Electronic Supplementary Information

1-Nitro-2-trinitromethyl substituted imidazoles: a new family of high performance energetic materials

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1. Crystal data and structure refinement for **11-15, 17** and **19**

Table S1. Crystal data and structure refinement for **11-13**.

	11	12a	12b	13
CCDC	1500624	1502271	1502272	1500626
Chemical formula	C5H6N6O8	C8H10N6O8	C8H10N6O8	C5H6N6O8
Formula weight / g mol^{-1}	278.16	318.22	318.22	278.16
Temperature / K	293(2)	293(2)	293(2)	293(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*1	*C*2/*c*	$P2_1/c$	$P2_1$
Crystal colour	colorless	colorless	colorless	colorless
a / Å	8.4150(17)	21.390(4)	11.267(2)	10.821(2)
b / Å	10.916(2)	12.501(3)	10.248(2)	8.8200(18)
c / Å	12.774(3)	9.957(2)	11.444(2)	11.286(2)
α / º	72.30(3)	90.00	90.00	90.00
β / º	83.98(3)	95.08(3)	91.41(3)	93.44(3)
γ / º	83.60(3)	90.00	90.00	90.00
Volume / $Å^3$	1107.8(4)	2652.0(9)	1321.0(5)	1075.2(4)
Z	4	8	4	4
D_{calc} / g cm^{-3}	1.668	1.594	1.600	1.718
Absorption coefficient / mm^{-1}	0.158	0.144	0.144	0.163
F(000)	568	1312	656	568
θ range / º	1.68-25.39	1.89-25.37	1.81-25.39	1.81-25.36
Index ranges	$0 \le h \le 10$, $-13 \le k \le 13$, $-15 \le l \le 15$	$0 \le h \le 25$, $0 \le k \le 15$, $-12 \le l \le 11$	$0 \le h \le 13$, $0 \le k \le 12$, $-13 \le l \le 13$	$0 \le h \le 13$, $0 \le k \le 10$, $-13 \le l \le 13$
Reflections collected	4072	2424	2432	2108
Goodness-of-fit on F^2	1.004	1.018	1.002	1.001
R indices (all data)	$R_1 = 0.1339$, $wR_2 = 0.1810$	$R_1=0.0921$, $wR_2=0.1711$	$R_1=0.1462$, $wR_2=0.1569$	$R_1 = 0.1087$, $wR_2 = 0.0981$
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0667$, $wR_2 = 0.1520$	$R_1=0.0556$, $wR_2=0.1492$	$R_1=0.0692$, $wR_2=0.1322$	$R_1 = 0.0525$, $wR_2 = 0.0828$
Largest diff. peak and hole / e $Å^{-3}$	0.339, -0.203	0.329, -0.270	0.202, -0.203	0.217, -0.167

Table S2. Crystal data and structure refinement for **14, 15, 17,** and **19**.

	14	15	17	19
CCDC	1502273	1500614	1500623	1500625
Chemical formula	C4H6N4O6	C6H8N4O6	C6H6N6O10	C8H8N6O12
Formula weight / g mol^{-1}	206.13	232.16	322.17	380.20
Temperature / K	293(2)	293(2)	298(2)	293(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P1$
Crystal colour	light yellow	colorless	colorless	colorless
a / Å	11.531(2)	10.125(2)	20.437(4)	8.6990(17)
b / Å	7.5300(15)	8.3450(17)	6.2410(12)	8.7890(18)
c / Å	17.166(3)	10.583(2)	20.588(4)	10.723(2)
α / º	90.00	90.00	90.00	86.59(3)
β / º	98.46(3)	106.10(3)	113.82(3)	89.54(3)
γ / º	90.00	90.00	90.00	72.16(3)
Volume / $Å^3$	1474.3(5)	859.1(3)	2402.3(8)	779.0(3)
Z	8	4	8	2
D_{calc} / g cm^{-3}	1.857	1.795	1.782	1.621
Absorption coefficient / mm^{-1}	0.175	0.162	0.172	0.155
$F(000)$	848	480	1312	388
θ range / º	1.79-25.36	2.09-25.38	1.18-25.46	1.90-25.39
Index ranges	$0 \le h \le 13$, $0 \le k \le 9$, $-20 \le l \le 20$	$0 \le h \le 12$, $0 \le k \le 10$, $-12 \le l \le 12$	$0 \le h \le 24$, $0 \le k \le 7$, $-24 \le l \le 22$	$0 \le h \le 10$, $-10 \le k \le 10$, $-12 \le l \le 12$
Reflections collected	2702	1577	4399	2867
Goodness-of-fit on F^2	1.041	1.000	1.000	1.003
R indices (all data)	R_1=0.0758 , wR_2=0.1644	R_1 = 0.0708, wR_2 = 0.1433	R_1 = 0.1810, wR_2 = 0.1715	R_1 = 0.1022, wR_2 = 0.1889
Final R indices [$I>2\sigma(I)$]	R_1=0.0570, wR_2=0.1528	R_1 = 0.0492, wR_2 = 0.1269	R_1 = 0.0785, wR_2 = 0.1403	R_1 = 0.0635, wR_2 = 0.1597
Largest diff. peak and hole / e $Å^{-3}$	0.378, -0.398	0.256, -0.351	0.264, -0.248	0.258, -0.307

2. Single-crystal X-ray Diffraction Analysis of Compound **11**

Table S3. Selected bond lengths [Å] and angles [^{o}] for compound **11**

O(1) – N(3)	1.209(4)	N(2) – N(3)	1.339(4)
O(2) – N(3)	1.225(4)	N(2) – C(3)	1.408(4)
O(3) – N(4)	1.191(4)	N(2) – C(2)	1.463(5)
O(4) – N(4)	1.191(4)	N(4) – C(5)	1.534(5)
O(5) – N(5)	1.195(4)	N(5) – C(5)	1.535(5)
O(6) – N(5)	1.205(5)	N(6) – C(5)	1.517(5)
O(7) – N(6)	1.195(4)	C(1) – C(4)	1.499(6)
O(8) – N(6	1.181(4)	C(1) – C(2)	1.527(5)
N(1) – C(3)	1.242(4)	C(3) – C(5)	1.501(5)
N(1) – C(1)	1.490(4)		
C(3) – N(1) – C(1)	108.3(3)	O(7) – N(6) – C(5)	116.9(4)
N(3) – N(2) – C(3)	127.6(3)	N(1) – C(1) – C(4)	108.7(3)
N(3) – N(2) – C(2)	123.4(3)	N(1) – C(1) – C(2)	106.1(3)
C(3) – N(2) – C(2)	108.3(3)	C(4) – C(1) – C(2)	113.5(4)
O(1) – N(3) – O(2)	125.1(4)	N(2) – C(2) – C(1)	101.4(3)
O(1) – N(3) – N(2)	117.5(3)	N(1) – C(3) – N(2)	115.2(3)
O(2) – N(3) – N(2)	117.3(3)	N(1) – C(3) – C(5)	120.9(3)
O(4) – N(4) – O(3)	127.2(4)	N(2) – C(3) – C(5)	123.9(3)
O(4) – N(4) – C(5)	114.9(4)	C(3) – C(5) – N(6)	112.6(3)
O(3) – N(4) – C(5)	117.8(4)	C(3) – C(5) – N(4)	111.6(3)
O(5) – N(5) – O(6)	127.1(4)	N(6) – C(5) – N(4)	114.2(3)
O(5) – N(5) – C(5)	117.4(4)	C(3) – C(5) – N(5)	107.7(3)
O(6) – N(5) – C(5)	115.4(4)	N(6) – C(5) – N(5)	105.1(3)
O(8) – N(6) – O(7)	126.8(4)	N(4) – C(5) – N(5)	104.9(3)
O(8) – N(6) – C(5)	116.1(4)		

Table S4. Selected torsion angles for **11** [^{o}]

C(2) – N(2) – N(3) – O(1)	1.9(5)	C(2) – N(2) – C(3) – C(5)	178.5(3)
C(2) – N(2) – N(3) – O(2)	-179.6(3)	N(1) – C(3) – C(5) – N(5)	2.3(5)
N(3) – N(2) – C(2) – C(1)	177.7(3)	N(2) – C(3) – C(5) – N(5)	-179.4(3)
C(1) – N(1) – C(3) – N(2)	-2.7(4)	O(7) – N(6) – C(5) – C(3)	-178.1(4)
C(2) – N(2) – C(3) – N(1)	-3.1(4)		

3. Single-crystal X-ray Diffraction Analysis of Compound **12a**

Table S5. Selected bond lengths [Å] and angles [^{o}] for compound **12a**

O(1) – N(3)	1.228(4)	N(4) – O(4)	1.191(4)
C(1) – N(1)	1.473(4)	N(4) – C(8)	1.522(4)
C(1) – C(6)	1.476(5)	C(4) – C(5)	1.516(5)
C(1) – C(2)	1.493(5)	N(5) – O(6)	1.194(3)
N(2) – C(7)	1.259(4)	N(5) – O(5)	1.211(4)
N(2) – C(6)	1.487(4)	N(5) – C(8)	1.528(4)
N(1) – N(3)	1.370(4)	C(5) – C(6)	1.469(5)
N(1) – C(7)	1.416(4)	N(6) – O(8)	1.198(4)
O(2) – N(3)	1.199(3)	N(6) – O(7)	1.202(3)
C(2) – C(3)	1.513(5)	N(6) – C(8)	1.541(4)
O(3) – N(4)	1.178(4)	C(7) – C(8)	1.497(4)
C(3) – C(4)	1.504(6)		
N(1) – C(1) – C(6)	100.2(2)	O(5) – N(5) – C(8)	113.3(3)
N(1) – C(1) – C(2)	125.2(3)	C(6) – C(5) – C(4)	109.4(3)
C(6) – C(1) – C(2)	113.2(3)	O(8) – N(6) – O(7)	128.0(3)
C(7) – N(2) – C(6)	105.6(2)	O(8) – N(6) – C(8)	116.1(3)
N(3) – N(1) – C(7)	123.7(3)	O(7) – N(6) – C(8)	116.0(3)
N(3) – N(1) – C(1)	124.0(2)	C(5) – C(6) – C(1)	114.6(3)
C(7) – N(1) – C(1)	104.9(2)	C(5) – C(6) – N(2)	120.8(3)
C(1) – C(2) – C(3)	106.8(3)	C(1) – C(6) – N(2)	106.4(3)
O(2) – N(3) – O(1)	125.8(3)	N(2) – C(7) – N(1)	115.0(3)
O(2) – N(3) – N(1)	116.5(3)	N(2) – C(7) – C(8)	119.6(3)
O(1) – N(3) – N(1)	117.7(3)	N(1) – C(7) – C(8)	125.3(3)
C(4) – C(3) – C(2)	116.7(3)	C(7) – C(8) – N(4)	112.5(2)
O(3) – N(4) – O(4)	126.6(3)	C(7) – C(8) – N(5)	112.5(2)
O(3) – N(4) – C(8)	114.0(3)	N(4) – C(8) – N(5)	112.7(3)
O(4) – N(4) – C(8)	119.2(3)	C(7) – C(8) – N(6)	108.4(2)
C(3) – C(4) – C(5)	114.6(3)	N(4) – C(8) – N(6)	104.4(2)
O(6) – N(5) – O(5)	127.4(3)	N(5) – C(8) – N(6)	105.8(2)
O(6) – N(5) – C(8)	119.2(3)		

Table S6. Selected torsion angles for **12a** [°]

C(6) – C(1) – N(1) – N(3)	176.5(3)	O(3) – N(4) – C(8) – C(7)	-9.1(4)
N(1) – C(1) – C(2) – C(3)	-177.4(3)	O(4) – N(4) – C(8) – C(7)	175.9(3)
C(6) – N(2) – C(7) – C(8)	174.9(3)	C(4) – C(5) – C(6) – N(2)	178.6(4)
N(2) – C(7) – C(8) – N(6)	-3.3(4)	C(6) – N(2) – C(7) – N(1)	-1.7(4)
N(1) – C(7) – C(8) – N(6)	172.9(3)		

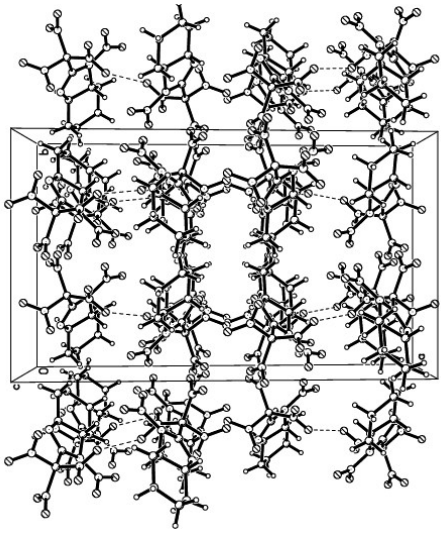


Fig. S1 Ball-and-stick packing diagram of **12a** viewed down the c axis

4. Single-crystal X-ray Diffraction Analysis of Compound **12b**

Table S7. Selected bond lengths [Å] and angles [°] for compound **12b**

N(1) – C(7)	1.256(4)	O(4) – N(4)	1.199(4)
N(1) – C(1)	1.500(5)	N(4) – C(8)	1.531(5)
O(1) – N(3)	1.241(4)	C(4) – C(5)	1.517(5)
C(1) – C(2)	1.518(5)	C(5) – C(6)	1.532(5)
C(1) – C(6)	1.537(5)	O(5) – N(5)	1.214(4)
N(2) – N(3)	1.370(4)	N(5) – O(6)	1.199(4)
N(2) – C(7)	1.424(5)	N(5) – C(8)	1.540(5)
N(2) – C(6)	1.500(4)	N(6) – O(8)	1.193(4)
O(2) – N(3)	1.191(4)	N(6) – O(7)	1.214(5)
C(2) – C(3)	1.500(6)	N(6) – C(8)	1.536(5)
O(3) – N(4)	1.202(4)	C(7) – C(8)	1.504(5)
C(3) – C(4)	1.506(6)		

C(7) – N(1) – C(1)	106.7(3)	O(6) – N(5) – C(8)	115.9(3)
N(1) – C(1) – C(2)	114.5(3)	O(5) – N(5) – C(8)	116.8(3)
N(1) – C(1) – C(6)	104.7(3)	O(8) – N(6) – O(7)	128.1(4)
C(2) – C(1) – C(6)	114.0(3)	O(8) – N(6) – C(8)	115.9(4)
N(3) – N(2) – C(7)	125.3(3)	O(7) – N(6) – C(8)	116.0(4)
N(3) – N(2) – C(6)	122.5(3)	N(2) – C(6) – C(5)	110.3(3)
C(7) – N(2) – C(6)	105.6(3)	N(2) – C(6) – C(1)	97.5(3)
C(3) – C(2) – C(1)	114.1(3)	C(5) – C(6) – C(1)	114.7(4)
O(2) – N(3) – O(1)	126.6(4)	N(1) – C(7) – N(2)	114.5(3)
O(2) – N(3) – N(2)	117.1(3)	N(1) – C(7) – C(8)	120.1(4)
O(1) – N(3) – N(2)	116.2(4)	N(2) – C(7) – C(8)	125.4(3)
C(2) – C(3) – C(4)	111.0(4)	C(7) – C(8) – N(4)	112.8(3)
O(4) – N(4) – O(3)	127.5(4)	C(7) – C(8) – N(6)	107.5(3)
O(4) – N(4) – C(8)	117.2(4)	N(4) – C(8) – N(6)	105.1(3)
O(3) – N(4) – C(8)	115.1(3)	C(7) – C(8) – N(5)	112.2(3)
C(3) – C(4) – C(5)	110.9(3)	N(4) – C(8) – N(5)	113.2(3)
C(4) – C(5) – C(6)	110.4(3)	N(6) – C(8) – N(5)	105.3(3)
O(6) – N(5) – O(5)	127.2(4)		

Table S8. Selected torsion angles for **12b** [^{o}]

N(3) – N(2) – C(6) – C(1)	177.6(3)	N(2) – C(7) – C(8) – N(6)	179.7(4)
C(1) – N(1) – C(7) – N(2)	3.1(5)	O(4) – N(4) – C(8) – C(7)	176.9(4)
C(1) – N(1) – C(7) – C(8)	-174.8(3)	O(3) – N(4) – C(8) – C(7)	-7.2(5)
N(1) – C(7) – C(8) – N(6)	-2.6(5)	O(5) – N(5) – C(8) – C(7)	-173.9(4)

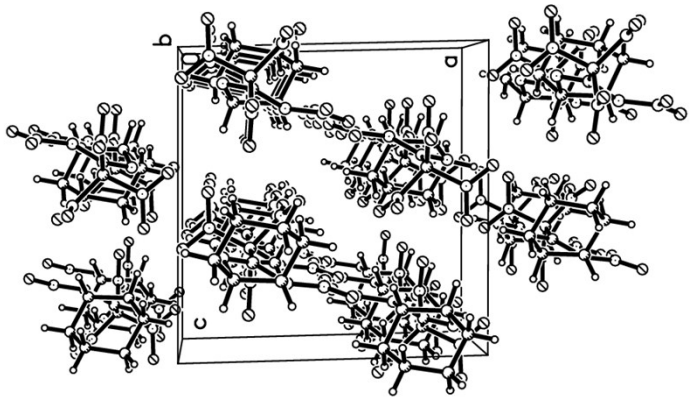


Fig. S2 Ball-and-stick packing diagram of **12b** viewed down the b axis

5. Single-crystal X-ray Diffraction Analysis of Compound **13**

Table S9. Selected bond lengths [Å] and angles [^{o}] for compound **13**

N(1) – C(4)	1.254(7)	N(4) – O(4)	1.075(16)
N(1) – C(1)	1.455(8)	N(4) – C(5)	1.576(11)
O(1) – N(3)	1.231(8)	N(5) – O(6)	1.162(6)
C(1) – C(2)	1.380(9)	N(5) – O(5)	1.167(7)
N(2) – C(4)	1.353(7)	N(5) – C(5)	1.457(8)
N(2) – N(3)	1.355(7)	C(5) – N(6)	1.521(8)
N(2) – C(3)	1.492(7)	C(6) – C(7)	1.450(8)
O(2) – N(3)	1.182(6)	C(6) – N(7)	1.473(7)
C(2) – C(3)	1.449(9)	N(6) – O(8)	1.163(7)
O(3) – N(4)	1.262(13)	N(6) – O(7)	1.194(7)
C(4) – C(5)	1.531(8)		
C(4) – N(1) – C(1)	118.9(6)	O(4) – N(4) – C(5)	113.9(14)
C(2) – C(1) – N(1)	113.3(7)	O(3) – N(4) – C(5)	109.5(11)
C(4) – N(2) – N(3)	125.0(5)	O(6) – N(5) – O(5)	122.7(8)
C(4) – N(2) – C(3)	120.0(5)	O(6) – N(5) – C(5)	124.8(7)
N(3) – N(2) – C(3)	114.8(5)	O(5) – N(5) – C(5)	112.3(6)
C(1) – C(2) – C(3)	117.3(8)	N(5) – C(5) – N(6)	108.1(5)
O(4) – N(4) – O(3)	136.7(15)	N(5) – C(5) – C(4)	118.4(5)
C(2) – C(3) – N(2)	109.6(5)	N(6) – C(5) – C(4)	111.4(5)
O(2) – N(3) – O(1)	124.4(7)	N(5) – C(5) – N(4)	106.0(7)
O(2) – N(3) – N(2)	119.6(7)	N(6) – C(5) – N(4)	102.5(7)
O(1) – N(3) – N(2)	115.5(6)	C(4) – C(5) – N(4)	109.1(5)
N(1) – C(4) – N(2)	124.8(6)	O(8) – N(6) – O(7)	120.5(8)
N(1) – C(4) – C(5)	112.1(5)	O(8) – N(6) – C(5)	123.6(7)
N(2) – C(4) – C(5)	123.0(5)	O(7) – N(6) – C(5)	115.9(6)

Table S10. Selected torsion angles for **13** [^{o}]

C(4) – N(2) – N(3) – O(2)	-177.9(6)	C(1) – N(1) – C(4) – C(5)	-179.7(8)
C(3) – N(2) – N(3) – O(2)	-3.6(10)	N(1) – C(4) – C(5) – N(4)	2.4(10)
C(3) – N(2) – N(3) – O(1)	-175.3(8)	N(2) – C(4) – C(5) – N(4)	-175.3(7)
C(1) – N(1) – C(4) – N(2)	-2.1(12)	C(3) – N(2) – C(4) – N(1)	-5.2(10)

6. Single-crystal X-ray Diffraction Analysis of Compound **14**

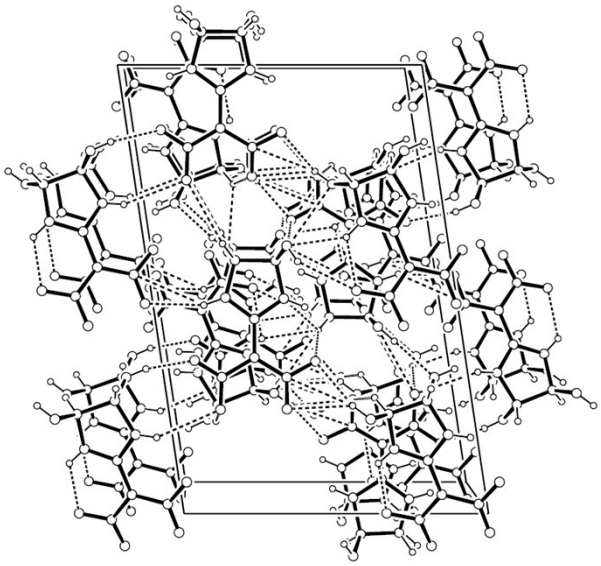
Table S11. Selected bond lengths [Å] and angles [^{o}] for compound **14**

O(1) – C(1)	1.403(4)	O(2) – H(2B)	0.9800
N(1) – C(3)	1.338(4)	N(3) – O(3)	1.151(4)
N(1) – C(1)	1.456(4)	N(3) – O(4)	1.219(3)
C(1) – C(2)	1.518(4)	N(3) – C(4)	1.410(4)
O(1) – H(1A)	0.8200	C(3) – C(4)	1.428(4)
N(2) – C(3)	1.319(4)	N(4) – O(6)	1.219(3)
N(2) – C(2)	1.457(4)	N(4) – O(5)	1.248(3)
O(2) – C(2)	1.400(4)	N(4) – C(4)	1.403(4)
C(1) – O(1) – H(1A)	109.5	C(2) – O(2) – H(2B)	109.5
C(3) – N(1) – C(1)	110.0(2)	O(4) – N(3) – C(4)	118.9(2)
O(1) – C(1) – N(1)	110.6(3)	N(2) – C(3) – N(1)	109.5(3)
O(1) – C(1) – C(2)	108.3(2)	N(2) – C(3) – C(4)	125.7(3)
N(1) – C(1) – C(2)	101.8(2)	N(1) – C(3) – C(4)	124.8(3)
C(3) – N(2) – C(2)	111.6(2)	O(6) – N(4) – O(5)	120.1(2)
O(2) – C(2) – N(2)	110.0(2)	O(6) – N(4) – C(4)	122.5(3)
O(2) – C(2) – C(1)	112.0(3)	O(5) – N(4) – C(4)	117.4(2)
N(2) – C(2) – C(1)	101.9(2)	N(4) – C(4) – N(3)	117.7(2)
O(3) – N(3) – O(4)	119.5(3)	N(4) – C(4) – C(3)	121.6(2)
O(3) – N(3) – C(4)	121.4(3)	N(3) – C(4) – C(3)	120.7(2)

Table S12. Selected torsion angles for **14** [^{o}]

C(2) – N(2) – C(3) – N(1)	6.1(4)	N(2) – C(3) – C(4) – N(4)	-0.2(5)
C(2) – N(2) – C(3) – C(4)	-174.8(3)	N(1) – C(3) – C(4) – N(4)	178.7(3)
O(4) – N(3) – C(4) – N(4)	-177.7(3)	N(2) – C(3) – C(4) – N(3)	-179.5(3)
O(4) – N(3) – C(4) – C(3)	1.6(5)	N(1) – C(3) – C(4) – N(3)	-0.6(5)

(a)



(b)

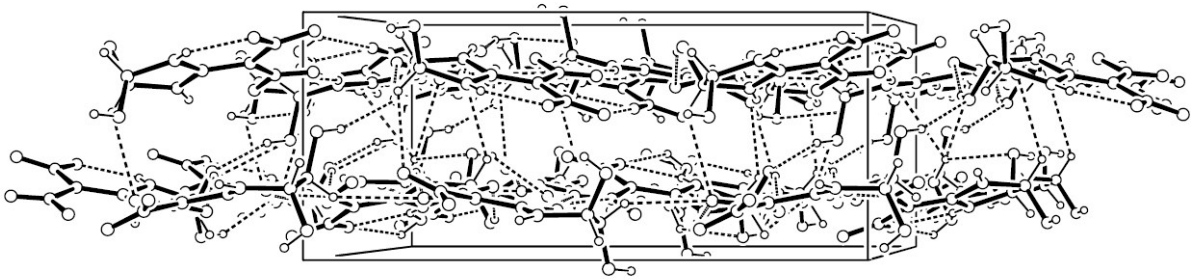


Fig. S3 (a) Ball-and-stick packing diagram of **14** viewed down the b axis; (b) Ball-and-stick packing diagram of **14** viewed down the a axis

7. Single-crystal X-ray Diffraction Analysis of Compound **15**

Table S13. Selected bond lengths [Å] and angles [^{o}] for compound **15**

O(1) – C(2)	1.383(3)	N(2) – H(2A)	0.8600
O(1) – C(1)	1.434(3)	C(2) – C(3)	1.527(4)
N(1) – C(5)	1.317(3)	N(3) – O(3)	1.223(3)
N(1) – C(2)	1.475(3)	N(3) – O(4)	1.243(3)
N(1) – H(1A)	0.8600	N(3) – C(6)	1.423(3)
C(1) – C(4)	1.499(4)	N(4) – O(5)	1.226(3)
O(2) – C(3)	1.424(4)	N(4) – O(6)	1.246(3)
O(2) – C(4)	1.432(3)	N(4) – C(6)	1.405(3)
N(2) – C(5)	1.350(3)	C(5) – C(6)	1.425(4)
N(2) – C(3)	1.433(3)		

C(2) – O(1) – C(1)	113.9(2)	O(4) – N(3) – C(6)	117.7(2)
C(5) – N(1) – C(2)	110.1(2)	O(2) – C(3) – N(2)	107.4(2)
C(5) – N(1) – H(1A)	124.9	O(2) – C(3) – C(2)	112.5(2)
C(2) – N(1) – H(1A)	124.9	N(2) – C(3) – C(2)	100.5(2)
O(1) – C(1) – C(4)	110.2(2)	O(5) – N(4) – O(6)	121.3(2)
C(3) – O(2) – C(4)	112.3(2)	O(5) – N(4) – C(6)	121.3(2)
C(5) – N(2) – C(3)	110.0(2)	O(6) – N(4) – C(6)	117.3(2)
C(5) – N(2) – H(2A)	125.0	O(2) – C(4) – C(1)	109.1(2)
C(3) – N(2) – H(2A)	125.0	N(1) – C(5) – N(2)	109.2(2)
O(1) – C(2) – N(1)	114.8(2)	N(1) – C(5) – C(6)	126.7(2)
O(1) – C(2) – C(3)	116.0(2)	N(2) – C(5) – C(6)	124.2(2)
N(1) – C(2) – C(3)	99.9(2)	N(4) – C(6) – N(3)	117.6(2)
O(3) – N(3) – O(4)	122.5(2)	N(4) – C(6) – C(5)	121.7(2)
O(3) – N(3) – C(6)	119.8(2)	N(3) – C(6) – C(5)	120.6(2)

Table S14. Selected torsion angles for **15** [^{o}]

N(1) – C(5) – C(6) – N(4)	-8.5(4)	C(2) – N(1) – C(5) – C(6)	172.3(2)
N(2) – C(5) – C(6) – N(4)	171.7(3)	C(2) – N(1) – C(5) – N(2)	-7.9(3)
N(1) – C(5) – C(6) – N(3)	174.8(2)	O(6) – N(4) – C(6) – N(3)	-175.1(2)
N(2) – C(5) – C(6) – N(3)	-5.0(4)	O(6)v N(4) – C(6) – C(5)	8.1(4)

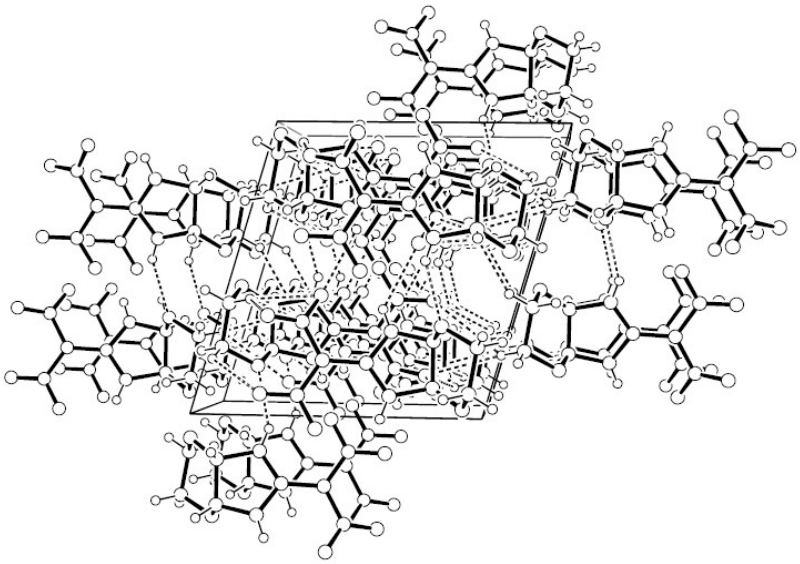


Fig. S4 Ball-and-stick packing diagram of **15** viewed down the b axis

8. Single-crystal X-ray Diffraction Analysis of Compound **17**

Table S15. Selected bond lengths [Å] and angles [^{o}] for compound **17**

C(1) – N(3)	1.503(6)	O(9) – C(3)	1.414(6)
C(1) – C(2)	1.506(6)	O(9) – C(4)	1.417(6)
C(1) – N(2)	1.559(6)	O(10) – C(6)	1.348(6)
C(1) – N(1)	1.559(7)	O(10) – C(5)	1.413(6)
O(1) – N(1)	1.138(6)	N(4) – N(5)	1.377(6)
O(2) – N(1)	1.225(6)	N(5) – C(2)	1.367(6)
O(3) – N(2)	1.178(5)	N(5) – C(6)	1.508(6)
O(4) – N(2)	1.180(5)	N(6) – C(2)	1.264(6)
O(5) – N(3)	1.251(5)	N(6) – C(3)	1.501(6)
O(6) – N(3)	1.193(5)	C(3) – C(6)	1.538(8)
O(7) – N(4)	1.230(5)	C(4) – C(5)	1.512(8)
O(8) – N(4)	1.232(5)		
N(3) – C(1) – C(2)	112.2(4)	O(7) – N(4) – N(5)	117.4(5)
N(3) – C(1) – N(2)	113.5(4)	O(8) – N(4) – N(5)	116.0(5)
C(2) – C(1) – N(2)	110.3(4)	C(2) – N(5) – N(4)	127.7(4)
N(3) – C(1) – N(1)	105.0(4)	C(2) – N(5) – C(6)	110.0(4)
C(2) – C(1) – N(1)	110.1(4)	N(4) – N(5) – C(6)	121.3(4)
N(2) – C(1) – N(1)	105.3(4)	C(2) – N(6) – C(3)	105.9(4)
C(3) – O(9) – C(4)	116.1(5)	N(6) – C(2) – N(5)	115.7(4)
C(6) – O(10) – C(5)	112.1(4)	N(6) – C(2) – C(1)	118.8(5)
O(1) – N(1) – O(2)	131.7(7)	N(5) – C(2) – C(1)	125.5(4)
O(1) – N(1) – C(1)	116.5(6)	O(9) – C(3) – N(6)	110.6(4)
O(2) – N(1) – C(1)	111.8(6)	O(9) – C(3) – C(6)	112.7(4)
O(3) – N(2) – O(4)	128.7(5)	N(6) – C(3) – C(6)	108.0(4)
O(3) – N(2) – C(1)	117.2(5)	O(10) – C(5) – C(4)	109.7(5)
O(4) – N(2) – C(1)	113.7(4)	O(10) – C(6) – N(5)	113.5(4)
O(6) – N(3) – O(5)	126.1(5)	O(10) – C(6) – C(3)	116.3(5)
O(6) – N(3) – C(1)	118.3(4)	N(5) – C(6) – C(3)	96.9(4)
O(5) – N(3) – C(1)	115.5(5)	O(7) – N(4) – O(8)	126.6(6)

Table S16. Selected torsion angles for **17** [°]

C(2) – C(1) – N(3) – O(6)	-6.6(6)	N(4) – N(5) – C(2) – C(1)	-0.1(8)
C(2) – C(1) – N(3) – O(5)	174.6(4)	N(1) – C(1) – C(2) – N(6)	-2.6(6)
O(7) – N(4) – N(5) – C(2)	178.6(5)	N(1) – C(1) – C(2) – N(5)	178.6(5)
O(8) – N(4) – N(5) – C(2)	-4.4(7)	N(4) – N(5) – C(6) – C(3)	-173.5(4)
O(8) – N(4) – N(5) – C(6)	-172.4(5)	C(3) – N(6) – C(2) – C(1)	178.3(4)
C(3) – N(6) – C(2) – N(5)	-2.8(6)	N(4) – N(5) – C(2) – N(6)	-179.0(4)

9. Single-crystal X-ray Diffraction Analysis of Compound **19**

Table S17. Selected bond lengths [Å] and angles [°] for compound **19**

O(1) – C(4)	1.374(4)	N(3) – O(5)	1.218(4)
O(1) – C(1)	1.417(4)	N(4) – O(8)	1.195(4)
N(1) – N(3)	1.370(4)	N(4) – O(7)	1.198(4)
N(1) – C(3)	1.396(4)	N(4) – C(8)	1.515(4)
N(1) – C(2)	1.447(4)	C(4) – C(5)	1.469(6)
C(1) – N(2)	1.467(4)	O(4) – C(6)	1.177(5)
C(1) – C(2)	1.535(5)	N(5) – O(10)	1.191(4)
N(2) – C(3)	1.254(4)	N(5) – O(9)	1.199(4)
C(2) – O(3)	1.411(4)	N(5) – C(8)	1.541(5)
O(2) – C(4)	1.186(5)	N(6) – O(11)	1.202(4)
O(3) – C(6)	1.363(4)	N(6) – O(12)	1.208(4)
C(3) – C(8)	1.506(4)	N(6) – C(8)	1.528(4)
N(3) – O(6)	1.206(4)	C(6) – C(7)	1.475(6)
C(4) – O(1) – C(1)	116.1(3)	O(2) – C(4) – O(1)	121.3(4)
N(3) – N(1) – C(3)	127.5(3)	O(2) – C(4) – C(5)	128.6(4)
N(3) – N(1) – C(2)	123.1(3)	O(1) – C(4) – C(5)	110.1(4)
C(3) – N(1) – C(2)	109.0(3)	O(10) – N(5) – O(9)	128.3(4)
O(1) – C(1) – N(2)	106.9(3)	O(10) – N(5) – C(8)	116.8(3)
O(1) – C(1) – C(2)	108.3(3)	O(9) – N(5) – C(8)	114.9(3)
N(2) – C(1) – C(2)	107.0(3)	O(11) – N(6) – O(12)	128.0(3)
C(3) – N(2) – C(1)	107.2(3)	O(11) – N(6) – C(8)	119.0(3)
O(3) – C(2) – N(1)	108.5(3)	O(12) – N(6) – C(8)	113.0(3)
O(3) – C(2) – C(1)	109.8(3)	O(4) – C(6) – O(3)	121.7(4)

N(1) – C(2) – C(1)	100.2(2)	O(4) – C(6) – C(7)	128.0(4)
C(6) – O(3) – C(2)	118.1(3)	O(3) – C(6) – C(7)	110.3(3)
N(2) – C(3) – N(1)	115.1(3)	C(3) – C(8) – N(4)	114.4(3)
N(2) – C(3) – C(8)	120.0(3)	C(3) – C(8) – N(6)	111.5(3)
N(1) – C(3) – C(8)	124.9(3)	N(4) – C(8) – N(6)	111.9(3)
O(6) – N(3) – O(5)	127.8(3)	C(3) – C(8) – N(5)	107.3(2)
O(6) – N(3) – N(1)	115.6(3)	N(4) – C(8) – N(5)	105.2(3)
O(5) – N(3) – N(1)	116.6(3)	N(6) – C(8) – N(5)	105.8(3)
O(8) – N(4) – O(7)	127.3(4)	O(7) – N(4) – C(8)	115.7(3)
O(8) – N(4) – C(8)	116.9(3)		

Table S18. Selected torsion angles for **19** [^{o}]

C(3) – N(1) – C(2) – C(1)	-9.3(3)	C(2) – N(1) – N(3) – O(5)	-173.9(3)
C(1) – N(2) – C(3) – N(1)	4.3(4)	C(1) – O(1) – C(4) – O(2)	6.2(5)
C(1) – N(2) – C(3) – C(8)	-175.1(3)	C(1) – O(1) – C(4) – C(5)	-174.0(3)
C(2) – N(1) – C(3) – N(2)	3.8(4)	C(2) – O(3) – C(6) – O(4)	0.3(6)
C(2) – N(1) – C(3) – C(8)	-176.8(3)	C(2) – O(3) – C(6) – C(7)	-179.2(3)
C(3) – N(1) – N(3) – O(6)	178.2(3)	N(2) – C(3) – C(8) – N(5)	-2.3(4)
C(2) – N(1) – N(3) – O(6)	6.2(5)	N(1) – C(3) – C(8) – N(5)	178.4(3)
C(3) – N(1) – N(3) – O(5)	-1.9(5)	O(7) – N(4) – C(8) – C(3)	-5.1(5)

10. ^{1}H NMR and ^{13}C NMR spectra of compounds **7-9**, **11-17**, and **19**.

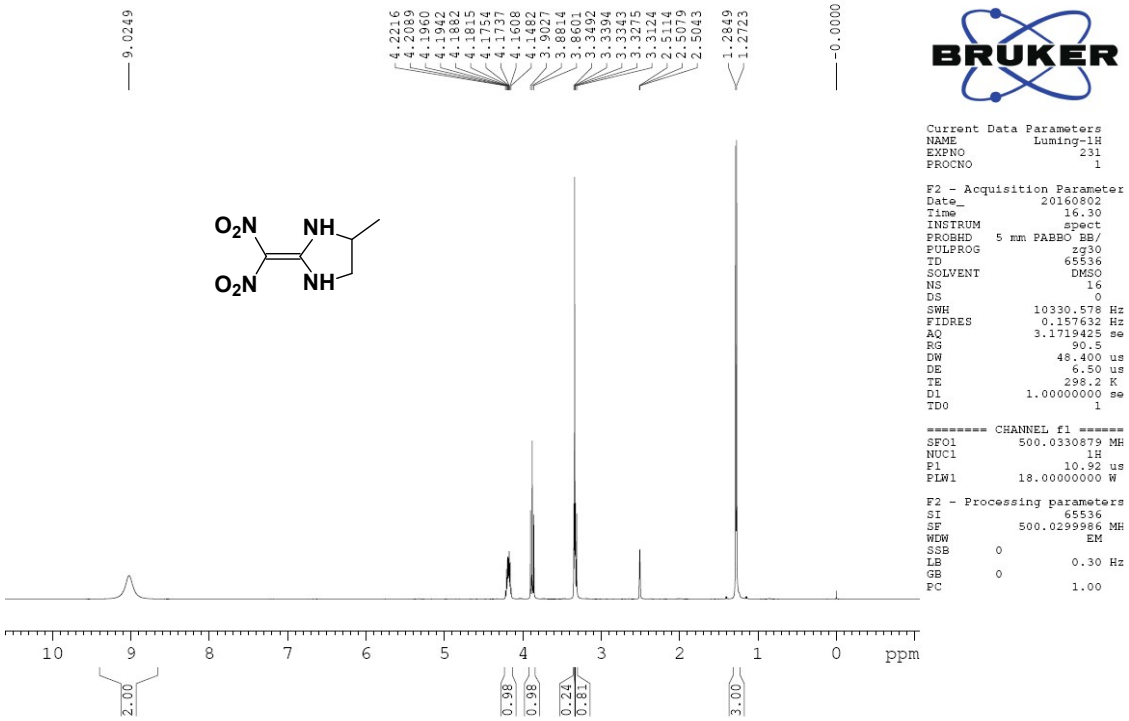


Fig. S5 ^{1}H-NMR spectrum of **7** in d_6-DMSO

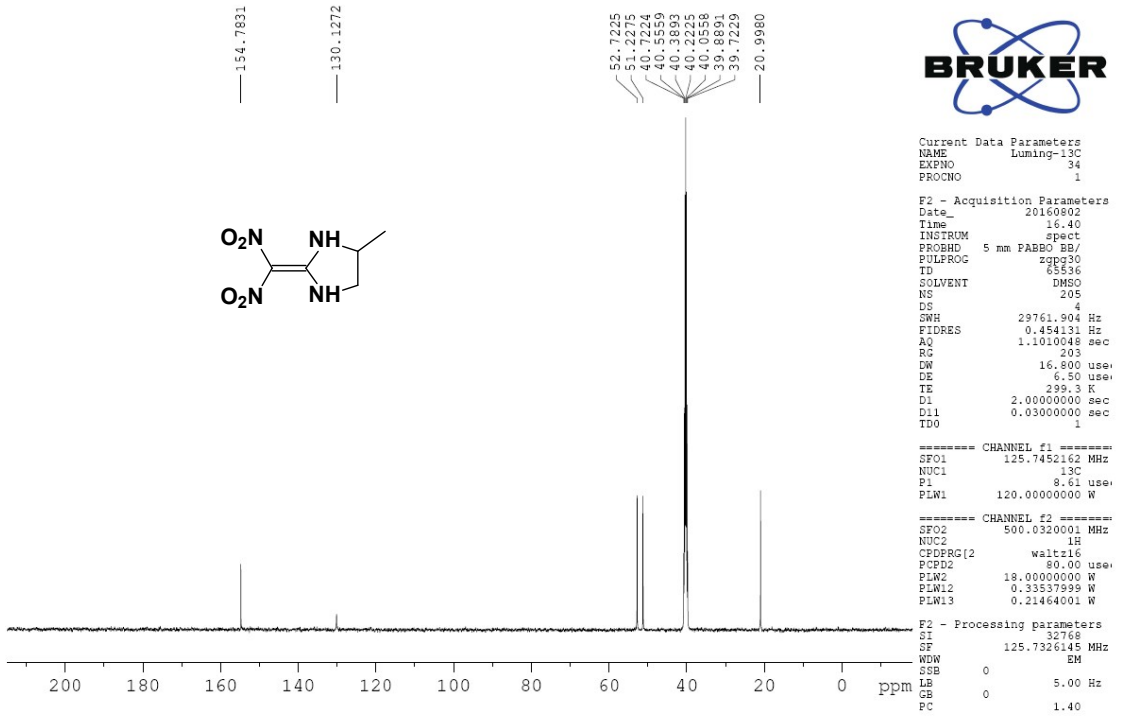


Fig. S6 ^{13}C-NMR spectrum of **7** in d_6-DMSO

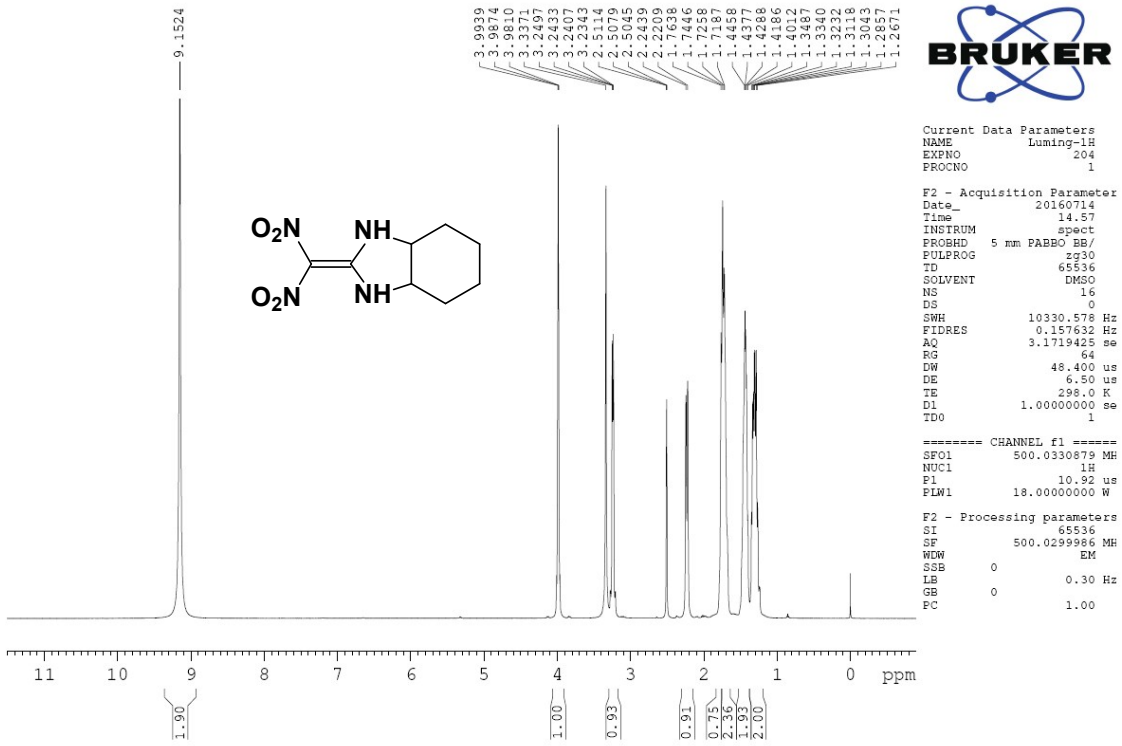


Fig. S7 ^{1}H-NMR spectrum of **8** in d_6-DMSO

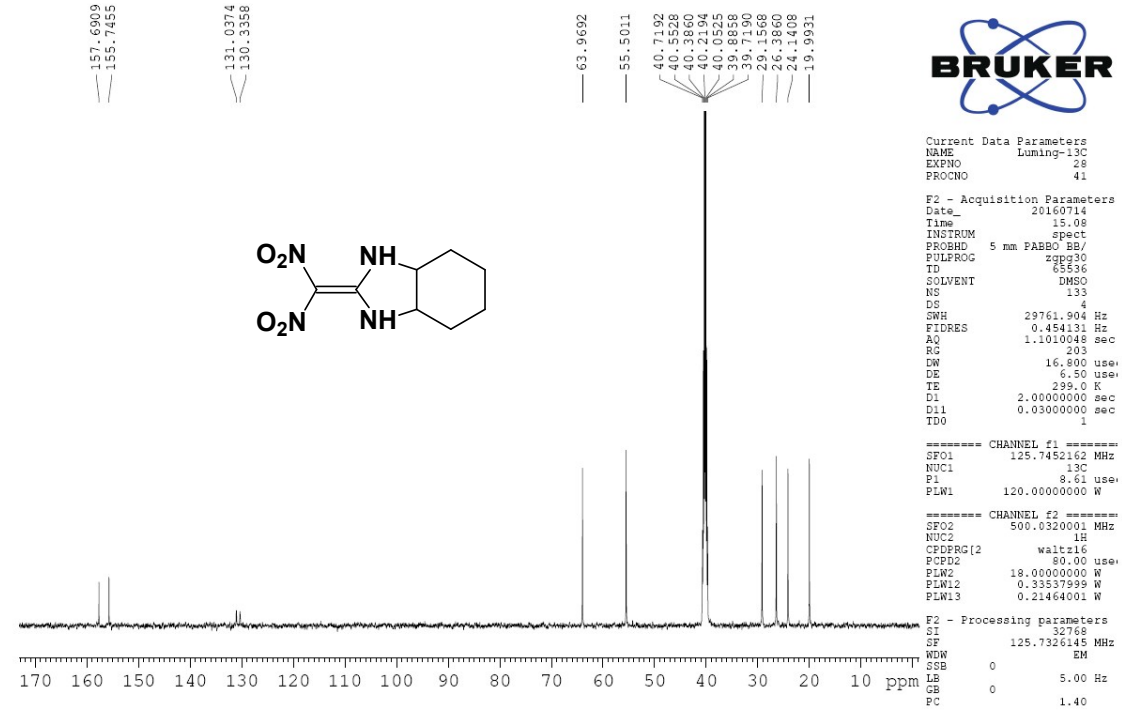


Fig. S8 ^{13}C-NMR spectrum of **8** in d_6-DMSO

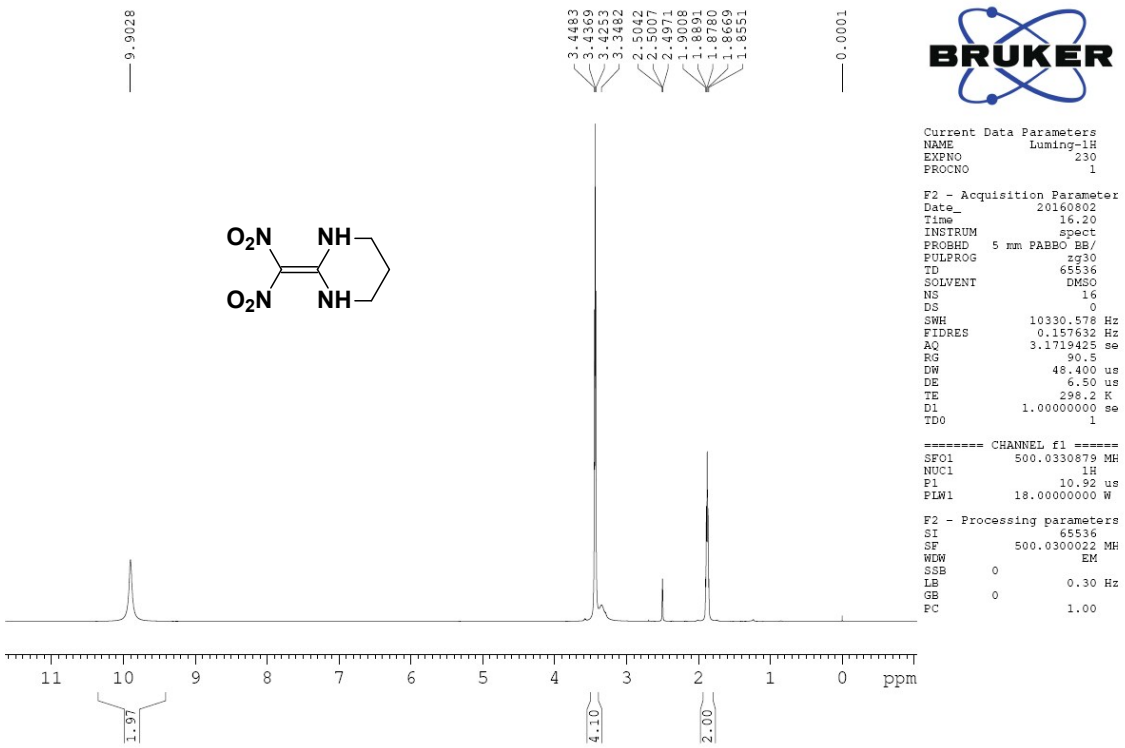


Fig. S9 ^{1}H-NMR spectrum of **9** in d_6-DMSO

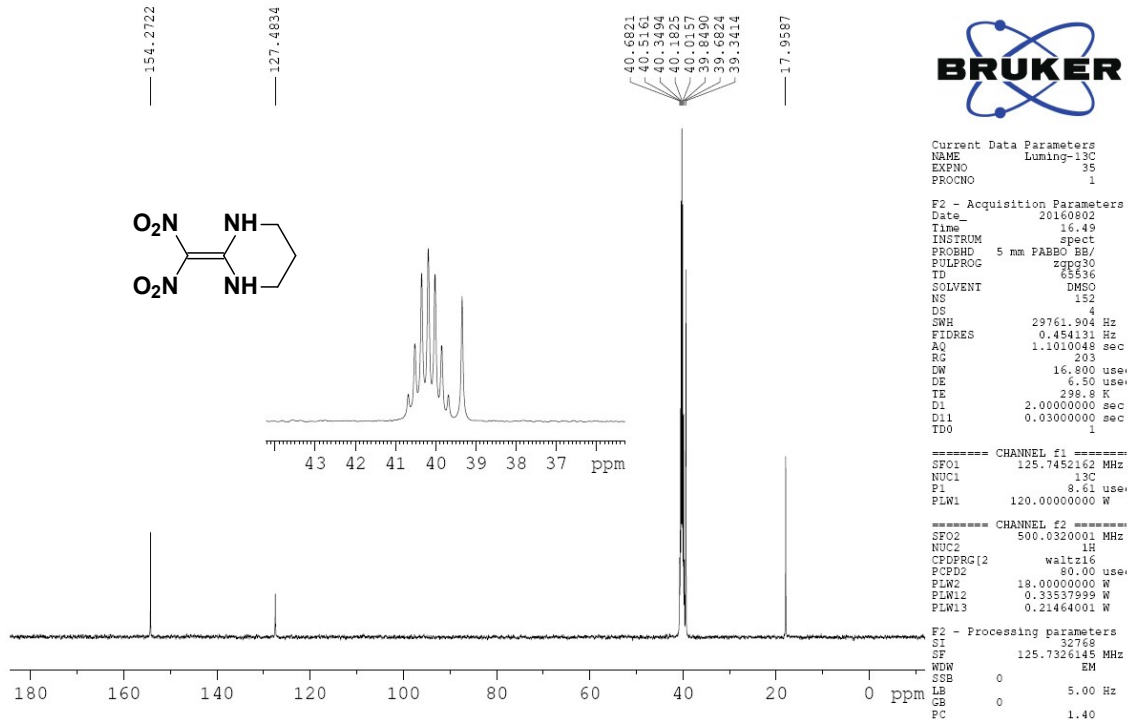


Fig. S10 ^{13}C-NMR spectrum of **9** in d_6-DMSO

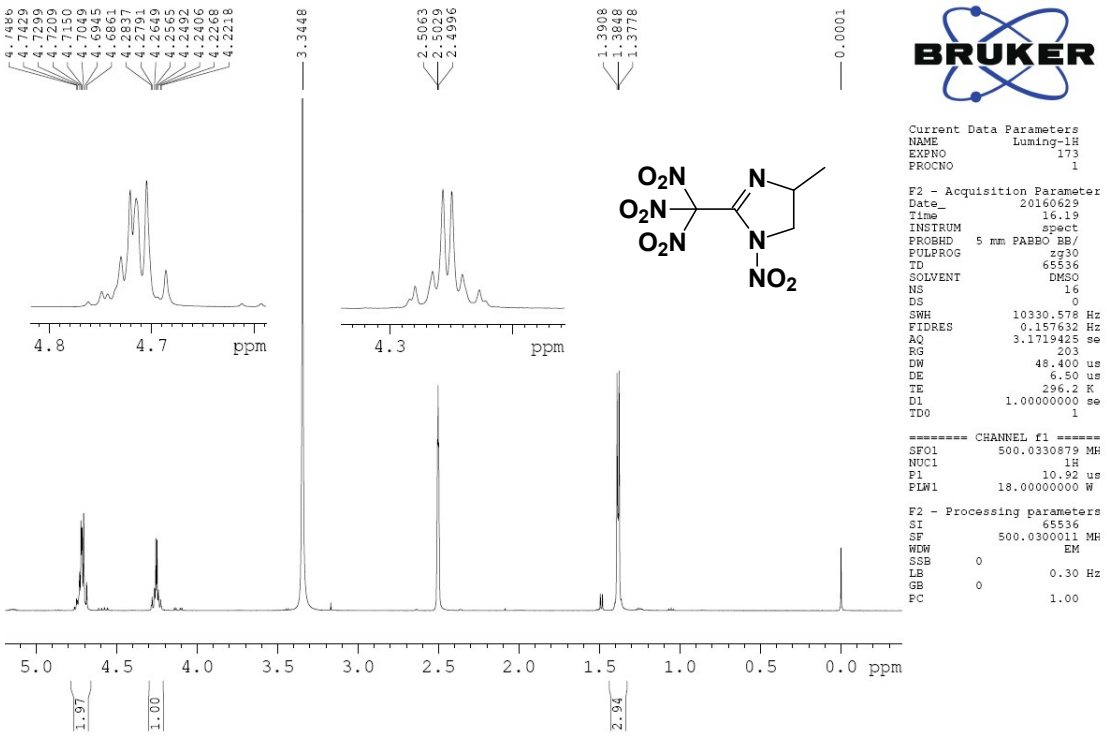


Fig. S11 ^{1}H-NMR spectrum of **11** in d_6-DMSO

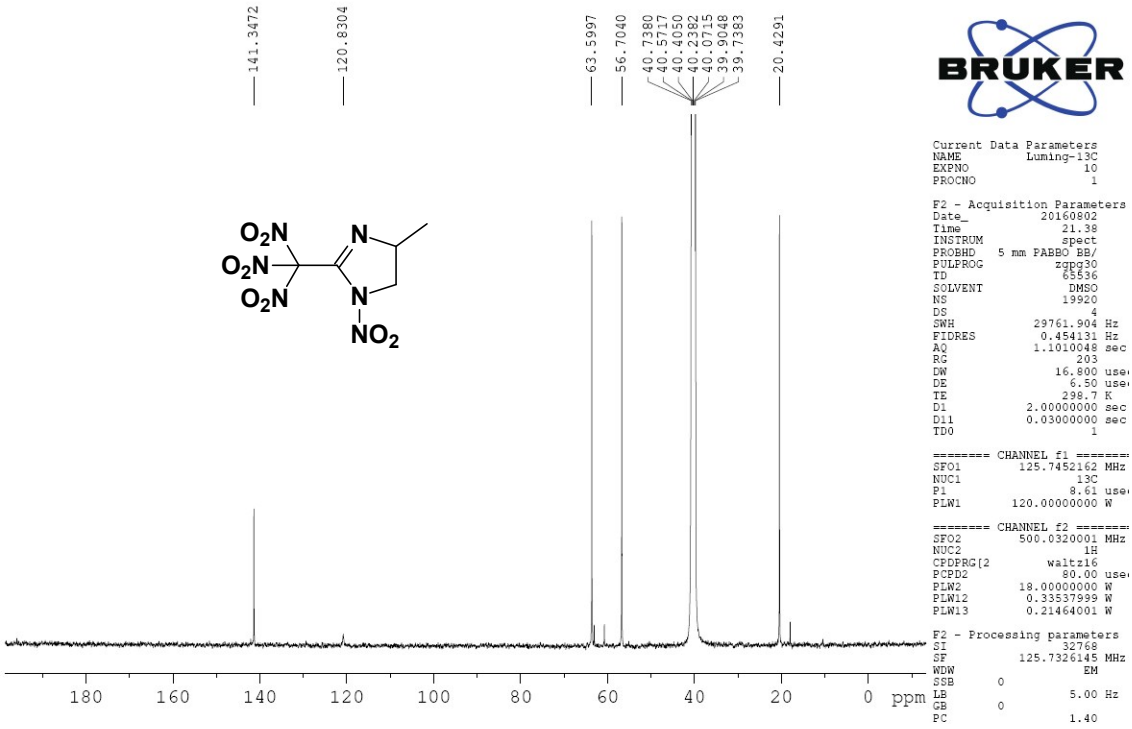


Fig. S12 ^{13}C-NMR spectrum of **11** in d_6-DMSO

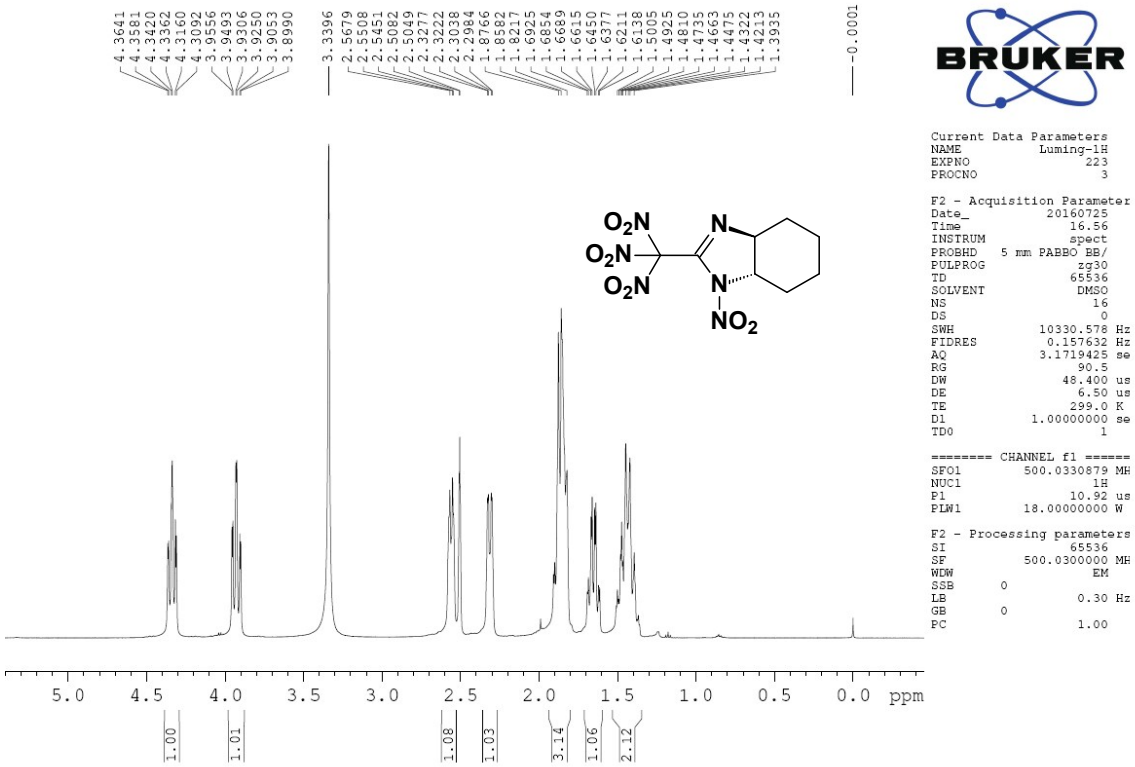


Fig. S13 ^{1}H-NMR spectrum of **12a** (trans-form) in d_6-DMSO

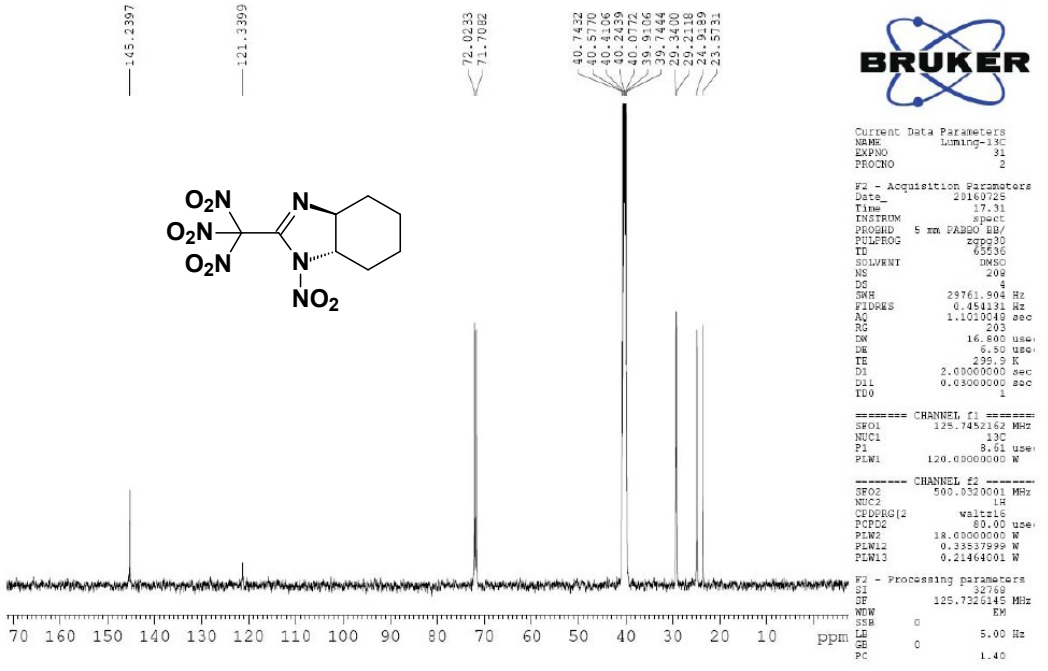


Fig. S14 ^{13}C-NMR spectrum of **12a** (trans-form) in d_6-DMSO

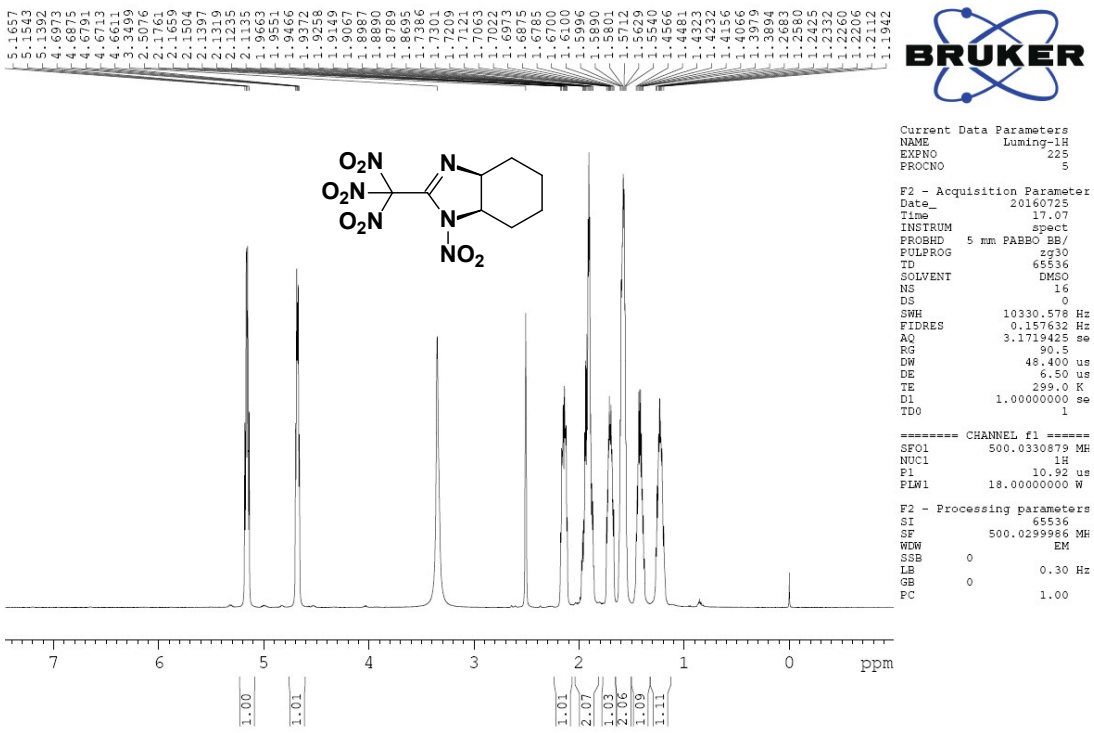


Fig. S15 ^{1}H-NMR spectrum of **12b** (cis-form) in d_6-DMSO

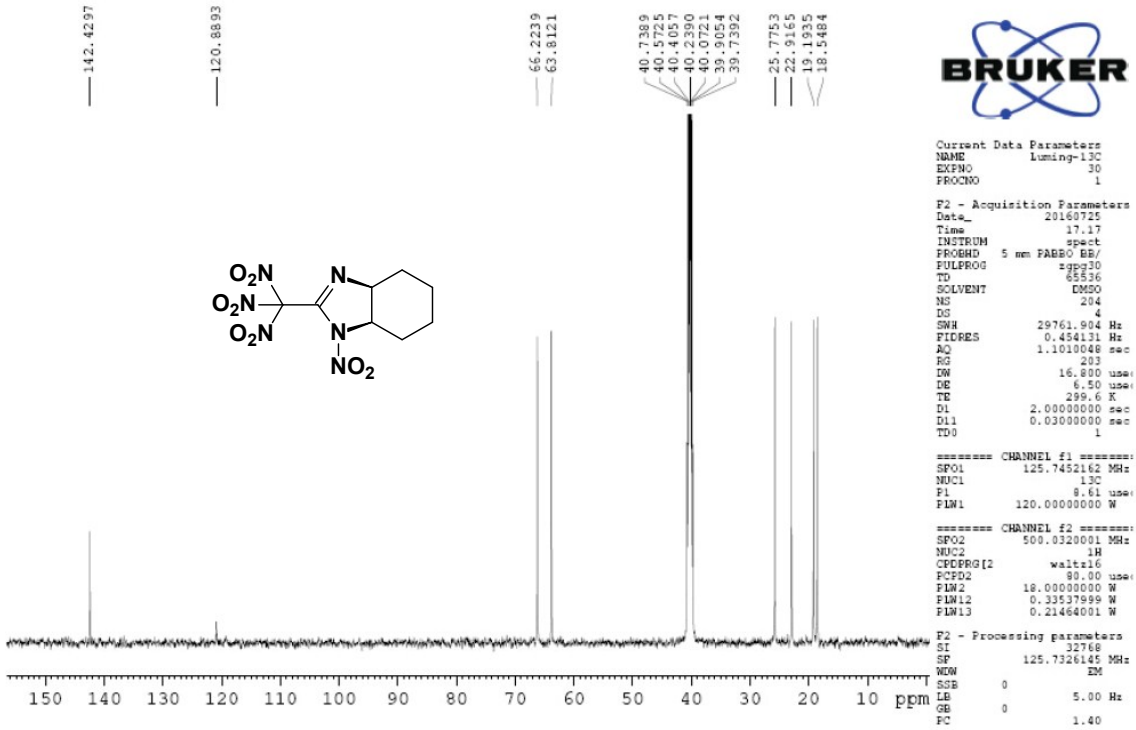


Fig. S16 ^{13}C-NMR spectrum of **12b** (cis-form) in d_6-DMSO

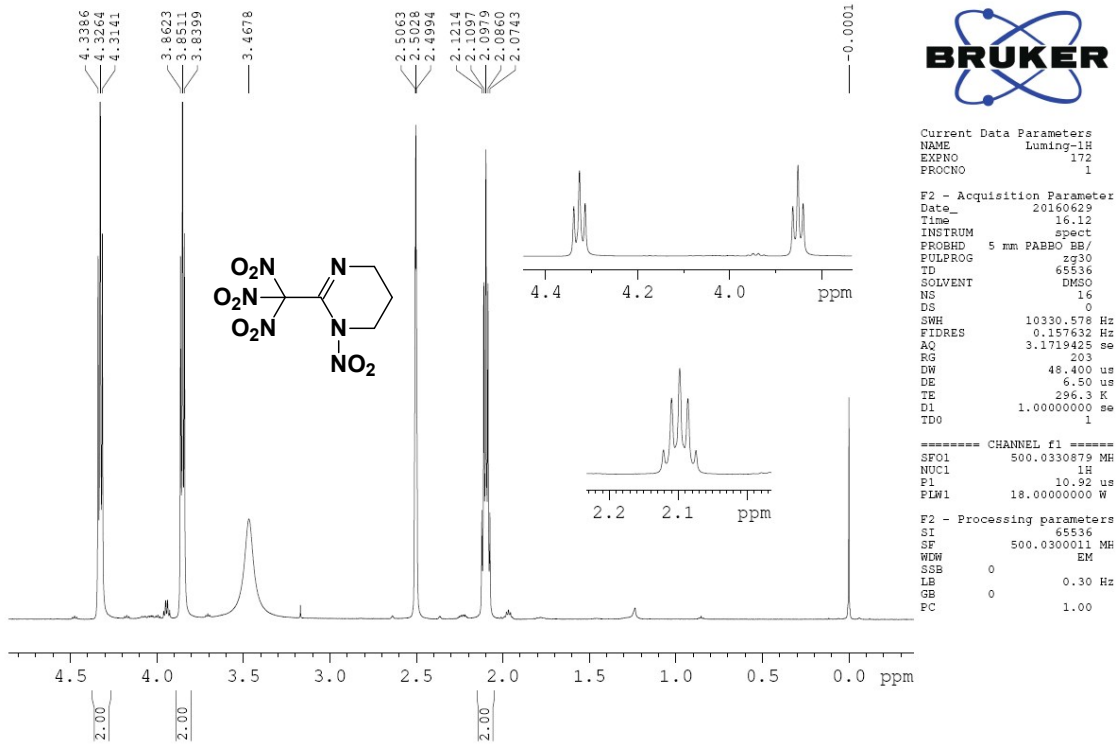


Fig. S17 ^{1}H-NMR spectrum of **13** in d_6-DMSO

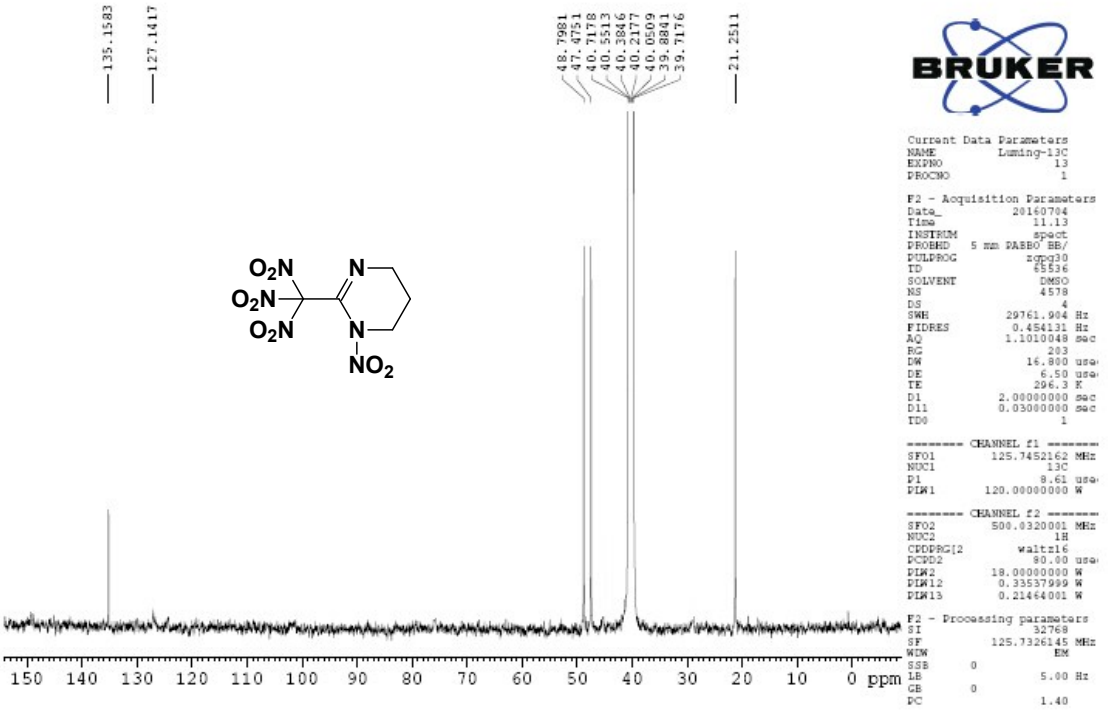


Fig. S18 ^{13}C-NMR spectrum of **13** in d_6-DMSO

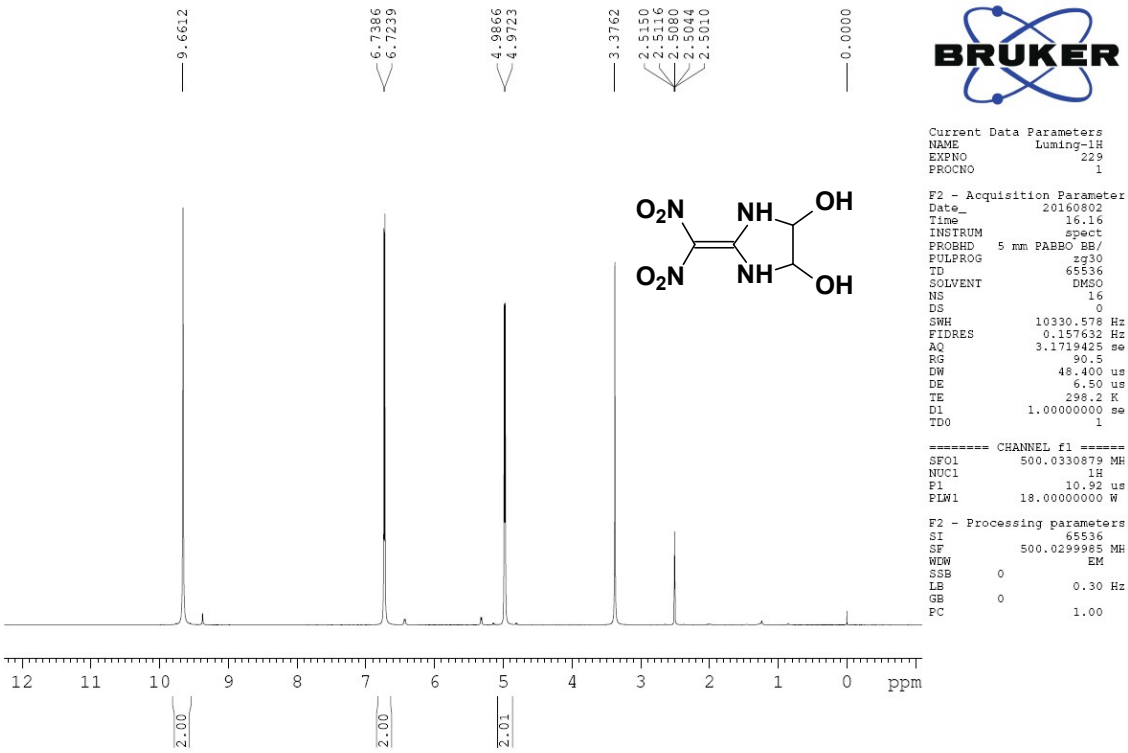


Fig. S19 ^{1}H-NMR spectrum of **14** in d_6-DMSO

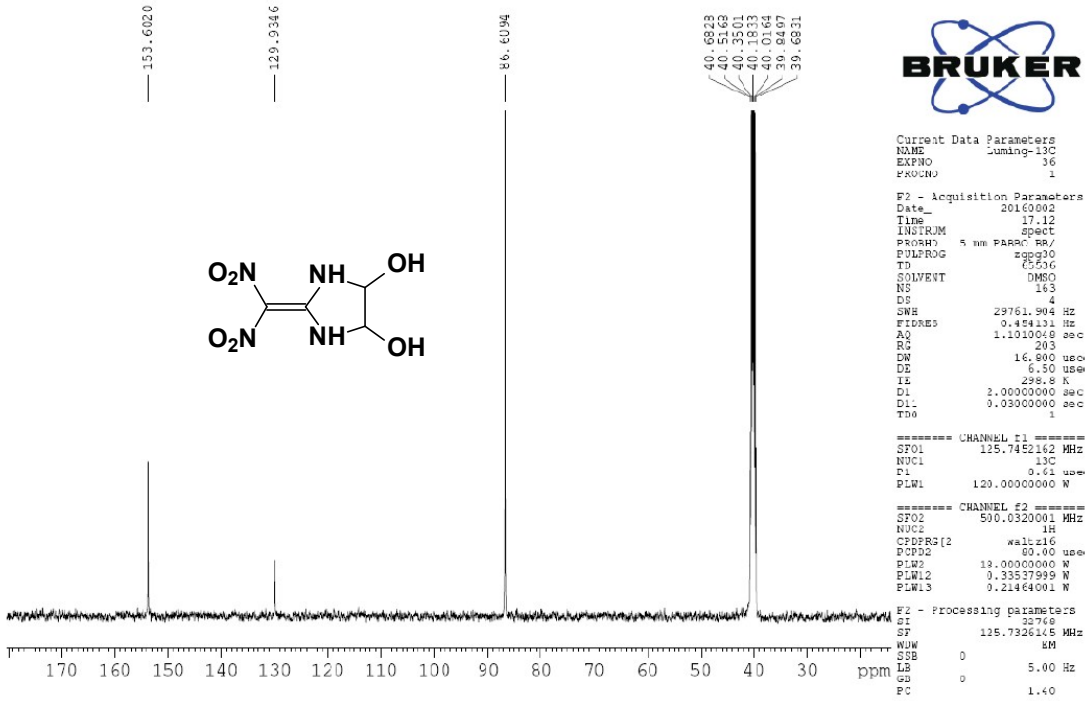


Fig. S20 ^{13}C-NMR spectrum of **14** in d_6-DMSO

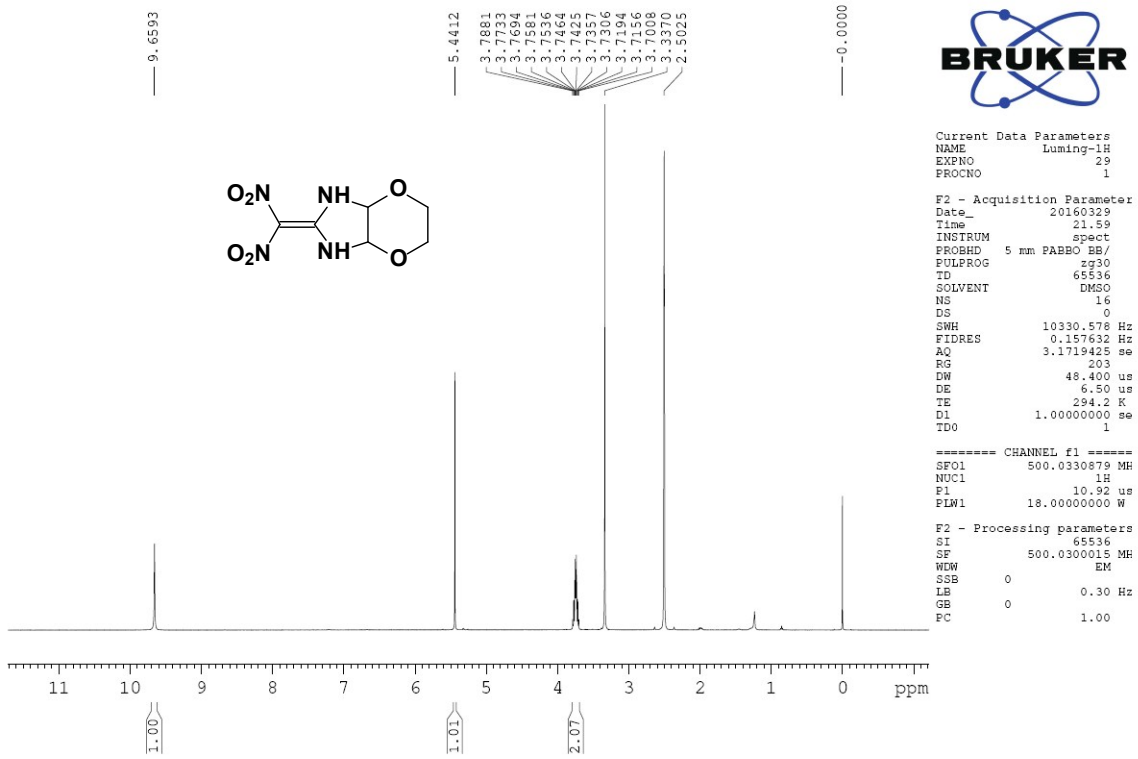


Fig. S21 ^{1}H-NMR spectrum of **15** in d_6-DMSO

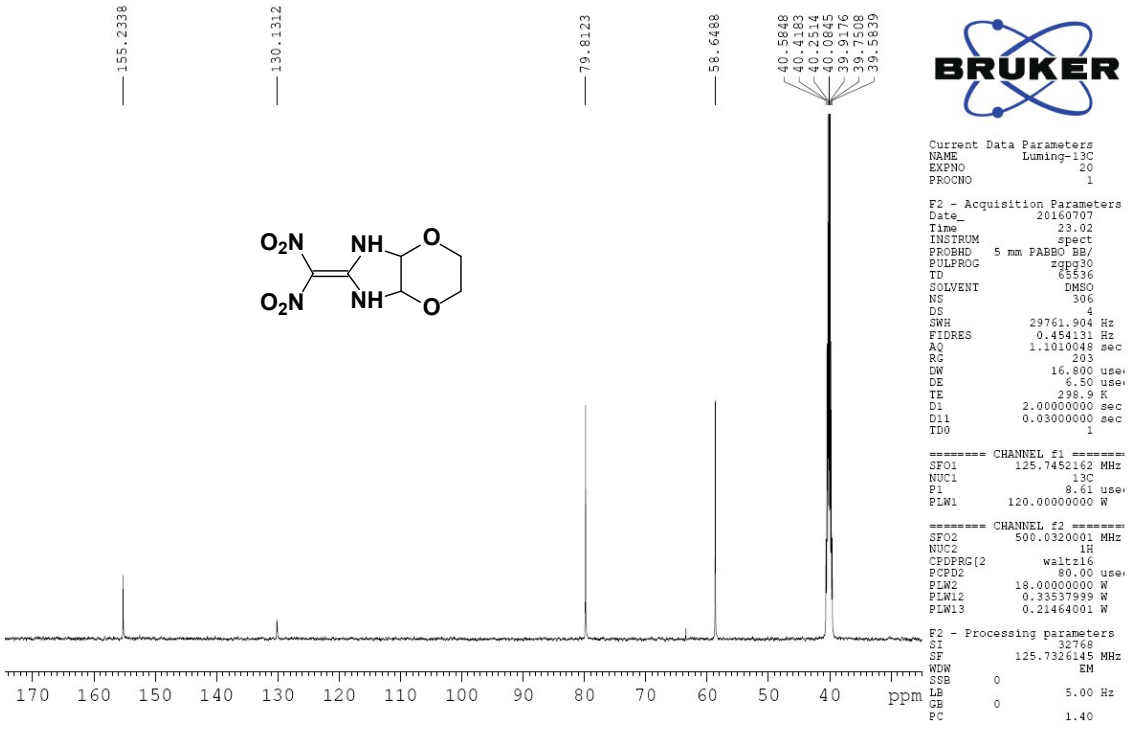


Fig. S22 ^{13}C-NMR spectrum of **15** in d_6-DMSO

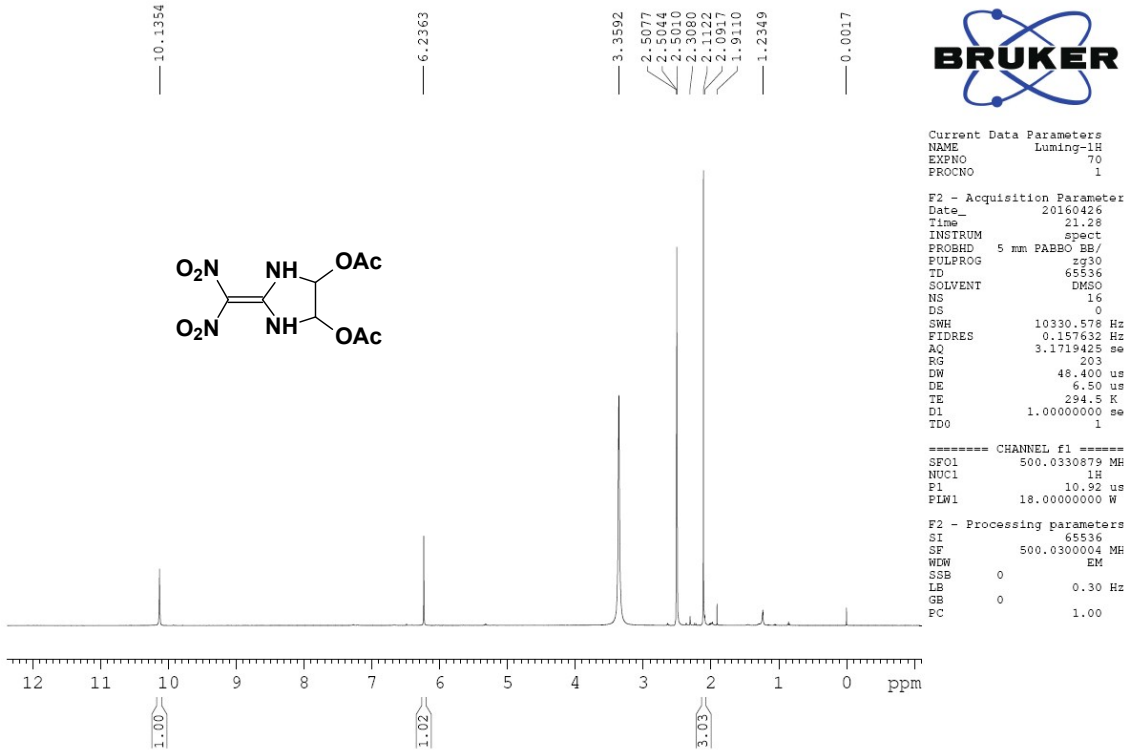


Fig. S23 ^{1}H-NMR spectrum of **16** in d_6-DMSO

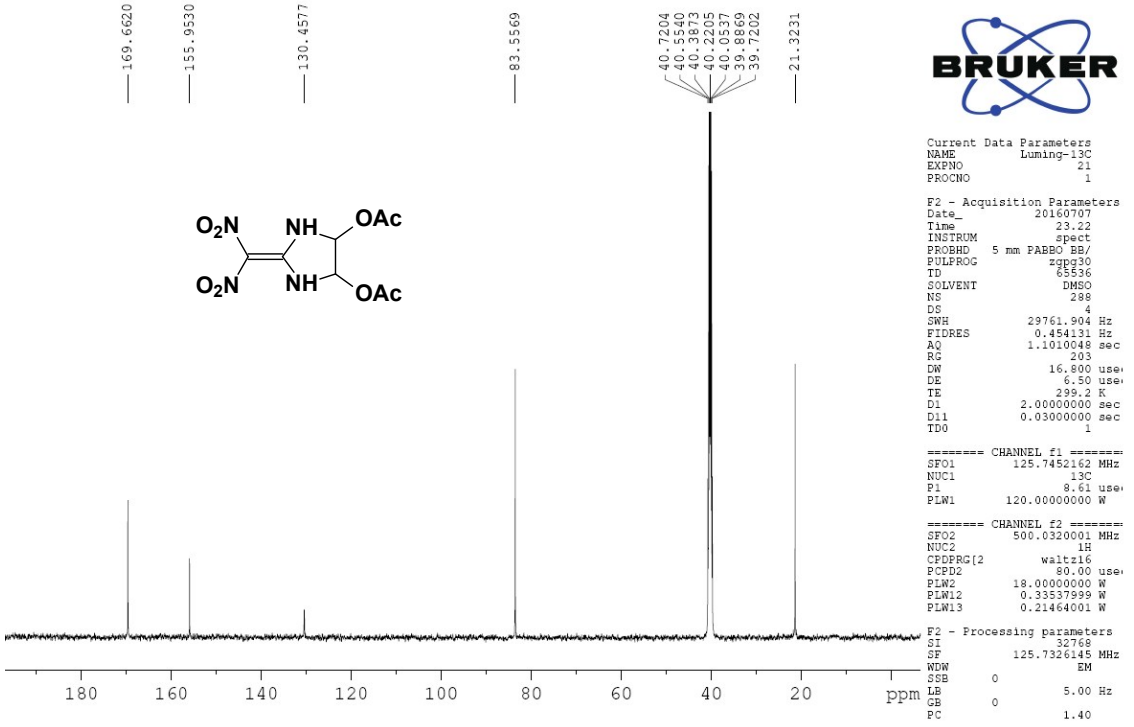


Fig. S24 ^{13}C-NMR spectrum of **16** in d_6-DMSO

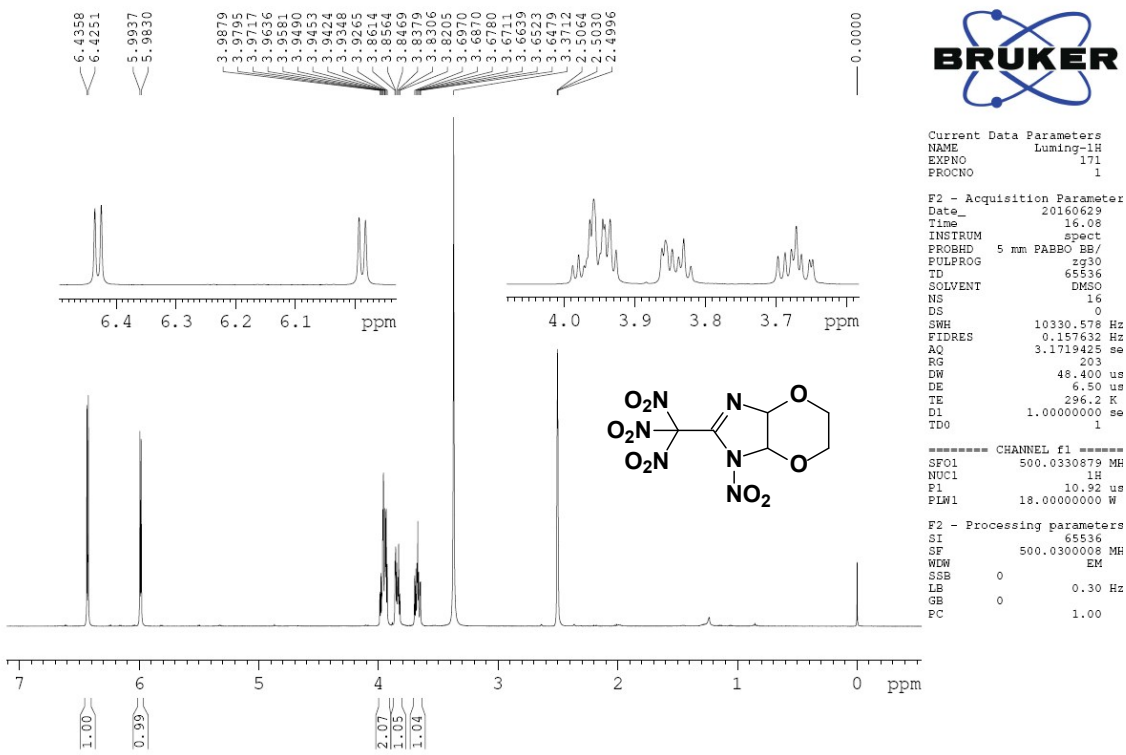


Fig. S25 ^{1}H-NMR spectrum of **17** in d_6-DMSO

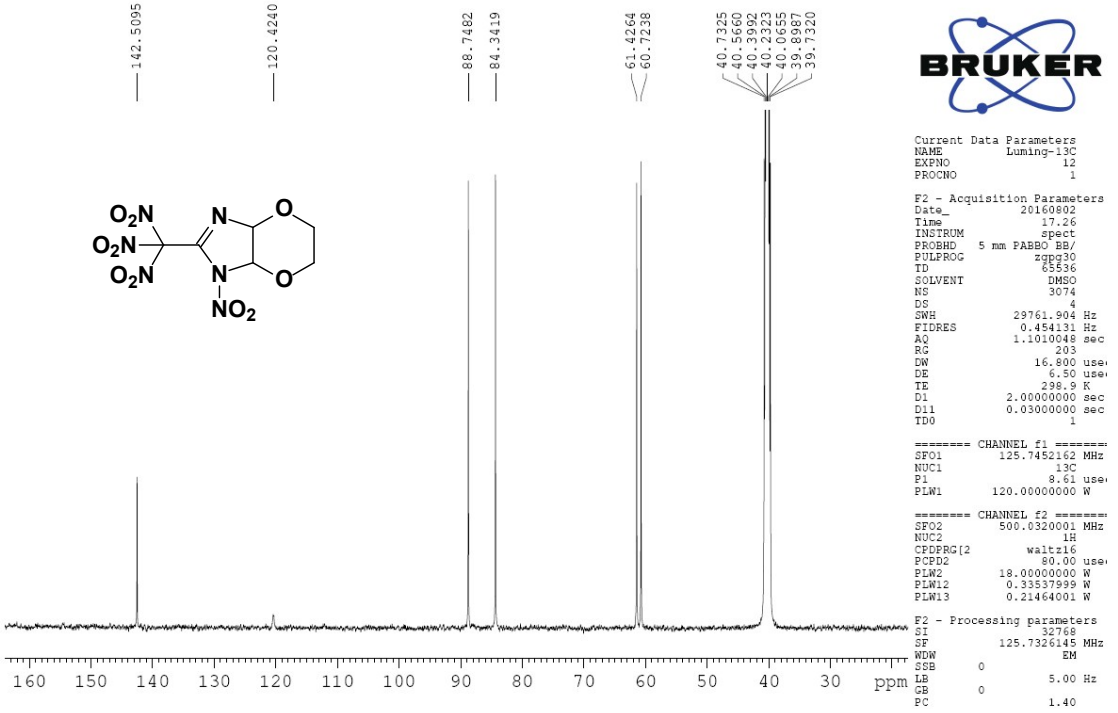


Fig. S26 ^{13}C-NMR spectrum of **17** in d_6-DMSO

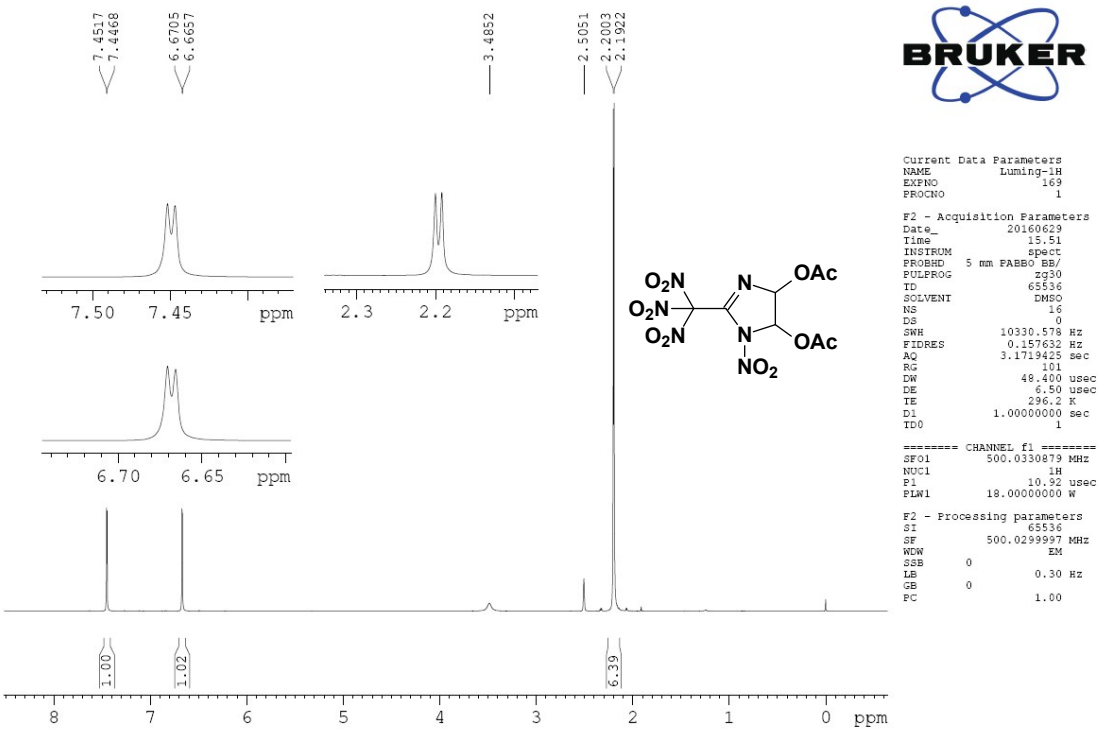


Fig. S27 ^{1}H-NMR spectrum of **19** in d_6-DMSO

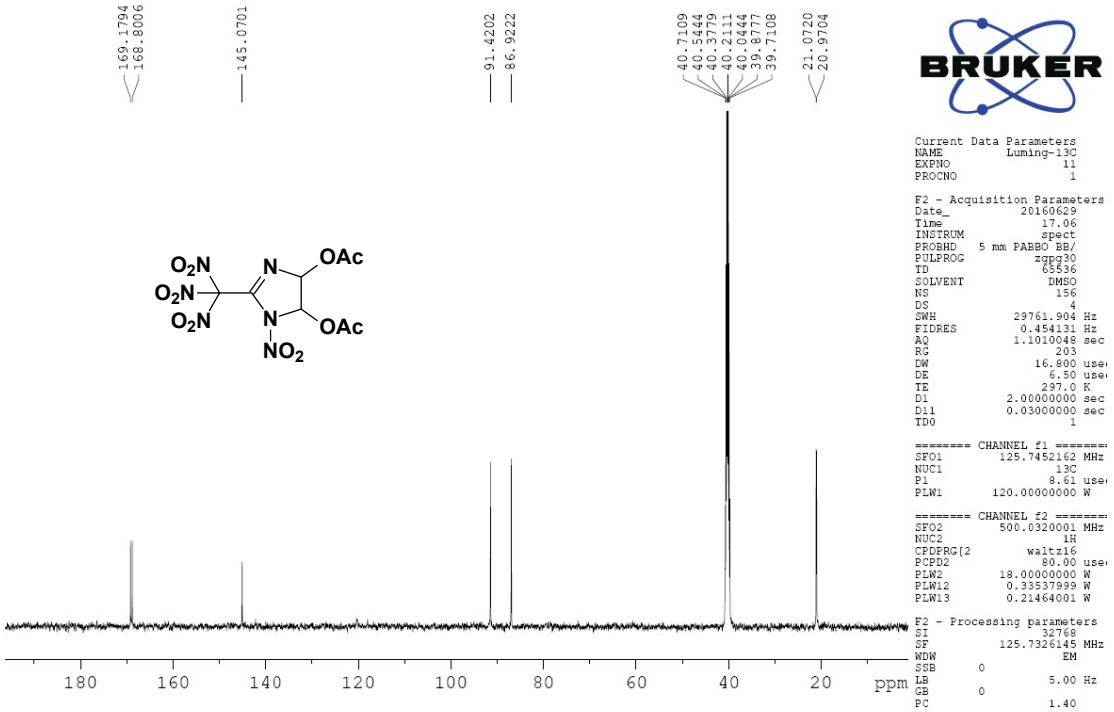


Fig. S28 ^{13}C-NMR spectrum of **19** in d_6-DMSO

11. DSC plots of **7-9**, and **14-16**

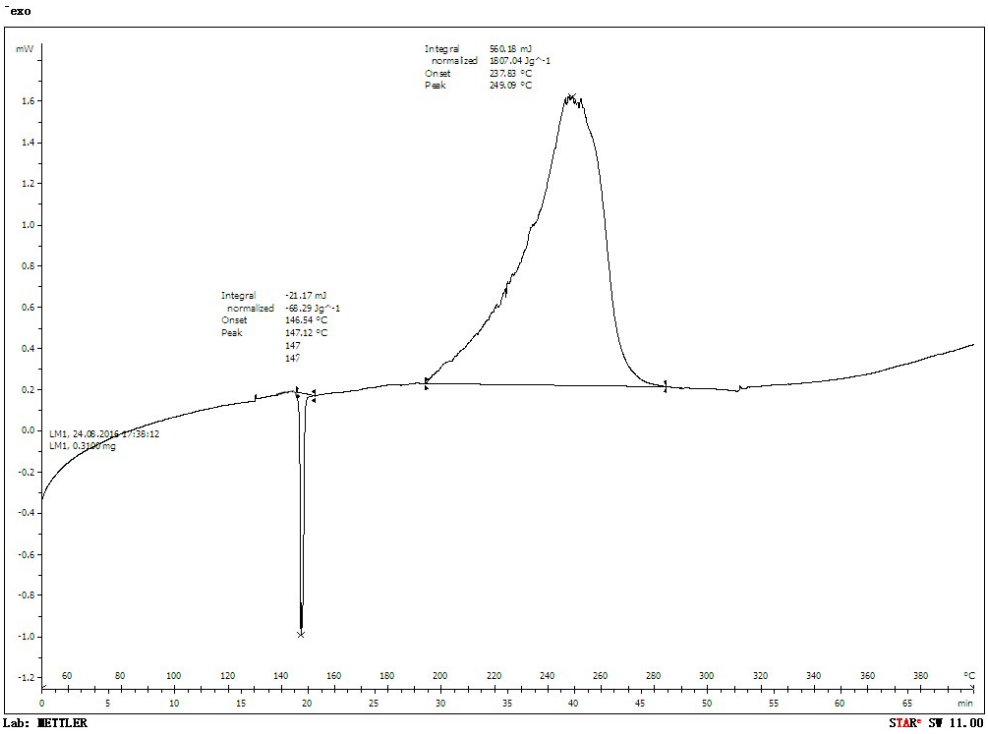


Fig. S29 The DSC plot (5 ^{o}C min^{-1}) of **7**

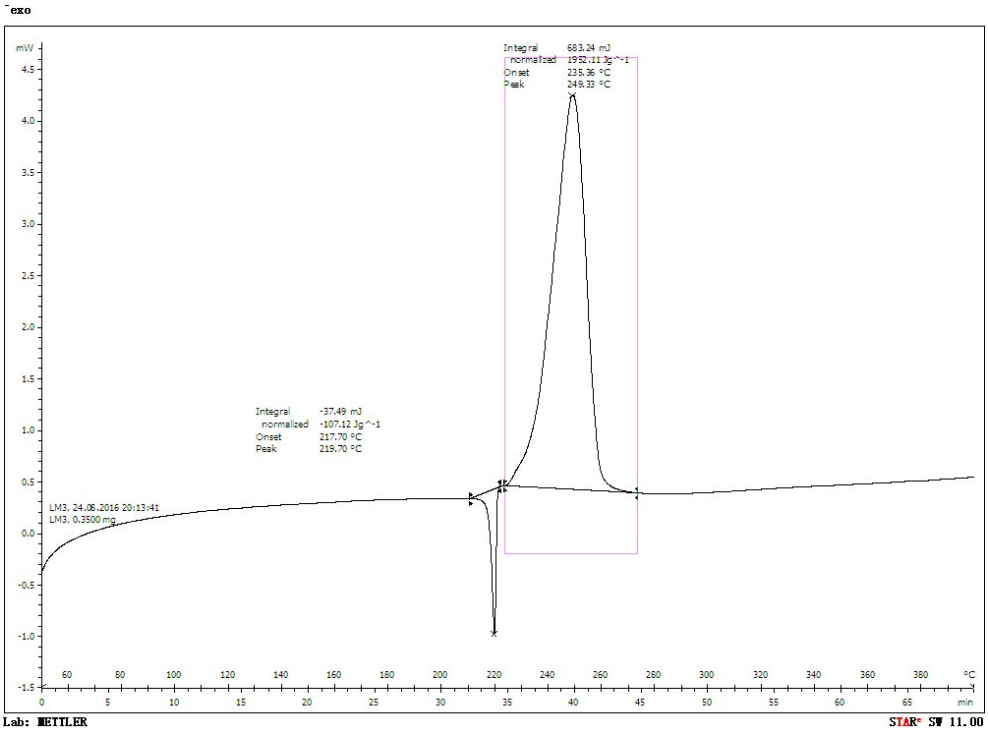


Fig. S30 The DSC plot (5 ^{o}C min^{-1}) of **8**

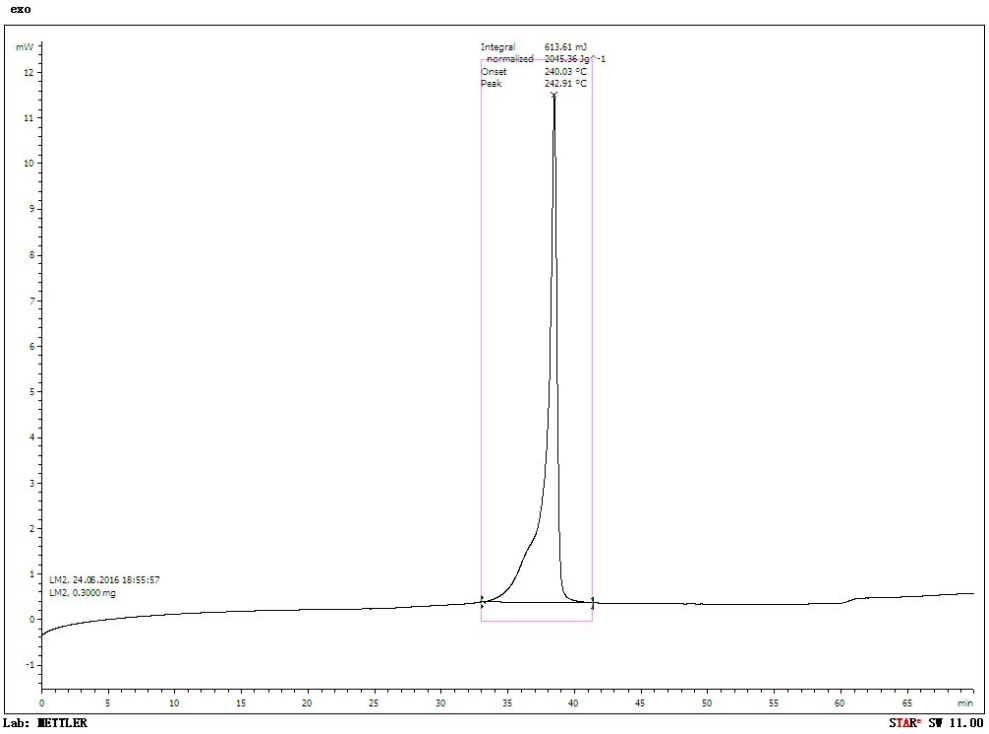


Fig. S31 The DSC plot (5 ^{o}C min^{-1}) of **9**

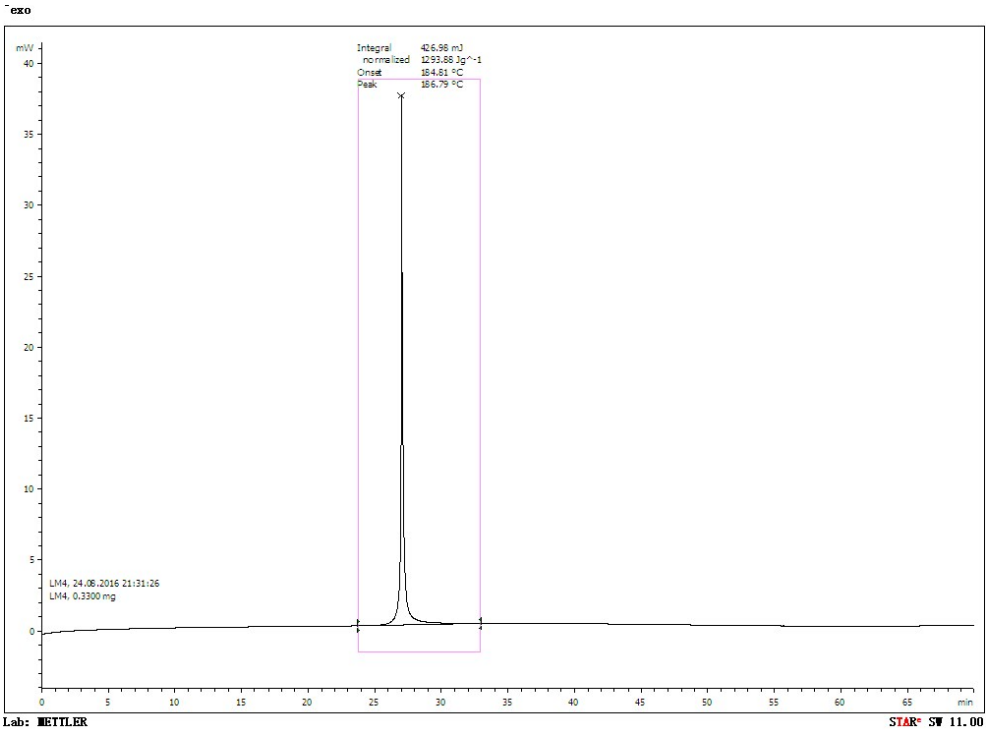


Fig. S32 The DSC plot (5 ^{o}C min^{-1}) of **14**

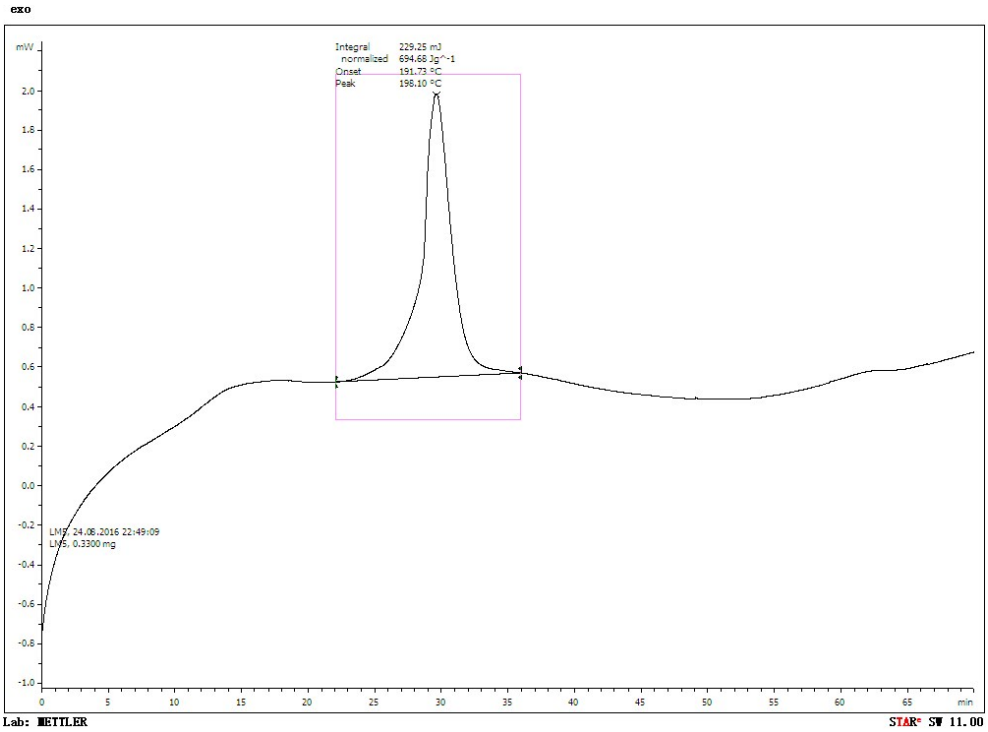


Fig. S33 The DSC plot (5 ^{o}C min^{-1}) of **15**

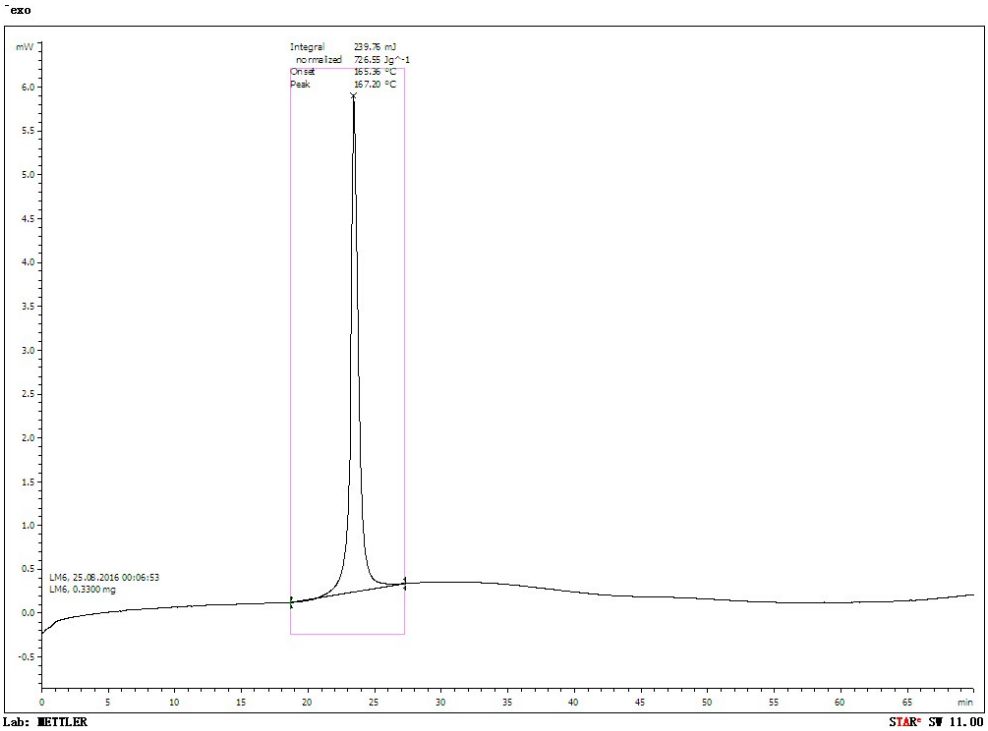


Fig. S34 The DSC plot (5 ^{o}C min^{-1}) of **16**

12. TGA plots of **11**-**13**, **17**, and **19**

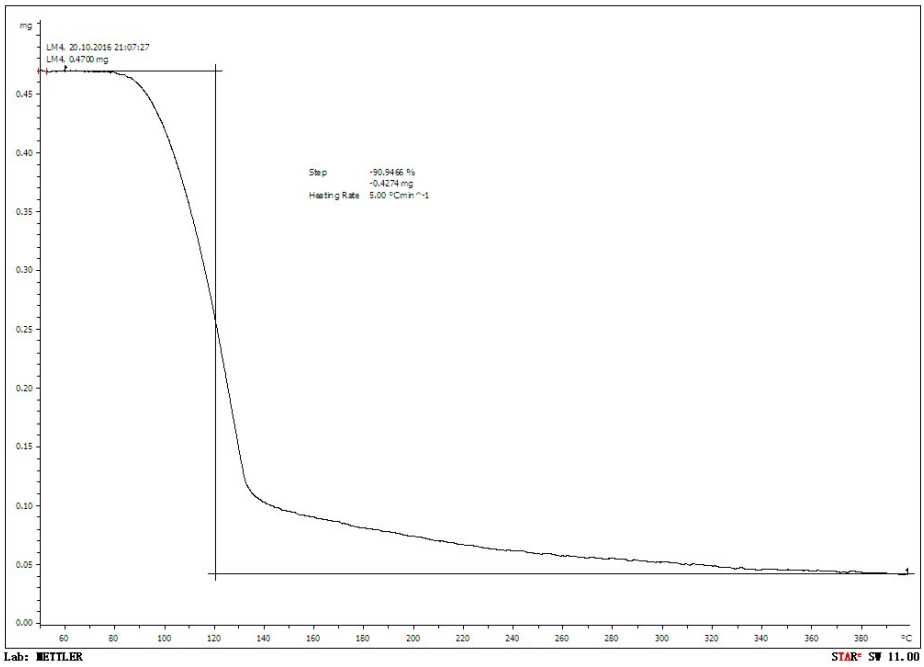


Fig. S35 The TGA plot (5 ^{o}C min^{-1}) of **11**

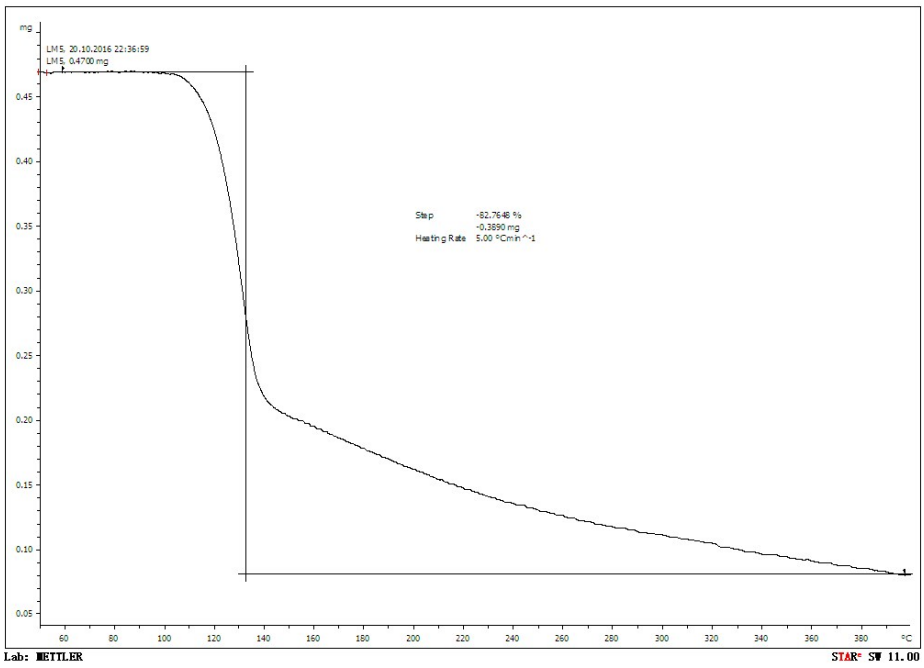


Fig. S36 The TGA plot (5 ^{o}C min^{-1}) of **12a**

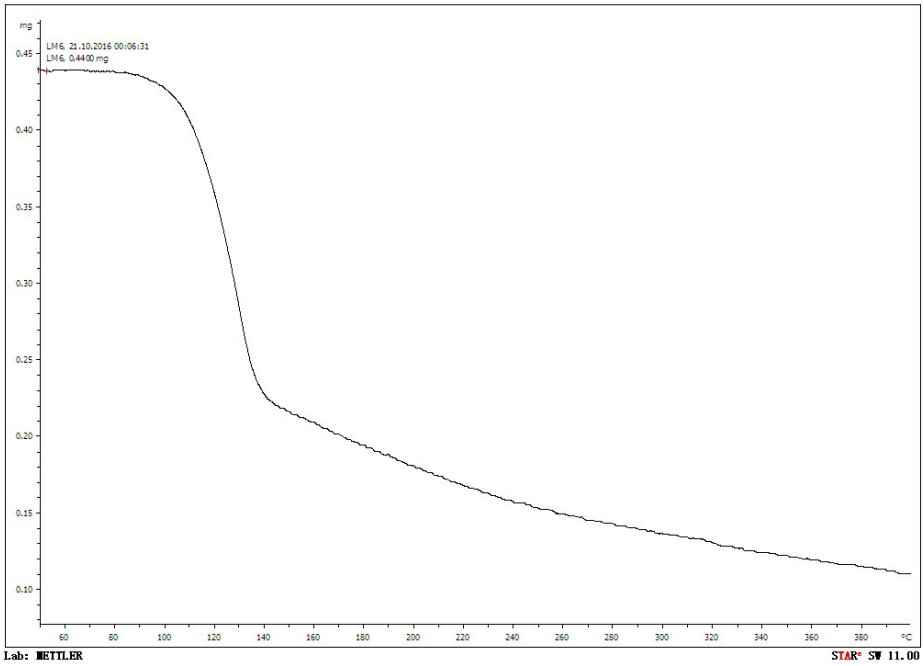


Fig. S37 The TGA plot (5 ^{o}C min^{-1}) of **12b**

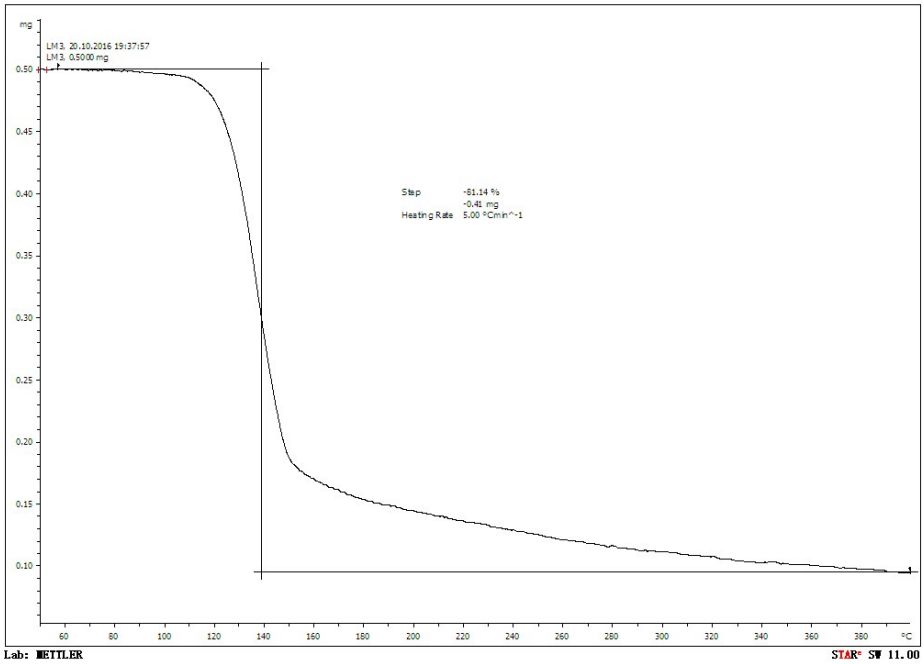


Fig. S38 The TGA plot (5 ^{o}C min^{-1}) of **13**

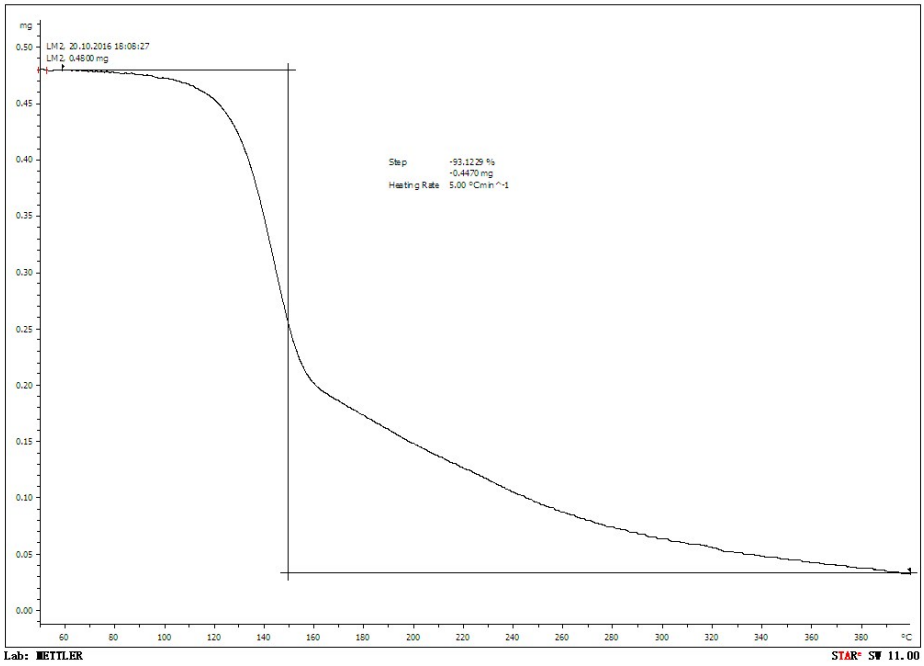


Fig. S39 The TGA plot (5 ^{o}C min^{-1}) of **17**

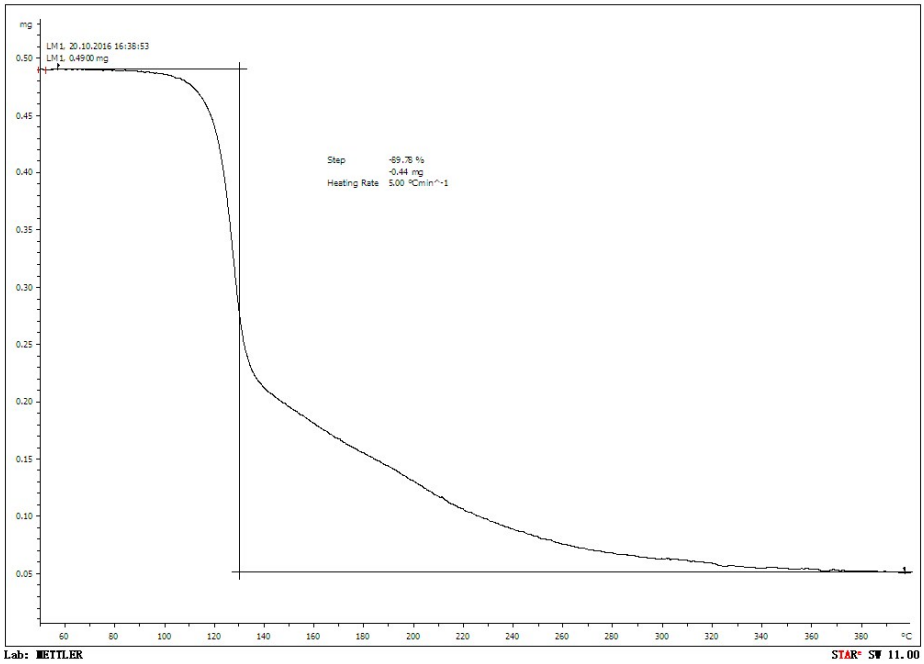


Fig. S40 The TGA plot (5 ^{o}C min^{-1}) of **19**

13. IR spectra of **7-9**, **11-17**, and **19**

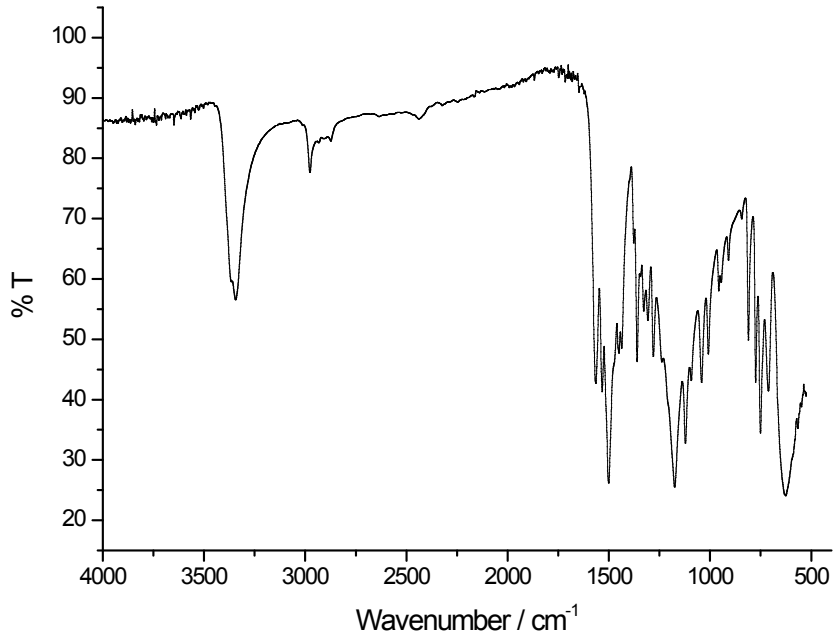


Fig. S41 The IR spectrum of **7**

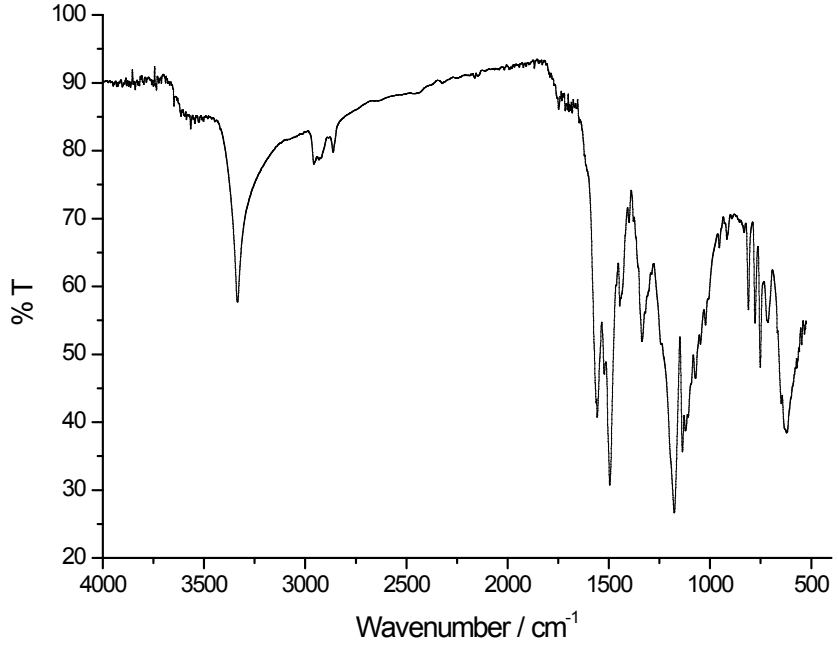


Fig. S42 The IR spectrum of **8**

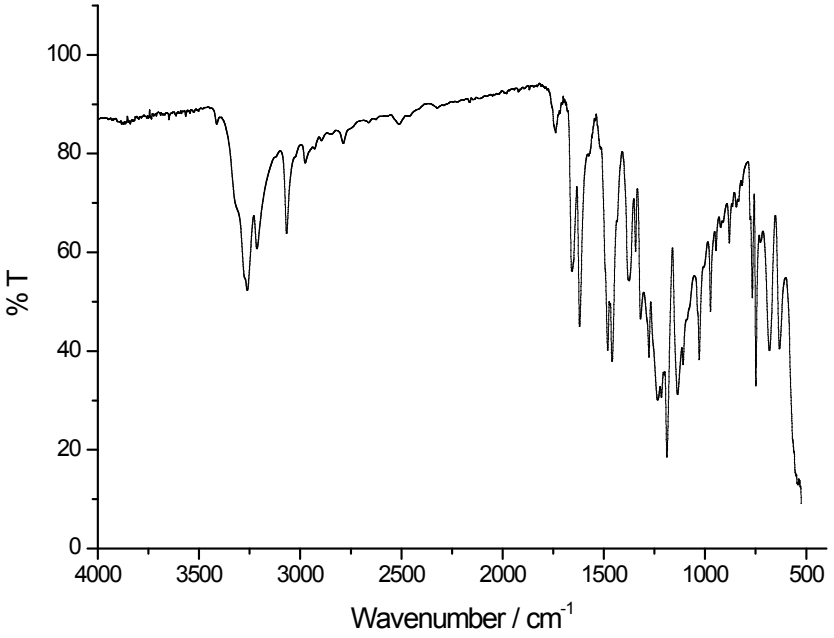


Fig. S43 The IR spectrum of **9**

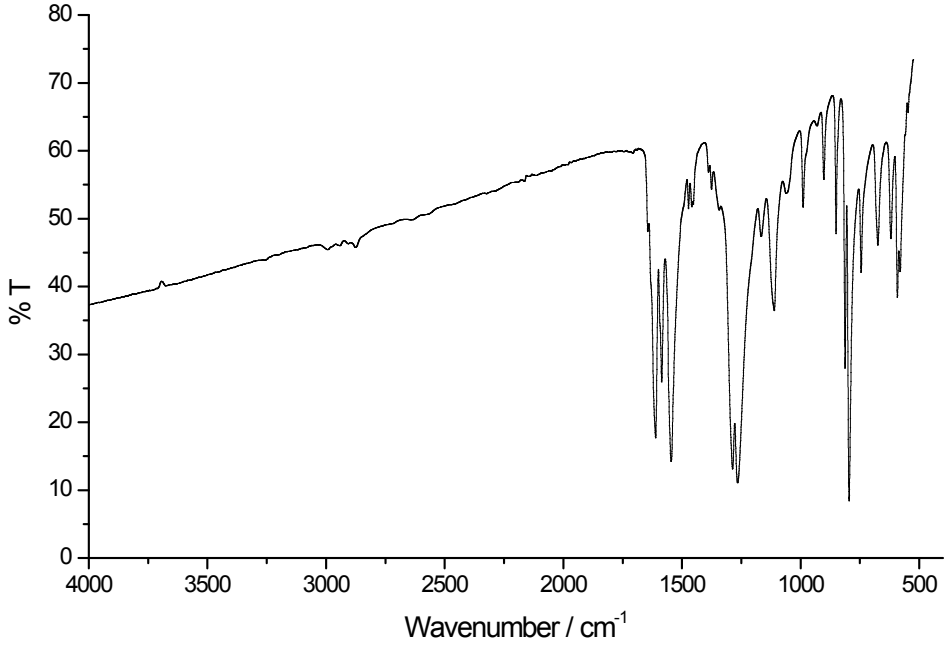


Fig. S44 The IR spectrum of **11**

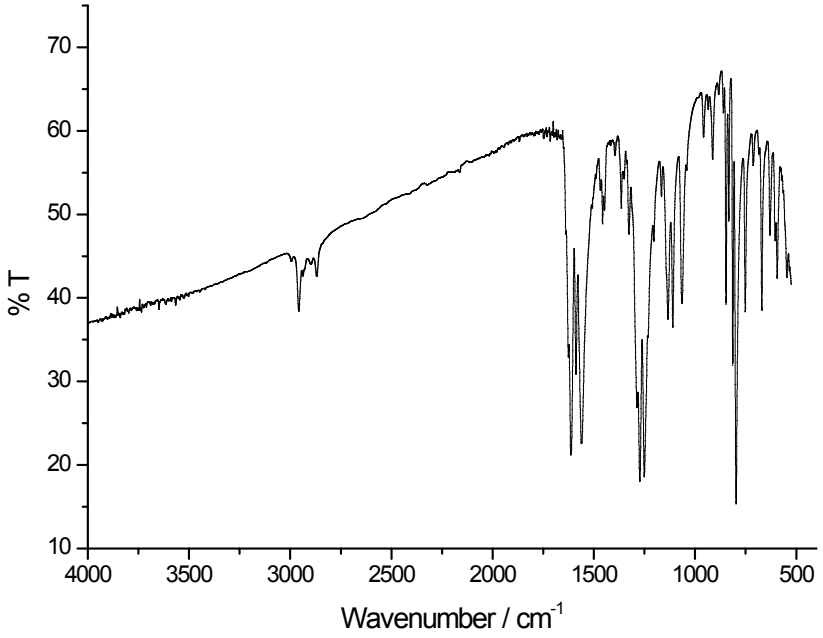


Fig. S45 The IR spectrum of **12a**

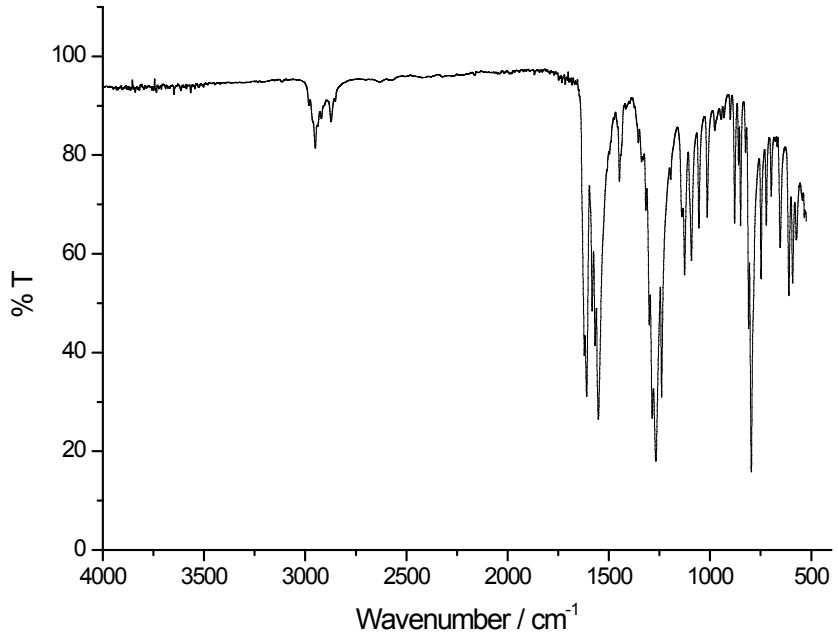


Fig. S46 The IR spectrum of **12b**

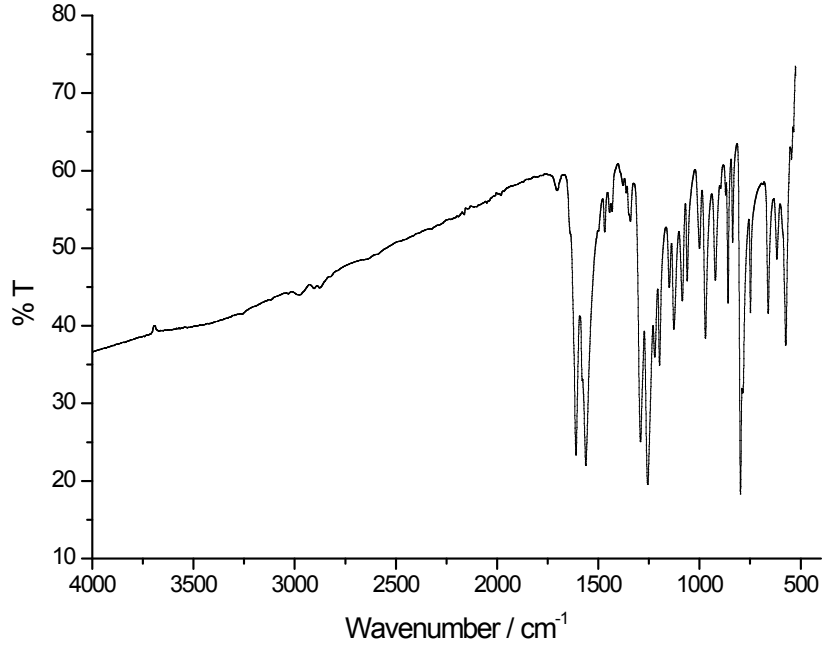


Fig. S47 The IR spectrum of **13**

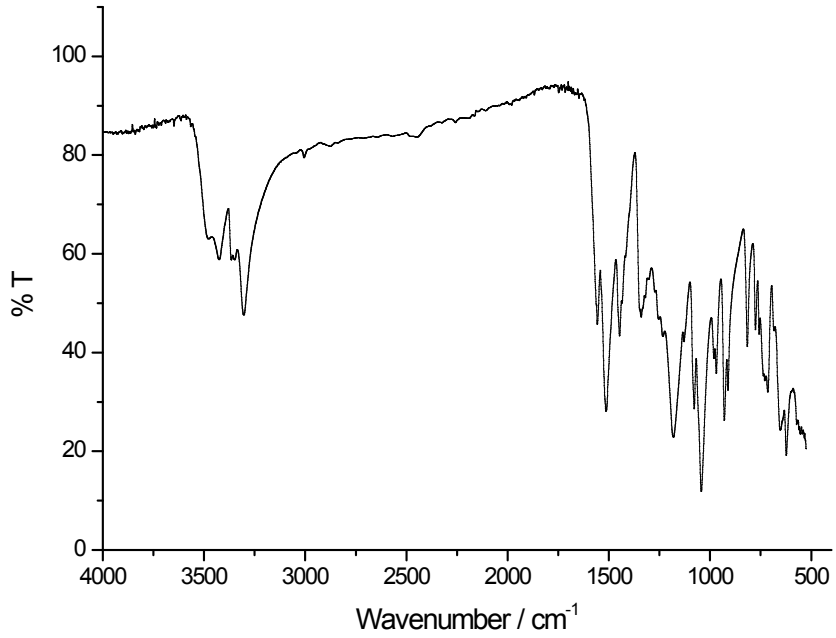


Fig. S48 The IR spectrum of **14**

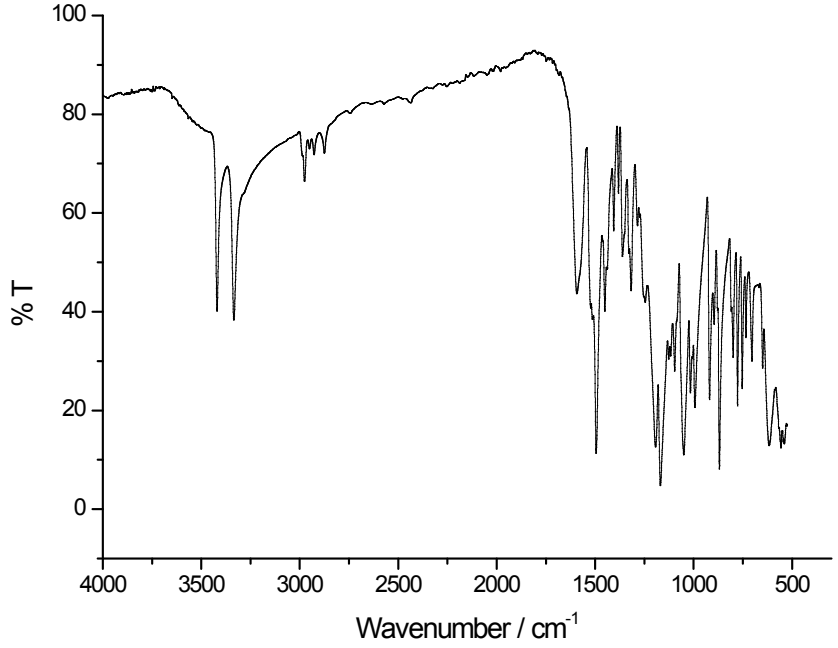


Fig. S49 The IR spectrum of **15**

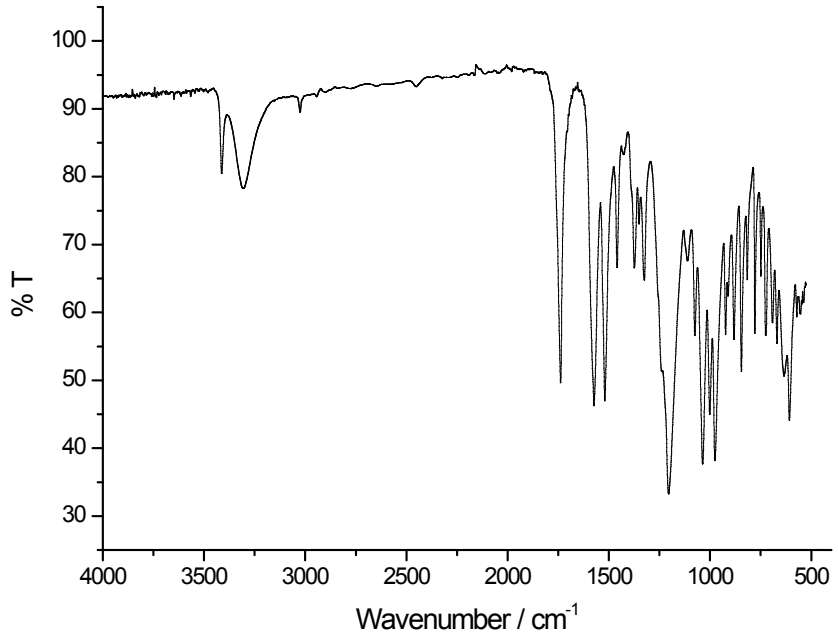


Fig. S50 The IR spectrum of **16**

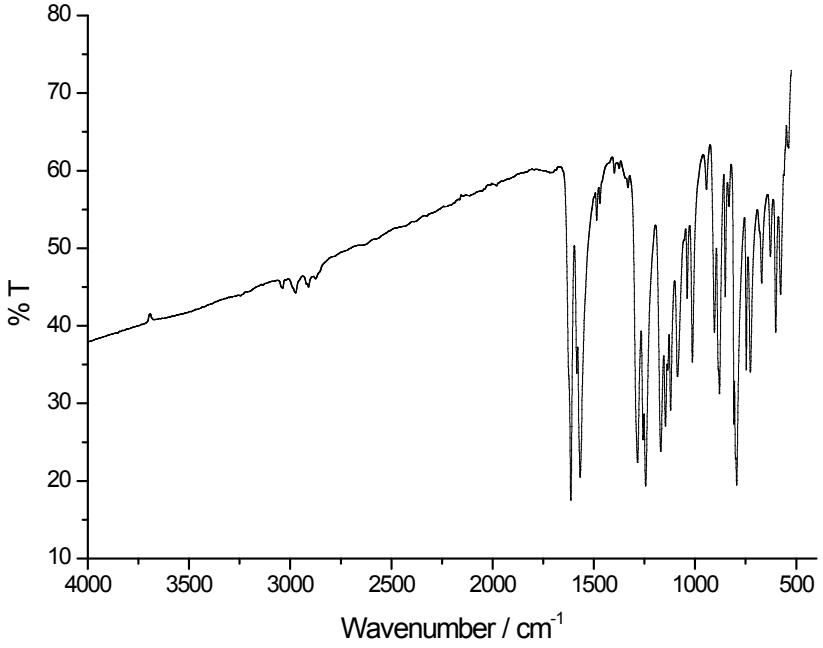


Fig. S51 The IR spectrum of **17**

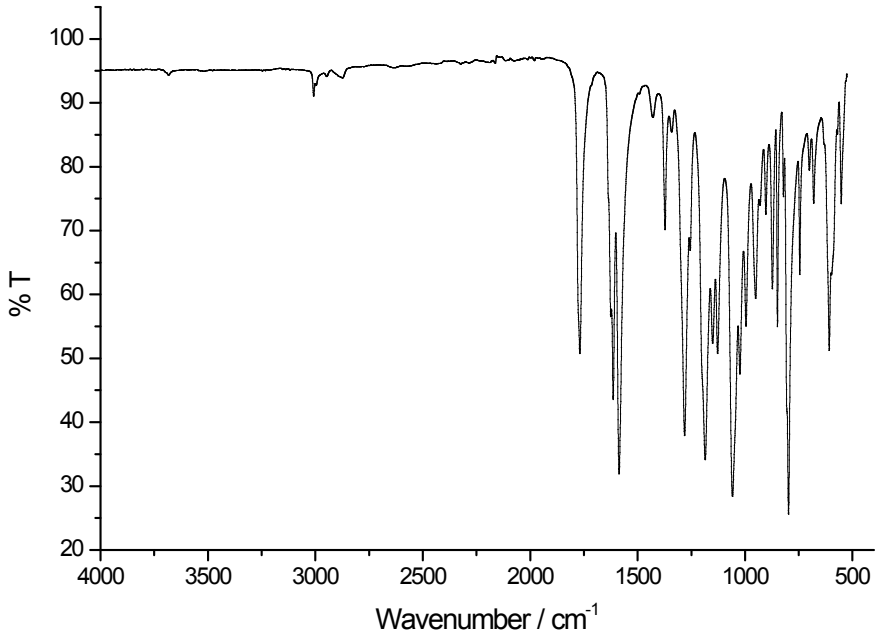


Fig. S52 The IR spectrum of **19**

14. Computational details

All of the *ab initio* calculations involved in this work were carried out using the Gaussian 09 suite of programs.[1] The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6-31++G(d, p) basis set. The geometrical configurations were optimized with no constraints imposed under default convergence criteria. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibration frequencies analysis.

Volume (V_m) was calculated based on the optimized structures. The surface electrostatic potential was calculated by Multiwfn program.[2]

The density was obtained using an improved equation proposed by Politzer et al. considering intermolecular interactions within the crystal.[3]

$$\rho(\text{crystal}) = \alpha[\tfrac{M}{V(0.001)}] + \beta(\upsilon\sigma_{tot}^2) + \gamma \quad (1)$$

Here $V(0.001)$ is the volume in cm^3/molecule and is encompassed by the 0.001 au contour of the electronic density, M is the molecular mass in g/molecule, υ is the balance of charges between positive potential and negative potential on molecular surface, and σ_{tot}^2 stands for strengths and variabilities of the overall surface potentials. The value of α, β, and γ have been reported by Peter Politzer et al.[3]

Heat of formation is another important parameter for energetic compounds. An isodesmic reaction processes is designed to screen the values of heat of formation for gas. So heats of formation of molecules can be given in terms of eq (2) [4]:

$$R(NO_2)_n + nCH_4 \rightarrow RH_n + nCH_3NO_2 \quad (2)$$

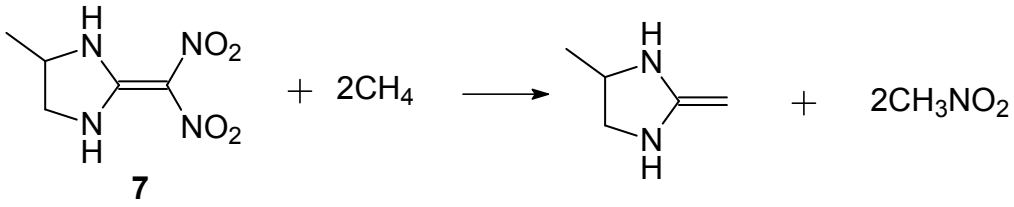
According to Hess' law of constant heat summation condensed-phase heats of formation can be determined.[5]

$$\Delta H(\text{solid}) = \Delta H(\text{gas}) - \Delta H(\text{sublimation}) \quad (3)$$

The enthalpy of sublimation can be represented as eq (4) and on the basis of the predicted electrostatic potential of a molecule.[6]

$$\Delta H(\text{sublimation}) = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + c \quad (4)$$

Here SA is the surface area of the 0.001 electrons $bohr^{-3}$ isosurface of the electronic density of the HEDMs, $\upsilon\sigma_{tot}^2$ is derived from the molecular electrostatic potential calculation, and a, b, c are fitting parameters reported by Politzer et al.[6a]



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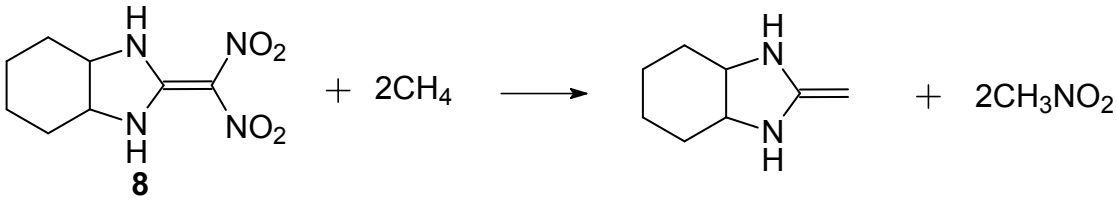

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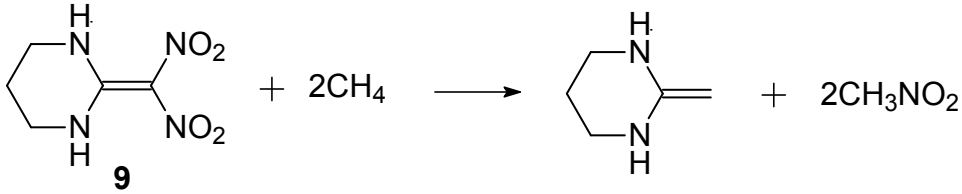

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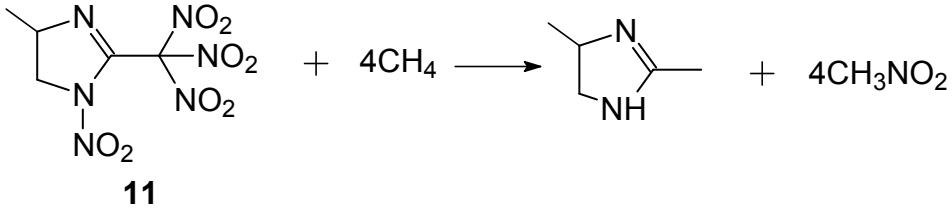

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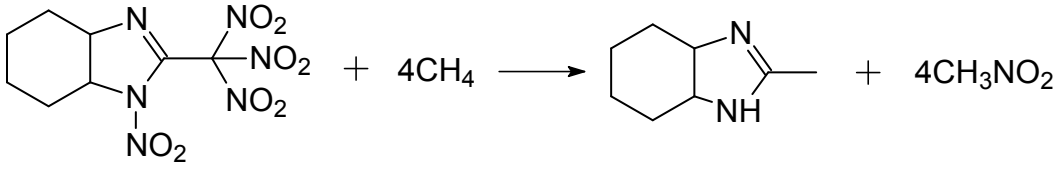
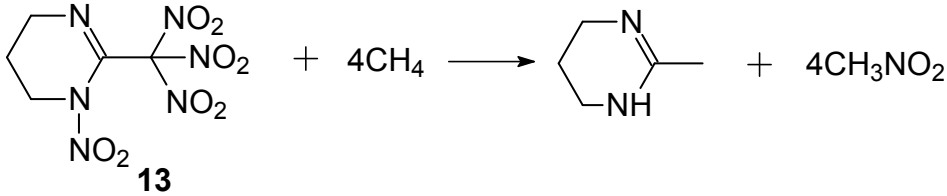


12 a, b



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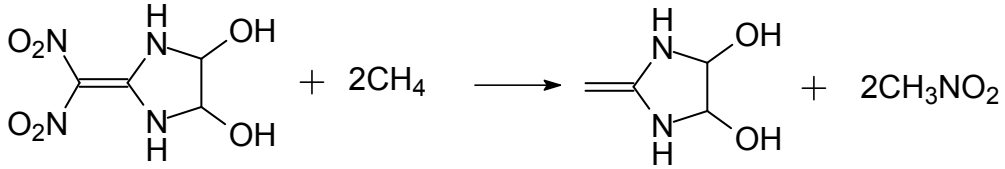

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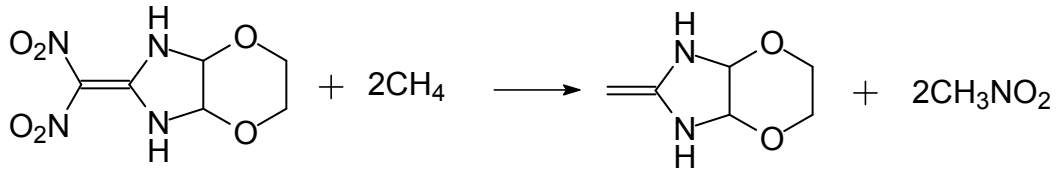

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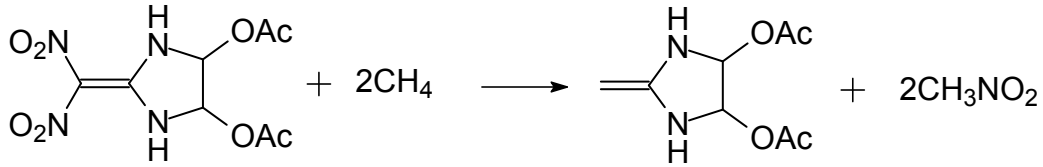

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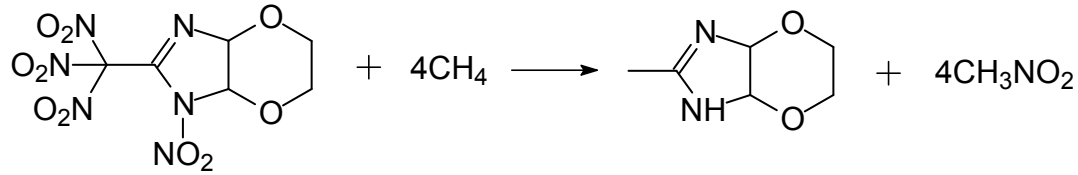

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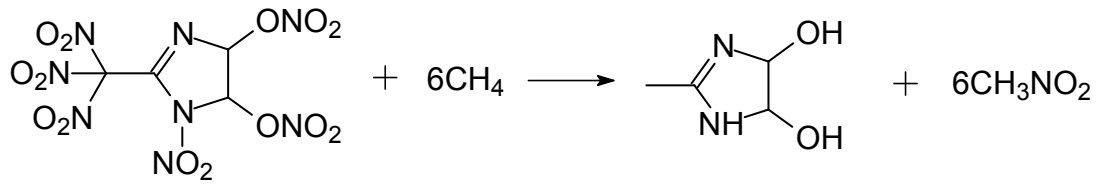

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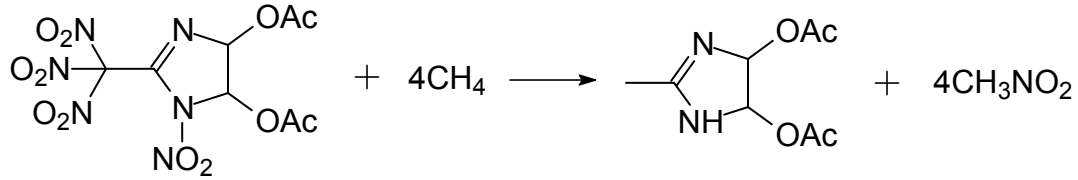

19

Scheme S1**.** Isodesmic reactions for **7-9**, and **11-19**

References

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