## Low Toxicity Functionalised Imidazolium Salts for Task Specific Ionic Liquid Electrolytes in Dye-Sensitised Solar Cells: A Step Towards Less Hazardous Energy Production.

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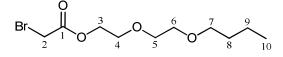
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#### General procedure A: 2-(2-Butoxyethoxy)ethyl-2-bromoacetate (10)<sup>1</sup>



To a stirred solution of di(ethyleneglycol)-*n*-butylether (23.83 g, 146.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at  $-5^{\circ}$ C was added sodium carbonate (23.35 g, 220.3 mmol) followed by bromoacetyl bromide (15.4 mL, 176 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then reaction mixture was filtered and washed with saturated sodium bicarbonate (50 mL) and brine solution (3 × 50 mL). The organic phase was then concentrated by rotary evaporation and crude product was purified by column chromatography (SiO<sub>2</sub>, EtOAc:Hexane, 20:80) to obtain the title compound as a colourless liquid in 98 % yield (40.82 g, 144.2 mmol).

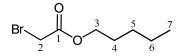
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>, δ)</u>: 4.26 (t, J = 4.8 Hz, 2H, H3), 3.82 (s, 2H, H2), 3.67 (t, J = 4.8 Hz, 2H, H4), 3.60-3.57(m, 2H, H5), 3.53-3.50 (m, 2H, H6), 3.39 (t, J = 6.8 Hz, 2H, H7), 1.50 (tt, J = 7.4, 6.8 Hz, 2H, H8), 1.30 (qt, J = 7.4, 7.2 Hz, 2H, H9), 0.85 (t, J = 7.2 Hz, 3H, H10).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 167.19 (COO, C1), 71.18 (OCH<sub>2</sub>, C7), 70.63 (OCH<sub>2</sub>, C5),
 70.01 (OCH<sub>2</sub>, C6), 68.70 (OCH<sub>2</sub>, C4), 65.31 (OCH<sub>2</sub>, C3), 31.65 (NCH<sub>2</sub>, C8), 25.85 (CH<sub>2</sub>,
 C2), 19.23 (CH<sub>2</sub>, C9), 13.89 (CH<sub>3</sub>, C10).

<u>IR (neat, cm<sup>-1</sup>)</u>: 2958, 2933, 2867, 1738, 1279, 1107, 1035, 962, 864, 666.

<sup>1</sup>H and <sup>13</sup>C-NMR spectra are in agreement with the literature data.<sup>1</sup>

**Pentyl 2-bromoacetate** (11)<sup>1</sup>



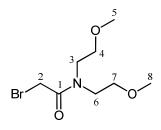
The title compound was prepared from pentan-1-ol (44.00 g, 500 mmol) and bromoacetyl bromide (101.00 g, 500 mmol) according to the general procedure A to obtain a pale yellow liquid in 64 % yield (66.88 g, 320 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm</u>: 4.09 (t, *J* = 6.8 Hz, 2H, *H3*), 3.75 (s, 2H, *H2*), 1.61-1.54 (m, 2H, *H4*), 1.28-1.23 (m, 4H, *H's* 5 and 6), 0.84 (t, *J* = 7.0 Hz, 3H, *H7*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 167.35 (CO, C1), 66.45 (OCH<sub>2</sub>, C3), 28.09 (CH<sub>2</sub>, C2), 27.87 (CH<sub>2</sub>, C4), 26.01 (CH<sub>2</sub>, C5), 22.27 (CH<sub>2</sub>, C6), 13.94 (CH<sub>3</sub>, C7).

<sup>1</sup>H and <sup>13</sup>C-NMR spectra are in agreement with the literature data.<sup>1</sup>

### 2-Bromo-*N*,*N*-*bis*(2-methoxyethyl)acetamide (12)<sup>2</sup>



To a stirred solution of *bis*(2-methoxyethyl)amine (40.10 g, 301.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) at -78 °C was added triethylamine (48.51 g, 479.4 mmol) followed by bromoacetyl bromide (34.8 mL, 400 mmol). The reaction mixture was stirred at -78 °C for 5 h. Then reaction mixture was washed with 10 % NH<sub>4</sub>Cl solution (200 mL), 10 % sodium bicarbonate (200 mL), water (200 mL) and brine solution (200 mL). The organic phase was then dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under high vacuum to obtain the title compound as a brown liquid in 76 % yield (58.15 g, 228.8 mmol).

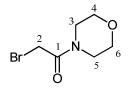
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm</u>: 3.96 (s, 2H, *H2*), 3.59 (t, *J* = 5.2 Hz, 2H, *H3/H6*), 3.52-3.48 (m, 4H, *H3/H6*, *H4/C7*), 3.48 (t, *J* = 5.2 Hz, 2H, *H4/H7*), 3.28 (s, 6H, *H5*, *H8*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 167.66 (COO, C1), 70.70 (OCH<sub>2</sub>, C4/C7), 70.28 (OCH<sub>2</sub>, C4/C7), 59.09 (OCH<sub>3</sub>, C5/C8), 58.89 (OCH<sub>3</sub>, C5/C8), 50.05 (NCH<sub>2</sub>, C3/C6), 46.83 (NCH<sub>2</sub>, C3/C6), 27.25 (CH<sub>2</sub>, C2).

<u>IR (neat, cm<sup>-1</sup>)</u>: 2984, 2929, 2890, 1643, 1456, 1419, 1365, 1189, 1112, 1012, 964, 825, 708.

<sup>1</sup>H and <sup>13</sup>C-NMR spectra are in agreement with the literature data.<sup>2</sup>

#### 2-Bromo-1-(morpholin-4-yl)ethan-1-one (13)



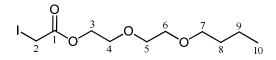
The title compound was prepared from morpholine (30.12 g, 345.7 mmol), sodium carbonate (54.97 g, 518.59 mmol) and bromoacetyl bromide (36.2 mL, 415 mmol) according to the general procedure A as a colourless liquid in 85 % yield (61.06 g, 293.5 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm</u>: 3.78 (s, 2H, *H2*), 3.63 (t, *J* = 4.8 Hz, 2H, *H4/H5*), 3.58 (t, *J* = 4.8 Hz, 2H, *H4/H5*), 3.51 (t, *J* = 4.8 Hz, 2H, *H3/H6*), 3.42 (t, *J* = 4.8 Hz, 2H, *H3/H6*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.27 (COO, *C1*), 66.35 (OCH<sub>2</sub>, *C4/C5*), 66.14 (OCH<sub>2</sub>, *C4/C5*), 46.92 (NCH<sub>2</sub>, *C3/C6*), 42.19 (NCH<sub>2</sub>, *C3/C6*), 25.48 (CH<sub>2</sub>, *C2*).

<u>IR (neat, cm<sup>-1</sup>):</u> 2966, 2857, 1636, 1459, 1436, 1361, 1274, 1217, 1109, 1068, 1036, 964, 846, 719.

2-(2-Butoxyethoxy)ethyl-2-iodoacetate (14)<sup>3</sup>

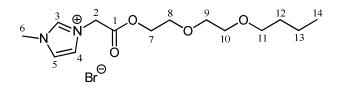


To a stirred solution of di(ethyleneglycol)-*n*-butylether (0.95 g, 5.87 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0°C was added sodium carbonate (0.65 g, 6.16 mmol) followed by iodoacetyl chloride (0.55 mL, 1.26 g, 6.16 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then reaction mixture was filtered and washed with saturated sodium bicarbonate (10 mL) and brine solution (5 mL). The organic phase was then concentrated by rotary evaporation and crude product was purified by column chromatography (SiO<sub>2</sub>, EtOAc:Hexane, 10:90) to obtain the title compound as a brown liquid in 68 % yield (1.31 g, 3.97 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ )</u>: 4.27 (t, *J* = 4.8 Hz, 2H, *H3*), 3.70 (s, 2H, *H2*), 3.69 (t, *J* = 4.8 Hz, 2H, *H4*), 3.63-3.62(m, 2H, *H5*), 3.57-3.55 (m, 2H, *H6*), 3.44 (t, *J* = 6.6 Hz, 2H, *H7*), 1.54 (tt, *J* = 7.4, 6.6 Hz, 2H, *H8*), 1.34 (qt, *J* = 7.4, 7.2 Hz, 2H, *H9*), 0.89 (t, *J* = 7.2 Hz, 3H, *H10*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 168.82 (COO, C1), 71.33 (OCH<sub>2</sub>, C7), 70.80 (OCH<sub>2</sub>, C5),
 70.17 (OCH<sub>2</sub>, C6), 68.84 (OCH<sub>2</sub>, C4), 65.29 (OCH<sub>2</sub>, C3), 31.80 (NCH<sub>2</sub>, C8), 19.36 (CH<sub>2</sub>, C9), 14.00 (CH<sub>3</sub>, C10), -5.50 (CH<sub>2</sub>, C2).

General procedure B: Bromide Ionic Liquids:3-{2-[2-(2-Butoxyethoxy)ethoxy]-2oxoethyl}-1-methyl-1H-imidazol-3-ium bromide (6a)<sup>1</sup>



To a stirred solution of **10** (20.18 g, 71.3 mmol) in diethyl ether (100 mL), 1-methylimidazole (5.85 g, 71.3 mmol) was added dropwise at RT under a  $N_2$  atmosphere. After stirring overnight the white solid of product was separated from the solvent by decantation. The solid was washed with diethyl ether (5 x 100 mL) and dried under high vacuum to obtain **6a** as a white solid in 90 % yield (23.5 g, 63.3 mmol). <u>Melting Point:</u> 78-80°C

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 10.13 (s, 1H, *H3*), 7.68 (t, J = 1.8, Hz, 1H, *H4/H5*), 7.51 (t, J = 1.8, Hz, 1H, *H4/H5*), 5.50 (s, 2H, *H2*), 4.33 (t, J = 4.8 Hz, 2H, *H7*), 4.06 (s, 3H, *H6*), 3.71 (t, J = 4.8 Hz, 2H, *H8*), 3.61 (t, J = 5.2 Hz, 2H, *H9*), 3.55 (t, J = 5.2 Hz, 2H, *H10*), 3.42 (t, J = 6.8 Hz, 2H, *H11*), 1.51 (tt, J = 7.6, 6.8 Hz, 2H, *H12*), 1.31 (tq, J = 7.6, 7.4 Hz, 2H, *H13*), 0.87 (t, J = 7.4 Hz, 3H, *H14*).

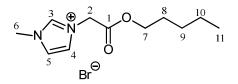
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 166.19 (COO, C1), 138.05 (ArCH, C3), 123.91 (ArCH, C4/C5), 123.15 (ArCH, C4/C5), 71.09 (OCH<sub>2</sub>, C11), 70.49 (OCH<sub>2</sub>, C9), 69.84 (OCH<sub>2</sub>, C10), 68.45 (OCH<sub>2</sub>, C8), 65.53 (OCH<sub>2</sub>, C7), 50.14 (NCH<sub>2</sub>, C2), 36.84 (NCH<sub>3</sub>, C6), 31.53 (CH<sub>2</sub>, C12), 19.14 (CH<sub>2</sub>, C13), 13.86 (CH<sub>3</sub>, C14).

<u>IR (neat, cm<sup>-1</sup>):</u> 3134, 3094, 2954, 2871, 1752, 1577, 1567, 1448, 1370, 1341, 1281, 1236, 1219, 1193, 1169, 1128, 1096, 1044, 967, 881, 850, 770, 713.

<u>HRMS (ESI<sup>+</sup>,m/z):</u> Calculated for [M-Br<sup>-</sup>]<sup>+</sup>, C<sub>14</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>, requires = 285.1814, found = 285.1803.

<sup>1</sup>H, <sup>13</sup>C-NMR spectra and melting point are in agreement with the literature data.<sup>1</sup>

3-Methyl-1-(pentoxycarbonylmethyl)imidazolium bromide (7a)<sup>1,4</sup>



The title compound **7a** was prepared from 1-methylimidazole (3.69g, 45.0 mmol) and **11** (54.0 mmol, 11.29 g) according to the general procedure B to afford a pale yellow liquid in 97 % yield (12.76 g, 43.8 mmol).

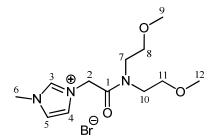
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm)</u>: 8.79 (s, 1H, *H3*), 7.30 (t, J = 1.8 Hz, 1H, *H4/H5*), 7.23 (t, J = 1.8 Hz, 1H, *H4/H5*), 4.95 (s, 2H, *H2*), 4.16 (t, J = 6.8 Hz, 2H, *H7*), 3.90 (s, 3H, *H6*), 1.65 (tt, J = 6.8, 7.2 Hz, 2H, *H8*), 1.30-1.23 (m, 4H, *H's 9 and 10*), 0.86 (t, J = 7.0 Hz, 3H, *H11*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (ppm): 166.16 (CO, C1), 138.39 (NCH<sub>2</sub>N, C3), 123.79 (NCH, C4), 123.08 (NCH, C5), 67.07 (OCH<sub>2</sub>, C7), 50.30 (NCH<sub>2</sub>, C2), 36.92 (NCH<sub>3</sub>, C6), 28.00 (CH<sub>2</sub>, C8), 27.79 (CH<sub>2</sub>, C9), 22.21 (CH<sub>2</sub>, C10), 13.19 (CH<sub>3</sub>, C11).

<u>IR (cm<sup>-1</sup>)</u>: 3095, 2959, 2931, 1750, 1578, 1569, 1559, 1495, 1455, 1398, 1230, 1177.

<u>HRMS m/z</u>: Found 211.1440 [M-Br<sup>-</sup>]<sup>+</sup>, Calcd. C<sub>11</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> = 211.1447

**3-{[bis(2-Methoxyethyl)carbamoyl]methyl}-1-methyl-1H-imidazol-3-ium bromide (8a)**<sup>1</sup>



The title compound **8a** was prepared from 1-methylimidazole (23.06 g, 280.8 mmol) and **12** (71.37 g, 280.9 mmol) according to the general procedure B to obtain a yellow solid in 83 % yield (78.04 g, 232.1 mmol). <u>Melting Point</u>: 68-70  $^{\circ}$ C

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.76 (s, 1H, *H3*), 7.47 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 7.41 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 5.57 (s, 2H, *H2*), 3.98 (s, 3H, *H6*), 3.62 (t, *J* = 4.8 Hz, 2H, *H7/H10*), 3.49 (t, *J* = 4.8 Hz, 2H, *H8/H11*), 3.47 (t, *J* = 4.8 Hz, 2H, *H8/H11*), 3.41(t, *J* = 4.8 Hz, 2H, *H7/H10*), 3.28 (s, 3H, *H9/H12*), 3.23 (s, 3H, H9/*H12*).

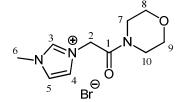
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.62 (COO, C1), 138.01 (ArCH, C3), 123.99 (ArCH, C4/C5), 122.61 (ArCH, C4/C5), 70.30 (OCH<sub>2</sub>, C8/C11), 70.04 (OCH<sub>2</sub>, C8/C11), 59.19 (OCH<sub>3</sub>, C9/C12), 58.80 (OCH<sub>3</sub>, C9/C12), 50.61 (NCH<sub>2</sub>, C2), 48.59 (NCH<sub>2</sub>, C7/C10), 46.68 (NCH<sub>2</sub>, C7/C10), 36.73 (NCH<sub>3</sub>, C6).

<u>IR (neat, cm<sup>-1</sup>):</u> 3420, 3078, 2930, 1651, 1570, 1470, 1424, 1350, 1175, 1111, 1014, 922, 827, 727.

<u>HRMS (ESI<sup>+</sup>, m/z)</u>: Calculated for [M-Br<sup>-</sup>]<sup>+</sup>, C<sub>12</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>, requires = 256.1661, found = 256.1653.

<sup>1</sup>H, <sup>13</sup>C-NMR spectra and melting point are in agreement with the literature data.<sup>1</sup>

#### 1-Methyl-3-[2-(morpholin-4-yl)-2-oxoethyl]-1H-imidazol-3-ium bromide (9a)



The title compound **9a** was prepared from 1-methylimidazole (23.37 mL, 293 mmol) and **13** (61.06 g, 293.5 mmol) according to the general procedure B to obtain a white solid in 85 % yield (72.29 g, 249.1 mmol). <u>Melting Point:</u>  $170-172^{\circ}C$ 

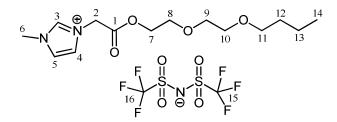
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.65 (s, 1H, *H3*), 7.64 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 7.38 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 5.75 (s, 2H, *H2*), 3.98 (s, 3H, *H6*), 3.76 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 3.64 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 3.59 (t, *J* = 4.8, Hz, 2H, *H7/H10*), 3.52 (t, *J* = 4.8, Hz, 2H, *H7/H10*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 163.34 (CON, *C1*), 137.94 (NCHN, *C3*), 124.56 (NCH, *C4/C5*), 122.33 (NCH, *C4/C5*), 66.50 (OCH<sub>2</sub>, *C8/C9*), 66.40 (OCH<sub>2</sub>, *C8/C9*), 50.75 (NCH<sub>2</sub>CO, C2), 45.51 (NCH<sub>2</sub>, *C7/C10*), 42.67 (NCH<sub>2</sub>, *C7/C10*), 36.83 (NCH<sub>3</sub>, *C6*).

<u>IR (neat, cm<sup>-1</sup>)</u>: 3364, 3076, 2864, 1640, 1574, 1425, 1242, 1165, 1113, 1042, 959, 857.

<u>HRMS (ESI<sup>+</sup>, m/z)</u>: Calculated for [M-Br<sup>-</sup>]<sup>+</sup>, C<sub>10</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>, requires = 210.1237, found = 210.1232.

General procedure C: [NTf<sub>2</sub>] Ionic Liquids: 3-{2-[2-(2-Butoxyethoxy)ethoxy]-2oxoethyl}-1-methyl-1H-imidazol-3-ium *bis*(trifluoromethylsulfonyl)imide (6b)<sup>1</sup>



To a stirred solution of bromide salt **6a** (126.03 g, 345.0 mmol) in distilled water (500 mL), LiNTf<sub>2</sub> was added (108.97 g, 379.6 mmol) at RT. After stirring for 4 h at RT the liquid product was separated from the water by decantation. The liquid was washed with distilled water (3 × 500 mL) and dried under high vacuum to obtain **6b** as a colourless oil in 80 % yield (155.39 g, 274.8 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 8.74 (s, 1H, *H3*), 7.39 (t, J = 1.6 Hz, 1H, *H4/H5*), 7.34 (t, J = 1.6 Hz, 1H, *H4/H5*), 5.00 (s, 2H, *H2*), 4.33 (t, J = 4.8 Hz, 2H, *H7*), 3.92 (s, 3H, *H6*), 3.70 (t, J = 4.8 Hz, 2H, *H8*), 3.61 (t, J = 4.8 Hz, 2H, *H9*), 3.56 (t, J = 4.8 Hz, 2H, *H10*), 3.43 (t, J = 6.8 Hz, 2H, *H11*), 1.52 (tt, J = 7.6, 6.8 Hz, 2H, *H12*), 1.32 (tq, J = 7.6, 7.2 Hz, 2H, *H13*), 0.88 (t, J = 7.2 Hz, 3H, *H14*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.84 (COO, C1), 137.49 (ArCH, C3), 123.97 (ArCH, C4/C5), 123.44 (ArCH, C4/C5), 119.76 (q, J = 320 Hz, 2CF<sub>3</sub>, C15, C16), 71.18 (OCH<sub>2</sub>, C11), 70.56 (OCH<sub>2</sub>, C9), 69.92 (OCH<sub>2</sub>, C10), 68.43 (OCH<sub>2</sub>, C8), 65.74 (OCH<sub>2</sub>, C7), 49.86 (CH<sub>2</sub>, C2), 36.47 (NCH<sub>3</sub>, C6), 31.66 (CH<sub>2</sub>, C12), 19.25 (CH<sub>2</sub>, C13), 13.90 (CH<sub>3</sub>, C14).

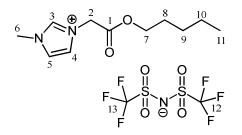
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) ppm: -79.20 (6F).

<u>IR (neat, cm<sup>-1</sup>)</u>: 3162, 2964, 2873, 1765, 1569, 1348, 1331, 1177, 1133, 1053, 976, 789, 740.

<u>MS (*m/z*):</u> 285.15 (M-NTf<sub>2</sub>)<sup>+</sup>

<sup>1</sup>H and <sup>13</sup>C-NMR spectra are in agreement with the literature data.<sup>1</sup>

# **3-Methyl-1-(pentoxycarbonylmethyl)imidazolium** *bis*(trifluoromethylsulfonyl)imide (7b)<sup>2</sup>



The title compound **7b** was prepared from **7a** (19.15 g, 39.0 mmol) and LiNTf2 (13.49 g, 47.0 mmol) according to the general procedure C as a colourless liquid in 93 % yield (17.78 g, 36.2 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm)</u>: 8.67 (s, 1H, *H3*), 7.32 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 7.27 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 4.91 (s, 2H, *H2*), 4.11 (t, *J* = 6.8 Hz, 2H, *H7*), 3.85 (s, 3H, *H6*), 1.65-1.57 (m, 2H, *H8*), 1.24-1.23 (m, 4H, *H9*, *H10*), 0.82 (t, *J* = 6.8 Hz, 3H, *H11*).

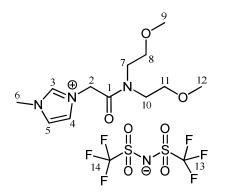
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (ppm): 165.76 (CO, C1), 137.52 (NCH<sub>2</sub>N, C3), 123.85 (NCH, C4), 123.25 (NCH, C5), 122.20 (q, J = 319 Hz, 2CF3's, C12, 13), 67.20 (OCH<sub>2</sub>, C7), 49.88 (NCH<sub>2</sub>, C2), 36.48 (NCH<sub>3</sub>, C6), 27.91 (CH<sub>2</sub>, C8), 27.73 (CH<sub>2</sub>, C9), 22.18 (CH<sub>2</sub>, C10), 13.82 (CH<sub>3</sub>, C11).

<u>IR (cm<sup>-1</sup>)</u>: 3164, 3124, 2963, 2928, 2862, 1750, 1582, 1569, 1558, 1495, 1455, 1354, 1197, 1136.

<u>MS *m/z*</u>: 211.2 [M-NTf<sub>2</sub><sup>-</sup>]<sup>+</sup>

<sup>1</sup>H and <sup>13</sup>C-NMR spectra are in agreement with the literature data.<sup>2</sup>

**3-{[bis(2-Methoxyethyl)carbamoyl]methyl}-1-methyl-1H-imidazol-3-ium** *bis*(trifluoromethylsulfonyl)imide (8b)



The title compound **8b** was prepared from bromide salt **8a** (74.99 g, 223 mmol) and LiNTf<sub>2</sub> (66.82 g, 232.7 mmol) according to the general procedure C to obtain a yellow oil in 74 % yield (88.64 g, 165.2 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 8.63 (s, 1H, *H3*), 7.27 (t, *J* = 1.8 Hz, 1H, *H4/H5*), 7.26 (t, *J* = 1.8 Hz, 1H, *H4/H5*), 5.24 (s, 2H, *H2*), 3.91 (s, 3H, *H6*), 3.58 (t, *J* = 4.8 Hz, 2H, *H7/H10*), 3.57-3.52 (m, 4H, *H7/H10*, *H8/H11*), 3.49 (t, *J* = 4.8 Hz, 2H, *H6/H11*), 3.34 (s, 3H, *H9/H12*), 3.30 (s, 3H, *H9/H12*).

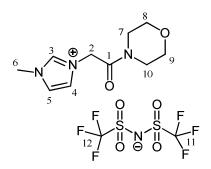
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.17 (COO, C1), 137.68 (ArCH, C3), 124.26 (ArCH, C4/C5), 122.72 (ArCH, C4/C5), 119.86 (q, J = 319 Hz, 2CF<sub>3</sub>'s, C13, C14), 70.52 (OCH<sub>2</sub>, C8/C11), 69.99 (OCH<sub>2</sub>, C8/C11), 59.16 (OCH<sub>3</sub>, C9/C12), 58.89 (OCH<sub>3</sub>, C9/C12), 50.52 (NCH<sub>2</sub>, C2), 48.63 (NCH<sub>2</sub>, C7/C10), 46.89 (NCH<sub>2</sub>, C7/C10), 36.45 (NCH<sub>3</sub>, C6).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) ppm: -78.97 (6F)

<u>IR (neat, cm<sup>-1</sup>):</u> 3161, 2938, 2898, 1659, 1575, 1473, 1427, 1348, 1330, 1175, 1133, 1116, 1052, 830, 789, 739.

<u>MS (*m/z*):</u> 256.15 (M-NTf<sub>2</sub>)<sup>+</sup>

1-Methyl-3-[2-(morpholin-4-yl)-2-oxoethyl]-1H-imidazol-3-ium *bis*(trifluoromethylsulfonyl)imide (9b)



The title compound **9b** was prepared from bromide salt **9a** (88.12 g, 303.7 mmol) and LiNTf<sub>2</sub> (95.93 g, 334.1 mmol) according to the general procedure C to afford a crystalline white solid 62 % yield (92.30 g, 188.2 mmol). <u>Melting Point:</u>  $63-65^{\circ}C$ 

<sup>1</sup><u>H NMR (400 MHz, DMSO-*d<sub>6</sub>*):</u> 9.41 (s, 1H, *H3*), 8.16 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 8.10 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 5.95 (s, 2H, *H2*), 4.57 (s, 3H, *H6*), 4.14 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 4.08 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 4.03-3.99 (m, 4H, *H7*, *H10*).

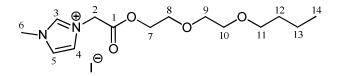
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): 163.93 (CON, C1), 137.91 (NCHN, C3), 124.04 (NCH, C4/C5), 123.00 (NCH, C4/C5), 119.56 (q, J =320 Hz, 2CF<sub>3</sub>'s, C11, C12), 65.95 (OCH<sub>2</sub>, C8/C9), 65.83 (OCH<sub>2</sub>, C8/C9), 49.99 (NCH<sub>2</sub>CO, C2), 44.70 (NCH<sub>2</sub>, C7/C10), 42.14 (NCH<sub>2</sub>, C7/C10), 35.87 (NCH<sub>3</sub>, C6).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) ppm: -78.99 (6F)

<u>IR (neat, cm<sup>-1</sup>):</u> 3164, 3109, 3000, 2872, 1656, 1579, 1564, 1475, 1440, 1348, 1328, 1275, 1184, 1136, 1108, 1050, 1033, 975, 845, 807, 771, 740.

<u>MS (*m/z*):</u> 210.10 [M-NTf<sub>2</sub>]<sup>+</sup>

General procedure D: Iodide Ionic Liquids: 3-{2-[2-(2-Butoxyethoxy)ethoxy]-2oxoethyl}-1-methyl-1H-imidazol-3-ium iodide (6c)



To a stirred solution of  $[NTf_2]$  salt **6b** (88.64 g, 156.7 mmol) in DCM (100 mL) was added a solution of tetrabutylammonium iodide (63.69 g, 172.4 mmol) in DCM (100 mL) slowly at

RT. After stirring for 3 h at RT the solvent was evaporated completely, the residue was dissolved in distilled water (100 mL). The aq. solution was washed with DCM (50 mL) and then evaporated on rota evaporator, dried under high vacuum to afford **6c** as yellow solid in 66 % yield (42.81 g, 103.8 mmol). <u>Melting Point:</u>  $52-54^{\circ}C$ 

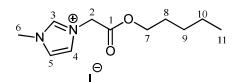
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.63 (s, 1H, *H3*), 7.68 (t, J = 1.8 Hz, 1H, *H4/H5*), 7.58 (t, J = 1.8 Hz, 1H, *H4/H5*), 5.37 (s, 2H, *H2*), 4.29 (t, J = 4.8 Hz, 2H, *H7*), 4.02 (s, 3H, *H6*), 3.67 (t, J = 4.8 Hz, 2H, *H8*), 3.56 (t, J = 4.4 Hz, 2H, *H9*), 3.50 (t, J = 4.4 Hz, 2H, *H10*), 3.36 (t, J = 6.8 Hz, 2H, *H11*), 1.45 (tt, J = 7.6, 6.8 Hz, 2H, *H12*), 1.25 (tq, J = 7.6, 7.2 Hz, 2H, *H13*), 0.82 (t, J = 7.2 Hz, 3H, *H14*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.86 (COO, C1), 137.53 (ArCH, C3), 123.93 (ArCH, C4/C5), 123.24 (ArCH, C4/C5), 71.03 (OCH<sub>2</sub>, C11), 70.45 (OCH<sub>2</sub>, C9), 69.80 (OCH<sub>2</sub>, C10), 68.42 (OCH<sub>2</sub>, C8), 65.63 (OCH<sub>2</sub>, C7), 50.46 (CH<sub>2</sub>, C2), 37.21 (NCH<sub>3</sub>, C6), 31.48 (CH<sub>2</sub>, C12), 19.09 (CH<sub>2</sub>, C13), 13.83 (CH<sub>3</sub>, C14).

<u>IR (neat, cm<sup>-1</sup>):</u> 3131, 3100, 2955, 2934, 2869, 1751, 1633, 1577, 1565, 1450, 1430, 1340, 1220, 1196, 1172, 1127, 1094, 1044, 969, 869, 841, 765.

<u>MS (m/z):</u> 285.20 (M-I)<sup>+</sup>

**3-Methyl-1-(pentoxycarbonylmethyl)imidazolium iodide** (7c)



The title compound **7c** was prepared using  $[NTf_2]$  salt **7b** (4.18 g, 9.26 mmol), tetrabutylammonium iodide (3.42 g, 9.26 mmol) and DCM (40 mL) according to the general procedure D to obtain a brown liquid in 72 % yield (2.25 g, 6.65 mmol).

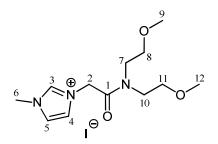
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) (ppm)</u>: 9.81 (s, 1H, *H3*), 7.65 (t, J = 1.8 Hz, 1H, *H4/H5*), 7.55 (t, J = 1.8 Hz, 1H, *H4/H5*), 5.39 (s, 2H, *H2*), 4.17 (t, J = 6.8 Hz, 2H, *H7*), 4.07 (s, 3H, *H6*), 1.65 (tt, J = 6.8, 7.2 Hz, 2H, *H8*), 1.31-1.27 (m, 4H, *H's 9 and 10*), 0.87 (t, J = 7.0 Hz, 3H, *H11*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (ppm): 165.92 (CO, C1), 137.81 (NCH<sub>2</sub>N, C3), 123.96 (NCH,
 C4), 123.24 (NCH, C5), 67.23 (OCH<sub>2</sub>, C7), 50.59 (NCH<sub>2</sub>, C2), 37.29 (NCH<sub>3</sub>, C6), 28.05 (CH<sub>2</sub>, C8), 27.83 (CH<sub>2</sub>, C9), 22.26 (CH<sub>2</sub>, C10), 13.99 (CH<sub>3</sub>, C11).

<u>IR (cm<sup>-1</sup>)</u>: 3091, 2948, 1757, 1559, 1534, 1489, 1423, 1388, 1229, 1167, 1023.

<u>MS m/z</u>: 211.2 [M-I<sup>-</sup>]<sup>+</sup>

3-{[bis(2-Methoxyethyl)carbamoyl]methyl}-1-methyl-1H-imidazol-3-ium iodide (8c)



The title compound **8c** was prepared from  $[NTf_2]$  salt **8b** (99.8 g, 186.0 mmol), tetrabutylammonium iodide (77.6 g, 210.1 mmol) and DCM (300 mL) according to the general procedure D to obtain a brown solid in 74 % yield (52.97 g, 138.3 mmol). <u>Melting Point:</u> 48-50°C

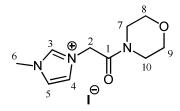
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.54 (s, 1H, *H3*), 7.45 (d, *J* = 2.4 Hz, 1H, *H4/H5*), 7.44 (d, *J* = 2.4 Hz, 1H, *H4/H5*), 5.59 (s, 2H, *H2*), 4.03 (s, 3H, *H6*), 3.67 (t, *J* = 4.8 Hz, 2H, *H7/H10*), 3.55-3.52 (m, 4H, *H7/H10*, *H8/H11*), 3.48 (t, *J* = 4.8 Hz, 2H, *H8/H11*), 3.35 (s, 3H, *H9/H12*), 3.29 (s, 3H, H9/*H12*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.12 (COO, C1), 137.66 (ArCH, C3), 124.10 (ArCH, C4/C5), 122.60 (ArCH, C4/C5), 70.44 (OCH<sub>2</sub>, C8/C11), 70.05 (OCH<sub>2</sub>, C8/C11), 59.32 (OCH<sub>3</sub>, C9/C12), 58.88 (OCH<sub>3</sub>, C9/C12), 50.85 (NCH<sub>2</sub>, C2), 48.84 (NCH<sub>2</sub>, C7/C10), 46.87 (NCH<sub>2</sub>, C7/C10), 37.07 (NCH<sub>3</sub>, C6).

<u>IR (neat, cm<sup>-1</sup>):</u> 3149, 3101, 2921, 2889, 1662, 1651, 1562, 1472, 1423, 1341, 1195, 1169, 1118, 1095, 1069, 1031, 1003, 831, 804, 751.

<u>MS (*m/z*):</u> 256.10 [M-I]<sup>+</sup>

#### 1-Methyl-3-[2-(morpholin-4-yl)-2-oxoethyl]-1H-imidazol-3-ium iodide (9c)



The title compound **9c** was prepared using  $[NTf_2]$  salt **9b** (5.61 g, 11.30 mmol), tetrabutylammonium iodide (4.18 g, 11.30 mmol) and DCM (50 mL) according to the general procedure D to obtain a yellow solid in 87 % yield (3.30 g, 9.79 mmol). <u>Melting Point:</u> 135-137°C

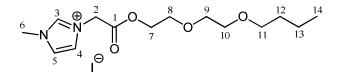
<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.48 (s, 1H, *H3*), 7.69 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 7.40 (t, *J* = 1.6 Hz, 1H, *H4/H5*), 5.78 (s, 2H, *H2*), 4.02 (s, 3H, *H6*), 3.83 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 3.70 (t, *J* = 4.8 Hz, 2H, *H8/H9*), 3.64 (t, *J* = 4.8, Hz, 2H, *H7/H10*), 3.57 (t, *J* = 4.8, Hz, 2H, *H7/H10*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 163.03 (CON, C1), 137.59 (NCHN, C3), 124.66 (NCH, C4/C5), 122.42 (NCH, C4/C5), 66.71 (OCH<sub>2</sub>, C8/C9), 66.48 (OCH<sub>2</sub>, C8/C9), 51.33 (NCH<sub>2</sub>CO, C2), 45.59 (NCH<sub>2</sub>, C7/C10), 42.82 (NCH<sub>2</sub>, C7/C10), 37.21 (NCH<sub>3</sub>, C6).

<u>IR (neat, cm<sup>-1</sup>):</u> 3351, 2938, 2861, 1631, 1572, 1435, 1212, 1175, 1111, 1045, 979.

<u>MS (*m/z*):</u> 210.09 [M-I<sup>-</sup>]<sup>+</sup>

Synthesis of 3-{2-[2-(2-Butoxyethoxy)ethoxy]-2-oxoethyl}-1-methyl-1H-imidazol-3-ium iodide (6c) from (14).<sup>1</sup>



To a stirred solution of **14** (1.09 g,3.30 mmol) in diethyl ether (10 mL), 1-methylimidazole (0.27 g, 3.30 mmol) was added dropwise at RT under a  $N_2$  atmosphere. After stirring overnight the yellow solid of product was separated from the solvent by decantation. The

solid was washed with diethyl ether (5 x 10 mL) and dried under high vacuum to obtain 6c as a yellow solid in 82 % yield (1.11 g, 2.69 mmol).

<sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>) ppm:</u> 9.79 (s, 1H, *H3*), 7.66 (t, J = 1.8 Hz, 1H, *H4/H5*), 7.48 (t, J = 1.8 Hz, 1H, *H4/H5*), 5.45 (s, 2H, *H2*), 4.36 (t, J = 4.8 Hz, 2H, *H7*), 4.08 (s, 3H, *H6*), 3.74 (t, J = 4.8 Hz, 2H, *H8*), 3.63 (m, 2H, *H9*), 3.58 (m, 2H, *H10*), 3.44 (t, J = 6.8 Hz, 2H, *H11*), 1.53 (tt, J = 7.6, 6.8 Hz, 2H, *H12*), 1.33 (tq, J = 7.6, 7.2 Hz, 2H, *H13*), 0.89 (t, J = 7.2 Hz, 3H, *H14*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) ppm: 165.92 (COO, C1), 137.90 (ArCH, C3), 124.02 (ArCH, C4/C5), 123.22 (ArCH, C4/C5), 71.18 (OCH<sub>2</sub>, C11), 70.62 (OCH<sub>2</sub>, C9), 69.96 (OCH<sub>2</sub>, C10), 68.56 (OCH<sub>2</sub>, C8), 65.77 (OCH<sub>2</sub>, C7), 50.60 (CH<sub>2</sub>, C2), 37.28 (NCH<sub>3</sub>, C6), 31.64 (CH<sub>2</sub>, C12), 19.22 (CH<sub>2</sub>, C13), 13.91 (CH<sub>3</sub>, C14).

<u>MS *m/z*</u>: 285.19 [M-I<sup>-</sup>]<sup>+</sup>

#### DSSC fabrication procedure:

The TiO<sub>2</sub> electrodes used for fabricating DSSC were manufactured by screen-printing,<sup>5</sup> which is based on a layer-by-layer deposition of  $TiO_2$  on fluorine doped tin oxide (FTO) conducting transparent glass substrates. In all cases, a non-porous dense blocking under-layer of TiO<sub>2</sub> was deposited on the FTO substrate via TiCl<sub>4</sub> treatment<sup>6</sup> in order to reduce charge recombination and dark currents. TiO<sub>2</sub> paste was then printed on the TiCl<sub>4</sub> treated glass using a TIFLEX Ltd manual screen-printer and involved several cycles. After each TiO<sub>2</sub> paste deposition, the films were kept in an ethanol chamber for 6 mins followed by drying at 125 °C for 6 min, while the final sintering involved gradual heating in an oven at 325°C (5 min), 375°C (5 min), 450°C (15 min) and 500°C (30 min). After sintering, the electrodes were again treated with TiCl<sub>4</sub> followed by another sintering at 500°C for 30 min. The TiO<sub>2</sub> active area was 0.28 cm<sup>2</sup> (consisting of a 6 mm diameter circular spot). The sintered electrodes were placed in a dye bath of N719 dissolved in acetonitrile:tert-butylalcohol:THF (vol 4.5:4.5:1) for 16-20 h. N719 [di-tetra butylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'dicarboxylato)ruthenium(II)] dye was procured from a commercial supplier (DyeSol Ltd) and used without further purification. The counter electrode was prepared with a thin film of Pt catalyst deposited via a drop of  $H_2PtCl_6$  solution (2 mg Pt in 1 mL ethanol) and heat treated at  $400^{\circ}$ C for 15 min. The dye coated TiO<sub>2</sub> electrode and Pt coated counter electrode were then

sandwiched together and sealed using a Bynel® polymer gasket (50 micron thick). This is followed by the electrolyte filling into the space between the two electrodes through a hole in the counter electrode *via* vacuum back filling. The back hole was sealed with a thin piece (0.1 mm thick) of glass heat sealed with Bynel® to complete the solar cell device fabrication.

Two TiO<sub>2</sub> printing pastes were employed: one is a "transparent" paste containing TiO<sub>2</sub> particles of average size 20 nm formed from P25 powder using a standard fabrication procedure.<sup>5</sup> Ethyl cellulose (Fluka, #46080 and #46070) and anhydrous Terpineol (Sigma-Aldrich, 86480) were used as received in making this paste. A second "scattering" paste was purchased from DyeSol Ltd (WER 2-0), which contains TiO<sub>2</sub> particles of size in the range of 150 nm to 250 nm, formulated to provide an opaque white scattering layer. Both pastes were screen printed with a 90 T mesh to yield a 7 + 2 electrode configuration (7 transparent layers + 2 scattering layers, total thickness = 15-16 micron after sintering).

#### DSSC measurement system:

Electro-optical characterization including: current/voltage (I-V) curves, open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ) and fill factor (FF), were studied using a *Newport 91195A-1000* solar simulator and *Newport 69920* Arc Lamp Power Supply and recorded with a GAMRY Instruments Potentiostat. A *Newport 81088A* Air Mass Filter was placed before the output of the solar simulator to simulate AM 1.5 spectrum with irradiance powers of 1000 W/m<sup>2</sup>.

Ionic Liquid	Water (% w/w)	ppm
1,3-Diethylimidiazolium iodide (DmimI) (1)	0.07	700
1-Ethyl-3methylimidiazolium iodide (EmimI) (2)	0.02	200
1-Ethyl-3-methylimidiazolium tetracyanoborate	0.17	1700
(EmimTCB) ( <b>3</b> )		
N-Butyl-1H-benzimidazole (NBB) (4)	0.51	5100
Guanadinium thiocyanate (GNCS) (5)	0.07	700
<u>6a</u>	0.22	2200
6b	0.42	4200
6с	0.17	1700
7a	0.15	1500
7c	0.17	1700
8a	0.45	4500
8b	0.16	1600
8c	0.6	6000
9a	1.07	10700
9b	0.43	4300
9c	0.43	4300

**Table S1**: Results from Karl Fischer analysis – after drying for 24 h under high vacuum (0.05 mBar).

	% change			
Compound (X)	J <sub>sc</sub>	$V_{oc}$	FF	η
2	8.7	8.4	9.4	28
6c	38.5	6.6	7.5	61.3
6a	34.7	3.6	15.4	62.6
6b	41.9	4.96	-11.3	32.3
7c	13.5	-2.1	7.1	18.1
7a	47.2	6.6	-26.2	15.2
8c	31.1	7.9	6.5	49.9
8a	39.7	6.2	-1.7	46.2
8b	53.5	9.4	-1.7	66.3
9c	18.7	1.2	9.4	31.1
9a	42.8	3.9	1.9	34.8
9b	85.6	8.5	-20.8	58.5

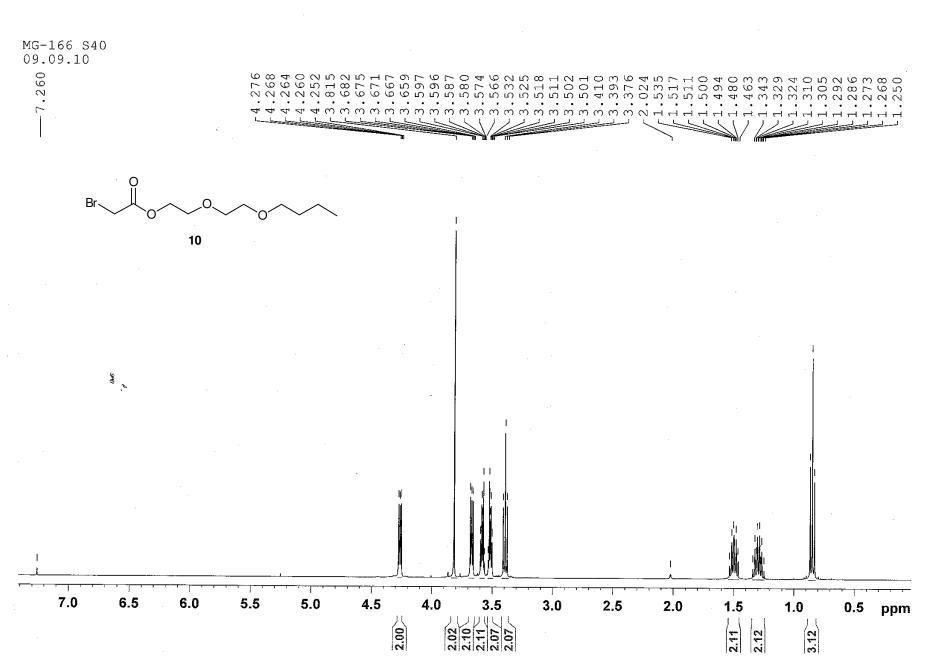
**Table S2:** Photovoltaic parameters percentage change of the DSSC devices made with DmimI /**X**/EmimTCB/I<sub>2</sub>/NBB/GNCS electrolyte following a small amount of moisture ingress tested at 1 sun (1000  $\text{Wm}^{-2}$ ) incident intensity of AM1.5 simulated solar light.

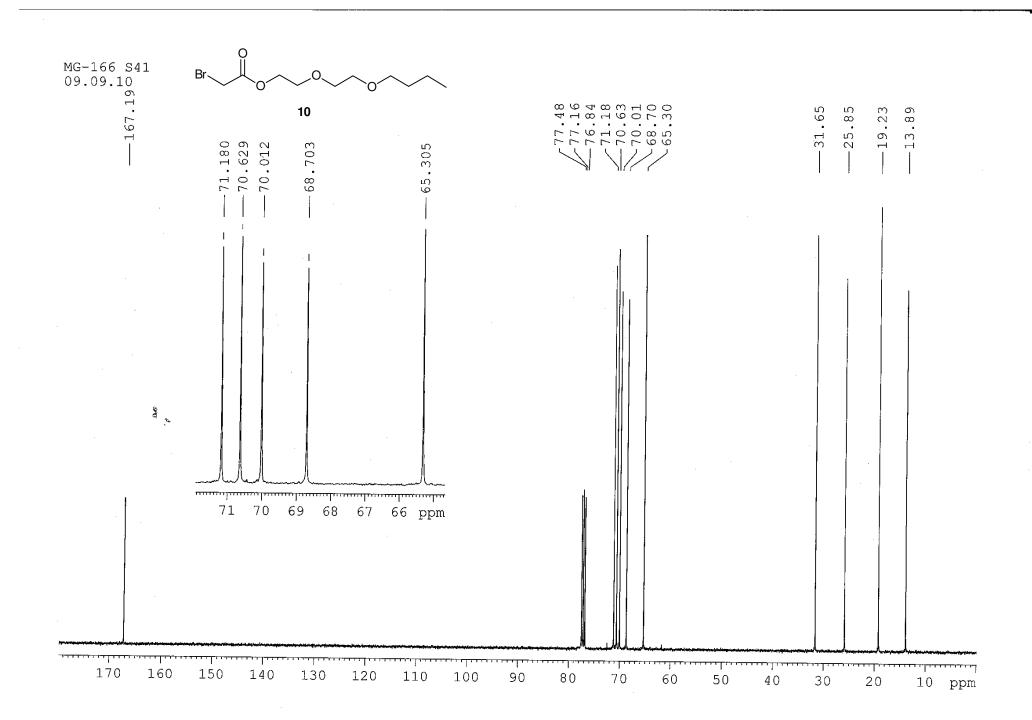
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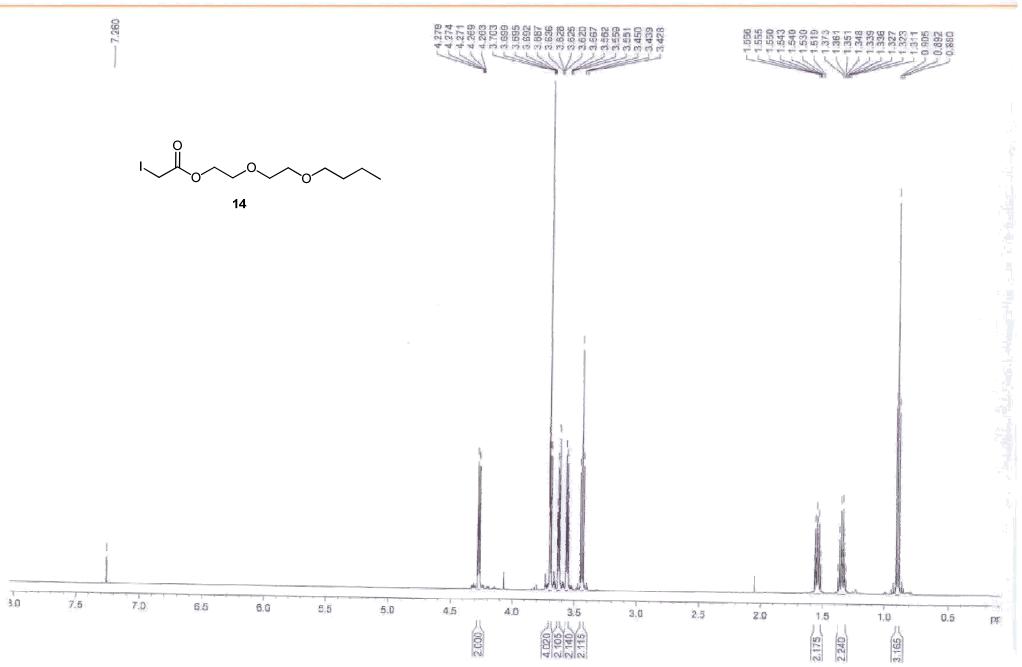
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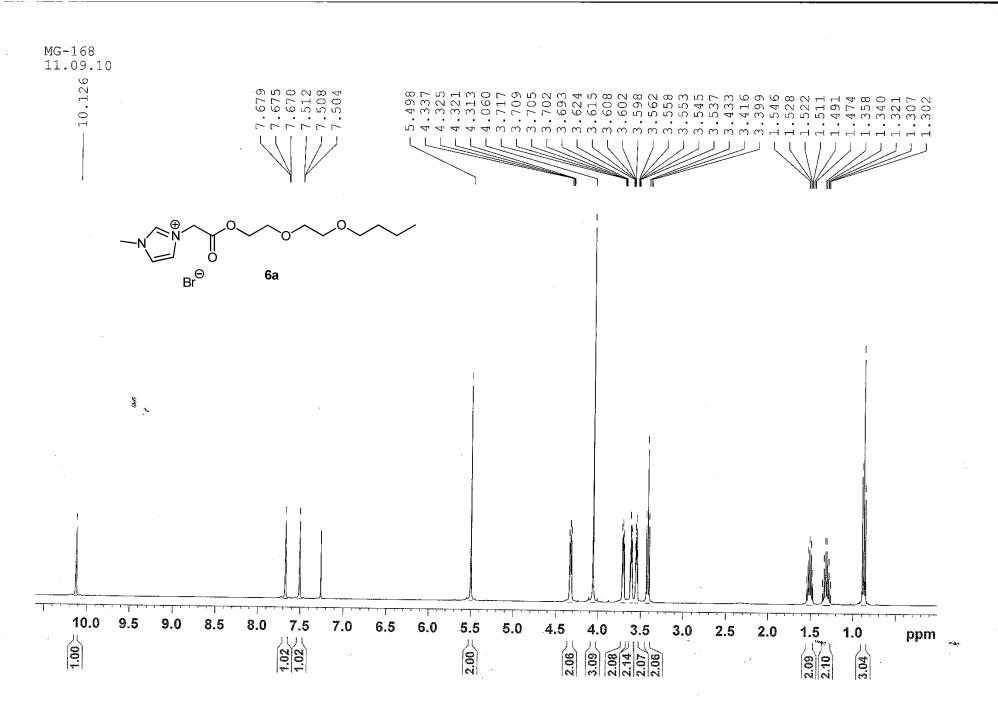
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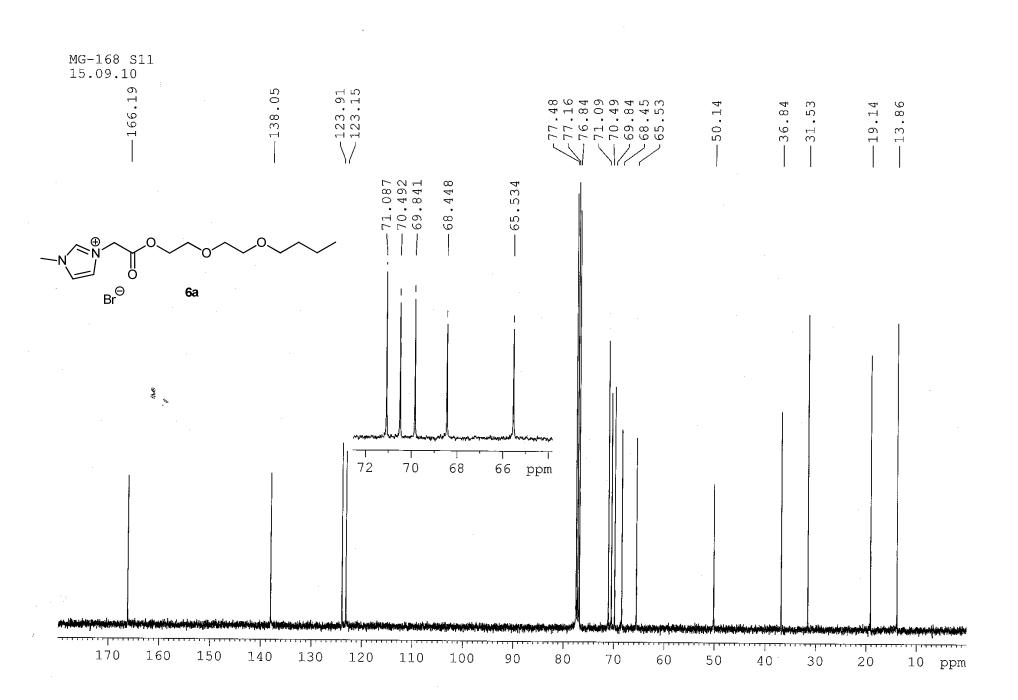


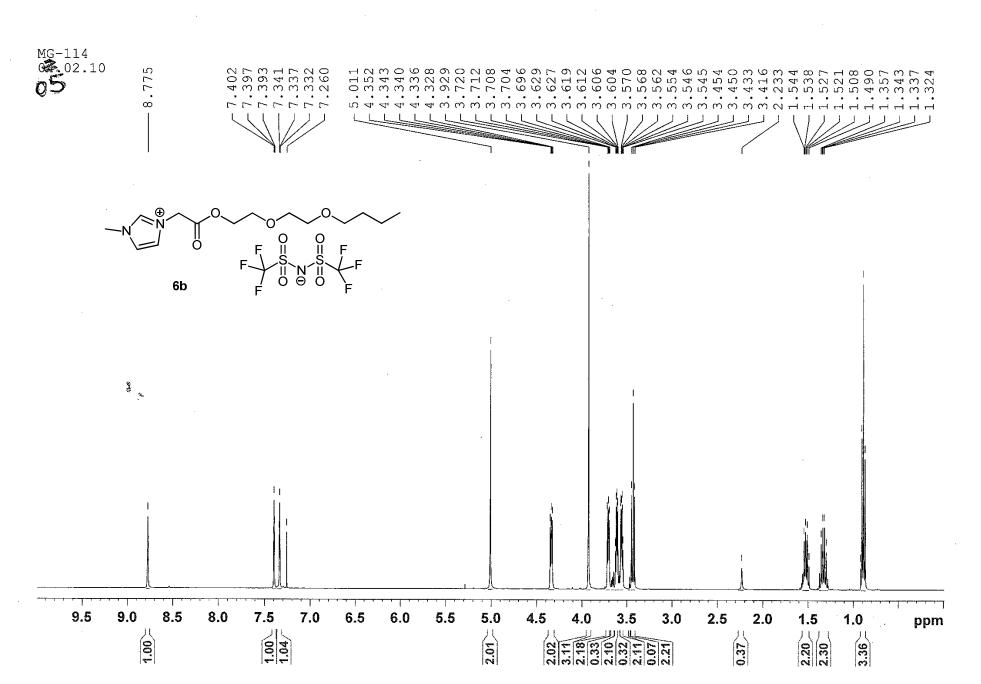


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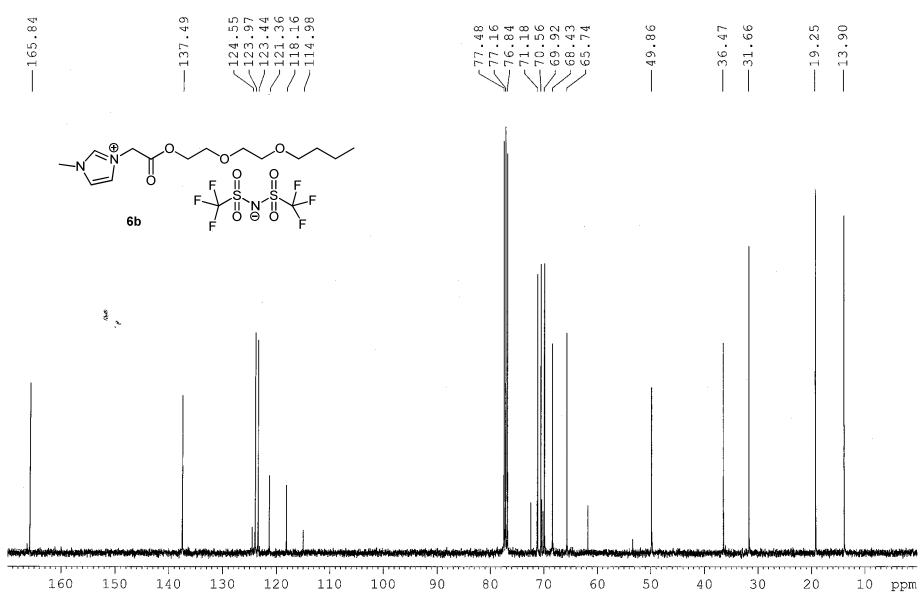


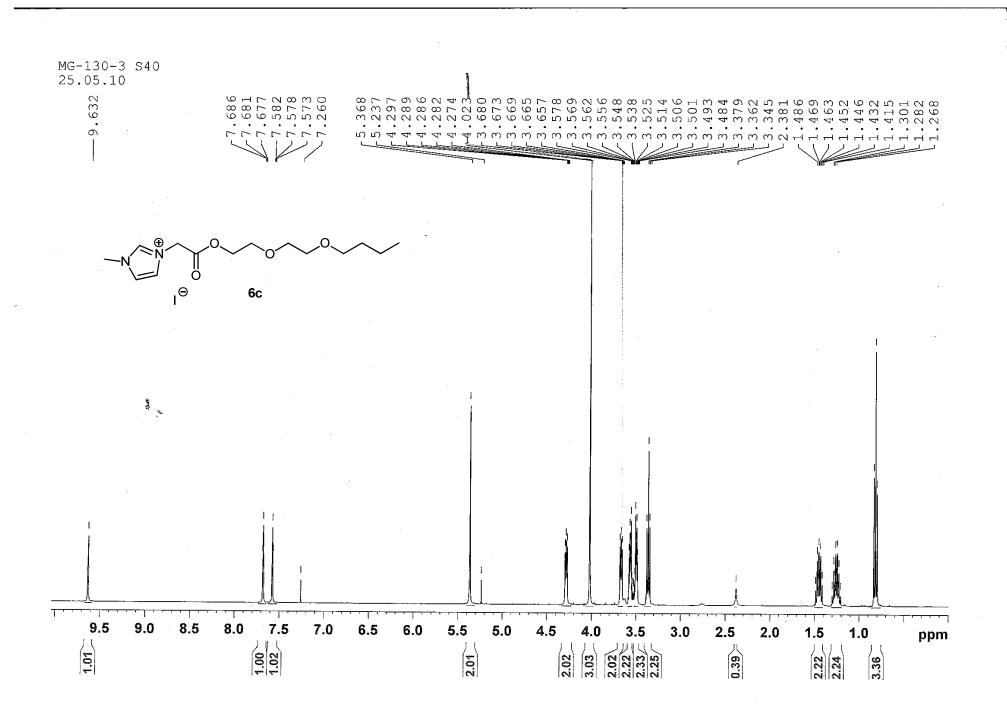
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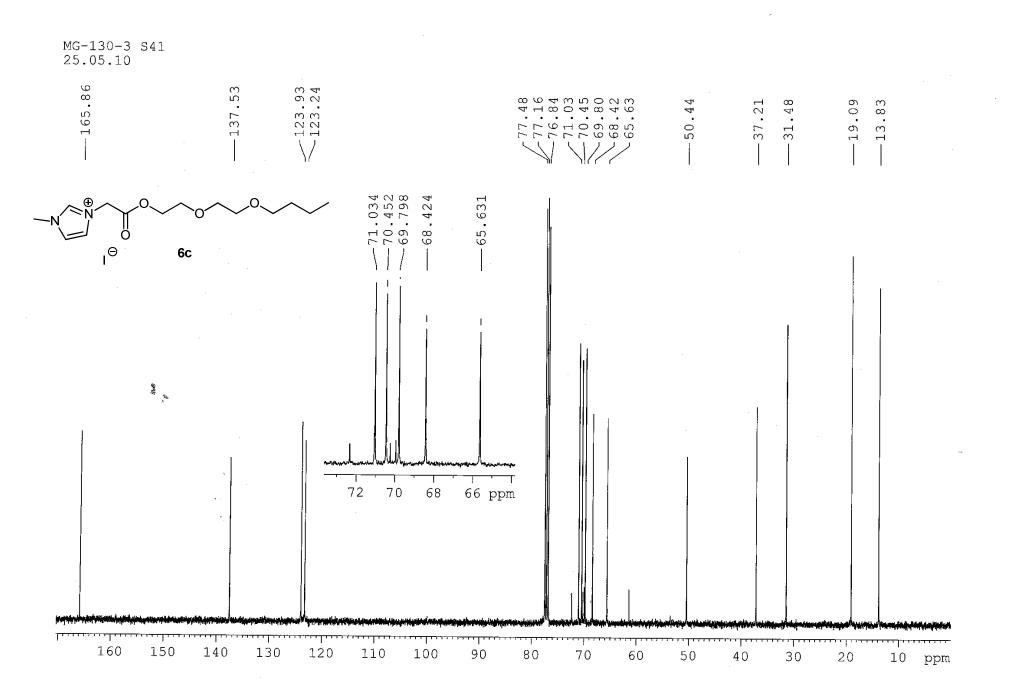


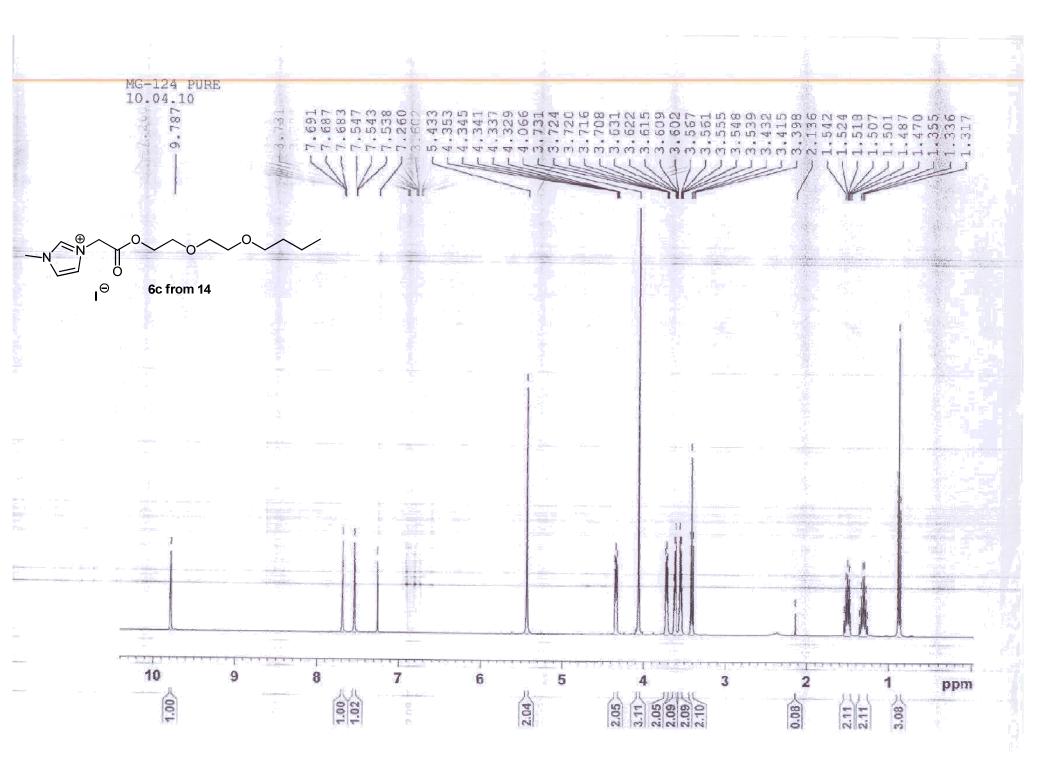


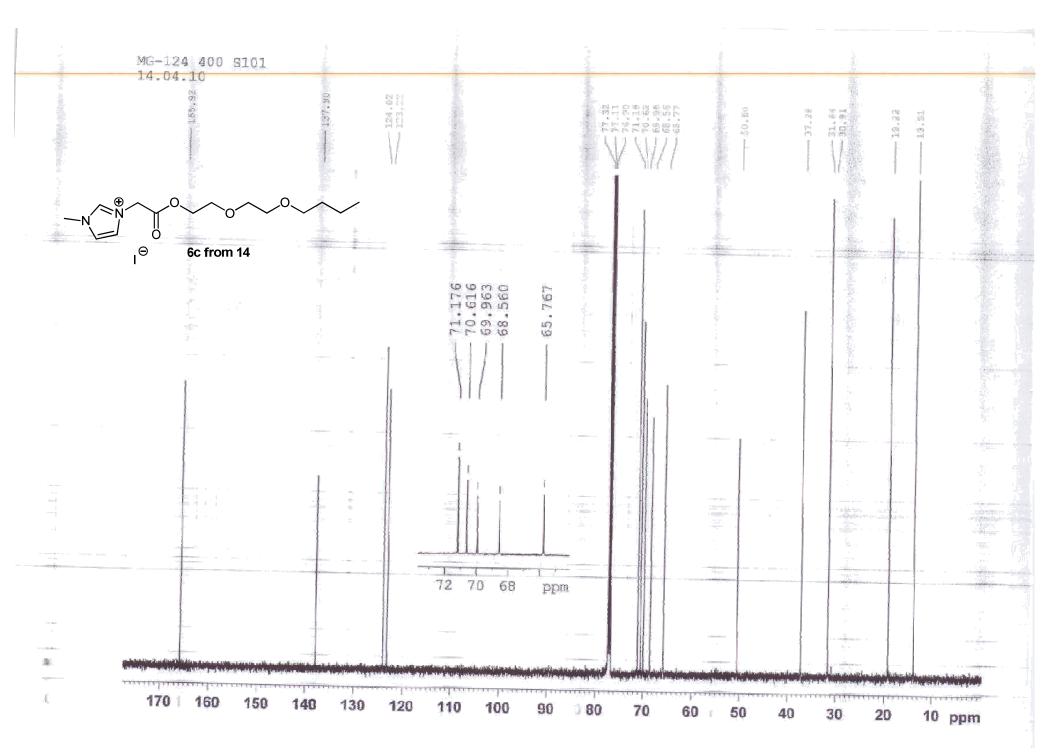
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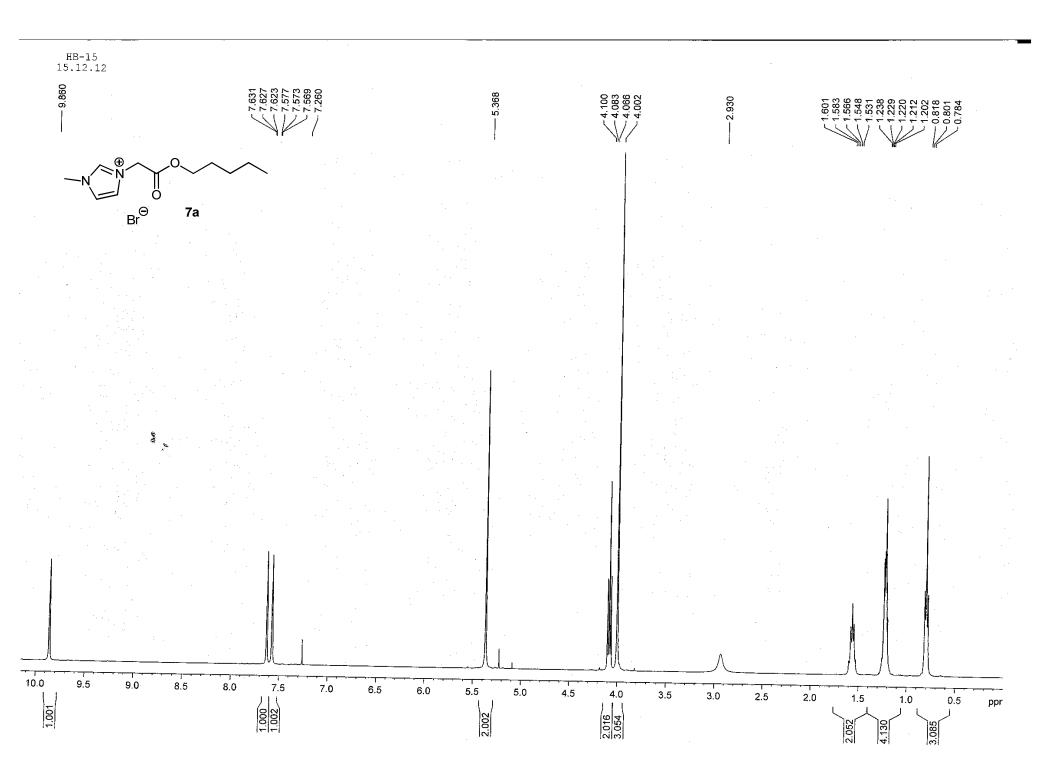


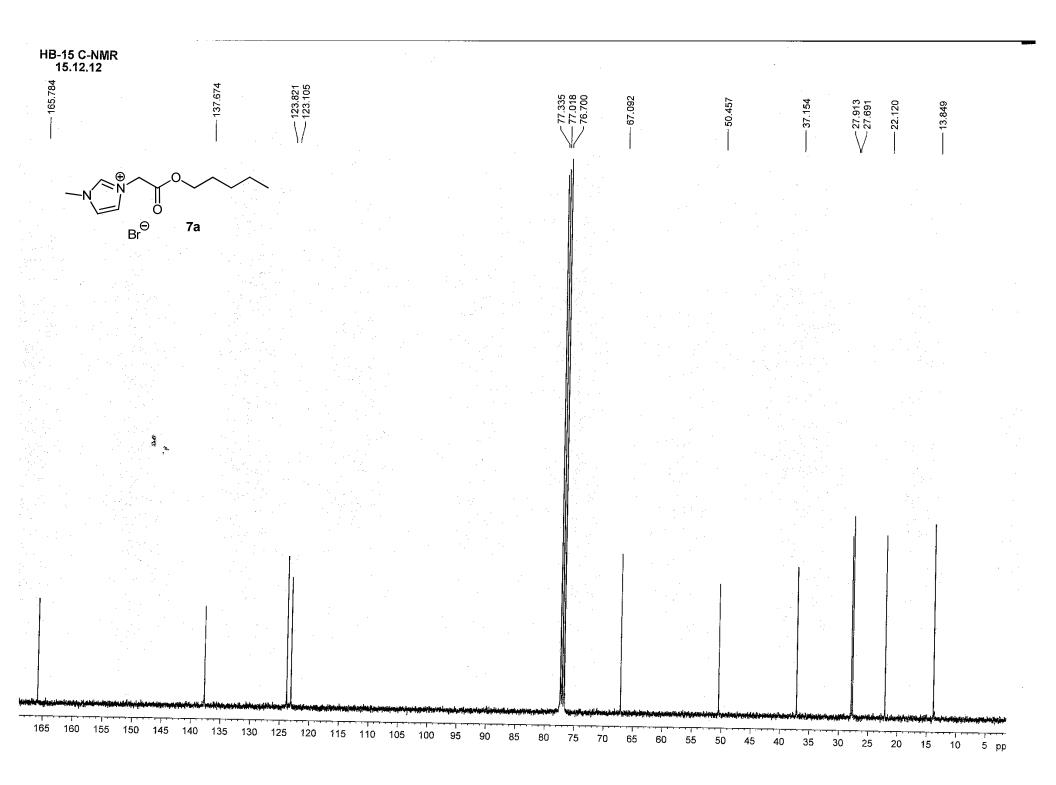


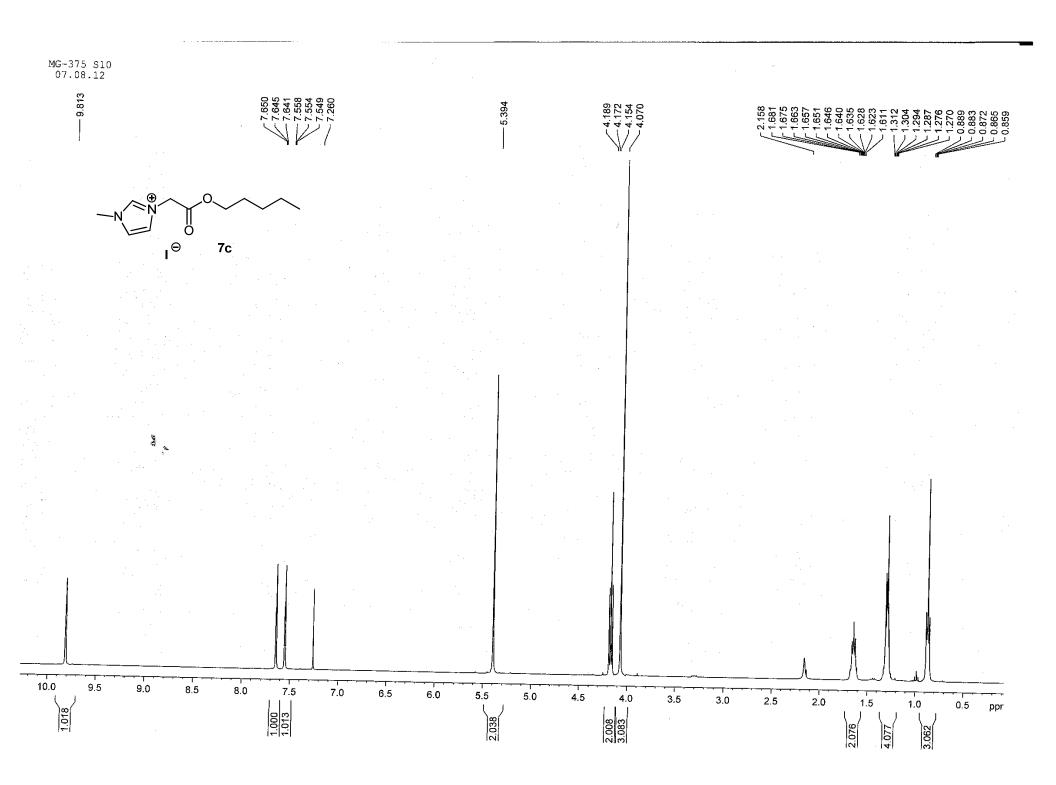


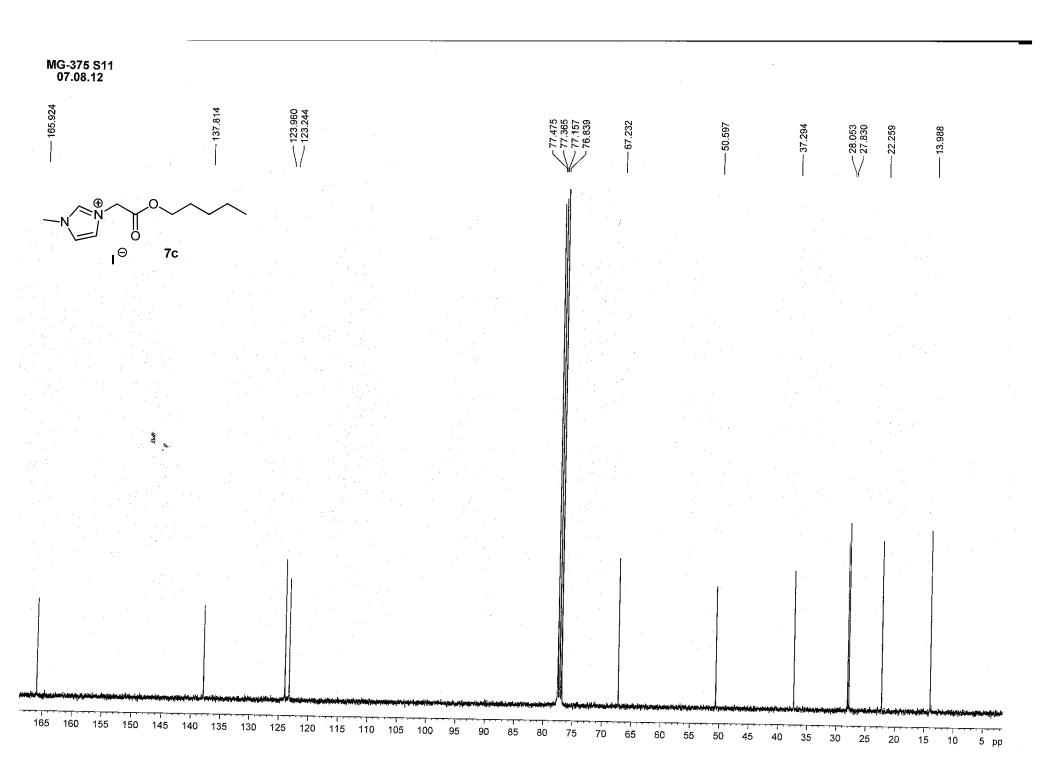


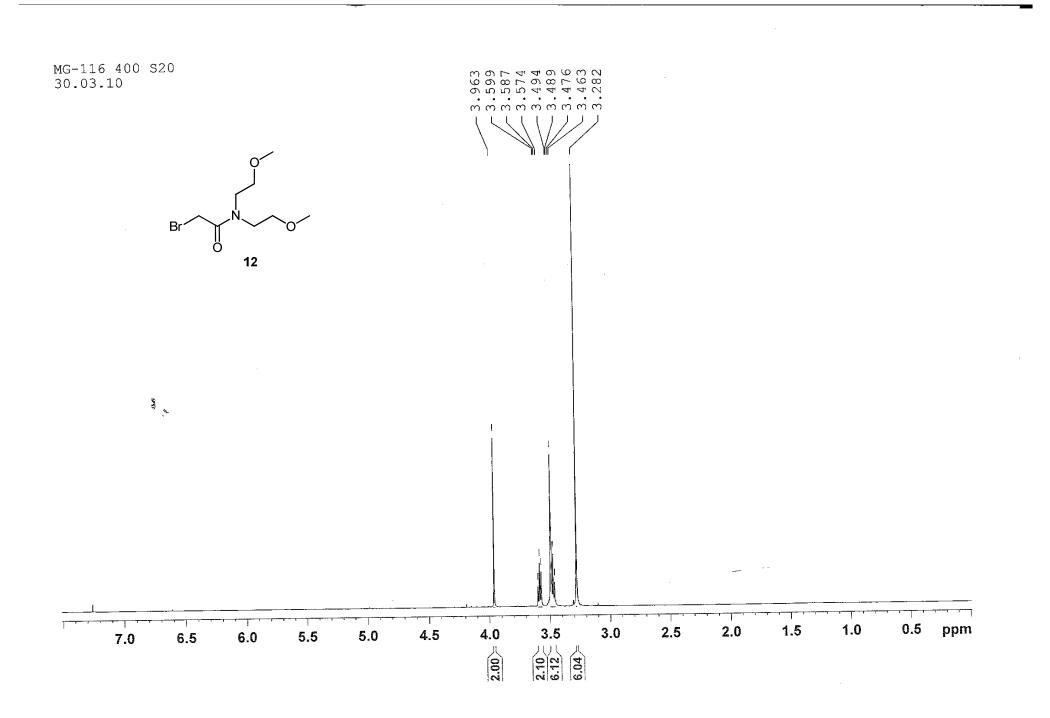


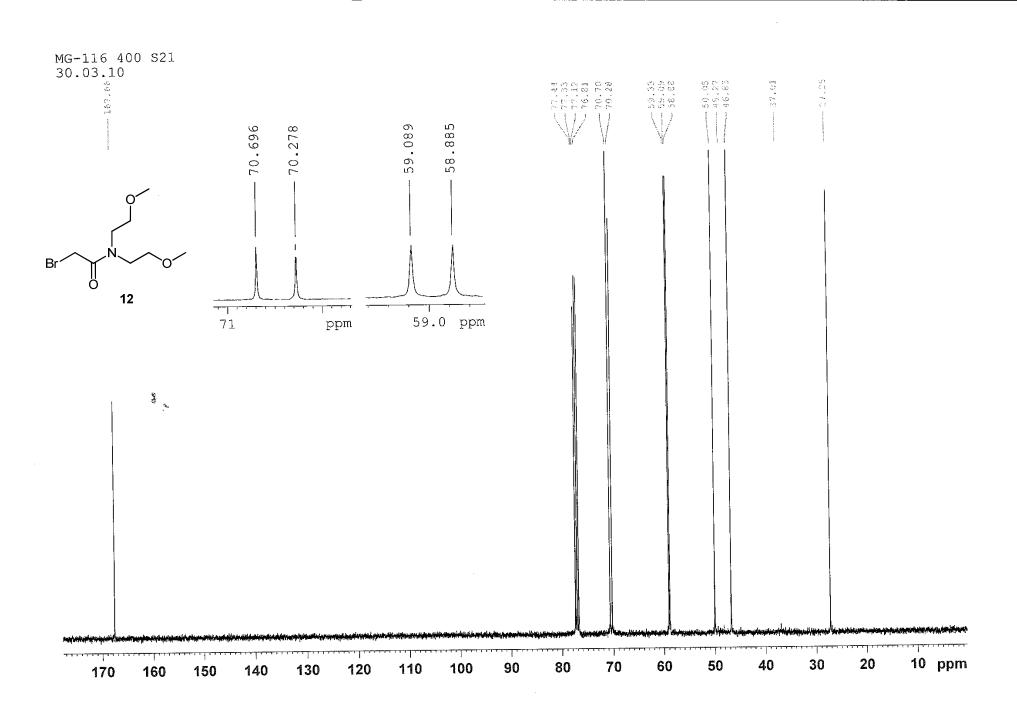


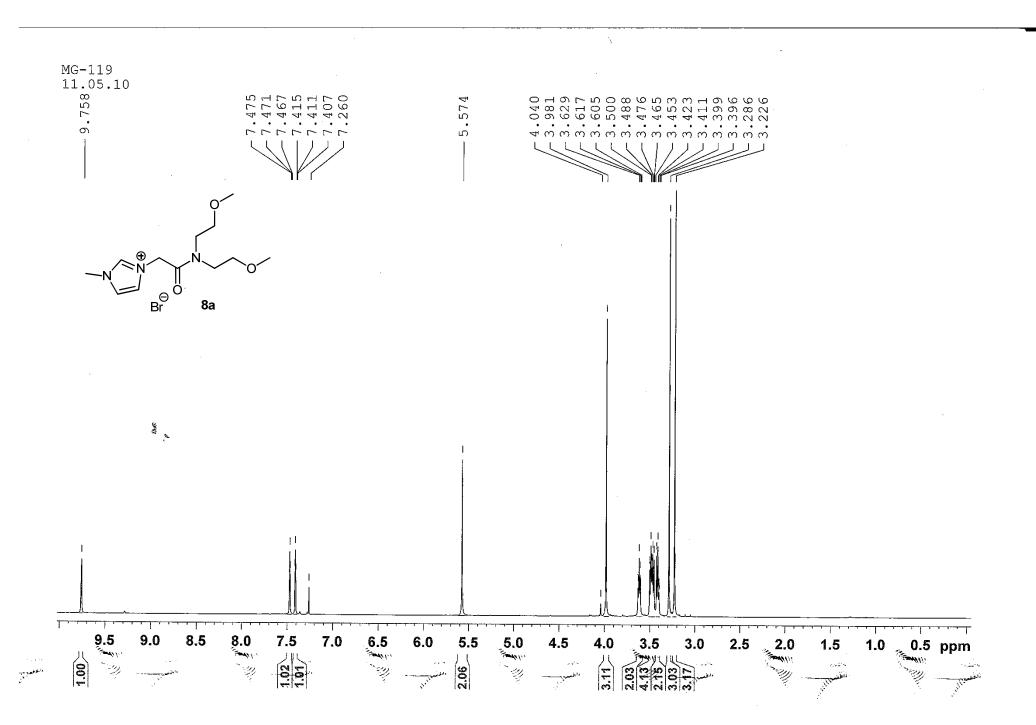




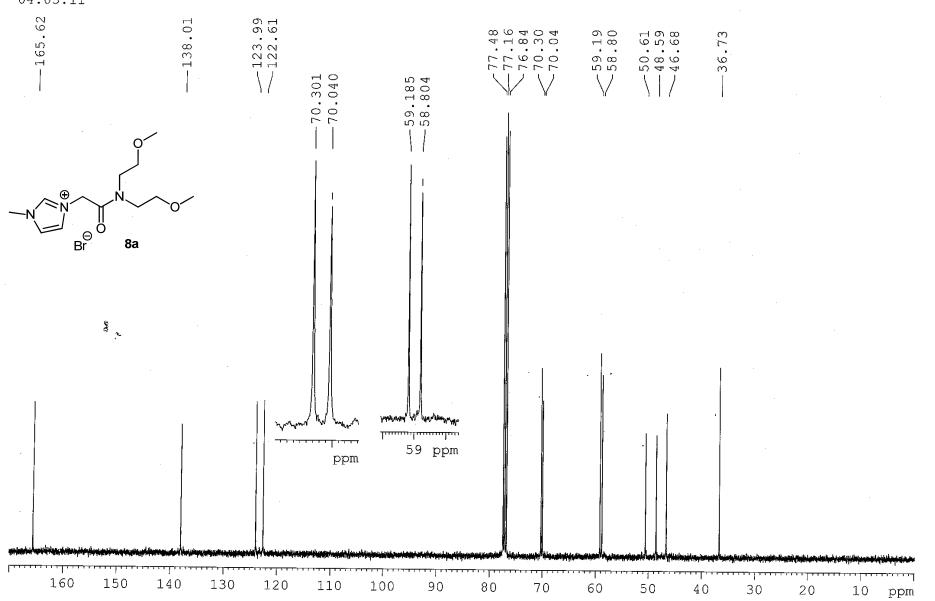


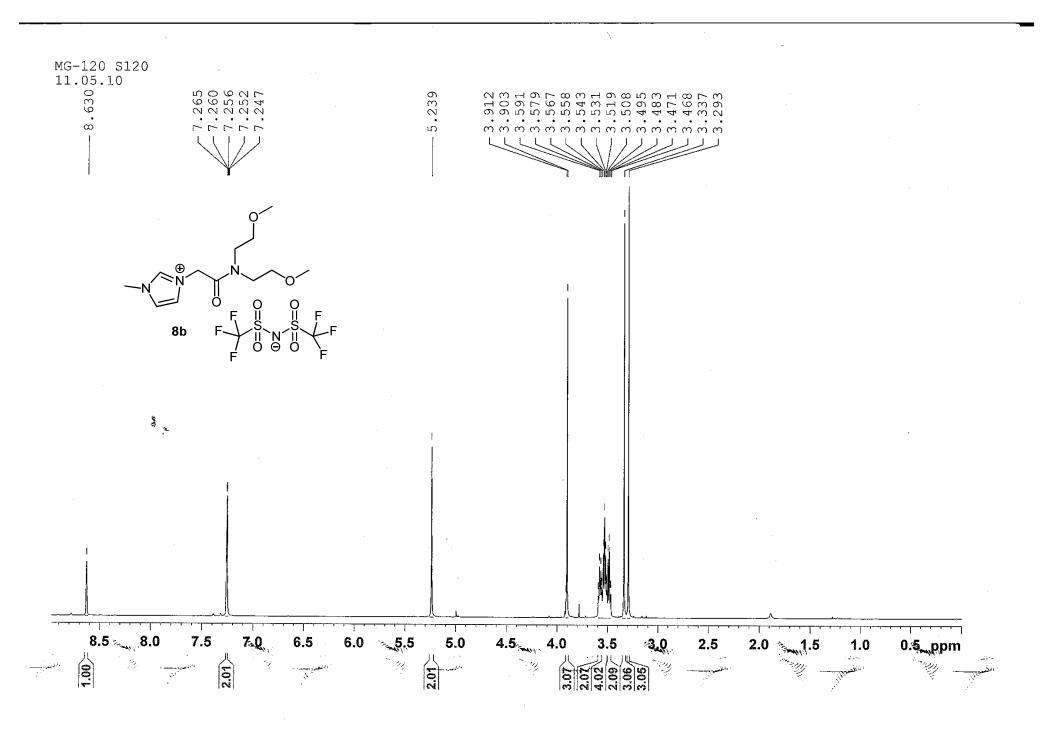


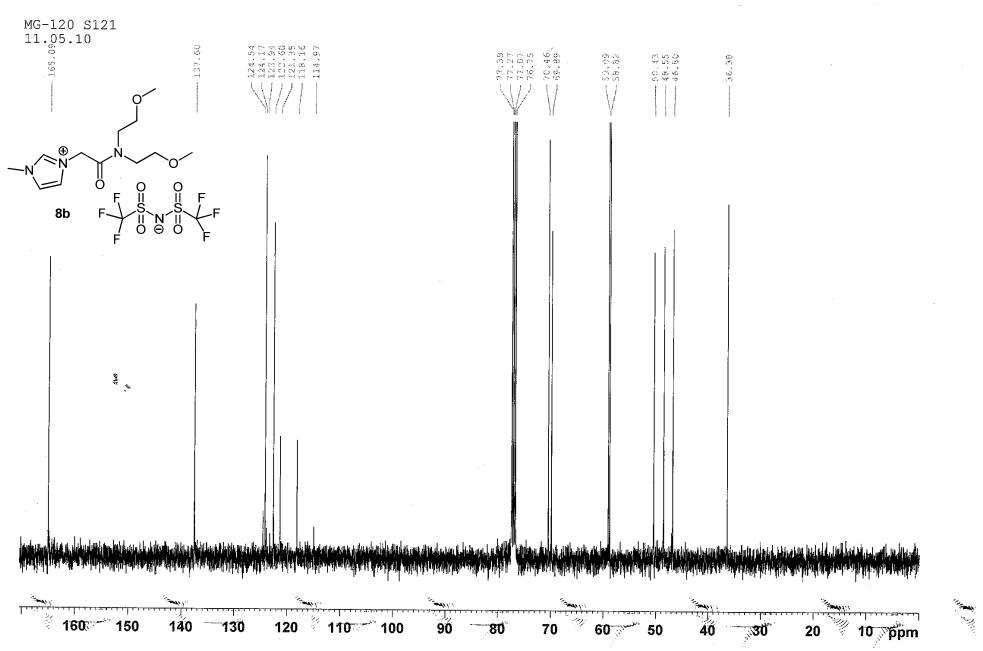


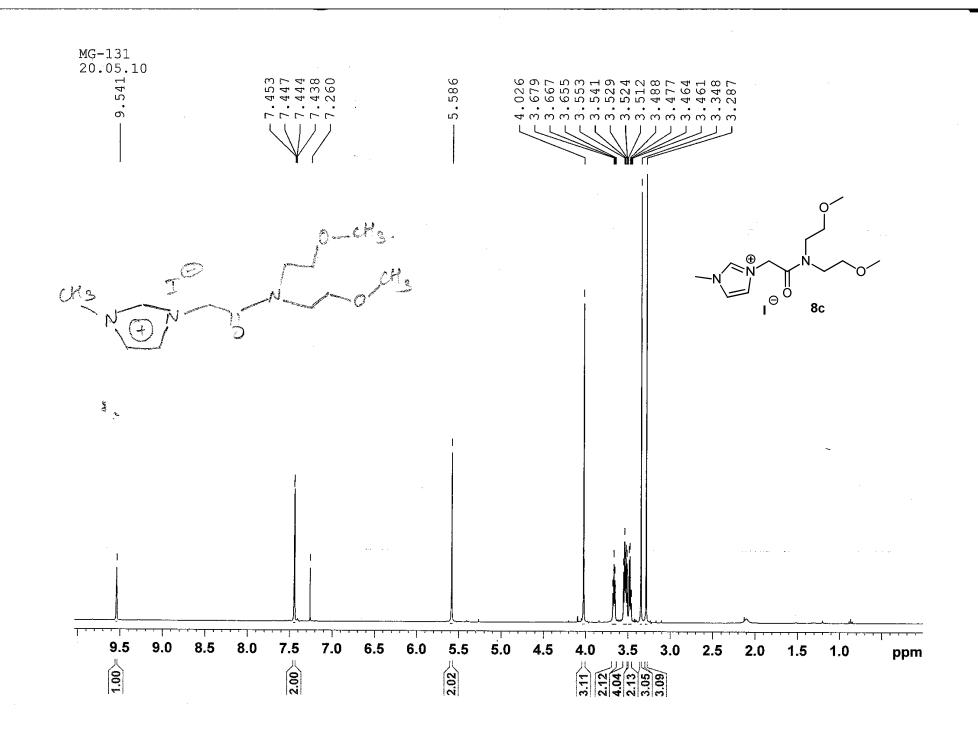


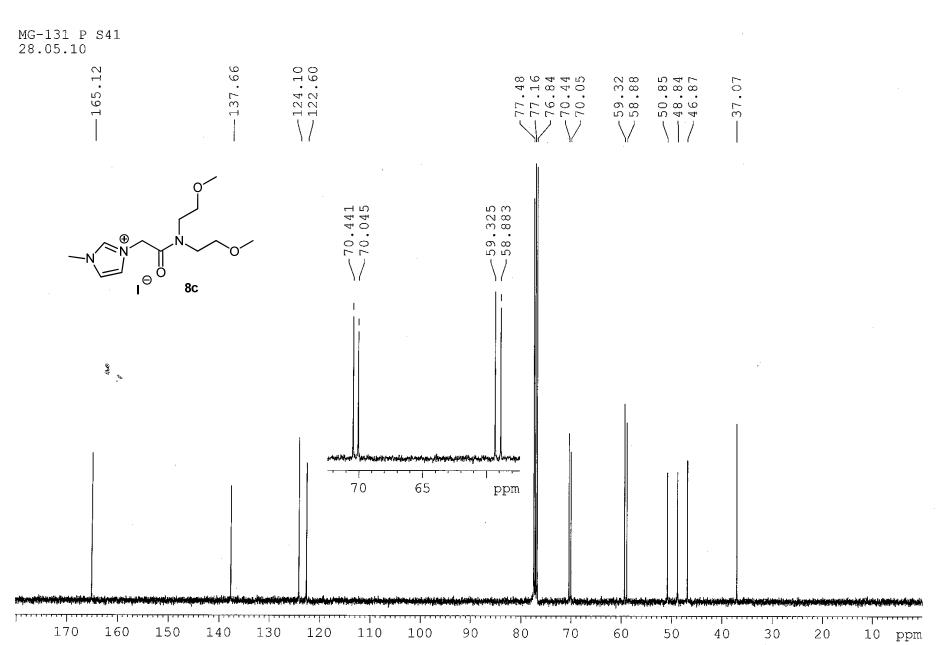
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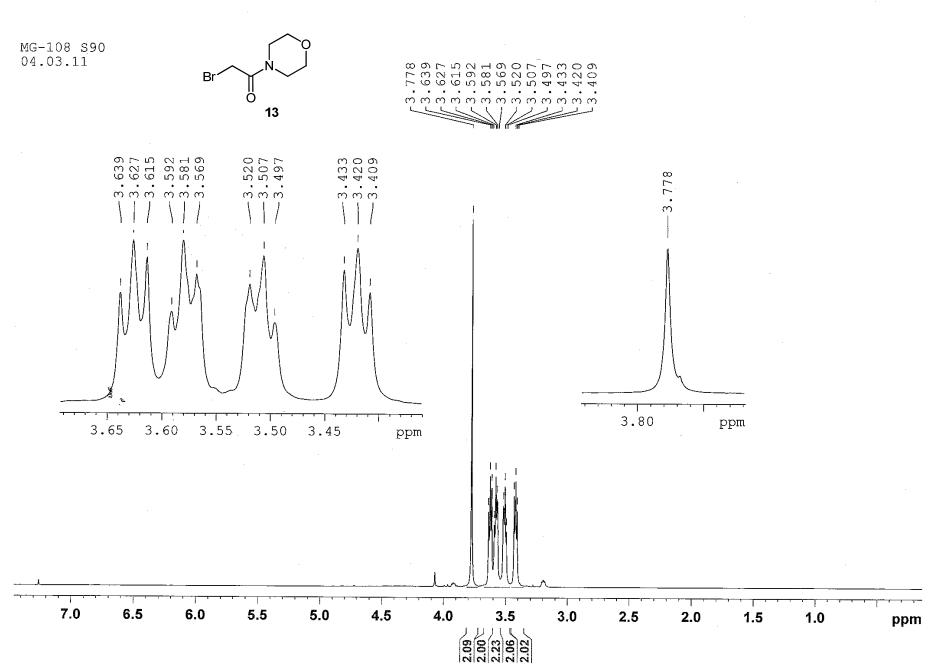


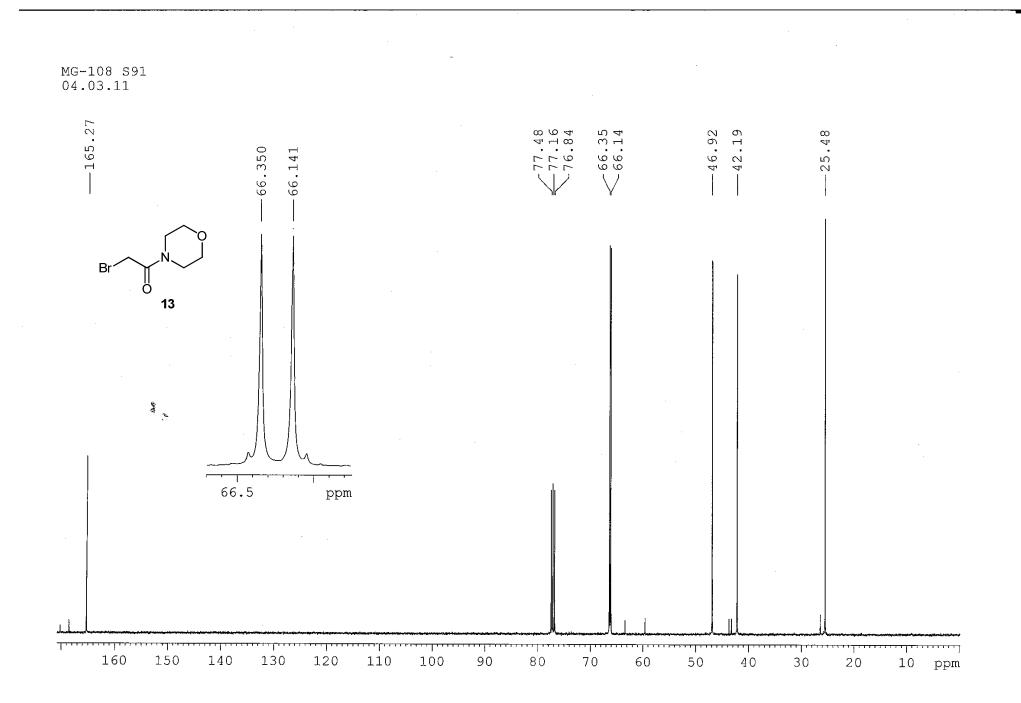


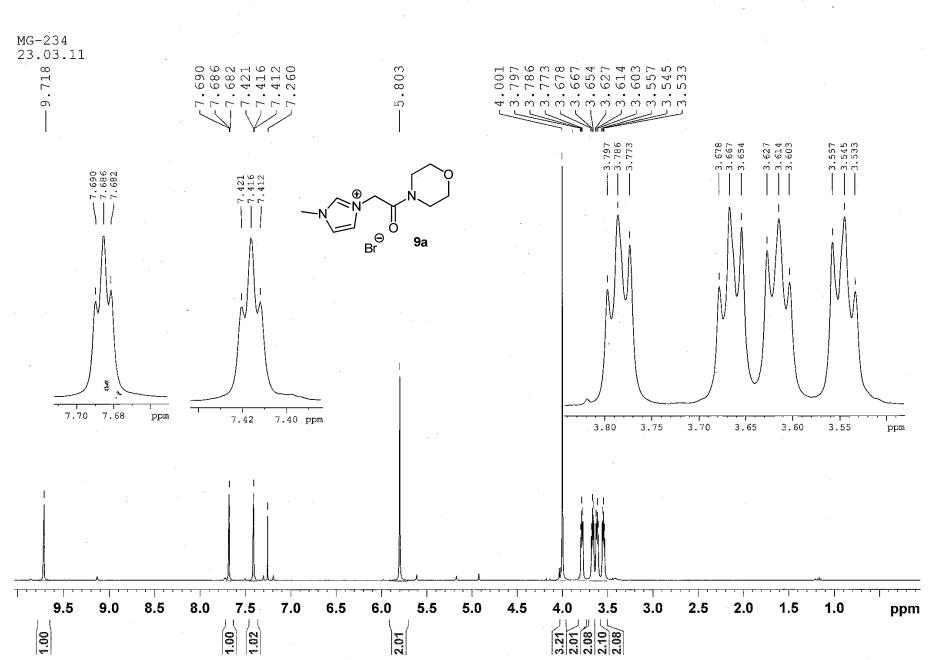




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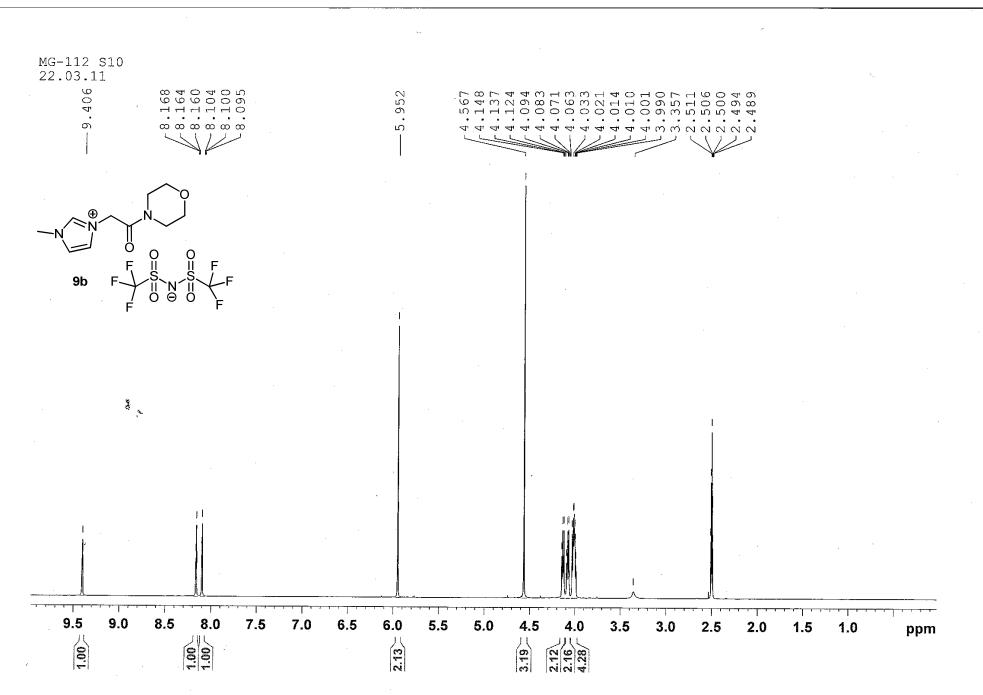


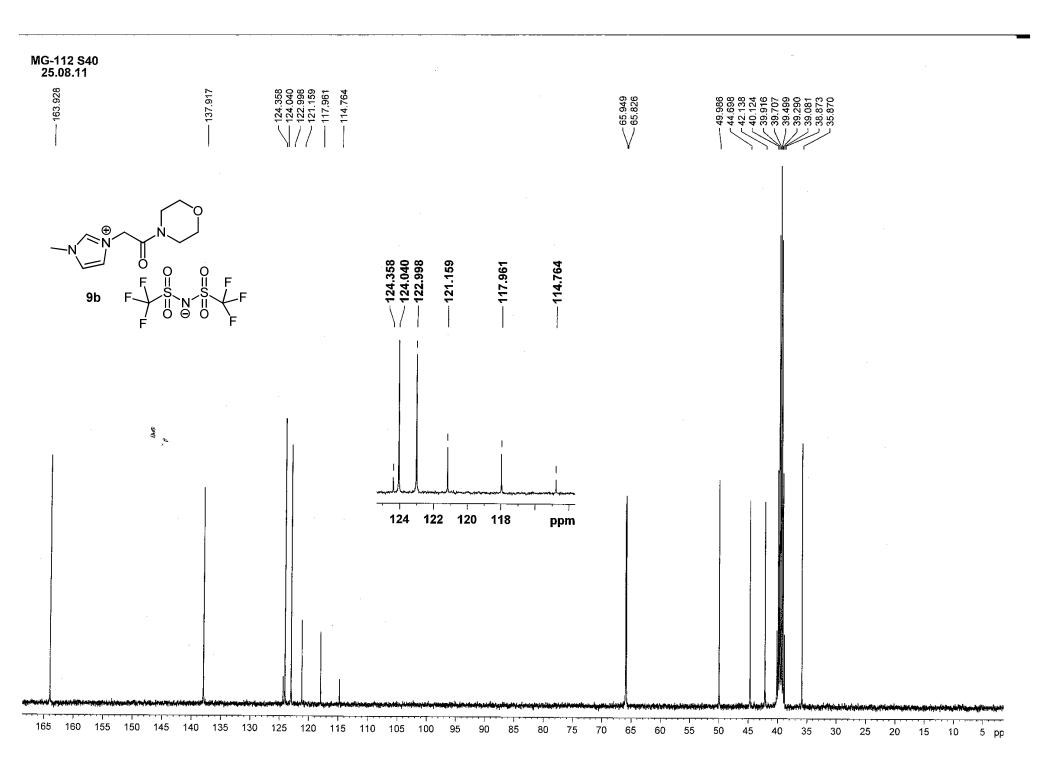


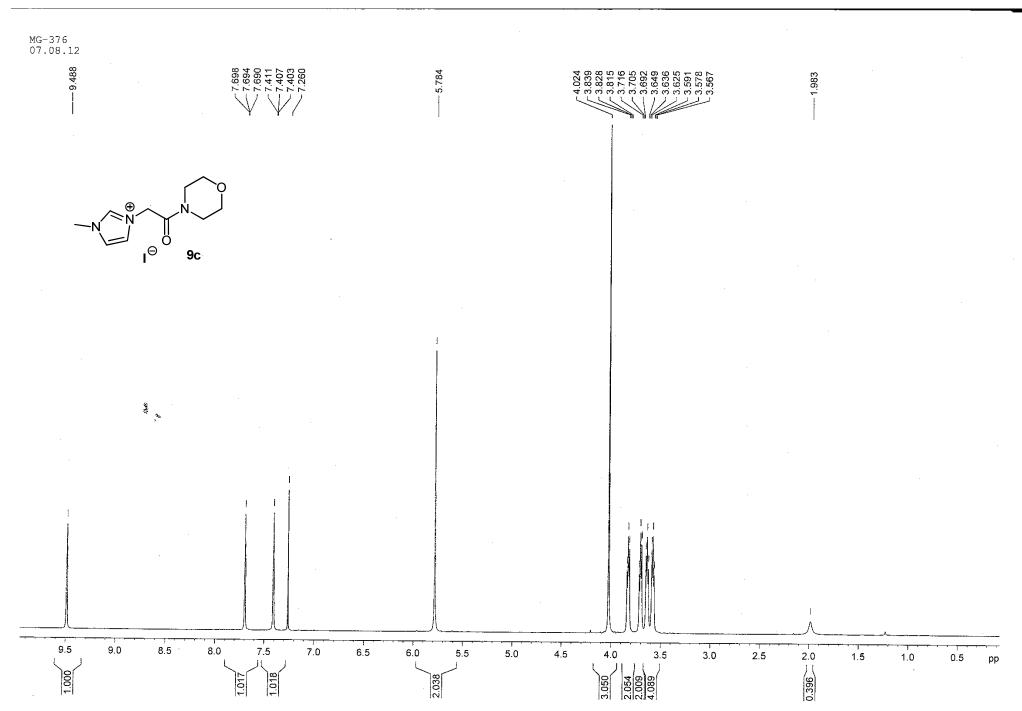


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