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Supporting Information

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Quadruple and double helices of 8-fluoroquinoline oligoamides

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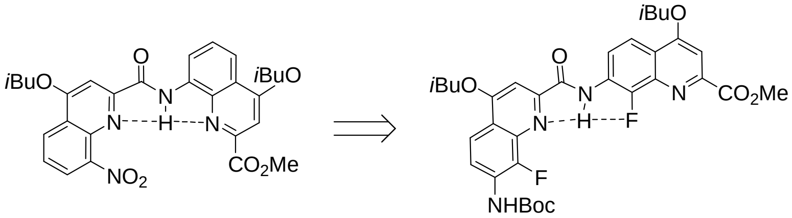
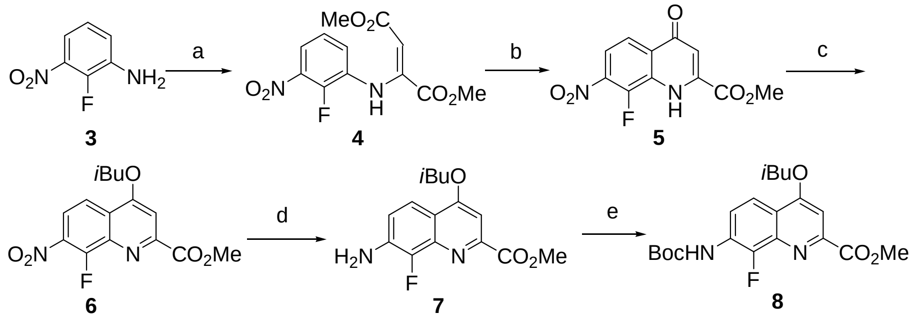
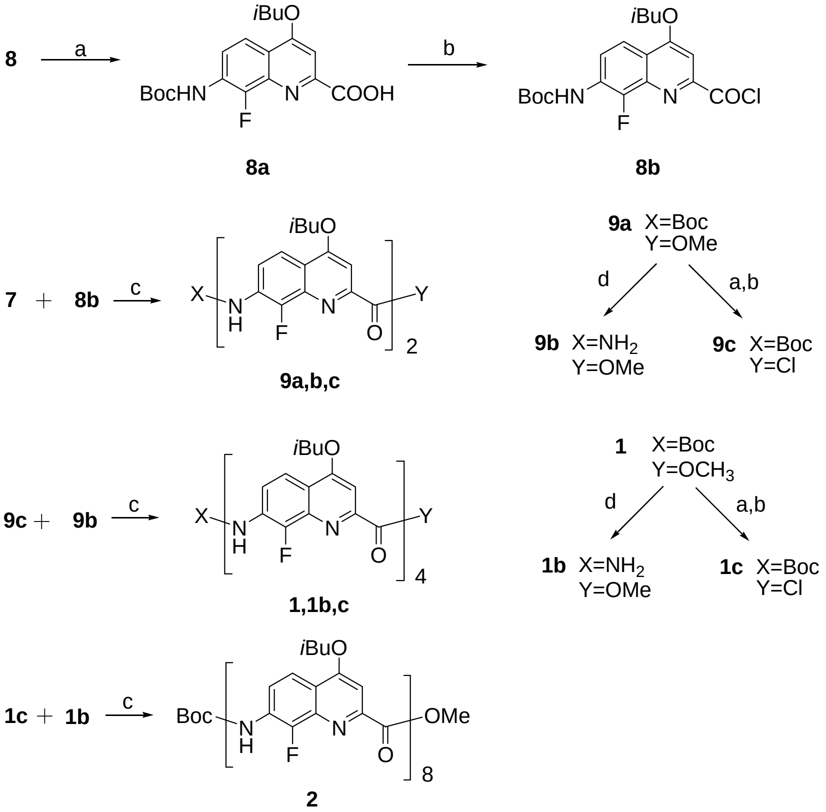
Synthetic schemes



Scheme S1 Expected change in curvature upon shifting the amine function from position 8 to position 7 in 2-quinolinecarboxamide oligomers.



Scheme S2. Synthesis of fluoroquinoline monomer **8**: a) dimethylacetylene dicarboxylate, MeOH, Δ; b) diphenyl ether, reflux; c) *i*BuOH, DIAD, PPh_3, THF, r.t.; d) Fe, AcOH, 120°C; e) di-*tert*-butyl dicarbonate, dioxane, heating for 7days.



Scheme S3. Synthesis of oligofluoroquinoline amides. a) NaOH, THF/water, rt; b) 1-chloro-N,N,2-trimethylpropenylamine, DCM, rt, 2h; c) DIEA, DCM; d) TFA/DCM, rt.

NMR studies of aggregation

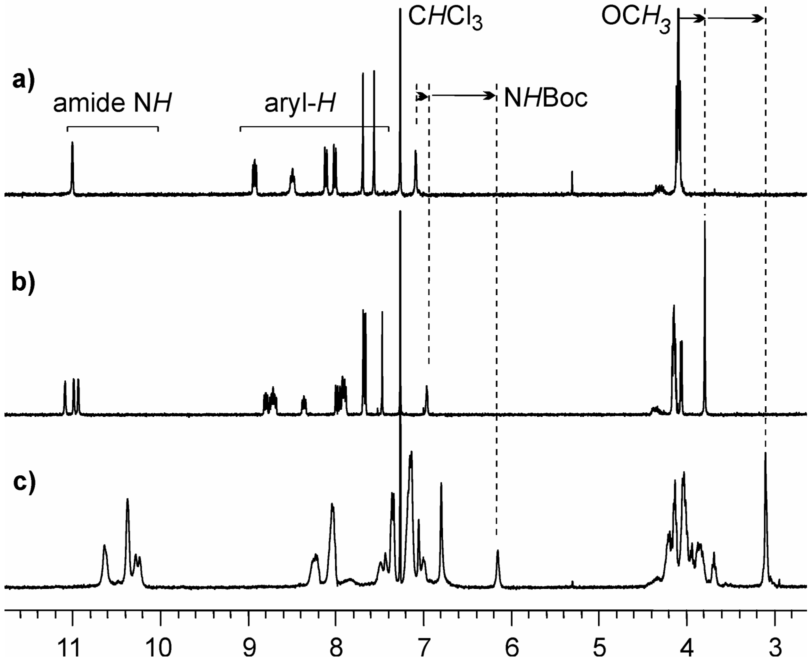


Figure S1: 400 MHz ^{1}H NMR spectra of a) dimer **9a**, b) tetramer **1**, c) octamer **2** in CDCl$_3$ (2mM) at 298K.

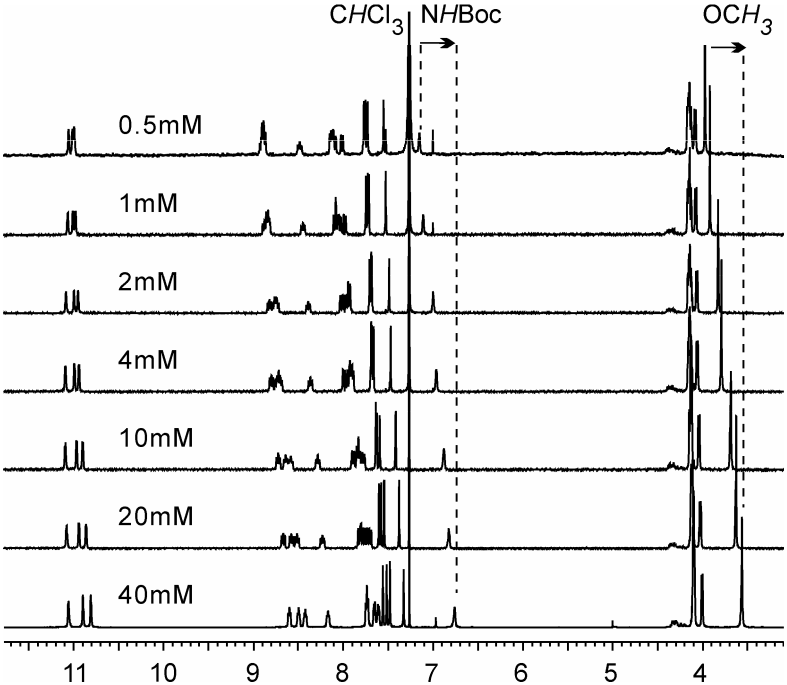


Figure S2 Part of 400MHz ^{1}H NMR of tetramer **1** at various concentrations in $CDCl_3$ at 25°C.

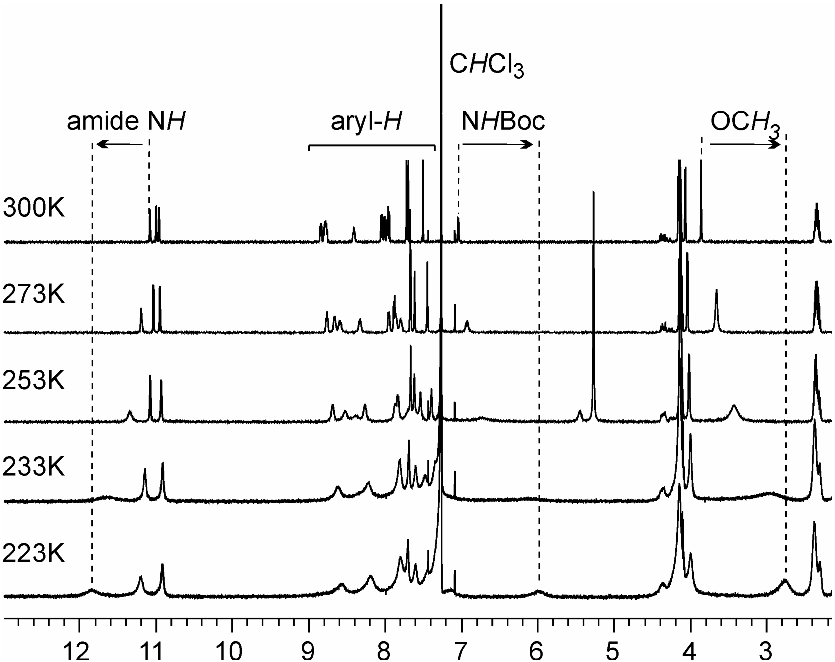


Figure S3 Temperature dependent ^{1}H NMR spectra (600 MHz) of tetramer **1** (2mM) in $CDCl_3$. The sharp signal at 5.4 ppm observed at 253K is not identified but likely associated with the solvent or water. It appears in the 243-253K range in the spectra of **1** and in the spectra of **2**.

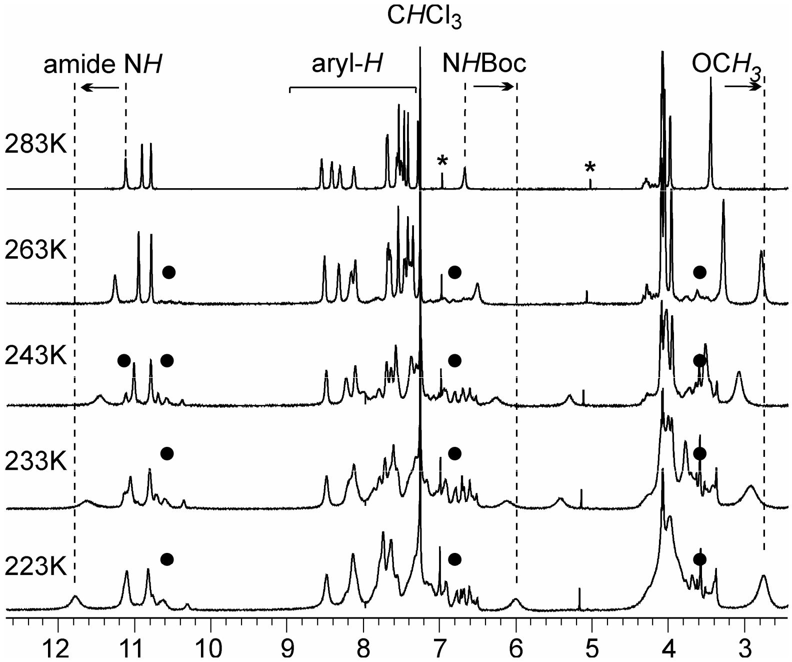


Figure S4 Temperature dependent ^{1}H NMR spectra (600 MHz) of tetramer **1** (40 mM) in $CDCl_3$. The black circles indicate signals of a new species appearing at low temperature. The stars indicate solvent signals

Table S1 Changes of chemical shifts of tetramer 1 with various concentrations at 298K and 223K.

	$\Delta\delta_{max}$ [a] (BocNH)	$\Delta\delta_{max}$ (OCH_3)	$\Delta\delta_{max}$ (aromatic)
2 mM	-1.07	-1.09	-0.60
10 mM	-0.77	-0.80	-0.38
20 mM	-0.77	-0.85	-0.42
40 mM	-0.75	-0.80	-0.35

[a] $\Delta\delta_{max} = \delta_{223K} - \delta_{298K}$

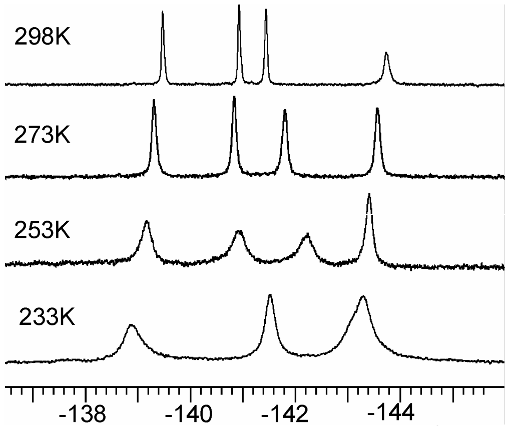


Figure S5. Temperature dependent ^{19}F NMR spectra (400 MHz) of tetramer **1** (10mM) in $CDCl_3$.

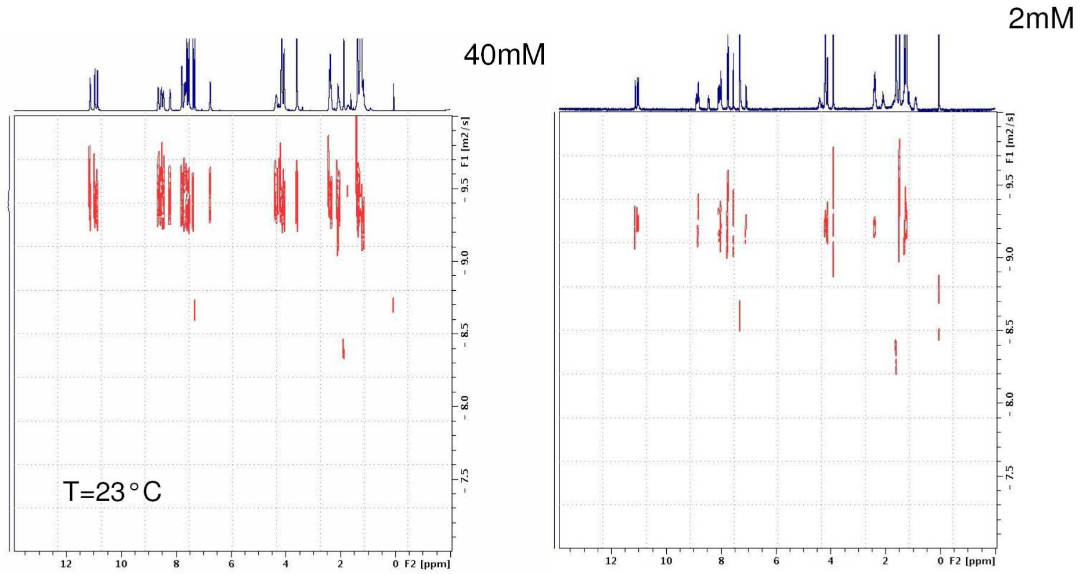


Figure S6. ^{1}H DOSY NMR spectra (400 MHz) of tetramer **1** at 40 mM and 2 mM in CDCl$_3$.

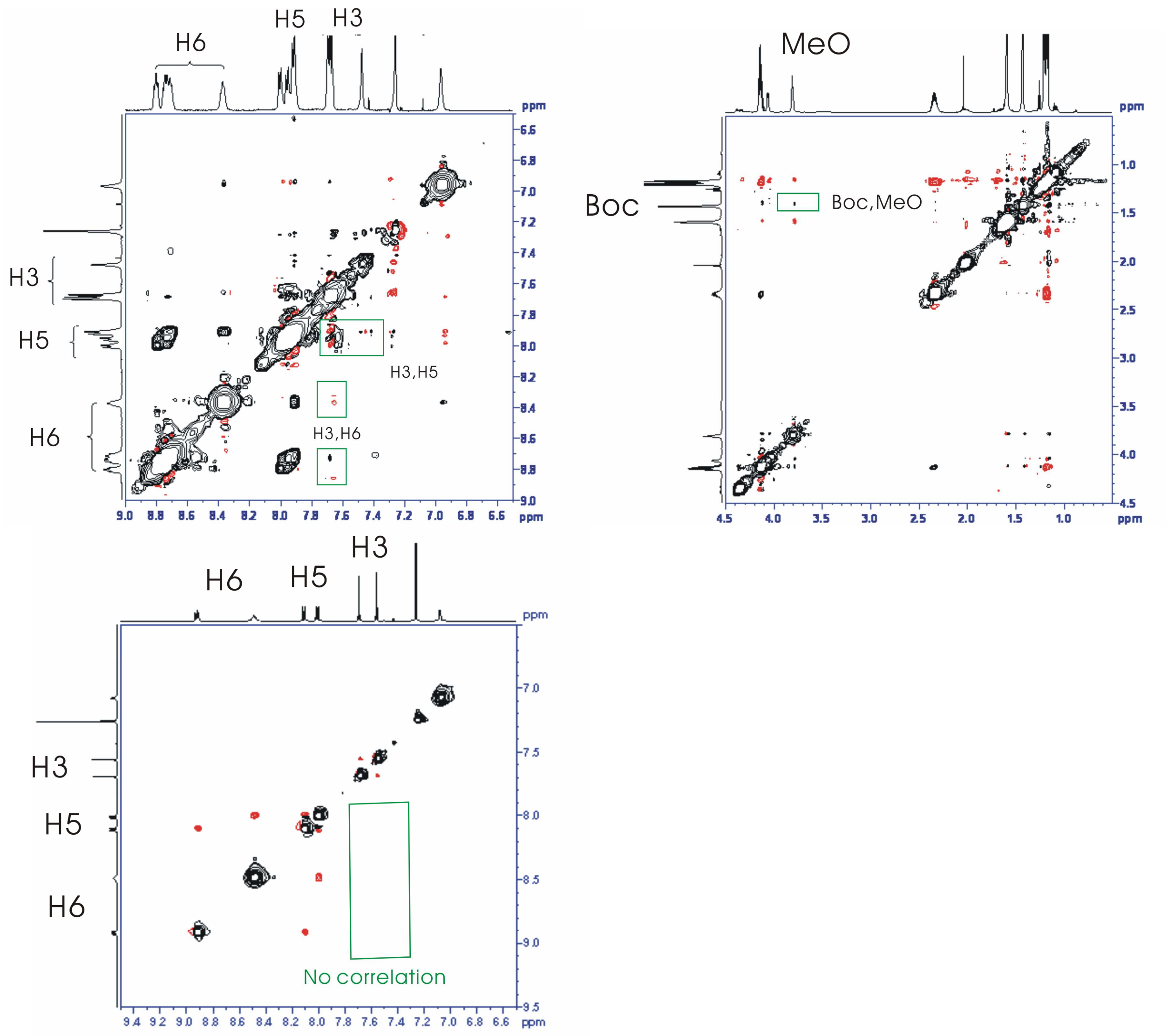


Figure S7. Partial NOESY spectra of tetramer **1** (top) and dimer **9a** (bottom) (4mM, CDCl$_3$, 600MHz). Correlations between H3 and H5/H6 are observed with **1** and not with **9a** suggesting that they correspond to intermolecular contacts associated with the aggregation of **1**, and not to intramolecular correlations. The N*H*Boc – C*H*$_3$ ester correlation in **1** (top right) is consistent both with the single helical conformation and with a head-to-tail arrangement of a duplex.

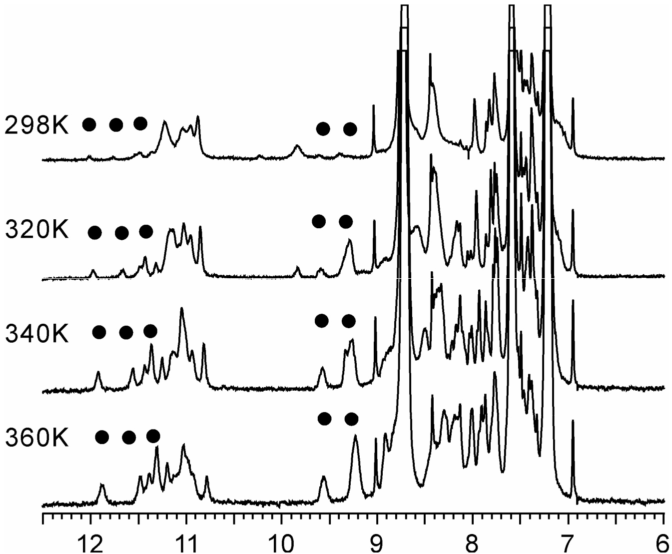


Figure S8. Partial ^{1}H NMR spectra (300 MHz) of Octamer **2** (1mM) in pyridine-d$_5$ at various temperatures, showing a second set of signals appearing downfield (•).

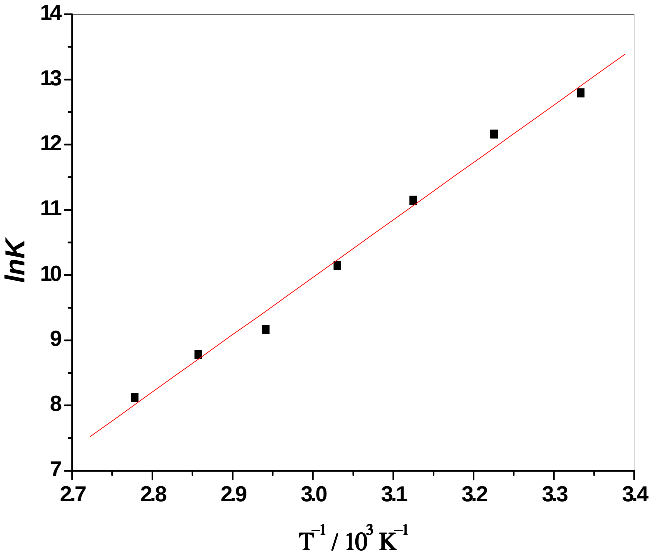


Figure S9. Van't Hoff plot of the dimerization of octamer **2** in pyridine-d$_5$. Experimental data were fitted to the Van't Hoff equation using linear regression analysis (red line, R=0.996). ΔH and ΔS were extracted to be -73.2 kJ.mol^{-1} and -136.3 J.K^{-1}, respectively.

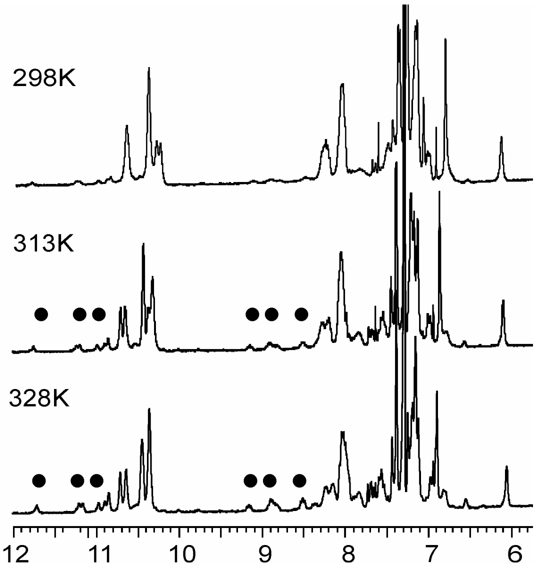


Figure S10. Partial ^{1}H NMR spectra (400 MHz) of Octamer **2** (1mM) in $CDCl_3$ at various temperatures, showing a second set of signals appearing downfield (•).

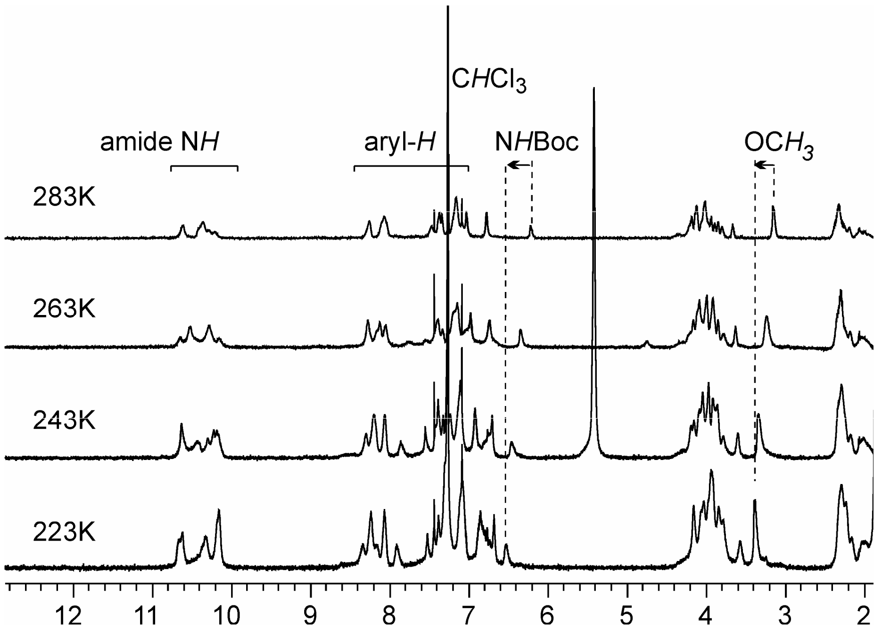


Figure S11 Temperature dependence of ^{1}H NMR spectra (400 MHz) of octamer **2** (1mM) in $CDCl_3$. The sharp signal at 5.4 ppm observed at 243K is not identified but likely associated with the solvent or water. It appears in the 243-253K range in the spectra of **1** and in the spectra of **2**.

Experimental section

General. All reactions were carried out under a dry nitrogen atmosphere. NMR spectra were recorded on Bruker AVANCE 600 (600 MHz), Bruker DMX 300 (300 MHz) and Bruker AVANCE 400 (400 MHz) 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). EI, ESI mass spectra and MALDI-TOF were obtained on GCT□LC-MS 2010 and Autotlex □ spectrometers, respectively.

2-Fluoro-3-nitroaniline 3 To glacial acetic acid (80 mL) was added 2-Fluoro-1,3-dinitrobenzene[1] (4.98 g, 26.8 mmol). The mixture was heated to 120°C. Reduced iron powder (4.35 g, 2.9 equiv) was added in portions over a period of 40 min and the mixture was heated to reflux for 2.5 h. The hot reaction mixture was poured into cold water and extracted with ether (3×50 mL). The combined organic fractions were washed with brine (5×40 mL), dried over Na_2SO_4, filtered and evaporated to dryness to give 2.4 g (57.6% yield) of the crude product as a brown-black solid. Recrystallization from carbon tetrachloride afforded 1.95 g (46.8%) of pure 2-fluoro-3-nitroaniline, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ

7.37-7.33 (m, 1H), 7.05-6.99 (m, 2H), 4.03 (s, 2H).[2] ^{13}C NMR ($CDCl_3$): δ 146.0, 142.6, 137.2, 137.0., 124.1, 124.1, 121.5, 121.5, 124.2, 124.2. MS (EI): 156.

Dimethyl N-(2-fluoro-3-nitro-phenyl)-amino-fumarate 4 To a solution of **3** (1.56 g, 0.010 mol) in MeOH (30 mL) was added dimethyl acetylenedicarboxylate (1.36 mL, 0.011 mol). After 18 h of stirring, the mixture was heated to reflux for 6 h and cooled. The resulting yellow prisms were collected by filtration to yield 2.0 g (67%) of the product. ^{1}H NMR ($CDCl_3$): δ 9.64 (s, 1H), 7.74-7.70 (m, 1H), 7.19-7.12 (m, 2H), 5.72 (s, 1H), 3.78 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 169.5, 163.4, 149.3, 146.7, 145.5, 138.1, 138.1, 131.3, 131.2, 127.2, 127.2, 123.8, 123.7, 120.3, 120.3, 97.7, 53.1, 51.7. MS (ESI) : 299.2 [M+H]$^+$, 321.1 [M+Na]$^+$, 337.1 [M+K]$^+$.

Methyl 8-fluoro-7-nitro-4-(*1H*)-quinolone-2-carboxylate 5 A mixture of **4** (3.00 g, 0.010mmol) and diphenyl ether (30.00 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 diluted with 100 ml of light petroleum ether to complete the precipitation. The solid was filtered off, washed well with hexane, and recrystallized from methanol in which it is sparingly soluble yield to give 2.3 g (86%) of the product. ^{1}H NMR (DMSO-d6): δ 12.85-12.56 (br, 1H), 8.20-8.10 (m, 3H), 3.96 (s, 3H). MS (ESI) : 267 [M+H]$^+$, 289 [M+Na]$^+$.

Methyl 8-fluoro-4-isobutoxy-7-nitro-2-quinolinecarboxylate 6 A mixture of **5** (3.64 g, 13.7 mmol) and triphenylphosphine (3.95 g, 1.1 equiv.), and 2-methyl-1-propanol (1.52 mL, 1.2 equiv.) in anhydrous THF (40 mL) was cooled to 0°C under nitrogen. Diisopropyl azodicarboxylate (2.96 mL, 1.1 equiv.) was added dropwise and the mixture was stirred at 0°C for 30 min, then at room temperature for 2 h. The solvent was evaporated. The product was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2 to yield 3.61 g (82%) of a white solid. ^{1}H NMR ($CDCl_3$): δ 8.10-8.04(m, 1H), 7.68 (s, 1H), 4.08 (d, *J*=16.4 Hz, 2H), 4.06 (s, 3H), 2.53-2.27 (m, 1H), 1.14 (d, *J*=6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 165.4, 162.2, 162.8, 153.9, 151.6, 151.1, 139.5, 139.4, 136.6, 126.5, 121.8, 121.8, 118.0, 117.9, 104.0, 76.1, 53.6, 28.2, 19.2. MS (ESI) : 323.2 [M+H]$^+$.

Methyl 7-amino-8-fluoro-4-isobutoxy-2-quinolinecarboxylate 7. The nitro quinoline **6** (0.32 g, 1.0 mmol) was dissolved in glacial acetic acid (9 mL) and the solution was heated to 120°C Reduced iron powder (0.17 g, 3.0 mmol) was added in one portion and the mixture was stirred at 120°Cfor 2 h. The hot mixture was poured into water, and the precipitate was filtered off and washed with cold water to give 0.23 g (80%) of the product as a yellow solid which was used without additional purification. ^{1}H NMR ($CDCl_3$): δ 7.86 (d, *J*=11.9 Hz, 1H), 7.41 (s, 1H), 7.10 (t, *J*=11.1 Hz, 1H), 4.15 (br, 2H), 4.04 (s, 3H), 4.02 (d, *J*=6.6 Hz, 2H), 2.30-2.24 (m, 1H) 2.53-2.27 (m, 1H), 1.12 (d, *J*=6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 166.5, 162.8, 149.7, 145.6, 142.3, 139.8, 139.7, 135.0, 134.8, 119.7, 117.7, 117.7, 116.0, 99.1, 75.1, 53.3, 28.2, 19.3. MS (ESI): 293.1 [M+H]$^+$, 315.2 [M+Na]$^+$, 331.1 [M+K]$^+$.

Methyl 7-(*tert*-butoxycarbonylamino)-8-fluoro-4-isobutoxy-2-quinolinecarboxylate 8 A solution of **7** (0.44 g, 1.5 mmol) in dioxane (30 mL) containing di-*tert*-butyl-dicarbonate (1.64 g, 7.5 mmol) was heated at 95°C for 7 days. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to afford the pure product (0.56 g, 95□). ^{1}H NMR ($CDCl_3$): δ 8.50 (t, *J*=8.0 Hz, 1H), 7.98 (d, *J*=9.3 Hz, 1H), 7.51 (s, 1H), 7.05 (d, *J*=1.2 Hz, 1H), 4.06 (s, 3H), 4.05 (d, *J*=6.9 Hz, 2H), 2.32-2.26 (m, 1H), 1.57 (s, 9H), 1.14 (d, *J*=6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 166.0, 162.6, 152.2, 149.8, 146.9, 144.4, 138.6, 138.5, 127.6, 127.5, 120.2, 118.6, 117.4, 100.3, 81.5, 75.2, 53.2, 28.2, 28.1, 19.2. MS (ESI): 393.2 [M+H]$^+$.

Dimer 9a. Monomer **8** (1.35 g, 3.44 mmol) was dissolved in a mixture of THF (60 mL) and H_2O (6 mL). To this solution was added NaOH (0.344 g, 2.5eq). The solution was stirred at room temperature for 5h. Then solution was neutralized with 1N HCl to pH = 4~5, and concentrated under reduced pressure to remove THF. H_2O (30 mL) was added to the residue. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were dried over Na_2SO_4, filtered, then evaporated to give monomer acid **8a** as a yellowish solid. It was dried in vacuo, and then dissolved in CH_2Cl_2 (40 mL). 1-chloro-*N*,*N*,2-trimethyl-propenylamine (0.92 g, 2 .0 eq) was added. The reaction mixture was stirred at RT for 2 h resulting in a homogeneous solution, and then evaporated to provide the corresponding acid chloride **8c**. To a solution of the monomer amine **7** (0.95 g, 3.26 mmol) in CH_2Cl_2 (40 mL) containing DIEA (2.3 mL, 13.04 mmol) was added a solution of acide chloride **8c** in CH_2Cl_2 (40 mL) via cannula. The reaction mixture was stirred at RT overnight. The solution was evaporated and the product was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2. Yield 2.01 g (95%) of a white solid. ^{1}H NMR ($CDCl_3$): δ 11.00 (s, 1H), 8.94-8.90 (d, *J*=9.2 Hz, *J*=2.4 Hz 1H), 8.497 (m, 1H), 8.11 (d, *J*=9.3 Hz, 1H), 8.01 ((d, *J*=9.3 Hz, 1H), 7.68 (s, 1H), 7.56 (s, 1H), 7.09 (s, 1H), 4.10 (d, *J*=17.3 Hz, 4H), 4.08 (s, 3H), 2.34-2.28 (m, 2H), 1.59 (m, 9H), 1.15 (t, *J*=6.2 Hz, 6H).

^{13}C NMR ($CDCl_3$): δ 165.9, 162.9, 162.9, 162.3, 162.2, 162.0, 152.1, 150.6, 149.6, 147.7, 146.4, 145.2, 143.8, 138.3, 138.2, 137.2, 137.1, 127.4, 127.3, 126.7, 126.6, 120.2, 119.7, 119.2, 118.3, 117.1, 100.3, 97.4, 81.4, 75.2, 75.1, 53.1, 28.2, 28.1, 28.0, 19.1. MS (ESI): 653.3 $[M+H]^+$.

Tetramer 1 Dimer **9a** (0.84 g 1.29 mmol) was dissolved in CH_2Cl_2 (10 mL), and excess TFA (5 mL) was added. The mixture was stirred 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 evaporated to give dimer amine **9b** as a yelllow solid. It was dried in vacuo, and used without further purification. Separately, dimer **9a** (0.89 g, 1.37 mmol) was dissolved in a mixture of THF (50 mL) and H_2O (5 mL). NaOH (0.137 g, 3.43 mmol) was added, and the solution was stirred at room temperature for 5h. The solution was neutralized with 1N HCl to pH = 4~5, then concentrated under reduced pressure to remove THF. H_2O (30 mL) was added to the residue. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were dried over Na_2SO_4 and then evaporated to give the corresponding dimer acid as a yellowish solid. It was dried in vacuo, and then dissolved in CH_2Cl_2 (40 mL). To this solution was added 1-chloro-*N*,*N*, 2-trimethylpropenylamine (0.36 g, 2.74 mmol). The reaction mixture was stirred at RT for 2 h resulting in a homogeneous solution, then evaporated to provide the corresponding acid chloride **9c**. To a solution of the dimer amine **9b** in CH_2Cl_2 (40 mL) containing DIEA (0.89 mL, 5.16 mmol) was added a solution of acid chloride **9c** in CH_2Cl_2 (40 mL) via cannula. The reaction mixture was stirred at RT overnight. The solution was evaporated and the product was purified by flash chromatography (SiO_2) eluting with CH_2Cl_2/EtOAc, 20:1. Yield 1.39 g (92%) of a white solid. ^{1}H NMR (4mM, $CDCl_3$): δ 11.08 (s, 1H), 10.98 (s, 1H), 10.93 (s, 1H), 8.31-8.67 (m, 3H), 8.36 (t, *J*=6.9 Hz, *J*=2.0 Hz, 1H), 8.00-7.88 (m, 4H), 7.68 (s, 1H), 7.67 (s, 1H), 7.65 (s, 1H), 7.47 (s, 1H), 6.96 (s, 1H), 4.16-4.05 (m, 8H), 3.79 (s, 3H), 2.38-2.29 (m, 4H), 1.42 (s, 9H), 1.22-1.17 (m, 24H). ^{13}C NMR ($CDCl_3$): δ 166.1, 163.0, 162.8, 162.2, 162.1, 152.0, 150.9, 150.7, 149.4, 148.1, 147.7, 147.3, 146.2, 145.6, 145.3, 144.8, 143.7, 138.4, 138.3, 137.2, 137.1, 136.9, 127.3, 127.2, 126.7, 126.7, 126.6, 119.5, 119.4, 119.2, 119.0, 118.9, 118.3, 116.2, 116.6, 100.2, 97.9, 97.6, 81.2, 75.4, 75.3, 75.2, 52.8, 28.4, 28.3, 28.1, 19.4. MS (MALDI-TOF) : 1195.6 $[M+Na]^+$, 1211.5 $[M+K]^+$.

Octamer 2 was prepared from tetramer 1 via saponification on one hand and TFA treatment on the other hand to get the tetramer acid and tetramer amine, respectively. The synthetic procedures are the same as used for the synthesis of **1**. Yield > 80%. ^{1}H NMR (4 mM, $CDCl_3$): δ 10.65 (s, 1H), 10.61 (s, 1H), 10.37 (s, 3H), 10.31 (s, 2H), 8.22 (br, 2H), 8.03 (br, 4H), 7.85 (br, 1H), 7.50-7.34 (m, 5H), 7.14 (br, 7H), 7.05 (s, 1H), 6.98 (br, 1H), 6.80 (s, 3H), 6.14 (s, 1H), 4.41-3.67 (m, 16H), 3.10 (s, 3H), 2.41-2.26 (m, 8H), 1.33-1.11 (m,41H). ^{13}C NMR ($CDCl_3$): δ 165.5, 162.1, 161.9, 161.7, 161.6, 161.4, 161.3, 161.1, 160.7, 151.6, 150.5, 150.2, 149.5, 149.3, 148.9, 148.1, 146.8, 146.6, 146.3, 145.3, 144.2, 144.0, 143.7, 142.8, 136.8, 136.4, 136.1, 136.0, 135.7, 126.2, 126.1, 125.8, 118.6, 118.4, 118.0, 117.8, 117.6, 117.5, 117.3, 115.6, 99.3, 98.0, 97.7, 97.5, 97.3, 96.8, 80.9, 75.1, 74.9, 74.7, 52.2, 28.5, 28.4, 28.3, 28.3, 28.2, 27.8, 19.6, 19.6, 19.5, 19.5, 19.4, 19.3, 19.3, 19.2, 19.2, 19.1, 19.1. MS (MALDI-TOF) : *m/*z 2236.8 $[M+H+Na]^+$, 2252.7 $[M+H+K]^+$

X-ray crystallography

Data were collected using a Rigaku Rapid diffractometer equipped with an MM007 micofocus rotating anode generator with monochromatized Cu-K_α radiation (1.54178 Å) and varimax optics. The data collection, unit cell refinement and data reduction were performed using the CrystalClear software package. The positions of non-H atoms were determined by the program SHELXS 87 and the position of the 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** (single helix), $[C_{62}H_{64}N_8O_{11}F_4(C_6H_5Cl)(H_2O)_3]$, were grown from chlorobenzene /n-hexane. A single colorless crystal of dimensions 0.3 × 0.2 × 0.2 mm was selected, mounted on a cryloop under oil and frozen into a N_2 stream at 223K. Crystals belong to the Triclinic space group P-1 with unit cell dimensions: a = 13.2847 (17) Å, b = 15.545 (2) Å, c = 16.933 (2) Å, α = 101.885 (3)°, β = 99.133 (5)°, γ = 97.076 (4)°, V = 3334.3 (7) Å^3, and Z = 2 (FW is 1333.76, ρ = 1.328 Mg m^{-3}). Reflections were collected from 2.72° ≤ θ ≤ 72.83° for a total of 45852 of which 12240 were unique (R_{int} = 0.2385) having I > 2σ (I); number of parameters is 859. Final *R* factors were R_1 = 0.1477 (I > 2σ (I)), wR_2 = 0.4603 (all data), GOF = 1.356 from SHELX, maximal residual electron density is 0.638 e Å^{-3}. CCDC deposition #665055

Single crystals of **1** (quadruple helix), $[C_{135}H_{133}N_{16}O_{35.55}Cl_2F_8]$, were grown from toluene/1,2-dichloroethane/n-hexane. A single colorless crystal of dimensions 0.1 × 0.2 × 0.3 mm was selected, mounted on a cryloop under oil and frozen into a N_2 stream at 223K. Crystals belong to the Orthorhombic space group Fdd2 with unit cell dimensions: a = 45.7987 (6) Å, b = 40.4084 (5) Å, c = 40.8397 (4) Å, α = 90°, β = 90°, γ = 90°, V = 75580 (2) Å^3, and Z = 48 (FW is 2771.46, ρ = 0.974 Mg m^{-3}). Reflections were collected from 2.90° ≤ θ ≤ 73.23° for a total of 177150 of which 35050 were unique (R_{int} = 0.1385) having I > 2σ (I);

number of parameters is 1764. Final *R* factors were $R_1 = 0.1653$ (I > 2σ (I)), $wR_2 = 0.4430$ (all data), GOF = 1.352 from SHELX, maximal residual electron density is 0.432 e $Å^{-3}$. CCDC deposition #665054

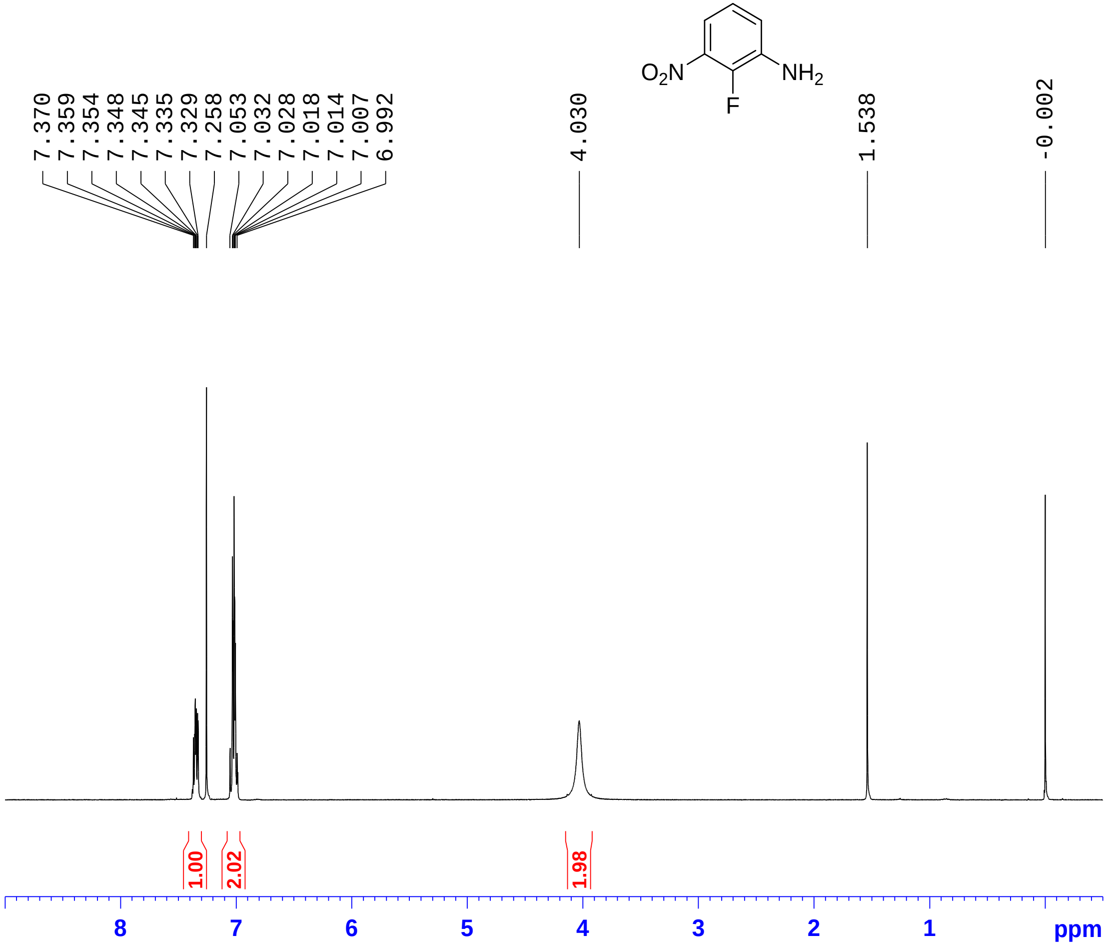
Single crystals of **2** (double helices), [$C_{944}H_{928}N_{128}O_{152}F_{64}$], were grown from 1,2 dichloroethane/n-hexane. A single colorless crystal of dimensions 0.1 × 0.2 × 0.2 mm was selected, mounted on a cryloop under oil and frozen into a N_2 stream at 223K. Crystals belong to the triclinic space group P-1 with unit cell dimensions: a = 25.391 (13) Å, b = 26.509 (13) Å, c = 27.909 (17) Å, α = 85.87 (3)°, β = 63.32 (3)°, γ = 62.56 (3)°, V = 14680 (2) $Å^3$, and Z = 2 (FW is 21511.84, ρ = 1.217 Mg m^{-3}). Reflections were collected from 6.60° ≤ θ ≤ 72.30° for a total of 153208 of which 47937 were unique ($R_{int} = 0.1655$) having I > 2σ (I); number of parameters is 3503. Final *R* factors were $R_1 = 0.1339$ (I > 2σ (I)), $wR_2 = 0.3812$ (all data), GOF = 0.660 from SHELX, maximal residual electron density is 0.695 e $Å^{-3}$. CCDC deposition #665053

References

1 J. F. K. Wilshire, *Aust. J. Chem.* **1967**, *20*, 2089–2811.

2 M. Hudlicky, H. M. Bell, *J. Fluorine Chem.* **1974**, *4*, 19–23.

^{1}H and ^{13}C NMR spectra of all relevant synthetic intermediates and title compounds.



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Current Data Parameters
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EXPNO                   53
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070725
Time                 14.08
INSTRUM              AV400
PROBHD       5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              11990.407 Hz
FIDRES            0.182959 Hz
AQ               2.7329011 sec
RG                   574.7
DW                  41.700 usec
DE                    6.00 usec
TE                   300.9 K
D1              2.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.50 usec
PL1                  -1.00 dB
SFO1           400.1332010 MHz

F2 - Processing parameters
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SF             400.1300106 MHz
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PC                    1.00
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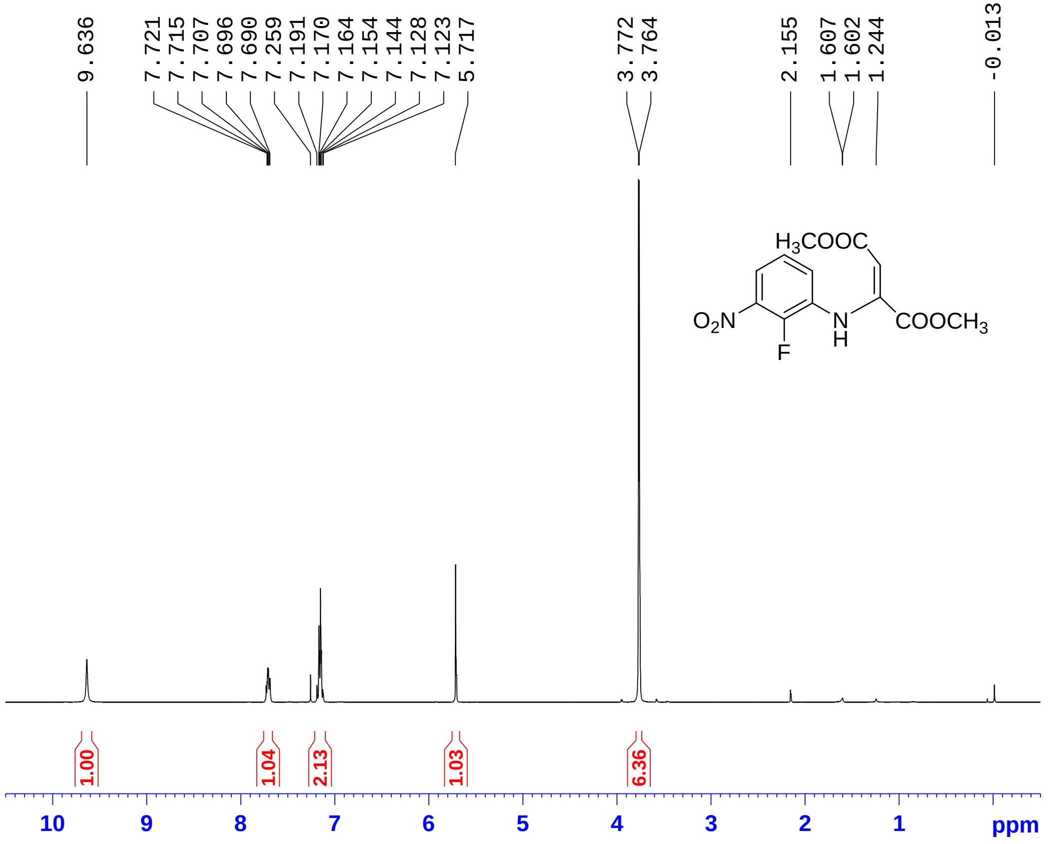

```
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EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070615
Time                    8.08
INSTRUM                AV400
PROBHD       5 mm BBO BB-1H
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                10822.511 Hz
FIDRES              0.165138 Hz
AQ                 3.0278132 sec
RG                     143.7
DW                    46.200 usec
DE                      6.00 usec
TE                     300.6 K
D1                4.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.00 usec
PL1                    -4.00 dB
SFO1             400.1332010 MHz

F2 - Processing parameters
SI                     32768
SF               400.1300092 MHz
WDW                       EM
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LB                      0.30 Hz
GB                         0
PC                      0.10
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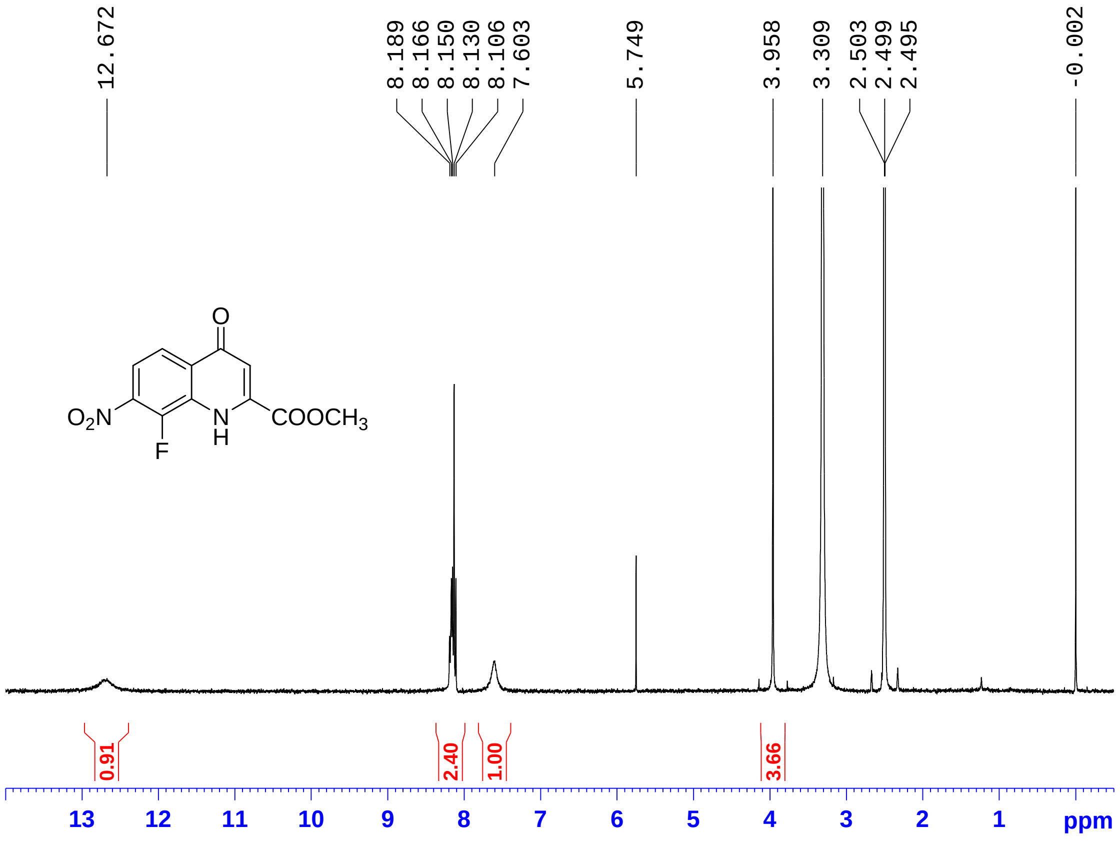

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NAME                         1h
EXPNO                        76
PROCNO                        1

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PROBHD          5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           16
DS                            0
SWH                   11990.407 Hz
FIDRES                 0.182959 Hz
AQ                    2.7329011 sec
RG                        645.1
DW                       41.700 usec
DE                         6.00 usec
TE                        300.5 K
D1                   2.00000000 sec
MCREST               0.00000000 sec
MCWRK                0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.50 usec
PL1                       -1.00 dB
SFO1                400.1332010 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300040 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
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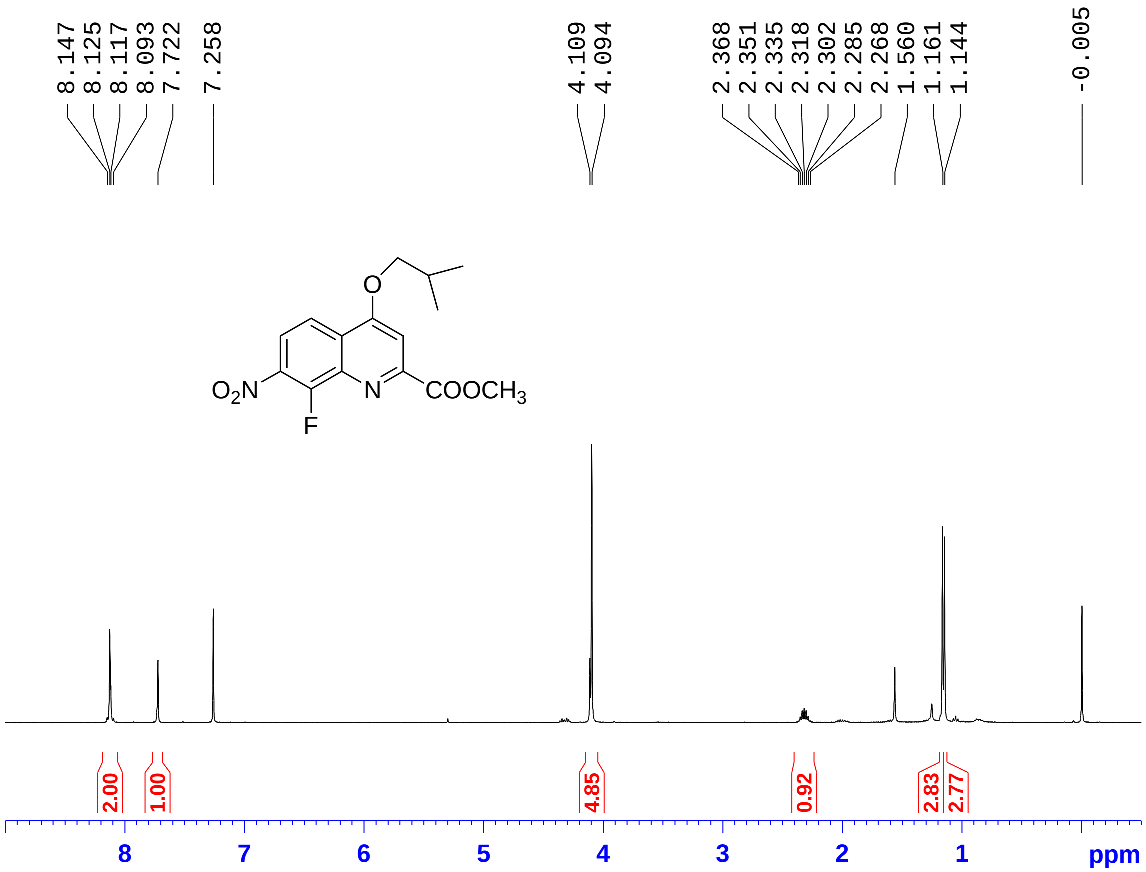

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Current Data Parameters
NAME                     gf-22
EXPNO                       15
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20061231
Time                     11.06
INSTRUM                  AV400
PROBHD          5 mm BBO BB-1H
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                           8
DS                           0
SWH                   9980.040 Hz
FIDRES                0.304567 Hz
AQ                   1.6417269 sec
RG                      1149.4
DW                      50.100 usec
DE                        6.00 usec
TE                       294.9 K
D1                  2.00000000 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                        8.00 usec
PL1                      -4.00 dB
SFO1            400.1326091 MHz

F2 - Processing parameters
SI                       32768
SF              400.1300094 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

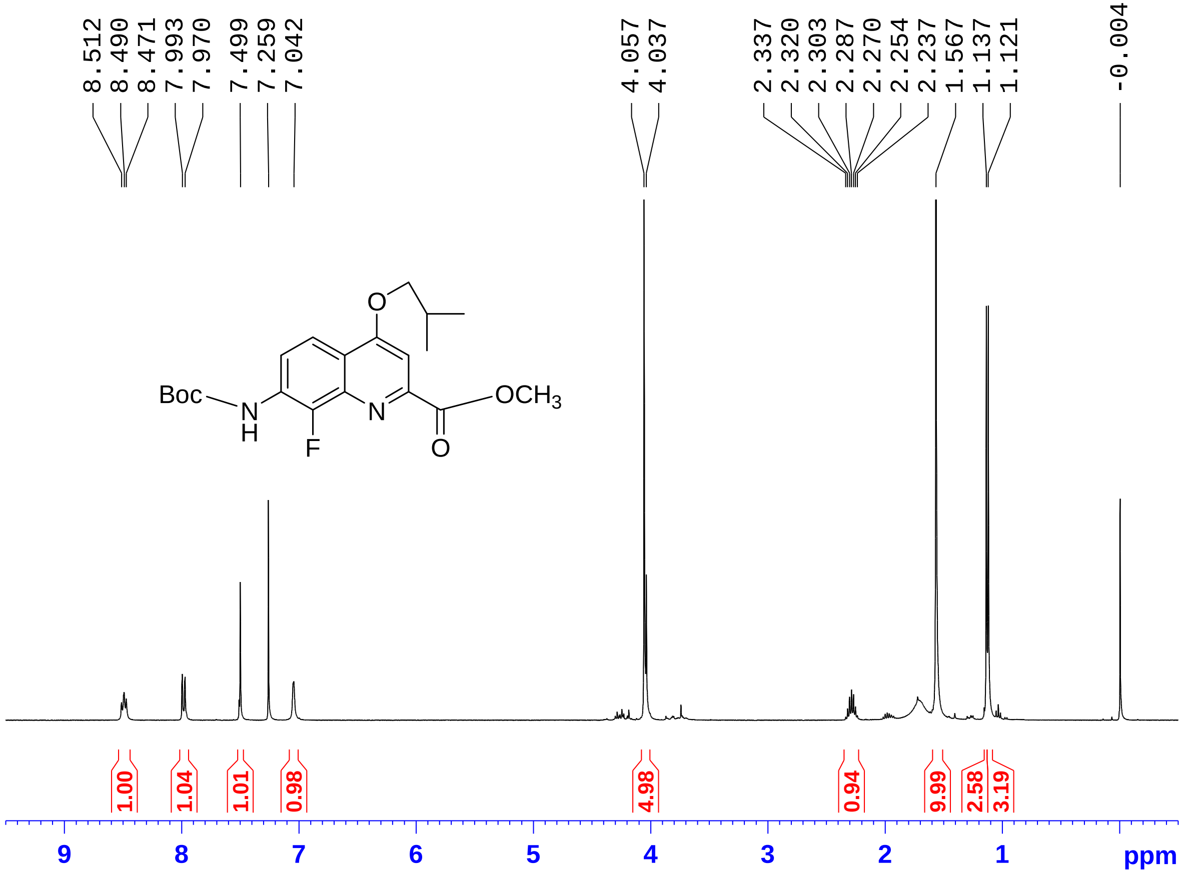

```
Current Data Parameters
NAME                         1h
EXPNO                        77
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070821
Time                      19.45
INSTRUM                   AV400
PROBHD         5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            0
SWH                   11990.407 Hz
FIDRES                 0.182959 Hz
AQ                    2.7329011 sec
RG                        574.7
DW                       41.700 usec
DE                         6.00 usec
TE                        300.2 K
D1                   2.00000000 sec
MCREST               0.00000000 sec
MCWRK                0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.50 usec
PL1                       -1.00 dB
SFO1                400.1332010 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300103 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
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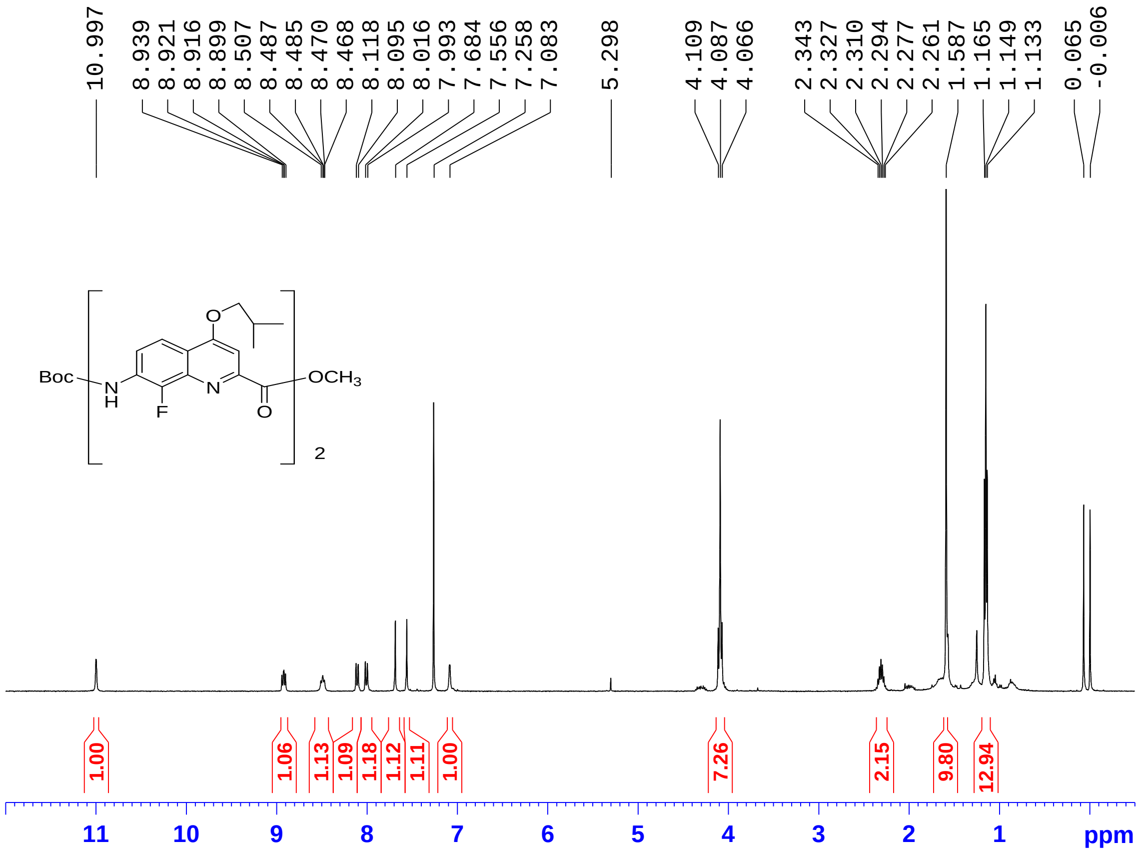

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Current Data Parameters
NAME                ganquan-h
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_                20070307
Time                     8.18
INSTRUM                 AV400
PROBHD         5 mm BBO BB-1H
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          0
SWH                 10822.511 Hz
FIDRES               0.165138 Hz
AQ                  3.0278132 sec
RG                      812.7
DW                     46.200 usec
DE                       6.00 usec
TE                      293.1 K
D1                 4.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       8.00 usec
PL1                     -4.00 dB
SFO1            400.1332010 MHz

F2 - Processing parameters
SI                      32768
SF              400.1300096 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       0.10
```
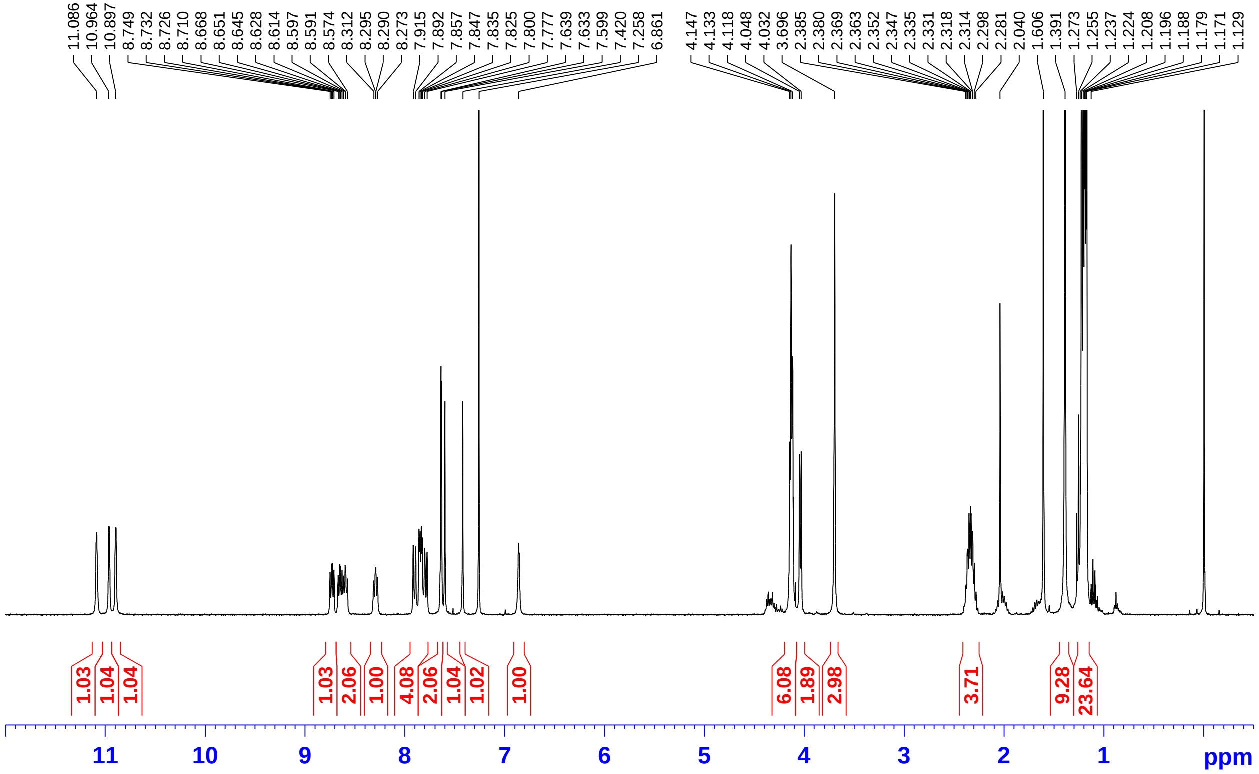
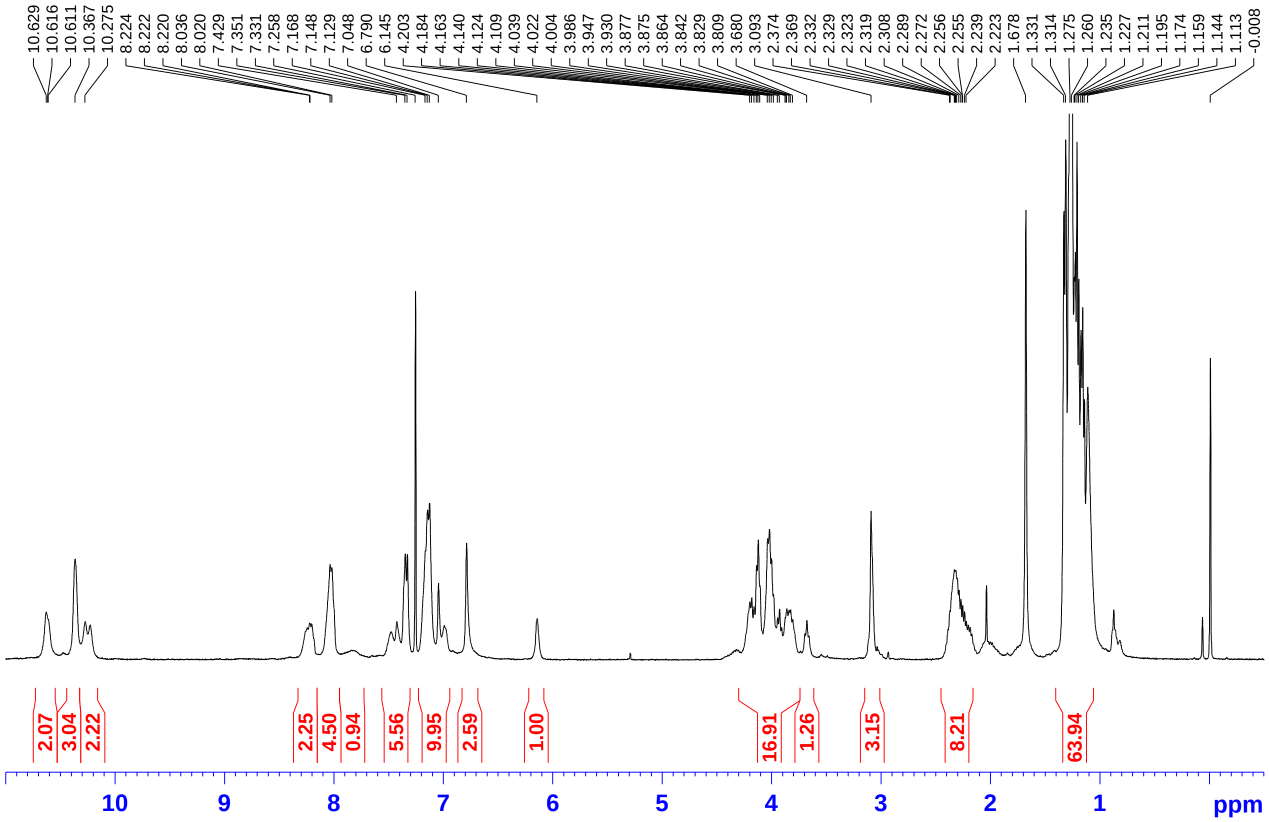

tetramer



```
Current Data Parameters
NAME                  ganquan-h2
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070612
Time                       13.51
INSTRUM                    AV400
PROBHD           5 mm BBO BB-1H
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             0
SWH                    10822.511 Hz
FIDRES                  0.165138 Hz
AQ                     3.0278132 sec
RG                         456.1
DW                        46.200 usec
DE                          6.00 usec
TE                         299.8 K
D1                    4.00000000 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                          1H
P1                          8.00 usec
PL1                        -4.00 dB
SFO1                 400.1332010 MHz

F2 - Processing parameters
SI                         32768
SF                   400.1300096 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          0.10
```

octamer



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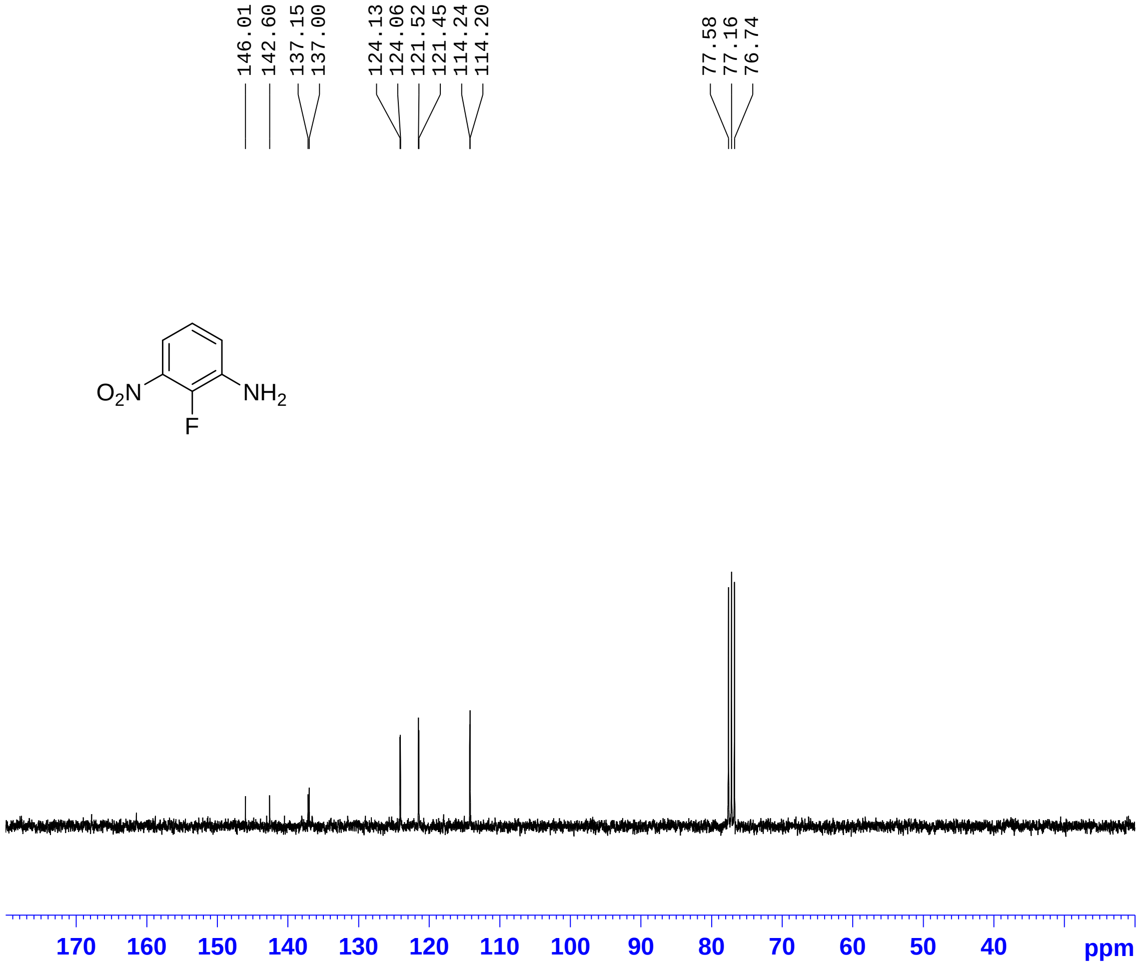
Current Data Parameters
NAME                  ganquan-h
EXPNO                        29
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070410
Time                      12.24
INSTRUM                   AV400
PROBHD          5 mm BBO BB-1H
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            0
SWH                   10822.511 Hz
FIDRES                 0.165138 Hz
AQ                    3.0278132 sec
RG                        228.1
DW                       46.200 usec
DE                         6.00 usec
TE                        297.4 K
D1                   4.00000000 sec
MCREST               0.00000000 sec
MCWRK                0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                         8.00 usec
PL1                       -4.00 dB
SFO1                400.1332010 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300098 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         0.10
```



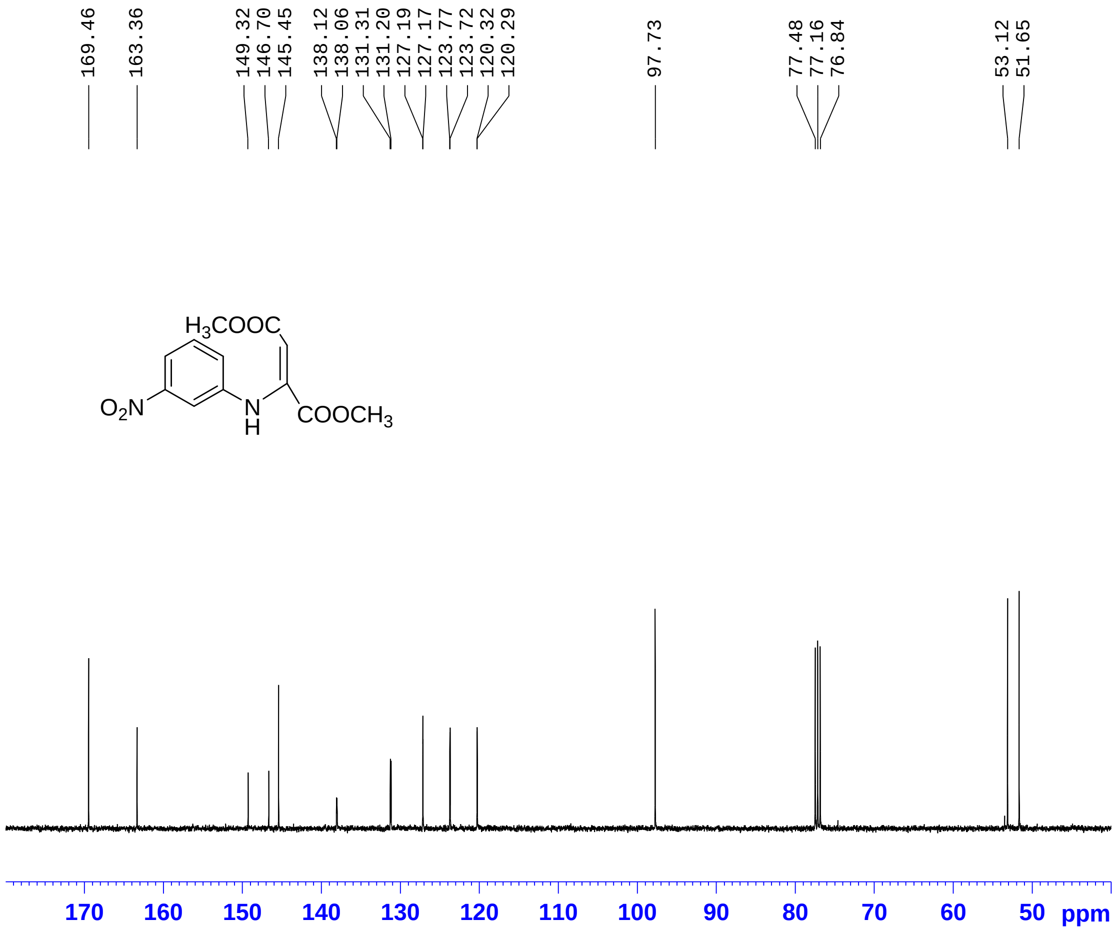
```
Current Data Parameters
NAME                             13c
EXPNO                              5
PROCNO                             1

F2 - Acquisition Parameters
Date_                       20071122
Time                           19.54
INSTRUM                        spect
PROBHD            5 mm BBI 1H-BB
PULPROG                       zgig30
TD                             65536
SOLVENT                        CDCl3
NS                               116
DS                                 0
SWH                    18939.395 Hz
FIDRES                  0.288992 Hz
AQ                     1.7302004 sec
RG                              2048
DW                        26.400 usec
DE                          6.00 usec
TE                           0.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                             13C
P1                          8.80 usec
PL1                         0.00 dB
SFO1                  75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                      waltz16
NUC2                              1H
PCPD2                      88.00 usec
PL2                         5.50 dB
PL12                       22.81 dB
SFO2                 300.1312005 MHz

F2 - Processing parameters
SI                             32768
SF                    75.4677426 MHz
WDW                               EM
SSB                                0
LB                          1.00 Hz
GB                                 0
PC                              1.40
```



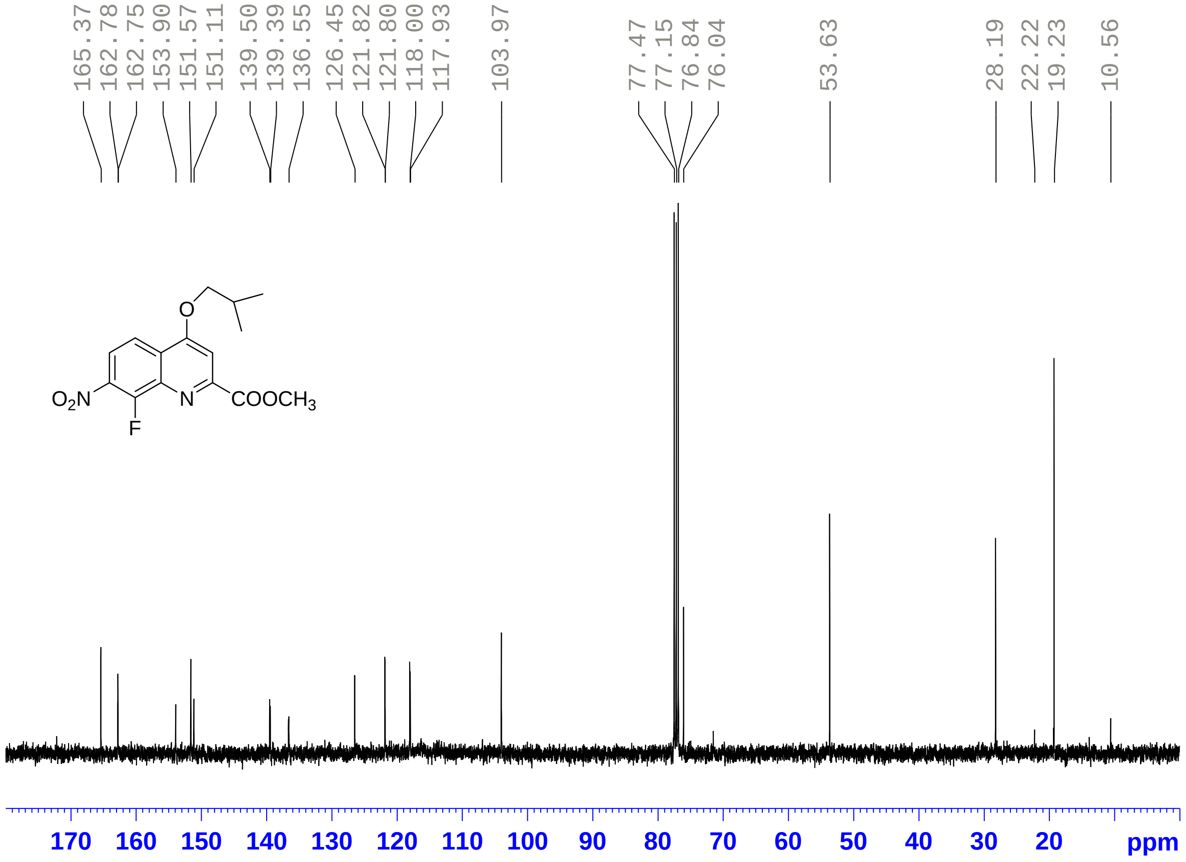
```
Current Data Parameters
NAME                              13c
EXPNO                              18
PROCNO                              1

F2 - Acquisition Parameters
Date_                        20071123
Time                            12.31
INSTRUM                         AV400
PROBHD              5 mm PABBO BB-
PULPROG                       zgig30
TD                              65536
SOLVENT                         CDCl3
NS                                 90
DS                                  0
SWH                         24154.590 Hz
FIDRES                       0.368570 Hz
AQ                          1.3566452 sec
RG                            14596.5
DW                             20.700 usec
DE                               6.00 usec
TE                              295.7 K
D1                         2.00000000 sec
d11                        0.03000000 sec
MCREST                     0.00000000 sec
MCWRK                      0.01500000 sec

======== CHANNEL f1 ========
NUC1                              13C
P1                               9.60 usec
PL1                             -3.00 dB
SFO1                      100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2                       waltz16
NUC2                               1H
PCPD2                           80.00 usec
PL2                             -1.00 dB
PL12                            14.46 dB
SFO2                      400.1316005 MHz

F2 - Processing parameters
SI                              32768
SF                        100.6127667 MHz
WDW                                EM
SSB                                 0
LB                               1.00 Hz
GB                                  0
PC                               1.40
```



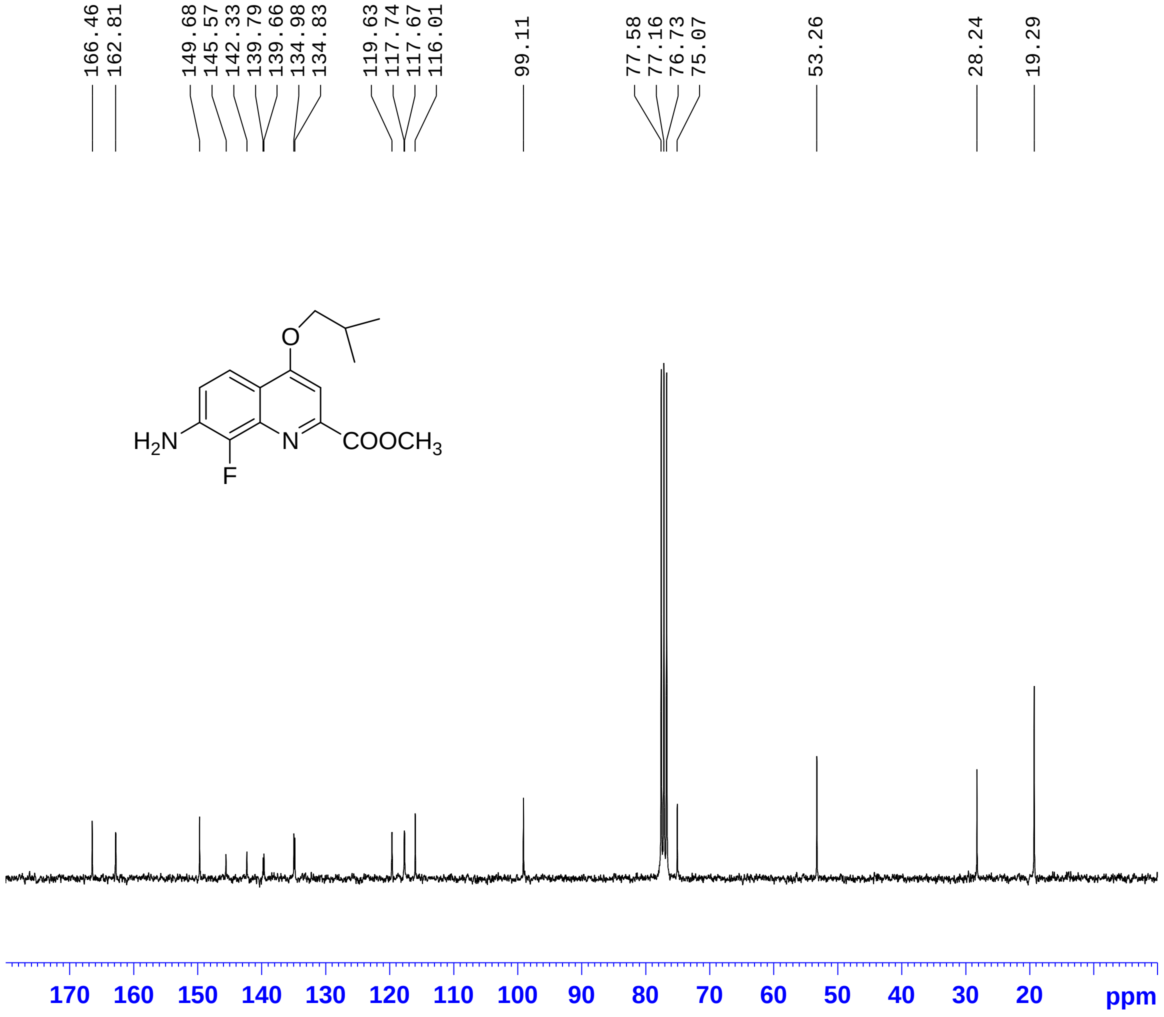
```
Current Data Parameters
NAME                         13c
EXPNO                          3
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070706
Time                       13.14
INSTRUM                    AV400
PROBHD           5 mm BBI 1H-BB
PULPROG                  zgig30
TD                         65536
SOLVENT                    CDCl3
NS                           333
DS                             0
SWH                    23980.814 Hz
FIDRES                  0.365918 Hz
AQ                     1.3664756 sec
RG                       14596.5
DW                        20.850 usec
DE                          6.00 usec
TE                         300.6 K
D1                    2.00000000 sec
d11                   0.03000000 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                         13C
P1                         21.30 usec
PL1                        -3.00 dB
SFO1                 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                      80.00 usec
PL2                         2.00 dB
PL12                       21.27 dB
SFO2                 400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                   100.6127583 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```



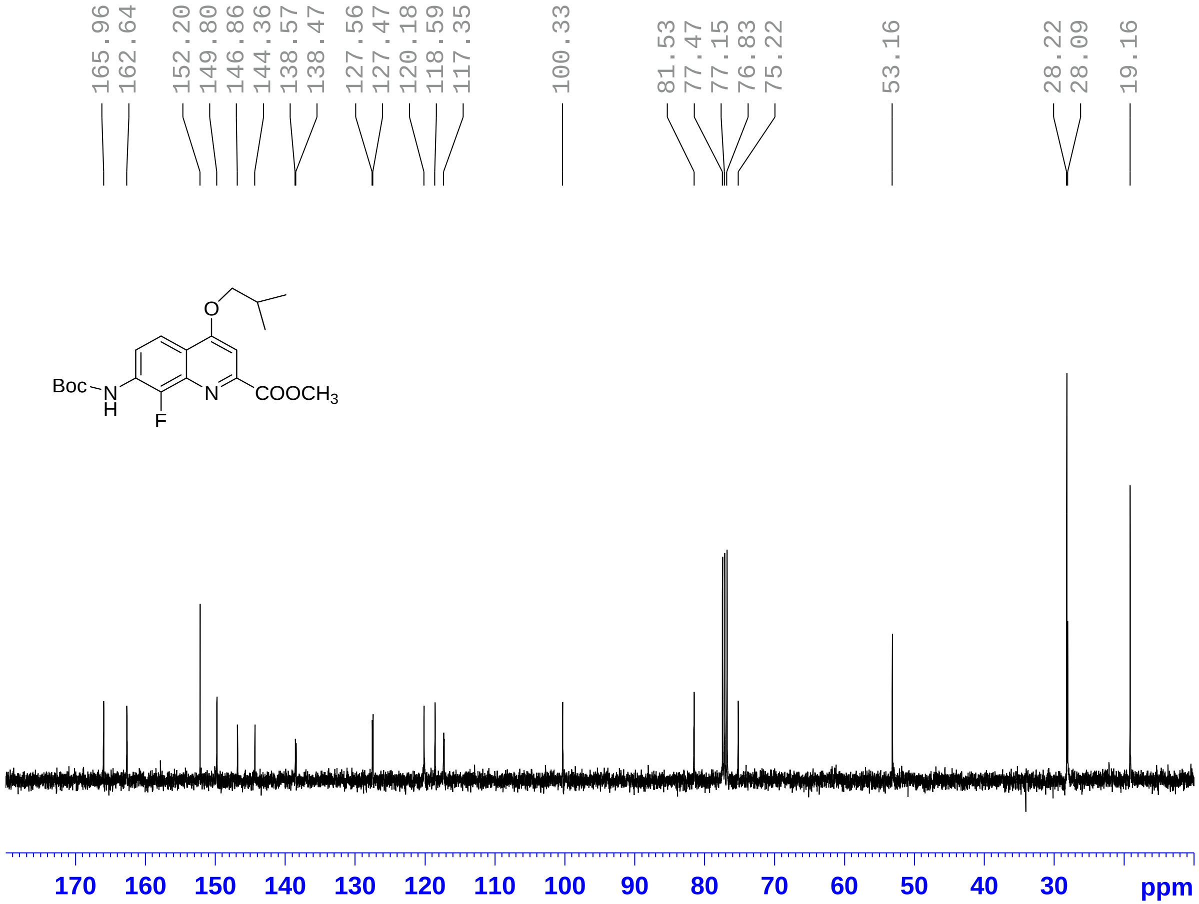
```
Current Data Parameters
NAME                          13c
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20071122
Time                         8.25
INSTRUM                     spect
PROBHD           5 mm BBI 1H-BB
PULPROG                   zgig30
TD                          65536
SOLVENT                     CDCl3
NS                            937
DS                              0
SWH                     18939.395 Hz
FIDRES                   0.288992 Hz
AQ                      1.7302004 sec
RG                           2048
DW                         26.400 usec
DE                           6.00 usec
TE                            0.0 K
D1                     2.00000000 sec
d11                    0.03000000 sec
MCREST                 0.00000000 sec
MCWRK                  0.01500000 sec

======== CHANNEL f1 ========
NUC1                          13C
P1                           8.80 usec
PL1                          0.00 dB
SFO1                   75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                           1H
PCPD2                       88.00 usec
PL2                          5.50 dB
PL12                        22.81 dB
SFO2                  300.1312005 MHz

F2 - Processing parameters
SI                          32768
SF                     75.4677431 MHz
WDW                            EM
SSB                             0
LB                           3.00 Hz
GB                              0
PC                           1.40
```



```
Current Data Parameters
NAME                    13c
EXPNO                    13
PROCNO                    1

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Time                  19.42
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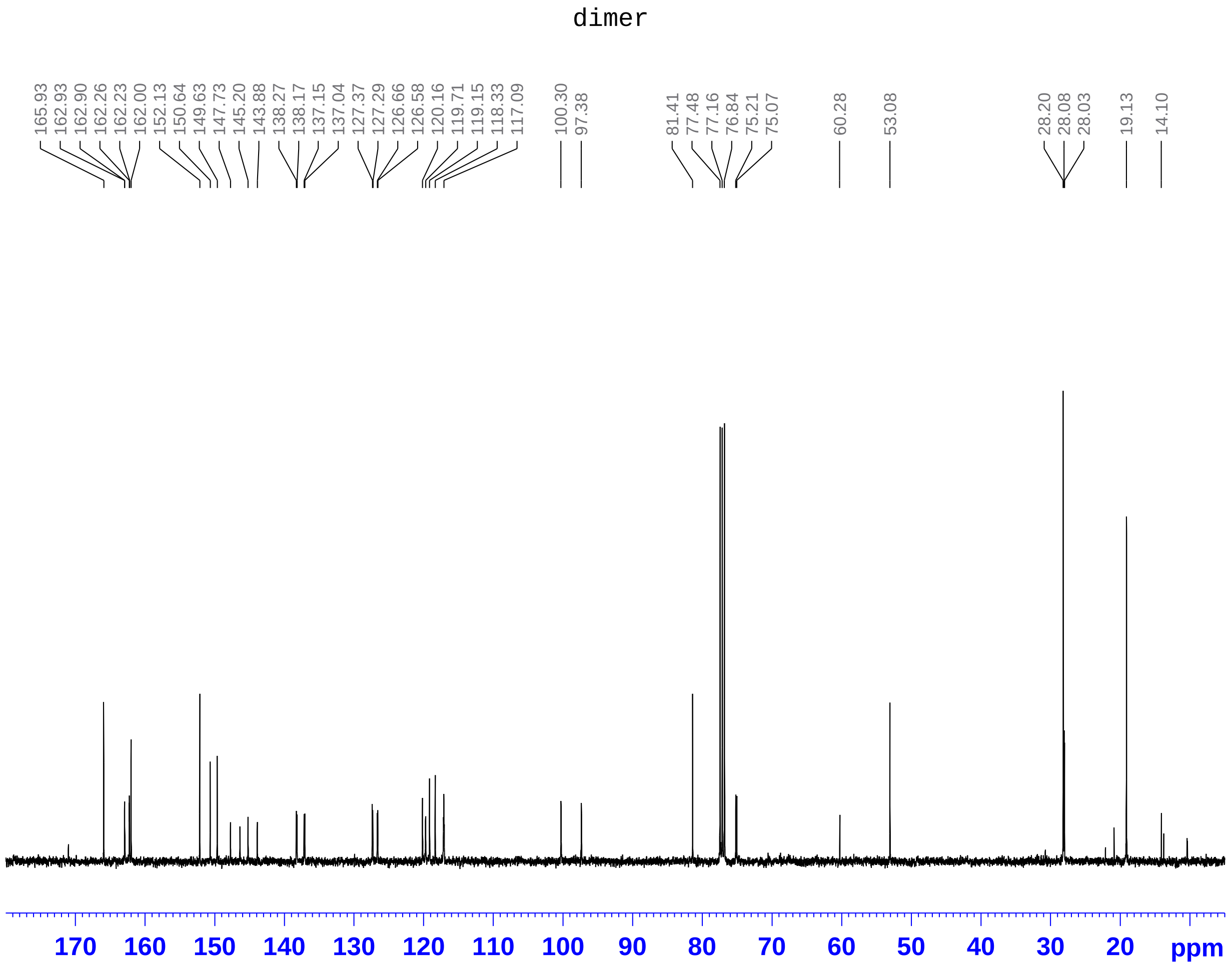
PROBHD       5 mm PABBO BB-
PULPROG              zgig30
TD                    65536
SOLVENT               CDCl3
NS                      480
DS                        0
SWH               24154.590 Hz
FIDRES             0.368570 Hz
AQ                1.3566452 sec
RG                  14596.5
DW                   20.700 usec
DE                     6.00 usec
TE                    301.9 K
D1               2.00000000 sec
d11              0.03000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.60 usec
PL1                   -3.00 dB
SFO1            100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -1.00 dB
PL12                  14.46 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF              100.6127663 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



```
Current Data Parameters
NAME                          13c
EXPNO                          15
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20070816
Time                        19.26
INSTRUM                     AV400
PROBHD          5 mm PABBO BB-
PULPROG                    zgig30
TD                          65536
SOLVENT                     CDCl3
NS                            228
DS                              0
SWH                     24154.590 Hz
FIDRES                   0.368570 Hz
AQ                      1.3566452 sec
RG                        14596.5
DW                         20.700 usec
DE                           6.00 usec
TE                          301.1 K
D1                     2.00000000 sec
d11                    0.03000000 sec
MCREST                 0.00000000 sec
MCWRK                  0.01500000 sec

======== CHANNEL f1 ========
NUC1                          13C
P1                           9.60 usec
PL1                         -3.00 dB
SFO1                  100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                           1H
PCPD2                       80.00 usec
PL2                         -1.00 dB
PL12                        14.46 dB
SFO2                  400.1316005 MHz

F2 - Processing parameters
SI                          32768
SF                    100.6127688 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
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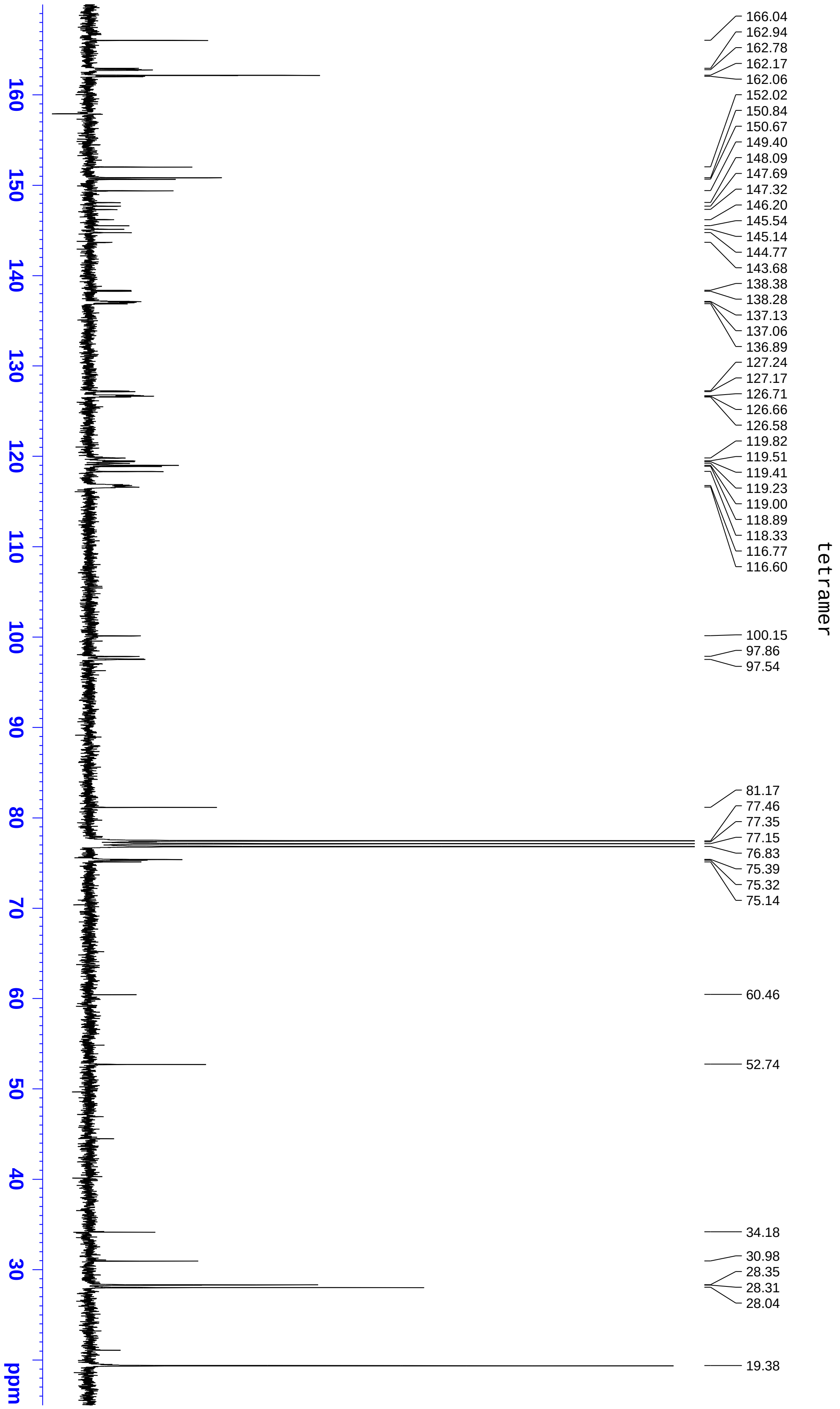
tetramer
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162.06
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147.32
146.20
145.54
145.14
144.77
143.68
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138.28
137.13
137.06
136.89
127.24
127.17
126.71
126.66
126.58
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119.51
119.41
119.23
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116.77
116.60
100.15
97.86
97.54
81.17
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75.14
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52.74
34.18
30.98
28.35
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50
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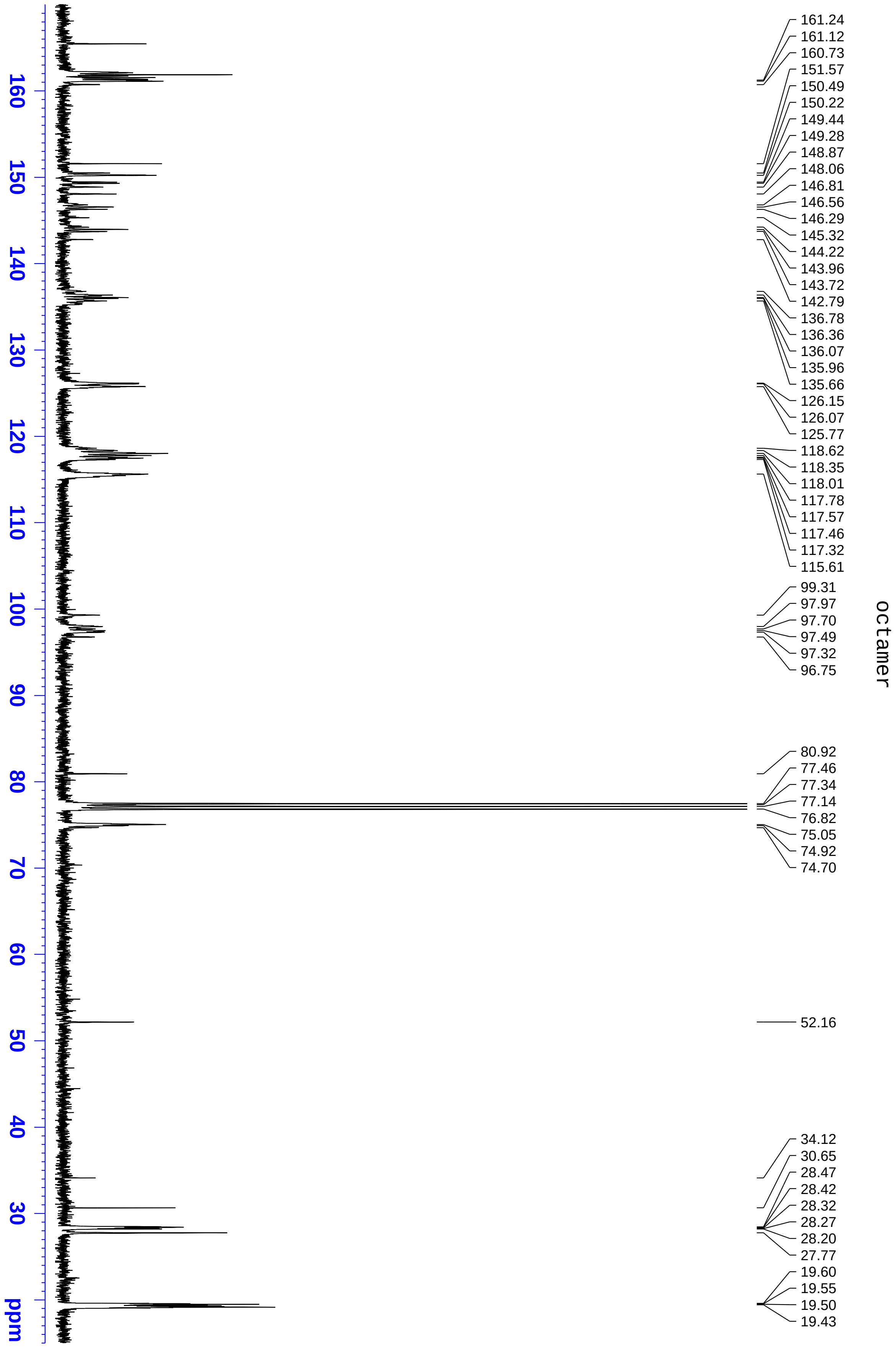
30
ppm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145.32
144.22
143.96
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40
30
ppm