Electronic Supplementary Material (ESI) for Dalton Transactions.

Nitration Pattern of Energetic 3,6-Diamino-1, 2, 4, 5-tetrazine Derivatives Containing Azole Functional Groups.

Supporting Information

Alexander Aizikovich, Avital Shlomovich, Adva Cohen and Michael Gozin*

School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel

E-mail: cogozin@gmail.com; Phone: +972-3-640-5878.

Content

X-ray Crystallography

Crystals of **16** suitable for X-ray diffraction were obtained by subjecting a solution of **16** in H_2O to vapors of perchloric acid, while suitable crystals of compound **20** were obtained by recrystallization from water and DMF. The crystals of **16** and **20**·4DMF. Data were collected using MoKa radiation (L = 0.71073 nm). An Oxford low-temperature device was used to keep the crystals at a constant temperature of 110K, during all data collection period. Details of the X-ray data collection and structure refinements are summarized in Table S1.

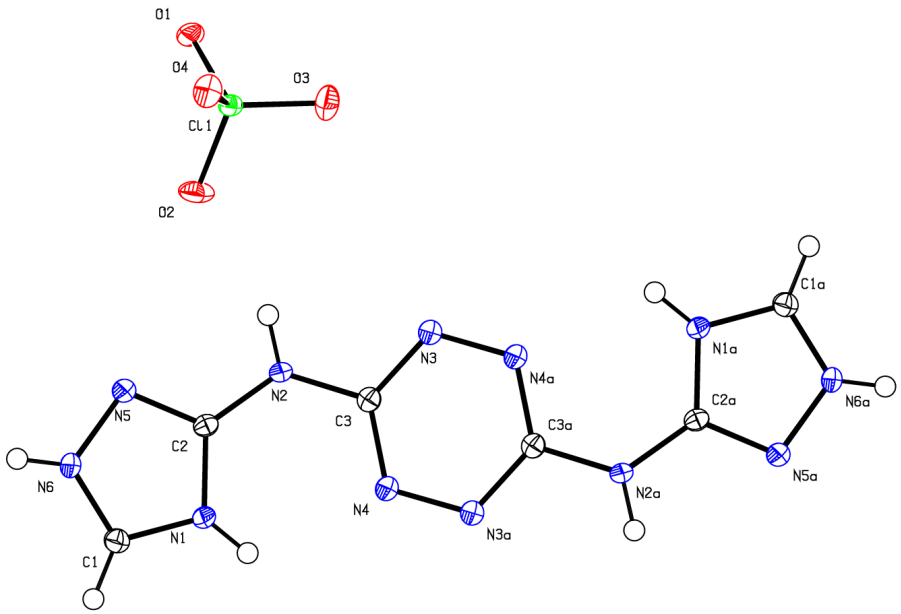

Figure S1. Structure of compound **16**, with contour probability level of 50%.

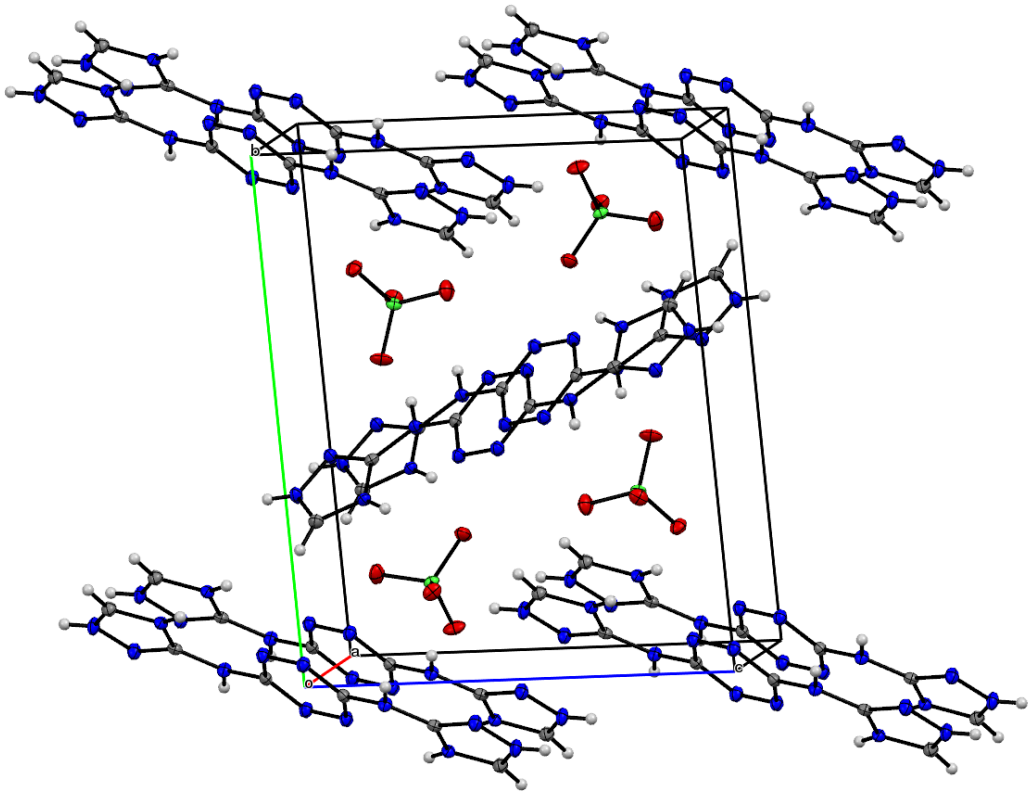

Figure S2. Arrangement of molecules of **16** in the obtained crystal.

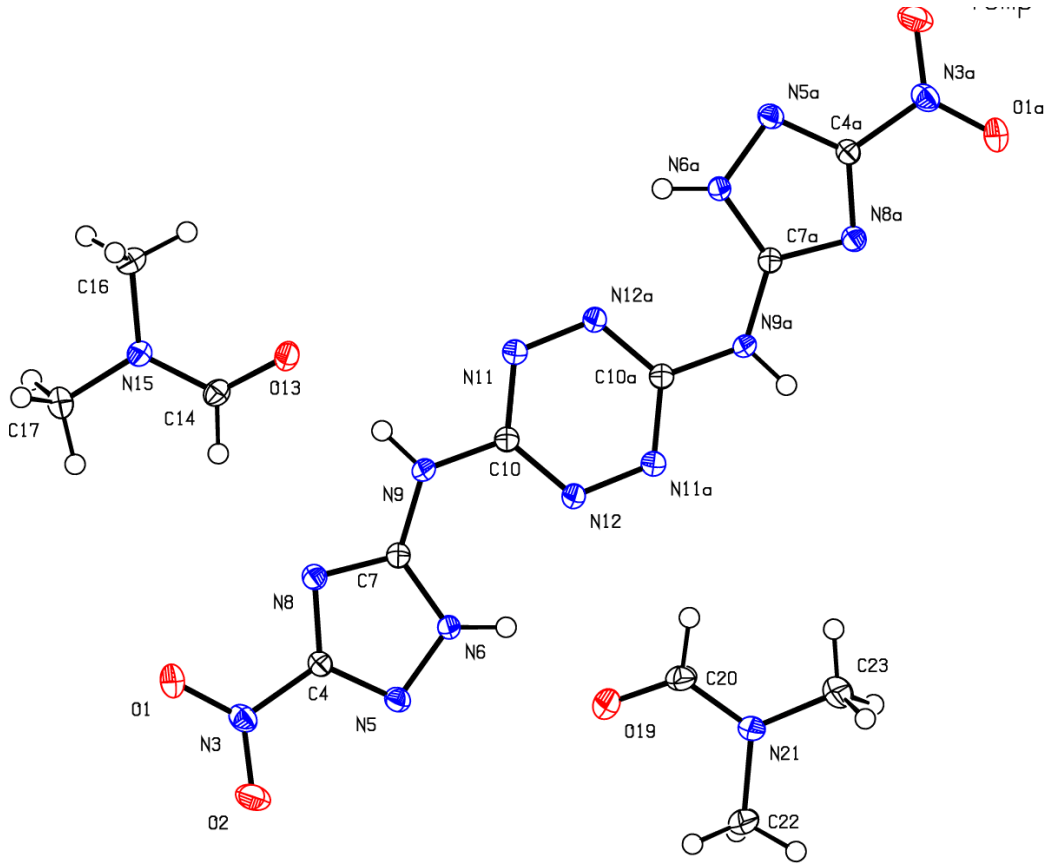

Figure S3. Structure of compound **20**, with contour probability level of 50%.

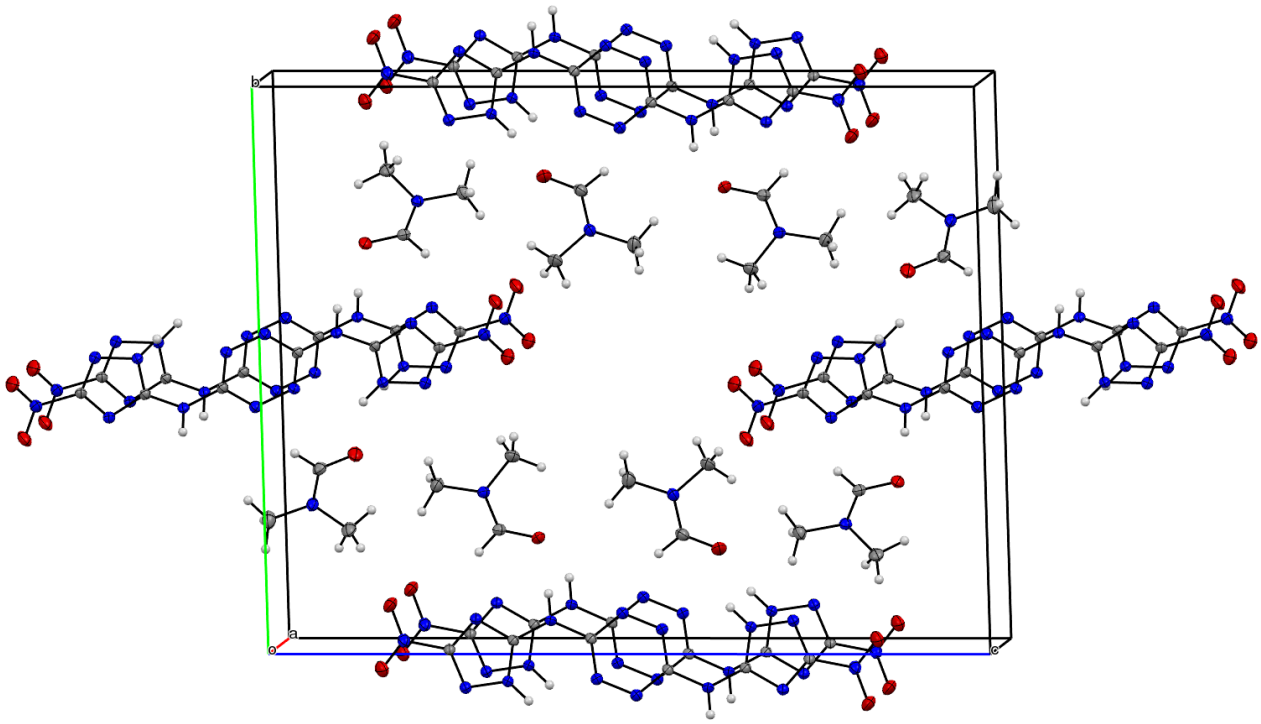

Figure S4. Arrangement of molecules of **20** in the obtained crystal.

Table S1. Crystallography data for compounds **16** and **20**.

	16	**20**
Formula	$C_6H_8N_{12}\cdot 2(ClO_4)$	$C_6H_4N_{14}O_4\cdot 4(C_3H_7NO)$
FW/ g mol^{-1}	447.14	628.26
Color	Yellow	Orange
Habit	Needle	Needle
Crystal size /mm	0.15 × 0.35 × 0.15	0.049 × 0.131 × 0.667
Crystal system	monoclinic	monoclinic
Space group	P 2_1/c	P 2_1/c
a/ Å	4.9063(2)	3.8323(4)
b/ Å	13.3753(5)	17.6530(19)
c/ Å	11.7380(4)	22.906(2)
α/ °	90	90
β/ °	100.4560(10)	93.488(5)
γ/ °	90	90
V/ Å^3	757.49(5)	1546.76
Z	2	2
$p_{calcd.}$/g·cm^{-3}	1.960	1.350
T /K	110 (2)	110 (2)
F (000)	452	660
μ/ mm^{-1}	0.508	0.109
Absorption correction	multi-scan	multi-scan
Dataset (h; k; l)	-5:6; -17:16; -15:12	-4:4; -20:20; -26:27
θ range /°	2.331:28.354	3.73:24.7
Reflections collected	7325	11663
Independent reflections	1882	2732
$R_{int.}$	0.0197	0.0252
Parameters	139	204
R1 [I>2σ(I)]	0.0297	0.0398
WR2 [I>2σ(I)]	0.0719	0.1182
R_1 (all data)	0.0328	0.0451
wR2 (all data)	0.0741	0.1223
S	1.055	1.046
Res. dens. /e·Å^{-3}	0.063	0.057
Solution	SHELXTL-2014	SHELXL-2013
Refinement	SHELXL-2014/6	SHELXS-97

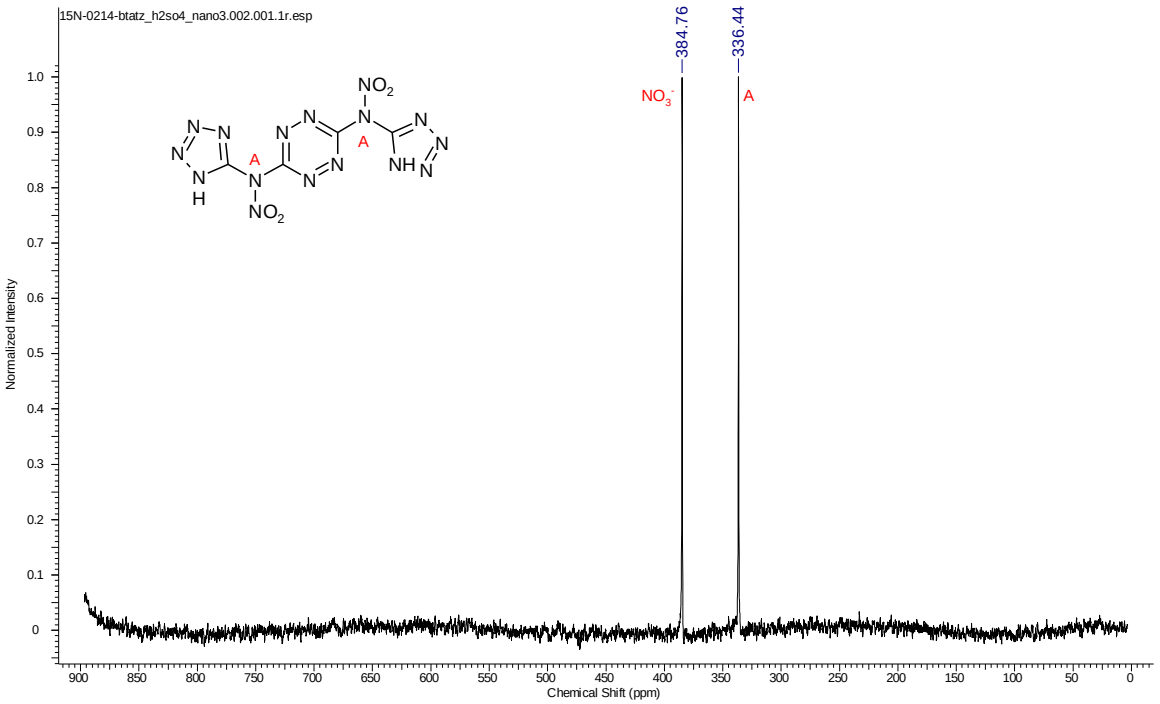

Figure S5. Study of nitration of compound **5** by ^{15}N NMR. *Reaction conditions: H_2SO_4, $Na^{15}NO_3$.*

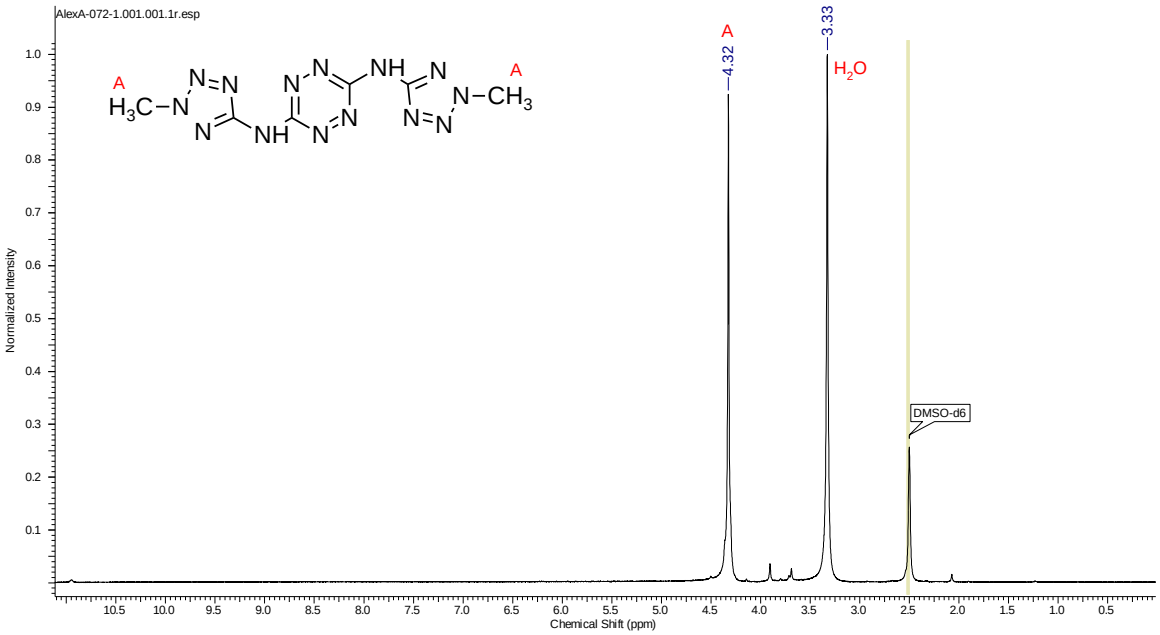

Figure S6. ^{1}H NMR of compound **12**.

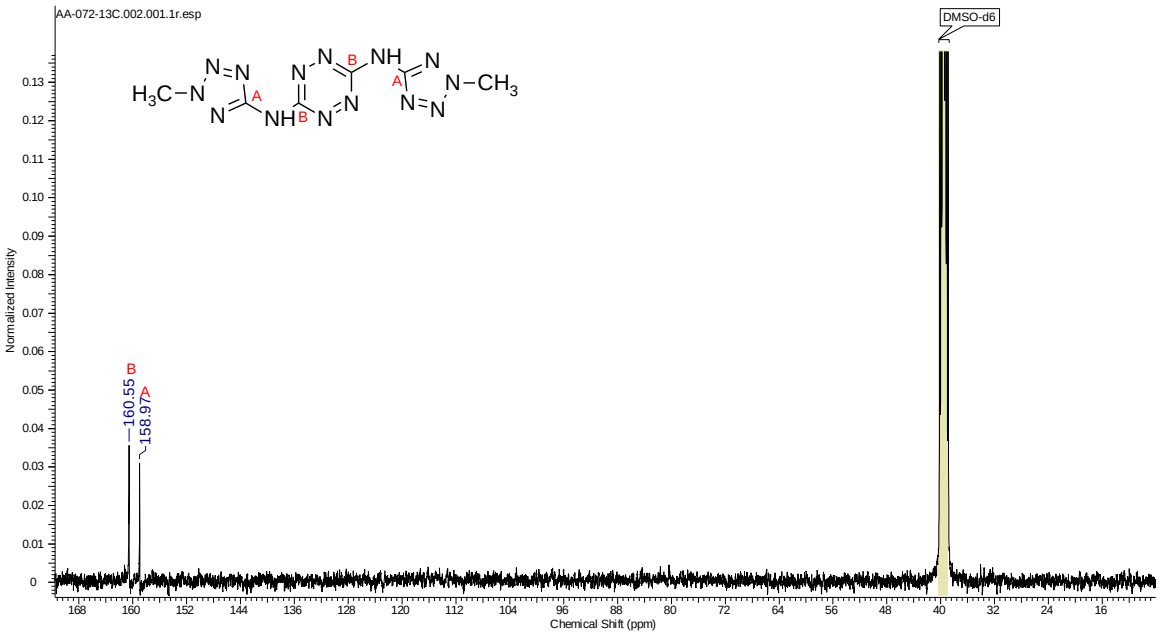

Figure S7. ^{13}C NMR of compound **12**.

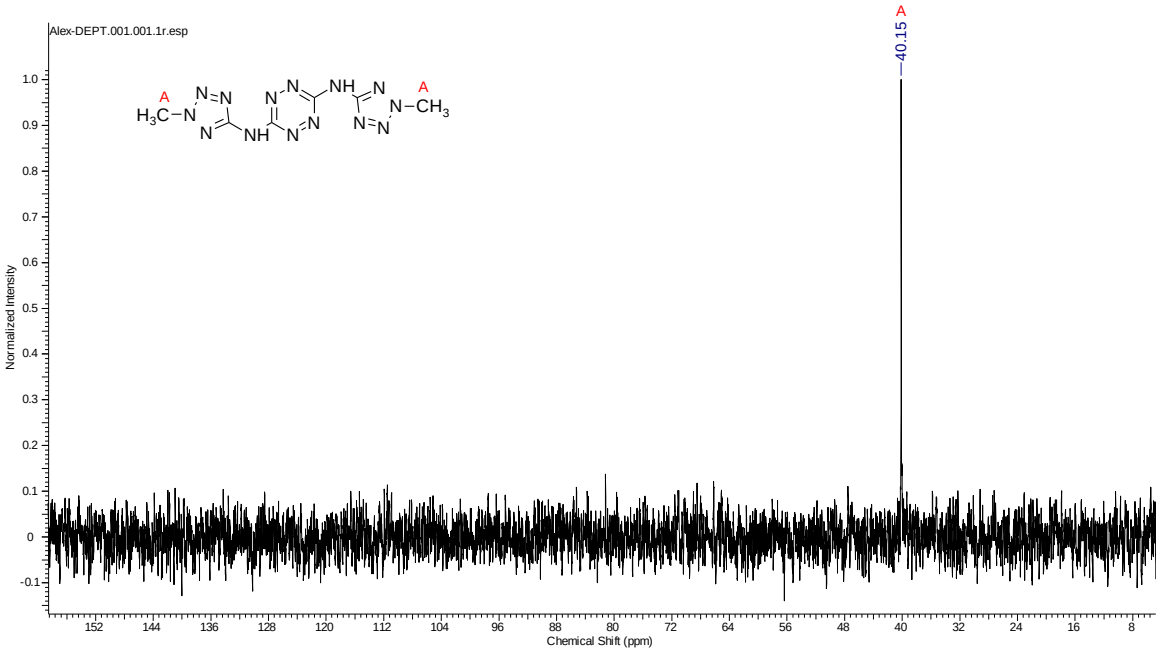

Figure S8. ^{13}C DEPT135 NMR of compound **12**.

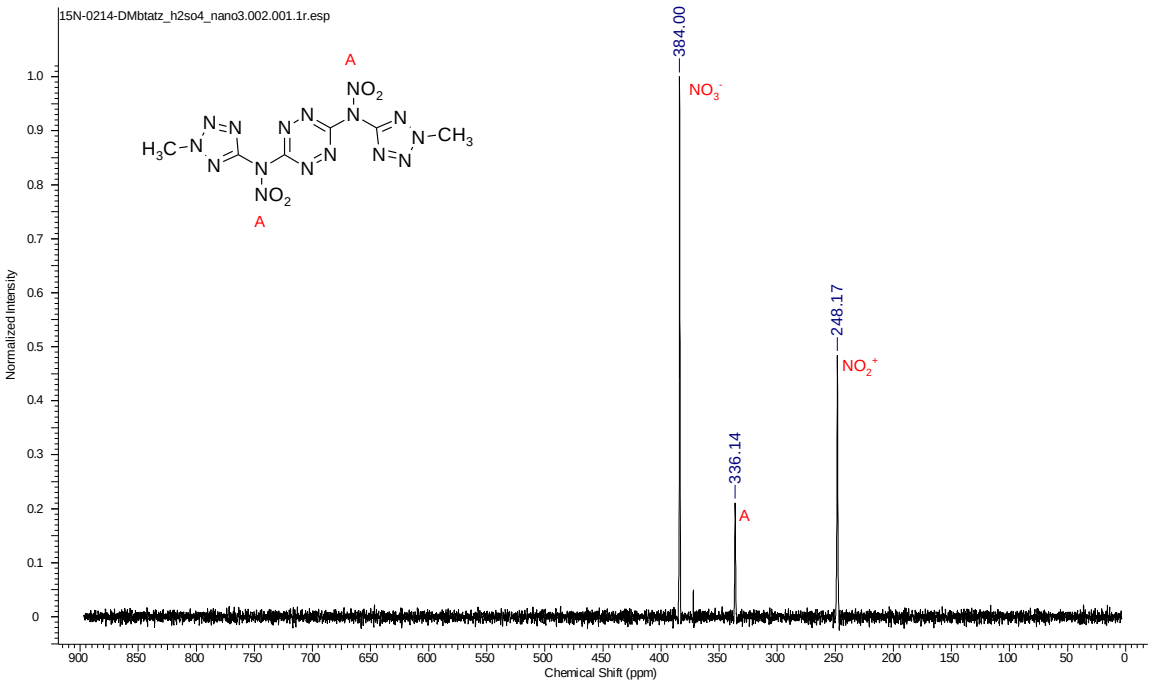

Figure S9. Study of nitration of compound **12** by ^{15}N NMR. *Reaction conditions:* H_2SO_4, $Na^{15}NO_3$.

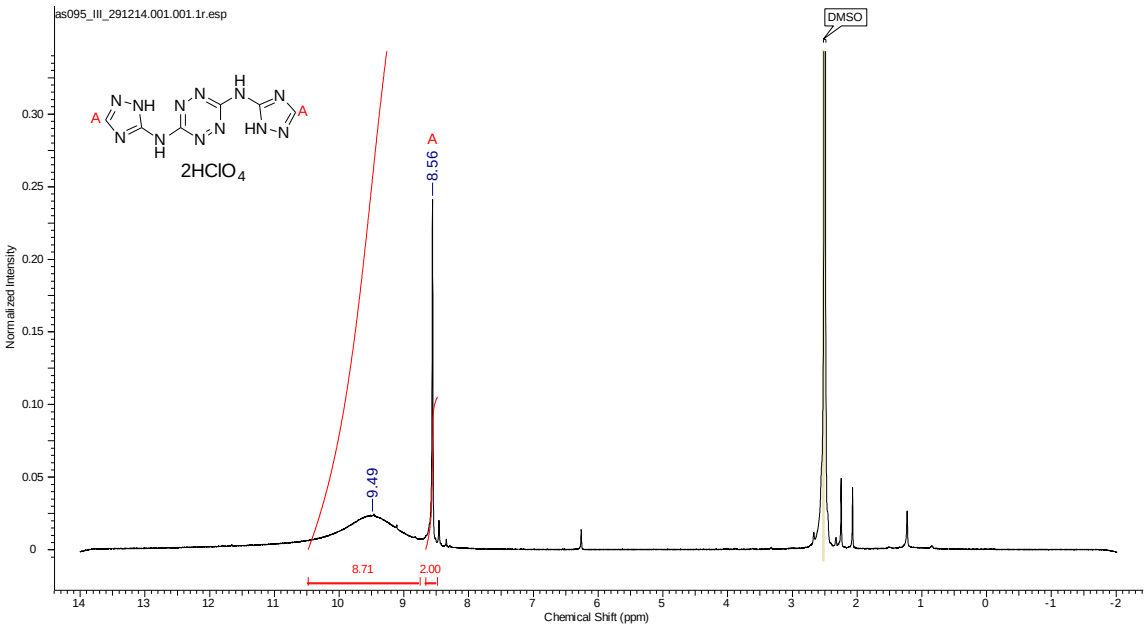

Figure S10. ^{1}H NMR of compound **16**.

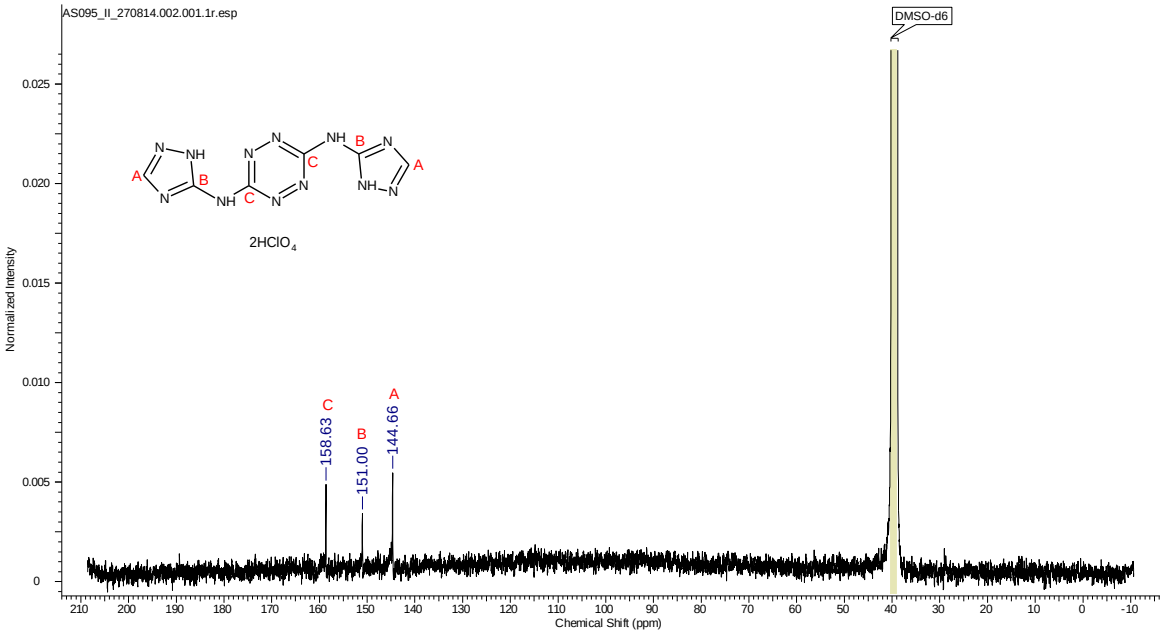

Figure S11. ^{13}C NMR of compound **16**.

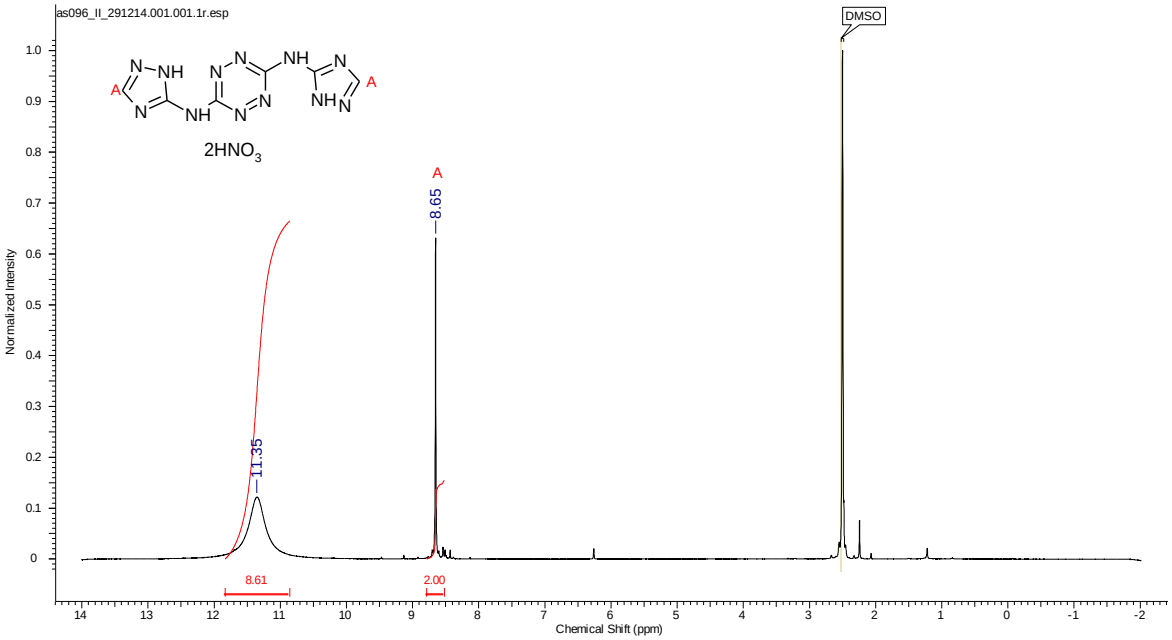

Figure S12. ^{1}H NMR of compound **17**.

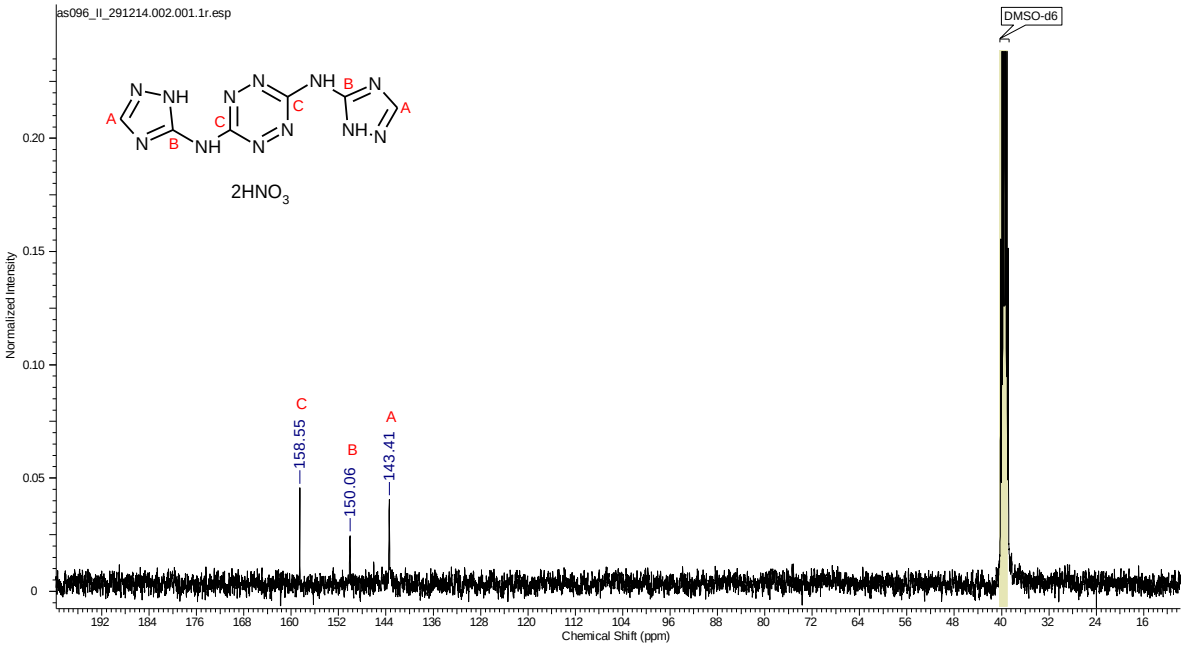

Figure S13. ^{13}C NMR of compound **17**.

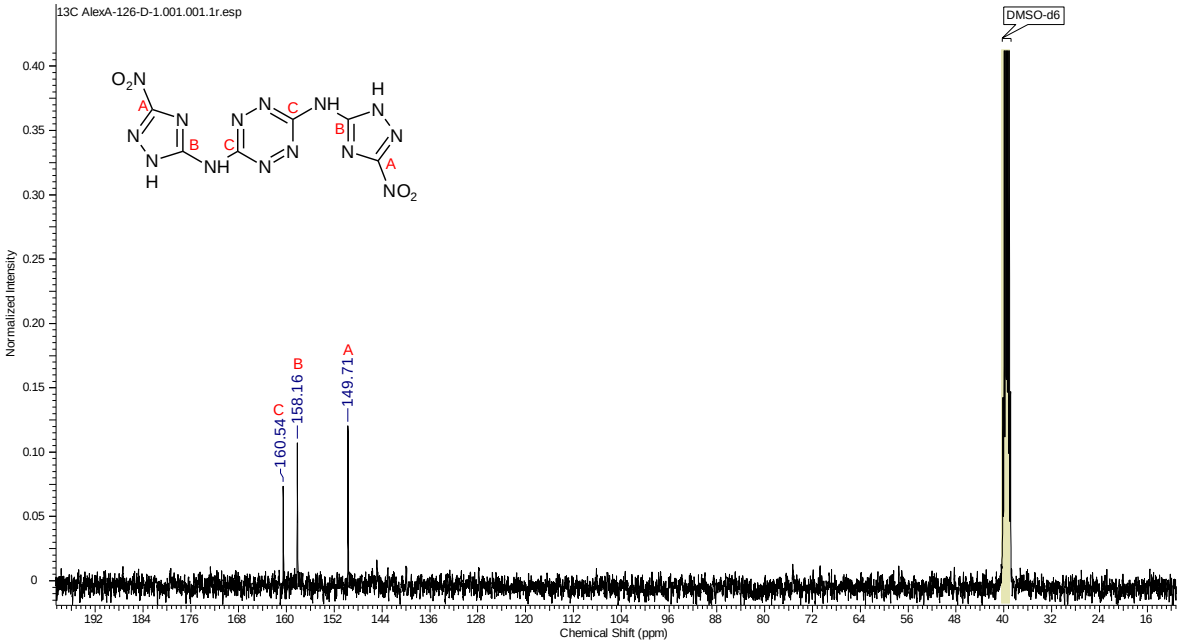

Figure S14. ^{13}C NMR of compound **20**.

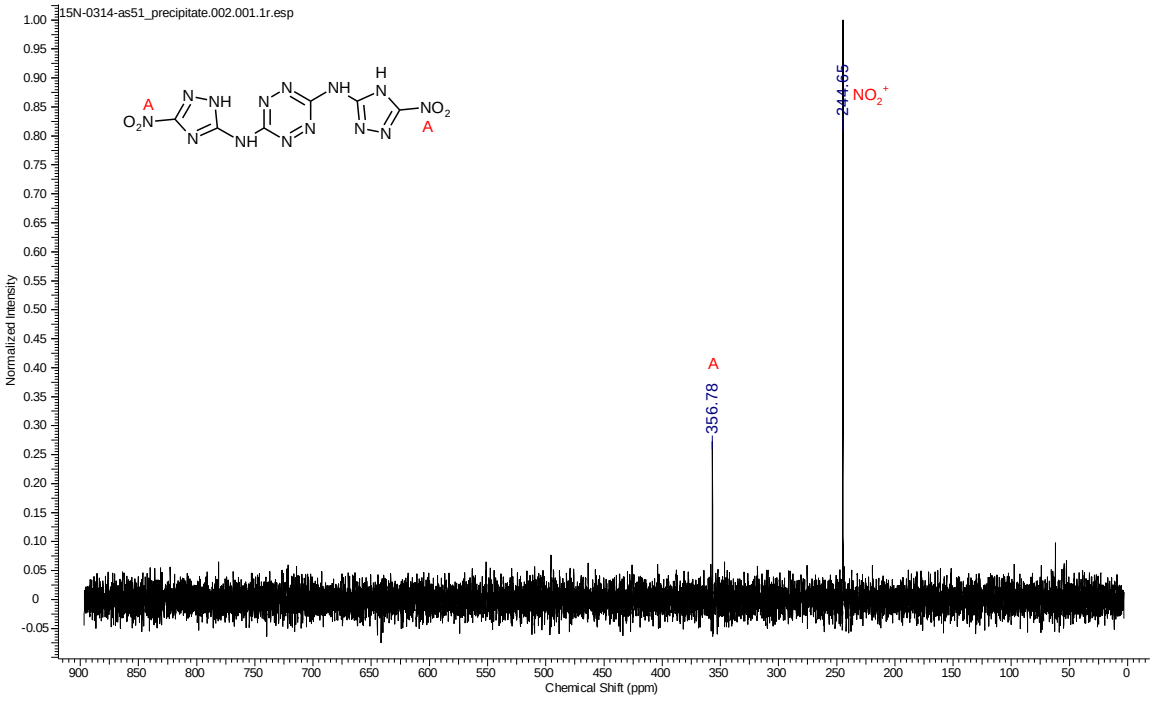

Figure S15. Study of the formation of compound **20** by ^{15}N NMR. *Reaction conditions:* Ac_2O, $Na^{15}NO_3$, HNO_3.