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**Supplementary Materials for**

# A Quantitative Metric for Organic Radical Stability and Persistence Using Thermodynamic and Kinetic Features

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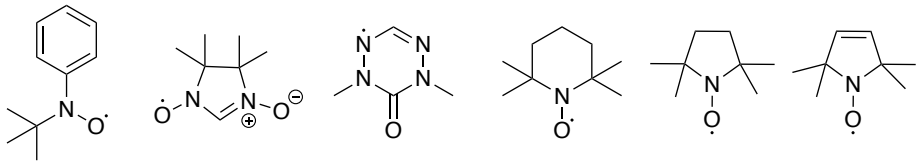
TABLE OF CONTENTS

| Section | Description | Page No. |
|---|---|---|
| 1. | Dependence of basis set for spin density calculations. | S2 |
| 2. | Distribution of fractional spin and buried volume of data set. | S3 |
| 3. | Structures considered for evaluating the organic radical stability metric. | S4 |
| 4. | Fractional spin and buried volumes for experimentally known radicals. | S5 |
| 5. | Plot of fractional spin vs. buried volume for radicals optimized in the gas phase. | S6 |
| 6. | Plot of pareto-front for radicals optimized in gas phase. | S7 |
| 7. | Comparison of Max fractional spin with thermodynamic quantities. | S8 |
| 8. | IQR plots for Radical Stability and Radical stabilization energies. | S9 |
| 9. | Structures of stable radicals for the comparison of C-H BDE values. | S10 |
| 10. | Fractional spins, buried volumes and thermochemistry of radical cascade reactions. | S11 |
| 11. | Correlation of RSS metric and relative bimolecular rates of radical decomposition. | S12 |
| 12. | RSS metrics generated with different radii used for buried volume analysis. | S13 |

## 1. Dependence of basis set for spin density calculations

**Table S1.** Largest Fractional Spin Density with M06-2X using two basis sets: def2TZVP and def2QZVP. There is small basis set dependence (0.01-0.03) for the value of the normalized fractional spin.




| Name | def2-TZVP | | def2-QZVP | |
|---|---|---|---|---|
| | spin density | fractional spin | spin density | fractional spin |
| nn | 0.31 | 0.20 | -0.37 | 0.21 |
| proxyl | 0.54 | 0.50 | 0.49 | 0.47 |
| s-proxyl | 0.53 | 0.48 | 0.49 | 0.46 |
| TBAN | 0.48 | 0.33 | 0.46 | 0.31 |
| TEMPO | 0.52 | 0.46 | 0.48 | 0.45 |
| verdazyl | 0.41 | 0.27 | 0.39 | 0.25 |

## 2. Distribution of fractional spin and buried volume of data set

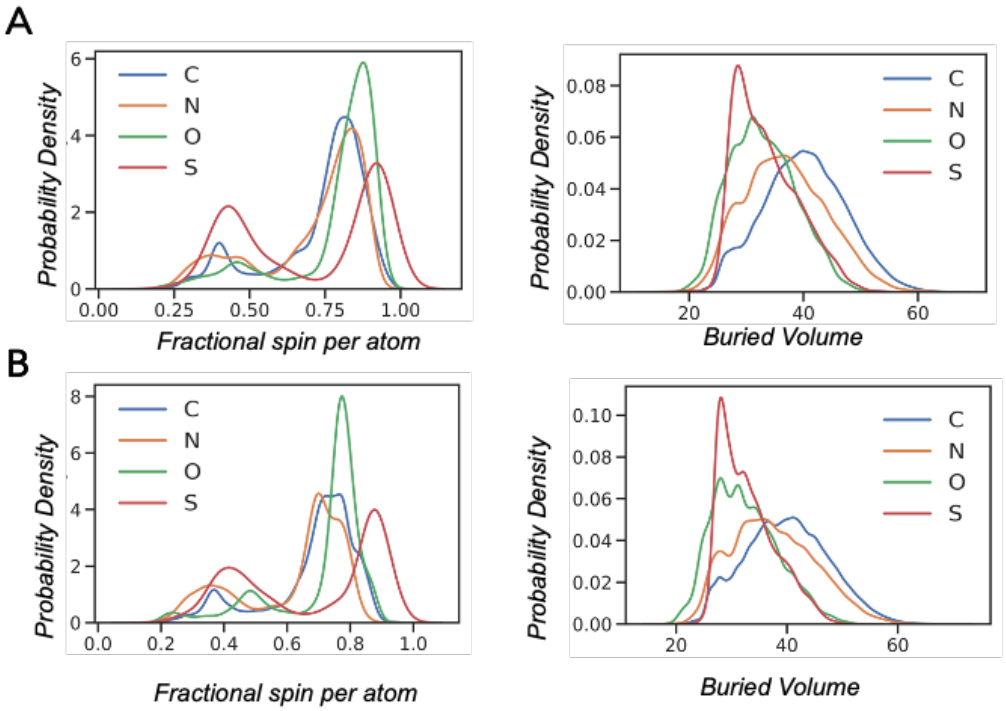



**Fig. S1.** The kernel density plots represent the spread of buried volume and fractional spin based on atom type in the data set. (A) in water phase (B) in gas phase

## 3. Structures considered for evaluating the organic radical stability metric

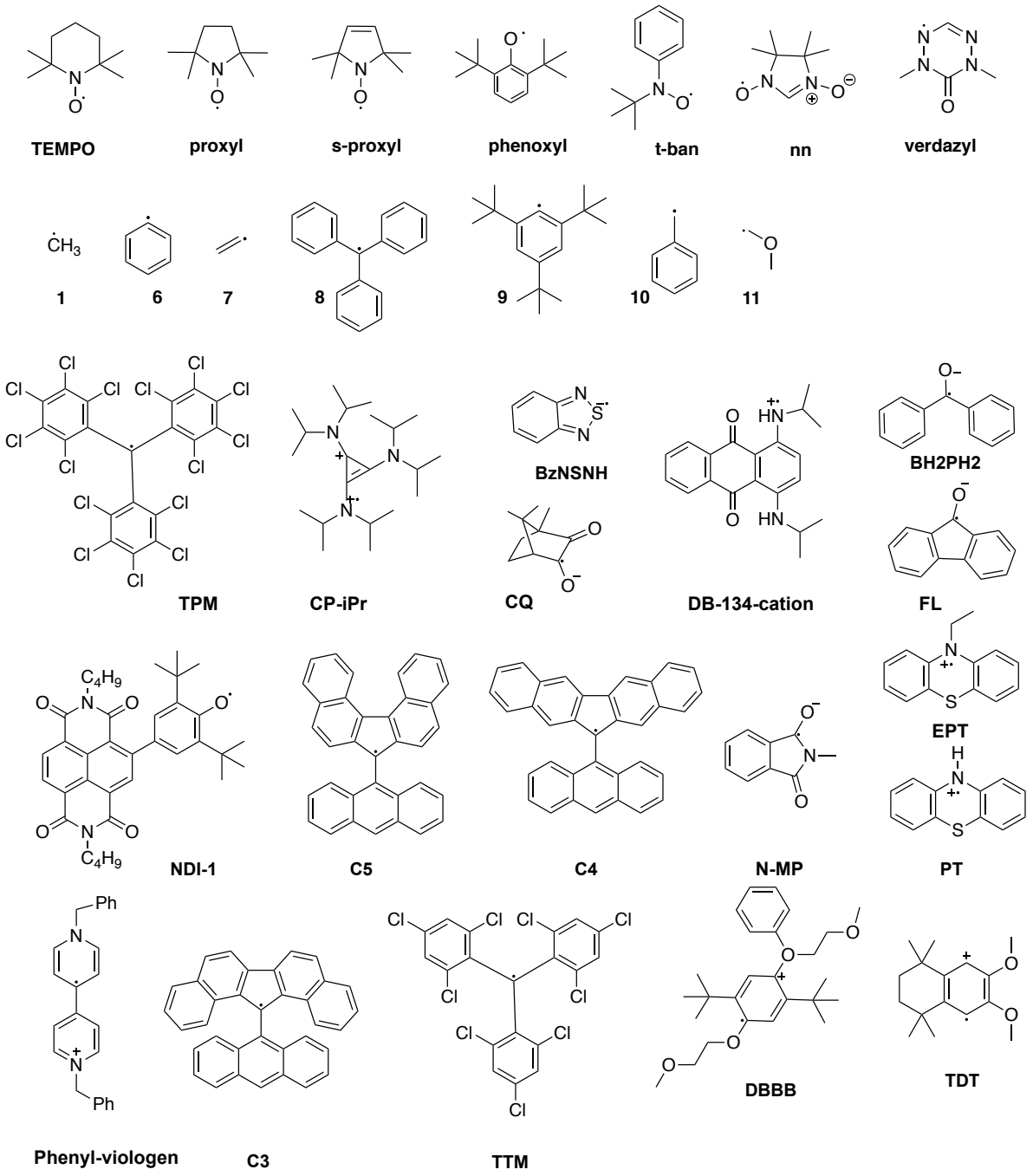



**Fig. S2**. Structures of radicals considered in the study of organic radical stability.

## 4. Fractional spin and buried volumes for experimentally known radicals

**Table S2.** M062X/def2-TZVP fractional Spin Density and $V_{bur}$ (%) for selected stable radicals in gas and water phase.

| | *Water* | | | *Gas phase* | | |
|---|---|---|---|---|---|---|
| **Radical** | **Atom** | **$V_{bur}$ (%)** | **Max. spin** | **Atom** | **$V_{bur}$ (%)** | **Max. spin** |
| **TPM** | C | 84.83 | 0.4275 | C | 84.80 | 0.4271 |
| **CP-iPr** | N | 69.47 | 0.2731 | N | 69.41 | 0.2569 |
| **Proxyl** | N | 64.13 | 0.4954 | O | 43.95 | 0.5037 |
| **CQ** | O | 33.12 | 0.2407 | O | 32.98 | 0.2922 |
| **TEMPO** | N | 66.92 | 0.4611 | O | 46.85 | 0.4865 |
| **NDI-1** | C | 61.13 | 0.2139 | C | 60.93 | 0.1999 |
| **s-proxyl** | N | 62.45 | 0.4840 | O | 43.52 | 0.4898 |
| **car-C5** | C | 67.99 | 0.2872 | C | 67.97 | 0.2840 |
| **verdazyl** | N | 38.75 | 0.2730 | N | 38.75 | 0.2808 |
| **car-C4** | C | 67.62 | 0.2384 | C | 67.62 | 0.2366 |
| **Phenoxyl** | C | 38.76 | 0.2306 | C | 38.70 | 0.2149 |
| **phenyl-viologen** | N | 53.19 | 0.1680 | N | 53.11 | 0.1667 |
| **car-C3** | C | 72.45 | 0.2585 | C | 72.51 | 0.2622 |
| **Nn** | N | 53.12 | 0.1984 | O | 36.12 | 0.2254 |
| **TTM** | C | 83.93 | 0.3929 | C | 83.89 | 0.3959 |
| **DBBB** | C | 61.05 | 0.2391 | C | 60.89 | 0.2236 |
| **TDT** | C | 69.35 | 0.1941 | C | 69.30 | 0.2251 |
| **Tban** | N | 59.13 | 0.3330 | O | 41.54 | 0.3491 |
| **BP** | C | 50.61 | 0.1736 | O | 36.47 | 0.1819 |
| **Trityl (8)** | C | 64.27 | 0.2460 | C | 64.31 | 0.2457 |
| **N-MP** | O | 33.09 | 0.1459 | C | 52.62 | 0.1595 |
| **FL** | O | 31.99 | 0.1778 | O | 32.08 | 0.2438 |
| **DB-134-cation** | N | 56.14 | 0.1181 | N | 56.13 | 0.1347 |
| **EPT** | N | 60.93 | 0.2565 | N | 60.92 | 0.2413 |
| **PT** | N | 47.83 | 0.2388 | S | 43.85 | 0.2460 |
| **BzNSN** | S | 31.68 | 0.2364 | S | 31.69 | 0.2098 |
| **11** | C | 24.61 | 0.9008 | C | 24.58 | 0.8963 |
| **1** | C | 13.32 | 1.0000 | C | 13.30 | 1.0000 |
| **10** | C | 30.77 | 0.3886 | C | 30.75 | 0.3914 |
| **7** | C | 19.63 | 0.8487 | C | 19.61 | 0.8501 |
| **6** | C | 36.39 | 0.7280 | C | 36.36 | 0.7317 |
| **9** | C | 61.18 | 0.7230 | C | 61.30 | 0.7249 |

## 5. Plot of fractional spin *vs.* buried volume for radicals optimized in the gas phase

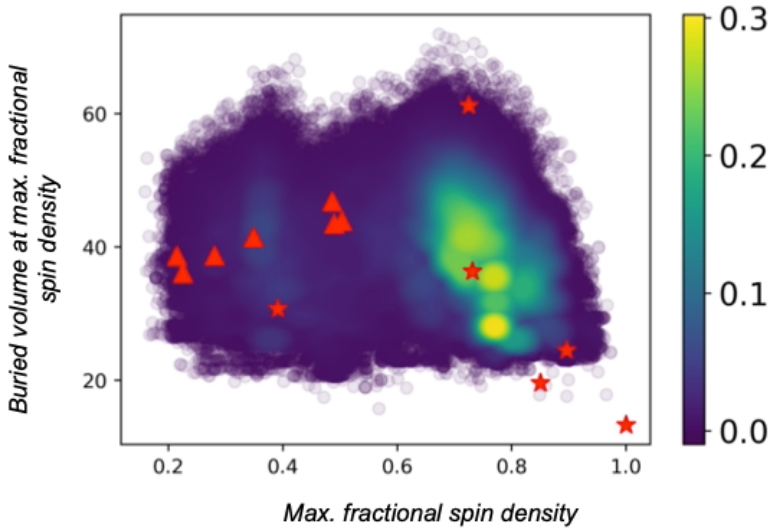



**Fig. S3.** Depiction of the stability metric to classify know radicals according to their stability. Experimentally stable radicals are shown as red triangles, located in the top left region of the graph.

## 6. Plot of pareto-front for radicals optimized in gas phase

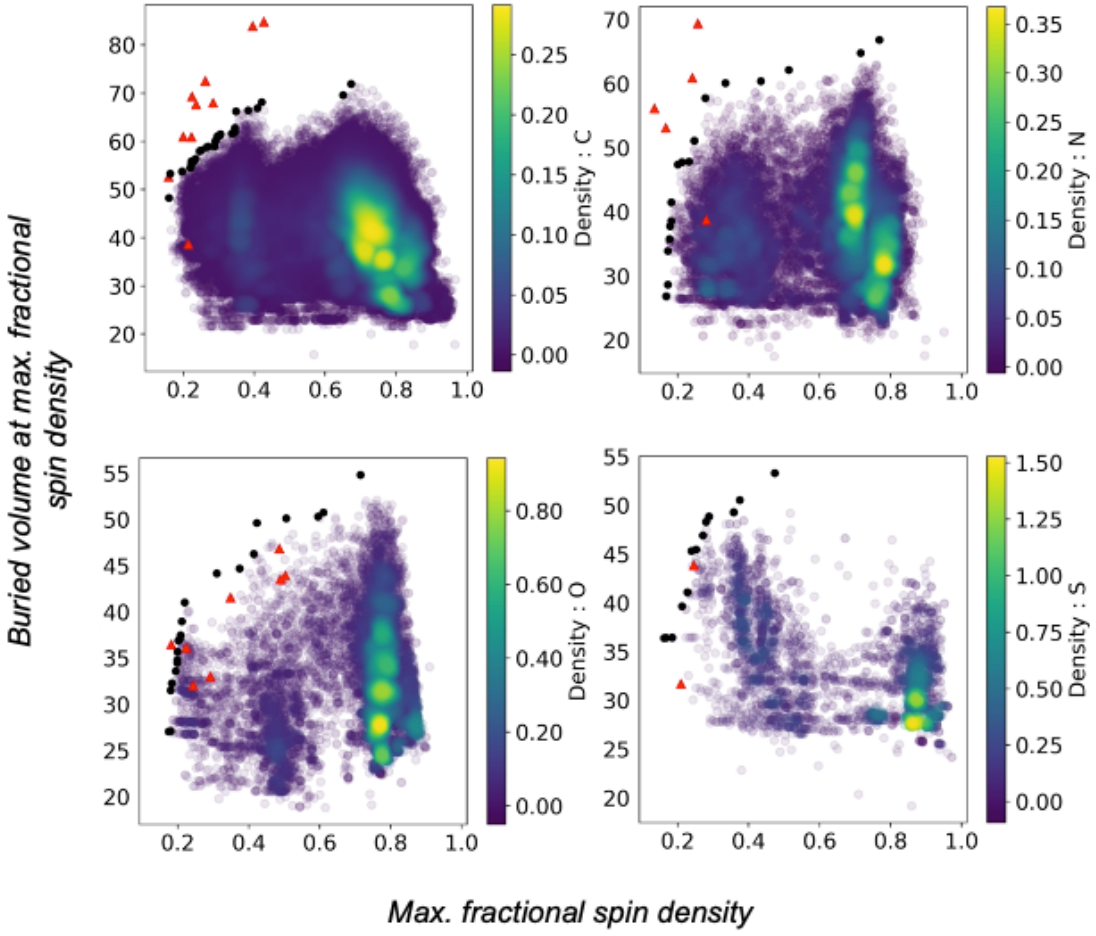
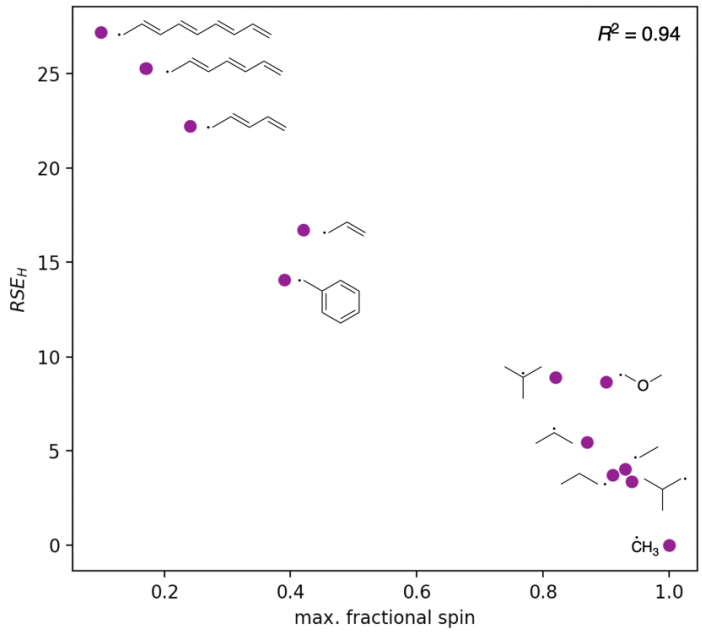



**Fig. S4.** Pareto front plots based on atom type (C, N, O, S) using fractional spin density and buried volume parameters.

## 7. Comparison of Max fractional spin with thermodynamic quantities.



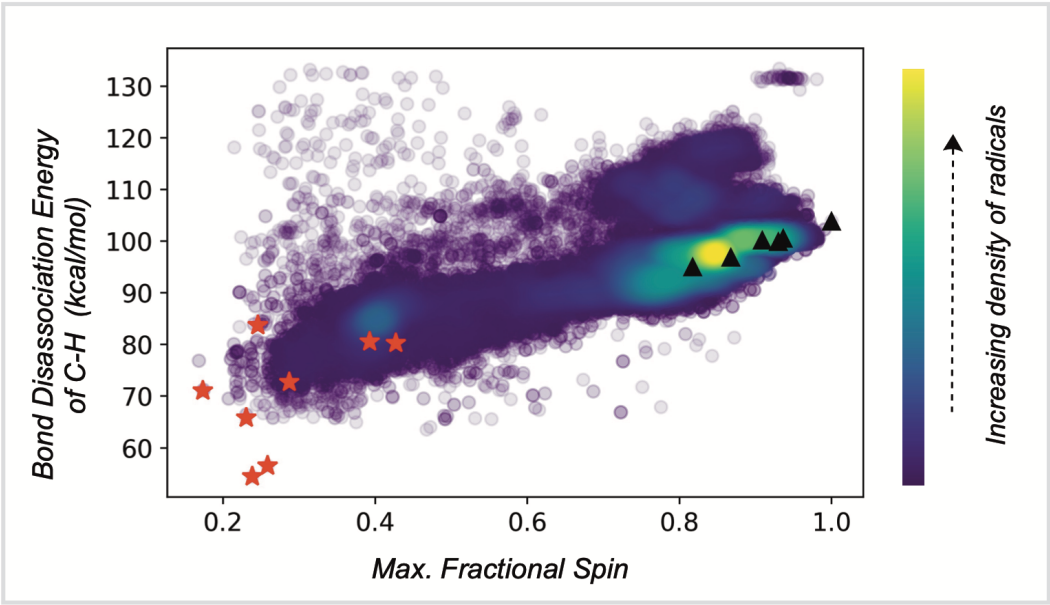




**Fig. S5.** Top: Correlation of max. fractional spin with RSE involving the cleavage of a C($sp^3$)-H bond. Bottom: Correlation of max. fractional spin with C–H BDE. The red stars are known stable radicals. The black triangles are aliphatic hydrocarbons

## 8. IQR plots for Radical Stability and Radical stabilization energies.

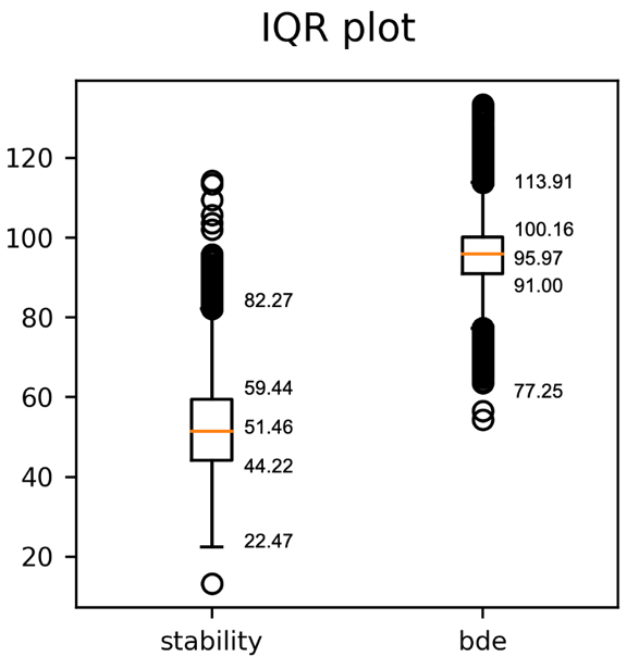



**Fig. S6.** Chemical molecular structures of stable radicals considered for comparison in C-H bond disassociation energies with the radical stability metric.

## 9. Structures of stable radicals for the comparison of C-H BDE values.

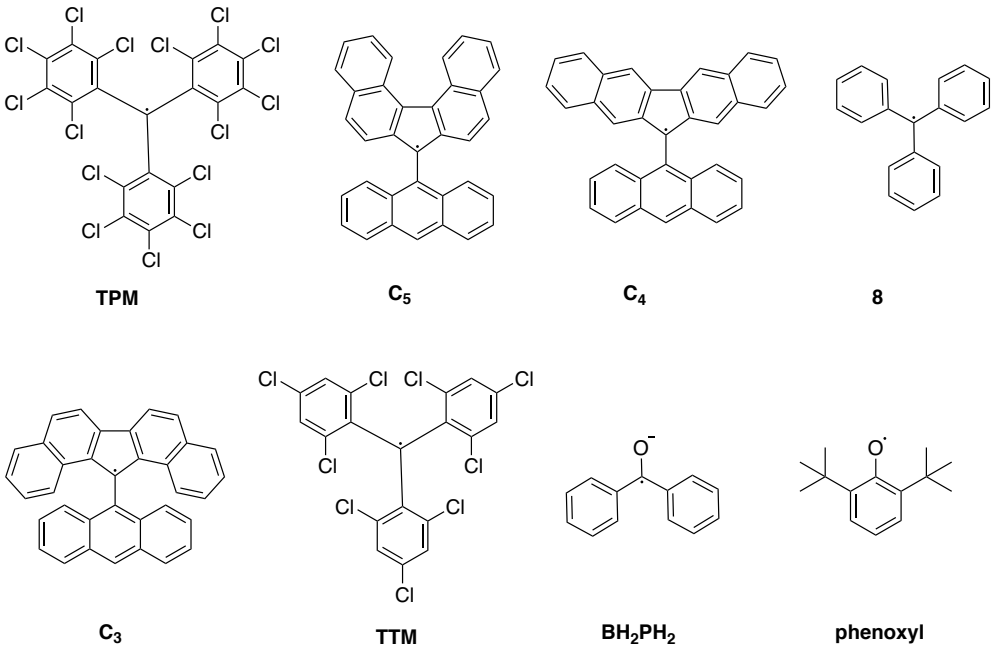



**Fig. S7.** Molecular structures of stable radicals for which C-H bond dissociation energies are compared with the radical stability (RSS) metric.

## 10. Fractional spins, buried volumes and thermochemistry of radical cascade reactions.

**Table S3.** Fractional Spin Density and Buried Volume for the Organic Reaction Cascades.

| Rxn | Int | Fractional Spin | Buried Volume | E (Hartree) | ZPE (Hartree) | H (Hartree) | G(T) (Hartree) | qh-G(T) (Hartree) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.8655 | 35.57 | -993.943240 | 0.274418 | -993.647487 | -993.722678 | -993.717100 |
| | 2 | 0.7850 | 61.24 | -993.988158 | 0.279212 | -993.689260 | -993.760967 | -993.755715 |
| | 3 | 0.3001 | 56.50 | -994.013187 | 0.281487 | -993.713355 | -993.779170 | -993.775948 |
| 2 | 1 | 0.8835 | 35.02 | -677.549588 | 0.332449 | -677.197937 | -677.265108 | -677.262000 |
| | 2 | 0.7830 | 49.50 | -677.572546 | 0.335977 | -677.218424 | -677.285767 | -677.281396 |
| | 3 | 0.3817 | 60.99 | -677.589464 | 0.338848 | -677.233884 | -677.297288 | -677.293643 |
| 3 | 1 | 0.7190 | 46.87 | -852.450664 | 0.400788 | -852.026430 | -852.099506 | -852.097533 |
| | 2 | 0.7718 | 56.66 | -852.490311 | 0.404021 | -852.064150 | -852.134397 | -852.132488 |
| | 3 | 0.6411 | 56.99 | -852.549563 | 0.407272 | -852.121107 | -852.190523 | -852.188037 |

## 11. Correlation of RSS metric and relative bimolecular rates of radical decomposition.

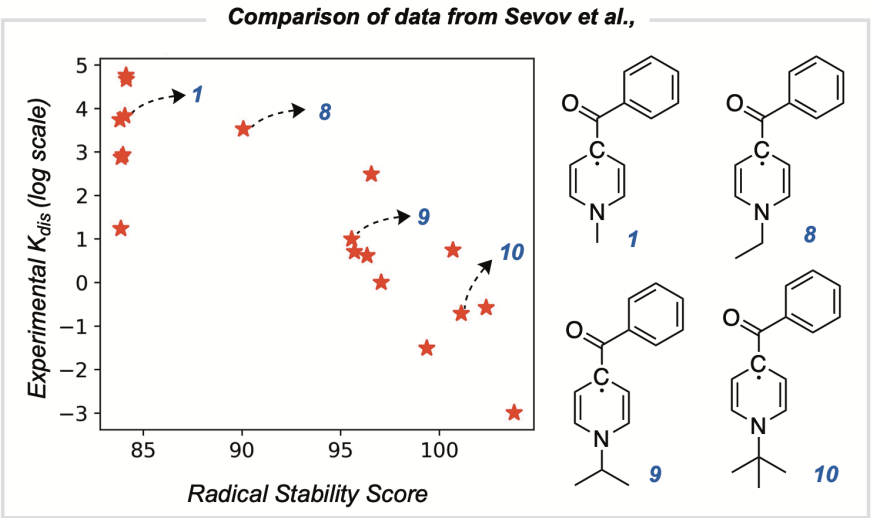



**Fig. S8.** Comparison of log($k_{rel}$) and RSS for 18 radicals originally studied by Sevov (*J. Am. Chem. Soc.* 2017, 139, 8, 2924–2927). Buried volumes were generated at the N atoms.

## 12. RSS metrics generated with different radii used for buried volume analysis.

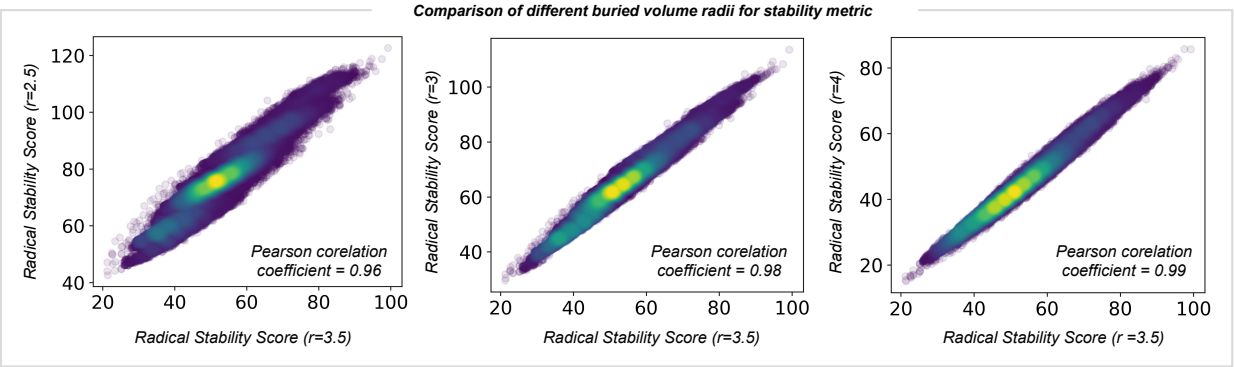



**Fig. S9.** Comparison of RSS metric generated with radii at 2.5, 3.0 and 4.0 Å against the more traditional value of 3.5 Å used for buried volume calculations.