Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Pillar[5]arene decaamine: synthesis, encapsulation of very long linear diacids and formation of ion pair-stopped [2]rotaxanes

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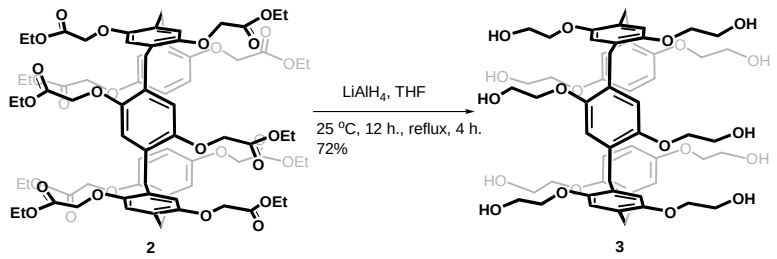
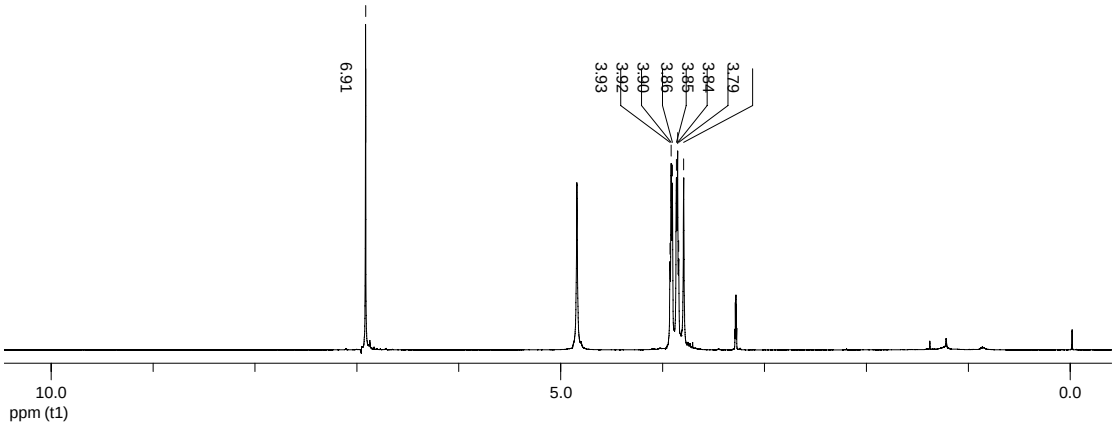
1. Synthesis and characterization of the compounds:

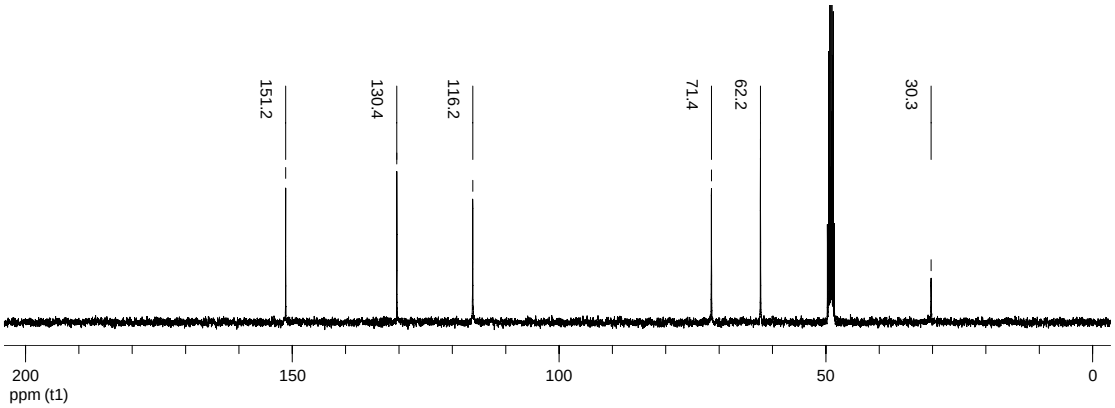


2 3

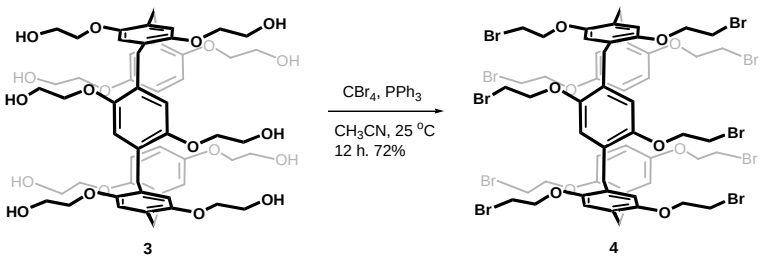
Compound 3: To a solution of compound **2**[1] (700 mg, 0.5 mmol) in anhydrous THF (30 mL) was added $LiAlH_4$ (380 mg, 10 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 12 h. and then heated under reflux for 4 h. To the cooled reaction mixture was added 1.0 M aqueous NaOH dropwisely until the end of gas evolution. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo* to give a white solid. The white solid was washed with water by sonication to produce compound **3** as a pure white solid (360mg, 72%). ^{1}H NMR (CH_3OH-d_4): δ 6.91 (s, 10 H), 3.92 (t, J = 4.6 Hz, 20 H), 3.85 (t, J = 4.6 Hz, 20 H), 3.79 (s, 10 H). ^{13}C NMR (CH_3OH-d_4): δ 151.2, 130.4, 116.2, 71.4, 62.2, 30.3. MS (ESI): *m/z* 1051 $[M + H]^+$, 1073 $[M + Na]^+$. HR-MS (ESI-TOF): Calcd. for $C_{55}H_{71}O_{20}$: 1051.4539. Found: 1051.4583.



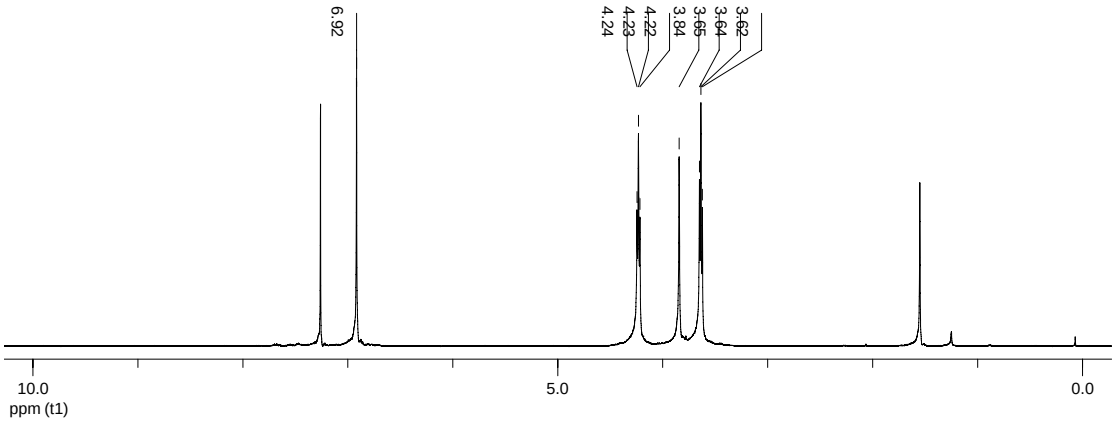
^{1}H NMR (400 MHz, 298 K) spectrum of **3** in CH_3OH-d_4.



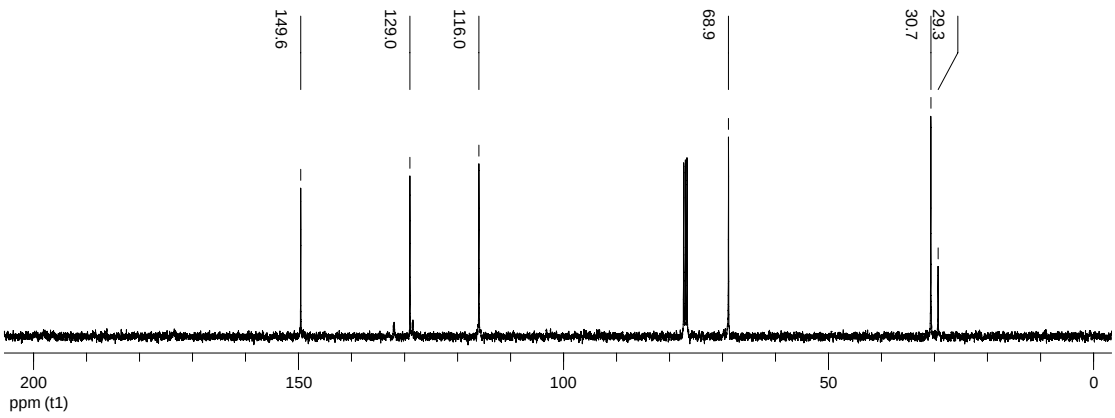
^{13}C NMR (400 MHz, 298 K) spectrum of **3** in CH_3OH-d_4.



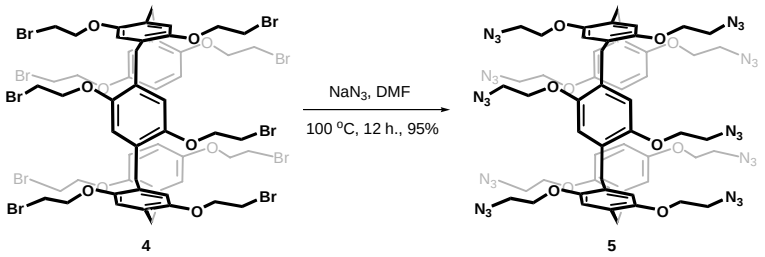
Compound 4: Carbontetrabromide (1.38 g, 4.16 mmol) was added slowly in small portions to a suspension of **3** (290 mg, 0.28 mmol) and triphenylphosphine (1.09 g, 4.16 mmol) in anhydrous acetonitrile (9 ml) at 0 °C with stirring. The reaction mixture was allowed to warm to room temperature, and the resulting mixture was stirred for 12 h. under nitrogen atmosphere. Then 200 mL of water was added to the reaction mixture, whereupon a white solid was precipitated. The precipitate was collected by filtration, and thoroughly washed with methanol to give **4** as a white solid (338 mg, 72%). ^{1}H NMR ($CDCl_3$): δ 6.92 (s, 10 H), 4.23 (t, J = 5.6 Hz, 20 H), 3.84 (s, 10 H), 3.64 (t, J = 5.6 Hz, 20 H). ^{13}C NMR ($CDCl_3$): δ 149.6, 129.0, 116.0, 68.9, 30.7, 29.3. MS (ESI): *m/z* 1680 $[M + H]^+$. HR-MS (ESI-TOF): Calcd. for $C_{55}H_{61}O_{10}Br_{10}$: 1680.5996. Found: 1680.5972.



^{1}H NMR (400 MHz, 298 K) spectrum of **4** in $CDCl_3$.

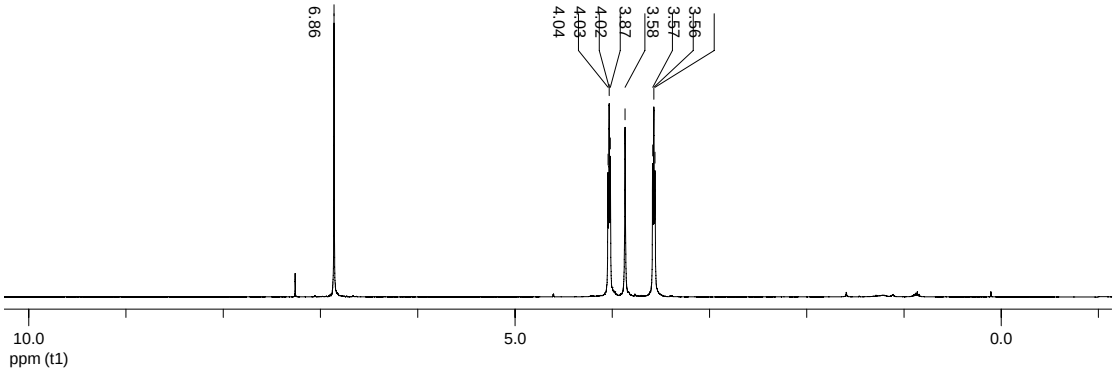


^{13}C NMR (400 MHz, 298 K) spectrum of **4** in $CDCl_3$.

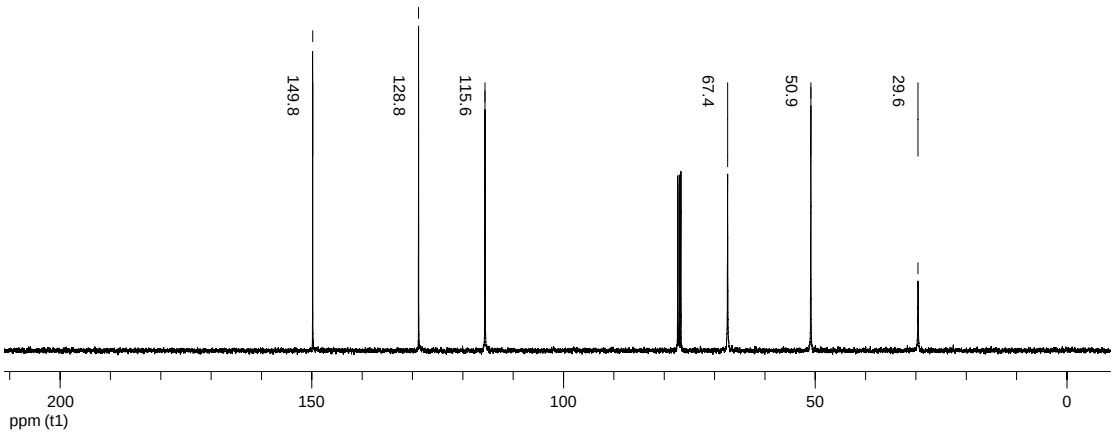


4 5

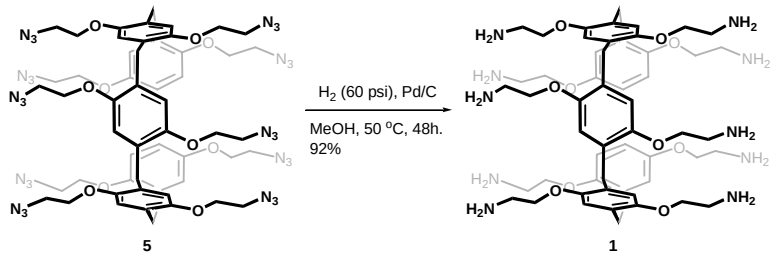
Compound 5: Sodium azide (193 mg, 3 mol) was added to the solution of **4** (100 mg, 0.06 mmol) in anhydrous DMF (5 ml). After stirring at 100 °C for 12 h. under nitrogen atmosphere, the mixture was cooled to room temperature and poured into water (80 ml). The precipitate was collected by filtration, and washed with water to yield **5** as white solid (74 mg, 95%). ^{1}H NMR ($CDCl_3$): δ 6.86 (s, 10 H), 4.03 (t, J = 4.8 Hz, 20 H), 3.87 (s, 10 H), 3.57 (t, J = 4.8 Hz, 20 H). ^{13}C NMR ($CDCl_3$): δ 149.8, 128.8, 115.6, 67.4, 50.9, 29.6. MS (ESI): *m/z* 1323 $[M + Na]^+$. HR-MS (ESI-TOF): Calcd. for $C_{55}H_{60}O_{10}N_{30}Na$: 1323.5006. Found: 1323.5013.



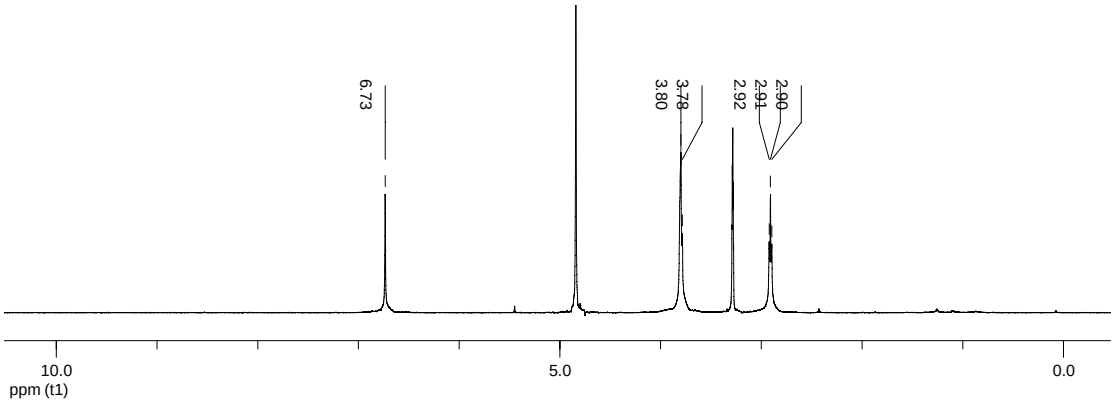
^{1}H NMR (400 MHz, 298 K) spectrum of **5** in $CDCl_3$.



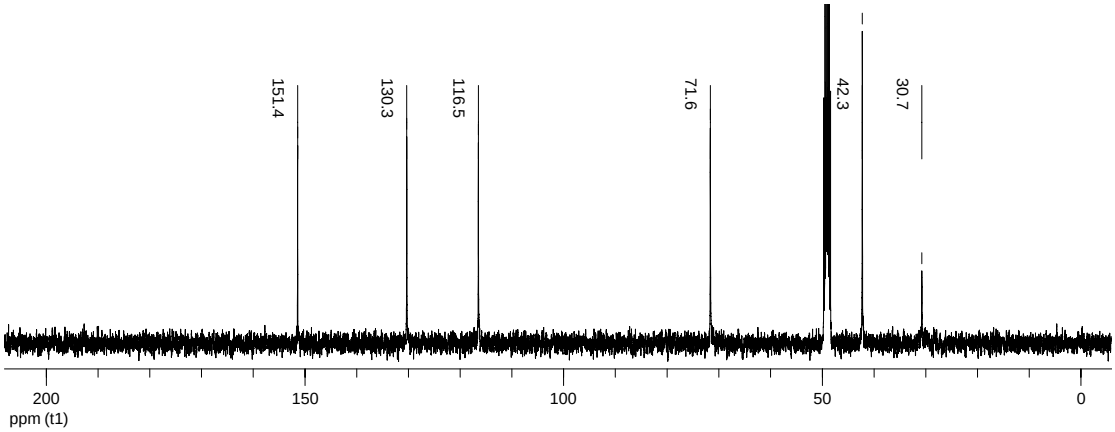
^{13}C NMR (400 MHz, 298 K) spectrum of **5** in $CDCl_3$.



Compound 1: A suspension of **5** (900 mg, 0.69 mmoL) and Pd/C (10%, 150 mg) in methanol was stirred at 50 °C under hydrogen atmosphere (60 psi) for 48 h. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by crystallization from chloroform to produce **1** as white solid (655 mg, 92%). ^{1}H NMR (CH_3OH-d_4): δ 6.73 (s, 10 H), 3.80 (br, 20 H), 3.78 (s, 10 H), 2.91 (t, J = 5.2 Hz, 20 H). ^{13}C NMR (CH_3OH-d_4): δ 151.4, 130.3, 116.5, 71.6, 42.3, 30.7. MS (ESI): *m/z* 1041 $[M + H]^+$. HR-MS (ESI-TOF): Calcd. for $C_{55}H_{81}O_{10}N_{10}$: 1041.6137. Found: 1041.6153.



^{1}H NMR (400 MHz, 298 K) spectrum of **1** in CH_3OH-d_4.



^{13}C NMR (400 MHz, 298 K) spectrum of **1** in CH_3OH-d_4.

Reference:

1. Ogoshi, T.; Hashizume, M.; Yamagishi, T.-A.; Nakamoto, Y. *Chem. Commun.* 2010, **46**, 3708-3710.

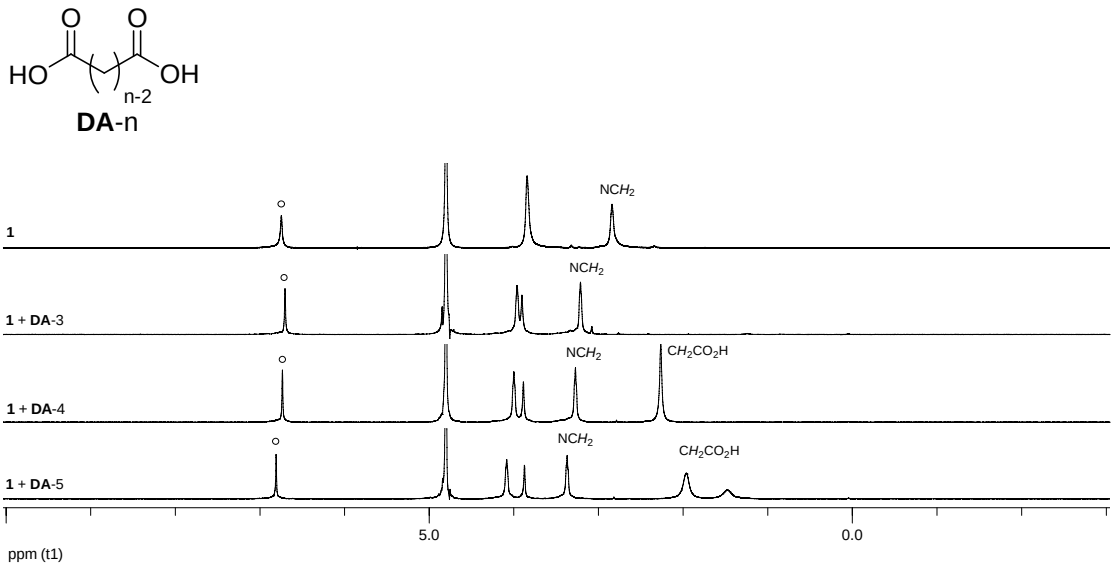


Fig SI-1: ^{1}H NMR spectra (400 MHz, 298 K) of **1** (2.8 mM) and its mixture with **DA**-3-5 (14.0 mM) in D_2O. (o: signal of Ar*H* on free **1**). For the acidity of CH_2 from **DA**-3, the signal of it was not observed.

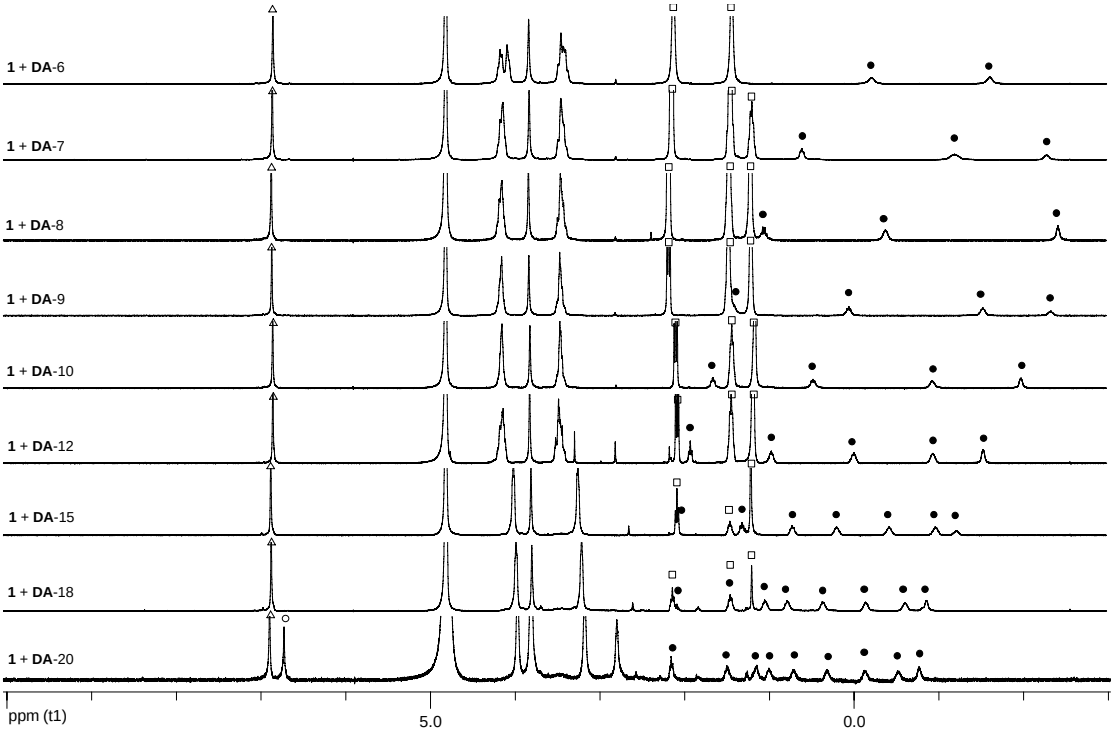


Fig SI-2: ^{1}H NMR spectra (400 MHz, 298 K) of **1** (2.8 mM) with **DA**-n (14.0 mM) in D_2O. (Δ: signal of Ar*H* from complexed **1**; o: signal of Ar*H* on free **1**; □: signal of free **DA**-n; •: signals from methylenes of encapsulated **DA**-n). For poor solubility, the longer of the diacids, the less of free diacids were observed.

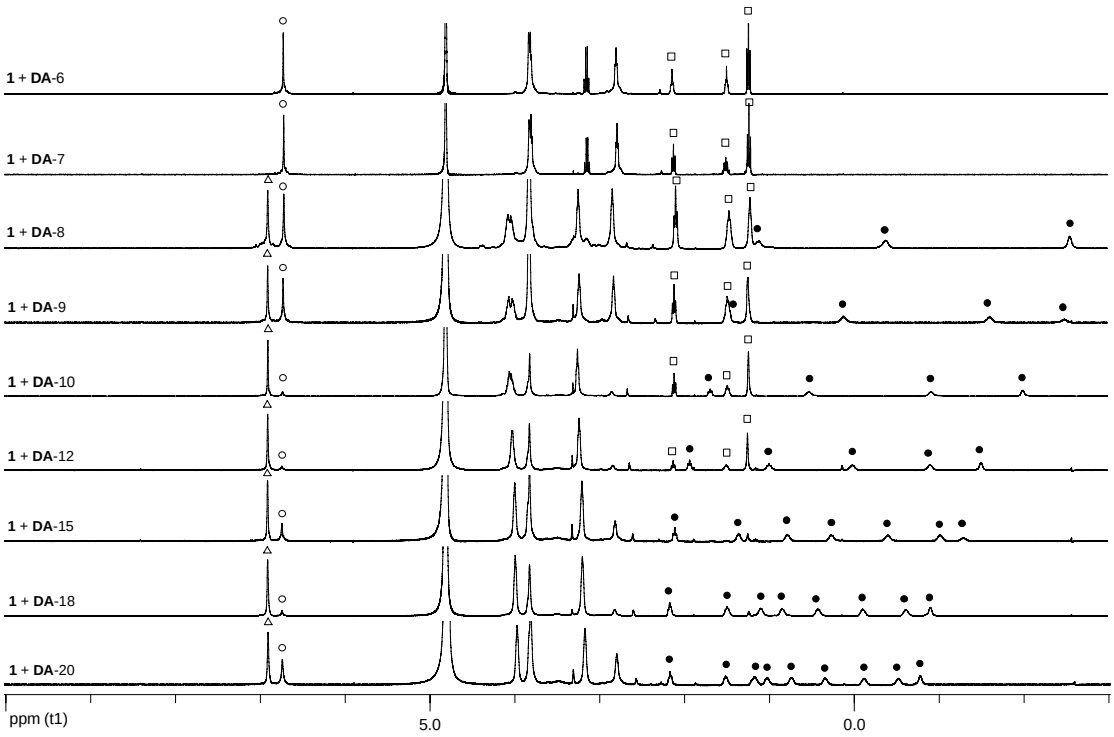


Fig SI-3: ^{1}H NMR spectra (400 MHz, 298 K) of **1** (2.8 mM) with **DA**-n (2.8 mM) in D_2O. (Δ: signal of Ar*H* from complexed **1**; o: signal of Ar*H* on free **1**; □: signal of free **DA**-n; •: signals from methylenes of encapsulated **DA**-n).

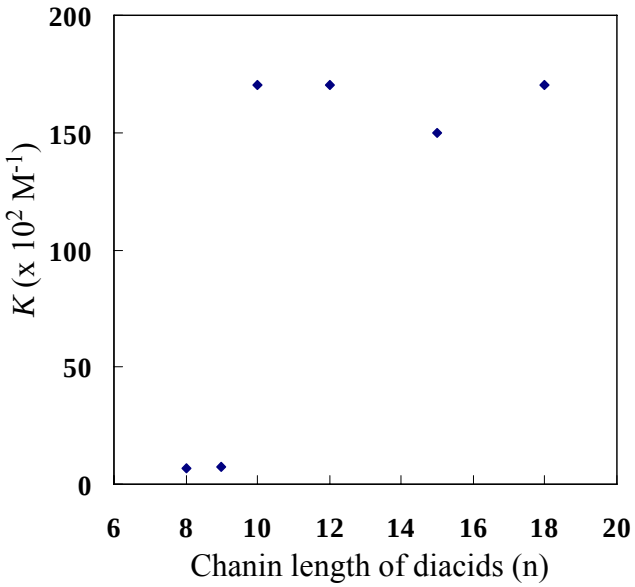


Fig SI-4: Plot of association constants (*K*) versus the chain length of diacids (n), indicating hydrophobic interaction contributed to the binding of **1** with **DA**-n (n = 10, 12, 15, 18). *K* was calculated from the integrated intensity of the Ar*H* signals of **1** exhibited in Fig SI-3.

Table SI-1: The length of diacids at extended state and results of ESI-TOF analysis on diacid⊂**1**.

Diacids (n)	Length of diacid (nm)	Fomula of diacid⊂**1**	HR-MS (ESI-TOF)[a]	Calculated mass[b] for diacid⊂**1**
Adipic acid (**DA**-6)	0.85	$C_{61}H_{90}N_{10}O_{14}$	1185.6567	1185.6560
Pimelic acid (**DA**-7)	0.98	$C_{62}H_{92}N_{10}O_{14}$	1199.6754	1199.6716
Suberic acid (**DA**-8)	1.10	$C_{63}H_{94}N_{10}O_{14}$	1213.6884	1213.6873
Azelaic acid (**DA**-9)	1.23	$C_{64}H_{96}N_{10}O_{14}$	1227.7064	1227.7029
Sebacic acid (**DA**-10)	1.36	$C_{65}H_{98}N_{10}O_{14}$	1241.7223	1241.7186
Dodecanedioic acid (**DA**-12)	1.62	$C_{67}H_{102}N_{10}O_{14}$	1269.7525	1269.7499
Pentadecanedioic acid (**DA**-15)	1.98	$C_{70}H_{108}N_{10}O_{14}$	1311.7970	1311.7968
Octadecanedioic acid (**DA**-18)	2.35	$C_{73}H_{114}N_{10}O_{14}$	1353.8472	1353.8438
Eicosanedioic acid (**DA**-20)	2.72	$C_{75}H_{118}N_{10}O_{14}$	1381.8790	1381.8751

[a]: negative mode; [b]: [diacid⊂**1** - H]$^-$.

Table SI-2: Chemical shifts (δ) and chemical shift changes (Δδ) of methylenes on free and encapsulated **DA**-n.

Diacids (n)	δ of CH_2 on free diacids (δ_{free}, ppm)			δ of CH_2 on encapsulated diacids ($\delta_{encapsulated}$, ppm)									Δδ (= $\delta_{free} - \delta_{encapsulated}$, ppm)								
	H-2	H-3	H-4-10	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H.-10	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10
DA-6	2.10	1.41	-	-0.25	-1.64	-	-	-	-	-	-	-	2.35	3.05	-	-	-	-	-	-	-
DA-7	2.12	1.43	1.17	0.58	-1.23	-2.32	-	-	-	-	-	-	1.54	2.66	3.49	-	-	-	-	-	-
DA-8	2.16	1.45	1.19	1.03	-0.41	-2.46	-	-	-	-	-	-	1.13	1.86	3.65	-	-	-	-	-	-
DA-9	2.16	1.45	1.18	1.40	0.02	-1.57	-2.37	-	-	-	-	-	0.76	1.43	2.75	3.55	-	-	-	-	-
DA-10	2.07	1.41	1.14	1.63	0.45	-0.97	-2.02	-	-	-	-	-	0.44	0.96	2.11	3.16	-	-	-	-	-
DA-12	2.06	1.42	1.16	1.90	0.94	-0.04	-0.97	-1.57	-	-	-	-	0.16	0.48	1.20	2.13	2.73	-	-	-	-
DA-15	2.06	1.43	1.19	2.06	1.29	0.69	0.17	-0.45	-1.00	-1.26	-	-	0.00	0.14	0.50	1.02	1.64	2.19	2.45	-	-
DA-18	2.11	1.43	1.17	2.11	1.43	1.02	0.76	0.34	-0.17	-0.64	-0.9	-	0.00	0.00	0.15	0.41	0.83	1.34	1.81	2.07	-
DA-20	2.16	1.50	1.15	2.16	1.50	1.15	1.01	0.72	0.32	-0.12	-0.52	-0.77	0.00	0.00	0.00	0.14	0.43	0.83	1.27	1.67	1.92

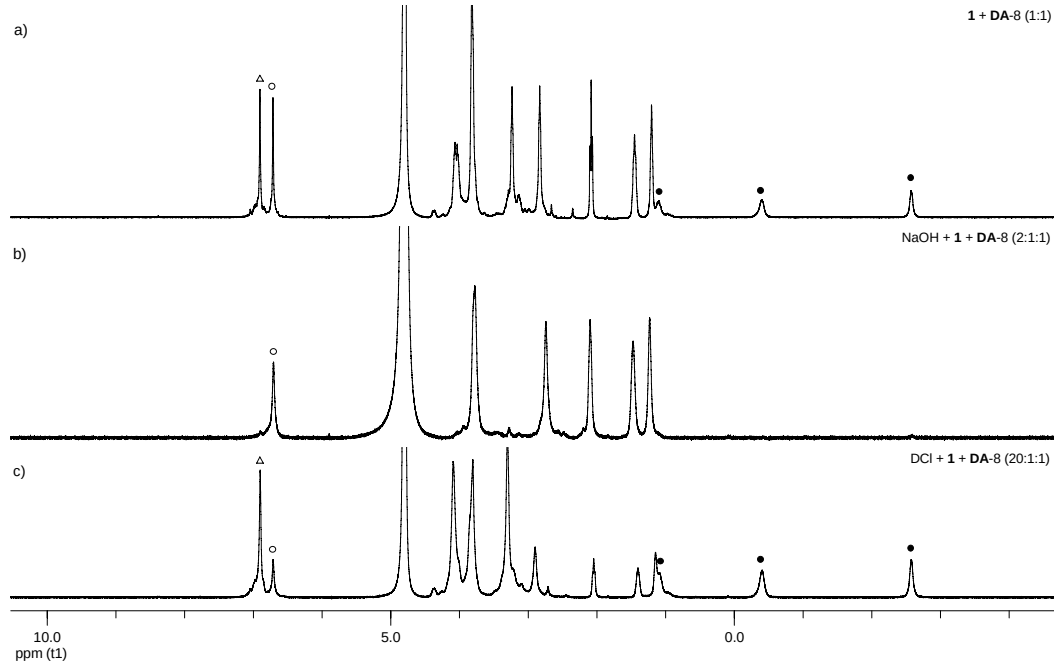


Fig SI-5: ^{1}H NMR spectra (400 MHz, 298 K, D_2O) of a) the mixture of **1** (2.8 mM) with **DA**-8 by titration with b) NaOH and c) DCl, indicating they deassembled in alkaline solution, and reassembled in acidic aqueous solution. (Δ: signal of Ar-*H* on complexed **1**; o: signal from Ar-*H* of free **1**; •: signals of methylenes on encapsulated **DA**-8)

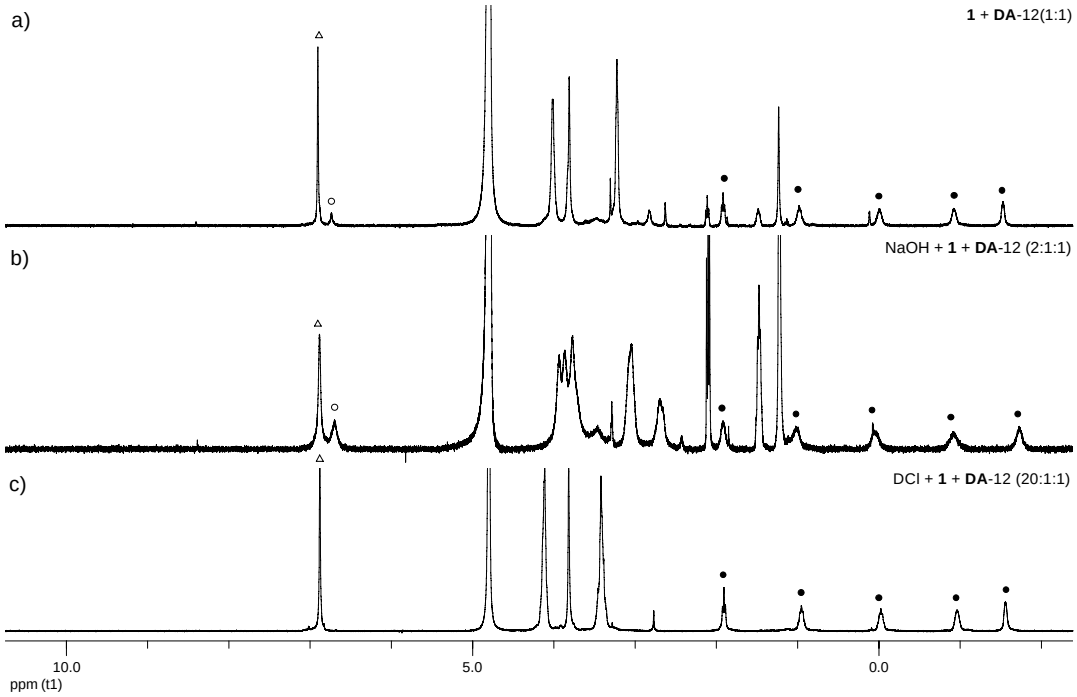


Fig SI-6: ^{1}H NMR spectra (400 MHz, 298 K, D_2O) of a) the mixture of **1** (2.8 mM) with **DA**-12 by titration with b) NaOH and c) DCl. (Δ: signal of Ar-*H* on complexed **1**; o: signal from Ar-*H* of free **1**; •: signals of methylenes on encapsulated **DA**-12).

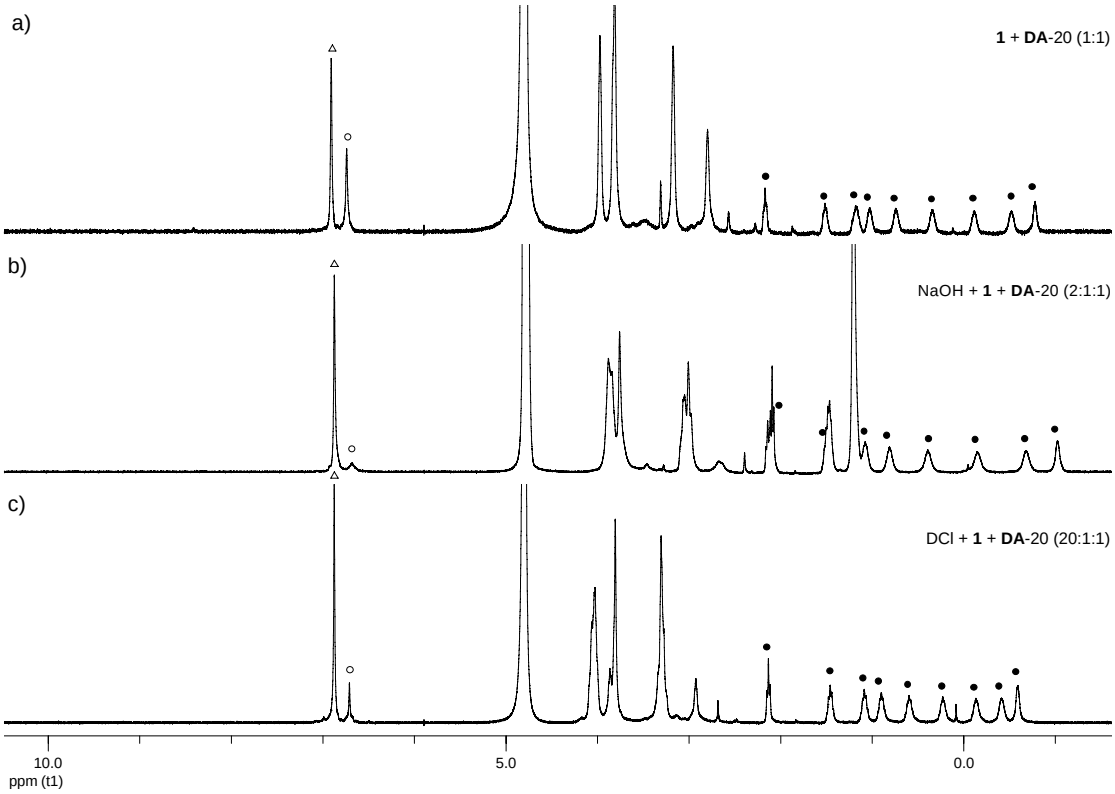


Fig SI-7: ^{1}H NMR spectra (400 MHz, 298 K, D_2O) of a) the mixture of **1** (2.8 mM) with **DA**-20 by titration with b) NaOH and c) DCl. (Δ: signal of Ar-*H* on complexed **1**; o: signal from Ar-*H* of free **1**; •: signals of methylenes on encapsulated **DA**-20).

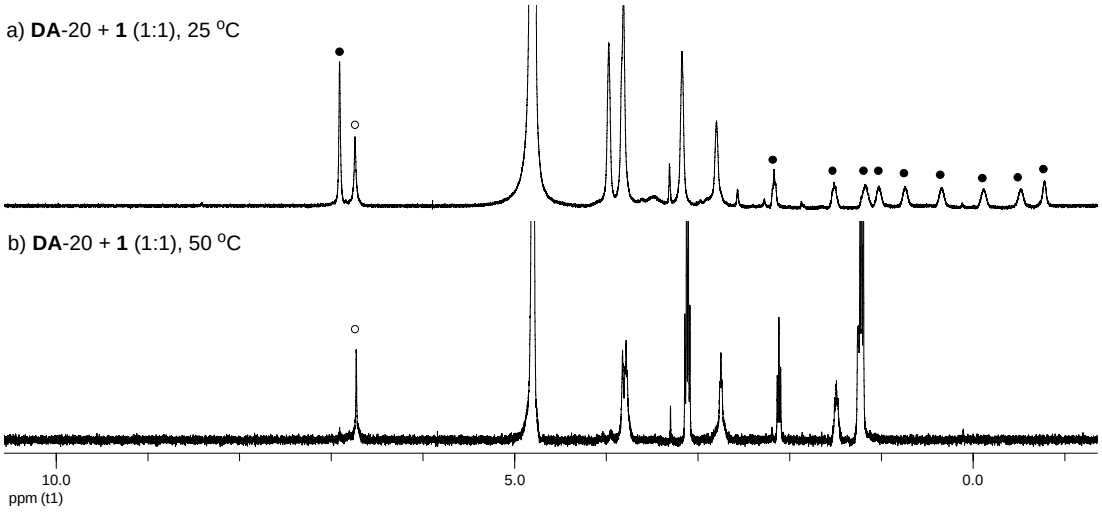


Fig SI-8: VT ^{1}H NMR spectra (400 MHz, D_2O) of **1** (2.8 mM) with **DA**-20, indicating the complex of them deassembled at 50 °C. (•: signal from Ar-*H* and methylene of the complex; o: signal of Ar-*H* on free **1**.)

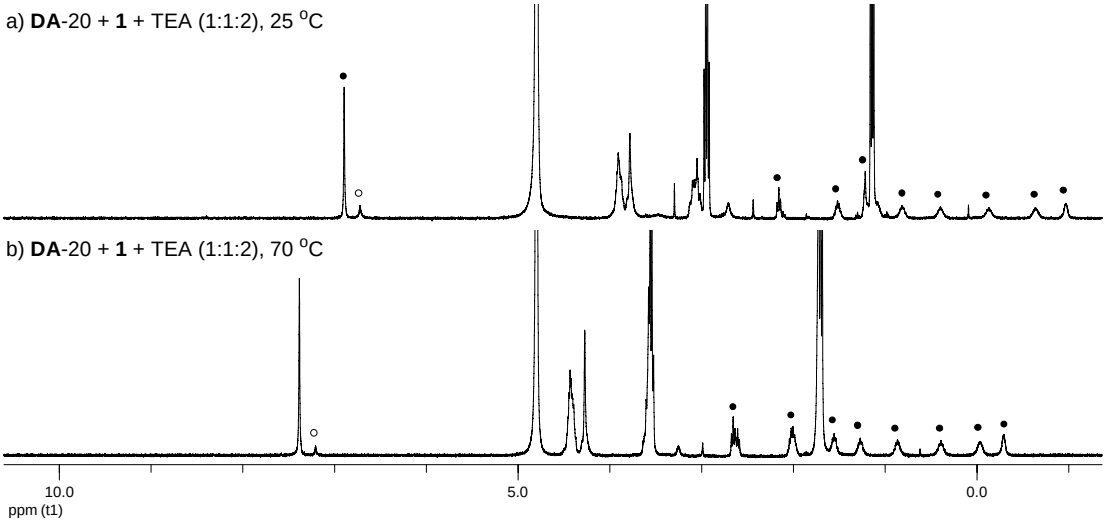


Fig SI-9: VT ^{1}H NMR spectra (400 MHz, D_2O) of **1** (2.8 mM) with **DA**-20 and TEA. (•: signal from Ar-*H* and methylene of the complex; o: signal of Ar-*H* on free **1**.)

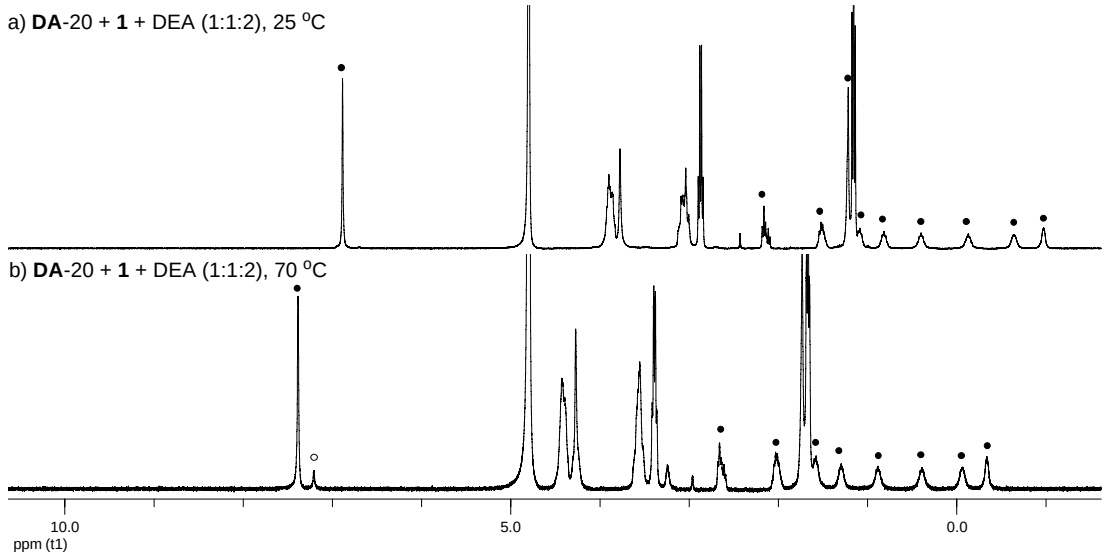


Fig SI-10: VT ^{1}H NMR spectra (400 MHz, D_2O) of **1** (2.8 mM) with **DA**-20 and DEA. (•: signal from Ar-*H* and methylene of the complex; o: signal of Ar-*H* on free **1**.)