Efficient Synthesis of *N*-(Chloromethyl)nitramines *via* $TiCl_4$-Catalyzed Chlorodeacetoxylation

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CONTENTS

X-ray experiments

The investigation of compounds **1e** and **1q** were carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα)=0.71073 Å, graphite monochromator, *ω*-scans) at 120K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [1]. 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 [2]. The CCDC numbers (2125221 for compounds **1e**, and 2125222 for **1q**) 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.

Crystallographic data for compounds **1e***:* $C_4H_8N_4O_4Cl_2$ are monoclinic, space group $P2_1/c$: a = 5.8212(4)Å, b = 11.9073(9)Å, c = 7.3664(5)Å, β = 112.7940(10)°, V = 470.72(6)Å^3, Z = 2, M = 247.04, d_{cryst} = 1.743 g·cm^{-3}. $wR2$=0.0615 calculated on F^2_{hkl} for all 1209 independent reflections with 2θ<57.7°, (*GOF*=1.066, R=0.0248 calculated on F_{hkl} for 1155 reflections with $I>2\sigma(I)$).

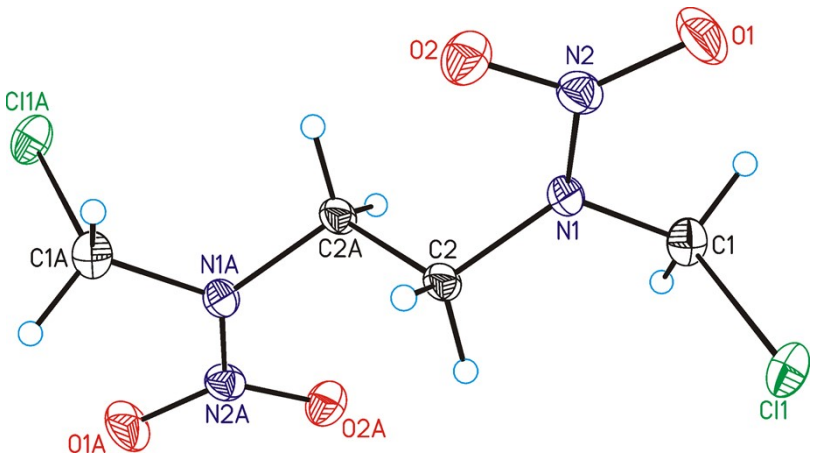

Figure 1. General view of compound **1e**. Thermal ellipsoids are drawn at 50% probability level.

***Crystallographic data for compounds* 1q**: $C_5H_{10}N_8O_8Cl_2$ are orthorhombic, space group *Pbcn*: a = 28.4221(9)Å, b = 5.9548(2)Å, c = 25.7279(9)Å, V = 4354.4(3)Å^3, Z = 12, M = 381.11, d_{cryst} = 1.744 g·cm^{-3}. $wR2$=0.1029 calculated on F^2_{hkl} for all 4304 independent reflections with 2θ<52.2°, (*GOF*=1.192, R=0.0569 calculated on F_{hkl} for 3615 reflections with $I>2\sigma(I)$).

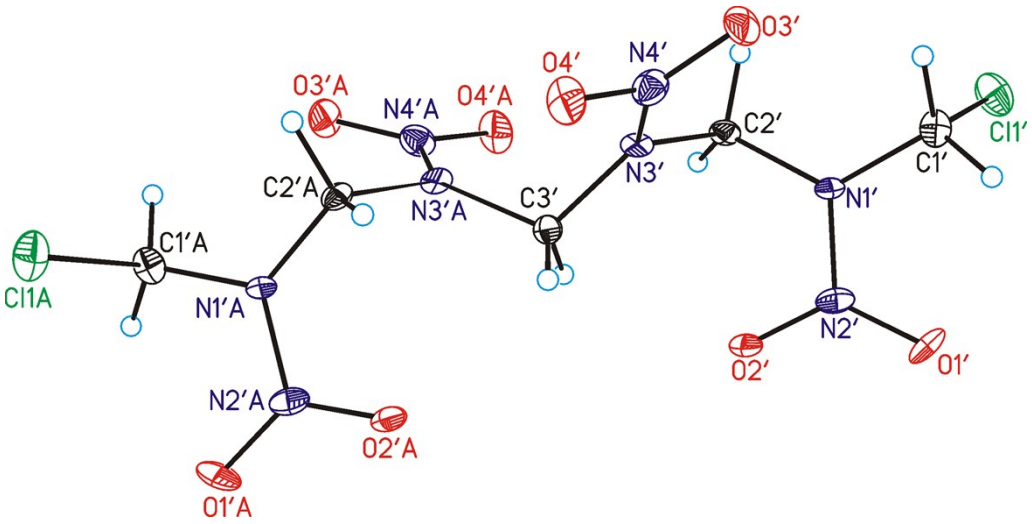

Figure 2. General view of compound **1q**. Thermal ellipsoids are drawn at 50% probability level.

Spectral data

1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane (**1a**): colorless needles, mp 143-144 °C (from $CHCl_3$) (lit.[3] mp 144-145°C), R_f = 0.45. ^1H NMR (CD_3CN) δ 5.80 (s, 2H, CH_2). IR and NMR data (^1H, ^{13}C, ^{14}N) agree well with previously reported values [4]. Anal. Calcd. for $C_4H_8Cl_2N_6O_6$ (307.04): C, 15.65; H, 2.63; N, 27.37. Found: C, 15.69; H, 2.66; N, 27.31.

2-Nitro-2-azapropyl chloride (**1b**): colorless liquid, bp 41-43°C /0.5 mm (lit.[4] bp 40-41°C/0.7 mm), R_f = 0.65. ^1H NMR ($CDCl_3$) δ 3.42 (s, 3H, CH_3), δ 5.64 (s, 2H, CH_2). NMR data agree well with previously reported values [5]. Anal. Calcd. for $C_2H_5ClN_2O_2$ (124.52): C, 19.29; H, 4.05; N, 22.50. Found: C, 19.33; H, 4.07; N, 22.44.

1,3-Dichloro-2-nitro-2-azapropane (**1c**): colorless liquid, bp 59-60 °C /0.5 mm, which crystallized on standing, mp 28-29 °C (lit.[3] bp 53-55°C /0.1 mm), R_f = 0.68. ^1H NMR ($CDCl_3$) δ 5.66 (s, 2H, CH_2). IR and NMR data (^1H, ^{13}C, ^{14}N) agree well with previously reported values [3]. Anal. Calcd. for $C_2H_4Cl_2N_2O_2$ (158.97): C, 15.11; H, 2.54; N, 17.62. Found: C, 15.07; H, 2.62; N, 17.79.

1,5-Dichloro-2,4-dinitro-2,4-diazapentane (**1d**): colorless needles, mp 91-94°C (from CCl_4, lit.[6] 89-90°C), R_f = 0.55. ^1H NMR ($CDCl_3$) δ 5.62 (s, 2H, CH_2), 5.81 (s, 2H, CH_2Cl). ^{13}C NMR ($CDCl_3$) δ 58.2, 63.4. ^{14}N NMR ($CDCl_3$) δ -37.9 (NO_2). IR (KBr): 3067, 3023, 1583, 1551, 1443, 1282, 1270, 1241, 912 cm^{-1}. Anal. Calcd. for $C_3H_6Cl_2N_4O_4$ (233.01): C, 15.46; H, 2.60; N, 24.05. Found: C, 15.39; H, 2.61; N, 23.96.

1,6-Dichloro-2,5-dinitro-2,5-diazapentane (**1e**): colorless needles, mp 107-109°C (from $CHCl_3$, lit. [6] mp 107-109°C), R_f = 0.62. ^{1}H NMR (DMSO-d_6) δ 4.02 (s, 2H, CH_2), 5.02 (s, 2H, CH_2Cl). ^{13}C NMR (DMSO-d_6) δ 46.9, 43.1. ^{14}N NMR (DMSO-d_6) δ -29.9 (NO_2). IR (KBr): 3598, 3456, 3412, 1550, 1454, 1424, 1343, 1264, 1160, 915, 669 cm^{-1}. Anal. Calcd. for $C_3H_6Cl_2N_4O_4$ (247.03): C, 15.46; H, 2.60; N, 24.05. Found: C, 15.39; H, 2.61; N, 23.96.

1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane (**1f):** colorless plates, mp 140-142°C (from $CHCl_3$, lit. [7] mp 139.5-141°C), R_f = 0.5. ^{1}H NMR (CD_3CN) δ 3.49 (s, 3H, CH_3), 5.67 (s, 2H, CH_2Cl), 5.80 (s, 2H, CH_2), 5.83 (s, 2H, CH_2). ^{13}C NMR (CD_3CN) δ 40.8, 60.2, 65.4, 67.2. ^{14}N NMR (CD_3CN) δ -35.7, -33.8, -29.5 (NO_2). IR (KBr): 3090, 3033, 1575, 1521, 1450, 1307, 1281, 1256, 946, 765 cm^{-1}. Anal. Calcd. for $C_4H_9ClN_6O_6$ (296.19): C, 17.62; H, 3.33; N, 30.83. Found: C, 17.67; H, 3.34; N, 30.72.

1-Chloro-2,4,6-trinitro-2,4,6-triazaoctane (**1g):** colorless plates, mp 115-117°C (from $CHCl_3$), R_f = 0.55. ^{1}H NMR (CD_3CN) δ 1.27 (t, 3H, J = 14 Hz, CH_3), 4.0-3.93 (q, 1H, J = 20.8 Hz, CH_2), 5.68 (s, 2H, CH_2Cl), 5.82 (s, 2H, $C\underline{H}_2NCH_2$), 5.85 (s, 2H, NCH_2N). ^{13}C NMR (CD_3CN) δ 12.3, 49.3, 60.2, 65.4, 66.5, 118.3. ^{14}N NMR (CD_3CN) δ -35.1, -33.3, -29.6 (NO_2). IR (KBr): 3084, 3040, 2991, 1575, 1552, 1516, 1468, 1442, 1409, 1273, 1247, 1201, 1153, 1096, 1076, 1042, 934, 911 cm^{-1}. Anal. Calcd. for $C_7H_{15}ClN_6O_6$ (310.22): C, 20.95; H, 3.87; N, 28.32. Found: C, 21.07; H, 3.91; N, 28.21.

1-Chloro-2,4,6-trinitro-2,4,6-triazanonane (**1h):** colorless plates, mp 109-111°C (from $CHCl_3$), R_f = 0.55. ^{1}H NMR (CD_3CN) δ 0.96 (t, 3H, J = 14.9 Hz, CH_3), 1.81-

1.68 (m, 2H, C$\underline{H}_2$CH$_3$), 3.89 (t, 2H, J = 15.1 Hz, NCH$_2$), 5.71 (s, 2H, CH$_2$Cl), 5.83 (s, 2H, C$\underline{H}_2$NCH$_2$), 5.86 (s, 2H, NCH$_2$N). ^{13}C NMR (CD$_3$CN) δ 10.3, 19.8, 54.5, 59.2, 64.5, 65.5. ^{14}N NMR (CD$_3$CN) δ -35.1, -33.4, -29.6 (NO$_2$). IR (KBr): 3081, 3036, 2976, 2937, 2876, 1575, 1527, 1445, 1416, 1272, 1246, 1232, 1186, 1150, 1111, 1058, 940, 915 cm^{-1}. Anal. Calcd. for $C_7H_{15}ClN_6O_6$ (324.25): C, 23.97; H, 4.36; N, 27.95. Found: C, 24.01; H, 4.42; N, 27.87.

1-Chloro-2,4,6-trinitro-2,4,6-triazadecane (**1i**)**:** colorless plates, mp 102-103°C (from CCl$_4$), R_f = 0.55. ^{1}H NMR (CD$_3$CN) δ 0.95 (t, 3H, J = 14.7 Hz, CH$_3$), 1.30-1.43 (m, 2H, CH$_2$), 1.63-1.73 (m, 2H, CH$_2$), 3.90 (t, 2H, J = 15.2 Hz, NCH$_2$), 5.69 (s, 2H, CH$_2$Cl), 5.81 (s, 2H, C$\underline{H}_2$NCH$_2$), 5.84 (s, 2H, NCH$_2$N). ^{13}C NMR (CD$_3$CN) δ 13.9, 20.6, 29.5, 53.8, 60.2, 65.4, 66.5. ^{14}N NMR (CD$_3$CN) δ -35.0, -33.3, -29.6 (NO$_2$). IR (KBr): 3086, 3035, 2963, 2933, 2875, 1572, 1523, 1435, 1413, 1273, 1243, 1149, 1100, 1056, 937, 906, 852, 764, 672, 644, 609 cm^{-1}. Anal. Calcd. for $C_7H_{15}ClN_6O_6$ (338.28): C, 26.72; H, 4.80; N, 26.71. Found: C, 26.75; H, 4.78; N, 26.77.

1-Bromo-10-chloro-5,7,9-trinitro-5,7,9-triazadecane (**1j**)**:** colorless plates, mp 96-97.5°C (from CCl$_4$), R_f = 0.62. ^{1}H NMR (CD$_3$CN) δ 1.86-1.88 (m, 4H, 2CH$_2$), 3.51 (t, 2H, J = 12.2 Hz, CH$_2$Br), 3.94 (t, 2H, J = 13.7 Hz, NCH$_2$), 5.69 (s, 2H, CH$_2$Cl), 5.82 (s, 2H, C$\underline{H}_2$NCH$_2$), 5.85 (s, 2H, NCH$_2$N). ^{13}C NMR (CD$_3$CN) δ 26.3, 30.6, 34.4, 53.1, 60.2, 65.5, 66.6. ^{14}N NMR (CD$_3$CN) δ -35.1, -33.4, -29.7 (NO$_2$). IR (KBr): 3087, 3039, 2966, 1566. 1525, 1448, 1431, 1408, 1273, 1109, 1086, 1063, 1022, 931, 908 cm^{-1}. Anal. Calcd. for $C_7H_{15}ClN_6O_6$ (417.17): C, 21.36; H, 3.59; N, 21.35. Found: C, 21.43; H, 3.63; N, 21.27.

1-Chloro-2,4,6-trinitro-2,4,6-triaza-9-methyldecane (**1k**)**:** colorless plates, mp 114-116°C (from CCl_4), R_f = 0.55. ^{1}H NMR (CD_3CN) δ 0.97 (t, 3H, J = 6.2 Hz, CH_3), 1.70-1.57 (m, 3H, C<u>H</u>C<u>H</u>$_2$), 3.94 (t, 2H, J = 15.2 Hz, NCH_2), 5.71 (s, 2H, CH_2Cl), 5.83 (s, 2H, $CH_2NC\underline{H}_2$), 5.86 (s, 2H, NCH_2N). ^{13}C NMR (CD_3CN) δ 21.6, 25.8, 34.9, 51.6, 59.2, 64.5, 65.5. ^{14}N NMR (CD_3CN) δ -35.1, -33.4, -29.7 (NO_2). IR (KBr): 3081, 3046, 2961, 2932, 2875, 1590, 1523, 1449, 1415, 1272, 1185, 1157, 1100, 1078, 942, 914 cm^{-1}. Anal. Calcd. for $C_7H_{15}ClN_6O_6$ (352.30): C, 29.23; H, 5.21; N, 25.57. Found: C, 29.34; H, 5.16; N, 25.43.

1-Chloro-2,5,7-trinitro-2,5,7-triazaoctane (**1l**)**:** colorless plates, mp 116-119°C (from CCl_4), R_f = 0.42. ^{1}H NMR (CD_3CN) δ 3.48 (s, 3H, CH_3), 4.12 (t, 2H, J = 11.3 Hz, CH_2), 4.25 (t, 2H, J = 11.5 Hz, CH_2), 5.50 (s, 2H, CH_2Cl), 5.66 (s, 2H, CH_2). ^{13}C NMR (CD_3CN) δ 40.6, 49.6, 51.0, 61.2, 68.4. ^{14}N NMR (CD_3CN) δ -32.6, -29.8, -28.7 (NO_2). IR (KBr): 3067, 3010, 1553, 1533, 1459, 1321, 1293, 1264, 1069, 968, 946, 905, 764, 676 cm^{-1}. Anal. Calcd. for $C_5H_{11}ClN_6O_6$ (310.22): C, 20.95; H, 3.87; N, 29.32. Found: C, 21.04; H, 3.82; N, 29.25.

1-Chloro-2,5,7-trinitro-2,5,7-triazanonane (**1m**)**:** colorless plates, mp 87-89.5°C (from CCl_4), R_f = 0.45. ^{1}H NMR (CD_3CN) δ 1.23 (t, 3H, J = 14 Hz, CH_3), 3.93 (q, 2H, J = 20.9 Hz, CH_2), 4.12 (t, 2H, J = 11.3 Hz, CH_2), 4.25 (t, 2H, J = 11.4 Hz, CH_2), 5.49 (s, 2H, CH_2Cl), 5.66 (s, 2H, CH_2). ^{13}C NMR (CD_3CN) δ 12.2, 49.0, 49.5, 50.9, 61.1, 67.6. ^{14}N NMR (CD_3CN) δ -32.6, -29.8 (NO_2). IR (KBr): 3081, 3019, 2978, 2938, 1551, 1510, 1456, 1286, 1246, 1065, 1034, 762 cm^{-1}. Anal. Calcd. for $C_6H_{13}ClN_6O_6$ (324.25): C, 23.97; H, 4.36; N, 27.95. Found: C, 24.10; H, 4.33; N, 28.28.

1-Chloro-7-cyclohexyl-2,5,7-trinitro-2,5,7-triazaheptane (**1n**)**:** colorless plates, mp 100-102°C (from CCl_4), R_f = 0.5. ^{1}H NMR (CD_3CN) δ 1.26-1.18 (m, 1H), 1.41-1.35 (m, 2H), 1.66 (d, 1H, *J* = 13.3 Hz), 1.81-1.74 (m, 2H), 1.86 (m, 4H), 4.13 (t, 2H, *J* = 11.5 Hz, $NCH_2C\underline{H}_2$), 4.21 (t, 1H, *J* = 9.6 Hz, NCH), 4.24 (t, 2H, *J* = 11.6 Hz, $NC\underline{H}_2CH_2$), 5.53 (s, 2H, CH_2Cl), 5.67 (s, 2H, CH_2). ^{13}C NMR (CD_3CN) δ 25.9, 26.5, 29.8, 49.5, 50.6, 61.1, 64.3, 65.3. ^{14}N NMR (CD_3CN) δ -32.5, -29.8 (NO_2). IR (KBr): 2947, 2859, 1565, 1534, 1456, 1421, 1334, 1275, 1151, 1129, 1058, 1001, 759, 661, 607 cm^{-1}. Anal. Calcd. for $C_{10}H_{19}ClN_6O_6$ (378.34): C, 33.86; H, 5.40; N, 23.69. Found: C, 33.79; H, 5.45; N, 23.63.

1-Bromo-9-chloro-3,5,8-trinitro-2,5,8-triazanonane (**1o**)**:** colorless plates, mp 100-102°C (from CCl_4), R_f = 0.43. ^{1}H NMR (CD_3CN) δ 3.68 (t, 2H, *J* = 13.3 Hz, $NCH_2C\underline{H}_2Br$), 4.14 (t, 2H, *J* = 11.5 Hz, $NC\underline{H}_2CH_2Br$), 4.26-4.33 (q, 4H, $NC\underline{H}_2C\underline{H}_2N$), 5.58 (s, 2H, CH_2Cl), 5.68 (s, 2H, CH_2). ^{13}C NMR (CD_3CN) δ 27.5, 48.5, 55.1, 53.7, 60.2, 67.1. ^{14}N NMR (CD_3CN) δ -32.5, -30.2 (NO_2). IR (KBr): 3075, 3023, 2955, 1547, 1513, 1458, 1446, 1413, 1334, 1291, 1276, 1248, 1218, 1195, 1155, 1124, 1084, 1064, 1032, 999, 951, 916, 877, 819, 759 cm^{-1}. Anal. Calcd. for $C_6H_{12}BrClN_6O_6$ (403.14): C, 18.99; H, 3.19; N, 22.14. Found: C, 19.07; H, 3.23; N, 22.03.

1-Bromo-9-chloro-3,6,8,11-tetranitro-3,6,8,11-tetraazaundecane (**1p**)**:** colorless plates, mp 163-165°C (from $C_2H_4Cl_2$), R_f = 0.45. ^{1}H NMR (CD_3CN) δ 3.68 (t, 2H, *J* = 12.7 Hz, CH_2Br), 4.11-4.17 (q, 4H, $C\underline{H}_2NC\underline{H}_2$), 4.26 (t, 2H, *J* = 11.7 Hz, $CH_2C\underline{H}_2N$), 5.70 (s, 2H, CH_2Cl), 5.82 (s, 2H, $CH_2NC\underline{H}_2$), 5.85 (s, 2H, NCH_2N). ^{13}C NMR (CD_3CN) δ 27.7, 49.9, 50.0, 53.8, 59.2, 64.4, 66.3. ^{14}N NMR (CD_3CN) δ -35.1, -33.5, -29.1 (NO_2). IR (KBr): 3085, 3029, 1574, 1534, 1457, 1443, 1418, 1330, 1271, 1248, 1236, 1218, 1133, 1112, 1070, 917, 764, 667, 640, 607 cm^{-1}.

Anal. Calcd. for $C_7H_{14}BrClN_8O_8$ (453.59): C, 18.54; H, 3.11; N, 24.70. Found: C, 18.62; H, 3.20; N, 24.57.

1,9-Dichloro-2,4,6,8-tetraitro-2,4,6,8-tetraazanonane (**1q**): colorless plates, mp 183-186°C (from $C_2H_4Cl_2$) (lit. [7] mp 195-198°C), R_f = 0.4. ^{1}H NMR (CD_3CN) δ 5.82 (s, 2H, CH_2Cl), 5.83 (s, 2H, NCH_2), 5.88 (s, 2H, NCH_2N). ^{13}C NMR (CD_3CN) δ 60.2, 65.5, 65.9. ^{14}N NMR (CD_3CN) δ -33.4 (NO_2). IR (KBr): 3069, 1586, 1565, 1443, 1370, 938, 912 cm^{-1}. Anal. Calcd. For $C_5H_{10}Cl_2N_8O_8$ (381.08): C, 15.76; H, 2.65; N, 29.40. Found: C, 15.84; H, 2.69; N, 29.34.

1,8-Dichloro-2,7-dinitro-2,7-diazaoctane (**1r**): colorless needles, mp 91-94°C (from CCl_4) (lit. [8] mp 82-83°C), R_f = 0.57. ^{1}H NMR ($CDCl_3$) δ 1.88 (m, 2H, $C\underline{H_2}C\underline{H_2}$), 3.87 (s, 2H, CH_2N), 5.63 (s, 2H, CH_2Cl). ^{13}C NMR ($CDCl_3$) δ 24.5, 50.3, 58.9. ^{14}N NMR ($CDCl_3$) δ -34.1 (NO_2). IR (KBr): 3059, 3003, 2966, 2955, 2933, 2864, 1535, 1452, 1298, 1268, 1154, 1058, 920, 908, 629 cm^{-1}. Anal. Calcd. for $C_6H_{12}Cl_2N_4O_4$ (275.09): C, 26.20; H, 4.40; N, 20.37. Found: C, 26.26; H, 4.42; N, 20.28.

References

1. *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, **2014**
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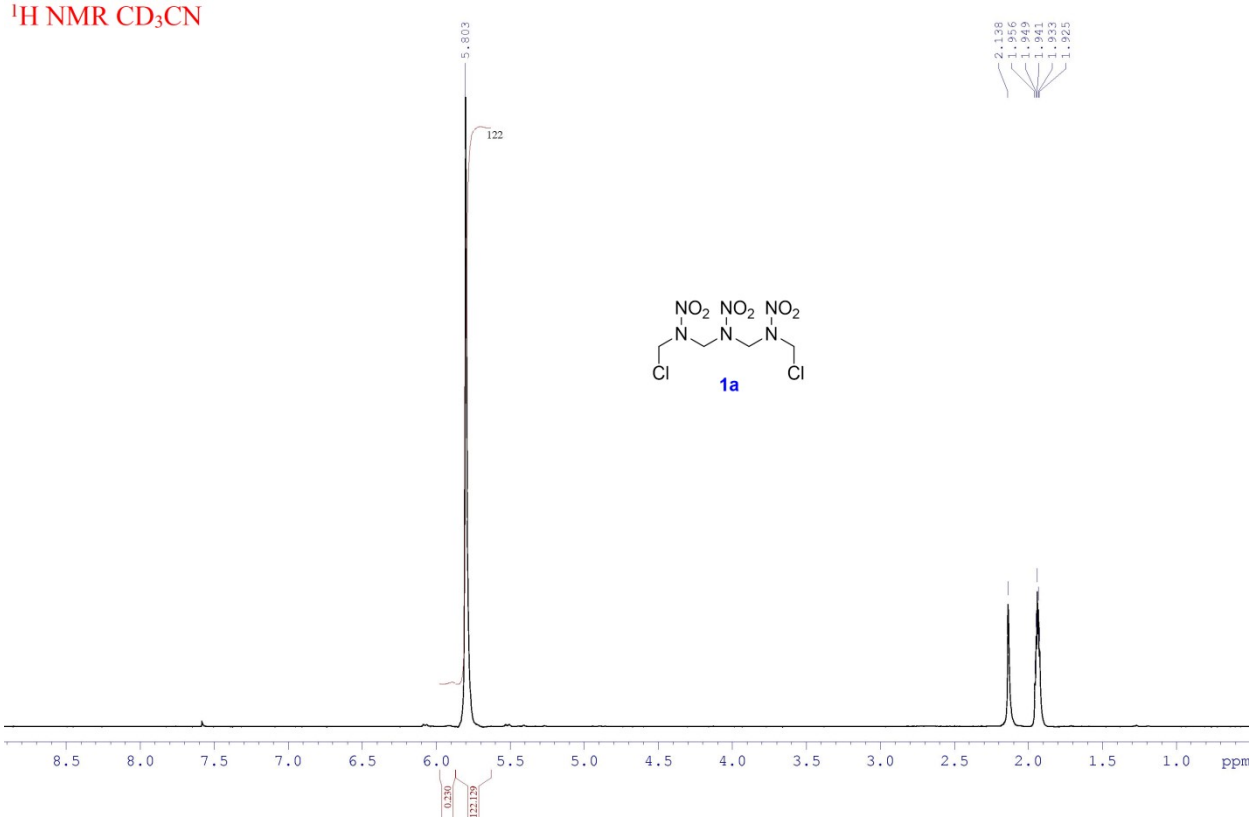
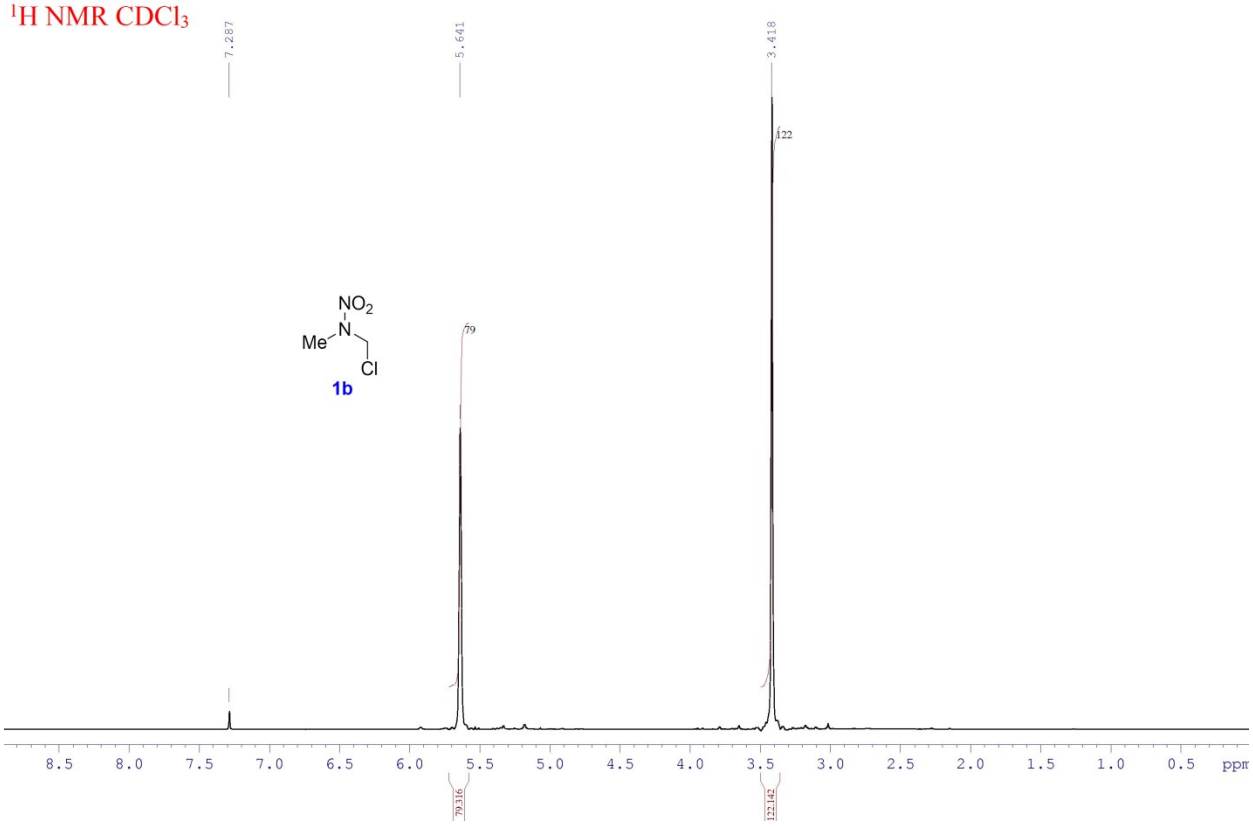
NMR spectra

^{1}H NMR CD_3CN



^{1}H NMR $CDCl_3$



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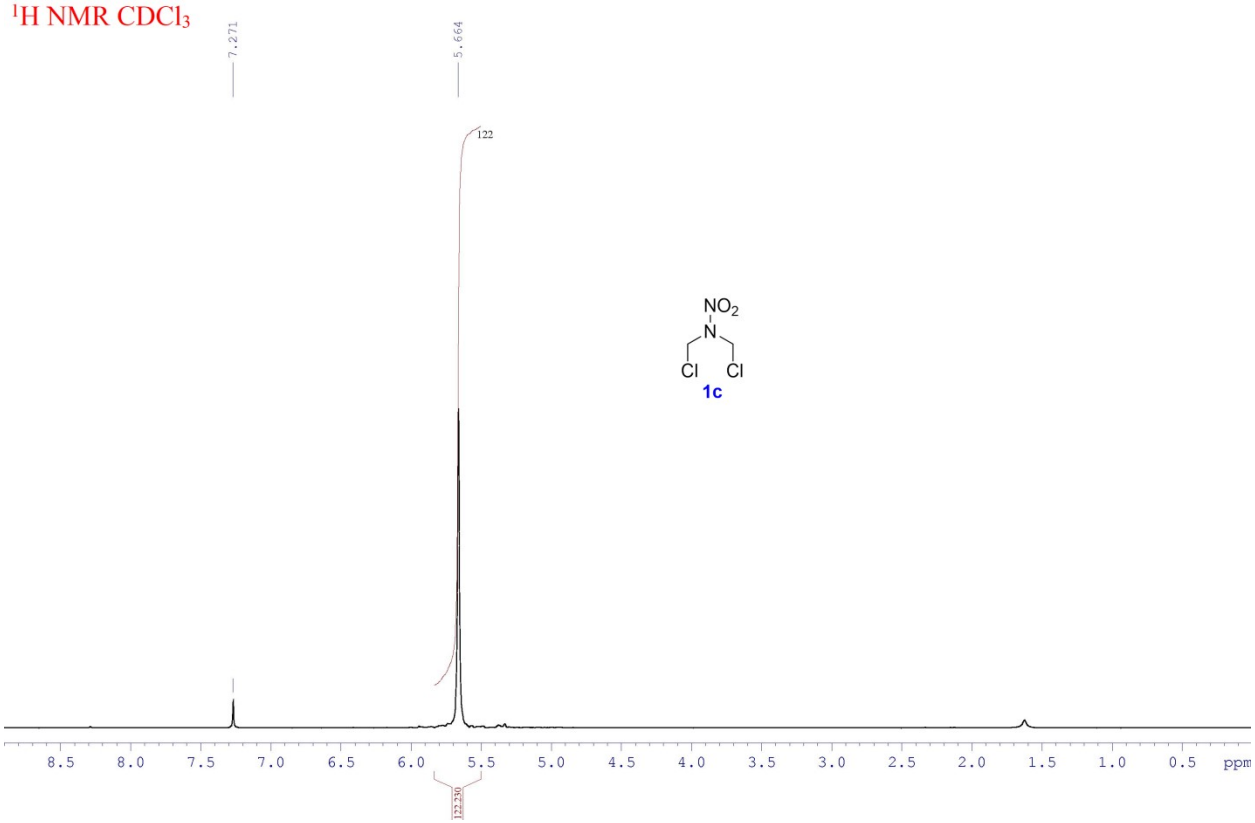

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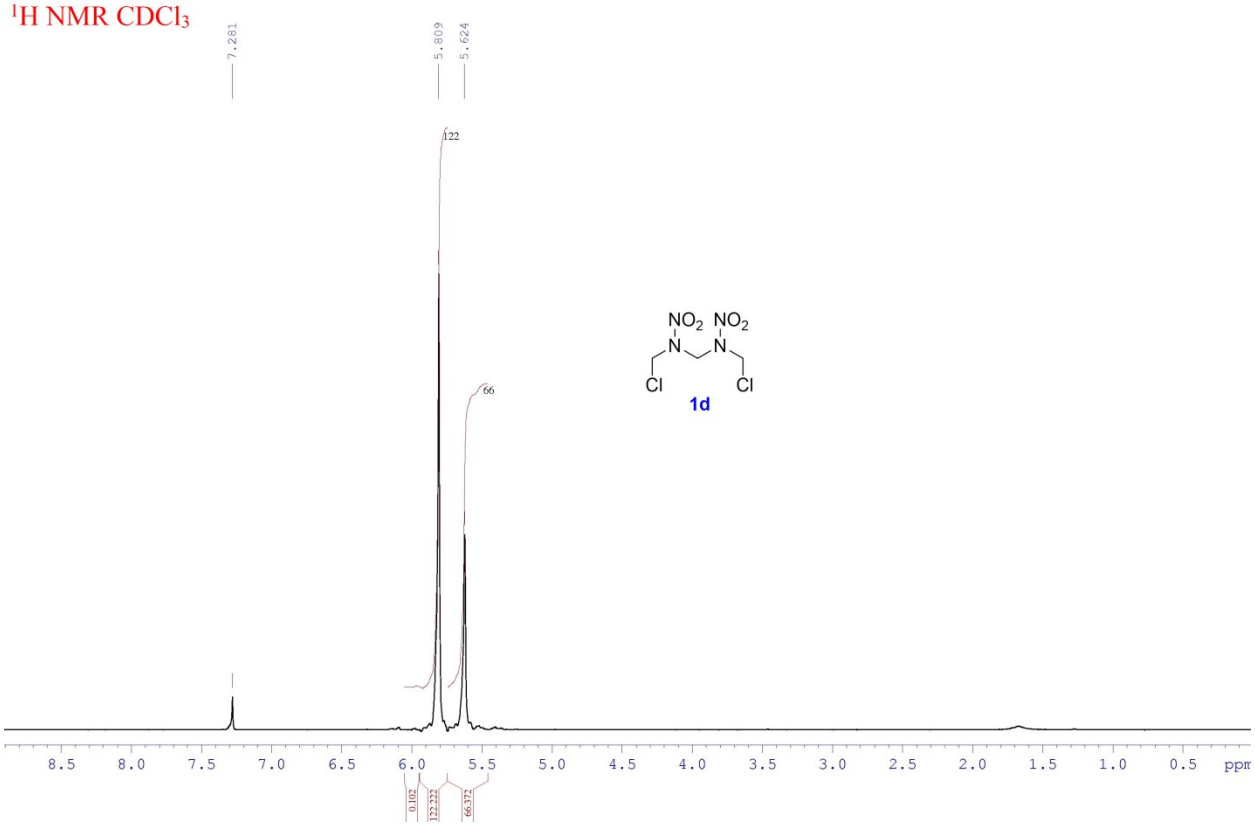

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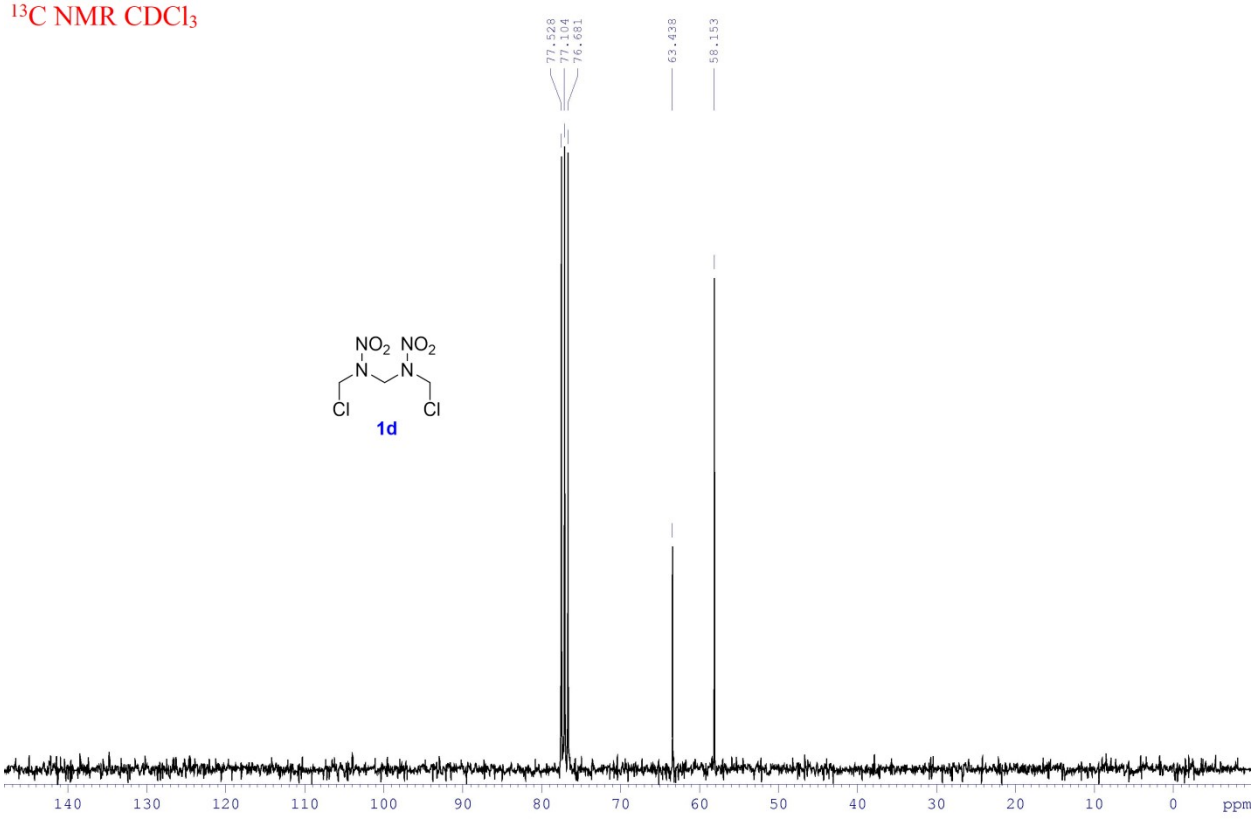

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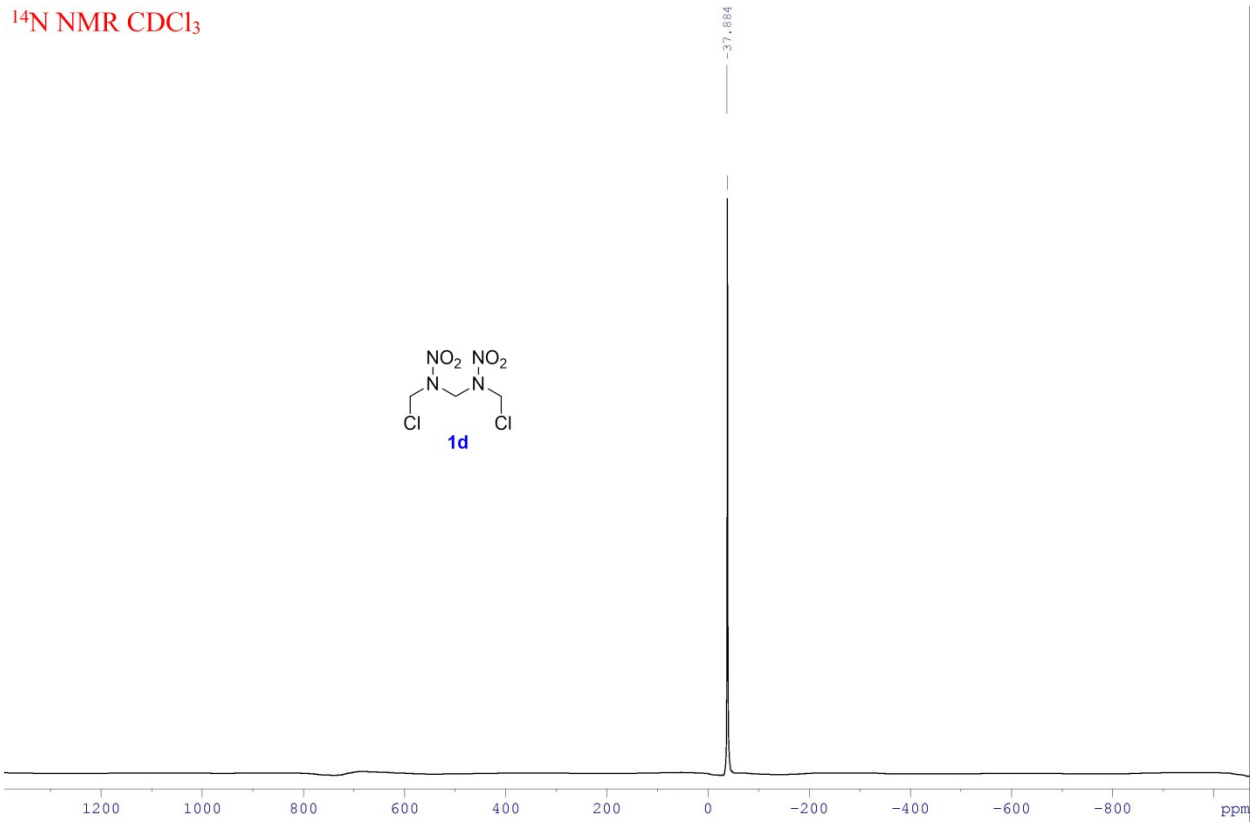

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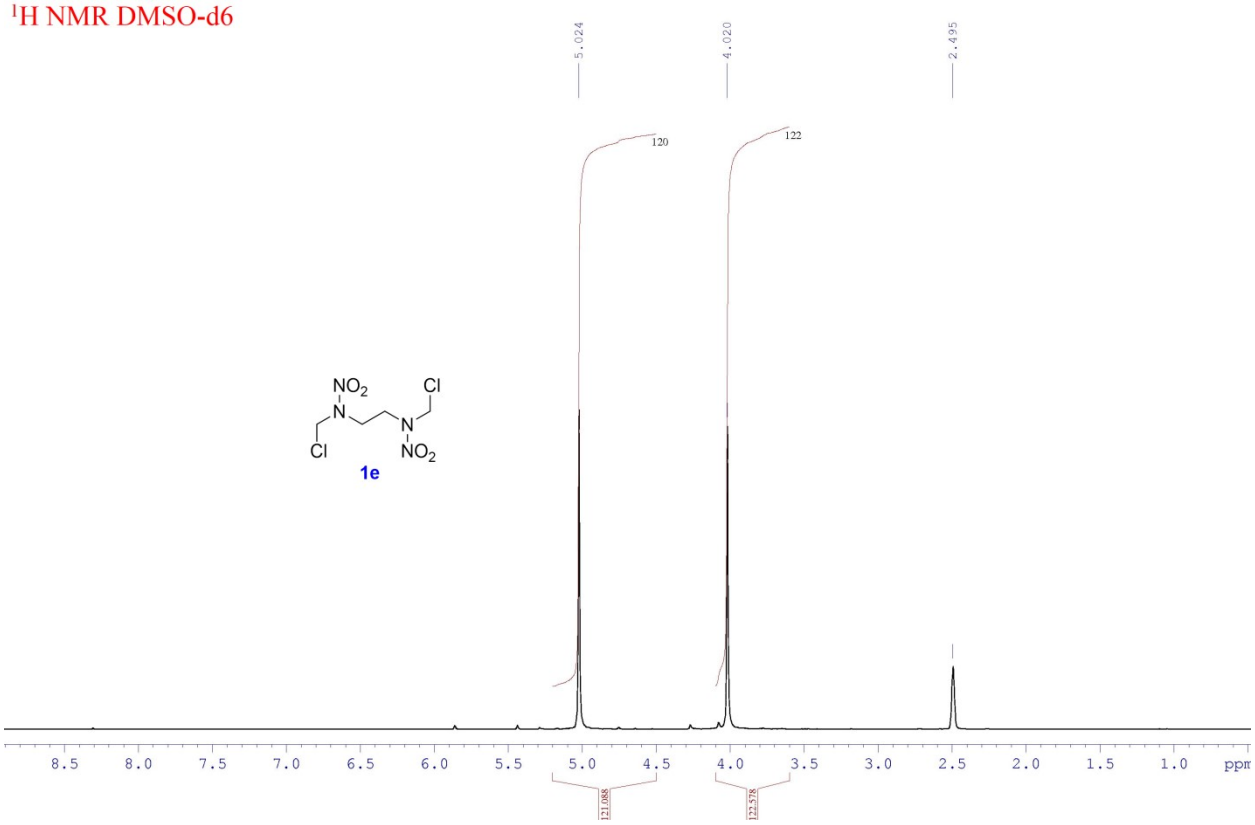

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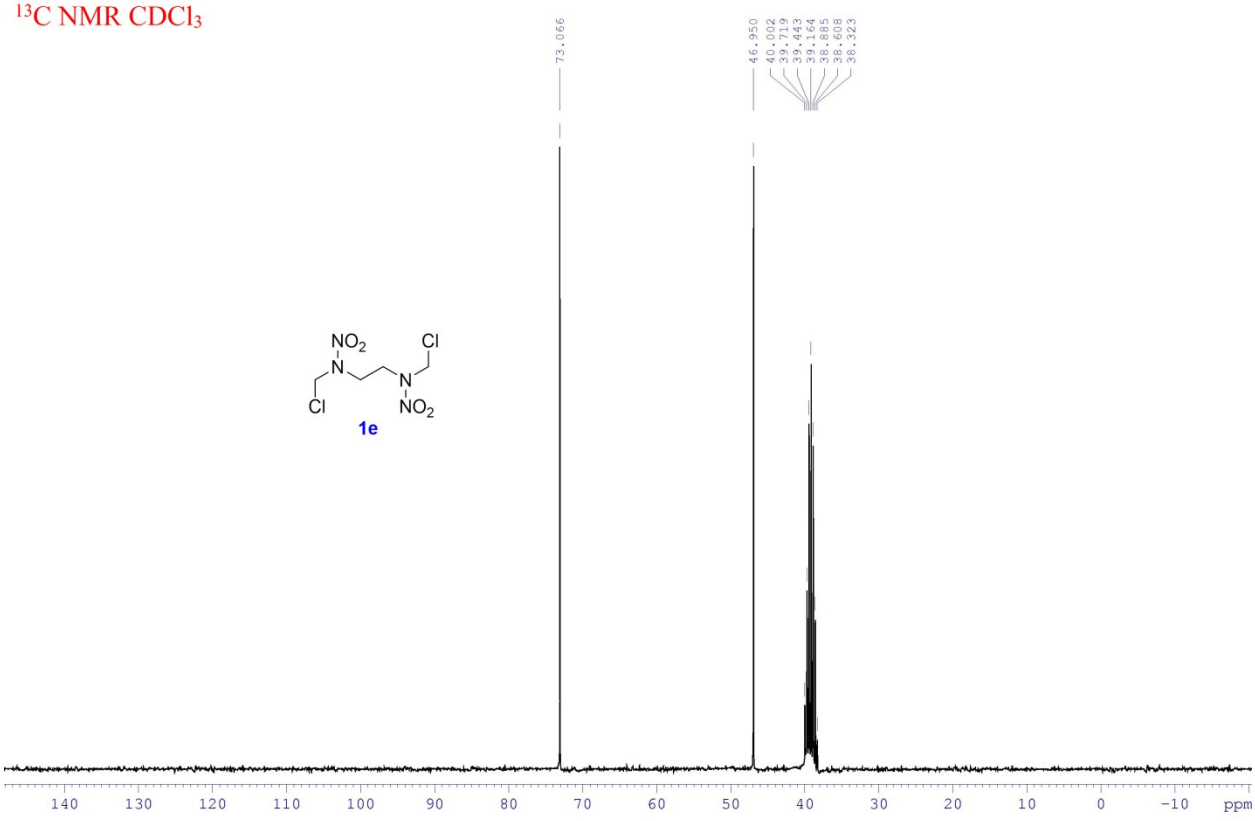

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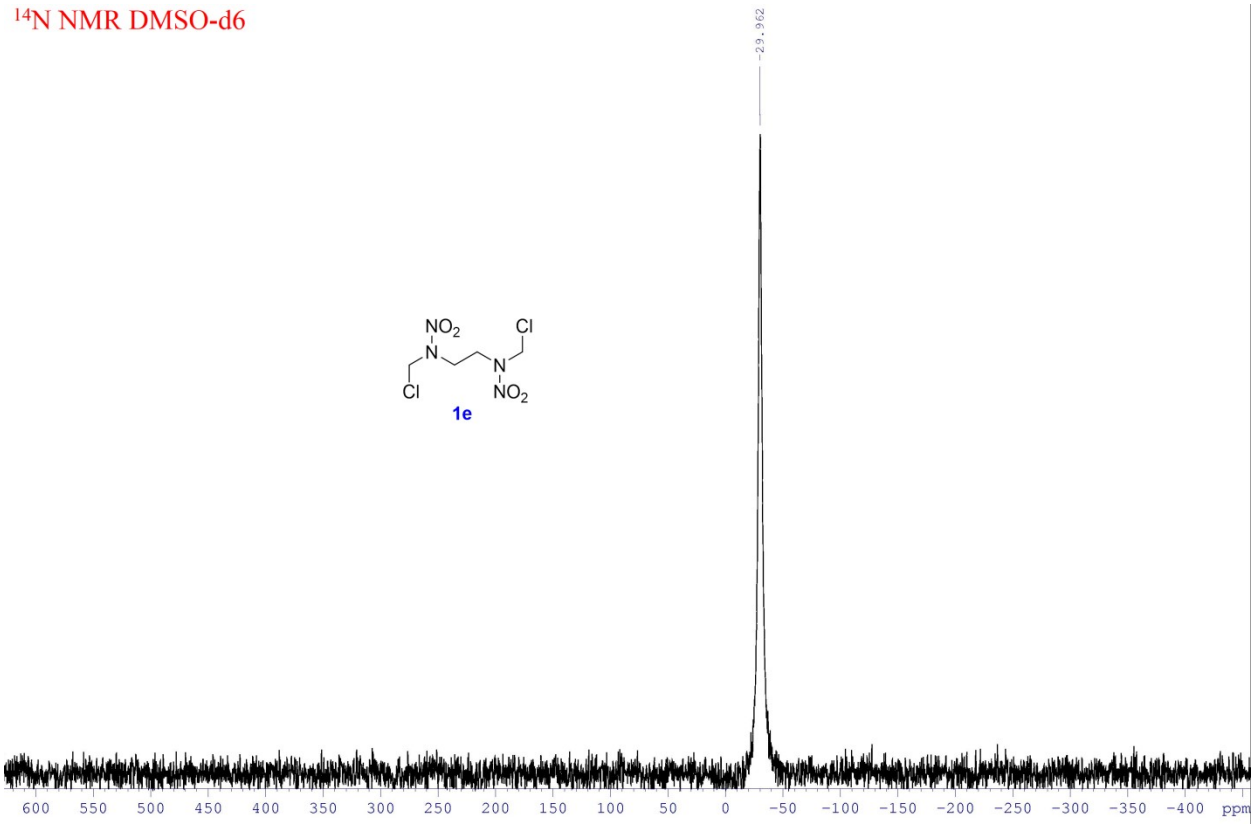

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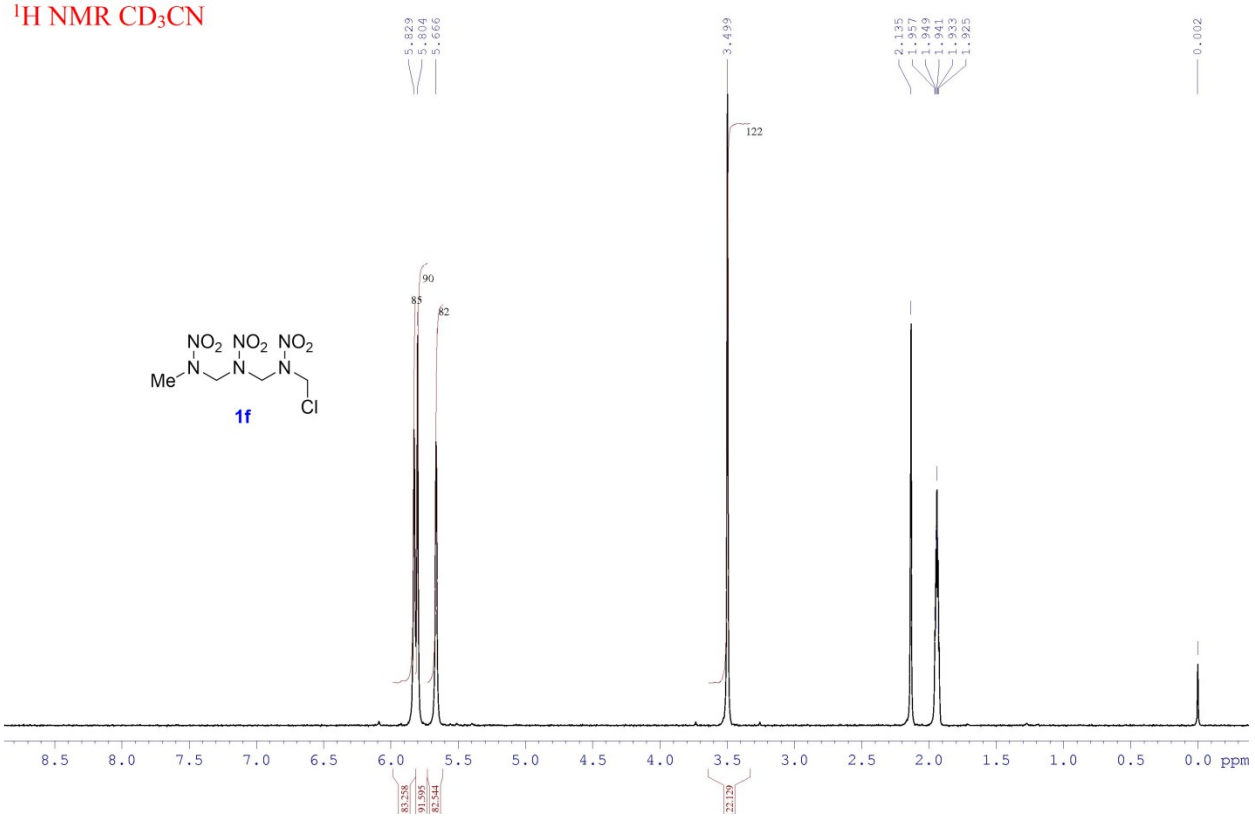

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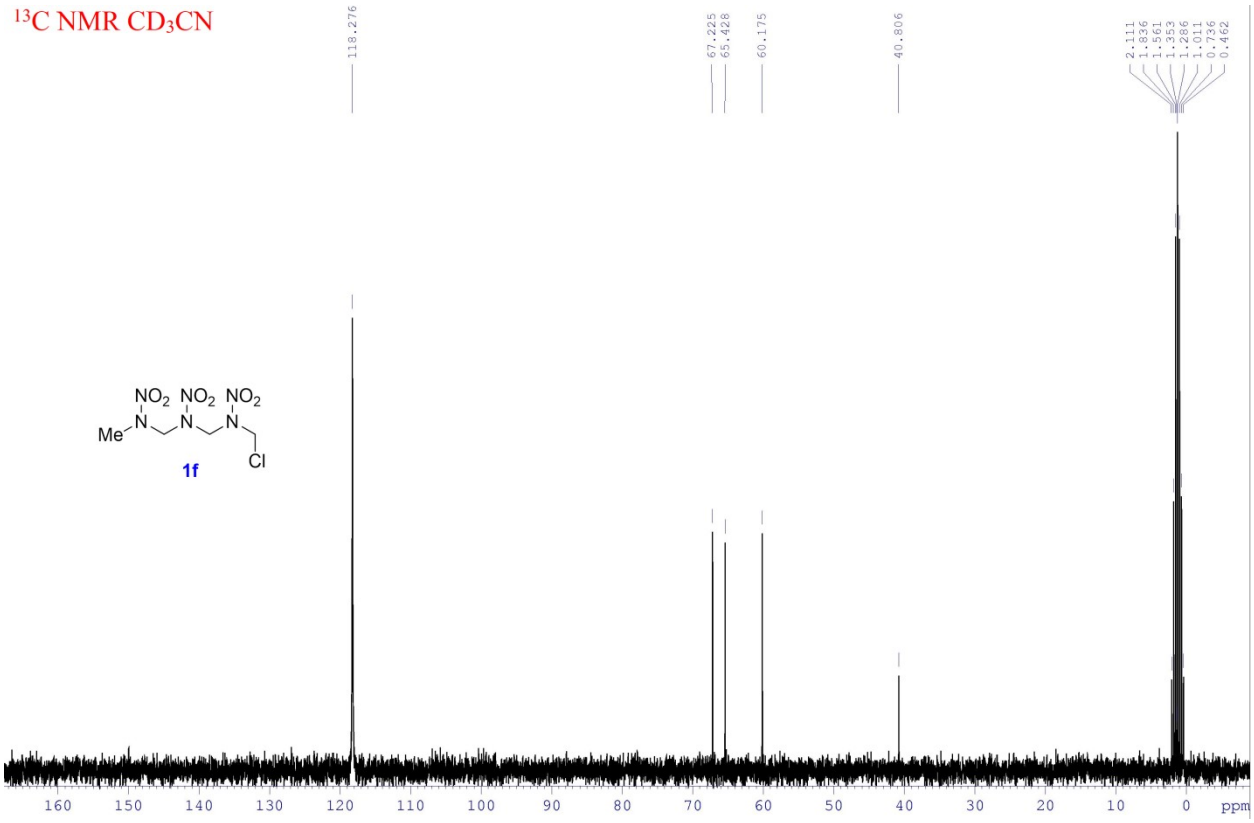

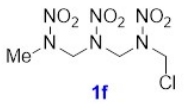

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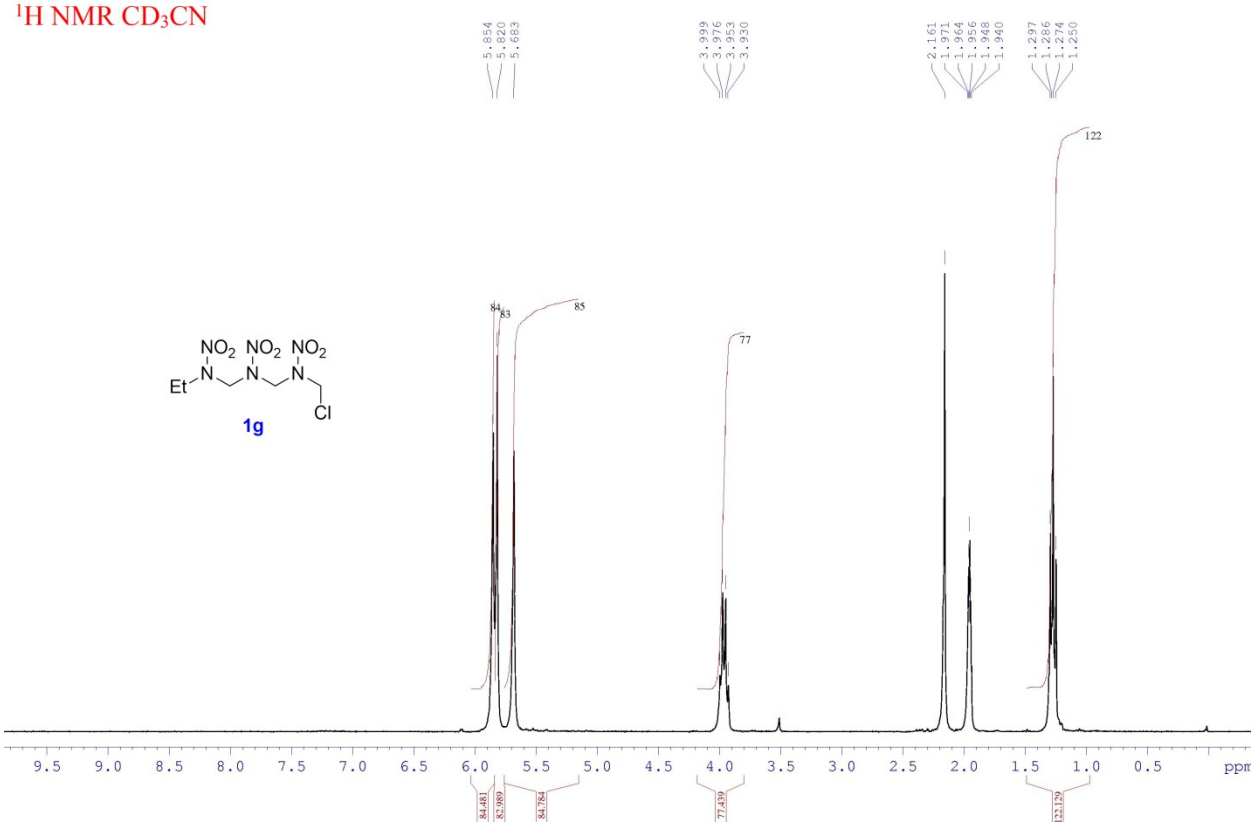

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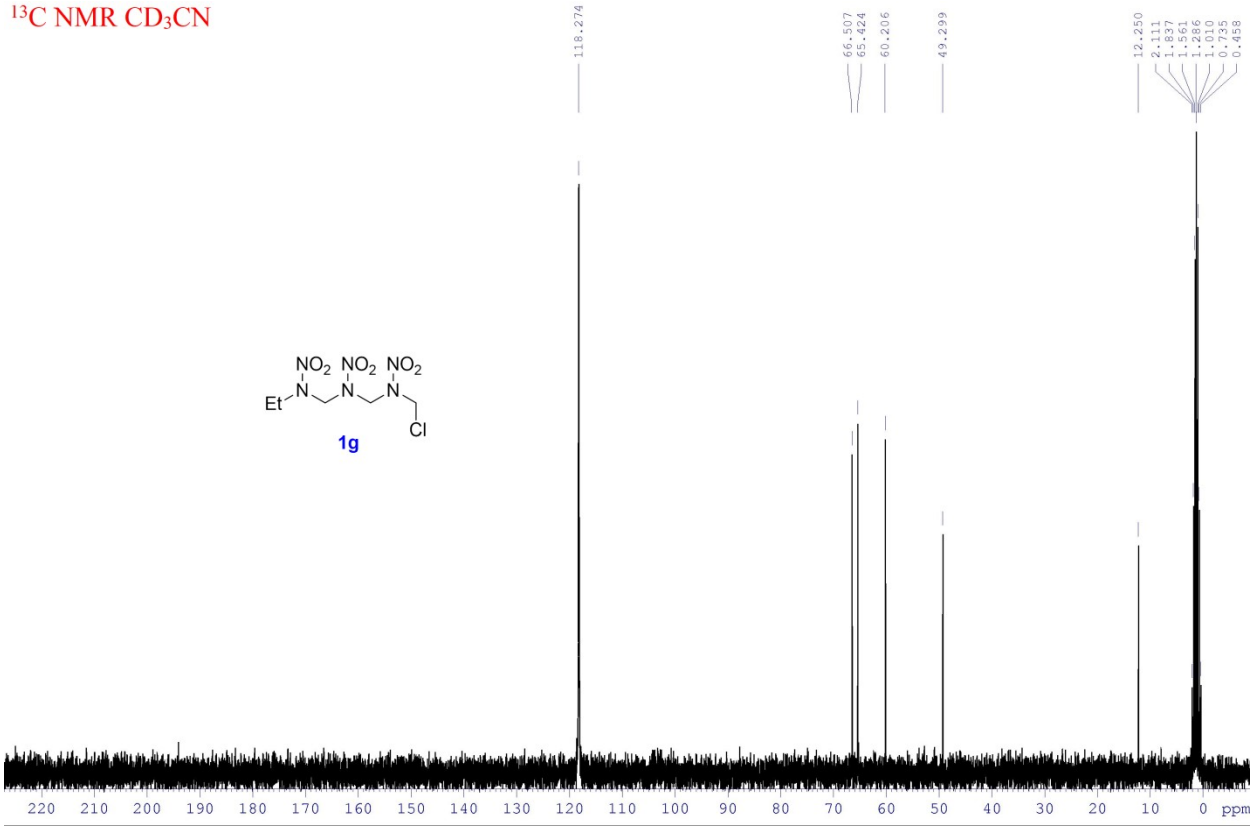

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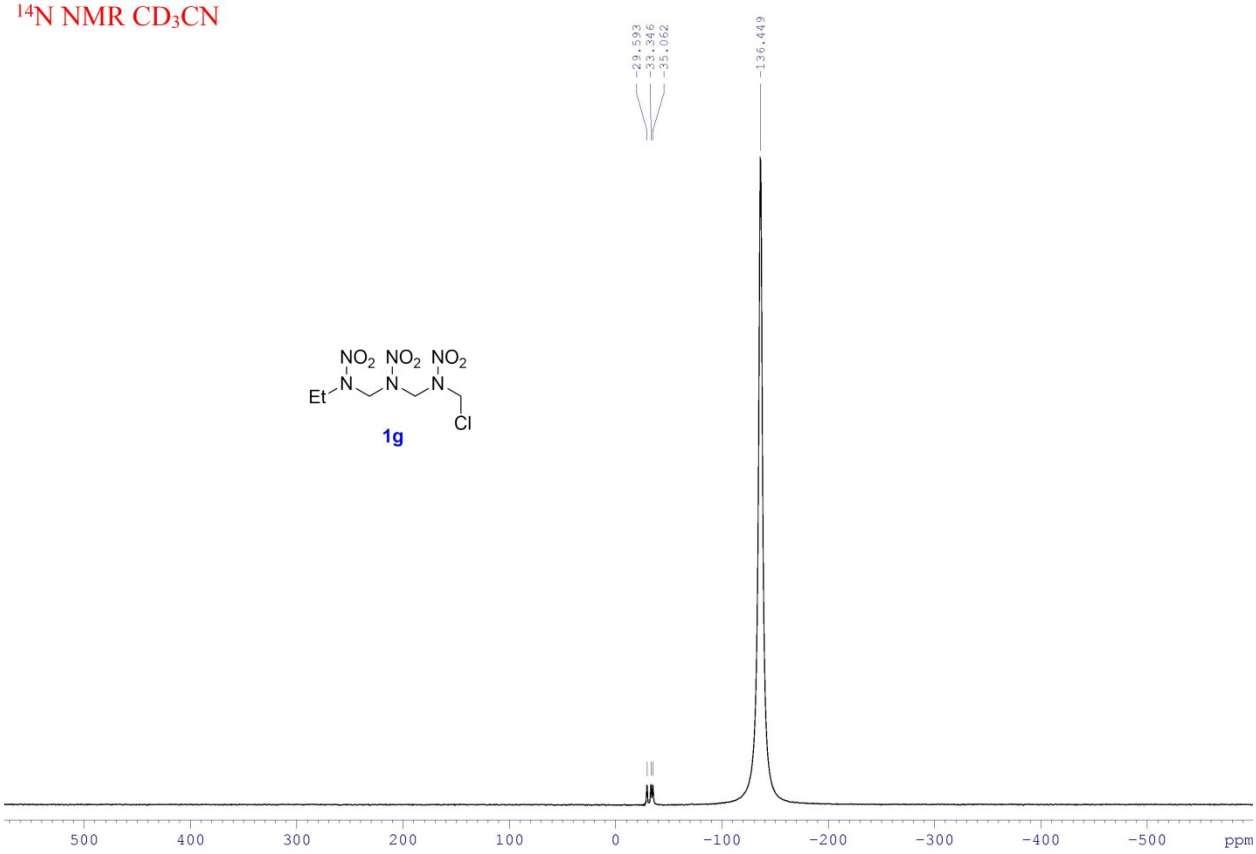

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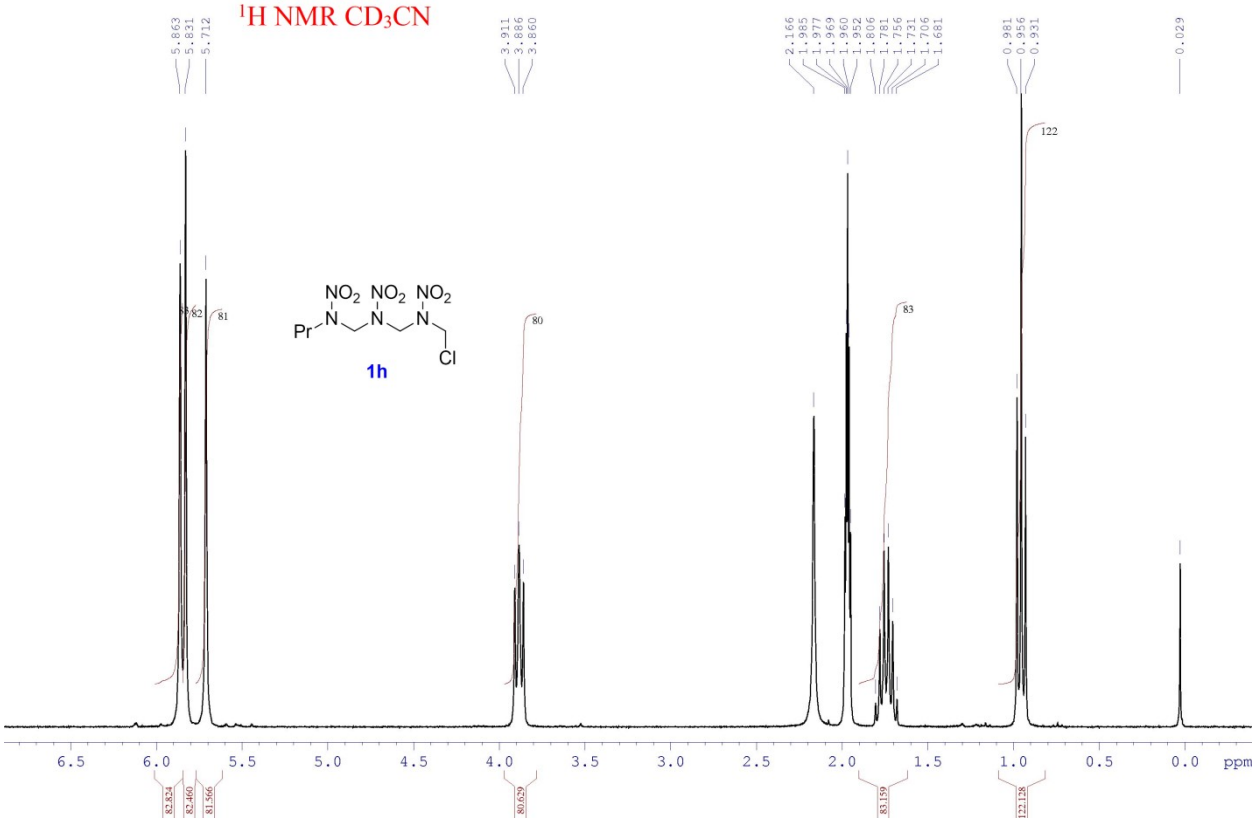

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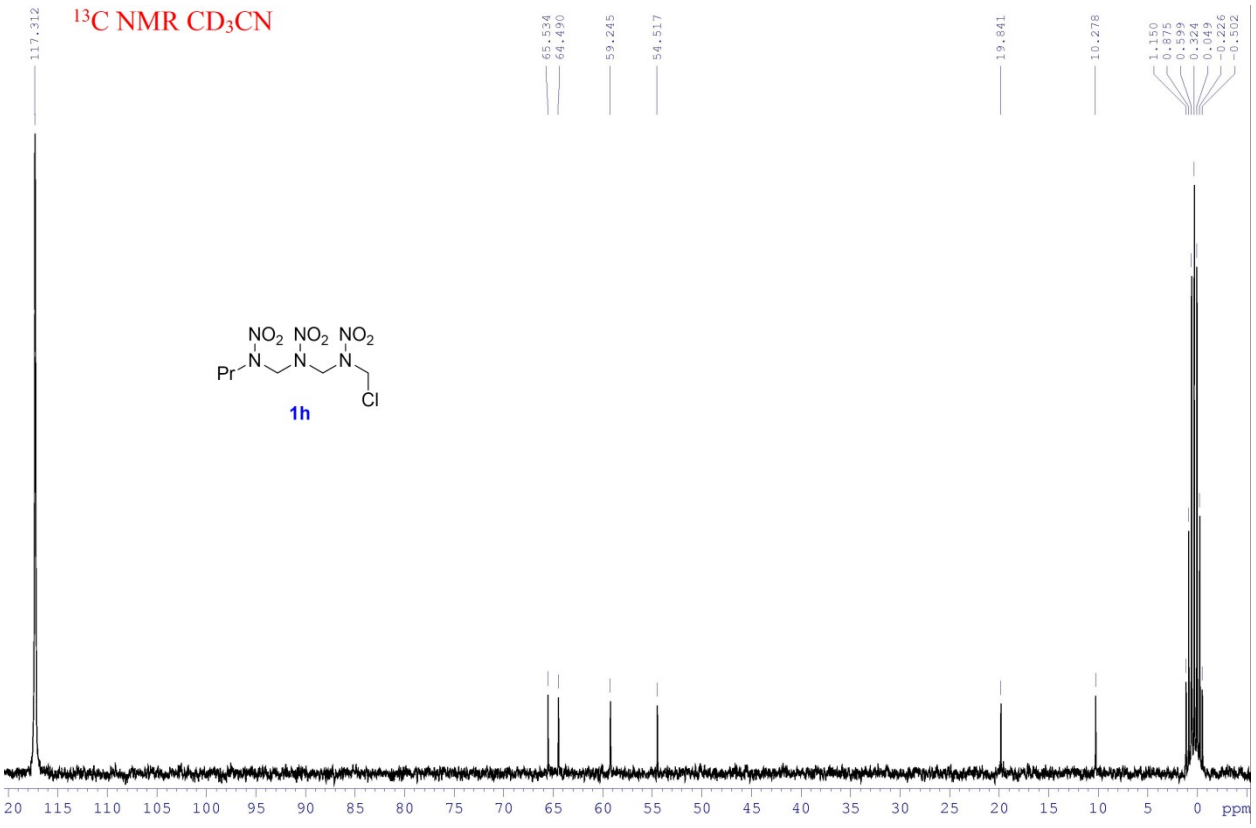

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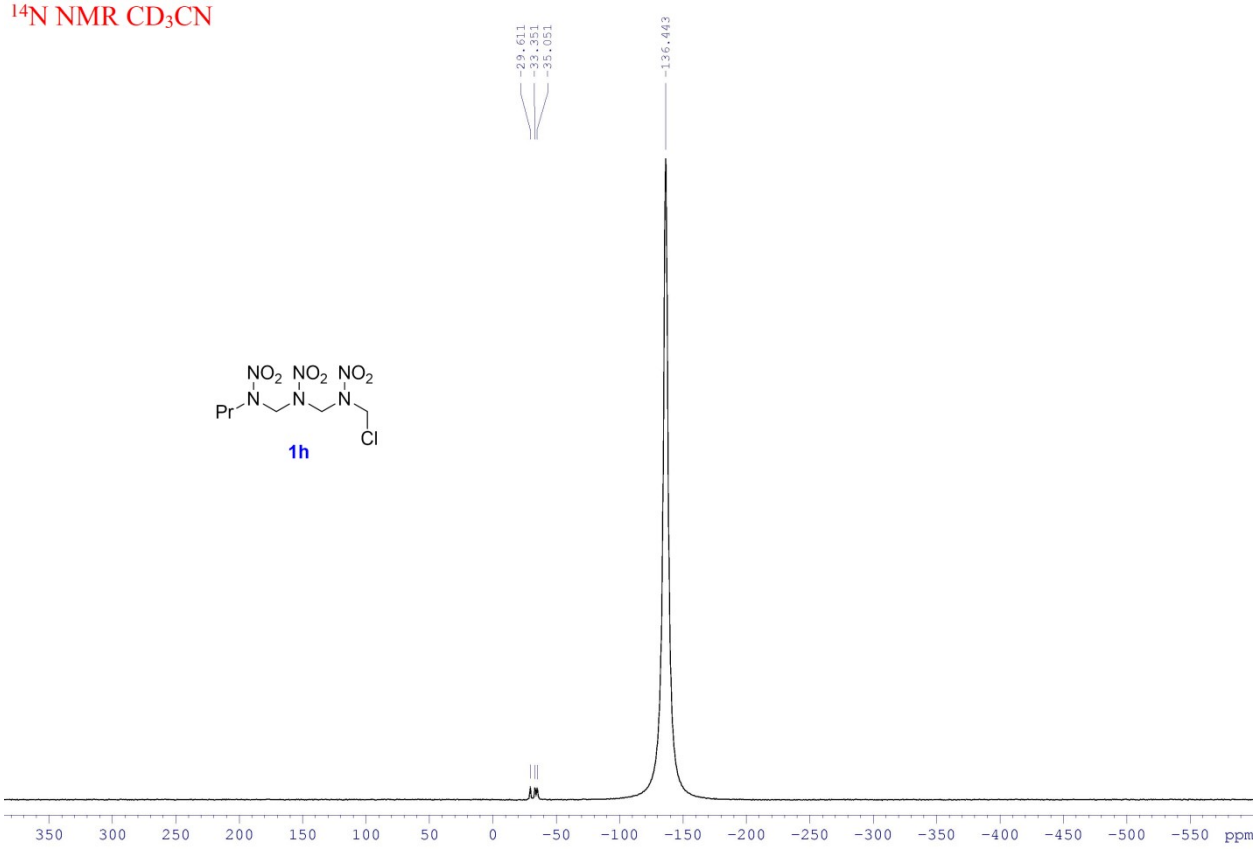

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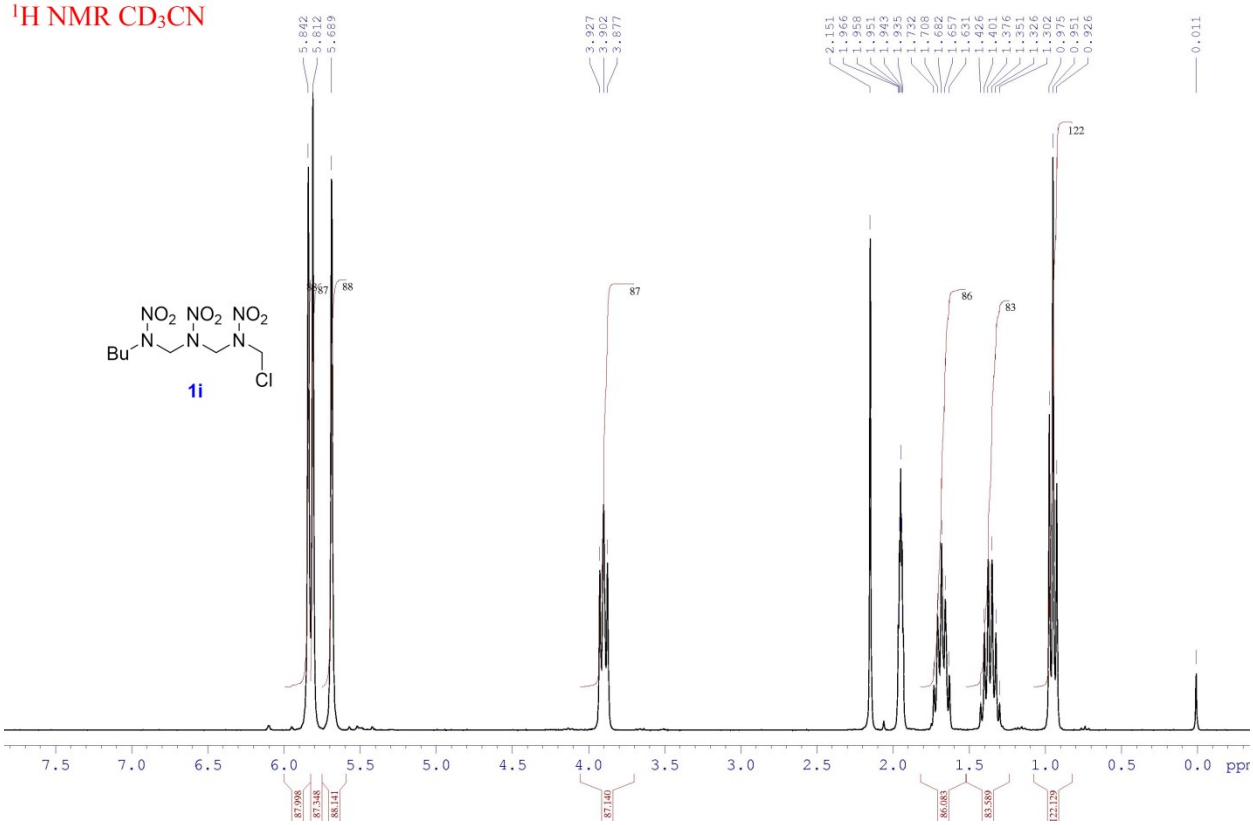

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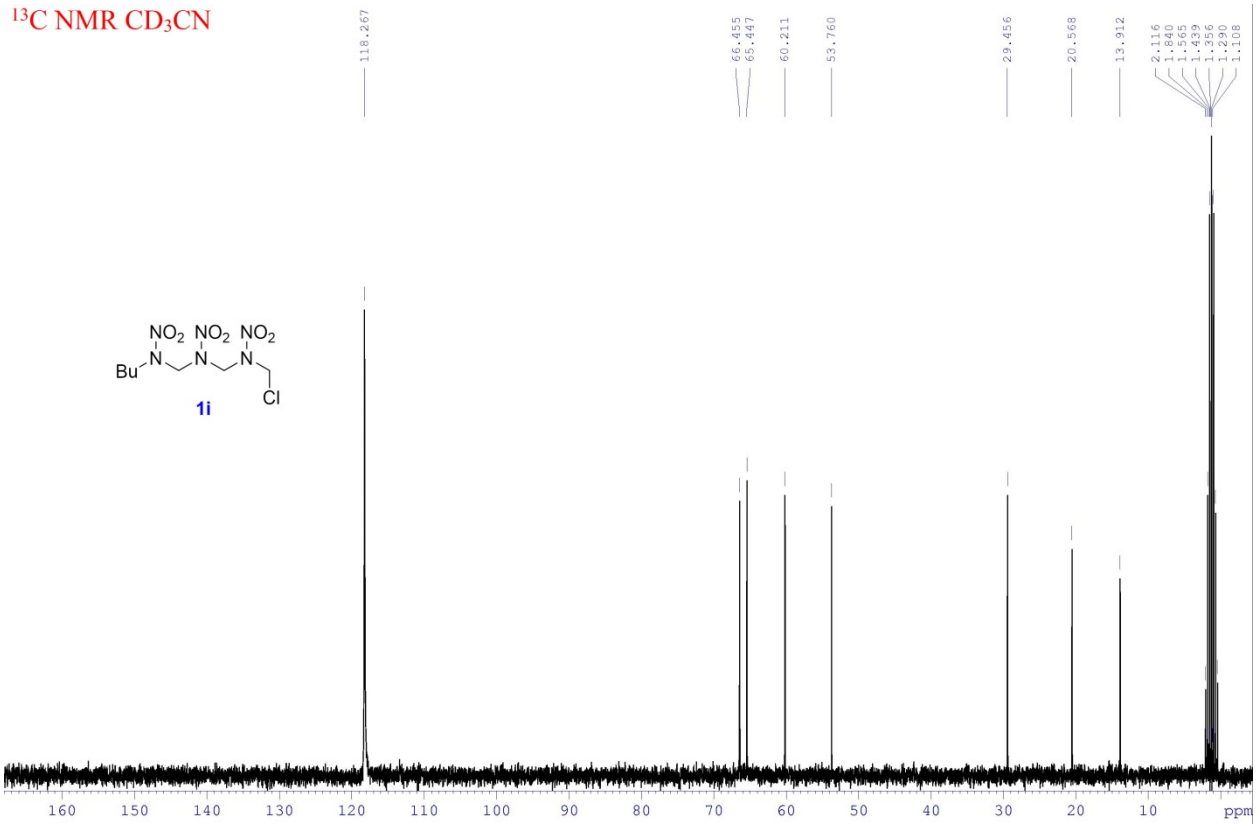

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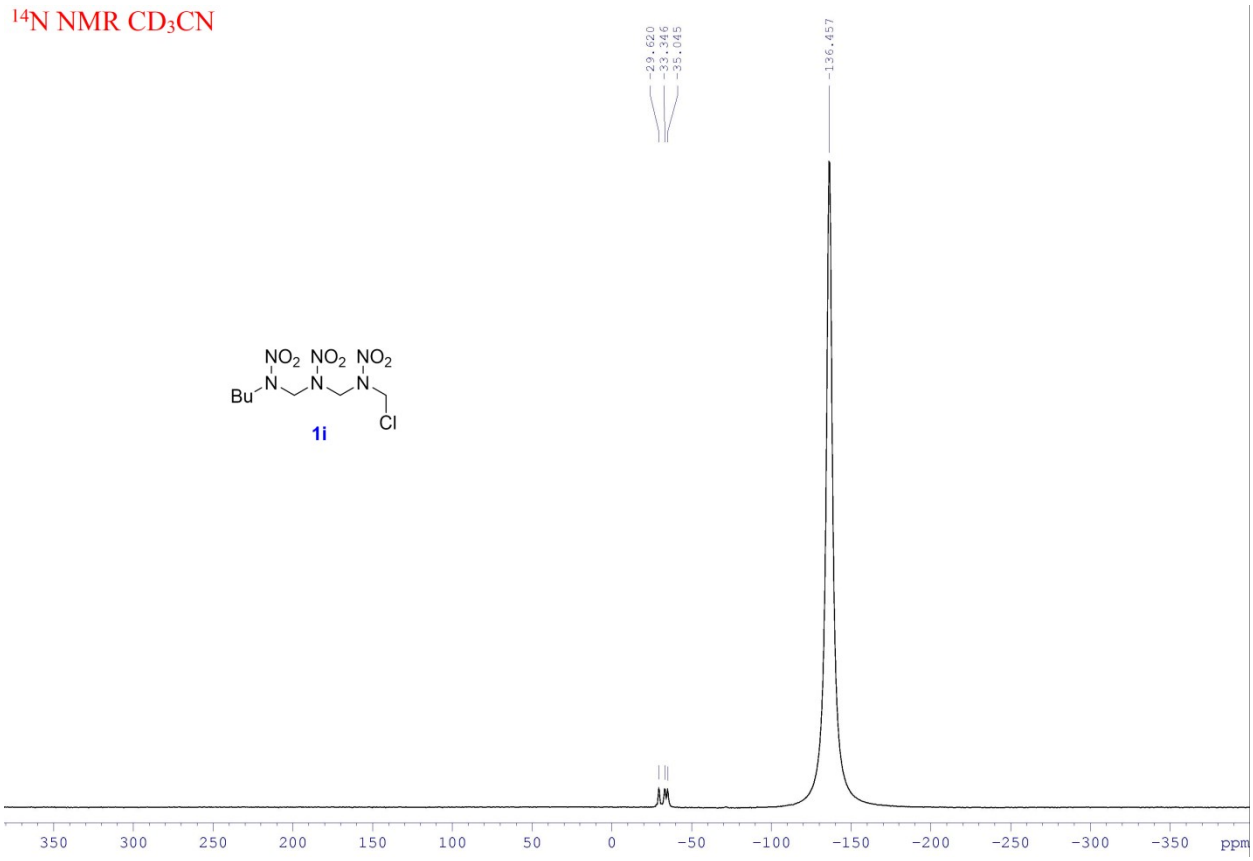

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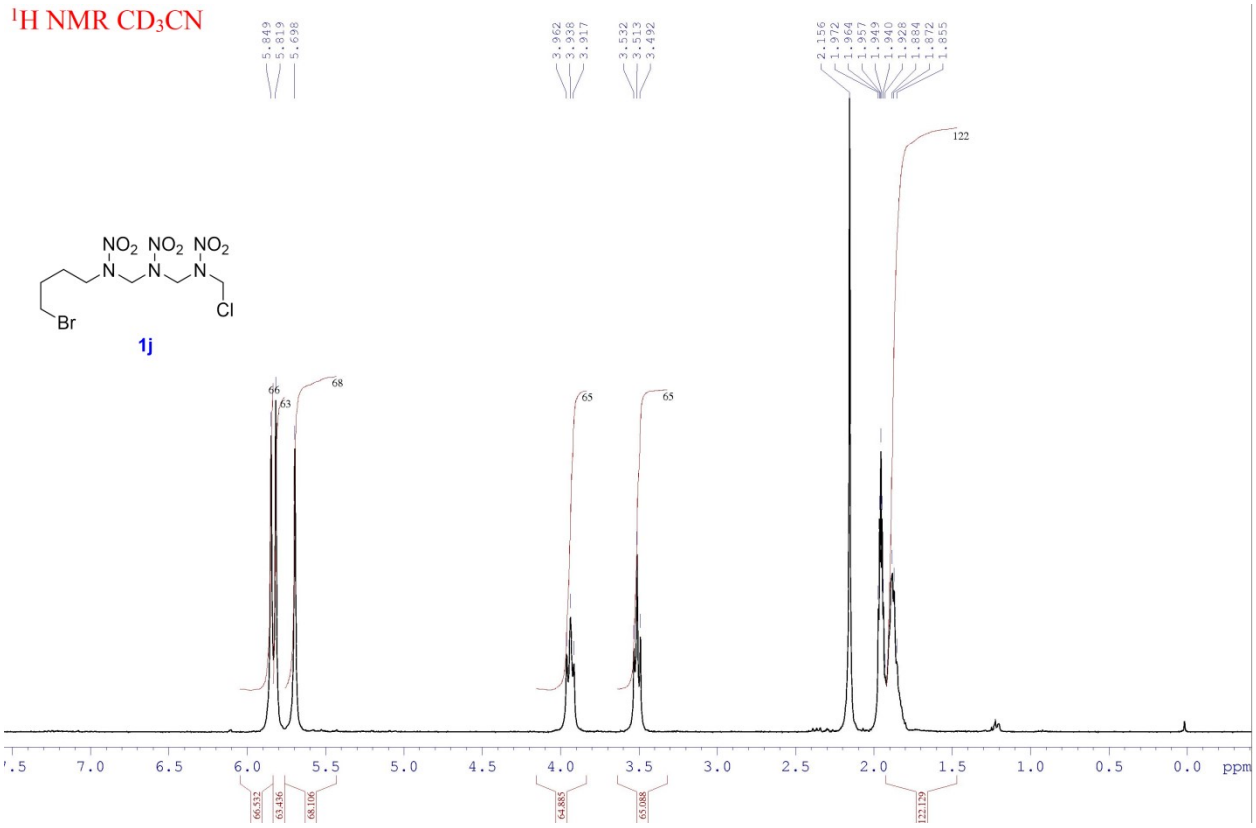

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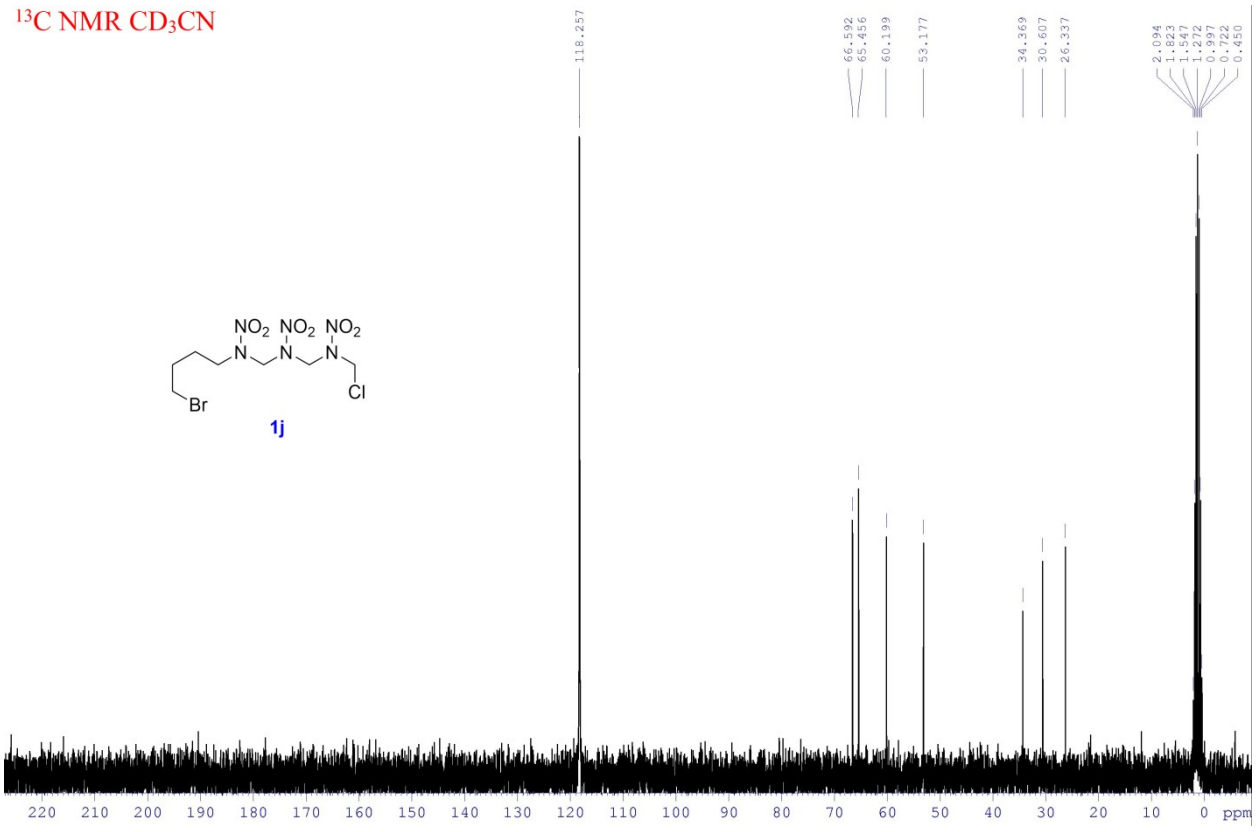

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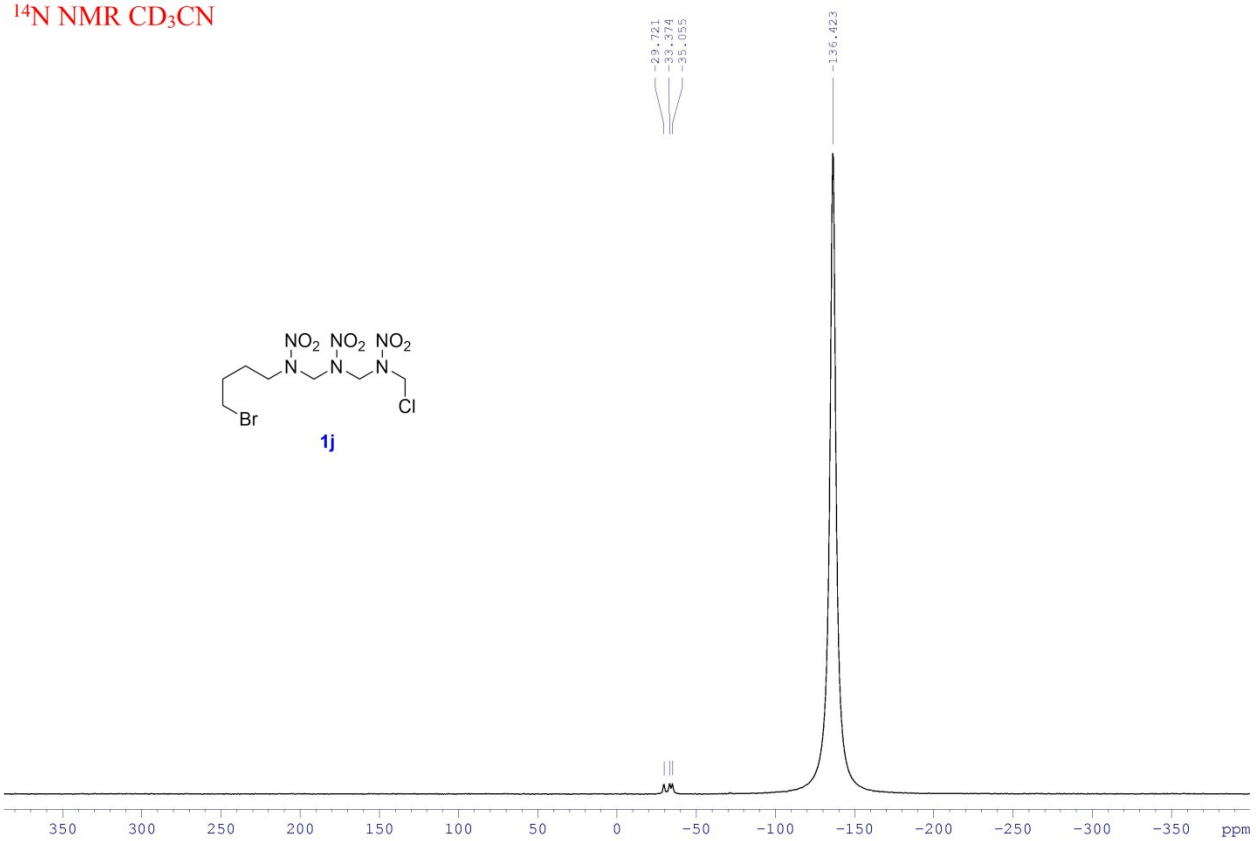

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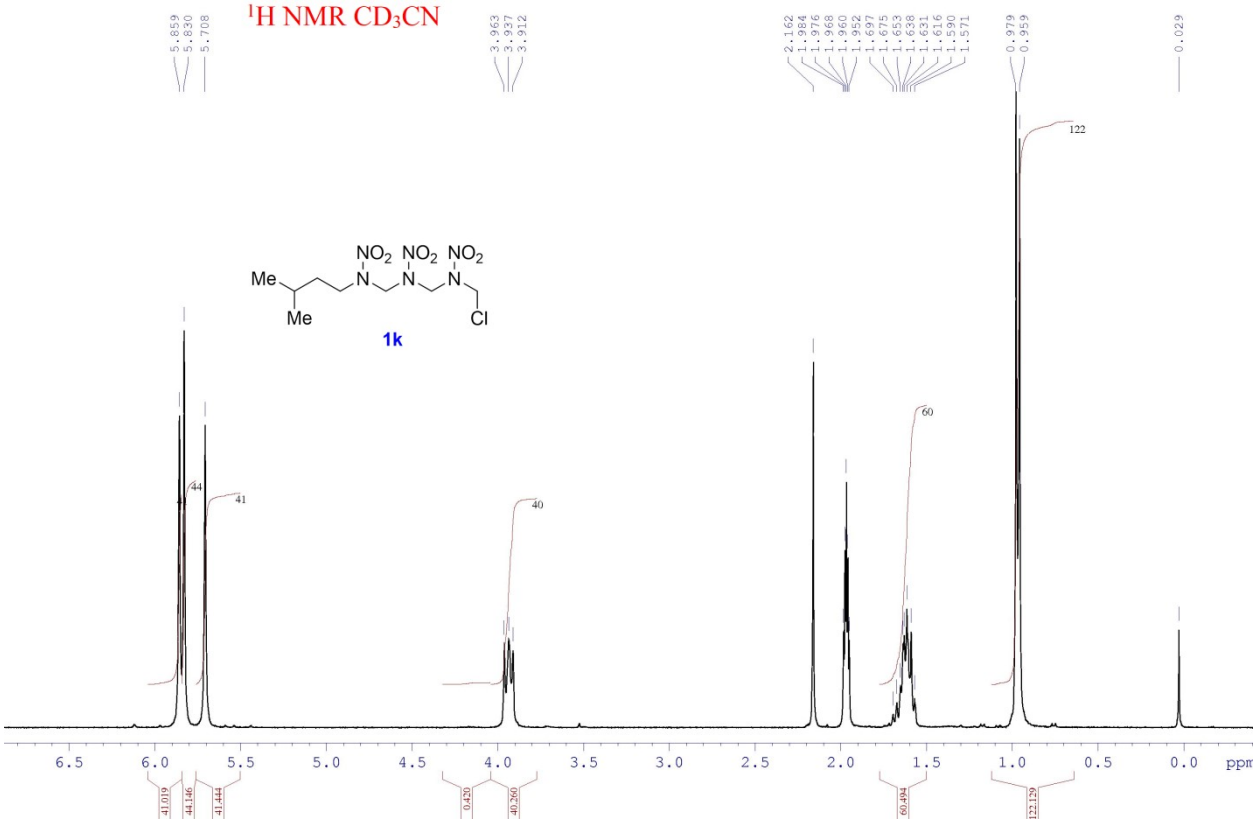

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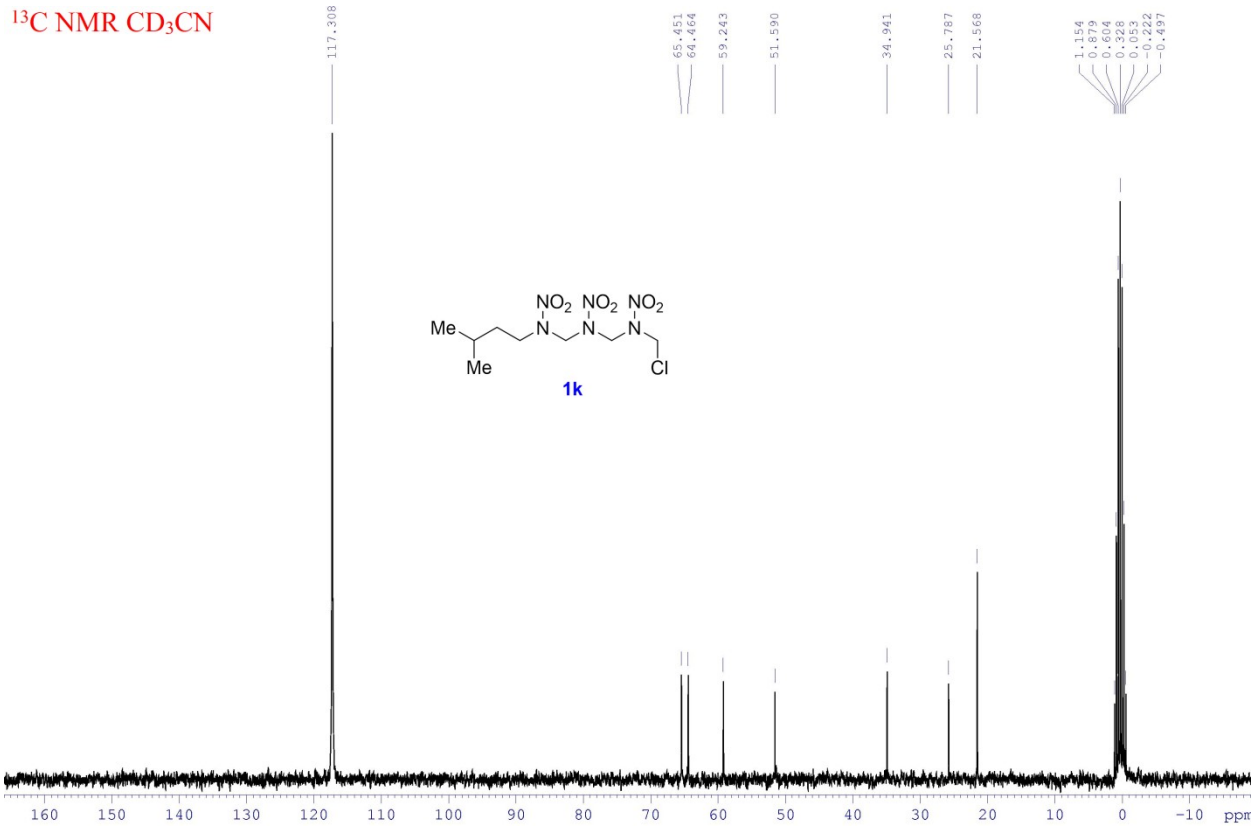

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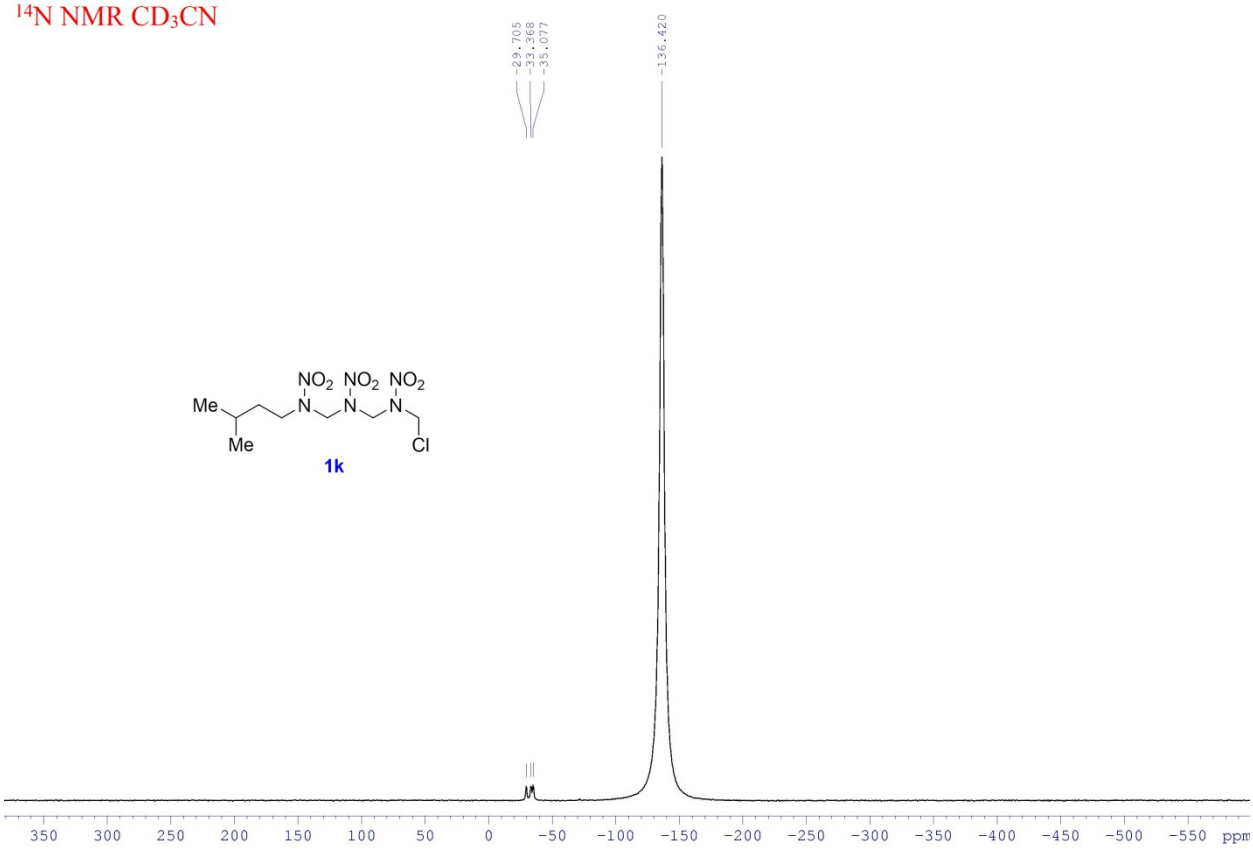

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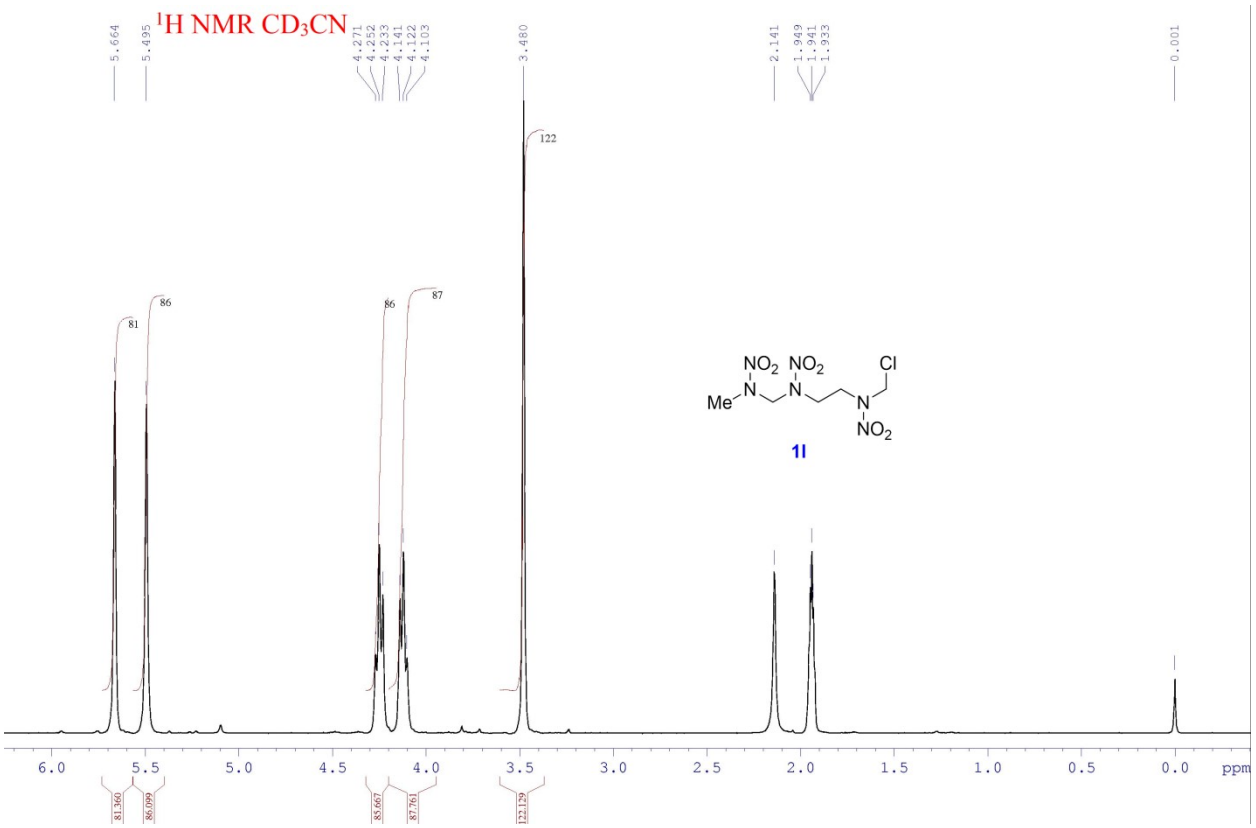

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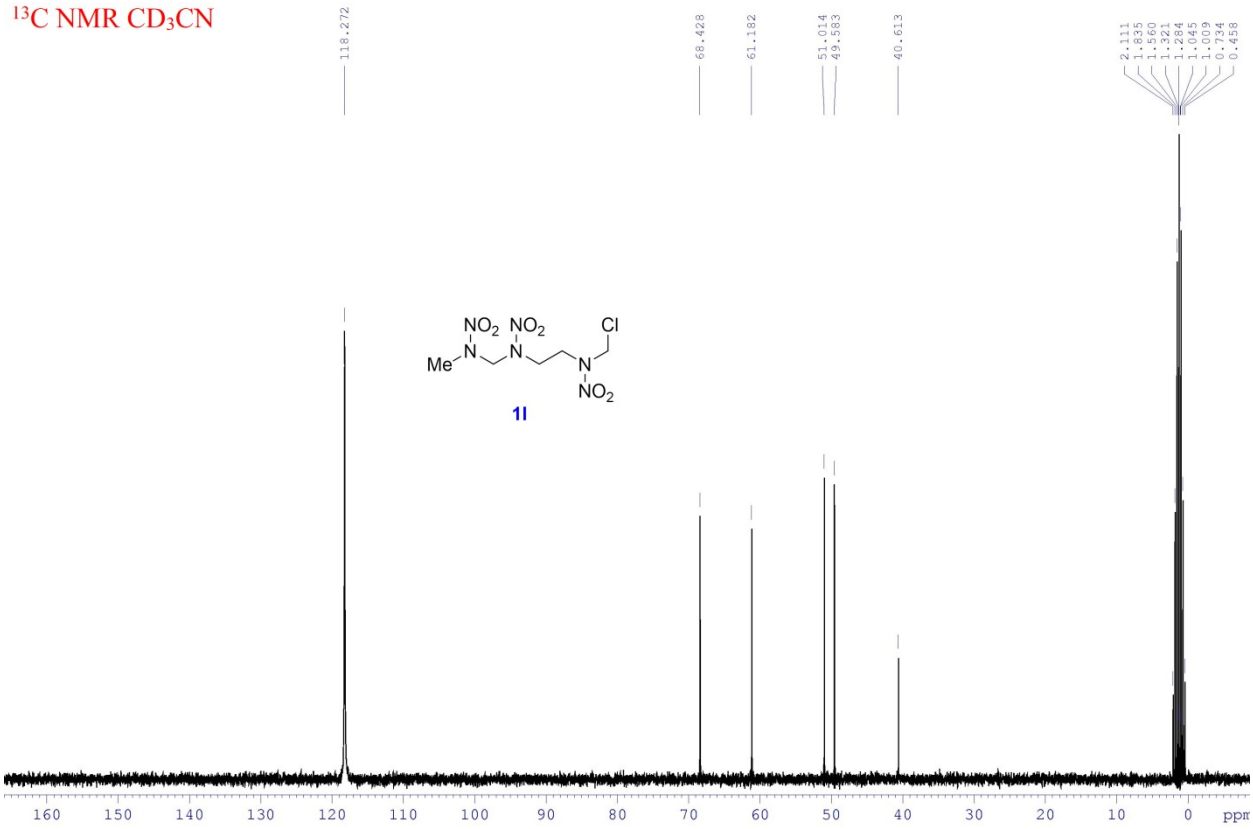

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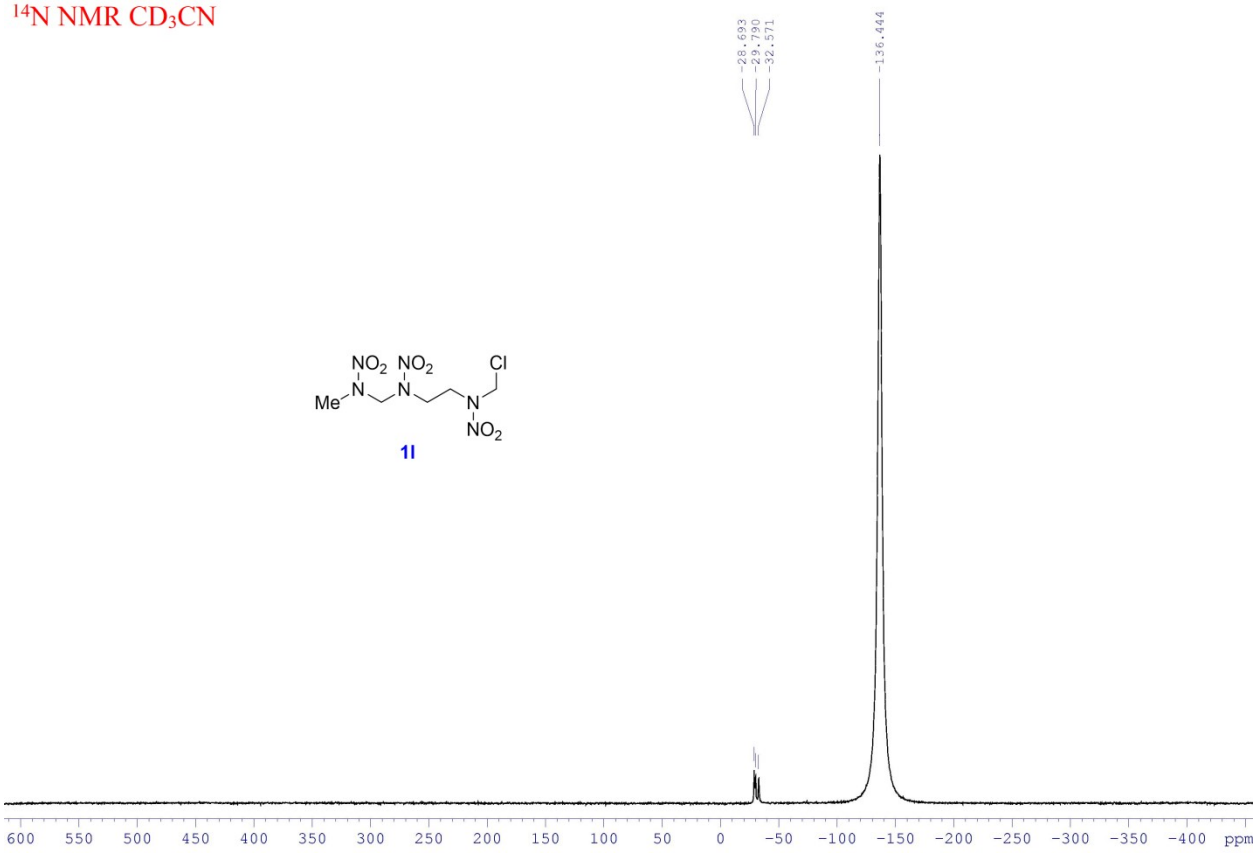

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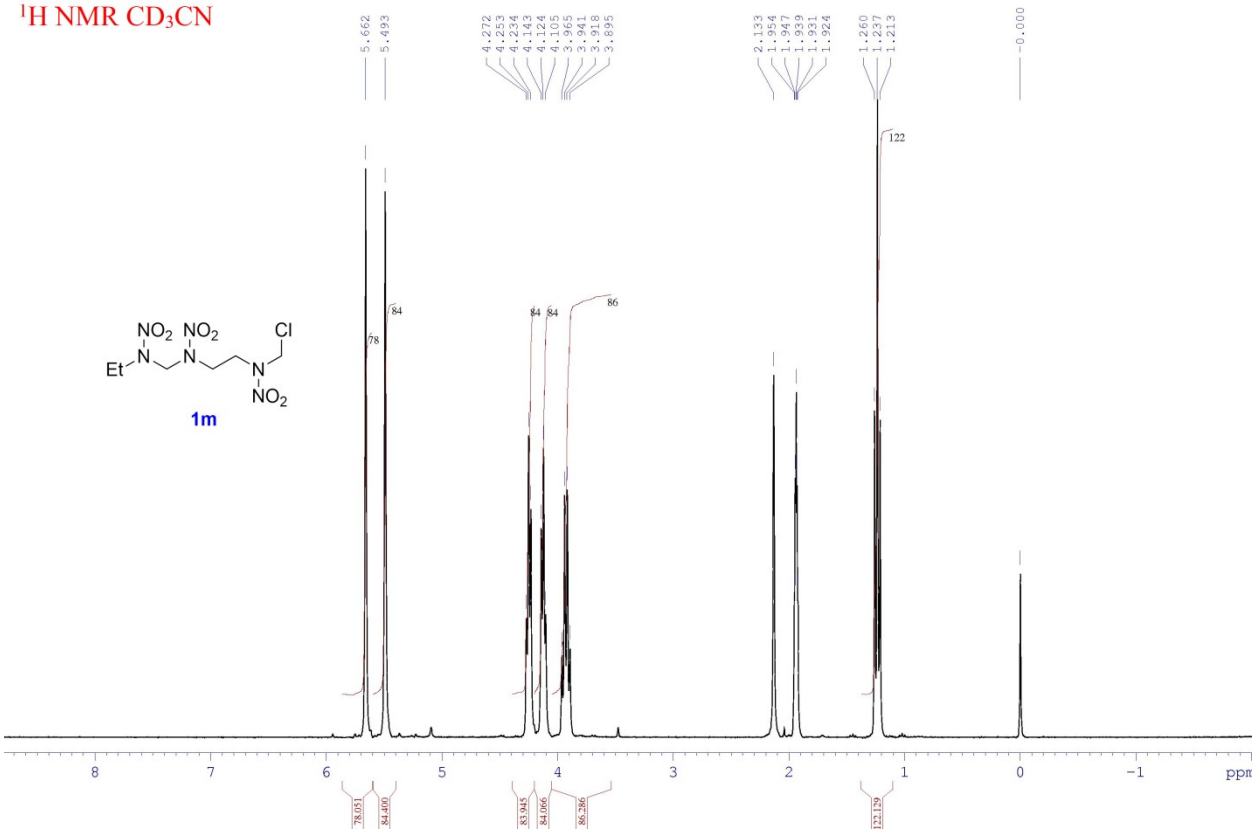

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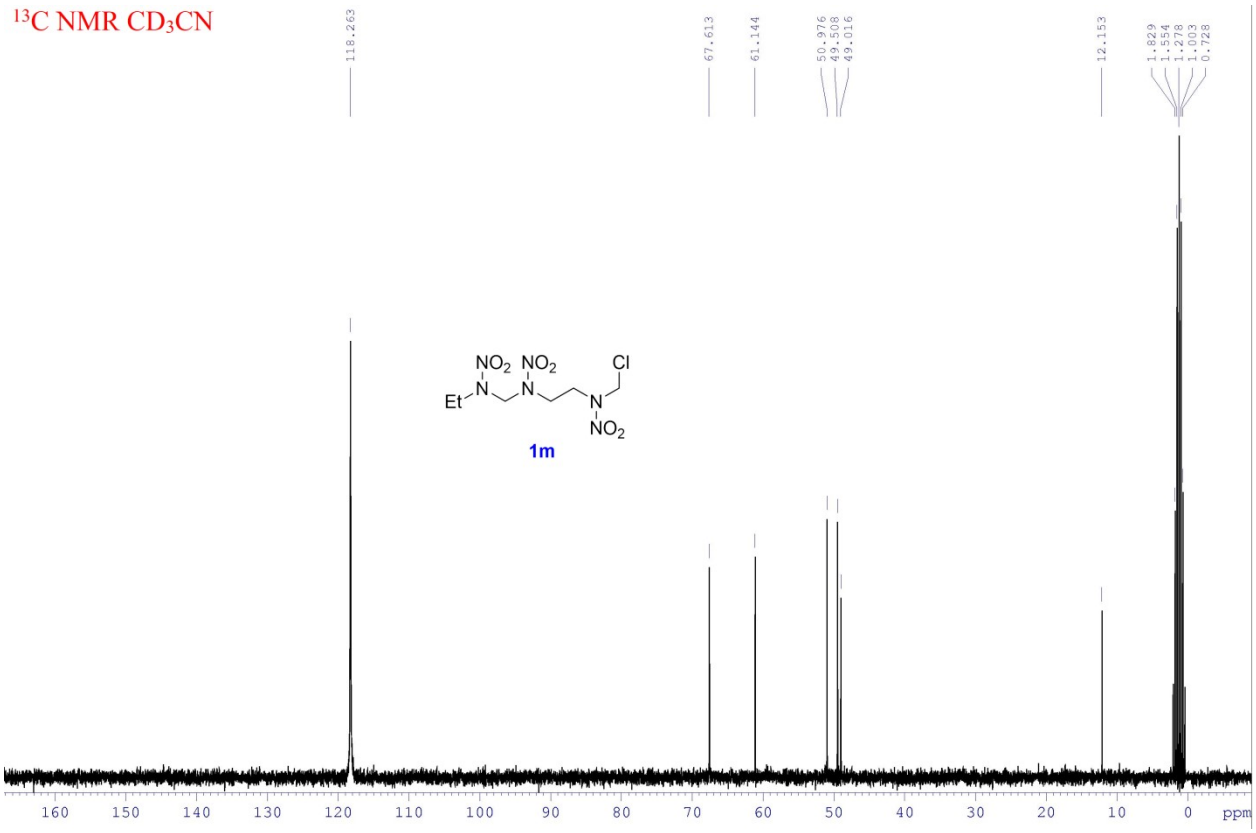

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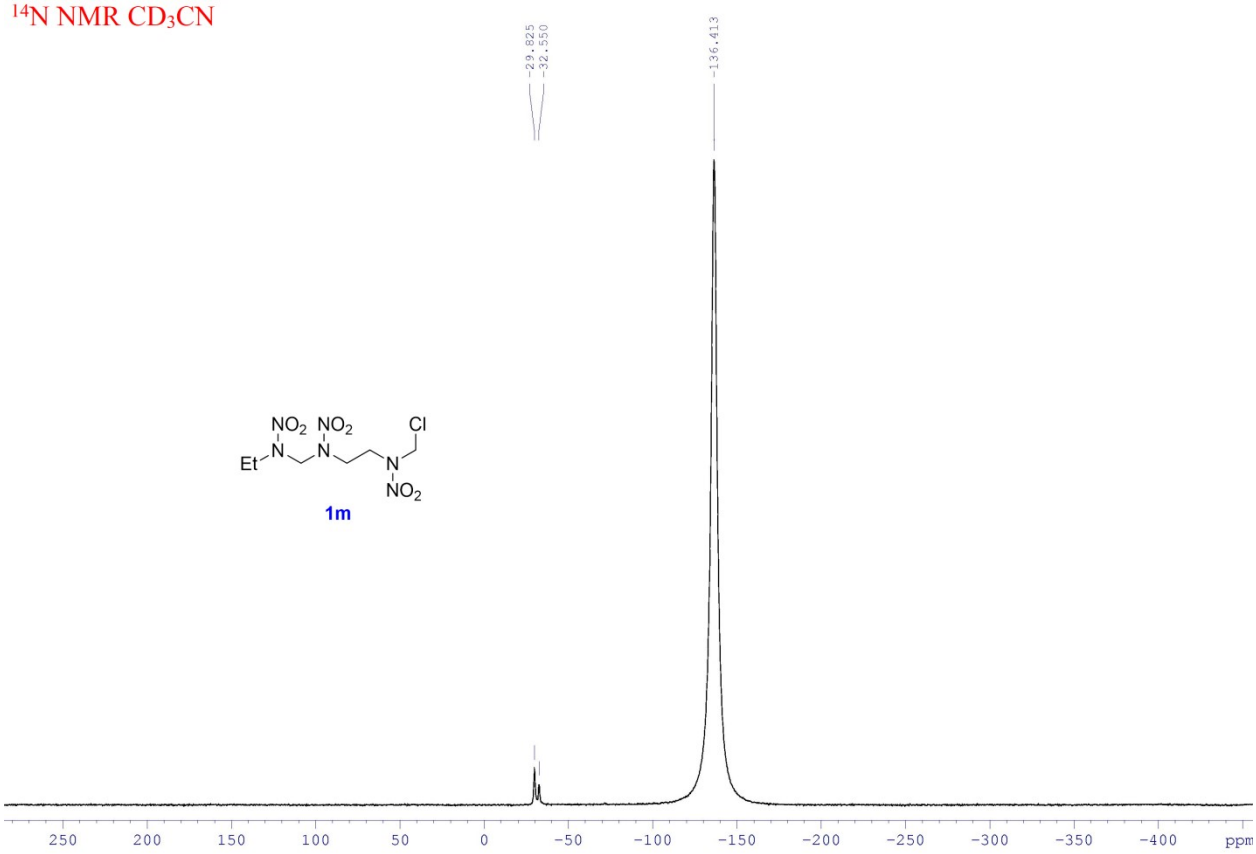

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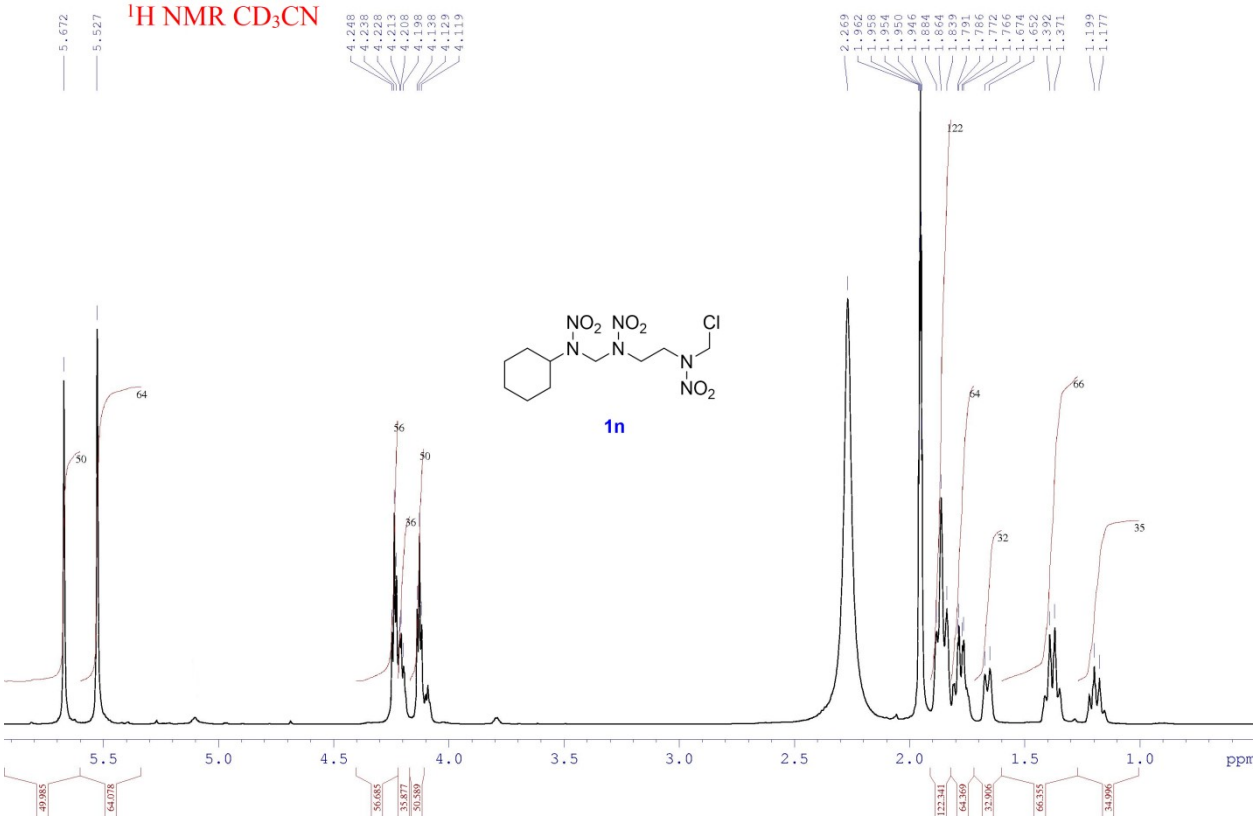

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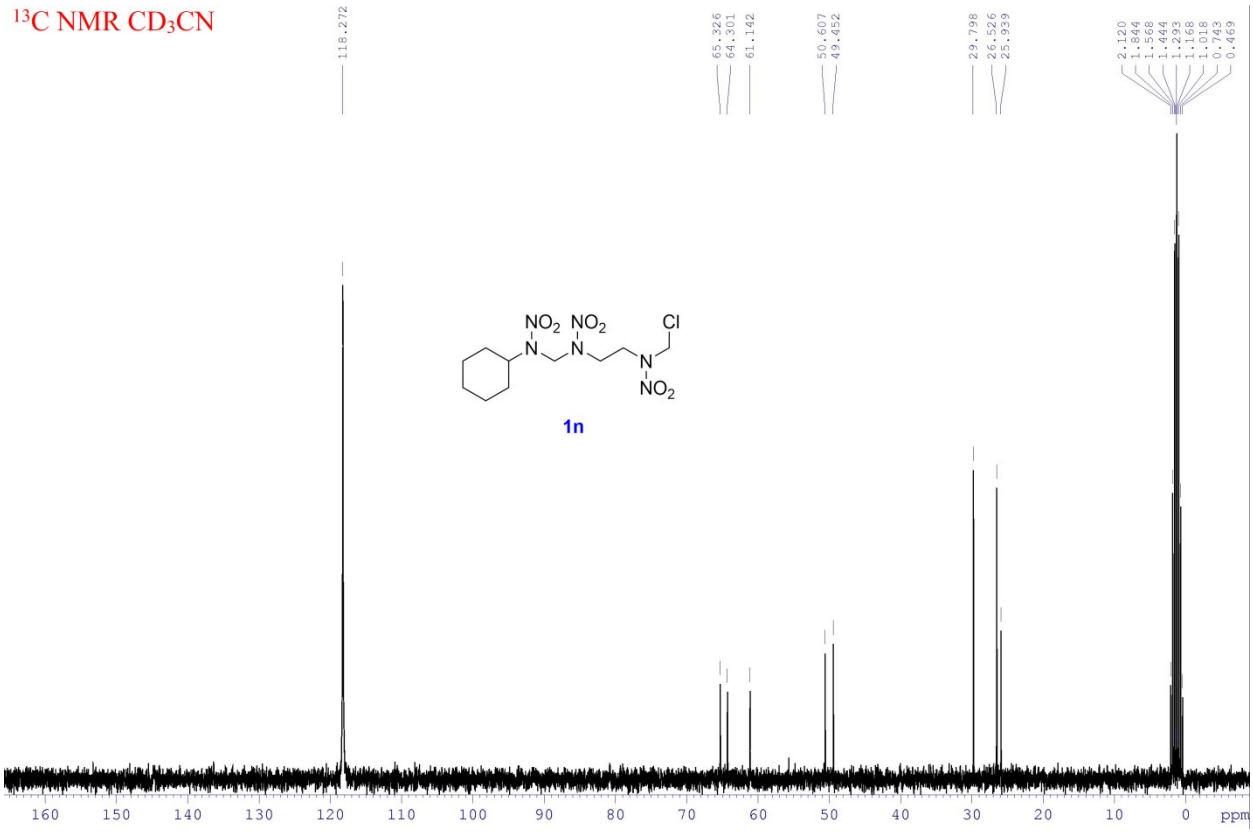

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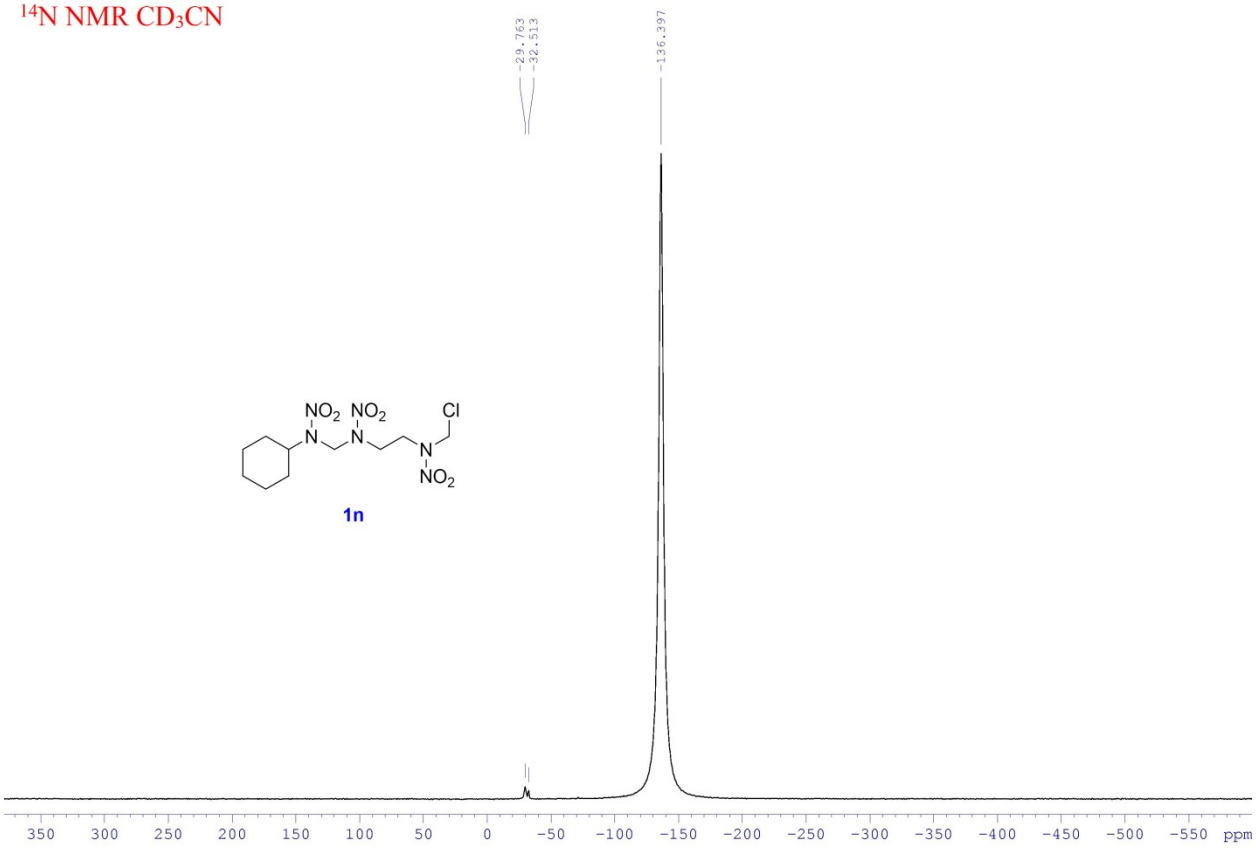

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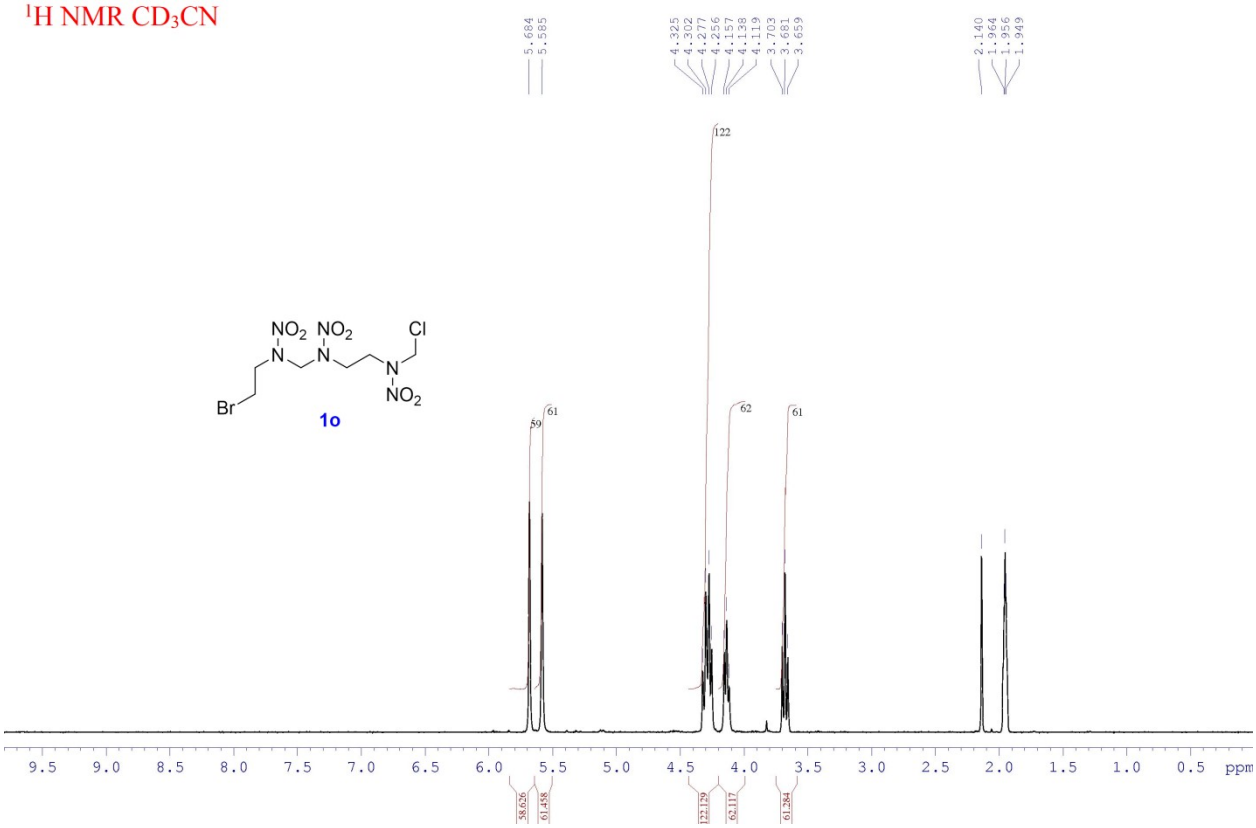

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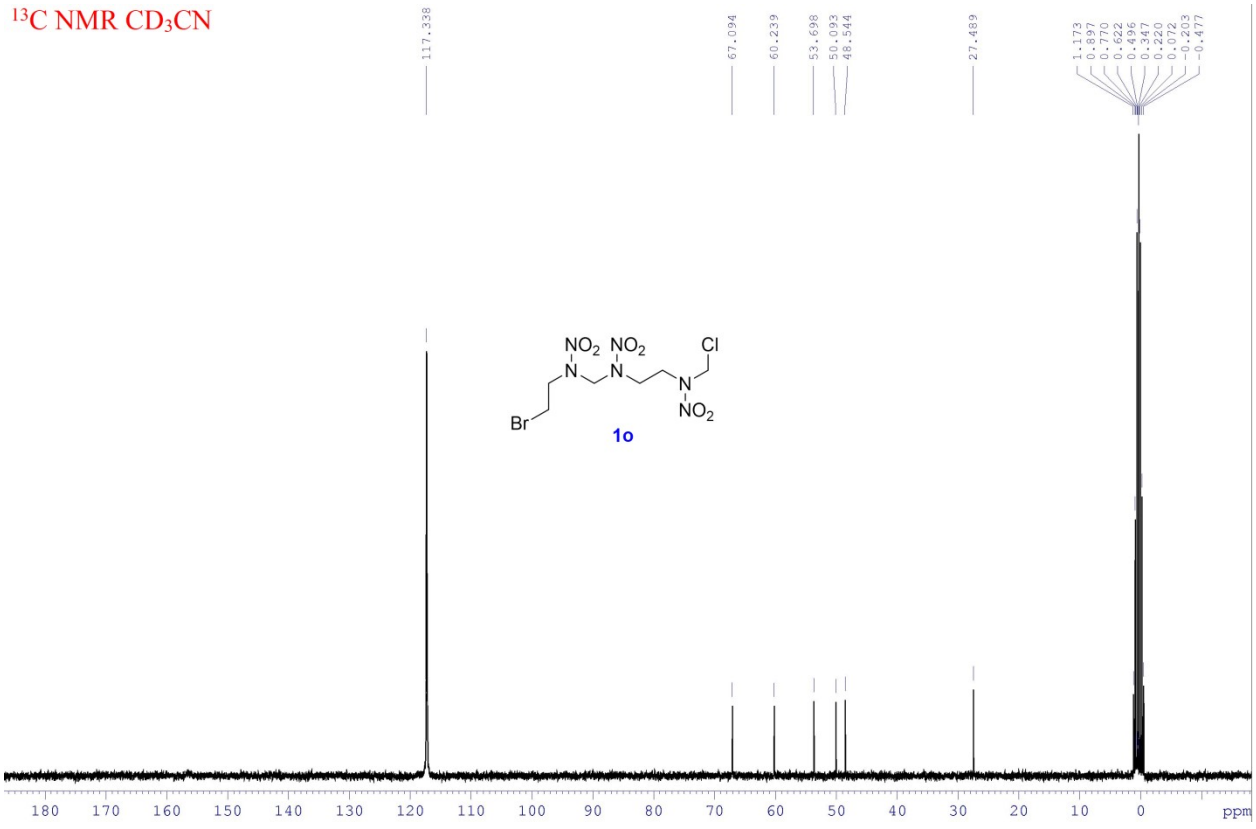

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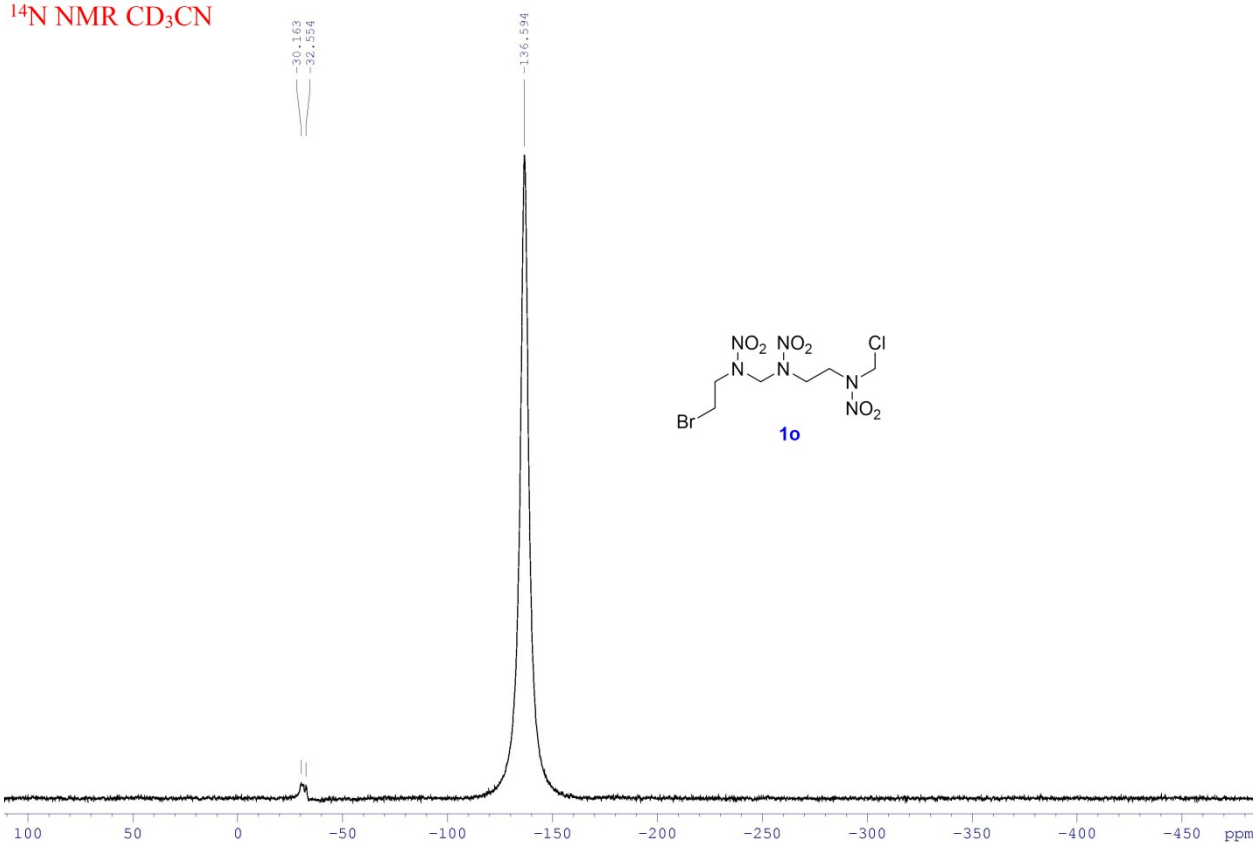

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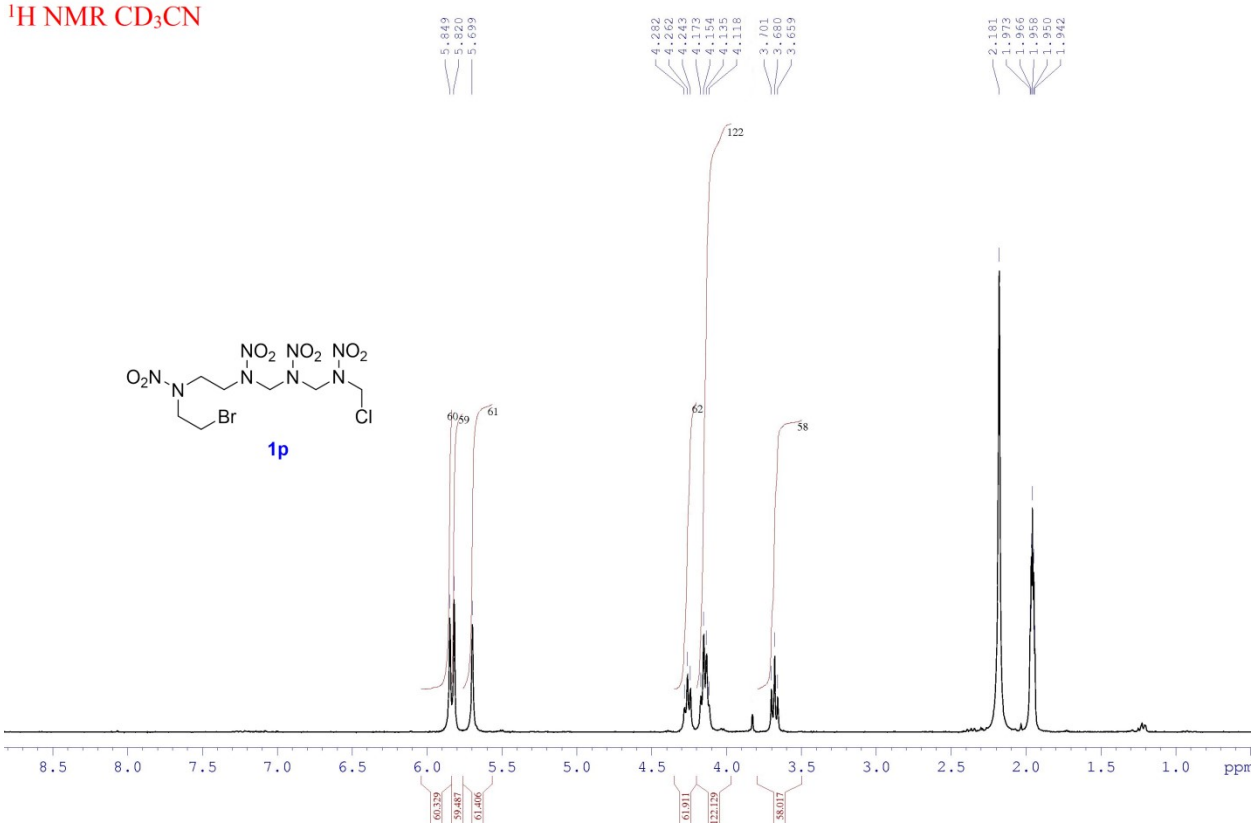

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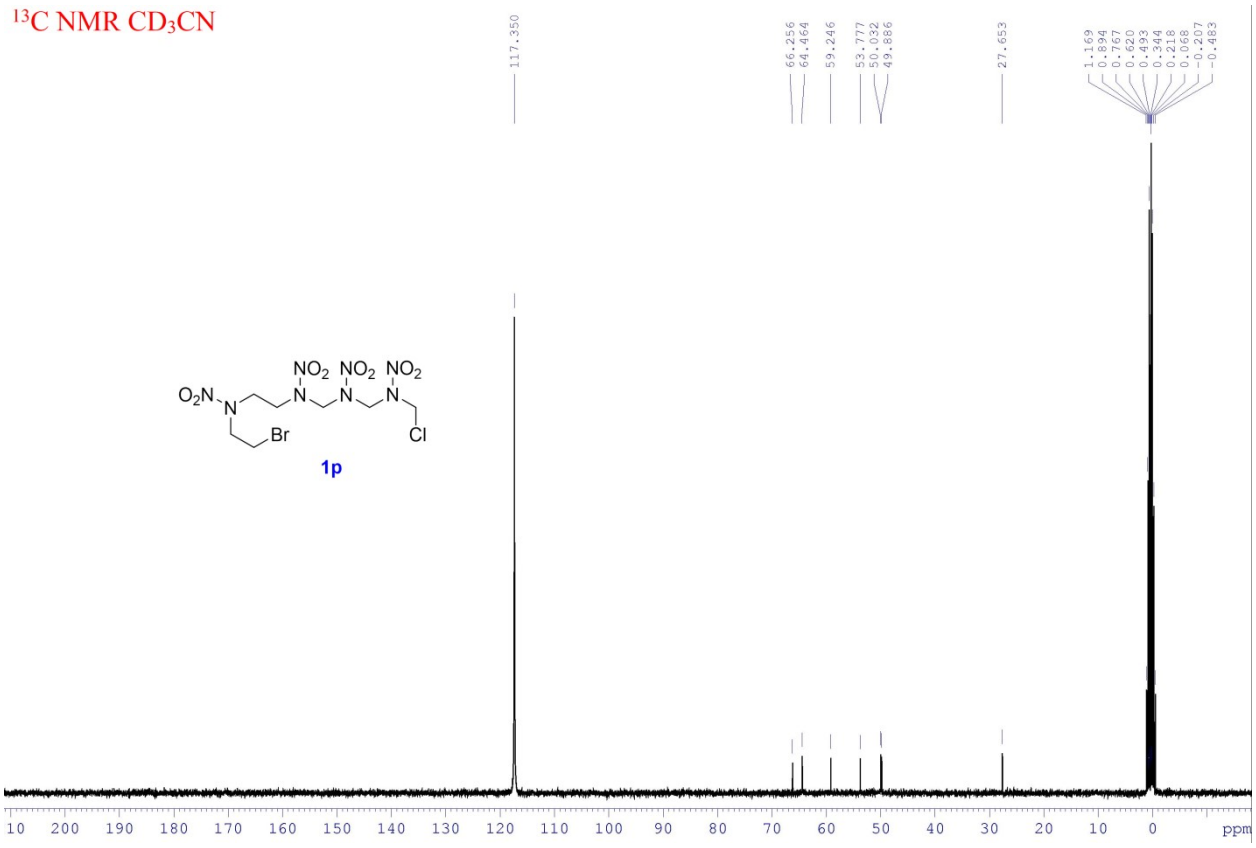

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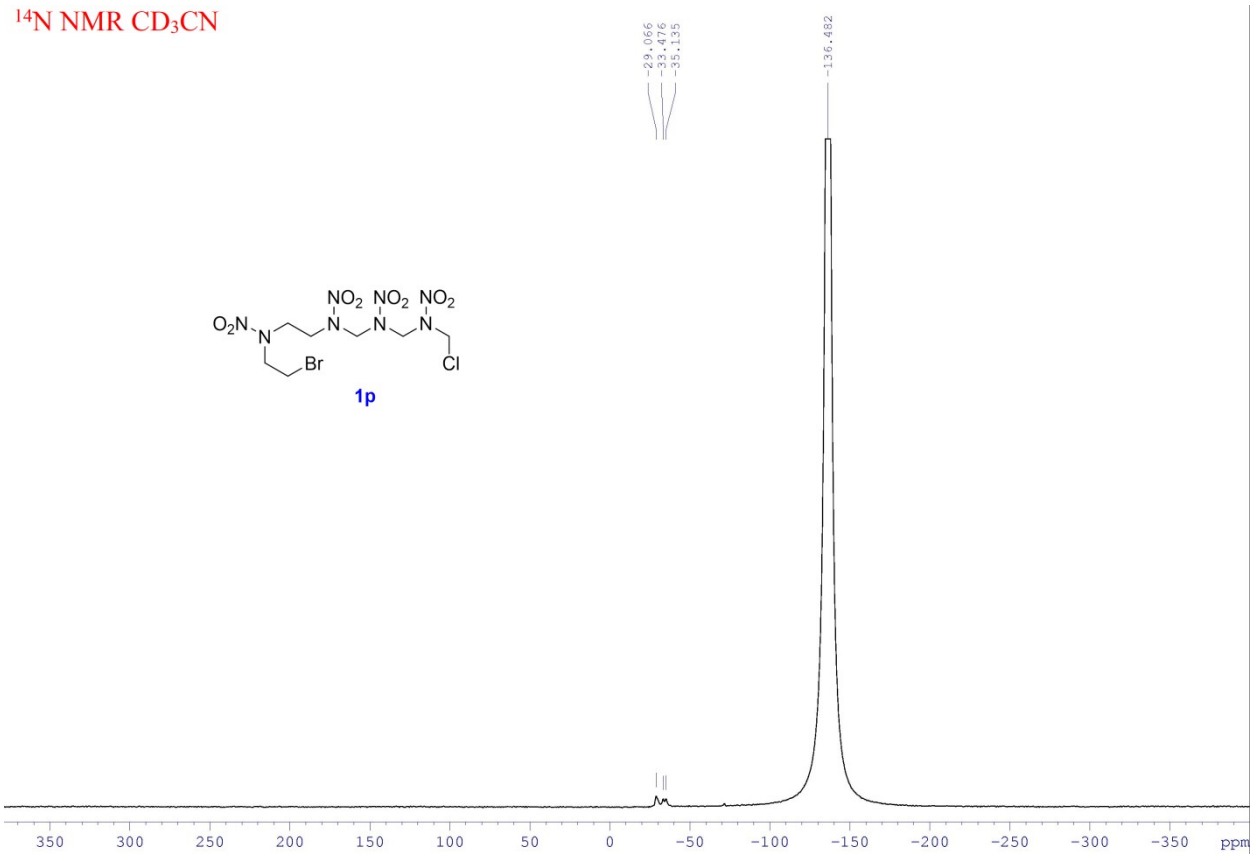

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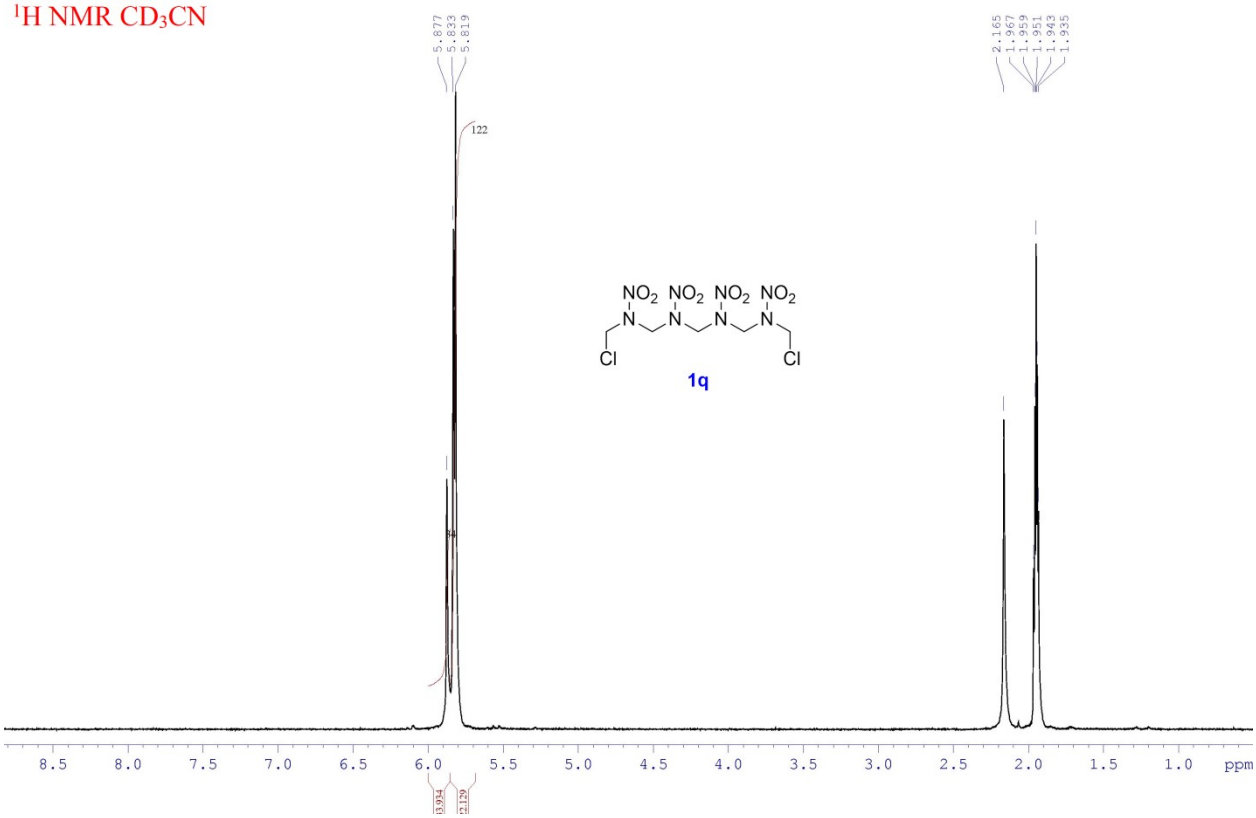

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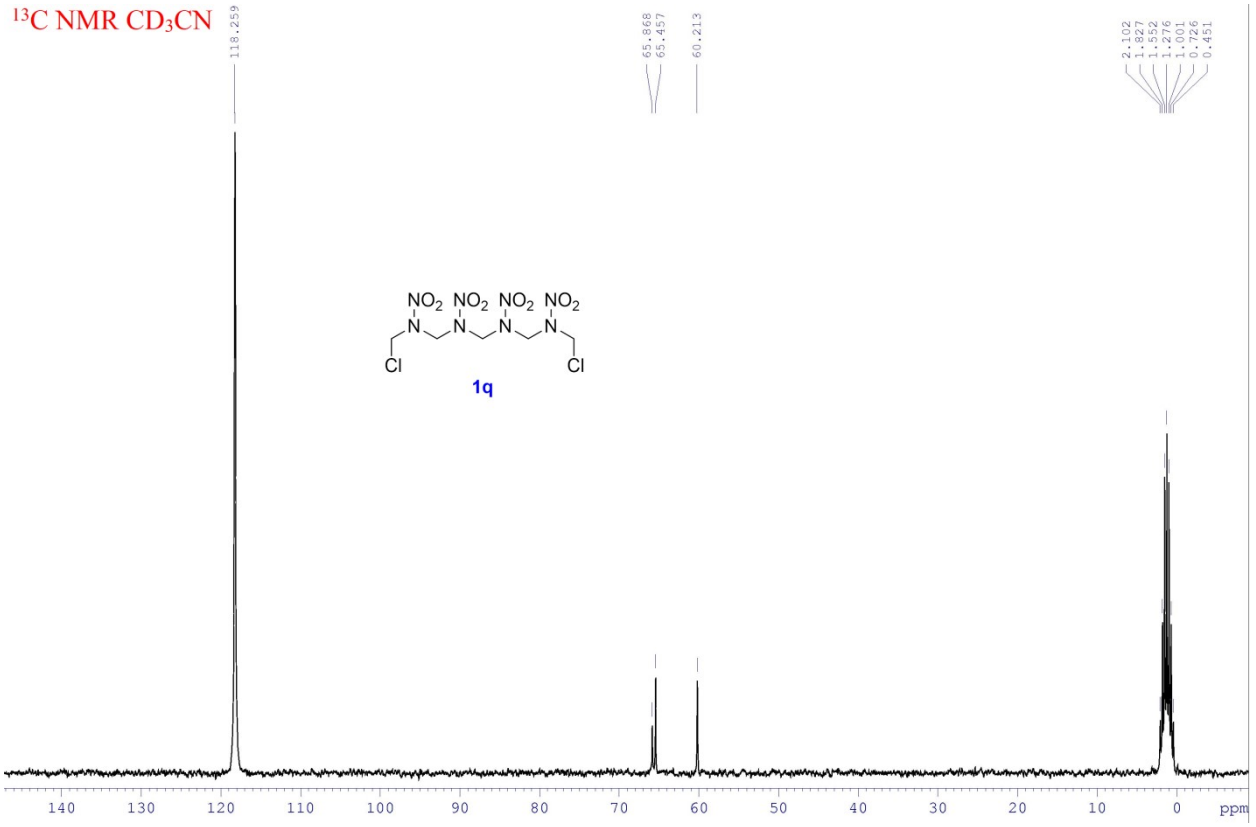

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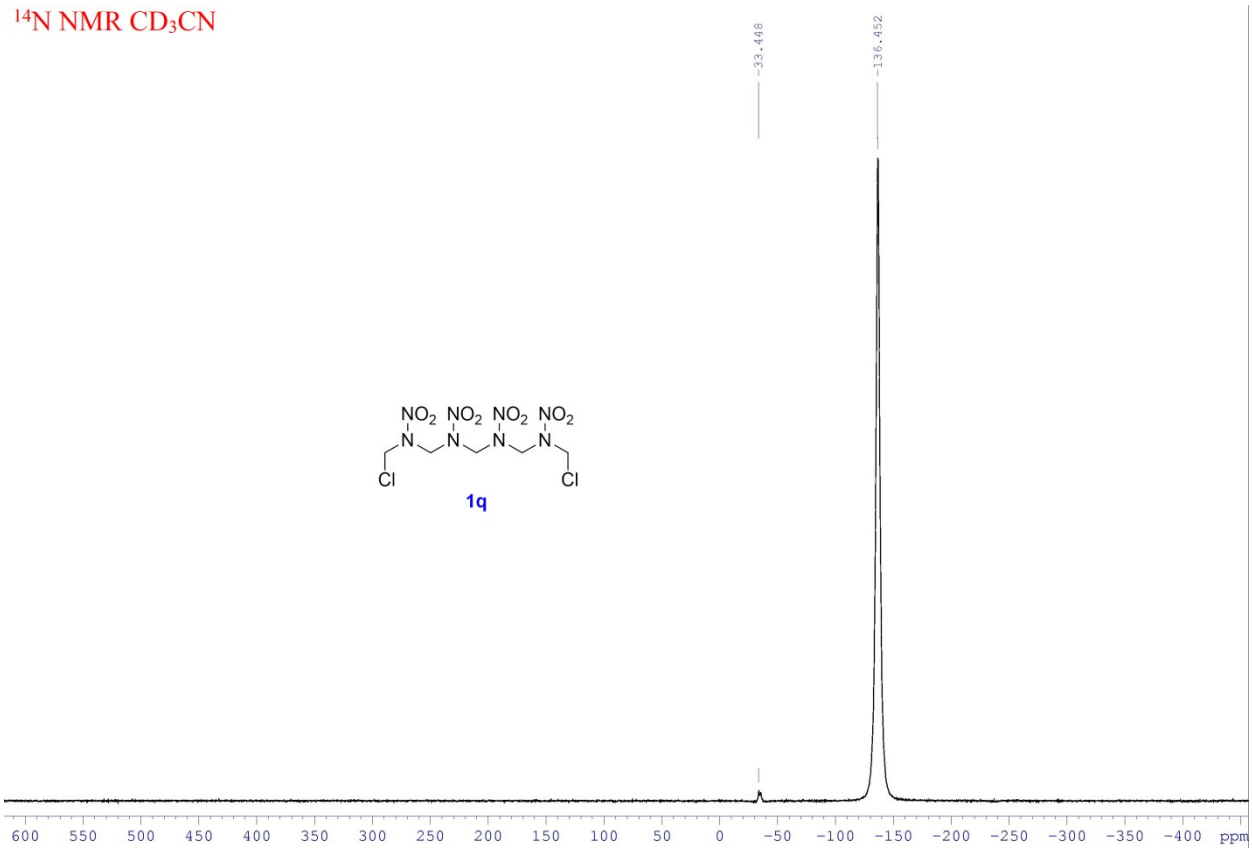

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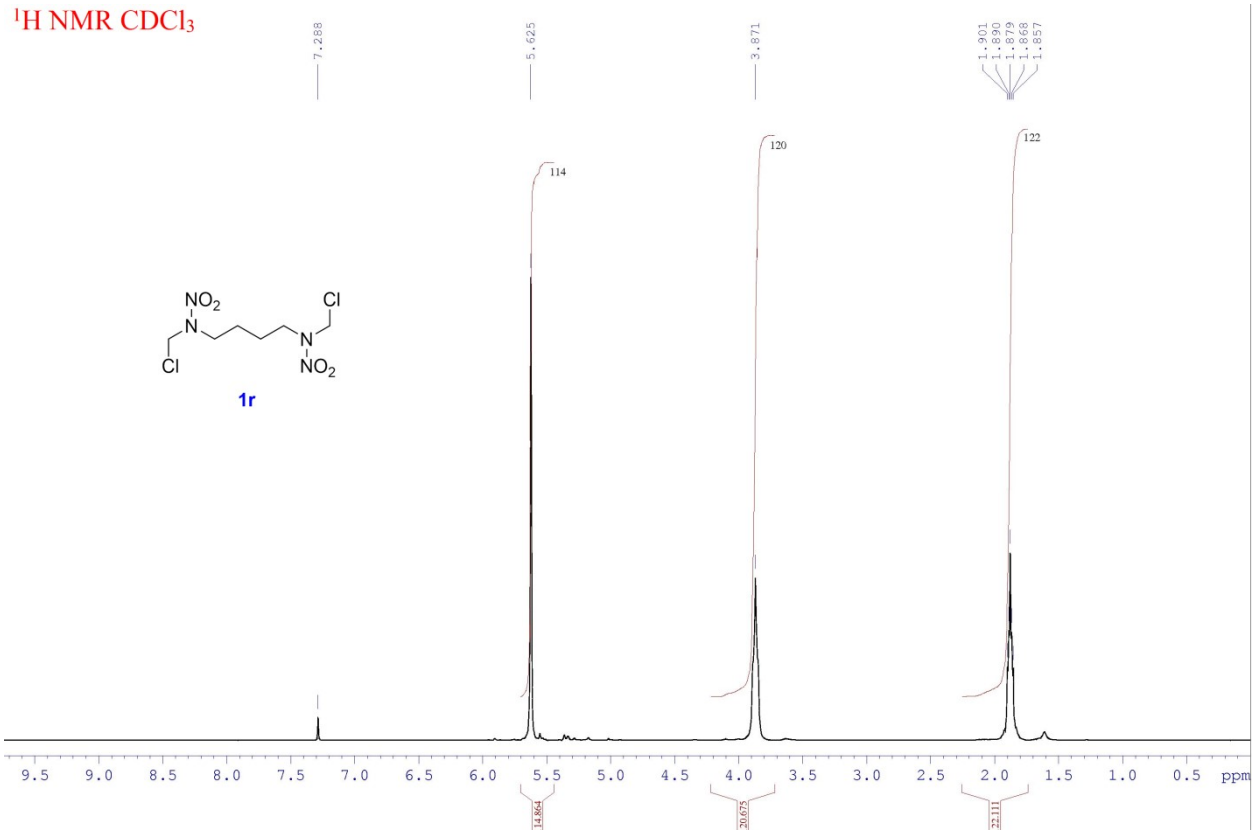

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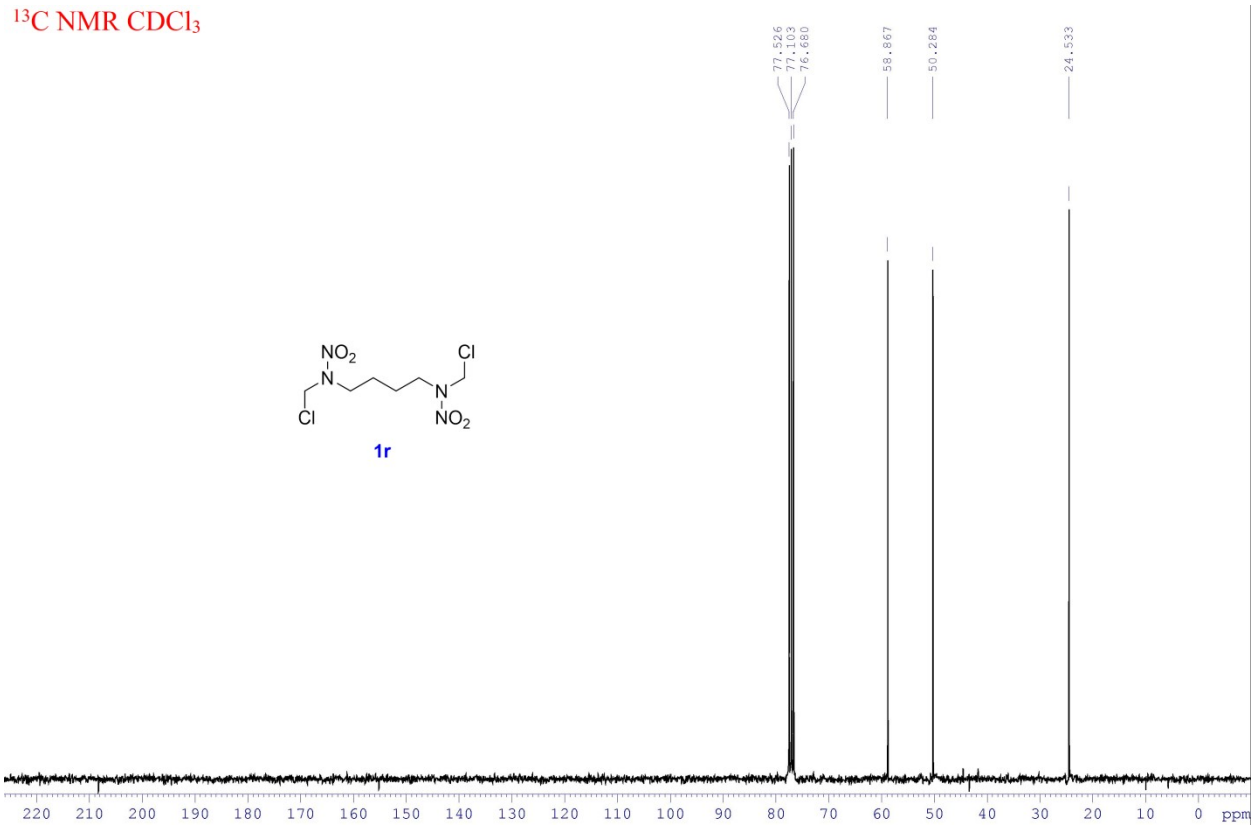

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