Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Potassium Complexes Containing Bidentate Pyrrole Ligands: Synthesis, Structures, and Catalytic Activity for the Cyclotrimerization of Isocyanates

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X-ray Crystallography.

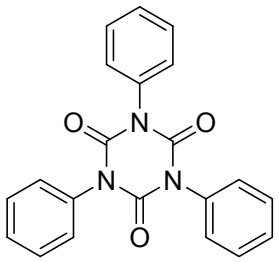
Single-crystal X-ray diffraction data of the compounds were collected on a Bruker Smart Apex CCD diffractometer using monochromated Mo Kα radiation, λ = 0.71073 Å. A total of N reflections were collected by using the ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (SADABS).[1] Each structure was solved by the direct method and refined on F^2 by full matrix least-squares (SHELX-14)[2] using all unique data. Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL-2014).[2] Details of the modeling of disorder in the crystals can be found in their CIF files. Data collection, and structure refinement details for complex **1** and **2** are gathered in Table 1. Details of the modeling of disorder in the crystals can be found in their CIF files.

Table 1. Single Crystal X-ray Data and Structure Refinement Details for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{13}H_{21}KN_2O$	$C_{18}H_{30}K_2N_4$
Formula weight	260.42	380.66
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
space group	Pnma	Pccn
a (Å)	12.2184(8)	17.8883(19)
b (Å)	7.5854(5)	22.588(2)
c (Å)	15.6270(10)	10.5492(11)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Volume ($Å^3$)	1448.33(16)	4262.6(8)
Z	4	8
D_c (g/cm^{-3})	1.194	1.186
M (mm^{-1})	0.355	0.451
F(000)	560	1632
Crystal size (mm)	0.30 x 0.30 x 0.20	0.30 x 0.30 x 0.20
Theta range for data collection	2.985 to 25.05 deg.	2.88 to 25.05 deg.
Reflections collected / unique	10514 / 1385 [R(int) = 0.0428]	26666 / 3776 [R(int) = 0.0603]
Completeness to theta = 25.05	99.8 %	99.7 %
Max. and min. transmission	0.9324 and 0.9010	0.9152 and 0.8765
Data / restraints / parameters	1385 / 8 / 103	3776 / 0 / 231
Goodness-of-fit	1.054	1.037
R_1 / wR_2 [I>2sigma(I)]	0.0654 / 0.1585	0.0657 / 0.1870
R_1 / wR_2 (all data)	0.0863 / 0.1720	0.0853 / 0.2036

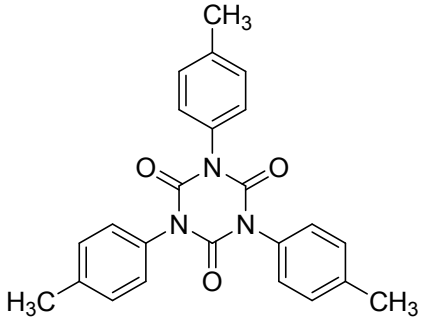
Characterization data of isocyanurates

(Isocyanurates were identified through comparisons with the corresponding ^{1}H NMR, ^{13}C NMR data reported in the literatures.)



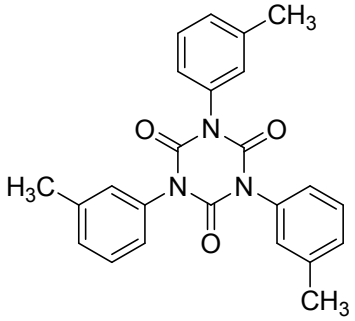
1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione[3]

White solid, yield: 98%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.82 (s), 133.73 (s), 129.50 (s), 128.55 (s). mp: 278-279 °C.



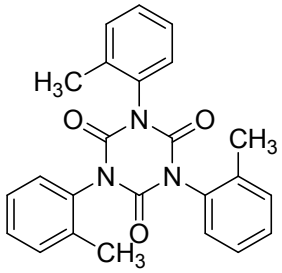
1,3,5-Tris(4-methylphenyl)-1,3,5-triazinane-2,4,6-trione[3]

White solid, yield: 97%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (q, J = 8.6 Hz, 4H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.01 (s), 139.40 (s), 131.23 (s), 130.11 (s), 128.20 (s), 21.37 (s). mp: 265.5-266.0 °C.



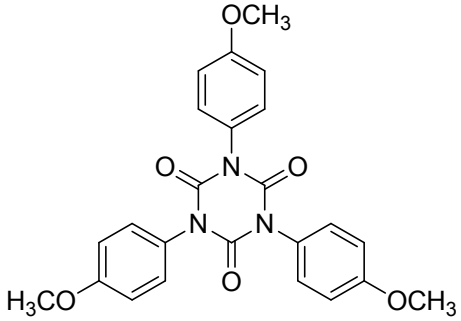
1,3,5-Tris(3-methylphenyl)-1,3,5-triazinane-2,4,6-trione[4]

White solid, yield: 95%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.92 (s), 139.57 (s), 133.59 (s), 130.26 (s), 129.26 (s), 129.05 (s), 125.45 (s), 21.39 (s). mp: 280.0-281.0 °C.



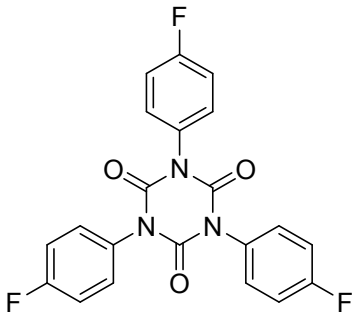
1,3,5-Tris(2-methylphenyl)-1,3,5-triazinane-2,4,6-trione[5]

White solid, yield: 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.23 (m, 4H), 2.31 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.11 (t, *J* = 5.9 Hz), 136.03 (s), 135.84 (s), 135.69 (s), 132.93 (s), 131.33 (t, *J* = 3.6 Hz), 129.89 (s), 128.78 (t, *J* = 10.1 Hz), 127.35 (t, *J* = 8.1 Hz), 17.56 (t, *J* = 10.6 Hz). mp: 157.0-158.0 °C.



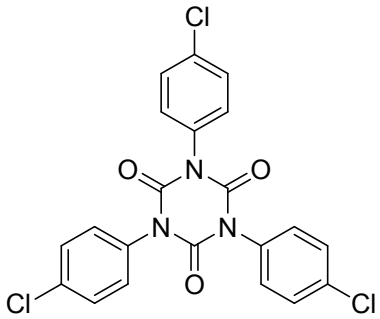
1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane-2,4,6-trione[3]

White solid, yield: 95%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.03 (s), 149.27 (s), 129.56 (s), 126.41 (s), 114.72 (s), 55.63 (s). mp: 258.0-258.5 °C.



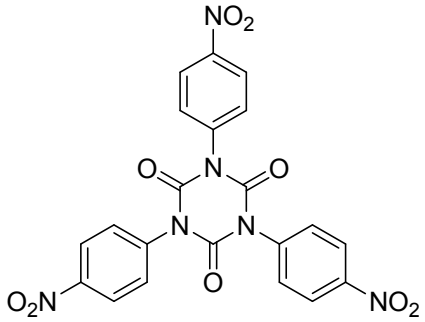
1,3,5-Tris(4-fluorophenyl)-1,3,5-triazinane-2,4,6-trione[6]

White solid, yield: 93%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.19 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.74 (s), 162.09 (s), 148.66 (s), 130.38 (d, *J* = 8.9 Hz), 129.33 (d, *J* = 3.4 Hz), 116.78 (s), 116.63 (s). mp: 267.5-268 °C.



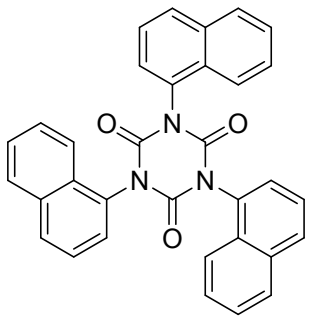
1,3,5-tris(4-chlorophenyl)-1,3,5-triazinane-2,4,6-trione[3]

White solid, yield: 94%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.28 (s), 135.75 (s), 131.86 (s), 129.88 (s). mp: 318.0-318.5 °C.



1,3,5-tris(4-nitrophenyl)-1,3,5-triazinane-2,4,6-trione[7]

Yellow solid, yield: 91%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H). mp: 408-409.5 °C.



1,3,5-tris(1-naphthyl)-1,3,5-triazinane-2,4,6-trione[7]

White solid, yield: 95%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02-7.91 (m, 3H), 7.71 (q, *J* = 7.9 Hz, 2H), 7.61-7.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.87 (s), 134.66 (s),

130.47 (s), 130.09 (s), 129.95 (s), 129.10 (s), 127.87 (s), 127.42 (s), 126.71 (s), 125.56 (s), 121.16 (s), 120.91 (s). mp: 339.0-340.0 °C.

References

[1] G. M. Sheldrick, Correction Software; University of Göttingen: Göttingen, Germany, 1996.

[2] (a) G. M. Sheldrick, *Acta Crystallographica Section A: Found. Adv.*, 2015, **71**, 3-8; (b) G. M. Sheldrick, *Acta Crystallographica Section C: Struct. Chem.*, 2015, **71**, 3-8.

[3] J. C. Shi, Z. Q. Guo, X. H. Wei, D. S. Liu, M. F. Lappert, *Synlett.*, 2011, 13, 1937-1939.

[4] B. Bantu, G. Manohar, U. Decker, K. Wurst, A. M. Schmidt, M. R. Buchmeiser, *Chem. Eur. J.* 2009, 15, 3103-3109.

[5] H. A. Duong, M. J. Cross, J, Louie, *Org. Lett.,* 2004, 6, 4679-4681.

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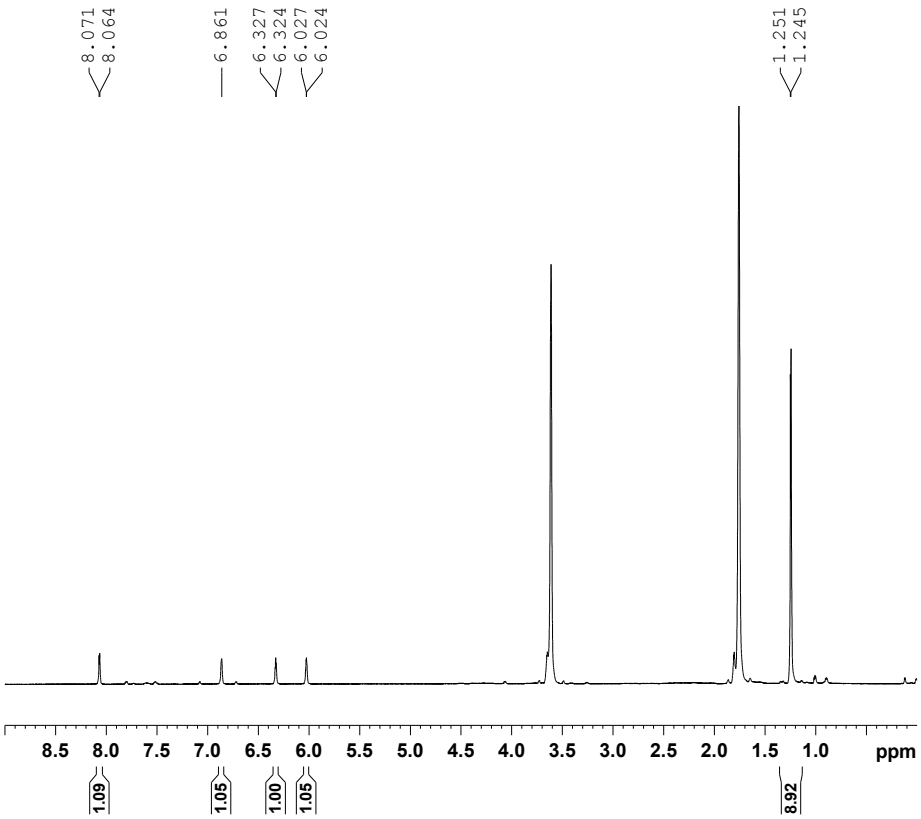
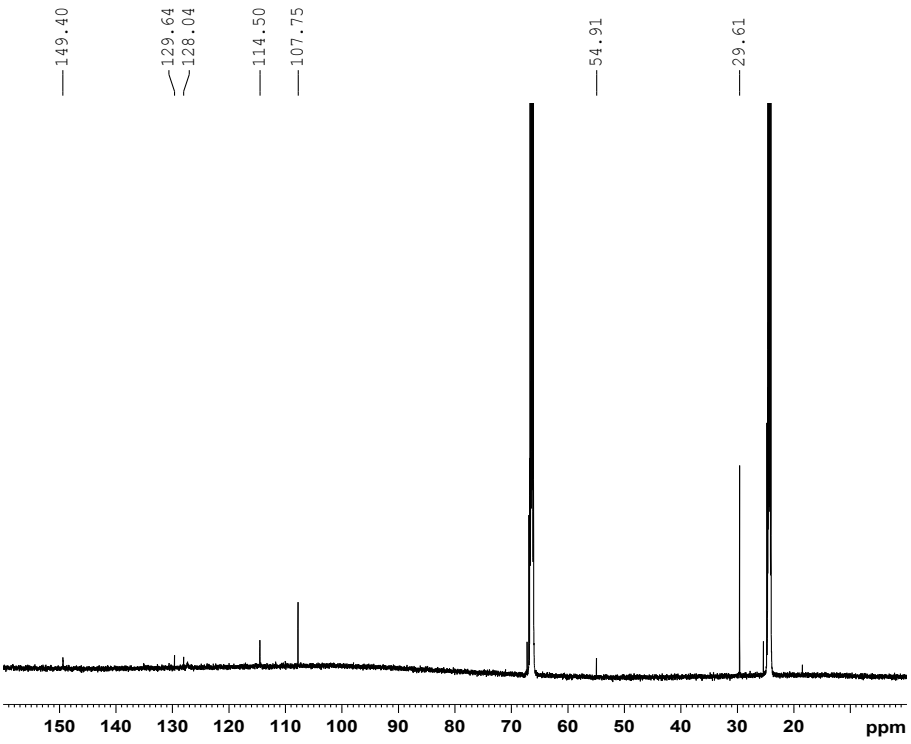
[7] S. M. Raders, J. G. Verkade, *J. Org. Chem.*, 2010, 75, 5308-5311.

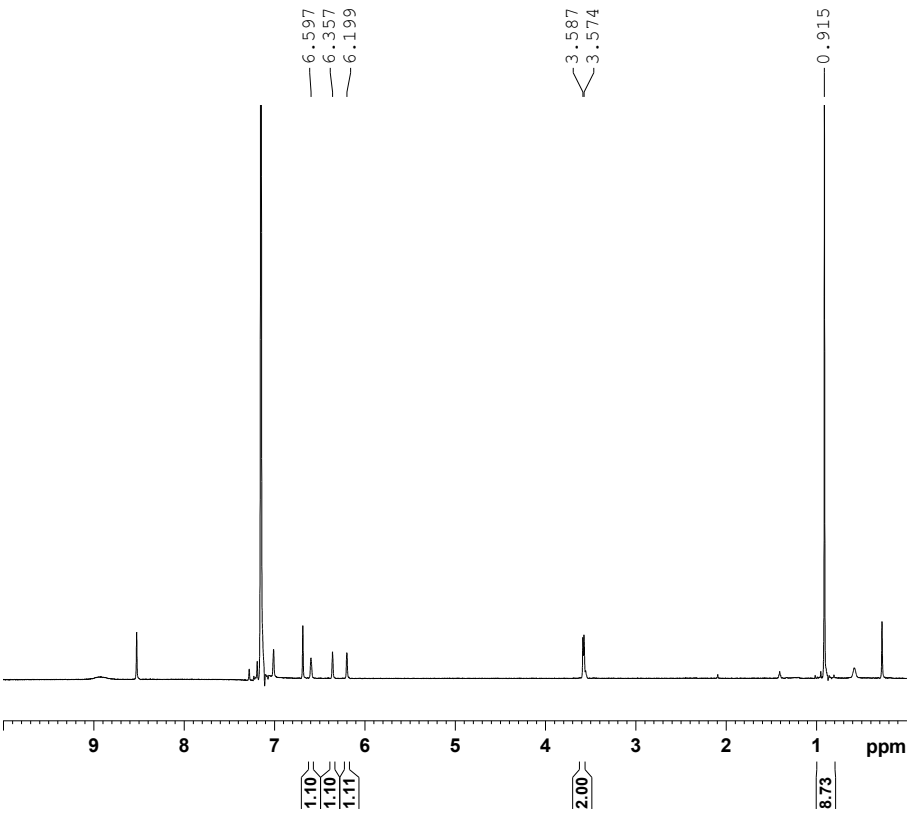
^{1}H and ^{13}C NMR Spectra of Potassium Complexes



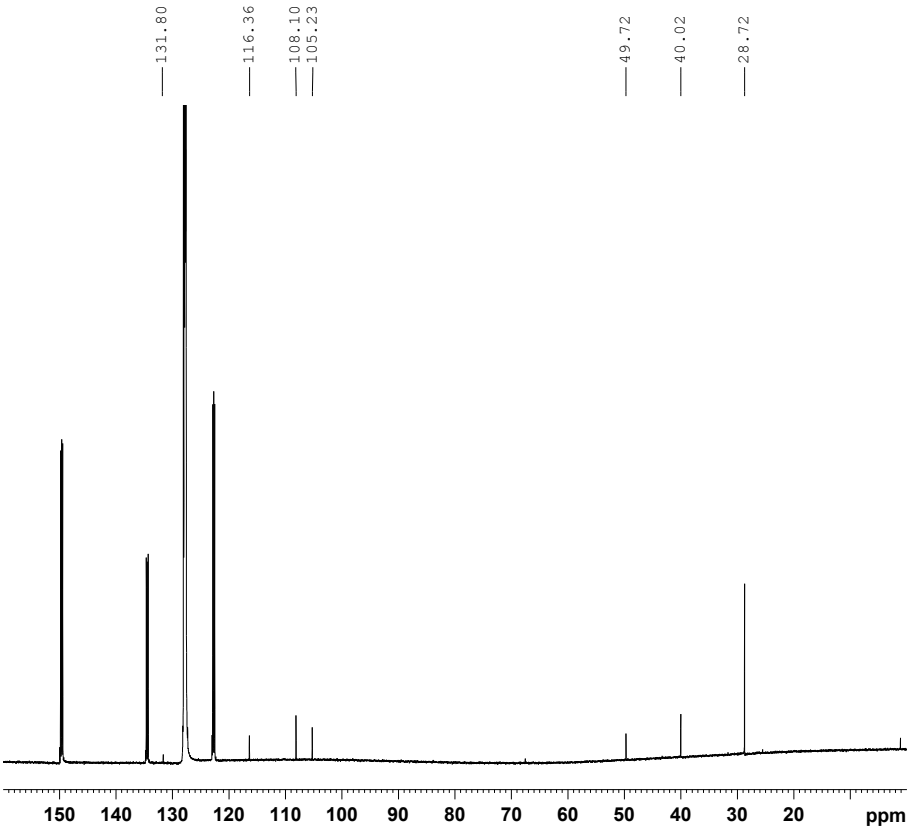
^{1}H NMR Spectra of Complex **1**



^{13}C NMR Spectra of Complex **1**

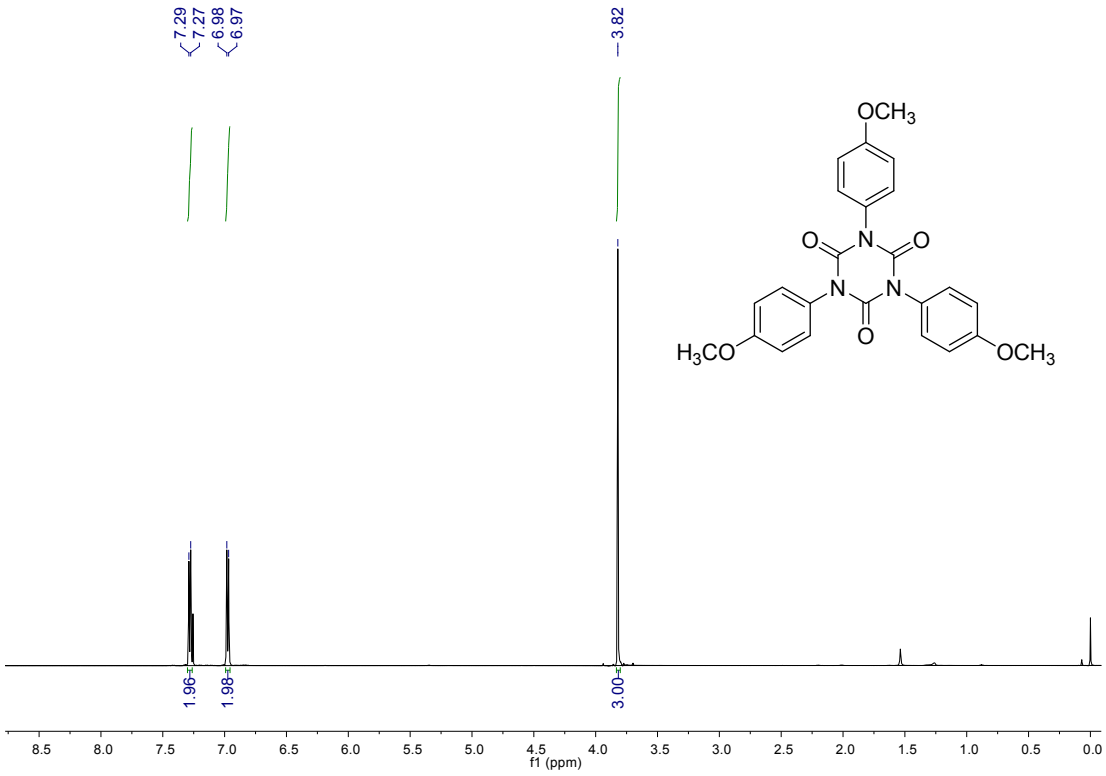


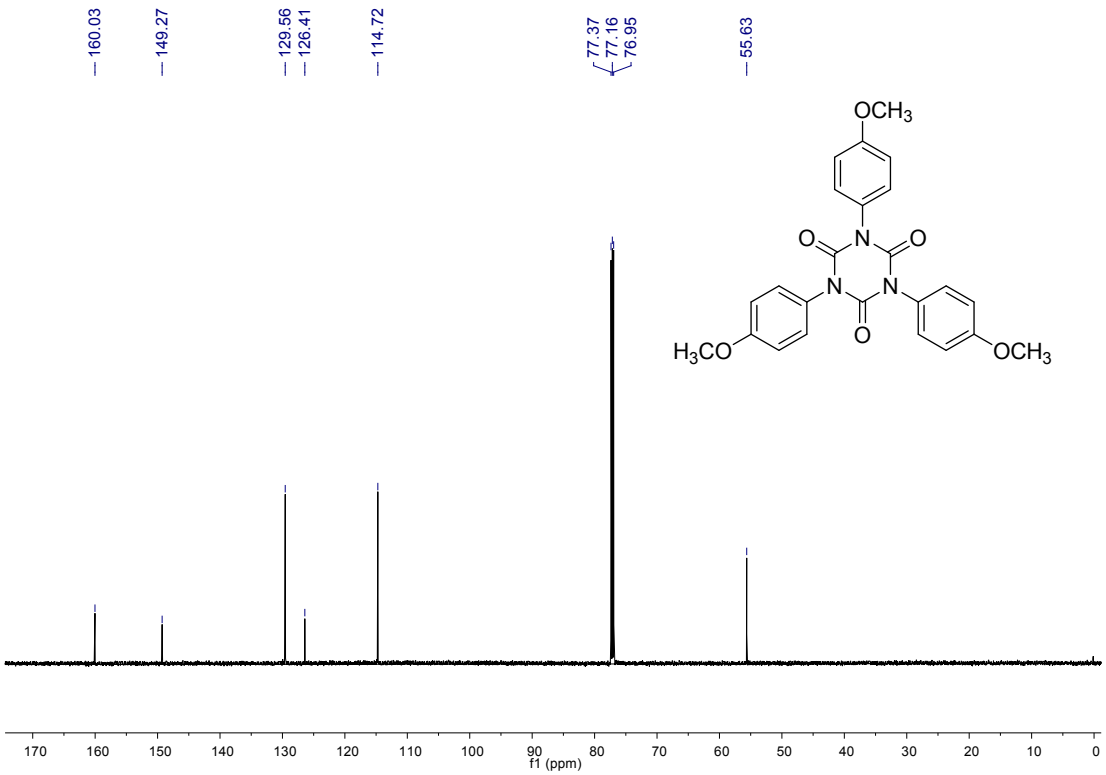
^{1}H NMR Spectra of Complex **2**

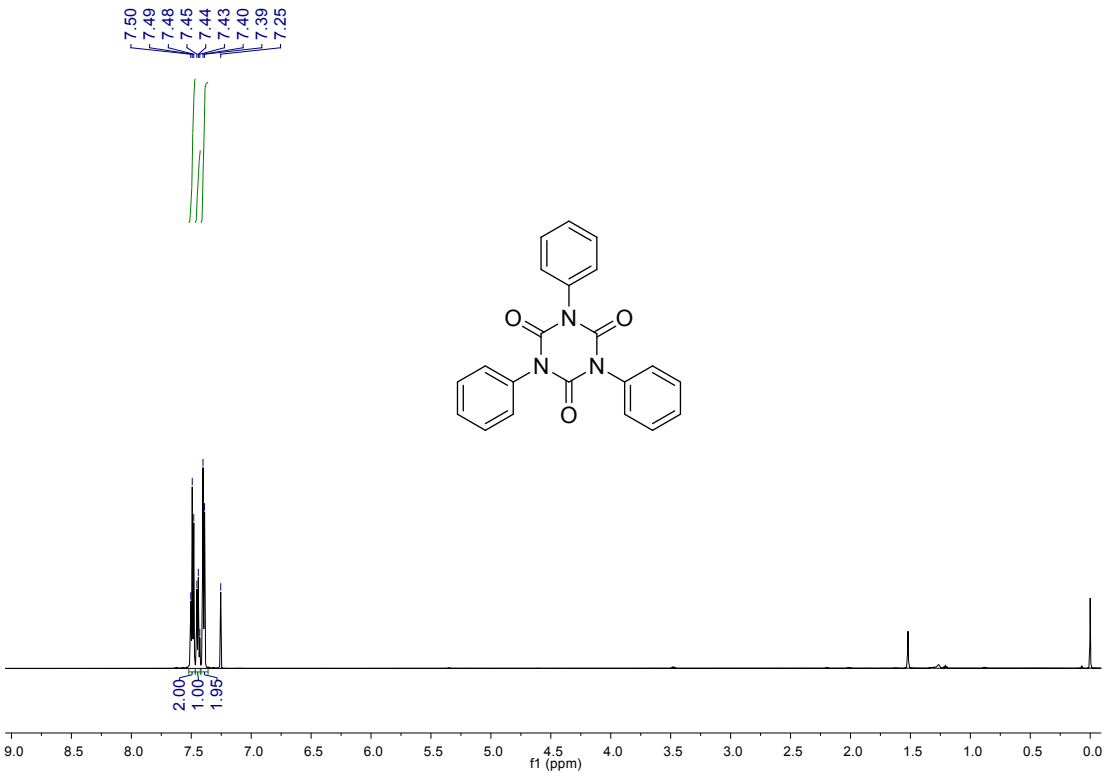


^{13}C NMR Spectra of Complex **2**

^{1}H and ^{13}C NMR Spectra of Isocyanurates



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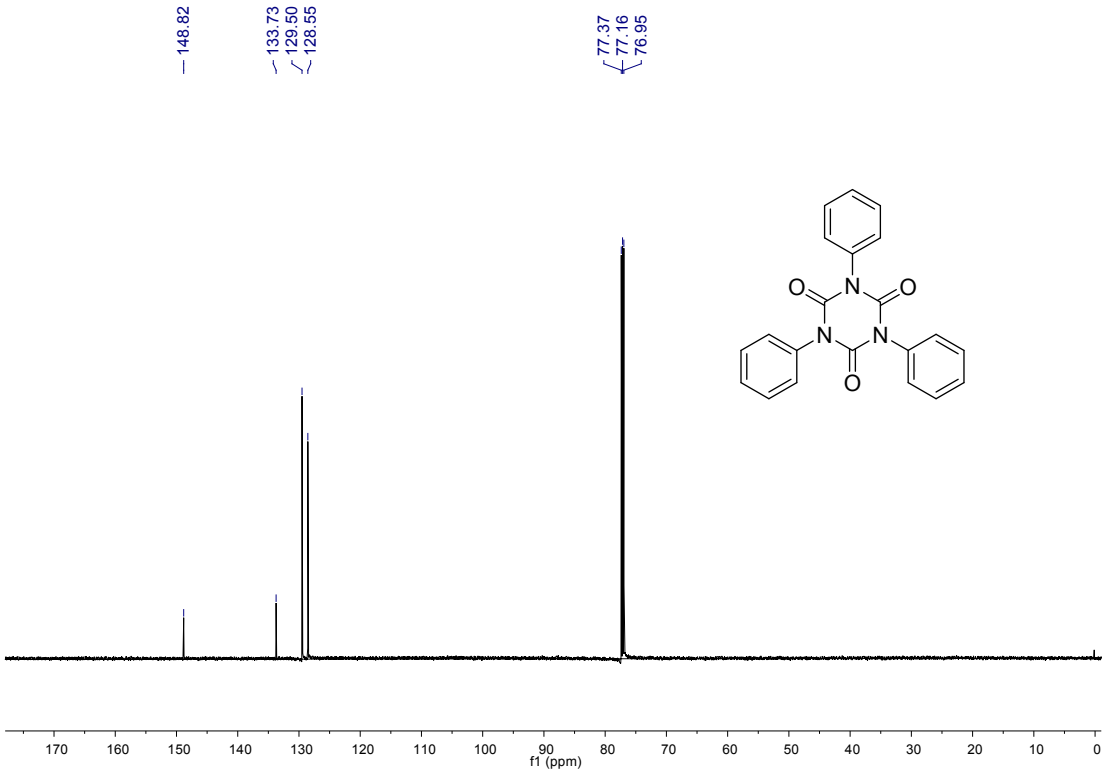
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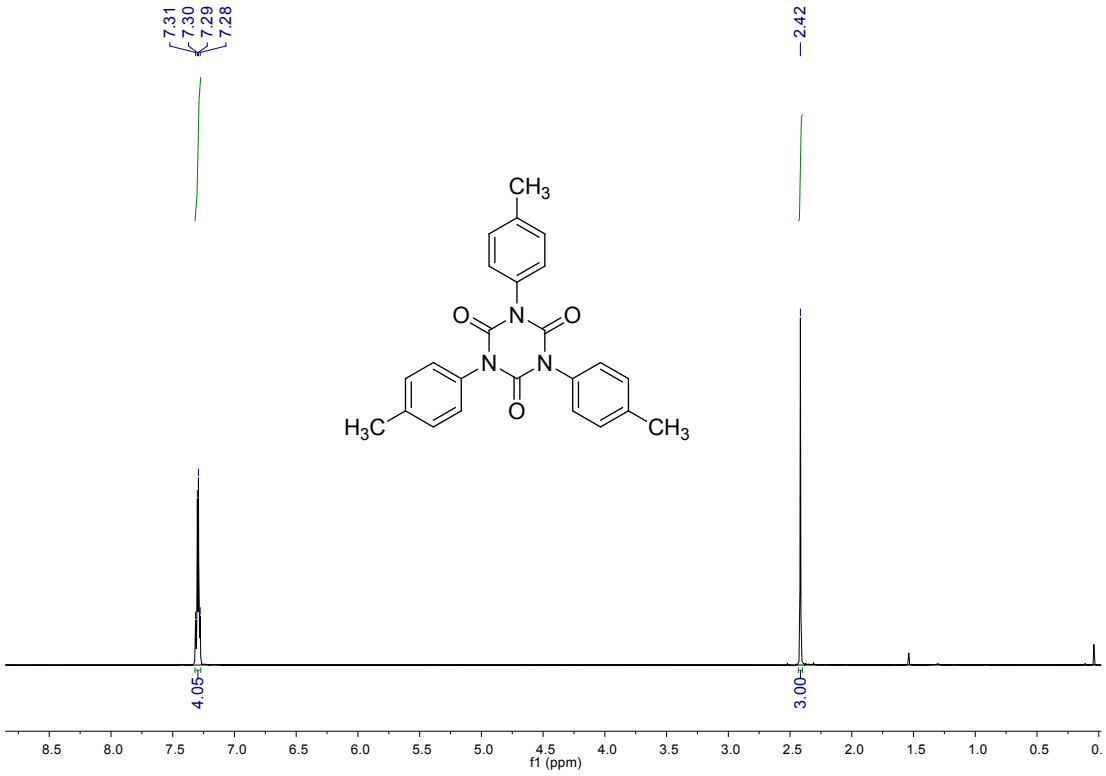
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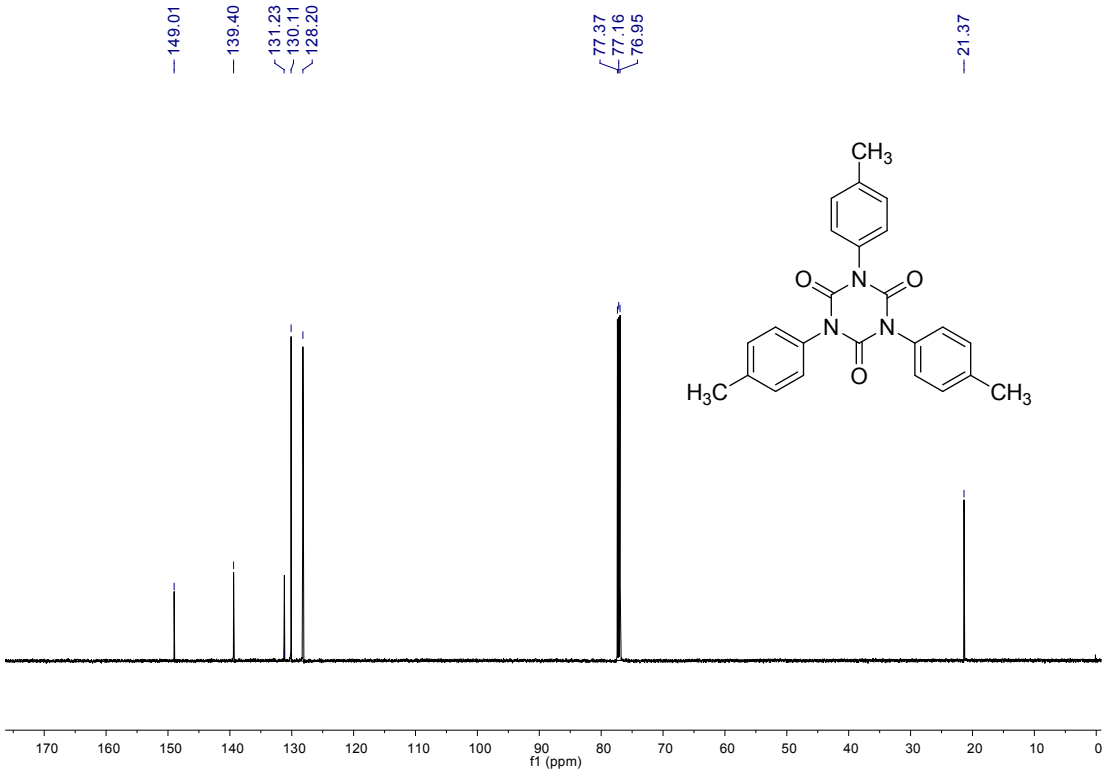
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H3C
CH3
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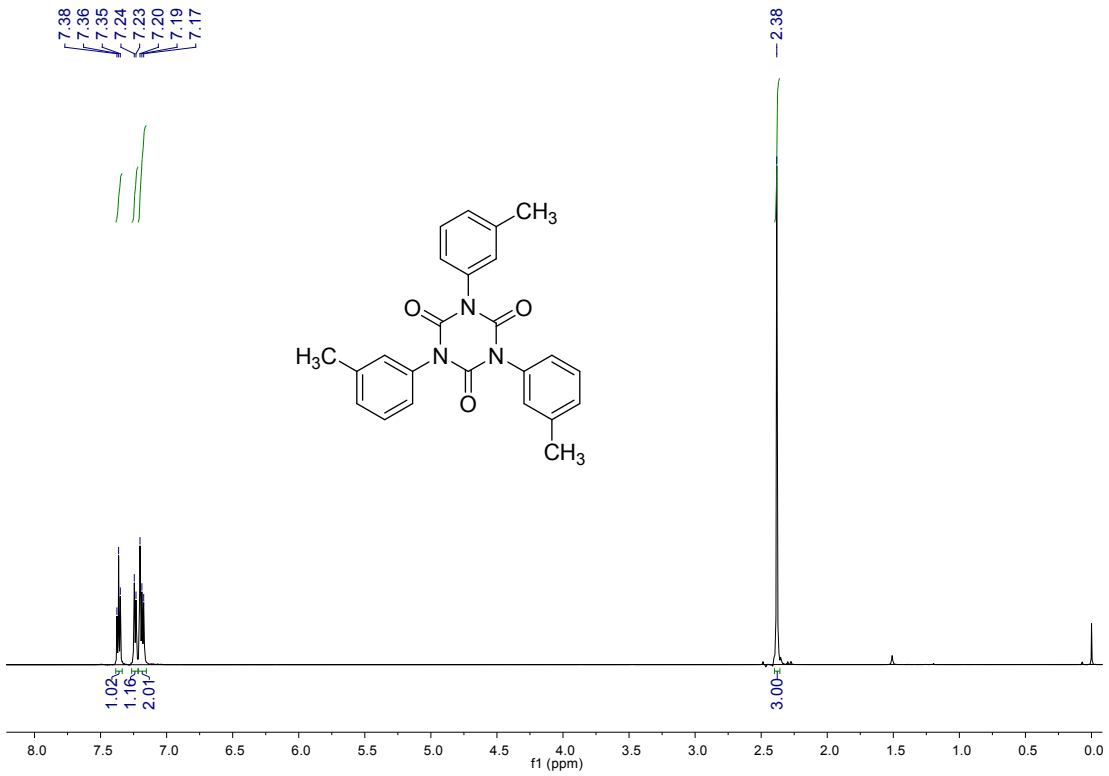
f1 (ppm)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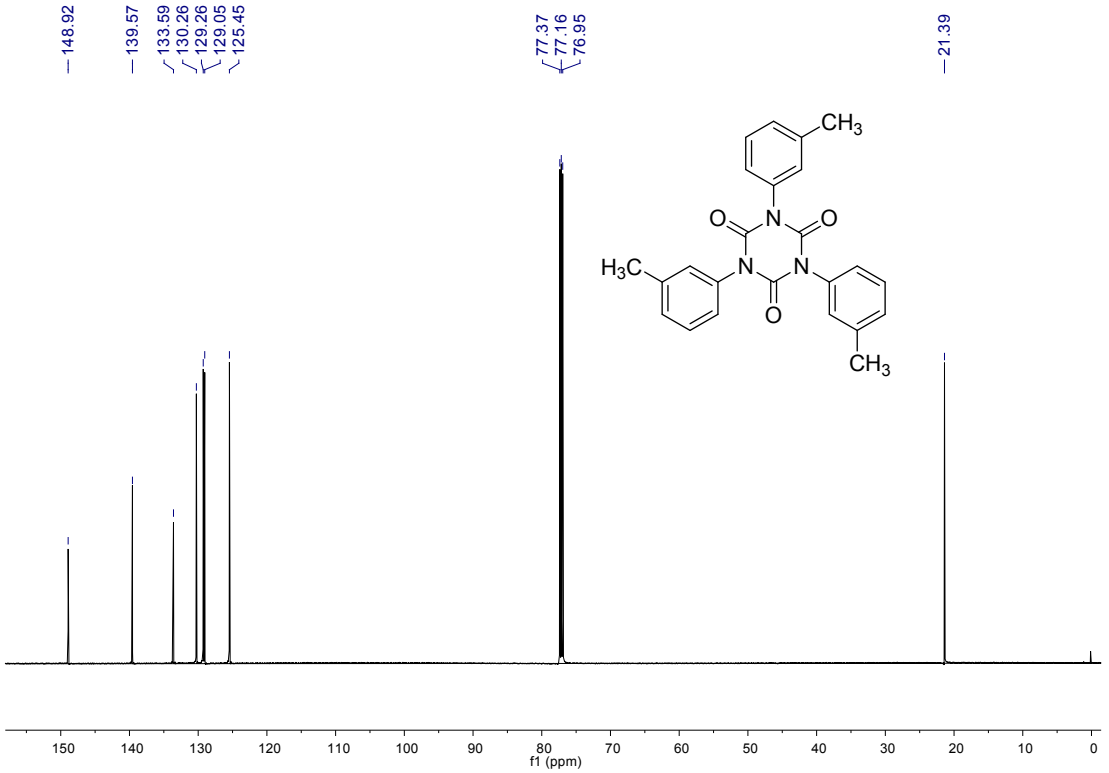
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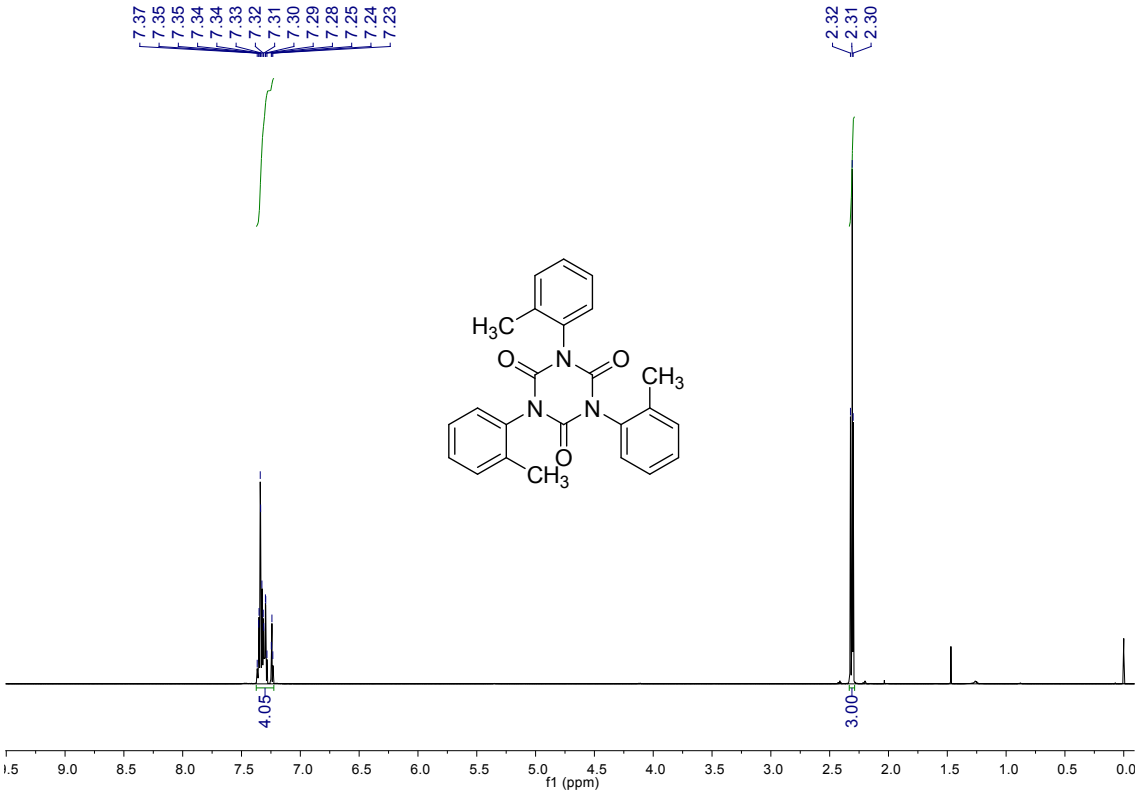
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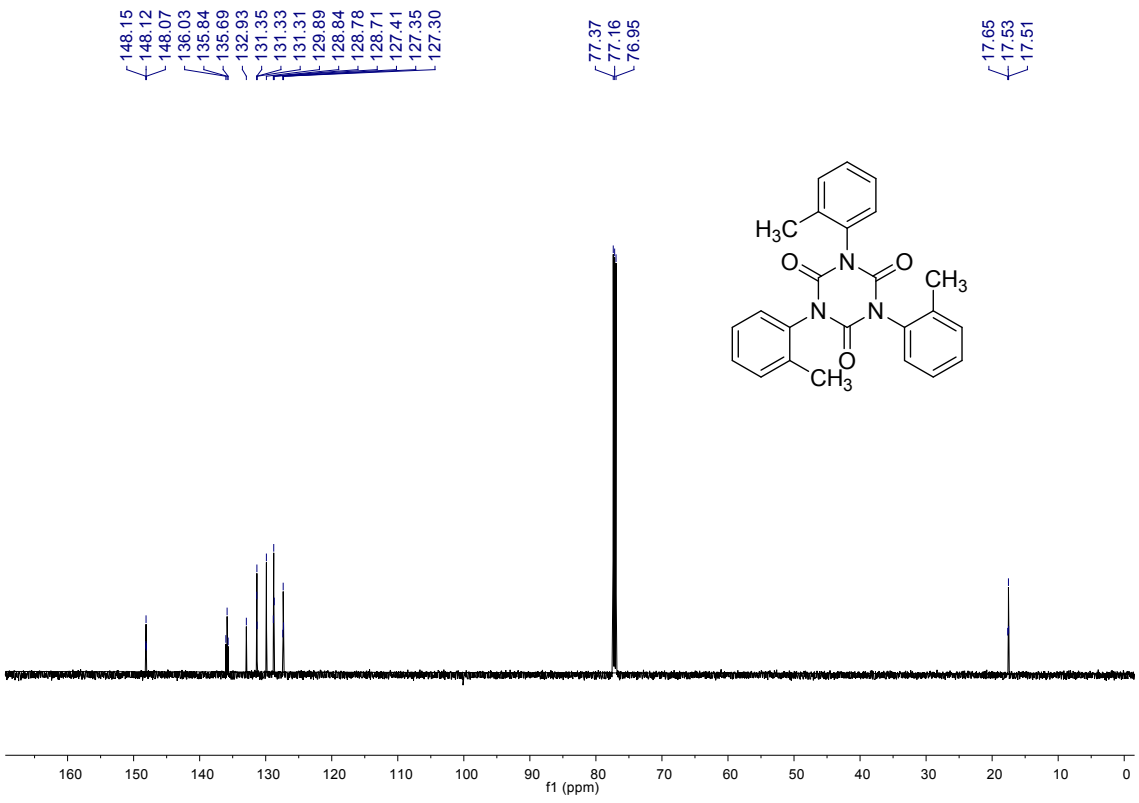
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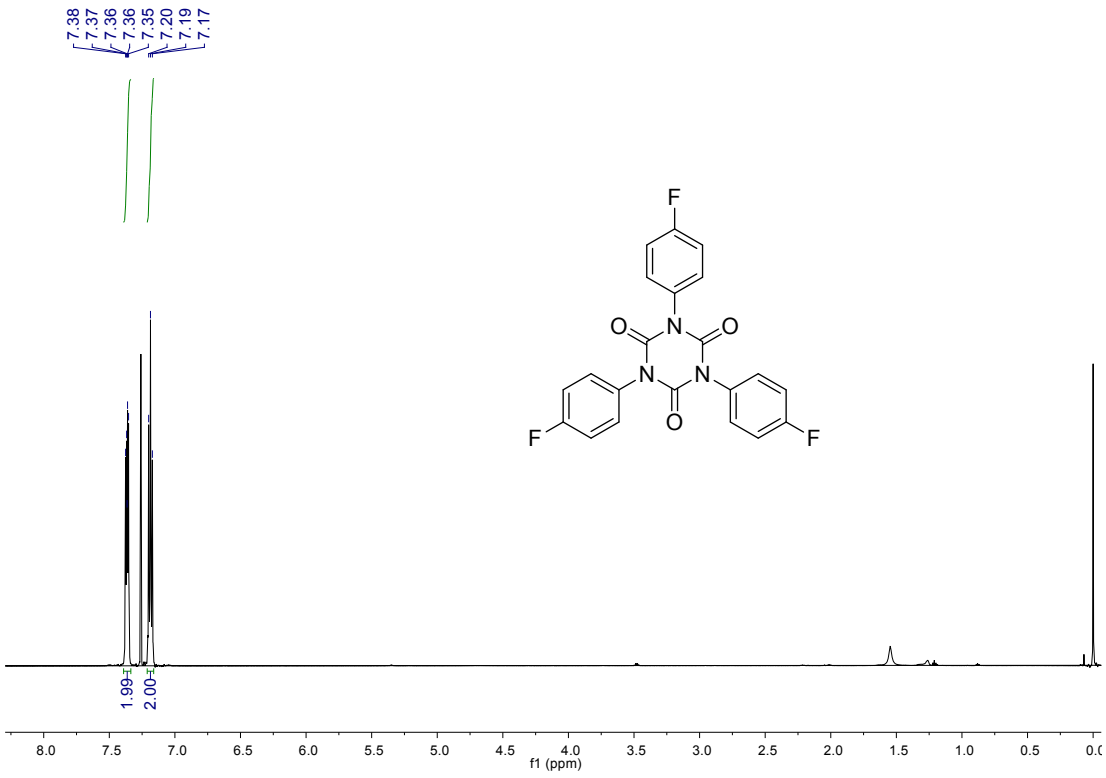
CH3
f1 (ppm)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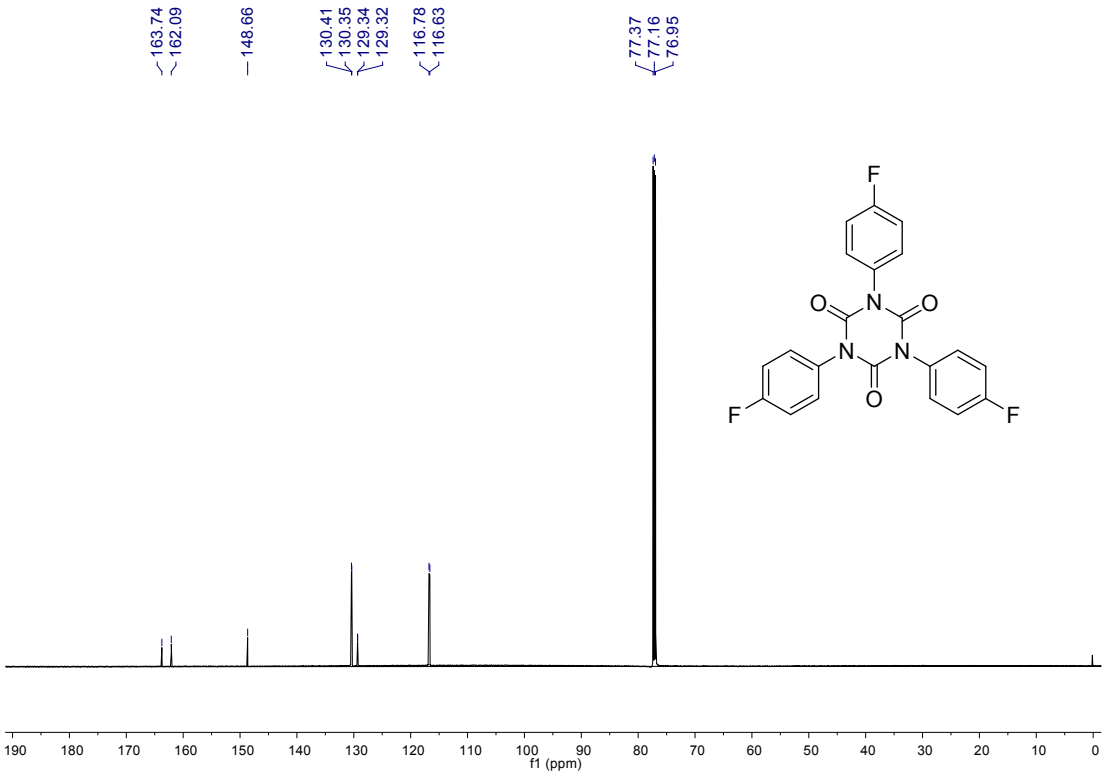
1.0
0.5
f1 (ppm)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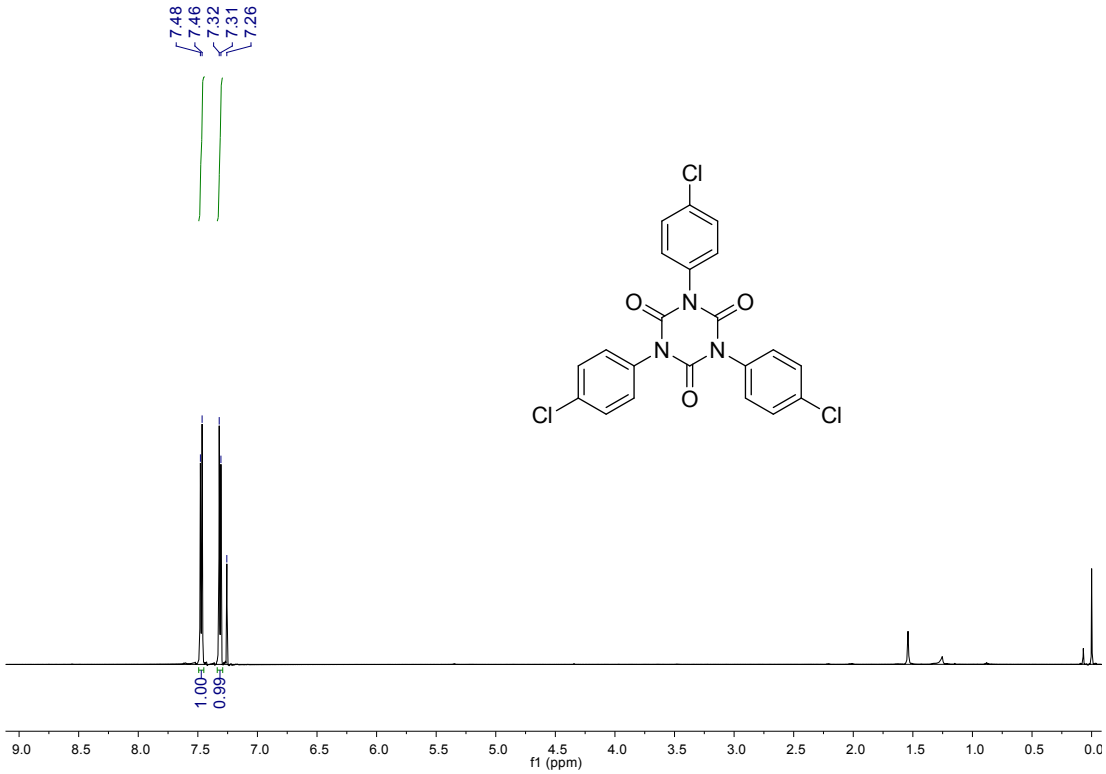
f1 (ppm)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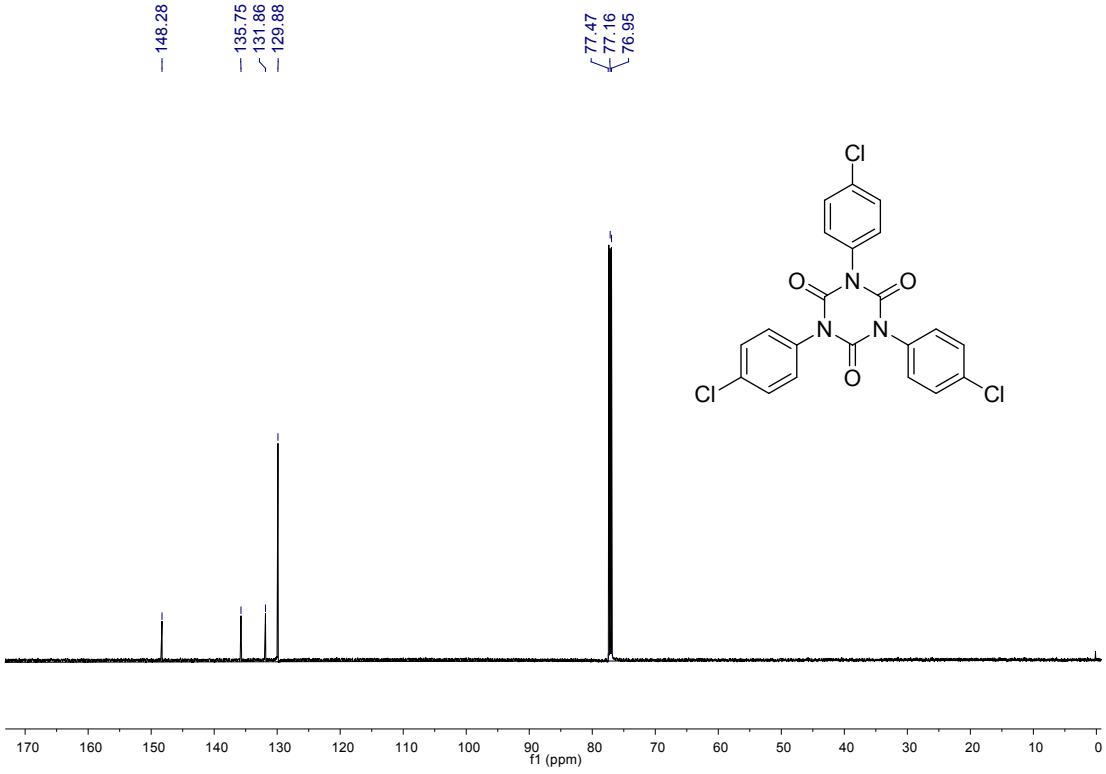
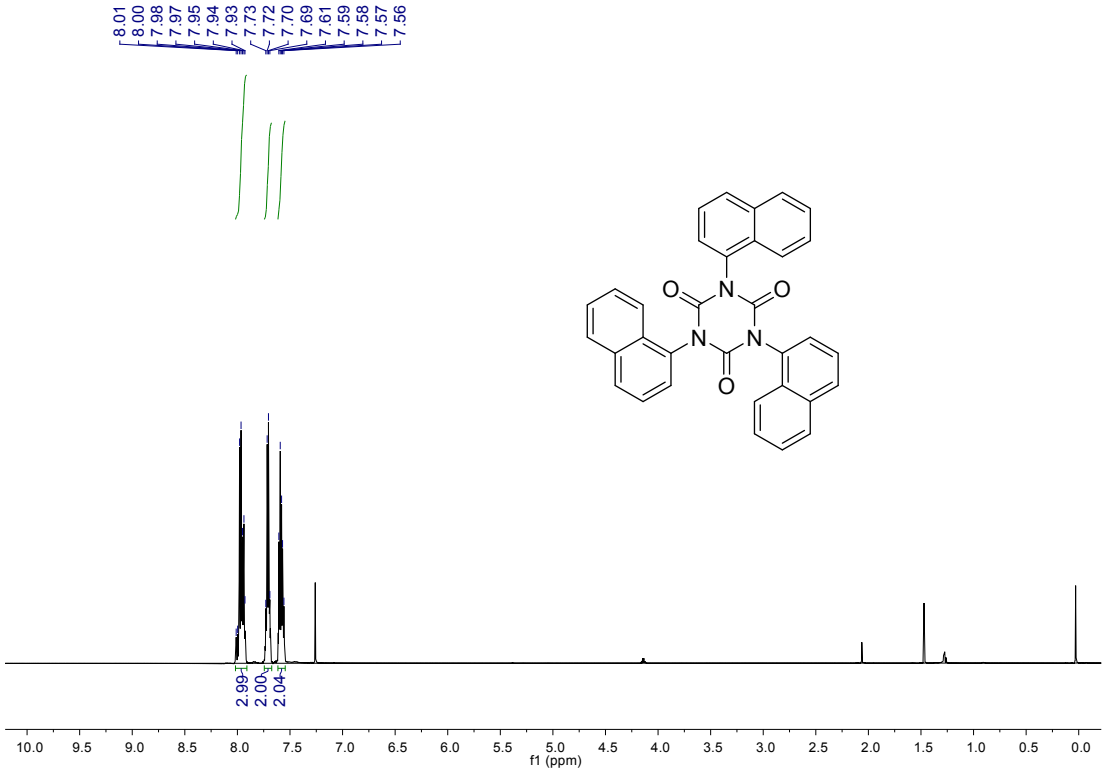
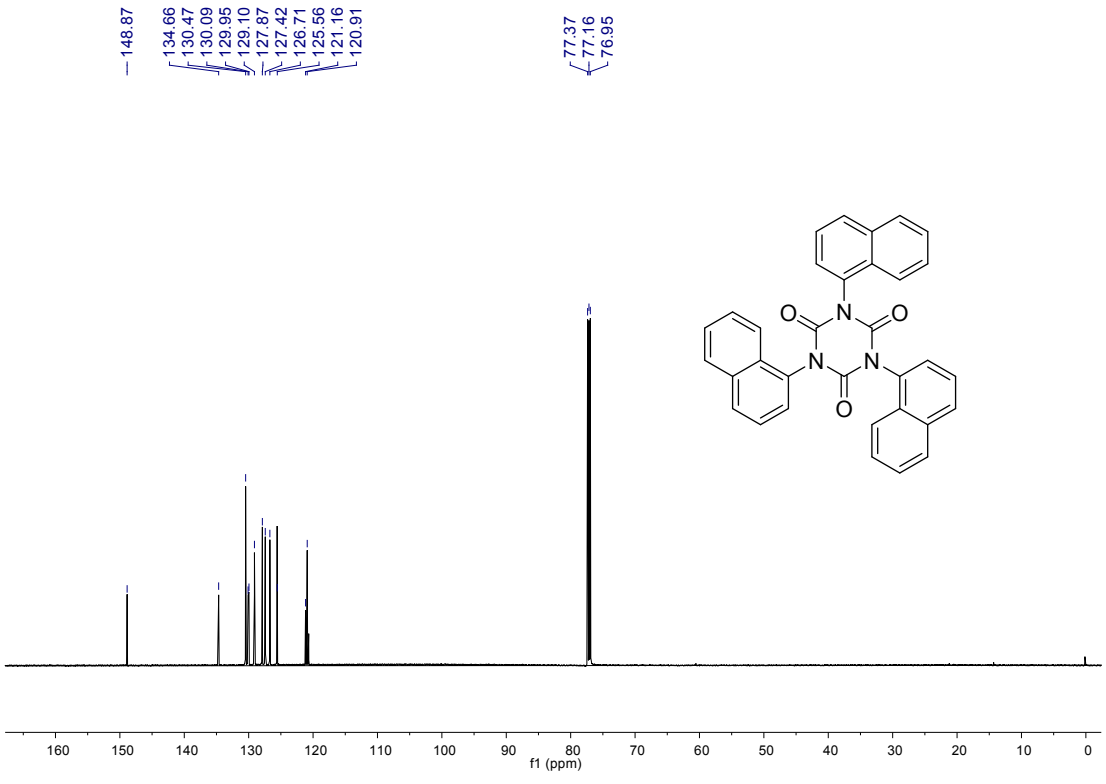
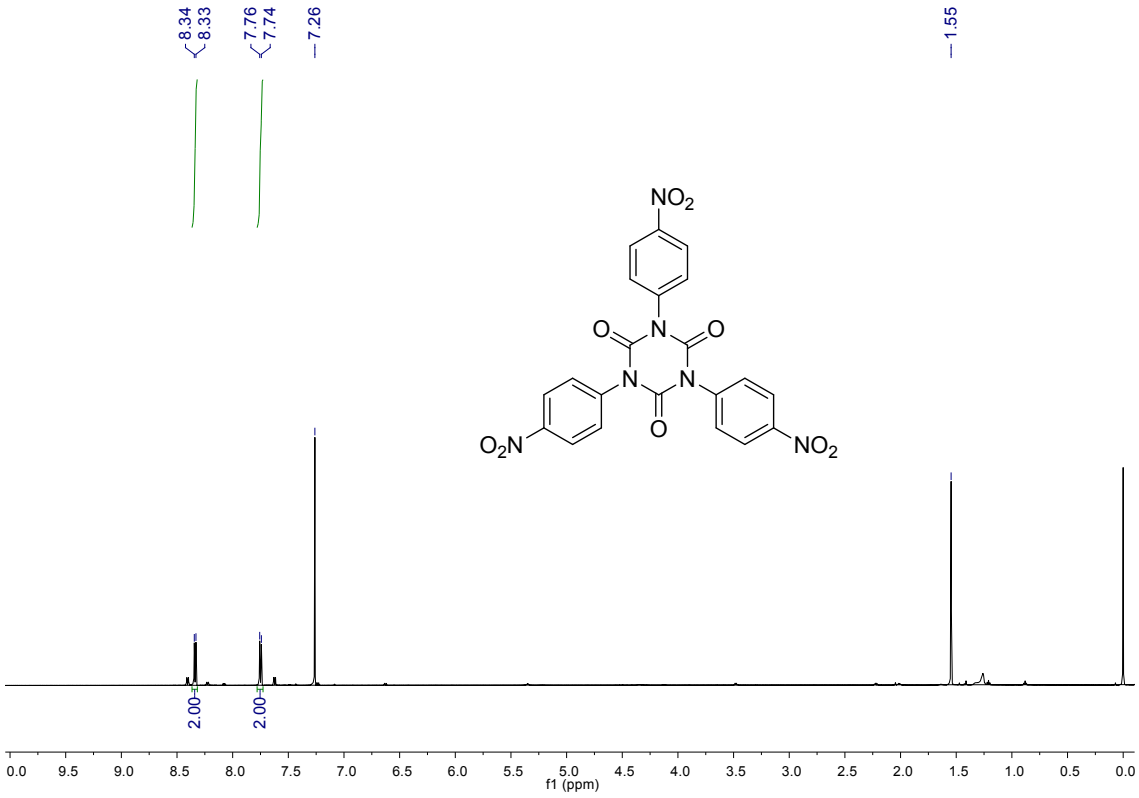
0.5
0.0
f1 (ppm)


148.28
135.75
131.86
129.88
77.47
77.16
76.95
Cl
O
N
O
N
N
O
Cl
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.01
8.00
7.98
7.97
7.95
7.94
7.93
7.73
7.72
7.70
7.69
7.61
7.59
7.58
7.57
7.56
O
N
O
N
N
O
2.99
2.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.87
134.66
130.47
130.09
129.95
129.10
127.87
127.42
126.71
125.56
121.16
120.91
77.37
77.16
76.95
O
N
O
N
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.34
8.33
7.76
7.74
7.26
1.55
NO2
O
N
O
N
N
O
O2N
NO2
2.00
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)