C. F. Bernasconi, M. Ali and J. C. Gunter, "Kinetic and Thermodynamic Acidities of Substituted 1-Benzyl-1-methoxy-2-nitroethylenes. Strong Reduction of the Transition State Imbalance Compared to Other Nitroalkanes."

**Figure S1**  Representative plots of absorbance versus $a_{H^+}$ according to eq 4 for the spectrophotometric $pK_a^{CH}$ determination. 2-CF$_3$ (O) and 2-NO$_2$ (●).
C. F. Bernasconi, M. Ali and J. C. Gunter, "Kinetic and Thermodynamic Acidities of Substituted 1-Benzyl-1-methoxy-2-nitroethylenes. Strong Reduction of the Transition State Imbalance Compared to Other Nitroalkanes."

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**Figure S2**  Representative plots of $k_{\text{obsd}}$ versus piperidinium ion concentration at pH 9.88. ▲, 2-CF$_3$; △, 2-NO$_2$; ■, 2-H; ○, 2-Me; ●, 2-MeO.
C. F. Bernasconi, M. Ali and J. C. Gunter, "Kinetic and Thermodynamic Acidities of Substituted 1-Benzyl-1-methoxy-2-nitroethylenes. Strong Reduction of the Transition State Imbalance Compared to Other Nitroalkanes."

**Figure S3**  Representative plots of slope versus $a_{H^+}$ according to eq 6 for the reactions of piperidine with 2-H (●) and 2-NO$_2$ (○), respectively.
Table S1. $^1$H NMR Chemical Shifts for 16-Z in CDCl$_3$.

<table>
<thead>
<tr>
<th>16-Z</th>
<th>CH$_2$NO$_2$</th>
<th>CH$_2$CO</th>
<th>C$_6$H$_4$</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-NO$_2$</td>
<td>5.33</td>
<td>3.95</td>
<td>7.43(d), 7.53(t), 7.62(d)</td>
<td></td>
</tr>
<tr>
<td>16-CF$_3$</td>
<td>5.31</td>
<td>3.95</td>
<td>7.43(d), 7.54(t), 7.62 (d)</td>
<td></td>
</tr>
<tr>
<td>16-Cl</td>
<td>5.28</td>
<td>3.85</td>
<td>7.11(d), 7.24(t), 7.33(m)</td>
<td></td>
</tr>
<tr>
<td>16-H</td>
<td>5.25</td>
<td>3.86</td>
<td>7.24(d), 7.36(d), 7.39(t)</td>
<td></td>
</tr>
<tr>
<td>16-Me</td>
<td>5.23</td>
<td>3.81</td>
<td>7.10(d), 7.19(d)</td>
<td>2.36</td>
</tr>
<tr>
<td>16-MeO</td>
<td>5.24</td>
<td>3.82</td>
<td>6.91(d), 7.14(d)</td>
<td>3.80</td>
</tr>
</tbody>
</table>

$^a$ 500 MHz.
C. F. Bernasconi, M. Ali and J. C. Gunter, "Kinetic and Thermodynamic Acidities of Substituted 1-Benzyl-1-methoxy-2-nitroethylenes. Strong Reduction of the Transition State Imbalance Compared to Other Nitroalkanes."

Table S2. $^{13}$C NMR Chemical Shifts for 16-Z in CDCl$_3$.$^a$

<table>
<thead>
<tr>
<th>16-Z</th>
<th>CH$_2$NO$_2$</th>
<th>CO</th>
<th>CH$_2$CO</th>
<th>C$_6$H$_4$</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-NO$_2$</td>
<td>82.6</td>
<td>192.9</td>
<td>46.9</td>
<td>125.0, 126.4, 129.7</td>
<td>132.2, 133.0</td>
</tr>
<tr>
<td>16-CF$_3$</td>
<td>82.6</td>
<td>192.8</td>
<td>47.0</td>
<td>125.1, 126.4, 129.2</td>
<td>129.7, 132.0, 175.4</td>
</tr>
<tr>
<td>16-Cl</td>
<td>82.5</td>
<td>192.9</td>
<td>47.2</td>
<td>127.7, 128.5, 129.7</td>
<td>130.6, 133.1</td>
</tr>
<tr>
<td>16-H</td>
<td>82.4</td>
<td>193.7</td>
<td>48.1</td>
<td>128.3, 129.5</td>
<td>129.6, 131.3</td>
</tr>
<tr>
<td>16-Me</td>
<td>82.5</td>
<td>194.1</td>
<td>47.9</td>
<td>128.4, 129.5</td>
<td>130.3, 138.3</td>
</tr>
<tr>
<td>16-MeO</td>
<td>82.3</td>
<td>194.1</td>
<td>47.3</td>
<td>114.9, 123.2</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>130.6, 159.6</td>
<td>55.4</td>
</tr>
</tbody>
</table>

$^a$500 MHz.
Table S3. $^1$H NMR Chemical Shifts for 2-Z in CDCl$_3$.

<table>
<thead>
<tr>
<th>2-Z</th>
<th>CHNO$_2$</th>
<th>CH$_3$O</th>
<th>CH$_2$</th>
<th>C$_6$H$_4$</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-NO$_2$ (Z)</td>
<td>6.96</td>
<td>3.82</td>
<td>4.24</td>
<td>7.51-7.56; 8.11-8.16</td>
<td></td>
</tr>
<tr>
<td>2-NO$_2$ (E)</td>
<td>7.58</td>
<td>4.14</td>
<td>4.55</td>
<td>7.83-7.87; 8.43-8.47</td>
<td></td>
</tr>
<tr>
<td>2-CF$_3$</td>
<td>6.93</td>
<td>3.81</td>
<td>4.16</td>
<td>7.44-7.54</td>
<td></td>
</tr>
<tr>
<td>2-Cl</td>
<td>6.91</td>
<td>3.79</td>
<td>4.04</td>
<td>7.11-7.23; 7.25-7.26</td>
<td></td>
</tr>
<tr>
<td>2-H</td>
<td>6.91</td>
<td>3.76</td>
<td>4.03</td>
<td>7.30-7.32</td>
<td></td>
</tr>
<tr>
<td>2-Me</td>
<td>6.90</td>
<td>3.77</td>
<td>4.00</td>
<td>7.13-7.14</td>
<td>2.31</td>
</tr>
<tr>
<td>2-MeO</td>
<td>6.89</td>
<td>3.77</td>
<td>3.98</td>
<td>6.87-6.90; 7.15-7.16</td>
<td>3.80</td>
</tr>
</tbody>
</table>

$^a$500 MHz.  $^b$See text.  $^c$Based on $\delta$ value for 2-NO$_2$ (Z) it is assumed that these compounds also have Z stereochemistry.
C. F. Bernasconi, M. Ali and J. C. Gunter, "Kinetic and Thermodynamic Acidities of Substituted 1-Benzyl-1-methoxy-2-nitroethylenes. Strong Reduction of the Transition State Imbalance Compared to Other Nitroalkanes."

Table S4. $^{13}$C NMR Chemical Shifts for 2-Z in CDCl$_3$.\(^a\)

<table>
<thead>
<tr>
<th>2-Z</th>
<th>CHNO$_2$</th>
<th>CO</th>
<th>CH$_3$O</th>
<th>CH$_2$</th>
<th>C$_6$H$_4$</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-NO$_2$</td>
<td>113.4</td>
<td>189.9</td>
<td>53.9</td>
<td>47.8</td>
<td>122.5, 124.9, 129.6</td>
<td>135.4, 136.2</td>
</tr>
<tr>
<td>2-CF$_3$</td>
<td>113.1</td>
<td>190.2</td>
<td>53.8</td>
<td>48.1</td>
<td>124.3, 124.3, 126.7</td>
<td>133.4, 134.4</td>
</tr>
<tr>
<td>2-Cl</td>
<td>112.8</td>
<td>190.1</td>
<td>53.6</td>
<td>47.9</td>
<td>127.5, 128.0</td>
<td>129.9, 134.5, 135.3</td>
</tr>
<tr>
<td>2-H</td>
<td>112.5</td>
<td>190.7</td>
<td>53.4</td>
<td>48.6</td>
<td>127.3, 128.8</td>
<td>129.7, 133.4</td>
</tr>
<tr>
<td>2-Me</td>
<td>112.6</td>
<td>190.9</td>
<td>53.5</td>
<td>48.4</td>
<td>129.4, 129.6</td>
<td>130.4, 137.1</td>
</tr>
<tr>
<td>2-MeO</td>
<td>112.6</td>
<td>191.1</td>
<td>53.5</td>
<td>47.8</td>
<td>114.4, 125.4</td>
<td>127.0, 130.9</td>
</tr>
</tbody>
</table>

\(^a\)500 MHz.