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A new conjugated tripoid N_4 system containing furazan and triazolofurazan cores linked by a nitrogen bridge

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Contents

Experimental section

CAUTION!!! Although we have encountered no difficulties during preparation and handling of the compounds described in this paper, they are potentially explosive energetic materials that are sensitive to impact and friction. Any manipulations must be carried out by using appropriate standard safety precautions.

General remarks. All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ^{1}H, ^{13}C, ^{14}N spectra were recorded with Bruker AM-300 (300.1, 75.5, 21.7 MHz) and Bruker AV600 (600.1, 150.9, 43.4) spectrometers. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N negative values of δ_N correspond to upfield shifts); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). IR spectra were recorded with a Bruker "ALPHA-T" spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}) as pellets with KBr. Elemental analyses were performed by the CHNSO Analyzer LecoTruSpec Micro. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F254 aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. Silica gel 60 Merck (15–40 μm) was used for preparative column chromatography. All reagents were purchased from Acros or Sigma–Aldrich. Solvents were purified before use, according to standard procedures. 3-Amino-4-azido-1,2,5-oxadiazole[S1] and diazomethane[S2] (ethyl ether solution) were prepared according to previously published procedures.

(E)-4,4'-(Triaz-1-ene-1,3-diyl)bis(3-azido-1,2,5-oxadiazole) **4**. ***!!!Caution!!! Compound 4 is sensitive to mechanical stimuli and explodes in porcelain mortar under slight pressure from the pestle.*** $NOBF_4$ (940 mg, 8 mmol) was added to a vigorously stirred solution of freshly prepared 3-amino-4-azido-1,2,5-oxadiazole **3** (1.01 g, 8 mmol) in dry CH_2Cl_2 (40 mL) at 20 °C under argon atmosphere. The reaction mixture was stirred for 30 min, after that it was transferred on silica gel and purified by flash chromatography (ethyl acetate/petroleum ether, 1:1). After evaporation of the solvent *in vacuo* slowly crystallizing viscous oil was obtained. Yield 693 mg (66%). Light yellow solid, m.p. 63°C (onset, for details see "Thermal behavior" section). IR (KBr): $\tilde{\nu}$ 1202, 1268, 1290, 1533, 1614, 2141, 3435 cm^{-1}. ^{13}C NMR (75.5 MHz, acetone-d_6) δ: 147.7 (br.s), 150.2 (br.s)) ppm. ^{14}N NMR (21.7 MHz, acetone-d_6). δ: –145 (N_3, $\Delta\nu_{1/2}$= 70 Hz). HRMS (ESI) *m*/*z* [*M*–H]$^-$calcd for $C_4HN_{13}O_2$: 262.0303, found: 262.0292.

[S1] S. P. Balabanova, A. A. Voronin, I. V. Fedyanin,A. N. Pivkina, D. B. Meerov, T. S. Kon'kova, Yu. N. Matyushin, Yu. A. Strelenkoand and L. L. Fershtat, *Dokl. Phys. Chem.*, 2023, **513**, 159; https://doi.org/10.1134/S0012501623600250

[S2] T. Sammakia, I. R. Ramazanov and A. V. Yaroslavova, in *Encyclopedia of Reagents for Organic Synthesis*, 2021; https://doi.org/10.1002/047084289X.rd017.pub2

(E)-4,4'-(3-Methyltriaz-1-ene-1,3-diyl)bis(3-azido-1,2,5-oxadiazole) **5**. To a stirred solution of triazene **4** (350 mg, 1.33 mmol) in MeCN (10 mL) a freshly prepared solution of diazomethane in Et_2O was added portionwise until no gas evolution was observed (TLC control, ethyl acetate/petroleum ether, 1:1). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (ethyl acetate/petroleum ether, 2:1). After evaporation of the solvent *in vacuo* viscous oil crystallizes to give light yellow solid, m.p. 57 °C (onset, for details see "Thermal behavior" section). ^{1}H NMR (600.1 MHz, acetone-d_6) δ: 3.84 (s, 3 H, CH_3) ppm. ^{13}C NMR (150.9 MHz, acetone-d_6) δ: 34.0, 147.3, 148.5, 149.9, 153.7 ppm. ^{14}N NMR (43.4 MHz, acetone-d_6) δ: –145 (N_3, $\Delta\nu_{½}$= 70 Hz). IR (KBr): $\tilde{\nu}$ 655, 869, 890, 1030, 1181, 1245, 1388, 1431, 1492, 1537, 1554, 1583, 2145, 2178 cm^{-1}. HRMS (ESI) *m*/*z* [*M*+Na]$^+$calcd for $C_5H_3N_{13}O_2$: 300.0425, found: 300.0419.

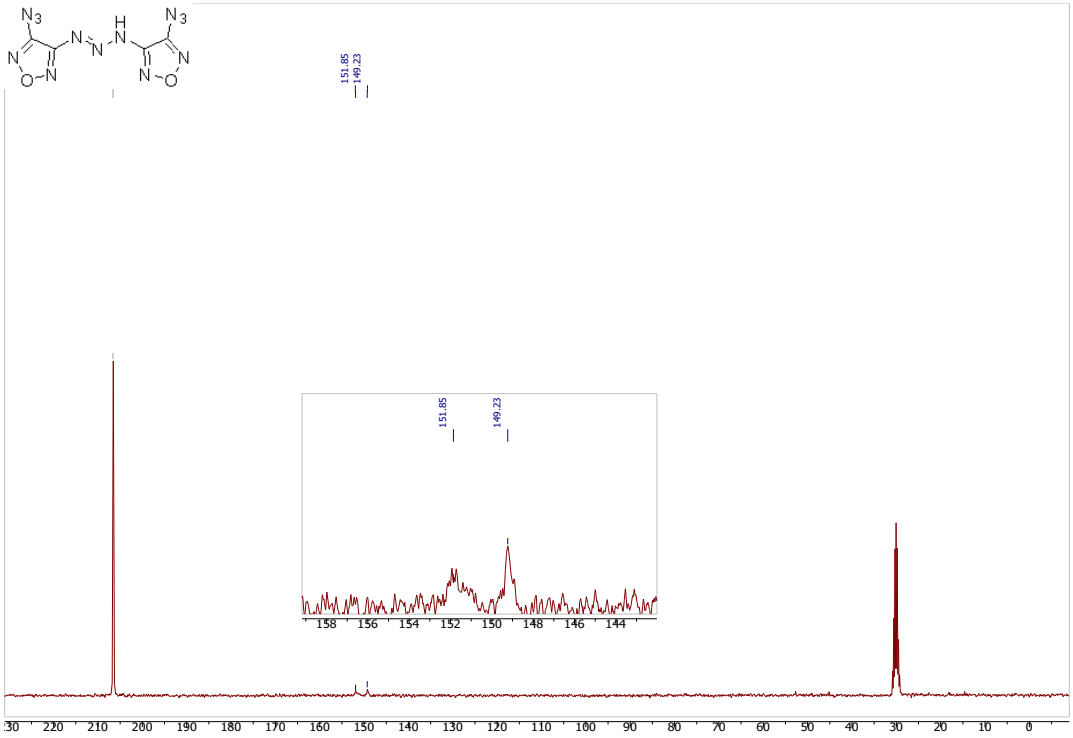
Thermal cyclization of (E)-4,4'-(3-methyltriaz-1-ene-1,3-diyl)bis(3-azido-1,2,5-oxadiazole) **5**. A solution of methyltriazene **5** (600 mg, 2.17mmol) in MeCN (20 mL) was refluxed for 40 h, and finally allowed to cool to rt. The solvent was evaporated *in vacuo* and the residue was separated by preparative chromatography (ethyl acetate/petroleum ether, 3:1) to give two compounds:

5-[N-(4-Azido-1,2,5-oxadiazol-3-yl)-N-methylamino]-[1,2,3]triazolo[4,5-c][1,2,5]oxa-diazol-5-ium-4-ide **1**. Yield 260 mg (48%). Yellow solid, m.p. 43 °C (onset, for details see "Thermal behavior" section). ^{1}H NMR (600.1 MHz, acetone-d_6) δ: 4.10 (s, 3 H, CH_3) ppm. ^{13}C NMR (150.9 MHz, acetone-d_6) δ: 43.0 (CH_3), 149.0 and 149.2 (C-3' and C-4'), 162.3 (C-3a and C-6a) ppm. ^{14}N NMR (43.4 MHz, acetone-d_6) δ: –64 (N-5, $\Delta\nu_{½}$= 210 Hz), –64 (N-4 and N-6, $\Delta\nu_{½}$= 760 Hz),–147 (N_3, $\Delta\nu_{½}$= 45 Hz). IR (KBr): $\tilde{\nu}$ 1015, 1191, 1296, 1309, 1327, 1345, 1428, 1456, 1533, 1583, 2145, 2950 cm^{-1}.

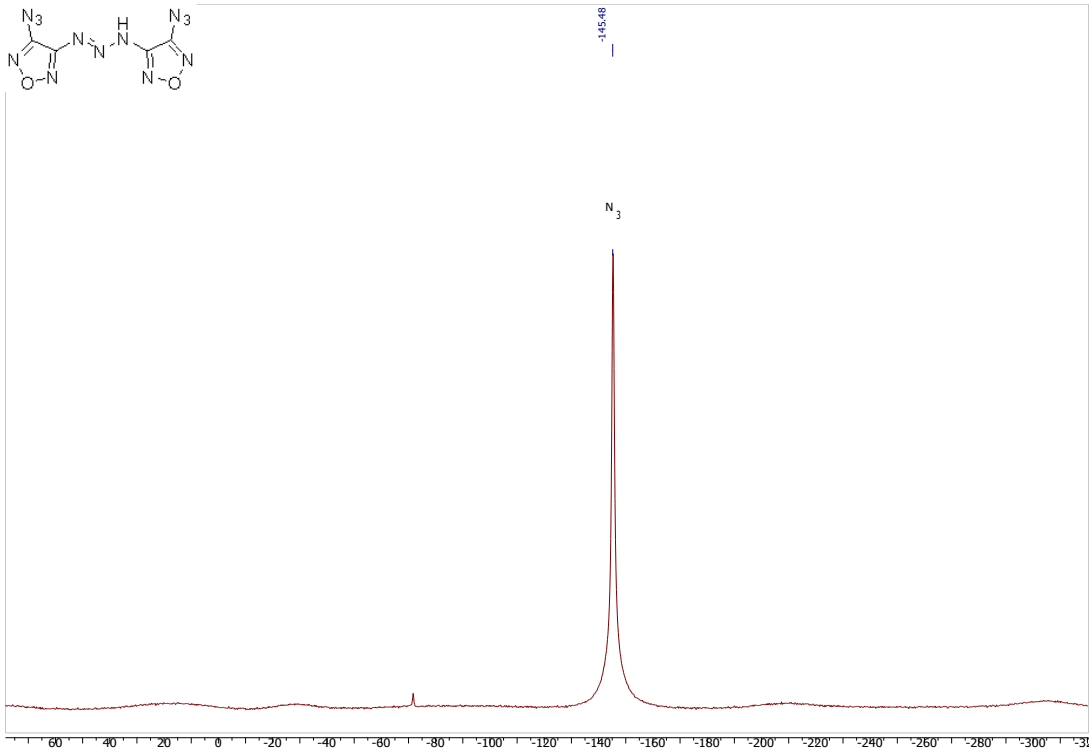
N-(4-Azido-1,2,5-oxadiazol-3-yl)-N-(4-methyl-4H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazol-5-ium-5-yl)amide **2**. Yield 205 mg (38%). Yellow solid, m.p. 158 °C (decomp., onset, for details see "Thermal behavior" section).^{1}H NMR (600.1 MHz, acetone-d_6) δ: 4.25 (s, 3 H, CH_3) ppm. ^{13}C NMR (150.9 MHz, acetone-d_6) δ: 35.3(CH_3), 148.0 (C-3a), 149.0 and 149.5(C-3' and C-4'), 153.7 (C-6a) ppm.^{14}N NMR (43.4 MHz, acetone-d_6) δ: –66 (N-5, $\Delta\nu_{½}$= 255 Hz), –146 (N_3, $\Delta\nu_{½}$= 50Hz). IR (KBr): $\tilde{\nu}$ 608, 769, 1018, 1282, 1485, 1510, 1533, 1684, 2146 cm^{-1}. HRMS (ESI) *m*/*z* [*M*+H]$^+$calcd for $C_5H_3N_{11}O_2$: 250.0544, found: 250. 0534.

NMR and IR section

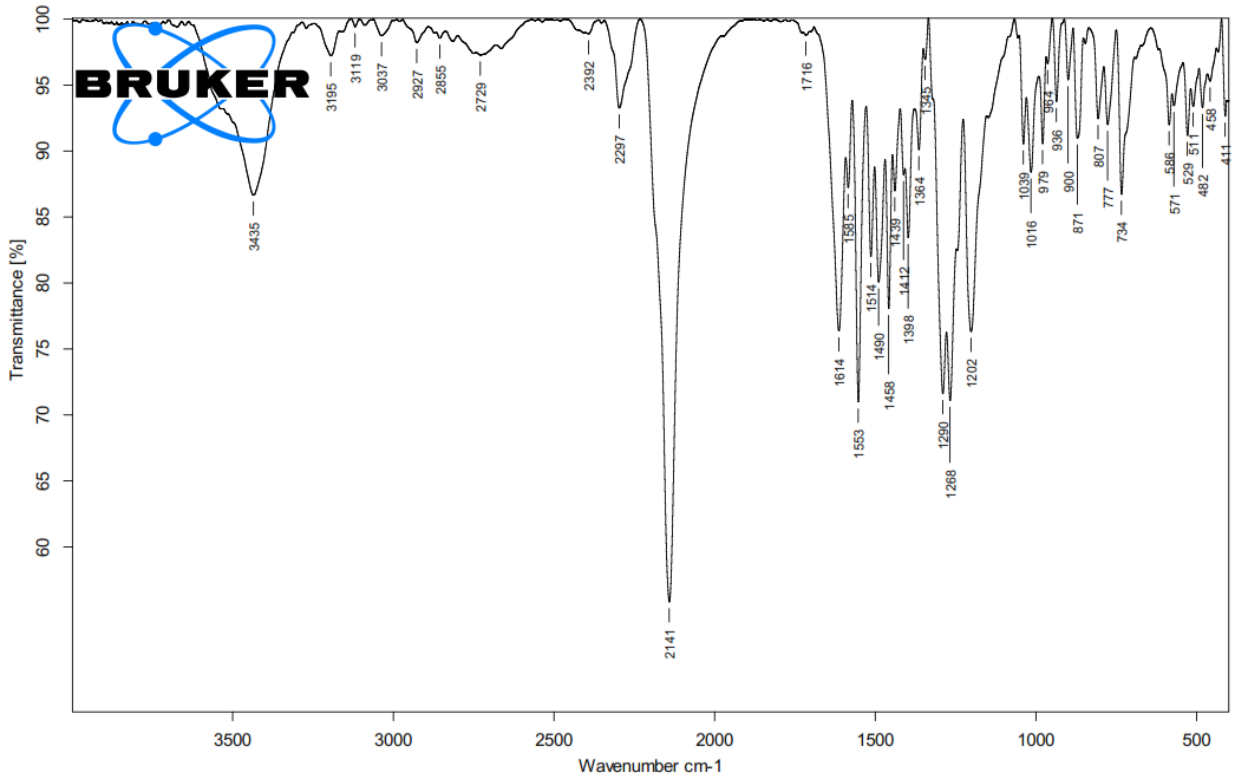
^{13}C NMR spectrum of triazene **4** in acetone-d_6



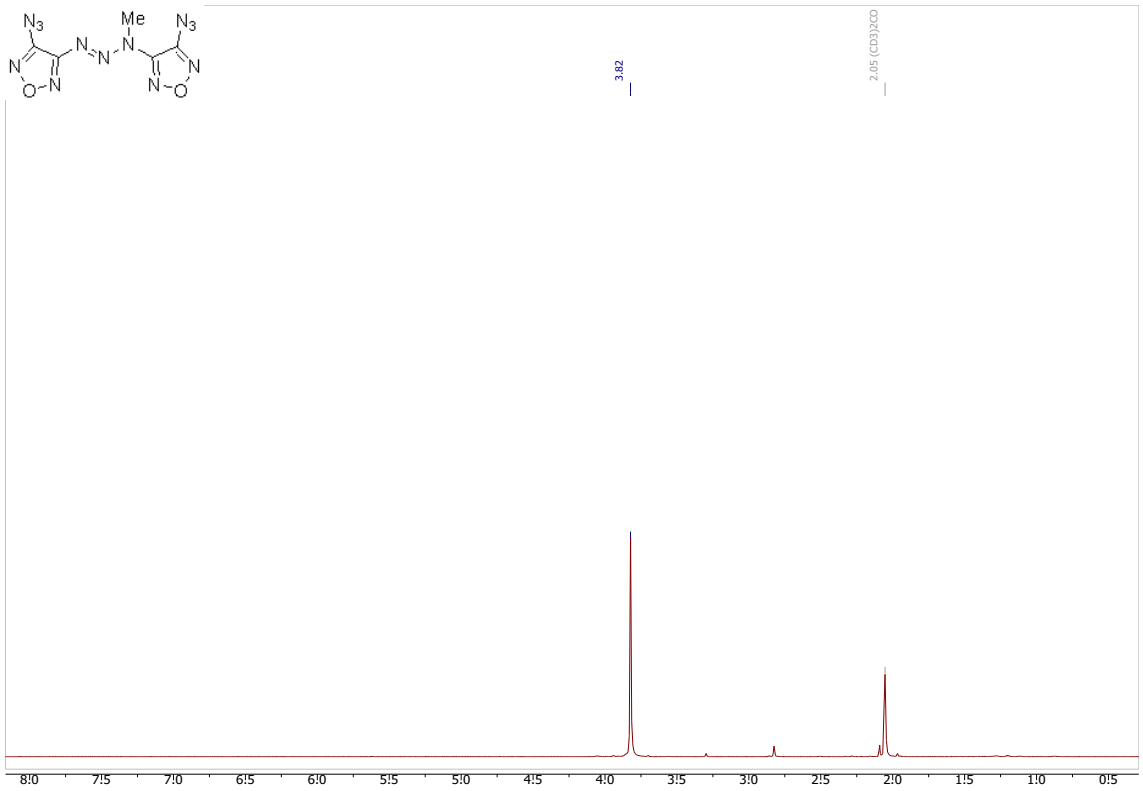
^{14}N NMR spectrum of triazene **4**in acetone-d_6



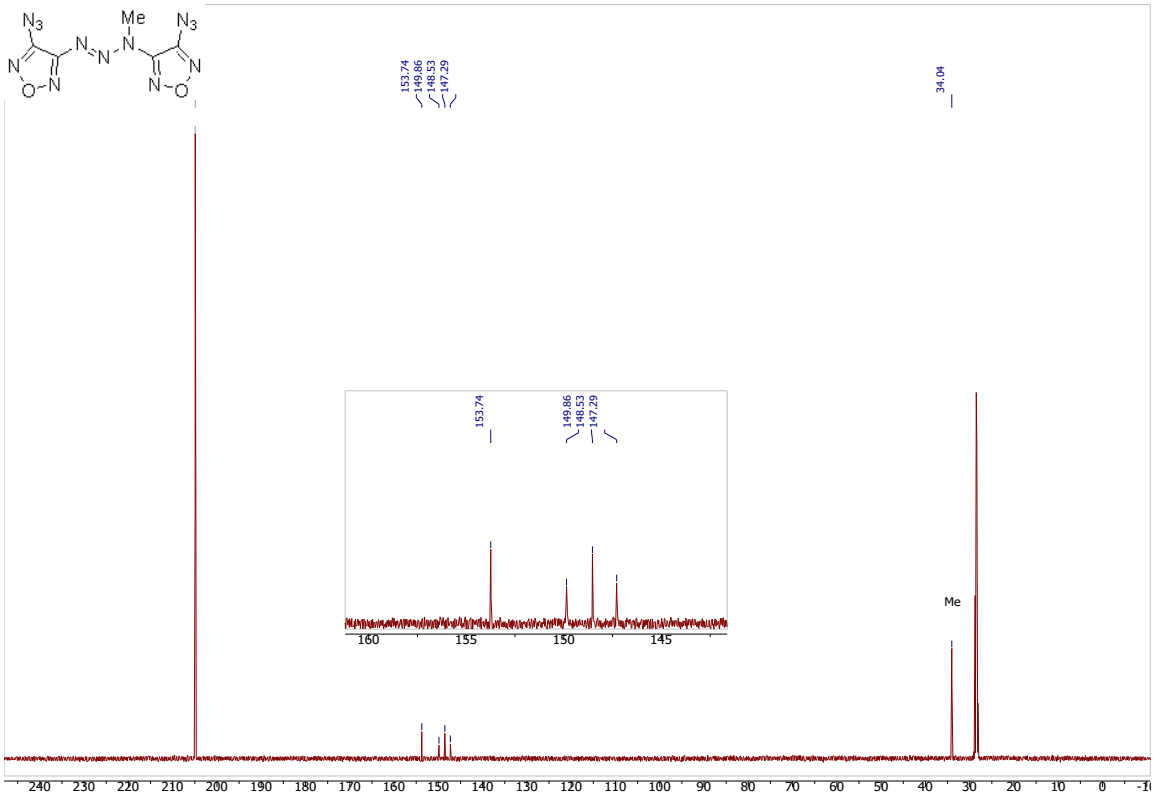
IR (KBr) spectrum of triazene **4**



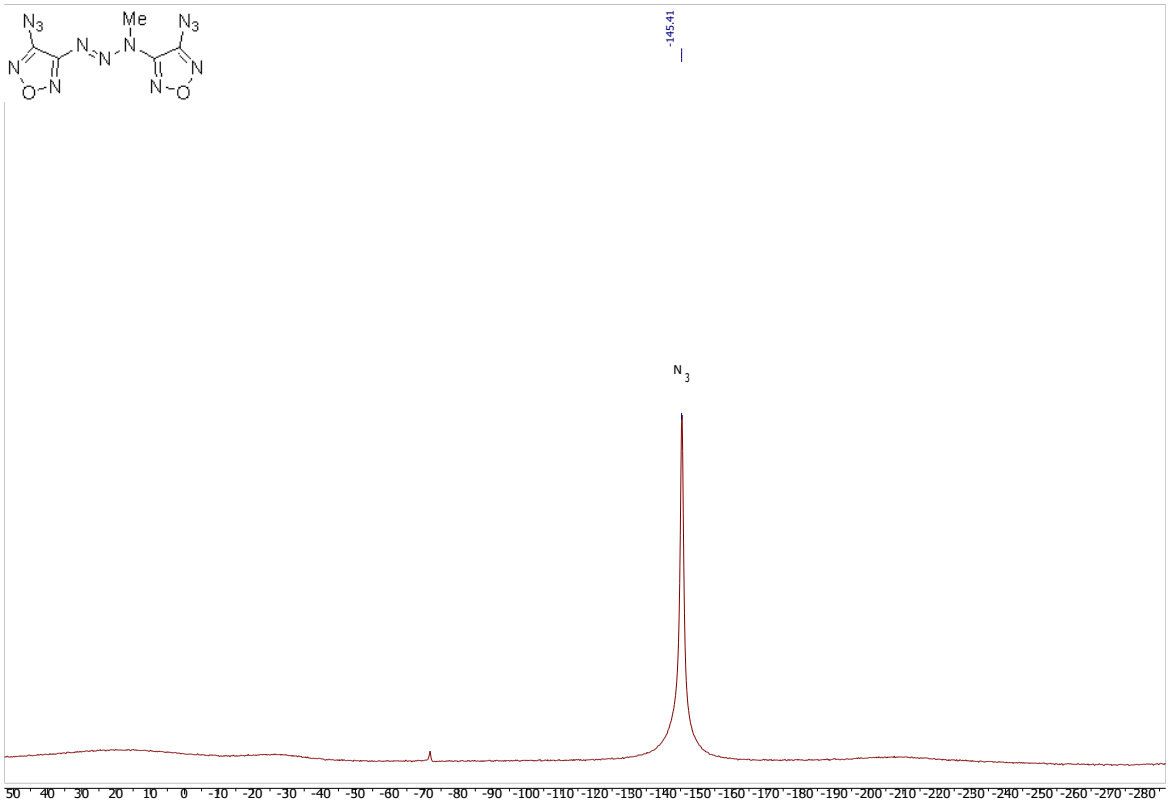
^{1}H NMR spectrum of methyltriazene **5** in acetone-d_6



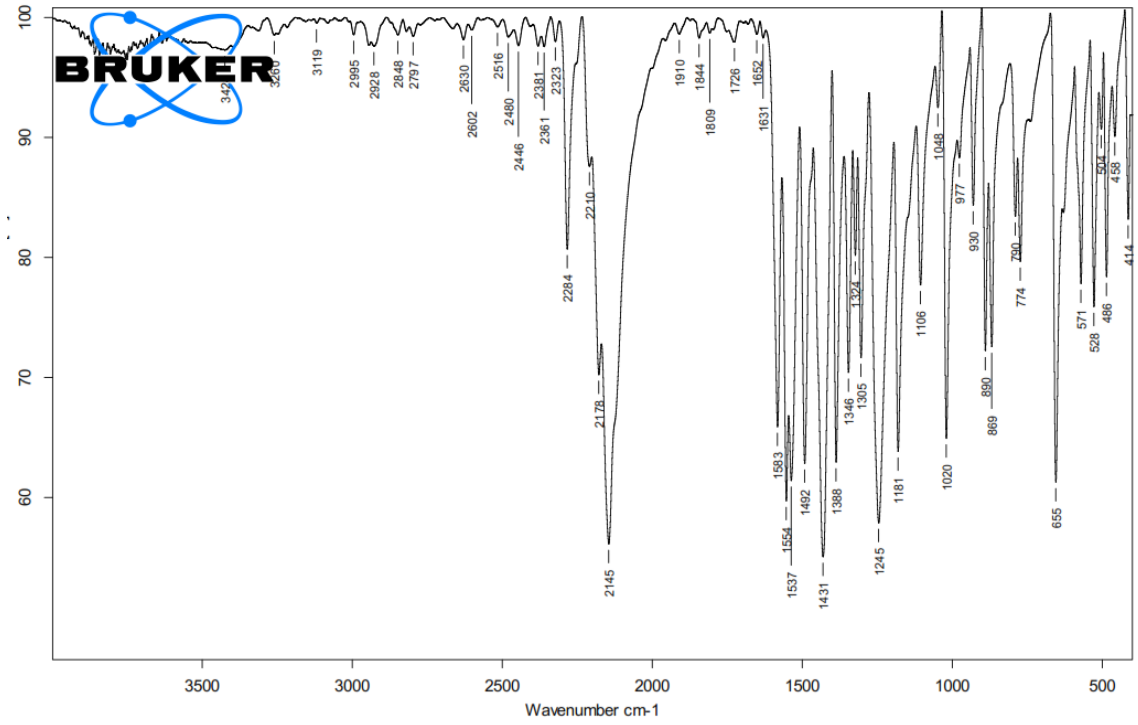
^{13}C NMR spectrum of methyltriazene **5** in acetone-d_6



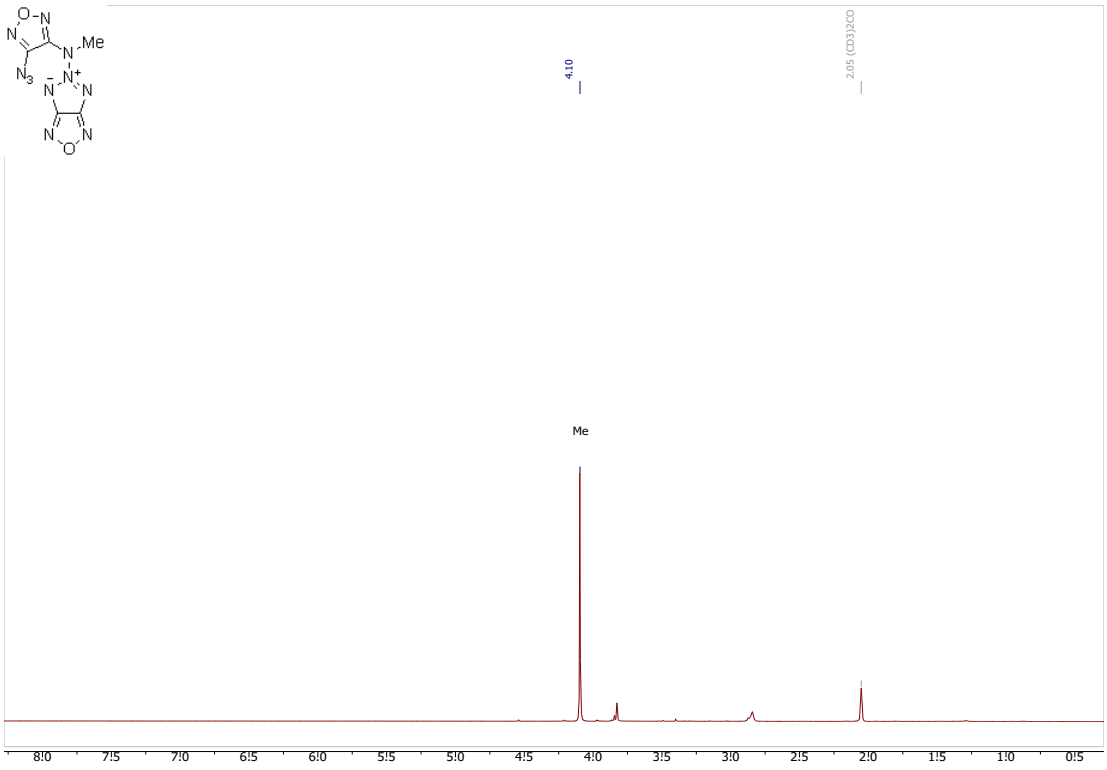
^{14}N NMR spectrum of methyltriazene **5** in acetone-d_6



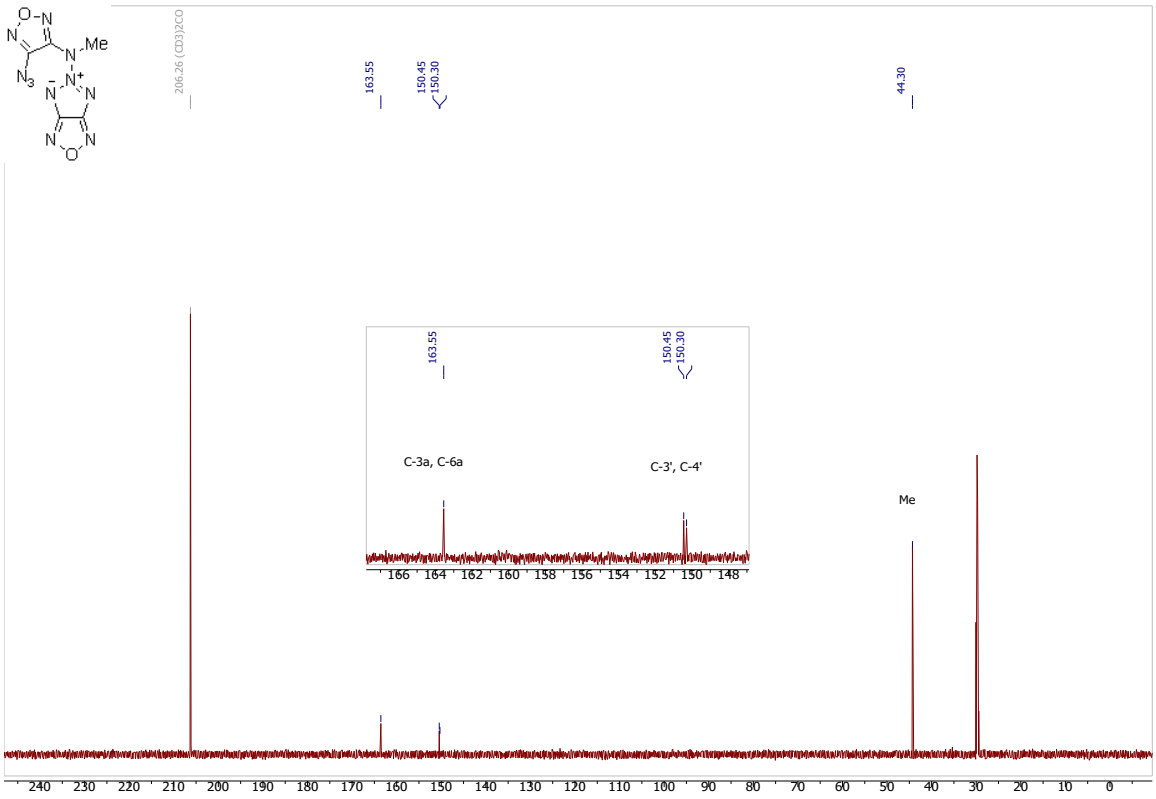
IR (KBr) spectrum of methyltriazene **5**



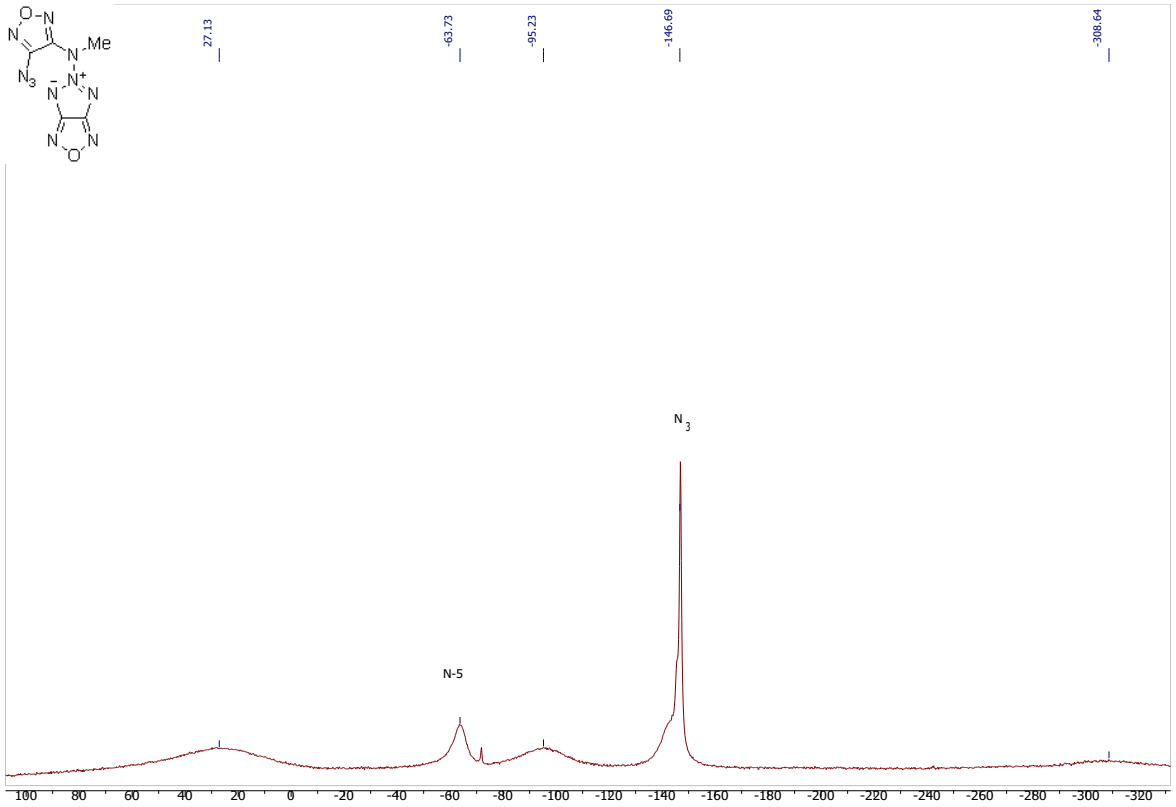
^{1}H NMR spectrum of FATF **1** in acetone-d_6



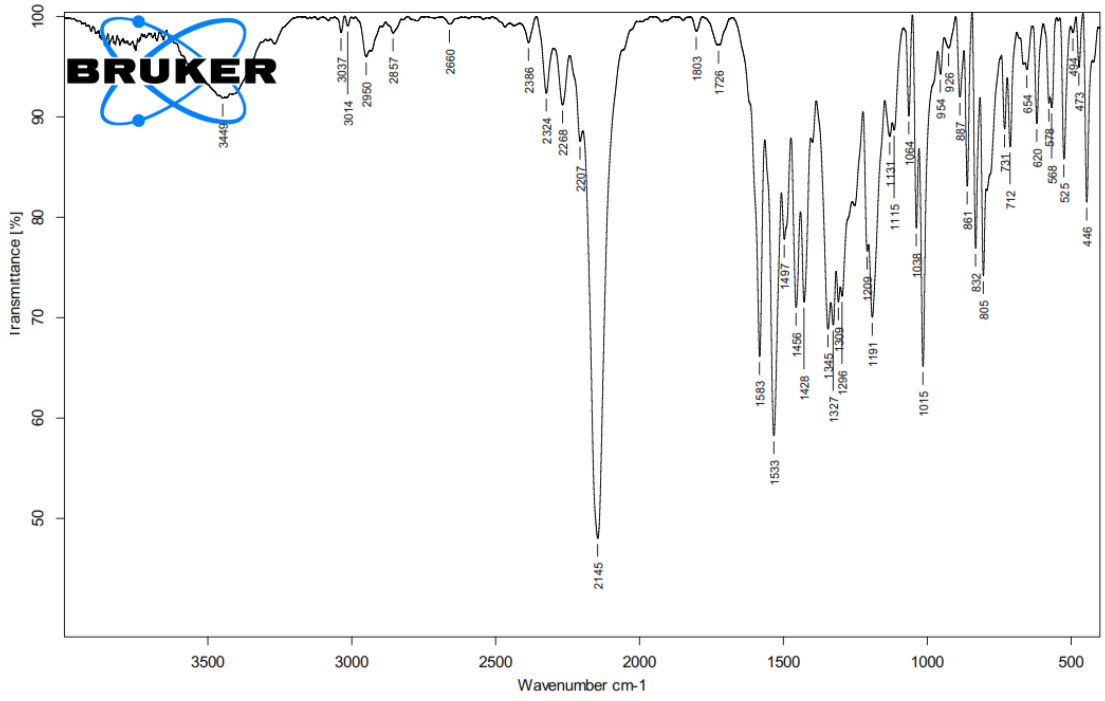
^{13}C NMR spectrum of FATF **1** in acetone-d_6



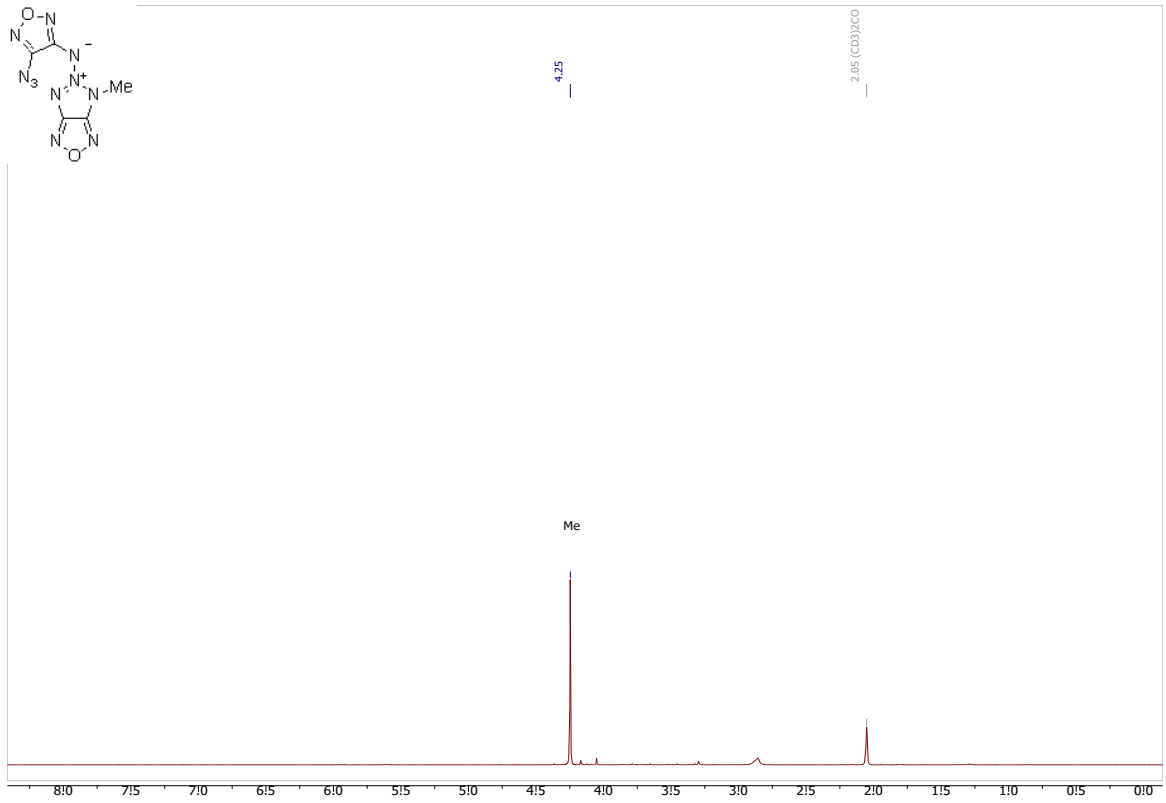
^{14}N NMR spectrum of FATF **1** in acetone-d_6



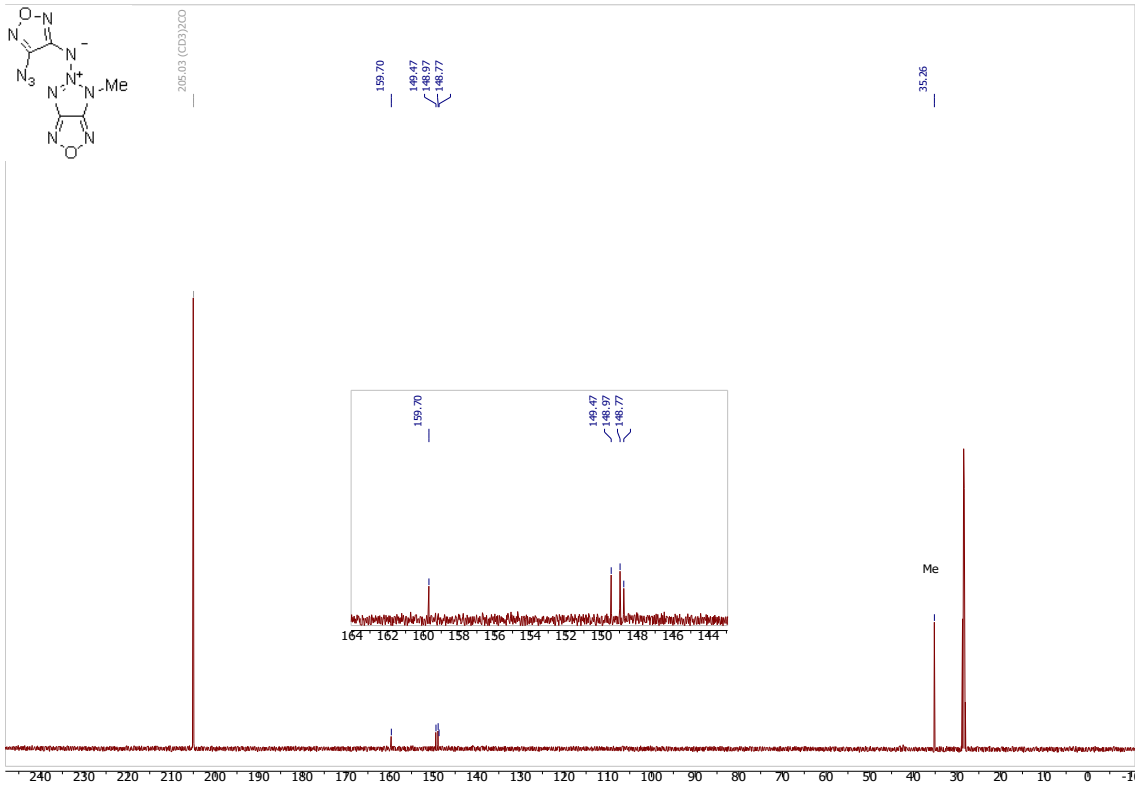
IR (KBr) spectrum of FATF **1**



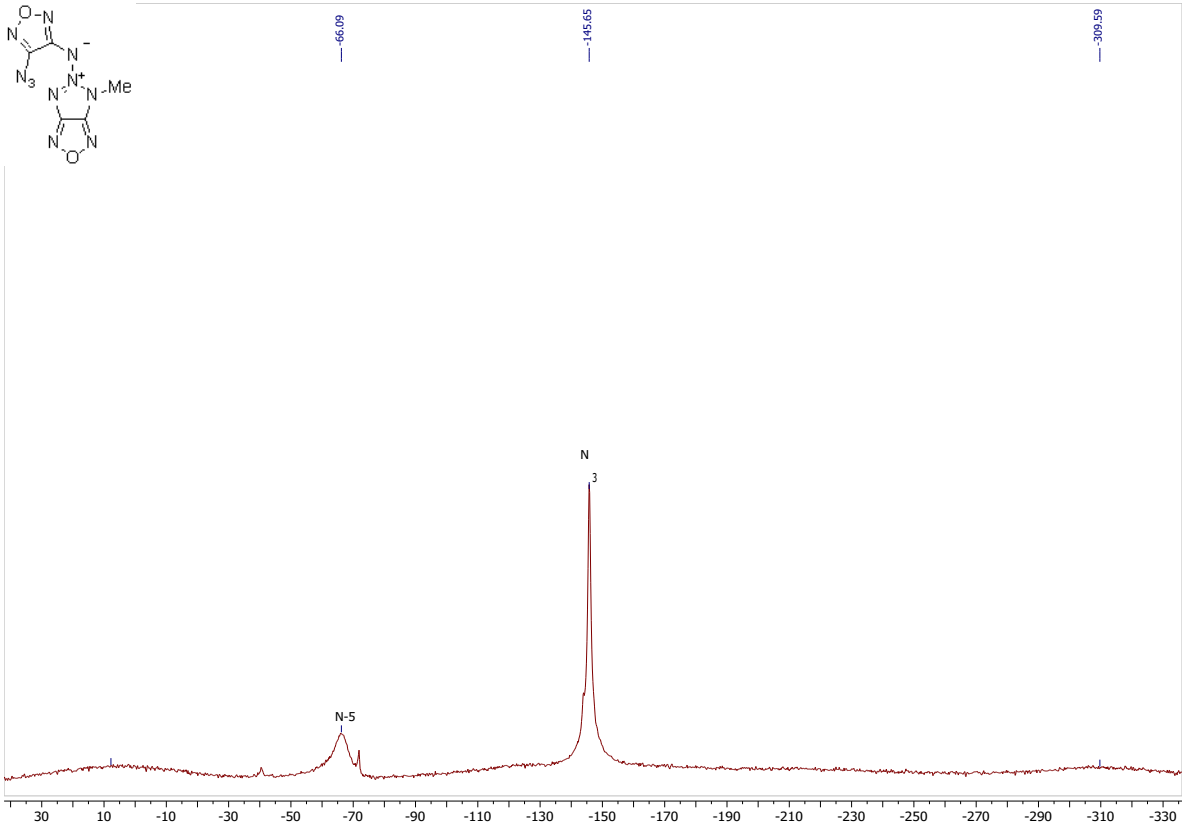
^{1}H NMR spectrum of amide **2** in acetone-d_6



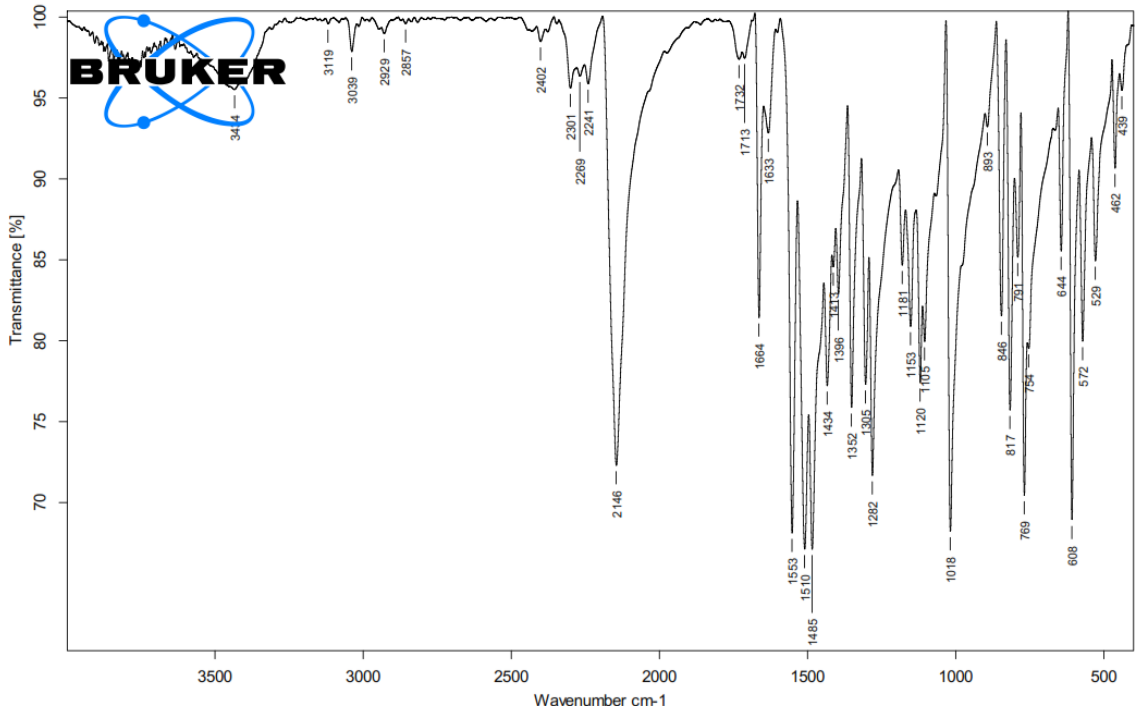
^{13}C NMR spectrum of amide **2** in acetone-d_6



^{14}N NMR spectrum of amide **2** in acetone-d_6

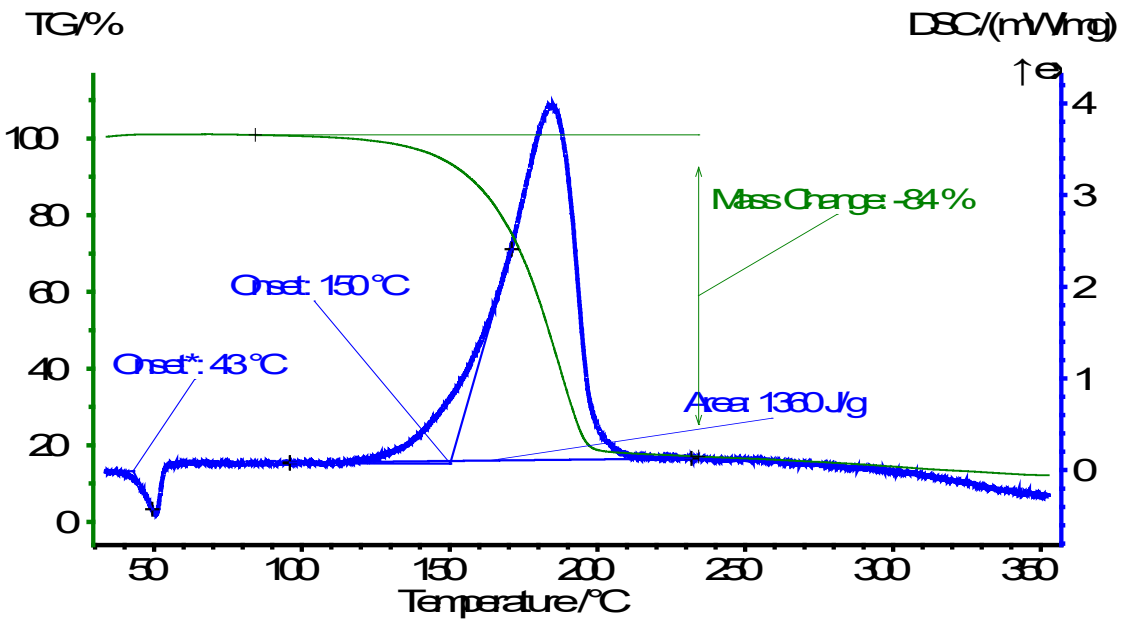


IR (KBr) spectrum of amide **2**

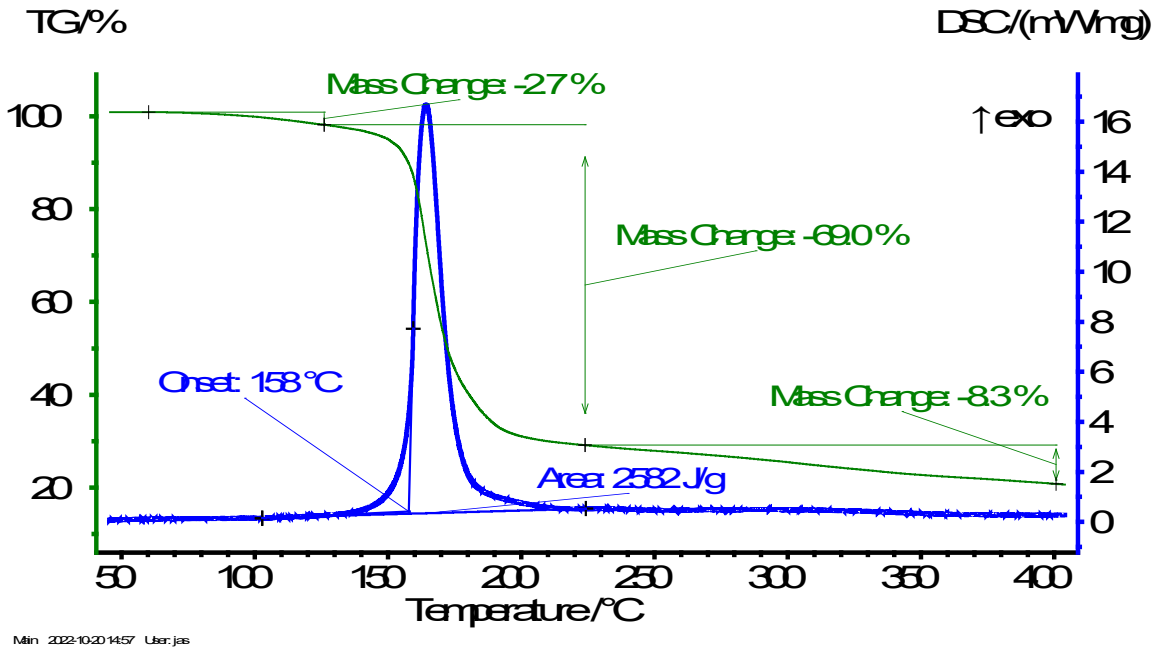


Thermal behavior

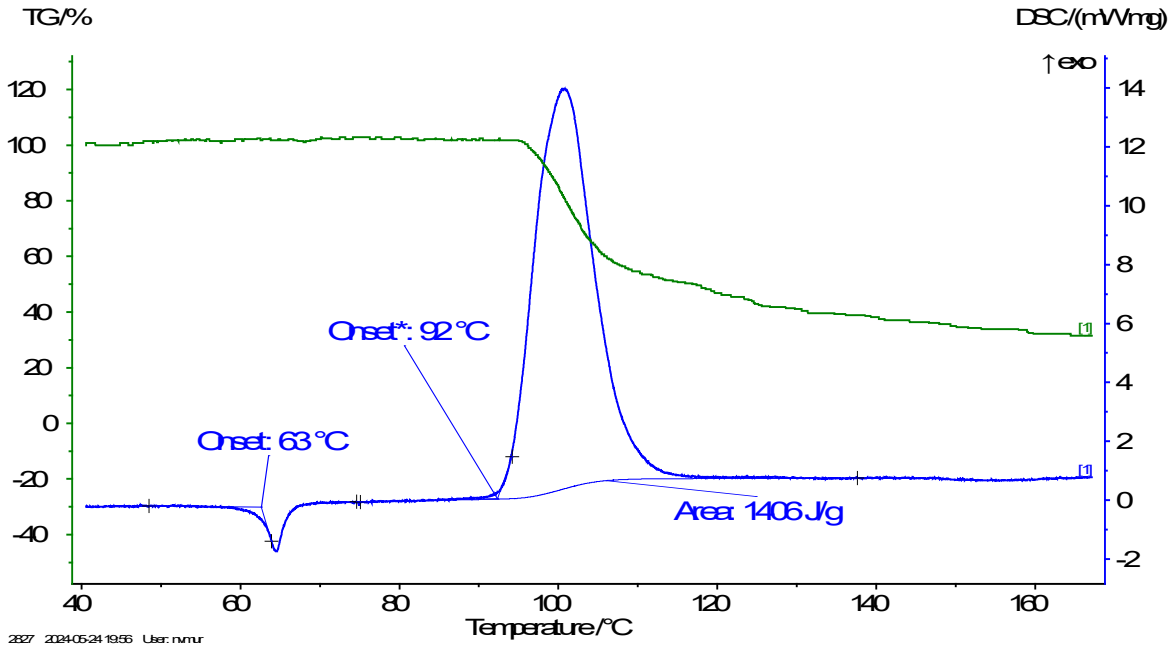
DSC (blue curve) and mass loss (TG, green curve) signals for FATF **1** heated at 5 K min^{-1} rate



DSC (blue curve) and mass loss (TG, green curve) signals for amide **2** heated at 5 K min^{-1} rate



DSC (blue curve) and mass loss (TG, green curve) signals for triazene **4** heated at 5 K min^{-1} rate



DSC (blue curve) and mass loss (TG, green curve) signals for methyltriazene **5** heated at 5 K min^{-1} rate