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# Trifluoroacetyl nitrate

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## Experimental

### General Details

Nitric acid ($d^{20}$ = 1.5 g·cm$^{-3}$) was preliminarily purified by distillation with the sulfuric acid additive; the colourless fraction was used in the syntheses. Dinitrogen pentoxide was prepared by the known procedure from $HNO_3$ and $P_2O_5$[1] and subjected to extra purification over $P_2O_5$ *in vacuo* (680 Torr). A receiver with $N_2O_5$ was cooled down to –40±5 °C.

The Raman spectra in the region 100–2000 cm$^{-1}$ were registered using a laser Raman spectrometer LabRAM Jobin-Yvon equipped with a cooled CCD detector. The excitation line was 632.8 nm of a He-Ne laser and the radiation power on the sample did not exceed 2 mW. Spectral resolution was 2 cm$^{-1}$. The spectra were recorded for the samples plugged in glass ampoules under argon atmosphere.

The $^{19}$F (282.40 MHz), $^{13}$C (75.47 MHz), $^{15}$N NMR (30.42 MHz) and $^{14}$N (21.69 MHz) spectra were recorded on a Bruker AM-300 spectrometer. A capillary with acetone-$d_6$ (TFAA, EtOAc, TFA, $CH_3NO_2$) or $CDCl_3$ ($CCl_4$) as a lock solvent were used for recording spectra of solutions in non-deuterated solvents. The $^{14}$N NMR spectra were recorded with $CH_3NO_2$ (10–15 mg) as internal standard unless otherwise specified (the high-field chemical shifts have negative values), $^{13}$C NMR spectra — with TMS as external standard and the $^{19}$F NMR spectra — with $CFCl_3$ as external standard. NMR spectra of compound **2** were recorded in $CDCl_3$: $^{1}$H (300.13 MHz), $^{13}$C NMR spectra with TMS and $^{14}$N NMR spectrum with $CH_3NO_2$ as external standard. The IR spectra were recorded on a Bruker ALPHA-T spectrometer. The mass spectrum was measured on a Kratos MS-300 instrument (EI, 70 eV).

The quantum chemical calculations of reaction equilibrium were performed using a set of programmes Gaussian 09 Revision D.01 DFT B3LYP/6-311++g(d,p)[2].

## Experimental Details

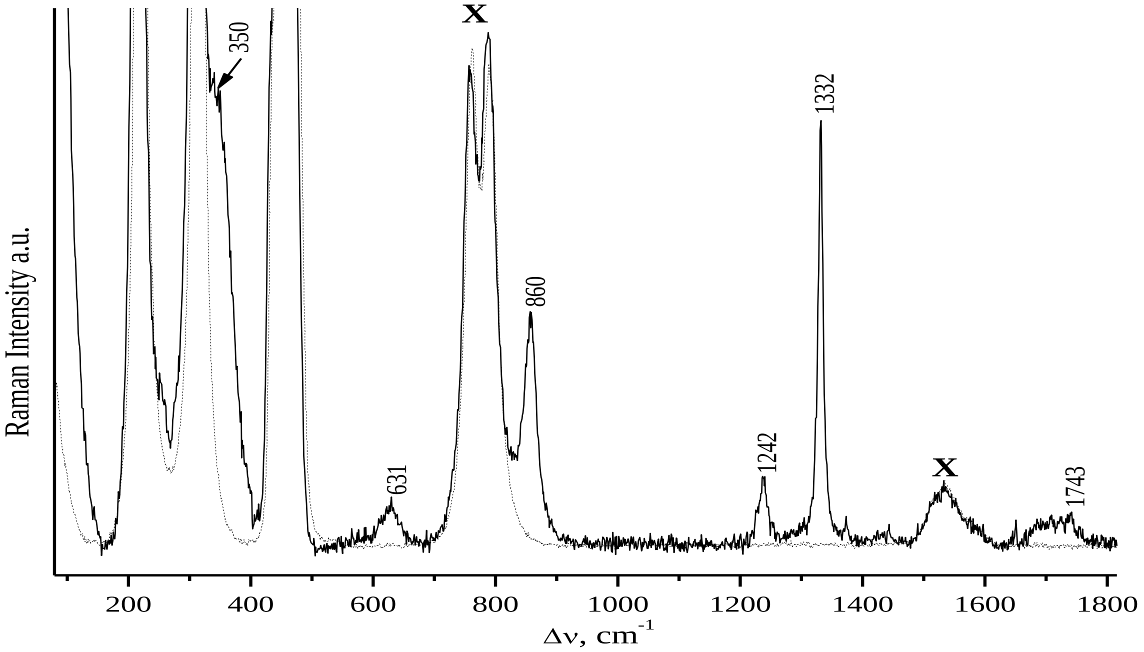

**Figure S1** Raman spectrum of $N_2O_5$ solution in $CCl_4$. Dashed line — the $CCl_4$ spectrum (**X**).

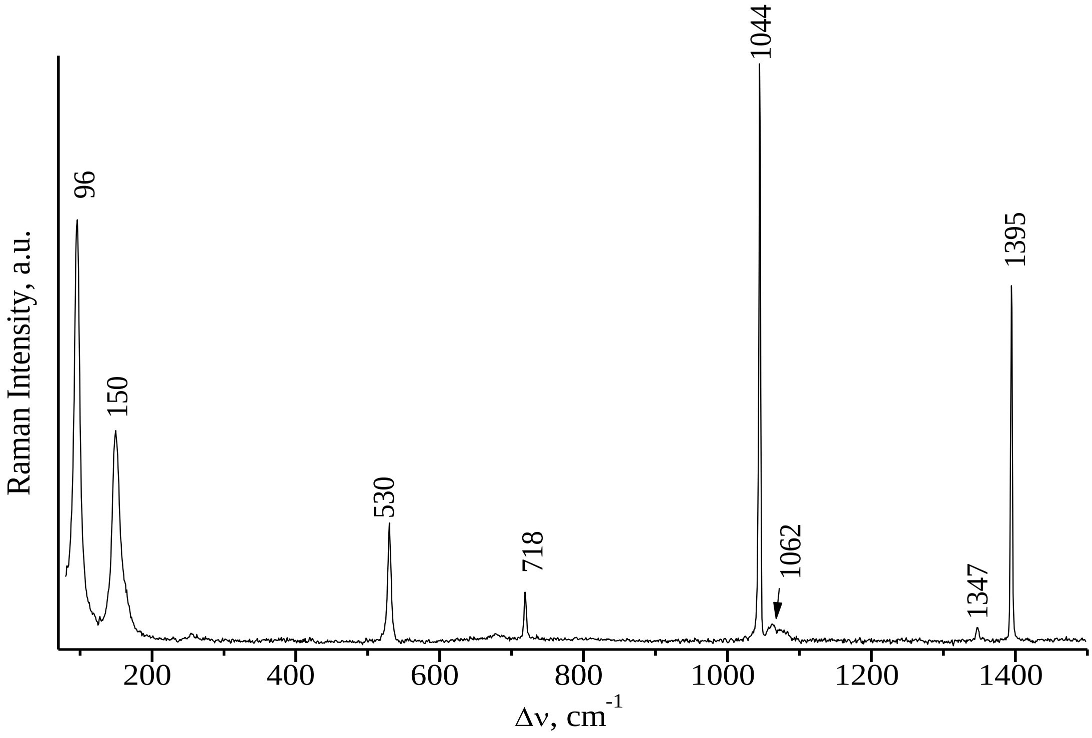

**Figure S2** Raman spectrum of solid $N_2O_5$.

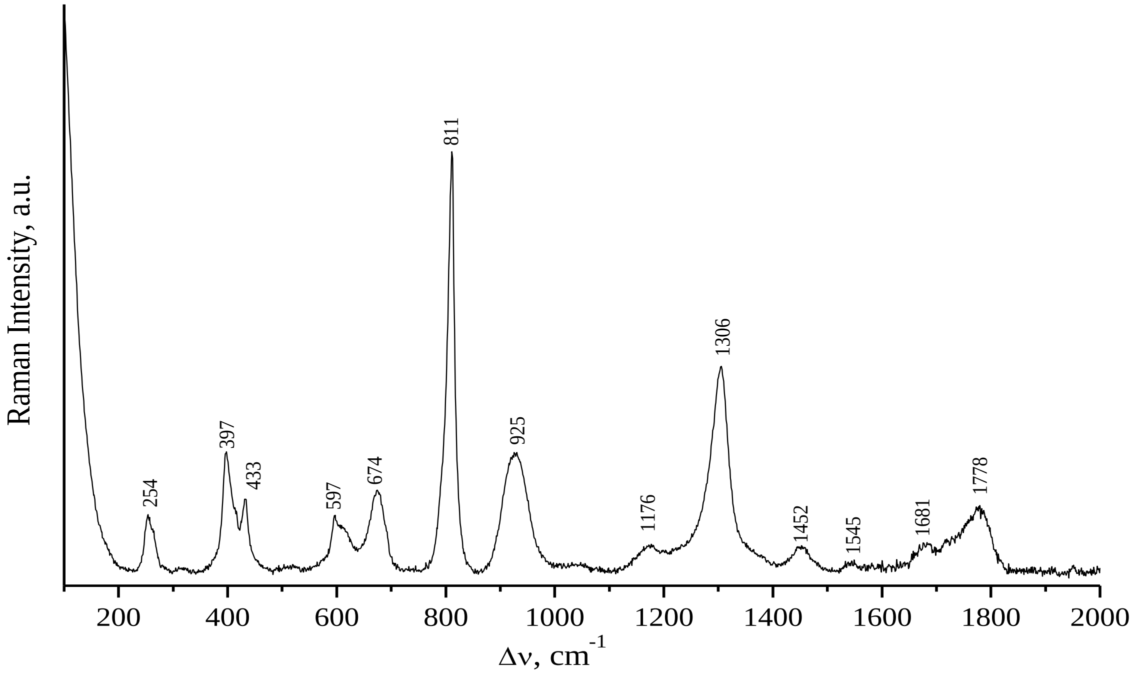

**Figure S3** Raman spectrum of the $HNO_3$—TFA mixture (1 : 1, mol).

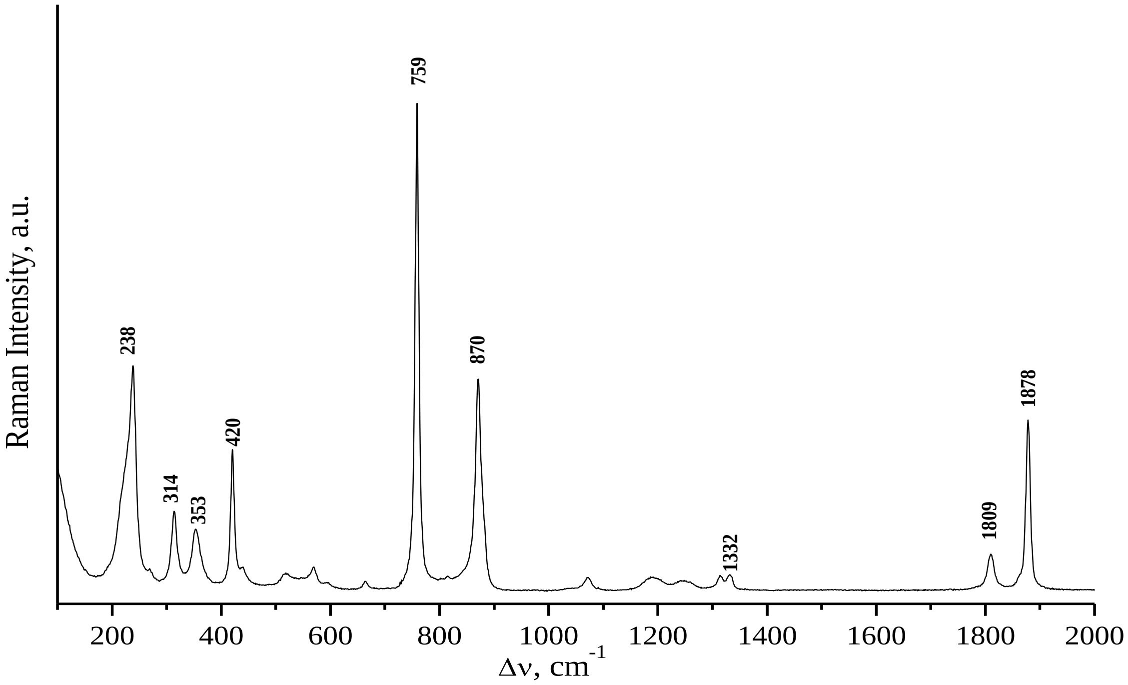

**Figure S4** Raman spectrum of TFAA.

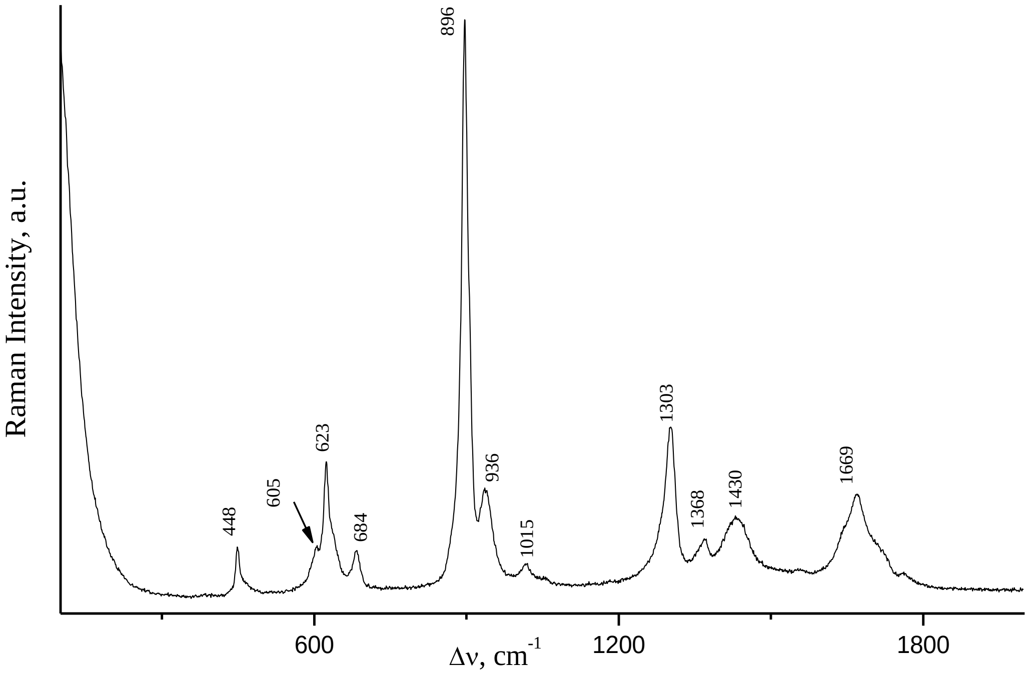

**Figure S5** Raman spectrum of the $HNO_3$—AcOH mixture (1 : 4, mol) at 0.5 h after dissolution.

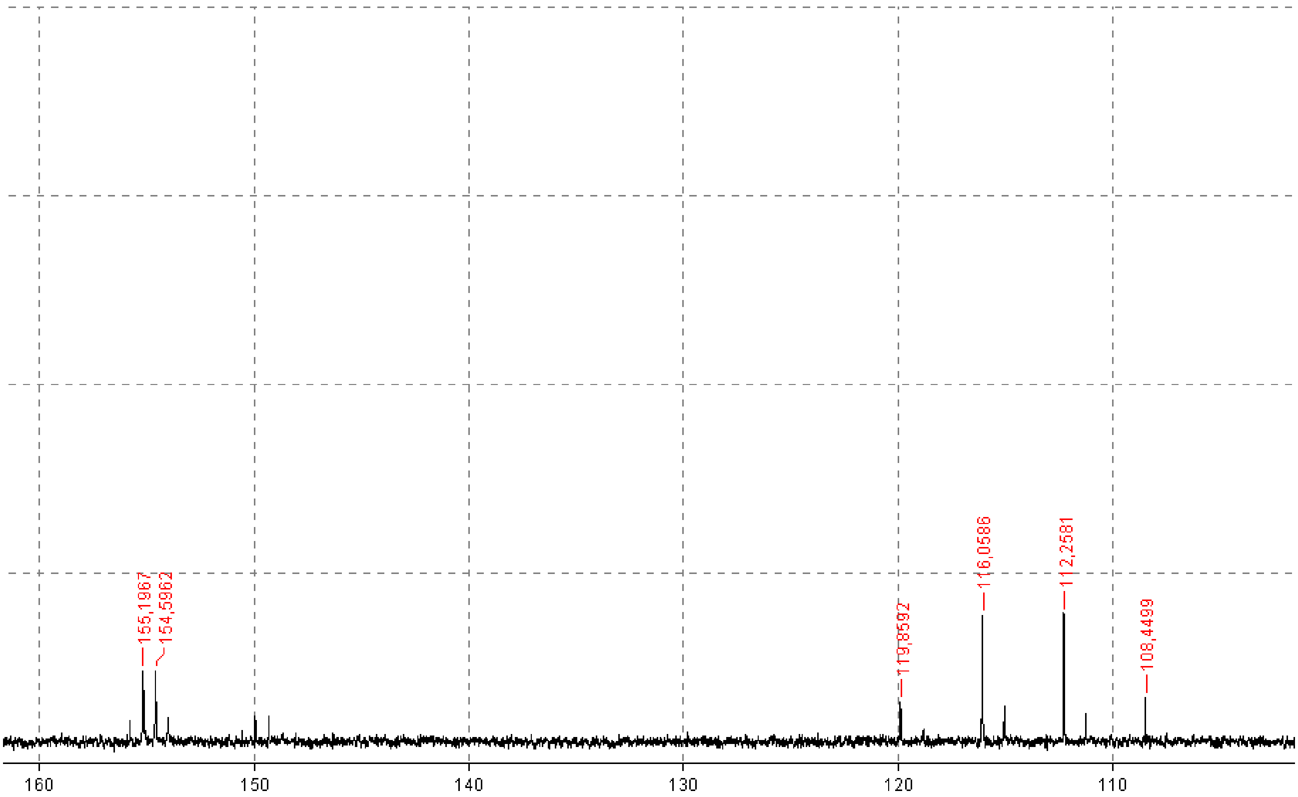

**Figure S6** $^{13}$C NMR spectrum of TFAN ($CDCl_3$). TFAA traces are present.

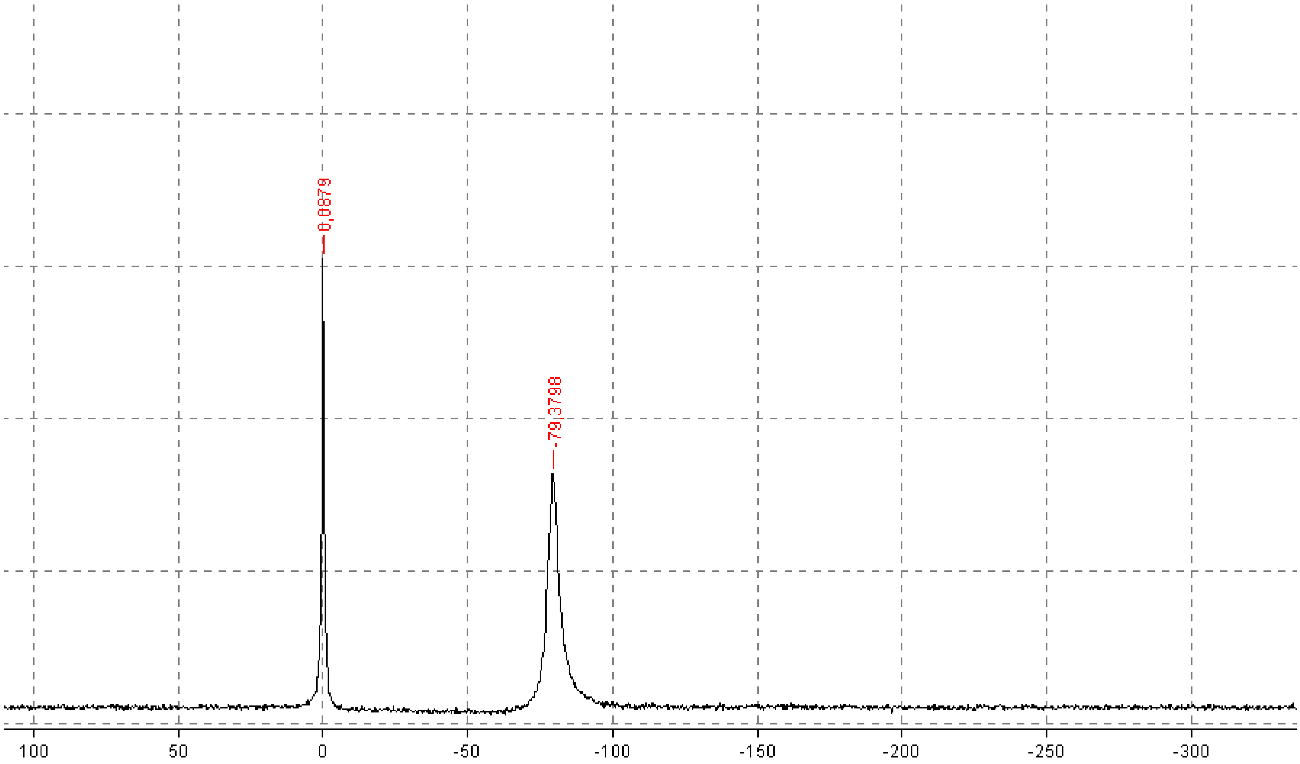

**Figure S7** $^{14}$N NMR spectrum of TFAN ($CDCl_3$), with $CH_3NO_2$ as internal standard.

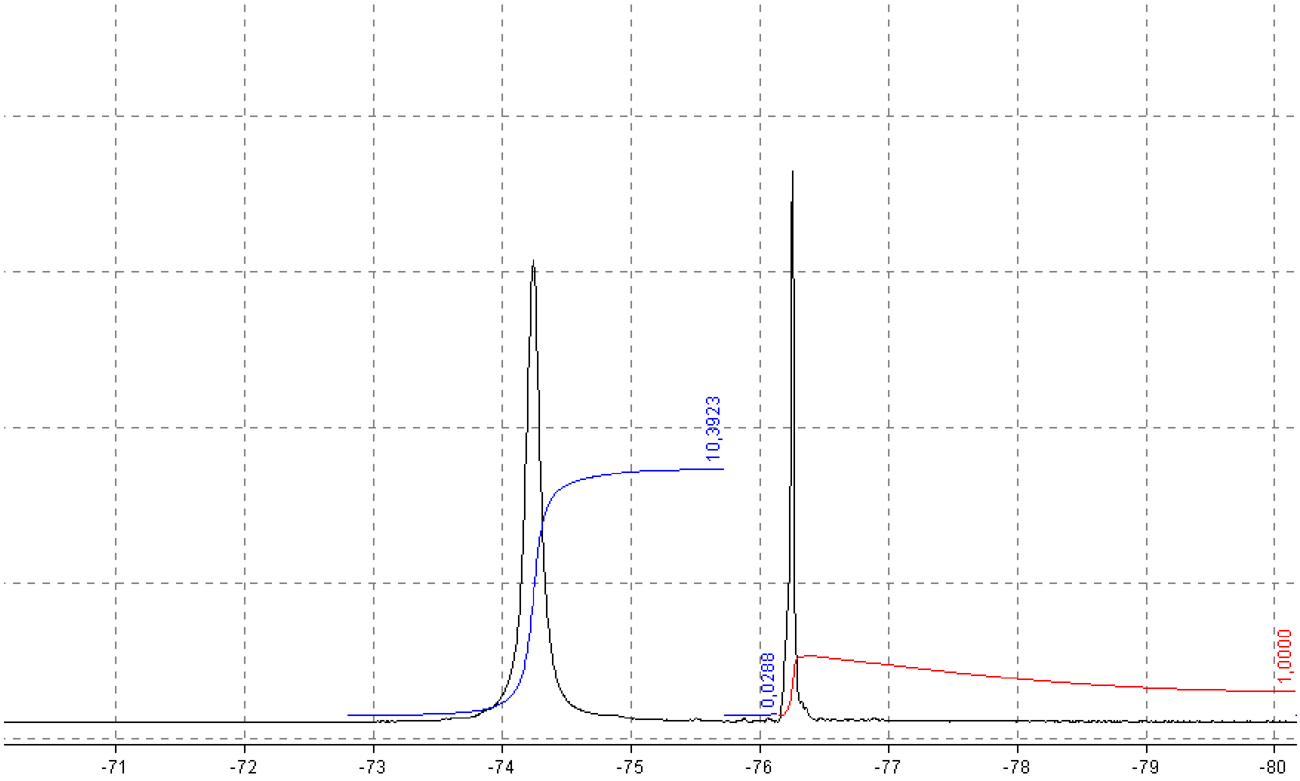

**Figure S8** $^{19}$F NMR spectrum of TFAN ($CDCl_3$). TFAA (≈ 9 mol. %) is present.

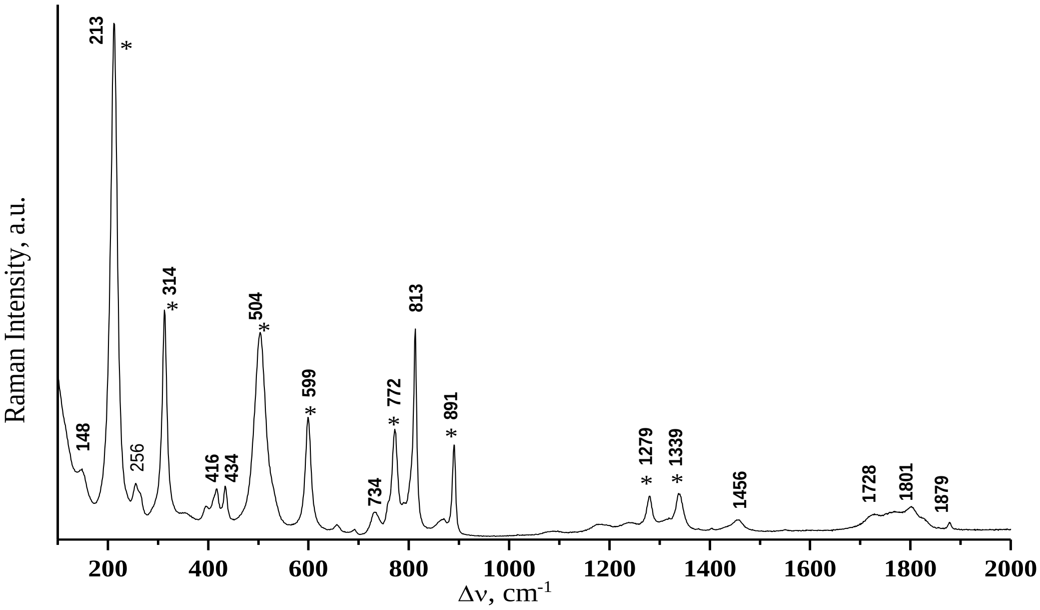

**Figure S9** Raman spectrum of the freshly prepared TFAN solution in TFA prepared from the TFAA—$HNO_3$ mixture (1 : 1, mol, 0–5 °C). The lines corresponding to the TFAN spectrum are marked with asterisks.

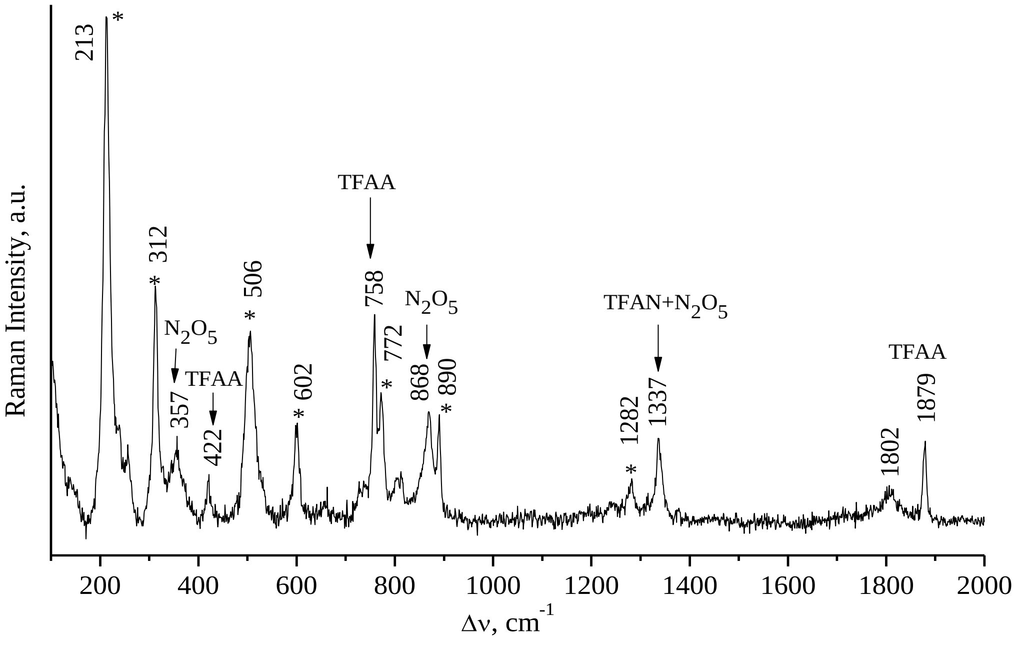

**Figure S10** Raman spectrum of the TFAN solution in TFAA prepared from the TFAA—$N_2O_5$ mixture (1.5 : 1, mol) at 6 h, 5 °C. The lines corresponding to the TFAN spectrum are marked with asterisks. The features of starting TFAA and $N_2O_5$ are also present.

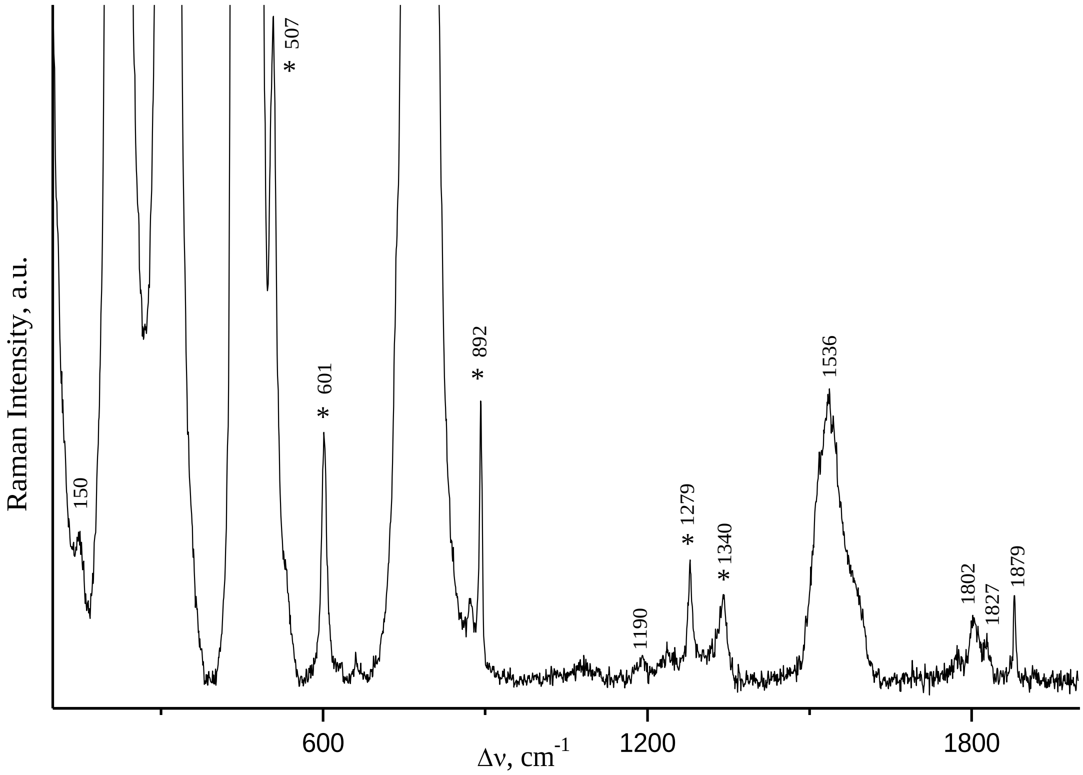

**Figure S11** Raman spectrum of the TFAN solution in $CCl_4$. The most intensive lines corresponding to the TFAN spectrum are marked with asterisks.

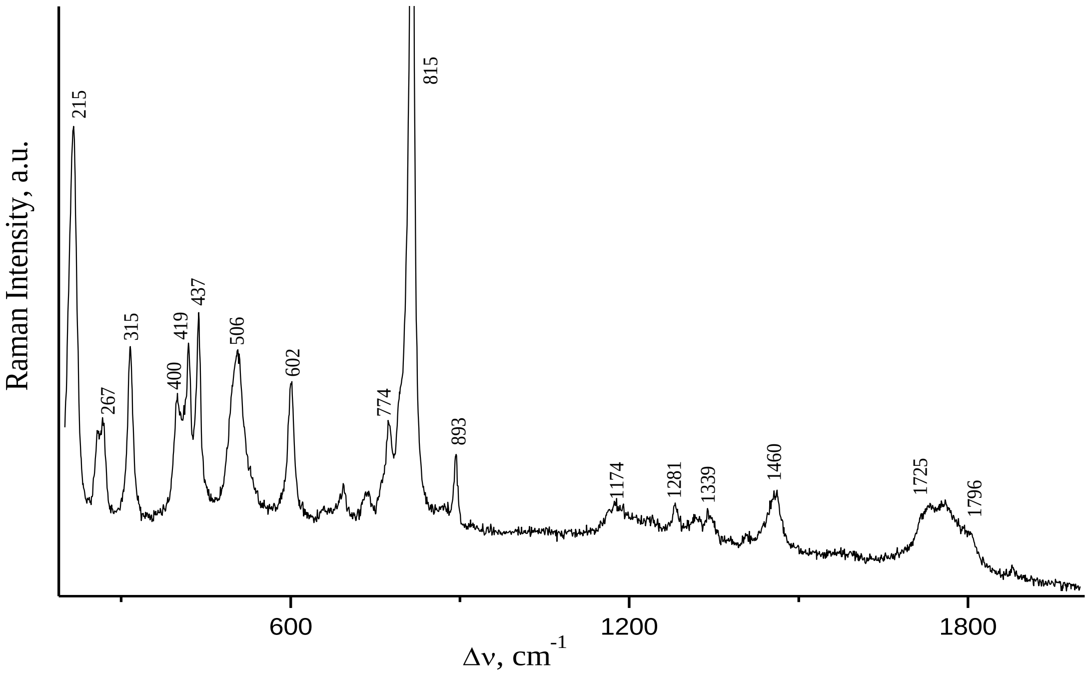

**Figure S12** Raman spectrum of the TFAN solution in TFA (1 : 4, mol) at 0.5 h, 0–5 °C (TFAN was prepared from $N_2O_5$—TFAA (1 : 1.2), 24 h, 5 °C).

**Table S1** $^{14}$N and $^{19}$F NMR monitoring of the TFAA reaction with $N_2O_5$, $HNO_3$ and $NH_4NO_3$.

| Time, h | $^{19}$F NMR, δ, ppm [% mol, conc. in the mixture] | | | $^{14}$N NMR, δ, ppm ($\Delta\nu_{1/2}$, Hz) [% mol, conc. in the mixture] |
|---|---|---|---|---|
| **No. 1 $(CF_3CO)_2O + N_2O_5$ (6 : 1, mol) → $CF_3COONO_2$** (neat, 0–5 °C) | | | | |
| 0.1 | — | — | — | –63 (45) ($N_2O_5$) |
| 0.7 | –76.7 [13] | –79.0 [87] | — | –73 (110) |
| 1.5 | –76.7 [28] | –79.0 [72] | — | –80 (40) (TFAN) |
| 7 | –76.7 [28] | –79.0 [72] | — | –80 (40) (TFAN) |
| **No. 2 $(CF_3CO)_2O + HNO_3$ (3.5 : 1, mol) → $CF_3COONO_2 + CF_3COOH$** (neat, 0–5 °C) | | | | |
| 0.1 | — | — | — | –47 (25) ($HNO_3$) |
| 0.2 | — | — | — | –69 (210) |
| 0.5 | –78.2 [27] | –79.1 [73] | — | –81 (40) (TFAN) |
| 48 | –78.2 [27] | –79.1 [73] | — | –81 (50) (TFAN) |
| **No. 3 $(CF_3CO)_2O + NH_4NO_3$ (2 : 1, mol) → $CF_3COONO_2 + CF_3COONH_4 + CF_3CONH_2$→ ($CF_3CONHNO_2$) → $N_2O + CF_3COOH$** (neat, 20 °C) | | | | |
| 1.5 | –79.1 [56] | –79.2 [39] | –80.1 [5] | –83 (40) (TFAN)<br>–146, –231 ($N_2O$)<br>–280 (370) ($CF_3CONH_2$)<br>–380 (m, *J* 53 Hz) ($NH_4^+$) |
| 2.5 | –79.2 [71] | –79.5 [27] | –80.1 [2] | — |
| 48 | –79.2 [53] | –79.7 [47] | — | –146, –231 ($N_2O$)<br>–360 (m, *J* 53 Hz) ($NH_4^+$) |
| **No. 4 $(CF_3CO)_2O + NH_4NO_3$ → ($CF_3COONO_2$ (gas) ↔ $(CF_3CO)_2O + N_2O_5$) → + solvent**[a] | | | | |
| Soln in $CCl_4$ | –73.6 [61] (TFAN) | –76.3 [39] (TFAA) | — | –58 (30) [11] ($N_2O_5$)<br>–77 (40) [87] (TFAN)<br>–147, –231 [2] ($N_2O$) |
| Soln in EtOAc | –76.6 [61] (TFAN) | –77.8 [39] (TFAA) | — | –80 (105) (TFAN)<br>–144, –229 ($N_2O$) |
| Soln in TFA | — | — | — | –84 (40) [97] (TFAN)<br>–146, –231 [3] ($N_2O$) |

[a] The solutions were prepared by distillation of reaction masses.

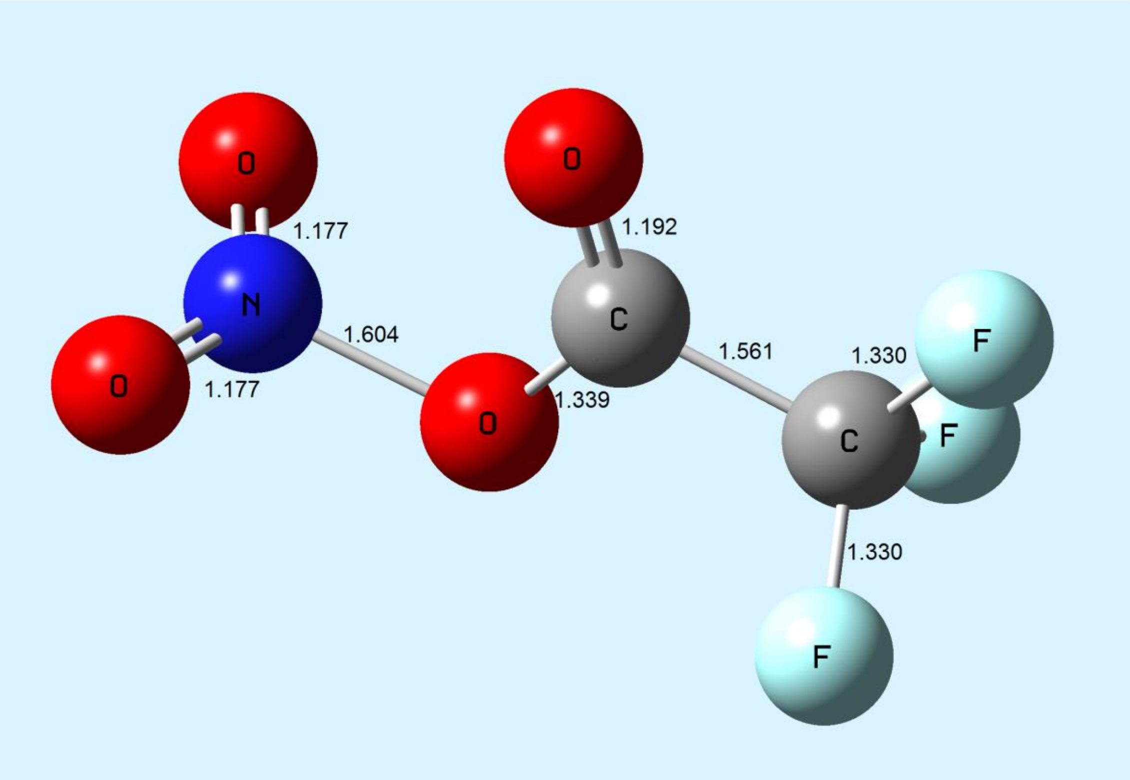

**Figure S13** *syn*-Conformer of TFAN. Bond lengths (Å) are shown.

**Table S2** Experimental Raman lines of *syn*-$CF_3COONO_2$ and calculated vibrational frequencies ($\nu$, $cm^{-1}$) obtained at the DFT level with the use of various functionals and basis sets.

| Raman exp. | B3LYP/ 6-31+G(d,p) | PBE/ aug-cc-pVTZ | TPSSh/ aug-cc-pVTZ | Normal mode assignment |
|---|---|---|---|---|
| | 51 | 62 | 61 | |
| | 69 | 74 | 73 | |
| | 130 | 116 | 120 | |
| 213 vs | 200 s | 188 | 193 | def. whole mol.*+$\nu_{CO\text{-}N}$ |
| | 253 | 244 | 249 | |
| 313 s | 315 s | 298 | 304 | def. whole mol. |
| | 407 | 387 | 401 | |
| 506 m | 508 vs | 475 | 498 | def. whole mol. +$\delta_{CON}$ |
| | 539 | 509 | 527 | |
| 601 m | 592 s | 564 | 587 | def. whole mol. |
| | 658 | 603 | 643 | |
| | 742 | 713 | 736 | |
| 772 m | 783 s | 752 | 772 | $\delta_{NO2}$ |
| 891 m | 900 m | 859 | 889 | def. whole mol. |
| | 1106 | 1095 | 1108 | $\nu_{C–F}$ + def. |
| | 1157 | 1107 | 1155 | $\nu_{C–F}$ |
| | 1206 | 1152 | 1205 | |
| 1280 w | 1283 s | 1221 | 1274 | $\nu_{C–C} + \nu^{s}_{NO2}$ +def. |
| 1340 w | 1371 s | 1328 | 1353 | $\nu^{s}_{NO2}$ (+ $\nu^{s}_{CO2}$) |
| | 1850 | 1758 | 1817 | $\nu^{s}_{C=O}$ (+$\nu^{s}_{NO2}$) |
| | 1877 | 1859 | 1864 s | $\nu^{as}_{NO2}$ |

Raman intensity in arbitrary units: vs – strong, s – strong, m - medium, w – weak.

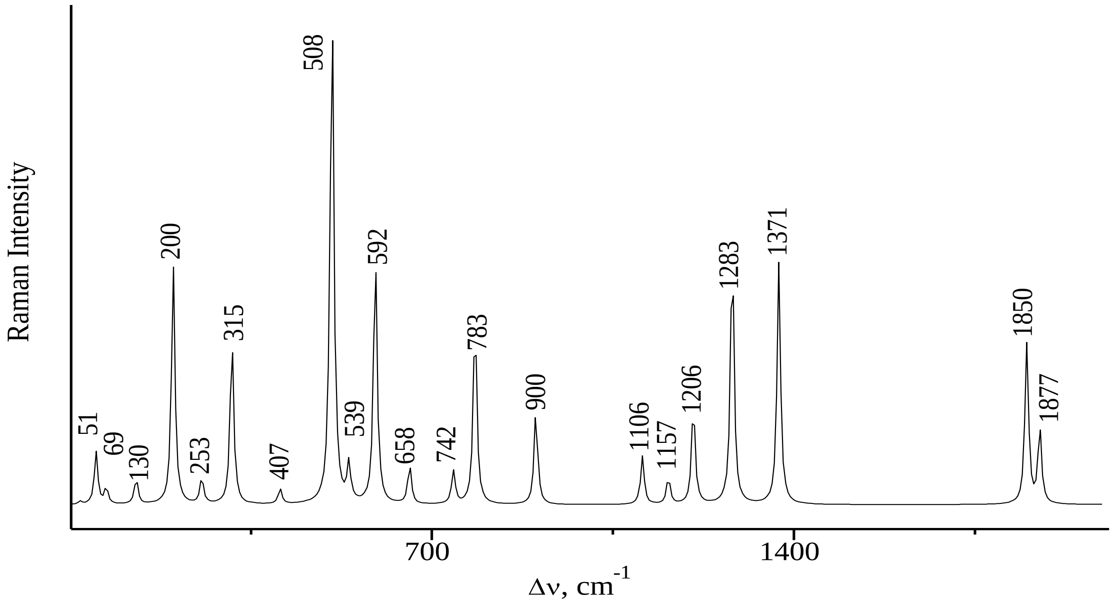

**Figure S14** Calculated Raman spectrum for TFAN at the B3LYP/6-31+G (d,p) level ($\nu$, $cm^{-1}$).

**Table S3** NMR monitoring of the reaction between TFAA and $N_2O_5$ in solutions, 0–5 °C.

| Solvent (research method) | TFAA : $N_2O_5$, mol | TFAN : TFAA ($^{19}$F) or TFAN : $N_2O_5$ ($^{14}$N) mol ratio at time after, h | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 3.5 | 7 | 24 | 3 day |
| $CDCl_3$ ($^{19}$F) | 1 : 1 | — | — | — | 3 : 1 | 10.4 : 1 |
| $CH_3NO_2$ ($^{19}$F) [a] | 1 : 1 | — | 2.6 : 1 | — | 3.1 : 1 | — |
| $CCl_4$ ($^{14}$N) | 1 : 1 | 1 : 1 | 3.5 : 1 | 7 : 1 | ≈ 80 : 1 [b] | — |
| | 3 : 1 | 25 : 1 | 40 : 1 | 60 : 1 | ∞ | — |
| | 7 : 1 [c] | ∞ | — | — | — | — |

[a] In $CH_3NO_2$ $\delta_F$: TFAN –75.3 ppm, TFAA –77.5 ppm, TFA –77.8 ppm.

[b] $N_2O_5$ signal was spectroscopically recorded, yet its intensity was close to noise.

[c] $N_2O_5$ solution in TFAA.

### Acetyl nitrate

Acetic anhydride (80 mg, 0.78 mmol) under argon atmosphere was mixed in an ampule with $N_2O_5$ (80 mg, 0.74 mmol), or with $HNO_3$ (47 mg, 0.75 mmol), then $CDCl_3$ (0.4 ml) was added and the ampule was sealed. The spectra were recorded after 0.5–1 h; $\delta_H$ ($CDCl_3$) 2.15 ($C\underline{H}_3$); $\delta_C$ ($CDCl_3$) 17.36 ($\underline{C}H_3$), 165.50 ($\underline{C}O$).

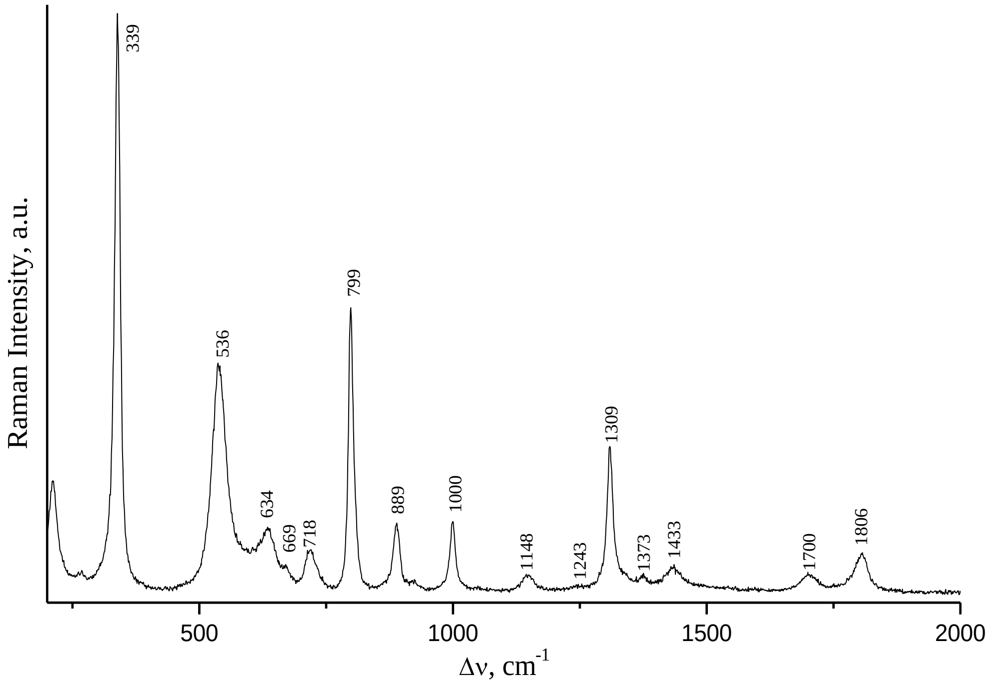

**Figure S15** Raman spectrum of $AcONO_2$ prepared from the $Ac_2O$—$N_2O_5$ mixture (1 : 1, mol, 1 day, 0–5 °C).

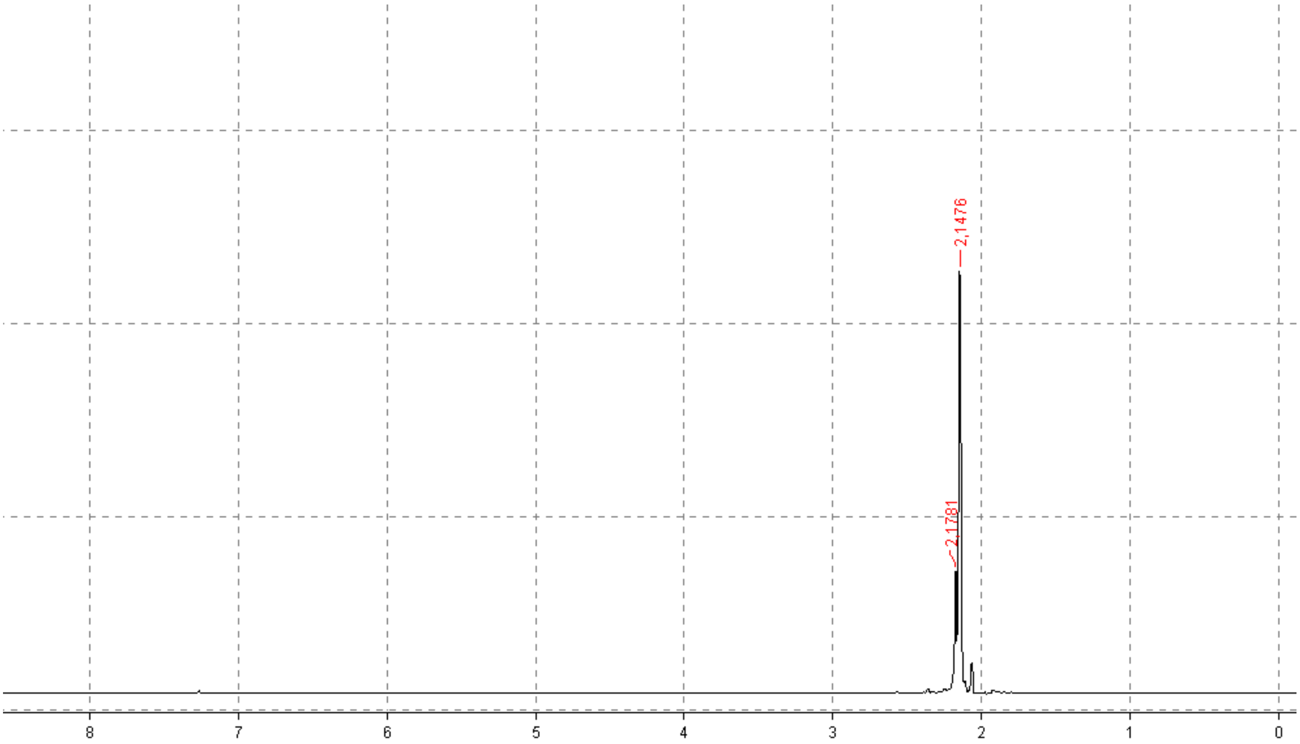

**Figure S16** $^1$H NMR spectrum of $AcONO_2$ obtained from $N_2O_5$ and $Ac_2O$ (ppm, $CDCl_3$). Excess $Ac_2O$ is present.

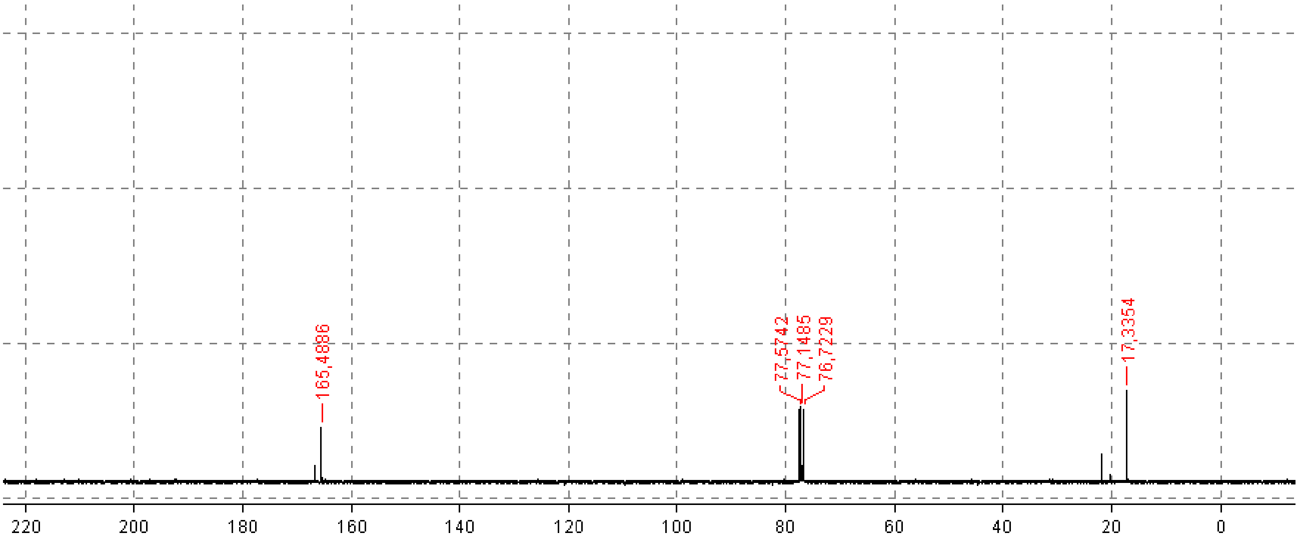

**Figure S17** $^{13}$C NMR spectrum of $AcONO_2$ obtained from $N_2O_5$ and $Ac_2O$ (ppm, $CDCl_3$). Excess $Ac_2O$ is present.

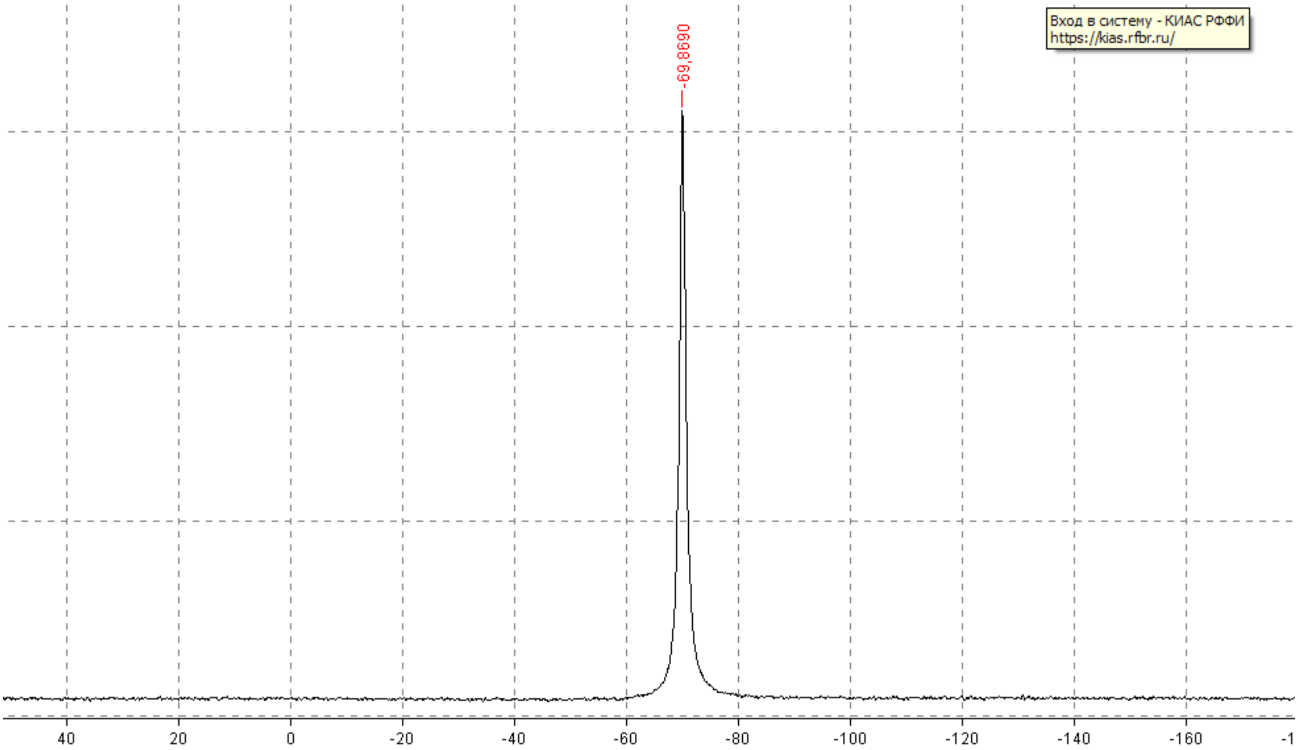

**Figure S18** $^{14}$N NMR spectrum of $AcONO_2$ obtained from $N_2O_5$ and $Ac_2O$ (ppm, $CDCl_3$).

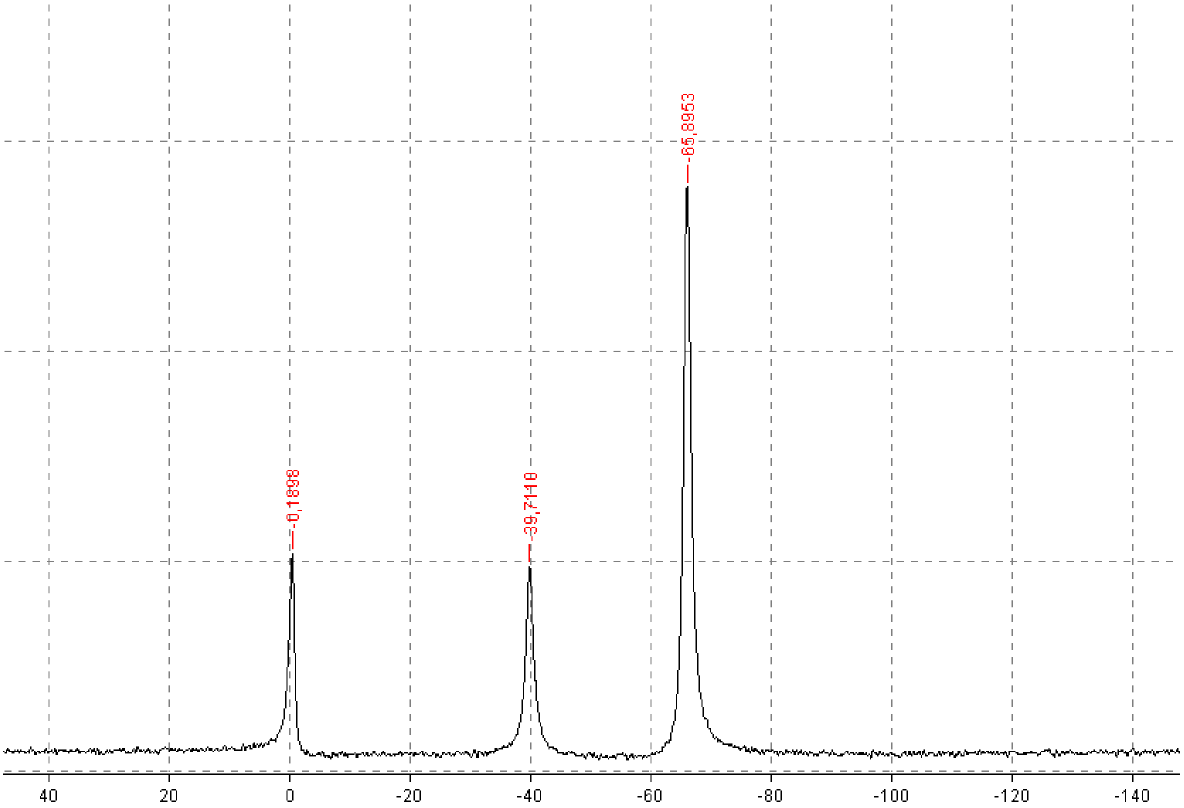

**Figure S19** $^{14}$N NMR spectrum of $AcONO_2$ obtained from $HNO_3$ and $Ac_2O$ (ppm, $CDCl_3$ with $MeNO_2$ as internal standard). $HNO_3$ is present.

**4-Nitro[2.2]paracyclophane (2)**

[2.2]Paracyclophane (**1**) (208 mg, 1 mmol), TFAA (1–1.5 ml) and $AgNO_3$ (or $KNO_3$, 1 mmol) were stirred in 1,2-dichloroethane (25 ml) at 25 °C for 2 h (in the case of $KNO_3$: 35 °C, 3 h). Water (15 ml) was added to the reaction mass and the organic layer was separated, washed with 1 % $NaHCO_3$ solution (1×5 ml) and water (1×10 ml), and dried ($MgSO_4$). The solvent was evacuated and the residue was purified on a column with silica gel (eluent — benzene : hexane = 1 : 5). Nitro compound **2** (195 mg, 77 %) was prepared (from $KNO_3$ — 157 mg, 62 %); mp 157–158 °C (from benzene : $CH_2Cl_2$ : hexane = 1 : 1 : 8 V), (lit. 155.5–156.5[3], 155–157[4] °C). IR (KBr, $cm^{-1}$): 511, 580, 635, 673, 694. 705, 758, 789, 807,872, 905, 930, 946, 1095, 1130, 1180, 1202, 1300, 1338 (vs, $NO_2$), 1401, 1411, 1438, 1452, 1482, 1516 (vs, $NO_2$), 1551, 1595, 2854, 2893, 2925, 2985, 3009, 3059, 3449 (br.); $^1H$ NMR: $\delta_H$ 2.90 (m, 1H, $CH_2$), 3.02–3.27 (m, 6H, $CH_2$), 4.10 (m, 1H, $CH_2$), 6.49 (d, 1H, *J* 8 Hz, CH), 6.55–6.65 (m, 4H, CH), 6.80 (d, 1H, *J* 8 Hz, CH), 7.26 (d, 1H, *J* 11 Hz, C(5)); $^{13}C$ NMR: $\delta_C$ 34.55, 34.89, 35.08, 36.07 (4$\underline{C}H_2$); 129.62, 130.07, 132.52, 133.21, 133.30, 137.43, 137.86 (7$\underline{C}$H); 136.54, 139.42, 139.87, 142.18 (4$\underline{C}$*ar*-C); 149.41 ($\underline{C}$-$NO_2$); $^{14}N$ NMR: $\delta_N$ –7 ($\Delta\nu_{1/2}$ 115 Hz). *m/z*: 253 [$M^+$], 208 [$C_{16}H_{16}^+$], 104 [main, $C_8H_8^+$].

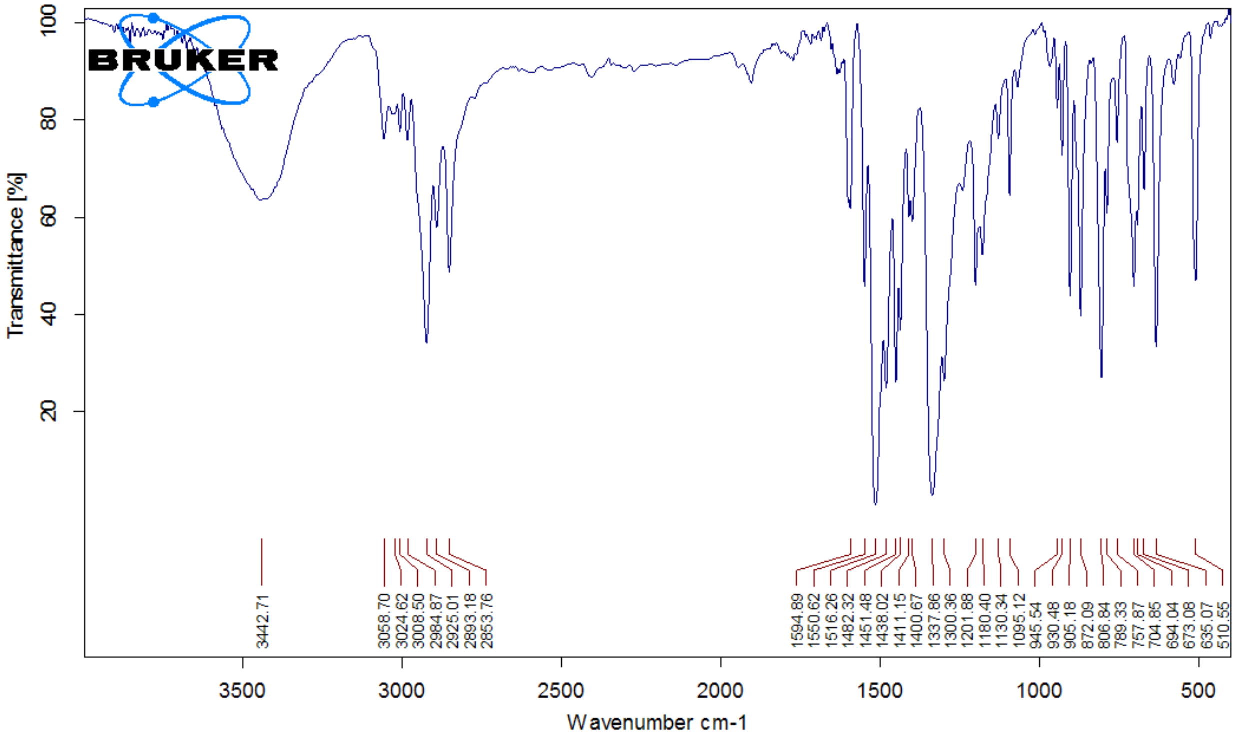

**Figure S19** IR spectrum of 4-nitro[2.2]paracyclophane (**2**) (KBr).

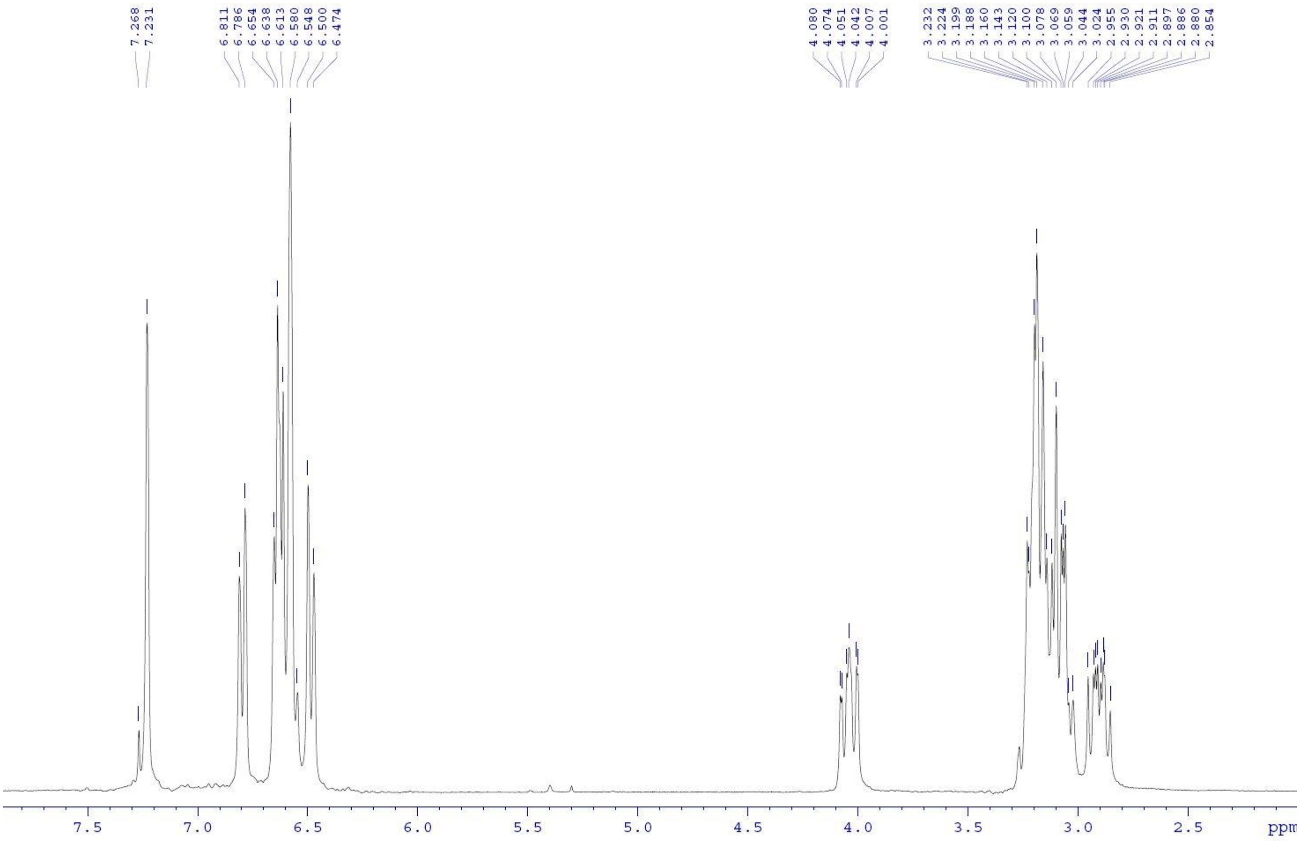

**Figure S20** $^{1}$H NMR spectrum of 4-nitro[2.2]paracyclophane (**2**).

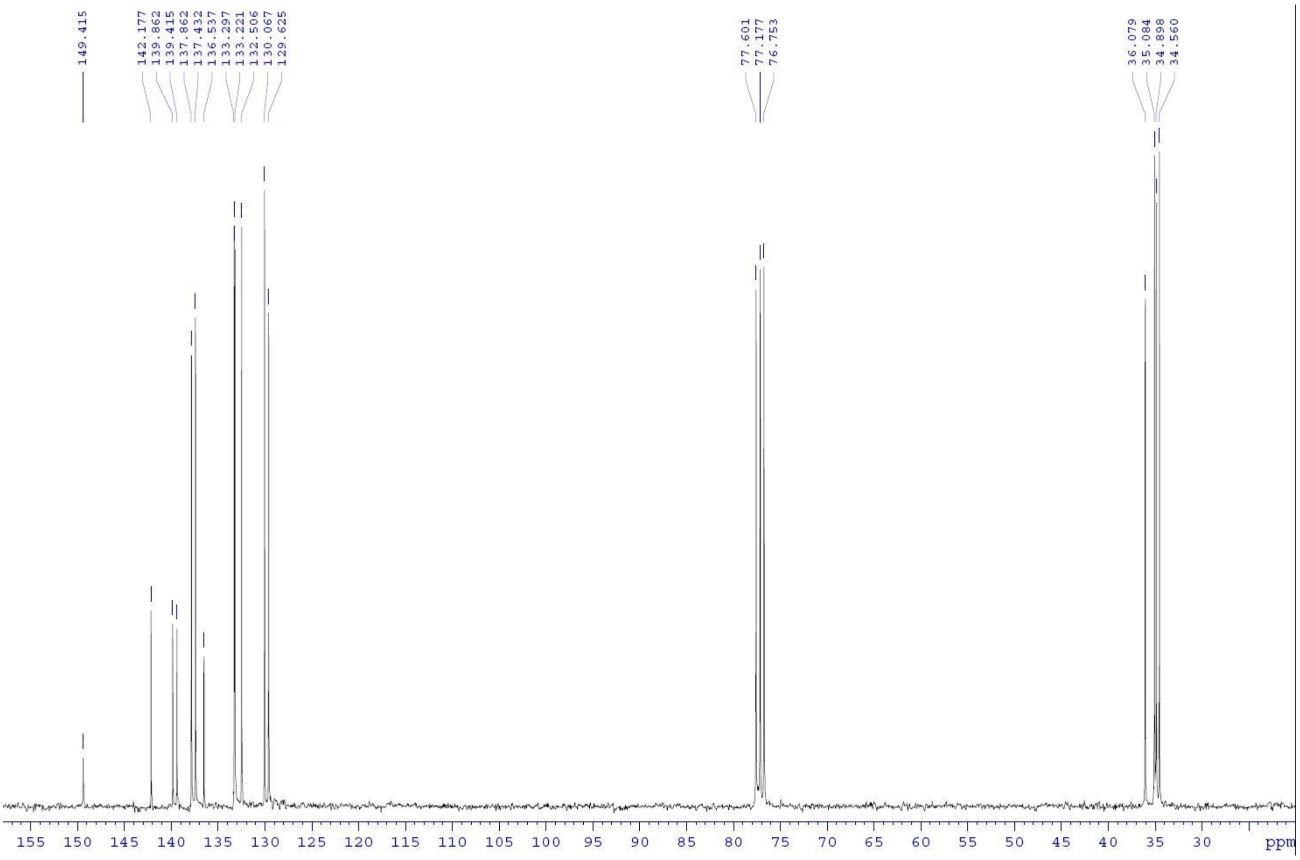

**Figure S21** $^{13}$C NMR spectrum of 4-nitro[2.2]paracyclophane (**2**).

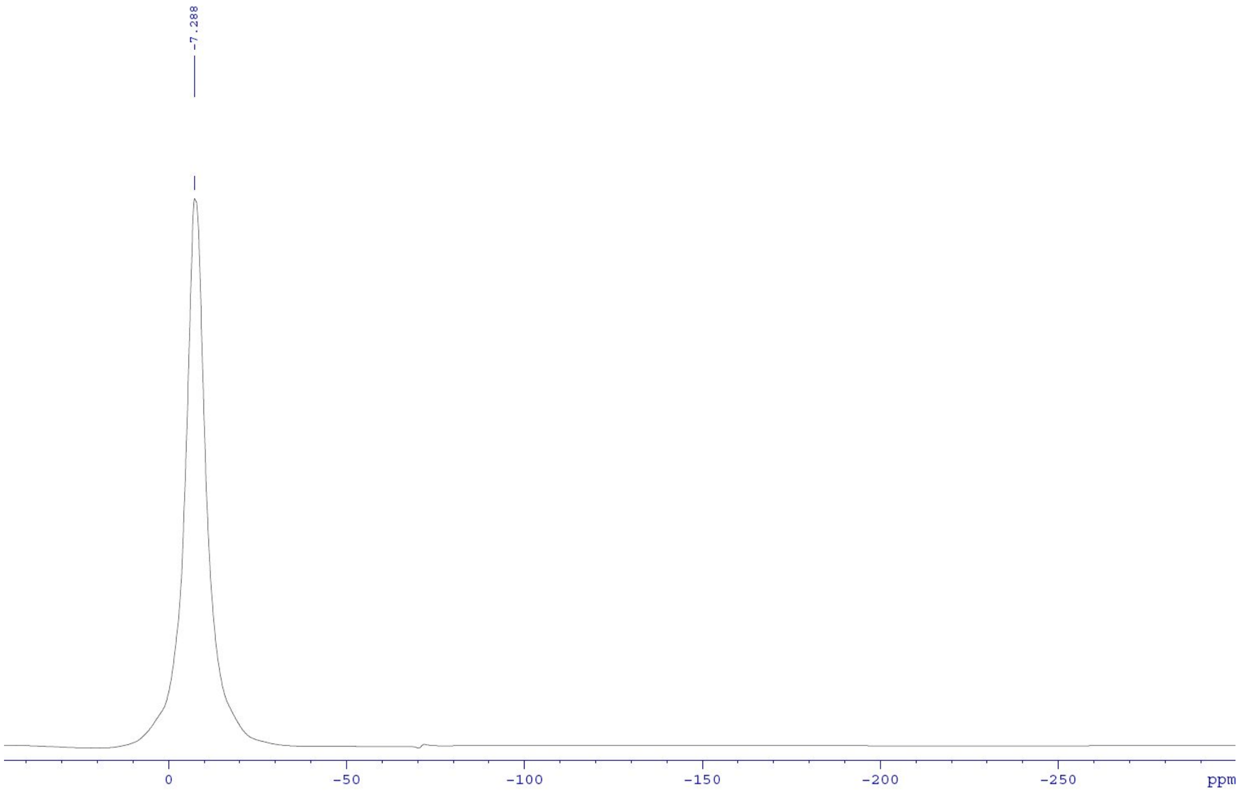

**Figure S22** $^{14}$N NMR spectrum of 4-nitro[2.2]paracyclophane (**2**).

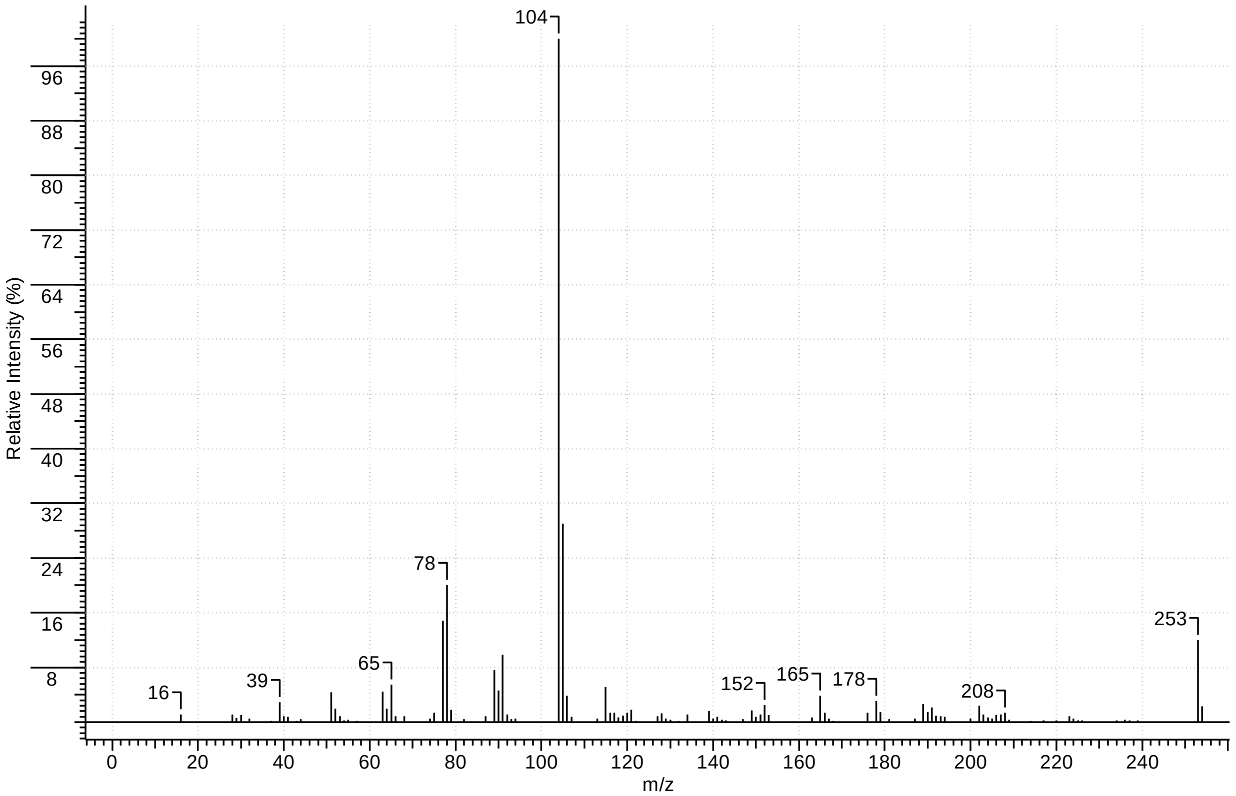

**Figure S23** Mass spectrum of 4-nitro[2.2]paracyclophane (**2**).

**Nitronium trifluoromethanesulfonate.** TFAN solution (1.90 g, 11.9 mmol) in $CCl_4$ (5 ml) prepared by distillation of the TFAA—$NH_4NO_3$ mixture was stored for 3 days in a refrigerator, then $CF_3SO_3H$ (1.40 g, 9.3 mmol) at 0 °C was added to it at stirring and the reaction mass was stirred for 10 min. The precipitate was filtered off on a Schott funnel with argon fed downward, washed with dry $CH_2Cl_2$ (2×5 ml) and dried *in vacuo*. The salt $NO_2^+[CF_3SO_3]^-$ (1.73 g, 95 %) was obtained as a loose white powder. Found (%): C, 6.38; N, 6.91. $CF_3NO_5S$. Calc. (%): C, 6.16; N, 7.18. The compound corresponds to that known from the IR[5,6] ($\nu^{as}_{NO2}$ 2394, $\nu^{comb}_{NO2}$ 3781 $cm^{-1}$) and Raman spectra[5,7,8] ($\nu^{s}_{NO2}$ 1410 $cm^{-1}$).

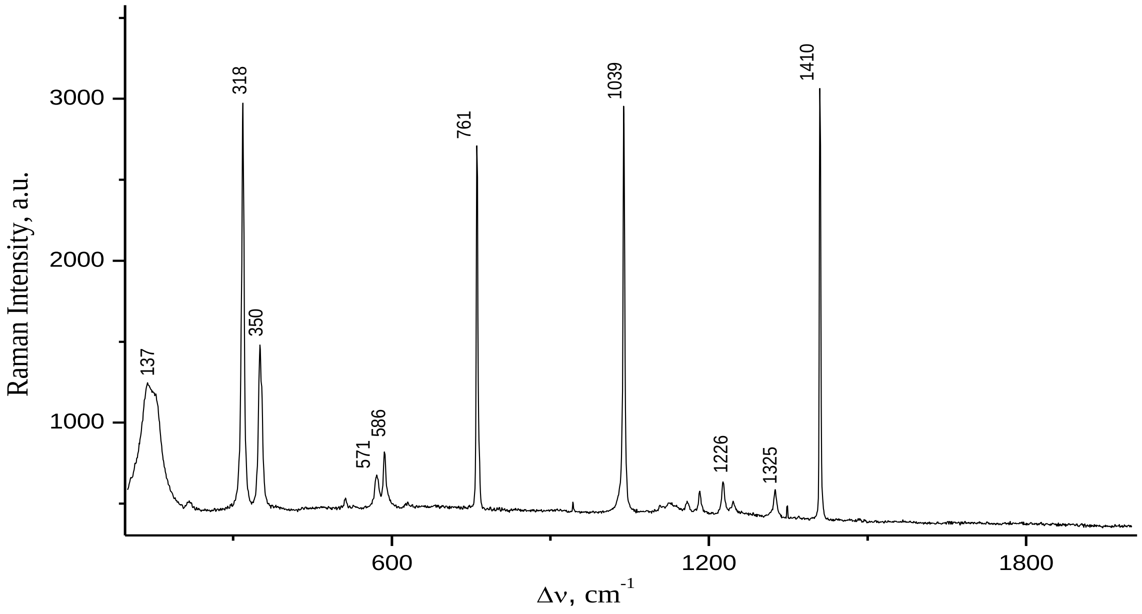

**Figure S24** Raman spectrum of nitronium trifluoromethanesulfonate.

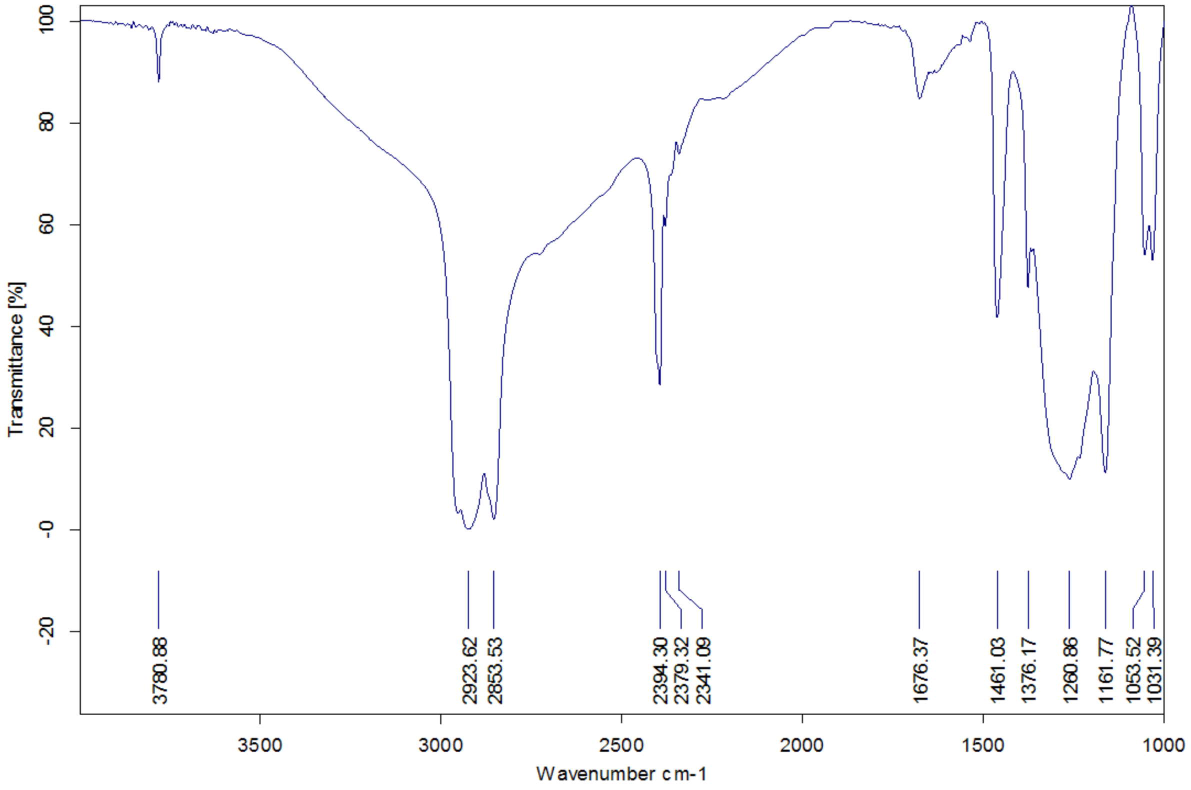

**Figure S25** IR spectrum of nitronium trifluoromethanesulfonate (Nujol, optics $CaF_2$).

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