SUPPORTING INFORMATION

Synthesis, Physicochemical Properties and Antimicrobial Activity of Mono-/Dinitroxyl Amides

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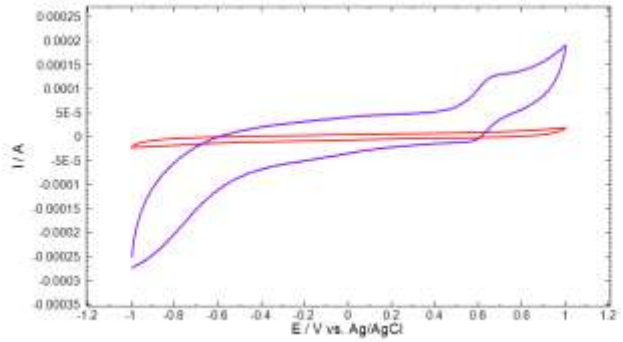
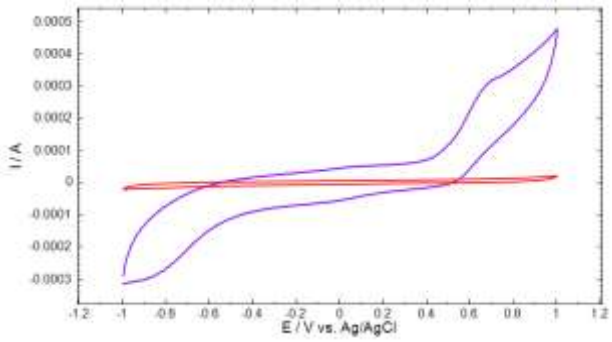
1. CYCLIC VOLTAMMETRY

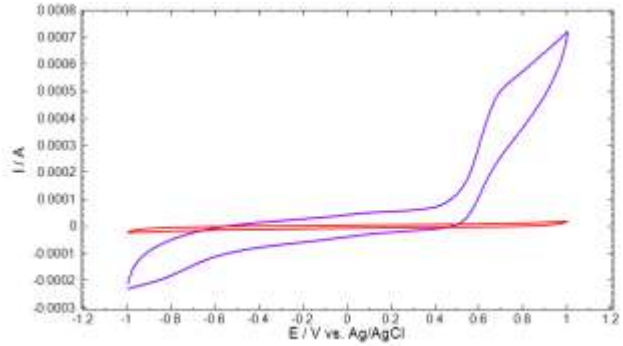
1.1 Cyclic voltammograms of mononitroxides 4–9 and dinitroxides 10–13.



Mononitroxide (4)



Mononitroxide (5)



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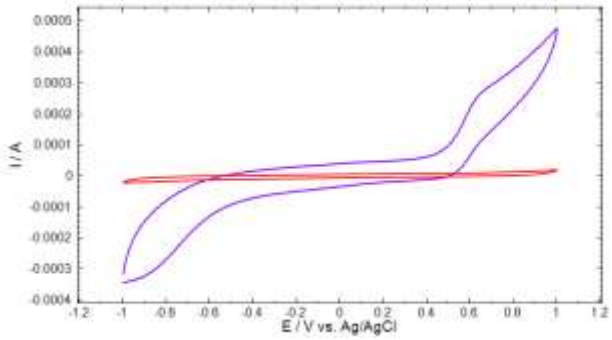

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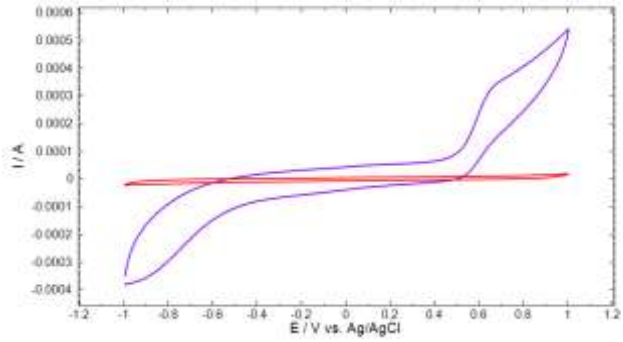
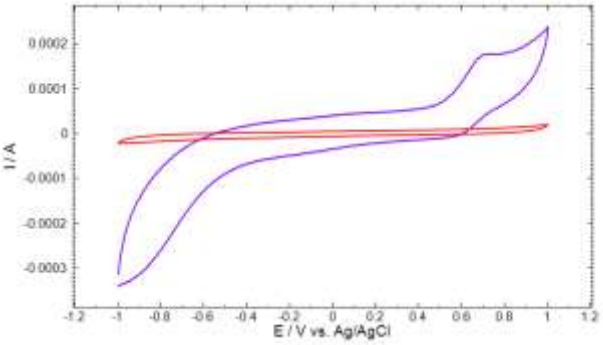
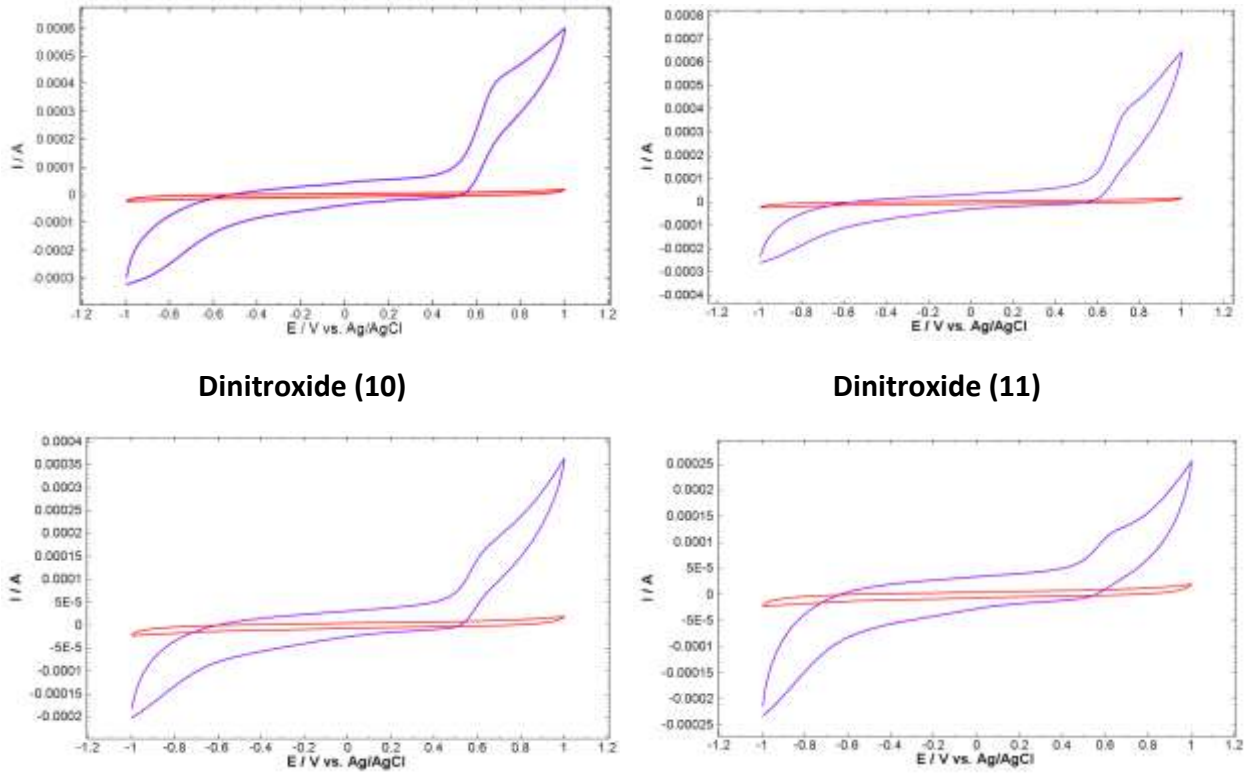


Mononitroxide (8)



Mononitroxide (9)



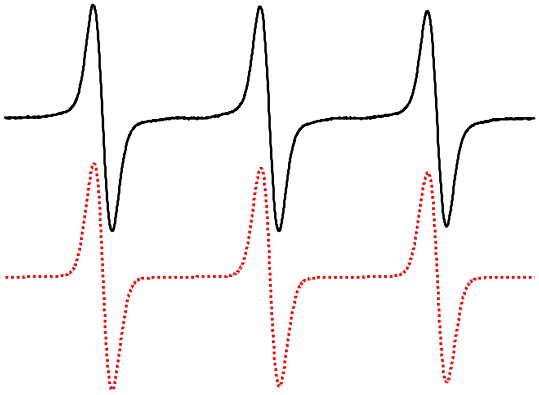
Dinitroxide (10) **Dinitroxide (11)**

Dinitroxide (12) **Dinitroxide (13)**

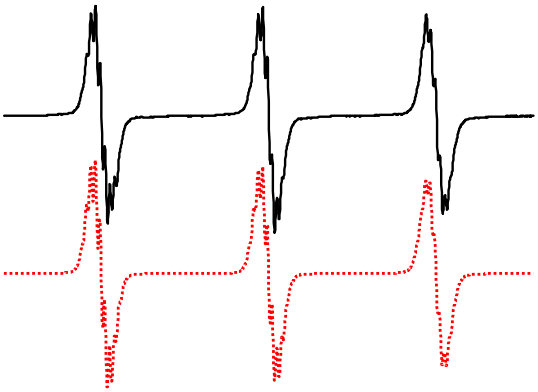
Figure S1: Cyclic voltammograms of mononitroxides **4**–**9** and dinitroxides **10**–**13**. Magenta – sample, Pink – control. Scan rate 100 mV s^{-1}, concentration 1× 10^{-4} mol L^{-1} in PBS at pH 7.0 on a PIGE electrode.

2. EPR SPECTROSCOPY

2.1 EPR spectra of mononitroxides 4–9 and dinitroxide 11.



Mononitroxide (4)



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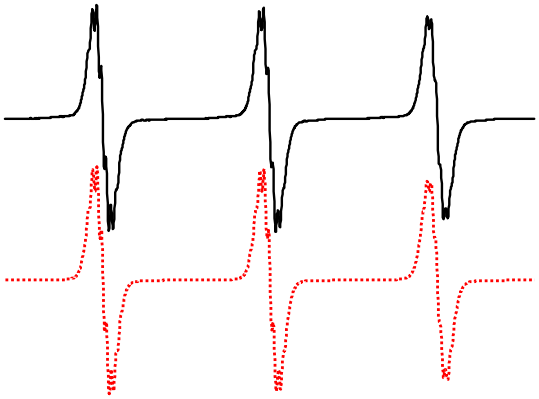
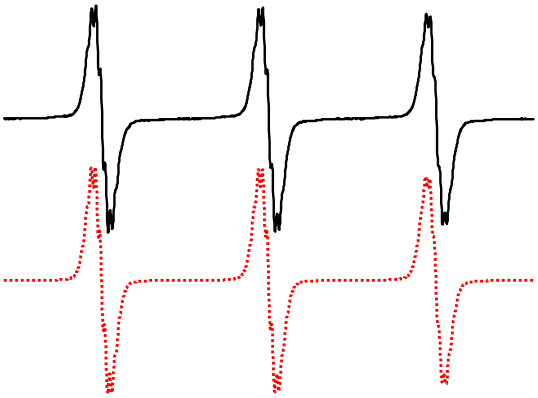
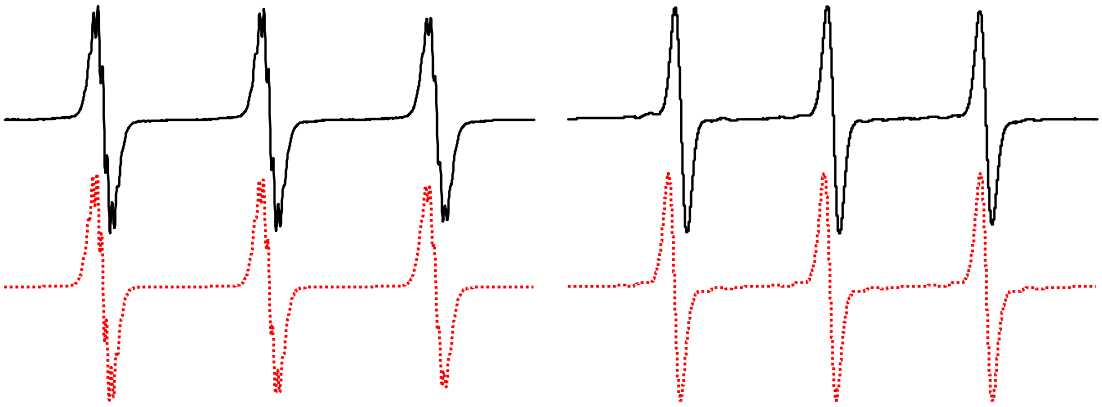


Mononitroxide (6)



Mononitroxide (7)



Mononitroxide (8) **Mononitroxide (9)**

Figure S2. Experimental (**–**) and simulated (¨) X-band EPR spectra of mononitroxides **4**–**9** obtained at 295 K in DCM under argon. Magnetic field sweep 6 mT; nitroxide concentration 0.1 mM. Spin Hamiltonian parameters elucidated from simulations are summarised in Table 2 (see Article).

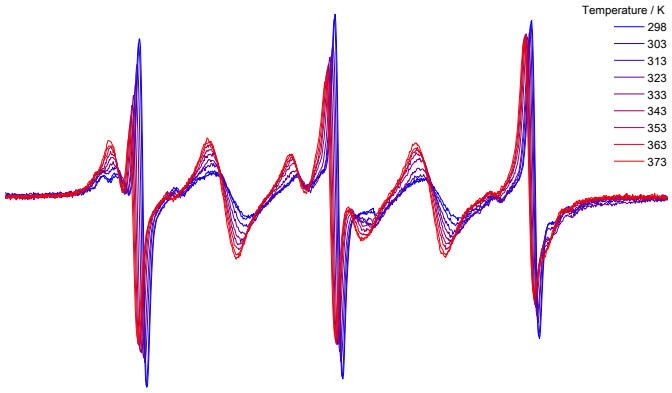
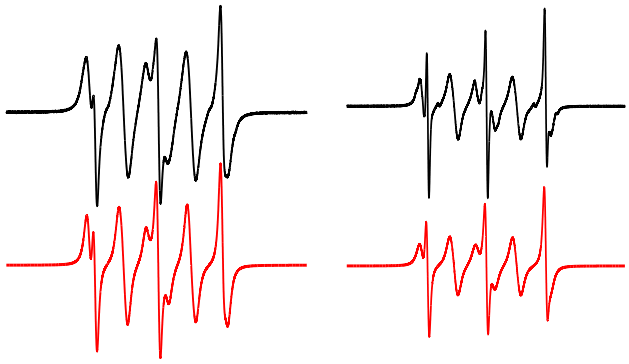


Figure S3. The set of X-band EPR spectra of dinitroxide **11** measured under argon at various temperatures (298–373 K) in DMSO (magnetic field sweep 6 mT; dinitroxide concentration 0.1 mM).



(a) **(b)**

Figure S4. Experimental (–) and simulated (–) X-band EPR spectra of dinitroxide **11** obtained at 295 K in DCM under Ar. Magnetic field sweep 7 mT; dinitroxide concentration 0.1 mM: (a) fresh solution, (b) solution stored for one month at +4 °C.

3. X-RAY CRYSTALLOGRAPHY

3.1 Selected geometric parameters for mononitroxides (4), (5), (8) and dinitroxides (10), (11).

Table S1. Summary of X-ray crystallographic data from single-crystal X-ray analyses of mono-/dinitroxides **4**, **5**, **8**, **10**, and **11**.

Compound	**4**	**5**	**8**	**10**	**11·0.5EtOH·0.5H_2O**
Chemical formula	$C_{14}H_{27}N_2O_3$	$C_{14}H_{27}N_2O_3$	$C_{11}H_{18}F_3N_2O_2$	$C_{20}H_{37}N_3O_3$	$C_{21}H_{34}F_3N_3O_3$· ·0.5C_2H_6O·0.5H_2O
M_r /.mol^{-1}	255.37	271.38	267.27	367.53	453.54
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	*P*bca	*P*nma	*P*nma	*P*bca	$P2_1/c$
T /K	293(2)	293(2)	293(2)	293(2)	293(2)
a /Å	11.7026(4)	11.9415(2)	11.9401(7)	19.4108(4)	14.2418(4)
b /Å	9.9471(3)	12.0243(2)	11.3109(7)	8.301(4)	9.4098(2)
c /Å	28.8577(12)	11.3190(2)	10.5933(5)	26.6839(5)	19.4980(6)
α /°	90	90	90	90	90
β /°	90	90	90	90	103.412(3)
γ /°	90	90	90	90	90
V /Å^3	3359.2(2)	1625.29(5)	1430.66(14)	4293.50(2)	2541.71(12)
Z	8	4	4	8	4
ρ_{calc} /g.cm^{-3}	1.010	1.109	1.241	1.137	1.185
μ /mm^{-1}	0.067	0.077	0.111	0.076	0.096
Crystal size /mm	0.95 x 0.59 x 0.29	0.93 x 0.44 x 0.25	0.78 x 0.40 x 0.28	0.89 x 0.69 x 0.59	0.75 x 0.30 x 0.21
F(000)	1128	596	564	1616	976
ϑ Range for data collection/°	3.04–26.37	2.48–26.37	3.61–26.45	2.10–26.37	2.94–25.24
Reflections collect.	15894	42154	6161	69062	30132
*R*1 (2σ)	0.0507	0.0580	0.0664	0.0498	0.0573
w*R*2 (all data)	0.1554	0.1727	0.2075	0.1435	0.1837
Data/restrains/ parameters	3417/27/184	1733/2/133	1523/104/116	4381/0/235	4546/154/310
S	1.067	1.076	1.094	1.069	1.030

$\Delta_{\rho max}$ /e Å^{-3}	0.215	0.193	0.219	0.292	0.567
$\Delta_{\rho min}$ /e Å^{-3}	–0.159	–0.248	–0.435	–0.216	–0.371

Table S2. Hydrogen bonds and intermolecular interactions data

Interactions / Hydrogen bonds	Distance [Å]	Symmetry code
Mononitroxide (4)		
N2–H2N···O2	2.120	-x-1/2,y-1/2,z
Mononitroxide (5)		
N2–H2N···O1	2.055	x -1/2, -y+1/2, -z+3/2
C2–H2B···H4B	2.474	-x+1, -y+1, -z+1
C8–H8B···H5A	2.629	-x +1/2, y-1/2, z-1/2
C5–H5B···H9A	2.870	x +1/2, -y+1/2, -z+3/2
Mononitroxide (8)		
N2–H2N···O1	2.000	x+1/2, -y+1/2, -z+3/2
N2–H2N···F1	2.241	x, y, z
C5A–H5A3···O2	2.636	-x+1/2, y-1/2, z-1/2
C2–H2B···O1	2.717	x+1/2, y, -z+3/2
C2–H2B*···O1	2.717	x+1/2, -y+1/2, -z+3/2
Dinitroxide (10)		
C15–H15A···H18B	2.420	x +1/2, y, -z+3/2
C15–H15A···H13B	2.325	
C4–H4A···O3	2.672	x -1/2, y, -z+3/2
C6–H6B···O2	2.469	-x +5/2, y-1/2, z
C20–H20B···O2	2.570	
C16–H16B···O1	2,696	-x+2, -y, -z+1
C17–H17A···O1	2.822	
C12–H12A···H2B	1.978	x, y, z
Dinitroxide (11·0.5EtOH·0.5H_2O)		

C2–H2B···O3	2.564	-x+1, y-1/2,- z+3/2
C3–H3···F1A	2.310	
C3–H3···F3A	2.292	
C3–H3···F1B	2.309	
C3–H3···F3B	2.292	
C7–H7A···O1S	2.571	x, y-1, z
C11–H11A···O3	2.440	
C11–H11B···F2A	2.615	-x+1, y-1/2,- z+3/2
C11–H11B···F2B	2.464	-x+1, y-1/2,- z+1/2
C13–H13B···O3	2.436	
O1W–H1WA···O1S	2.390	x, y-1, z
O1W–H1WB···O2	2.190	-x, y-1/2,- z+3/2
O1S–H1S···O1W	2.267	x, y+1, z

3.2 ORTEP drawings and/or packing diagrams of mononitroxides (4), (5), (8) and dinitroxides (10), (11).

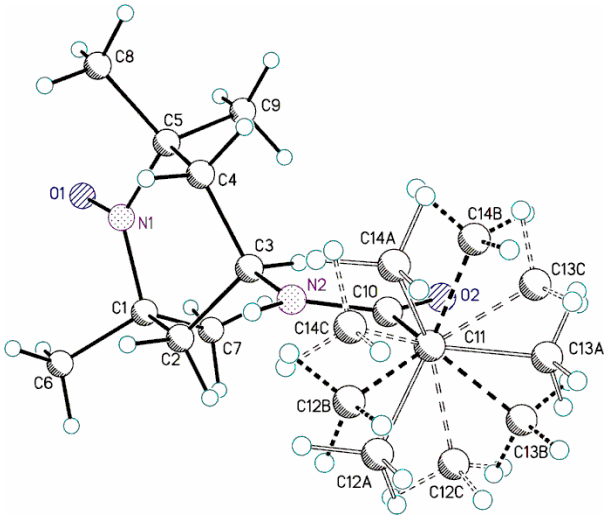


Figure S5. The disordered *tert*-butyl group (open lines and dashed lines) in mononitroxide **4**.

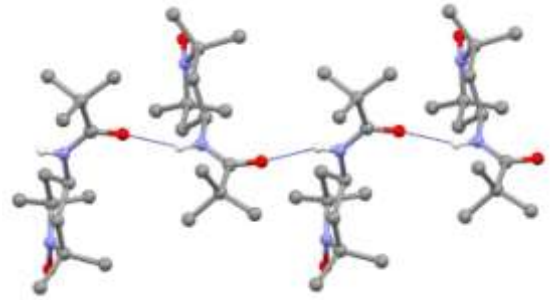


Figure S6. The N–H···O hydrogen bonds and H···H intermolecular contacts in the crystal structure of mononitroxide **4**.

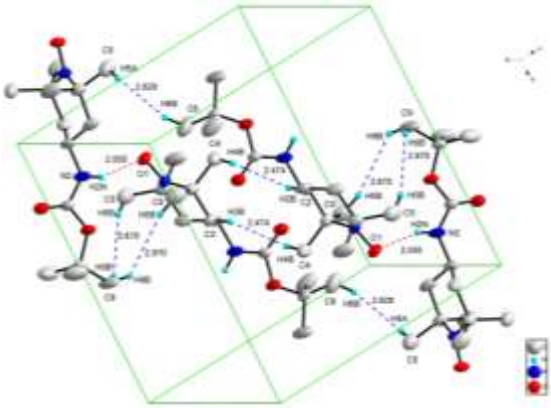


Figure S7. The N–H···O hydrogen bonds and H···H intermolecular contacts in the crystal structure of mononitroxide **5**.

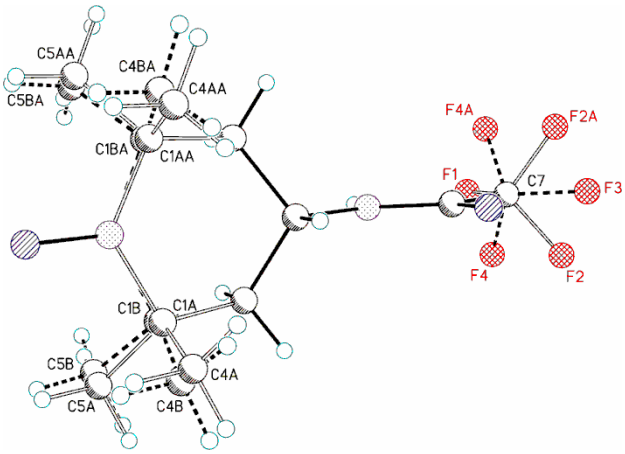


Figure S8. The disordered trifluoroacetyl and *gem*-dimethyl groups (open lines and dashed lines) in mononitroxide **8**.

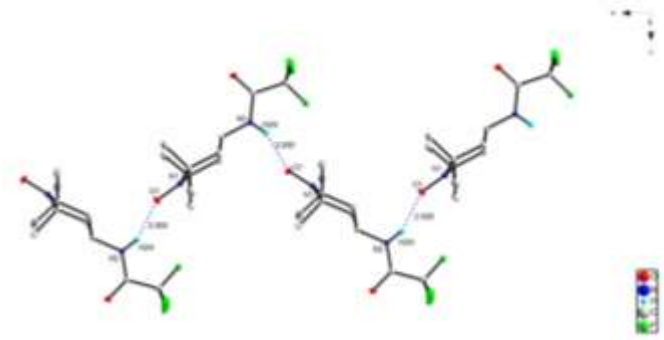


Figure S9. The N–H···O hydrogen bonds in the crystal structure of mononitroxide **8**.

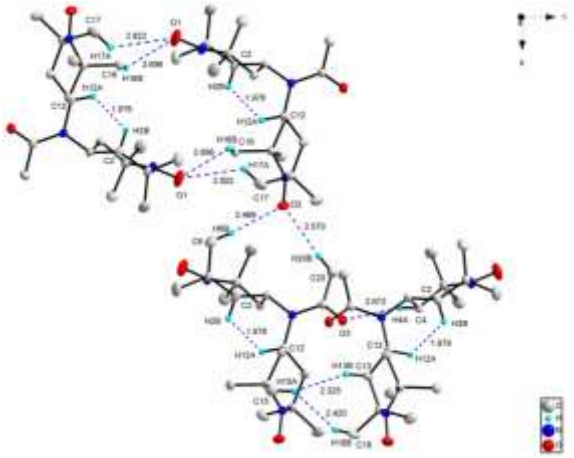


Figure S10. The C–H···O hydrogen bonds and H···H intermolecular contacts in the crystal structure of dinitroxide **10**.

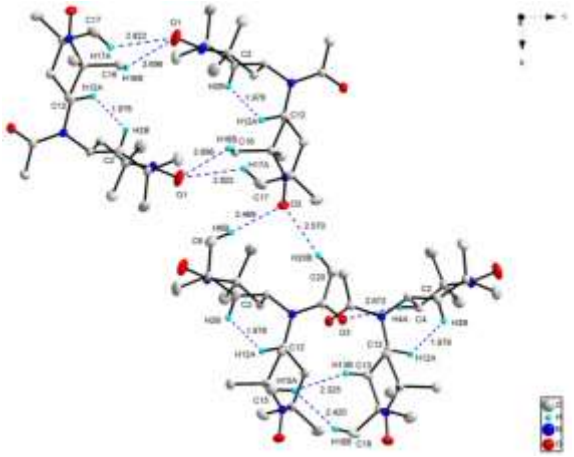


Figure S11. The C–H···O hydrogen bonds and H···H intermolecular contacts in the crystal structure of dinitroxide **10**.

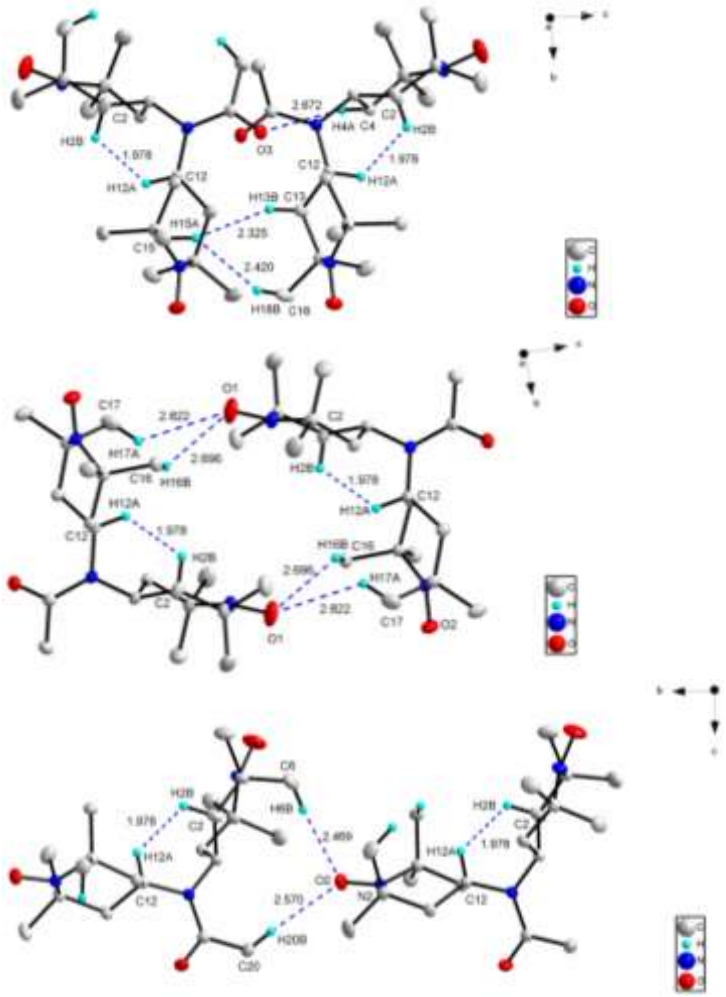


Figure S12. Details of the C–H···O hydrogen bonds and H···H intermolecular contacts in the crystal structure of dinitroxide **10**.

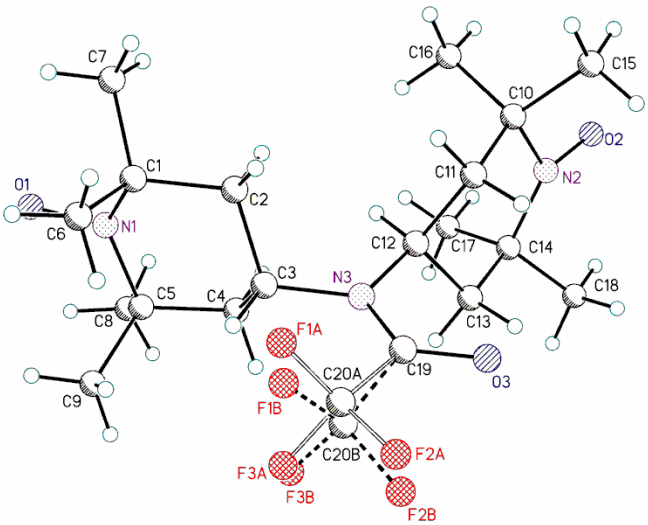


Figure S13. The disordered trifluoroacetyl group (open lines and dashed lines) of dinitroxide **11**. The solvent molecules (EtOH, H_2O) were omitted for clarity.

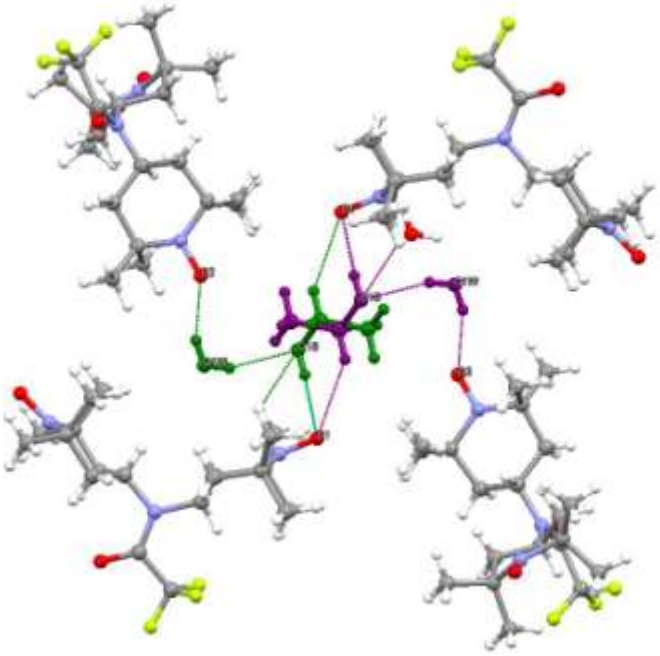


Figure S14. The disordered solvents (EtOH and H_2O) in the crystal structure of dinitroxide **11**.

4. ANALYTICAL DATA

4.1 HRMS spectra of nitroxides (8), (9) and (11).

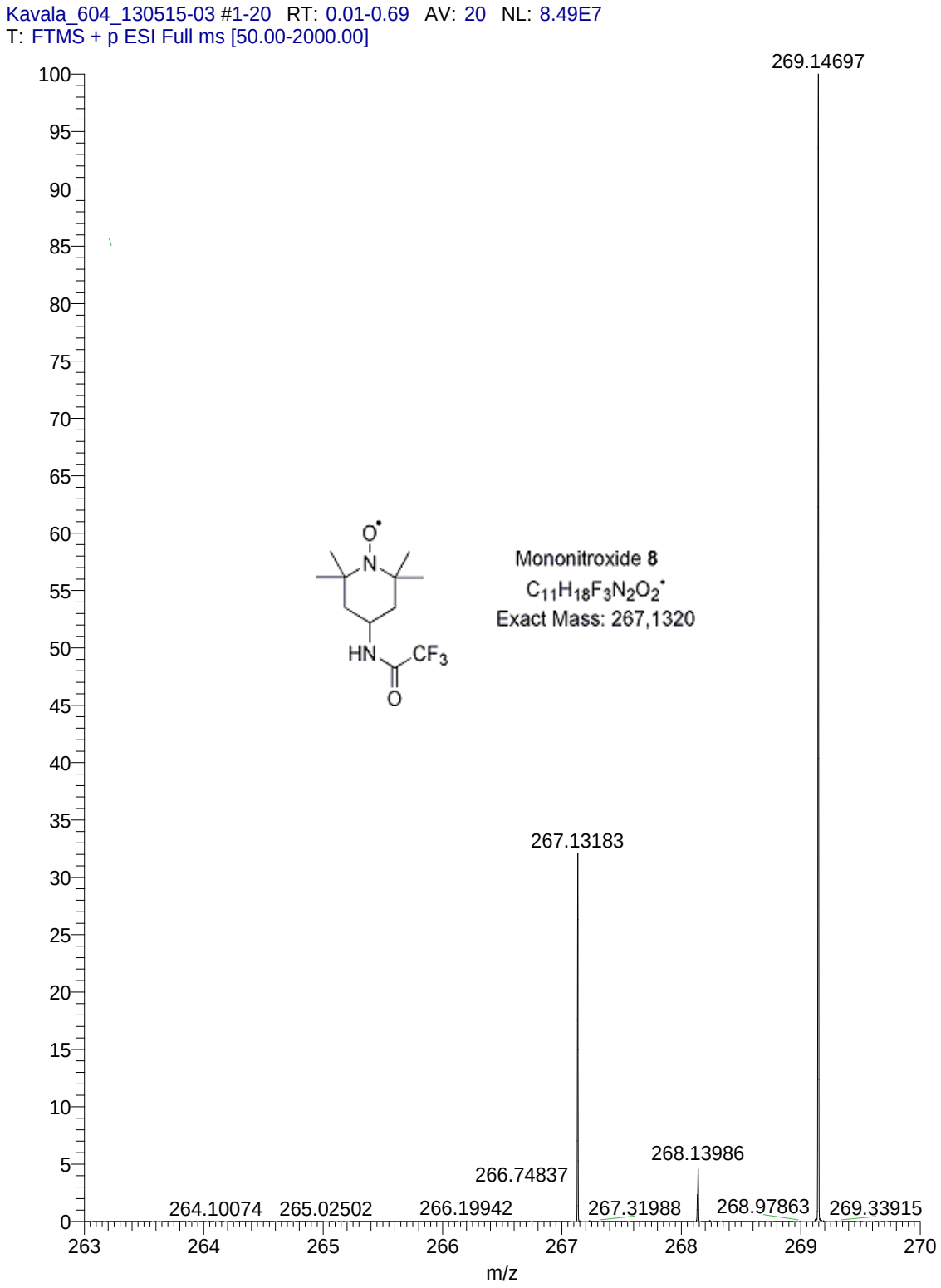


Figure S15. HRMS (ESI) spectrum of mononitroxide **8**.

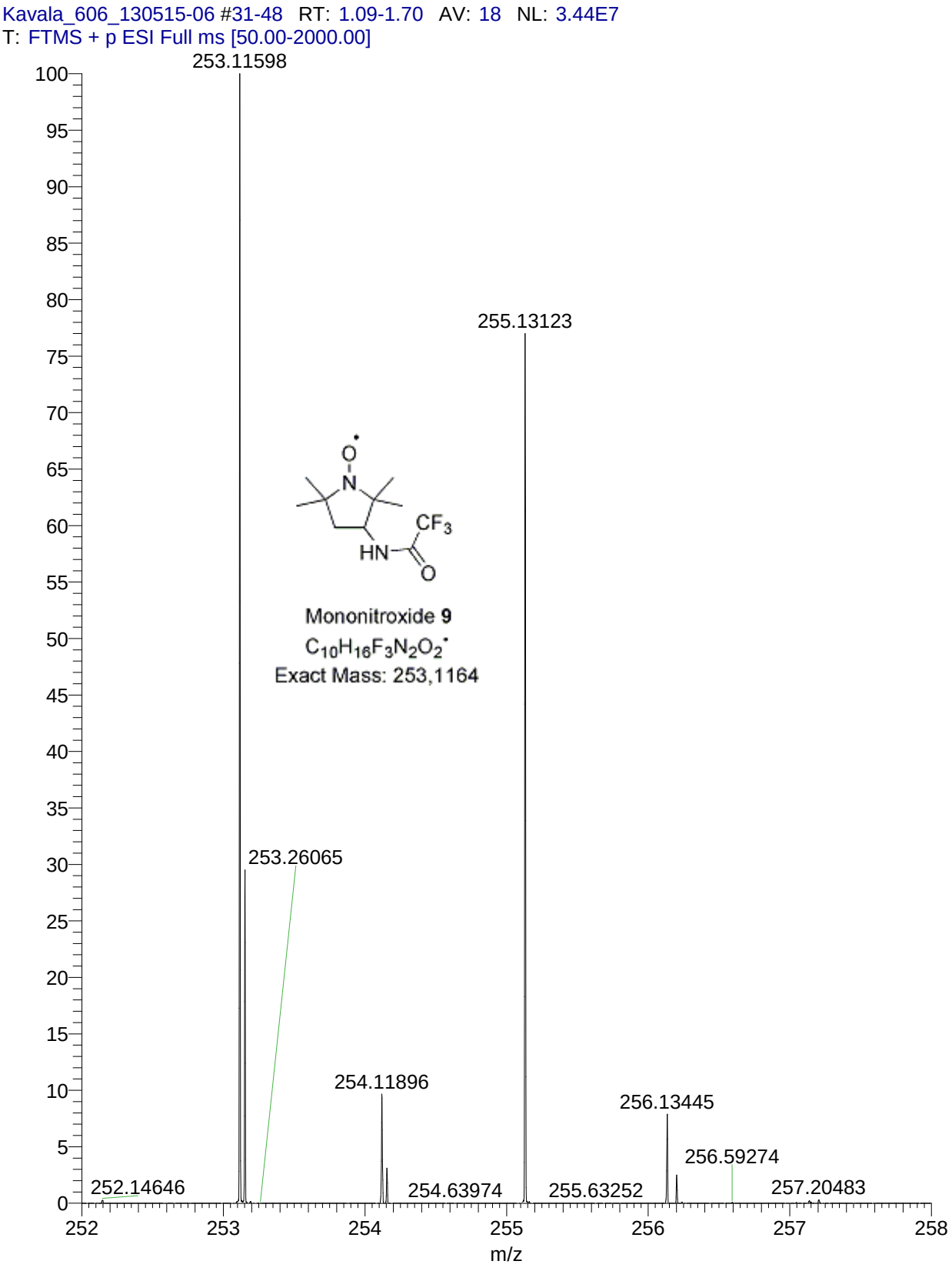


Figure S16. HRMS (ESI) spectrum of mononitroxide **9**.

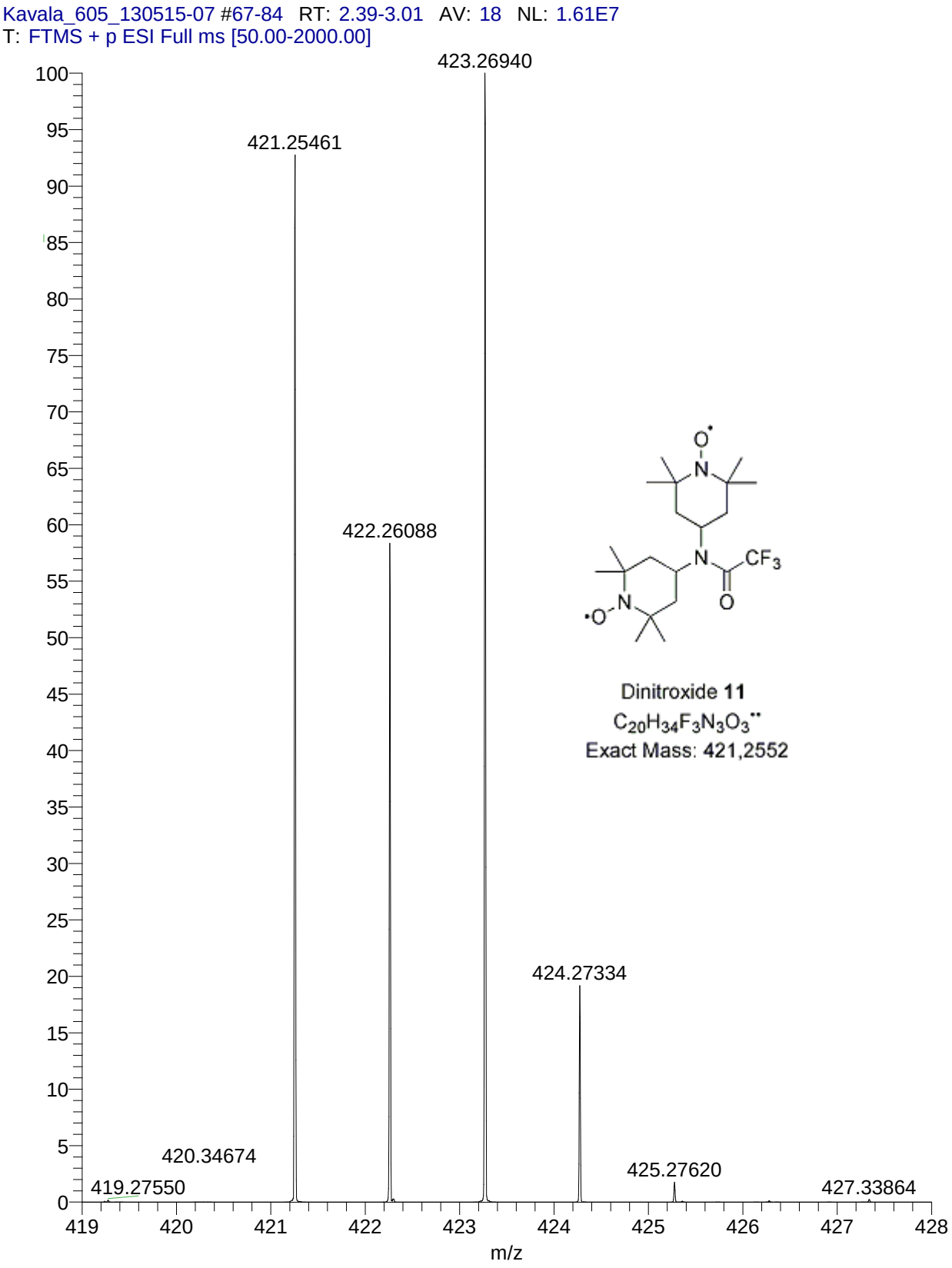


Figure S17. HRMS (ESI) spectrum of dinitroxide **11.**