Electronic Supplementary Information

N-(2-Fluoro-2,2-dinitroethyl)azoles: Novel assembly of diverse explosophoric building blocks for energetic compounds design

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General Information

All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in KBr pellets on a BrukerALPHA spectrometer. The ^{1}H, ^{19}F, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 282.00, 75.47, 21.68 and 30.42 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard without correction nitromethane (^{14}N) and $CClF_3$ (^{19}F). Analytical TLC was performed using commercially pre-coated silica gel plates (Silufol UV_{254}), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected.

CAUTION! All compounds are potentially explosive and should be handled with appropriate precautions.

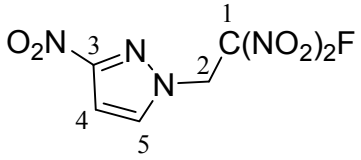
Characterization of Compounds 12-29

General Procedure for the Preparation of K-salts of N-(dinitroethyl)azoles. A mixture of a NH-azole (2.5 mmol) and t-BuOK (5 mmol) in methanol (10 mL) was stirred for 5 min under reflux. 1,1,1-Trinitroethan (2.6 mmol) in methanol (10 mL) was then added dropwise, keeping the flask temperature about 65 °C. After the addition was complete, the reaction mixture was heated under reflux. The reaction was stirred until the starting azole could no longer be detected by thin-layer chromatography, which typically took 1-2 h. The mixture was then cooled to 20 °C, and the yellow-orange solid which separated was collected by filtration and washed with methanol (5 mL) and diethyl ether (3×5 mL), and dried to give crude K-salt **3**. The crude compound was used directly in the next step without any further purification. If necessary, a pure sample could be prepared for analysis by recrystallization; however, the purification is accompanied by large losses.

General Procedure for the Preparation of Compounds 12-29.

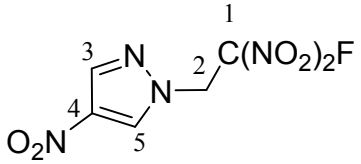
Selectfluor™ was added with stirring to a slurry of crude K-salt (2 mmol; from the previous stage) in acetonitrile (10 mL) at room temperature. After 1 h of stirring, the reaction mixture was diluted with CH_2Cl_2 (200 mL), washed with brine (2×50 mL), passed through silica gel, and dried over $MgSO_4$. The solution was evaporated and the residue was purified by recrystallization from a suitable solvent or column chromatography on silica gel to give fluorinated product as a white solid:

1-(2-Fluoro-2,2-dinitroethyl)-3-nitro-1H-pyrazole, 12



The compound was prepared followed by **General Procedure**. After recrystallization from $CHCl_3$ colorless solid **12** was obtained in 68% yield; mp 88-89°C. ^{1}H NMR (DMSO-d_6): 6.18 (d, J_{HF} = 15.3 Hz, 2H, NC<u>H</u>$_2$), 7.17 (s, 1H, C<u>H</u>), 8.16 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 52.2 (d, J_{CF} = 17.6 Hz, C2), 100.9 (C5), 119.4 (d, J_{CF} = 293.9 Hz, C1), 137.2 (C4), 156.9 (C3); ^{19}F NMR (DMSO-d_6): 108.95 (t, 1F, J = 14.32 Hz); IR: ν = 3164, 3131, 3035, 2976, 2896, 1618, 1553, 1510, 1458, 1429, 1381, 1355, 1317, 1302, 1220,1187, 1078, 1061, 1027, 998, 888, 849, 827, 810, 784, 755, 736, 618, 593, 447 cm^{-1}; Anal. calcd. (%) for $C_5H_4FN_5O_6$ (249,11): C 24.11, H 1.62, N 28.11; found: C 24.31; H 1.74; N 28.20.

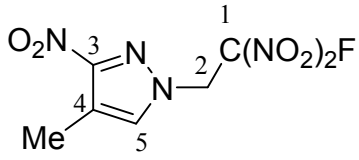
1-(2-Fluoro-2,2-dinitroethyl)-4-nitro-1H-pyrazole, 13



The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **13** was obtained in 68% yield; mp 101-102ºC. ^{1}H NMR (DMSO-d_6): 6.11 (d, 2H, J_{HF} = 15.1 Hz, NC<u>H</u>$_2$), 8.45 (s, 1H, C<u>H</u>), 9.01 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 51.8 (d, J_{CF} = 17.6 Hz, C2), 119.2 (d, J_{CF} = 294.0 Hz, C1), 133.2 (C5), 135.9 (C4), 137.6 (C3); ^{19}F NMR (DMSO-d_6): 109.14 (t, 1F, J = 14.86 Hz); ^{14}N NMR (DMSO-d_6): -18.85 (bs, <u>N</u>O$_2$); ^{15}N NMR (DMSO-d_6): -182.2 (<u>N</u>CH$_2$), -70.8(C=<u>N</u>-N), -21.5 (C(<u>N</u>O$_2$) F), -21.0 (C(<u>N</u>O$_2$)F), -18.0 (<u>N</u>O$_2$); IR: ν = 3435, 3147, 3129, 3026, 2984,1624, 1604, 1536, 1510, 1413, 1332, 1309, 1210, 1191, 1139, 1082, 1003, 966, 885, 851, 822, 806, 756, 740, 658, 613, 586,

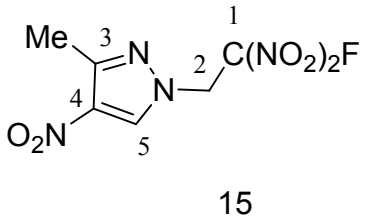
548, 451 cm^{-1}; Anal. calcd. (%) for $C_5H_4FN_5O_6$ (249,11): C 24.11, H 1.62, N 28.11; found C 24.19; H 1.71; N 28.03.

1-(2-Fluoro-2,2-dinitroethyl)-4-methyl-3-nitro-1H-pyrazole, 14

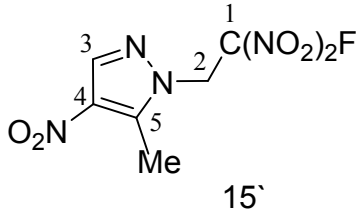


The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **13** was obtained in 32% yield; mp 100-101ºC. ^{1}H NMR (DMSO-d_6): 2.27 (s, 3H, C<u>H</u>$_3$), 6.09 (d, 2H, J_{HF} = 15.3 Hz, NC<u>H</u>$_2$), 7.98 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 9.12 (s, <u>C</u>H$_3$), 52.1 (d, J_{CF} = 17.4 Hz, C2), 119.3 (d, J_{CF} = 293.5 Hz, C1), 114.9 (C4), 127.3 (C5), 135.8 (C3); ^{19}F NMR (DMSO-d_6): -109.12 (t, 1F, J = 15.09 Hz); ^{14}N NMR (DMSO-d_6): -18.70 (bs, <u>N</u>O$_2$); ^{15}N NMR (DMSO-d_6): -189.0 (<u>N</u>CH$_2$), -76.7 (C=<u>N</u>-N), -21.5 (C(<u>N</u>O$_2$)F), -21.0 (C(<u>N</u>O$_2$)F), -18.1; IR: ν = 3421, 3121, 3031, 3002, 2979, 1622, 1591, 1525, 1425, 1377, 1337, 1305, 1220, 1187, 1148, 1076, 1027, 1000, 891, 849, 814, 777, 758, 627, 591, 522 cm^{-1}; Anal. calcd. (%) for $C_6H_6FN_5O_6$ (263,14): C 27.39; H 2.30; N 26.61; found C 27.31; H 2.35; N 26.51.

1-(2-Fluoro-2,2-dinitroethyl)-5-methyl-4-nitro-1H-pyrazole, 15
1-(2-Fluoro-2,2-dinitroethyl)-3-methyl-4-nitro-1H-pyrazole, 15`



15

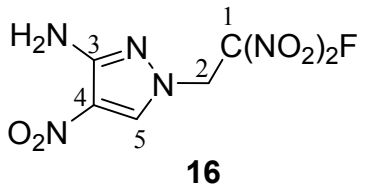


15`

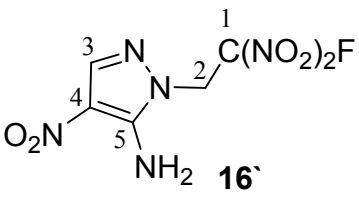
The mixture of isomers **15** and **15`** is not separated (ratio 1/1). The mixture of compounds **15** and **15`** was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **15** and **15`** was obtained in 65% yield; mp 85-90ºC.

NMR data for the mixture of isomers **15** and **15`:**
^{1}H NMR (DMSO-d_6): 2.39 (s, 3H, C<u>H</u>$_3$, **15`**), 2.69 (s, 3H, C<u>H</u>$_3$, **15**), 5.93 (d, 2H, $J_{HF}$ = 2.1 Hz, NC<u>H</u>$_2$, **15`**), 5.98 (d, 2H, J_{HF} = 2.2 Hz, NC<u>H</u>$_2$, **15**), 8.28 (s, 1H, C<u>H</u>, **15`**); 8.85 (s, 1H, C<u>H</u>, **15**); $^{13}$C NMR (DMSO-$d_6$): 10.54 (s, <u>C</u>H$_3$, **15`**), 12.87 (s, <u>C</u>H$_3$, **15**), 49.52 (d, J_{CF} = 17.45 Hz, C2, **15`**), 51.6 (d, $J_{CF}$ = 17.68 Hz, C2, **15**), 119.24 (d, $J_{CF}$ = 294.04 Hz, C1, **15+15`**), 133.34 (C4, **15**), 133.85 (C4, **15`**), 133.99 (C3, **15`**), 134.46 (C5, **15**), 143.24 (C5, **15`**), 147.07 (C3, **15**); $^{19}$F NMR (DMSO-$d_6$): -109.12 (t, 1F, $J$ = 14.86 Hz), -111.02 (t, 1F, $J$ = 14.75 Hz); $^{14}$N NMR (DMSO-$d_6$): -23.18 (bs, <u>N</u>O$_2$); $^{15}$N NMR (DMSO-$d_6$): -182.8 (<u>N</u>CH$_2$, **15`**), -189.6 (<u>N</u>CH$_2$, **15**), -78.1 (C=<u>N</u>-N, **15**), -75.5 (C=<u>N</u>-N, **15`**), -21.2 (C(<u>N</u>O$_2$)F), -21.3 (C(<u>N</u>O$_2$)F), -20.8 (C(<u>N</u>O$_2$)F), -20.9 (C(<u>N</u>O$_2$)F), -16.4 (<u>N</u>O$_2$, **15**), -16.1 (<u>N</u>O$_2$, **15`**).

1-(2-Fluoro-2,2-dinitroethyl)-4-nitro-1H-pyrazol-3-amine, 16
1-(2-Fluoro-2,2-dinitroethyl)-4-nitro-1H-pyrazol-5-amine, 16`



16



16`

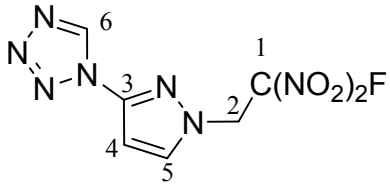
The mixture of compounds **16** and **16`** was prepared followed by **General Procedure**. Solid **16** and **16`** were obtained in 38% yield

(ratio 1/1). The mixture of isomers **16** and **16`** is separated by column chromatography on silica gel (Eluent is $CHCl_3$, $R_f$ (**16**) = 0.79, $R_f$ (**16`**) = 0.45).

After purified by silica gel chromatography, yelow solid **16** was obtained in 18% yield; mp 167-168°C ($CHCl_3$). ^{1}H NMR (DMSO-d_6): 5.76 (d, 2H, J_{HF} = 14.40 Hz, NC$\underline{H}_2$), 7.91 (s, 2H, N$\underline{H}_2$), 8.08 (s, 1H, C$\underline{H}$); ^{13}C NMR (DMSO-d_6): 47.96 (d, J_{CF} = 17.7 Hz, C2), 119.0 (d, J_{CF} = 291.92 Hz, C1), 117.3 (C4), 137.2 (C5), 147.7 (C3); ^{19}F NMR (DMSO-d_6): -110.31 (t, 1F, J = 14.33 Hz); ^{14}N NMR (DMSO-d_6): -20.58 (bs, $\underline{N}O_2$); IR: ν = 3467, 3341, 3251, 3146, 3017, 2964, 1641, 1605, 1583, 1506, 1474, 1340, 1318, 1278, 1209, 1082, 848, 807, 763, 700, 666, 592, 547, 498 cm^{-1}; Anal. calcd. (%) for $C_5H_5FN_6O_6$ (264,13): C 22.74; H 1.91; N 31.82; found C 22.87; H 1.82; N 31.71.

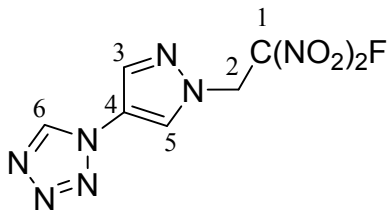
After purified by silica gel chromatography, colorless solid **16`** was obtained in 20% yield; mp 189-190 °C ($CHCl_3$). ^{1}H NMR (DMSO-d_6): 5.79 (d, 2H, J_{HF} =14.90 Hz, NC$\underline{H}_2$), 6.30 (bs, 2H, N$\underline{H}_2$), 8.62 (s, 1H, C$\underline{H}$); ^{13}C NMR (DMSO-d_6): 51.7 (d, J_{CF} = 17.54 Hz, C2), 119.2 (d, J_{CF} = 293.55 Hz, C1), 122.2 (C4), 133.2 (C3), 151.8 (C5); ^{19}F NMR (DMSO-d_6): -109.56 (t, 1F, J = 14.52 Hz); ^{14}N NMR (DMSO-d_6): -22,38 (bs, $\underline{N}O_2$); ^{15}N NMR (DMSO-d_6): -322.8 ($\underline{N}H_2$), -201.7 ($\underline{N}CH_2$), -199.6 (C=$\underline{N}$-N), -21.2 (C($\underline{N}O_2$)F), -20.1 (C($\underline{N}O_2$)F), -15.0 ($\underline{N}O_2$); IR: ν = 3467, 3341, 3146, 3017, 2964, 1641, 1605, 1583, 1506, 1474, 1415, 1403, 1340, 1318, 1278, 1209, 1082, 1002, 980, 848, 807, 763, 700, 666, 592, 547, 498 cm^{-1}; Anal. calcd. (%) for $C_5H_5FN_6O_6$ (264,13): C 22.74; H 1.91; N 31.82; found C 22.67; H 2.02; N 31.95.

1-(1-(2-Fluoro-2,2-dinitroethyl)-1H-pyrazol-3-yl)-1H-tetrazole, 17



The compound was prepared followed by **General Procedure**. After recrystallization from CCl_4 colorless solid **17** was obtained in 55% yield; mp 121ºC.^{1}H NMR (DMSO-d_6): 6.11 (d, 2H, J_{HF} = 15.5 Hz, NC$\underline{H}_2$), 6.97(d, 1H, J = 1.7 Hz, C$\underline{H}$), 8.17 (d, 1H, J = 1.7 Hz, C$\underline{H}$-Pz), 9.96 (s, 1H, c, C$\underline{H}$-Tz); ^{13}C NMR (DMSO-d_6): 51.8 (d, J_{CF} = 17.6 Hz, C2), 119.4 (d, J_{CF} = 293.2 Hz, C1), 100.6 (C5), 136.4 (C4), 142.4 (C6), 144.3 (C3); ^{19}F NMR (DMSO-d_6): -109.29 (t, 1F, J = 15.37 Hz); ^{14}N NMR (DMSO-d_6): -22.85 (bs, $\underline{N}O_2$); IR: ν = 3155, 3121, 3025, 2974, 1617, 1549, 1351, 1304, 1265, 1207, 1122, 1092, 1077, 1018, 962, 888, 849, 810, 787, 729, 658, 626, 588 cm^{-1}; Anal. calcd. (%) for $C_6H_5FN_8O_4$ (272,16): C 26.48; H 1.85; N 41.17; found C 26.35; H 1.94; N 41.37.

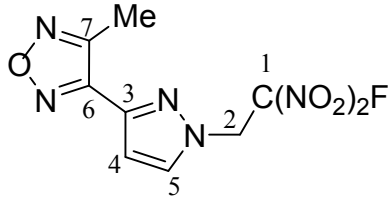
1-(1-(2-Fluoro-2,2-dinitroethyl)-1H-pyrazol-4-yl)-1H-tetrazole, 18



The compound was prepared followed by **General Procedure**. After recrystallization from CCl_4 colorless solid **18** was obtained in 55% yield; mp 109-110ºC.^{1}H NMR (DMSO-d_6): 6.15 (d, 2H, J_{HF} = 15.2 Hz, NC$\underline{H}_2$), 8.27(s, 1H, C$\underline{H}$-Pz), 8.66(s, 1H, C$\underline{H}$-Pz), 9.93 (s, 1H, C$\underline{H}$-Tz); ^{13}C NMR (DMSO-d_6): 51.8 (d, J_{CF} = 17.6 Hz, C2), 119.5 (d, J_{CF} = 292.8 Hz, C1), 118.8 (C4), 127.3 (C5), 135.3 (C3), 143.3 (C6); ^{19}F NMR (DMSO-d_6): -109.67 (t, 1F, J = 15.08 Hz); ^{14}N NMR (DMSO-d_6): -17.38 (bs, $\underline{N}O_2$); ^{15}N NMR (DMSO-d_6):): -186.6 ($\underline{N}CH_2$), -149.7, -72.1, -49.2, -21.1 (C($\underline{N}O_2$)F), -20.6 (C($\underline{N}O_2$)F), -14.5, 13.6; IR: ν = 3139, 3046, 3018, 2971, 1614, 1593, 1482,

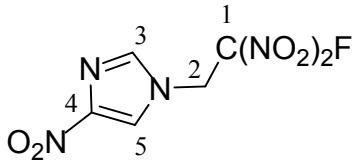
1316, 1298, 1261, 1165, 1098, 1075, 971, 945, 863, 849, 803, 736, 626, 584 cm^{-1}; Anal. calcd. (%) for $C_6H_5FN_8O_4$ (272,16): C 26.48; H 1.85; N 41.17; found C 26.57; H 1.74; N 41.26.

3-(1-(2-Fluoro-2,2-dinitroethyl)-1H-pyrazol-3-yl)-4-methyl-1,2,5-oxadiazole, 19



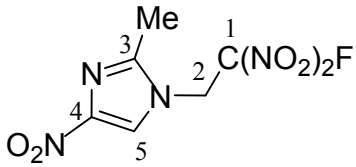
The compound was prepared followed by **General Procedure**. After recrystallization from CCl_4 colorless solid **19** was obtained in 43% yield; mp 132ºC. ^{1}H NMR (DMSO-d_6): 2.47 (s, 3H, C<u>H</u>$_3$), 6.05 (d, 2H, J_{HF} = 15.30 Hz, NC<u>H</u>$_2$), 6.94 (d, 1H, CH, J_{HF} = 2.1 Hz,), 8.08 (d, 1H, C<u>H</u>, J_{HF} = 2.4 Hz,); ^{13}C NMR (DMSO-d_6): 10.5 (s, <u>C</u>H$_3$), 52.6 (d, J_{CF} = 17.63 Hz, C2), 108.1 (C4), 120.60 (d, J_{CF} = 292.97 Hz, C1), 136.3 (C5), 141.9 (C3), 148.9 (C6), 151.3 (C7); ^{19}F NMR (DMSO-d_6): -110.11 (t, 1F, J = 15.10 Hz); ^{14}N NMR (DMSO-d_6): -22.70 (bs, <u>N</u>O$_2$); ^{15}N NMR (DMSO-d_6): -322.8 (<u>N</u>H$_2$), -183.1 (<u>N</u>CH$_2$), -74.6 (C=<u>N</u>-N), -20.8 (C(<u>N</u>O$_2$)F), -20.2 (C(<u>N</u>O$_2$)F), 27.7 (N-furazan ring), 28.9 (N- furazan ring); IR: ν = 3159, 3138, 3022, 2983, 1619, 1542, 1507, 1429, 1415, 1395, 1364, 1348, 1333,1312, 1298, 1243, 1215, 1114, 1074, 1040, 1013, 989, 951, 893, 852, 812, 778, 729, 682, 668, 623, 604 , 589, 566, 495 cm^{-1}; Anal. calcd. (%) for $C_8H_7FN_6O_5$ (286,18): 33.58; H 2.47; N 29.37; found C 33.63; H 2.39; N 29.46.

1-(2-Fluoro-2,2-dinitroethyl)-4-nitro-1H-imidazole, 21



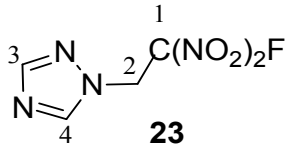
The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **21** was obtained in 70% yield; mp 129-130ºC. ^{1}H NMR (DMSO-d_6): 5.96 (d, 2H, J_{HF} = 16.0 Hz, NC<u>H</u>$_2$), 7.94 (s, 1H, C<u>H</u>), 8.38 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 47.2 (d, J_{CF} = 18.05 Hz, C2), 119.3 (d, J_{CF} = 292.59 Hz, C1), 122.1 (C5), 138.5 (C3), 147.5 (C4); ^{19}F NMR (DMSO-d_6): -107.11 (t, 1F, J = 15.62 Hz); ^{14}N NMR (DMSO-d_6): -23.39 (bs, <u>N</u>O$_2$); ^{15}N NMR (DMSO-d_6): -17.6 (<u>N</u>O$_2$), -21.1 (C(<u>N</u>O$_2$)F), -21.2 (C(<u>N</u>O$_2$)F), -123.0 (C-<u>N</u>=C), -217.3 (<u>N</u>CH$_2$); IR: ν = 3144, 3018, 2961, 1613, 1550, 1521, 1493, 1384, 1348, 1290, 1248, 1216, 1140, 1076, 1042, 983, 900, 852, 826, 809, 752, 709, 670, 602, 566 cm^{-1}; Anal. calcd. (%) for $C_5H_4FN_5O_6$ (249,11): C 24.11; H 1.62; N 28.11; found C 24.23; H 1.71; N 28.02.

1-(2-Fluoro-2,2-dinitroethyl)-2-methyl-4-nitro-1H-imidazole, 22

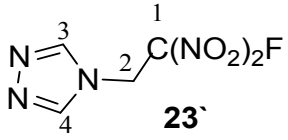


The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **22** was obtained in 36% yield; mp 159ºC. ^{1}H NMR (DMSO-d_6): 2.4 (s, 3H, C<u>H</u>$_3$), 5.96 (d, 2H, J_{HF} = 16.3 Hz, NC<u>H</u>$_2$), 8.21 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 12.49 (d, J_{CF} = 2.88 Hz, <u>C</u>H$_3$), 46.5 (d, J_{CF} = 17.63 Hz, C2), 119.5 (d, J_{CF} = 292.64 Hz, C1), 122.2 (C5), 146.1 (C3), 146.8 (C4); ^{19}F NMR (DMSO-d_6): -108.25 (t, 1F, J = 15.47 Hz); ^{14}N NMR (DMSO-d_6): -19.12 (bs, NO$_2$); ^{15}N NMR (DMSO-d_6): -219.8 (<u>N</u>CH$_2$), -126.2 (C-<u>N</u>=C), -21.5 (C(<u>N</u>O$_2$)F), -21.0 (C(<u>N</u>O$_2$)F), -17.3 (<u>N</u>O$_2$); IR: ν = 3140, 3041, 2954, 1616, 1513, 1439, 1412, 1366, 1344, 1310, 1279, 1210, 1141, 1072, 1008, 991, 955, 907, 880, 851, 814, 765, 725, 676, 644, 594, 530 cm^{-1}; Anal. calcd. (%) for $C_6H_6FN_5O_6$ (263,14): C 27.39; H 2.30; N 26.61; found C 27.25; H 2.27; N 26.74.

1-(2-Fluoro-2,2-dinitroethyl)-1H-1,2,4-triazole, 23
4-(2-Fluoro-2,2-dinitroethyl)-4H-1,2,4-triazole, 23`



23

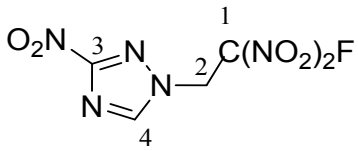


23`

The mixture of compounds **23** and **23`** was prepared followed by **General Procedure** in 62% yield .
NMR data for the mixture of isomers **23** and **23`** (ratio 10/1)**:**
^{1}H NMR (DMSO-d_6): 5.59 (2H, д, J_{HF} = 15.32 Hz, NC$\underline{H}_2$, **23`**), 6.10 (2H, д, $J_{HF}$ = 15.30 Hz, NC$\underline{H}_2$, **23**), 8.10 (1H, c, C$\underline{H}$, **23**), 8.60 (1H, c, C$\underline{H}$, **23`**), 8.70 (1H, c, C$\underline{H}$, **23**);

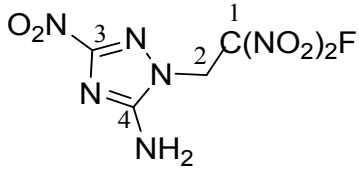
After recrystallization from CH_2Cl_2 colorless solid **23** was obtained in 50% yield; mp 83ºC. ^{1}H NMR (DMSO-d_6): 6.10 (d, 2H, J_{HF} = 15.30 Hz, NC$\underline{H}_2$), 8.10 (s, 1H, C$\underline{H}$), 8.70 (s, 1H, C$\underline{H}$); ^{13}C NMR (DMSO-d_6): 49.24 (d, J_{CF} = 17.93 Hz, C2), 119.6 (d, J_{CF} = 292.74 Hz, C1), 147.1 (C5), 153.5 (C3); ^{19}F NMR (DMSO-d_6): -109.50 (t, 1F, J = 14.89 Hz); ^{14}N NMR (DMSO-d_6): -23. 62 (bs, $\underline{N}O_2$); ^{15}N NMR (DMSO-d_6): -188.27 ($\underline{N}CH_2$), -123.35, -84.99, -21.20 (C($\underline{N}O_2$)F) , -20.70 (C($\underline{N}O_2$)F); IR: ν = 3140, 3041, 2954, 2899, 1616, 1594, 1513, 1439, 1412, 1383, 1366, 1344, 1329, 1310, 1293, 1279, 1210, 1193, 1141, 1072, 1008, 991, 955, 907, 880, 851, 814, 765, 725, 676, 644, 594, 530 cm^{-1}; Anal. calcd. (%) for $C_4H_4FN_5O_4$ (205,11): C 23.42; H 1.97; N 34.15; found C 23.34; H 2.05; N 34.24.

1-(2-Fluoro-2,2-dinitroethyl)-3-nitro-1H-1,2,4-triazole, 24



The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **24** was obtained in 9% yield; mp 217ºC; ^{1}H NMR (DMSO-d_6): 6.30 (d, 2H, J_{HF} = 15.10 Hz, NC$\underline{H}_2$), 9.02 (s, 1H, C$\underline{H}$); ^{13}C NMR (DMSO-d_6): 50.27 (d, J_{CF} = 17.82 Hz, C2), 119.2 (d, J_{CF} = 293.93 Hz, C1), 150.0 (C4), 163.3 (C3); ^{19}F NMR (DMSO-d_6): -108.41 (t, 1F, J = 14.76 Hz); ^{14}N NMR (DMSO-d_6): -24.14 (bs, NO_2); ^{15}N NMR (DMSO-d_6): -174.78 ($\underline{N}CH_2$), -131.40, -86.17, -25.90 (C($\underline{N}O_2$) F) , -22.31 (C($\underline{N}O_2$) F), -21.81 ($\underline{N}O_2$); IR: ν = 3135, 3015, 2970, 2361, 2343, 1608, 1595, 1562, 1510, 1425, 1384, 1466, 1313, 1291, 1216, 1080, 1029, 884, 839, 812, 765, 740, 647, 581 cm^{-1}; Anal. calcd. (%) for $C_4H_3FN_6O_6$ (250,10): C 19.21; H 1.21; N 33.60; found C 19.30; H 1.11; N 33.71.

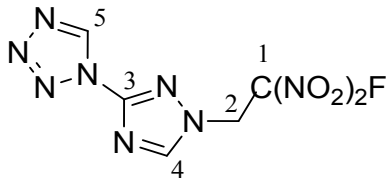
1-(2-Fluoro-2,2-dinitroethyl)-3-nitro-1H-1,2,4-triazol-5-amine, 26



The compound was prepared followed by **General Procedure**. After recrystallization from $CHCl_3$/ MeCN 5/1 colorless solid **26** was obtained in 15% yield; mp 218ºC; ^{1}H NMR (DMSO-d_6): 5.89 (2H, д, J_{HF} = 14.80 Hz, NC$\underline{H}_2$), 7.56 (2H, c, N$\underline{H}_2$); ^{13}C NMR (DMSO-d_6): 47.4 (д, J_{CF} = 17.43 Hz, C2), 118.7 (д, J_{CF} = 293.26 Hz, C1), 158.0 (C4), 160.4 (C5); ^{19}F NMR (DMSO-d_6): -109.37 (1F, т, J = 14.00 Hz); ^{14}N NMR (DMSO-d_6): -23. 67 (уш. с, NO_2); ^{15}N NMR (DMSO-d_6): -319.05 ($\underline{N}H_2$), -214.33, -176.33 ($\underline{N}CH_2$), -104.37, -23.39 ($\underline{N}O_2$), -21.32 (C($\underline{N}O_2$) F), -20.81 (C($\underline{N}O_2$) F); IR: ν = 3415, 3314, 3246, 3153, 1655, 1609, 1533, 1423, 1317, 1271, 1159, 1070,

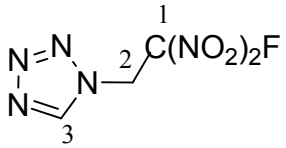
1000, 867, 849, 816, 729, 709, 629 cm^{-1}; Anal. calcd. (%) for $C_4H_4FN_7O_6$ (265,12): C 18.12; H 1.52; N 36.98; found C 18.01; H 1.63; N 37.05.

1-(1-(2-Fluoro-2,2-dinitroethyl)-1H-1,2,4-triazol-3-yl)-1H-tetrazole, 27



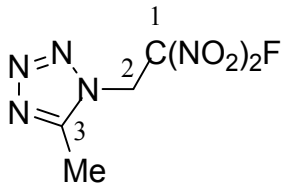
The compound was prepared followed by **General Procedure**. After recrystallization from $CHCl_3$ colorless solid **27** was obtained in 15% yield; mp 130ºC; ^{1}H NMR (DMSO-d_6): 6.24 (d, 2H, J_{HF} = 14.80 Hz, NC<u>H</u>$_2$), 9.01 (s, 1H, C<u>H</u>), 10.08 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 49.5 (d, J_{CF} = 17.84 Hz, C2), 118.8 (d, J_{CF} = 293.92 Hz, C1), 143.1 (C3), 149.1(C5), 153.4 (C4); ^{19}F NMR (DMSO-d_6): -108.74 (t, 1F, J = 14.84 Hz); ^{14}N NMR (DMSO-d_6): -24. 08 (bs, NO_2); ^{15}N NMR (DMSO-d_6): -179.50 (<u>N</u>CH$_2$), -144.94, -130.16, -103.94, -48.54, -22.02 (C(<u>N</u>O$_2$) F), -21.51 (C(NO_2) F), -16.64, 16.28; IR: ν = 3116, 3034, 1623, 1575, 1503, 1422, 1359, 1303, 1267, 1223, 1203, 1185, 1083, 1029, 980, 865, 848, 814, 771, 735, 655, 643, 611, 500 cm^{-1}; Anal. calcd. (%) for $C_5H_4FN_9O_4$ (273,14): C 21.99; H 1.48; N 46.15; found C 21.90; H 1.59; N 46.27.

1-(2-Fluoro-2,2-dinitroethyl)-1H-tetrazole, 28



The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **28** was obtained in 16% yield; mp 86-89ºC; ^{1}H NMR (DMSO-d_6): 6.45 (, 2H, J_{HF} = 15.2 Hz, NC<u>H</u>$_2$), 9.61 (s, 1H, C<u>H</u>); ^{13}C NMR (DMSO-d_6): 47.6 (d, J_{CF} = 18.42 Hz, C2), 118.6 (d, J_{CF} = 293.64 Hz, C1), 145.7 (C3); ^{19}F NMR (DMSO-d_6): -107.93 (t, 1F, J = 14.09 Hz); ^{14}N NMR (DMSO-d_6): -24. 23 (bs, NO_2); ^{15}N NMR (DMSO-d_6): -158.60, -47.98, -22.323 (<u>N</u>O$_2$), -21.81 (<u>N</u>O$_2$), -12.01, 17.91.; IR: ν = 3151, 2989, 2956, 1604, 1479, 1432, 1324, 1296, 1268, 1177, 1103, 1065, 1020, 994, 958, 886, 850, 810, 763, 705, 686, 650, 593 cm^{-1}; Anal. calcd. (%) for $C_3H_3FN_6O_4$ (273,14): C 17.48; H 1.47; N 40.78; found C 17.55; H 1.42; N 40.69.

1-(2-Fluoro-2,2-dinitroethyl)-5-methyl-1H-tetrazole, 29



The compound was prepared followed by **General Procedure**. After recrystallization from CH_2Cl_2 colorless solid **28** was obtained in 18% yield; mp 122-123 ºC; ^{1}H NMR (DMSO-d_6): 2.59 (s, 3H, C<u>H</u>$_3$), 6.26 (d, 2H, J_{HF} = 15.1 Hz, NC<u>H</u>$_2$); ^{13}C NMR (DMSO-d_6): 8.2 (<u>C</u>H$_3$), 46.8 (d, J_{CF} = 17.63 Hz, C2), 118.8 (d J_{CF} = 292.64 Hz, C1), 154.5 (<u>C</u>3);. ^{19}F NMR (DMSO-d_6): -109.87 (t, 1F, J = 14.53 Hz); ^{15}N NMR (DMSO-d_6): -272.20, -51.08, -22.33 (<u>N</u>O$_2$), -21.85 (<u>N</u>O$_2$), 15.74; IR: ν = 3014, 2978, 2940, 1602, 1529, 1422, 1371, 1315, 1293, 1253,1143, 1060, 1006, 898, 850, 814, 744, 670, 571, 499 cm^{-1}; Anal. calcd. (%) for $C_4H_5FN_6O_4$ (220,12): C 21.83; H 2.29; N 38.18; found C 21.85; H 2.21 N 38.08.

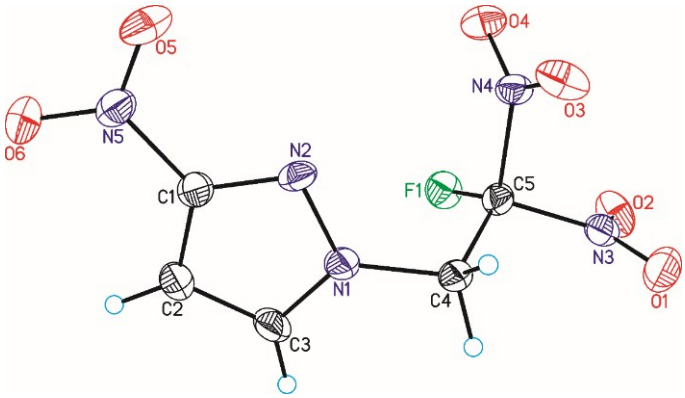
X-ray analysis of the involved materials.

X-ray experiments for compounds **12,13,21,28** were carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα)=0.71073 Å, graphite monochromator, *ω*-scans) at 100K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package.[1S] The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program.[2S] The details of data collection and crystal structures refinement are summarized in Table 1S along with CCDC numbers which contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

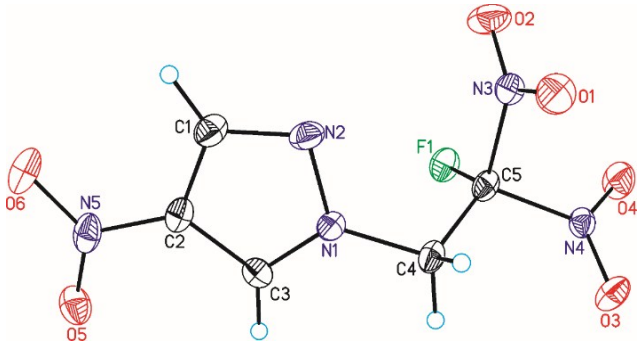
Table 1S. Crystallographic data for azasydnone derivatives **12,13,21,28**.

	12	**13**	**21**	**28**
formula	$C_5H_4N_5FO_6$	$C_5H_4N_5FO_6$	$C_5H_4N_5FO_6$	$C_5H_4N_5FO_6$
fw	249.13	249.13	249.13	206.11
crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
space group	*P*-1	$P2_1$	*Pbca*	$Pna2_1$
a, Å	7.976(3)	5.4659(12)	6.6055(3)	11.4331(11)
b, Å	8.218(3)	10.477(2)	11.5186(5)	5.7212(6)
c, Å	15.344(6)	8.1322(17)	23.4809(10)	11.2434(11)
α, deg.	94.059(8)	90	90	90
β, deg.	104.850(7)	94.857(4)	90	90
γ, deg.	97.364(8)	90	90	90
V, Å^3	958.5(6)	464.02(17)	1786.57(14)	735.44(13)
Z	4	4	8	4
d_{cryst}, g·cm^{-3}	1.727	1.783	1.852	1.862
F(000)	504	252	1008	416
μ, mm^{-1}	0.169	0.174	0.181	0.182
θ range, deg.	2.5 – 28.0	2.5 – 27.15	3.5 – 30.08	3.6 – 28.9
reflections collected	14158	4928	22344	7221
independent reflections/R_{int}	4628 / 0.0587	2039 / 0.0603	2621 / 0.0166	1930 / 0.0335
Completeness to theta *θ*,%	100	100	99.9	99.9
refined parameters	307	154	154	127
GOF (F^2)	1.009	0.987	1.039	1.045
reflections with $I>2\sigma(I)$	2968	1475	2288	1773
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0448	0.0431	0.0317	0.0289
$wR_2(F^2)$ (all data)[b]	0.1034	0.0781	0.0878	0.0648
Max diff. peak/hole, *e*·Å^{-3}	0.279 / -0.312	0.218 / -0.223	0.393 / -0.257	0.202 / -0.241
CCDC number	1874345	1874346	1874347	1874348

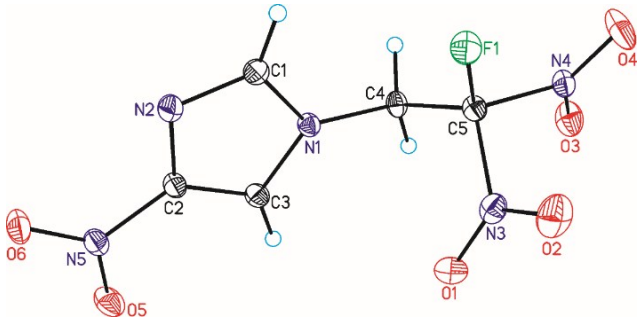
[a] $R_1 = \sum||F_o| - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$



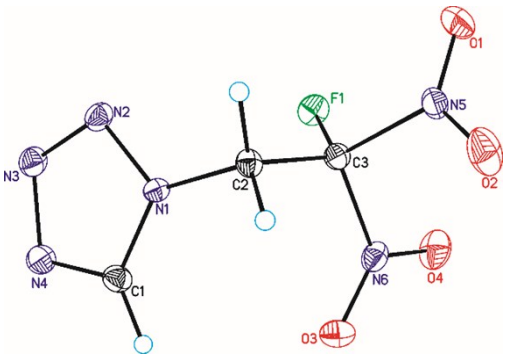
12



13



21



28

Figure 1S. General view of compounds **12**, **13**, **21**, and **28** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

Table 2S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **12** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction	Molecular pair
1	-1+x,y,z	No close contcts			van der Waals	A…A
2	1+x,y,z	No close contcts			van der Waals	A…A
3	2-x,1-y,-z	F1	O4	2.858	F…O	A…A
		O4	F1	2.858		
4	2-x,2-y,-z	O5	C4	3.315	C-H…O C-H…N	A…A
		O5	H4B	2.531		
		C4	O5	3.315		
		H4B	O5	2.531		
		N2	H4B	2.511		
		H4B	N2	2.511		
5	1+x,y,z	O2	C4'	3.184	C-H…O	A…A'
		O2	H4'A	2.398		
6	1+x,1+y,z	O1	F1'	2.939	F…O	A…A'
7	-x,1-y,-z	No close contcts			van der Waals	A…A'
8	1-x,1-y,-z	O5	C4'	3.140	C-H…O	A…A'
		O5	H4'A	2.347		
9	1-x,1-y,1-z	N3	O5'	2.914	NO_2…NO_2 C-H…O	A…A'
		C4	O5'	3.089		
		H4A	O5'	2.361		
10	2-x,1-y,1-z	O2	O6'	2.997	NO_2…NO_2 C-H…O	A…A'
		O2	C2'	3.305		
		O2	H2'	2.524		
		N3	O6'	3.024		

Table 3S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A' of compound **12** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction	Molecular pair
1'	-1+x,y,z	O3' O3'	C3' H3'	3.146 2.483	C-H…O	A'…A'
2'	1+x,y,z	C3' H3'	O3' O3'	3.146 2.483	C-H…O	A'…A'
3'	-x,-y,1-z	F1' O4'	O4' F1'	2.910 2.910	F…O	A'…A'
4'	-x,1-y,1-z	O1' O5' N2' H4'B	O5' O1' H4'B N2'	2.891 2.891 2.438 2.438	NO_2…NO_2 C-H…N	A'…A'
5'	-1+x,y,z	C4' H4'A	O2 O2	3.184 2.398	C-H…O	A'…A
6'	-1+x,-1+y,z	F1'	O1	2.939	F…O	A'…A
7'	-x,1-y,-z	No	close	contacts	van-der-Waals	A'…A
8'	1-x,1-y,-z	C4' H4'A	O5 O5	3.140 2.347	C-H…O	A'…A
9'	1-x,1-y,1-z	O5' O5' O5'	N3 C4 H4A	2.914 3.089 2.361	NO_2…NO_2 C-H…O	A'…A
10'	2-x,1-y,1-z	O6' O6' C2' H2'	O2 N3 O2 O2	2.997 3.024 3.305 2.524	NO_2…NO_2 C-H…O	A'…A

Table 4S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **13** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction
1	-1+x,y,z	O1 C1 H1	N4 O5 O5	2.973 3.170 2.464	NO_2…NO_2 C-H…O
2	1+x,y,z	O5 O5 N4	C1 H1 O1	3.170 2.464 2.973	NO_2…NO_2 C-H…O
3	x,y,-1+z	No close contacts			van-der-Waals
4	x,y,1+z	No close contacts			van-der-Waals
5	-1-x,-1/2+y,-3-z	O6 O6 O6	N2 C4 H4A	3.100 3.268 2.508	N…NO_2 C-H…O
6	-1-x,1/2+y,-3-z	N2 C4 H4A	O6 O6 O6	3.100 3.268 2.508	N…NO_2 C-H…O
7	-1-x,-1/2+y,-2-z	No close contacts			van-der-Waals
8	-1-x,1/2+y,-2-z	No close contacts			van-der-Waals
9	-x,-1/2+y,-3-z	O5 O5	C4 H4B	3.129 2.576	C-H…O
10	-x,1/2+y,-3-z	C4 H4B	O5 O5	3.129 2.576	C-H…O
11	-x,-1/2+y,-2-z	F1	O3	2.806	F…O
12	-x,1/2+y,-2-z	O3	F1	2.806	F…O

Table 5S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **21** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction
1	-1+x,y,z	No close contacts			van-der-Waals
2	1+x,y,z	No close contacts			van-der-Waals
3	-x,-1/2+y,1/2-z	C4 H4B	O5 O5	3.300 2.321	C-H…O
4	-x,1/2+y,1/2-z	O5 O5	C4 H4B	3.300 2.321	C-H…O
5	-1/2+x,1/2-y,-z	F1	O2	2.838	F…O
6	1/2+x,1/2-y,-z	O2	F1	2.838	F…O
7	-x,-y,-z	O4	O4	3.029	NO_2…NO_2
8	1-x,-y,-z	O2	O4	3.072	NO_2…NO_2
9	-1/2+x,y,1/2-z	O6 N5 C2	O5 O5 O5	3.000 3.022 3.251	O…π
10	1/2+x,y,1/2-z	O5 O5 O5	O6 N5 C2	3.000 3.022 3.251	O…π
11	-1/2-x,-1/2+y,z	C4 H4A	N2 N2	3.168 2.461	C-H…N
12	-1/2-x,1/2+y,z	N2 N2	C4 H4A	3.168 2.461	C-H…N
13	1/2-x,-1/2+y,z	O1	O6	2.876	NO_2…NO_2
14	1/2-x,1/2+y,z	O6	O1	2.876	NO_2…NO_2

Comments

It is seen that predominant contribution into intermolecular bonding for all three compounds is provided by C-H…O(N) and van-der-Waals interactions. In addition, short F…O and NO_2…NO_2 contacts are also observed. Each molecule in the crystal of all three compounds forms nearly the same numbers of intermolecular interactions. However in compound **13** and especially in compound **12** some of the closest neighbours are connected simultaneously by two different types of interactions. As a result, number of closest neighbours of a molecule in the crystals of **12** and **13** are equal to 10 and 12 respectively. In contrary, in compound **21**, intermolecular contacts are distributed over 14 neighbours thereby inducing less constrain for optimal packing.

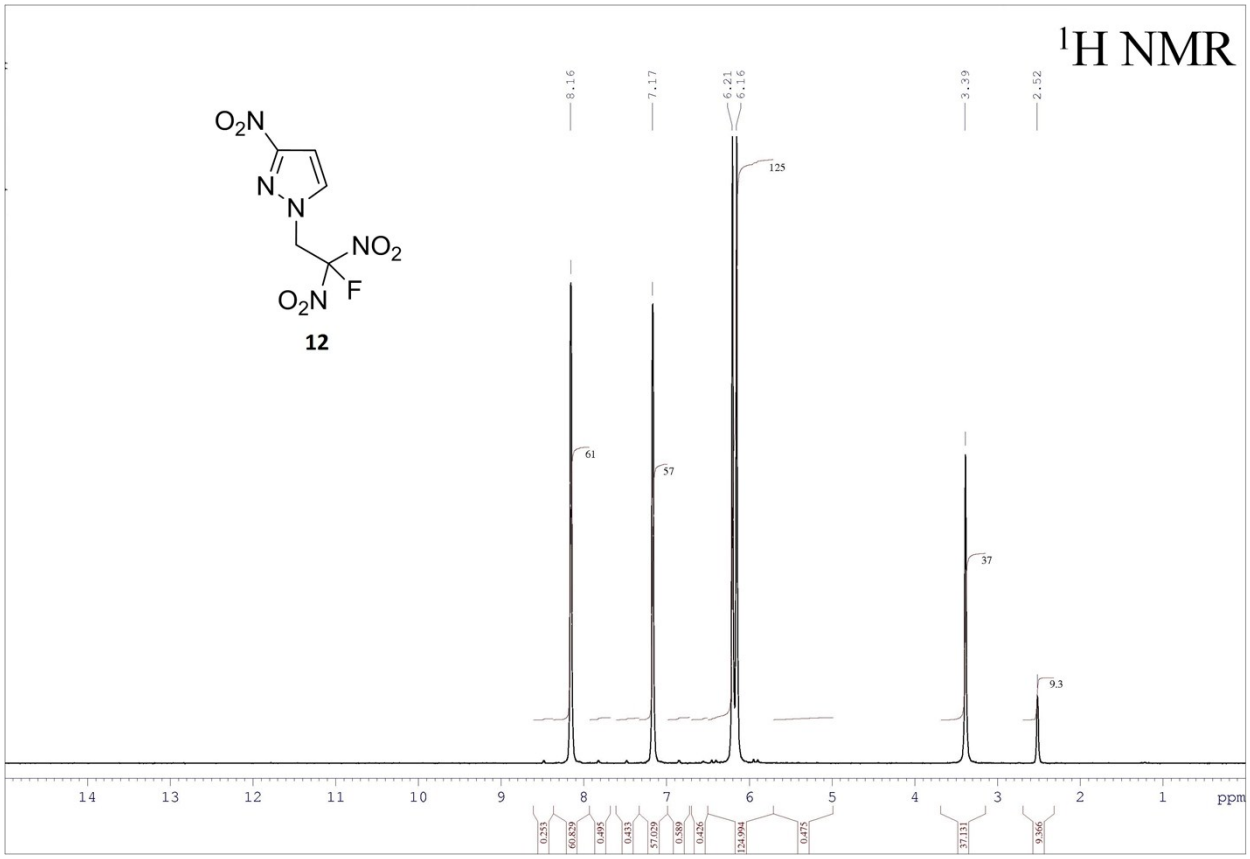
Table 6S. Tightness of crystal packing as defined by Kitaigorodsky packing coefficient and Δ_{OED} criterion for compounds **12**, **13**, **21**

Crystal packing tightness	compound **12**	compound **13**	compound **21**
Kitaigorodsky packing coefficient	0.703	0.728	0.756
Δ_{OED} criterion	0.151	0.202	0.271

References

1S. *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, **2009**.
2S. G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122.

NMR spectra


^{1}H NMR
O_2N
N
N
NO_2
F
O_2N
12
8.16
7.17
6.21
6.16
3.39
2.52
125
61
57
37
9.3
14
13
12
11
10
9
8
7
6
5
4
3
2
1
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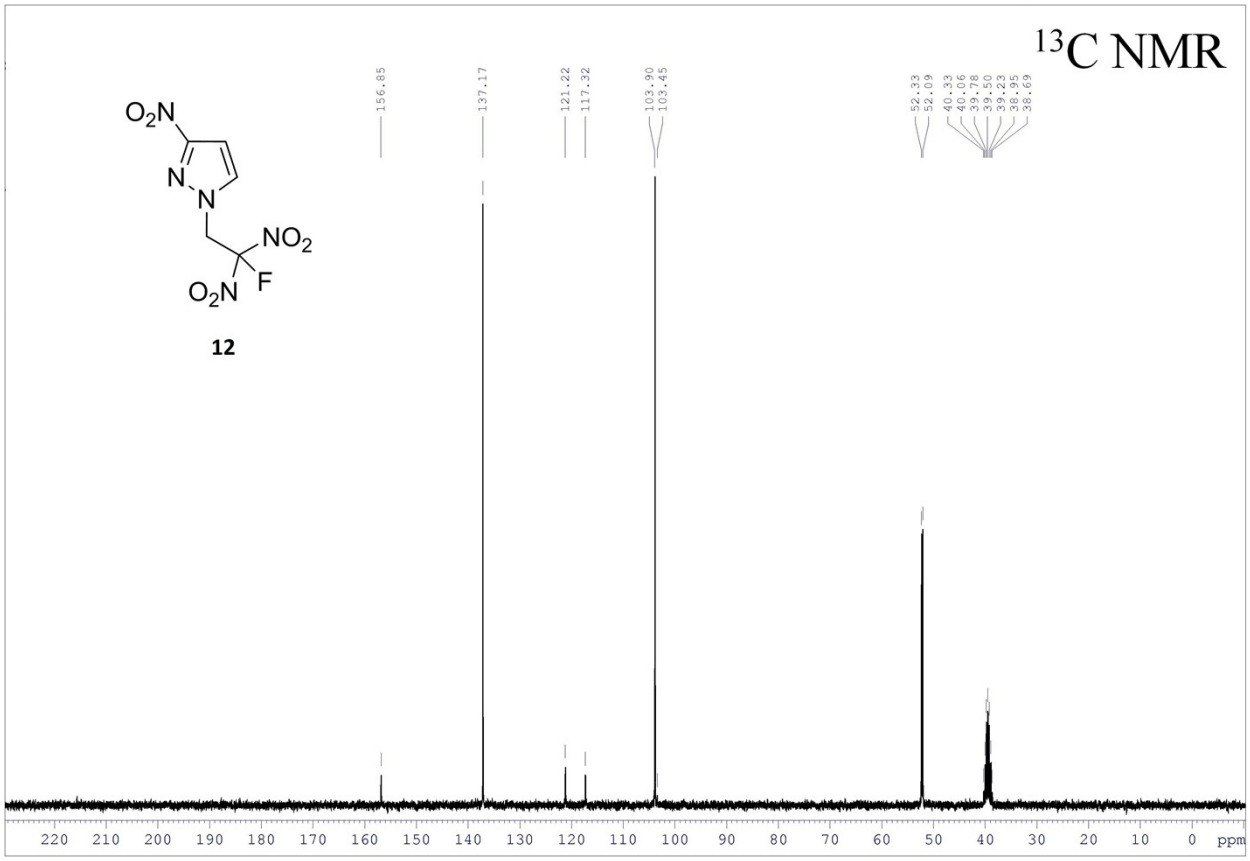
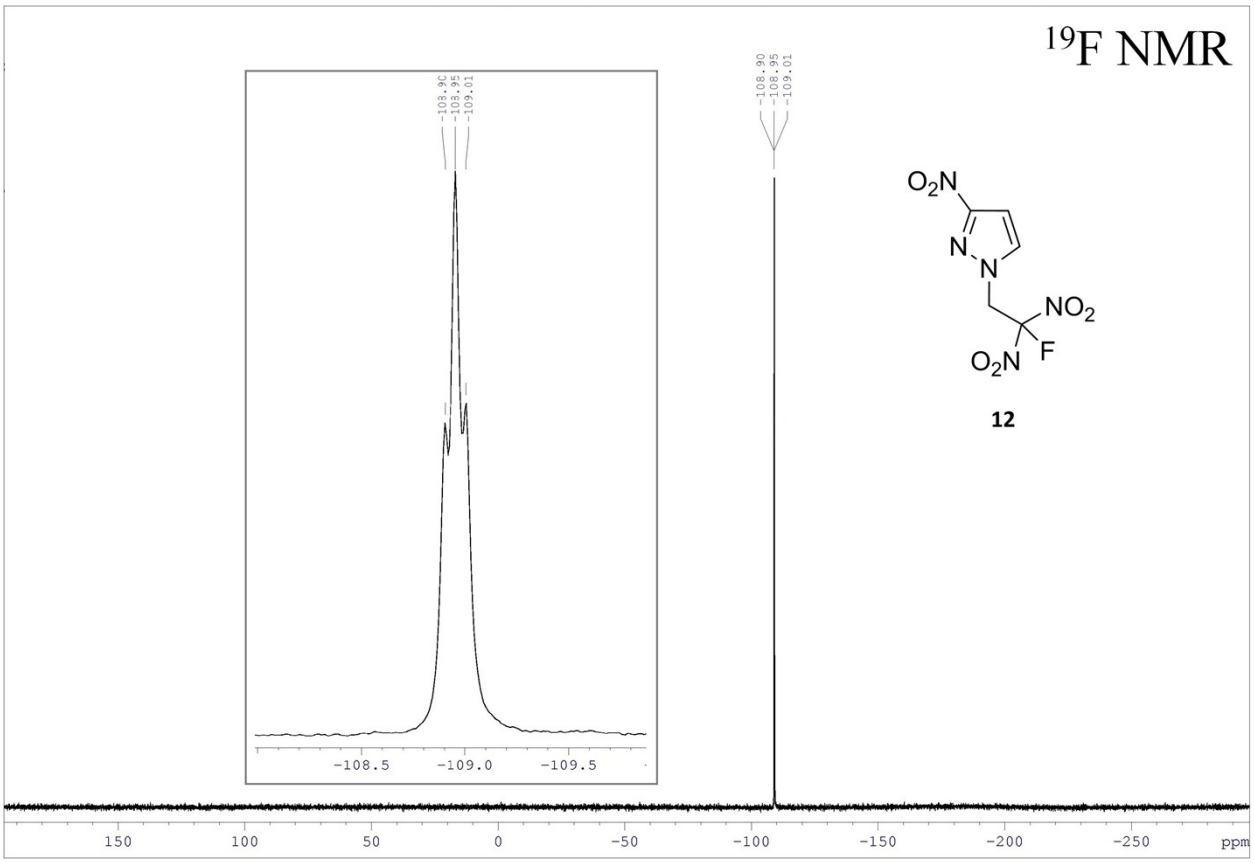
0.495
0.433
57.029
0.589
0.426
124.994
0.475
37.133
9.366


^{13}C NMR
O_2N
N
N
NO_2
F
O_2N
12
156.85
137.17
121.22
117.32
103.90
103.45
52.33
52.09
40.33
40.06
39.78
39.50
39.23
38.95
38.69
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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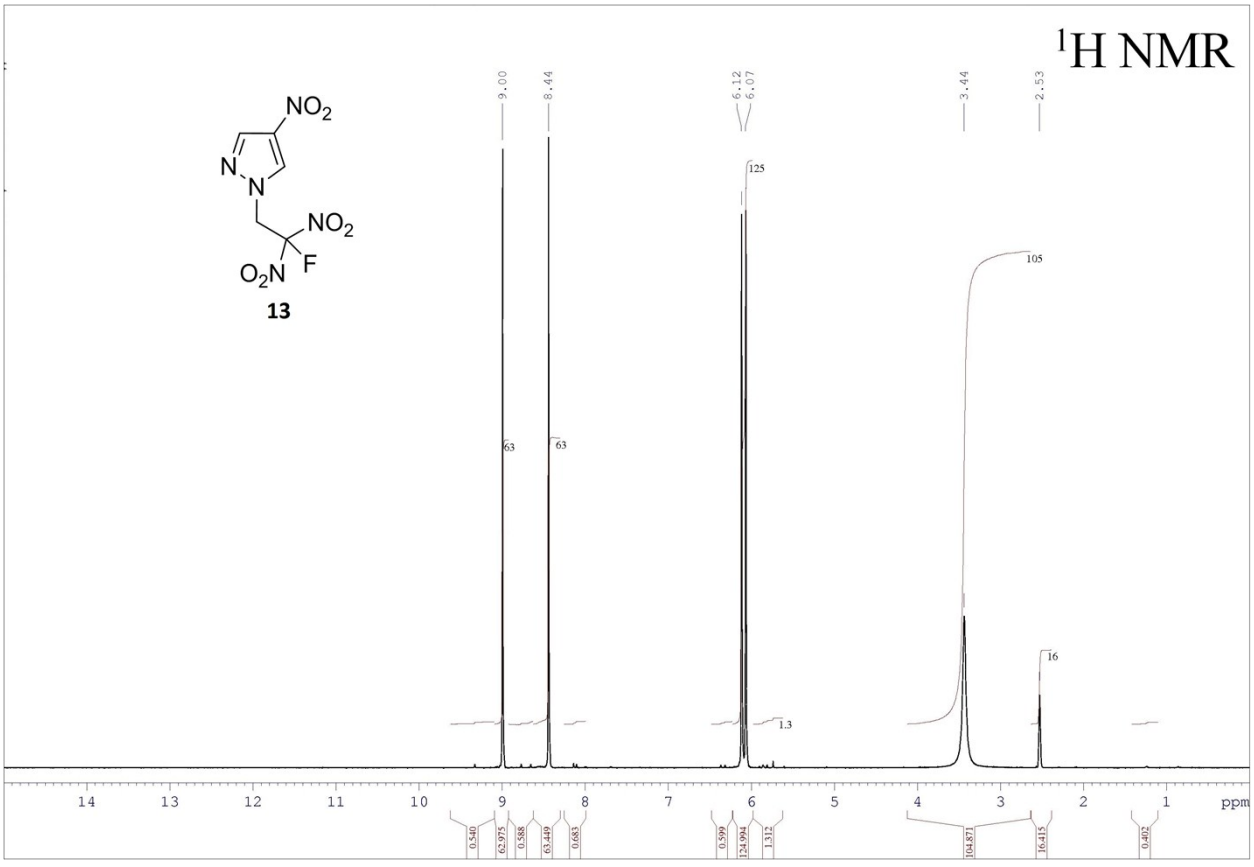
-103.90
-103.95
-109.01
-108.90
-108.95
-109.01
-108.5
-109.0
-109.5
O2N
N
N
NO2
O2N
F
12
150
100
50
0
-50
-100
-150
-200
-250
ppm


1H NMR
NO2
N
N
NO2
O2N
F
13
9.00
8.44
6.12
6.07
3.44
2.53
125
105
63
63
16
1.3
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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0.588
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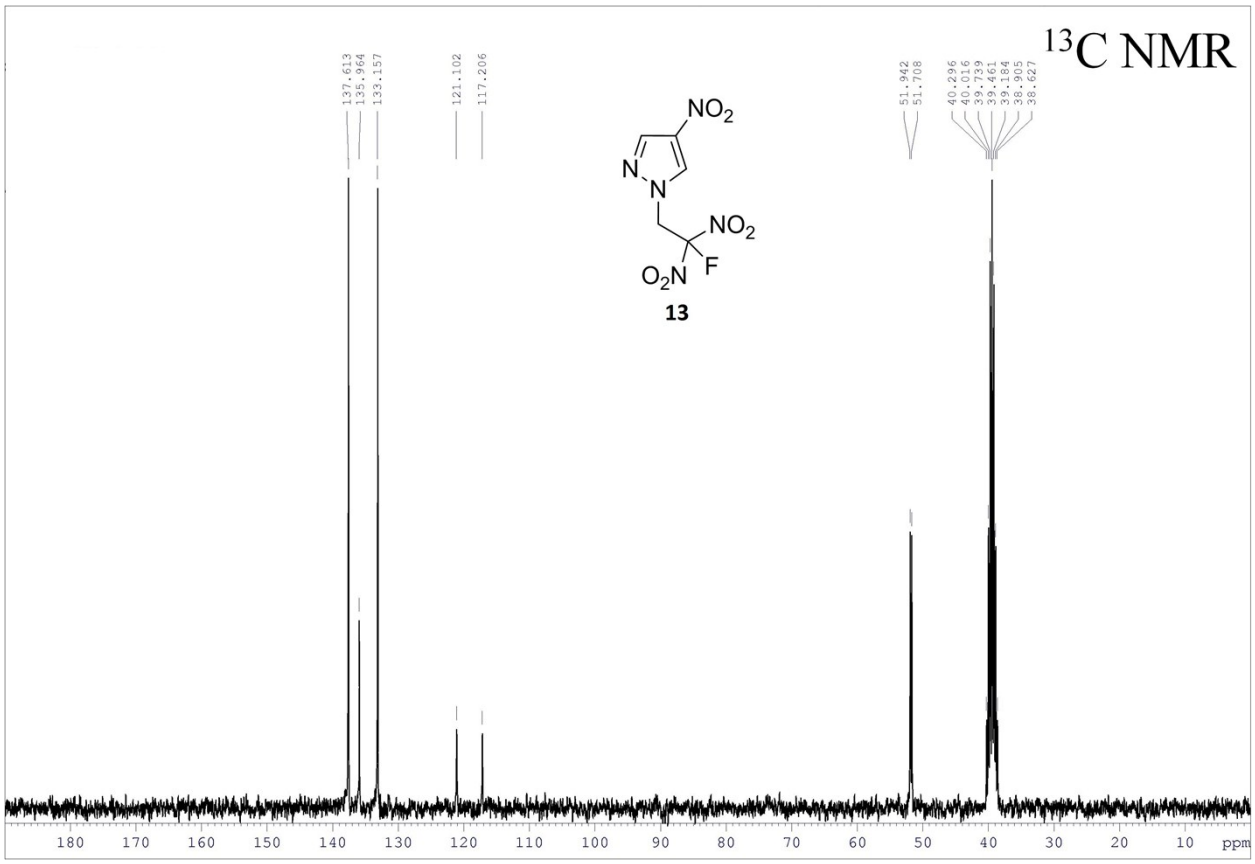
0.688
0.599
124.994
1.312
104.871
16.415
0.402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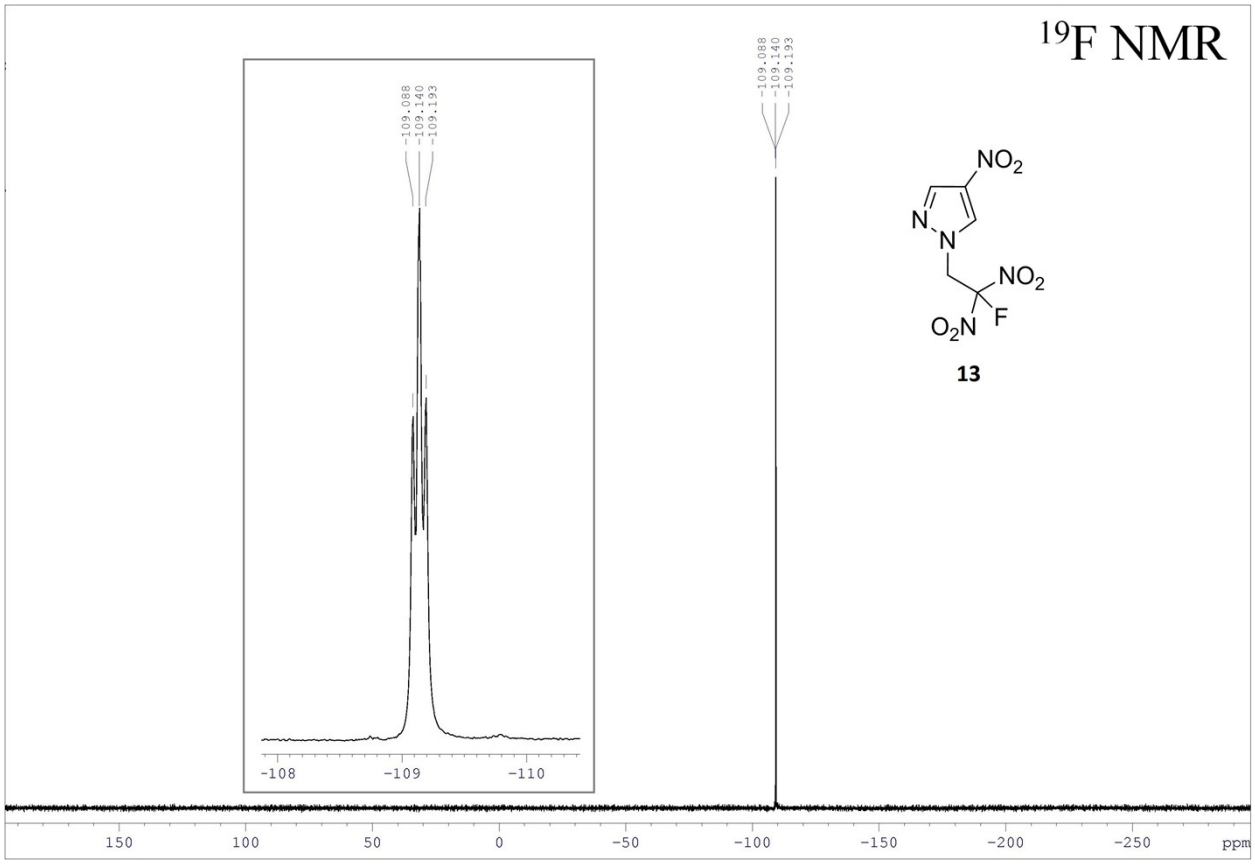
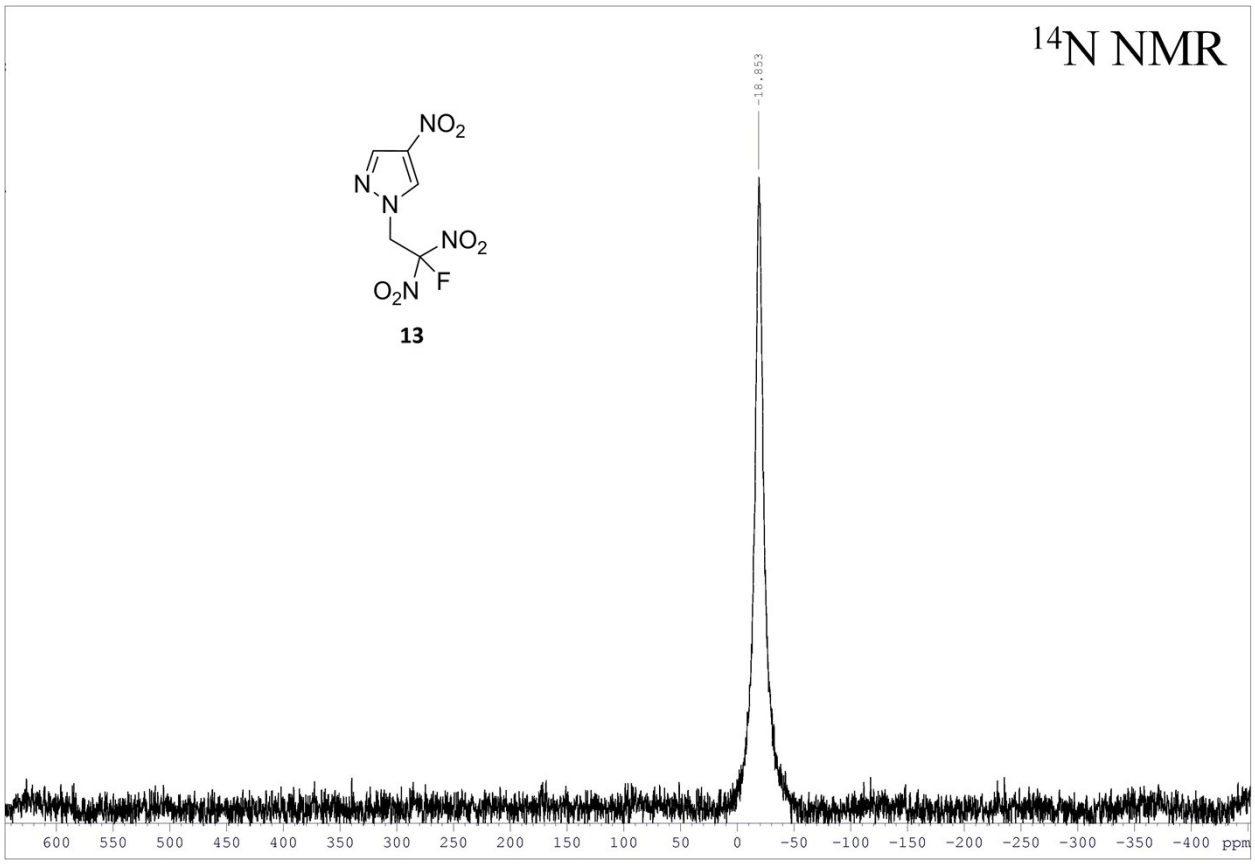
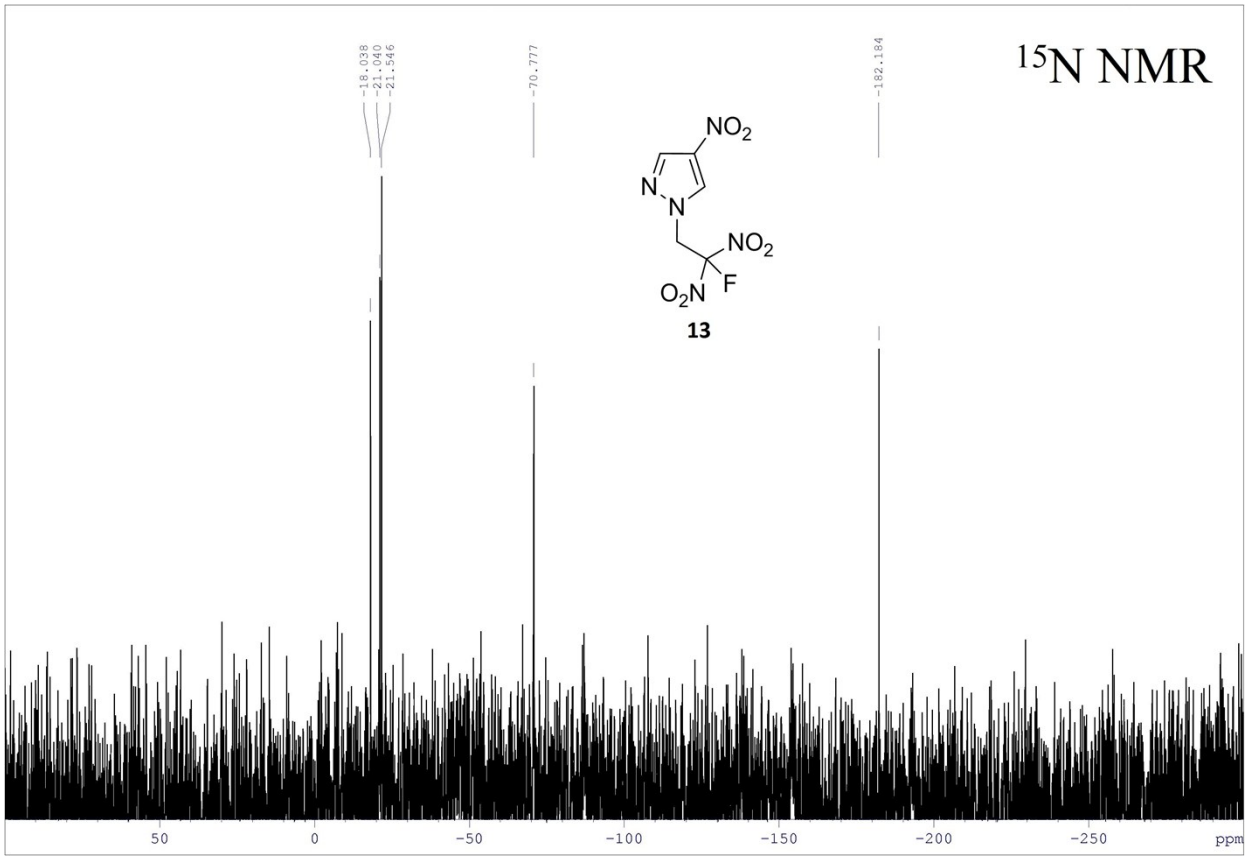
137.613
135.964
133.157
121.102
117.206
51.942
51.708
40.296
40.016
39.739
39.461
39.184
38.905
38.627
NO2
N
N
NO2
O2N
F
13
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{19}F NMR
-109.088
-109.140
-109.193
-108
-109
-110
NO2
N
N
NO2
O2N
F
13
150 100 50 0 -50 -100 -150 -200 -250 ppm


^{14}N NMR
-18.853
NO2
N
N
NO2
O2N
F
13
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm


^{15}N NMR
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-21.040
-21.546
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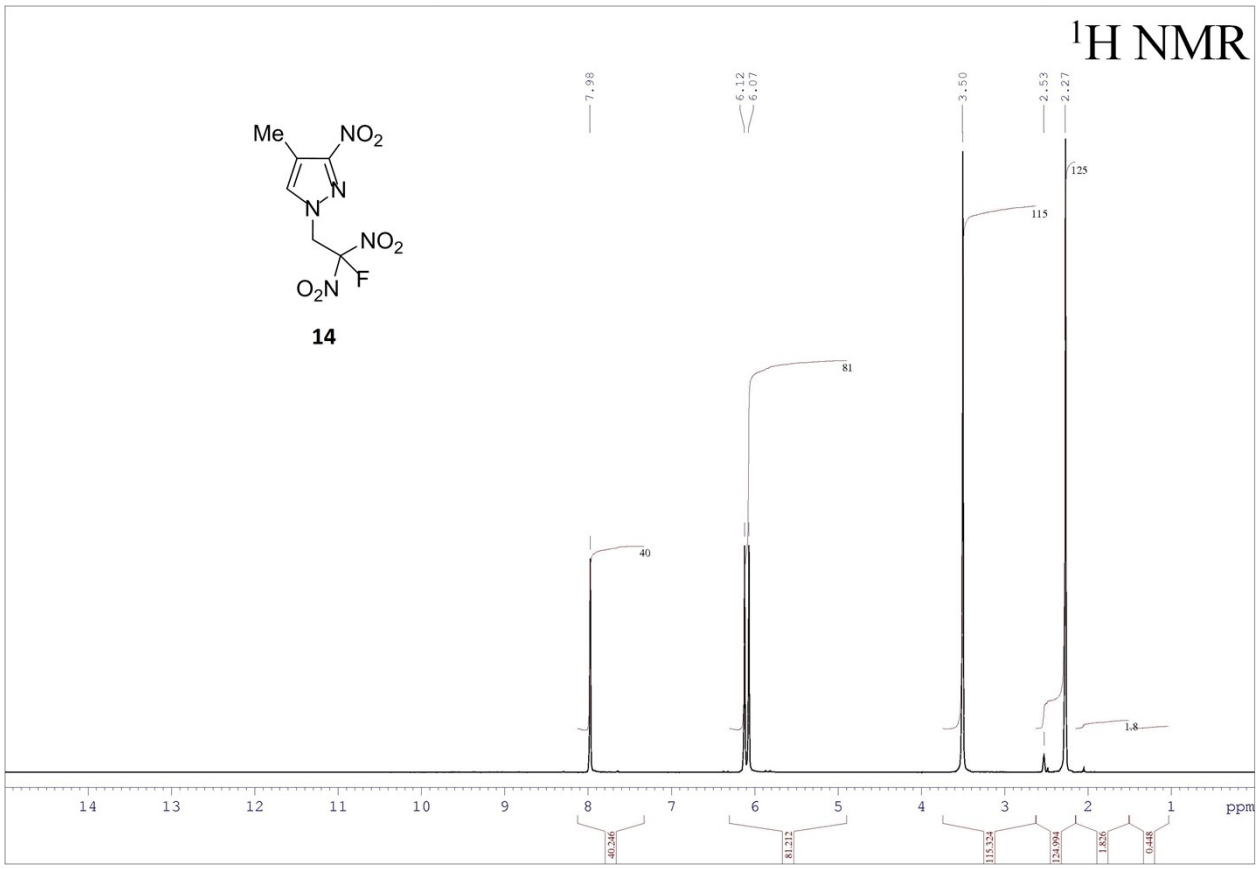
NO2
N
N
NO2
O2N
F
13
50 0 -50 -100 -150 -200 -250 ppm


^{1}H NMR
Me
NO2
N
N
NO2
O2N
F
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7.98
6.12
6.07
3.50
2.53
2.27
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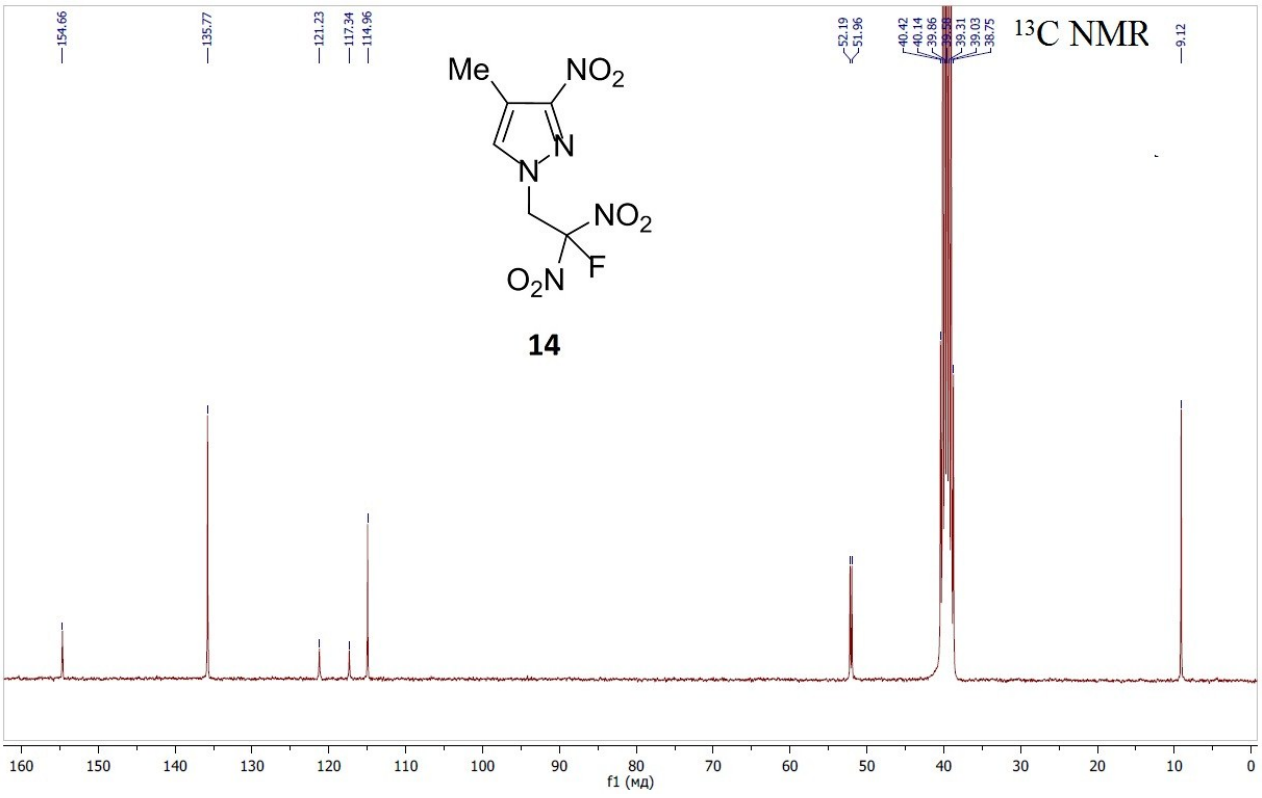
115
81
40
1.8
ppm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154.66
135.77
121.23
117.34
114.96
52.19
51.96
40.42
40.14
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38.75
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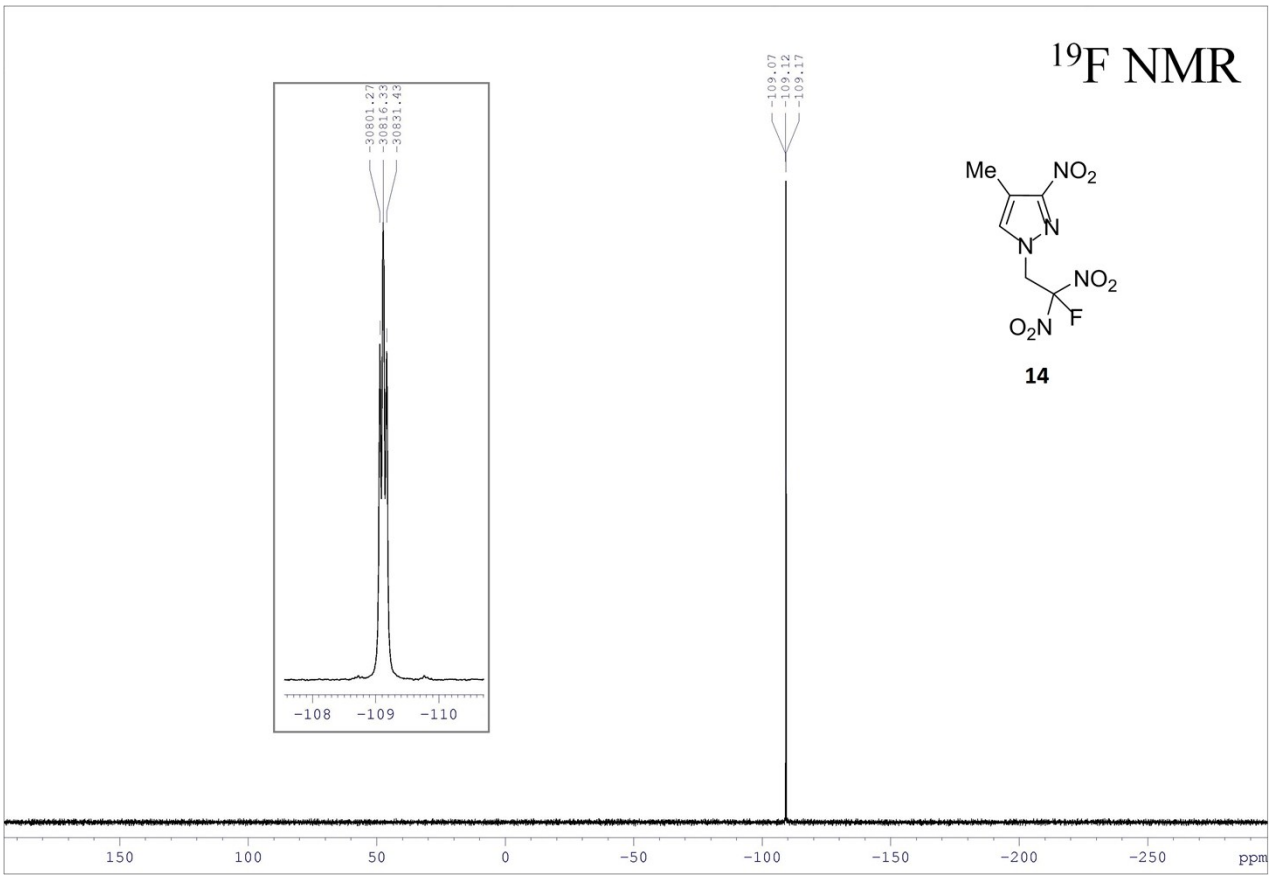
Me
NO2
N
N
NO2
O2N
F
14
f1 (мд)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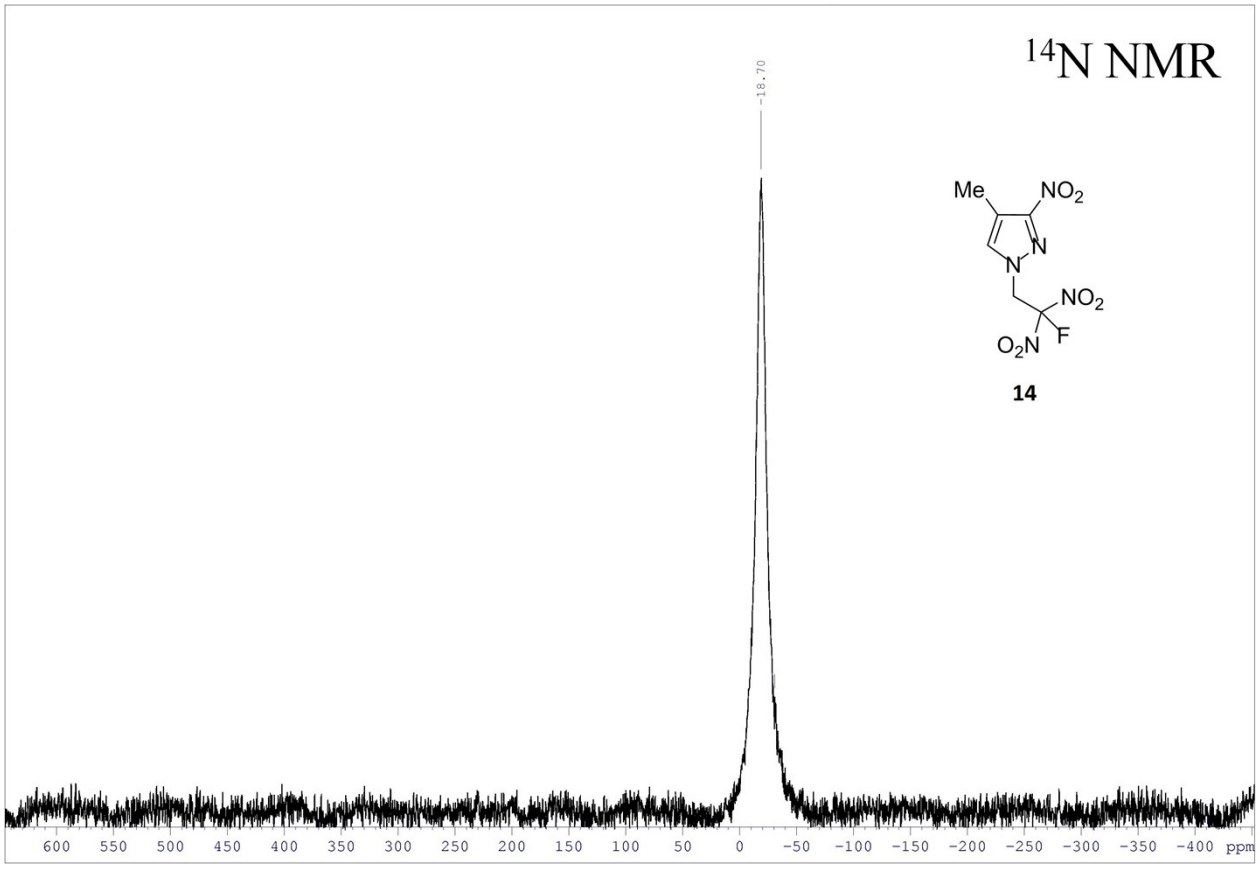
-30801.27
-30816.33
-30831.43
-109.07
-109.12
-109.17
Me
NO2
N
N
NO2
O2N
F
14
-108
-109
-110
150
100
50
0
-50
-100
-150
-200
-250
ppm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NO2
N
N
NO2
O2N
F
14
600
550
500
450
400
350
300
250
200
150
100
50
0
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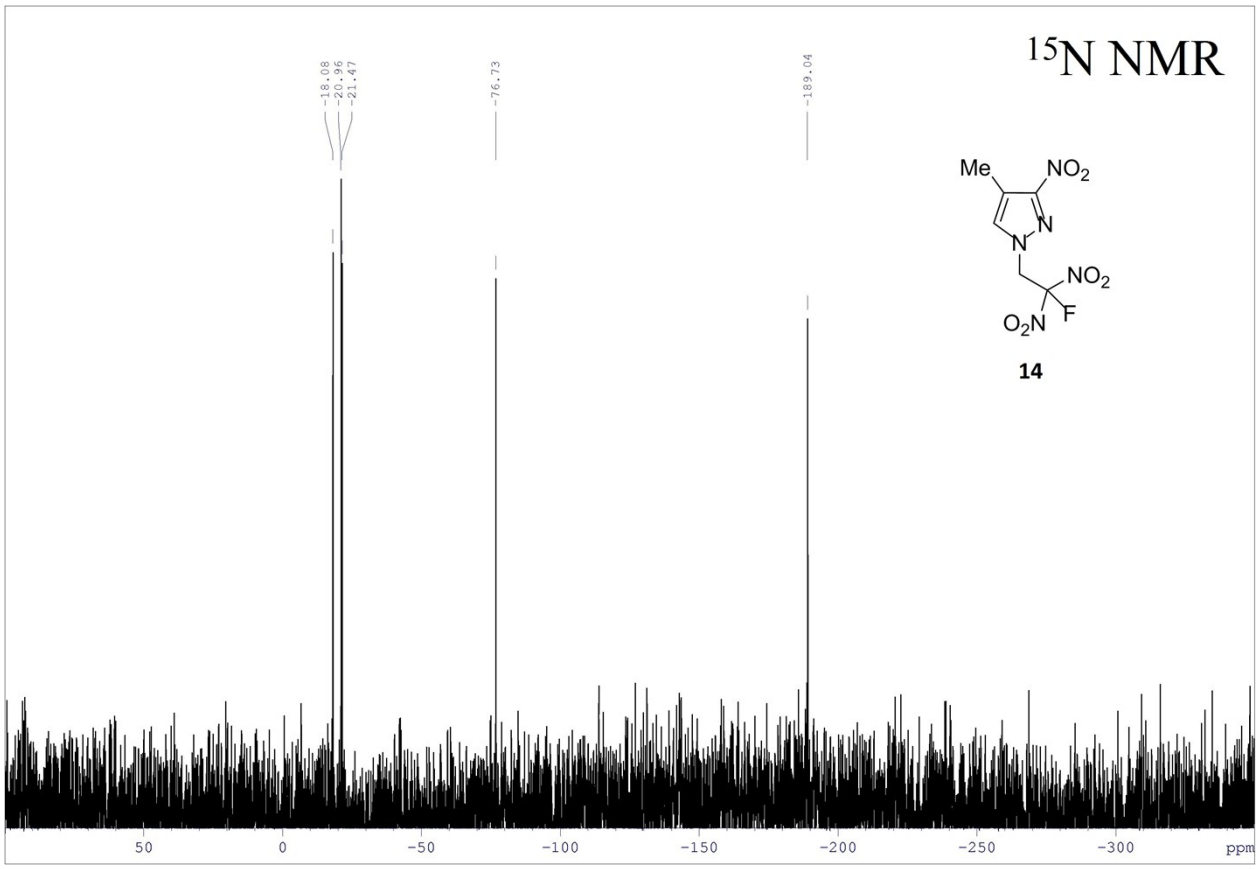
-100
-150
-200
-250
-300
-350
-400
ppm


15N NMR
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-20.96
-21.47
-76.73
-189.04
Me
NO2
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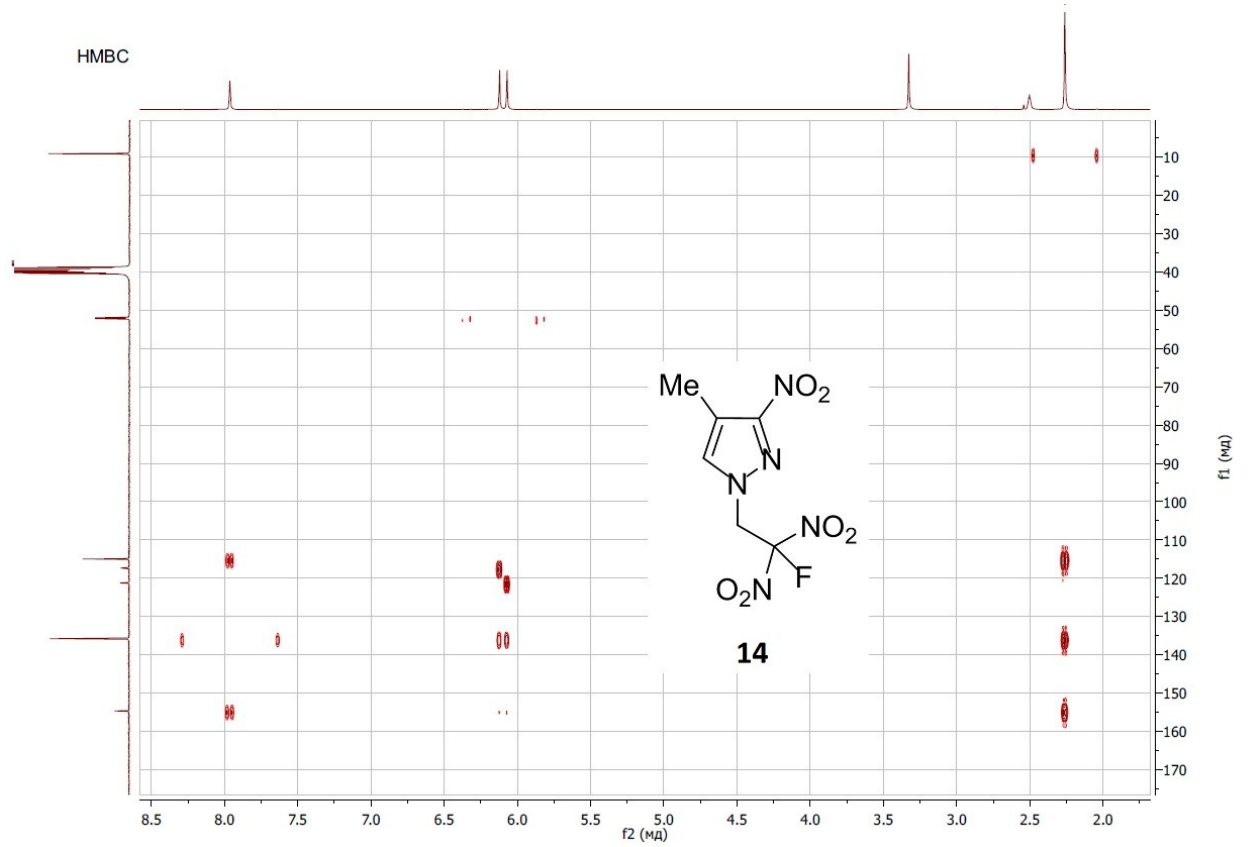
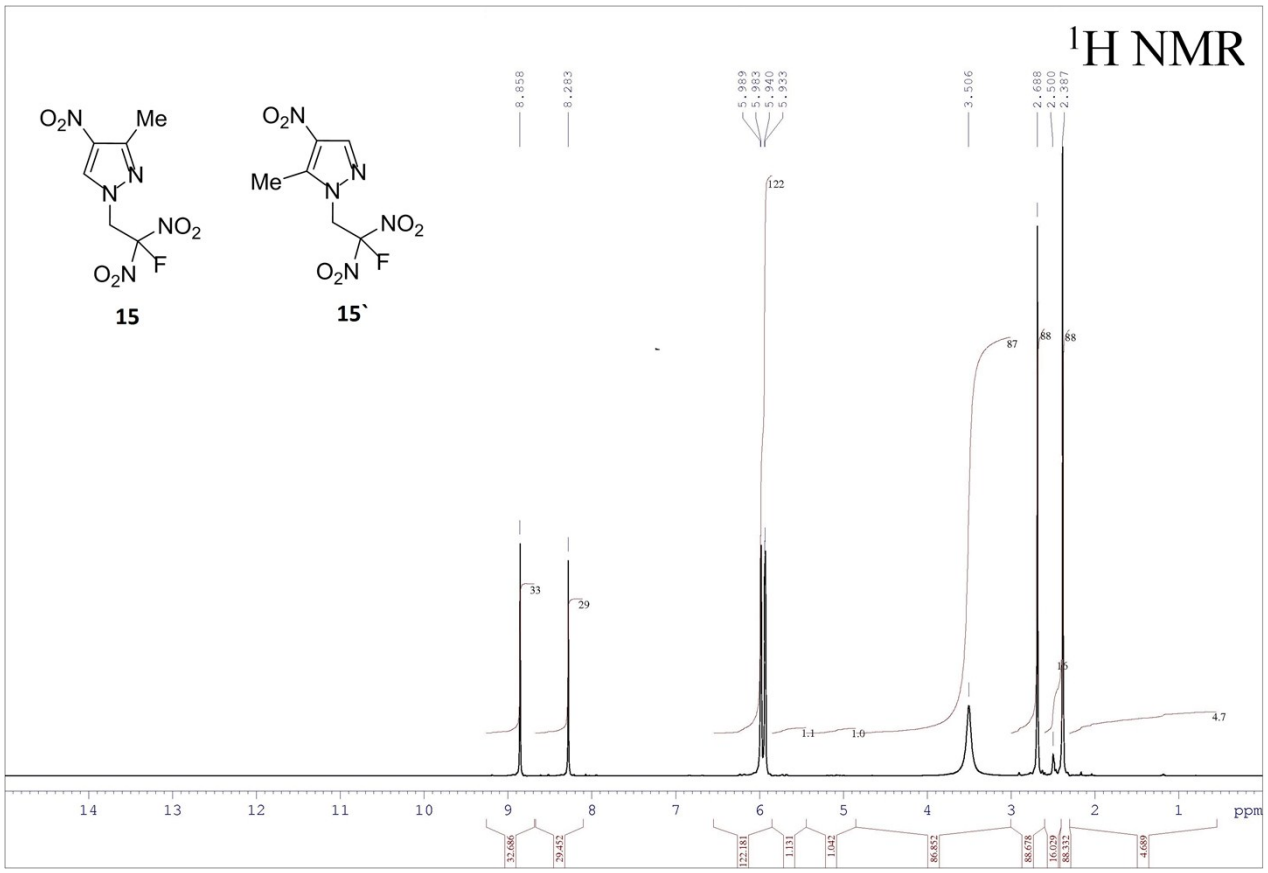
N
NO2
O2N
F
14
50
0
-50
-100
-150
-200
-250
-300
ppm


HMBC
Me
NO2
N
N
NO2
O2N
F
14
f2 (мд)
f1 (мд)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O_2N
Me
NO_2
F
15
15`
8.858
8.283
5.989
5.983
5.940
5.933
3.506
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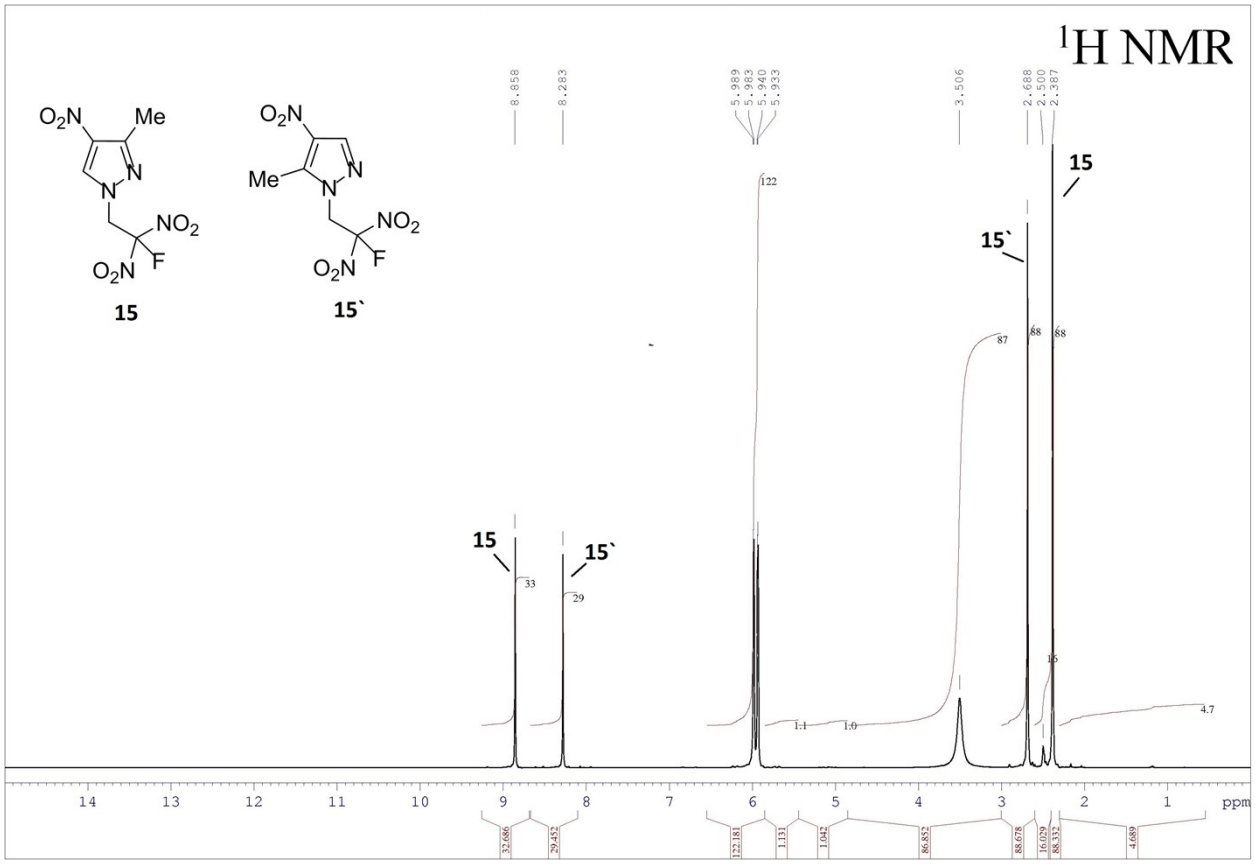
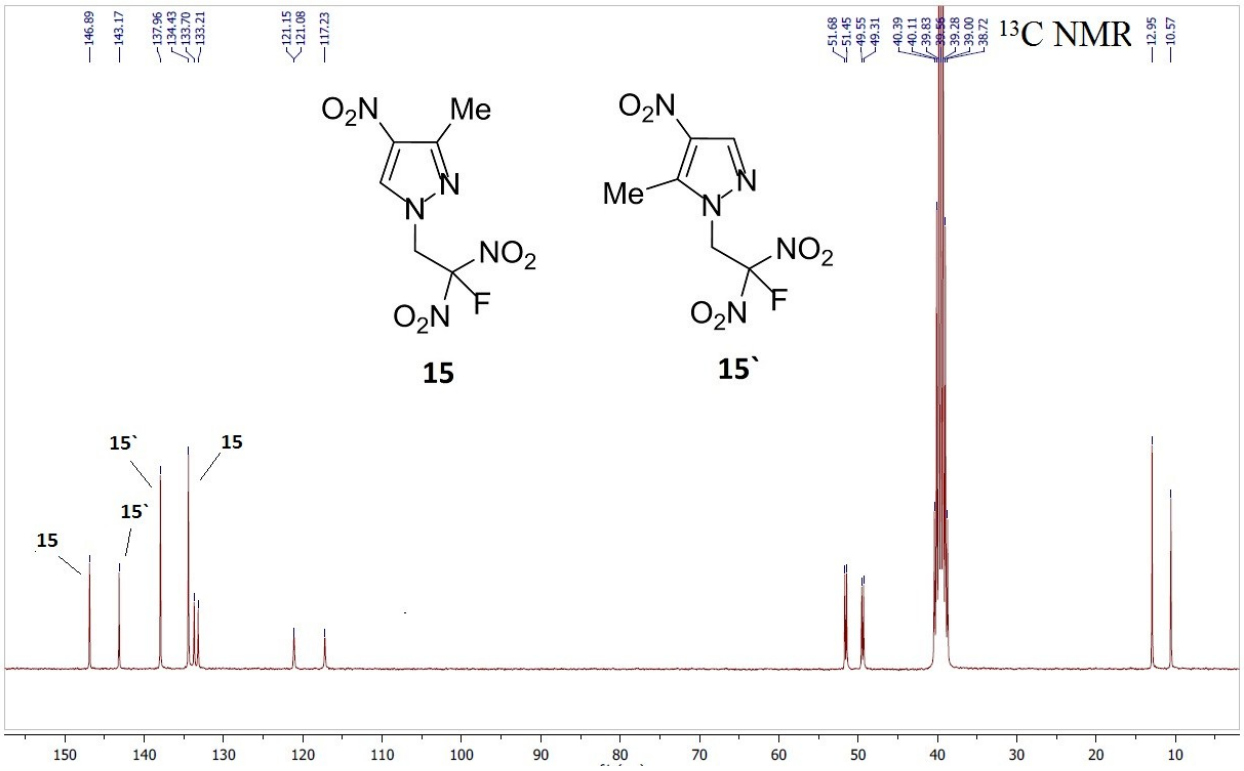
2.500
2.387
122
87
88
33
29
15
4.7
1:1
1:0
ppm


^{1}H NMR
O_2N
Me
NO_2
F
15
15`
8.858
8.283
5.989
5.983
5.940
5.933
3.506
2.688
2.500
2.387
122
87
88
33
29
15
4.7
1:1
1:0
ppm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133.21
121.15
121.08
117.23
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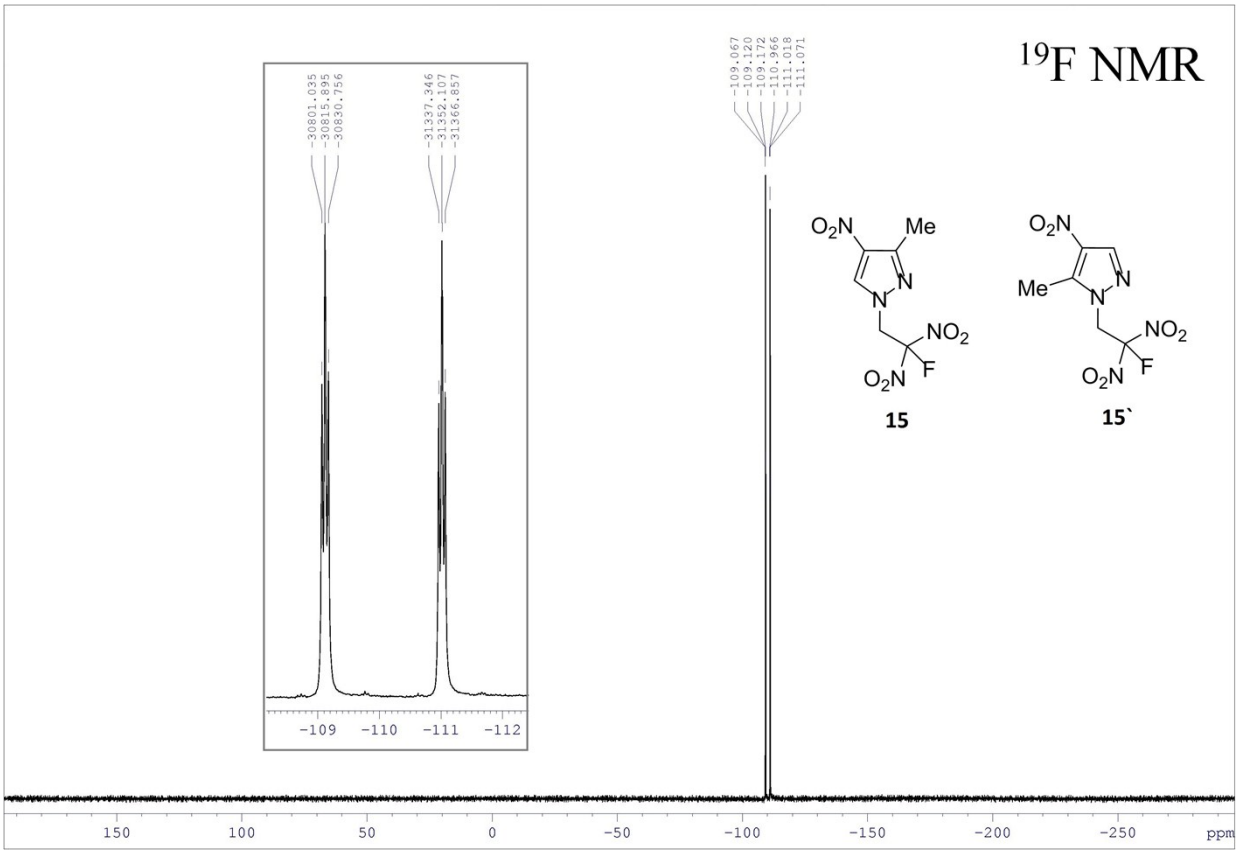
51.45
49.55
49.31
40.39
40.11
39.83
39.56
39.28
39.00
38.72
12.95
10.57
13C NMR
O2N
Me
N
N
NO2
O2N
F
15
O2N
Me
N
N
NO2
O2N
F
15`
15`
15
15`
15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


19F NMR
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-30830.756
-31337.346
-31352.107
-31366.857
-109.067
-109.120
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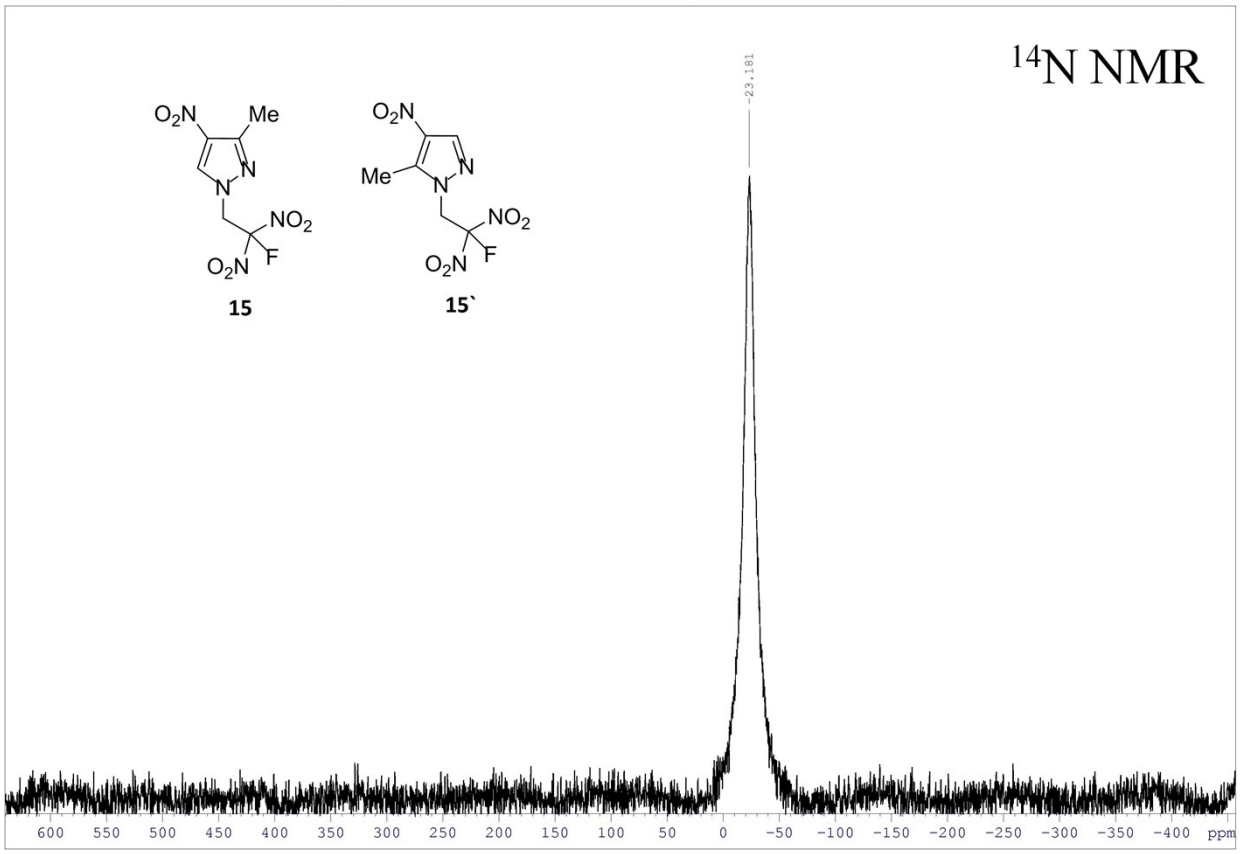
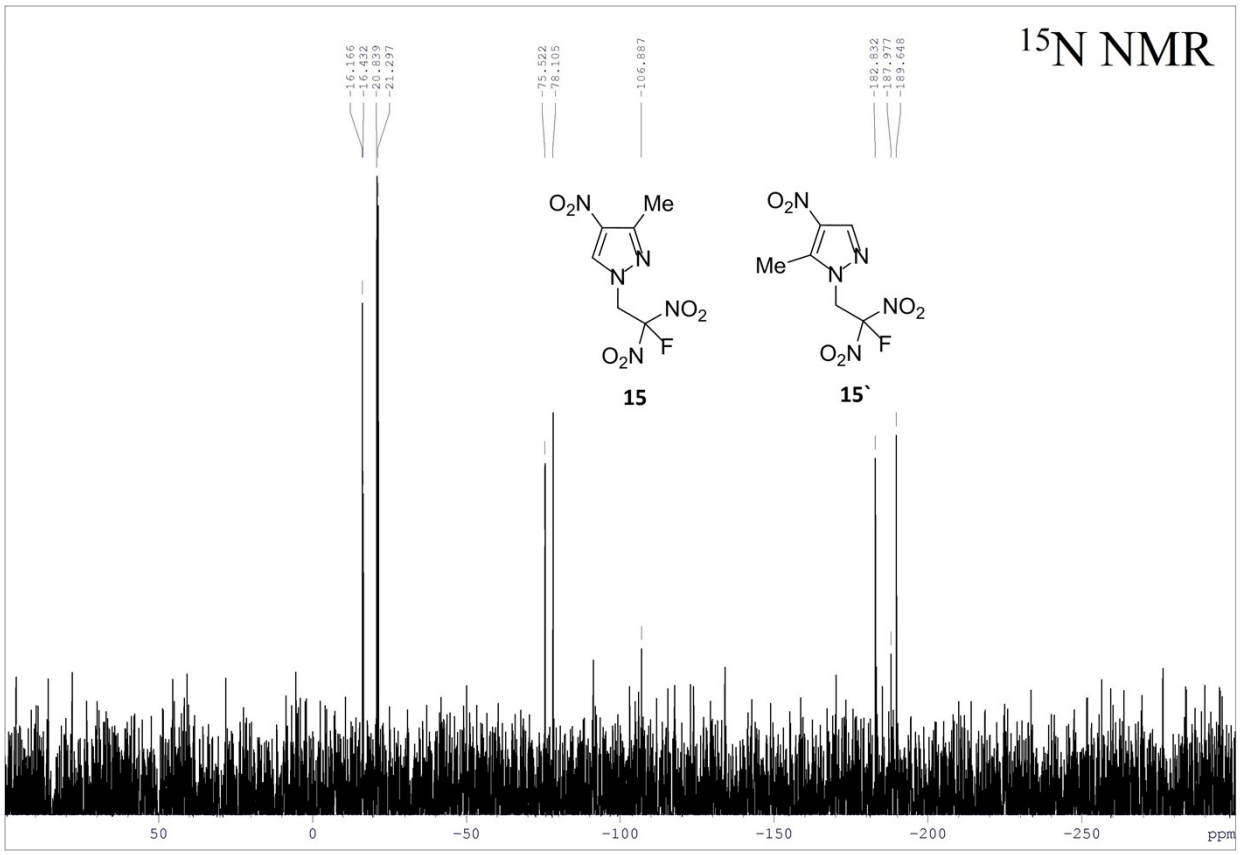
-110.966
-111.018
-111.071
-109
-110
-111
-112
O2N
Me
N
N
NO2
O2N
F
15
O2N
Me
N
N
NO2
O2N
F
15`
150
100
50
0
-50
-100
-150
-200
-250
ppm


^{14}N NMR
-23.181
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm

15 **15`**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-20.839
-21.297
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-78.105
-106.887
-182.832
-187.977
-189.648
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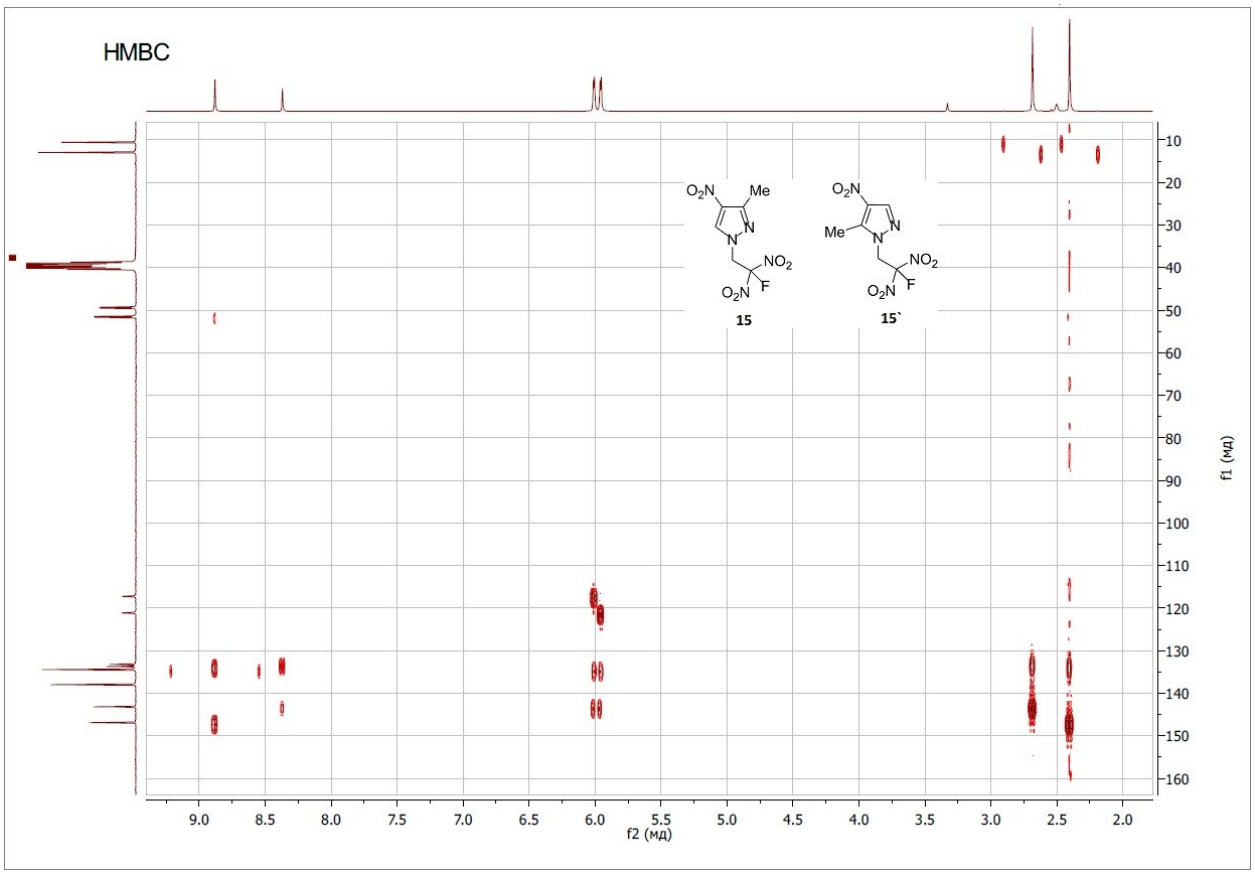
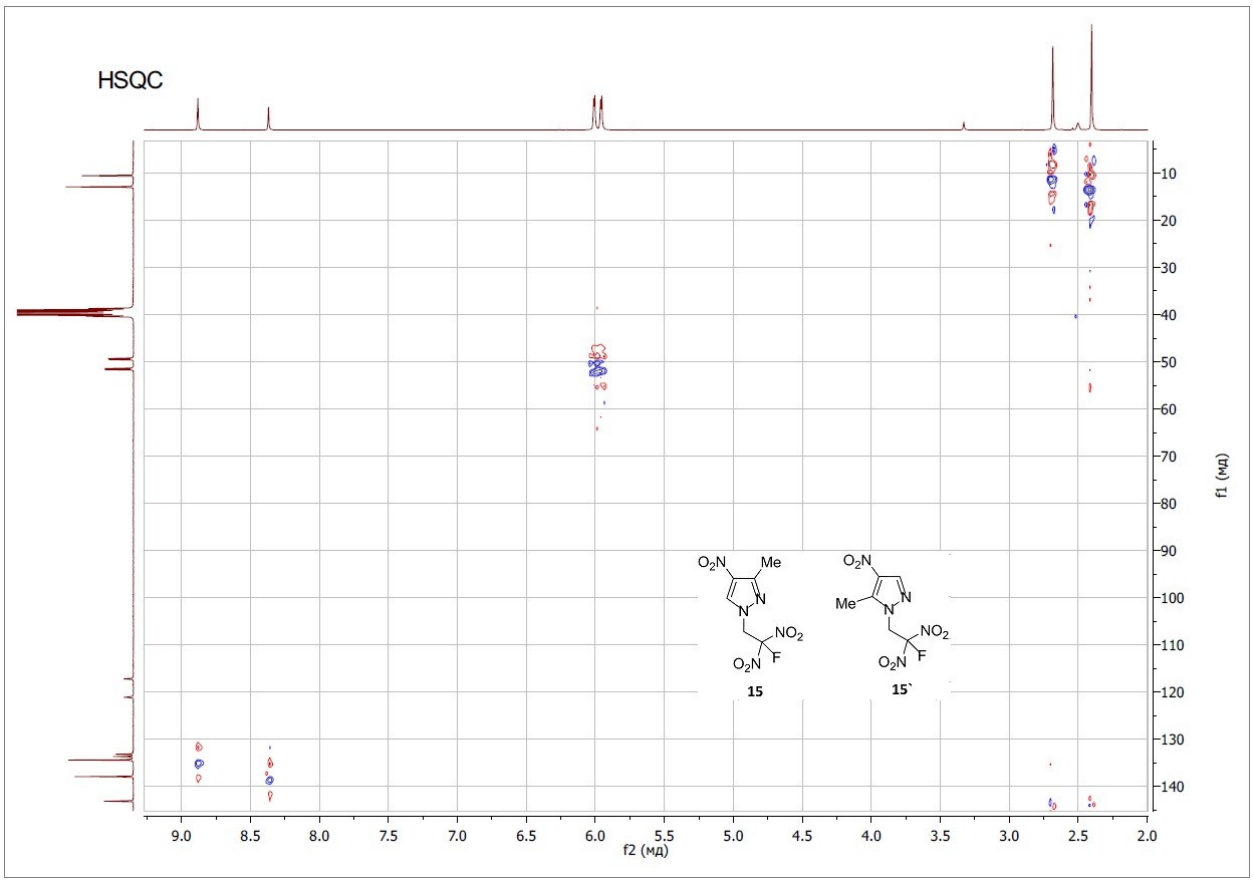
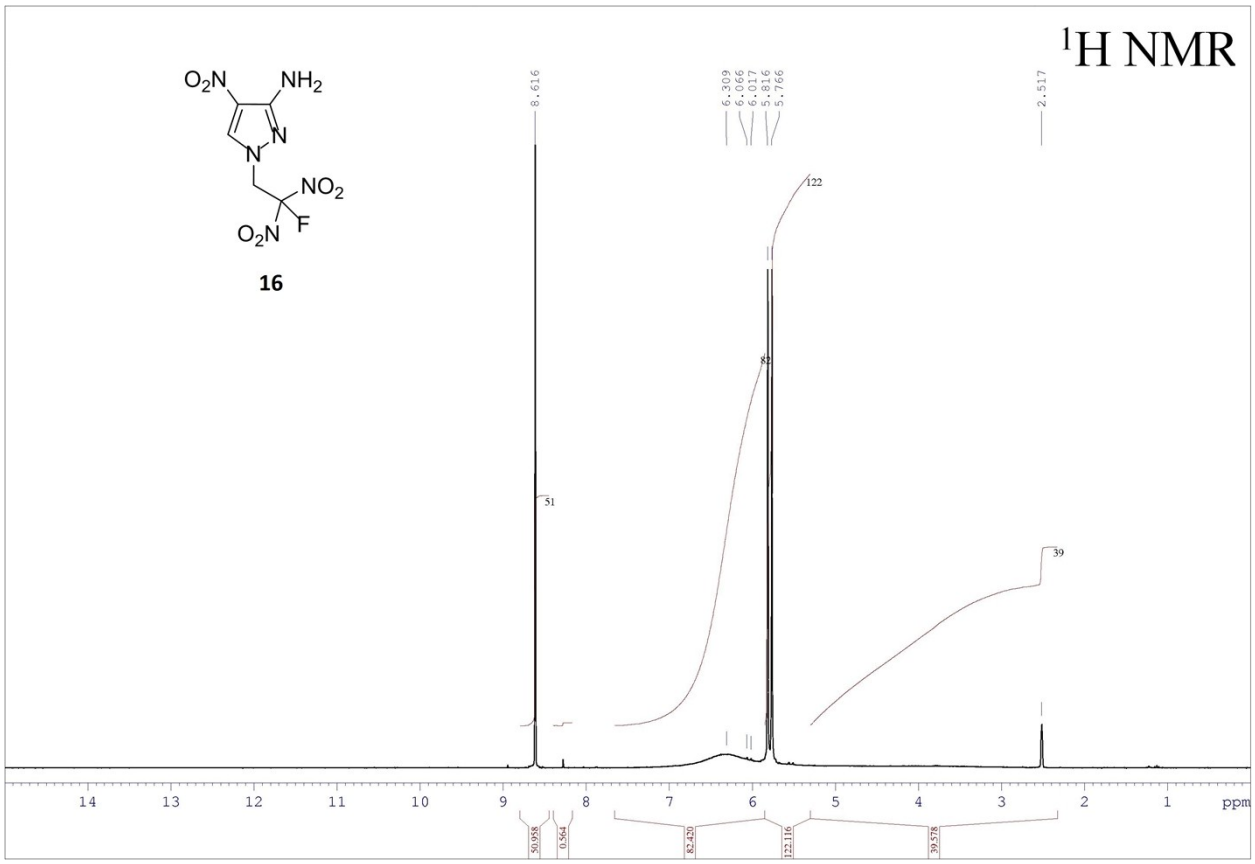
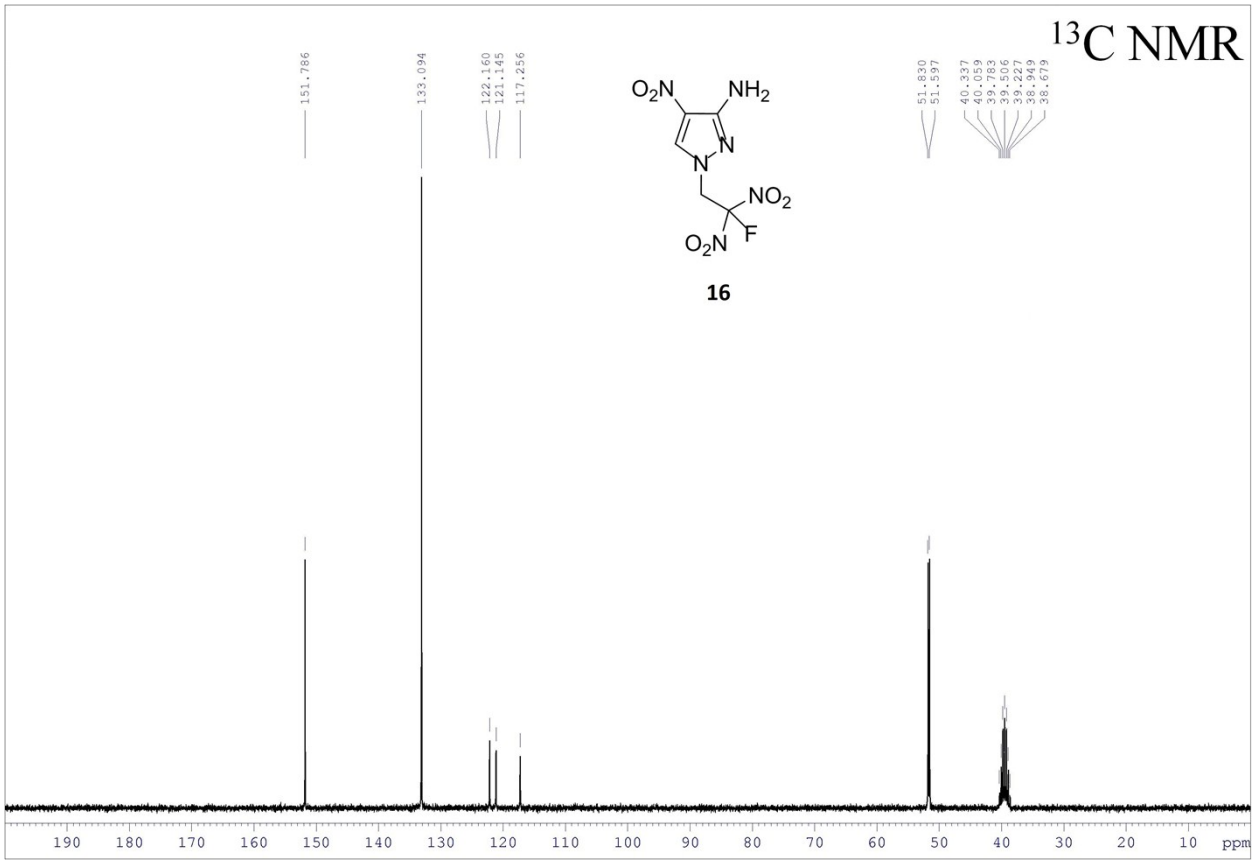
15 **15`**


HMBC
15
15`
f2 (мд)
f1 (мд)


HSQC
15
15`
f2 (мд)
f1 (мд)


^{1}H NMR
16
8.616
6.309
6.066
6.017
5.816
5.766
2.517
122
51
39
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm


^{13}C NMR
16
151.786
133.094
122.160
121.145
117.256
51.830
51.597
40.337
40.059
39.783
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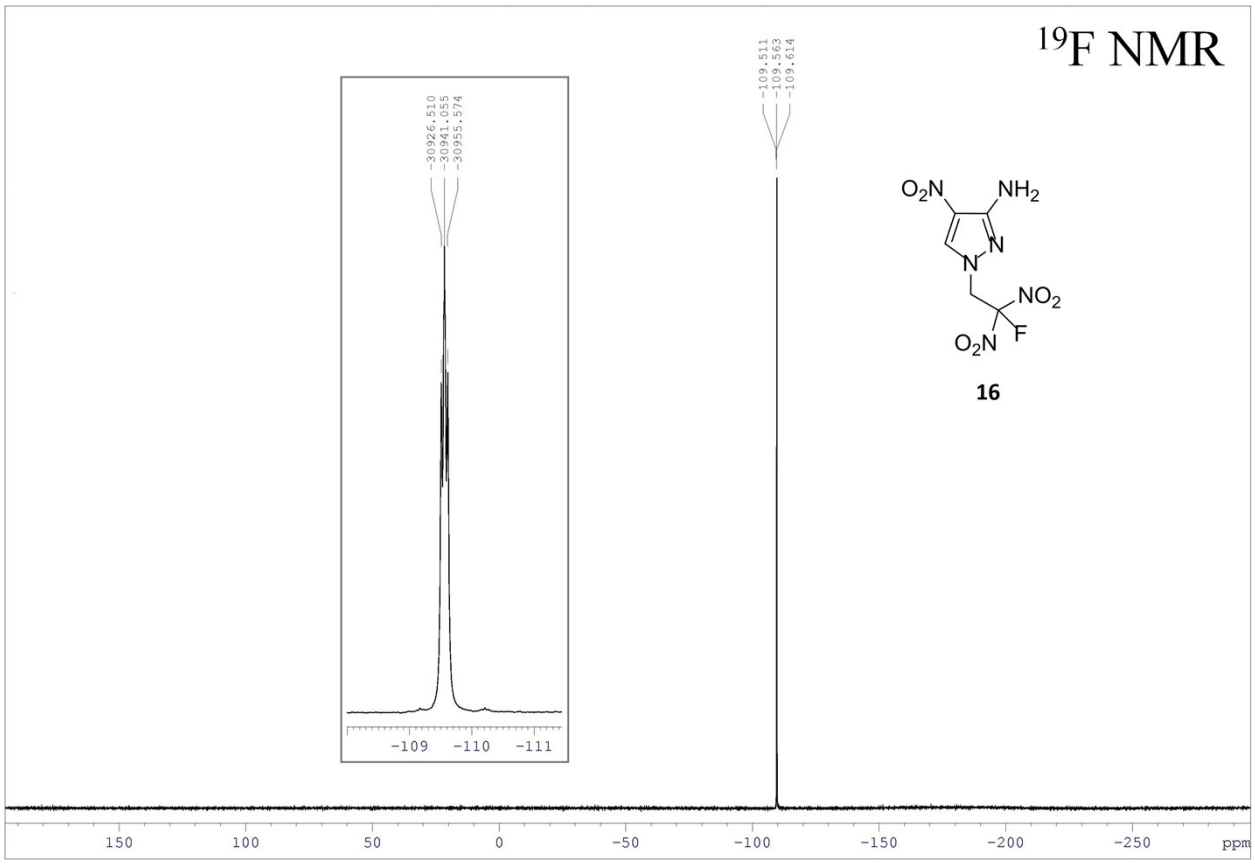
39.227
38.949
38.679
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


19F NMR
-109.511
-109.563
-109.614
-30926.510
-30941.055
-30955.574
-109
-110
-111
O2N
NH2
N
N
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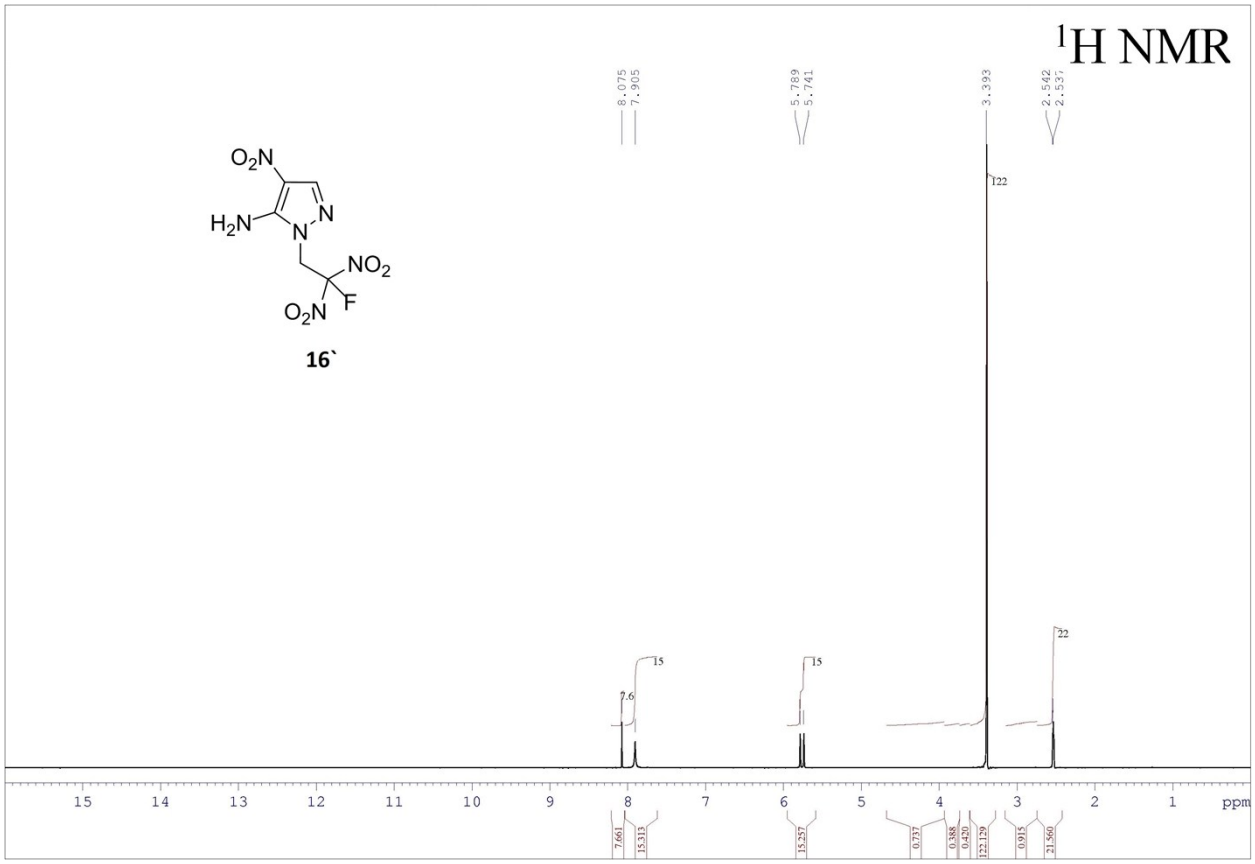
O2N
F
16
150
100
50
0
-50
-100
-150
-200
-250
ppm


1H NMR
8.075
7.905
5.789
5.741
3.393
2.542
2.537
O2N
H2N
N
N
NO2
O2N
F
16`
22
15
15
7.6
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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0.388
0.420
122.129
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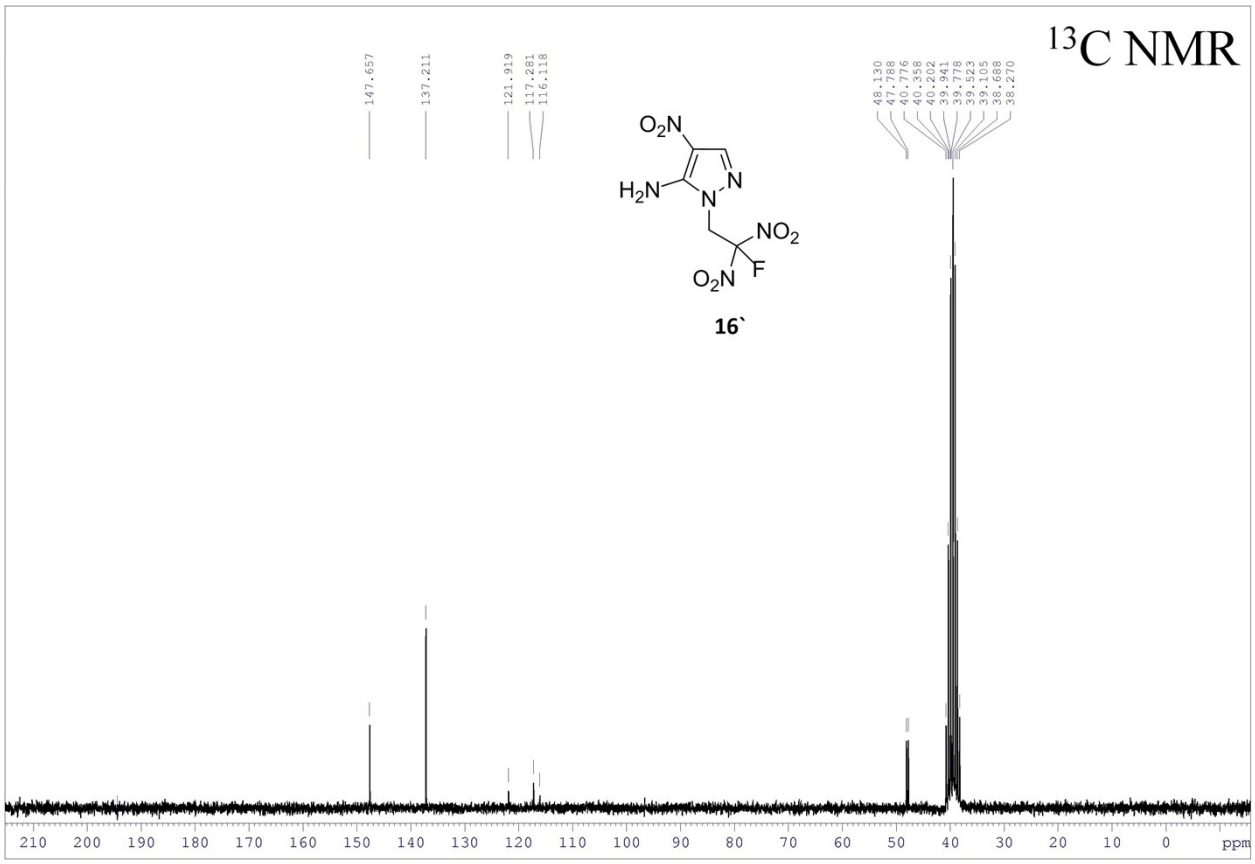
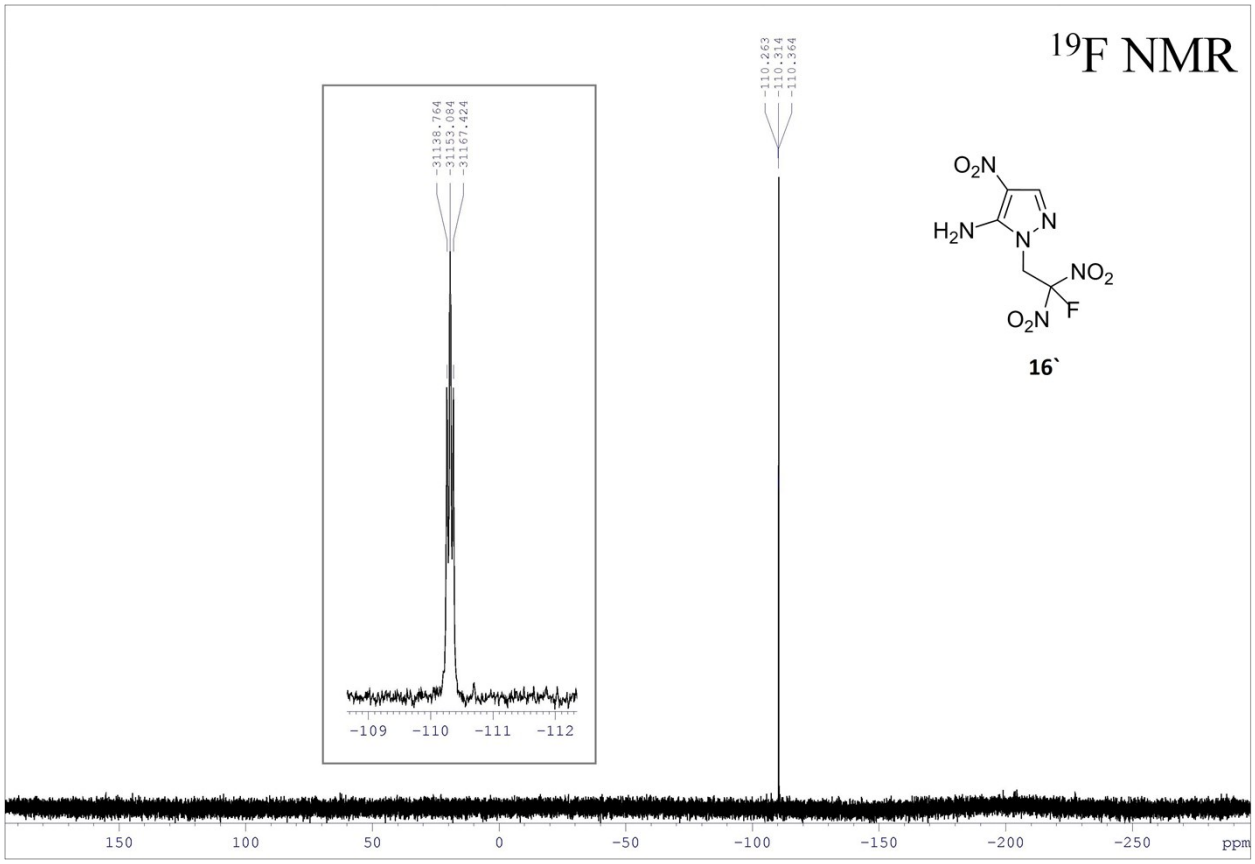
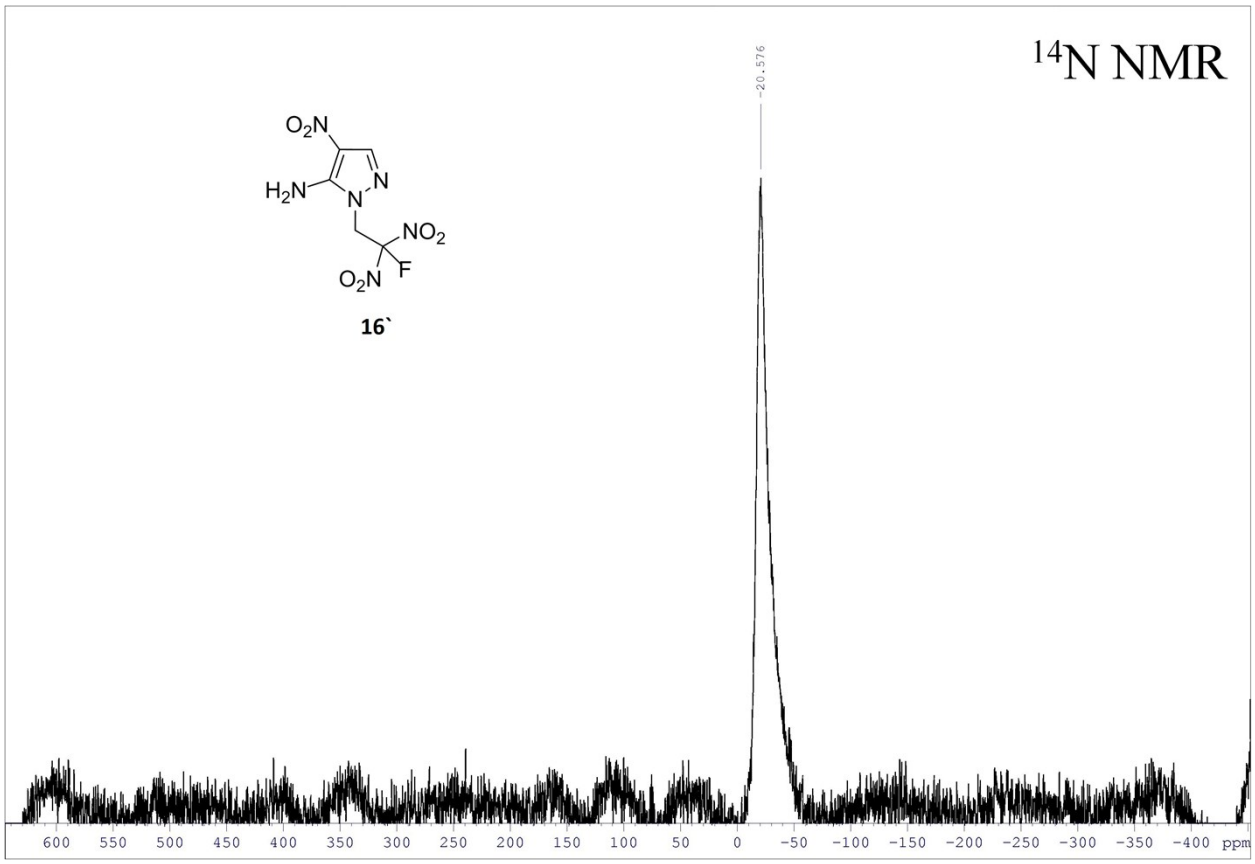
21.560


^{13}C NMR
147.657
137.211
121.919
117.281
116.118
48.130
47.788
40.776
40.358
40.202
39.941
39.778
39.523
39.105
38.688
38.270
O_2N
H_2N
N
N
NO_2
O_2N
F
16`
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


^{19}F NMR
-110.263
-110.314
-110.364
-31138.764
-31153.084
-31167.424
O_2N
H_2N
N
N
NO_2
O_2N
F
16`
-109 -110 -111 -112
150 100 50 0 -50 -100 -150 -200 -250 ppm


^{14}N NMR
-20.576
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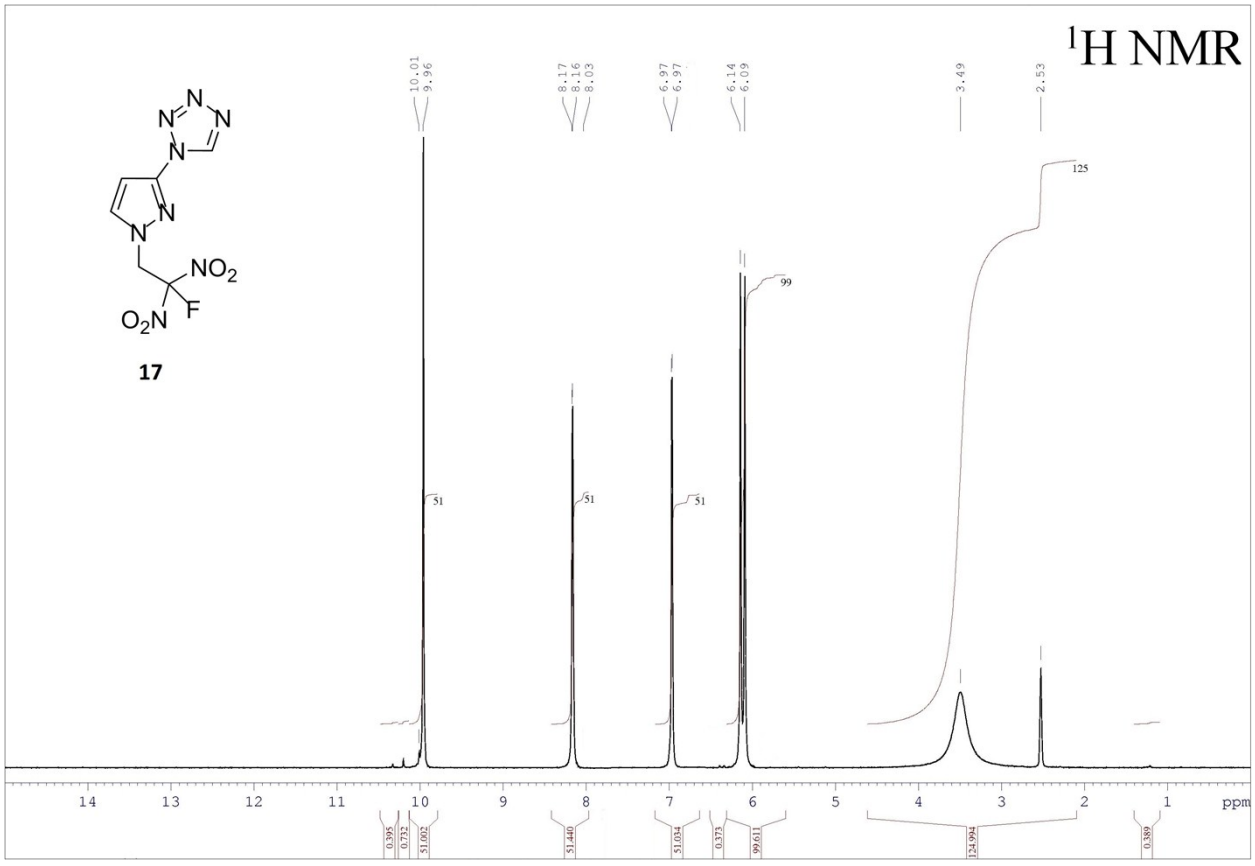
16`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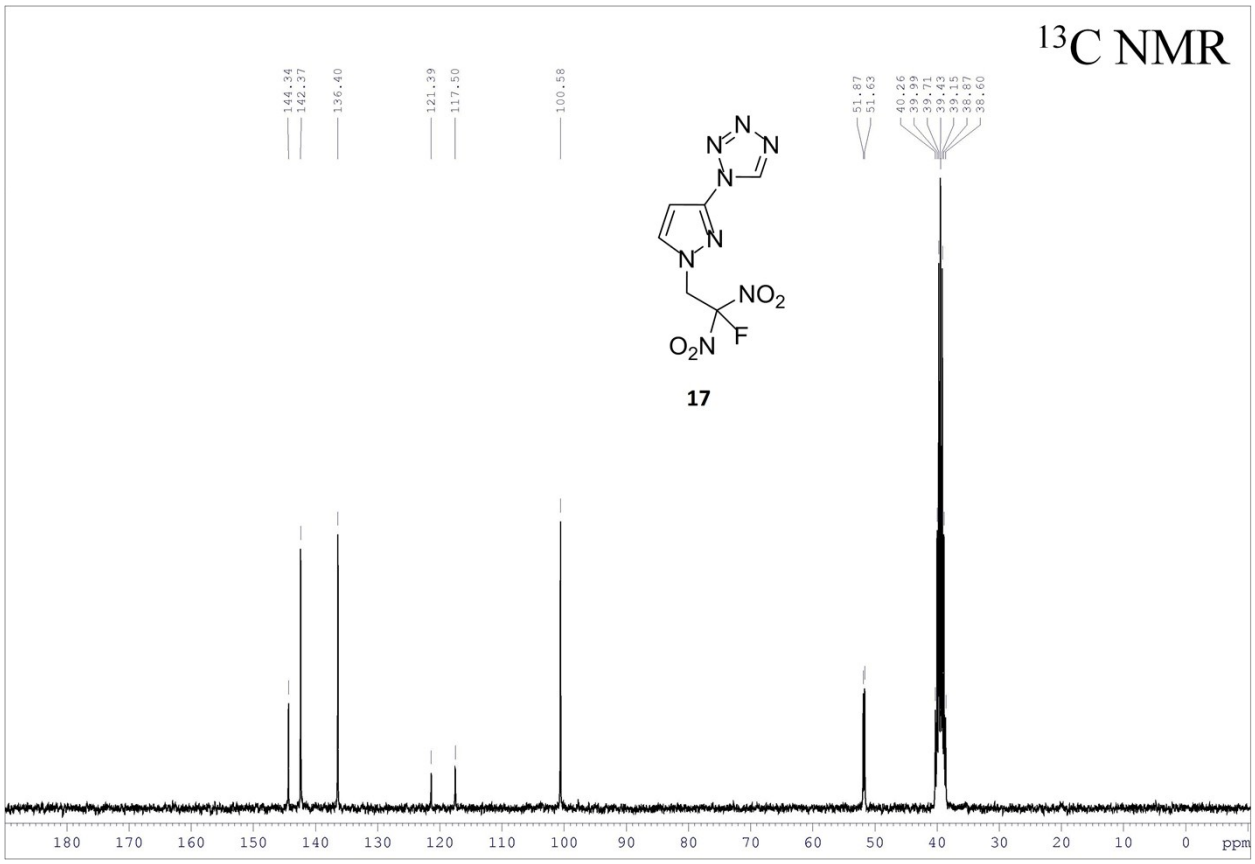
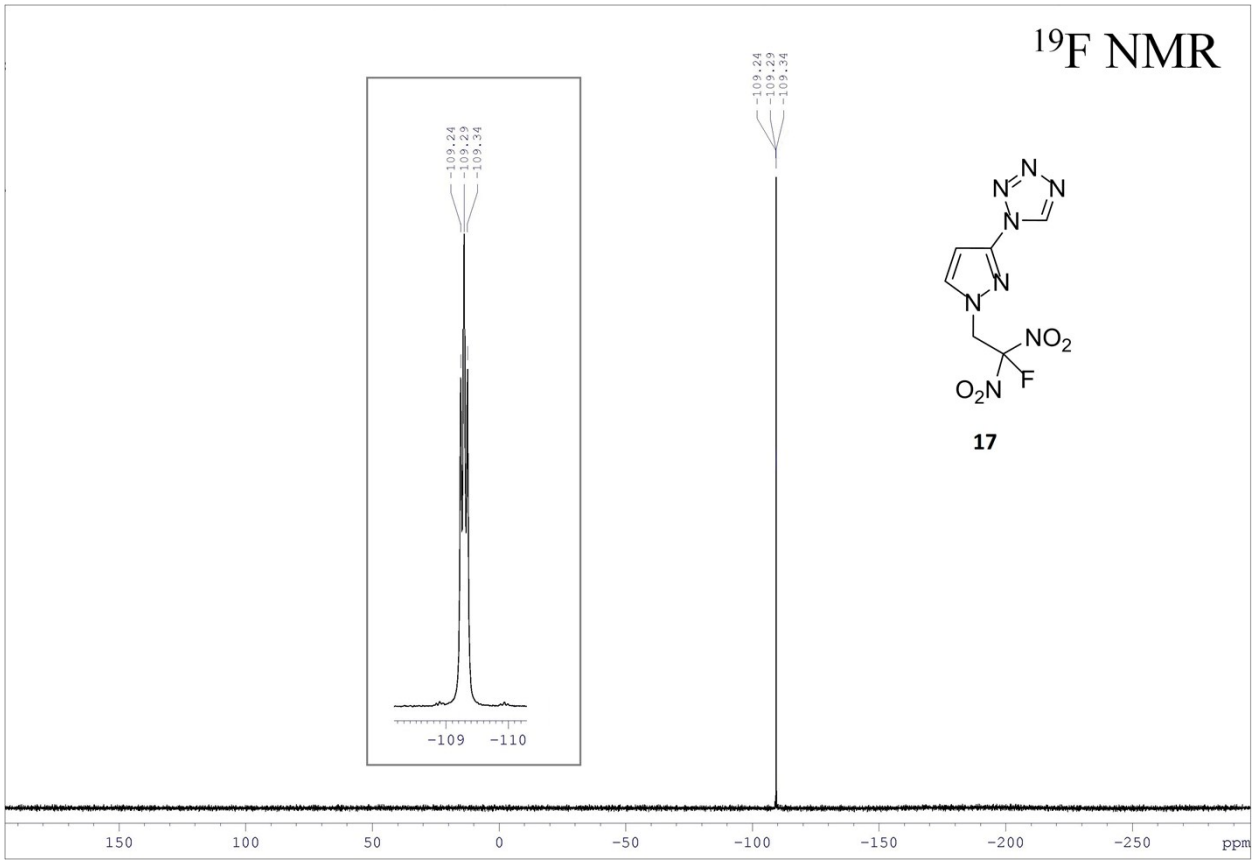
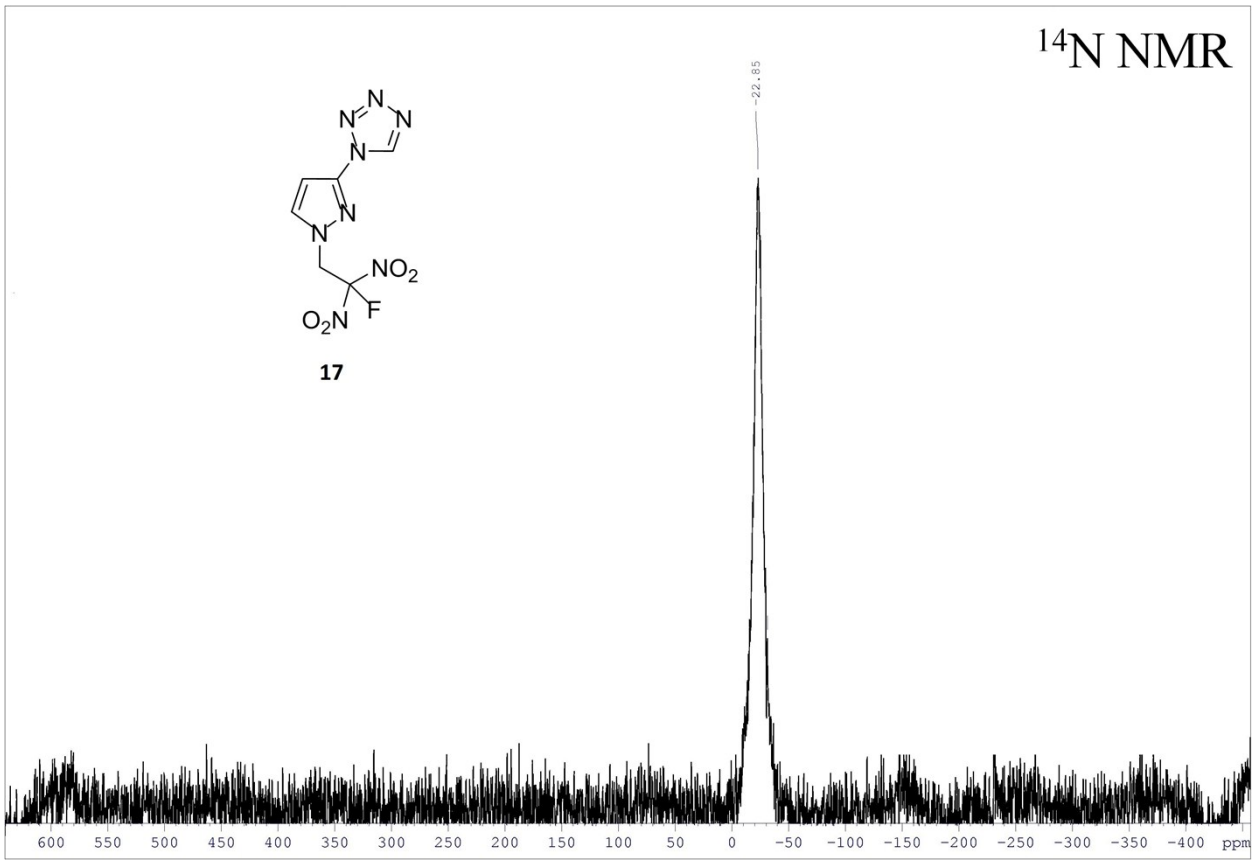
10.01
9.96
8.17
8.16
8.03
6.97
6.97
6.14
6.09
3.49
2.53
125
99
51
51
51
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.395
0.732
51.092
51.440
51.034
0.373
99.661
124.994
0.389

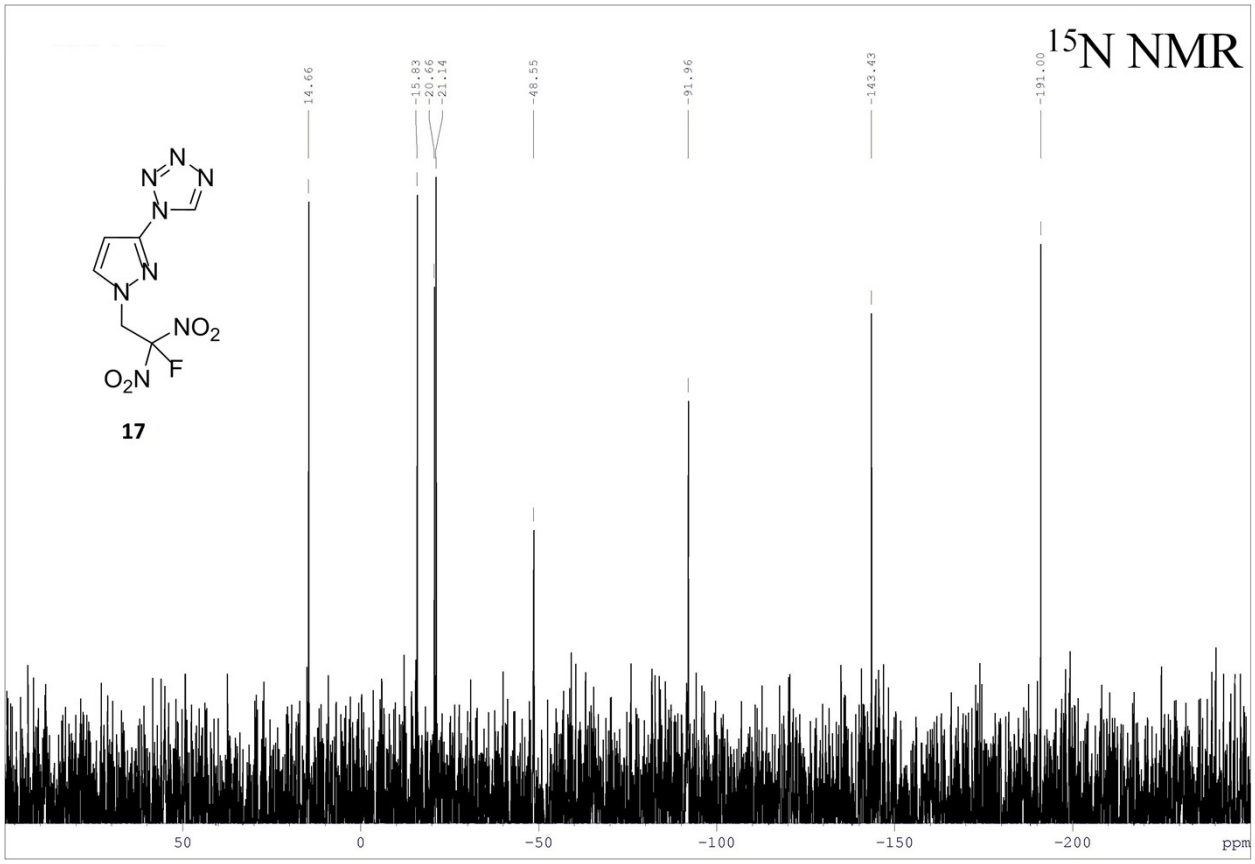
17


13C NMR
144.34
142.37
136.40
121.39
117.50
100.58
51.87
51.63
40.26
39.99
39.71
39.43
39.15
38.87
38.60
NO2
O2N
F
17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

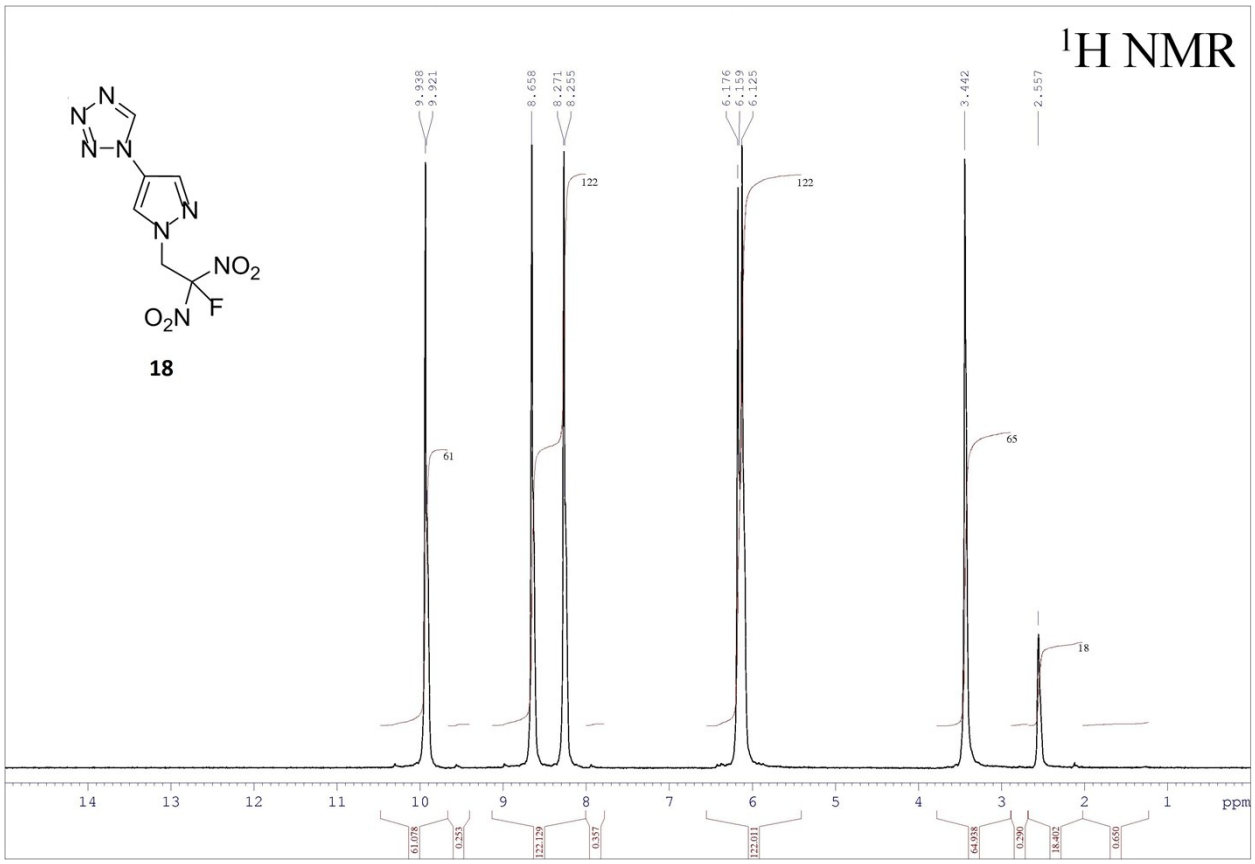

19F NMR
-109.24
-109.29
-109.34
-109 -110
150 100 50 0 -50 -100 -150 -200 -250 ppm
NO2
O2N
F
17


^{14}N NMR
-22.85
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm

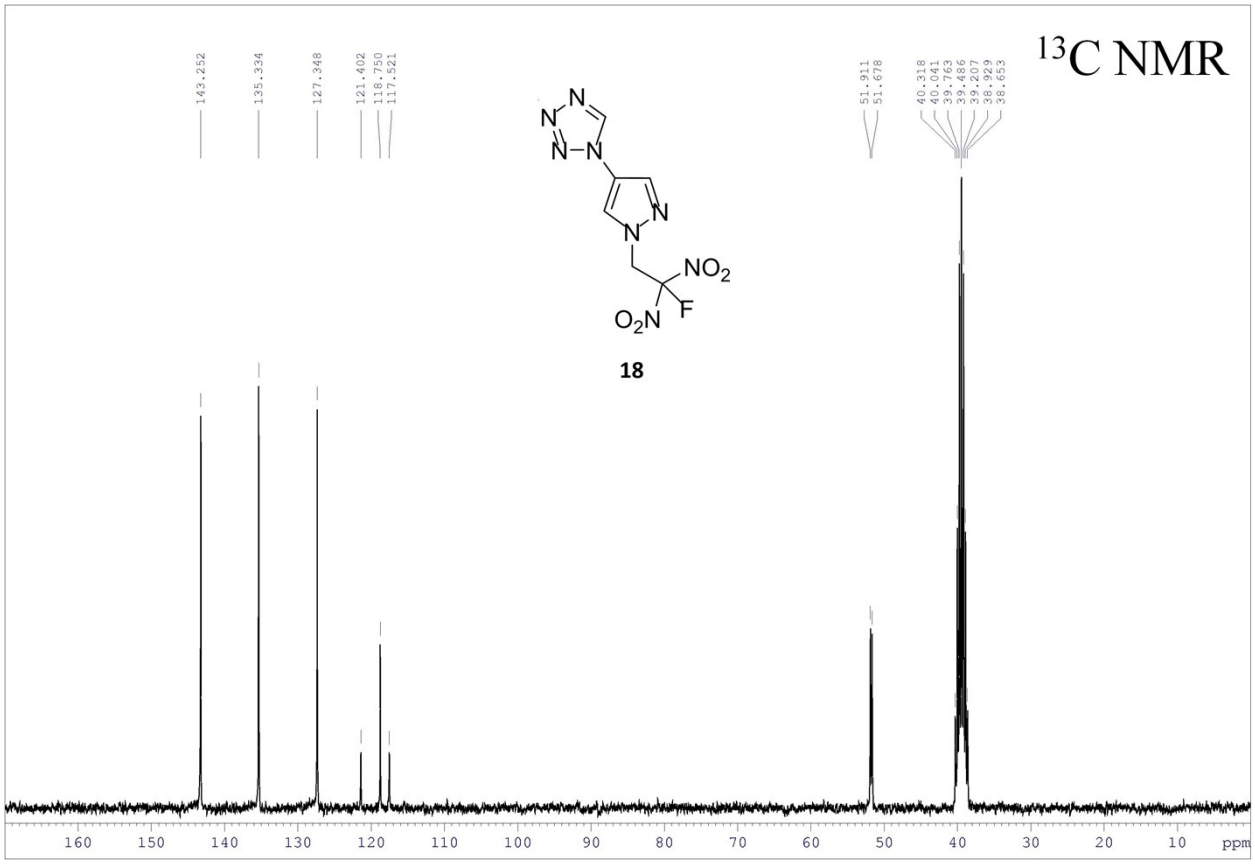
17


^{15}N NMR
14.66
-15.83
-20.66
-21.14
-48.55
-91.96
-143.43
-191.00
50 0 -50 -100 -150 -200 ppm

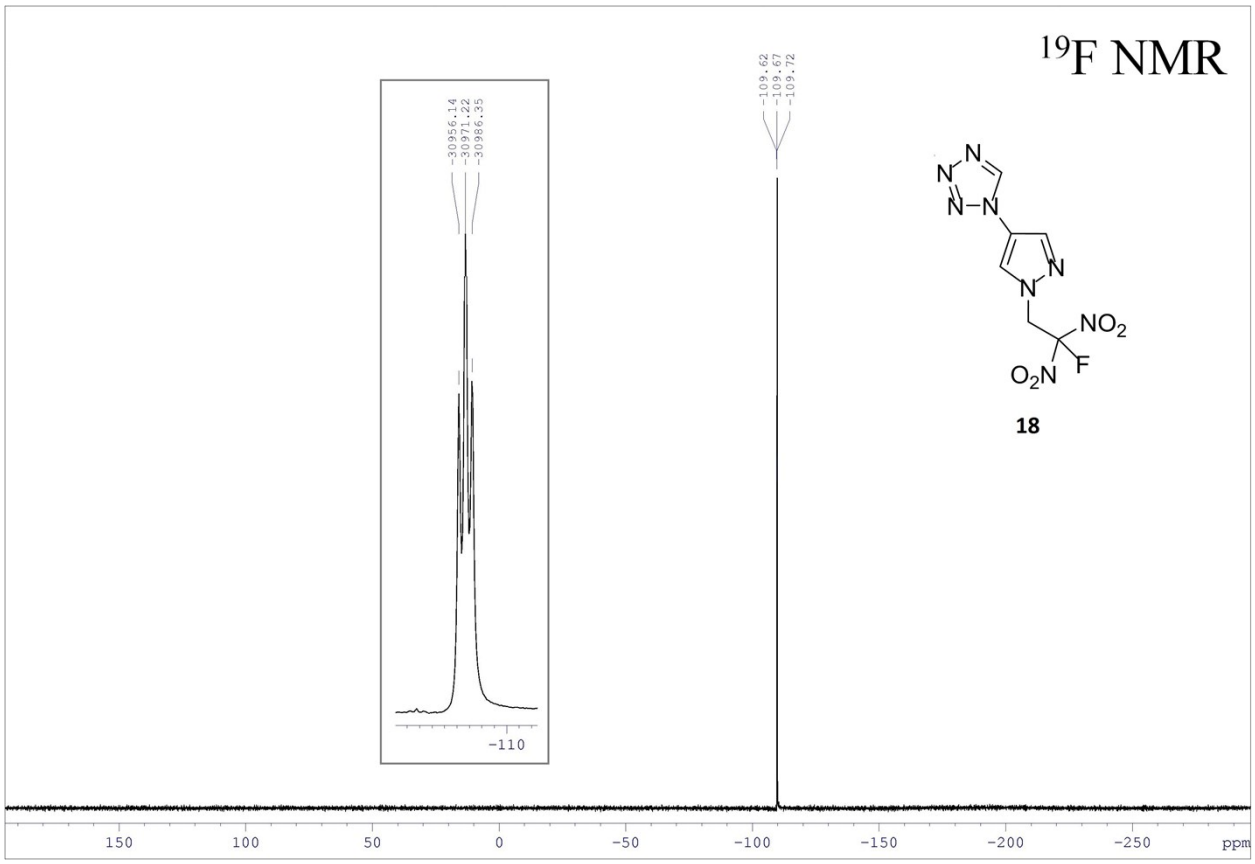
17


^{1}H NMR
9.938
9.921
8.658
8.271
8.255
6.176
6.159
6.125
3.442
2.557
122
122
61
65
18
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
61.078
0.253
122.129
0.357
122.011
64.938
0.290
18.402
0.650

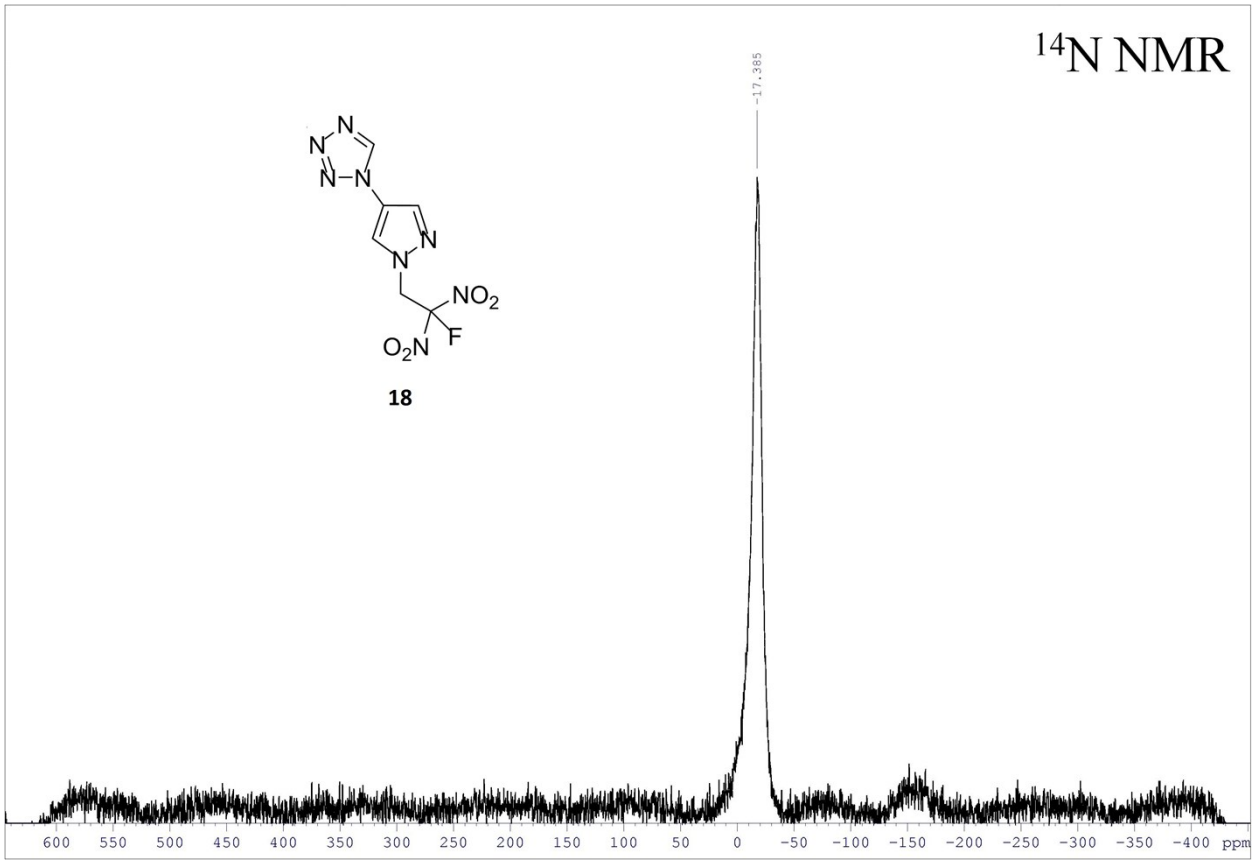
18


^{13}C NMR
143.252
135.334
127.348
121.402
118.750
117.521
51.911
51.678
40.318
40.041
39.763
39.486
39.207
38.929
38.653
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

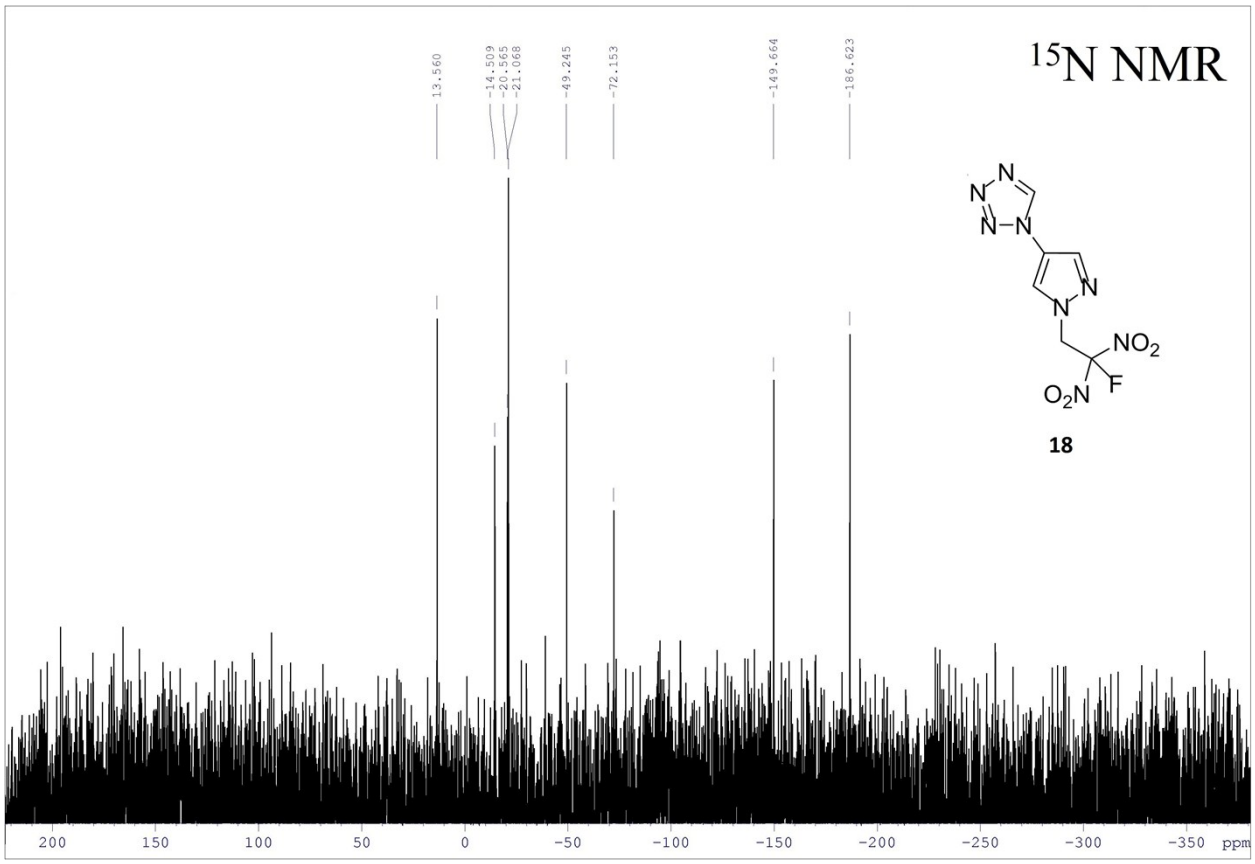
18

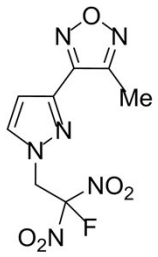

19F NMR
-30956.14
-30971.22
-30986.35
-109.62
-109.67
-109.72
-110
150
100
50
0
-50
-100
-150
-200
-250
ppm

18


14N NMR
-17.385
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
ppm

18


^{15}N NMR
13.560
-14.509
-20.565
-21.068
-49.245
-72.153
-149.664
-186.623
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

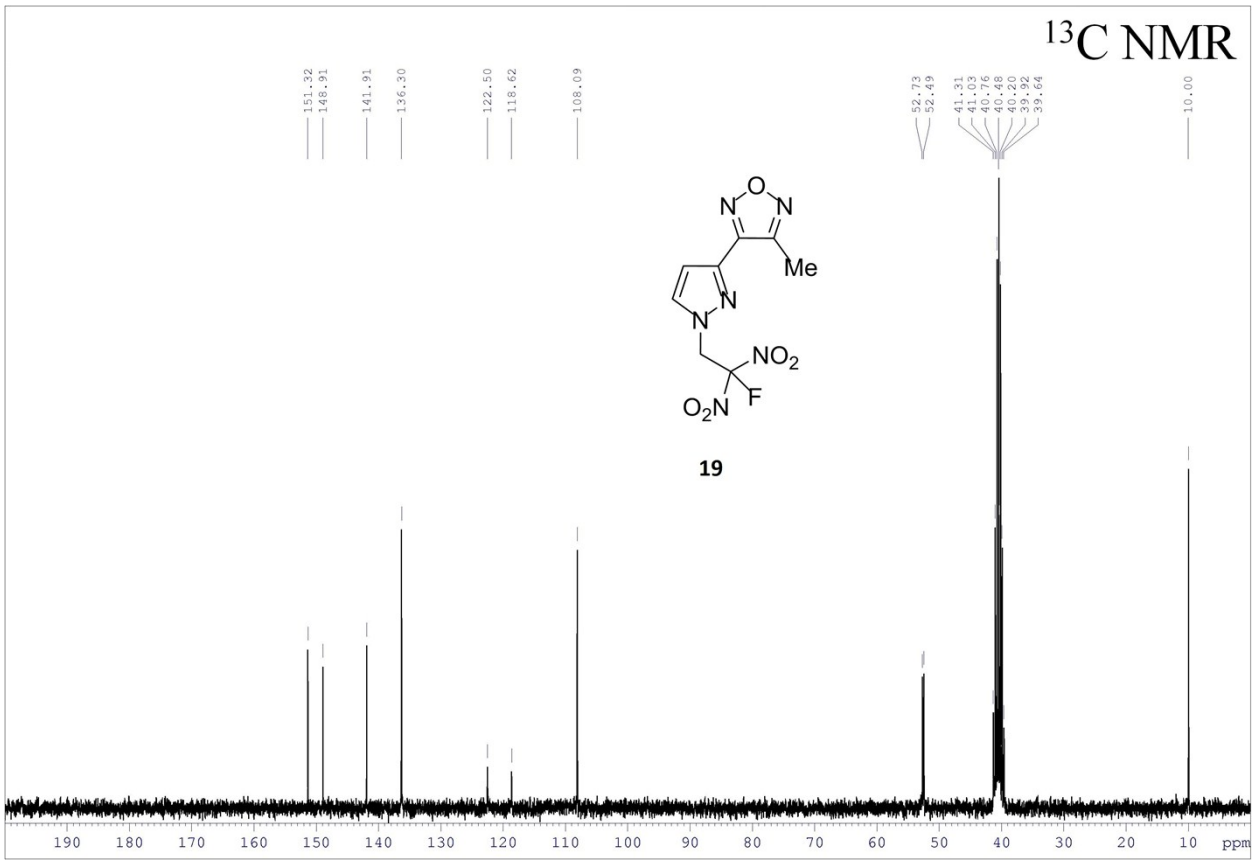


18

^{1}H NMR
8.09
8.08
6.95
6.94
6.11
6.06
3.41
2.49
2.47
66
33
30
16
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
33.345
30.333
66.141
0.287
0.337
16.557
0.246
125.077

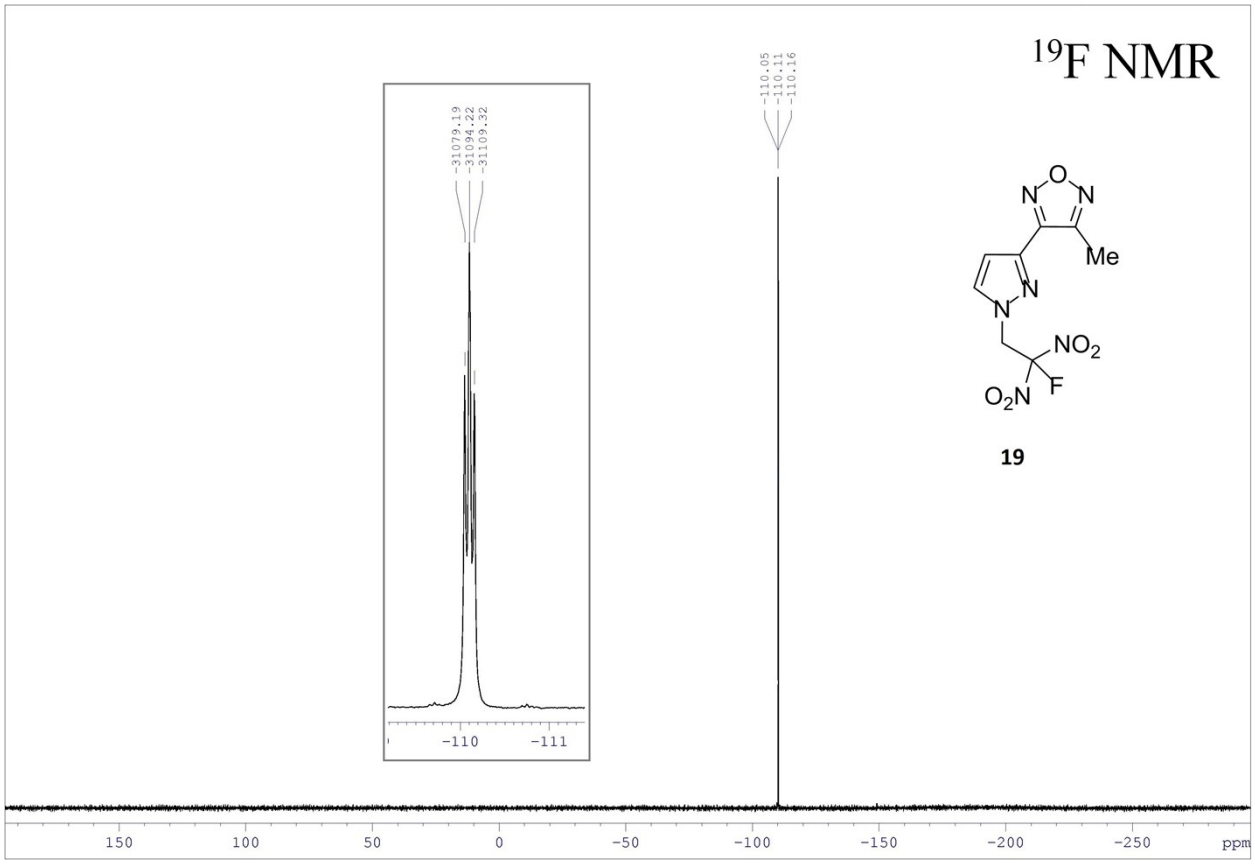
19

^{13}C NMR

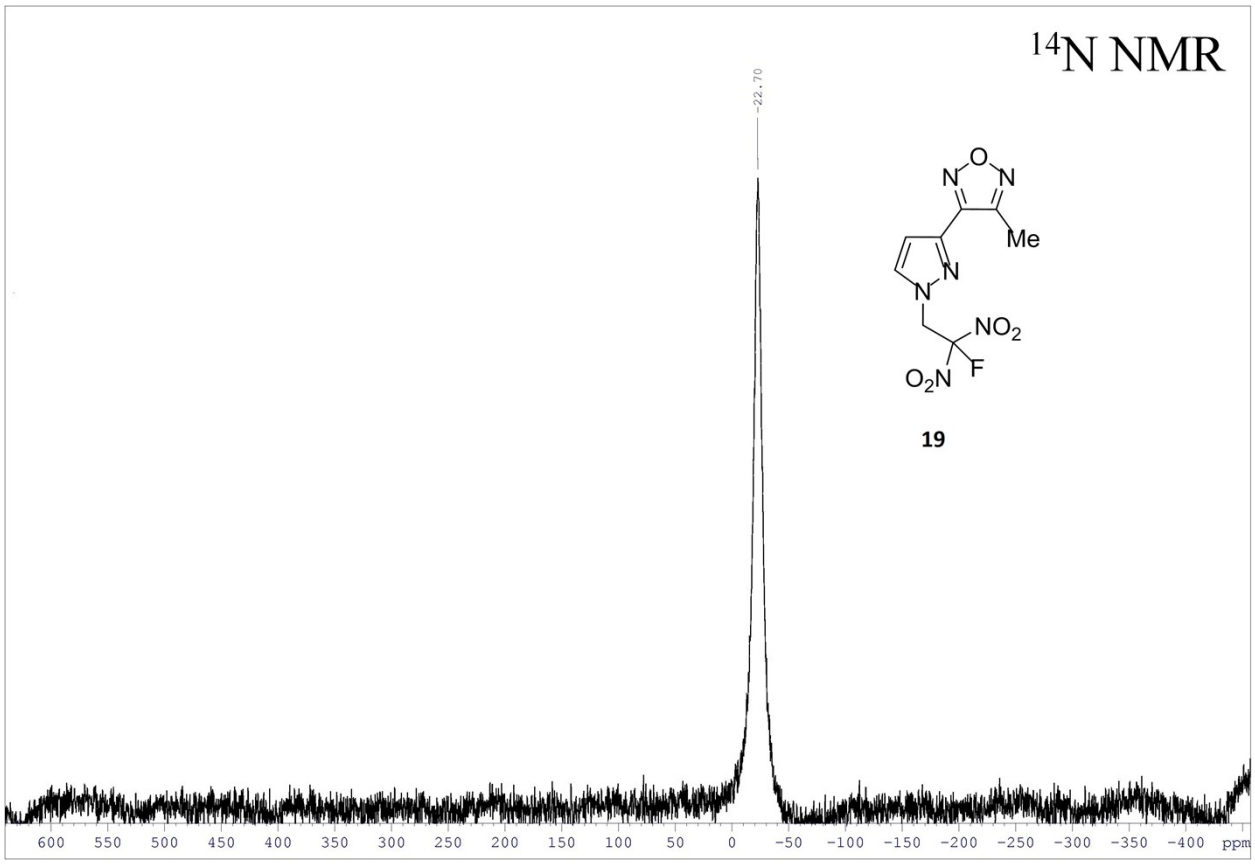


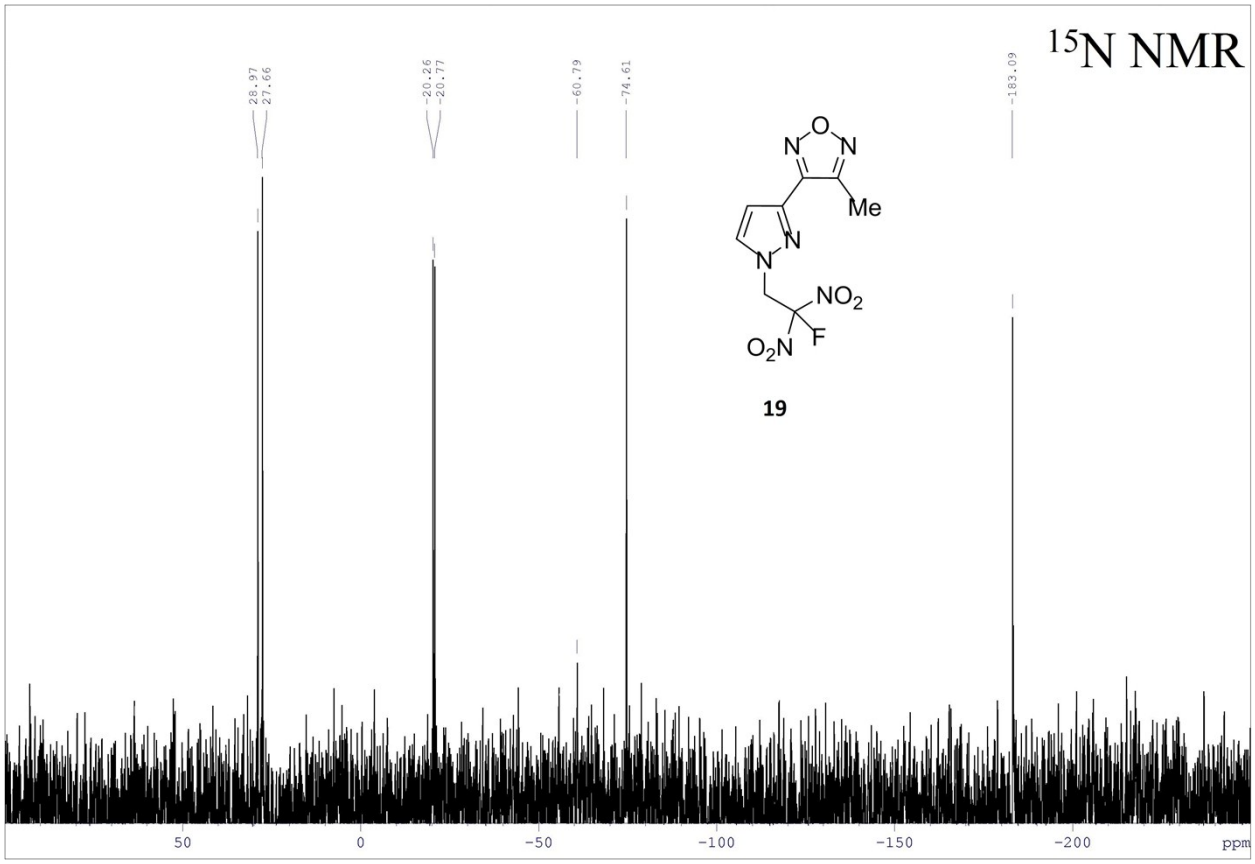
19

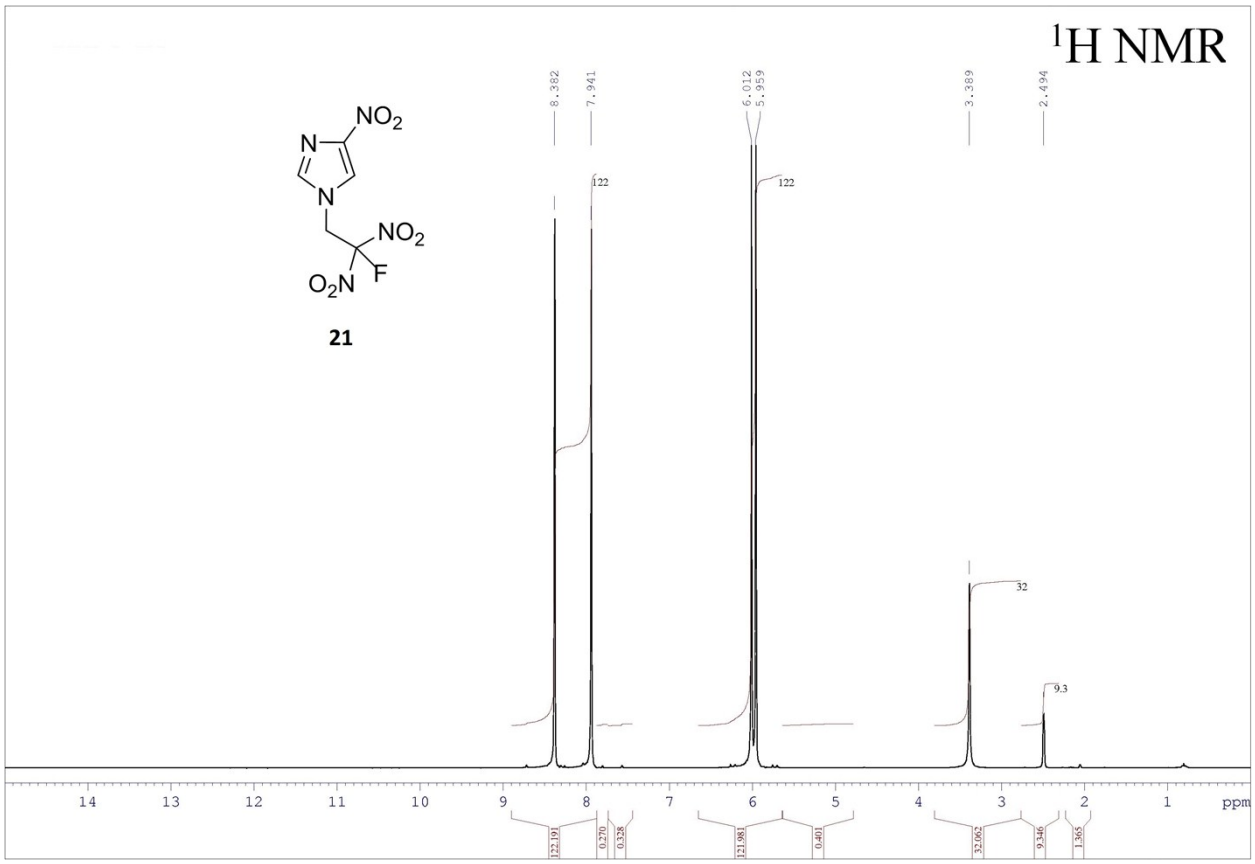
^{19}F NMR



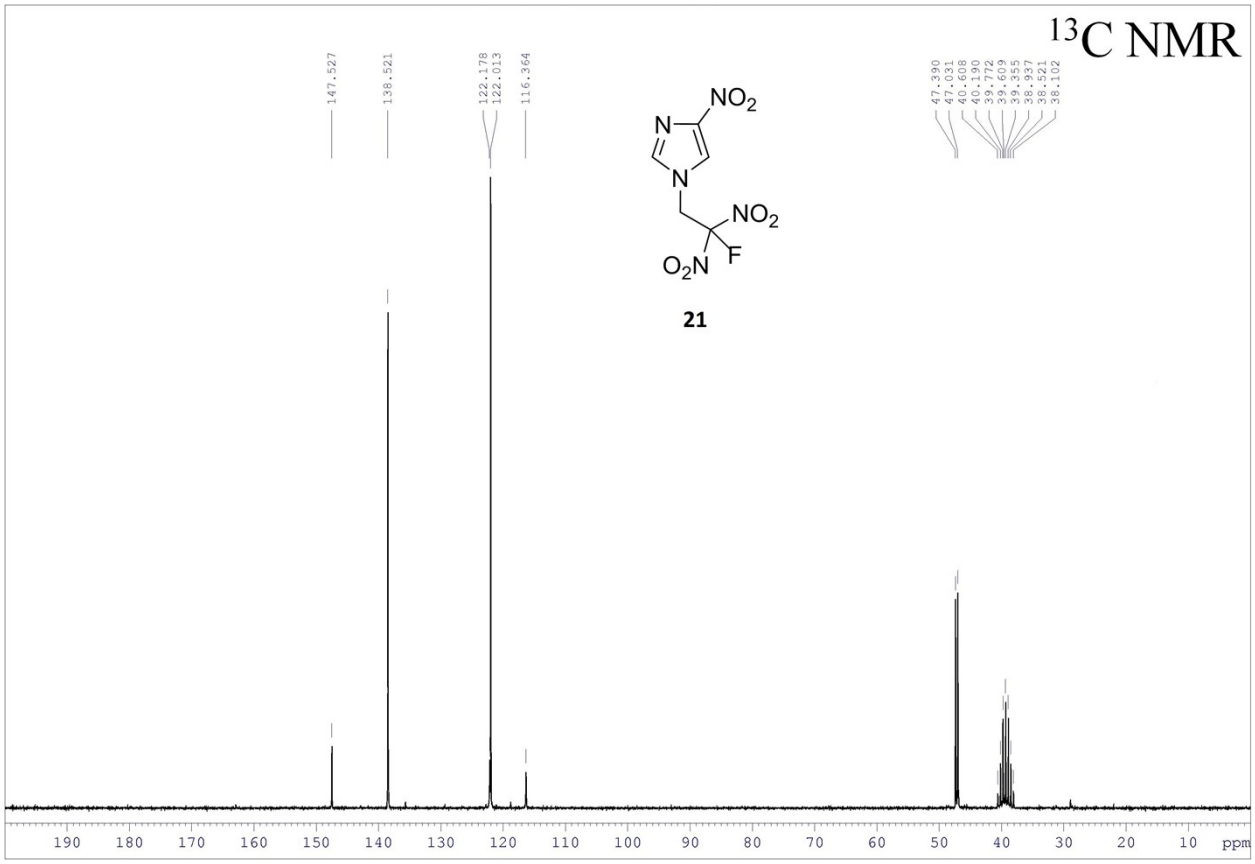
19


^{14}N NMR
-22.70
Me
NO2
O2N
F
19
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm

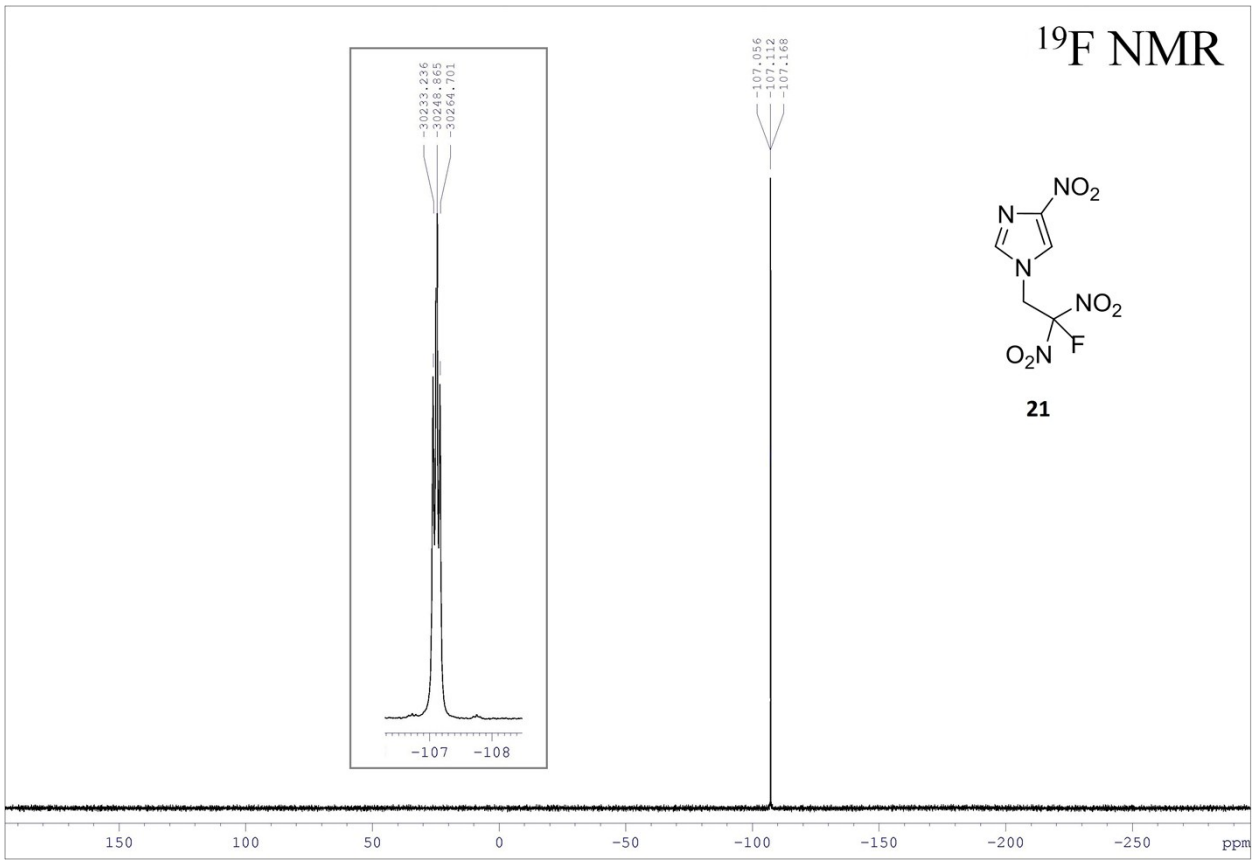

^{15}N NMR
28.97
27.66
-20.26
-20.77
-60.79
-74.61
-183.09
Me
NO2
O2N
F
19
50 0 -50 -100 -150 -200 ppm

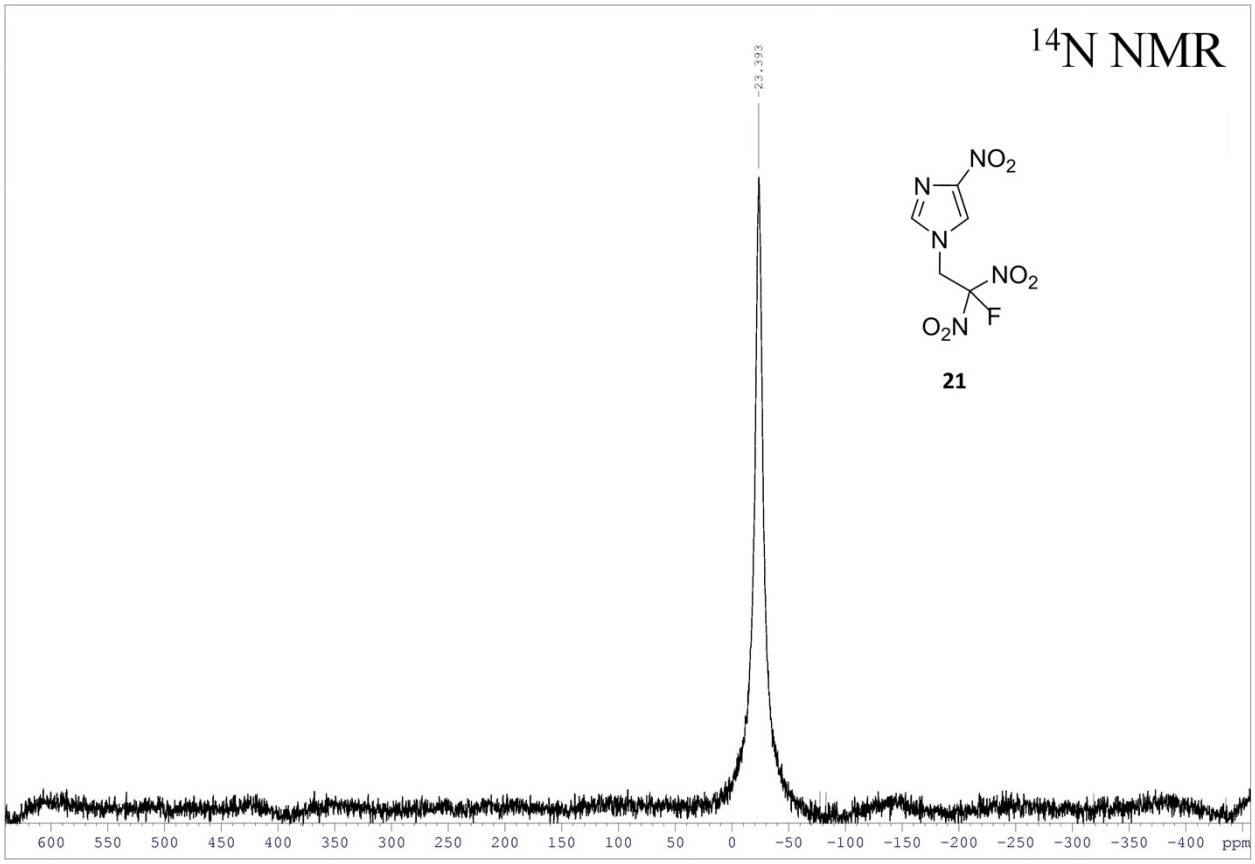

^{1}H NMR
8.382
7.941
6.012
5.959
3.389
2.494
122
122
32
9.3
ppm
122.191
0.270
0.328
121.981
0.401
32.062
9.346
1.365

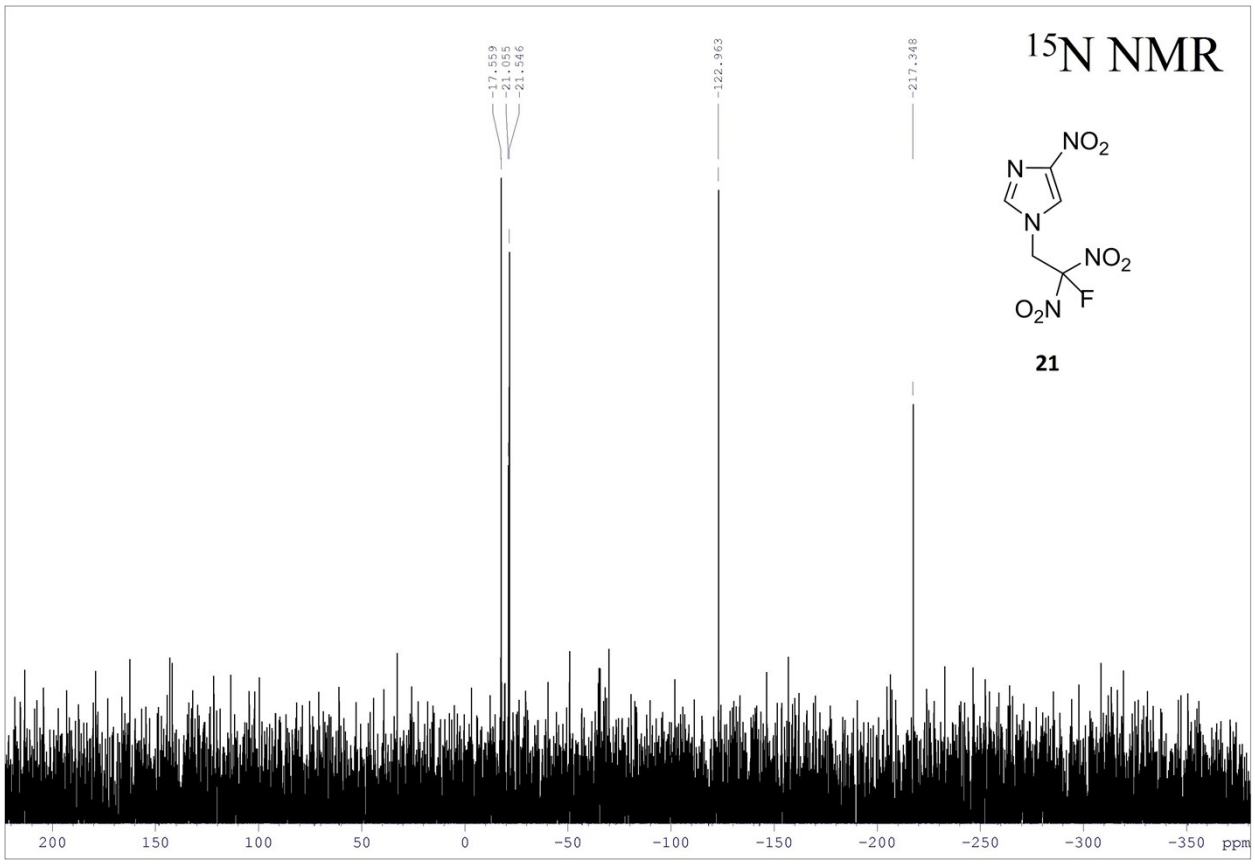
21

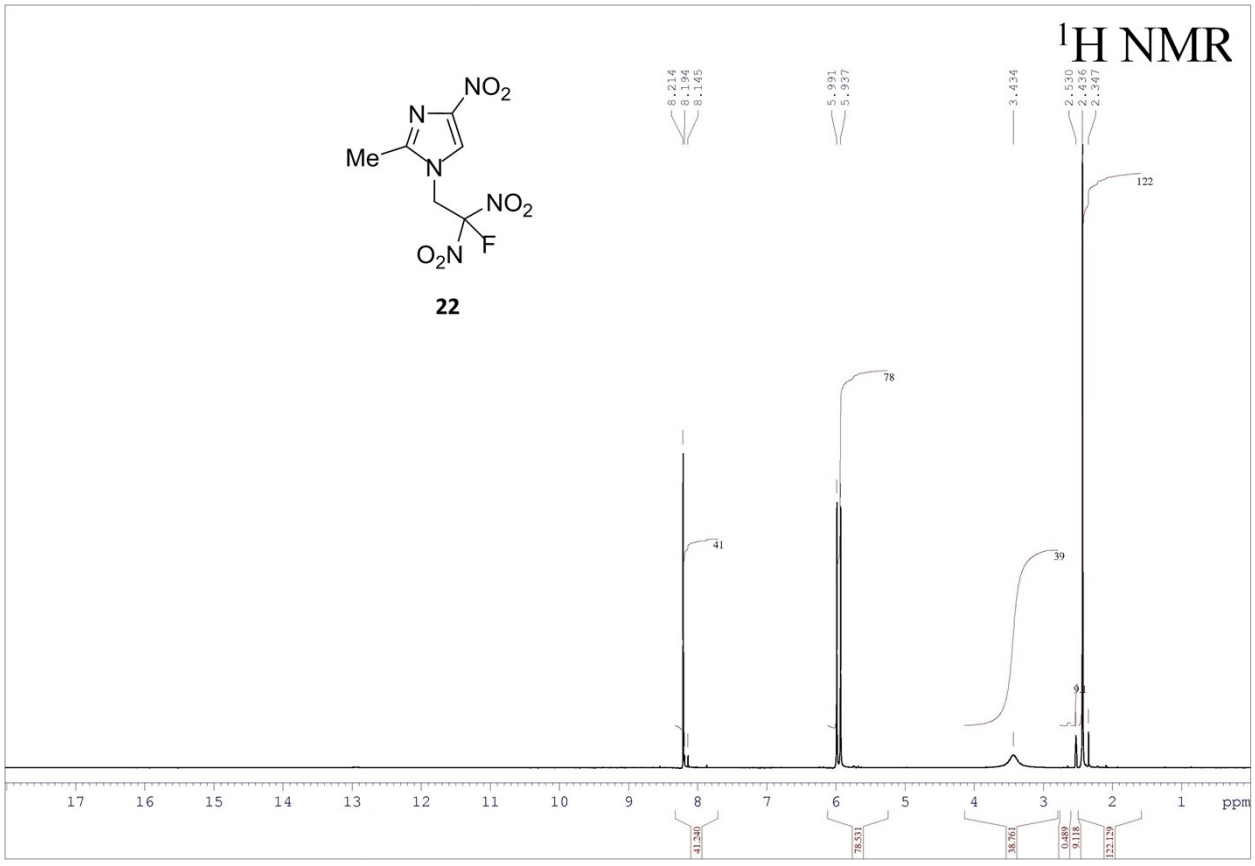

^{13}C NMR
147.527
138.521
122.178
122.013
116.364
47.390
47.031
40.608
40.190
39.772
39.609
39.355
38.937
38.521
38.102
ppm

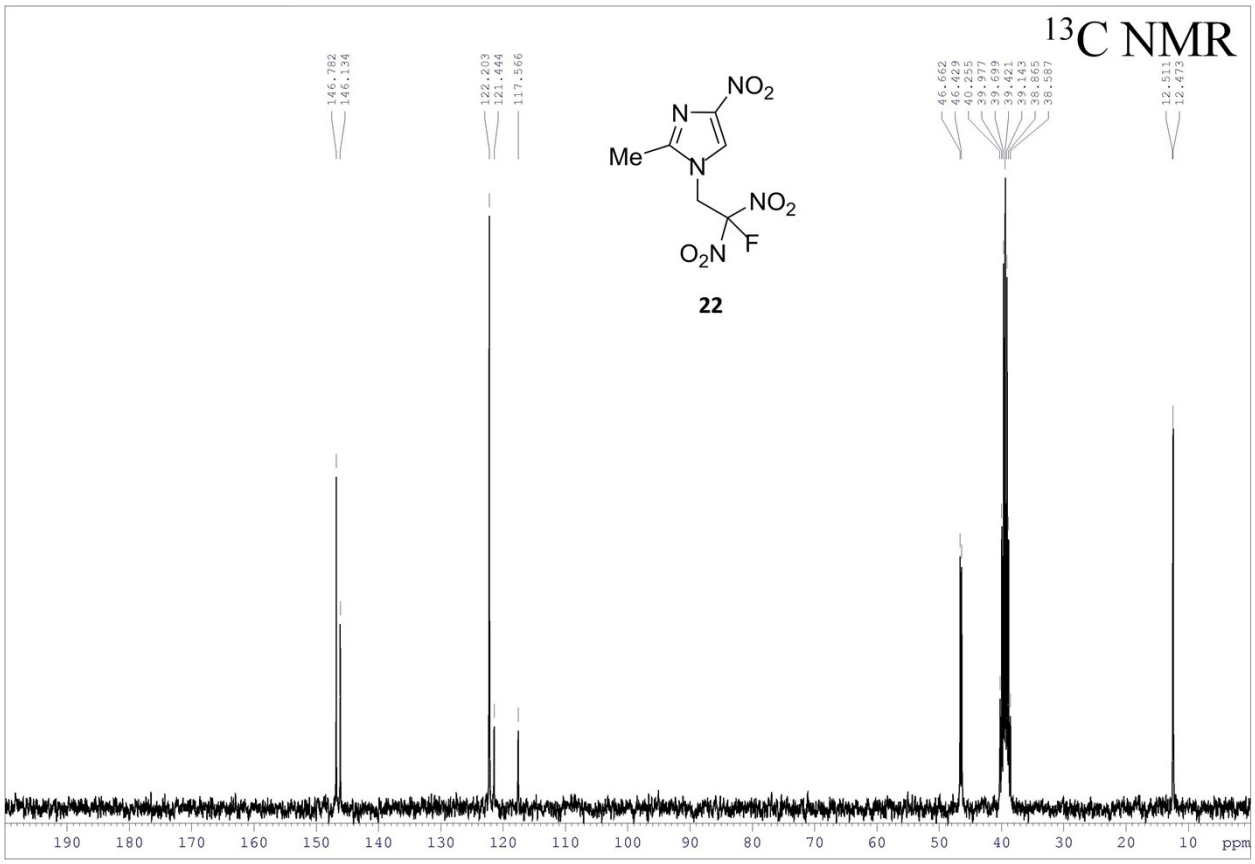
21

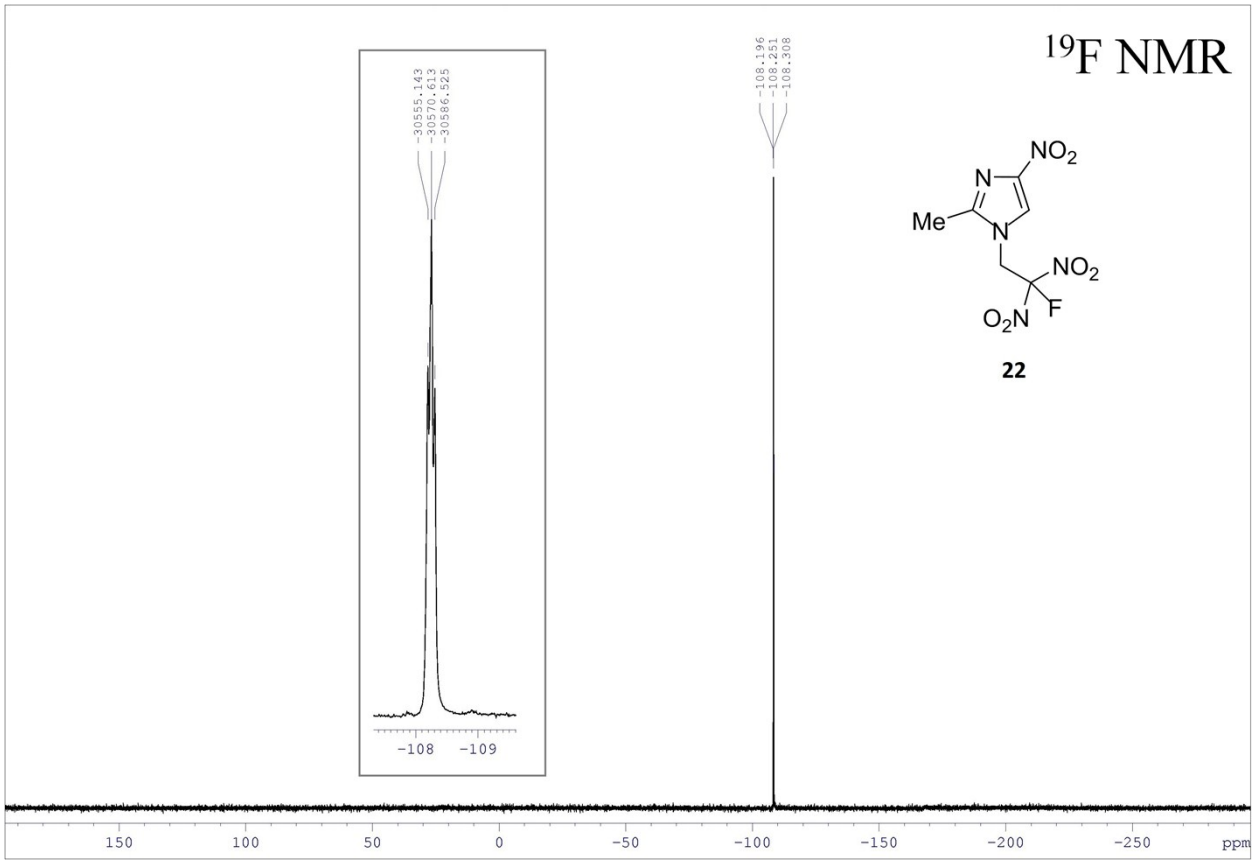

19F NMR
-30233.236
-30248.865
-30264.701
-107.056
-107.112
-107.168
-107
-108
NO2
N
N
NO2
O2N
F
21
150
100
50
0
-50
-100
-150
-200
-250
ppm

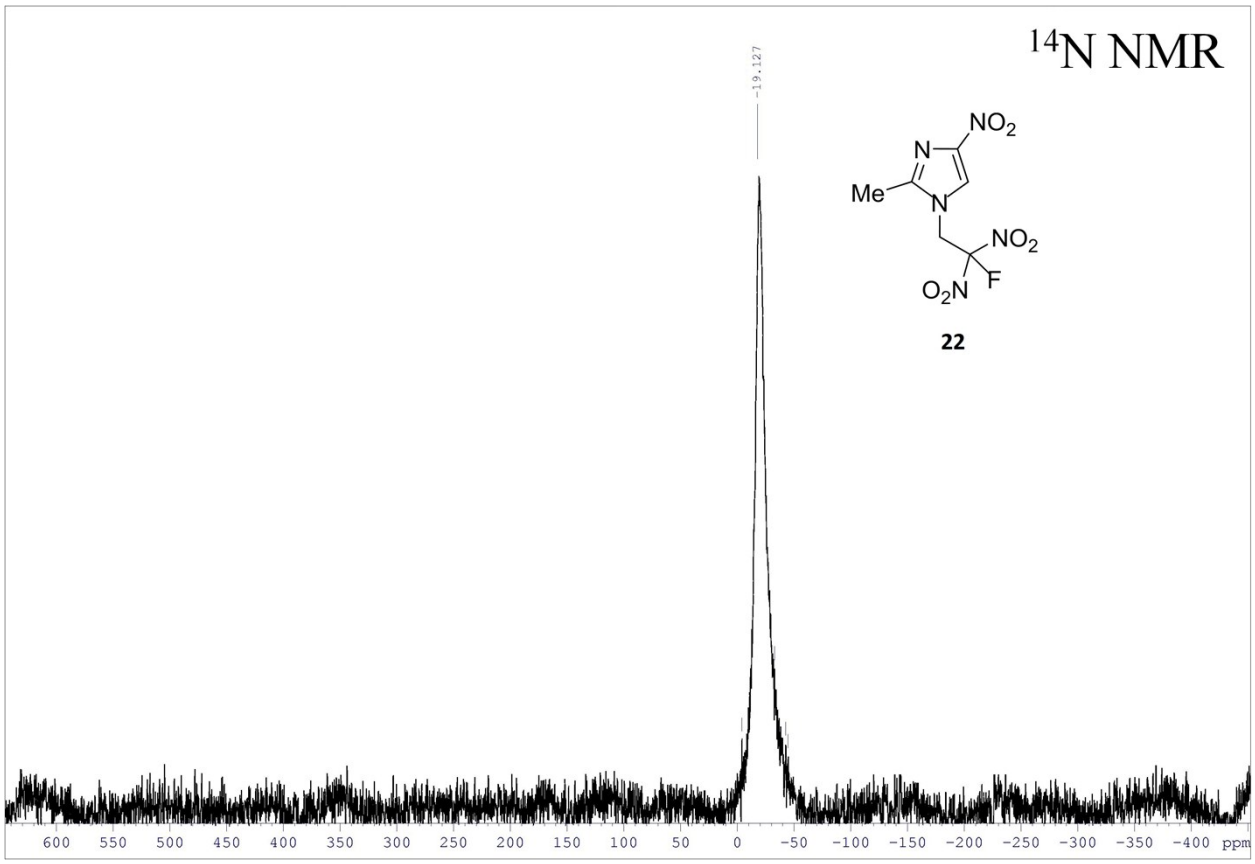

14N NMR
-23.393
NO2
N
N
NO2
O2N
F
21
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
ppm

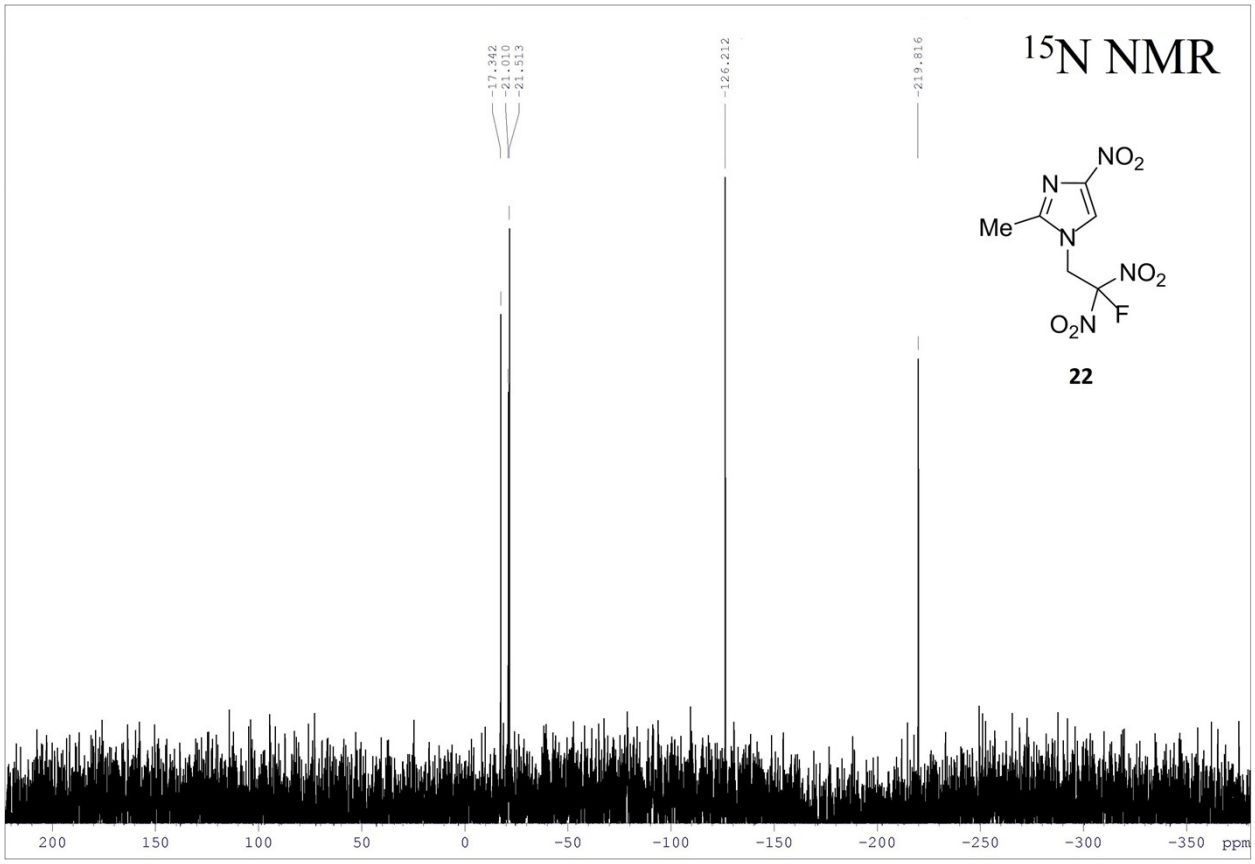

15N NMR
-17.559
-21.055
-21.546
-122.963
-217.348
NO2
N
N
NO2
O2N
F
21
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

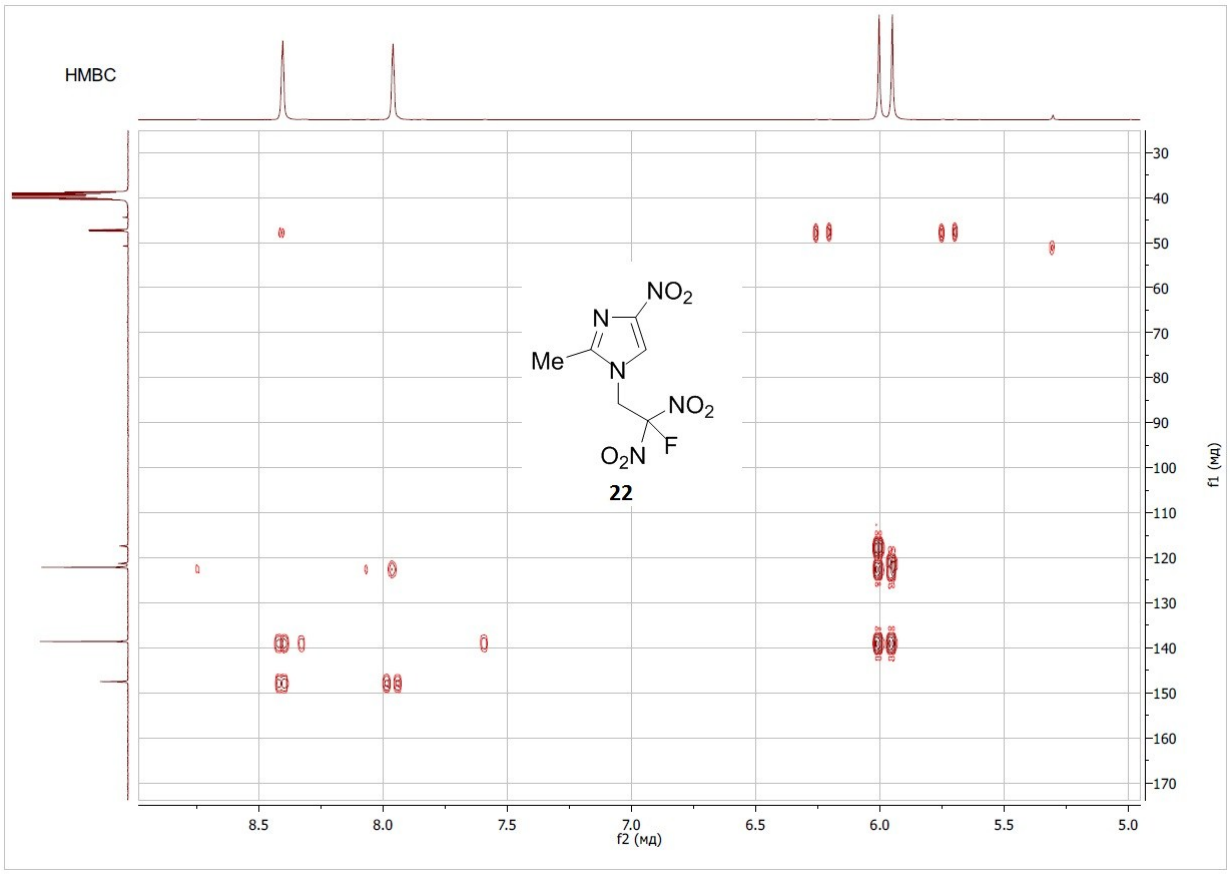

1H NMR
NO2
N
Me
N
NO2
O2N
F
22
8.214
8.194
8.145
5.991
5.937
3.434
2.530
2.436
2.347
122
78
41
39
91
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
41.240
78.531
38.761
0.489
9.118
122.129

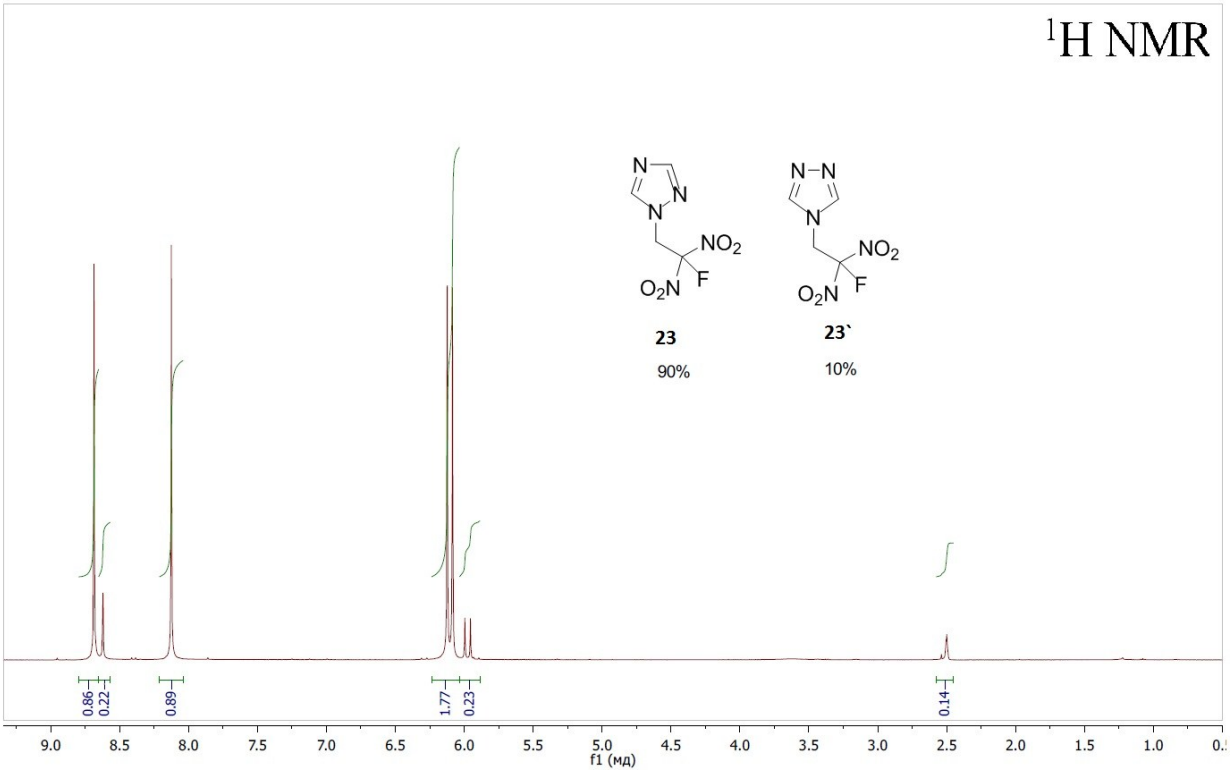

^{13}C NMR
146.782
146.134
122.203
121.444
117.566
46.662
46.429
40.255
39.677
39.469
39.421
39.143
38.865
38.587
12.511
12.473
NO2
N
Me
N
NO2
O2N
F
22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{19}F NMR
-30555.143
-30570.613
-30586.525
-108.196
-108.251
-108.308
NO2
N
Me
N
NO2
O2N
F
22
-108 -109
150 100 50 0 -50 -100 -150 -200 -250 ppm

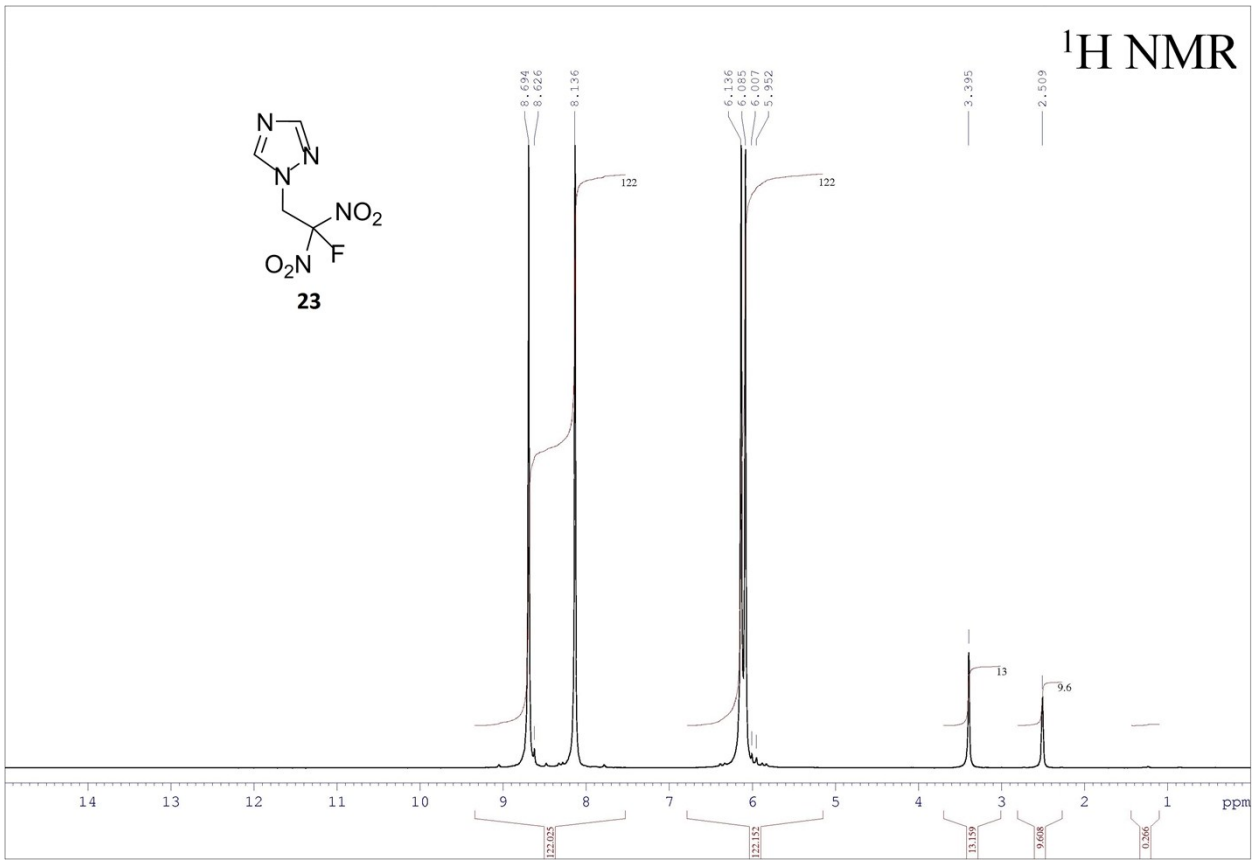

^{14}N NMR
-19.127
NO2
N
Me
N
NO2
O2N
F
22
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm


^{15}N NMR
-17.342
-21.010
-21.513
-126.212
-219.816
NO2
N
Me
N
NO2
O2N
F
22
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm


HMBC
NO2
N
Me
N
NO2
O2N
F
22
f1 (мд)
f2 (мд)

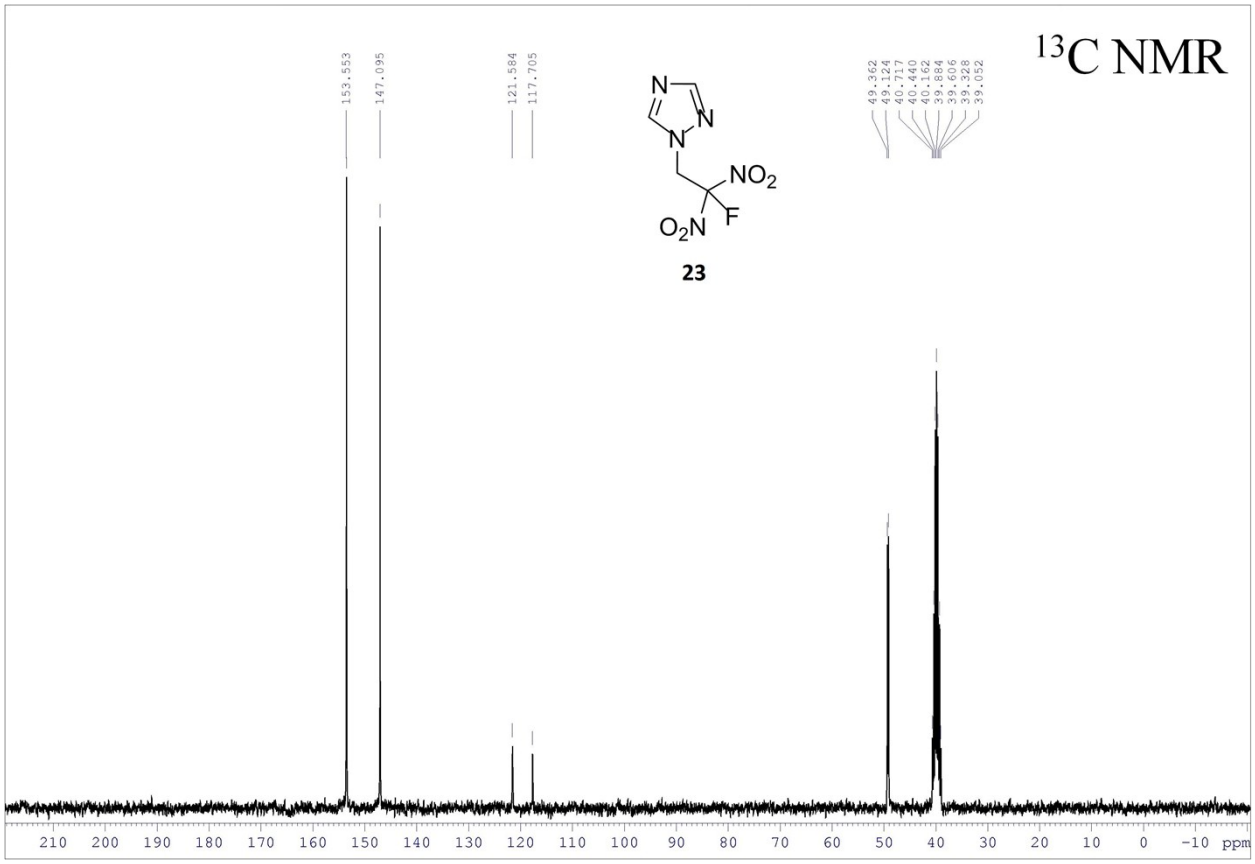

1H NMR
N
N
N
NO2
O2N
F
23
90%
N–N
N
NO2
O2N
F
23`
10%
0.86
0.22
0.89
1.77
0.23
0.14
f1 (мд)

^{1}H NMR

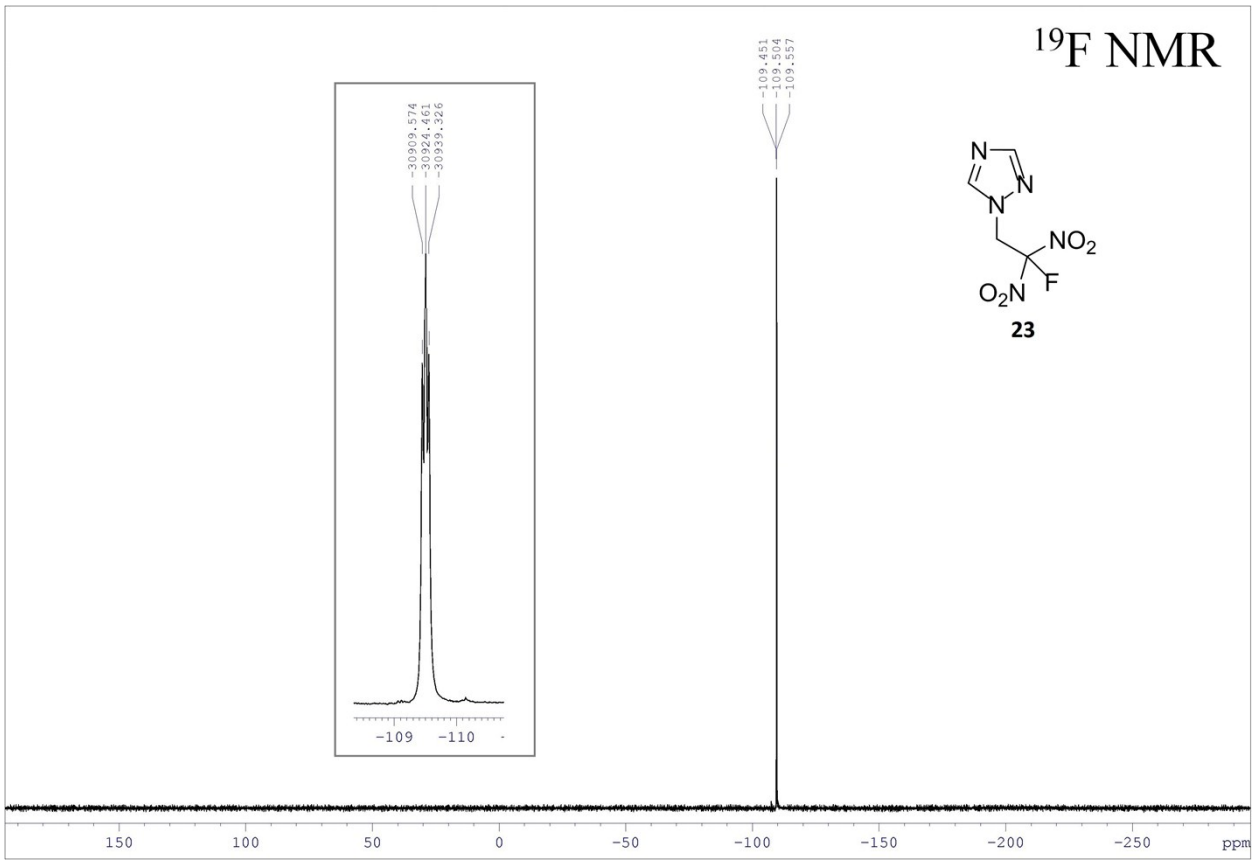


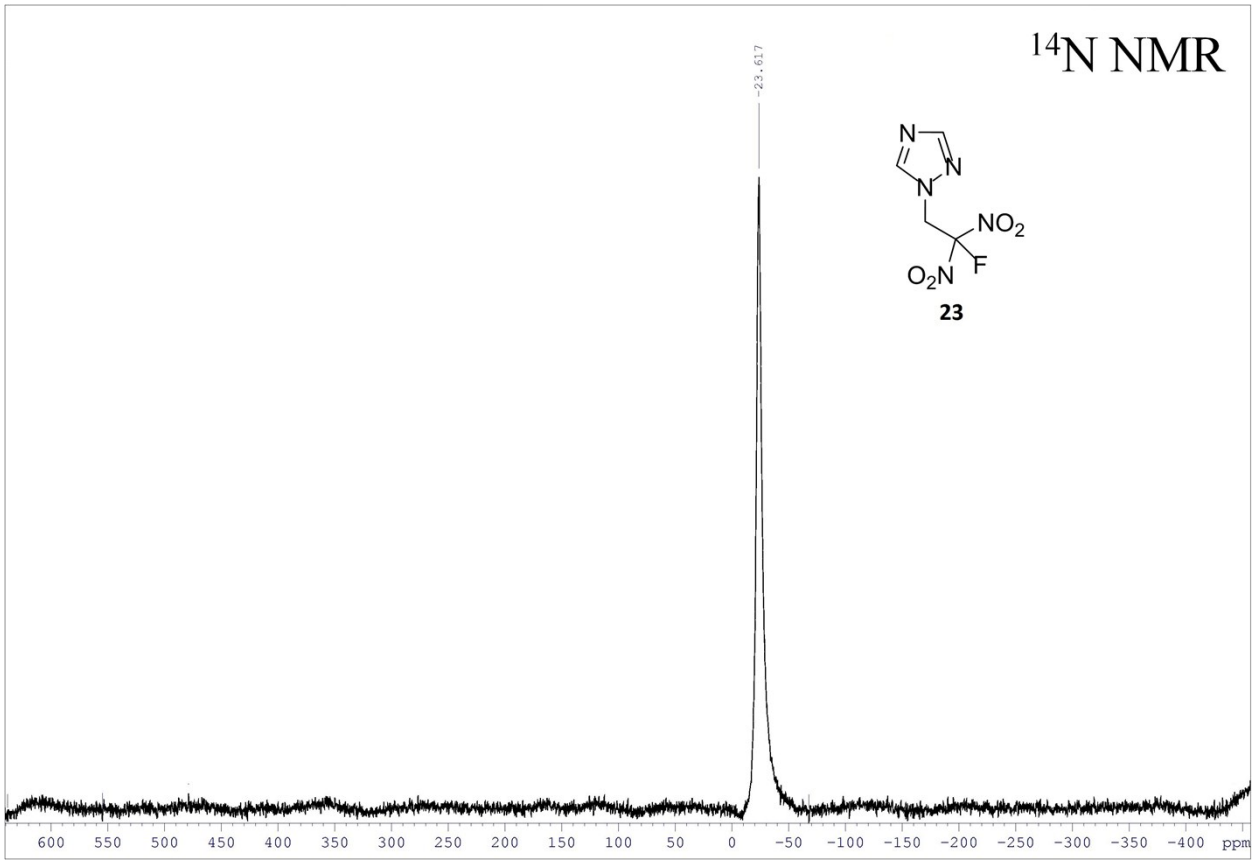
23

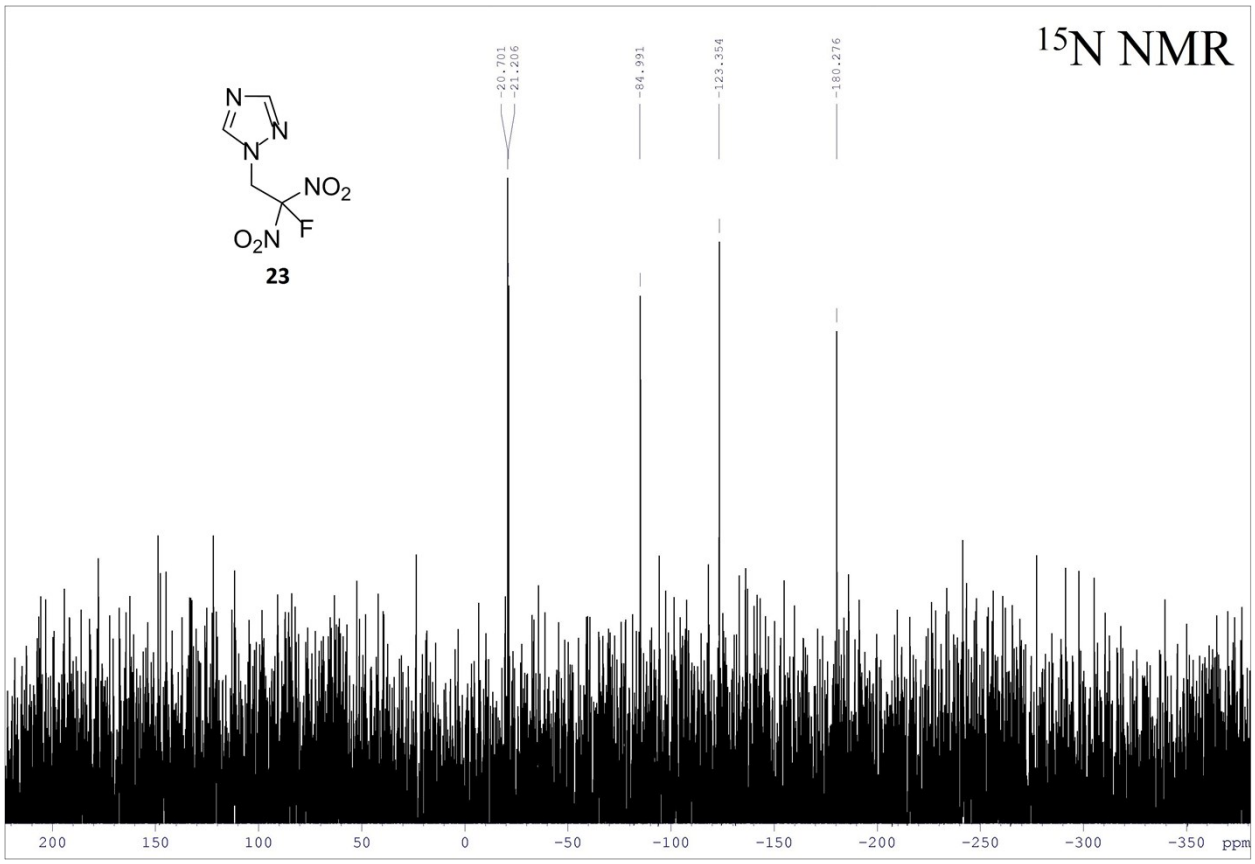
^{13}C NMR



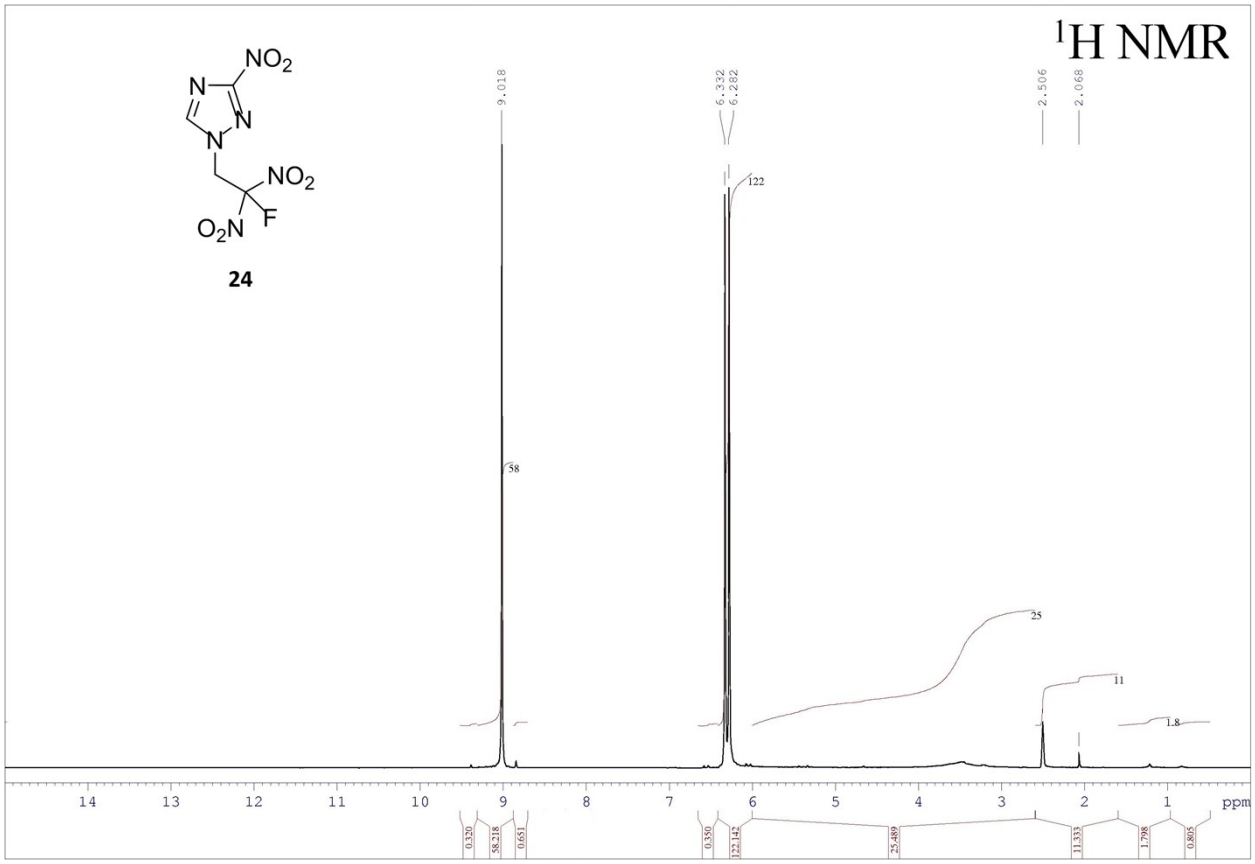
23


19F NMR
-109.451
-109.504
-109.557
-30909.574
-30924.461
-30939.326
-109
-110
N
N
N
NO2
O2N
F
23
150
100
50
0
-50
-100
-150
-200
-250
ppm

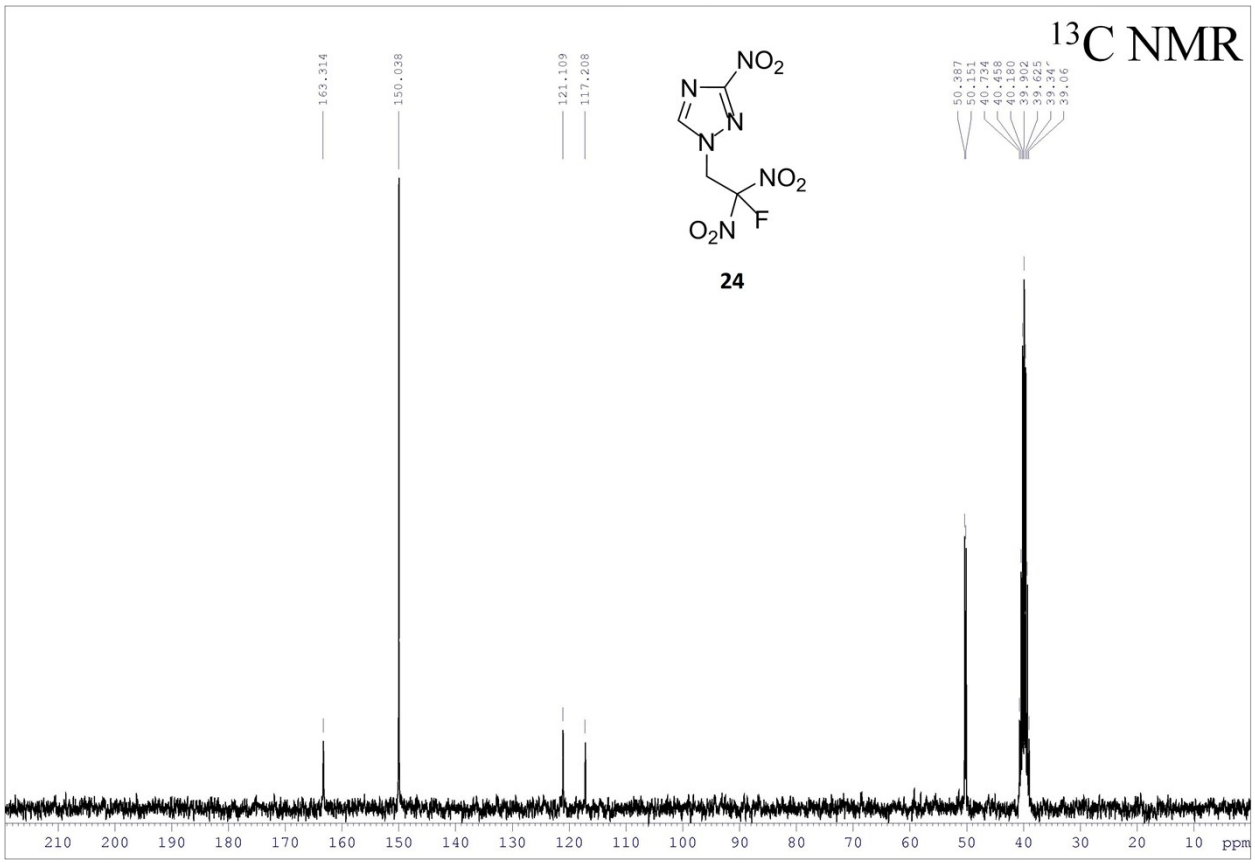

14N NMR
-23.617
N
N
N
NO2
O2N
F
23
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
ppm

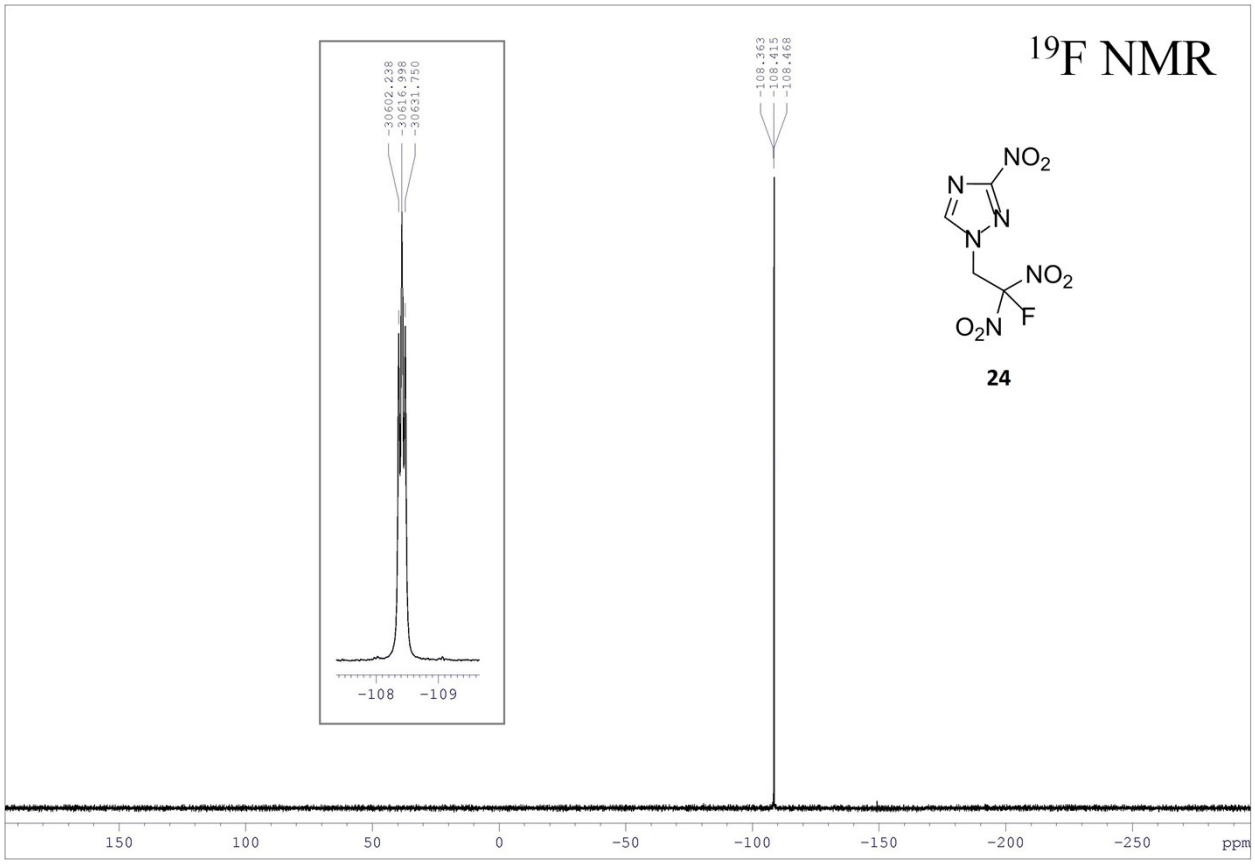

^{15}N NMR
-20.701
-21.206
-84.991
-123.354
-180.276
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

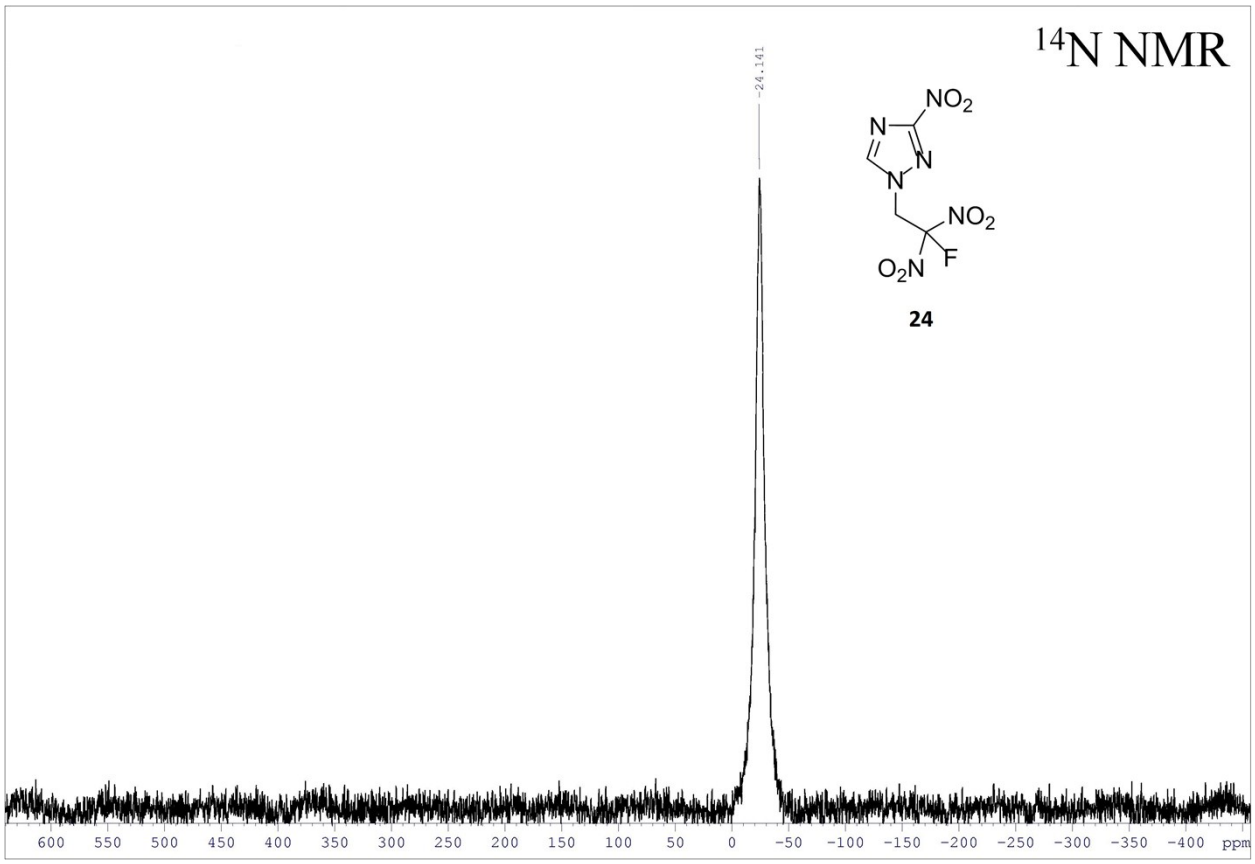
23

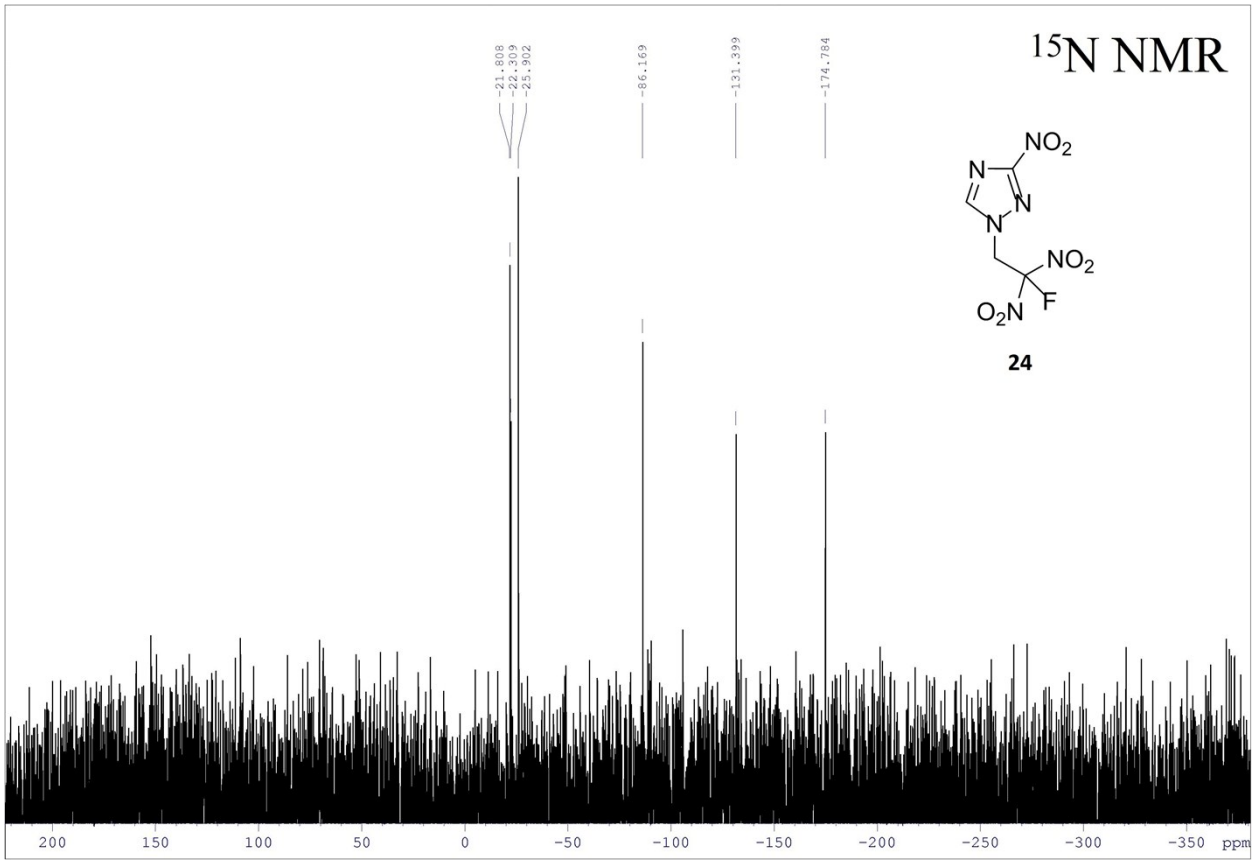

^{1}H NMR
9.018
6.332
6.282
2.506
2.068
122
58
25
11
1.8
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.320
58.218
0.651
0.350
122.142
25.489
11.333
1.798
0.805

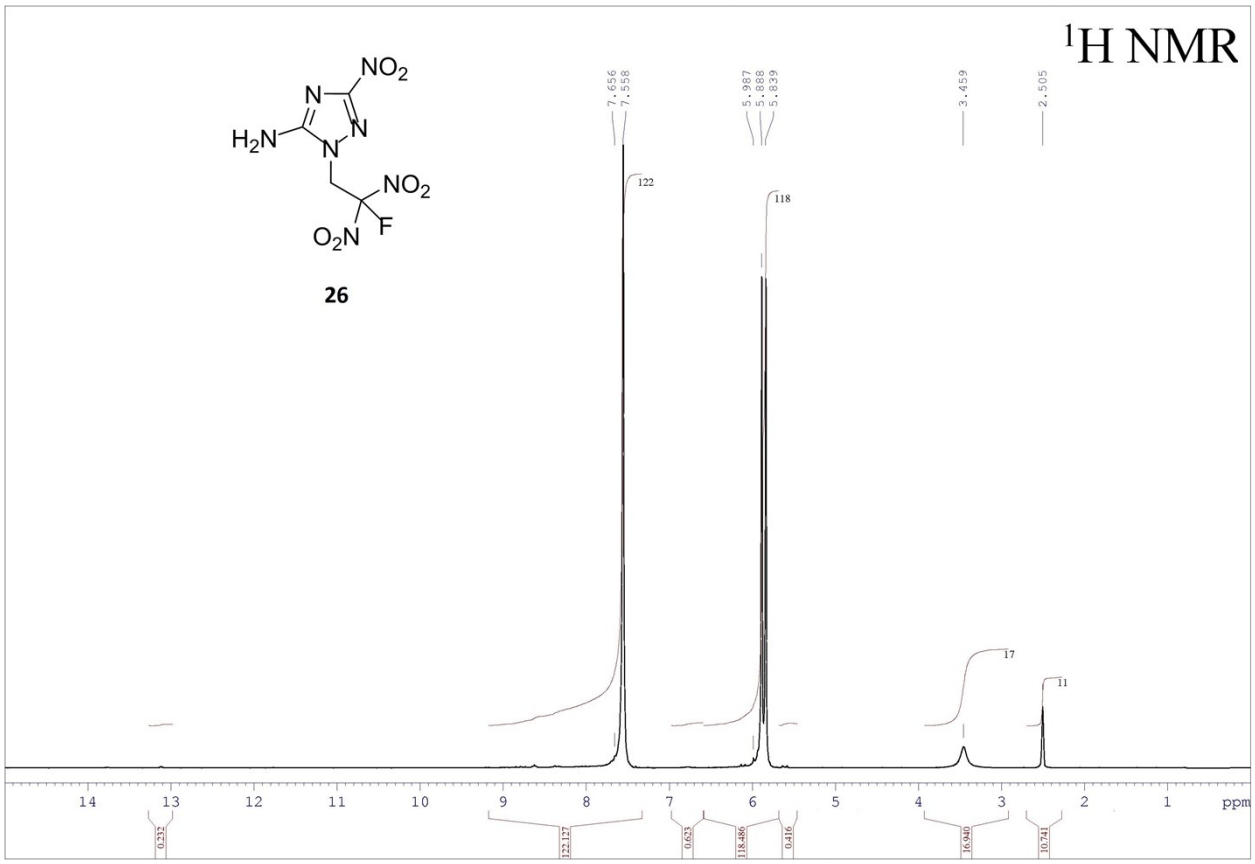
24

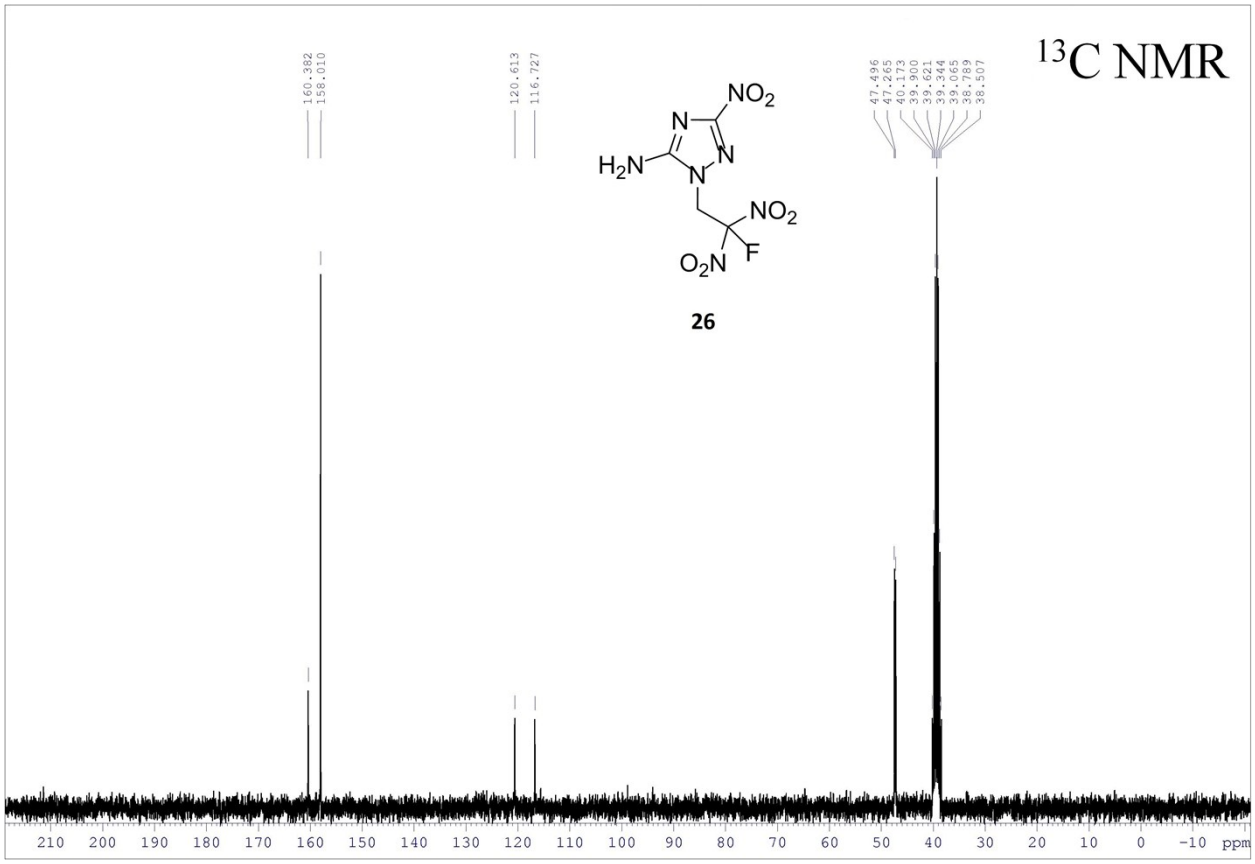

^{13}C NMR
163.314
150.038
121.109
117.208
50.387
50.151
40.734
40.458
40.180
39.902
39.625
39.347
39.06
NO2
N
N
N
NO2
O2N
F
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

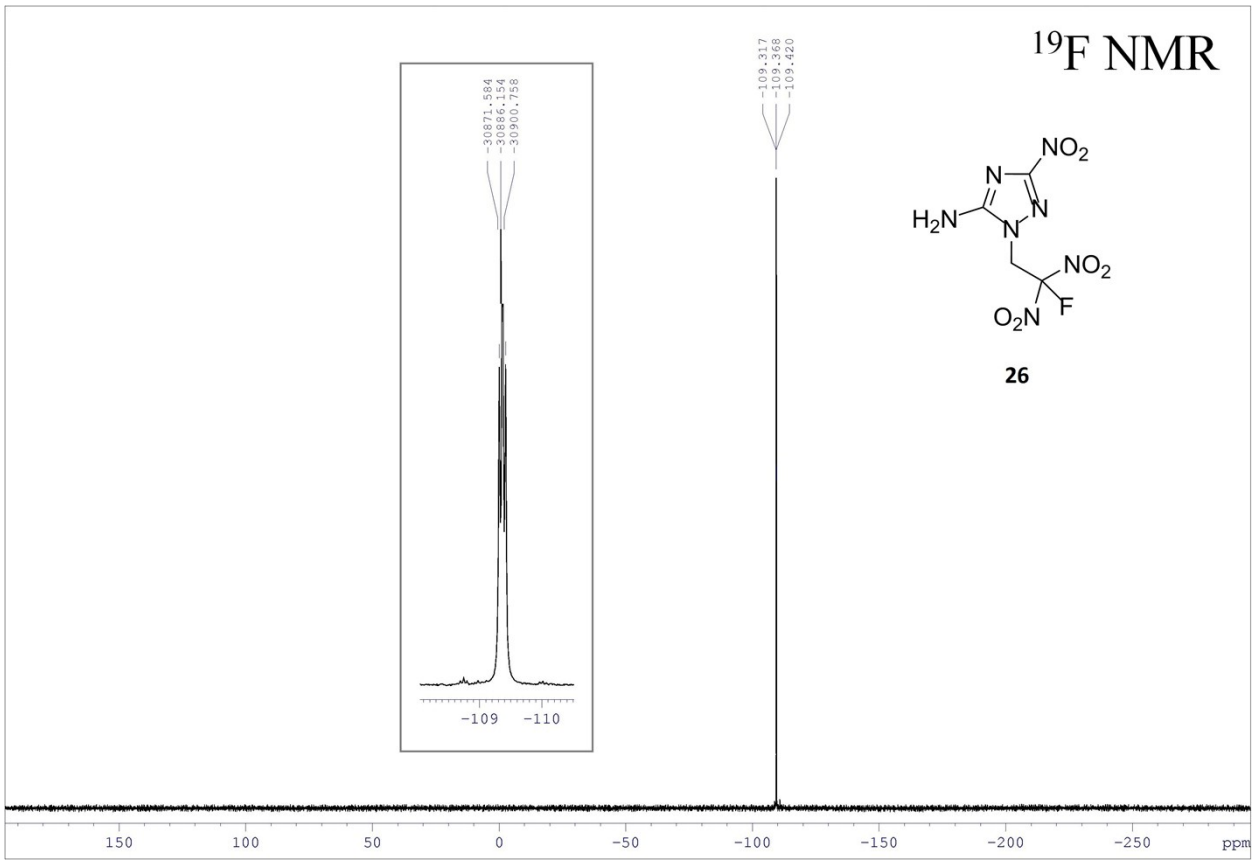

^{19}F NMR
-30602.238
-30616.998
-30631.750
-108.363
-108.415
-108.468
NO2
N
N
N
NO2
O2N
F
24
-108 -109
150 100 50 0 -50 -100 -150 -200 -250 ppm

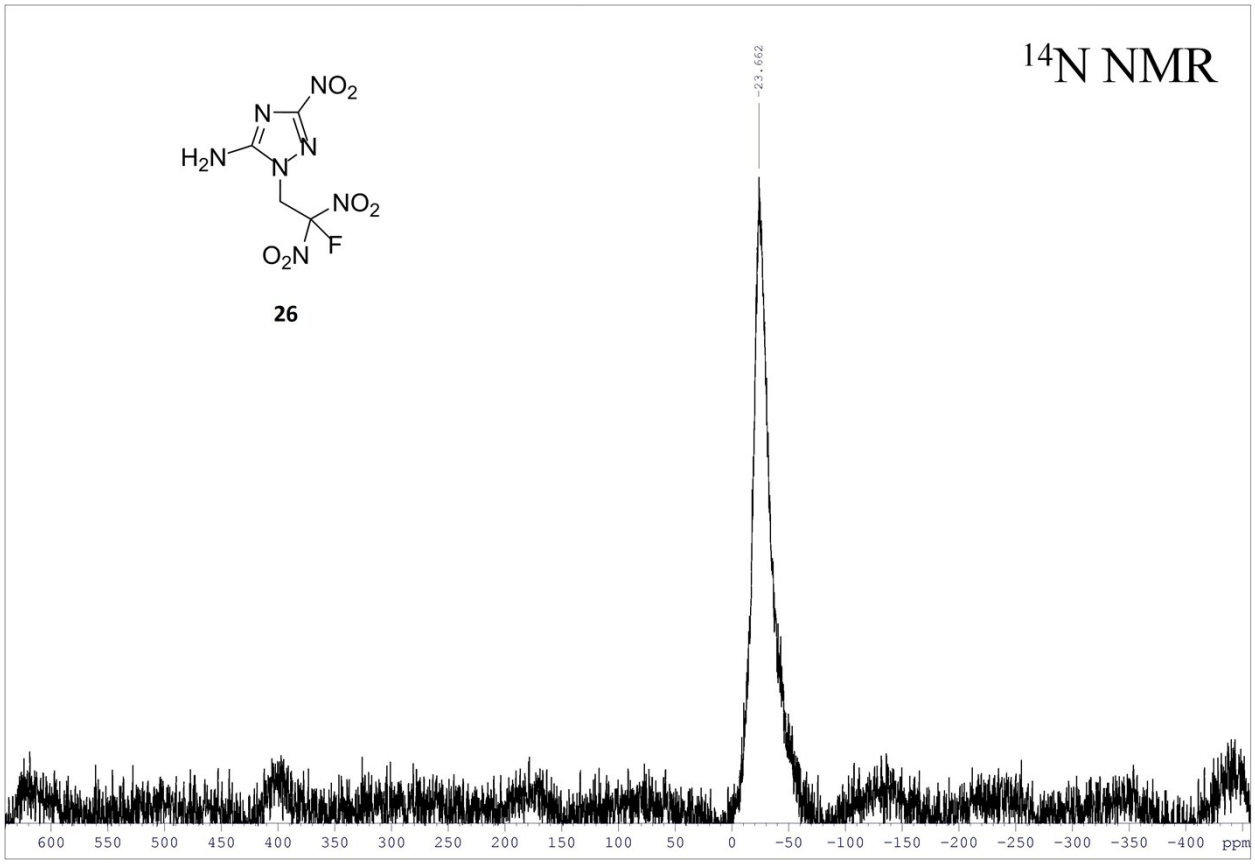

^{14}N NMR
-24.141
NO2
N
N
N
NO2
O2N
F
24
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm

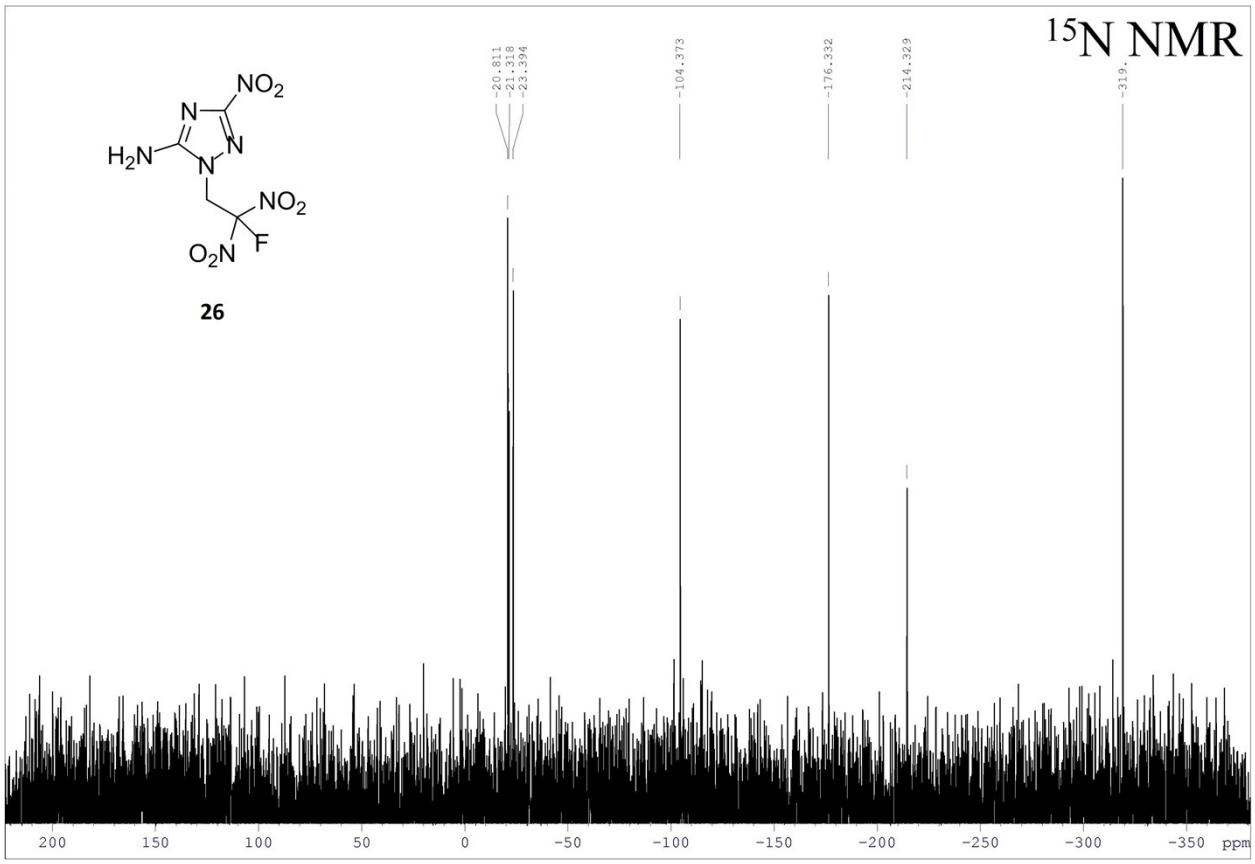

^{15}N NMR
-21.808
-22.309
-25.902
-86.169
-131.399
-174.784
NO2
N
N
N
NO2
O2N
F
24
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm


^{1}H NMR
26
7.656
7.558
5.987
5.888
5.839
3.459
2.505
122
118
17
11
ppm

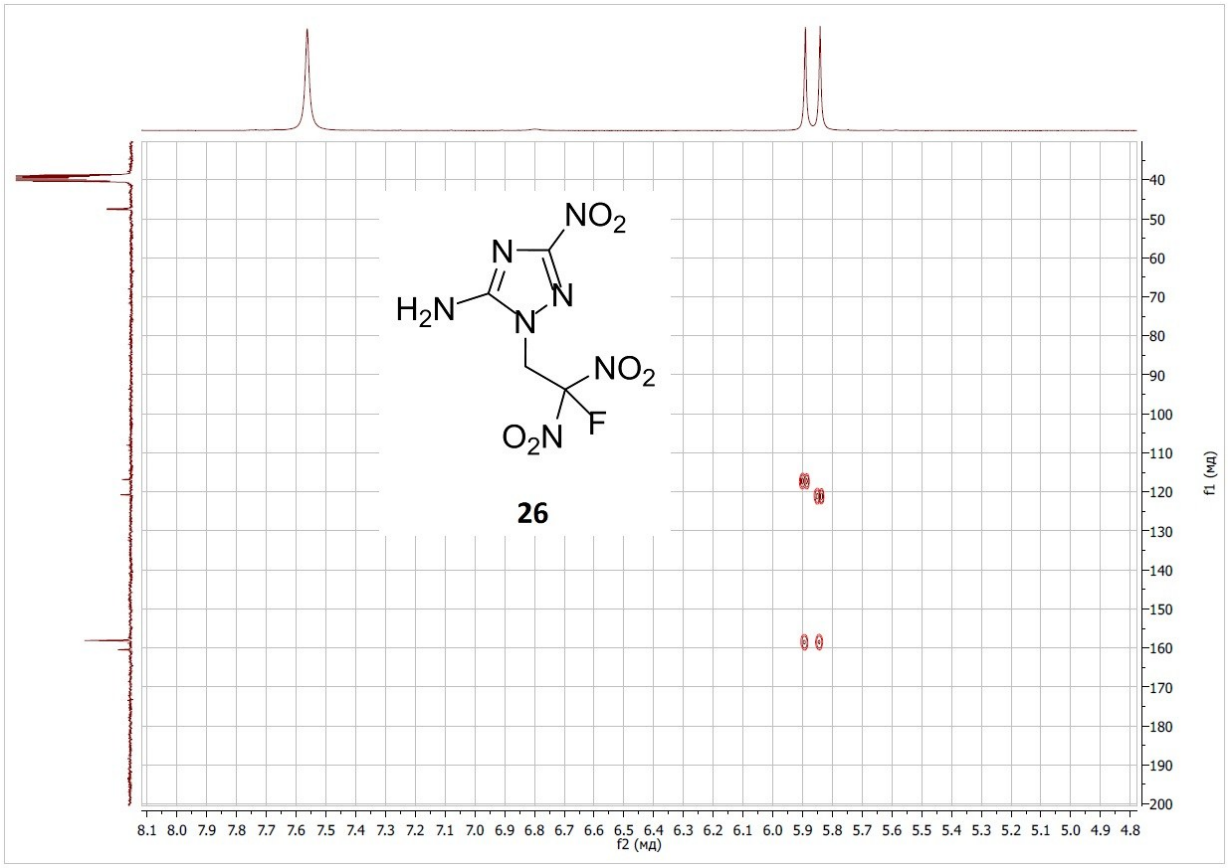

^{13}C NMR
26
160.382
158.010
120.613
116.727
47.496
47.265
40.173
39.900
39.621
39.344
39.065
38.789
38.507
ppm


19F NMR
-30871.584
-30886.154
-30900.758
-109.317
-109.368
-109.420
-109 -110
NO2
N
H2N
N
N
NO2
O2N
F
26
150 100 50 0 -50 -100 -150 -200 -250 ppm

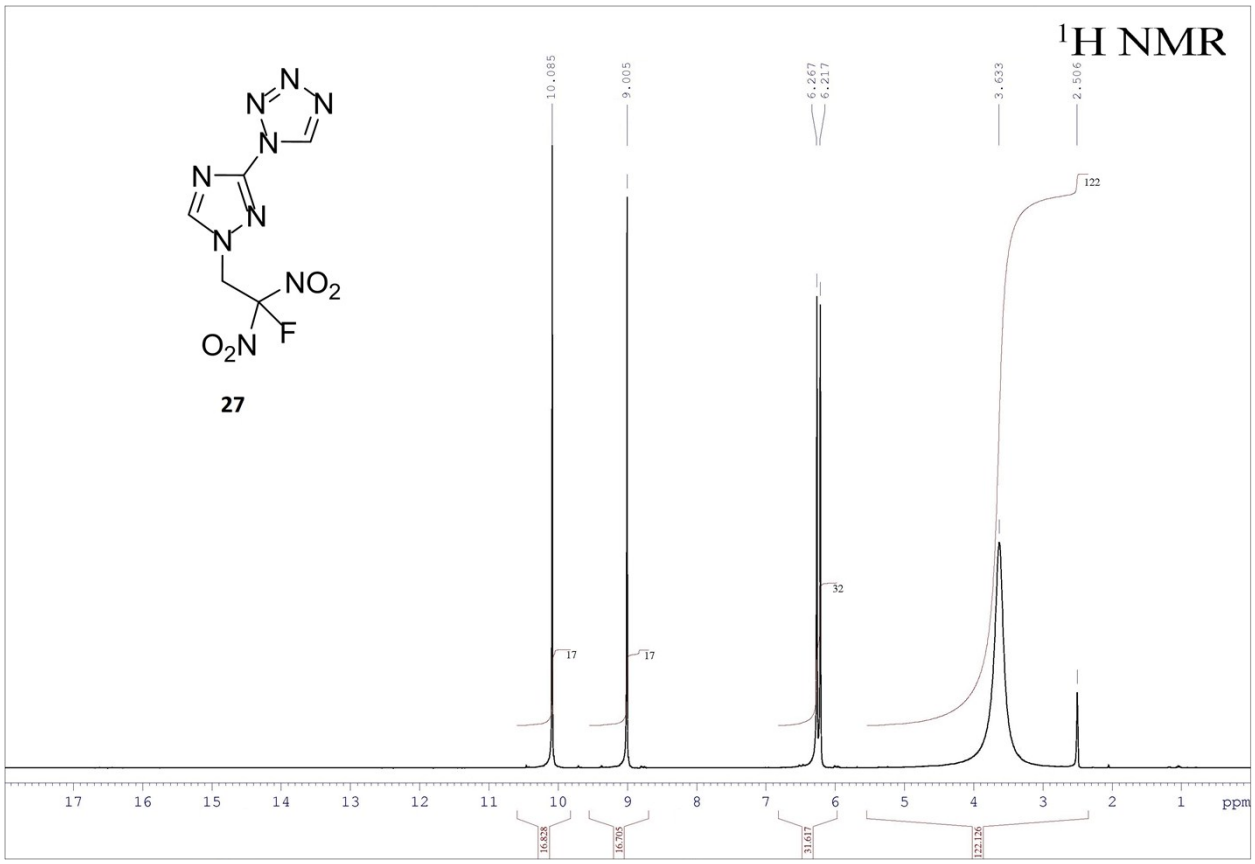

14N NMR
-23.662
NO2
N
H2N
N
N
NO2
O2N
F
26
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm


^{15}N NMR
-20.811
-21.318
-23.394
-104.373
-176.332
-214.329
-319.
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

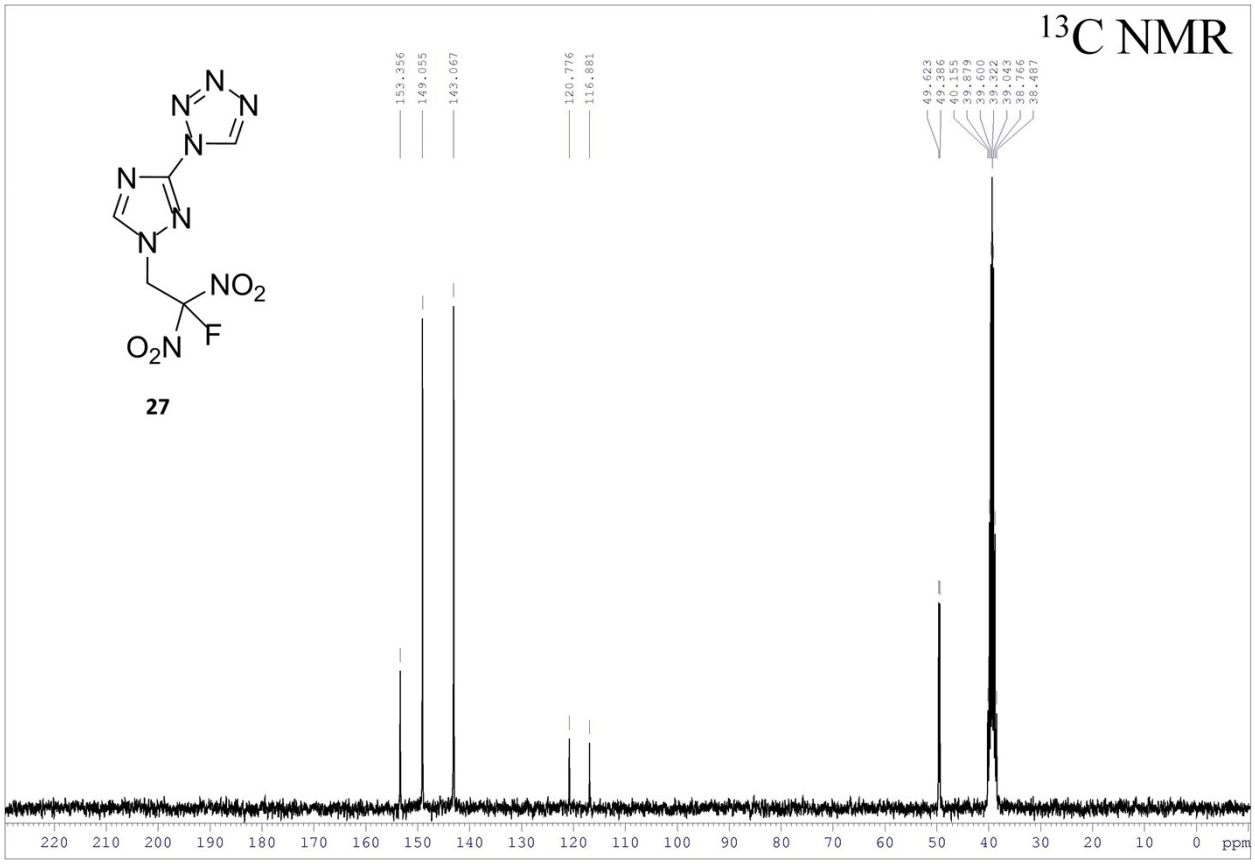
26


f1 (мд)
f2 (мд)

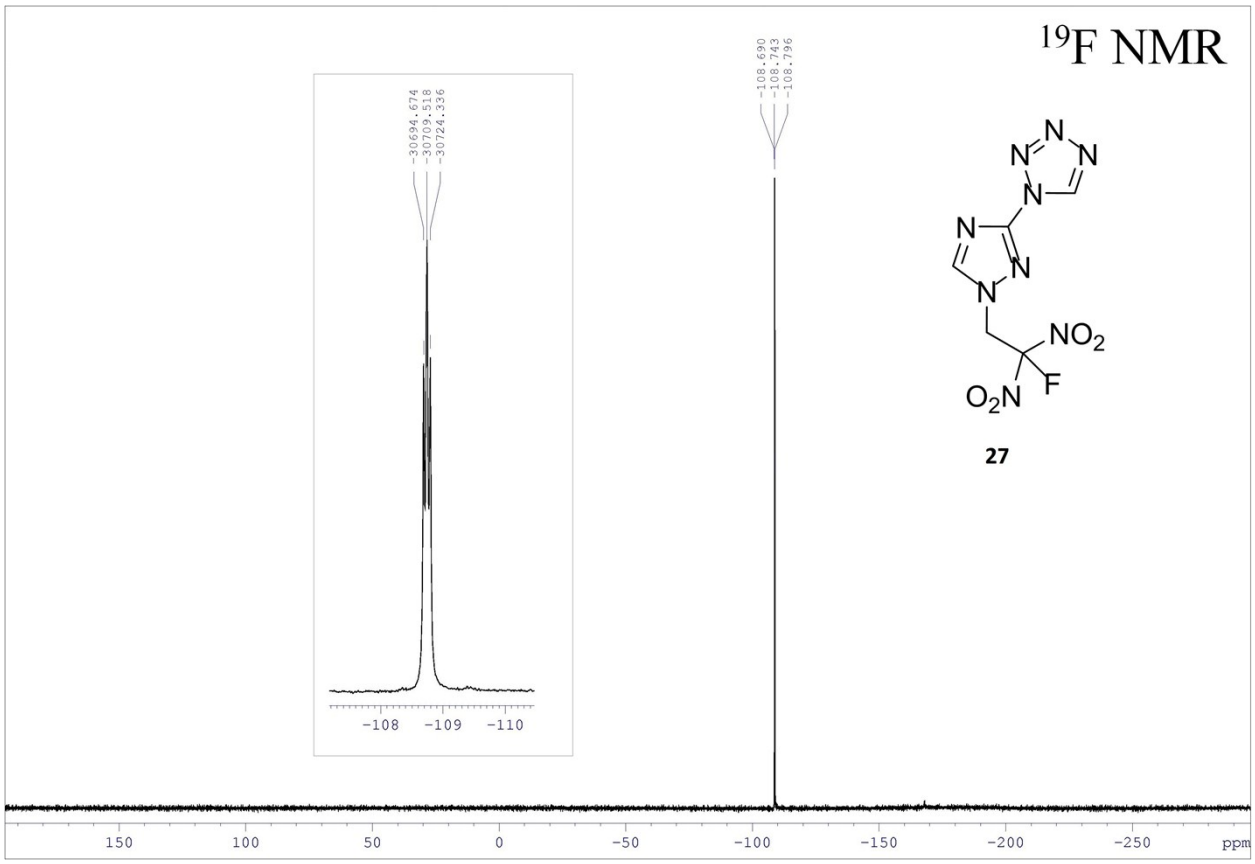
26

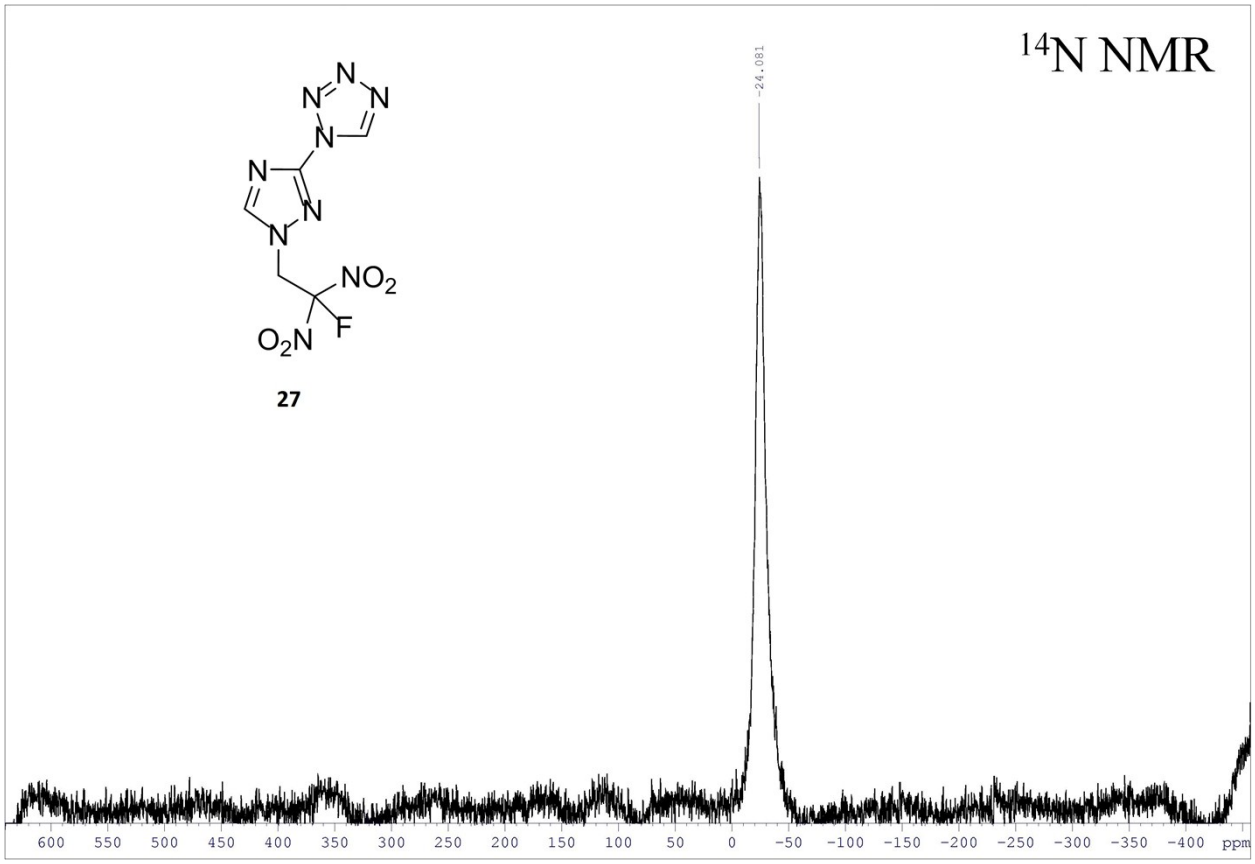

^{1}H NMR
10.085
9.005
6.267
6.217
3.633
2.506
122
32
17
17
16.828
16.705
31.617
122.126
ppm

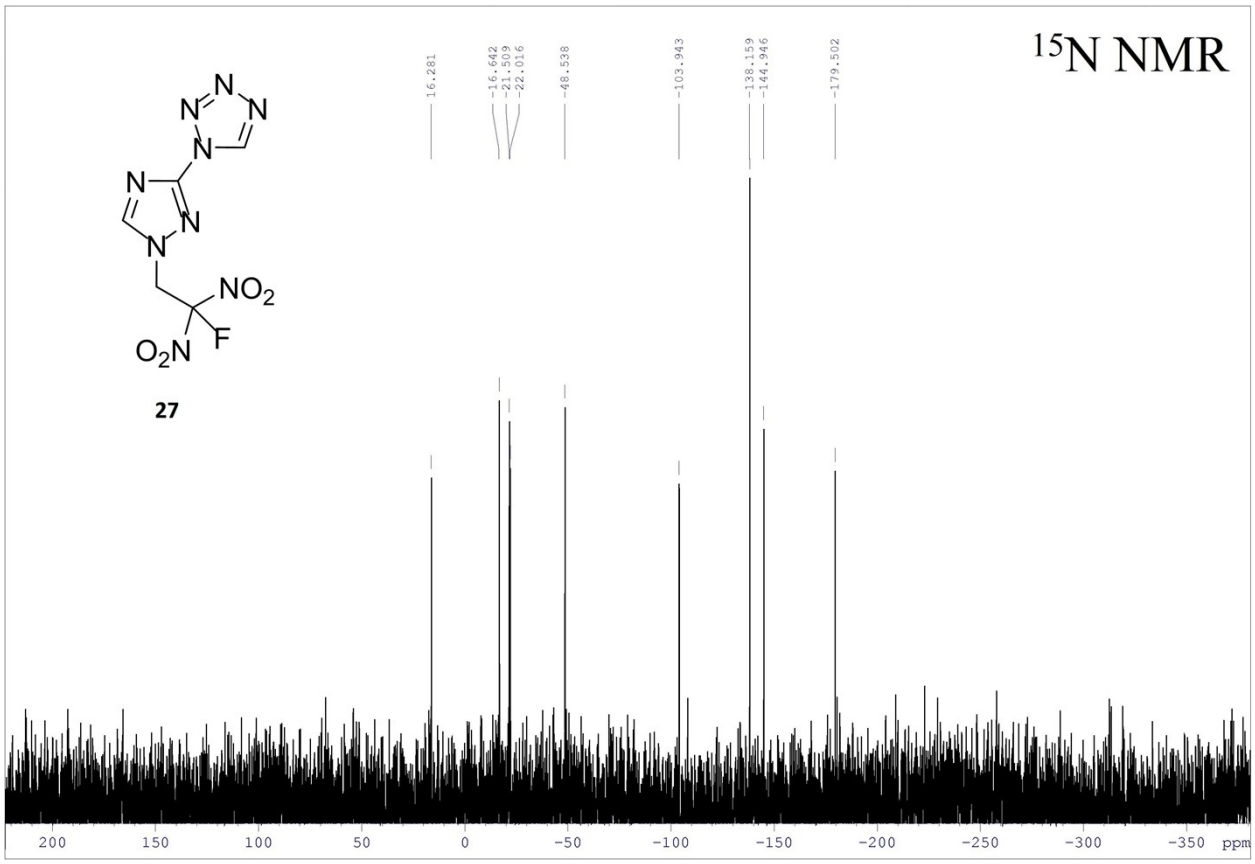
27


^{13}C NMR
153.356
149.055
143.067
120.776
116.881
49.623
49.386
49.155
48.919
39.600
39.322
39.043
38.766
38.487
ppm

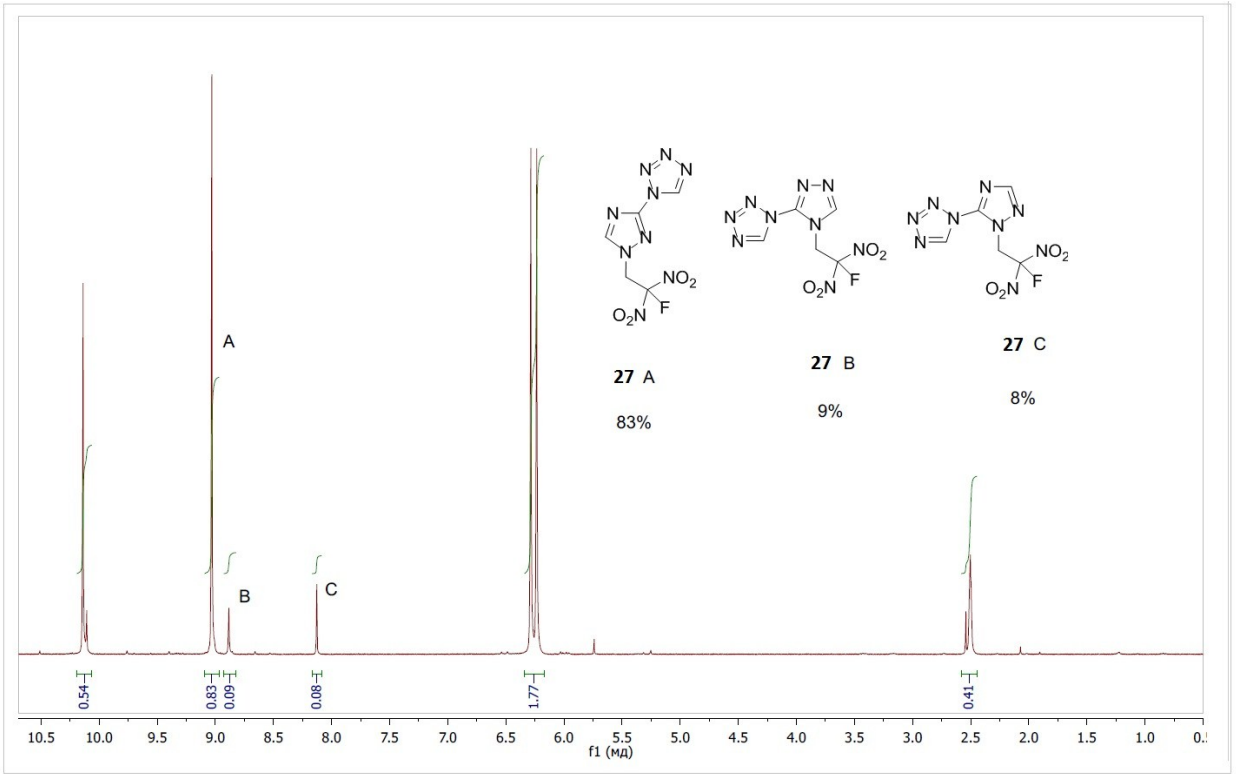
27


19F NMR
-30694.674
-30709.518
-30724.336
-108.690
-108.743
-108.796
-108
-109
-110
150
100
50
0
-50
-100
-150
-200
-250
ppm
NO2
O2N
F
27


14N NMR
-24.081
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
ppm
NO2
O2N
F
27



27



27 A

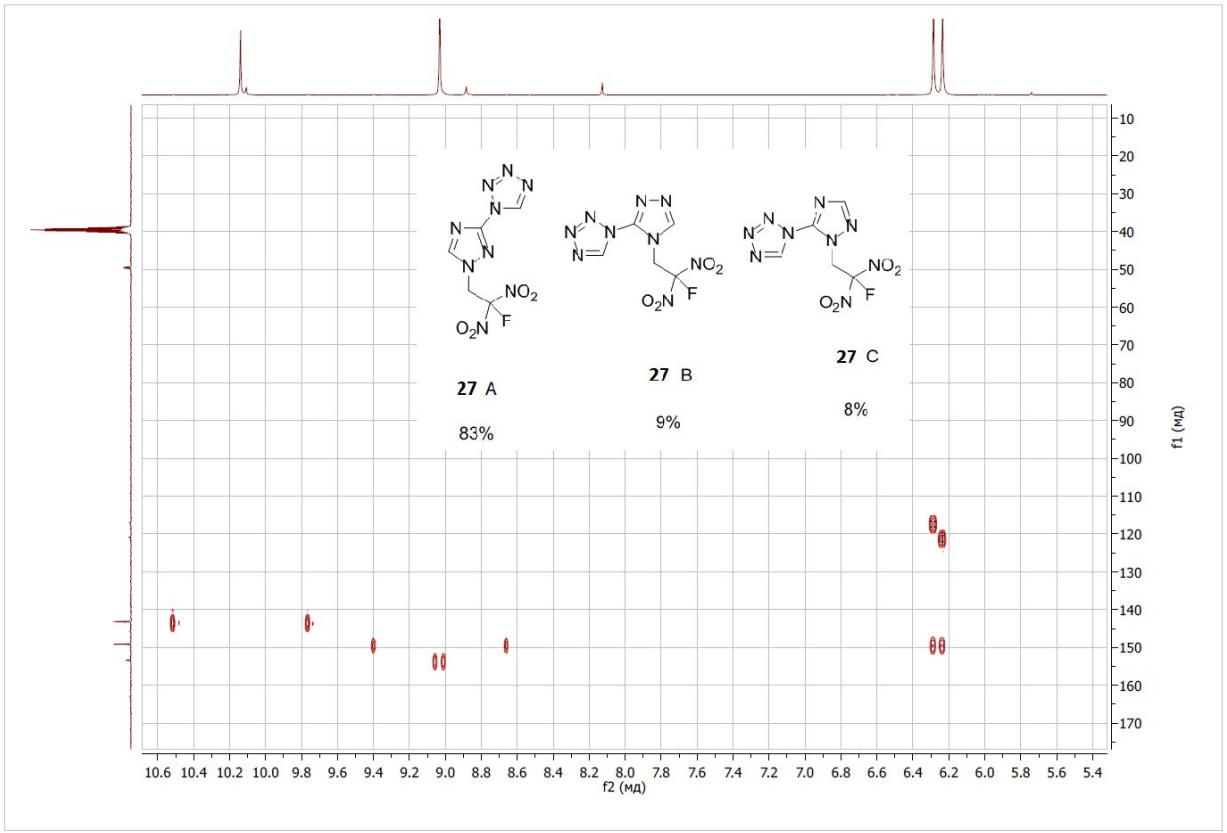
83%

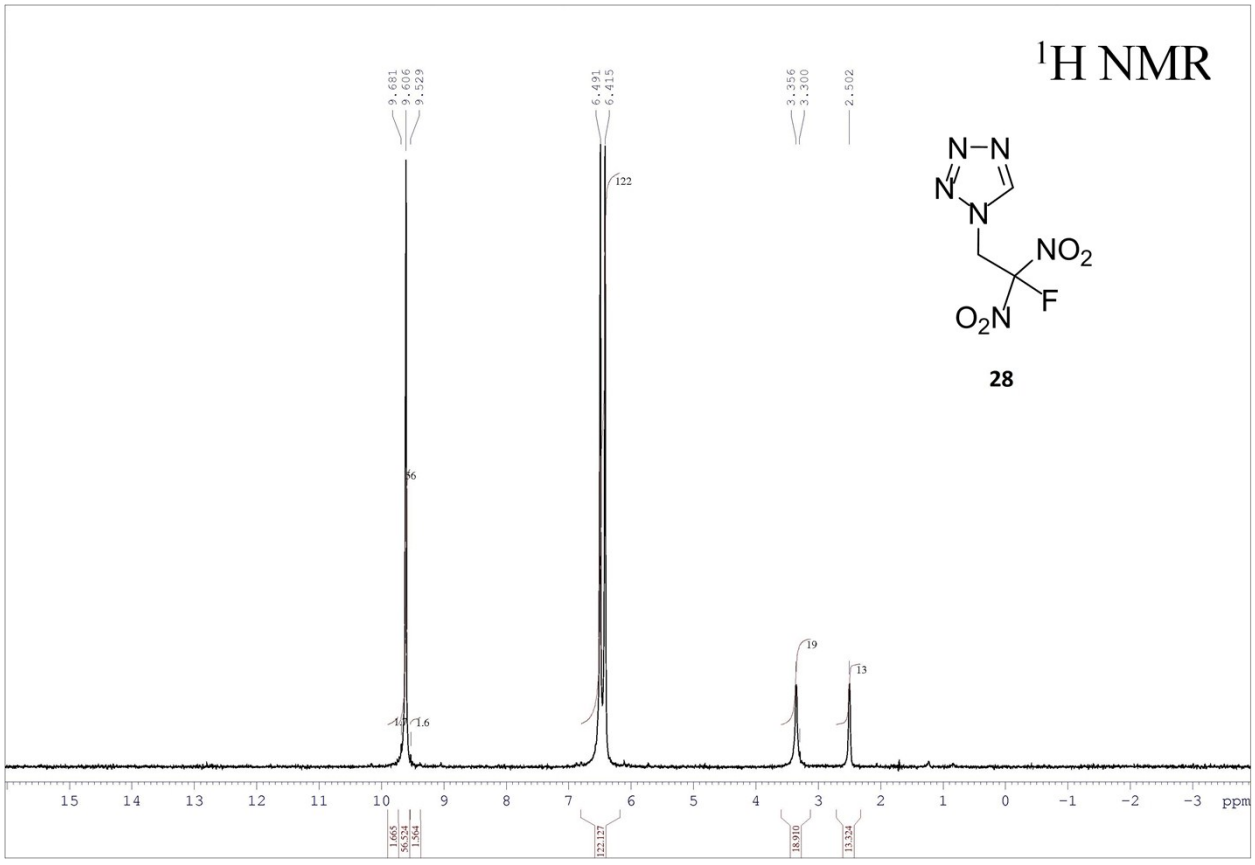
27 B

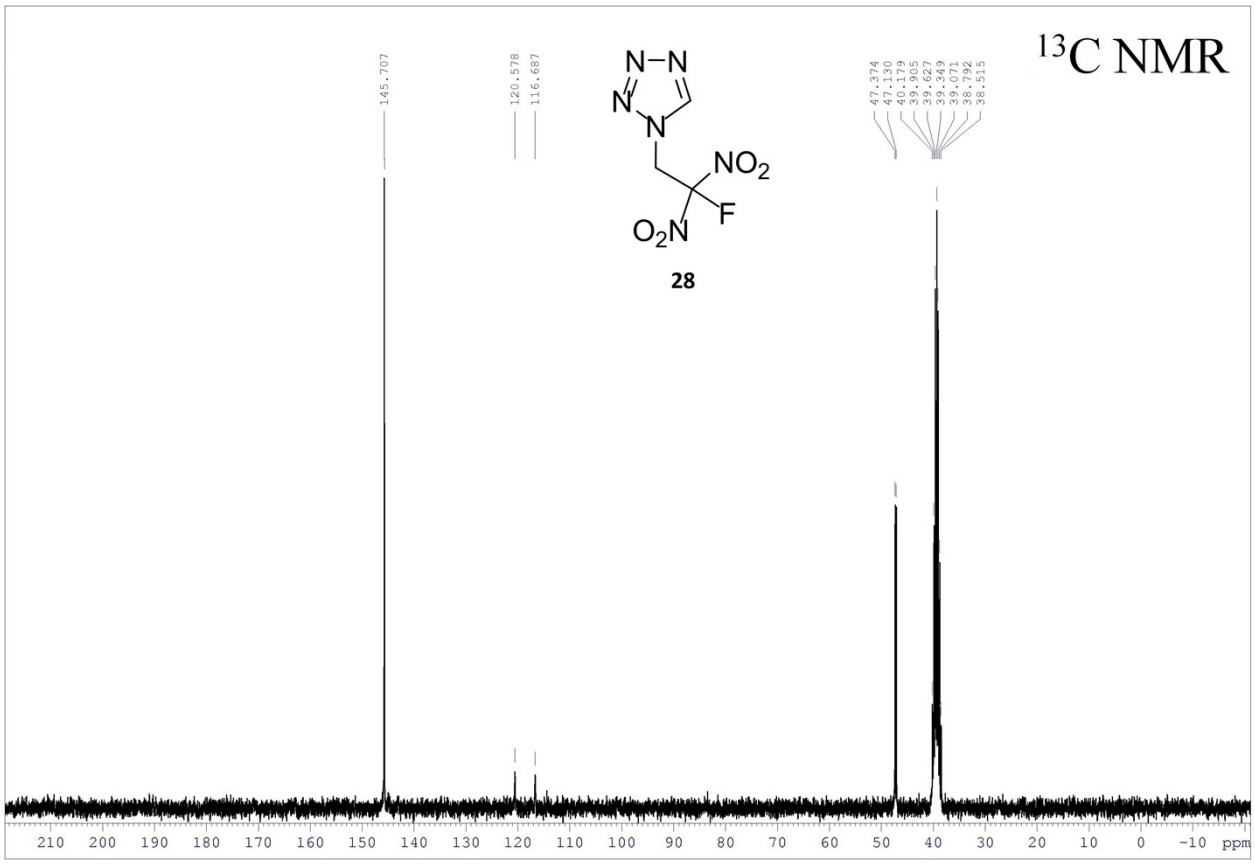
9%

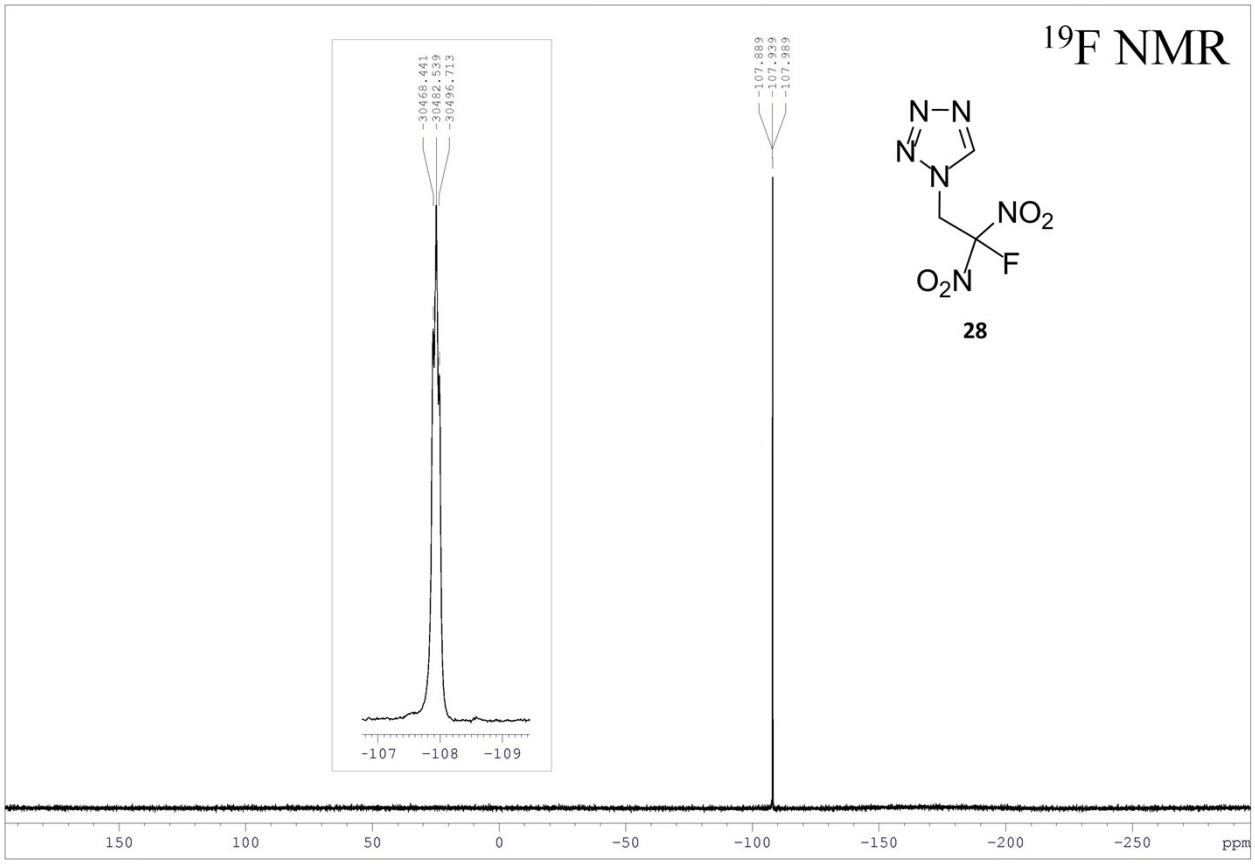
27 C

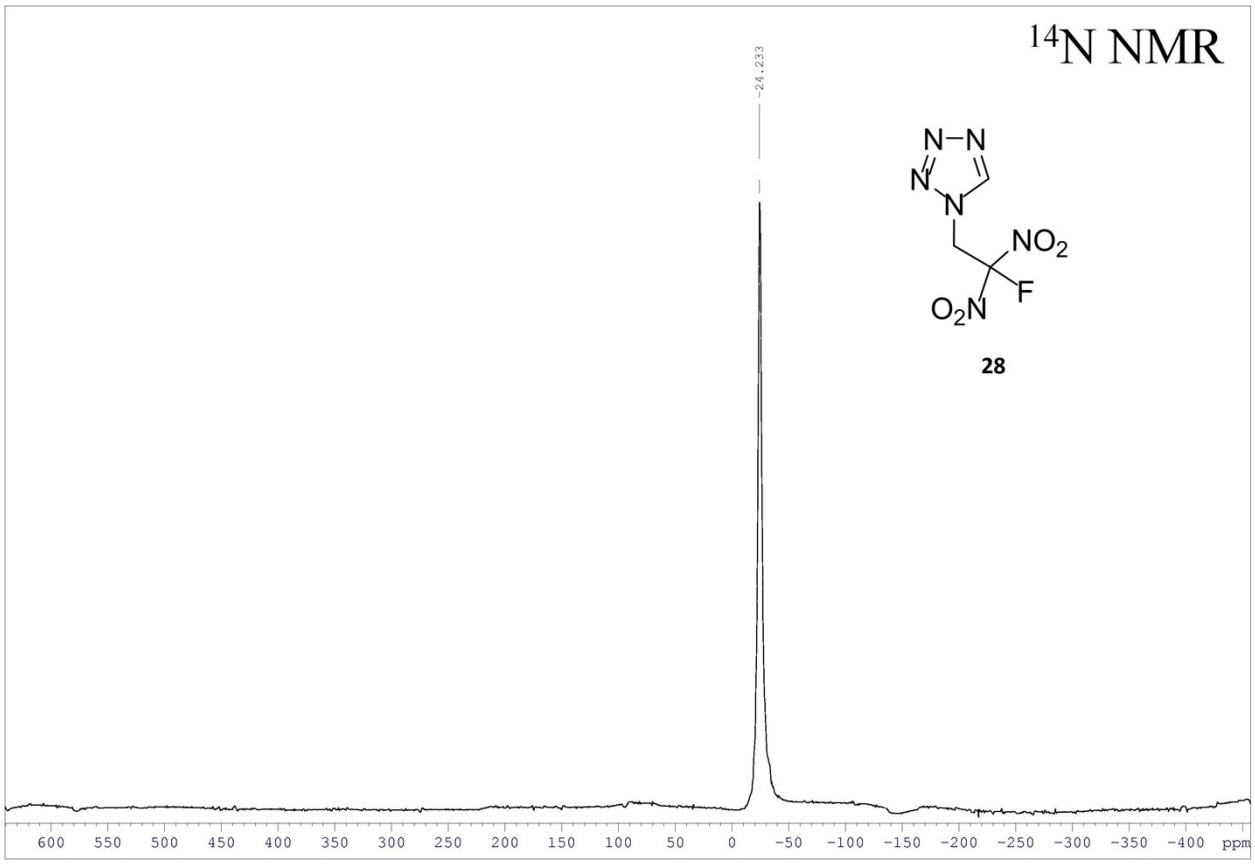
8%

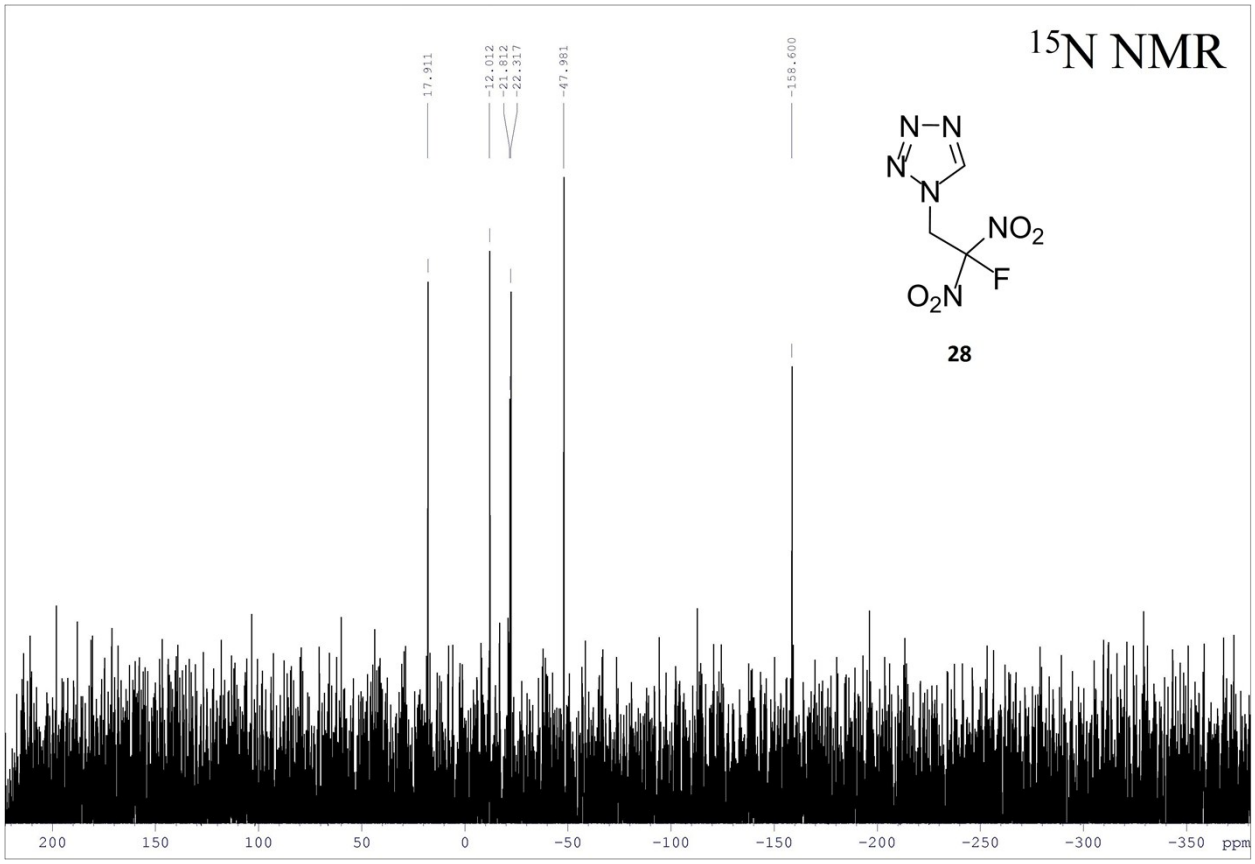

27 A
83%
27 B
9%
27 C
8%
f2 (мд)
f1 (мд)

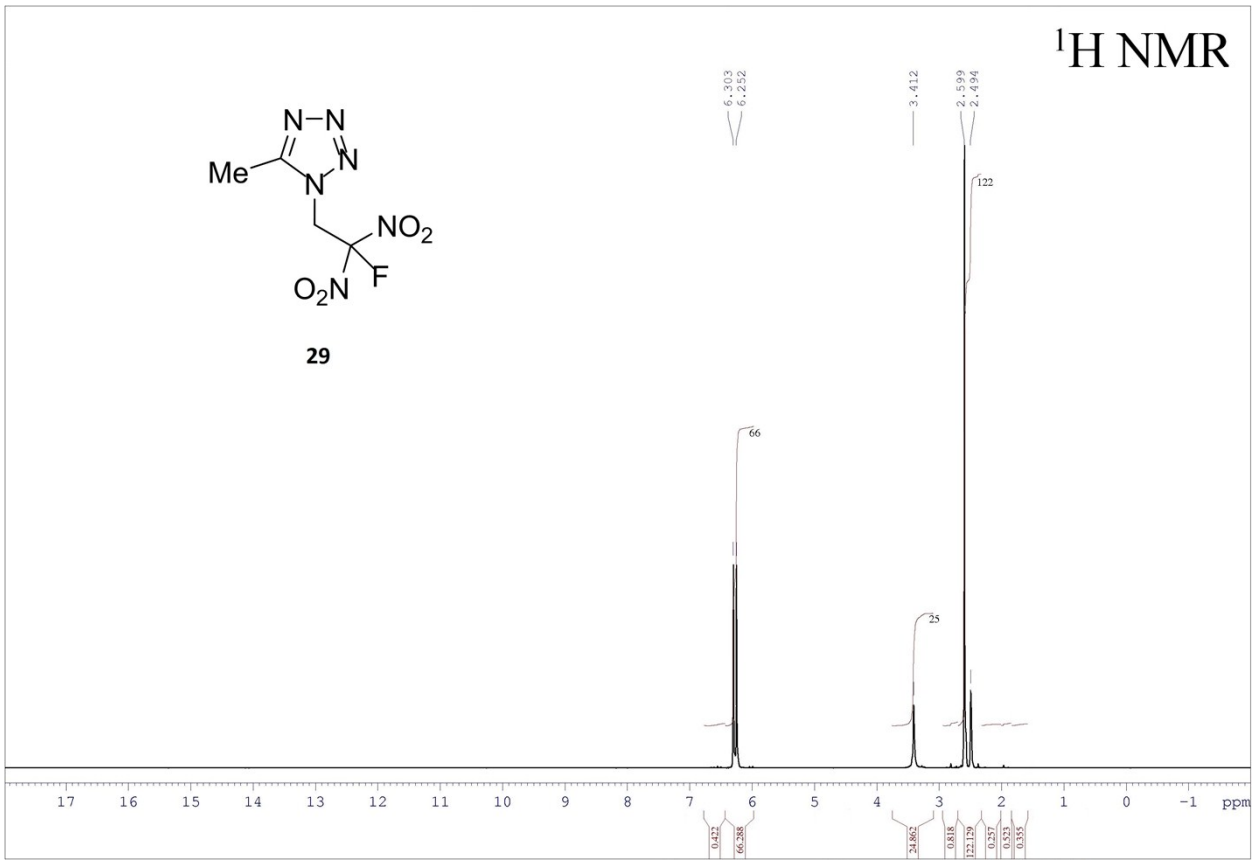

^{1}H NMR
9.681
9.606
9.529
6.491
6.415
3.356
3.300
2.502
28
ppm

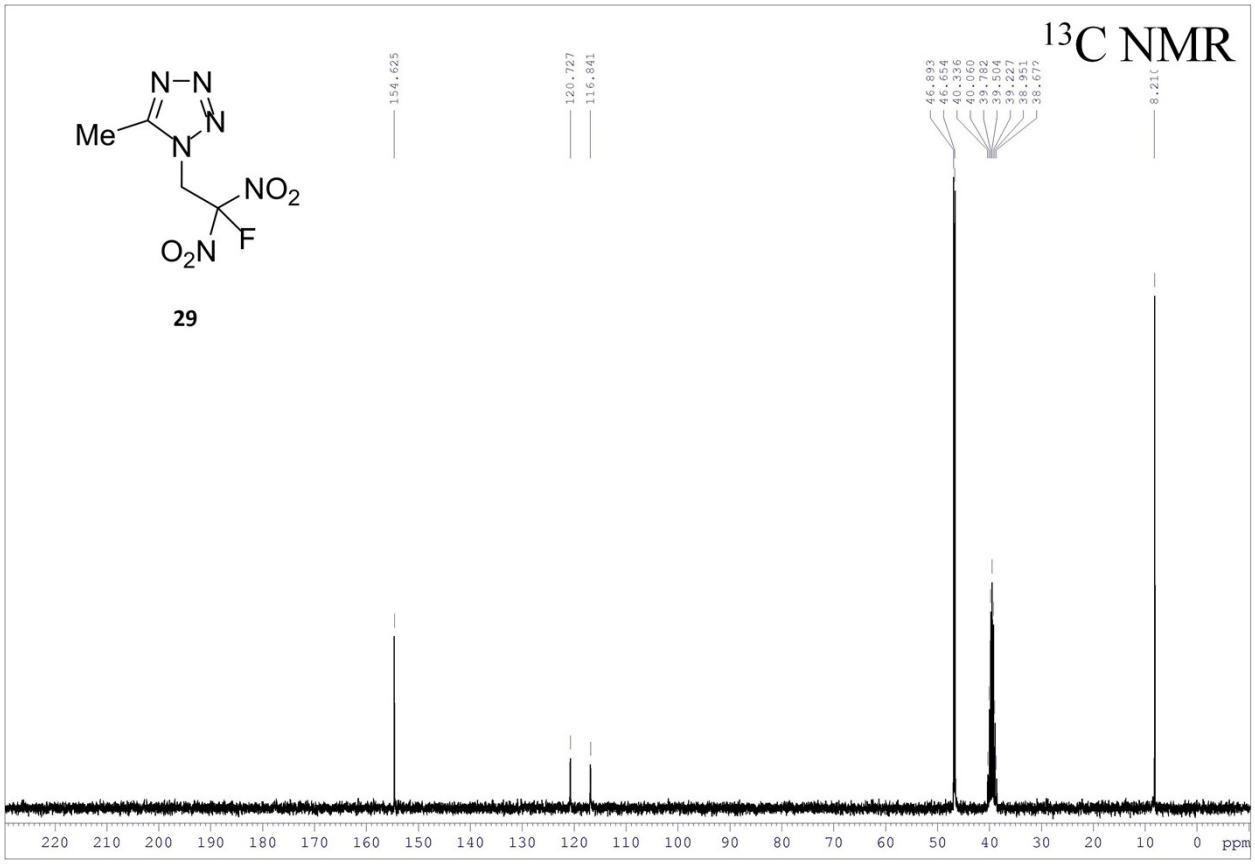

^{13}C NMR
145.707
120.578
116.687
47.374
47.130
40.179
39.905
39.627
39.349
39.071
38.792
38.515
N–N
NO2
F
O2N
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

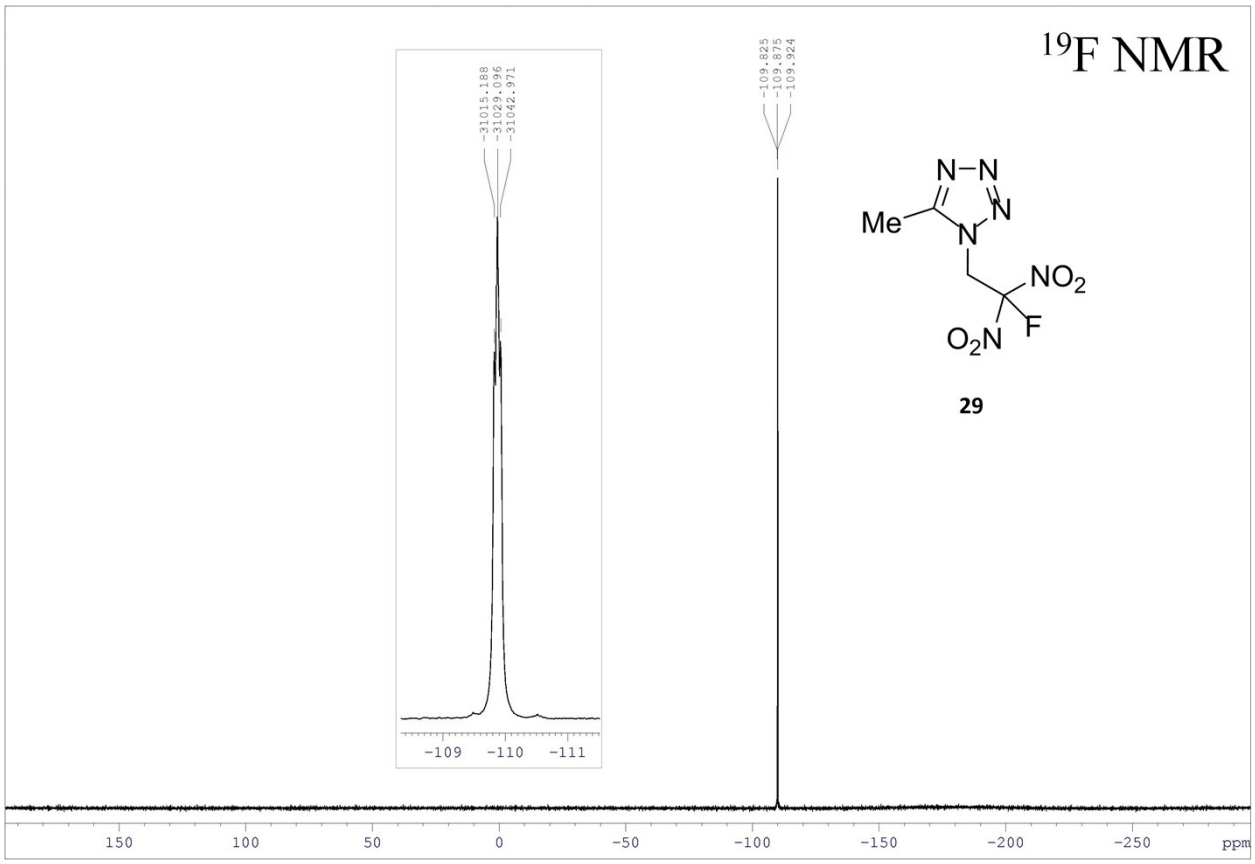

^{19}F NMR
-30468.441
-30482.539
-30496.713
-107.883
-107.939
-107.989
N–N
NO2
F
O2N
28
-107 -108 -109
150 100 50 0 -50 -100 -150 -200 -250 ppm


^{14}N NMR
-24.233
28
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 ppm


^{15}N NMR
17.911
-12.012
-21.812
-22.317
-47.981
-158.600
28
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm


^{1}H NMR
Me
N–N
N
N
NO2
O2N
F
29
6.303
6.252
3.412
2.599
2.494
122
66
25
0.422
66.288
24.862
0.818
122.129
0.257
0.523
0.355
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm


^{13}C NMR
Me
N–N
N
N
NO2
O2N
F
29
154.625
120.727
116.841
46.893
46.654
40.336
40.060
39.782
39.504
39.227
38.951
38.675
8.210
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


19F NMR
-31015.188
-31029.096
-31042.971
-109.825
-109.875
-109.924
-109
-110
-111
150
100
50
0
-50
-100
-150
-200
-250
ppm
Me
N
N
N
NO2
O2N
F

29