New Biobased-Zwitterionic Ionic Liquids : efficiency and biocompatibility for the development of sustainable biorefinery processes

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1. Synthesis of iodide derivatives

4-(3-methoxy-3-oxopropyl)-1,3-diimethyl-1*H*-imidazol-3-ium iodide (1)

5g (32.4 mmol) of **A**, 9g (65 mmol) of K_2CO_3 and iodomethane (8.1 mL, 130 mmol) were stirred in 100 mL of acetone at 70°C for 1h to afford after work-up, 9.7 g (97%) of pure compound **1** as a white solid. Mp = 134°C. ^{1}H NMR ($CDCl_3$, 300 MHz) : δ (ppm) 9.76 (s, 1 H, NCHN), 7.35 (s, 1 H, NCH), 3.99, 3.94 (s, 6 H, 2 x NCH_3), 3.64 (s, 3 H, OCH_3), 2.95 (dd, 2 H, J = 6.5 Hz, J = 7.5 Hz, CH_2), 2.73 (t, 2 H, J = 7.0 Hz, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 171.7 (CO), 136.7 (NCHN), 134.5 (Cq), 120;7 (NCH), 52.2 (OCH_3), 36.9, 34.4 (2 x NCH_3), 31.8 (CH_2), 18.9 (CH_2). HRMS (ESI^+) calc. for $C_9H_{15}N_2O_2^+$: 183.1232, found 183.1139.

4-(3-methoxy-3-oxopropyl)-1,3-diethyl-1*H*-imidazol-3-ium iodide (**2**)

5g (32.4 mmol) of **A**, 9g (65 mmol) of K_2CO_3 and iodoethane (7.8 mL, 97 mmol) were stirred in 100 mL of acetone at 70°C overnight to afford after work-up, 10.4 g (94%) of pure compound **2** as a slight yellow solid. Mp = 111°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 9.86 (s, 1 H, NCHN), 7.41 (s, 1 H, NCH), 4.30 (dd, 2 H, *J* = 7.3 Hz, *J* = 14.7 Hz, NCH_2), 4.24 (dd, 2 H, *J* = 7.3 Hz, *J* = 14.7 Hz, NCH_2), 3.61 (s, 3 H, OCH_3), 2.92 (m, 2 H, CH_2), 2.72 (t, 2 H, *J* = 6.7 Hz, CH_2), 1.52 (m, 6 H, 2 x CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 171.8 (CO), 135.2 (NCHN), 133.8 (Cq), 119.2 (NCH), 52.1 (OCH_3), 45.2, 42.6 (2 x NCH_2), 31.8 (CH_2), 18.9 (CH_2), 15.6, 15.5 (2 x CH_3). HRMS (ESI$^+$) calc. for $C_{11}H_{19}N_2O_2^+$: 211.1447, found 211.1446.

4-(3-methoxy-3-oxopropyl)-1,3-dipropyl-1*H*-imidazol-3-ium iodide (**3**)

4.6g (29.7 mmol) of **A**, 8.2g (59.4 mmol) of K_2CO_3 and 1-iodopropane (8.7 mL, 89 mmol) were stirred in 100 mL of acetone at 70°C for 3 days to afford after work-up, 15.0 g (99%) of pure compound **3** as a viscous liquid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 9.25 (s, 1 H, NCHN), 7.66 (s, 1 H, NCH), 4.13 (m, 4 H, 2 x NCH_2), 3.63 (s, 3 H, OCH_3), 2.93 (m, 2 H, CH_2), 2.75 (m, 2 H, CH_2), 1.81 (m, 4 H, 2 x CH_2), 0.88 (m, 6 H, 2 x CH_3). ^{13}C NMR (DMSO-d_6, 75 MHz): δ (ppm) 172.3 (CO), 136.0 (NCHN), 134.2 (Cq), 119.6 (NCH), 52.1 (OCH_3), 50.8, 48.2 (2 x NCH_2), 31.5, 23.1, 22.8, 18.8 (4 x CH_2), 10.9, 10.8 (2 x CH_3). HRMS (ESI$^+$) calc. for $C_{13}H_{23}N_2O_2^+$: 239.1760, found 239.1760.

4-(3-methoxy-3-oxopropyl)-1,3-dibutyl-1*H*-imidazol-3-ium iodide (**4**)

5g (32.4 mmol) of **A**, 8.9g (65 mmol) of K_2CO_3 and 1-iodobutane (7.7 mL, 68 mmol) were stirred in 100 mL of acetone at 70°C for 3 days to afford after work-up, 12.2 g (95%) of pure compound **4** as a viscous liquid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 9.35 (s, 1 H, NCHN), 7.71 (s, 1 H, NCH), 4.17 (m, 4 H, 2 x NCH_2), 3.61 (s, 3 H, OCH_3), 2.93 (t, 2 H, *J* = 7.2 Hz, CH_2), 2.74 (t, 2 H, *J* = 7.2 Hz, CH_2), 1.76 (m, 4 H, 2 x CH_2), 1.26 (m, 4 H, 2 x CH_2), 0.88 (m, 6 H, 2 x CH_3). ^{13}C NMR (DMSO-d_6, 75 MHz): δ (ppm) 172.3 (CO), 135.9 (NCHN), 134.0 (Cq), 119.7 (NCH), 52.2 (OCH_3), 49.0, 46.6 (2 x NCH_2), 31.7, 31.6, 31.3, 19.4, 19.2, 18.9 (6 x CH_2), 13.8, 13.7 (2 x CH_3). HRMS (ESI$^+$) calc. for $C_{15}H_{27}N_2O_2^+$: 267.2073, found 267.2081.

4-(3-methoxy-3-oxopropyl)-1,3-dipentyl-1*H*-imidazol-3-ium iodide (**5**)

5g (32.4 mmol) of **A**, 8.9g (65 mmol) of K_2CO_3 and 1-iodopentane (8.8 mL, 68 mmol) were stirred in 100 mL of acetone at 70°C for 3 days to afford after work-up, 13.2 g (99%) of pure compound **5** as a viscous liquid. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 9.25 (s, 1 H, NCHN), 7.66 (s, 1 H, NCH), 4.15 (t, 4 H, *J* = 7.4 Hz, 2 x NCH_2), 3.63 (s, 3 H, OCH_3), 2.93 (t, 2 H, *J* = 7.2 Hz, CH_2), 2.76 (t, 2 H, *J* = 7.2 Hz, CH_2), 1.79 (m, 4 H, 2 x CH_2), 1.29 (m, 8 H, 4 x CH_2), 0.88 (m, 6 H, 2 x CH_3). ^{13}C NMR (DMSO-d_6, 75 MHz): δ (ppm) 172.3 (CO), 136.0 (NCHN), 134.1 (Cq), 119.6 (NCH), 52.1 (OCH_3), 49.3, 46.7 (2 x NCH_2), 31.5, 29.3, 29.0, 28.2, 28.0, 22.0, 21.9, 18.8 (8 x CH_2), 14.2 (2 x CH_3). HRMS (ESI$^+$) calc. for $C_{17}H_{31}N_2O_2^+$: 295.2386, found 295.2382.

2. Synthesis of ZILs derivatives

3-(1,3-dimethyl-1*H*-imidazol-3-ium-4-yl)propanoate (**ZIL1**)

7.72g (24.90 mmol) of 4-(3-methoxy-3-oxopropyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide and 46g of Amberlite IRN78 OH resin (1/6 ratio) in 38.6 mL of MeOH were used to obtain pure **ZIL1** as a white solid (4.10g, >99% yield). Mp = 109°C. ^{1}H) NMR (CD_3OD, 400 MHz) δ : 8.74 (s, 1H, NCHN residual), 7.30 (s, 1 H, CH=C), 3.88 (s, 3 H, NCH_3), 3.86 (s, 3 H, NCH_3), 2.93 (t, 2 H, *J* = 7.1 Hz, CH_2), 2.53 (t, 2 H, *J* = 7.1 Hz, CH_2). ^{13}C) NMR (CD_3OD, 100 MHz) δ : 177.9 (CO_2), 136.4 (C*q*), 135.9, 135.6 (m, NCHN residual), 119.8 (CH=N), 34.9 ($CH_2CO_2^-$), 34.8 (NCH_3), 32.4 (NCH_3), 19.9 (CH_2). HRMS (ESI^+) calc. for $C_8H_{13}N_2O_2$ $[M+H]^+$ 169.0977, found 169.0981.

3-(1,3-diethyl-1*H*-imidazol-3-ium-4-yl)propanoate (**ZIL2**)

8.80g (26.03 mmol) of 4-(3-methoxy-3-oxopropyl)-1,3-diethyl-1*H*-imidazol-3-ium iodide et 53g of resin Amberlite IRN78 OH (1/6 ratio) in 44 mL of MeOH were used to obtain pure **ZIL2** as a white solid (4.37g, 85% yield). Mp = 98°C. ^{1}H) NMR (CD_3OD, 400 MHz) δ : 9.03 (s, 1H, NCHN residual), 7.44 (s, 1 H, CH=N), 4.25 (m, 4 H, 2 x NCH_2), 2.97 (t, 2 H, *J* = 7.2 Hz, CH_2), 2.56 (t, 2 H, *J* = 7.2 Hz, CH_2), 1.55 (m, 6 H, 2 x CH_3). ^{13}C) NMR (CD_3OD, 100 MHz) δ : 177.8 (CO_2^-), 135.9 (C*q*), 134.4, 133.8 (m, NCHN residual), 118.4 (CH=C), 44.5, 41.8 (2 x NCH_2), 34.9 (CH_2), 20.0 (CH_2), 14.2, 13.9 (2 x CH_3). HRMS (ESI^+) calc. for $C_{10}H_{17}N_2O_2$ $[M+H]^+$ 197.1290, found 197.1294.

3-(1,3-dipropyl-1*H*-imidazol-3-ium-4-yl)propanoate (**ZIL3**)

2.42g (6.61 mmol) of 4-(3-methoxy-3-oxopropyl)-1,3-dipropyl-1*H*-imidazol-3-ium iodide and 14.5g of resin Amberlite IRN78 OH (1/6 ratio) in 12 mL of MeOH were used to obtain pure **ZIL3** as a viscous liquid (1.60g, >99% yield). ^{1}H) NMR ($CDCl_3$, 400 MHz) δ : 8.99 (s, 1H, NCHN residual), 7.42 (s, 1 H, CH=C), 4.16 (m, 4 H, 2 x NCH_2), 2.96 (t, 2 H, *J* = 6.9 Hz, CH_2), 2.56 (t, 2 H, *J* = 6.9 Hz, CH_2), 1.92 (m, 4 H, 2 x CH_2), 1.00 (m, 6 H, 2 x CH_3). ^{13}C) NMR ($CDCl_3$, 100 MHz) δ : 177.9 (CO_2^-), 136.1 (C*q*), 135.2, 134.8, 134.5 (t, $^{1}J_{C\text{-}D}$ = 33 Hz, NCHN residual),[1] 118.7 (CH=C), 50.8, 48.0 (2 x NCH_2), 34.9 (CH_2), 22.9 (CH_2), 22.7 (CH_2), 20.1 (CH_2), 9.6 (CH_3), 9.5 (CH_3). HRMS (ESI^+) calc. for $C_{12}H_{21}N_2O_2$ $[M+H]^+$ 225.1603, found 225.1611.

3-(1,3-dibutyl-1*H*-imidazol-3-ium-4-yl)propanoate (**ZIL4**)

3.40g (8.63 mmol) of 4-(3-methoxy-3-oxopropyl)-1,3-dibutyl-1*H*-imidazol-3-ium iodide and 20.4g of resin Amberlite IRN78 OH (1/6 ratio) in 17 mL of MeOH were used to obtain pure **ZIL4** as a slight yellow solid (1.87g, 86% yield). Mp = 64°C. ^{1}H) NMR ($CDCl_3$, 400 MHz) δ : 10.84 (s, 1 H, NCHN), 6.93 (s, 1 H, CH=C), 4.15 (m, 4 H, 2 x NCH_2), 2.85 (t, 2 H, *J* = 7.1 Hz, CH_2), 2.48 (t, 2 H, *J* = 7.1 Hz, CH_2), 1.75 (m, 4 H, 2 x CH_2), 1.28 (m, 4 H, 2 x CH_2), 0.86 (m, 6 H, 2 x CH_3). ^{13}C) NMR ($CDCl_3$, 100 MHz) δ : 176.0 (CO_2^-), 138.4 (NCHN), 136.4 (C*q*), 117.3 (CH=C), 49.0, 46.5 (2 x NCH_2), 35.7 (CH_2), 32.0, 31.9 (2 x CH_2), 21.0 (CH_2), 19.5, 19.4 (2 x CH_2), 13.4, 13.3 (2 x CH_3). HRMS (ESI^+) calc. for $C_{14}H_{25}N_2O_2$ $[M+H]^+$ 253.1913, found 253.1918.

^{1}H) NMR (MeOD, 400 MHz) δ : 9.00 (s, 1H, NCHN residual), 7.42 (s, 1 H, CH=C), 4.20 (m, 4 H, 2 x NCH_2), 2.96 (m, 2 H, CH_2), 2.55 (t, 2 H, *J* = 7.0 Hz, CH_2), 1.87 (m, 4 H, 2 x CH_2), 1.41 (m, 4 H, 2 x CH_2), 1.02 (m, 6 H, 2 x CH_3). ^{13}C) NMR (MeOD, 100 MHz) δ : 177.9 (CO_2^-), 136.4 (C*q*), 135.0, 134.8, 134.4 (t, $^{1}J_{C\text{-}D}$ = 29 Hz, NCHN residual),[1] 118.7 (CH=C), 49.0, 46.4 (2 x NCH_2), 34.9 (CH_2), 31.6, 31.5, 31.4 (3 x CH_2), 20.1 (CH_2), 19.2, 19.1 (2 x CH_2), 12.5, 13.4 (2 x CH_3).

3-(1,3-dipentyl-1*H*-imidazol-3-ium-4-yl)propanoate (ZIL5)

6.20g (14.69 mmol) of 4-(3-methoxy-3-oxopropyl)-1,3-dipentyl-1*H*-imidazol-3-ium iodide and 37g of resin Amberlite IRN78 OH (1/6 ratio) in 31 mL of MeOH were used to obtain pure **ZIL5** as a viscous liquid (4.13g, >99% yield). ^{1}H) NMR ($CDCl_3$, 400 MHz) δ : 8.92 (s, 1 H, NCHN residual), 7.39 (s, 1 H, CH=C), 4.19 (m, 4 H, 2 x NCH_2), 2.94 (t, 2 H, *J* = 6.9 Hz, CH_2), 2.54 (t, 2 H, *J* = 6.9 Hz, CH_2), 1.89 (m, 4 H, 2 x CH_2), 1.32 (m, 8 H, 4 x CH_2), 0.95 (t, 6 H, *J* = 6.5 Hz, 2 x CH_3). ^{13}C) NMR ($CDCl_3$, 100 MHz) δ : 177.9 (CO_2^-), 136.1 (C*q*), 134.9, 134.6 (m, NCHN residual), 118.7 (CH=N), 49.3, 46.6 (2 x NCH_2), 34.8 (CH_2), 29.2, 29.0 (2 x CH_2), 28.1, 28.0 (2 x CH_2), 21.8, 21.7 (2 x CH_2), 20.0 (CH_2), 12.8, 12.7 (2 x CH_3). HRMS (ESI^+) calc. for $C_{16}H_{29}N_2O_2$ $[M+H]^+$ 281.2229, found 281.2231.

3. Composition of the simulated systems (number of molecules)

ERGO	DOPA	PIPA	POPA	DOPC	PIPC	POPC	DOPE	PIPE	POPE
180	4	4	12	138	132	330	64	62	154

DOPS	PIPS	POPS	PIPI	POPI	ZIL	W (0/1/2 bead)
18	18	44	52	188	409	9645/9256/8645

4. SEM micrographs

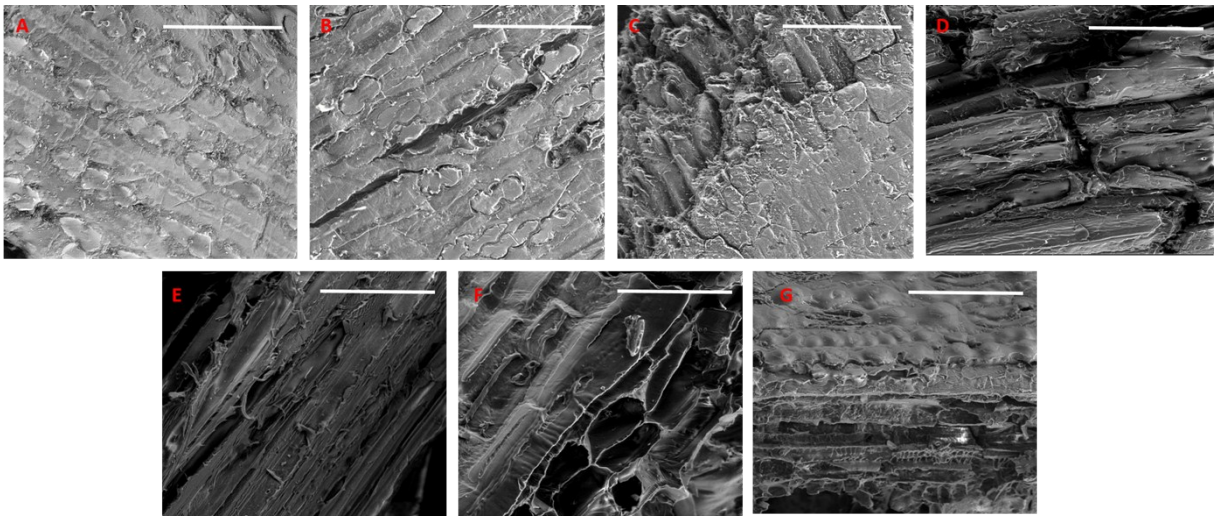
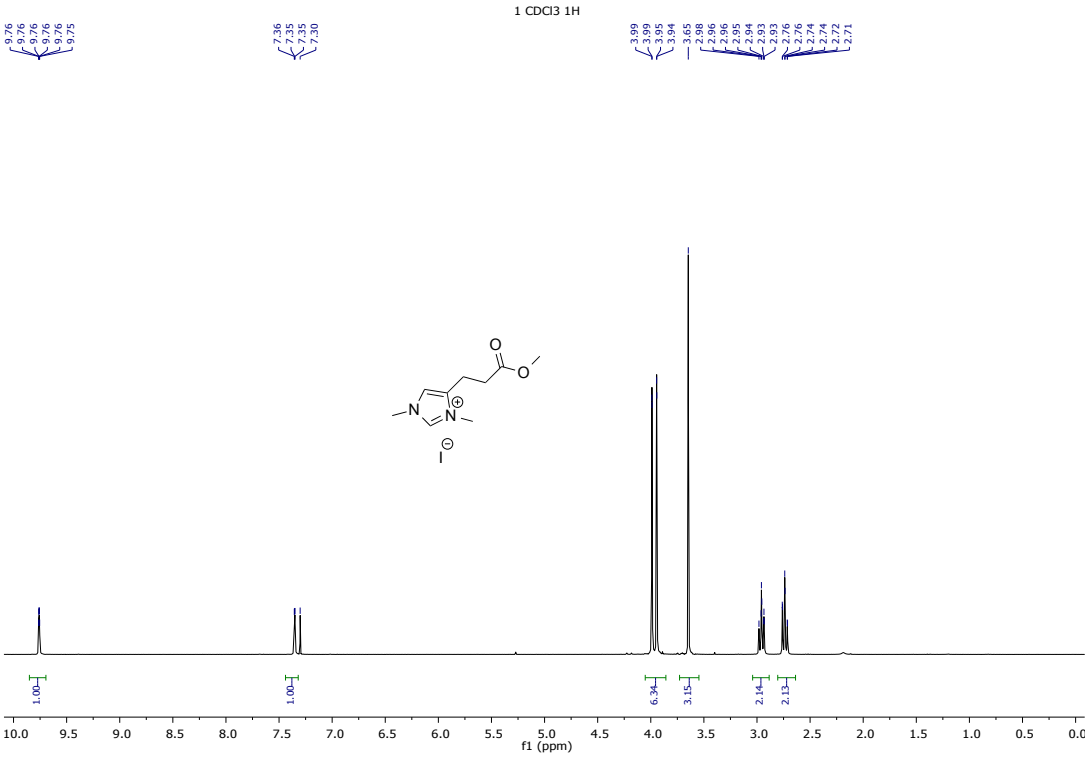


Figure S1. SEM micrographs of untreated miscanthus (A), [C_2mim][OAc]-pretreated miscanthus (B), pretreated miscanthus with ZIL1 (C), ZIL2 (D), ZIL3 (E), ZIL4 (F) and ZIL5 (G), (scale = 50µm)

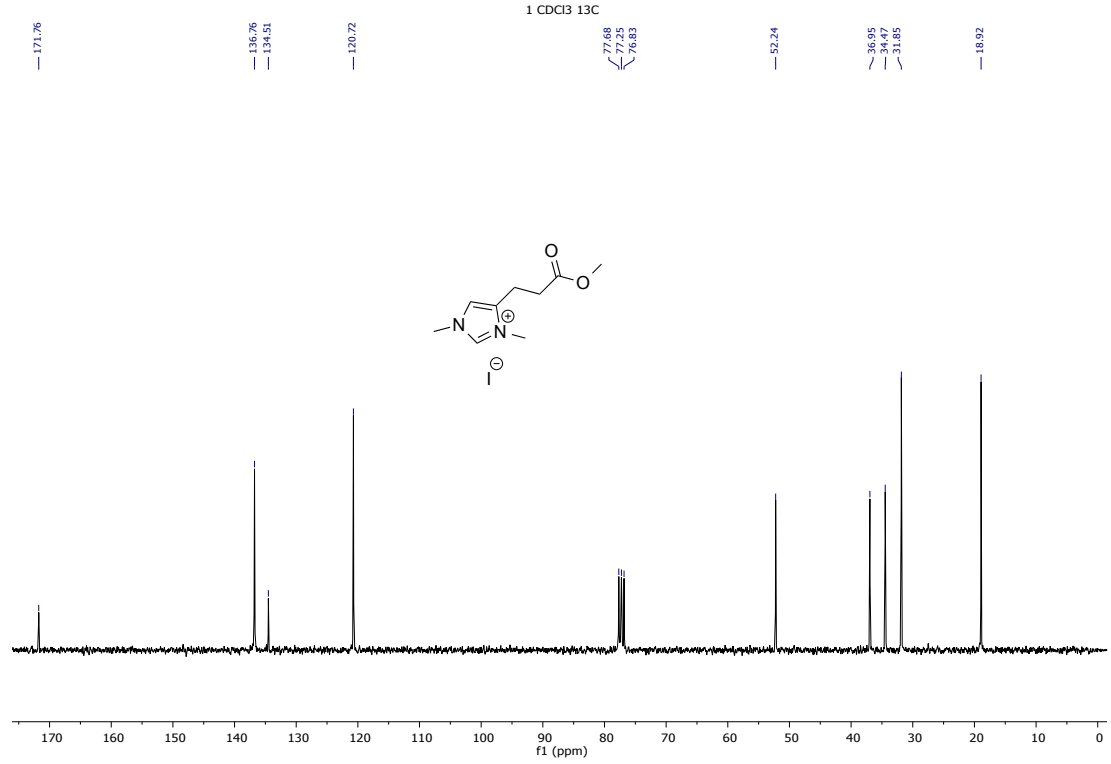
References

1 I. Tommasi and F. Sorrentino, *Tet. Lett.*, 2006, **47**, 6453-6456.

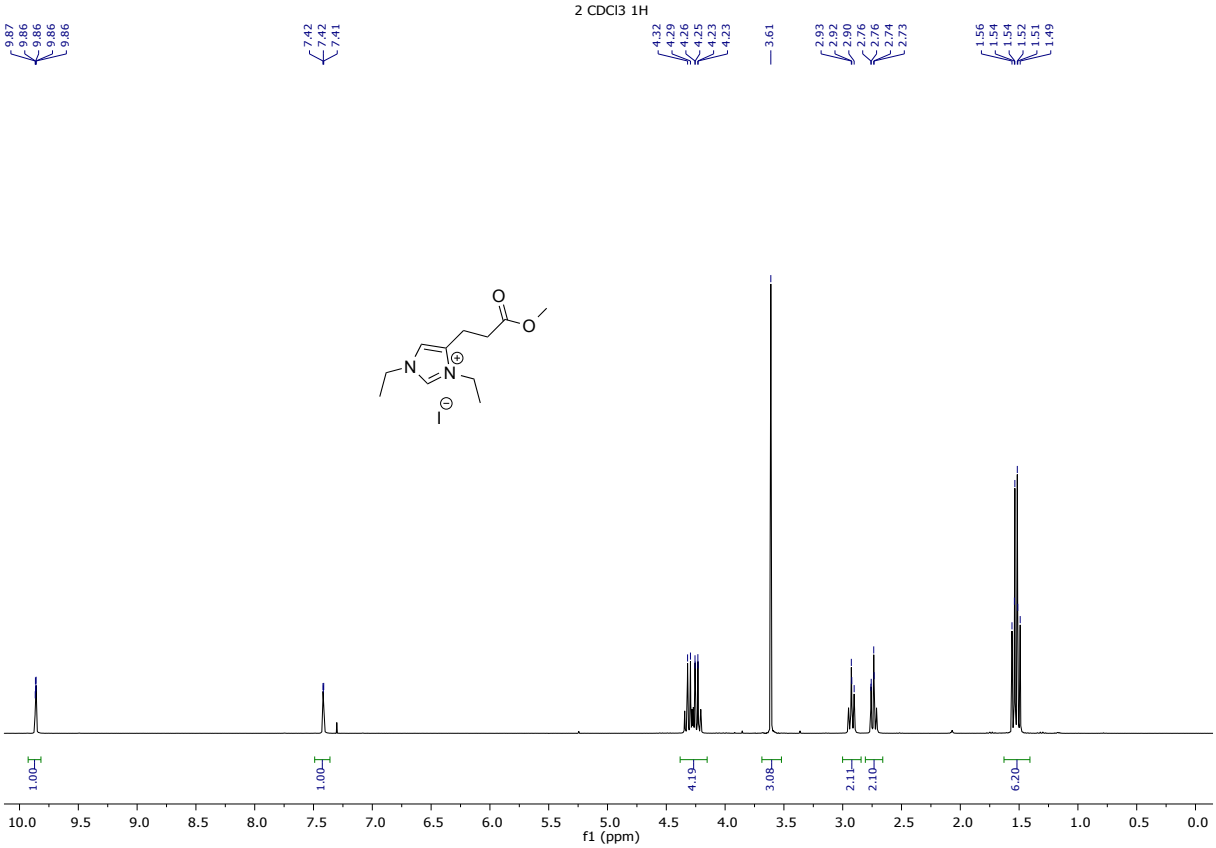
5. ^{1}H and ^{13}C NMR spectra of ZIL derivatives



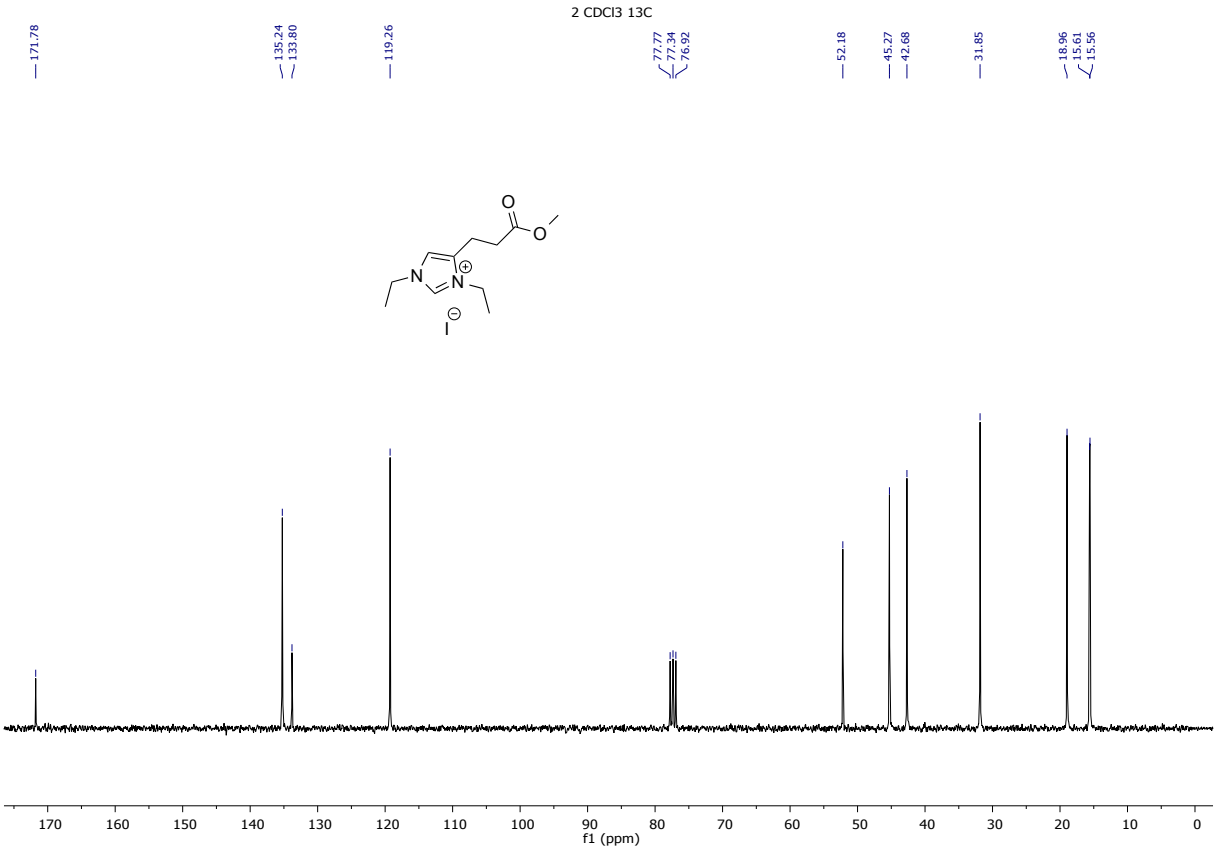
^{1}H NMR of compound **1**



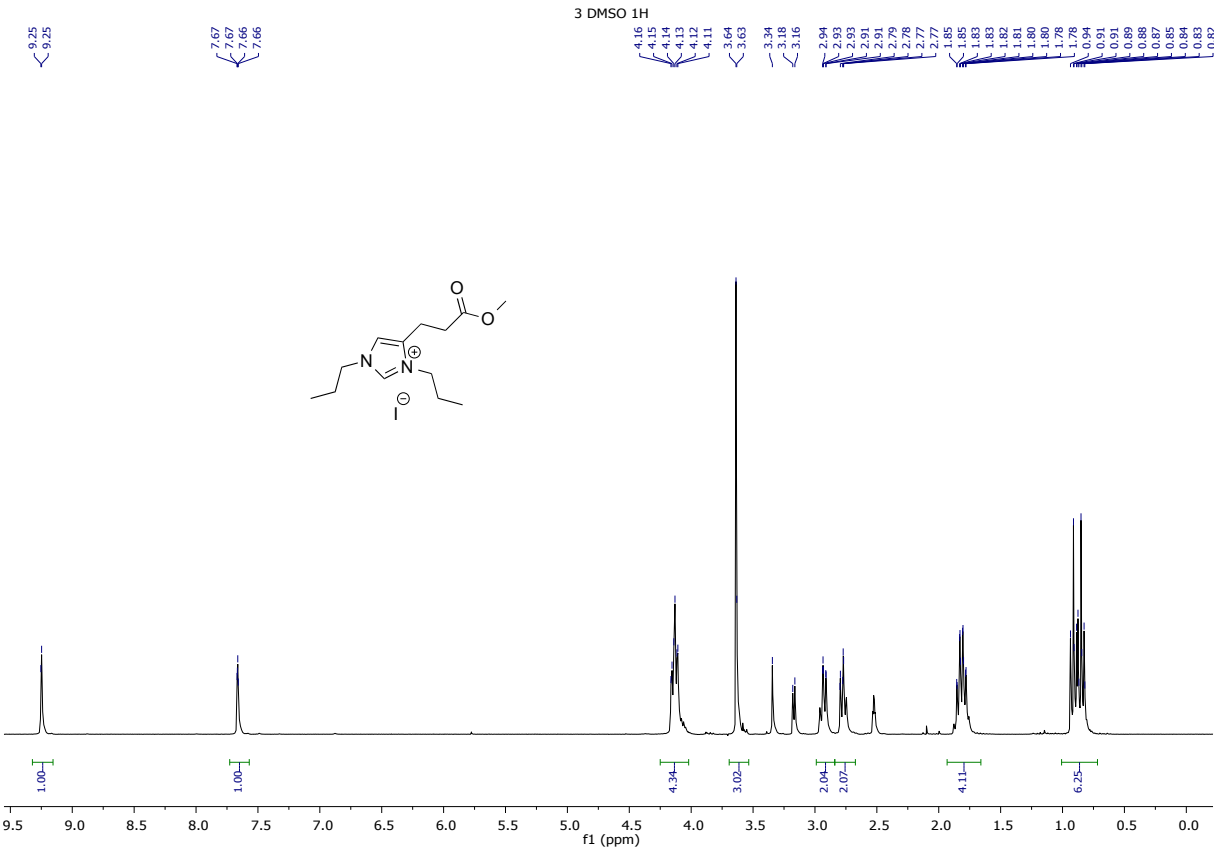
^{13}C NMR of compound **1**



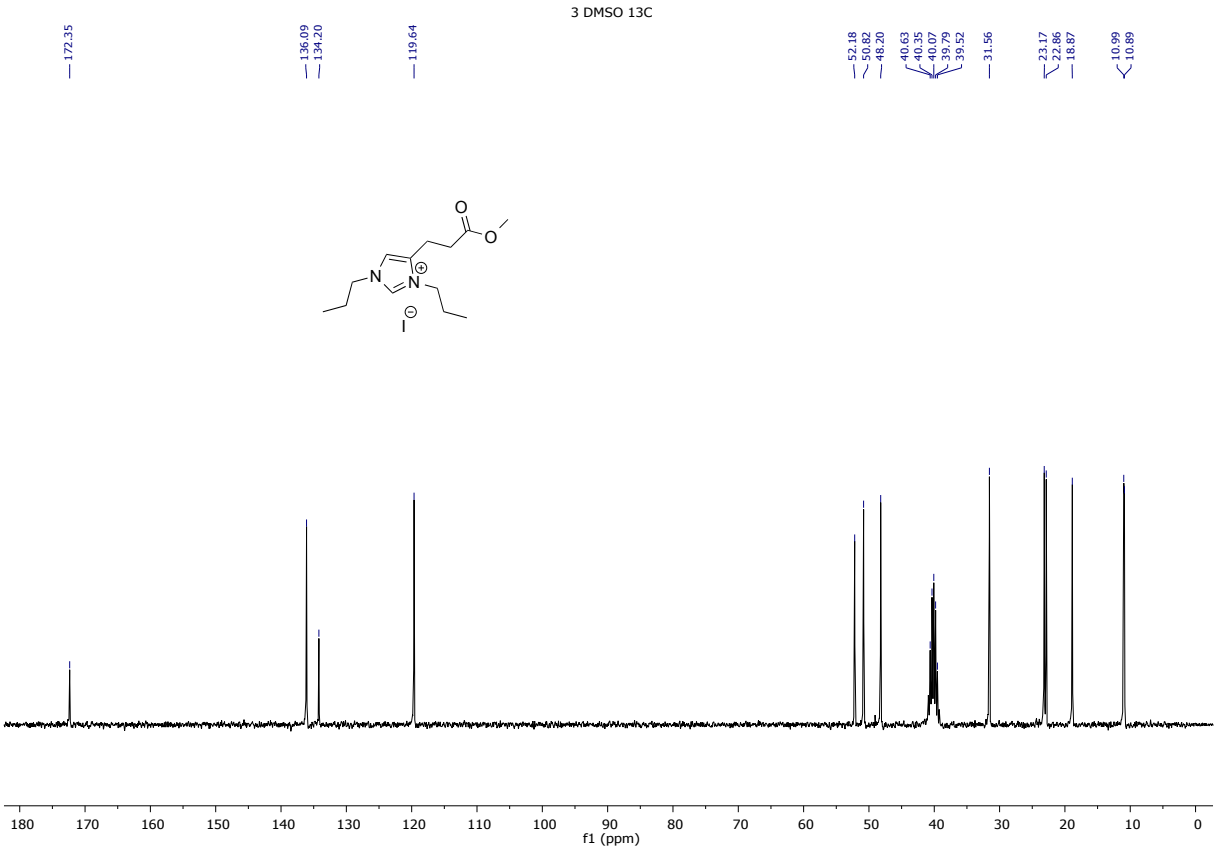
^{1}H NMR of compound **2**



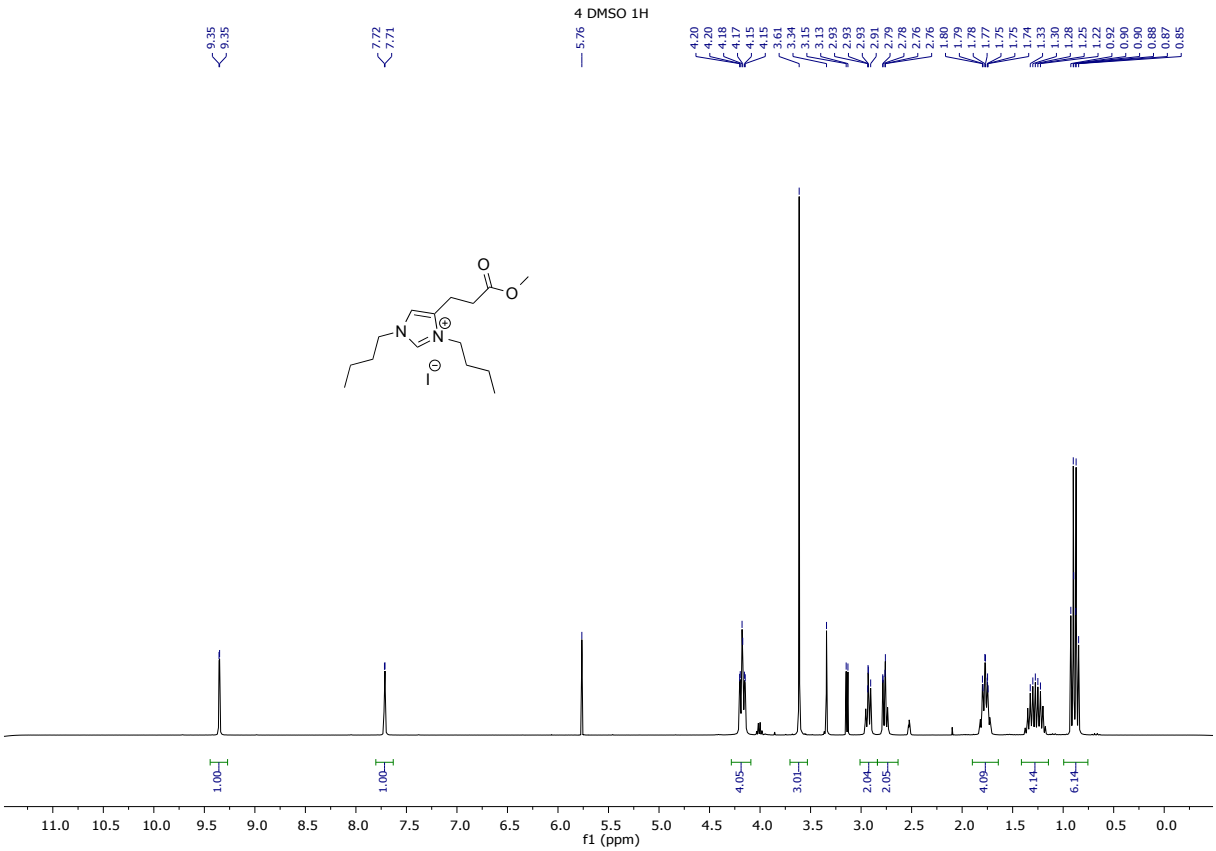
^{13}C NMR of compound **2**



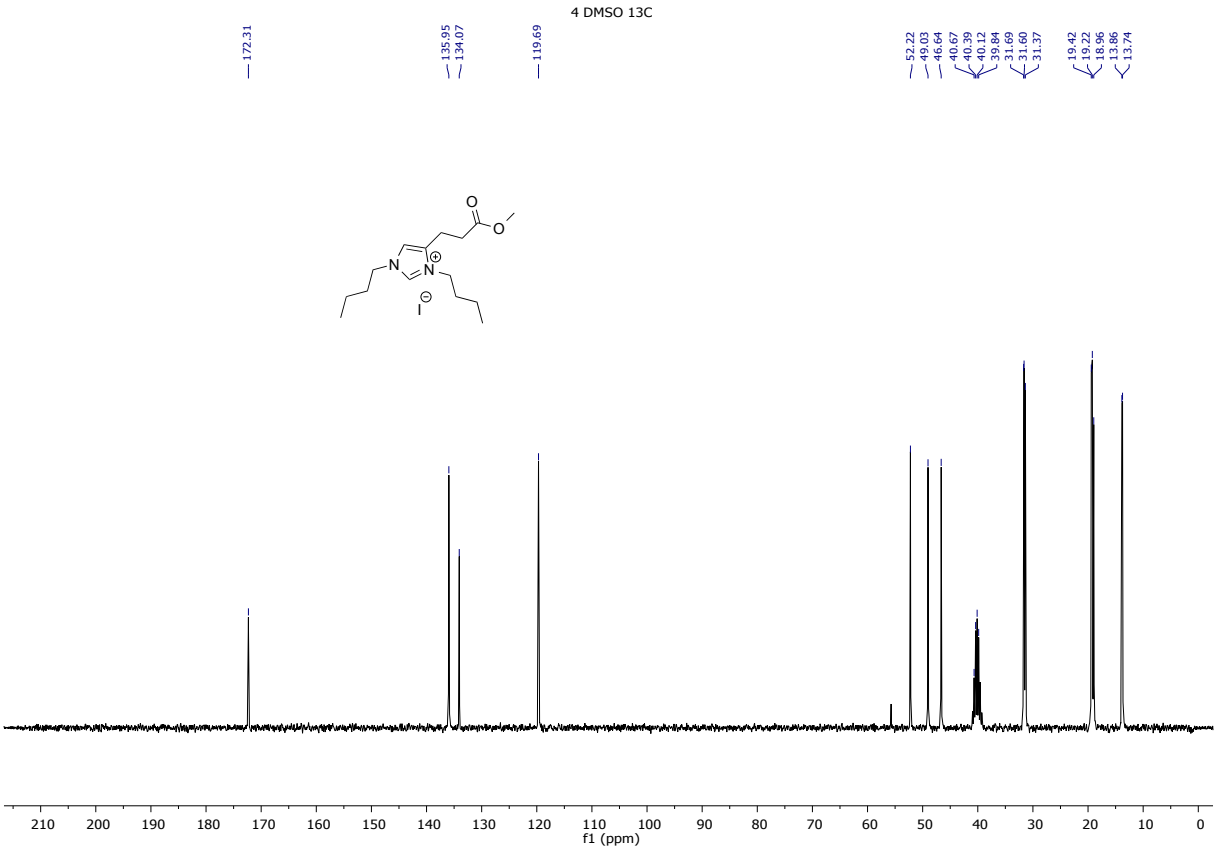
^{1}H NMR of compound **3**



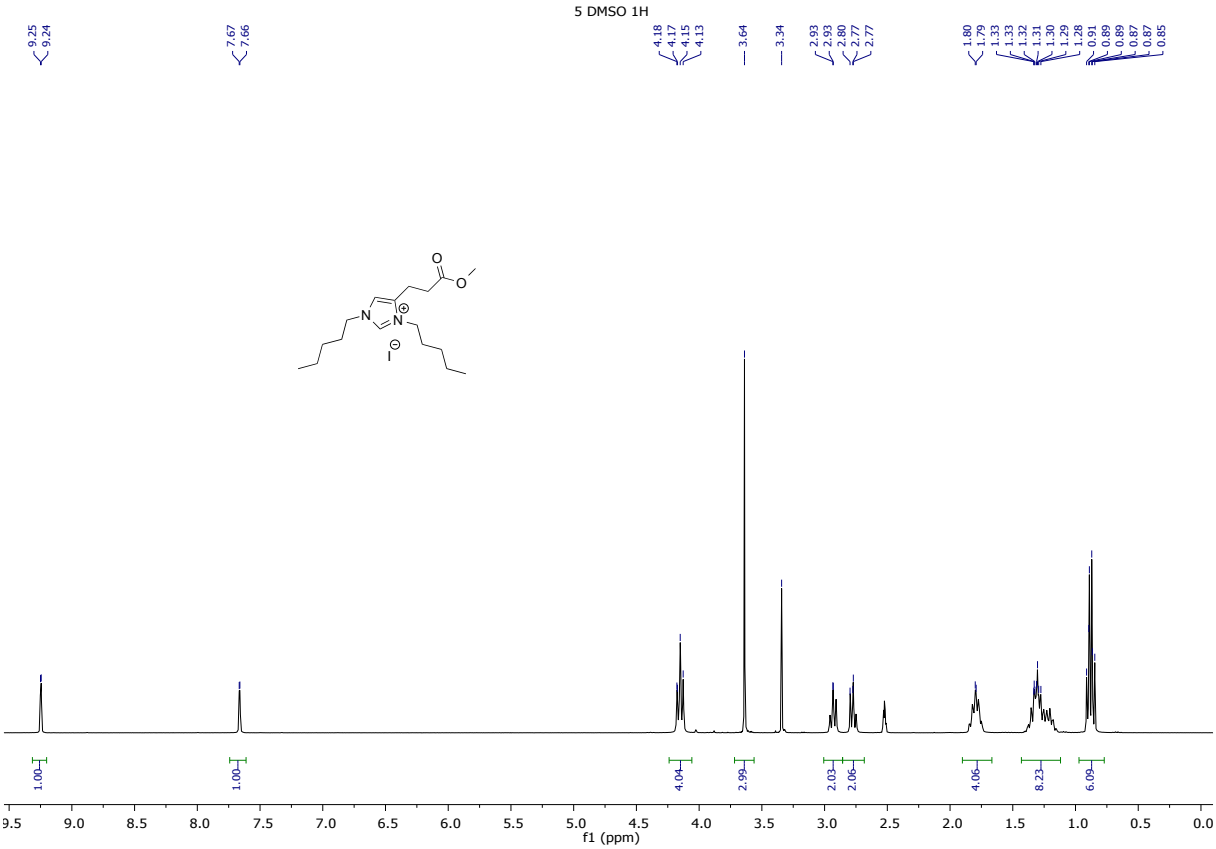
^{13}C NMR of compound **3**



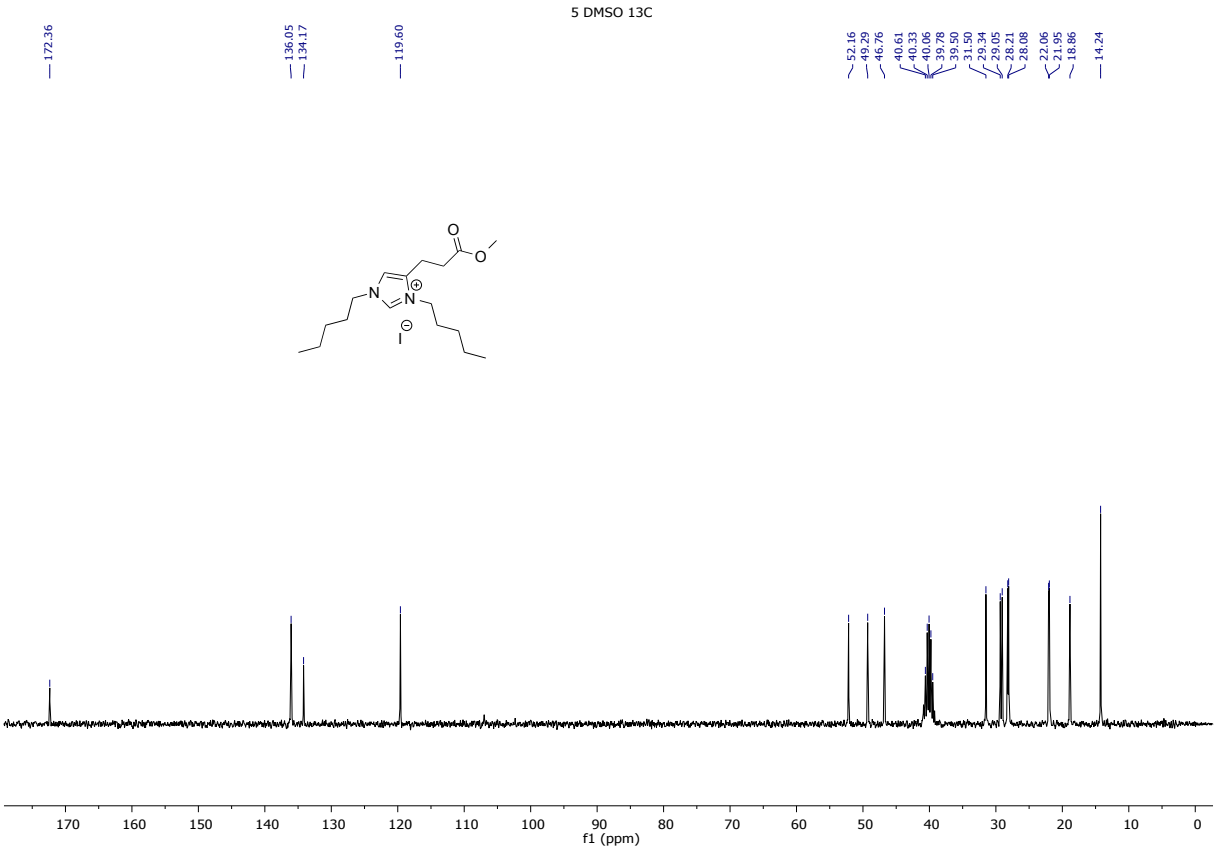
^{1}H NMR of compound **4**



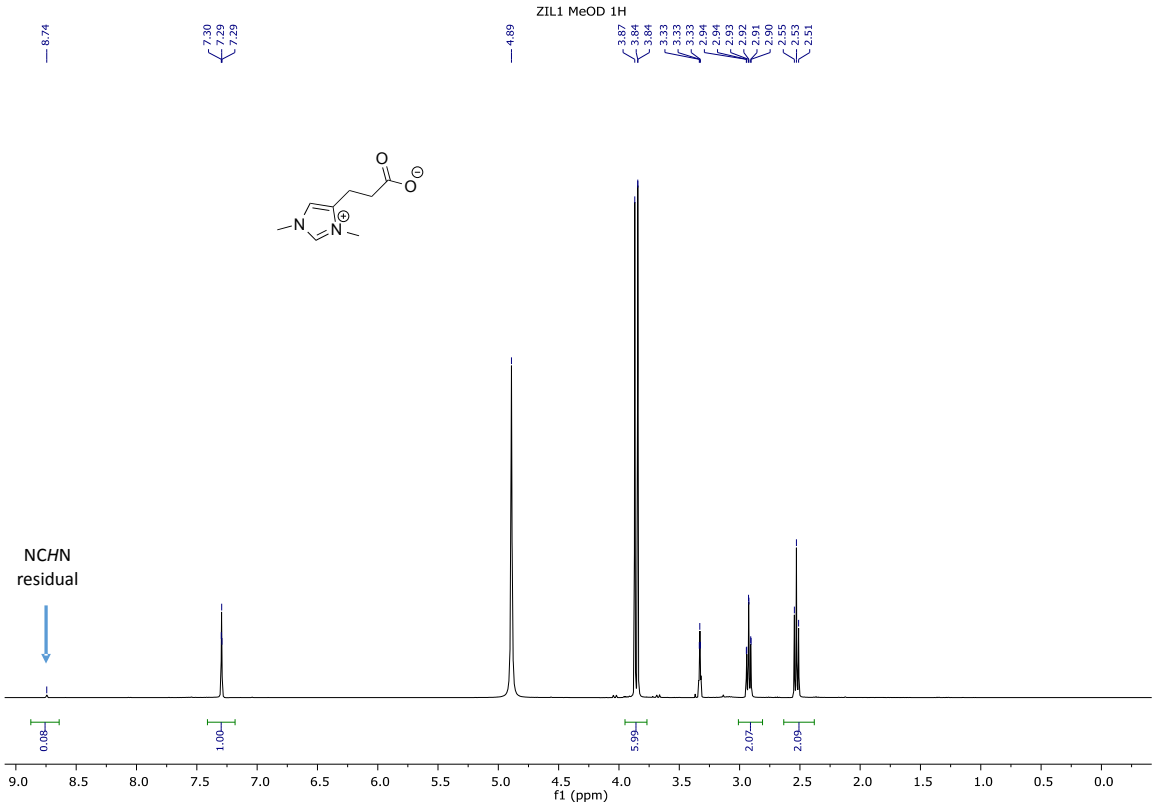
^{13}C NMR of compound **4**



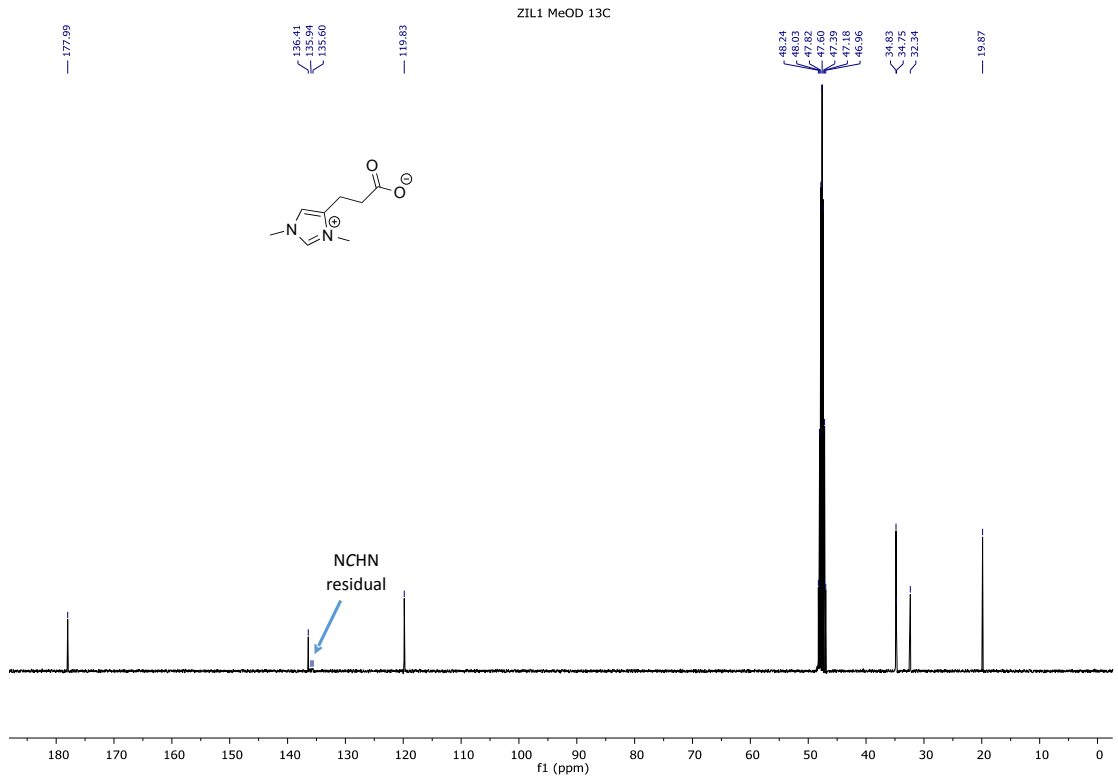
^{1}H NMR of compound **5**



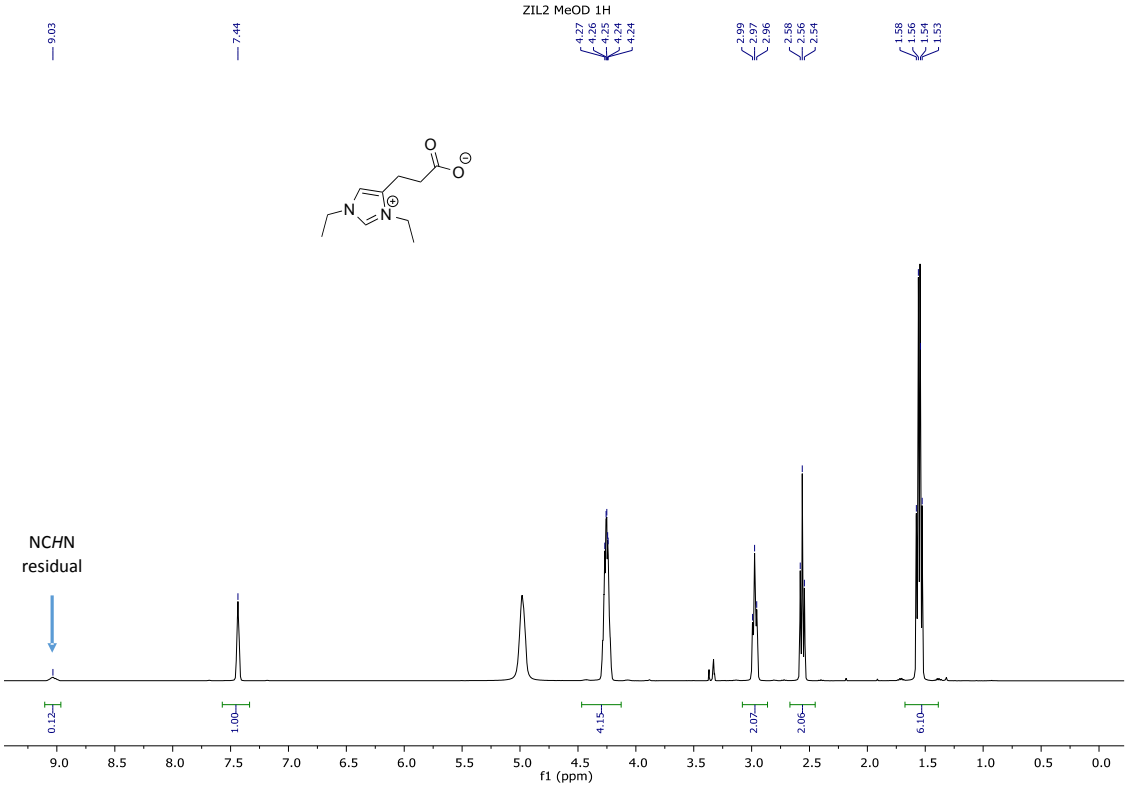
^{13}C NMR of compound **5**



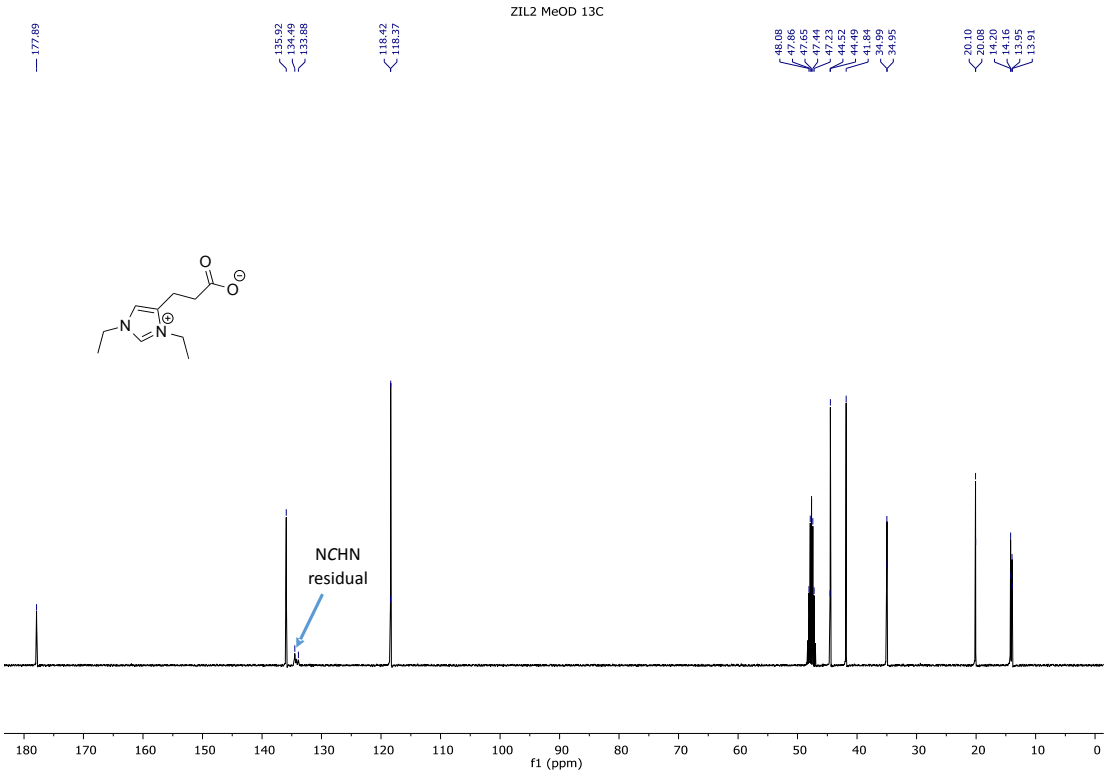
^{1}H NMR of compound **ZIL1**



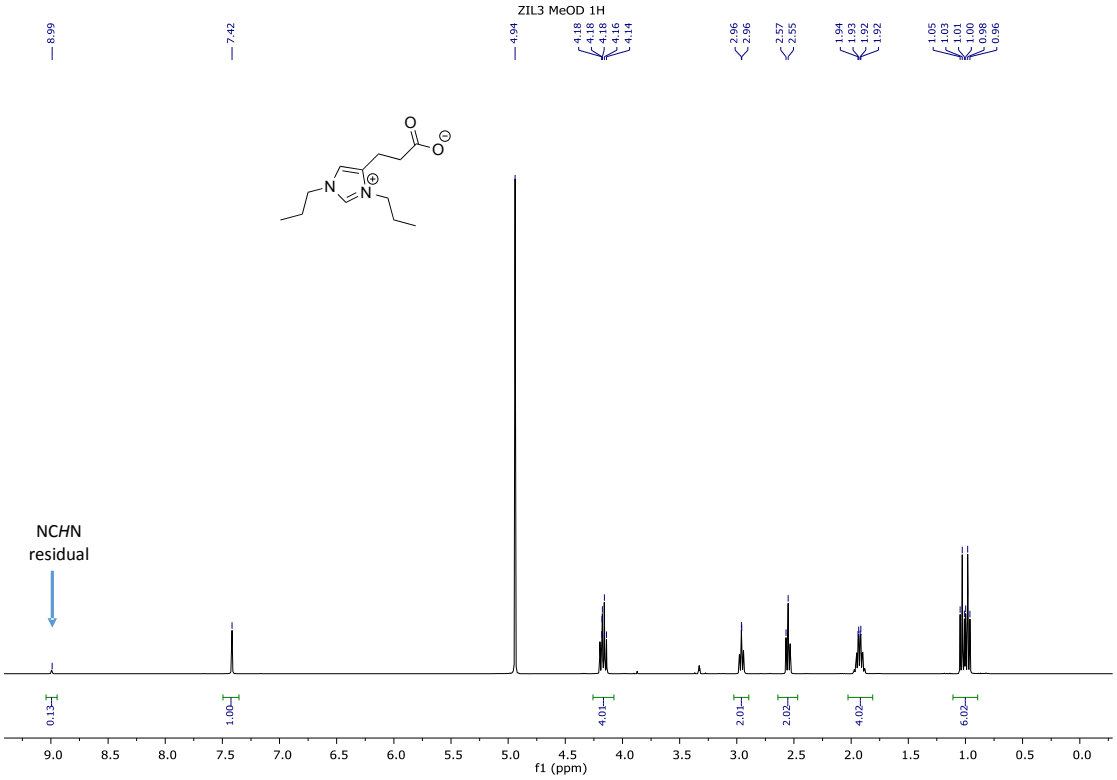
^{13}C NMR of compound **ZIL1**



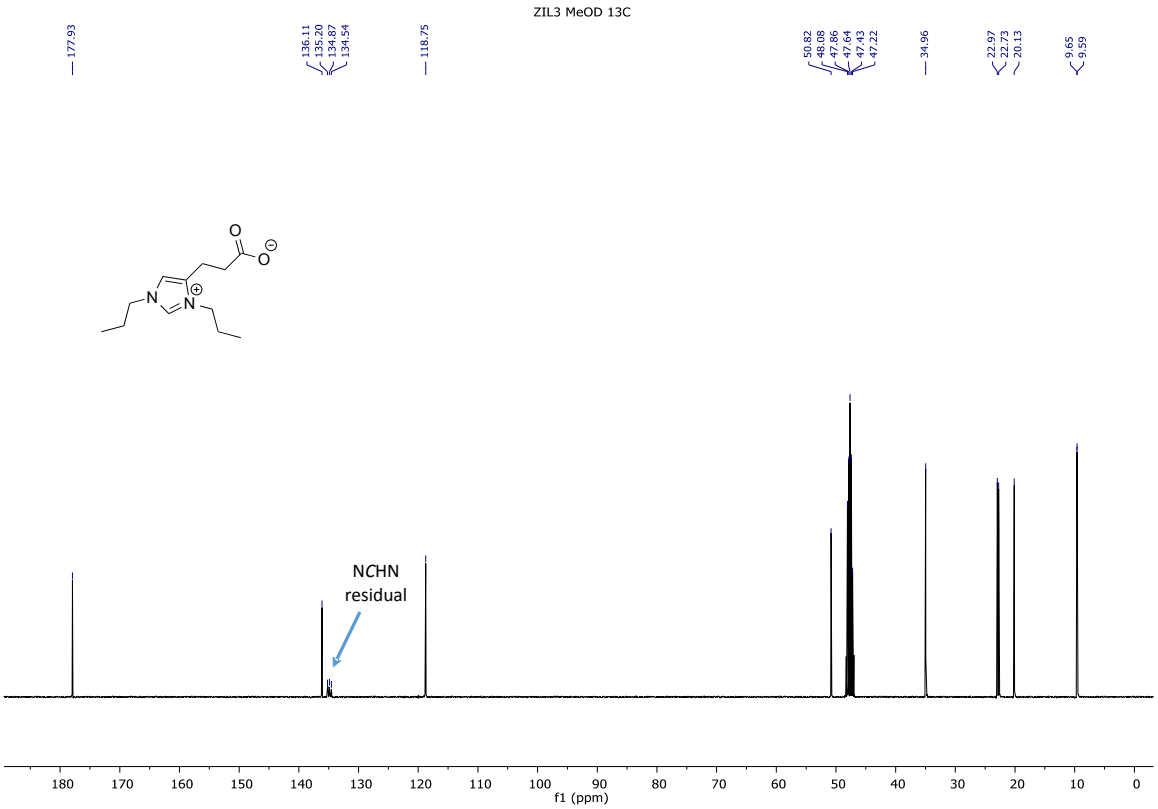
^{1}H NMR of compound **ZIL2**



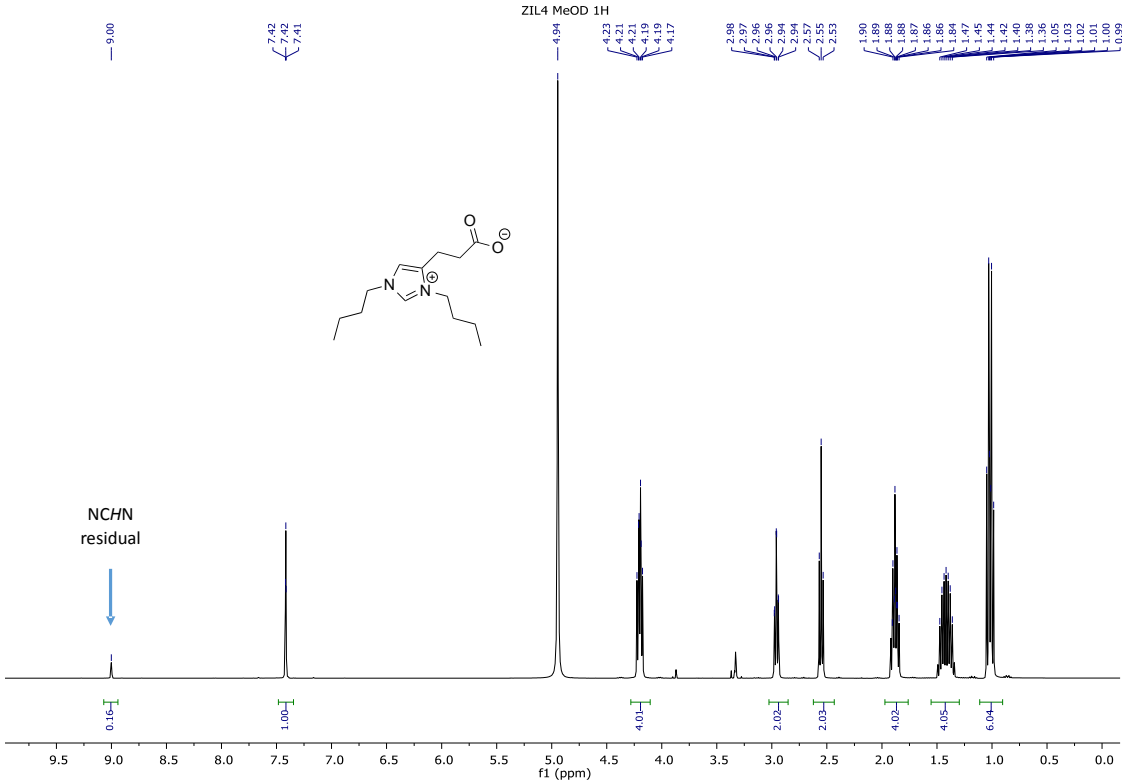
^{13}C NMR of compound **ZIL2**



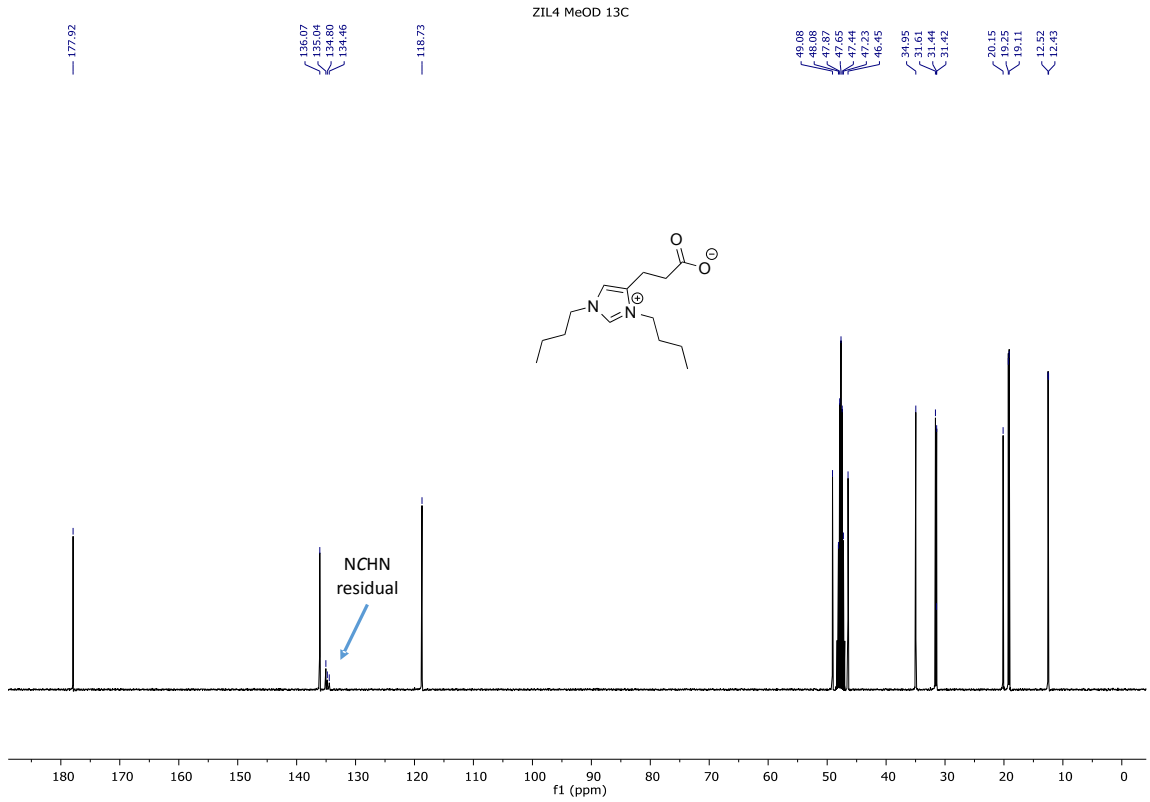
^{1}H NMR of compound **ZIL3**



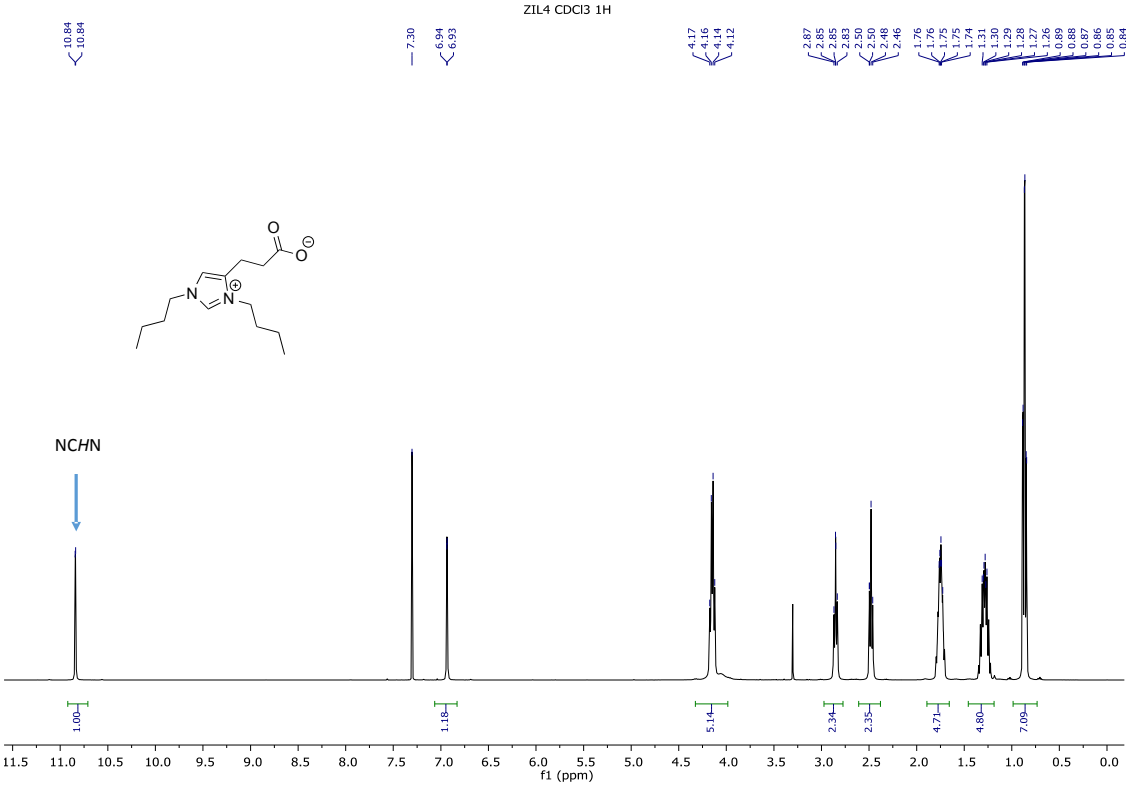
^{13}C NMR of compound **ZIL3**



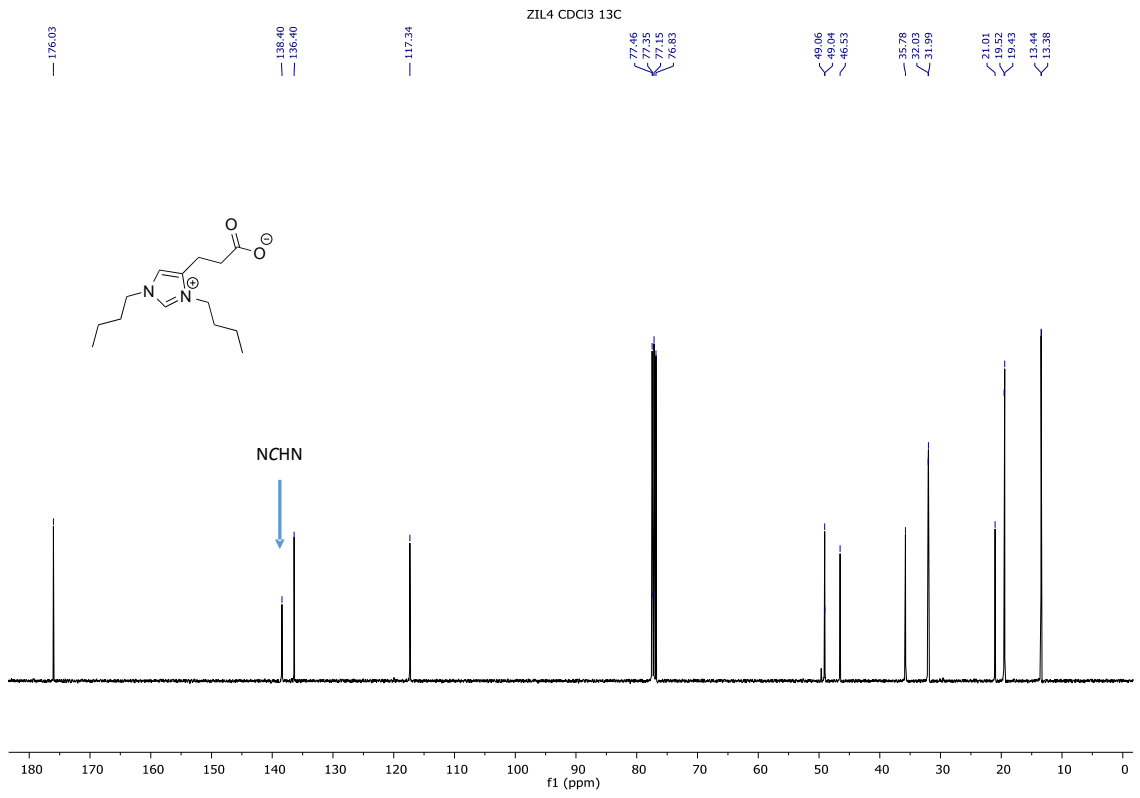
^{1}H NMR of compound **ZIL4** (MeOD)



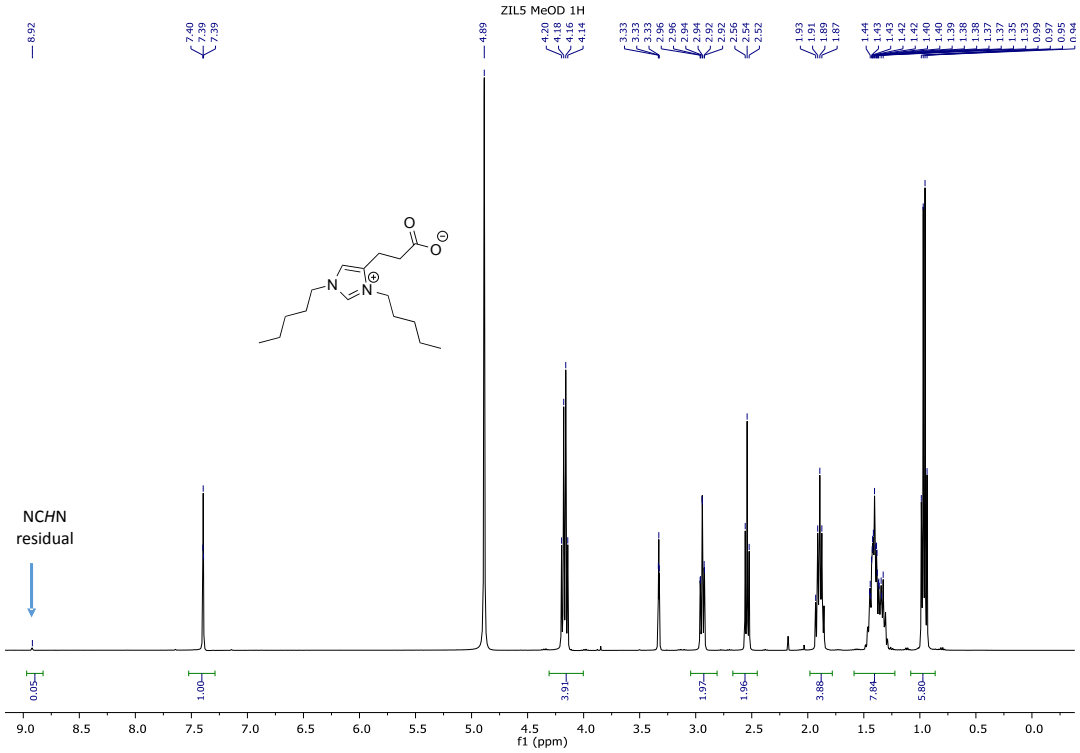
^{13}C NMR of compound **ZIL4** (MeOD)



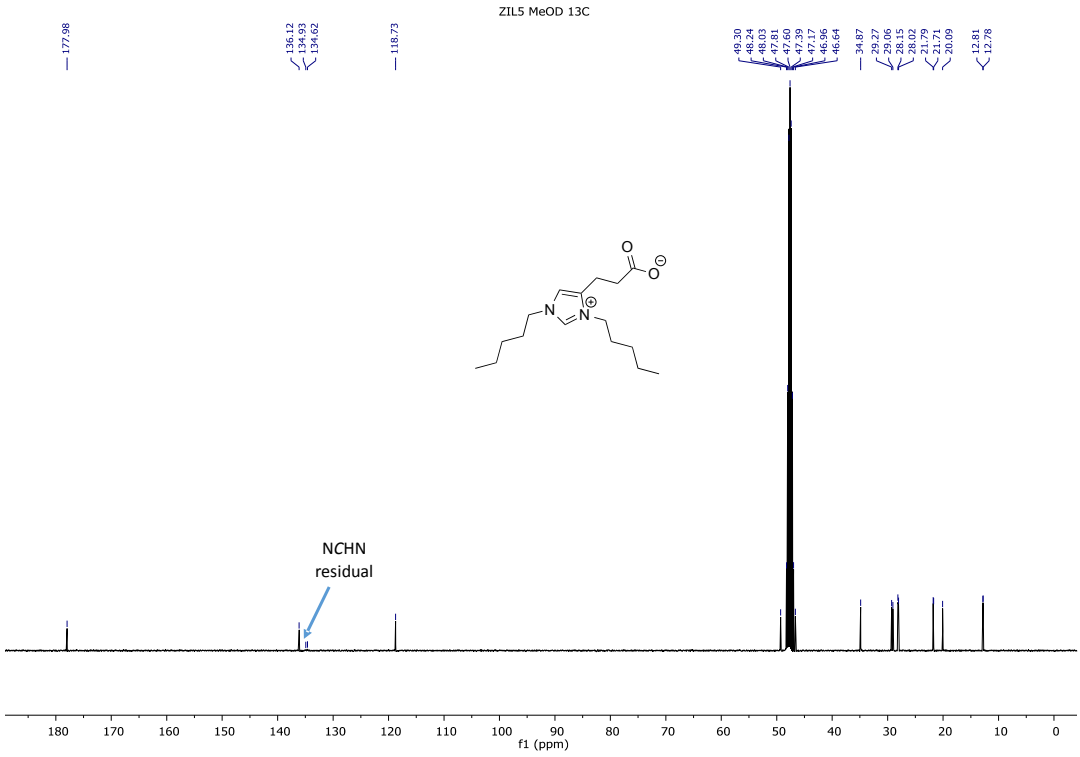
^{1}H NMR of compound **ZIL4** ($CDCl_3$)



^{13}C NMR of compound **ZIL4** ($CDCl_3$)



^{1}H NMR of compound **ZIL5**



^{13}C NMR of compound **ZIL5**