Redox potentials of trifluoromethyl-containing compounds

Yuanye Jiang¹, Haizhu Yu²,³, Yao Fu¹* & Lei Liu³*

¹Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
²Department of Polymer Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China
³Department of Chemistry, Tsinghua University, Beijing 100084, China

Received March 26, 2014; accepted June 5, 2014; published online October 11, 2014

1  Detail results of ionization potential, electron affinity, bond dissociation enthalpy and redox potentials

Table S1  Experimental and calculated ionization potentials and electron affinities of trifluoromethylated and trifluorinated compounds (V) a)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Exp.</th>
<th>B3LYP</th>
<th>M06-2X</th>
<th>oB97X-D</th>
<th>TPSS</th>
<th>mPW1PW9</th>
<th>CAM-B3LY</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF₂</td>
<td>IP</td>
<td>8.73</td>
<td>8.91</td>
<td>8.81</td>
<td>8.74</td>
<td>8.78</td>
<td>8.86</td>
<td>8.91</td>
</tr>
<tr>
<td>CF₃CF₂</td>
<td>EA</td>
<td>1.84</td>
<td>1.81</td>
<td>1.71</td>
<td>1.66</td>
<td>1.72</td>
<td>1.55</td>
<td>1.78</td>
</tr>
<tr>
<td>CH₃F</td>
<td>IP</td>
<td>12.5</td>
<td>12.33</td>
<td>12.44</td>
<td>12.30</td>
<td>12.07</td>
<td>12.25</td>
<td>12.36</td>
</tr>
<tr>
<td>BF₃</td>
<td>IP</td>
<td>15.8</td>
<td>15.20</td>
<td>15.63</td>
<td>15.29</td>
<td>14.47</td>
<td>15.20</td>
<td>15.38</td>
</tr>
<tr>
<td>PF₃</td>
<td>IP</td>
<td>12.3</td>
<td>11.48</td>
<td>11.41</td>
<td>11.41</td>
<td>11.24</td>
<td>11.32</td>
<td>11.48</td>
</tr>
<tr>
<td>R</td>
<td>–</td>
<td>0.9975</td>
<td>0.9978</td>
<td>0.9980</td>
<td>0.9957</td>
<td>0.9909</td>
<td>0.9974</td>
<td>0.9964</td>
</tr>
<tr>
<td>SD</td>
<td>–</td>
<td>0.3183</td>
<td>0.2766</td>
<td>0.2727</td>
<td>0.4481</td>
<td>0.7743</td>
<td>0.3085</td>
<td>0.3497</td>
</tr>
<tr>
<td>RMSD</td>
<td>–</td>
<td>0.3384</td>
<td>0.3034</td>
<td>0.3716</td>
<td>0.5652</td>
<td>0.5963</td>
<td>0.3156</td>
<td>0.4092</td>
</tr>
</tbody>
</table>


*Corresponding authors (email: fuyao@ustc.edu.cn; liu@mail.tsinghua.edu.cn)
Table S2  Experimental and calculated bond dissociation enthalpy of trifluoromethylated compounds (kcal/mol) a)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Exp.</th>
<th>B3LYP</th>
<th>CAM-B3LYP</th>
<th>M06-2X</th>
<th>wB97X-D</th>
<th>TPSS</th>
<th>mPW1PW91</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF3</td>
<td>102.6 ± 1.2</td>
<td>95.3</td>
<td>96.8</td>
<td>103.2</td>
<td>100.9</td>
<td>92.7</td>
<td>97.1</td>
</tr>
<tr>
<td>CF3H</td>
<td>95 ± 2</td>
<td>89.1</td>
<td>92.5</td>
<td>98.0</td>
<td>94.6</td>
<td>86.4</td>
<td>91.0</td>
</tr>
<tr>
<td>CF3F2</td>
<td>97.3 ± 2.3</td>
<td>86.2</td>
<td>89.9</td>
<td>95.9</td>
<td>91.7</td>
<td>83.1</td>
<td>88.2</td>
</tr>
<tr>
<td>CF3F</td>
<td>98.7 ± 1.2</td>
<td>87.0</td>
<td>91.1</td>
<td>97.5</td>
<td>92.9</td>
<td>83.7</td>
<td>89.3</td>
</tr>
<tr>
<td>CHF3H2</td>
<td>107 ± 3</td>
<td>100.8</td>
<td>104.4</td>
<td>108.6</td>
<td>106.2</td>
<td>98.3</td>
<td>102.6</td>
</tr>
<tr>
<td>CF3OH2</td>
<td>110.7 ± 3</td>
<td>101.9</td>
<td>106.0</td>
<td>110.4</td>
<td>108.3</td>
<td>98.7</td>
<td>103.7</td>
</tr>
<tr>
<td>CH3CF3</td>
<td>87.4 ± 3</td>
<td>78.5</td>
<td>83.0</td>
<td>90.4</td>
<td>86.6</td>
<td>76.3</td>
<td>81.4</td>
</tr>
<tr>
<td>CF3Ph2</td>
<td>84.2 ± 4</td>
<td>67.0</td>
<td>73.2</td>
<td>82.4</td>
<td>78.1</td>
<td>64.7</td>
<td>70.5</td>
</tr>
<tr>
<td>CF3OCH3</td>
<td>89.5 ± 4</td>
<td>53.5</td>
<td>61.1</td>
<td>72.2</td>
<td>67.1</td>
<td>52.0</td>
<td>57.6</td>
</tr>
<tr>
<td>CF3–CO2H</td>
<td>96.9 ± 1.5</td>
<td>86.9</td>
<td>90.5</td>
<td>96.7</td>
<td>92.8</td>
<td>84.4</td>
<td>89.1</td>
</tr>
<tr>
<td>CF3–CO2Me</td>
<td>85.5 ± 2.5</td>
<td>74.7</td>
<td>78.7</td>
<td>85.2</td>
<td>81.3</td>
<td>72.7</td>
<td>77.6</td>
</tr>
<tr>
<td>CF3–CF2•</td>
<td>58.6 ± 2</td>
<td>54.0</td>
<td>57.5</td>
<td>59.2</td>
<td>57.5</td>
<td>53.0</td>
<td>59.3</td>
</tr>
<tr>
<td>CF3–CO</td>
<td>12.4 ± 1</td>
<td>6.6</td>
<td>8.1</td>
<td>6.7</td>
<td>8.6</td>
<td>8.6</td>
<td>10.2</td>
</tr>
<tr>
<td>CF3–F</td>
<td>130.7 ± 0.5</td>
<td>123.3</td>
<td>127.2</td>
<td>130.2</td>
<td>127.3</td>
<td>123.0</td>
<td>124.3</td>
</tr>
<tr>
<td>CF3–Cl</td>
<td>87.3 ± 0.9</td>
<td>80.0</td>
<td>81.7</td>
<td>87.3</td>
<td>85.0</td>
<td>81.8</td>
<td>83.4</td>
</tr>
<tr>
<td>CF3–Br</td>
<td>70.8 ± 0.3</td>
<td>65.0</td>
<td>65.7</td>
<td>74.4</td>
<td>68.8</td>
<td>65.8</td>
<td>67.7</td>
</tr>
<tr>
<td>CF3–I</td>
<td>54.3 ± 0.3</td>
<td>53.2</td>
<td>53.0</td>
<td>61.5</td>
<td>55.8</td>
<td>54.6</td>
<td>55.3</td>
</tr>
<tr>
<td>CF3–OH</td>
<td>115.2 ± 0.3</td>
<td>106.4</td>
<td>110.4</td>
<td>115.5</td>
<td>111.8</td>
<td>104.7</td>
<td>108.6</td>
</tr>
<tr>
<td>CF3–OCOF3</td>
<td>86.4 ± 2</td>
<td>73.7</td>
<td>77.8</td>
<td>85.7</td>
<td>79.0</td>
<td>71.9</td>
<td>75.7</td>
</tr>
<tr>
<td>CF3–CO2</td>
<td>40.4</td>
<td>33.2</td>
<td>36.4</td>
<td>40.0</td>
<td>36.2</td>
<td>32.5</td>
<td>34.8</td>
</tr>
<tr>
<td>CF3–NO</td>
<td>39.9</td>
<td>33.9</td>
<td>35.9</td>
<td>40.3</td>
<td>37.6</td>
<td>34.0</td>
<td>35.7</td>
</tr>
<tr>
<td>CF3–NF2</td>
<td>67.1</td>
<td>53.9</td>
<td>57.8</td>
<td>65.3</td>
<td>58.9</td>
<td>51.2</td>
<td>56.2</td>
</tr>
<tr>
<td>CF3–N3CF3</td>
<td>55.2</td>
<td>50.8</td>
<td>54.6</td>
<td>59.5</td>
<td>56.5</td>
<td>49.2</td>
<td>53.9</td>
</tr>
</tbody>
</table>

R = 0.9937 0.9965 0.9965 0.9970 0.9905 0.9938

SD = 3.8396 2.9302 3.2381 2.7964 4.8069 3.7986

RMSD = 9.2190 5.8003 3.1767 4.1223 10.7290 7.0300


Table S3  Experimental (in V vs aqueous SCE) and calculated (in V vs NHE) reduction potentials for Test Group 1

<table>
<thead>
<tr>
<th>Methods</th>
<th>CF3Br</th>
<th>CF3I</th>
<th>C6F13I</th>
<th>R</th>
<th>SD</th>
<th>ΔE1</th>
<th>ΔE2</th>
<th>MAD</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>–2.10</td>
<td>–1.54</td>
<td>–1.32</td>
<td>–1.32</td>
<td>0.58</td>
<td>0.20</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B3LYP</td>
<td>–1.16</td>
<td>–0.88</td>
<td>–0.57</td>
<td>0.9543</td>
<td>0.1518</td>
<td>0.28</td>
<td>0.31</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>–1.23</td>
<td>–0.94</td>
<td>–0.67</td>
<td>0.9680</td>
<td>0.1513</td>
<td>0.29</td>
<td>0.27</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>M06-2X</td>
<td>–1.95</td>
<td>–1.13</td>
<td>–0.95</td>
<td>0.9968</td>
<td>0.1332</td>
<td>0.82</td>
<td>0.18</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>wB97X-d</td>
<td>–1.79</td>
<td>–0.89</td>
<td>–0.62</td>
<td>0.9996</td>
<td>0.2079</td>
<td>0.90</td>
<td>0.27</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>TPSS</td>
<td>–1.84</td>
<td>–1.00</td>
<td>–0.72</td>
<td>1.0000</td>
<td>0.1778</td>
<td>0.84</td>
<td>0.28</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>mPW1PW91</td>
<td>–1.78</td>
<td>–0.90</td>
<td>–0.59</td>
<td>1.0000</td>
<td>0.2122</td>
<td>0.88</td>
<td>0.31</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>wB97X-d</td>
<td>–1.50</td>
<td>–0.96</td>
<td>–0.68</td>
<td>0.9957</td>
<td>0.0400</td>
<td>0.54</td>
<td>0.28</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>B3LYP/PCM</td>
<td>–1.53</td>
<td>–1.12</td>
<td>–0.89</td>
<td>0.9936</td>
<td>0.0907</td>
<td>0.41</td>
<td>0.23</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The redox potentials versus NHE were converted to those versus SCE by adding a constant of –0.24 V to get the values in Table 2. We note that the test samples in Test Group 1 was too little, we turned to examine the performance of methods on predicting the difference between the measured redox potentials. The reduction potential of CF3Br minus that of CF3I to get ΔE1, and the reduction potential of CF3I minus that of C6F13I to get ΔE2. MAD and RMSD (V) in Table S3 were based on the ΔE.
### Table S4  Experimental (in V vs Ag/AgCl) and calculated (in V vs NHE) redox potentials in CH$_2$Cl$_2$ for Test Group 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Exp.  $E_{pc}$</th>
<th>M06-2X  $E_{pc}$</th>
<th>$\omega$B97X-D  $E_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-1.81$</td>
<td>$-1.38$</td>
<td>$-1.46$</td>
</tr>
<tr>
<td></td>
<td>$0.28$</td>
<td>$1.10$</td>
<td>$0.84$</td>
</tr>
<tr>
<td>2</td>
<td>$-1.79$</td>
<td>$-1.41$</td>
<td>$-1.52$</td>
</tr>
<tr>
<td></td>
<td>$0.32$</td>
<td>$0.85$</td>
<td>$0.69$</td>
</tr>
<tr>
<td>3</td>
<td>$-1.76$</td>
<td>$-1.41$</td>
<td>$-1.54$</td>
</tr>
<tr>
<td></td>
<td>$0.24$</td>
<td>$0.97$</td>
<td>$0.74$</td>
</tr>
<tr>
<td>4</td>
<td>$-1.90$</td>
<td>$-1.57$</td>
<td>$-1.59$</td>
</tr>
<tr>
<td></td>
<td>$0.13$</td>
<td>$0.87$</td>
<td>$0.68$</td>
</tr>
<tr>
<td>5</td>
<td>$-1.95$</td>
<td>$-1.68$</td>
<td>$-1.80$</td>
</tr>
<tr>
<td></td>
<td>$0.12$</td>
<td>$0.70$</td>
<td>$0.57$</td>
</tr>
</tbody>
</table>

---

### Table S5  The differences between the measured and calculated redox potentials (V)

<table>
<thead>
<tr>
<th>Methods</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
<th>$\Delta E_4$</th>
<th>$\Delta E_5$</th>
<th>$\Delta E_6$</th>
<th>$\Delta E_7$</th>
<th>$\Delta E_8$</th>
<th>MAD</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>$+0.02$</td>
<td>$+0.05$</td>
<td>$-0.09$</td>
<td>$-0.14$</td>
<td>$+0.04$</td>
<td>$-0.04$</td>
<td>$-0.15$</td>
<td>$-0.16$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M06-2X</td>
<td>$-0.03$</td>
<td>$-0.03$</td>
<td>$-0.19$</td>
<td>$-0.30$</td>
<td>$-0.25$</td>
<td>$-0.13$</td>
<td>$-0.23$</td>
<td>$-0.40$</td>
<td>$0.1363$</td>
<td>$0.1584$</td>
</tr>
<tr>
<td>$\omega$B97X-D</td>
<td>$-0.06$</td>
<td>$-0.08$</td>
<td>$-0.13$</td>
<td>$-0.34$</td>
<td>$-0.15$</td>
<td>$-0.16$</td>
<td>$-0.27$</td>
<td>$0.1025$</td>
<td>$0.1208$</td>
<td></td>
</tr>
</tbody>
</table>

The redox potentials versus NHE were converted to those versus Ag/AgCl by adding a constant of $-0.22$ V to get the values in Table 3. $\Delta E_n$ ($n = 1-4$) were the differences between the oxidation peak potentials of compound 2 to 5 and that of compound 1. $\Delta E_n$ ($n = 5-8$) were the difference between the reduction peak potentials of compound 2 to 5 and that of compound 1. MAD and RMSD (V) were calculated based on the $\Delta E_n$ ($n = 1-8$).

### Table S6  Calculated bond dissociation free energy and the bond dissociation enthalpies (BDE) from literature of various R–Cl, R–CN and R–CF$_3$ compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>BDE from literatures a)</th>
<th>Calc. BDFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl–CH$_3$</td>
<td>$83.7 \pm 0.4$</td>
<td>77.9</td>
</tr>
<tr>
<td>Cl–F</td>
<td>$84.6 \pm 1.5$</td>
<td>74.2</td>
</tr>
<tr>
<td>Cl–F$_2$</td>
<td>$84.1 \pm 1.5$</td>
<td>72.8</td>
</tr>
<tr>
<td>Cl–F$_3$</td>
<td>$82.4$</td>
<td>73.0</td>
</tr>
<tr>
<td>Cl–CH$_2$</td>
<td>$86.1 \pm 2$</td>
<td>76.2</td>
</tr>
<tr>
<td>Cl–F$_3$</td>
<td>$87.3 \pm 0.9$</td>
<td>76.2</td>
</tr>
<tr>
<td>Cl–CH$_2$–CH$_2$</td>
<td>$71.3 \pm 1.2$</td>
<td>61.1</td>
</tr>
<tr>
<td>Cl–CH$_2$Ph</td>
<td>$71.7 \pm 1.1$</td>
<td>64.0</td>
</tr>
<tr>
<td>Cl–CH=CH$_2$</td>
<td>$94.8 \pm 1.2$</td>
<td>85.5</td>
</tr>
<tr>
<td>Cl–Ph</td>
<td>$95.5 \pm 1.5$</td>
<td>86.5</td>
</tr>
<tr>
<td>Cl–CO$_2$Me</td>
<td>$84.6 \pm 2$</td>
<td>75.5</td>
</tr>
<tr>
<td>Cl–CO$_2$Ph</td>
<td>$81.5 \pm 2$</td>
<td>74.2</td>
</tr>
<tr>
<td>Cl–C$_2$H$_4$</td>
<td>$104.1 \pm 2$</td>
<td>102.8</td>
</tr>
<tr>
<td>Cl–C$_2$F$_4$</td>
<td>$63.4 \pm 0.5$</td>
<td>66.1</td>
</tr>
<tr>
<td>Cl–C$_2$F$_5$</td>
<td>$91.6 \pm 2$</td>
<td>85.3</td>
</tr>
<tr>
<td>Cl–O$_2$F</td>
<td>$90.0$</td>
<td>77.4</td>
</tr>
<tr>
<td>Cl–NO</td>
<td>$38.0 \pm 0.2$</td>
<td>31.3</td>
</tr>
<tr>
<td>Cl–NO$_2$</td>
<td>$33.9 \pm 0.3$</td>
<td>25.1</td>
</tr>
<tr>
<td>Cl–NH$_2$</td>
<td>$60.5$</td>
<td>53.8</td>
</tr>
<tr>
<td>Cl–SO$_2$H</td>
<td>$70 \pm 3$</td>
<td>56.1</td>
</tr>
</tbody>
</table>

a) (To be continued on the next page)
Compounds BDE from literatures a) Calc. BDFE

<table>
<thead>
<tr>
<th>Compounds</th>
<th>BDE from literatures a)</th>
<th>Calc. BDFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN•CN</td>
<td>136.7 ± 1.6</td>
<td>137.0</td>
</tr>
<tr>
<td>CN•O(H)</td>
<td>108 ± 2</td>
<td>102.2</td>
</tr>
<tr>
<td>CN•S(H)</td>
<td>126.7 ± 2</td>
<td>107.7</td>
</tr>
<tr>
<td>CN•CF₃</td>
<td>112.1 ± 1.0</td>
<td>106.6</td>
</tr>
<tr>
<td>CN•CH₂</td>
<td>133.4 ± 1.8</td>
<td>129.5</td>
</tr>
<tr>
<td>CN•H⁺</td>
<td>155.5 ± 2.5</td>
<td>150.2</td>
</tr>
<tr>
<td>CN•Ar</td>
<td>120.4 ± 2.0</td>
<td>115.5</td>
</tr>
<tr>
<td>CN•FeBu</td>
<td>117.2 ± 2.0</td>
<td>112.4</td>
</tr>
<tr>
<td>CN•H₂</td>
<td>120.0 ± 2.0</td>
<td>115.9</td>
</tr>
<tr>
<td>CN•H₂</td>
<td>121.9 ± 2.0</td>
<td>117.7</td>
</tr>
<tr>
<td>CN•H₂</td>
<td>132.3 ± 2.0</td>
<td>130.2</td>
</tr>
<tr>
<td>CN•CHPh</td>
<td>107.4 ± 2</td>
<td>106.8</td>
</tr>
<tr>
<td>CN•CH₂CH₂H</td>
<td>108.1 ± 2</td>
<td>104.0</td>
</tr>
<tr>
<td>CN•CH₂CN</td>
<td>101.9 ± 3</td>
<td>104.1</td>
</tr>
<tr>
<td>CN•CH₂Me</td>
<td>113.5</td>
<td>111.3</td>
</tr>
<tr>
<td>CN•O(O)CN</td>
<td>96.0 ± 2.5</td>
<td>95.9</td>
</tr>
<tr>
<td>F₅-C-H₃</td>
<td>102.6 ± 1.2</td>
<td>94.8</td>
</tr>
<tr>
<td>F₅-C-F₃</td>
<td>98.7 ± 1.2</td>
<td>82.5</td>
</tr>
<tr>
<td>F₅-C-CH=CH₂</td>
<td>107 ± 3</td>
<td>96.6</td>
</tr>
<tr>
<td>F₅-C-OF=CF₂</td>
<td>100.5</td>
<td>96.8</td>
</tr>
<tr>
<td>F₅-C-CCCH</td>
<td>123.2</td>
<td>115.8</td>
</tr>
<tr>
<td>F₅-C-CH₂H₁</td>
<td>110.7 ± 3</td>
<td>97.4</td>
</tr>
<tr>
<td>F₅-C-CH=CH₃</td>
<td>87.4 ± 3</td>
<td>77.4</td>
</tr>
<tr>
<td>F₅-C-CH₃H</td>
<td>69.5 ± 4</td>
<td>54.3</td>
</tr>
<tr>
<td>F₅-C-CH₄H</td>
<td>130.7 ± 0.5</td>
<td>117.5</td>
</tr>
<tr>
<td>F₅-C-Cl</td>
<td>87.3 ± 0.9</td>
<td>76.2</td>
</tr>
<tr>
<td>F₅-C-Br</td>
<td>70.8 ± 0.3</td>
<td>60.4</td>
</tr>
<tr>
<td>F₅-C-I</td>
<td>54.3 ± 0.3</td>
<td>49.5</td>
</tr>
<tr>
<td>F₅-C-OH</td>
<td>115.2 ± 0.3</td>
<td>102.6</td>
</tr>
<tr>
<td>F₅-C-OOCF₃</td>
<td>86.4 ± 2</td>
<td>65.7</td>
</tr>
<tr>
<td>F₅-C-OO •</td>
<td>40.4</td>
<td>25.6</td>
</tr>
<tr>
<td>F₅-C-H₂CH²</td>
<td>96.9 ± 1.5</td>
<td>83.9</td>
</tr>
<tr>
<td>F₅-C-O(O)O₂Me</td>
<td>85.5 ± 2.5</td>
<td>78.5</td>
</tr>
<tr>
<td>F₅-C-NO</td>
<td>39.9</td>
<td>29.2</td>
</tr>
<tr>
<td>F₅-C-N₂O₃H²</td>
<td>55.2</td>
<td>45.5</td>
</tr>
<tr>
<td>F₅-C-NF₂</td>
<td>67.1</td>
<td>47.9</td>
</tr>
</tbody>
</table>


2 Examples for redox potential calculation

For a better understanding about redox potential calculation, we use three examples including neutral, catonic and anionic species to illustrate it. According to half reactions shown in Scheme 3, the calculations of the redox potential $E_{\text{ox-radical}}$, $E_{\text{ox-cation}}$, $E_{\text{re-radical}}$ and $E_{\text{re-anion}}$ of CF₃CH₃ need to know the free energies of the species CF₃CH₃, CF₃•, CF₃⁺, CF₃⁻, CH₃•, CH₃⁺ and CH₃⁻ in MeCN. First, we conduct the geometry optimization of each individual species with a moderate basis set (Lanl2dz+p for Br, I and 6-31+G(d) for the rest atoms) in solvent MeCN (solvation model is SMD), to get their stable structures. Based on the optimized structures, frequency analysis is conducted as the same level of theory to obtain the thermodynamic corrections of Gibbs free energies of each species (Table S7). Also, based on the optimized structures, single point energies are calculated to obtain more accurate electronic energies with the oB97X-D method associated with a larger basis set (def2-TZVP for Br, I and 6-311++G(2df,2p) for the rest atoms) in MeCN (solvation model is SMD). Plus the thermodynamic correction and the solution-phase single point energy of each species together to get the solution-phase Gibbs free energy $\Delta G_{\text{sol}}$. 
Table S7  Energies of some calculated species (Hartree)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Thermodynamic corrections to Gibbs free energy</th>
<th>Solution-phase single point energies</th>
<th>Solution-phase Gibbs free energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃CH₃</td>
<td>0.024737</td>
<td>-377.6014321</td>
<td>-377.5766951</td>
</tr>
<tr>
<td>CF₃⁻</td>
<td>-0.017149</td>
<td>-337.7448908</td>
<td>-337.7620398</td>
</tr>
<tr>
<td>CF₃⁺</td>
<td>-0.013795</td>
<td>-337.5871714</td>
<td>-337.6009664</td>
</tr>
<tr>
<td>CH₃⁻</td>
<td>-0.0114</td>
<td>-337.3745914</td>
<td>-337.3859914</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>0.011307</td>
<td>-39.9492833</td>
<td>-39.9379773</td>
</tr>
<tr>
<td>CF₃⁻</td>
<td>0.011126</td>
<td>-39.8357407</td>
<td>-39.8246147</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>0.013035</td>
<td>-39.61049558</td>
<td>-39.59746058</td>
</tr>
</tbody>
</table>

According to Eqs. (1) and (2), we can get the following equations:

\[
E_{\text{ox-radical}}(\text{CF}_3\text{CH}_3) = \frac{\Delta G_{\text{sol}}(\text{CH}_3^+) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}(\text{CF}_3\text{CH}_3)}{F} - 4.44
\]

\[
= \frac{(-39.59746058) + (-337.6009664) - (-377.5766951)}{23.06} \times 627.51 - 4.44 = 5.85 \text{ (eV)}
\]

\[
E_{\text{ox-cation}}(\text{CF}_3\text{CH}_3) = \frac{\Delta G_{\text{sol}}(\text{CH}_3^+) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}(\text{CF}_3\text{CH}_3)}{F} - 4.44
\]

\[
= \frac{(-39.8246147) + (-337.3859914) - (-377.5766951)}{23.06} \times 627.51 - 4.44 = 5.52 \text{ (eV)}
\]

\[
E_{\text{re-radical}}(\text{CF}_3\text{CH}_3) = \frac{\Delta G_{\text{sol}}(\text{CH}_3^+) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}(\text{CF}_3\text{CH}_3)}{F} - 4.44
\]

\[
= \frac{(-39.9379773) + (-337.6009664) - (-377.5766951)}{23.06} \times 627.51 - 4.44 = 5.47 \text{ (eV)}
\]

\[
E_{\text{re-anion}}(\text{CF}_3\text{CH}_3) = \frac{\Delta G_{\text{sol}}(\text{CH}_3^+) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}(\text{CF}_3\text{CH}_3)}{F} - 4.44
\]

\[
= \frac{(-39.8246147) + (-377.7620398) - (-377.5766951)}{23.06} \times 627.51 - 4.44 = 4.17 \text{ (eV)}
\]

where 627.51 is the conversion factor from Hartree to kcal/mol, \(F\) is Faraday constant (23.06 kcal/(mol V)) and 4.44 is the free energy change associated with the reference NHE half-reaction (i.e., \(\text{H}^+ (\text{aq}) + \text{e}^- (g) \rightarrow \frac{1}{2}\text{H}_2 (g)\)).

Similarly, the redox potentials \(E_{\text{ox-radical}}, E_{\text{ox-cation}}\) and \(E_{\text{re-anion}}\) of \([\text{CF}_3(\text{BF}_3)]^-\) are calculated by starting from the geometry optimization of the species \([\text{CF}_3(\text{BF}_3)]^-\), BF₃, BF₃⁺ and BF₃⁻ and finally to get their solution-phase Gibbs free energies. Then the redox potentials of \([\text{CF}_3(\text{BF}_3)]^-\) are calculated according to the following equations:

\[
E_{\text{ox-radical}}([\text{CF}_3(\text{BF}_3)]^-) = \frac{\Delta G_{\text{sol}}(\text{BF}_3) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}([\text{CF}_3(\text{BF}_3)]^-)}{F} - 4.44
\]

\[
= +1.76 \text{ (eV)}
\]

\[
E_{\text{ox-cation}}([\text{CF}_3(\text{BF}_3)]^-) = \frac{\Delta G_{\text{sol}}(\text{BF}_3) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}([\text{CF}_3(\text{BF}_3)]^-)}{F} - 4.44
\]

\[
= +5.78 \text{ (eV)}
\]

\[
E_{\text{re-anion}}([\text{CF}_3(\text{BF}_3)]^-) = \frac{\Delta G_{\text{sol}}(\text{BF}_3) + \Delta G_{\text{sol}}(\text{CF}_3^\bullet) - \Delta G_{\text{sol}}([\text{CF}_3(\text{BF}_3)]^-)}{F} - 4.44
\]

\[
= -4.43 \text{ (eV)}
\]
The redox potentials $E_{\text{ox–cation}}$, $E_{\text{re–radical}}$, and $E_{\text{re–anion}}$ of cationic species $[\text{CF}_3(\text{NPh}_3)]^+$ can be calculated according the following equations:

$$
E_{\text{ox–cation}} ([\text{CF}_3(\text{NPh}_3)]^+) = \frac{\Delta G_{\text{sol}} ([\text{NPh}_3]) + \Delta G_{\text{sol}} (\text{CF}_3^+) - \Delta G_{\text{sol}} ([\text{CF}_3(\text{NPh}_3)]^+) }{F} - 4.44
= +2.06 \text{ (eV)}
$$

$$
E_{\text{re–radical}} ([\text{CF}_3(\text{NPh}_3)]^+) = \frac{\Delta G_{\text{sol}} ([\text{NPh}_3]) + \Delta G_{\text{sol}} (\text{CF}_3^*) - \Delta G_{\text{sol}} ([\text{CF}_3(\text{NPh}_3)]^+) }{F} - 4.44
= +0.07 \text{ (eV)}
$$

$$
E_{\text{re–anion}} ([\text{CF}_3(\text{NPh}_3)]^+) = \frac{\Delta G_{\text{sol}} ([\text{NPh}_3]) + \Delta G_{\text{sol}} (\text{CF}_3^*) - \Delta G_{\text{sol}} ([\text{CF}_3(\text{NPh}_3)]^+) }{F} - 4.44
= -0.71 \text{ (eV)}
$$

3 Species with high-spin ground state

In addition to the energies of the singlet (or doublet) states of all studied species, these of their triplet (or quartet) states are all calculated to find the ground states. These species with triplet (or quartet) states as ground states are shown in Table S8 and the energies of their triplet (or quartet) states were used for redox potential calculations. Note that the geometry optimizations of some high-spin-state species led to their decompositions. For example, triplet $\text{CF}_3\text{SiPh}_3$ decomposes to $[\text{CF}_3]$ and $[\text{SiPh}_3]$ after geometry optimization. We did not investigate the redox potentials involving those cases.

Table S8  Ground states of calculated compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Singlet or doublet state</th>
<th>Triplet or quartet state</th>
<th>Compounds</th>
<th>Singlet or doublet state</th>
<th>Triplet or quartet state</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^-$</td>
<td>√</td>
<td>C≡N$^+$</td>
<td>NO$^-$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH$^+$</td>
<td>√</td>
<td>NMe$_2^+$</td>
<td>OH$^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>O$_2$</td>
<td>√</td>
<td>CF=CF$_2^+$</td>
<td>O$_2$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>F$^+$</td>
<td>√</td>
<td>F$^+$</td>
<td>F$^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Br$^+$</td>
<td>√</td>
<td>I$^+$</td>
<td>Br$^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2-MeO-C$_6$H$_4^+$</td>
<td>√</td>
<td>4-NH$_2$C$_6$H$_4^+$</td>
<td>2-MeO-C$_6$H$_4^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C≡C-OMe$^+$</td>
<td>√</td>
<td>C≡CH$^+$</td>
<td>C≡C-OMe$^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>[(CF$_3$)BF$_3$]$^+$</td>
<td>N/A</td>
<td>[(CF$_3$)NPh$_3$]$^+$</td>
<td>[(CF$_3$)BF$_3$]$^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3^-$</td>
<td>N/A</td>
<td>N(SO$_2$Ph)$_2$</td>
<td>CF$_3^-$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>N/A</td>
<td>NF$_2^-$</td>
<td>CF$_3$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3^+$</td>
<td>N/A</td>
<td>NF$_2$</td>
<td>CF$_3^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>BF$_3^-$</td>
<td>N/A</td>
<td>CF$_3$-CH$_3$</td>
<td>BF$_3^-$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>BF$_3^+$</td>
<td>N/A</td>
<td>CH$_3$</td>
<td>BF$_3^+$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$-CF$_3$</td>
<td>N/A</td>
<td>CF$_3$-i-Pr</td>
<td>CF$_3$-CF$_3$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>i-Pr</td>
<td>N/A</td>
<td>CF$_3$-NMe</td>
<td>i-Pr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$-t-Bu</td>
<td>N/A</td>
<td>NH$\cdot$Me</td>
<td>CF$_3$-t-Bu</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>t-Bu</td>
<td>N/A</td>
<td>CF$_3$-OH</td>
<td>t-Bu</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$-CH$_2$OMe</td>
<td>N/A</td>
<td>OH</td>
<td>CF$_3$-CH$_2$OMe</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OMe</td>
<td>N/A</td>
<td>CF$_3$-OMe</td>
<td>CH$_2$OMe</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$-CH$_2$OH</td>
<td>N/A</td>
<td>OMe$^-$</td>
<td>CF$_3$-CH$_2$OH</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>N/A</td>
<td>OMe</td>
<td>CH$_2$OH</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF$_3$-I</td>
<td>N/A</td>
<td>CF$_3$-F</td>
<td>CF$_3$-I</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF=CF$_2$-</td>
<td>N/A</td>
<td>CF$_3$-Cl</td>
<td>CF=CF$_2$-</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COO$Me^-$</td>
<td>N/A</td>
<td>CF$_3$-Br</td>
<td>COO$Me^-$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

(To be continued on the next page)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Singlet or doublet state</th>
<th>Triplet or quartet state</th>
<th>Compounds</th>
<th>Singlet or doublet state</th>
<th>Triplet or quartet state</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>N/A</td>
<td>N/A</td>
<td>OOCF₃⁺</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF₃⁻SiMe₃</td>
<td>N/A</td>
<td>N/A</td>
<td>CF₃⁻Si(Ph)₃</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SiMe₃</td>
<td>N/A</td>
<td>N/A</td>
<td>CF₃⁻P(O)OEt₂</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CF₃⁻SMe</td>
<td>N/A</td>
<td>N/A</td>
<td>SiMe⁻</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SMe</td>
<td>N/A</td>
<td>N/A</td>
<td>CF₃SO₂⁻</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOOC⁻CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>Ph⁻Ph</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>F⁻CF₃</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MeO⁻CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>·CF₃</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H₂N⁻CF₃</td>
<td>N/A</td>
<td>N/A</td>
<td>NH₂</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) N/A means that the species decompose after geometry optimization.
### Table S9  Calculated redox potentials of trifluoromethylated radicals

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{ox}$</td>
<td>$E_{re}$</td>
<td>$E_{ox}$</td>
</tr>
<tr>
<td>$\text{O}^{-}\cdot\text{CF}_3$</td>
<td>+2.21</td>
<td>+0.17</td>
<td>+0.47</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$ $\text{NO}_2$</td>
<td>+2.05</td>
<td>+1.13</td>
<td>+0.62</td>
</tr>
<tr>
<td>$\text{NC}^{-}\cdot\text{CF}_3$</td>
<td>+2.27</td>
<td>−0.52</td>
<td>+0.29</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$ $\text{CN}$</td>
<td>+1.84</td>
<td>−1.09</td>
<td>+0.38</td>
</tr>
<tr>
<td>$\text{HOOCC}^{-}\cdot\text{CF}_3$</td>
<td>+1.84</td>
<td>−0.50</td>
<td>+0.23</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$ $\text{CO}_2\text{H}$</td>
<td>+1.68</td>
<td>−1.21</td>
<td>+0.33</td>
</tr>
<tr>
<td>$\text{NH}_2\text{CO}^{-}\cdot\text{CF}_3$</td>
<td>+0.91</td>
<td>−0.81</td>
<td>+0.11</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$ $\text{CONNH}_2$</td>
<td>+1.44</td>
<td>−1.34</td>
<td>−0.01</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$</td>
<td>+0.85</td>
<td>−1.34</td>
<td>+0.39</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$</td>
<td>+1.04</td>
<td>+0.96</td>
<td>−0.30</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$</td>
<td>+0.48</td>
<td>−1.93</td>
<td>−0.52</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$</td>
<td>+0.58</td>
<td>−1.49</td>
<td>+0.30</td>
</tr>
<tr>
<td>$\cdot\text{CF}_3$</td>
<td>+0.15</td>
<td>−2.24</td>
<td>−0.81</td>
</tr>
</tbody>
</table>

(To be continued on the next page)


<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{ox}$</th>
<th>$E_{re}$</th>
<th>Compounds</th>
<th>$E_{ox}$</th>
<th>$E_{re}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.60</td>
<td>-1.51</td>
<td>NH$_2$·CF$_3$</td>
<td>-0.58</td>
<td>-1.81</td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.49</td>
<td>-1.95</td>
<td>+0.97</td>
<td>-0.90</td>
<td></td>
</tr>
<tr>
<td>MeO·CF$_3$</td>
<td>-0.29</td>
<td>-2.04</td>
<td>+0.67</td>
<td>-1.17</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>-0.34</td>
<td>-1.31</td>
<td>+1.18</td>
<td>-0.63</td>
<td></td>
</tr>
<tr>
<td>H$_2$N·CF$_3$</td>
<td>-1.13</td>
<td>-2.19</td>
<td>+0.98</td>
<td>-1.12</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>-1.32</td>
<td>-1.38</td>
<td>+1.04</td>
<td>-0.89</td>
<td></td>
</tr>
<tr>
<td>H$_2$N·CF$_3$</td>
<td>-0.70</td>
<td>-2.19</td>
<td>+0.91</td>
<td>-1.22</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>-0.84</td>
<td>-2.17</td>
<td>+1.24</td>
<td>-0.65</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.09</td>
<td>-1.96</td>
<td>+0.76</td>
<td>-0.88</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.12</td>
<td>-1.72</td>
<td>+0.43</td>
<td>-1.10</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.28</td>
<td>-1.67</td>
<td>+1.18</td>
<td>-0.75</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.23</td>
<td>-1.75</td>
<td>-1.83</td>
<td>-0.38</td>
<td></td>
</tr>
<tr>
<td>$\cdot$CF$_3$</td>
<td>+0.01</td>
<td>-1.89</td>
<td>+0.72</td>
<td>-0.14</td>
<td></td>
</tr>
<tr>
<td>Me·CF$_3$·CF$_3$</td>
<td>+0.18</td>
<td>-1.81</td>
<td>+0.97</td>
<td>-0.89</td>
<td></td>
</tr>
</tbody>
</table>

(To be continued on the next page)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>$E_{ox}$</td>
<td>$E_{re}$</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>F&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;Me&lt;/sub&gt;·</td>
<td>-0.08</td>
<td>-2.03</td>
<td>+2.24</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>+0.29</td>
<td>-1.71</td>
<td>+0.10</td>
</tr>
<tr>
<td><img src="image4.png" alt="Image" /></td>
<td>+0.67</td>
<td>-1.45</td>
<td>+0.49</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td>+0.61</td>
<td>-1.32</td>
<td>+0.70</td>
</tr>
<tr>
<td><img src="image6.png" alt="Image" /></td>
<td>+0.92</td>
<td>-1.03</td>
<td>+0.33</td>
</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td>-0.27</td>
<td>-1.93</td>
<td>+0.44</td>
</tr>
<tr>
<td><img src="image8.png" alt="Image" /></td>
<td>-0.37</td>
<td>-1.89</td>
<td>+1.55</td>
</tr>
<tr>
<td><img src="image9.png" alt="Image" /></td>
<td>-0.09</td>
<td>-1.58</td>
<td>+0.59</td>
</tr>
<tr>
<td><img src="image10.png" alt="Image" /></td>
<td>+0.36</td>
<td>-1.41</td>
<td>+1.90</td>
</tr>
<tr>
<td><img src="image11.png" alt="Image" /></td>
<td>-0.54</td>
<td>-1.98</td>
<td>+0.13</td>
</tr>
<tr>
<td><img src="image12.png" alt="Image" /></td>
<td>+0.20</td>
<td>-1.84</td>
<td>-0.36</td>
</tr>
<tr>
<td><img src="image13.png" alt="Image" /></td>
<td>+0.05</td>
<td>-1.64</td>
<td>-0.23</td>
</tr>
<tr>
<td><img src="image14.png" alt="Image" /></td>
<td>+0.76</td>
<td>-1.21</td>
<td>+1.23</td>
</tr>
</tbody>
</table>

(To be continued on the next page)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
<th>Compounds</th>
<th>Redox potentials (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{ox}$</td>
<td>$E_{re}$</td>
<td></td>
</tr>
<tr>
<td>NHO$_2$</td>
<td>+2.69</td>
<td>-0.61</td>
<td>NHO$_2$</td>
</tr>
<tr>
<td>CO$_3$H$_2$</td>
<td>+1.49</td>
<td>-0.33</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>OCN</td>
<td>+0.52</td>
<td>-1.39</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+0.09</td>
<td>-1.58</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+1.64</td>
<td>+0.04</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+1.14</td>
<td>-0.13</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>+0.82</td>
<td>-1.01</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CN</td>
<td>+1.18</td>
<td>-0.23</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CN</td>
<td>+0.98</td>
<td>-0.66</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CN</td>
<td>+0.75</td>
<td>-1.04</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CN</td>
<td>+1.02</td>
<td>-0.66</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CO$_3$H$_2$</td>
<td>+0.82</td>
<td>-0.82</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>CO$_3$H$_2$</td>
<td>+0.55</td>
<td>-1.26</td>
<td>CF$_3$</td>
</tr>
<tr>
<td></td>
<td>+0.77</td>
<td>-0.81</td>
<td></td>
</tr>
</tbody>
</table>