Electronic Supplemental Information (ESI)

Impact of 1 mmol dm^{-3} concentrations small molecules containing nitrogen-based cationic groups on the oxygen reduction reaction on polycrystalline platinum in aqueous KOH (1 mol dm^{-3}).

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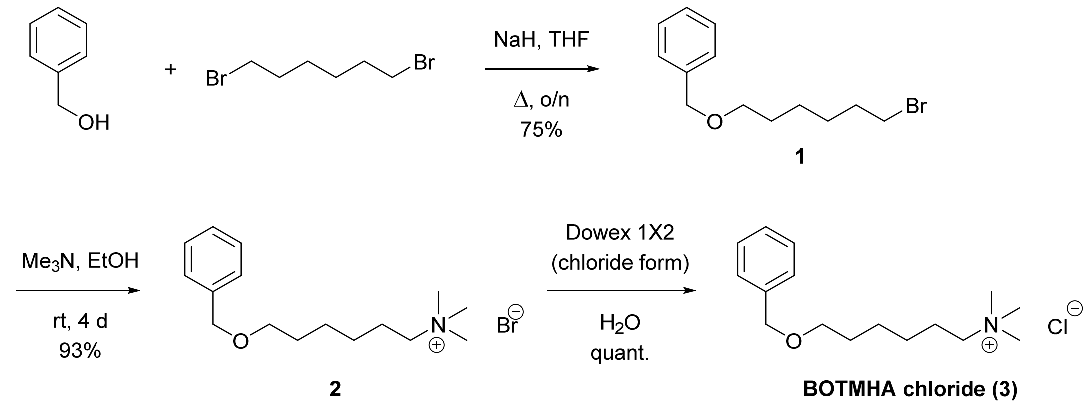
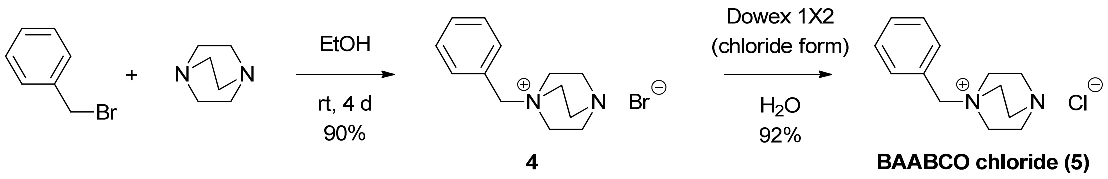
Synthetic Schemes

BOTMHA and BAABCO were synthesised as shown in Scheme ESI1 and scheme ESI2, respectively.



Scheme ESI1 The synthesis of 6-(benzyloxy)-N,N,N-trimethylhexan-1-aminium chloride (BOTMHA)

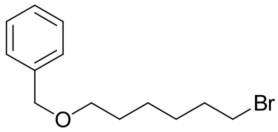


Scheme ESI2 The synthesis of 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (BAABCO)

General Experimental

Starting materials, reagents and solvents for reactions were reagent grade and, unless otherwise stated, used as purchased. THF was distilled from sodium benzophenone ketyl under nitrogen. Infra-red (IR) spectra were recorded in the range 600-4000 cm^{-1} using an Agilent Clary 600 FTIR spectrometer fitted with a MKII Golden Gate Single Reflection ATR System. NMR spectra were obtained on a Bruker 500 MHz spectrometer. ^{1}H NMR spectra were referenced to TMS at 0 ppm. The data is given as follows: chemical shift (δ) in ppm, integration, multiplicity, coupling constants (J, accurate to 0.5 Hz), assignment (if deduced using COSY and HSQC). ^{13}C spectra were referenced to TMS at 0 ppm. The data is given as follows: chemical shift (δ) in ppm, multiplicity. GCMS spectra were recorded on an Agilent 7890A GC system connected to an Agilent 5975C inert XL EI/CI with Triple-Axis Detectors. GC conditions were as follows: inj. vol. 1 μL, inj. temp. 250 °C, column Zebron ZB-5MS (30 m × 0.25 mm), oven temperature gradient 0-3 min, 50 °C; 3-23 min, 50-250 °C (10 °C ramp per minute); 23-35 min, 250 °C. High-resolution mass spectrometry (HRMS) was performed on a Waters QTOF Premier with electrospray ionisation. Elemental analysis was performed by Exeter Analytical Service, UK.

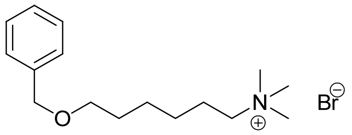
Benzyl 6-bromohexyl ether (1)



1

To a stirred solution of benzyl alcohol (0.81 g, 7.53 mmol) and 1,6-dibromohexane (14.7 g, 60.2 mmol) in THF (203 mL) was added NaH (60% w/w suspension in oil, 1.81 g, 75.3 mmol) portionwise.[1] The reaction mixture was heated at reflux overnight then filtered through celite and the solvent evaporated. Silica gel flash column chromatography (gradient elution, hexane only, hexane/ethyl acetate 97:3, 80:20) gave the title compound as a colourless oil (1.52 g, 75%); R_f (hexane/ethyl acetate 95:5) 0.6; IR (cm^{-1}) 2934, 2856, 1453, 1361, 1099; ^{1}H-NMR ($CDCl_3$) 7.36-7.32 (4H, m), 7.29-7.26 (1H, m), 4.50 (2H, s), 3.47 (2H, t, J = 7 Hz), 3.40 (2H, t, J = 7 Hz), 1.86 (2H, pentet, J = 7 Hz), 1.63 (2H, pentet, J = 7 Hz), 1.48-1.37 (4H, m); ^{13}C NMR ($CDCl_3$) 138.6, 128.4, 127.6, 127.5, 72.9, 70.2, 33.9, 32.8, 29.6, 28.0, 25.4; GCMS (EI) 18.8 min, *m/z* = 272 (0.3%), 270 (0.3%), 181 (0.5%), 179 (0.5%) 163 (1%), 161 (1%), 118 (2%), 108 (6%), 107 (6%), 92 (71%), 91 (100%). ^{1}H NMR and MS data is in approximate agreement with that given in the literature.[2]

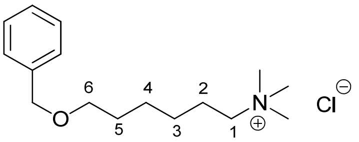
6-(Benzyloxy)-*N,N,N*-trimethylhexan-1-aminium bromide (2)



2

Bromo-ether **1** (0.4 g, 1.48 mmol) was dissolved in ethanol (10 mL). Trimethylamine solution (31% w/w in ethanol, 3.1 mL, 12.9 mmol) was added and the mixture was stirred at room temperature for 4 d.[3] The solvent was evaporated, the mixture was dissolved in water (30 mL) and the resulting aqueous solution was washed with diethyl ether (3 × 30 mL). The aqueous phase was lyophilised and the resulting pinkish-white solid was washed with diethyl ether and dried under high vacuum to give the title product (0.43 g, 93%); m.p. 143 ºC (sharp); IR (cm^{-1}) 3004, 2926, 2861, 1494, 1478, 1450, 1366, 1124; ^{1}H-NMR (MeOD) 7.37-7.34 (4H, m), 7.32-7.28 (1H, m), 4.51 (2H, s), 3.54 (2H, t, J = 6 Hz), 3.37-3.33 (2H, m), 3.14 (9H, s), 1.84-1.78 (2H, m), 1.70-1.64 (2H, m), 1.54-1.47 (2H, m), 1.45-1.39 (2H, m); ^{13}C NMR (MeOD) 139.8, 129.4, 128.9, 128.7, 73.9, 71.2, 67.8 (t, J_{CN} = 2.7 Hz), 53.5 (t, J_{CN} = 4.0 Hz), 30.4, 27.1, 26.8, 23.8; HRMS (ESI) (not done).

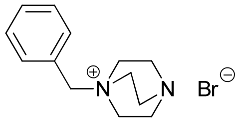
6-(Benzyloxy)-*N,N,N*-trimethylhexan-1-aminium chloride (BOTMHA chloride, 3)



BOTMHA chloride (3)

Bromide salt **2** (52 mg, 0.16 mmol) was dissolved in deionised water (~0.2 mL) and passed through a column containing Dowex® 1X2 (chloride form, 200-400 mesh, wet bed volume 0.7 mEq/mL) anion exchange resin (1 mL wet volume).[4] The column was eluted with deionised water (20 mL) and fractions containing product (UV active TLC spot) were combined and lyophilised to give the product (45 mg, quantitative); IR (cm^{-1}) 2935, 2855, 1481, 1451, 1365, 1122; ^{1}H-NMR (MeOD) 7.35-7.32 (4H, m, Ph), 7.30-7.25 (1H, m, Ph), 4.49 (2H, s, $PhC\underline{H}_2$-), 3.51 (2H, t, J = 6.5 Hz, 6-H), 3.31 (2H, m, 1-H), 3.11 (9H, s, -$N(C\underline{H}_3)_3$, 1.79 (2H, m, 2-H), 1.65 (2H, m, 5-H), 1.49 (2H, m, 4-H), 1.40 (2H, m, 3-H); ^{13}C NMR (MeOD) 139.8 (Ph), 129.4 (Ph), 128.9 (Ph), 128.7 (Ph), 73.9 (-$C\underline{H}_2Ph$), 71.2 (6-C), 67.8 (t, J_{CN} = 2.7 Hz, 1-C)), 53.5 (t, J_{CN} = 4.0 Hz, -$N(\underline{C}H_3)_3$), 30.4 (5-C), 27.1 (3-C), 26.8 (4-C), 23.8 (2-C); HRMS (ESI) found [M$^+$] 250.2174, $C_{16}H_{28}NO$ [M$^+$] requires 250.2171; elemental analysis found C, 60.58; H, 9.85; Cl, 11.78; N, 4.45, $C_{16}H_{28}ClNO$ requires C, 67.23; H, 9.87; Cl, 12.40; N, 4.90. The poor correlation of the elemental analysis reflects the hygroscopic nature of the compound. However the C:Cl ratio of 5.14:1 (5.4:1 is required) shows the salt has been entirely converted to the chloride form.

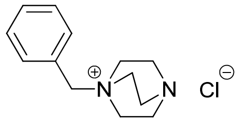
1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (4)



4

Benzylbromide (3.02 g, 0.018 mol) was dissolved in ethanol (30 mL). 1,4-diazabicyclo[2.2.2]octane (DABCO, 2.52 g, 0.023 mol) was added and the mixture was stirred at room temperature for 4 d. The solvent was evaporated, the mixture was dissolved in water (200 mL) and the resulting aqueous solution was washed with diethyl ether (3 × 200 mL). The aqueous phase was lyophilised and the resulting solid was washed with diethyl ether and dried under high vacuum to give the product as a white solid (4.6 g, 90%); m.p. 225 ºC (sharp); IR (cm^{-1}) 2961, 2889, 1454, 1314; ^{1}H-NMR (MeOD) 7.56-7.51 (5H, m), 4.54 (2H, s), 3.44 (6H, t (broad), J = 7.5 Hz), 3.18 (6H, t (broad), J = 7.5 Hz); ^{13}C NMR (MeOD) 134.4, 131.9, 130.5, 127.9, 69.3, 53.5, 46.2; HRMS (ESI) found [M$^+$] 203.1535, $C_{13}H_{18}N_2$ [M$^+$] requires 203.1548.

1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (BAABCO chloride, 5)



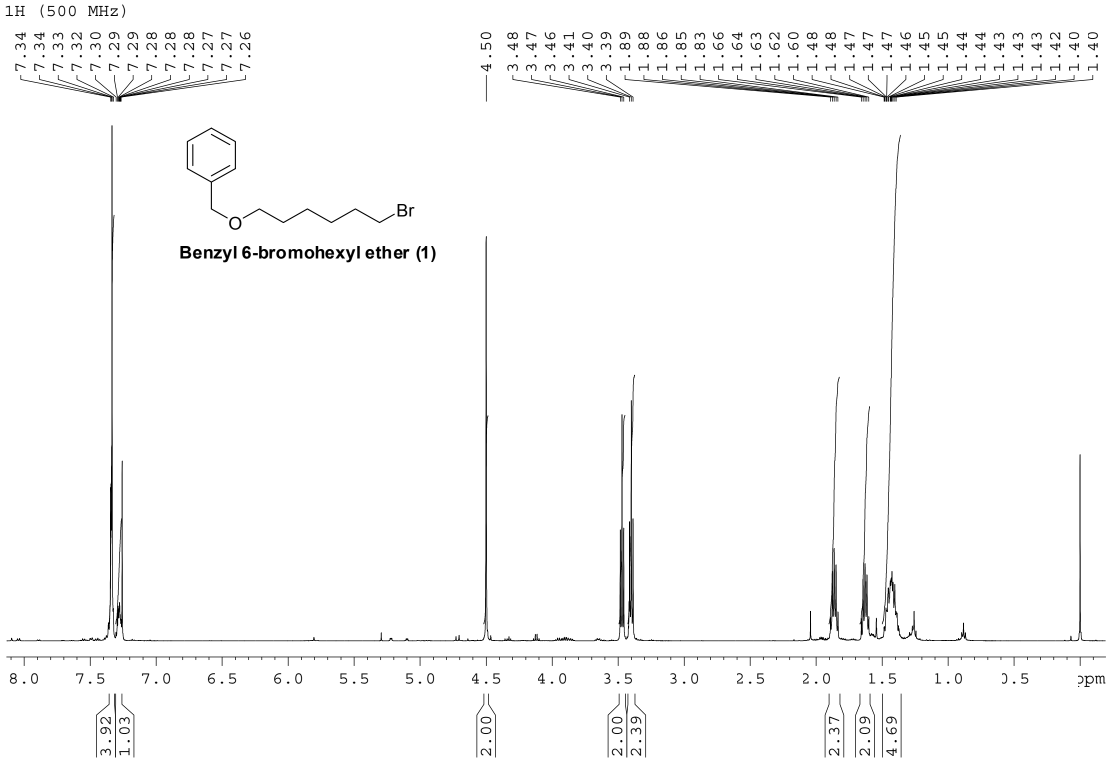
BAABCO chloride (5)

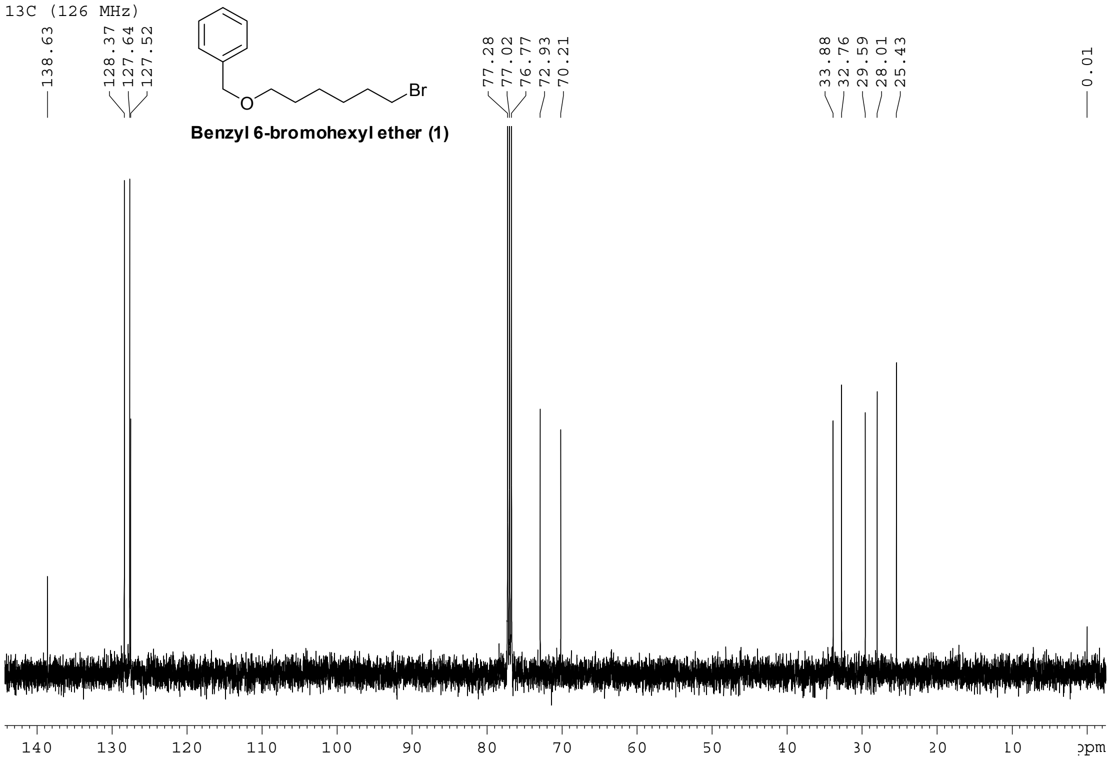
Bromide salt **4** (1.53 g, 5.69 mmol) was dissolved in deionised water and passed through a column containing Dowex® 1X2 (chloride form, 200-400 mesh) anion exchange resin (30 g).[4] The resulting aqueous solution was lyophilised to give the product as a fine, white powder (1.25 g, 92%); m.p. 153 ºC (sharp); IR (cm^{-1}) 2977, 2946, 2896, 1609, 1459, 1217, 1054; ^{1}H-NMR (MeOD) 7.57-7.51 (5H, m), 4.50 (2H, s), 3.40 (6H, t (broad), J = 7.5 Hz), 3.17 (6H, t (broad), J =7.5 Hz); ^{13}C NMR (MeOD) 134.4, 131.9, 130.5, 127.8, 69.4, 53.6, 46.2; HRMS (ESI) found [M$^+$] 203.1540, $C_{13}H_{19}N_2$ [M$^+$] requires 203.1548; elemental analysis found C, 60.20; H, 8.14; Cl, 13.79; N, 10.85, $C_{13}H_{19}ClN$ requires C, 65.40; H, 8.02; Cl, 14.85; N, 11.73. The poor correlation of the elemental analysis reflects the hygroscopic nature of the compound. However the C:Cl ratio of 4.37:1 (4.4:1 is required) shows the salt has been entirely converted to the chloride form.

References to the ESI

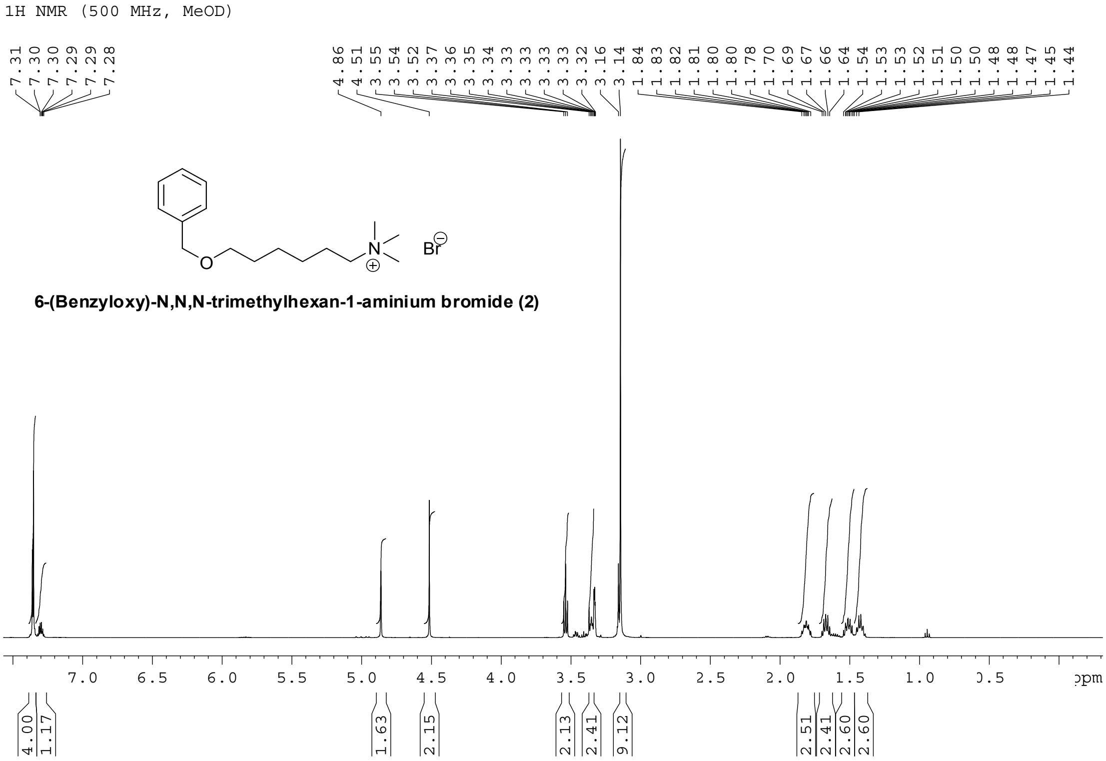
(1) Yuan, Z.; Chen, J.; Zeng, Y.; Li, Y.-Y.; Han, Y.; Li, Y. *Org. Biomol. Chem.* 2011, **9**, 6256.
(2) Tsuda, Y.; Hosoi, S.; Goto, Y. *Chem. Pharm. Bull.* 1991, **39**, 18.
(3) Menger, F. M.; Shi, L. *J. Am. Chem. Soc.* 2006, **128**, 9338.
(4) Zhang, J.; Jing, B.; Janout, V.; Regen, S. L. *Langmuir* 2007, **23**, 8709.

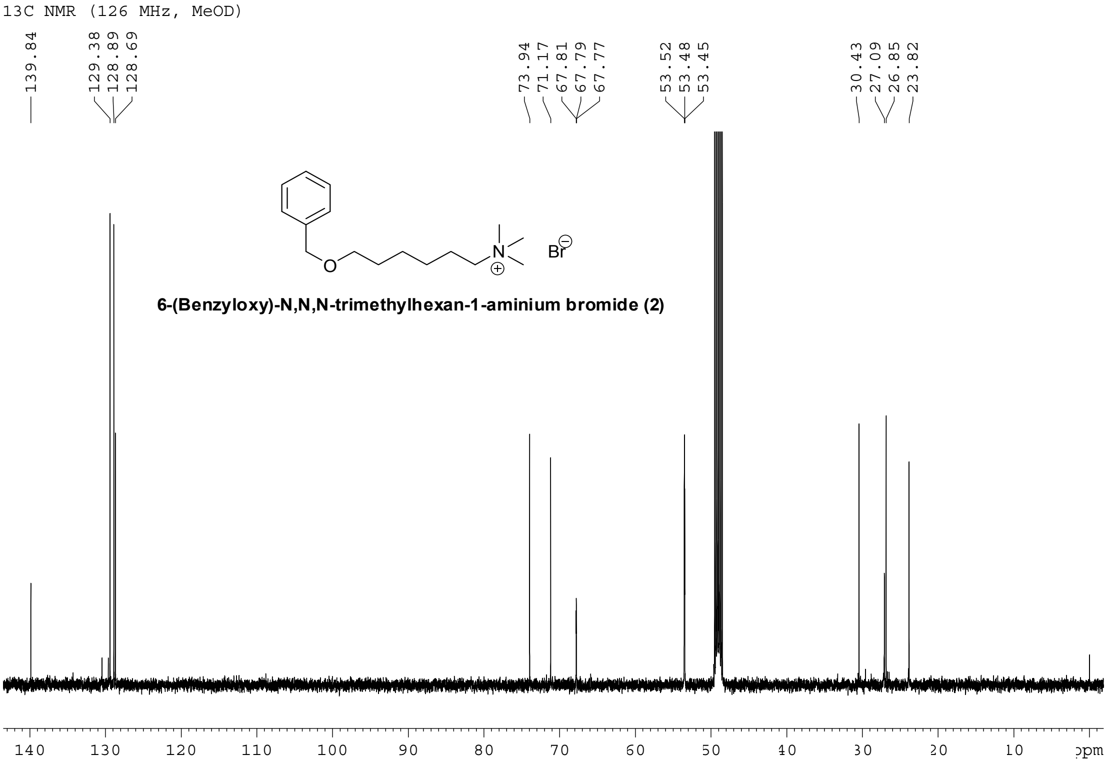
NMR ESI1 Benzyl 6-bromohexyl ether (**1**)





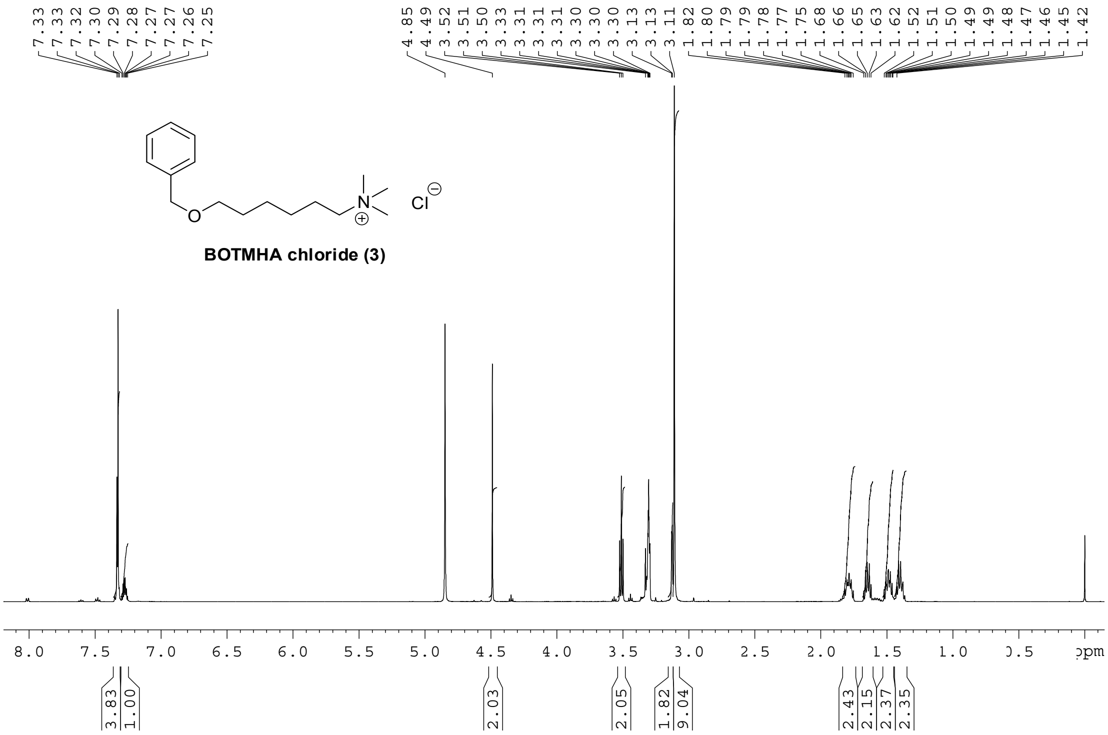
NMR ESI2 6-(Benzyloxy)-*N,N,N*-trimethylhexan-1-aminium bromide (**2**)



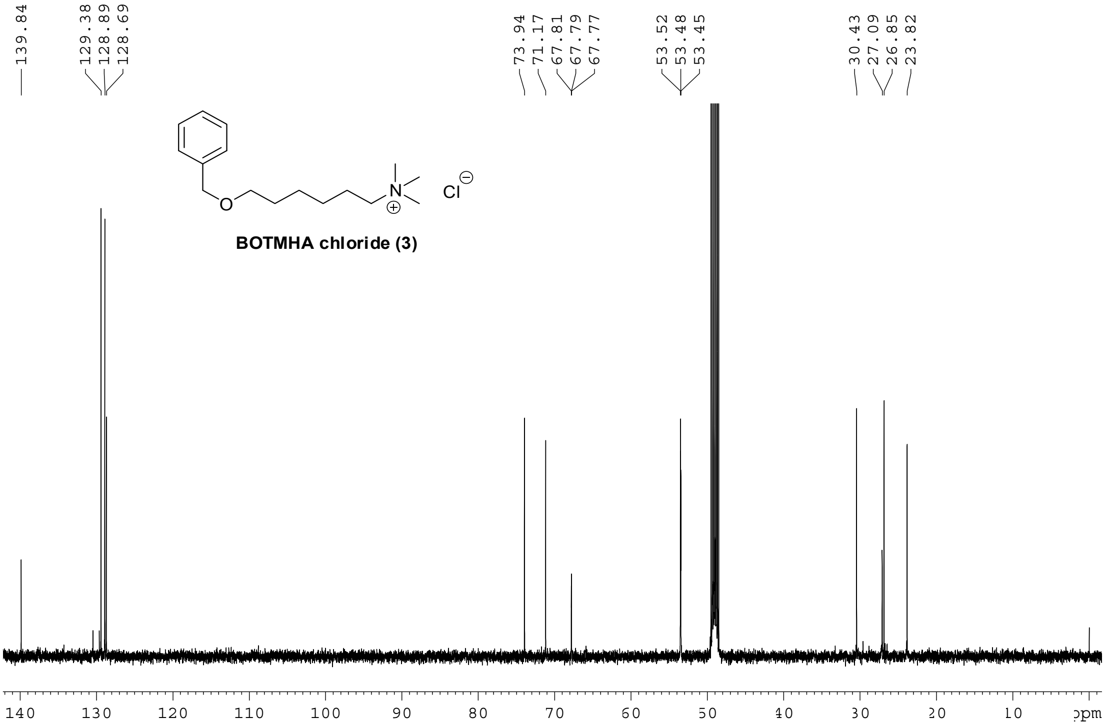


NMR ESI3 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (BOTMHA chloride, **4**)

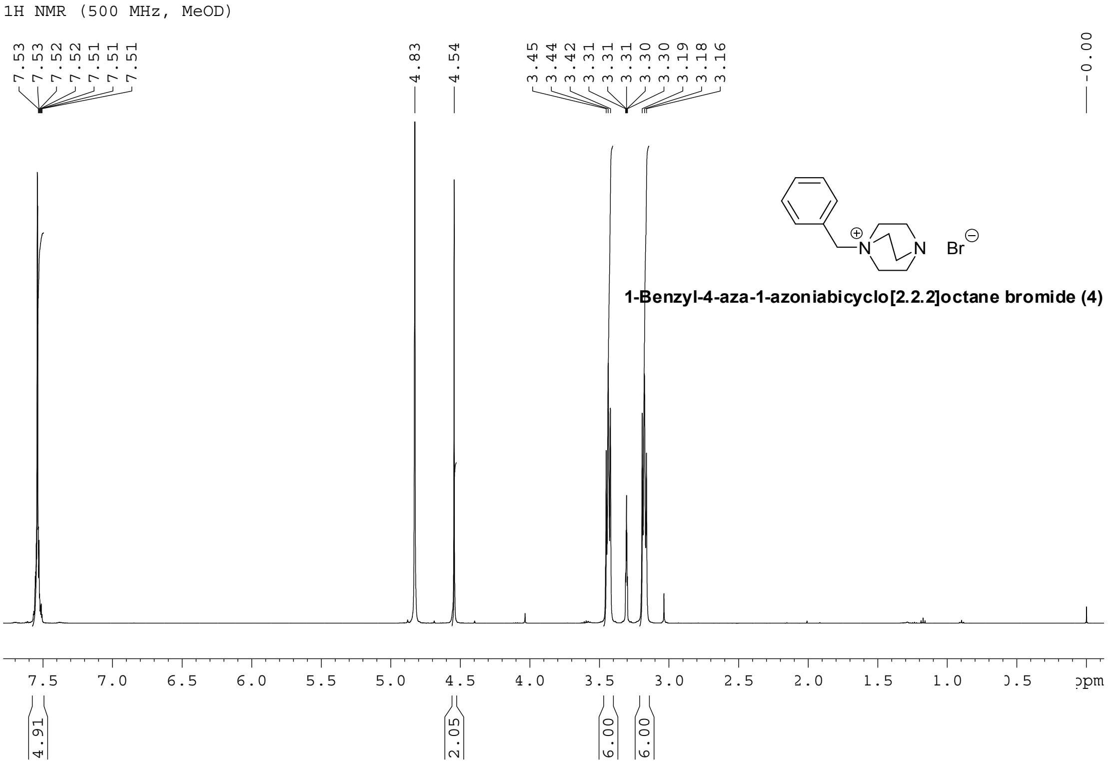
1H NMR (500 MHz, MeOD)

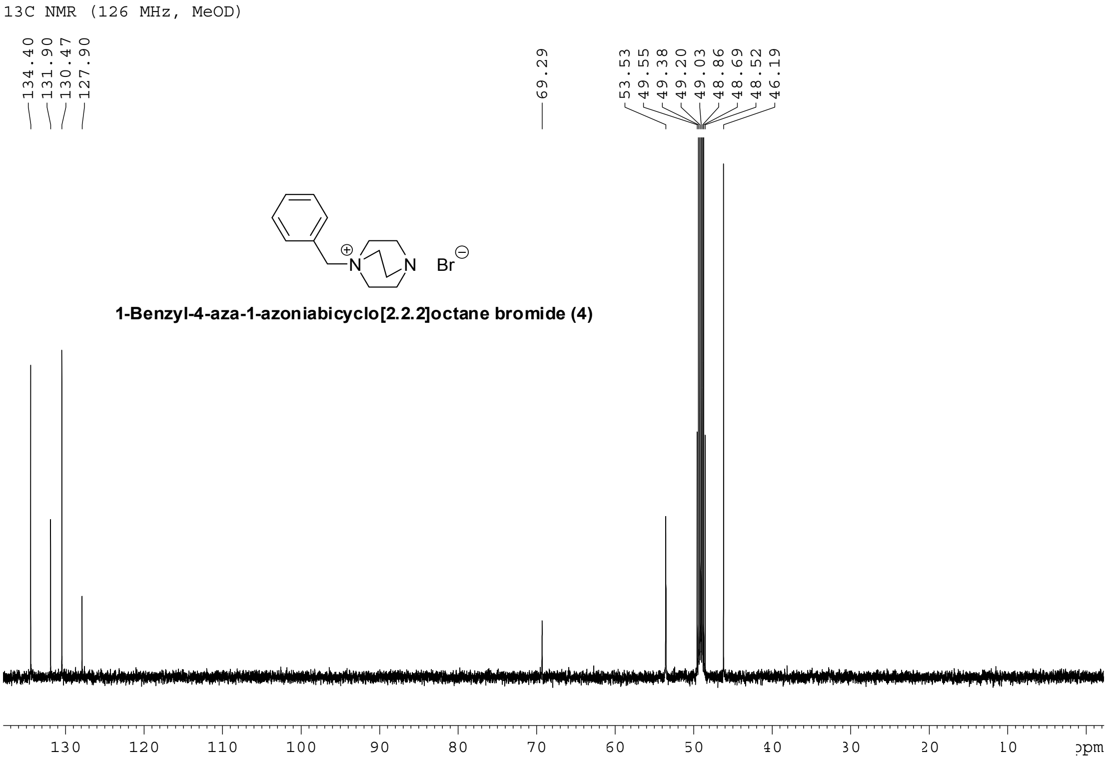


13C NMR (126 MHz, MeOD)

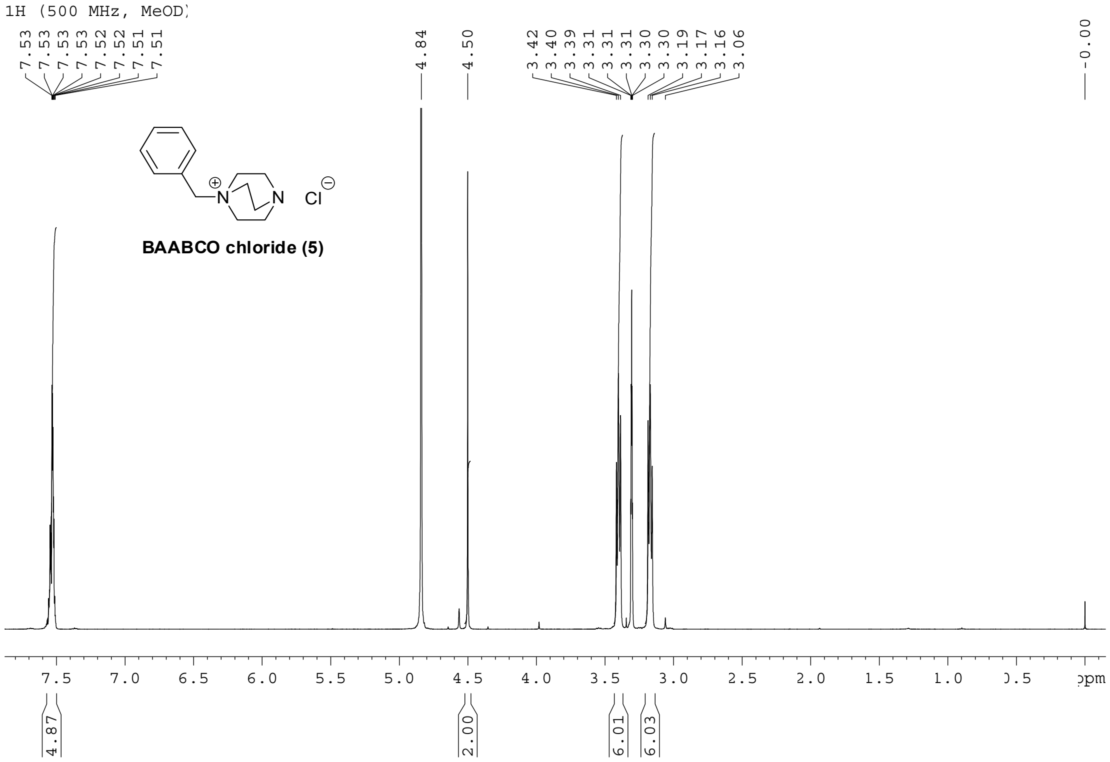


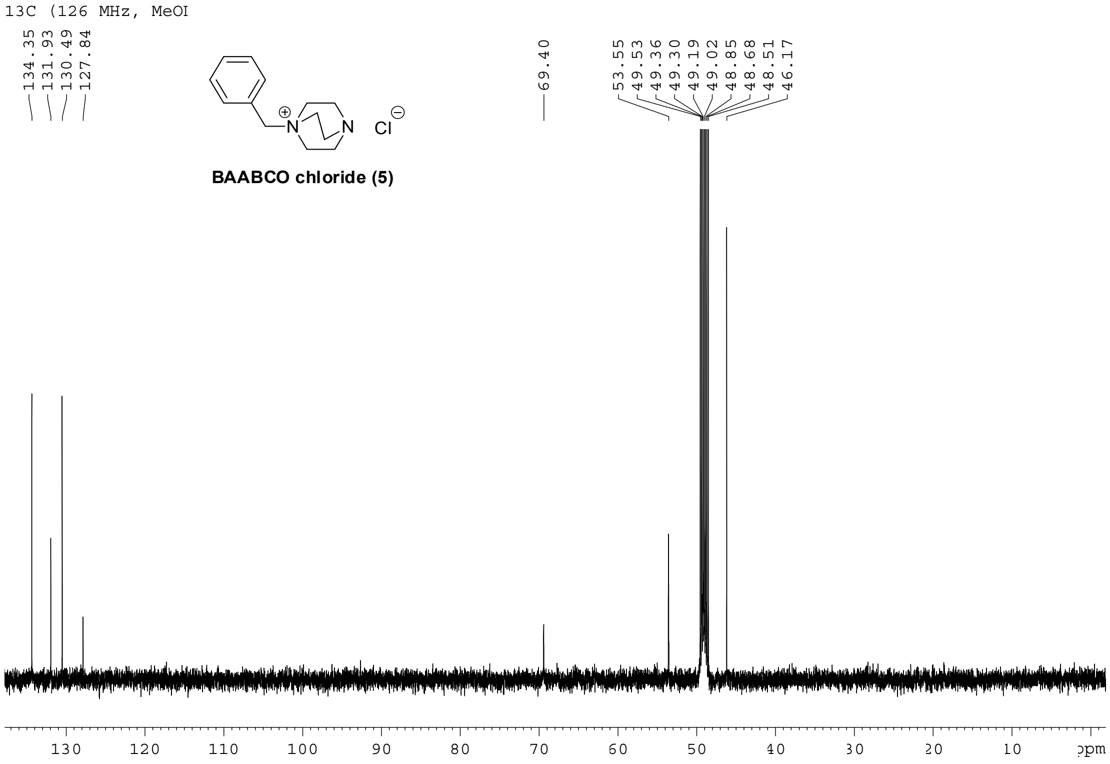
NMR ESI4 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (**4**)





NMR ESI5 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (BAABCO chloride, **5**)





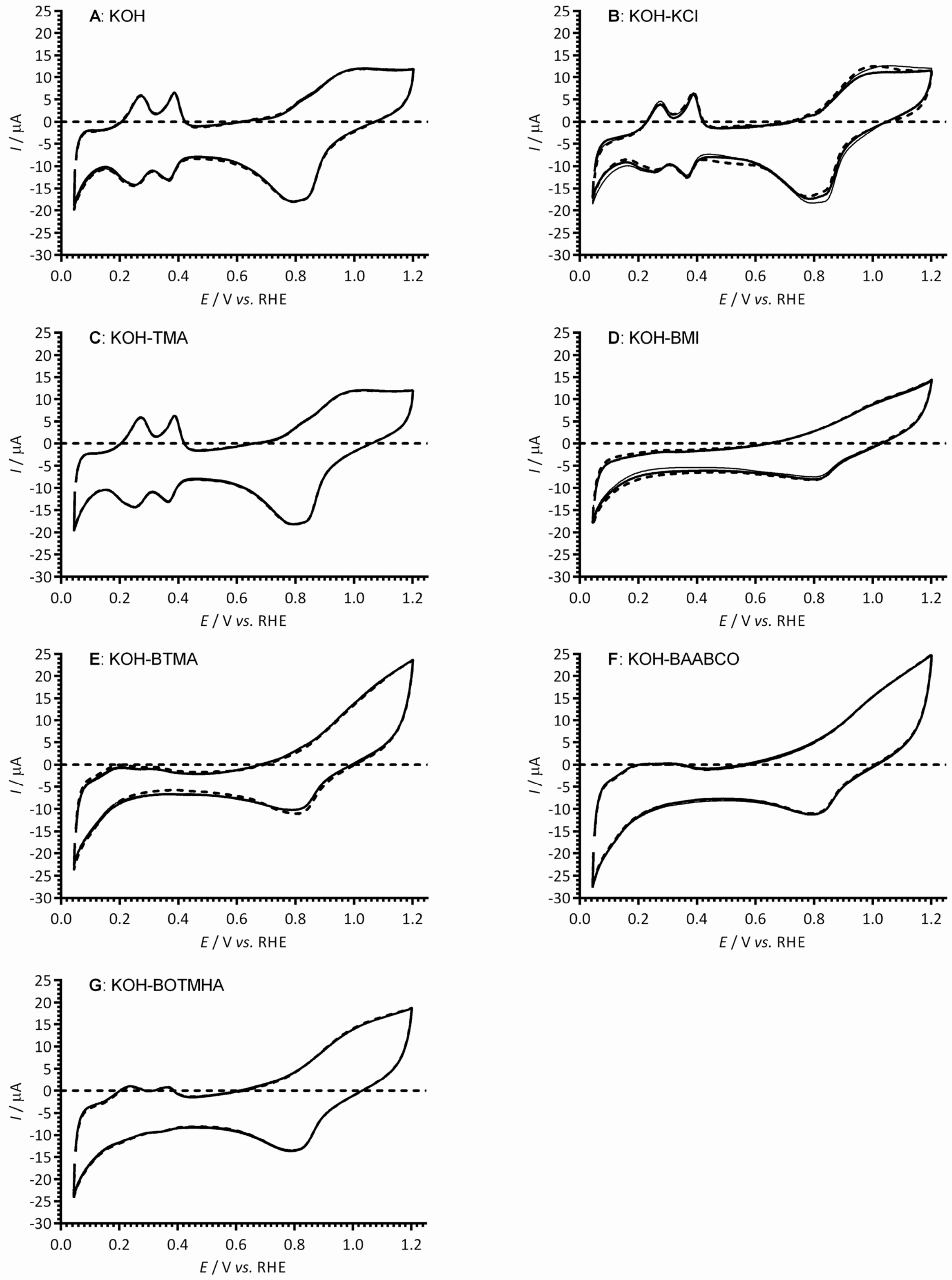


Fig. ESI1 The three repeat cyclic voltammograms of a polycrystalline Pt disk electrode in N_2-saturated aqueous KOH (1 mol dm^{-3}) electrolytes at 25 °C with and without addition of 1 mmol dm^{-3} of KCl or model cationic head-group molecules. Scan rate = 50 mV s^{-1}. This is the raw data linked to Figures 1 and 2 in the main article.

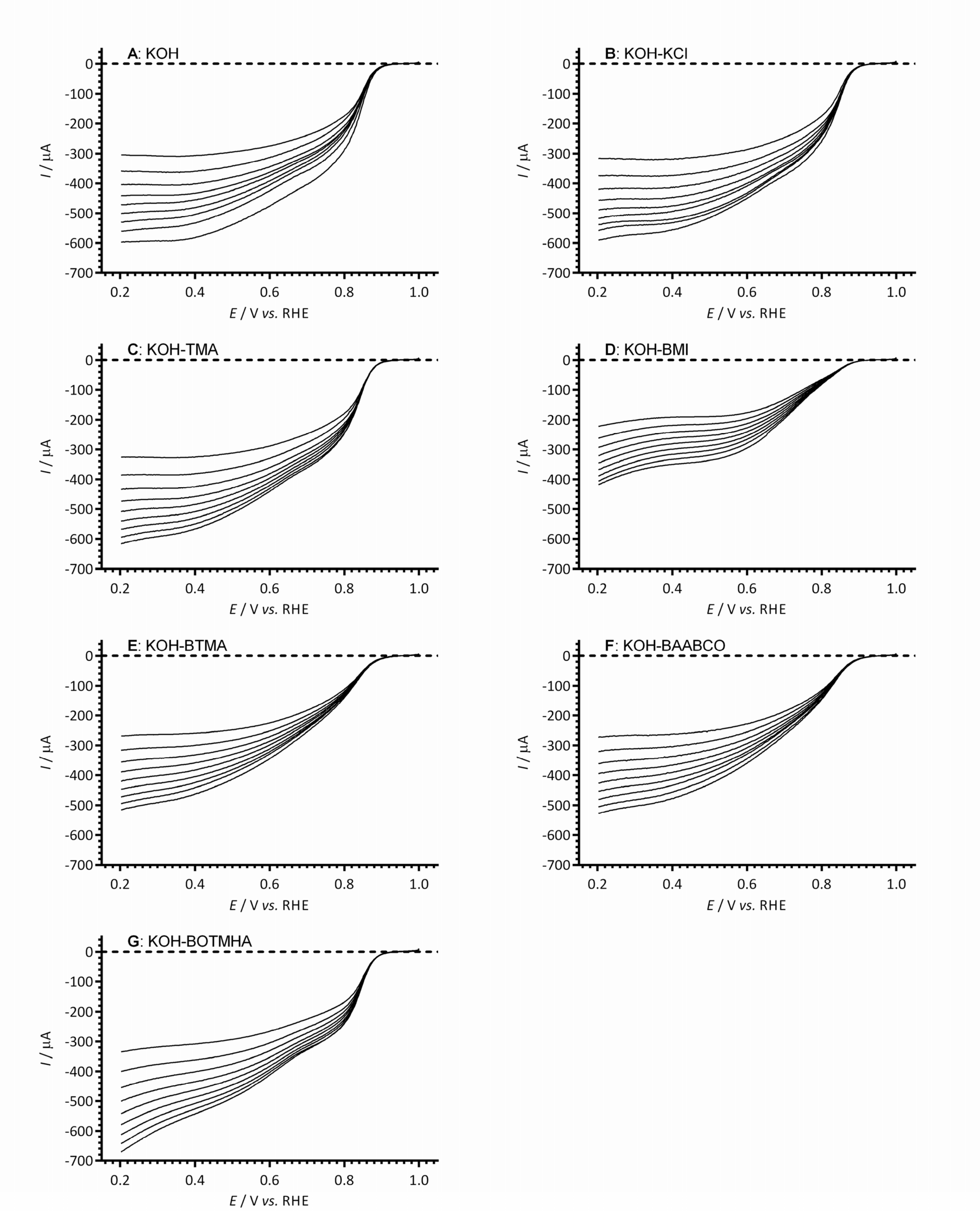


Fig. ESI2 The linear sweep hydrodynamic voltammograms at 25 °C of a polycrystalline Pt disk electrode in the O_2-saturated alkaline electrolytes with and without addition of 1 mmol dm^{-3} of KCl or the model cationic head-group molecules. Scan rate = 5 mV s^{-1} and RDE rotation rates in the range 400 - 2000 rpm. This is the raw data linked to Figure 6 and 7 and Table 1 in the main article.

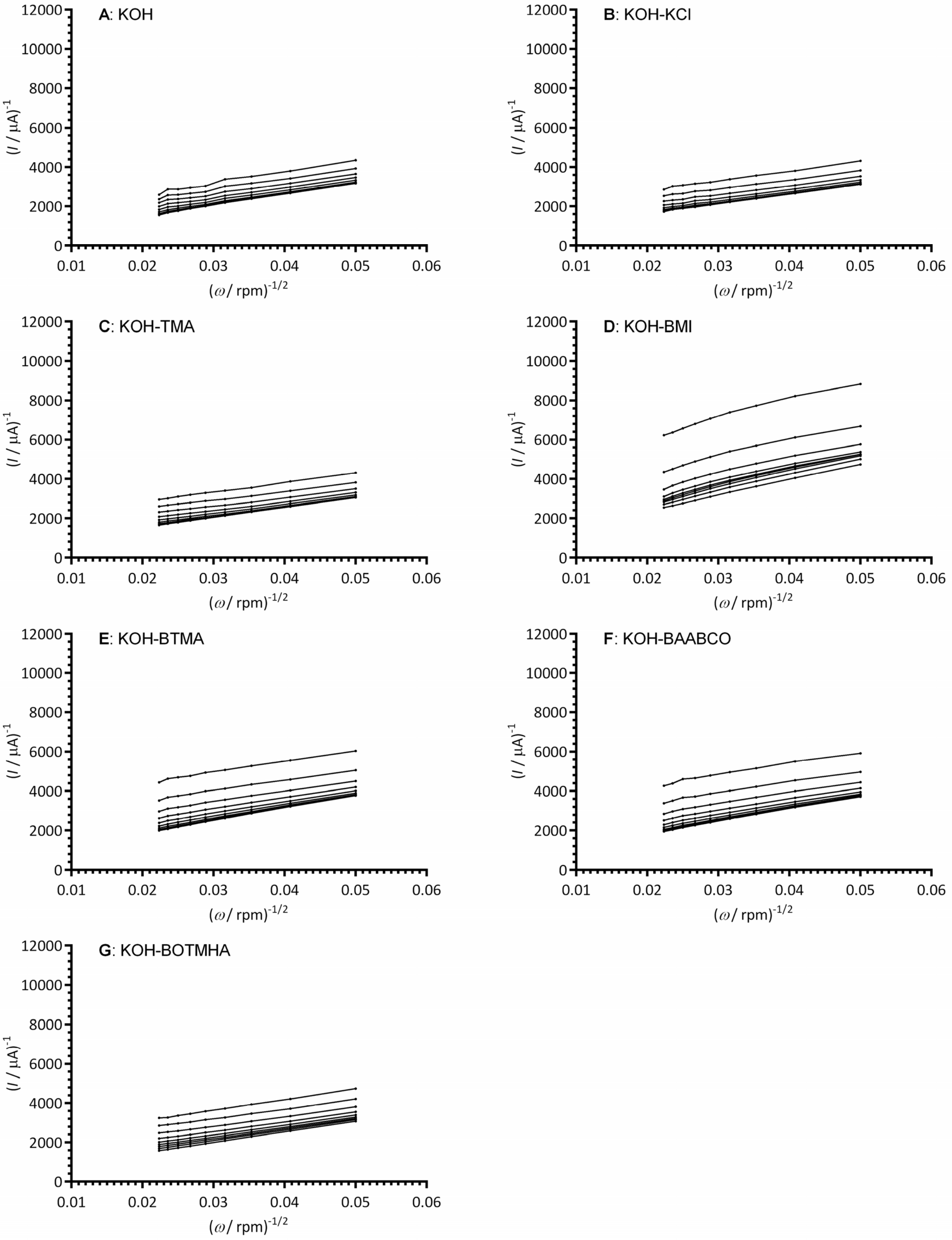


Fig. ESI3 The Koutecky - Levich plots of a polycrystalline Pt disk electrode in the O_2-saturated alkaline electrolytes at 25 °C with and without addition of 1 mmol dm^{-3} of KCl or the model cationic head-group molecules. Scan rate = 5 mV s^{-1} and RDE rotation rates in the range 400 - 2000 rpm. This is the raw data linked to Figures 6 and 7 and Table 1 in the main article.