Electronic Supporting Information (ESI) for:

The facile alkylation and iodination of imidazol(in)ium salts in the presence of cesium carbonate

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1. Experimental procedures

1.1 General information

All the syntheses were carried out under a normal atmosphere with analytical grade reagents and solvents used without any further purification. The imidazol(in)ium salts used as starting materials were prepared according to published procedures.[1] All the other chemicals were purchased from Aldrich or TCI. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Electrospray mass spectra were obtained using a Bruker Daltonics SolariX XR 9.4 T instrument. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

1.2 Alkylation reactions

1.2.1 Typical procedure for C2 alkylation reactions

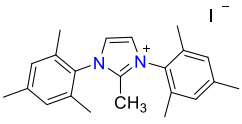
A 25 mL Schlenk tube equipped with a magnetic stirring bar and a septum was loaded with an imidazol(in)ium salt (1 mmol), Cs_2CO_3 (500 mg, 1.5 mmol), an alkyl halide (8 mmol), and acetonitrile (5 mL). The suspension was stirred in an oil bath set at a given temperature for 1–90 h (see Tables 1, 2, and Scheme 2 for details). After cooling to room temperature, the volatiles were removed on a rotary evaporator and the residue was taken up with dichloromethane (15 mL) and a 1 M aqueous NH_4Cl solution (30 mL). The biphasic mixture was vigorously stirred for 30 min at room temperature. It was then transferred into a separatory funnel and the Schlenk tube was rinsed with deionized water (15 mL). The aqueous phase was separated and extracted with dichloromethane (3 × 15 mL). The organic phases were combined and washed with brine (15 mL). After drying over $MgSO_4$, the solvent was evaporated and the remaining solid was recrystallized from isopropanol.

1.2.2 Typical procedure for C2α alkylation reactions

A 25 mL Schlenk tube equipped with a magnetic stirring bar and a septum was loaded with a C2-alkylated imidazolium iodide (0.2 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), an alkyl halide (1.6 mmol, 8 equiv or 4 mmol, 20 equiv), and acetonitrile (3 mL). The suspension was stirred in an oil bath at 80 °C for 24 h. After cooling to room temperature, the volatiles were removed on a rotary evaporator and the residue was taken up with dichloromethane (15 mL) and deionized water (15 mL). The biphasic mixture was transferred into a separatory funnel. The aqueous phase was separated and extracted with dichloromethane (3 × 15 mL). The organic phases were combined and washed with brine (15 mL). After drying over $MgSO_4$, the solvent was evaporated and the remaining solid was recrystallized from isopropanol.

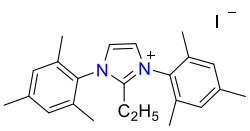
1.2.3 Analytical data

1,3-Dimesityl-2-methylimidazolium iodide (1a)



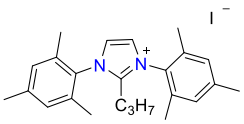
Pale yellow powder (370 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 2H, NCH), 7.06 (s, 4H, *m*-CH_{ar} Mes), 2.34 (s, 6H, *p*-CH_3 Mes), 2.19 (s, 3H, $NCCH_3$), 2.05 ppm (s, 12H, *o*-CH_3 Mes). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.8 (C^2 Im), 142.0 (*p*-C Mes), 134.1 (*o*-C Mes), 130.4 (*i*-C Mes), 129.6 (*m*-CH Mes), 124.9 ($CH^{4,5}$ Im), 21.2 (*p*-CH_3), 17.7 (*o*-CH_3), 10.5 ppm (CH_3). These data matched those reported in the literature.[2,3] Elemental analysis calcd for $C_{22}H_{27}IN_2$: C 59.20, H 6.10, N 6.28; found: C 58.38, H 6.10, N 6.36.

2-Ethyl-1,3-dimesitylimidazolium iodide (1b)



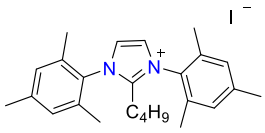
Pale brown powder (364 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 2H, NCH), 7.04 (s, 4H, *m*-CH_{ar} Mes), 2.48 (q, J = 7.6 Hz, 2H, CH_2CH$_3$), 2.31 (s, 6H, *p*-CH_3 Mes), 2.04 (s, 12H, *o*-CH_3 Mes), 0.83 (t, J = 7.7 Hz, 3H, CH$_2$CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.2 (C^2 Im), 141.9 (*p*-C Mes), 133.9 (*o*-C Mes), 130.3 (*i*-C Mes), 129.5 (*m*-CH Mes), 125.2 (CH^{4,5} Im), 21.1 (*p*-CH_3), 18.0 (*C*H$_2$CH$_3$), 17.6 (*o*-CH_3), 10.4 (CH$_2$*C*H$_3$) ppm. Elemental analysis calcd for $C_{23}H_{29}IN_2$: C 60.00, H 6.35, N 6.08; found: C 60.17, H 6.29, N 6.28.

1,3-Dimesityl-2-propylimidazolium iodide (1c)



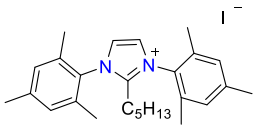
Pale brown powder (382 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 2H, NCH), 7.04 (s, 4H, *m*-CH_{ar} Mes), 2.40 – 2.33 (m, 2H, CH_2CH$_2$CH$_3$), 2.32 (s, 6H, *p*-CH_3 Mes), 2.04 (s, 12H, *o*-CH_3 Mes), 1.18 (h, J = 7.4 Hz, 2H, CH$_2$CH_2CH$_3$), 0.66 (t, J = 7.3 Hz, 3H, CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.3 (C^2 Im), 141.9 (*p*-C Mes), 133.9 (*o*-C Mes), 130.4 (*i*-C Mes), 129.6 (*m*-CH Mes), 125.3 (CH^{4,5} Im), 26.1 (*C*H$_2$CH$_2$), 21.1 (*p*-CH_3), 19.5 (CH$_2$*C*H$_2$), 17.7 (*o*-CH_3), 14.1 (CH$_2$*C*H$_3$) ppm. Elemental analysis calcd for $C_{24}H_{31}IN_2$: C 60.76, H 6.59, N 5.90; found C 60.01, H 6.85, N 5.75.

2-Butyl-1,3-dimesitylimidazolium iodide (1d)



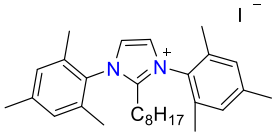
Microcrystalline pale brown powder (330 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 2H, NCH), 7.10 (s, 4H, *m*-CH_{ar} Mes), 2.45 – 2.39 (m, 2H, CH_2(CH$_2$)$_2$CH$_3$), 2.38 (s, 6H, *p*-CH_3 Mes), 2.09 (s, 12H, *o*-CH_3 Mes), 1.22 – 1.10 (m, 2H, CH$_2$CH_2CH$_2$CH$_3$), 1.06 (h, J = 7.1 Hz, 2H, CH$_2$CH$_2$CH_2CH$_3$), 0.59 ppm (t, J = 7.2 Hz, 3H, CH$_2$(CH$_2$)$_2$CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.4 (C^2 Im), 142.1 (*p*-C Mes), 134.1 (*o*-C Mes), 130.5 (*i*-C Mes), 129.8 (*m*-CH Mes), 125.7 (CH^{4,5} Im), 27.8 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 23.9 (*C*H$_2$CH$_2$CH$_3$), 22.3 (*C*H$_2$CH$_3$), 21.3 (*p*-CH_3), 17.9 (*o*-CH_3), 13.0 (CH$_2$*C*H$_3$) ppm. Elemental analysis calcd for $C_{25}H_{33}IN_2$: C 61.47, H 6.81, N 5.74; found C 60.61, H 6.82, N 5.51.

1,3-Dimesityl-2-pentylimidazolium iodide (1e)



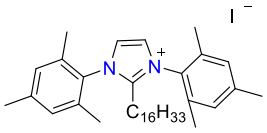
Pale brown powder (377 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 2H, NCH), 7.07 (s, 4H, *m*-CH_{ar} Mes), 2.39 (d, J = 8.1 Hz, 2H, CH_2(CH$_2$)$_3$CH$_3$), 2.35 (s, 6H, *p*-CH_3 Mes), 2.07 (s, 12H, *o*-CH_3 Mes), 1.16 (p, J = 6.8 Hz, 2H, CH$_2$CH_2(CH$_2$)$_2$CH$_3$), 1.05 – 0.85 (m, 4H, CH$_2$CH$_2$(CH_2)$_2$CH$_3$), 0.61 (t, J = 7.1 Hz, 3H, (CH$_2$)$_4$CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.4 (C^2 Im), 142.0 (*p*-C Mes), 134.0 (*o*-C Mes), 130.4 (*i*-C Mes), 129.7 (*m*-CH Mes), 125.5 (CH^{4,5} Im), 30.9 (*C*H$_2$(CH$_2$)$_3$CH$_3$), 25.3 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 24.0 (*C*H$_2$CH$_2$CH$_3$), 21.3 (*C*H$_2$CH$_3$), 21.2 (*p*-CH_3), 17.8 (*o*-CH_3), 13.2 (CH$_2$*C*H$_3$) ppm. Elemental analysis calcd for $C_{26}H_{35}IN_2$: C 62.15, H 7.02, N 5.58; found C 61.71, H 7.03, N 6.04.

1,3-Dimesityl-2-octylimidazolium iodide (1f)



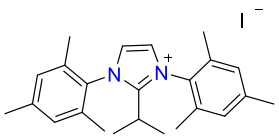
Pale orange oil (408 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 2H, NCH), 7.10 (s, 4H, *m*-CH_{ar} Mes), 2.39 (s, 8H, *p*-CH_3 Mes + $CH_2(CH_2)_6CH_3$), 2.11 (s, 12H, *o*-CH_3 Mes), 1.24 – 1.11 (m, 4H, $CH_2(CH_2)_2(CH_2)_4CH_3$), 1.11 – 0.87 (m, 8H, $(CH_2)_3(CH_2)_4CH_3$), 0.82 ppm (t, J = 7.2 Hz, 3H, $(CH_2)_7CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.2 (C^2 Im), 142.1 (*p*-C Mes), 134.2 (*o*-C Mes), 130.5 (*i*-C Mes), 129.9 (*m*-CH Mes), 125.9 ($CH^{4,5}$ Im), 31.6 ($CH_2(CH_2)_6CH_3$), 28.9 (CH_2 octyl), 28.5 (CH_2 octyl), 28.2 (CH_2 octyl), 25.7 (CH_2 octyl), 24.0 (CH_2 octyl), 22.6 (CH_2 octyl), 21.3 (*p*-CH_3), 17.9 (*o*-CH_3), 14.1 (CH_2CH_3) ppm. Highly viscous oil unsuitable for elemental analysis.

2-Hexadecyl-1,3-dimesitylimidazolium iodide (1g)



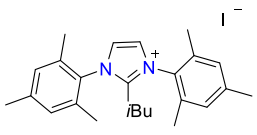
Microcrystalline white powder (208 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 2H, NCH), 7.10 (s, 4H, *m*-CH_{ar} Mes), 2.40 (s, 8H, *p*-CH_3 Mes + $CH_2(CH_2)_{14}CH_3$), 2.11 (s, 12H, *o*-CH_3 Mes), 1.32 – 1.12 (m, 20H, $CH_2(CH_2)_{10}(CH_2)_4CH_3$), 1.09 – 0.90 (m, 8H, $CH_2(CH_2)_{10}(CH_2)_4CH_3$), 0.87 ppm (t, J = 6.9 Hz 3H, $(CH_2)_{15}CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.1 (C^2 Im), 142.1 (*p*-C Mes), 134.2 (*o*-C Mes), 130.5 (*i*-C Mes), 129.9 (*m*-CH Mes), 126.0 ($CH^{4,5}$ Im), 32.1 ($CH_2(CH_2)_{14}CH_3$), 29.82 (CH_2), 29.79 (CH_2), 29.76 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 25.7 (CH_2), 24.0 (CH_2), 22.8 (CH_2), 21.4 (*p*-CH_3), 17.9 (*o*-CH_3), 14.3 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{37}H_{57}IN_2$: C 67.66, H 8.75, N 4.27; found C 67.11, H 8.72, N 4.87.

2-Isopropyl 1,3-dimesityl-imidazolium iodide (1h)



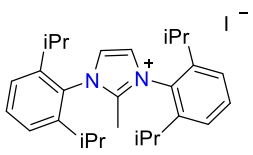
Orange oil (250 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (s, 2H, NCH), 7.03 (s, 4H, *m*-CH_{ar} Mes), 2.89 (hept, J = 7.2 Hz, 1H, $CH(CH_3)_2$), 2.31 (s, 6H, *p*-CH_3 Mes), 2.04 (s, 12H, *o*-CH_3 Mes), 0.99 (d, J = 7.3 Hz, 6H, $CH(CH_3)_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.9 (C^2 Im), 141.9 (*p*-C Mes), 134.2 (*o*-C Mes), 130.2 (*i*-C Mes), 130.0 (*m*-CH Mes), 125.7 ($CH^{4,5}$ Im), 26.5 ($CH(CH_3)_2$), 21.1 (*p*-CH_3), 18.8 ($CH(CH_3)_2$), 17.7 (*o*-CH_3) ppm. Highly viscous oil unsuitable for elemental analysis.

2-Isobutyl-1,3-Dimesitylimidazolium iodide (1j)



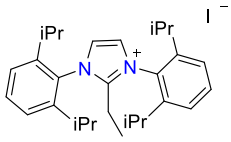
Pale yellow powder (392 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 2H, NCH), 7.10 (s, 4H, *m*-CH_{ar} Mes), 2.39 (s, 6H, *p*-CH_3 Mes), 2.36 (d, J = 6.5 Hz, 2H, CH_2CH), 2.12 (s, 12H, *o*-CH_3 Mes), 1.51 (h, J = 13.7, 6.9 Hz, 1H, CH iBu), 0.70 ppm (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.7 (C^2 Im), 142.0 (*p*-C Mes), 134.2 (*o*-C Mes), 130.6 (*i*-C Mes), 130.0 (*m*-CH Mes), 126.2 ($CH^{4,5}$ Im), 33.6 (CH_2CH), 26.9 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$), 21.3 (*p*-CH_3), 18.1 (*o*-CH_3) ppm. Elemental analysis calcd for $C_{25}H_{33}IN_2$: C 61.47, H 6.81, N 5.74; found C 60.00, H 6.78, N 5.81.

1,3-Bis(2,6-diisopropylphenyl)-2-methylimidazolium iodide (2a)



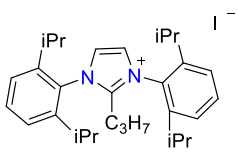
White powder (448 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 2H, NCH), 7.61 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.38 (d, J = 7.8 Hz, 4H, m-CH_{ar} Dip), 2.28 (hept, J = 6.9 Hz, 4H, CH iPr), 2.11 (s, 3H, CCH_3), 1.27 (d, J = 6.7 Hz, 12H, CH_3 iPr), 1.18 ppm (d, J = 6.8 Hz, 12H, CH_3 iPr). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.3 (C^2 Im), 145.0 (o-C Dip), 132.7 (p-CH Dip), 129.0 (i-C Dip), 126.5 ($CH^{4,5}$ Im), 125.5 (m-CH Dip), 29.2 ($CH(CH_3)_2$ Dip), 24.7 (CH_3 Dip), 23.5 (CH_3 Dip), 11.1 (CH_3) ppm. These data matched those reported in the literature.[2] Elemental analysis calcd for $C_{28}H_{39}IN_2$: C 63.39, H 7.41, N 5.28; found C 61.72, H 7.23, N 5.72.

1,3-Bis(2,6-diisopropylphenyl)-2-ethylimidazolium iodide (2b)



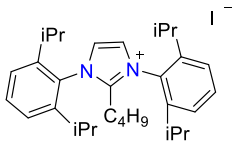
Beige powder (441 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 2H, NCH), 7.58 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.34 (d, J = 7.8 Hz, 4H, m-CH_{ar} Dip), 2.46 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.21 (hept, J = 6.8 Hz, 4H, CH iPr), 1.22 (d, J = 3.3 Hz, 12H, CH_3 iPr), 1.20 (d, J = 3.2 Hz, 12H, CH_3 iPr), 0.82 ppm (t, J = 7.6 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.8 (C^2 Im), 144.9 (o-C Dip), 132.6 (p-CH Dip), 128.9 (i-C Dip), 126.4 ($CH^{4,5}$ Im), 125.3 (m-CH Dip), 29.2 ($CH(CH_3)_2$ Dip), 25.7 (CH_3 Dip), 22.8 (CH_3 Dip), 18.1 (CH_2), 10.3 (CH_3) ppm. Elemental analysis calcd for $C_{29}H_{41}IN_2$: C 63.96, H 7.59, N 5.14; found C 63.74, H 7.58, N 5.64.

1,3-Bis(2,6-diisopropylphenyl)-2-propylimidazolium iodide (2c)



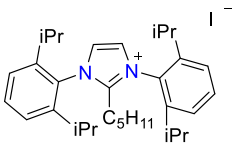
Pale green powder (443 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 2H, NCH), 7.62 (t, J = 7.9 Hz, 2H, p-CH_{ar} Dip), 7.37 (d, J = 7.9 Hz, 4H, m-CH_{ar} Dip), 2.38 – 2.27 (m, 2H, $CH_2CH_2CH_3$), 2.22 (h, J = 6.8 Hz, 4H, CH iPr), 1.24 (d, J = 1.9 Hz, 12H, CH_3 iPr), 1.23 (d, J = 2.0 Hz, 12H, CH_3 iPr), 1.20 – 1.10 (m, 2H, $CH_2CH_2CH_3$), 0.66 ppm (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.9 (C^2 Im), 144.9 (o-C Dip), 132.7 (p-C Dip), 129.0 (i-CH Dip), 126.7 ($CH^{4,5}$ Im), 125.4 (m-CH Dip), 29.3 ($CH(CH_3)_2$ Dip), 26.4 ($CH_2CH_2CH_3$), 25.8 (CH_3 Dip), 22.8 (CH_3 Dip), 19.5 (CH_2CH_3), 14.2 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{30}H_{43}IN_2$: C 64.51, H 7.76, N 5.02; found C 64.20, H 7.77, N 5.55.

2-Butyl 1,3-bis(2,6-diisopropylphenyl)imidazolium iodide (2d)



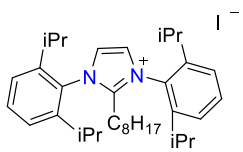
Pale purple powder (412 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 2H, NCH), 7.64 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.40 (d, J = 7.9 Hz, 4H, m-CH_{ar} Dip), 2.40 – 2.31 (m, 2H, $CH_2(CH_2)_2CH_3$), 2.26 (h, J = 6.9 Hz, 4H, CH iPr), 1.34 – 1.11 (m, 24H, CH_3 iPr), 1.18 – 1.08 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.03 (h, J = 7.1 Hz, 2H, $(CH_2)_2CH_2CH_3$), 0.58 ppm (t, J = 7.2 Hz, 3H, $(CH_2)_3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.9 (C^2 Im), 145.0 (o-C Dip), 132.6 (p-CH Dip), 129.0 (i-C Dip), 126.8 ($CH^{4,5}$ Im), 125.3 (m-CH Dip), 29.3 ($CH(CH_3)_2$ Dip), 27.8 (CH_2 butyl), 25.8 (CH_3 Dip), 24.0 (CH_2 butyl), 22.8 (CH_3 Dip), 22.4 (CH_2 butyl), 12.9 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{31}H_{45}IN_2$: C 65.02, H 7.92, N 4.89; found C 66.57, H 8.13, N 5.50.

1,3-Bis(2,6-diisopropylphenyl)-2-pentylimidazolium iodide (2e)



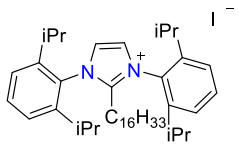
Pale beige powder (452 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 2H, NCH), 7.63 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.39 (d, J = 7.8 Hz, 4H, m-CH_{ar} Dip), 2.36 – 2.30 (m, 2H, CH_2(CH_2)$_3$$CH_3$), 2.25 (h, J = 6.8 Hz, 4H, CH iPr), 1.26 (t, J = 6.9 Hz, 24H, CH_3 iPr), 1.19 – 1.07 (m, 2H, CH_2CH_2(CH_2)$_2$$CH_3$), 1.02 – 0.93 (m, 4H, ($CH_2$)$_2$(C$H_2$)$_2$$CH_3$), 0.62 (t, J = 6.7 Hz, 3H, (CH_2)$_4$$CH_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.0 (C^2 Im), 145.1 (o-C Dip), 132.7 (p-CH Dip), 129.1 (i-C Dip), 126.8 ($CH^{4,5}$ Im), 125.4 (m-CH Dip), 31.3, 29.4 (CH(CH_3)$_2$ Dip), 25.9 (CH_2 pentyl), 25.5 (CH_3 Dip), 24.5 (CH_2 pentyl), 22.9 (CH_3 Dip), 21.6 (CH_2 pentyl), 13.3 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{32}H_{47}IN_2$: C 65.52, H 8.08, N 4.78; found C 66.05, H 8.29, N 4.60.

1,3-Bis(2,6-diisopropylphenyl)-2-octylimidazolium iodide (2f)



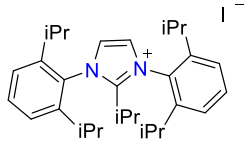
White powder (400 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 2H, NCH), 7.64 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.40 (d, J = 7.9 Hz, 4H, m-CH_{ar} Dip), 2.40 – 2.31 (m, 2H, CH_2(CH_2)$_6$$CH_3$), 2.27 (h, J = 6.9 Hz, 4H, CH iPr), 1.29 (d, J = 6.8 Hz, 12H, CH_3 iPr), 1.26 (d, J = 6.9 Hz, 12H, CH_3 iPr), 1.24 – 1.07 (m, 4H, CH_2(CH_2)$_2$(CH_2)$_4$$CH_3$), 1.08 – 0.83 (m, 8H, ($CH_2$)$_3$(C$H_2$)$_4$$CH_3$), 0.79 ppm (t, J = 7.2 Hz, 3H, (CH_2)$_7$$CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.9 (C^2 Im), 145.2 (o-C Dip), 132.7 (p-CH Dip), 129.2 (i-C Dip), 127.0 ($CH^{4,5}$ Im), 125.4 (m-CH Dip), 31.5 (CH_2 octyl), 29.4 (CH(CH_3)$_2$ Dip), 29.2 (CH_2 octyl), 28.5 (CH_2 octyl), 28.4 (CH_2 octyl), 25.9 (CH_2 octyl), 25.8 (CH_3 Dip), 24.5 (CH_2 octyl), 23.0 (CH_2 octyl), 22.5 (CH_3 Dip), 14.1 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{35}H_{53}IN_2$: C 66.86, H 8.50, N 4.46; found C 66.53, H 8.45, N 4.94.

1,3-Bis(2,6-diisopropylphenyl)-2-hexadecylimidazolium iodide (2g)



White powder (194 mg, 26% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 2H, NCH), 7.64 (t, J = 7.9 Hz, 2H, p-CH_{ar} Dip), 7.40 (d, J = 7.8 Hz, 4H, m-CH_{ar} Dip), 2.35 (t, J = 8.7 Hz, 2H, CH_2(CH_2)$_{14}$$CH_3$), 2.28 (p, J = 6.8 Hz, 4H, CH iPr), 1.30 (d, J = 6.7 Hz, 12H, CH_3 iPr), 1.28 – 0.90 (m, 40H, CH_3 iPr + CH_2(CH_2)$_{14}$$CH_3$), 0.87 ppm (t, J = 7.2 Hz, 3H, (CH_2)$_{15}$$CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.8 (C^2 Im), 145.2 (o-C Dip), 132.7 (p-CH Dip), 129.2 (i-C Dip), 127.2 ($CH^{4,5}$ Im), 125.4 (m-CH Dip), 32.1 (CH_2(CH_2)$_{14}$$CH_3$), 29.81 ($CH_2$), 29.78 ($CH_2$), 29.74 ($CH_2$), 29.68 ($CH_2$), 29.6 ($CH_2$), 29.49 ($CH_2$), 29.45 ($CH_2$), 29.40 (C$H$($CH_3$)$_2$ Dip), 29.2 (CH_2), 28.9 (CH_2), 28.4 (CH_2), 26.0 (CH_2), 25.8 (CH_3 Dip), 24.5 (CH_2), 23.0 (CH_2), 22.8 (CH_3 Dip), 14.3 (CH_2CH_3) ppm. Elemental analysis calcd for $C_{43}H_{69}IN_2$: C 69.70, H 9.39, N 3.78; found C 69.14, H 9.29, N 4.28.

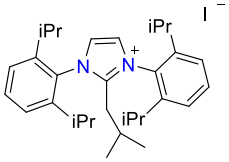
1,3-Bis(2,6-diisopropylphenyl)-2-isopropylimidazolium iodide (2h)



Pale yellow powder (485 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 2H, NCH), 7.63 (t, J = 7.8 Hz, 2H, p-CH_{ar} Dip), 7.39 (d, J = 7.8 Hz, 4H, m-CH_{ar} Dip), 3.02 (hept, J = 7.2 Hz, 1H, CH(CH_3)$_2$), 2.31 (hept, J = 6.9 Hz, 4H, CH iPr), 1.32 (d, J = 6.8 Hz, 12H, CH_3 Dip), 1.28 (d, J = 6.8 Hz, 12H, CH_3 Dip), 1.03 ppm (d, J = 7.2 Hz, 6H,

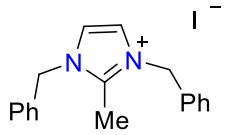
CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.2 (C^2 Im), 145.5 (*o*-C Dip), 132.7 (*p*-CH Dip), 129.7 (*i*-C Dip), 127.3 ($CH^{4,5}$ Im), 125.2 (*m*-CH Dip), 29.7 (*C*H(CH_3)$_2$ Dip), 26.5 (*C*H(CH_3)$_2$), 22.4 (CH_3 Dip), 19.4 (CH(*C*H_3)$_2$) ppm. Elemental analysis calcd for $C_{30}H_{43}IN_2$: C 64.51, H 7.76, N 5.02; found C 64.36, H 7.77, N 5.27.

1,3-Bis(2,6-diisopropylphenyl)-2-isobutylimidazolium iodide (2j)



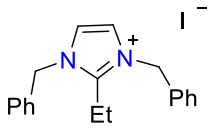
White powder (385 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.27 (s, 2H, NCH), 7.63 (t, *J* = 7.8 Hz, 2H, *p*-CH_{ar} Dip), 7.40 (d, *J* = 7.9 Hz, 4H, *m*-CH_{ar} Dip), 2.33 (d, *J* = 7.3 Hz, 2H, CH_2CH), 2.28 (q, *J* = 6.8 Hz, 4H, CH iPr), 1.50 (dq, *J* = 14.4, 7.2 Hz, 1H, CH(CH_3)$_2$), 1.29 (d, *J* = 6.9 Hz, 12H, CH_3 iPr), 1.26 (d, *J* = 6.8 Hz, 12H, CH_3 iPr), 0.67 (d, *J* = 6.6 Hz, 6H CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 147.6 (C^2 Im), 145.1 (*o*-C Dip), 132.7 (*p*-CH Dip), 129.3 (*i*-C Dip), 127.2 ($CH^{4,5}$ Im), 125.5 (*m*-CH Dip), 33.9 (CH_2), 29.5 (*C*H(CH_3)$_2$ Dip), 26.4 (*C*H(CH_3)$_2$), 22.7 (CH_3 Dip), 22.6 (CH(*C*H_3)$_2$) ppm. Elemental analysis calcd for $C_{31}H_{45}IN_2$: C 65.02, H 7.92, N 4.89; found C 64.82, H 7.89, N 4.95.

1,3-Dibenzyl-2-methylimidazolium iodide (3a)



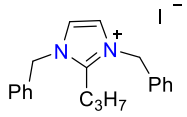
Pale yellow powder (320 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 6.7 Hz, 6H, CH_{ar}), 7.32 – 7.27 (m, 4H, CH_{ar}), 7.21 (s, 2H, CH_{ar}), 5.35 (s, 4H, NCH_2), 2.70 ppm (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.7 (C^2 Im), 132.5 (*i*-CH Ph), 129.7 (*p*-CH Ph), 129.4 (*m*-CH Ph), 128.4 (*o*-CH Ph), 121.6 ($CH^{4,5}$ Im), 52.6 (CH_2), 11.4 (CH_3) ppm. Elemental analysis calcd for $C_{18}H_{19}IN_2$: C 55.40, H 4.91, N 7.18; found C 55.84, H 5.18, N 7.34.

1,3-Dibenzyl-2-ethylimidazolium iodide (3b)



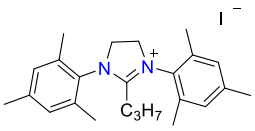
Pale yellow powder (325 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.31 (m, 8H, CH_{ar}), 7.31 – 7.27 (m, 4H, CH_{ar}), 5.39 (s, 4H, NCH_2), 3.15 (q, *J* = 7.7 Hz, 2H, C*H*$_2$CH$_3$), 0.93 ppm (t, *J* = 7.7 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.5 (C^2 Im), 132.9 (*i*-CH Ph), 129.6 (*p*-CH Ph), 129.4 (*m*-CH Ph), 128.3 (*o*-CH Ph), 121.9 ($CH^{4,5}$ Im), 52.4 (PhCH$_2$), 18.3 (*C*H$_2$CH$_3$), 11.3 (CH_3) ppm. Elemental analysis calcd for $C_{19}H_{21}IN_2$: C 56.45, H 5.24, N 6.93; found C 58.63, H 5.45, N 7.10.

1,3-Dibenzyl-2-propylimidazolium iodide (3c)



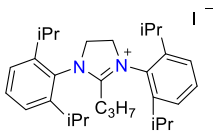
Brown oil (322 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.39 – 7.34 (m, 7H, CH_{ar}), 7.34 – 7.24 (m, 5H, CH_{ar}), 5.38 (s, 4H, NCH_2), 3.09 – 3.01 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.29 (dq, *J* = 15.2, 7.4 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 0.89 ppm (t, *J* = 7.3 Hz, 3H, (CH$_2$)$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 147.6 (C^2 Im), 132.9 (*i*-CH Ph), 129.5 (*p*-CH Ph), 129.4 (*m*-CH Ph), 128.3 (*o*-CH Ph), 121.9 ($CH^{4,5}$ Im), 52.4 (PhCH$_2$), 26.2 (*C*H$_2$CH$_2$CH$_3$), 20.7 (*C*H$_2$CH$_3$), 13.9 (CH_3) ppm.

1,3-Dimesityl-2-propylimidazolinium iodide (4)



Pale yellow powder (142 mg, 30% yield). ^{1}H NMR (400 MHz, dmso-d_6): δ = 7.14 (s, 4H, *m*-CH_{ar} Mes), 4.38 (s, 4H, NCH_2), 2.32 (s, 12H, *o*-CH_3 Mes), 2.31 (s, 6H, *p*-CH_3 Mes), 2.12 – 2.03 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.12 (dt, *J* = 15.2, 7.6 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 0.60 ppm (t, *J* = 7.3 Hz, 3H, (CH$_2$)$_2$C*H*$_3$). ^{13}C NMR (101 MHz, dmso-d_6): δ = 169.0 (C^2 Im), 140.0 (*p*-C Mes), 135.2 (*o*-C Mes), 130.2 (*i*-C Mes), 130.0 (*m*-CH Mes), 50.0 (CH$_2^{4,5}$ Im), 26.6 (*C*H$_2$CH$_2$CH$_3$), 20.6 (*p*-CH_3), 17.5 (*o*-CH_3), 17.3 (*C*H$_2$CH$_3$), 14.0 (CH_3) ppm. Elemental analysis calcd for $C_{24}H_{33}IN_2$: C 60.50, H 6.98, N 5.88; found C 60.08, H 6.99, N 6.07.

1,3-Bis(2,6-diisopropylphenyl)-2-propylimidazolinium iodide (5)



Pale brown powder (215 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.8 Hz, 2H, *p*-CH_{ar} Dip), 7.33 (d, *J* = 7.8 Hz, 4H, *m*-CH_{ar} Dip), 4.76 (s, 4H, NCH_2), 2.97 (hept, *J* = 6.9 Hz, 4H, CH iPr), 2.04 – 1.95 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.42 (d, *J* = 6.8 Hz, 12H, CH_3 iPr), 1.31 (d, *J* = 6.8 Hz, 12H, CH_3 iPr), 1.21 (d, *J* = 6.1 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 0.66 ppm (t, *J* = 7.3 Hz, 3H, (CH$_2$)$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.6 (C^2 Im), 146.3 (*o*-C Dip), 131.8 (*p*-CH Dip), 129.6 (*i*-C Dip), 125.8 (*m*-CH Dip), 54.2 (CH$_2^{4,5}$ Im), 29.3 (*C*H$_2$CH$_2$CH$_3$), 27.6 (*C*H(CH$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 18.3 (*C*H$_2$CH$_3$), 14.4 (CH$_2$*C*H$_3$) ppm. Elemental analysis calcd for $C_{30}H_{45}IN_2$: C 64.27, H 8.09, N 5.00; found C 63.99, H 8.07, N 5.44.

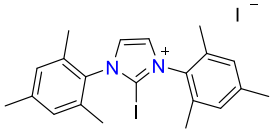
1.3 Iodination reactions

1.3.1 Typical procedure

A 25 mL round-bottomed flask equipped with a magnetic stirring bar and a septum was loaded with an imidazol(in)ium salt (1 mmol), Cs_2CO_3 (375 mg, 1.15 mmol), iodine (292 mg, 1.15 mmol), and acetonitrile (5 mL). The suspension was stirred in an oil bath at 70 °C for 2 h. After cooling to room temperature, the volatiles were removed on a rotary evaporator and the residue was taken up with dichloromethane (15 mL) and a 1 M aqueous NH_4Cl solution (30 mL). The biphasic mixture was vigorously stirred for 30 min at room temperature. It was then transferred into a separatory funnel and the Schlenk tube was rinsed with deionized water (15 mL). The aqueous phase was separated and extracted three times with dichloromethane (15 mL each). The organic phases were combined and washed with brine (15 mL). After drying over $MgSO_4$, the solvent was evaporated on a rotary evaporator. The residue was transferred in a vial and suspended in diethylether (5 mL) to remove the potential excess of molecular iodine. The supernatant solution was removed with a pipette and the remaining solid was dried under high vacuum.

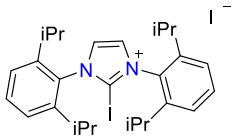
1.3.2 Analytical data

2-Iodo-1,3-dimesitylimidazolium iodide (6)



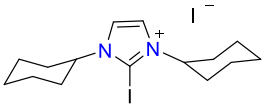
White microcrystalline powder (372 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 2H, NCH), 7.01 (s, 4H, *m*-CH_{ar} Mes), 2.35 (s, 6H, *p*-CH_3 Mes), 1.98 ppm (s, 12H, *o*-CH_3 Mes). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.7 (*p*-C Mes), 134.2 (*o*-C Mes), 132.3 (*i*-C Mes), 130.1 (*m*-CH Mes), 125.3 ($CH^{4,5}$ Im), 118.5 (C^2 Im), 21.3 (*p*-CH_3), 17.7 (*o*-CH_3) ppm. These data matched those reported in the literature.[4] Elemental analysis calcd for $C_{21}H_{24}I_2N_2$: C 45.18, H 4.33, N 5.02; found C 43.36, H 4.30, N 4.80.

1,3-Bis(2,6-diisopropylphenyl)-2-iodoimidazolium iodide (7)



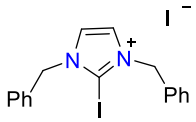
White powder (425 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, *J* = 7.8 Hz, 2H, *p*-CH_{ar} Dip), 7.46 (s, 2H, NCH), 7.34 (d, *J* = 7.9 Hz, 4H, *m*-CH_{ar} Dip), 2.28 (hept, *J* = 6.9 Hz, 4H, CH iPr), 1.29 (d, *J* = 6.9 Hz, 12H, CH_3 iPr), 1.18 ppm (d, *J* = 6.9 Hz, 12H, CH_3 iPr). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0 (*o*-C Dip), 132.3 (*p*-CH Dip), 132.1 (*i*-C Dip), 125.6 ($CH^{4,5}$ Im), 125.2 (*m*-CH Dip), 123.3 (C^2 Im), 29.4 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$) ppm. These data matched those reported in the literature.[5] Elemental analysis calcd for $C_{27}H_{36}I_2N_2$: C 50.48, H 5.65, N 4.36; found C 50.46, H 5.68, N 4.28.

1,3-Dicyclohexyl-2-iodoimidazolium iodide (8)



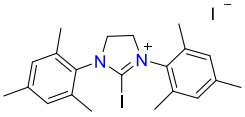
Microcrystalline pale orange powder (385 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 1.2 Hz, 2H, NCH), 4.46 (tt, *J* = 12.0, 3.9 Hz, 2H, CH cyclohexyl), 2.11 – 2.02 (m, 4H, CH_2 cyclohexyl), 1.93 (dt, *J* = 13.8, 3.4 Hz, 4H, CH_2 cyclohexyl), 1.79 (dt, *J* = 13.1, 3.4 Hz, 2H, CH_2 cyclohexyl), 1.62 (qd, *J* = 12.3, 3.2 Hz, 4H, CH_2 cyclohexyl), 1.49 (qt, *J* = 13.1, 3.3 Hz, 4H, CH_2 cyclohexyl), 1.25 ppm (qt, *J* = 12.9, 3.7 Hz, 2H, CH_2 cyclohexyl). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 120.6 ($CH^{4,5}$ Im), 113.3 (C^2 Im), 61.8 (CH Cy), 33.3 (CH_2), 25.2 (CH_2), 24.8 (CH_2) ppm. Elemental analysis calcd for $C_{15}H_{24}I_2N_2$: C 37.06, H 4.98, N 5.76; found C 37.87, H 4.71, N 5.48.

1,3-Dibenzyl-2-iodoimidazolium iodide (9)



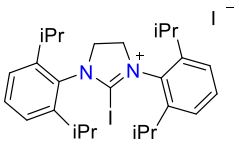
Yellow powder (327 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (qd, *J* = 4.9, 4.0, 1.8 Hz, 6H, CH_{ar} benzyl), 7.33 (dd, *J* = 7.3, 2.3 Hz, 4H, CH_{ar} benzyl), 7.12 (s, 2H, NCH), 5.39 ppm (s, 4H, NCH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.6 (*i*-C Ph), 129.8 (*p*-CH Ph), 129.7 (*m*-CH Ph), 128.7 (*o*-CH Ph), 123.2 ($CH^{4,5}$ Im), 117.1 (C^2 Im), 55.9 (CH_2) ppm. Elemental analysis calcd for $C_{17}H_{16}I_2N_2$: C 40.66, H 3.21, N 5.58; found C 41.64, H 3.35, N 5.86.

2-Iodo-1,3-dimesitylimidazolinium iodide (10)



Pale yellow powder (452 mg, 81% yield). ^{1}H NMR (400 MHz, dmso-d_6): δ = 7.14 (s, 4H, *m*-CH_{ar} Mes), 4.47 (s, 4H, NCH_2), 2.32 (s, 6H, *p*-CH_3 Mes), 2.28 ppm (s, 12H, *o*-CH_3 Mes). ^{13}C NMR (101 MHz, dmso-d_6): δ = 140.1 (*p*-C Mes), 136.0 (C^2 Im), 135.4 (*o*-C Mes), 132.7 (*i*-C Mes), 129.8 (*m*-CH Mes), 51.4 ($CH^{4,5}$ Im), 20.7 (*p*-CH_3), 17.2 (*o*-CH_3) ppm. Elemental analysis calcd for $C_{21}H_{26}I_2N_2$: C 45.02, H 4.68, N 5.00; found C 44.66, H 4.64, N 5.16.

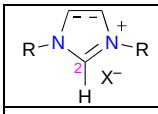
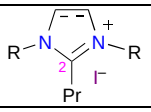
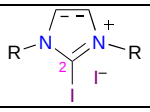
1,3-Bis(2,6-diisopropylphenyl)-2-iodoimidazolinium iodide (11)



White powder (486 mg, 75% yield). ^{1}H NMR (400 MHz, dmso-d_6): δ = 7.58 (t, J = 7.8 Hz, 2H, *p*-CH_{ar} Dip), 7.46 (d, J = 7.8 Hz, 4H, *m*-CH_{ar} Dip), 4.48 (s, 4H, NCH_2), 2.92 (hept, J = 6.9 Hz, 4H, CH iPr), 1.33 (d, J = 7.0 Hz, 12H, CH_3 iPr), 1.30 ppm (d, J = 7.0 Hz, 12H, CH_3 iPr). ^{13}C NMR (101 MHz, dmso-d_6): δ = 146.1 (*o*-C Dip), 145.9 (C^2 Im), 132.4 (*p*-CH Dip), 131.3 (*i*-C Dip), 125.3 (*m*-CH Dip), 54.0 ($CH_2^{4,5}$ Im), 28.6 (CH(CH_3)$_2$), 24.7 (CH(CH$_3$)$_2$), 23.8 (CH(CH$_3$)$_2$) ppm. Elemental analysis calcd for $C_{27}H_{38}I_2N_2$: C 50.32, H 5.94, N 4.35; found C 53.08, H 6.24, N 5.05.

2. Structural analysis

Table S1. ^{13}C NMR chemical shifts of various imidazol(in)ium salts with C2–H, C2–Pr, or C2–I groups.

	δ C$_2$ (ppm)[a]		δ C$_2$ (ppm)		δ C$_2$ (ppm)
IMes·HCl	138.8	**1c**	147.3	**6**	125.3
IDip·HCl	139.4	**2c**	147.9	**7**	123.3
IBn·HBF$_4$	135.5	**3c**	147.6	**9**	117.1
SIMes·HCl	160.0	**4**	169.0	**10**	136.0
SIDip·HCl	160.1	**5**	169.6	**11**	145.9

[a] Data from ref. 1.

3. Mass Spectrometry

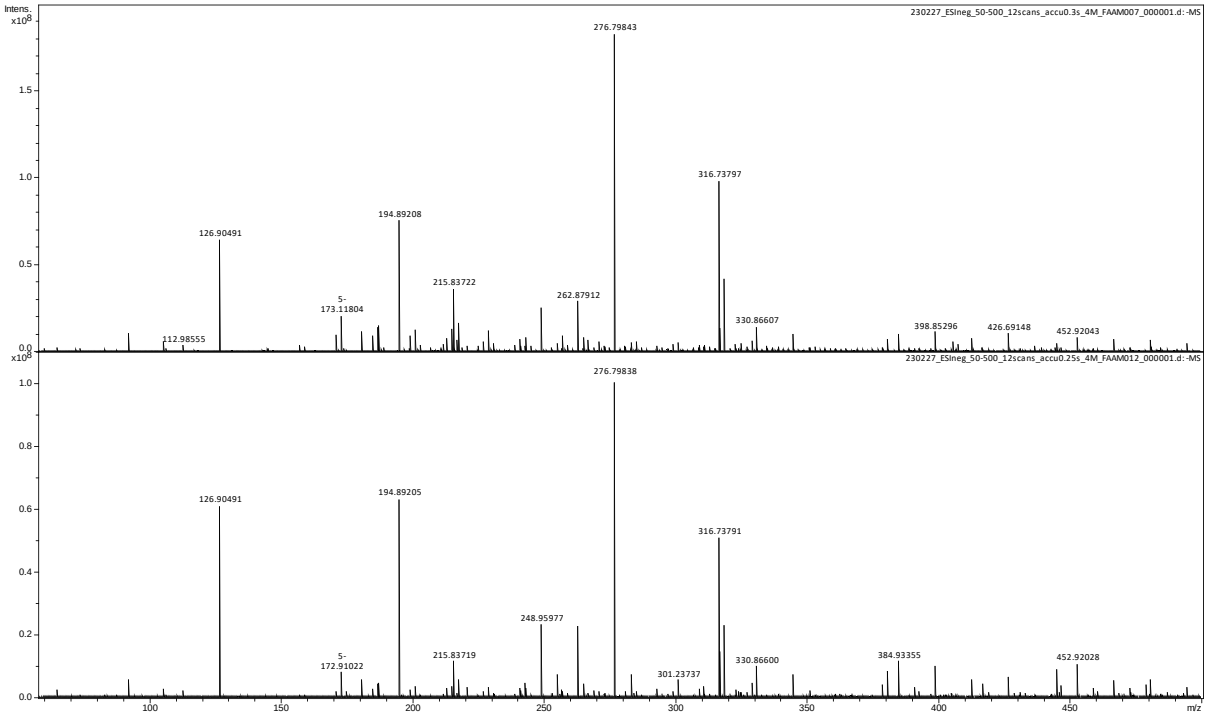


Fig. S1. ESI-MS spectra of 1,3-dimesityl-2-methylimidazolium iodide (**1a**, top) and 1,3-bis-(2,6-diisopropylphenyl)-2-methylimidazolium iodide (**2a**, bottom) in the negative mode

4. Crystallography

4.1 General information

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane in a $CDCl_3$ solution at –18 °C. Data were collected on a Bruker D8 VENTURE PHOTON III-14 diffractometer using an Incoatec multilayer mirror monochromated with the Mo-*K*α radiation (λ = 0.71073 Å) from a microfocus sealed tube source at 100 K and with a detector resolution of 7.3910 pixels mm^{-1}. Data for crystal structure determination was collected by omega and phi scans. Data reduction was performed using the APEX3 v2018.7-2 software package.[6] An empirical absorption correction based on the multiscan method[7] was applied using SADABS 2016/2.[8] The structure was solved using SHELXT 2018/2.[9] and finally refined by full-matrix least-squares based on F^2 by SHELXL 2018/3.[10] All non-hydrogen atoms were anisotropically refined and the hydrogen atom positions were calculated and refined using a riding model.

4.2 Crystal data

2-Ethyl-1,3-dimesitylimidazolium iodide chloroform solvate (1b·$CHCl_3$). Colorless prism, 0.09 × 0.07 × 0.06 mm, MF = $C_{23}H_{29}N_2{\cdot}I{\cdot}CHCl_3$, MW = 579.75, orthorhombic, space group *Pbca* (no. 61), a = 19.2342(15), b = 10.1167(7), c = 26.9285(17) Å, V = 5239.9(6) $Å^3$, Z = 8, μ = 1.54 mm^{-1}, reflections collected/unique = 53950/5778 (R_{int} = 0.054), final refinement converged with R_1 = 0.065 (I > 2σ(I)) and wR_2 = 0.133 (all data), *GOF* = 1.23, $\Delta\rho_{max}/\Delta\rho_{min}$ = 0.66/–0.46 e·$Å^{-3}$.

1,3-Bis(2,6-diisopropylphenyl)-2-ethylimidazolium iodide chloroform solvate (2b·$CHCl_3$). Colorless needle, 0.18 × 0.08 × 0.05 mm, MF = $C_{29}H_{41}N_2{\cdot}I{\cdot}2(CHCl_3)$, MW = 783.27, monoclinic, space group $P2_1/c$ (no. 14), a = 17.5644(10), b = 44.896(3), c = 9.5243(5) Å, β = 98.986(2)°, V = 7418.4(7) $Å^3$, Z = 8, μ = 1.32 mm^{-1}, reflections collected/unique = 16362/13715 (R_{int} = 0.072), final refinement converged with R_1 = 0.029 (I > 2σ(I)) and wR_2 = 0.071 (all data), *GOF* = 1.03, $\Delta\rho_{max}/\Delta\rho_{min}$ = 1.56/–1.20 e·$Å^{-3}$.

2-Iodo-1,3-dimesitylimidazolium iodide (6). Colorless plate, 0.16 × 0.06 × 0.02 mm, MF = $C_{21}H_{24}I_2N_2$, MW = 558.22, triclinic, space group $P1^-$ (no. 2), a = 8.0999 (4), b = 9.3367(5), c = 15.5240(9) Å, α = 87.968(2)°, β = 79.642(2)°, γ = 74.3022(18)°, V = 1111.71(10) $Å^3$, Z = 2, μ = 2.83 mm^{-1}, reflections collected/unique = 42392/5503 (R_{int} = 0.054), final refinement converged with R_1 = 0.043 (I > 2σ(I)) and wR_2 = 0.100 (all data), *GOF* = 1.24, $\Delta\rho_{max}/\Delta\rho_{min}$ = 1.65/–2.08 e·$Å^{-3}$.

Deposition Numbers 2300133 (for **1b**), 2300134 (for **2b**), and 2300132 (for **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

4.3 ORTEP plots

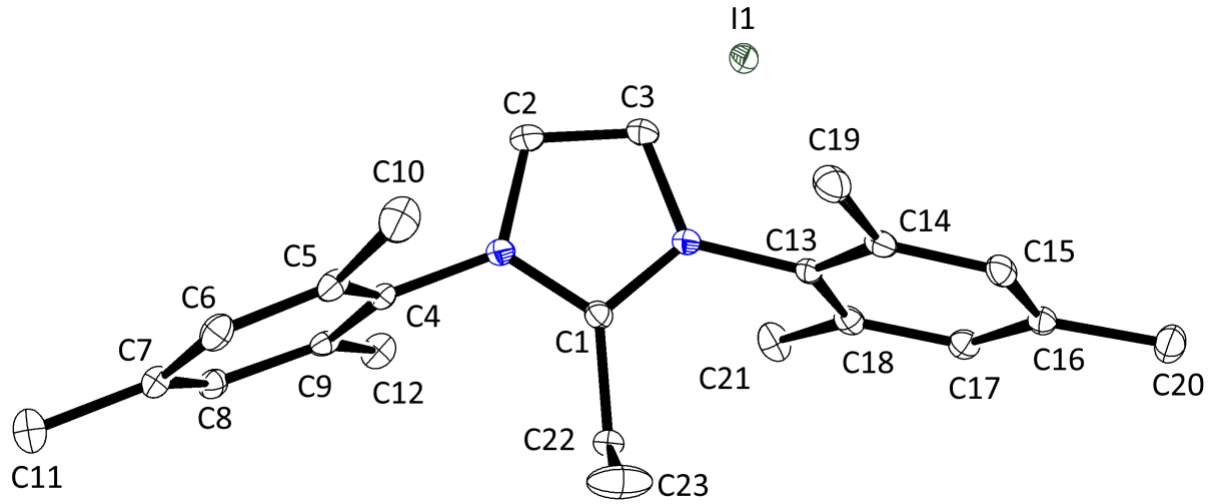


Fig. S2. ORTEP representation of 2-ethyl-1,3-dimesitylimidazolium iodide chloroform solvate (**1b**·$CHCl_3$). Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms and the cocrystallized solvent were omitted for clarity.

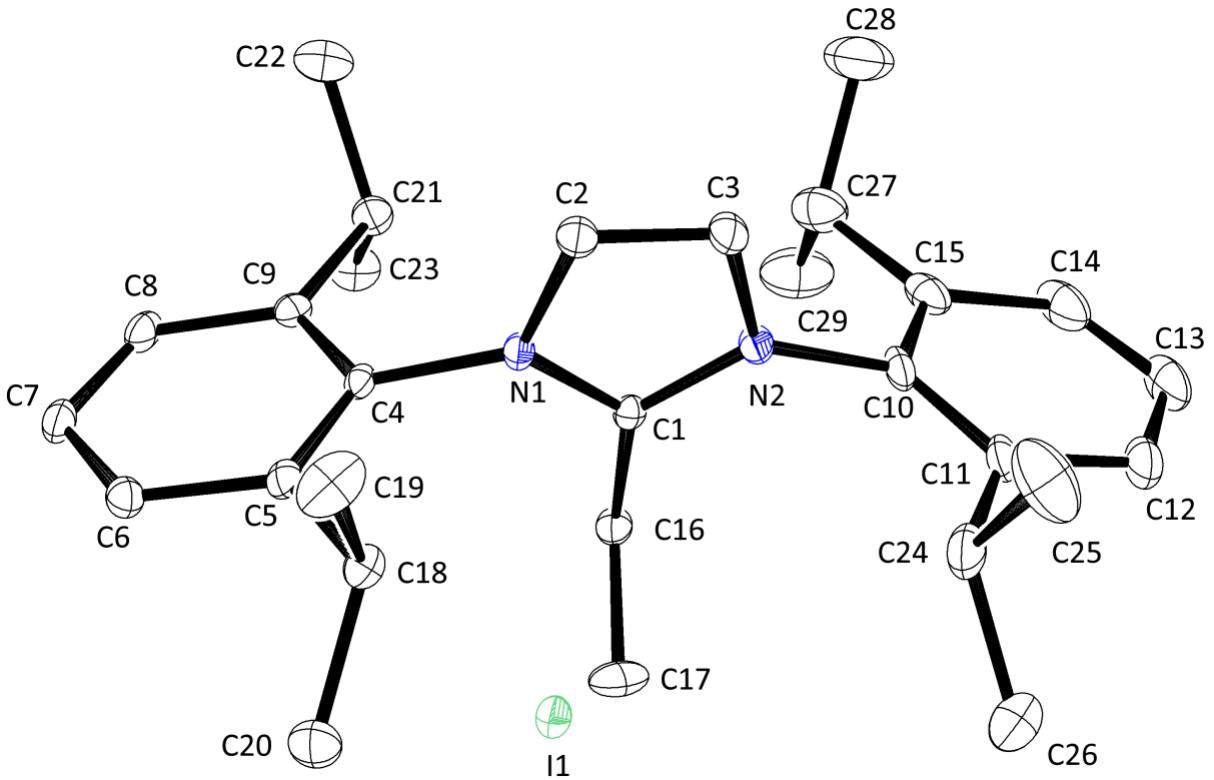


Fig. S3. ORTEP representation of 1,3-bis(2,6-diisopropylphenyl)-2-ethylimidazolium iodide chloroform solvate (**2b**·2 $CHCl_3$). Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms and the cocrystallized solvent were omitted for clarity.

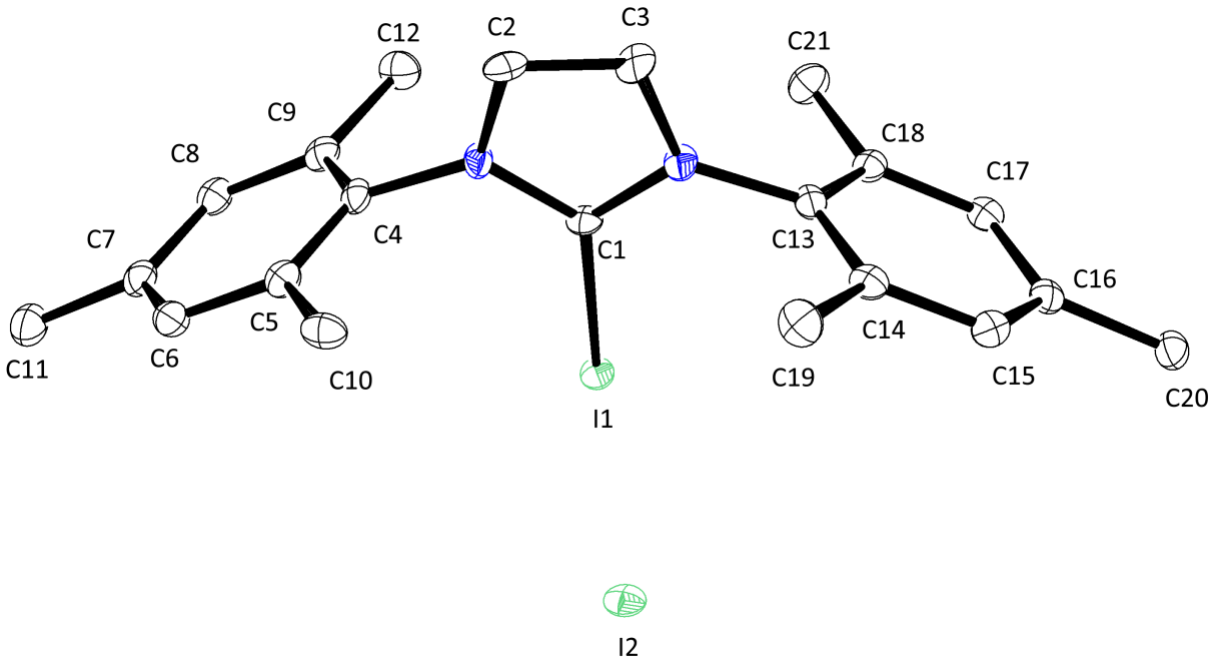


Fig. S4. ORTEP representation of 2-iodo-1,3-dimesitylimidazolium iodide (**6**). Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

5. NMR spectra

5.1 NMR spectra of alkylated products

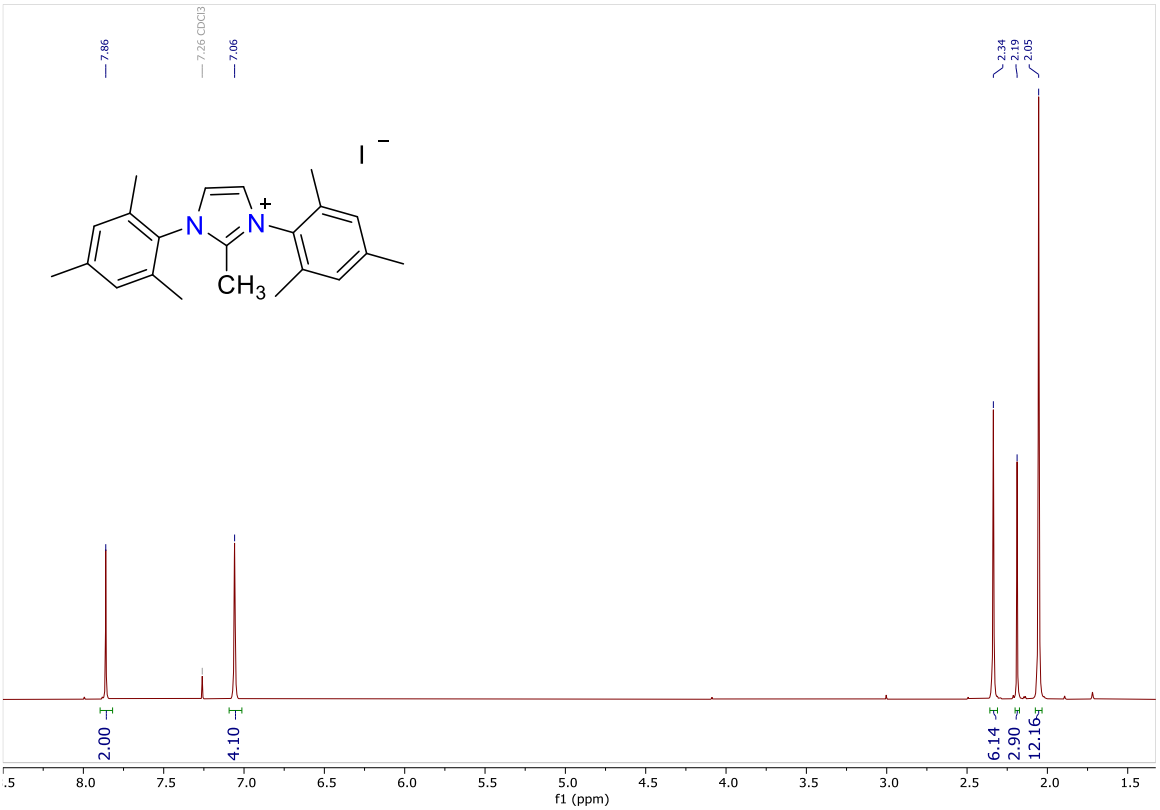


Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-methylimidazolium iodide (**1a**)

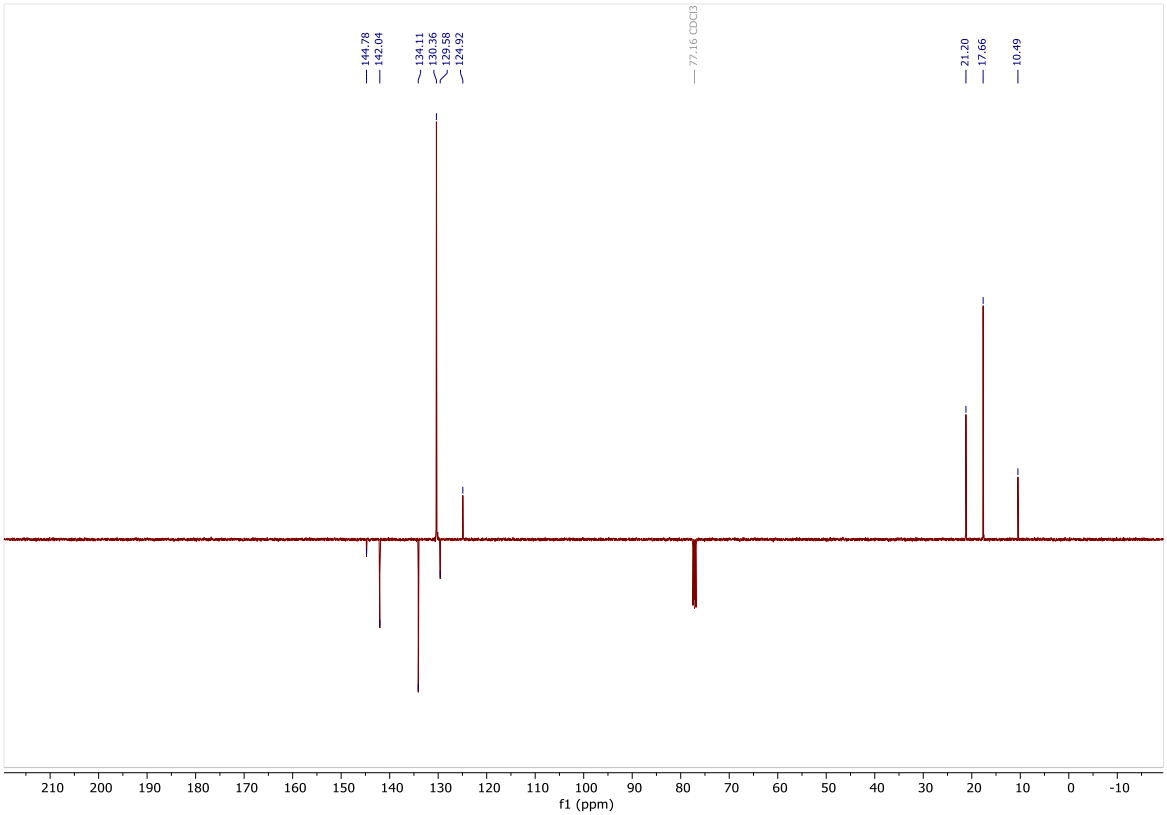


Fig. S6. $^{13}C\{^{1}H\}$ APT NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-methylimidazolium iodide (**1a**)

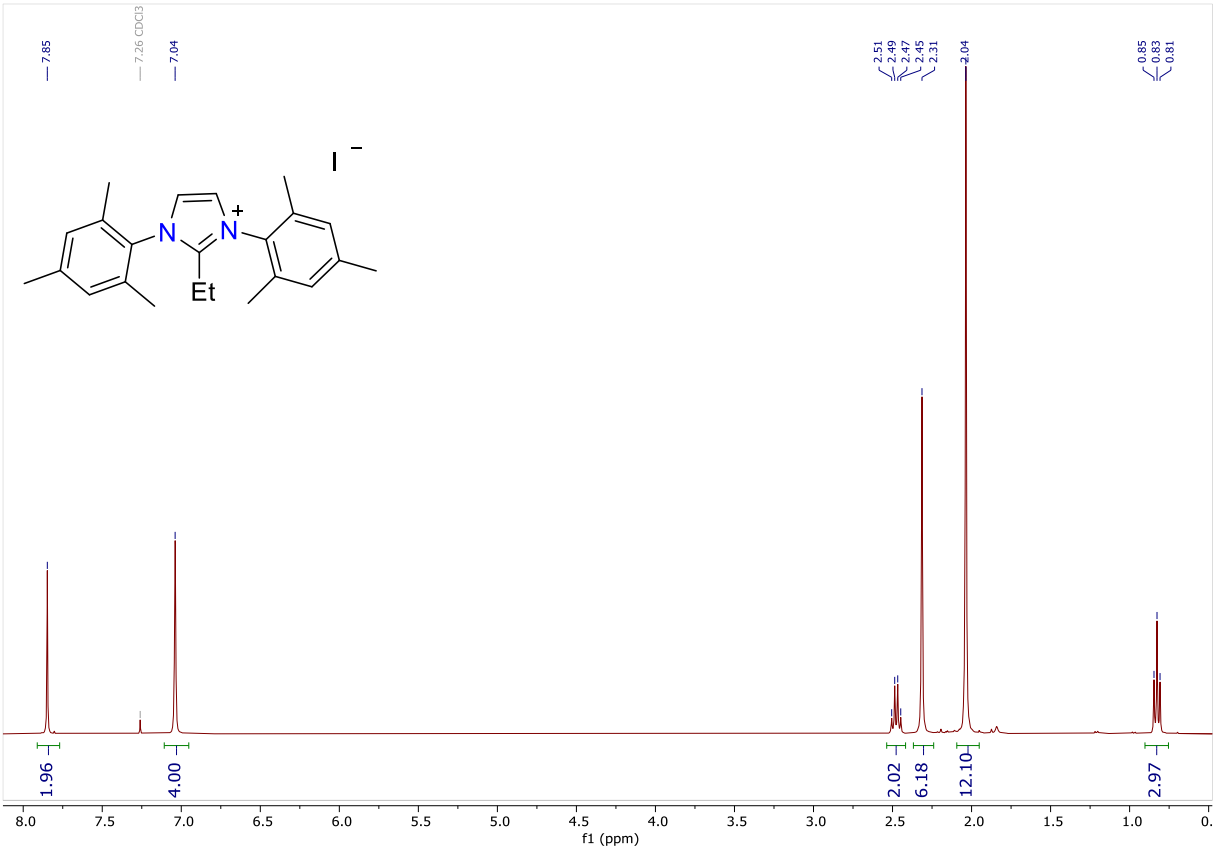


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-ethyl-1,3-dimesitylimidazolium iodide (**1b**)

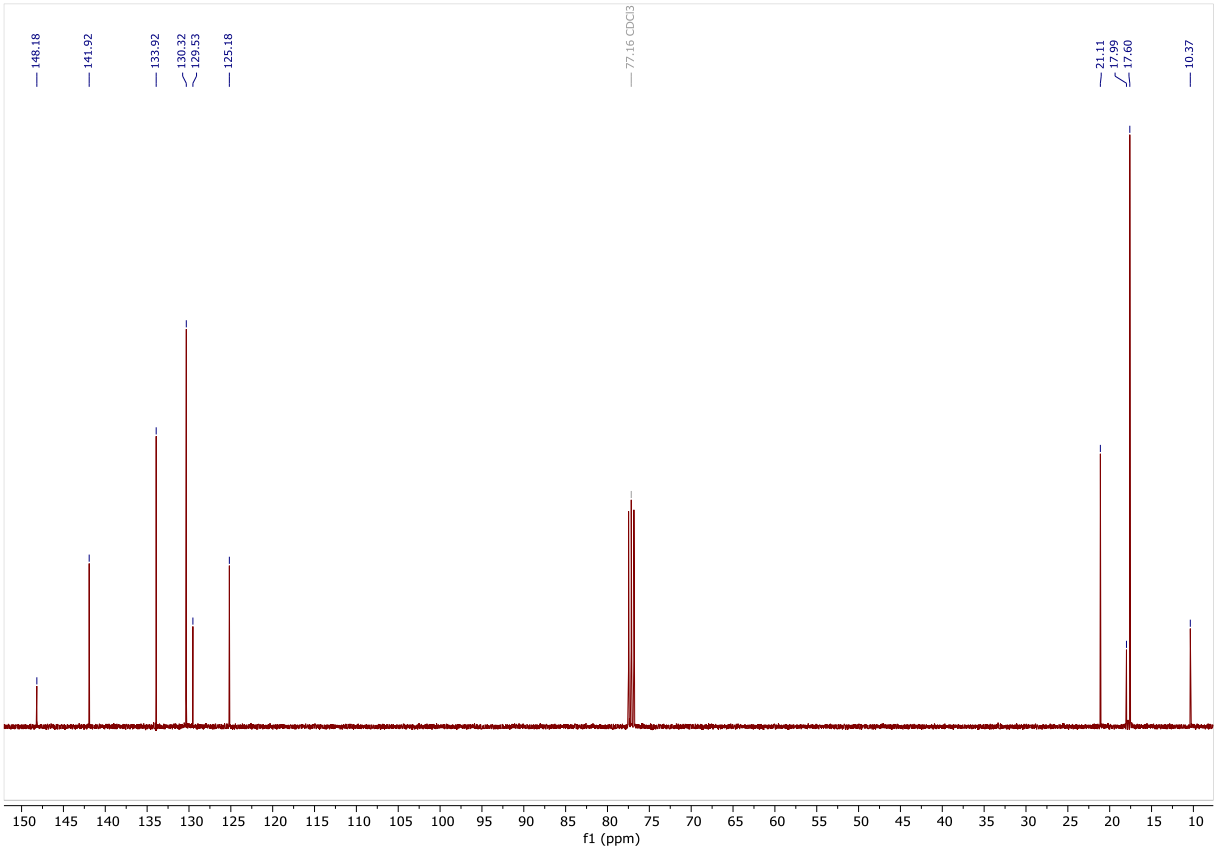


Fig. S8. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-ethyl-1,3-dimesityl-imidazolium iodide (**1b**)

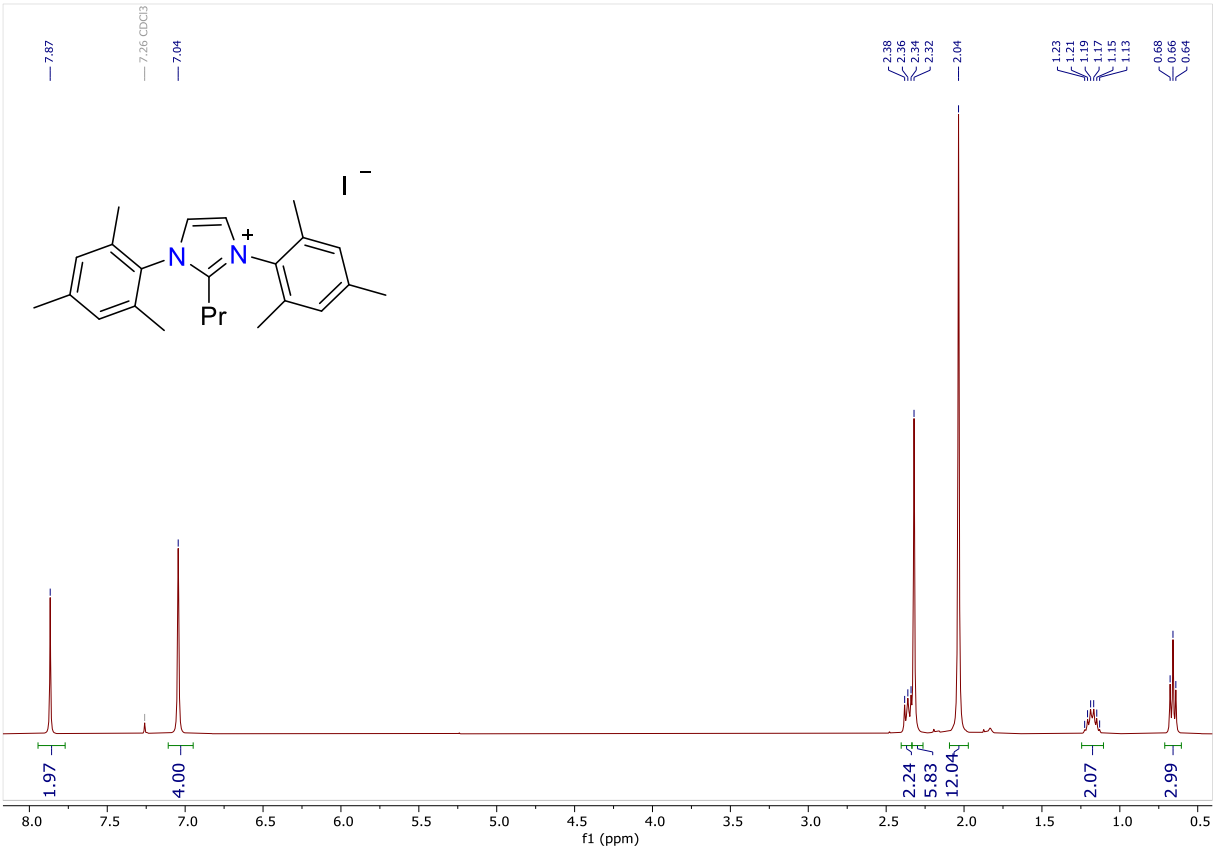


Fig. S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-propylimidazolium iodide (**1c**)

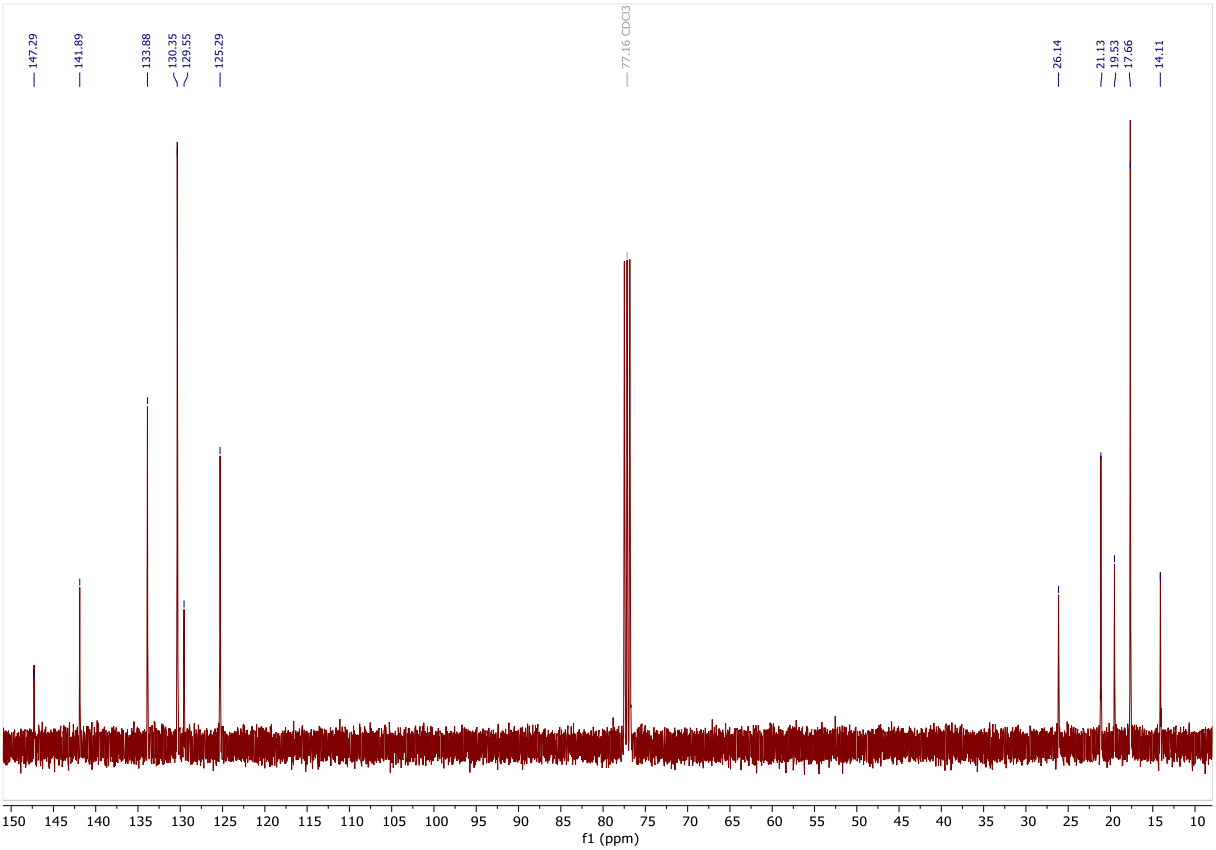


Fig. S10. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-propylimidazolium iodide (**1c**)

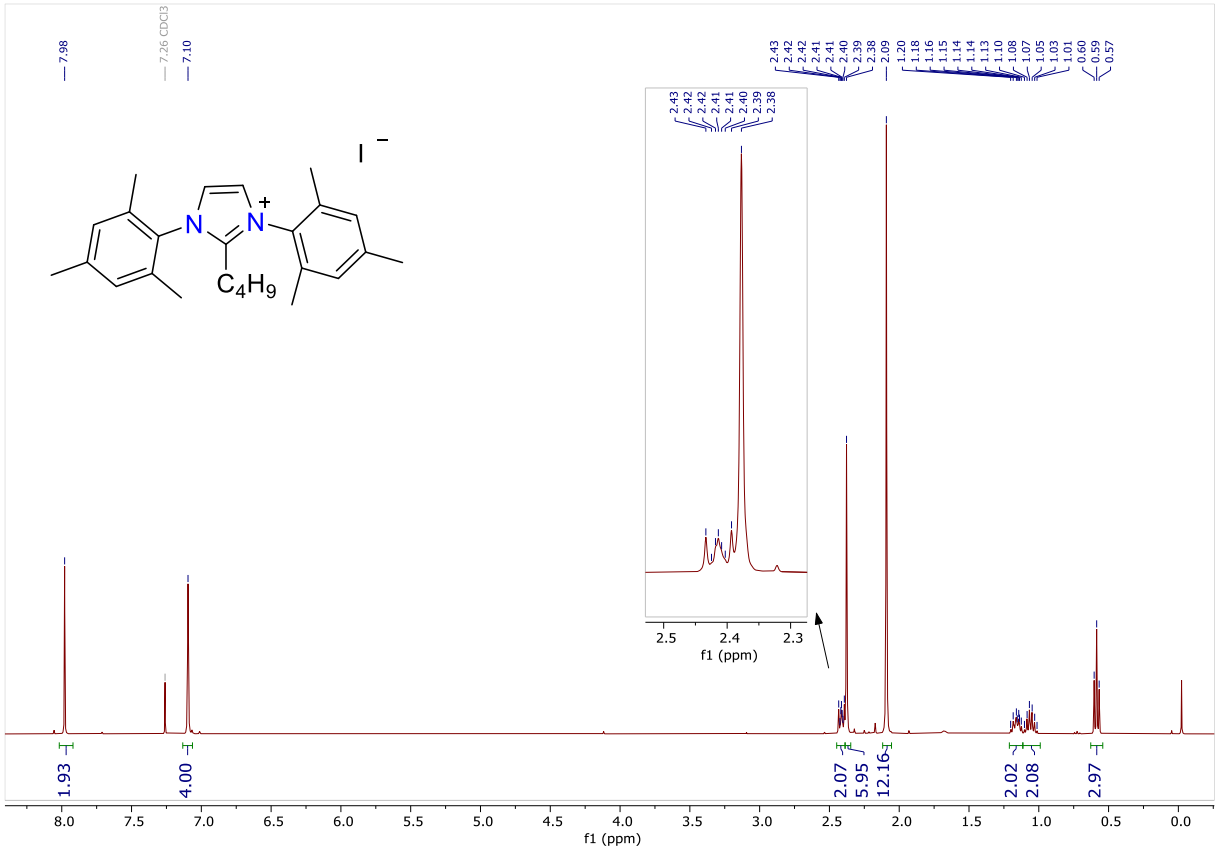


Fig. S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-butyl-1,3-dimesitylimidazolium iodide (**1d**)

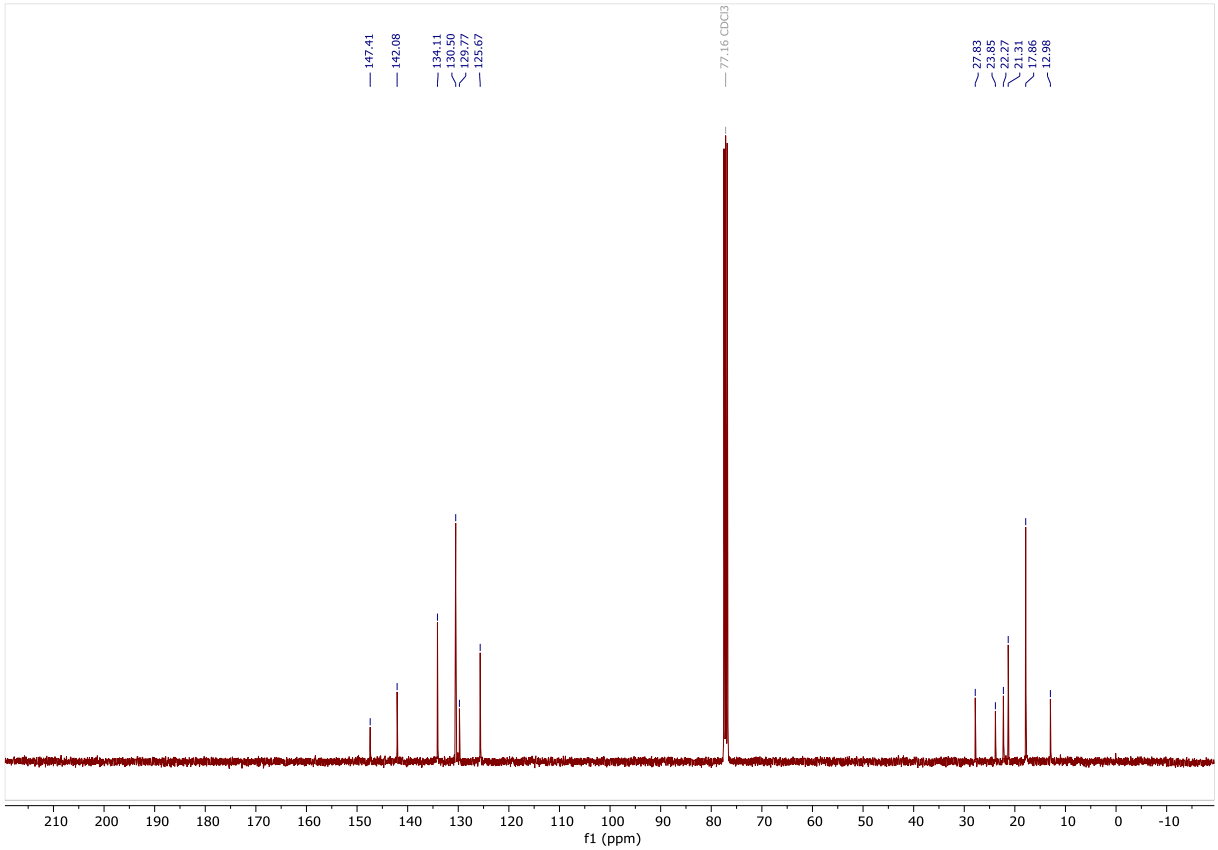


Fig. S12. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-butyl-1,3-dimesityl-imidazolium iodide (**1d**)

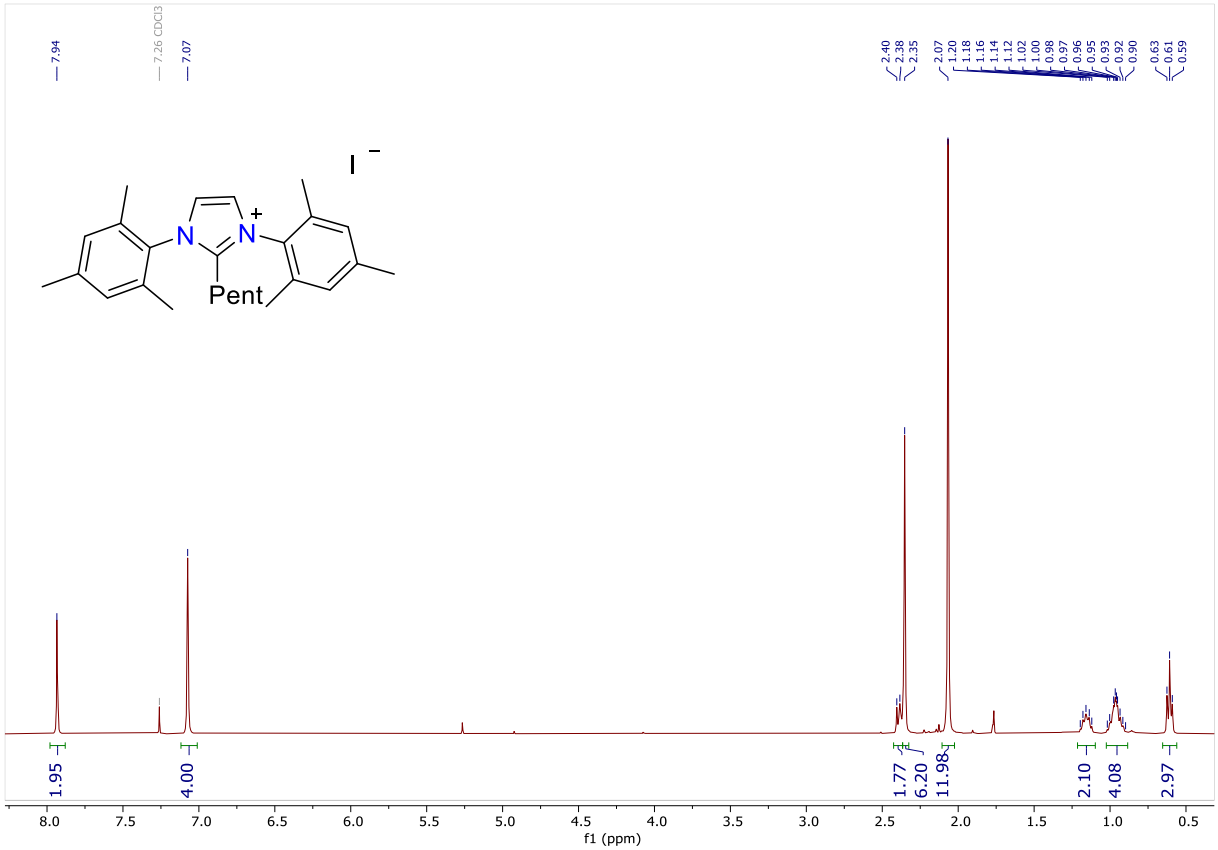


Fig. S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-pentylimidazolium iodide (**1e**)

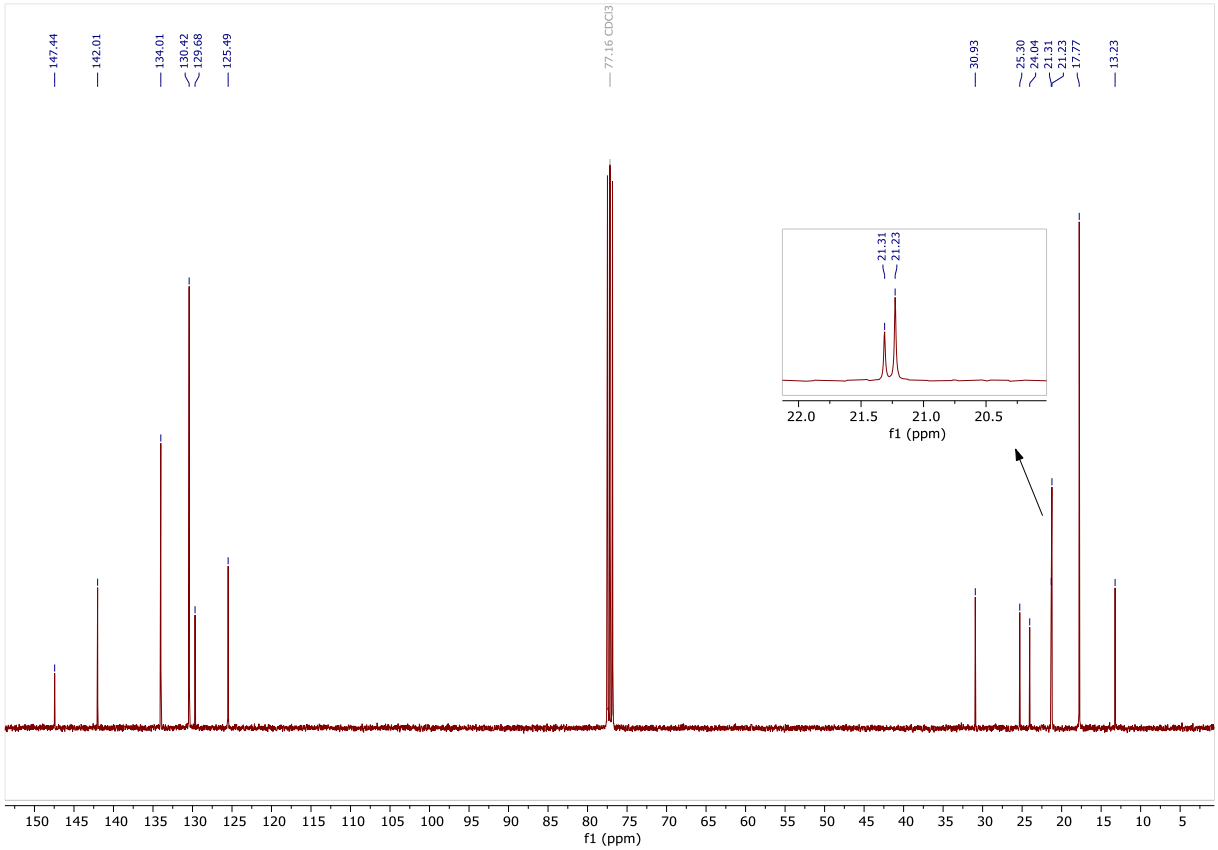


Fig. S14. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-pentylimidazolium iodide (**1e**)

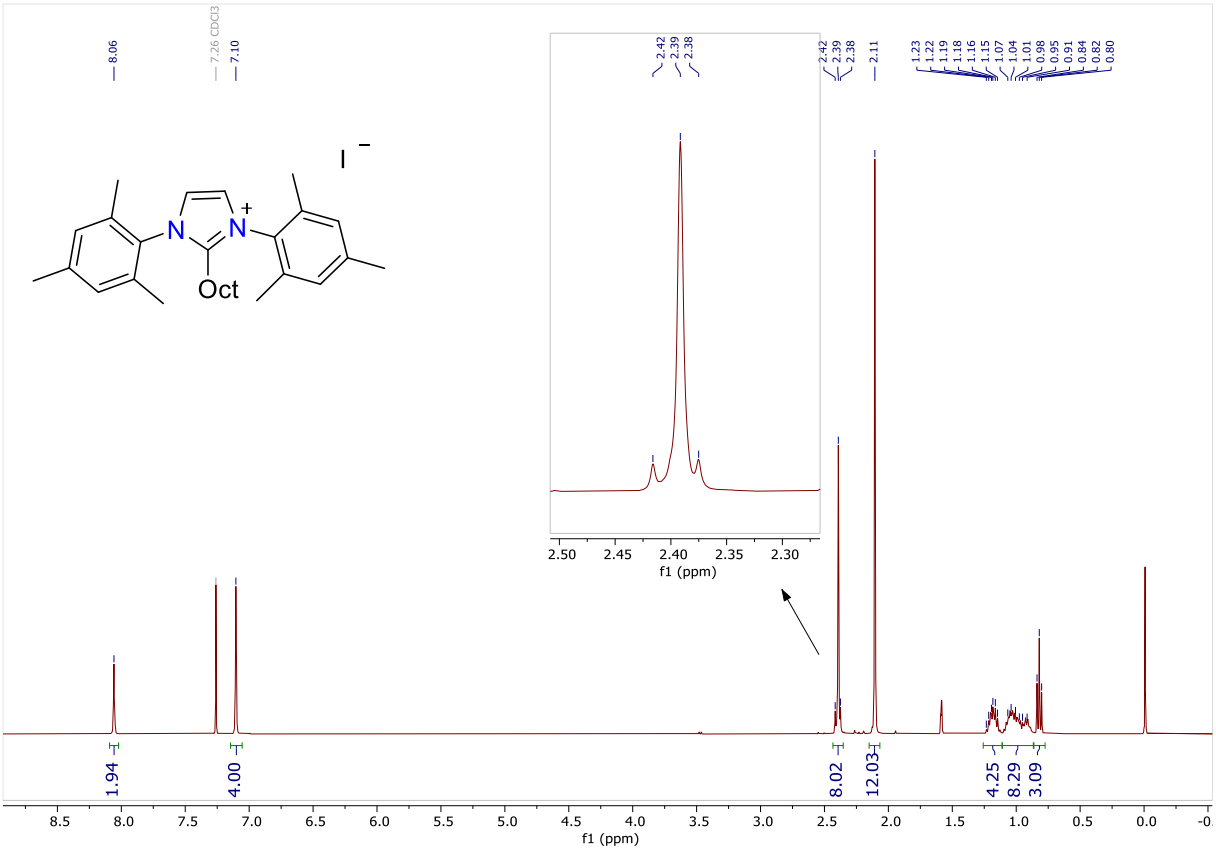


Fig. S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-octylimidazolium iodide (**1f**)

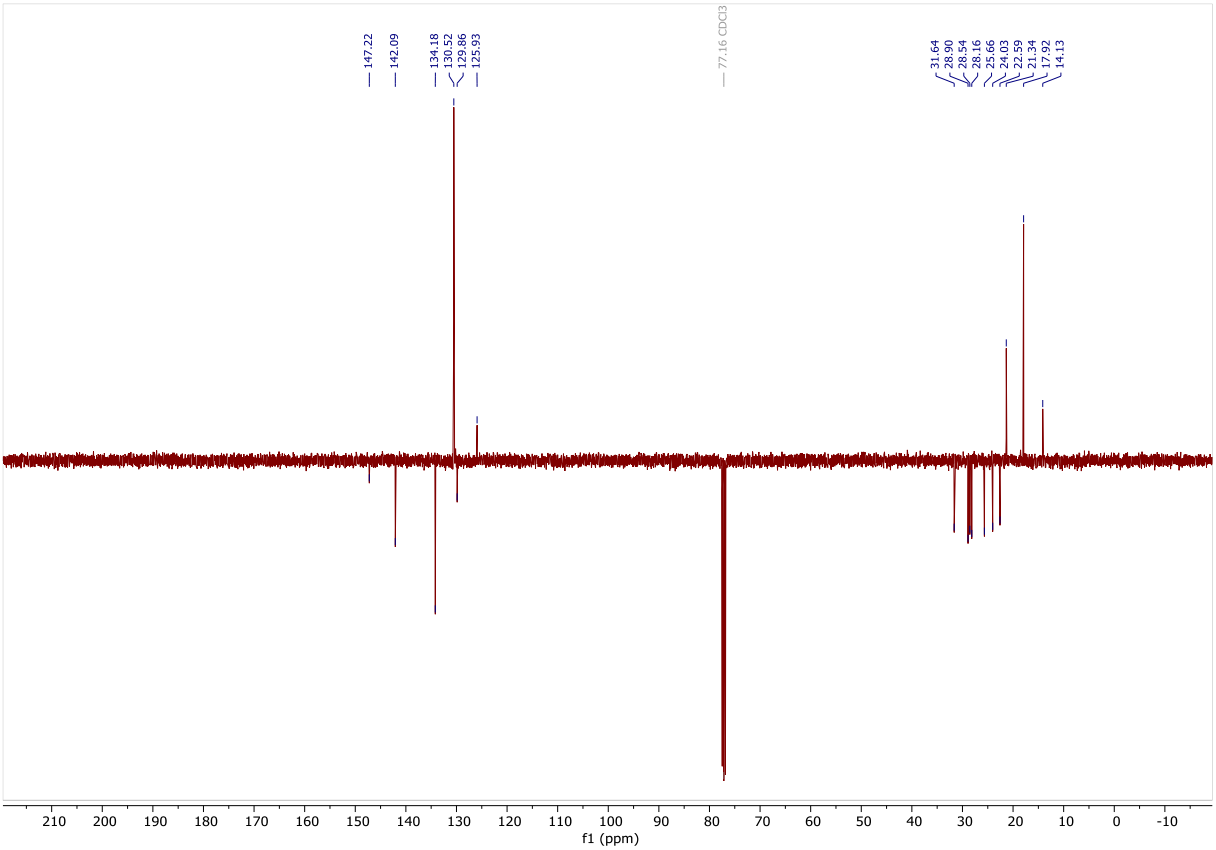


Fig. S16. ^{13}C{^{1}H} APT NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dimesityl-2-octyl-imidazolium iodide (**1f**)

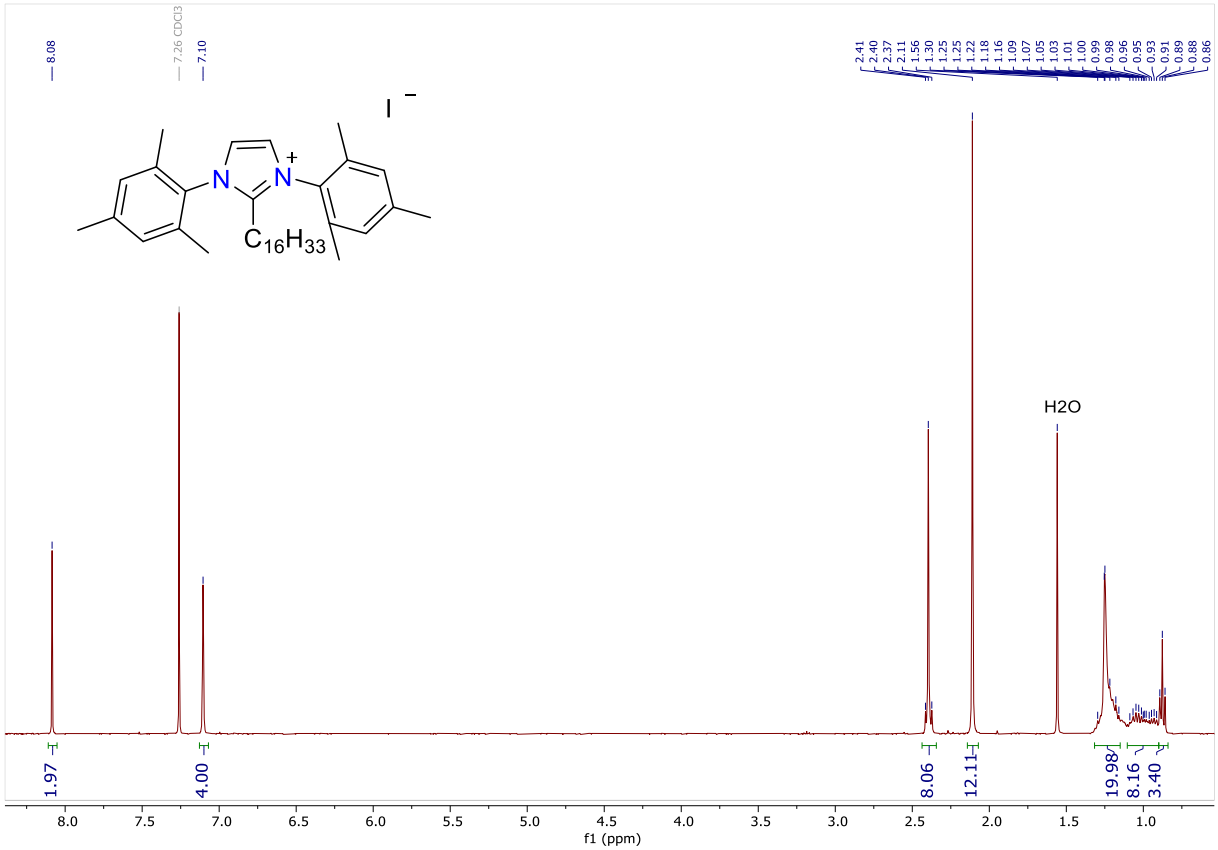


Fig. S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-hexadecyl-1,3-dimesitylimidazolium iodide (**1g**)

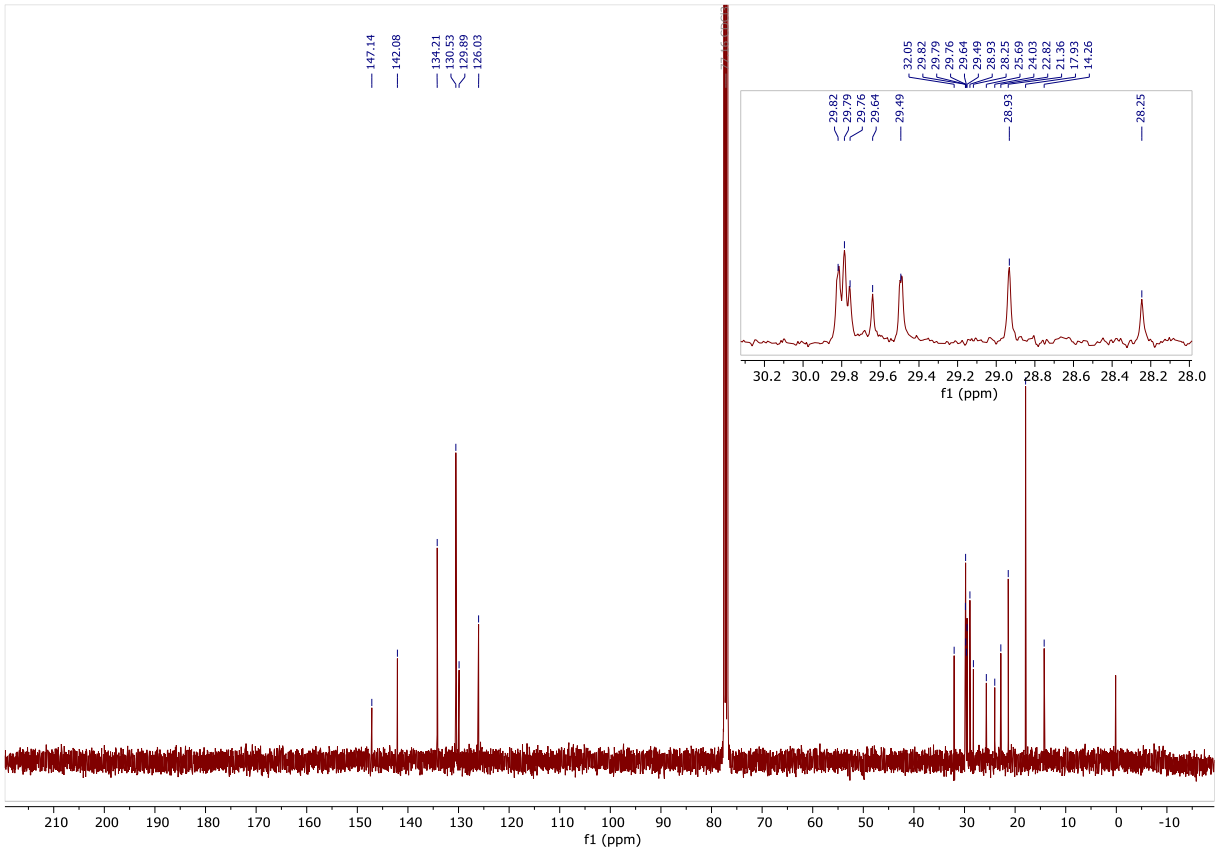


Fig. S18. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-hexadecyl-1,3-dimesitylimidazolium iodide (**1g**)

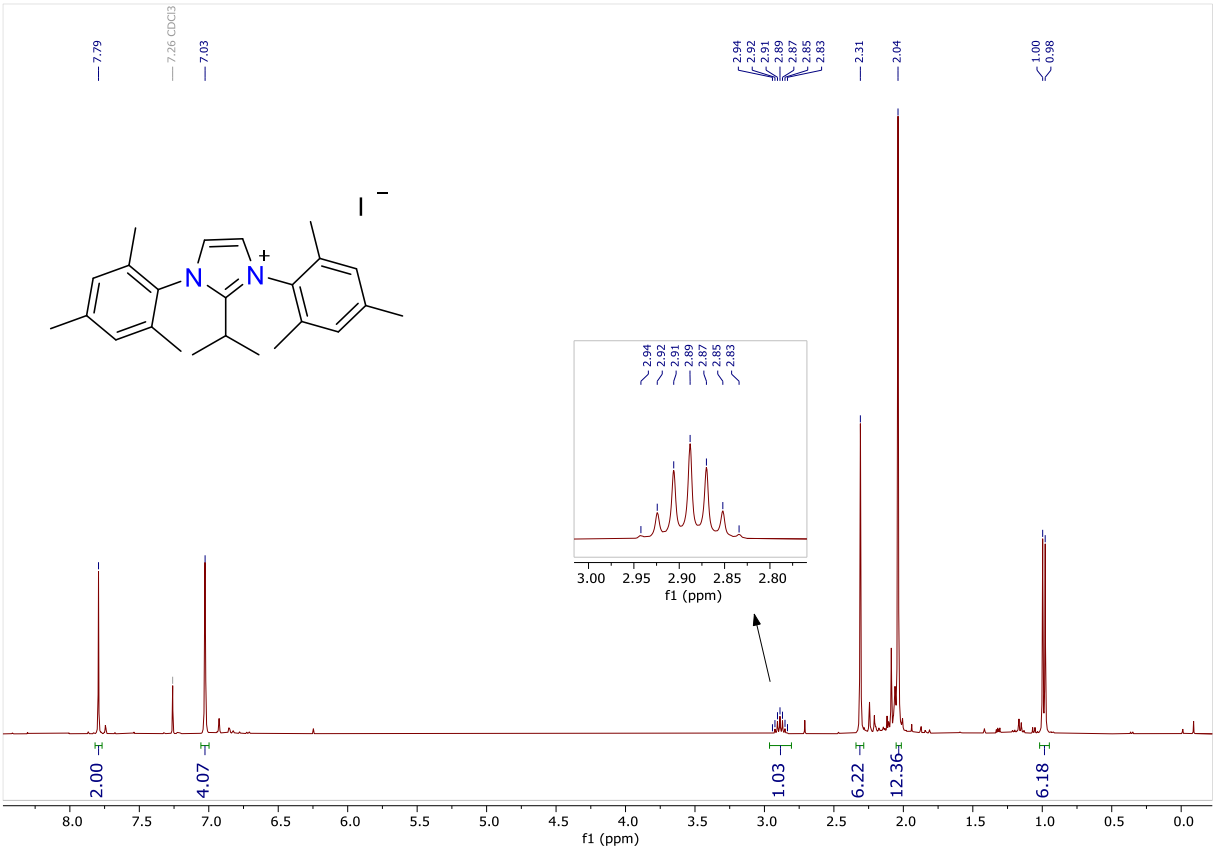


Fig. S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-isopropyl-1,3-dimesitylimidazolium iodide (**1h**)

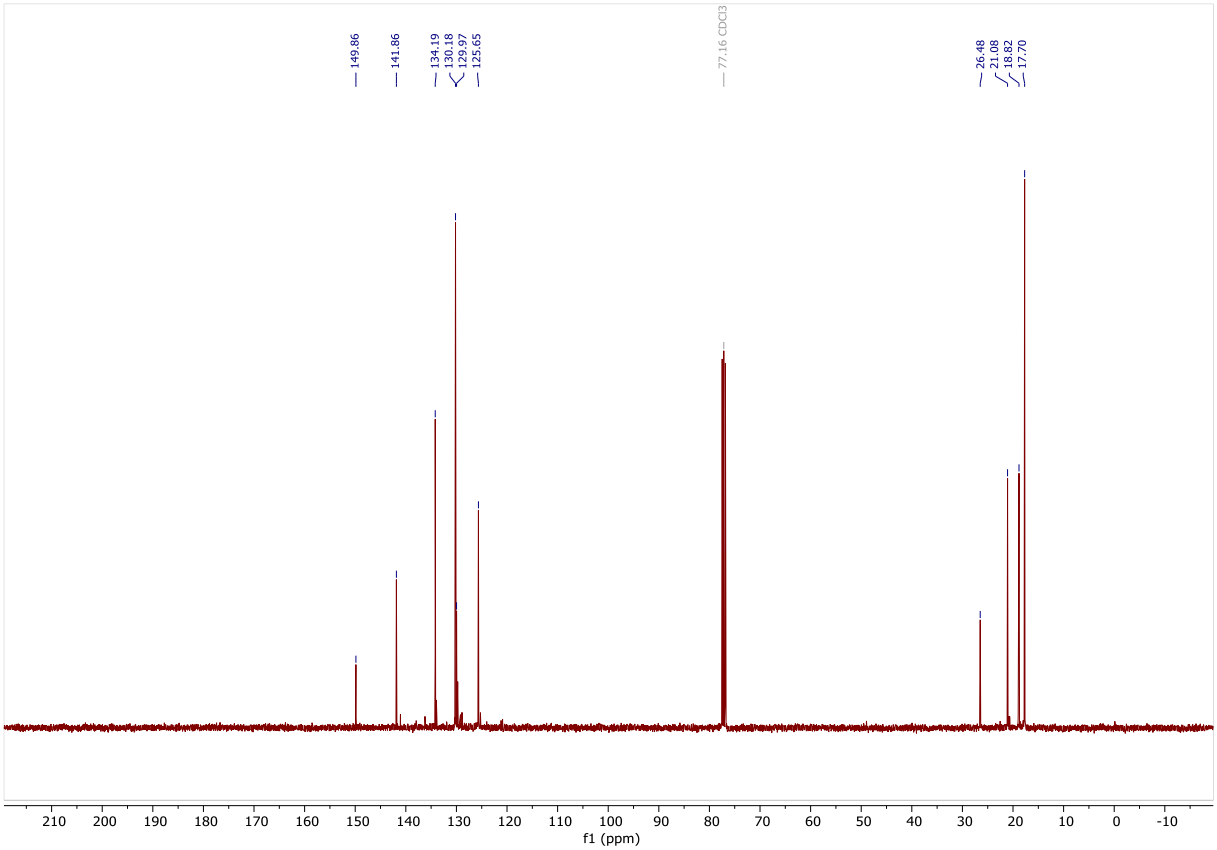


Fig. S20. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-isopropyl-1,3-dimesitylimidazolium iodide (**1h**)

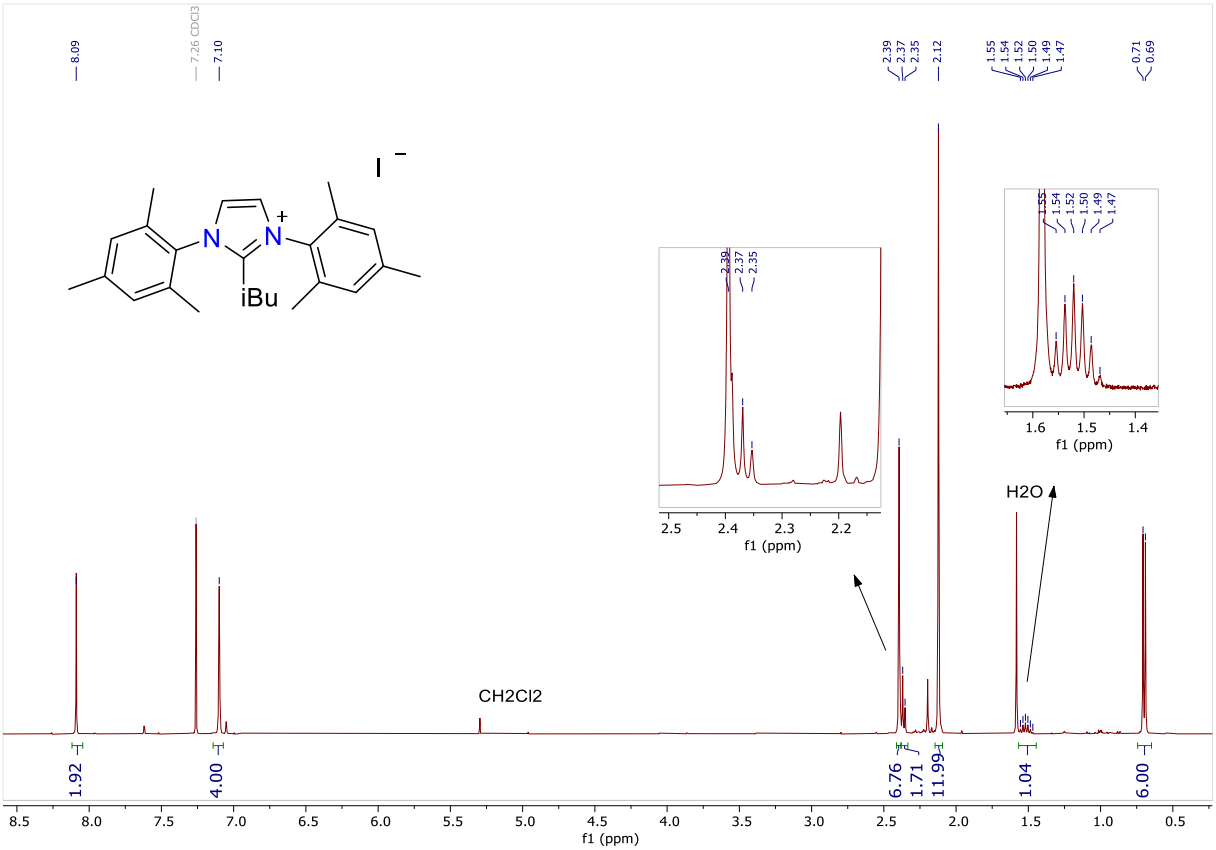


Fig. S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-isobutyl-1,3-dimesitylimidazolium iodide (**1j**)

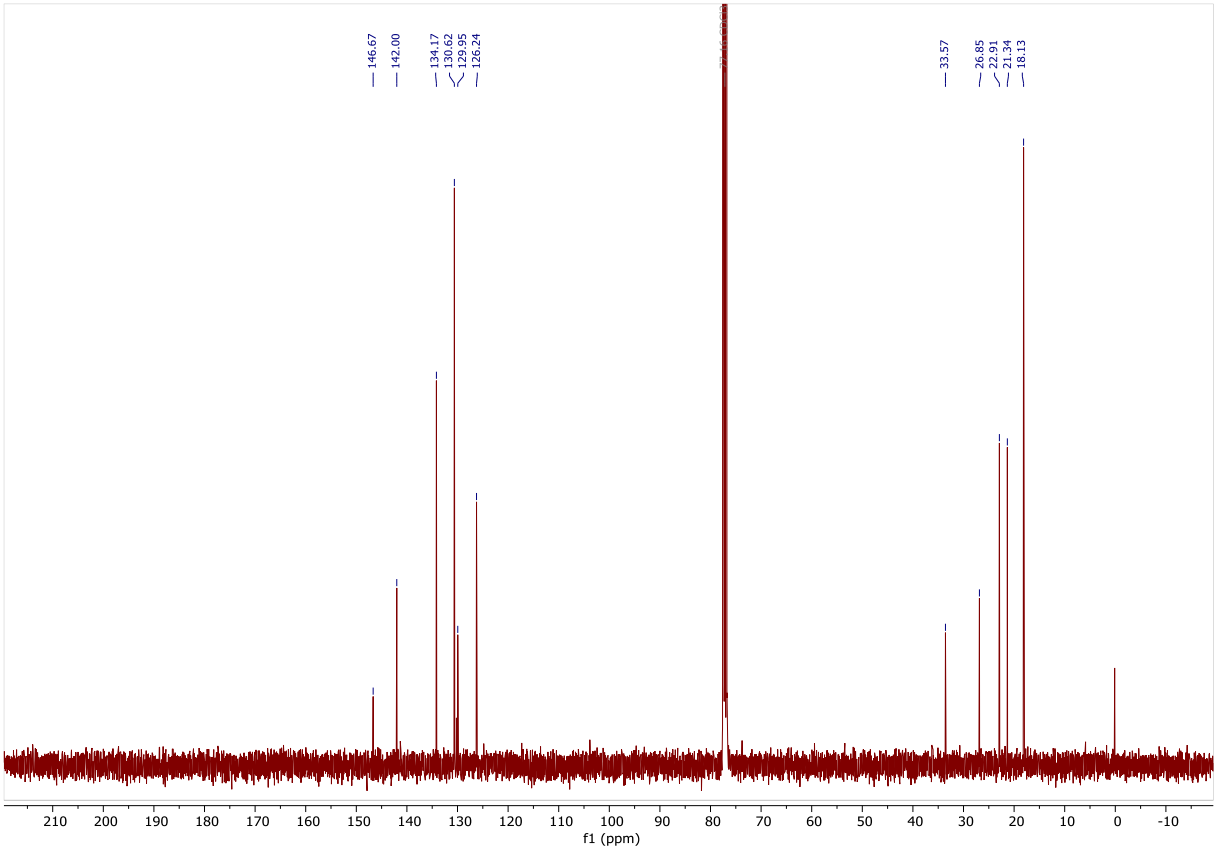


Fig. S22. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-isobutyl-1,3-dimesitylimidazolium iodide (**1j**)

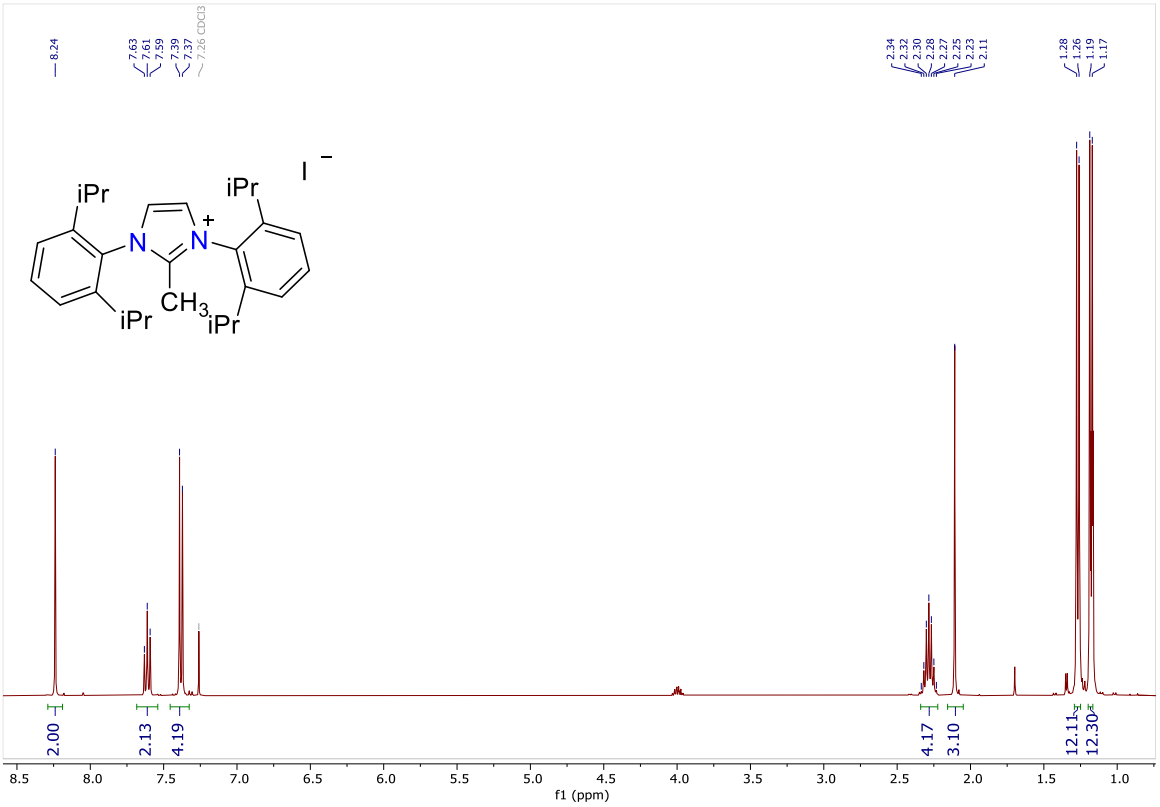


Fig. S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-methylimidazolium iodide (**2a**)

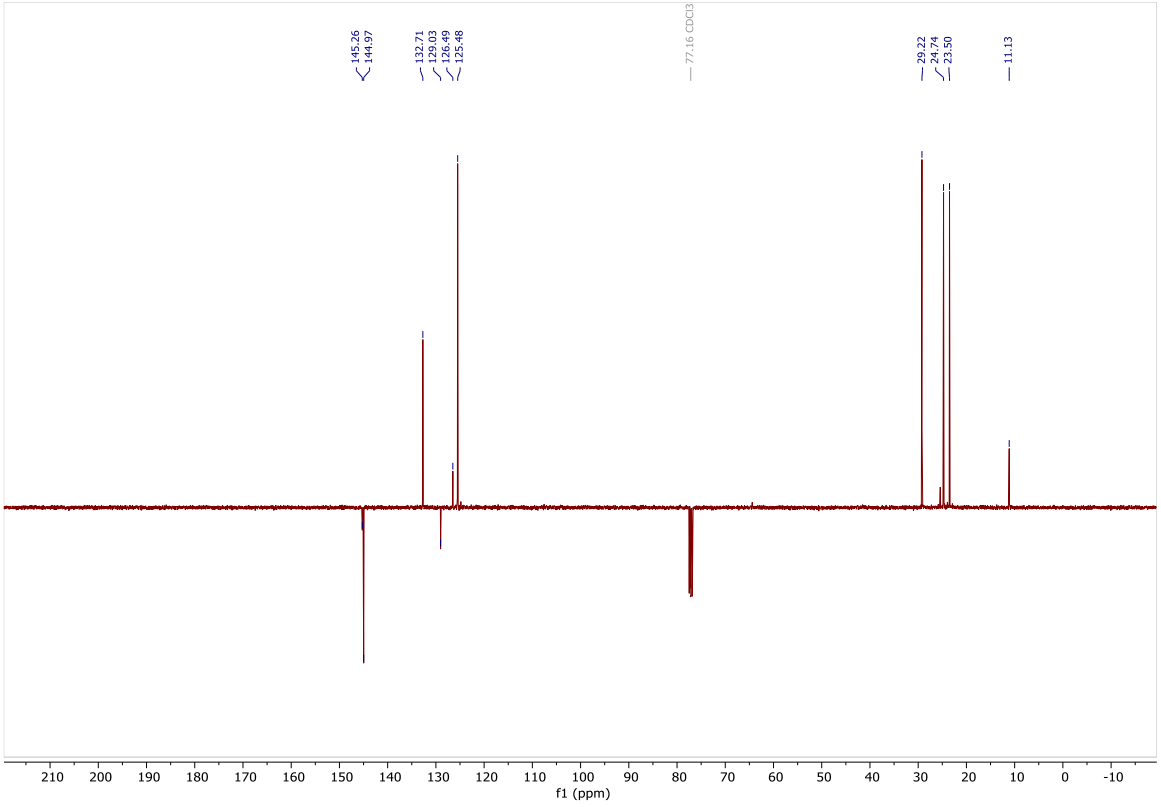


Fig. S24. ^{13}C{^{1}H} APT NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-methylimidazolium iodide (**2a**)

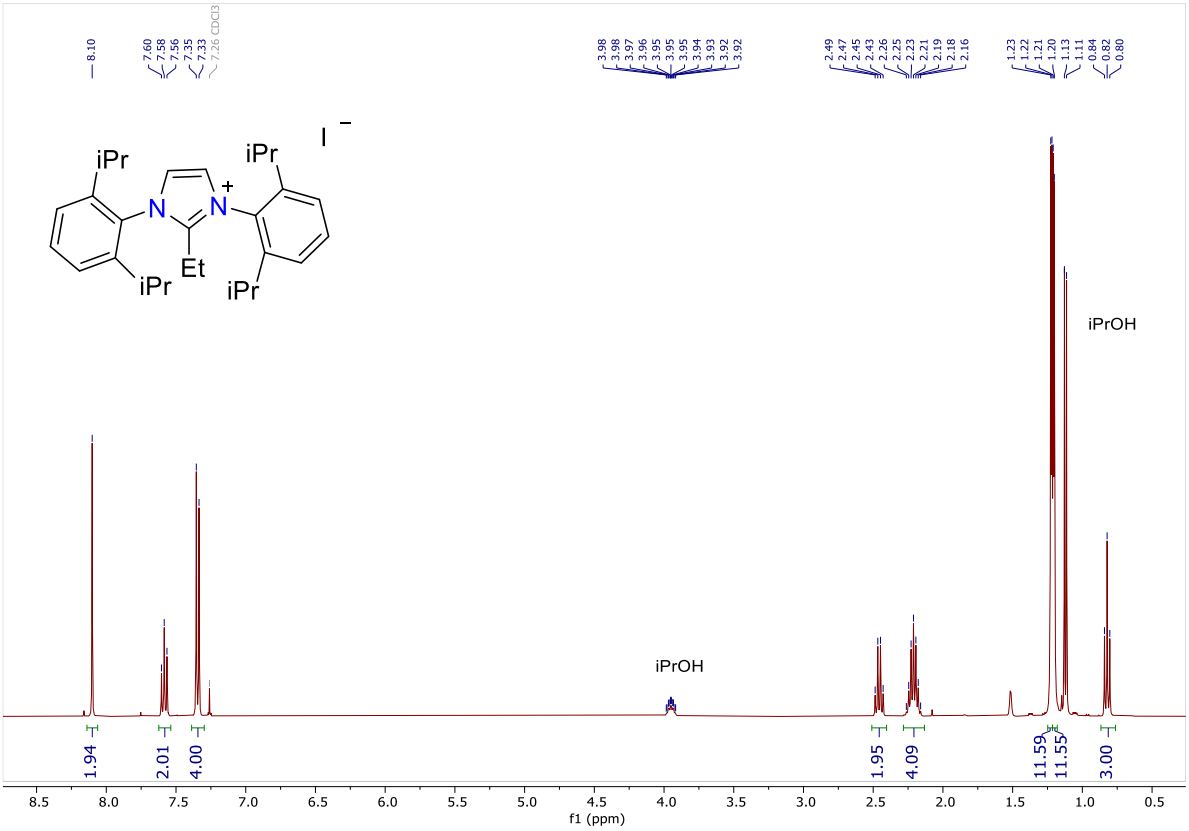


Fig. S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-ethylimidazolium iodide (**2b**)

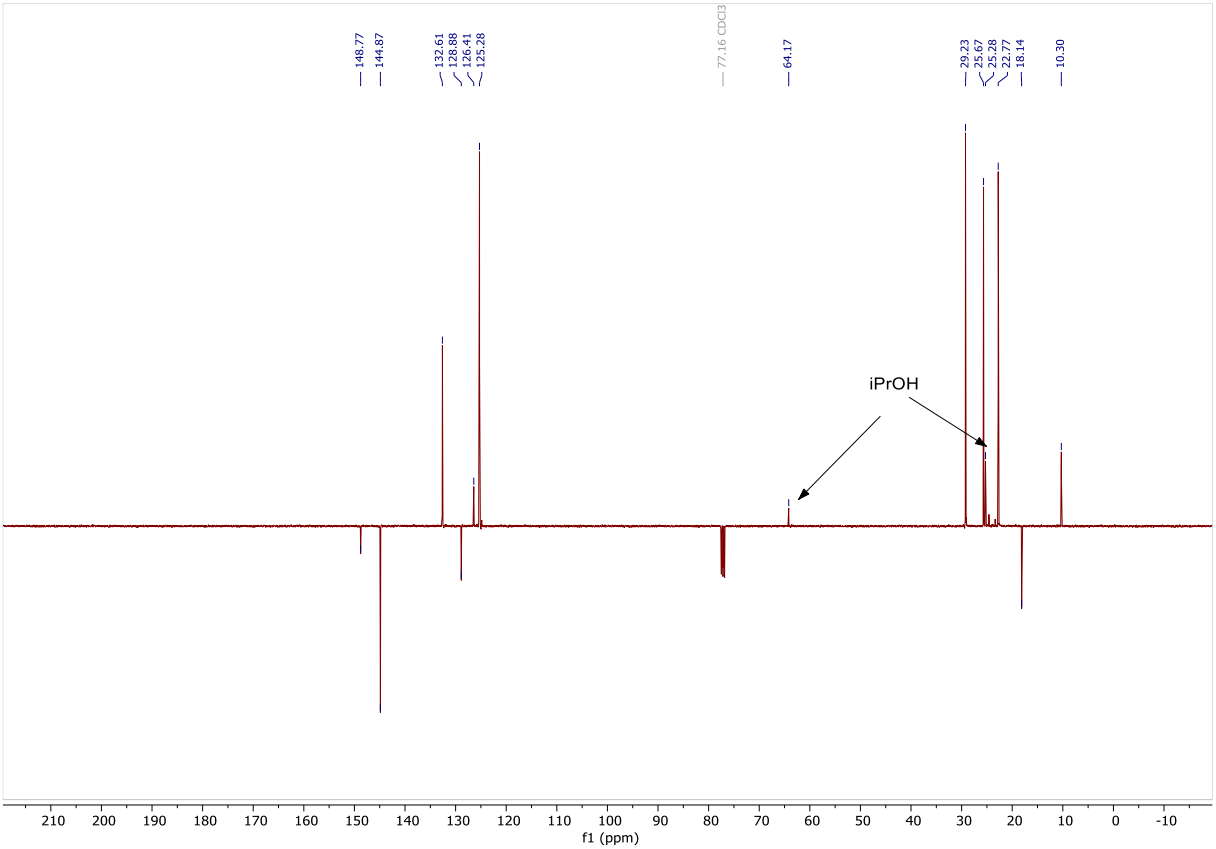


Fig. S26. ^{13}C{^{1}H} APT NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-ethylimidazolium iodide (**2b**)

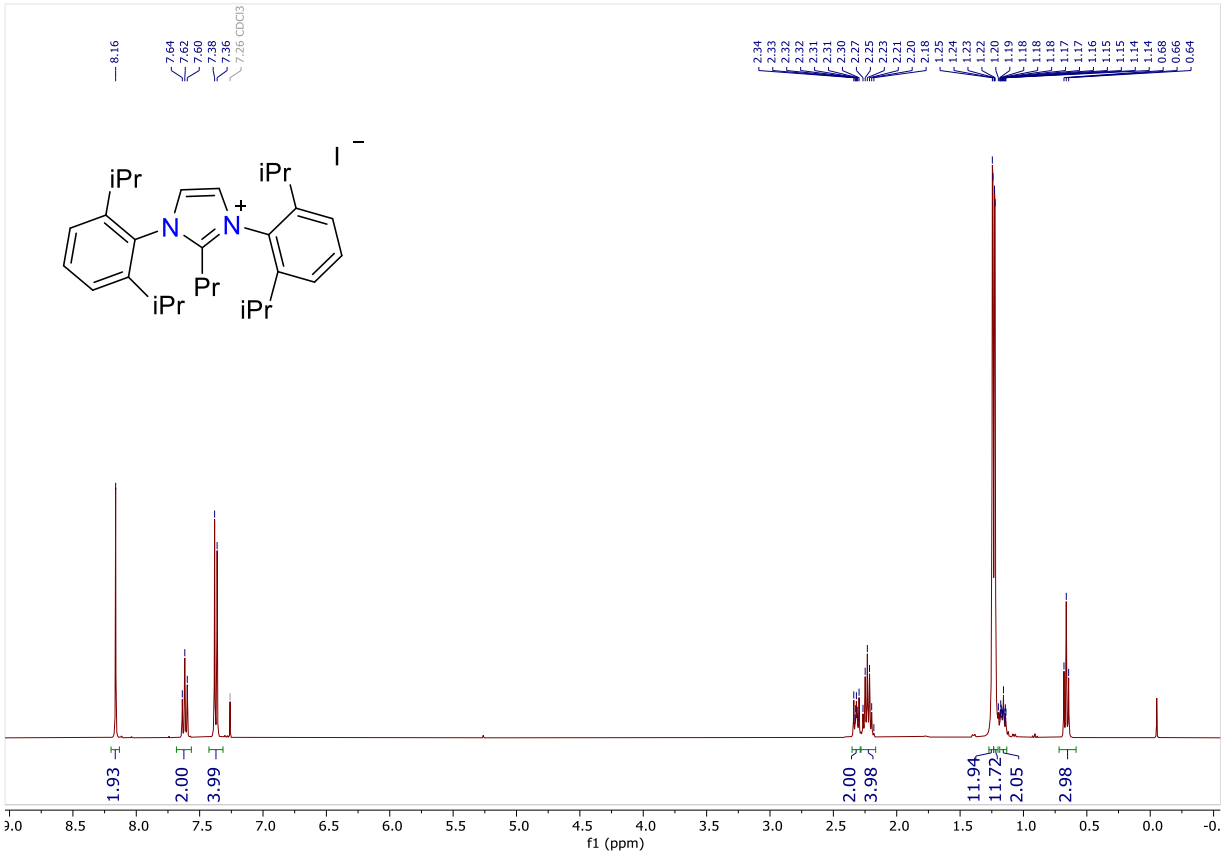


Fig. S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-propylimidazolium iodide (**2c**)

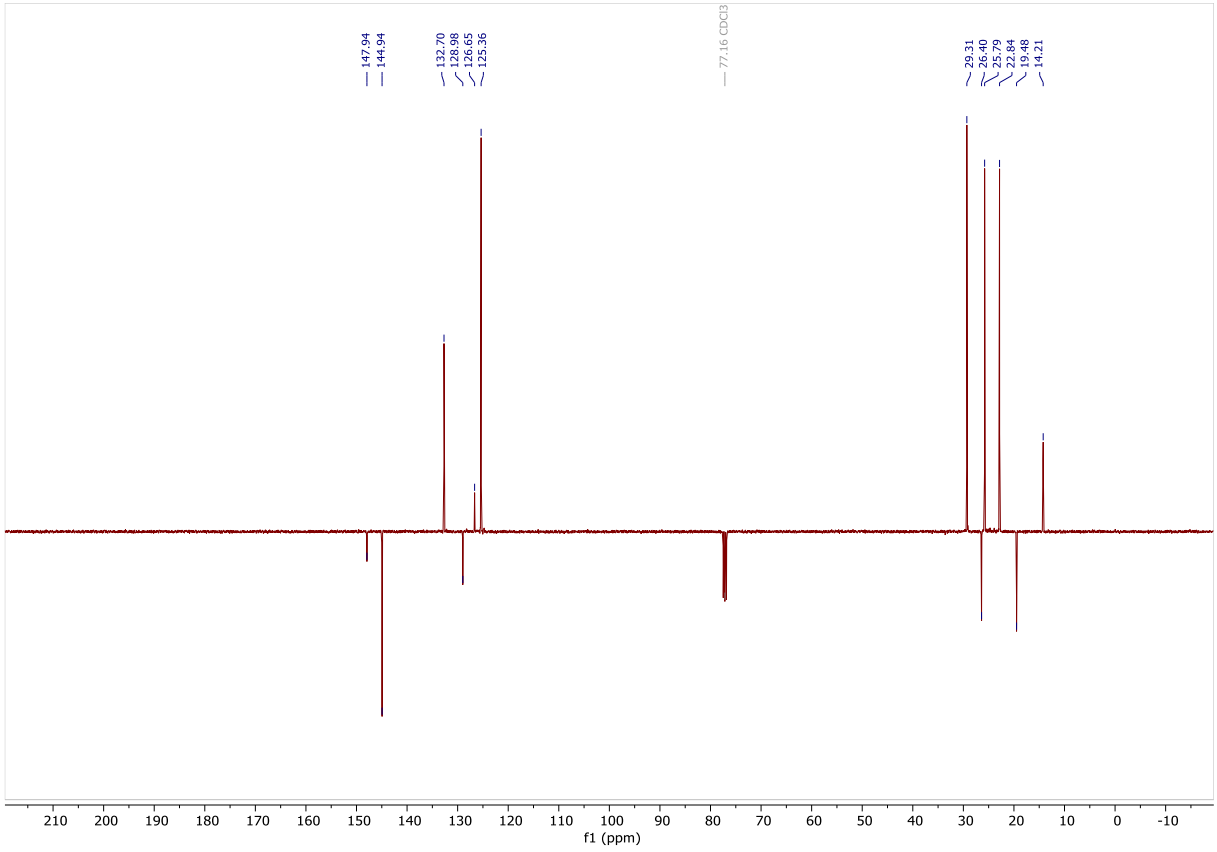


Fig. S28. ^{13}C{^{1}H} APT NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-propylimidazolium iodide (**2c**)

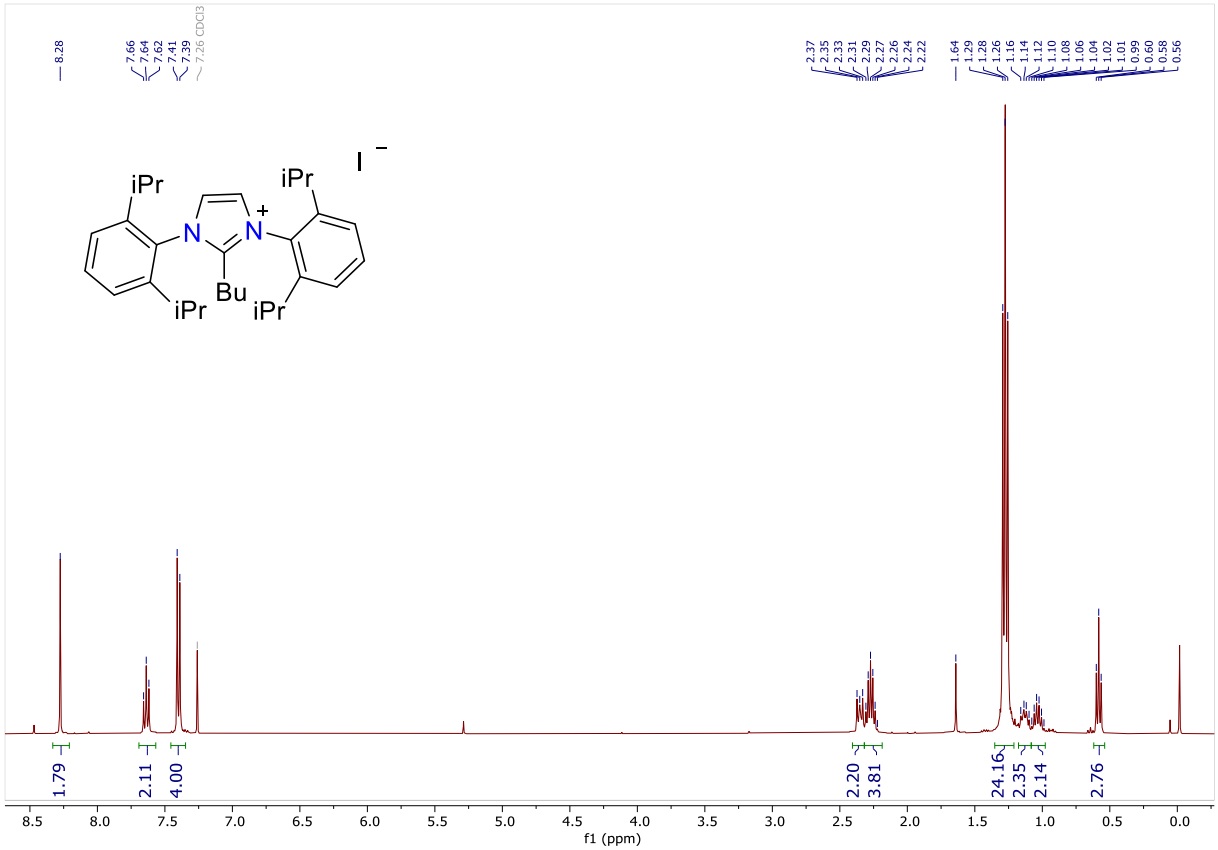


Fig. S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-butyl-1,3-bis(2,6-diisopropyl-phenyl)imidazolium iodide (**2d**)

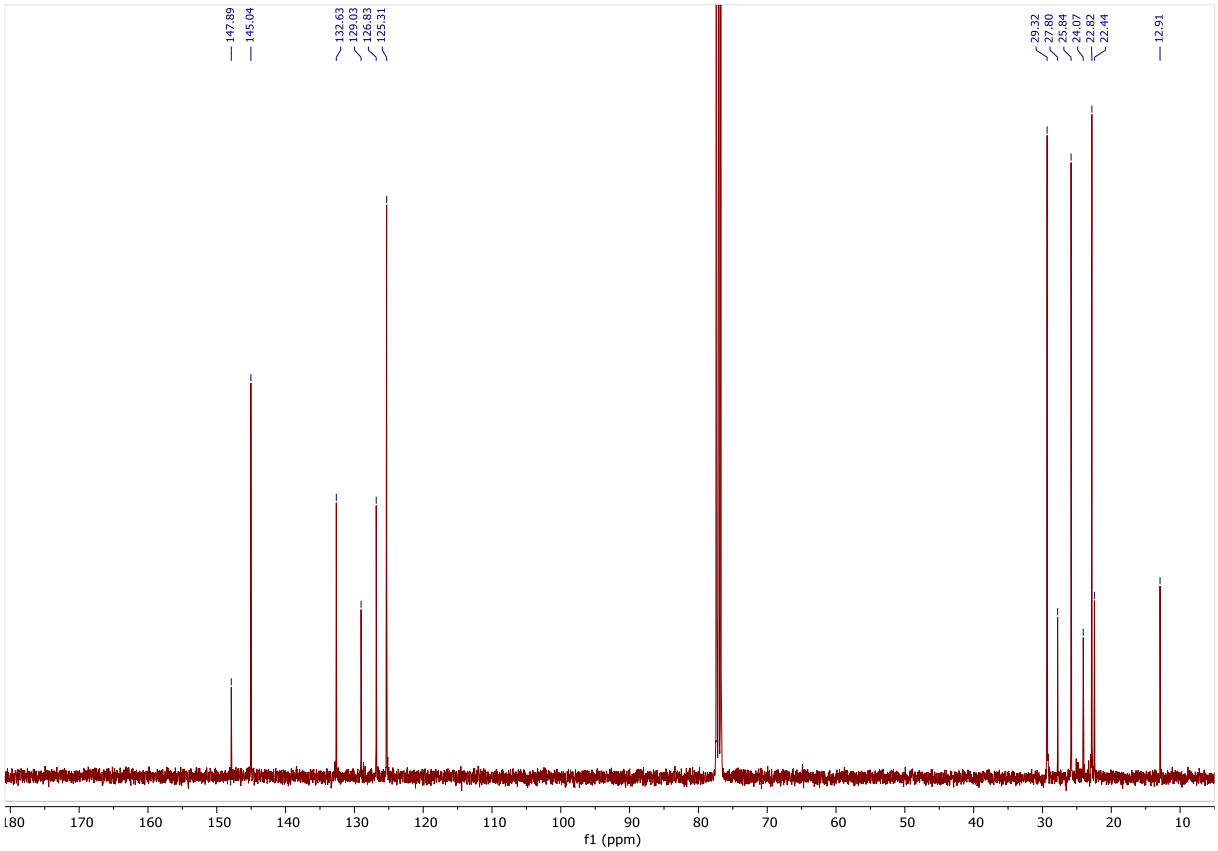


Fig. S30. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-butyl-1,3-bis(2,6-di-isopropylphenyl)imidazolium iodide (**2d**)

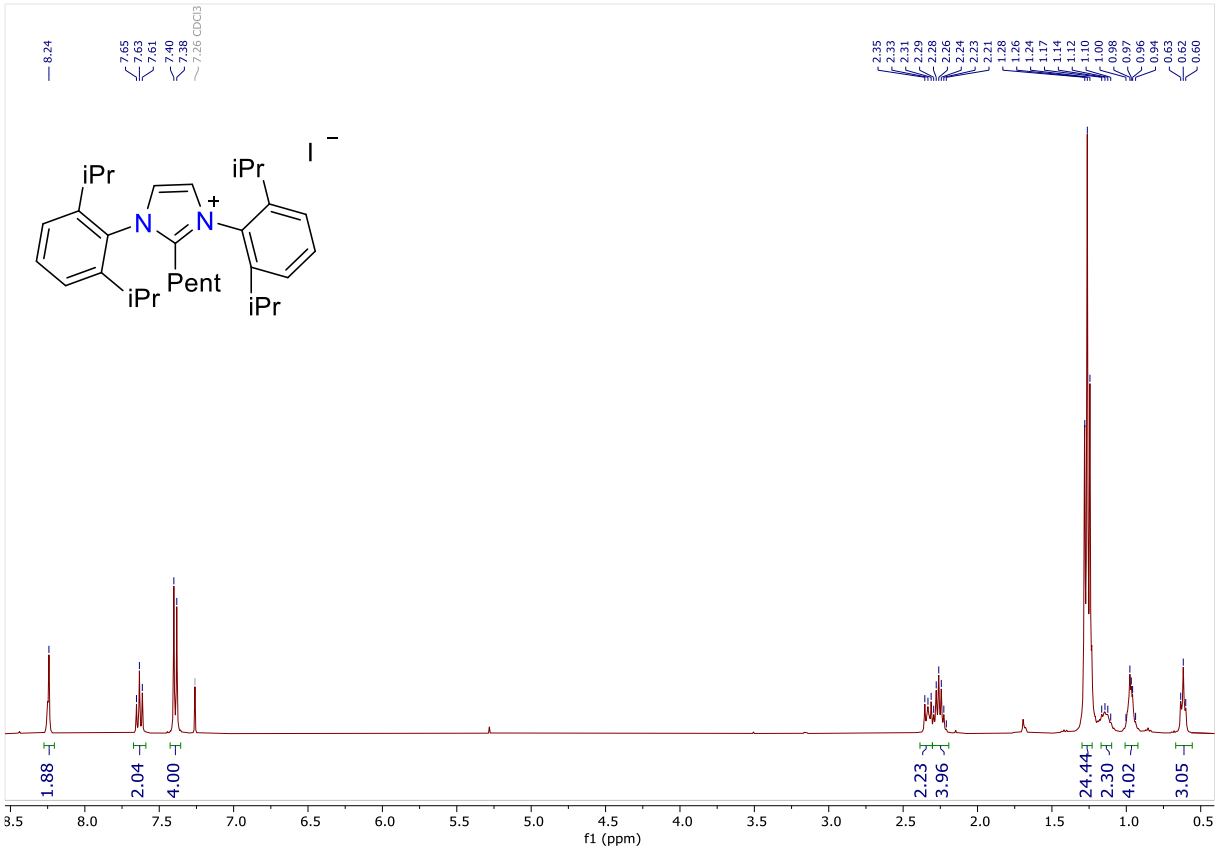


Fig. S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-pentylimidazolium iodide (**2e**)

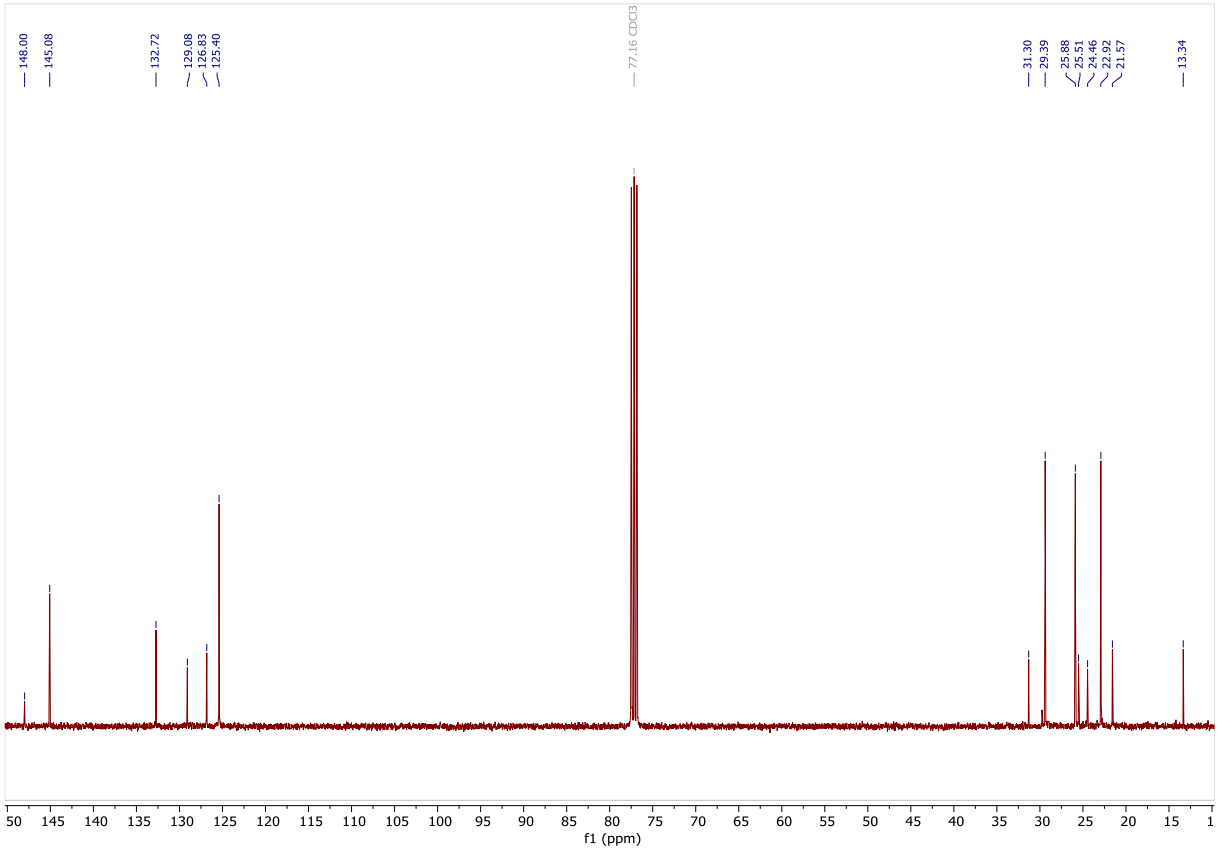


Fig. S32. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-pentylimidazolium iodide (**2e**)

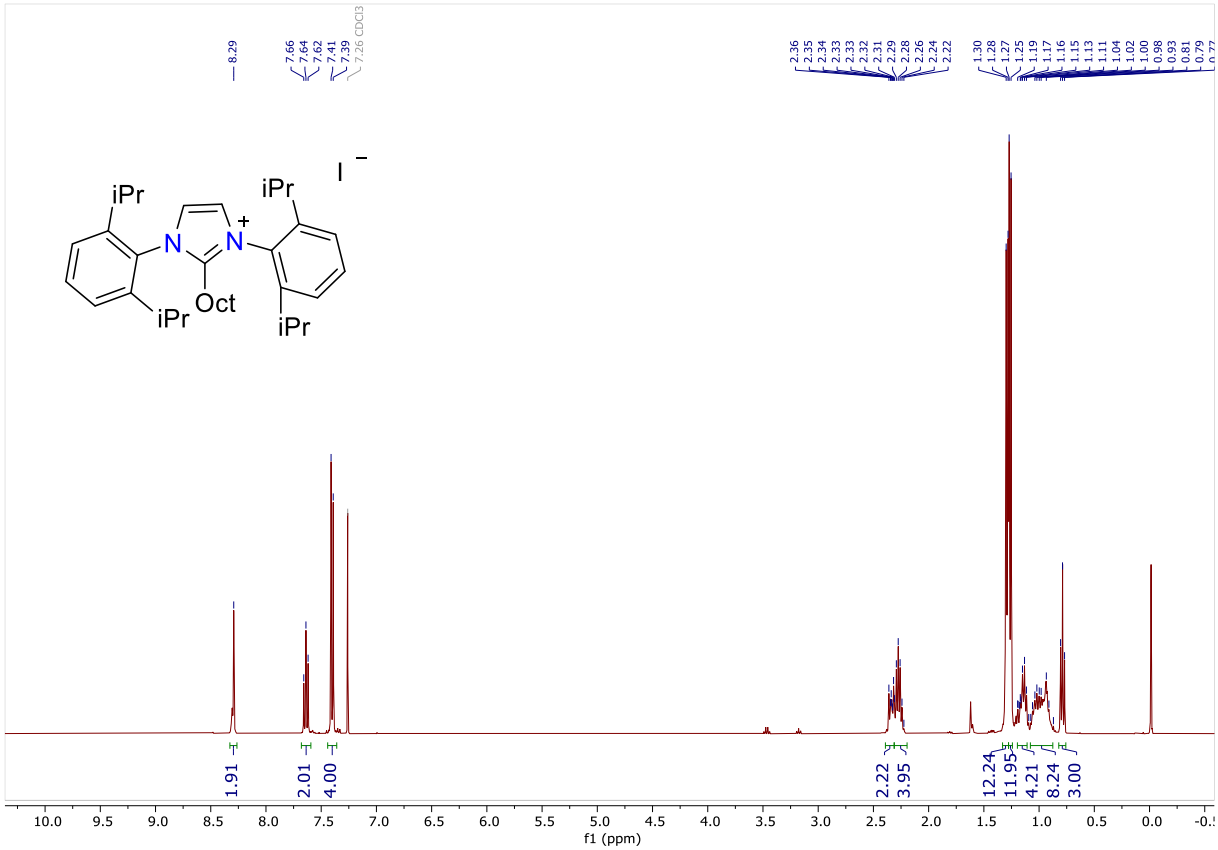


Fig. S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-octylimidazolium iodide (**2f**)

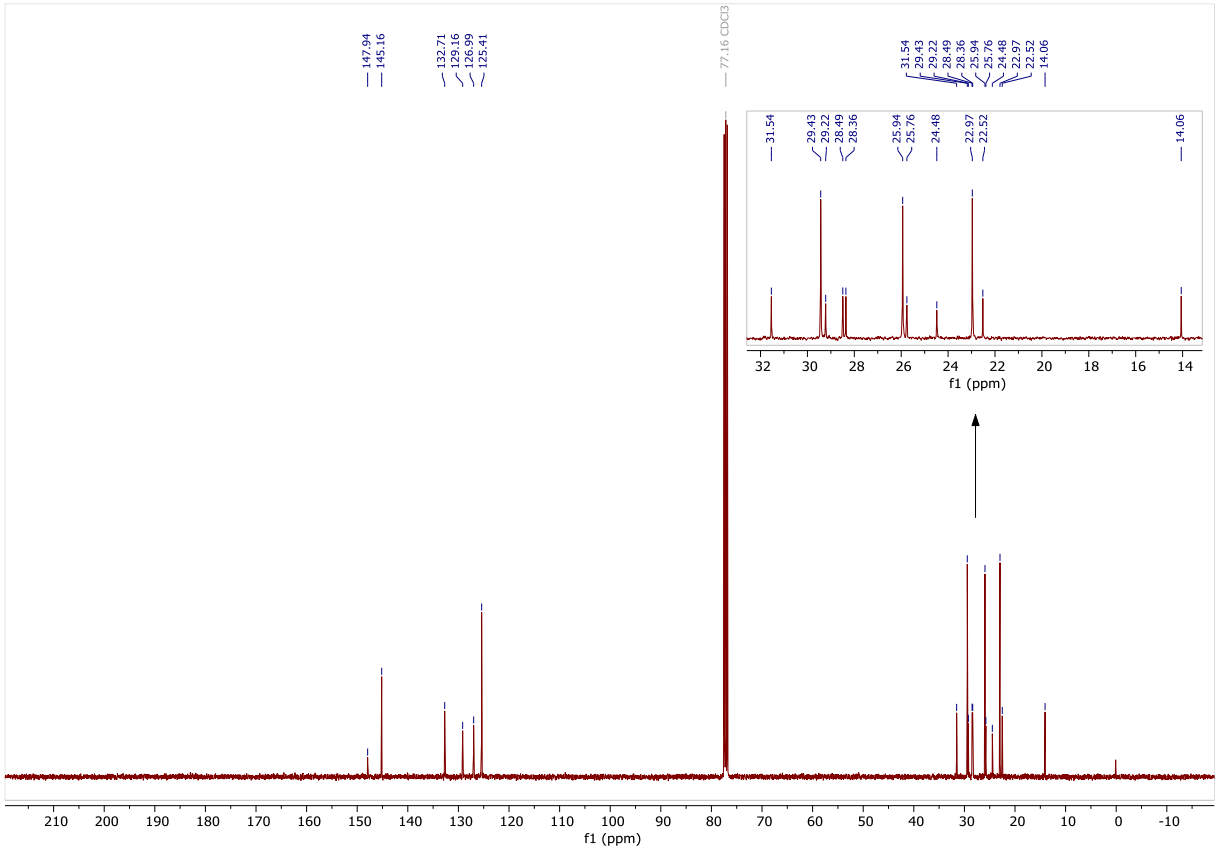


Fig. S34. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-octylimidazolium iodide (**2f**)

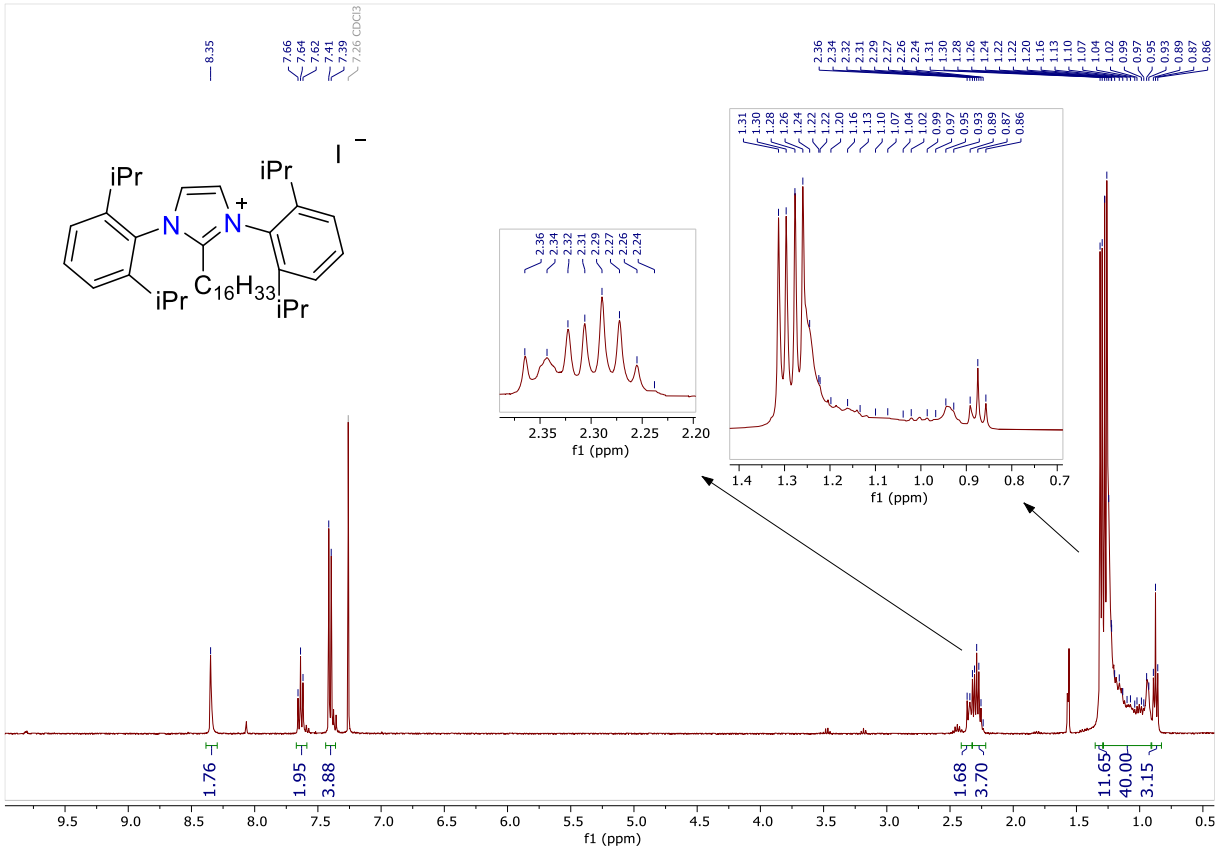


Fig. S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-hexadecylimidazolium iodide (**2g**)

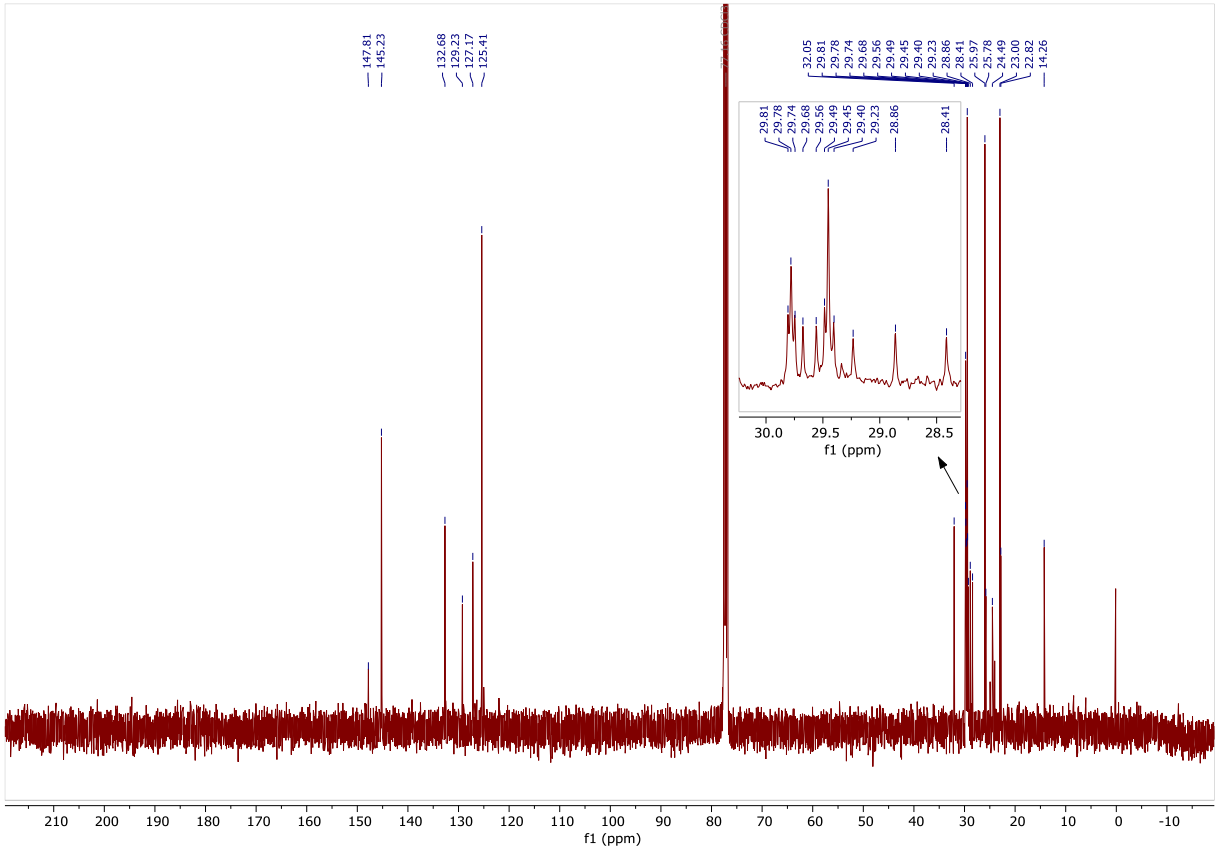


Fig. S36. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-hexadecylimidazolium iodide (**2g**)

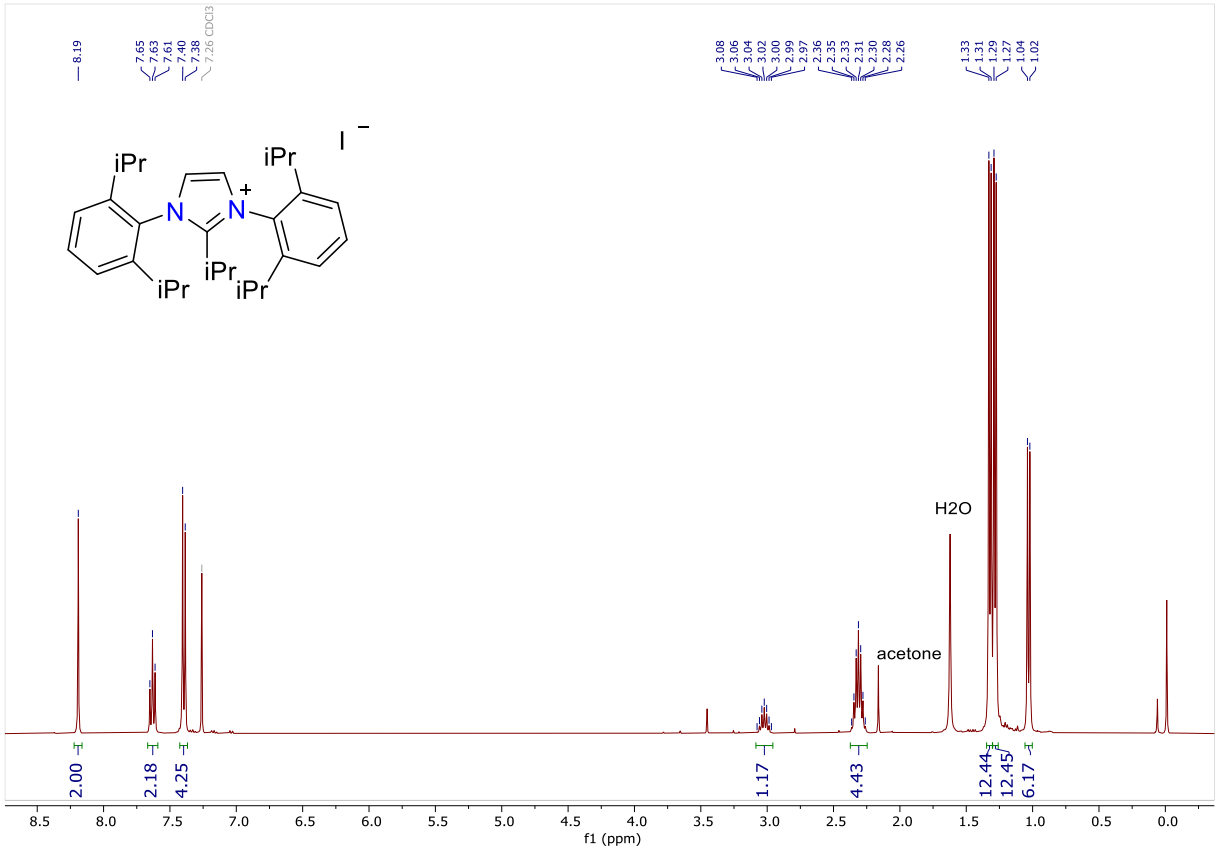


Fig. S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-isopropylimidazolium iodide (**2h**)

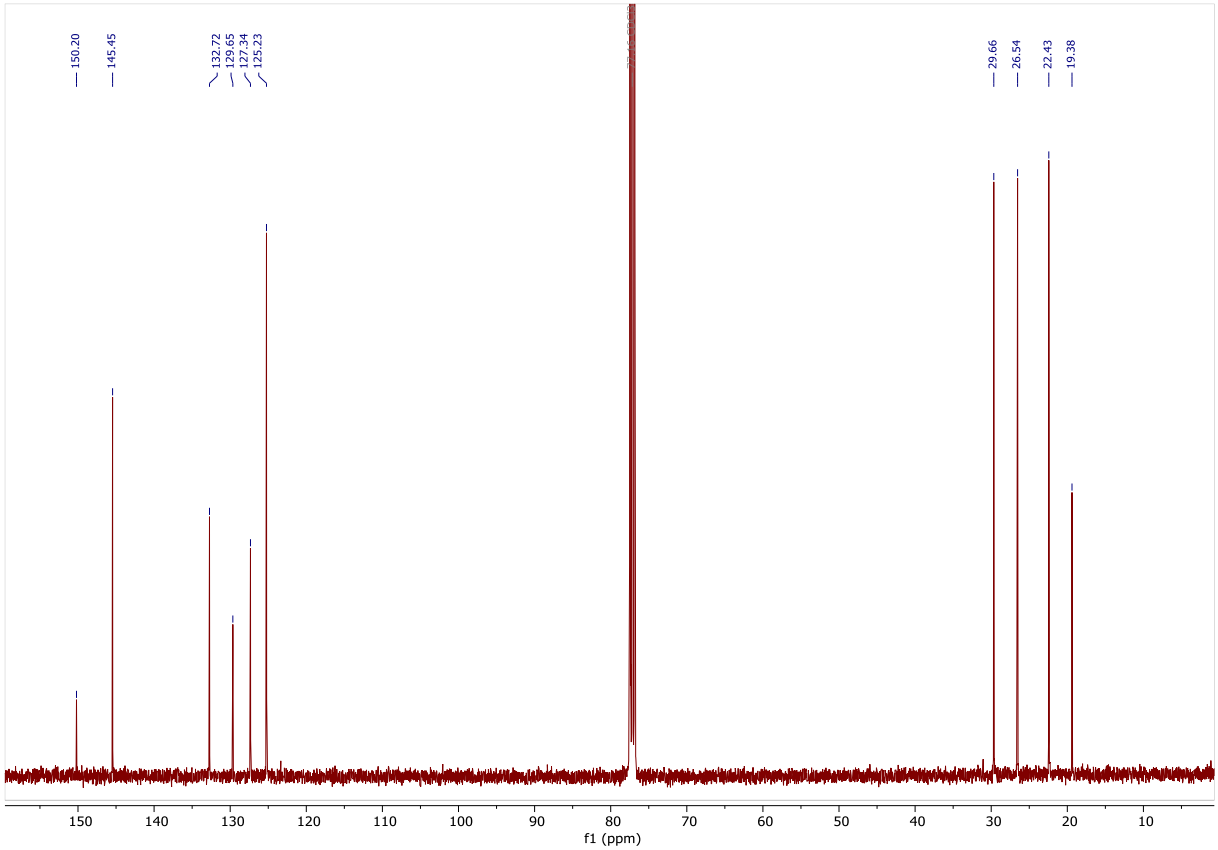


Fig. S38. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-isopropylimidazolium iodide (**2h**)

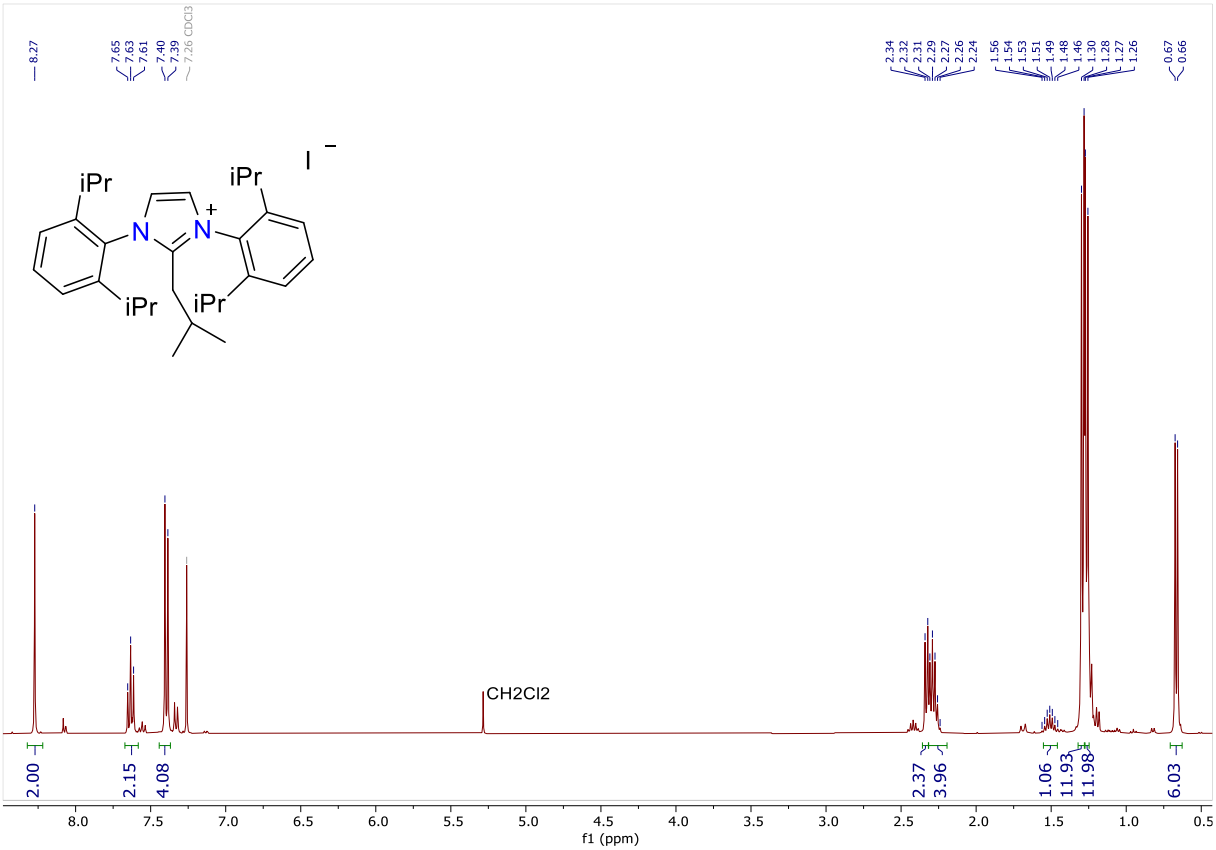


Fig. S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-isobutylimidazolium iodide (**2j**)

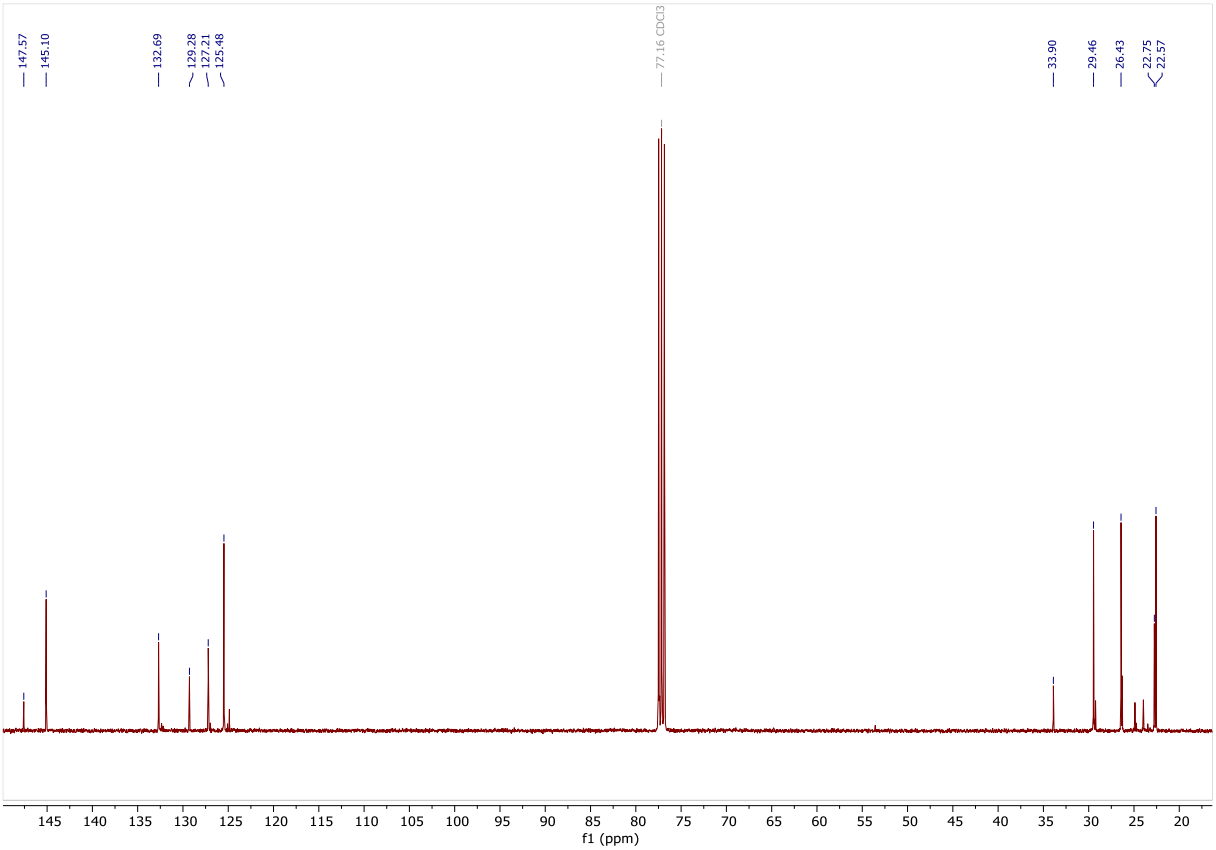


Fig. S40. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-isobutylimidazolium iodide (**2j**)

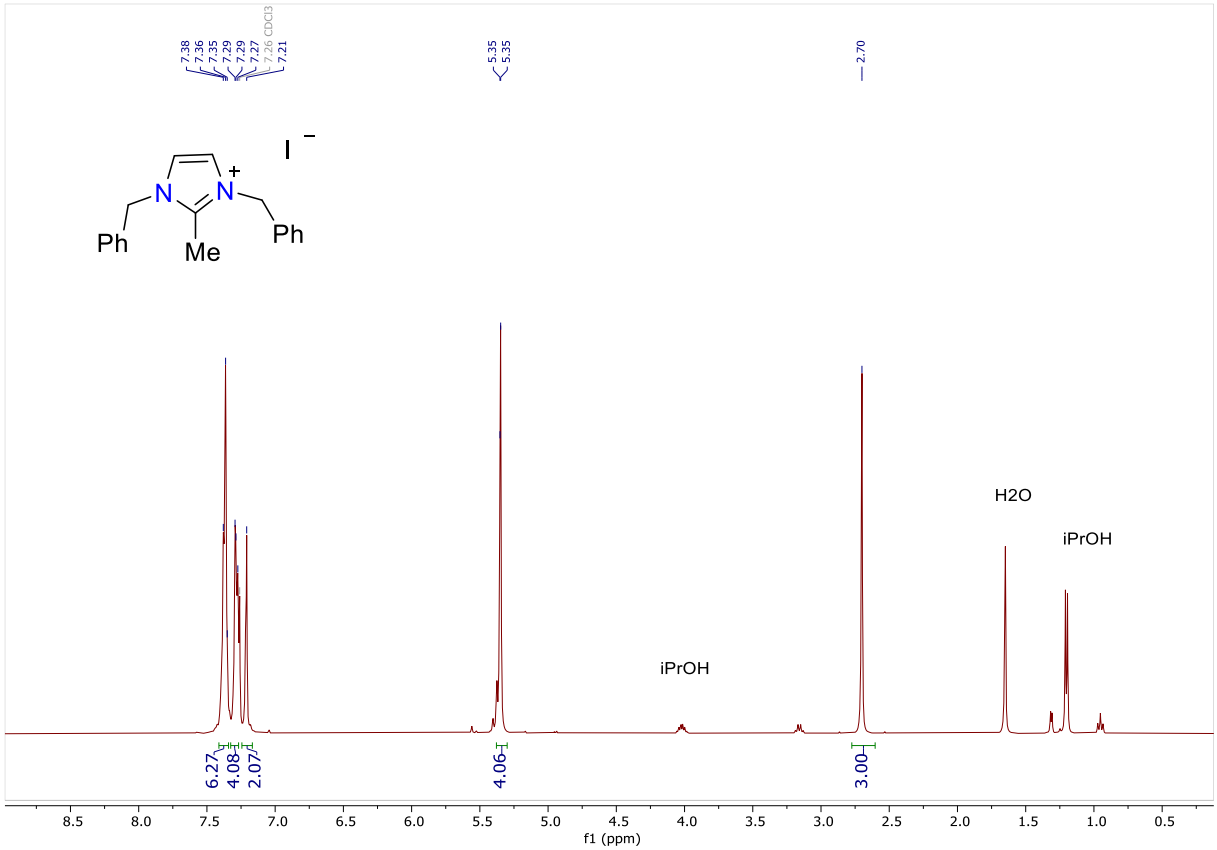


Fig. S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-methylimidazolium iodide (**3a**)

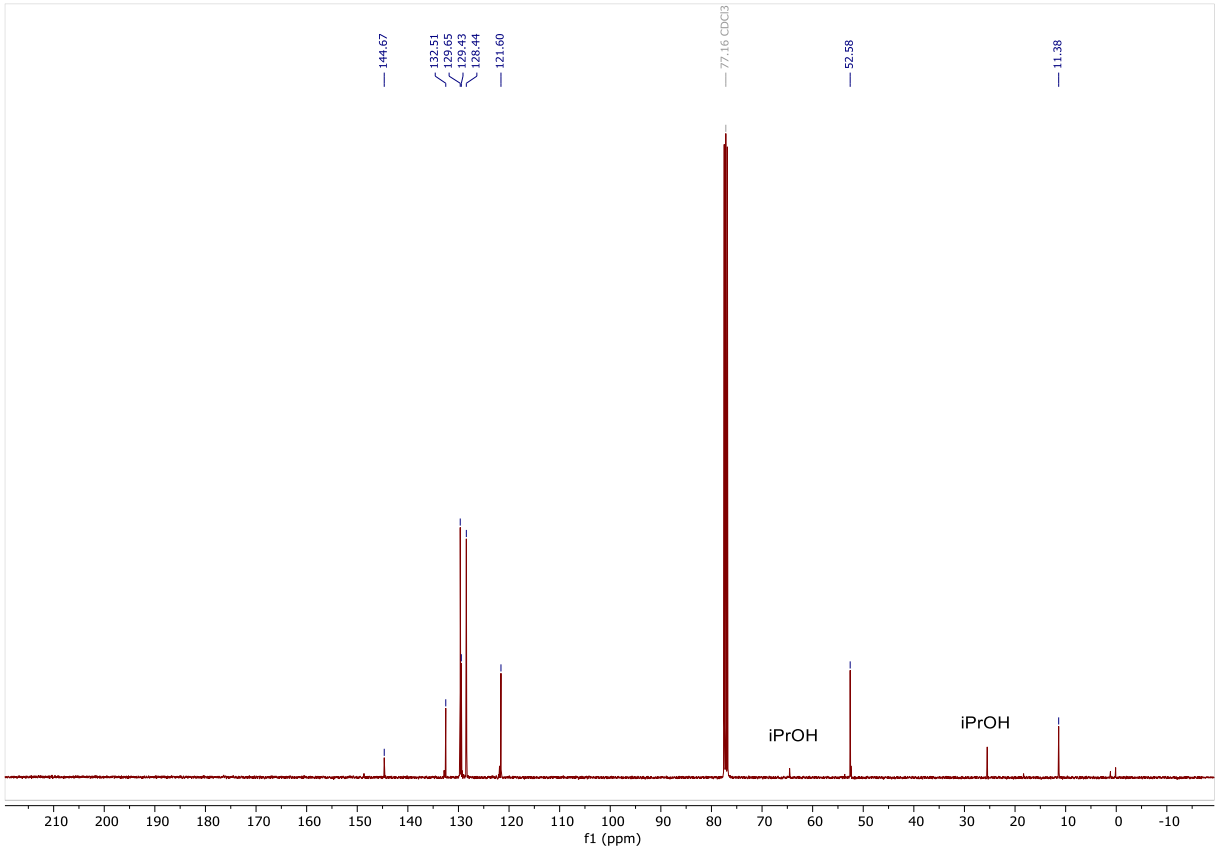


Fig. S42. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-methylimidazolium iodide (**3a**)

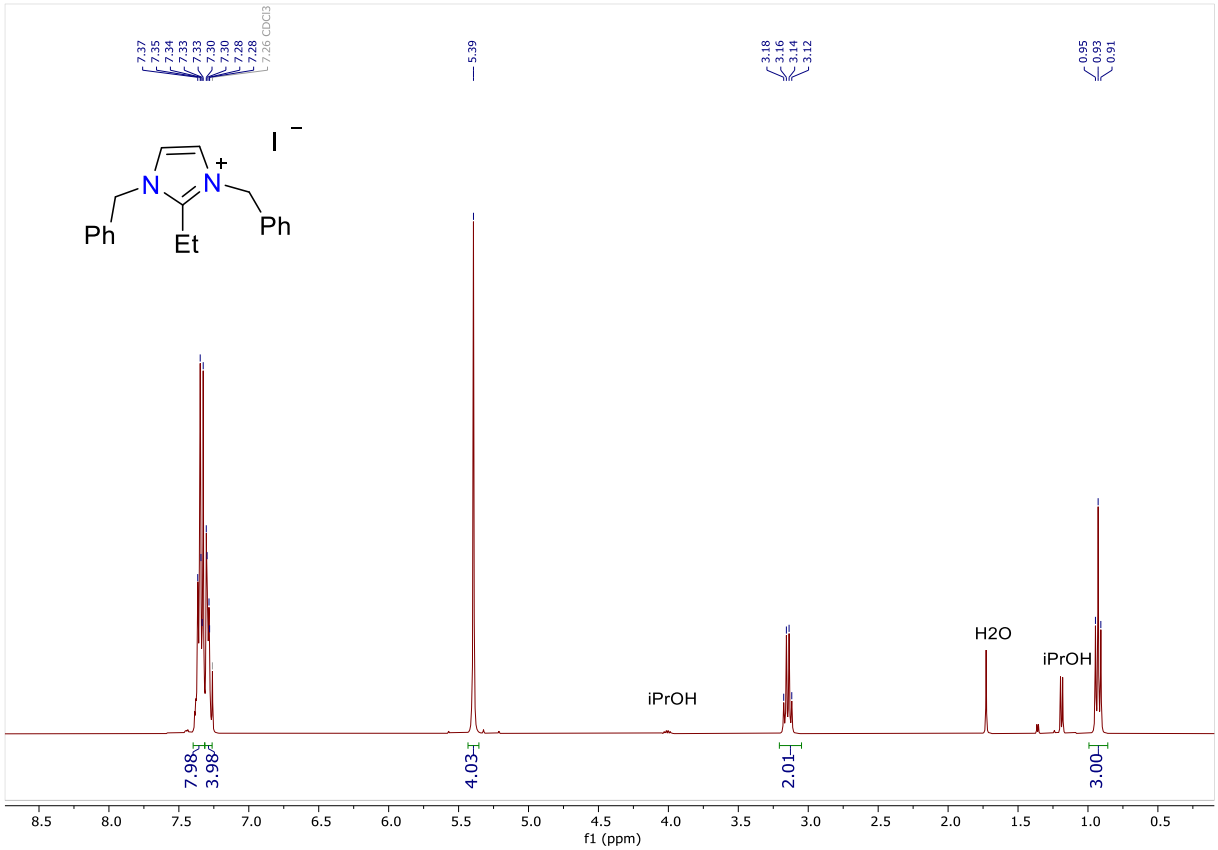


Fig. S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-ethylimidazolium iodide (**3b**)

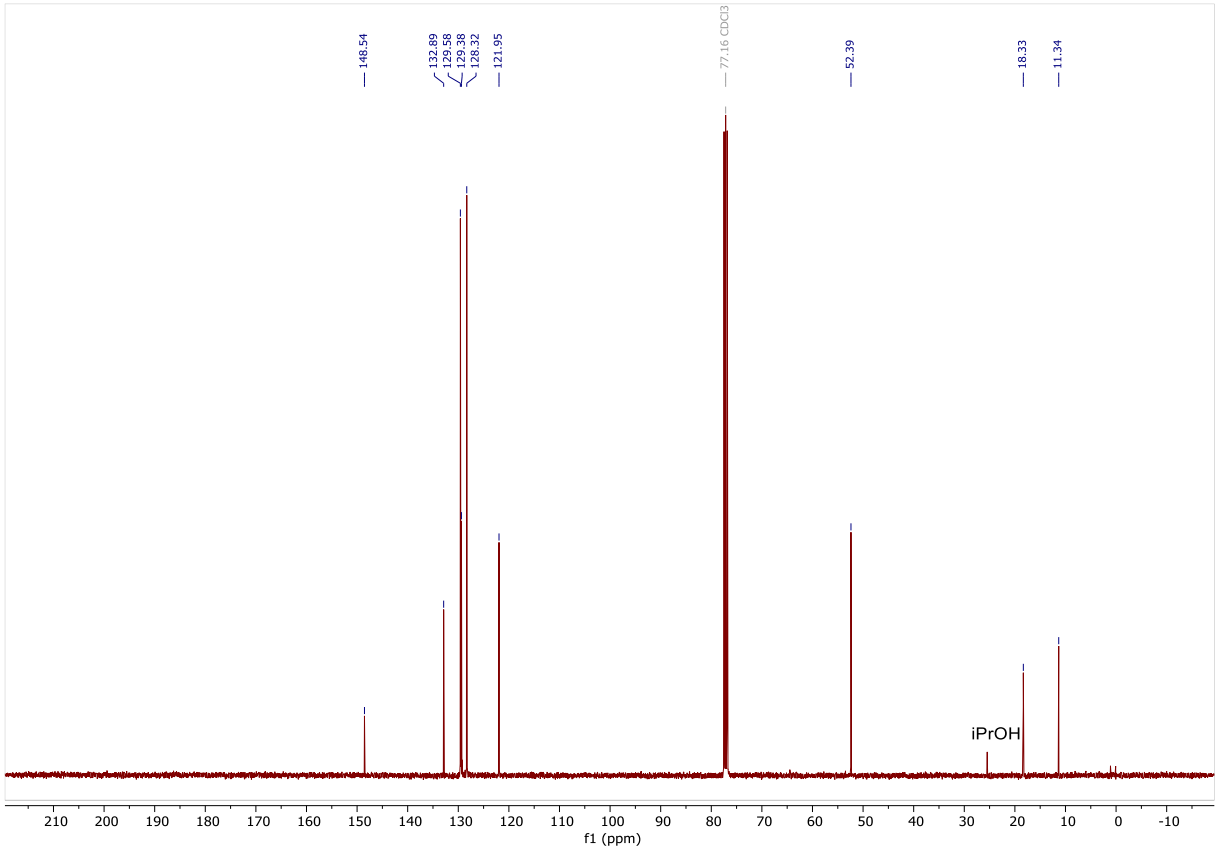


Fig. S44. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-ethyl-imidazolium iodide (**3b**)

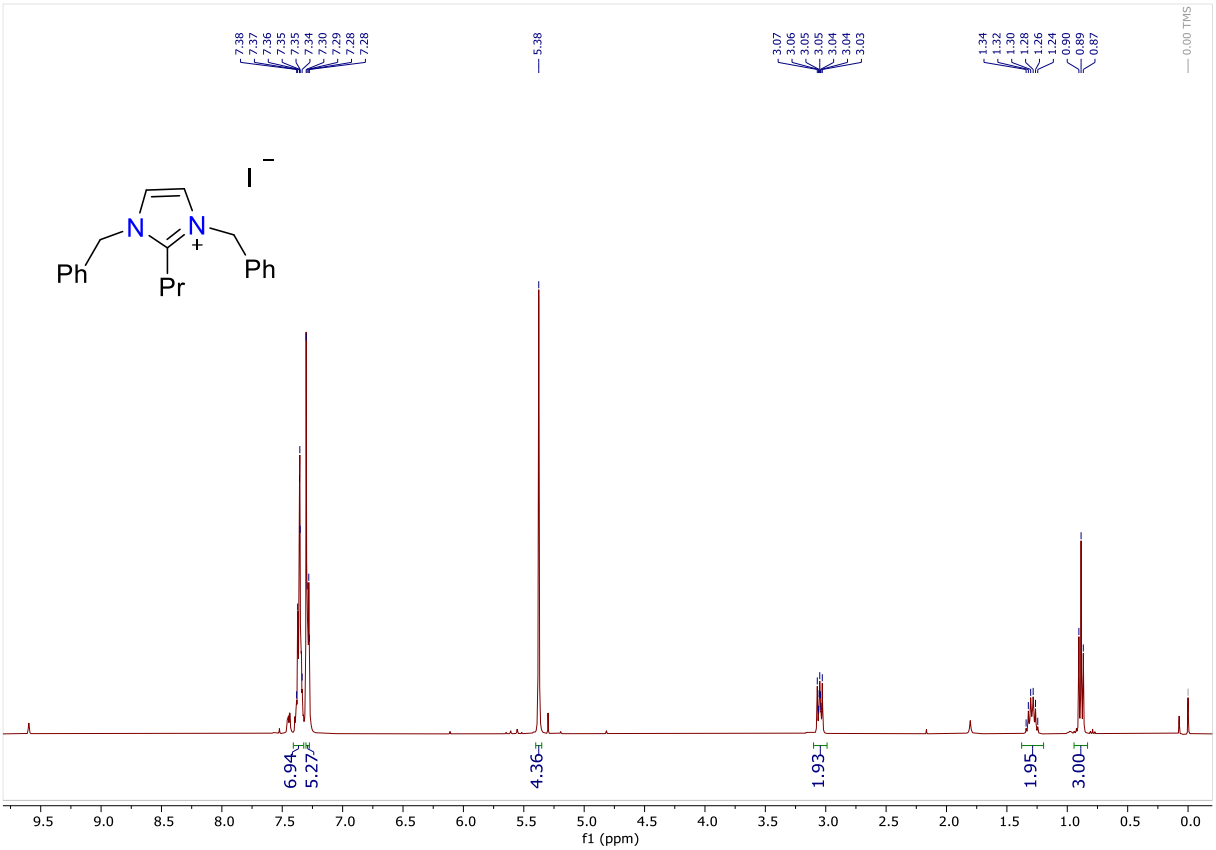


Fig. S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-propylimidazolium iodide (**3c**)

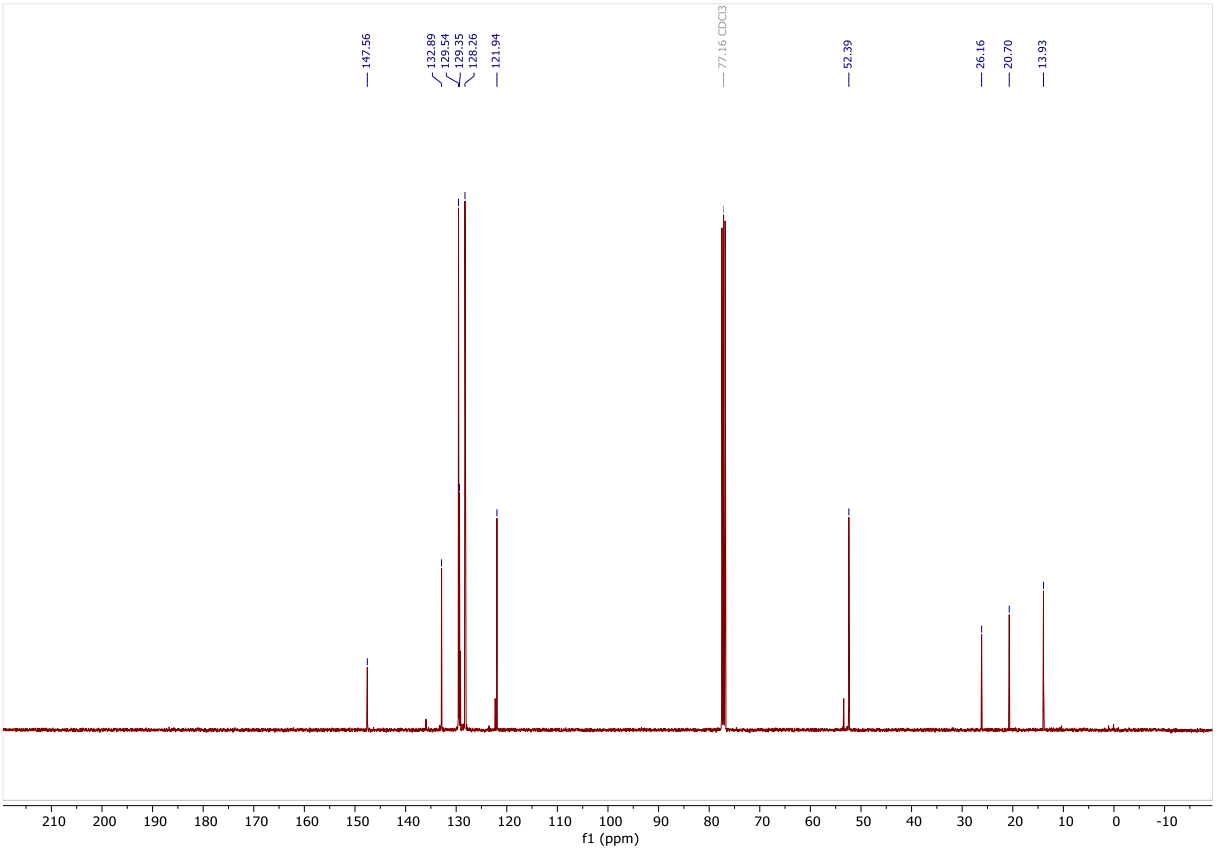


Fig. S46. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-propyl-imidazolium iodide (**3c**)

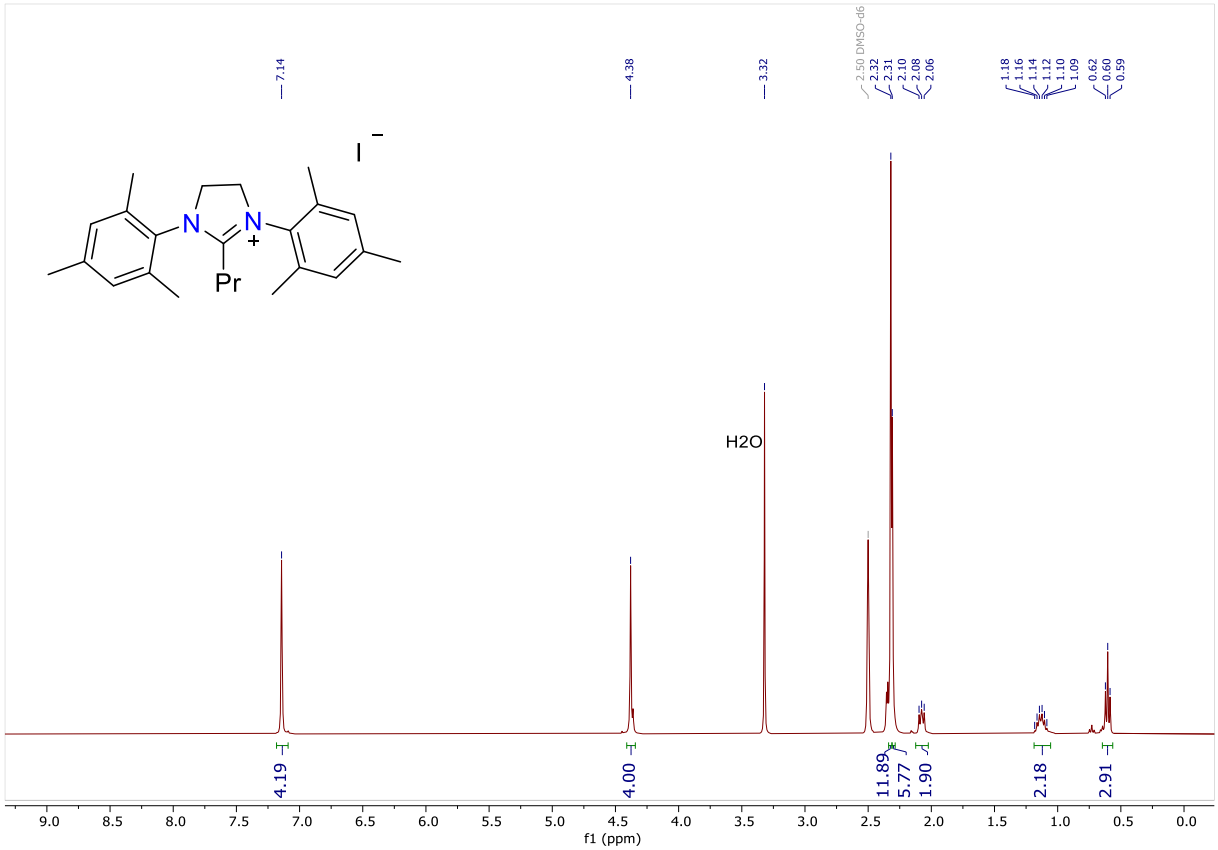


Fig. S47. ^{1}H NMR spectrum (400 MHz, dmso-d_6, 298 K) of 1,3-dimesityl-2-propylimidazolinium iodide (**4**)

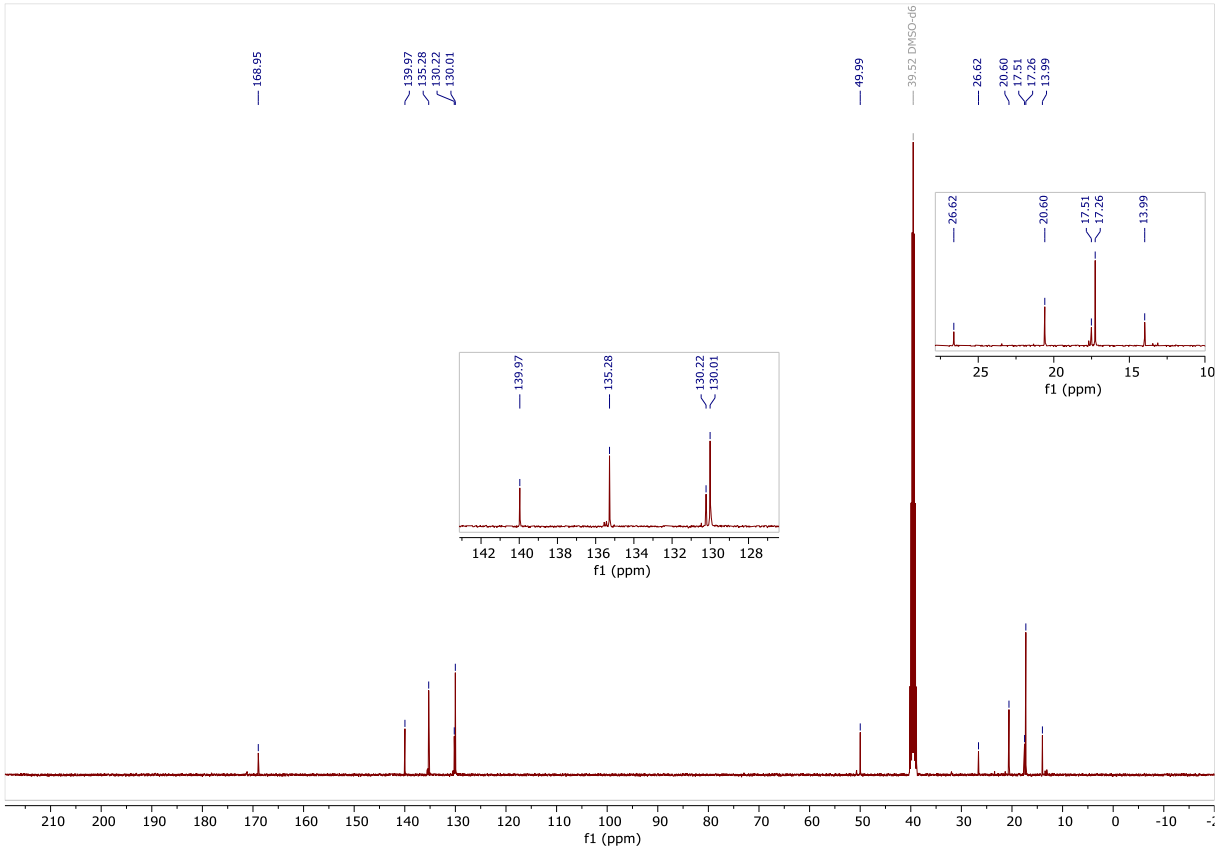


Fig. S48. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, dmso-d_6, 298 K) of 1,3-dimesityl-2-propylimidazolinium iodide (**4**)

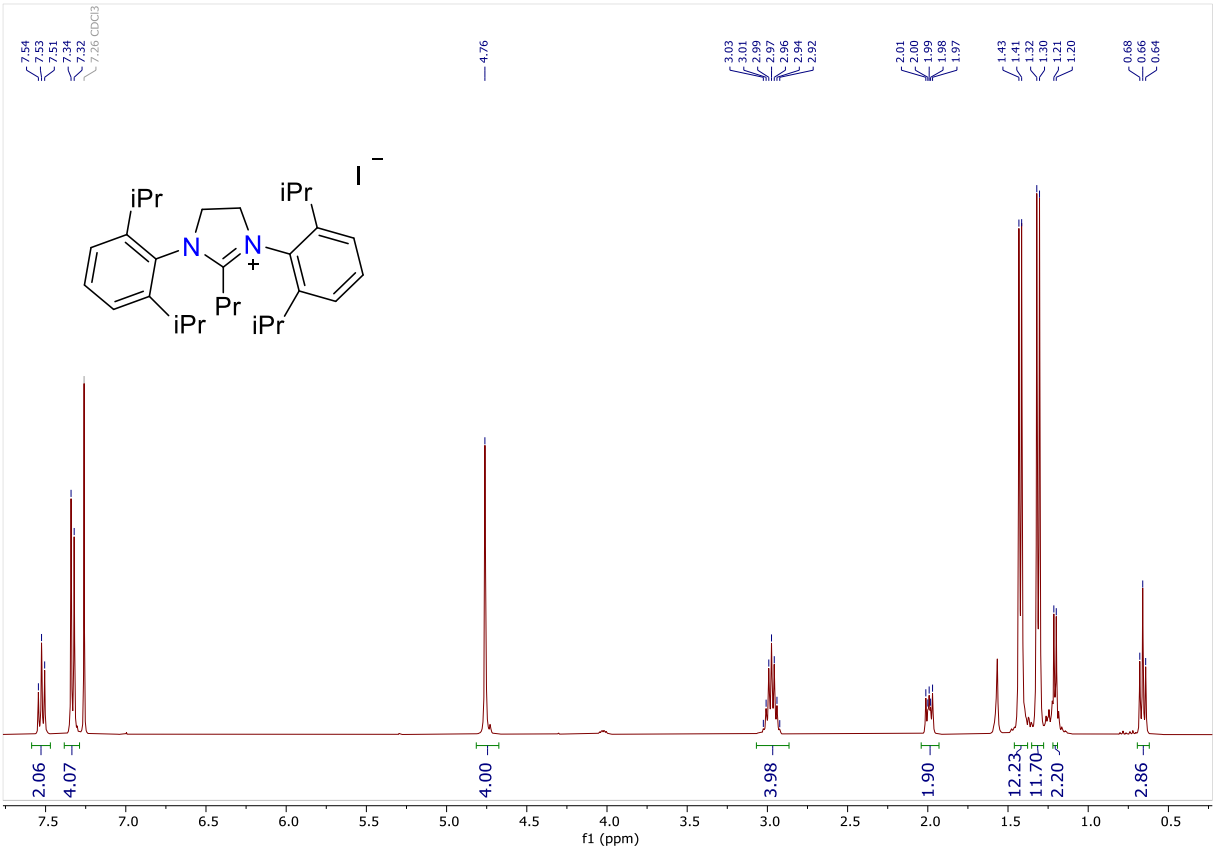


Fig. S49. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-propylimidazolinium (**5**)

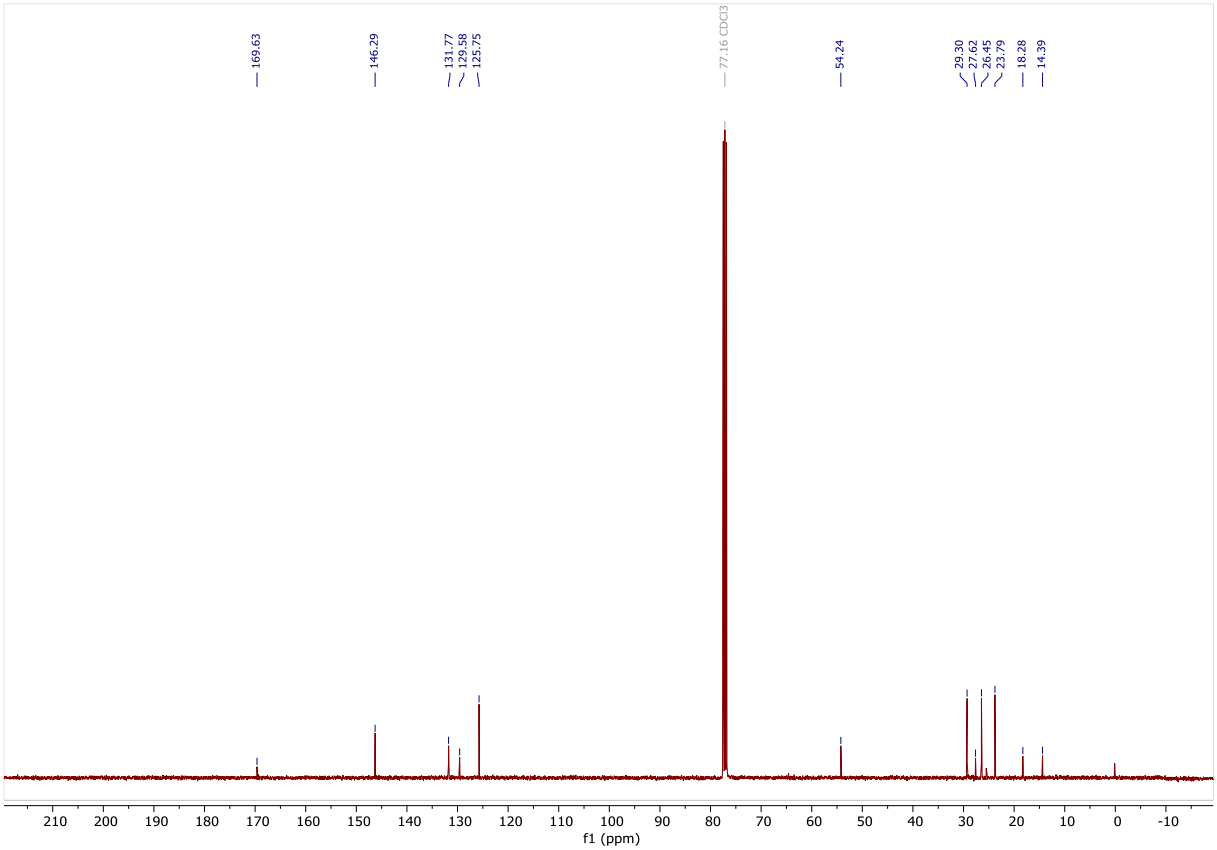


Fig. S50. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-propylimidazolinium (**5**)

5.2 NMR spectra of iodinated products

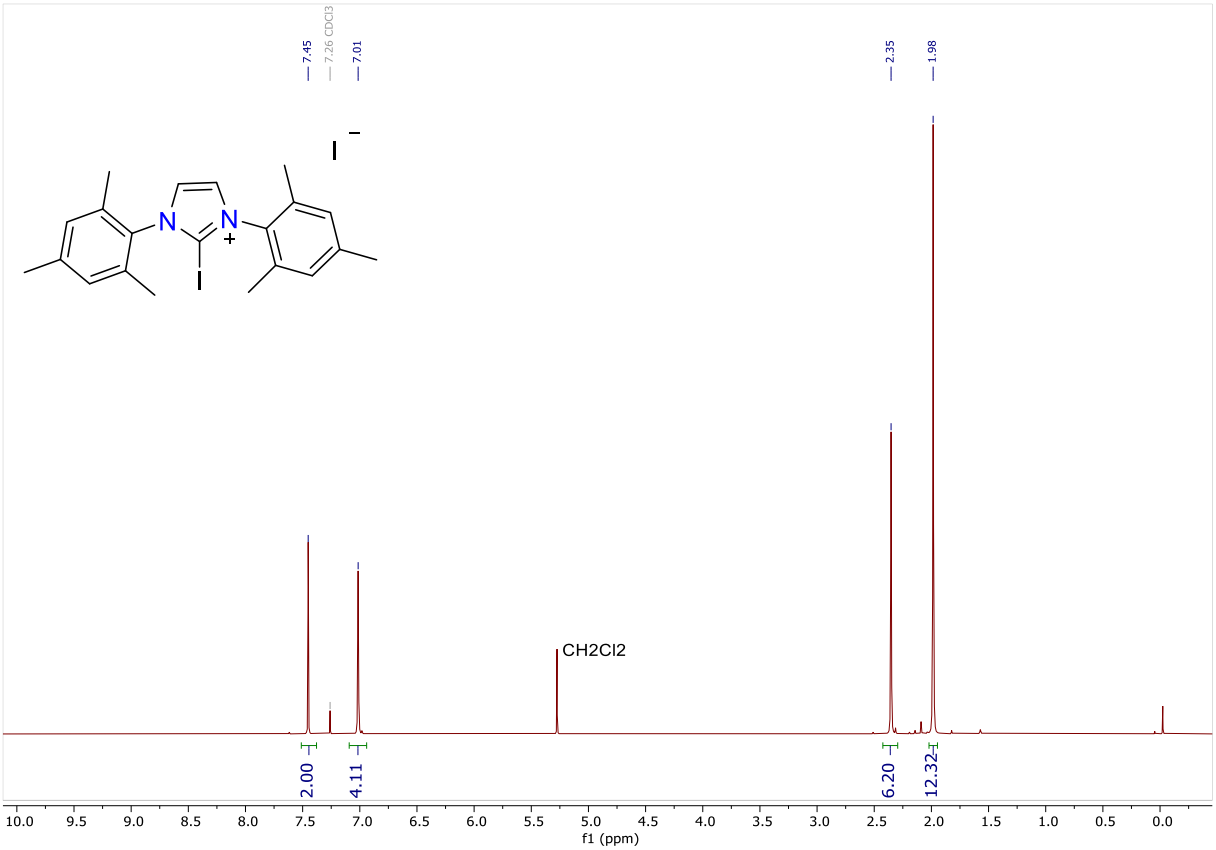


Fig. S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 2-iodo-1,3-dimesitylimidazolium iodide (**6**)

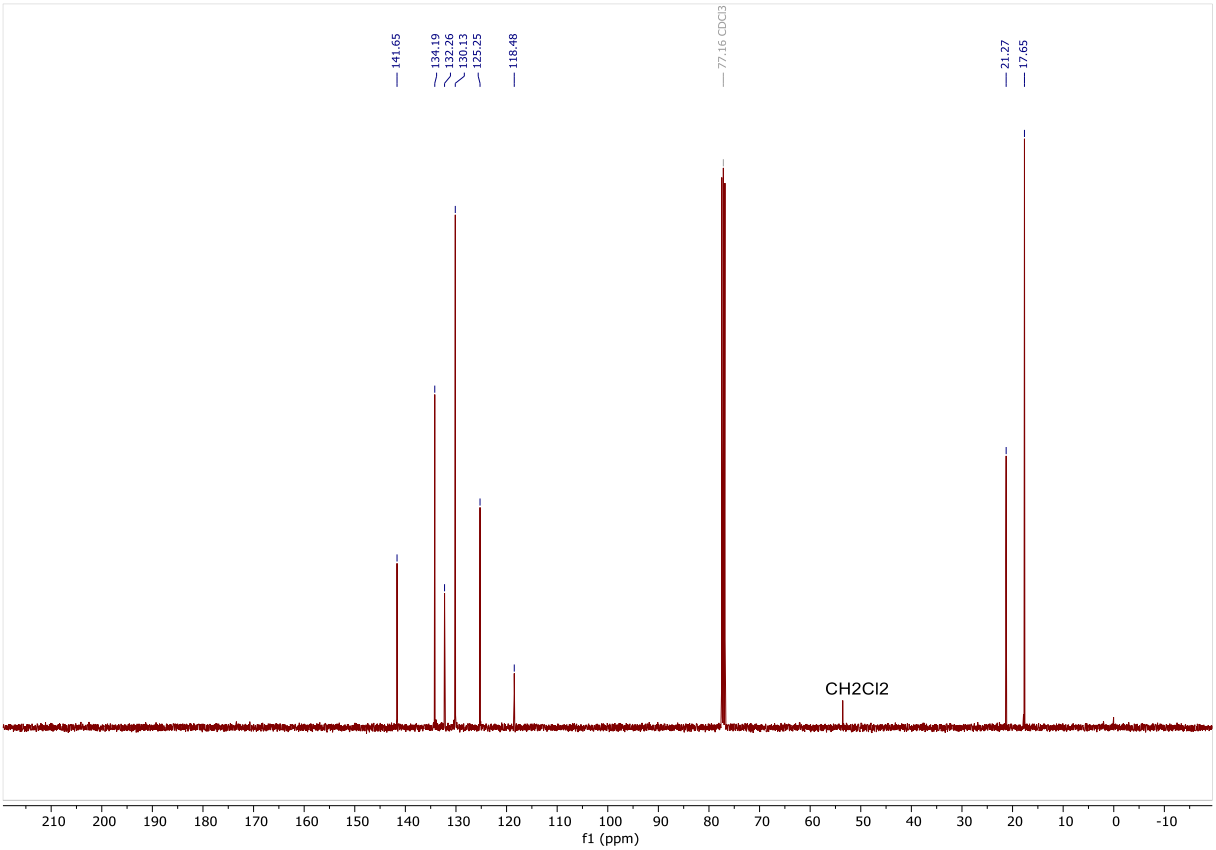


Fig. S52. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 2-iodo-1,3-dimesityl-imidazolium iodide (**6**)

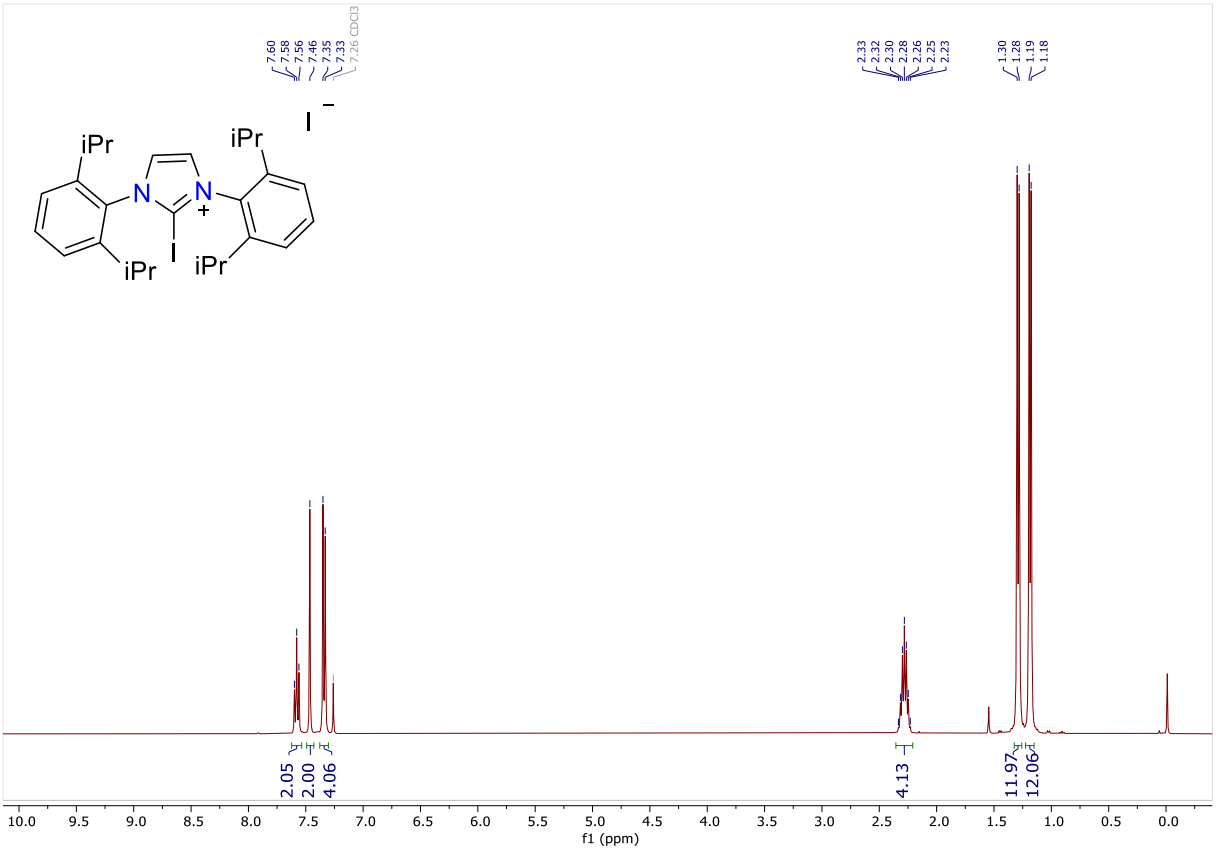


Fig. S53. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-iodoimidazolium iodide (**7**)

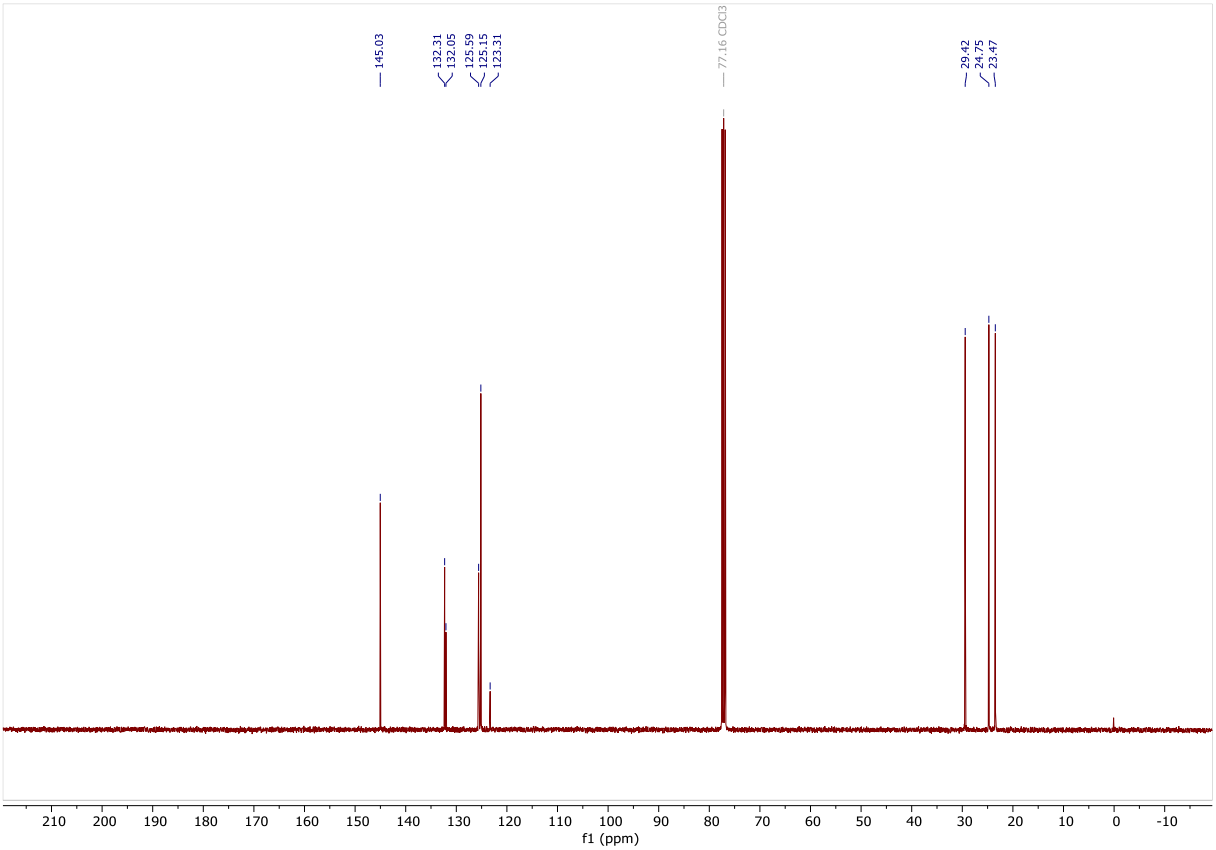


Fig. S54. $^{13}C\{^{1}H\}$ CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-iodoimidazolium iodide (**7**)

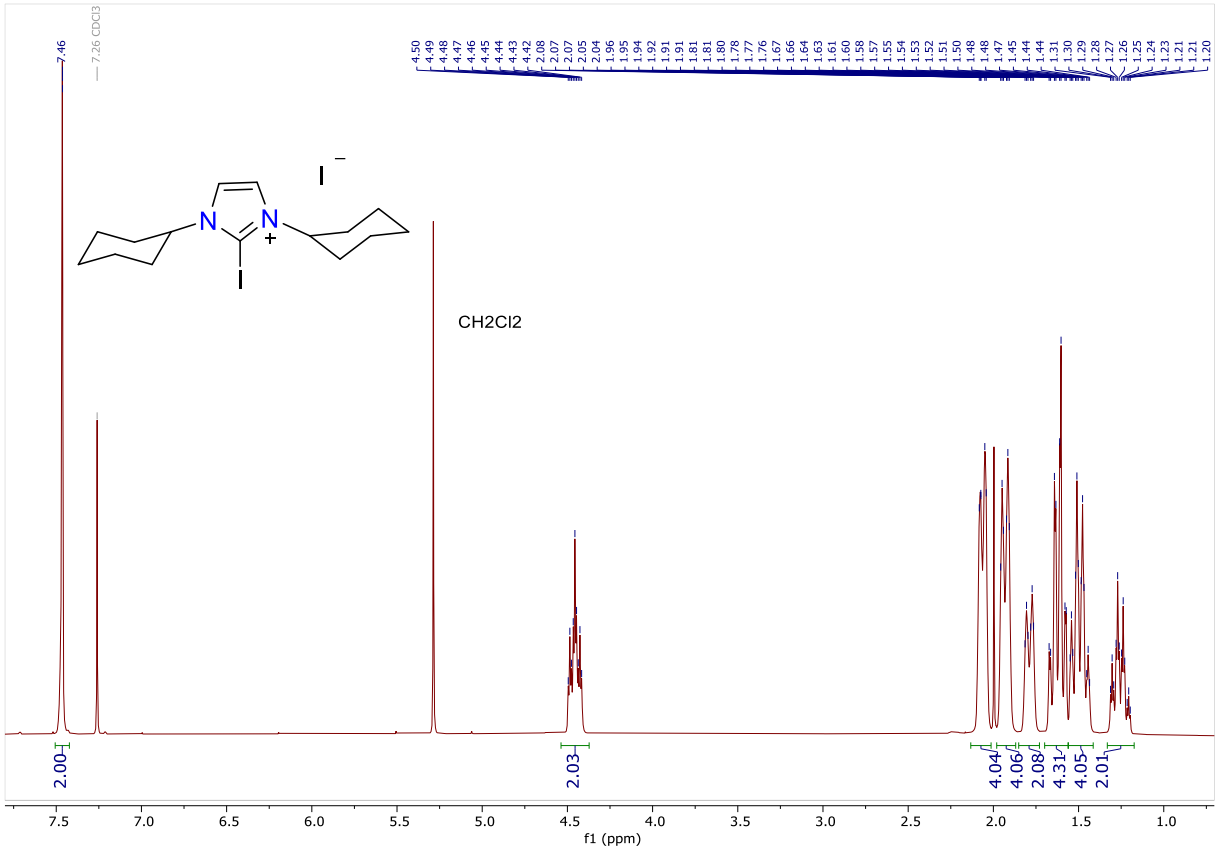


Fig. S55. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dicyclohexyl-2-iodoimidazolium iodide (**8**)

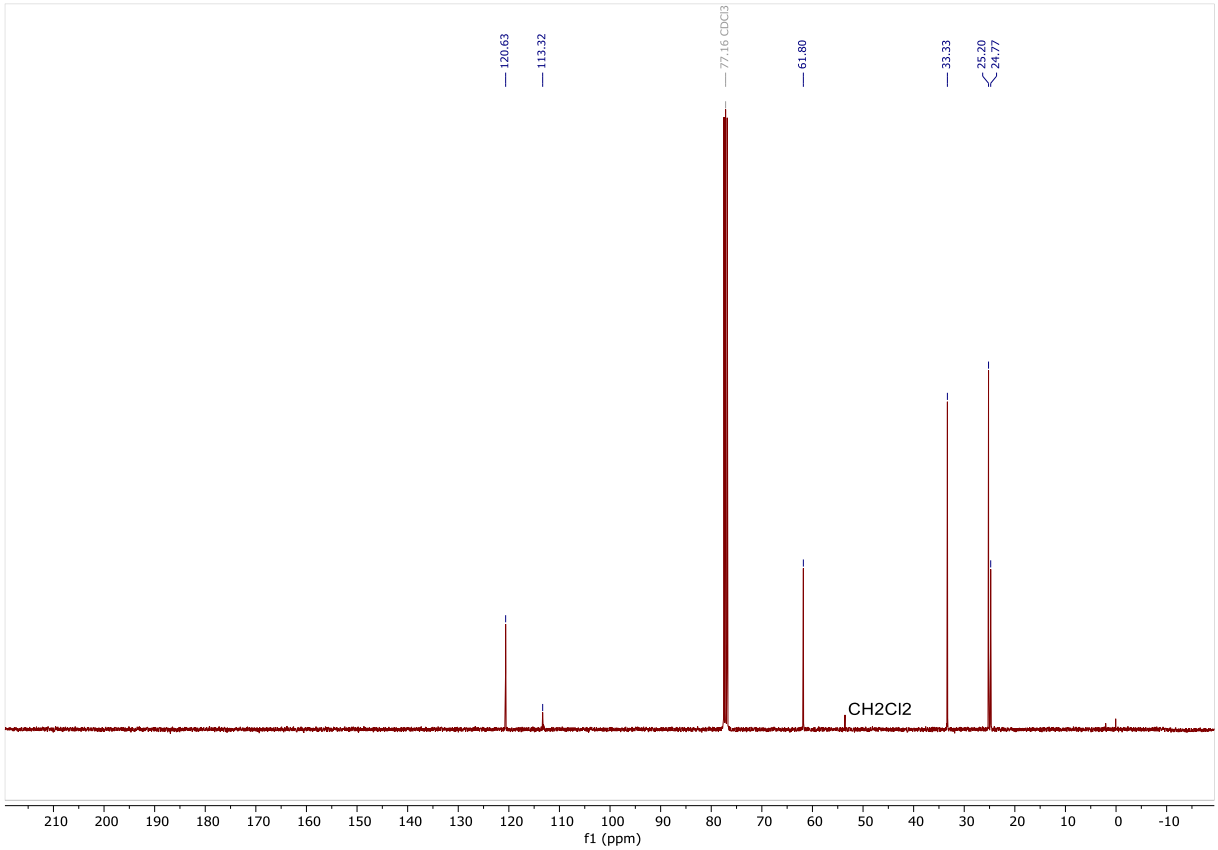


Fig. S56. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dicyclohexyl-2-iodoimidazolium iodide (**8**)

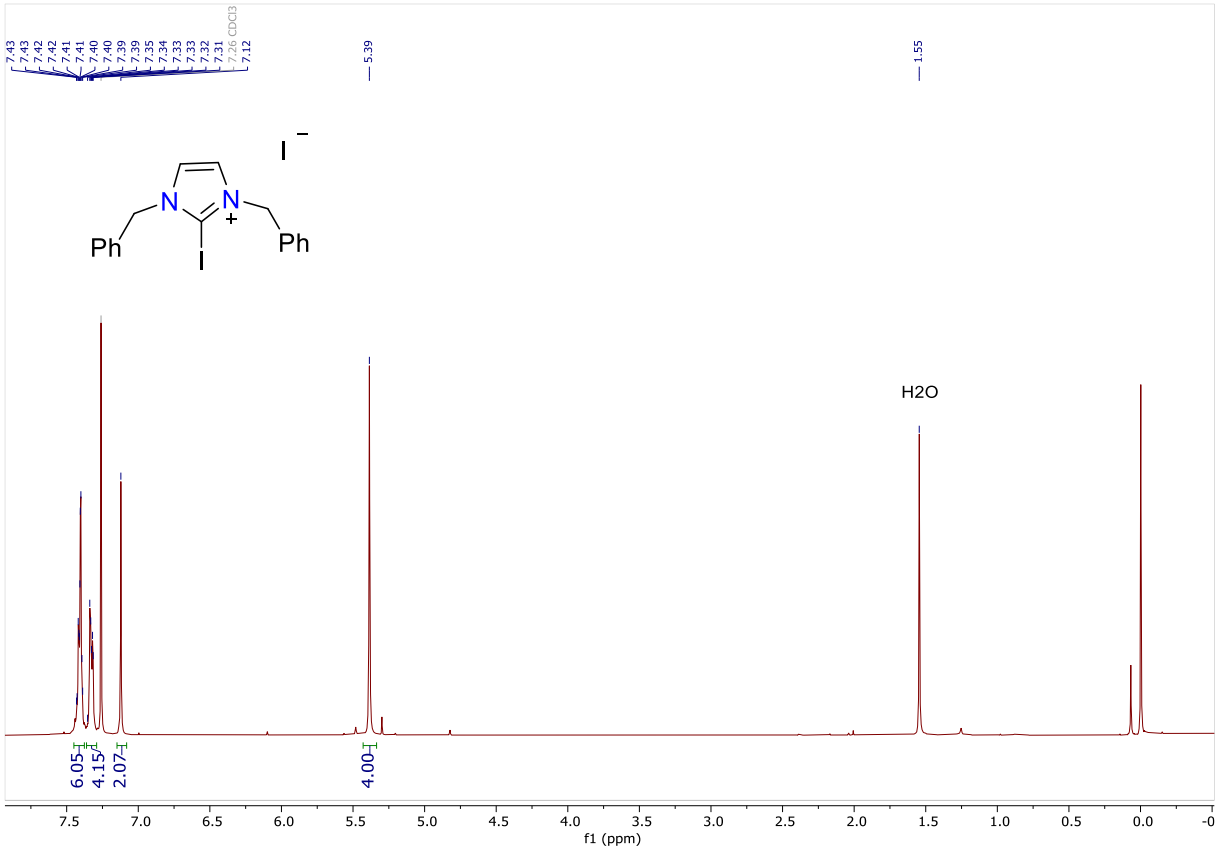


Fig. S57. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-iodoimidazolium iodide (**9**)

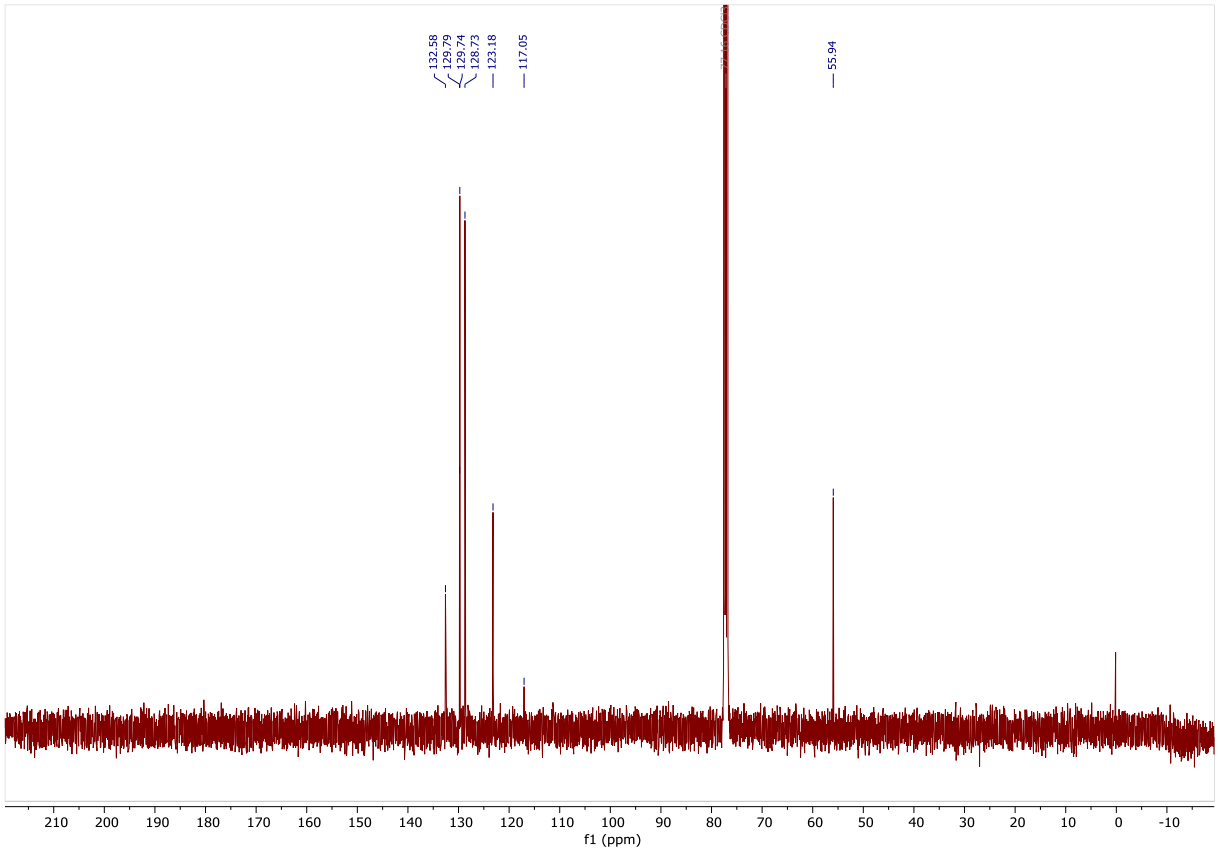


Fig. S58. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1,3-dibenzyl-2-iodo-imidazolium iodide (**9**)

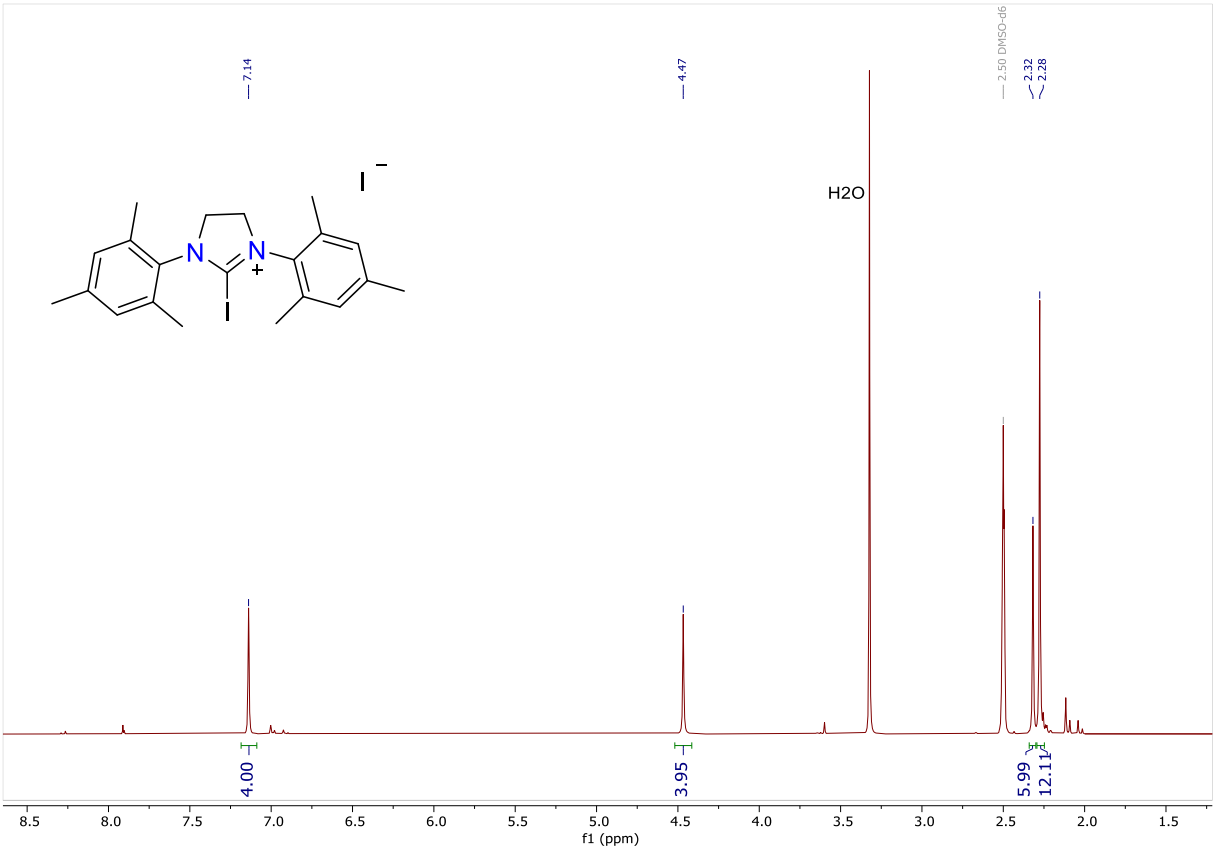


Fig. S59. ^{1}H NMR spectrum (400 MHz, dmso-d_6, 298 K) of 2-iodo-1,3-dimesitylimidazolinium iodide (**10**)

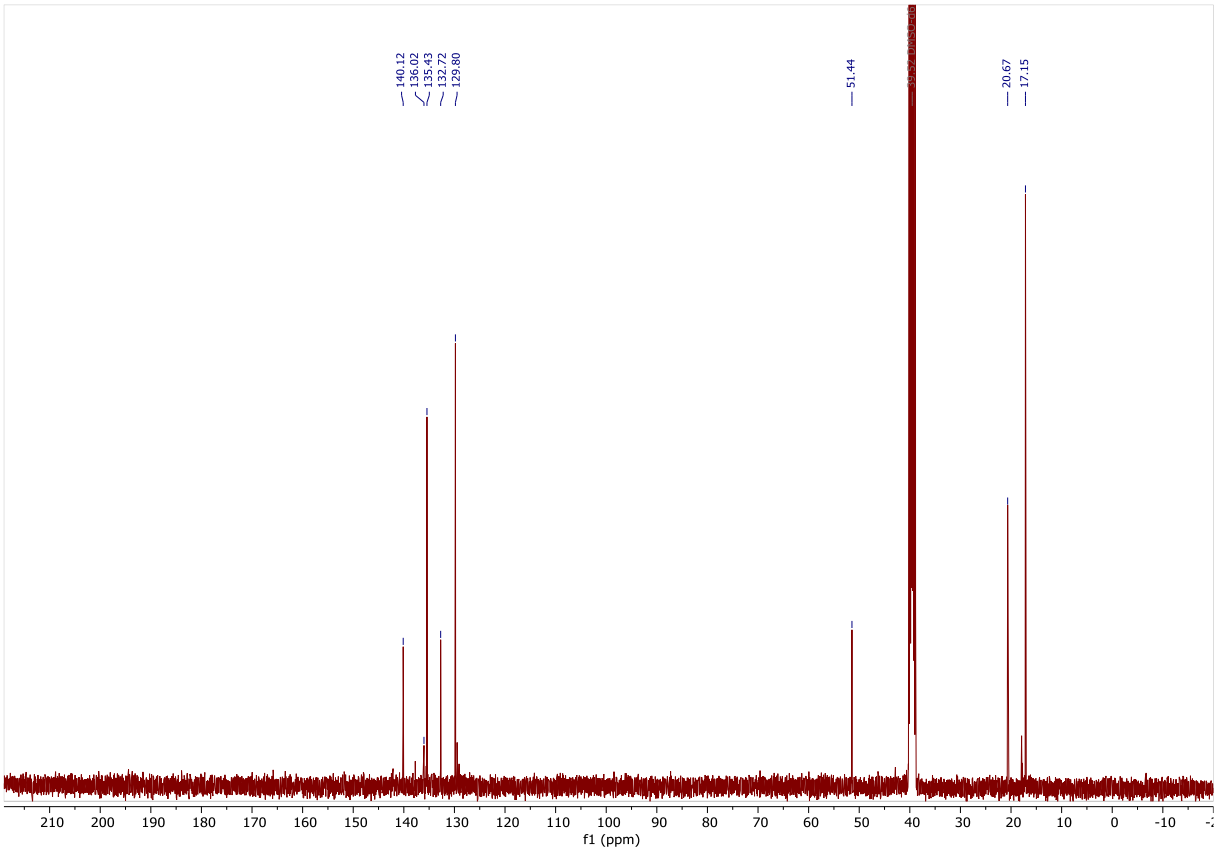


Fig. S60. ^{13}C{^{1}H} CPD NMR spectrum (101 MHz, dmso-d_6, 298 K) of 2-iodo-1,3-dimesitylimidazolinium iodide (**10**)

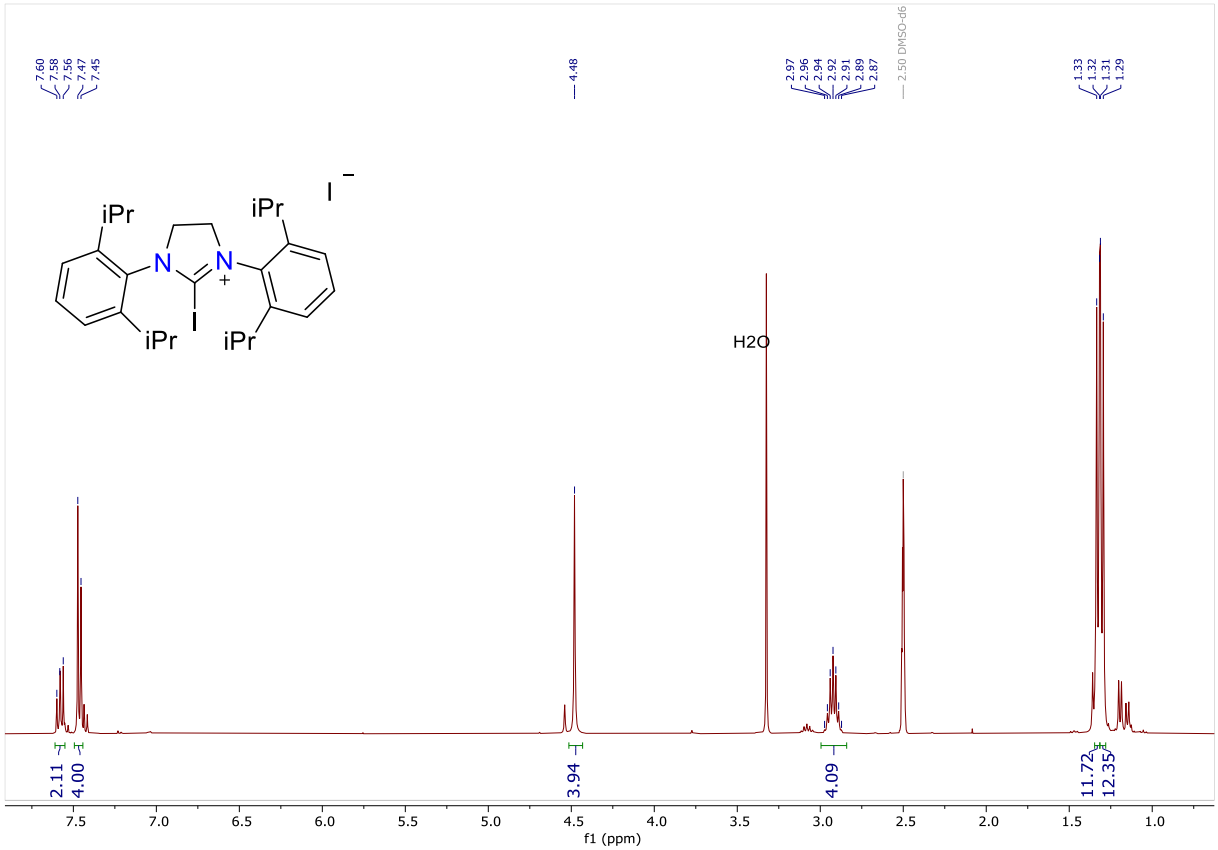


Fig. S61. ^{1}H NMR spectrum (400 MHz, dmso-d_6, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-iodoimidazolinium iodide (**11**)

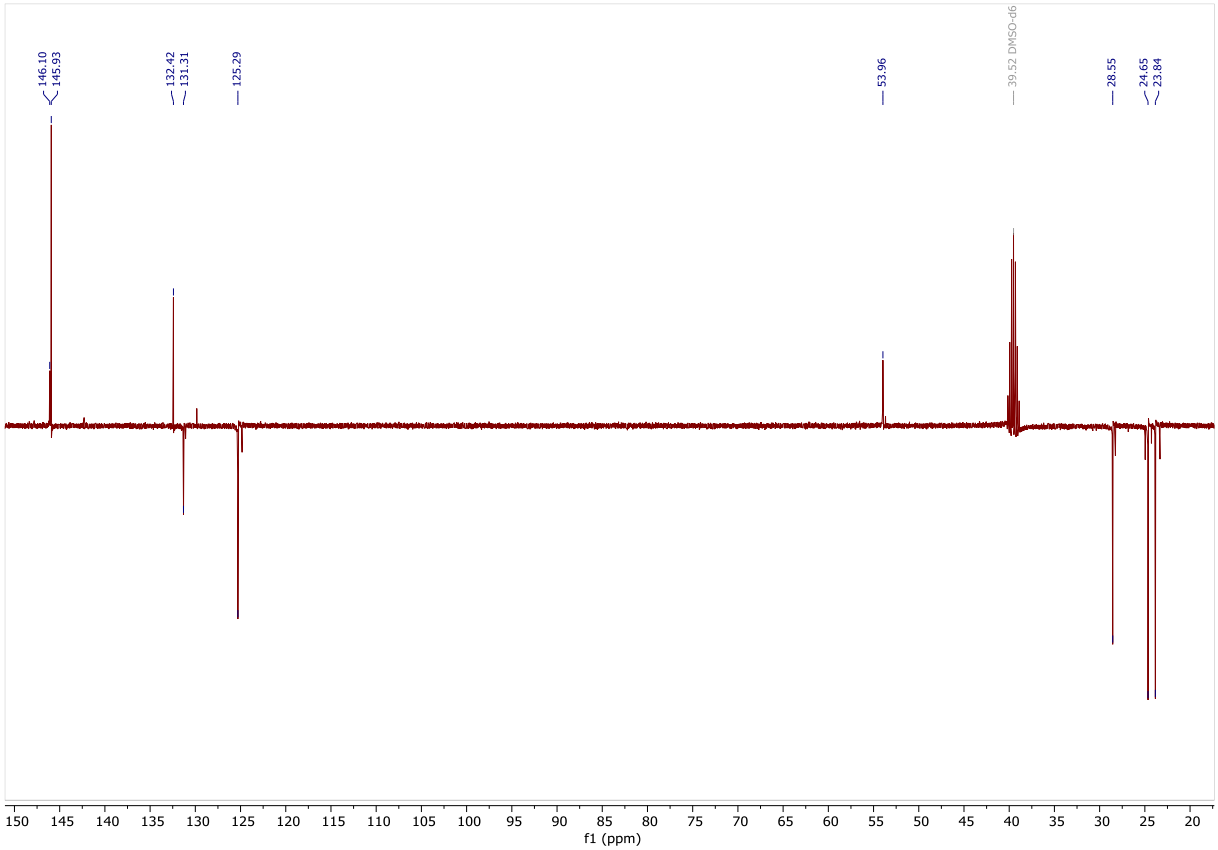


Fig. S62. ^{13}C{^{1}H} APT NMR spectrum (101 MHz, dmso-*d*6, 298 K) of 1,3-bis(2,6-diisopropylphenyl)-2-iodoimidazolinium iodide (**11**)

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