Electronic Supporting Information

Dynamic Covalent and Noncovalent Assembly of o-Nitrosocumene in Organic Solvents and Water

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1. General information and procedures

NMR spectra were recorded on Bruker AM-360, AM-500 and NEO-500 spectrometers using deuterated solvents (Cambridge Isotopes) with chemical shifts referenced to residual nondeuterated solvent signal. Signal quantitation was performed by signal integration relative to that for added internal standard (NaOAc, MeOH, mesitylene, or Me_2SO_2). ACS grade dichloromethane (DCM, CH_2Cl_2) and deionized water (DI H_2O) were used without further purification for all reactions of *o*-NC.

VT-NMR

Variable Temperature (VT) ^{1}H-NMR spectroscopy was conducted with probe cooling on a 360 MHz NMR spectrometer. From a N_2 cylinder equipped with a regulator, a line of N_2 gas is plumbed directly to the spectrometer via a Cu coil fully submerged in liquid N_2. The gas flow (L/h) and temperature (K) are controlled using Topspin "EDTE" command at the instrument console until target temperature is achieved and remains constant for ~5 min. Evidence of M,D equilibration may be obtained by collecting multiple spectra at a target temperature at different times (waiting 5-30 min as needed). Sample temperature was measured using a sealed capillary of CD_3OD included in the sample tube as a CD_3OD chemical thermometer according to the method and calibrations reported by Griesinger and coworkers.[1] Integral values relative to a given internal standard were scaled based on the number of nuclei for each signal to subsequently calculate Km for $D_E \rightleftharpoons 2M$ and $D_Z \rightleftharpoons 2M$. Van't Hoff plots of ln (K_m) vs. 1/T (1/K) were created. Using the LINEST function in excel, the slope and intercept were obtained (along with respective errors) and used to extract ΔH° and ΔS° for the monomerizations. Vertical error bars were added based on the standard deviation (2σ) of the y-values (ln (K_m)).

***o*-NC VT-NMR general methods:**

Solids were weighed on a (Ohaus Adventurer) analytical balance to 0.1 mg and volumes were measured in oven-dried 1.00 mL volumetric flasks or using Hamilton GASTIGHT® microliter syringes to 0.1 mL. All deuterated solvents were used as purchased from Cambridge Isotopes. Cleaned, dried 3 mm precision NMR tubes were used. A clean, flame-sealed capillary tube of CD_3OD (99.8%) was added to all samples as a chemical thermometer to measure the internal temperature of the sample (see ref 1). The 4th degree polynomial shown below was used to calibrate the temperature for a given ^{1}H-NMR spectrum based on the chemical shift difference between residual CH_3 and OH signals.

$$T/\mathrm{K} = \sum_{i=0}^{4} a_i (\Delta\delta/\mathrm{ppm})^i. \qquad \textit{Eq 1.}$$

i	0	1	2	3	4
a_i	416.4745	−39.5133	−36.0620	11.4869	−2.4340

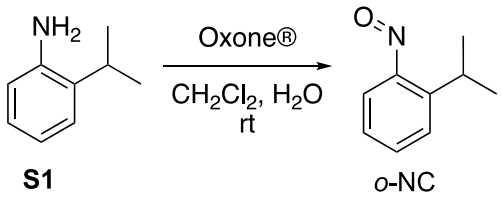
[1] N. Karschin, S. Krenek, D. Heyer and C. Griesinger, *Magn. Reson. Chem.*, 2022, **60**, 203-209.

***o*-NC VT-NMR sample preparation (by solvent):**

- $CDCl_3$: 0.363 M *o*-NC and 0.166 M dimethylsulfone in $CDCl_3$, respectively.
- $(CD_3)_2CO$: 0.275 M *o*-NC and 0.180 M mesitylene in $(CD_3)_2CO$, respectively.
- CD_3OD: 0.190 M *o*-NC and 0.180 M mesitylene in CD_3OD, respectively. The CD_3OD residual nondeuterated solvent signals were used in place of a sealed capillary of CD_3OD.
- CD_3CN: 0.109 M *o*-NC and 0.0358 M mesitylene in CD_3CN, respectively.
- D_2O: From 0.0697 M *o*-NC stock solution in DMSO-d_6 was prepared 2.37 mM *o*-NC and 1.96 mM NaOAc in D_2O, respectively.

  For D_2O concentration studies, subsequent volumes of an *o*-NC DMSO-d_6 stock solution (in 5-10 μL increments) were added and the ^{1}H-NMR spectrum was obtained after each addition.

2. Preparation of *o*-nitrosocumene, *o*-NC[2]



2-aminocumene (2.00 g, 0.0148 mol) (Ambeed) was weighed into a 250 mL round bottom flask equipped with a large stir bar and dissolved in 60 mL CH_2Cl_2 (DCM). Separately, Oxone® [$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$] (BeanTown Chemical) (18.2 g, 0.0296 mol) was dissolved in a minimal amount of deionized H_2O (~100 mL) giving a saturated solution, which was then added to the solution of aminocumene **S1** and the mixture was stirred vigorously. The reaction was monitored by TLC (silica gel, 1:4 EtOAc:hexane) for consumption of starting material, which occurred at ~3.5 hours. The colored organic layer was then removed using a separatory funnel, and the aqueous layer washed with DCM (3 x 25 mL). The combined organic layers were dried over anhydr Na_2SO_4, filtered, concentrated *in vacuo* to a volume of ~ 5 mL, capped, and placed in the freezer (-15 ˚C) overnight. Crystals of *o*-NC formed, were filtered, and washed with a minimal amount of cold DCM, and subsequently recrystallized in ~1 mL of DCM with slow cooling to -15 ˚C to provide pure, colorless crystalline solid (0.592 g, 26.8%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69 (m, 2H), 7.13 (t, J = 8.2 Hz, 1H), 6.09 (d, J = 8.2 Hz, 1H), 5.29 (septet, J = 6.9 Hz, 1H), 1.57 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 164.0 (C), 152.9 (C), 136.9 (CH), 128.2 (CH), 125.5 (CH), 105.6 (CH), 27.4 (CH), 24.5 (CH_3).

[2] Biphasic CH_2Cl_2/oxone is a generally useful for N-oxygenation reactions (a) S. C. Blackstock, K. Poehling and M. L. Greer, *J. Am. Chem. Soc.*, 1995, **117**, 6617-6618; (b) M. L. Greer, B. J. McGee, R. D. Rogers and S. C. Blackstock, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1864-1866; (c) B. Priewisch and K. Rück-Braun, *J. Org. Chem.*, 2005, **70**, 2350-2352. *o*-NC preparations: (a) R.-Q. Ran, S.-D. Xiu and C.-Y. Li, *Org. Lett.*, 2014, **16**, 6394-6396; (b) S. A. Kelley, Ph.D. Dissertation, The University of Alabama, 2021.

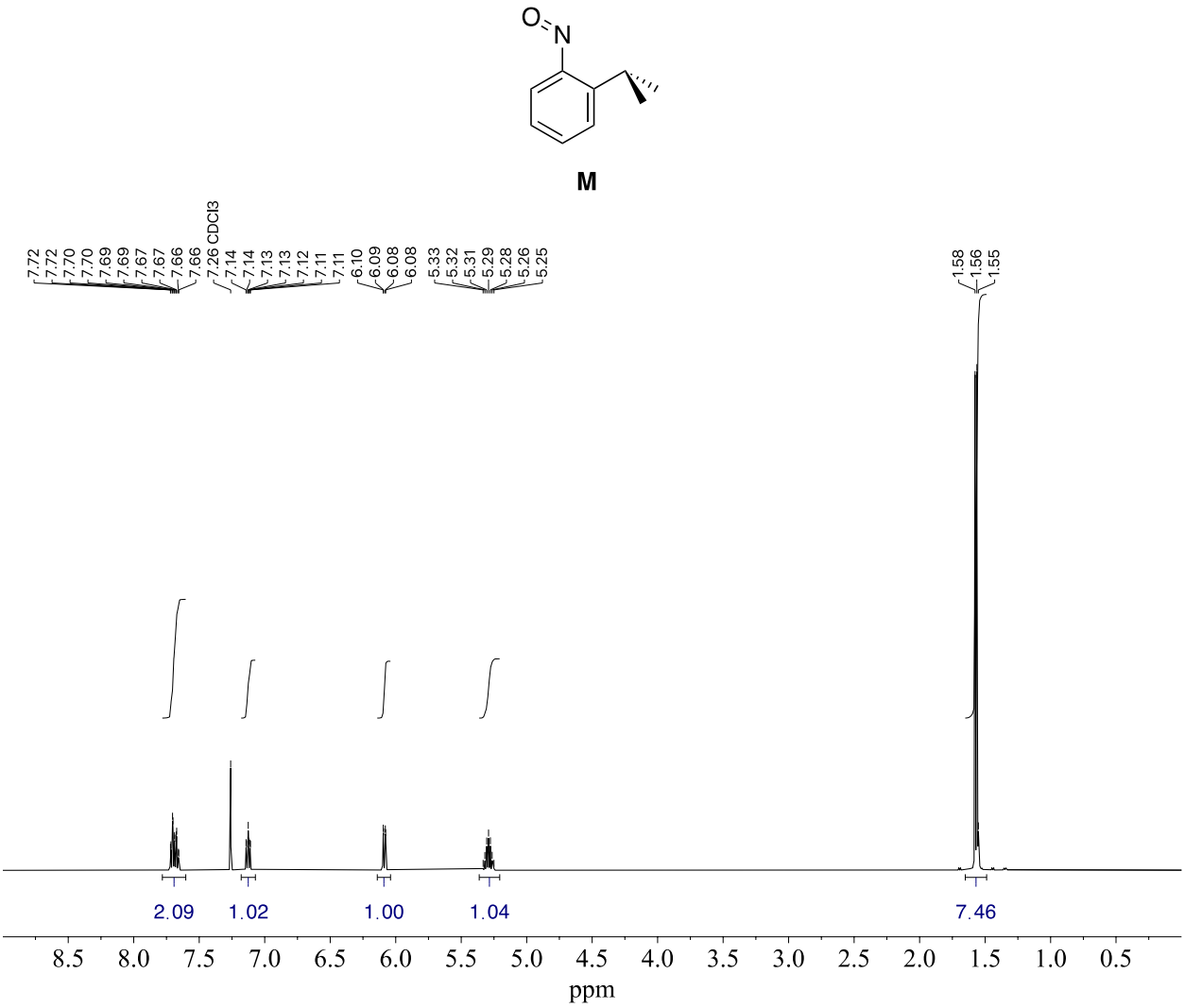


Figure S1. ^{1}H-NMR spectrum (500 MHz) 0.0544 M *o*-NC in $CDCl_3$

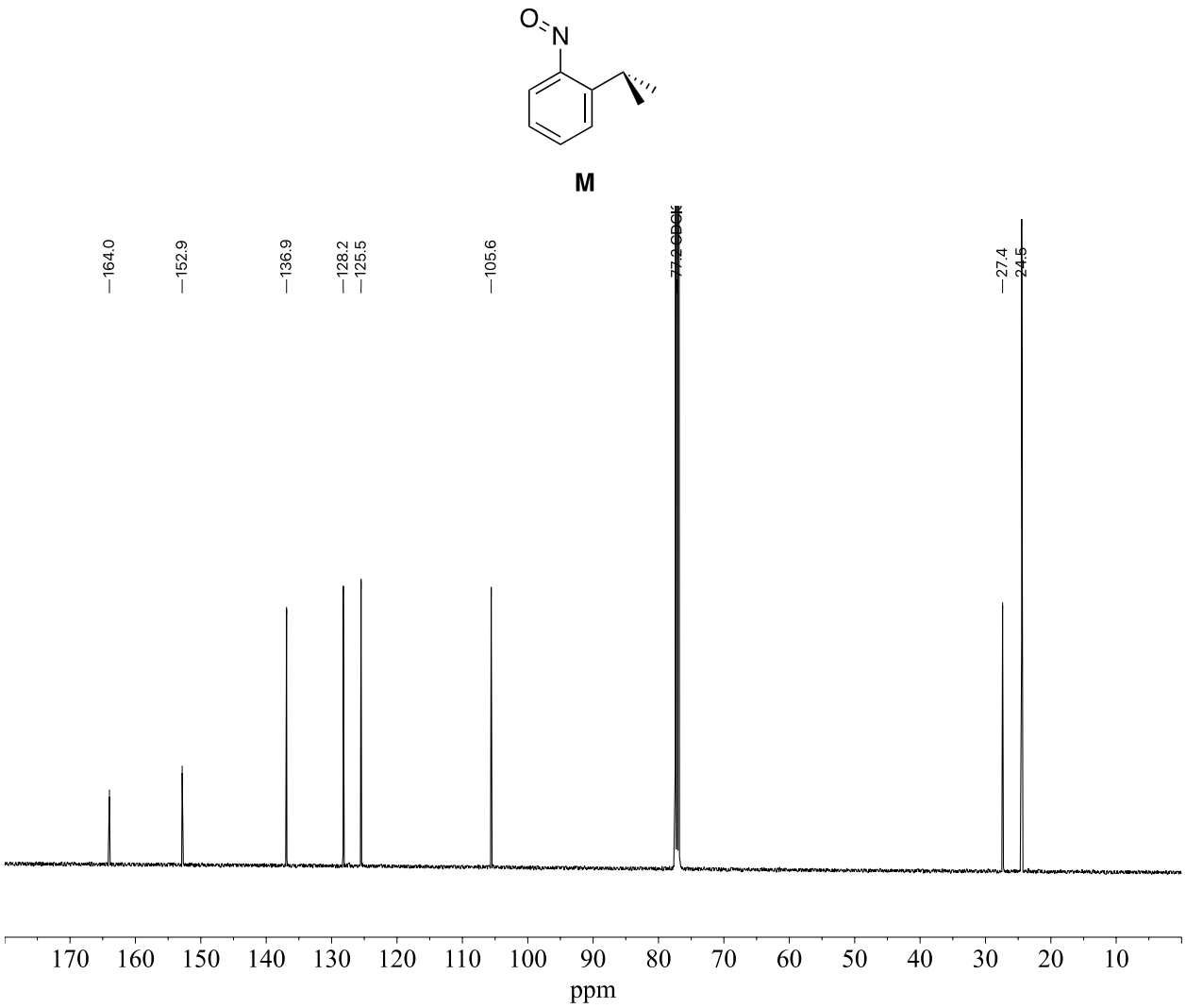


Figure S2. ^{13}C-NMR spectrum (126 MHz) 0.0544 M *o*-NC in $CDCl_3$

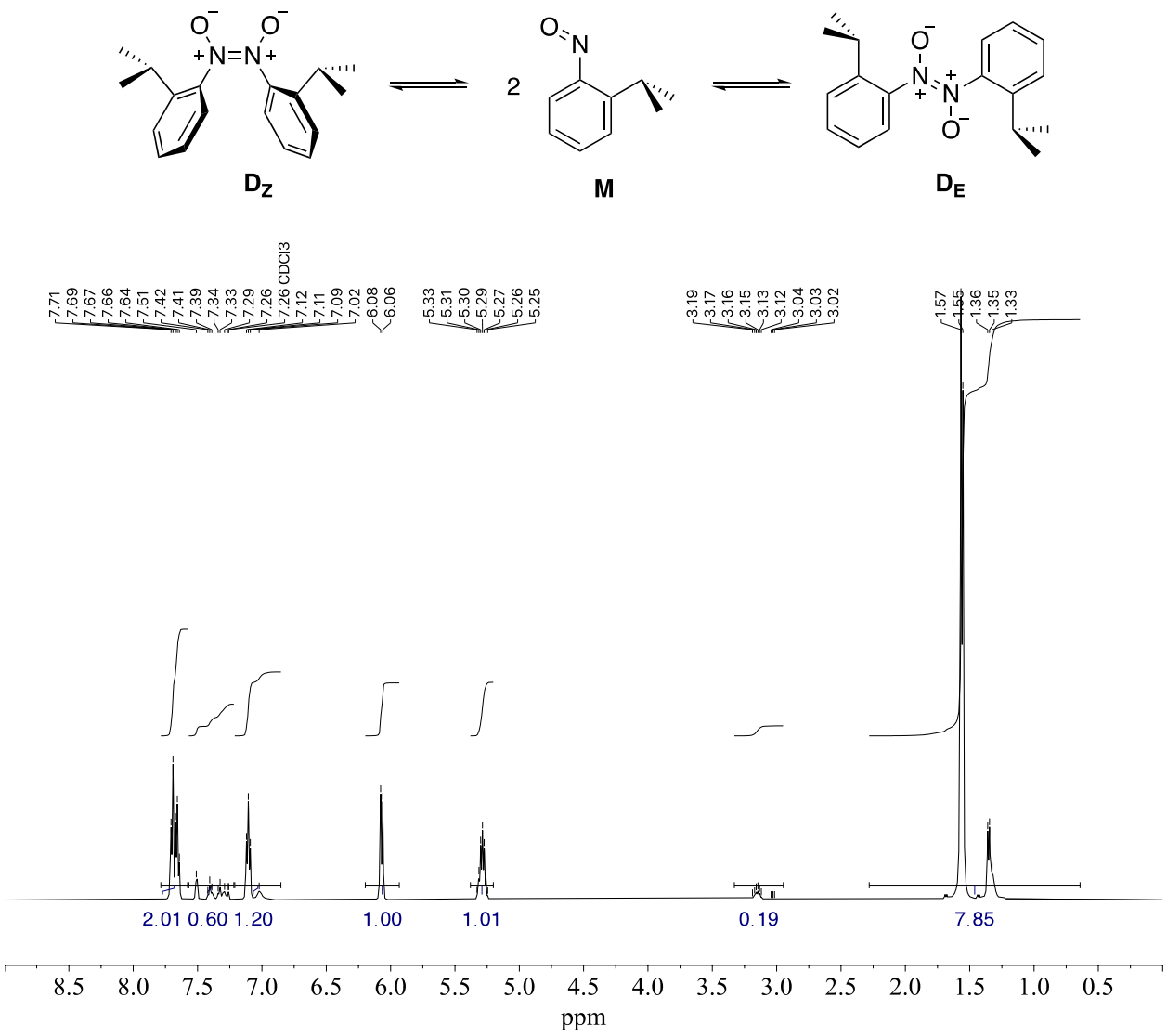


Figure S3. ^{1}H-NMR spectrum (500 MHz) 0.976 M *o*-NC in $CDCl_3$ (showing some D_Z and D_E dimer signals)

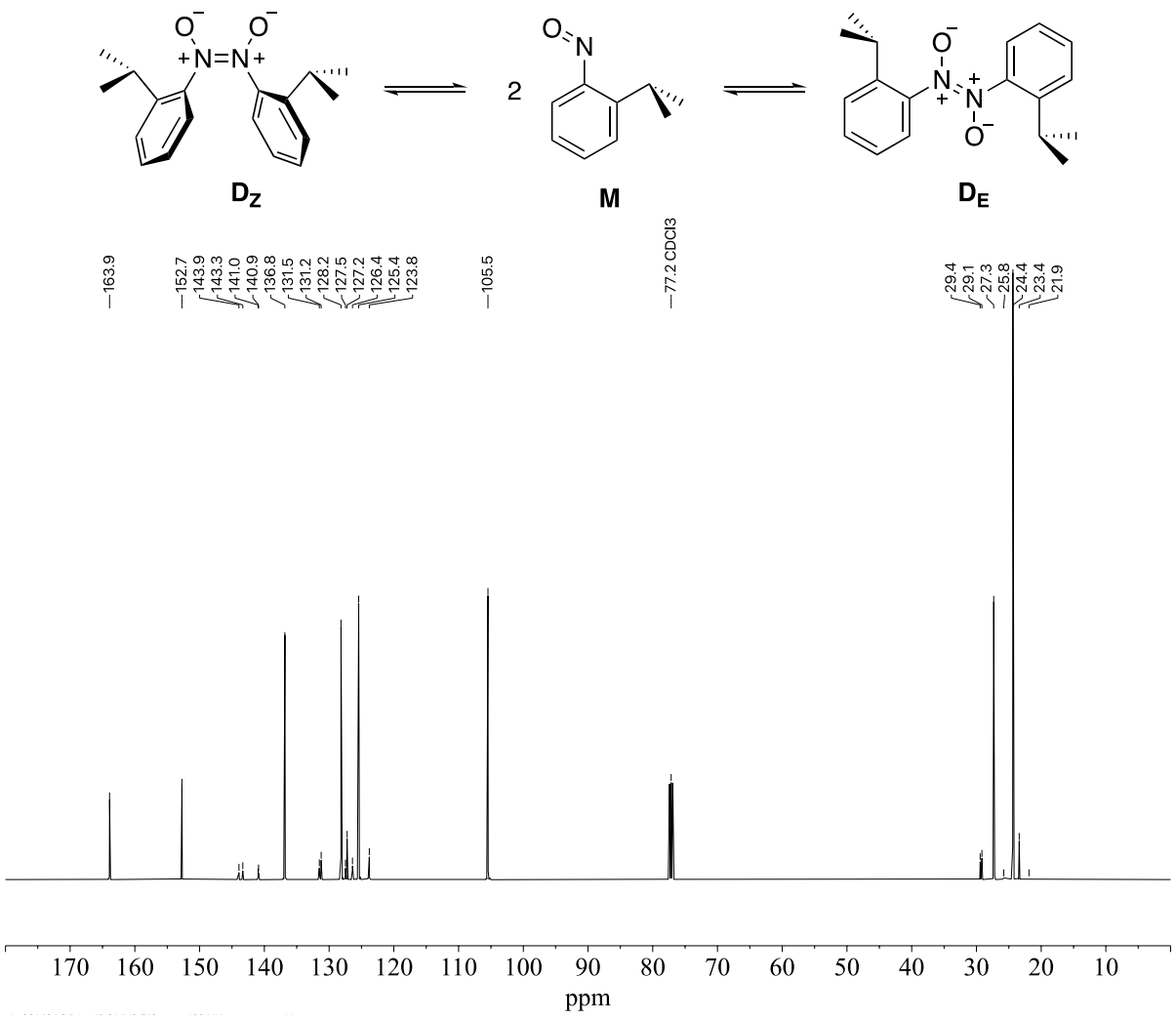


Figure S4. ^{13}C-NMR spectrum (126 MHz) 0.976 M *o*-NC in $CDCl_3$ (showing M, D_Z, and D_E signals)

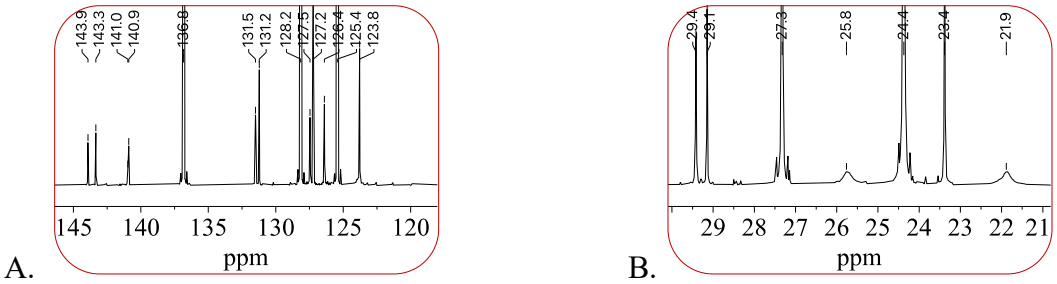


Figure S5. ^{13}C-NMR spectra (126 MHz) 0.976 M *o*-NC in $CDCl_3$ (A) aromatic CH region and (B) isopropyl CH and CH_3 region

Note: the broad ^{13}C signals at 21.9 and 25.8 ppm are assigned as diastereotopic methyl carbons for the D_Z (anti) dimer of *o*-NC

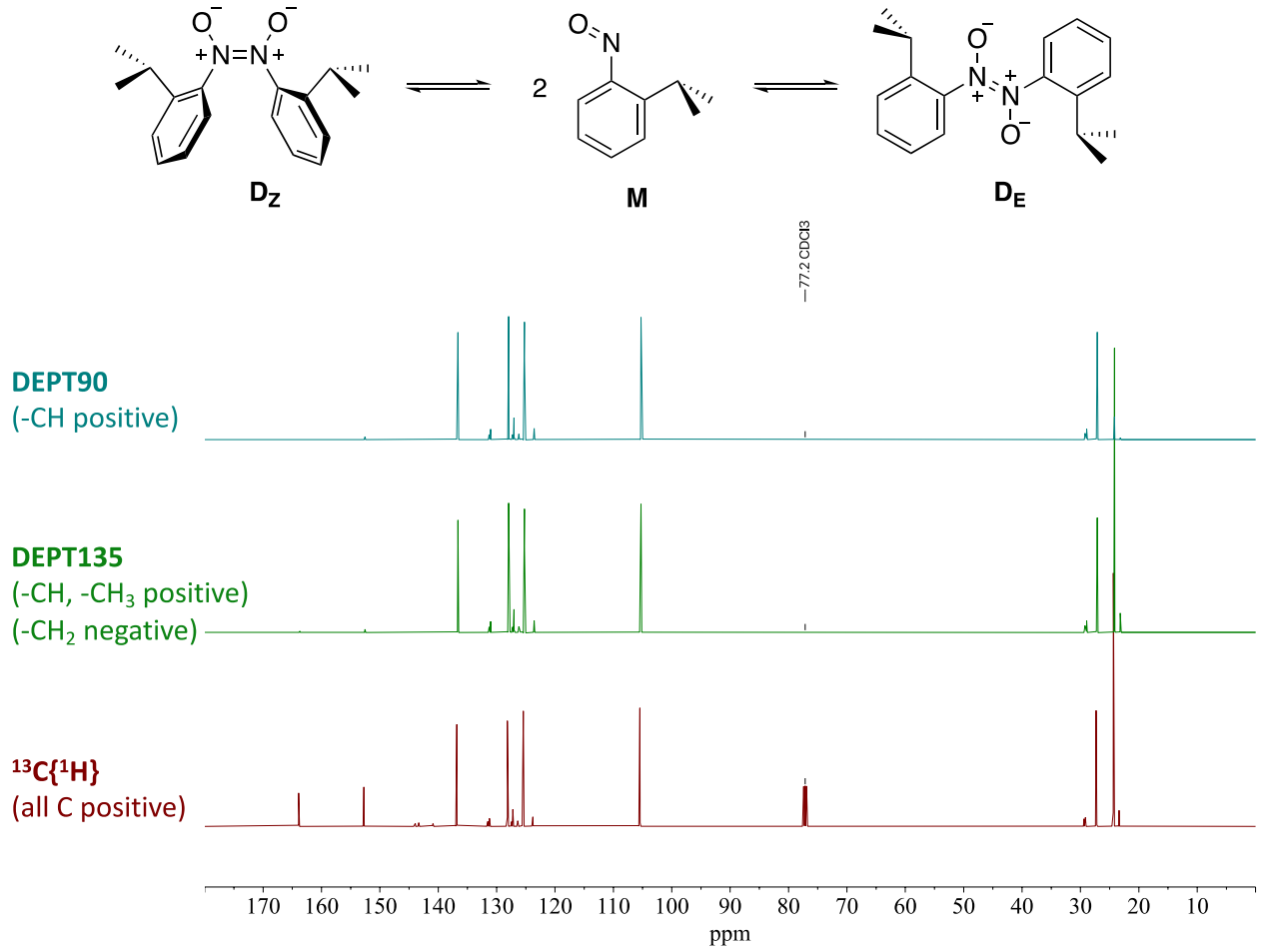


Figure S6. ^{13}C-NMR spectra (126 MHz) 0.976 M *o*-NC in $CDCl_3$ (maroon) $^{13}C\{^1H\}$ spectrum, (green) DEPT135 spectrum, and (blue) DEPT90 spectrum

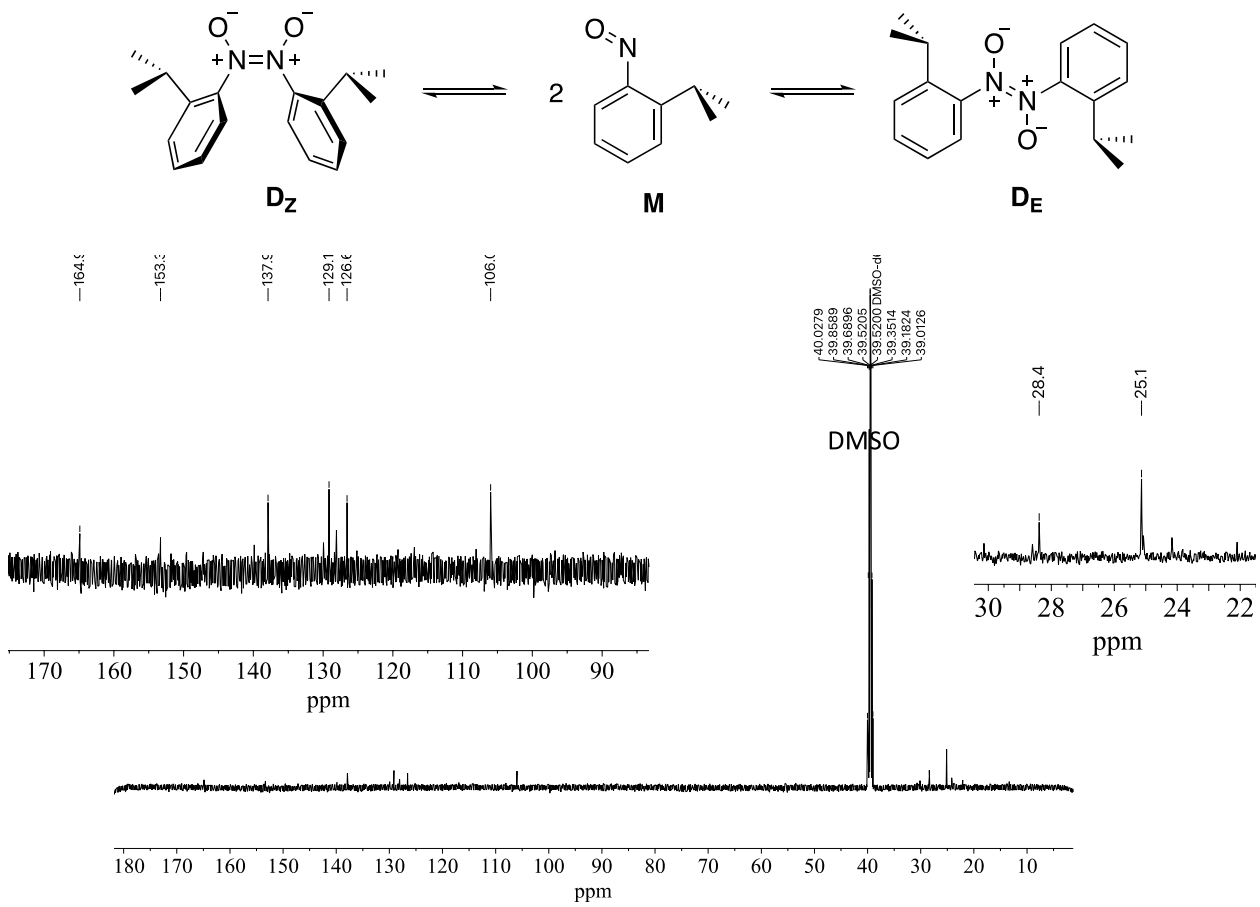


Figure S7. ^{13}C-NMR spectrum (126 MHz) 3.8 mM *o*-NC in D_2O from (DMSO-d_6 stock solution) with large amount aggregate

For ^{1}H-NMR of *o*-NC in D_2O see manuscript, Figure 3.

3. X-ray crystallography of *o*-NC and cold NMR analysis of dissolved crystals in CD_3OD

Single, clear, colorless crystals of *o*-NC [SCB297_Cu_3] were grown from a green solution of DCM upon slow cooling (-15 ˚C). A suitable crystal with dimensions 0.026 × 0.023 × 0.018 mm^3 was selected and mounted using Parabar® 10312 Immersion Oil with a MiTeGen dual thickness microloop on a Rigaku XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 117(20) K during data collection. Using Olex2,[3] the structure was solved with the SHELXT[4] structure solution program using intrinsic phasing and refined with the SHELXL[5] refinement package using Least Squares minimization using calculated H-atom positions. The structure has been deposited as CCDC 2313924.

[3] G. M. Sheldrick, SHELXT – Integrated Space-Group and Crystal- Structure Determination. *Acta Cryst., Sect. A* 2015, **71**, 3-8.
[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst*. 2009, **42**, 339-3416.
[5] G. M. Sheldrick, Crystal Structure Refinement with ShelXL. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 2015, **71**, 3-8.

Table S1. Crystal data and structure refinement for *o*-NC D_Z (anti) SCB297_Cu_3.

Identification code	SCB297_Cu_3
Empirical formula	$C_{18}H_{22}N_2O_2$
Formula weight	298.37
Temperature/K	117(20)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7459(4)
b/Å	10.4541(3)
c/Å	13.4750(4)
α/°	90
β/°	111.592(4)
γ/°	90
Volume/Å^3	1669.51(10)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.620
F(000)	640.0
Crystal size/mm^3	0.026 × 0.023 × 0.018
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.168 to 142.534
Index ranges	$-9 \leq h \leq 15$, $-11 \leq k \leq 12$, $-16 \leq l \leq 15$
Reflections collected	7988
Independent reflections	3150 [R_{int} = 0.0364, R_{sigma} = 0.0444]
Data/restraints/parameters	3150/0/203
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.1133
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1192
Largest diff. peak/hole / e Å^{-3}	0.20/-0.20

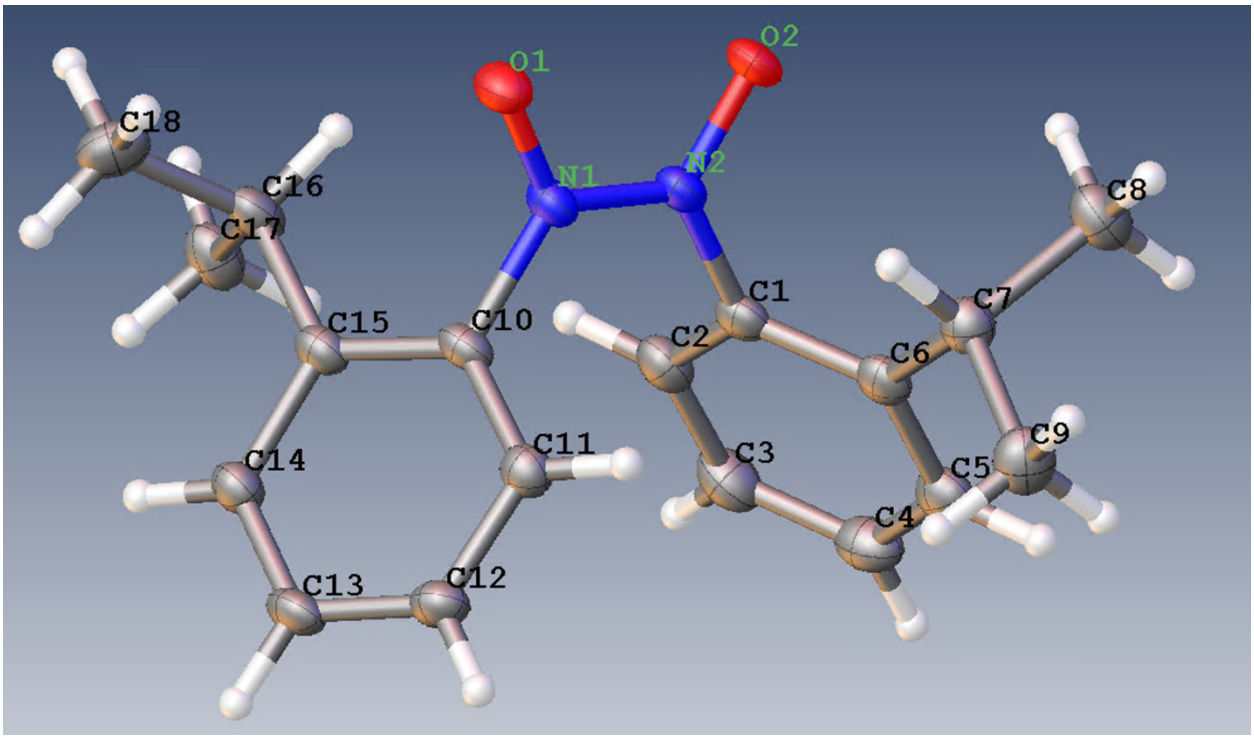


Figure S8. Crystal structure of *o*-NC D_Z (anti)

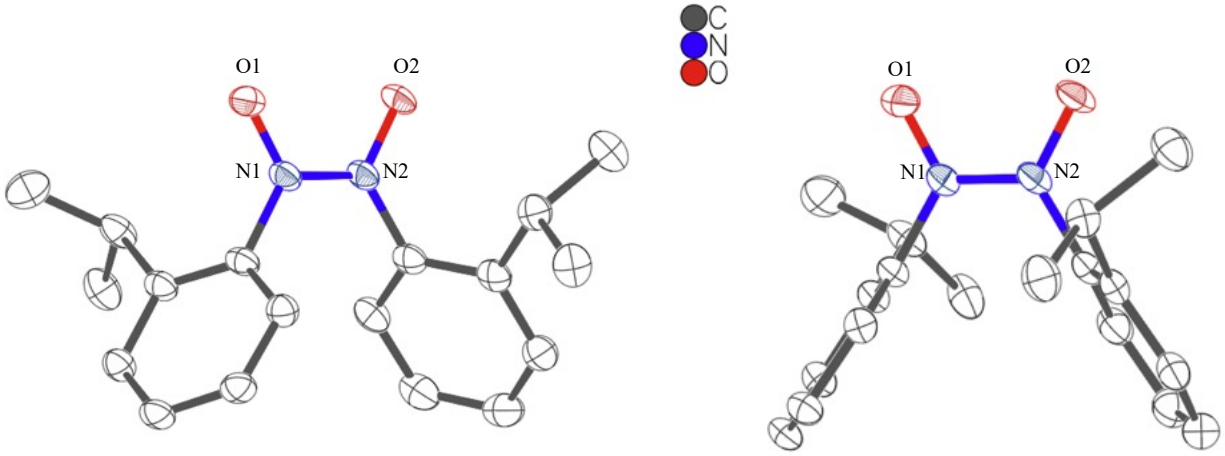


Figure S9. ORTEP (50% thermal ellipsoids) diagram of *o*-NC D_Z (anti) with heteroatoms labelled and hydrogen atoms omitted for clarity.

Table S2. Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.2602(17)	C12	C13	1.382(2)
O2	N2	1.2668(16)	C14	C13	1.388(2)
N2	N1	1.3241(18)	C6	C7	1.521(2)
N2	C1	1.451(2)	C6	C5	1.395(2)
N1	C10	1.4582(19)	C7	C9	1.526(2)
C15	C10	1.389(2)	C7	C8	1.532(2)
C15	C14	1.402(2)	C16	C17	1.531(2)
C15	C16	1.517(2)	C16	C18	1.530(3)
C1	C6	1.394(2)	C2	C3	1.387(3)
C1	C2	1.388(2)	C5	C4	1.388(3)
C10	C11	1.392(2)	C3	C4	1.380(3)
C11	C12	1.383(2)			

Table S3. Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	N2	N1	119.02(13)	C13	C12	C11	119.54(15)
O2	N2	C1	119.31(12)	C13	C14	C15	121.15(15)
N1	N2	C1	121.63(12)	C1	C6	C7	122.45(15)
O1	N1	N2	119.26(12)	C1	C6	C5	115.86(15)
O1	N1	C10	120.00(12)	C5	C6	C7	121.69(15)
N2	N1	C10	120.73(13)	C12	C13	C14	121.01(15)
C10	C15	C14	116.00(15)	C6	C7	C9	111.93(14)
C10	C15	C16	123.23(14)	C6	C7	C8	110.92(13)
C14	C15	C16	120.77(15)	C9	C7	C8	110.97(15)
C6	C1	N2	117.82(14)	C15	C16	C17	111.93(14)
C2	C1	N2	118.53(15)	C15	C16	C18	110.52(13)
C2	C1	C6	123.44(15)	C18	C16	C17	110.02(15)
C15	C10	N1	118.20(14)	C3	C2	C1	118.81(17)
C15	C10	C11	123.74(14)	C4	C5	C6	121.80(17)
C11	C10	N1	117.87(14)	C4	C3	C2	119.47(16)
C12	C11	C10	118.54(15)	C3	C4	C5	120.61(17)

Table S4. Torsional Angles

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	C10	C15	67.36(18)	C1	C2	C3	C4	-0.7(2)
O1	N1	C10	C11	-107.75(17)	C10	C15	C14	C13	1.1(2)
O2	N2	N1	O1	1.9(2)	C10	C15	C16	C17	123.19(16)
O2	N2	N1	C10	-179.02(13)	C10	C15	C16	C18	-113.81(17)
O2	N2	C1	C6	63.75(18)	C10	C11	C12	C13	0.5(2)
O2	N2	C1	C2	-111.26(16)	C11	C12	C13	C14	0.4(2)
N2	N1	C10	C15	-111.71(17)	C14	C15	C10	N1	-175.02(13)
N2	N1	C10	C11	73.18(19)	C14	C15	C10	C11	-0.2(2)
N2	C1	C6	C7	4.3(2)	C14	C15	C16	C17	-57.3(2)
N2	C1	C6	C5	-175.14(13)	C14	C15	C16	C18	65.7(2)
N2	C1	C2	C3	175.50(14)	C6	C1	C2	C3	0.8(2)
N1	N2	C1	C6	-114.07(16)	C6	C5	C4	C3	0.1(3)
N1	N2	C1	C2	70.93(19)	C7	C6	C5	C4	-179.53(15)
N1	C10	C11	C12	174.28(14)	C16	C15	C10	N1	4.5(2)
C15	C10	C11	C12	-0.5(2)	C16	C15	C10	C11	179.27(15)
C15	C14	C13	C12	-1.2(2)	C16	C15	C14	C13	-178.44(15)
C1	N2	N1	O1	179.72(13)	C2	C1	C6	C7	179.07(14)
C1	N2	N1	C10	-1.2(2)	C2	C1	C6	C5	-0.4(2)
C1	C6	C7	C9	133.36(16)	C2	C3	C4	C5	0.3(3)
C1	C6	C7	C8	-102.09(18)	C5	C6	C7	C9	-47.2(2)
C1	C6	C5	C4	-0.1(2) C	5	C6	C7	C8	77.33(19)

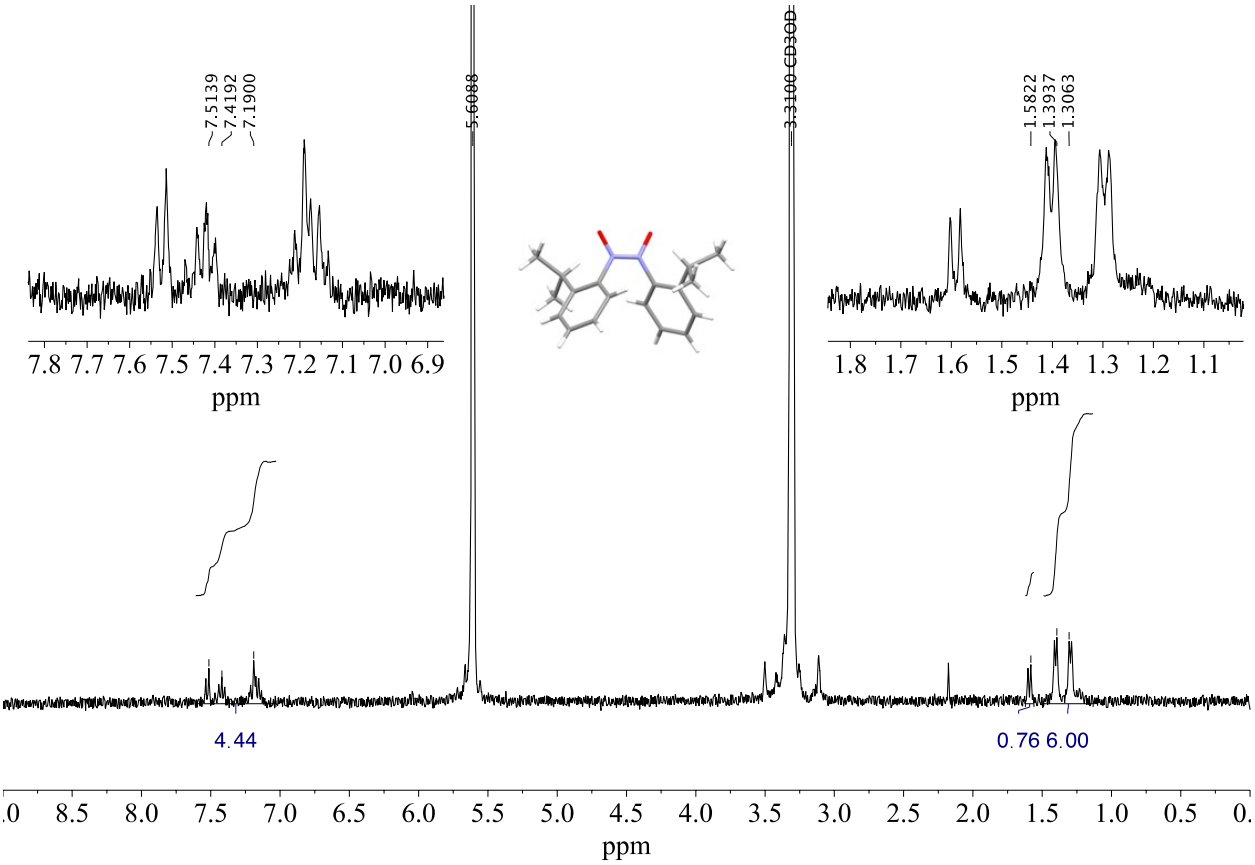


Figure S10. ^{1}H-NMR spectrum (360 MHz, CD_3OD) D_Z (anti) crystal dissolved at –68.0 ˚C in precooled CD_3OD (used to fully assign D_Z (anti) signals in solution)

Note: the small doublet at ~1.60 ppm is due to a small amount of monomerization that occurred during *o*-NC addition to cold CD_3OD. At -68.0 ˚C, the equilibrium of this monomer with the bulk D_Z (anti) is slow.

4. EXSY ^{1}H-NMR spectrum of *o*-NC in $CDCl_3$ and M, D_Z, and D_E signal assignments

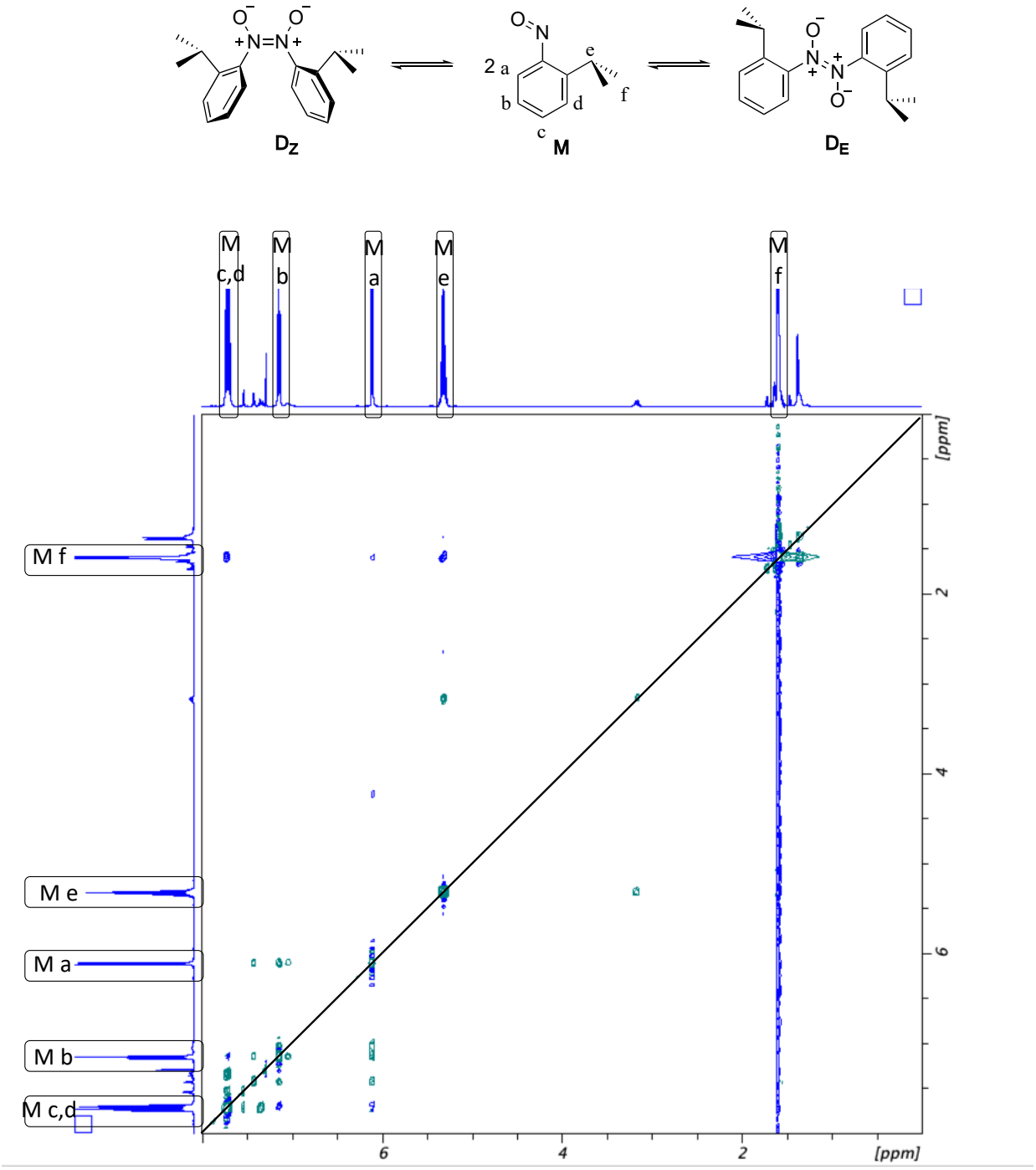


Figure S11. 2D EXSY ^{1}H-NMR spectrum (500 MHz) 0.349 M *o*-NC in $CDCl_3$ full spectrum.

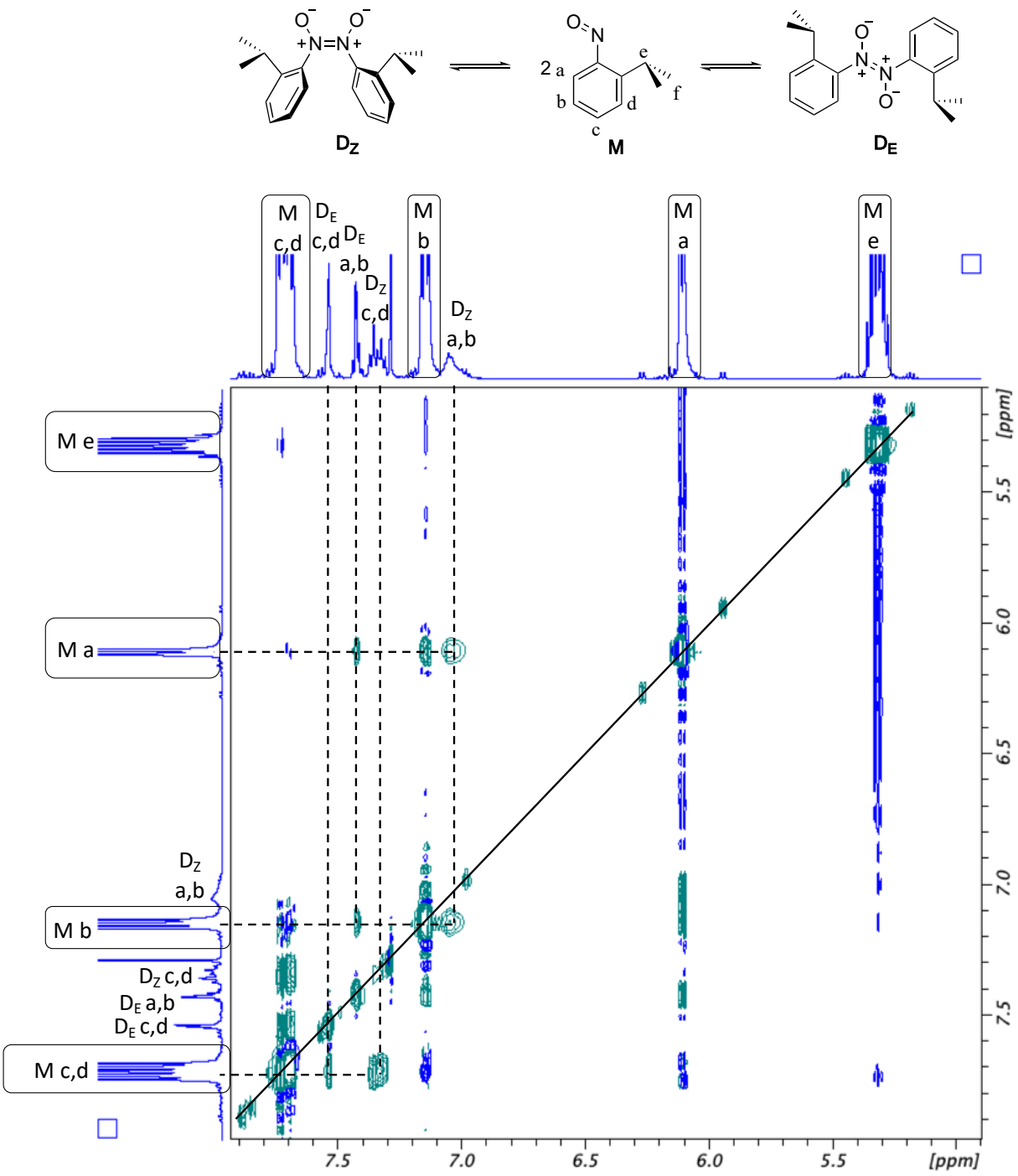


Figure S12. 2D EXSY ^{1}H-NMR spectrum (500 MHz) 0.349 M *o*-NC in $CDCl_3$ methine region. Based on these EXSY exchange peaks, D_Z and D_E a,b and c,d dimer signals are confirmed by exchange with the known signals of M (as indicated by dashed lines).

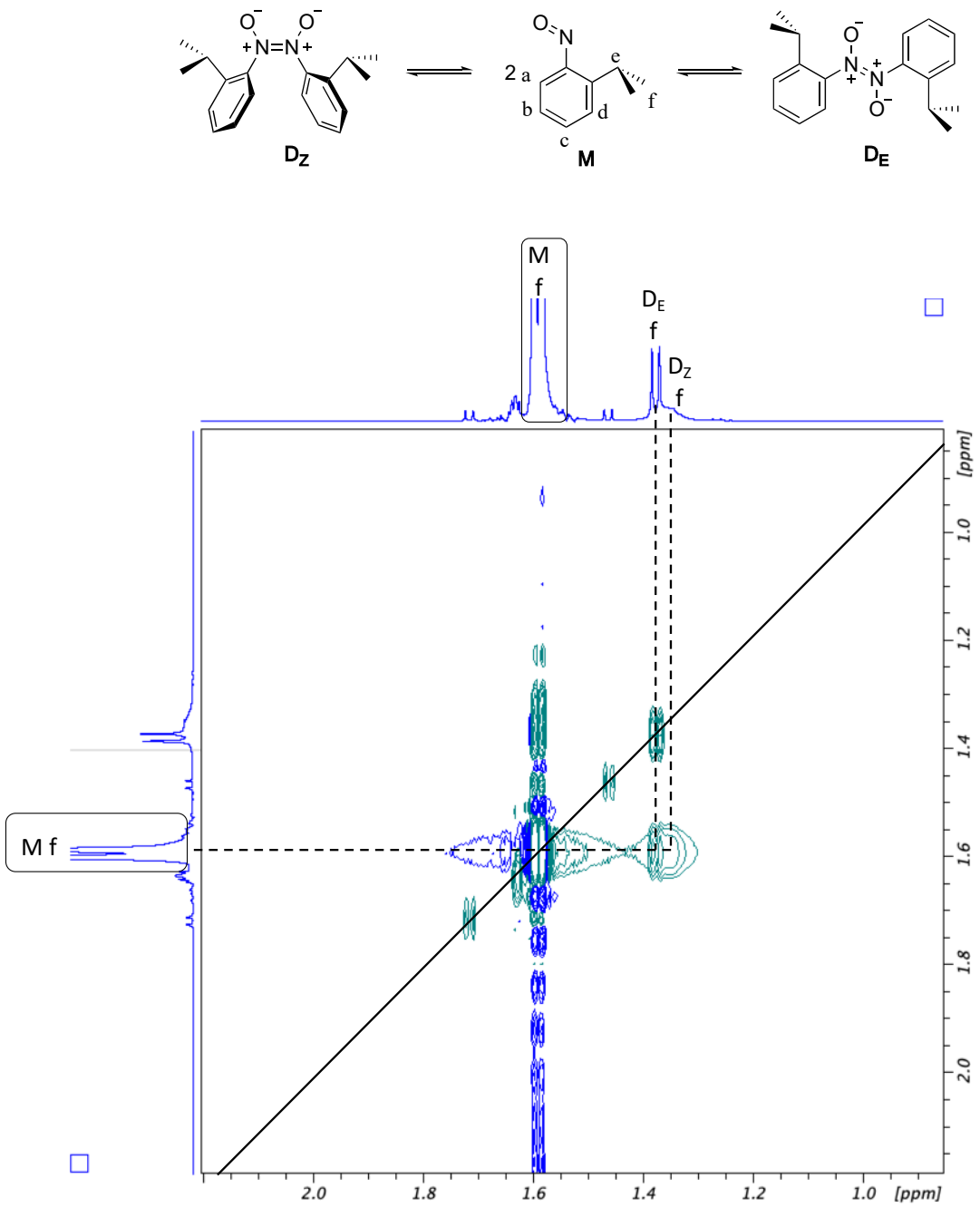


Figure S13. 2D EXSY ^{1}H-NMR spectrum ($CDCl_3$, 500 MHz) 0.349 M *o*-NC in $CDCl_3$ methyl region. Based on these EXSY exchange peaks, D_Z and D_E a,b and c,d dimer signals are confirmed by exchange with the known signals of M (as indicated by dashed lines).

5. VT-NMR analysis for monomer and dimer distributions of *o*-NC in $CDCl_3$, $(CD_3)_2CO$, CD_3OD, CD_3CN, and D_2O

Figure S14. VT ^{1}H-NMR spectra (500 MHz) of 0.363 M *o*-NC in $CDCl_3$ (Run 3). For full signal assignment, see Figures S11-13.

- Within the red box region is the M 'c,d' signal which was integrated and used directly to quantify M.
- Within the green box region are the D_E the 'c,d' protons which were integrated and used directly to quantify D_E.
- Within the blue box region are the D_Z the 'a,b' protons which were integrated and used directly to quantify D_Z.

Table S5. A) M and D signal integrations (Figure S14) of *o*-NC (VT-NMR) B) M and D concentrations of *o*-NC in $CDCl_3$ (Run 3).

Figure S15. Van't Hoff Plot for *o*-NC monomerization (D ⇌ 2M) in $CDCl_3$

Table S6. Summary of VT-NMR data for *o*-NC monomerization in $CDCl_3$

* used in manuscript

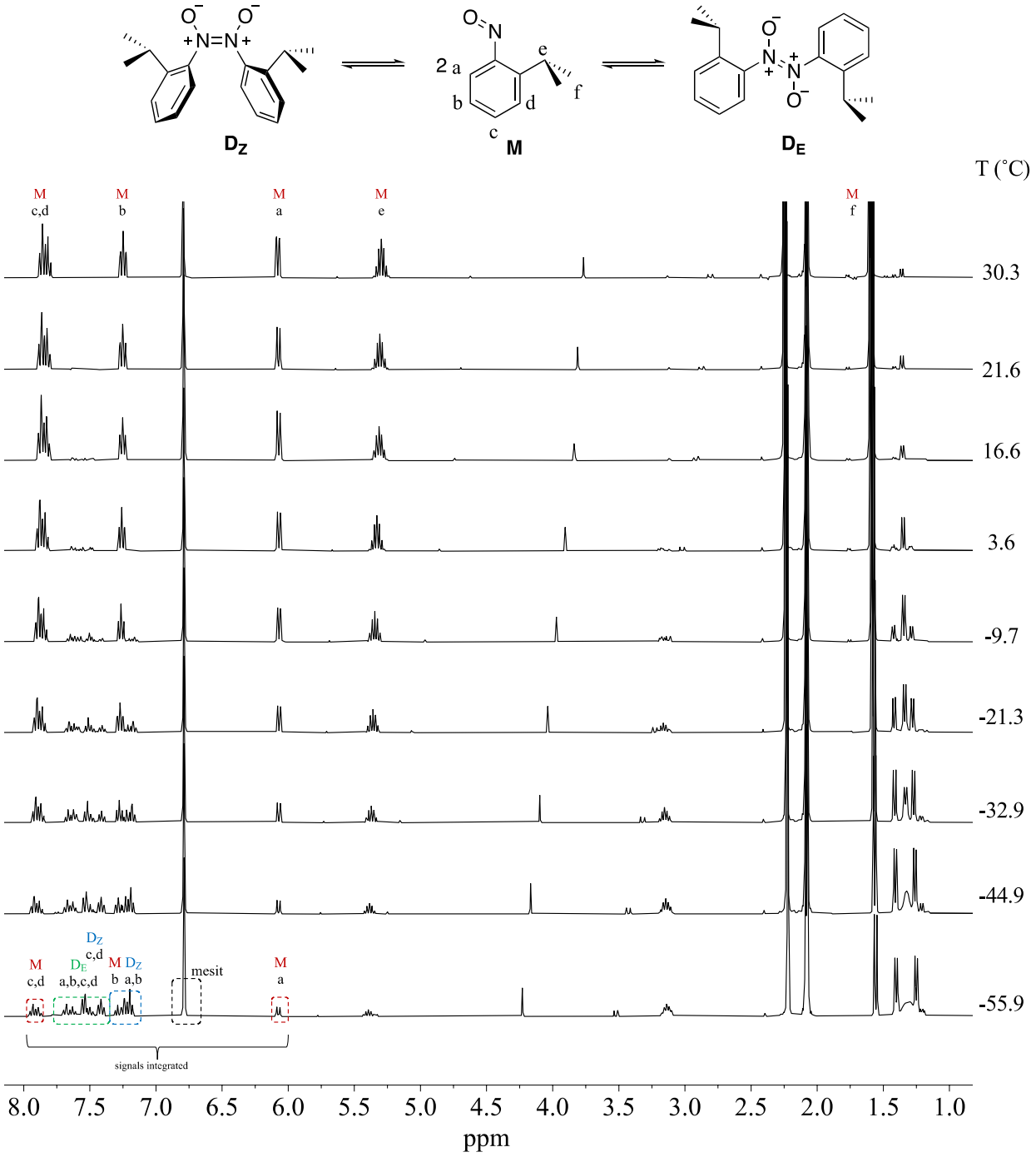


Figure S16. VT ^{1}H-NMR spectra (500 MHz) of 0.275 M *o*-NC in $(CD_3)_2CO$ (Run 3). For full signal assignment, see Figures S11-13.

- Within the red box region are the M 'c,d' signals which were integrated and used directly to quantify M.

- Within the blue box region are the D_Z ‘a,b’ signals and the M ‘b’ signal. The D_Z ‘a,b’ integration value was obtained subtracting the analogous value of the M ‘a’ signal integration (red box region labelled ‘a’).
- Within the green box region are the D_E ‘a,b,c,d’ signals and the D_Z ‘c,d’ signals. The D_E ‘a,b,c,d’ integration value was obtained subtracting the determined integration value of D_Z ‘a,b’ signals (second bullet point).

Table S7. A) M and D signal integrations (Figure S16) of *o*-NC (VT-NMR) B) M and D concentrations of *o*-NC in $(CD_3)_2CO$ (Run 3).

Figure S17. Van't Hoff Plot for *o*-NC monomerization (D ⇌ 2M) in $(CD_3)_2CO$ (Run 3).

Table S8. Summary of VT-NMR data in $(CD_3)_2CO$

* used in manuscript

Figure S18. VT-^{1}H NMR spectra (500 MHz) of 0.190 M *o*-NC in CD_3OD (Run 3). For full signal assignment, see Figures S11-13.

- Within the red box region are the M ‘c,d’ signals which were integrated and used directly to quantify M.
- Within the blue box region are the D_Z ‘a,b’ signals and the M ‘b’ signal. The D_Z ‘a,b’ integration value was obtained subtracting the analogous value of the M ‘a’ signal integration (red box region labelled ‘a’).
- Within the green box region are the D_E ‘a,b,c,d’ signals and the D_Z ‘c,d’ signals. The D_E ‘a,b,c,d’ integration value was obtained subtracting the determined integration value of D_Z ‘a,b’ signals (second bullet point).

Table S9. A) M and D signal integrations (Figure S18) of *o*-NC (VT-NMR) B) M and D concentrations of *o*-NC in CD_3OD (Run 3).

Figure S19. Van't Hoff Plot for *o*-NC monomerization (D ⇌ 2M) in CD_3OD (Run 1).

Table S10. Summary of VT-NMR data in CD_3OD

* used in manuscript

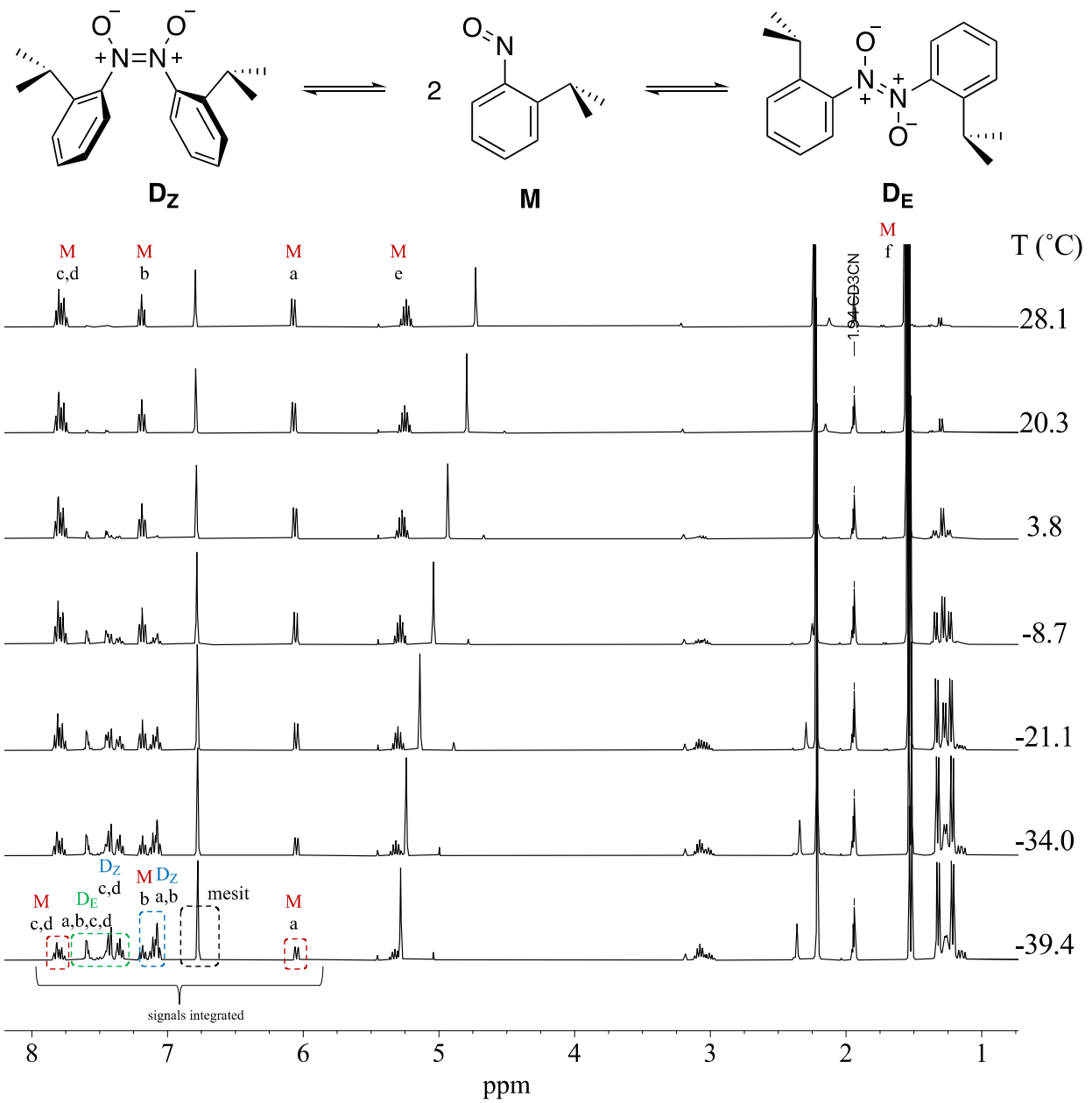


Figure S20. VT-^{1}H NMR spectra (500 MHz) of 0.109 M *o*-NC in CD_3CN (Run 2). For full signal assignment, see Figures S11-13.

- Within the red box region are the M 'c,d' signals which were integrated and used directly to quantify M.
- Within the blue box region are the D_Z 'a,b' signals and the M 'b' signal. The D_Z 'a,b' integration value was obtained subtracting the analogous value of the M 'a' signal integration (red box region labelled 'a').
- Within the green box region are the D_E 'a,b,c,d' signals and the D_Z 'c,d' signals. The D_E 'a,b,c,d' integration value was obtained subtracting the determined integration value of D_Z 'a,b' signals (second bullet point).

Table S11. A) M and D signal integrations (Figure S20) of *o*-NC (VT-NMR) B) M and D concentrations of *o*-NC in CD_3CN (Run 2).

Figure S21. Van't Hoff Plot for *o*-NC monomerization (D ⇌ 2M) in CD_3CN (Run 2).

Table S12. Summary of VT-NMR data in CD_3CN data

* used in manuscript

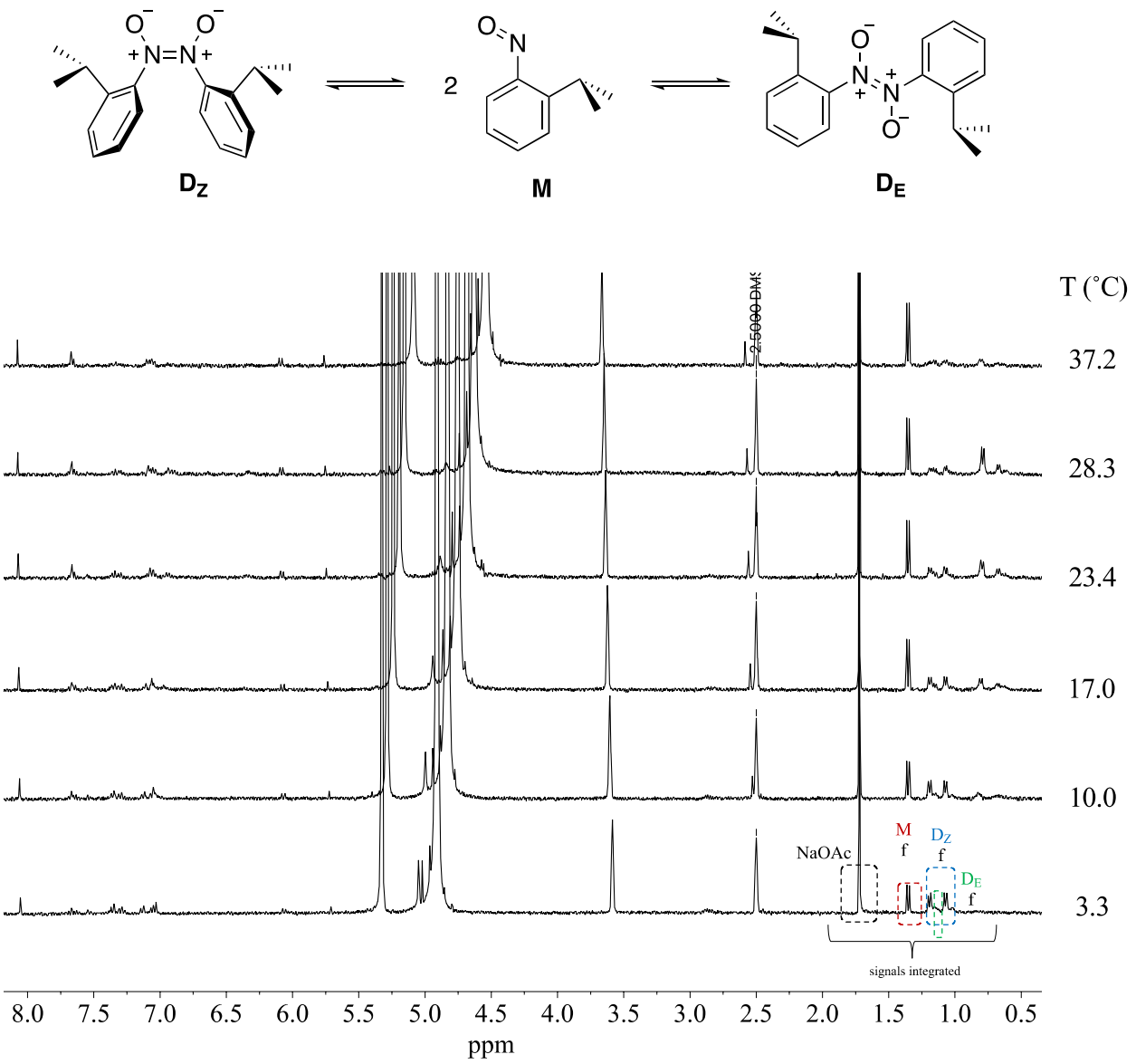


Figure S22. VT-^{1}H NMR spectra (500 MHz) of 0.546 mM *o*-NC in D_2O (Run 1). For full signal assignment, see Figures S11-13.

- For directly quantifying M, the 'f' proton was integrated
- For indirectly quantifying D_Z & D_E, the 'f' region of both was integrated and manual heights were analyzed for changes in inflection of the integral above D_E allowing it to be determined and ultimately subtracted from the total dimer integral

Table S13. A) M and D distribution in D_2O based on the integration of the methyl NMR signals of *o*-NC (VT-NMR). B) M and D distribution of *o*-NC in D_2O (VT-NMR) by concentration.

A

Run 1	Integration Data (methyl-H)				M:D Ratio (adjusted for #H)		
T Correct (K)	M	D_E	D_Z	NaOAc	M	D_E	D_Z
301	38.52	7.31	29.23	100	68%	6%	26%
297	35.27	7.88	33.57	100	63%	7%	30%
290	29.64	7.92	38.67	100	56%	7%	37%
283	26.03	8.62	48.82	100	48%	8%	45%
276	20.94	9.77	55.39	100	39%	9%	52%
310 (warmup)	43.38	6.27	16.94	100	79%	6%	15%

B

Run 1	Concentrations (M)					
T Correct (K)	[M]	$[D_Z]$	$[D_E]$	[NaOAc]	K_m $D_Z \rightleftharpoons 2M$	K_m $D_E \rightleftharpoons 2M$
301	3.79E-04	3.59E-05	1.44E-04	1.97E-03	3.79E-04	3.59E-05
297	3.47E-04	3.87E-05	1.65E-04	1.97E-03	3.47E-04	3.87E-05
290	2.91E-04	3.89E-05	1.90E-04	1.97E-03	2.91E-04	3.89E-05
283	2.56E-04	4.24E-05	2.40E-04	1.97E-03	2.56E-04	4.24E-05
276	2.06E-04	4.80E-05	2.72E-04	1.97E-03	2.06E-04	4.80E-05
310 (warmup)	4.26E-04	3.08E-05	8.33E-05	1.97E-03	4.26E-04	3.08E-05

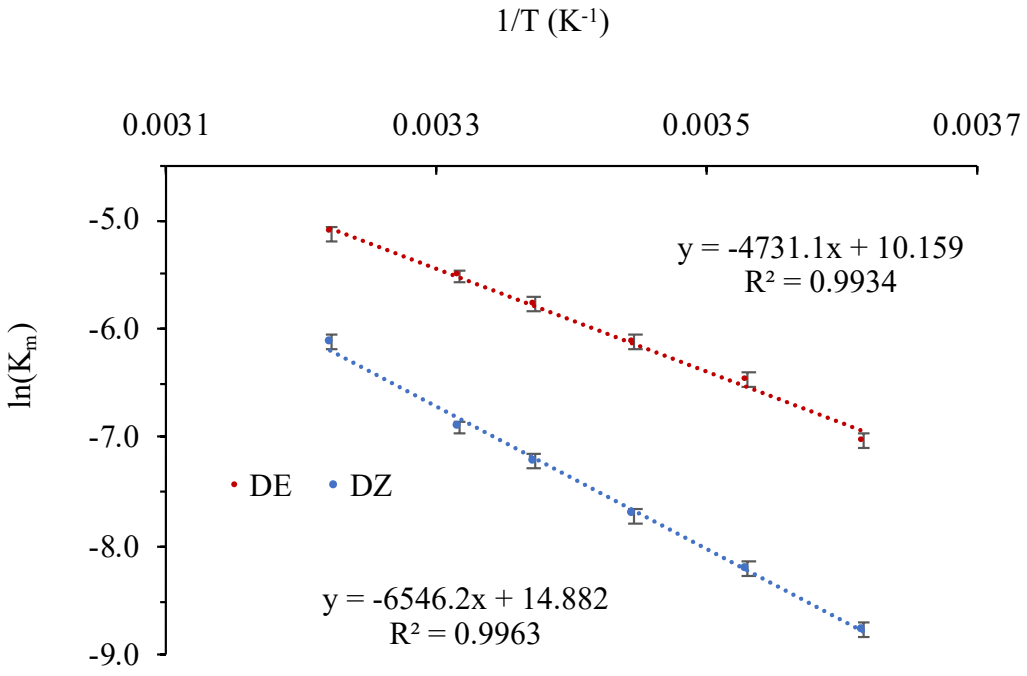


Figure S23. Van't Hoff Plots for *o*-NC monomerization (D ⇌ 2M) in D_2O (Run 1).

Table S14. Summary of VT-NMR data in D_2O

D_2O (80)		[total *o*-NC]	ΔH˚ (kJ/mol)	ΔS˚ (J/mol*k)	ΔG˚ 298 K (kJ/mol)	K_m 298 K (M)	ΔT (˚C)
Run 1*	D_Z	0.546 mM	54.4 ±1.7	124 ± 6	17.4 ± 0.1	0.00088 ± 0.00003	3.33 – 37.2
	D_E		39.3 ± 1.6	84 ± 5	14.3 ± 0.1	0.0032 ± 0.0001	
Run 2	D_Z	0.586 mM	58.2 ± 4.7	140 ± 16	16.5	0.00131	2.77 - 25.8
	D_E		46.8 ± 3.7	113 ± 13	13.1	0.00508	
Average	D_Z	0.586 mM	56.3 ± 3.2	132 ± 11	17.0	0.00108	2.77 – 37.2
	D_E		43.1 ± 2.7	98.5 ± 9	13.7	0.00408	

* used in manuscript

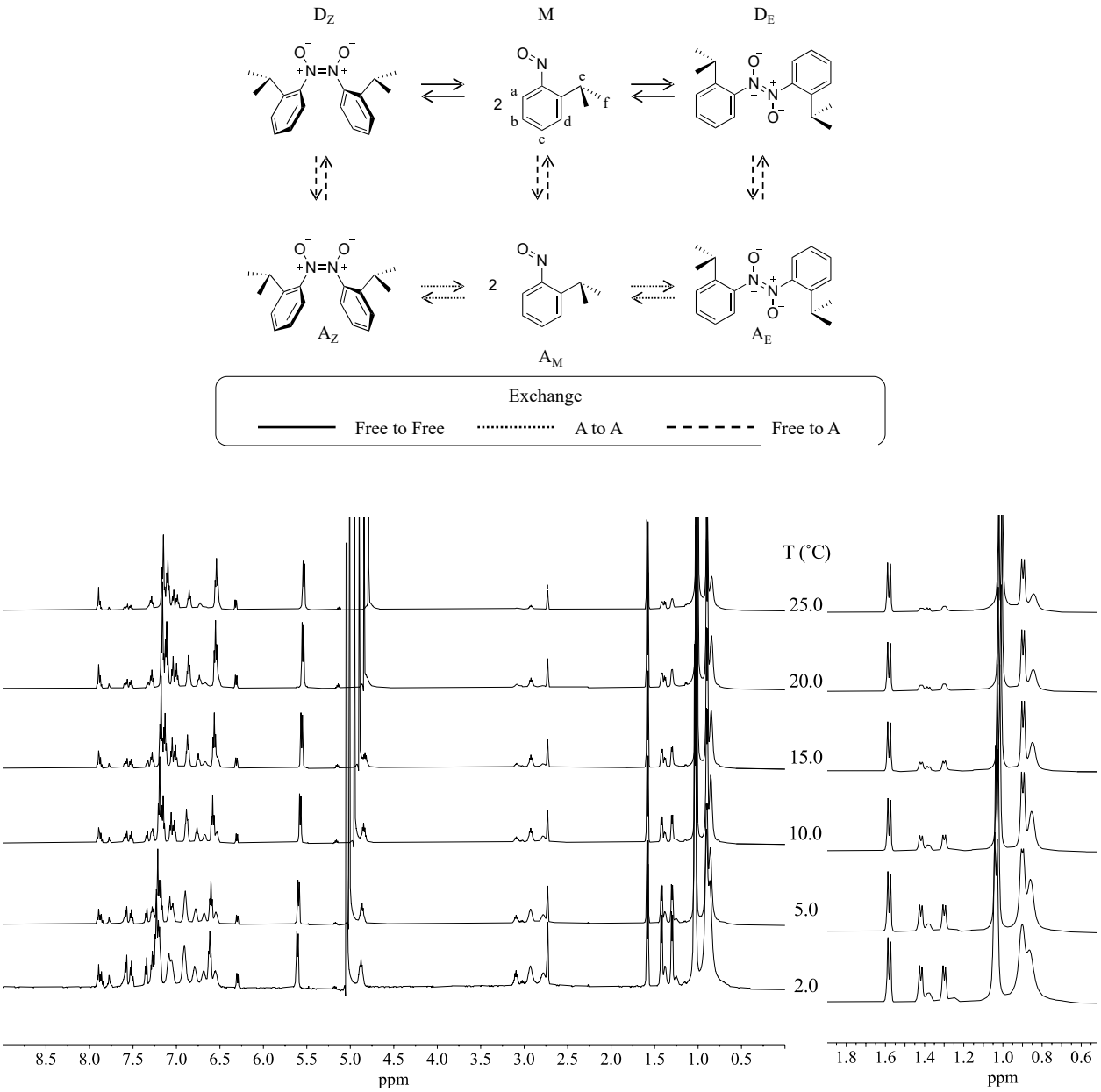


Figure S24. Higher resolution, VT ^{1}H-NMR spectra (500 MHz) of ~5.0 mM *o*-NC in D_2O (approximate temperatures).

6. ^{1}H-NMR of *o*-NC aggregate formation in D_2O at variable concentrations and times

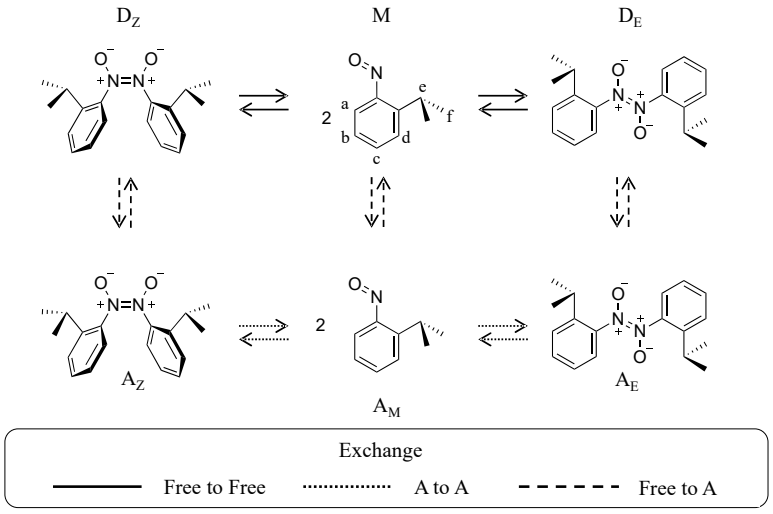
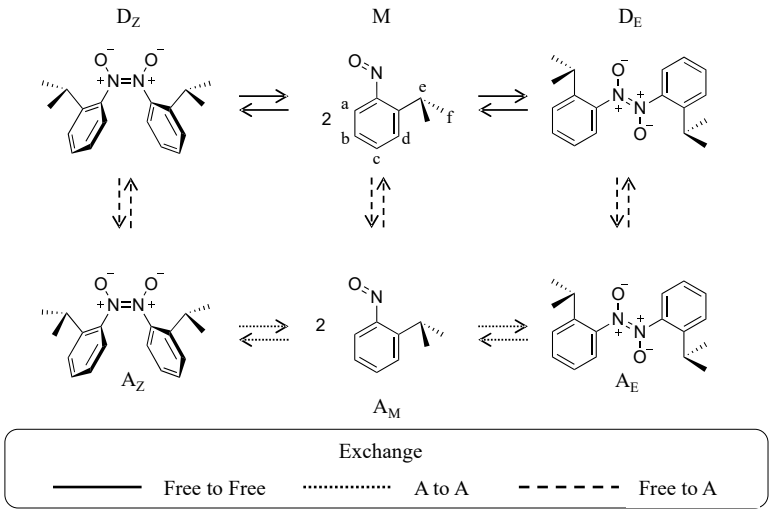


Figure S25. Concentration (mM) dependence of *o*-NC in D_2O by ^{1}H-NMR spectroscopy



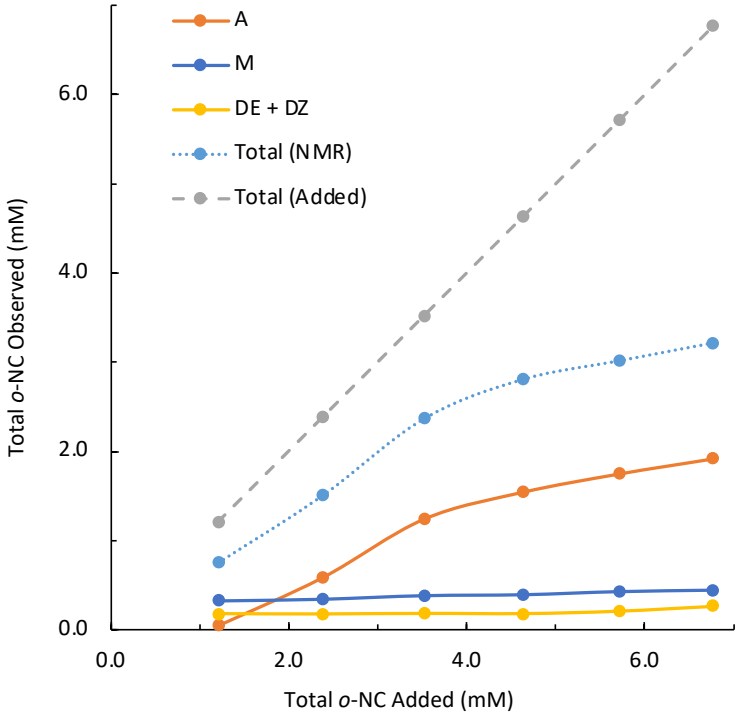


Figure S26. Concentration (mM) profile of *o*-NC structures in D_2O at 25 ˚C.

Figure 5 shows the concentration profile of *o*-NC components in D_2O as *o*-NC concentration is increased beyond 1 mM. Dissolved M and D signals remain steady at their saturation values, while the aggregate signals grow in intensity with added *o*-NC (added as stock solution in DMSO-d_6). The solution also continues to grow more turbid. Not all the added *o*-NC is being observed in the NMR spectrum as determined by quantitation using Me_2SO_2 as internal standard.

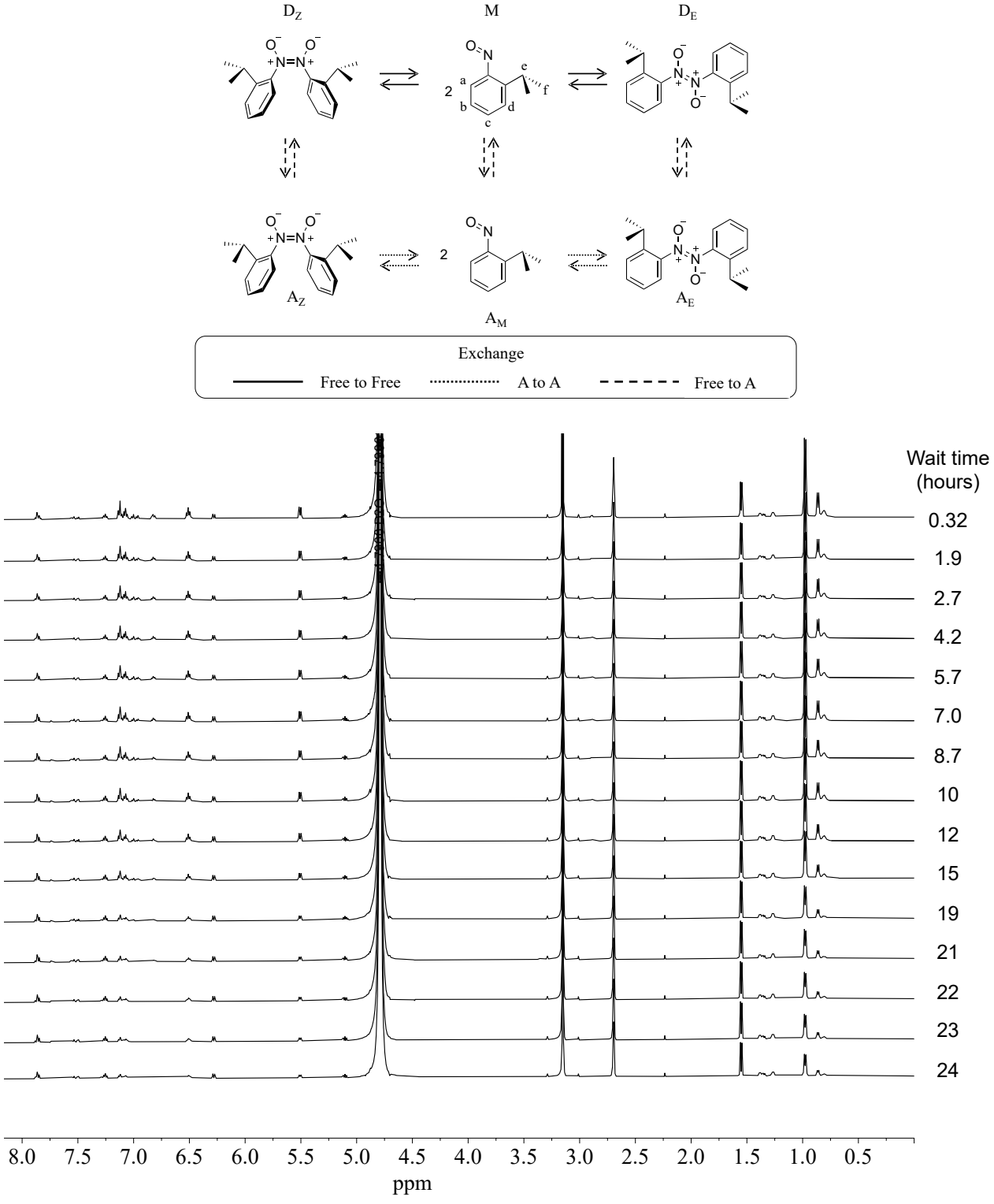
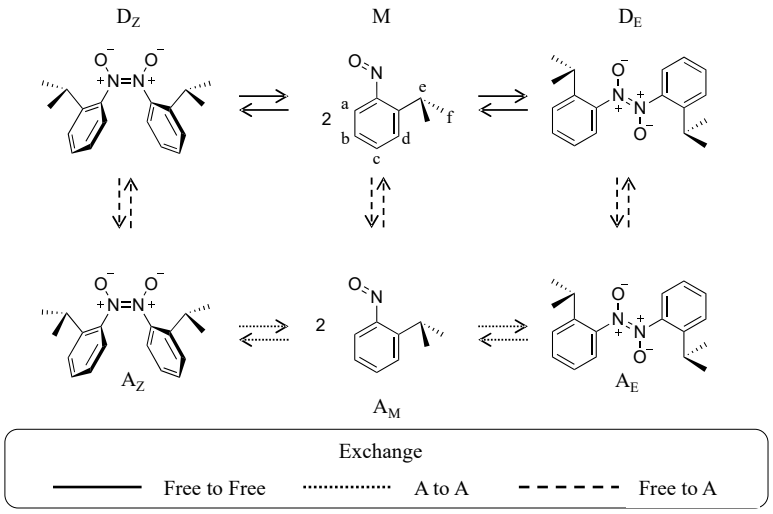


Figure S27. ^{1}H NMR spectra (D_2O, 500 MHz) Concentration of 2.40 mM *o*-NC solution species (M, D, A) as a function of time (after preparation of sample).



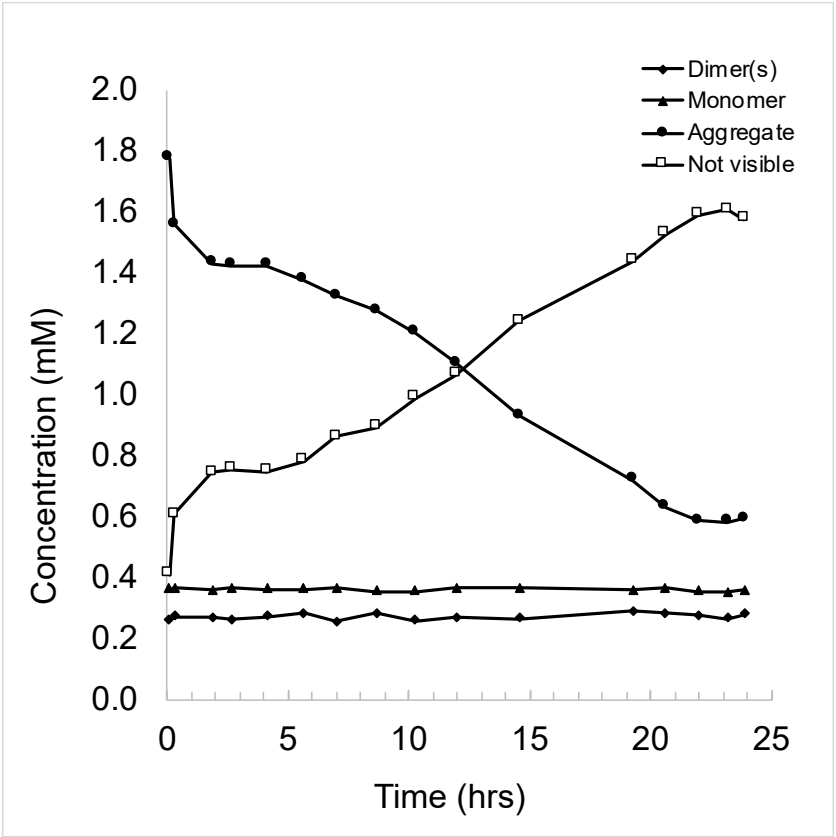


Figure S28. Plot of 2.40 mM *o*-NC solution species (M, D, A) as a function of time (since preparation of sample).

7. *o*-NC aggregate analysis in water via COSY, EXSY, DOSY NMR spectroscopy

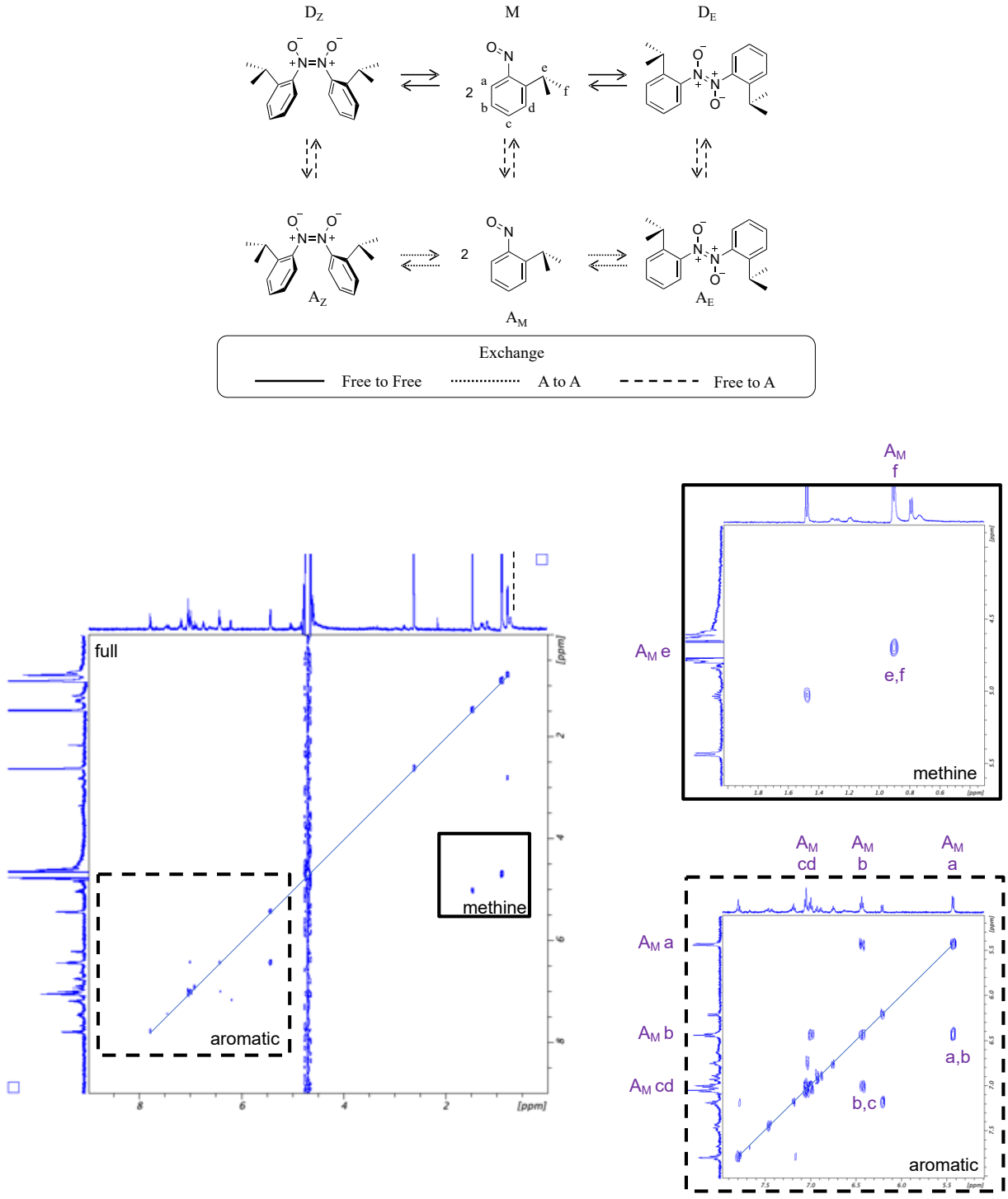


Figure S29. 2D COSY spectrum (D_2O, 500 MHz) ~4.1 mM *o*-NC in D_2O

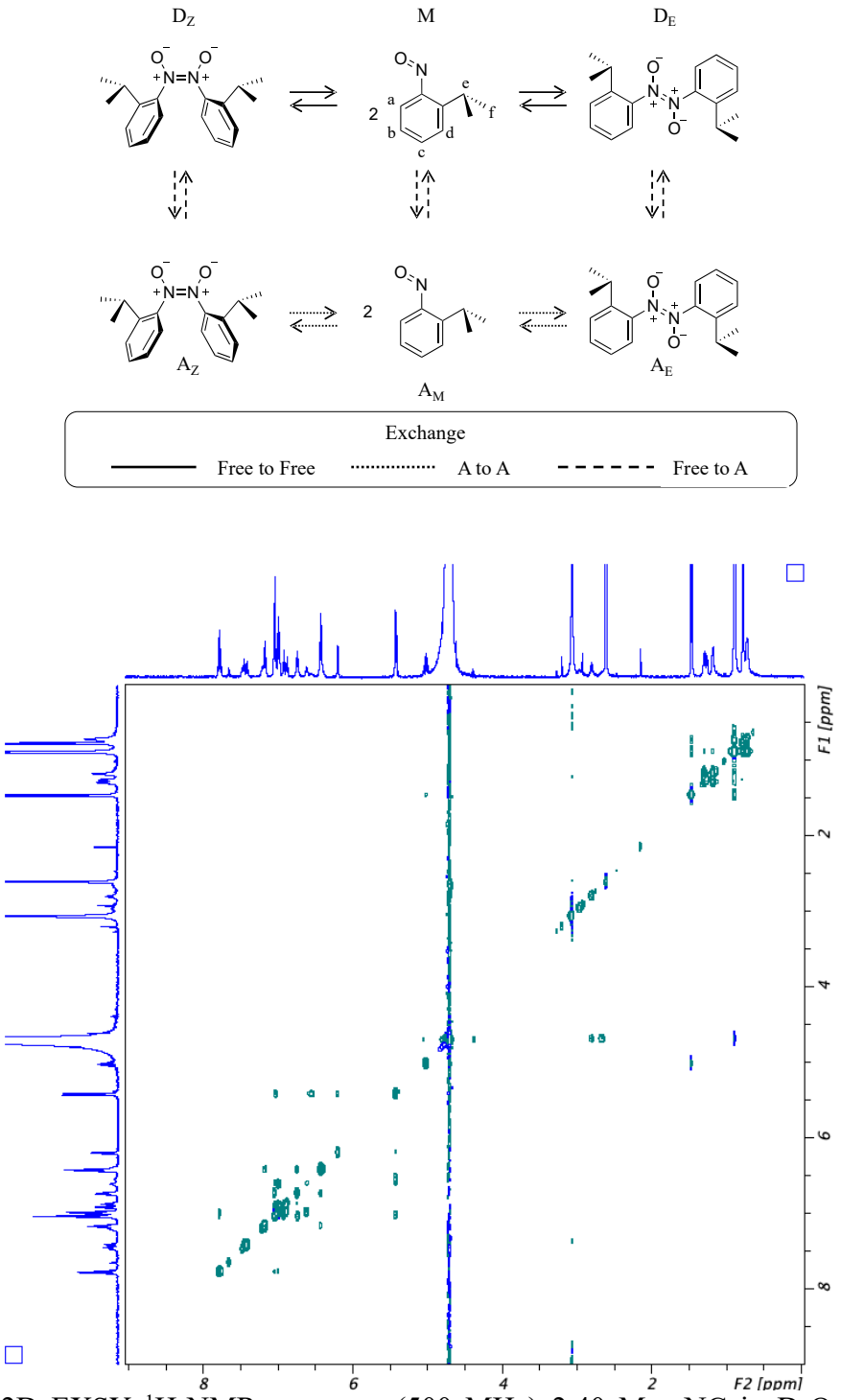


Figure S30. 2D EXSY ^{1}H-NMR spectrum (500 MHz) 2.40 M *o*-NC in D_2O. In this EXSY exchange peaks (green) observed for M ⇌ D, M ⇌ A, D ⇌ A but not D ⇌ D.

For zoomed aromatic and methyl regions, refer to pages S45 and S46.

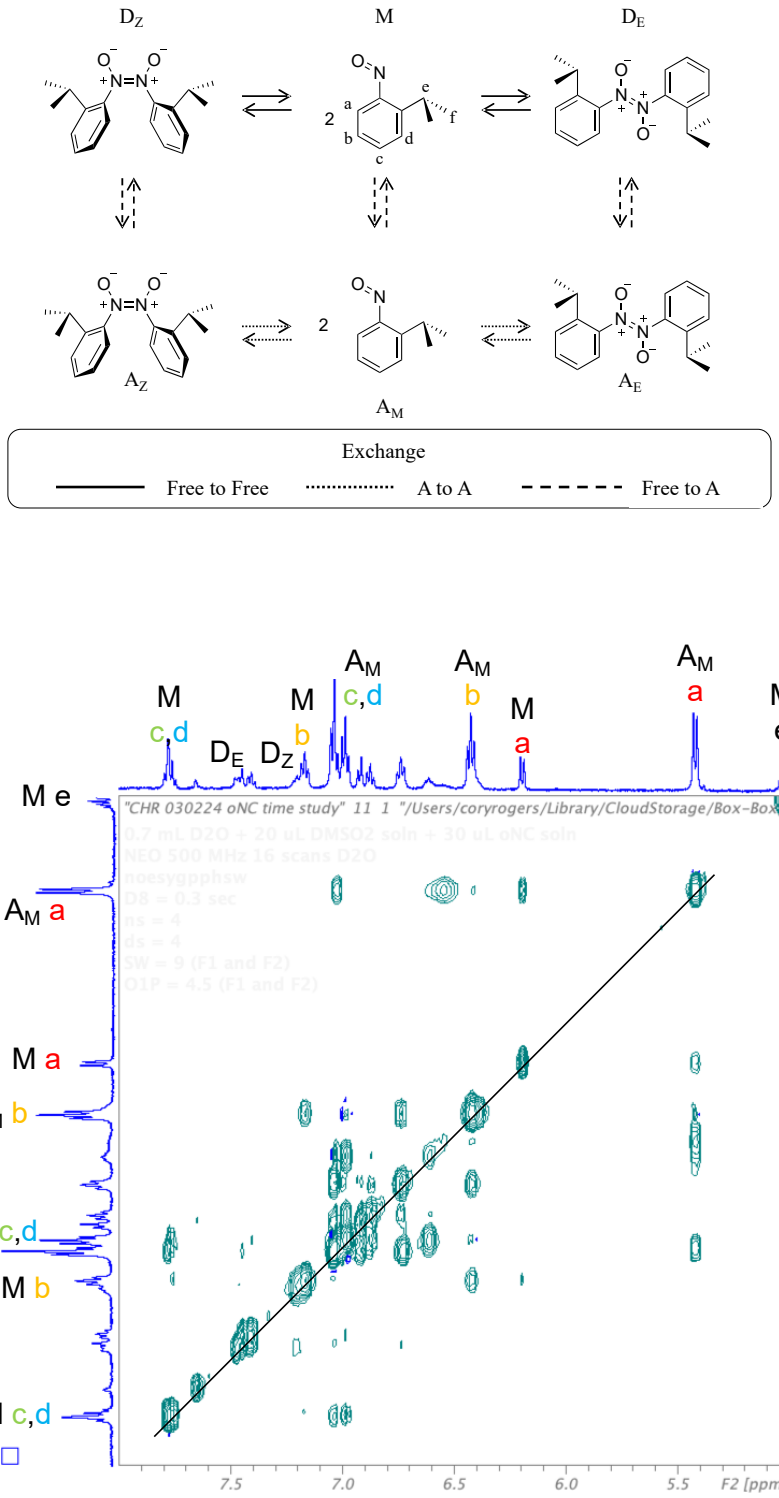


Figure S31. 2D EXSY ^{1}H-NMR spectrum (500 MHz) aromatic region of 2.40 M *o*-NC in D_2O. In this EXSY exchange peaks (green) observed for M ⇌ D, M ⇌ A, D ⇌ A but not D ⇌ D.

Note: major exchange signals representing M ⇌ A_M are indicated by dashed lines.

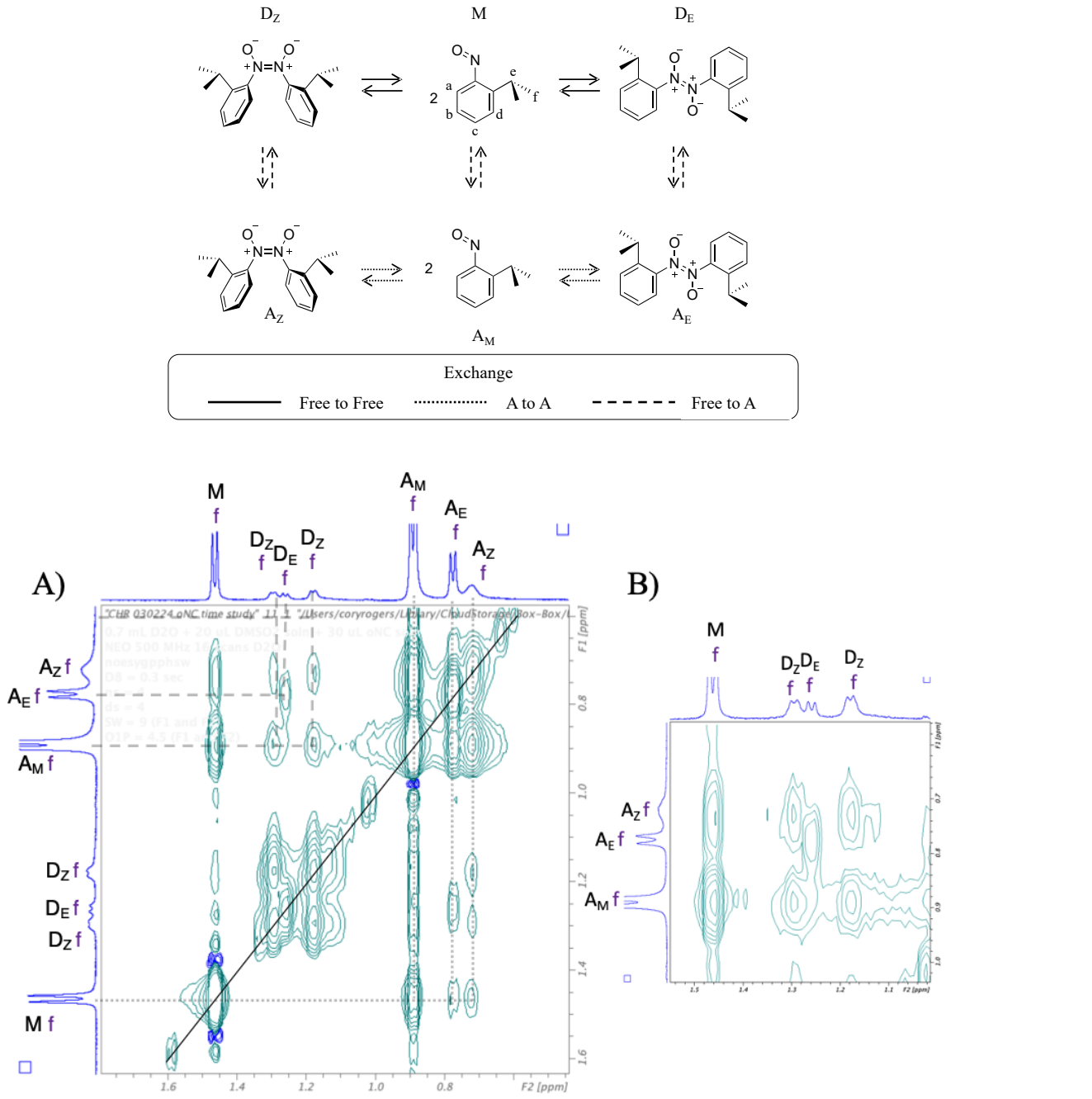


Figure S32. A) 2D EXSY ^{1}H-NMR spectrum (500 MHz) methyl region of 2.40 M *o*-NC in D_2O. In this EXSY exchange peaks (green) observed for M ⇌ D, M ⇌ A, D ⇌ A but not D ⇌ D and B) Zoom region for D ⇌ A_M

Note: diastereotopic methyl signals for D_Z (anti) exchange ~1.1-1.3 ppm.

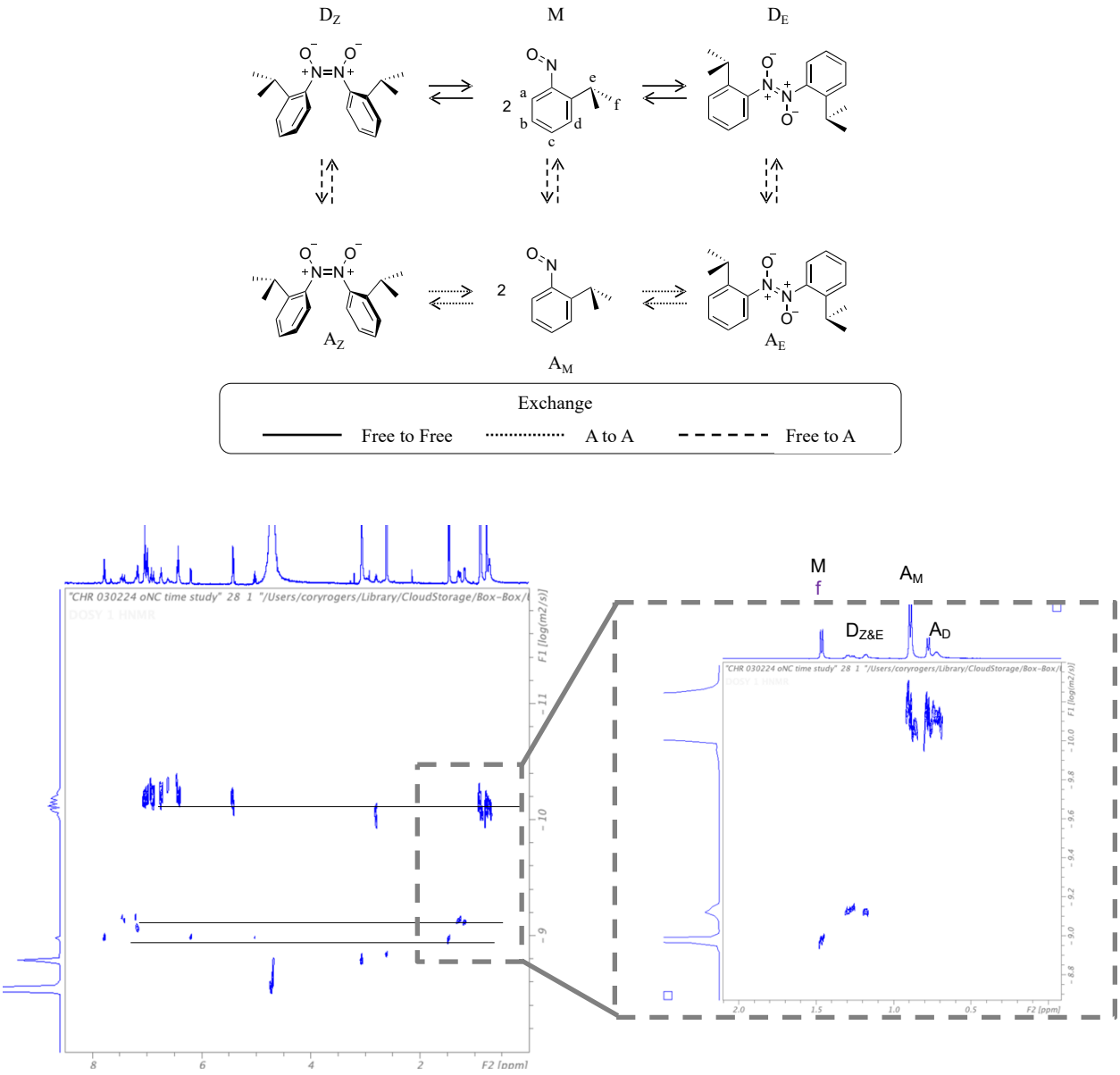


Figure S33. 2D DOSY spectrum (500 MHz) 2.40 mM *o*-NC in D_2O

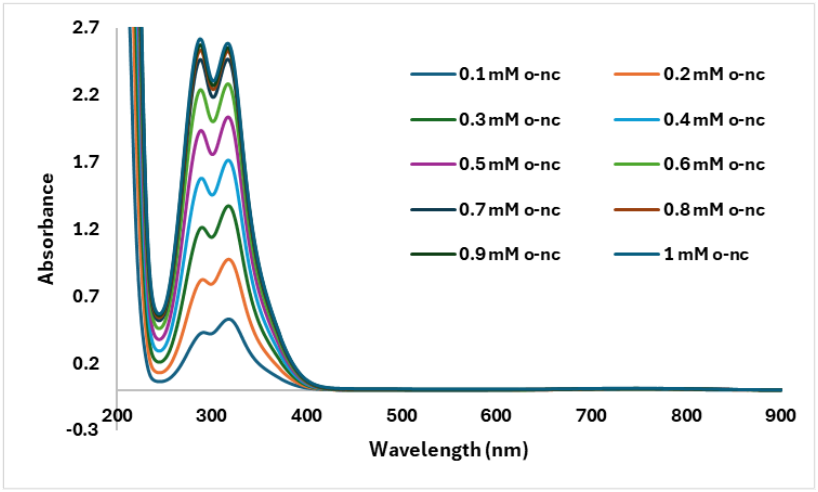
Table S15. Diffusion coefficients and hydrodynamic radii from DOSY analysis of M, D, and A assemblies of 2.40 mM *o*-NC over time.

Stokes-Einstein Eq.

$$D = \frac{K_B T}{6\pi\eta R}$$

	Monomer		Dimer(s)		Aggregate	
time	D	R	D	R	D	R
hrs	10^{10} m²/s	Å	10^{10} m²/s	Å	10^{10} m²/s	Å
1.8	9.07	2.71	6.10	4.0	0.180	136
3.2	9.67	2.54	6.34	3.87	0.624	39.3
4.7	10.1	2.43	7.17	3.42	0.650	37.7
6.2	10.1	2.42	7.18	3.41	0.692	35.5
7.5	10.3	2.39	7.59	3.23	0.717	34.2
9.2	10.2	2.41	7.46	3.29	0.744	33.0
11	10.2	2.40	7.49	3.27	0.768	31.9
12	10.2	2.42	7.35	3.34	0.733	33.4
15	9.92	2.47	6.70	3.66	0.743	33.0
20	10.1	2.44	7.17	3.42	0.872	28.1
22	9.92	2.47	6.66	3.68	0.786	31.2
23	10.1	2.43	7.14	3.44	0.820	29.9
avg	9.97	2.46	7.03	3.50	0.74	33.4
stdev	0.33	0.09	0.47	0.25	0.18	3.2

A)



B)

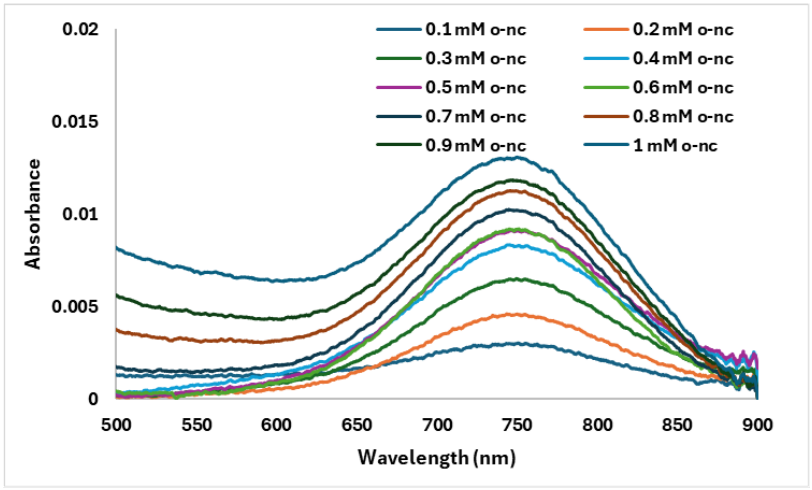


Figure S34. Concentration based UV-Vis titrations of *o*-NC in water.

Figure S35. Dynamic light scattering (DLS) of 2.0 mM *o*-NC in water at different times (0, 2, 4, 6, 24 hours) after initial sample preparation.

8. DFT calculation data supporting *o*-NC assembly in organic solvents and water

Computational details

Density functional theory (DFT) calculations were performed using Gaussian 16.[6] Geometry optimizations were performed with the ωB97X-D functional,[7] using the 6-31+G(d,p) basis set, and SMD implicit solvation[8] to model the effects of chloroform or water. Vibrational analysis on all stationary points allowed for the confirmation of minima structures (zero imaginary frequencies) and transition structures (TS, exactly one imaginary frequency). Zero-point energy, enthalpy and free energy corrections were obtained with a state of 1 atm pressure and 298.15 K temperature using Goodvibes version 2.0.3,[9] applying Grimme's quasiharmonic oscillator approximation with a frequency cut-off value of 100 cm^{-1}. To obtain accurate energies, single point energy refinements were then performed at the ωB97X-D/aug-cc-pVTZ level of theory, using the SMD implicit solvation model. The free energy values reported were then obtained by adding the free energy corrections obtained from the frequency analysis to the single-point electronic energies. The free energy values for the chloroform or water solvation models are different, but the geometries of the structures are similar, see Figure S33 and S35. Visualizations of the computed structures were prepared using CYLview.[10]

Additional figures and schemes

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[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Rev. C.01, Wallingford, CT, 2016.

[7] J. D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys Chem Chem Phys* 2008, **10**, 6615-20.

[8] A. V. C. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* 2009, **113**, 6378–6396.

[9] I. P. Funes-Ardoiz, R. S. GoodVibes: GoodVibes 2.0.3 2018.

[10] C. Y. Legault, CYLview, 1.0.565b. Université de Sherbrooke 2009.

Additional figures and schemes

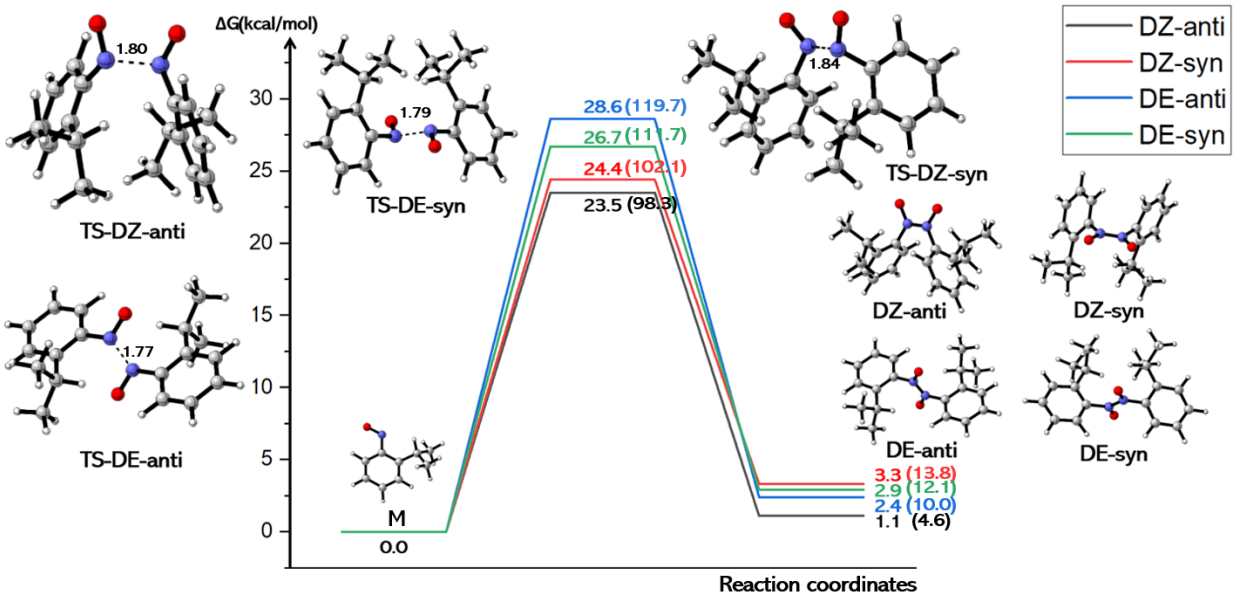

Figure S36. PES from Monomer to Dimers in chloroform: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(chloroform)//ωB97X-D/aug-cc-pVTZ/SMD(chloroform). Energies are in kcal/mol with (kJ/mol in parenthesis). Bond lengths in Å.

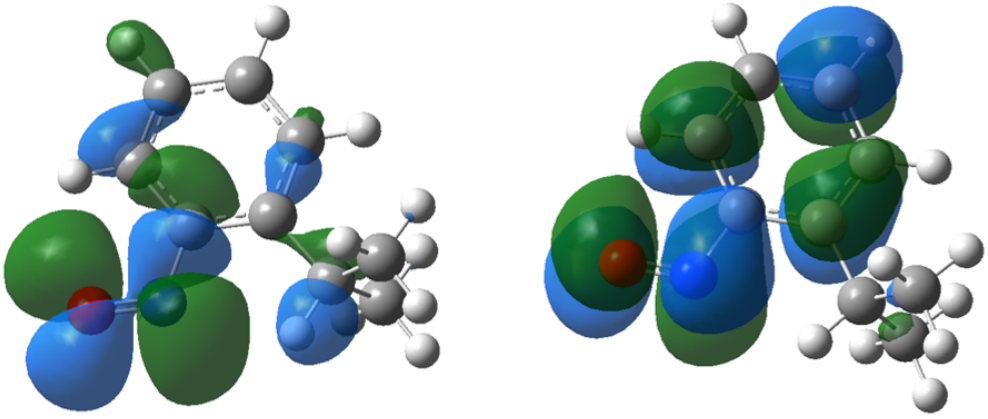

Figure S37. HOMO and LUMO for monomer in chloroform: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(chloroform).

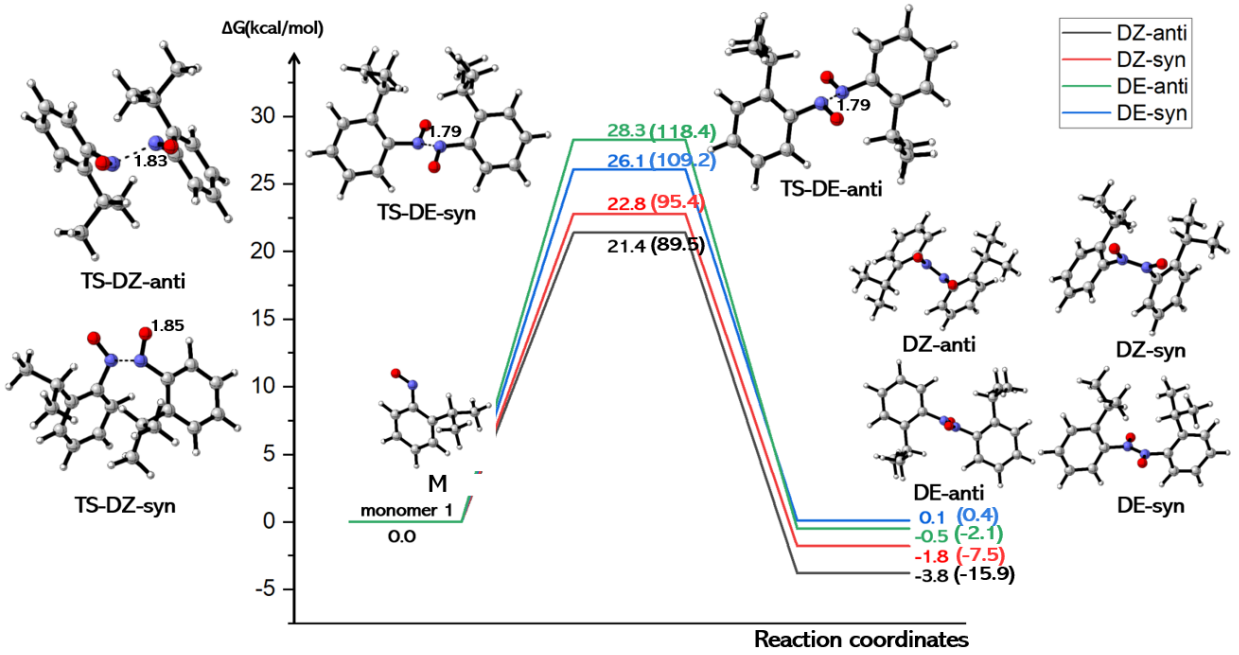

Figure S38. PES from Monomer to Dimers in water: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(water)//ωB97X-D/aug-cc-pVTZ/SMD(water). Energies are in kcal/mol with (kJ/mol in parenthesis). Bond length in Å.

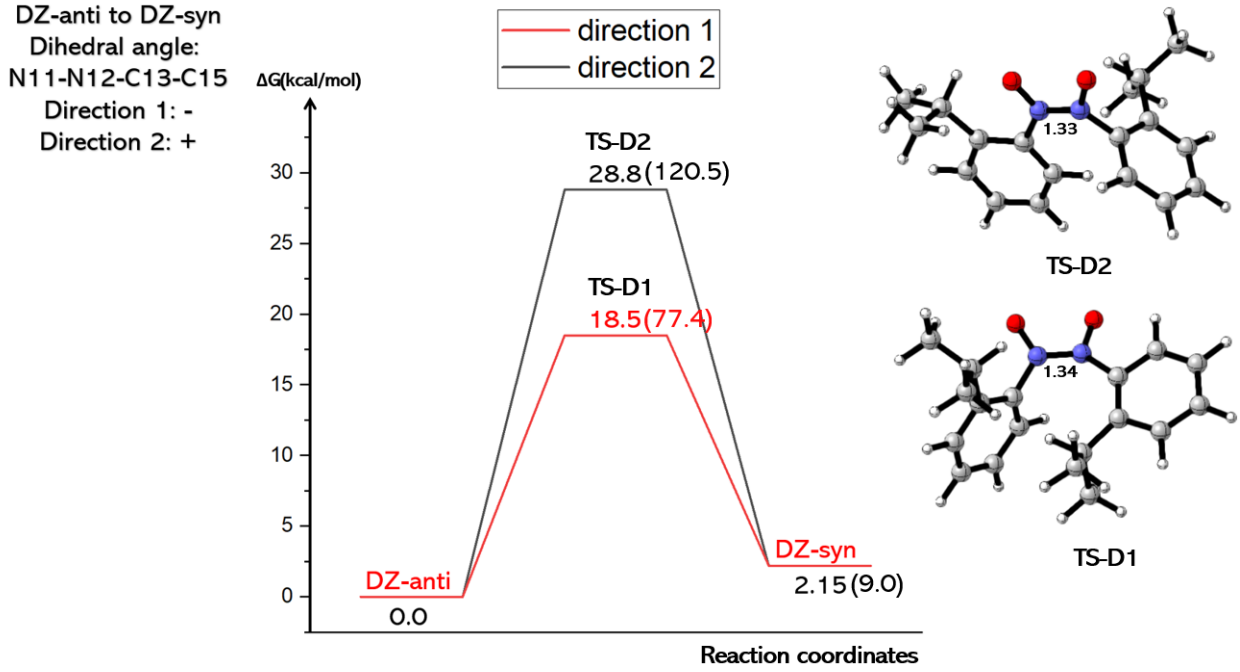

Figure S39. PES of phenyl rotation within the D_Z dimer: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(chloroform)//ωB97X-D/aug-cc-pVTZ/SMD(chloroform). Energies are in kcal/mol with (kJ/mol in parenthesis). Bond length in Å.

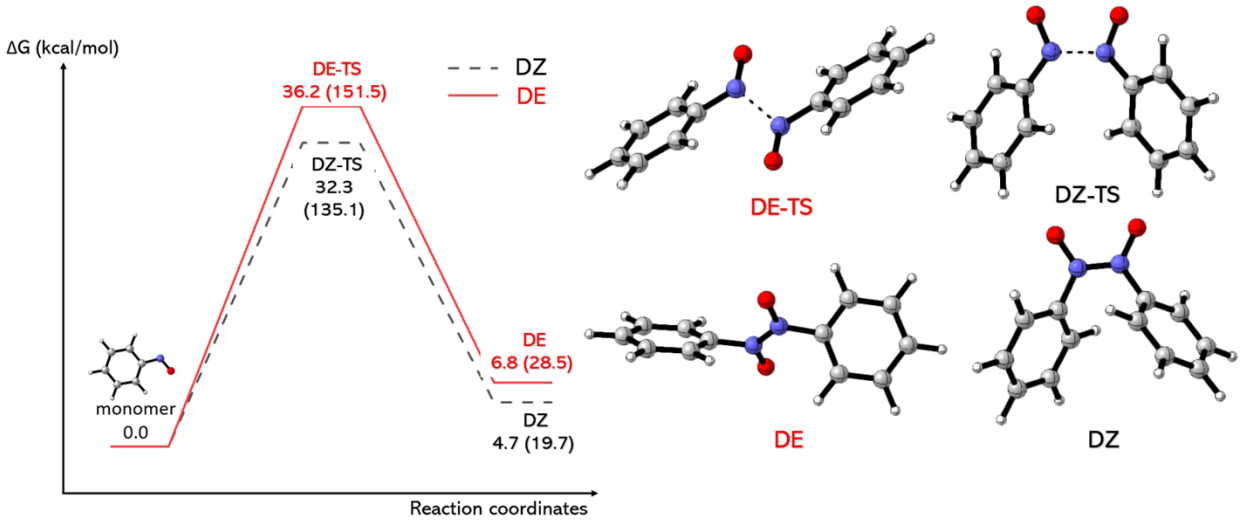

Figure S40. PES for nitrosobenzene from Monomer to Dimers in chloroform: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(chloroform)//ωB97X-D/aug-cc-pVTZ/SMD(chloroform). Energies are in kcal/mol with (kJ/mol in parenthesis). Bond lengths in Å.

Figure S41. Modeling of specific solvation effect of M to D_Z in water: Calculation performed at ωB97X-D/6-31G(d,p)/SMD(water)//ωB97X-D/aug-cc-pVTZ/SMD(water). Energies are in kcal/mol with (kJ/mol).

With explicit water molecules added into the calculation, the M → D_Z free energy of reaction becomes even more exergonic. This suggests that the dimer is preferentially stabilized by polar, hydrogen bond-donating solvents.

Complete energy data

Energy (E), enthalpy (H) and quasi-harmonic-corrected free energy (qh-G(T)) are obtained from the ωB97X-D/6−31+G(d,p)/SMD optimizations and frequency calculations. Single-point refinements (SPE) are obtained at the ωB97X-D/aug-cc-pVTZ/SMD level of theory.

Table S16. Absolute energy (in Hartrees) of all computed structures

Name (**chloroform**)	E	H	qh-G(T)	aug-cc-pVTZ
DZ-anti	-958.759889	-958.365463	-958.433394	-959.029407
DZ-syn	-958.756871	-958.362511	-958.430065	-959.026292
M	-479.366399	-479.171419	-479.218096	-479.500639
DE-anti	-958.755055	-958.361219	-958.43093	-959.024149
DE-syn	-958.757017	-958.363101	-958.431923	-959.025998
TS-DZ-anti	-958.72224	-958.331283	-958.399367	-958.990158
TS-DZ-syn	-958.720604	-958.3295	-958.397752	-958.98856
TS-DE-anti	-958.716521	-958.325689	-958.394301	-958.984379
TS-DE-syn	-958.713142	-958.322276	-958.391133	-958.98112

Name (**water**)	E	H	qh-G(T)	aug-cc-pVTZ
DZ-anti	-958.752662	-958.358369	-958.426026	-959.020865
DZ-syn	-958.749449	-958.355205	-958.422796	-959.017588
M	-479.358453	-479.163682	-479.210335	-479.492186
DE-anti	-958.743715	-958.350138	-958.41988	-959.011734
DE-syn	-958.746695	-958.352733	-958.421059	-959.01449
TS-DZ-anti	-958.708988	-958.318541	-958.387036	-958.975948
TS-DZ-syn	-958.706798	-958.316344	-958.384776	-958.973843
TS-DE-anti	-958.7012	-958.310769	-958.3795	-958.968165
TS-DE-syn	-958.698333	-958.307609	-958.376071	-958.965318

Name (**chloroform**)	E	H	qh-G(T)	aug-cc-pVTZ
TS1-DZ-anti to DZ-syn-dihedral	-958.715235	-958.322136	-958.38815	-958.98418
TS2-DZ-anti to DZ-syn-dihedral	-958.730766	-958.337724	-958.404032	-959.00017

Name (**water**)	E	H	qh-G(T)	aug-cc-pVTZ
M-H_2O	-555.787533	-555.565178	-555.61965	-555.780396
DZ-anti-2H_2O	-1111.619344	-1111.169379	-1111.248078	-1111.569871

Nitrosobenzene

Name (**chloroform**)	E	H	qh-G(T)	aug-cc-pVTZ
DZ	-722.90532	-722.689971	-722.74175	-723.115852

DE	-722.901598	-722.686555	-722.738878	-723.111655
Monomer	-361.443102	-361.337666	-361.375132	-361.54787
DZ-TS	-722.868856	-722.656489	-722.708751	-723.068498
DE-TS	-722.863023	-722.650872	-722.703548	-723.061631

XYZ coordinates of all DFT-optimized geometries and vibrational frequencies for TS

DE-anti (chloroform)

C	2.97375	2.71719	-0.05798
C	1.74080	2.11608	-0.27198
C	1.65893	0.72807	-0.24598
C	2.75301	-0.10683	-0.02698
C	3.98095	0.53129	0.18102
C	4.09482	1.91830	0.16902
H	3.06065	3.79820	-0.07198
H	0.84875	2.70600	-0.45998
H	4.86601	-0.07363	0.35602
H	5.06378	2.37839	0.33502
N	0.35699	0.15495	-0.53598
N	-0.36598	-0.23911	0.46602
O	-0.05101	0.07691	-1.73198
O	0.04502	-0.16808	1.66202
C	-1.68493	-0.76824	0.17402
C	-2.76601	0.11066	0.10502
C	-1.79880	-2.14625	0.03602
C	-4.01596	-0.47145	-0.13498
C	-3.05575	-2.69136	-0.19598
H	-0.91574	-2.77217	0.11102
C	-4.16183	-1.84746	-0.28398
H	-4.89201	0.16547	-0.20598
H	-3.16865	-3.76537	-0.30698
H	-5.14779	-2.26456	-0.46798
C	2.64015	-1.61984	-0.01498
C	3.00720	-2.18980	1.36002
C	3.49121	-2.24676	-1.12698
H	1.59717	-1.88793	-0.21598
H	2.39016	-1.74386	2.14702
H	2.85130	-3.27382	1.37302
H	4.06018	-1.99971	1.59802
H	3.21217	-1.85179	-2.10898
H	4.55719	-2.04966	-0.96898
H	3.34931	-3.33277	-1.14198
C	-2.60015	1.61368	0.24802
C	-3.58920	2.20959	1.25602
C	-2.71421	2.29967	-1.11998
H	-1.59517	1.80877	0.63702
H	-3.51716	1.70759	2.22602
H	-3.37130	3.27161	1.40502
H	-4.62320	2.13049	0.90402
H	-1.98618	1.89173	-1.82798
H	-3.71620	2.16058	-1.54198
H	-2.53631	3.37568	-1.01998

DE-syn (chloroform)

C	3.92201	0.16191	-0.14905
C	2.55401	0.26596	0.12995
C	1.83897	-0.93102	0.14995
C	2.41392	-2.17604	-0.07705
C	3.77492	-2.24508	-0.34505
C	4.52596	-1.06911	-0.38205
H	4.52404	1.06389	-0.18505
H	1.79889	-3.06901	-0.04605
H	4.24489	-3.20610	-0.52305
H	5.58996	-1.11315	-0.59305
N	0.42697	-0.90597	0.48895
N	-0.42603	-0.90494	-0.48905
O	0.06197	-0.89095	1.70195
O	-0.06203	-0.88995	-1.70205
C	-1.83903	-0.93088	-0.15005
C	-2.55399	0.26614	-0.13005

C	-2.41408	-2.17586	0.07695
C	-3.92199	0.16119	0.14795
C	-3.77508	-2.24482	0.34495
H	-1.79811	-3.06889	0.04595
C	-4.52604	-1.06979	0.38195
H	-4.52496	1.06421	0.18495
H	-4.24411	-3.20580	0.52295
H	-5.59004	-1.11375	0.59295
C	1.88806	1.61198	0.35395
C	1.77608	2.37999	-0.96905
C	2.60209	2.44196	1.42595
H	0.87505	1.42702	0.72095
H	1.25506	1.78901	-1.72905
H	1.22412	3.31401	-0.82005
H	2.76809	2.63295	-1.36005
H	2.68307	1.88796	2.36595
H	3.61010	2.73192	1.10995
H	2.03812	3.35998	1.61895
C	-1.88894	1.61212	-0.35405
C	-1.77592	2.38011	0.96995
C	-2.60191	2.44214	-1.42505
H	-0.87495	1.42808	-0.72105
H	-1.25494	1.78809	1.72895
H	-1.22388	3.31409	0.82095
H	-2.76891	2.63215	1.35995
H	-2.68293	1.88814	-2.36605
H	-3.60990	2.73218	-1.11005
H	-2.03888	3.36112	-1.61805

DZ-anti (chloroform)

C	-2.70293	0.92910	-1.46542
C	-2.19901	0.35138	-0.29574
C	-1.03597	0.92497	0.22361
C	-0.41286	2.03325	-0.34073
C	-0.93678	2.58097	-1.50442
C	-2.08282	2.02140	-2.06677
H	-3.60296	0.51944	-1.91368
H	0.46817	2.45390	0.13053
H	-0.45770	3.43919	-1.96292
H	-2.50276	2.44196	-2.97454
N	-0.49704	0.42220	1.47733
N	0.49689	-0.42389	1.47687
C	1.03587	-0.92521	0.22259
C	2.19893	-0.35001	-0.29606
C	0.41278	-2.03283	-0.34307
C	2.70290	-0.92738	-1.46738
C	0.93676	-2.57920	-1.50737
H	-0.46826	-2.45402	0.12767
C	2.08282	-2.01797	-2.06903
H	3.60295	-0.51720	-1.91412
H	0.45769	-3.43689	-1.96688
H	2.50280	-2.43848	-2.97826
O	0.97883	-0.82456	2.56764
O	-0.97903	0.82161	2.56856
C	-2.90712	-0.80395	0.38857
C	-3.31820	-1.90535	-0.59407
C	-4.11909	-0.28630	1.17785
H	-2.21318	-1.24643	1.11133
H	-2.47622	-2.22906	-1.21424
H	-3.69129	-2.77364	-0.04158
H	-4.12116	-1.57189	-1.26090
H	-3.81804	0.46424	1.91329
H	-4.85504	0.16715	0.50309
H	-4.60518	-1.11157	1.70736
C	2.90702	0.80253	0.38963
C	3.31914	1.90606	-0.59173
C	4.11896	0.28396	1.17835
H	2.21304	1.24517	1.11287
H	2.47718	2.23049	-1.21155
H	3.69220	2.77371	-0.03821
H	4.12112	1.57338	-1.25790
H	3.81687	-0.46743	1.91391
H	4.85493	-0.16871	0.50411
H	4.60502	1.10961	1.70884

DZ-syn (chloroform)

C	2.51301	-0.97408	-1.49489
C	2.01803	-0.33907	-0.34989
C	1.03801	-1.03704	0.36711
C	0.60697	-2.31303	0.01511
C	1.12195	-2.91404	-1.12589
C	2.07097	-2.23407	-1.88589
H	3.27002	-0.47310	-2.08889
H	-0.12205	-2.82800	0.63011
H	0.78792	-3.90503	-1.41289
H	2.48096	-2.69208	-2.78089
N	0.52502	-0.44502	1.59211
N	-0.70596	-0.00498	1.66811
C	-1.68397	-0.28996	0.62611
C	-2.47301	-1.41793	0.83311
C	-1.88094	0.59805	-0.43389
C	-3.47801	-1.71990	-0.07489
H	-2.28802	-2.04794	1.69811
C	-2.90395	0.26308	-1.33089
C	-3.68499	-0.87489	-1.16389
H	-4.09404	-2.60088	0.06911
H	-3.09993	0.91409	-2.17689
H	-4.46800	-1.09687	-1.88289
O	-1.09395	0.55703	2.72511
O	1.29603	-0.27804	2.57211
C	2.58007	0.99892	0.10311
C	2.75110	1.99191	-1.05089
C	3.91206	0.78488	0.83711
H	1.88108	1.43894	0.82111
H	1.84110	2.07894	-1.64989
H	2.99213	2.98190	-0.64989
H	3.57009	1.70289	-1.71789
H	3.78504	0.11988	1.69511
H	4.65905	0.34985	0.16311
H	4.29909	1.74386	1.19911
C	-1.09491	1.89003	-0.56489
C	-1.80587	3.01305	0.20611
C	-0.84689	2.29902	-2.01889
H	-0.11791	1.73600	-0.09689
H	-1.93888	2.75005	1.25911
H	-1.21784	3.93603	0.15411
H	-2.79287	3.21108	-0.22589
H	-0.38092	1.49100	-2.59289
H	-1.77288	2.59005	-2.52489
H	-0.18087	3.16800	-2.04589

M (chloroform)

C	-2.12773	1.56953	0.00000
C	-2.09600	0.18853	0.00000
C	-0.86113	-0.48072	0.00000
C	0.36301	0.21604	0.00000
C	0.29628	1.61605	0.00000
C	-0.92159	2.28229	0.00000
H	-3.07562	2.09772	0.00000
H	-3.00912	-0.39629	0.00000
H	1.21639	2.19287	0.00000
H	-0.93737	3.36830	0.00000
N	-0.78641	-1.90473	0.00000
O	-1.85453	-2.49252	0.00000
C	1.71387	-0.48023	0.00000
C	2.50894	-0.13338	1.26600
C	2.50894	-0.13338	-1.26600
H	1.53866	-1.55719	0.00000
H	1.94888	-0.39427	2.17000
H	3.45183	-0.69057	1.27800
H	2.75015	0.93457	1.31100
H	1.94888	-0.39427	-2.17000
H	2.74915	0.93457	-1.31100
H	3.45183	-0.69057	-1.27800

TS-DE-anti (chloroform)

Imaginary frequency: -428.19 cm^{-1}

C	3.11280	2.67824	0.09704
C	1.88584	2.15814	-0.28496
C	1.71894	0.77413	-0.33696
C	2.74501	-0.12679	-0.02996
C	3.97697	0.42830	0.33804

C	4.15886	1.80532	0.40704
H	3.25671	3.75225	0.15704
H	1.04879	2.80308	-0.53396
H	4.81002	-0.22764	0.57204
H	5.12483	2.20339	0.70304
N	0.44098	0.22903	-0.73596
N	-0.44098	-0.22903	0.73604
O	-0.20307	0.86899	-1.56096
O	0.20307	-0.86899	1.56104
C	-1.71894	-0.77413	0.33704
C	-2.74501	0.12679	0.03004
C	-1.88584	-2.15814	0.28504
C	-3.97697	-0.42830	-0.33796
C	-3.11280	-2.67824	-0.09696
H	-1.04879	-2.80308	0.53404
C	-4.15886	-1.80532	-0.40696
H	-4.81002	0.22764	-0.57296
H	-3.25671	-3.75225	-0.15696
H	-5.12483	-2.20339	-0.70296
C	2.56112	-1.62481	-0.18796
C	3.16218	-2.42176	0.97304
C	3.13516	-2.08576	-1.53596
H	1.48414	-1.82589	-0.20296
H	2.78716	-2.06179	1.93604
H	2.89326	-3.47778	0.87504
H	4.25618	-2.36268	0.98404
H	2.66512	-1.55380	-2.36896
H	4.21514	-1.90568	-1.58196
H	2.96224	-3.15877	-1.67396
C	-2.56112	1.62481	0.18704
C	-3.13516	2.08576	1.53604
C	-3.16218	2.42176	-0.97296
H	-1.48414	1.82589	0.20304
H	-2.66512	1.55380	2.36904
H	-2.96224	3.15877	1.67404
H	-4.21514	1.90568	1.58204
H	-2.78716	2.06179	-1.93596
H	-4.25618	2.36268	-0.98396
H	-2.89326	3.47778	-0.87496

TS-DE-syn (chloroform)

Imaginary frequency: -438.01 cm^{-1}

C	-3.93703	-0.00224	0.21096
C	-2.60604	0.23383	-0.15004
C	-1.83298	-0.90014	-0.44504
C	-2.34293	-2.19516	-0.36304
C	-3.67492	-2.39422	-0.02404
C	-4.47097	-1.28826	0.26396
H	-4.57206	0.84074	0.46596
H	-1.68689	-3.03313	-0.57904
H	-4.08187	-3.39824	0.02496
H	-5.51196	-1.42431	0.54196
N	-0.43799	-0.85708	-0.84404
N	0.54702	-0.93203	0.64796
O	-0.09702	-0.03006	-1.68104
O	0.20406	-1.77305	1.46896
C	1.94502	-0.91697	0.27196
C	2.54596	0.32006	0.01896
C	2.64007	-2.12494	0.18796
C	3.90296	0.30212	-0.32804
C	3.97807	-2.11287	-0.17304
H	2.11612	-3.05296	0.39396
C	4.60802	-0.89185	-0.42904
H	4.41492	1.24115	-0.51804
H	4.52911	-3.04385	-0.25804
H	5.65702	-0.87280	-0.70804
C	-2.04110	1.64485	-0.11304
C	-1.81612	2.08386	1.34096
C	-2.91815	2.64881	-0.87004
H	-1.07410	1.63390	-0.61604
H	-1.17209	1.37689	1.87396
H	-1.33916	3.06988	1.36796
H	-2.76512	2.15182	1.88396
H	-3.08713	2.32680	-1.90204
H	-3.89315	2.78477	-0.39004
H	-2.42319	3.62483	-0.89504

C	1.79390	1.62503	0.19896
C	1.93286	2.55703	-1.00704
C	2.23087	2.31905	1.49696
H	0.73591	1.37498	0.30896
H	1.64388	2.05002	-1.93204
H	1.28382	3.42900	-0.87804
H	2.95884	2.92408	-1.12004
H	2.07690	1.67004	2.36496
H	3.29286	2.59009	1.45996
H	1.65283	3.23702	1.64896

TS-DZ-anti (chloroform)

Imaginary frequency: -393.17 cm^{-1}

C	-2.54977	-0.21164	-1.44440
C	-1.67485	-0.68802	-0.45851
C	-1.67609	0.00040	0.75882
C	-2.49225	1.10418	1.00525
C	-3.33217	1.56456	0.00136
C	-3.35794	0.89916	-1.22596
H	-2.59659	-0.71718	-2.40365
H	-2.43643	1.59872	1.96950
H	-3.95830	2.43441	0.17070
H	-4.01387	1.24846	-2.01788
N	-0.77817	-0.45300	1.80472
N	0.77772	0.45018	1.80536
C	1.67591	-0.00121	0.75925
C	1.67499	0.68838	-0.45841
C	2.49201	-1.10523	1.00382
C	2.55017	0.21396	-1.44353
C	3.33220	-1.56464	-0.00029
H	2.43595	-1.60070	1.96858
C	3.35828	-0.89704	-1.22596
H	2.59724	0.72044	-2.40228
H	3.95828	-2.43465	0.16837
H	4.01342	-1.24558	-2.01905
O	1.22158	0.46068	2.94242
O	-1.22231	-0.46461	2.94165
C	-0.84367	-1.94282	-0.66601
C	-0.33247	-2.10006	-2.10002
C	-1.64658	-3.17812	-0.22972
H	0.02824	-1.87203	-0.01087
H	0.16247	-1.19083	-2.45152
H	0.39464	-2.91695	-2.14233
H	-1.14135	-2.34582	-2.79725
H	-1.95672	-3.10267	0.81728
H	-2.54749	-3.29393	-0.84389
H	-1.03946	-4.08300	-0.34108
C	0.84387	1.94338	-0.66291
C	0.33303	2.10302	-2.09690
C	1.64666	3.17827	-0.22621
H	-0.02821	1.87196	-0.00806
H	-0.16281	1.19313	-2.44941
H	-0.39406	2.91995	-2.13860
H	1.14210	2.34845	-2.79468
H	1.95754	3.10180	0.82079
H	2.54673	3.29467	-0.84004
H	1.03957	4.08325	-0.33585

TS-DZ-syn (chloroform)

Imaginary frequency: -382.08 cm^{-1}

C	-2.70099	-1.40176	-0.71194
C	-2.17193	-0.16179	-0.33894
C	-1.10190	0.31316	-1.11194
C	-0.54894	-0.41787	-2.16094
C	-1.11100	-1.63784	-2.51894
C	-2.19602	-2.12279	-1.79094
H	-3.52901	-1.81673	-0.14394
H	0.30308	-0.00991	-2.69694
H	-0.70202	-2.20486	-3.34794
H	-2.64306	-3.07577	-2.05394
N	-0.47584	1.60313	-0.89594
N	0.72215	1.55507	0.49606
C	1.91912	0.82602	0.12406
C	2.93215	1.48597	-0.57094
C	1.99606	-0.52599	0.47606
C	4.06312	0.77991	-0.95194

H	2.80820	2.53597	-0.81894
C	3.15702	-1.20804	0.09206
C	4.17205	-0.57209	-0.61594
H	4.85314	1.27287	-1.50894
H	3.27197	-2.25505	0.35506
H	5.05503	-1.13213	-0.90694
O	0.87621	2.68207	0.93406
O	-1.21080	2.56616	-0.76594
C	-2.71489	0.59224	0.86306
C	-2.87693	-0.31376	2.09006
C	-4.03986	1.28530	0.51706
H	-1.99085	1.37020	1.12806
H	-1.94796	-0.84480	2.32406
H	-3.14690	0.29326	2.96106
H	-3.66897	-1.05672	1.94906
H	-3.91783	1.96829	-0.32894
H	-4.80689	0.54734	0.25606
H	-4.40083	1.86232	1.37406
C	0.92302	-1.19194	1.32006
C	1.34702	-1.20896	2.79606
C	0.56196	-2.59592	0.83006
H	0.02305	-0.57690	1.24706
H	1.54207	-0.19597	3.16406
H	0.55600	-1.64992	3.41206
H	2.25800	-1.80200	2.93506
H	0.31196	-2.59291	-0.23494
H	1.37892	-3.30696	0.99206
H	-0.30906	-2.96588	1.38106

TS1-dihedra-DZ-anti-to-syn-direction1 (chloroform)

Imaginary frequency: -54.85 cm^{-1}

C	3.62701	0.75494	0.21395
C	2.53701	-0.12005	0.29495
C	1.76300	-0.24505	-0.86005
C	2.05701	0.40195	-2.05705
C	3.14701	1.26094	-2.10305
C	3.92602	1.43994	-0.95905
H	4.25401	0.89894	1.08895
H	1.42501	0.23895	-2.92305
H	3.38702	1.78394	-3.02205
H	4.77902	2.11193	-0.98505
N	0.66900	-1.19104	-0.87305
N	-0.58900	-0.97903	-0.50605
C	-1.19199	0.30697	-0.11905
C	-0.40998	1.46596	-0.02605
C	-2.58499	0.36598	0.16895
C	-0.95898	2.69197	0.31595
H	0.64802	1.44696	-0.21305
C	-3.08998	1.63298	0.49895
C	-2.31798	2.78198	0.57495
H	-0.31297	3.56196	0.37495
H	-4.14898	1.72099	0.70995
H	-2.77597	3.72998	0.83695
O	-1.31401	-2.00003	-0.54805
O	0.97799	-2.36904	-1.20905
C	2.20800	-0.85405	1.58295
C	1.83401	0.13095	2.69795
C	3.36300	-1.76806	2.00895
H	1.33900	-1.49504	1.40095
H	0.99301	0.76796	2.40595
H	1.54700	-0.41705	3.60195
H	2.68001	0.77895	2.95295
H	3.61899	-2.47506	1.21395
H	4.26000	-1.19006	2.25695
H	3.07799	-2.34106	2.89695
C	-3.60600	-0.77602	0.10695
C	-4.06400	-0.98601	-1.34505
C	-4.82600	-0.57401	1.01495
H	-3.11500	-1.68502	0.43895
H	-3.21900	-1.20202	-2.00405
H	-4.76201	-1.82801	-1.40205
H	-4.57899	-0.09201	-1.71805
H	-4.53800	-0.31701	2.03995
H	-5.51699	0.19199	0.64595
H	-5.38600	-1.51501	1.05195

TS2-dihedra-DZ-anti-to-syn-direction2 (chloroform)

Imaginary frequency: -52.86 cm^{-1}

C	-3.01799	-1.05891	-0.24193
C	-2.19496	-0.00294	0.15807
C	-1.23894	0.41503	-0.77293
C	-1.12096	-0.12397	-2.04893
C	-1.95600	-1.17394	-2.41293
C	-2.90001	-1.64191	-1.50193
H	-3.76901	-1.43488	0.44607
H	-0.37795	0.27000	-2.73493
H	-1.86901	-1.61895	-3.39793
H	-3.55704	-2.46189	-1.77593
N	-0.43890	1.58100	-0.47593
N	0.89310	1.64596	-0.61393
C	1.95707	0.70192	-0.10593
C	3.16009	1.41688	0.05307
C	1.93302	-0.68408	0.18707
C	4.33407	0.81383	0.46407
H	3.16213	2.47388	-0.15593
C	3.16100	-1.25312	0.57707
C	4.34302	-0.55117	0.71807
H	5.23009	1.41580	0.57607
H	3.17296	-2.31813	0.78107
H	5.25001	-1.06320	1.02607
O	1.29814	2.79494	-0.91493
O	-1.06486	2.67302	-0.56693
C	-2.32593	0.64107	1.52707
C	-2.44197	-0.39193	2.65307
C	-3.51790	1.60811	1.54707
H	-1.41791	1.22604	1.70807
H	-1.62400	-1.11796	2.62107
H	-2.40795	0.11607	3.62207
H	-3.38799	-0.94189	2.60507
H	-3.41387	2.37611	0.77607
H	-4.45692	1.06915	1.37607
H	-3.58488	2.10411	2.52207
C	0.79098	-1.69204	0.14007
C	0.63696	-2.46304	1.46007
C	0.96295	-2.65305	-1.04393
H	-0.14000	-1.17101	-0.00093
H	0.60798	-1.78503	2.31807
H	-0.30206	-3.02700	1.43807
H	1.44493	-3.18406	1.62507
H	1.02897	-2.11005	-1.99193
H	1.87093	-3.25708	-0.93693
H	0.10793	-3.33302	-1.09993

DZ-anti-H_2O (water)

C	-3.12302	0.30494	1.53405
C	-2.45301	-0.13305	0.38505
C	-1.13700	-0.55502	0.57405
C	-0.50000	-0.58400	1.81005
C	-1.19401	-0.13702	2.92705
C	-2.50702	0.30995	2.78105
H	-4.15003	0.64492	1.44805
H	0.51701	-0.94998	1.88705
H	-0.71401	-0.14201	3.89905
H	-3.05803	0.65994	3.64805
N	-0.39499	-1.08900	-0.55795
N	0.50400	-0.37198	-1.15595
C	0.69597	1.02402	-0.79895
C	1.79396	1.37105	-0.00895
C	-0.19305	1.94600	-1.33995
C	1.95393	2.73805	0.24405
C	-0.00708	3.29300	-1.06195
H	-1.01205	1.60598	-1.96495
C	1.06991	3.68403	-0.26695
H	2.78992	3.06707	0.85305
H	-0.69310	4.02899	-1.46695
H	1.22588	4.73503	-0.04595
O	1.19401	-0.88897	-2.08495
O	-0.58496	-2.28201	-0.92695
C	-3.14201	-0.17706	-0.96595
C	-3.87304	1.13092	-1.28595

C	-4.09998	-1.37508	-1.02795
H	-2.37700	-0.32305	-1.73595
H	-3.21006	1.99594	-1.18895
H	-4.24803	1.09891	-2.31395
H	-4.73204	1.28190	-0.62395
H	-3.57196	-2.31507	-0.83995
H	-4.89498	-1.27110	-0.28095
H	-4.56498	-1.43309	-2.01695
C	2.77698	0.34507	0.52205
C	3.08398	0.54807	2.00905
C	4.06398	0.36910	-0.31395
H	2.32700	-0.64794	0.41305
H	2.16698	0.59205	2.60505
H	3.69000	-0.28591	2.37405
H	3.64896	1.47009	2.18005
H	3.85598	0.17209	-1.36995
H	4.55496	1.34510	-0.23595
H	4.76400	-0.39189	0.05005
O	1.25207	-3.71897	0.87605
H	1.94206	-3.45595	0.23605
H	0.43806	-3.39199	0.46505
O	3.02805	-2.85393	-1.12295
H	3.74904	-2.35291	-0.72295
H	2.42304	-2.17694	-1.47895

M-H_2O (water)

C	-1.10777	2.67712	0.00210
C	0.12516	2.06099	-0.00290
C	0.20302	0.65398	-0.00390
C	-0.95307	-0.15590	0.00010
C	-2.18900	0.50423	0.00510
C	-2.26785	1.88924	0.00610
H	-1.18065	3.75913	0.00310
H	1.04123	2.64189	-0.00590
H	-3.10406	-0.07967	0.00810
H	-3.24180	2.36835	0.00910
N	1.44294	-0.01716	-0.00790
O	2.44102	0.69874	-0.01190
C	-0.90824	-1.67290	-0.00090
C	-1.57229	-2.23683	-1.26390
C	-1.56130	-2.23783	1.26810
H	0.13773	-1.98402	-0.00490
H	-1.10025	-1.84188	-2.16890
H	-1.47641	-3.32684	-1.27590
H	-2.63927	-1.99172	-1.29690
H	-1.08225	-1.84388	2.16910
H	-2.62827	-1.99172	1.31110
H	-1.46641	-3.32784	1.27810
O	4.86386	-0.78952	-0.01590
H	5.55293	-0.15260	0.20210
H	4.03592	-0.27543	-0.00990

Nitrosobenzene-DE (chloroform)

C	4.02101	0.57802	-0.92696
C	2.64501	0.77902	-0.99696
C	1.83901	0.19703	-0.02796
C	2.35801	-0.55897	1.01804
C	3.73601	-0.73798	1.08204
C	4.56501	-0.17699	0.11104
H	4.66601	1.01801	-1.67996
H	2.20101	1.37803	-1.78496
H	1.70300	-0.99697	1.76204
H	4.16100	-1.31998	1.89404
H	5.63901	-0.32699	0.16504
N	0.42201	0.49503	-0.08396
N	-0.42199	-0.49496	-0.08496
O	0.04502	1.70204	-0.16396
O	-0.04500	-1.70196	-0.16696
C	-1.83899	-0.19696	-0.02796
C	-2.64500	-0.77695	-0.99896
C	-2.35799	0.55605	1.02004
C	-4.02099	-0.57595	-0.92796
H	-2.20200	-1.37295	-1.78796
C	-3.73599	0.73605	1.08404
H	-1.70299	0.99204	1.76504
C	-4.56499	0.17706	0.11104

H	-4.66600	-1.01294	-1.68296
H	-4.16099	1.31605	1.89704
H	-5.63899	0.32806	0.16604

Nitrosobenzene-DZ (chloroform)

C	-3.02203	-1.11108	0.82899
C	-2.26808	0.05195	0.94099
C	-1.39810	0.37999	-0.09201
C	-1.28106	-0.39400	-1.24001
C	-2.04301	-1.55404	-1.33901
C	-2.90700	-1.91507	-0.30601
H	-3.70102	-1.38911	1.62799
H	-2.34511	0.69495	1.81199
H	-0.60908	-0.09597	-2.03801
H	-1.96399	-2.17203	-2.22701
H	-3.49796	-2.82110	-0.38801
N	-0.65415	1.61902	0.02099
N	0.65385	1.61908	-0.02101
C	1.39790	0.38011	0.09199
C	2.26792	0.05215	-0.94101
C	1.28094	-0.39289	1.23999
C	3.02197	-1.11081	-0.82901
H	2.34489	0.69416	-1.81201
C	2.04399	-1.55386	1.33899
H	0.60992	-0.09492	2.03799
C	2.90700	-1.91482	0.30599
H	3.70098	-1.38878	-1.62801
H	1.96501	-2.17186	2.22799
H	3.49904	-2.82079	0.38799
O	1.27380	2.71211	-0.08101
O	-1.27420	2.71200	0.08099

Nitrosobenzene-DE-TS (chloroform)

Imaginary frequency: -454.36 cm^{-1}

C	-4.02811	-1.04470	0.39279
C	-2.67982	-1.27507	0.15246
C	-1.88509	-0.21704	-0.28954
C	-2.41030	1.05480	-0.50417
C	-3.76677	1.26999	-0.27137
C	-4.57092	0.22554	0.18013
H	-4.65935	-1.85407	0.74547
H	-2.23717	-2.25383	0.30305
H	-1.77086	1.85408	-0.86045
H	-4.19255	2.25357	-0.44072
H	-5.62626	0.39867	0.36711
N	-0.48785	-0.42356	-0.59604
N	0.48786	0.42342	0.59616
O	-0.14219	-1.56597	-0.87852
O	0.14214	1.56581	0.87870
C	1.88510	0.21699	0.28958
C	2.67972	1.27509	-0.15246
C	2.41041	-1.05481	0.50416
C	4.02801	1.04481	-0.39287
H	2.23700	2.25382	-0.30301
C	3.76688	-1.26991	0.27127
H	1.77105	-1.85414	0.86047
C	4.57093	-0.22539	-0.18027
H	4.65918	1.85424	-0.74559
H	4.19273	-2.25346	0.44057
H	5.62627	-0.39845	-0.36732

Nitrosobenzene-DZ-TS (chloroform)

Imaginary frequency: -388.06 cm^{-1}

C	-3.68167	-0.47164	-0.63399
C	-2.78848	0.57453	-0.43356
C	-1.64113	0.33866	0.32054
C	-1.37485	-0.90333	0.88726
C	-2.28404	-1.94045	0.69120
C	-3.43080	-1.72598	-0.07189
H	-4.57566	-0.31066	-1.22804
H	-2.96274	1.55848	-0.85682
H	-0.47606	-1.04616	1.47847
H	-2.09658	-2.91298	1.13473
H	-4.13506	-2.53720	-0.22843
N	-0.68459	1.39711	0.57844
N	0.68441	1.39687	-0.57823

C	1.64076	0.33820	-0.32041
C	1.37397	-0.90427	-0.88587
C	2.78902	0.57470	0.43215
C	2.28352	-1.94113	-0.69005
H	0.47450	-1.04789	-1.47580
C	3.68250	-0.47123	0.63247
H	2.96365	1.55900	0.85445
C	3.43112	-1.72601	0.07158
H	2.09568	-2.91397	-1.13274
H	4.57707	-0.30975	1.22550
H	4.13566	-2.53704	0.22785
O	1.12377	2.53032	-0.66980
O	-1.12361	2.53068	0.67015