Supporting Information

# Structure-property relations in oligomers of linear aliphatic diisocyanates

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Totals - 18 pages, 31 figures and 1 table.

# 1. Crystallographic Details

**Table S1**:.Crystal structure refinement table of compounds **10a**, **11**.

| | **10a** | **11** |
|---|---|---|
| empirical formula | C14H20N4O4 | C9H12N4O2 |
| M [g/mol] | 308.34 | 208.23 |
| λ [Å] | 1.54178 | 1.54178 |
| T [K] | 110 | 106 |
| crystal system | monoclinic | orthorombic |
| space group | $P2_1/c$ | *Pbca* |
| Z | 4 | 12 |
| a [Å] | 14.1020(13) | 8.0638(7) |
| b [Å] | 5.5694(3) | 15.8581(8) |
| c [Å] | 19.3126(12) | 21.5715(13) |
| α [°] | 90 | 90 |
| β [°] | 98.478(8) | 90 |
| γ [°] | 90 | 90 |
| V [$Å^3$] | 1500.22(18) | 2758.5(3) |
| $D_c$ [$g/cm^3$] | 1.365 | 1.504 |
| μ [$mm^{-1}$] | 0.848 | 0.921 |
| F(000) | 656 | 1320 |
| crystal size [mm] | 0.20×0.08×0.03 | 0.20×0.10×0.06 |
| θ range [°] | 3.638 to 67.693 | 4.099 to 65.684 |
| limiting indices | $-16 \le h \le 14$,<br>$-6 \le k \le 6$,<br>$-22 \le l \le 19$ | $-9 \le h \le 9$,<br>$-9 \le k \le 18$,<br>$-24 \le l \le 24$ |
| reflections collected | 9890 | 14617 |
| independent | 2596 | 2357 |
| $R_{int}$ | 0.0771 | 0.0901 |
| completeness | 0.976 | 0.987 |
| absorption correction | semi-empirical from equivalents | semi-empirical from equivalents |
| max. / min. transmission | 1.0 / 0.85 | 1.00 / 0.42 |
| Data / restraints / parameter | 2596 / 0 / 204 | 2357 / 0 / 196 |
| $R_1$, $\omega R_2$ [$I>2\sigma(I)$] | 0.0787, 0.2044 | 0.0534, 0.1295 |
| $R_1$, $\omega R_2$ (all data) | 0.1086, 0.2281 | 0.0781, 01495 |
| GooF on $F^2$ | 1.047 | 1.027 |
| peak / hole [$eÅ^{-3}$] | 0.383 / −0.336 | 0.451 / −0.300 |
| CCDC | 1823829 | 1823830 |

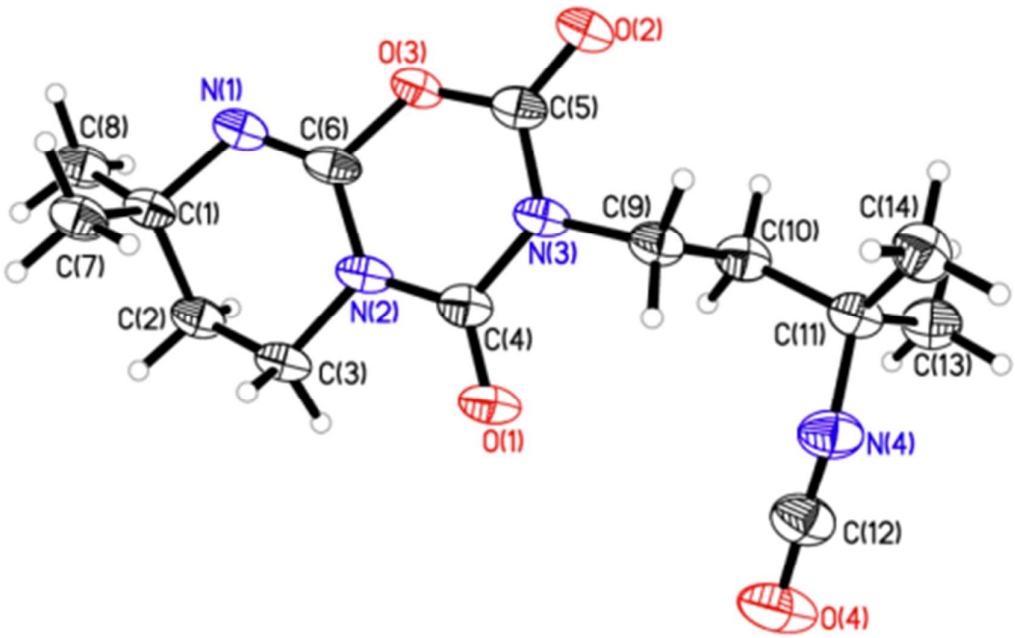



**Figure S1:** ORTEP-Plot of the molecular structure of **10a**. Thermal ellipsoids are shown at 50% probability level.

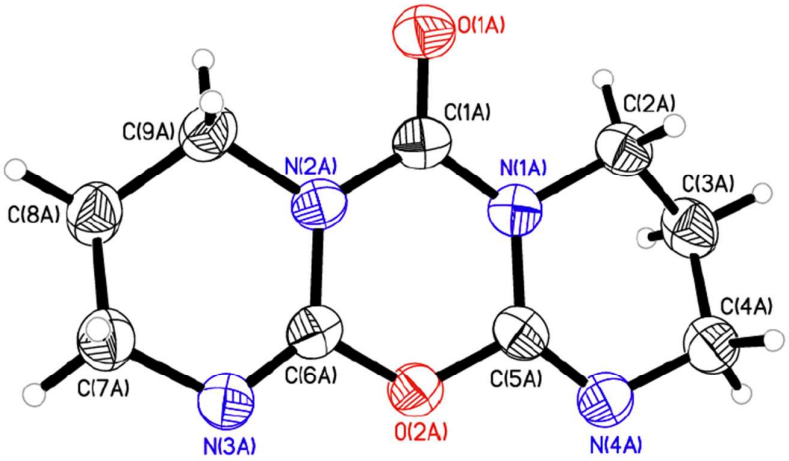



**Figure S2**: ORTEP-Plot of the molecular structure of **11**. Thermal ellipsoids are shown at 50% probability level.

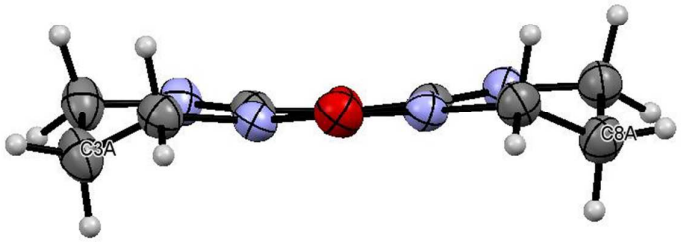



**Figure S3**: ORTEP-Plot of the molecular structure of **11** (side view). Thermal ellipsoids are shown at 50% probability level.

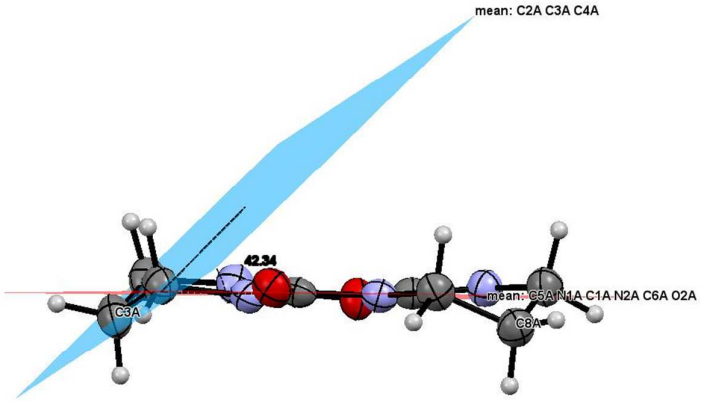



**Figure S4**: ORTEP-Plot of the molecular structure of **11** (side view). Thermal ellipsoids are shown at 50% probability level. The defined planes (dihedral angle: 42.34 °) elucidate the half-chair conformation of the annelated rings.

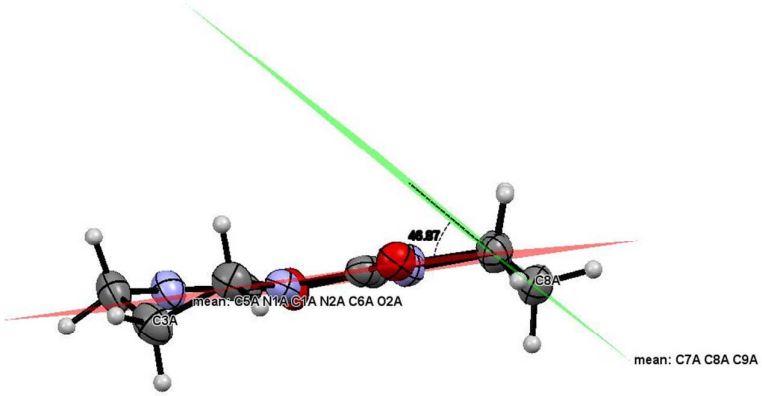
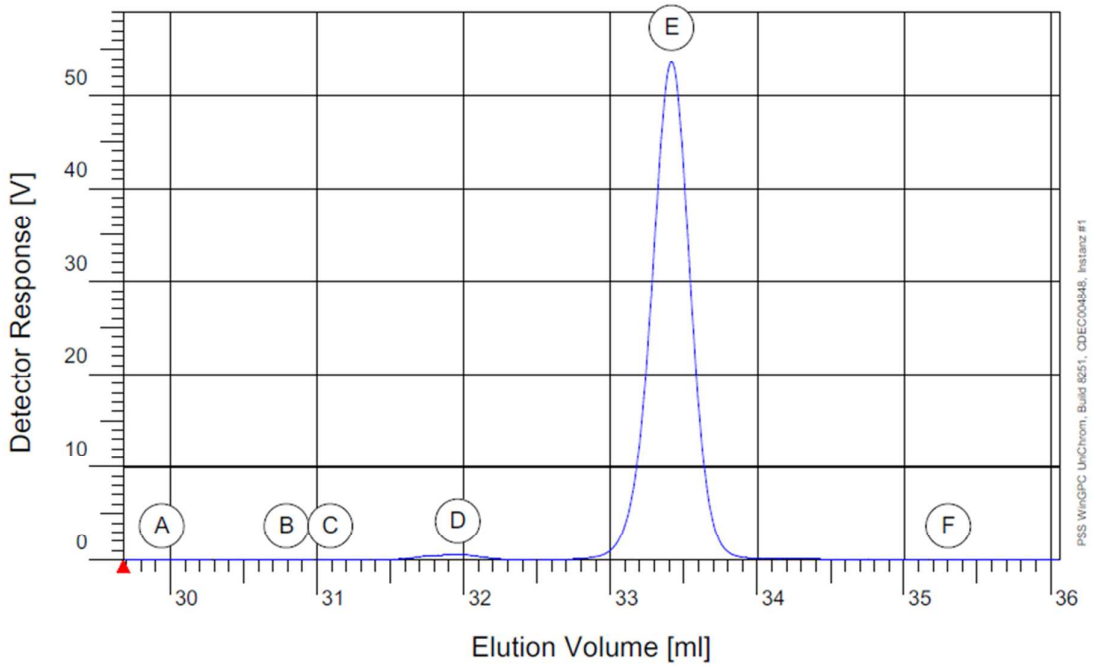



**Figure S5**: ORTEP-Plot of the molecular structure of **11** (side view).Thermal ellipsoids are shown at 50% probability level. The defined planes (dihedral angle: 46.87 °) elucidate the half-chair conformation of the annelated rings.

# 2. Size Exclusion Chromatography (SEC)

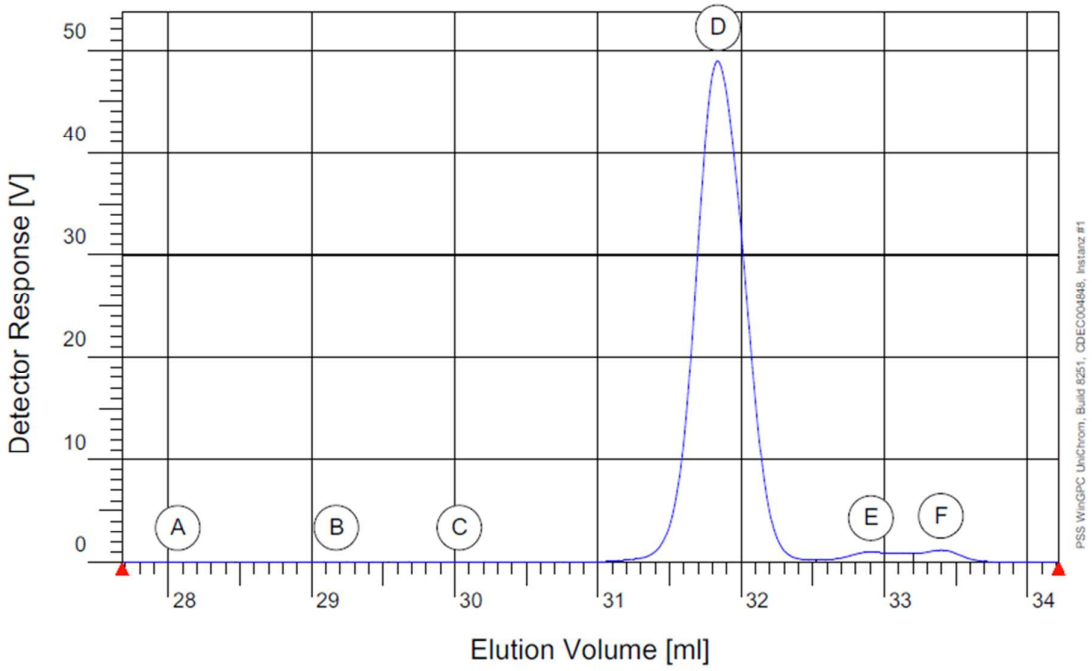
Bis-(6-isocyanatohexyl) uretdione **6a**




| Peak | Komponente | VP [ml] | YP [V] | MP [Da] | F [V*ml] | F [%] | C [g/l] | C [%] |
|---|---|---|---|---|---|---|---|---|
| A : | | 29.9432 | 0.0306 | 1077.897 | 0.0102 | 0.0587 | | |
| B : | | 30.7917 | 0.0540 | 861.6381 | 0.0228 | 0.1313 | | |
| C : | | 31.0911 | 0.0437 | 795.8407 | 0.0111 | 0.0636 | | |
| D : | | 31.9595 | 0.5649 | 630.1614 | 0.2664 | 1.5313 | | |
| E : | | 33.4169 | 53.7003 | 420.6857 | 17.0611 | 98.0819 | | |
| F : | | 35.3035 | 0.0505 | 248.0675 | 0.0232 | 0.1332 | | |
| Summe | | | | | 17.3948 | 100.0000 | 0.0000 | 100.0000 |

**Figure S6**: SEC of **6a**.

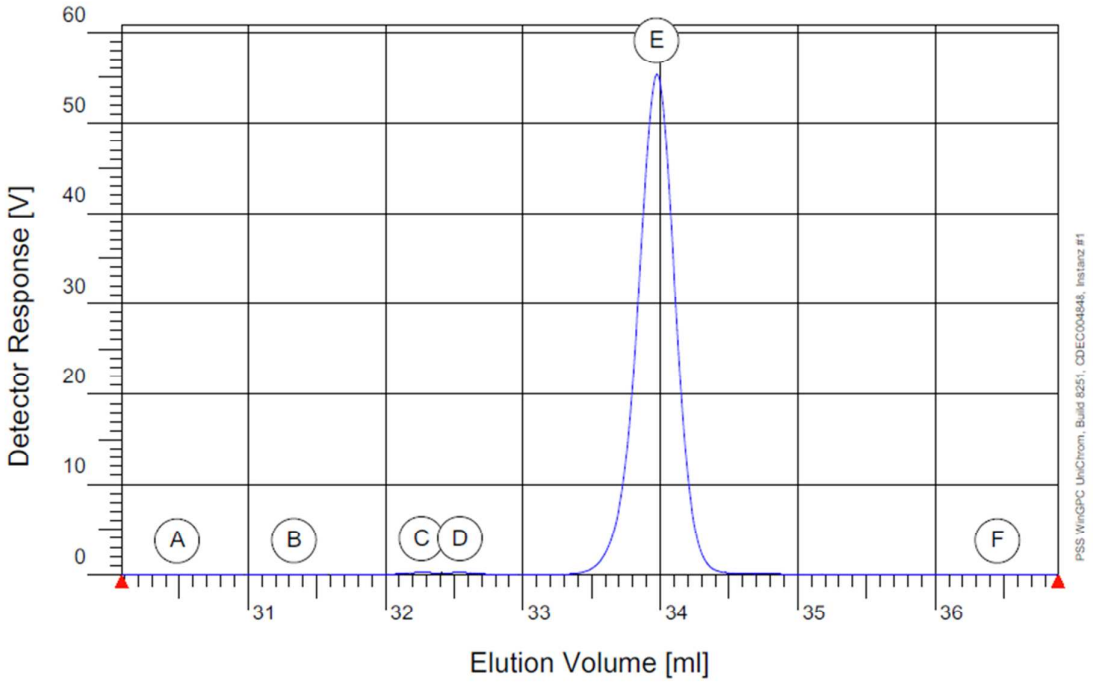
Tris-6-isocyanatohexyl iminooxadiazinedione / isocyanurate mixture **7a** / **8a**




| Peak | Komponente | VP [ml] | YP [V] | MP [Da] | F [V*ml] | F [%] | C [g/l] | C [%] |
|---|---|---|---|---|---|---|---|---|
| A : | | 28.0658 | 0.0404 | 1803.731 | 0.0152 | 0.0738 | | |
| B : | | 29.1739 | 0.0586 | 1323.162 | 0.0420 | 0.2038 | | |
| C : | | 30.0324 | 0.0816 | 1052.805 | 0.0530 | 0.2574 | | |
| D : | | 31.8392 | 48.8547 | 651.0856 | 19.6075 | 95.1359 | | |
| E : | | 32.9073 | 1.0010 | 485.3058 | 0.4967 | 2.4098 | | |
| F : | | 33.3965 | 1.2035 | 423.1115 | 0.3956 | 1.9193 | | |
| Summe | | | | | 20.6100 | 100.0000 | 0.0000 | 100.0000 |

**Figure S7**: SEC of **7a** / **8a**.

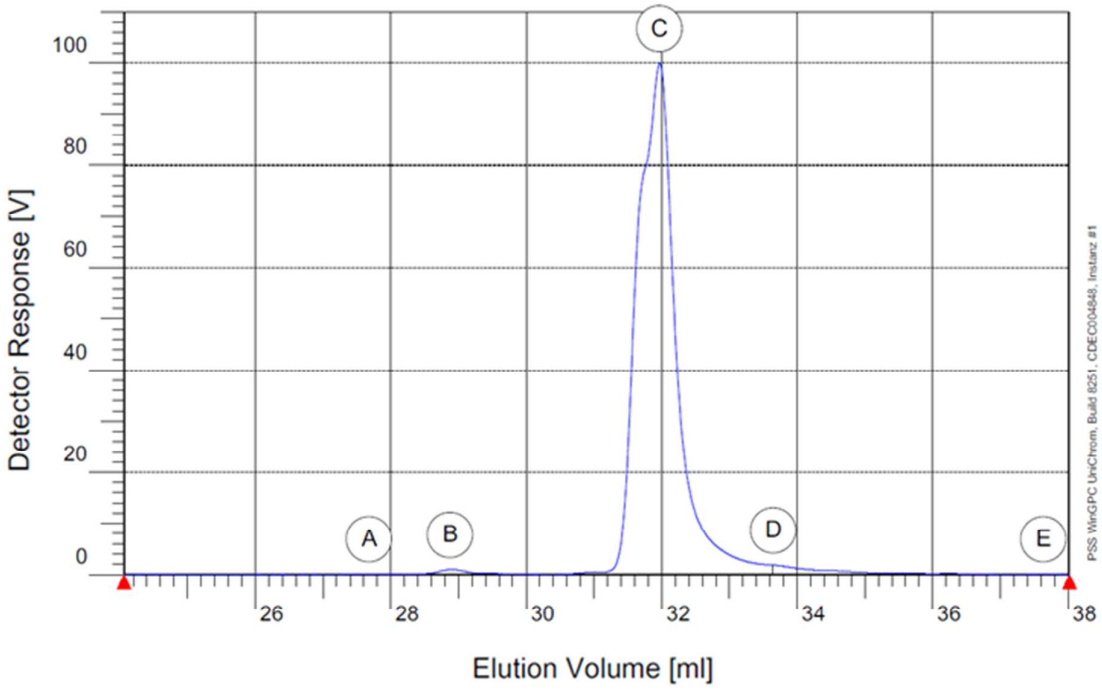
Bis-(5-isocyanatopentyl) uretdione **6b**




| Peak | Komponente | VP [ml] | YP [V] | MP [Da] | F [V*ml] | F [%] | C [g/l] | C [%] |
|---|---|---|---|---|---|---|---|---|
| A : | | 30.4834 | 0.0294 | 934.7464 | 0.0152 | 0.0832 | | |
| B : | | 31.3333 | 0.0566 | 746.0733 | 0.0196 | 0.1073 | | |
| C : | | 32.2631 | 0.2668 | 580.0139 | 0.0920 | 0.5032 | | |
| D : | | 32.5431 | 0.2589 | 536.9736 | 0.0747 | 0.4087 | | |
| E : | | 33.9729 | 55.3679 | 359.5702 | 18.0674 | 98.8332 | | |
| F : | | 36.4526 | 0.0297 | 184.4946 | 0.0117 | 0.0642 | | |
| Summe | | | | | 18.2807 | 100.0000 | 0.0000 | 100.0000 |

**Figure S8**: SEC of **6b**.

Tris-(5-isocyanatopentyl) iminooxadiazinedione / isocyanurate mixture **7b** / **8b**




| Peak | Komponente | VP [ml] | YP [V] | MP [Da] | F [V*ml] | F [%] | C [g/l] | C [%] |
|---|---|---|---|---|---|---|---|---|
| A : | | 27.6781 | 0.0002 | 2077.604 | 0.0001 | 0.2235 | | |
| B : | | 28.8768 | 0.0009 | 1462.994 | 0.0007 | 1.0541 | | |
| C : | | 31.9695 | 0.0904 | 633.7799 | 0.0602 | 96.3146 | | |
| D : | | 33.6477 | 0.0017 | 395.4788 | 0.0014 | 2.3093 | | |
| E : | | 37.6394 | 0.0002 | 141.0381 | 0.0001 | 0.0985 | | |
| Summe | | | | | 0.0625 | 100.0000 | 0.0000 | 100.0000 |

**Figure S9**: SEC of **7b** / **8b**.

# 3. Nuclear Magnetic Resonance (NMR)

1,3 Diisocyanatopropane: GDI **4**

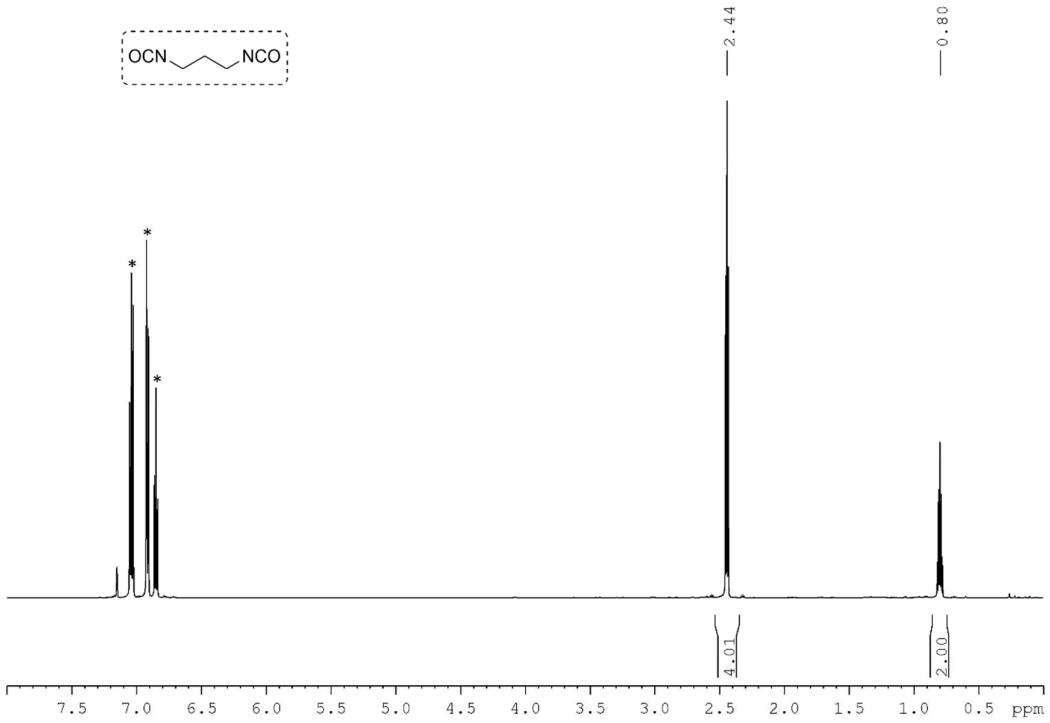



**Figure S10**: $^{1}$H-NMR (600 MHz, $C_6D_6$) of **4**. Signals indicated with * are from the solvent (diphenyl ether).

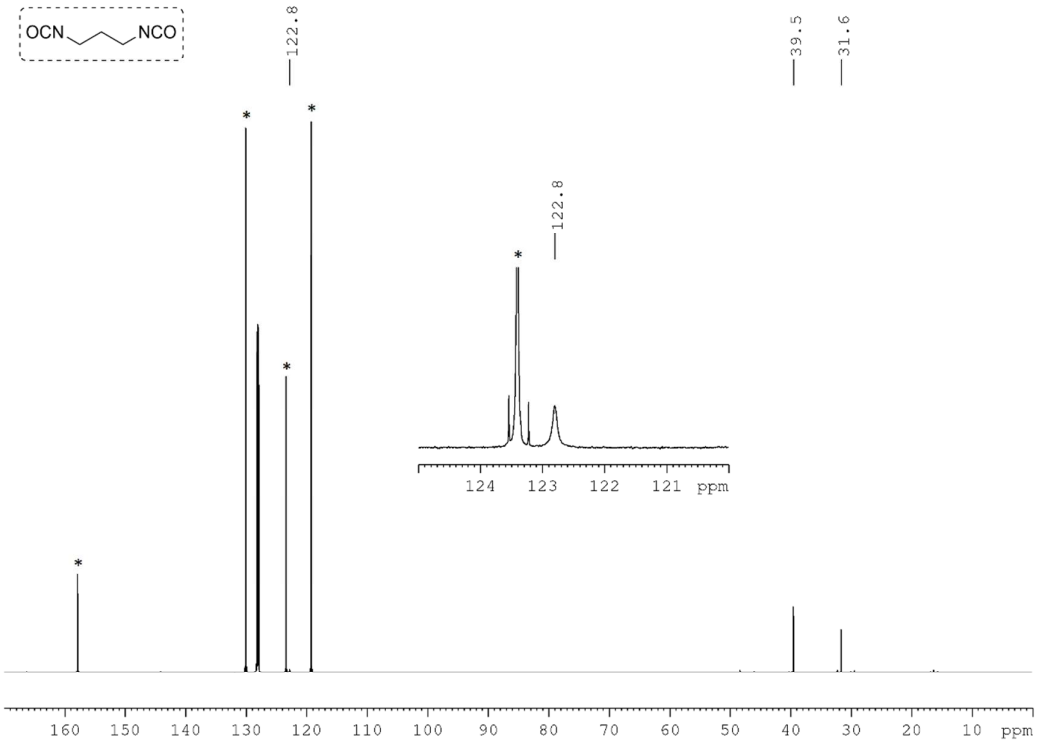



**Figure S11**: $^{13}C\{^{1}H\}$-NMR (176.10 MHz, $C_6D_6$) of **4**. Signals indicated with * are from the solvent (diphenyl ether).

1,3-Diisocyanato-3-methylbutane: MBDI **5**

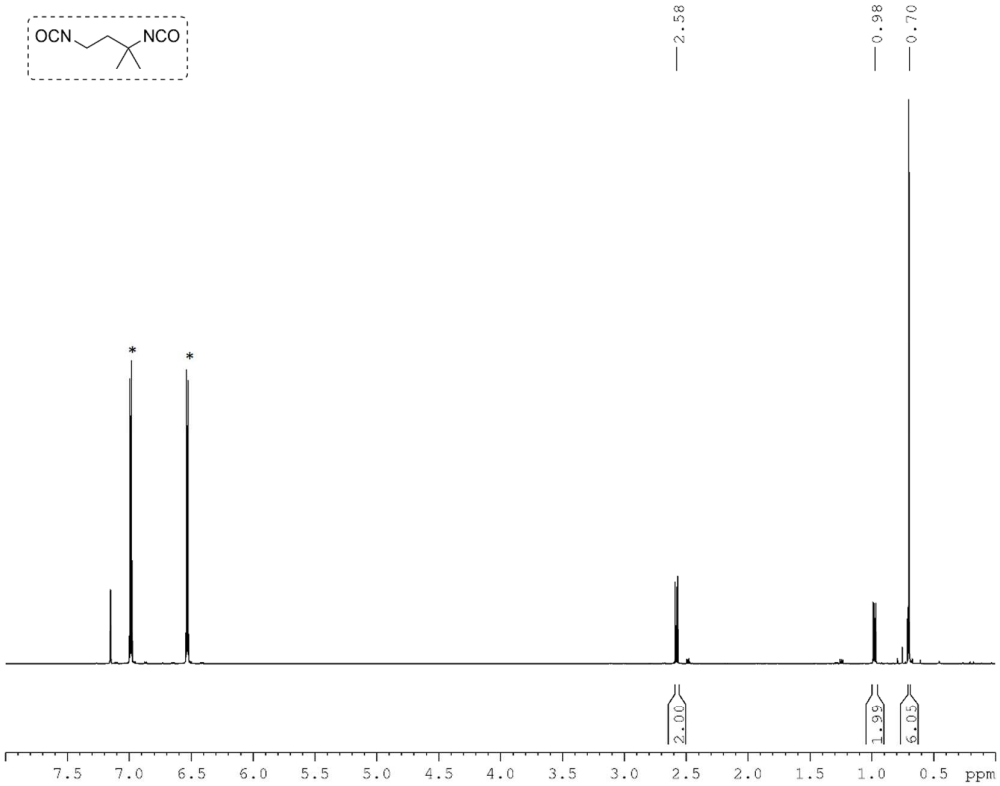



**Figure S12**: $^{1}$H-NMR (700 MHz, $C_6D_6$) of **5**. Signals indicated with * are from the solvent (1,2-dichlorobenzene).

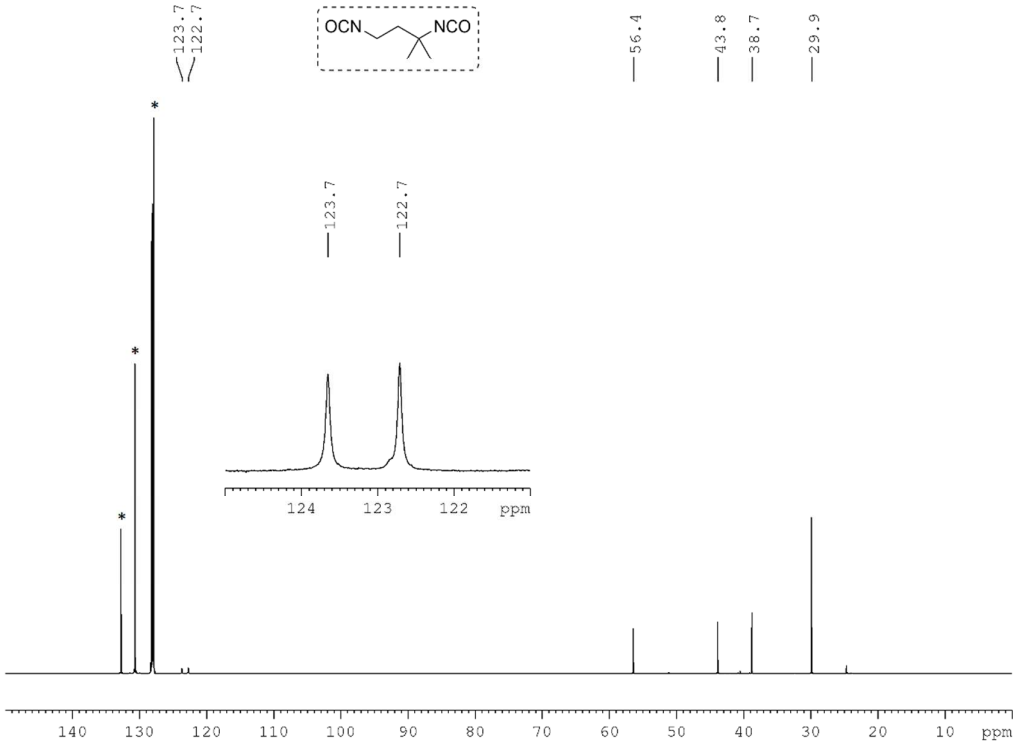



**Figure S13**: $^{13}$C{$^{1}$H}-NMR (176.10 MHz, $C_6D_6$) of **5**. Signals indicated with * are from the solvent (1,2-dichlorobenzene).

Bis-(6-isocyanatohexyl) uretdione **6a**

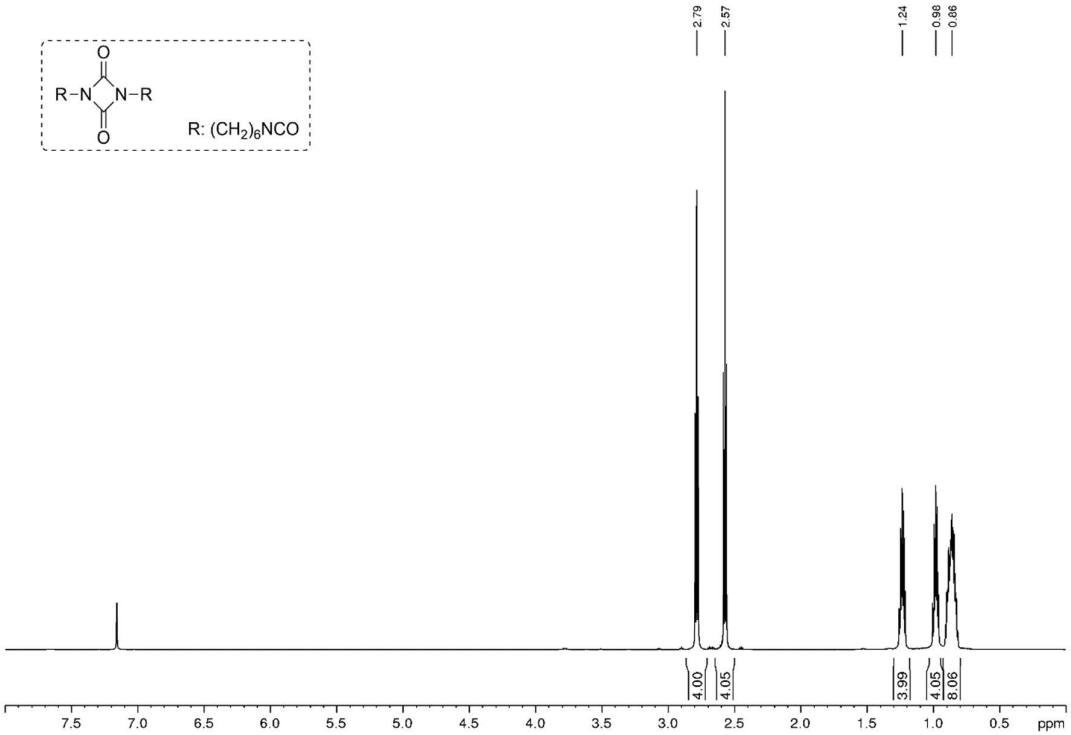



**Figure S14**: $^1$H-NMR (600 MHz, $C_6D_6$) of **6a**.

Tris-(6-isocyanatohexyl) iminooxadiazinedione / isocyanurate mixture **7a** / **8a**

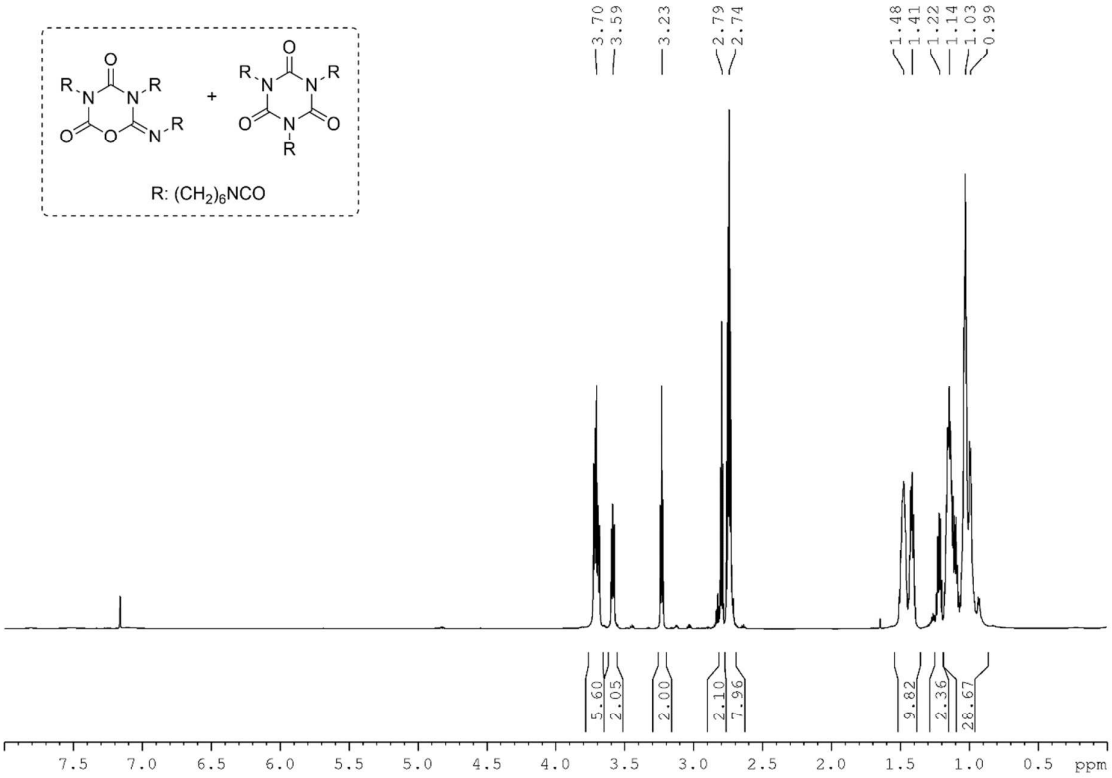



**Figure S15**: $^1$H-NMR (600 MHz, $C_6D_6$) of **7a** / **8a**.

Bis-(6-isocyanatopentyl) uretdione **6b**

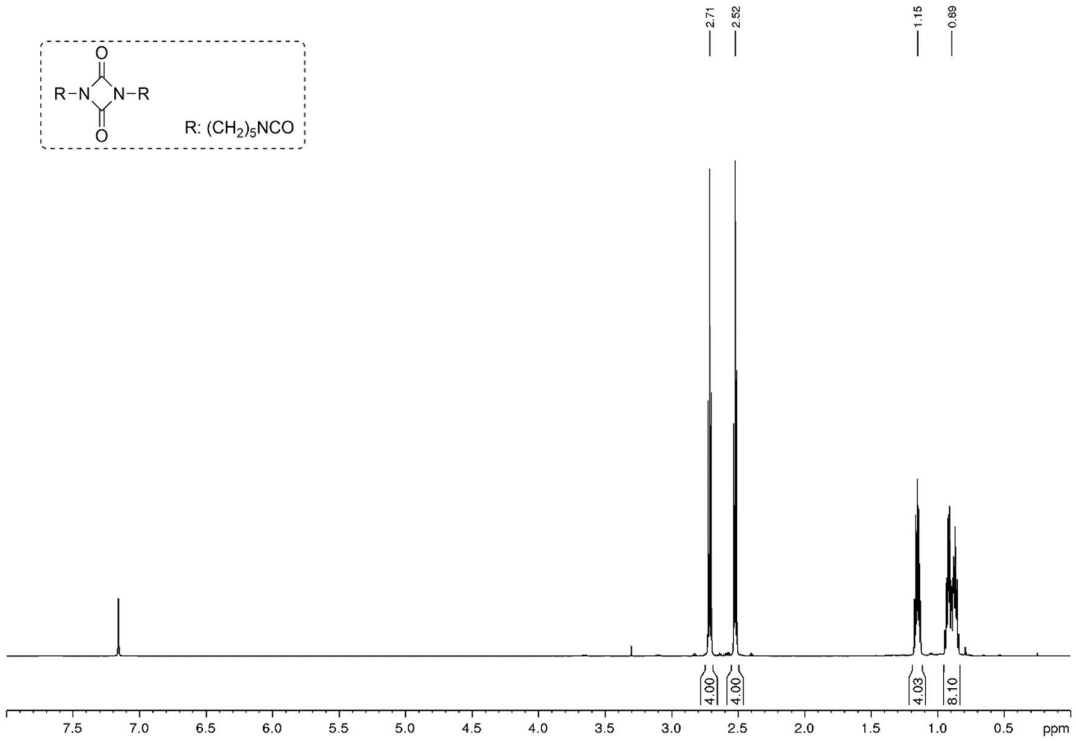



**Figure S16**: $^1$H-NMR (600 MHz, $C_6D_6$) of **6b**.

Tris-(5-isocyanatopentyl) iminooxadiazinedione / isocyanurate mixture **7b** / **8b**

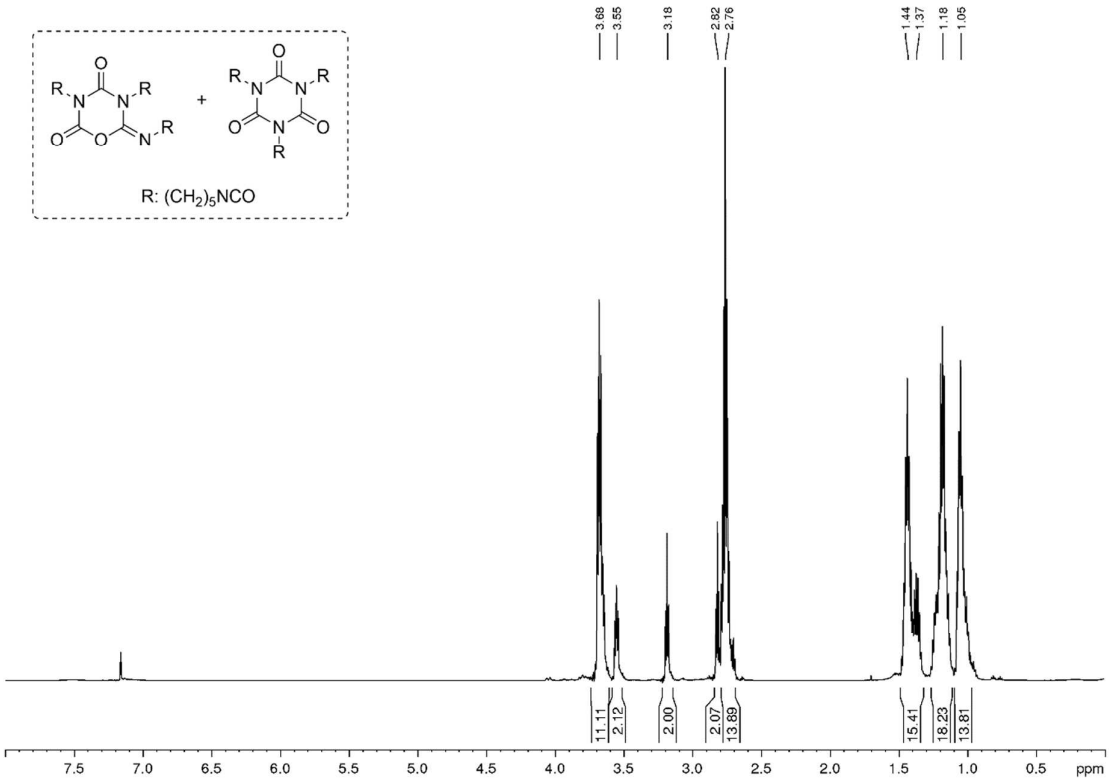



**Figure S17**: $^1$H-NMR (600 MHz, $C_6D_6$) of **7b** / **8b**.

3-(3-Isocyanatopropyl)-7,8-dihydro-2*H*,6*H*-pyrimido[2,1-*b*][1,3,5]oxadiazine-2,4(3*H*)-dione **9** (Bicyclic iminooxadiazinedione of **4**)

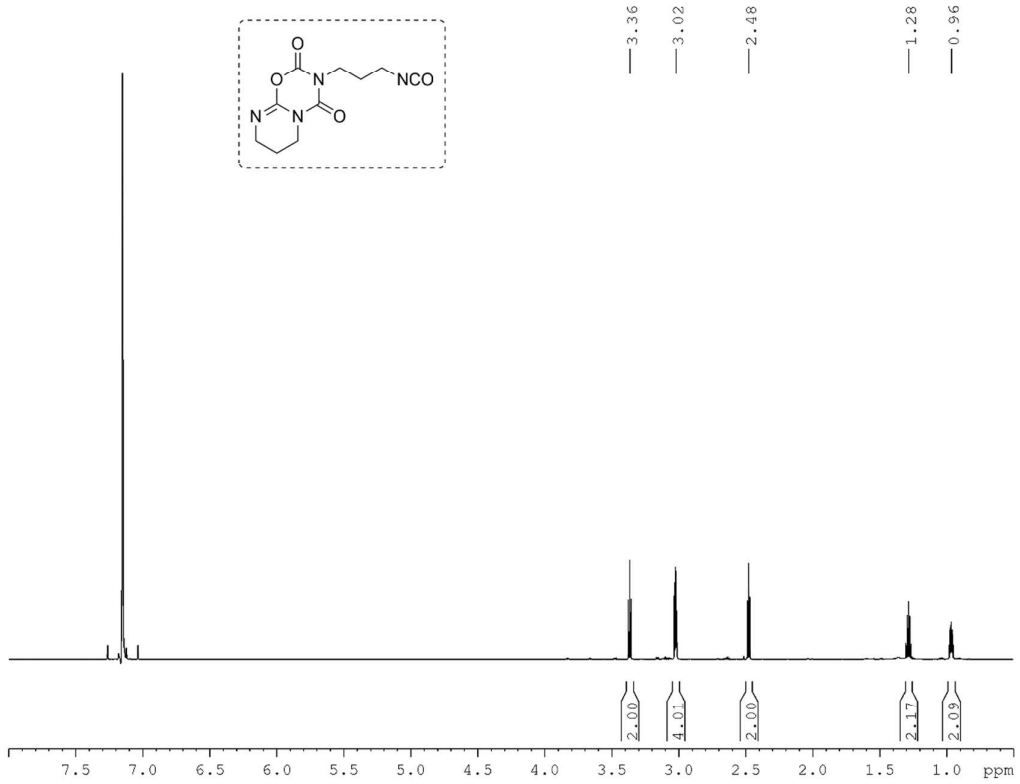



**Figure S18**: $^{1}$H-NMR (700 MHz, $C_6D_6$) of **9**.

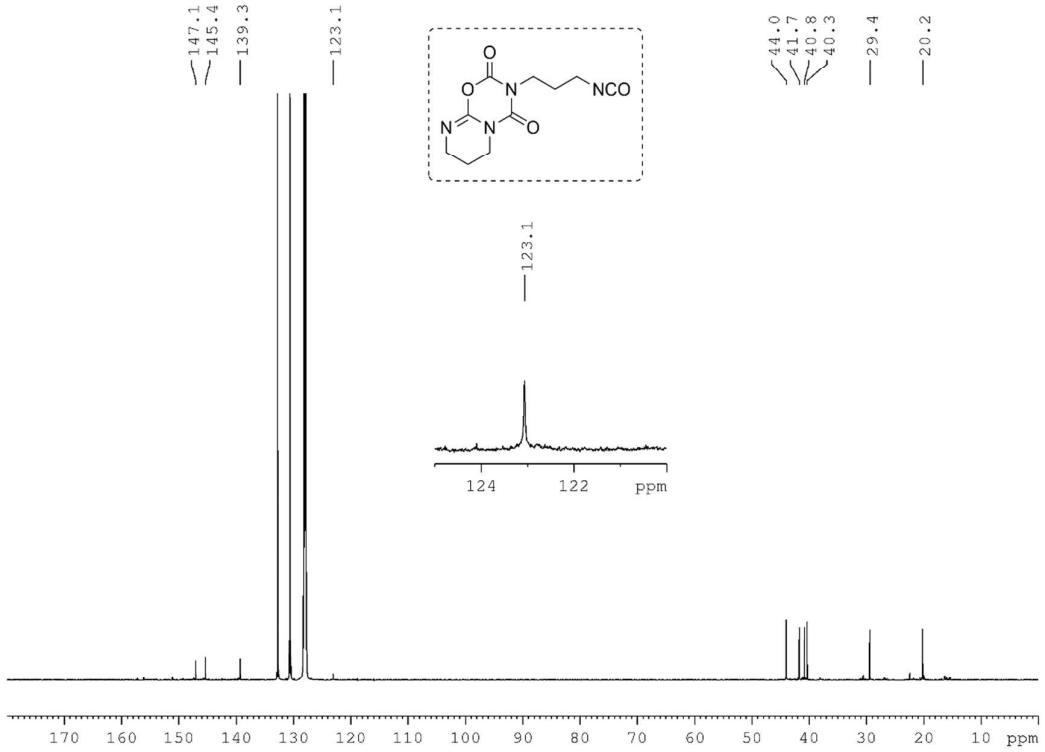



**Figure S19**: $^{13}$C{$^{1}$H}-NMR (176.10 MHz, $C_6D_6$) of **9**.

3-(3-isocyanato-3-methylbutyl)-8,8-dimethyl-7,8-dihydro-2*H*,6*H*-pyrimido[2,1-*b*][1,3,5]oxadiazine-2,4(3*H*)-dione **10a** (Bicyclic iminooxadiazinedione of **5**)

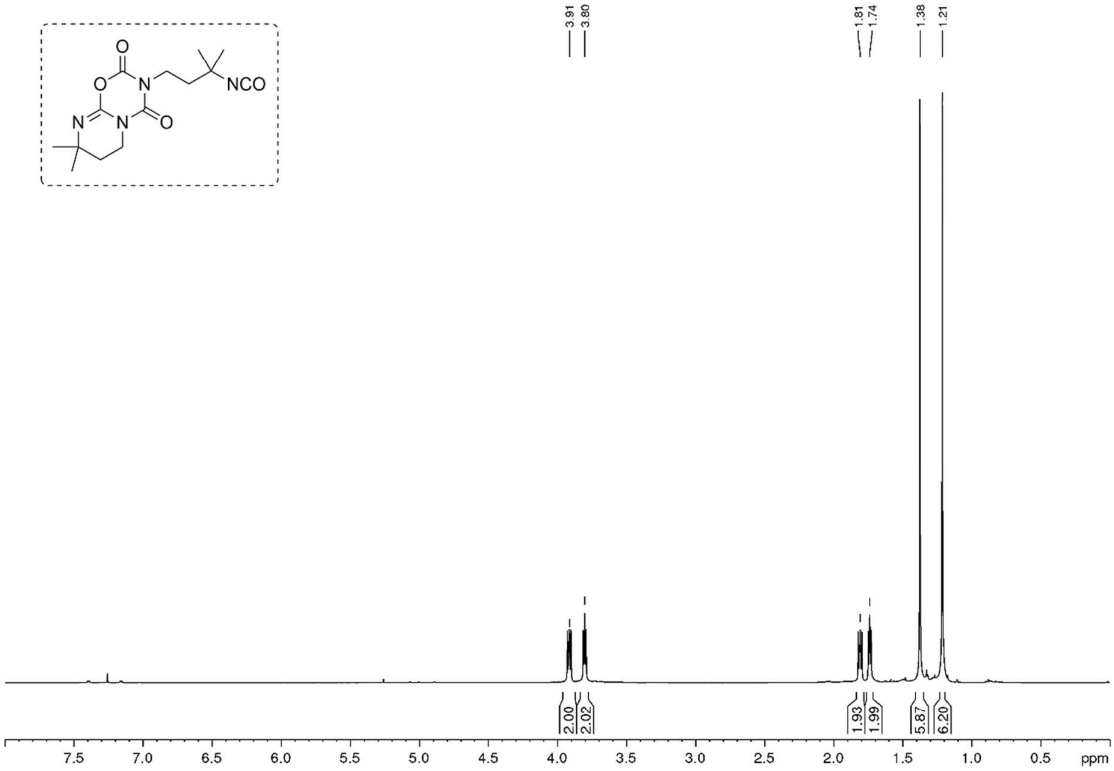



**Figure 1**: $^{1}$H-NMR (600 MHz, $CDCl_3$) of **10a**.

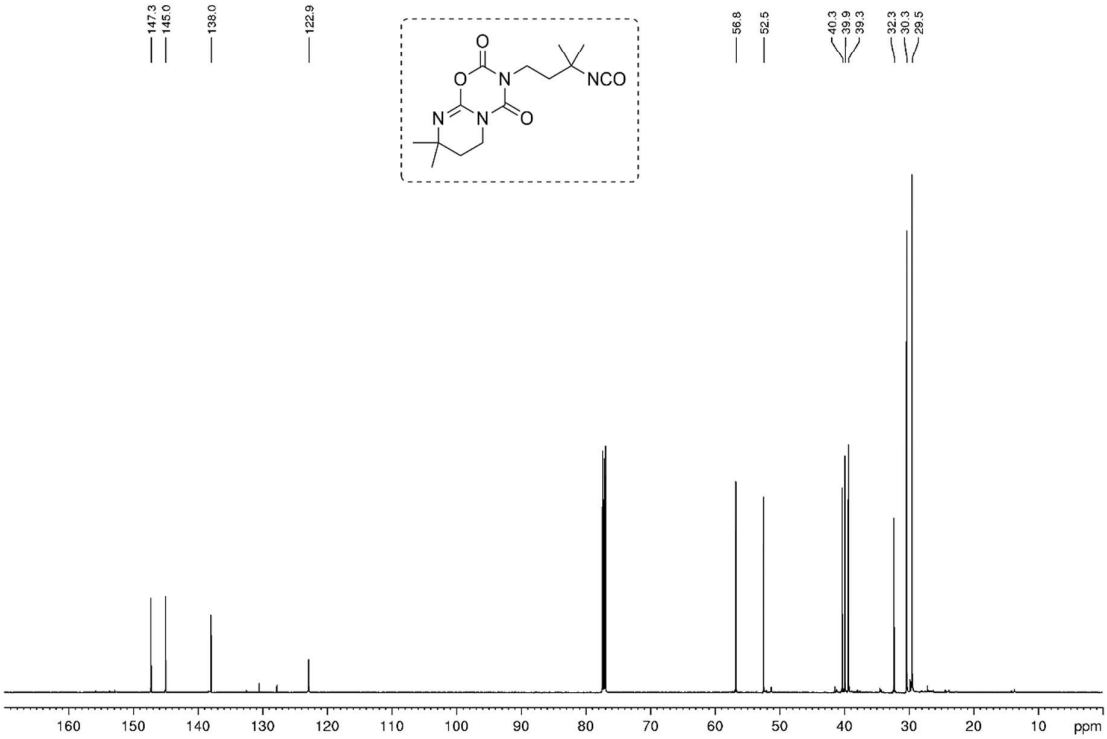



**Figure 2**: $^{13}$C{$^{1}$H}-NMR (150.96 MHz, $CDCl_3$) of **10a**.

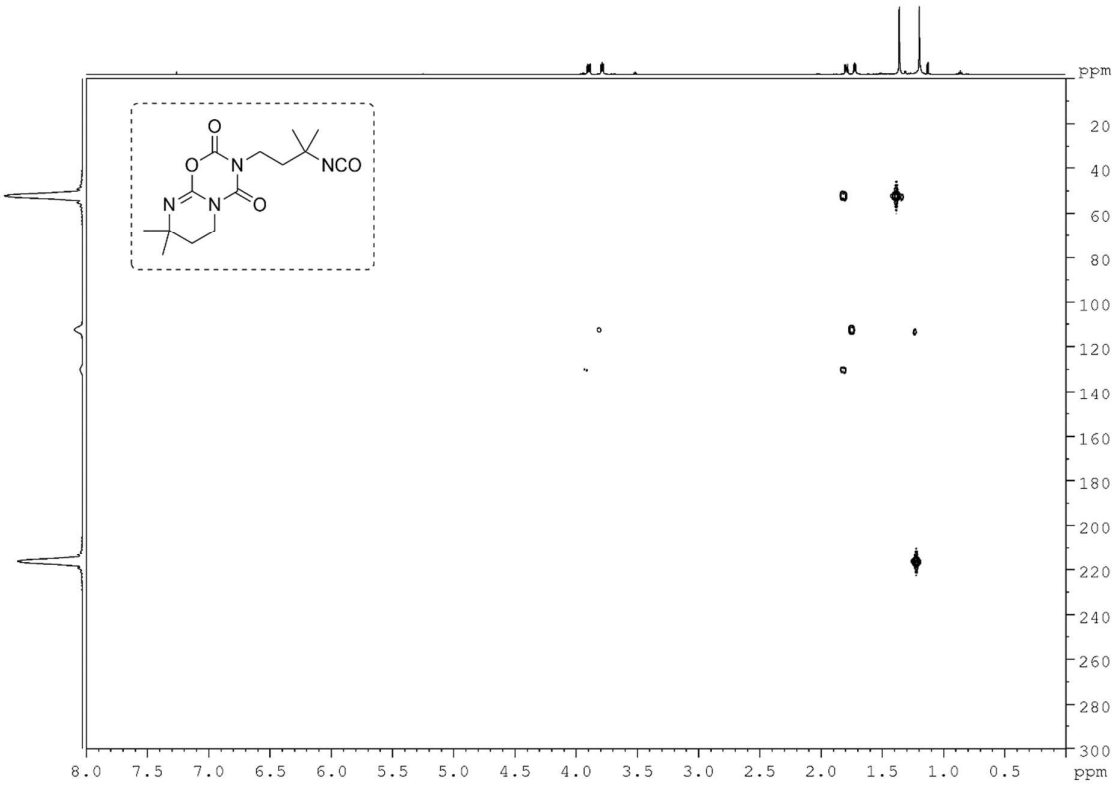



**Figure S22**: $^{1}$H-$^{15}$N-HMBC (700 MHz, 70.97 MHz, $CDCl_3$) of **10a**.

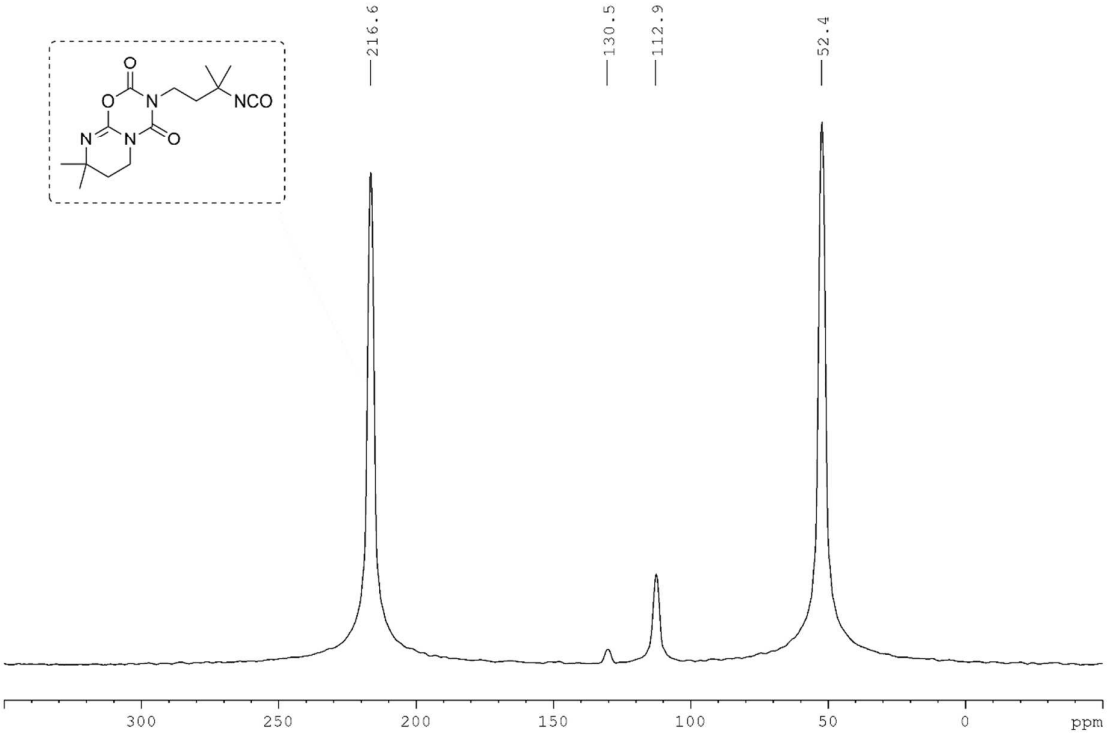



**Figure S23**: $^{15}$N-NMR (70.97 MHz, $CDCl_3$) of **10a** (taken from the $^{1}$H-$^{15}$N-HMBC, see Figure S22).

3,4,9,10-tetrahydro-2H,6H,8H-dipyrimido[2,1-b:1',2'-e][1,3,5]oxadiazin-6-one **11**

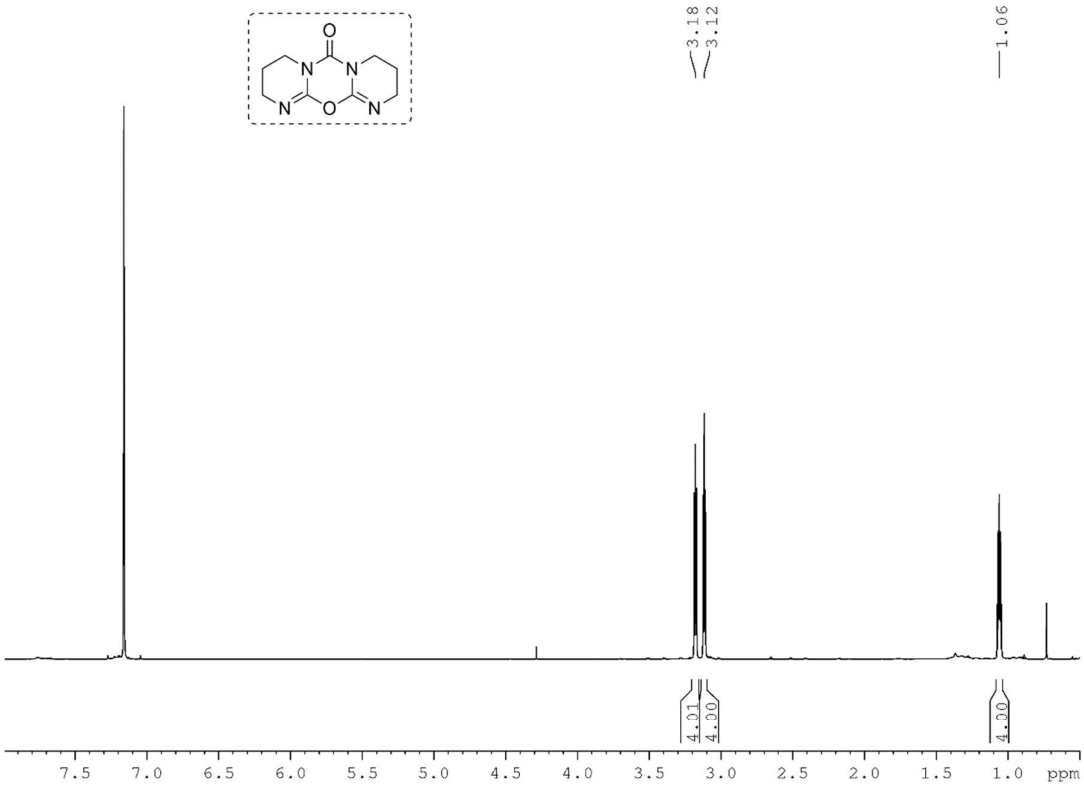



**Figure 3**: $^{1}$H-NMR (700 MHz, $C_6D_6$) of **11**.

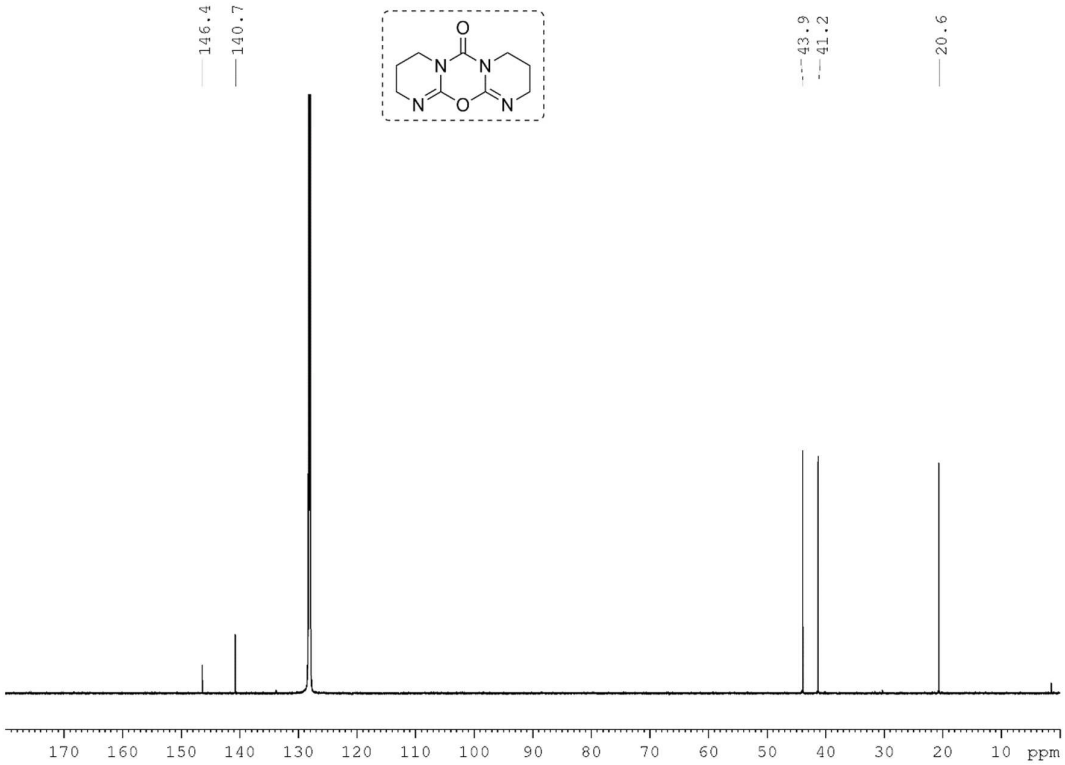



**Figure 45**: $^{13}$C{$^{1}$H}-NMR (176.10 MHz, $C_6D_6$) of **11**.

# 4. Gas chromatography – mass spectrometry (GC – MS)

3-(3-Isocyanatopropyl)-7,8-dihydro-2*H*,6*H*-pyrimido[2,1-*b*][1,3,5]oxadiazine-2,4(3*H*)-dione **9** (Bicyclic iminooxadiazinedione of **4**)

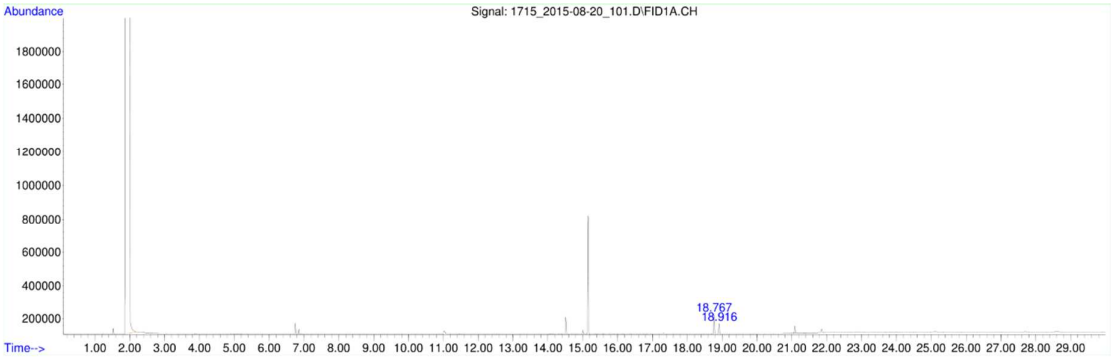



**Figure S26**5: Gas chromatogram of **9** (reaction mixture). The peak at 18.8 min indicates structure **11**, the peak at 18.9 min indicates structure **9**.

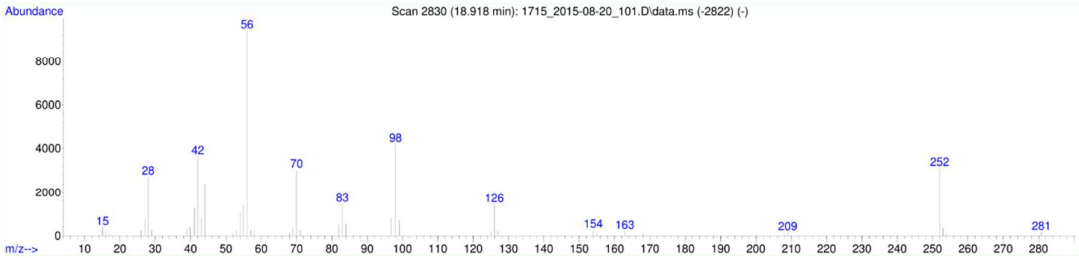



**Figure S276**: Mass spectrum of the compound eluting at 18.9 min (see Figure S26), indicating structure **9**.

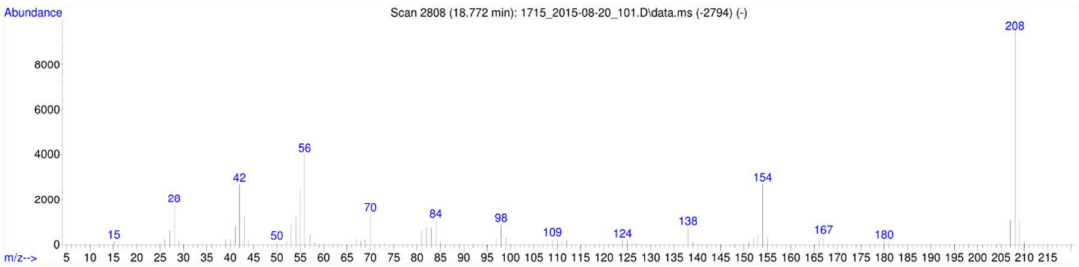



**Figure S28**: Mass spectrum of the compound eluting at 18.8 min (see Figure S26), indicating structure **11** (the tricyclic decarboxylation product of **9** formed during the GC-MS process (compare Figure S27): m/z 252 → 208, m/z -44 ($-CO_2$)).

3-(3-isocyanato-3-methylbutyl)-8,8-dimethyl-7,8-dihydro-2*H*,6*H*-pyrimido[2,1-*b*][1,3,5]oxadiazine-2,4(3*H*)-dione **10a** (Bicyclic iminooxadiazinedione of **5**)

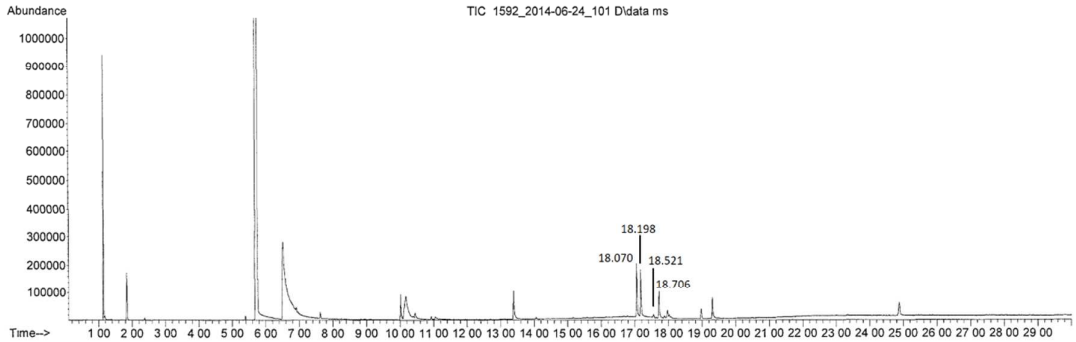



**Figure S29**: Gas chromatogram of **10** (reaction mixture). The peaks at 18.5 and at 18.7 min indicate **10**. The peaks at 18.1 and 18.2 min indicate tricyclic decarboxylation products of **10**, analogous to structure **11**.

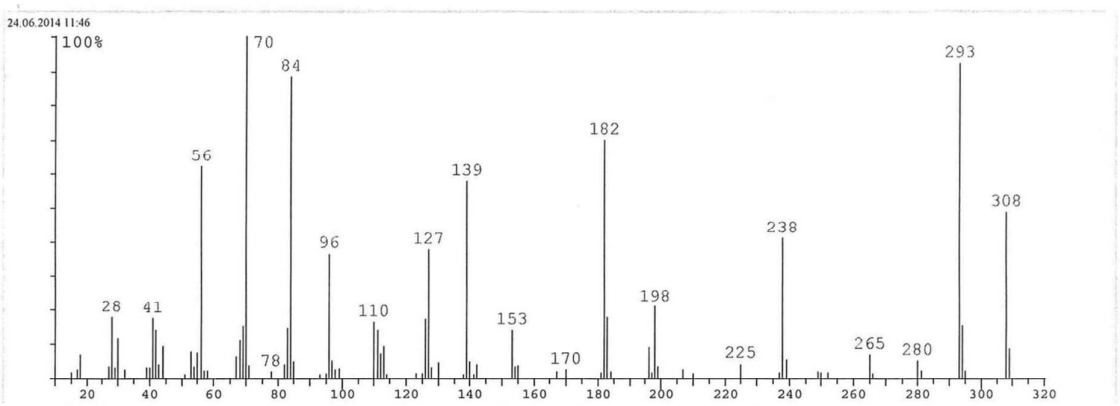



**Figure S30**: Mass spectrum of the compounds eluting at 18.5 and 18.7 min (see Figure S29), indicating structure **10**.

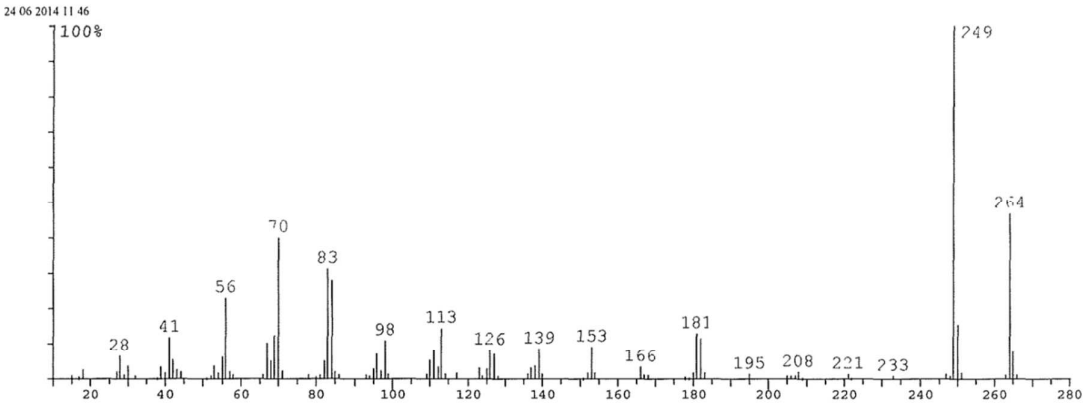



**Figure S31**: Mass spectrum of the compounds eluting at 18.1 and 18.2 min (see Figure S29), indicating decarboxylation products of **10** formed during the GC-MS process (compare Figure S30): m/z 308 → 264 / m/z 293 → 249, m/z -44 (-$CO_2$)).