

Supporting Information for

Surface- and Redox-Active Multi-Functional Polyphenol-Derived Poly(ionic liquid)s: Controlled Synthesis and Characterization

Nagaraj Patil,¹ Daniela Cordella,¹ Abdelhafid Aqil,¹ Antoine Debuigne,¹ Shimelis

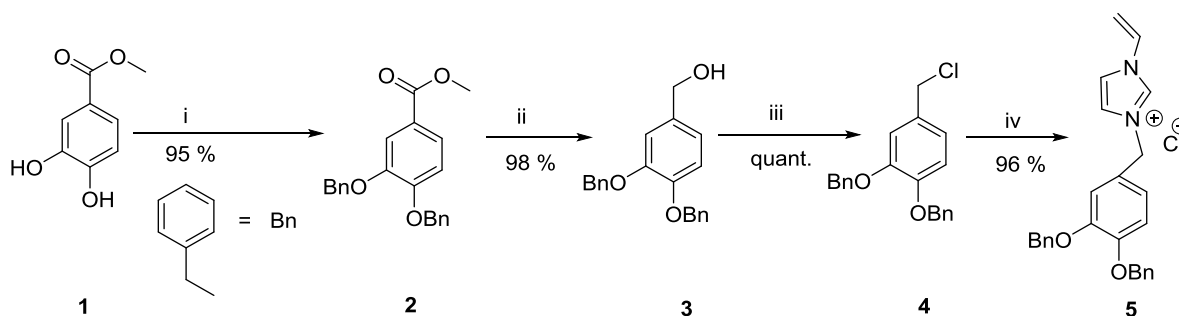
Admassie,^{2,3} Christine Jérôme,^{1} Christophe Detrembleur^{1*}*

¹Centre for Education and Research on Macromolecules (CERM), CESAM Research Unit,
Department of Chemistry, University of Liege, Allée de la Chimie B6A, 4000 Liège,
Belgium

²Biomolecular and organic electronics, IFM, Linköping University, S-581 83, Linköping,
Sweden

³Department of Chemistry, Addis Ababa University, PO Box 1176, Addis Ababa, Ethiopia

Supporting Scheme S1. Synthesis of VIm-cat⁺-Cl⁻ (5)



Reagents and Conditions: (i) BnCl, K₂CO₃, DMF, 75 °C, 12 h; (ii) LiAlH₄, THF, 2 h; (iii) SOCl₂, cat. DMF, DCM, 4 h; (iv) 1-vinylimidazole, THF, 70 °C, 48 h.

Methyl 3,4-bis(benzyloxy)benzoate (2): A two-necked round-bottom flask was charged with 20.0 g (118.9 mmol, 1 eqv.) of **1** and 49.3 g (356.7 mmol, 3 eqv.) of finely grinded, oven dried K₂CO₃. The flask was evacuated by three consecutive vacuum-argon cycles and backfilled with argon, before transferring 400 mL of degassed anhydrous DMF using cannula. 31.6 g (29 mL, 249.6 mmol, 2.1 eqv.) of degassed benzyl chloride in degassed anhydrous DMF (50 mL) was slowly added to the above suspension under argon atmosphere at room temperature. The suspension was brought to reflux and continued vigorous stirring for 12 h under argon atmosphere. The reaction mixture was cooled to room temperature and poured into cold water. The solid precipitated was collected by vacuum filtration and re-dissolved in CH₂Cl₂. After being washed with saturated NaHCO₃, water and brine, the organic phase was dried over anhydrous MgSO₄, filtered and passed through a short column of basic alumina using CH₂Cl₂ as an eluent. The solvent was rotaevaporated under reduced pressure, affording 39.4 g of **2** (112.9 mmol, 95 % yield), as a cream colored solid. ¹H NMR (400 MHz, DMSO-*d*₆, δ (ppm)): 7.62 – 7.55 (m, 2H, ArH, #1, 5), 7.51 – 7.28 (m, 10H, ArH of Bn), 7.23 – 7.16 (m, 1H, ArH, #4), 5.23 (s, 2H, ArOCH₂-, #26), 5.19 (s, 2H, ArOCH₂-, #18), 3.81 (s, 3H, ArCO₂CH₃). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 166.32 (C=O), 152.90 (ArC, #3), 148.19 (ArC, #2), 137.39 (ArC of Bn, #12), 137.08 (ArC of Bn, #20),

128.92, 128.87, 128.41, 128.31, 128.02, 127.94 (ArC of Bn) 123.92 (ArC, #5), 122.56 (ArC, #6), 114.83 (ArC, #4), 113.67 (ArC, #1), 70.56 (ArOCH₂, #18), 70.36 (ArOCH₂, #26), 52.39 (ArCO₂CH₃).

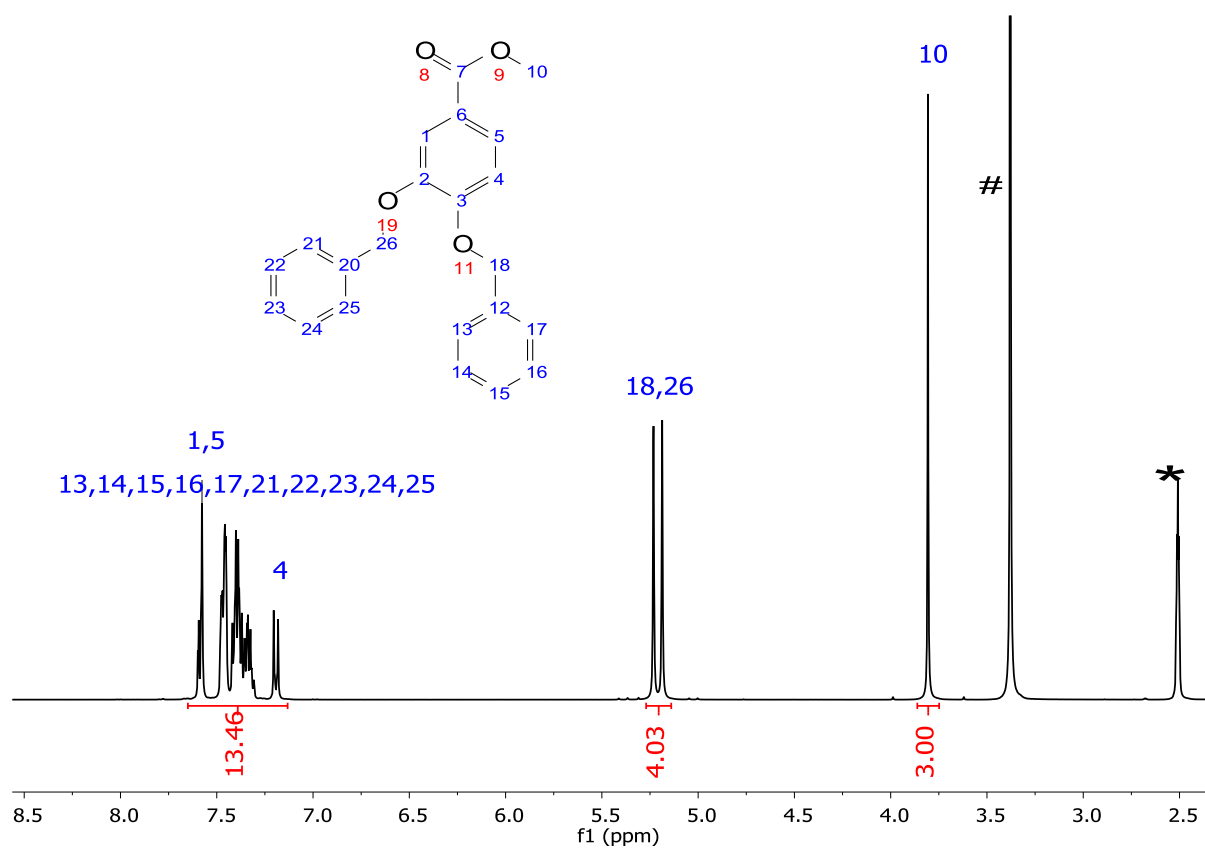


Figure S1. ¹H NMR spectrum of **2** in DMSO-*d*₆. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

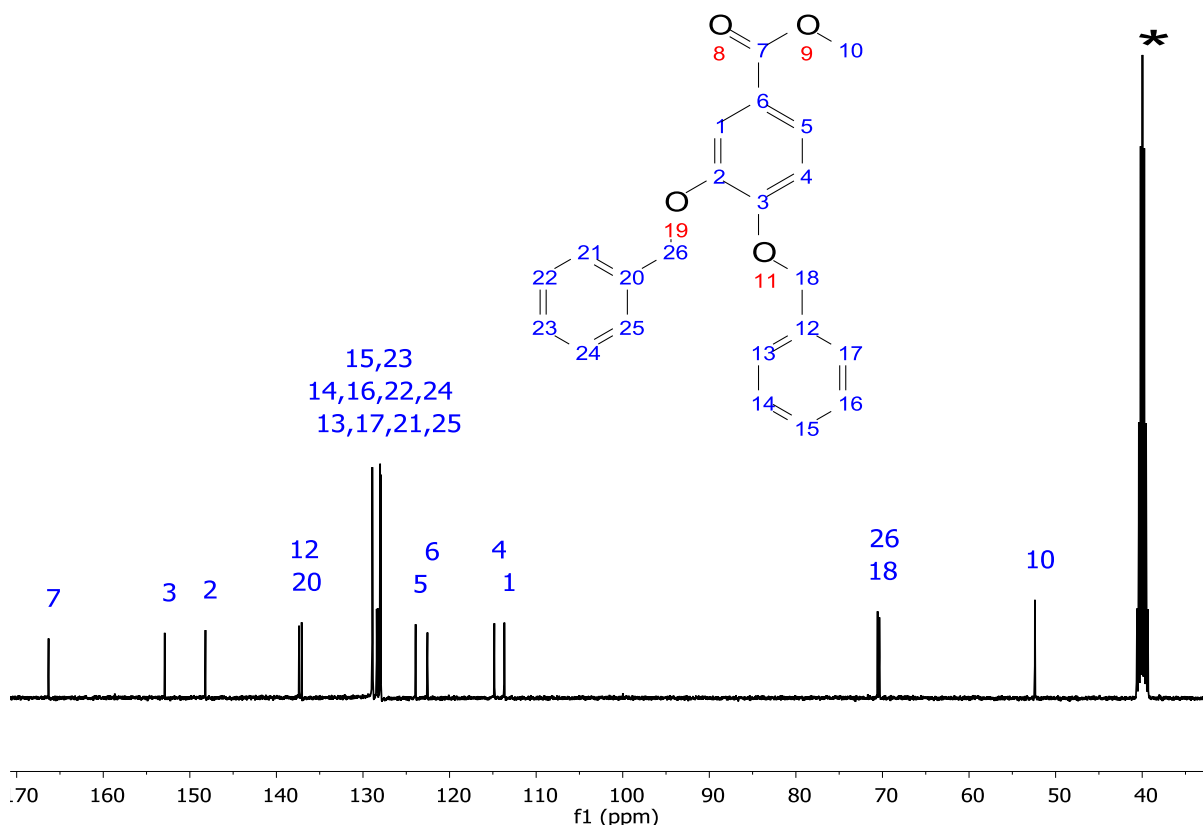


Figure S2. ^{13}C NMR spectrum of **2** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

(3,4-bis(benzyloxy)phenyl)methanol (3). To a suspension of LiAlH_4 (4.9 g, 129.1 mmol, 1.5 eqv.) in dry THF (200 mL) at 0°C was added dropwise a solution of methyl 3,4-bis(benzyloxy)benzoate (**2**) (30.0 g, 86.1 mmol, 1 eqv.) in 150 mL of dry THF under argon atmosphere. The reaction mixture was stirred at room temperature for 2 h, before being quenched by successive addition of 5 mL H_2O , 5 mL of 15% NaOH and 15 mL of H_2O . The granular salts were filtered, washed with THF and dried over anhydrous MgSO_4 . The solvent was fully rotaevaporated under reduced pressure and the remaining solid was re-dissolved in CH_2Cl_2 and passed through a short column of basic alumina using CH_2Cl_2 as an eluent. The solvent was rotaevaporated under reduced pressure, affording 27.0 g of **3** (84.4 mmol, 98 %

yield), as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.52 – 7.27 (m, 10H, ArH of Bn), 7.07 (d, $J = 2.0$ Hz, 1H, ArH, #1), 7.01 (d, $J = 8.2$ Hz, 1H, ArH, #4), 6.85 (dd, $J = 8.3, 1.9$ Hz, 1H, ArH, #5), 5.12 (m, 5H, $\text{OHCH}_2\text{ArOCH}_2$ -, #8, 16, 24), 4.42 (d, $J = 5.7$ Hz, 2H, ArCH_2OH). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ (ppm)): 148.70 (ArC, #2), 147.49 (ArC, #3), 137.91 (ArOCH_2ArC of Bn, #10), 136.24 (ArOCH_2ArC of Bn, #18), 128.83, 128.80, 128.61, 128.20, 127.97, 127.93 (ArC of Bn), 128.15 (ArC, #6), 119.66 (ArC, #5), 114.95 (ArC, #4), 113.59 (ArC, #1), 70.71, 70.57 (ArOCH_2 -), 63.18 (ArCH_2OH).

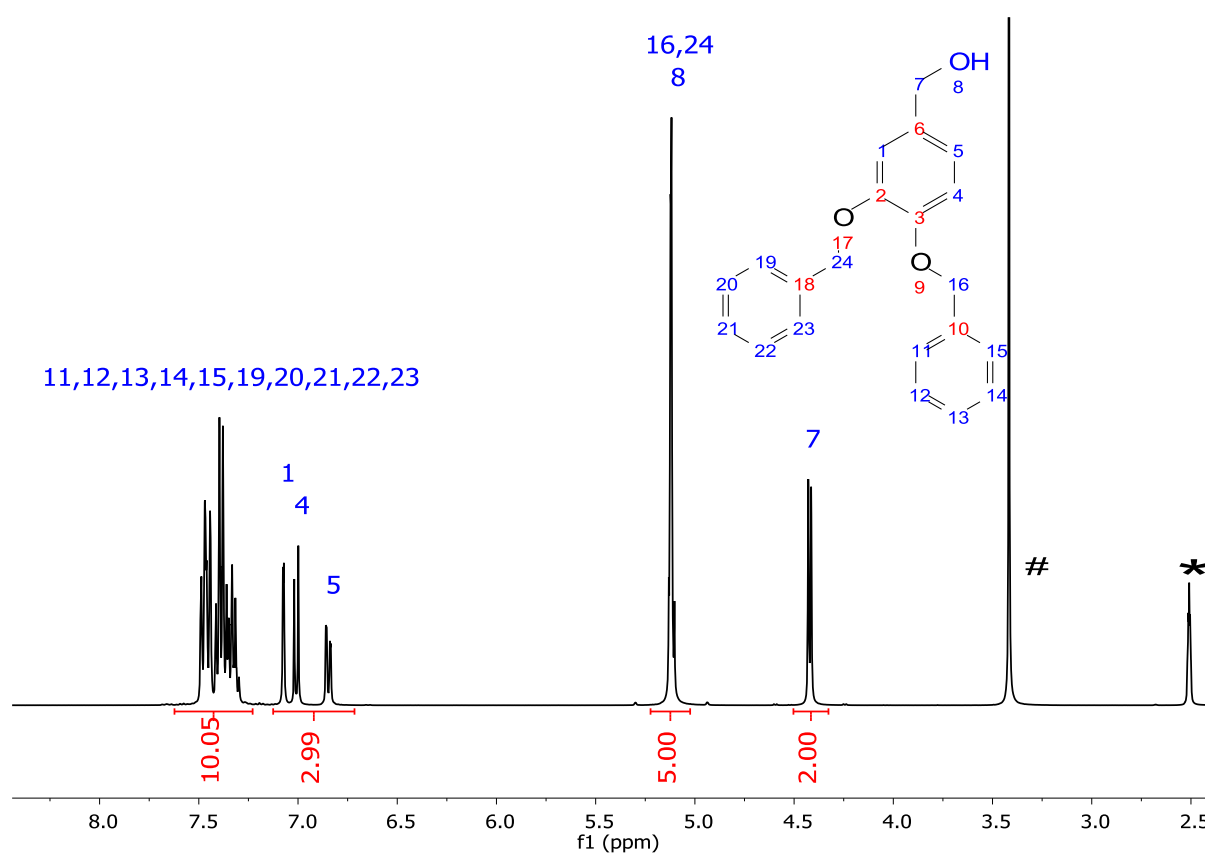


Figure S3. ^1H NMR spectrum of **3** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

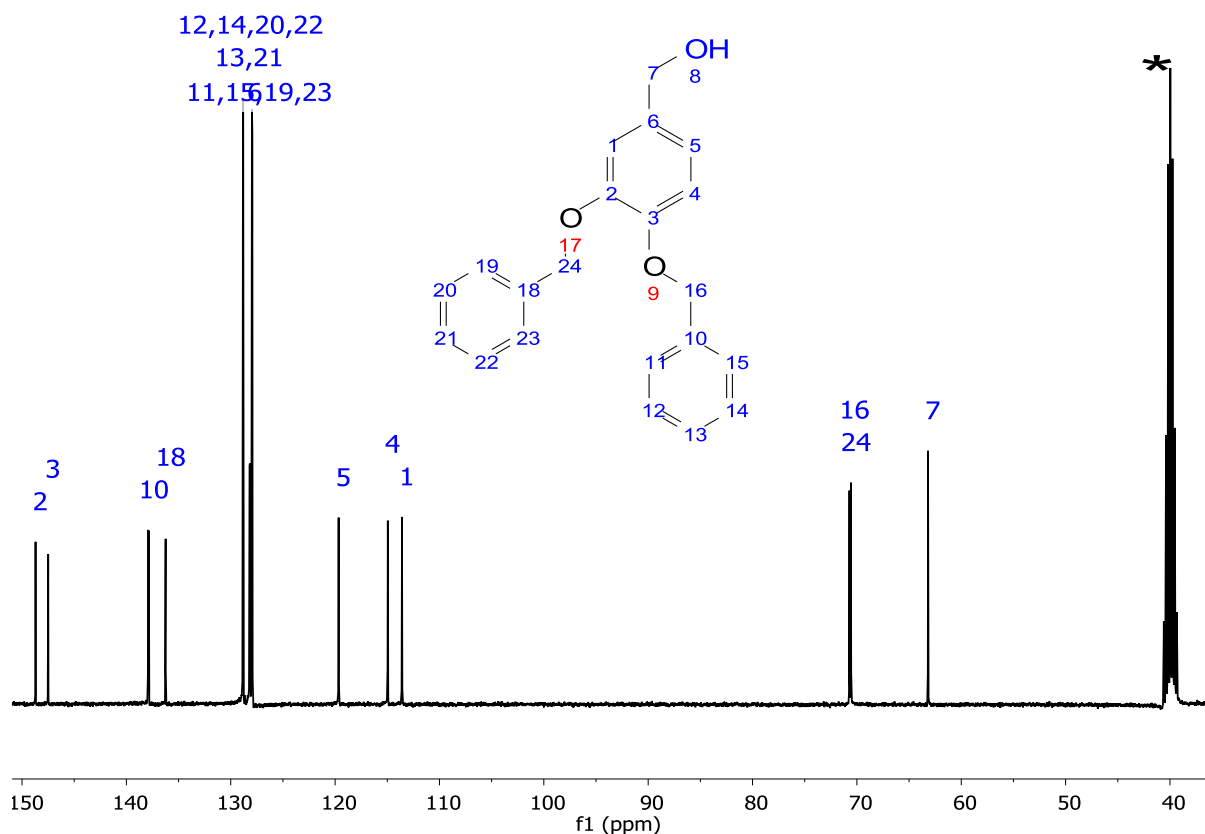


Figure S4. ^{13}C NMR spectrum of **3** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

(((4-(chloromethyl)-1,2-phenylene)bis(oxy))bis(methylene))dibenzene (4). 16.7g of thionyl chloride (10.2 mL, 140.4 mmol, 1.5 eqv. in 25 mL of dry CH_2Cl_2) was added dropwise under argon atmosphere to a 0 °C solution of (3,4-bis(benzyloxy)phenyl)methanol, (**3**) (30.0 g, 93.6 mmol, 1 eqv.) in dry CH_2Cl_2 (150 mL) with a catalytic amount of DMF (2 mL). Upon addition, reaction was allowed to stir for 4 h under argon atmosphere. Upon completion, all the organic volatiles being removed by repeated (x5, with toluene) rotaevaporation under reduced pressure and the residue was taken up with CH_2Cl_2 . The product was washed with aqueous NaHCO_3 , water and brine, then dried over anhydrous MgSO_4 and concentrated to give **4**, as a straw colored solid (31.4 g, 92.7 mmol, quantitative

yield). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.51 – 7.27 (m, 10H, ArH of Bn), 7.18 (d, J = 2.1 Hz, 1H, ArH , #1), 7.05 (d, J = 8.3 Hz, 1H, ArH , #4), 6.97 (dd, J = 8.3, 2.0 Hz, 1H, ArH , #5), 5.13 (d, J = 6.8 Hz, 4H, ArOCH_2 -, #16, 24), 4.69 (s, 2H, ArCH_2Cl). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ (ppm)): 148.80 (ArC , #2), 148.62 (ArC , #3), 137.61 (ArOCH_2ArC of Bn, #10), 137.56 (ArOCH_2ArC of Bn, #18), 130.91 (ArC , #6), 128.94, 128.85, 128.29, 128.24, 128.19, 128.10, 127.98, 127.93 (ArC of Bn), 122.47 (ArC , #5), 115.62 (ArC , #4), 114.69 (ArC , #1), 70.63, 70.47 (ArOCH_2 -), 46.98 (ArCH_2Cl).

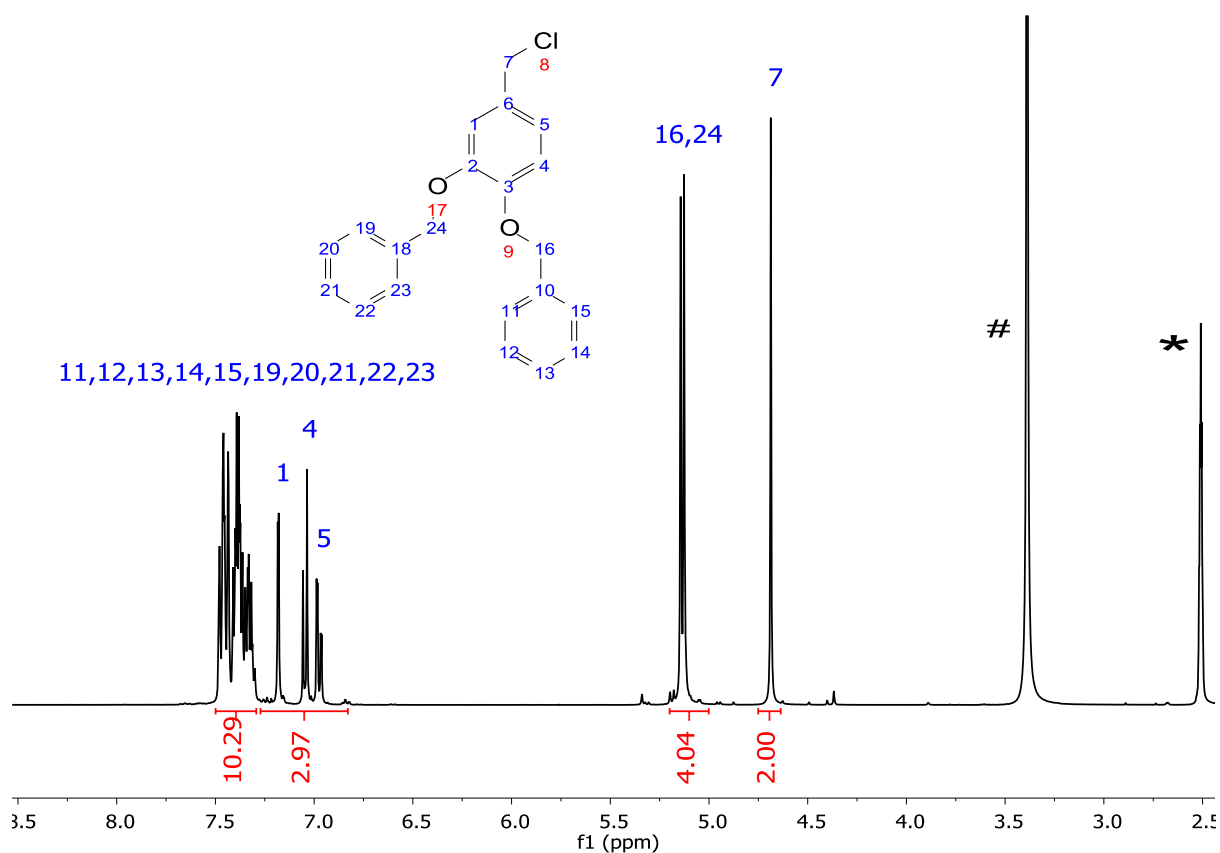


Figure S5. ^1H NMR spectrum of **4** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

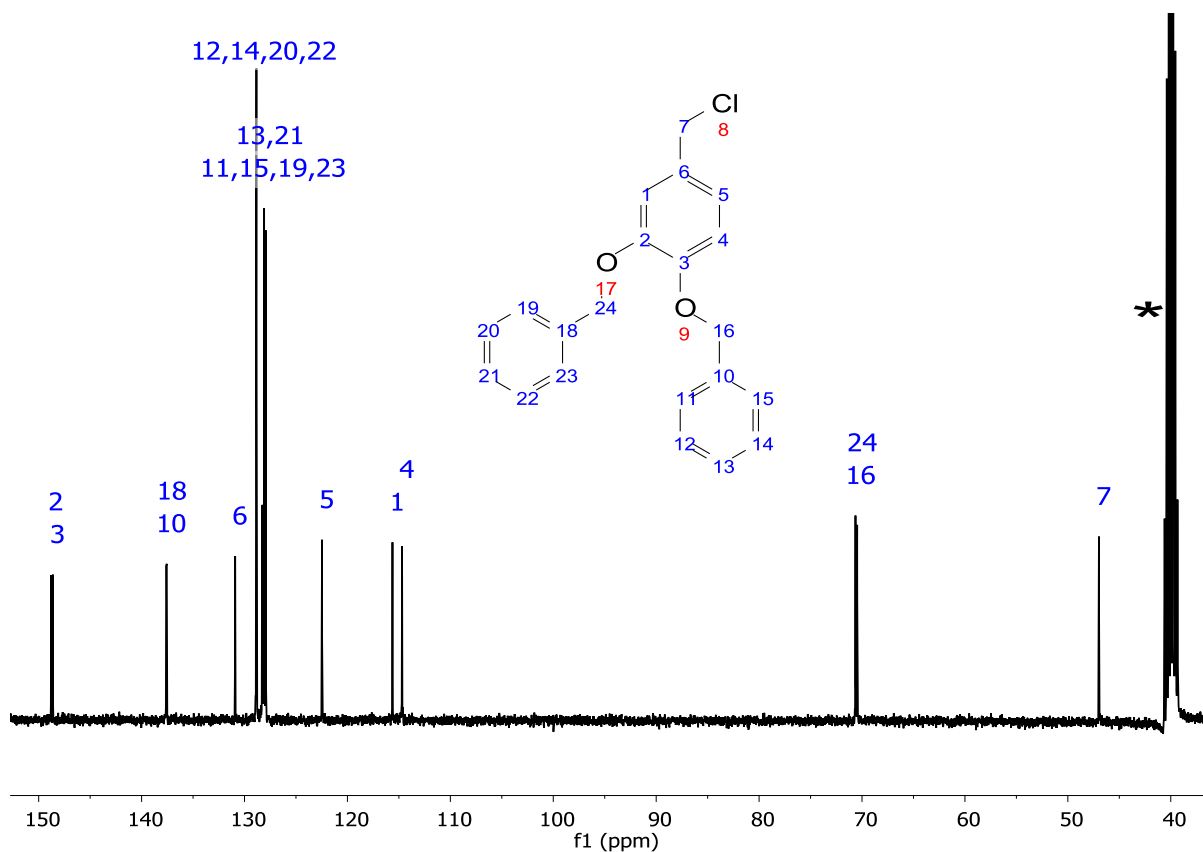


Figure S6. ^{13}C NMR spectrum of **4** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

3-(3,4-bis(benzyloxy)benzyl)-1-vinyl-1H-imidazol-3-ium chloride (5**, VIm-cat⁺-Cl).** Under vigorous stirring, 25.0 g of **4** (73.8 mmol, 1.1 eqv.) in 15 mL of anhydrous THF was added dropwise to 6.3 g (67.1 mmol, 6.1 mL, 1 eqv.) of 1-vinylimidazole in a 50 mL, one-necked round-bottom flask. The reaction mixture was then refluxed at 70 °C for 48 h and the resulting pale brown viscous liquid was cooled to room temperature. The crude product was purified by repeated precipitation from methanol/diethyl ether (x10) and dried under vacuum at 40 °C to obtain 30.6 g (70.8 mmol, 96 % yield) of **5**, as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 9.67 (s, 1H, -NCHN-), 8.22 (t, $J = 1.9$ Hz, 1H, -NCH=CHN-, #4), 7.91 (t, $J = 1.8$ Hz, 1H, -NCH=CHN-, #3), 7.48 – 7.26 (m, ArH of Bn (10H),

HCH=CHN- (1H), ArH (1H), #13), 7.10 (d, $J = 8.3$ Hz, 1H, ArH, #12), 7.04 (dd, $J = 8.3$, 2.0 Hz, 1H, ArH, #9), 5.99 (dd, $J = 15.7$, 2.4 Hz, 1H, CH₂=CHN-), 5.43 (dd, $J = 8.7$, 2.4 Hz, 1H, HCH=CHN-), 5.34 (s, 2H, ArCH₂N-), 5.15 (s, 4H, ArOCH₂-, #22, 30). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 149.19, 148.77 (ArC, #10, 11), 137.54, 137.39 (ArOCH₂ArC of Bn, #16, 24), 135.80 (-NCHN-), 129.40 (-NCH=CHN-, #3), 128.89, 128.85, 128.34, 128.29, 128.16, 127.93 (ArC of Bn), 127.34 (ArC, #14), 123.58 (CH₂=CHN-), 122.38 (NCH=CHN-, #4), 119.75 (ArC, #13), 115.59 (ArC, #9), 114.80 (ArC, #12), 109.17 (CH₂=CHN-), 70.61, 70.40 (ArOCH₂-, #22, 30), 52.57 (ArCH₂N-).

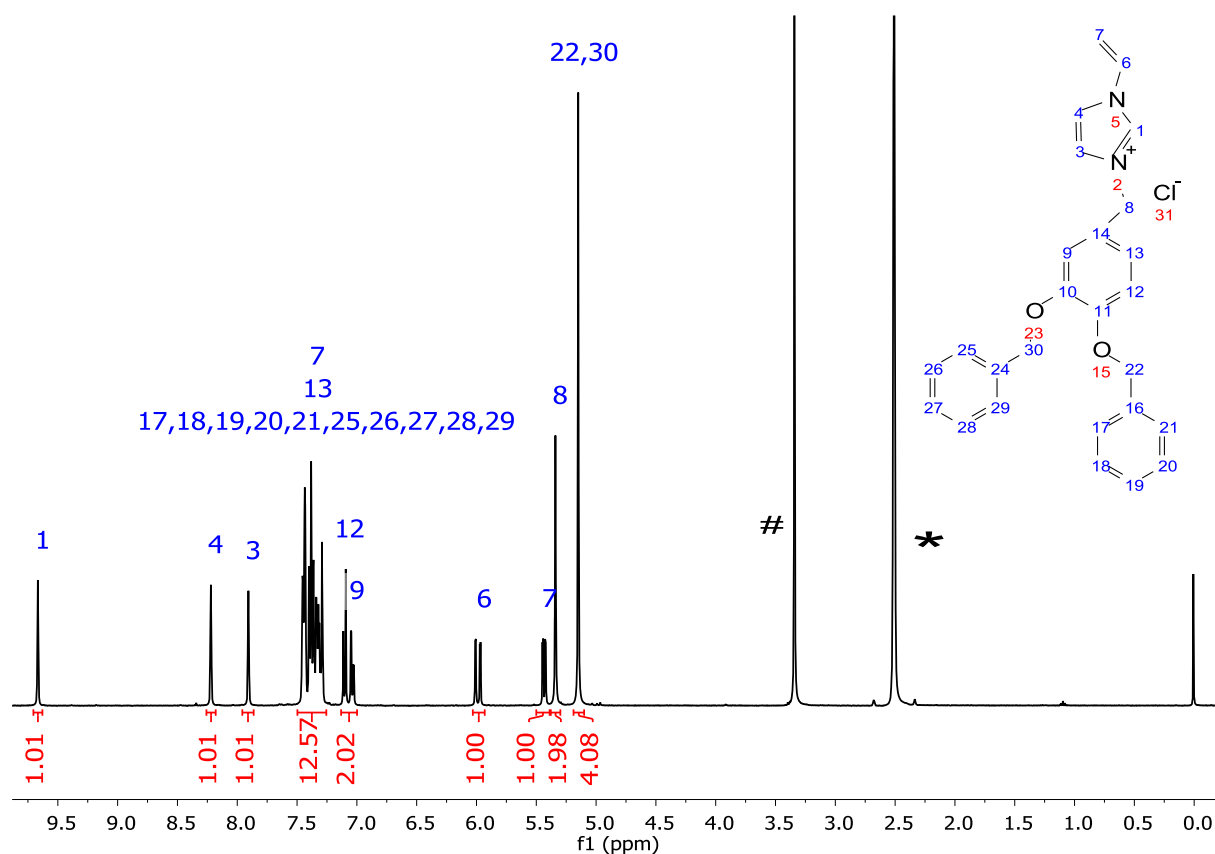


Figure S7. ¹H NMR spectrum of **5** in DMSO-*d*₆. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

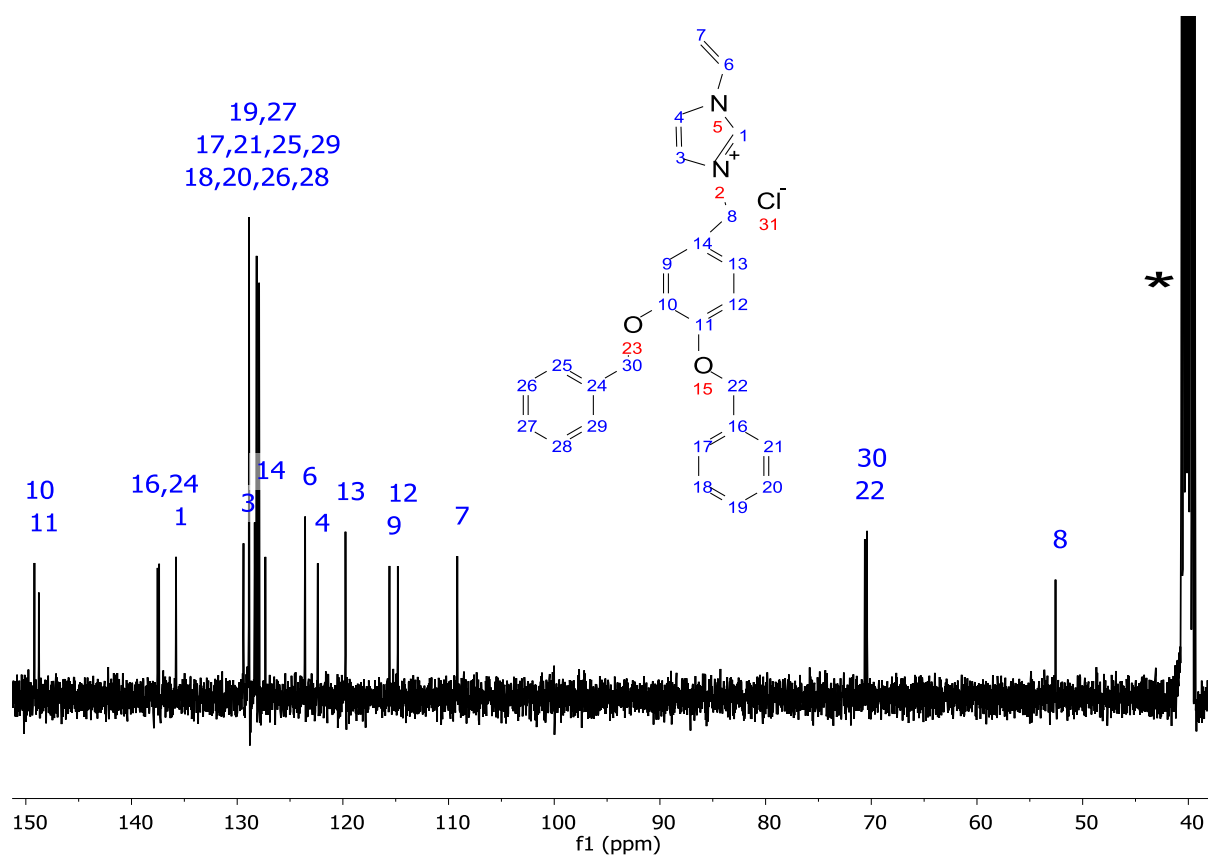
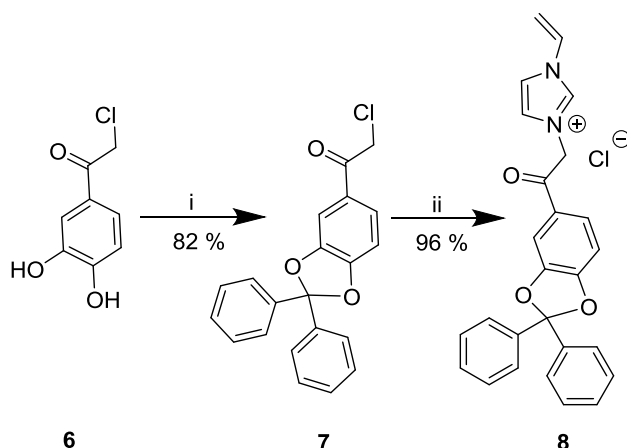


Figure S8. ^{13}C NMR spectrum of **5** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

Supporting Scheme S2. Synthesis of VIm-cat=O⁺-Cl⁻ (8)



Reagents and Conditions: (i) α,α -dichlorodiphenylmethane, toluene, 170 °C, 12 h; (ii) 1-vinylimidazole, MeOH, 70 °C, 48 h.

2-chloro-1-(2,2-diphenylbenzo[d][1,3]dioxol-5-yl)ethan-1-one (7). A two-necked round-bottom flask was charged with 12.5 g (67.0 mmol, 1 eqv.) of 2-chloro-1-(3,4-dihydroxyphenyl)ethan-1-one (**6**) and evacuated by three consecutive vacuum-argon cycles, followed by addition of 50.0 mL of degassed anhydrous toluene under argon atmosphere. 19.06 g of α,α -dichlorodiphenylmethane (80.4 mmol, 1.2 eqv.) was added and continued stirring for 1 h at room temperature. The flask was then attached to a reflux condenser and an oil bubbler and placed in an oil bath. Temperature of the oil bath was gradually raised to 170 °C to avoid strong evolution of gaseous HCl and the reaction mixture was stirred vigorously overnight, cooled to room temperature and washed with water (5 x 100 mL). The aqueous phase was then extracted with CH₂Cl₂ (3 x 100 mL) and the combined organic phases dried over MgSO₄, filtered and the solvent was removed by rotaevaporation to afford 19.3 g of **7** (55.0 mmol, 82 % yield) as a pale yellow solid, which was used in the next step without further purification. ¹H NMR (400 MHz, DMSO-*d*₆, δ (ppm)): 7.67 (dd, *J* = 8.3, 1.8 Hz, 1H, ArH, #10), 7.66 – 7.49 (m, 5H, ArH of PG), 7.52 – 7.38 (m, 5H, ArH of PG, 1H, ArH, #6), 7.25 – 7.14 (m, 1H, ArH, #9), 5.12 (s, 2H, -ArCOCH₂Cl). ¹³C NMR (101 MHz, DMSO-*d*₆, δ

(ppm): 190.14 ($-\text{Ar}\underline{\text{C}}\text{OCH}_2\text{Cl}$), 151.90 ($\text{Ar}\underline{\text{C}}$, #8), 147.39 ($\text{Ar}\underline{\text{C}}$, #7), 139.59 ($\text{Ar}\underline{\text{C}}$, #4), 130.12, 130.07 ($\text{Ar}\underline{\text{C}}$ of PG, #14,15), 129.69, 129.13, 129.11, 129.04, 128.98, 126.54, 126.25 ($\text{Ar}\underline{\text{C}}$ of PG), 125.64 ($\text{Ar}\underline{\text{C}}$, #10), 118.13 ($(\text{Ar})_2\underline{\text{C}}(\text{O})_2\text{Ar}-$), 109.23, 108.82 ($\text{Ar}\underline{\text{C}}$, #6,9), 47.90 ($-\text{ArCO}\underline{\text{C}}\text{H}_2\text{Cl}$).

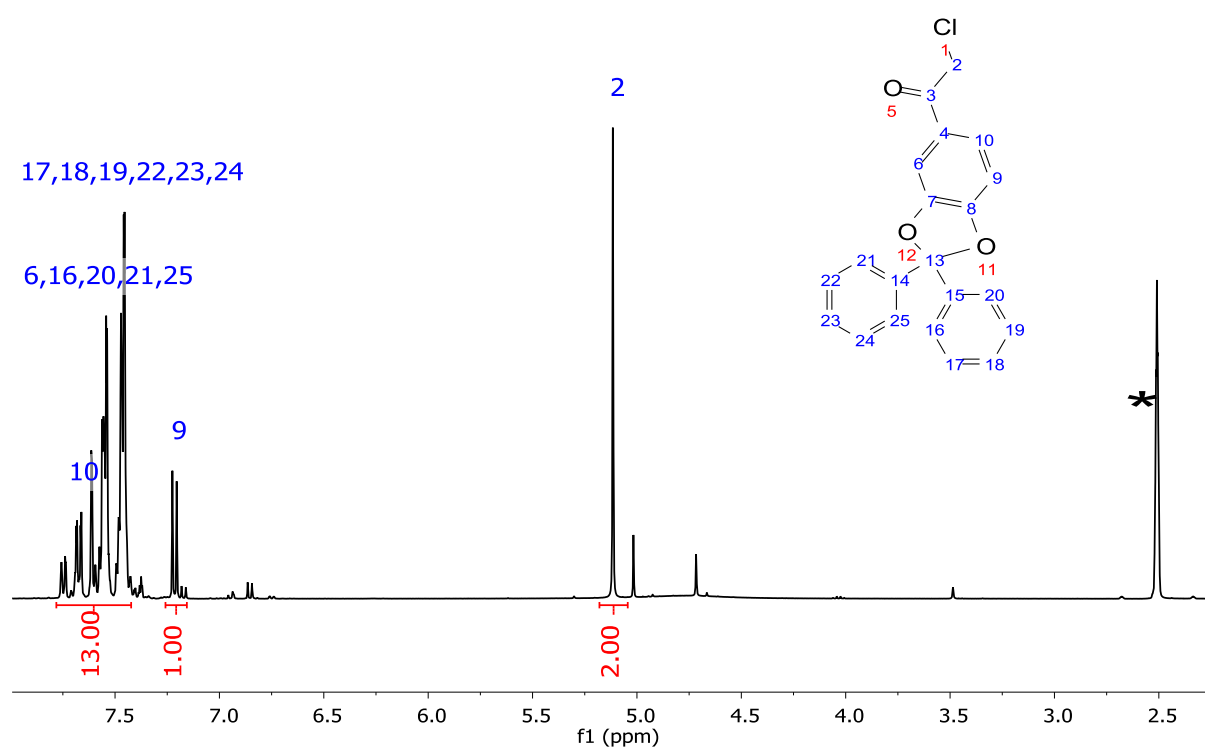


Figure S9. ^1H NMR spectrum of **7** in $\text{DMSO}-d_6$. * in the spectrum corresponds to the deuterated solvent signal.

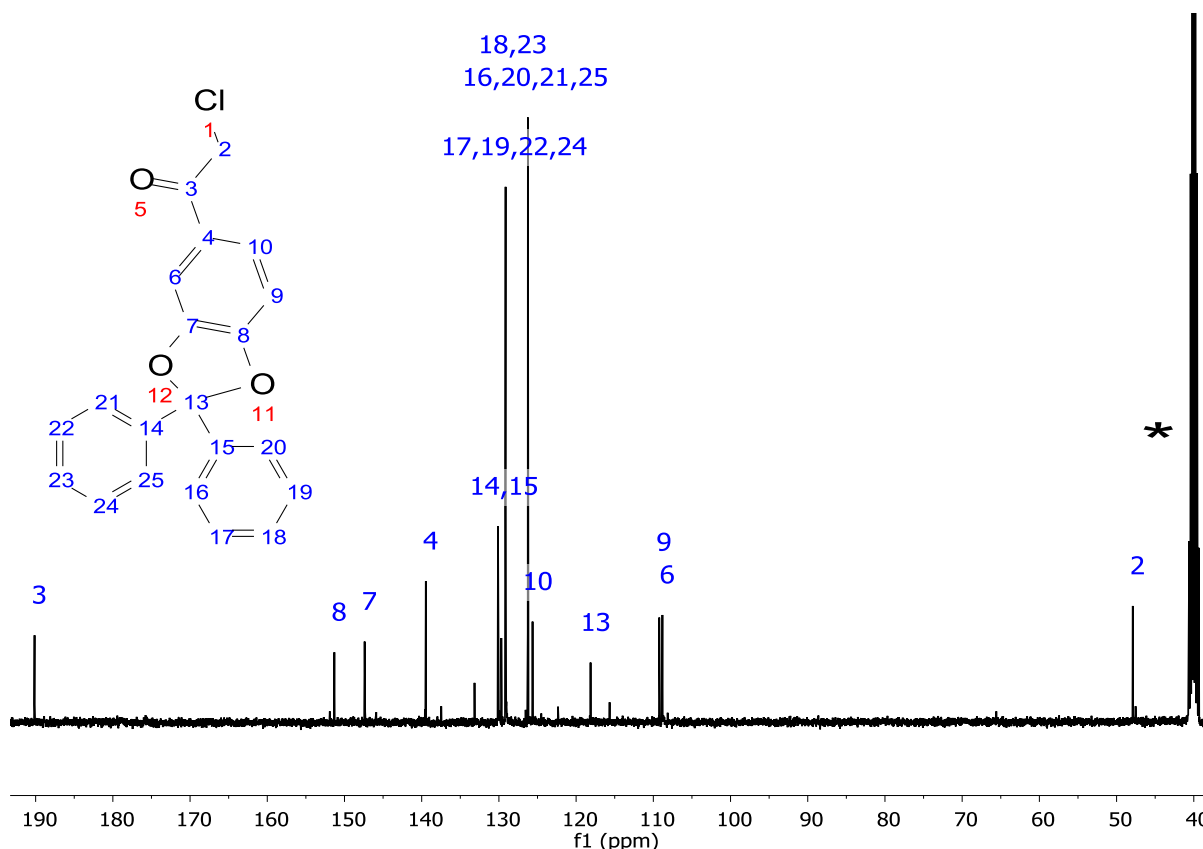


Figure S10. ^{13}C NMR spectrum of **7** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

3-(2-(2,2-diphenylbenzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-1-vinyl-1H-imidazol-3-ium chloride (8**, VIm-cat=O⁺-Cl).** Under vigorous stirring, 18.0 g of **7** (51.3 mmol, 1.1 eqv.) in 10 mL of anhydrous methanol was added dropwise to 4.39 g (46.6 mmol, 4.22 mL, 1 eqv.) of 1-vinylimidazole in a 50 mL, one-necked round-bottom flask. The reaction mixture was then refluxed at 70 °C for 30 h and the resulting pale brown viscous liquid was cooled to room temperature. The crude product was purified by repeated precipitation from methanol/diethyl ether (x10) and dried under vacuum at 40 °C to obtain 21.9 g (49.3 mmol, 96 % yield) of **8**, as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 9.52 (s, 1H, -NCHN-), 8.33 (s, 1H, -NCH=CHN-, #4), 7.85 (t, J = 1.8 Hz, 1H, -NCH=CHN-, #3), 7.77 (dd,

$J = 8.2, 1.8$ Hz, 1H, ArH, #16), 7.71 (d, $J = 1.7$ Hz, 1H, ArH, #12), 7.61 – 7.42 (m, 10H, ArH of PG), 7.32 (d, $J = 8.2$ Hz, 1H, ArH, #15), 6.05 (s, 2H, -ArCOCH₂Cl), 6.05 (dd, $J = 15.7, 2.5$ Hz, 1H, CH₂=CHN-), 5.48 (dd, $J = 8.8, 2.4$ Hz, 1H, HCH=CHN-). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 189.59 (-ArC(=O)CH₂Cl), 151.85 (-ArOCArC of PG, #14), 147.61 (-ArOCArC of PG, #13), 139.33 (ArC, #10), 137.27 (-NCHN-), 130.21 (ArC of PG, #20, 21), 129.39 (-NCH=CHN-, #3), 129.18 (ArC of PG), 126.25 (ArC of PG), 125.71 (CH₂=CHN-), 125.35 (ArC, #16), 119.02 (NCH=CHN-, #4), 118.37 ((Ar)₂C(O)₂Ar-), 109.57, 109.45 (ArC, #12,15), 108.64 (CH₂=CHN-), 55.87 (-ArCOCH₂Cl).

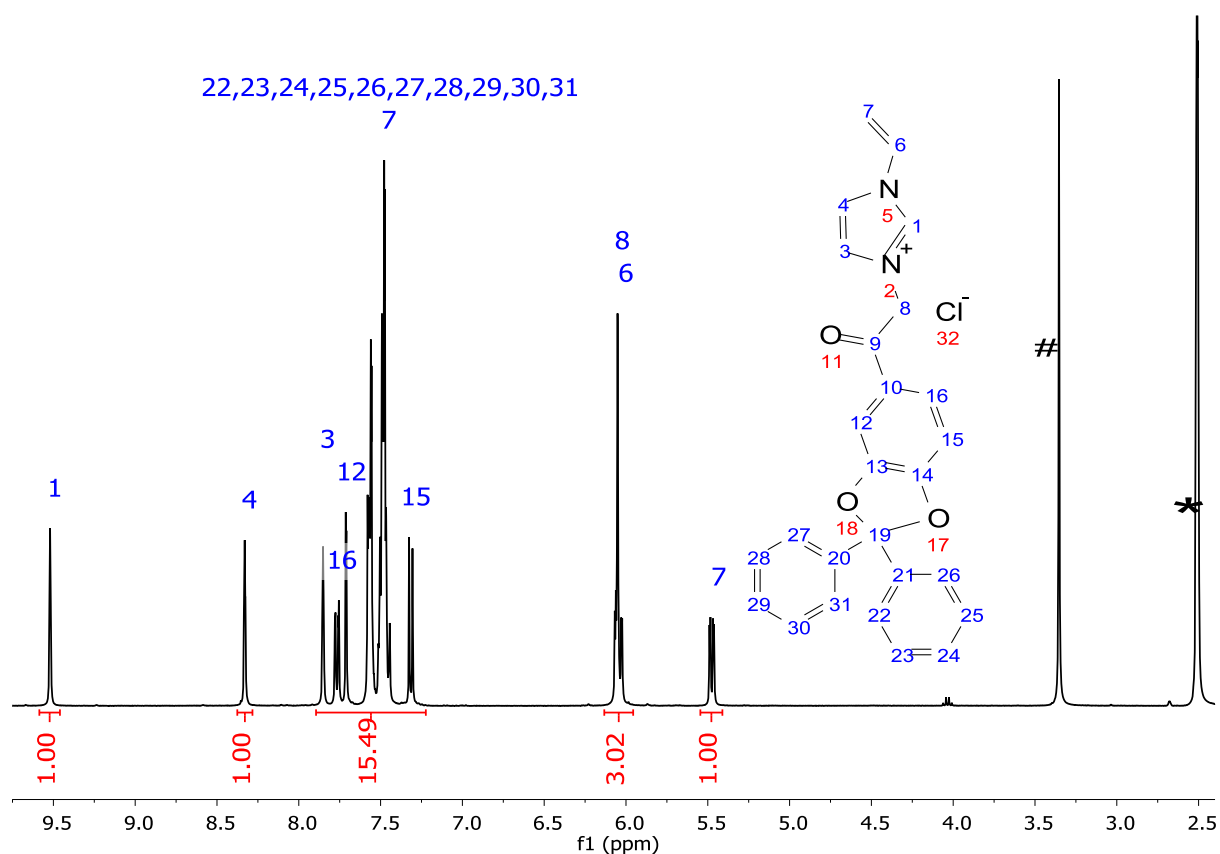


Figure S11. ¹H NMR spectrum of **8** in DMSO-*d*₆. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

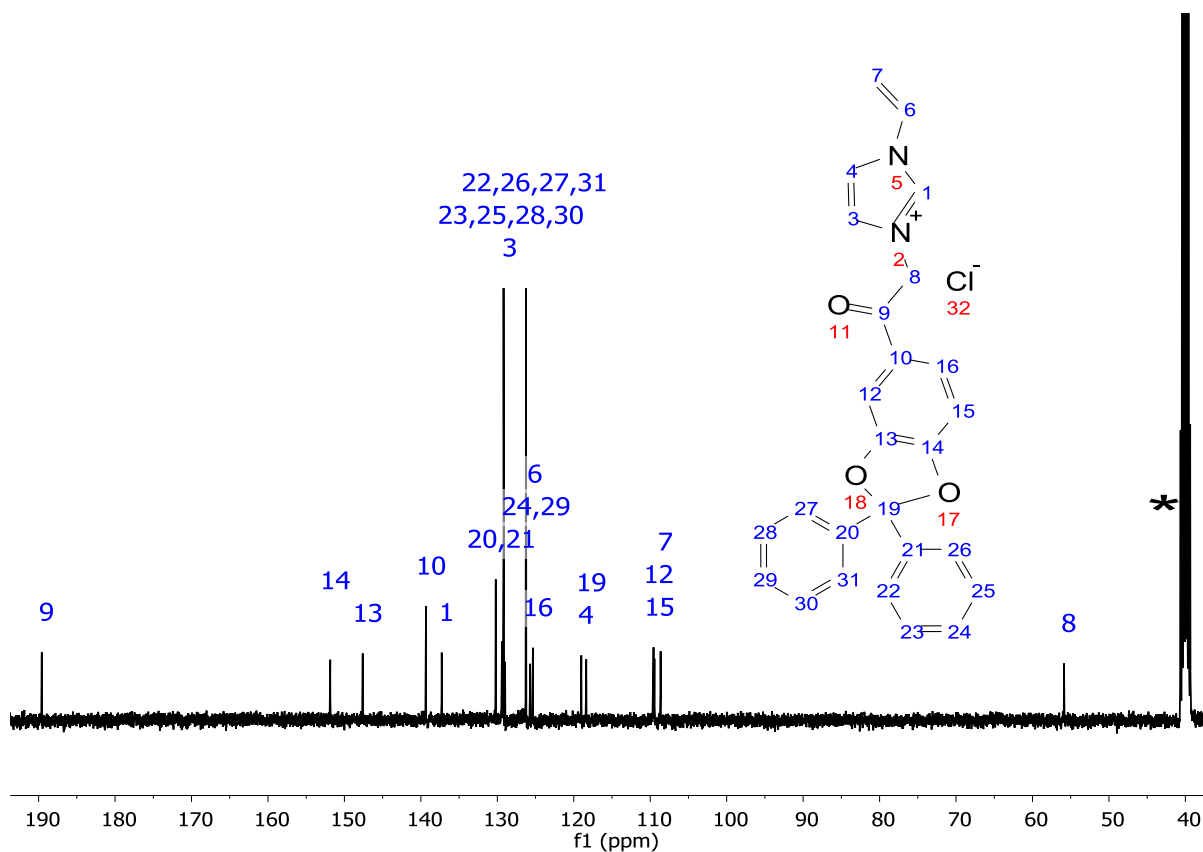
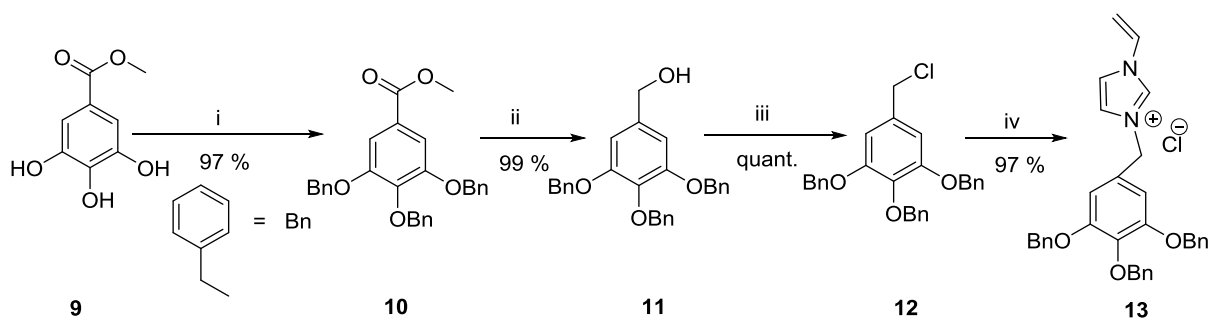


Figure S12. ^{13}C NMR spectrum of **8** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

Supporting Scheme S3. Synthesis of VIm-pyr $^{\oplus}$ -Cl (13)



Reagents and Conditions: (i) BnCl , K_2CO_3 , DMF, 75°C , 12 h; (ii) LiAlH_4 , THF, 2 h; (iii) SOCl_2 , cat. DMF, DCM, 4 h; (iv) 1-vinylimidazole, THF, 70°C , 48 h.

Methyl 3,4,5-tris(benzyloxy)benzoate (10). A two-necked round-bottom flask was charged with 20.0 g (108.6 mmol, 1 eqv.) of **9** and 68.0 g (492.0 mmol, 4.5 eqv.) of finely grinded, oven dried K₂CO₃. The flask was evacuated by three consecutive vacuum-argon cycles and backfilled with argon, before transferring 400 mL of degassed anhydrous DMF using cannula. 43.3 g (39.4 mL, 342.1 mmol, 3.15 eqv.) of degassed benzyl chloride in degassed anhydrous DMF (50 mL) was slowly added to the above suspension under argon atmosphere at room temperature. The suspension was brought to reflux and continued vigorous stirring for 12 h under argon atmosphere. The reaction mixture was cooled to room temperature and poured into cold water. The solid precipitated was collected by vacuum filtration and re-dissolved in CH₂Cl₂. After being washed with saturated NaHCO₃, water and brine, the organic phase was dried over anhydrous MgSO₄, filtered and passed through a short column of basic alumina using CH₂Cl₂ as an eluent. The solvent was rotaevaporated under reduced pressure, affording 47.9 g of **10** (105.3 mmol, 97 % yield), as a cream colored solid. ¹H NMR (400 MHz, DMSO-*d*₆, δ (ppm)): 7.51 – 7.28 (m, ArH of Bn (15H), ArH (2H)), 5.19 (s, 4H, ArOCH₂-, #26, 34), 5.05 (s, 2H, ArOCH₂-, #18), 3.84 (s, 3H, ArCO₂CH₃). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 166.22 (C=O), 152.60 (ArC, #2, 4), 141.78 (ArC, #3), 137.74 (ArC of Bn, #12), 137.19 (ArC of Bn, #20, 28), 128.89, 128.66, 128.58, 128.55, 128.39, 128.07 (ArC of Bn), 125.25 (ArC, #6), 108.55 (ArC, #1, 5), 74.71 (ArOCH₂-, #18), 70.76 (ArOCH₂-, #26, 34), 52.71 (ArCO₂CH₃).

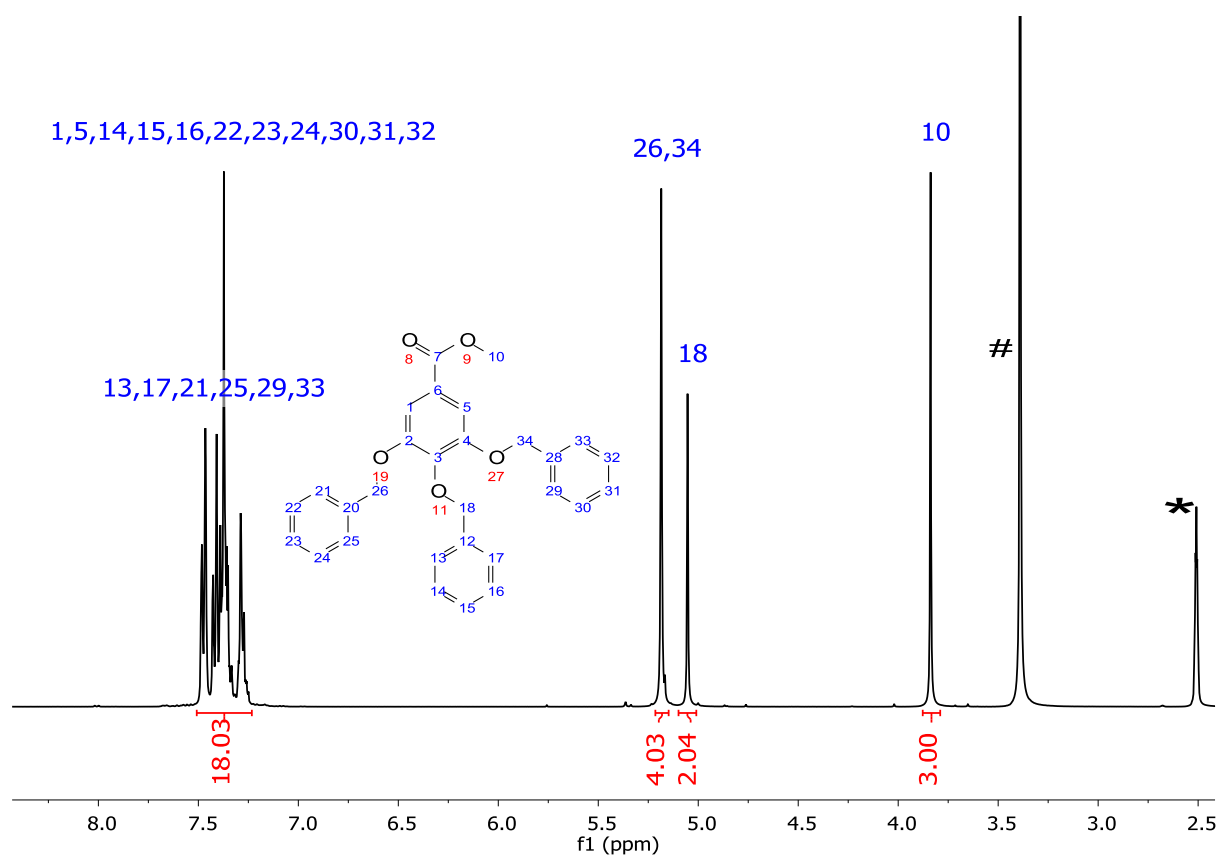


Figure S13. ^1H NMR spectrum of **10** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

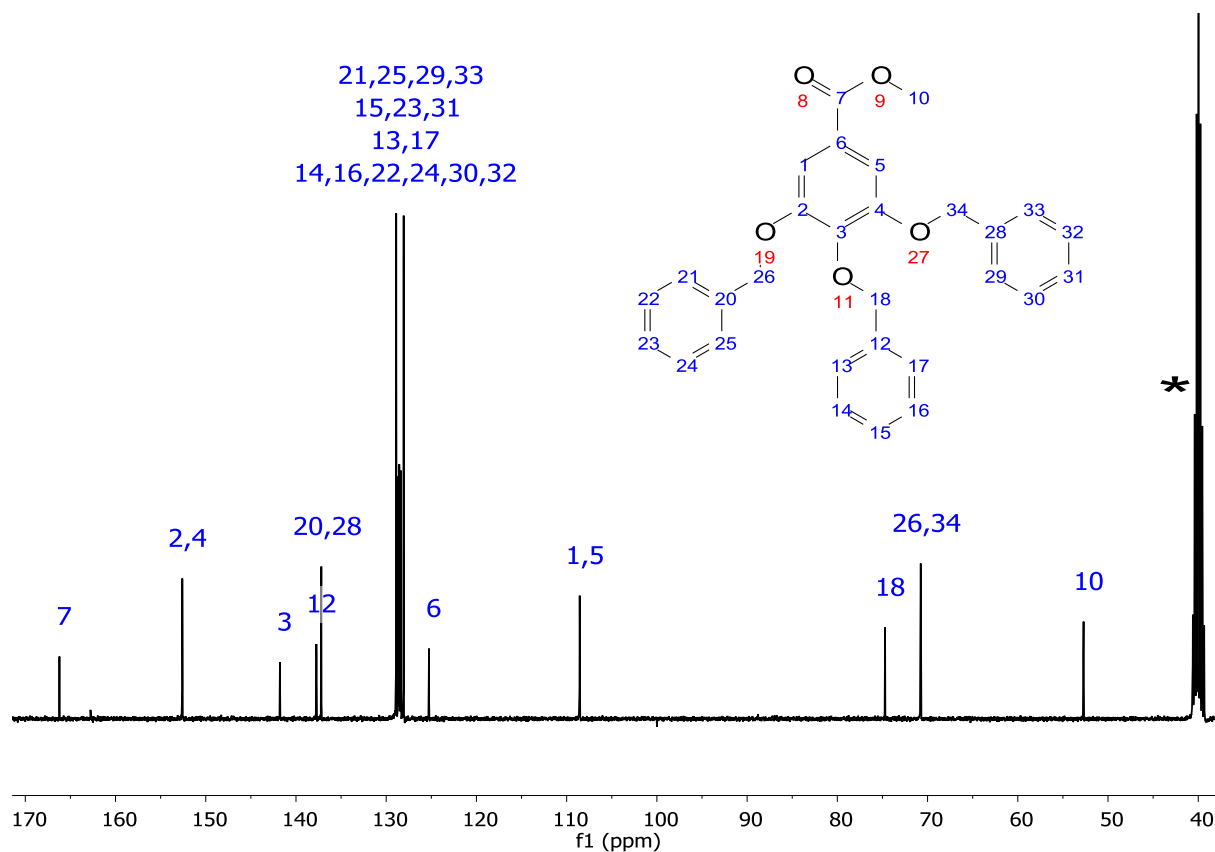


Figure S14. ^{13}C NMR spectrum of **10** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

(3,4,5-tris(benzyloxy)phenyl)methanol (11). To a suspension of LiAlH_4 (5.0 g, 131.8 mmol, 1.5 eqv.) in dry THF (250 mL) at 0 °C was added dropwise a solution of methyl 3,4,5-tris(benzyloxy)benzoate (**10**) (40.0 g, 88.0 mmol, 1 eqv.) in 150 mL of dry THF under argon atmosphere. The reaction mixture was stirred at room temperature for 2 h, before being quenched by successive addition of 5 mL H_2O , 5 mL of 15% NaOH and 15 mL of H_2O . The granular salts were filtered, washed with THF and dried over anhydrous MgSO_4 . The solvent was fully rotaevaporated under reduced pressure and the remaining solid was re-dissolved in CH_2Cl_2 and passed through a short column of basic alumina using CH_2Cl_2 as an eluent. The solvent was rotaevaporated under reduced pressure, affording 37.2 g of **11** (87.1 mmol, 99 %

yield), as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.51 – 7.43 (m, 4H, ArH of Bn), 7.45 – 7.31 (m, 8H, ArH of Bn), 7.35 – 7.22 (m, 3H, ArH of Bn), 6.78 (s, 2H, ArH), 5.20 (t, $J = 5.7$ Hz, 1H, ArCH_2OH), 5.11 (s, 4H, ArOCH_2 -, #24, 32), 4.93 (s, 2H, ArOCH_2 -, #16), 4.43 (d, $J = 5.3$ Hz, 2H, ArCH_2OH). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ (ppm)): 152.54 (ArC , #2, 4), 138.85 (ArC , #6), 138.30 (ArC , #3), 137.67 (ArOCH_2ArC of Bn, #18, 26), 136.27 (ArOCH_2ArC of Bn, #10), 128.85, 128.59, 128.52, 128.49, 128.26, 128.18, 128.01 (ArC of Bn), 105.66 (ArC , #1, 5), 74.74 (ArOCH_2 -, #16), 70.55 (ArOCH_2 -, #24, 32), 63.39 (ArCH_2OH).

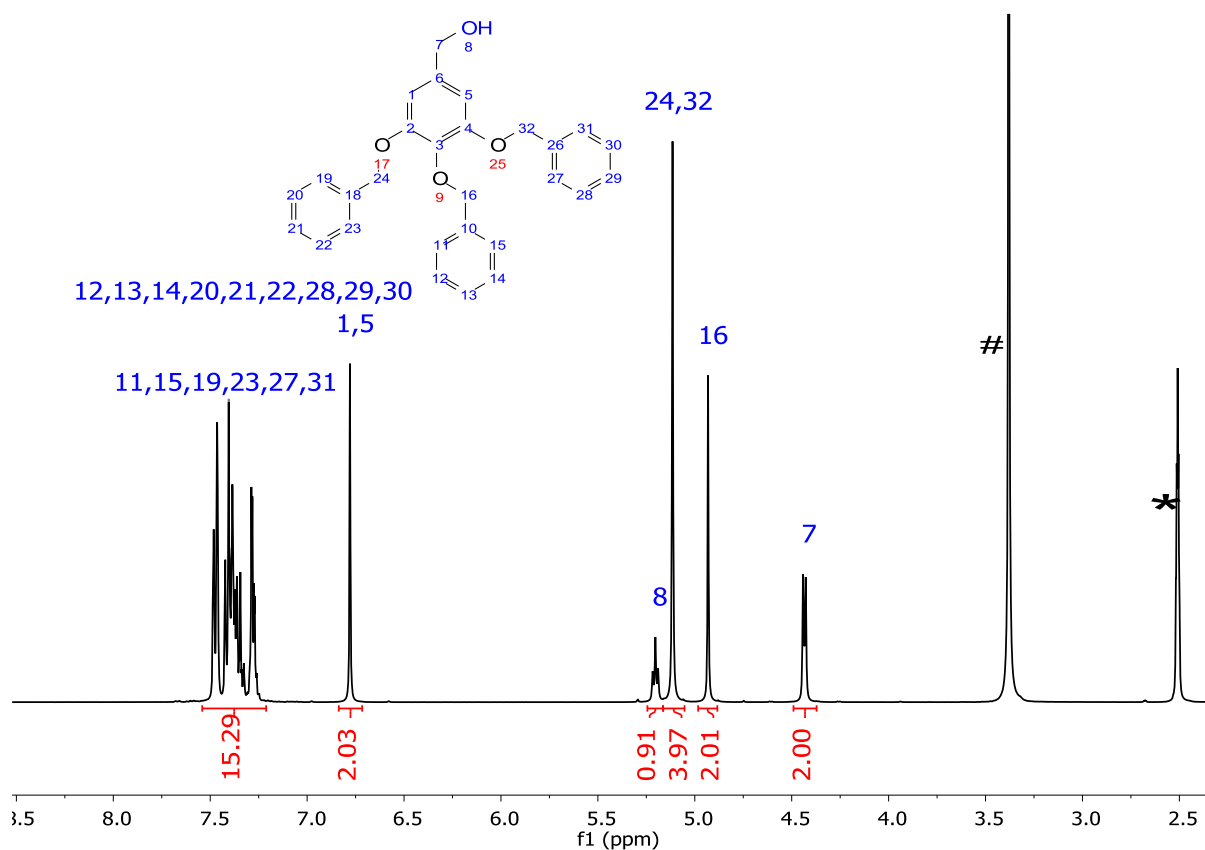


Figure S15. ^1H NMR spectrum of **11** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

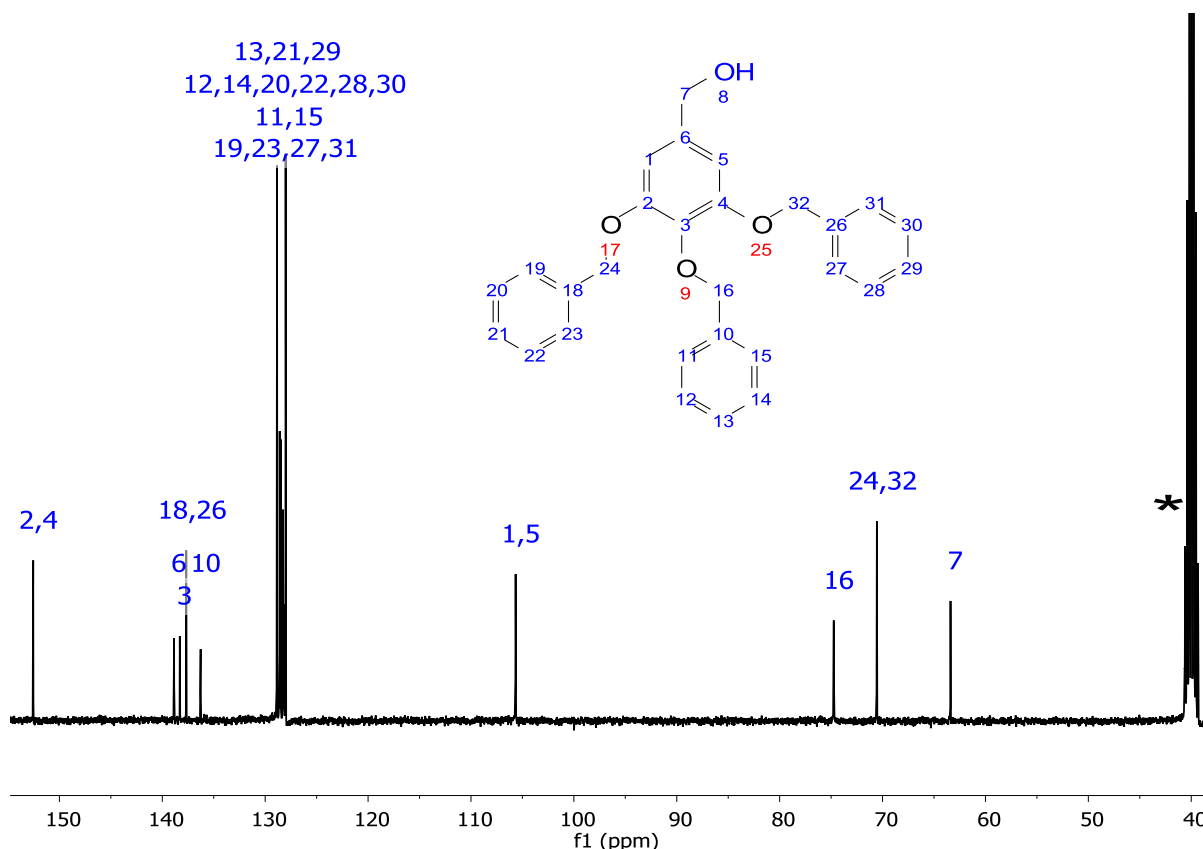


Figure S16. ^{13}C NMR spectrum of **11** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

(((5-(chloromethyl)benzene-1,2,3-triyl)tris(oxy))tris(methylene))tribenzene (12**).**

10.5 g of thionyl chloride (6.4 mL, 87.9 mmol, 1.5 eqv. in 20 mL of dry CH_2Cl_2) was added dropwise under argon atmosphere to a 0 °C solution of (3,4-bis(benzyloxy)phenyl)methanol, (**11**) (25.0 g, 58.6 mmol, 1 eqv.) in dry CH_2Cl_2 (150 mL) with a catalytic amount of DMF (2 mL). Upon addition, reaction was allowed to stir for 4 h under argon atmosphere. Upon completion, all the organic volatiles being removed by repeated (x5, with toluene) rotaevaporation under reduced pressure and the residue was taken up with CH_2Cl_2 . The product was washed with aqueous NaHCO_3 , water and brine, then dried over anhydrous MgSO_4 and concentrated to give **12**, as a straw colored solid (25.9 g, 58.3 mmol, quantitative

yield). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.52 – 7.44 (m, 4H, ArH of Bn), 7.46 – 7.30 (m, 8H, ArH of Bn), 7.33 – 7.22 (m, 3H, ArH of Bn), 6.93 (s, 2H, ArH), 5.13 (s, 4H, ArOCH_2 -, #24, 32), 4.95 (s, 2H, ArOCH_2 -, #16), 4.69 (s, 2H, ArCH_2Cl). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ (ppm)): 152.66 (ArC -, #2, 4), 138.09 (ArC -, #6), 137.65 (ArC -, #3), 137.38 (ArOCH_2ArC of Bn, #18, 26), 133.61 (ArOCH_2ArC of Bn, #10), 128.87, 128.67, 128.61, 128.51, 128.36, 128.25, 128.16 (ArC of Bn), 108.45 (ArC -, #1, 5), 74.76 (ArOCH_2 -, #16), 70.70 (ArOCH_2 -, #24, 32), 47.08 (ArCH_2Cl).

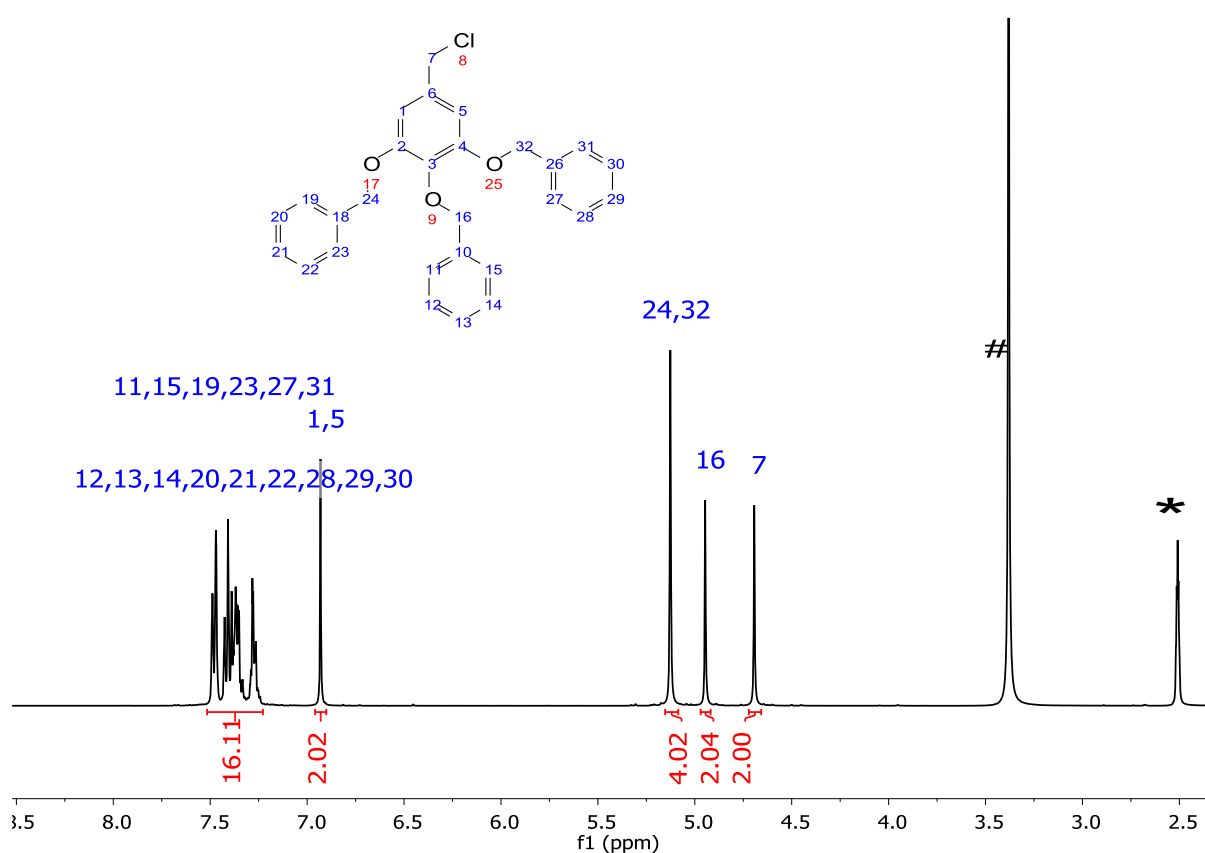


Figure S17. ^1H NMR spectrum of **12** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

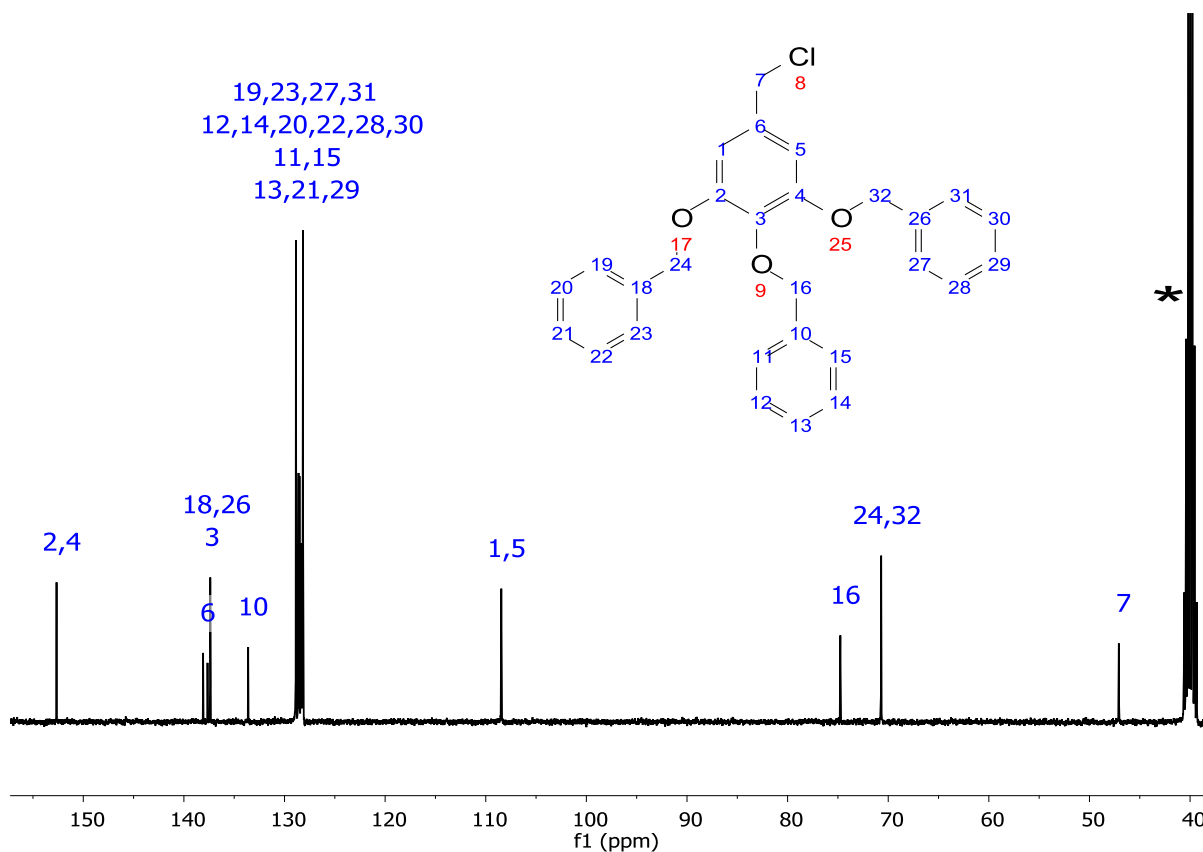


Figure S18. ^{13}C NMR spectrum of **12** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

3-(3,4,5-tris(benzyloxy)benzyl)-1-vinyl-1H-imidazol-3-ium chloride (13, VIm-pyr⁺-Cl). Under vigorous stirring, 25.0 g of **12** (56.2 mmol, 1.1 eqv.) in 15 mL of anhydrous THF was added dropwise to 4.8 g (51.1 mmol, 4.6 mL, 1 eqv.) of 1-vinylimidazole in a 50 mL, one-necked round-bottom flask. The reaction mixture was then refluxed at 70 °C for 48 h and the resulting pale brown viscous liquid was allowed to cool down to room temperature. The crude product was purified by repeated precipitation from methanol/diethyl ether (x10) and dried under vacuum at 40 °C to obtain 29.0 g (54.5 mmol, 97 % yield) of **13**, as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 9.76 (s, 1H, -NCHN-), 8.25 (t, $J = 1.9$ Hz, 1H, -NCH=CHN-, #4), 7.95 (s, 1H, -NCH=CHN-, #3), 7.46 (m, 4H, ArH of Bn), 7.45 – 7.28 (m, ArH of Bn (8H), HCH=CHN- (1H)), 7.32 – 7.22 (m, 3H,

ArH of Bn), 7.04 (s, 2H, ArH), 6.02 (dd, $J = 15.6, 2.4$ Hz, 1H, CH₂=CHN-), 5.46 (dd, $J = 8.8, 2.4$ Hz, 1H, HCH=CHN-), 5.36 (s, 2H, ArCH₂N-), 5.15 (s, 4H, ArOCH₂-, #30, 38), 4.93 (s, 2H, ArOCH₂-, #22). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 152.88 (ArC, #10, 12), 138.02 (ArOCH₂ArC of Bn, #16), 137.21 (ArC, #11), 135.93 (-NCHN-), 130.15 (-NCH=CHN-, #3), 129.44 (ArC, #14), 128.89, 128.59, 128.53, 128.43, 128.30, 128.22 (ArC of Bn), 123.64 (CH₂=CHN-), 119.76 (NCH=CHN-, #4), 109.24 (CH₂=CHN-), 108.60 (ArC, #9, 13), 74.74 (ArOCH₂-, #22), 70.74 (ArOCH₂-, #30, 38), 52.91 (ArCH₂N-).

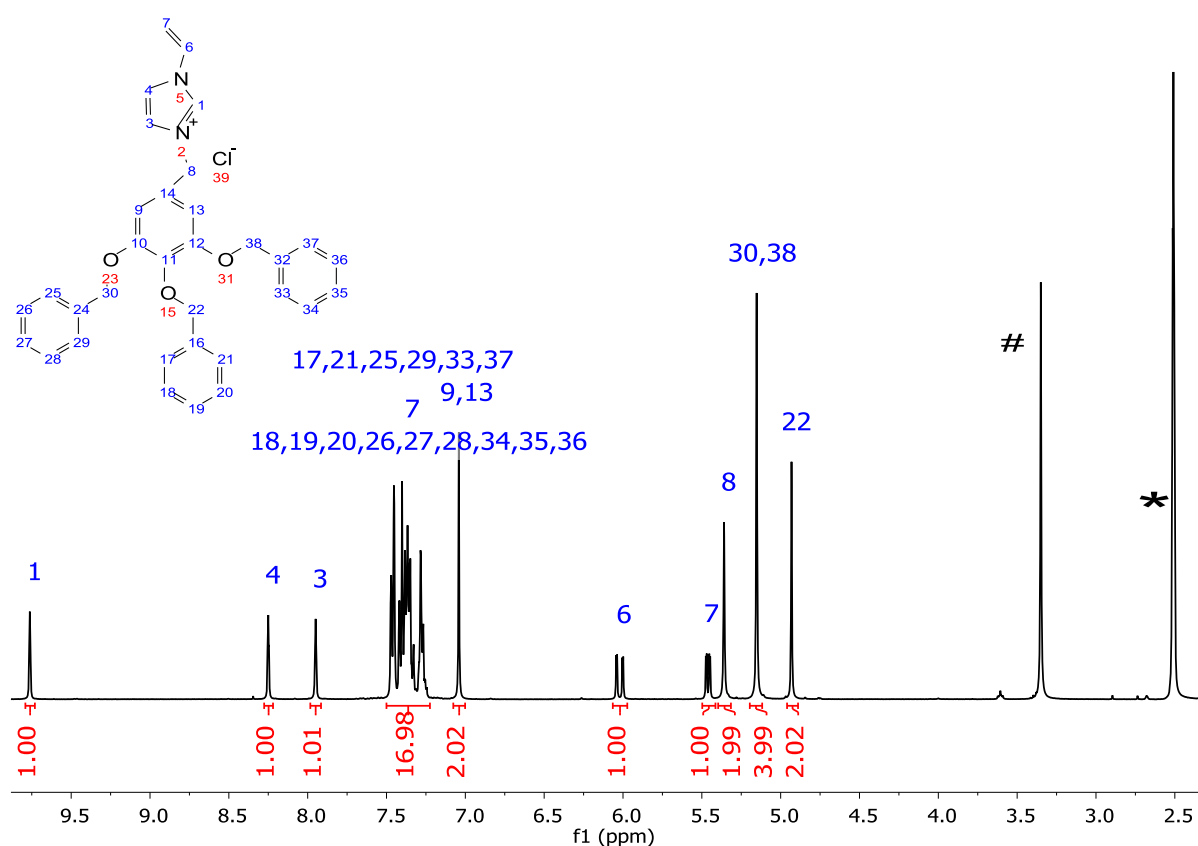


Figure S19. ¹H NMR spectrum of **13** in DMSO-*d*₆. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

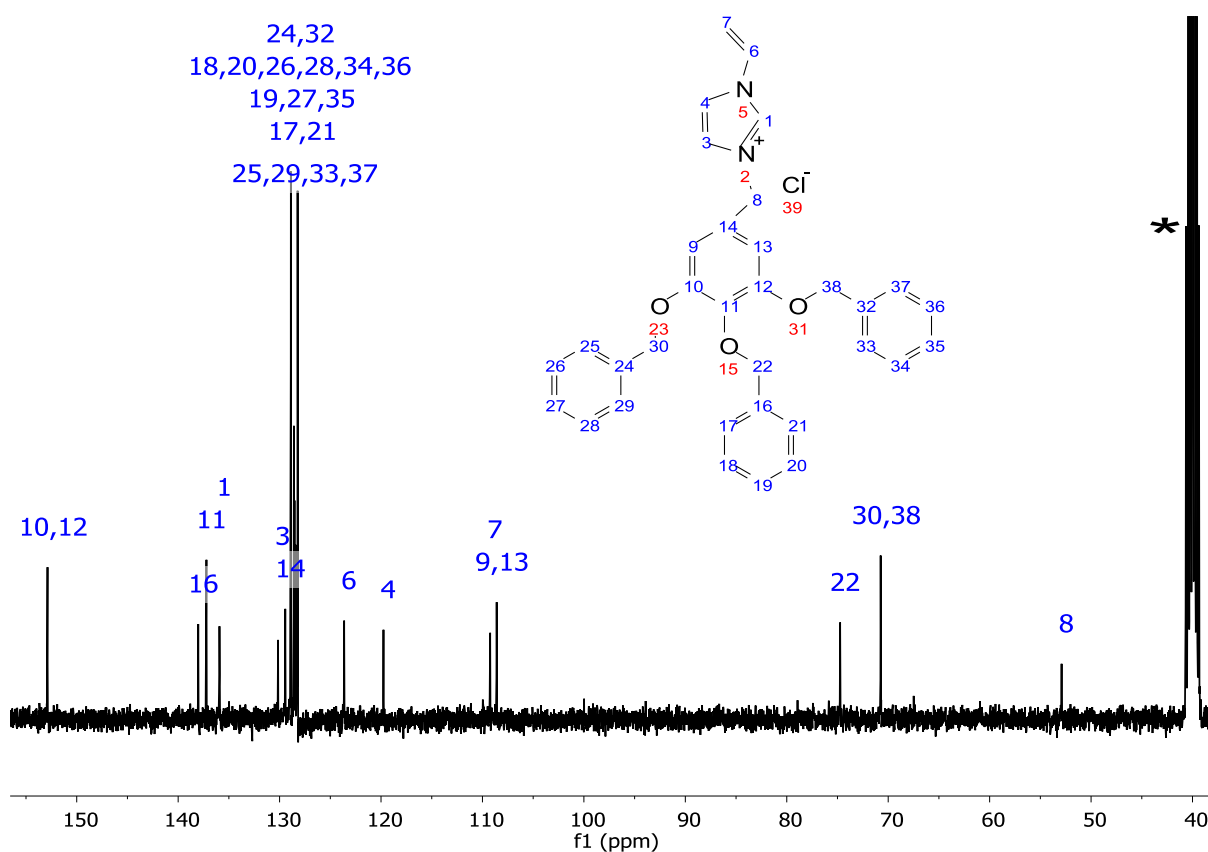
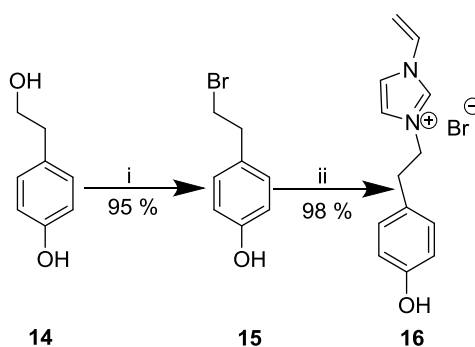


Figure S20. ^{13}C NMR spectrum of **13** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

Supporting Scheme S4. Synthesis of VIm-phe-Br (**16**)



Reagents and Conditions: (i) HBr , 85°C , 12 h; (ii) 1-vinylimidazole, MeOH , 80°C , 36 h.

4-(2-bromoethyl)phenol (15). 4-(2-Hydroxyethyl)phenol, **14** (25.0 g, 181 mmol), was dissolved in a solution of 48% HBr (w/w) in water (150 mL). This light yellow solution was allowed to stir vigorously at a temperature of 85 °C for 12 h. The reaction mixture was allowed to cool to room temperature and was then extracted with CH₂Cl₂ (3 x 100 mL). The combined extracts were dried over anhydrous MgSO₄, filtered, concentrated under reduced pressure, and dried under vacuum at ambient temperature to afford 35.0 g (174 mmol, 95 % crude yield) of a tan solid, which was used in the next step without further purification. ¹H NMR (400 MHz, DMSO-*d*₆, δ (ppm)): 9.28 (s, 1H, ArOH), 7.12 – 7.02 (m, 2H, ArH, #1, 5), 6.76 – 6.64 (m, 2H, ArH, #2, 4), 3.63 (t, *J* = 7.4 Hz, 2H, ArCH₂CH₂Br), 3.00 (t, *J* = 7.4 Hz, 2H, ArCH₂CH₂Br). ¹³C NMR (101 MHz, DMSO-*d*₆, δ (ppm)): 156.54 (ArC, #3), 130.28 (ArC, #1, 5), 129.54 (ArC, #6), 115.58 (ArC, #2, 4), 38.28 (ArCH₂CH₂Br), 35.42 (ArCH₂CH₂Br).

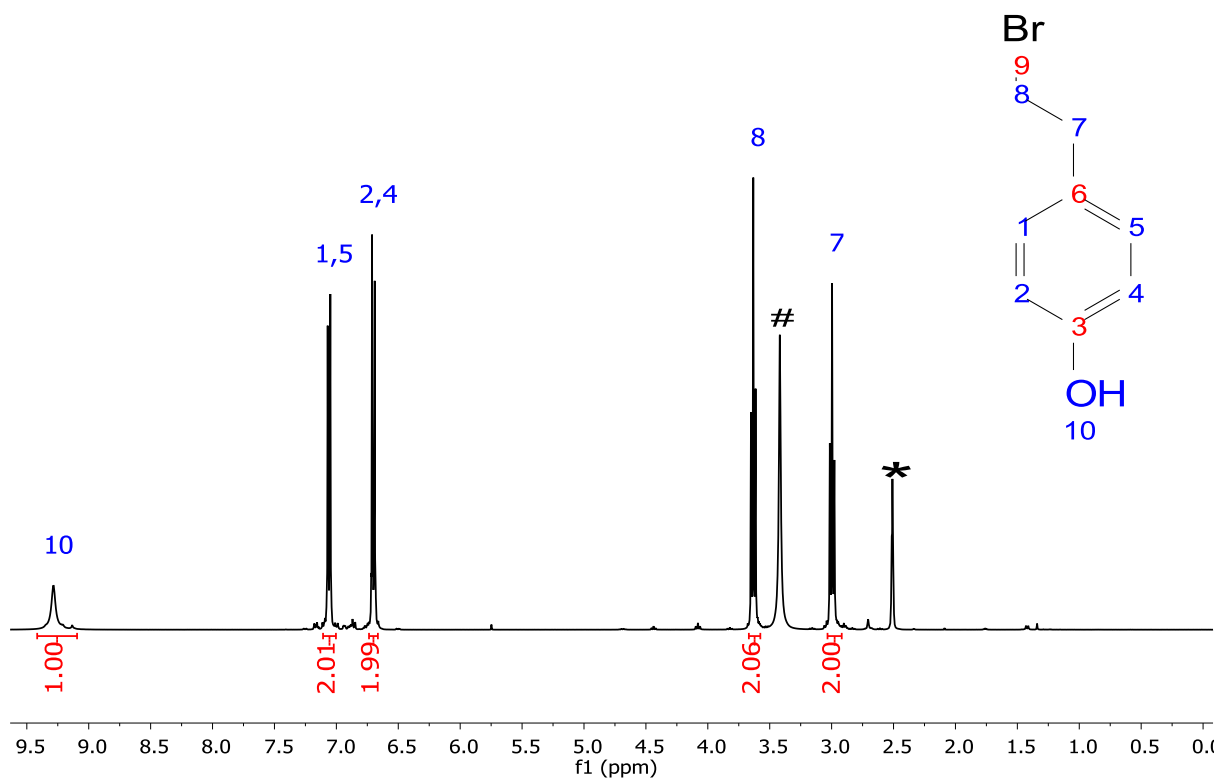


Figure S21. ^1H NMR spectrum of **15** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

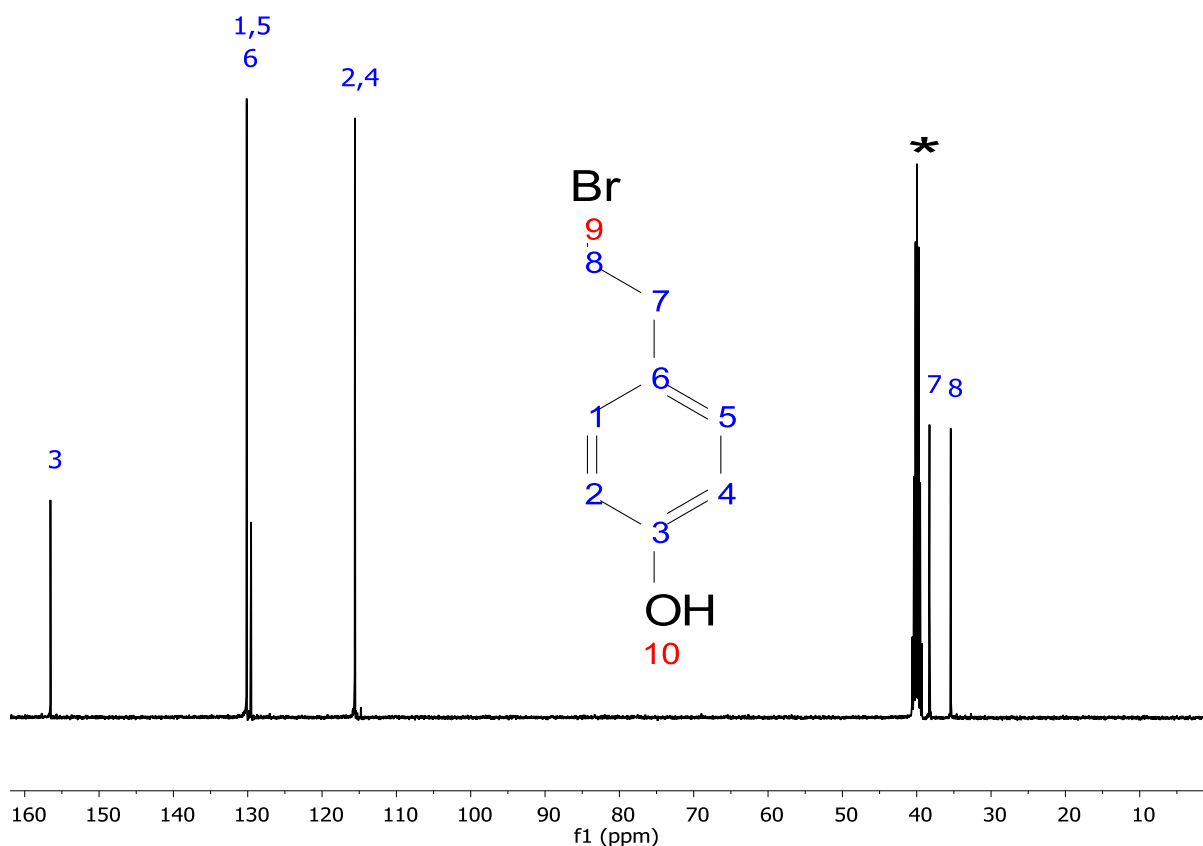


Figure S22. ^{13}C NMR spectrum of **15** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

3-(4-hydroxyphenethyl)-1-vinyl-1H-imidazol-3-ium bromide (**16**, VIm-phe-Br).

Under vigorous stirring, 25.0 g of **15** (124.3 mmol, 1.1 eqv.) in 25 mL of anhydrous methanol was added dropwise to 10.6 g (113.1 mmol, 10.2 mL, 1 eqv.) of 1-vinylimidazole in a 100 mL, one-necked round-bottom flask. The reaction mixture was then refluxed at 80 °C for 36 h and the resulting pale brown viscous liquid was allowed to cool down to room temperature. The crude product was purified by repeated precipitation from methanol/diethyl ether (x5) and ethyl acetate (x5) and dried under vacuum at 40 °C to obtain 36.0 g (121.9 mmol, 98 %

yield) of **16** as a colourless solid. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ (ppm)): 9.43 (s, 1H, -NCHN-), 9.32 (s, 1H, ArOH), 8.19 (t, $J = 1.9$ Hz, 1H, -NCH=CHN-, #4), 7.89 (t, $J = 1.8$ Hz, 1H, -NCH=CHN-, #3), 7.28 (dd, $J = 15.6, 8.8$ Hz, 1H, HCH=CHN-), 7.04 – 6.95 (m, 2H, ArH, #11, 15), 6.74 – 6.64 (m, 2H, ArH, #12, 14), 5.94 (dd, $J = 15.6, 2.4$ Hz, 1H, $\text{CH}_2=\text{CHN-}$), 5.41 (dd, $J = 8.7, 2.4$ Hz, 1H, HCH=CHN-), 4.40 (t, $J = 7.3$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{N-}$), 3.05 (t, $J = 7.3$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{N-}$). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, δ (ppm)): 156.69 (ArC, #13), 135.70 (-NCHN-), 130.09 (ArC, #11, 15), 129.27 (ArC, #10), 127.09 (-NCH=CHN-, #3), 123.78 ($\text{CH}_2=\text{CHN-}$), 119.47 (-NCH=CHN-, #4), 115.85 (ArC, #12, 14), 109.18 ($\text{CH}_2=\text{CHN-}$), 51.05 ($\text{ArCH}_2\text{CH}_2\text{N-}$), 34.86 ($\text{ArCH}_2\text{CH}_2\text{N-}$).

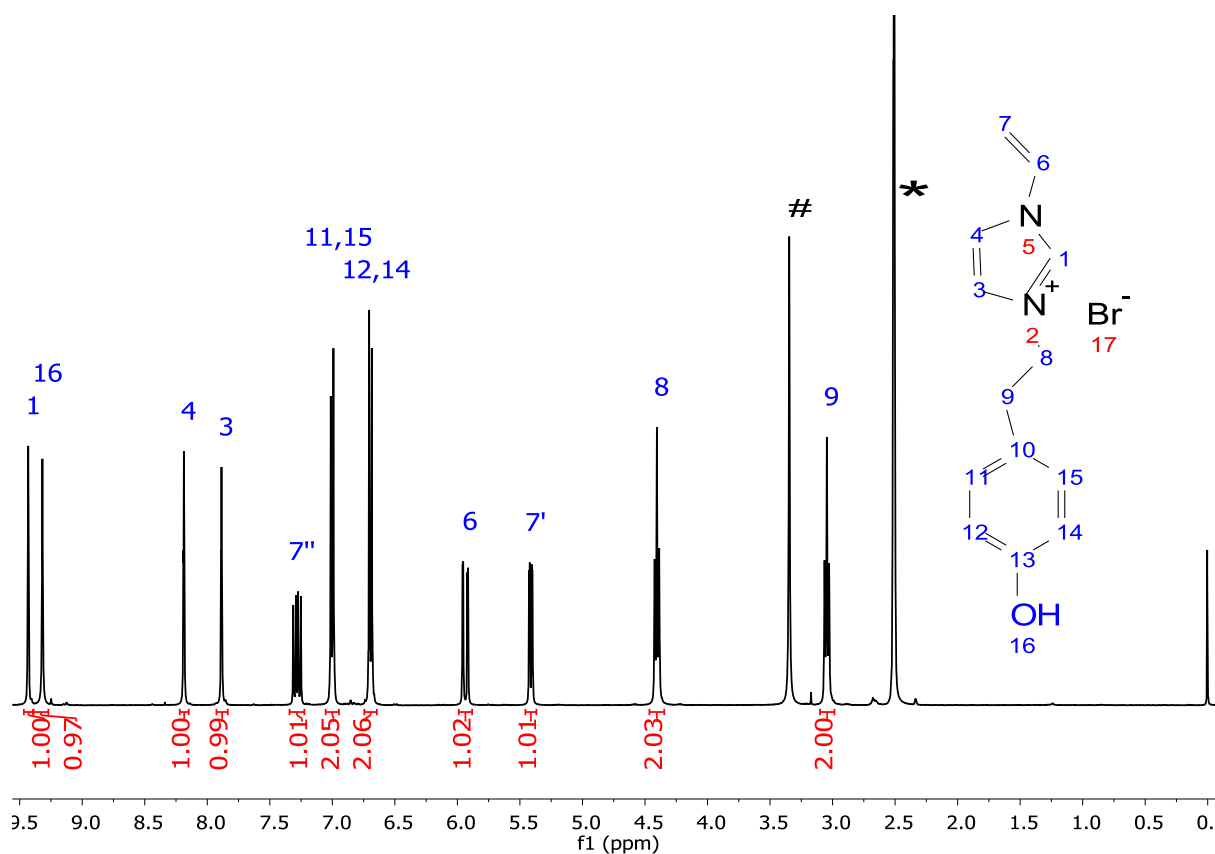


Figure S23. ^1H NMR spectrum of **16** in $\text{DMSO-}d_6$. * and # in the spectrum corresponds to the deuterated solvent and its residual water signals, respectively.

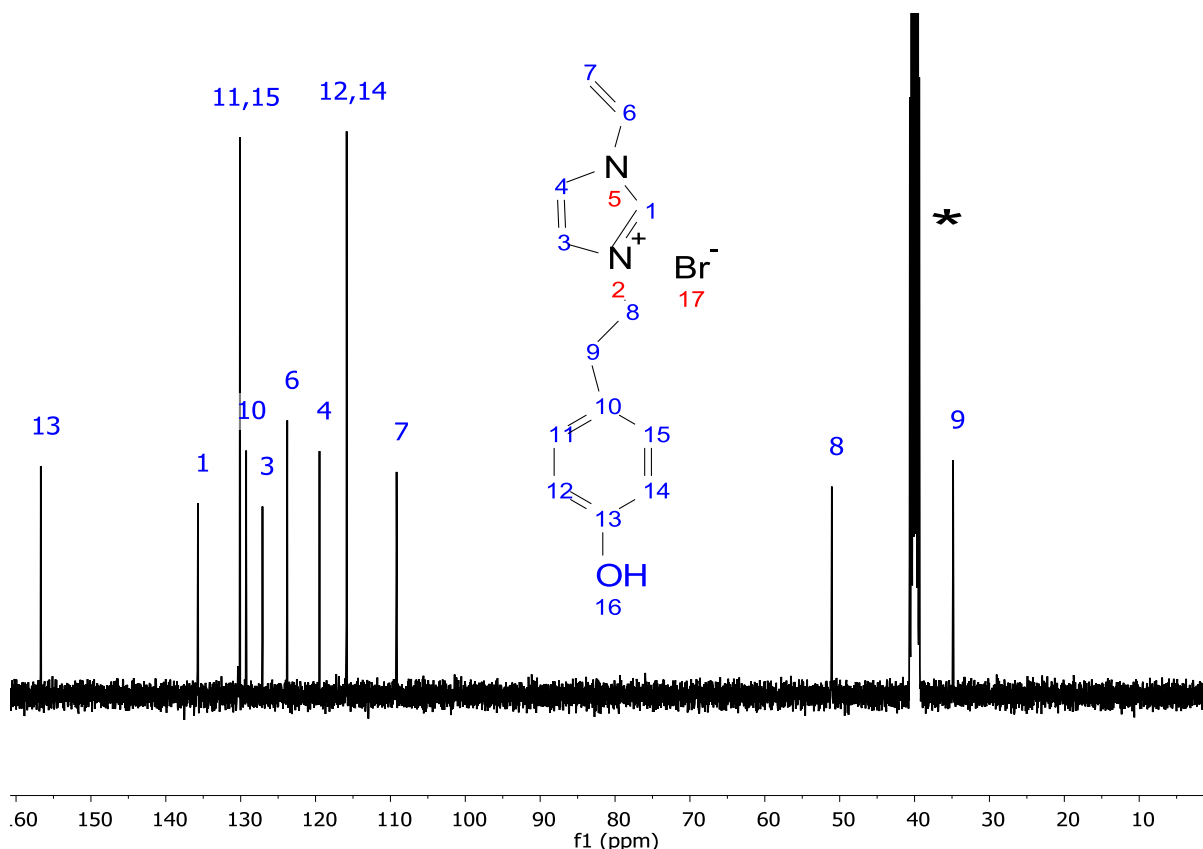


Figure S24. ^{13}C NMR spectrum of **16** in $\text{DMSO-}d_6$. * in the spectrum corresponds to the deuterated solvent signal.

Synthesis of VIm-phe-TFSI and VIm-cat/cat=o/pyr @-TFSI Monomers from their Halide Analogues. The synthesis and characterization of hydrophobic IL- monomers featuring TFSI⁻ counteranion from their halide analogues can be found elsewhere and also described in detail for their polymeric versions in the main manuscript. In brief, 1.0 mmol of 1-vinyl-3-alkylimidazolium salt with halide counteranion (Br^-/Cl^-) was dissolved in 10 mL of deionized water, followed by drop-wise addition of 1.1 mmol of LiTFSI in 5 mL of water, and continued stirring overnight at room temperature. So obtained oily product was then extracted with ethyl acetate and washed several time with deionized water (until no precipitate of AgCl is observed, upon testing with AgNO_3 solution). Concentrated product

was dried under vacuum to yield monomers with TFSI⁻ counteranion, as a grey colored (semi)solid in quantitative yield.

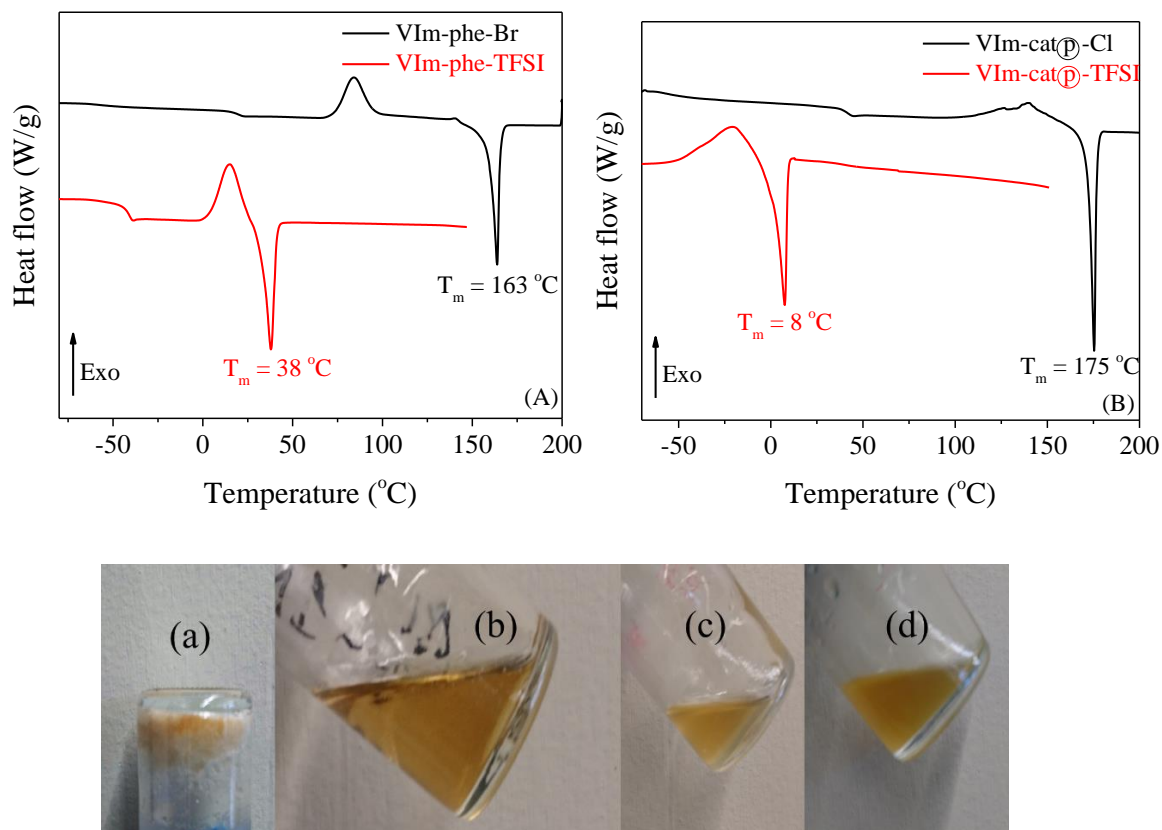


Figure S25. DSC thermograms of (A) VIm-phe-Br/TFSI, and (B) VIm-cat[Ⓟ]-Cl/TFSI monomers, under nitrogen atmosphere at 10 °C min^{-1} (top). Digital images of (a) VIm-phe-TFSI, (b) VIm-cat[Ⓟ]-TFSI, (C) VIm-cat[Ⓟ]-TFSI, and (d) VIm-pyr[Ⓟ]-TFSI monomers (bottom).

Note: The unprotected phenol functional monomer VIm-phe-TFSI melts at around 38 °C , whereas, all other monomers with TFSI counteranion (VIm-cat[Ⓟ]-TFSI, VIm-cat[Ⓟ]-TFSI and VIm-pyr[Ⓟ]-TFSI) exist as room-temperature ionic liquids (RTIL). A representative DSC thermograms of benzyl ether protected catechol monomer VIm-cat[Ⓟ]-TFSI is shown in Figure S25B, and the digital images of other monomers with the same counteranion is shown

above. None of the monomers with halide counteranion exhibits melting point below 100 °C (Figure S25). Therefore, all the monomers with TFSI⁻ counteranion can be defined as a new example of IL monomers.

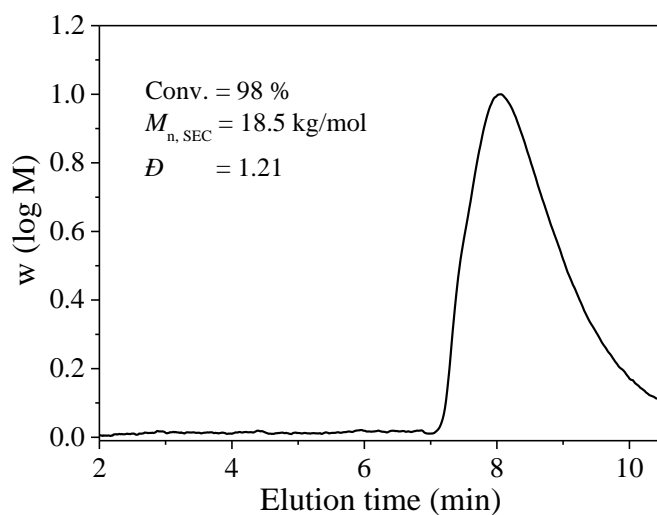


Figure S26. RI-SEC trace as a function of elution time for PVIm-cat@-Cl prepared by OMRP with [monomer]:[R-Co(acac)₂] = 75:1 in DMF at 30 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange (Cl⁻/TFSI⁻) of the polymer, using PS calibration.

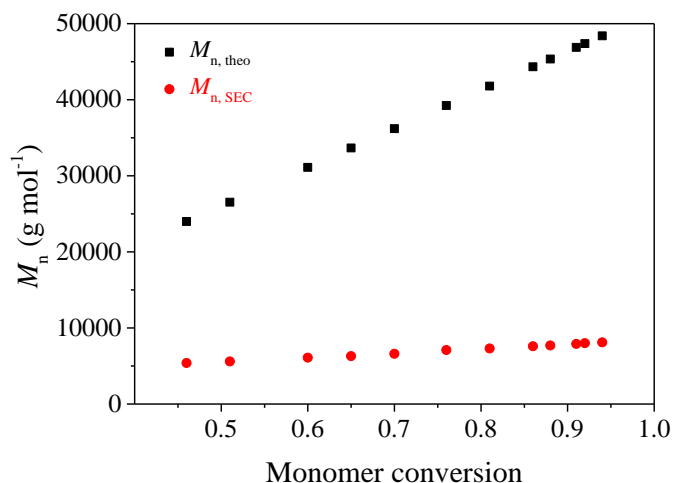


Figure S27. The number-average molar mass (M_n) versus monomer conversion plot for the OMRP of VIm-cat⁺-Cl, with a molar ratio of 75:1 ([monomer]:[R-Co(acac)₂]) in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange (Cl⁻/TFSI⁻) of the polymer, using PS calibration.

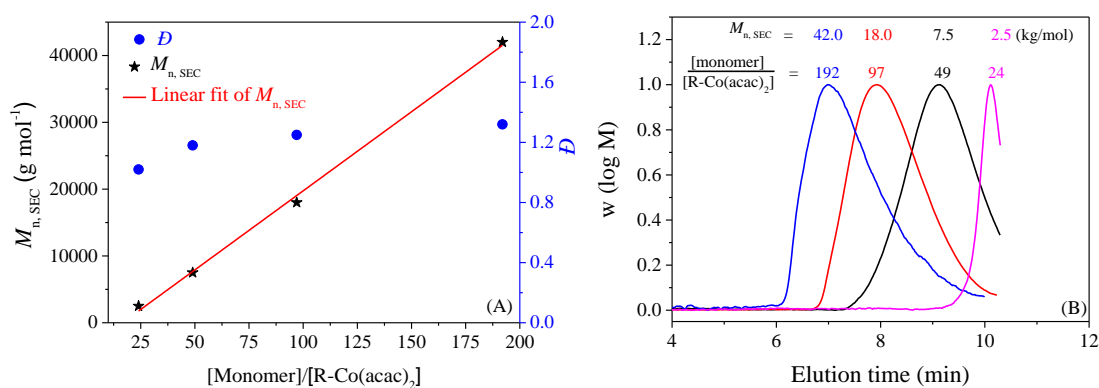


Figure S28. (A) $M_{n,SEC}$ with D values, and (B) the corresponding RI-SEC traces obtained from the OMRP of VIm-cat⁺-Cl, with different [monomer]/[R-Co(acac)₂] ratios in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange (Cl⁻/TFSI⁻) of the polymer, using PS calibration.

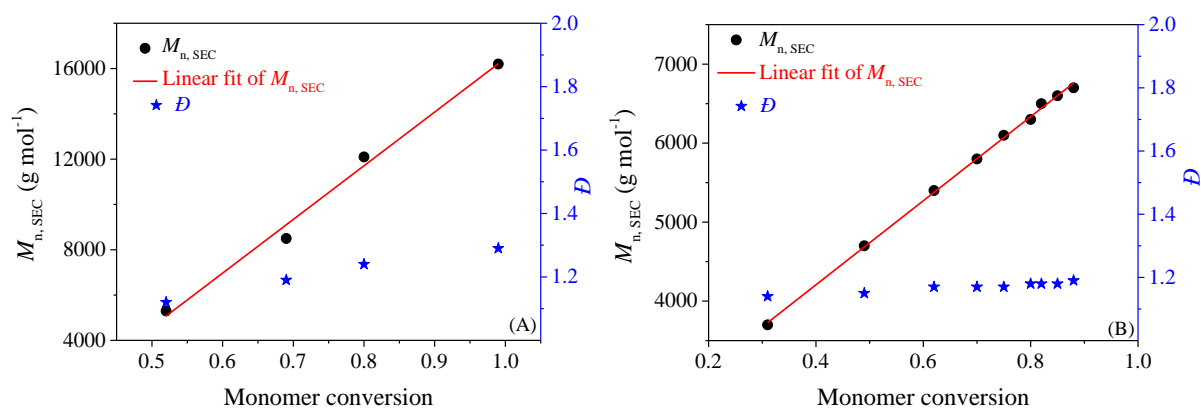


Figure S29. $M_{n,SEC}$ versus monomer conversion plots for the OMRP of (A) VIm-cat=o \oplus -Cl, and (B) VIm-pyr \oplus -Cl, with a molar ratio of 75:1 ([monomer]:[R-Co(acac) $_2$]) in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange (Cl $^-$ /TFSI $^-$) of the polymer, using PS calibration.

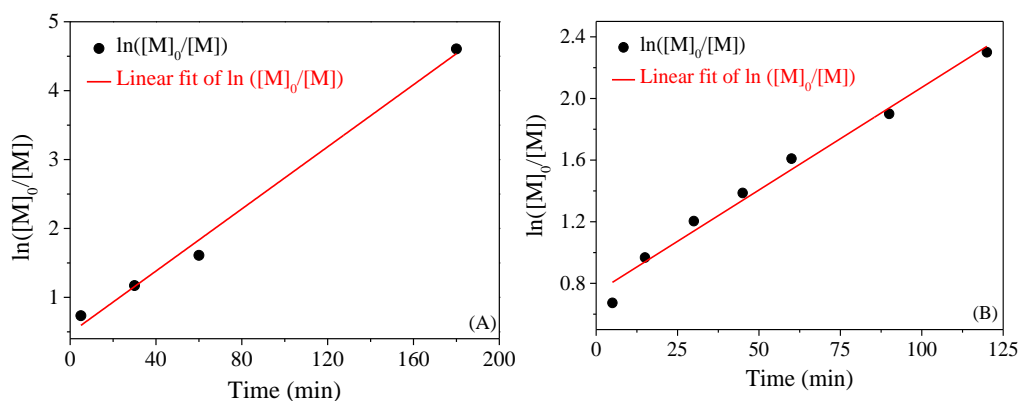


Figure S30. Semilogarithmic plots against polymerization time for the OMRP of (A) VIm-cat=o \oplus -Cl, and (B) VIm-pyr \oplus -Cl, with a molar ratio of 75:1 ([monomer]:[R-Co(acac) $_2$]) in DMF at 0–2 °C.

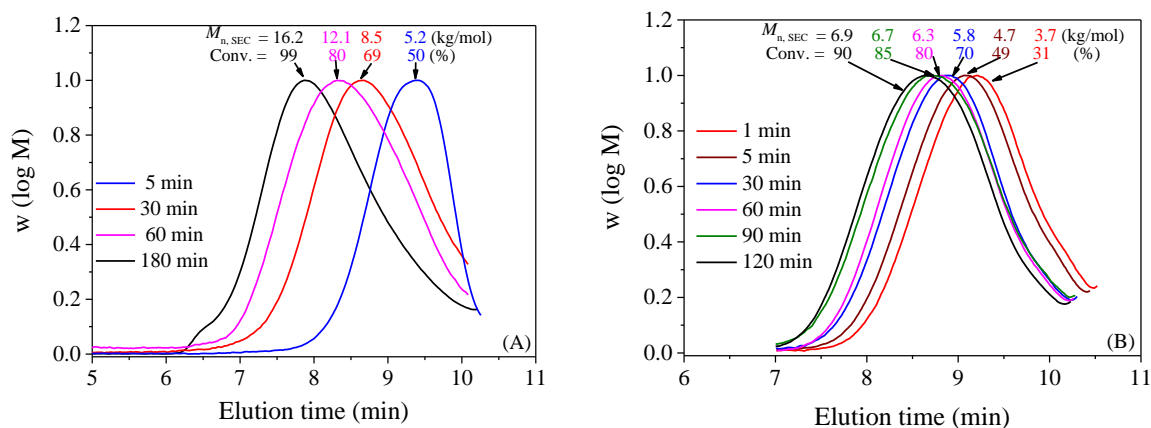


Figure S31. RI-SEC traces as a function of elution time, obtained from the OMRP of (A) VIm-cat=o@-Cl, and (B) VIm-pyr@-Cl, with a molar ratio of 75:1 ([monomer]:[R-Co(acac)₂]) in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange ($Cl^-/TFSI^-$) of the polymer, using PS calibration.

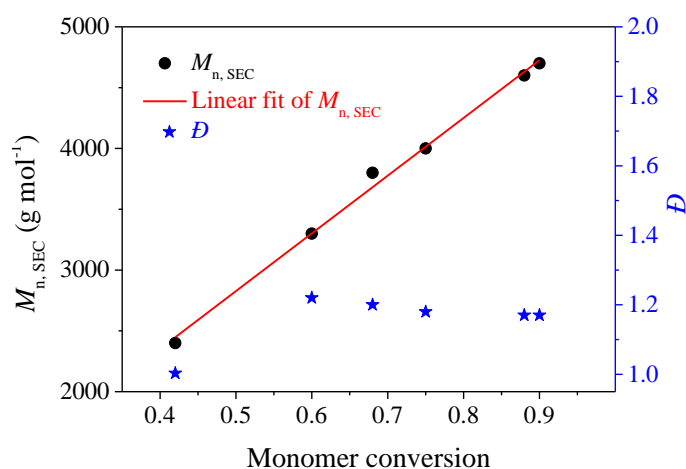


Figure S32. $M_{n, SEC}$ versus monomer conversion plot for the OMRP of VIm-phe-Br, with a molar ratio of 75:1 ([monomer]:[R-Co(acac)₂]) in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange ($Cl^-/TFSI^-$) of the polymer, using PS calibration.

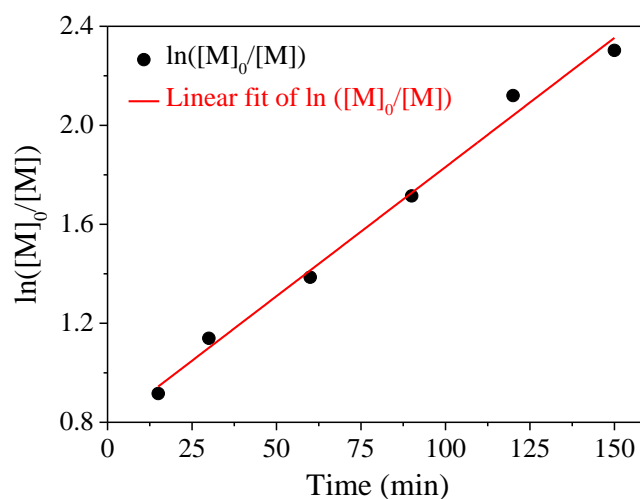


Figure S33. Semilogarithmic plot against polymerization time for the OMRP VIm-phe-Br, with a molar ratio of 75:1 ([monomer]:[R-Co(acac)₂]) in DMF at 0–2 °C.

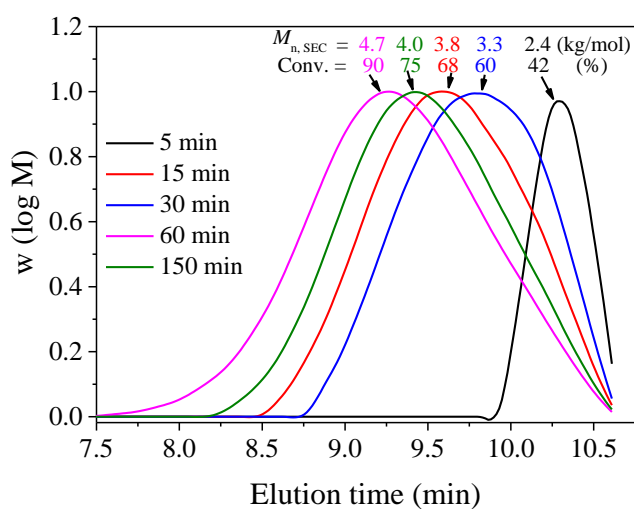


Figure S34. RI-SEC traces as a function of elution time, obtained from the OMRP of VIm-phe-Br, with a molar ratio of 75:1 ([monomer]:[R-Co(acac)₂]) in DMF at 0–2 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange ($Cl^-/TFSI^-$) of the polymer, using PS calibration.

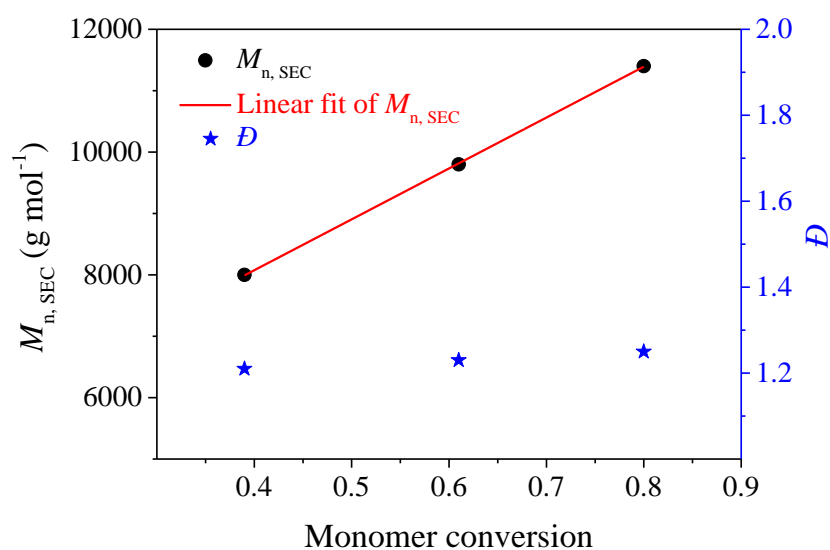


Figure S35. $M_{n, SEC}$ versus monomer conversion plot for the synthesis of P(VIm-pyr[⊕]-Cl)-*b*-P(VIm-et-Br) by sequential OMRP, with [VIm-et-Br]:[P(VIm-pyr[⊕]-Cl)-Co(acac)₂] = 50:1 in DMF at 30 °C. SEC in THF (containing 10mM LiTFSI) was realized after anion exchange (Cl⁻/TFSI⁻) of the polymer, using PS calibration.

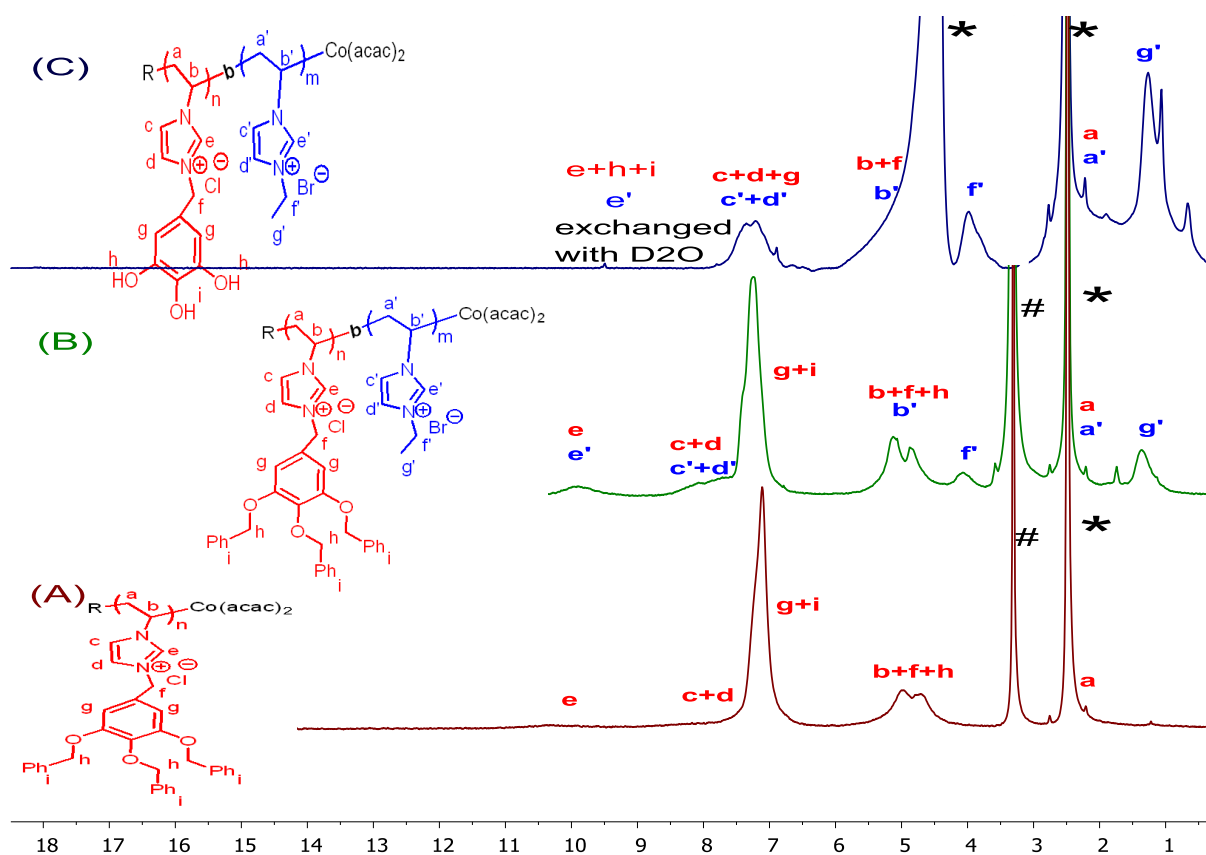


Figure S36. ^1H NMR spectra of (A) P(VIm-pyr@-Cl), (B) P(VIm-pyr@-Cl)- b -P(VIm-et-Br) in $\text{DMSO}-d_6$, and (C) P(VIm-pyr-Cl)- b -P(VIm-et-Br) in $\text{DMSO}-d_6 + \text{D}_2\text{O}$. * and # in the spectrum corresponds to the deuterated and residual solvent signals, respectively.

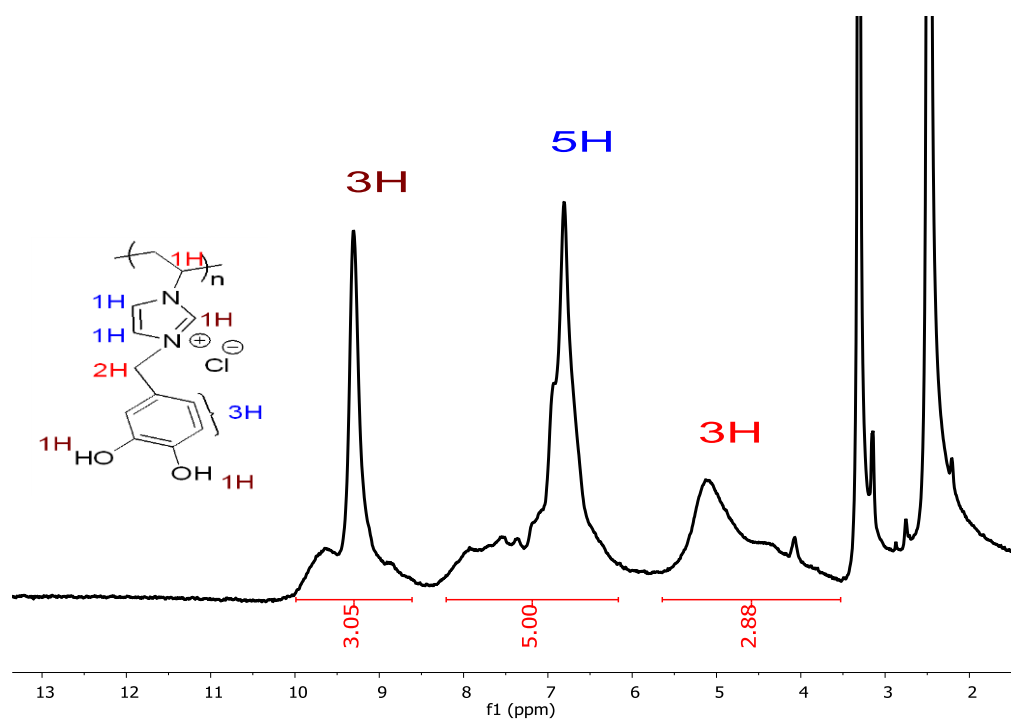


Figure S37. ^1H NMR spectrum of PVIm-cat-Cl in $\text{DMSO-}d_6$.

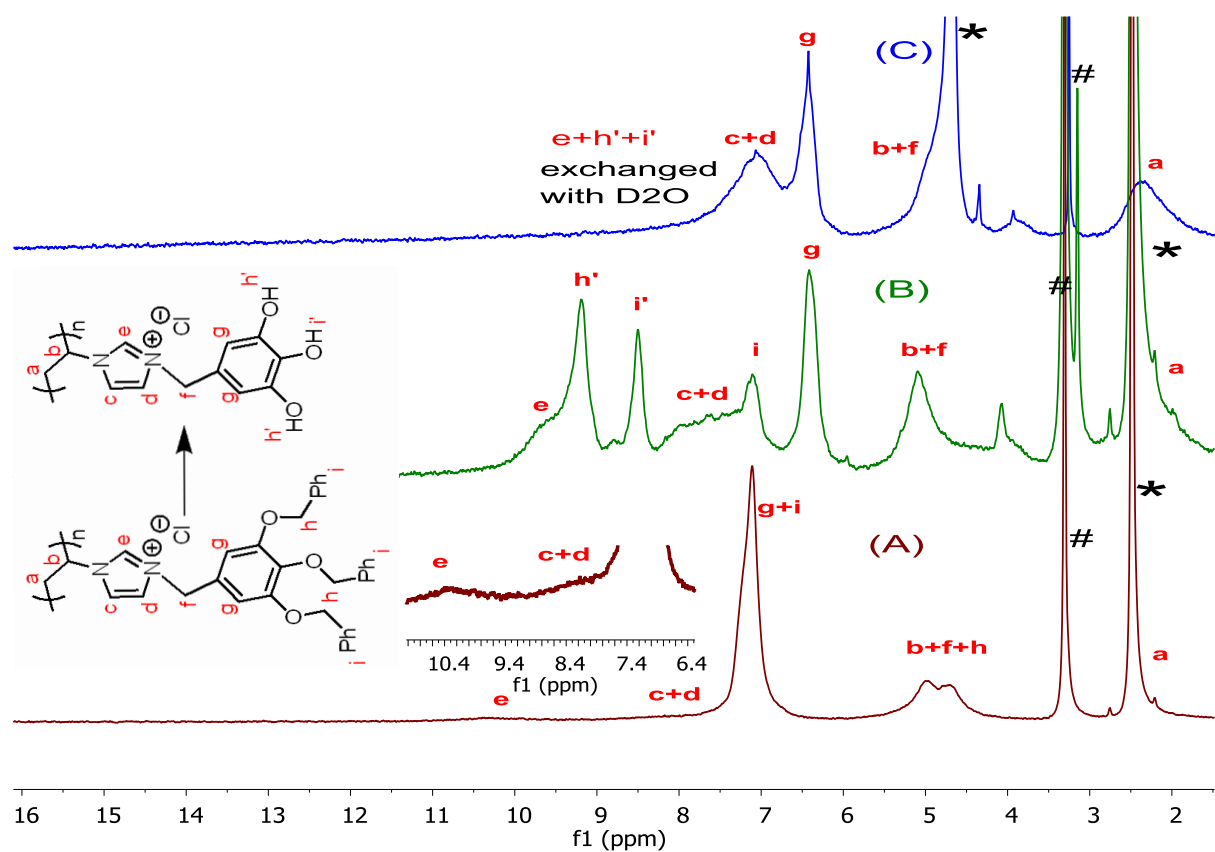
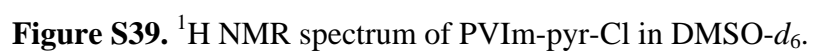


Figure S38. ^1H NMR spectra of (A) PVIm-pyr@-Cl, (B) PVIm-pyr-Cl in $\text{DMSO}-d_6$, and (C) PVIm-pyr-Cl in D_2O . * and # in the spectrum corresponds to the deuterated and residual solvent signals, respectively.



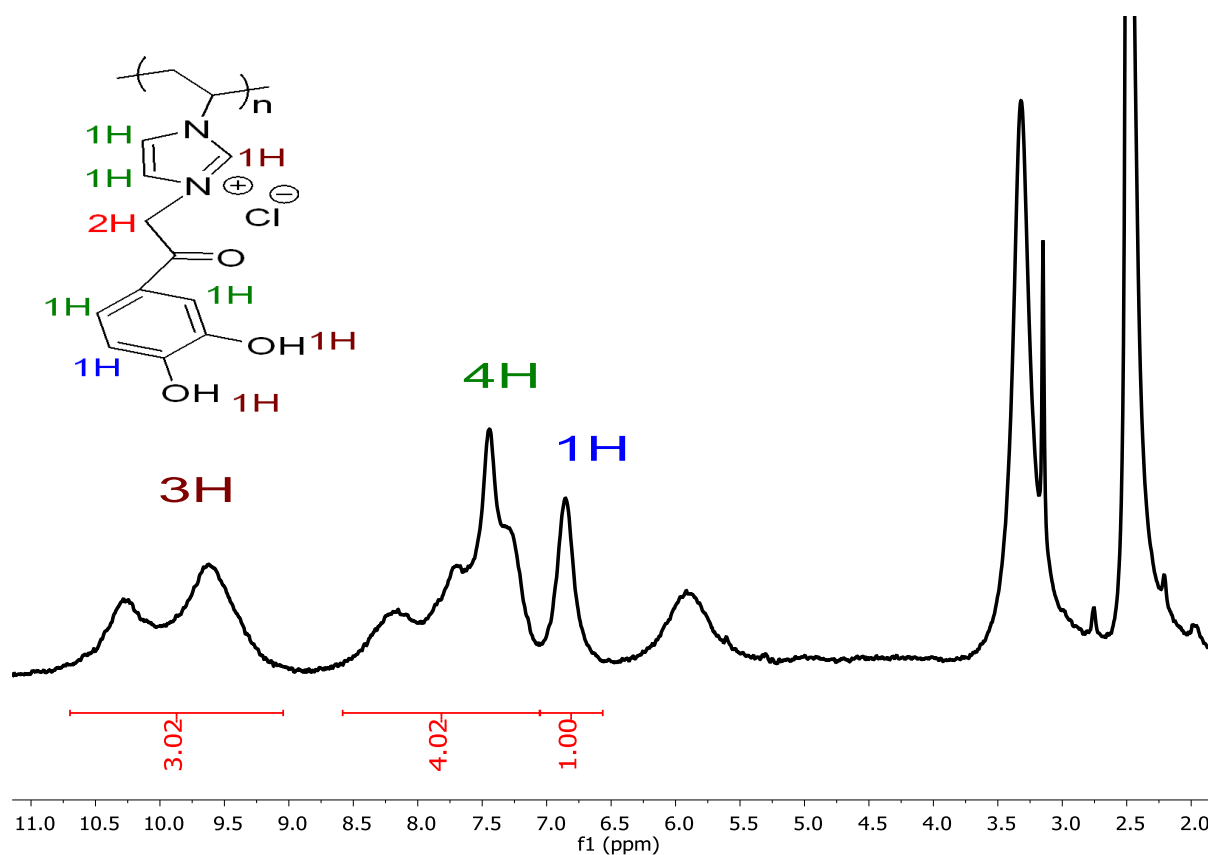


Figure S40. ^1H NMR spectrum of PVIm-cat=o-Cl in $\text{DMSO-}d_6$.

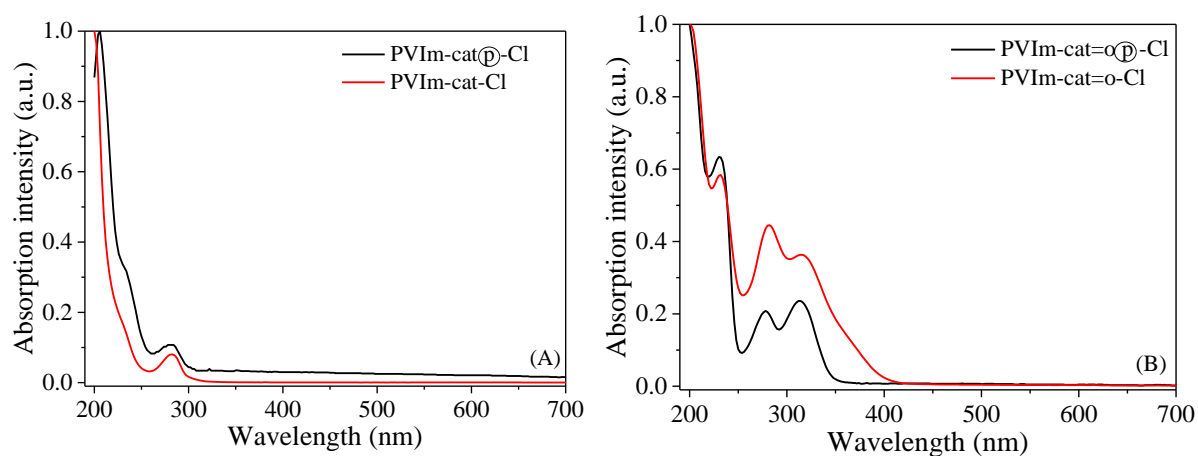


Figure S41. UV-vis spectra of (A) PVIm-cat@-Cl, PVIm-cat-Cl (after deprotection), and (B) PVIm-cat=o@-Cl, PVIm-cat=o-Cl (after deprotection) in methanol/water (1:1, V/V%).

Note: Aerobic/chemical oxidation of free catechols (upon deprotection) results in the formation of -aryloxyradicals and o -quinones. The reaction between free radicals and/or nucleophilic addition of -hydroxyl groups on o -quinones is known to form crosslinks, which can be seen from UV-vis spectroscopy (≥ 400 nm). The absence of such peaks in Figure S41 proves the deprotected polymers didn't oxidize and become crosslinked at any stage in our studies.

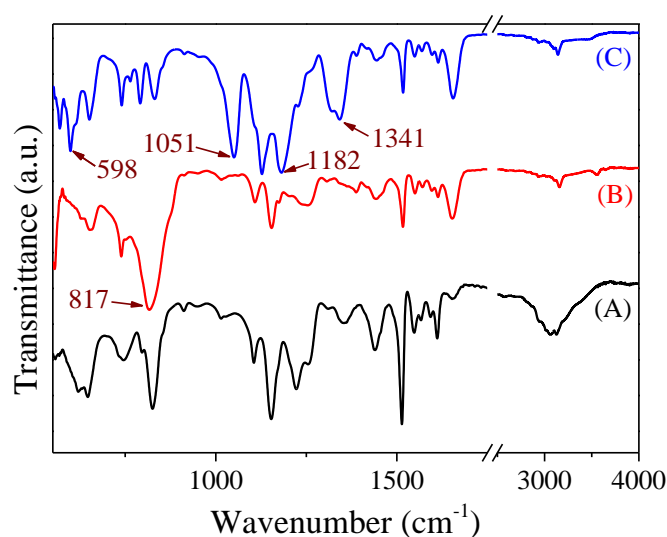


Figure S42. ATR-FTIR spectra of (A) PVIm-phe-Cl, (B) PVIm-phe-PF₆, and (C) PVIm-phe-TFSI.

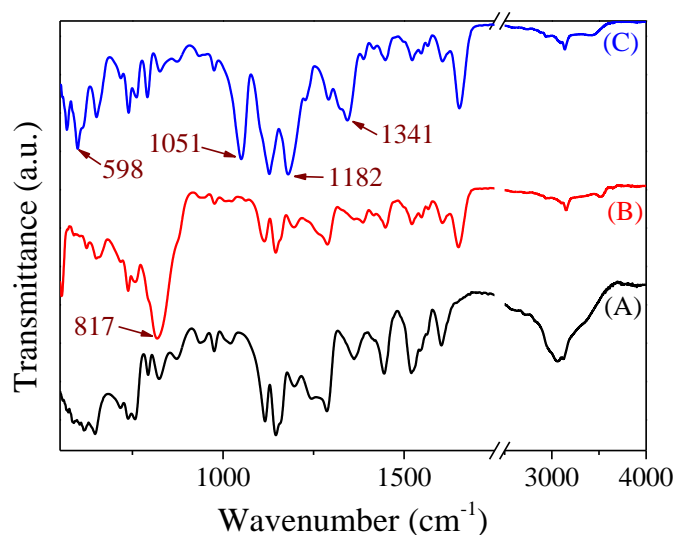


Figure S43. ATR-FTIR spectra of (A) PVIm-cat-Cl, (B) PVIm-cat-PF₆, and (C) PVIm-cat-TFSI.

Table S1. Solubility of PILs in Different Solvents^a

Solvent	PVIm-phe-Br	PVIm-phe-PF ₆ /TFSI	PVIm-cat [⊕] /cat=o [⊕] /pyr [⊕] -Cl	PVIm-cat/cat=o/pyr-Cl	PVIm-cat/cat=o/pyr-PF ₆ /TFSI
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
Water	—	—	—	+	—
Methanol	—	+	—	—	+
Acetone	—	+	—	—	+
THF	—	+	—	—	+
Ethyl acetate	—	+	—	—	+
DCM	—	+	—	—	+

^aat room temperature at a concentration of 1.0 wt %.

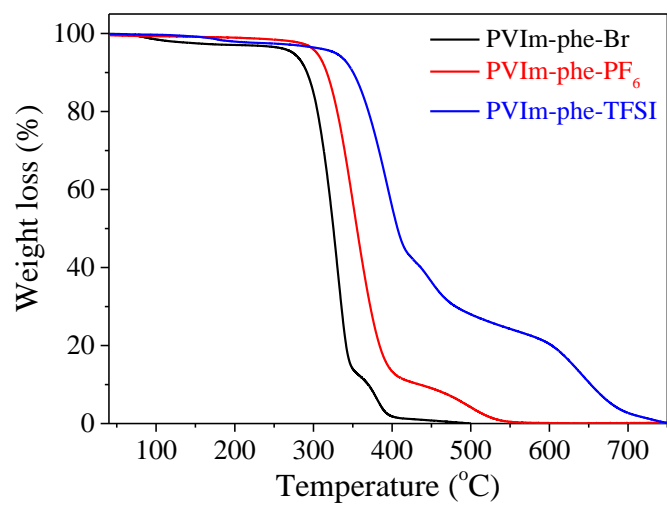


Figure S44. TGA of PVIm-phe-X series ($X = \text{Cl}^-$, PF_6^- , and TFSI^-), under nitrogen atmosphere at $10\text{ }^\circ\text{C min}^{-1}$.

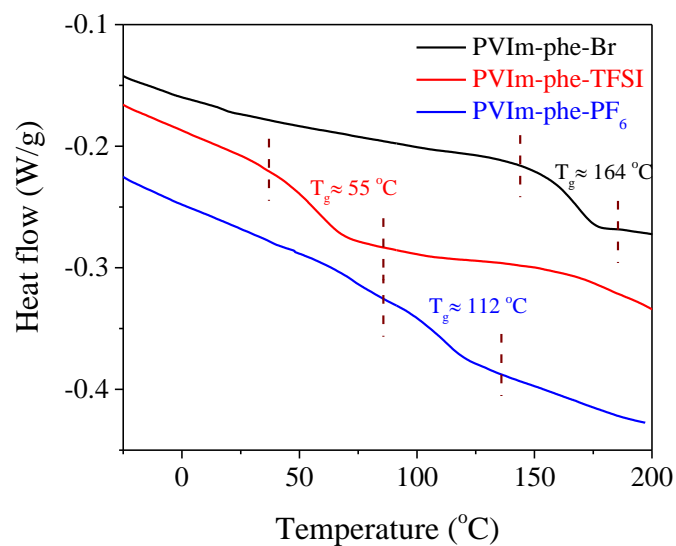


Figure S45. DSC thermograms of PVIm-phe-X series ($X = \text{Cl}^-$, PF_6^- , and TFSI^-), under nitrogen atmosphere at $10\text{ }^\circ\text{C min}^{-1}$.

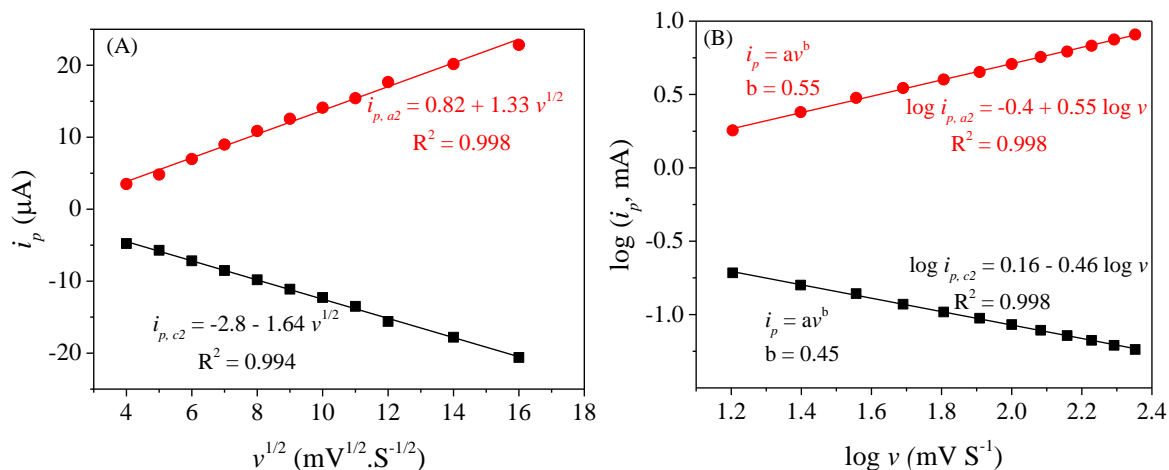


Figure S46. (A) peak current (i_p) as a function of the square root of the scan rate ($v^{1/2}$), and (B) $\log i_p$ vs. $\log v$ correspond to the redox processes, 9A(A2) (HQ^{+}/Q) // 9A(C2) ($\text{Q}^{\bullet-}/\text{Q}^{2-}$) of Figure 9.

Note: In a CV experiment, the current is a function of the scan rate and can generally be expressed as

$$i(V) = av^b \quad (\text{eq S1})$$

$$\log i(V) = \log a + b \log v \quad (\text{eq S2})$$

Where i is the current at a given potential (V), v is the scan rate of the experiment (in mV s^{-1}), and a and b are adjustable constants. A plot of $\log i(V)$ vs $\log v$ is a straight line (Eq S2) whose slope is b and intercept $\log a$. For a redox process involving semi-infinite linear diffusion kinetics, the current is diffusion-controlled and vary as $v^{1/2}$ with $b \approx 0.5$. In contrast, currents resulting from surface adsorption processes vary linearly with v and have b value of 1.

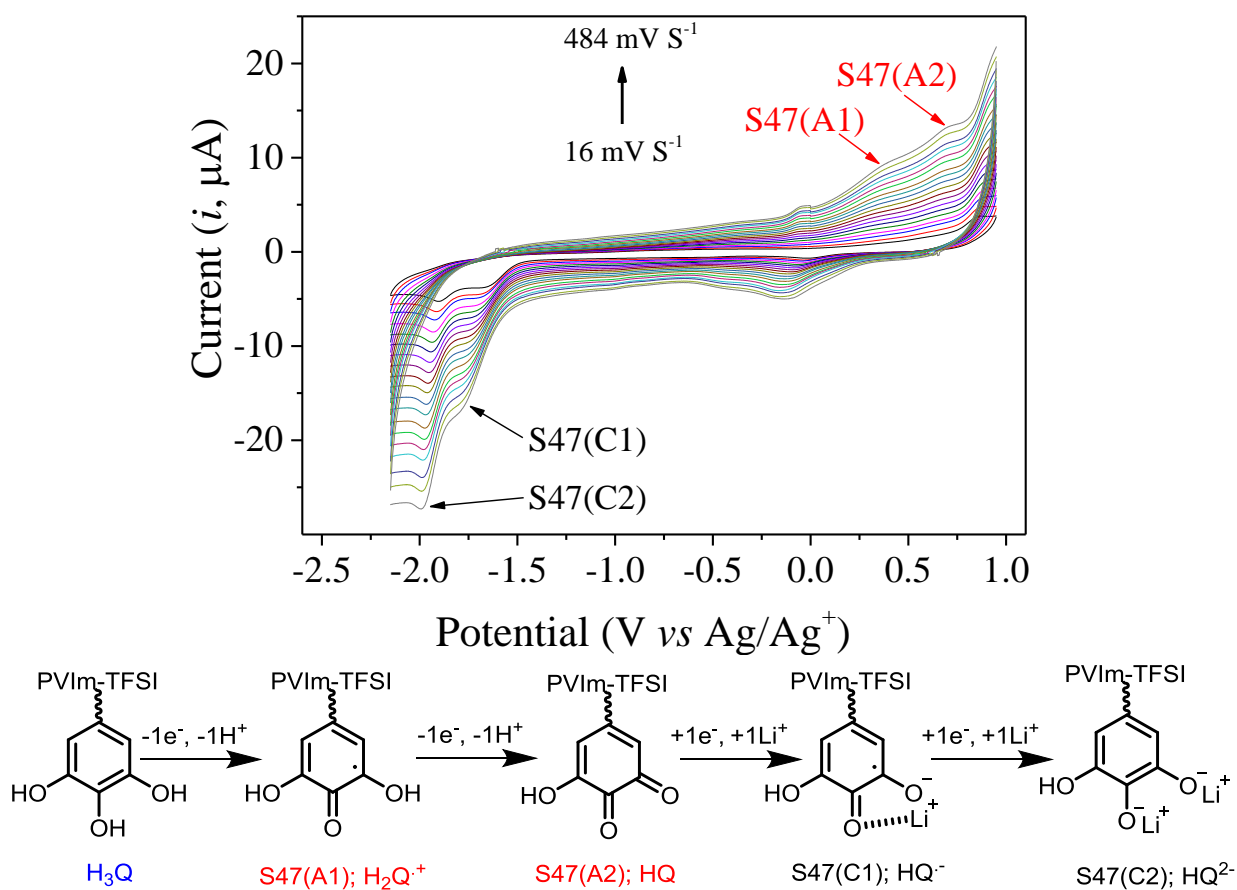


Figure S47. Cyclic voltammograms of 8.0 mM PVIm-pyr-TFSI at a glassy carbon electrode, in DMSO containing 0.1M LiTFSI. Scan rate = 16–484 mV s^{-1} . Plausible chemical scheme for the corresponding redox process is represented under the graph.

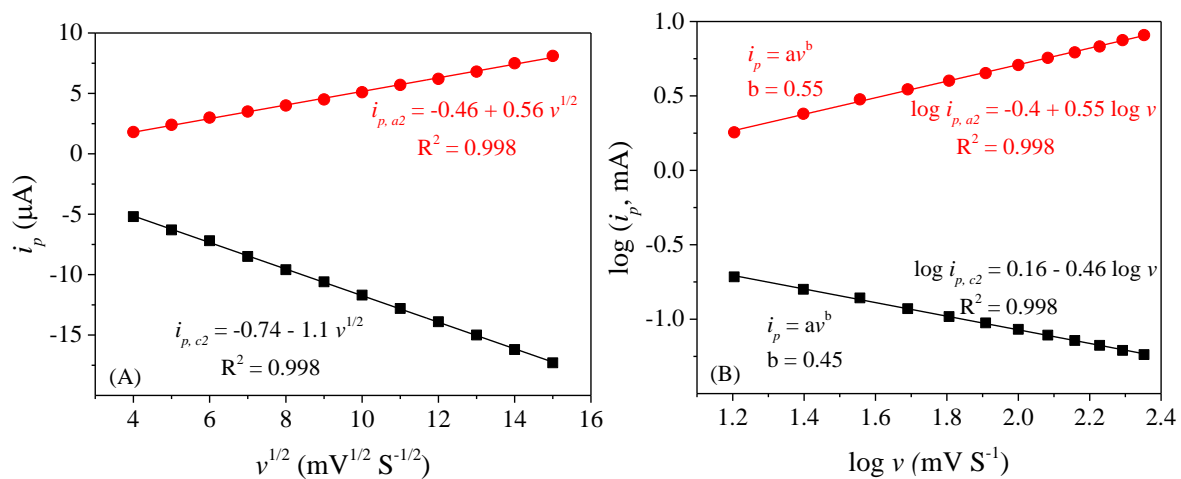


Figure S48. (A) peak current (i_p) as a function of the square root of the scan rate ($v^{1/2}$), and (B) $\log i_p$ vs. $\log v$ correspond to the redox processes, S47(A2) ($\text{H}_2\text{Q}^{*+}/\text{HQ}$) // S47(C2) ($\text{HQ}^{*-}/\text{HQ}^{2-}$) of graph S47.

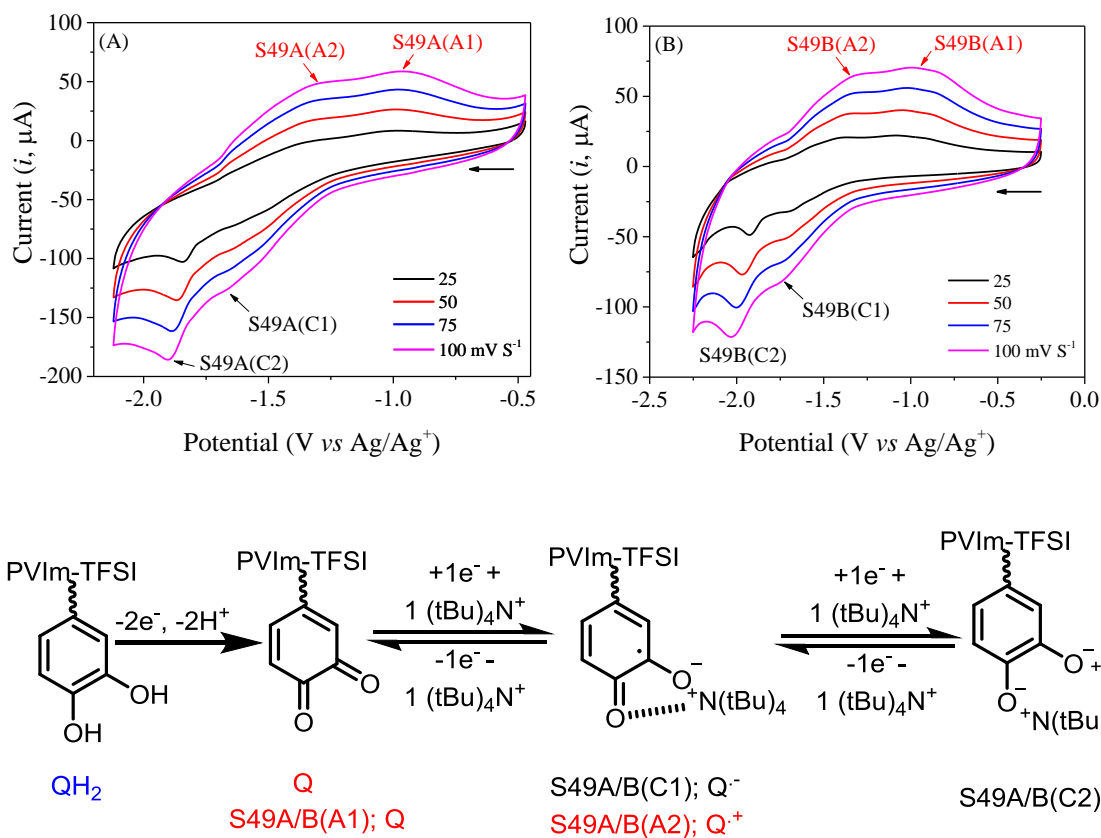


Figure S49. Cyclic voltammograms of (A) PVIm-cat-TFSI, and (B) PVIm-cat=o-TFSI drop-casted film at a glassy carbon electrode, in DMSO containing 0.1M TBA-TFSI at various scan rates. Plausible chemical scheme for the corresponding redox process is represented under the graph.

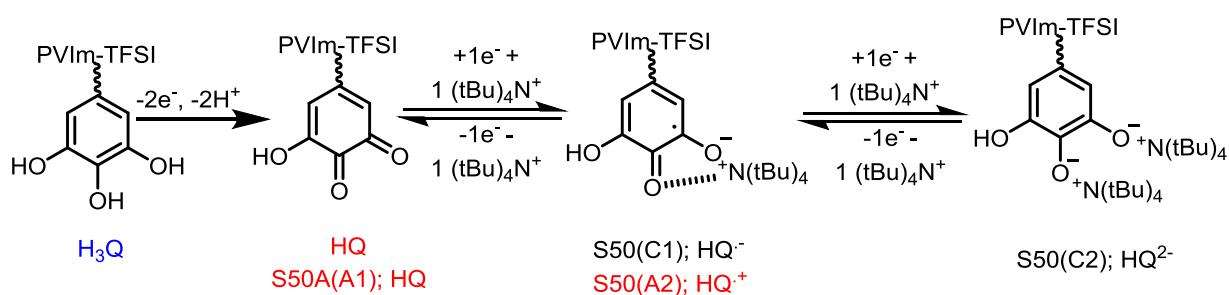
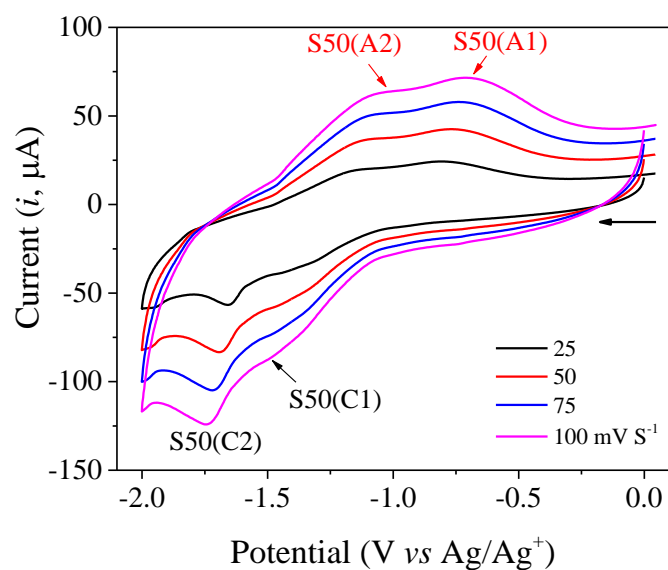


Figure S50. Cyclic voltammograms of PVIm-pyr-TFSI drop-casted film at a glassy carbon electrode, in DMSO containing 0.1M TBA-TFSI at various scan rates. Plausible chemical scheme for the corresponding redox process is represented under the graph.

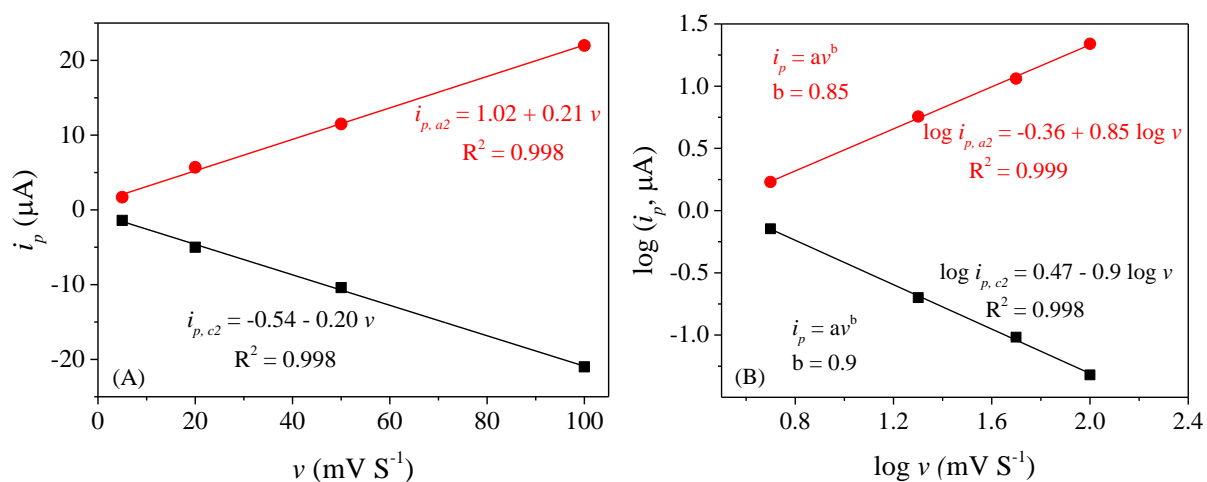


Figure S51. (A) peak current (i_p) as a function of the scan rate (v), and (B) $\log i_p$ vs. $\log v$ correspond to the first redox couple, 9B(C1) (Q/Q^{•-}) // 9B(A1) (HQ^{•+}/Q) of graph 9B.

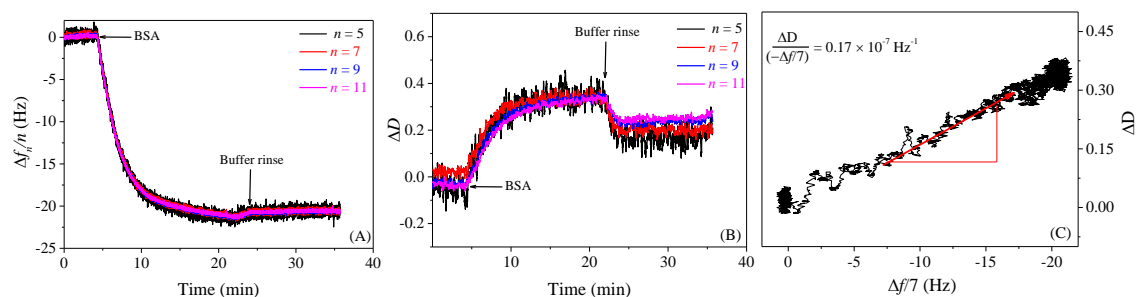


Figure S52. (A) Shift in frequency (Δf), (B) shift in dissipation (ΔD), and (C) $\Delta D / (\Delta f/7)$ data plots induced by the adsorption of BSA (1.0 mg mL⁻¹) onto gold surface measured by QCM-D as a function of time. ΔD and Δf are measured simultaneously at different overtones ($n = 5, 7, 9, 11$), and Δf_n normalized by their overtone numbers.

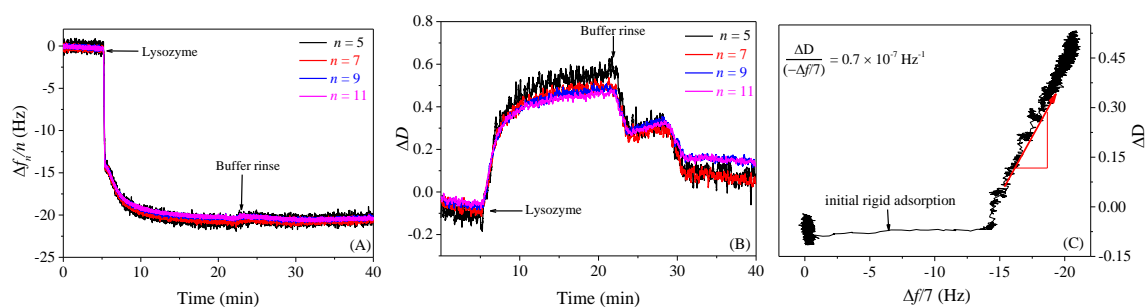


Figure S53. (A) Δf , (B) ΔD , and (C) $\Delta D / (\Delta f/7)$ data plots induced by the adsorption of Lysozyme (1.0 mg mL^{-1}) onto gold surface measured by QCM-D as a function of time. ΔD and Δf are measured simultaneously at different overtones ($n = 5, 7, 9, 11$), and Δf_n normalized by their overtone numbers.

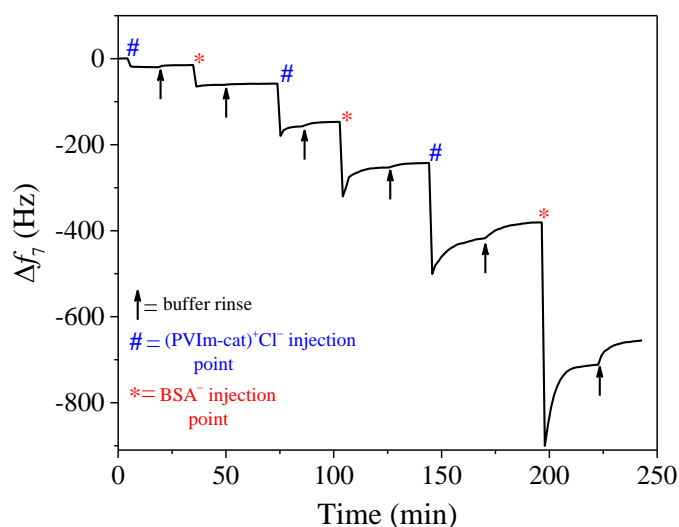


Figure S54. Δf measurements during LBL assembly on gold surface obtained by QCM-D analysis of the $[(\text{PVIm-cat})^+\text{Cl}^-/(\text{BSA})^-]_3$ system assembly as a function of time. The concentration of LBL partners was 1.0 mg mL^{-1} .

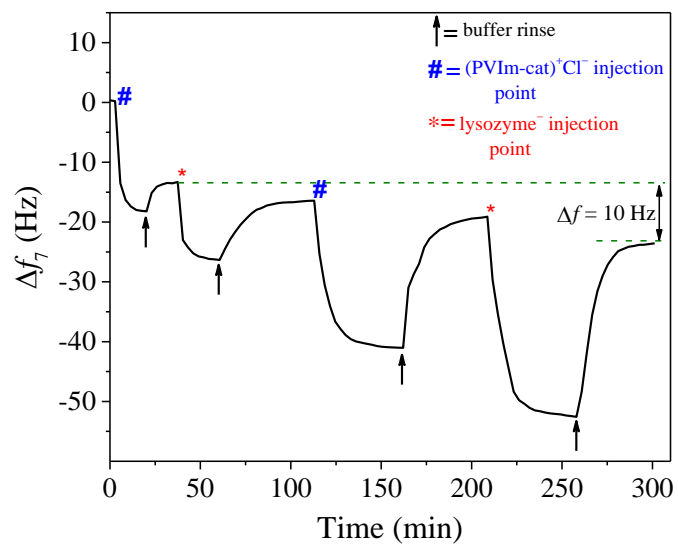


Figure S55. A representative Δf measurements during deposition of (PVIm-cat)⁺Cl⁻ and (Lysozyme)⁺ on gold surface obtained by QCM-D analysis as a function of time. The concentration of polymer and lysozyme was 1.0 mg mL⁻¹.