Supplementary Information for:

Singlet-assisted diffusion-NMR (SAD-NMR): redefining the limits when measuring tortuosity in porous media

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S1. Synthesis of water-soluble $^{13}$C$_2$ labelled perdeuterated naphthalene derivative 1 (labeled as I in the main paper)

S1.1 General Experimental
All air/moisture sensitive reactions were carried out under an inert atmosphere (N$_2$ or Ar), using oven or flame-dried glassware. THF (from Na/benzophenone) was distilled before use. All other solvents and reagents were used as received from standard chemical suppliers unless otherwise stated. TLC was performed on aluminium plates pre-coated with silica gel 60 with an F$_{254}$ indicator; visualised under UV light (254 nm) and/or by staining with KMnO$_4$ (10% aq.). Flash column chromatography was performed with Merck Kieselgel 60 silica gel. Fourier-transform infrared (FT-IR) spectra are reported in wavenumbers (cm$^{-1}$) and were collected on a Nicolet 380 spectrometer fitted with a Diamond platform, as solids or neat liquids. $^1$H NMR
and $^{13}$C NMR spectra were recorded in CDCl$_3$ solutions using Bruker DPX400, Bruker AVII-400 or AVIIIHD-400 (400 and 100 MHz respectively) spectrometers. Chemical shifts are reported in $\delta$ units using CHCl$_3$ ($\delta$ 7.27 ppm $^1$H, $\delta$ 77.0 ppm $^{13}$C) as internal standards. $^2$H NMR spectra were recorded in CHCl$_3$ or H$_2$O solutions using a Bruker AVIIIHD-500 (76.8 MHz $^2$H) spectrometer. Chemical shifts are reported in $\delta$ units using CDCl$_3$ as an internal standard ($\delta$ 7.27 ppm $^2$H). Coupling constants (J) are reported in Hz and are rounded to the nearest 0.1 Hz. Matching coupling constants are corrected. High-resolution mass spectra (HRMS) were obtained using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. HRMS were recorded using positive ion electrospray ionisation (ESI$^+$).

**S1.2 Dimethyl-2,2′-((1,2,3,4,6-pentakis(methoxy- $d_3$)-7-(propan-2-yl- $d_7$) naphthalene-5,8-diyl)bis (oxy)) diacetate-4a,8a- $^{13}$C$_2$ (4)**

A solution of cyclobutenones 3a and 3b (1:1, 300 mg, 0.39 mmol) in THF (3 mL) was purged with N$_2$ atm and sonicated for 30 min, then heated under microwave irradiation in a sealed tube at 135 °C for 5 h. The reaction mixture was diluted with THF (15 mL), treated with KOH (94 mg, 1.68 mmol) and methyl bromoacetate-2,2-$d_2$ (0.18 mL, 1.91 mmol) and stirred at rt for 1 h. The mixture was filtered and the solvent removed in vacuo. Purification by column chromatography eluting with Et$_2$O:petroleum ether (20:80) afforded the title compound 4 as a white solid (250 mg, 0.46 mmol, 60%). R$_f$ 0.41 (eluent EtOAc/hexane 1:1); mp 85–87 °C; FT-IR $\nu_{\text{max}}$ 2983, 2937, 2856, 1764, 1743, 1588, 1446, 1382, 1351 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.85 (3H, s), 3.84 (3H, s) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 118.22, 188.20 ppm; LRMS (ESI$^+$) m/z 541.5 [M+H]$^+$, 563.4 [M+Na]$^+$; HRMS (ESI$^+$) for C$_{22}$H$_2$D$_{26}$O$_{12}$ [M+H]$^+$ calcd 541.3666, found 541.3673.

**S1.3 2,2′-((1,2,3,4,6-Pentakis(methoxy- $d_3$)-7-(propan-2-yl- $d_7$) naphthalene-5,8-diyl)bis(oxy)) diacetic acid-4a,8a- $^{13}$C$_2$ (5)**
To a suspension of diester 4 (220 mg, 0.41 mmol) in MeOH (5 mL) was added KOH (114 mg, 2.04 mmol) in one portion and the reaction heated at 75 °C for 5 h, then concentrated *in vacuo*. The white residue was dissolved in H$_2$O (5 mL) and washed with EtOAc (3 x 5 mL) to remove any organic impurities. The aqueous phase was acidified to pH 2 with 1M HCl and extracted with EtOAc (3 x 5 mL). The combined organic phases were dried (Na$_2$SO$_4$) and concentrated *in vacuo* to afford the title compound 5 as white solid (190 mg, 0.37 mmol, 91%).

Mp 148–150 °C; FT-IR $\nu_{max}$ 3115, 1765, 1769, 1588, 1467, 1362, 1191, 1091 cm$^{-1}$; $^2$H NMR (76.8 MHz, CHCl$_3$) δ 4.79 (s, 4D), 4.55 (s, 1D), 4.01 (s, 6D), 3.97 (s, 3D), 3.93 (s, 3D), 3.90 (s, 3D), 1.35 (s, 6D) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 116.76 ppm; LRMS (ESI$^+$) m/z 513.6 [M+H]$^+$, 535.4 [M+Na]$^+$; HRMS (ESI$^+$) for C$_{20}$H$_{23}$D$_3$O$_{12}$ [M+H]$^+$ calcd 513.3353, found 513.3356.

S1.4 Sodium-2,2'-(((1,2,3,4,6-pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}$C$_2$ (1)

To neat diacid 5 (230 mg, 0.45 mmol) was added NaOH (0.92 mL of a 1M solution in H$_2$O, 0.92 mmol) turning the suspension from white to a pale pink colour. The reaction mixture was concentrated *in vacuo* to afford the title compound 1 as a pale pink solid (250 mg, 0.45 mmol, 100%). Mp >290 °C; FT-IR $\nu_{max}$ 3350, 1606, 1586, 1396, 1359, 1187, 1089, 1020, 969 cm$^{-1}$; $^2$H NMR (76.8 MHz, H$_2$O) 4.78 (s, 2D), 4.30 (s, 1D), 3.93 (s, 9D), 3.81 (s, 6D), 3.28 (s, 2D), 1.25 (s, 6D) ppm; $^{13}$C NMR (100 MHz, H$_2$O) δ 118.57 ppm.
S1.5 $^1$H NMR (400 MHz, CDCl$_3$) Dimethyl-2,2'-(1,2,3,4,6-pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)naphthalene-5,8-diyl)bis (oxy))diacetate-4,8a-13C$_2$ (4)

S1.6 $^{13}$C NMR (100 MHz, CDCl$_3$) Dimethyl-2,2'-(1,2,3,4,6-pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)naphthalene-5,8-diyl)bis (oxy))diacetate-4,8a-13C$_2$ (4)
S1.7 $^2$H NMR (76.8 MHz, CHCl$_3$) 2,2'-(1,2,3,4,6-Pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)naphthalene-5,8-diyl)bis(oxy)) diacetic acid-4a,8a-$^{13}$C$_2$ (5)

S1.8 $^{13}$C NMR (100 MHz, CDCl$_3$) 2,2'-(1,2,3,4,6-Pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)naphthalene-5,8-diyl)bis(oxy)) diacetic acid-4a,8a-$^{13}$C$_2$ (5)
S1.9 $^2$H NMR (76.8 MHz, H$_2$O) Sodium-2,2'-$'$(1,2,3,4,6-pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)-naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}$C$_2$ (1)

S1.10 $^{13}$C NMR (100 MHz, H$_2$O) Sodium-2,2'-$'$(1,2,3,4,6-pentakis(methoxy-$d_3$)-7-(propan-2-yl-$d_7$)-naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}$C$_2$ (1)