SUPPORTING INFORMATION

Synthesis of Nitrate Ester and Nitramine Derivatives of Polyfluoro Alkyl Compounds for High Energy Materials

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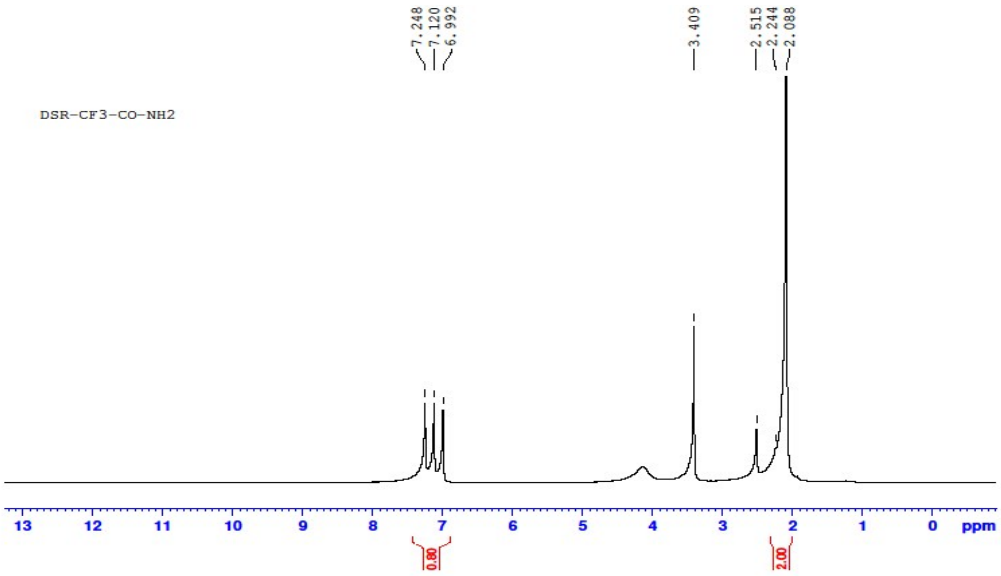
1. Spectral data

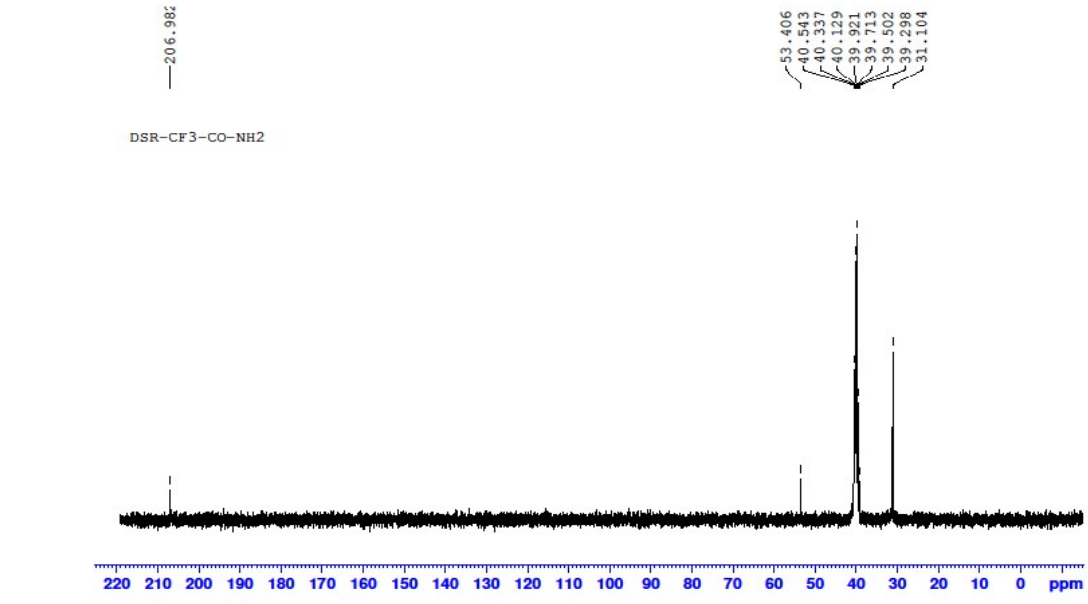
Sr. No.	Compound
1	2,2,2-Trifluoroethyl carbamate **(1)** a. ^{1}HNMR, b. ^{13}CNMR
2	2,2,2-Trifluoroethyl nitrocarbamate **(2)** a. ^{1}HNMR, b. ^{13}CNMR
3	2,2,3,3-Tetrafluorobutane-1,4-diyl dicarbamate **(3)** a. ^{1}HNMR, b. ^{13}CNMR
4	2,2,3,3-Tetrafluorobutane-1,4-diyl bis(nitrocarbamate) **(4)** a. ^{1}HNMR, b. ^{13}CNMR
5	2,2,3,3-Tetrafluorobutane-1,4-diyl dinitrate **(5)** a. ^{1}HNMR, b. ^{13}CNMR
6	2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl dicarbamate **(6)** a. ^{1}HNMR, b. ^{13}CNMR
7	2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl bis(nitrocarbamate) **(7)** a. ^{1}HNMR, b. ^{13}CNMR
8	2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl dinitrate **(8)** a. ^{1}HNMR, b. ^{13}CNMR

1. 2,2,2-trifluoroethyl carbamate (1)

a. ^{1}H NMR

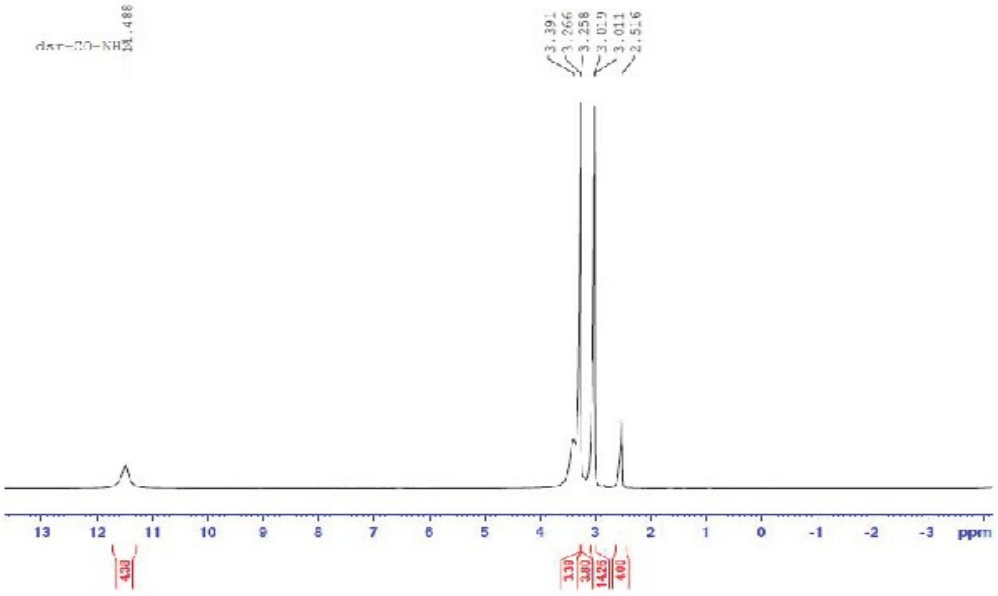


b. ^{13}CNMR

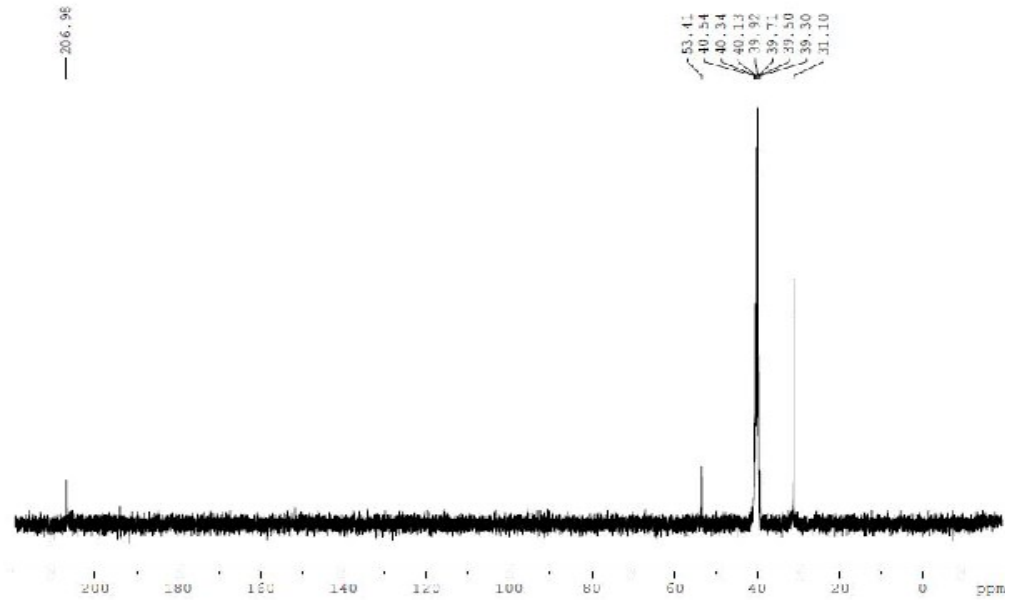


2. 2,2,2-Trifluoroethyl nitrocarbamate (2)

a. ^{1}H NMR

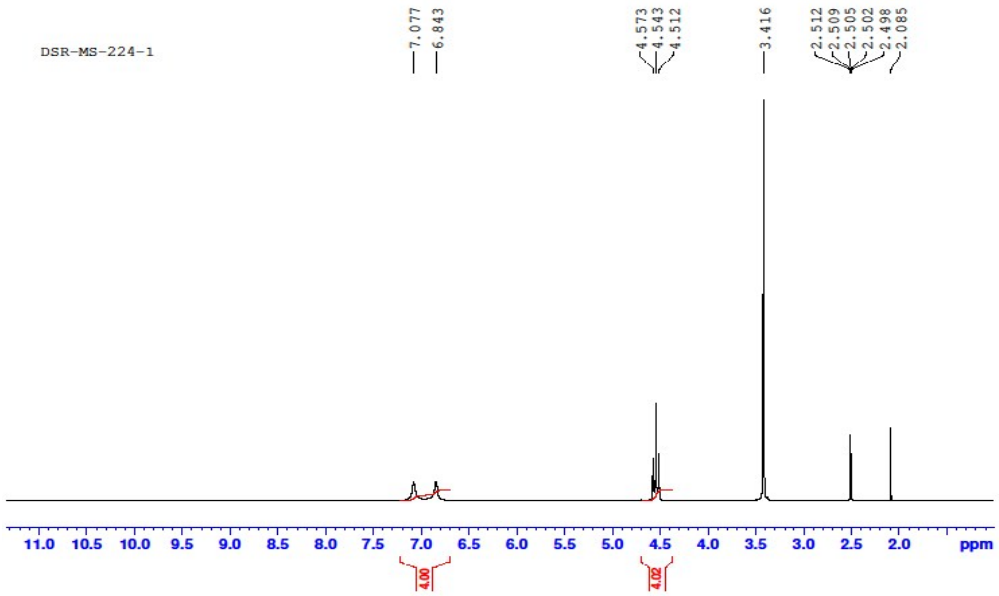


b. ^{13}C NMR

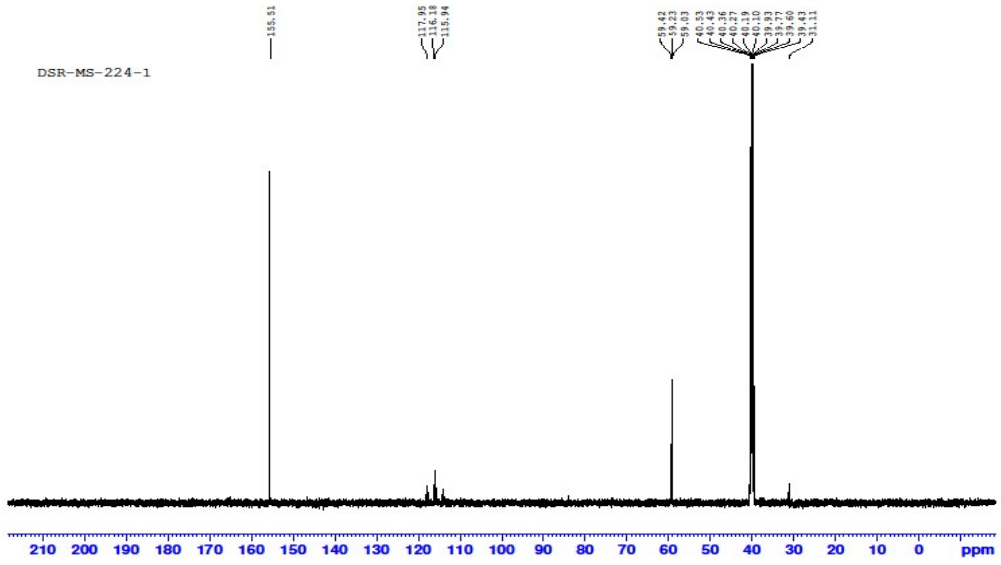


3. 2,2,3,3-Tetrafluorobutane-1,4-diyl dicarbamate (3)

a. ^{1}H NMR

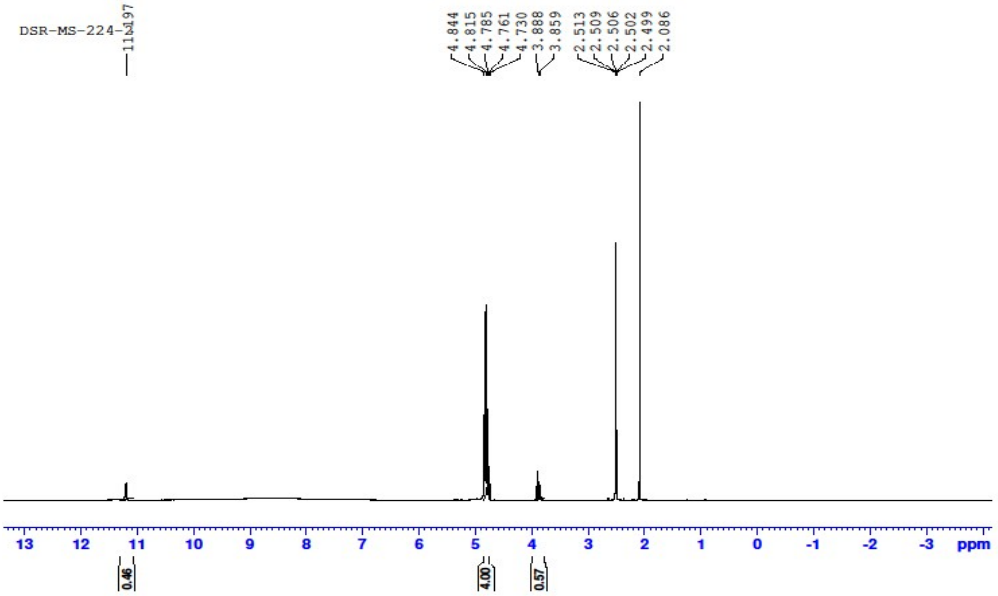


b. ^{13}C NMR

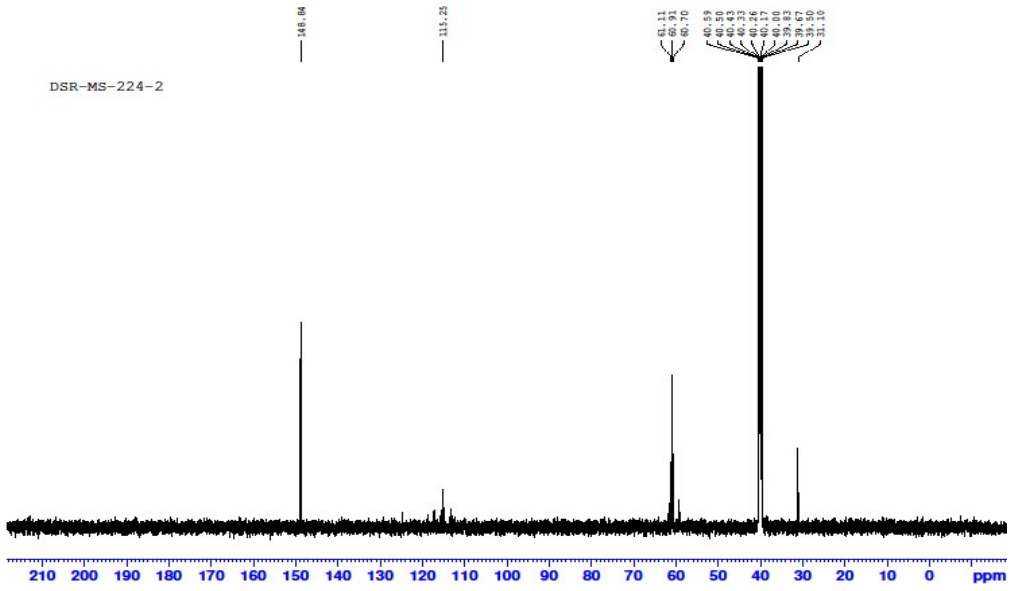


4. 2,2,3,3-Tetrafluorobutane-1,4-diyl bis(nitrocarbamate) (4)

a. ^{1}H NMR

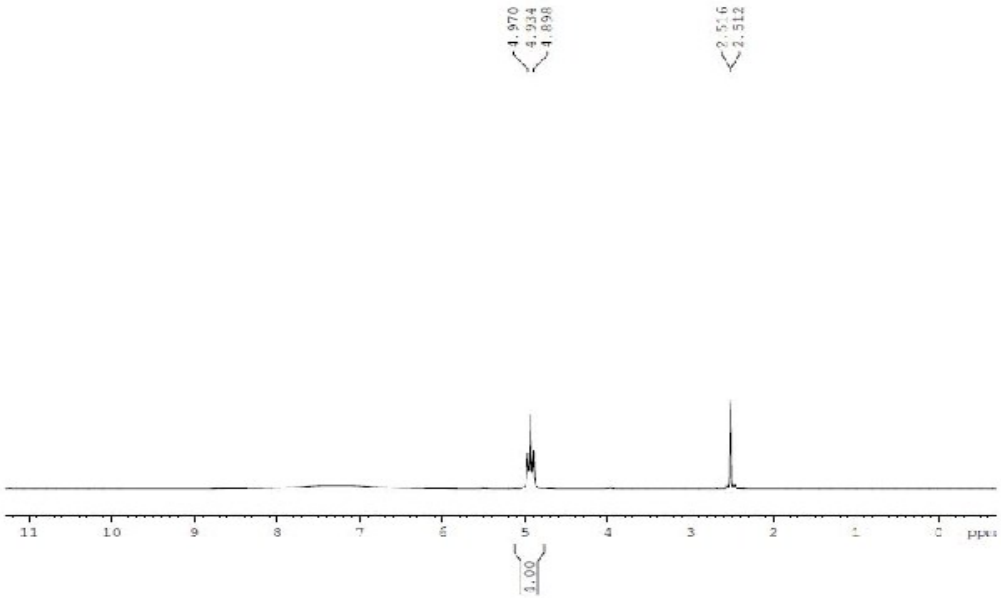


b. ^{13}C NMR.

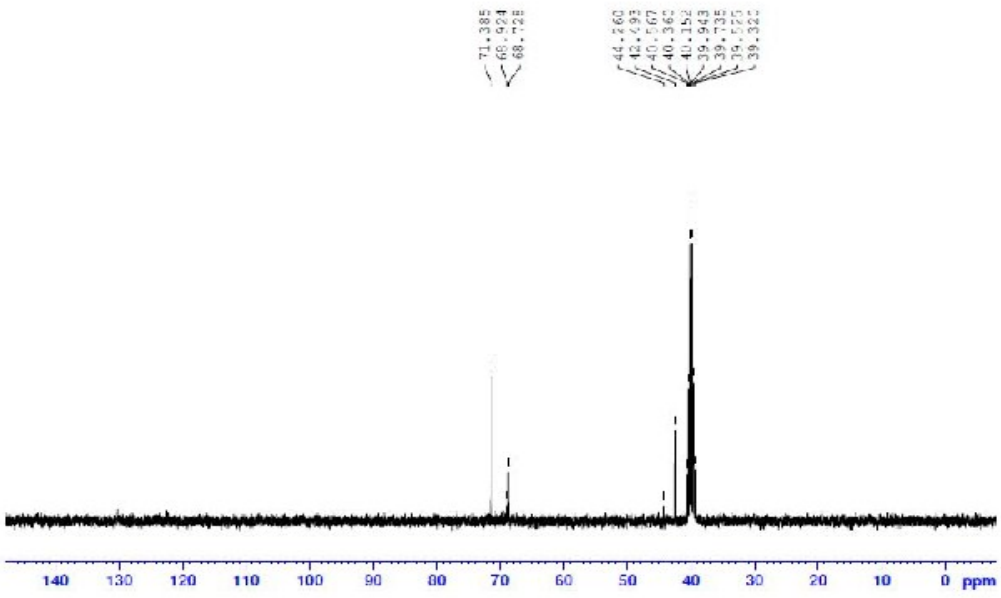


5. 2,2,3,3-Tetrafluorobutane-1,4-diyl dinitrate (5)

a. ^{1}H NMR

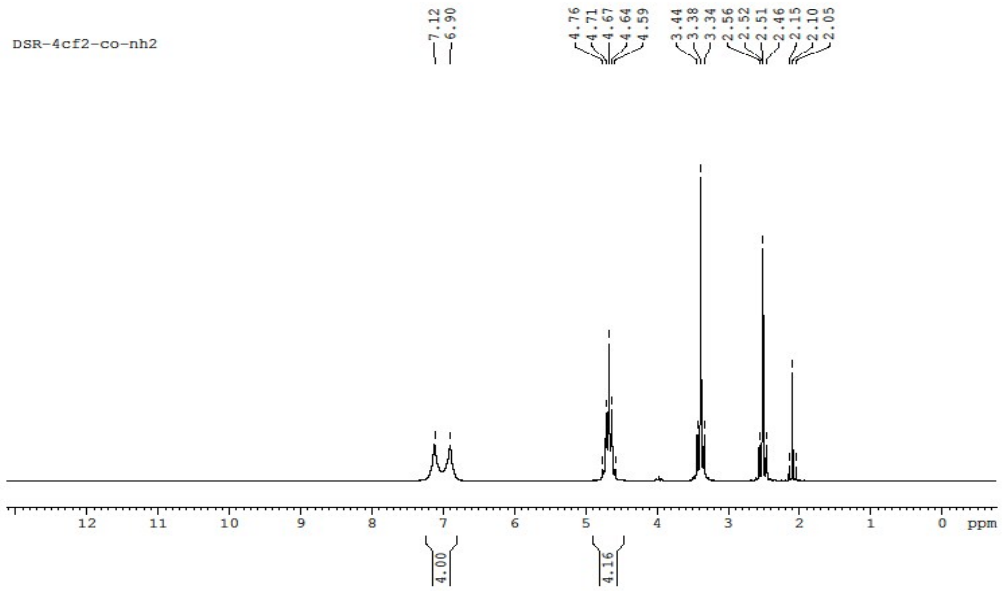


b. ^{13}C NMR

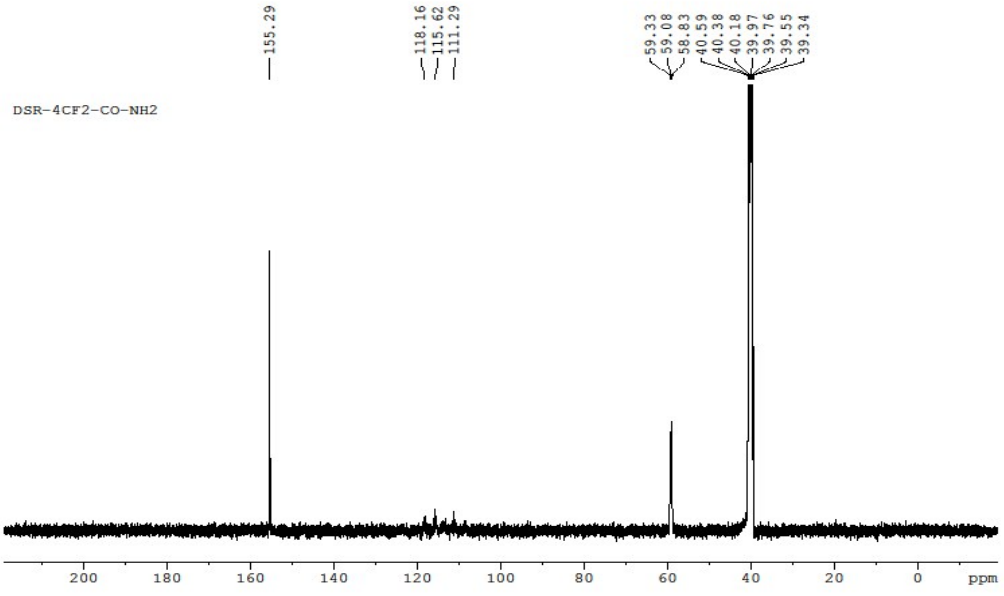


6. 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl dicarbamate (6)

a. ^{1}H NMR

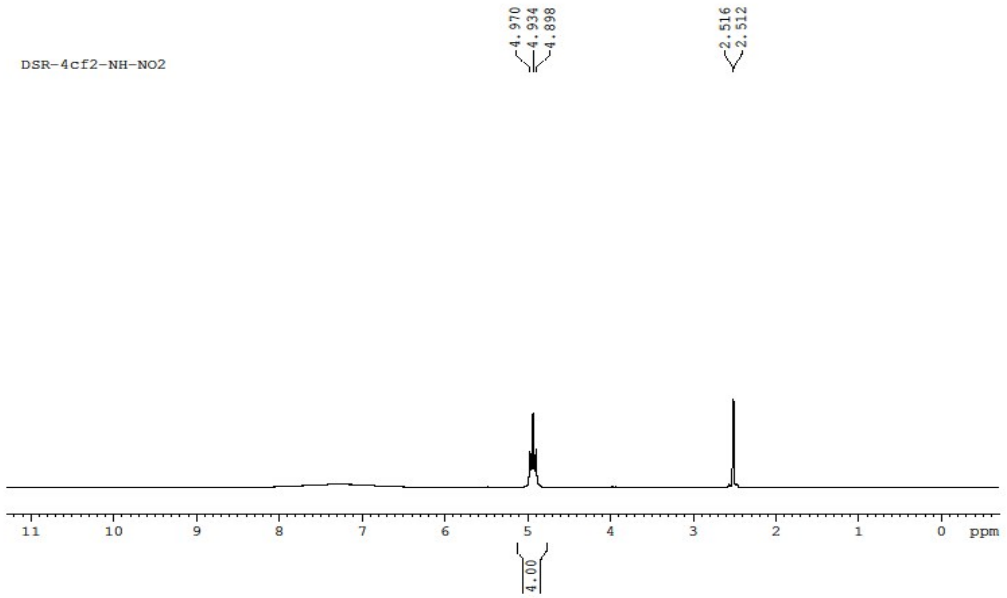


b. ^{13}C NMR

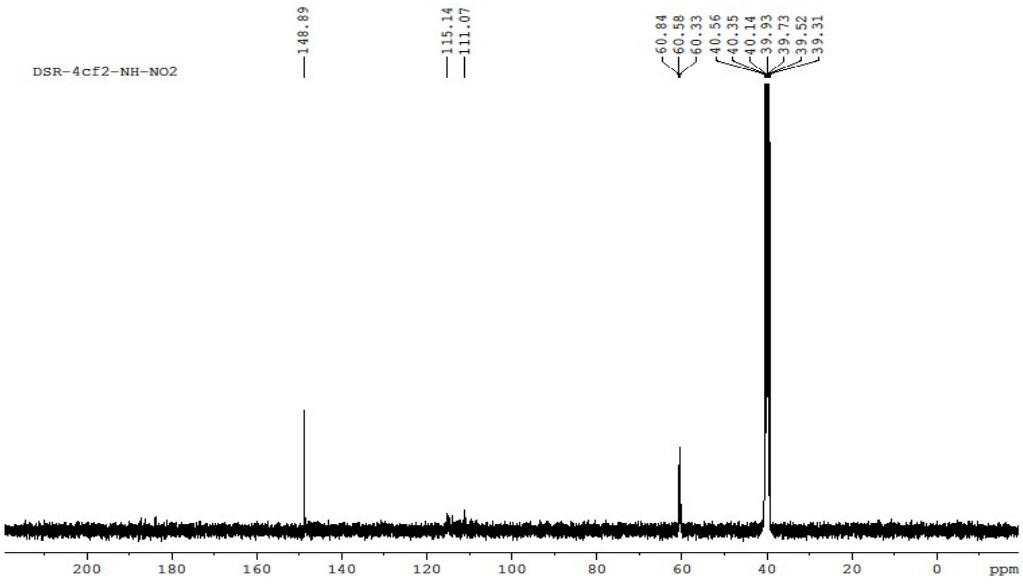


7. 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl bis(nitrocarbamate) (7)

a. ^{1}H NMR

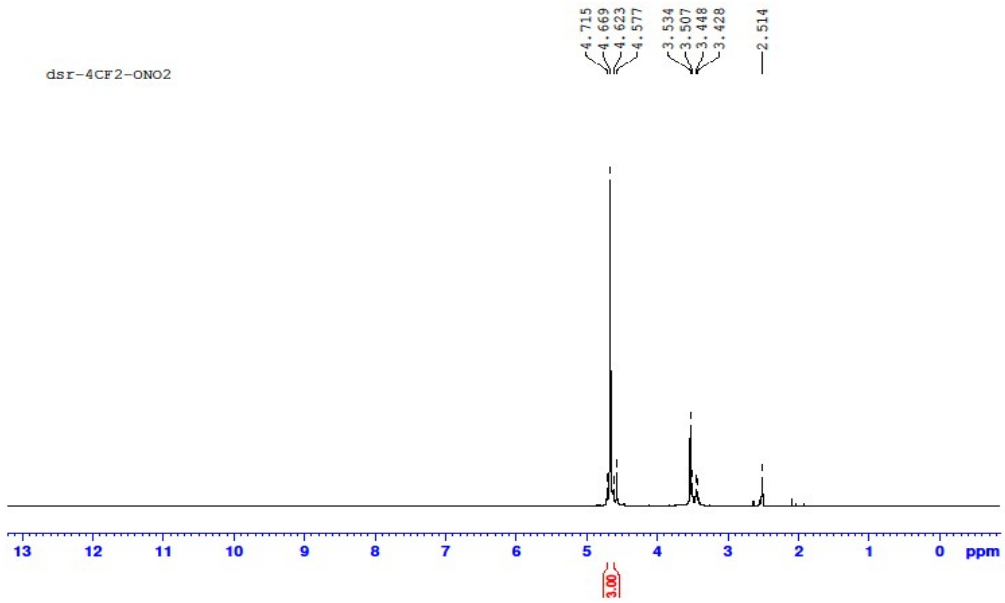


b. ^{13}C NMR

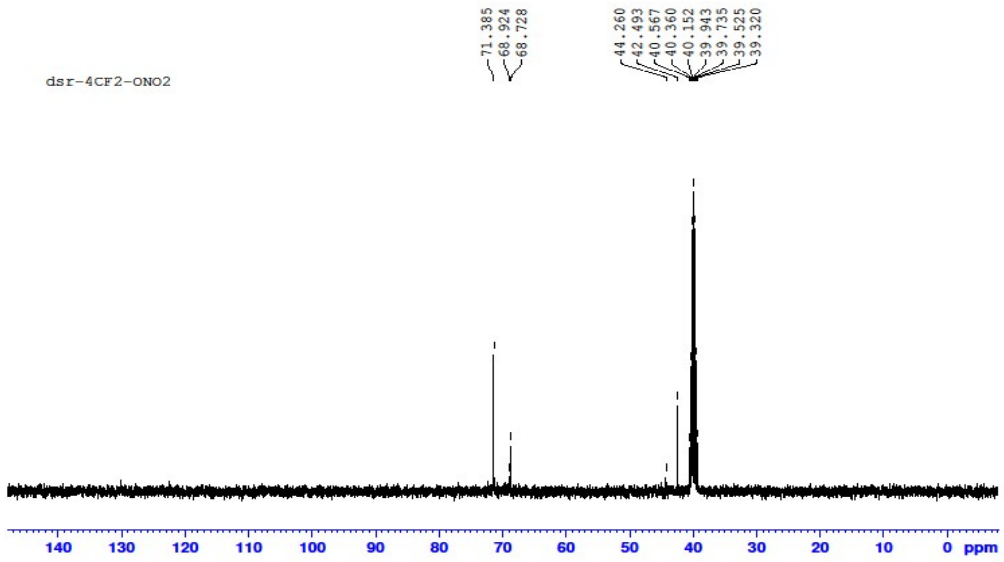


8. 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl dinitrate (8)

a. ^{1}H NMR



b. ^{13}C NMR



2. Theoretical calculations

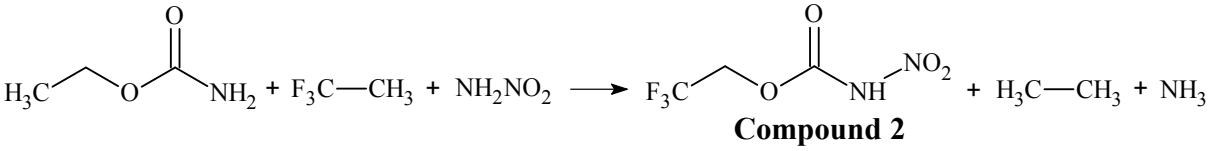
All quantum chemical calculations were performed using the Gaussian G09 program package.[1] The geometries of all the compounds were fully optimized at the DFT (B3PW91) level with 6-31G(d,p) basis set and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were found. Isodesmic reactions were used to compute the heats of formation and presented in Figure S1. The usage of the gas phase HOF (HOF_{gas}) in the calculation of detonation properties slightly overestimates the values of detonation velocity and detonation pressure, and hence, the solid phase HOF (HOF_{solid}) can efficiently reduce the errors. The HOF_{solid} is calculated as the difference between HOF_{gas} and heat of sublimation (HOF_{sub}) as,

$$HOF_{solid} = HOF_{gas} - HOF_{sub} \quad (1)$$

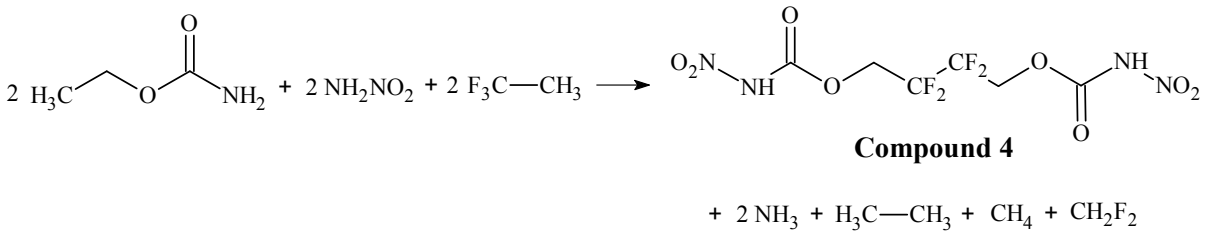
The heat of sublimation (HOF_{Sub}), which is required to convert the HOF_{Gas} to the solid state (HOF_{Solid}), was calculated from Equation (2),[2]

$$HOF_{sub} = 4.4307\ x\ 10^{-4}A^2 + 2.0599\left(v\sigma_{tot}^2\right)^{0.5} - 2.4825 \quad (2)$$

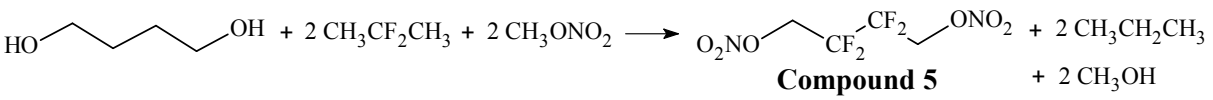
where A represent the surface area of the 0.001 electrons/bohr^3 isosurface of electronic density, *v* denotes the degree of balance between the positive and negative surface potentials, and σ_{tot}^2 is the electrostatic potential variance. These molecular surface properties were obtained using the Multiwfn program.[3]



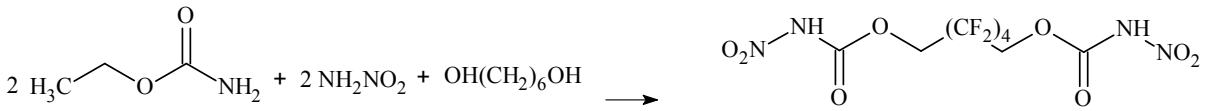
Compound 2



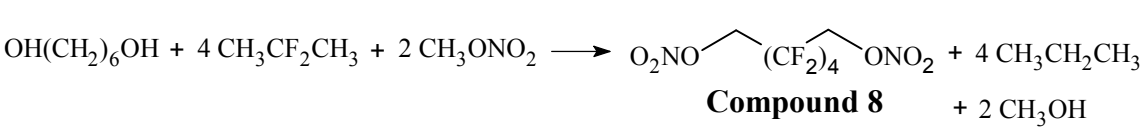
Compound 4



Compound 5



Compound 7



Compound 8

Scheme S1. Isodesmic reactions for compounds **2**, **4**, **5**, **7** and **8**.

3. Crystallographic data

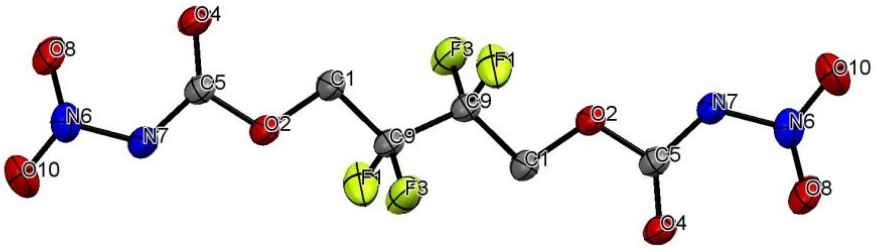


Figure 1. Molecular structure of Compound **4**.

Table 1: Selected bond lengths and bond angles for the Compound **4**.

Bond lengths (Å)					
Parameter	Value	Parameter	Values	Parameter	Value
F1–C9	1.353(3)	C5–N7	1.377(4)	N6–O10	1.204(4)
O2–C5	1.333(3)	C5–O4	1.186(4)	C9–C9	1.530(5)
O2–C1	1.434(3)	N6–N7	1.389(3)	C9–C1	1.501(4)
F3–C9	1.350(3)	N6–O8	1.203(4)		
Bond angles (°)					
C5–O2–C1	114.6(2)	O8–N6–O10	126.6(3)	F3–C9–F1	106.0(3)
O2–C5–N7	106.0(2)	O10–N6–N7	114.2(3)	F3–C9–C9	107.7(3)
O4–C5–O2	126.0(3)	C5–N7–N6	123.4(3)	F3–C9–C1	110.4(2)
O4–C5–N7	127.9(2)	F1–C9–C9	107.2(3)	C1–C9–C9	114.6(3)
O8–N6–N7	119.2(3)	F1–C9–C1	110.5(2)	O2–C1–C9	105.3(2)

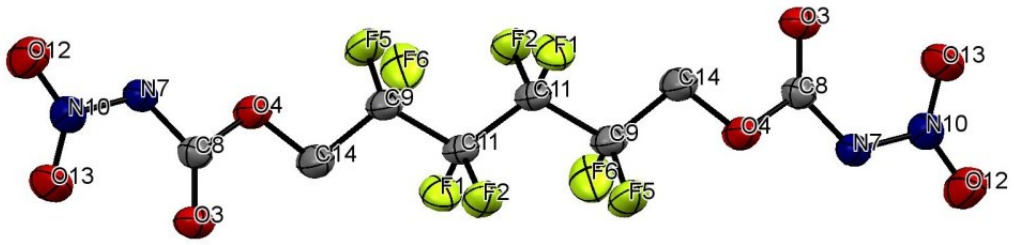


Figure 2. Crystal packing diagram for compound **7**.

Table 2: Selected bond lengths and bond angles for the Compound **7**.

Bond lengths (Å)					
Parameter	Value	Parameter	Values	Parameter	Value
F1–C11	1.339(2)	F5–C9	1.344(3)	C9–C14	1.507(3)
F2–C11	1.341(2)	F6–C9	1.346(2)	N10–O12	1.200(3)
O3–C8	1.182(3)	N7–C8	1.390(3)	N10–O13	1.198(3)
O4–C8	1.342(2)	N7–N10	1.377(3)	C11–C11	1.550(4)
O4–C14	1.430(2)	C9–C11	1.557(3)		
Bond angles (°)					
C8–O4–C14	114.19(17)	F5–C9–C14	110.72(18)	F1–C11–F2	108.72(15)
N10–N7–C8	123.28(17)	F6–C9–C11	108.08(17)	F1–C11–C9	107.58(15)
O3–C8–O4	125.63(19)	F6–C9–C14	110.56(18)	F1–C11–C11	108.58(18)
O3–C8–N7	128.45(18)	C14–C9–C11	111.83(16)	F2–C11–C9	106.75(16)
O4–C8–N7	105.88(16)	O12–N10–N7	114.5(2)	F2–C11–C11	108.97(18)
F5–C9–F6	105.94(18)	O13–N10–N7	119.1(2)	C11–C11–C9	116.04(19)
F5–C9–C11	109.51(16)	O13–N10–O12	126.4(2)	O4–C14–C9	104.68(17)

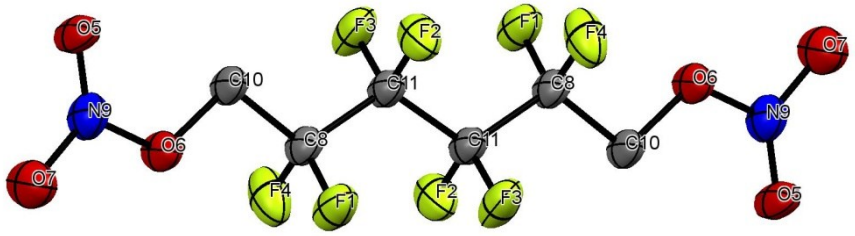


Figure 3. Molecular structure of Compound **8**.

Table 3: Selected bond lengths and bond angles for the Compound **8**.

Bond lengths (Å)					
Parameter	Value	Parameter	Values	Parameter	Value
F1–C8	1.350(4)	O5–N9	1.204(4)	C8–C10	1.517(4)
F2–C11	1.342(4)	O6–N9	1.350(3)	C8–C11	1.543(4)
F3–C11	1.333(4)	O6–C10	1.427(4)	C11–C11	1.554(5)
F4–C8	1.342(4)	O7–N9	1.326(4)		
Bond angles (°)					
N9–O6–C10	116.2(2)	C10–C8–C11	112.8(3)	F2–C11–C11	108.6(3)
F1–C8–C10	109.5(2)	O5–N9–O6	122.7(3)	F3–C11–F2	108.2(3)
F1–C8–C11	108.4(2)	O5–N9–O7	127.0(3)	F3–C11–C8	107.1(2)
F4–C8–F1	106.1(3)	O7–N9–O6	110.2(3)	F3–C11–C11	108.8(3)
F4–C8–C10	111.0(3)	O6–C10–C8	103.5(3)	C8–C11–C11	115.9(3)
F4–C8–C11	108.8(2)	F2–C11–C8	107.9(2)		

Compound 4: CCDC structure deposit information
CCDC 1437815

Summary of Data CCDC 1437815

Compound Name:
Formula: C6 H6 F4 N4 O8
Unit Cell Parameters: a 11.4164(17) b 13.6481(9) c 4.9679(8) P21/n

Compound 7: CCDC structure deposit information
CCDC 1428609

Summary of Data CCDC 1428609

Compound Name:
Formula: C8 H6 F8 N4 O8
Unit Cell Parameters: a 4.99141(16) b 20.7151(8) c 7.2618(2) P21/c

Compound 8: CCDC structure deposit information
CCDC 1424012

Summary of Data CCDC 1424012

Compound Name:
Formula: C6 H4 F8 N2 O6
Unit Cell Parameters: a 5.1438(5) b 6.2912(9) c 9.9448(12) P-1

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. V. Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. L. G. Liu, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al- Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision D. 01*, Gaussian, Inc., Wallingford, CT, **2004**.

2. P. Politzer, Y. Ma, P. Lane, M. C. Concha, *Int. J. Quant. Chem.* 2005, **105**, 341–347.

3. T. Lu, F. Chen, *J. Comput. Chem.* 2012, **33**, 580–592.