Supporting Information

Mutual activation of two radical trapping agents: unusual “win-win synergy” of resveratrol and TEMPO during scavenging of dpph’ radical in methanol.

Adrian Konopko, 1,2 & Grzegorz Litwinienko1,*

1 Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093, Warsaw, Poland
2 Nencki Institute of Experimental Biology, Polish Academy of Sciences, Pasteura 3, Warsaw, 02-093, Poland

*Corresponding author (GL) e-mail: litwin@chem.uw.edu.pl

SYMBOLS and ABBREVIATIONS

dpph’ 2,2-diphenyl-1-picrylhydrazyl radical
TEMPO’ 2,2,6,6-tetramethylpiperidine-1-oxyl radical
4-OH-TEMPO’ • hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl radical
RSV resveratrol
TEMPO-H 2,2,6,6-tetramethylpiperidin-1-ol
3,5-DHA 3,5-dihydroxybenzyl alcohol
AcOH acetic acid
MeOH methanol

TABLE OF CONTENTS

| Figure | Table | Description | Page |
|--------|-------|-------------|------|
| S1     | S1    | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO’ in MeOH, linear fitting. | S-3  |
| S2     | S2    | Data and kinetic parameters for reaction of dpph’ with excess of 4-OH-TEMPO’ in MeOH, linear fitting. | S-4  |
| S3     | S3    | Data and kinetic parameters for reaction of dpph’ with excess RSV in MeOH, linear fitting. | S-5  |
| S4     | S4    | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO’ in EtOAc, linear fitting. | S-6  |
| S5     | S5    | Data and kinetic parameters for reaction of dpph’ with excess of 4-OH-TEMPO’ in EtOAc, linear fitting. | S-7  |
| S6     | S6    | Data and kinetic parameters for reaction of dpph’ with excess of RSV in EtOAc, linear fitting. | S-8  |
| S7     | S7    | Data and kinetic parameters for reaction of dpph’ with excess of RSV and TEMPO’ 1:1 mol/mol in MeOH, linear fitting. | S-9  |
| S8     | S8    | Data and kinetic parameters for reaction of dpph’ with excess of RSV and TEMPO’ 1:1 mol/mol in EtOAc, linear fitting. | S-10 |
| Figure S9. Table S9. | Data and kinetic parameters for reaction of dpph’ with excess of RSV and 4-OH-TEMPO’ 1:1 mol/mol in MeOH, linear fitting. | S-11 |
|----------------------|-------------------------------------------------------------------------------------------------|------|
| Figure S10. Table S10. | Data and kinetic parameters for reaction of dpph’ with excess of RSV and 4-OH-TEMPO’ 1:1 mol/mol in EtOAc, linear fitting. | S-12 |
| Figure S11. Table S11. | Data and kinetic parameters for reaction of dpph’ with excess 3,5-DHA in MeOH, linear fitting. | S-13 |
| Figure S12. Table S12. | Data and kinetic parameters for reaction of dpph’ with excess of 3,5-DHA and TEMPO’ 1:1 mol/mol in MeOH, linear fitting. | S-14 |
| Figure S13. Table S13. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO’ in acidified MeOH (10mM AcOH), linear fitting. | S-15 |
| Figure S14. Table S14. | Data and kinetic parameters for reaction of dpph’ with excess of 4-OH-TEMPO’ in acidified MeOH (10mM AcOH), linear fitting. | S-16 |
| Figure S15. Table S15. | Data and kinetic parameters for reaction of dpph’ with excess of RSV in acidified MeOH (10mM AcOH), linear fitting. | S-17 |
| Figure S16. Table S16. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO’ with 10 mM HFIP, linear fitting. | S-18 |
| Figure S17. Table S17. | Data and kinetic parameters for reaction of dpph’ with excess TEMPO-H in MeOH, linear fitting. | S-19 |
| Figure S18. Table S18. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO-H in acidified MeOH (10mM AcOH), linear fitting. | S-20 |
| Figure S19. Table S19. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO-H in EtOAc, linear fitting. | S-21 |
| Figure S20. Table S20. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO-H and RSV 1:1 mol/mol in MeOH, linear fitting. | S-22 |
| Figure S21. Table S21. | Data and kinetic parameters for reaction of dpph’ with excess of TEMPO-H and RSV 1:1 mol/mol in EtOAc, linear fitting. | S-23 |
| Table S22. | Literature values of oxidation and reduction potentials (vs NHE) for TEMPO’, 4-OH-TEMPO’, TEMPOH**, TEMPOinium’, resveratrol and dpph’. | S-24 |
Table S1. Pseudo-first-order rate constant ($k_{exp}$) for reaction of dpph’ (constant initial concentration) with excess of TEMPO’ in MeOH and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{exp}$ plotted against concentration of nitroide: $k_{exp} = k^s[\text{TEMPO’}] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^s_{90\%}$ calculated as standard deviation for confidential level 90%.

| [TEMPO’] / mM | $k_{exp}$ / s$^{-1}$ | [TEMPO’] / mM | $k_{exp}$ / s$^{-1}$ |
|---------------|----------------------|---------------|----------------------|
| 12.7          | 0.52                 | 12.5          | 0.38                 |
| 9.53          | 0.40                 | 9.36          | 0.33                 |
| 5.10          | 0.28                 | 7.02          | 0.26                 |
| 3.65          | 0.24                 | 3.58          | 0.19                 |
| 2.43          | 0.18                 | 2.39          | 0.13                 |
| 1.62          | 0.14                 | 1.59          | 0.09                 |
| 0.97          | 0.11                 | 0.96          | 0.07                 |

$k^s = 33.28 \text{ M}^{-1}\text{s}^{-1}$  
$\Delta k^s_{90\%} = 4.0$  
$R^2 = 0.9904$

$k^s = 27.89 \text{ M}^{-1}\text{s}^{-1}$  
$\Delta k^s_{90\%} = 3.9$  
$R^2 = 0.9781$

$k^{\text{MeOH}} = 30.6 \pm 3.8 \text{ M}^{-1}\text{s}^{-1}$

Figure S1. Plots of $k_{exp}$ versus concentration of TEMPO’ (data taken from Table S1).
**Table S2.** Pseudo-first-order rate constant \( (k_{\text{exp}}) \) for reaction of dpph\(^{\bullet}\) (constant initial concentration) with excess of 4-OH-TEMPO\(^{\bullet}\) in MeOH and bimolecular rate constant \( k^S \) calculated as a slope from linear dependence of \( k_{\text{exp}} \) plotted against concentration of nitroxide: \( k_{\text{exp}} = k^S [\text{4-OH-TEMPO}^{\bullet}] + \text{const} \), with regression coefficient (R\(^2\)) and error \( \Delta k^S_{90\%} \) calculated as standard deviation for confidential level 90%.

| Neat MeOH | Neat MeOH |
|-----------|-----------|
| [4-OH-TEMPO\(^{\bullet}\)] / mM | \( k_{\text{exp}} / \text{s}^{-1} \) | [4-OH-TEMPO\(^{\bullet}\)] / mM | \( k_{\text{exp}} / \text{s}^{-1} \) |
| 12.6      | 0.17      | 9.35      | 0.13      |
| 9.78      | 0.14      | 7.01      | 0.09      |
| 7.33      | 0.13      | 5.26      | 0.06      |
| 5.50      | 0.09      | 2.68      | 0.03      |
| 3.93      | 0.08      | 1.79      | 0.02      |
| 2.81      | 0.06      | 1.19      | 0.01      |
| 1.87      | 0.05      | 0.30      | 0.00      |
| 1.25      | 0.05      | 0.12      | 0.00      |

\( k^S = 11.4 \text{ M}^{-1}\text{s}^{-1} \) \( \Delta k^S_{90\%} = 1.7 \) \( R^2 = 0.9839 \)

\( k^S = 13.8 \text{ M}^{-1}\text{s}^{-1} \) \( \Delta k^S_{90\%} = 0.8 \) \( R^2 = 0.9965 \)

\( k^{\text{MeOH}} = 12.6 \pm 1.7 \text{ M}^{-1}\text{s}^{-1} \)

**Figure S2.** Plots of \( k_{\text{exp}} \) versus concentration of 4-OH-TEMPO\(^{\bullet}\) (data taken from Table S2).
**Table S3** Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph• (constant initial concentration) with excess of RSV in MeOH and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}}=k^S[RSV] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| Neat MeOH | Neat MeOH |
|-----------|-----------|
| [RSV] / mM | $k_{\text{exp}}$ / s$^{-1}$ | [RSV] / mM | $k_{\text{exp}}$ / s$^{-1}$ |
| 12.3 | 2.77 | 12.8 | 2.91 |
| 9.56 | 2.26 | 9.97 | 2.47 |
| 7.17 | 1.92 | 7.48 | 1.99 |
| 5.38 | 1.53 | 5.61 | 1.69 |
| 3.84 | 1.26 | 4.00 | 1.41 |
| 2.74 | 0.87 | 2.86 | 1.09 |
| 1.83 | 0.74 | 1.91 | 0.95 |
| 1.22 | 0.62 | 1.27 | 0.71 |

$k^S = 196.24 \text{ M}^{-1}\text{s}^{-1}$ \hspace{1cm} $k^S = 187.06 \text{ M}^{-1}\text{s}^{-1}$

$\Delta k^S_{90\%} = 16.8$ \hspace{1cm} $\Delta k^S_{90\%} = 11.3$

$R^2 = 0.9914$ \hspace{1cm} $R^2 = 0.9937$

$k_{\text{MeOH}} = 191.7 \pm 6.5 \text{ M}^{-1}\text{s}^{-1}$

---

**Figure S3.** Plots of $k_{\text{exp}}$ versus concentration of RSV (data taken from Table S3).
Table S4 Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dppe$^\cdot$ (constant initial concentration) with excess of TEMPO$^\cdot$ in EtOAc and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of nitroxide: $k_{\text{exp}}=k^s[\text{TEMPO}^\cdot]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^s_{90\%}$ calculated as standard deviation for confidential level 90%.

| Neat EtOAc | Neat EtOAc |
|------------|------------|
| [TEMPO$^\cdot$] / mM | $k_{\text{exp}} \times 10^4$ / s$^{-1}$ | [TEMPO$^\cdot$] / mM | $k_{\text{exp}} \times 10^4$ / s$^{-1}$ |
| 12.1 | 6.00 | 12.2 | 1.80 |
| 9.41 | 4.73 | 9.50 | 1.61 |
| 7.06 | 4.00 | 7.13 | 1.21 |
| 5.29 | 3.33 | 5.35 | 0.88 |
| 3.78 | 2.75 | 3.82 | 0.51 |
| 2.70 | 2.50 | 2.73 | 0.39 |
| 1.80 | 2.00 | 1.82 | 0.36 |
| 1.20 | 1.47 | | |

$k^s = 0.039 \text{ M}^{-1}\text{s}^{-1}$  
$\Delta k^s_{90\%} = 0.003$  
$R^2 = 0.9913$

$k^s = 0.015 \text{ M}^{-1}\text{s}^{-1}$  
$\Delta k^s_{90\%} = 0.002$  
$R^2 = 0.9755$

$K_{\text{EtOAc}} = 0.027 \pm 0.016 \text{ M}^{-1}\text{s}^{-1}$

Figure S4. Plots of $k_{\text{exp}}$ versus concentration of TEMPO$^\cdot$ (data taken from Table S4).

S-6
Table S5 Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph• (constant initial concentration) with excess of 4-OH-TEMPO• in EtOAc and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of nitroxide: $k_{\text{exp}}=k^S[4\text{-OH-TEMPO}•]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| Neat EtOAc | Neat EtOAc |
|------------|------------|
| [4-OH-TEMPO•] / mM | $k_{\text{exp}} \times 10^4$ / s⁻¹ | [4-OH-TEMPO•] / mM | $k_{\text{exp}} \times 10^4$ / s⁻¹ |
| 11.6 | 11.0 | 10.2 | 6.9 |
| 9.04 | 9.0 | 7.93 | 5.4 |
| 5.09 | 5.2 | 5.95 | 4.9 |
| 3.63 | 4.0 | 4.46 | 4.3 |
| 2.60 | 3.0 | 3.19 | 3.9 |
| 1.73 | 2.0 | 2.28 | 3.3 |
| 1.15 | 1.0 | 1.52 | 2.6 |

$k^S = 0.094 \text{ M}^{-1}\text{s}^{-1}$

$\Delta k^S_{90\%} = 0.006$

$R^2 = 0.9913$

$K_{\text{EtOAc}} = 0.07 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$

$k^S = 0.045 \text{ M}^{-1}\text{s}^{-1}$

$\Delta k^S_{90\%} = 0.006$

$R^2 = 0.9755$

Figure S5. Plots of $k_{\text{exp}}$ versus concentration of 4-OH-TEMPO• (data taken from Table S5).
Table S6 Pseudo-first-order rate constant \((k_{\text{exp}})\) for reaction of dpph\(^-\) (constant initial concentration) with excess of RSV in EtOAc and bimolecular rate constant \(k^S\) calculated as a slope from linear dependence of \(k_{\text{exp}}\) plotted against concentration of phenol: \(k_{\text{exp}}=k^S[RSV]+\text{const}\), with regression coefficient \((R^2)\) and error \(\Delta k_{90\%}\) calculated as standard deviation for confidential level 90%.

| Neat EtOAc | Neat EtOAc |
|------------|------------|
| [RSV] / mM | \(k_{\text{exp}} \times 10^3 / \text{s}^{-1}\) | [RSV] / mM | \(k_{\text{exp}} \times 10^3 / \text{s}^{-1}\) |
| 12.4       | 12.2       | 12.7       | 13.3       |
| 9.66       | 10.0       | 9.86       | 10.6       |
| 7.24       | 7.7        | 7.39       | 8.1        |
| 5.43       | 5.9        | 5.55       | 6.1        |
| 3.88       | 4.4        | 3.96       | 4.8        |
| 2.77       | 3.1        | 2.83       | 3.3        |
| 1.85       | 2.1        | 1.89       | 2.2        |
| 1.23       | 1.4        | 1.26       | 1.6        |

\[k^S = 0.97 \text{ M}^{-1} \text{s}^{-1}\]

\[\Delta k_{90\%} = 0.04\]

\[R^2 = 0.997\]

\[K_{\text{EtOAc}} = 1.00 \pm 0.04 \text{ M}^{-1} \text{s}^{-1}\]

Figure S6. Plots of \(k_{\text{exp}}\) versus concentration of RSV (data taken from Table S6).
Table S7  Pseudo-first-order rate constant ($k_{exp}$) for reaction of dpph\textsuperscript{•} (constant initial concentration) with excess of TEMPO\textsuperscript{•} + RSV, 1:1 mol/mol in MeOH and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{exp}$ plotted against concentration of phenol: $k_{exp} = k^s[RSV] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^s_{90\%}$ calculated as standard deviation for confidential level 90%.

| [TEMPO\textsuperscript{•}] / mM | [RSV] / mM | $k_{exp}$ / s\textsuperscript{-1} | [TEMPO\textsuperscript{•}] / mM | [RSV] / mM | $k_{exp}$ / s\textsuperscript{-1} |
|-----------------|-------------|-----------------|-----------------|-------------|-----------------|
| 10.8            | 10.8        | 17.7            | 10.8            | 7.01        | 9.4             |
| 8.13            | 8.13        | 13.5            | 8.13            | 5.26        | 7.7             |
| 6.10            | 6.10        | 10.7            | 6.10            | 3.94        | 6.4             |
| 4.36            | 4.36        | 8.3             | 4.36            | 2.82        | 5.1             |
| 3.11            | 3.11        | 6.1             | 3.11            | 2.01        | 4.1             |
| 2.07            | 2.07        | 4.4             | 2.07            | 1.34        | 2.9             |
| 1.38            | 1.38        | 3.0             | 1.38            | 0.89        | 2.4             |
| 0.83            | 0.83        | 2.1             | 0.83            | 0.54        | 1.8             |

$k^s = 1543$ M\textsuperscript{-1}s\textsuperscript{-1}  \quad \Delta k^s_{90\%} = 36 \quad R^2 = 0.9977

$k^s = 1179$ M\textsuperscript{-1}s\textsuperscript{-1}  \quad \Delta k^s_{90\%} = 56 \quad R^2 = 0.9905

$k_{MeOH} = 1360 \pm 260$ M\textsuperscript{-1}s\textsuperscript{-1}

Figure S7. Plots of $k_{exp}$ versus concentration of RSV (data taken from Table S7).
Table S8 Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph• (constant initial concentration) with excess of TEMPO• + RSV, 1:1 mol/mol in EtOAc and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}}=k^S[RSV] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| [TEMPO•] / mM | [RSV] / mM | $k_{\text{exp}} \times 10^3$ / s⁻¹ | [TEMPO•] / mM | [RSV] / mM | $k_{\text{exp}} \times 10^3$ / s⁻¹ |
|---------------|------------|-----------------|---------------|------------|-----------------|
| 10.5          | 10.5       | 9.5             | 10.5          | 1.13       | 12.7            |
| 8.14          | 8.14       | 7.7             | 8.14          | 8.76       | 9.8             |
| 6.11          | 6.11       | 6.1             | 6.11          | 6.57       | 7.1             |
| 4.58          | 4.58       | 4.5             | 4.58          | 4.93       | 5.3             |
| 3.27          | 3.27       | 3.8             | 3.27          | 3.52       | 4.7             |
| 2.34          | 2.34       | 2.6             | 2.34          | 2.51       | 2.9             |
| 1.56          | 1.56       | 1.4             | 1.56          | 1.68       | 2.6             |
| 1.04          | 1.04       | 1.4             | 1.04          | 1.04       | 1.04            |

$k^S = 0.88$ M⁻¹s⁻¹  
$\Delta k^S_{90\%} = 0.06$  
$R^2 = 0.9918$

$k^S = 1.06$ M⁻¹s⁻¹  
$\Delta k^S_{90\%} = 0.09$  
$R^2 = 0.9906$

$k_{\text{EtOAc}} = 0.97 \pm 0.13$ M⁻¹s⁻¹

Figure S8. Plots of $k_{\text{exp}}$ versus concentration of RSV (data taken from Table S8).
Table S9  Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph$^\cdot$ (constant initial concentration) with excess of 4-OH-TEMPO$^\cdot$ + RSV, 1:1 mol/mol in MeOH and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}} = k^S[RSV] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| [4-OH-TEMPO$^\cdot$] / mM | [RSV] / mM | $k_{\text{exp}}$ / s$^{-1}$ | [4-OH-TEMPO$^\cdot$] / mM | [RSV] / mM | $k_{\text{exp}}$ / s$^{-1}$ |
|-----------------|------------|-----------------|-----------------|------------|-----------------|
| 9.13            | 9.13       | 5.3             | 9.73            | 9.73       | 5.4             |
| 7.10            | 7.10       | 4.1             | 7.57            | 7.57       | 4.1             |
| 5.33            | 5.33       | 2.9             | 5.68            | 5.68       | 3.0             |
| 4.00            | 4.00       | 2.1             | 4.26            | 4.26       | 2.0             |
| 2.85            | 2.85       | 1.3             | 3.04            | 3.04       | 1.3             |
| 2.04            | 2.04       | 1.0             | 2.17            | 2.17       | 1.0             |
| 1.36            | 1.36       | 0.7             | 1.45            | 1.45       | 0.7             |
| 0.91            | 0.91       | 0.5             | 0.97            | 0.97       | 0.5             |

$k^S = 591$ M$^{-1}$s$^{-1}$

$\Delta k^S_{90\%} = 32$

$R^2 = 0.9951$

$k^S = 568$ M$^{-1}$s$^{-1}$

$\Delta k^S_{90\%} = 28$

$R^2 = 0.9959$

$k^\text{MeOH} = 580 \pm 16$ M$^{-1}$s$^{-1}$

Figure S9. Plots of $k_{\text{exp}}$ versus concentration of RSV (data taken from Table S9).
Table S10  Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpbh• (constant initial concentration) with excess of 4-OH-TEMPO• + RSV, 1:1 mol/mol in EtOAc and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}}=k^S[\text{RSV}]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| [4-OH-TEMPO•] / mM | [RSV] / mM | $k_{\text{exp}}\times10^3$ / s⁻¹ | [4-OH-TEMPO•] / mM | [RSV] / mM | $k_{\text{exp}}\times10^3$ / s⁻¹ |
|---------------------|-------------|----------------------|---------------------|-------------|----------------------|
| 10.0                | 10.0        | 12.0                 | 9.46                | 9.46        | 10.8                 |
| 7.78                | 7.78        | 8.6                  | 7.36                | 7.36        | 8.7                  |
| 5.84                | 5.84        | 6.5                  | 5.52                | 5.52        | 6.4                  |
| 4.38                | 4.38        | 4.4                  | 4.14                | 4.14        | 4.3                  |
| 3.13                | 3.13        | 3.5                  | 2.96                | 2.96        | 2.6                  |
| 2.23                | 2.23        | 2.0                  | 1.41                | 1.41        | 1.4                  |
| 1.49                | 1.49        | 1.1                  | 0.94                | 0.94        | 1.2                  |
| 0.99                | 0.99        | 0.8                  |                     |             |                      |

$k^S = 1.23$ M⁻¹s⁻¹
$\Delta k^S_{90\%} = 0.06$
$R^2 = 0.9954$

$k^S = 1.18$ M⁻¹s⁻¹
$\Delta k^S_{90\%} = 0.09$
$R^2 = 0.9913$

$K_{\text{EtOAc}} = 1.21 \pm 0.04$ M⁻¹s⁻¹

Figure S10. Plots of $k_{\text{exp}}$ versus concentration of RSV (data taken from Table S10).
Table S11. Pseudo-first-order rate constant \((k_{\text{exp}})\) for reaction of dpnh \(^{-}\) (constant initial concentration) with excess of 3,5-DHA in MeOH and bimolecular rate constant \(k^{S}\) calculated as a slope from linear dependence of \(k_{\text{exp}}\) plotted against concentration of phenol: \(k_{\text{exp}}=k^{S}[3,5\text{-DHA}]+\) const, with regression coefficient \((R^{2})\) and error \(\Delta k^{S}_{90\%}\) calculated as standard deviation for confidential level 90\%.

| Neat MeOH | Neat MeOH |
|-----------|-----------|
| [3,5-DHA] / mM | \(k_{\text{exp}} \times 10^{-2} / \text{s}^{-1}\) | [3,5-DHA] / mM | \(k_{\text{exp}} \times 10^{-2} / \text{s}^{-1}\) |
| 10.2 | 10.2 | 13.1 | 11.2 |
| 7.62 | 8.4 | 9.82 | 9.4 |
| 5.71 | 7.1 | 7.37 | 8.2 |
| 2.91 | 5.2 | 5.52 | 7.3 |
| 1.94 | 4.8 | 3.95 | 6.3 |
| 1.30 | 4.2 | 1.88 | 4.4 |

\[ k^{S} = 0.67 \text{ M}^{-1}\text{s}^{-1} \]

\[ \Delta k^{S}_{90\%} = 0.03 \]

\[ R^{2} = 0.9984 \]

\[ k^{S} = 0.58 \text{ M}^{-1}\text{s}^{-1} \]

\[ \Delta k^{S}_{90\%} = 0.07 \]

\[ R^{2} = 0.9781 \]

\[ k^{\text{MeOH}} = 0.63 \pm 0.06 \text{ M}^{-1}\text{s}^{-1} \]

Figure S11. Plots of \(k_{\text{exp}}\) versus concentration of 3,5-DHA (data taken from Table S11).
Table S12  Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph$^\cdot$ (constant initial concentration) with excess of TEMPO' + 3,5-DHA, 1:1 mol/mol in MeOH and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}}=k^S[3,5\text{-DHA}]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| [TEMPO$^\cdot$] / mM | [3,5-DHA] / mM | $k_{\text{exp}}$ / s$^{-1}$ | [TEMPO$^\cdot$] / mM | [3,5-DHA] / mM | $k_{\text{exp}}$ / s$^{-1}$ |
|----------------------|----------------|---------------------|----------------------|----------------|---------------------|
| 12.0                 | 12.0           | 1.50                | 11.9                 | 11.9           | 1.42                |
| 9.4                  | 9.4            | 1.11                | 9.3                  | 9.3            | 1.12                |
| 5.3                  | 5.3            | 0.73                | 4.7                  | 4.7            | 0.75                |
| 3.6                  | 3.6            | 0.55                | 3.2                  | 3.2            | 0.54                |
| 2.6                  | 2.6            | 0.46                | 2.3                  | 2.3            | 0.42                |
| 1.7                  | 1.7            | 0.38                | 1.5                  | 1.5            | 0.31                |
| 1.2                  | 1.2            | 0.23                | 1.0                  | 1.0            | 0.22                |

$k^S = 108.4$ M$^{-1}$ s$^{-1}$
$\Delta k^S_{90\%} = 8.1$
$R^2 = 0.9923$

$k^S = 106.3$ M$^{-1}$ s$^{-1}$
$\Delta k^S_{90\%} = 9.1$
$R^2 = 0.9902$

$k_{\text{MeOH}} = 107.4 \pm 1.5$ M$^{-1}$ s$^{-1}$

Figure S12. Plots of $k_{\text{exp}}$ versus concentration of 3,5-DHA (data taken from Table S12).
**Table S13.** Pseudo-first-order rate constant \( (k_{\text{exp}}) \) for reaction of dpph\( ^\cdot \) (constant initial concentration) with excess of TEMPO\( ^\cdot \) in acidified MeOH and bimolecular rate constant \( k^S \) calculated as a slope from linear dependence of \( k_{\text{exp}} \) plotted against concentration of nitroxide: 
\[ k_{\text{exp}} = k^S[\text{TEMPO}^\cdot] + \text{const}, \]
with regression coefficient \( (R^2) \) and error \( \Delta k^S_{90\%} \) calculated as standard deviation for confidential level 90%.

| MeOH / 10 mM AcOH | MeOH / 10 mM AcOH |
|-------------------|-------------------|
| [TEMPO\( ^\cdot \)] / mM | \( k_{\text{exp}} \) / s\(^{-1} \) | [TEMPO\( ^\cdot \)] / mM | \( k_{\text{exp}} \) / s\(^{-1} \) |
| 12.5 | 1.7 | 12.3 | 1.8 |
| 9.36 | 1.4 | 9.22 | 1.4 |
| 7.02 | 1.1 | 6.91 | 1.1 |
| 5.01 | 0.9 | 4.94 | 0.9 |
| 3.58 | 0.7 | 3.53 | 0.7 |
| 2.39 | 0.4 | 2.35 | 0.5 |
| 1.59 | 0.4 | 1.57 | 0.3 |
| 0.96 | 0.3 | \( k^S = 130.2 \text{ M}^{-1}\text{s}^{-1} \) | \( k^S = 133.5 \text{ M}^{-1}\text{s}^{-1} \) |
| \( \Delta k^S_{90\%} = 6.7 \) | \( \Delta k^S_{90\%} = 5.9 \) |
| \( R^2 = 0.9955 \) | \( R^2 = 0.9781 \) |

\( k^{\text{MeOH}} = 132 \pm 2 \text{ M}^{-1}\text{s}^{-1} \)

**Figure S13.** Plots of \( k_{\text{exp}} \) versus concentration of TEMPO\( ^\cdot \) (data taken from Table S13).
Table S14. Pseudo-first-order rate constant ($k_{exp}$) for reaction of dppe$^\bullet$ (constant initial concentration) with excess of 4-OH-TEMPO$^\bullet$ in acidified MeOH and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{exp}$ plotted against concentration of nitroxide: $k_{exp}=k^s[4$-OH-TEMPO$^\bullet$] + const, with regression coefficient ($R^2$) and error $\Delta k^s_{90\%}$ calculated as standard deviation for confidential level 90%.

| MeOH / 10 mM AcOH | MeOH / 10 mM AcOH |
|--------------------|--------------------|
| [4-OH-TEMPO$^\bullet$] / mM | $k_{exp}$ / s$^{-1}$ | [4-OH-TEMPO$^\bullet$] / mM | $k_{exp}$ / s$^{-1}$ |
|---------------------|-------------------|---------------------|-------------------|
| 8.90                | 0.19              | 12.9                | 0.23              |
| 6.67                | 0.15              | 10.1                | 0.20              |
| 5.00                | 0.13              | 7.55                | 0.16              |
| 3.57                | 0.10              | 5.66                | 0.14              |
| 2.55                | 0.08              | 4.05                | 0.12              |
| 1.70                | 0.06              | 2.89                | 0.11              |
| 1.22                | 0.06              | 1.93                | 0.09              |

$k^s = 18.3$ M$^{-1}$s$^{-1}$

$\Delta k^s_{90\%} = 1.1$

$R^2 = 0.9954$

$k_{MeOH} = 15.6 \pm 3.8$ M$^{-1}$s$^{-1}$

Figure S14. Plots of $k_{exp}$ versus concentration of 4-OH-TEMPO$^\bullet$ (data taken from Table S14).
Table S15. Pseudo-first-order rate constant (k_{exp}) for reaction of dpph• (constant initial concentration) with excess of RSV in acidified MeOH and bimolecular rate constant k^S calculated as a slope from linear dependence of k_{exp} plotted against concentration of phenol: k_{exp}=k^S[RSV] + const, with regression coefficient (R^2) and error Δk^S_{90%} calculated as standard deviation for confidential level 90%.

| MeOH / 10 mM AcOH | MeOH / 10 mM AcOH |
|-------------------|-------------------|
| [RSV] / mM        | k_{exp} \times 10^3 / s^-1 | [RSV] / mM        | k_{exp} \times 10^3 / s^-1 |
| 12.2              | 38.9              | 12.2              | 33.0              |
| 9.47              | 31.2              | 9.52              | 30.3              |
| 7.10              | 25.8              | 7.14              | 24.0              |
| 5.33              | 20.7              | 3.83              | 16.7              |
| 3.81              | 17.5              | 2.73              | 13.9              |
| 2.72              | 12.8              | 1.21              | 10.9              |
| 1.81              | 12.2              |                   |                   |
| 1.21              | 9.9               |                   |                   |

k^S = 2.6 \text{ M}^{-1} \text{s}^{-1} \quad k^S = 2.1 \text{ M}^{-1} \text{s}^{-1}

Δk^S_{90%} = 0.1 \quad Δk^S_{90%} = 0.2

R^2 = 0.9965 \quad R^2 = 0.9877

k^{\text{MeOH}} = 2.4 \pm 0.4 \text{ M}^{-1} \text{s}^{-1}

Figure S15. Plots of k_{exp} versus concentration of RSV (data taken from Table S15).
Table S16. Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph$^\cdot$ (constant initial concentration) with excess of TEMPO$^\cdot$ in MeOH with 10 mM HFIP and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of nitroxide: $k_{\text{exp}}=k^s[\text{TEMPO}^\cdot]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k_{90%}^s$ calculated as standard deviation for confidential level 90%.

| MeOH / 10 mM HFIP | MeOH / 10 mM HFIP |
|-------------------|-------------------|
| [TEMPO$^\cdot$] / mM | $k_{\text{exp}}$ / s$^{-1}$ | [TEMPO$^\cdot$] / mM | $k_{\text{exp}}$ / s$^{-1}$ |
| 11.9 | 1.07 | 12.0 | 1.15 |
| 9.3  | 0.81 | 9.3  | 0.89 |
| 6.9  | 0.78 | 5.2  | 0.69 |
| 5.2  | 0.60 | 3.7  | 0.66 |
| 3.7  | 0.54 | 2.7  | 0.56 |
| 2.7  | 0.48 | 1.8  | 0.50 |
| 1.2  | 0.35 |      |      |

$k^s = 63.3$ M$^{-1}$s$^{-1}$  \hspace{1cm} $k^s = 59.3$ M$^{-1}$s$^{-1}$

$\Delta k_{90%}^s = 8.7$  \hspace{1cm} $\Delta k_{90%}^s = 9.2$

$R^2 = 0.9745$  \hspace{1cm} $R^2 = 0.9751$

$k^\text{MeOH} = 61.3 \pm 2.8$ M$^{-1}$s$^{-1}$

Figure S16. Plots of $k_{\text{exp}}$ versus concentration of TEMPO$^\cdot$ (data taken from Table S16).
Table S17. Pseudo-first-order rate constant \((k_{\text{exp}})\) for reaction of dpph\(^*\) (constant initial concentration) with excess of TEMPO-H in MeOH and bimolecular rate constant \(k^s\) calculated as a slope from linear dependence of \(k_{\text{exp}}\) plotted against concentration of TEMPO-H: \(k_{\text{exp}} = k^s [\text{TEMPO-H}] + \text{const}\), with regression coefficient \(R^2\) and error \(\Delta k^s_{90\%}\) calculated as standard deviation for confidential level 90%.

| Neat MeOH | Neat MeOH |
|-----------|-----------|
| [TEMPO-H] / mM | \(k_{\text{exp}} / \text{s}^{-1}\) | [TEMPO-H] / mM | \(k_{\text{exp}} / \text{s}^{-1}\) |
| 5.2       | 0.24      | 5.2       | 0.20      |
| 4.1       | 0.19      | 4.0       | 0.17      |
| 3.1       | 0.15      | 3.1       | 0.14      |
| 2.3       | 0.13      | 2.3       | 0.11      |
| 1.6       | 0.11      | 1.5       | 0.09      |
| 1.2       | 0.09      | 1.2       | 0.08      |
| 0.8       | 0.08      | 0.8       | 0.05      |

\(k^s = 35.0 \text{ M}^{-1}\text{s}^{-1}\) \(\Delta k^s_{90\%} = 2.0\) \(R^2 = 0.9966\)

\(k_{\text{MeOH}} = 34.5 \pm 0.5 \text{ M}^{-1}\text{s}^{-1}\)

Figure S17. Plots of \(k_{\text{exp}}\) versus concentration of TEMPO-H (data taken from Table S17).
Table S18. Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph$^\bullet$ (constant initial concentration) with excess of TEMPO-H in acidified MeOH and bimolecular rate constant $k^s$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of TEMPO-H: $k_{\text{exp}}=k^s[\text{TEMPO-H}]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^s_{90\%}$ calculated as standard deviation for confidential level 90%.

| MeOH / 10 mM AcOH | MeOH / 10 mM AcOH |
|-------------------|-------------------|
| [TEMPO-H] / mM    | $k_{\text{exp}}$ / s$^{-1}$ | [TEMPO-H] / mM | $k_{\text{exp}}$ / s$^{-1}$ |
| 5.4 mM            | 0.28              | 6.5 mM          | 0.29              |
| 4.2 mM            | 0.23              | 3.8 mM          | 0.19              |
| 2.4 mM            | 0.14              | 2.9 mM          | 0.15              |
| 1.7 mM            | 0.12              | 2.0 mM          | 0.12              |
| 1.2 mM            | 0.09              | 1.5 mM          | 0.09              |
| 0.8 mM            | 0.07              | 1.9 mM          | 0.07              |
| 0.5 mM            | 0.05              | 0.6 mM          | 0.04              |

$k^s = 46$ M$^{-1}$s$^{-1}$  \hspace{1cm}  $k^s = 41$ M$^{-1}$s$^{-1}$  
$\Delta k^s_{90\%} = 3.0$  \hspace{1cm}  $\Delta k^s_{90\%} = 3.0$  
$R^2 = 0.9958$  \hspace{1cm}  $R^2 = 0.9908$

$k_{\text{MeOH}} = 43.5 \pm 3.5$ M$^{-1}$s$^{-1}$

Figure S18. Plots of $k_{\text{exp}}$ versus concentration of TEMPO-H (data taken from Table S18).
Table S19. Pseudo-first-order rate constant \((k_{\text{exp}})\) for reaction of dpph\(^{\bullet}\) (constant initial concentration) with excess of TEMPO-H in EtOAc and bimolecular rate constant \(k^S\) calculated as a slope from linear dependence of \(k_{\text{exp}}\) plotted against concentration of TEMPO-H: \(k_{\text{exp}} = k^S[\text{TEMPO-H}] + \text{const}\), with regression coefficient \((R^2)\) and error \(\Delta k^S_{90\%}\) calculated as standard deviation for confidential level 90%.

| Neat EtOAc | Neat EtOAc |
|------------|------------|
| [TEMPO-H] / mM & \(k_{\text{exp}} \times 10^2 / \text{s}^{-1}\) | [TEMPO-H] / mM & \(k_{\text{exp}} \times 10^2 / \text{s}^{-1}\) |
| 4.9 & 4.63 & 5.2 & 3.22 |
| 3.8 & 3.51 & 4.0 & 2.60 |
| 2.9 & 2.71 & 3.0 & 1.89 |
| 2.1 & 2.05 & 2.3 & 1.51 |
| 1.5 & 1.52 & 1.6 & 1.10 |
| 1.1 & 1.14 & 1.2 & 0.82 |
| 0.7 & 0.67 & 0.7 & 0.51 |
| 0.5 & 0.48 & 0.5 & 0.38 |

\(k^s = 9.3 \text{ M}^{-1}\text{s}^{-1}\) \(\Delta k^S_{90\%} = 0.3\) \(R^2 = 0.9987\)

\(k^s = 6.1 \text{ M}^{-1}\text{s}^{-1}\) \(\Delta k^S_{90\%} = 0.2\) \(R^2 = 0.9985\)

\(k_{\text{MeOH}} = 7.7 \pm 2.2 \text{ M}^{-1}\text{s}^{-1}\)

Figure S19. Plots of \(k_{\text{exp}}\) versus concentration of TEMPO-H (data taken from Table S19).
Table S20. Pseudo-first-order rate constant ($k_{exp}$) for reaction of dpph$^*$ (constant initial concentration) with excess of RSV + TEMPO-H, 1:1 mol/mol in MeOH and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{exp}$ plotted against concentration of phenol: $k_{exp}=k^S[RSV]+\text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| Neat MeOH | Neat MeOH |
|-----------|-----------|
| [TEMPO-H] / mM | [RSV] / mM | $k_{exp}$ / s$^{-1}$ | [TEMPO-H] / mM | [RSV] / mM | $k_{exp}$ / s$^{-1}$ |
| 10.4 | 10.4 | 20.2 | 10.1 | 10.1 | 21.3 |
| 8.1 | 8.1 | 16.0 | 7.9 | 7.9 | 16.8 |
| 6.1 | 6.1 | 11.7 | 5.9 | 5.9 | 12.4 |
| 4.6 | 4.6 | 8.4 | 4.4 | 4.4 | 9.0 |
| 3.3 | 3.3 | 5.8 | 3.2 | 3.2 | 6.0 |
| 2.3 | 2.3 | 3.8 | 2.3 | 2.3 | 4.2 |
| 1.6 | 1.6 | 2.2 | 1.5 | 1.5 | 2.5 |
| 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.5 |

$k^S = 2048$ M$^{-1}$s$^{-1}$

$\Delta k^S_{90\%} = 37$

$R^2 = 0.9994$

$k^S = 2196$ M$^{-1}$s$^{-1}$

$\Delta k^S_{90\%} = 37$

$R^2 = 0.9995$

$K^{MeOH} = 2122 \pm 105$ M$^{-1}$s$^{-1}$

Figure S20. Plots of $k_{exp}$ versus concentration of RSV (data taken from Table S20).
### Table S21.
Pseudo-first-order rate constant ($k_{\text{exp}}$) for reaction of dpph• (constant initial concentration) with excess of RSV + TEMPO-H, 1:1 mol/mol in EtOAc and bimolecular rate constant $k^S$ calculated as a slope from linear dependence of $k_{\text{exp}}$ plotted against concentration of phenol: $k_{\text{exp}}=k^S[RSV] + \text{const}$, with regression coefficient ($R^2$) and error $\Delta k^S_{90\%}$ calculated as standard deviation for confidential level 90%.

| [TEMPO-H] / mM | [RSV] / mM | $k_{\text{exp}} \times 10^2$ / s⁻¹ | [TEMPO-H] / mM | [RSV] / mM | $k_{\text{exp}} \times 10^2$ / s⁻¹ |
|---------------|------------|-------------------------------|---------------|------------|-------------------------------|
| 9.8           | 9.8        | 7.0                           | 9.6           | 9.6        | 10.2                          |
| 7.6           | 7.6        | 5.4                           | 7.5           | 7.5        | 7.7                           |
| 5.7           | 5.7        | 3.8                           | 5.6           | 5.6        | 5.7                           |
| 4.3           | 4.3        | 2.8                           | 4.2           | 4.2        | 4.2                           |
| 3.1           | 3.1        | 2.0                           | 3.0           | 3.0        | 2.9                           |
| 2.2           | 2.2        | 1.4                           | 2.2           | 2.2        | 2.1                           |
| 1.5           | 1.5        | 0.9                           | 1.4           | 1.4        | 1.3                           |
| 1.0           | 1.0        | 0.7                           | 0.9           | 0.9        | 0.9                           |

$k^S = 7.3$ M⁻¹s⁻¹
$\Delta k^S_{90\%} = 0.2$
$R^2 = 0.9981$

$K_{\text{EtOAc}} = 9.0 \pm 2.4$ M⁻¹s⁻¹

### Figure S21.
Plots of $k_{\text{exp}}$ versus concentration of RSV (data taken from Table S21).
Table S22. Literature values of oxidation and reduction potentials (vs NHE) for TEMPO’, 4-OH-TEMPO*, TEMPOH+, TEMPO+ium+, resveratrol and dpph*.

|          | $E_{\text{ox}}$ / mV | $E_{\text{red}}$ / mV |
|----------|----------------------|----------------------|
| TEMPO*   | 750±5, 734, 864, 730-750 (pH 7) | 804 (pH 9.3) |
| 4-OH-TEMPO* | 818±806, 830 | 229, 233 |
| TEMPOH+  | 955 ± 15 |  |
| TEMPO+ium+ | 750±5, 804 (pH 9.3) |  |
| RSV      | 849 (pH 3.2), ~650 (pH 7.0) |  |
| dpph*    | 545, 424 |  |

* In water, pH 7.

b Cyclic voltammetry 0.003 M TEMPO, in MeOH/MeCN (1:1), 0.1 M Bu4NBF4, half-wave potential (620mV vs. SCE), here recalculated to NHE.

c Values collected by Tikhonov et al. 2, 7

*d 560V vs. SCE in t-butanol/water (1:1).

c Reversible half-wave potential of the reduction of TEMPO (or 4-OH-TEMPO) at pH 7 determined experimentally by Kato et al.9

For the resulting half-wave potentials (versus SHE) for one electron oxidation and reduction potentials calculated theoretically by Hodgson et al. 10 of several nitroxides.

$g$ Standard reduction potential for TEMPOH+/TEMPOH$_2$ pair calculated from $E_{\text{ox}}$(TEMPO+ium+/TEMPO+), and equilibrium constant for TEMPOH+/TEMPO+.$E_{\text{ox}}$(TEMPO+ium+/TEMPO+). 1

$h$ -0.65V vs. SCE in t-butanol/water (1:1). 8

i In ethanol/water, measured versus Ag/AgCl and recalculated into NHE. Those potentials correspond to the oxidation of the phenol moiety (the slope is ~45 mV/pH), the oxidation of the resorcinol group occurs at potential ca 200mV higher and the slope is -59 mV/pH.11

j For dpph*/dpph+,H redox pair in water-methanol 1:1 at pH =7.12

k In acetonitrile.13

REFERENCES

1. V. D. Sen and V. A. Golubev, J Phys Org Chem, 2009, 22, 138-143.
2. V. D. Sen’, I. V. Tikhonov, L. I. Borodin, E. M. Pliss, V. A. Golubev, M. A. Syroeshkin and A. I. Rusakov, J. Phys. Org. Chem., 2015, 28, 17-24.
3. T. Yamasaki, Y. Matsuoka, F. Mito, M. Yamato and K. i. Yamada, Asian J. Org. Chem., 2013, 2, 388-391.
4. A. Orita, M. G. Verde, M. Sakai and Y. S. Meng, J. Power Source, 2016, 321, 126-134.
5. J. R. Fish, S. G. Swarts, M. D. Sevilla and T. Malinski, J. Phys. Chem., 1988, 92, 3745-3751.
6. X.-Y. Qian, S.-Q. Li, J. Song and H.-C. Xu, ACS Catalysis, 2017, 7, 2730-2734.
7. I. V. Tikhonov, V. D. Sen’, L. I. Borodin, E. M. Pliss, V. A. Golubev and A. I. Rusakov, J. Phys. Org. Chem., 2014, 27, 114-120.
8. R. A. Green, J. T. Hill-Cousins, R. C. D. Brown, D. Pletcher and S. G. Leach, Electrochim. Acta, 2013, 113, 550-556.
9. Y. Kato, Y. Shimizu, L. Yijing, K. Unoura, H. Utsumi and T. Ogata, Electrochim. Acta, 1995, 40, 2799-2802.
10. J. L. Hodgson, M. Namazian, S. E. Bottle and M. L. Coote, J. Phys. Chem. A, 2007, 111, 13595-13605.
11. O. Corduneanu, P. Janeiro and A. M. O. Brett, Electroanalysis, 2006, 18, 757-762.
12. Q.-k. Zhuang, F. Scholz and F. Pragst, Electrochem. Comm., 1999, 1, 406-410.
13. I. Nakanishi, K. Fukuhara, T. Shimada, K. Ohkubo, Y. Iizuka, K. Inami, M. Mochizuki, S. Urano, S. Itoh and N. Miyata, J. Chem. Soc. Perkin 2, 2002, 1520-1524.