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Supporting Information

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Supporting Information

Converting sequences of aromatic amino acid monomers into function: second generation helical capsules

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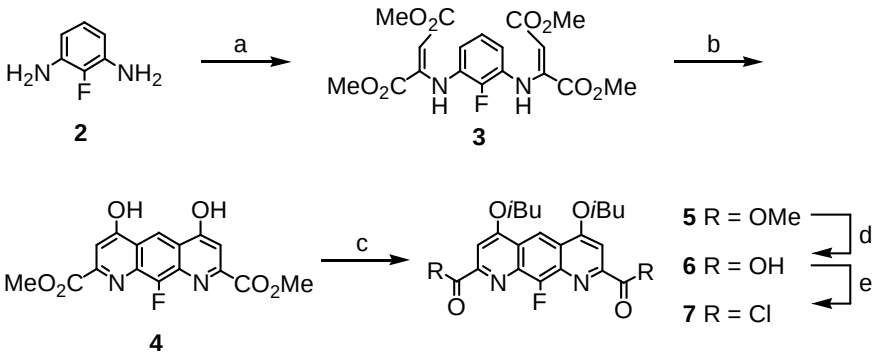
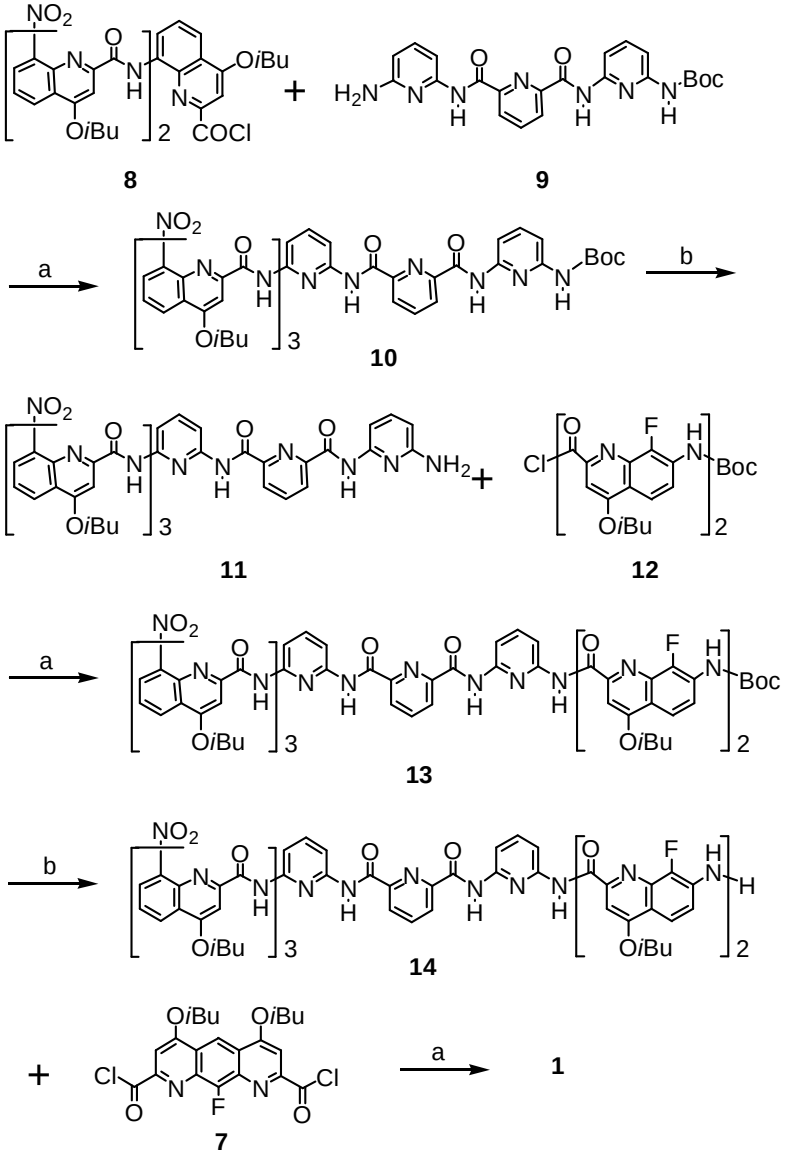
Synthetic schemes



Scheme S1. Synthesis of 1,8-diaza-9-fluoro-2,7-anthracenedicarboxylic acid **6**. a) dimethylacetylenedicarboxylate, MeOH, reflux; b) diphenylether, reflux; c) iBuOH, PPh_3, DIAD, THF, rt; d) NaOH, rt; e) 1-chloro-N,N,2-trimethylpropenylamine, $CHCl_3$, rt, 3h.



Scheme S2. Synthesis of capsule **1**. a) DIEA, THF, rt; b) TFA/DCM, rt.

NMR binding studies

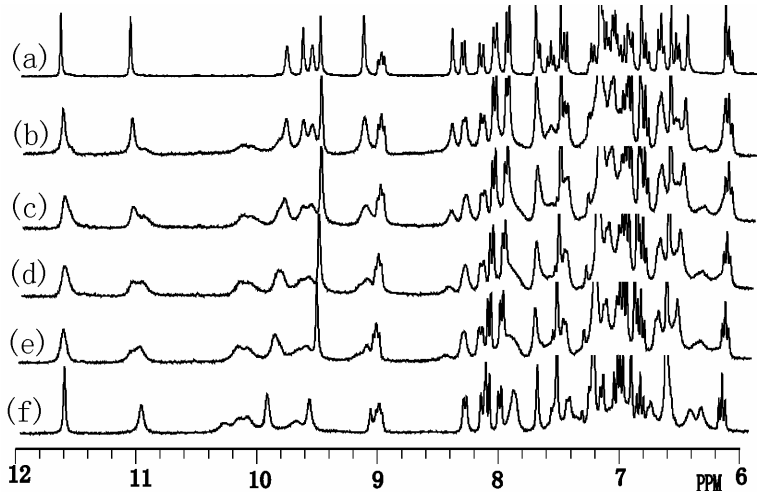


Figure S1. Part of representative 300 MHz NMR titration of **1** in $CDCl_3$ (2 mM) at 25°C with 1,2-ethylene glycol: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv.; (f) 4.5 equiv.

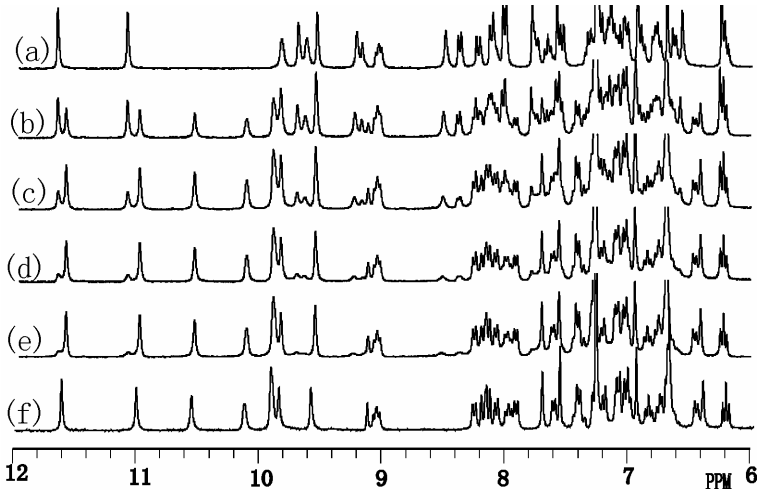


Figure S2. Part of representative 300 MHz NMR titration of **1** in $CDCl_3$ (2 mM) at 25°C with 1,3-propanediol: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv.; (f) 4.5 equiv.

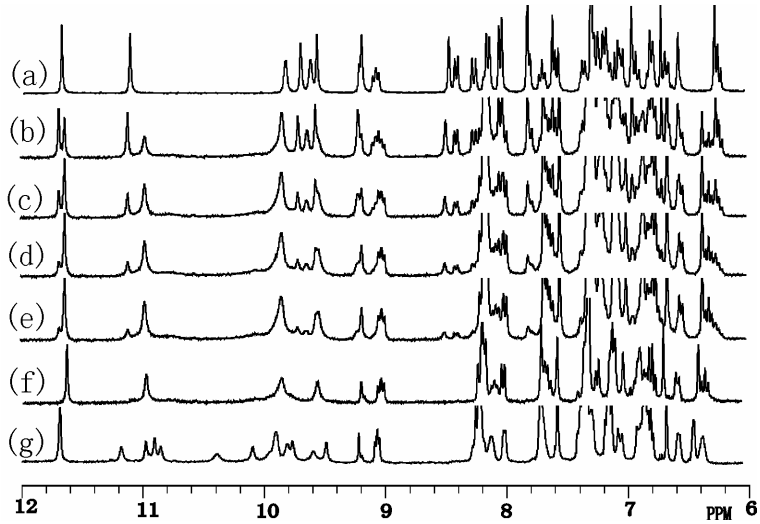


Figure S3. Part of representative 300 MHz NMR titration of **1** in $CDCl_3$ (2 mM) at 25°C with 4-amino butanol: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv.; (f) 4.5 equiv; (g) 4.5 equiv of 400 MHZ NMR spectra at 273K.

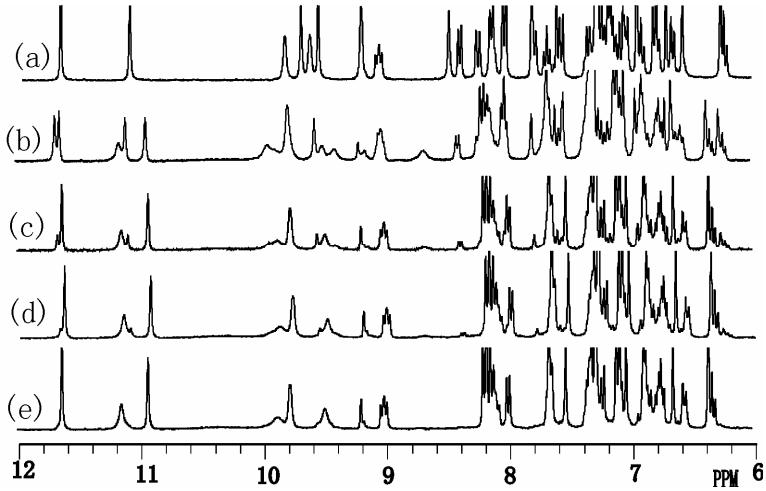


Figure S4. Part of representative 300 MHz NMR titration of **1** in $CDCl_3$ (2 mM) at 25°C with 1,4-butanediamine: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv.

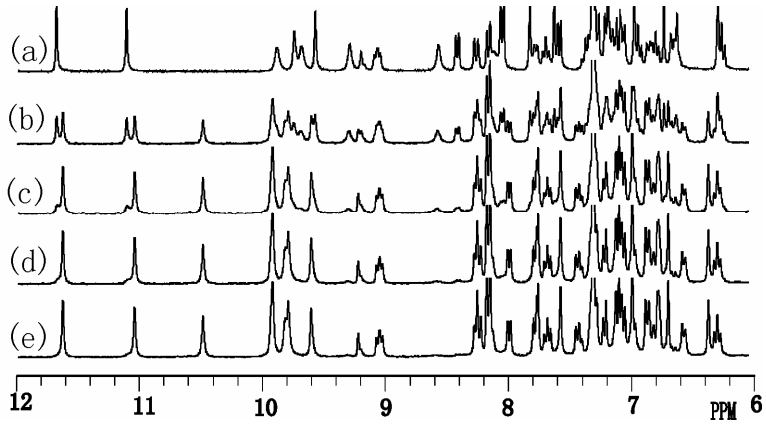


Figure S5. Part of representative 300 MHz NMR titration of **1** in $CDCl_3$ (2 mM) at 25°C with 2-butenediol: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv.

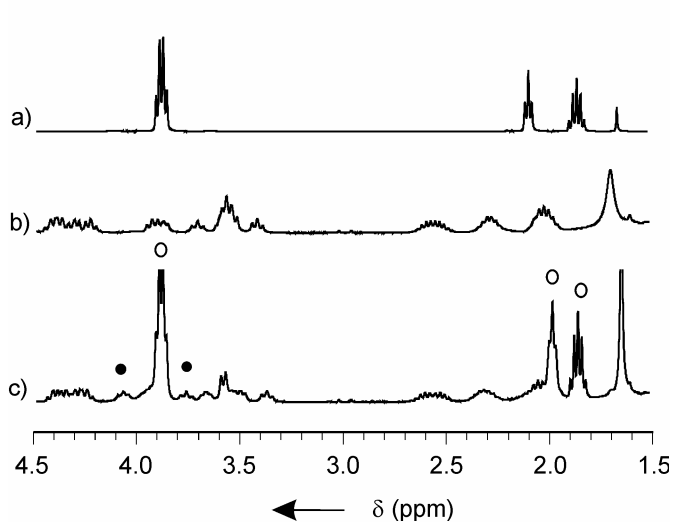


Figure S6. Part of the 300 MHz NMR spectra in $CDCl_3$ of: (a) 1,3-propanediol; (b) capsule **1** (2 mM); (c) capsule **1** (2 mM) in the presence of 5 equiv. of 1,3-propoanediol. White circles indicate signals of the free guest and black circles indicate signals of the encapsulated guests unambiguously assigned on the basis of COSY experiments. Signals at 3.75 an 4.1 ppm indicate diastereotopic protons of the guest in the helical capsule.

Experimental section

General. All reactions were carried out under a dry nitrogen or argon atmosphere. Unless otherwise noted, the original materials were used directly from commercial supplies without any purification. Dry THF was distilled from Na/Benzephenone, dry dichloromethane and diisopropylethylamine (DIEA) were distilled from CaH_2 prior to use. NMR spectra were recorded on Bruker DMX 300 and Bruker AVANCE 400 spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) using residual solvent protons as internal standards (chloroform: δ 7.26 ppm; DMSO: δ 2.50 ppm). Coupling constants are expressed in Hertz EI, ESI mass spectra and MALDI-TOF were obtained on GCT, LC-MS 2010, and Autoflex spectrometers, respectively.

2,6-Diaminofluorobenzene (2) A mixture of 2-fluoro-1,3-dinitrobenzene (2.5 g, 13.4 mmol) dissolved in MeOH (30 mL) and 10% Pd/C (0.25 g) was stirred at ambient temperature under 1 bar atmosphere of hydrogen for 5 h. The solution was then filtered through Celite, and the solvent was evaporated rapidly to dryness to give 1.6 g (92% yield) of the product, which was used without further purification. ^{1}H NMR ($CDCl_3$, ppm): δ 6.72 (t, *J*(H, H) = 8.0, 1H), 6.19 (t, *J*(H, H) = 8.0, 2H), 3.69 (br, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 142.5, 140.3, 134.8, 134.7, 124.3, 124.2, 107.0, 107.0. MS (ESI): 127.1 $[M+H]^+$.

2,6-Bis(1,2-dicarbomethoxyvinylamino)-fluorobenzene (3) To a solution of **2** (1.26 g, 0.01 mol) in MeOH (100 mL) was added dimethyl acetylenedicarboxylate (2.70 mL, 0.022 mol). The mixture was heated to reflux for 24 h, and then cooled. The resulting yellow prisms were collected by filtration to yield 3.85 g (93.9%) of the product. ^{1}H NMR ($CDCl_3$, ppm): δ 9.51 (s, 2H) 6.93 (t, *J*(H, H) = 7.9, 1H), 6.63 (t, *J*(H, H) = 7.7, 2H), 5.54 (s, 2H), 3.75 (s, 6H), 3.74 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.8, 164.1, 148.8, 147.2, 146.3, 129.5, 129.4, 123.8, 123.8, 118.0, 95.3, 53.0, 51.5. MS (ESI): 411.2 $[M+H]^+$, 433.2 $[M+Na]^+$.

Dimethyl 1,8-diaza-4,5-dihydroxy-9-fluoro-2,7-anthracenedicarboxylate (4) A mixture of **3** (0.41 g, 1 mmol) and diphenyl ether (4.10 g) was heated with stirring at 240-250°C for 10 min. The product began to precipitate in the hot reaction medium. After cooling, the mixture was poured into 100 ml of light petroleum ether to complete the precipitation. The solid was filtered off, washed well with hexane and chloroform. A yield of 0.31g (89.6%) of the product was obtained. The compound was sufficiently pure to use for the next step without further purification. However, all attempts to acquire NMR spectra failed due to its poor solubility in most organic solvents. MS (ESI): 347.2$[M+H]^+$, 369.2 $[M+Na]^+$.

Dimethyl 1,8-diaza-4,5-diisobutoxy-9-fluoro-2,7-anthracene dicarboxylate (5) A mixture of **4** (1.04 g, 3 mmol), triphenylphosphine (1.89 g, 2.4 equiv.), and 2-methyl-1-propanol (0.67 mL, 2.4 equiv.) in anhydrous THF (80 mL) was cooled to 0°C under nitrogen. Diisopropyl azodicarboxylate (1.3 mL, 2.2 equiv.) was added dropwise and the mixture was stirred at 0°C for 30 min, then at room temperature for 12 h. The solvent was evaporated to dryness and the residue was purified by chromatography on silica eluting with DCM/ethyl acetate from 100:1 to 100:10 vol/vol to afford the product (1.26 g, 91.3% yield). ^{1}H NMR ($CDCl_3$, ppm): δ 9.00 (m, 1H), 7.55 (s, 2H), 4.16 (d, *J*(H, H) = 6.3, 4H), 4.10 (s, 6H), 2.42-2.32 (m, 2H), 1.21 (d, *J*(H, H) = 6.6, 12H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.8, 162.9, 162.8, 155.4, 152.7, 151.2, 136.1, 136.0, 122.1, 110.6, 110.5, 99.5, 75.3, 53.4, 28.2, 19.1. MS (MALDI-TOF): 459.6 $[M+H]^+$ 481.7 $[M+Na]^+$, 497.7 $[M+K]^+$.

1,8-diaza-4,5-diisobutoxy-2,7-anthracenedicarboxylic acid (6). Under protection from light, diester **5** (400 mg, 0.87 mmol) was dissolved in THF (40 mL). A solution of NaOH (87.3 mg) in water (10 mL) was added and the reaction was kept stirring at RT for 12 h. Acetic acid was added until the pH value is below 7. The obtained yellow precipitate was filtered and washed with water. Then the wet product was dried with a toluene azeotrope with three times to yield diacid **6**, which was used without further purification. ^{1}H NMR (DMSO-d_5, 300 MHz): δ = 8.84 (s, 1H), 7.48 (s, 2H), 4.19 (d, *J*(H, H) = 6.0, 4H), 2.30-2.21 (m, 2H), 1.13 (d, *J*(H, H) = 6.6, 12H). MS (ESI) : m/z: 431.0 $[M + H]^+$.

Hexameric oligomer (10). To a solution of the Boc monoprotected pyridine trimer amine **9**[1] (300 mg, 0.67 mmol) in dry THF (20 mL) containing DIEA (0.25 mL, 3.2 mmol) was added a solution of acid chloride **8**[2] (532 mg, 0.67 mmol) in dry THF (10 mL) via a syringe. The reaction mixture was stirred at RT overnight. The solution was evaporated and the crude was purified by flash chromatography (SiO_2) eluting with EtOAc/CH_2Cl_2 (2:98 to 5:95 vol/vol) to obtain hexameric oligomer **10** as a light yellow solid (565 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.05 (s, 1H), 11.71 (s, 1H), 9.92 (s, 1H), 9.36 (s, 1H), 9.24 (d, *J*(H, H) = 7.8, 1H), 8.92 (s, 1H), 8.61(m, 4H), 8.27 (t, *J*(H, H) = 7.8, 1H), 8.19 (d, *J*(H, H) = 7.8, 1H), 8.09 (d, *J*(H, H) = 8.7, 1H), 8.02-7.99 (m, 1H), 7.81-7.71 (m, 5H), 7.62-7.58 (m, 1H), 7.51 (d, *J*(H, H) = 8.1, 1H), 7.46 (s, 1H), 7.42 (d, *J*(H, H) = 7.8, 1H), 7.24 (s, 1H), 7.16 (s, 1H), 6.66 (t, *J*(H, H) = 8.1, 1H), 6.55 (s, 1H), 4.05-4.00 (m, 4H), 3.80-3.78 (m, 2H), 2.44-2.26 (m, 3H), 1.30-1.17 (m, 18H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.1, 161.9, 161.5, 160.4, 160.2, 159.8, 159.6, 153.1, 150.6, 149.5, 149.2, 148.5,

147.6, 147.5, 147.4, 147.2, 146.5, 143.9, 139.1, 139.0, 138.3, 138.0, 137.6, 134.1, 133.3, 127.3, 127.0, 125.4, 124.9, 124.6, 124.4, 123.4, 122.4, 121.3, 121.2, 118.3, 116.3, 115.3, 115.0, 109.4, 107.9, 107.1, 106.9, 98.2, 98.1, 96.7, 79.4, 74.5, 74.3, 73.9, 28.7, 27.2, 27.1, 26.4, 18.4, 18.3, 18.2. MS (ESI) : m/z : 1206.0 $[M+H]^+$.

Hexameric oligomer (11). Excess TFA (1.5 mL) was added dropwise to a solution of **10** (560 mg, 0.46 mmol) in CH_2Cl_2 (10 mL). The mixture was allowed to stir at room temperature for 3h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL), washed with saturated $NaHCO_3$, dried over Na_2SO_4 and then concentrated to give hexamer amine **11** as a yellow solid which was used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.08 (s, 1H), 11.87 (s, 1H), 9.90 (s, 1H), 9.57 (s, 1H), 9.20 (d, *J*(H, H) = 7.5, 1H), 9.06 (s, 1H), 8.60-8.54 (m, 4H), 8.27-8.20 (m, 2H), 8.09 (d, *J*(H, H) = 8.4, 1H), 7.81-7.67 (m, 4H), 7.59 (d, *J*(H, H) = 7.5, 1H), 7.52-7.40 (m, 4H), 7.28 (s, 1H), 7.13 (s, 1H), 6.65 (t, *J*(H, H) = 7.8, 1H), 6.26 (d, *J*(H, H) = 7.8, 1H), 4.08-3.99 (m, 4H), 3.78 (d, *J*(H, H) = 6.6, 2H), 2.45-2.25 (m, 3H), 1.27-1.16 (m, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.2, 163.1, 163.0, 162.9, 161,4, 161.2, 160.7, 160.2, 156.8, 153.9, 150.2, 149.6, 148.5, 148.4, 148.3, 147.7, 144.8, 140.0, 139.7, 139.2, 139.1, 139.0, 138.7, 134.8, 134.2, 128.1, 128.0, 126.4, 125.9, 125.5, 125.2, 124.2, 123.4, 122.3, 122.1, 119.2, 117.2, 116.4, 115.8, 110.7, 108.7, 104.7, 102.9, 99.3, 99.1, 97.8, 75.5, 75.3, 74.8, 28.1, 28.0, 19.4, 19.3, 19.2. MS (ESI): m/z : 1106.3 $[M+H]^+$.

Octameric oligomer (13). To a solution of hexamer amine **11** (520 mg, 0.47 mmol) in THF (20 mL) containing DIEA (0.25 mL, 3.2 mmol) was added a solution of acid chloride **12**[3] (381 mg, 0.58 mmol) in THF (10 mL) dropwise via a syringe. The reaction mixture was stirred at RT overnight. The solution was evaporated and the product was purified by flash chromatography (SiO_2) eluting with cyclohexane/EtOAc (1:1 vol/vol) to obtain octamer **13** (480 mg, 60% yield) as a light yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.01 (s, 1H), 11.47 (s, 1H), 10.66 (s, 1H), 10.48 (s, 1H), 9.86 (s, 1H), 9.66 (s, 1H), 9.15 (s, 1H), 8.84 (d, *J*(H, H) = 7.8, 1H), 8.89 (d, *J*(H, H) = 7.5, 1H), 8.62 (d, *J*(H, H) = 7.5, 1H), 8.53-8.46 (m, 2H), 8.34-8.27 (m, 4H), 8.20 (d, *J*(H, H) = 7.8, 1H), 8.06 (d, *J*(H, H) = 9.0, 1H), 7.66 (s, 1H), 7.64-7.50 (m, 3H), 7.42 (s, 1H), 7.37-7.33 (m, 3H), 7.23-7.20 (m, 1H), 7.11 (t, *J*(H, H) = 8.1, 1H), 7.02 (s, 1H), 6,99 (d, *J*(H, H) = 8.1, 1H), 6.73-6.70 (m, 1H), 6.66 (t, *J*(H, H) = 8.1, 1H), 6.58 (s, 1H), 4.25-4.02 (m, 6H), 3.97-3.65 (m, 4H), 2.44-2.16 (m, 5H), 1.73 (s, 9H), 1.37-1.18 (m, 24H), 1.06 (d, *J*(H, H) = 6.6, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.1, 161.6, 161.3, 161.2, 160.3, 160.2, 159.5, 152.6, 151.5, 149.4, 149.3, 149.2, 148.9, 148.1, 147.8, 147.3, 146.4, 143.6, 139.2, 138.2, 138.0, 137.8, 137.7, 136.9, 133.5, 132.7, 126.8, 126.2, 126.0, 125.7, 125.6, 125.4, 125.0, 124.9, 124.7, 124.5, 124.4, 123.1, 122.3, 121.1, 120.0, 117.5, 117.4, 117.1, 116.7, 116.2, 116.1, 116.0, 115.7, 114.8, 114.6, 108.9, 108.4, 108.0, 107.4, 98.1, 97.8, 96.4, 96.2, 80.7, 74.3, 74.2, 73.7, 73.9, 73.8, 28.7, 27.3, 27.2, 27.1, 27.0, 26.9, 18.4, 18.3, 18.2, 18.1. MS (ESI) : m/z : 1726.3 $[M+H]^+$, 1748.3 $[M+Na]^+$.

Octameric oligomer (14). Octamer **13** (250 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (10 mL), and excess TFA (1.5 mL) was added dropwise. The mixture was allowed to stir at room temperature for 3h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL), washed with saturated $NaHCO_3$, dried over Na_2SO_4 and then concentrated to give octamer amine **14** as a yellow solid which was used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.00 (s, 1H), 11.46 (s, 1H), 10.66 (s, 1H), 10.48 (s, 1H), 9.83 (s, 1H), 9.67 (s, 1H), 9.18 (s, 1H), 8.89 (d, *J*(H, H) = 8.1, 1H), 8.65 (d, *J*(H, H) = 7.5, 1H), 8.60 (d, *J*(H, H) = 7.5, 1H), 8.47 (d, *J*(H, H) = 6.9, 1H), 8.34-8.26 (m, 4H), 8.17 (d, *J*(H, H) = 8.1, 1H), 7.94-7.85 (m, 2H), 7.64 (d, *J*(H, H) = 7.2, 1H), 7.58 (s, 1H), 7.55-7.49 (m, 2H), 7.39-7.34 (m, 3H), 7.25 (s, 1H), 7.23-7.03 (m, 5H), 7.01 (s, 1H), 6.66 (t, *J*(H, H) = 7.8, 1H), 6.54 (s, 1H), 4.21-3.90 (m, 6H), 3.84-3.80 (m, 4H), 2.44-2.00 (m, 5H), 1.39-1.17 (m, 24H), 1.04 (d, *J*(H, H) = 6.6, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.9, 162.7, 162.6, 162.2, 162.0, 161.9, 161.6, 161.4, 161.3, 160.7, 160.4, 153.8, 150.4, 150.2, 149.9, 149.4, 149.1, 148.7, 148.5, 148.0, 147.3, 144.8, 140.2, 139.4, 138.9, 138.7, 138.6, 137.8, 134.6, 134.5, 134.4, 134.1, 127.8, 126.8, 126.3, 125.8, 125.7, 125.5, 124.9, 124.1, 123.2, 122.1, 121.0, 118.8, 118.3, 117.8, 117.3, 117.2, 116.6, 115.8, 115.6, 109.6, 109.1, 108.9, 108.7, 99.0, 98.8, 97.6, 97.2, 95.9, 75.1, 74.9, 74.7, 74.6, 29.7, 28.3, 28.2, 28.2, 28.1, 27.8, 19.5, 19.4, 19.3, 19.1. MS (ESI): 1626.4 $[M+H]^+$, 1648.4 $[M+Na]^+$.

Helical capsule (1). Diacid **6** (33 mg, 0.077 mmol) was suspended in anhydrous $CHCl_3$ (10 mL). 1-chloro-N,N, 2-trimethylpropenylamine (0.12 mL, 0.87 mmol) was added and the reaction was allowed to stir at RT for 3 h. The reaction mixture remains a suspension, but the reaction does work under these conditions. The solvent and excess reagents were removed under vacuum and the residue was dried under vacuum for at least 2 h to yield acid chloride **7** as a yellow-orange solid. To a solution of octamer amine **14** (200 mg, 0.12 mmol) and distilled DIEA (0.2 mL, 1.1 mmol) in dry THF (10 mL) was added dropwise at RT a solution of the freshly prepared diacid chloride **7** in THF (10 mL). The reaction was allowed to proceed at RT overnight. The solution was evaporated and the product was purified by flash chromatography (SiO_2) eluting with EtOAc/DCM (2:98 to 5:95, vol/vol) to obtain **1** as a yellowish solid (70 mg, 31% yield). ^{1}H NMR ($CDCl_3$,

300 MHz): δ = 11.68 (s, 2H), 11.10 (s, 2H), 9.91 (s, 2H), 9.75 (s, 2H), 9.72 (s, 2H), 9.55 (s, 2H), 9.33 (s, 2H), 9.16 (s, 1H), 9.03 (t, *J*(H, H) = 6.9, 2H), 8.60 (s, 2H), 8.38 (d, *J*(H, H) = 7.8, 2H), 8.22 (d, *J*(H, H) = 9.0, 2H), 8.02 (d, *J*(H, H) = 7.5, 2H), 7.78 (s, 2H), 7.72-7.54 (m, 8H), 7.25-7.23 (m, 5H), 7.18-7.02 (m, 11H), 6.93-6.84 (m, 4H), 6.75 (t, *J*(H, H) = 7.8, 2H), 6.69 (s, 2H), 6.61-6.56 (m, 4H), 6.25 (s, 2H), 6.21 (d, *J*(H, H) = 7.5, 2H), 4.45-4.20 (m, 8H), 3.96-3.86 (m, 4H), 3.70 (t, *J*(H, H) = 7.8, 2H), 3.62-3.52 (m, 8H), 3.42 (t, *J*(H, H) = 7.8, 2H), 2.63-2.48 (m, 2H), 2.29-2.25 (m, 4H), 2.04-1.97 (m, 6H), 1.44-1.22 (m, 60H), 0.99-0.94 (m, 12H). MS (TOF-ESI): m/z: 1823.6 $[M + 2H]^{2+}$, 1835.6 $[M+H+Na]^{2+}$, 1840.6 $[M+H+K]^{2+}$, 1846.6 $[M+2Na]^{2+}$, 1851.6 $[M+K+Na]^{2+}$, 3669.86 $[M+Na]^{+}$. Crystals suitable for x-ray analysis were obtained upon diffusing hexane into $CDCl_3$.

X-ray crystallography

Data were collected using a Rigaku Rapid diffractometer equipped with an MM007 microfocus rotating anode generator with monochromatized Cu-K_α radiation (1.54178 Å), varimax optics and a RAPID image plate for three of the structures. The data collected on the crystal of 1 grown in pure water were collected on a Cu-K_α Bruker AXS rotating anode with Helios optics and a Platinum CCD camera. The data collection, unit cell refinement and data reduction were performed using the CrystalClear and Proteum2 software packages. The positions of non-H atoms were determined by the program SHELXD[4^4] and the position of H atoms were deduced from coordinates of the non-H atoms and confirmed by Fourier Synthesis. H atoms were included for structure factor calculations but not refined.

Single crystals of **1** (helical capsule) cocrystallized with encapsulated 1,3-propanediol (size 0.2 x 0.2 x 0.4 mm), 1,4-butanediol (size 0.2 x 0.2 x 0.2 mm), 1-amino-4-butanol (size 0.3 x 0.2 x 0.2 mm) and water (size 0.2 x 0.2 x 0.2) were all grown from chloroform/n-hexane and mounted on a cryoloop under oil and frozen into a N_2 stream at 123K for the structures complexed with 1,3-propanediol, 1,4-butanediol, 1-amino-4-butanol and at 100K for the structure with water.

Crystals of **1** crystallized with 1,3-propanediol belong to the Triclinic space group *P*-1 with unit cell dimensions: a = 18.8716 (6) Å, b = 25.0352 (2) Å, c = 27.0598 (8) Å, α = 80.890 (7)°, β = 84.806 (8)°, γ = 70.220 (6)°, V = 11869.1 (5) $Å^3$, and Z = 2 (FW is 4675.79, ρ = 1.308 Mg m^{-3}). Reflections were collected from 1.65° ≤ θ ≤ 73.04° for a total of 105326 of which 39624 were unique (R_{int} = 0.1873) having I > 2σ (I); number of parameters is 2702. Final *R* factors were R_1 = 0.2237 (I > 2σ (I)), wR_2 = 0.4256 (all data), GOF = 1.431 from SHELX, maximal residual electron density is 0.709 e $Å^{-3}$. CCDC # 677158

Crystals of **1** crystallized with 1,4-butanediol belong to the Triclinic space group *P*-1 with unit cell dimensions: a = 18.6735 (3) Å, b = 24.7835 (3) Å, c = 26.9042 (7) Å, α = 80.820 (6)°, β = 85.094 (6)°, γ = 70.093 (4)°, V = 11553.1 (5) $Å^3$, and Z = 2 (FW is 4702.65, ρ = 1.352 Mg m^{-3}). Reflections were collected from 2.97° ≤ θ ≤ 73.06° for a total of 114450 of which 39372 were unique (R_{int} = 0.2867) having I > 2σ (I); number of parameters is 2689. Final *R* factors were R_1 = 0.2245 (I > 2σ (I)), wR_2 = 0.5367 (all data), GOF = 1.252 from SHELX, maximal residual electron density is 0.807 e $Å^{-3}$. CCDC # 677155

Crystals of **1** crystallized with 1-amino-4-butanediol belong to the Triclinic space group *P*-1 with unit cell dimensions: a = 18.8692 (12) Å, b = 25.2437 (14) Å, c = 27.1316 (16) Å, α = 81.545 (4)°, β = 86.193 (4)°, γ = 69.820 (4)°, V = 11996.7 (12) $Å^3$, and Z = 2 (FW is 3963.12, ρ = 1.097 Mg m^{-3}). Reflections were collected from 6.57° ≤ θ ≤ 73.98° for a total of 165540 of which 42733 were unique (R_{int} = 0.1949) having I > 2σ (I); number of parameters is 2803. Final *R* factors were R_1 = 0.1402 (I > 2σ (I)), wR_2 = 0.3486 (all data), GOF = 0.677 from SHELX, maximal residual electron density is 0.634 e $Å^{-3}$. CCDC # 677157

Crystals of **1** crystallized with water belong to the Triclinic space group *P*-1 with unit cell dimensions: a = 22.460 (3) Å, b = 24.252 (4) Å, c = 24.970 (4) Å, α = 76.770 (7)°, β = 89.903 (8)°, γ = 73.669 (8)°, V = 12678 (3) $Å^3$, and Z = 2 (FW is 4960.5, ρ = 1.299 Mg m^{-3}). Reflections were collected from 1.82° ≤ θ ≤ 46.74° for a total of 69091 of which 20826 were unique (R_{int} = 0.0549) having I > 2σ (I); number of parameters is 2849. Final *R* factors were R_1 = 0.2250 (I > 2σ (I)), wR_2 = 0.5325 (all data), GOF = 1.535 from SHELX, maximal residual electron density is 1.533 e $Å^{-3}$. CCDC # 677156

References

[1] V. Berl, I. Huc, R. G. Khoury, J.-M. Lehn, *Chem. J. Eur.* **2001**, 7, 2798.

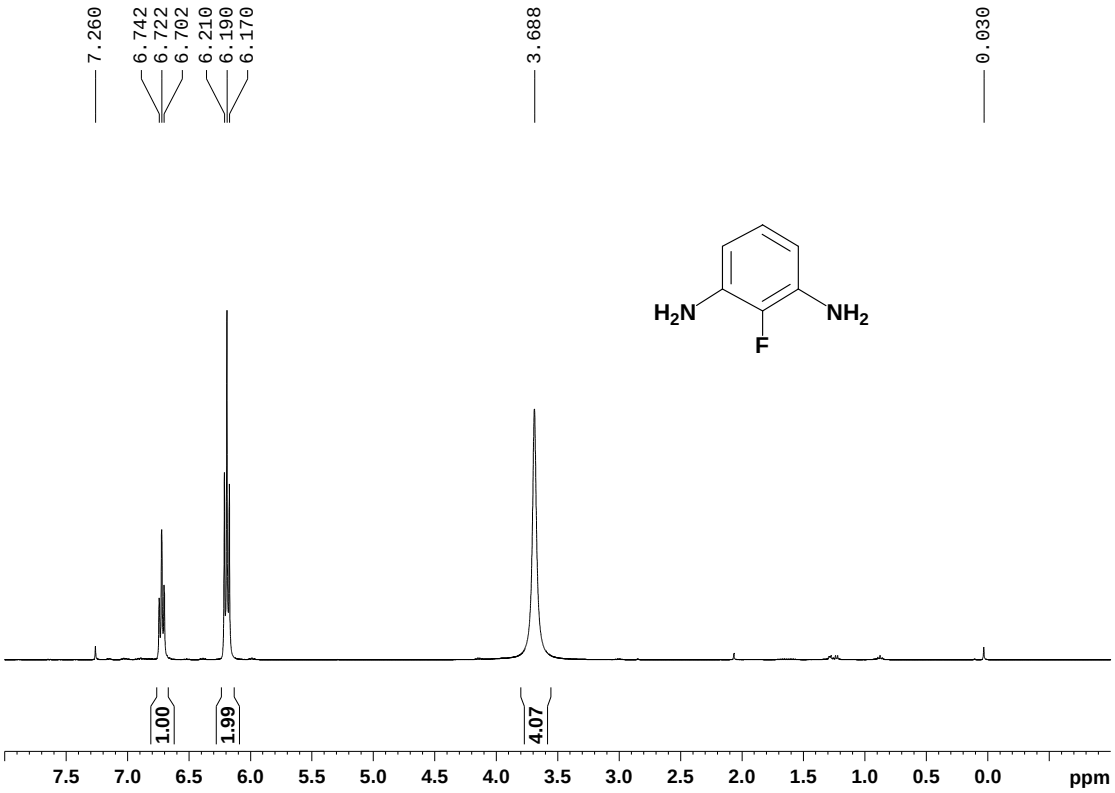
[2] H. Jiang, J.-M. Léger, C. Dolain, P. Guionneau, I. Huc *Tetrahedron* **2003**, *59*, 8365.

[3] Q. Gan, C. Bao, B. Kauffmann, A. Grélard, J. Xiang, S. Li, I. Huc, H. Jiang, *Angew. Chem. Int. Ed.* **2008**, DOI: 10.1002/anie.200704938.

[4] G. M. Sheldrick, *Acta Cryst.* 2008, *A64*, 112-122.

^{1}H spectra of all relevant synthetic intermediates and title compounds.

2,6-Diaminofluorobenzene (2)



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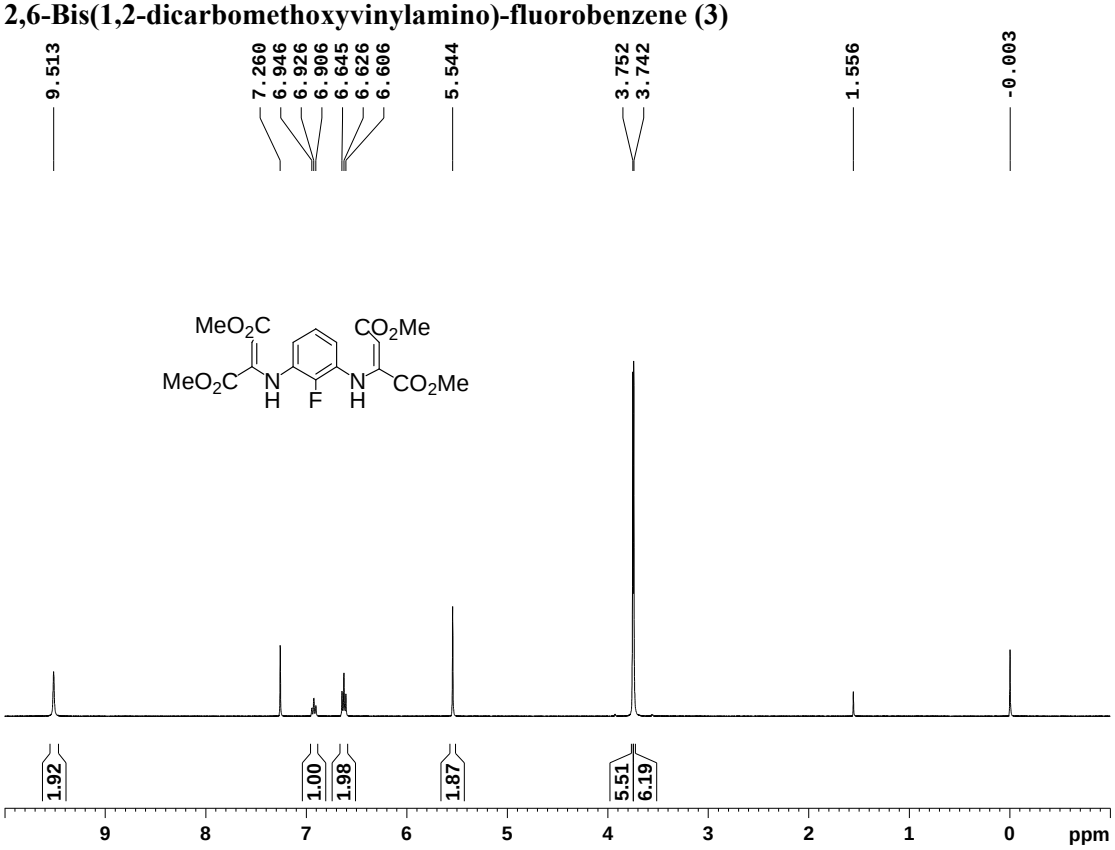

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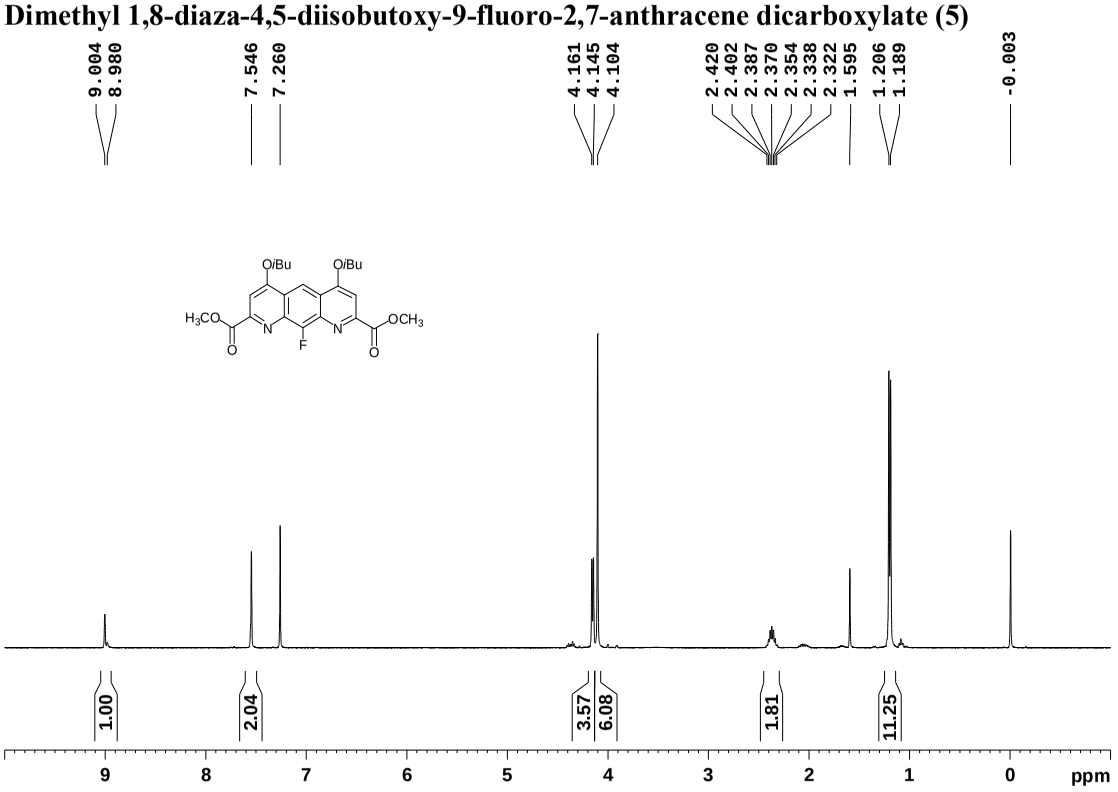

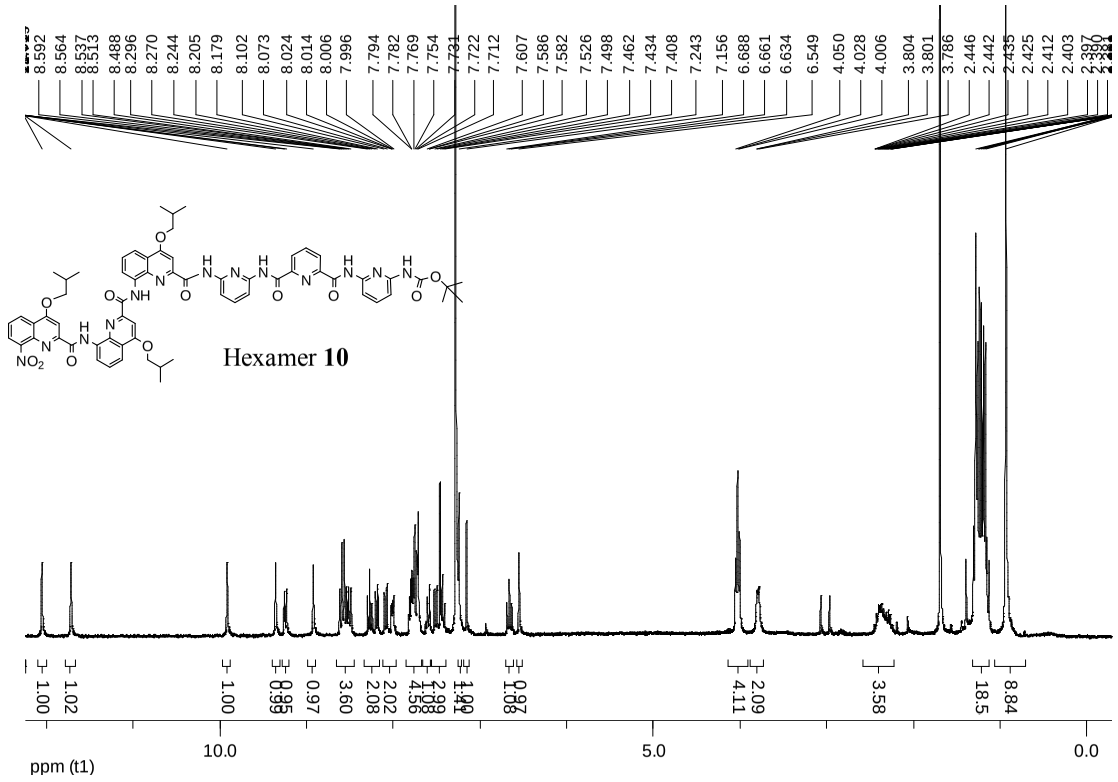

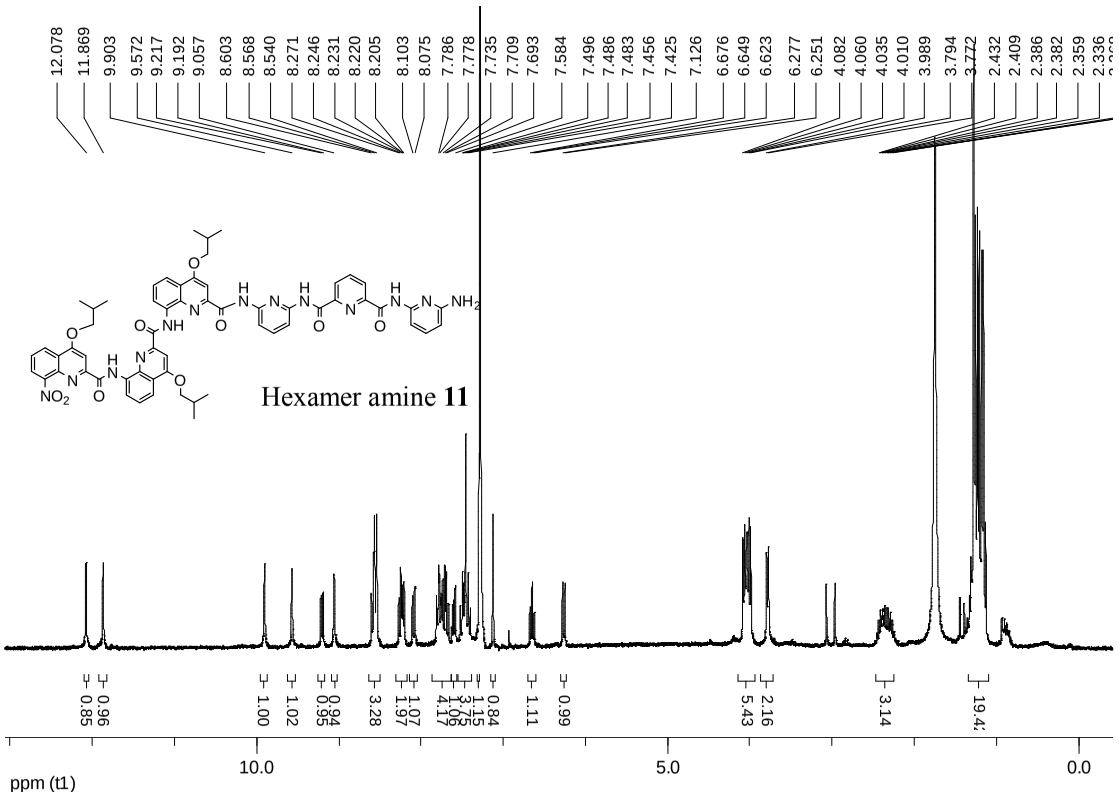
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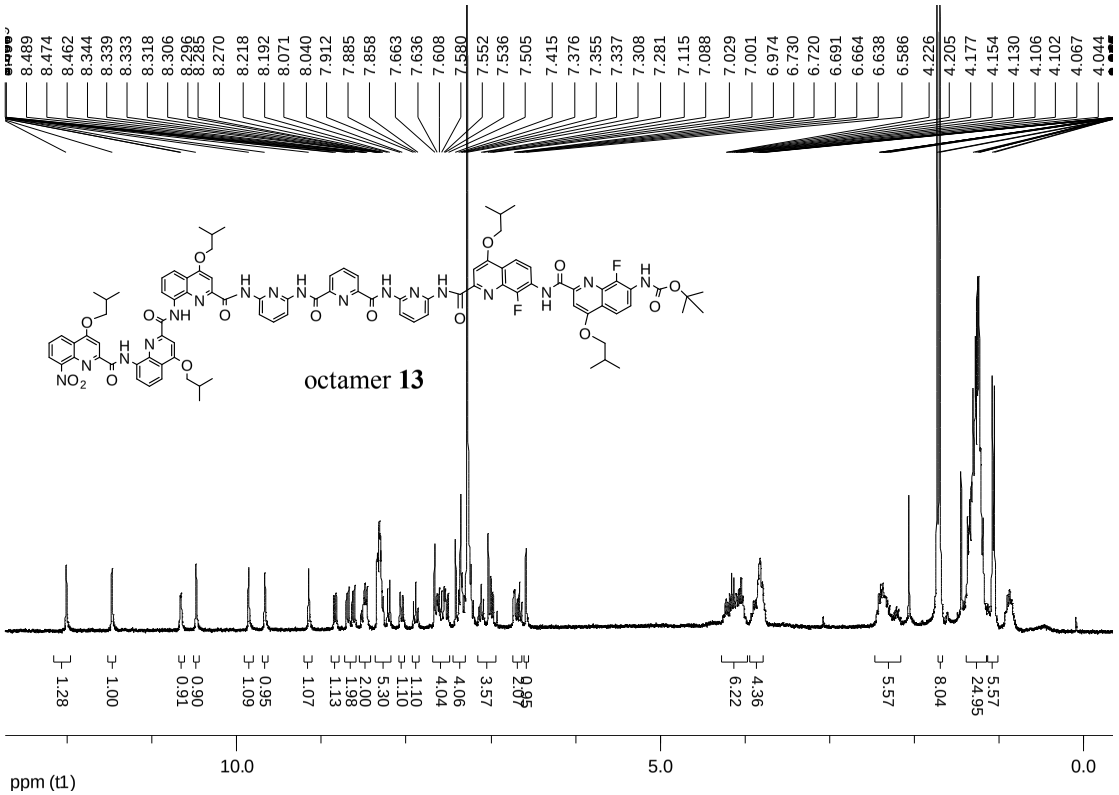
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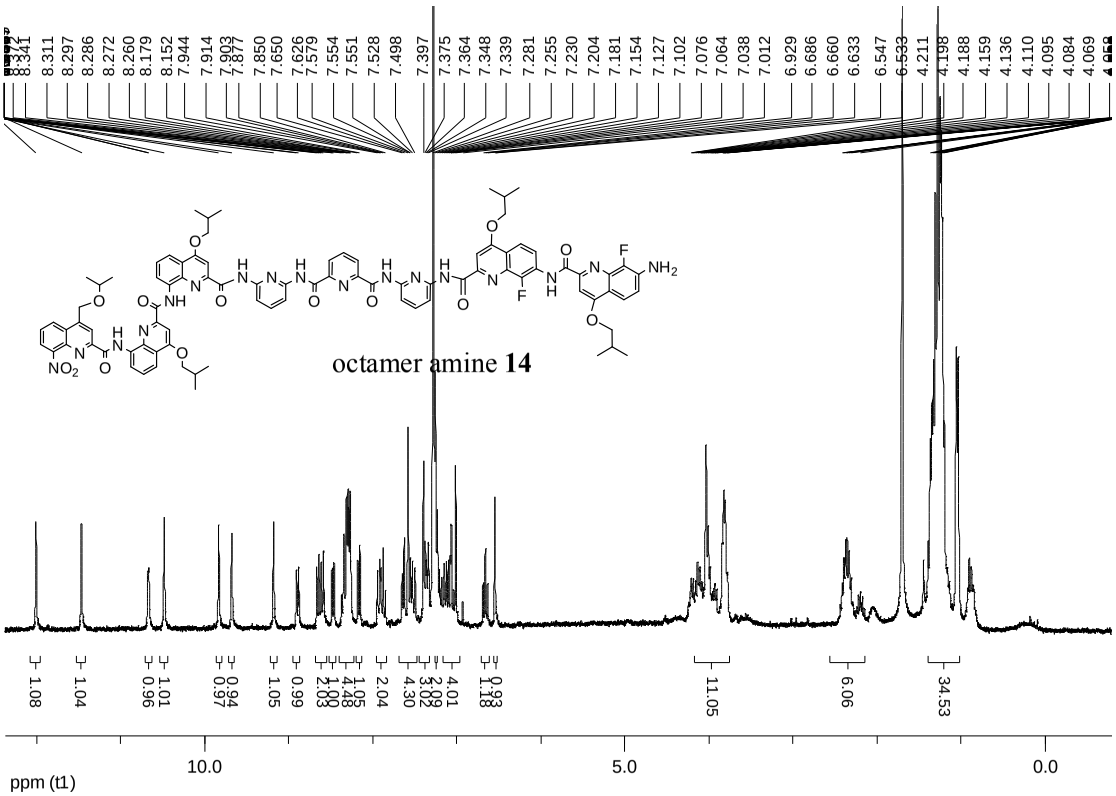
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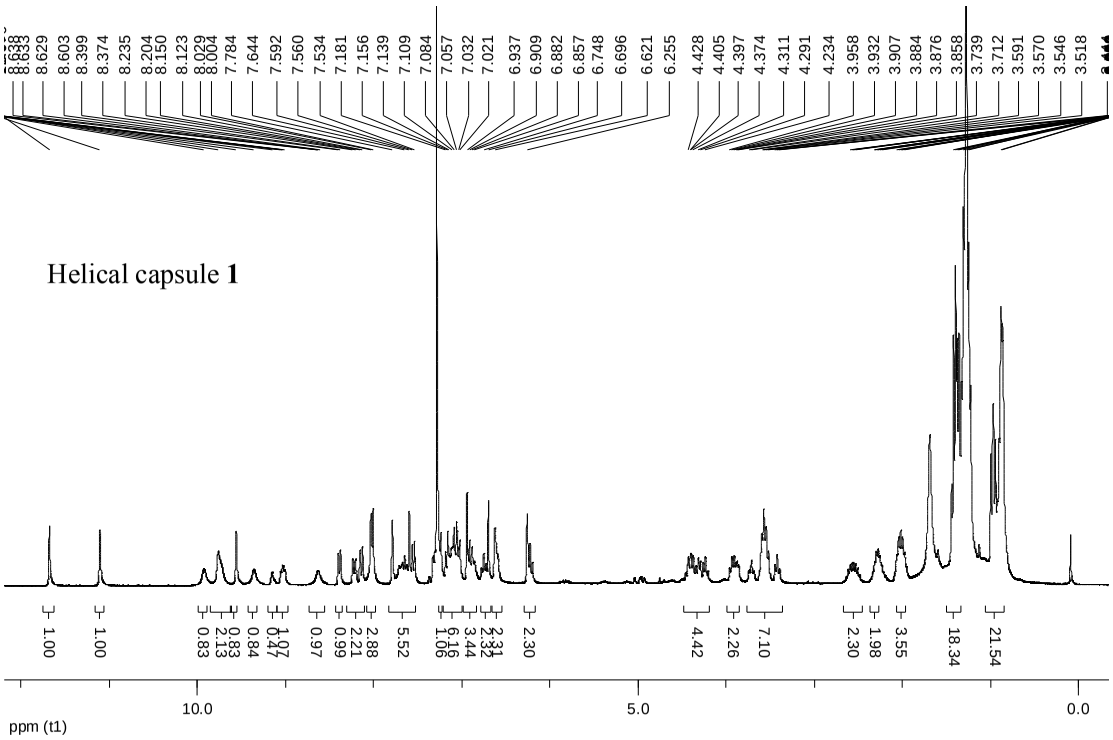
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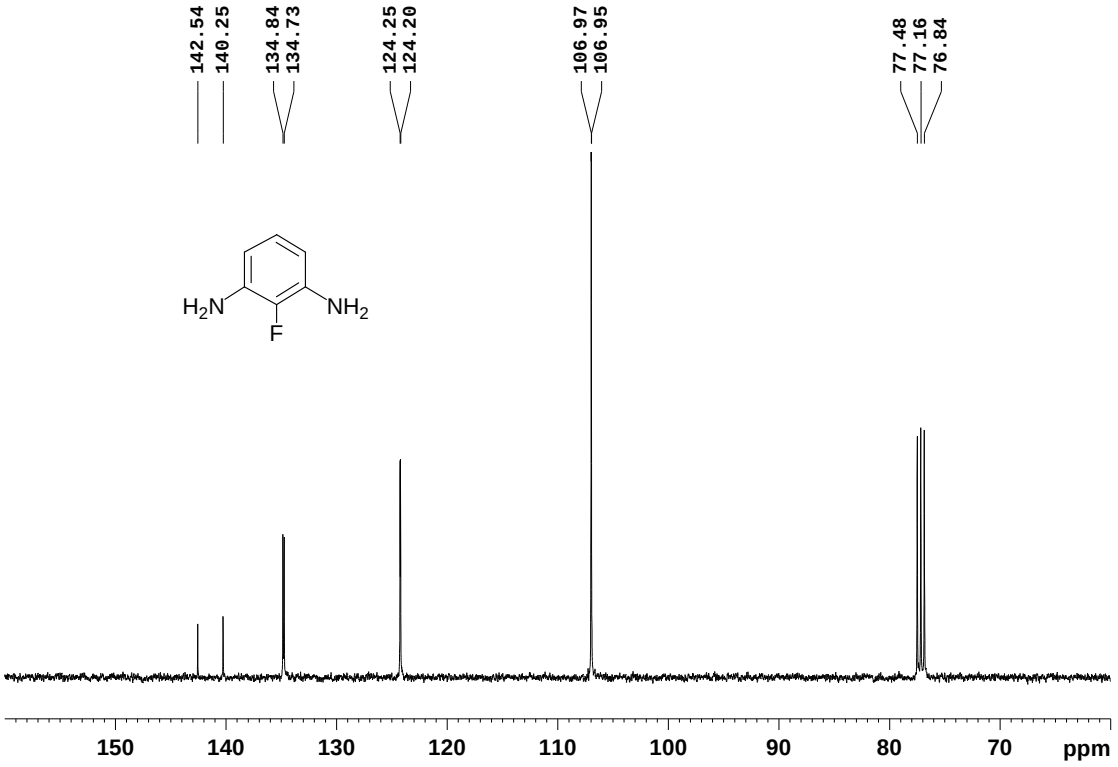
^{13}C spectra of all relevant synthetic intermediates and title compounds.
The splitting of some ^{13}C signals corresponds to scalar couplings with ^{19}F

2,6-Diaminofluorobenzene (2)



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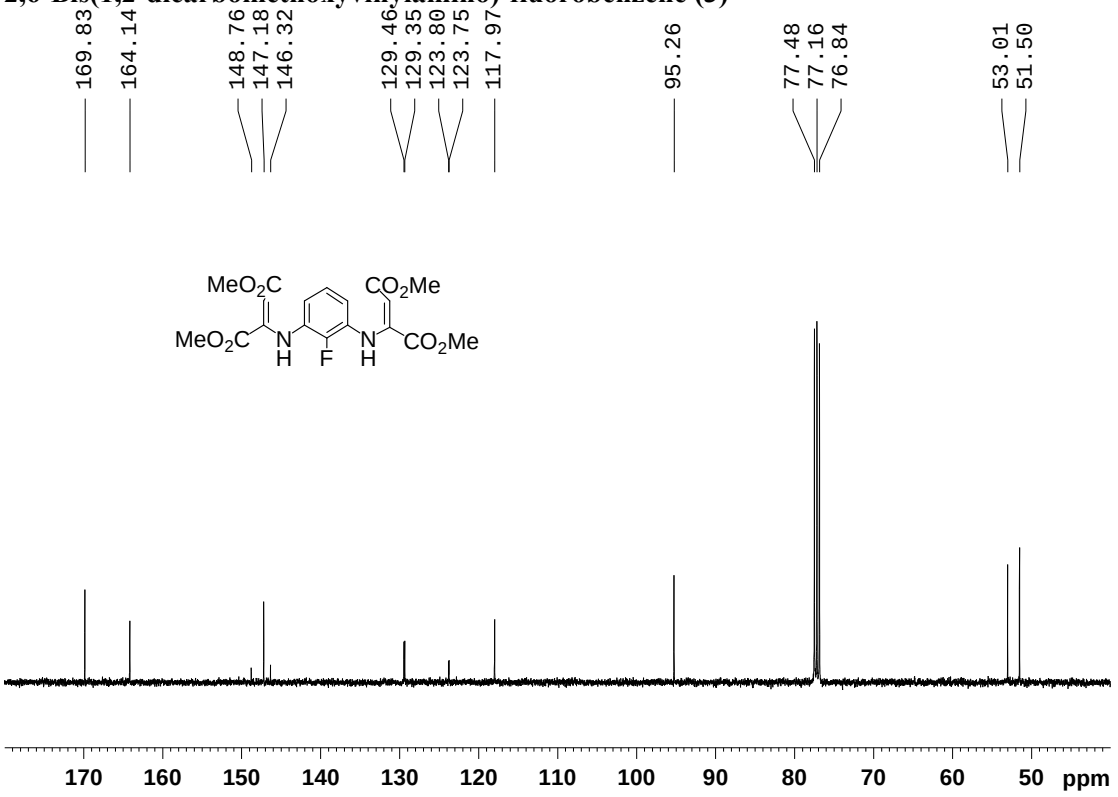
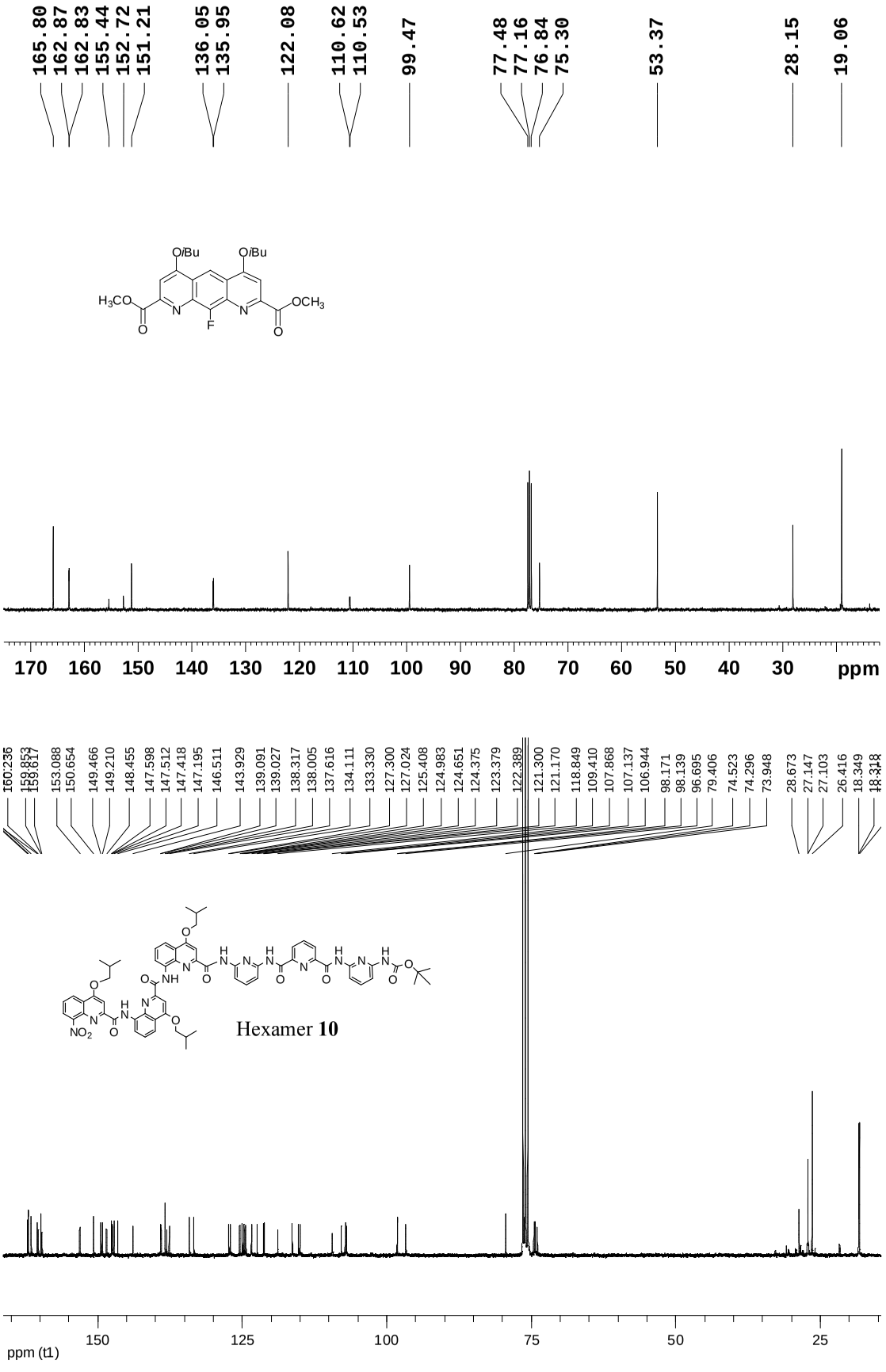
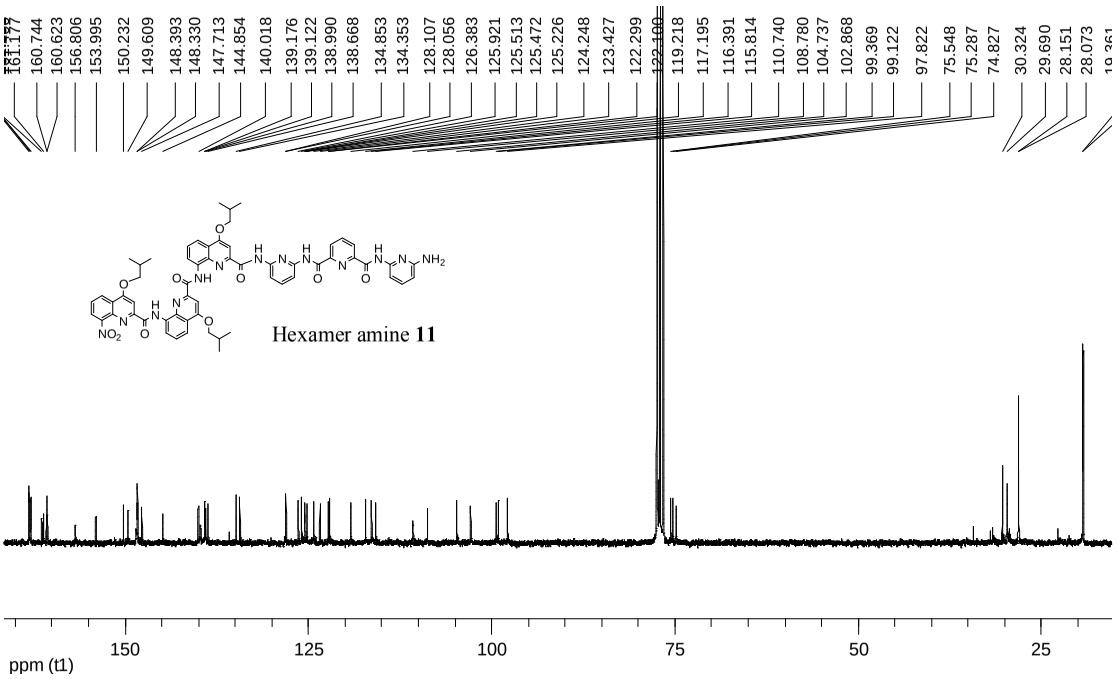


Dimethyl 1,8-diaza-4,5-diisobutoxy-9-fluoro-2,7-anthracene dicarboxylate (5)

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122.108
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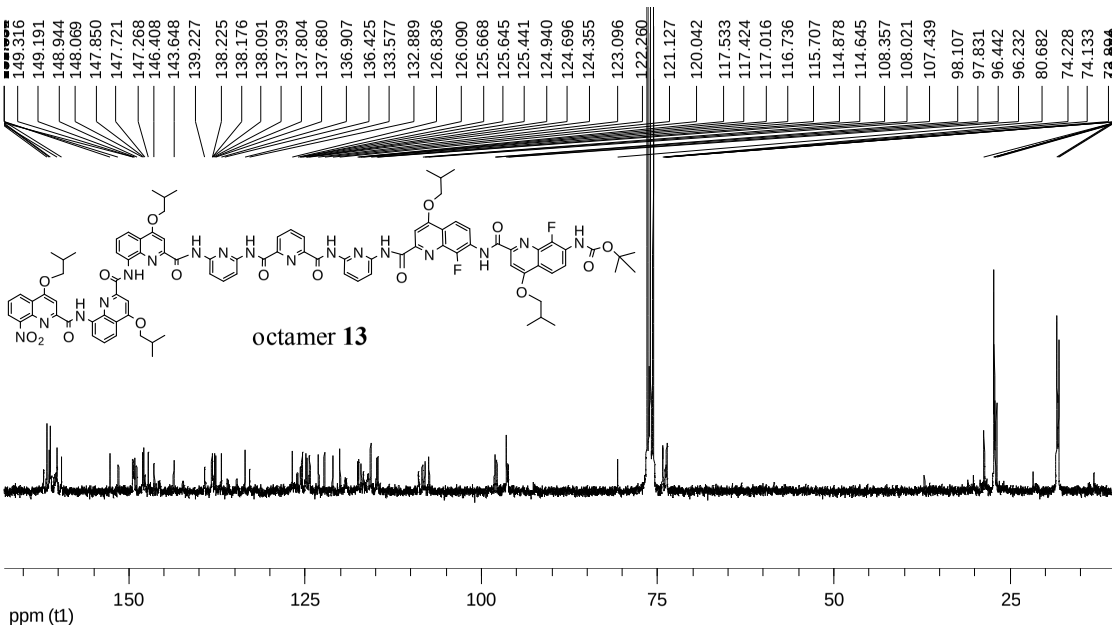
50
25
ppm (t1)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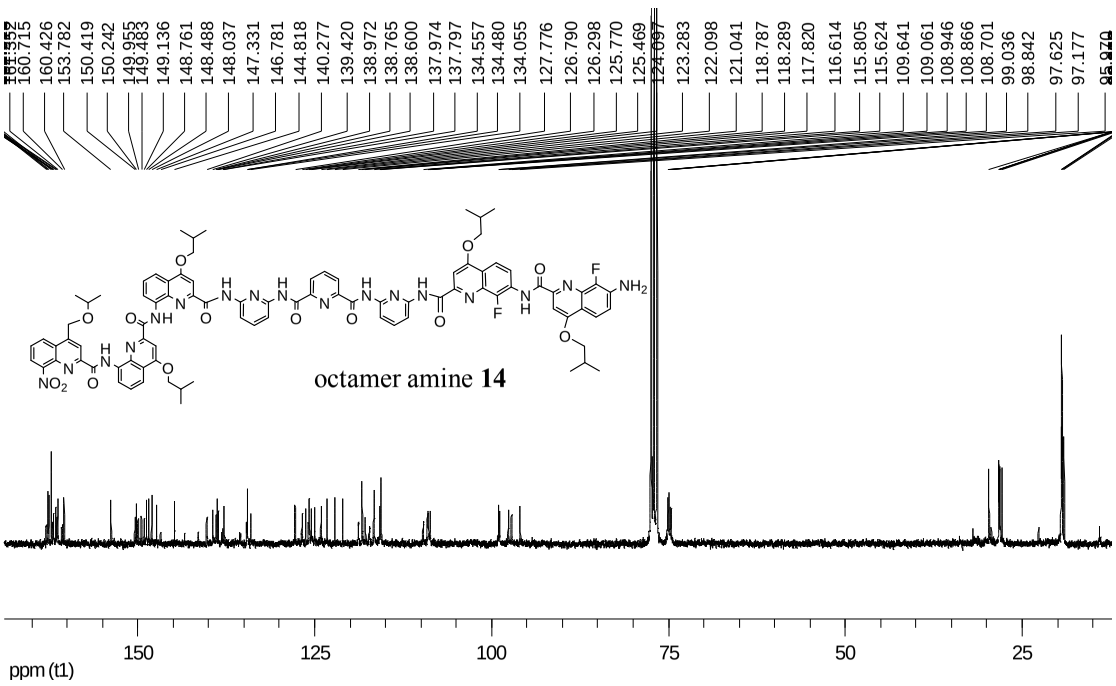
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50
25
ppm (t1)