Supporting Information

Unravelling the limits of the transfer of asymmetry in supramolecular polymers

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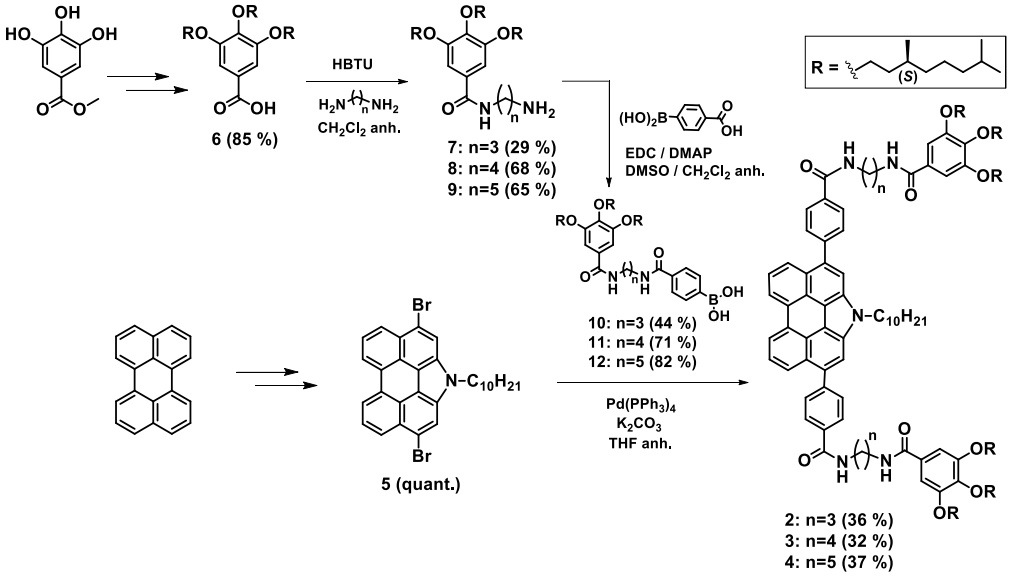
Contents:

1. Experimental section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) and on a Bruker Avance 700 (^{1}H: 700 MHz; ^{13}C: 175 MHz) spectrometer using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. FT-IR spectra in film were recorded on a Bruker Tensor 27 (ATR device) spectrometer. FT- IR spectra in solution were recorded on a JASCO-FT-IR-6800 equipped with a CaF_2 cell with a path length of 0.1 mm. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 500 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm, by using a quartz cuvette (Hellma). Thermal experiments were performed at constant heating rates of 1 ºC/min from 10 to 90 ºC in methylcyclohexane (MCH). Circular dichroism (CD) measurements were performed on a JASCO-1500 dichrograph equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 500 nm, with a wavelength increment of 0.2 nm, a response time of 1 s, and a bandwidth of 2 nm using a quartz cuvette (Hellma). Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer. AFM measurements were performed under ambient conditions using a MultiMode 8HR SPM from Bruker operating in tapping mode in air. Silicon cantilevers with a resonance frequency of 300 kHz were used. Solutions of compounds **2-4** were heated up to 90 ºC and cooled down to 20 ºC prior to be spin-coated onto mica.

2. Synthetic details and characterization



Scheme S1. Synthesis of chiral *N*-annulated perylenetetracarboxamides **2-4**.

Compounds **5** [S1] and **6** [S2] were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

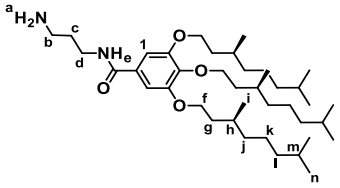
[S1] F. García, J. Buendía, S. Ghosh, A. Ajayaghosh, L. Sánchez. Luminescent and conductive supramolecular polymers obtained from an *N*-annulated perylenedicarboxamide. *Chem. Comm*. **2013**, *49*, 9278–9280.

[S2] S. Ghosh, X-Q. Li, V. Stepanenko, F. Würthner. Control of H- and J-Type p Stacking by Peripheral Alkyl Chains and Self-Sorting Phenomena in Perylene Bisimide Homo- and Heteroaggregates. *Chem. Eur. J.* **2008**, *14*, 11343–11357.

Synthesis of benzamides 7-9. General procedure.

Compound **6** (1.00 g, 1.69 mmol) was dissolved in dry CH_2Cl_2 (100 mL) under Argon atmosphere. Then, HBTU (0.57 g, 2.03 mmol) and the corresponding diamine (propane-1,3-diamine for **7**, putrescine for **8** or cadaverine for **9**) (2.40 mL, 23.69 mmol) were added. The reaction mixture was stirred at room temperature overnight. The organic layer was washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/methanol 10/0.2).

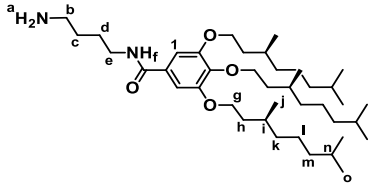
3,4,5-tris((*S*)-3,7-dimethyloctyloxy)-*N*-(3-aminopropyl)benzamide (7).



$C_{40}H_{74}N_2O_4$
Exact Mass: 646.5649
Mol. Wt.: 647.0266

Compound **7** was obtained as a pale yellow oil (0.42 g, 29 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) δ 7.31 (1H, H_e, br), 7.05 (2H, H_1, s), 4.00 (6H, H_f, m), 3.51 (2H, H_d, br), 3.07 (2H, H_b, br), 2.02 (2H, H_c, br), 1.82 (3H, H_h, sept, J=6.4 Hz), 1.68 (3H, H_m, br), 1.51 (6H, H_g, m), 1.34−1.08 (20H, $H_{a+j+k+l}$, m), 0.89 (9H, H_i, d, J=6.5 Hz), 0.85 (18H, H_n, d, J=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) δ 169.1, 153.3, 141.4, 128.1, 105.8, 77.4, 71.9, 67.7, 39.5, 39.4, 37.7, 37.6, 37.5, 36.5, 29.9, 29.8, 28.1, 24.9, 24.9, 22.9, 22.8, 19.7, 19.6; FTIR (neat) 737, 763, 846, 1112, 1230, 1334, 1382, 1429, 1465, 1495, 1542, 1579, 1634, 2870, 2925, 2953 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{40}H_{75}N_2O_4$ $[M+H]^+$, 647.565; found, 647.447.

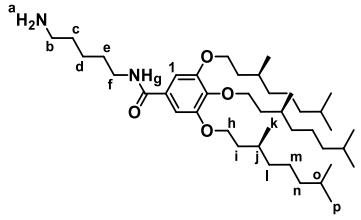
3,4,5-tris((*S*)-3,7-dimethyloctyloxy)-*N*-(4-aminobutyl)benzamide (8).



$C_{41}H_{76}N_2O_4$
Exact Mass: 660.5805
Mol. Wt.: 661.0531

Compound **8** was obtained as a pale yellow oil (0.77 g, 68 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) δ 7.36 (1H, H_f, br), 7.04 (2H, H_1, s), 4.53 (2H, H_a, br), 3.94 (6H, H_g, m), 3.33 (2H, H_e, br), 2.73 (2H, H_b, br), 1.77 (3H, H_i, m), 1.67−1.41 (13H, $H_{c+d+h+n}$, br), 1.31−1.04 (18H, H_{k+l+m}, m), 0.86 (9H, H_j, d, J=4.7 Hz), 0.81 (18H, H_o, d, J=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) δ 167.5, 153.0, 140.8, 129.3, 105.6, 77.4, 71.7, 67.4, 40.6, 39.7, 39.3, 39.2, 37.5, 37.4, 37.3, 36.4, 29.7, 29.6, 28.4, 28.2, 28.0, 27.7, 26.8, 24.7, 24.7, 22.7, 22.6, 19.7, 19.5, 19.4; FTIR (neat) 671, 761, 848, 996, 1113, 1231, 1333, 1382, 1428, 1465, 1496, 1545, 1579, 1634, 2869, 2926, 2953, 3320 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{41}H_{77}N_2O_4$ $[M+H]^+$, 661.588; found, 661.312.

3,4,5-tris((*S*)-3,7-dimethyloctyloxy)-*N*-(5-aminopentyl)benzamide (9).



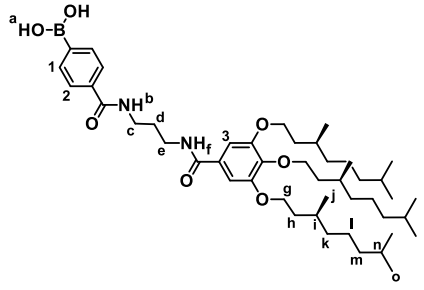
$C_{42}H_{78}N_2O_4$
Exact Mass: 674.5962
Mol. Wt.: 675.0797

Compound **9** was obtained as a pale yellow oil (0.72 g, 65 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) δ 6.98 (2H, H_1, s), 6.41 (1H, H_g, t, J=5.6 Hz), 4.01 (6H, H_h, m), 3.55 (2H, H_a, br), 3.40 (2H, H_f, q, J=6.7 Hz), 2.78 (2H, H_b, t, J=6.8 Hz), 1.83 (3H, H_j, m), 1.68 (3H, H_o, br), 1.63−1.41 (12H, $H_{c+d+e+i}$, m), 1.35−1.09 (18H, H_{l+m+n}, br), 0.91 (9H, H_k, d, J=6.5 Hz), 0.85 (18H, H_p, d, J=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) δ 167.7, 153.2, 141.1, 129.7, 105.7, 77.4, 71.8, 67.7, 41.3, 40.1, 39.5, 39.4, 37.6, 37.5, 37.4, 36.5, 31.2, 29.9, 29.8, 29.4, 28.1, 24.9, 24.8, 24.1, 22.8, 22.7, 19.7; FTIR (neat) 762, 849, 996, 1114, 1230, 1334, 1382, 1428, 1466, 1496, 1545, 1579, 1634, 2869, 2926, 2953, 3303 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{42}H_{79}N_2O_4$ $[M+H]^+$, 675.604; found, 675.504.

Synthesis of phenylboronic acids 10-12. General procedure.

4-(Dihydroxyboryl)benzoic acid (0.15 g, 0.90 mmol) was dissolved in dry DMSO (1 mL) and in dry CH_2Cl_2 (15 mL) under Argon atmosphere. The solution was cooled to 0 ºC and a mixture of 4-dimethylaminopyridine (0.12 g, 0.99 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (0.19 g, 0.99 mmol) was slowly added. The mixture was stirred for 30 minutes. After that, the corresponding amine (compounds **7-9**) (0.67 g, 0.99 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and added portionwise. The reaction mixture was stirred at room temperature overnight. The organic layer was washed with water, HCl 1 M, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/methanol 10/0.5).

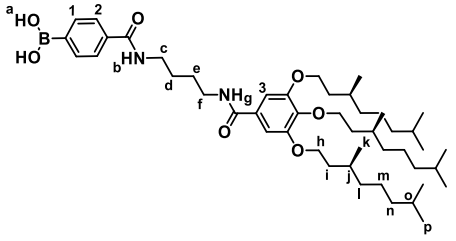
4-(3-(3,4,5-tris((*S*)-3-methyloctyloxy)benzamido)propylcarbamoyl)phenylboronic acid (10).



$C_{47}H_{79}BN_2O_7$
Exact Mass: 794.598
Mol. Wt.: 794.9504

Compound **10** was obtained as a pale, yellow, viscous oil (161 mg, 44 %). ^{1}H NMR (MeOD-d_4, 300 MHz, 25 ºC) δ 7.76 (4H, H_{1+2}, br), 7.18 (2H, H_3, s), 4.04 (6H, H_g, m), 3.47 (4H, H_{c+e}, br), 1.92−1.69 (8H, H_{d+i+n}, br), 1.53 (6H, H_h, m), 1.40−1.12 (18H, H_{k+l+m}, br), 0.94 (9H, H_j, d, J=6.5 Hz), 0.87 (18H, H_o, d, J=6.7 Hz); ^{13}C NMR (MeOD-d_4, 75 MHz, 25 ºC) δ 168.3, 152.8, 140.4, 133.3, 129.1, 125.9, 105.4, 71.2, 66.9, 48.5, 48.2, 47.9, 47.6, 47.3, 47.1, 46.8, 39.2, 39.1, 37.3, 37.1, 37.0, 36.9, 36.2, 29.6, 29.4, 29.0, 27.8, 24.6, 24.5, 21.8, 21.7, 21.6, 18.9, 18.6; FTIR (neat) 672, 714, 763, 993, 1018, 1111, 1229, 1331, 1376, 1430, 1463, 1497, 1544, 1579, 1637, 1712, 2094, 2868, 2925, 2953, 3332 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{47}H_{80}BN_2O_7$ $[M+H]^+$, 795.598; found, 795.433.

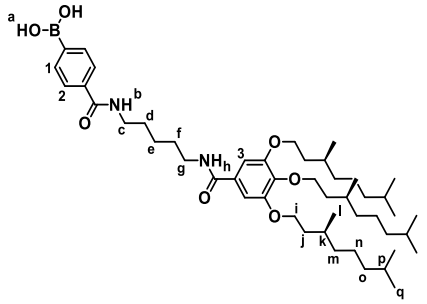
4-(4-(3,4,5-tris((*S*)-3-methyloctyloxy)benzamido)butylcarbamoyl)phenylboronic acid (11).



$C_{48}H_{81}BN_2O_7$
Exact Mass: 808.6137
Mol. Wt.: 808.9769

Compound **11** was obtained as a pale, yellow, viscous oil (0.38 g, 71 %). ^{1}H NMR (MeOD-d$_4$, 300 MHz, 25 ºC) δ 7.76 (4H, H$_{1+2}$, br), 7.15 (2H, H$_3$, s), 4.02 (6H, H$_h$, br), 3.41 (4H, H$_{c+f}$, br), 1.88−1.65 (10H, H$_{d+e+j+o}$, br), 1.52 (6H, H$_i$, m), 1.39−1.11 (18H, H$_{l+m+n}$, br), 0.93 (9H, H$_k$, d, J=6.4 Hz), 0.87 (18H, H$_p$, d, J=6.6 Hz); ^{13}C NMR (MeOD-d$_4$, 75 MHz, 25 ºC) δ 169.5, 154.1, 141.7, 135.0, 130.6, 127.2, 106.7, 79.5, 72.5, 68.2, 40.8, 40.6, 40.5, 40.4, 38.6, 38.5, 38.5, 37.6, 30.9, 30.8, 29.2, 28.1, 27.9, 26.0, 25.9, 23.2, 23.1, 23.1, 20.3, 20.0; FTIR (neat) 653, 714, 762, 857, 997, 1016, 1046, 1114, 1196, 1232, 1332, 1366, 1379, 1402, 1425, 1466, 1497, 1543, 1579, 1634, 2869, 2926, 2953, 3314 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{48}H_{81}BN_2O_7$ [M], 808.614; found, 808.449.

4-(5-(3,4,5-tris((*S*)-3-methyloctyloxy)benzamido)pentylcarbamoyl)phenylboronic acid (12).



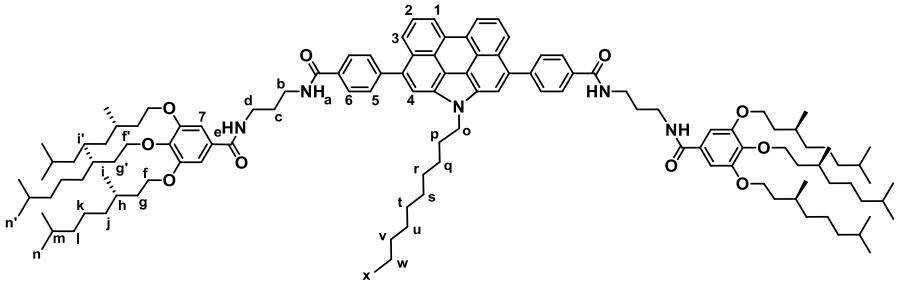
$C_{49}H_{83}BN_2O_7$
Exact Mass: 822.6293
Mol. Wt.: 823.0035

Compound **11** was obtained as a pale, yellow, viscous oil (0.61 g, 82 %). ^{1}H NMR (MeOD-d$_4$, 300 MHz, 25 ºC) δ 7.69 (4H, H$_{1+2}$, br), 7.15 (2H, H$_3$, s), 4.02 (6H, Hi, br), 3.38 (4H, H$_{c+g}$, t, J=6.9 Hz), 1.89−1.61 (10H, H$_{d+f+k+p}$, br), 1.58−1.41 (8H, H$_{e+j}$, m), 1.39−1.12 (18H, H$_{m+n+o}$, br), 0.94 (9H, H$_l$, d, J=6.5 Hz), 0.87 (18H, H$_q$, d, J=6.6 Hz); ^{13}C NMR (MeOD-d$_4$, 75 MHz, 25 ºC) δ 169.5, 154.1, 141.7, 136.6, 134.6, 130.6, 127.3, 106.8, 72.5, 68.2, 40.9, 40.8, 40.6, 40.5, 38.6, 38.5, 37.6, 30.9, 30.8, 30.1, 26.0, 25.9, 25.4, 23.2, 23.1, 23.1, 20.3, 20.0; FTIR (neat) 649, 715, 760, 858, 1014, 1046, 1111, 1231, 1325, 1374, 1435, 1501, 1550, 1578, 1628, 2473, 2869, 2926, 2953, 3323 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{49}H_{83}BN_2O_7$ [M], 822.629; found, 822.578.

Synthesis of *N*-annulated perylene tetracarboxamides 2-4. General procedure.

Compound **5** (51 mg, 0.09 mmol), the corresponding boronic acid (compound **10-12**) (160 mg, 0.21 mmol), tetrakis(triphenylphosphine) palladium(0) (10 mg, 0.01 mmol) were dissolved in dry THF (20 mL). K_2CO_3 (63 mg, 0.46 mmol) was dissolved in water (1.1 mL) and added to the solution under Argon atmosphere. The reaction mixture was heated at reflux overnight. After evaporation of the solvent under reduced pressure, the residue was washed with water, extracted with chloroform, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After that, the residue was purified by column chromatography.

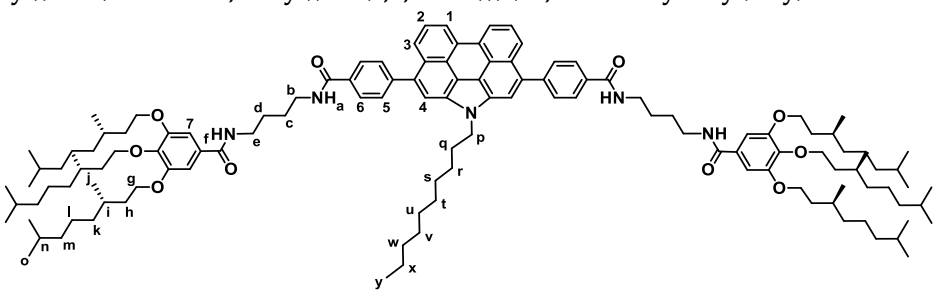
***N,N'*-(((4,4'-(1-decyl-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,10-diyl)bis(benzoyl))bis-(azanediyl))-bis(propane-3,1-diyl))bis(3,4,5-tris(((*S*)-3,7-dimethyloctyl)oxy)benzamide) (2).**



$C_{124}H_{183}N_5O_{10}$
Exact Mass: 1902.3965
Mol. Wt.: 1903.8073

Column chromatography (silica gel, chloroform/methanol 10/0.05) affords compound **2** as a yellow solid (62 mg, 36 %). ^{1}H NMR ($CDCl_3$, 700 MHz, 25 ºC) δ 8.69 (2H, H_1, d, J=7.5 Hz), 8.11 (6H, H_{6+3}, m), 7.82 (4H, H_5, d, J=7.6 Hz), 7.78 (2H, H_2, t, J=7.6 Hz), 7.75 (2H, H_4, s), 7.48 (2H, H_a, br), 7.18 (2H, H_e, br), 7.16 (4H, H_7, s), 4.64 (2H, H_o, br), 4.11 (8H, H_f, m), 4.04 (4H, $H_{f'}$, m), 3.65 (8H, H_{b+d}, br), 2.07 (2H, H_p, quin, J=6.8 Hz), 1.92−1.81 (10H, H_{h+c}, br), 1.72 (6H, H_m, br), 1.62 (4H, $H_{g'}$, m), 1.51 (8H, H_g, m), 1.36−1.12 (50H, $H_{j+k+l+q+r+s+t+u+v+w}$, m), 0.95 (12H, H_i, d, J=6.5 Hz), 0.92 (6H, $H_{i'}$, d, J=6.4 Hz), 0.86 (12H, $H_{n'}$, d, J=6.6 Hz), 0.84 (24H, H_n, d, J=7.1 Hz), 0.81 (3H, H_x, t, J=6.4 Hz); ^{13}C NMR ($CDCl_3$, 175 MHz, 25 ºC) δ 168.4, 167.9, 153.3, 145.5, 141.2, 136.7, 133.0, 132.0, 130.8, 130.7, 129.3, 127.6, 127.4, 125.0, 125.0, 124.1, 121.3, 117.3, 114.3, 105.7, 77.4, 71.9, 67.7, 45.9, 39.5, 39.4, 37.7, 37.5, 37.5, 36.5, 36.4, 36.3, 32.1, 31.9, 31.4, 30.1, 30.0, 29.8, 29.8, 29.6, 29.5, 29.4, 29.4, 28.1, 27.3, 24.9, 24.9, 22.8, 22.8, 22.7, 19.7, 19.7, 14.3, 14.2; FTIR (neat) 609, 668, 719, 741, 759, 803, 848, 954, 1019, 1117, 1237, 1261, 1339, 1366, 1381, 1426, 1467, 1500, 1538, 1581, 1609, 1633, 1735, 2853, 2869, 2924, 2954, 3047, 3291 cm^{-1}. HRMS (MALDI-TOF, exact mass) calcd. for $C_{124}H_{183}N_5O_{10}$ [M], 1902.3965; found, 1902.4022.

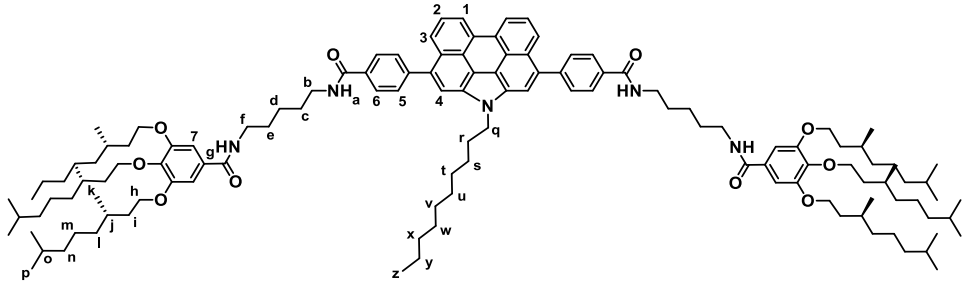
***N,N'*-(((4,4'-(1-decyl-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,10-diyl)bis(benzoyl))bis-(azanediyl))-bis(buthane-4,1-diyl))bis(3,4,5-tris(((*S*)-3,7-dimethyloctyl)oxy)benzamide) (3).**



$C_{126}H_{187}N_5O_{10}$
Exact Mass: 1930.4278
Mol. Wt.: 1931.8605

Column chromatography (silica gel, chloroform/methanol 10/0.1) affords compound **3** as a yellow solid (98 mg, 32 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) δ 8.60 (2H, H_1, d, J=7.7 Hz), 8.06 (2H, H_3, d, J=8.3 Hz), 8.00 (4H, H_6, d, J=8.2 Hz), 7.72 (6H, H_{2+5}, m), 7.63 (2H, H_4, s), 7.11 (4H, H_7, s), 6.85 (4H, H_{a+f}, m), 4.45 (2H, H_p, t, J=6.6 Hz), 4.04 (12H, H_g, m), 3.61 (8H, H_{b+e}, m), 1.97 (2H, H_q, quin, J=6.7 Hz), 1.89−1.77 (14H, H_{c+d+i}, br), 1.69 (6H, H_n, br), 1.52 (12H, H_h, m), 1.33−1.09 (50H, $H_{k+l+m+r+s+t+u+v+w+x}$, br), 0.90 (18H, H_j, d, J=6.5 Hz), 0.87 (39H, H_{o+y}, d, J=6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) δ 167.9, 167.8, 153.2, 145.3, 141.1, 136.5, 133.2, 131.9, 130.6, 130.6, 129.6, 127.4, 127.4, 124.8, 124.0, 121.2, 117.1, 114.1, 105.8, 77.4, 71.8, 67.7, 45.6, 40.0, 39.9, 39.5, 39.4, 37.7, 37.5, 37.5, 36.5, 31.9, 31.2, 29.9, 29.8, 29.6, 29.3, 29.3, 28.1, 28.1, 27.5, 27.2, 27.0, 24.9, 22.8, 22.7, 22.7, 19.7, 14.2; FTIR (neat) 668, 734, 759, 803, 850, 1114, 1195, 1234, 1314, 1334, 1366, 1382, 1427, 1467, 1500, 1541, 1580, 1609, 1633, 2870, 2925, 2954, 3290 cm^{-1}. HRMS (MALDI-TOF, exact mass) calcd. for $C_{126}H_{187}N_5O_{10}$ [M], 1930.4278; found, 1930.4347.

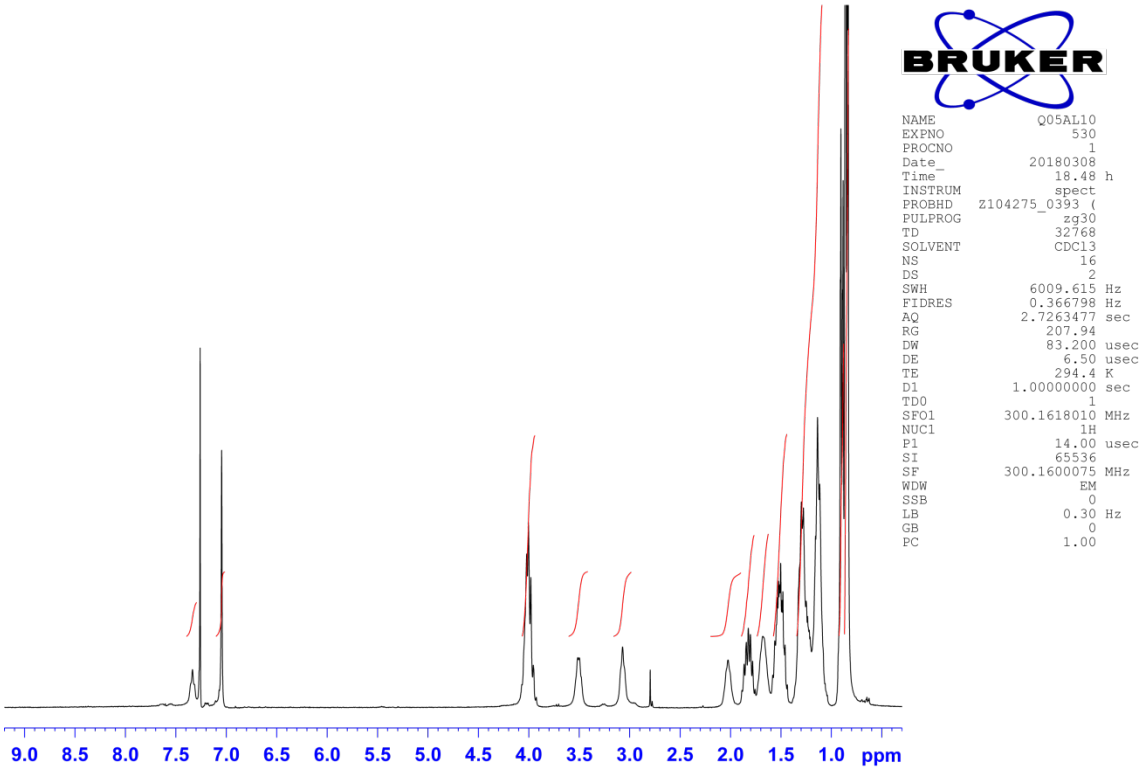
***N,N'*-(((4,4'-(1-decyl-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,10-diyl)bis(benzoyl))bis-(azanediyl))-bis(penthane-5,1-diyl))bis(3,4,5-tris(((*S*)-3,7-dimethyloctyl)oxy)benzamide) (4).**



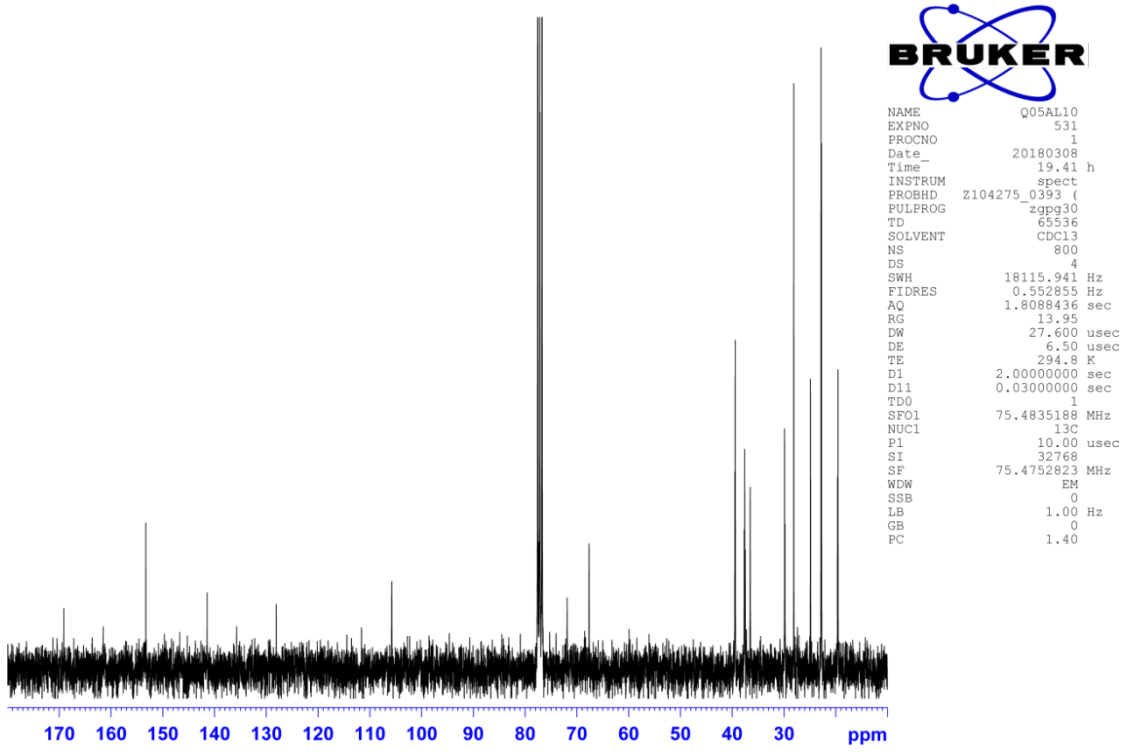
$C_{128}H_{191}N_5O_{10}$
Exact Mass: 1958.4591
Mol. Wt.: 1959.9136

Column chromatography (silica gel, chloroform/methanol 10/0.1) affords compound **4** as a yellow solid (96 mg, 37 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) δ 8.60 (2H, H_1, d, J=7.7 Hz), 8.05 (2H, H_3, d, J=8.3 Hz), 7.96 (4H, H_6, d, J=8.3 Hz), 7.71 (6H, H_{5+2}, m), 7.64 (2H, H_4, s), 7.05 (4H, H_7, s), 6.62 (2H, H_a, t, J=5.7 Hz), 6.48 (2H, H_g, t, J=5.7 Hz), 4.48 (2H, H_q, t, J=6.5 Hz), 4.01 (12H, H_h, m), 3.57 (4H, $H_{b\ or\ f}$, q, J=6.5 Hz), 3.50 (4H, $H_{f\ or\ b}$, q, J=6.5 Hz), 1.98 (2H, H_r, quin, J=6.7 Hz), 1.78 (14H, H_{c+e+j}, m), 1.66 (6H, H_o, br), 1.52 (16H, H_{i+d}, m), 1.33–1.07 (50H, $H_{l+m+n+s+t+u+v+w+x+y}$, m), 0.90 (18H, H_k, d, J=6.6 Hz), 0.84 (39H, H_{p+z}, m); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) δ 167.8, 167.8, 153.2, 145.3, 141.1, 136.5, 133.3, 131.9, 130.7, 130.6, 129.8, 127.5, 127.3, 124.9, 124.9, 124.0, 121.2, 117.2, 114.2, 105.7, 77.4, 71.8, 67.7, 45.7, 40.1, 40.0, 39.5, 39.4, 37.6, 37.5, 37.4, 36.5, 31.9, 31.3, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.1, 27.2, 24.8, 24.8, 24.3, 22.8, 22.7, 19.6, 19.6, 14.2; FTIR (neat) 760, 849, 1116, 1236, 1337, 1378, 1430, 1466, 1501, 1543, 1581, 1634, 1719, 2855, 2926, 2955, 3289, 3337, 3742, 3803 cm^{-1}. HRMS (MALDI-TOF, exact mass) calcd. for $C_{128}H_{191}N_5O_{10}$ [M], 1958.4591; found, 1958.4548.

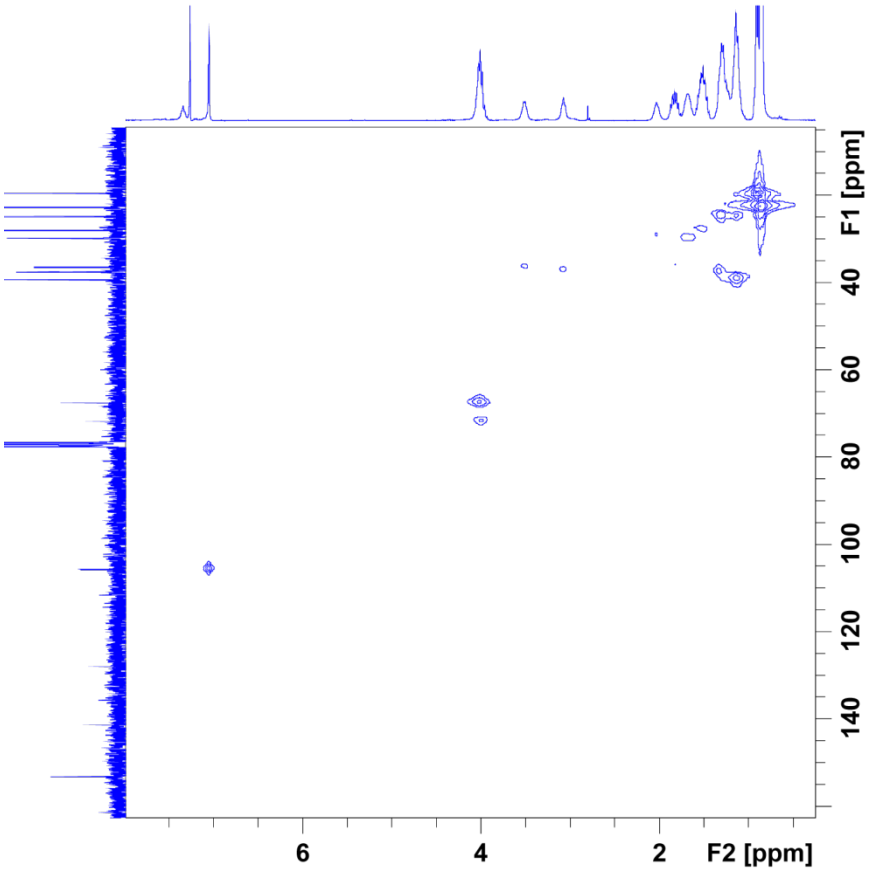
3. Collection of spectra



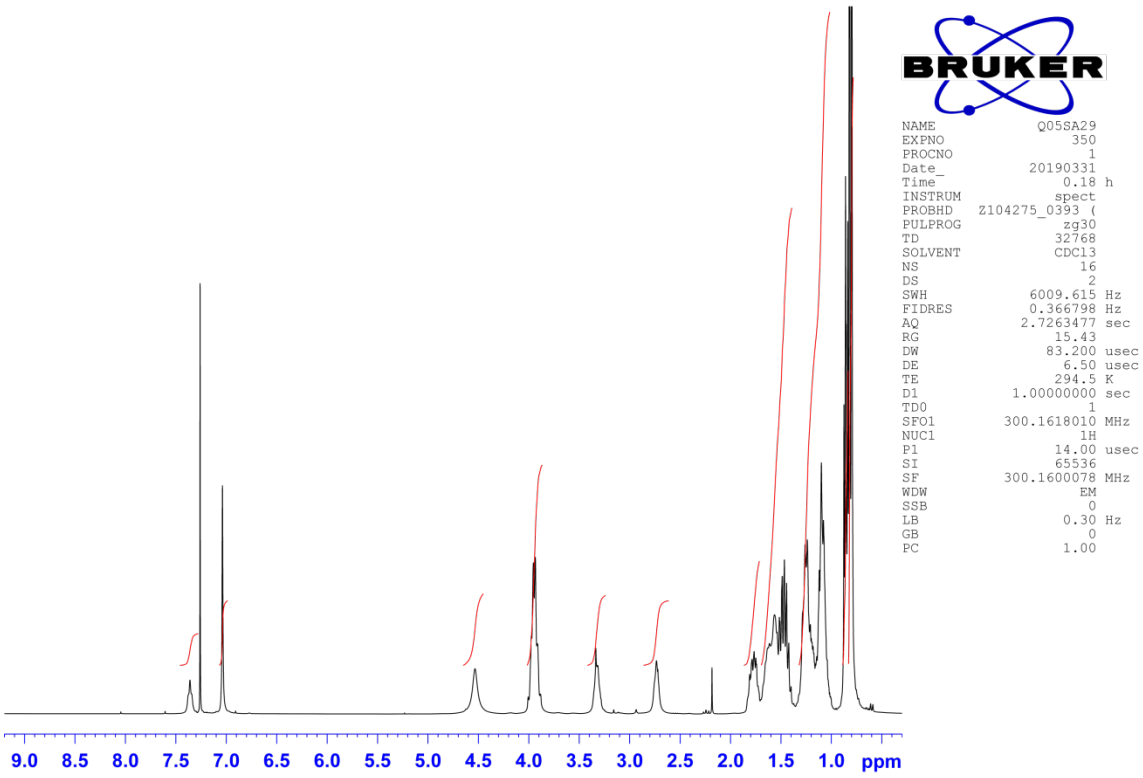
^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) of compound **7**.



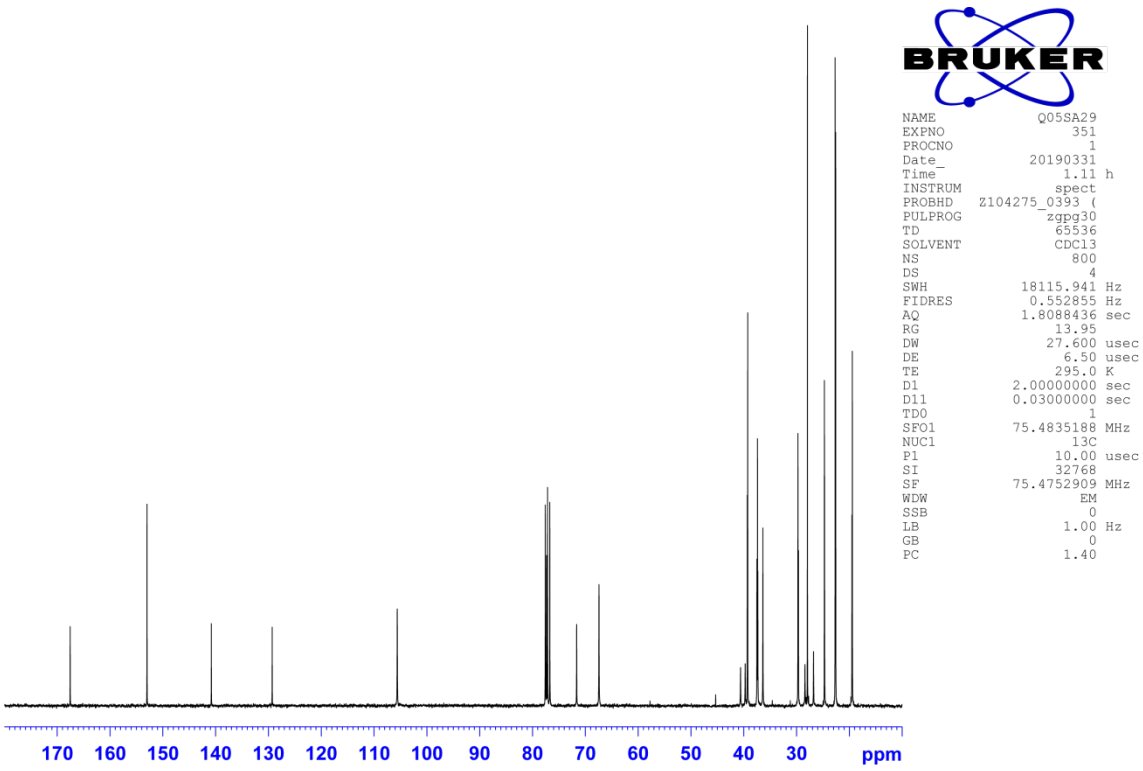
^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) of compound **7**.



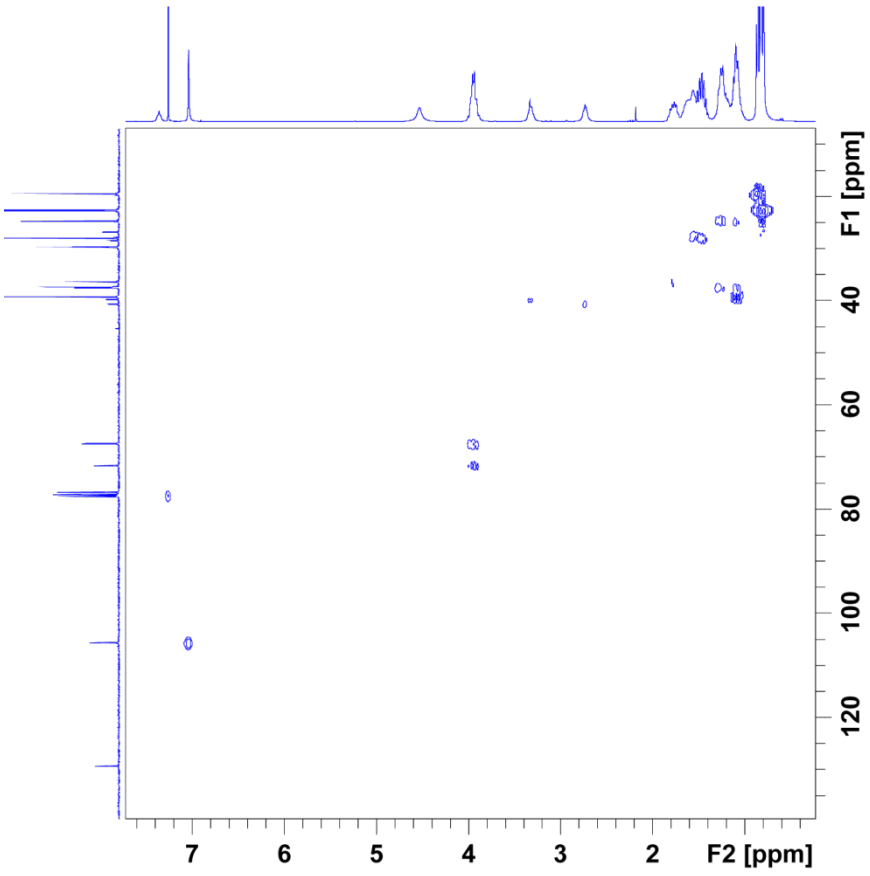
$^{1}H,^{13}C$-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **7**.



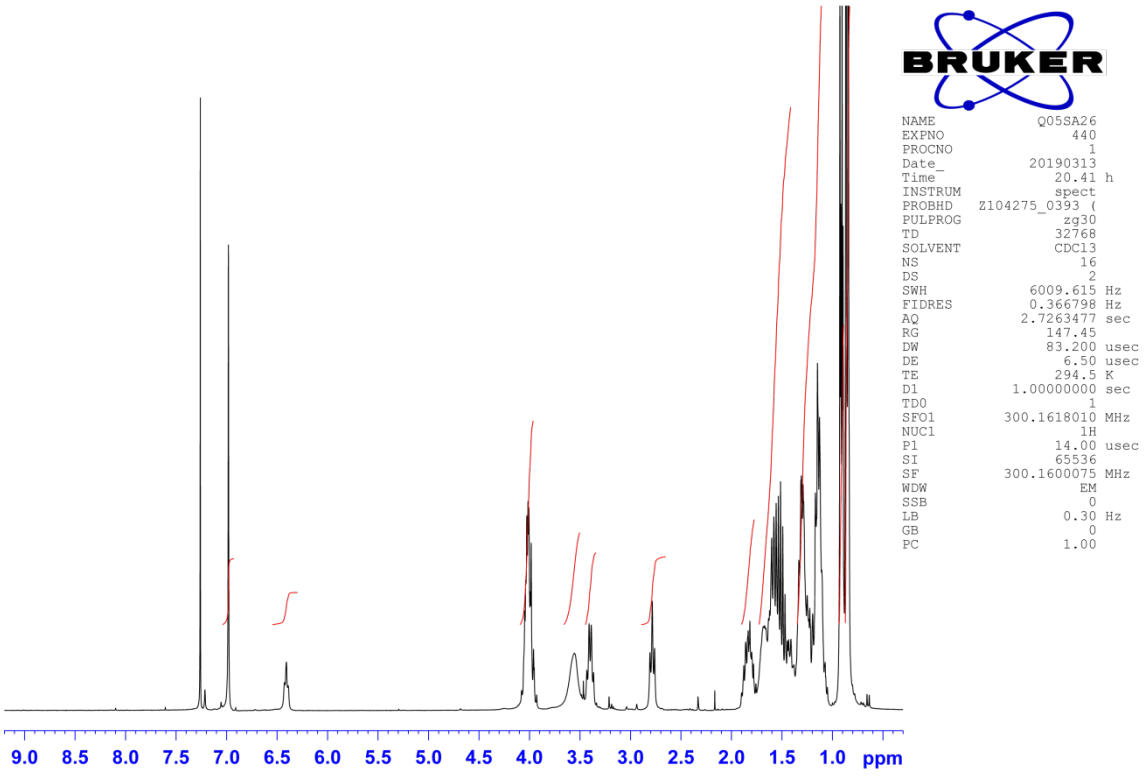
^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) of compound **8**.



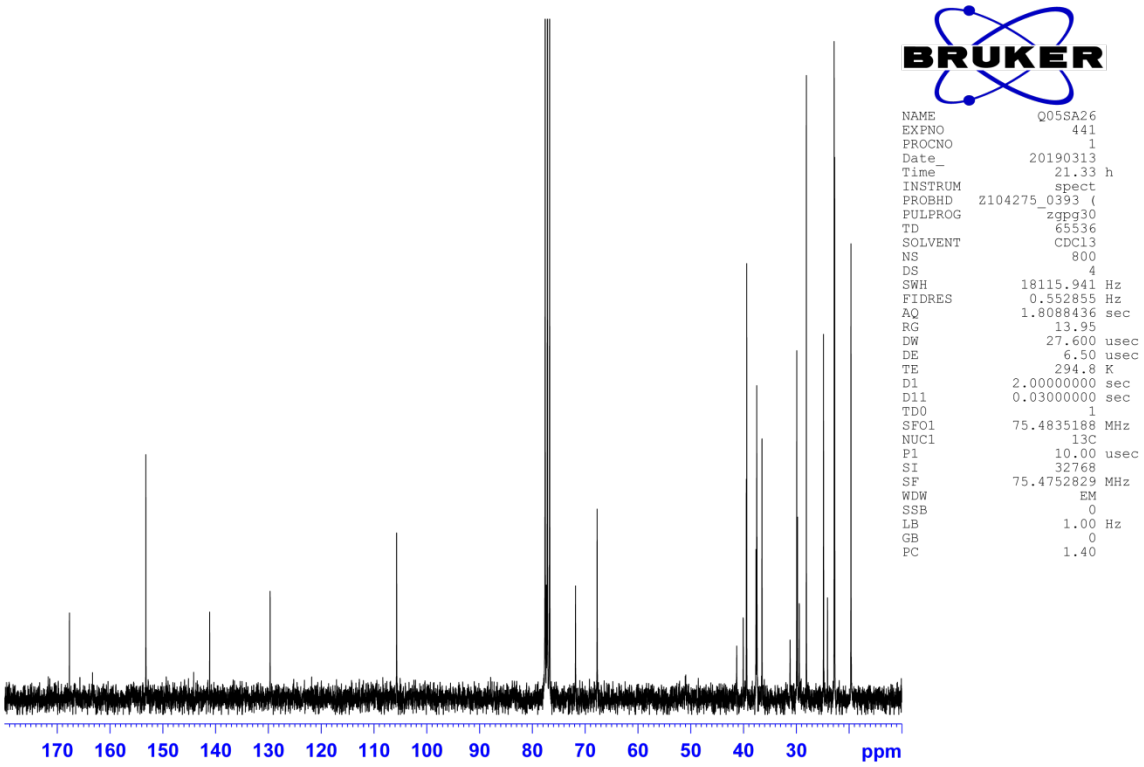
^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) of compound **8**.



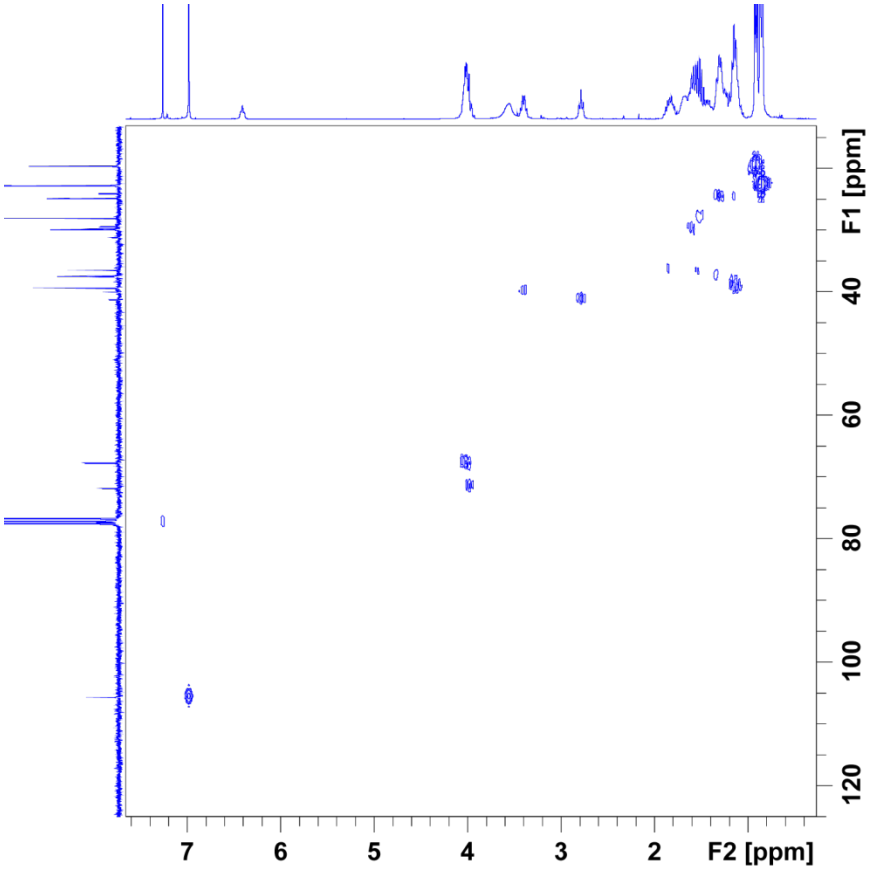
^{1}H,^{13}C-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **8**.



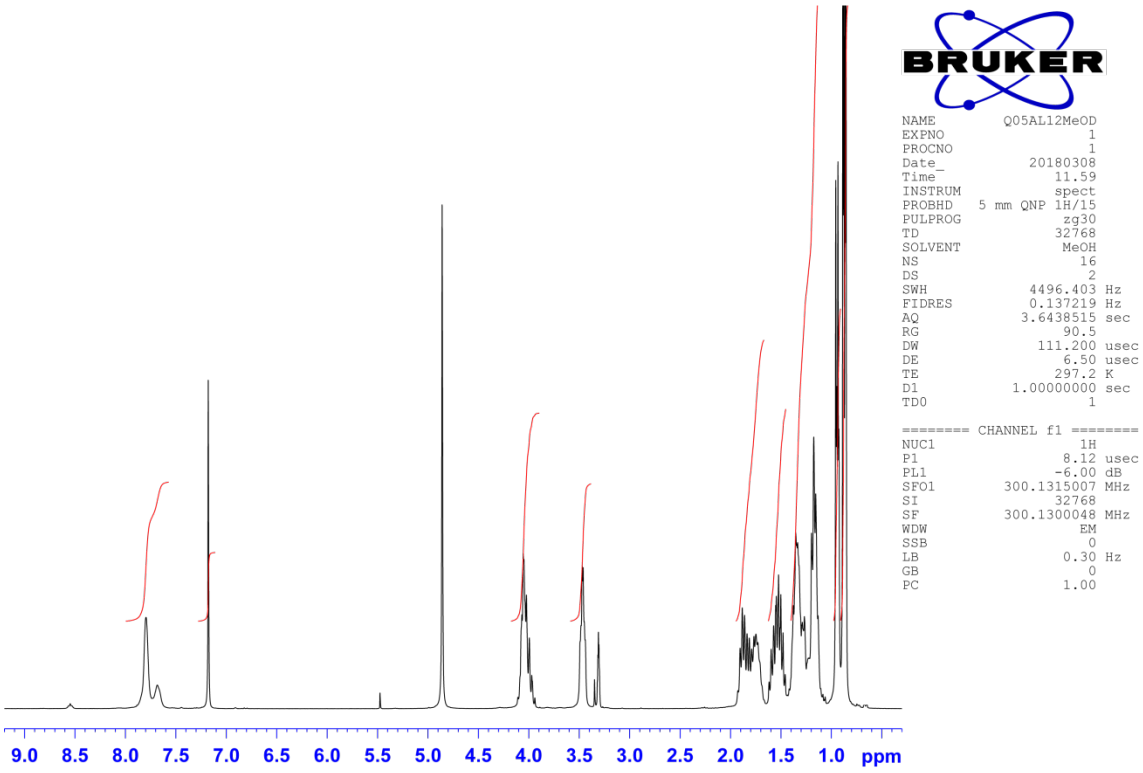
^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) of compound **9**.



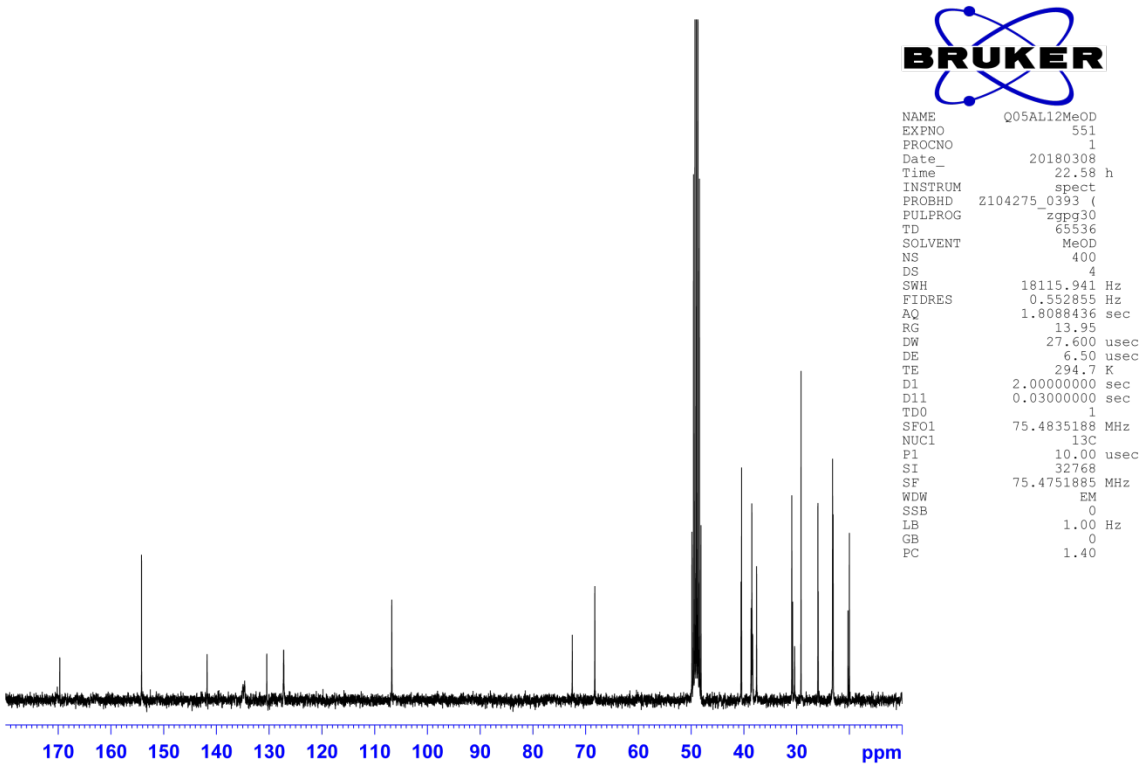
^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) of compound **9**.



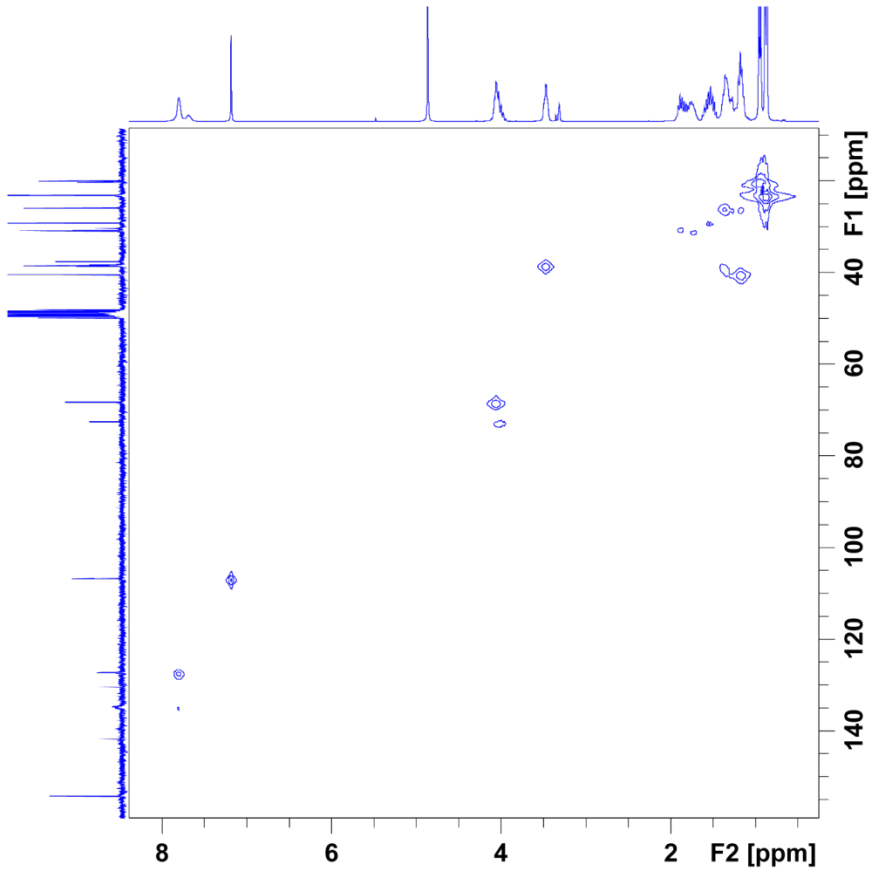
$^{1}H,^{13}C$-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **9**.



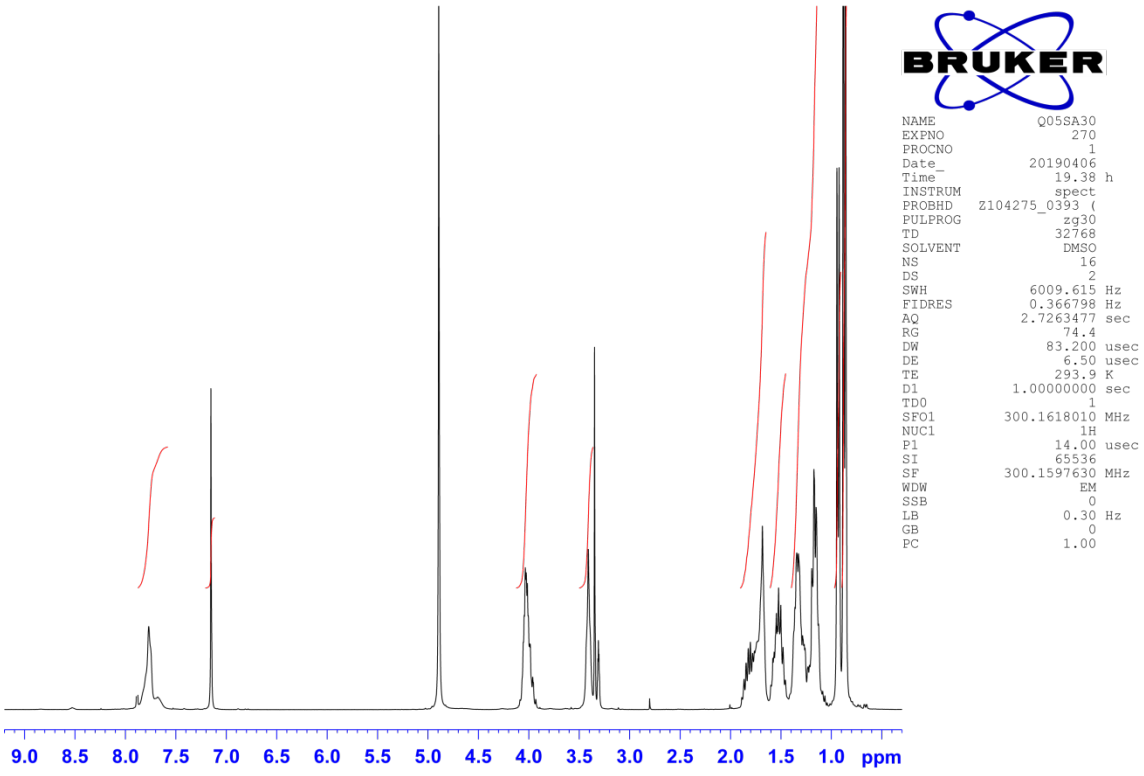
^{1}H NMR (MeOD-d_4, 300 MHz, 25 ºC) of compound **10**.



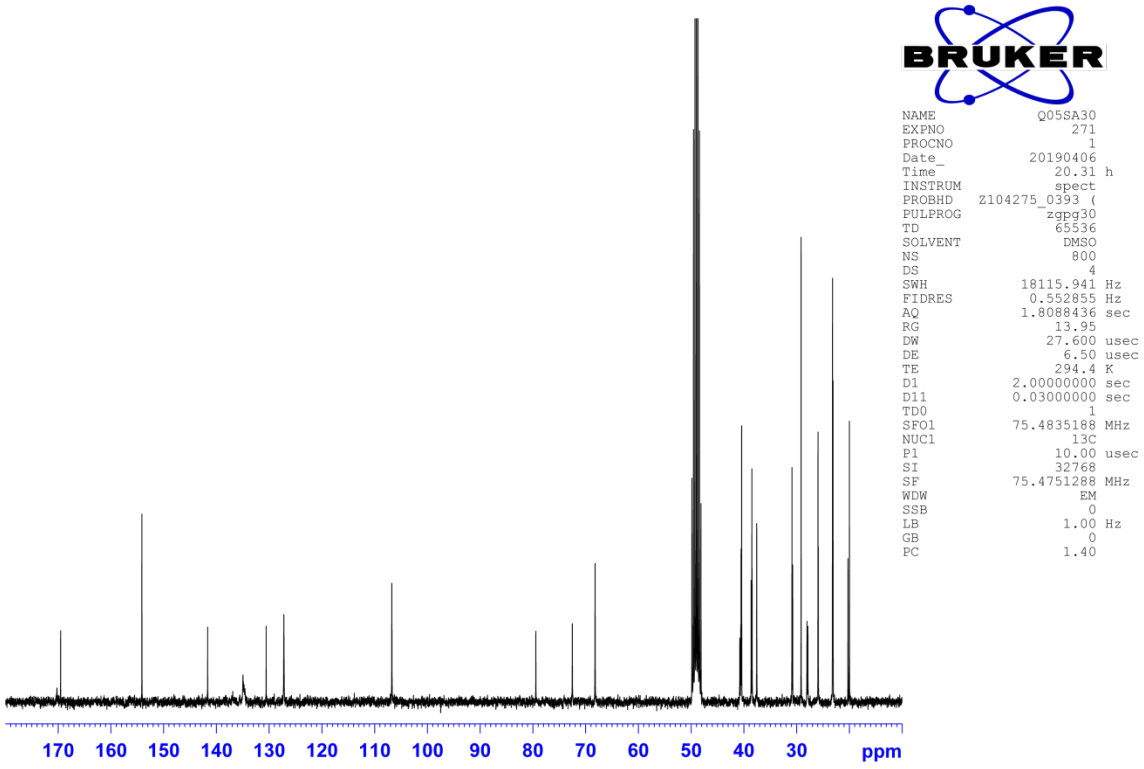
^{13}C NMR (MeOD-d$_4$, 75 MHz, 25 ºC) of compound **10**.



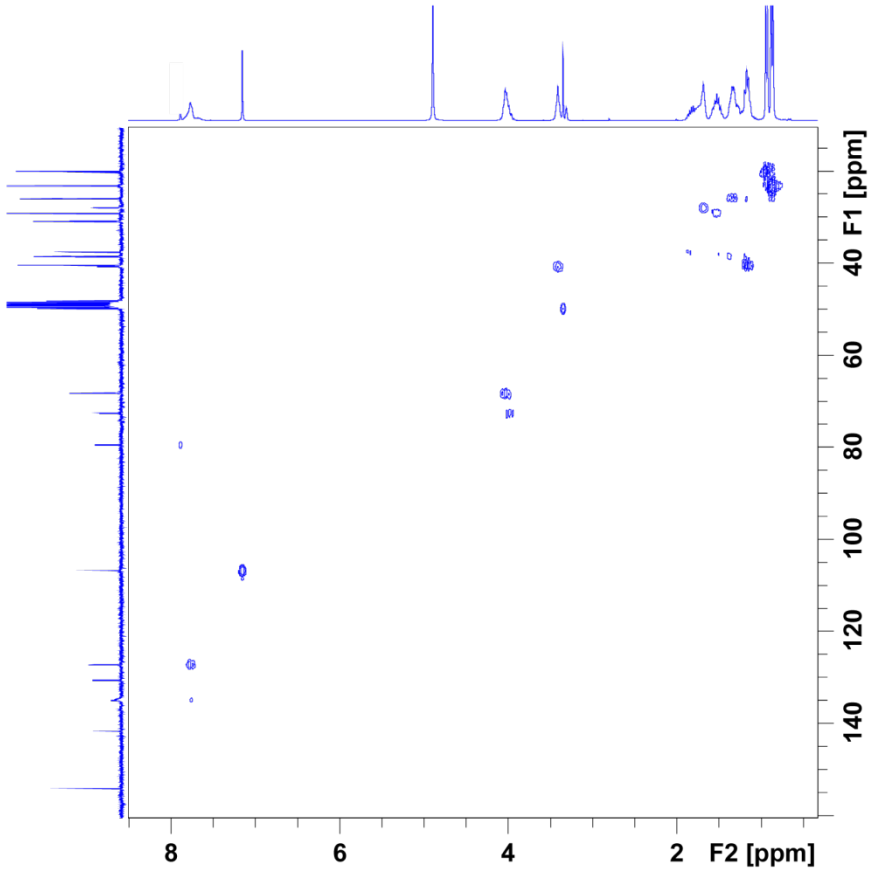
^{1}H,^{13}C-HMQC spectrum (MeOD-d$_4$, 25 ºC) of compound **10**.



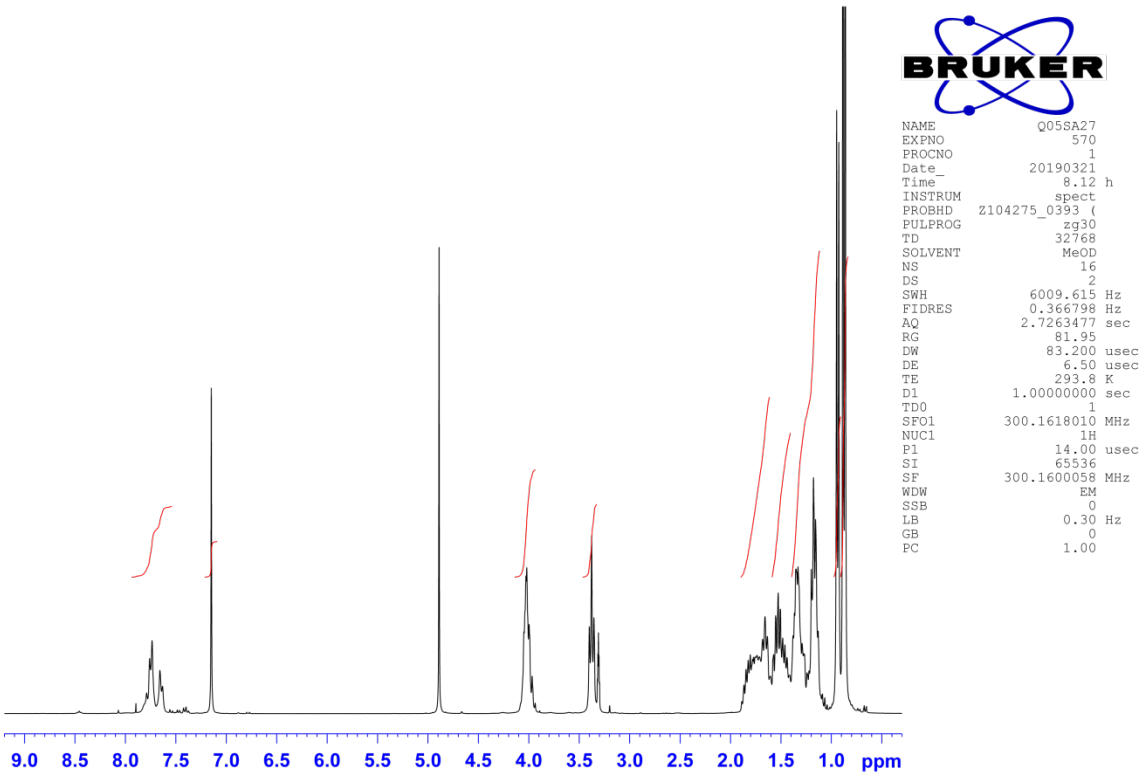
^{1}H NMR (MeOD-d$_4$, 300 MHz, 25 ºC) of compound **11**.



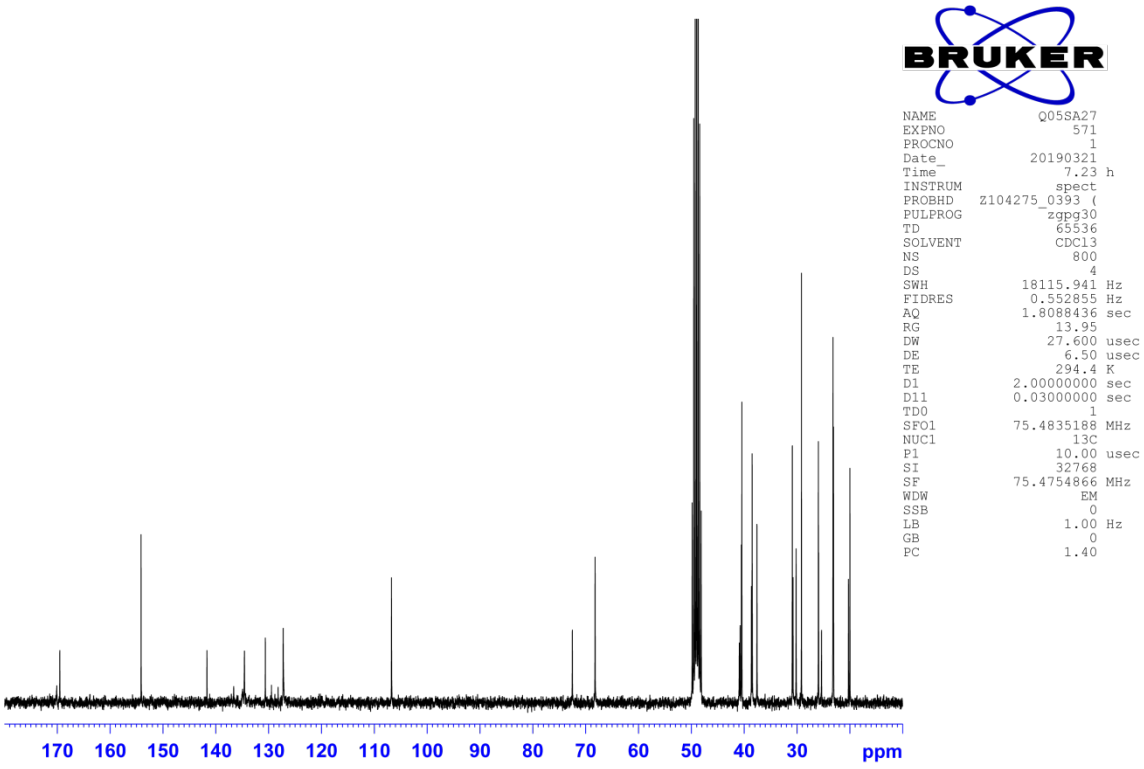
^{13}C NMR (MeOD-d$_4$, 75 MHz, 25 ºC) of compound **11**.



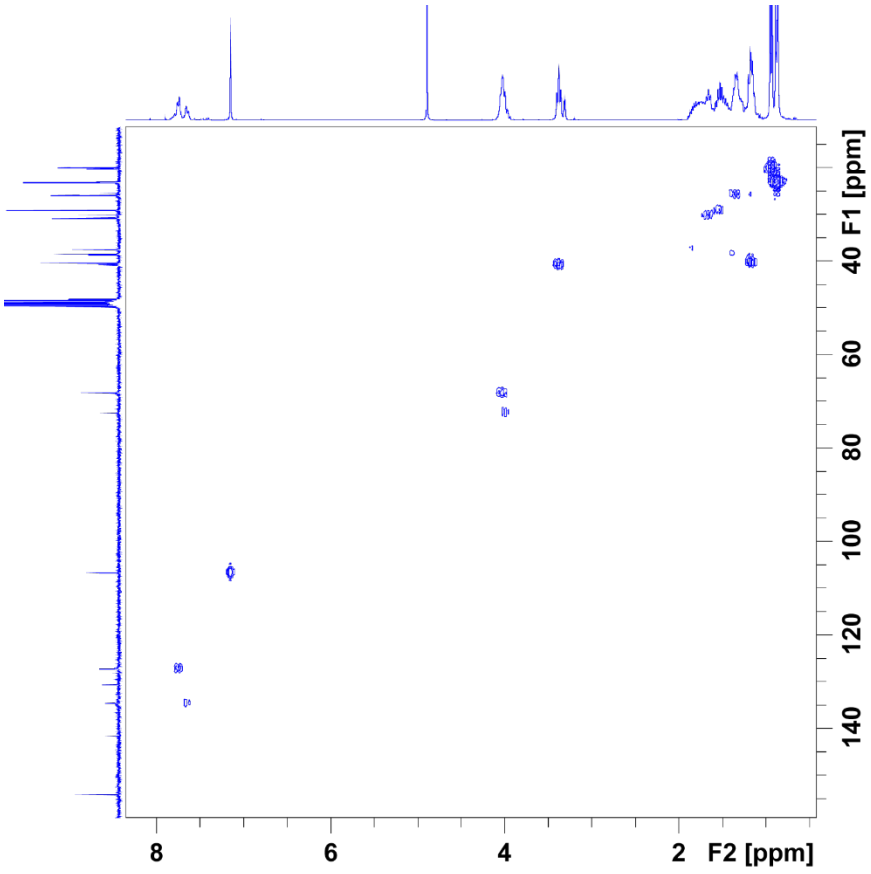
$^{1}H,^{13}C$-HMQC spectrum (MeOD-d_4, 25 ºC) of compound **11**.



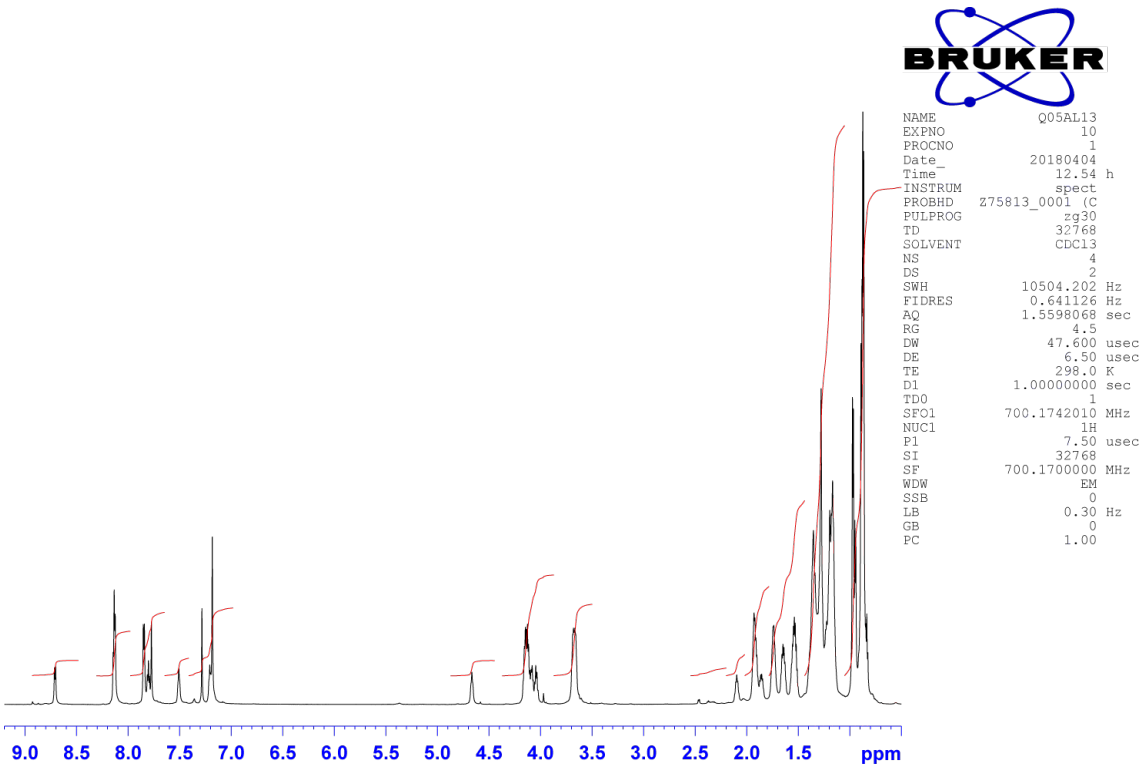
^{1}H NMR (MeOD-d_4, 300 MHz, 25 ºC) of compound **12**.



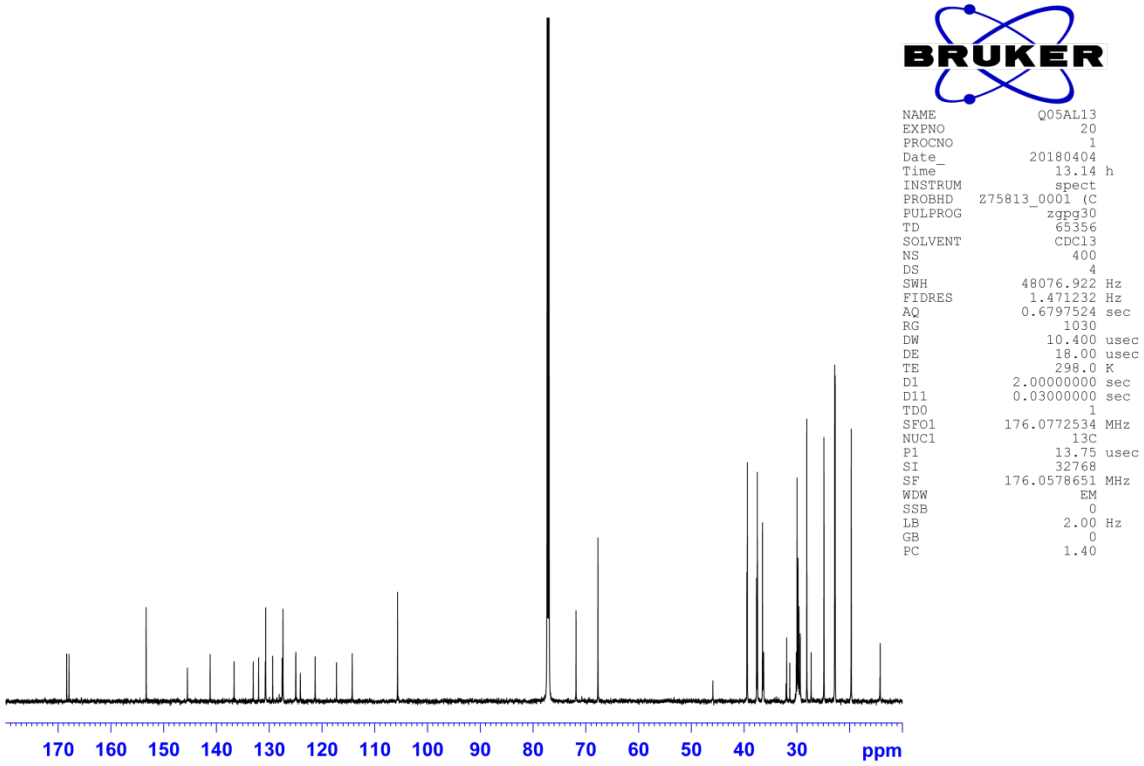
^{13}C NMR (MeOD-d$_4$, 75 MHz, 25 ºC) of compound **12**.



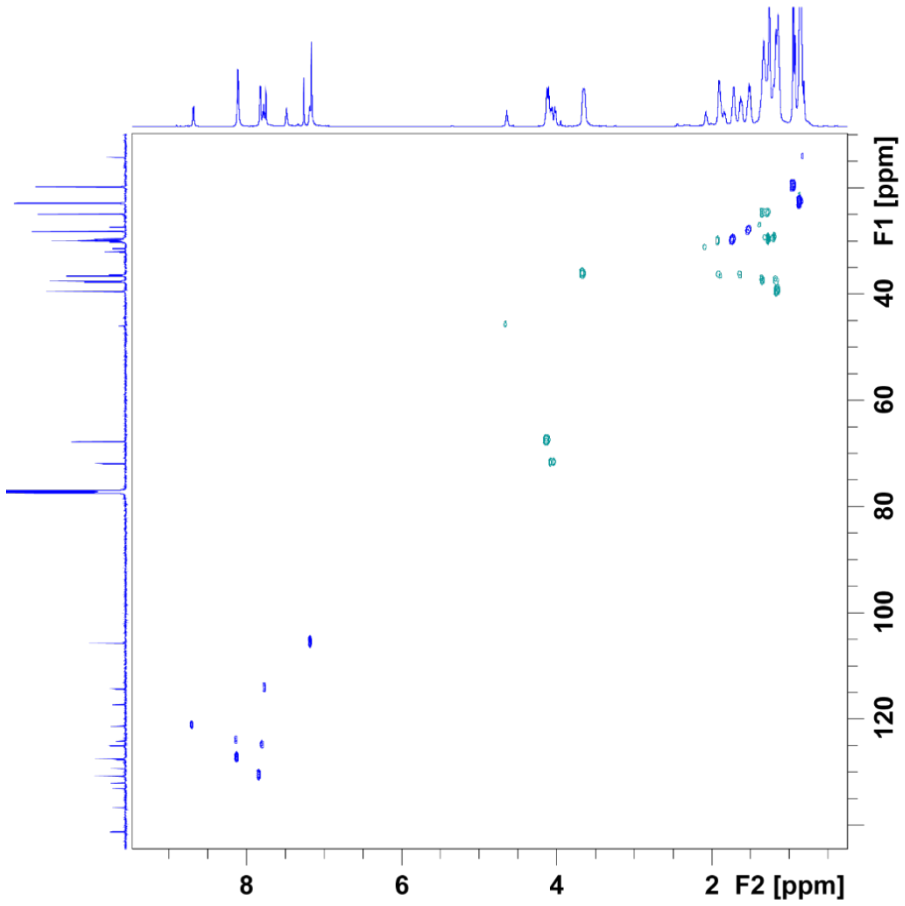
^{1}H,^{13}C-HMQC spectrum (MeOD-d$_4$, 25 ºC) of compound **12**.



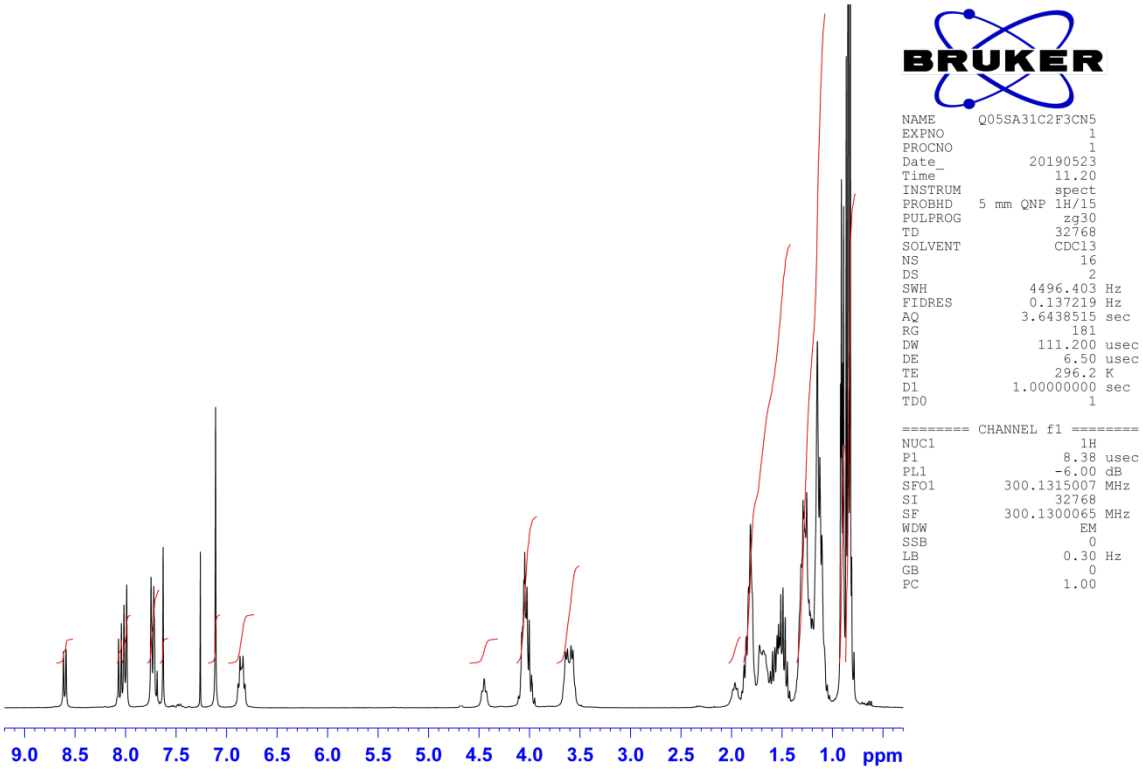
^{1}H NMR ($CDCl_3$, 700 MHz, 25 ºC) of compound **2**.



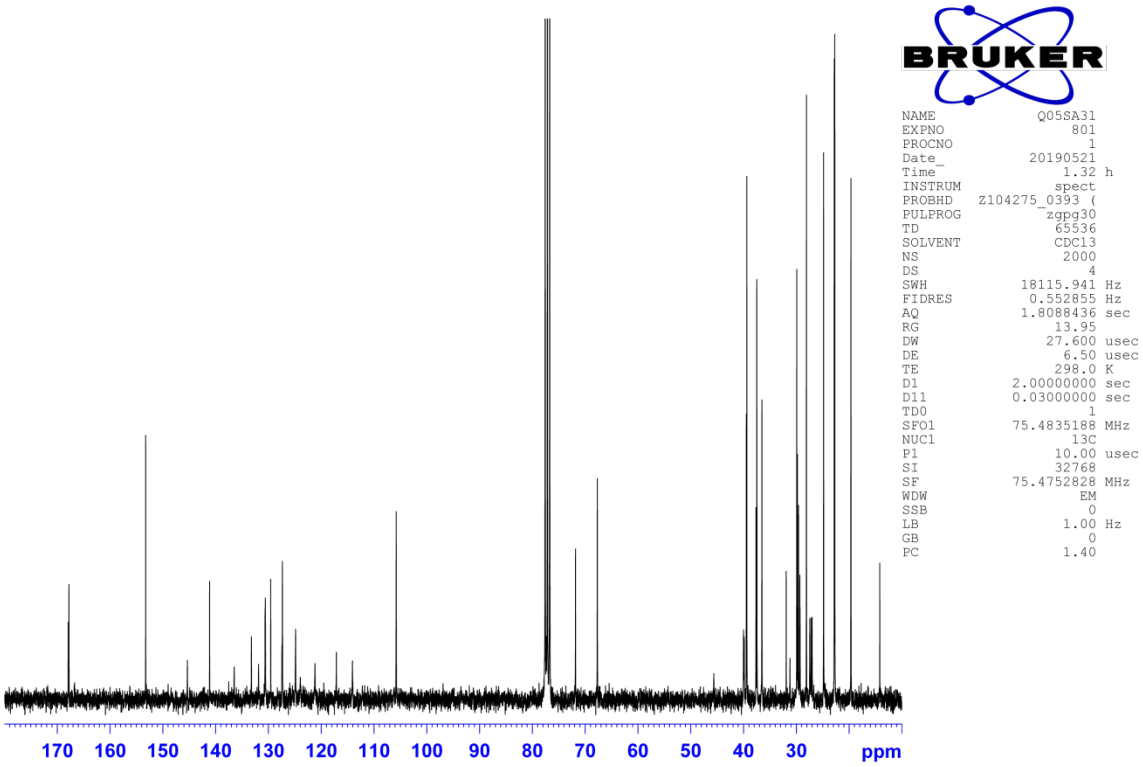
^{13}C NMR ($CDCl_3$, 175 MHz, 25 ºC) of compound **2**.



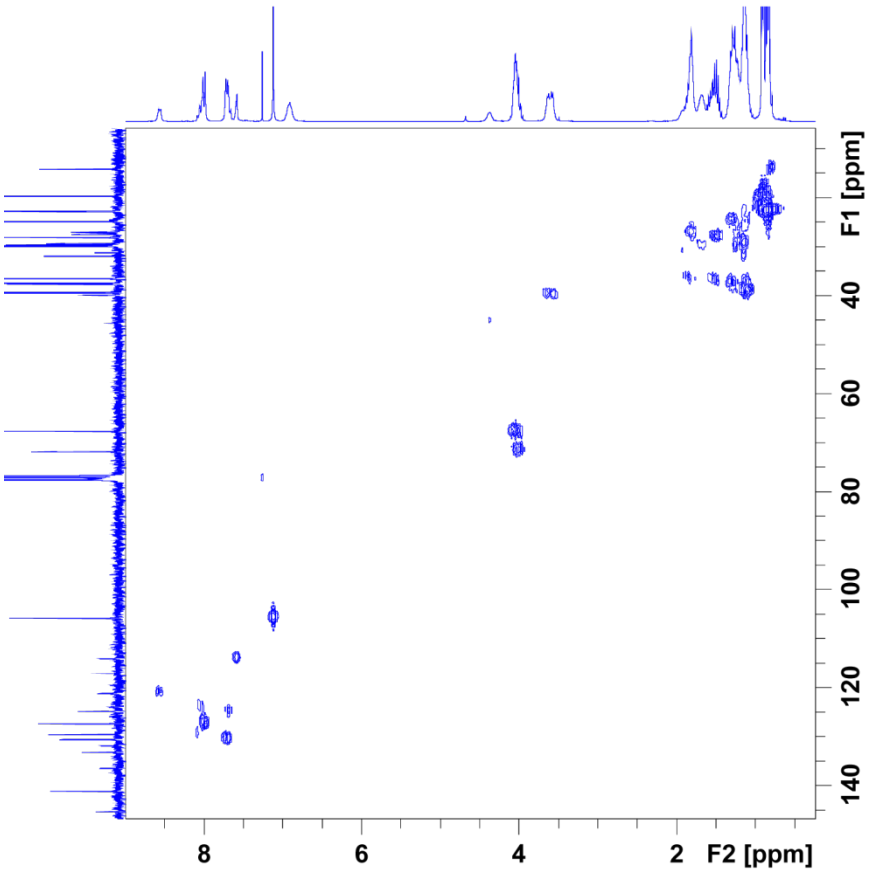
$^{1}H,^{13}C$-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **2**.



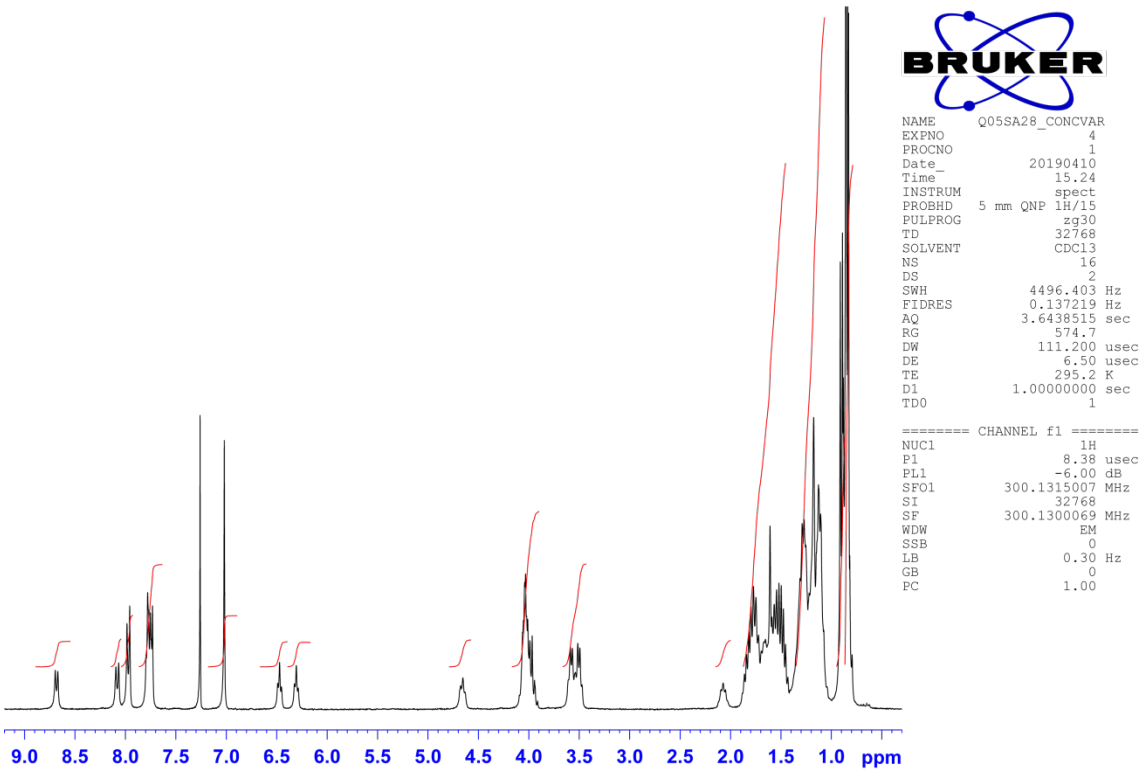
^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) of compound **3**.



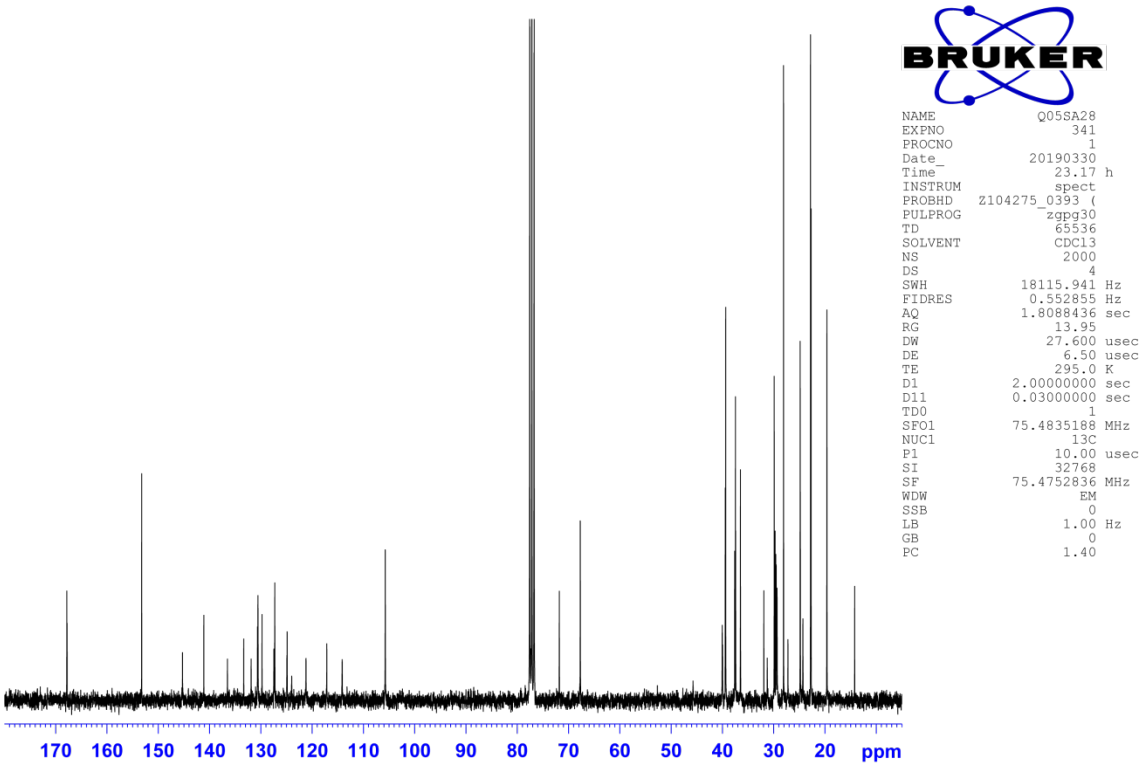
^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) of compound **3**.



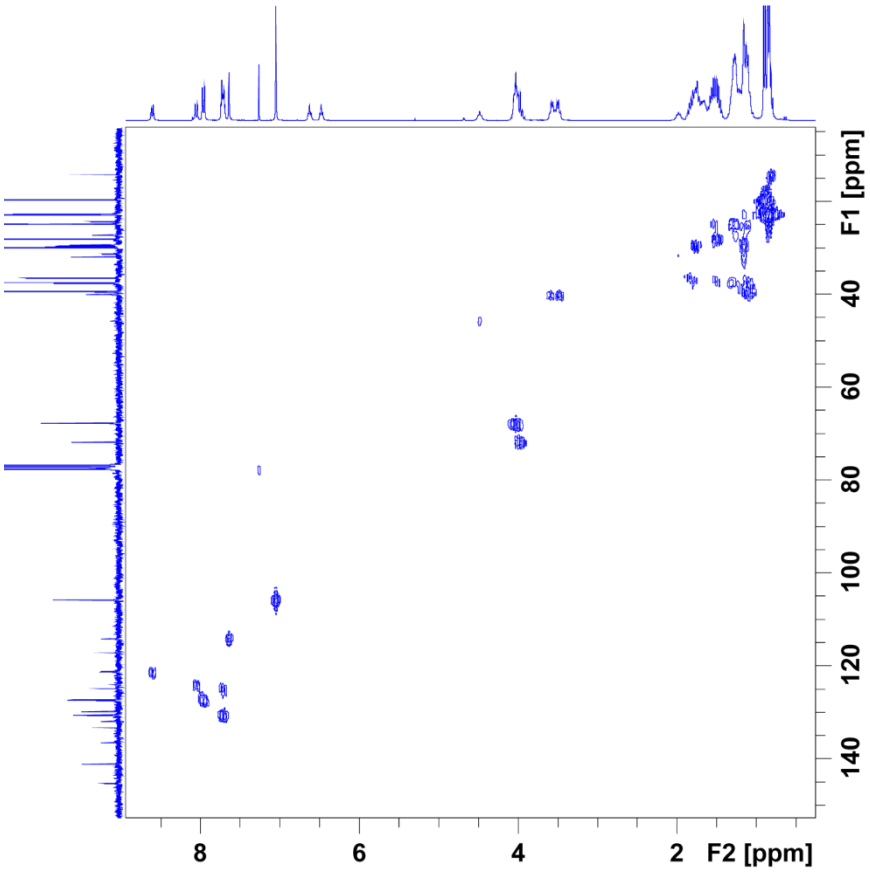
^{1}H,^{13}C-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **3**.



^{1}H NMR ($CDCl_3$, 300 MHz, 25 ºC) of compound **4**.



^{13}C NMR ($CDCl_3$, 75 MHz, 25 ºC) of compound **4**.



$^{1}H,^{13}C$-HMQC spectrum ($CDCl_3$, 25 ºC) of compound **4**.

4. Supplementary Figures and Tables

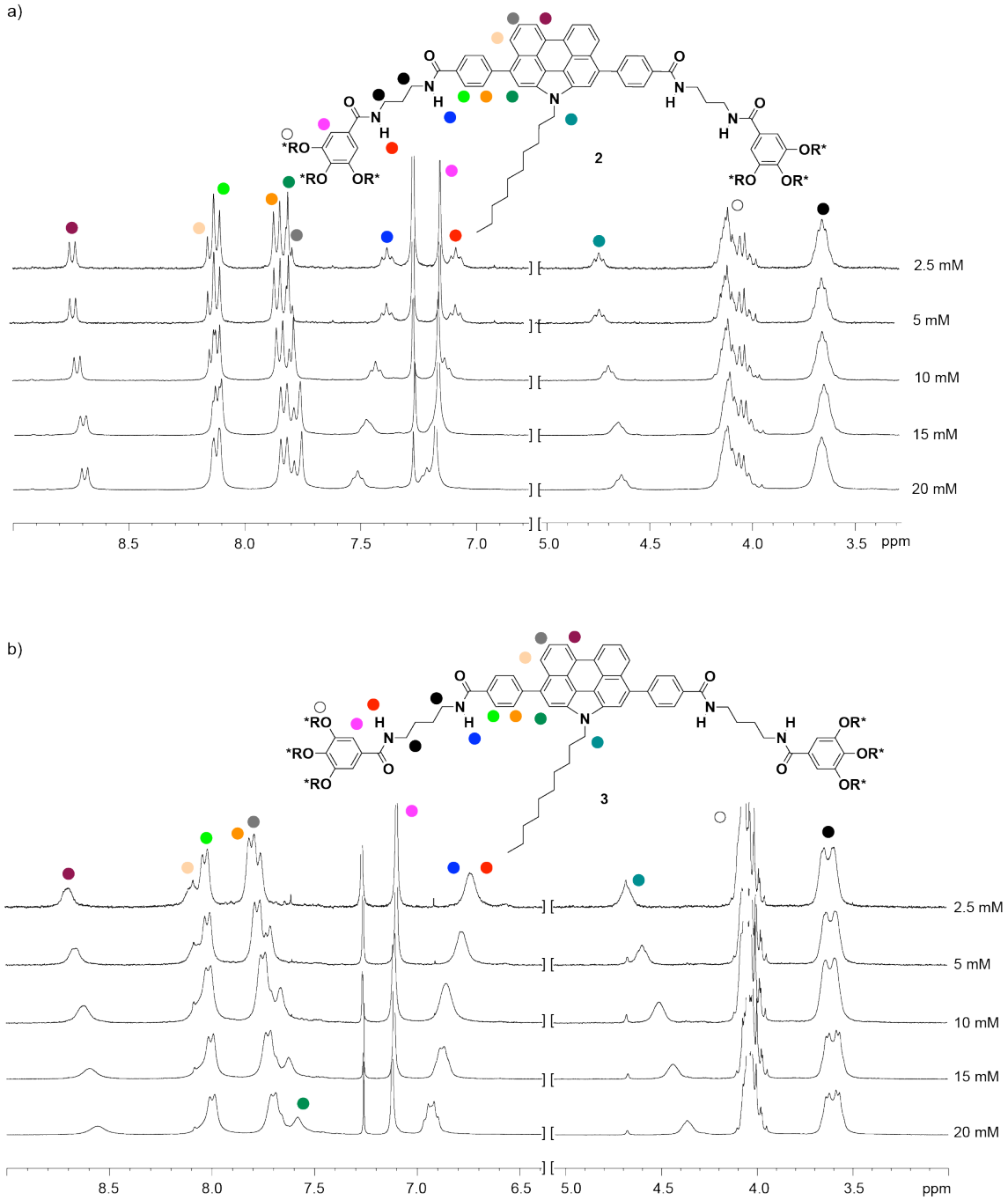


Figure S1. Partial ^{1}H NMR spectra of **2** (a) and **3** (b) in $CDCl_3$ at different concentrations (300 MHz, 25 ºC).

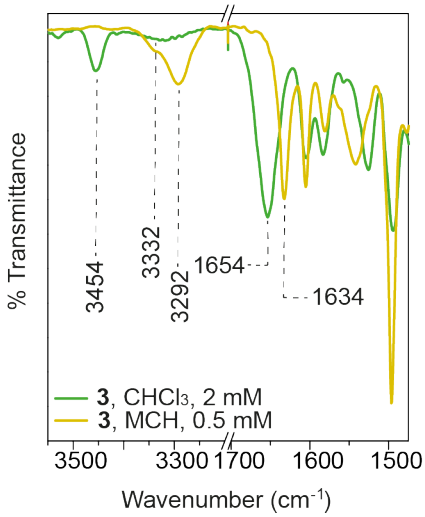


Figure S2. Partial FTIR spectra of **3** in solution showing the region in which the stretching N-H and Amide I bands are observed.

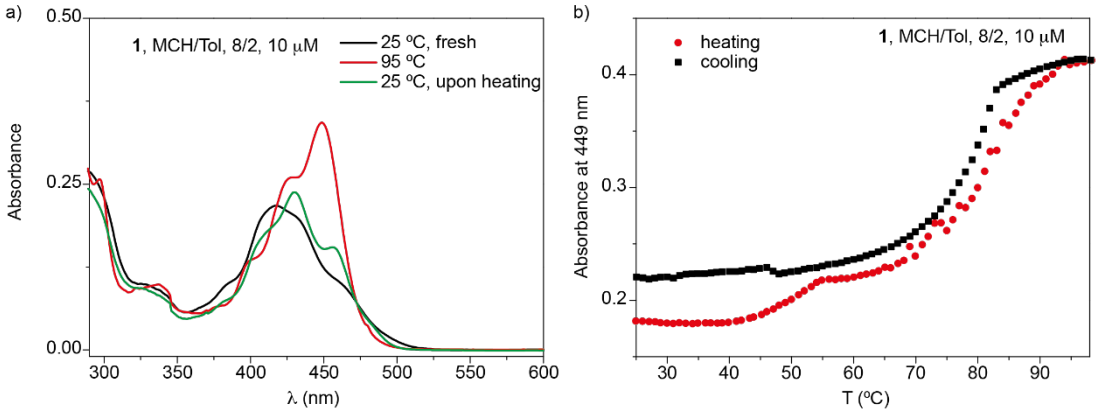


Figure S3. UV-Vis spectra (a) and variation of the absorbance at λ = 449 nm (b) of a diluted solution of **1** (MCH/Tol (8/2); c_T = 10 μM; cooling and heating rate = 1 ºC/min).

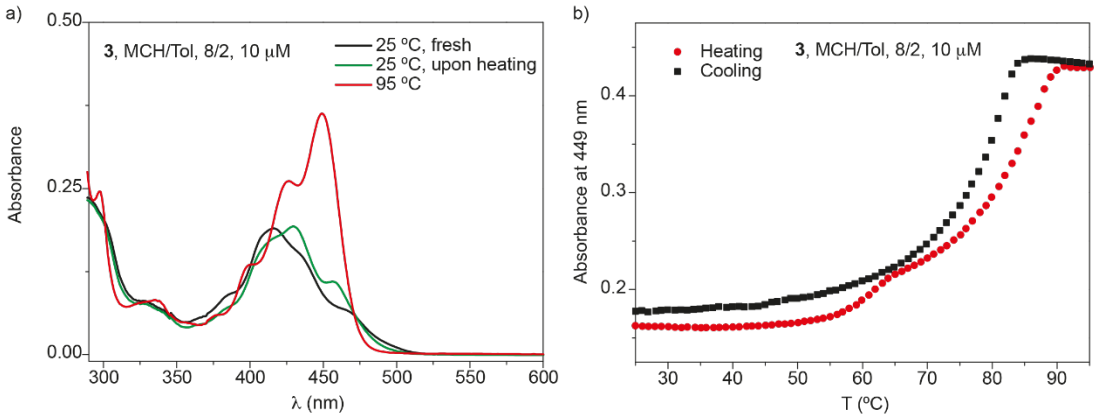


Figure S4. (a) UV-Vis spectra of **3**; (b) Variation of the absorbance at λ = 449 nm of a diluted solution of **3** (experimental conditions: MCH/Tol (8/2); c_T = 10 μM; cooling and heating rate = 1 ºC/min).

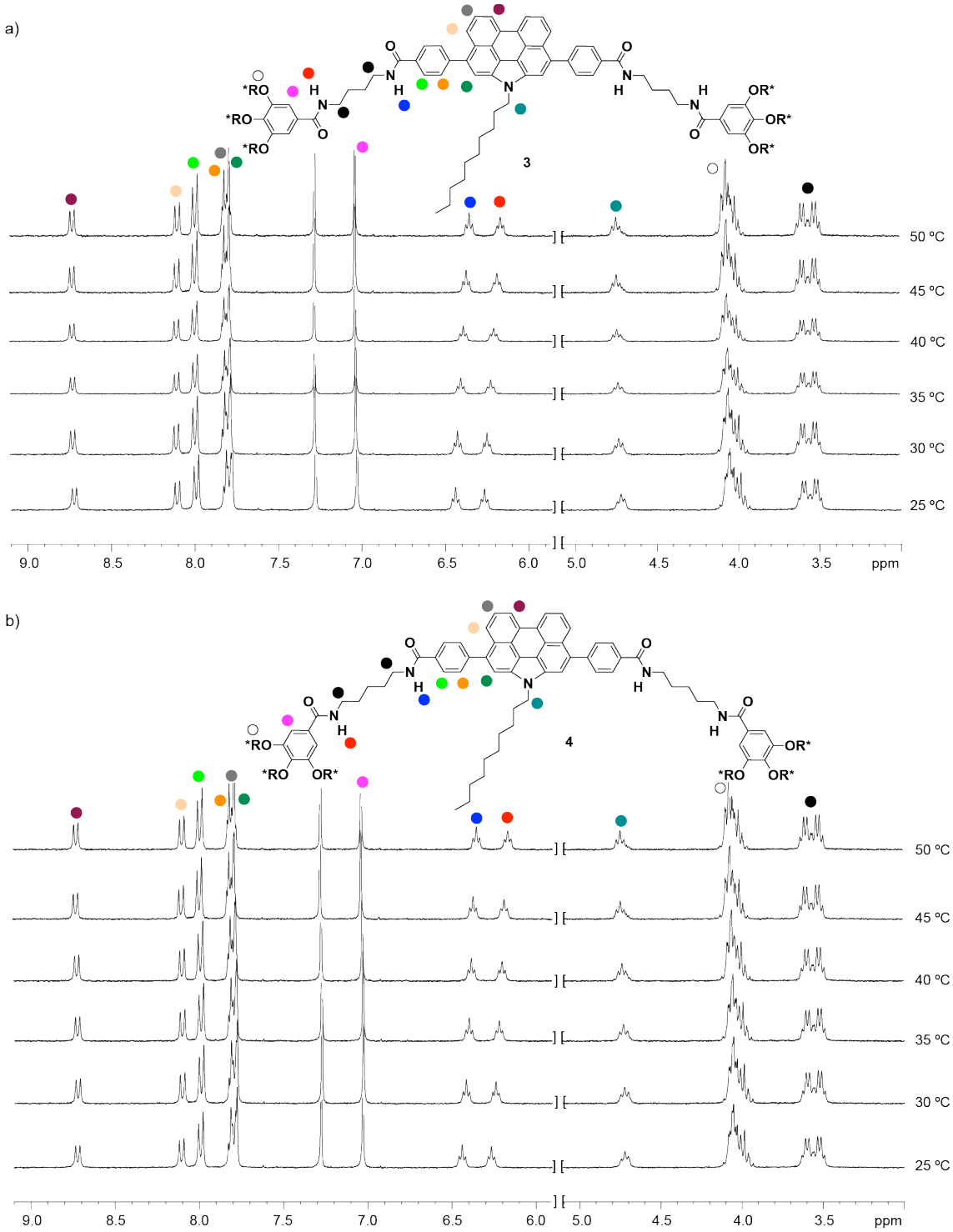


Figure S5. Partial VT-^{1}H NMR spectra of **3** (a) and **4** (b) (c_T = 2 mM; $CDCl_3$, 300 MHz).

Table S1. Chemical shifts for the inner and outer amide protons at different temperatures ($CDCl_3$; 300 MHz; 2 mM).

Compound	T (ºC)	δ inner NH	δ outer NH
2	25	7.34	7.06
	30	7.31	7.04
	35	7.28	7.02
	40	*	7.01
	45	7.21	6.99
	50	7.18	6.97
3	25	6.68	6.64
	30	6.64	6.61
	35	6.62	6.57
	40	6.60	6.54
	45	6.58	6.51
	50	6.56	6.48
4	25	6.42	6.24
	30	6.40	6.22
	35	6.38	6.20
	40	6.36	6.18
	45	6.35	6.16
	50	6.34	6.15

*Coincides with the resonance corresponding to the solvent

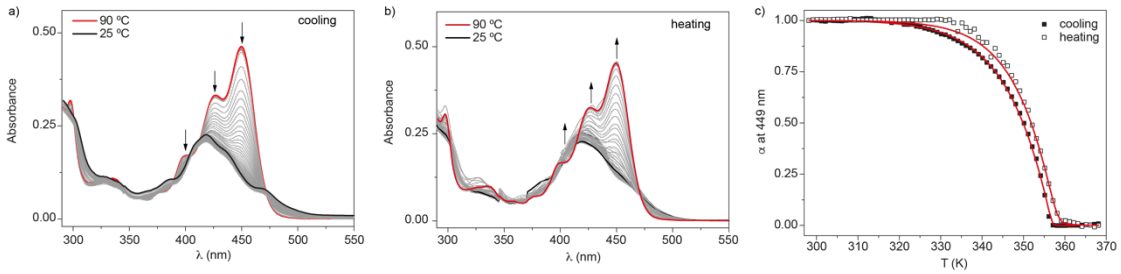


Figure S6. UV-Vis spectra of **4** upon cooling (a) and heating (b) a solution at c_T = 10 μM in MCH/Tol 8/2 by applying a cooling or heating rate of 1 ºC/min. Arrows indicate the spectral changes observed upon decreasing (a) or increasing the (b) the temperature. (c) Variation of the degree of aggregation with the temperature upon cooling or heating at 1 ºC/min. Red lines in (c) correspond to the fitting to the EQ model to guide the eye.

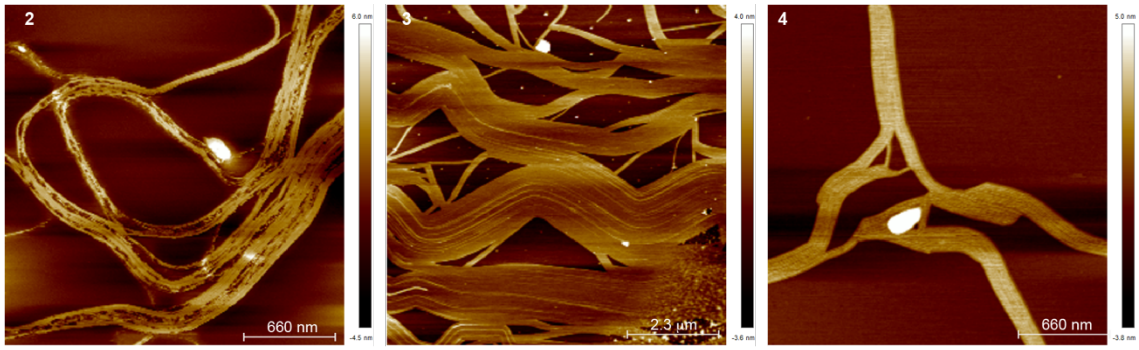


Figure S7. AFM images of the fibrillar bundles formed by the supramolecular polymers of compounds **2-4**. Experimental conditions: MCH/Tol 8/2 as solvent, c_T = 10 µM, mica as surface.

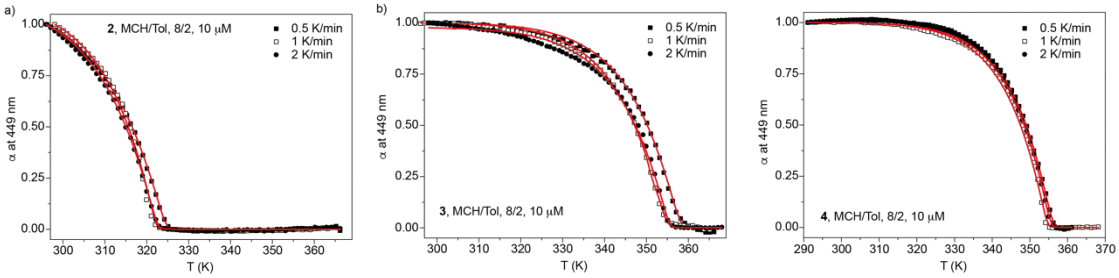


Figure S8. Plot of the variation of the degree of aggregation (α) versus temperature for compounds **2** (a), **3** (b) and **4** (c) at different cooling rates (0.5, 1 or 2 ºC/min). The red lines depict the fitting to the one-component EQ model. Experimental conditions: MCH/Tol 8/2 as solvent, c_T = 10 µM.