

## A flavin-based [2]catenane

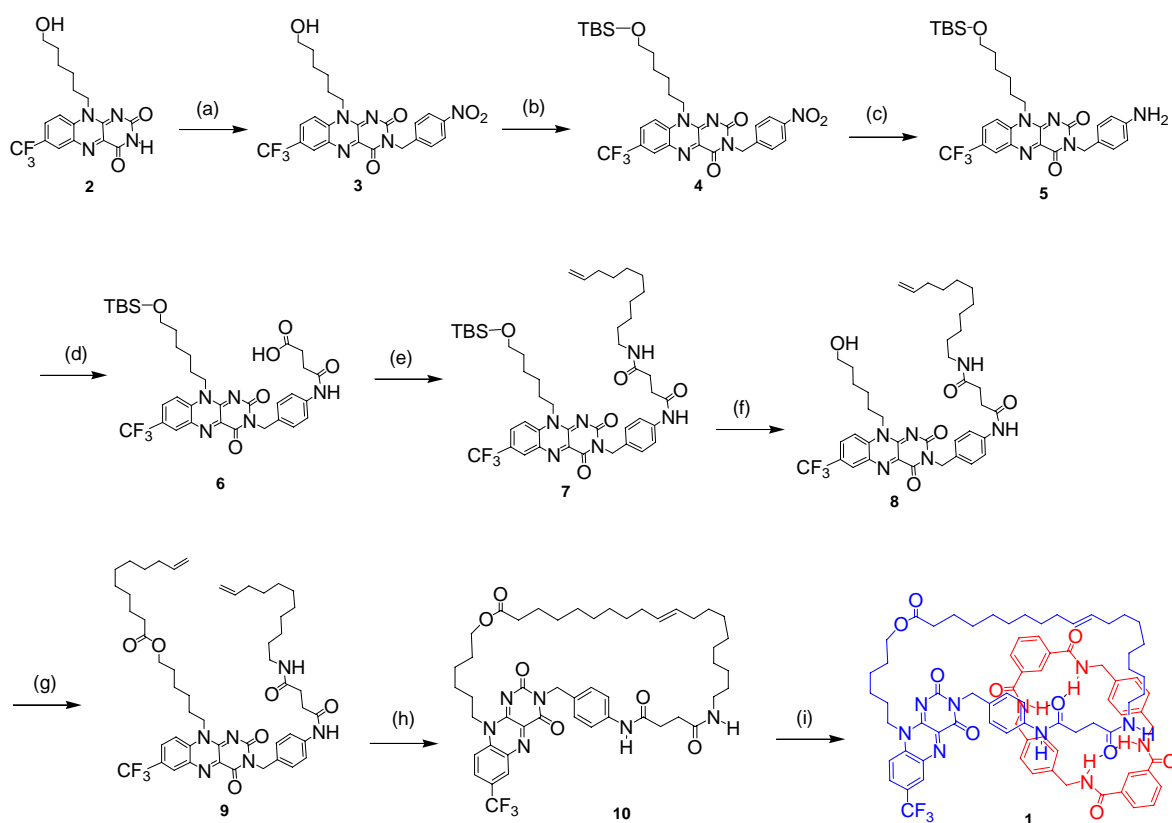
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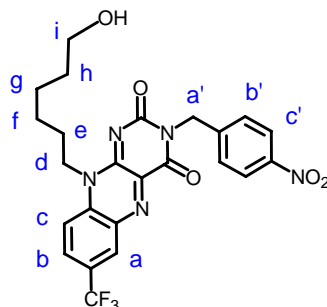
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### (a) Synthesis.



(a). Nitrobenzyl chloride,  $K_2CO_3$  in MeCN (30°C, 3d, Yield = 68%); (b). *Tert*-Butyl Dimethyl Silyl Chloride, DMAP,  $NEt_3$ , DMF, (r.t., 1h, Yield = 96%); (c). Pd(C) in MeOH, (r.t., 1h, Yield = 75%); (d). Succinic anhydride, DMAP,  $CH_2Cl_2$  (50°C, overnight, Yield = 85%); (e). 10-undecen-amine, EDCI, HOBt, cat DMAP, in  $CH_2Cl_2$  (r.t., 18h, Yield = 96%); (f). 10% aq HCl in THF (r.t., 1h, Yield = 94%); (g). 10-undecenoic acid, HOBt, EDCI, cat DMAP,  $CH_2Cl_2$  (r.t., 24h, Yield = 77%); (h). 2<sup>nd</sup> generation Grubbs' catalyst, dry  $CH_2Cl_2$ , (40°C, 18h, Yield = 50%); (i). Isophthyl chloride (in dry  $CH_2Cl_2$  10 mL), *p*-xylylenediamine (in dry  $CH_2Cl_2$  10 mL) simultaneously added dropwise over 3h to **10** in dry  $CH_2Cl_2$  and  $NEt_3$  (Yield = 26%).

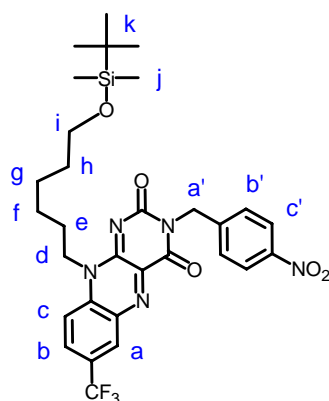
## Synthesis of compound 2.



7-Trifluoromethyl-10-hydroxyhexyl isoalloxazine (5.0 g, 13.1 mmol), nitrobenzyl chloride (8.07 g, 47.0 mmol, 3.6eq) and  $K_2CO_3$  (5.4 g, 39.1 mmol, 3eq) were stirred in MeCN (200 ml) at 30°C (protected from light) for 3 d. The solvent was evaporated under vacuum and the crude mixture dissolved in  $CH_2Cl_2$  then filtered to remove the  $K_2CO_3$ . The  $CH_2Cl_2$  was reduced in volume and the product isolated by column chromatography (eluent initially  $CH_2Cl_2$ , increasing polarity to  $CH_2Cl_2$ /acetone (8:2)). All fractions containing the product were combined, concentrated under reduced pressure, dissolved in minimum amount acetone and precipitated by adding petroleum ether to give pure product **2**. Yield = 4.58 g (68 %). m.p. = 163-165°C.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.59 (1H, br s, ArH-a), 8.16 (2H, d,  $J=8.8$ Hz, ArH-b' x2), 8.09 (1H, dd,  $J=9.0$  and 1.7Hz, ArH-b), 7.76 (1H, d,  $J=7.7$ Hz, ArH-c and 2H, d,  $J=8.8$ Hz, ArH-c' x2), 5.36 (2H, s,  $CH_2$ -a'), 4.69 (2H, br t,  $CH_2$ -d), 3.67 (2H, t,  $J=6.0$ Hz,  $CH_2$ -i), 1.89 (2H, quint,  $J=7.5$ Hz,  $CH_2$ -e), 1.65-1.50 (6H, m,  $CH_2$ -f,g,h).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  158.9 (ArC=O), 154.9 (ArC=O), 149.1 (ArC=N), 147.4 (ArC=N), 143.5 (ArC), 138.3 (ArC), 135.0 (ArC), 134.5 (ArC), 131.7 (ArCH, q,  $J=3$ Hz), 130.8 (ArCH, q,  $J=3.9$ Hz), 130.3 (2x ArCH, AB), 128.8 (q,  $J=35$ Hz, ArC- $CF_3$ ), 122.8 (q,  $J=272$ Hz,  $CF_3$ ), 123.7 (2x ArCH, AB), 116.3 (ArCH), 62.4 ( $CH_2$ ), 45.1 ( $CH_2$ ), 44.6 ( $CH_2$ ), 32.2 ( $CH_2$ ), 26.7 ( $CH_2$ ), 26.3 ( $CH_2$ ), 25.0 ( $CH_2$ ).  $\nu_{max}$  (thin film)/ $cm^{-1}$  3400 br, 2916, 2858, 1703, 1660, 1596, 1566, 1344, 1285, 1224, 1197, 1128. MS (m/z, FAB) = 518.3 ( $[M+H]^+$ , 100%), 502.3 (9), 418 (8), 137 (19). HRMS found 518.1649.  $C_{24}H_{23}F_3N_5O_5$  requires  $[M+H]^+$ , 518.1651.

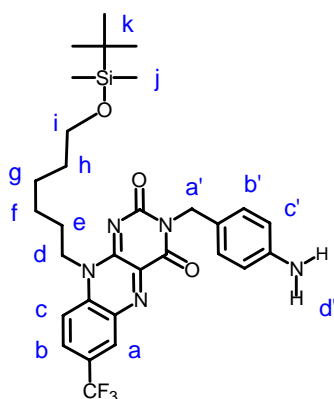
### Synthesis of compound 3:



Compound **2** (3.30 g, 6.38 mmol) was dissolved in DMF (5 ml) and then *tert*-butyldimethylsilyl chloride (1.44 g, 9.56 mmol, 1.5eq) and DMAP (150 mg, 1.28 mmol, 0.2eq) were added. The mixture was then stirred at r.t. for 30 min before adding NEt<sub>3</sub> (2.0 ml, 14.4 mmol, 2eq) dropwise by pipette over 10 min. The reaction was allowed to continue stirring for 1h, then diluted with distilled water (100 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 ml x2), dried (MgSO<sub>4</sub>) and the CH<sub>2</sub>Cl<sub>2</sub> evaporated under vacuum. The product was isolated using column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/petroleum Ether (80:20)) to give an orange crystalline solid. The compound was dissolved in a minimum amount of ether and precipitated with petroleum ether to afford **3** as a yellow solid. Yield = 3.85 g (96 %). m.p. = 163-165°C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.59 (1H, d, J=1.2Hz, ArH-a), 8.16 (2H, d, J=8.9Hz, Ar-b' x2), 8.09 (1H, dd, J=9.2 and 1.9Hz, ArH-b), 7.75 (2H, d, J=8.9Hz, ArH-c' x2), 7.74 (1H, d, J=9.2Hz, ArH-c), 5.36 (2H, s, CH<sub>2</sub>-a'), 4.68 (2H, t, broad, J=7.5, CH<sub>2</sub>-d), 3.61 (2H, t, J=6.2Hz, CH<sub>2</sub>-i), 1.87 (2H, quint, J=7.6Hz, CH<sub>2</sub>-e), 1.60-1.40 (6H, m, CH<sub>2</sub>-f,g,h), 0.88 (9H, s, CH<sub>3</sub>-k x3), 0.04 (6H, s, CH<sub>3</sub>-j x2). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 158.9 (ArC=O), 154.8 (ArC=O), 149.1 (ArC=N), 147.4 (ArC=N), 143.5 (ArC), 138.3 (ArC), 134.9 (ArC), 134.5 (ArC), 131.6 (ArCH, q, J=3Hz), 130.7 (ArCH, q, J=3.9Hz), 130.3 (2x ArCH, AB), 128.7 (q, J=35Hz, ArC-CF<sub>3</sub>), 124.2 (ArCH), 123.6 (q, J=272Hz, CF<sub>3</sub>), 116.3 (2x ArCH, AB), 62.8 (CH<sub>2</sub>), 45.3 (CH<sub>2</sub>), 44.6 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 25.9 (3x CH<sub>3</sub>), 25.5 (CH<sub>2</sub>), 18.3 (CSi), -5.3 (2x CH<sub>3</sub>). ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 2939, 2860, 1717, 1669, 1596, 1559, 1457, 1337, 1239, 1192, 1127, 1014. MS (m/z, FAB) = 632.4 ([M+H]<sup>+</sup>, 100%), 616.4(20), 574.3(40). HRMS found 632.2513. C<sub>30</sub>H<sub>37</sub>O<sub>5</sub>N<sub>5</sub>F<sub>3</sub>Si requires [M+H]<sup>+</sup>, 632.2516.

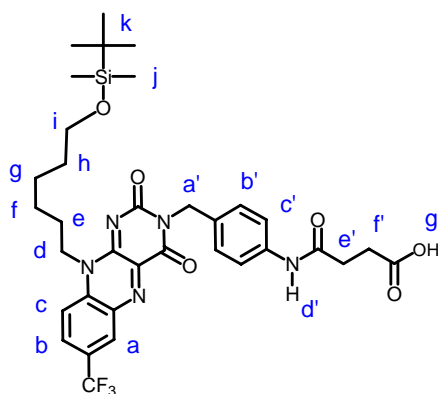
#### Synthesis of compound 4.



Compound **3** (1.30 g, 2.05 mmol), ammonium formate (2.50 g, 39.6 mmol) and 10% Pd(C) (350 mg) were stirred in MeOH (50 ml) at r.t. for 1h. The Pd(C) was removed by filtration under an N<sub>2</sub> blanket. The filtrate was evaporated under vacuum, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with water (3 x 100 ml), dried (MgSO<sub>4</sub>), concentrated under reduced pressure and then purified by column chromatography (eluent initially CH<sub>2</sub>Cl<sub>2</sub>, increasing polarity to CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (9:1)) to yield **4** as a yellow solid. Yield = 924 mg (75%). m.p. = 94-95°C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.55 (1H, d, J=1.38Hz, ArH-a), 8.03 (1H, dd, J=8.96 and 1.95Hz, ArH-b), 7.69 (1H, d, J=8.96Hz, ArH-c), 7.42 (2H, d, J=8.57Hz, ArH-b' x2), 6.58 (2H, d, J=8.57Hz, ArH-c'), 5.15 (2H, s, CH<sub>2</sub>-a'), 4.63 (2H, br t, J=6.5Hz, CH<sub>2</sub>-d), 3.63 (2H, s, NH<sub>2</sub>-d'), 3.61 (2H, t, J=6.5Hz, CH<sub>2</sub>-i), 1.83 (2H, quint, J=7.7Hz, CH<sub>2</sub>-e), 1.58-1.38 (6H, m, CH<sub>2</sub>-f,g,h), 0.88 (9H, s, CH<sub>3</sub>-k x3), 0.04 (6H, s, CH<sub>3</sub>-j x2). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 158.8 (ArC=O), 155.2 (ArC=O), 148.9 (ArC=N), 146.1 (ArC=N), 138.7 (ArC), 134.7 (ArC), 134.5 (ArC), 131.2 (2x ArCH AB), 131.1 (ArCH, br s), 130.6 (ArCH, q, J=3.9Hz), 128.3 (q, J=35Hz, ArC-CF<sub>3</sub>), 126.5 (ArC), 122.9 (q, J=272Hz, CF<sub>3</sub>), 116.1 (ArCH), 114.7 (2x ArCH AB), 62.8 (CH<sub>2</sub>), 45.0 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 25.9 (3x CH<sub>3</sub>), 25.5 (CH<sub>2</sub>), 18.3 (CSi), -5.3 (2x CH<sub>3</sub>). ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3452, 3357, 2939, 2859, 1712, 1664, 1600, 1559, 1459, 1331, 1284, 1242, 1192, 1128, 1005. MS (m/z, FAB) = 624.4 ([M+ Na]<sup>+</sup>, 92%), 601.4 (23), 519.4 (23), 439.3 (48), 107.7 (95), 75.2 (100). HRMS found 624.2596. C<sub>30</sub>H<sub>38</sub>O<sub>3</sub>N<sub>5</sub>F<sub>3</sub>SiNa requires [M+Na]<sup>+</sup>, 624.2594.

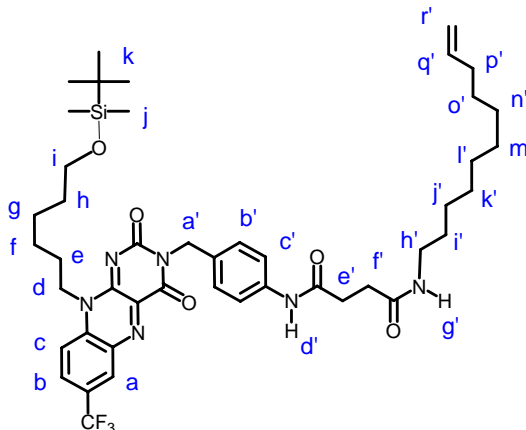
## Synthesis of compound 5.



Compound **4** (800 mg, 1.33 mmol), succinic anhydride (266 mg, 2.66 mmol, 2eq) and DMAP (17 mg, 0.14 mmol, 0.1eq) were heated under reflux in  $\text{CH}_2\text{Cl}_2$  (50 ml) for 22h. The mixture was allowed to cool to r.t. and stirred for 2 days. The mixture was concentrated under reduced pressure and then purified by column chromatography (eluent initially  $\text{CH}_2\text{Cl}_2$ /petroleum ether (90:10), increasing polarity to  $\text{CH}_2\text{Cl}_2$ /acetone (80:20)) to yield **5** as a yellow solid. Yield = 775 mg (85%). m.p. = 104-105°C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  9.78 (1H, br s, OH-g'), 8.86 (1H, s, NH-d'), 8.52 (1H, d,  $J=1.4\text{Hz}$ , ArH-a), 8.03 (1H, dd,  $J=9.0$  and  $2.0\text{Hz}$ , ArH-b), 7.71 (1H, d,  $J=9.0\text{Hz}$ , ArH-c), 7.68 (2H, d,  $J=8.5\text{Hz}$ , ArH-b' x2), 7.16 (2H, d,  $J=8.5\text{Hz}$ , ArH-c' x2), 5.26 (2H, s,  $\text{CH}_2$ -a'), 4.62 (2H, t, broad,  $J=6\text{Hz}$ ,  $\text{CH}_2$ -d), 3.58 (2H, t,  $J=6.2\text{Hz}$ ,  $\text{CH}_2$ -i), 2.851 (4H, br s,  $\text{CH}_2$ -e' and f'), 1.82 (2H, quint,  $J=7.4\text{Hz}$ ,  $\text{CH}_2$ -e), 1.55-1.35 (6H, m,  $\text{CH}_2$ -f, g and h), 0.85 (9H, s,  $\text{CH}_3$ -k x3), 0.01 (6H, s,  $\text{CH}_3$ -j x2).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  176.2 (C=O), 170.6 (C=O), 158.9 (ArC=O), 155.4 (ArC=O), 148.8 (ArC=N), 138.3 (ArC=N), 137.5 (ArC), 134.7 (ArC), 134.3 (ArC), 131.8 (ArC), 131.2 (ArCH, br s), 130.3 (ArCH, br s), 129.7 (2x ArCH AB), 128.2 (q,  $J=35\text{Hz}$ , ArC-CF<sub>3</sub>), 122.8 (q,  $J=272\text{Hz}$ , CF<sub>3</sub>), 119.7 (2x ArCH AB), 116.4 (ArCH), 62.8 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 44.6 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 25.8 (3x CH<sub>3</sub>), 25.4 (CH<sub>2</sub>), 18.2 (CSi), -5.5 (2x CH<sub>3</sub>).  $\nu_{\text{max}}$  (thin film)/ $\text{cm}^{-1}$  3740, 3508, 3323, 2938, 2860, 1715, 1659, 1600, 1557, 1459, 1419, 1329, 1244, 1194, 1132, 1010. MS (m/z, FAB) = 702.4 ( $[\text{M}+\text{H}]^+$ , 52%), 644.3(20), 497.3 (25), 439.3 (40), 206.5 (70). HRMS found 702.2938.  $\text{C}_{34}\text{H}_{43}\text{O}_6\text{N}_5\text{F}_3\text{Si}$  requires  $[\text{M}+\text{H}]^+$ , 702.2935.

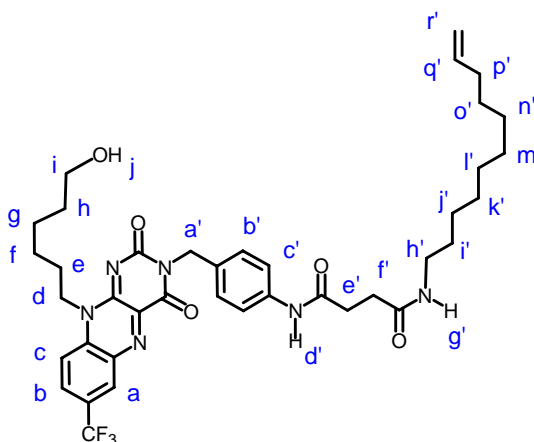
## Synthesis of compound 7.



Compound **6** (2.3 g, 3.28 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) before adding EDCI (817 mg, 4.26 mmol, 1.3eq), HOBt (575 mg, 4.26 mmol, 1.3eq), 10-undecen-amine (1.3g, 7.68 mmol, 2eq) and DMAP (40 mg, 0.33 mmol, 0.1eq). The reaction was stirred at r.t. for 18h then the product was concentrated under reduced pressure and purified by subjecting the mixture to column chromatography (eluent initially CH<sub>2</sub>Cl<sub>2</sub>, increasing polarity to CH<sub>2</sub>Cl<sub>2</sub>/acetone (8:2)) to yield **7** as a yellow solid. Yield = 2.68 g (96%). m.p. = 148-149°C.

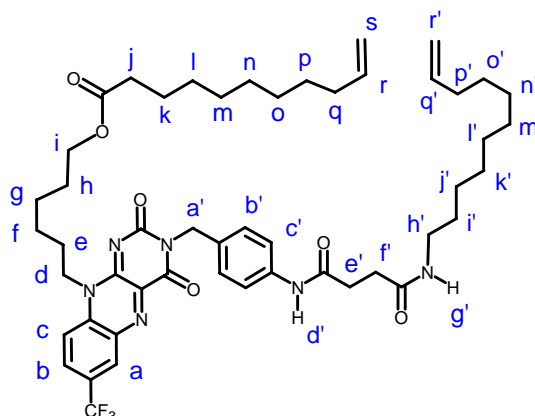
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.56 (1H, d, J=1.3Hz, ArH-a), 8.54 (1H, s, NH-d'), 8.04 (1H, dd, J=9.1 and 2.0Hz, ArH-b), 7.70 (1H, d, J=9.1Hz, ArH-c), 7.55 (2H, d, J=8.6Hz, ArH-b'), 7.44 (2H, d, J=8.6Hz, ArH-c'), 5.86 (1H, br t, J=4.9Hz, NH-g'), 5.86-5.74 (1H, m, CH-q'), 5.23 (2H, s, CH<sub>2</sub>-a'), 5.02-4.90(2H, m, CH<sub>2</sub>-r'), 4.64 (2H, br t, J=6.6Hz, CH<sub>2</sub>-d), 3.61 (2H, t, J=6.1Hz, CH<sub>2</sub>-i), 3.25-3.16 (2H, m, CH<sub>2</sub>-h'), 2.68-2.64 and 2.57-2.53 (4H, mx2, CH<sub>2</sub>-e' and f'), 2.07-1.98 (2H, m, CH<sub>2</sub>-p'), 1.84 (2H, quint, J=7.3Hz, CH<sub>2</sub>-e), 1.58-1.40 (6H, m, CH<sub>2</sub>-f, g and h), 1.40-1.30 (2H, m, CH<sub>2</sub>-i'), 1.32-1.20 (12H, m, CH<sub>2</sub>-j', k', l', m', n', o'), 0.88 (9H, s, CH<sub>3</sub>-k x3), 0.04 (6H, s, CH<sub>3</sub>-j x2). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 172.2 (C=O), 170.6 (C=O), 158.8 (ArC=O), 155.0 (ArC=O), 149.0 (ArC=N), 139.2 (CH alkene), 138.7 (ArC=N), 137.7 (ArC), 134.8 (ArC), 134.5 (ArC), 132.1 (ArC), 131.3 (ArCH, q, J=3Hz), 130.7 (ArCH, q, J=3.9Hz), 130.4 (2x ArCH AB), 128.5 (q, J=35Hz, ArC-CF<sub>3</sub>), 122.9 (q, J=272Hz, CF<sub>3</sub>), 119.7 (2x ArCH AB), 116.1 (ArCH), 114.1 (CH<sub>2</sub> alkene), 62.9 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 44.8 (CH<sub>2</sub>), 39.8 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.41 (CH<sub>2</sub>), 29.36 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 25.9 (3x CH<sub>3</sub>), 25.6 (CH<sub>2</sub>), 18.3 (CSi), -5.3 (2x CH<sub>3</sub>). ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3302, 2927, 2856, 1709, 1656, 1600, 1556, 1459, 1421, 1330, 1243, 1193, 1130, 1006. MS (m/z, FAB) = 853.5 ([M+H]<sup>+</sup>, 20%), 795.4(10), 439.3 (30), 252.4 (90), 107.7 (100). HRMS found 853.4654. C<sub>45</sub>H<sub>64</sub>N<sub>6</sub>O<sub>5</sub>F<sub>3</sub>Si requires [M+H]<sup>+</sup>, 853.4660.

## Synthesis of compound 8.



Compound **7** (560 mg, 0.657 mmol) was dissolved in THF (17 ml) and distilled water (14 ml) was added, followed by conc. HCl (1.5 ml). The mixture was allowed to continue stirring at r.t. for 1h. The mixture was then diluted by addition of distilled water (100 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 100 ml). The organic layers were combined, washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to give **8** as a yellow/orange solid. Yield = 453 mg (94 %). m.p. = 135-136°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.86 (1H, s, NH-d'), 8.54 (1H, d, J=1.2Hz, ArH-a), 8.04 (1H, dd, J=9.02 and 1.9Hz, ArH-b), 7.72 (1H, d, J=9.02Hz, ArH-c), 7.47 (2H, d, J=8.57Hz, ArH-b'), 7.41 (2H, d, J=8.57Hz, ArH-c'), 6.12 (1H, t, J=5.5Hz, NH-g'), 5.86-5.73 (1H, m, CH-q'), 5.20 (2H, s, CH<sub>2</sub>-a'), 5.02-4.89 (2H, m, CH<sub>2</sub>-r'), 4.64 (2H, br t, J=6.5Hz, CH<sub>2</sub>-d), 3.64 (2H, t, J=6.1Hz, CH<sub>2</sub>-i), 3.22-3.15 (2H, m, CH<sub>2</sub>-h'), 2.67-2.61 and 2.54-2.49 (4H, mx2, CH<sub>2</sub>-e' and f'), 2.05-1.98 (2H, m, CH<sub>2</sub>-p'), 1.84 (2H, quint, J=7.7Hz, CH<sub>2</sub>-e), 1.62-1.40 (6H, m, CH<sub>2</sub>-f, g and h), 1.39-1.30 (2H, m, CH<sub>2</sub>-i'), 1.30-1.19 (12H, m, CH<sub>2</sub>-j', k', l', m', n', o'). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 172.2 (C=O), 170.7 (C=O), 158.8 (ArC=O), 155.3 (ArC=O), 149.0 (ArC=N), 139.2 (CH alkene), 138.6 (ArC=N), 137.8 (ArC), 134.9 (ArC), 134.5 (ArC), 132.0 (ArC), 131.3 (ArCH, q, J=3Hz), 130.6 (ArCH, q, J=3.9Hz), 130.2 (2x ArCH AB), 128.4 (q, J=35Hz, ArC-CF<sub>3</sub>), 122.9 (q, J=272Hz, CF<sub>3</sub>), 119.7 (2x ArCH AB), 116.2 (ArCH), 114.1 (CH<sub>2</sub> alkene), 62.4 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 39.7 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.43 (CH<sub>2</sub>), 29.42 (CH<sub>2</sub>), 29.38 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>). ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3440 br, 3303, 2925, 2855, 1653, 1601, 1555, 1426, 1329, 1236, 1188, 1133. MS (m/z, FAB) = 739.6 ([M+H]<sup>+</sup>, 100%), 421.6 (60), 252.4 (100), 107.7 (85). HRMS found 739.3788. C<sub>39</sub>H<sub>50</sub>O<sub>5</sub>N<sub>6</sub>F<sub>3</sub> requires [M+H]<sup>+</sup>, 739.3795.

## Synthesis of compound 9.

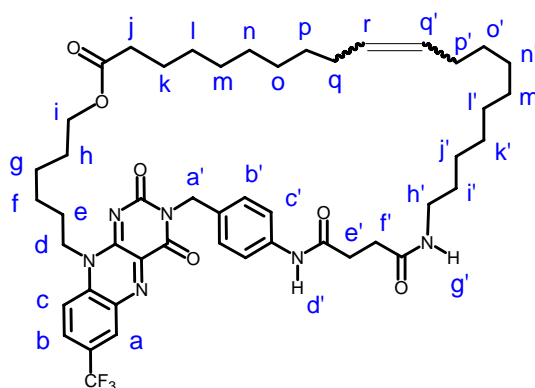


EDCI (774 mg, 4.04 mmol, 1.4 eq) was added to a stirred solution of compound **8** (2.05 g, 2.78 mmol), HOBt (550 mg, 4.07 mmol, 1.4 eq), DMAP (495 mg, 4.05 mmol, 1.4 eq) and 10-undecenoic acid (765 mg, 0.8 mmol, 1.4 eq) in  $\text{CH}_2\text{Cl}_2$  (40 ml). The reaction was stopped after 2 days, washed with distilled water (3 x 100 ml), dried ( $\text{MgSO}_4$ ) and the solvent removed under reduced pressure. The product was purified by column chromatography, (eluent initially  $\text{CH}_2\text{Cl}_2$ , increasing polarity to  $\text{CH}_2\text{Cl}_2$ /methanol (96:4)) to yield **9** as a yellow solid. Yield = 1.93 g (77 %). m.p. = 170 °C.

$^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.56 (2H, s, NH-d' and ArH-a), 8.03 (1H, dd, J=8.9 and 1.8Hz, ArH-b), 7.70 (1H, d, J=8.9Hz, ArH-c), 7.54 (2H, d, J=8.57Hz, ArH-b' x2), 7.44 (2H, d, J=8.57Hz, ArH-c' x2), 5.86 (1H, t, J=5.2Hz, NH-g'), 5.86-5.74 (2H, m, CH-r and q'), 5.23 (2H, s,  $\text{CH}_2$ -a'), 5.01-4.89 (4H, m,  $\text{CH}_2$ -s and r'), 4.64 (2H, br t, J=6.2Hz,  $\text{CH}_2$ -d), 4.06 (2H, t, J=6.65Hz,  $\text{CH}_2$ -i), 3.22 (2H, q, J=6.7Hz,  $\text{CH}_2$ -h'), 2.68-2.64 and 2.57-2.53 (4H, mx2,  $\text{CH}_2$ -e' and f'), 2.29 (2H, t, J=7.6Hz,  $\text{CH}_2$ -j), 2.02 (4H, q, J=7.1Hz,  $\text{CH}_2$ -q and p'), 1.85 (2H, quint, J=7.5Hz,  $\text{CH}_2$ -e), 1.69-1.50 (6H, m,  $\text{CH}_2$ -f,g and h), 1.50-1.40 (4H, m,  $\text{CH}_2$ -k and i'), 1.40-1.32 (4H, m,  $\text{CH}_2$ -p and o'), 1.32-1.20 (18H, m,  $\text{CH}_2$ -l,m,n,o,j',k',l',m',n).  $^{13}\text{C}$ NMR (400MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  174.0 (C=O), 172.2 (C=O), 170.6 (C=O), 158.7 (ArC=O), 155.0 (ArC=O), 148.9 (ArC=N), 139.2 (CH alkene), 139.1 (CH alkene), 138.6 (ArC=N), 137.7 (ArC), 134.8 (ArC), 134.4 (ArC), 132.1 (ArC), 131.3 (q, J=3Hz ArCH), 130.7 (q, J=3.9Hz, ArCH), 130.4 (2x ArCH AB), 128.5 (q, J=35Hz, ArC-CF<sub>3</sub>), 122.9 (q, J=272Hz, CF<sub>3</sub>), 119.7 (2x ArCH AB), 116.1 (ArCH), 114.13 (CH<sub>2</sub> alkene), 114.10 (CH<sub>2</sub> alkene), 63.8 (CH<sub>2</sub>), 45.0 (CH<sub>2</sub>), 44.8 (CH<sub>2</sub>), 39.8 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.42 (CH<sub>2</sub>), 29.36 (CH<sub>2</sub>), 29.30 (CH<sub>2</sub>), 29.26 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.11 (CH<sub>2</sub>), 29.06 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>).  $\nu_{\text{max}}$  (thin film)/ $\text{cm}^{-1}$  3302, 2925, 2855, 1721, 1655, 1599, 1557, 1532, 1458, 1420, 1328, 1238, 1183, 1130, 1074, 1005. MS (m/z, FAB) = 905.5 ([M+H]<sup>+</sup>, 80%), 653 (25), 383 (40), 252(100), 106 (80). HRMS found 905.5167.  $\text{C}_{50}\text{H}_{68}\text{O}_6\text{N}_6\text{F}_3$  requires [M+H]<sup>+</sup>, 905.5152.



## Synthesis of compound 10.

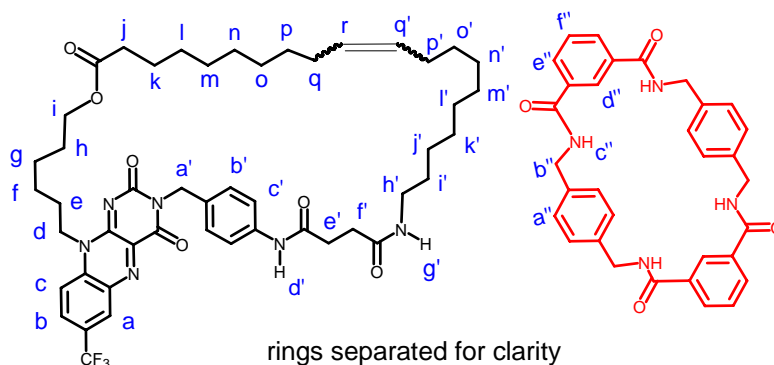


Compound **9** (181 mg, 0.2 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (150 ml) and degassed by  $\text{N}_2$  bubbling for 10 minutes before adding the 2<sup>nd</sup> generation Grubbs' catalyst (4.25 mg, 2.5 mol %). The mixture was then heated under reflux and  $\text{N}_2$  at 40°C for 18h. The solvent was evaporated under reduced pressure and the remaining solid subjected to column chromatography (eluent  $\text{CH}_2\text{Cl}_2$ /methanol (90:10)) to afford **10** as a yellow solid. Yield = 90 mg (50%). m.p. = 226°C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.57 (1H, d,  $J=1.3\text{Hz}$ , ArH-a), 8.54 (1H, s, NH-d'), 8.05 (1H, dd,  $J=9.0$  and  $1.9\text{Hz}$ , ArH-b), 7.70 (1H, d,  $J=9.0\text{Hz}$ , ArH-c), 7.56 (2H, d,  $J=8.6\text{Hz}$ , ArH-b' x2), 7.45 (2H, d,  $J=8.6\text{Hz}$ , ArH-c' x2), 5.90 (1H, t,  $J=5.65$ , NH-g'), 5.34 (2H, t,  $J=3.5\text{Hz}$ , (E)alkene, [4:1 ratio minor triplet at 5.30,  $J=5.0\text{Hz}$ , (Z)alkene]), 5.24 (2H, s,  $\text{CH}_2$ -a'), 4.65 (2H, br t,  $J=6.2\text{Hz}$ ,  $\text{CH}_2$ -d), 4.07 (2H, t,  $J=6.3\text{Hz}$ ,  $\text{CH}_2$ -i), 3.21 (2H, q,  $J=6.6\text{Hz}$ ,  $\text{CH}_2$ -h'), 2.68-2.64 and 2.57-2.53 (4H, mx2,  $\text{CH}_2$ -e' and f'), 2.29 (2H, t,  $J=7.4\text{Hz}$ ,  $\text{CH}_2$ -j), 2.00-1.88 (4H, m,  $\text{CH}_2$ -q and p' and e), 1.88-1.80 (2H, m,  $\text{CH}_2$ -e), 1.75-1.40 (10H, m,  $\text{CH}_2$ -f, g, h, k and i'), 1.33-1.17 (22H, m,  $\text{CH}_2$ -l,m,n,o,p,j',k',l',m',n',o').  $^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ )  $\delta_{\text{H}}$  9.93 (1H, s, NH-d'), 8.58 (1H, s, ArH-c), 8.23 (2H, br s, ArH-a and ArH-b), 7.80 (1H, t,  $J=5.5\text{Hz}$ , NH-g'), 7.52 (2H, d,  $J=8.5\text{Hz}$ , ArH-c' x2), 7.33 (2H, d,  $J=8.5\text{Hz}$ , ArH-b' x2), 5.32 (2H, t,  $J=3.5\text{Hz}$ , (E)alkene, [4:1 ratio minor triplet at 5.28,  $J=4.8\text{Hz}$ , (Z)alkene]), 5.08 (2H, s,  $\text{CH}_2$ -a'), 4.65 (2H, br t,  $J=6.7\text{Hz}$ ,  $\text{CH}_2$ -d), 4.03 (2H, t,  $J=6.1\text{Hz}$ ,  $\text{CH}_2$ -i), 3.03 (2H, q,  $J=5.9\text{Hz}$ ,  $\text{CH}_2$ -h'), 2.54 (2H, obscured by solvent peak,  $\text{CH}_2$ -e'), 2.38 (2H, t,  $J=6.6\text{Hz}$ ,  $\text{CH}_2$ -f'), 2.28 (2H, t,  $J=7.2\text{Hz}$ ,  $\text{CH}_2$ -j), 1.97-1.86 (4H, m,  $\text{CH}_2$ -q and p'), 1.76 (2H, quin,  $J=7.1\text{Hz}$ ,  $\text{CH}_2$ -e), 1.60 (2H, quin,  $J=6.7\text{Hz}$ ,  $\text{CH}_2$ -h), 1.55-1.44 (4H, m,  $\text{CH}_2$ -f and k), 1.44-1.36 (2H, m,  $\text{CH}_2$ -g), 1.36-1.28 (2H, m,  $\text{CH}_2$ -i'), 1.28-1.16 (22H, m,  $\text{CH}_2$ -l,m,n,o,p,j',k',l',m',n',o').  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  174.0 (C=O), 172.2 (C=O), 170.6 (C=O), 158.7 (ArC=O), 154.9 (ArC=O), 148.9 (ArC=N), 138.6 (ArC), 137.7 (ArC), 134.8 (ArC=N), 134.5 (ArC), 132.2 (ArC), 131.3 (q,  $J=3\text{Hz}$ , ArCH), 130.7 (q,  $J=3.9\text{Hz}$ , ArCH), 130.5 (2x ArCH AB), 130.4 (CH alkene), 130.3 (CH alkene), 128.5 (q,  $J=35\text{Hz}$ , ArC- $\text{CF}_3$ ), 122.9 (q,  $J=272\text{Hz}$ ,  $\text{CF}_3$ ), 119.7 (2x ArCH AB), 116.0 (ArCH), 63.8 ( $\text{CH}_2$ ), 45.0 ( $\text{CH}_2$ ), 44.7 ( $\text{CH}_2$ ), 39.7 ( $\text{CH}_2$ ), 34.3 ( $\text{CH}_2$ ), 33.1 ( $\text{CH}_2$ ), 32.4 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.40

(CH<sub>2</sub>), 29.35 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.98 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>).  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 3300, 2924, 2854, 1721, 1652, 1598, 1560, 1531, 1458, 1417, 1329, 1241, 1176, 1134, 1075, 1015. MS (m/z, FAB) = 877.5 ([M+H]<sup>+</sup>, 100%), 722 (15), 383 (20), 106 (23). HRMS found m/z = 877.4836. C<sub>48</sub>H<sub>64</sub>N<sub>6</sub>O<sub>6</sub>F<sub>3</sub> requires [M+H]<sup>+</sup>, 877.4839.

## Synthesis of catenane **1**.



Macrocyclic **10** (190 mg, 0.21 mmol) was dissolved by warming in dry  $\text{CH}_2\text{Cl}_2$  (100 mL stabilized with amines not ethanol) before adding  $\text{NEt}_3$  (1.0 mL, 7.2 mmol, 34 eq). After cooling to r.t., two separate solutions, isophthaloyl chloride (213 mg, 1.05 mmol, 5eq) in  $\text{CH}_2\text{Cl}_2$  (10 mL), and *p*-xylylenediamine (145 mg 1.06 mmol, 5eq) in  $\text{CH}_2\text{Cl}_2$  (10 mL), were simultaneously added into the reaction mixture over 3h using a motor-driven syringe pump. The  $\text{NEt}_3\cdot\text{HCl}$  salt was removed by filtration and the filtrate was concentrated under reduced pressure. The product was then purified by careful column chromatography (eluent:  $\text{CH}_2\text{Cl}_2$ /methanol: 98:2). Yield = 76 mg (26 %). m.p = 188 - 189°C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) at 25°C,  $\delta_{\text{H}}$  9.86 (1H, br s, NH-d'), 8.47 (3H, m, ArH-a and ArH-d'' x2), 8.09 (1H, dd,  $J=9.1$  and 1.7Hz, ArH-b), 7.93 (4H, br s, ArH-e''), 7.78-7.70 (5H, m, ArH-c and NH-c'' x4), 7.40-7.32 (4H, m, ArH-b' x2 and ArH-c' x2), 7.22-7.10 (10H, m, ArH-f'' and ArH-a''), 6.55 (1H, br s, NH-g'), 5.31-5.26 (2H, m, CH-r and q'), 5.11 (2H, br s,  $\text{CH}_2$ -a'), 4.60-4.28 (10H, m,  $\text{CH}_2$ -b'' x4 and  $\text{CH}_2$ -i), 3.88 (2H, t,  $J=5.4\text{Hz}$ ,  $\text{CH}_2$ -d), 3.03 (2H, br s,  $\text{CH}_2$ -h'), 2.17 (2H, t,  $J=7.5\text{Hz}$ ,  $\text{CH}_2$ -j), 1.90-1.75 (6H, m,  $\text{CH}_2$ -q,p' and e'), 1.70-1.55 (2H, m,  $\text{CH}_2$ -h), 1.55-1.42 (4H, m,  $\text{CH}_2$ -k and i'), 1.42-1.35 (2H, m,  $\text{CH}_2$ -e), 1.55-1.05 (28H, m,  $\text{CH}_2$ -f,g,l,m,n,o,p,j'k'l'm'n'o' and f').  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) at 55°C,  $\delta_{\text{H}}$  9.31 (1H, br s, NH-d'), 8.45 (2H, br s, ArH-d''), 8.29 (1H, br s, ArH-a), 7.99 (1H, d,  $J=8.2\text{Hz}$ , ArH-b), 7.90 (4H, br s, ArH-e''), 7.63 (1H, d,  $J=8.2\text{Hz}$ , ArH-c), 7.38 (4H, br s, NH-c''), 7.38-7.24 (4H, m, ArH-b' and c'), 7.18 (2H, s, ArH-f''), 7.04 (8H, s, ArH-a''), 6.04 (1H, br s, NH-g'), 5.24-2.18 (2H, m, CH-r and q'), 5.02 (2H, s,  $\text{CH}_2$ -a'), 4.50-4.30 (10H, m,  $\text{CH}_2$ -b'' x4 and  $\text{CH}_2$ -i), 3.81 (2H, t,  $J=6.0\text{Hz}$ ,  $\text{CH}_2$ -d), 2.99-2.91 (2H, m,  $\text{CH}_2$ -h'), 2.12-2.04 (2H, m,  $\text{CH}_2$ -j), 1.90-1.67 (6H, m,  $\text{CH}_2$ -q,p' and e'), 1.67-1.55 (2H, m,  $\text{CH}_2$ -h), 1.90-1.75 (6H, m,  $\text{CH}_2$ -e,k and i'), 1.40-1.05 (28H, m,  $\text{CH}_2$ -f,g,l,m,n,o,p,j'k'l'm'n'o' and f').  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta_{\text{H}}$  9.78 (1H, s, NH-d'), 8.94 (4H, br t,  $J=5.4\text{Hz}$  ArH-c''), 8.65 (1H, br s, ArH-a), 8.33 (1H, d,  $J=8.7\text{Hz}$ , ArH-b), 8.07 (2H, br s, ArH-d'' x2), 8.91 (4H, d,  $J=7.8\text{Hz}$ , ArH-e'' x4), 7.87 (1H, d,  $J=9.4\text{Hz}$ , ArH-c), 7.76 (1H, t,  $J=5.2\text{Hz}$ , NH-g'), 7.50 (2H, t,  $J=7.8\text{Hz}$ , ArH-f''), 7.21 (2H, d,  $J=8.3\text{Hz}$ ,  $\text{CH}_2$ -b'), 7.05 (2H, d,  $J=8.3\text{Hz}$ ,  $\text{CH}_2$ -c'), 7.00 (8H, s,  $\text{CH}_2$ -a''), 5.35-5.30 (2H, m,  $\text{CH}_2$ -r and  $\text{CH}_2$ -q'), 5.05 (2H,

s, CH<sub>2</sub>-a'), 4.40-4.19 (10H, m, CH<sub>2</sub>-i and CH<sub>2</sub>-b" x4), 3.33 (2H, t, J=6.5Hz, CH<sub>2</sub>-d), 2.94 (2H, q, J=6.0Hz, CH<sub>2</sub>-h'), 2.43 (2H, t, J=6.6Hz, CH<sub>2</sub>-e'), 2.30 (2H, t, J=6.6Hz, CH<sub>2</sub>-f'), 2.03 (2H, t, J=7.3Hz, CH<sub>2</sub>-j), 1.95-1.87 (4H, m, CH<sub>2</sub>-q and p'), 1.38-1.31 (2H, m, CH<sub>2</sub>-k), 1.31-1.21 (6H, m, CH<sub>2</sub>-i', p and o'), 1.21-1.10 (18H, m, CH<sub>2</sub>-l,m,n,o,j',k',l',m',n), 0.87-0.77 (2H, m, CH<sub>2</sub>-h), 0.60-0.50 (2H, m, CH<sub>2</sub>-e), 0.42-0.32 (2H, m, CH<sub>2</sub>-g), 0.31-0.21 (2H, m, CH<sub>2</sub>-f).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 172.8 (C=O), 171.1 (C=O), 170.3 (C=O), 165.5 (4x C=O), 159.1 (ArC=O), 156.2 (ArC=O), 149.9 (ArC=N), 140.1 (ArC=N), 138.0 (4x ArC), 137.9 (ArC), 134.6 (4x ArC), 134.4 (ArC), 131.13 (ArC), 130.7 (ArCH, br s), 130.1 (CH alkene), 130.0 (CH alkene), 129.7 (ArC), 129.4 (4x ArCH), 128.9 (ArCH, br s), 128.2 (2x ArCH), 127.8 (8x ArCH), 127.5 (2x ArCH), 126.5 (2x ArCH), 126.0 (q, J=33.5Hz, ArC-CF<sub>3</sub>), 123.7 (q, J=272.0Hz, CF<sub>3</sub>), 118.5 (2x ArCH), 118.3 (ArCH), 63.2 (CH<sub>2</sub>), 43.8 (CH<sub>2</sub>), 42.4 (4x CH<sub>2</sub>), 38.4 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.69 (CH<sub>2</sub>), 28.66 (2x CH<sub>2</sub>), 28.61 (2x CH<sub>2</sub>), 28.57 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 27.3 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>).

ν<sub>max</sub> (thin film)/cm<sup>-1</sup> 3309 br, 2926, 2855, 1719, 1652, 1599, 1531, 1422, 1326, 1236, 1192, 1131, 1081. MS (m/z, FAB) = 1409.7 ([M+H]<sup>+</sup>, 24%), 877.4 (10), 460.1 (12), 307.0 (100), 289.0 (50). Elemental analysis calcd. (%) for C<sub>80</sub>H<sub>91</sub>F<sub>3</sub>N<sub>10</sub>O<sub>10</sub>: C, 68.16; H, 6.51; N, 9.94; found: C, 68.35; H, 6.63; N, 9.90.

## References:

Synthesis of 10-undecen-amine:

Kai Cheng and Christopher C. Landry *J. Am. Chem. Soc.* 2007, **129**, 9674-9685.

## Abbreviations:

DMAP: 4-(Dimethylamino) pyridine

DMF: Dimethylformamide

EDCI: 1-ethyl 3-(3-dimethylaminopropyl) carbodiimide HCl.

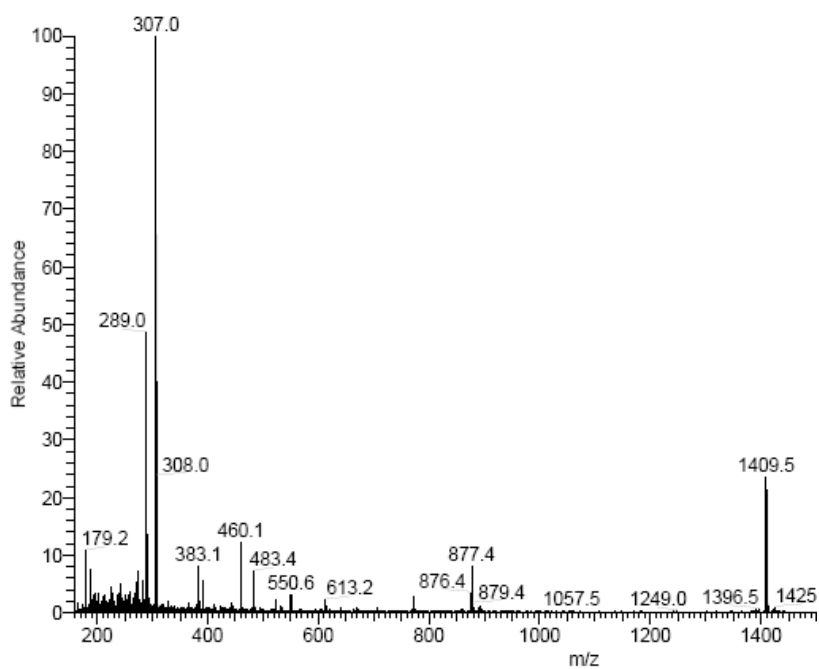
HOBt: 1-Hydroxybenzotriazole hydrate

NEt<sub>3</sub>: triethylamine

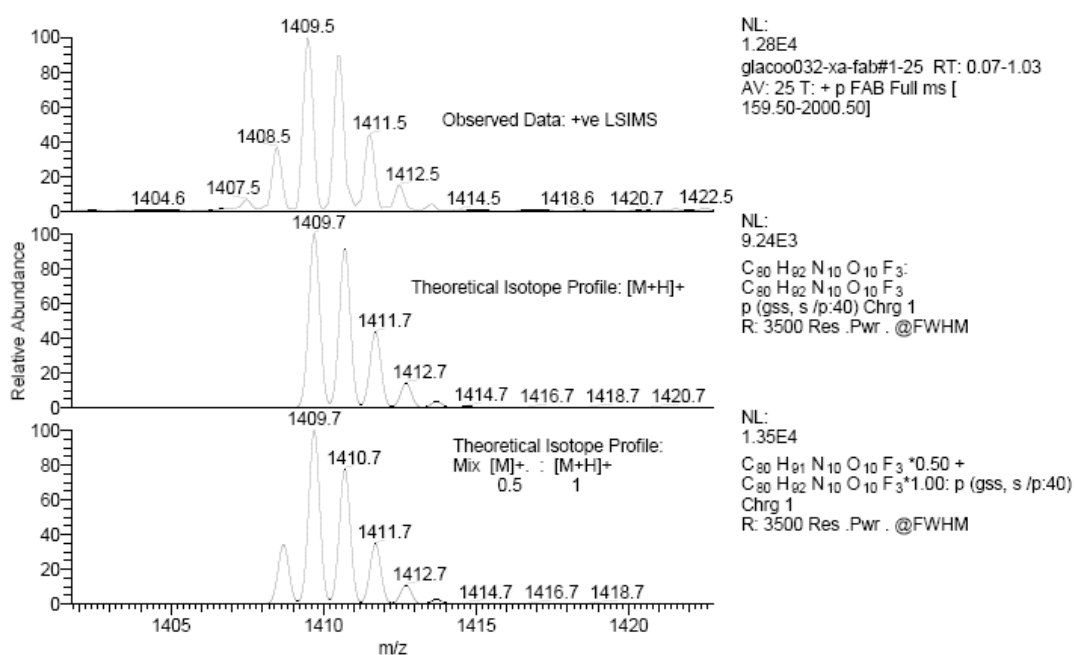
TBDMS: t-butyl dimethyl silane.

2<sup>nd</sup> generation Grubbs' catalyst = benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium.

**(b) Mass spectrometry**

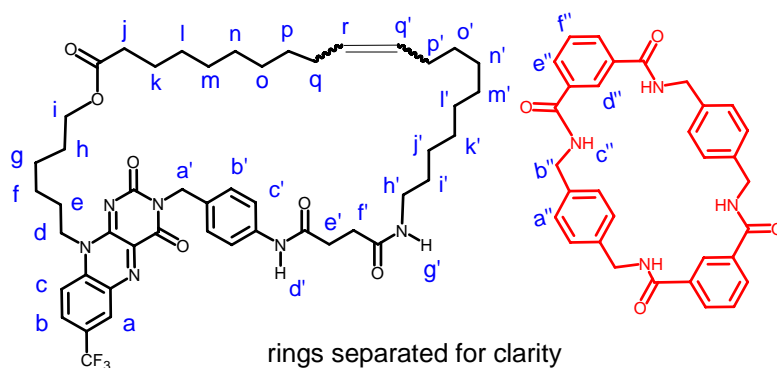


**Figure S1:** FAB MS of **1** (NOBA MATRIX).



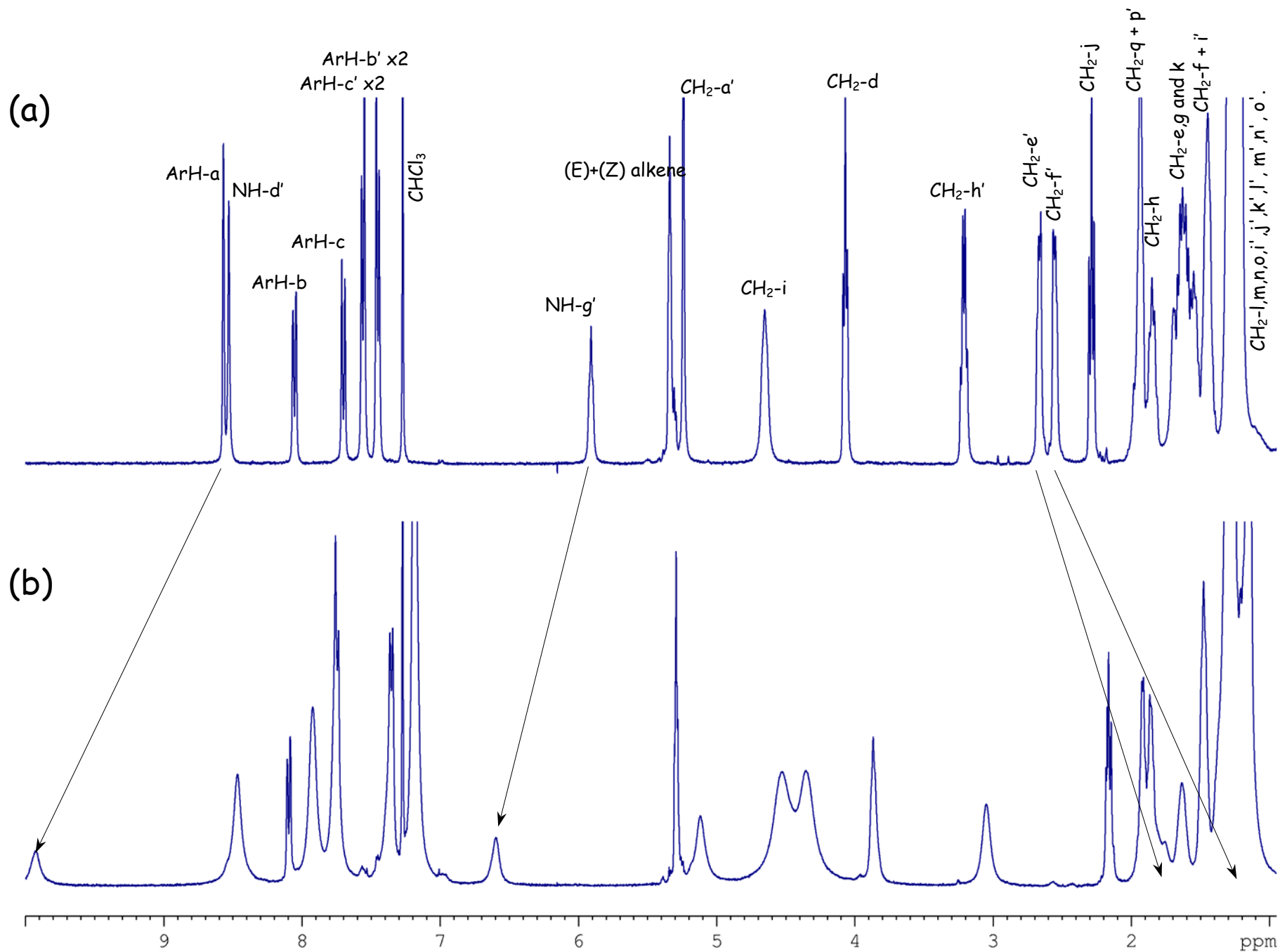
**Figure S2:** Comparison of observed and theoretical FAB MS of **1**.

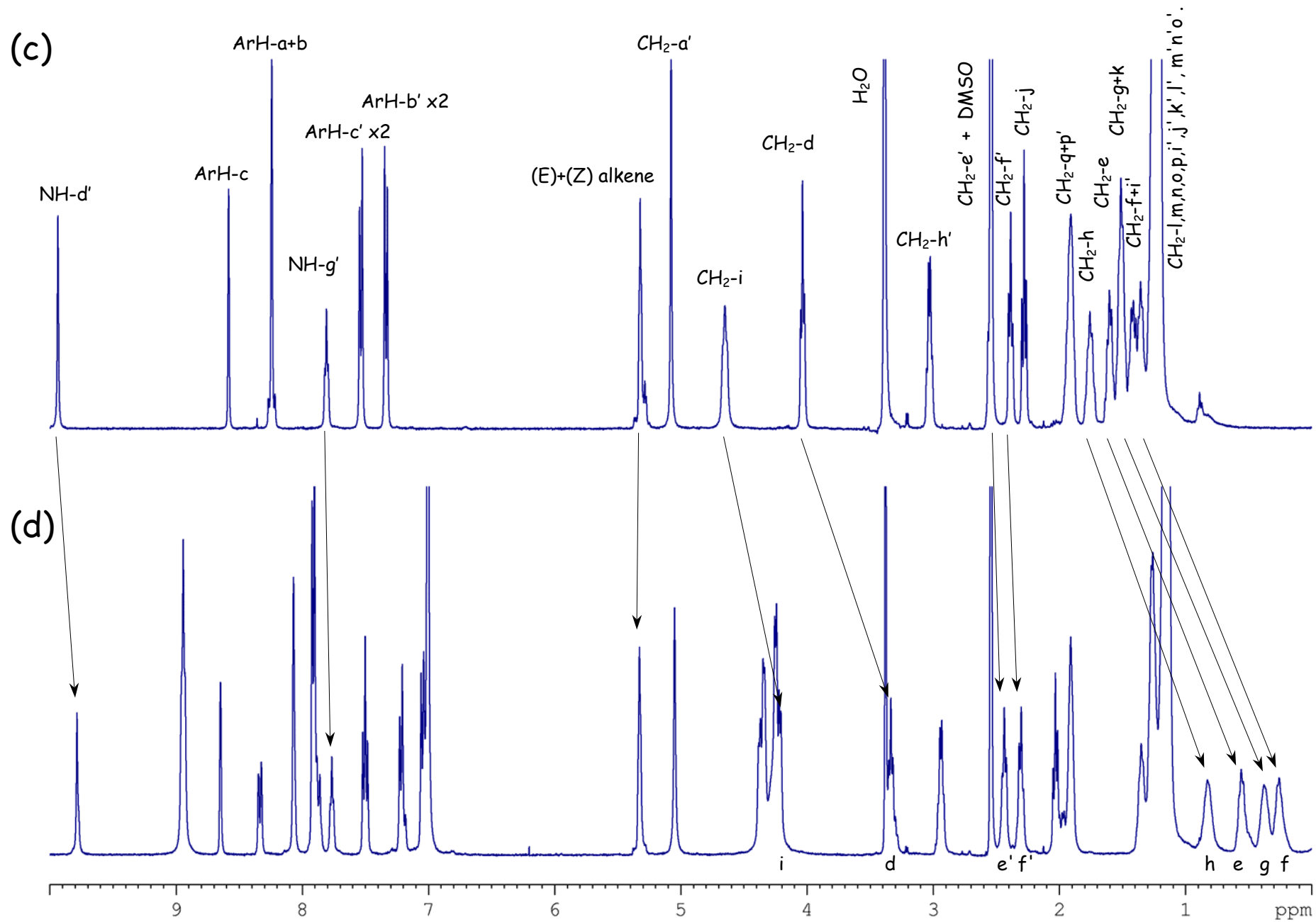
**(c) NMR Spectroscopy**



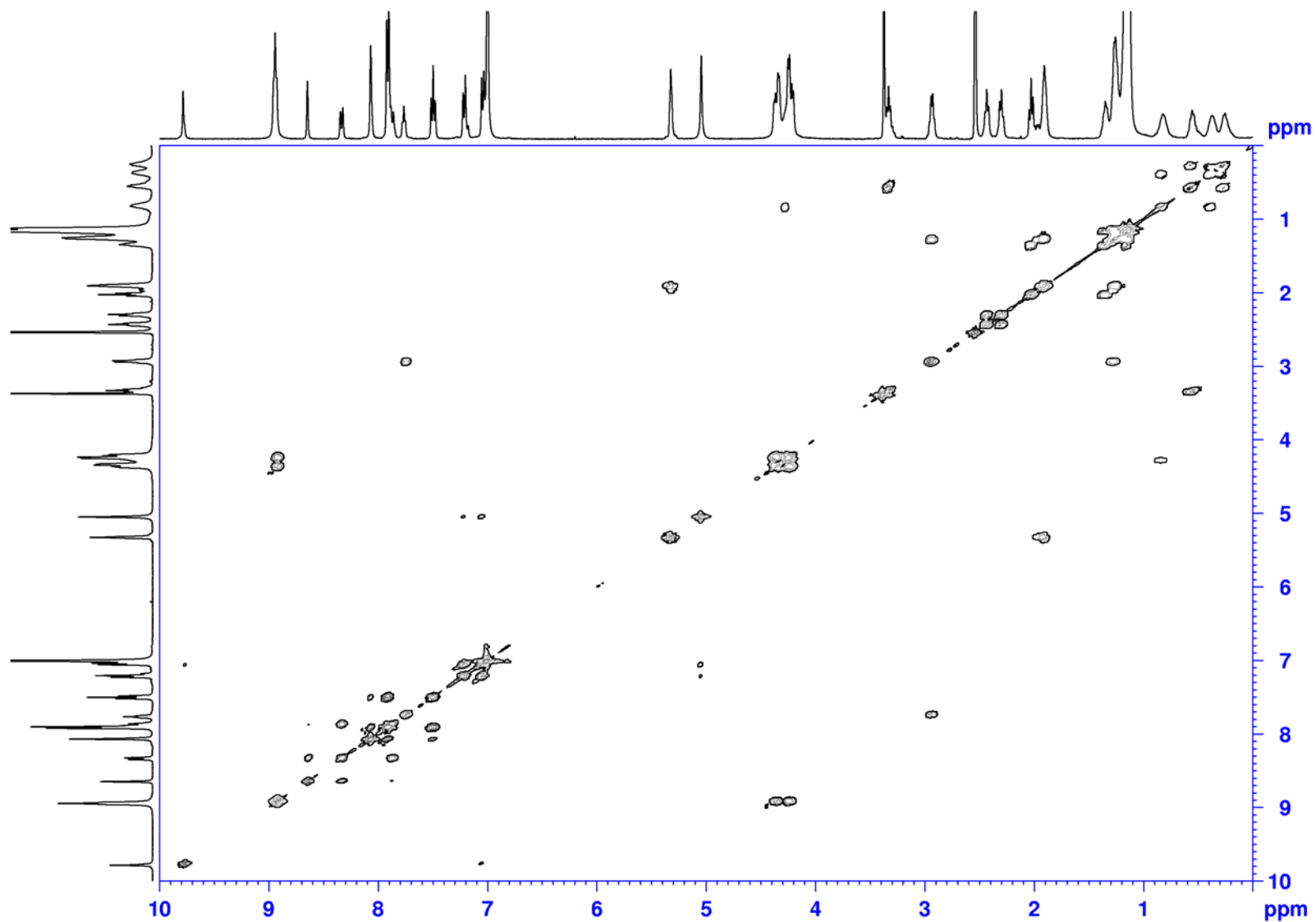
**Figure S3:** Lettering scheme used in NMR assignment of **1**.

**Figure S4:** Partial  $^1\text{H}$  NMR spectra (a) and (b) below show macrocycle **10** and catenane **1**, respectively recorded in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR spectra (c) and (d) show macrocycle **10** and catenane **1**, respectively, recorded in  $\text{DMSO}-d_6$ . Spectra are displayed on pages 15 and 16.

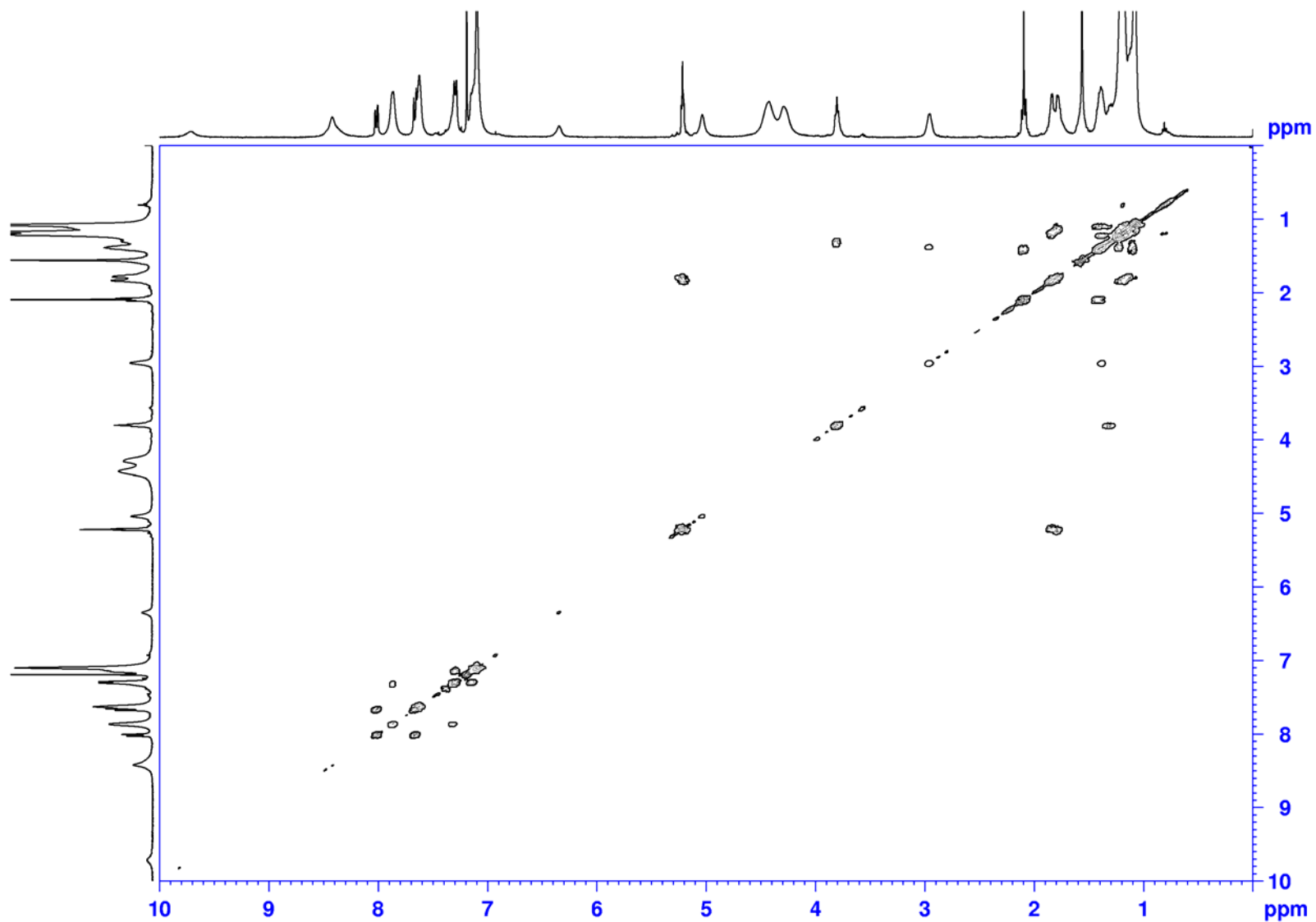






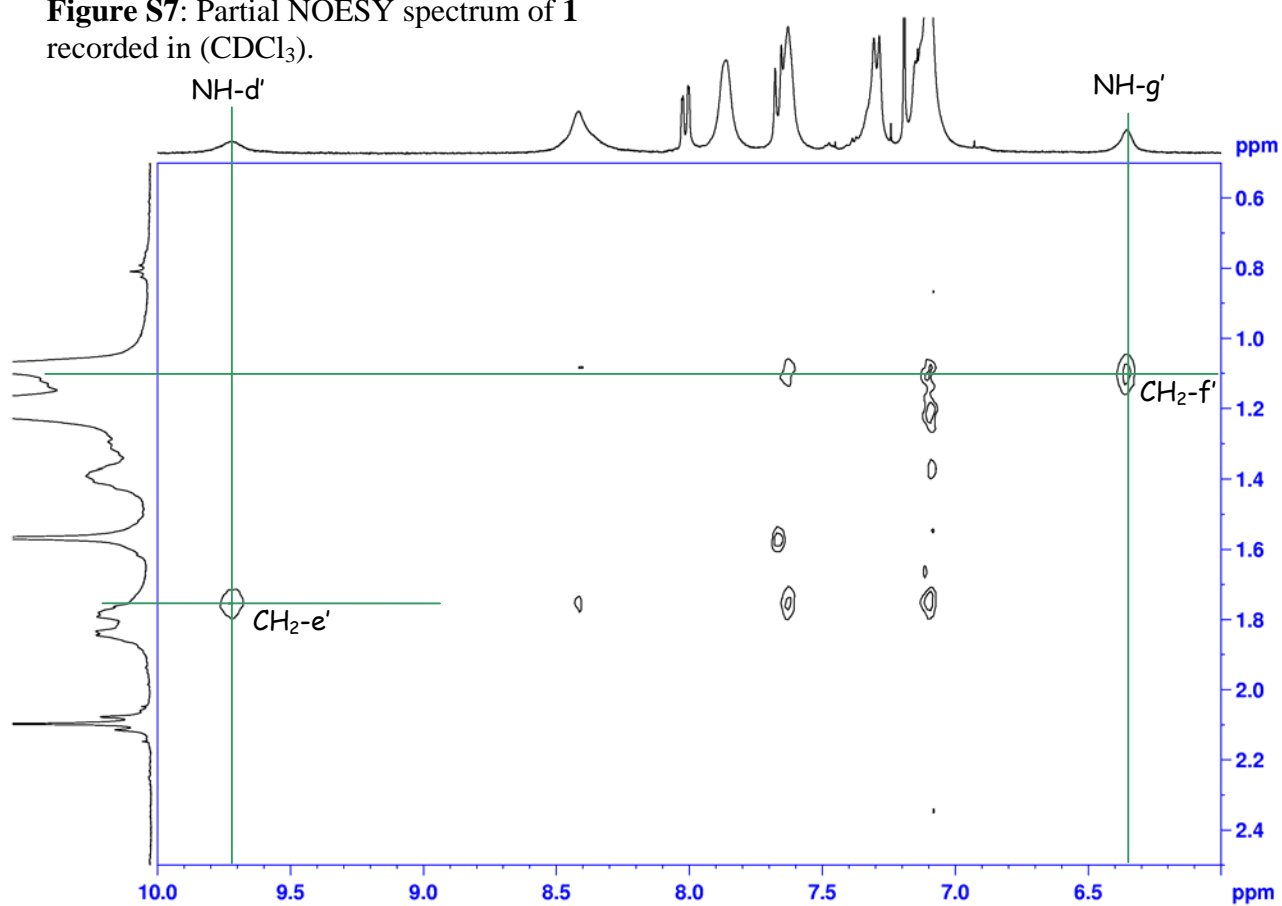


**Figure S5:** COSY spectrum of **1** recorded in DMSO-d<sub>6</sub>

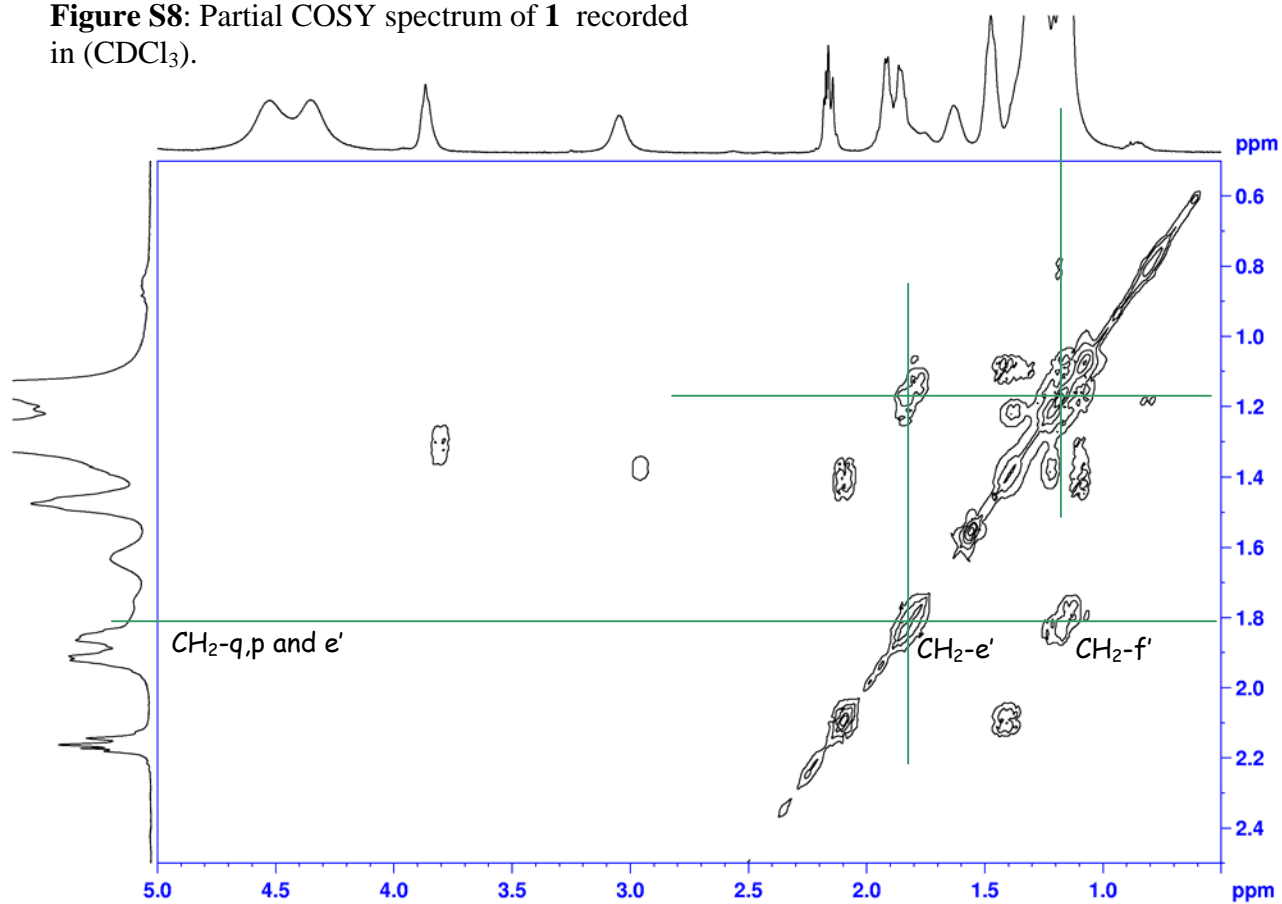


**Figure S6:** COSY spectrum of **1** recorded in CDCl<sub>3</sub>

**Figure S7:** Partial NOESY spectrum of **1** recorded in (CDCl<sub>3</sub>).



**Figure S8:** Partial COSY spectrum of **1** recorded in (CDCl<sub>3</sub>).



### (d) Crystallographic Studies of 1.

A suitable single crystal of **1** was selected and mounted onto the top of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150(2) K on a Oxford Diffraction Gemini CCD-detector diffractometer [ $\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}$ ]. Because of the large structure and weak crystal diffraction, it was only possible to collect diffraction data to  $2\theta$  max  $48.8^\circ$ . The data were collected and processed using software CrysAlis CCD and RED, Oxford Diffraction Ltd., Version 1.171.32.15. Structure solution and refinement were carried out with SHELXS-97<sup>1</sup> and SHELXL-97<sup>2</sup> via WinGX.<sup>3</sup> Corrections for incident and diffracted beam absorption effects were applied using analytical methods.<sup>4</sup>

#### References:

- (1) Sheldrick, G. M. *Acta Crystallogr. , Sect. A* 1998, **A46**, 467.
- (2) Sheldrick, G. M. SHELXL-97. Program for Crystal structure analysis, University of Göttingen, Germany, 1997.
- (3) Farrugia, L. J. *J. Appl. Cryst.* 1999, **32**, 837.
- (4) Clark, R. C. & Reid, J. S. *Acta Cryst.* 1995, **A51**, 887.

Crystal data and structure refinements for **1**:  $\text{C}_{84}\text{H}_{107}\text{F}_3\text{N}_{10}\text{O}_{14}$ ,  $M = 1537.80$ ; block crystal:  $0.27 \times 0.25 \times 0.16 \text{ mm}^3$ ;  $T = 150(2) \text{ K}$ . Monoclinic, space group  $\text{P}2_1/c$ ,  $a = 13.9514(5)$ ,  $b = 29.1721(10)$ ,  $c = 20.3132(7) \text{ \AA}$ ,  $\beta = 102.463(3)^\circ$ ,  $V = 8072.5(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.265 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.091 \text{ mm}^{-1}$ ,  $F(000) = 3280$ , 33859 reflections measured, of which 10751 are independent ( $R_{\text{int}} = 0.048$ ), 949 refined parameters,  $R1 = 0.0665$ ,  $wR2 = 0.1895$ . All non-hydrogens were found from the electron density map (asymmetric unit). Most of the hydrogens were theoretically calculated and refined in riding model. No attempt was made to add hydrogen atoms to the solvent molecules which accounts for the number difference of H atoms between given formula and atom list sum. Due to variable orientations, part of the long chain involving C27 cannot be well defined. A two-part disorder model was applied to the section from C27 to C34 of this long chain. 17 Restraints of SADI and DFIX were set for the C-C distances within this disorder model. H addition to this section was attempted to both disordered parts. The oxygen atom O14 on a solvent ethanol molecule was also assigned two disordered positions. Below is the list of H-bonds of interest. As no H atoms were found for water molecules, no H bond calculation was attempted for H bonds involving water molecules.

Hydrogen bonds with  $\text{H}\cdots\text{A} < r(\text{A}) + 2.000 \text{ Angstroms}$  and  $\langle \text{DHA} \rangle > 110 \text{ deg}$ .

D-H	d(D-H)	d(H..A)	$\langle \text{DHA} \rangle$	d(D..A)	A
N5-H5	0.860	2.140	164.83	2.978	O1 [ -x+1, -y+1, -z+1 ]
N6-H6	0.860	2.371	143.35	3.104	O11 [ x, -y+1/2, z-1/2 ]
N7-H7	0.860	2.087	152.44	2.877	O11 [ x, -y+1/2, z-1/2 ]
N8-H8	0.860	2.164	164.82	3.002	O4
N9-H9	0.860	2.038	166.75	2.882	O12
N10-H10	0.860	2.092	152.64	2.883	O3
O13-H13	0.820	2.087	133.23	2.715	O7

**(e) Electrochemistry**

Cyclic voltammetry experiments were performed using a CH Instruments 440A electrochemical workstation. The electrolyte solution (0.1 M) was prepared from recrystallised  $\text{Bu}_4\text{NPF}_6$  and dry  $\text{CH}_2\text{Cl}_2$ . A three electrode configuration was used with a platinum disc working electrode, a platinum wire counter electrode and a silver/silver chloride reference electrode. The solution was purged with nitrogen prior to recording the electrochemical data, and all measurements were recorded under a nitrogen atmosphere.