

## Acidic *N*-dealkylation in nitrotriazolium salts

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### General Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III spectrometer (400.13 and 100.61 MHz, respectively) in Me<sub>2</sub>CO-*d*<sub>6</sub>: 2.07 ppm for nuclear <sup>1</sup>H, 29.8 и 206.3 ppm for nuclear <sup>13</sup>C; in DMSO-*d*<sub>6</sub>: 2.50 ppm for nuclear <sup>1</sup>H, 39.5 ppm for nuclear <sup>13</sup>C, internal standard Me<sub>2</sub>CO-*d*<sub>6</sub> or DMSO-*d*<sub>6</sub>. IR spectra (KBr): Simex FT-801 FTIR spectrometer. The melting point was determined on a Stuart SMP30 apparatus. Elemental analyses were done on a Thermo Scientific Flash EA1112 CHNS elemental analyzer for carbon, hydrogen, nitrogen and oxygen contents and on a Analytik Jena multi EA 4000 for chlorine content. The XRD analysis was performed on an Bruker KAPPA APEX II CCD diffractometer [ $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$ ,  $\varphi, \omega$ -scans of narrow (0.5°) frames].

### Preparation of reagents and components

**1,3-Dialkyl-4-nitro-1H-[1,2,3]triazol-4-ium perchlorates 1a-m** were obtained as described [G. T. Sukhanov, G. V. Sakovich, Yu. V. Filippova, I. Yu. Bagryanskaya, and A. G. Sukhanova, *Mendeleev Commun.*, 2014, **24**, 280; O. A. Ivashkevich, Vad. E. Matulis, A. S. Lyakhov, I. N. Grigorieva, P. N. Gaponik, G. T. Sukhanov, Yu. V. Filippova, A. G. Sukhanova, *Chem. Heterocycl. Comp.*, 2009, **10**, 1218 (*Khim. Geterotsikl. Soedin.*, 2009, 1519)].

**1-tert-Butyl-4-alkyl-5-nitro-1H-[1,2,4]triazol-4-ium perchlorates 5a,b** were obtained as described [G. T. Sukhanov, G. V. Sakovich, Yu. V. Filippova, I. Yu. Bagryanskaya, and A. G. Sukhanova, *Mendeleev Commun.*, 2014, **24**, 280].

**1,4,5-Trimethyl-3-nitro-1H-[1,2,4]triazol-4-ium perchlorate 5c** and **1,4-diethyl-3-nitro-1H-[1,2,4]triazol-4-ium perchlorate 5d** were obtained as described [G. T. Sukhanov, A. G. Sukhanova and Yu. V. Sheikov, *Chem. Heterocycl. Comp.*, 2007, **43**, 786 (*Khim. Geterotsikl. Soedin.*, 2007, 927)].

All others reagents (hydrochloric acid, hydrobromic acid) and solvents were obtained from commercial sources and used without purification.

### Synthetic procedures and characterization of isolated compounds

**Dealkylation of 1,3-dialkyl-4-nitro-1,2,3-triazolium salts 1a-n.** A solution (10 mmol) of the corresponding salt **1a-n** was refluxed in 36% HCl (45 ml). The reaction time for each substrate is specified in Scheme 1. The reaction mixture was then cooled to room temperature and extracted with dichloromethane (3×20 ml). The dichloromethane solutions were combined and washed with aqueous Na<sub>2</sub>CO<sub>3</sub> and then with water until neutral pH. The solvent was evacuated at reduced pressure to furnish the respective 1-alkyl-5-nitro-(**2a-e**) or 1-alkyl-4-nitro-1,2,3-triazoles (**3a-e**).

The dealkylation of salt **1n** brought about mixed triazoles **2f** and **3f** whose recrystallization from ethanol furnished pure **3f**.

The properties of triazoles **3b** and **2f** are reported previously [S. V. Voitekhovich, P. N. Gaponik, A. S. Lyakhov, J. V. Filipova, A. G. Sukhanova, G. T. Sukhanov and O. A. Ivashkevich, *Tetrahedron Lett.*, 2009, **50**, 2577; Yu. V. Filippova, A. G. Sukhanova, S. V. Voitekhovich, Vad. E. Matulis, G. T. Sukhanov, Yu. V. Grigoriev and O. A. Ivashkevich, *J. Het. Chem.*, 2012, **49**, 965.].

**1-Ethyl-5-nitro-1,2,3-triazole (2a)**: Yield (79%), yellow liquid, bp 59–60 °C/1–2 Torr. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 8.67 (s, 1H, C-H); 4.73–4.78 (q, 2H, *J*=7.0 Hz, -CH<sub>2</sub>-); 1.51–1.54 (t, 3H, *J*=7.0 Hz, -CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 144.26 (C-NO<sub>2</sub>); 133.94 (C-H); 47.24 (N-CH<sub>2</sub>); 14.79 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3146, 1727, 1564, 1510, 1487, 1440, 1402, 1376, 1357, 1261, 1200, 1163, 1101, 1040, 960, 876, 831, 747, 705. Anal. calcd. for C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 33.81; H, 4.26; N, 39.42; O, 22.52. Found (%): C, 33.67; H, 4.14; N, 39.21; O, 22.14.

**5-Nitro-1-*n*-propyl-1,2,3-triazole (2b)**: Yield (97%), yellow liquid, bp 77–78 °C/1–2 Torr. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 8.73 (s, 1H, C-H); 4.65–4.69 (t, 2H, *J*=7.0 Hz, N-CH<sub>2</sub>-); 1.87–1.96 (sextet, 2H, -CH<sub>2</sub>-); 0.90–0.93 (t, 3H, *J*=7.4 Hz, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 144.26 (C-NO<sub>2</sub>); 133.32 (C-H); 53.05 (N-CH<sub>2</sub>); 22.64 (C-CH<sub>2</sub>); 11.00 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3152, 1731, 1568, 1511, 1468, 1441, 1405, 1379, 1361, 1257, 1201, 1158, 1107, 1041, 965, 864, 829, 751, 708. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 38.46; H, 5.16; N, 35.88; O, 20.49. Found (%): C, 38.21; H, 5.02; N, 35.72; O, 20.17.

**1-*n*-Butyl-5-nitro-1,2,3-triazole (2c)**: yellow liquid, bp 98–99 °C/1–2 Torr. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 8.71 (s, 1H, C-H); 4.66–4.70 (t, 2H, *J*=7.2 Hz, N-CH<sub>2</sub>-); 1.81–1.88 (m, 2H, C-CH<sub>2</sub>-); 1.26–1.35 (m, 2H, C-CH<sub>2</sub>-); 0.88–0.92 (t, 3H, *J*=7.4 Hz, C-CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 144.38 (C-NO<sub>2</sub>); 133.44 (C-H); 51.28 (N-CH<sub>2</sub>); 31.14 (C-CH<sub>2</sub>); 19.53 (C-CH<sub>2</sub>); 13.70 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3143, 2962, 1544, 1498, 1469, 1357, 1286, 1181, 1105, 1070, 966, 856, 823, 746. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 42.35; H, 5.92; N, 32.92; O, 18.80. Found (%): C, 42.27; H, 5.89; N, 32.78; O, 18.76.

**1-(4-Methylbutyl)-5-nitro-1,2,3-triazole (2d)**: yellow liquid, bp 126–127 °C/1–2 Torr. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 8.72 (s, 1H, C-H); 4.69–4.73 (t, 2H, *J*=7.4 Hz, N-CH<sub>2</sub>-); 1.75–1.80 (q, 2H, *J*=7.2 Hz, C-CH<sub>2</sub>-); 1.55–1.65 (m, 1H, C-CH-); 0.93–0.95 (d, 6H, *J*=7.6 Hz, C-(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 144.37 (C-NO<sub>2</sub>); 133.50 (C-H); 50.05 (N-CH<sub>2</sub>); 37.89 (C-CH<sub>2</sub>); 25.53 (C-CH); 22.47 (C-(CH<sub>3</sub>)<sub>2</sub>). FTIR (ν, cm<sup>-1</sup>): 3144, 2959, 1545, 1498, 1468, 1357, 1276, 1183, 1106, 1078, 961, 826, 746. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 45.64; H, 6.57; N, 30.42; O, 17.37. Found (%): C, 45.57; H, 6.51; N, 30.57; O, 17.75.

**1-(2-Ethylhexyl)-5-nitro-1,2,3-triazole (2e)**: yellow liquid, bp 134–135 °C/1–2 Torr. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 8.75 (s, 1H, C-H); 4.60–4.61 (d, 2H, *J*=7.2 Hz, N-CH<sub>2</sub>-); 1.93–1.99 (m, 1H, C-CH-); 1.18–1.33 (m, 9H, C-(CH<sub>2</sub>CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>); 0.83–0.88 (m, 5H, C-CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 144.53 (C-NO<sub>2</sub>); 133.67 (C-H); 54.69 (N-CH<sub>2</sub>); 38.95 (C-CH); 30.06 (C-CH<sub>2</sub>); 28.14 (C-CH<sub>2</sub>); 23.49 (C-CH<sub>3</sub>); 22.79 (C-CH<sub>2</sub>); 14.28 (C-CH<sub>2</sub>); 10.49 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3151, 2946, 1543, 1499, 1468, 1356, 1285, 1182, 1105, 1075, 963, 824, 745. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 53.08; H, 8.02; N, 24.76; O, 14.14. Found (%): C, 53.11; H, 8.07; N, 24.54; O, 14.01.

**1-Methyl-4-nitro-1,2,3-triazole (3a)**: white crystals, mp 125–126 °C (EtOH). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 9.26 (s, 1H, C-H); 4.16 (s, 3H, N-CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 153.35 (C-NO<sub>2</sub>); 126.10 (C-H); 38.11 (N-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3118, 1760, 1542, 1509, 1410, 1395, 1377, 1320, 1279, 1233, 1107, 1040, 1005, 883, 827, 760, 692. Anal. calcd. for C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 28.13; H, 3.15; N, 43.74; O, 24.98. Found (%): C, 28.01; H, 3.11; N, 43.42; O, 24.77.

**1-*n*-Butyl-4-nitro-1,2,3-triazole (3c)**: white crystals, mp 52–53 °C (EtOH). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 9.34 (s, 1H, C-H); 4.45–4.49 (t, 2H, *J*=7.1 Hz, N-CH<sub>2</sub>); 1.83–1.90 (m, 2H, C-CH<sub>2</sub>), 1.22–1.31 (m, 2H, C-CH<sub>2</sub>), 0.87–0.91 (t, 3H, C-CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 153.37 (C-NO<sub>2</sub>); 125.21 (C-H); 51.02 (N-CH<sub>2</sub>); 31.58 (C-CH<sub>2</sub>); 19.33 (C-CH<sub>2</sub>);

13.60 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3110, 2962, 1755, 1542, 1514, 1469, 1396, 1305, 1262, 1118, 1046, 1016, 879, 829, 760, 737. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 42.35; H, 5.92; N, 32.92; O, 18.80. Found (%): C, 42.32; H, 5.87; N, 32.76; O, 18.71.

**1-(4-Methylbutyl)-4-nitro-1,2,3-triazole (3d)**: mp 75-76 °C (EtOH). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 9.37 (s, 1H, C-H); 4.47-4.51 (t, 2H, *J* = 7.4 Hz, N-CH<sub>2</sub>); 1.76-1.81 (q, 2H, *J* = 7.2 Hz, C-CH<sub>2</sub>); 1.45-1.55 (m, 1H, C-CH-); 0.91-0.92 (d, 6H, *J* = 6.6 Hz, C-(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 153.39 (C-NO<sub>2</sub>); 125.29 (C-H); 49.75 (N-CH<sub>2</sub>); 38.31 (C-CH<sub>2</sub>)<sub>2</sub>; 25.27 (C-CH); 22.41 (C-(CH<sub>3</sub>)<sub>2</sub>). FTIR (ν, cm<sup>-1</sup>): 3104, 2959, 1753, 1542, 1513, 1467, 1396, 1305, 1238, 1130, 1047, 1017, 879, 829, 759, 729, 690. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 45.64; H, 6.57; N, 30.42; O, 17.37. Found (%): C, 45.60; H, 6.51; N, 30.38; O, 17.32.

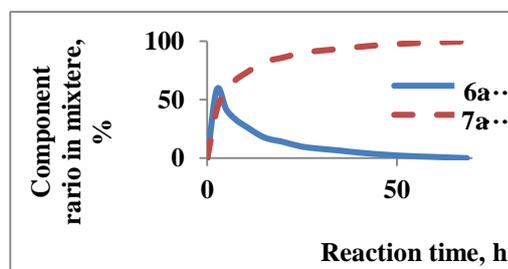
**1-Isopropyl-4-nitro-1,2,3-triazole (3e)**: white crystals, mp 39-40 °C (EtOH). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 9.43 (s, 1H, C-H); 4.89-4.96 (m, 1H, CH); 1.54-1.56 (d, 6H, *J* = 6.7 Hz, (CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 153.44 (C-NO<sub>2</sub>); 123.68 (C-H); 54.92 (N-C); 22.60 (CH<sub>3</sub>)<sub>2</sub>. FTIR (ν, cm<sup>-1</sup>): 3115, 1748, 1551, 1501, 1405, 1391, 1373, 1318, 1266, 1228, 1110, 1040, 1003, 891, 829, 761, 689. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 38.46; H, 5.16; N, 35.88; O, 20.49. Found (%): C, 38.32; H, 5.08; N, 35.34; O, 20.24.

**1-Benzyl-4-nitro-1,2,3-triazole (3f)**: mp 89-90 °C (EtOH). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 9.45 (s, 1H, C-H); 7.36-7.42 (m, 5H, CH<sub>aromat</sub>); 5.72 (s, 2H, N-CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ, ppm: 153.57 (C-NO<sub>2</sub>); 135.14 (C<sub>aromat</sub>); 128.71-129.37 (CH<sub>aromat</sub>); 125.56 (C-H); 54.59 (N-CH<sub>2</sub>). FTIR (ν, cm<sup>-1</sup>): 3139, 3009, 1534, 1510, 1455, 1391, 1275, 1104, 1040, 857, 829, 780, 757, 718, 696. Anal. calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 52.94; H, 3.95; N, 27.44; O, 15.67. Found (%): C, 52.81; H, 3.91; N, 27.38; O, 15.54.

**Dealkylation of 1-tert-butyl-3-*R*-4-nitro-1,2,3-triazolium salts 10-s.** The procedure is identical to that of dealkylation of salts **1a-n**. The reaction mixture was extracted with dichloromethane to yield **4**, **4'** mixture. The spectral data of compounds **4**, **4'** are in agreement with the literature data [Yu. V. Filippova, A. G. Sukhanova, S. V. Voitekhovich, V. E. Matulis, G. T. Sukhanov, Yu. V. Grigoriev and O. A. Ivashkevich, *J. Heterocycl. Chem.*, 2012, **49**, 965]. The residue of the reaction mixture after it was extracted with CH<sub>2</sub>Cl<sub>2</sub> was evaporated *in vacuo*. The residue was recrystallized from alcohol to give 4-nitro-1,2,3-triazole. Yield of **4**, **4'** mixture was 14.0%. Yield of 4-nitro-1,2,3-triazole: 78.0–78.8%.

**General procedure for the synthesis of compounds 6a-g, 7a,b.** A mixture of the corresponding salt **5a-d** (5 mmol) and concentrated HCl (in the synthesis of compounds **6a-d**, **7a,b**) or 48% aq. HBr (in the synthesis of compounds **6e-g**) (25.0 ml) was refluxed for 5-10 h, then evaporated to dryness *in vacuo*. The residue was recrystallized from organic solvent to give desired product.

The prolonged keeping the reaction mixture facilitated complete de-*tert*-butylation of salt **6a** and conversion into **7a** (Figure S1).



**Figure S1** A change in composition of transformation products of salt **5a** in HCl

**1-tert-Butyl-5-chloro-4-methyl-1*H*-[1,2,4]triazol-4-ium perchlorate (6a).** Yield 0.32 g (90%), white crystals, mp 221 °C (ethanol). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.15 (s, 1H, C-H), 4.10 (s, 3H, CH<sub>3</sub>), 1.76 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm:

143.09 (C-Cl); 132.78 (C-H); 64.87 (-C-); 33.75 (-CH<sub>3</sub>); 27.44 ((CH<sub>3</sub>)<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3154, 3098, 2989, 1571, 1507, 1465, 1446, 1373, 1216, 1180, 1104, 995, 625. Anal. calcd. for C<sub>7</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 30.67; H, 4.78; Cl, 28.87; N, 15.33; O, 23.35. Found (%): C, 30.65; H, 4.77; Cl, 28.81; N, 15.36; O, 23.31.

**5-Chloro-4-methyl-1H-[1,2,4]triazol-4-ium perchlorate (7a).** The compound was obtained by recrystallization of the reaction mixture residue after compound **6a** was isolated with propan-2-ol/dichloromethane (1:1) from the mixture. Yield 0.96 g (95%), white crystals, mp 127 °C (propan-2-ol/dichloromethane). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.11 (s, 1H, C-H); 4.16 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 145.66 (C-Cl); 136.51 (C-H); 33.82 (-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 2985, 2697, 2651, 1726, 1562, 1525, 1455, 1404, 1358, 1320, 1085, 934, 862, 677, 626. Anal. calcd. for C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 16.53; H, 2.31; Cl, 32.53; N, 19.28; O, 29.36. Found (%): C, 16.50; H, 2.30; Cl, 32.37; N, 19.24; O, 29.29.

**1-tert-Butyl-5-chloro-4-ethyl-1H-[1,2,4]triazol-4-ium perchlorate (6b).** Yield 0.3 g (88%), white crystals, mp 194 °C (ethanol). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.16 (s, 1H, C-H); 4.46-4.52 (q, 2H, *J*=7.32 Hz, -CH<sub>2</sub>-); 1.76 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>); 1.62-1.66 (t, 3H, *J*=7.32 Hz, -CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 142.27 (C-Cl); 131.24 (C-H); 64.88 (-C-); 43.87 (-CH<sub>2</sub>-); 27.41 ((CH<sub>3</sub>)<sub>3</sub>); 13.07 (CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3146, 3084, 2989, 1562, 1502, 1392, 1375, 1211, 1100, 996, 662, 625. Anal. calcd. for C<sub>8</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 33.35; H, 5.25; Cl, 24.61; N, 14.58; O, 22.21. Found (%): C, 33.30; H, 5.21; Cl, 24.58; N, 14.54; O, 22.18.

**5-Chloro-4-ethyl-1H-[1,2,4]triazol-4-ium perchlorate (7b).** The compound was obtained by recrystallization of the reaction mixture residue after compound **6b** was isolated with propan-2-ol/dichloromethane (1:1) from the mixture. Yield 0.6 g (91%), white crystals, mp 96 °C (propan-2-ol/dichloromethane). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.13 (s, 1H, C-H); 4.54-4.60 (q, 2H, *J*=6.83 Hz, -CH<sub>2</sub>-); 1.64-1.70 (t, 3H, *J*=7.22 Hz, -CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 144.28 (C-Cl); 135.08 (C-H); 43.79 (-CH<sub>2</sub>-); 13.05 (CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 2988, 2680, 2662, 1563, 1515, 1450, 1400, 1364, 1325, 1102, 976, 870, 672, 625. Anal. calcd. for C<sub>4</sub>H<sub>7</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 20.71; H, 3.04; Cl, 30.56; N, 18.11; O, 27.58. Found (%): C, 20.73; H, 3.00; Cl, 30.46; N, 18.05; O, 27.47.

**3-Chloro-1,4,5-trimethyl-1H-[1,2,4]triazol-4-ium perchlorate (6c).** Yield 1.12 g (91%), white crystals, mp 187 °C (H<sub>2</sub>O). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 4.15 (s, 3H, N-CH<sub>3</sub>); 3.97 (s, 3H, N-CH<sub>3</sub>); 2.97 (s, 3H, C-CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 154.54 (C-Cl); 143.39 (C-CH<sub>3</sub>); 37.82 (N-CH<sub>3</sub>); 32.69 (N-CH<sub>3</sub>); 9.94 (C-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3448, 2965, 1589, 1554, 1478, 1384, 1293, 1094, 807, 735, 683, 625. Anal. calcd. for C<sub>5</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 24.41; H, 3.69; Cl, 28.82; N, 17.08; O, 26.01. Found (%): C, 24.40; H, 3.67; Cl, 28.75; N, 17.04; O, 25.95.

**3-Chloro-1,4-diethyl-1H-[1,2,4]triazol-4-ium perchlorate (6d).** Yield 1.18 g (91%), white crystals, mp 156 °C (H<sub>2</sub>O). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.11 (s, 1H, C-H); 4.56-4.62 (q, 2H, *J*=7.22 Hz, -CH<sub>2</sub>-); 4.48-4.53 (q, 2H, *J*=7.32 Hz, -CH<sub>2</sub>-); 1.60-1.67 (m, 6H, *J*=7.02 Hz, 2(-CH<sub>3</sub>)). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 143.80 (C-Cl); 132.5 (C-H); 48.86 (-CH<sub>2</sub>-); 43.84 (-CH<sub>2</sub>-); 13.09 (-CH<sub>3</sub>); 13.02 (-CH<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3161, 3095, 2998, 1578, 1516, 1455, 1396, 1188, 1092, 984, 625. Anal. calcd. for C<sub>6</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 27.71; H, 4.26; Cl, 27.26; N, 16.16; O, 24.61. Found (%): C, 27.70; H, 4.23; Cl, 27.20; N, 16.16; O, 24.58.

**5-Bromo-1-tert-butyl-4-methyl-1H-[1,2,4]triazol-4-ium perchlorate (6e).** Yield 1.37 g (86%), white crystals, mp 175 °C (Me<sub>2</sub>CO). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.13 (s, 1H, C-H); 4.11 (s, 3H, CH<sub>3</sub>); 1.81 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 144.08 (C-Br); 133.55 (C-H); 50.15 (-C-); 64.66 (-CH<sub>3</sub>); 25.49 ((CH<sub>3</sub>)<sub>3</sub>). FTIR (ν, cm<sup>-1</sup>): 3154, 3092, 2999, 1722, 1566, 1501, 1442, 1371, 1244, 1201, 1150, 1096, 997, 624. Anal. calcd. for C<sub>7</sub>H<sub>13</sub>BrClN<sub>3</sub>O<sub>4</sub> (%): C, 26.39; H, 4.11; Cl, 11.13; N, 13.19; O, 20.09. Found (%): C, 26.40; H, 4.11; Cl, 11.00; N, 13.18; O, 20.07.

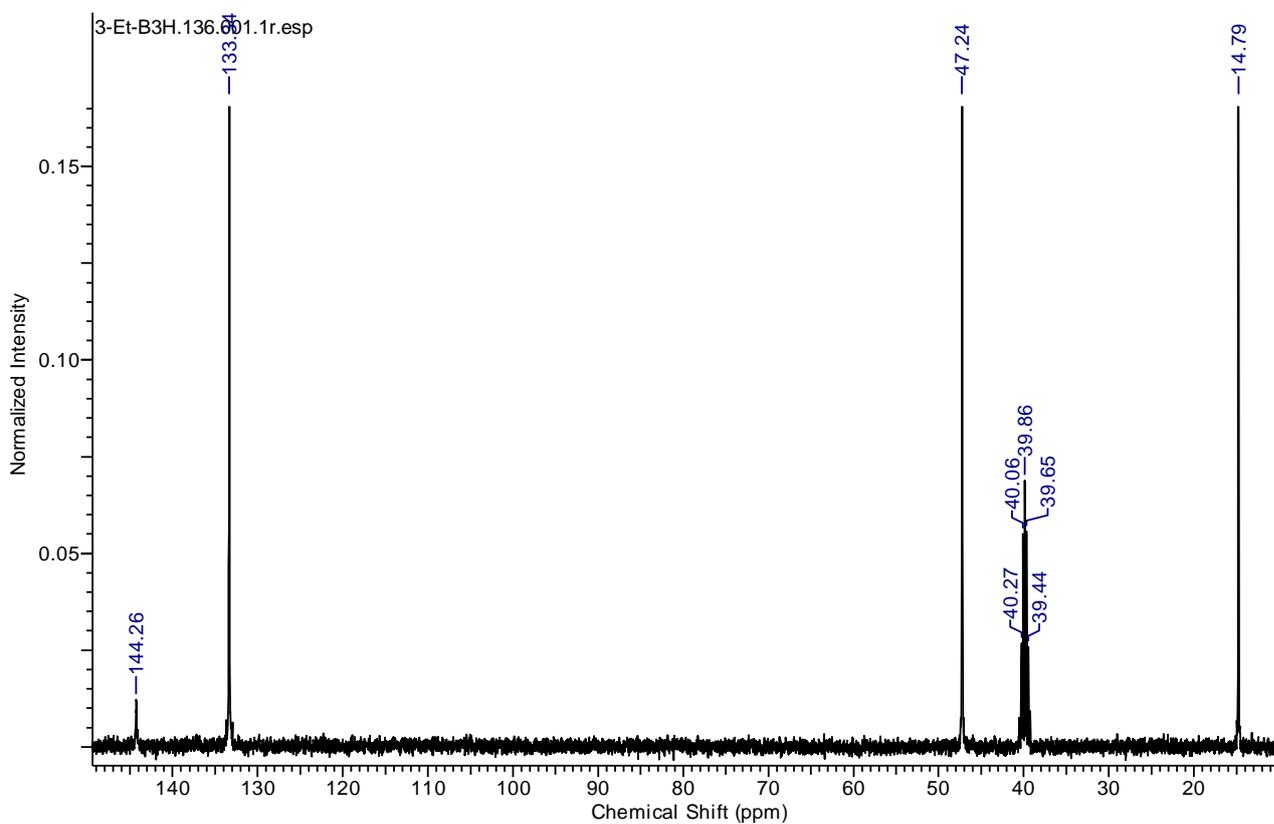
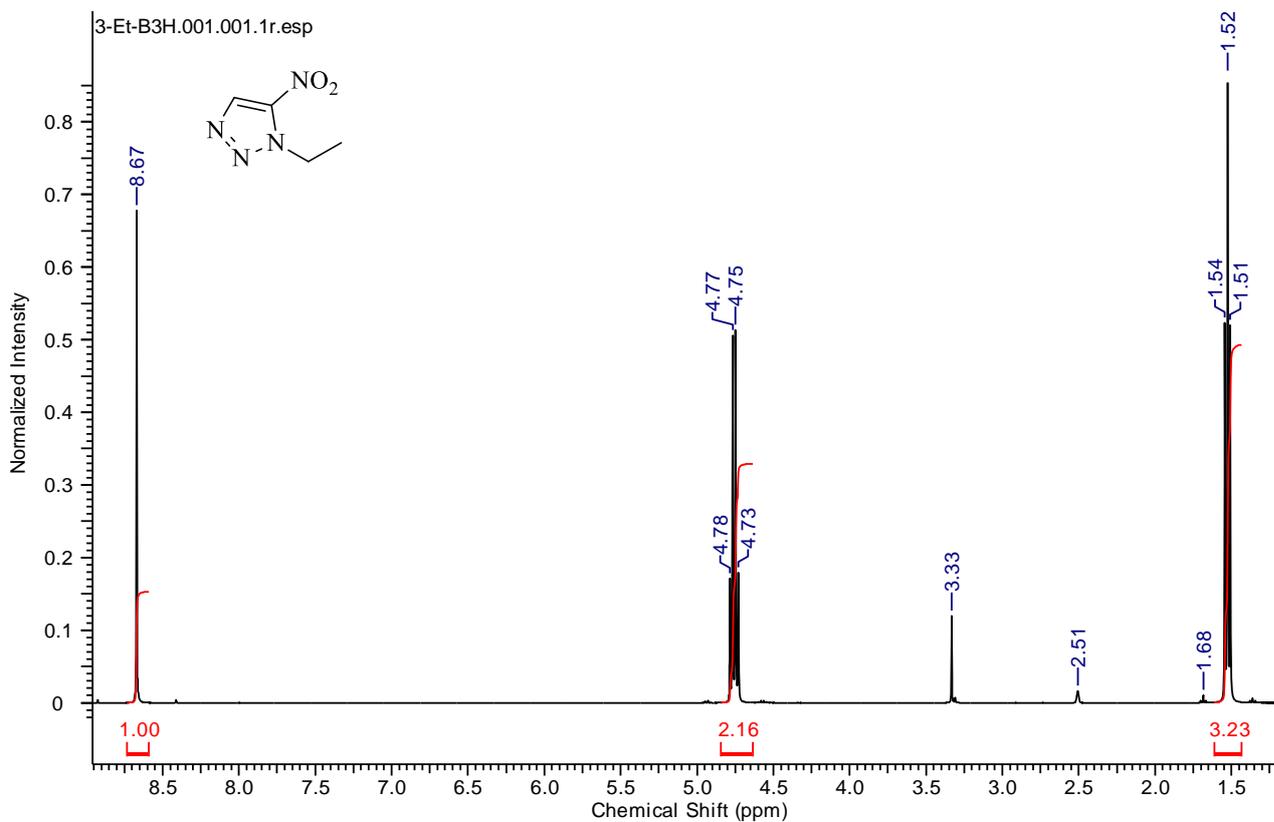
**3-Bromo-1,4,5-trimethyl-1H-[1,2,4]triazol-4-ium perchlorate (6f).** Yield 1.43 g (99%), white crystals, mp 205 °C (H<sub>2</sub>O). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 4.17 (s, 3H, N-CH<sub>3</sub>); 3.98 (s, 3H, N-CH<sub>3</sub>); 3.00 (s, 3H, C-CH<sub>3</sub>). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 154.68

(C-Br); 132.15 (C-CH<sub>3</sub>); 37.83(N-CH<sub>3</sub>); 33.80 (N-CH<sub>3</sub>); 9.95 (C-CH<sub>3</sub>). FTIR (v, cm<sup>-1</sup>): 3464, 3400, 2962, 1592, 1546, 1458, 1374, 1286, 1087, 789, 732, 676, 624. Anal. calcd. for C<sub>5</sub>H<sub>9</sub>BrClN<sub>3</sub>O<sub>4</sub> (%): C, 20.67; H, 3.12; Cl, 12.20; N, 14.46; O, 22.03. Found (%): C, 20.67; H, 3.08; Cl, 12.15; N, 14.44; O, 22.00.

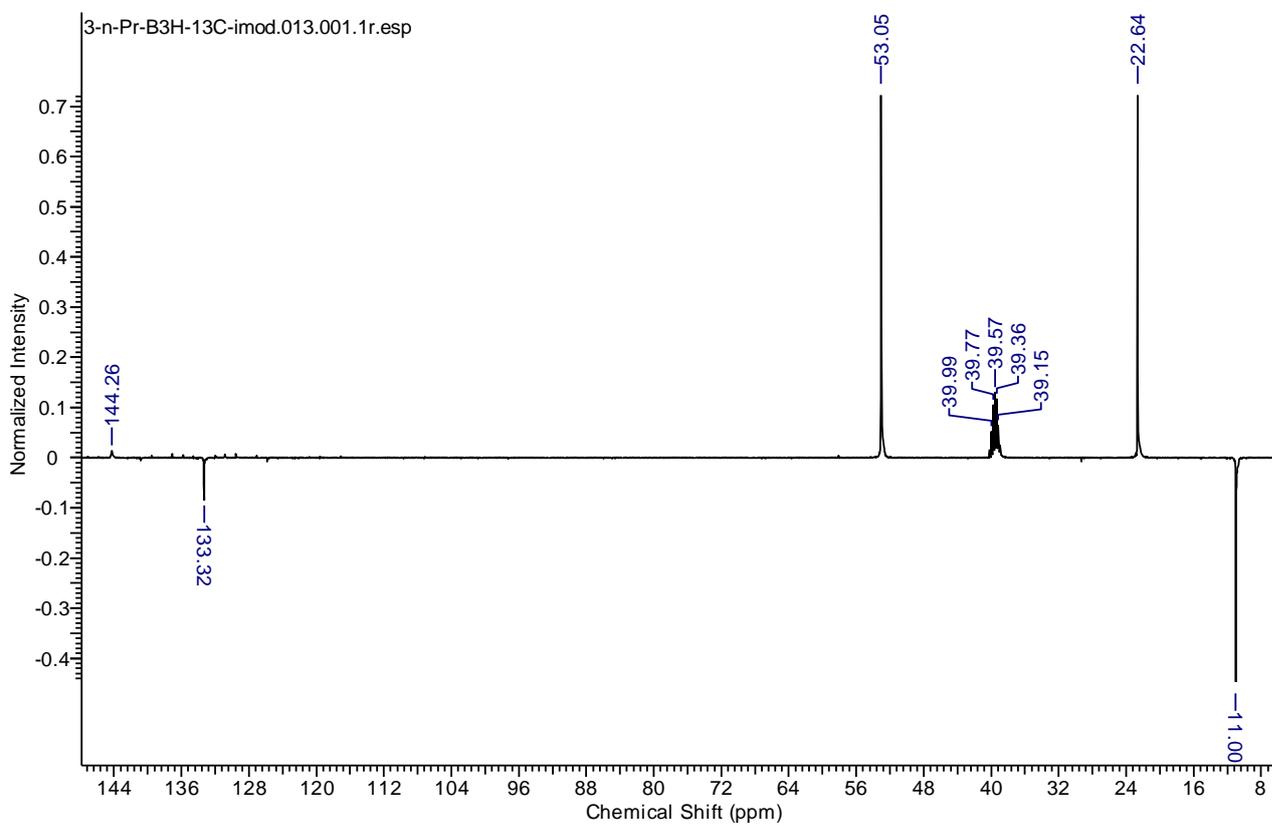
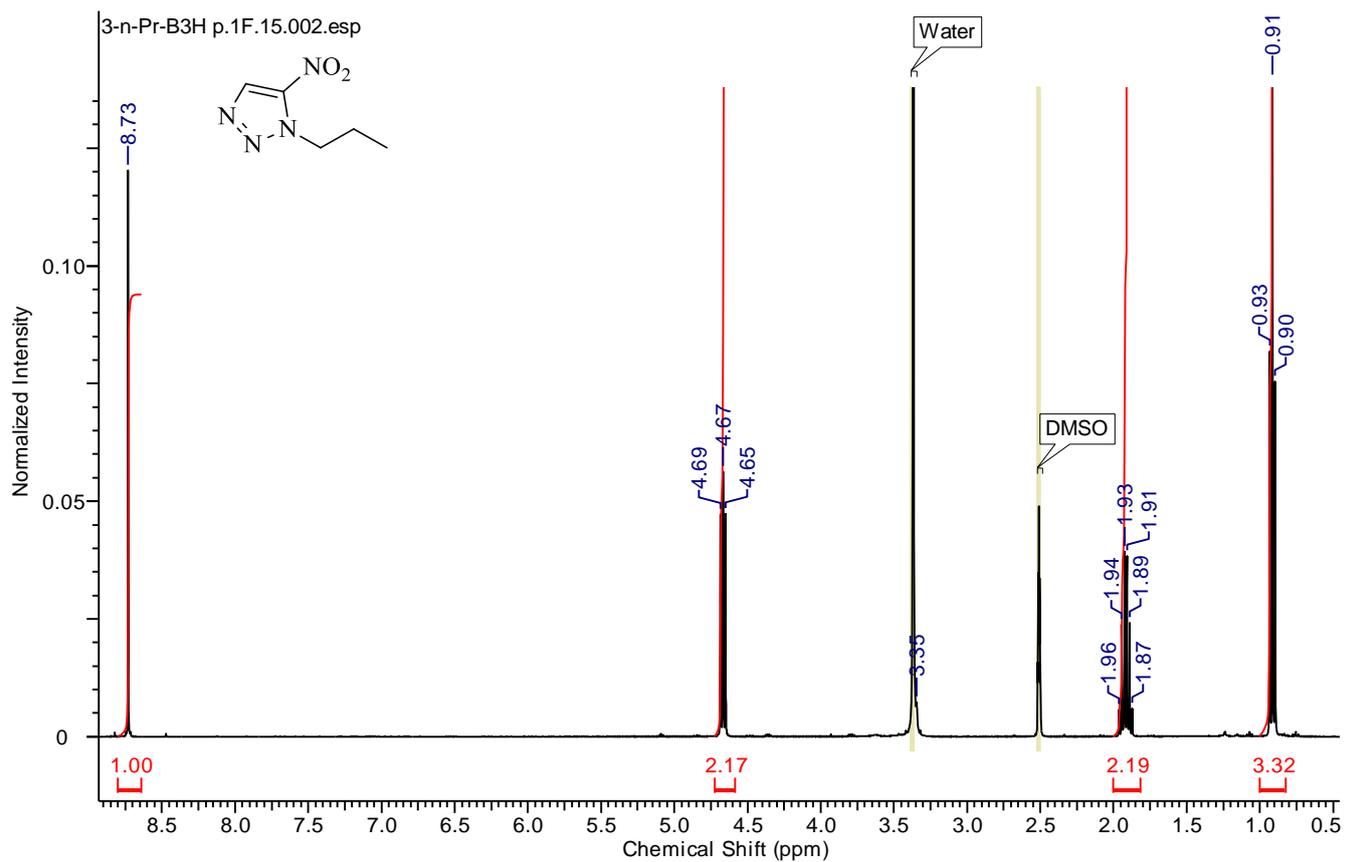
**3-Bromo-1,4-diethyl-1*H*-[1,2,4]triazol-4-ium perchlorate (6g).** Yield 1.38 g (91%), white crystals, mp 155 °C (H<sub>2</sub>O). <sup>1</sup>H NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 10.09 (s, 1H, C-H); 4.57-4.62 (q, 2H, *J*=7.22 Hz, -CH<sub>2</sub>-); 4.45-4.50 (q, 2H, *J*=7.12 Hz, -CH<sub>2</sub>-); 1.60-1.66 (m, 6H, *J*=5.95 Hz, 2(-CH<sub>3</sub>)). <sup>13</sup>C NMR (Me<sub>2</sub>CO-*d*<sub>6</sub>) δ, ppm: 144.10 (C-Br); 132.74 (C-H); 48.74 (-CH<sub>2</sub>-); 44.74 (-CH<sub>2</sub>-); 13.30 (-CH<sub>3</sub>); 13.07 (-CH<sub>3</sub>). FTIR (v, cm<sup>-1</sup>): 3156, 3091, 2992, 1573, 1509, 1452, 1393, 1312, 1086, 879, 731, 625. Anal. calcd. for C<sub>6</sub>H<sub>11</sub>BrClN<sub>3</sub>O<sub>4</sub> (%): C, 23.66; H, 3.64; Cl, 11.64; N, 13.80; O, 21.02. Found (%): C, 23.63; H, 3.59; Cl, 11.62; N, 13.72; O, 21.05.

# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of novel compounds

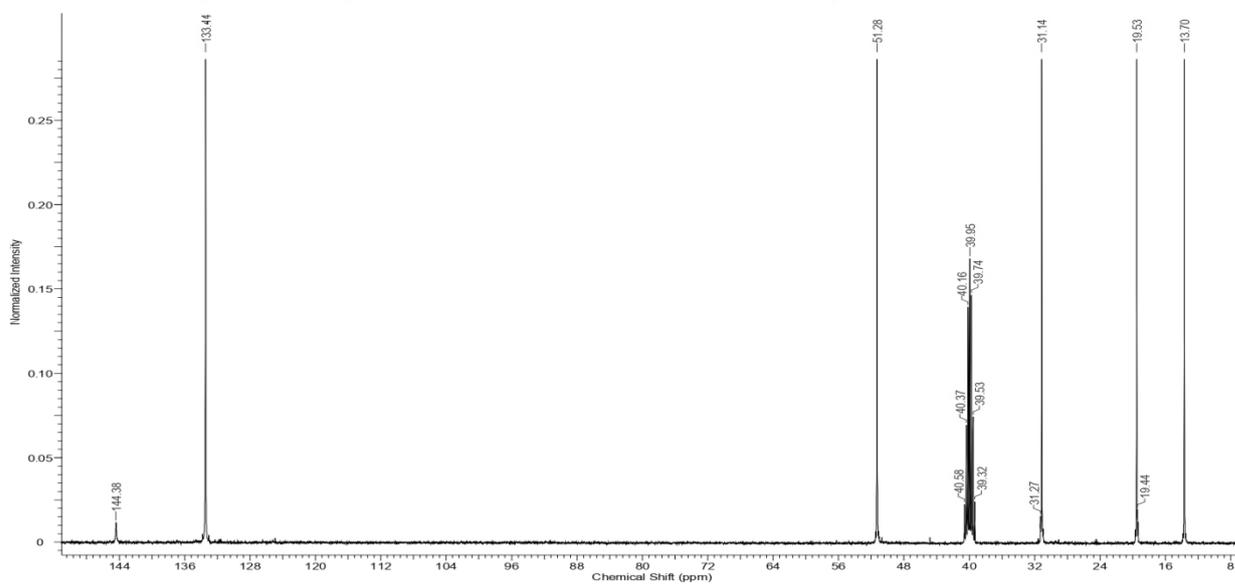
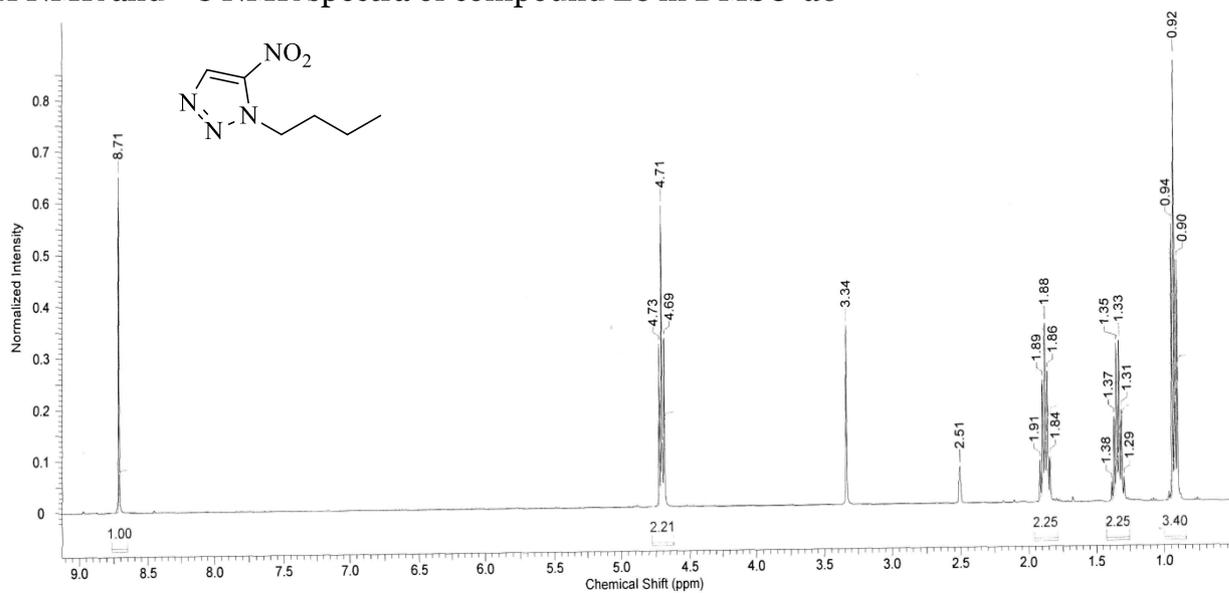
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **2a** in  $\text{DMSO}-d_6$



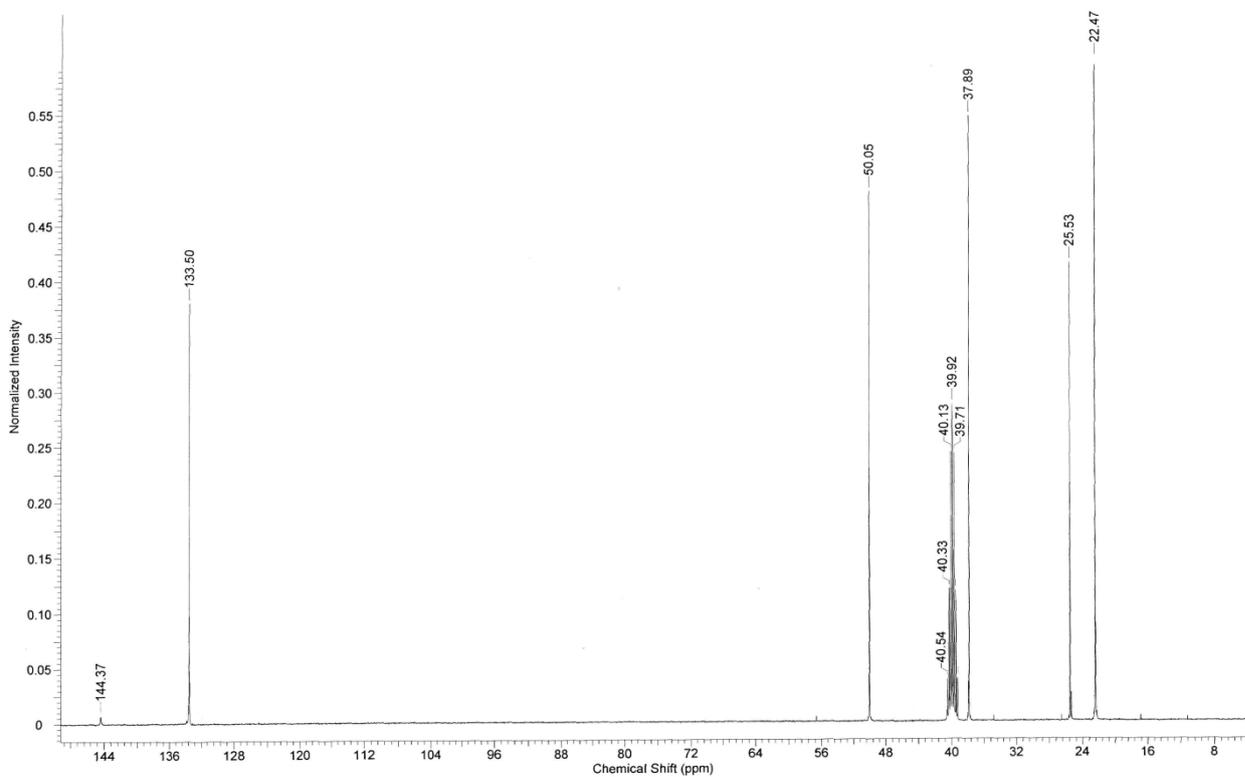
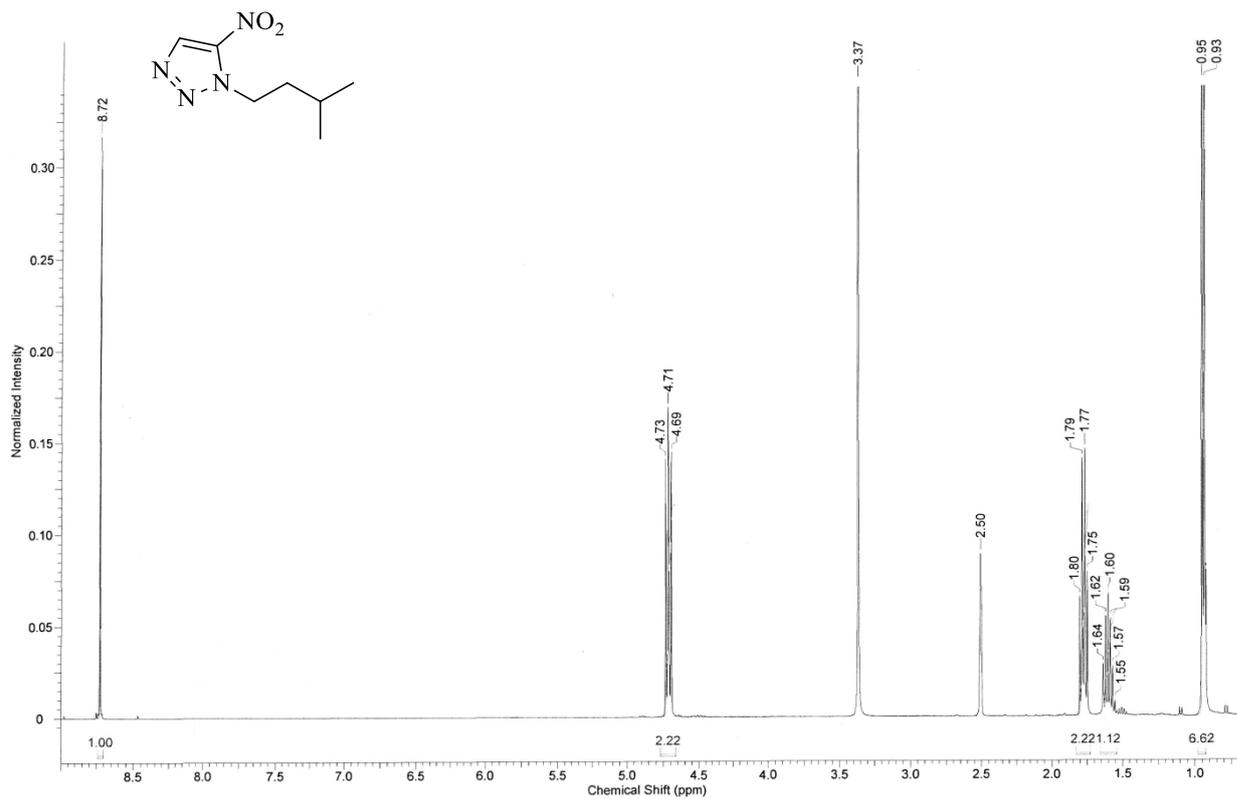
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound **2b** in DMSO-*d*<sub>6</sub>



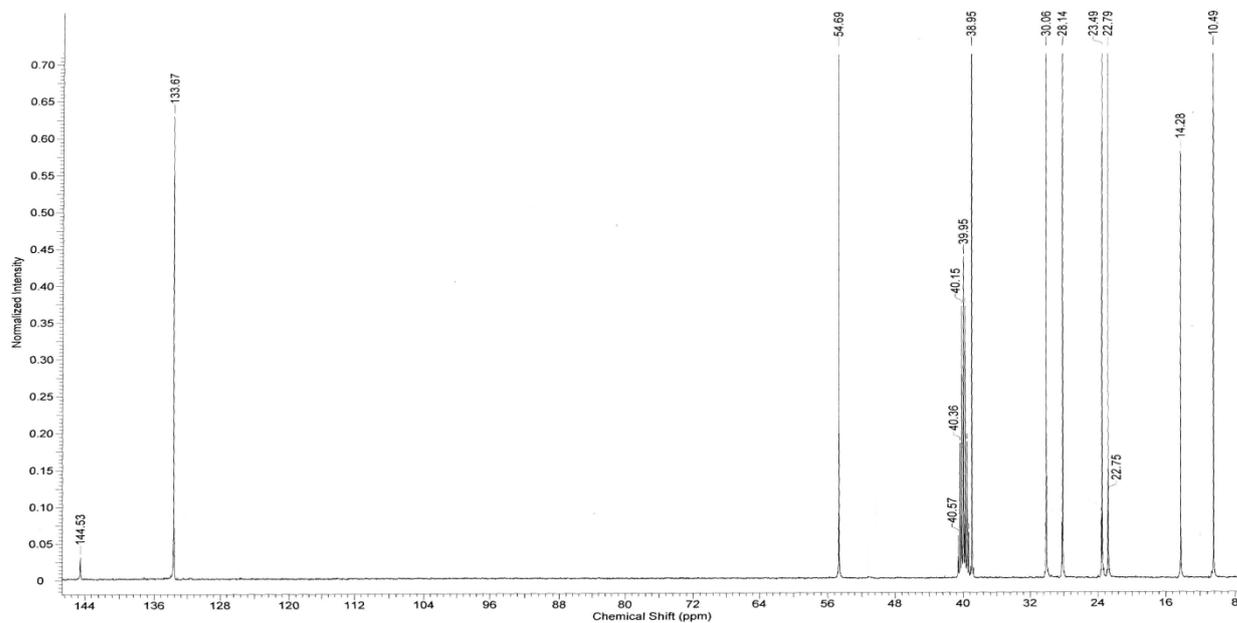
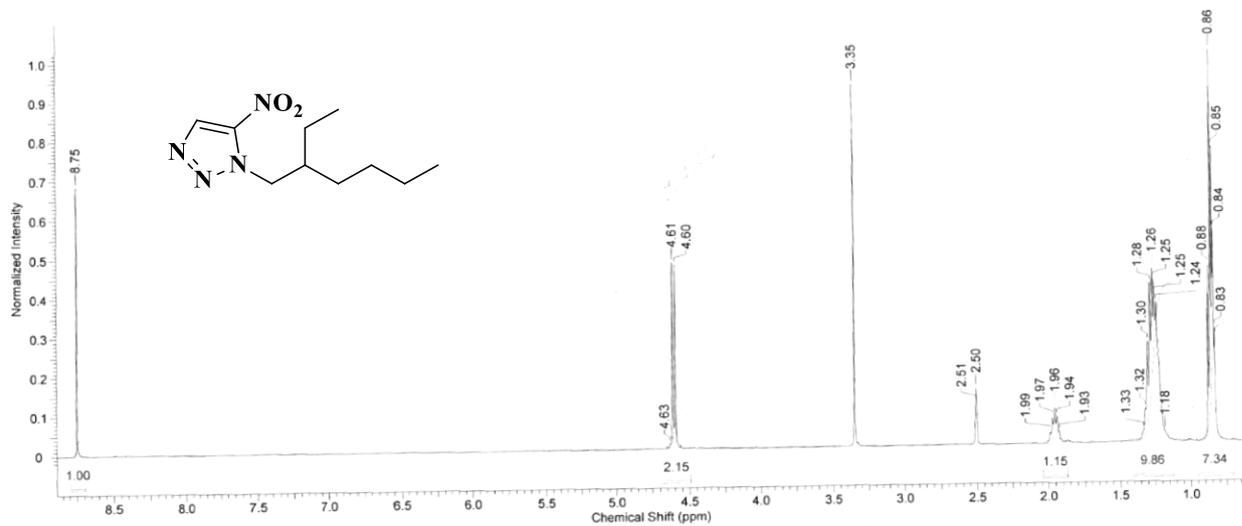
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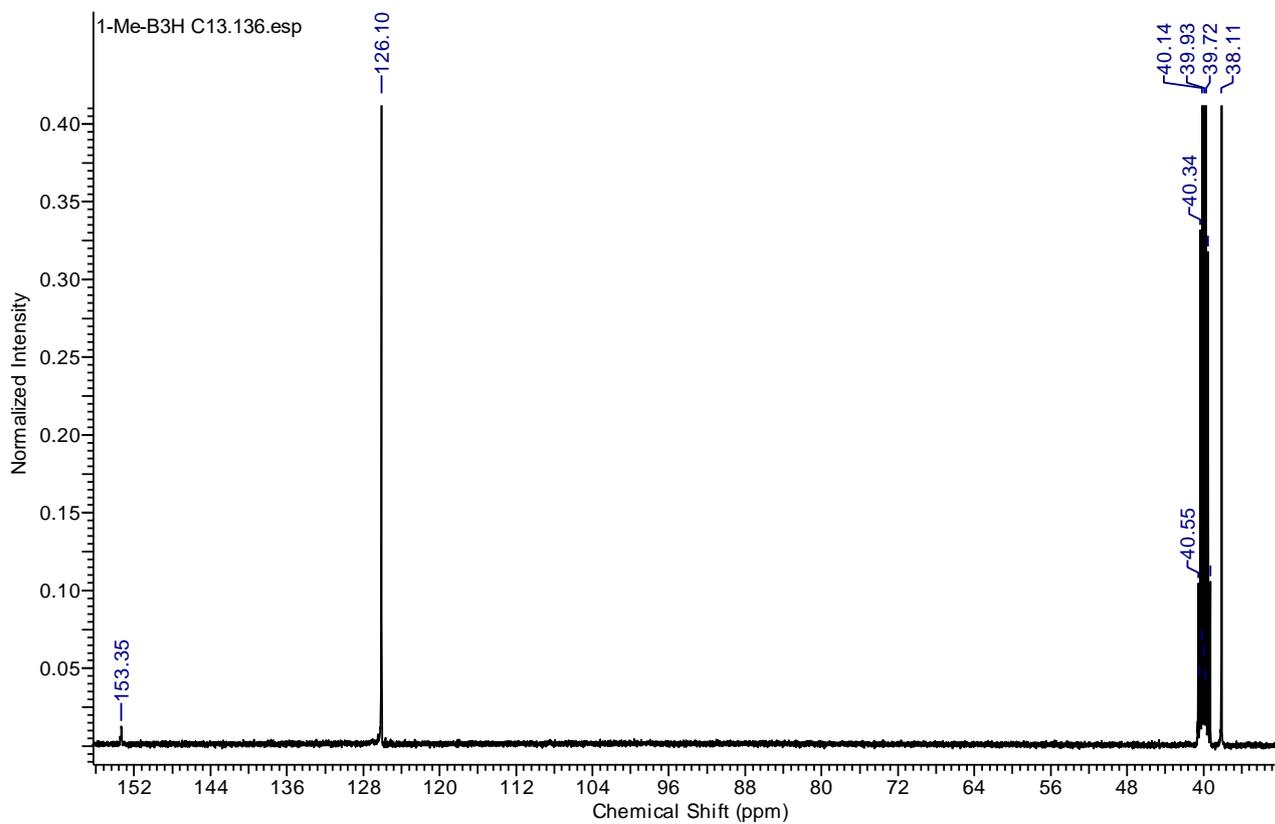
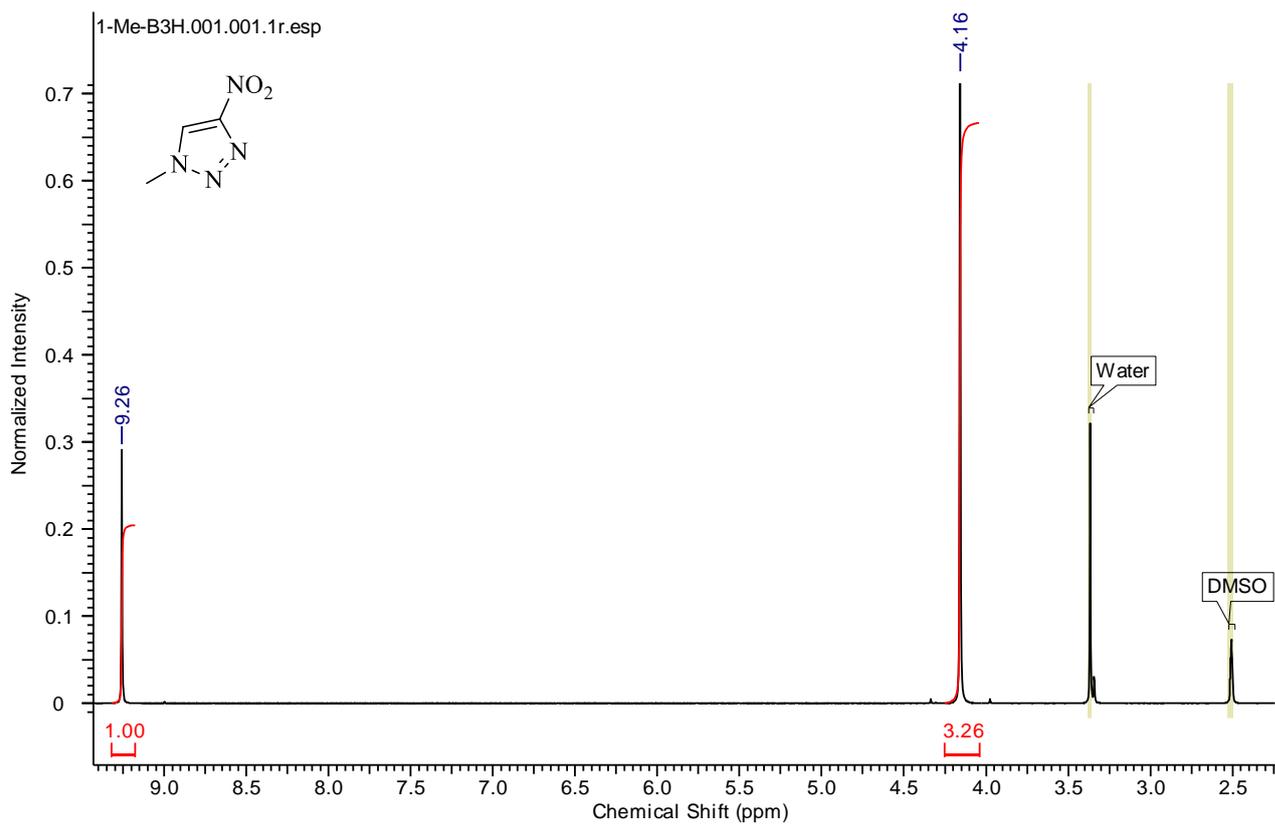
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **2d** in DMSO- $d_6$



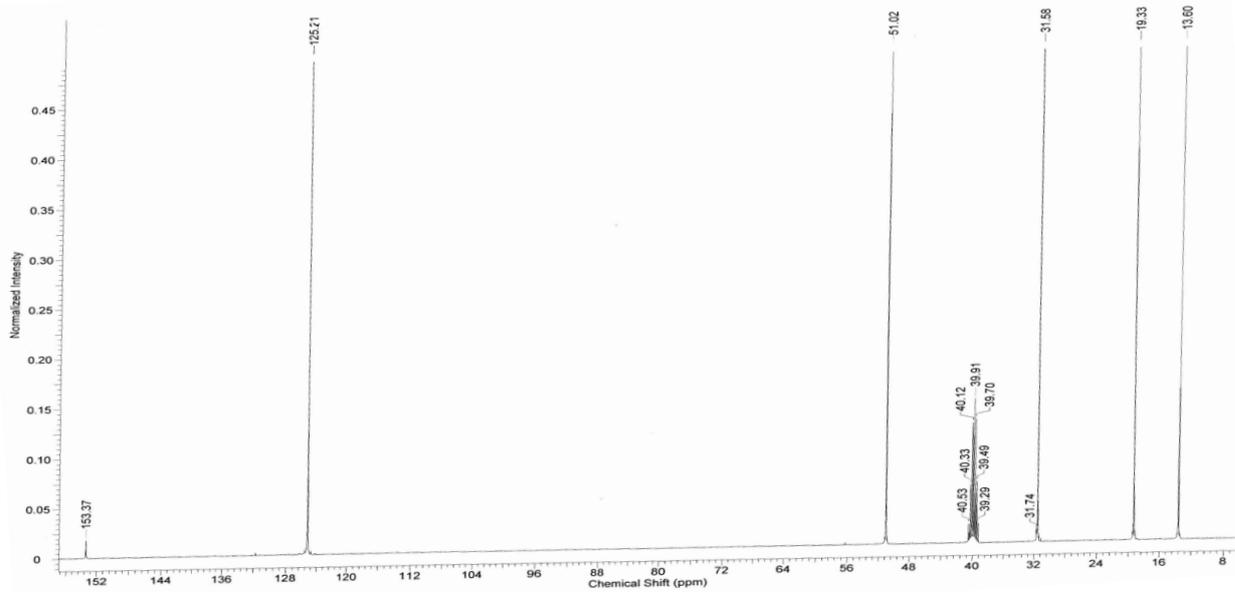
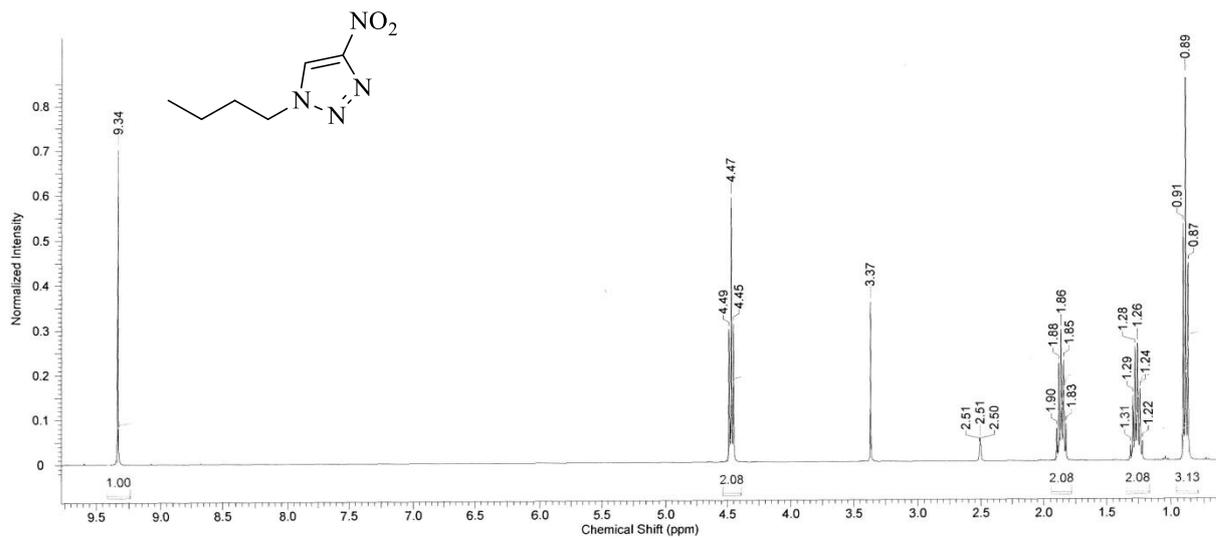
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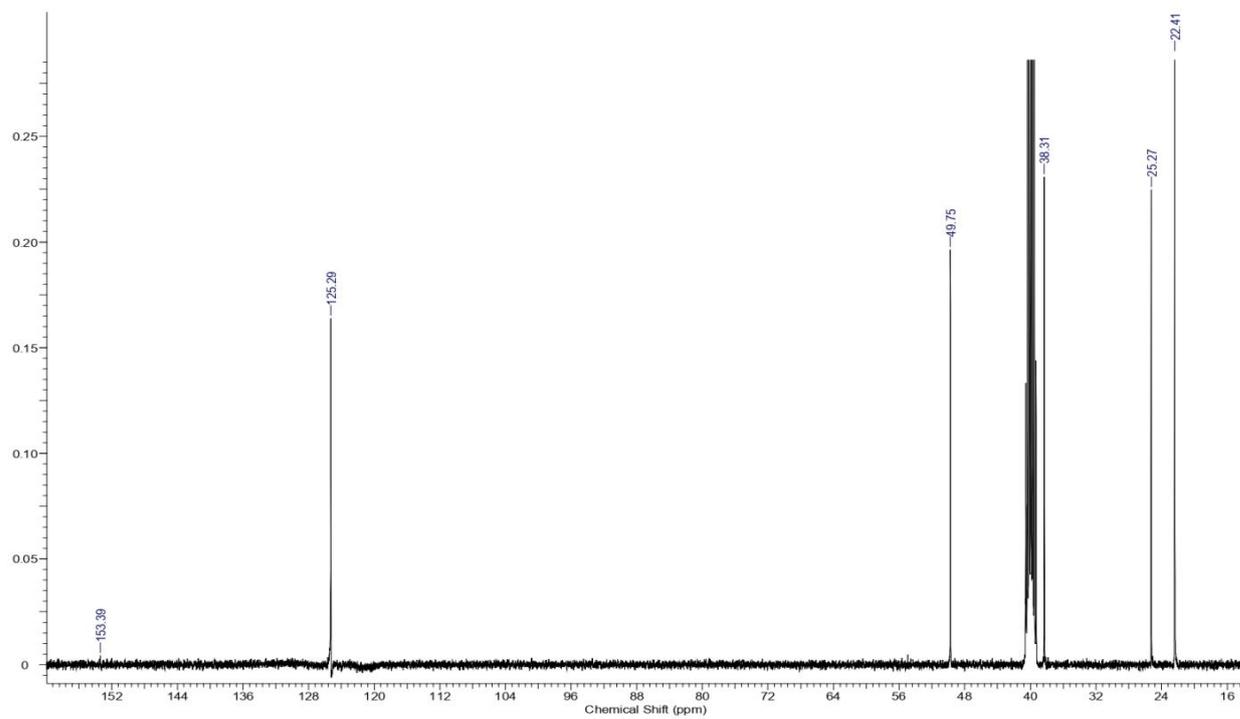
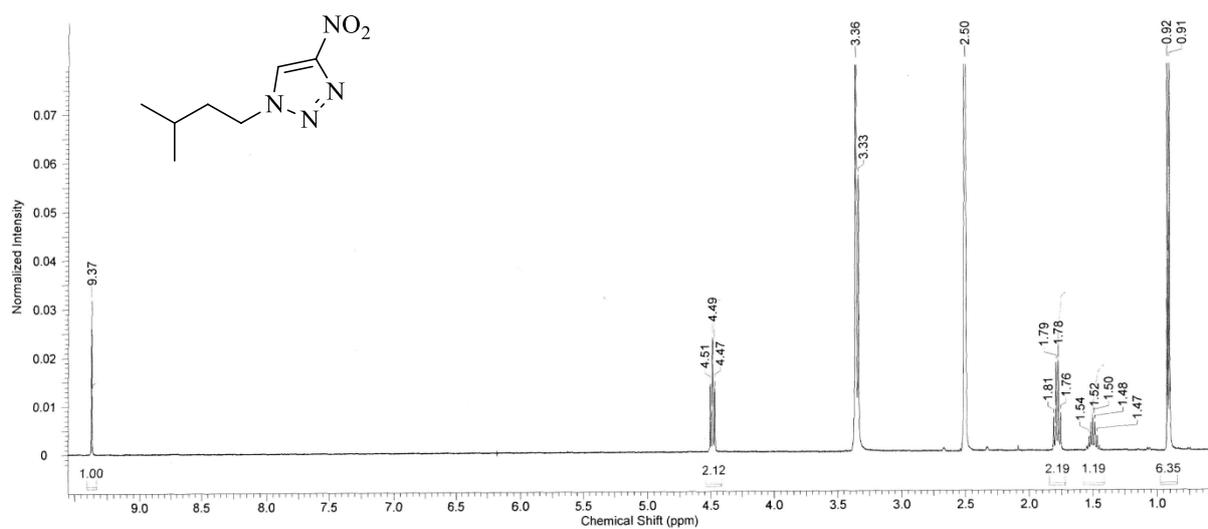
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **3a** in  $\text{DMSO-}d_6$



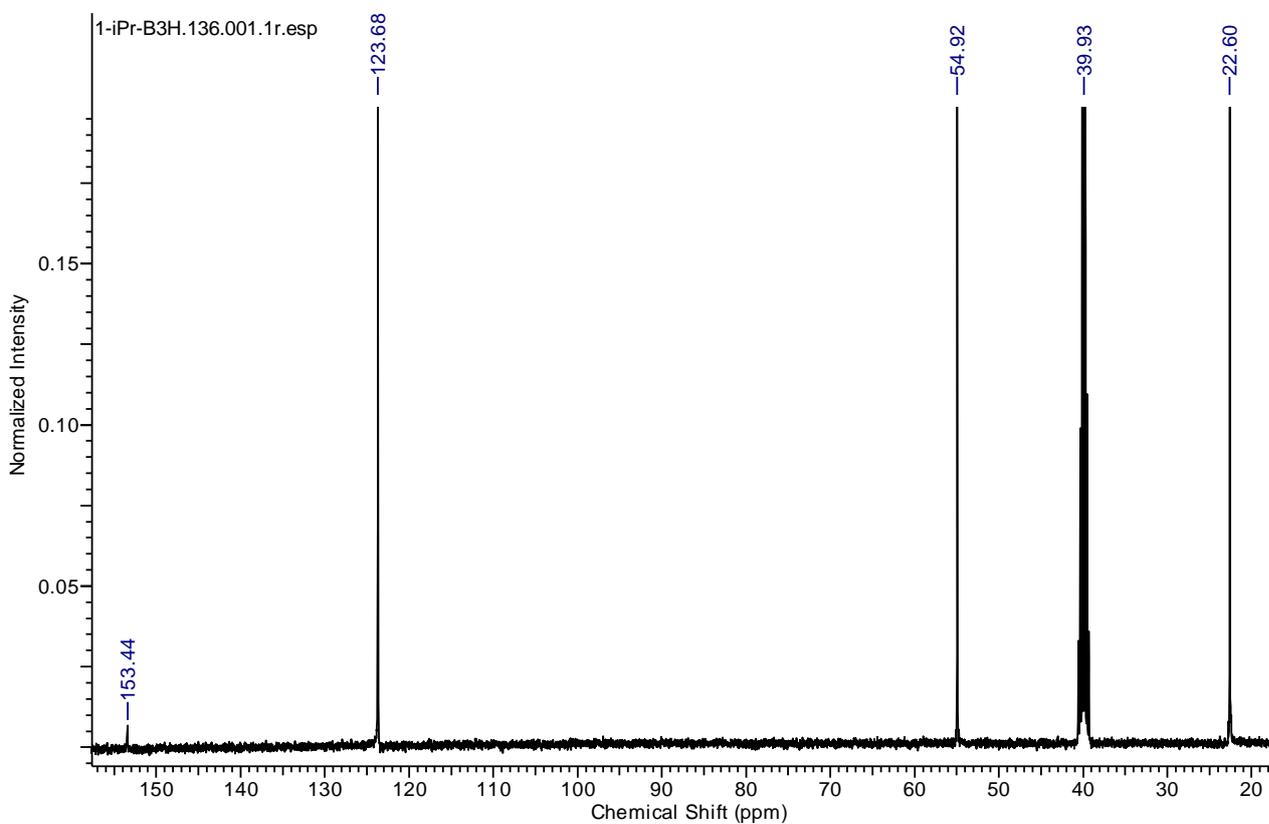
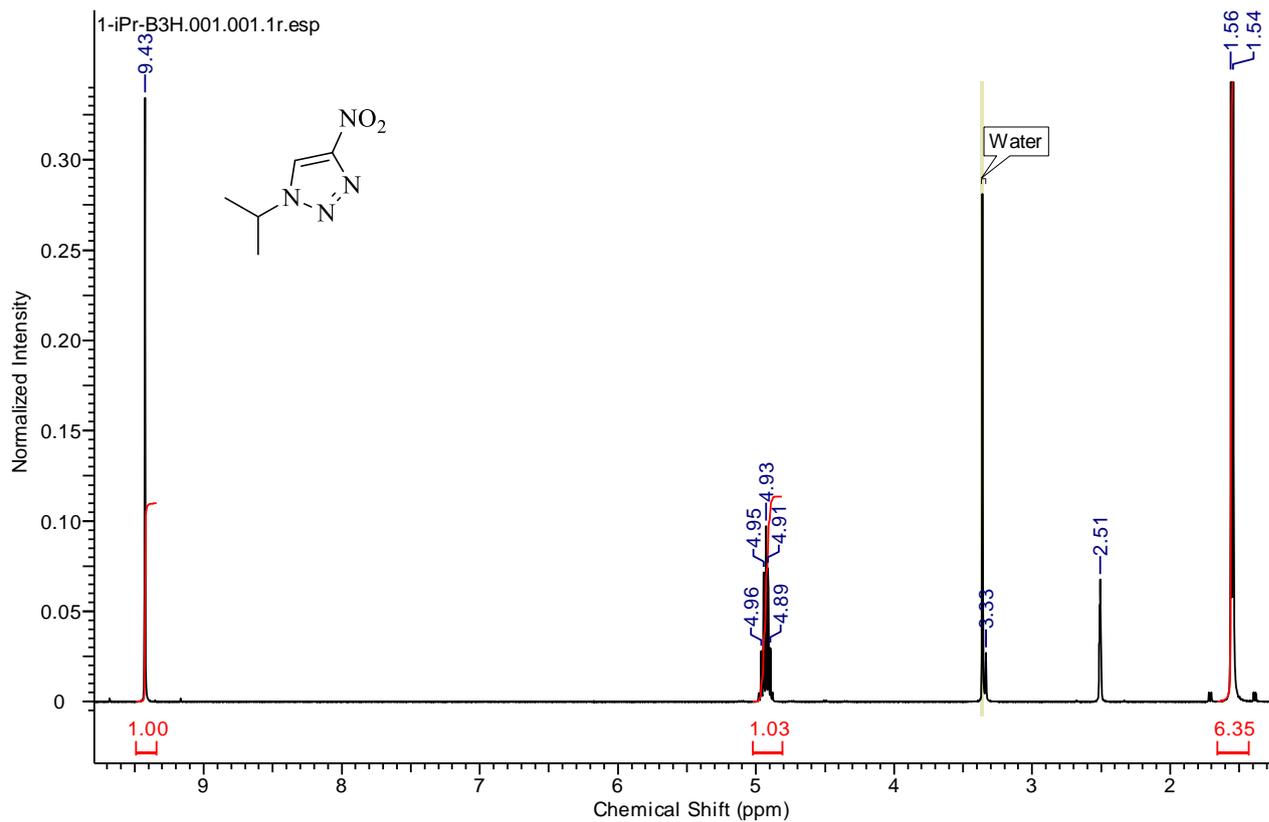
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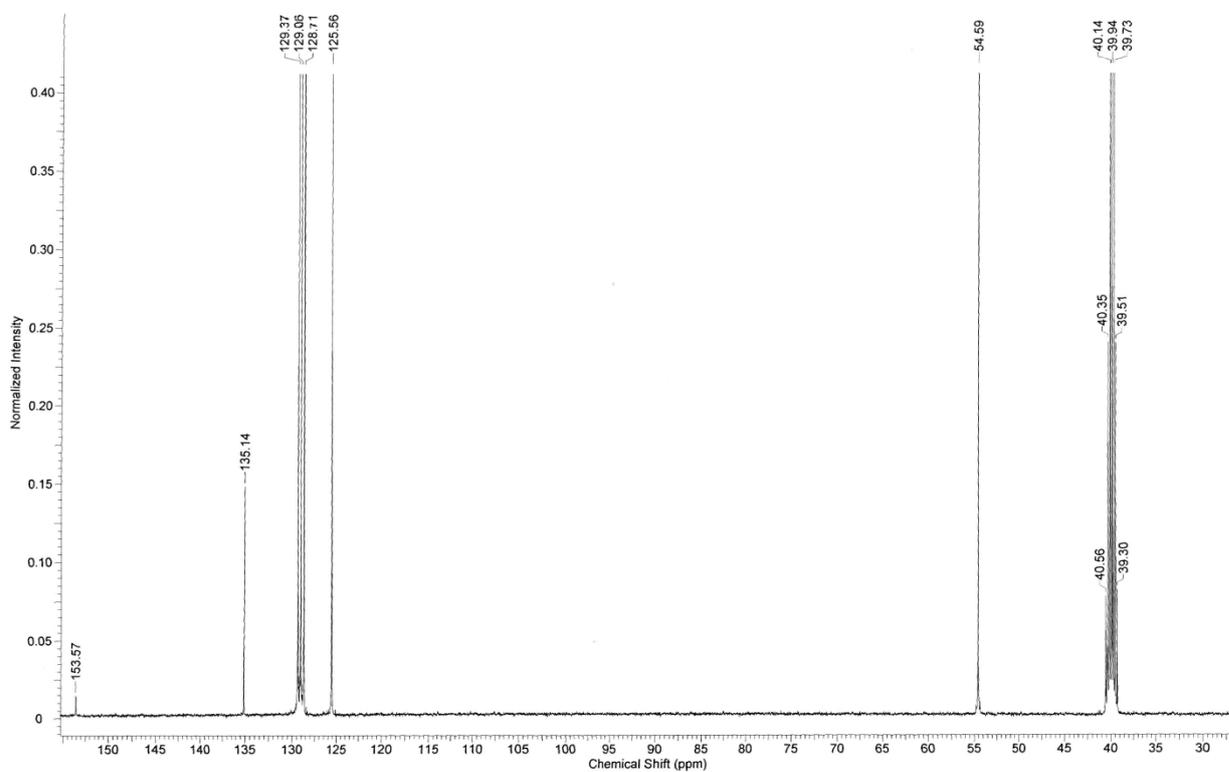
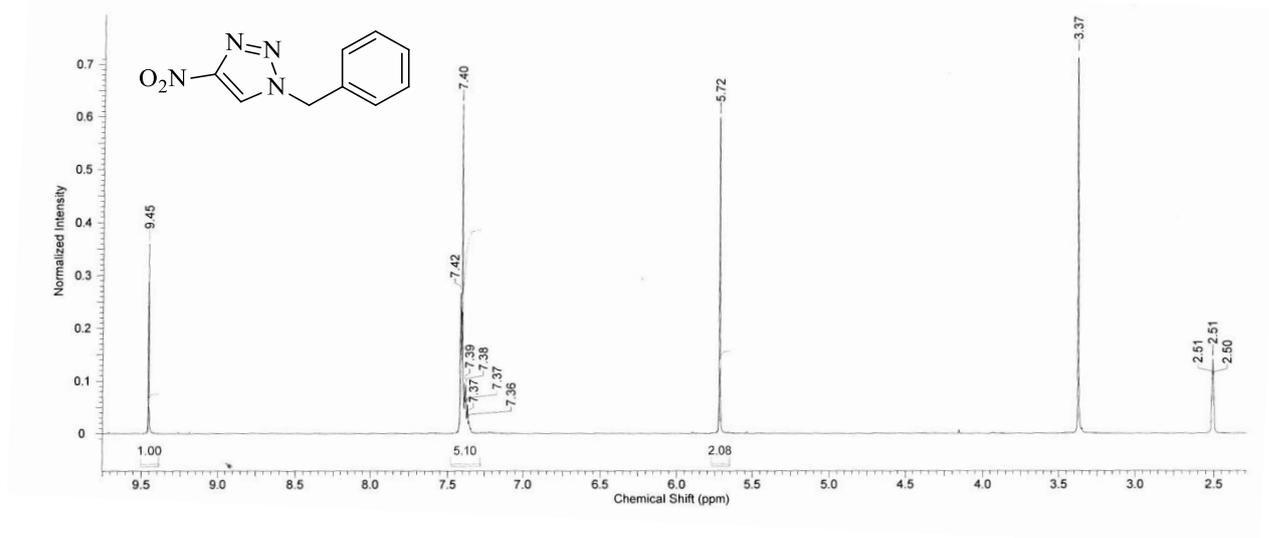
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **3d** in  $\text{DMSO-}d_6$



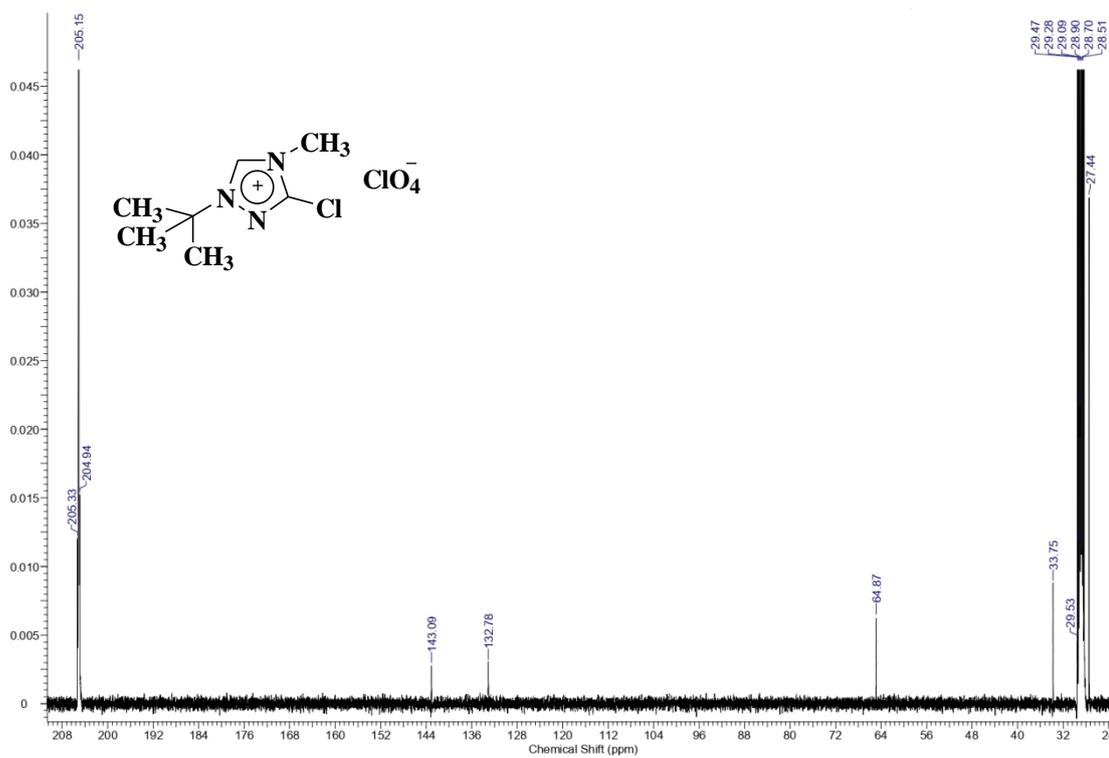
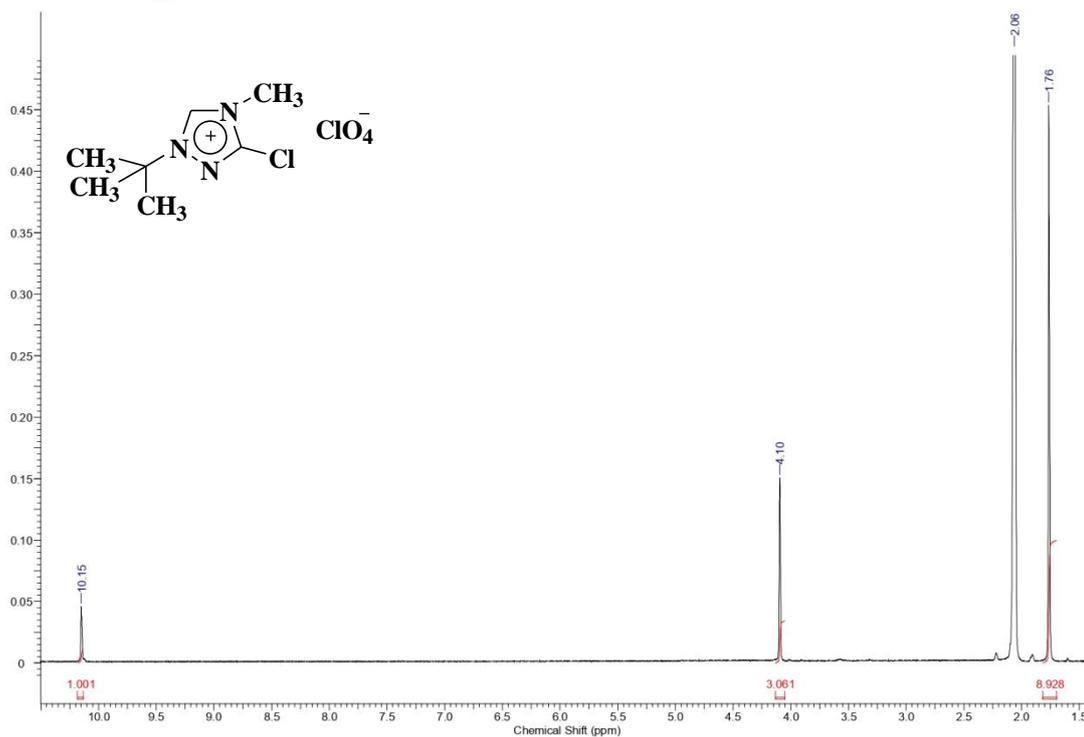
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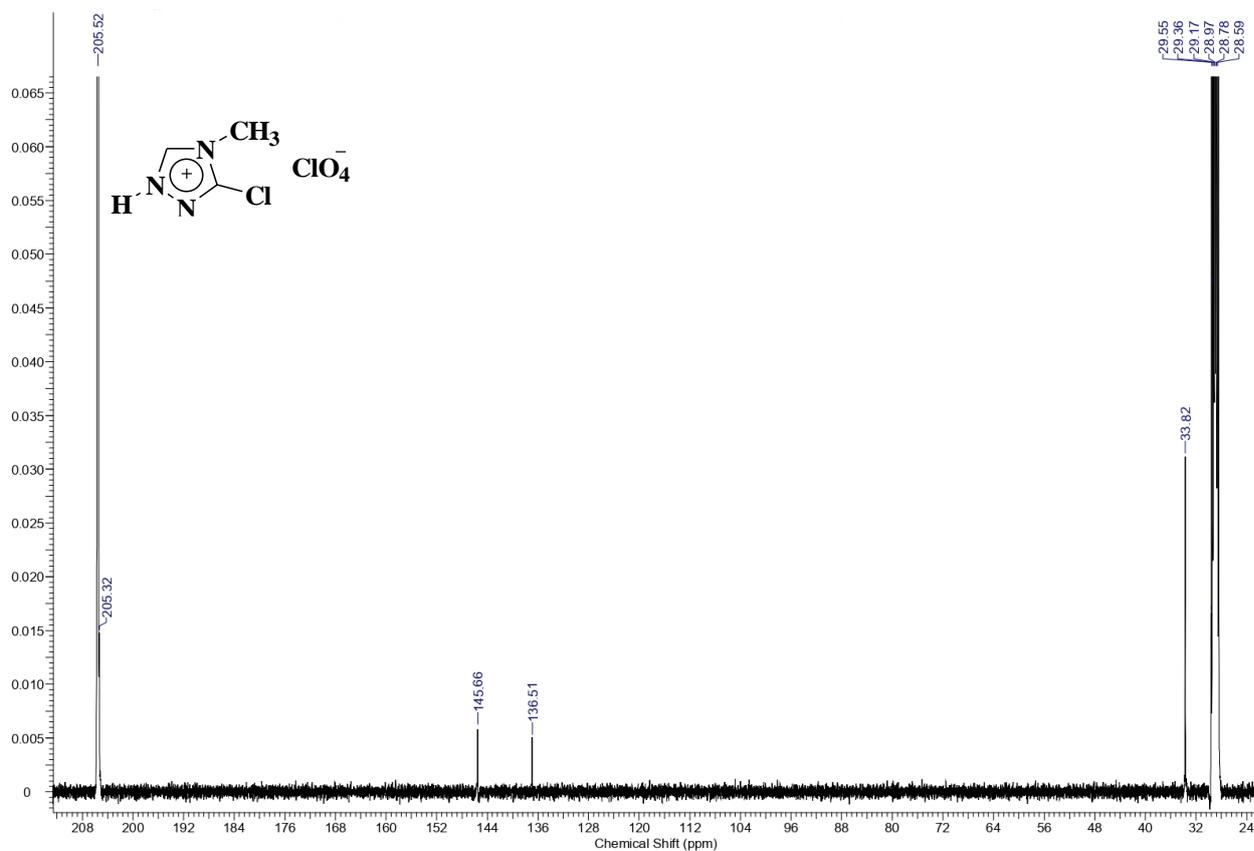
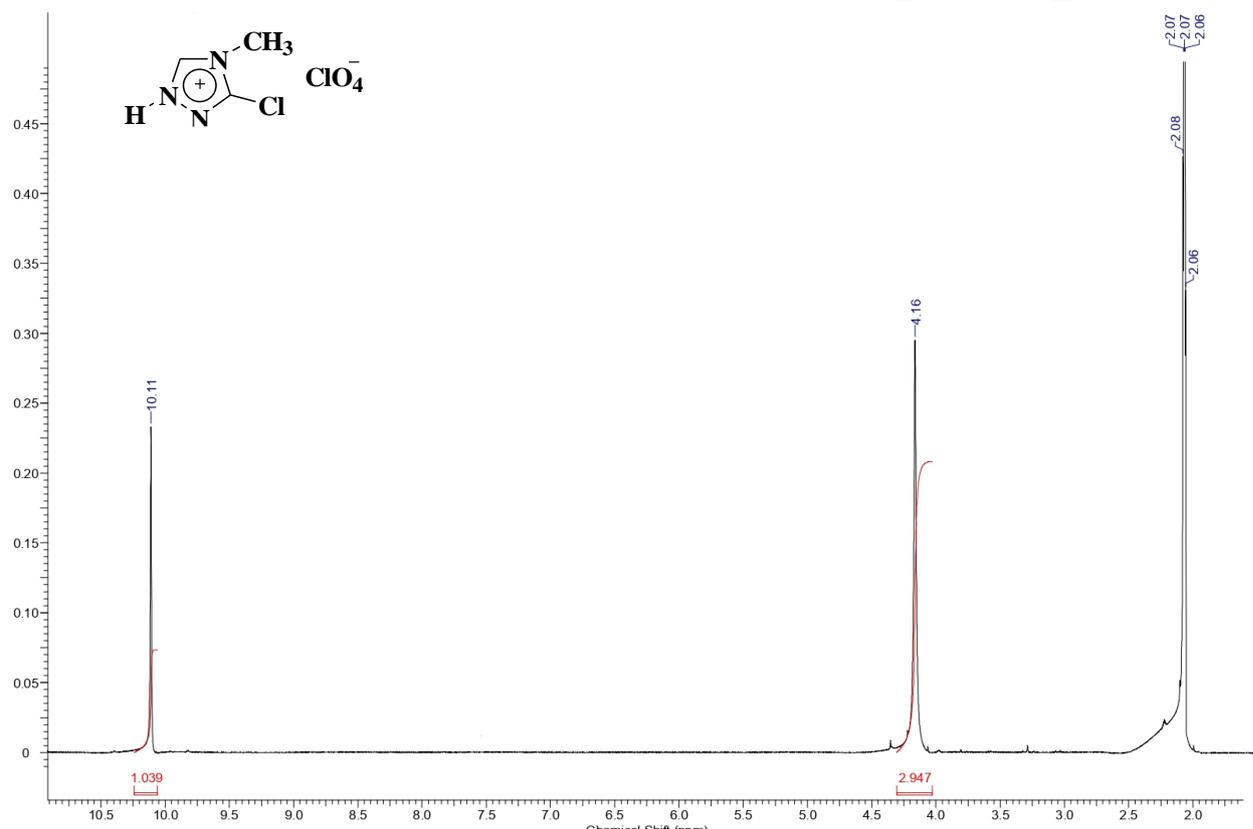
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **3f** in  $\text{DMSO-}d_6$



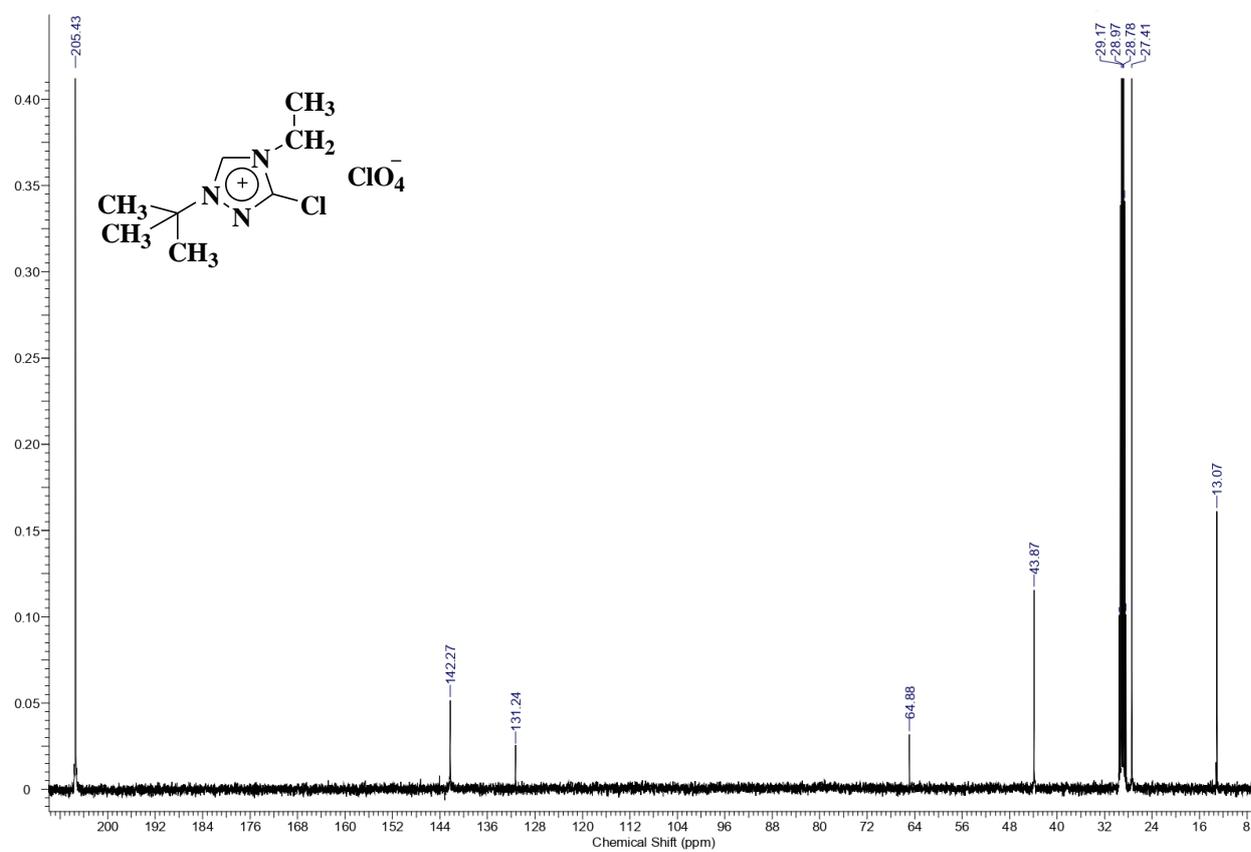
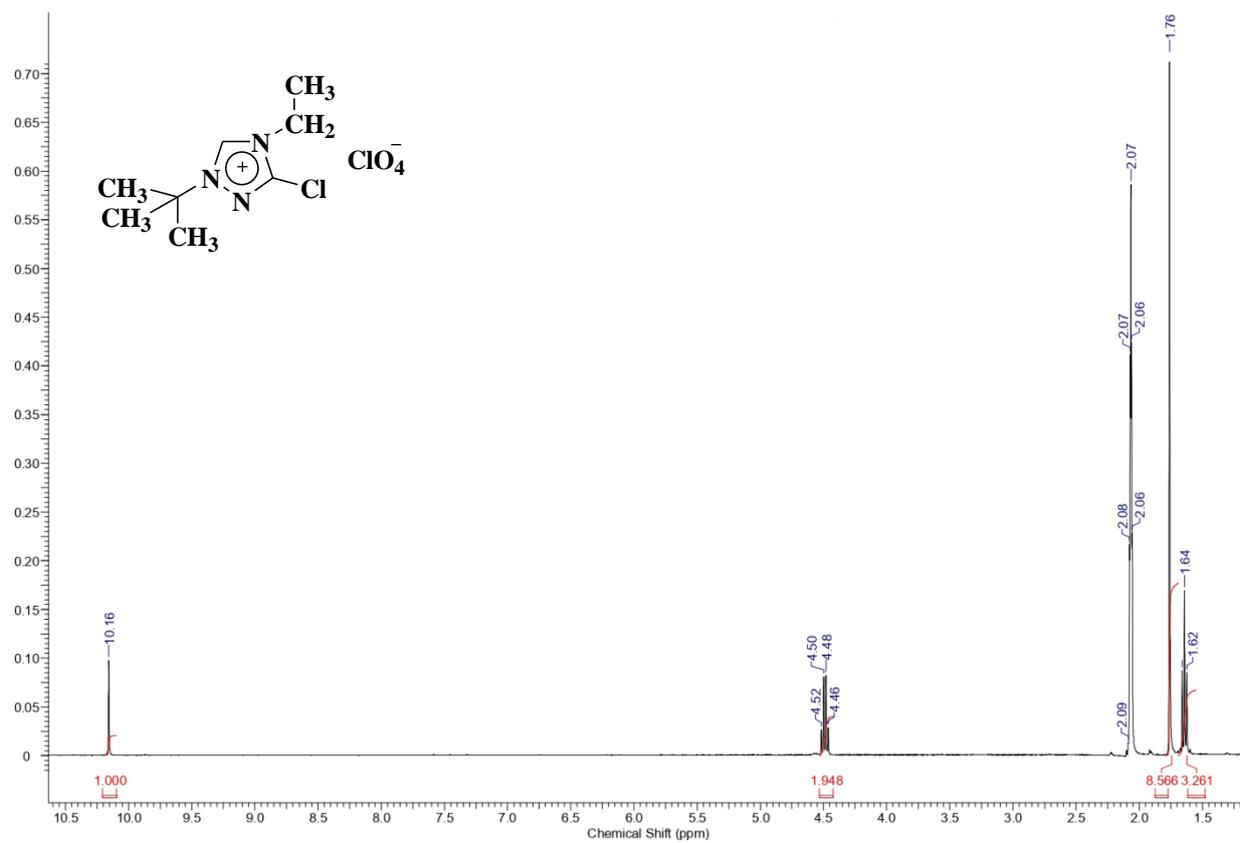
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6a** in  $\text{Me}_2\text{CO}-d_6$



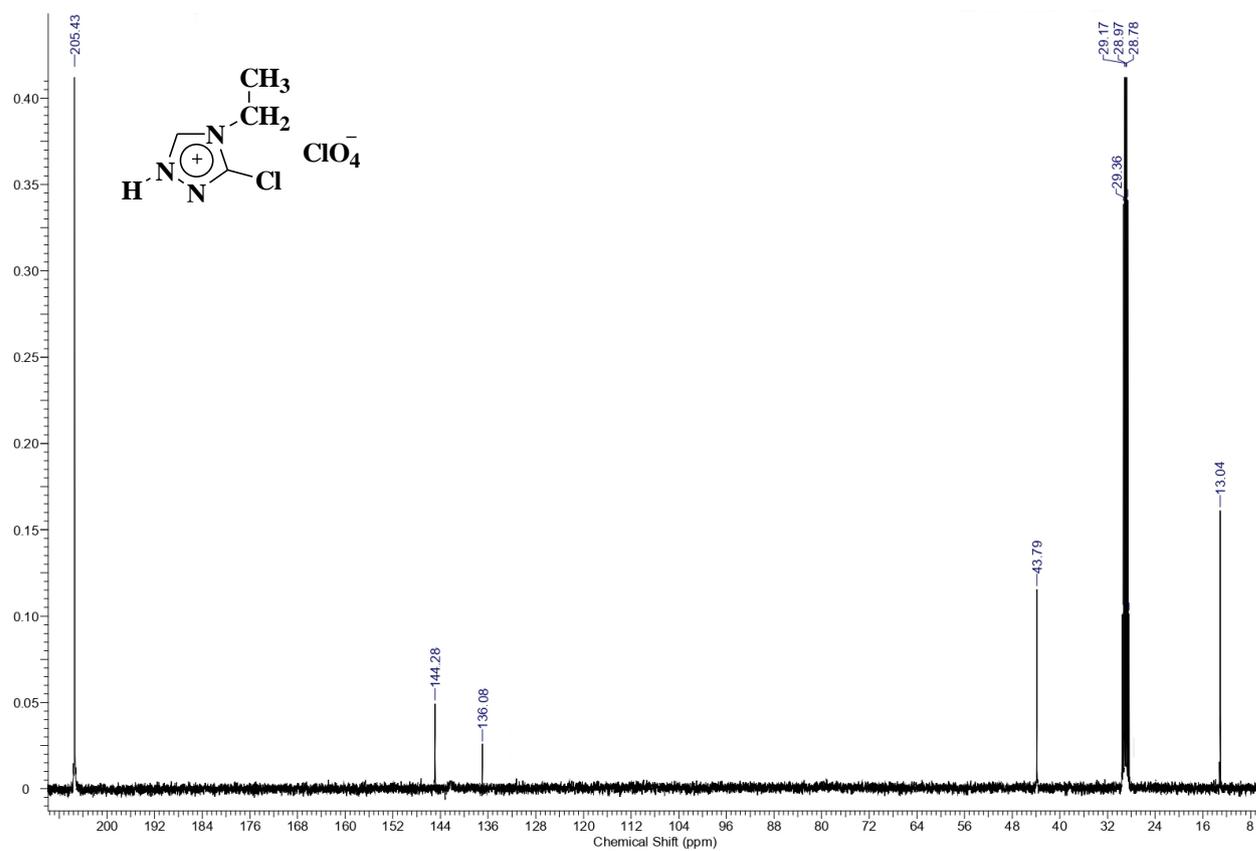
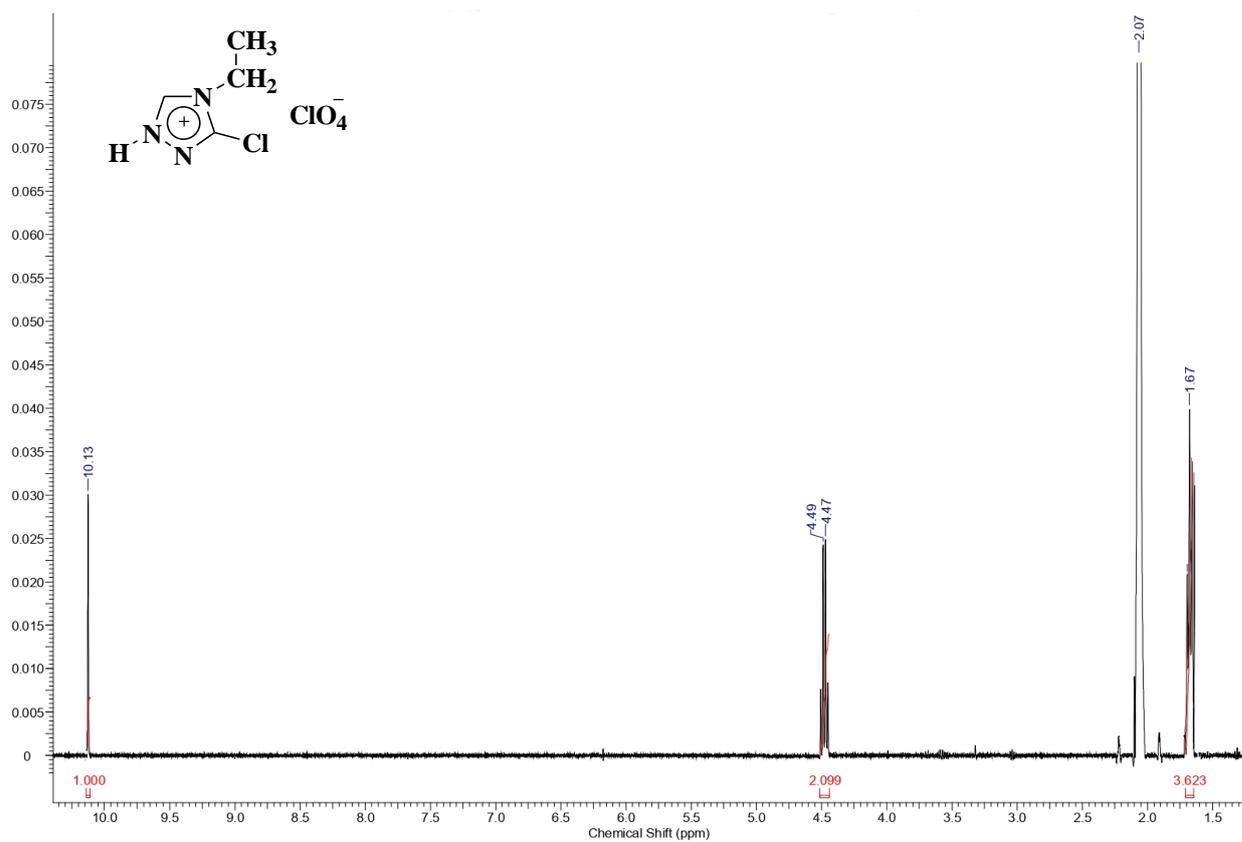
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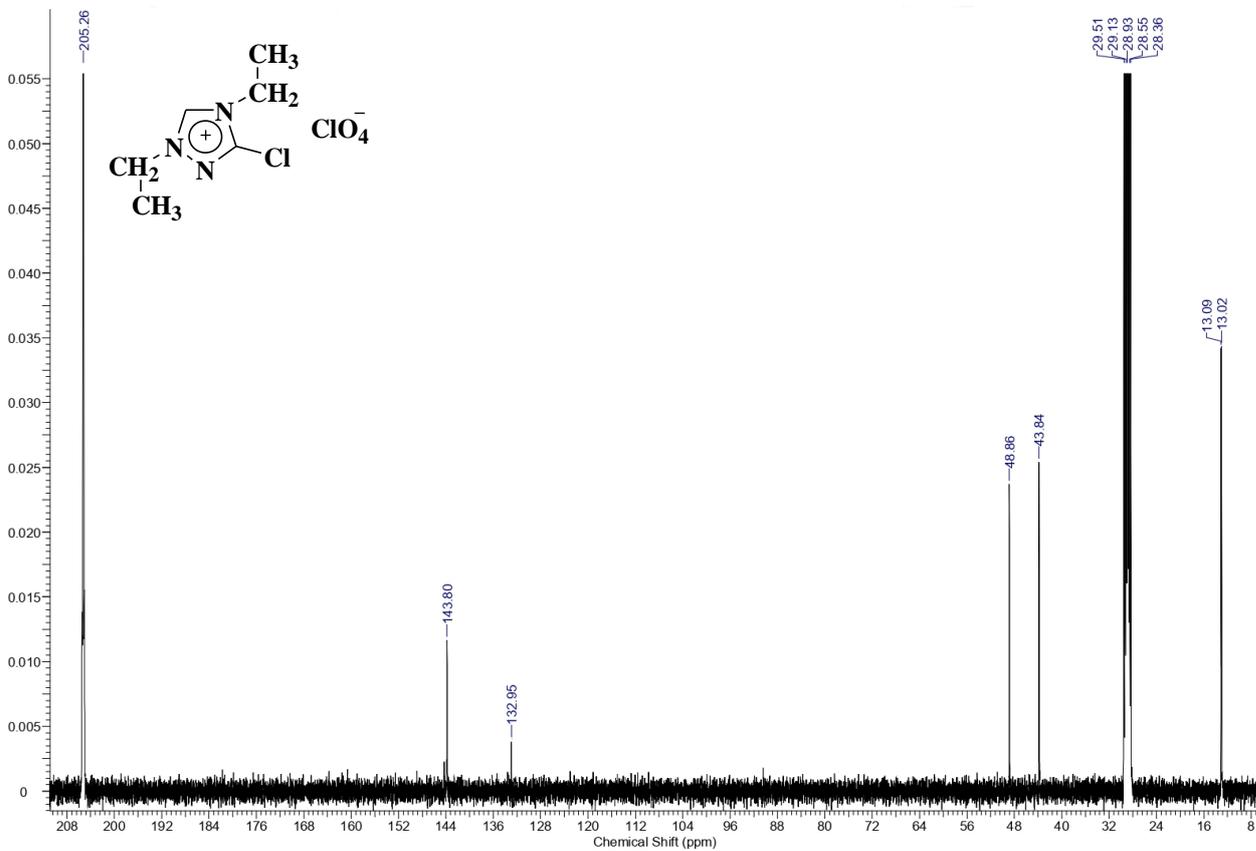
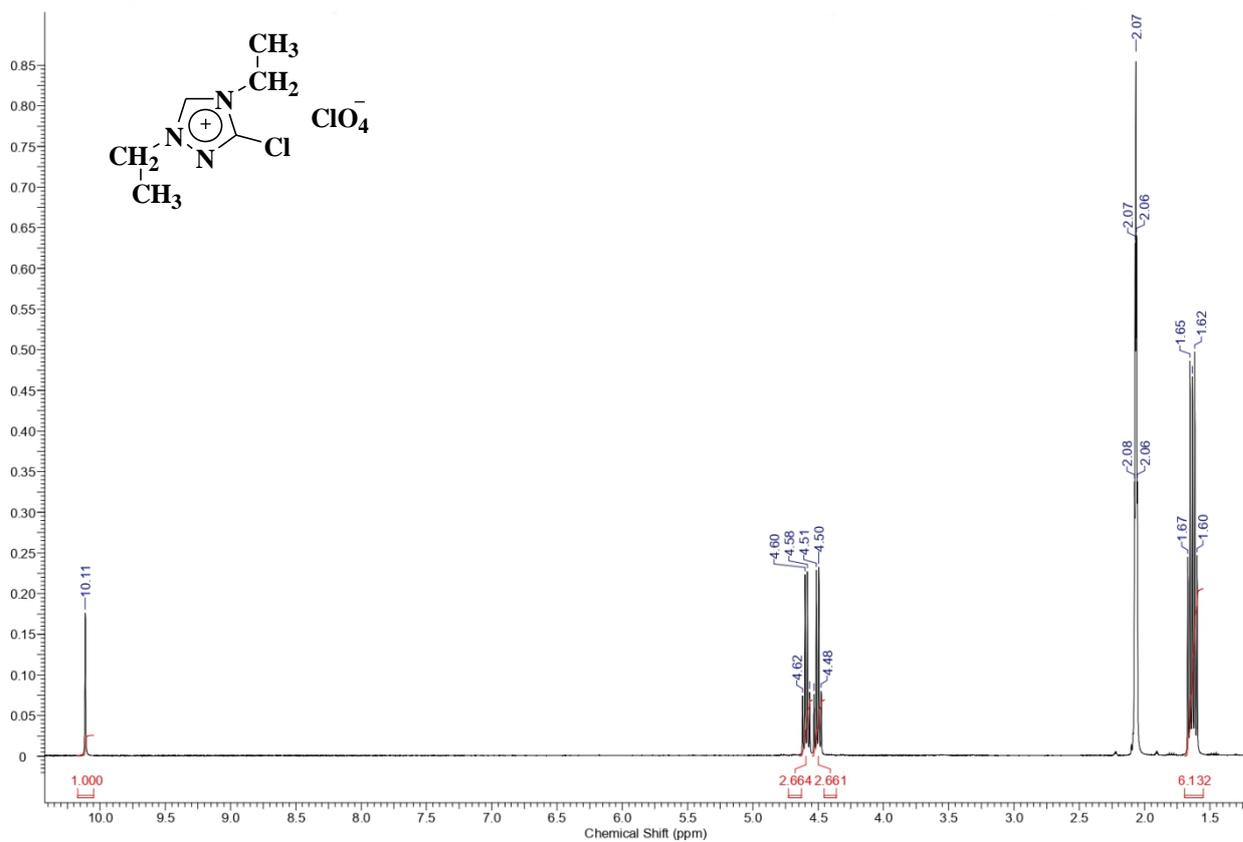
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6b** in  $\text{Me}_2\text{CO}-d_6$



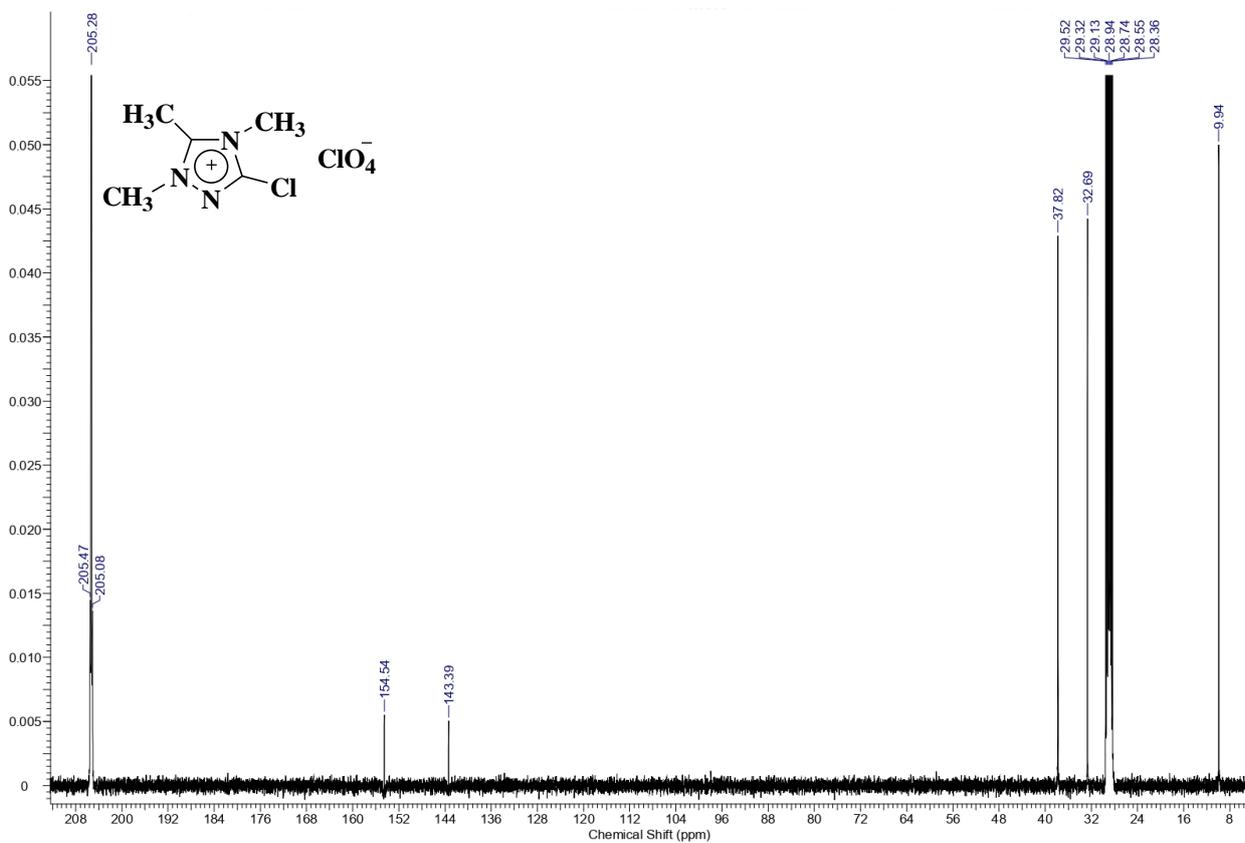
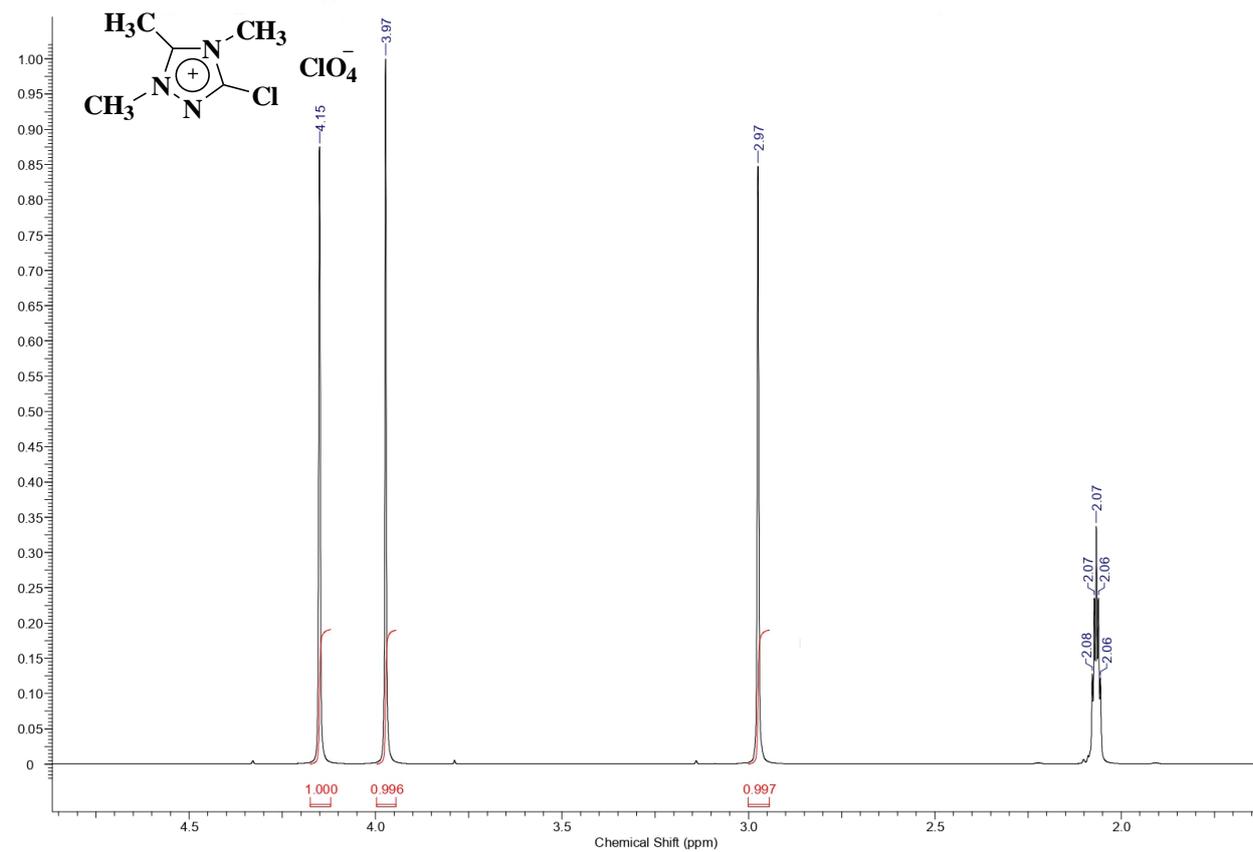
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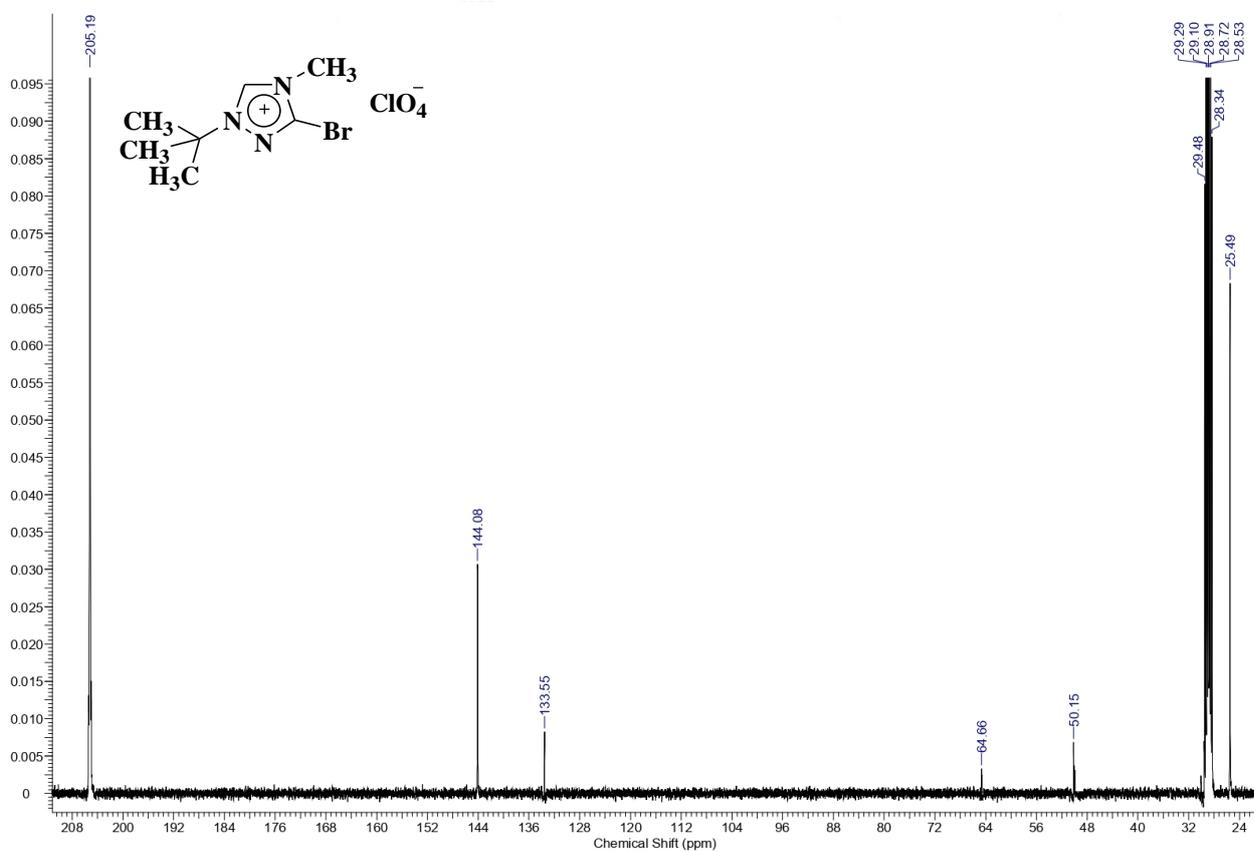
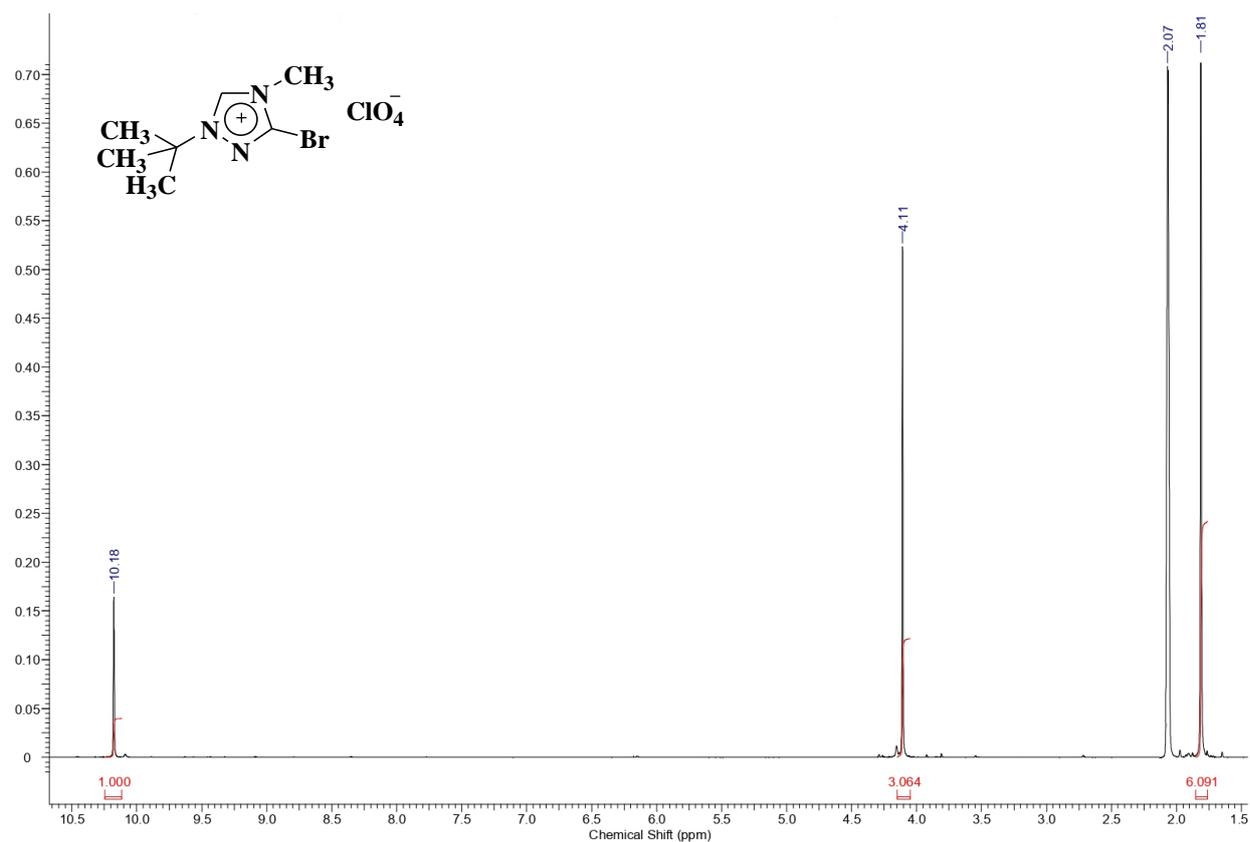
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6d** in  $\text{Me}_2\text{CO}-d_6$



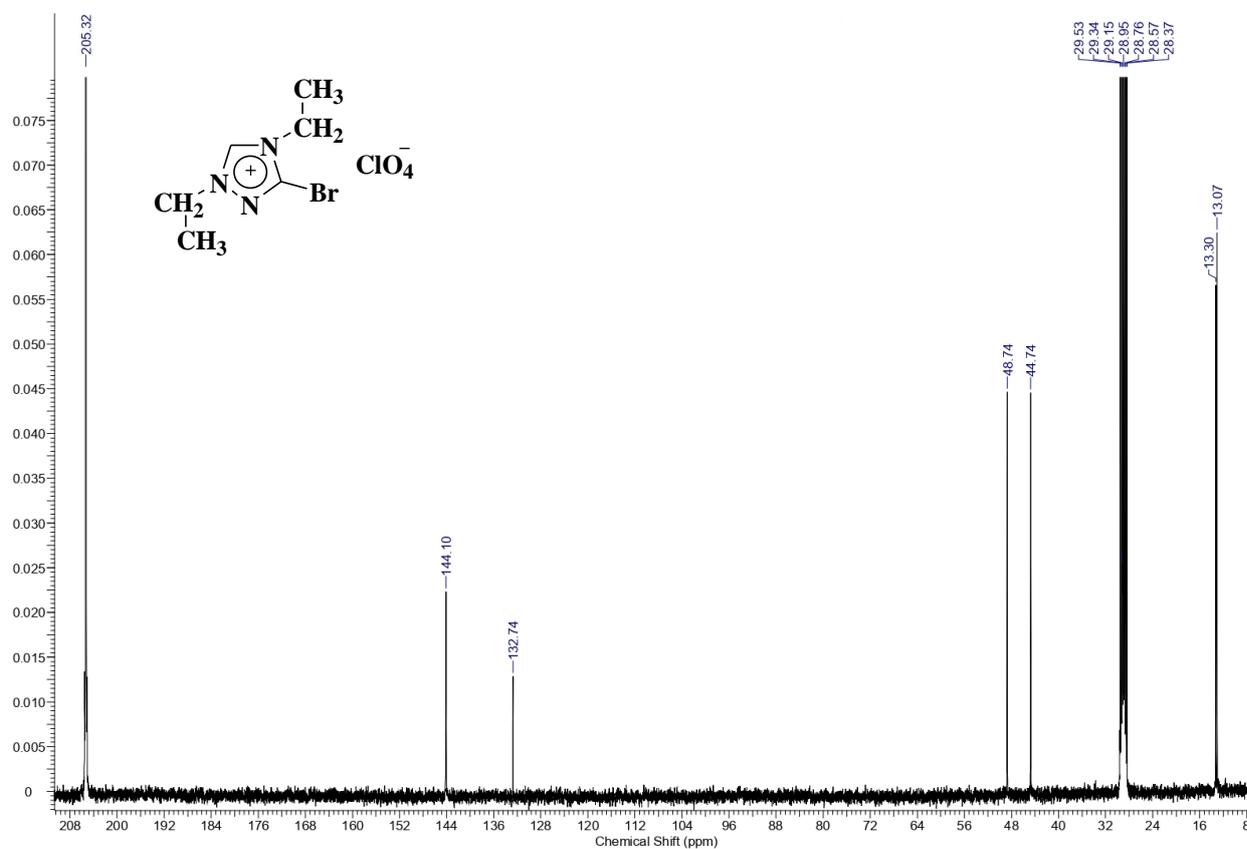
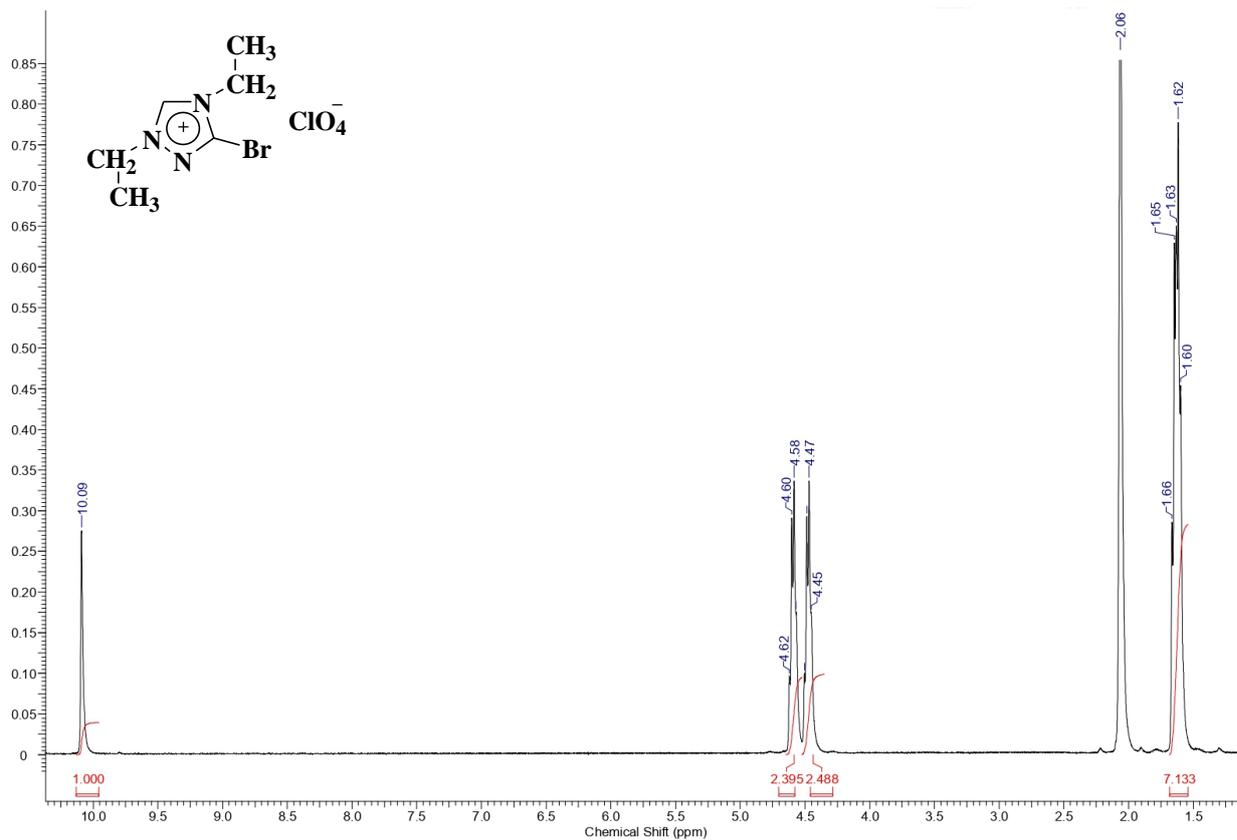
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6c** in  $\text{Me}_2\text{CO}-d_6$



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6e** in  $\text{Me}_2\text{CO}-d_6$



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6g** in  $\text{Me}_2\text{CO}-d_6$



$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **6f** in  $\text{Me}_2\text{CO}-d_6$

