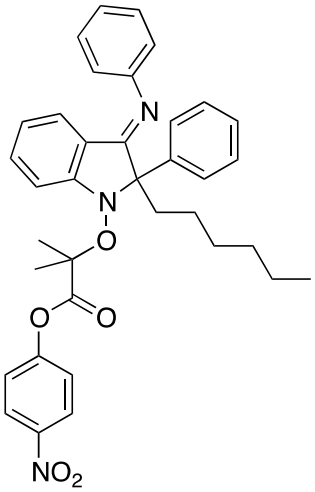
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.85 (m, 3 H, CH_3); 1.16 (t, J = 7.1 Hz, 3 H, CH_3); 1.28-1.41 (m, 14 H, 2 CH_3 + 4 CH_2); 2.54-2.75 (m, 2 H, CH_2); 3.75 (m, 2 H, CH_2); 6.34 (d, J = 7.8 Hz, 1 H, CH); 6.65 (m, 1 H, CH); 6.71 (d, J = 7.8 Hz, 2 H, CH); 7.07 (m, 2 H, CH); 7.25-7.42 (m, 8 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 14.08 (CH_3); 14.28 (CH_3); 22.78 (CH_2); 23.73 (CH_3); 24.08 (CH_2); 25.40 (CH_3); 29.91 (CH_2); 31.56 (CH_2); 34.88 (CH_2); 61.13 (CH_2); 79.22 [-N-C(Ph)-CH_2]; 81.13 [-$(CH_3)_2$C-C(O)]; 114.07; 118.50; 121.79; 123.51; 125.85; 127.32; 129.51; 133.56; 152.22 (aryl carbons); 160.55 (-C=N-); 173.18 (-C=O).

ESI HRMS: calcd for $C_{32}H_{38}N_2O_3$ $[M]^+$ 498.2884; found 498.2882.

m.p. 75 °C.

FT-IR, ν, cm^{-1}: 1732 (C=O),1657 (>C=N-); 1596 [PhN(OR')-C(2)].



Alcoxyamine **2b,y**: 2-Phenyl-2-hexyl-3-phenyimino-indoline-1-yloxy-O-(*p*-nitrophenyl)-methylpropanoate

70% yield.

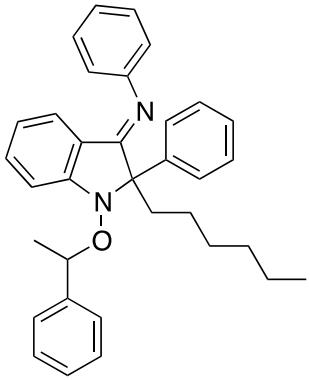
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.79 (m, 3 H, CH_3); 1.18-1.30 (m, 8 H, CH_2); 1.41 (s, 3 H, CH_3); 1.53 (s, 3 H, CH_3); 2.59 (m, 2 H, CH_2); 6.30 (d, J = 7.82 Hz, 1 H, CH); 6.64 (d, J = 7.30 Hz, 2 H, CH); 6.88 (d, J = 9.02 Hz, 2 H, CH); 7.01 (t, J = 7.39 Hz, 1 H, CH); 7.19-7.31 (m, 8 H, CH); 7.35 (d, J = 7.36 Hz, 2 H, CH); 8.13 (d, J = 9.08 Hz, 2 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 14.26 (CH_3); 22.39 (CH_2); 22.75 (CH_2); 23.88 (CH_3); 24.11 (CH_2); 25.56 (CH_3); 29.89 (CH_2); 31.55 (CH_2); 34.93 (CH_2); 79.47 [-N-C(Ph)-CH_2-]; 83.49 [-$(CH_3)_2$C-C(O)]; 114.06; 118.41; 122.30; 122.69; 123.69; 125.22; 129.58; 133.70; 144.25; 145.52; 151.95; 155.40; (aryl carbons); 160.15 (-C=N-); 170.83 (C-NO2); 171.31 (-C=O).

ESI HRMS: calcd for $C_{36}H_{37}N_3O_5$ $[M]^+$ 591.27332, found 591.2733

m.p. 130 °C.

FT-IR, ν, cm^{-1}: 1778 (C=O); 1658 (>C=N-); 1595 [PhN(OR')-C(2)]; 1523 (NO_2).



Alkoxyamine **2b,z**: 2-Phenyl-2-hexyl-3-phenyimino-indoline-1-yloxy-O-styryl

75% yield.

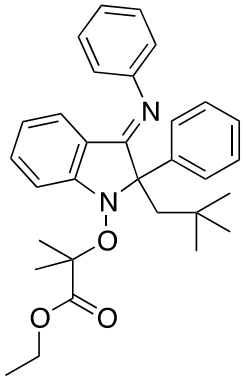
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.85 (m, 3 H, CH_3); 1.22-1.43 (m, 8 H, CH_2); 1.52 (d, J = 6.32 Hz, 3 H, CH_3); 2.40-2.53 (m, 2 H, CH_2); 4.64 (m, 1 H, CH); 6.32 (m, 1 H, CH); 6.57 (m, 1 H, CH); 6.75 (dd, J_1 = 7.27 Hz, J_2 = 12.29 Hz, 2 H, CH); 7.07 (dd, J_1 = 7.40 Hz, J_2 = 14.81 Hz, 2 H, CH); 7.16 (d, J = 7.63 Hz, 2 H, CH); 7.31 (m, 9 H, CH); 7.45 (d, J = 7.37 Hz, 2 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 14.26 (CH_3); 21.12 (CH_3); 22.78 (CH_2); 24.26 (CH_2); 24.11 (CH_2); 29.94 (CH_2); 31.70 (CH_2); 78.63 [-N-C(Ph)-CH_2-]; 82.28 (CH); 112.89; 118.56; 118.99; 121.02; 123.56; 126.12-127.84 (m); 128.38; 133.59; 141.98; 142.43; 143.64; 152.18; 171.42 (aryl carbons); 160.15 (-C=N-); 173.17 (C=O).

ESI HRMS: calcd for $C_{34}H_{36}N_2O$ $[M]^+$ 488.28276, found 488,2828.

m.p. 98 °C.

FT-IR, ν, cm^{-1}: 1658 (>C=N-); 1597 [PhN(OR')-C(2)].



Alkoxyamine **2c,x**: 2-Phenyl-2-neopentyl-3-phenyimino-indoline-1-yloxy-O-ethyl-methylpropanoate

68% yield.

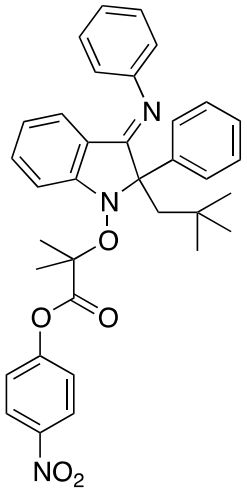
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.96 (s, 9 H, CH_3); 1.20 (t, J = 7.14 Hz, 3 H, CH_3); 1.35 (s, 3 H, CH_3); 1.36 (s, 3 H, CH_3); 2.78 (AB, J_1 = 14.30, J_2 = 58.78 Hz, 2 H, CH_2); 3.83 (quad, J_1 = 6.98, 2 H, CH_2); 6.44 (d, J = 7.45 Hz, 1 H, CH); 6.64 (t, J = 7.84 Hz, 1 H, CH); 6.77 (d, J = 7.5 Hz, 2 H, CH); 7.07 (t, J = 7.39 Hz, 1 H, CH); 7.18-7.53 (m, 9 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 14.07 (CH_3); 23.33 (CH_3); 25.44 (CH_3); 31.62 (Cq); 32.41 $(CH_3)_3$; 45.49 (CH_2); 61.14 (CH_2); 79.53 [-N-C(Ph)-(CH_2-$(CH_3)_3$)]; 83.27 (-CH_3)2C-C(O)); 113.35; 117.77; 118.65; 120.56; 123.51; 126.01; 127.15; 128.03; 129.60; 133.52; 146.22; 152.25; 171.42 (aryl carbons); 160.12 (-C=N-); 173.17 (C=O).

ESI HRMS: calcd for $C_{31}H_{36}N_2O_3$ $[M+H]^+$ 484.27259, found 484.2726.

m.p. 109 °C.

FT-IR, ν , cm^{-1}: 1730 (C=O); 1645 (>C=N-); 1596 [PhN(OR')-C(2)].



Alkoxyamine **2c,y**: 2-phenyl-2-neopentyl-3-phenyimino-indoline-1-yloxy-O-(*p*-nitrophenyl)-methylpropanoate

64% yield.

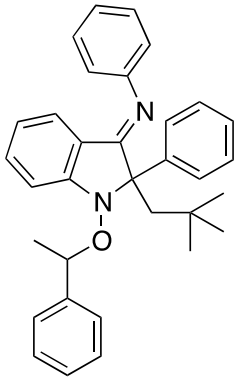
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.96 (s, 9 H, CH_3); 1.51 (s, 6 H, CH_3); 2.80 (AB, J_1 = 14.38, J_2 = 51.7 Hz, 2 H, CH_2); 6.46 (d, J = 7.75 Hz, 1 H, CH); 6.71 (m, 3 H, CH); 7.05 (m, 3 H, CH); 7.32 (m, 9 H, CH); 8.23 (d, J = 9.7 Hz, 2 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 23.53 (CH_3); 25.52 (CH_3); 31.67 (Cq); 32.45 $(CH_3)_3$; 45.57 (CH_2); 79.83 [-N-C(Ph)-(CH_2-$(CH_3)_3$)]; 83.60 [$(-CH_3)_2$C-C(O)]; 118.07; 121.68; 122.26; 125.25; 125.52; 126.37; 127.37; 129.54; 133.67; 145.52; 152.00; 155.41 (aryl carbons); 159.79 (-C=N-); 170.82 (C-NO_2); 173.17 (C=O).

ESI HRMS: calcd for $C_{35}H_{35}N_3O_5$ $[M]^+$ 577.25767, found 577.2577.

m.p. 137 °C.

FT-IR, ν, cm^{-1}: 1774 (C=O); 1652 (>C=N-); 1593 [PhN(OR')-C(2)]; 1521 (NO_2).



Alkoxyamine **2c,z**: 2-phenyl-2-neopentyl-3-phenyimino-indoline-1-yloxy-O-styryl

66% yield.

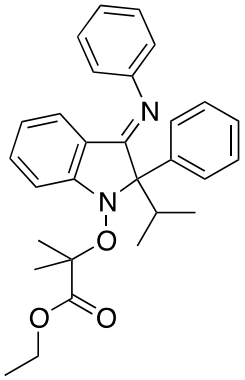
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.93 (s, 9 H, CH_3); 1.42 (d, J = 6.56 Hz, 3 H, CH_3); 2.63 (m, 2 H, CH_2); 4.55 (m, 1 H, CH); 6.47 (m, 2 H, CH); 6.80 (m, 2 H, CH); 7.06-7.50 (m, 15 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 21.08 (CH_3); 29.11 (Cq); 31.69 $(CH_3)_3$; 46.17 (CH_2); 79.26 [-N-C(Ph)-(CH_2-$(CH_3)_3$)]; 82.20 (CH_3-CH-Ph); 112.78; 118.21; 120.62; 123.54; 125.64; 127.31; 128.05; 129.48; 133.56; 141.95; 145.59; 152.11; 171.17 (aryl carbons); 158.87 (-C=N-)

ESI HRMS: calcd for $C_{33}H_{34}N_2O_5$ $[M]^+$474.26711, found 474.2671.

m.p. 52 °C.

FT-IR, ν, cm^{-1}: 1657 (>C=N-); 1596 [PhN(OR')-C(2)].



Alkoxyamine **2d,x**: 2-phenyl-2-isopropyl-3-phenyimino-indoline-1-yloxy-O-ethyl-methylpropanoate

65% yield.

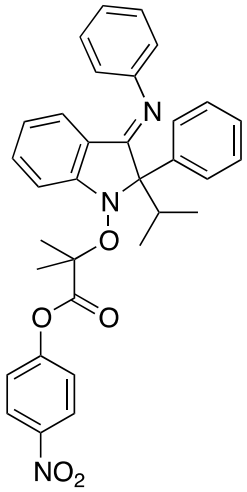
^{1}H NMR ($CDCl_3$, 300.13 MHz) : δ 0.88 (s, 3 H, CH_3); 1.15 (s, 3 H, CH_3); 1.22-1.31 (m, 9 H, CH_3); 1.57 (s, 1 H, CH); 4.07 (m, 2 H, CH_2); 6.37 (d, *J* = 7.80 Hz, 1 H, CH); 6.60 (t, *J* = 7.56 Hz, 1 H, CH); 6.85 (d, *J* = 7.57 Hz, 2 H, CH); 7.10 (t, *J* = 8.38 Hz, 2 H, CH); 7.23-7.35 (m, 6 H, CH); 7.44 (d, *J* = 7.34 Hz, 2 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 14.17 (CH_3); 17.41 $(CH_3)_2$; 25.36 $(CH_3)_2$; 30.57 (CH); 61.26 (CH_2); 77.44 [-N-C(Ph)-CH]; 83.42 [$-(CH_3)_2$C-C(O)]; 118.48; 120.97; 123.50; 125.49; 127.46; 129.62; 130.11; 133.57; 152.34; 169.31 (aryl carbons); 159.74 (-C=N-); 173.41 (-C=O).

ESI HRMS: calcd for $C_{29}H_{32}N_2O_3$ $[M]^+$ 456.24129, found 456.2413.

m.p. 83 °C.

FT-IR, ν, cm^{-1}: 1737 (C=O); 1656 (>C=N-); 1597 [PhN(OR')-C(2)].



Alkoxyamine **2d,y**: 2-phenyl-2-isopropyl-3-phenyimino-indoline-1-yloxy-O-(*p*-nitrophenyl)-methylpropanoate

65% yield.

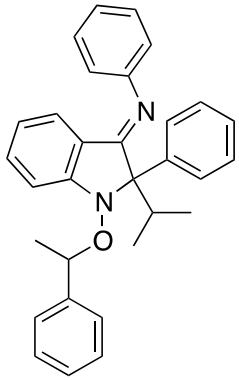
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.91 (m, 3 H, CH_3); 1.25-1.33 (m, 6 H, CH_3); 1.49 (br s, 3 H, CH_3); 1.66 (s, 1 H, CH); 6.40 (d, *J* = 7.79 Hz, 1 H, CH); 6.65 (t, *J* = 7.24 Hz, 1 H, CH); 6.85 (d, *J* = 7.50 Hz, 2 H, CH); 7.12 (d, *J* = 7.74 Hz, 2 H, CH); 7.7 (d, *J* = 9.0 Hz, 2 H, CH); 7.30 (m, 6 H, CH); 7.45 (d, *J* = 6.91 Hz, 2 H, CH); 8.27 (d, *J* = 9.0 Hz, 2 H, CH).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 23.67 (CH_3); 25.03 (CH_3); 25.61(CH_3)$_2$; 30.91 (CH); 81.83 [-N-C(Ph)-(CH-(CH_3)$_3$)]; 83.53 [-CH_3)$_2$C-C(O)]; 118.38; 121.46; 122.26; 125.31; 125.60; 127 .60; 128.00; 129.63; 130.07; 145.51; 151.98; 155.43 (aryl carbons); 159.34 (-C=N-); 169.03 (C-NO2); 170.85 (C=O).

ESI HRMS: calcd for $C_{33}H_{31}N_3O_5$ $[M]^+$542.22637, found 549.2264.

m.p. 92 °C.

FT-IR, ν, cm^{-1}: 1769 (C=O); 1656 (>C=N-); 1593 [PhN(OR')-C(2)]; 1525 (NO_2).



Alkoxyamine **2d,z**: 2-phenyl-2-isopropyl-3-phenyimino-indoline-1-yloxy-O-styryl

69% yield.

^{1}H NMR ($CDCl_3$, 300.13 MHz) : δ 0.94 (m, 3 H, CH_3); 1.23 (m, 3 H, CH_3); 1.46 (m, 3 H, CH_3); 1.53 (s, 1 H, CH); 3.27 (m, 1 H, CH); 6.31 (m, 1 H, CH); 6.48 (m, 1 H, CH); 6.84 (d, *J* = 8.17 Hz, 2 H, CH); 7.09 (m, 2 H, CH); 7.20 (d, *J* = 6.94 Hz, 2 H, CH); 7.30-7.37 (m, 9 H, CH); 7.56 (d, *J* = 7.49 Hz, 2 H, CH).

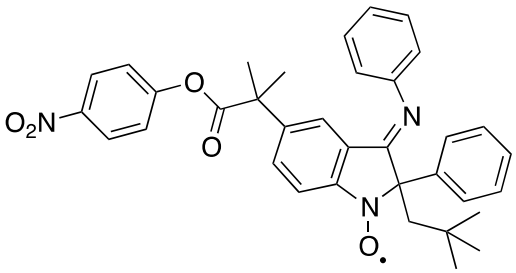
^{13}C NMR ($CDCl_3$, 75.47 MHz): 21.08 (CH_3); 29.11 $(CH_3)_2$; 31.69 (CH); 79.26 [-N-C(Ph)-(CH-(CH3)3)]; 82.20 (CH); 112.78; 118.21; 120.62; 123.54; 125.64; 127.31; 128.05; 129.48; 133.56; 141.95; 145.59; 152.11; 171.17 (aryl carbons); 158.87 (-C=N-).

ESI HRMS: calcd for $C_{31}H_{30}N_2O$ $[M]^+$446.23581, found 446.2358.

m.p. 79 °C.

FT-IR, ν, cm^{-1}: 1655 (>C=N-); 1594 [PhN(OR')-C(2)].

3. Spectroscopic data and X-ray analysis of 2,3-dihydro-2-neopentyl-2-phenyl-(3-iminophenyl)indole-5-[(*p*-nitrophenyl)-2-methylpropanoate-2-yl]-1-oxyl



M.p. 135-6°C from ethanol. HRMS: calcd for $C_{26}H_{20}N_2$ $[M]^+$ 577.2571, found 577.2575. FT-IR, ν, cm^{-1}: 1761 (C=O); 1649 (>C=N-); 1593 [PhN(OR')-C(2)]; 1526 (NO_2). H.f.c.cs in $CHCl_3$: a_N(NO) = 9.28; $a_{H\text{-}7}$ = 3.06; $a_{H\text{-}4/6}$ = 1.19(1H); $a_{H\text{-}4/6}$ = 0.99(1H), $a_{N\text{-}N=C}$ = 0.78 Gauss; g-factor 2.0061(3)

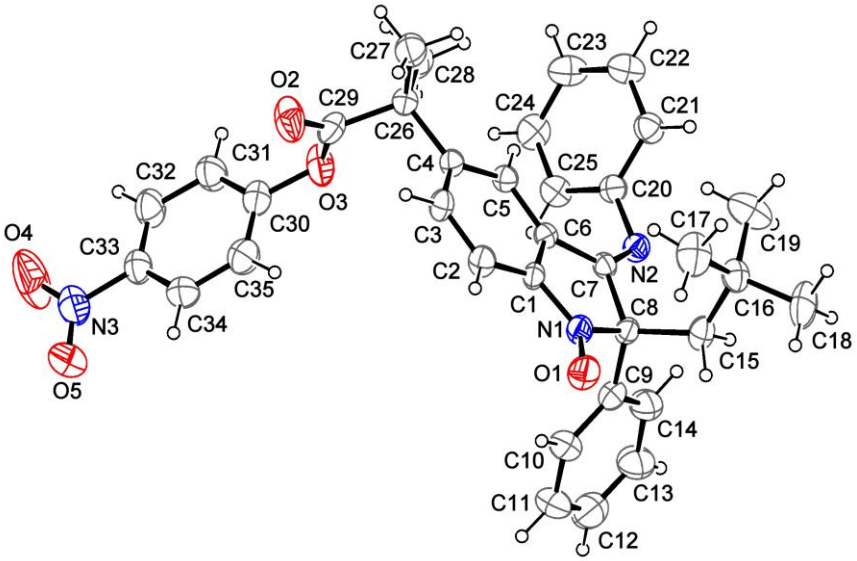


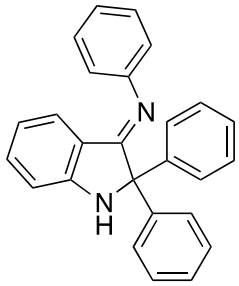
Figure S1. Molecular structure of side-product obtained from compound **2cy** with displacement ellipsoids drawn at the 50% probability level.

Crystallographic data were collected at room temperature on a Bruker SMART 1000 diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using SIR97[1] and anisotropically refined for all the non-H atoms. The refinements were performed on F^2 using SHELXL-97[2]. All H atoms were placed at calculated positions and refined using a riding model approximation, with C–H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl H atoms. One reflection (0 0 1) was omitted from the refinement as possibly partially obscured by the beam stop. $C_{35}H_{34}N_3O_5$, M_r = 576.65, triclinic, space group *P*-1, *a* = 9.1861(12), *b* = 13.0550(17), *c* = 13.3338(17) Å, α = 75.872(3), β = 81.166(3), γ = 89.590(3)°, V = 1531.5(3) $Å^3$, Z = 2, ρ_{calc} = 1.250 g cm^{-3}, μ = 0.84 mm^{-1}; colourless plate, crystal dimensions 0.02 x 0.06 x 0.10 mm, *T* = 294(2) K, 393 parameters, R = 0.051, *w*R2 = 0.065 for 5685 unique reflections, S =0.870, Δρ(min/max) = -0.15/0.14 e $Å^{-3}$.

1. A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.

2. G.M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122

Synthesis of 2,2-diphenyl-3-phenyliminoindoline.[3]



DPAIO nitroxide **1a** (375 mg, 1mmol) and iron powder (280 mg, 5mmol) were heated in acetic acid (10 ml) at 50°C for 10 hours. After cooling, the precipitate was filtered off and solid sodium carbonate was added to the filtrate to give a solid mixture. This mixture was extracted with dichloromethane and the extract was evaporated to dryness. Finally, the amine was purified over silica column (eluant 10% Et_2O in pentane).

Yield 44%;

m.p. 193°C from petroleum ether 80-100°C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 4.93 (s, 1H); 6.45 (d, J = 7.07 Hz, 2H); 6.83 (m, 3H); 6.99 (m, 1H); 7.10 (t, J = 8.98 Hz, 1H); 7.22-7.39 (m, 8H); 7.54 (d, *J* = 12.10 Hz, 4H).

^{13}C NMR ($CDCl_3$, 75.47 MHz): 73.84 [-C(Ph)$_2$]; 111.62; 118.26; 123.24; 127.26; 127.34; 127.76; 128.19; 129.29; 133.86; 144.17; 151.90 (aryl carbons); 155.93 (-C=N-).

ESI HRMS: calcd for $C_{26}H_{20}N_2$ $[M+H]^+$ 360.1626, found 360.1626.

3. C. Berti, L. Greci, L. Marchetti, *J. Chem. Soc. Perkin Trans. 2*, 1977, 1032-1035.

5. HPLC experiments

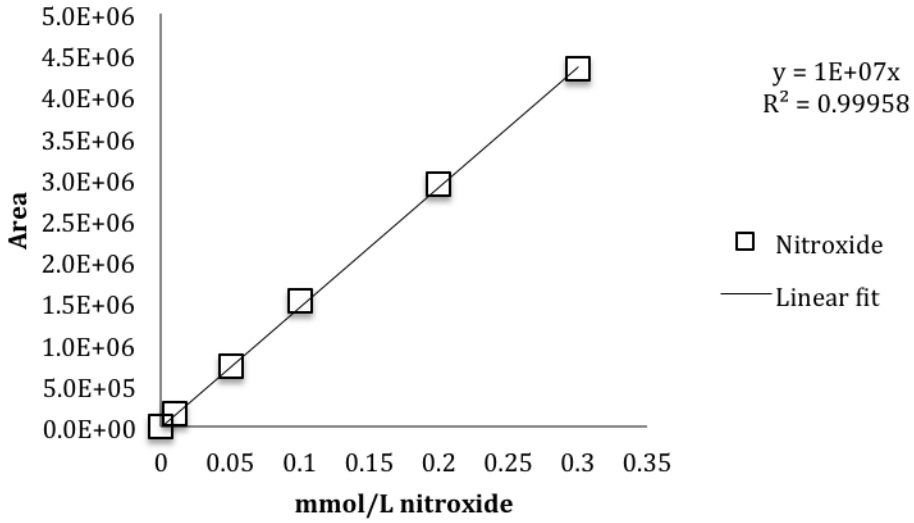


Figure S2. Calibration curve for the DPAIO nitroxide.

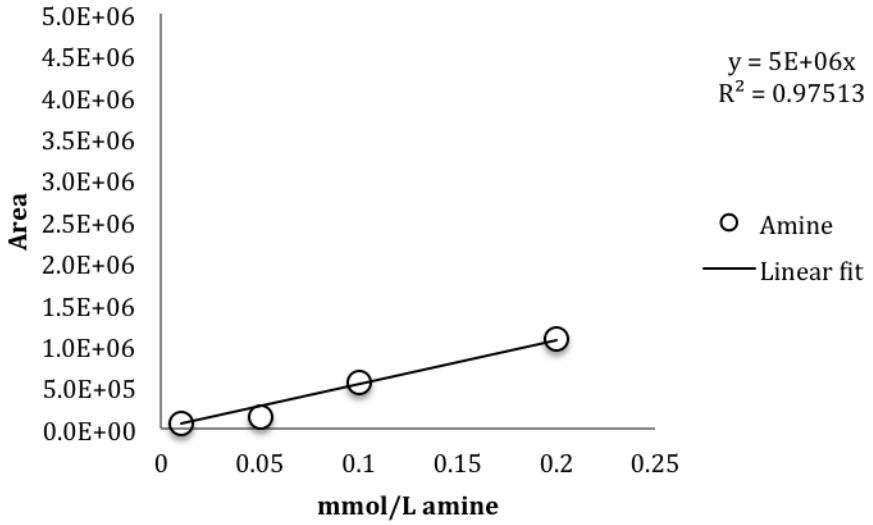
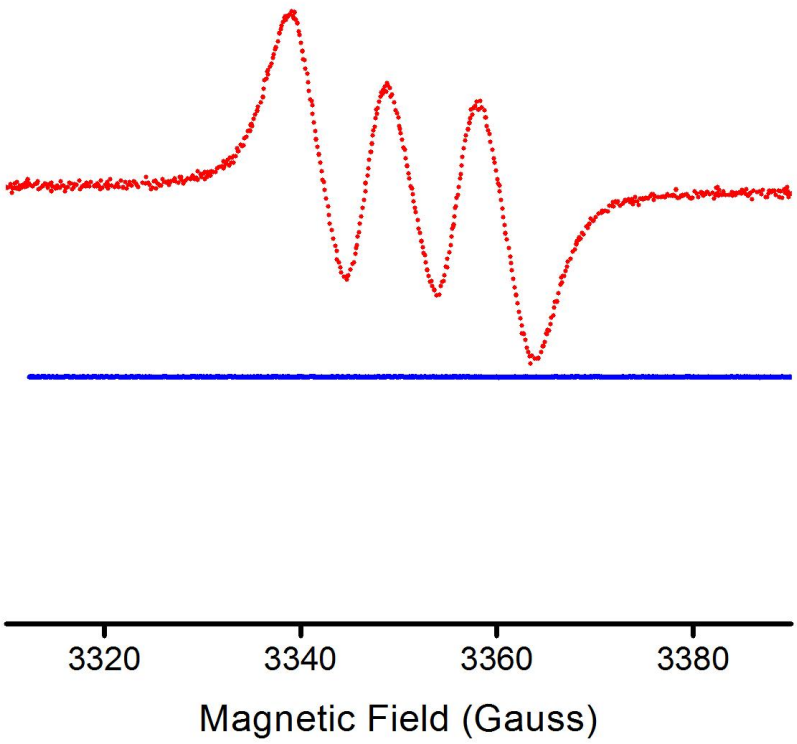


Figure S3. Calibration curve for the amine.

6. ESR experiment

Figure S4. ESR spectra obtained before (solid blue line) and after heating (short dotted red line) (2 h) a 10-4 M solution of PMMA-DPAIO macroinitiator in *tert*-butylbenzene.



7. Polymerization experiments

Figure S5. Kinetics of the bulk MMA polymerization initiated with **2a,y** (▲) at 100 °C **, 2c,y** (●) and **2d,y** (■) at 85 °C with $[MMA]_0$: $[alkoxyamine]_0$ = 400:1 .

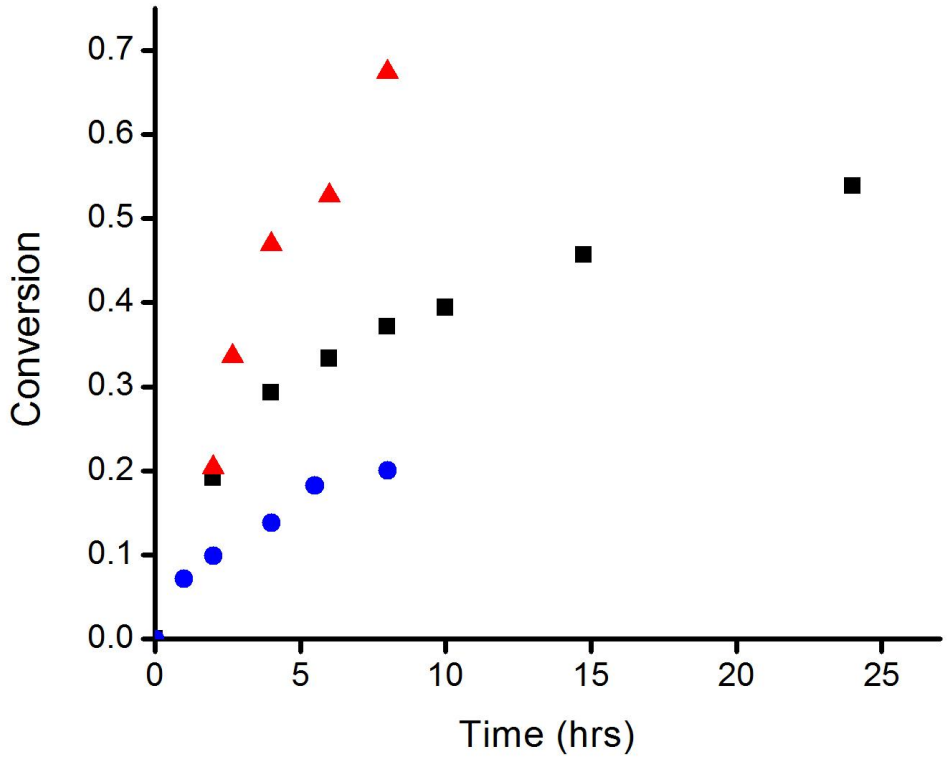


Figure S6. Evolution of number-average molar mass (M_n ■) and polydispersity index (PDI ▲) vs conversion for the bulk MMA polymerization initiated with **2a,y** ($[MMA]_0$: $[\mathbf{2a,y}]_0$ = 400:1) at 100 °C. The solid line corresponds to the theoretical M_n. b) Molar Mass Distribution obtained from the bulk MMA polymerization initiated with **2a,y**.

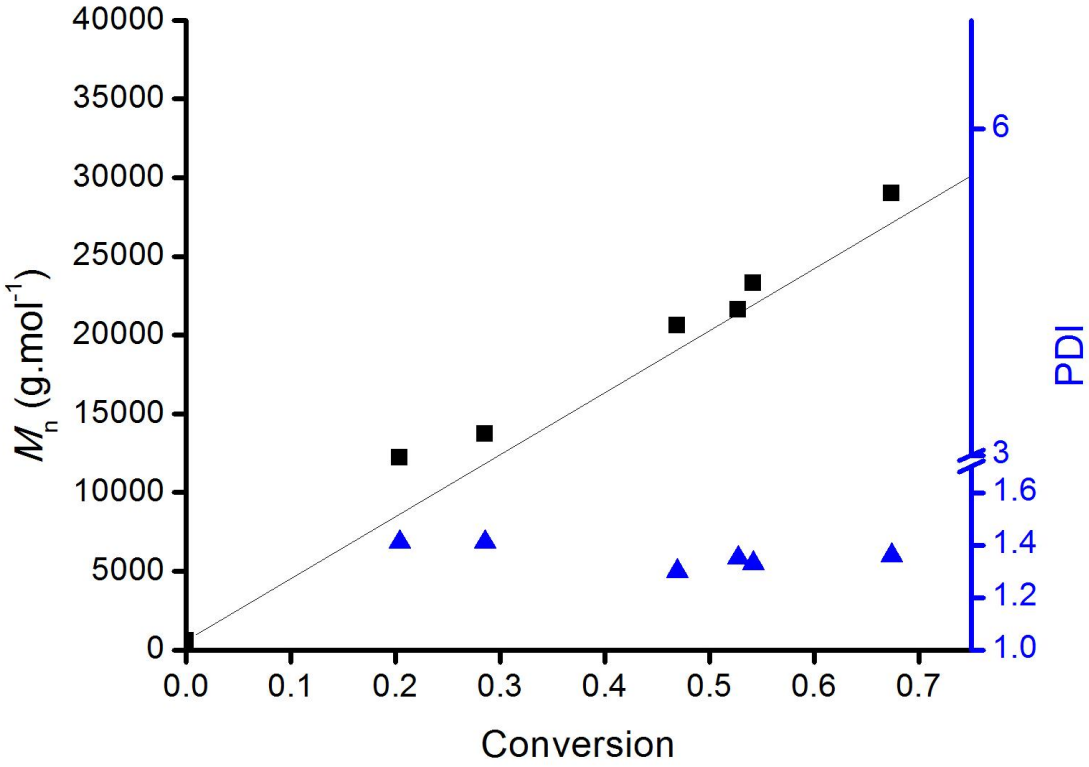


Figure S7. Evolution of number-average molar mass (M_n ■) and polydispersity index (PDI ▲) vs conversion for the bulk MMA polymerization initiated with **2c,y** ($[MMA]_0$: $[\mathbf{2c,y}]_0$ = 400:1) at 85 °C. The solid line corresponds to the theoretical M_n. b) Molar Mass Distribution obtained from the bulk MMA polymerization initiated with **2c,y**.

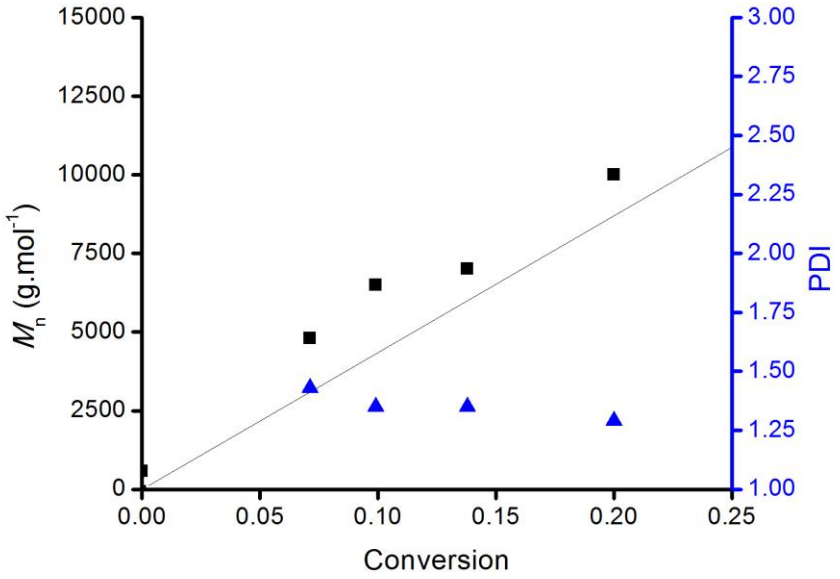


Figure S8. Kinetics of the bulk styrene polymerization initiated with **2c,y** (●) and **2d,y** (◆) at 120 °C with $[Sty]_0$: $[alkoxyamine]_0$ = 400:1 .

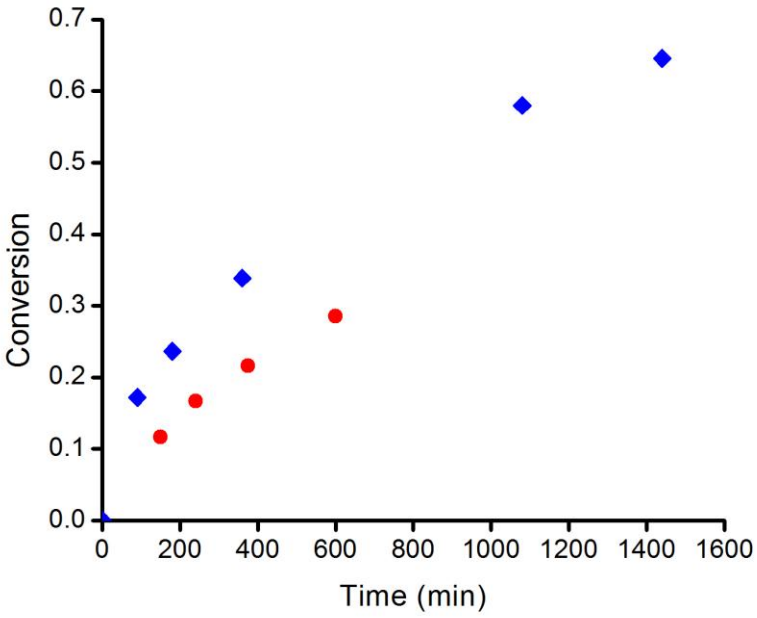


Figure S9. Evolution of number-average molar mass (M_n ■) and polydispersity index (PDI ▲) vs conversion for the bulk styrene polymerization initiated with **2c,y** ($[Sty]_0$: $[\mathbf{2c,y}]_0$ = 400:1) at 120 °C. The solid line corresponds to the theoretical M_n. b) Molar Mass Distribution obtained from the bulk styrene polymerization initiated with **2c,y**.