Electronic supporting information

Synthesis and intramolecular ring transformation of *N,N'*-dialkylated 2,6,9-triazabicyclo[3.3.1]nonadienes

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1. Crystallographic data for 2a and 3d

Table S1. Crystallographic data for **2a** and **3d**.

	2a	**3d**
Empirical formula	$C_{12}H_{19}N_5O_4$	$C_{20}H_{19}N_5O_4$
Formula weight	297.32	393.40
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a / Å	17.8252(6)	14.4032(16)
b / Å	7.4804(2)	9.8582(2)
c / Å	10.9523(4)	19.916(2)
α / °	90	90
β / °	105.159(4)	140.02(2)
γ / °	90	90
Volume / Å^3	1409.56(8)	1817.0(6)
Z	4	4
ρ_{calc} / g cm^{-3}	1.401	1.438
μ(Mo Kα) / mm^{-1}	0.107	0.103
F(000)	632	824
Crystal size / mm^3	0.294 × 0.082 × 0.033	0.796 × 0.532 × 0.413
2θ range / °	4.736 to 52.74	5.01 to 52.744
Temperature / K	123.15	93.15
Reflections collected	10670	13775
Independent reflections	2885	3711
Goodness-of-fit on F^2	1.053	1.057
R_1 (I ≥ 2σ(I))[a]	0.0343	0.0351
wR_2 (all data)[b]	0.0871	0.0892

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

2. Temperature depending NMR spectra

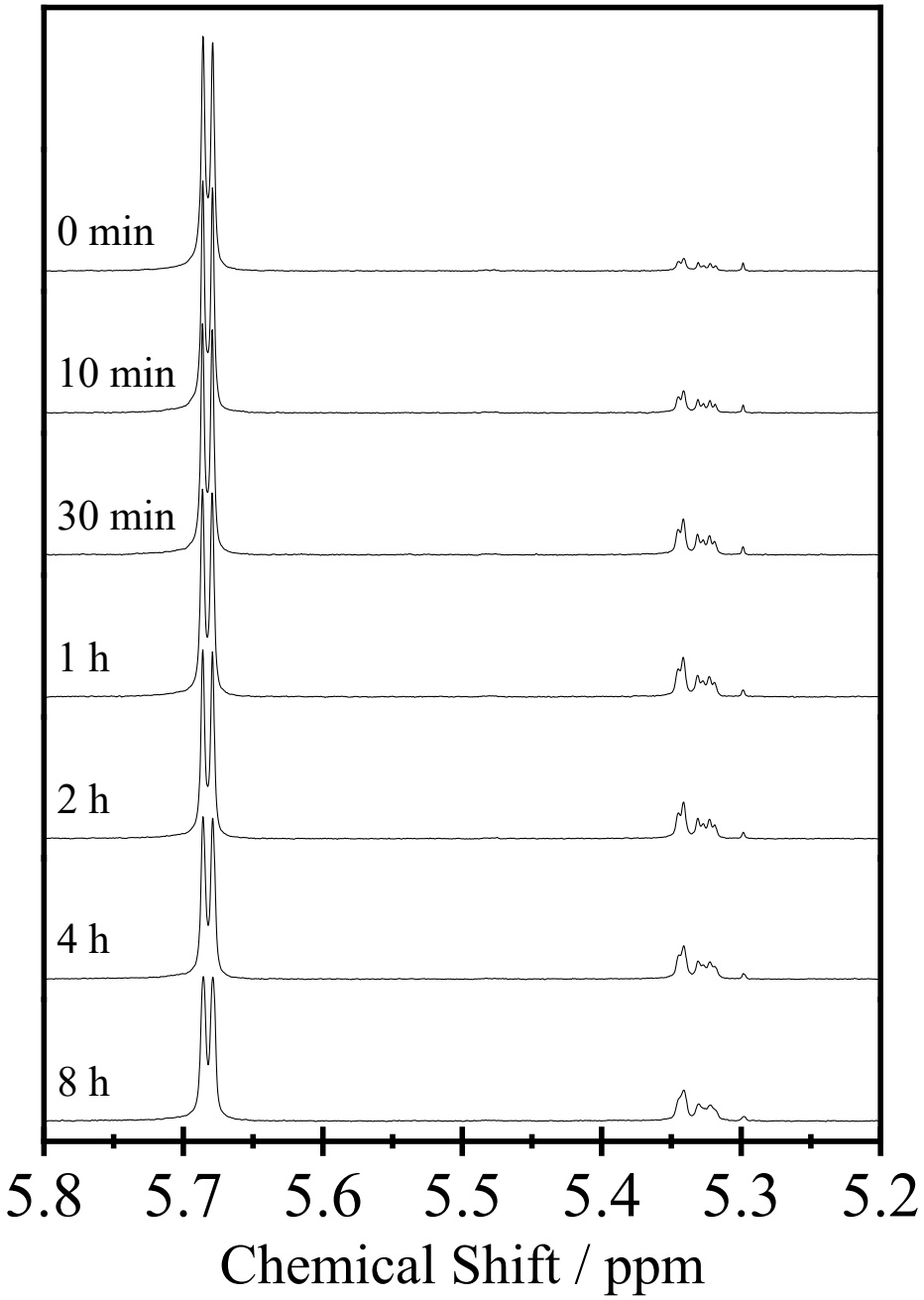


Figure S1. Time variation in ^{1}H NMR spectrum of **2a** in $CDCl_3$.

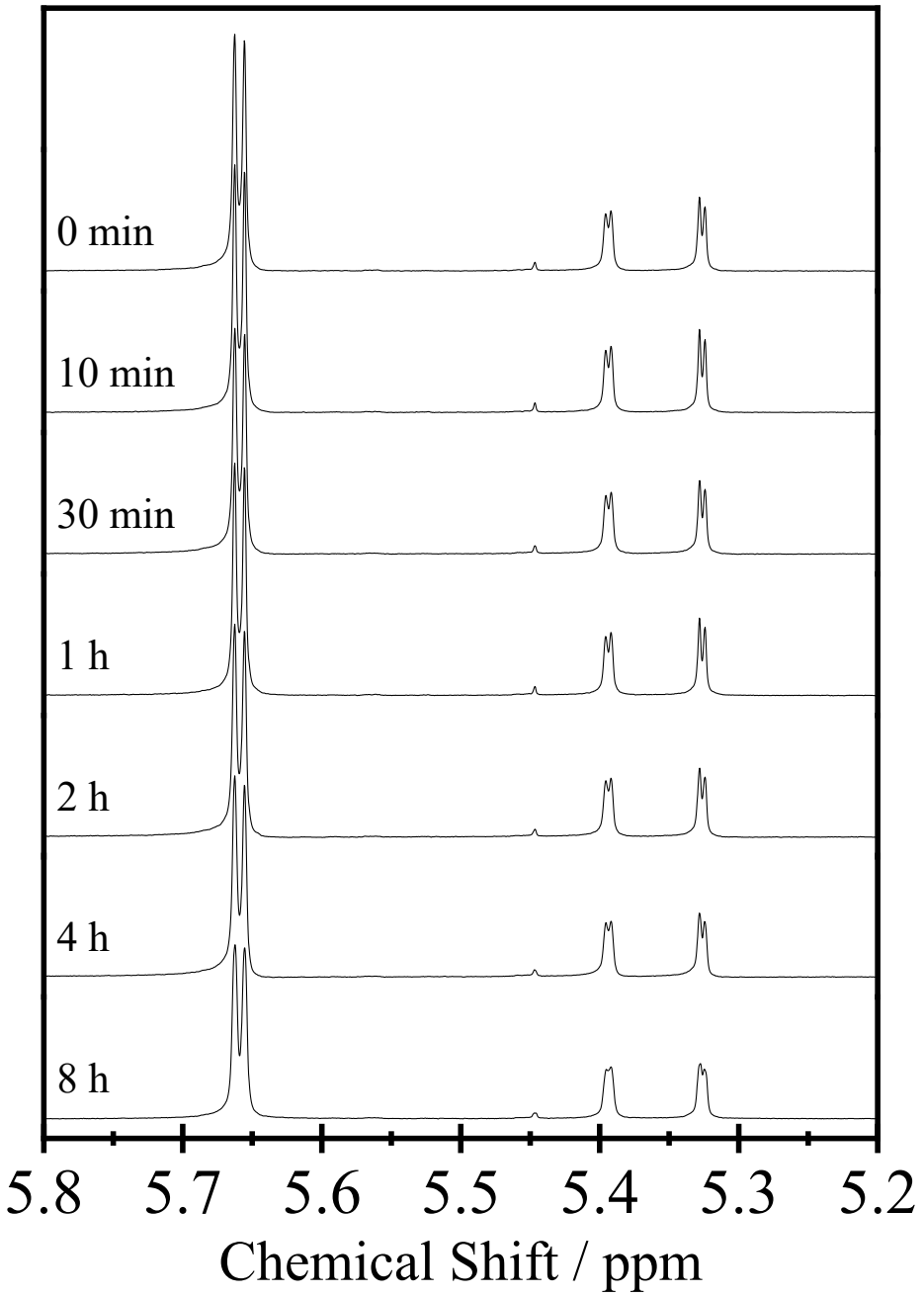


Figure S2. Time variation in ^{1}H NMR spectrum of **2a** in CD_3CN.

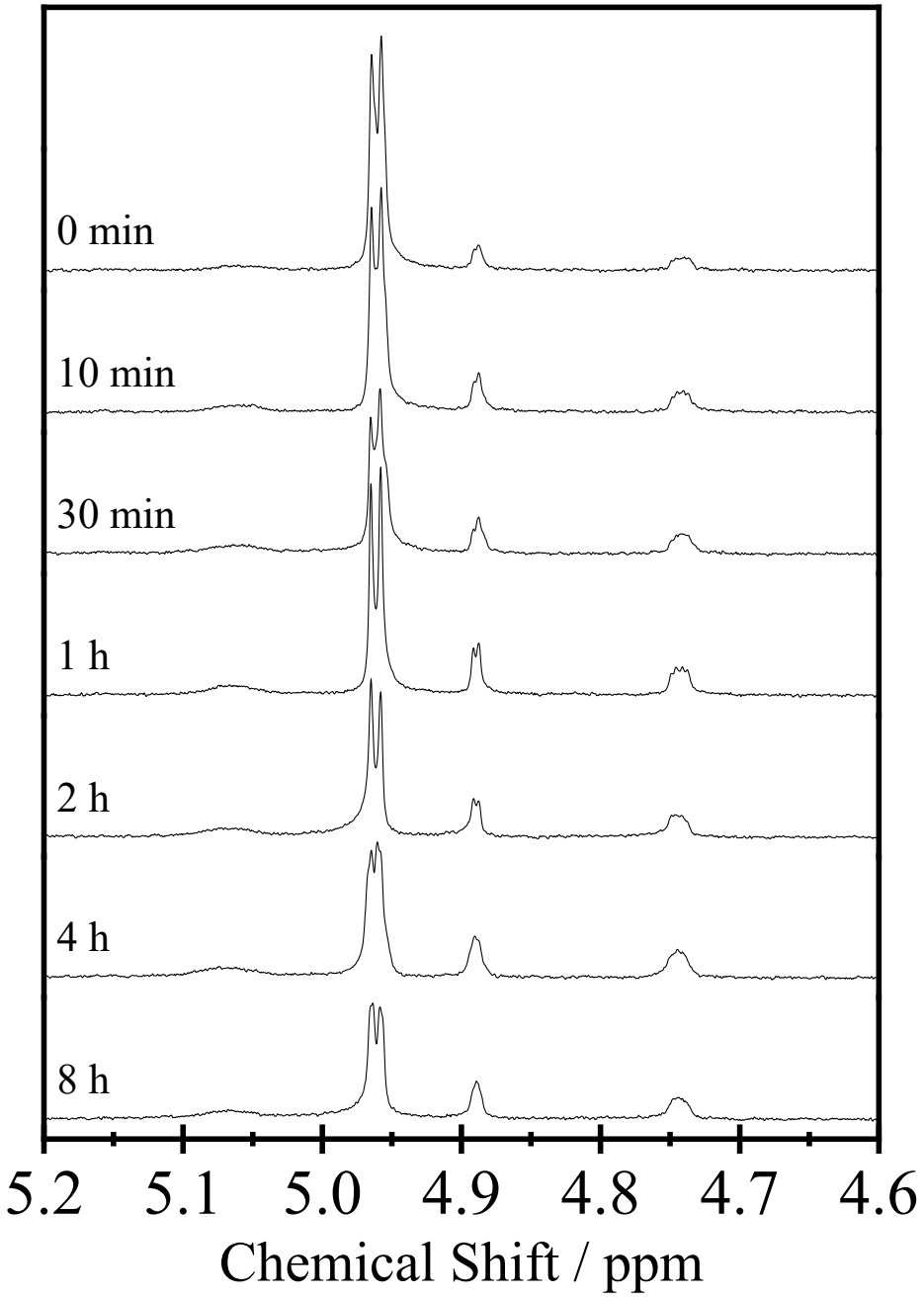


Figure S3. Time variation in ^{1}H NMR spectrum of **2a** in C_6D_6.

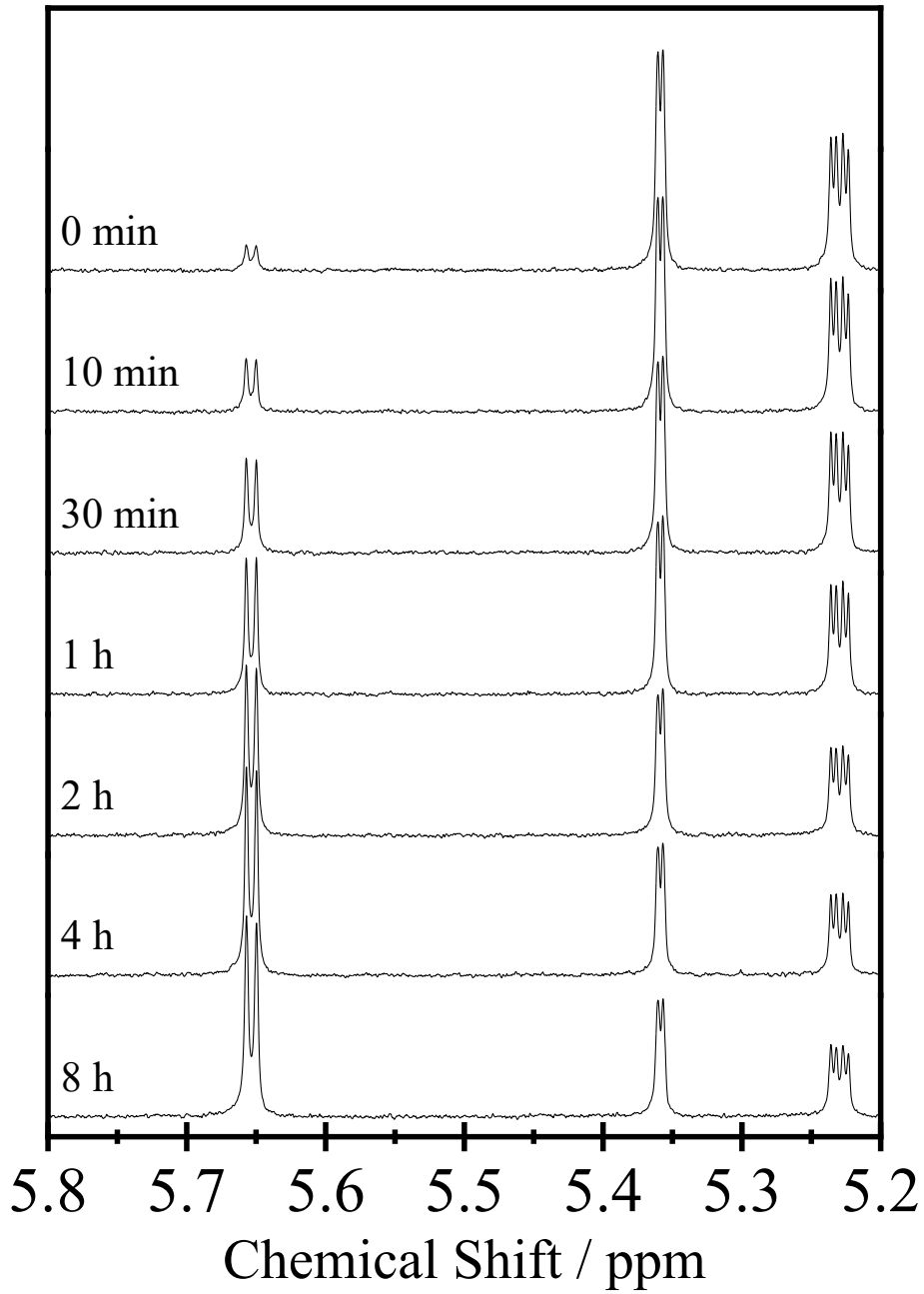


Figure S4. Time variation in ^{1}H NMR spectrum of **3d** in $CDCl_3$.

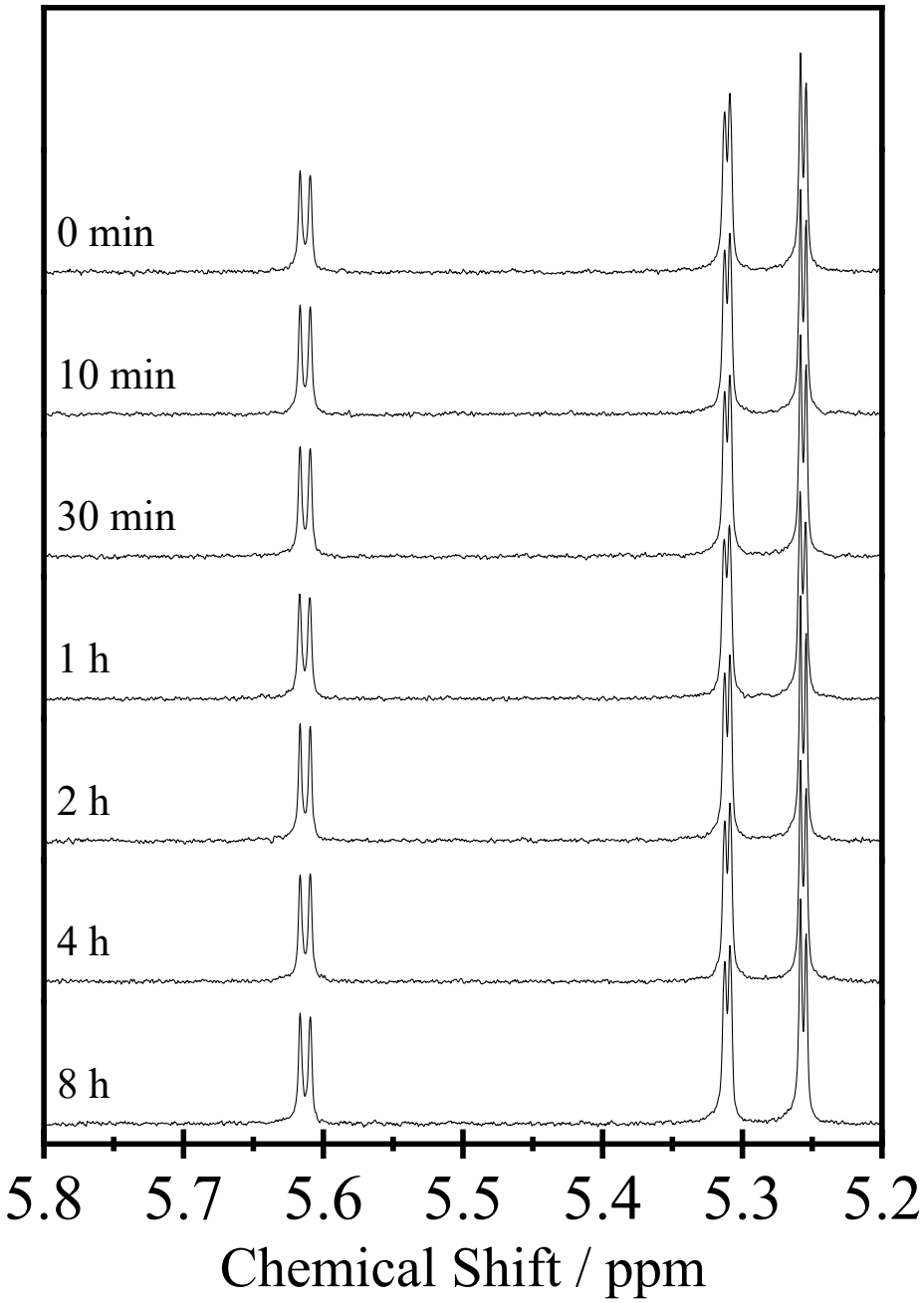


Figure S5. Time variation in ^{1}H NMR spectrum of **3d** in CD_3CN.

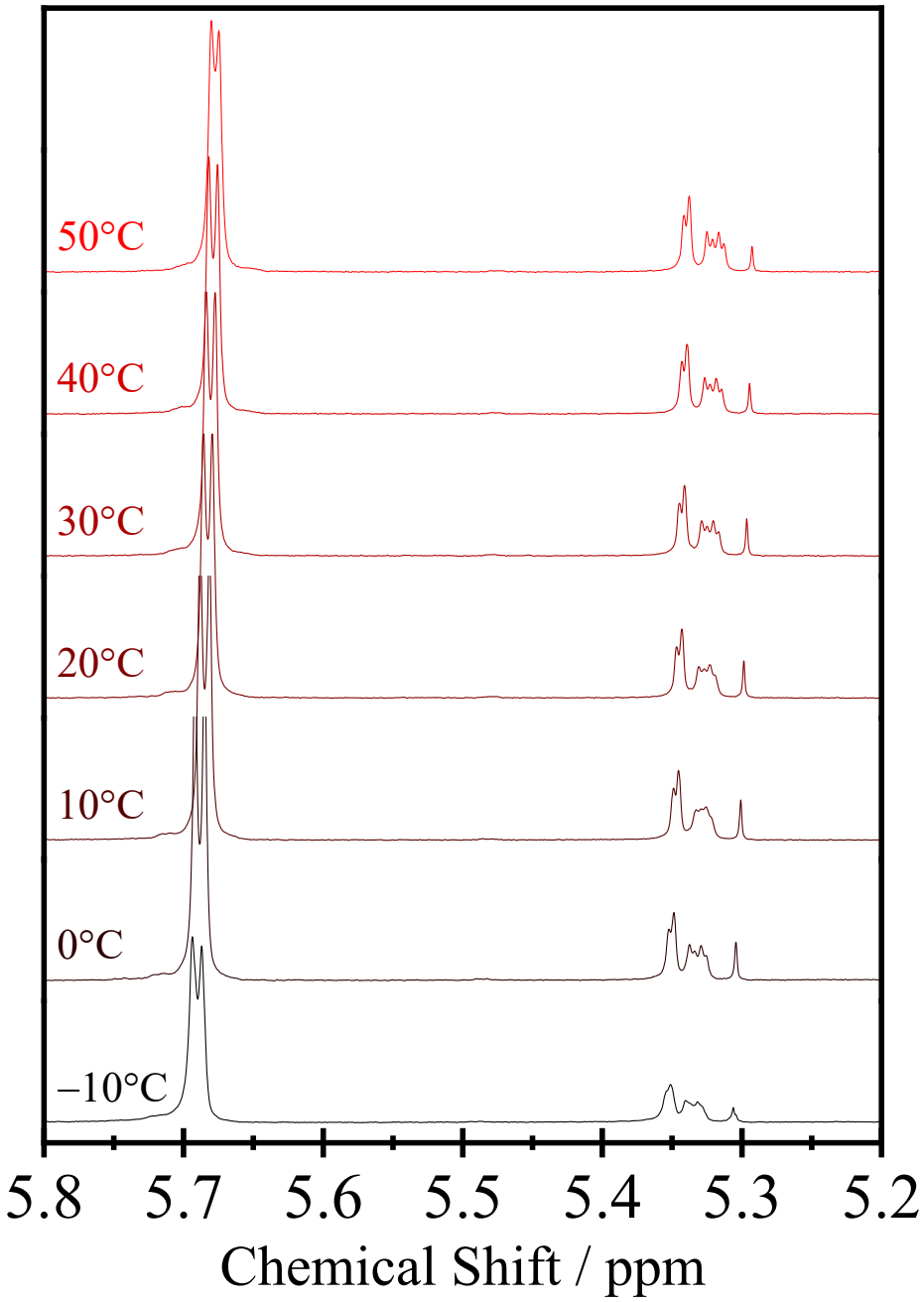


Figure S6. Temperature depending ^{1}H NMR spectrum of **3a**/**2a** in $CDCl_3$.

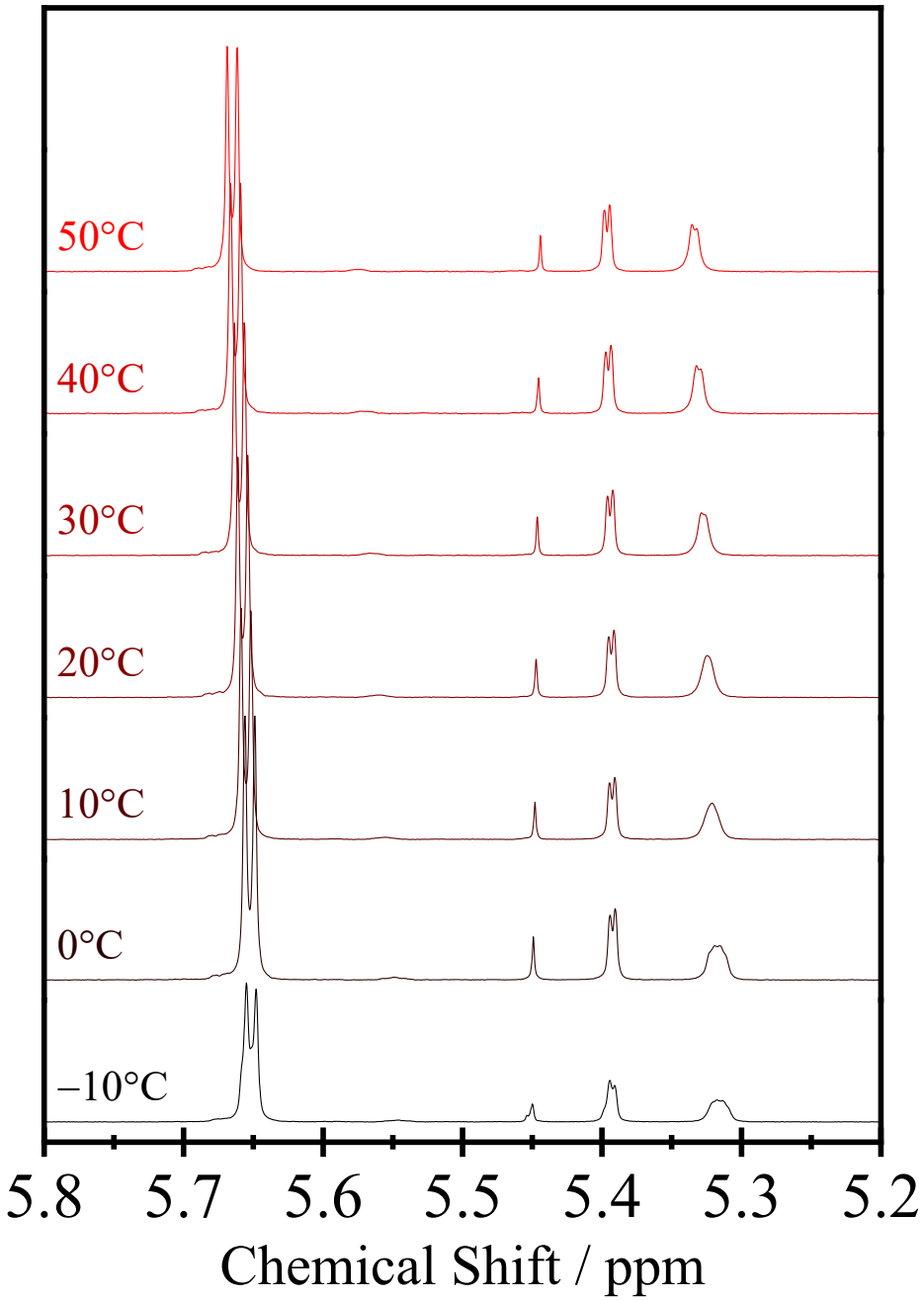


Figure S7. Temperature depending ^{1}H NMR spectrum of **3a**/**2a** in CD_3CN.

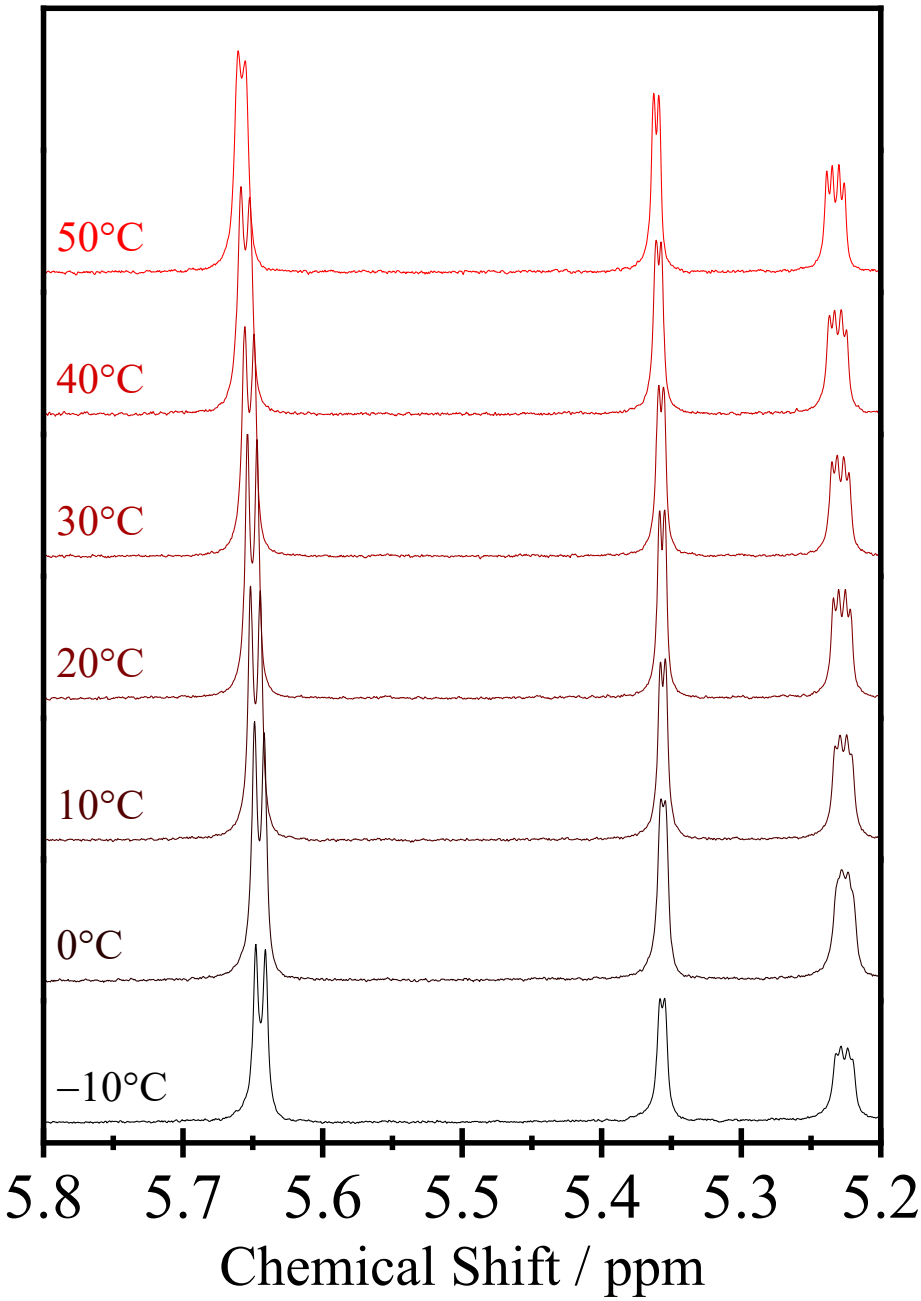


Figure S8. Temperature depending ^{1}H NMR spectrum of **3d**/**2d** in $CDCl_3$.

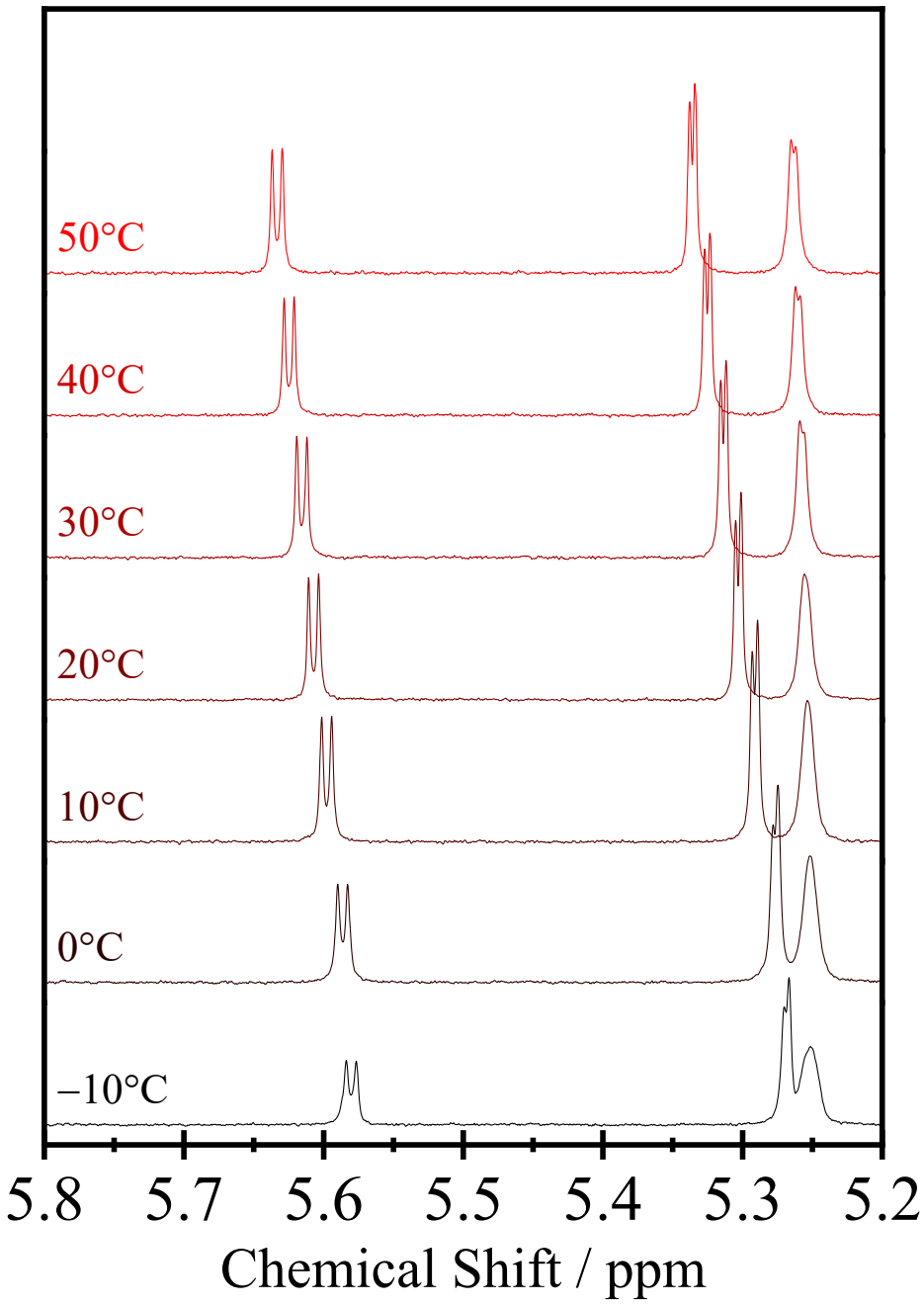
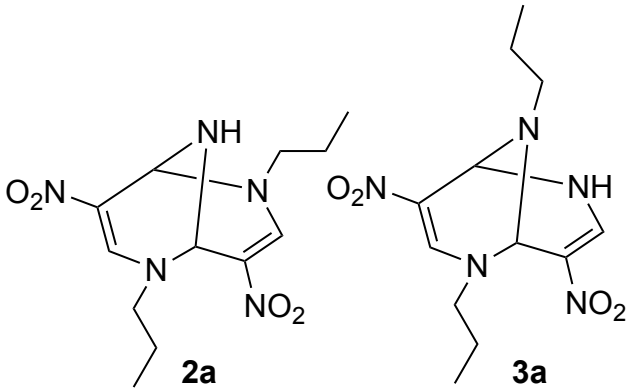


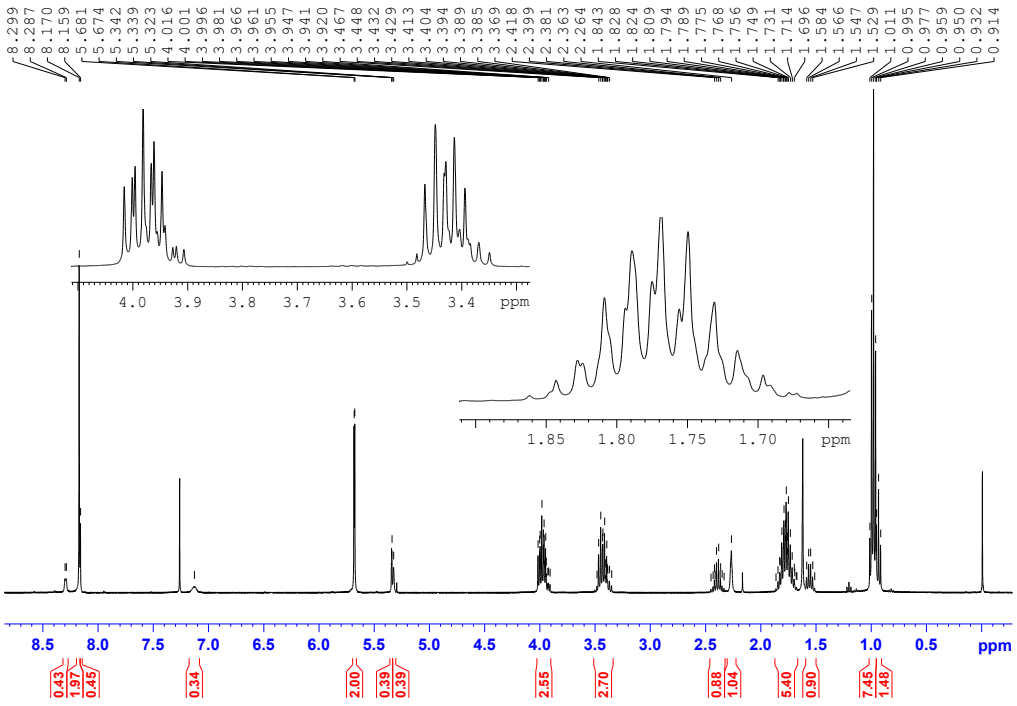
Figure S9. Temperature depending ^{1}H NMR spectrum of **3d**/**2d** in CD_3CN.

3. Copies of NMR spectra

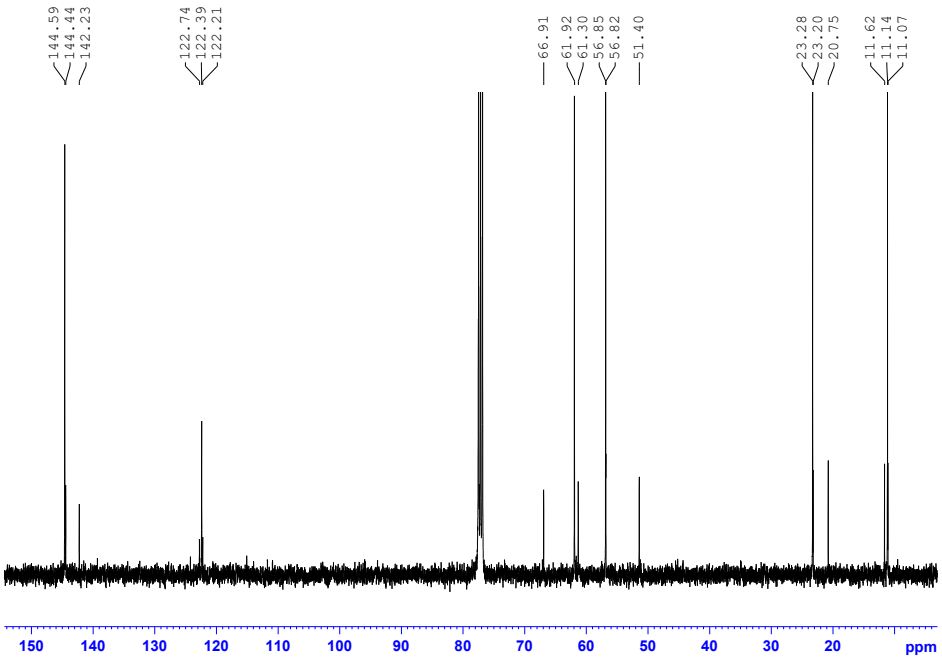
2,6,9-Triaza-4,8-dinitro-2,6-dipropylbicyclo[3.3.1]nona-3,7-diene (2a)
2,6,9-Triaza-4,8-dinitro-2,9-dipropylbicyclo[3.3.1]nona-3,7-diene (3a)



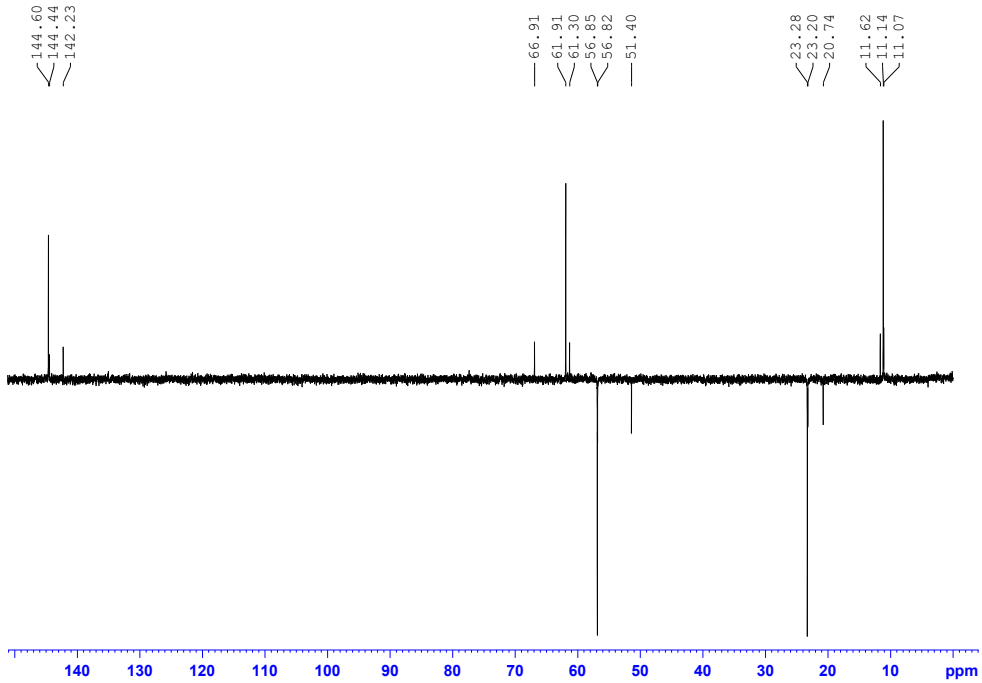
^{1}H NMR (400 MHz, $CDCl_3$)



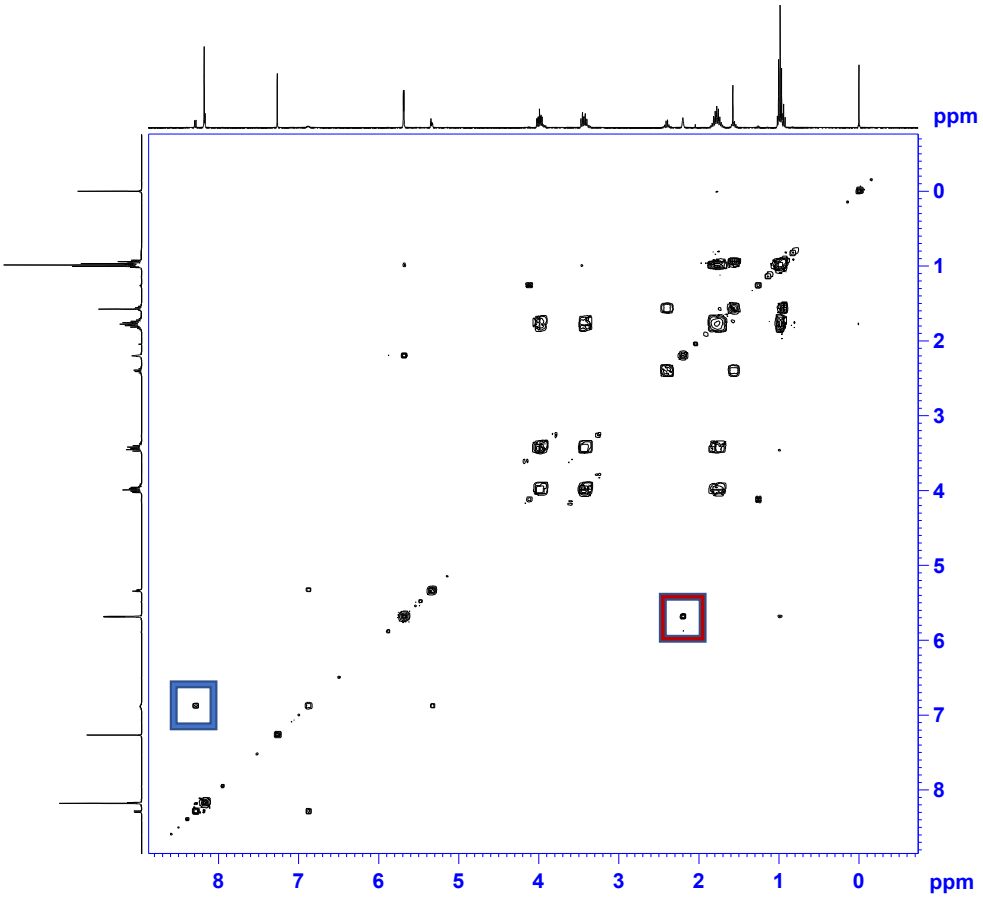
^{13}C NMR (100 MHz, $CDCl_3$)

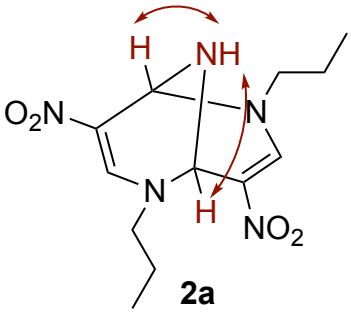


DEPT NMR (100 MHz, $CDCl_3$)

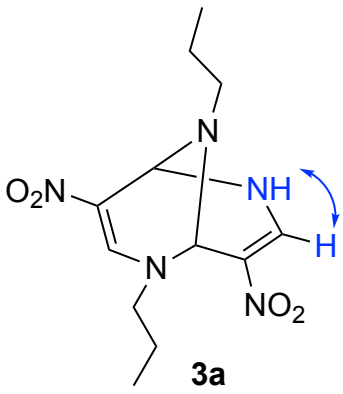


1H-1H 2D COSY NMR



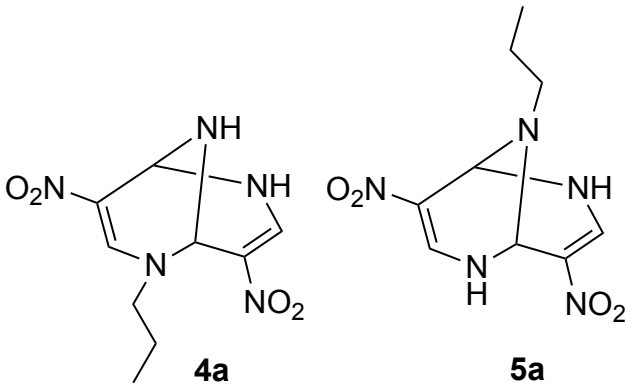


2a

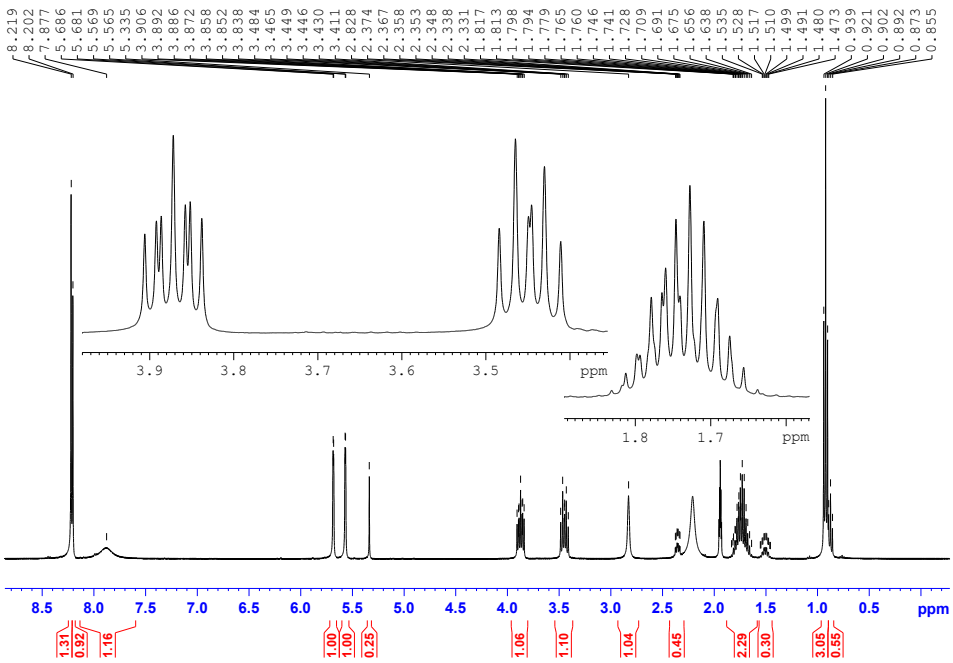


3a

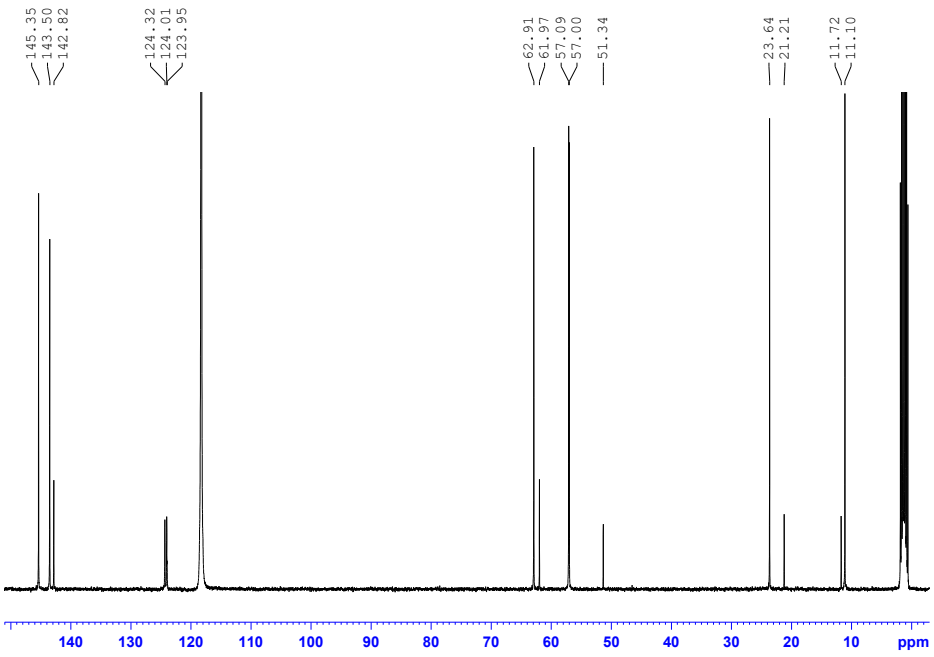
2,6,9-Triaza-4,8-dinitro-2-propylbicyclo[3.3.1]nona-3,7-diene (4a)
2,6,9-Triaza-4,8-dinitro-9-propylbicyclo[3.3.1]nona-3,7-diene (5a)



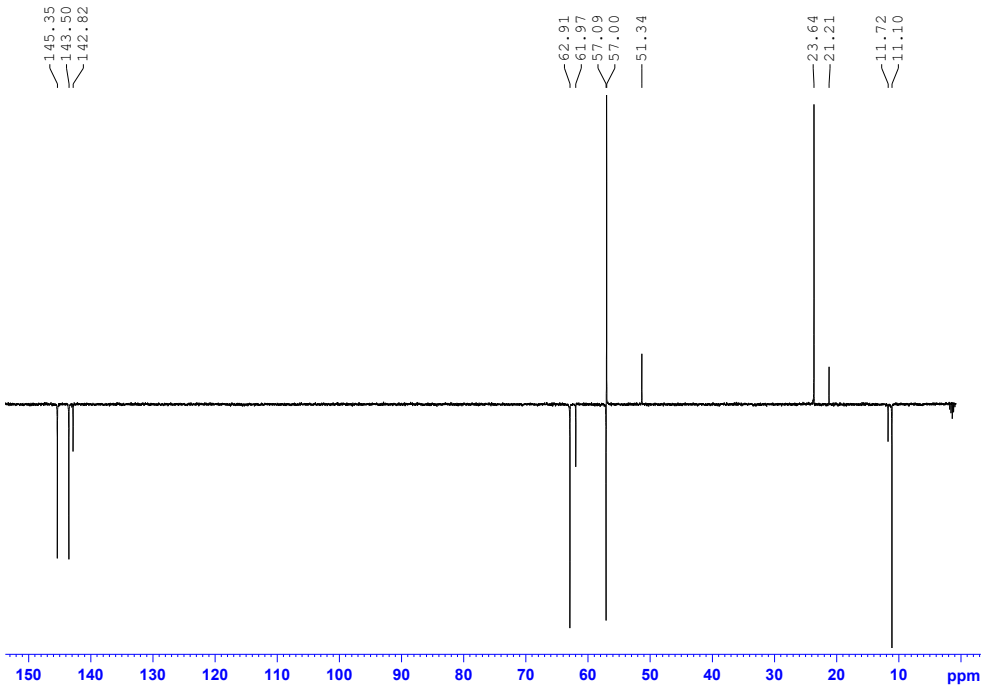
^{1}H NMR (400 MHz, CD_3CN)



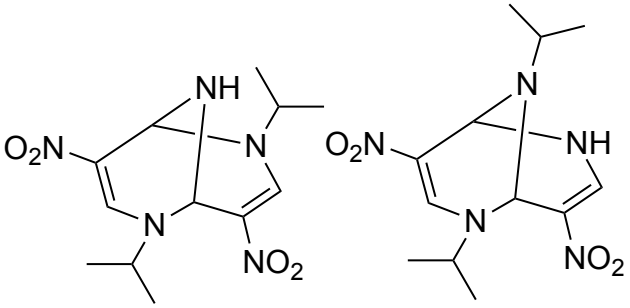
^{13}C NMR (100 MHz, $CDCl_3$)



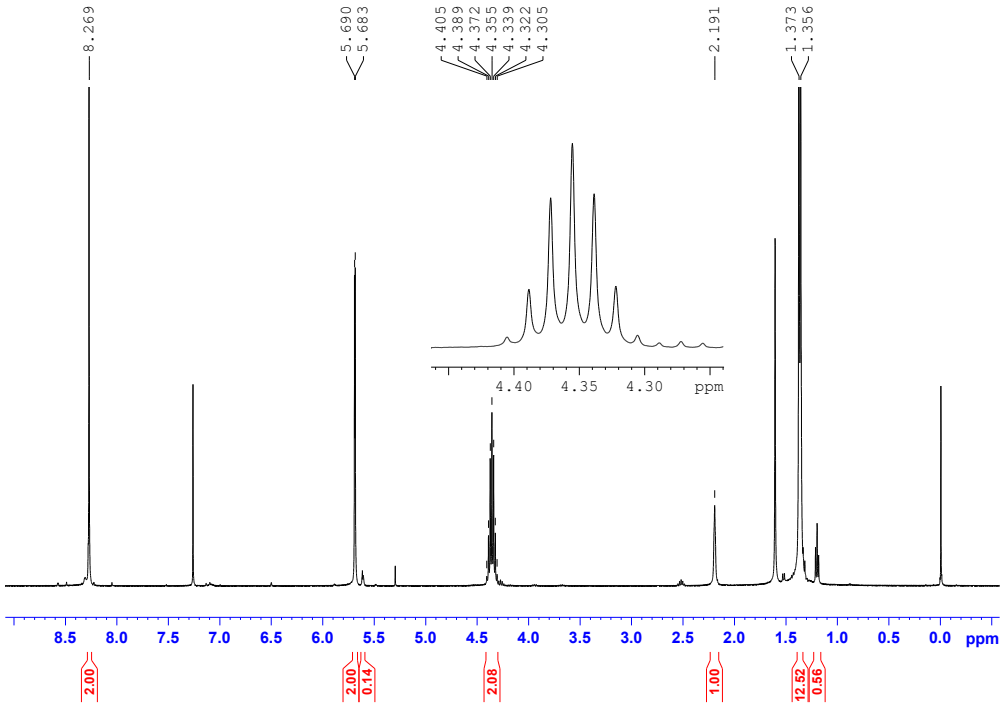
DEPT NMR (100 MHz, $CDCl_3$)



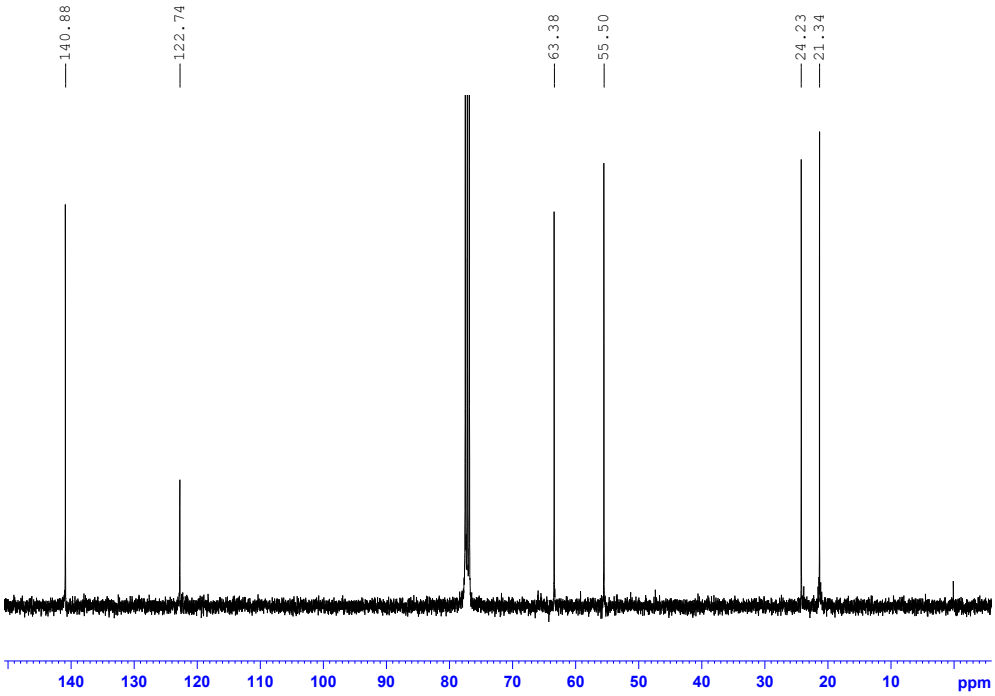
2,6,9-Triaza-2,6-di(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (2b)
2,6,9-Triaza-2,9-di(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (3b)



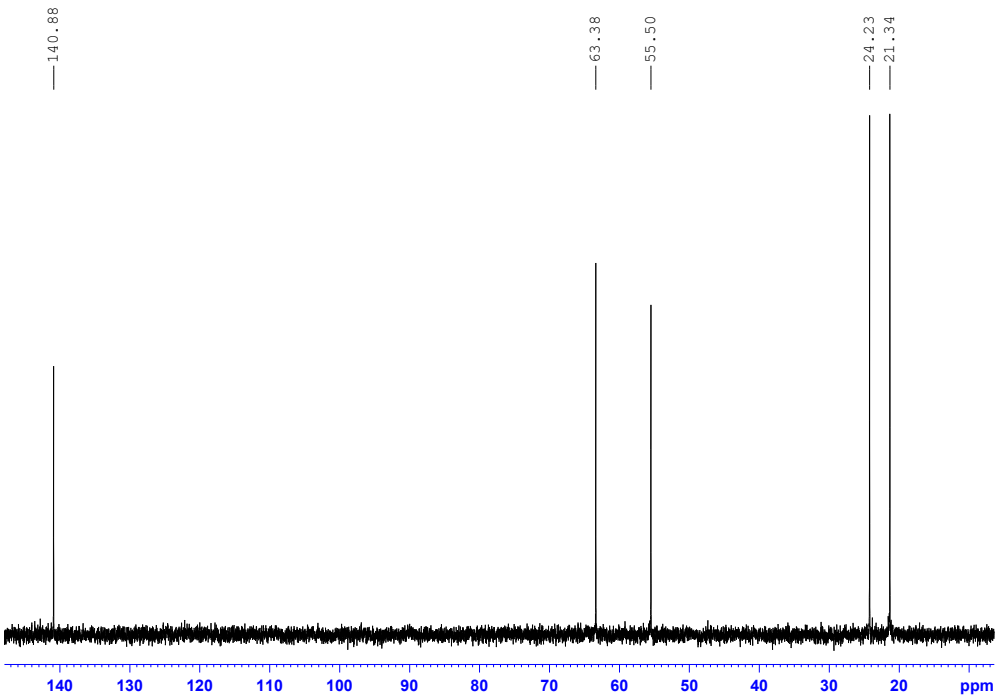
^{1}H NMR (400 MHz, $CDCl_3$)



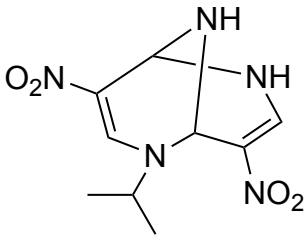
^{13}C NMR (100 MHz, $CDCl_3$)



DEPT NMR (100 MHz, $CDCl_3$)

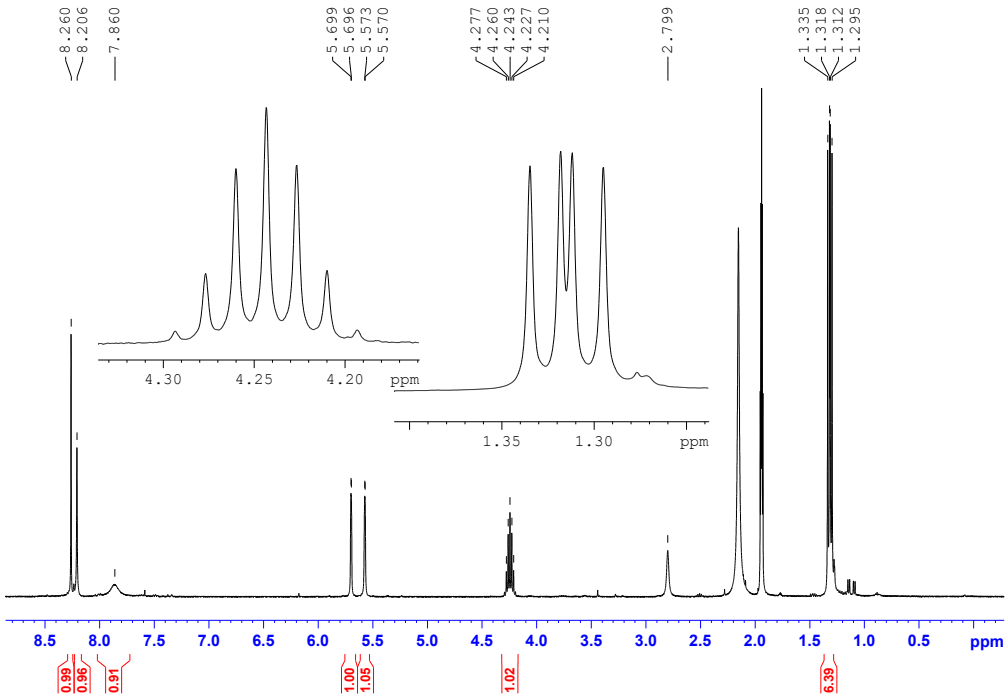


2,6,9-Triaza-2-(2-methylethyl)-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (4b)

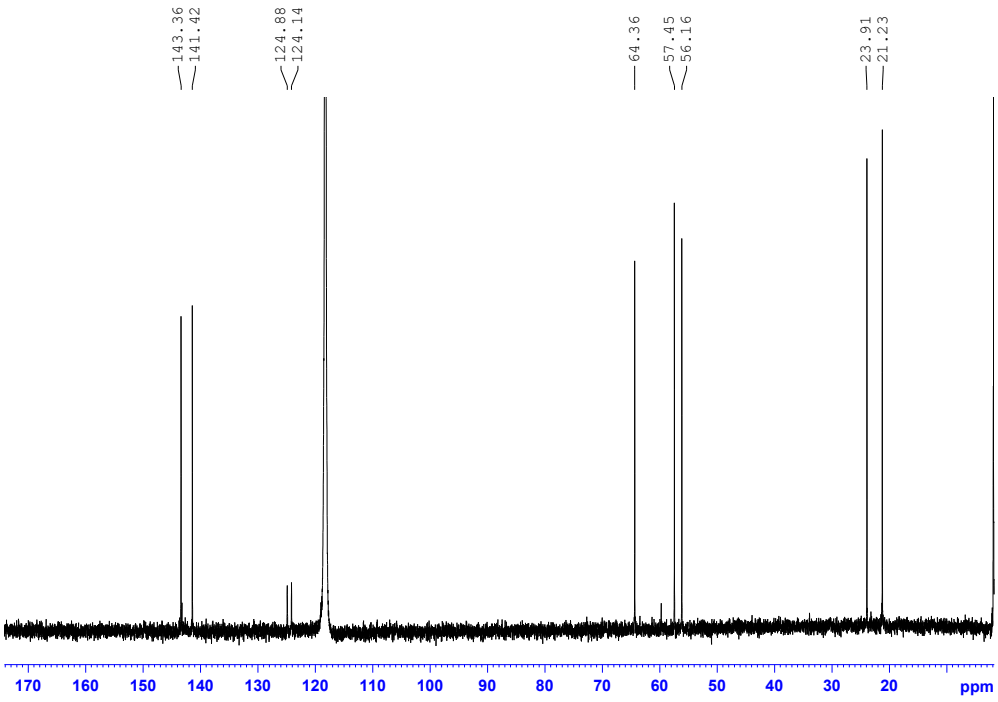


4b

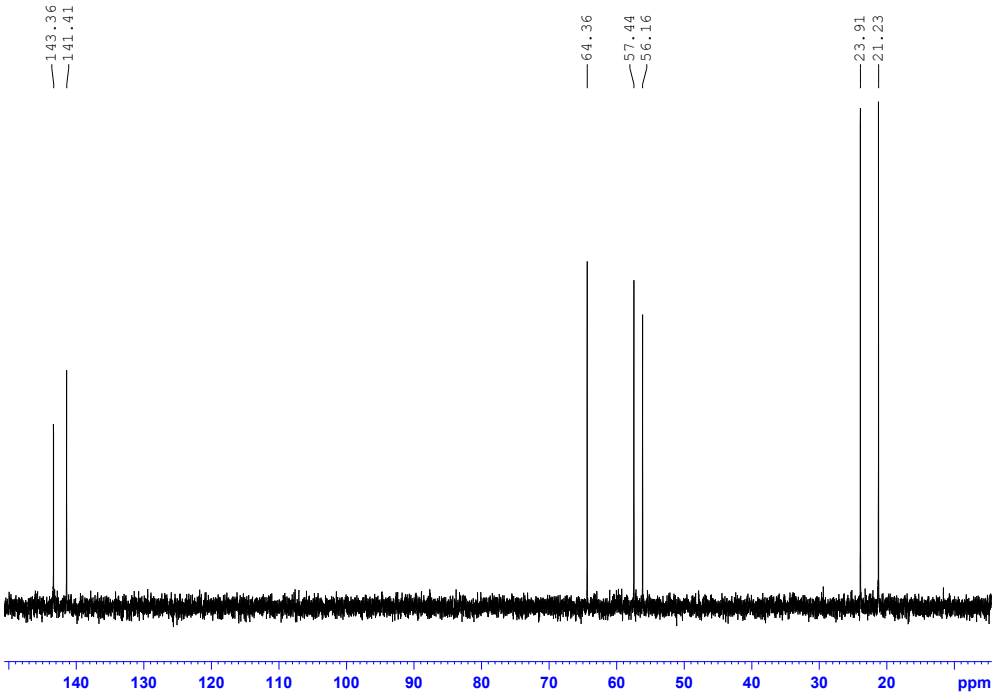
^{1}H NMR (400 MHz, CD_3CN)



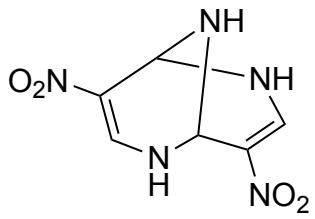
^{13}C NMR (100 MHz, CD_3CN)



DEPT NMR (100 MHz, CD_3CN)

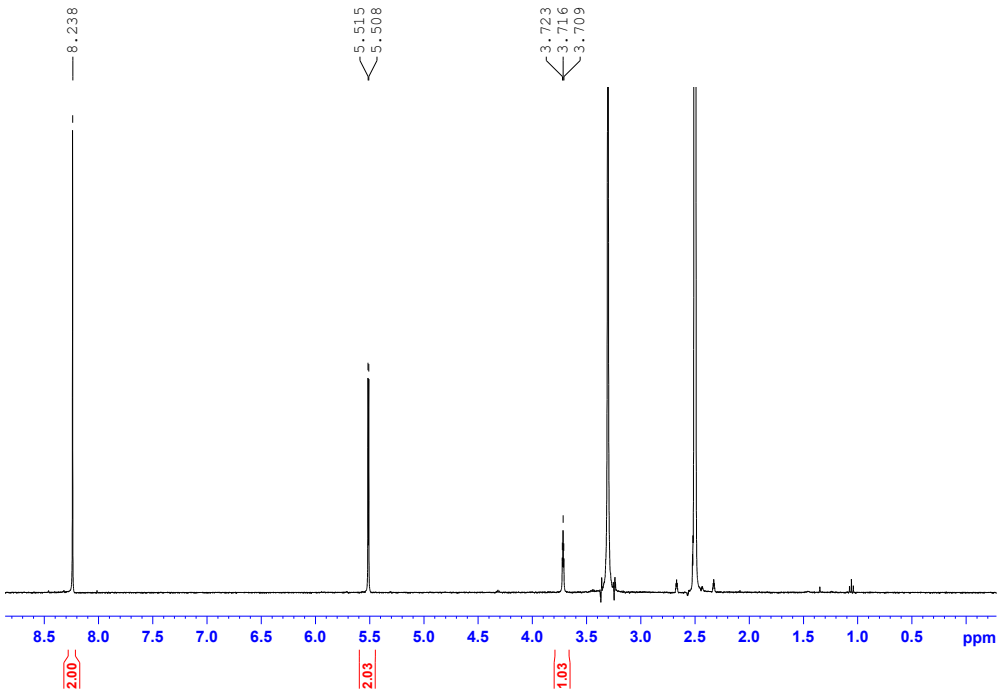


2,6,9-Triaza-4,8-dinitro[3.3.1]nona-3,7-diene (6)

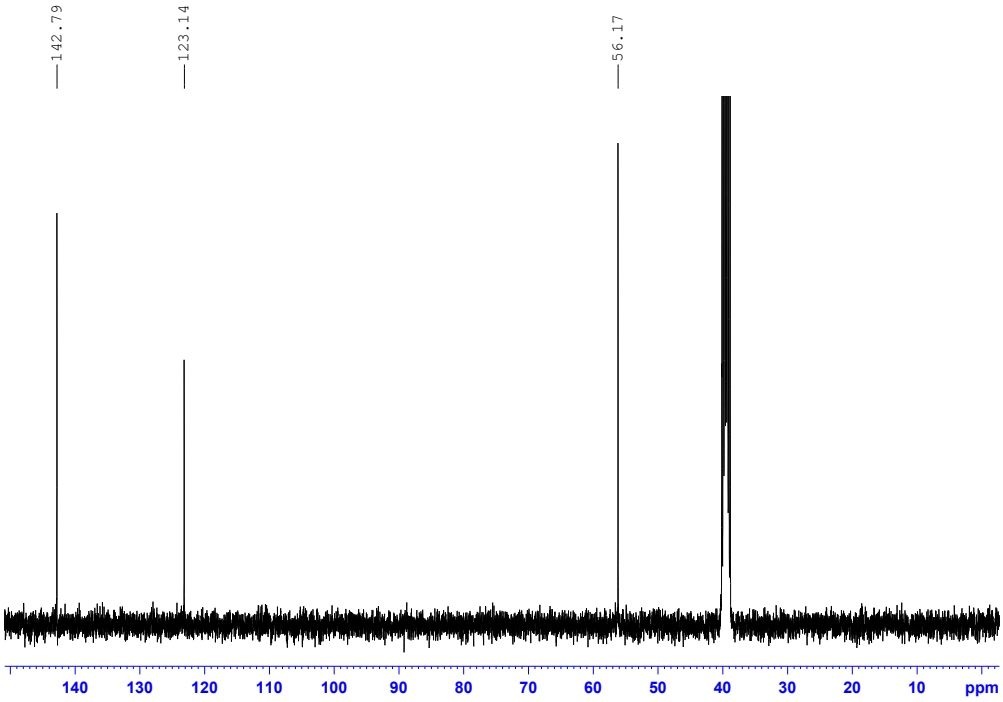


6

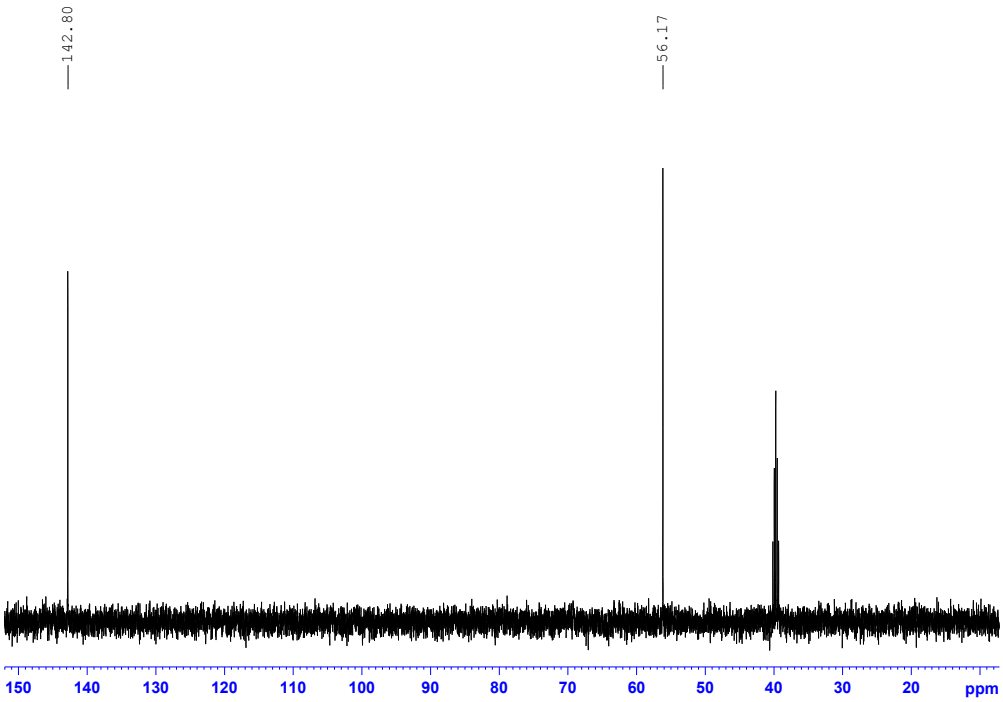
^{1}H NMR (400 MHz, DMSO-d_6)



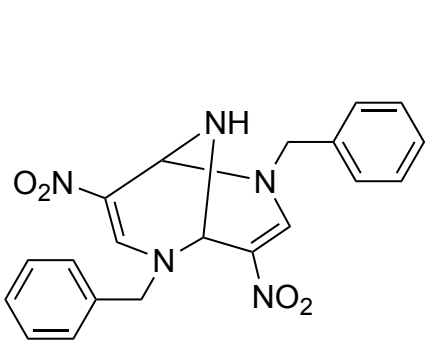
^{13}C NMR (100 MHz, DMSO-d_6)



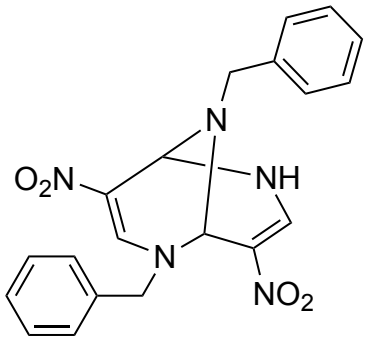
DEPT NMR (100 MHz, DMSO-d_6)



2,6,9-Triaza-2,6-dibenzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (2d)
2,6,9-Triaza-2,9-dibenzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (3d)

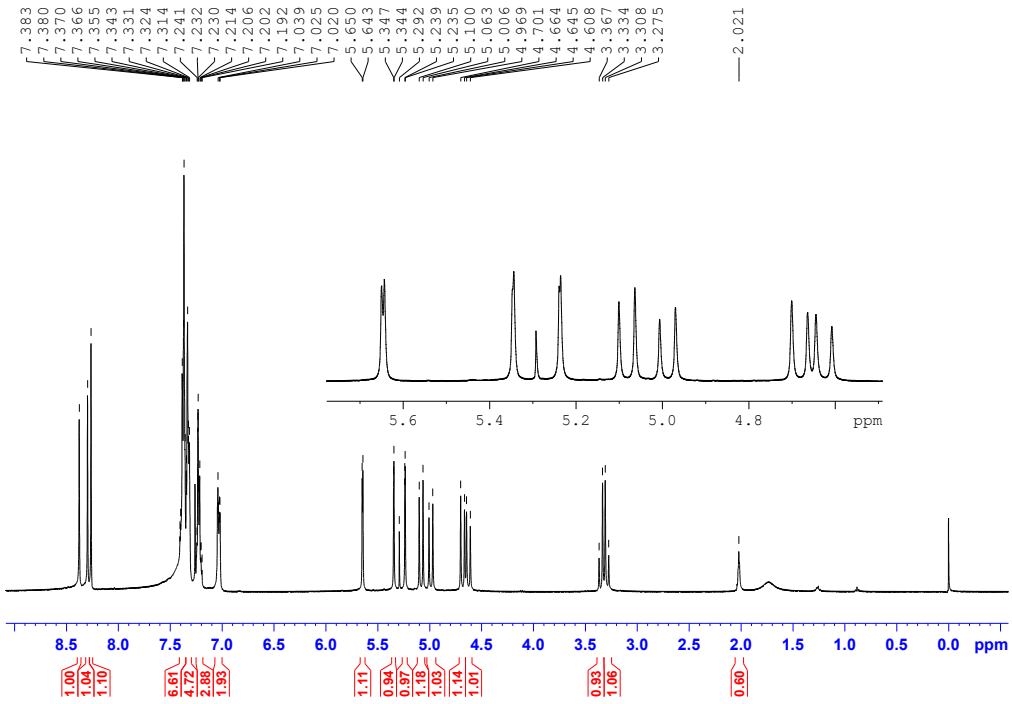


2d

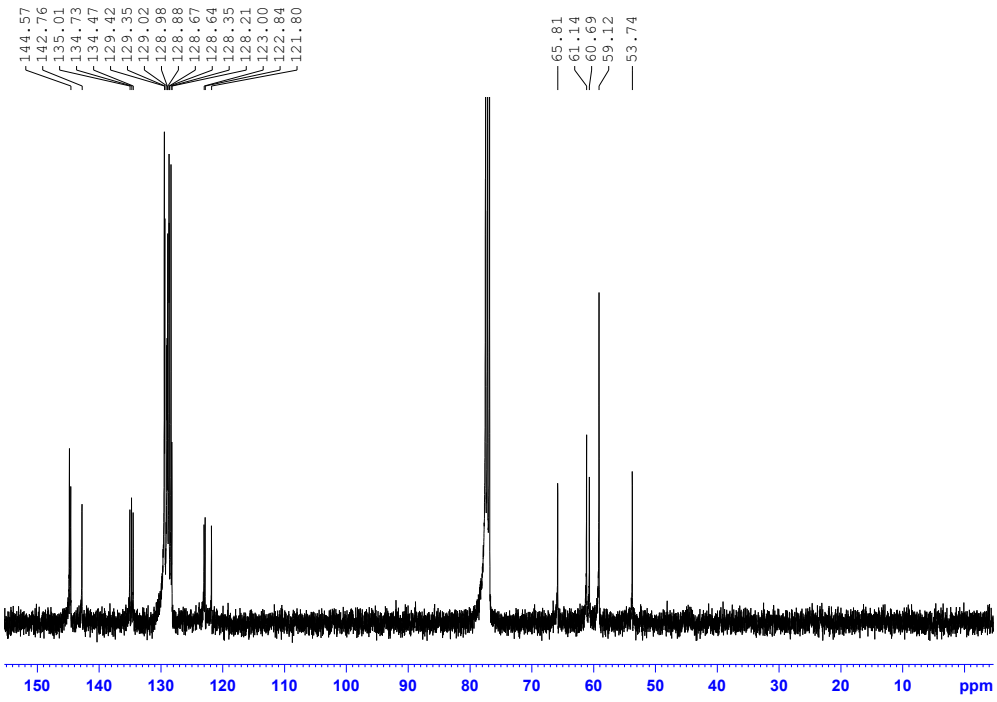


3d

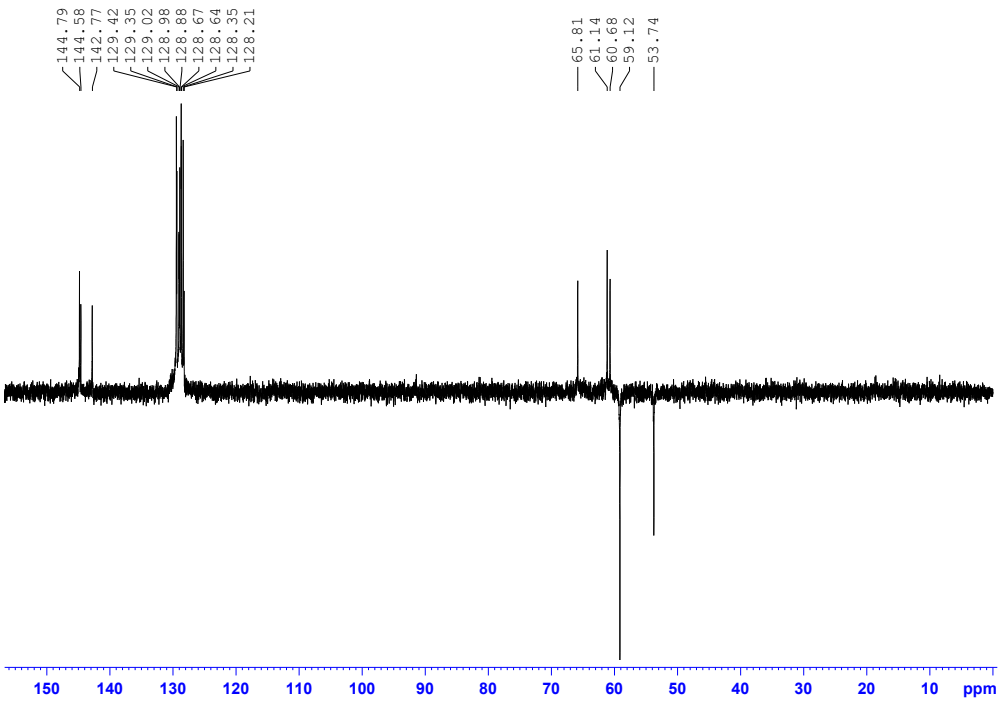
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

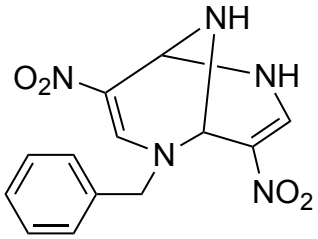


DEPT NMR (100 MHz, $CDCl_3$)

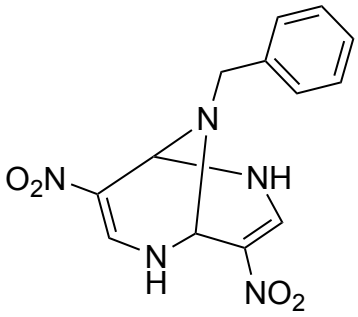


2,6,9-Triaza-2-benzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (4d)

2,6,9-Triaza-9-benzyl-4,8-dinitrobicyclo[3.3.1]nona-3,7-diene (5d)

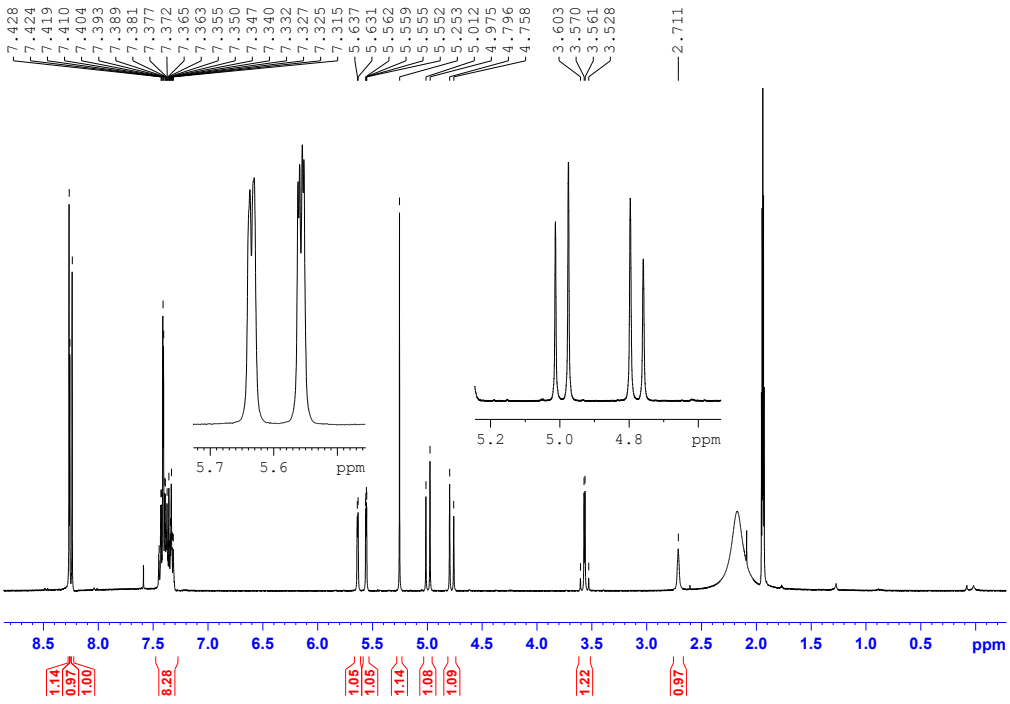


4d



5d

^{1}H NMR (400 MHz, CD_3CN)



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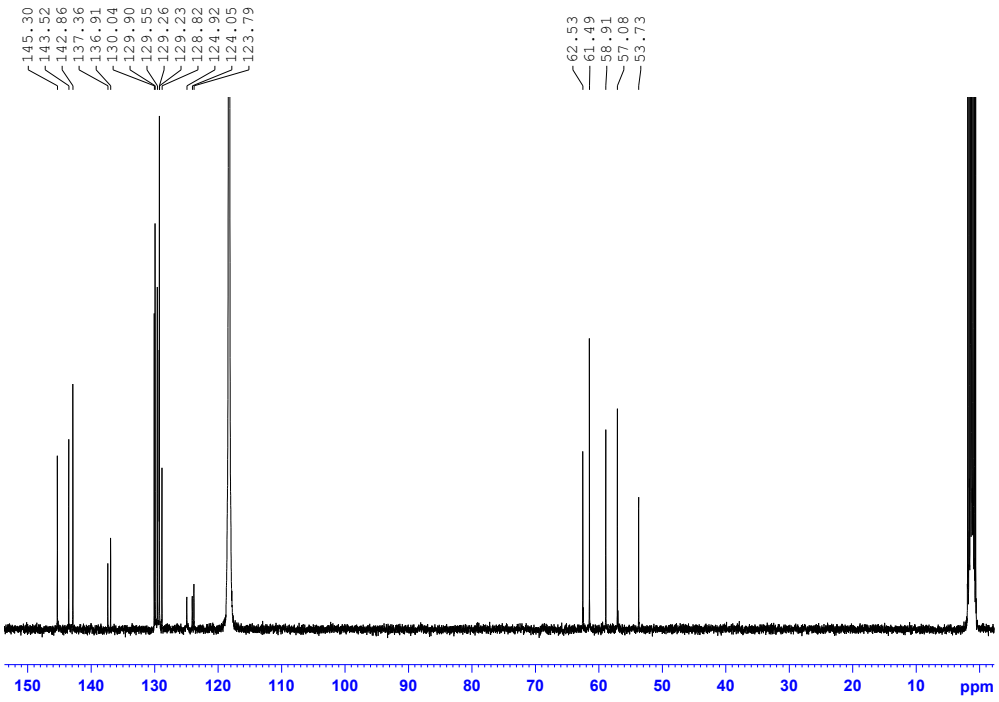
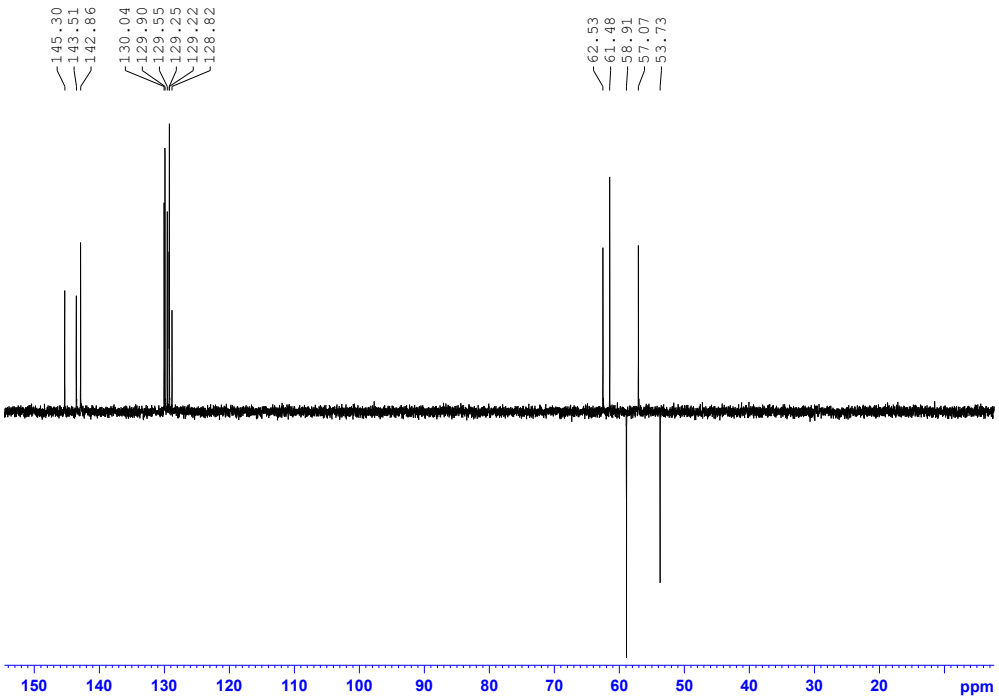
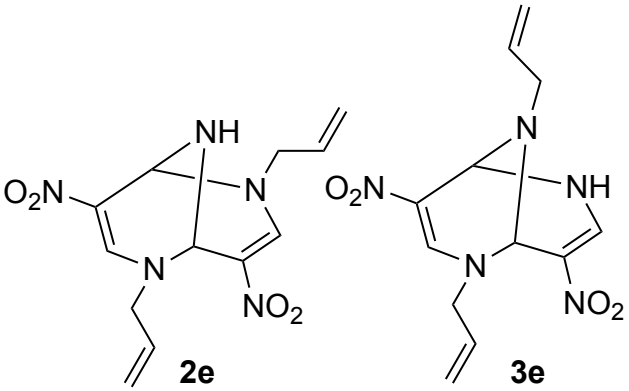


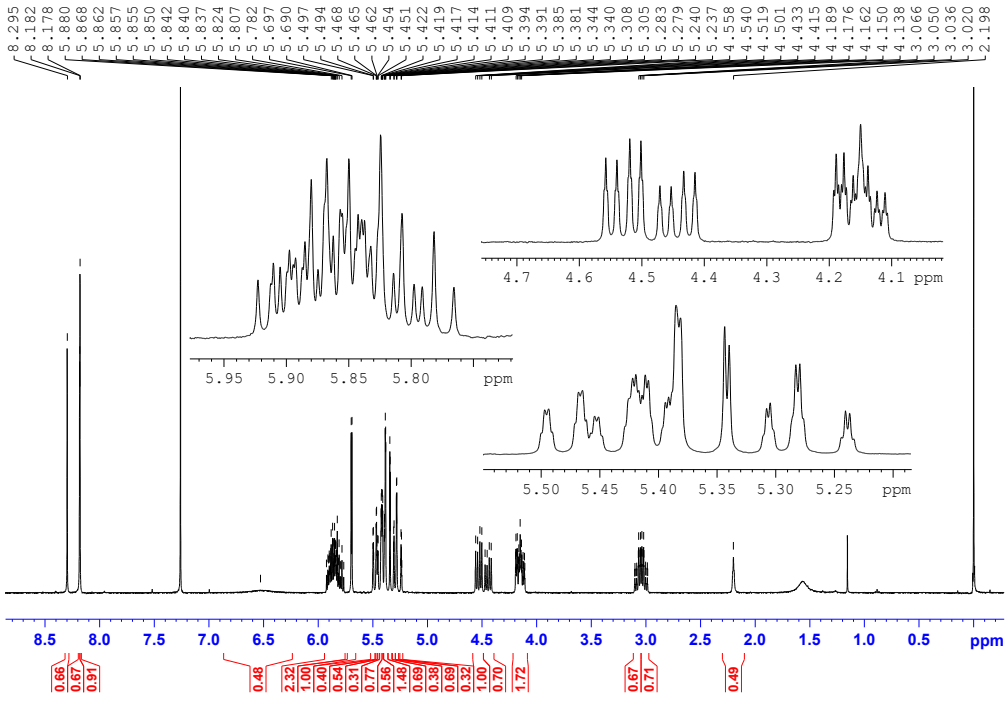
DEPT NMR (100 MHz, CD_3CN)



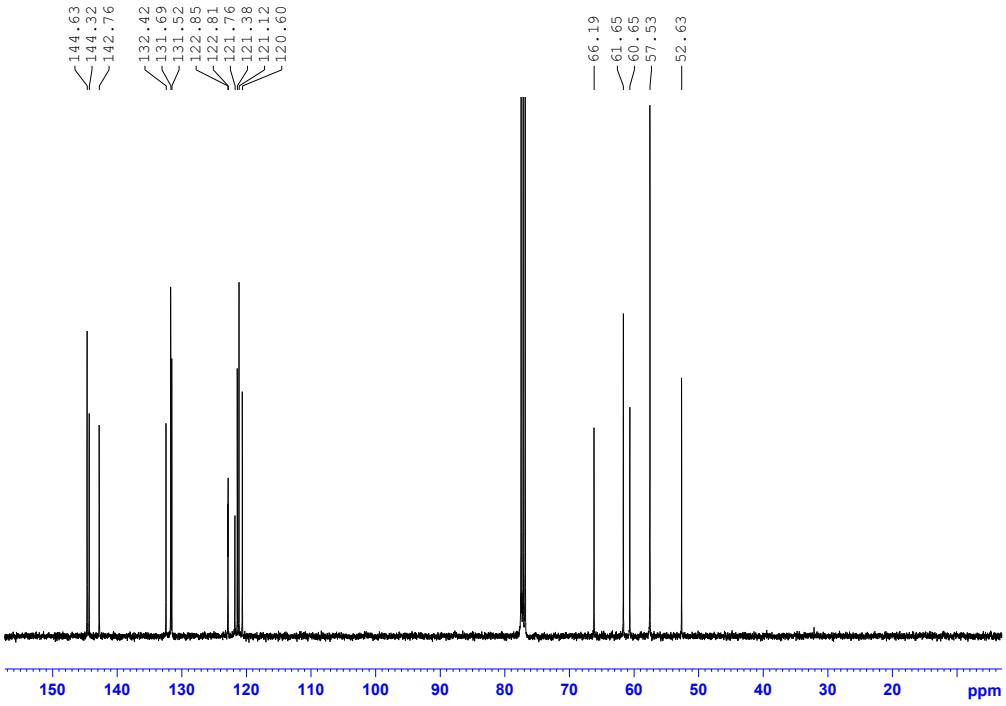
2,6,9-Triaza-4,8-dinitro-2,6-di(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (2e)
2,6,9-Triaza-4,8-dinitro-2,9-di(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (3e)



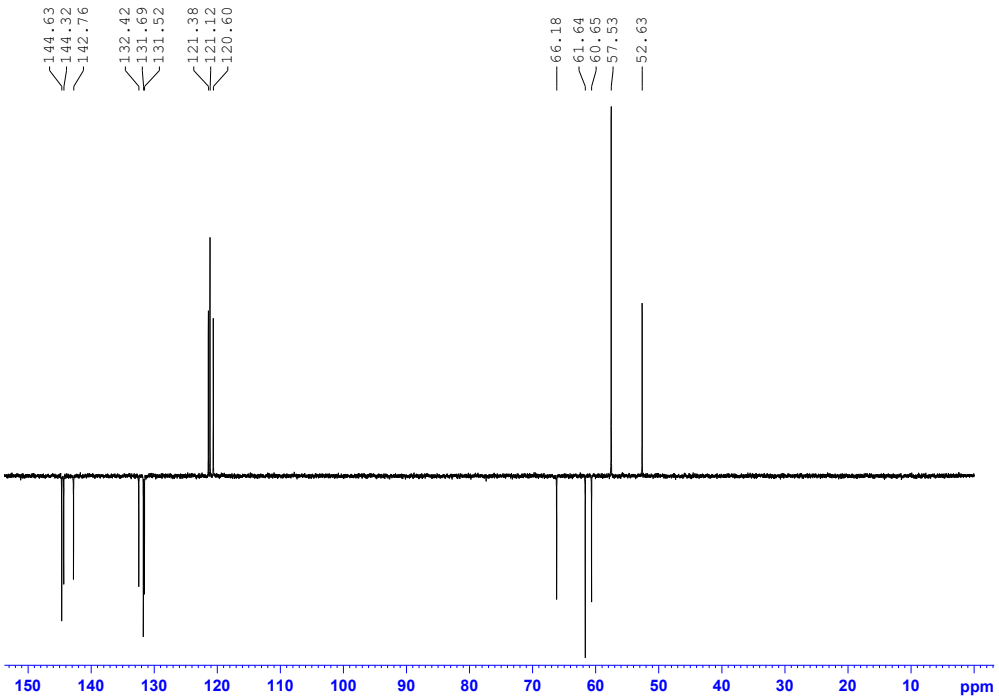
^{1}H NMR (400 MHz, $CDCl_3$)



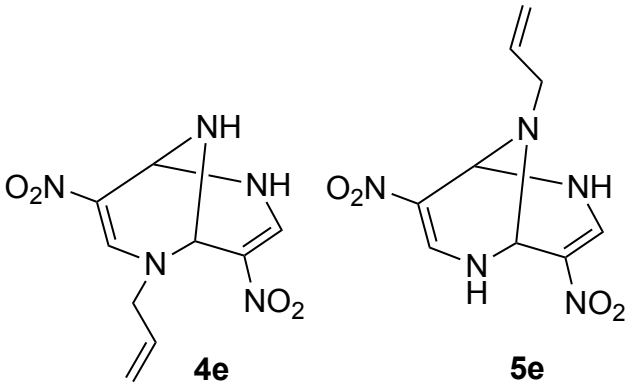
^{13}C NMR (100 MHz, $CDCl_3$)



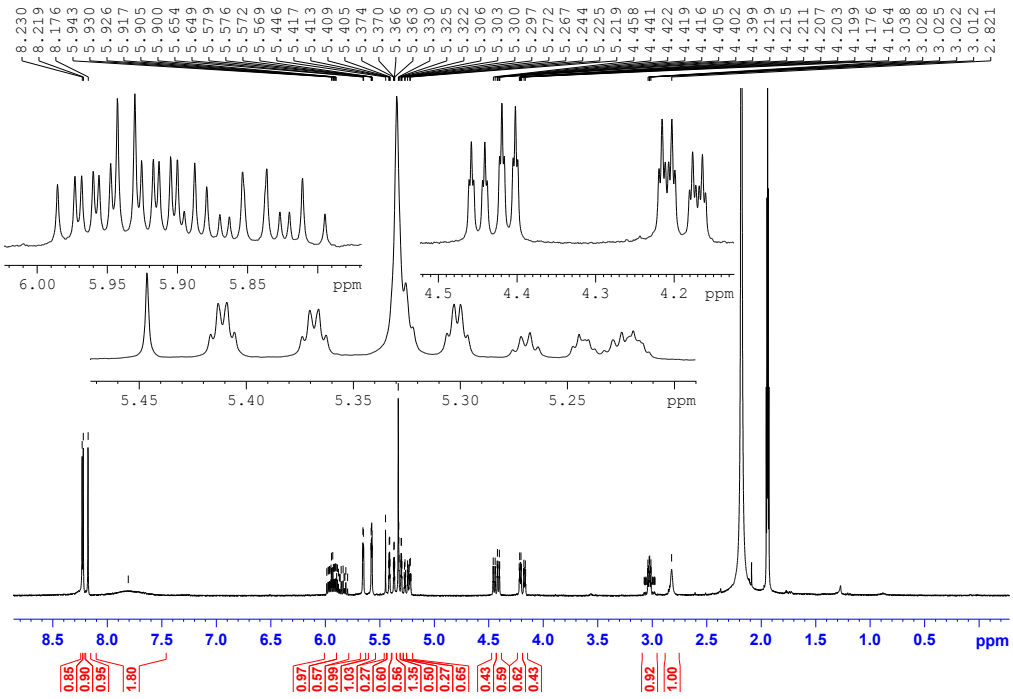
DEPT NMR (100 MHz, CD_3CN)



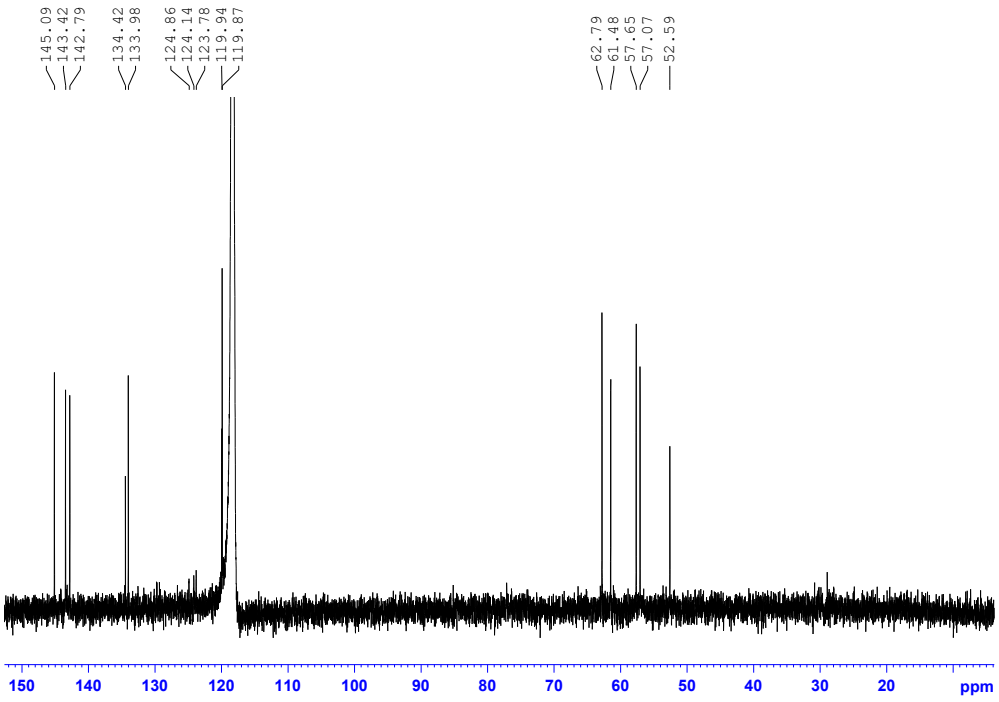
2,6,9-Triaza-4,8-dinitro-2-(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (4e)
2,6,9-Triaza-4,8-dinitro-9-(3-propen-1-yl)bicyclo[3.3.1]nona-3,7-diene (5e)



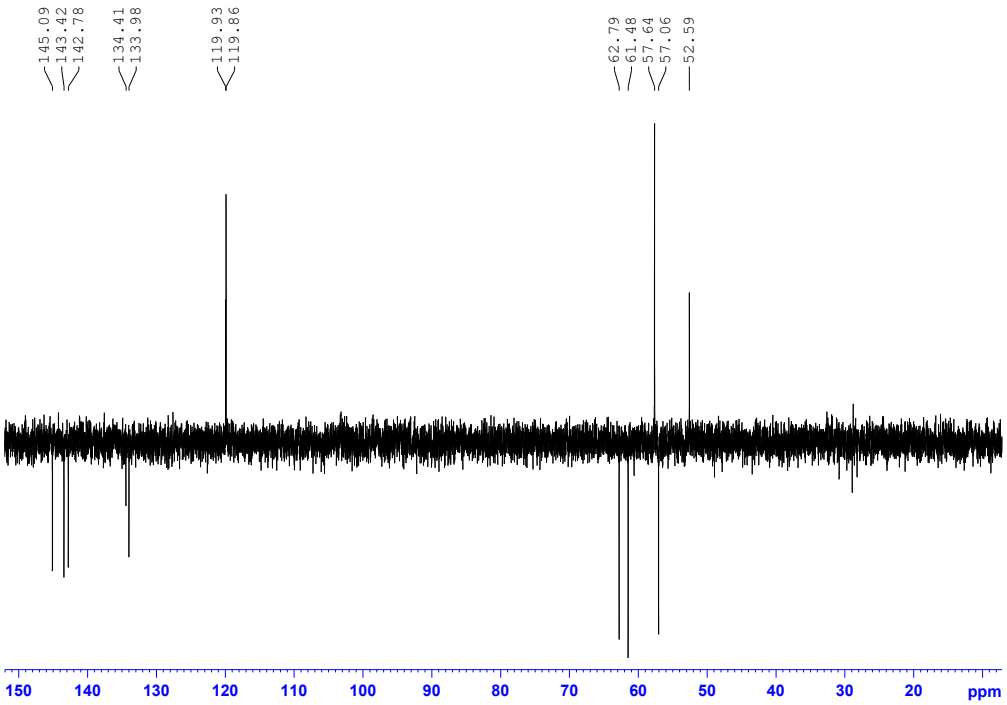
^{1}H NMR (400 MHz, CD_3CN)



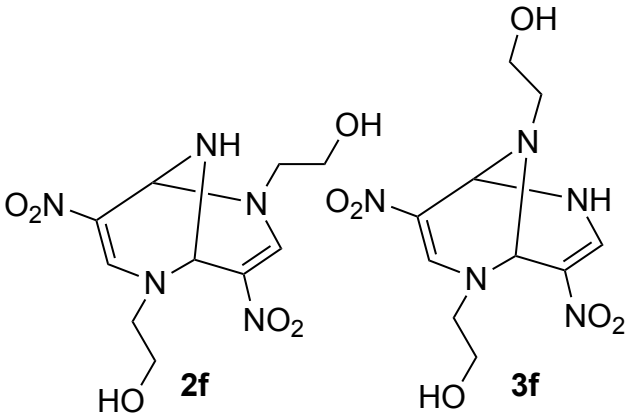
^{13}C NMR (100 MHz, CD_3CN)



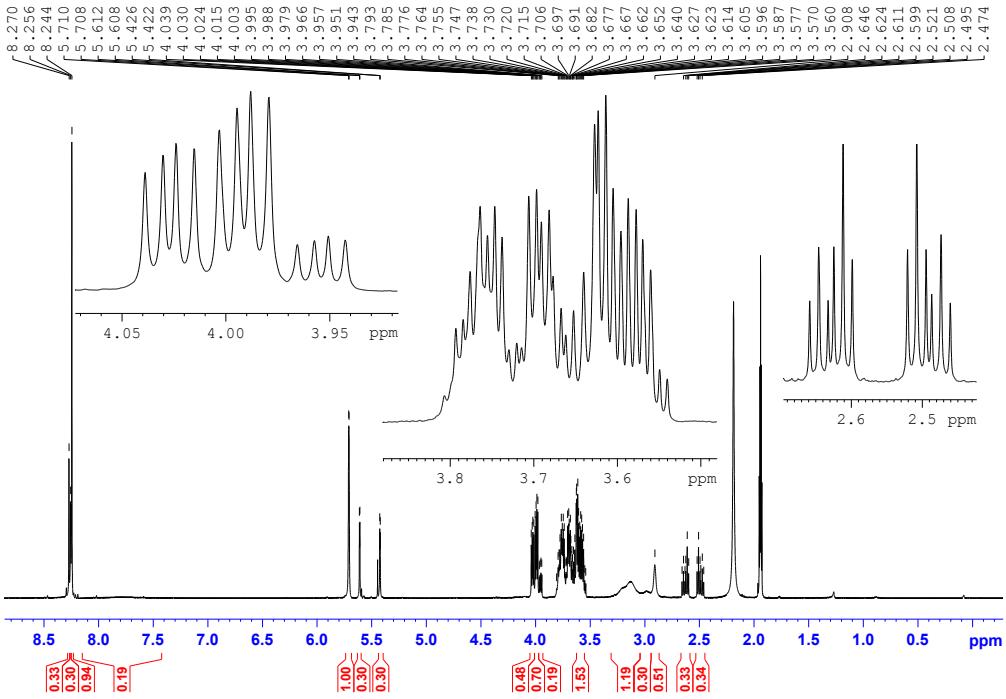
DEPT NMR (100 MHz, CD_3CN)



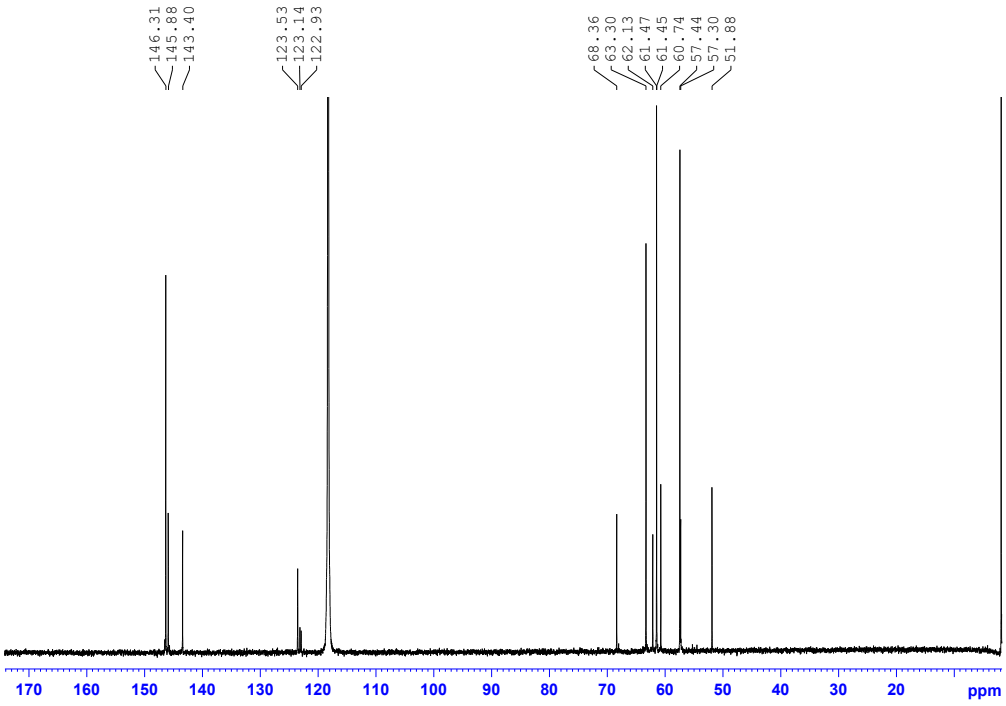
2,6,9-Triaza-2,6-di(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (2f)
2,6,9-Triaza-2,9-di(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (3f)



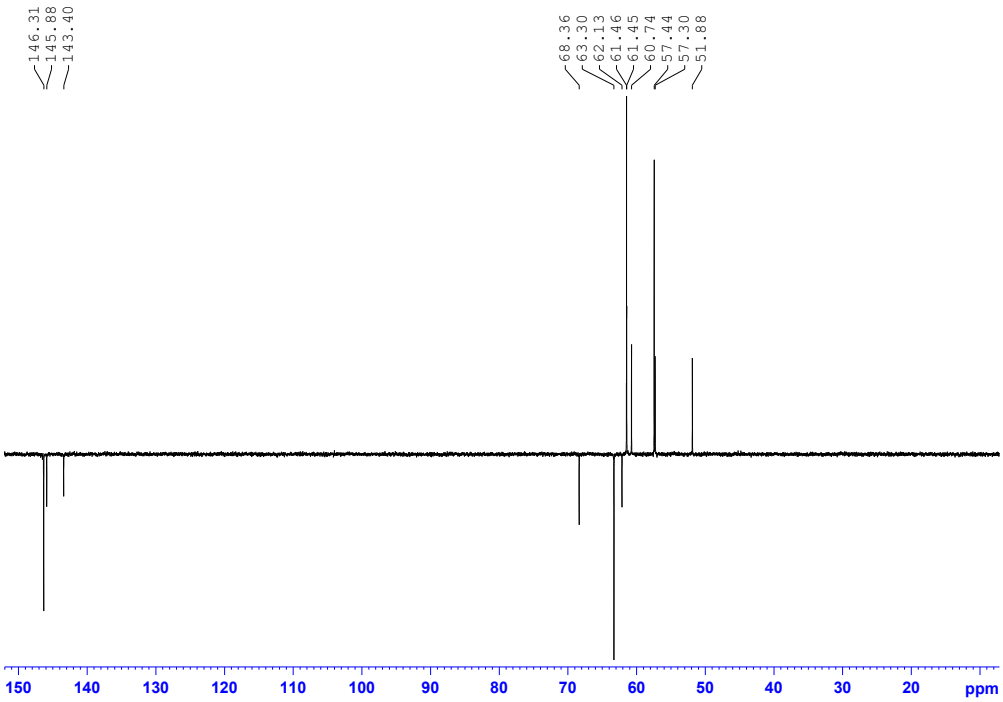
^{1}H NMR (400 MHz, CD_3CN)



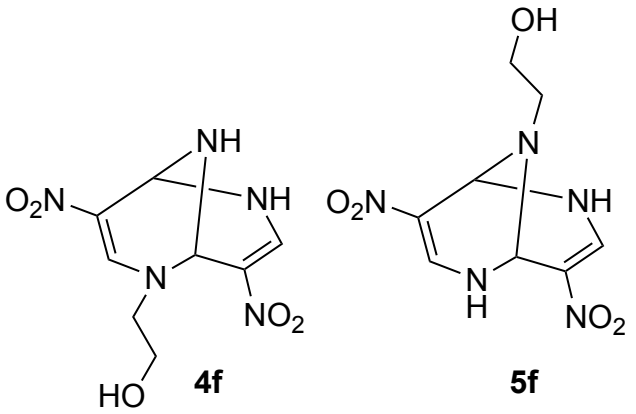
^{13}C NMR (100 MHz, CD_3CN)



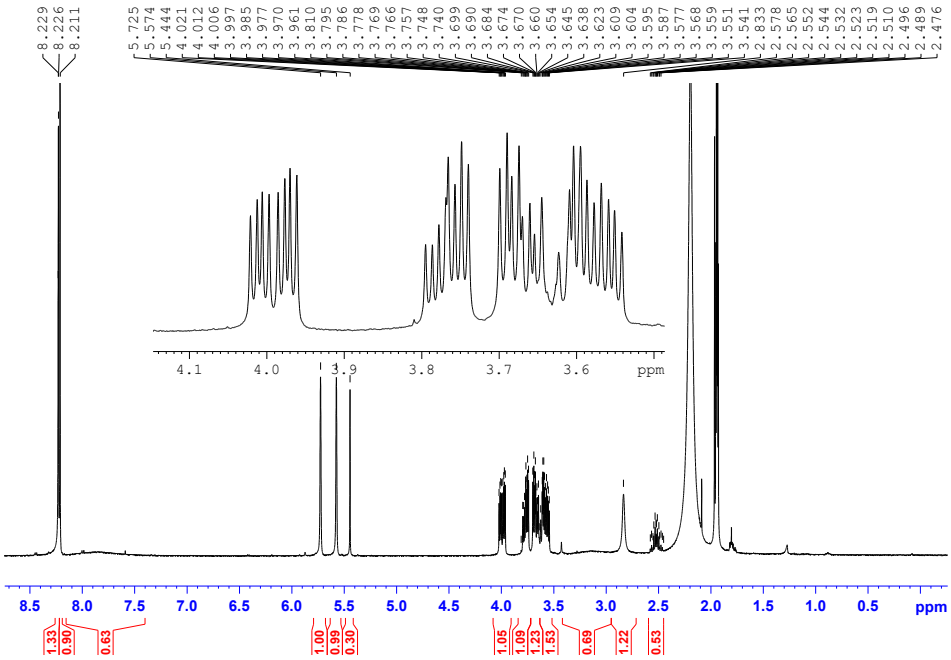
DEPT NMR (100 MHz, CD_3CN)



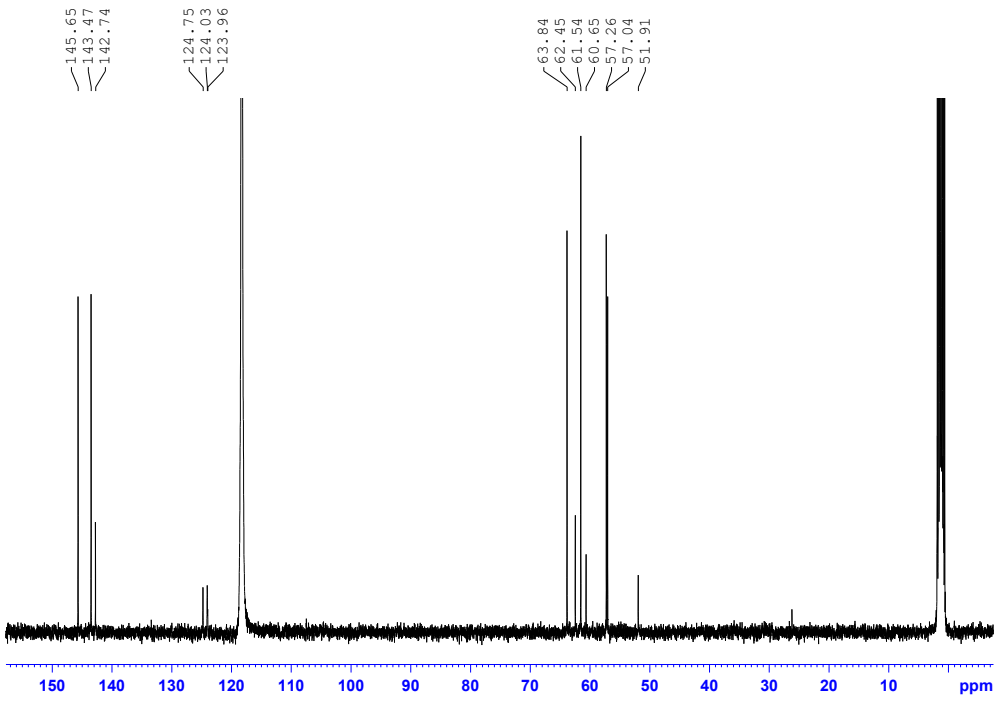
2,6,9-Triaza-2-(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (4f)
2,6,9-Triaza-9-(2-hydroxyethyl)-4,8-dinitro[3.3.1]nona-3,7-diene (5f)



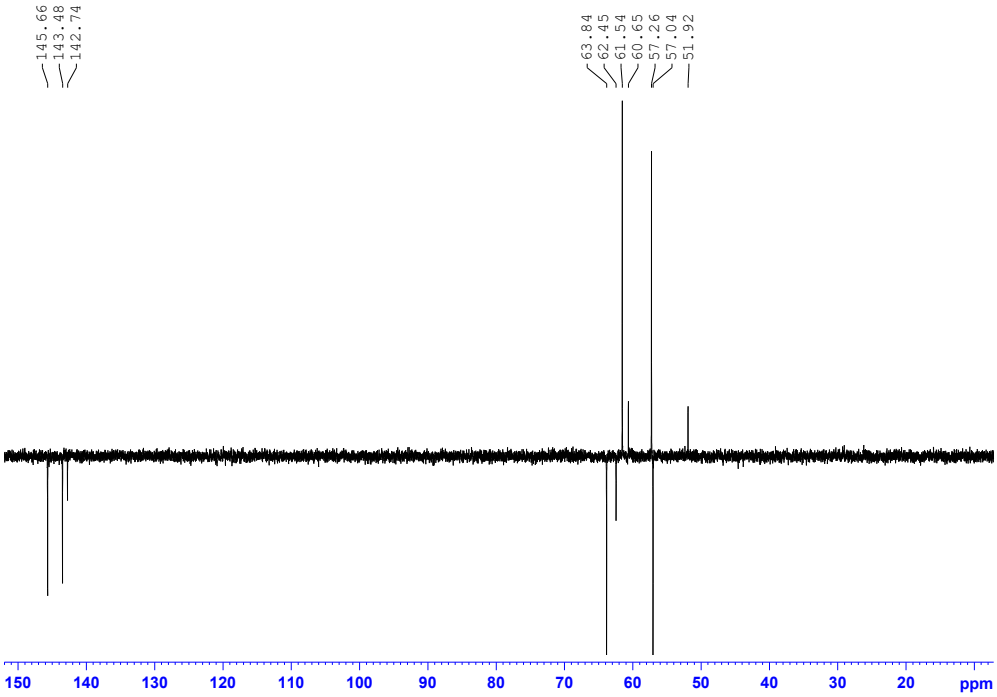
^{1}H NMR (400 MHz, CD_3CN)



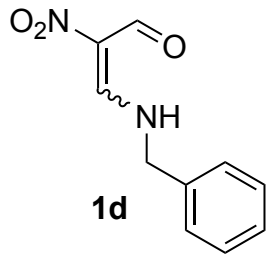
^{13}C NMR (100 MHz, CD_3CN)



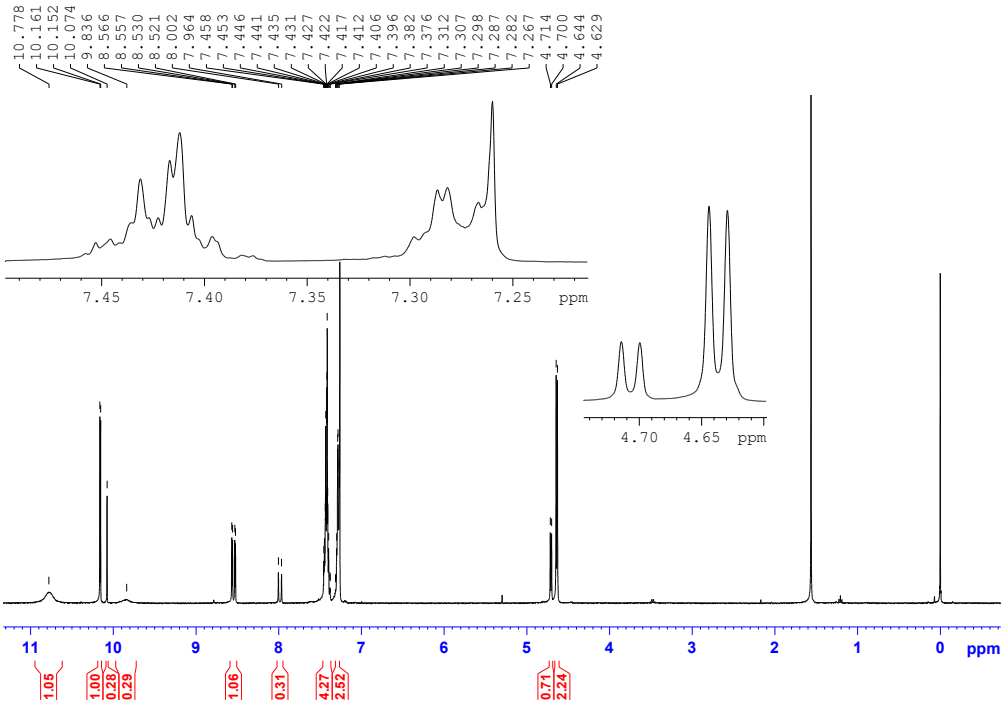
DEPT NMR (100 MHz, CD_3CN)



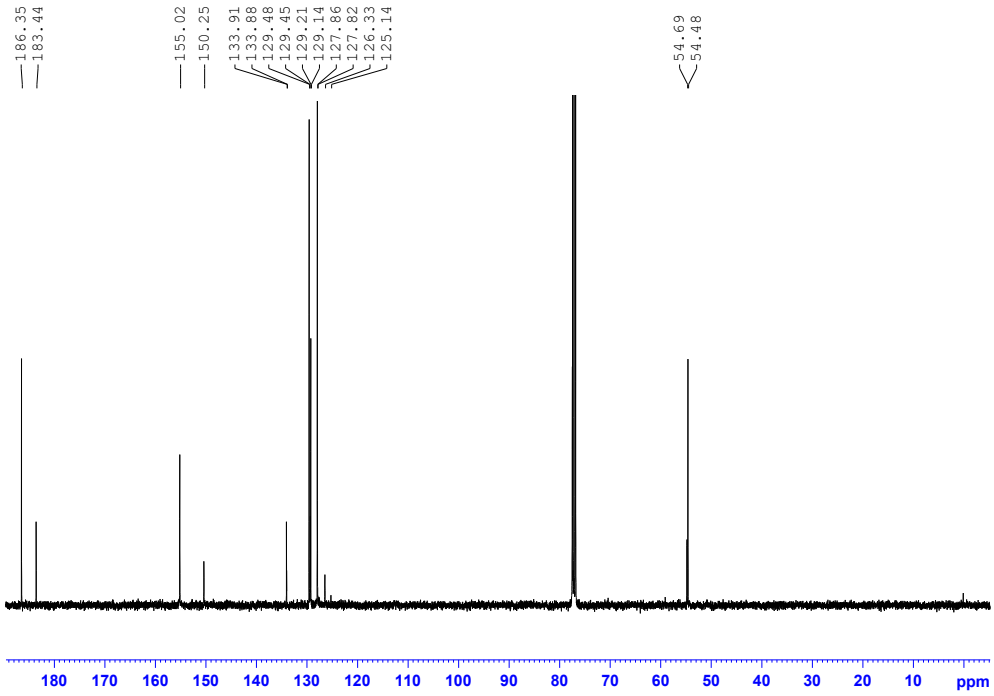
4-Aza-2-nitro-5-phenyl-2-pentenal (1d)



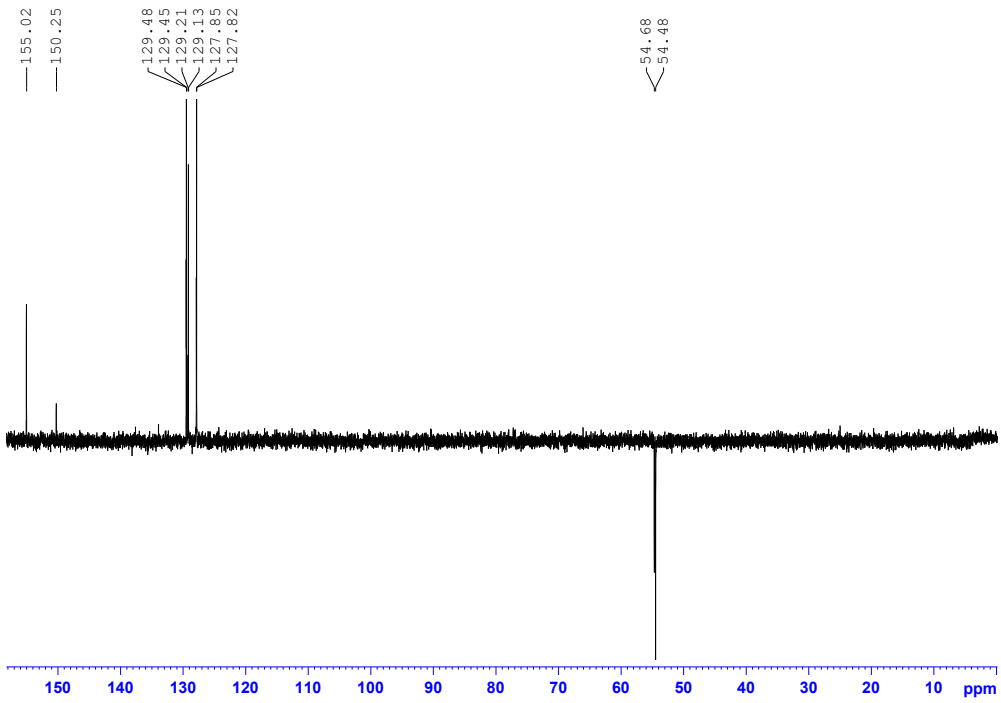
^{1}H NMR (400 MHz, $CDCl_3$)



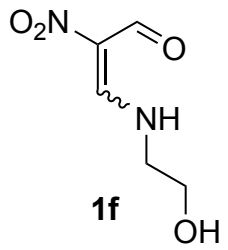
^{13}C NMR (100 MHz, $CDCl_3$)



DEPT NMR (100 MHz, $CDCl_3$)

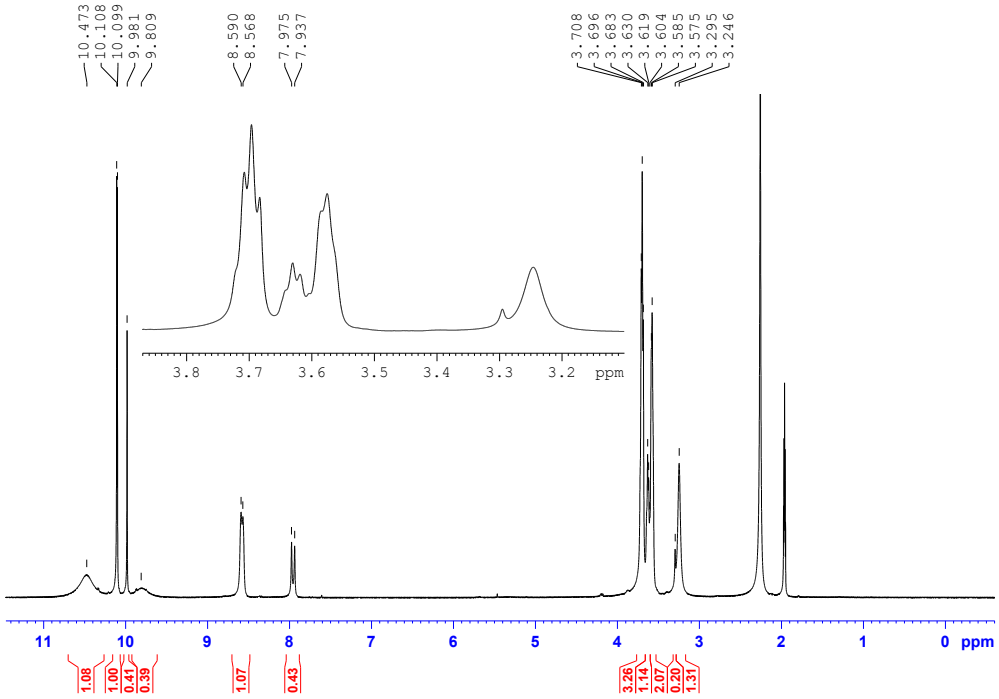


4-Aza-6-hydroxy-2-nitro-2-hexenal (1f)

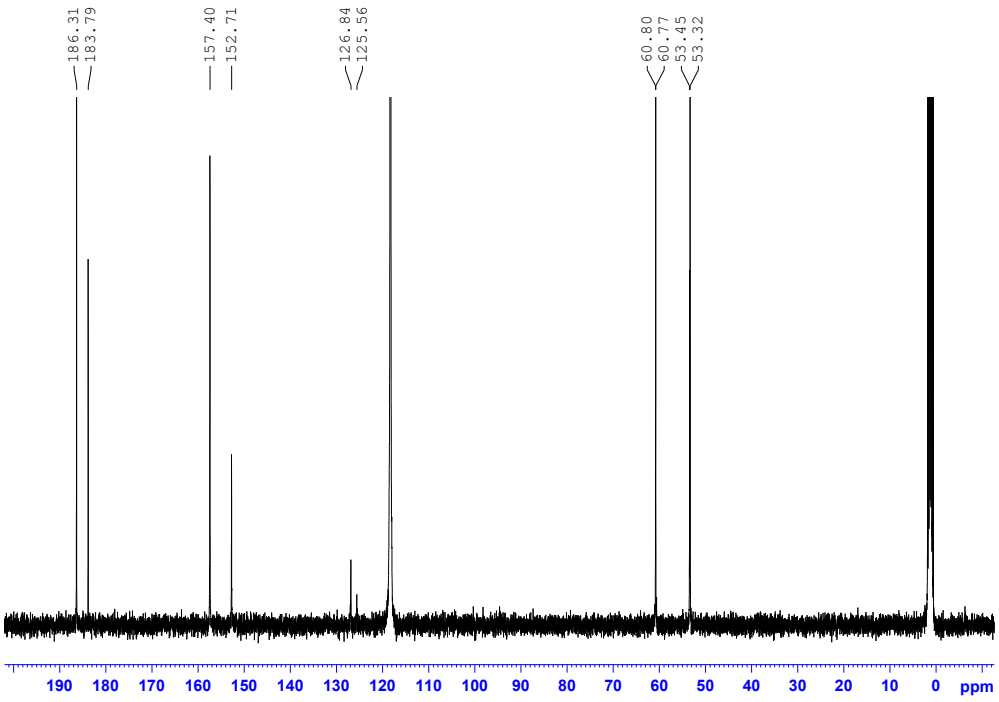


1f

^{1}H NMR (400 MHz, CD_3CN)



^{13}C NMR (100 MHz, CD_3CN)



DEPT NMR (100 MHz, CD_3CN)