Supplementary Information for:

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

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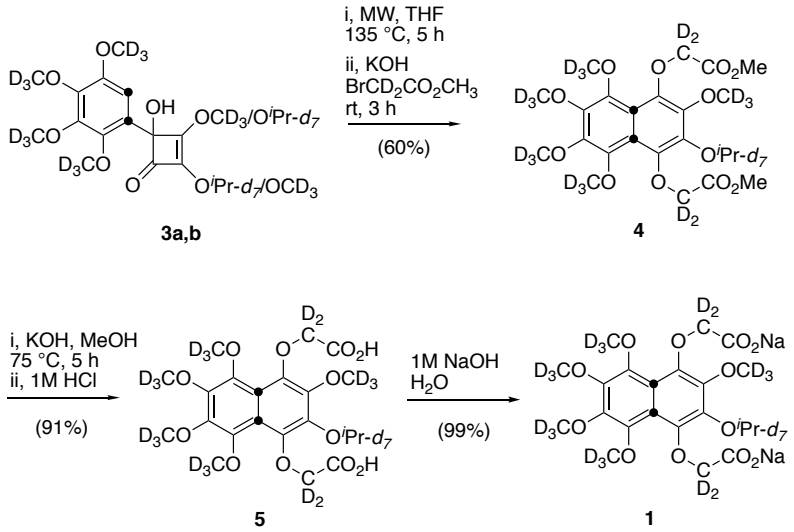
S1. Synthesis of water-soluble $^{13}C_2$ labelled perdeuterated naphthalene derivative 1 (labeled as I in the main paper)

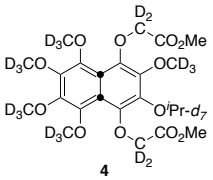


S1.1 General Experimental

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 δ units using $CHCl_3$ (δ 7.27 ppm ^1H, δ 77.0 ppm ^{13}C) as internal standards. ^2H NMR spectra were recorded in $CHCl_3$ or H_2O solutions using a Bruker AVIIIHD-500 (76.8 MHz ^2H) spectrometer. Chemical shifts are reported in δ units using $CDCl_3$ as an internal standard (δ 7.27 ppm ^2H). 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)



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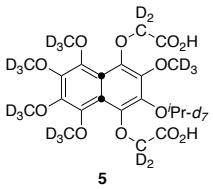
A solution of cyclobutenones **3a** and **3b** (1:1, 300 mg, 0.39 mmol) in THF (3 mL) was purged with N_2 atm and sonicated for 30 min, then heated under microwave irradiation in a sealed tube at 135 °C for 5 h. The reaction mixture was diluted with THF (15 mL), treated with KOH (94 mg, 1.68 mmol) and 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_2O: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 ν_{max} 2983, 2937, 2856, 1764, 1743, 1588, 1446, 1382, 1351 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 3.84 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.22, 188.20 ppm; LRMS (ESI^+) m/z 541.5 $[M+H]^+$, 563.4 $[M+Na]^+$; HRMS (ESI^+) for $C_{22}{}^{13}C_2H_7D_{26}O_{12}$ $[M+H]^+$ 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)

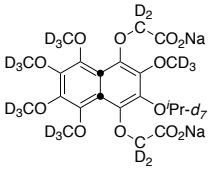


5

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_2O (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_2SO_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 ν_{max} 3115, 1765, 1769, 1588, 1467, 1403, 1362, 1191, 1091 cm^{-1}; ^2H 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 $C_{20}{}^{13}C_2H_3D_{26}O_{12}$ $[M+H]^+$ calcd 513.3353, found 513.3356.

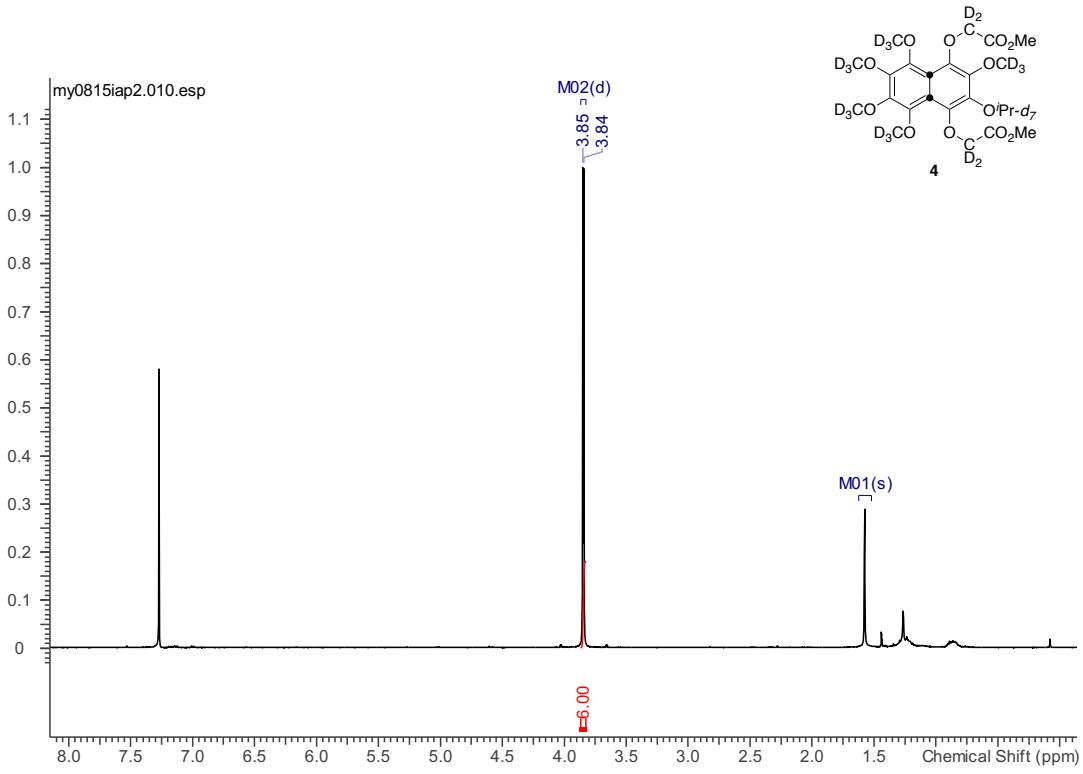
S1.4 Sodium-2,2'-((1,2,3,4,6-pentakis(methoxy-d_3)-7-(propan-2-yl-d_7)naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}C_2$ (1)



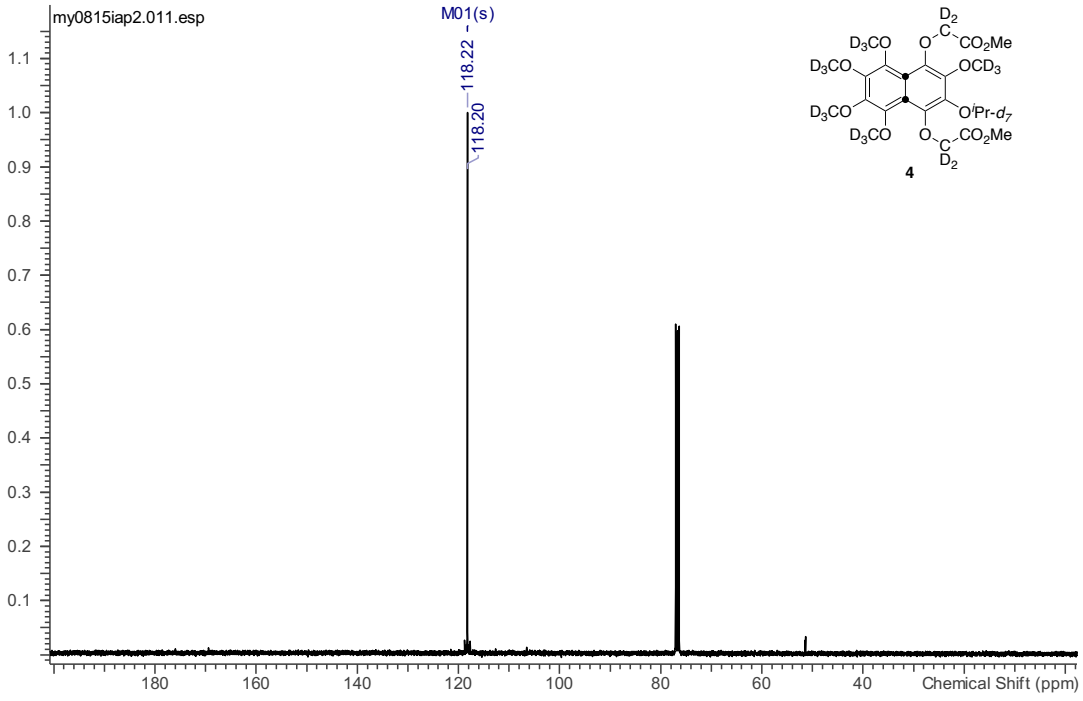
1

To neat diacid **5** (230 mg, 0.45 mmol) was added NaOH (0.92 mL of a 1M solution in H_2O, 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 ν_{max} 3350, 1606, 1586, 1396, 1359, 1187, 1089, 1020, 969 cm^{-1}; ^2H NMR (76.8 MHz, H_2O) 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_2O) δ 118.57 ppm.

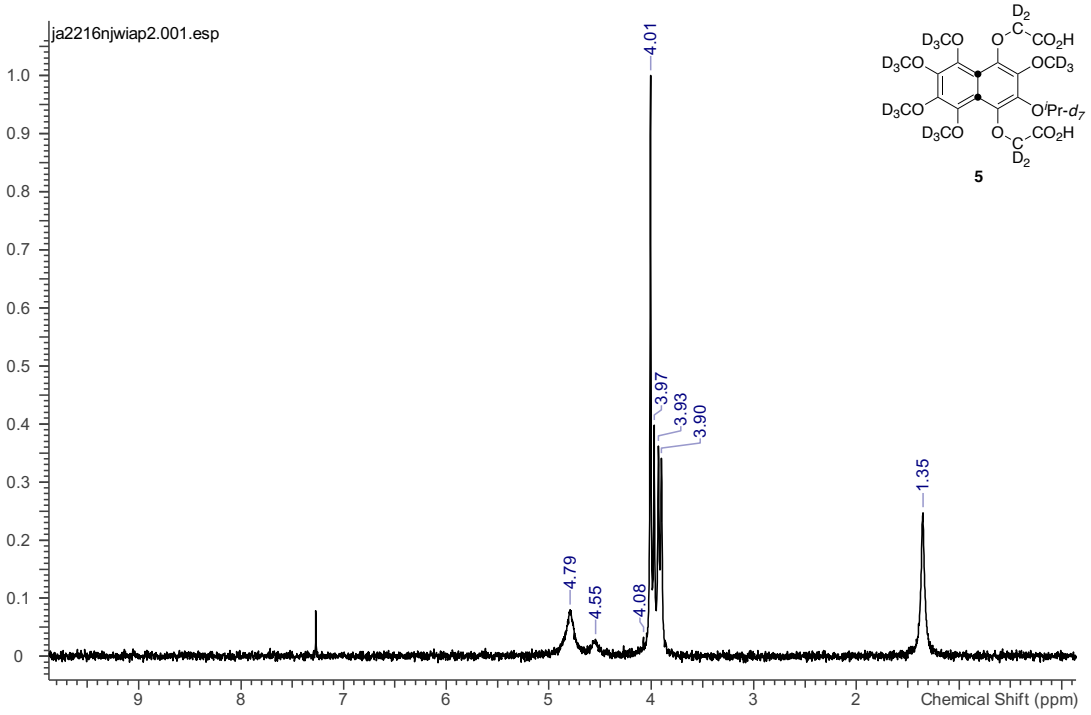
S1.5 ^{1}H NMR (400 MHz, $CDCl_3$) Dimethyl-2,2'-((1,2,3,4,6-pentakis(methoxy-d_3)-7-(propan-2-yl-d_7)naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}C_2$ (4)



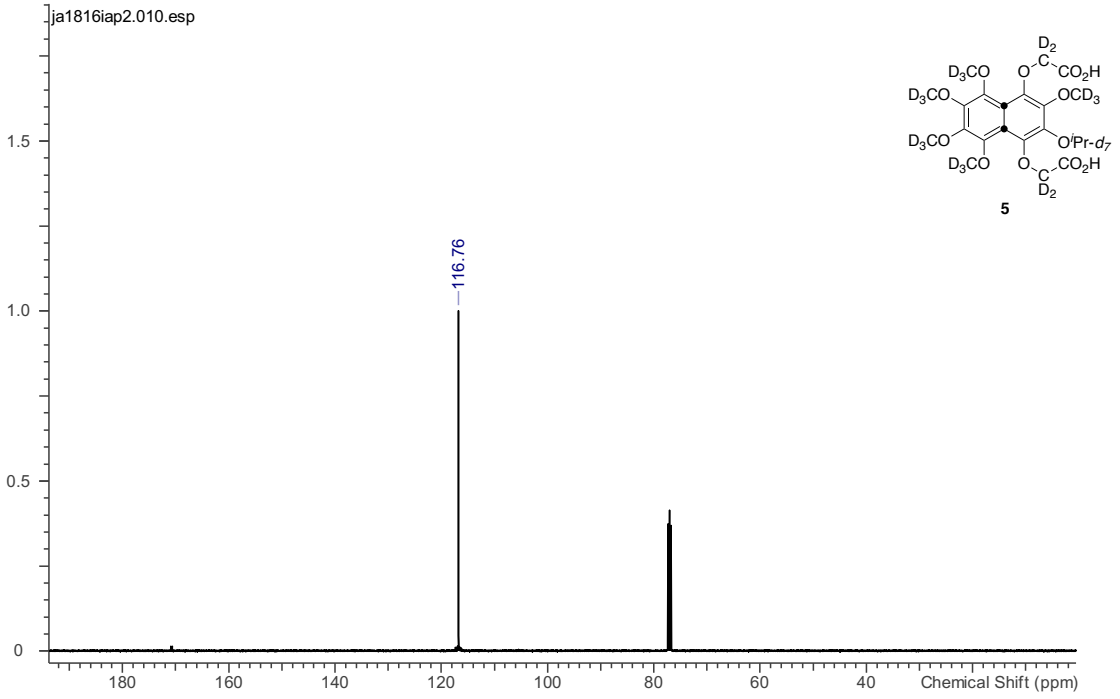
S1.6 ^{13}C NMR (100 MHz, $CDCl_3$) Dimethyl-2,2'-((1,2,3,4,6-pentakis(methoxy-d_3)-7-(propan-2-yl-d_7)naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}C_2$ (4)



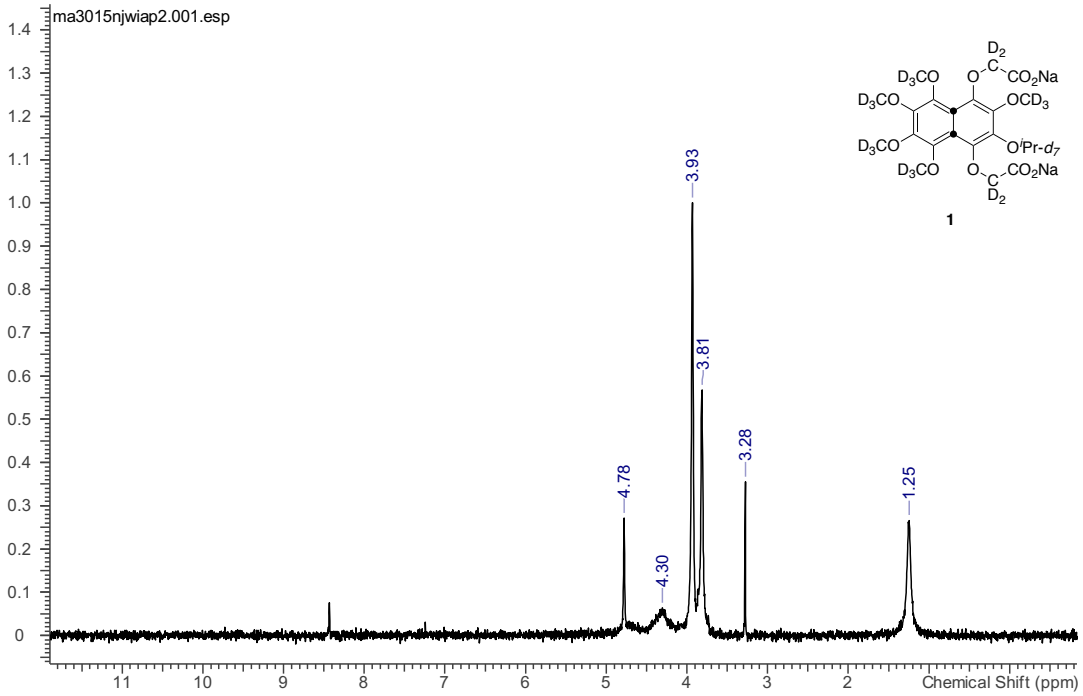
S1.7 ^{2}H NMR (76.8 MHz, $CHCl_3$) 2,2'-((1,2,3,4,6-Pentakis(methoxy-d_3)-7-(propan-2-yl-d_7)naphthalene-5,8-diyl)bis(oxy)) diacetic acid-4a,8a-$^{13}C_2$ (5)



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_2O) Sodium-2,2'-((1,2,3,4,6-pentakis(methoxy-d_3)-7-(propan-2-yl-$_7$)naphthalene-5,8-diyl)bis (oxy))diacetate-4a,8a-$^{13}C_2$ (1)



S1.10 ^{13}C NMR (100 MHz, H_2O) 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)