Supplementary Information

Radical exchange reaction of multi-spin isoindoline nitroxides followed by EPR spectroscopy

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1) Materials and Methods

NMR spectra were recorded on a BRUKER *Avance* 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) on solutions in CDCl$_3$ or CD$_2$Cl$_2$. Chemical shifts (δ) are expressed in parts per million (ppm) and are referenced to CHCl$_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm) respectively CH$_2$Cl$_2$ (^{1}H: 5.32 ppm, ^{13}C: 53.8 ppm) as internal standard. All coupling constants (J) are absolute values and J values are expressed in Hertz (Hz). The description of signals includes: s = singlet, bs = broad singlet, m = multiplet, dd = doublet of doublets, qd = quartet of doublets and AAʹBBʹ for a more complex system (no first order). The spectra were analyzed according to first order. The signal structure in ^{13}C-NMR was analyzed by DEPT (Distortionless Enhancement by Polarization Transfer) and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal) and C$_q$ = quaternary C-atom (no signal). IR spectra were recorded with a FT-IR BRUKER *IFS 88* spectrometer with OPUS software using the attenuated total reflection technique (ATR). The absorption band is given in wave numbers $\tilde{\nu}$ in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong $0 - 9\%$ T, s = strong $10 - 39\%$ T, m = medium $40 - 69\%$ T, w = weak $70 - 89\%$ T, vw = very weak, $90 - 100\%$ T. Analytical thin layer chromatography (TLC) was carried out on MERCK silica gel coated aluminum plates (silica gel 60, F$_{254}$), detected under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. EI (Electron Ionization) and FAB (Fast Atom Bombardment) mass spectra were obtained using FINNIGAN *MAT* 95 mass spectrometer. The indication of the molecular fragments was carried out as the ratio of mass to charge *m/z*; the intensity of the signals was expressed in percent relative to the intensity of the base signal (100%). The EA measurements were performed on an ELEMENTAR VARIO *MICRO* device using a SARTORIUS *M2P* precision balance. The following abbreviations were used: calcd. = calculated data, found = measured data. The EPR spectra were recorded on a *Bruker ESP300E* spectrometer. The compounds were dissolved in toluene and deoxygenated by bubbling Argon for several minutes. The spectra were taken at 298 K. The instrument settings were as follows: microwave power 2.00 mW, modulation amplitude 0.0452 mT, modulation frequency 100 kHz, scan time 180 s. Solvents, reagents and chemicals were purchased from SIGMA-ALDRICH, ABCR, ALFA AESAR and FISHER SCIENTIFIC. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Absolute toluene was obtained by refluxing over sodium, followed by distillation and was kept under Argon. Reactions with air- and/or water sensitive reagents were done under Argon using standard *Schlenk* technique. Tetrakis(4-azidophenyl)methane (**1**) was synthesized by Dr. Laure Monnereau according to literature procedures.[1] The synthesis of isoindoline derivatives[2-7] and the monoalkoxyamine[8] are based on literature procedures.
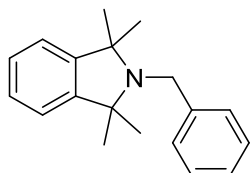
2) Synthetic Procedures

N-Benzylphthalimide:[2] 75.0 g phthalic anhydride (506 mmol, 1.00 equiv.) and 65.0 mL benzylamine (63.9 g, 592 mmol, 1.17 equiv.) in 300 mL glacial acetic acid were refluxed for 4 h. After cooling to room temperature 700 mL water were added. The precipitate was filtered off and washed with water. The crude product was recrystallized in ethanol. 106 g of a colorless solid (446 mmol) were obtained. Yield: 88%. – mp: 115–117 °C. – ^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 4.85 (s, 2 H, CH_2), 7.23–7.36 (m, 3 H, C$_{Ar}H$), 7.41–7.46 (m, 3 H, C$_{Ar}H$), 7.70 (AAʹBBʹ, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 3.1 Hz, 2 H, C$_{Ar}H$), 7.84 (AAʹBBʹ, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 3.1 Hz, 2 H, C$_{Ar}H$). – ^{13}C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 41.7 (–, CH$_2$), 123.5 (+, C_{Ar}H), 127.9 (+, C_{Ar}H), 128.7 (+, C_{Ar}H), 128.8 (+, C_{Ar}H), 132.2 (C$_{quart.}$, C_{Ar}), 134.1 (+, C_{Ar}H), 136.5 (C$_{quart.}$, C_{Ar}), 168.2 (C$_{quart.}$, CO). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3458 (vw), 3057 (vw), 2946 (vw), 1763 (w), 1705 (m), 1491 (w), 1465 (w), 1431 (w), 1389 (m), 1330 (w),
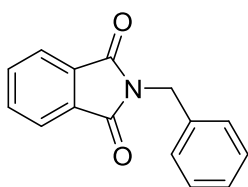
1296 (w), 1204 (w), 1184 (w), 1156 (w), 1101 (w), 1086 (w), 1061 (w), 935 (w), 824 (vw), 792 (w), 762 (w), 713 (m), 694 (m), 623 (w), 589 (w), 521 (w), 404 (vw). – MS (70 eV, EI), m/z (%): 237/238/239 (100/16/1.7) [M$^+$], 209 (12) [M$^+$ – CO], 104/105 (6.7/1.9) [C$_7$H$_4$O$^+$]. – HR-MS (C$_{15}$H$_{11}$NO$_2$): calcd. 237.0784, found 237.0784.

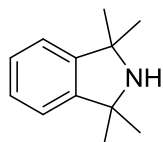The experimental data are consistent with the literature.[2]

2-Benzyl-1,1,3,3-tetramethylisoindoline:[3, 4] Under an Argon atmosphere, 800 mL of a 3 M MeMgI-solution (2.40 mol, 6.70 equiv. MeMgI) in diethyl ether and 50 mL of abs. toluene were placed in a 2 L three-necked flask with reflux condenser, thermometer and attached cooling trap. The diethyl ether was distilled off the solution at vacuum and 30 °C until the mixture was slightly cloudy. A solution of 85.0 g *N*-benzylphthalimide (0.358 mol, 1.00 equiv.) in 600 mL abs. toluene were added slowly. After, more solvent was removed by distillation until the reaction mixture refluxed at 110 °C and it was refluxed for additional 19 h. Then toluene was removed by distillation, cooled to room temperature and 1 L of *n*-hexane was added. The mixture was refluxed for another 16 h and again cooled to room temperature. The mixture was filtered over Celite® and the filter cake was washed tree times with *n*-hexane. Air was bubbled through the filtrate overnight and then passed over a column of basic alumina using *n*-pentane as eluent until the eluent was amine-free. The solvent was removed under reduced pressure and the crude product recrystallized in ethanol. A slightly beige solid was obtained (20.6 g, 77.7 mol). Yield: 22%. – mp: 62–63 °C. – ^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.32 (s, 12 H, C*H$_3$*), 4.00 (s, 2 H, C*H$_2$*), 7.12–7.17 (m, 2 H, C$_{Ar}$*H*), 7.20–7.27 (m, 3 H, C$_{Ar}$*H*), 7.27–7.33 (m, 2 H, C$_{Ar}$*H*), 7.45–7.50 (m, 2 H, C$_{Ar}$*H*). – ^{13}C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 28.6 (+, *C*H$_3$), 46.4 (–, *C*H$_2$), 65.3 (C$_{quart.}$, *C*(CH$_3$)$_2$), 121.5 (+, *C$_{Ar}$*H), 126.5 (+, *C$_{Ar}$*H), 126.9 (+, *C$_{Ar}$*H), 128.0 (+, *C$_{Ar}$*H), 128.5 (+, *C$_{Ar}$*H), 143.6 (C$_{quart.}$, *C$_{Ar}$*), 148.0 (C$_{quart.}$, *C$_{Ar}$*). – IR (ATR): ṽ (cm^{-1}) = 3020 (vw), 2958 (w), 2922 (w), 1602 (vw), 1487 (w), 1446 (w), 1371 (w), 1356 (w), 1321 (w), 1300 (w), 1266 (w), 1212 (w), 1195 (w), 1161 (w), 1104 (w), 1073 (w), 1026 (w), 945 (w), 905 (w), 874 (w), 791 (vw), 743 (m), 701 (m), 624 (w), 572 (w), 551 (w), 526 (w), 480 (vw), 440 (vw). – MS (70 eV, EI), m/z (%): 265/266 (3.9/0.87) [M$^+$], 250/251 (100/19) [M$^+$ – CH$_3$], 144/145 (4.0/1.5) [M$^+$ – Bn – 2 × CH$_3$], 91/92 (56/3.7) [Bn$^+$]. – HR-MS (C$_{19}$H$_{23}$N): calcd. 265.1825, found 265.1825.

The experimental data are consistent with the literature.[3, 4]

1,1,3,3-Tetramethylisoindoline: A suspension of 9.28 g 2-benzyl-1,1,3,3-tetramethylisoindoline (35.0 mmol, 1.00 equiv.) and 1.12 g Pd/C (10%, 1.05 mmol (Pd), 3 mol%) in 120 mL glacial acetic acid was stirred for 24 h under a hydrogen atmosphere at ambient pressure at room temperature. After this, the reaction mixture was filtered over Celite® and the filter cake was washed with conc. acetic acid, water and little diethyl ether. The filtrate was extracted by diethyl ether three times and the organic phase was discarded. Afterwards the aqueous phase was made alkaline (pH = 10) using NaOH and again extracted with diethyl ether three times. The organic phase was washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the obtained colorless solid (4.36 g, 24.9 mmol) was used without further purification. Yield: 71%. – ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) = 1.42 (s, 12 H, 4 × C*H$_3$*), 1.81 (bs, 1 H, N*H*), 7.10–7.15 (m, 2 H, Ar*H*), 7.20–7.26 (m, 2 H, Ar*H*). – ^{13}C-NMR (101 MHz, CD$_2$Cl$_2$): δ (ppm) = 32.5 (+, *C*H$_3$), 63.1 (C$_{quart.}$, *C*CH$_3$), 121.9 (+, *C$_{Ar}$*H), 127.5 (+, *C$_{Ar}$*H), 149.6 (C$_{quart.}$, *C$_{Ar}$*). – IR (ATR): ṽ (cm^{-1}) = 2959 (m), 2920 (w), 1481 (w), 1448 (w), 1372 (w), 1360 (w), 1317 (w), 1237 (vw), 1166 (w), 1107 (w), 1022 (w), 991 (w), 883 (vw), 723 (m), 671 (w), 524 (w), 414 (vw). – MS (70 eV, EI), m/z (%): 175 (1.7)

[M⁺], 174 (12) [M⁺ – H], 160/161 (100/13) [M⁺ – CH₃], 159 (9.0) [M⁺ – CH₃ – H], 145/146 (34/5.1) [M⁺ – 2 × CH₃], 144 (29) [M⁺ – 2 × CH₃ – H]. – HR-MS ($C_{12}H_{17}N$): calcd. 175.1356, found. 175.1354.

The experimental data are consistent with the literature.[3, 4]

1,1,3,3-Tetramethylisoindolin-2-yloxyl: To a solution of 4.35 g (24.9 mmol, 1.00 equiv.) in 150 mL dichloromethane were added 9.12 g *m*CPBA (70%, 37.4 mmol, 1.00 equiv.). After stirring at room temperature for 8 h the reaction mixture was washed with 10% NaOH solution three times and brine and was dried over Na_2SO_4. The solvent was removed under reduced pressure and the obtained yellow solid (4.61 g, 24.2 mmol) was used without further purification. Yield: 97%. – mp: 123–125 °C. – IR (ATR): ṽ (cm⁻¹) = 2973 (w), 2926 (vw), 1483 (w), 1450 (w), 1373 (vw), 1355 (w), 1317 (vw), 1279 (w), 1165 (w), 1120 (w), 1022 (vw), 760 (m), 678 (vw), 614 (vw), 550 (w), 466 (vw). – MS (70 eV, EI), *m/z* (%): 190/191 (67/9.8) [M⁺], 175/176 (54/16) [M⁺ – CH₃], 160/161 (58/9.5) [M⁺ – 2 × CH₃], 158 (20), 145/146 (100/12) [M⁺ – 3 × CH₃], 129 (10), 117 (16). HR-MS ($C_{12}H_{16}NO·$): calcd. 190.1226, found 190.1225.

The experimental data are consistent with the literature.[3-5]

5-Iodo-1,1,3,3-tetramethylisoindolin-2-yloxyl: At 0 °C, 2.21 g KI (13.3 mmol, 0.550 equiv.) were added in small portions to a solution of 1.00 g periodic acid in 80 mL conc. sulfuric acid. After the addition was completed the mixture was stirred for further 15 min. Then, 4.61 g 1,1,3,3-tetramethylisoindolin-2-yloxyl (24.2 mmol, 1.00 equiv.) were added at 0 °C. The reaction mixture was warmed up slowly to room temperature while stirring for further 3 h. Afterwards the mixture was poured on 200 mL ice and was made alkaline (pH = 10) using NaOH pellets and 7 M NaOH-solution. The aqueous phase was extracted with dichloromethane three times and the combined organic phases were washed with sodium thiosulfate solution, water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, 7 × 20 cm, CH/CH_2Cl_2 = 1:5). 3.05 g of a yellow solid (9.65 mmol) was obtained as clean product as well as 0.725 g of starting material and a mixed fraction of both starting material and a small amount of product (3%). Yield (clean fraction): 40%. – mp: 135–138 °C. – Rf (CH/CH_2Cl_2 = 1:5) = 0.36. – IR (ATR): ṽ (cm⁻¹) = 3040 (vw), 2969 (w), 2924 (vw), 1598 (vw), 1447 (vw), 1429 (vw), 1398 (vw), 1372 (vw), 1356 (vw), 1306 (w), 1277 (w), 1164 (w), 1120 (w), 1076 (w), 910 (vw), 887 (vw), 830 (w), 820 (w), 790 (vw), 771 (vw), 625 (vw), 548 (w), 494 (w), 382 (vw). – MS (70 eV, EI), *m/z* (%): 316/317 (100/18) [M⁺], 301/302 (30/22) [M⁺ – CH₃], 286/287 (46/7.3) [M⁺ – 2 × CH₃], 271 (37/4.3) [M⁺ – 3 × CH₃], 144 (29) [M⁺ – 3 × CH₃ – I], 143 (11) [M⁺ – 2 × CH₃ – I –O], 129 (20), 128 (17). – HR-MS ($C_{12}H_{15}INO$): calcd. 316.0193, found 316.0193.

The experimental data are consistent with the literature.[6]
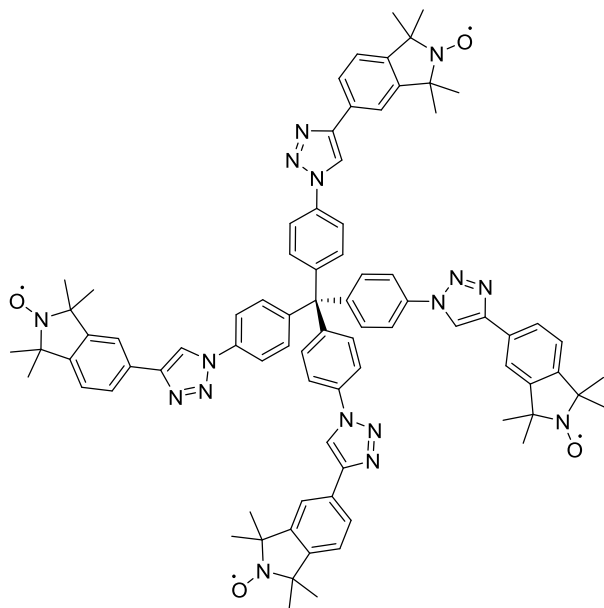
5-Ethynyl-1,1,3,3-tetramethylisoindolin-2-yloxyl (2): Under an argon atmosphere, 3.03 g 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxyl (9.58 mmol, 1.00 equiv.), 23.0 mg copper(I)iodide (0.120 mmol, 1.25 mol%), 0.151 mg [Pd(PPh₃)₂]Cl₂ (0.216 mmol, 2.25 mol%) were placed in 10 mL degassed triethylamine. Then, 2.80 mL trimethylsilylacetylene (1.93 g, 2.11 mmol, 2.22 equiv.) were added

and the reaction mixture was stirred at 50 °C for 6 h. After cooling to room temperature, the precipitate was filtered off and the solvent removed under reduced pressure. The residue was passed over a short column of neutral alumina (CH/EE = 15:1) and the solvent was again removed under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, 5 × 20 cm, CH/EE = 9:1). 1.01 g of a yellow solid (3.54 mmol, 37%) were obtained and used directly in the next step. A second mixed fraction was further purified by a second column (SiO$_2$, 4 × 20 cm, CH/EE = 15:1) to obtain additional 1.16 g of a yellow solid (4.03 mmol, 42%) with little impurities. – R_f (CH/EE = 9:1) = 0.28. – MS (70 eV, EI), m/z (%): 286/287 (99/19) [M$^+$], 271/272 (100/30) [M$^+$ – CH$_3$], 256/257 (58/12) [M$^+$ – 2 × CH$_3$], 241/242 (68/14) [M$^+$ – 3 × CH$_3$]. – HR-MS (C$_{17}$H$_{24}$NOSi$^{\cdot}$): calcd. 286.1622, found 286.1622.

7.10 mL of a 1 M KOH-solution (0.397 g, 7.08 mmol, 2.00 equiv. in water) were added to a solution of 1.01 g 5-[2-(trimethylsilyl)ethynyl]-1,1,3,3-tetramethylisoindoline (3.54 mmol, 1.00 equiv.) in 50 mL methanol. After stirring for 2.5 h at room temperature the reaction mixture was diluted with 45 mL water and extracted with diethyl ether three times. The combined organic phases were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO$_2$, 4 × 20 cm, CH$_2$Cl$_2$). 0.735 g of a yellow solid (3.43 mmol) were obtained. Yield: 97%. - mp: 121 °C. – R_f (CH$_2$Cl$_2$) = 0.41. – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3194 (w), 2977 (vw), 2928 (vw), 1572 (vw), 1487 (vw), 1454 (vw), 1428 (vw), 1362 (w), 1311 (vw), 1279 (vw), 1164 (w), 1121 (w), 993 (vw), 901 (vw), 836 (w), 699 (w), 663 (vw), 625 (vw), 596 (vw), 549 (w), 492 (vw), 411 (vw). – MS (70 eV, EI), m/z (%): 214 (89) [M$^+$], 199/200 (100/18) [M$^+$ – CH$_3$], 184/185 (54/7.7) [M$^+$ – 2 × CH$_3$], 182 (19) [M$^+$ – CH$_3$ – O – H], 169/170 (79/9.3) [M$^+$ – 3 × CH$_3$], 145 (21) [M$^+$ – 4 × CH$_3$], 153 (28) [M$^+$ – 3 × CH$_3$ – O], 152 (33) [M$^+$ – 3 × CH$_3$ – O – H], 141 (20), 128 (15) [M$^+$ – 3 × CH$_3$ –O – CCH], 115 (25). – HR-MS (C$_{14}$H$_{16}$NO$^{\cdot}$): calcd. 214.1226, found 214.1227.

The experimental data are consistent with the literature.[7]

Tetrakis(4-(4'-(1'',1'',3'',3''-tetramethylisondolin-2-oxyl-5''yl)-1',2',3'-triazol-1'-yl)phenyl)methane (3):
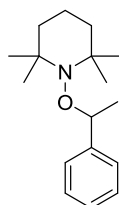

In a closed vial, 226 mg tetrakis(4-azidophenyl)methane (0.467 mmol, 1.00 equiv.), 11.7 mg copper sulfate, (46.7 μmol, 0.100 equiv.), 37.0 mg sodium ascorbate (187 μmol, 0.400 equiv.) und 601 mg 5-ethynyl-1,1,3,3-tetramethylisoindoline-2-yloxyl (2.80 mmol, 6.00 equiv.) in 17 mL of a ^{t}BuOH/H$_2$O-mixture (1:1) were stirred at 70 °C for 72 h. After cooling to room temperature 15 mL methanol were added and the precipitate was filtered off, washed with 50 mL of water, 50 mL of methanol and little diethyl ether. The solid was dried in vacuum to obtain 0.551 g of a beige solid (0.411 mmol). Yield: 88%. – mp: 320–325 °C (decomposition). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2972 (vw), 2928 (vw), 1605 (vw), 1512 (w), 1483 (vw), 1439 (vw), 1402 (vw), 1357 (vw), 1313 (vw), 1287 (vw), 1228 (vw), 1164 (ve), 1121 (vw), 1032 (w), 995 (vw), 980 (vw), 899 (vw), 826 (w), 731 (vw), 691 (vw), 635 (vw), 549 (w), 497 (vw). – MS (3-NBA, FAB), m/z (%): 1359/1360 [M$^+$ + H$_2$O], 1341/1342/1344/1345 [M$^+$], 1327

[M$^+$ – CH$_3$], 1311 [M$^+$ – CH$_3$ – O]. – C$_{81}$H$_{80}$N$_{16}$O$_4$· • 2 H$_2$O (1359.6): calcd. C 70.62, H 6.15, N 16.27; found C 70.60, H 6.07, N 15.90.

According to the mass and elemental analysis, tetranitroxide **3** coordinates water from the reaction mixture which cannot be removed in vacuum.

2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (4):[8] Under an Argon atmosphere, 2.54 g TEMPO (16.1 mmol, 1.10 equiv.), 0.978 g copper powder, (15.4 mmol, 1.05 equiv.), 53.0 mg Cu(OTf)$_2$ (147 µmol, 1.00 mol%) and 157 mg 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.586 mmol, 4.00 mol%) in 15 mL abs. toluene were suspended. After, 2.00 mL 1-bromo-1-phenylethane (2.71 g, 14.7 mmol, 1.00 equiv.) were added and the mixture was stirred at 75 °C for 3 d. After cooling to room temperature the mixture was filtrated over silica gel and the filter cake was washed with CH$_2$Cl$_2$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO$_2$, 4×20 cm, Cyclohexane/CH$_2$Cl$_2$ = 2:1➔ 1:1). 3.19 g of a colorless solid (12.2 mmol) were obtained. Yield: 83%. – mp: 45–48 °C. – R_f (CH/CH$_2$Cl$_2$ = 1:1) = 0.82. – ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) = 0.66 (s, 3 H, TEMPO-CH$_3$), 1.03 (s, 3 H, TEMPO-CH$_3$), 1.17 (s, 3 H, TEMPO-CH$_3$), 1.23 – 1.65 (m, 9 H, TEMPO-CH$_3$, TEMPO-CH$_2$), 1.48 (dd, ^{3}J = 6.7, 1.0 Hz, 3 H, CH$_3$), 4.79 (qd, ^{3}J = 6.7, 1.0 Hz, 3 H, CH), 7.19 – 7.27 (m, 1 H, H$_{aromat.}$), 7.27 – 7.35 (m, 4 H, H$_{aromat.}$). – ^{13}C-NMR (101 MHz, CD$_2$Cl$_2$): δ (ppm) = 17.8 (–, CH$_2$), 20.6 (+, CH$_3$), 23.8 (+, CH$_3$), 26.2 (+, CH$_3$), 34.5 (+, CH$_3$), 34.7 (+, CH$_3$), 41.0 (–, CH$_2$), 60.1 (C$_{quart.}$, CMe), 68.3 (C$_{quart.}$, CMe), 83.5 (+, CH), 127.2 (+, C$_{arom.}$H), 127.3 (+, C$_{arom.}$H), 128.5 (+, C$_{arom.}$H), 146.4 (C$_{quart.}$, C$_{aromat.}$). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2971 (w), 2926 (m), 1493 (vw), 1451 (w), 1374 (w), 1360 (w), 1280 (vw), 1257 (w), 1241 (w), 1194 (w), 1132 (w), 1060 (m), 1028 (w), 987 (w), 956 (w), 934 (w), 882 (w), 845 (vw), 759 (w), 697 (m), 624 (w), 547 (w). MS (70 eV, EI), *m/z* (%): 261/262 (<1) [M$^+$], 246/247 (<1) [M$^+$ – CH$_3$], 188 (<1) [M$^+$ – 5 × CH$_3$], 156 (57) [TEMPO$^+$], 142 (100) [TEMPO$^+$ – CH$_3$], 123 (16), 105 (79) [C$_8$H$_9^+$], 69 (30). – HR-MS (C$_{17}$H$_{27}$NO): calcd. 261.2087, found 261.2085.

The experimental data are consistent with the literature.[9]

3) EPR measurements

For the EPR experiments, stock solutions of all compounds investigated were prepared in toluene with a concentration of 0.1 mM (referred to nitroxide or alkoxyamine moieties).

For the reference EPR measurements shown in Figure 2 of the main manuscript, TPM NO **3** and TEMPO **5** solutions were mixed as follows:

100% TPM NO **3**: 1.0 mL TPM NO **3** solution + 0.0 mL TEMPO **5** solution

90% TPM NO **3**: 0.90 mL TPM NO **3** solution + 0.10 mL TEMPO **5** solution

50% TPM NO **3**: 0.50 mL TPM NO **3** solution + 0.50 mL TEMPO **5** solution

10% TPM NO **3**: 0.10 mL TPM NO **3** solution + 0.90 mL TEMPO **5** solution

0% TPM NO **3**: 0.0 mL TPM NO **3** solution + 1.0 mL TEMPO **5** solution

For the EPR measurements shown in Figure 3 of the main manuscript mixtures of TPM NO **3** solution (2 mL) and alkoxyamine **4** solution (2 mL) were measured after degassing and heating under nitrogen for 15 min, 1 h, 2 h, 14 h, 48 h and 96 h.

For the EPR measurements shown in Figure 4 in the main manuscript, TPM NO **3** and alkoxyamine **4** solutions were mixed as follows:

1/1   2.0 mL TPM NO **3** solution + 2.0 mL alkoxyamine **4** solution + 2.0 mL toluene

1/2   2.0 mL TPM NO **3** solution + 4.0 mL alkoxyamine **4** solution

1/5   1.0 mL TPM NO **3** solution + 5.0 mL alkoxyamine **4** solution

Afterwards the solutions were degassed and heated under nitrogen for 1 h (left column) or 24 h (right column).

4) EPR data analysis

Spectra of TPM NO **3** and TEMPO **5** were visually fitted with the 'garlic' routine of EasySpin[10] under the assumption of fast isotropic Brownian rotational diffusion. A virtually perfect fit was obtained for TEMPO **5** with g tensor principal values of 2.0092, 2.007, and 2.0028 and a ^{14}N hyperfine tensor with coinciding principal axes frame and principal values (12.61, 12.61, 105.6) MHz. Gaussian and Lorentzian line broadening with 0.09 mT full width at half height was assumed and a rotational correlation time of 4 ps (fast limit) was fitted. For TPM NO **3**, ^{13}C satellite peaks of the three lines of the ^{14}N hyperfine triplet were not accounted for by such fitting, a problem that was not affecting later decomposition of the two-component spectra. The same linewidth parameters gave a good fit of the main lines, but now with all g tensor principal values reduced by 0.00022, with hyperfine tensor principal values (12.61, 12.61, 94) MHz and a fitted rotational correlation time of 29.5 ps. Note that the g and hyperfine tensor principal values should not be considered as experimental results. Only the isotropic values can be extracted from such spectra. To estimate anisotropy, we started from values given in literature[11].

Two-component spectra were then least-square fitted with a home-written Matlab® script. In order to obtain good fits, we found it necessary to vary the microwave frequency, the isotropic g value difference (varying between 0.00015 and 0.00022), intrinsic linewidth (as the same multiple of 0.09 mT Gaussian and Lorentzian linewidths for both species), and the normalized fraction p of TEMPO **5** (the fraction of TMP NO **3** is 1-p). Other spin Hamiltonian parameters and the rotational correlation times could be kept constant. The fraction p multiplied by 100 (expressed as percent exchanged) is plotted in Figure 3 of the main text.

5) Calculations

Computational details

The quantum chemical calculations reported in this work have been performed with the TURBOMOLE program package[12] using standard density functional theory (DFT) methods and orbital basis sets of type "def2". [13] The geometries of **3**, **4**, **5** and **6** were optimized at the TPSS [14]/TZVP, B3LYP[15]/SVP and B3LYP/TZVP levels of theory employing tight convergence criteria (SCF energy: 10^{-8} Eh, energy gradient: 10^{-5} E$_h$/a$_0$ and inclusion of the derivatives of quadrature weights) and fine quadrature grids

(m5). All structures were confirmed to be minima on the potential energy surface by calculation of the vibrational frequencies. Thermodynamic data (ΔH, ΔS, ΔG) were computed for a standard pressure of 0.1 MPa and various temperatures (0 K, 353.15 K, 373.15 K). For the evaluation of the partition functions the vibrational frequencies were scaled[16] by a factor of 0.9914 for TPSS and 0.9614 for B3LYP, respectively.

Calculation of the Gibbs free energy of reaction

The Gibbs free energy of reaction, ΔG, can be obtained according to the following equation:

$$\Delta G = \Delta H - T\Delta S$$

Due to many low-frequency vibrations found for **3** and **6**, the harmonic oscillator approximation used for the calculation of the partition sums is introducing large errors, especially for the entropic contribution ΔS which should be small. We therefore rather consider ΔH for estimation of the experimental ΔG.

Table S1: Computed values (in kJ/mol) for the enthalpy of reaction, ΔH.

	ΔH (0 K)	ΔH (353.15 K)	ΔH (373.15 K)
TPSS/TZVP	5.1	4.4	4.4
B3LYP/SVP	−3.7	−3.6	−3.7
B3LYP/TZVP	−3.1	−3.2	−3.2

Calculation of the equilibrium constant and the limit of exchange in equilibrium

We consider the reaction

$$A \ + \ 4B \ \rightleftharpoons \ C \ + \ 4D$$
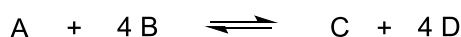
with TPM-NO **3** (= A), TEMPO-alkoxyamine **4** (= B), TPM-NO-alkoxyamine **6** (= C) and TEMPO **5** (= D). The equilibrium constant is then given as

$$K = \frac{[C][D]^4}{[A][B]^4}$$

where the equilibrium concentrations are determined by the initial amount of A and B and the limit of exchange in equilibrium, x_{eq}. Using molar ratios of 1/1, 1/2 and 1/5, the following polynomial equations have to be solved:

$$1/1: \ K \cdot (1-\xi_{eq}) \cdot (1-\xi_{eq})^4 - \xi_{eq}^5 = 0$$

$$1/2: \ K \cdot (1-\xi_{eq}) \cdot (2-\xi_{eq})^4 - \xi_{eq}^5 = 0$$

$$1/5: \ K \cdot (1-\xi_{eq}) \cdot (5-\xi_{eq})^4 - \xi_{eq}^5 = 0$$

x_{eq} may take values between 0 (0 % exchange) and 1 (100 % exchange). The equilibrium constant K can be obtained for a given temperature T via the following relation:

$$\Delta G = -RT \cdot \ln K$$

Table S2: Calculated limit of exchange, x_{eq}, for the radical exchange process of TPM-NO **3** and TEMPO-alkoxyamine **4** (T = 80°C = 353.15 K).

Molar ratio of 3/4	$\Delta G = -15$ kJ/mol	$\Delta G = -10$ kJ/mol	$\Delta G = -5$ kJ/mol	$\Delta G = 0$ kJ/mol
1/1	0.7353	0.6639	0.5843	0.5000
1/2	0.9942	0.9737	0.9153	0.8159
1/5	0.9999	0.9998	0.9992	0.9961

Molar ratio of 3/4	$\Delta G = 5$ kJ/mol	$\Delta G = 10$ kJ/mol	$\Delta G = 15$ kJ/mol
1/1	0.4156	0.3360	0.2646
1/2	0.6945	0.5693	0.4525
1/5	0.9808	0.9256	0.8112

Table S3: Calculated limit of exchange, x_{eq}, for the radical exchange process of TPM-NO **3** and TEMPO-alkoxyamine **4** (T = 100°C = 373.15 K).

Molar ratio of 3/4	$\Delta G = -15$ kJ/mol	$\Delta G = -10$ kJ/mol	$\Delta G = -5$ kJ/mol	$\Delta G = 0$ kJ/mol
1/1	0.7245	0.6558	0.5798	0.5000
1/2	0.9925	0.9696	0.9109	0.8159
1/5	0.9999	0.9998	0.9992	0.9961

Molar ratio of 3/4	$\Delta G = 5$ kJ/mol	$\Delta G = 10$ kJ/mol	$\Delta G = 15$ kJ/mol
1/1	0.4201	0.3442	0.2754
1/2	0.7012	0.5825	0.4704
1/5	0.9824	0.9345	0.8328

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