

Supporting information for
Environ. Sci. Technol.

**Isotopic analysis of oxidative pollutant
degradation pathways exhibiting
large H isotope fractionation**

Reto S. Wijker^{1,2}, Pawel Adamczyk³, Jakov Bolotin¹, Piotr Paneth^{*,3},
and Thomas B. Hofstetter^{*,1,2}

¹Eawag, Swiss Federal Institute of Aquatic Science and Technology

²Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zürich

³Institute of Applied Radiation Chemistry, Technical University of Lodz, Zeromskiego
116, 90-924 Lodz, Poland

*Corresponding authors: piotr.paneth@p.lodz.pl, thomas.hofstetter@eawag.ch

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S1 Chemicals

Chemicals and gases were purchased from various manufacturers and used without further treatment. A list of compound names, purities, and suppliers follows. 2-nitrotoluene (99%), 4-nitrotoluene (98%), 2,6-dinitrotoluene (98%), 2,4-dinitrotoluene (97%), nitrobenzene (99%), potassium permanganate (KMnO_4 , 99%), sodium thiosulfate (NaS_2O_3 , 98%) from Sigma-Aldrich (Buchs SG, Switzerland), toluene (99.9%) from VWR International (Dietikon, Switzerland) and hexane (99%, Macron Fine Chemicals, USA). The carrier and reference gas for GC and GC/IRMS included helium (He , 99.999%), N_2 (99.9999%), CO_2 (99.999%), H_2 (99.999%), synthetic air ($20 \pm 1\%$ O_2 in N_2 (99.9995%)), O_2 (99.9995%) and, N_2 (99.9995%) from Carbagas (Rümlang, Switzerland). All aqueous solutions were prepared in nanopure water (18.2 $\text{M}\Omega\text{-cm}$, Barnstead NANOpure Diamond Water Purification System).

S2 Data Evaluation

S2.1 Apparent kinetic isotope effects

^2H -, ^{13}C -, and ^{15}N -AKIEs were calculated using established methods² to support the interpretation of the modeling approach in the main manuscript. All AKIEs were derived from eqs. S1-S2 and the results are compiled in Table S1.

$$\ln \left(\frac{\delta^h \text{E}_0 + n/x \cdot \Delta \delta^h \text{E} + 1}{\delta^h \text{E}_0 + 1} \right) = \epsilon_{\text{E,rp}} \cdot \ln \left(\frac{c}{c_0} \right) \quad (\text{S1})$$

$$\text{AKIE}_{\text{E}} = \frac{1}{1 + z \cdot \epsilon_{\text{E,rp}}} \quad (\text{S2})$$

where E stands for the element (C, H, or N), $\epsilon_{\text{E,rp}}$ is the isotope enrichment factor for the reactive position, $\delta^h \text{E}$ is the isotope signature during oxidation, $\delta^h \text{E}_0$ its initial value, and $\Delta \delta^h \text{E}$ the extent of isotope fractionation. n is the total number of atoms of element E, x represents the number of reactive sites, and z accounts for intramolecular isotopic competition among reactive sites. c/c_0 is the fraction of remaining reactant. Notice that the derivation of z for the dioxygenation of nitrobenzene is illustrated explicitly in Tables S2 and S3 for C and H isotopes, respectively.

Table S1: Apparent kinetic isotope effects (AKIEs) quantified according to eqs. S1 and S2.

Pathway & Compound	Element	n	x	z	AKIE
Dioxygenation of nitrobenzene	C	6	6	3	1.027 ± 0.002
	H	5	5	3	0.965 ± 0.003
	N	1	1	1	1.0017 ± 0.0002
CH ₃ -group oxidation of toluene	C	7	1	1	1.0394 ± 0.0026
	H	8	3	3	no quantification possible

Table S2: Allocation of light and heavy reaction rate constants (^{12}k vs. ^{13}k) for **nitrobenzene dioxygenation** depending on position of ^{13}C substitution and position of MnO_4^- attack to account for intramolecular competition. C numbering scheme from Figure S1.

Position of ^{13}C	Position of MnO_4^- attack						$\frac{n^{13}k}{n^{12}k + n^{13}k} = \frac{1}{z}$
	C ₁ –C ₂	C ₂ –C ₃	C ₃ –C ₄	C ₄ –C ₅	C ₅ –C ₆	C ₆ –C ₁	
C ₁	^{13}k	^{12}k	^{12}k	^{12}k	^{12}k	^{13}k	1/3
C ₂	^{13}k	^{13}k	^{12}k	^{12}k	^{12}k	^{12}k	1/3
C ₃	^{12}k	^{13}k	^{13}k	^{12}k	^{12}k	^{12}k	1/3
C ₄	^{12}k	^{12}k	^{13}k	^{13}k	^{12}k	^{12}k	1/3
C ₅	^{12}k	^{12}k	^{12}k	^{13}k	^{13}k	^{12}k	1/3
C ₆	^{12}k	^{12}k	^{12}k	^{12}k	^{13}k	^{13}k	1/3
average							1/3

Table S3: Allocation of light and heavy reaction rate constants (1k vs. 2k) for **nitrobenzene dioxygenation** depending on position of ^2H substitution and position of MnO_4^- attack to account for intramolecular competition. H numbering scheme from Figure S1.

Position of ^2H	Position of MnO_4^- attack						$\frac{n^2k}{n^1k + n^2k} = \frac{1}{z}$
	C ₁ –C ₂	C ₂ –C ₃	C ₃ –C ₄	C ₄ –C ₅	C ₅ –C ₆	C ₆ –C ₁	
H _{C₂}	2k	2k	1k	1k	1k	1k	1/3
H _{C₃}	1k	2k	2k	1k	1k	1k	1/3
H _{C₄}	1k	1k	2k	2k	1k	1k	1/3
H _{C₅}	1k	1k	1k	2k	2k	1k	1/3
H _{C₆}	1k	1k	1k	1k	2k	2k	1/3
average							1/3

S2.2 Equations for interpretation of multi-element isotope fractionation

It follows from the Rayleigh equation that the fraction of remaining compound, f is proportional to the extent of C and H isotope fractionation as quantified by isotope enrichment factors, ϵ , in eqs. S3-S4 regardless if determined from C and H isotope fractionation (eq. S5). It follows from this equivalence that the slope of the linear relationship in eq. S6 that the characteristic slope $\Lambda^{\text{H/C}}$ is the ratio of ϵ -values (S7).

$$\left(\frac{\delta^2\text{H} + 1}{\delta^2\text{H}_0 + 1} \right) = f_{\text{H}}^{\epsilon_{\text{H}}} \quad (\text{S3})$$

$$\left(\frac{\delta^{13}\text{C} + 1}{\delta^{13}\text{C}_0 + 1} \right) = f_{\text{C}}^{\epsilon_{\text{C}}} \quad (\text{S4})$$

$$f_{\text{H}} = f_{\text{C}} \quad (\text{S5})$$

$$\ln \left(\frac{\delta^2\text{H} + 1}{\delta^2\text{H}_0 + 1} \right) = \frac{\epsilon_{\text{H}}}{\epsilon_{\text{C}}} \cdot \ln \left(\frac{\delta^{13}\text{C} + 1}{\delta^{13}\text{C}_0 + 1} \right) \quad (\text{S6})$$

$$\Lambda^{\text{H/C}} = \frac{\epsilon_{\text{H}}}{\epsilon_{\text{C}}} \quad (\text{S7})$$

Equation S6 can be simplified to yield the typically used comparison of isotope signatures for different elements (eq. 1 in the main manuscript and eq. S10 below). To this end, one applies a Taylor series expansion to the \ln -terms as shown below to obtain eq. S10.

$$\ln(x + 1) = \sum_{n=1}^{\infty} (-1)^{n+1} \cdot \frac{x^n}{n} = \sum_{n=1}^{\infty} x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (\text{S8})$$

$$\delta^2\text{H} - \delta^2\text{H}_0 \approx \frac{\epsilon_{\text{H}}}{\epsilon_{\text{C}}} \cdot (\delta^{13}\text{C} - \delta^{13}\text{C}_0) \quad (\text{S9})$$

$$\frac{\Delta\delta^2\text{H}}{\Delta\delta^{13}\text{C}} \approx \frac{\epsilon_{\text{H}}}{\epsilon_{\text{C}}} \quad (\text{S10})$$

S3 Isotopomer-specific modeling of experimental data

The trends of toluene, nitrobenzene, and substituted nitrotoluene concentrations, $\delta^2\text{H}$ -, and $\delta^{13}\text{C}$ - values were quantified using a numerical model, in which a series of C and H isotopologs and isotopomers were included (eq. 6 in the main manuscript). A compilation of the different isotopologs and isotopomers for all compounds is shown in Tables S4-S7. Isotopomers were numbered according to a numbering scheme shown in Figure S1. Also shown therein are stoichiometric coefficients used to account for intramolecular isotopic competition, γ_j^E . Initial isotopomer distribution was assumed to follow binomial distribution according to the initial isotope signatures determined for each compound. The numerical model was implemented in Aquasim⁴ as shown previously³ using measured concentration and isotope signature time courses as described in the main manuscript.

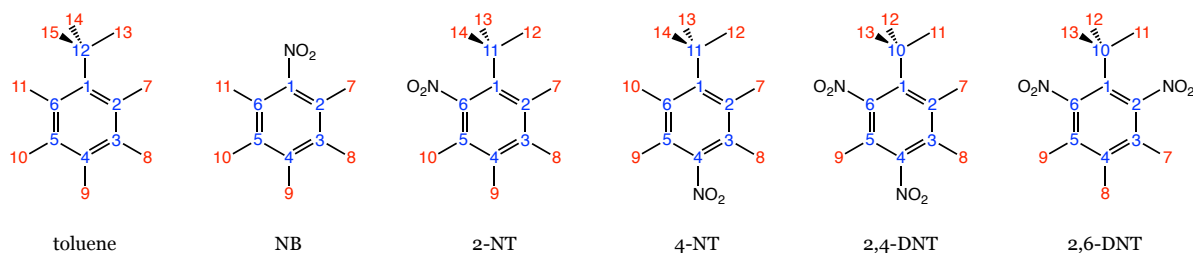


Figure S1: Atom numbering scheme used to label C (blue numbers) and H (red numbers) isotopomers.

S4 Theoretical evaluation of mono- and dinitrotoluene oxidation by MnO_4^- and intrinsic position-specific kinetic isotope effects

Theoretical evaluation of MnO_4^- -catalyzed oxidations by density functional theory (DFT) were carried out at the IEFPCM/B3LYP/6-31+G(d,p) level of theory. The results for mono- and dinitrotoluenes are shown in tables S8 (2-NT), S9 (3-NT), S10 (4-NT), S11 (2,4-DNT), S12 (2,6-DNT), and illustrative optimized ground and transition state geometries are shown in table S13-S33. Additional examples can be found in the companion paper.¹

Table S4: C and H isotopomers of **toluene** included in the numerical model. γ is used to account for intramolecular competition of randomly distributed heavy ^{13}C and ^2H isotopes.

Isotopomer	Atom number and position of isotopic substitution ^a											Stoichiometric coefficient / intramolecular competition											
	aromatic moiety						aliphatic moieties					CH ₃ -group oxidation				dioxygenation							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	¹² C γ _{C_{mox}}	¹³ C γ _{C_{mox}}	¹ H γ _{C_{mox}}	² H γ _{C_{mox}}	¹² C γ _{diox}	¹³ C γ _{diox}	¹ H γ _{diox}	² H γ _{diox}
i1	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	1	0
i21	¹³ C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i22	¹² C	¹³ C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i23	¹² C	¹² C	¹³ C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i24	¹² C	¹² C	¹² C	¹³ C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i25	¹² C	¹² C	¹² C	¹² C	¹³ C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i26	¹² C	¹² C	¹² C	¹² C	¹² C	¹³ C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	2/3	1/3	1	0
i212	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹³ C	¹ H	¹ H	¹ H	0	1	1	0	1	0	1	0
i27	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	² H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	2/3	1/3
i28	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	2/3	1/3
i29	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	² H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	2/3	1/3
i210	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	² H	¹ H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	2/3	1/3
i211	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	² H	¹² C	¹ H	¹ H	¹ H	1	0	1	0	1	0	2/3	1/3
i213	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	² H	¹ H	¹ H	1	0	2/3	1/3	1	0	1	0
i214	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	² H	¹ H	1	0	2/3	1/3	1	0	1	0
i215	¹² C	¹² C	¹² C	¹² C	¹² C	¹² C	¹ H	¹ H	¹ H	¹ H	¹ H	¹² C	¹ H	¹ H	² H	1	0	2/3	1/3	1	0	1	0

^a See numbering scheme in Figure S1

Table S5: C and H isotopomers of **nitrobenzene** included in the numerical model. γ is used to account for intramolecular competition of randomly distributed heavy ^{13}C and ^2H isotopes.

Isotopomer	Atom number and position of isotopic substitution ^a											Stoichiometric coefficient / intramolecular competition			
	aromatic moiety											dioxygenation			
	1	2	3	4	5	6	7	8	9	10	11	$\gamma_{\text{diox}}^{12\text{C}}$	$\gamma_{\text{diox}}^{13\text{C}}$	$\gamma_{\text{diox}}^{1\text{H}}$	$\gamma_{\text{diox}}^{2\text{H}}$
i1	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^1H	1	0	1	0
i21	^{13}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i22	^{12}C	^{13}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i23	^{12}C	^{12}C	^{13}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i24	^{12}C	^{12}C	^{12}C	^{13}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i25	^{12}C	^{12}C	^{12}C	^{12}C	^{13}C	^{12}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i26	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{13}C	^1H	^1H	^1H	^1H	^1H	2/3	1/3	1	0
i27	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^2H	^1H	^1H	^1H	^1H	1	0	2/3	1/3
i28	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^2H	^1H	^1H	^1H	1	0	2/3	1/3
i29	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^2H	^1H	^1H	1	0	2/3	1/3
i210	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^2H	^1H	1	0	2/3	1/3
i211	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^2H	1	0	2/3	1/3

^a See numbering scheme in Figure S1

Table S6: C and H isotopomers of **2-nitrotoluene (2-NT)** and **4-nitrotoluene (4-NT)** included in the numerical model. γ is used to account for intramolecular competition of randomly distributed heavy ^{13}C and ^2H isotopes.

Isotopomer	Atom number and position of isotopic substitution ^a										Stoichiometric coefficient / intramolecular competition												
	aromatic moiety										aliphatic moieties				CH ₃ -group oxidation				dioxygenation				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	$\gamma_{\text{C}_{\text{m ox}}^{12}\text{C}}$	$\gamma_{\text{C}_{\text{m ox}}^{13}\text{C}}$	$\gamma_{\text{C}_{\text{m ox}}^{1\text{H}}}$	$\gamma_{\text{C}_{\text{m ox}}^{2\text{H}}}$	$\gamma_{\text{diox}}^{12}\text{C}$	$\gamma_{\text{diox}}^{13}\text{C}$	$\gamma_{\text{diox}}^{1\text{H}}$	$\gamma_{\text{diox}}^{2\text{H}}$	
i1	^{12}C						^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	1	0	0	1	0
i21	^{13}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i22	^{12}C	^{13}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i23	^{12}C	^{12}C	^{13}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i24	^{12}C	^{12}C	^{12}C	^{13}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i25	^{12}C	^{12}C	^{12}C	^{12}C	^{13}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i26	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{13}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	2/3	1/3	1	0	0
i211	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{13}C	^1H	^1H	^1H	0	1	1	0	1	0	1	0	0
i27	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^2H	^1H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	1	0	2/3	1/3	0
i28	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^2H	^2H	^1H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	1	0	2/3	1/3	0
i29	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^2H	^1H	^{12}C	^1H	^1H	^1H	1	0	1	0	1	0	2/3	1/3	0
i210	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^2H	^{12}C	^1H	^1H	^1H	1	0	1	0	1	0	2/3	1/3	0
i212	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^2H	^1H	^1H	1	0	2/3	1/3	1	0	1	0	0
i213	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^2H	^1H	1	0	2/3	1/3	1	0	1	0	0
i214	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^{12}C	^1H	^1H	^1H	^1H	^{12}C	^1H	^1H	^2H	1	0	2/3	1/3	1	0	1	0	0

^a See numbering scheme in Figure S1

Table S7: C and H isotopomers of **2,4-dinitrotoluene** (2,4-DNT) and **2,6-dinitrotoluene** (2,6-DNT) included in the numerical model. γ is used to account for intramolecular competition of randomly distributed heavy ^{13}C and ^2H isotopes.

Isotopomer	Atom number and position of isotopic substitution ^a													Stoichiometric coefficient / intramolecular competition																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
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	aromatic moiety													¹² C γ _{C_{mox}}	¹³ C γ _{C_{mox}}	¹ H γ _{C_{mox}}	² H γ _{C_{mox}}	¹² C γ _{diox}	¹³ C γ _{diox}	¹ H γ _{diox}	² H γ _{diox}																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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^a See numbering scheme in Figure S1

Table S8: Oxidation of **2-nitrotoluene** by MnO_4^- : Gibbs free energies of reaction (ΔG_R), branching ratios for MnO_4^- attack at reactive position (θ_p^*), as well as ^2H -, ^{13}C -, and ^{15}N -KIEs for the different reactive positions p . Theoretical C, H, and N isotope enrichment factors are denoted ϵ_E^* .

Parameter	2-nitrotoluene									
	$p =$	C_m	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_1	<i>average</i> ^a	
ΔG_R	(kcal mol ⁻¹)	-19.10	-4.98	-7.73	-2.65	0.20	-0.65	-0.40		
θ_p^*	(-)	0.931	0.001	0.010	0.032	0.006	0.018	0.002		
^2H -KIE	(-)									
	H_{C_2}	-	-	-	-	-	-	-		
	H_{C_3}	0.9945	1.0080	0.8722	0.8842	1.0120	1.0065	0.9997	0.9901	
	H_{C_4}	1.0076	1.0194	1.0378	0.9333	0.9420	1.0252	1.0076	1.0055	
	H_{C_5}	1.0012	1.0103	1.0070	1.0155	0.8875	0.8971	1.0114	0.9992	
	H_{C_6}	1.0097	1.0322	1.0196	1.0043	1.0279	0.9429	0.9348	1.0084	
	$\text{H}_{\text{C}_{m1}}$	3.6829	1.0183	1.0076	0.9897	1.0008	1.0219	0.9435	3.4978	
	$\text{H}_{\text{C}_{m2}}$	1.0817	1.0280	0.9947	0.9992	0.9868	1.0012	1.0129	1.0760	
	$\text{H}_{\text{C}_{m3}}$	1.0639	0.9178	1.0148	1.0246	1.0078	1.0035	1.0149	1.0605	
	<i>average</i>	1.4059	1.0049	0.9934	0.9787	0.9807	0.9555	0.9893	1.3768	
ϵ_{H}^*	(‰)								-274	
^{13}C -KIE	(-)									
	C_1	1.0033	1.0407	0.9984	0.9989	0.9990	0.9985	1.0010	1.0030	
	C_2	1.005	1.0135	1.0361	1.0008	1.0000	1.0010	1.0181	1.0009	
	C_3	1.0040	1.0014	1.0148	1.0306	1.0007	0.9998	1.0022	1.0049	
	C_4	1.0012	1.0011	1.0010	1.0187	1.0172	1.0011	1.0019	1.0019	
	C_5	1.0006	1.0011	1.0009	1.0006	1.0321	1.0173	1.0007	1.0011	
	C_6	1.0013	1.0020	1.0007	1.0024	1.0027	1.0318	1.0349	1.0020	
	C_m	1.0300	0.9991	1.0004	0.9981	0.9984	0.9990	0.9988	1.0278	
	<i>average</i>	1.0058	1.0003	1.0075	1.0072	1.0072	1.0069	1.0082	1.0059	
ϵ_{C}^*	(‰)								-5.9	
^{15}N -KIE	(-)									
	N_{C_2}	1.0042	1.0030	1.0028	1.0028	1.0027	1.0030	1.0037	1.0041	
ϵ_{N}^*	(‰)								-4.1	

^a Average, atom-specific KIEs are calculated from the weighted average of position-specific MnO_4^- -attack as in eq. 11 of the main manuscript.

Table S9: Oxidation of **3-nitrotoluene** by MnO_4^- : Gibbs free energies of reaction (ΔG_R), branching ratios for MnO_4^- attack at reactive position (θ_p^*), as well as ^2H -, ^{13}C -, and ^{15}N -KIEs for the different reactive positions p . Theoretical C, H, and N isotope enrichment factors are denoted ϵ_E^* .

Parameter	3-nitrotoluene									
	$p =$	C_m	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_1	<i>average</i> ^a	
ΔG_R	(kcal mol ⁻¹)	-22.33	-1.96	-4.36	-4.07	0.56	0.97	0.55		
θ_p^*	(-)	0.873	0.031	0.042	0.018	0.001	0.003	0.031		
^2H -KIE	(-)									
	H_{C_2}	1.0056	0.8842	0.8790	1.0217	1.0095	1.0119	1.0118	0.9979	
	H_{C_3}			—	(none)	—				
	H_{C_4}	1.0040	1.0028	1.0182	0.8801	0.8841	1.0090	1.0036	1.0022	
	H_{C_5}	0.9979	1.0105	1.0187	1.0333	0.9354	0.9496	1.0292	1.0006	
	H_{C_6}	1.0095	1.0084	1.0017	1.0075	1.0151	0.8878	0.9016	1.0053	
	$\text{H}_{\text{C}_{m1}}$	3.6218	1.0179	0.9545	1.0060	0.9527	1.0119	1.0198	3.2882	
	$\text{H}_{\text{C}_{m2}}$	1.1533	1.0213	1.0736	1.0208	1.0689	1.0198	0.9987	1.1381	
	$\text{H}_{\text{C}_{m3}}$	1.0117	0.9593	1.0111	1.0066	0.9993	1.0088	0.9976	1.0095	
	<i>average</i>	1.4005	0.9863	0.9938	0.9966	0.9807	0.9855	0.9946	1.3491	
ϵ_{H}^*	(‰)								-259	
^{13}C -KIE	(-)									
	C_1	1.0023	1.0173	1.0003	1.0009	1.0021	0.9992	1.0140	1.0030	
	C_2	1.0011	1.0322	1.0364	1.0009	1.0010	1.0009	1.0005	1.0035	
	C_3	1.0007	1.0006	1.0127	1.0125	1.0004	1.0019	1.0018	1.0015	
	C_4	1.0014	1.0005	1.0013	1.0350	1.0307	1.0007	1.0008	1.0020	
	C_5	1.0007	1.0022	1.0018	1.0005	1.0189	1.0164	1.0005	1.0009	
	C_6	1.0011	1.0007	1.0006	1.0007	1.0009	1.0334	1.0339	1.0022	
	C_m	1.0276	0.9988	1.0001	1.0002	1.0002	1.0000	0.9989	1.0240	
	<i>average</i>	1.0050	1.0075	1.0076	1.0072	1.0077	1.0075	1.0072	1.0053	
ϵ_{C}^*	(‰)								-5.3	
^{15}N -KIE	(-)									
ϵ_{N}^*	(‰)									
	N_{C_2}	1.0001	1.0027	1.0023	1.0022	1.0024	1.0031	1.0033	1.0004	
									-0.4	

^a Average, atom-specific KIEs are calculated from the weighted average of position-specific MnO_4^- -attack as in eq. 11 of the main manuscript.

Table S10: Oxidation of **4-nitrotoluene** oxidation by MnO_4^- : Gibbs free energies of reaction (ΔG_R), branching ratios for MnO_4^- attack at reactive position (θ_p^*), as well as ^2H -, ^{13}C -, and ^{15}N -KIEs for the different reactive positions p . Theoretical C, H, and N isotope enrichment factors are denoted ϵ_E^* .

Parameter	4-nitrotoluene					
	$p =$	C_m	C_1-C_2	C_2-C_3	C_3-C_4	<i>average</i> ^a
ΔG_R (kcal mol ⁻¹)		-20.26	1.97	-3.47	-3.69	
θ_p^* (-)		0.623	0.001	0.372	0.004	
^2H -KIE (-)	H_{C_2}	1.0055	0.9705	0.9375	1.0360	0.9803
	H_{C_3}	1.0021	1.0100	0.8915	0.8788	0.9605
	H_{C_4}	-	-	-	-	-
	H_{C_5}	1.0001	1.0054	1.0089	1.0110	1.0034
	H_{C_6}	1.0122	1.0291	1.0045	1.0240	1.0094
	$\text{H}_{C_{m_1}}$	3.5531	0.9970	0.9880	0.9706	2.5860
	$\text{H}_{C_{m_2}}$	1.1318	0.9572	1.0662	1.0447	1.1069
	$\text{H}_{C_{m_3}}$	1.0404	1.0198	0.9732	0.9950	1.0152
ϵ_H^* (‰)	<i>average</i>	1.3922	0.9984	0.9814	0.9943	1.2374 -192
^{13}C -KIE (-)	C_1	1.0008	1.0355	1.0002	1.0020	1.0006
	C_2	1.0028	1.0152	1.0302	1.0015	1.0130
	C_3	1.0006	1.0006	1.0201	1.0136	1.0079
	C_4	1.0012	1.0016	1.0006	1.0358	1.0011
	C_5	1.0015	1.0011	1.0020	1.0006	1.0017
	C_6	1.0005	0.9998	1.0009	1.0002	1.0006
	C_m	1.0306	0.9983	0.9999	0.9999	1.0190
ϵ_C^* (‰)	<i>average</i>	1.0054	1.0074	1.0077	1.0077	1.0063 -6.2
^{15}N -KIE (-)	N_{C_4}	1.0033	1.0028	1.0025	1.0019	1.0030
ϵ_N^* (‰)						-3.0

^a Average, atom-specific KIEs are calculated from the weighted average of position-specific MnO_4^- -attack as in eq. 11 of the main manuscript.

Table S11: Oxidation of **2,4-dinitrotoluene** oxidation by MnO_4^- : Gibbs free energies of reaction (ΔG_R), branching ratios for MnO_4^- attack at reactive position (θ_p^*), as well as ^2H -, ^{13}C -, and ^{15}N -KIEs for the different reactive positions p . Theoretical C, H, and N isotope enrichment factors are denoted ϵ_E^* .

Parameter	2,4-dinitrotoluene									
	$p =$	C_m	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_1	<i>average</i> ^a	
ΔG_R	(kcal mol ⁻¹)	-21.56	-5.76	-12.51	-9.61	-4.89	-4.77	0.00		
θ_p^*	(-)	0.215	0.0	0.141	0.582	0.007	0.054	0.001		
^2H -KIE	(-)			— (none)	—					
	H_{C_2}	0.9912	0.9997	0.8472	0.8511	1.0055	0.9971	0.9947	0.8898	
	H_{C_3}			— (none)	—					
	H_{C_4}	1.0018	1.0090	1.0077	1.0136	0.8691	0.8667	1.0097	1.0013	
	H_{C_5}	1.0120	1.0410	1.0167	1.0165	1.0401	0.9755	0.9975	1.0135	
	H_{C_6}	3.9883	1.0284	1.0042	0.9959	1.0064	1.0149	0.9124	1.6415	
ϵ_{H}^*	$\text{H}_{\text{C}_{m1}}$	1.0387	1.0287	1.0066	0.9863	0.9819	1.0050	1.0253	1.0014	
	$\text{H}_{\text{C}_{m2}}$	1.0857	0.9123	1.0023	1.0290	1.0130	0.9998	1.0306	1.0357	
	$\text{H}_{\text{C}_{m3}}$	1.5196	1.0032	0.9808	0.9821	0.9860	0.9765	0.9950	1.0972	
	<i>average</i>								-89	
	(‰)									
	(-)									
^{13}C -KIE	C_1	1.0043	1.0440	1.0012	1.0007	1.0004	1.0015	1.0433	1.0016	
	C_2	1.0034	1.0107	1.0127	1.0022	1.0030	1.0033	1.0024	1.0040	
	C_3	0.9999	1.0008	1.0398	1.0396	1.0009	1.0002	1.0002	1.0287	
	C_4	1.0018	1.0019	1.0008	1.0111	1.0131	1.0009	1.0023	1.0071	
	C_5	1.0006	1.0010	1.0005	1.0007	1.0373	1.0382	1.0010	1.0029	
	C_6	1.0009	1.0015	1.0027	1.0027	1.0015	1.0115	1.0084	1.0028	
ϵ_{C}^*	C_m	1.0290	0.9991	1.0001	1.0003	1.0000	1.0000	0.9988	1.0064	
	<i>average</i>	1.0057	1.0084	1.0083	1.0082	1.0080	1.0079	1.0081	1.0076	
	(‰)								-7.6	
	(-)									
	N_{C_2}	1.0042	1.0038	1.0032	1.0041	1.0038	1.0034	1.0035	1.0040	
	N_{C_4}	1.0032	1.0037	1.0033	1.0026	1.0028	1.0029	1.0039	1.0028	
^{15}N -KIE	<i>average</i>	1.0037	1.0038	1.0033	1.0034	1.0033	1.0032	1.0037	1.0034	
	(‰)								-3.4	
	(-)									
	ϵ_{N}^*									
	(‰)									
	(-)									

^a Average, atom-specific KIEs are calculated from the weighted average of position-specific MnO_4^- -attack as in eq. 11 of the main manuscript.

Table S12: Oxidation of **2,6-dinitrotoluene** oxidation by MnO_4^- : Gibbs free energies of reaction (ΔG_R), branching ratios for MnO_4^- attack at reactive position (θ_p^*), as well as ^2H -, ^{13}C -, and ^{15}N -KIEs for the different reactive positions p . Theoretical C, H, and N isotope enrichment factors are denoted ϵ_E^* .

Parameter	2,6-dinitrotoluene					
	$p =$	C_m	C_1-C_2	C_2-C_3	C_3-C_4	average ^a
ΔG_R	(kcal mol ⁻¹)	-19.27	-7.62	-10.37	-0.70	
θ_p^*	(-)	0.676	0.001	0.025	0.298	
^2H -KIE	(-)		— (none)	—		
	H_{C_2}	0.9888	1.0051	0.8513	0.8680	0.9494
	H_{C_3}	1.0095	1.0158	1.0400	0.9721	0.9991
	H_{C_4}	0.9972	0.9979	1.0061	1.0096	1.0011
	H_{C_5}	— (none)	—	—	—	—
	H_{C_6}	3.0379	0.9879	0.9786	0.9834	2.3721
	$\text{H}_{\text{C}_{m1}}$	1.0720	1.0680	1.0696	1.0078	1.0528
	$\text{H}_{\text{C}_{m2}}$	1.0872	0.9295	0.9380	0.9989	1.0570
	$\text{H}_{\text{C}_{m3}}$	1.3654	1.0007	0.9806	0.9733	1.2386
	average					-193
ϵ_{H}^*	(‰)					
^{13}C -KIE	(-)					
	C_1	1.0054	1.0451	1.0025	1.0011	1.0041
	C_2	1.0048	1.0109	1.0155	1.0026	1.0044
	C_3	1.0001	1.0008	1.0374	1.0365	1.0119
	C_4	1.0017	1.0026	1.0003	1.0123	1.0048
	C_5	1.0001	1.0002	1.0009	1.0006	1.0003
	C_6	1.0036	1.0044	1.0038	1.0039	1.0037
	C_m	1.0344	1.0003	0.9996	0.9999	1.0232
	average	1.0072	1.0092	1.0086	1.0081	1.0075
ϵ_{C}^*	(‰)					-7.4
^{15}N -KIE	(-)					
	N_{C_2}	1.0029	1.0044	1.0051	1.0037	1.0032
	N_{C_6}	1.0048	1.0054	1.0026	1.0033	1.0043
	average	1.00385	1.0049	1.00385	1.0035	1.0037
ϵ_{N}^*	(‰)					-3.7

^a Average, atom-specific KIEs are calculated from the weighted average of position-specific MnO_4^- -attack as in eq. 11 of the main manuscript.

Table S13: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **CH₃-group oxidation**.

Reactant			
Mn	-2.80653000	-0.90123300	-0.09500200
O	-2.33499600	-1.29748500	1.38141300
O	-2.02018300	-1.79609100	-1.16238200
O	-4.37922000	-1.15657100	-0.24010200
O	-2.48909500	0.64536000	-0.35846900
H	-1.25092900	2.06777400	1.41705500
C	-0.30073900	2.11460600	1.95637600
C	0.73720800	1.24932100	1.29565000
C	1.45974000	0.33251900	2.08174100
C	2.42320500	-0.51606900	1.55055600
C	2.67205900	-0.46846900	0.17774400
C	1.98143500	0.39994300	-0.65630100
C	1.03632900	1.24912700	-0.08495800
H	0.01275700	3.16208800	1.97042500
H	-0.45616600	1.78062200	2.98395500
H	1.25057600	0.28801400	3.14494700
H	2.96947700	-1.20556800	2.18152200
H	2.17484000	0.42526700	-1.71942000
N	0.35735900	2.15960700	-1.02089100
O	0.30935200	1.83270500	-2.21006500
O	-0.11077000	3.21101200	-0.58165400
N	3.68205700	-1.35440300	-0.40558200
O	3.87774300	-1.29505500	-1.62262800
O	4.28859200	-2.11758400	0.35101500

Table S14: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **CH_3 -group oxidation**.

Transition state			
Mn	-3.36112300	-0.55094500	-0.33124800
O	-2.77705000	-1.14837300	1.03514800
O	-3.08587100	-1.53513000	-1.54530900
O	-4.89273000	-0.16685000	-0.17281200
O	-2.41437700	0.84686200	-0.48468200
H	-1.68456600	0.90694200	0.33543500
C	-0.73211100	1.00605800	1.53295700
C	0.48326100	0.47105300	1.01627200
C	0.77157900	-0.90785300	1.28514800
C	1.91188400	-1.54087700	0.85453800
C	2.85400500	-0.81036500	0.09999400
C	2.64141100	0.52507900	-0.20638700
C	1.47564700	1.15347500	0.23086100
H	-0.87127300	2.07824300	1.58496400
H	-1.20925500	0.41611100	2.30726900
H	0.03995500	-1.46484000	1.86002800
H	2.09362100	-2.58264500	1.08587600
H	3.36663800	1.07854700	-0.78518800
N	1.33972000	2.54849500	-0.15446000
O	2.32645800	3.13082200	-0.63358500
O	0.24441400	3.10820000	-0.00681300
N	4.06028700	-1.45592900	-0.36626700
O	4.87288700	-0.79633300	-1.03252500
O	4.23362400	-2.64996100	-0.07722300

Table S15: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **CH_3 -group oxidation**.

Product			
Mn	3.29007700	-0.57847900	0.14632500
O	2.09597200	0.15481300	-1.03171700
O	3.09494200	-2.15641500	0.12340000
O	4.69717900	0.12832000	-0.07102200
O	2.56974200	0.04662700	1.69494500
H	1.74968300	0.54288900	1.56873800
C	1.09161700	1.09550300	-0.77439100
C	-0.27145600	0.45916800	-0.51075000
C	-0.39085000	-0.93294700	-0.65807300
C	-1.59111700	-1.60288900	-0.45398100
C	-2.71650400	-0.86607900	-0.08030500
C	-2.66034800	0.50933400	0.09171800
C	-1.44409300	1.15270200	-0.13233000
H	1.34653200	1.78374100	0.04336800
H	0.99415900	1.73812600	-1.66139800
H	0.49618400	-1.48671200	-0.93794300
H	-1.65912100	-2.67599900	-0.58070300
H	-3.53441000	1.07297800	0.38530600
N	-1.45376700	2.61039500	0.05248600
O	-2.42514000	3.12311900	0.61571300
O	-0.49173800	3.25801200	-0.36930300
N	-3.99226500	-1.55349000	0.13857100
O	-4.97231200	-0.87670600	0.46119600
O	-4.02192200	-2.77778800	-0.01124100

Table S16: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₁–C₂-attack**

Reactant			
O	-2.21152900	0.60135900	-0.43206500
O	-1.57498300	-1.84666800	0.21668200
Mn	-2.77848600	-0.87650100	-0.19481900
O	-3.45764700	-1.41030700	-1.54159800
O	-3.86725600	-0.84809600	0.97700700
H	1.71365600	-0.23526400	1.79275000
C	1.06886200	1.71715000	-0.96465900
C	1.02611200	1.21619500	0.35612800
C	1.78097400	0.12245400	0.77515900
C	2.62297100	-0.48682200	-0.14459100
C	2.71112100	-0.03819700	-1.46347400
C	1.93176200	1.04501300	-1.85025400
H	3.37165300	-0.53025000	-2.16602100
H	1.98611500	1.38940600	-2.87713000
C	0.25474100	2.86976200	-1.48568900
H	-0.80090400	2.75483100	-1.22729800
H	0.59129800	3.81589100	-1.05278400
H	0.35242800	2.92561000	-2.57159800
N	0.17123400	1.82549600	1.38730000
O	-0.11439100	1.14548500	2.37694100
O	-0.20399800	2.98832000	1.22831500
N	3.43302100	-1.62815700	0.28727000
O	4.17316600	-2.15972500	-0.54496100
O	3.33649600	-2.00316700	1.45903400

Table S17: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₁–C₂-attack**

Transition state			
O	-1.90619200	-0.03797300	-0.53603800
O	0.10548700	-1.33531300	0.29427100
Mn	-1.41288700	-1.56735800	-0.41079500
O	-1.25329000	-2.22873000	-1.84463100
O	-2.35666800	-2.38440800	0.57190400
H	0.84218200	-0.02894300	1.76731800
C	0.02060800	2.01707400	-0.83269100
C	-0.15175000	1.22731100	0.34245600
C	0.76278300	0.15226400	0.70248600
C	2.02277700	0.16924200	-0.02636100
C	2.18347400	0.90245000	-1.17680500
C	1.16240200	1.77760600	-1.59485700
H	3.10527700	0.82866100	-1.74101600
H	1.29657000	2.32862500	-2.51897900
C	-0.95376100	3.05957500	-1.31279500
H	-1.98073800	2.68933700	-1.28010100
H	-0.91861000	3.95287800	-0.68276000
H	-0.70446100	3.34608200	-2.33704400
N	-1.10089400	1.58105000	1.37781100
O	-1.19294000	0.83516400	2.36774600
O	-1.78053100	2.61019900	1.25610000
N	3.09031800	-0.65415100	0.46155200
O	4.15188500	-0.71094200	-0.18433900
O	2.91684900	-1.27976200	1.52227400

Table S18: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₁–C₂-attack**

Product			
O	-1.57030400	0.66922700	0.13042200
O	-0.26472400	-1.44616000	-0.17144000
Mn	-2.03963000	-1.07892600	-0.19571900
O	-2.61666300	-1.20654700	-1.66593000
O	-2.74413300	-1.74437700	1.05463900
H	0.63116300	-0.57914700	1.47000100
C	0.21220800	1.77068200	-1.03104400
C	-0.22833300	0.92812900	0.15684200
C	0.53720100	-0.41211200	0.39031300
C	1.89243200	-0.43458700	-0.25440600
C	2.24525600	0.41056900	-1.24736600
C	1.36120100	1.46913600	-1.67904800
H	3.21358700	0.30549700	-1.72363300
H	1.66535200	2.05889900	-2.53803400
C	-0.69081900	2.89156300	-1.44323100
H	-1.68849000	2.51063800	-1.68464600
H	-0.81964200	3.61403700	-0.62728000
H	-0.28746000	3.41784500	-2.31051600
N	0.05786700	1.80632100	1.46937500
O	-0.74043300	1.73514600	2.39289000
O	1.09996500	2.45953300	1.48894200
N	2.80959900	-1.46486900	0.16976200
O	3.90316000	-1.58189800	-0.40539400
O	2.46177000	-2.19555600	1.11096600

Table S19: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₂–C₃-attack**

Reactant			
O	-2.21152900	0.60135900	-0.43206500
O	-1.57498300	-1.84666800	0.21668200
Mn	-2.77848600	-0.87650100	-0.19481900
O	-3.45764700	-1.41030700	-1.54159800
O	-3.86725600	-0.84809600	0.97700700
H	1.71365600	-0.23526400	1.79275000
C	1.06886200	1.71715000	-0.96465900
C	1.02611200	1.21619500	0.35612800
C	1.78097400	0.12245400	0.77515900
C	2.62297100	-0.48682200	-0.14459100
C	2.71112100	-0.03819700	-1.46347400
C	1.93176200	1.04501300	-1.85025400
H	3.37165300	-0.53025000	-2.16602100
H	1.98611500	1.38940600	-2.87713000
C	0.25474100	2.86976200	-1.48568900
H	-0.80090400	2.75483100	-1.22729800
H	0.59129800	3.81589100	-1.05278400
H	0.35242800	2.92561000	-2.57159800
N	0.17123400	1.82549600	1.38730000
O	-0.11439100	1.14548500	2.37694100
O	-0.20399800	2.98832000	1.22831500
N	3.43302100	-1.62815700	0.28727000
O	4.17316600	-2.15972500	-0.54496100
O	3.33649600	-2.00316700	1.45903400

Table S20: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₂–C₃-attack**

Transition state			
O	-1.90619200	-0.03797300	-0.53603800
O	0.10548700	-1.33531300	0.29427100
Mn	-1.41288700	-1.56735800	-0.41079500
O	-1.25329000	-2.22873000	-1.84463100
O	-2.35666800	-2.38440800	0.57190400
H	0.84218200	-0.02894300	1.76731800
C	0.02060800	2.01707400	-0.83269100
C	-0.15175000	1.22731100	0.34245600
C	0.76278300	0.15226400	0.70248600
C	2.02277700	0.16924200	-0.02636100
C	2.18347400	0.90245000	-1.17680500
C	1.16240200	1.77760600	-1.59485700
H	3.10527700	0.82866100	-1.74101600
H	1.29657000	2.32862500	-2.51897900
C	-0.95376100	3.05957500	-1.31279500
H	-1.98073800	2.68933700	-1.28010100
H	-0.91861000	3.95287800	-0.68276000
H	-0.70446100	3.34608200	-2.33704400
N	-1.10089400	1.58105000	1.37781100
O	-1.19294000	0.83516400	2.36774600
O	-1.78053100	2.61019900	1.25610000
N	3.09031800	-0.65415100	0.46155200
O	4.15188500	-0.71094200	-0.18433900
O	2.91684900	-1.27976200	1.52227400

Table S21: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₂–C₃-attack**

Product			
O	-1.57030400	0.66922700	0.13042200
O	-0.26472400	-1.44616000	-0.17144000
Mn	-2.03963000	-1.07892600	-0.19571900
O	-2.61666300	-1.20654700	-1.66593000
O	-2.74413300	-1.74437700	1.05463900
H	0.63116300	-0.57914700	1.47000100
C	0.21220800	1.77068200	-1.03104400
C	-0.22833300	0.92812900	0.15684200
C	0.53720100	-0.41211200	0.39031300
C	1.89243200	-0.43458700	-0.25440600
C	2.24525600	0.41056900	-1.24736600
C	1.36120100	1.46913600	-1.67904800
H	3.21358700	0.30549700	-1.72363300
H	1.66535200	2.05889900	-2.53803400
C	-0.69081900	2.89156300	-1.44323100
H	-1.68849000	2.51063800	-1.68464600
H	-0.81964200	3.61403700	-0.62728000
H	-0.28746000	3.41784500	-2.31051600
N	0.05786700	1.80632100	1.46937500
O	-0.74043300	1.73514600	2.39289000
O	1.09996500	2.45953300	1.48894200
N	2.80959900	-1.46486900	0.16976200
O	3.90316000	-1.58189800	-0.40539400
O	2.46177000	-2.19555600	1.11096600

Table S22: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₃–C₄-attack**

Reactant			
O	1.34427600	-1.44056900	0.48337700
O	2.14243400	0.86343500	-0.44257000
Mn	2.53284500	-0.67855600	-0.26984500
O	2.76105600	-1.33736000	-1.70996800
O	3.87660000	-0.79834500	0.59069800
C	-1.85861800	-0.49955700	0.30914000
C	-1.15774700	0.58829200	0.82519200
C	-1.04698300	1.72711900	0.04143700
C	-1.63723200	1.80621200	-1.22109100
C	-2.35251800	0.71175200	-1.69116900
C	-2.48261700	-0.48212600	-0.95705300
H	-1.54134400	2.70705400	-1.81370800
H	-2.83005100	0.77477200	-2.66286000
H	-0.69654700	0.53365300	1.80041700
C	-3.28036600	-1.61285600	-1.55007600
H	-3.83103900	-1.25494600	-2.42205800
H	-2.62375900	-2.43022100	-1.86225700
H	-3.98879600	-2.03340000	-0.83202900
N	-1.90387500	-1.68805700	1.17275300
O	-2.07864000	-2.78957900	0.64821400
O	-1.75240700	-1.52590600	2.38720400
N	-0.29113400	2.86904300	0.55922100
O	-0.13243600	3.84194200	-0.18354300
O	0.14561300	2.80726800	1.71115200

Table S23: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₃–C₄-attack**

Transition state			
O	0.38232700	-1.10273200	0.53546000
O	1.97628000	0.25079700	-0.88712800
Mn	1.78178900	-1.27172300	-0.39258800
O	1.50743600	-2.23868300	-1.62171200
O	3.00147600	-1.72005100	0.52159900
C	-1.79212700	0.05230400	0.26653500
C	-0.45057400	0.35323400	0.76874100
C	0.22556900	1.42634800	0.07674200
C	-0.26758500	1.94390200	-1.13410900
C	-1.43871000	1.44682800	-1.65901900
C	-2.26219900	0.51093600	-0.96031700
H	0.28374200	2.72601500	-1.64064500
H	-1.78900300	1.81888100	-2.61519000
H	-0.35513400	0.37038300	1.84709500
C	-3.58035500	0.15191000	-1.59444300
H	-3.67175800	0.65042200	-2.56138500
H	-3.67141100	-0.92792800	-1.73724500
H	-4.42028400	0.45053300	-0.96070100
N	-2.57619900	-0.79288600	1.13013700
O	-3.68536500	-1.20193600	0.74877700
O	-2.11385300	-1.08394300	2.24848100
N	1.26680800	2.13349000	0.78156300
O	1.75207500	3.14923700	0.25955800
O	1.63471700	1.69828100	1.88447800

Table S24: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₃–C₄-attack**

Product			
O	-0.52174200	-1.23955800	-0.31552500
O	-1.71413500	0.78592400	0.55381300
Mn	-2.20492300	-0.96354700	0.28871000
O	-2.40815300	-1.68391600	1.68566000
O	-3.25050300	-1.08853500	-0.89251800
C	1.68135700	-0.33891300	-0.13975400
C	0.25056700	-0.06424600	-0.54217000
C	-0.42316000	1.10522800	0.23686300
C	0.31487200	1.59293800	1.44742000
C	1.53650000	1.14269100	1.76797000
C	2.30583200	0.20515500	0.93995400
H	-0.22447600	2.28387400	2.08847900
H	2.01292800	1.49010700	2.67944100
H	0.23047200	0.16204600	-1.61410000
C	3.72775600	-0.02991000	1.37249800
H	4.06939100	0.80757700	1.98509400
H	3.78990900	-0.94098400	1.97930000
H	4.40479000	-0.16554900	0.52885100
N	2.35338300	-1.28031600	-1.01302800
O	3.32077500	-1.92666900	-0.58506900
O	1.92023600	-1.41167900	-2.16903200
N	-0.46951300	2.32744800	-0.79972700
O	0.58878000	2.92506400	-0.99270200
O	-1.52393200	2.56987100	-1.36865400

Table S25: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₄–C₅-attack**

Reactant			
O	2.66881400	-0.76545300	1.32221700
O	2.02601300	0.27436000	-0.98433700
Mn	2.94813500	-0.80892700	-0.25236700
O	2.60746200	-2.26744000	-0.81512800
O	4.48777900	-0.47433400	-0.53124900
C	-1.47183400	-0.22563500	2.04623900
C	-0.65723700	0.85291700	1.72263500
C	-0.78557200	1.43318200	0.46013000
C	-1.70109400	0.95833700	-0.46788300
C	-2.48584700	-0.13807800	-0.11625300
C	-2.40690000	-0.76790400	1.14591300
H	-1.38583900	-0.67056400	3.03156600
H	-1.79774100	1.41699800	-1.44180400
H	0.06210900	1.24180300	2.43171700
C	-3.25338700	-1.93001500	1.59253200
H	-4.31115000	-1.77570600	1.36433500
H	-2.95074400	-2.85031300	1.08466800
H	-3.14186200	-2.07200700	2.66906000
N	0.05709300	2.57582900	0.09948700
O	-0.07652600	3.06690700	-1.02427900
O	0.85390000	2.99530700	0.94232300
N	-3.42159000	-0.60458300	-1.15076200
O	-3.79291500	-1.77941700	-1.12017400
O	-3.78145700	0.20474900	-2.01078600

Table S26: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₄–C₅-attack**

Transition state			
O	1.46158600	-0.91156300	1.03947000
O	1.38731200	0.27749600	-1.19739600
Mn	2.14631400	-0.96641700	-0.51296900
O	1.76497900	-2.32907500	-1.23000500
O	3.70969000	-0.69816500	-0.43286400
C	-0.85433500	-0.73438200	1.82433200
C	0.29009400	0.13241700	1.52655200
C	0.02307500	1.13448200	0.50668500
C	-1.15017300	1.11758200	-0.25597700
C	-2.09360000	0.13520900	-0.03514400
C	-1.98465400	-0.80996900	1.06161400
H	-0.75837500	-1.37565200	2.69418500
H	-1.30284000	1.86149500	-1.02461700
H	0.81657600	0.51511100	2.39753200
C	-3.07419300	-1.78049800	1.45211400
H	-4.04889400	-1.29061000	1.52711100
H	-3.17686600	-2.58228600	0.71655400
H	-2.83141600	-2.22401500	2.42054400
N	-3.22913700	0.13275400	-0.94036400
O	-3.92687200	-0.88841700	-1.01453400
O	-3.45438400	1.14626400	-1.62165200
N	0.87529500	2.29460100	0.44327500
O	0.57685900	3.21802600	-0.33077400
O	1.87877400	2.32241400	1.17418900

Table S27: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₄–C₅-attack**

Product			
O	1.32907800	-0.83675200	1.22900700
O	1.38698200	0.39574800	-0.95660400
Mn	2.43774400	-0.91273200	-0.20018800
O	2.23629900	-2.27479700	-0.98572400
O	3.86919000	-0.35898000	0.18548100
C	-0.84458500	-0.10030100	1.91055500
C	0.45217200	0.29020000	1.25588100
C	0.31366400	0.79884000	-0.20987800
C	-0.97468600	0.44204000	-0.89227000
C	-1.97962800	-0.12564400	-0.20992300
C	-1.99465600	-0.33846600	1.25189700
H	-0.81285000	-0.21445000	2.99031300
H	-1.01569000	0.56995800	-1.96802500
H	0.92937000	1.08101000	1.85192700
C	-3.26290100	-0.71732200	1.97654000
H	-4.09808100	-0.07082200	1.68448400
H	-3.55941600	-1.74715800	1.76177600
H	-3.11323600	-0.61400900	3.05332100
N	0.36096300	2.39220500	-0.12551300
O	-0.70909300	2.98035300	0.02281800
O	1.45797300	2.93126900	-0.16268300
N	-3.11463300	-0.60585200	-1.02098400
O	-3.61012300	-1.69310100	-0.71554800
O	-3.49209300	0.08291300	-1.97179800

Table S28: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₅–C₆-attack**

Reactant			
O	1.71799000	-1.83313300	0.49685700
O	2.15277100	0.49509100	-0.60102400
Mn	2.84271500	-0.84880300	-0.07443300
O	3.61420400	-1.56183400	-1.28150200
O	3.88329300	-0.49535100	1.08860900
H	-0.38524600	2.01411600	2.31224200
C	-2.39215100	-0.54814100	1.21846700
C	-1.68632400	0.30864200	2.08285700
C	-0.92874000	1.37945600	1.62393000
C	-0.88345000	1.62759700	0.25141200
C	-1.57502100	0.83480500	-0.65287300
C	-2.30602800	-0.24361700	-0.15821200
H	-1.53982900	1.03714500	-1.71398400
H	-1.73707700	0.12127700	3.14979900
C	-3.18834000	-1.67981000	1.81107200
H	-2.71427300	-2.64209400	1.59711500
H	-3.25283000	-1.55508600	2.89356400
H	-4.19941300	-1.72696000	1.39876400
N	-2.99773500	-1.05650600	-1.17063800
O	-3.26548000	-2.22878900	-0.90040000
O	-3.26661100	-0.52496300	-2.25204100
N	-0.09379700	2.75272500	-0.25498700
O	-0.09624400	2.96741000	-1.46953600
O	0.53030700	3.43463800	0.56188400

Table S29: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₅–C₆-attack**

Transition state			
O	1.30884700	-1.73950000	0.22575400
O	1.75357200	0.74737500	0.16660300
Mn	2.35251900	-0.70252200	-0.44764500
O	2.22857800	-0.72244300	-2.03247300
O	3.82843100	-0.95973200	0.08915600
H	0.85695100	1.41404600	1.95585300
C	-1.19325700	-1.12470200	0.99455800
C	-0.05954200	-0.49043600	1.53631800
C	0.35806400	0.84742500	1.17754300
C	-0.60070600	1.57800900	0.36719400
C	-1.66951600	0.96425600	-0.23014400
C	-1.94679600	-0.39155000	0.04939100
H	-2.32137400	1.51760200	-0.89093700
H	0.43380100	-0.96252900	2.37582400
C	-1.52573600	-2.50387800	1.49282200
H	-1.34695000	-3.24919300	0.71236500
H	-0.89939200	-2.74433200	2.35396500
H	-2.57769200	-2.59115700	1.77508600
N	-3.08983700	-0.95697700	-0.63466400
O	-3.28776900	-2.17924300	-0.57014800
O	-3.83235500	-0.19612800	-1.27912200
N	-0.38804300	2.98618600	0.15296900
O	-1.15472000	3.60671200	-0.60189500
O	0.55688700	3.53038500	0.74646900

Table S30: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C₅–C₆-attack**

Product			
O	1.59771100	-1.00627200	1.08934000
O	1.27647800	0.90304300	-0.52150200
Mn	2.52787100	-0.40431300	-0.35955900
O	2.41168300	-1.45085300	-1.54848900
O	3.91426400	0.22468900	0.09080400
H	0.89115300	1.66761600	1.36314500
C	-0.77589400	-1.30527300	0.68842800
C	0.32460100	-0.40134400	1.24504000
C	0.42989400	0.99972300	0.62712300
C	-0.90951300	1.53388900	0.21417100
C	-1.95892100	0.73614900	-0.05836100
C	-1.84476800	-0.69947500	0.09655300
H	-2.89360300	1.14920600	-0.41369500
H	0.10521300	-0.32130200	2.32420600
C	-0.59780200	-2.76385500	0.95449200
H	-0.15222000	-3.24394300	0.07403300
H	0.09227100	-2.90601700	1.78738800
H	-1.54388100	-3.27108600	1.14652000
N	-3.00356900	-1.46286200	-0.37264800
O	-2.84847500	-2.64440200	-0.69409700
O	-4.09148100	-0.87650500	-0.43294400
N	-1.04386700	2.96331500	0.00421000
O	-2.12716200	3.42147400	-0.38582400
O	-0.05417200	3.67023700	0.23793200

Table S31: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C_6-C_1 -attack**

Reactant			
O	-2.97030900	0.18340300	1.28730200
O	-1.76765500	-1.32106100	-0.47870400
Mn	-3.10174600	-0.50000400	-0.15344600
O	-3.31356400	0.63287000	-1.26334800
O	-4.35595400	-1.49384800	-0.15914200
C	1.14846200	1.27793000	1.63875400
C	1.49918000	0.00948900	2.08446100
C	2.04946000	-0.96894500	1.23591000
C	2.24518200	-0.58165600	-0.10845000
C	1.92389000	0.68701500	-0.58685700
C	1.36734400	1.59944000	0.29811500
H	0.71753000	2.00731300	2.31274300
H	2.09698200	0.94625600	-1.62178700
H	1.34456100	-0.24076600	3.12828000
C	2.40837600	-2.31062200	1.81590800
H	1.72192300	-3.08445100	1.46040300
H	3.41483500	-2.62331500	1.52609000
H	2.35148000	-2.26578200	2.90498500
N	1.01050200	2.93286200	-0.19394600
O	0.52831900	3.73552800	0.60930800
O	1.21041200	3.18791700	-1.38453500
N	2.81608100	-1.50619600	-1.10038300
O	3.36498400	-1.01955300	-2.09340600
O	2.71112800	-2.71797100	-0.90264000

Table S32: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C_6-C_1 -attack**

Transition state			
O	1.22227300	-1.92618100	0.31162500
O	1.61483500	0.57368200	0.05303900
Mn	2.20494700	-0.91581500	-0.46721100
O	2.02769600	-1.04832900	-2.04029400
O	3.70586100	-1.11066700	0.02428200
C	-1.22013000	-1.16776400	1.24646600
C	-0.10025300	-0.45157100	1.62970700
C	0.26591600	0.85016600	1.06534800
C	-0.75274900	1.36388600	0.12402900
C	-1.83125100	0.61831800	-0.29451400
C	-2.06444300	-0.65120400	0.25769600
H	-1.44848200	-2.11689600	1.71453900
H	-2.50934700	1.01971100	-1.03401300
H	0.48738100	-0.80616400	2.46701000
C	0.91071100	1.78080700	2.08988600
H	1.47962300	2.57401500	1.61289000
H	0.13183100	2.22966900	2.71579800
H	1.57305300	1.19727800	2.73372000
N	-3.20911200	-1.40433200	-0.17603600
O	-3.41493900	-2.51865300	0.33502200
O	-3.95194100	-0.91613200	-1.04529000
N	-0.61435400	2.67341100	-0.47979500
O	-1.54375700	3.10846400	-1.18266200
O	0.42493500	3.32011600	-0.28704200

Table S33: Optimized geometries for **2,4-dinitrotoluene** oxidation by MnO_4^- by **C_6-C_1 -attack**

Product			
O	1.49989500	-1.23957500	1.08395000
O	1.23694400	0.65684200	-0.54175000
Mn	2.39022500	-0.73919000	-0.42310700
O	2.12734900	-1.78778100	-1.58631600
O	3.84710700	-0.21628100	-0.06646700
C	-0.86670700	-1.42403500	0.84157300
C	0.27340200	-0.55636500	1.28708500
C	0.39375800	0.84186100	0.60057700
C	-0.96564400	1.31665200	0.09131300
C	-2.03346800	0.51622900	-0.08975200
C	-1.94385600	-0.89024000	0.24046900
H	-0.80662800	-2.48478100	1.05873600
H	-2.95051600	0.90269400	-0.51327300
H	0.13062000	-0.41765800	2.37267500
C	1.04351100	1.81100100	1.60383200
H	1.35612400	2.73072100	1.11123300
H	0.35095600	2.05656000	2.41605900
H	1.92344200	1.32663800	2.03711300
N	-3.08056300	-1.74862300	-0.11613200
O	-3.01643800	-2.95127400	0.14743500
O	-4.04969700	-1.21455100	-0.66396000
N	-1.12044300	2.69845700	-0.37072500
O	-2.26307000	3.16486900	-0.47457200
O	-0.10191000	3.34101800	-0.64175100

S5 Figures

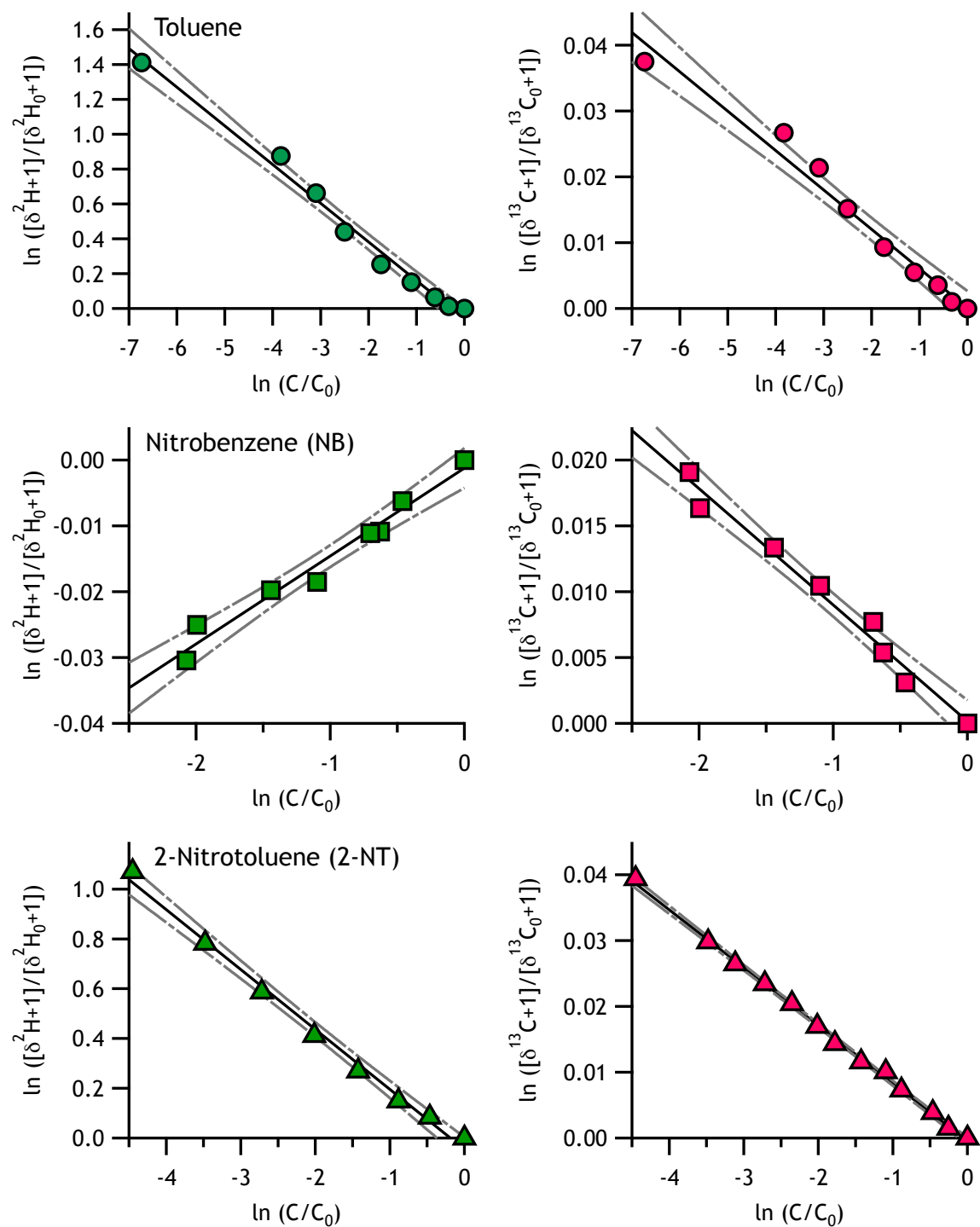


Figure S2: Linearized isotope Rayleigh plots for H (left panels) and C (right panels) isotope fractionation of toluene, nitrobenzene, and 2-nitrotoluene. Solid lines indicate linear regression fits, dashed lines show 95% confidence intervals. The corresponding H and C isotope enrichment factors, ϵ_H and ϵ_C , are listed in Table 1 of the main manuscript.

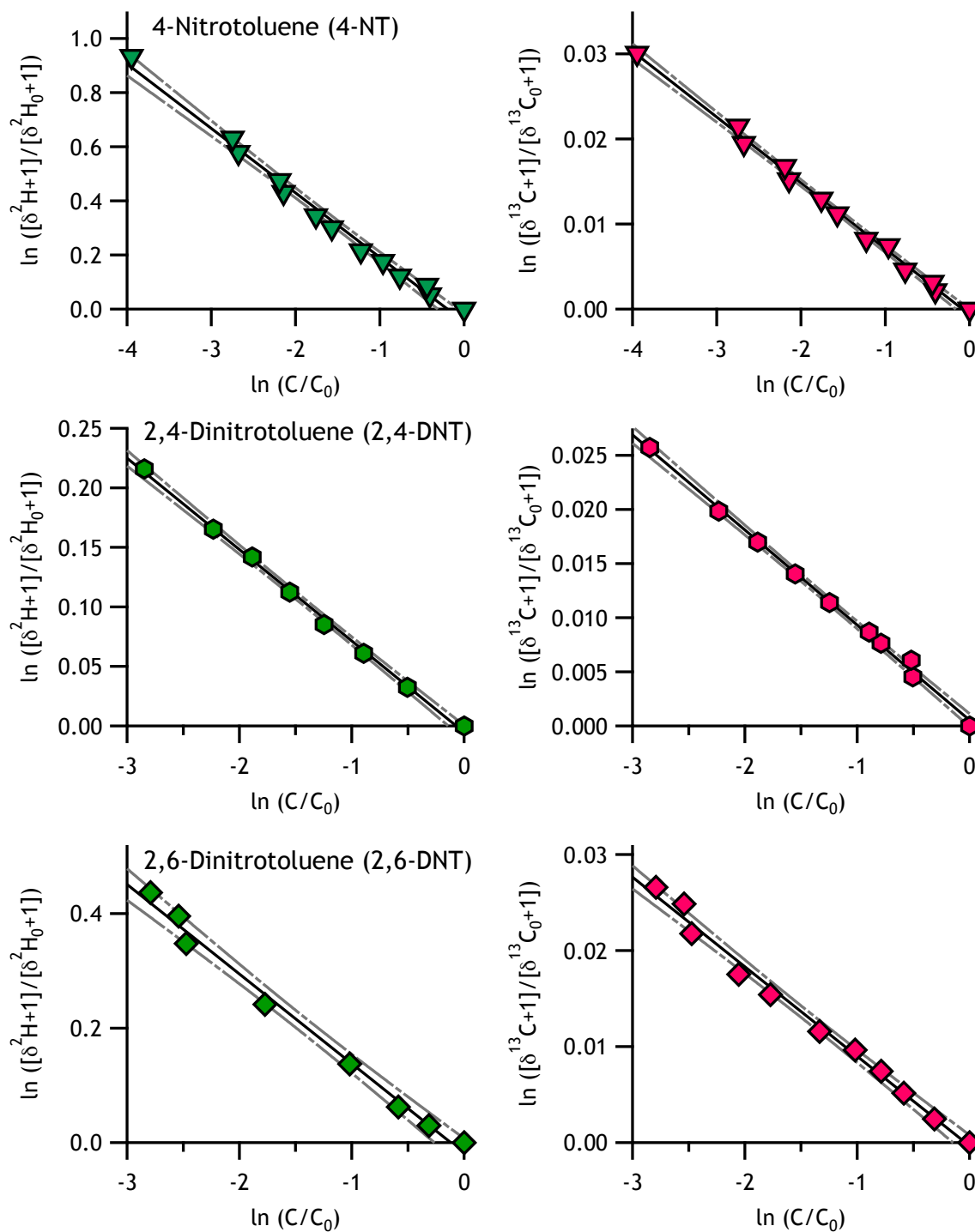


Figure S3: Linearized isotope Rayleigh plots for H (left panels) and C (right panels) isotope fractionation of 4-nitrotoluene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene. Solid lines indicate linear regression fits, dashed lines show 95% confidence intervals. The corresponding H and C isotope enrichment factors, ϵ_{H} and ϵ_{C} , are listed in Table 1 of the main manuscript.

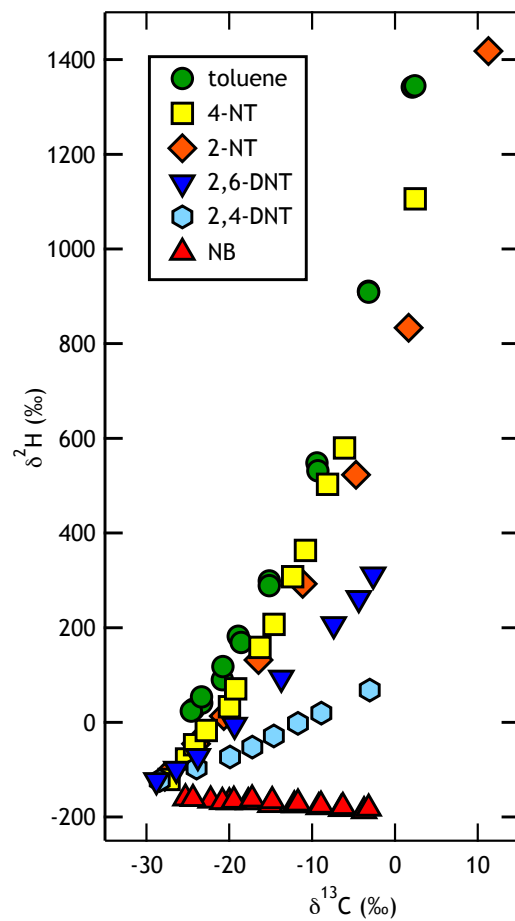


Figure S4: H vs. C isotope fractionation plots according to eqs. S10 and eq. 3 in the main manuscript illustrating the nonlinearity due to substantial H isotope fractionation. Measurement uncertainties are smaller than marker size.

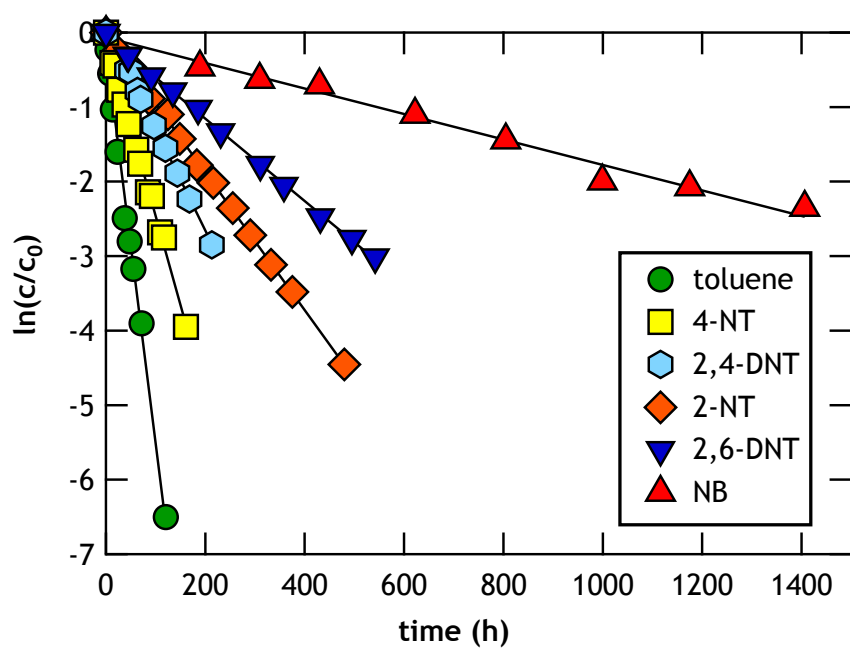


Figure S5: Semi-logarithmic plot of oxidation kinetics of all compounds analyzed in this study illustrating pseudo-1st-order reaction kinetics. c/c_0 stands for the fraction of remaining reactant.

S6 References

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