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May the First Addition of Alkyl Radical Play a Role in the Fate of NMP?

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Experimental section

4-Phenyl-1-[(1-phenylethyl)-oxy]-2,2,5,5-tetramethyl-2,5-dihydroimidazole (1e). Colorless oil, 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.63-6.92 (m, 10H, CH); 4.69 (q, $^3J_{H\text{-}H}$ = 6 Hz, 1H, $CHCH_3$); 1.54, 1.49, 1.48, 1.46, 1.43, 1.51, 1.25, 0.90, 0.82 (15H, CH_3).

2-methyl-2-[2,2,5,5-tetramethyl-4-phenylimidazoline-1-oxyl]propionic acid 4-nitrophenyl ester (1g). Yellow powder, 58% yield. Anal. calcd. for $C_{23}H_{27}N_3O_5$ (425): C, 64.94; H, 6.35; N, 9.88; O, 18.82; Found: C, 64.32; H, 6.35; N, 9.46; O, 19.25. ^{1}H NMR ($CDCl_3$): δ = 8.30 (d, $^2J_{H\text{-}H}$ = 8 Hz, 2 H, CH), 7.75–7.60 (m, 2 H, CH), 7.45-7.30 (m, 3 H, CH), 7.25 (m, 2 H, CH), 1.67 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3) 1.56 (s, 3 H, CH_3), 1.51 (s, 6 H, CH_3), 1.42 (s, 3 H, CH_3) ppm. LRMS *m/z* 426 $[M+H]^+$, *m/z* 448 $[M+Na]^+$.

2,2,3,4,4,5,5-Heptamethyl-1-[(1-phenylethyl)-oxy]-imidazolidine (5e). Colorless oil, 52% yield. ^{1}H NMR: δ = 7.55–7.05 (m, 5 H, CH), 4.85-4.60 (m, J = 9 Hz, 1 H, CH), 2.20-2.09 (2s, 3 H, NCH_3), 1.52-1.47 (2d, J = 9 Hz, 3 H, CH_3), 1.30-1.21 (2s, 3 H, CH_3), 1.15 (d, J = 3 Hz, 3 H, CH_3), 1.02-1.00 (2s, 3 H, CH_3), 0.95-0.85 (2s, 3 H, CH_3), 0.91-0.89 (2s, 3 H, CH_3), 0.58-0.54 (2s, 3H, CH_3) ppm. ^{13}C NMR: δ = 145.56-144.96 (2s, *C*-CH), 128.00 (s, 2CH), 127.12-126.99 (2s, 2CH), 82.60-82.32 (2s, C-*C*H-CH_3), 79.18-78.65 (2s, N*C*N), 66.96-66.58 (2s, N*C*$(CH_3)_2$), 61.35-61.18 (2s, N*C*$(CH_3)_2$), 27.60-27.11 (3s, CH_3), 26.00 (s, CH_3), 24.63-24.41 (2s, CH_3), 23.36-22.89 (2s, CH_3), 22.72-22.59 (2s, CH_3), 22.02 (s, CH_3), 17.89-17.78 (2s, 2CH_3) ppm. LRMS *m/z* 291 $[M+H]^+$, *m/z* 308 $[M+NH_4]^+$.

5,5-Diphenyl-2,2,3,4,4-pentamethyl-1-[(1-phenylethyl)-oxy]-imidazolidine (6e). Colorless oil, 48% yield. ESI-MS m/z 415.2746 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ = 7.8-7.18 (m, 15 H, CH); 5.07 (q, ^{3}J = 6 Hz, 1H, CH); 2.26 (bs, 3H, CH_3), 1.53-0.47 (m, 15H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 134.73 (s, C_{ar}), 129.93 (s, C_{ar}), 127.87(s, CH_{ar}), 127.18 (s, CH_{ar}), 126.41 (s, CH_{ar}), 126.05 (s, CH_{ar}), 128.29 (s, CH_{ar}), 81.68 (s, *C*H-CH_3), 81.60 (s, *C*), 80.89 (s, C), 64.56 (s, C), 27.66 (s, CH_3), 26.18 (s, CH_3), 23.05 (s, CH_3), 23.03 (s, CH_3), 27.15 (s, CH_3).

2-Methyl-2-[(2,2,3,4,4-pentamethyl-5,5-diphenylimidazolidine-1-yl)oxy]-propionic acid 4-nitrophenyl ester (6g). Yellowish powder, 72% yield. ^{1}H NMR: δ = 8.09 (d, $^{2}J_{H,H}$ = 8 Hz, 2 H, CH), 8.05–7.80 (m, 2 H, CH), 7.70-7.50 (m, 2 H, CH), 7.40-7.15 (m, 3 H, CH), 7.15-6.95 (m, 3 H, CH), 6.49 (d, $^{2}J_{H,H}$ = 8 Hz, 2 H, CH), 2.37 (s, 3 H, NCH_3), 1.76 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 0.45 (s, 3 H, CH_3) ppm. LRMS *m/z* 518 $[M+H]^+$, *m/z* 540 $[M+Na]^+$.

Methyl 2-[(2,2,3,4,5,5-hexamethylimidazolidin-1-yl)oxy]propanoate (10a), a mixture of diastereomers, colorless oil, 37 % yield. Anal. Calc. for $C_{13}H_{26}N_2O_3$: C, 60.44; H, 10.14; N, 10.84; found: C, 60.68; H, 10.28; N, 11.06. ν_{max} (neat)/cm^{-1} 2976, 2844, 2786, 2621, 1757, 1450, 1376, 1364, 1273, 1239, 1202, 1181, 1146, 1094, 1042 and 994. δ_H(400 MHz; $CDCl_3$):

4.17 (total 1 H, m, O-C<u>H</u>(CH_3)), 3.57, 3.58 (total 3 H, each s, O-CH_3), 2.28, 2.13 (total 1 H, each m, 4-C<u>H</u>(CH_3)), 2.00, 1.99 (total 3 H, each s, N-CH_3), 1.21, 1.20 (total 3 H, each d, J 3.5, O-CH(C<u>H</u>$_3$)), 1.09, 1.03, 0.97, 0.94 (total 6 H, each s, 2-C(CH_3)$_2$), 0.84, 0.85, 0.87, 0.89 (total 6 H, each s, 5-C(CH_3)$_2$), 0.77, 0.78 (3 H, each d, J 3, 4-CH_3),; δ_C(100 MHz, $CDCl_3$): 12.58, 12.63, 12.79, 12.88 (4-CH_3), 13.63, 13.74, 15.42, 15.56 (O-CH(<u>C</u>H_3)), 16.81, 17.06, 23.16, 23.70, 23.95, 24.34, 25.21, 25.56, 25.95, 26.63, 27.03, 27.81 (2,5-C(<u>C</u>H_3)$_2$), 32.26, 32.48 (N-CH_3), 51.04, 51.06 (O-CH_3), 61.60, 62.07, 64.39, 64.76 (C-4), 62.75, 63.31, 64.55, 64.90 (C-5), 79.40, 80.05, 80.21 (O-<u>C</u>H(CH_3)), 80.02, 81.64 (C-2), 173.53, 173.63, 173.88, 174.08 (C=O).

***tert*-Butyl 2-[(2,2,3,4,5,5-hexamethylimidazolidin-1-yl)oxy]-2-methylpropanoate (10d)**, a mixture of conformers, colorless oil, 44 % yield. Anal. Calc. for $C_{17}H_{34}N_2O_3$: C, 64.93; H, 10.90; N, 8.91, found: C, 65.12; H, 10.86; N, 8.74. ν_{max} (neat)/cm^{-1} 2977, 2934, 2843, 2785, 2621, 1731, 1460, 1366, 1273, 1240, 1220, 1164, 1136 and 850. δ_H(200 MHz; $CDCl_3$): 0.81, 0.82 (total 3 H, each d, J 6, 4-CH_3), 0.84, 0.87, 0.90, 0.92, 0.94, 0.97, 1.07, 1.09 (total 12 H, each s, 2,5-CH_3), 1.27 (total 6 H, s, O-C(CH_3)$_2$), 1.36 (total 9 H, s, C(CH_3)$_3$), 2.04, 2.05 (total 3 H, each s, N-CH_3), 2.16, 2.20 (total 1 H, each m, 4-C<u>H</u>(CH_3)); δ_C(50 MHz, $CDCl_3$): 12.60, 13.99 (4-CH_3), 13.15, 15.56 (O-C(<u>C</u>H_3)$_2$), 22.48, 23.44, 24.14, 24.38, 24.81, 25.07, 25.69, 27.31 (2,5-C(<u>C</u>H_3)$_2$), 27.63 (C(<u>C</u>H_3)$_3$), 32.61, 32.79 (N-CH_3), 62.23, 64.55 (C-4), 63.05, 64.48 (C-5), 80.17 (<u>C</u>(CH_3)$_3$), 80.44, 81.21 (O-<u>C</u>(CH_3)$_2$), 81.10, 81.74 (C-2), 173.44 (C=O).

1,2,2,4,4,5-Hexamethyl-3-[(1-phenylethyl)-oxy]imidazolidine (10e), a mixture of diastereomers, colorless oil, 45 % yield. Anal. calc. for $C_{17}H_{28}N_2O$: C, 73.87; H, 10.21; N, 10.13; found: C, 73.65; H, 10.25; N, 9.91. ν_{max} (neat)/cm^{-1} 3086, 3064, 3032, 2974, 2929, 2842, 2784, 2708, 2680, 2620, 1603, 1494, 1452, 1374, 1361, 1273, 1239, 1220, 1178, 1065, 1009, 996, 892 and 760. δ_H(400 MHz; $CDCl_3$): 0.59, 1.02 (total 3 H, each d, J 3, 4-CH_3), 0.77, 0.89, 0.91, 0.93, 0.94, 0.95, 0.97, 1.07, 1.09, 1.11, 1.21, 1.24, 1.28, 1.31 (total 12 H,

each s, 2,5-CH_3), 1.35, 1.38, 1.53 (total 3 H, each d, J 3, O-CH-C<u>H</u>$_3$) 2.11, 2.13, 2.20 (total 3 H, each s, N-CH_3), 2.26, 2.33, 2.43, 2.48 (total 1 H, m, 4-C<u>H</u>(CH_3)), 4.73 (total 1 H, m, O-C<u>H</u>-CH_3), 7.26–7.38 (total 5 H, m, Ph); δ_C(100 MHz, $CDCl_3$): 13.19, 13.91 (O-CH(<u>C</u>H_3)Ph), 13.06, 13.21, 15.70, 15.90 (4-CH_3), 21.66, 21.74, 22.13, 23.47, 23.84, 24.39, 24.49, 24.57, 25.43, 26.08 (2,5-C(<u>C</u>H_3)$_2$), 32.47, 32.54, 32.64, 32.82 (N-CH_3), 62.02, 62.33, 64.59, 64.75 (C-4), 62.34, 62.63, 64.28, 64.54 (C-5), 79.64, 80.31 (C-2), 82.25, 82.35, 82.50 (O-<u>C</u>H(CH_3)Ph), 126.85, 126.94, 127.00, 127.07, 127.13, 127.74, 127.81 (*o*,*m*,*p*-Ph), 144.36, 144.50 (*i*-Ph).

2,2-Dibutyl-[(1-phenylethyl)-oxy]-3,4,5,5-tetramethylimidazolidine (12e). Colorless oil, 51% yield. ^{1}H NMR: δ = 7.39-7.17 (m, 5H, CH), 5.21 (q, J=6 Hz, 1H, C*H*N), 4.68 (m, 1H, C*H*Ph).

2,2-Diethyl-5,5-diphenyl-[(1-phenylethyl)-oxy]-3,4,4-trimethylimidazolidine (16e). Colorless oil, 50% yield. $C_{30}H_{38}N_2O$ (442.2984) ESI-MS m/z 443.3051 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ = 7.50-7.02 (m, 15 H, CH); 5.12 (q, ^{3}J = 9 Hz, 1H, CH); 2.40 (s, 3H, CH_3), 1.55-0.57 (m, 19H, CH_2 + CH_3). ^{13}C NMR ($CDCl_3$): δ = 145.11 (s, C_{ar}), 130.02 (s, C_{ar}), 128.25(s, CH_{ar}), 128.23 (s, CH_{ar}), 127.73 (s, CH_{ar}), 127.53 (s, CH_{ar}), 126.86 (s, CH_{ar}), 126.50 (s, CH_{ar}), 126.10 (s, CH_{ar}), 84.91 (s, *C*), 81.25 (s, C), 81.22 (s, *C*H-CH_3), 64.09 (s, C), 29.75 (s, CH_3), 29.44 (s, CH_2), 23.85 (s, CH_3), 23.03 (s, CH_3), 21.00 (s, CH3), 10.47 (s, CH_3).

2,2-Diethyl-3,4,5,5-tetramethyl-[(1-phenylethyl)-oxy]-imidazolidine (17e). Colourless oil, mixture of diastereomers, yield 60%. Anal. calcd. for $C_{19}H_{32}N_2O$ (304.25): C, 74.95; H, 10.59; N, 9.20. Found: C, 74.70; H, 10.25; N, 8.87. ν_{max}(KBr)/cm^{-1} 3087, 3065, 3032, 2973, 2795, 1494, 1452, 1377, 1227, 1064, 1009, 997, 965, 912, 841, 760 and 699; δ_H(300 MHz; $CDCl_3$) 0.84, 1.01, 1.49 (total 6 H t J 7, CH_3, Et), 0.93 (3 H m 4-CH_3), 1.09, 1.12, 1.23, 1.28 (total 6 H each s, 5-Me) 1.34-1.90 (total 4 H m, CH_2), 1.46 and 1.51 (total 3H, both d J 6.6, C<u>H</u>$_3$CHPh), 2.26, 2.30 (total 3 H, each s, NCH_3), 2.49, 2.60 (total 1H, both q J 6.6, 4-CH),

4.71 (1H m, $CH_3C\underline{H}Ph$), 7.35 (5H m, Ph); δ_C(100 MHz; $CDCl_3$) 9.41, 9.69, 9.89, 9.95 (CH_3, Et), 13.94, 13.99 (4-Me), 16.47, 16.65 (O-CH-$\underline{C}H_3$), 22.20, 22.42, 25.69, 26.38, 26.69 (5-Me) 28.87, 29.23, 30.48, 30.92 (CH_2), 32.97, 33.15 (N-CH_3), 63.54, 63.64 (N-CH), 63.87, 64.08 (C-5), 81.92, 82.07 (O-CH), 82.95, 83.63 (C-2), Ph: 126.66, 127.00 (C_o), 127.77, 127.81 (C_m), 128.17, 128,51 (C_p), 144.61, 144,86 (C_i).

2-Methyl-2-[(2,2-diethyl-3,4,5,5-tetramethylimidazolidine-1-yl)oxy]propionic acid 4-nitrophenyl ester (17g). Colourless oil, yield 50%. Anal. calcd. for $C_{21}H_{33}N_3O_5$ (407,50): C, 61.90; H, 8.16; N, 10.31. Found: C, 61.70; H, 8.25; N, 9.04. ν_{max}(KBr)/cm^{-1} 3117, 3085, 2978, 2797, 1767, 1616, 1592, 1525, 1490, 1455, 1347, 1204, 1163, 1012, 863, 711, 687 and 661; δ_H(300 MHz; $CDCl_3$) 0.90 – 0.98 (total 6 H, m, CH_3, Et), 0.99 (total 3 H, d, J 7, 4-CH_3), 1.09, 1.12 (each 3 H s, 5-Me), 1.40-1.53, 1.55-1.72 and 1.75-1.90 (1 H, 2H and 1 H, each m, CH_2) 1.62 and 1.64 (3 H and 3 H m, O-C(CH_3)$_2$CO), 2.33 (3 H s, N-CH_3), 2.46 (1H q J 7, CH) 7.35 and 8.31 (AA'BB' J 9, C_6H_4); δ_C(75 MHz; $CDCl_3$) 8.98, 9.36 (CH_3, Et), 13.50 (4-CH_3), 15.78 and 23.36 (5-Me), 24.52, 25.20 (O-C($\underline{C}H_3$)$_2$CO), 28.86, 29.87 (CH_2), 32.28 (N-CH_3), 62.89 (CH), 63.59 (C-5), 80.56 (O-$\underline{C}$(CH_3)$_3$), 83.34 (C-2), 121.31 and 124.34 (CH, Ar), 144.32 (C-N, Ar), 154.81 (C-O, Ar), 171.33 (C=O).

Methyl 2-[(2,2,3,4-tetramethyl-1,4-diazaspiro[4.4]non-1-yl)oxy]propanoate (19a), a mixture of diastereomers, colorless oil, 30 % yield. ν_{max} (neat)/cm^{-1} 2952, 2869, 2841, 2784, 2634, 1757, 1454, 1363, 1325, 1272, 1250, 1252, 1203, 1147, 1088, 1041, 982, 944, and 848. δ_H(400 MHz; $CDCl_3$): 0.82 (total 3 H, d, J 6, 4-CH_3), 0.91, 0.93, 0.94, 1.01, 1.04, 1.05, 1.06, 1.10 (total 6 H, each s, 5-CH_3), 1.28, 1.30 (total 3 H, each d, J 6.5, O-CH(C$\underline{H}_3$)), 1.34–2.09 (total 8 H, m, CH_2), 2.04, 2.05, 2.09 (total 3 H, each s, N-CH_3), 2.20, 2.33, 2.55 (total 1 H, m, 4-C$\underline{H}$(CH_3)), 3.60, 3.63 (total 3 H, each s, O-CH_3), 4.23, 4.34 (total 1 H, each m, O-C$\underline{H}$-(CH_3)); δ_C(100 MHz, $CDCl_3$): 13.16, 13.30, 13.51, 13.66 (4-CH_3), 16.19, 16.33, 17.22, 17.54 (O-CH($\underline{C}H_3$)), 21.68, 21.79, 24.61, 24.66, 24.82, 25.04, 25.12, 26.91, 27.19, 29.41, 32.08,

32.21, 33.54, 34.76, 36.08, 36.74 (CH_2), 23.67, 23.78, 25.22, 26.05, 26.54 (5-CH_3), 31.97, 32.01, 32.54, 32.60 (N-CH_3), 51.22, (O-CH_3), 61.95, 62.20, 64.96, 65.12 (C-5), 63.34, 63.92, 65.96, 66.06 (C-4), 78.69, 79.58, 79.67, 80.11 (O-$\underline{C}$H(CH_3)), 90.17, 92.44, 92.63 (C-2), 173.53, 173.73, 173.84, 174.0 (C=O).

2,2-**Diethyl-3,4-dimethyl-1-[(1-phenylethyl)-oxy]-1,4-diaza-spiro[4,5]decan (20e)**, a mixture of diastereomers, colorless oil, 50% yield. Anal. calcd. for $C_{22}H_{36}N_2O$ (344): C, 76.69; H, 10.53; N, 8.13; Found: C, 76.77; H, 10.13; N, 8.30; ν_{max} (neat)/cm^{-1} 3031, 2930, 2876, 2786, 1454, 1494, 1452, 1371, 1292, 1204, 1061, 1030, 1007, 993, 960, 909, 885, 760, and 700; δ_H(300 MHz; $CDCl_3$) 0.37, 0.39, 0.54, 0.78, 0.83, 1.06, 1, 10, 1.12 (total 6H, each t J= 7 Hz, CH_3, Et), 0.92, 0.95, 1.00, 1.01 (total 3H, each d, J= 7 Hz, 4-CH_3), 1.25-2.20 (14 H, m, CH_2), 1.51, 1.55 (total 3H, both d, J= 7 Hz, CH_3, PhCHCH_3), 2.27, 2.31, 2.34, 2.36 (total 3H, each s, N-CH_3), 2.46, 2.53, 2.88, 2.95 (total 1H, each q, J= 7 Hz, N-CH), 4.74, 4.79, 5.24, 5.21 (total 1H, each q, J= 7 Hz, O-CH), 7.29-7.44 (5H, m, Ph); δ_C(100 MHz; $CDCl_3$) 8.11, 8.29, 8.97, 9.36, 9.68, 9.99, 10.18, 11.04 (CH_3, Et), 13.56, 13.63, 14.80, 14,93 (4-CH_3), 22.11, 22.39, 22.83, 22.92 (CH_3, PhCHCH_3), 21.24, 22.48, 22.77, 23.77, 23.90, 24.77, 25.16, 25.28, 25.38, 25.82, 26.61, 26.88, 26.93, 27.26, 27.69, 29.19, 29.54, 30.41, 31.39, 32.48, 33.77, 35.78, 36.23 (CH_2), 34.61, 34.69, 35.16, 35.69 (N-CH_3), 58.56, 58.67, 62.66, 62.84 (N-CH), 66.63, 67.33, 69.05, 69.52 (CEt_2), 81.77, 81.95, 82.02, 82.69 (O-$\underline{C}$H(CH_3)Ph), 81.34, 82.21 (C-2), 125.96, 126.06, 126.16, 126.65, 126.73, 126.79, 126.90, 126.96, 127.15, 127.19, 127.70, 127.75, 127.84, 127.88, 127.98, 128.16, 128.51 (*o*,*m*,*p*-Ph), 143.96, 144.34, 144.64, 144.74 (C_i, Ph).

2-[(2,2,5,5-tetraethyl-3,4-dimethylimidazolidine-1-yl)oxy]propionic acid methyl ester (21a). Colorless oil, mixture of 4 isomers, 70% yield. Anal. calcd. for $C_{17}H_{34}N_2O_3$ (314): C, 64.93; H, 10.90; N, 8.91. Found: C, 65.27; H, 10.96; N, 8.44. ν_{max}(KBr)/cm^{-1} 2970, 2937, 2880, 2793, 1758, 1465, 1373, 1275, 1202, 1149, 1090 and 1048; δ_H(400 MHz; $CDCl_3$) 0.60

– 1.0 (total 15 H, m, 5CH_3, 4Et and 4-CH_3), 1.23, 1.27, 1.29 and 1.30 (total 3 H, each d, J 7, O-CH(C$\underline{H}_3$)CO), 1.3-2.0 (total 8 H, m, CH_2), 2.04, 2.20 and 2.24 (total 3H, each s, N-CH_3), 2.62 – 2.83 (1H, m, NCH), 3.66, 3.67 (total 3 H, each s, OCH_3), 4.29 (1H, m, OCH); δ_C(100 MHz; $CDCl_3$) 6.82, 6.97, 7.86, 7.93, 9.02, 9.17, 9.21, 9.31, 9.36, 9.44, 9.61, 9.64, 10.39, 10.91, 10.95 (CH_3, Et), 14.13, 14.22, 15.17, 15.28 (4-CH_3), 17.00, 17.64, 17.72, 17.77 (OCH-C$\underline{H}$3), 21.26, 21.88, 23.32, 23.43, 24.92, 25.26, 25.59, 25.78, 26.72, 27.83, 28.06, 28.45, 29.56, 29.88, 30.35, 31.18 (CH_2), 31.47, 31.70, 33.34, 33.49 (N-CH_3), 51.28 (OCH_3), 58.93, 59.30, 62.31, 62.50 (NCH), 66.62, 67.71, 67.89, 67.98 (C-5), 77.88, 78.60, 78.94, 79.00 (OCH), 80.11 (O-$\underline{C}(CH_3)_3$), 82.50, 83.37, 84.15, 84.60 (C-2), 174.36, 174.46, 174.55 (C=O).

2-methyl-2-[2,2,5,5-tetraethyl-3,4-dimethylimidazolidine-1-oxyl]propionic acid tert-butyl ester (21d). Colorless oil, mixture of diastereomers, 60% yield. Anal. calcd. for $C_{21}H_{42}N_2O_3$ (370): C, 68.06; H, 11.42; N, 7.56. Found: C, 68.49; H, 10.95; N, 7.56. ν_{max}(KBr)/cm^{-1} 2975, 2937, 2880, 2809, 2793, 1731, 1464, 1368, 1287, 1250, 1224, 1136, 1036, 996, 967, 943, 900, 849, 767 and 751; δ_H(400 MHz; $CDCl_3$) 0.80 – 0.92 (total 12 H, m, CH_3, Et), 0.95 and 1.01 (total 3 H, both d, J 6, 4-CH_3), 1.34, 1.35, 1.36 and 1.37 (total 6 H, each s, O-C$(CH_3)_2$CO), 1.3-2.1 (total 8 H, m, CH_2), 1.41 (9 H, s, *t*-Bu), 2.04 and 2.26 (total 3H, each s, N-CH_3), 2.77 (1H, m, CH); δ_C(100 MHz; $CDCl_3$) 7.12, 8.49, 9.05, 9.41, 9.84(double intensity), 10.62, 10.87 (CH_3, Et), 14.47, 15.19 (4-CH_3), 20.68, 22.81, 24.84, 25.38, 27.05, 28.47, 30.84, 31.27 (CH_2), 24.61, 24.80 (O-C($\underline{C}H_3)_2$CO), 27.54 (C($\underline{C}H_3)_3$), 32.06, 32.51 (N-CH_3), 59.57, 62.02 (CH), 66.83, 67.77 (C-5), 80.11 (O-$\underline{C}(CH_3)_3$), 81.27, 81.43 (O-$\underline{C}(CH_3)_2$CO), 83.17, 84.13 (C-2), 173.15, 173.34 (C=O).

2-methyl-2-[(2,2,5,5-tetraethyl-3,4-dimethylimidazolidine-1-yl)oxy]propionic acid phenyl ester (21f). 30% yield. δ_H(300 MHz, $CDCl_3$) 7.28-7.09 (m, 5 H, CH); 2.89-2.80 (m, 1H, CH); 2.07 (s, 3H, CH_3); 2.03-1.50 (m, 14H, CH_2 + CH_3), 1.08-0.88 (m, 15H, CH_3).

Thermal decomposition of alkoxyamine was performed until the EPR signal reached a plateau, meaning that all alkoxyamine was decomposed. For each experiment, the plateau was reached for more than 90% conversion. Therefore, each alkoxyamines exhibited more than 90% purity.

Results

In a recent work,[1] we reported for the homolysis of the C—ON bond for **1a** and **2a**: ΔE_a = E_a(**1a**) – E_a(**2a**) = 0.7 kJ·mol^{-1}. It was assumed this value also held for the difference between E_a for **1e** and **2e**, i.e. E_a(**2e**) = 140.3 kJ·mol^{-1}. The E_a for **17e** was estimated applying the increment +12.8 kJ·mol^{-1} (**c•→e•**),[2] providing the effect of the phenyl group in **17f** was accounted for by $k_{d,\mathbf{c}} = k_{d,\mathbf{f}}/3$,[3,4] i.e. E_a(**17c**) = 117.4 kJ·mol^{-1}. The E_a for **7e** (Table S1) was obtained by applying the increment +12.8 kJ·mol^{-1} (**d•→e•**),[2] assuming no effect of the alkyl ester group.[5] The E_a for **18e** (Table S1) was obtained by applying the increment -8.7 kJ·mol^{-1}, assuming that the E_a difference of E_a for **2a** (E_a = 144.8 kJ·mol^{-1})[1] and **18a** (E_a = 136.1 kJ·mol^{-1})[1] held. The conversion of E_a for **19a** (see Table 1) into E_a for **19e** (Table S1) was done applying the increment -6.3 kJ·mol^{-1}.[2] The value of E_a(**21e**) was given by averaging the values obtained applying the increment +6.3 kJ·mol^{-1} to E_a(**21a**),[2] and +12.8 to E_a(**21d**) and to E_a(**21c**),[2] providing that $k_{d,\mathbf{c}} = k_{d,\mathbf{f}}/3$,[3,4] i.e. E_a(**21c**) = 110.7 kJ·mol^{-1}.

Multi-parameter approach. The analysis of k_d in terms of polar/stabilization and steric effects (eq. S1) has already been applied to 40 cyclic nitroxyl fragments carrying fragment **e**.[6,7] The polar/stabilization effect is accounted for by the polar Hammett constant σ_L and given by eq. S2 (as exemplified in Figure S1).[6,7] The missing σ_L constants were estimated with eqs. S3 and S4.[8,9] The steric effect is accounted for by eqs. S5 and S6 (as exemplified in Figure S1).[6,7,10] It was assumed that the steric effects E_s^{AorB} of the two alkyl groups flanking the nitroxyl fragment were linearly combined (eq. S5) and that each E_s value was given by eq.

S6.[6,7] The individual Fujita steric constants r_i for the alkyl group R are negative, meaning that the larger alkyl group, the smaller r(R) value.[10] All the values of σ_L and E_s needed for eq. S1 are gathered in Table S1.

$$\log\left(k_{d,n}/s^{-1}\right) = \log\left(k_{d0}/s^{-1}\right) + \rho_L \cdot \sigma_{L,\mathbf{n}} + \delta \cdot E_{s,\mathbf{n}} \quad \text{(S1)}$$

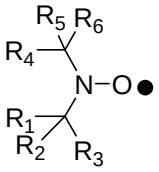
$$\sigma_{L,\mathbf{n}} = \sum_{i=1}^{6} \sigma_L(R_i) \quad \text{(S2)}$$

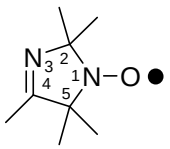
$$\sigma_{L,R_1R_2CH} = 0.297 \times \sum \sigma_{L,R} + 0.00482 \quad \text{(S3)}$$

$$\sigma_{L,R_1R_2R_3C} = 0.248 \times \sum \sigma_{L,R} + 0.00398 \quad \text{(S4)}$$

$$E_{s,\mathbf{n}} = E_s^A + E_s^B \quad \text{(S5)}$$

$$E_s^{AorB} = -2.104 + 3.429 \times r_1(R_1) + 1.978 \times r_2(R_2) + 0.649 \times r_3(R_3) \quad \text{(S6)}$$





2●

$\sigma_L = 4\sigma_{L,Me} + \sigma_{L,MeC=NR} + \sigma_{L,N=CR}$

$E_s^A = E_s^B$ = -2.104 + 3.429r_1(C5') + 1.978r_2(Me) + 0.649r_3(Me)

Figure S1. Examples of steric (E_s)and polar (σ_I)constants estimate.

The very close values of k_d for **2a** (1.4 10^{-5} s^{-1} at 120 °C in PhCl)[1] and **1a** (1.1 10^{-5} s^{-1} at 120 °C in PhCl)[1] show that the replacement of the methyl group in **2a** by the phenyl ring in **1a** has no significant influence (ΔE_a = 0.7 kJ·mol^{-1}) either on the polarity or on the bulkiness of the nitroxyl fragment.[11] In a previous work, it was shown that the cyclic strain for the five-membered ring for nitroxyl fragments **3**, **9**, **11**, **13**, and **14** was accounted for by the steric constant r(C5[12]) = 0.31. As in the case of fragments **3**, carbons 3 and 4 on the ring of fragments **1**, **2**, **7**, and **18** are bounded by a double bond, and therefore, r(C5) was applied to

estimate the corresponding E_s. Unexpectedly, molecules **1e** and **2e** are outliers whereas **7e** and **18e** lie on the regression line (eq. 7). Such discrepancies might be due to the difficulty to estimate both the E_a for an alkyl fragment other than **e** and the polar effect of the imine function.[8,9,13] When the steric cyclic constant *r*(C5) was applied to estimate E_s for fragments **4**, **5**, **8**, **10**, **17**, **20**, and **21**, the data strikingly deviated from the correlation line (Triangles in Figure 5). Thus, assuming that fragment **10** lay on the correlation line, a new steric cyclic constant *r*(C5") was developed applying eqs. S5 and S6 and given as 0.15. Hence, using this new value, fragments **4**, **5**, **8**, **17**, **20**, and **21** were shifted close to the regression line (Figure 5 and eq. 7). In a previous work,[7] the difficulty to estimate E_s when the substituents were cycles was mentioned. The comparison of the k_d for **19e** and **17e** (Table S1) shows that the values are very close, meaning that the 5-membered ring is sterically as demanding as two ethyl groups although it has been reported to be the size of the methyl group.[7,10] On the other hand, *r*(C6") was applied successfully to estimate E_s of **4e**, **7e**, **8e**, and **20e** (Table S1). Interestingly, **12e** and **15e** are deviated strongly (Figure 4) when *r*(*n*-Bu) and *r*(*n*-Pr) were used, respectively, whereas assuming *r*(*n*-Bu) = *r*(*n*-Pr) = *r*(Et), the data were shifted closer to the regression line (for discussion, see the levelled steric effect section). When the value of *r* = –1.4 was applied for the phenyl group[6,7] as for $E_{s,\mathbf{11}}$, the data for **6e** and **16e** deviated dramatically from the regression line whatever, the ring constant *r*(C5) or *r*(C5").[14] In fact, phenyl group is known as a Janus group[15] i.e. a group capable of changing its steric demand when the surrounding groups vary. Therefore, for the sake of simplicity, it was assumed that the two phenyl groups exhibited the same bulkiness, hence, the data for **6e** and **16e** were shifted on the straight line when *r*(Ph) was assumed around –0.23 (Figure 5) to estimate $E_{s,\mathbf{6e}}$ and $E_{s,\mathbf{16e}}$, using *r*(C5").[16]

Table S1. Activation energies E_a and homolysis rate constants k_d at 120 °C for the release of alkyl radical **e•**, polar/stabilization Hammett constants[a] σ_L and Fujita steric constants[b] E_s for nitroxides **1•– 21•.**

Nitroxyl fragment	E_a (kJ·mol^{-1})[c]	k_d (s^{-1})[d]	σ_L[e]	E_s[f]
1	141.0	4.4 10^{-5}	0.29[g]	-2.08[h)i)]
2	140.3[j]	9.4 10^{-5}	0.29[g]	-2.08[h)i)]
3[k]	139.8	6.3 10^{-5}	0.08	-2.08
4	139.4[l]	7.1 10^{-5}	0.5	-2.87[h)i)m)]/-3.97[i)m)n)]
5	138.1	1.1 10^{-4}	0.17[o]	-2.08[h)i)]/-3.18[i)n)]
6	137.7	1.2 10^{-4}	0.43[o]	-3.78[i)n)p)]
7	137.5[j]	1.3 10^{-4}	0.29[g]	-3.47[i)h)m)]
8	137.4[l]	1.3 10^{-4}	0.50	-2.87[h)i)m)]/-3.97[i)m)n)]
9[k]	137.0	1.5 10^{-4}	-0.06	-2.08
10	135.9	2.1 10^{-4}	0.18[o,q)]	-2.08[h)i)]/-3.18[i)n)]
11[k]	133.5	4.3 10^{-4}	0.07	-2.99
12	132.8	5.4 10^{-4}	0.18[o,q)]	-3.92[h)i)]/-4.18[i)n)r)]
13[k]	132.3	6.2 10^{-4}	0.09	-3.44
14[k]	131.1	9.0 10^{-4}	0.08	-4.08
15[k]	130.9	9.6 10^{-4}	0.08	-4.08[s)]
16	130.2	1.2 10^{-3}	0.43[o)]	-4.78[i)p)]
17	130.2[j]	7.7 10^{-4}	0.18[o,q)]	-3.08[h)i)]/-4.18[i)n)]
18	131.6[j]	1.3 10^{-3}	0.29[g)]	-4.08[h)i)]
19	128.5[j]	2.0 10^{-3}	0.18[o,q)]	-2.19[h)i)]/-4.18[i)n)t)]
20	124.3	7.2 10^{-3}	0.18[o,q)]	-3.47[h)i)m)]/-4.57[i)m)n)]
21	121.9[j]	1.6 10^{-2}	0.18[o,q)]	-4.08[h)i)]/-5.17[i)n)]

[a] Value of σ_L given in reference [8] unless otherwise mentioned, $\sigma_{L,Me} = \sigma_{L,Et} = \sigma_{L,n\text{-}Pr} = \sigma_{L,n\text{-}Bu} = -0.01$, $\sigma_{L,ring} = 2\times\sigma_{L,Me} = -0.02$, $\sigma_{L,Ph} = 0.12$.

[b] Values for the basic groups E_s(Me) = 0, E_s(Et) = -0.38, E_s(*n*-Pr) = -0.67, E_s(*n*-Bu) = -0.70 are given in reference [10].

[c] Errors estimated around 2 kJ·mol^{-1}. Values given for the released alkyl radical **e•** and re-estimated with the averaged frequency factor A = 2.4 10^{14} s^{-1}, see references [7], [17], and [18].

[d] Estimated using A = 2.4 10^{14} s^{-1} and the E_a listed in the second column.

[e] Given by eq. 2, see text.

[f] Given by eqs. 5 and 6, see text.

[g] $\sigma_{L,PhHC=N}$ = 0.14 see ref. [8] and $\sigma_{L,PhC=NH}$ = 0.19 using $F_{PhC=NH}$ = 0.19 as given in reference [13].

[h] E_s was estimated with r(C5) = 0.31, see references [6] and [7].

[i] It was assumed that there was no steric influence of the substituent attached to the double bond or to the nitrogen atom.

[j] See text.

[k] Given in ref. [6].

[l] Given in reference [7].

[m] r(C6") = -0.15.

[n] E_s was estimated with r(C5") = 0.15, see text.

[o] σ_{L,NMe_2} = 0.17. σ_{L,Me_2CNMe_2} = 0.04 as given by eq. 4.

[p] E_s was estimated with r(Ph) = -0.23, see text.

[q] σ_{L,NMe_2} = 0.17. $\sigma_{L,MeHCNMe_2}$ = 0.05 as given by eq. 3.

[r] It was assumed r(*n*-Bu) = r(Et), see text. Otherwise, E_s(**12**) = -5.02.

[s] It was assumed r(*n*-Pr) = r(Et), see SI. Otherwise, E_s(**15**) = -5.60.

[t] r(C5') = r(Et) was used, see SI. For r(C5') = -0.04, E_s(**19**) = -3.28 (empty circle in Figure 4).

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[12] The code for cyclic steric constants is given in reference **Fehler! Textmarke nicht definiert.**, i.e., *r*(C5) for $CR_2(CH_2)_2CR_2$ and $CR_2CR{=}XCR_2$, *r*(C5') for $(CH_2)_4$, and *r*(C5'') for $CR_2CHRNMeCR_2$ and $CR_2CR_2NMeCR_2$ and $CR_2NRC(O)CR_2$.

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[14] When *r*(Ph) = -1.4 and *r*(C5'') = 0.15 were used for estimating E_s, E_s(**6**) = -6.86 and *E*s(**16**) = -7.86.

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