

Supplementary Information

Polymerization mechanism of dopamine resolved: A story of strong π stacking

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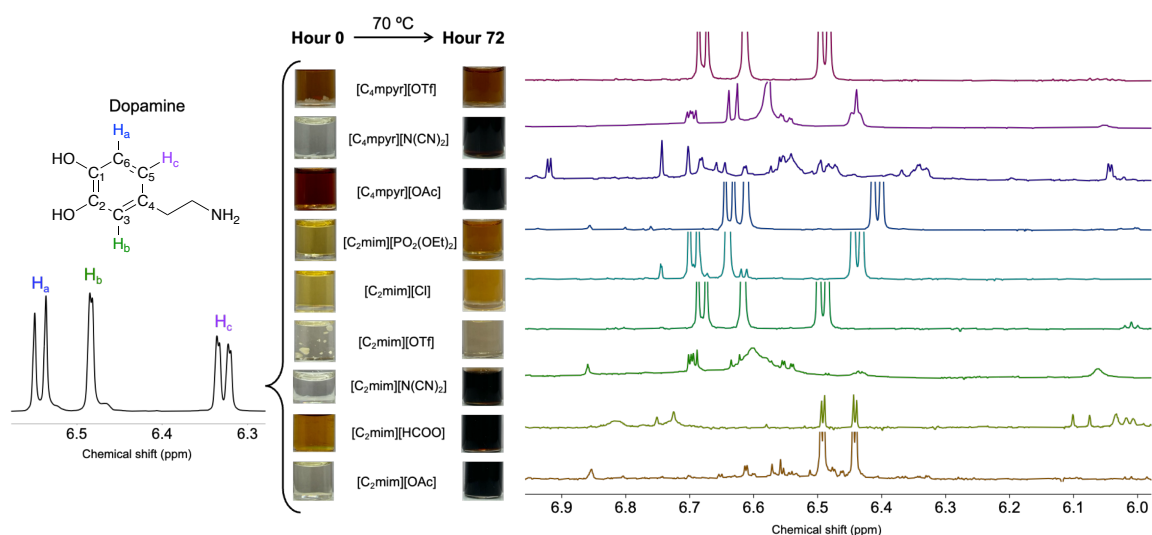


Figure S1: Initial ^1H NMR spectra of dopamine with proton assignments (left) and resultant spectra collected from various 10 mg/mL DA/IL samples (20 μL in 580 μL DMSO- d_6) after heating at 70 $^\circ\text{C}$ for 72 hours. Images of the samples before and after heating are also shown. Developing a black coloured solution whilst producing many new aromatic proton environments indicates evidence of DA polymerisation in the IL.

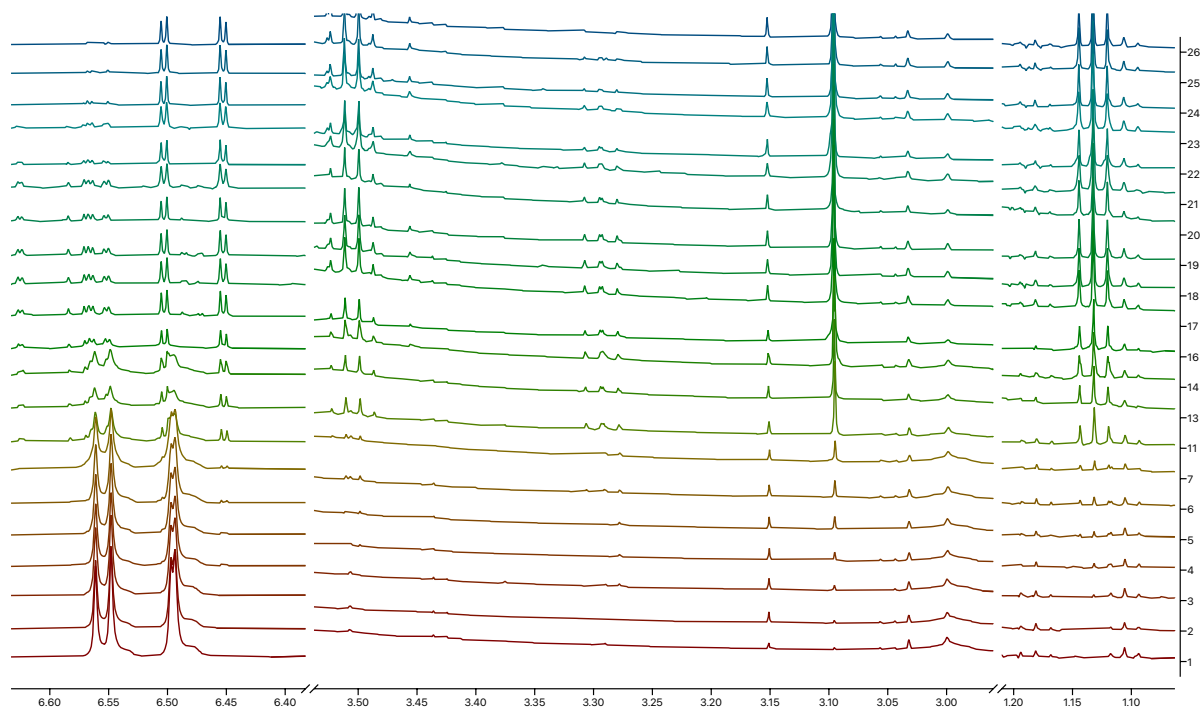


Figure S2: Full stacked spectra for *in-situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO- d_6), showing the growth of imidazole byproduct peaks.

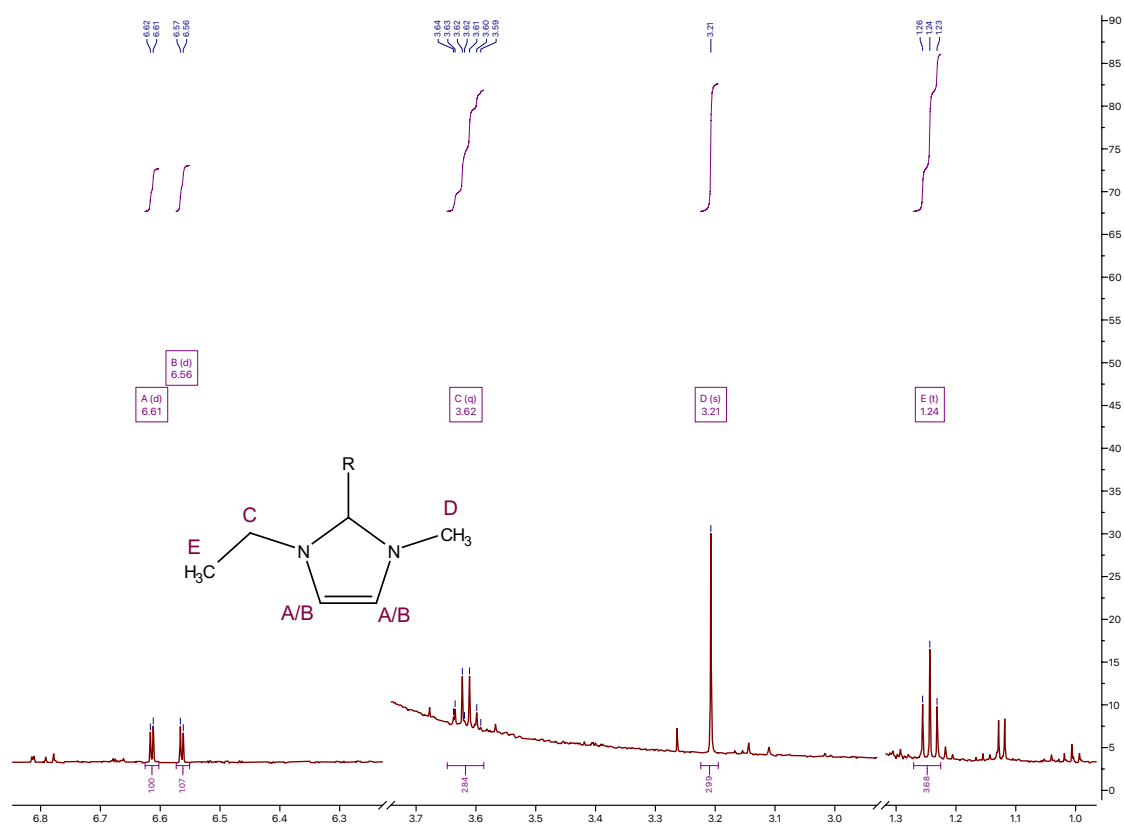


Figure S3: 184 hour time point of *in situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO-d_6). Peak assignments for the imidazole byproduct are shown. ^1H NMR (600 MHz, DMSO-d_6) δ 6.61 (d, $J = 2.9$ Hz, 1H), 6.56 (d, $J = 2.9$ Hz, 1H), 3.62 (q, $J = 7.2$, 2H), 3.21 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H).

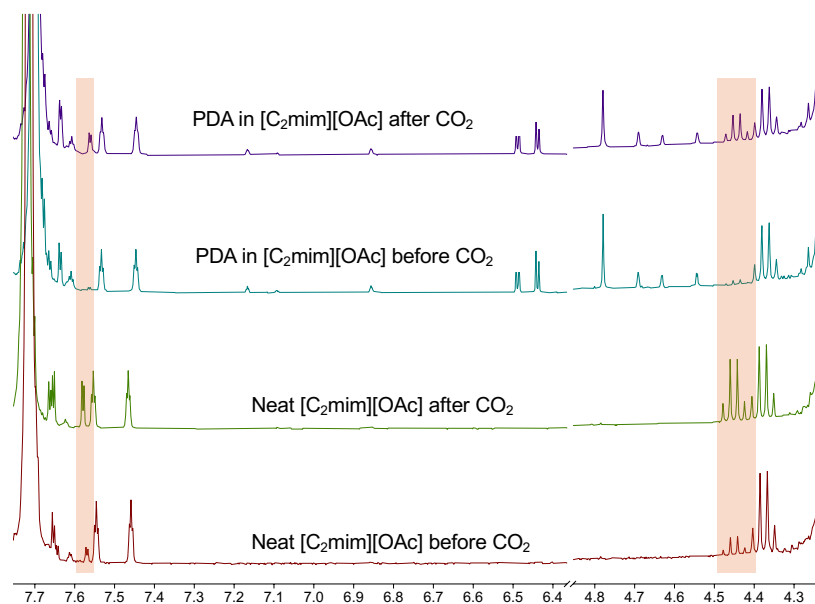


Figure S4: Effect of introducing CO₂ (as a dry ice pellet) into both neat [C₂mim][OAc] and a solution of DA in [C₂mim][OAc] (80 mg/mL, polymerised for 6 days at 80°C) to track the formation of carbenes in imidazolium ILs via the formation of a carboxylated cation.¹ After the CO₂ addition, C₂mim⁺ resonance signals as reported by Seo et al.,² were observed, confirming the presence of the C₂mim carbene.

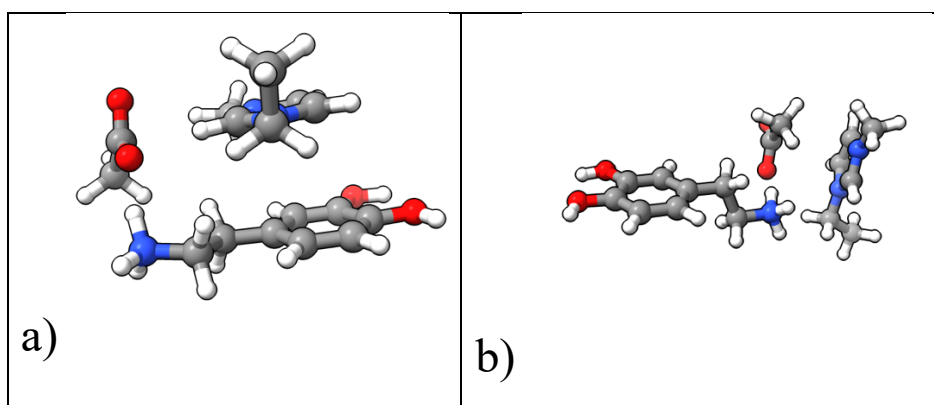


Figure S5: Configurations used in the DFT investigations of DA/DQ-NH₃⁺ deprotonation (Step 1) using 1IP with a) cation stacked above the catechol ring (conf1) or b) interacting only with the anion (conf2).

Table S1: pK_a values of conjugate acids of the anions used in this study. This outcome is consistent with the ability of the ionic liquid anion to hydrogen bond with the deprotonated form, as does water.

Conjugate acid	Anion	pK_a	Ref
CH_3COOH	CH_3COO^-	4.75	³
$HCOOH$	$HCOO^-$	3.75	³
$HPO_2(OEt)_2$	$PO_2(OEt)_2^-$	1.37	⁴
$HN(CN)_2$	$N(CN)_2^-$	-	-
HCl	Cl^-	-6.6	⁵
$CFSO_3H$	OTf^-	-14.6	⁵

Table S2: Calculated final deprotonation energies ($\Delta H_{(ave)}$) of dopamine and dopamine-quinone with single ion pairs of various ionic liquids, noting the success of the forced proton transfer. In this study, DFT calculations were used to probe the viability of this proton transfer at the atomic level. Each system included a protonated, with the anion engaging in hydrogen bonding with the NH_3^+ group. After initial clusters were optimised, a proton transfer (from NH_3^+ in DAH^+ to the acceptor atom on the anion) was manually forced before undergoing a second geometry optimisation. A stable geometry was only found in systems with $[C_2mim][OAc]$ and $[C_4mpyr][OAc]$. All other systems reverted to the original geometry after the forced proton transfer, indicating that the process is not energetically favourable. The calculated $\Delta H_{(ave)}$ values of $+9.0 \text{ kJ mol}^{-1}$ in $[C_2mim][OAc]$ and $+2.6 \text{ kJ mol}^{-1}$ in $[C_4mpyr][OAc]$ indicate that deprotonated DA could be stabilised by the IL environment. These findings match all experimental results except in the case of $[C_2mim][HCOO]$. Previous reports suggest that DAH^+ is first oxidised to dopamine-quinone (DQ) before the deprotonation occurs. For completion, the same protocol of proton transfer was applied to a single protonated DQ molecule (DQH^+). A stable geometry for the proton transfer system was found in all three ILs, $[C_2mim][HCOO]$, $[C_2mim][OAc]$, and $[C_4mpyr][OAc]$, now aligning well with the experimental data, suggesting that the proton transfer in $[C_2mim][HCOO]$ could

be facilitated after oxidation of DA. These findings vindicate the hypothesis that the anion's basicity drives the initial deprotonation of DAH⁺ and DQH⁺, thus facilitating the following cyclisation of DQ.

Ionic Liquid	$\Delta H_{(ave)}$ (DA) (kJ mol⁻¹)	Complete proton transfer?	$\Delta H_{(ave)}$ (DQ) (kJ mol⁻¹)	Complete proton transfer?
[C ₂ mim][HCOO]	-	No	+11.4	Yes
[C ₂ mim][OAc]	+9.0	Yes	+6.0	Yes
[C ₂ mim][N(CN) ₂]	-	No	-	No
[C ₂ mim][OTf]	-	No	-	No
[C ₄ mpyr][OAc]	+2.6	Yes	+5.4	Yes
[C ₄ mpyr][N(CN) ₂]	-	No	-	No
[C ₄ mpyr][OTf]	-	No	-	No

Table S3: Data used to calculate the DA-NH₃⁺ deprotonation energies.

Configuration	Transfer complete?	State 1 SRS/aug-cc- pVDZ (Hartree)	State 1 ZPVE ωB97XD /aug-cc- pVDZ (Hartree)	PT SRS/aug- cc-pVDZ (Hartree)	PT ZPVE ωB97XD/ aug-cc- pVDZ (Hartree)	Boltzmann- weighted energy (298.15 K) (kJ mol⁻¹)
DA-NH ₃ ⁺ [C ₂ mim][N(CN) ₂] Conf 1	No	-1099.437898	0.393294	-1099.437666	0.393559	0.765
DA-NH ₃ ⁺ [C ₂ mim][N(CN) ₂] Conf 2	No	-1099.432801	0.392992	-1099.432818	0.393241	
DA-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 1	No	-1048.350052	0.392687	-1048.349920	0.392268	-0.624

DA-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 2	No	-1048.336988	0.392147	-1048.337337	0.392313	
DA-NH ₃ ⁺ [C ₂ mim][OAc] Conf 1	Yes	-1087.552547	0.421062	-1087.546662	0.418729	9.024
DA-NH ₃ ⁺ [C ₂ mim][OAc] Conf 2	Yes	-1087.543615	0.420271	-1087.538581	0.418582	
DA-NH ₃ ⁺ [C ₂ mim][OTf] Conf 1	No	-1819.398750	0.399425	-1819.398675	0.399307	-0.354
DA-NH ₃ ⁺ [C ₂ mim][OTf] Conf 2	No	-1819.387151	0.397797	-1819.387287	0.397722	
DA-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 1	Yes	-1152.317597	0.537124	-1152.312179	0.535232	2.581
DA-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 2	Yes	-1152.313109	0.536660	-1152.310369	0.534757	
DA-NH ₃ ⁺ [C ₄ mpyr][OTf] Conf 1	No	-1884.158214		-1884.158233		
DA-NH ₃ ⁺ [C ₄ mpyr][OTf] Conf 2	No	-1884.153865		-1884.153921		
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 1	No	-1164.198717		-1164.200441		
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 2	No	-1164.193289		-1164.193365		

Table S4: Raw data used to calculate the DQ-NH₃⁺ deprotonation energies.

Configuration	Transfer complete?	State 1 SRS/aug-cc- pVDZ (Hartree)	State 1 ZPVE ωB97XD /aug-cc- pVDZ (Hartree)	PT SRS/aug- cc-pVDZ (Hartree)	PT ZPVE ωB97XD/ aug-cc- pVDZ (Hartree)	Boltzmann- weighted energy (298.15 K) (kJ mol ⁻¹)
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DQ-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 1	Yes	-1047.112071	0.369081	-1047.104146	0.366405	11.448
DQ-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 2	Yes	-1047.101686	0.368574	-1047.095128	0.366114	
DQ-NH ₃ ⁺ [C ₂ mim][OAc] Conf 1	Yes	-1086.313482	0.397403	-1086.308445	0.395317	6.037
DQ-NH ₃ ⁺ [C ₂ mim][OAc] Conf 2	Yes	-1086.305326	0.397091	-1086.301403	0.395217	
DQ-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 1	Yes	-1151.077377	0.514582	-1151.072267	0.512909	5.402
DQ-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 2	Yes	-1151.077700	0.513988	-1151.073770	0.511869	
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 2	No	-1098.189522	0.369677	-1098.189476	0.369662	5.402

Table S5: N-H and A-H (acceptor atom, either O or N) bond lengths following the geometry optimisation of the forced proton transfer.

Configuration	N-H Bond Length (Å)	A-H Bond Length (Å)
DA-NH ₃ ⁺ [C ₂ mim][N(CN) ₂] Conf 1	1.042	1.884
DA-NH ₃ ⁺ [C ₂ mim][N(CN) ₂] Conf 2	1.044	1.848
DA-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 1	1.066	1.636
DA-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 2	1.071	1.602
DA-NH ₃ ⁺ [C ₂ mim][OAc] Conf 1	1.542	1.053

DA-NH ₃ ⁺ [C ₂ mim][OAc] Conf 2	1.573	1.044
DA-NH ₃ ⁺ [C ₂ mim][OTf] Conf 1	1.035	1.867
DA-NH ₃ ⁺ [C ₂ mim][OTf] Conf 2	1.041	1.77
DA-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 1	1.572	1.044
DA-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 2	1.557	1.047
DA-NH ₃ ⁺ [C ₄ mpyr][OTf] Conf 1	1.038	1.823
DA-NH ₃ ⁺ [C ₄ mpyr][OTf] Conf 2	1.039	1.776
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 1	1.04	1.914
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 2	1.041	1.892
DQ-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 1	1.509	1.073
DQ-NH ₃ ⁺ [C ₂ mim][HCOO] Conf 2	1.505	1.068
DQ-NH ₃ ⁺ [C ₂ mim][OAc] Conf 1	1.561	1.045
DQ-NH ₃ ⁺ [C ₂ mim][OAc] Conf 2	1.597	1.036
DQ-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 1	1.616	1.031
DQ-NH ₃ ⁺ [C ₄ mpyr][OAc] Conf 2	1.595	1.037
DA-NH ₃ ⁺ [C ₄ mpyr][N(CN) ₂] Conf 2	1.046	1.834

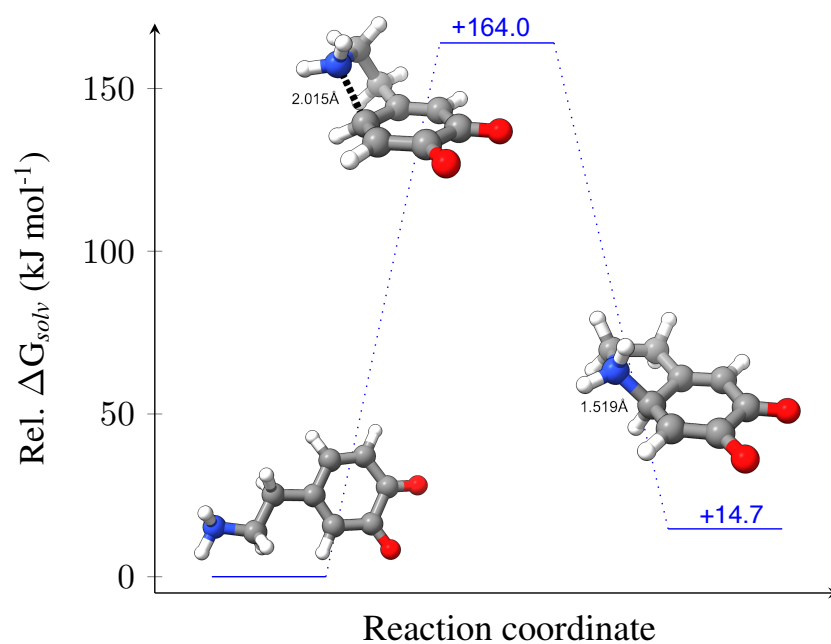


Figure S6: Free energy barrier (ΔG_{solv} in kJ mol^{-1}) for the cyclization of dopamine-quinone to form the cyclised DQ intermediate.

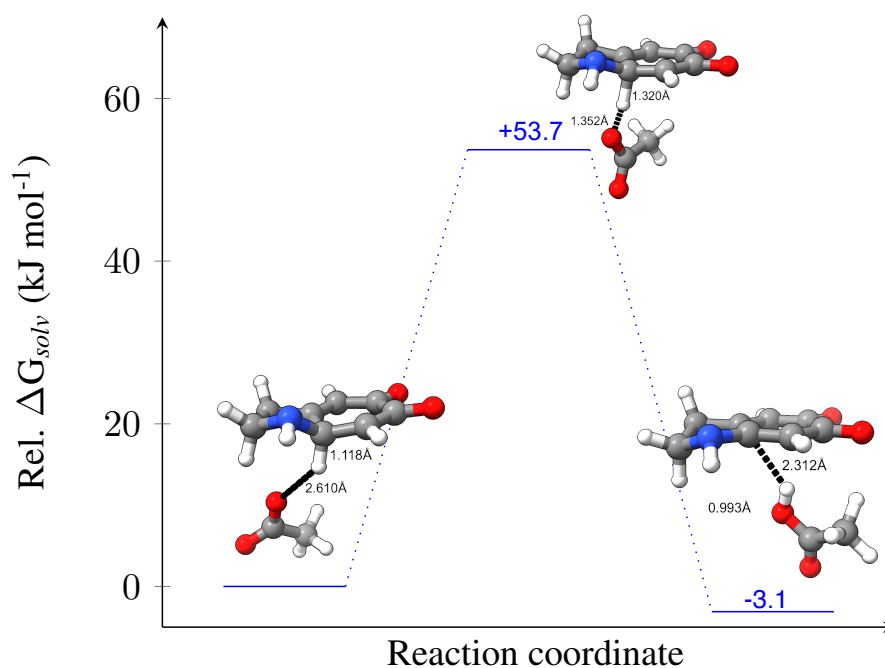


Figure S7: Free energy barrier (ΔG_{solv} in kJ mol^{-1}) for the removal of the C8 proton from the dieone intermediate, allowing for the formation of leukodopaminechrome.

Table S6: Raw data used to calculate the free energy barriers of the cyclization of DQ and the deprotonation of the dieone (via acetate).

Molecule	ZPVE M062X/ cc-pVTZ (Hartrees)	TC (298.15 K) (Hartrees)	S (cal mol ⁻¹ K ⁻¹)	ωB97XD/ aug-cc-pVTZ Gas (Hartrees)	M05-2X/ 6-311+G** SMD Ethanol (Hartrees)	M05-2X/ 6-311+G** Gas (Hartrees)
DQ	0.160008	0.170383	100.793000	-515.435159	-515.507356	-515.482132
TS-Dieone (+H ⁺)	0.194158	0.207928	118.19	-743.3197961	-743.6727634	-743.3738394
Dieone (+H ⁺)	0.163700	0.172567	93.063000	-515.379513	-515.509713	-515.428580
Dieone + Acetate	0.198830	0.213782	129.876000	-743.346723	-743.692492	-743.399748
TS-Dieone + Acetate	0.194158	0.207928	118.19	-743.3197961	-743.6727634	-743.3738394
LDC + Acetate	0.199266	0.213384	121.023000	-743.328614	-743.701819	-743.385969

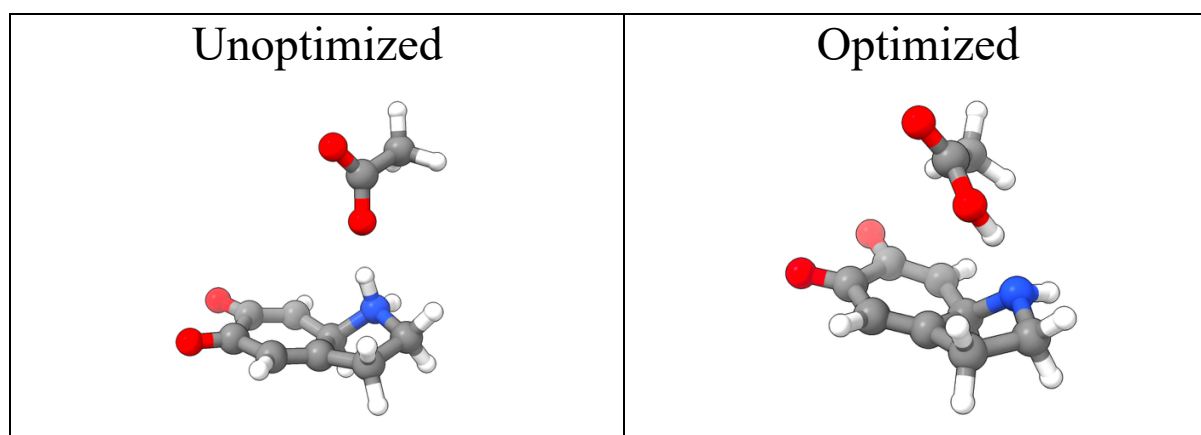


Figure S8: Initial and geometry optimized structure of the protonated dieone with an acetate molecule, demonstrating the barrierless proton transfer.

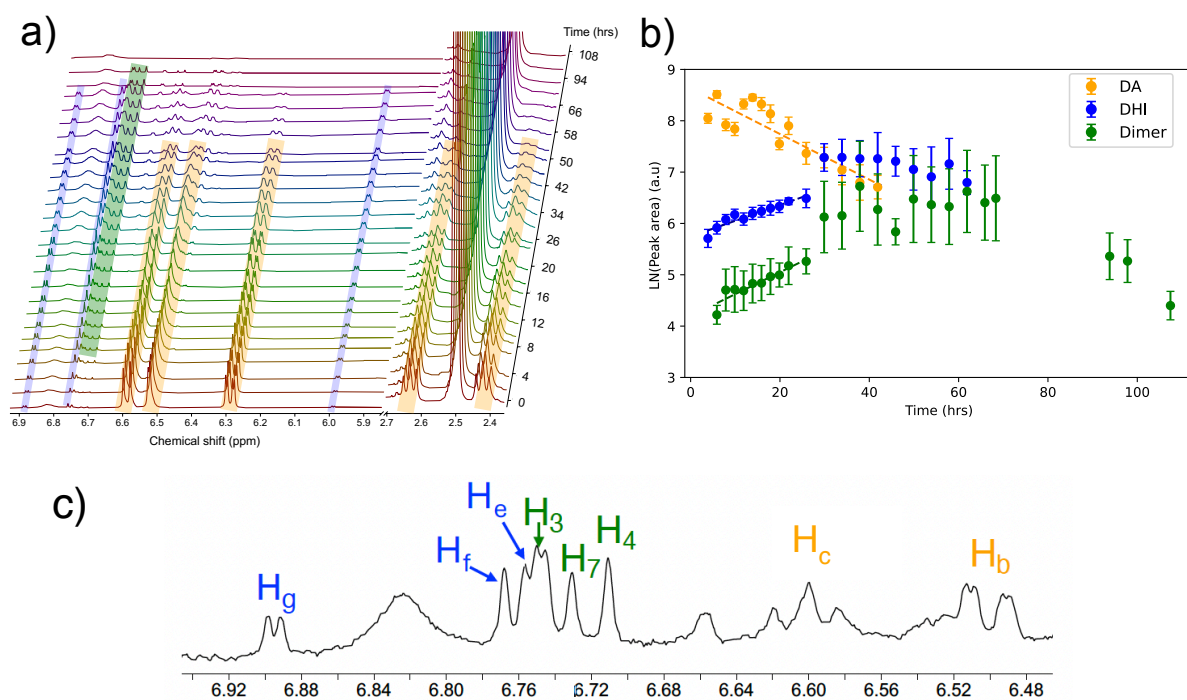


Figure S9: a) The full spectrum over 108 hours of *in situ*, room temperature ¹H NMR reaction monitoring of dopamine in [C₄mpyr][OAc] (80 mg/mL) (20 μL in 580 μL DMSO-d₆). Highlighted areas correspond to the colouring and data points used in the b) natural logarithm of a peak area vs. time for peaks associated with dopamine ($R^2 = 0.7811$), DHI ($R^2 = 0.8974$), and the 2-2' dimer ($R^2 = 0.8719$) in [C₄mpyr][OAc]. Errors correspond to one standard deviation from the average normalised peak area for each proton signal. c) Zoomed aromatic region and resultant proton assignments after 50 hours.

The analysis of the NMR data shows a linear decrease of $\ln(\text{peak area})$, proportionally to concentration. This correlation suggests that the rate determining step is first order. Does this provide information on the mechanism?

Intuitively, the rate determining step might be expected to be the cyclisation step; this is supported literature.⁶ Hence the rate for the cyclisation step can be expressed as such ...

$$\text{rate} = k[\text{DQ}]$$

Now, formally, [DQ] will be dependent on the position of any pre-equilibria, but the overall process will be first order, so the data is consistent with our proposed mechanism.

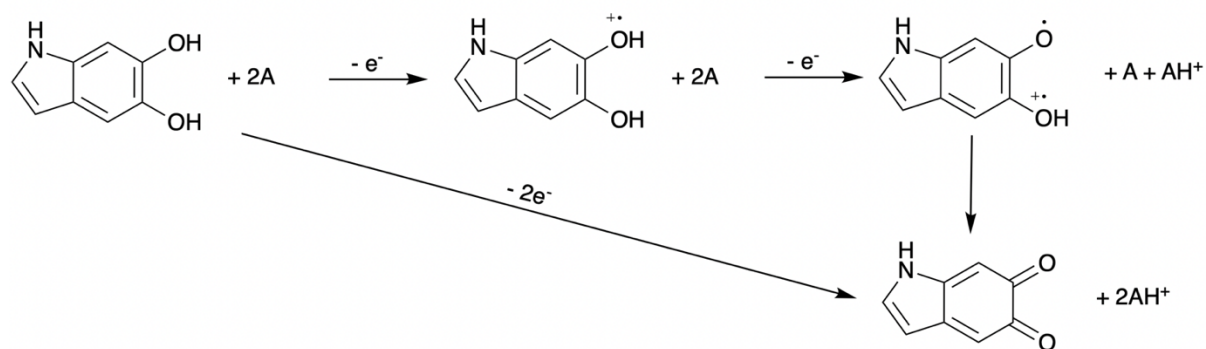


Figure S10: Potential pathways for the two-electron, two-proton oxidation of 5,6-dihydroxyindole (DHI).

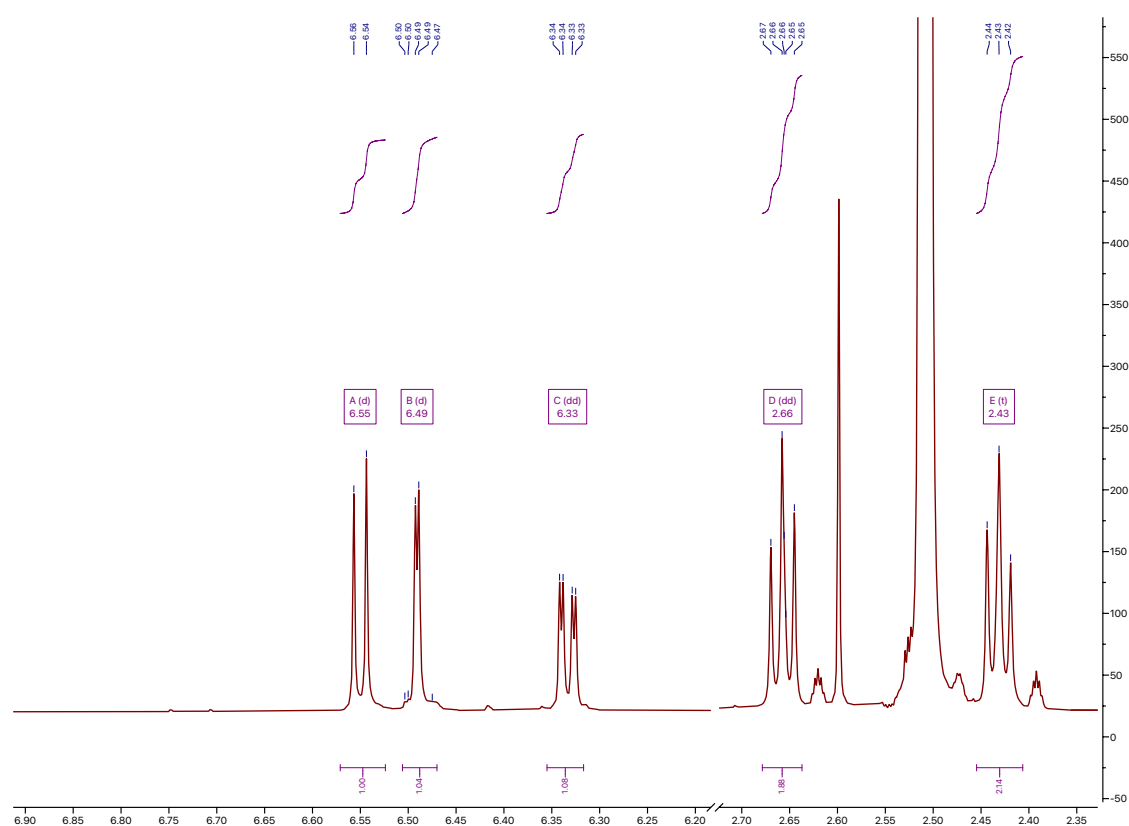


Figure S11: Zoomed ^1H NMR spectrum of 25 mg/mL DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6) after 4 days under a N_2 atmosphere at 70 $^\circ\text{C}$. ^1H NMR (600 MHz, DMSO-d_6) δ 6.55 (d, $J = 7.9$ Hz, 1H), 6.49 (d, $J = 2.2$ Hz, 1H), 6.33 (dd, $J = 7.9, 2.2$ Hz, 1H), 2.66 (t, $J = 7.5\text{--}8.4$ Hz, 2H), 2.43 (t, $J = 7.5\text{--}8.4$ Hz, 2H).

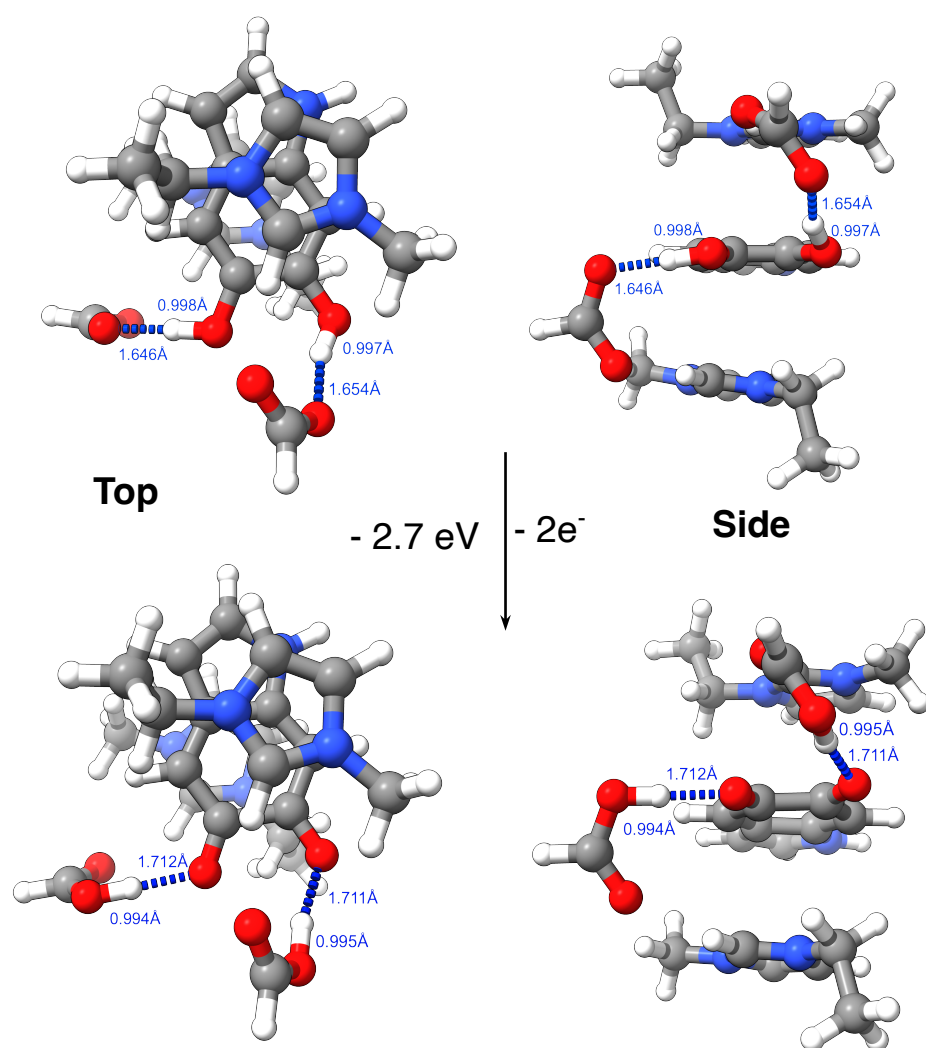


Figure S12: Example of an optimised DHI system with proton transfers to two formate anions in $[\text{C}_2\text{mim}][\text{HCOO}]$ (stacked configuration), following the removal of two electrons.

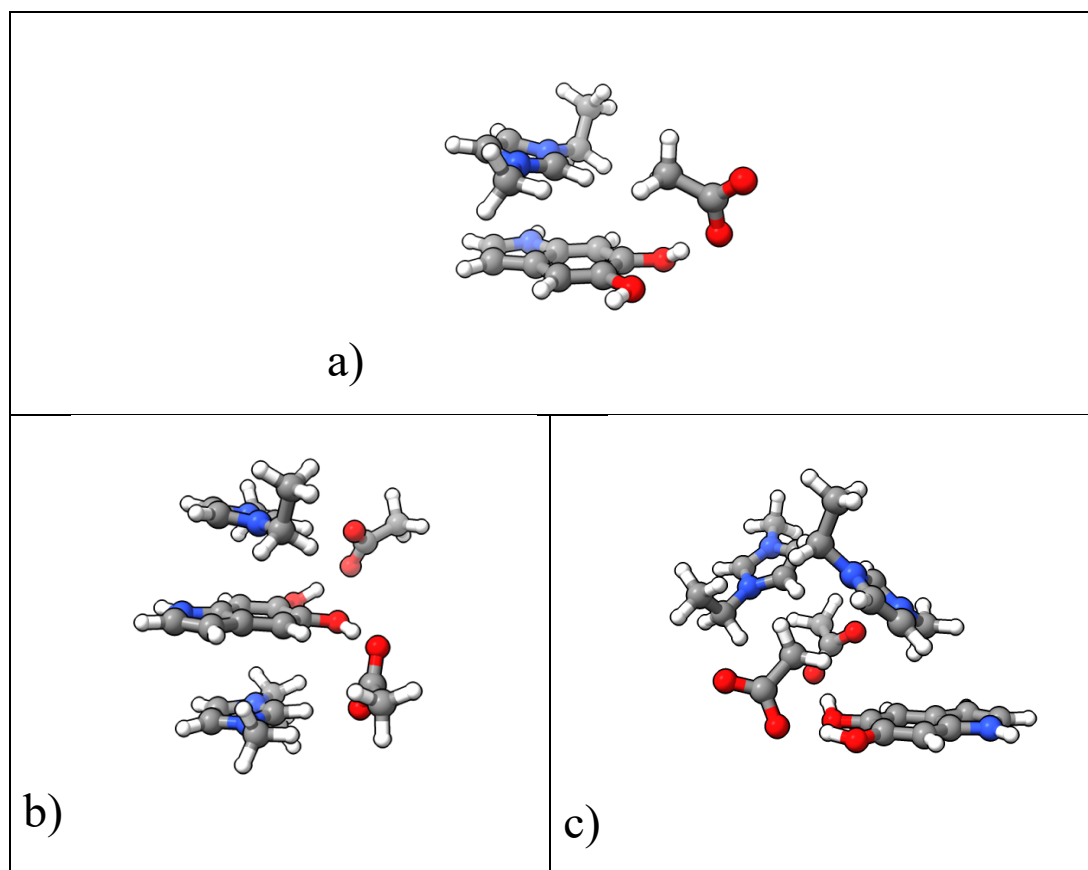


Figure S13: Configurations used in the DFT investigations, including: a) 1IP DHI deprotonation; and 2IP DHI deprotonation with either b) DHI sandwiched by the cations or c) cations only interacting with their corresponding anions (non-stacked).

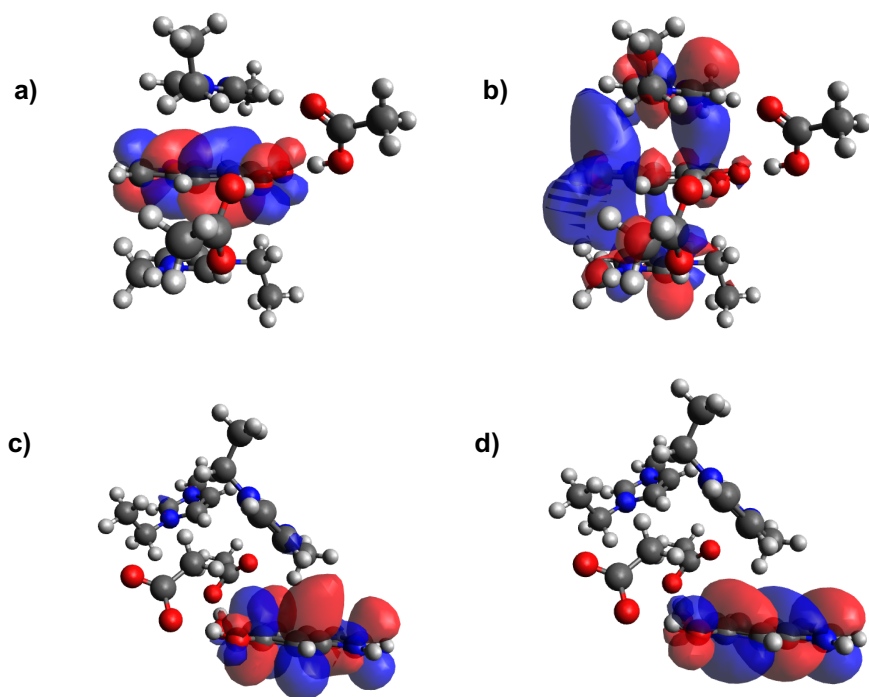


Figure S14: Calculated molecular orbitals of DHI with 2 ion pairs of [C₂mim][OAc] in the stacked configuration a) HOMO, b) LUMO, and the non-stacked configuration c) HOMO, d) LUMO.

Table S7: Raw data used to calculate ΔH_{2e} of each DHI + 2IP system.

System	0 Charge SRS/aug-cc- pVDZ (Hartree)	0 Charge ZPVE ω B97XD /aug-cc- pVDZ (Hartree)	+2 charge SRS/aug-cc- pVDZ (Hartree)	+2 charge ZPVE ω B97XD/ aug-cc- pVDZ (Hartree)	Total energy (Hartrees)	Total energy (eV)	HOMO- LUMO Gap (0 charge)
DHI 2 H ₂ O	-665.474774	0.185628	-665.092074	0.386484	0.3865	10.52	10.64
DHI 2 IP [C ₂ mim][HCOO] Stacked	-1577.616066	0.526742	-1577.720378	0.528987	-0.102066	-2.78	10.40
DHI 2 IP [C ₂ mim][HCOO] Non-stacked	-1578.020273	0.524630	-1577.671771	0.528735	0.352607	9.60	10.66
DHI 2 IP [C ₂ mim][OAc] Stacked	-1656.024196	0.579441	-1656.136042	0.584306	-0.106982	-2.91	8.05
DHI 2 IP [C ₂ mim][OAc] Non-stacked	-1656.444869	0.583566	-1656.120847	0.586269	0.326725	8.89	10.56

Table S8: Raw data used to calculate ΔH_{1e} of each DHI + 1IP system.

System	0 Charge SRS/aug-cc- pVDZ (Hartree)	0 Charge ZPVE ω B97XD /aug-cc-pVDZ (Hartree)	+1 charge SRS/aug-cc- pVDZ (Hartree)	+1 charge ZPVE ω B97XD/ aug-cc-pVDZ (Hartree)	Total energy (Hartrees)	Total energy (eV)
DHI 1IP [C ₂ mim][HCOO]	-1048.422619	0.332669	-1048.249425	0.333770	0.174294	4.74
DHI 1IP [C ₂ mim][OAc]	-1087.749996	0.360166	-1087.583012	0.361314	0.168132	4.58
DHI 1IP [C ₄ mpyr][OAc]	-1152.758745	0.478293	-1152.590296	0.478796	0.168951	4.60

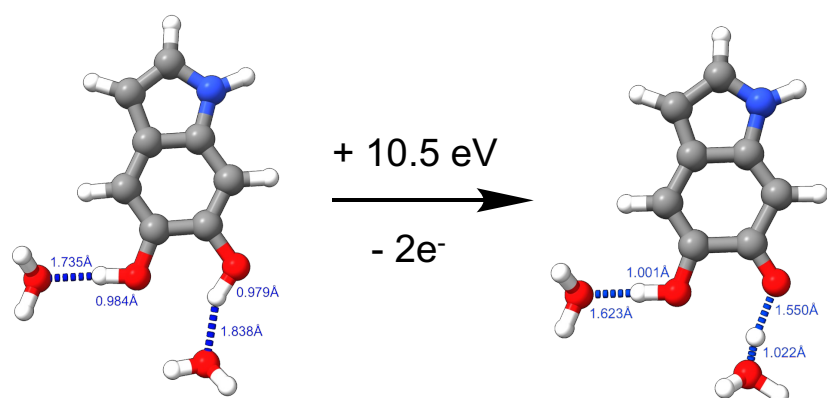


Figure S15: Optimized structures of the DHI + 2 H₂O system with the calculated ΔH_{2e} .

Table S9: Raw data used to calculate free energy barriers of dimerization.

Molecule	ZPVE M062X/ cc-pVTZ (Hartrees)	TC (298.15 K) (Hartrees)	S (cal mol ⁻¹ K ⁻¹)	ω B97XD/ aug-cc- pVTZ Gas (Hartrees)	M05-2X/ 6-311+G** SMD Ethanol (Hartrees)	M05-2X/ 6-311+G** Gas (Hartrees)
DHI (-H ⁺)	0.125861	0.133880	87.592000	-513.716841	-513.881909	-513.777804
2-2' (-H ⁺)	0.243941	0.261208	135.784000	-1026.766743	-1027.012157	-1026.892304
IQ	0.114847	0.123073	89.985000	-513.014804	-513.105487	-513.077423
2-4' (-H ⁺)	0.243917	0.260644	132.204000	-1026.768444	-1027.001728	-1026.894822
2-7' (-H ⁺)	0.244045	0.260737	131.851000	-1026.758624	-1026.996913	-1026.884412
TS 2-2' (-H ⁺)	0.241104	0.258305	136.185000	-1026.745302	-1026.978636	-1026.877993
TS 2-4' (-H ⁺)	0.241825	0.258387	129.510000	-1026.730387	-1026.978041	-1026.862948
TS 2-7' (-H ⁺)	0.241545	0.258186	130.059000	-1026.721966	-1026.973037	-1026.854051

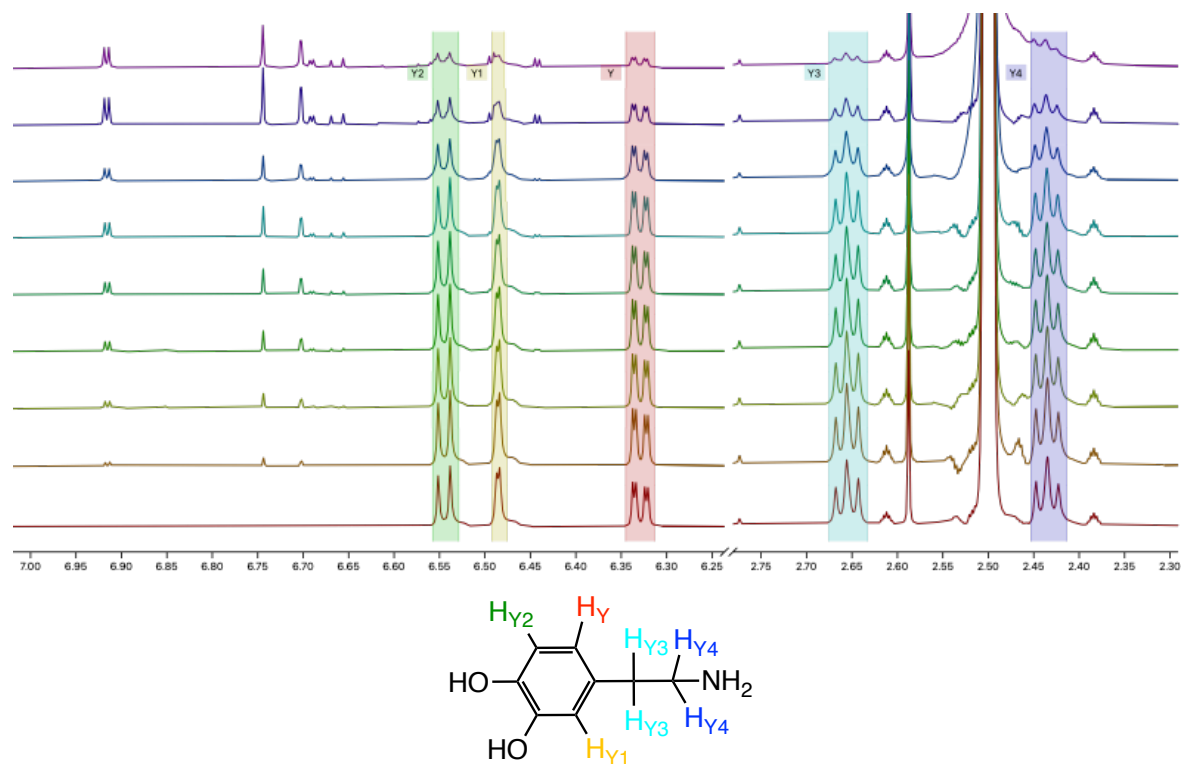


Figure S16: Areas of integration and relative proton assignments for dopamine signals in the *in situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO- d_6).

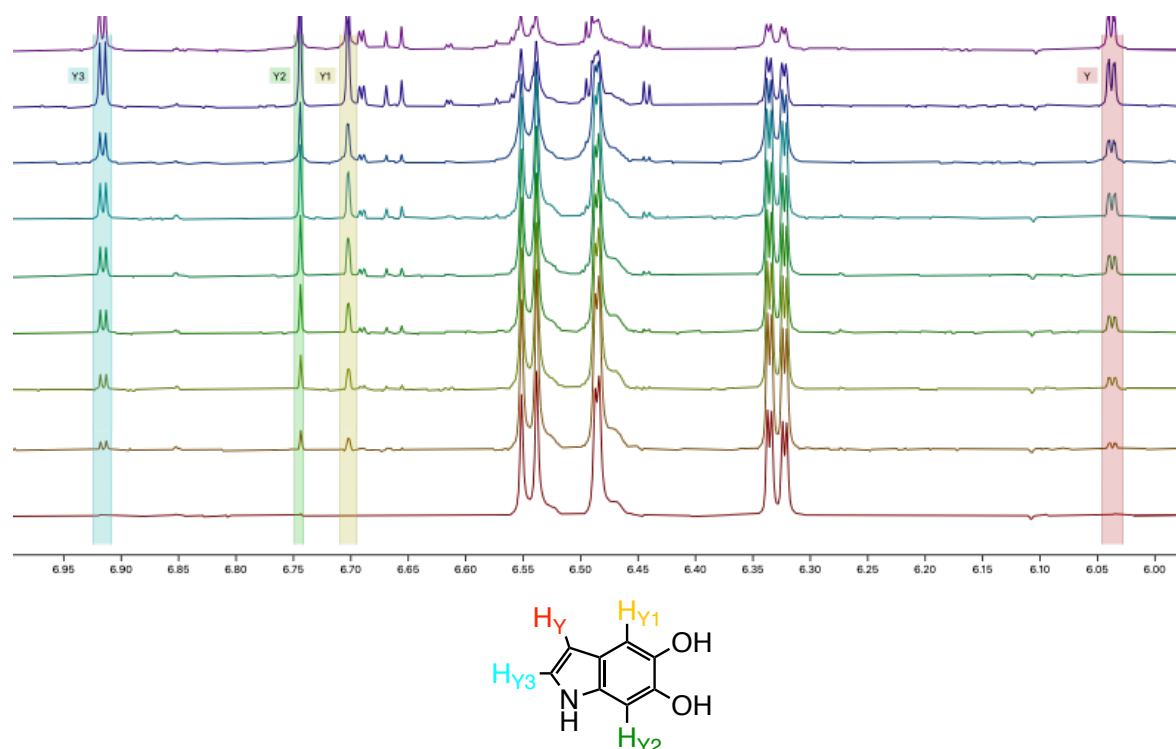


Figure S17: Areas of integration and relative proton assignments for DHI signals in the *in situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO- d_6). DHI has 2 ortho protons at the C4 ($\text{Y1} = \text{H}_e$) and C7 positions ($\text{Y2} = \text{H}_f$), which produce a doublet at 6.70 ppm and a singlet at 6.75 ppm, respectively. The C3 proton ($\text{Y} = \text{H}_d$) is the least deshielded at 6.04 ppm and engages in $3J$ coupling ($J = 0.9$ Hz) to the C2 (H_g) (6.92 ppm) and $4J$ coupling ($J = 3.0$ Hz) to the C4 proton ($\text{Y3} = \text{H}_e$).

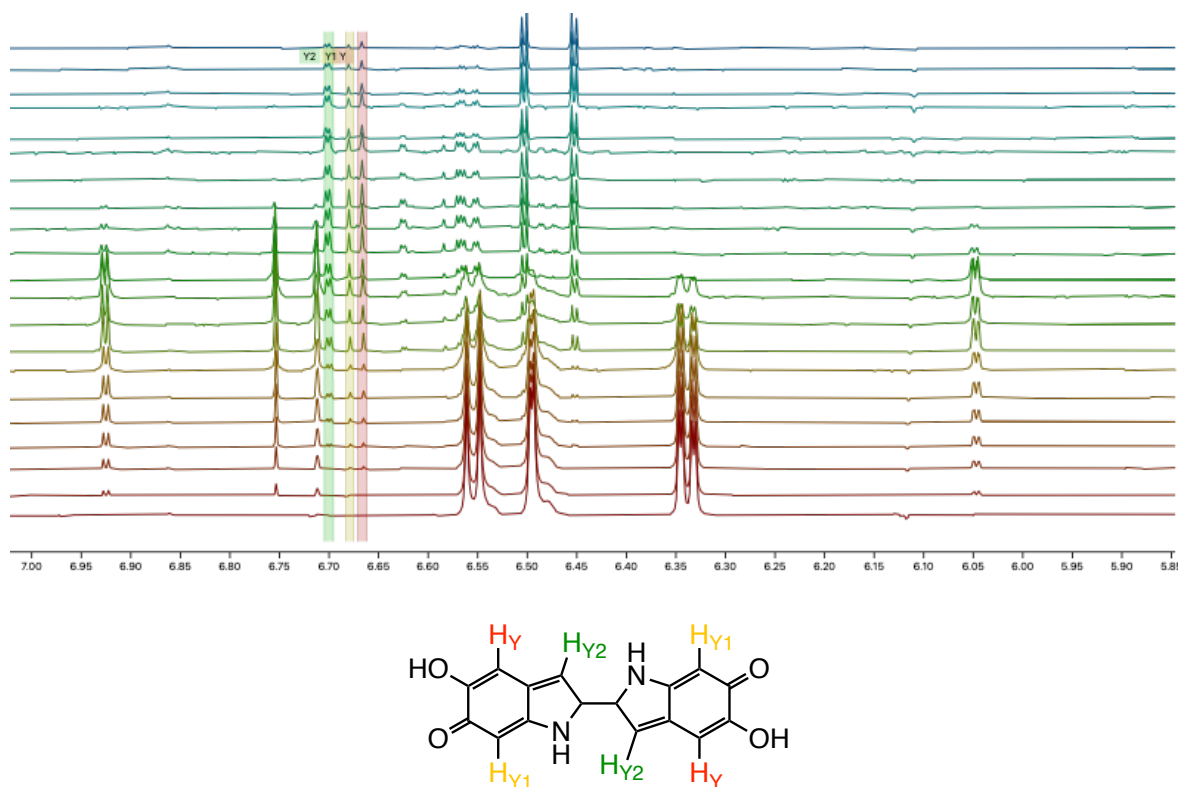


Figure S18: Areas of integration and relative proton assignments for 2-2' signals in the *in situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO-d_6). As a symmetric molecule, the 2-2' dimer only has four proton environments (discounting OH and NH protons). The H_2 protons give rise to peaks at a much lower chemical shift (closer to the aliphatic region). This is not visible due to the large IL peaks in the range of 3.5 to 4.5 ppm. In contrast, both 2-4' and 2-7' dimers would produce at least 6 different aromatic proton environments.

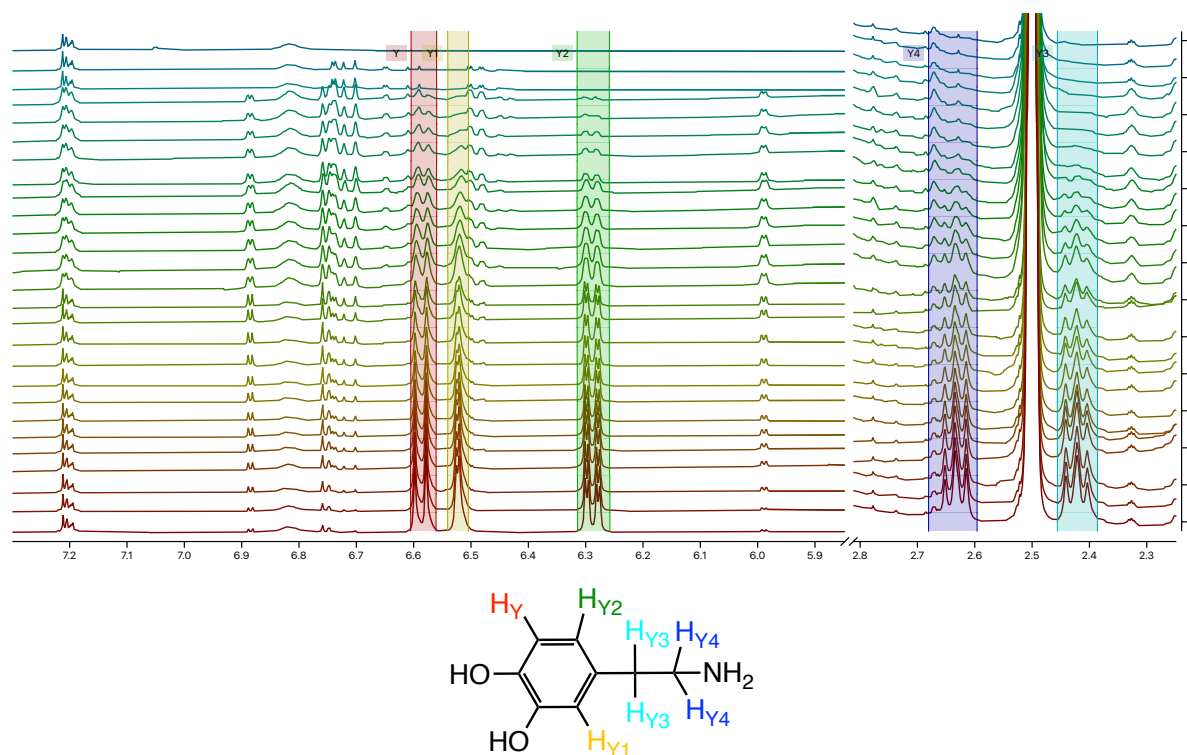


Figure S19: Labelled areas of integration and relative proton assignments for dopamine signals in the *in situ*, room temperature ¹H NMR reaction monitoring of DA in [C₄mpyr][OAc] (80 mg/mL) (20 μL in 580 μL DMSO-d₆). DA proton assignments at 0 hr: (600 MHz, DMSO-d₆) δ Y = 6.55 (d, *J* = 7.9 Hz, 1H), Y1 = 6.49 (d, *J* = 2.2 Hz, 1H), Y2 = 6.34 (dd, *J* = 7.9, 2.2 Hz, 1H), Y4 = 2.67 (t, *J* = 7.5-8.4 Hz, 2H), Y3 = 2.43 (t, *J* = 7.5-8.4 Hz, 2H).

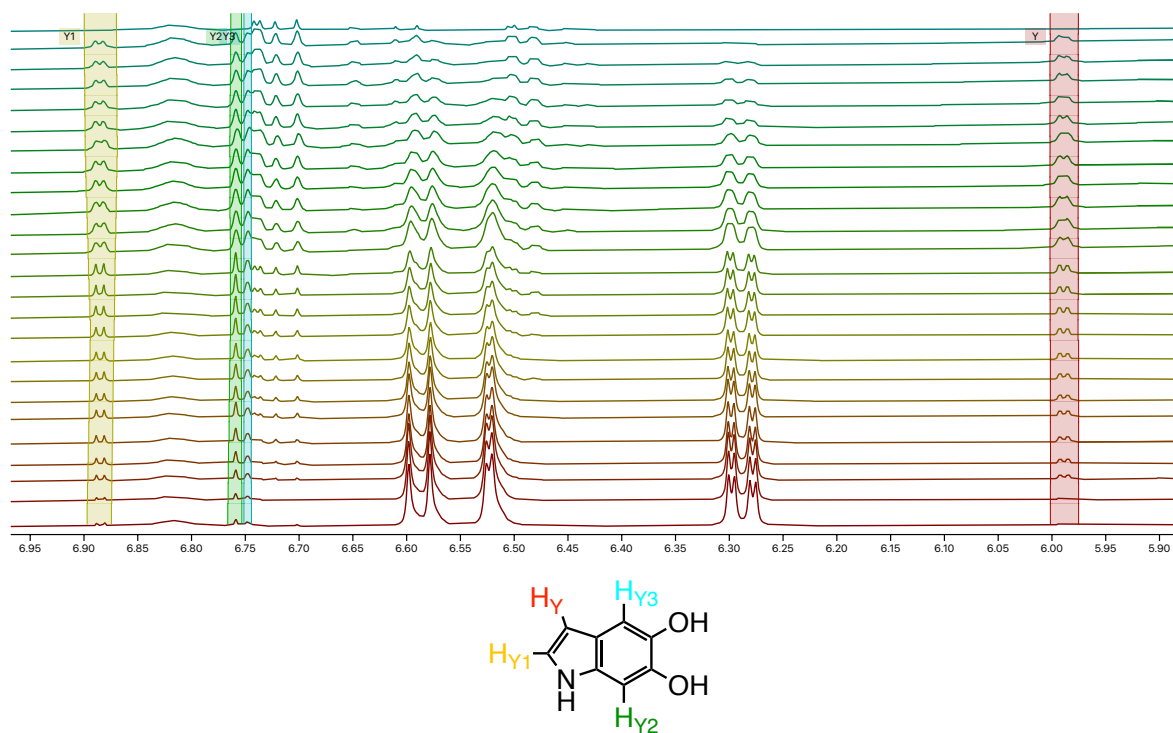


Figure S20: Labelled areas of integration and relative proton assignments for DHI signals in the *in situ*, room temperature ^1H NMR reaction monitoring of DA in $[\text{C}_4\text{mpyr}][\text{OAc}]$ (80 mg/mL) (20 μL in 580 μL DMSO- d_6). DHI proton assignments at 24 hr: (600 MHz, DMSO- d_6) δ Y1 = 6.86 (d, J = 3.0 Hz, 1H), Y2 = 6.76 (s, 1H), Y3 6.74 (s, 1H), Y = 5.98 (dd, J = 3.9, 2.2 Hz, 1H).

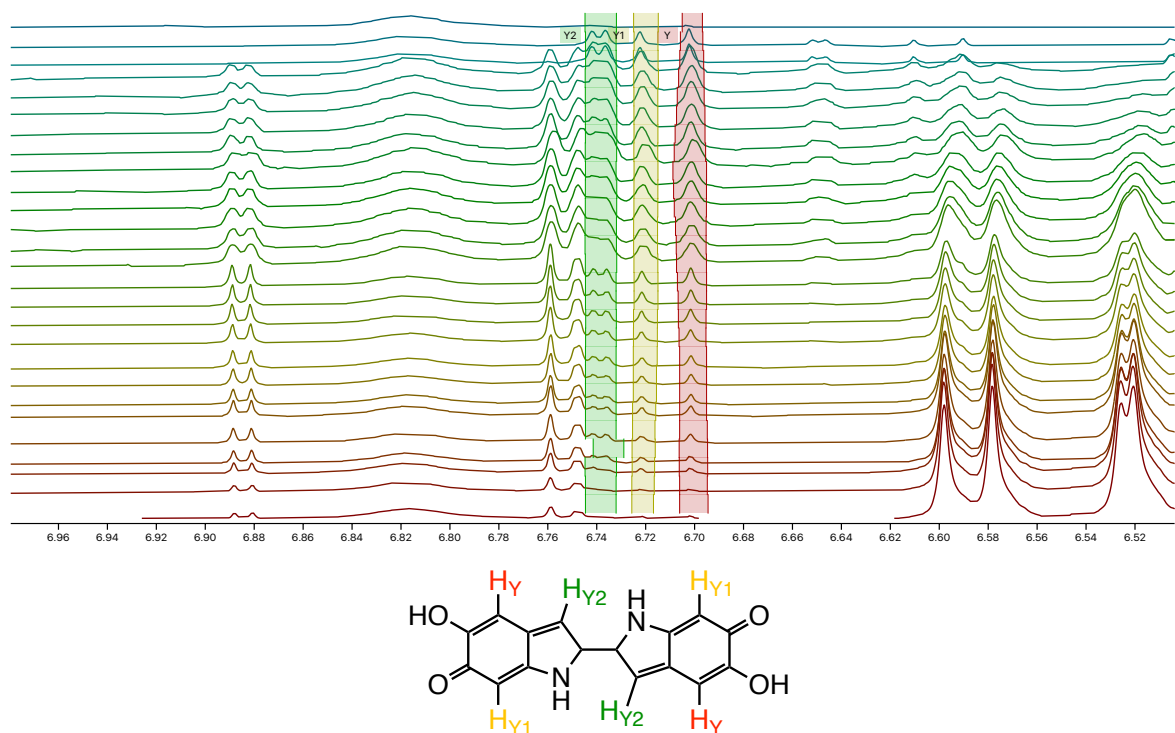


Figure S21: Labelled areas of integration and relative proton assignments for 2-2' dimer signals in the *in situ*, room temperature ¹H NMR reaction monitoring of DA in [C₄mpyr][OAc] (80 mg/mL) (20 μL in 580 μL DMSO-d₆). 2-2' dimer proton assignments at 72 hr: (600 MHz, DMSO-d₆) δ Y2 = 6.74 (d, J = 2.1 Hz, 1H), Y1 = 6.72 (s, 1H), Y = 6.70 (s, 1H).¹

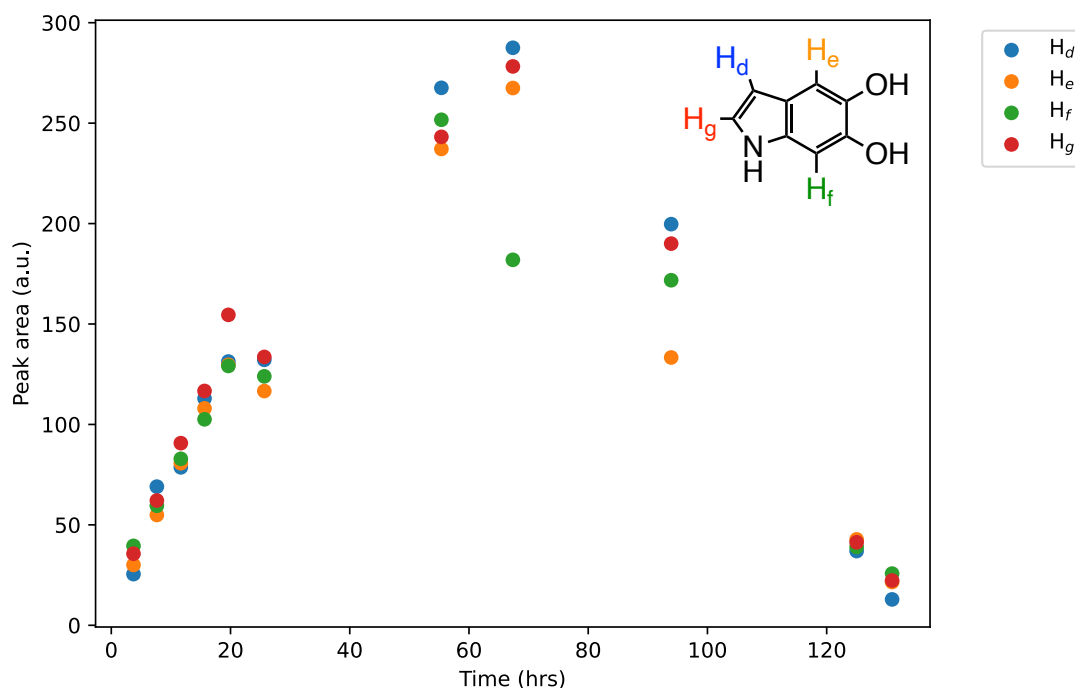


Figure S22: Peak area of each DHI signal over time in the *in situ*, room temperature ¹H NMR reaction monitoring of DA in [C₂mim][OAc] (80 mg/mL) (20 μL in 580 μL DMSO-d₆).

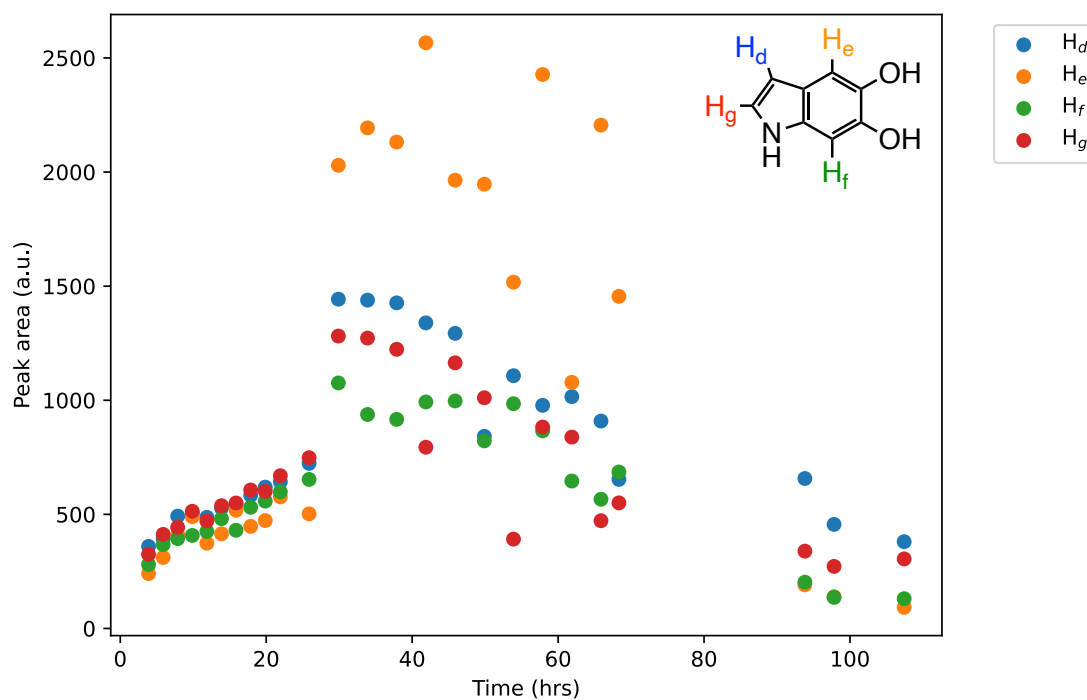


Figure S23: Peak area of each DHI signal over time in the *in situ*, room temperature ¹H NMR reaction monitoring of DA in [C₄mpyr][OAc] (80 mg/mL) (20 μL in 580 μL DMSO-d₆). Large signals due to the overlapping peaks with dimer.

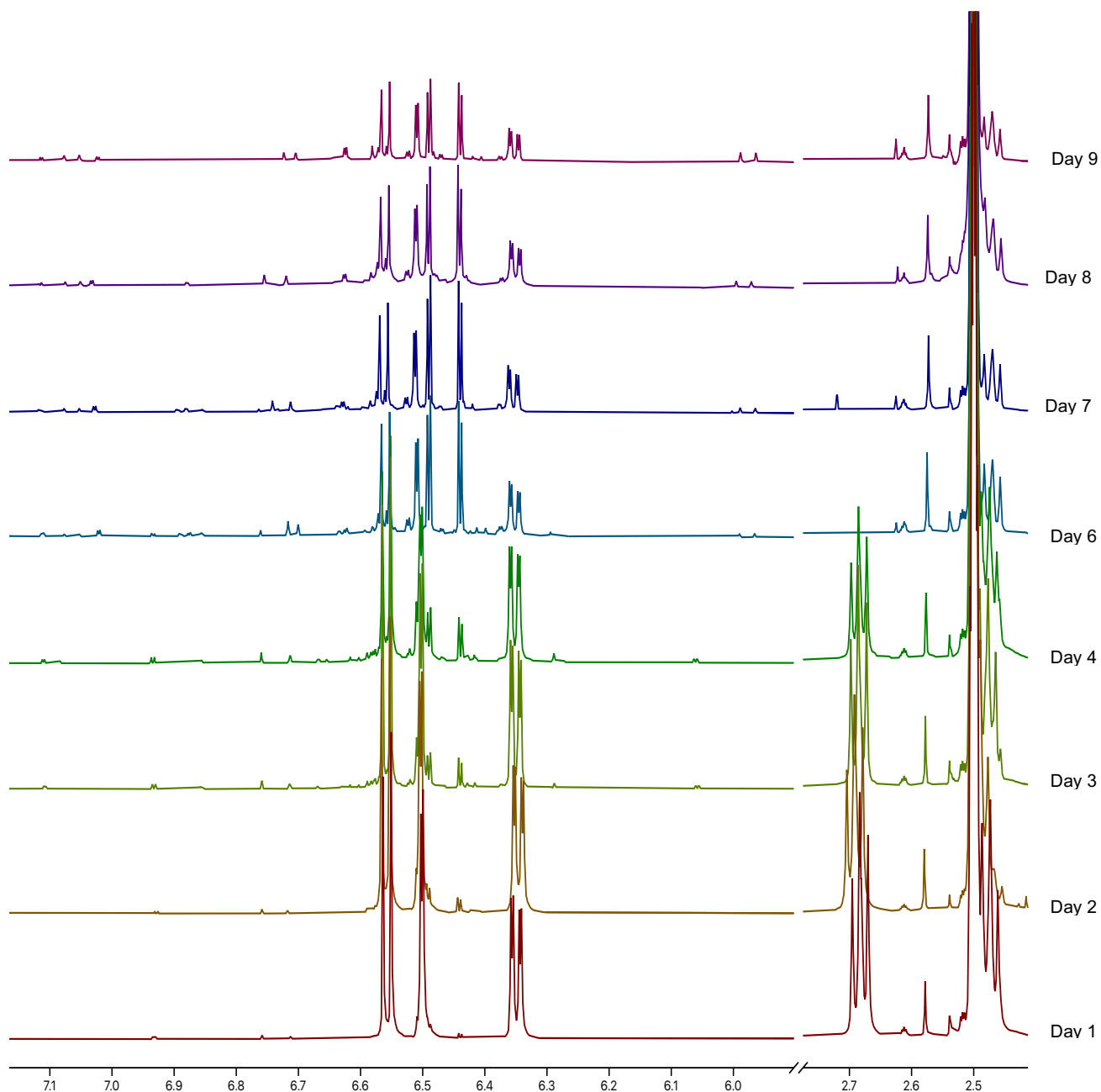


Figure S24: Aliphatic and aromatic regions of 80°C *ex situ* ^1H NMR reaction monitoring of 160 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO- d_6). DA peaks after 1 day: ^1H NMR (600 MHz, DMSO- d_6) δ 6.57 (d, J = 7.9 Hz, 1H), 6.51 (d, J = 2.2 Hz, 1H), 6.36 (dd, J = 7.9, 2.2 Hz, 1H), 2.69 (t, J = 7.5-8.4 Hz, 2H), 2.48 (t, J = 7.5-8.4 Hz, 2H).

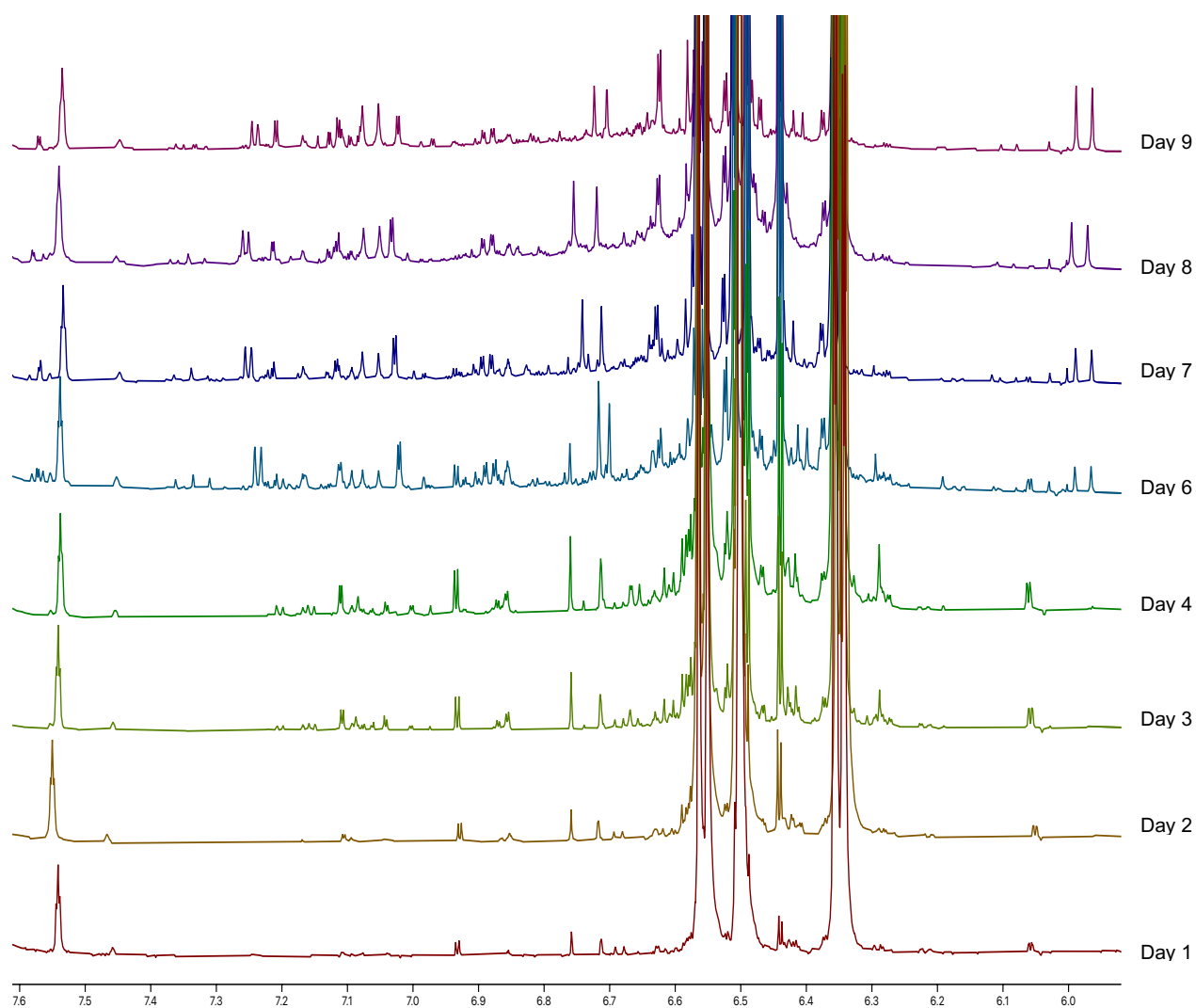


Figure S25: Zoomed aromatic region of 80°C *ex situ* ^1H NMR reaction monitoring of 160 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6) (Same as Figure 2e in main text, but with no highlights). DHI peaks after 1 day: ^1H NMR (600 MHz, DMSO-d_6) δ 6.94 (d, $J = 3.0$ Hz, 1H), 6.77 (s, 1H), 6.72 (d, $J = 0.9$ Hz, 1H), 6.04 (dd, $J = 3.0, 0.9$ Hz, 1H).

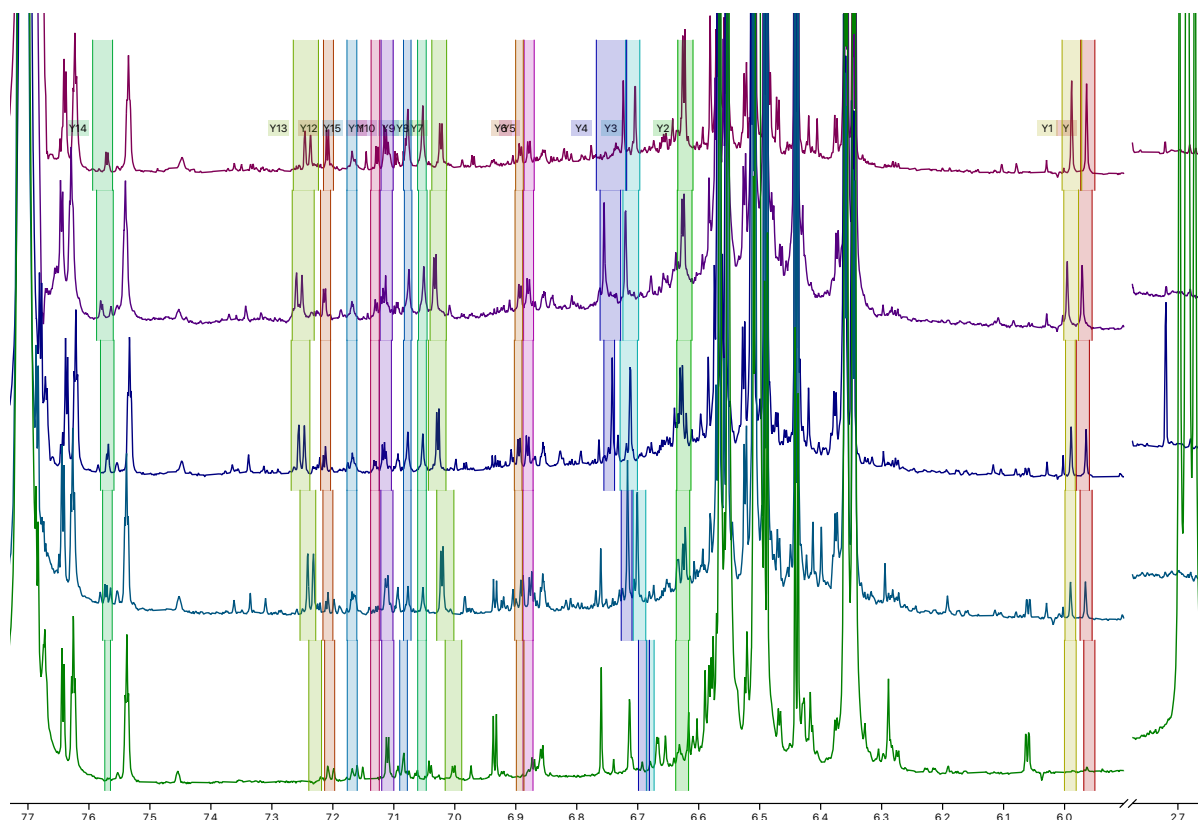


Figure S26: Labelled integration areas of dimer signals (for correlation analysis) for the 80°C *ex situ* ^1H NMR reaction monitoring of 160 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6). Dimer peaks after 7 days: ^1H NMR (600 MHz, DMSO-d_6) δ Y14 = 7.58 (d, J = 1.8 Hz, 1H), Y13 = 7.27 (d, J = 0.8 Hz, 1H), Y12 = 7.26 (s, 1H), Y15 = 7.22 (d, J = 2.1 Hz, 1H), Y11 = 7.13 (d, J = 2.3 Hz, 1H), Y9 = 7.09 (s, 1H), Y8 = 7.06 (s, 1H), Y7 = 7.04 (d, J = 2.2 Hz, 2H), Y6 = 6.90 (d, J = 2.3 Hz, 1H), Y5 = 6.89 (d, J = 2.2 Hz, 1H), Y4 = 6.75 (s, 2H), Y3 = 6.72 (d, J = 0.8 Hz, 2H), Y2 = 6.64 (d, J = 2.2 Hz, 2H), Y1 = 6.00 (s, 1H), Y = 5.97 (s, 1H).

Table S10: Raw peak areas of DHI signals for the 80°C *ex situ* ^1H NMR reaction monitoring of 160 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6).

Time (days)	Integral Range (H_d) (6.094227, 6.044489) Y	Integral Range (H_e) (6.791839, 6.754457) Y3	Integral Range (H_f) (6.948816, 6.919715) Y2	Integral Range (H_g) (6.732319, 6.705407) Y1	Average peak area
1	114.472	148.778	152.271	108.627	131.037
2	154.525	184.74	193.204	186.191	179.665
3	332.2	290.683	330.585	330.137	320.90125

4	260.71	434.971	252.9	513.47	365.51275
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Table S11: Raw peak areas of dimer signals (5.95-7.04 ppm) for the 80°C *ex situ* ¹H NMR reaction monitoring of 160 mg DA in 1 mL [C₂mim][OAc] (20μL in 580μL DMSO-d₆).

Time (days)	Integral Range (5.980918, 5.950320) Y	Integral Range (6.004150, 5.971852) Y1	Integral Range (6.637655, 6.609323) Y2	Integral Range (6.728884, 6.673174) Y3	Integral Range (6.771949, 6.680720) Y4	Integral Range (6.888110, 6.869845) Y5	Integral Range (6.902276, 6.886602) Y6	Integral Range (7.043370, 6.988654) Y7
4	30.5093	169.533	139.908	56.0238	56.9373	71.7358	16.9633	161.353
6	250.118	227.757	265.415	644.768	1036.59	554.06	180.505	695.224
7	282.426	303.1	756.676	671.182	792.08	271.443	278.617	527.987
8	438.48	461.149	820.62	617.004	701.067	321.758	243.361	568.73
9	531.062	541.492	1008.21	459.449	504.962	208.026	201.914	421.631

Table S12: Raw peak areas of dimer signals (7.04 – 7.59 ppm) for the 80°C *ex situ* ¹H NMR reaction monitoring of 160 mg DA in 1 mL [C₂mim][OAc] (20μL in 580μL DMSO-d₆).

Time (days)	Integral Range (7.061089, 7.045395) Y8	Integral Range (7.090279, 7.070327) Y9	Integral Range (7.123833, 7.100029) Y10	Integral Range (7.137999, 7.123069) Y11	Integral Range (7.176931, 7.159992) Y15	Integral Range (7.22016, 7.197008) Y12	Integral Range (7.268327, 7.218462) Y13	Integral Range (7.59387, 7.558886) Y14
4	-12.5539	161.659	382.629	-44.2675	217.439	156.806	-138.817	-30.9939
6	230.384	180.444	473.383	32.6865	324.384	134.157	761.91	161.589
7	300.604	319.497	275.786	74.4658	247.229	147.888	561.051	246.653
8	530.744	308.502	342.623	110.411	172.263	246.598	295.224	157.229
9	593.228	615.985	356.922	152.497	192.732	237.64	541.591	179.338

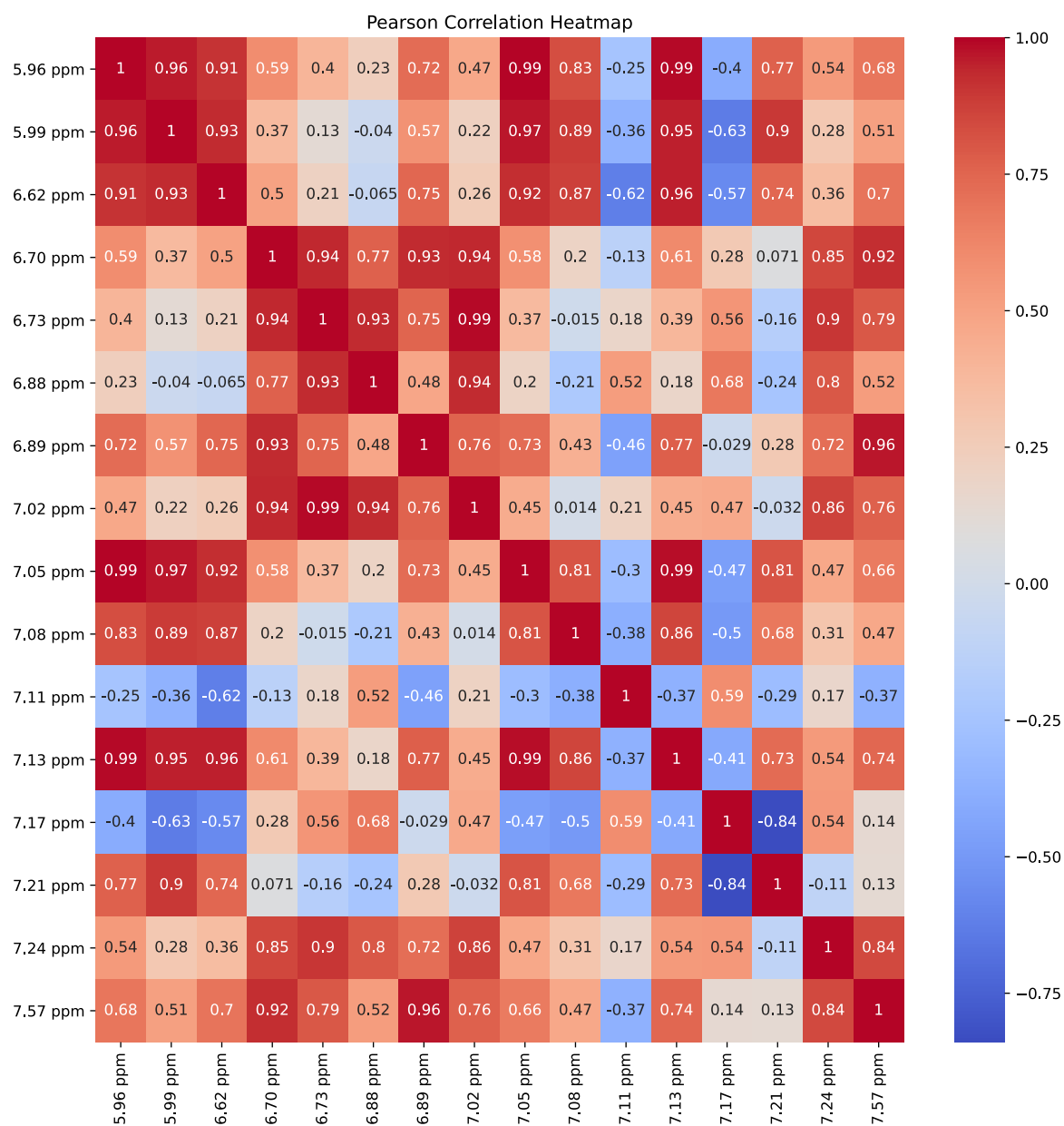


Figure S27: Pearson correlation heatmap of peaks of interest in Table S11-12 (dimer peaks in 80°C *ex situ* ^1H NMR reaction monitoring of 160 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$).

Table S13: Summary table of the Pearson correlation heatmap of dimer peaks in 80°C *ex situ* ¹H NMR reaction monitoring of 160 mg DA in 1 mL [C₂mim][OAc]. The number of other correlated peaks (above specific thresholds) for each peak of interest is listed below. The colouring was assigned to groups of correlated peaks, representative of a single chemical species with several proton environments. For example, the 3 peaks in the green set all have at least 3 correlated peaks above R² = 0.9 (including self-correlation), which are to the other members of the same set. Furthermore, they are also the only peaks with 2H integration. As a symmetric molecule, the 2-2' dimer only has four proton environments (discounting OH and NH protons). The H₂ protons give rise to peaks at a much lower chemical shift (closer to the aliphatic region). This is not visible due to the large IL peaks in the range of 3.5 to 4.5 ppm. Therefore, the green set is most likely the 2-2' dimer. In contrast, both 2-4' and 2-7' dimers would produce at least 6 different aromatic proton environments. Theoretically, the 2-4' dimer must include two singlets, two doublets with 3J coupling and two doublets with 4J coupling. On the other hand, the 2-7' dimer must include one singlet, three doublets with 4J coupling, one doublet with 3J coupling and one doublet of doublets with 3J and 4J coupling. Due to the high potential for peak overlap in this narrow region, it is difficult to identify every peak present in each species, and lower correlation coefficients are expected. Therefore, at R² = 0.7-0.75, the purple and light blue sets demonstrate similar patterns to the 2-4' and 2-7' dimers, respectively. The light blue set includes singlets at 7.26 (doublet with J = 0.8 Hz) and 7.27 ppm, and doublets at 6.88 (J = 2.2 Hz), 6.89 (J = 2.3 Hz), 7.21 (J = 2.1 Hz) and 7.57 ppm (J = 1.8 Hz), 7.09 (J = 2.1 Hz) and 7.19 ppm (J = 2.0 Hz), whereas the purple set includes four 1H singlets at 5.97, 5.99, 7.05, and 7.08 ppm, a doublet (J = 2.2 Hz, 2H) at 6.62 ppm, and a multiplet at 7.13 ppm.

		# Correlated peaks above threshold (R ²)						Integration
δ (ppm)	Splitting	0.7	0.75	0.8	0.9	0.93	0.95	
5.97	s	7	6	5	4	3	3	1
5.99	s	6	6	6	4	4	3	1
6.62	d	7	5	5	4	2	1	2 (overlap)
6.70	s	6	6	5	4	3	0	2
6.73	s	6	6	4	3	2	1	2
6.88	d	4	4	2	2	1	0	1
6.89	d	9	5	2	2	2	0	1
7.02	d	6	6	4	3	3	1	2
7.05	s	7	6	6	4	3	3	1
7.08	s	5	5	5	0	0	0	1
7.13	d	8	6	5	4	3	4	1
7.21	d	5	3	2	0	0	0	1

7.26	s	6	5	4	0	0	0	1
7.27	s	6	5	4	0	0	0	1
7.57	d	6	5	3	0	0	0	1

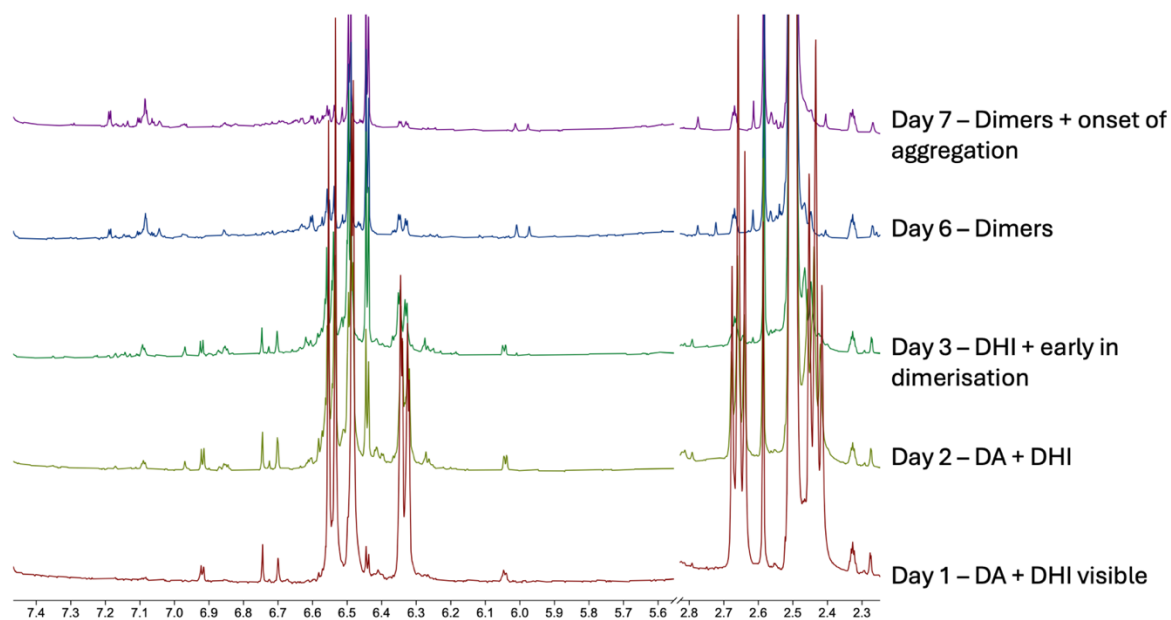


Figure S28: ^1H NMR spectra of the 80 mg/mL DA in $[\text{C}_2\text{mim}][\text{OAc}]$ (polymerised at 100 °C for 7 days) used in the FTIR and SAXS studies.

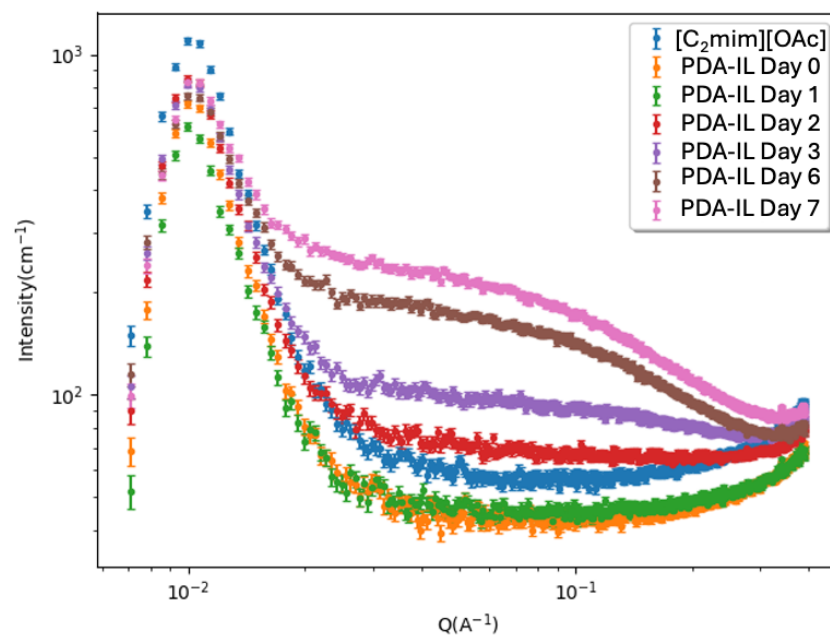


Figure S 29: Raw SAXS traces of IL blank and 80 mg/mL DA in $[C_2mim][OAc]$ (polymerised at 100 °C for 7 days).

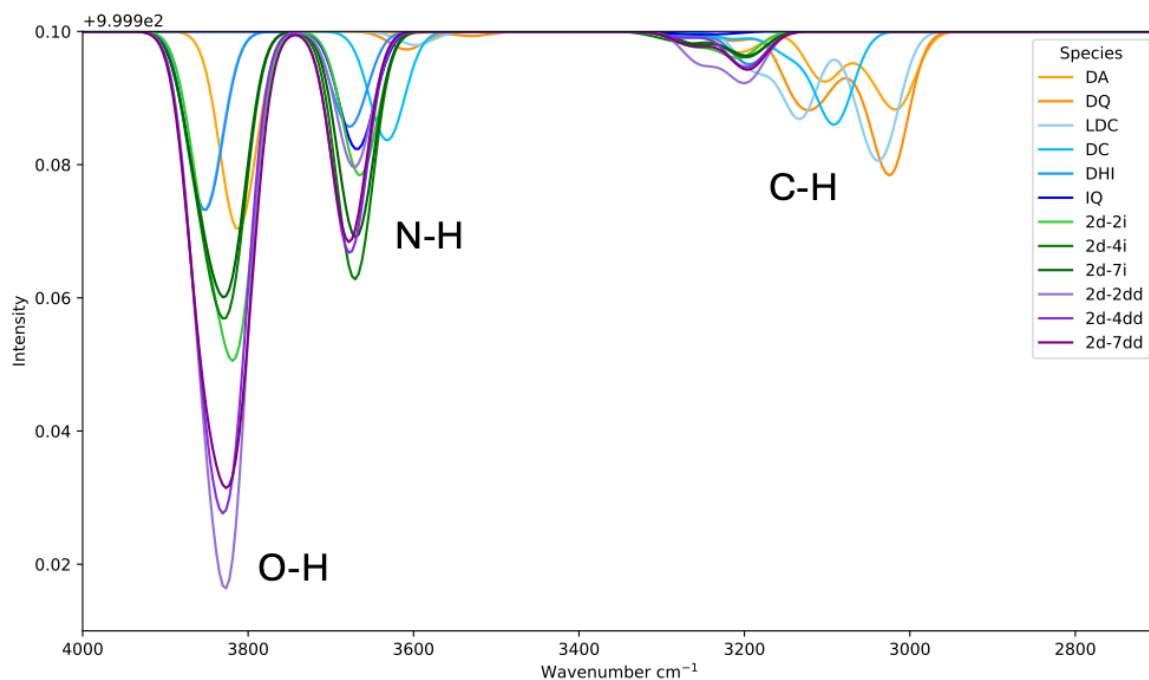


Figure S30: Zoomed C-H/N-H/O-H region of the theoretical FTIR spectra calculated at the $\omega B97XD/aug-cc-pVDZ$ level of theory (with SMD ethanol solvation model).

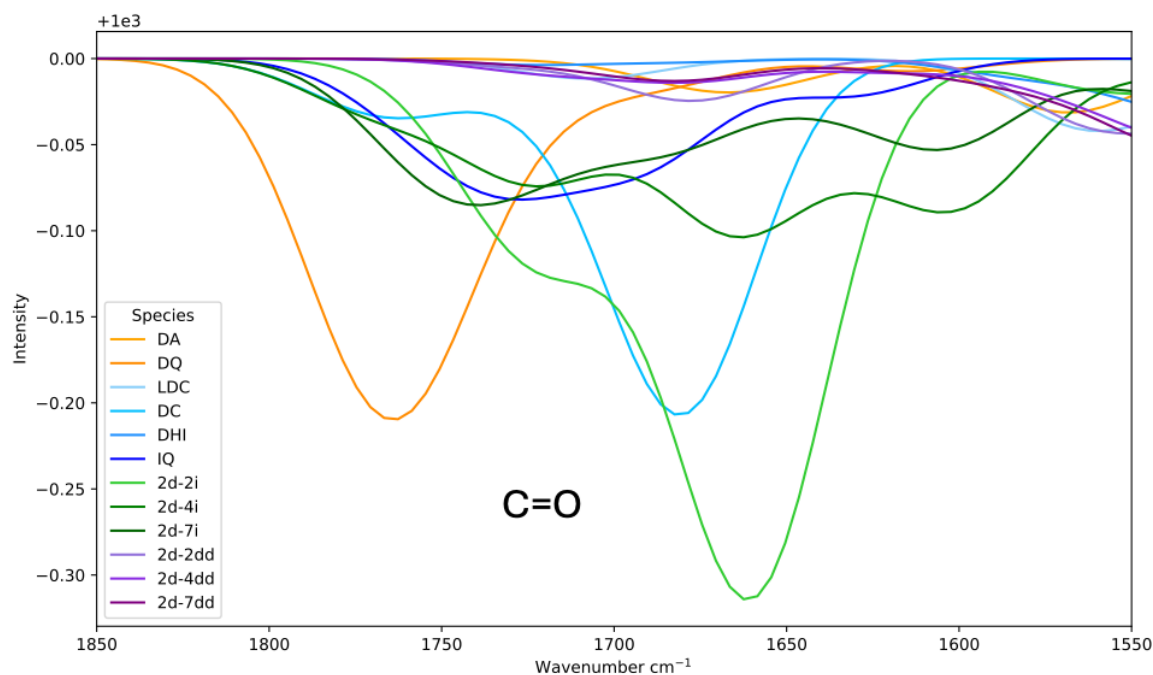


Figure S31: Zoomed C=O region of the theoretical FTIR spectra calculated at the ω B97XD/aug-cc-pVDZ level of theory (with SMD ethanol solvation model).

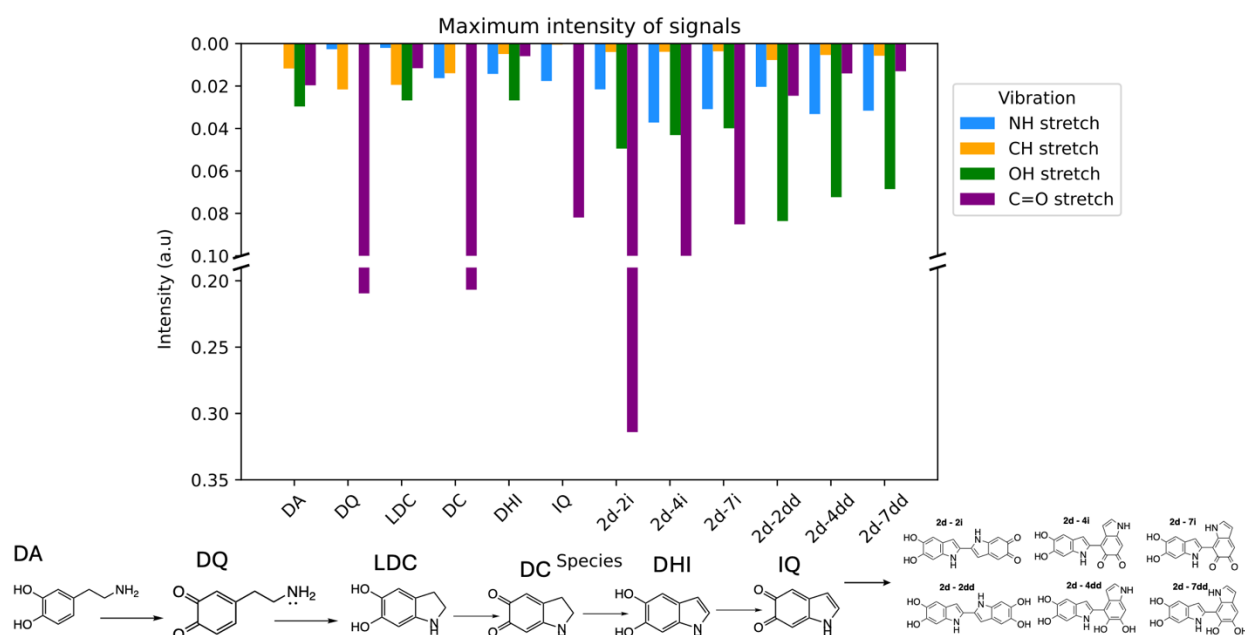


Figure S32: Maximum intensity of vibrational signals taken from the predicted IR spectrum of various polymerization intermediates (Figure S30-31), calculated at the ω B97XD/aug-cc-pVDZ level of theory (with SMD ethanol solvation model). The structures of intermediates are presented.

Table S14: Fitting parameters for SAXS traces. Despite low errors, ellipsoid models fitted to the scattering data were excluded due to discrepancies in the polar and equatorial radii.

	Sphere		Cylinder			Ellipsoid		
Day	Radius	Error	Radius	Length	Error	Polar	Equatorial	Error
0	-	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-	-
2	9.4	0.8	5.0	20.9	0.8	1.0	10.9	0.8
3	9.7	2.3	5.2	21.6	0.9	6.5	10.8	0.9
6	11.3	2.4	5.4	32.4	0.9	21.6	6.0	0.8
7	11.9	4.1	6.0	35.8	1.0	24.0	6.6	0.9

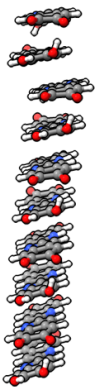
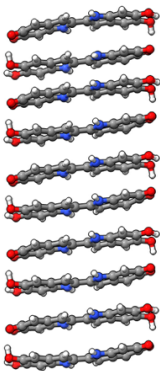
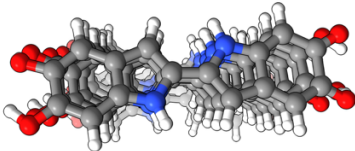
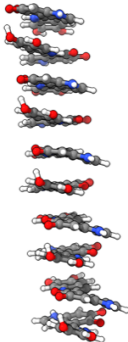
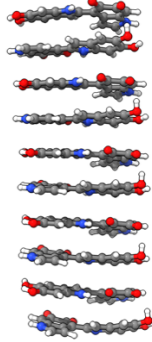
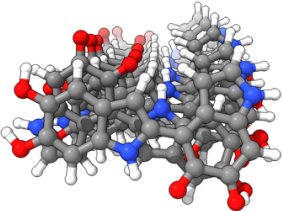
Cluster	X	Y	Z
2-2'			
2-4'			

Figure S33: Geometry optimized structures of the 2-2' and 2-4' 10-dimer aggregates, viewed along the specified cartesian axis.

Table S15: Distance between each the centre of mass (COM) of each fragment in the 2-2' 10-dimer aggregate. The average distance between adjacent fragments is 3.54 Å whilst the total height along all 10 fragments is 31.86 Å.

	Frag_1	Frag_2	Frag_3	Frag_4	Frag_5	Frag_6	Frag_7	Frag_8	Frag_9	Frag_10
Frag_1	0.000000	3.529222	6.511782	9.825747	13.348793	16.737916	20.284509	23.686527	27.240165	30.659333
Frag_2	3.529222	0.000000	3.605399	6.529276	10.031554	13.358284	16.925728	20.296829	23.868321	27.264491
Frag_3	6.511782	3.605399	0.000000	3.476287	6.981584	10.392638	13.921158	17.326557	20.865486	24.288743
Frag_4	9.825747	6.529276	3.476287	0.000000	3.624948	6.964475	10.539159	13.913644	17.479277	20.880800
Frag_5	13.348793	10.031554	6.981584	3.624948	0.000000	3.446354	6.947994	10.361552	13.901481	17.329027
Frag_6	16.737916	13.358284	10.392638	6.964475	3.446354	0.000000	3.617910	6.954325	10.530663	13.925946
Frag_7	20.284509	16.925728	13.921158	10.539159	6.947994	3.617910	0.000000	3.458191	6.956335	10.397327
Frag_8	23.686527	20.296829	17.326557	13.913644	10.361552	6.954325	3.458191	0.000000	3.609592	6.972926
Frag_9	27.240165	23.868321	20.865486	17.479277	13.901481	10.530663	6.956335	3.609592	0.000000	3.488321
Frag_10	30.659333	27.264491	24.288743	20.880800	17.329027	13.925946	10.397327	6.972926	3.488321	0.000000

Table S16: Distance between each the centre of mass (COM) of each fragment in the 2-4' 10-dimer aggregate. The average distance between adjacent fragments is 3.46 Å, whilst the total height along all 10 fragments is 31.10 Å.

	Frag_1	Frag_2	Frag_3	Frag_4	Frag_5	Frag_6	Frag_7	Frag_8	Frag_9	Frag_10
Frag_1	0.000000	3.141337	6.570889	9.598995	13.196664	16.181191	19.844571	22.788730	26.475026	29.445259
Frag_2	3.141337	0.000000	3.805778	6.597934	10.314550	13.200332	16.932974	19.814226	23.547751	26.487817
Frag_3	6.570889	3.805778	0.000000	3.170160	6.628758	9.642991	13.280847	16.239417	19.916814	22.882772
Frag_4	9.598995	6.597934	3.170160	0.000000	3.819064	6.604633	10.362600	13.224853	16.971279	19.893217
Frag_5	13.196664	10.314550	6.628758	3.819064	0.000000	3.157352	6.653501	9.640750	13.292294	16.261945
Frag_6	16.181191	13.200332	9.642991	6.604633	3.157352	0.000000	3.866766	6.624626	10.396703	13.289471
Frag_7	19.844571	16.932974	13.280847	10.362600	6.653501	3.866766	0.000000	3.127056	6.640224	9.631982
Frag_8	22.788730	19.814226	16.239417	13.224853	9.640750	6.624626	3.127056	0.000000	3.867366	6.685071
Frag_9	26.475026	23.547751	19.916814	16.971279	13.292294	10.396703	6.640224	3.867366	0.000000	3.149016
Frag_10	29.445259	26.487817	22.882772	19.893217	16.261945	13.289471	9.631982	6.685071	3.149016	0.000000

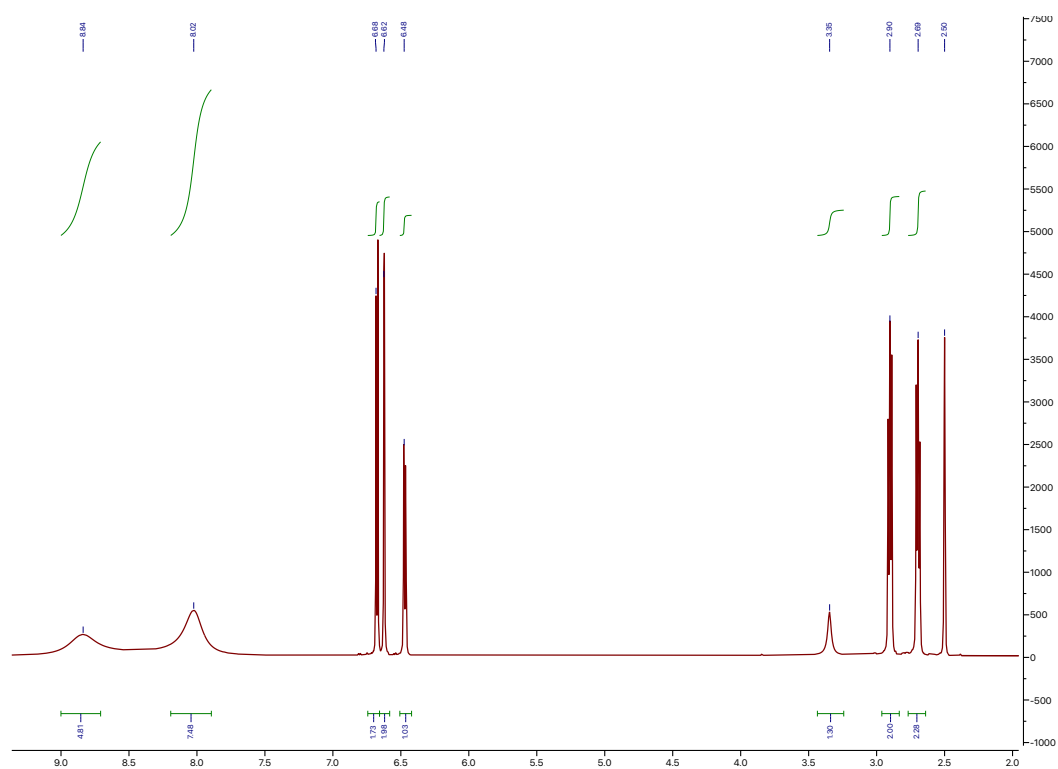


Figure S34: ^1H NMR spectrum of dopamine hydrochloride in DMSO-d_6 . ^1H NMR (600 MHz, DMSO-d_6): δ 8.84 (s, broad), 8.02 (s, broad), 6.68 (d, $J = 8.0$ Hz, 1H), 6.62 (d, $J = 2.1$ Hz, 1H), 6.48 (dd, $J = 8.0, 2.1$ Hz, 1H), 3.35 (s, 2H), 2.90 (t, $J = 7.5-8.4$ Hz, 2H), 2.69 (t, $J = 7.5-8.4$ Hz, 2H).

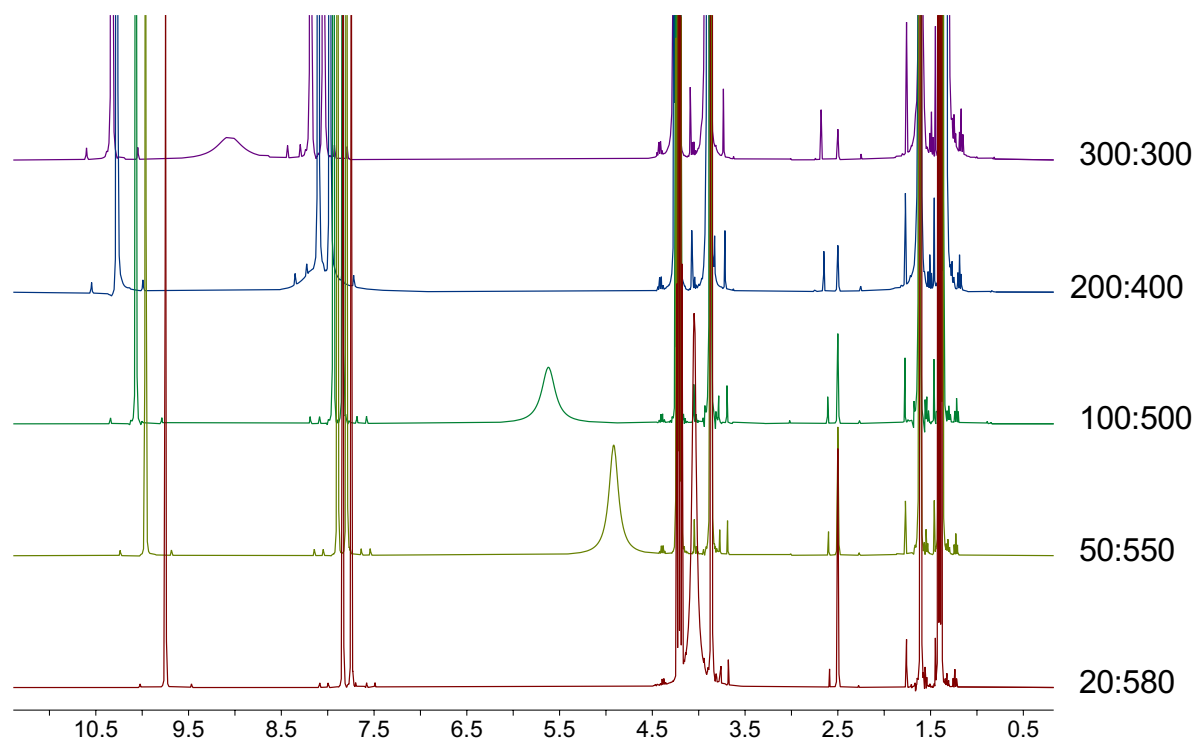


Figure S35: ^1H NMR broad peaks produced by varying the ratio of $[\text{C}_2\text{mim}][\text{OAc}]$ (left number) and DMSO-d_6 (right number) in a total of $600\ \mu\text{L}$.

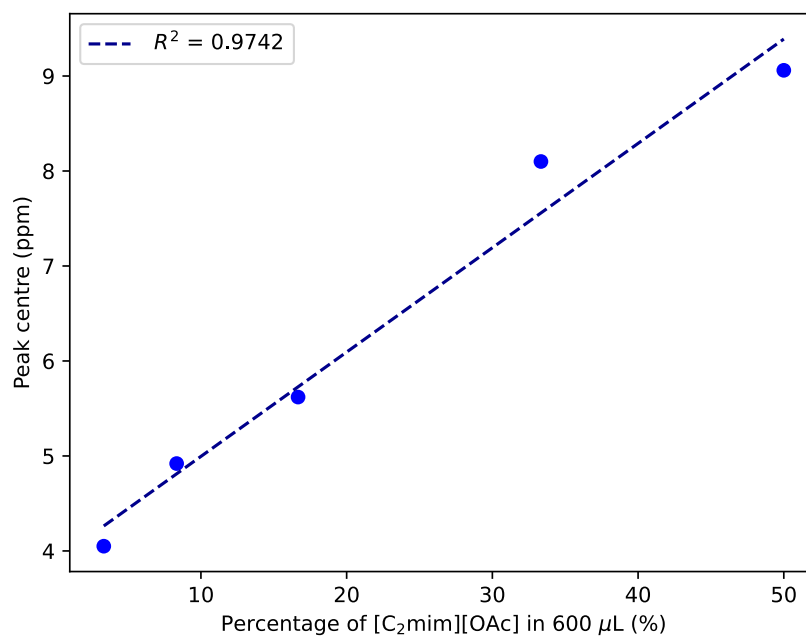


Figure S36: Graphical representation of the linear relationship between the broad peak position (in ppm) and the percentage of $[\text{C}_2\text{mim}][\text{OAc}]$ and DMSO-d_6 in a total of $600\ \mu\text{L}$.

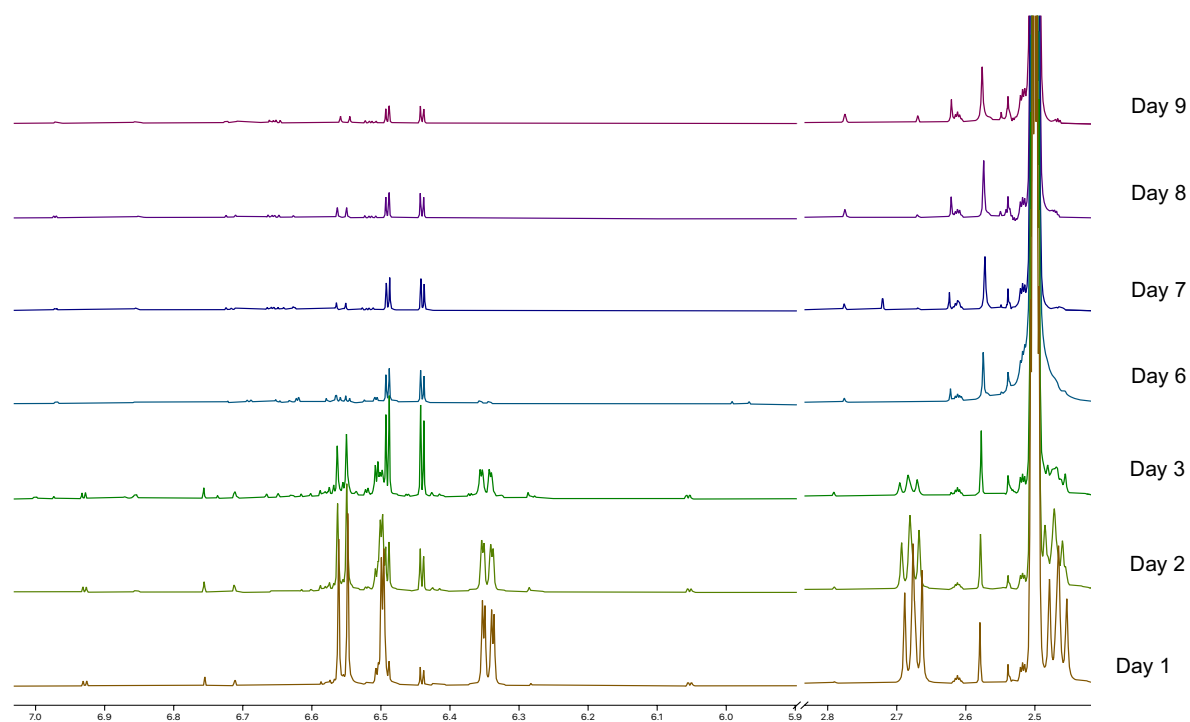


Figure S37: Aliphatic and aromatic regions of 80°C *ex situ* ^1H NMR reaction monitoring of 80 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6).

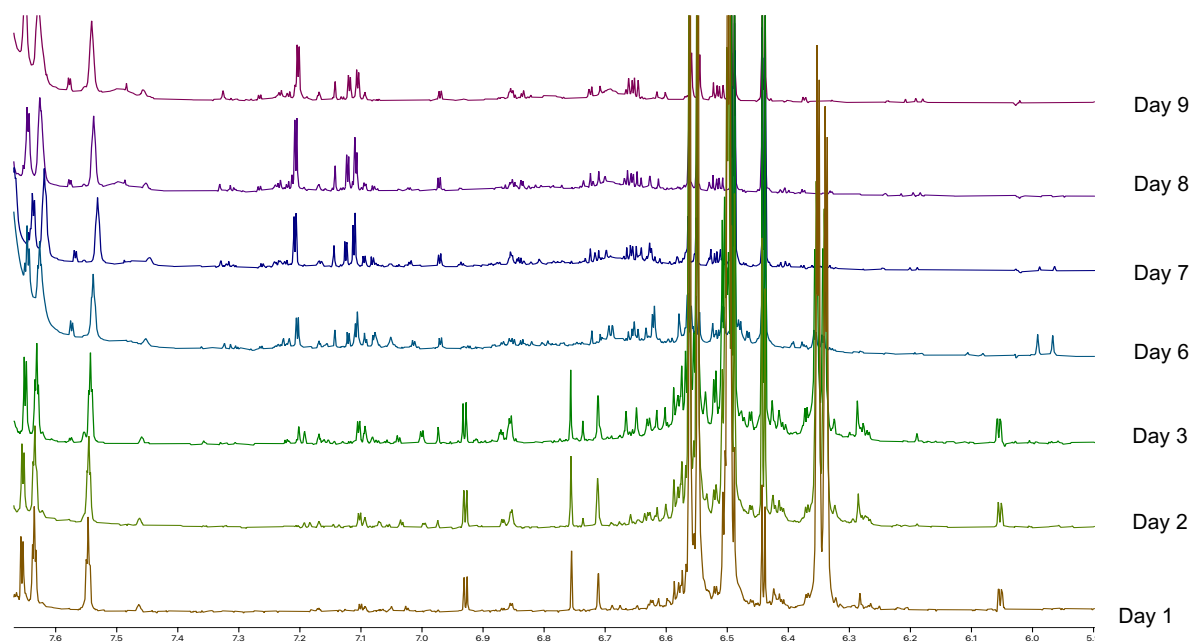


Figure S38: Zoomed aromatic region of 80°C *ex situ* ^1H NMR reaction monitoring of 80 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6).

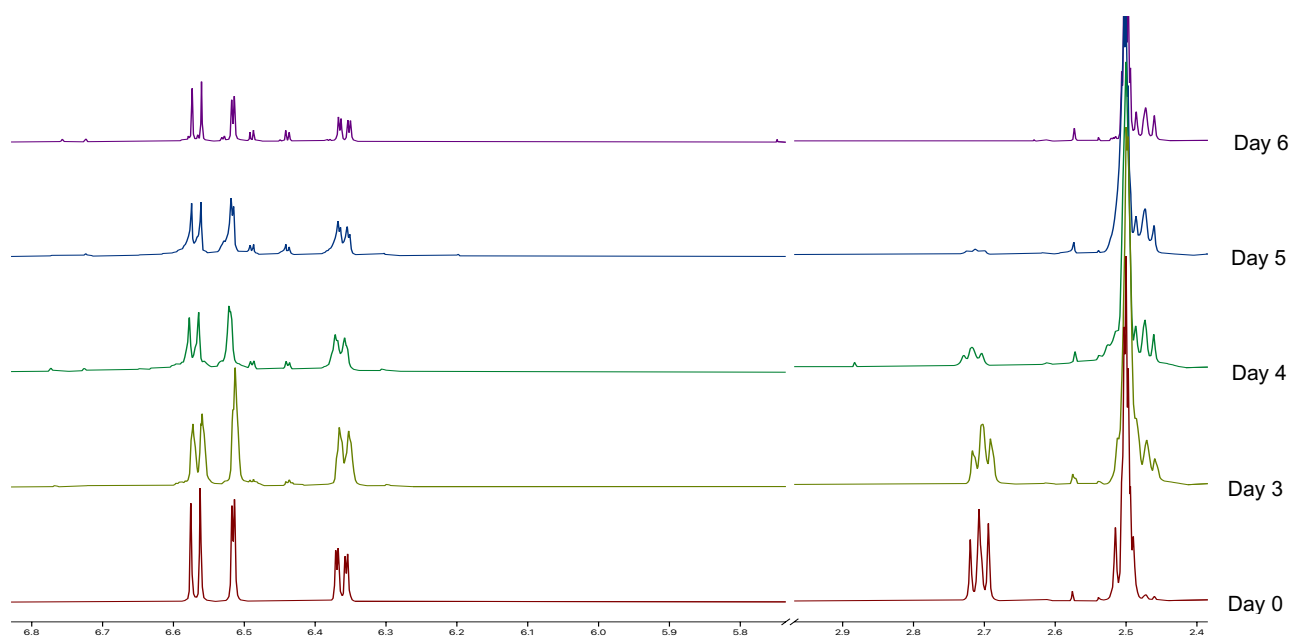


Figure S39: Aliphatic and aromatic regions of 80°C *ex situ* ^1H NMR reaction monitoring of 250 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6).

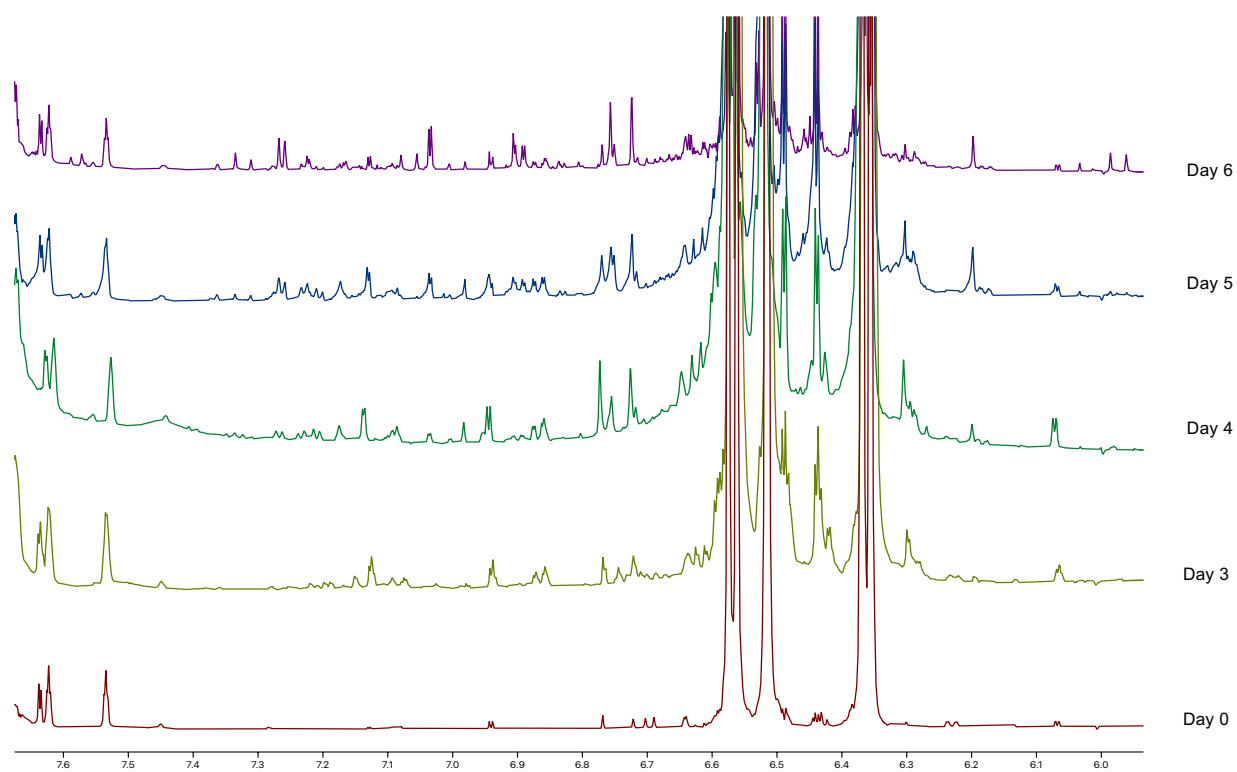


Figure S40: Zoomed aromatic region of 80°C *ex situ* ^1H NMR reaction monitoring of 250 mg DA in 1 mL $[\text{C}_2\text{mim}][\text{OAc}]$ (20 μL in 580 μL DMSO-d_6).

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