SUPPORTING INFORMATION FOR:

Molecular Fibers and Wires in Solid-State and Solution Self-Assemblies of Cyclodextrin [2]-Rotaxanes

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Synthesis

6: A mixture of α-cyclodextrin **3** (3.0 g, 3.1 mmol) and 4,4'-dicarboxyazobenzene **2** (100 mg, 0.37 mmol) in 0.2 mol dm^{-3} carbonate buffer (pH 10, 25 cm^3) was stirred at room temperature for two hours. 3,5-Dimethylaniline **5** (180 mg, 1.48 mmol) and DMT-MM (370 mg, 1.55 mmol) were then added, and the mixture was stirred at room temperature for an additional ten hours. The resulting solution was washed with ethyl acetate (5 × 25 cm^3), and then it was concentrated under reduced pressure. The residue was dissolved in water (40 cm^3) and the solution was applied to a Diaion HP-20 column (310 × 25 mm). The column was eluted with water (*ca.* 3.0 dm^3) until no more unreacted α-cyclodextrin **3** was detected by TLC. The column was then eluted with a water–methanol solvent gradient. The desired product was obtained when the column was eluted with 50% aqueous methanol. That fraction was concentrated under reduced pressure to give an orange powder (147 mg, 27%); TLC (5:4:3:2 v/v/v/v *i*-propanol–ethanol–water–acetic acid) R_f 0.8 (relative to solvent front), 1.5 (relative to α-cyclodextrin **3**); ^{1}H NMR (500 MHz, Methanol-d_4) δ_H 8.64 (2H, d, *J* 8.5), 8.24 (2H, d, *J* 8.5), 8.20 (2H, d, *J* 8.5), 8.03 (2H, d, *J* 8.5), 7.47 (2H, s), 7.39 (2H, s), 6.87 (1H, s), 6.86 (1H, s), 4.86 (6H, d, *J* 4.0), 3.84–3.80 (6H, m), 3.77–3.74 (6H, m), 3.74–3.72 (6H, m), 3.50–3.57 (6H, m), 3.53–3.50 (6H, m), 3.43–3.42 (6H, m), 2.35 (6H, s), 2.34 (6H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 166.3, 164.0, 153.1, 153.0, 138.7, 137.6, 136.8, 128.7, 127.6, 125.6, 124.5, 122.2, 118.7, 118.5, 102.0, 81.4, 73.1, 72.1, 71.6, 59.4, 21.2; ESI-MS (positive) *m/z* 1472 ($M+Na^+$); Elemental analysis: Found C, 50.19; H, 6.12; N, 3.80. $C_{66}H_{88}N_4O_{32}.7H_2O$ requires C, 50.31; H, 6.53; N, 3.56%.

7: (132 mg, 25%); TLC (5:4:3 v/v/v *n*-butanol–ethanol–water) R_f 0.8 (relative to solvent front), 2.9 (relative to α-cyclodextrin **3**); HPLC: t_R 3.7 min (column: YMC ODS-AQ, 250 × 10 mm; 45% aq. CH_3CN; flow rate: 3.0 cm^3 min^{-1}); ^{1}H NMR (500 MHz, MeOH-d_4) δ_H 8.14 (4H, s), 8.10 (2H, d, *J* 8.0), 7.72 (2H, d, *J* 8.0), 7.51 (1H, d, *J* 16.5), 7.33 (1H, d, *J* 16.5), 7.16 (6H, m), 4.94 (6H, d, *J* 3.5), 3.91–3.87 (12H, m), 3.74 (6H, dd, *J* 3.5 and 12.3), 3.61 (6H, dd, *J* 1.5 and 12.0), 3.57 (6H, t, *J* 9.0), 3.48 (6H, dd, *J* 3.5 and 9.5), 2.35 (6H, s), 2.30 (6H, s); ^{13}C NMR (125 MHz, MeOH-d_4) δ_C 169.5, 168.3, 141.0, 140.5, 137.6, 137.4, 136.0, 135.9, 135.3, 131.9, 130.6, 129.7, 129.4(1), 129.3(6), 129.3(3), 129.2(7), 128.7, 128.2, 104.2, 83.6, 75.3, 74.0, 73.9, 61.7, 18.9, 18.6; ESI-MS (negative) *m/z* 1445 ($M-H^+$); Elemental analysis: Found C, 50.04; H, 6.55; N, 1.91. $C_{68}H_{90}N_2O_{32}.10H_2O$ requires C, 50.18; H, 6.81; N, 1.72%.

8: (30 mg, yield 5%); TLC (5:4:3 v/v/v *n*-butanol–ethanol–water) R_f 0.65 (relative to solvent front), 1.7 (relative to α-cyclodextrin **3**); HPLC: t_R 22.7 min (column: SymmetryPrep C18, 300 × 20 mm; gradient aq. MeCN; flow rate: 10 $cm^3\ min^{-1}$); ^1H NMR (500 MHz, Methanol-d_4) δ_H 7.22 (2H, s), 7.20 (2H, s), 6.87 (1H, s), 6.83 (1H, s), 4.98 (6H, d, *J* 2.5), 4.02–3.99 (12H, m), 3.93–3.90 (6H, m), 3.57–3.54 (6H, m), 3.52–3.51 (6H, m), 3.51–3.50 (6H, m), 2.48–2.32 (4H, m), 2.28 (6H, s), 2.26 (6H, s), 1.81–1.66 (4H, m), 1.56–1.40 (12H, m); ^{13}C NMR (75.5 MHz, Methanol-d_4) δ_C 175.3, 174.1, 139.7, 139.6, 139.4, 126.7, 119.2, 118.9, 104.1, 83.6, 75.3, 74.0, 73.8, 61.8, 38.4, 35.2, 32.7, 32.5, 32.1, 31.8, 30.9, 30.4, 28.7, 27.2, 21.5(3), 21.4(8); ESI-MS (positive) *m/z* 1409 (M^+); Elemental analysis: Found C, 49.07; H, 7.24; N, 1.80. $C_{64}H_{100}N_2O_{32}.8.5H_2O$ requires C, 49.19; H, 7.55; N, 1.79%.

9: 4,4'-Dicarboxyazobenzene **2** (50 mg, 0.19 mmol) was dissolved in THF (15 cm^3) and water (5 cm^3). 3,5-Dimethylaniline (90 mg, 0.74 mmol) and DMT-MM (200 mg, 0.82 mmol) were added and the mixture was stirred for 24 h at room temperature. The resultant precipitate was collected by filtration and dried under vacuum to give the diamide **9** as an orange powder (45 mg, 50%). M.p. >250 °C; ^1H NMR (300 MHz, DMSO-d_6) δ_H 10.30 (2H, s), 8.17 (4H, d, *J* 8.1), 8.06 (4H, d, *J* 8.1), 7.43 (4H, s), 6.77 (2H, s), 2.27 (12H, s); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ_C 165.2, 153.4, 139.5, 138.3, 132.3, 129.8, 126.2, 123.4, 118.9, 21.84; ESI-MS (positive) *m/z* (%): 477 (100) [$M+H^+$], 499 (45) [$M+Na^+$]; Elemental analysis: Found C, 75.00; H, 5.88; N, 12.01. $C_{30}H_{28}N_4O_2$ requires: C, 75.61; H, 5.92; N, 11.76%.

10: 2,6-Dimethylaniline (30 mg, 0.25 mmol) and Et_3N (0.12 ml) were added to a solution of 4,4'-dicarboxystilbene[1] (14 mg, 0.06 mmol) and BOP (50 mg, 0.12 mmol) in anhydrous DMF (2 cm^3) and the mixture was stirred overnight at room temperature, before it was concentrated under reduced pressure. The residue was partitioned between brine and EtOAc. The organic layer was washed with aqueous citric acid, aqueous sodium bicarbonate and brine, then it was dried over $MgSO_4$ and concentrated under reduced pressure. The residue recrystallized from EtOH to give the diamide **10** as a colorless powder (14 mg, 57%). M.p. >250 °C; ^1H NMR (300 MHz, DMSO-d_6) δ_H 9.80 (2H, s), 8.03 (4H, d, *J* 8.7), 7.80 (4H, d, *J* 8.7), 7.52 (1H, d, *J* 16.0), 7.40 (1H, d, *J* 16.0), (4H, apparent s), 7.13 (6H, apparent s), 2.18 (12H, s); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ_C 165.2, 140.5, 136.4, 136.0, 134.1, 130.1, 128.8, 128.4, 127.4, 18.8; ESI-MS (positive) *m/z* (%): 475 (95) [$M+H^+$], 497 (100) [$M+Na^+$].

X-Ray Crystallography

The crystal data, data collection and refinement parameters are listed below. Measurements were made with a Nonius KappaCCD area detector using Mo Kα (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz and polarization effects and absorption.

Structures **6** and **7** were solved by direct methods using SHELXD[2] and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. In the structure of **6** two of the hydroxymethyl groups were disordered over two positions. Hydrogen atoms were included in calculated positions except that water molecules were included only as oxygen atoms.

Structure **9** was solved using SIR92[3] and refined on F with data where $I>2\sigma(I)$ using CRYSTALS.[4] Disorder was observed in the central section of the molecule and this has been incorporated into the model. Hydrogen atoms of the methyl groups and of the amine were refined positionally, while the remaining hydrogen atoms ride on the atoms to which they are bonded.

Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre. Free copies can be obtained from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

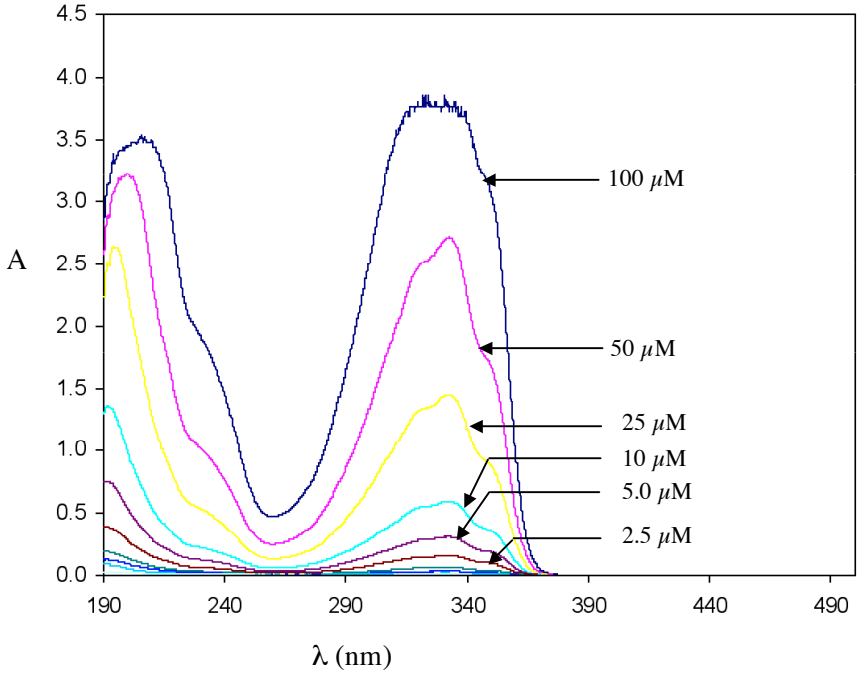
Table 1. Principal crystallographic data for the rotaxanes **6** and **7** and the diamide **9**.

	6	**7**	**9**
CCDC number	675081	675082	675083
formula	$C_{66}H_{88}N_4O_{39.5}$	$C_{68}H_{90}N_2O_{39}$	$C_{30}H_{28}N_4O_2$
M_r	1569.40	1559.42	476.58
crystal system	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a [Å]	13.629 (5)	13.8320 (3)	5.0641 (1)
b [Å]	16.304 (5)	22.7978 (5)	10.9910 (3)
c [Å]	34.170 (11)	24.1251 (5)	22.2770 (5)
β [°]	90.00	90.00	90.9020 (14)
V [Å^3]	7592.6 (4)	7607.6 (3)	1239.77 (5)
Z	4	4	2
T [K]	200	200	200
morphology	orange needle	colorless block	orange needle
D_x (Mgm^{-3})	1.373	1.362	1.277
μ (mm^{-1})	0.115	0.113	0.082
F(000)	3312	3296	504
Crystal size (mm)	0.57 × 0.19 × 0.17	0.53 × 0.51 × 0.45	0.40 × 0.10 × 0.04
θ-range (°)	2.6 – 25.2	2.7 – 27.5	2.6 – 27.5
Data collected	49838	68680	22556
Independent data [$R_{(int)}$]	12851 [0.122]	17084 [0.038]	2848 [0.049]
Observed data [$I>2\sigma(I)$]	11460	15786	1743
Parameters	1032	1004	213
R_1 [$I>2\sigma(I)$]	0.064	0.055	0.043
wR_2	0.169[a]	0.166[a]	0.078[b]

[a]All data. [b]$I>2\sigma(I)$.

Ultraviolet-Visible Spectra

a)



b)

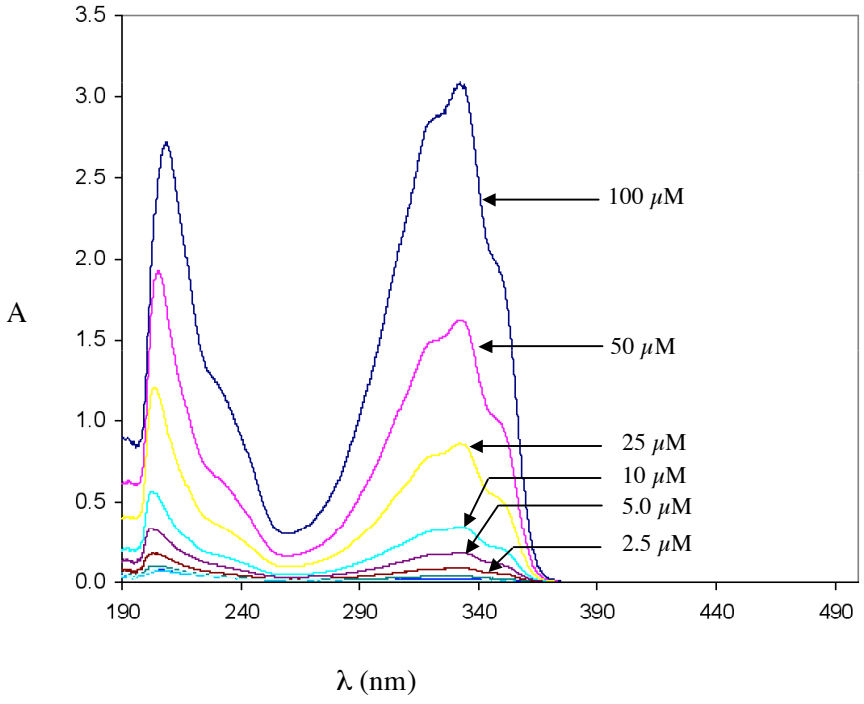


Figure S1. Absorption spectra of the rotaxane **7** in a) water and b) methanol at concentrations ranging from 2.5–100 μM, recorded at room temperature.

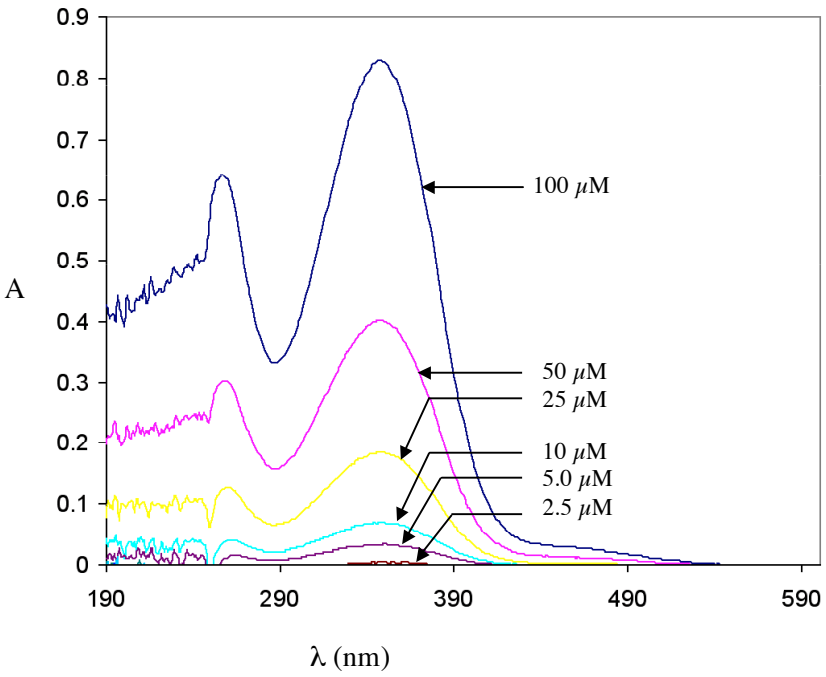


Figure S2. Absorption spectra of the diamide **9** in DMSO at concentrations ranging from 2.5–100 μM, recorded at room temperature.

Graphs of Ultraviolet-Visible Absorbance and Fluorescence Emission Intensity *vs* Concentration for Aqueous Solutions of the Rotaxane 6

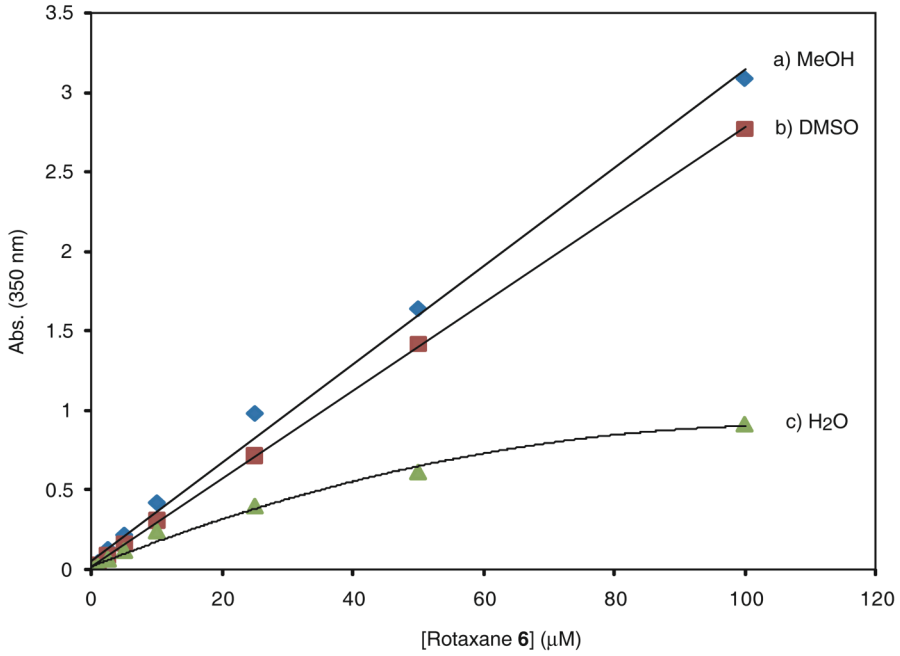


Figure S3. Absorbance at 350 nm of solutions of the rotaxane **6** as a function of concentration, recorded at room temperature in the solvents indicated.

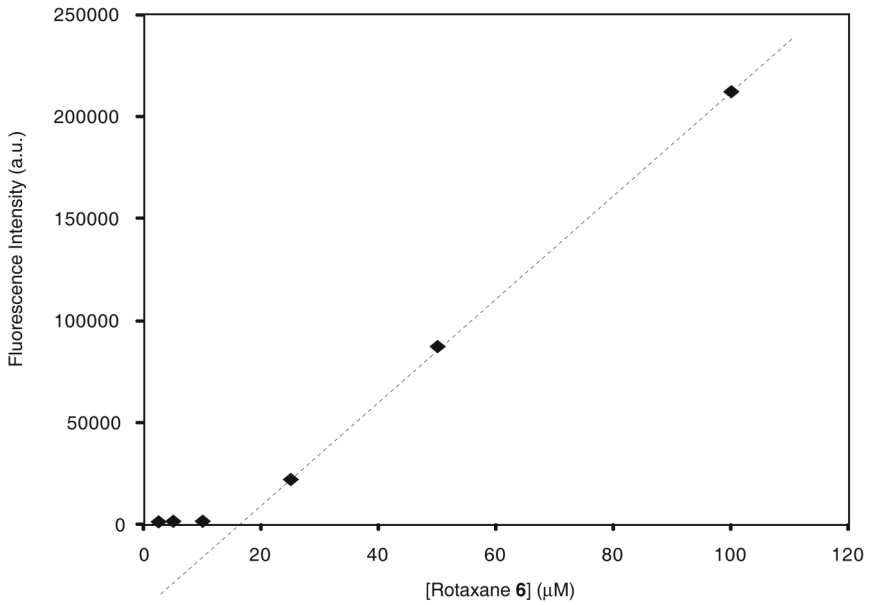
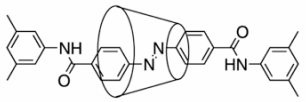


Figure S4. Fluorescence emission intensity at 520 nm of aqueous solutions of the rotaxane **6** as a function of concentration, recorded at room temperature (λ_{ex} = 480 nm).

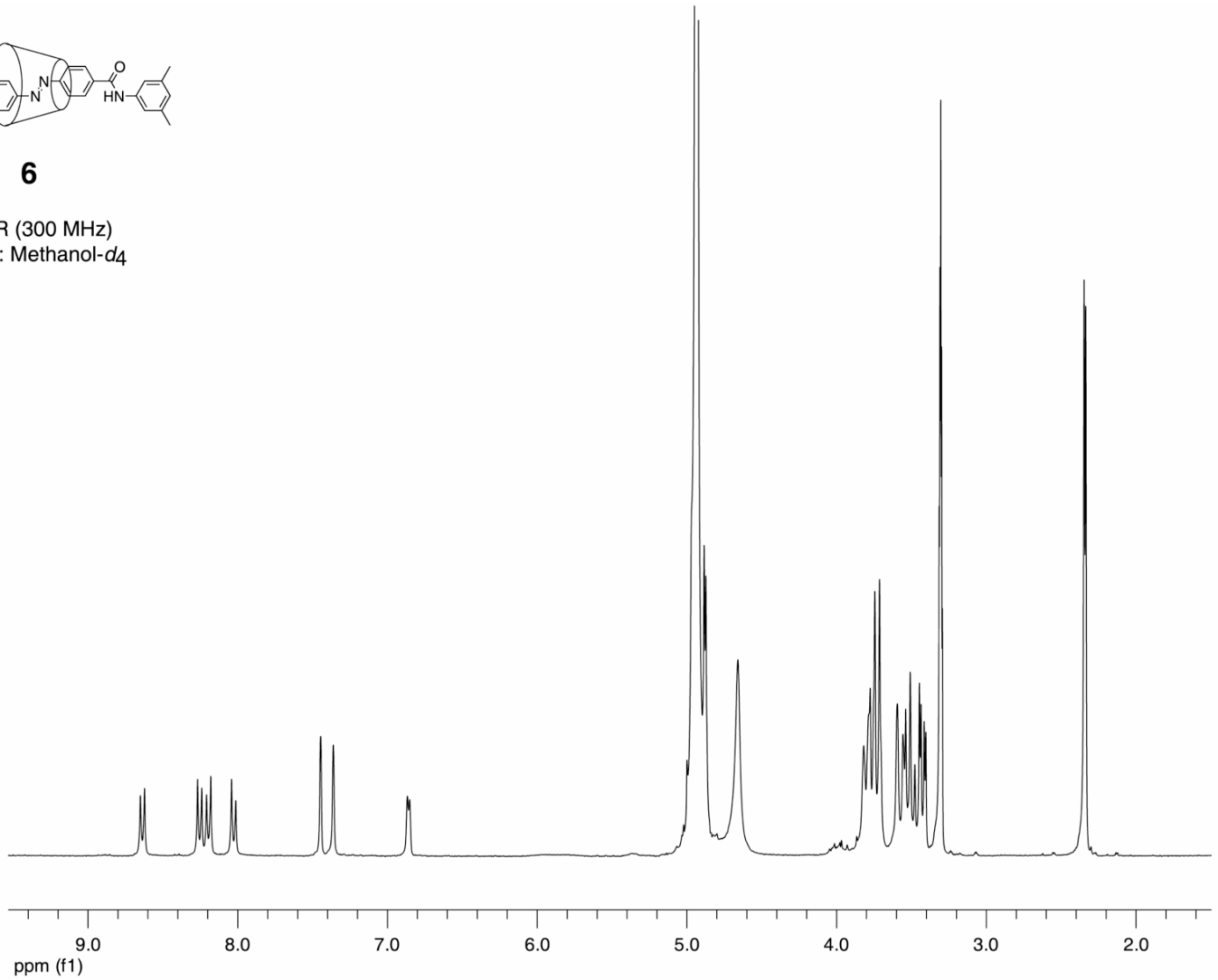
References

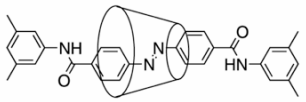
1. Eastoe, J.; Dominguez, M. S.; Wyatt, P.; Beeby, A.; Heenan, R. K. *Langmuir* **2002**, *18*, 7837–7844.
2. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
3. SIR92. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
4. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.



6

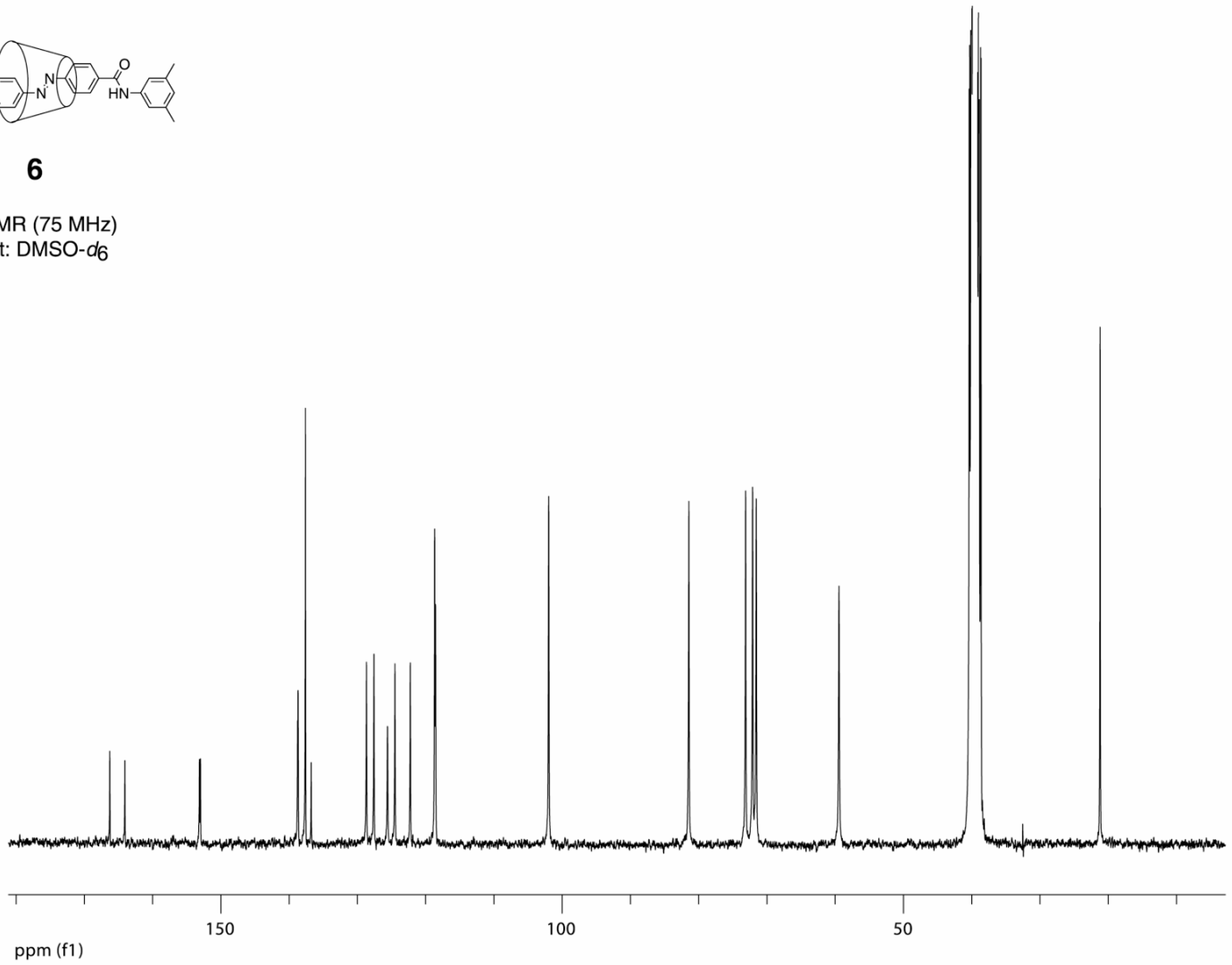
1H NMR (300 MHz)
Solvent: Methanol-d_4

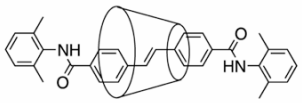




6

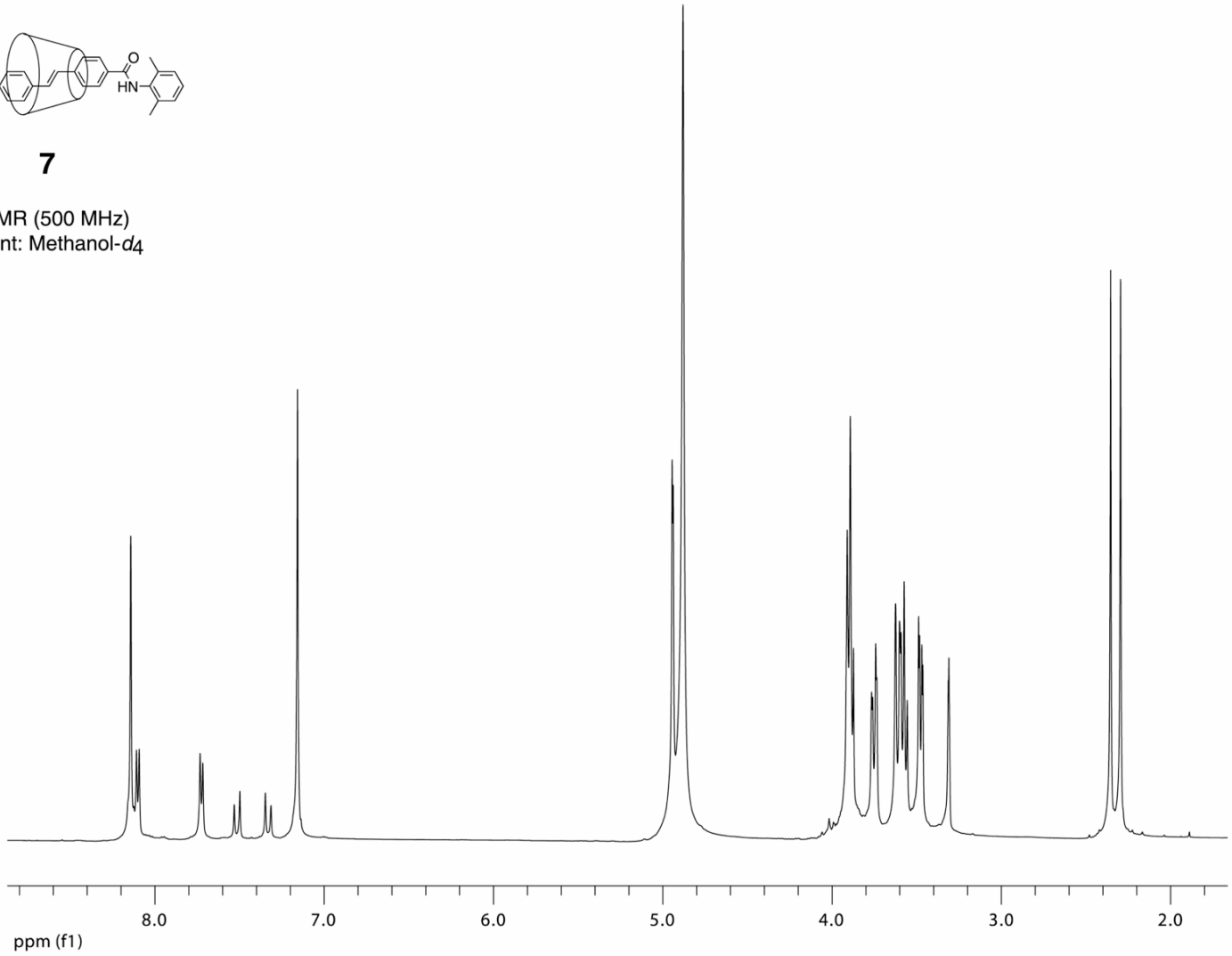
13C NMR (75 MHz)
Solvent: DMSO-d_6

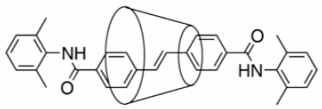




7

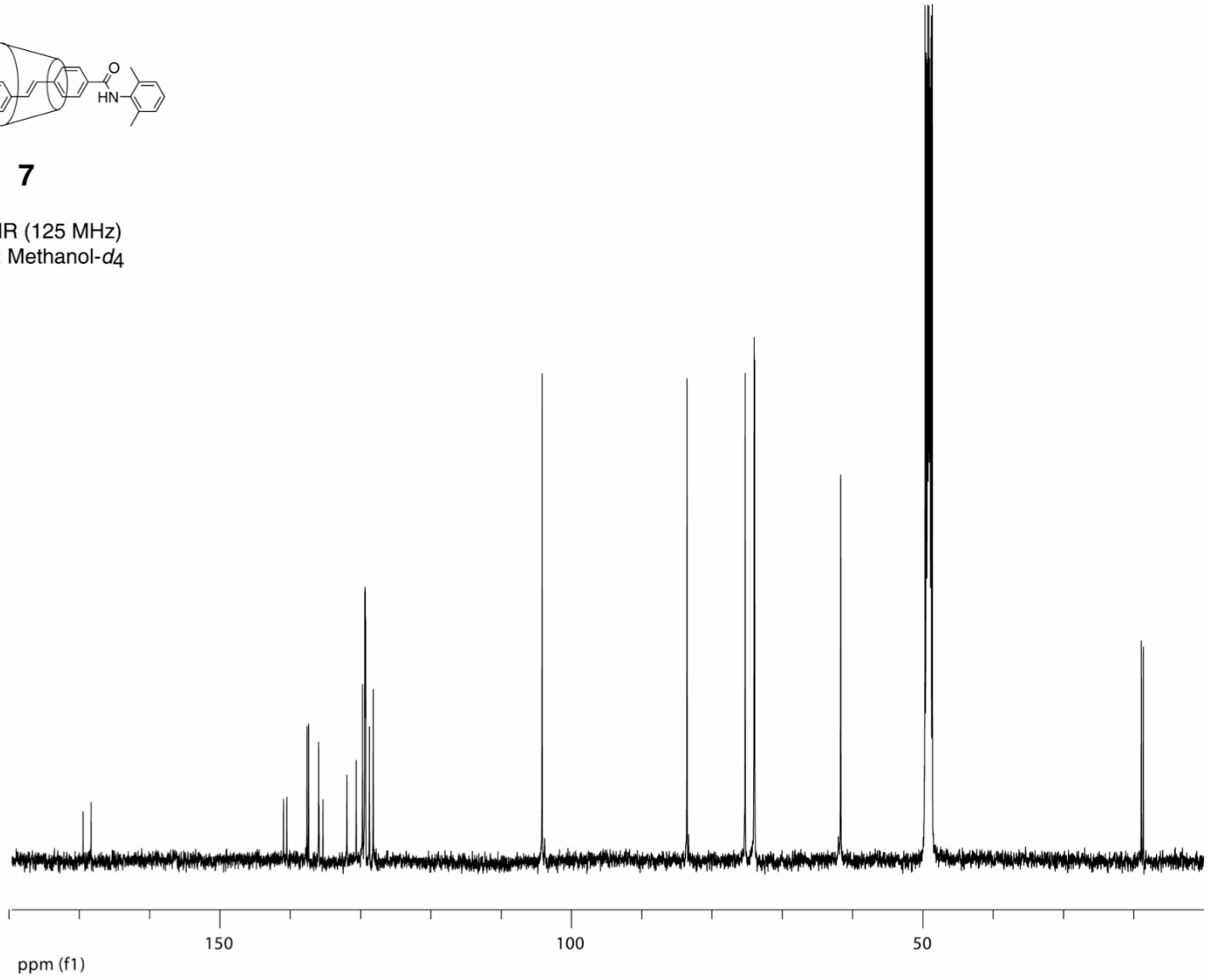
1H NMR (500 MHz)
Solvent: Methanol-d_4

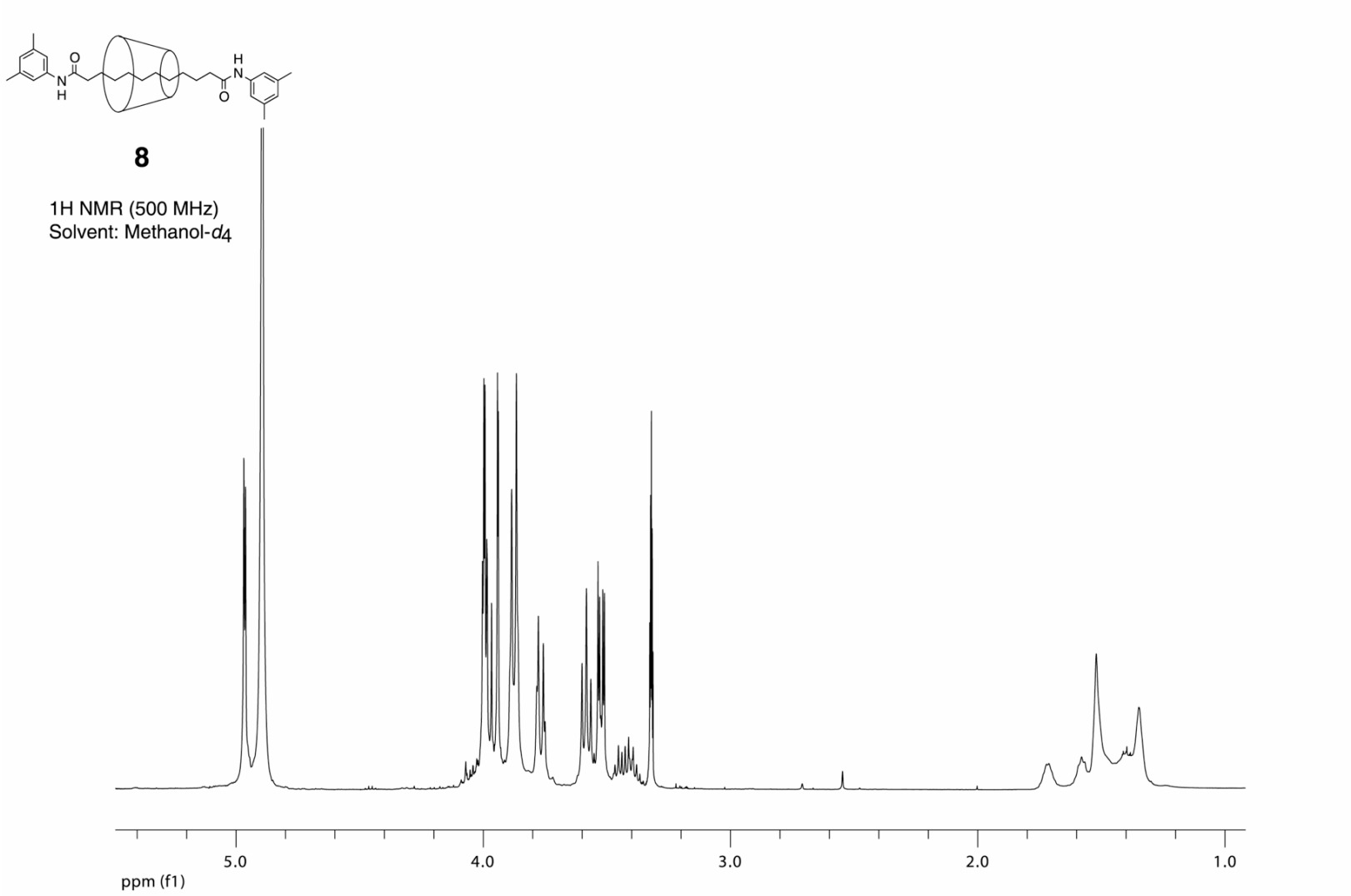


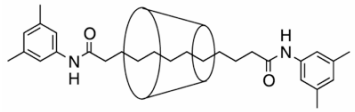


7

13C NMR (125 MHz)
Solvent: Methanol-d_4

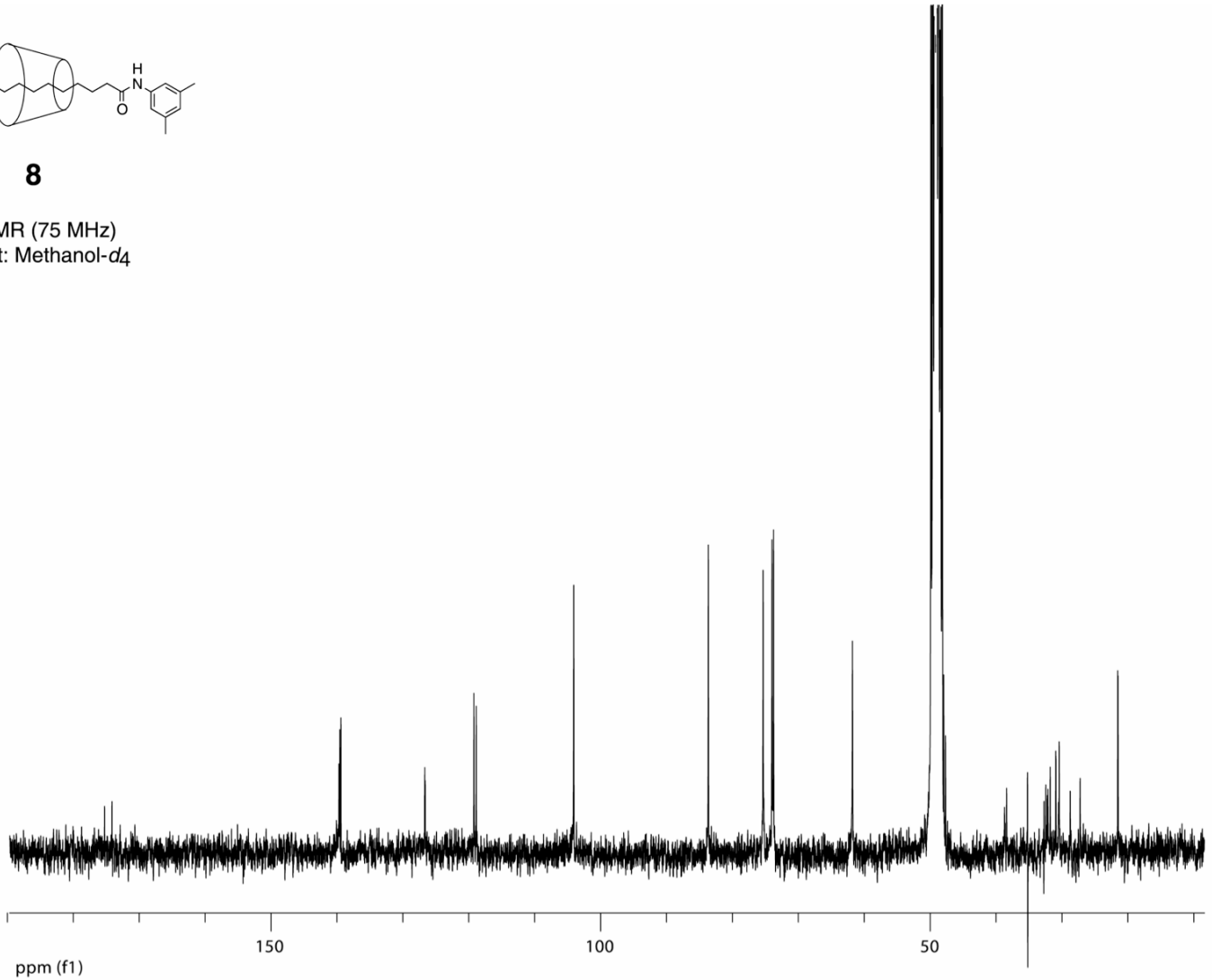


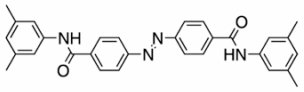

8
1H NMR (500 MHz)
Solvent: Methanol-d_4
5.0
4.0
3.0
2.0
1.0
ppm (f1)



8

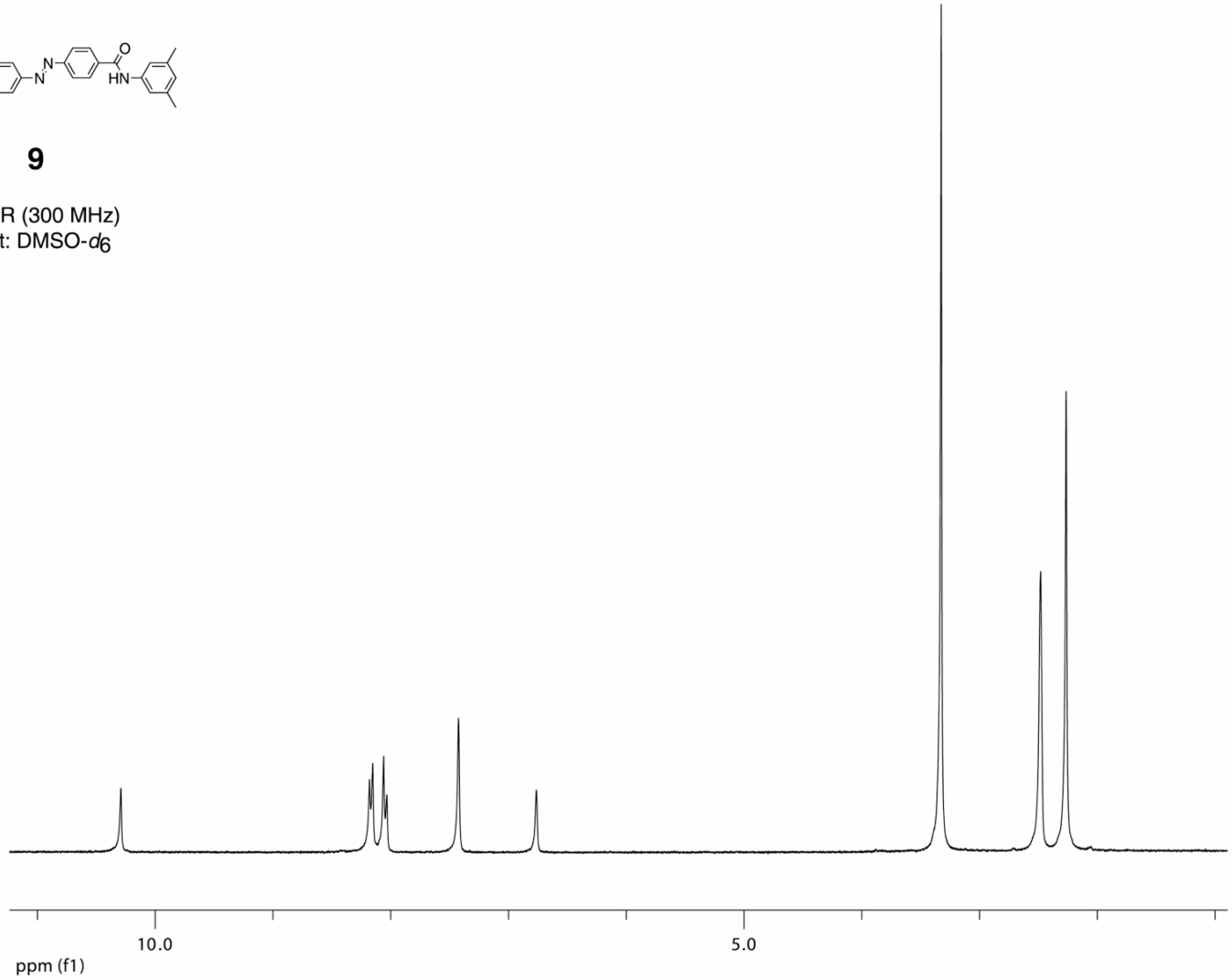
13C NMR (75 MHz)
Solvent: Methanol-d_4

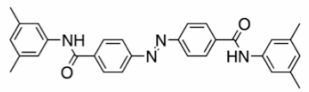




9

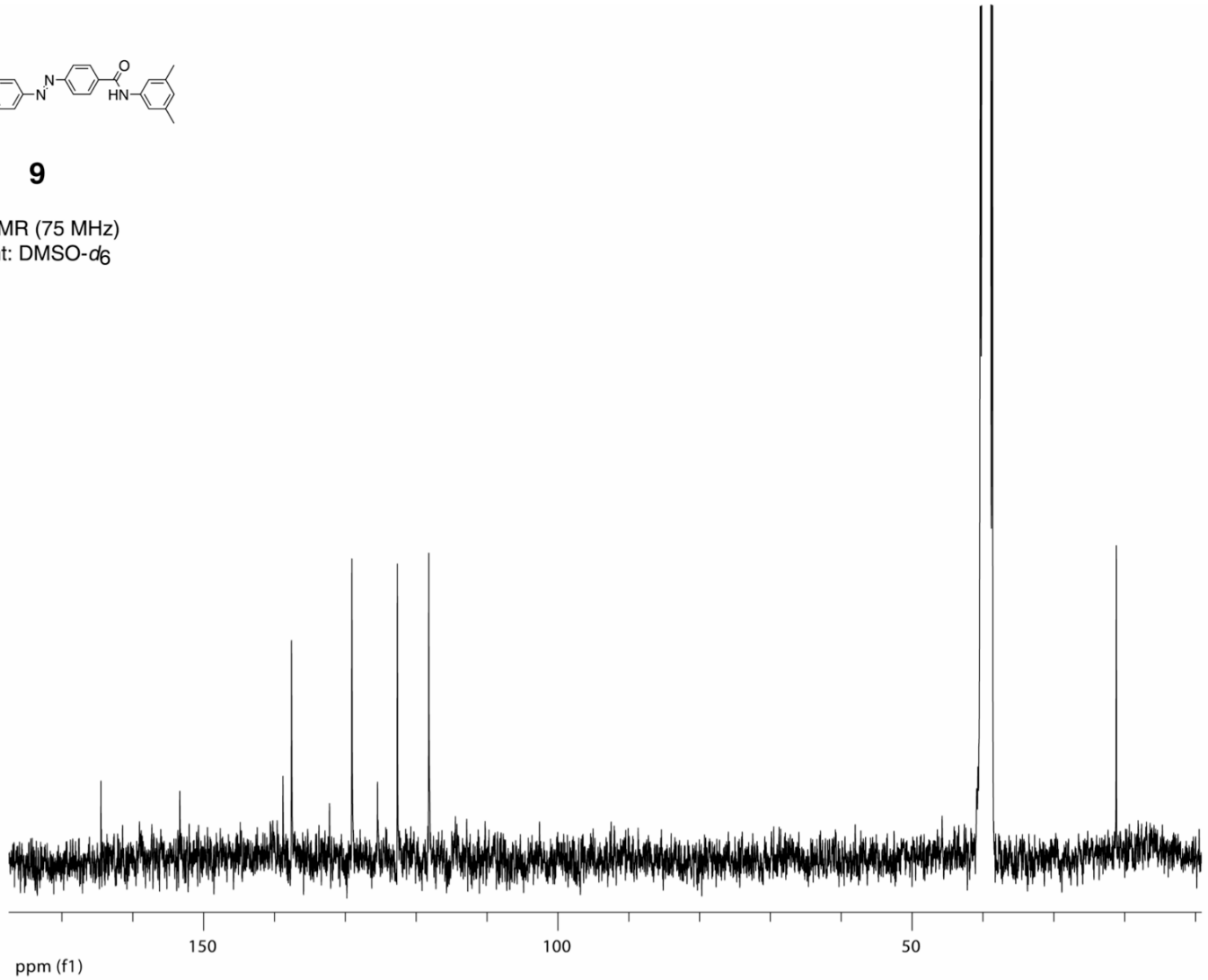
1H NMR (300 MHz)
Solvent: DMSO-d_6

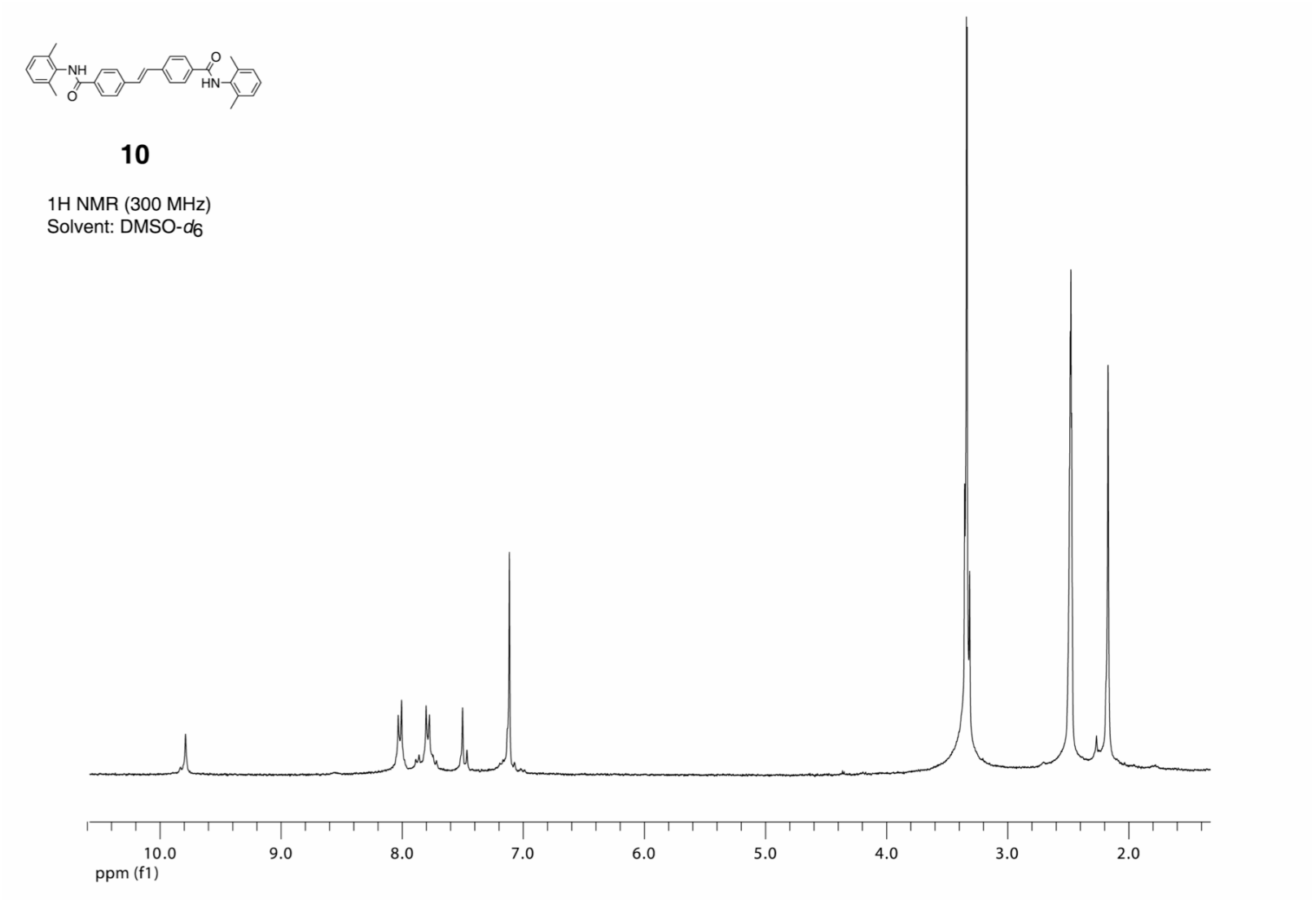


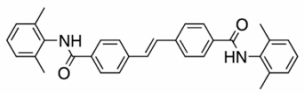


9

13C NMR (75 MHz)
Solvent: DMSO-d_6




NH
O
O
HN
10
1H NMR (300 MHz)
Solvent: DMSO-d6
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)



10

13C NMR (75 MHz)
Solvent: DMSO-d_6