Supporting Information

O^2-Functionalized Methylamine Diazeniumdiolates: Evidence for $E \rightleftharpoons Z$ Equilibration in an Acyclic System

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Dynamic NMR Experiments. Data used to derive the rate of exchange involving the anion and its conjugate acid were recorded on a 400 MHz NMR spectrometer. Samples were prepared in D_2O and the pD was adjusted to 3, 7, and 13 using NaOD and/or DCl.

UV-Visible Spectra for Determination of pK_a for 13.

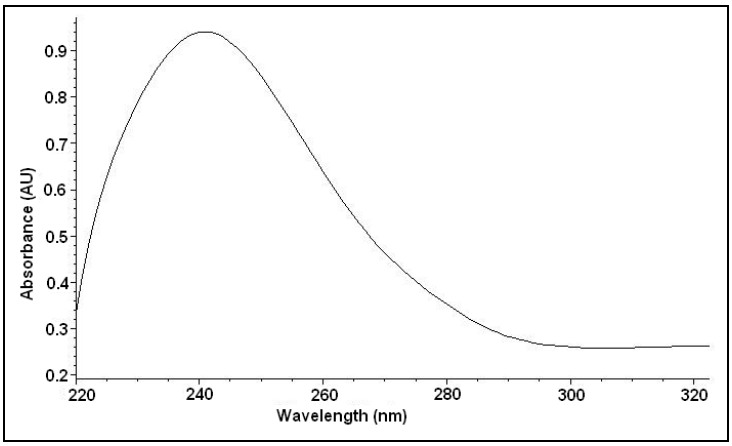

Figure S1. UV spectrum of **13** (λ_{max} = 241 nm) in pH 7.4 buffer.

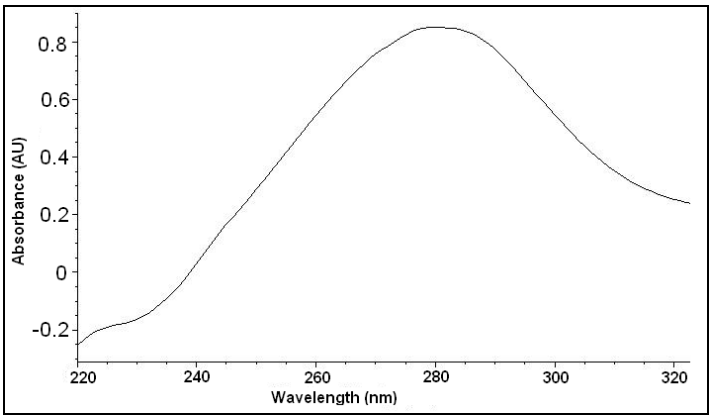

Figure S2. UV spectrum of **13** (λ_{max} = 278 nm) in 1 M NaOH solution.

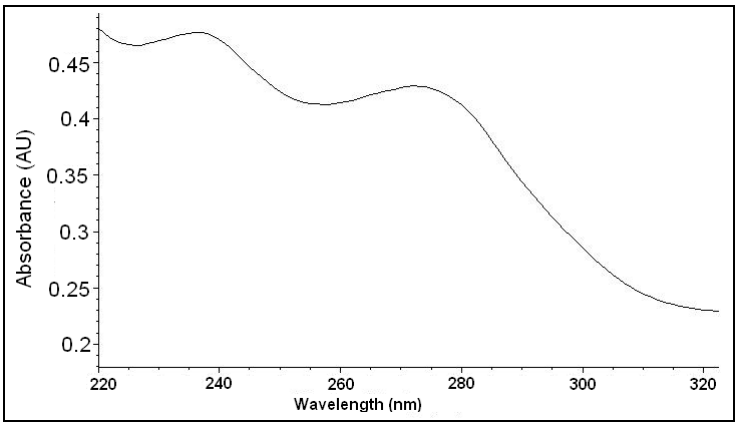

Figure S3. UV spectrum of **13** (λ_{max} = 241 and 278 nm) in pH 11.7 buffer.

LC/MS Analysis. A mixture of the two isomeric forms of **13** was injected on a HPLC, and the separations were performed on a reverse phase C18 column (3 µm, 2.1x150 mm), with a water-acetonitrile 90:10 mobile phase and a flow rate of 0.2 mL/min. The solvent line was split prior to entering the mass spectrometer. High resolution mass spectra (HRMS) were recorded on an Accurate-Mass quadrupole time-of-flight (Q-TOF) mass spectrometer. Positive ions were generated using electrospray ionization (ESI) with a capillary voltage of 3500 V, a fragmenter voltage of 175 V, and a nebulizer pressure of 25 psi.

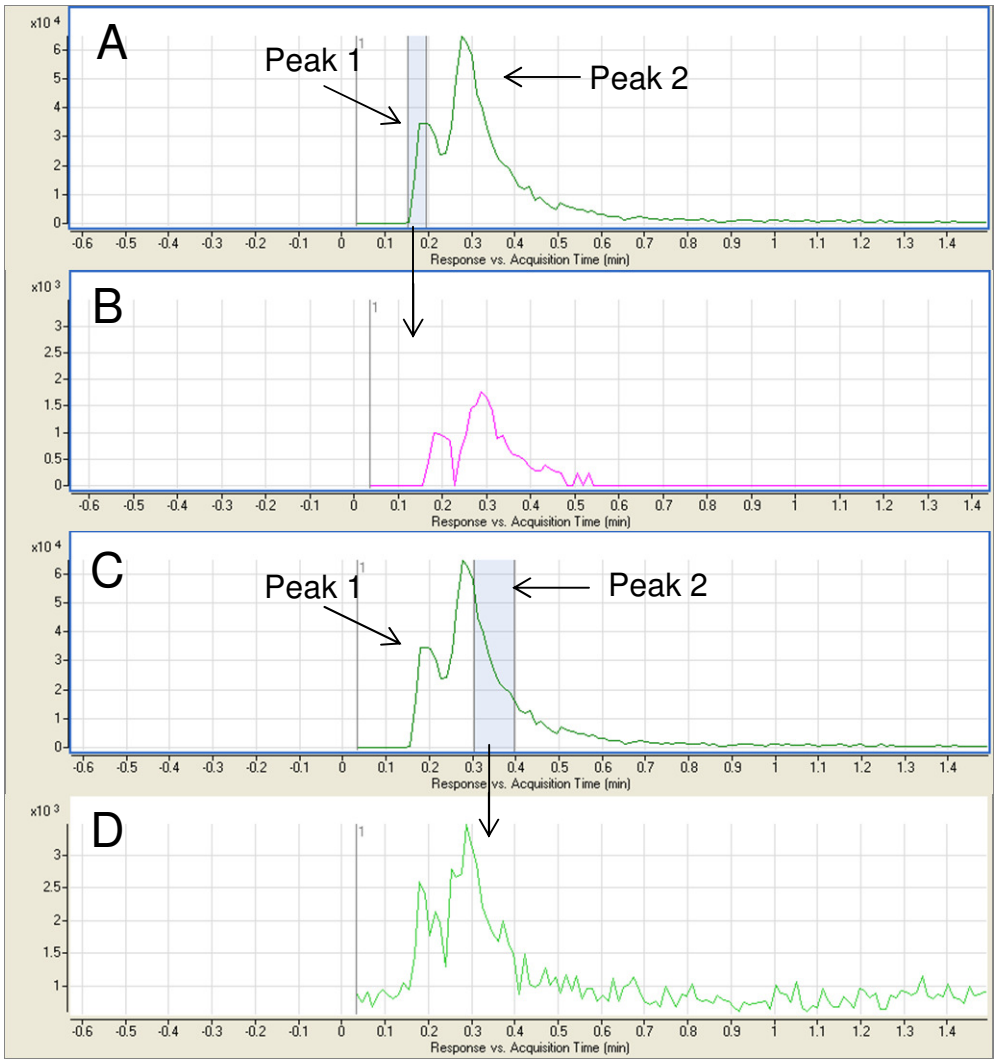

Figure S4. Equilibration of compound **13** between two isomeric forms that is partially separable by HPLC. **Panel A** is an HPLC trace illustrating the partial separation, with the shaded area representing the portion of the eluate richest in the smaller component; this portion was collected at 0 ^{o}C and immediately reinjected to obtain the chromatogram of **Panel B**, showing re-equilibration. **Panel C**, same as **A** except that the eluate that was collected cold and immediately reinjected (shaded area) was enriched in the major isomer. **D**, as in the experiment of **Panel B**, the resulting HPLC trace showed complete re-equilibration. Each trace is an extracted ion chromatogram, *m/z* 120.077. Photodiode array detector responses confirm that the two peaks in each chromatogram also had identical ultraviolet spectra (λ_{max} = 240 nm).

Peak 1

m/z	Ion	Formula	Abundance
120.07682	(M+H)+	C3 H10 N3 O2	24124.2

Best	Formula (M)	Ion Formula	m/z	Calc m/z	Mass	Calc Mass	Abs Diff (pp	Score	Mass Match	Abund Match	Spacing Match	DBE
☑	C3 H9 N3 O2	C3 H10 N3 O2	120.07682	120.07675	119.06954	119.06948	0.57	87.58	99.94	87.77	62.65	1

Peak 2

m/z	Ion	Formula	Abundance
120.07692	(M+H)+	C3 H10 N3 O2	62731.2

Best	Formula (M)	Ion Formula	m/z	Calc m/z	Mass	Calc Mass	Abs Diff (pp	Score	Mass Match	Abund Match	Spacing Match	DBE
☑	C3 H9 N3 O2	C3 H10 N3 O2	120.07692	120.07675	119.06965	119.06948	1.42	99.2	99.6	98.45	99.28	1

m/z	Ion	Formula	Abundance
142.05889	(M+Na)+	C3 H9 N3 Na O2	2241.5

Best	Formula (M)	Ion Formula	m/z	Calc m/z	Mass	Calc Mass	Abs Diff (pp	Score	Mass Match	Abund Match	Spacing Match	DBE
☑	C3 H9 N3 O2	C3 H9 N3 Na O2	142.05889	142.0587	119.06967	119.06948	1.63	47.39	99.52	0	0	1

Figure S5. Molecular formula calculations from the $[M+H]^+$ ion in peak 1 and both the $[M+H]^+$ and $[M+Na]^+$ ions in peak 2 of Figure S13. These calculations confirm that both peaks in the chromatograms of **13** have the same molecular formula, $C_3H_9N_3O_2$.

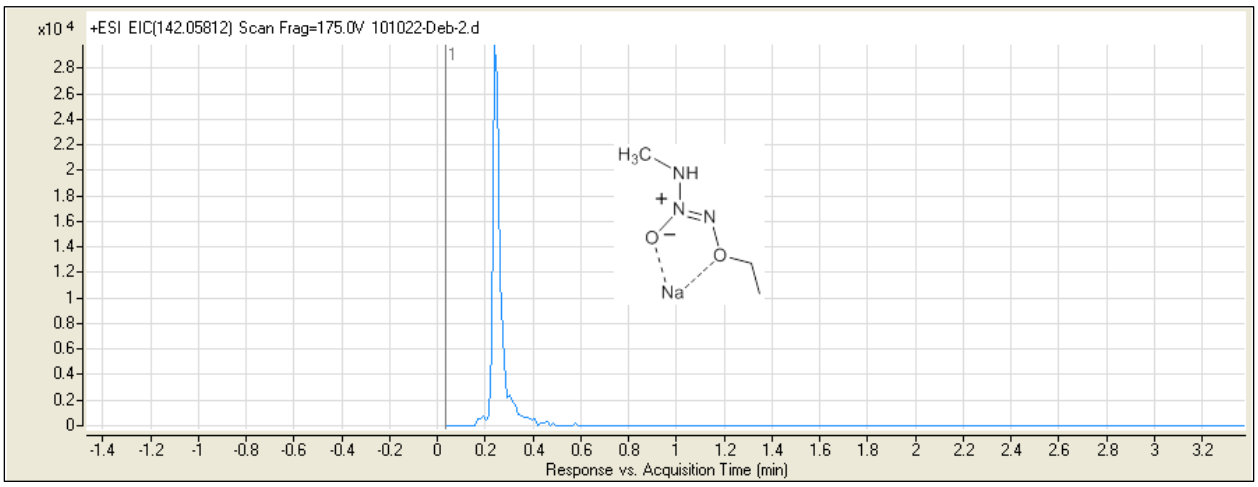

Figure S6. Extracted ion chromatogram of the ion of *m/z* 142.058 in the spectrum of **13**, which is the $[M+Na]^+$ ion detected in peak 2. This analysis shows that only peak 2 formed detectable sodium adducts.

Single-crystal X-ray Diffraction Analysis of *Z*-4. Single-crystal X-ray diffraction data on ***Z*-4** were collected at 100 K using MoKα radiation (λ = 0.71073 Å) and a CCD area detector. The sample was prepared for data collection by coating with high viscosity microscope oil. The oil-coated crystal was mounted on a MicroMesh mount and transferred immediately to the diffractometer. The 0.618 x 0.514 x 0.277 mm^3 crystal was monoclinic in space group $P2_{1/c}$ with unit cell dimensions a = 22.122(4) Å, b = 5.3670(10) Å, c = 16.713(3) Å, and β = 112.172(4) °. Corrections were applied for Lorentz, polarization, and absorption effects. The structure was solved by direct methods and refined by full-matrix least squares on F^2 values. using appropriate programs. Parameters refined included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on carbons were included using a riding model [coordinate shifts of C applied to H atoms] with C-H distance set at 0.96 Å. The asymmetric unit contained a single molecule. Data were 96.3% complete to 25.00° θ. The asymmetric unit contains two molecules.

Table S1. Crystal data and structure refinement for **Z-4**.

Empirical formula	$C_8H_{11}N_3O_2$	
Formula weight	181.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_{1/c}$	
Unit cell dimensions	a = 22.122(4) Å	α= 90°
	b = 5.3670(10) Å	β= 112.172(4)°
	c = 16.713(3) Å	γ = 90°
Volume	1837.6(6) $Å^3$	
Z	8	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	768	

Crystal size	0.618 x 0.514 x 0.277 mm^3
θ range for data collection	8.18 to 25.35°
Index ranges	-26<=h<=26, -6<=k<=6, -20<=l<=20
Reflections collected	19649
Independent reflections	3249 [R(int) = 0.0574]
Completeness to θ = 25.00°	96.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9736 and 0.9425
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3249 / 156 / 237
Goodness-of-fit on F^2	1.083
Final R indices [I>2σ(I)]	R1 = 0.0451, wR2 = 0.1089
R indices (all data)	R1 = 0.0527, wR2 = 0.1105
Largest diff. peak and hole	0.423 and -0.440 e.$Å^{-3}$

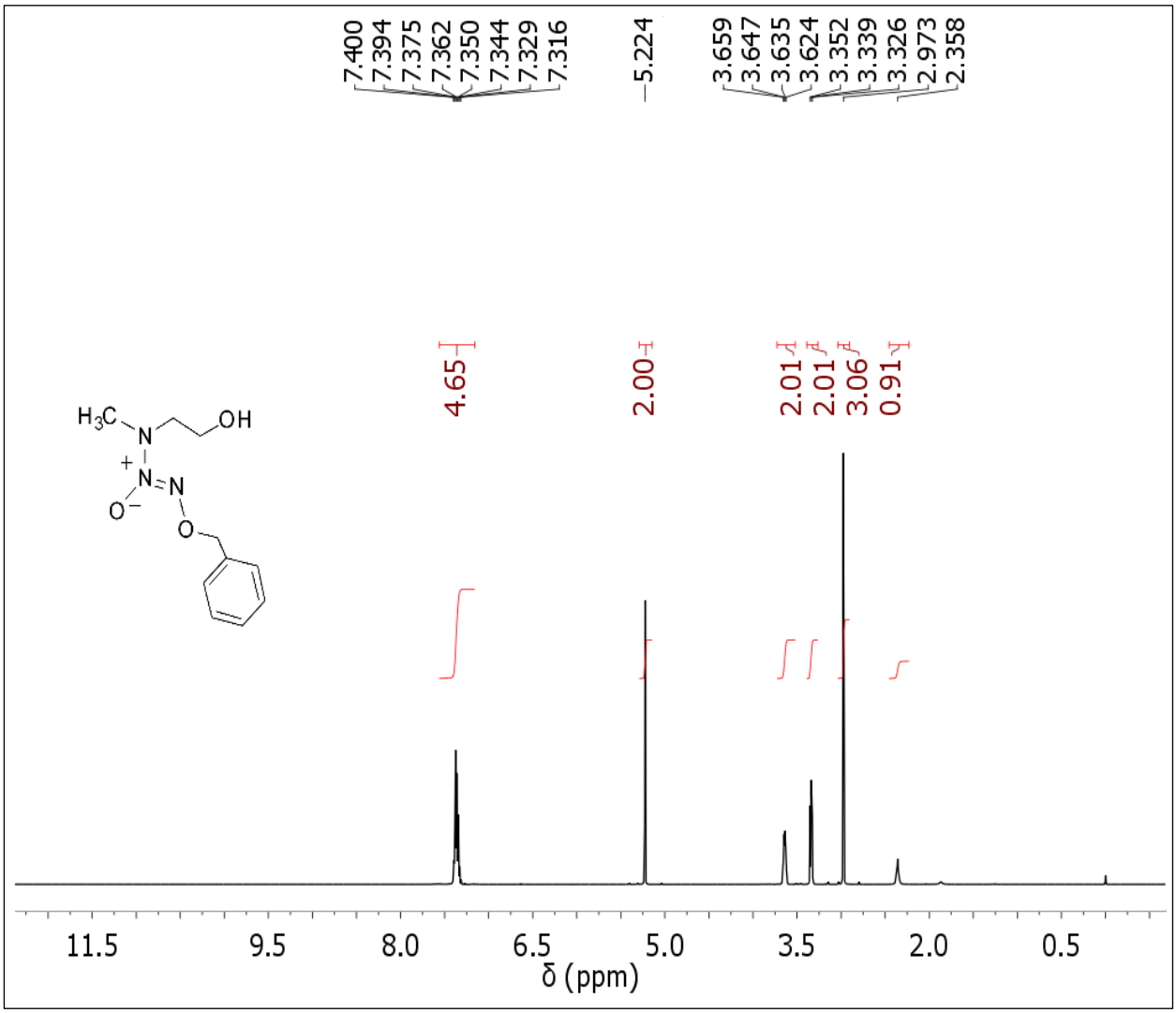

Figure S7. ^{1}H NMR spectra of compound **7** in $CDCl_3$ at 25 ^{o}C.

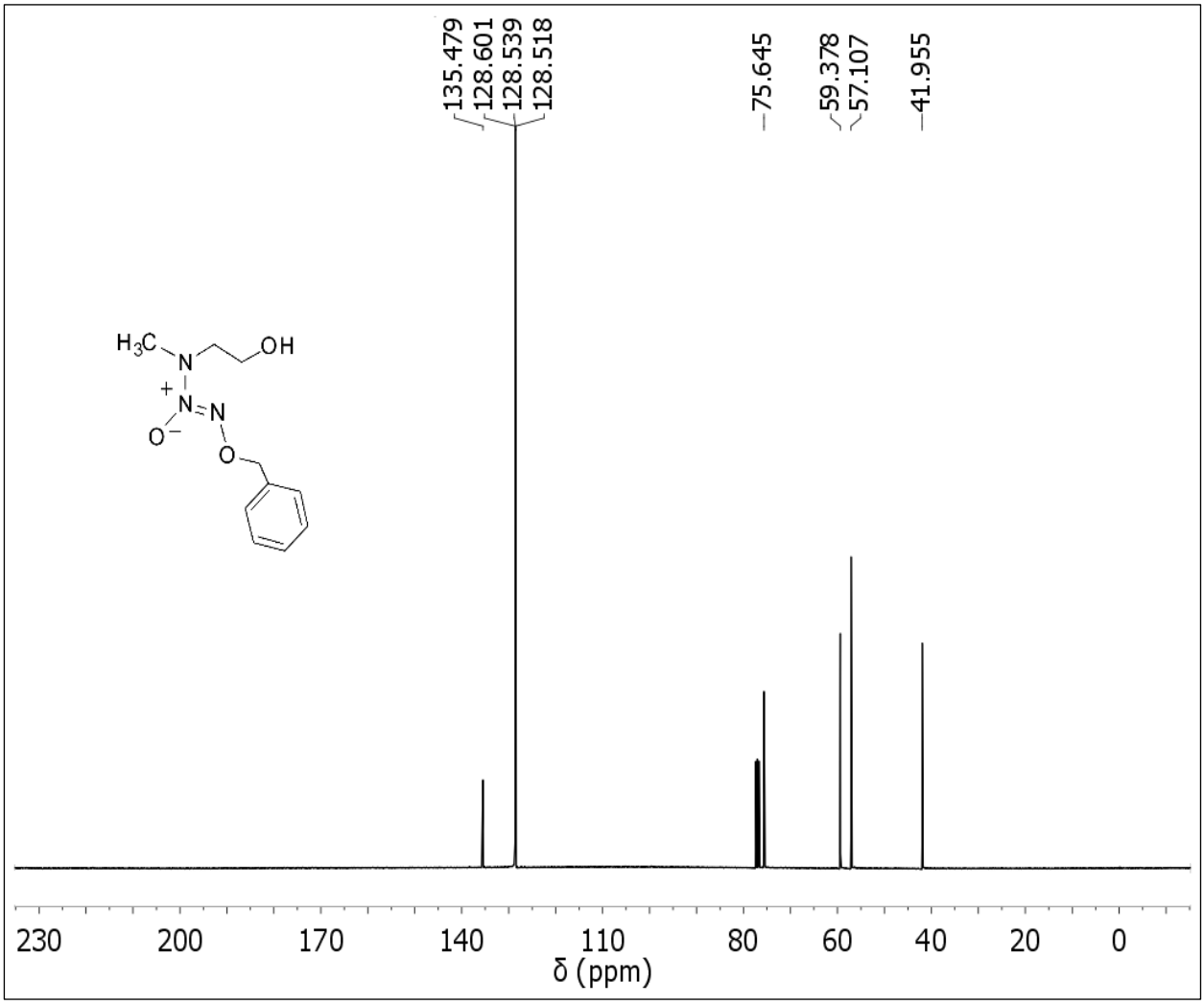

Figure S8. ^{13}C NMR spectra of compound **7** in $CDCl_3$ at 25 ^{o}C.

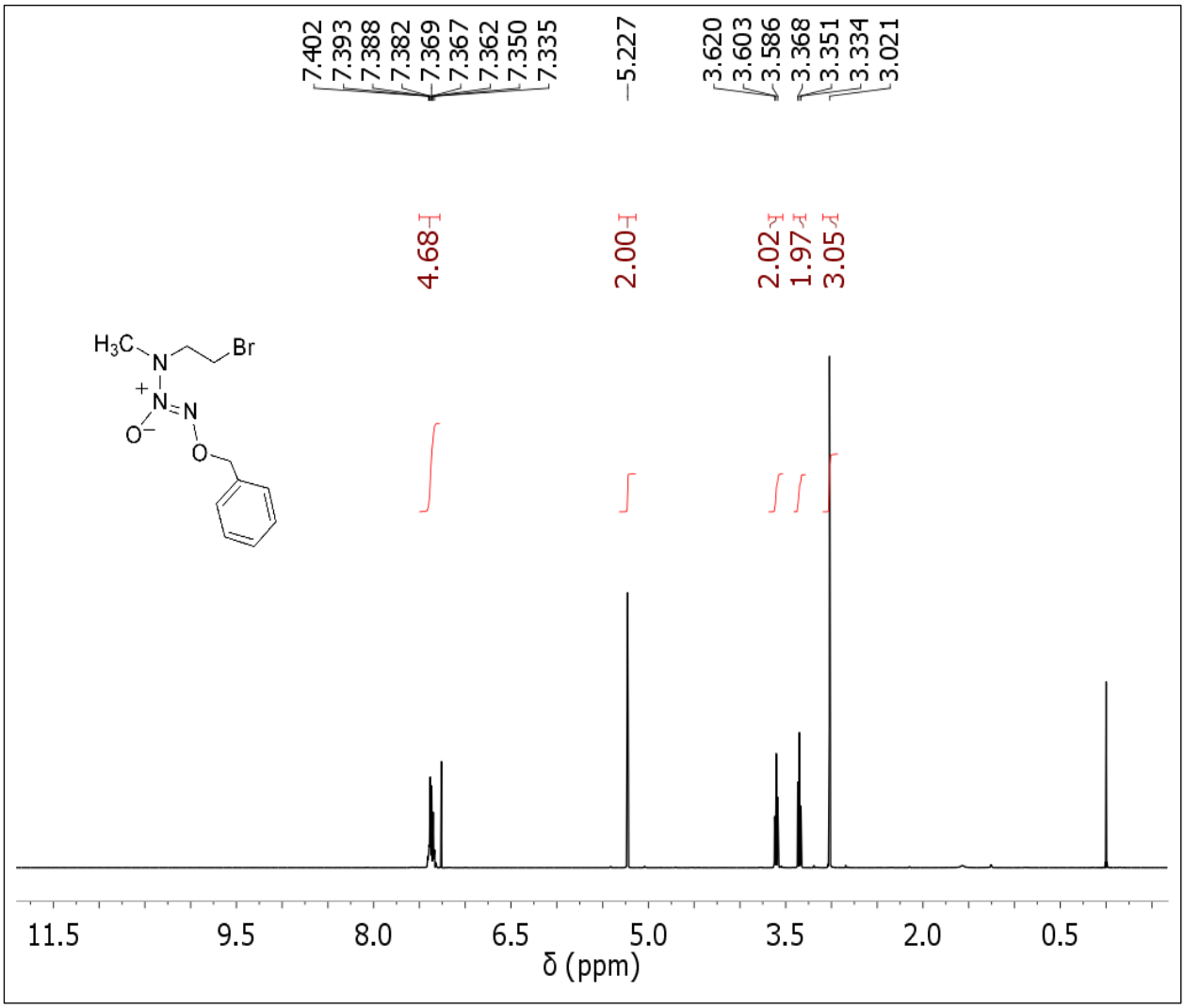

Figure S9. ^{1}H NMR spectra of compound **8** in $CDCl_3$ at 25 ^{o}C.

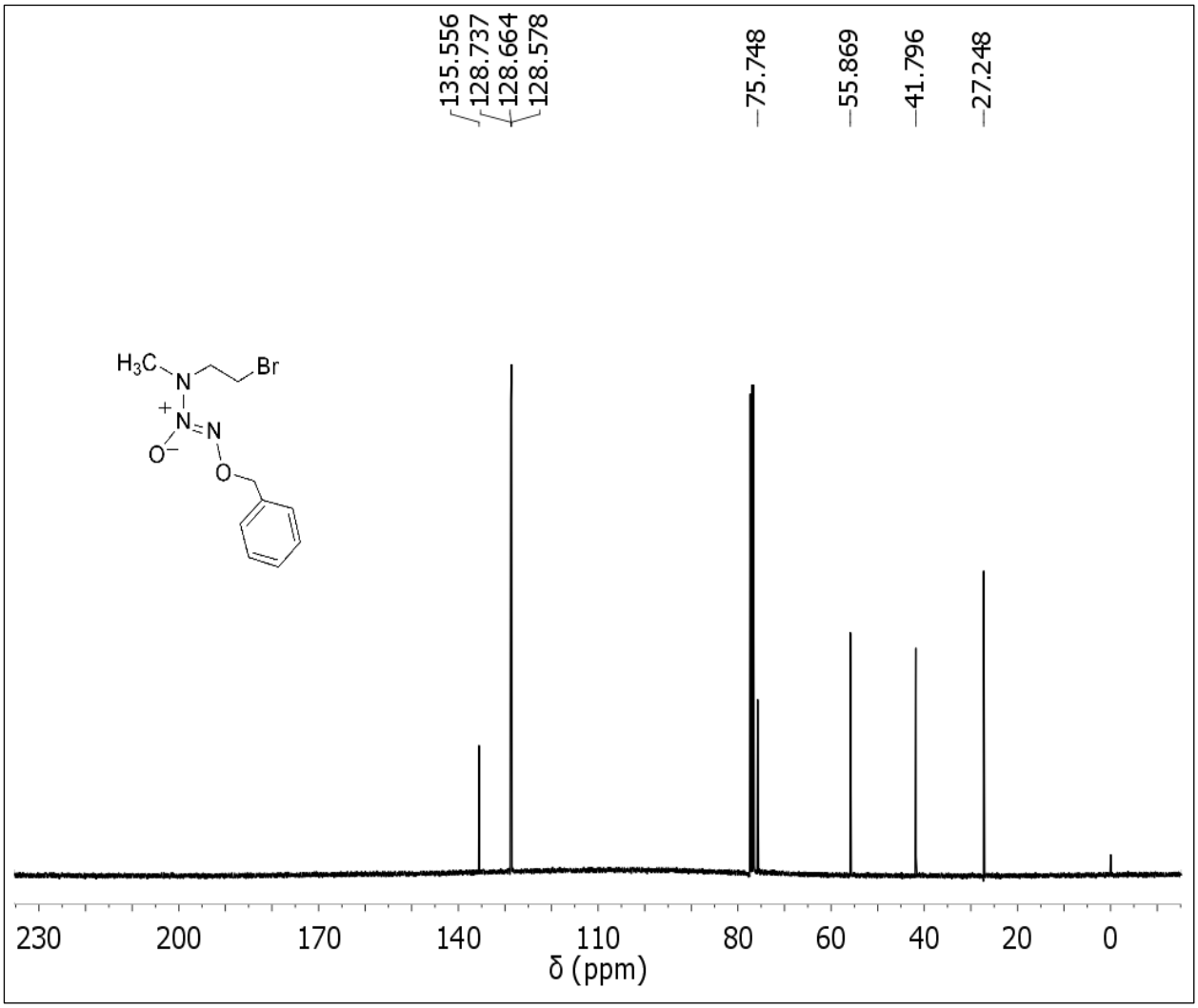

Figure S10. ^{13}C NMR spectra of compound **8** in $CDCl_3$ at 25 ^{o}C.

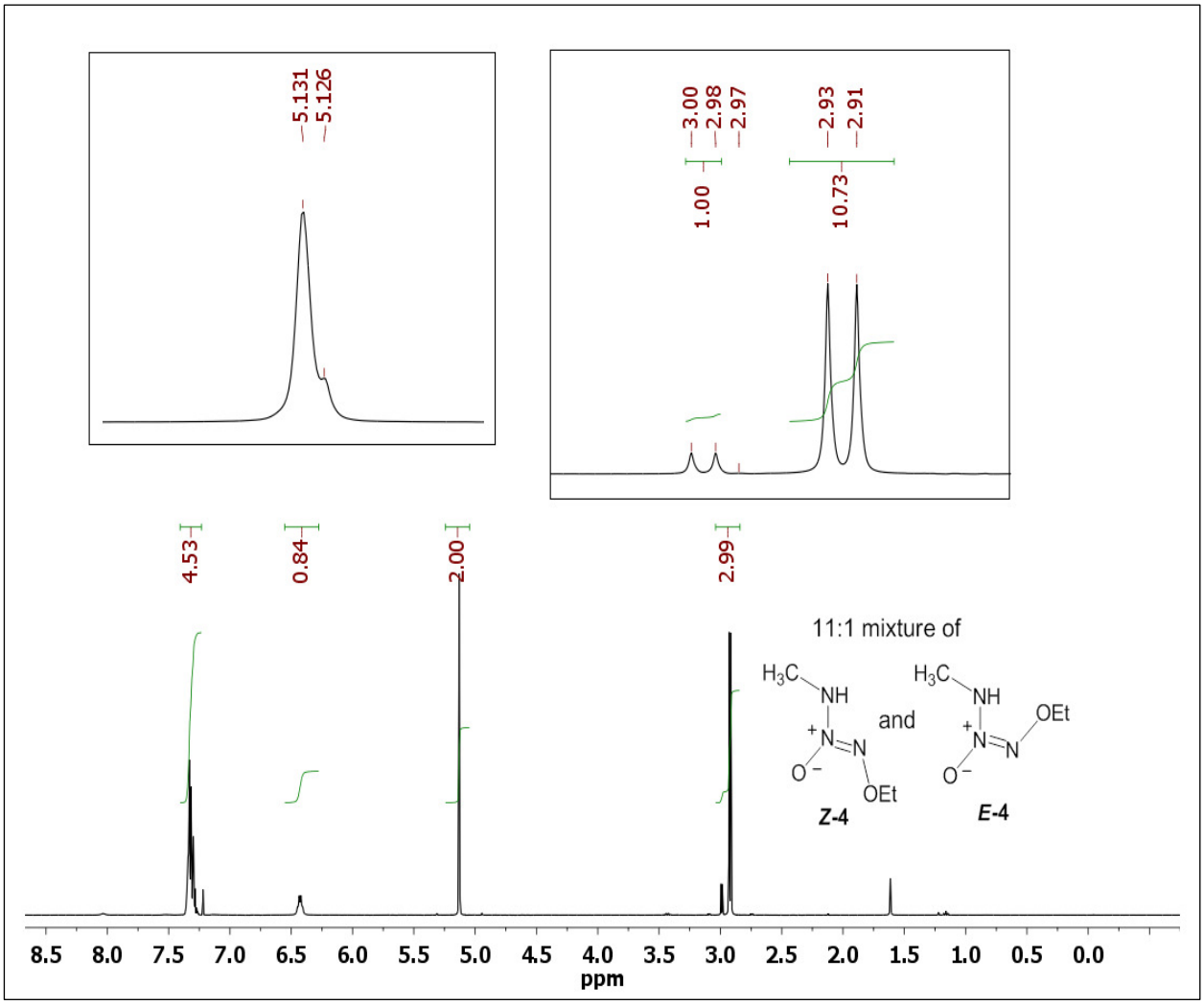

Figure S11. ^{1}H NMR spectrum of an equilibrium mixture of compounds ***Z*-4** and ***E*-4** in $CDCl_3$ at 25 ^{o}C.

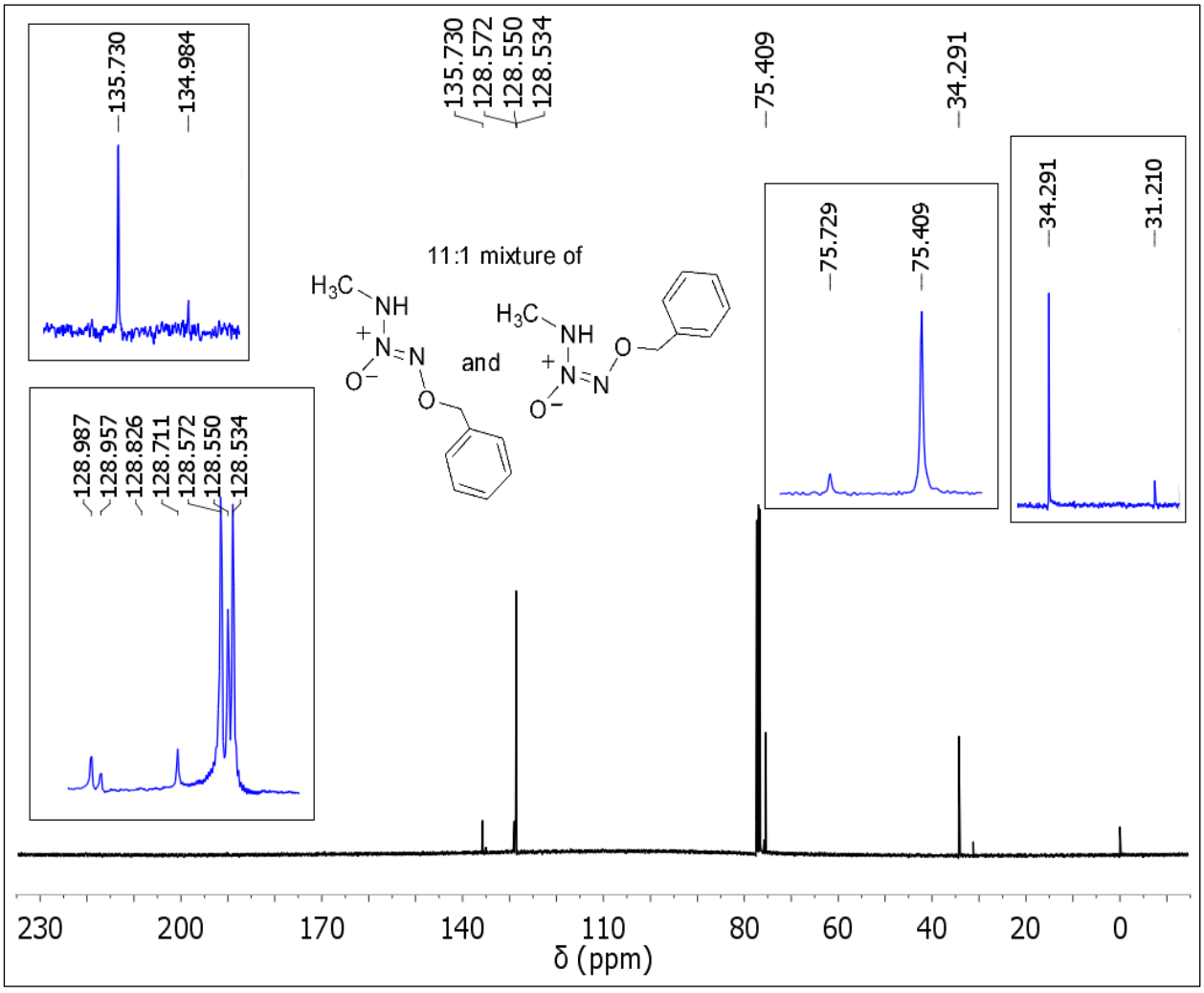

Figure S12. ^{13}C NMR spectrum of an equilibrium mixture of compounds ***Z*-4** and ***E*-4** in $CDCl_3$ at 25 ^{o}C.

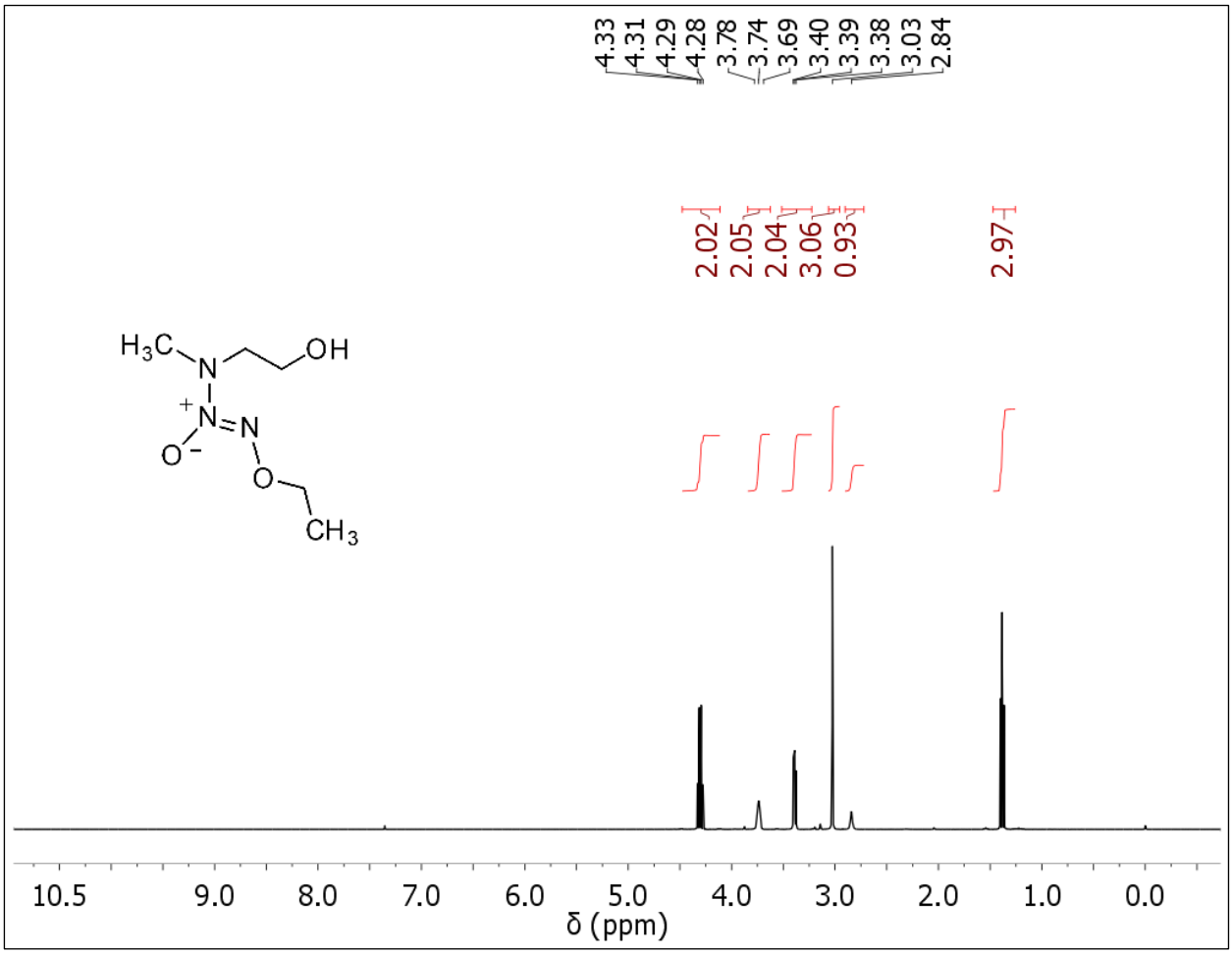

Figure S13. ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 25 ^{o}C.

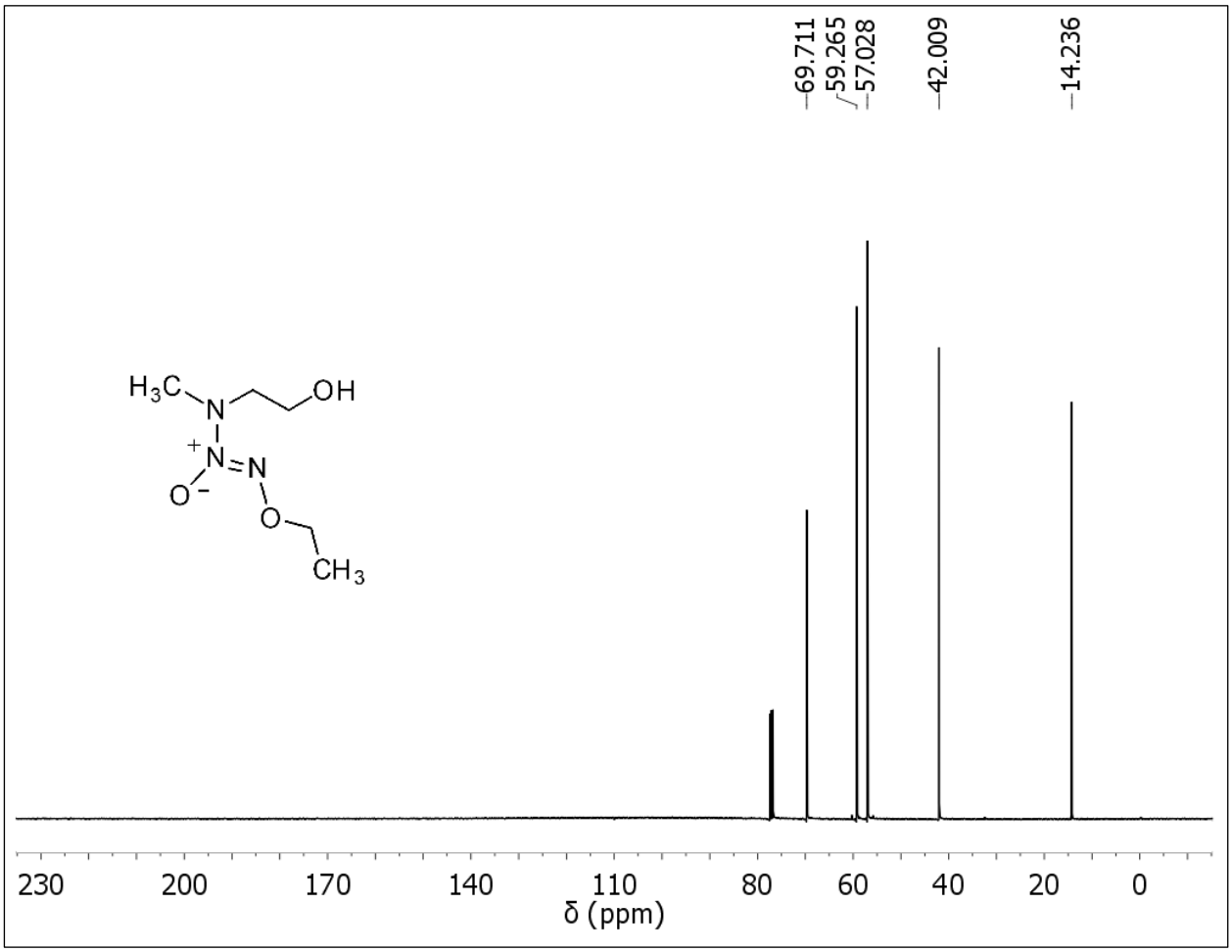

Figure S13. ^{13}C NMR spectrum of compound **10** in $CDCl_3$ at 25 ^{o}C.

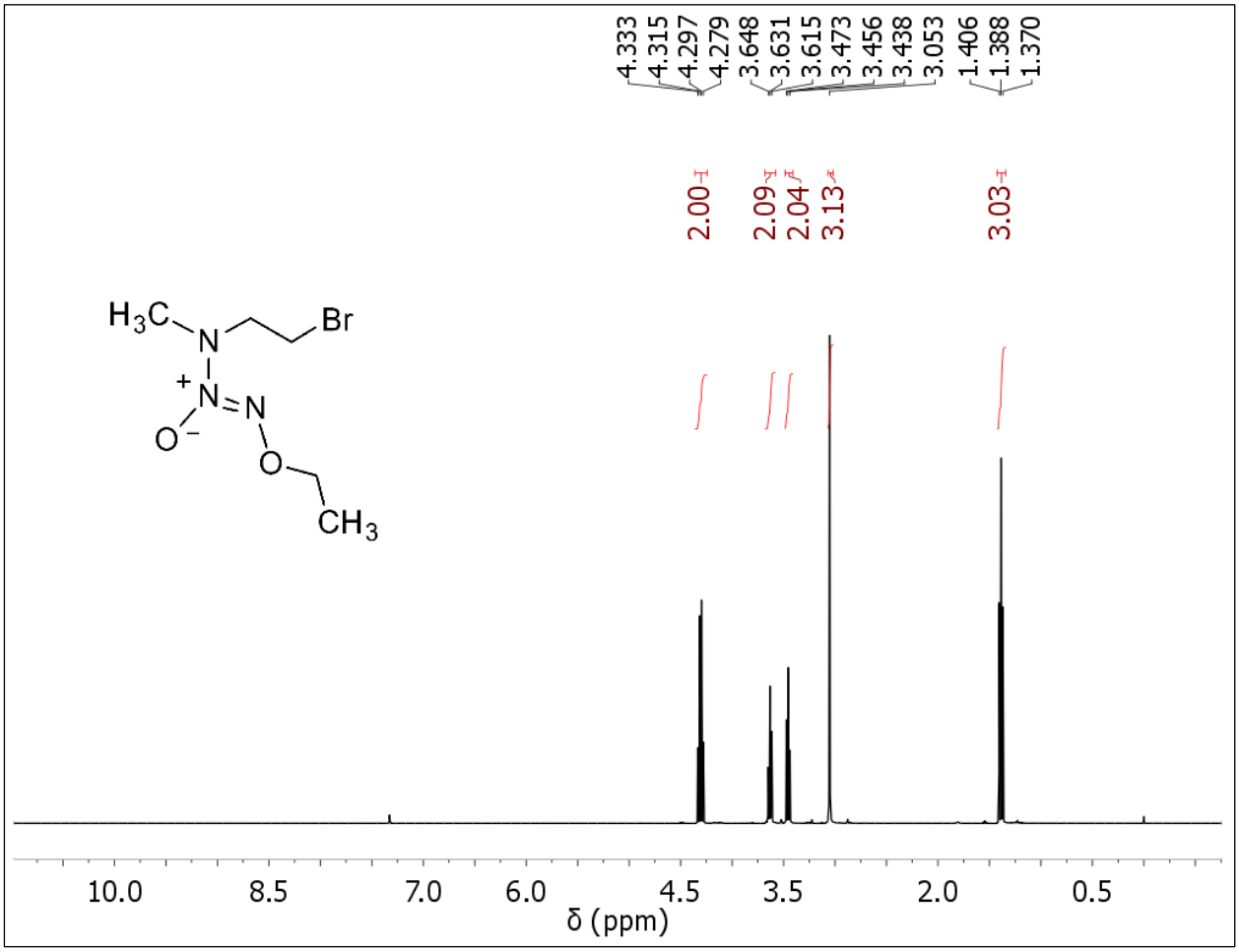

Figure S15. ^{1}H NMR spectrum of compound **11** in $CDCl_3$ at 25 ^{o}C.

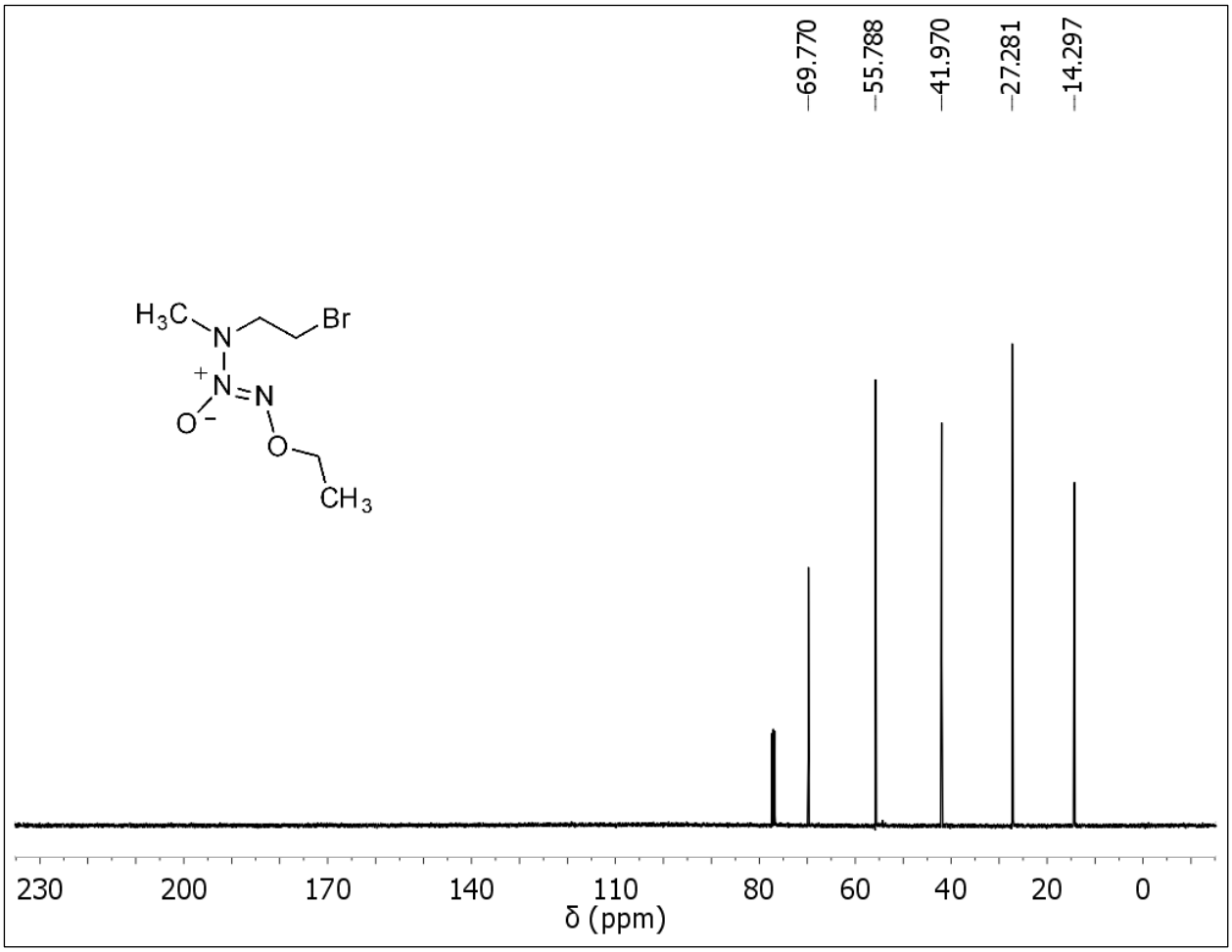

Figure S16. ^{13}C NMR spectrum of compound **11** in $CDCl_3$ at 25 ^{o}C.

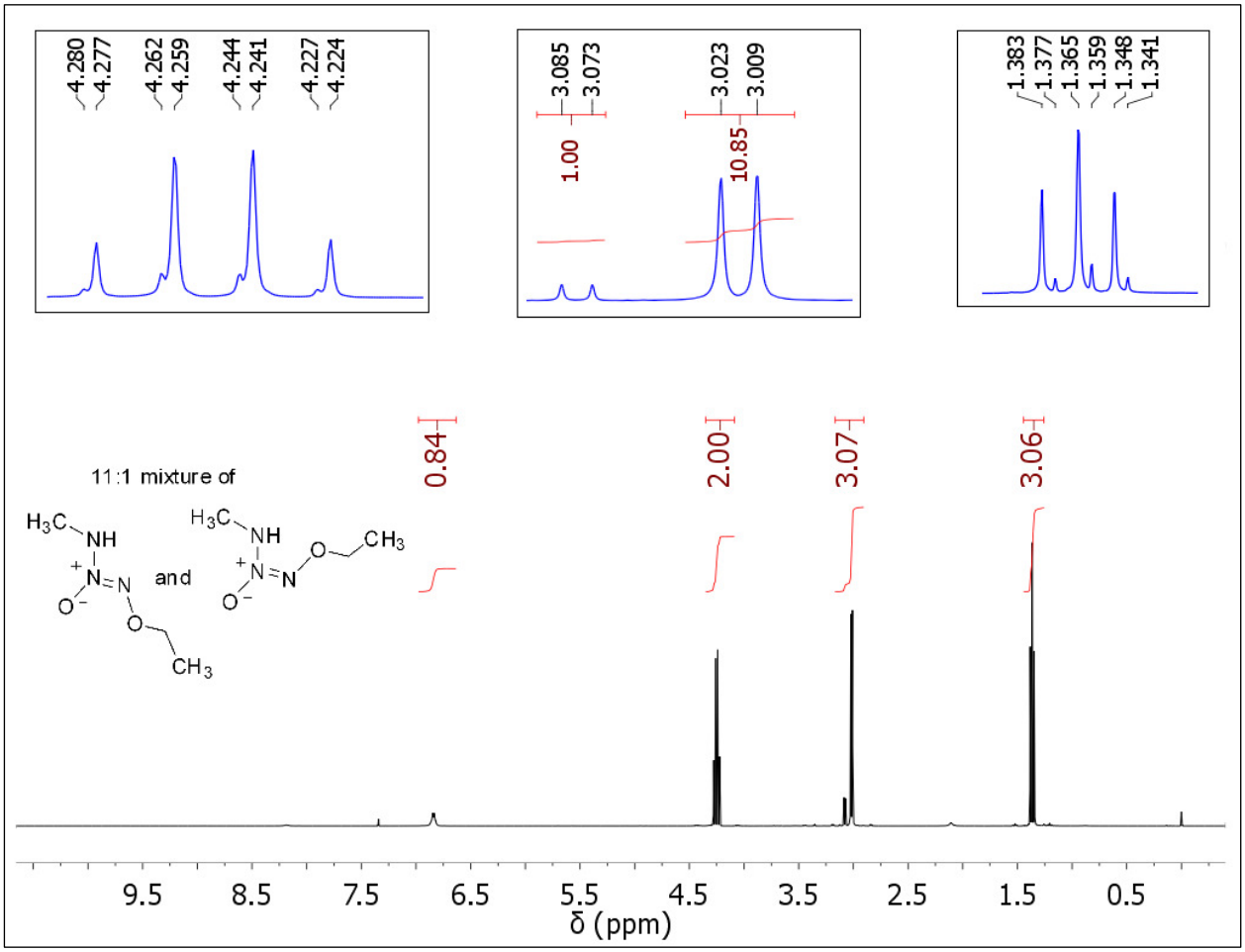

Figure S17. ^{1}H NMR spectrum of an equilibrium mixture of compounds ***Z*-13** and ***E*-13** in $CDCl_3$ at 25 ^{o}C.

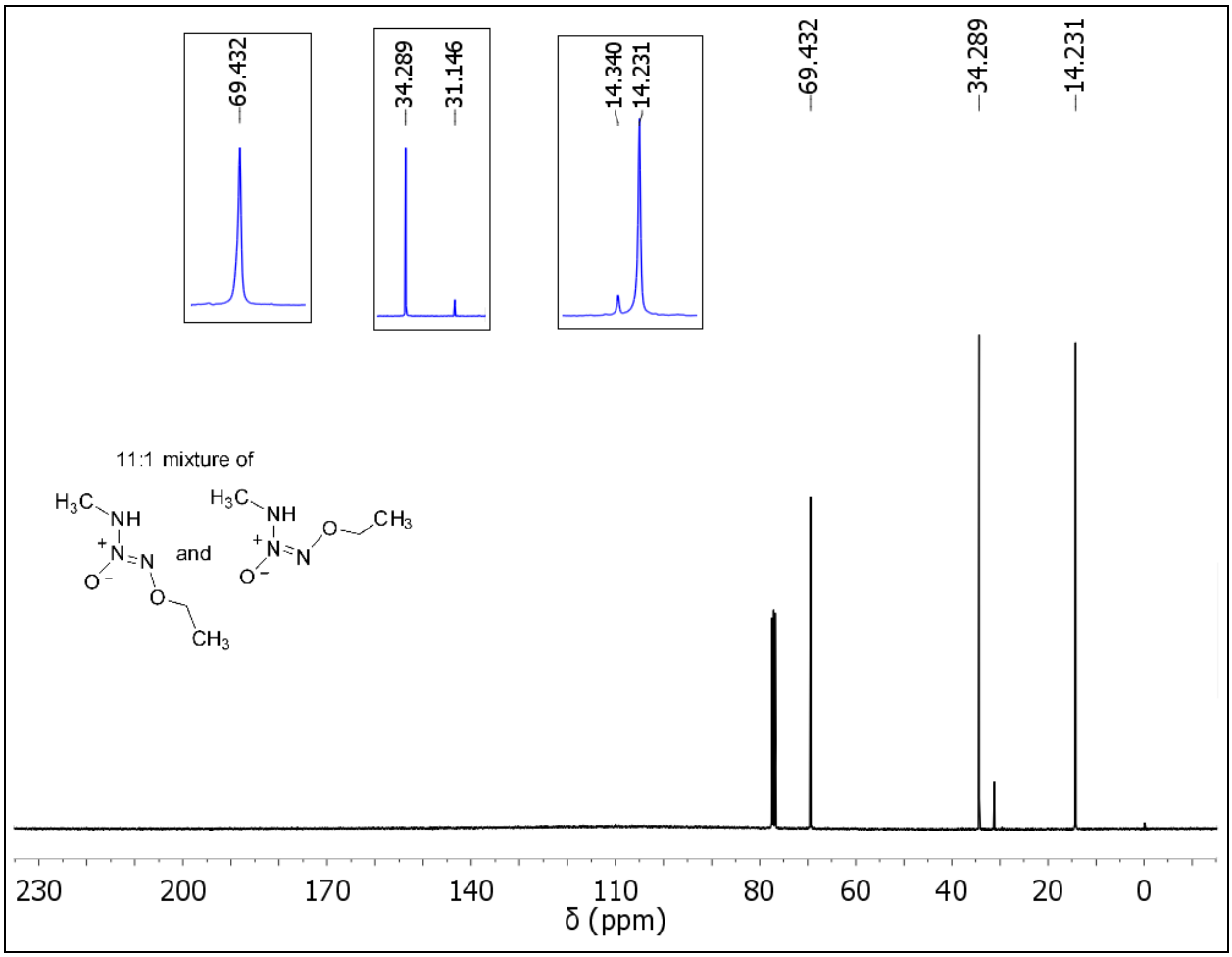

Figure S18. ^{13}C NMR spectrum of an equilibrium mixture of compounds ***Z*-13** and ***E*-13** in $CDCl_3$ at 25 ^{o}C.

References

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