Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea (ZXC-19): A Multifluorine Explosive with Superior Performance

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Table S1: Crystallographic data and structure refinement details for 1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea (ZXC-19)

CCDC	**Deposition Number**		**1877092**
Bond precision:	C-C = 0.0028 A		Wavelength=0.71073
Cell:	a=12.2579(5)	b=9.7269(4)	c=29.1802(12)
	alpha=90	beta=92.889(4)	gamma=90
Temperature: 173 K			
	Calculated		Reported
Volume	3474.8(2)		3474.8(2)
Space group	P 21/n		P 21/n
Hall group	: -P 2yn		-P 2yn
Moiety formula	C13 H2 F6 N6 O9		C13 H2 F6 N6 O9
Sum formula	C13 H2 F6 N6 O9		C13 H2 F6 N6 O9
Mr	500.21		500.21
Dx,g cm^{-3}	1.912		1.912
Z	8		8
Mu (mm^{-1})	0.200		0.200
F000	1984.0		1984.0
F000'	1985.80		
h,k,lmax	15,12,37		15,12,37
Nref	7593		7524
Tmin,Tmax	0.959,0.984		0.781,1.000
Tmin'	0.959		
Correction method= # Reported T Limits: Tmin=0.781 Tmax=1.000 AbsCorr = MULTI-SCAN			
Data completeness= 0.991		Theta(max)= 26.997	
R(reflections)= 0.0394(5455)		wR2(reflections)= 0.1052(7524)	
S = 1.068		Npar= 644	

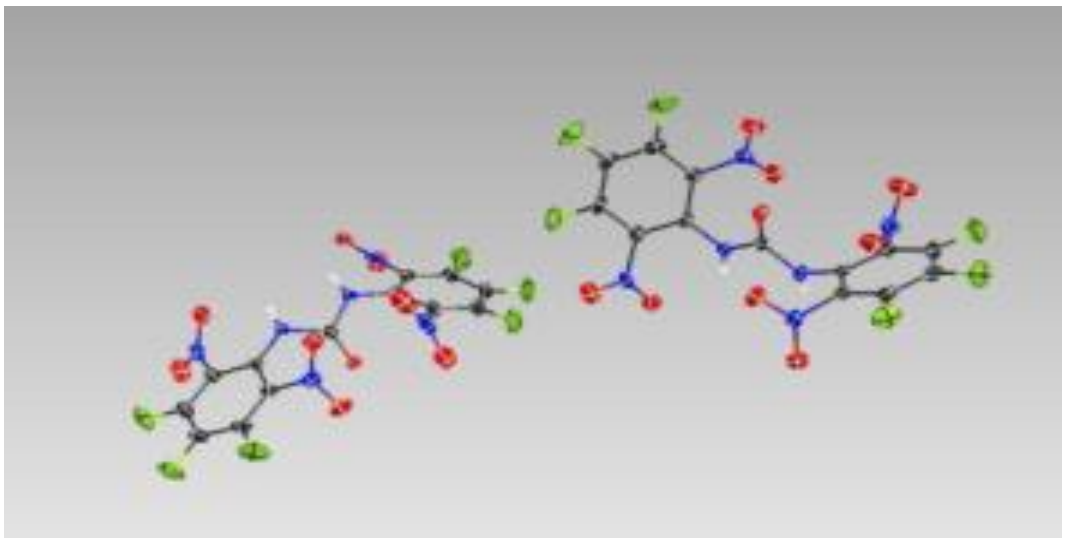

Figure 1 Single-crystal X-ray structure of ZXC-19

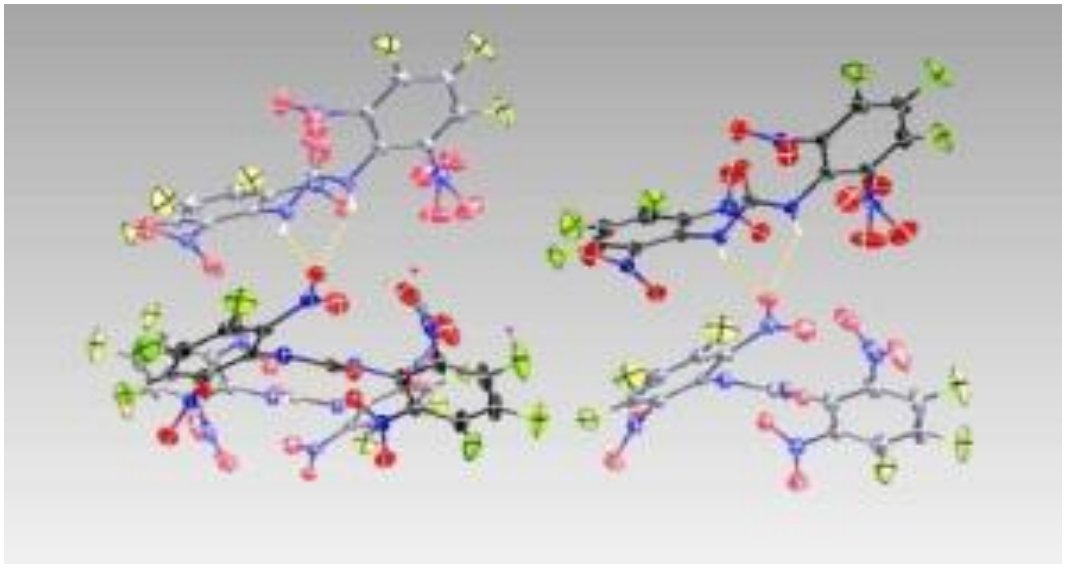

Figure 2 Expand all contacts' X-ray structure of ZXC-19

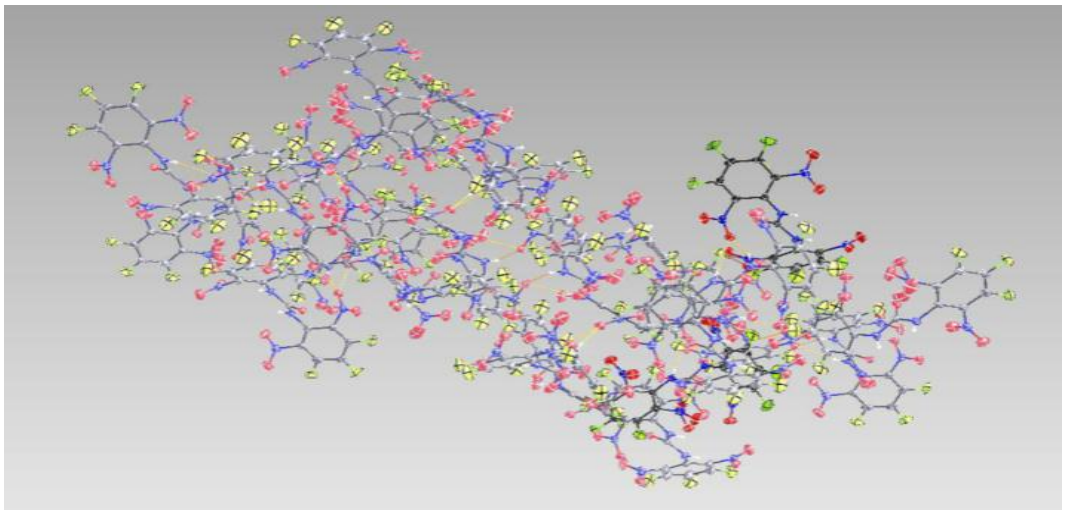

Figure 3 Crystal packing of ZXC-19

Table 2. Atomic parameters

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Å^2]
C1A		4e	1		0.95132	1.00289	0.11868	
C2A		4e	1		1.29502	1.09610	0.19623	
C3A		4e	1		1.26533	1.04765	0.23769	
C4A		4e	1		1.16983	0.97496	0.24038	
C5A		4e	1		1.10310	0.95124	0.20155	
C6A		4e	1		1.12965	1.00202	0.15859	
C7A		4e	1		1.22772	1.07577	0.15721	
C8A		4e	1		0.64148	1.10983	0.02097	
C9A		4e	1		0.56769	1.07183	0.05230	
C10A		4e	1		0.60186	0.99862	0.09008	
C11A		4e	1		0.71075	0.96379	0.09773	
C12A		4e	1		0.78943	1.00438	0.06734	
C13A		4e	1		0.75113	1.07670	0.02826	
C1B		4e	1		0.34748	0.52762	0.06255	
C2B		4e	1		0.32182	0.44450	0.02571	
C3B		4e	1		0.21913	0.38979	0.01993	
C4B		4e	1		0.14049	0.41968	0.05070	
C5B		4e	1		0.16371	0.50240	0.08899	
C6B		4e	1		0.26944	0.55639	0.09402	
C7B		4e	1		0.02764	0.41796	0.13911	
C8B		4e	1		-0.15055	0.20174	0.25036	
C9B		4e	1		-0.25362	0.17434	0.23190	
C10B		4e	1		-0.28871	0.23651	0.19147	
C11B		4e	1		-0.22154	0.32696	0.16972	
C12B		4e	1		-0.11768	0.35890	0.18822	
C13B		4e	1		-0.08425	0.29291	0.22862	
F1A		4e	1		1.39065	1.15947	0.19419	
F2A		4e	1		1.33002	1.06842	0.27537	
F3A		4e	1		1.14653	0.92189	0.28053	
F4A		4e	1		0.60450	1.17596	-0.01661	
F5A		4e	1		0.46186	1.10370	0.04471	
F6A		4e	1		0.52661	0.95601	0.11829	
F1B		4e	1		0.44721	0.58106	0.06751	
F2B		4e	1		0.39695	0.41650	-0.00468	
F3B		4e	1		0.19593	0.31155	-0.01676	
F4B		4e	1		-0.11554	0.14065	0.28915	
F5B		4e	1		-0.31902	0.08882	0.25325	
F6B		4e	1		-0.38894	0.20978	0.17383	

N1A		4e	1		1.06259	0.98028	0.11924	
H1AA		4e	1		1.09039	0.97550	0.09501	-1.2000
N2A		4e	1		0.90054	0.97890	0.07596	
H2AA		4e	1		0.93751	0.96985	0.05363	-1.2000
N3A		4e	1		1.01017	0.85804	0.20690	
N4A		4e	1		1.26226	1.13595	0.11458	
N5A		4e	1		0.73804	0.87399	0.13672	
N6A		4e	1		0.82552	1.11967	-0.00652	
N1B		4e	1		0.08660	0.52546	0.12176	
H1BA		4e	1		0.08672	0.59764	0.13448	-1.2000
N2B		4e	1		-0.05028	0.45828	0.16811	
H2BA		4e	1		-0.06731	0.53801	0.17087	-1.2000
N3B		4e	1		0.03049	0.36319	0.04104	
N4B		4e	1		0.30061	0.64553	0.13293	
N6B		4e	1		0.02241	0.32556	0.25117	
O1A		4e	1		0.94966	0.88159	0.23779	
O2A		4e	1		1.00153	0.75957	0.18066	
O3A		4e	1		1.24650	1.06905	0.07928	
O4A		4e	1		1.30554	1.24859	0.11658	
O5A		4e	1		0.90352	1.03705	0.15192	
O6A		4e	1		0.70361	0.90424	0.17392	
O7A		4e	1		0.79207	0.77220	0.12892	
O8A		4e	1		0.89881	1.03853	-0.01521	
O9A		4e	1		0.81018	1.22927	-0.02558	
O1B		4e	1		0.02417	0.24157	0.03122	
O2B		4e	1		-0.04692	0.44203	0.04340	
O3B		4e	1		0.23443	0.73322	0.14324	
O4B		4e	1		0.38958	0.62710	0.15267	
O5B		4e	1		0.04393	0.29862	0.12940	
O8B		4e	1		0.10407	0.28349	0.23344	
O9B		4e	1		0.02220	0.39360	0.28602	
N5B		4e	1		-0.26173	0.38868	0.12606	
O6B		4e	1		-0.29042	0.30686	0.09589	
O7B		4e	1		-0.25678	0.50883	0.12269	

Table 3. Some hydrogen bonding parameters of ZXC-19

Donor---Hydrogen...Acceptor	Don--Hyd [Å]	Hyd--Acc [Å]	Don--Acc [Å]	D--H-----A
N1B---H1BA...O2A»4	0.79	2.35	3.067	150.4°
N2B---H2BA...O2A»4	0.81	2.33	3.018	143.9°

N1B»1---H1BA»1...O2A»5	0.79	2.35	3.067	150.4°
N2B»1---H2BA»1...O2A»5	0.81	2.33	3.018	143.9°
N1B»2---H1BA»2...O2A»6	0.79	2.35	3.067	150.4°
N2B»2---H2BA»2...O2A»6	0.81	2.33	3.018	143.9°
N1B»3---H1BA»3...O2A»7	0.79	2.35	3.067	150.4°

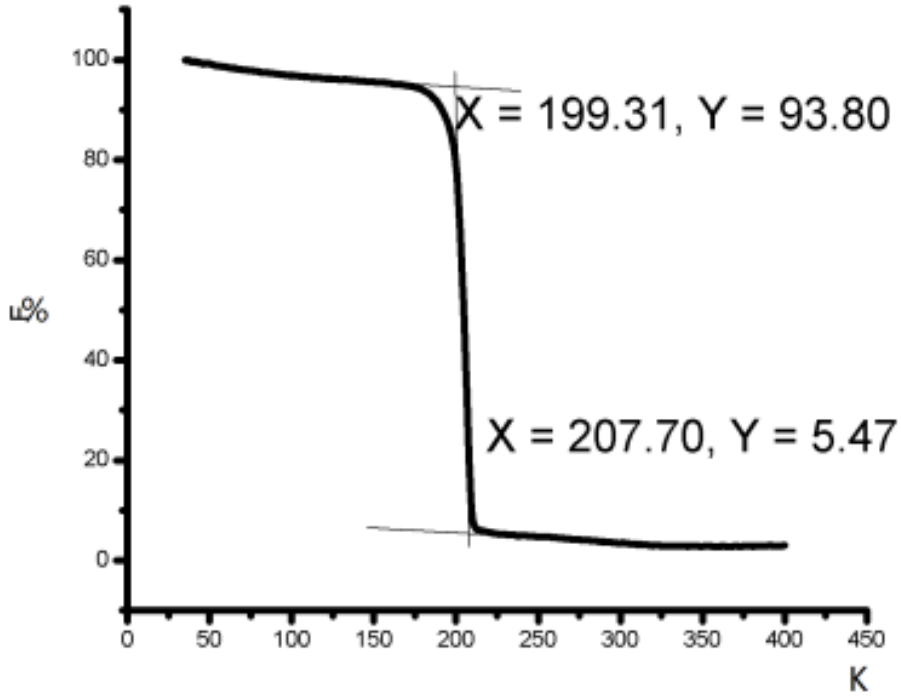

Figure 4 The TG curve diagram of ZXC-19

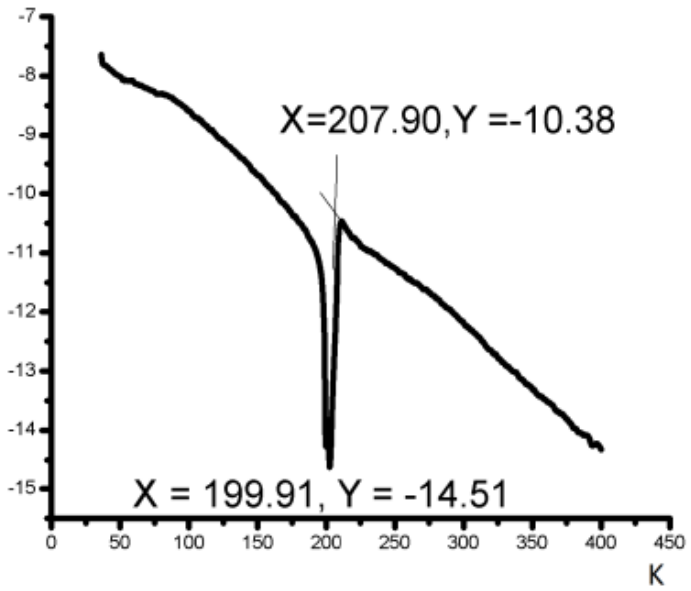

Figure 5 The DSC curve diagram of ZXC-19

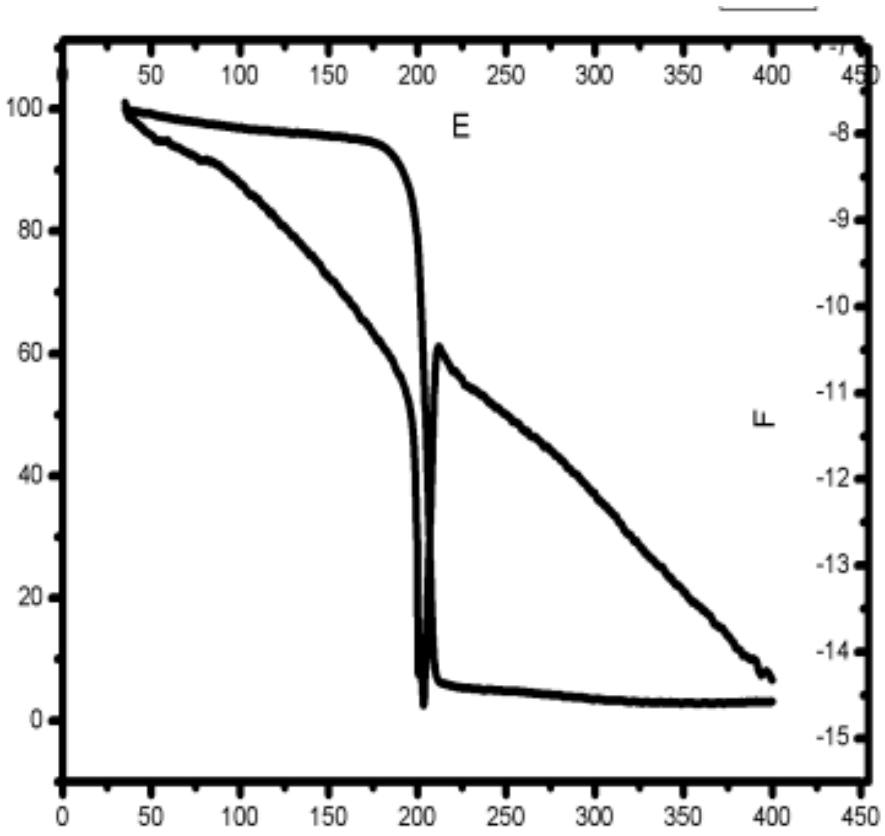

Figure 6 The TG-DSC curve diagram of ZXC-19

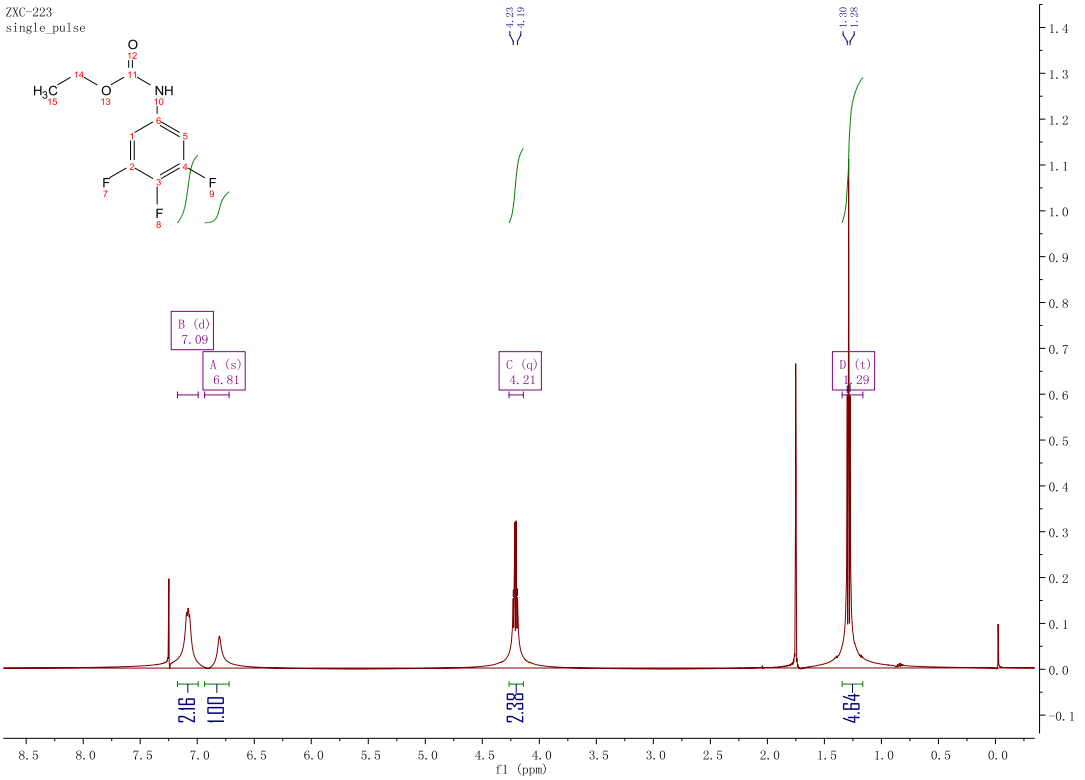

Figure 7 ^{1}H NMR spectrum (600 MHz) of ethyl (3,4,5-trifluorophenyl)carbamate in CDCl3-d_1 at 25 ^{o}C

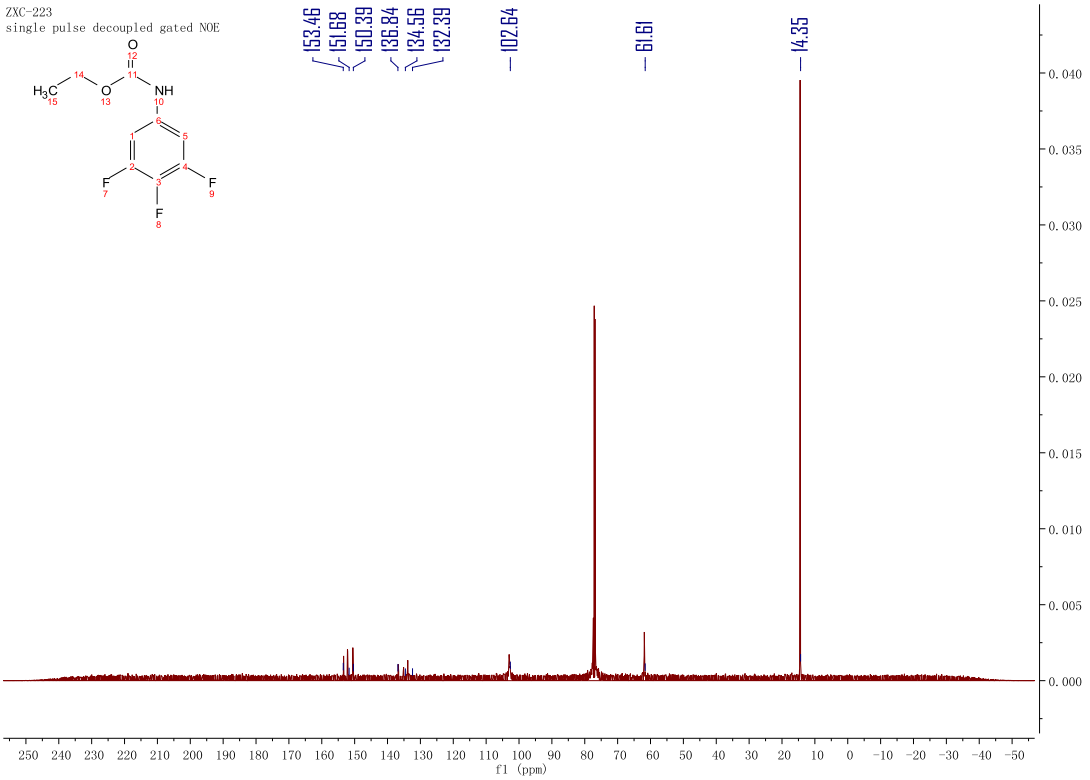

Figure 8 ^{13}C NMR spectrum (125 MHz) of ethyl (3,4,5-trifluorophenyl)carbamate in CDCl3-d_1 at 25 ^{o}C

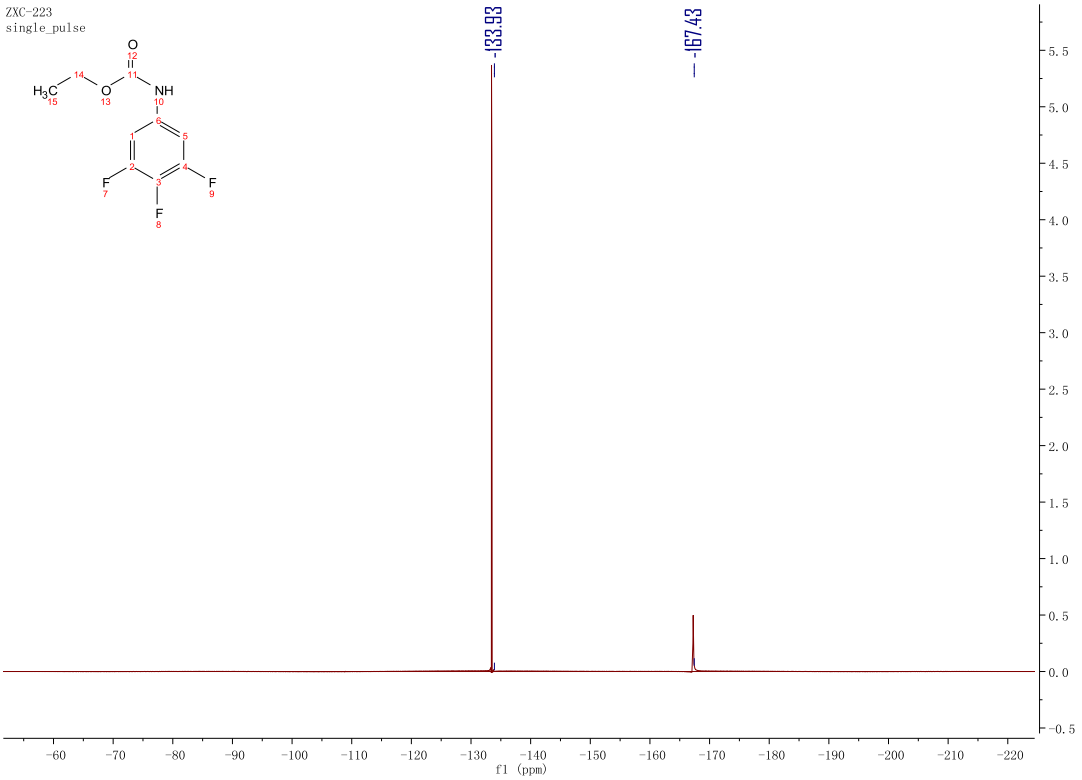

Figure 9 ^{19}F NMR spectrum (564 MHz) of ethyl (3,4,5-trifluorophenyl)carbamate in CDCl3-d_1 at 25 ^{o}C

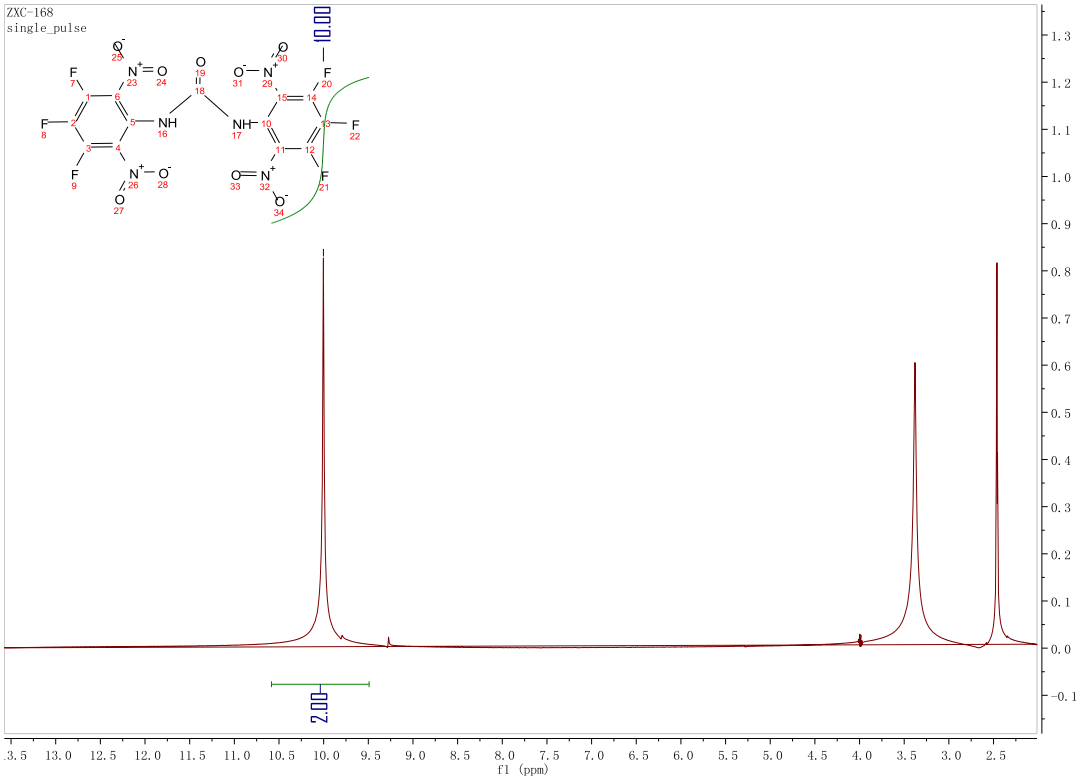

Figure 10 ^{1} H NMR spectrum (600 MHz) of 1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea in DMSO-d_6 at 25 ^{o}C

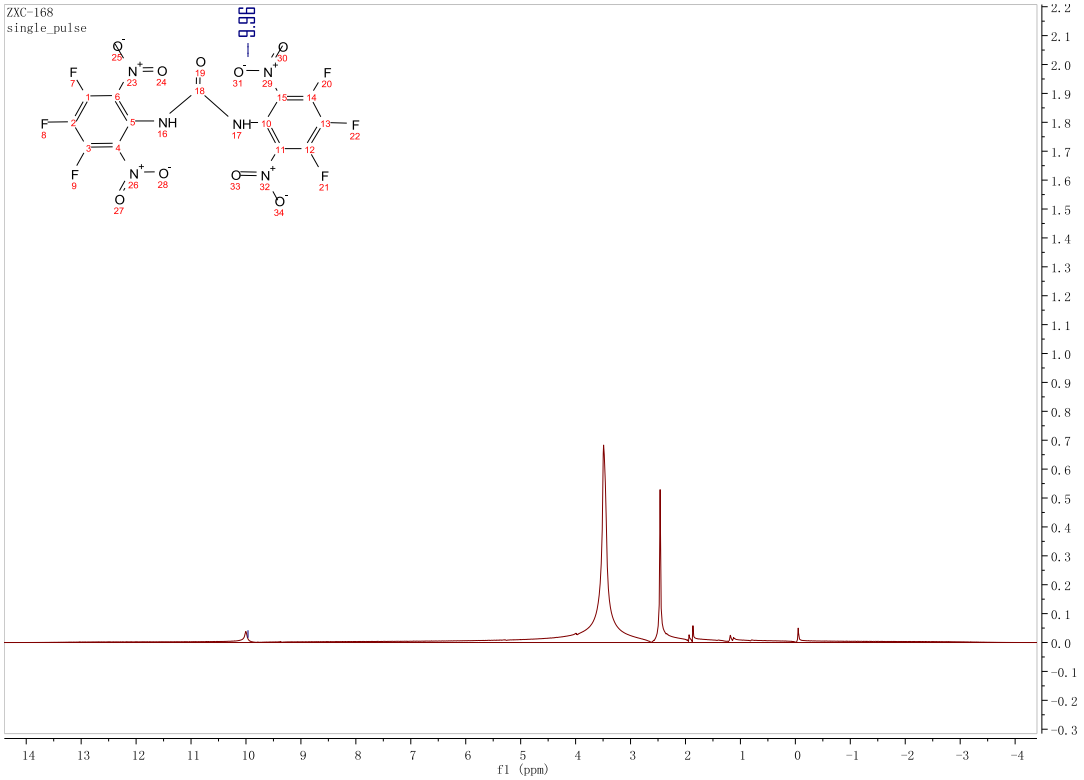

Figure 11 ^{1}H NMR spectrum (600 MHz) of 1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea in DMSO-d_6 +2d D_2O-d_2 at 25 ^{o}C

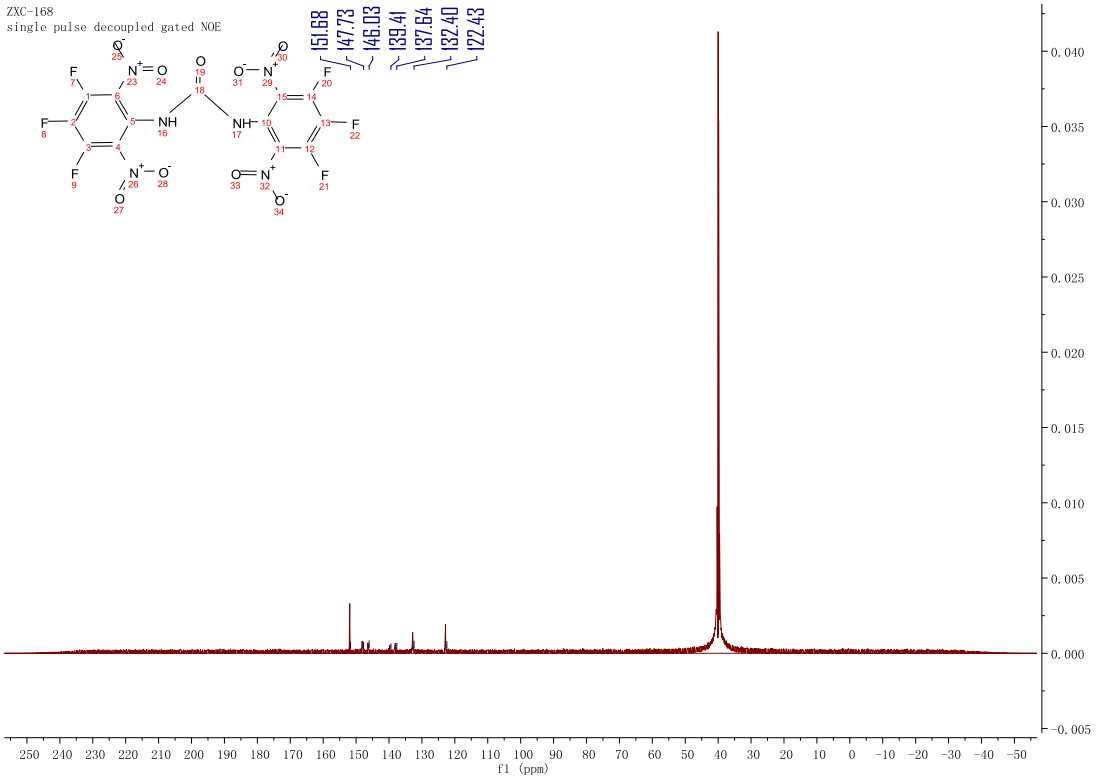

Figure12 ^{13}C NMR spectrum (150 MHz) of (1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea) in DMSO-d_6 at 25 ^{o}C

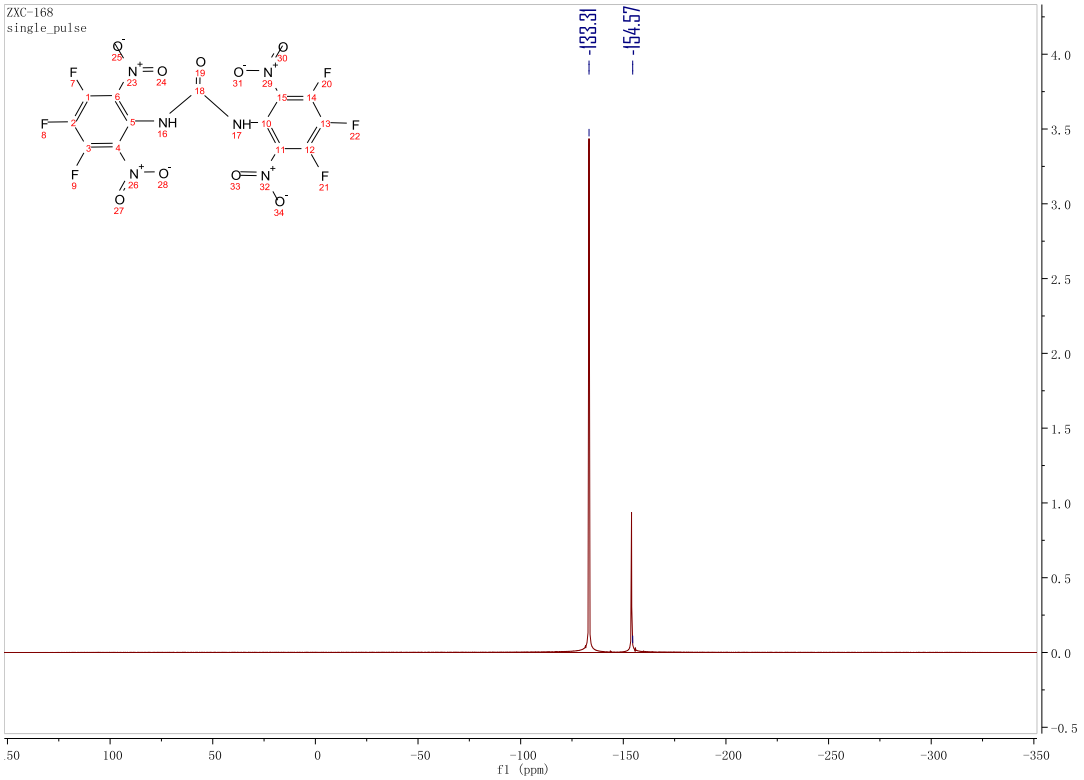

Figure 13 ^{19}F NMR spectrum (564 MHz) of 1,3-bis(3,4,5-trifluoro-2,6-dinitrophenyl)urea in DMSO-d_6 at 25 ^{o}C

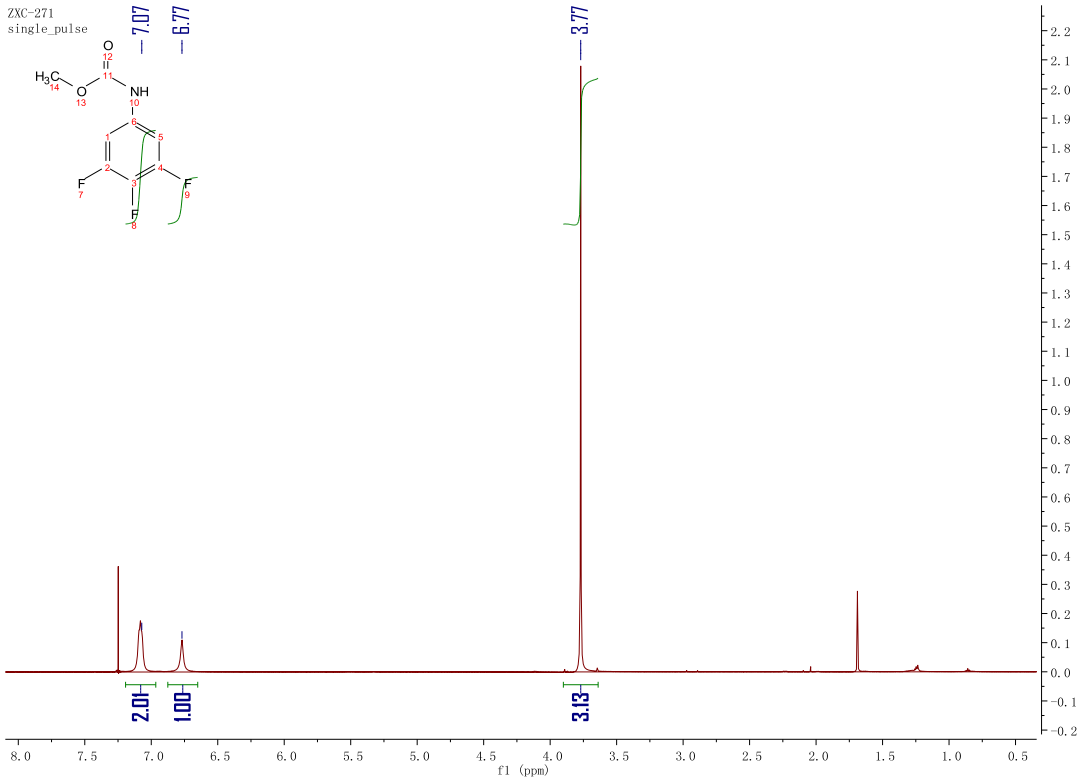

Figure 14 ^{1}H NMR spectrum (600 MHz) of methyl (3,4,5-trifluorophenyl)carbamate in CDCl3-d_1 at 25 ^{o}C

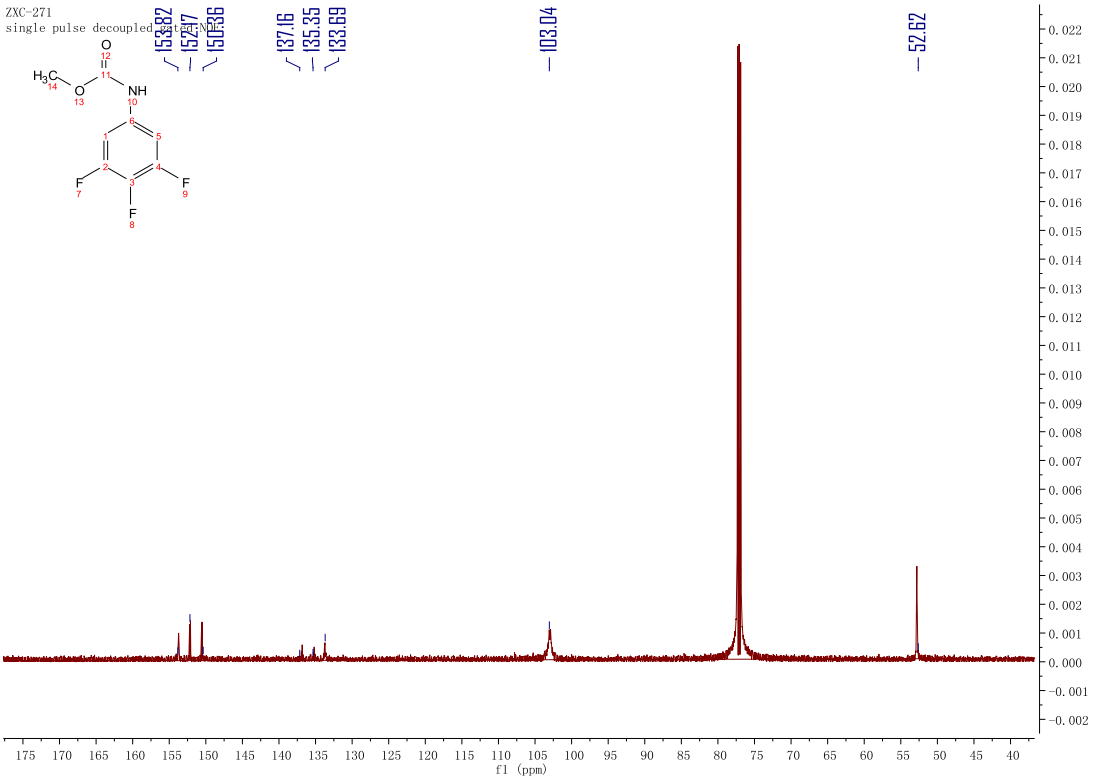

Figure 15 ^{13}C NMR spectrum (125 MHz) of methyl (3,4,5-trifluorophenyl)carbamate in $CDCl_3$-d_1 at 25 ^{o}C

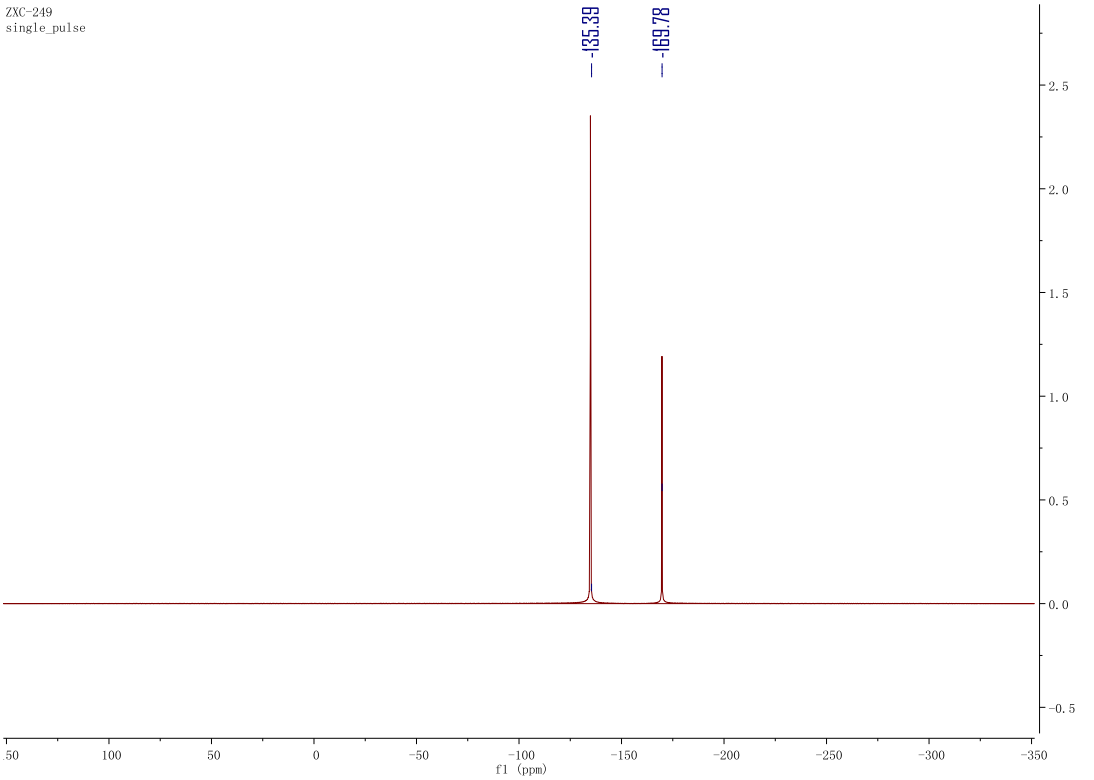

Figure 16 ^{19}F NMR spectrum (564 MHz) of methyl (3,4,5-trifluorophenyl)carbamate in $CDCl_3$-d_1 at 25 ^{o}C

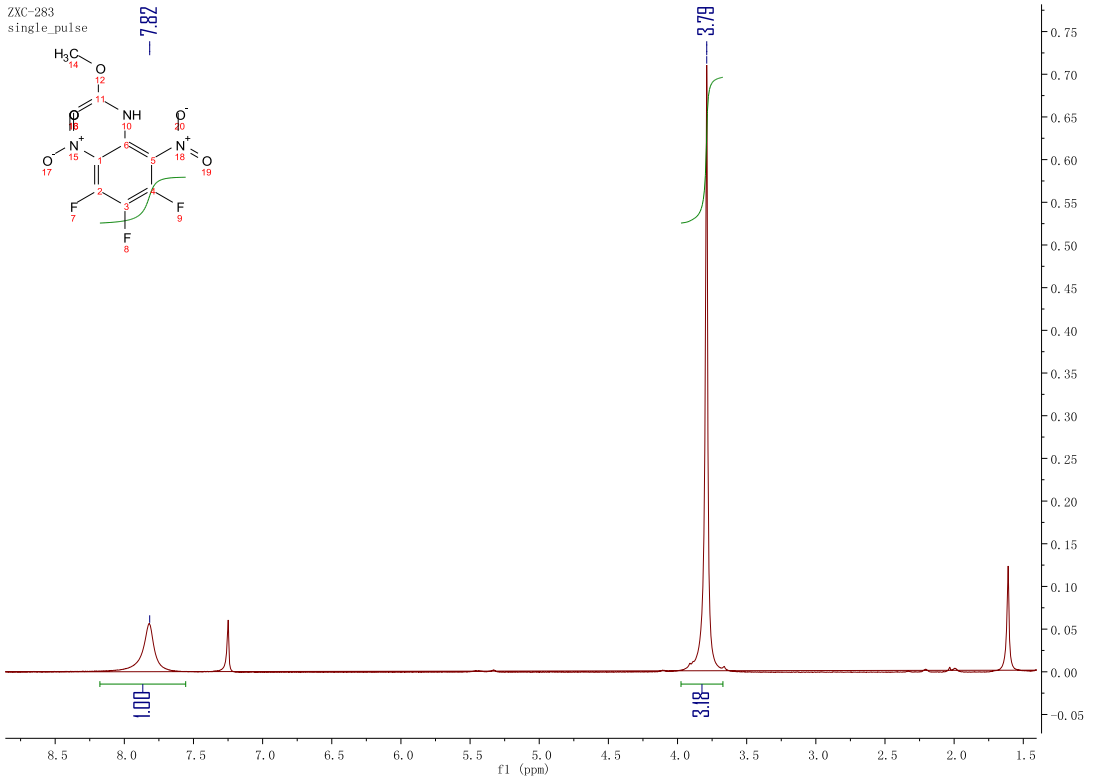

Figure 17 ^{1}H NMR spectrum (600 MHz) of methyl (3,4,5-trifluoro-2,6-dinitrophenyl)carbamate in CDCl3-d_1 at 25 ^{o}C

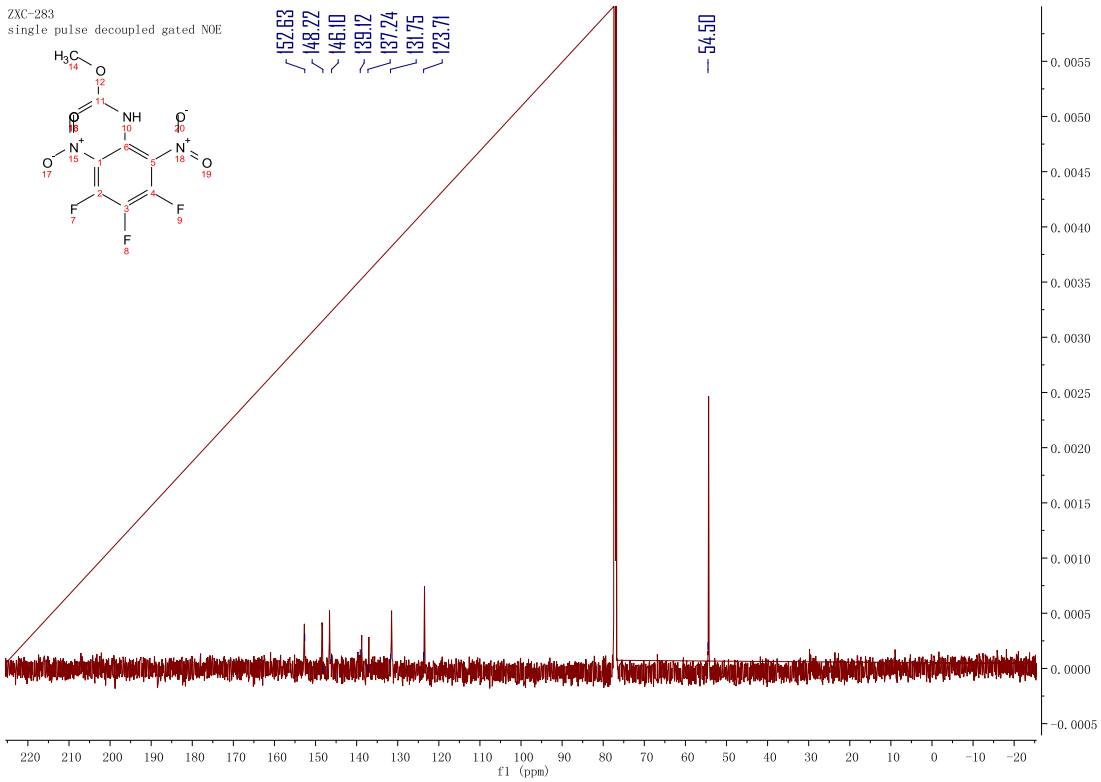

Figure 18 ^{13}C NMR spectrum (125 MHz) of methyl (3,4,5-trifluoro-2,6-dinitrophenyl)carbamate in $CDCl_3$-d_1 at 25 ^{o}C

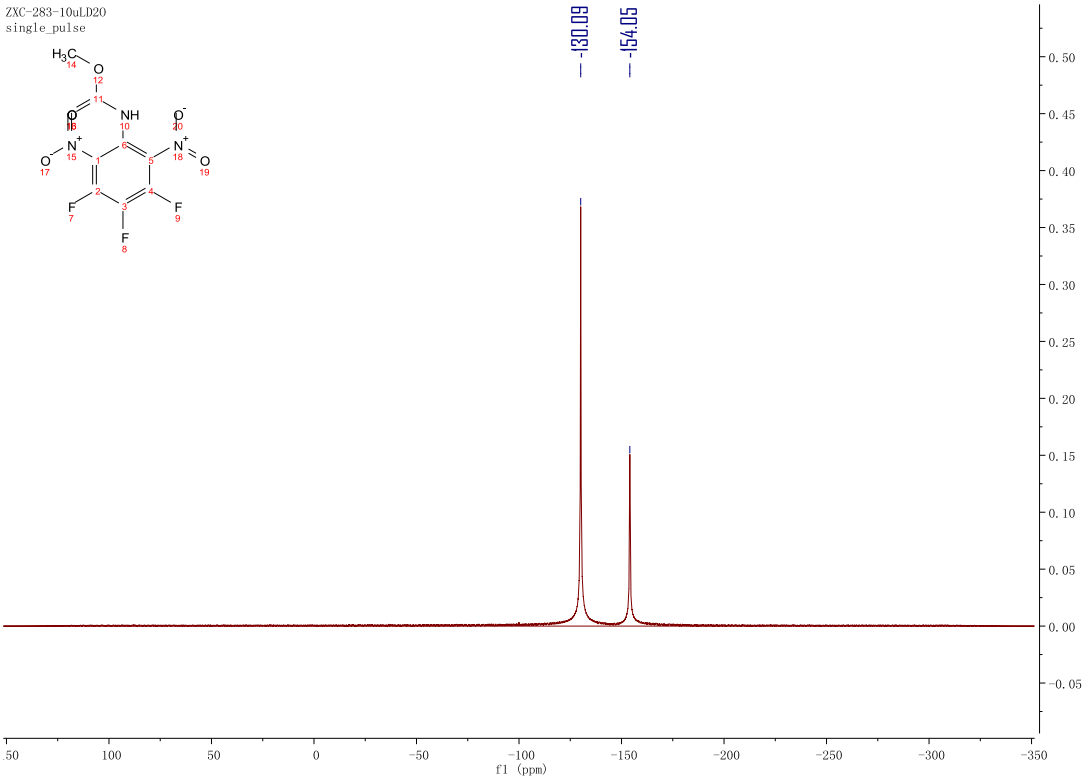

Figure 19 ^{19}F NMR spectrum (564 MHz) of methyl (3,4,5-trifluoro-2,6-dinitrophenyl)carbamate in $CDCl_3$-d_1 at 25 °C

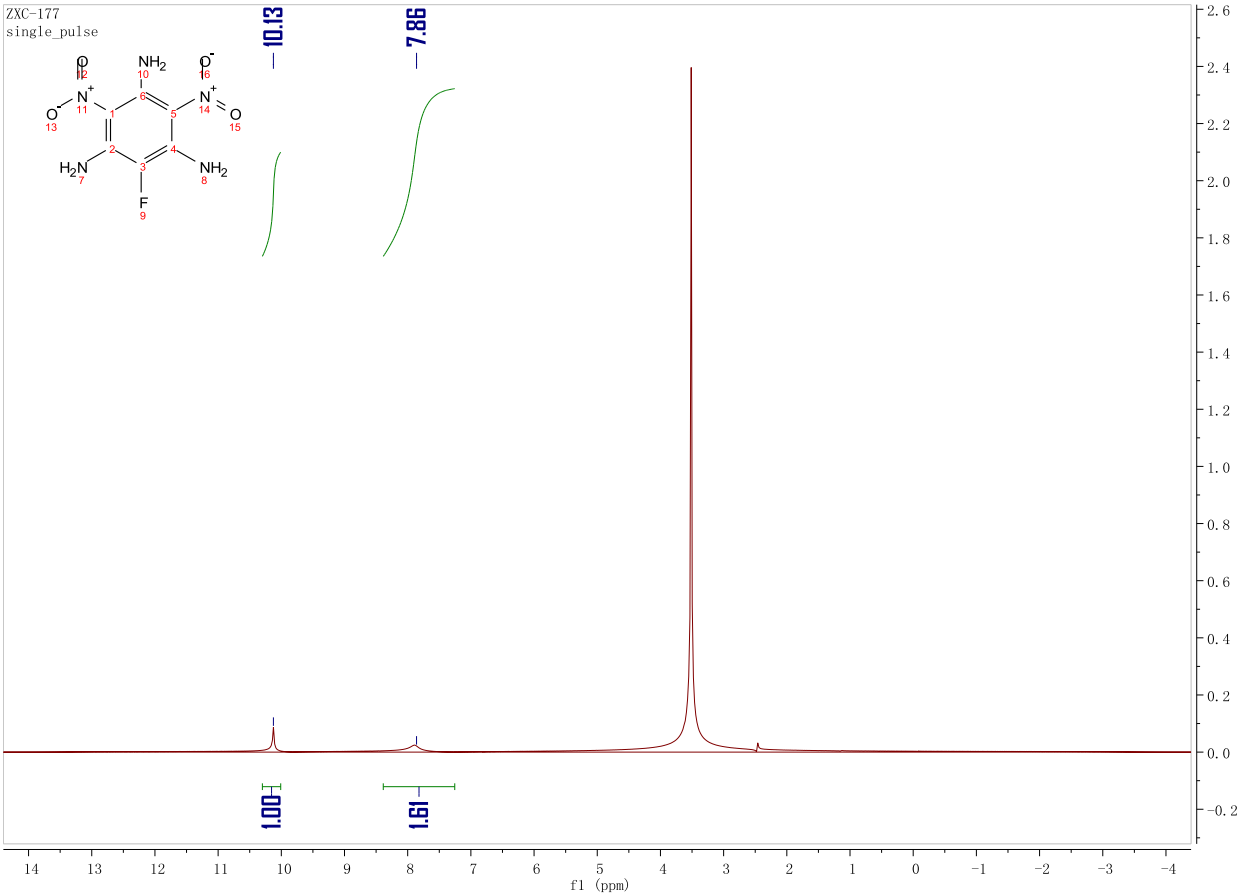

Figure 20 ^{1}H NMR spectrum (600 MHz) of ZXC-8 in DMSO-d_6 at 25 °C

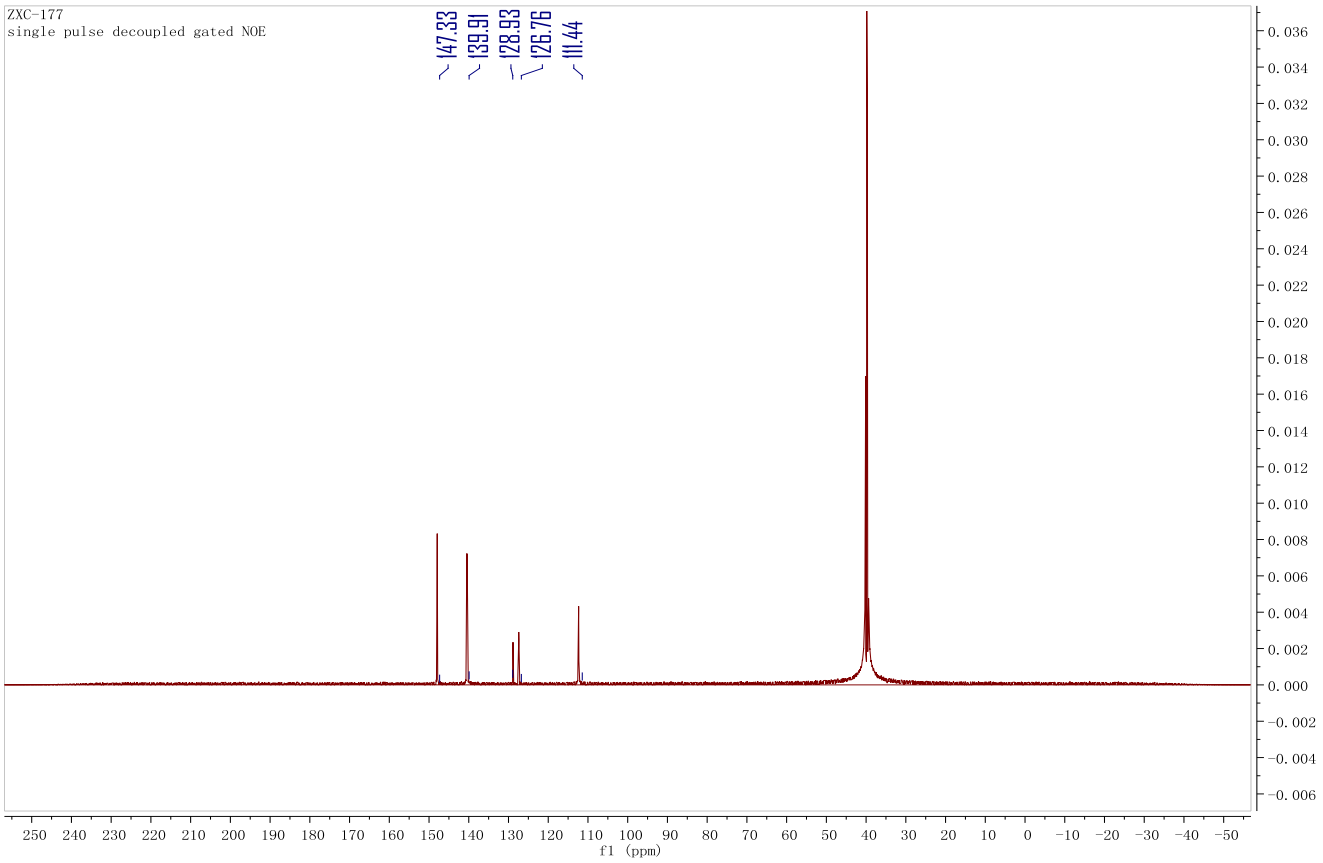

Figure 21 ^{13}C NMR spectrum (150 MHz) of ZXC-8 in DMSO-d_6 at 25 °C

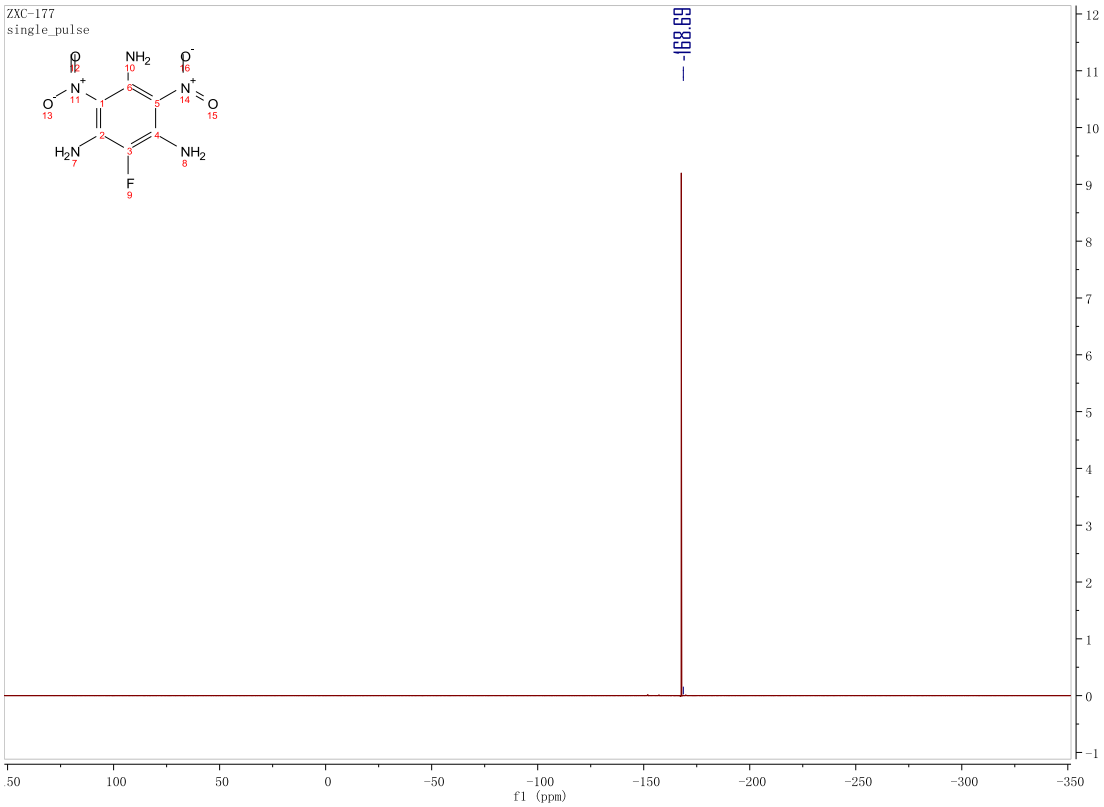

Figure 22 ^{19}F NMR spectrum (564 MHz) of ZXC-8 in DMSO-d_6 at 25 °C

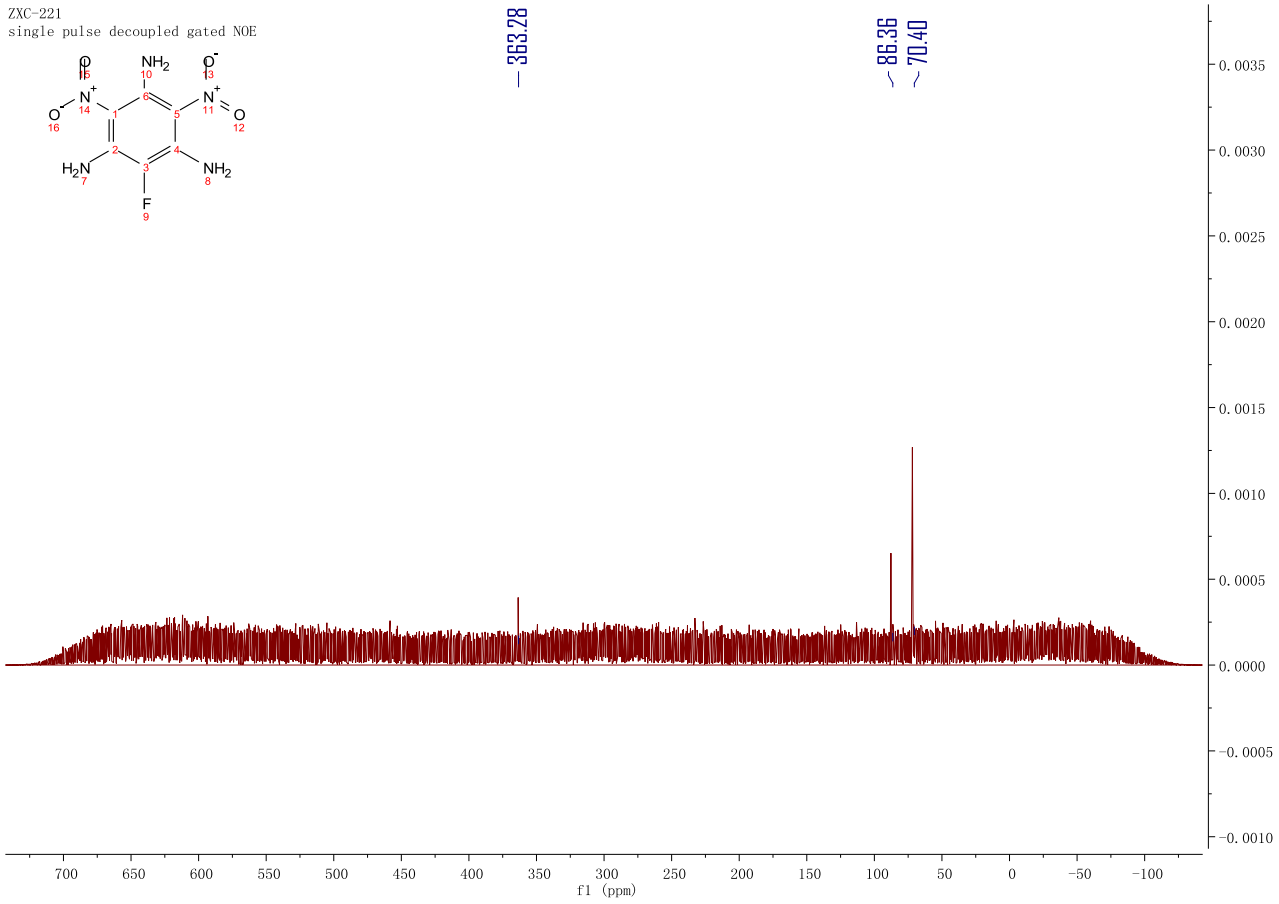

Figure 23 ^{15}N NMR spectrum (60.81 MHz) of ZXC-8 in DMSO-d_6 at 25 ^{o}C

Computation details

The predictions of heats of formation (HOF) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are in Scheme 1. The change of enthalpy for the reactions at 298 K can be expressed as

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \quad (1)$$

Where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE

is the difference between the zero-point energies (*ZPE*) of the products and the reactants at 0 K; ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq (2) is the *PV* work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOFs of reference compounds are available from the experiments.

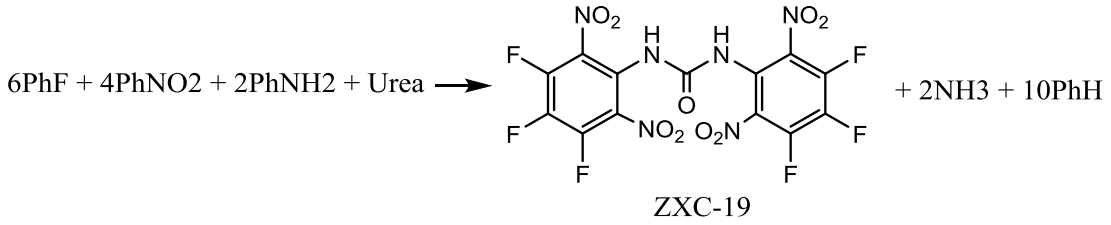

Figure 14. Isodesmic reactions for ZXC-19

Detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet formula

as

P = 1.558 ρ 2 Φ (1)

D = 1.01 Φ 1/2 (1+1.30ρ0) (2)

Φ = 0.4889 N (MQ) 1/2 (3)

where D is the predicted detonation velocity (km/s) and P is the detonation pressure (GPa), ρ is the density of a compound (cm^3 /mol). Φ, N, M and Q are characteristic parameters of an explosive, Q is chemical energy of detonation (kJ/g). The crystal densities and the calculated heats of formation were used in computing the D and P values.

Table 4 Total energy at B3LYP/6-311+G level, vibrational zero-point energy, thermal correction to enthalpy and heat of formation for title compounds and reference compounds [a]**

Species	*E*	ZPE	ΔH_T	HOF
ZXC-19	-2101.293637	484.21	562.19	-891.65
PhNH2	-287.6876277	306.16	323.98	87.50 [b]
PhF	-331.5801118	241.3	257.32	-115.90 [b]
Benzene	-232.3112363	262.92	276.95	82.9 [b]
Nitrobenzene	-436.8746216	269.3	289.78	68.5 [b]
Urea	-225.3498071	166.76	180.91	-245.8 [b]
NH3	-56.5826356	89.89	99.9	-45.9 [b]

[a] E in a.u., ZPE, ΔH_T and HOF are in kJ/mol. [b] Data from Ref [Dean, J. A. *LANGE'S Handbook of Chemistry*, 15th ed., McGraw-Hill Book Co, New York, **1999**].

Table 5 The detonation properties of of ZXC- 19

	T_d[a] (℃)	$\Delta_f H$ (J/g)	d[b](g cm^{-3})	$\Delta_f H$[c] (kJ mol^{-1})	P[d] (GPa)	D[e] (m s^{-1})	IS[f] (J)	FS[g] (N)
ZXC-19	207.9	4916.86	1.90	292.30	32.54	8260	24.5	360
TATB	375.0	-	1.93	21.74	27.88	7880	>60	360

RDX	210.0	-	1.81	86.30	38.00	8983	7	120

[a] Decomposition temperature; [b] Density based on XRD at 298K; [c] Formation heat; [d] Detonation pressure; [e] Detonation velocity; [f] Impact sensitivity; [g] Friction sensitivity

Note: V_D is the predicted detonation velocity (km/s); P is the detonation pressure (GPa); d is measured density (cm^3 /mol); ΔH_T is the thermal correction to enthalpy (kJ/mol); *IS* is impact sensitivity (BAM drophammer, 1 of 6); *FS* is friction sensitivity (BAM friction tester, 1 of 6);

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