

Macromolecules

Macromolecules, 1998, 31(17), 5955-5957, DOI:[10.1021/ma9807264](https://doi.org/10.1021/ma9807264)

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Supporting Information

Synthesis of ((2,2,6,6-Tetramethylpiperidinyloxy)methyl)benzene (2). To a Schlenk flask was added benzyl bromide, 0.50 mL (4.2 mmol); TEMPO, 0.79 g (5.04 mmol); copper powder, 0.28 g (4.4 mmol); Cu(OTf)₂, 0.015 g (0.042 mmol); dTbpy, 45 mg (0.17 mmol) and 5.0 mL of benzene. The reaction solution was degassed, put under argon and heated to 75 °C for 12 h. The reaction solution was loaded onto an alumina column and eluted with 95:5 hexanes:CH₂Cl₂. **2** eluted as a colorless fraction before the excess TEMPO. Solvent was removed to yield 0.99 g (4.01 mmol) of **2** as a very pale yellow oil. Isolated yield = 96 %. ¹H NMR: CDCl₃ (δ vs TMS): δ 7.41-7.20 ppm, m, 5H (Ph); 4.82 ppm, s, 2H (benzyl CH₂); 1.65-0.90 ppm, broad, 18H (TEMPO). ¹³C NMR. CDCl₃ (δ vs TMS): 138.2, 128.2, 127.4, 127.3, 78.8, 60.0, 39.8, 33.1, 20.3, 17.1. Protonated **2** has m/z = 248.0 by electrospray LCQ-MS.

Synthesis of Methyl 2-(2,2,6,6-Tetramethylpiperidinyloxy)propionate (3). To a Schlenk flask was added methyl-2-bromopropionate, 0.50 mL (4.5 mmol); TEMPO, 0.84 g (5.4 mmol); copper powder, 0.30 g (4.7 mmol); Cu(OTf)₂, 0.016 g (0.045 mmol); dTbpy, 48 mg (0.18 mmol) and 5.0 mL of benzene. The reaction solution was degassed, put under argon and heated to 75 °C for 12 h. The reaction solution was loaded onto an alumina column and eluted with 95:5 hexanes:CH₂Cl₂. **3** eluted as a colorless fraction and some mixed with the excess TEMPO. Two fractions were collected. Solvent was removed from the first fraction to yield 0.56g (2.3 mmol) of **3**. The second fraction was taken to dryness and dissolved in a minimal amount of hexanes and loaded on another alumina column and eluted with with 95:5 hexanes:CH₂Cl₂. The fraction before the excess TEMPO eluted was collected as a colorless solution. Solvent was removed to yield 0.27 g

(1.1 mmol) of **3** as a very pale yellow oil. Combined isolated yield = 75 %. ^1H NMR: CDCl_3 (δ vs TMS): δ 4.34 ppm, q, $^3J_{\text{HH}} = 7$ Hz, 1H (C-CHCH₃O); 3.70 ppm, s, 3H (methoxy group); 1.50 - 1.00 ppm, broad, 18H (TEMPO); 1.40 ppm, d, $^3J_{\text{HH}} = 7$ Hz, 3H (C-CHCH₃O). ^{13}C NMR: CDCl_3 (δ vs TMS): 174.4, 81.6, 51.4, 40.3, 33.7, 32.9, 20.2, 18.2, 17.2. Protonated **3** has $m/z = 244.1$ by electrospray LCQ-MS.

Synthesis of Ethyl 2-(2,2,6,6-Tetramethylpiperidinyloxy)isobutyrate (4). To a Schlenk flask was added ethyl-2-bromoisobutyrate, 0.10 mL (0.68 mmol); TEMPO, 0.128 g (0.82 mmol); copper powder, 0.045 g (0.72 mmol); $\text{Cu}(\text{OTf})_2$, 0.002 g (0.0068 mmol); dNbpy, 0.011 g (0.027 mmol) and 1.0 mL of benzene. The reaction solution was degassed, put under argon and heated to 55 °C for 18 h. The reaction solution was loaded onto an alumina column and eluted with 9:1 hexanes: CH_2Cl_2 . **4** eluted as a colorless fraction before the excess TEMPO. Solvent was removed to yield 0.17 g (0.63 mmol) of **4** as a very pale yellow oil. Isolated yield = 92 %. ^1H NMR: CDCl_3 (δ vs TMS): δ 4.17 ppm, q, $^3J_{\text{HH}} = 7$ Hz, 2H ($\text{CH}_3\text{CH}_2\text{O}$); 1.61-1.36 ppm, m, 4H (TEMPO methylene); 1.35-1.21 ppm, m, 2H (TEMPO methylene); 1.29 ppm, t, $^3J_{\text{HH}} = 7$ Hz, 3H ($\text{CH}_3\text{CH}_2\text{O}$); 1.48 ppm, s, 6H; 1.16 ppm, s, 6H; 1.02 ppm, s, 6H ($(\text{CH}_3)_2\text{C}$; TEMPO methyls). ^{13}C NMR: CDCl_3 (δ vs TMS): 81.1, 60.5, 59.5, 40.6, 33.4, 24.5, 20.4, 17.1, 14.1, carbonyl C was not observed. Protonated **4** has $m/z = 272.0$ by electrospray LCQ-MS.

Synthesis of 2-(2,2,6,6-Tetramethylpiperidinyloxy)propionitrile (5). To a Schlenk flask was added 2-bromo propionitrile, 0.50 mL (5.8 mmol); TEMPO, 1.08 g (6.9 mmol); copper powder, 0.38 g (6.07 mmol); $\text{Cu}(\text{OTf})_2$, 0.021 g (0.058 mmol); dTbpy, 62 mg (0.23 mmol) and 5.0 mL of benzene. The reaction solution was degassed, put under argon and heated to 75 °C for 8 h. The reaction solution was loaded onto an alumina

column and eluted with 95:5 hexanes:CH₂Cl₂. **5** eluted as a colorless fraction and some mixed with the excess TEMPO. Two fractions were collected. Solvent was removed from the first fraction to yield 0.80 g (3.8 mmol) of **5**. The second fraction was taken to dryness and dissolved in a minimal amount of hexanes and loaded on another alumina column and eluted with with 95:5 hexanes:CH₂Cl₂. The fraction before the excess TEMPO eluted was collected as a colorless solution. Solvent was removed to yield 0.12 g (0.57 mmol) of **5** as a very pale yellow oil. Combined isolated yield = 76 %. ¹H NMR (CDCl₃, δ vs TMS): 4.65 ppm, q, ³J_{HH} = 7 Hz, 1H (methine proton); 1.56 ppm, d, ³J_{HH} = 7 Hz, 3H (propionitrile methyl); diastereotopic methylene protons in a range from 1.54 - 1.40 ppm, m, 6H (TEMPO methylene protons); 1.35 ppm, 1.16 ppm, 1.11 ppm, 1.10 ppm, 12H (TEMPO methyl groups). ¹³C NMR (CDCl₃, δ vs TMS): 120.3, 70.0, 60.7, 59.7, 39.9, 34.1, 33.5, 20.3, 20.1, 19.2, 17.0. Protonated **5** has m/z = 232.8 by electrospray LCQ-MS.

Synthesis of 1-(2,2,6,6-tetramethyl-4-hydroxypeperidinyloxy)-1-phenylethane (6). **6** was prepared under similar conditions as **1**. Protonated **6** has m/z = 278.0 by electrospray LCQ-MS.