Supporting Information

Single-Step Synthesis of 3,5-diazido 1,2,4-triazole: Environmentally Benign High-Performance Primary Explosives

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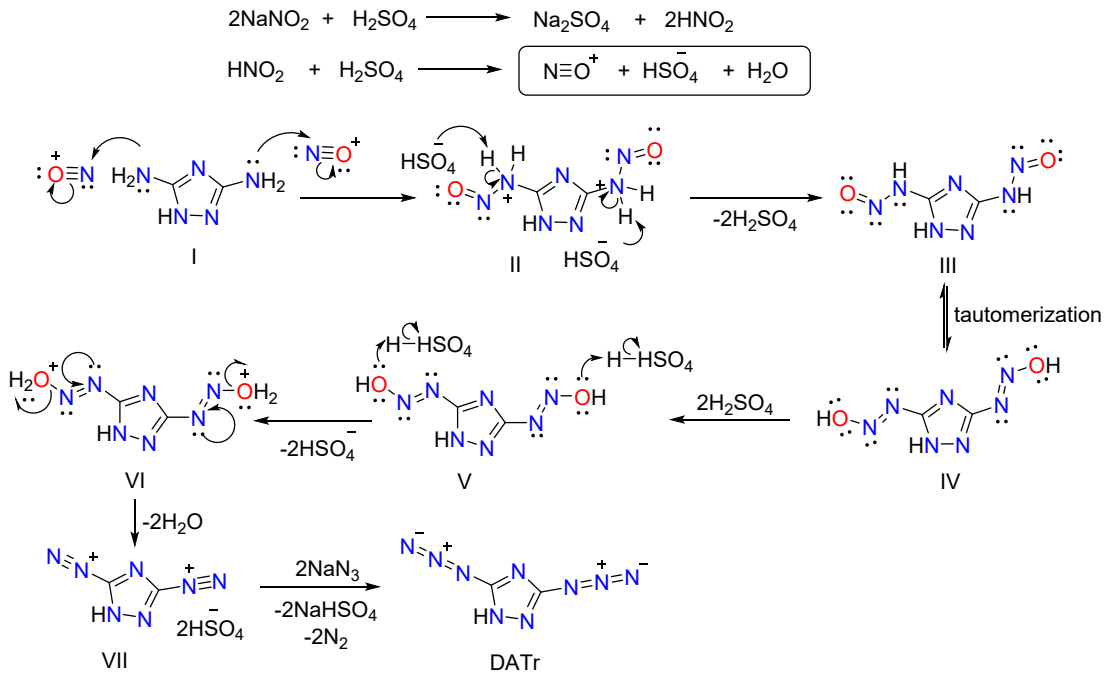
Plausible reaction mechanism for the synthesis of 3,5-Diazido-1,2,4-triazole from 3,5-Diamino-1,2,4-triazole:

Step 1: Generation of Nitrosyl Cation: Sodium nitrite reacts with sulfuric acid to generate nitrous acid, which is protonated to form the electrophile nitrosonium ion $(NO)^{+}$.

Step 2: Nitrosation of the Amino Groups: The amino groups at the 3- and 5-positions of 3,5-diamino-1,2,4-triazole attack the nitrosonium ion.

Step 3: Formation of Diazonium Intermediates: Under strongly acidic conditions, the nitrosamine tautomerizes to the diazohydroxide form. Protonation of the hydroxyl group converts it into a good leaving group followed by loss of water gives the diazonium ion (R-N_2^{+}). Because there are two amino groups, a bis-diazonium triazole salt forms.

Step 4: Nucleophilic Substitution by Azide: Azide ion attacks the diazonium carbon and displaces nitrogen functionality. This substitution occurs at both diazonium centres to form DATr as the final product.



Scheme S1. Plausible reaction mechanism for the synthesis of 3,5-Diazido-1,2,4-triazole from 3,5-Diamino-1,2,4-triazole

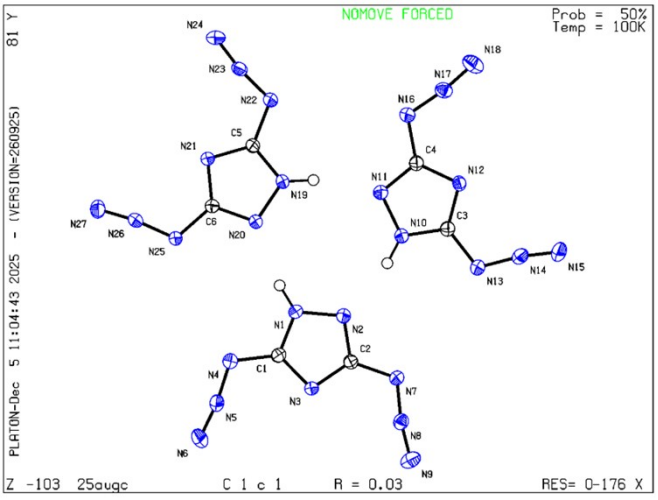


Figure S1: Molecular Structure of **DATr.**

Table S1: Crystal data and structure refinement for DATr.

CCDC No.	2513812
Empirical formula	C_2HN_9
Formula weight	151.12
Temperature/K	100.0
Crystal system	monoclinic
Space group	Cc

a/Å	12.0395(10)
b/Å	23.364(2)
c/Å	8.0029(6)
α/°	90
β/°	125.292(2)
γ/°	90
Volume/Å3	1837.5(3)
Z	12
ρcalcg/cm3	1.639
μ/mm-1	0.131
F(000)	912.0
Crystal size/mm3	0.17 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.496 to 56.928
Index ranges	-16 ≤ h ≤ 16, -31 ≤ k ≤ 31, -10 ≤ l ≤ 10
Reflections collected	14578
Independent reflections	4580 [Rint = 0.0266, Rsigma = 0.0269]
Data/restraints/parameters	4580/2/299
Goodness-of-fit on F2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0257, wR2 = 0.0672
Final R indexes [all data]	R1 = 0.0266, wR2 = 0.0684
Largest diff. peak/hole / e Å-3	0.21/-0.26

NMR, IR Spectra, HRMS & TG-DSC plots:

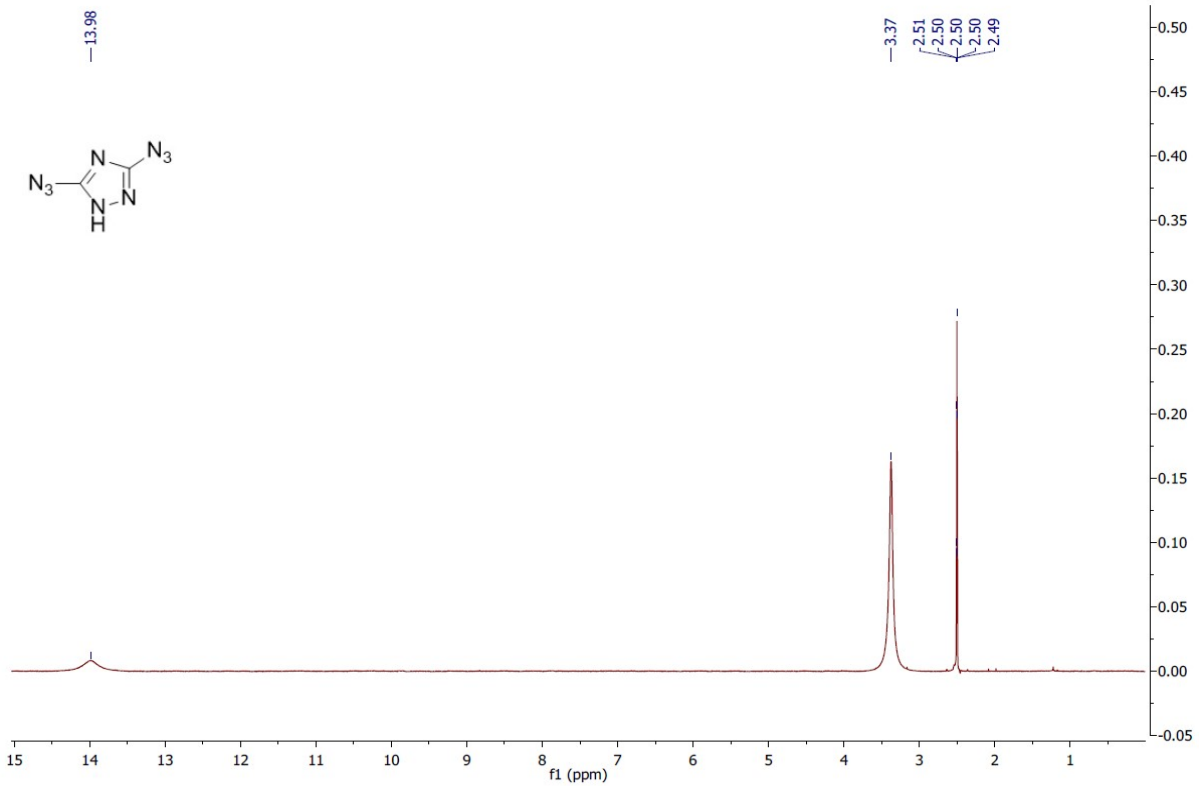


Figure S2: ^{1}H NMR spectrum of **DATr** (Fresh) in **DMSO-*d*$_6$** in 500 MHz**.**

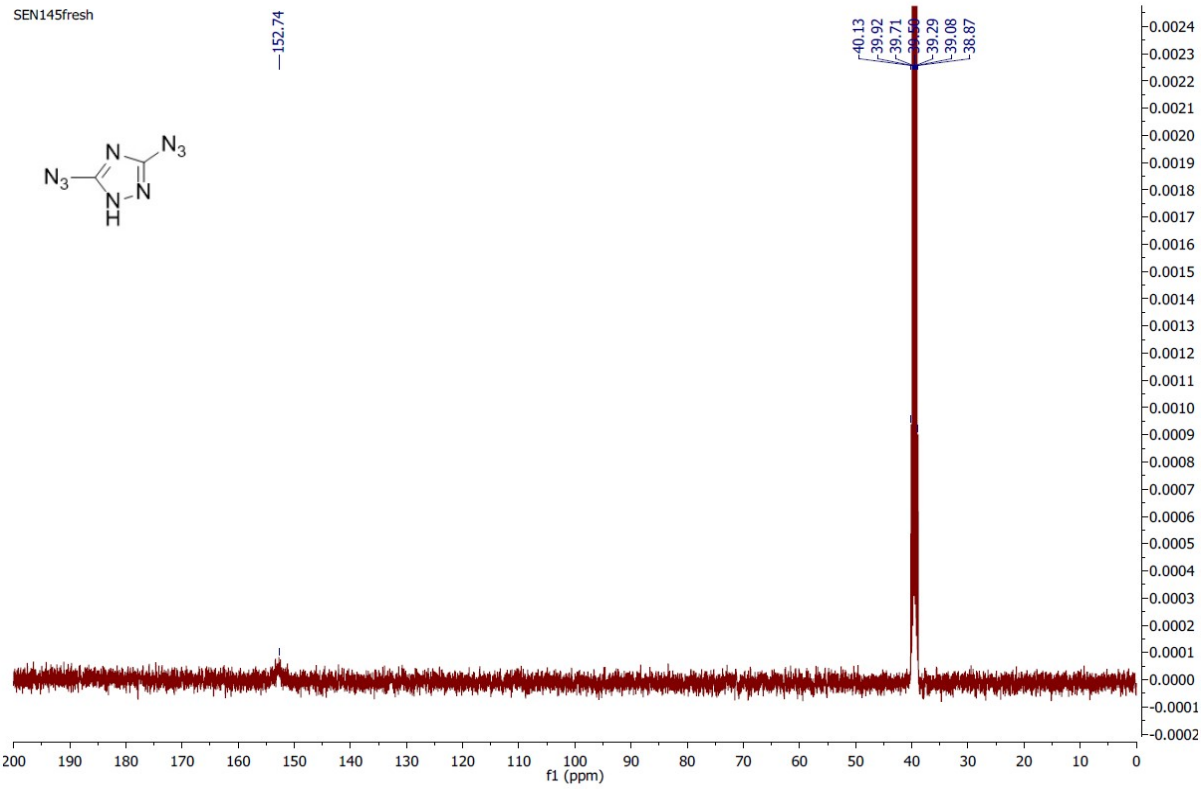


Figure S3: ^{13}C NMR spectrum of **DATr** (Fresh) in **DMSO-*d*$_6$** in 126 MHz.

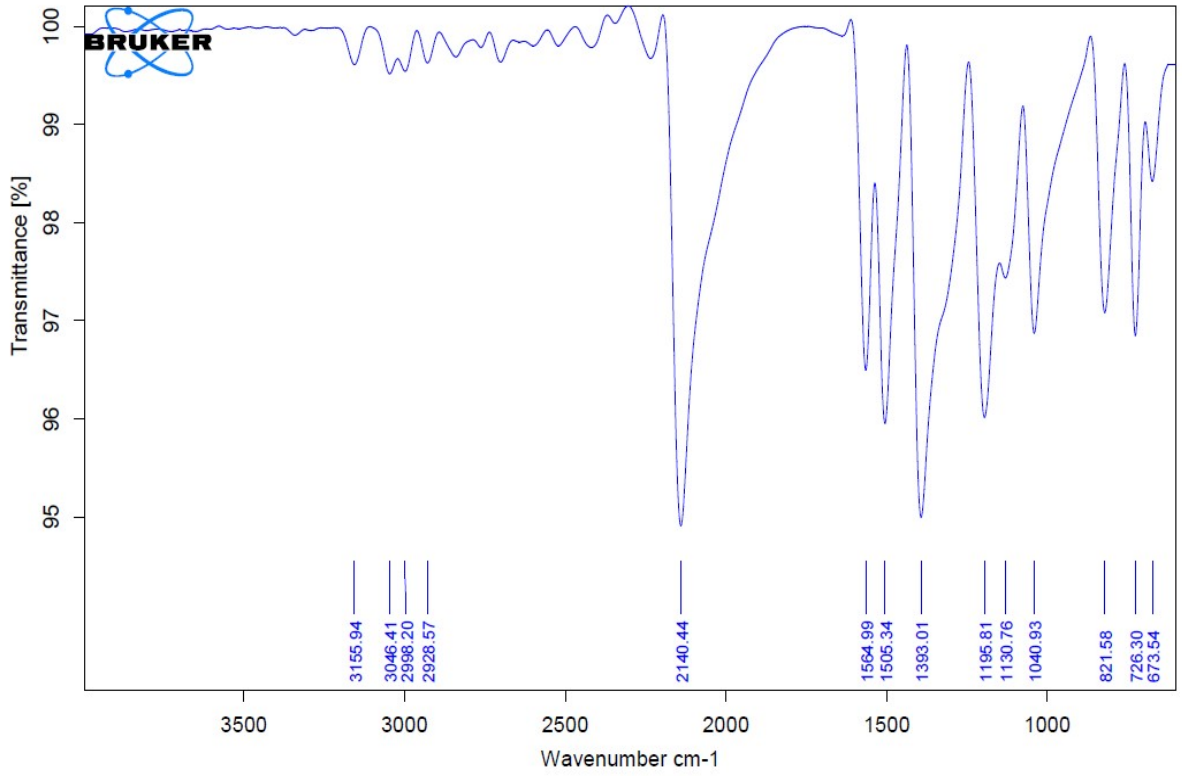


Figure S4: IR spectrum of **DATr** (Fresh).

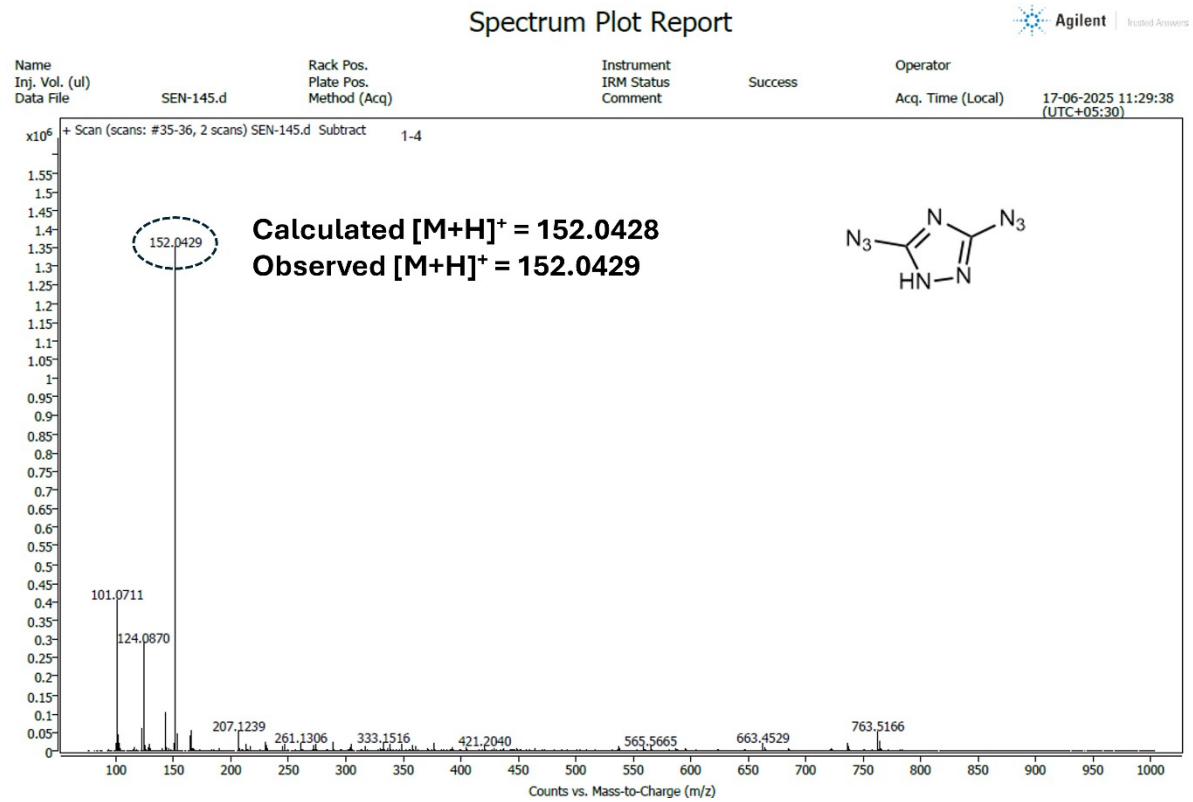


Figure S5: Mass spectrum of **DATr** (Fresh).

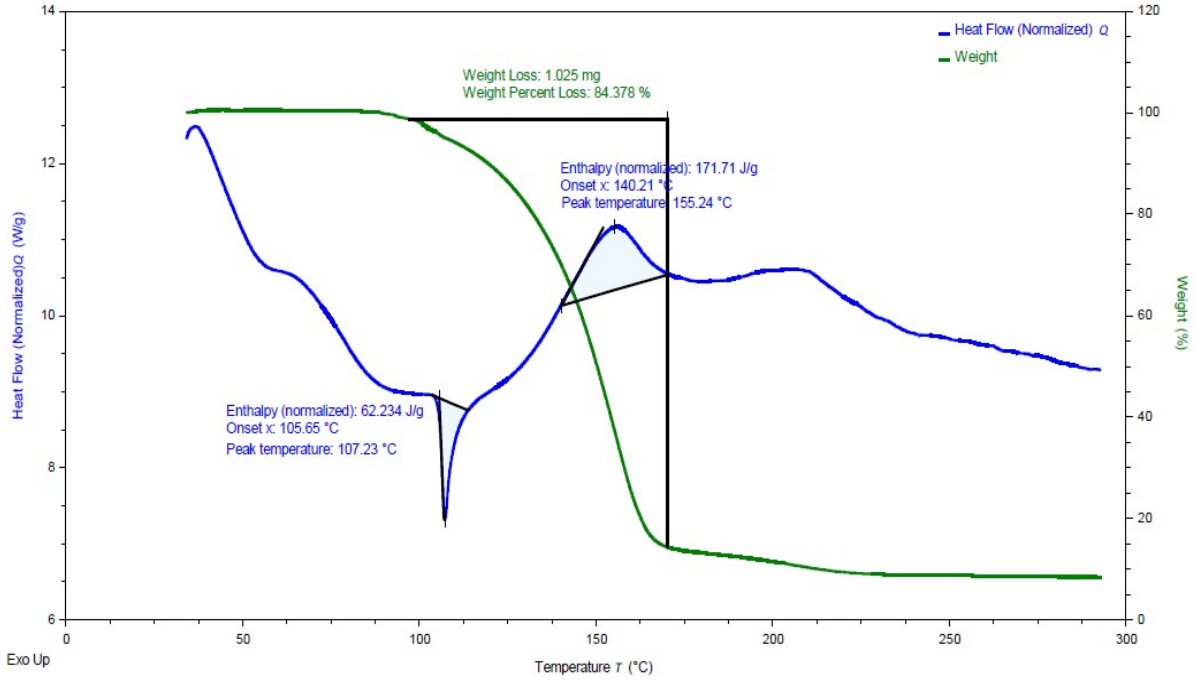


Figure S6: DSC spectra of **DATr** (Fresh) at a heating rate of 5 ˚C min^{-1}.

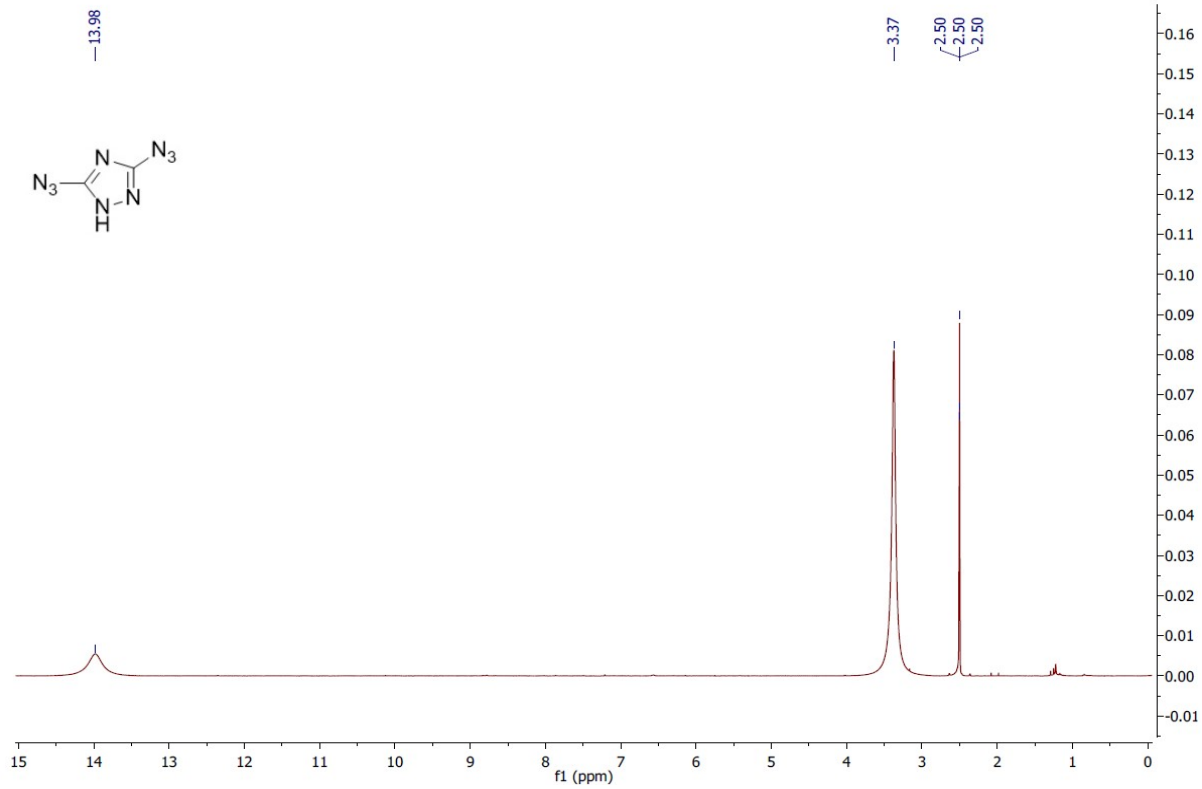


Figure S7: ^{1}H NMR spectrum of **DATr** (2 months in sunlight) in **DMSO-*d*$_6$** in 500 MHz**.**

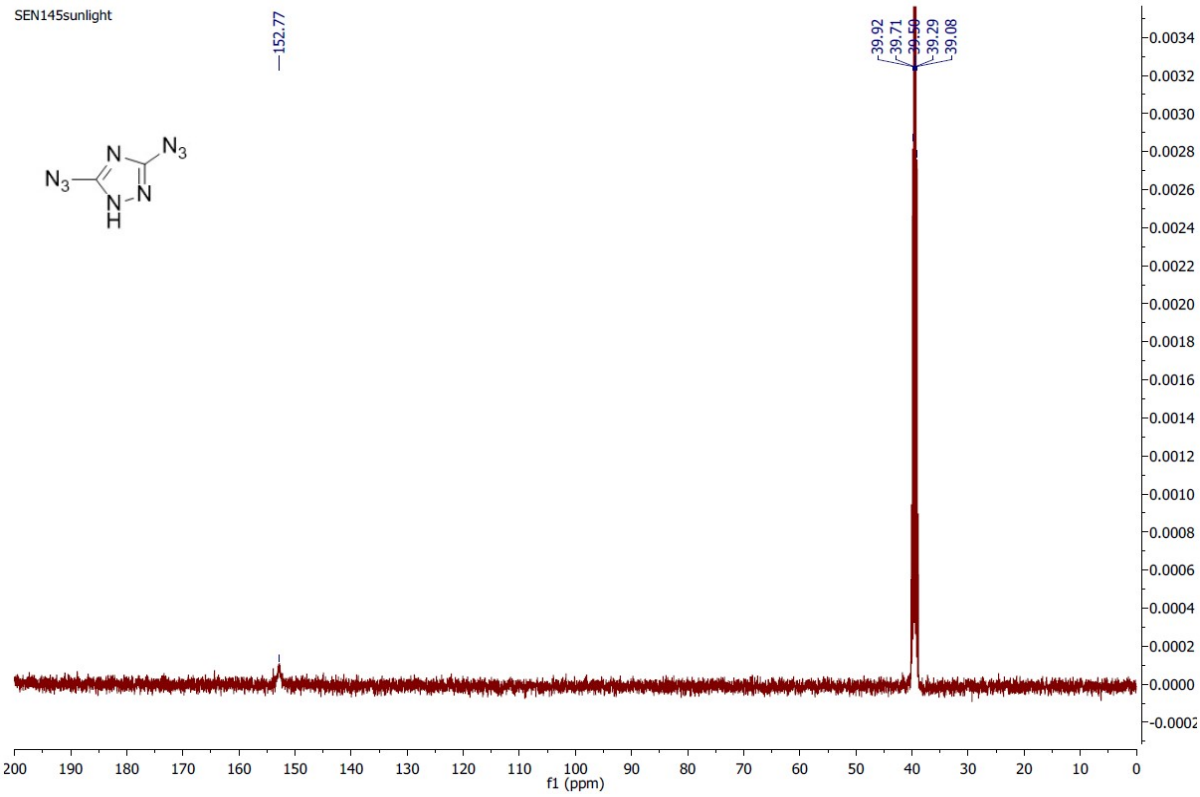


Figure S8: ^{13}C NMR spectrum of **DATr** (2 months in sunlight) in **DMSO-*d*$_6$** in 126 MHz.

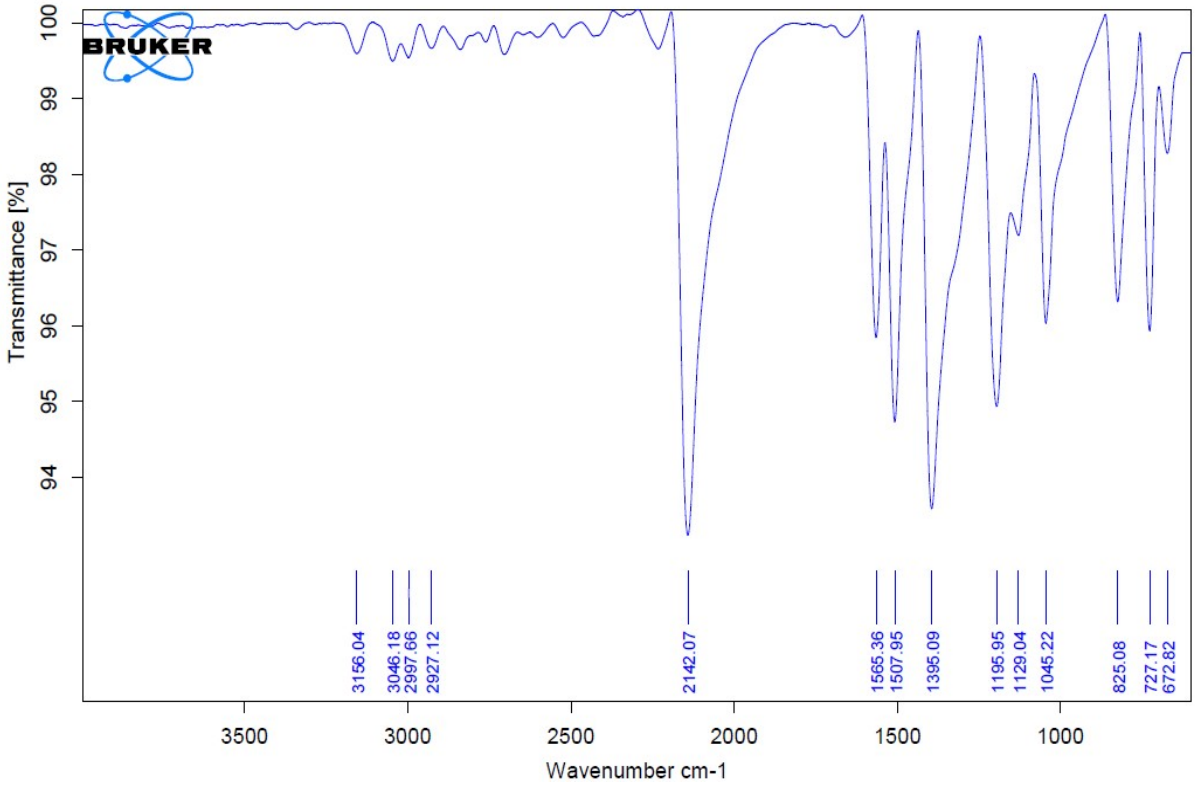


Figure S9: IR spectrum of **DATr** (2 months in sunlight).

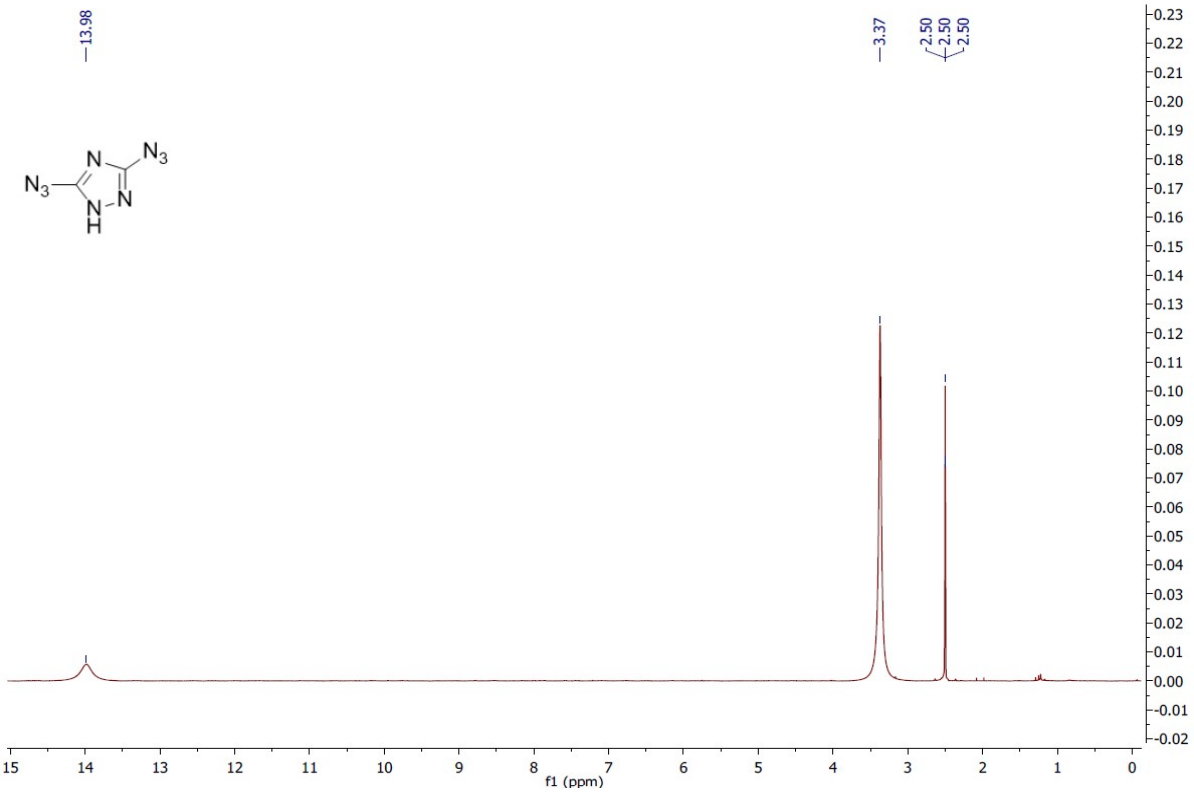


Figure S10: ^{1}H NMR spectrum of **DATr** (48 h at 70 ˚C) in **DMSO-*d*$_6$** in 500 MHz**.**

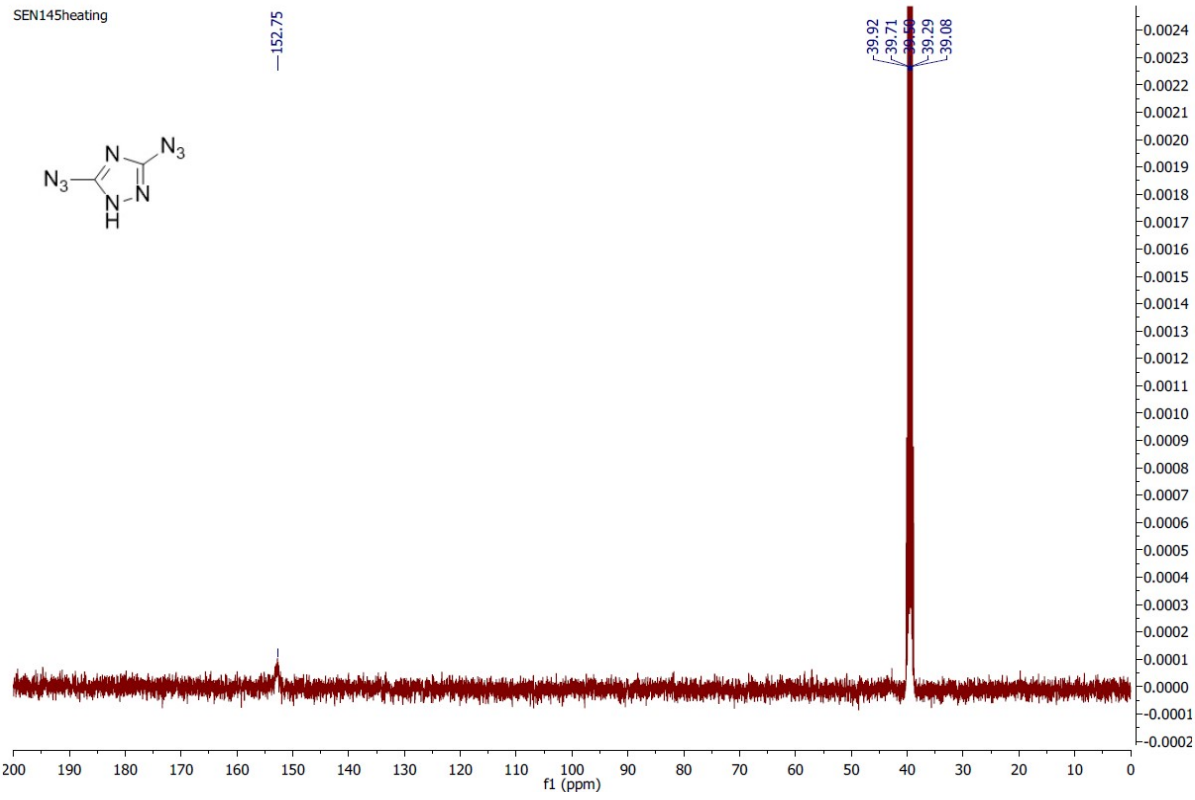


Figure S11: ^{13}C NMR spectrum of **DATr** (48 h at 70 ˚C) in **DMSO-*d*$_6$** in 126 MHz.

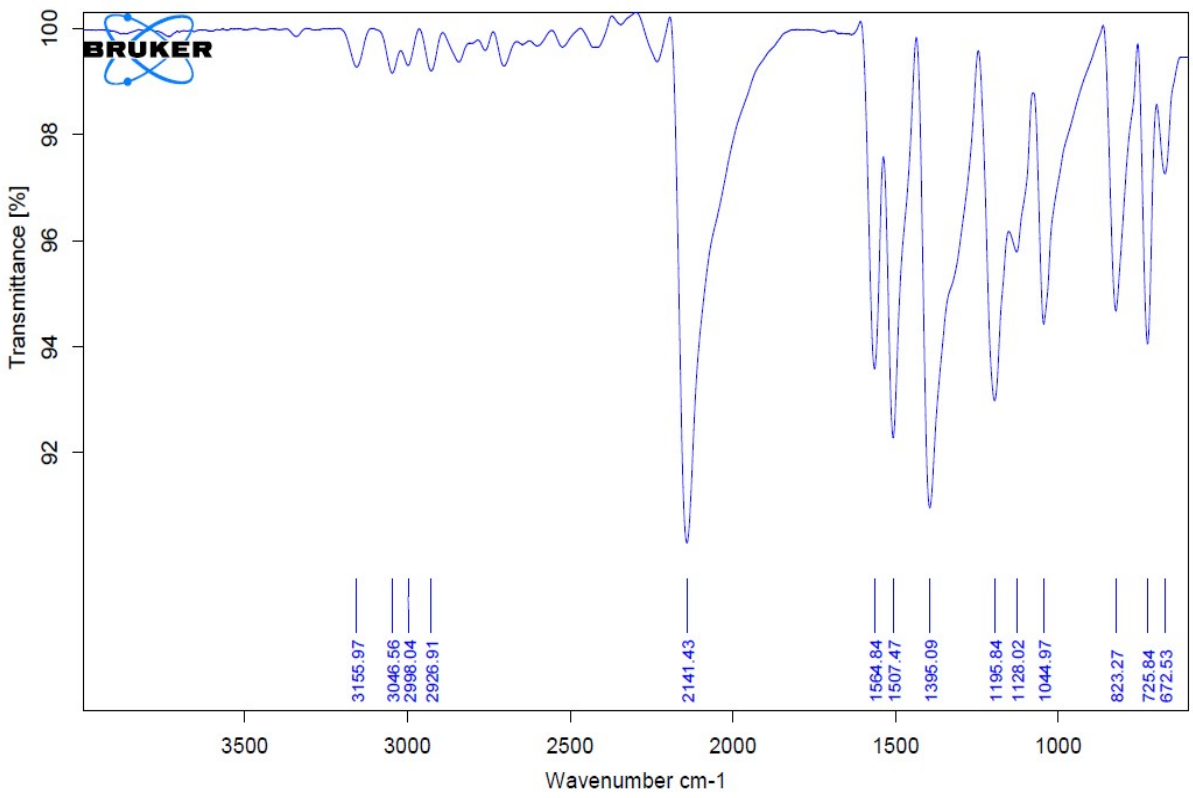


Figure S12: IR spectrum of **DATr** (48 h at 70 ˚C).

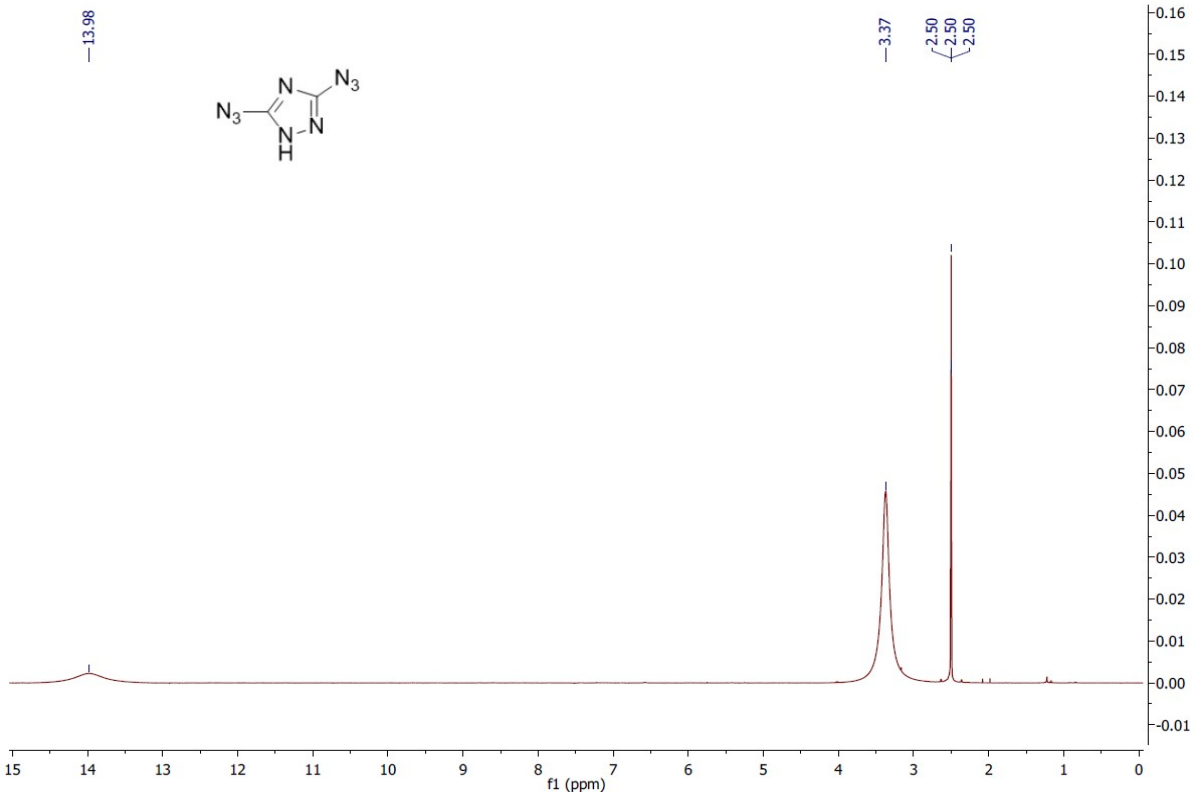


Figure S13: [1]H NMR spectrum of **DATr** (6 months in open air) in **DMSO-*d*$_6$** in 500 MHz**.**

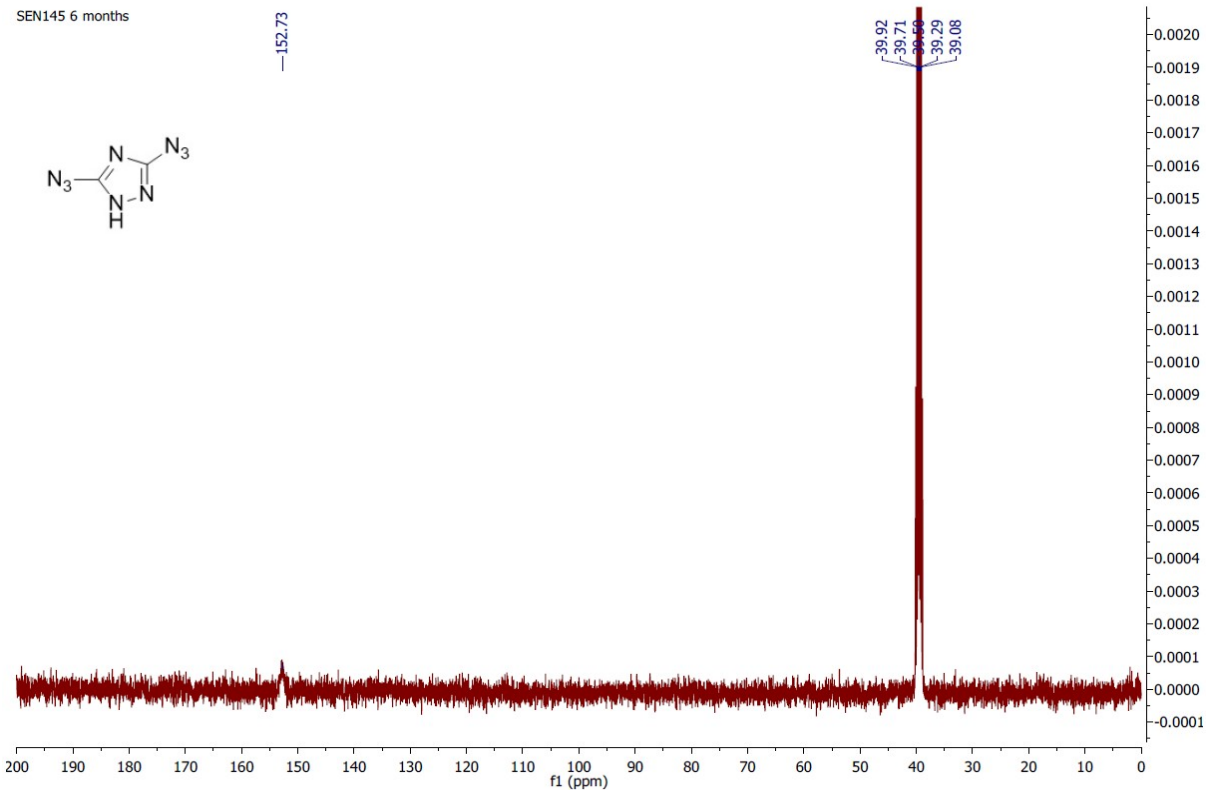


Figure S14: ^{13}C NMR spectrum of **DATr** (6 months in open air) in **DMSO-*d*$_6$** in 126 MHz.

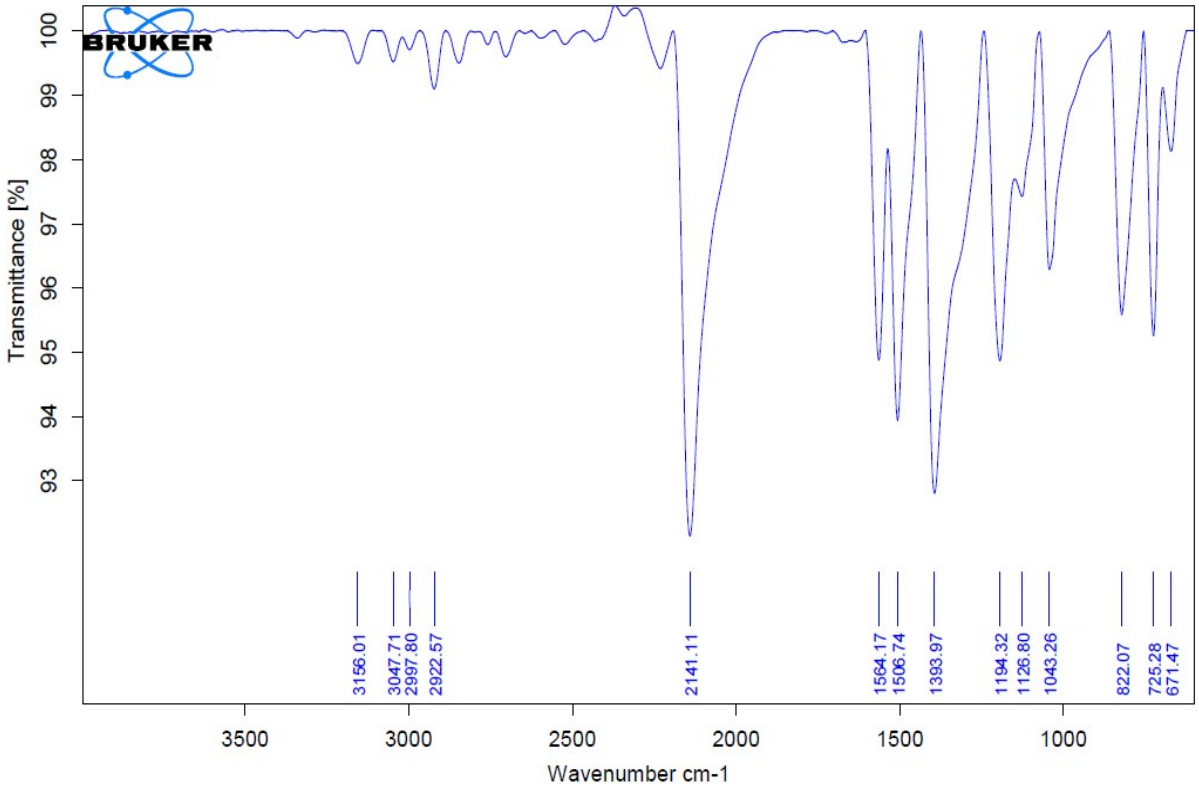


Figure S15: IR spectrum of **DATr** (6 months in open air).