Supporting Information

Synthesis of Huge Macrocycles using Two Calix[4]arenes as Templates

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General.

Solvents and other chemicals were purchased from commercial sources and were used without further purification. Column chromatography was performed on silica gel (Merck, 0.040-0.063 mm). ^{1}H NMR spectra were recorded on Bruker DRX400 Avance Instrument (400 MHz). Chemical shifts were calibrated to the residual signal of a deuterated solvent. ESI-mass spectra were obtained on a Q-TOF Ultima3 (from Micromass) instrument.

Multimacrocycle 6 (m = 10, Y = C_5H_{11})

A suspension of **4** (n = 6, Y = C_5H_{11}, 200 mg, 98.7 µmol) and **5** (230 mg, 148 µmol) in a mixture of benzene and dichloromethane (1:1 v/v, 400 mL) was stirred during 1.5 hours (55 °C, oil bath). After cooling, the mixture was purged with nitrogen during 30 minutes and a solution of the Grubbs' catalyst (bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride, 32.5 mg, 39.5 µmol) in dichloromethane (10 mL) was added in one portion. The mixture was stirred at ambient temperature during 6 days. Triethylamine (1 mL) was added and after 1 hour the mixture was evaporated. The hydrogenation was carried out with platinum (IV) oxide (85%, 40.3 mg) in THF (20 mL) under hydrogen atmosphere (12 h). Then the mixture was filtered and evaporated. The crude product was purified by the column chromatography on silica (THF / hexane = 1:2). After crystallisation from chloroform / methanol (5 : 50 mL), 160.9 mg (85%) of the desired product were obtained. m. p. > 290°C (partly decomposed); ^{1}H NMR (dmso-d_6) δ 7.38 (s, 4H, NH), 7.17 (s, 4H, NH), 6.89 (s, 8H, Calix-ArH), 6.51 (d, ^4J = 1.8 Hz, 8H, ArH), 6.04 (br t, ^4J = 1.8 Hz, 4H, ArH), 4.35 and 3.14 (d, ^2J=12.3 Hz, 4H + 4H, $ArCH_2Ar$), 3.86 (t, ^3J = 6.5 Hz, 16H, $-OCH_2-$), 3.82 (t, ^3J = 7.6 Hz, 8H, $-OCH_2-$), 1.95 (t, ^3J = 7.3 Hz, 8H, $-OCH_2C\mathit{H_2}-$), 1.64 (t, ^3J = 7.3 Hz, 16H, $-OCH_2C\mathit{H_2}-$), 1.45-1.20 (two m, 64H, -

$OCH_2CH_2CH_2CH_2$), 0.95 (t, ^3J = 6.8, 12H, $-CH_3$); ESI-MS m/z: calcd for $C_{116}H_{160}N_8O_{16}Na$ (M + Na) 1945.6, found 1944.9.

General procedure for the synthesis of macrocycles 7:

The compound **6** (m = 8, 10, 14, 20) (0.025 mmol) was refluxed in acetic acid (20 mL) for 24 hours. After cooling, acetic acid was removed in vacuo. The residue was separated and purified by column chromatography on silica gel (CH_2Cl_2 / MeOH =20:1) giving **7** as the first eluted compound and **8**.

7 (m = 8):

Yield: 50 %. m.p. >300°C, phase transition 136-140°C; ^{1}H NMR (dmso-d_6): δ = 9.79 (s, 4H, -NH), 6.77 (br d, 8H, -ArH), 6.14 (br t, 4H, -ArH), 3.87 (t, ^3J = 6.5 Hz, 16H, $-OCH_2-$), 1.99 (s, 12H, $-COCH_3$), 1.66 (m, 16H, $-OCH_2CH_2-$), 1.38-1.24 (m, 32H, $-OCH_2CH_2CH_2CH_2-$); ESI-MS m/z: calcd for $C_{64}H_{92}N_4O_{12}Na$ (M + Na) 1132.5, found 1132.7.

7 (m = 10):

Yield: 66 %. m.p. >300°C, phase transition 130-135°C; ^{1}H NMR (dmso-d_6): δ = 9.78 (s, 4H, -NH), 6.77 (d, ^4J = 2.0 Hz, 8H, ArH), 6.14 (br t, 4H, -ArH), 3.87 (t, ^3J = 6.5 Hz, 16H, $-OCH_2-$), 1.99 (s, 12H, $-COCH_3$), 1.67-1.63 (m, 16H, $-OCH_2CH_2-$), 1.36-1.23 (m, 48H, $-OCH_2CH_2CH_2CH_2-$); ESI-MS m/z: calcd for $C_{72}H_{108}N_4O_{12}Na$ (M + Na) 1244.7, found 1243.6.

7 (m = 14):

Yield: 72 %. m.p. >300°C, phase transition 100-105°C; ^{1}H NMR (dmso-d_6): δ = 9.78 (s, 4H, -NH), 6.77 (br d, 8H, -ArH), 6.12 (br t, 4H, -ArH), 3.86 (t, ^3J = 6.3 Hz 16H, $-OCH_2-$), 1.99 (s, 12H, $-COCH_3$), 1.65 (m, 16H, $-OCH_2CH_2-$), 1.35-1.22 (m, 80H, $-OCH_2CH_2CH_2CH_2-$); ESI-MS m/z: calcd for $C_{88}H_{140}N_4O_{12}Na$ (M + Na) 1469.1, found 1467.8.

7 (m = 20):

Yield: 67 %. m.p. >300°C, phase transition 95-100°C; ^{1}H NMR (dmso-d_6, 80 °C): δ = 9.42 (s, 4H, -NH), 6.78 (d, ^4J = 2.0 Hz, 8H, -ArH), 6.14 (t, ^4J = 2.0 Hz, 4H, -ArH), 3.91 (t, ^3J = 6.4 Hz, 16H, $-OCH_2-$), 2.00 (s, 12H, $-COCH_3$), 1.70 (m, 16H, $-OCH_2C\mathit{H_2}-$), 1.40-1.26 (m, 128H, $-OCH_2CH_2C\mathit{H_2}C\mathit{H_2}-$); ESI-MS m/z: calcd for $C_{112}H_{188}N_4O_{12}Na$ (M + Na) 1805.8, found 1805. 4.

Multimacrocycle 10 (n = 1, Y = C_5H_{11})

10 was synthesized from **9** (n = 1, 204mg, 0.1mmol) and tetratosyl urea calix[4]arene **5** (230 mg, 0.15mmol) in a way similar to **6** (see above). After purification of the crude product on the silica column (eluant: CH_2Cl_2/THF = 4:1) a white solid (120mg, 62%) was obtained.

m.p. >300°C (partly decomposed); ^{1}H NMR (THF-d_8) δ 7.57 (d, 8H, NH), 6.91(s, 8H, Calix-ArH), 6.62 (s, 8H, ArH), 6.03 (s, 4H, ArH), 4.47 and 3.10 (d, 4H + 4H, $ArCH_2Ar$), 3.97-3.89 (m, 16H + 8H, OCH_2-), 3.63 and 3.45 (m, 32H, $-OC\mathit{H_2}C\mathit{H_2}O-$), 2.01 (m, 8H, $-OCH_2C\mathit{H_2}-$), 1.58 (m, 16H, $-OCH_2C\mathit{H_2}C\mathit{H_2}CH_2O-$), 1.45-1.23(m, 16H, $-OCH_2CH_2C\mathit{H_2}C\mathit{H_2}CH_3$), 0.99 (t, 12H, $-CH_3$); ESI-MS m/z: calcd for $C_{108}H_{144}N_8O_{24}Na$ (M + Na) 1961.4, found 1960.9.

11 (n = 1): Macrocycle **11** was prepared in a similar way to **7**.

Yield: 65 %. m.p. >300 °C, phase transition 65-70°C; ^{1}H NMR (dmso-d_6): δ = 9.80 (s, 4H, -NH), 6.79 (br d, 8H, -ArH), 6.20 (br t, 4H, -ArH), 3.99 (br t, 16H, $-OCH_2CH_2OC\mathit{H_2}-$), 3.63 (br t, 16H, $-OC\mathit{H_2}C\mathit{H_2}O-$), 3.43(br t, 16H, $-OC\mathit{H_2}C\mathit{H_2}O-$), 1.99 (s, 12H, $-COCH_3$), 1.53 (m, 16H, $-OCH_2C\mathit{H_2}C\mathit{H_2}-$); ESI-MS m/z: calcd for $C_{64}H_{92}N_4O_{20}Na$ (M + Na) 1260.4, found 1259.6.

Table S1. Crystal data and structure refinement for **6** (Y = CH_3, m = 10).

Identification code	boeh33	
Empirical formula	C108 H163 N8 O25.50	
Formula weight	1981.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 18.8106(15) Å	α= 98.409(6)°.
	b = 23.1537(18) Å	β= 104.443(6)°.
	c = 28.968(2) Å	γ = 102.706(6)°.
Volume	11645.5(15) Å^3	
Z	4	
Density (calculated)	1.130 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	4284	
Crystal size	0.42 x 0.40 x 0.36 mm^3	
Theta range for data collection	3.56 to 25.03°.	
Index ranges	-22<=h<=22, -27<=k<=27, -34<=l<=34	
Reflections collected	93167	
Independent reflections	38675 [R(int) = 0.1984]	
Completeness to theta = 25.00°	94.0 %	
Absorption correction	None	
Max. and min. transmission	0.9718 and 0.9672	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	38675 / 42 / 2548	
Goodness-of-fit on F^2	1.252	
Final R indices [I>2sigma(I)]	R1 = 0.1560, wR2 = 0.3756	
R indices (all data)	R1 = 0.2387, wR2 = 0.4450	
Largest diff. peak and hole	1.379 and -0.590 e.Å^{-3}	

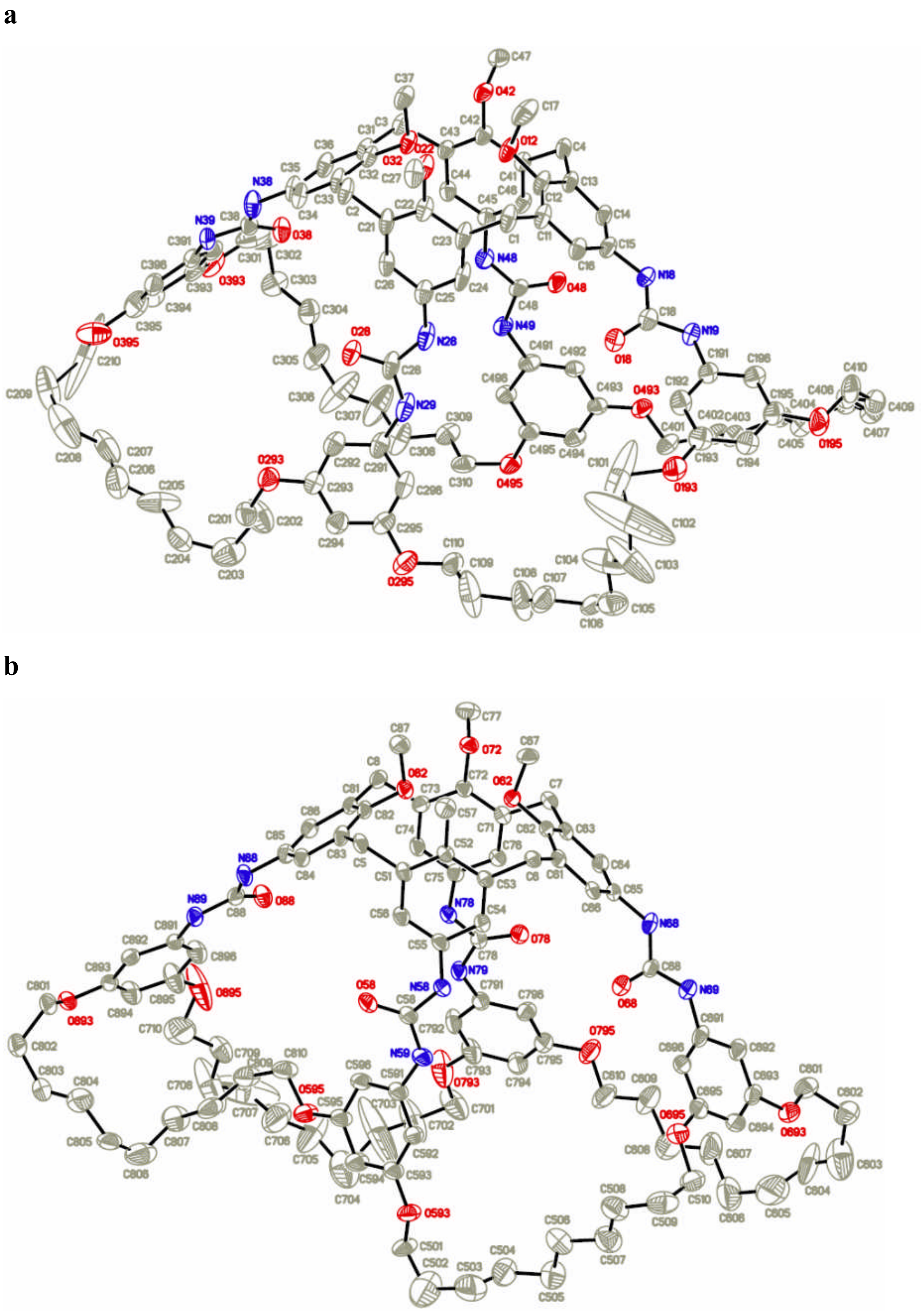

Figure S1. Single crystal X-ray structure (ORTEP-diagrams) of **6** (m=10, Y=CH_3). The two independent molecules (a and b), are shown.

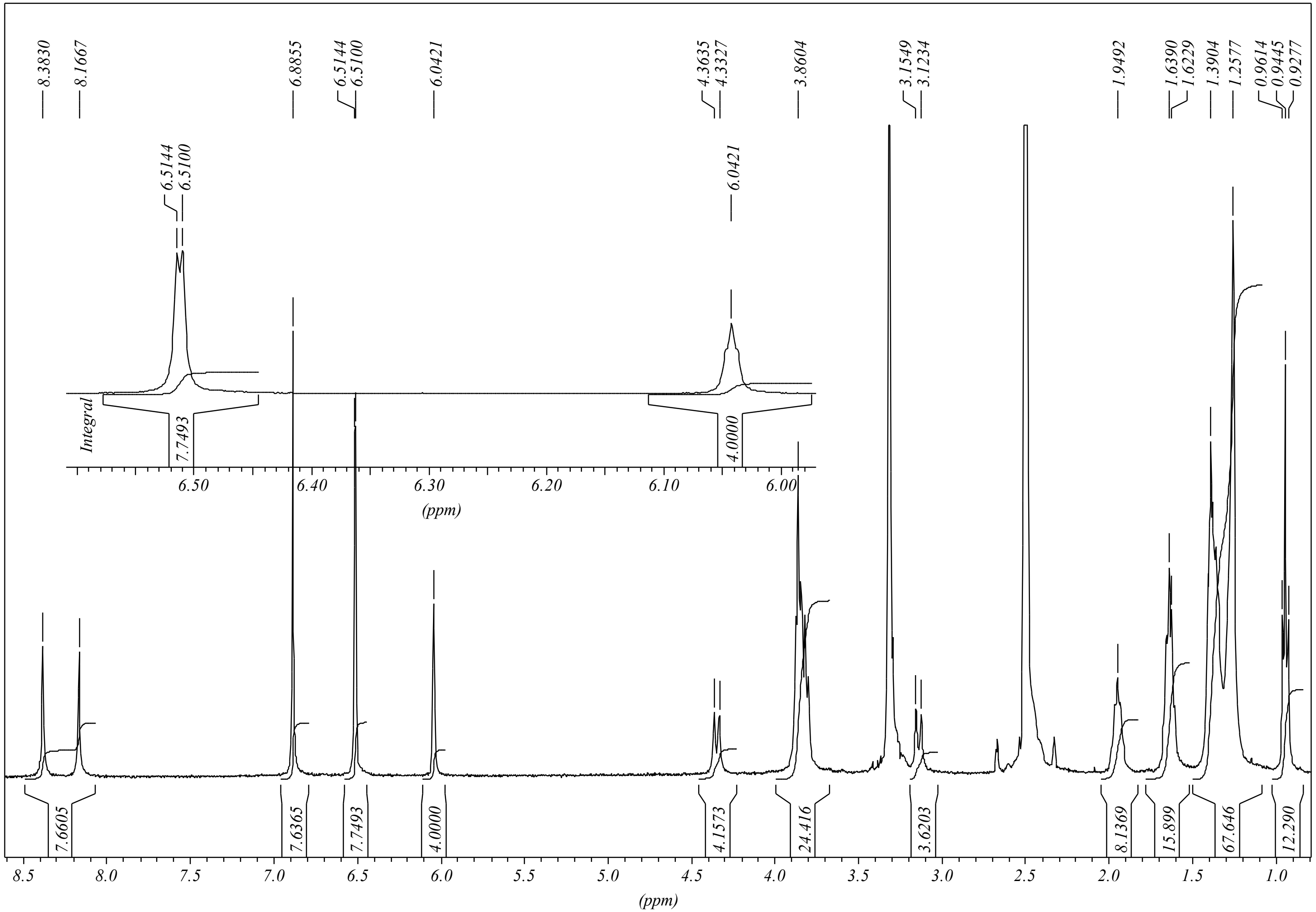

Figure S2. ^{1}H NMR spectrum of **6** (m = 10, Y = C_5H_{11}, 400 MHz, THF-d_8, 25 °C).

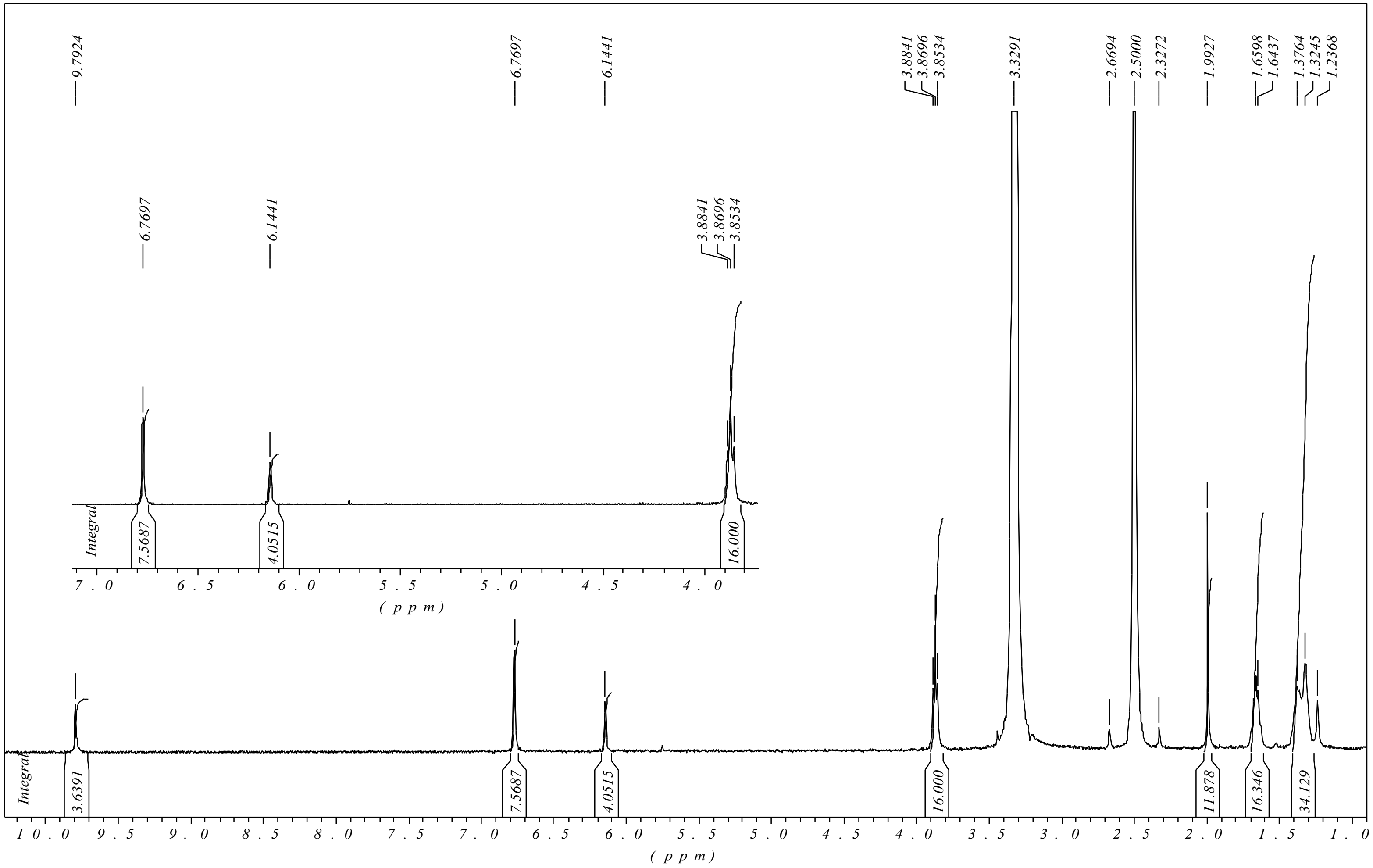

Figure S3. ^{1}H NMR spectrum of **7** (m = 8, 400 MHz, dmso-d_6, 25 °C).

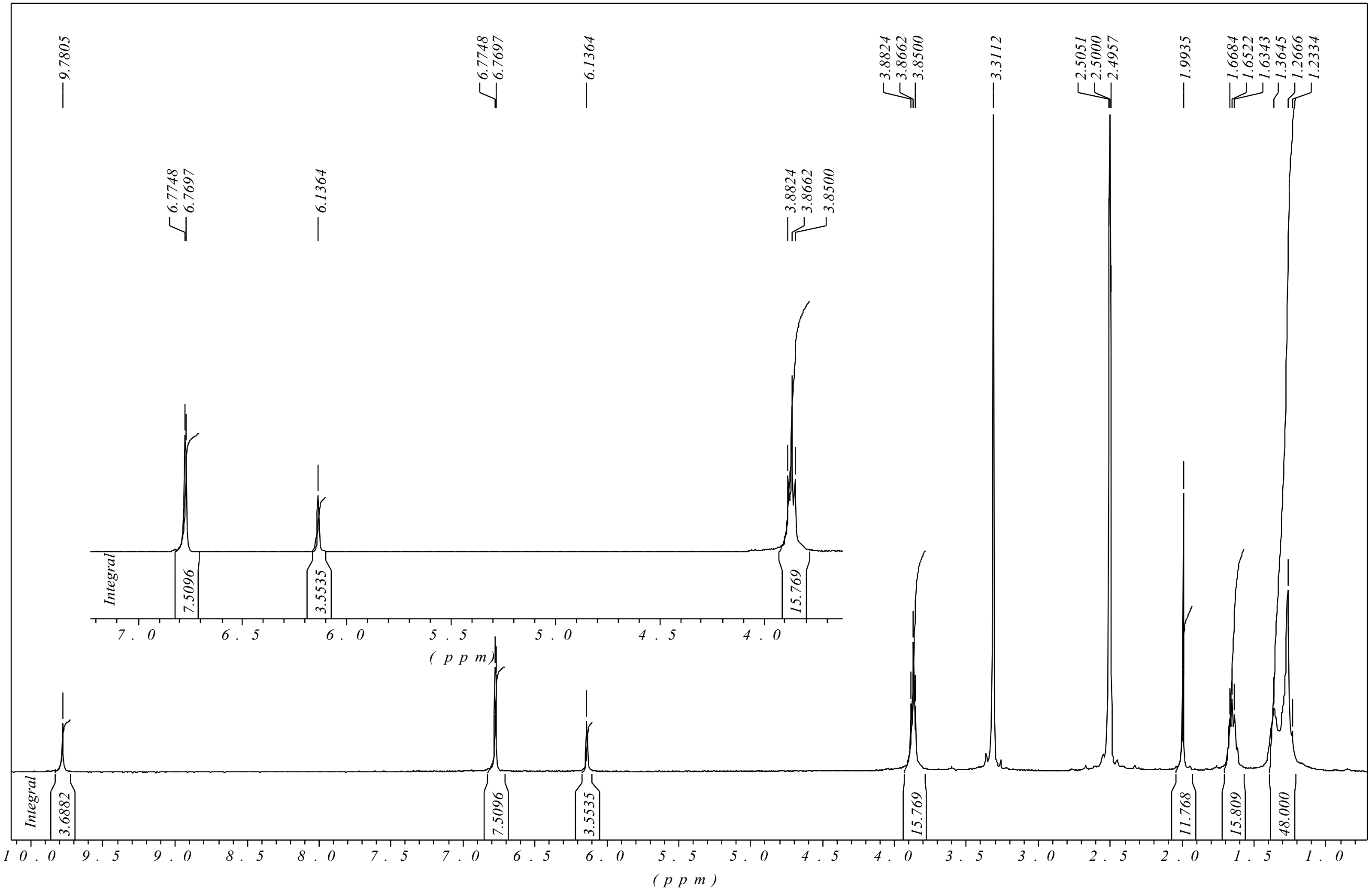

Figure S4. ^{1}H NMR spectrum of **7** (m = 10, 400 MHz, dmso-d_6, 25 °C).

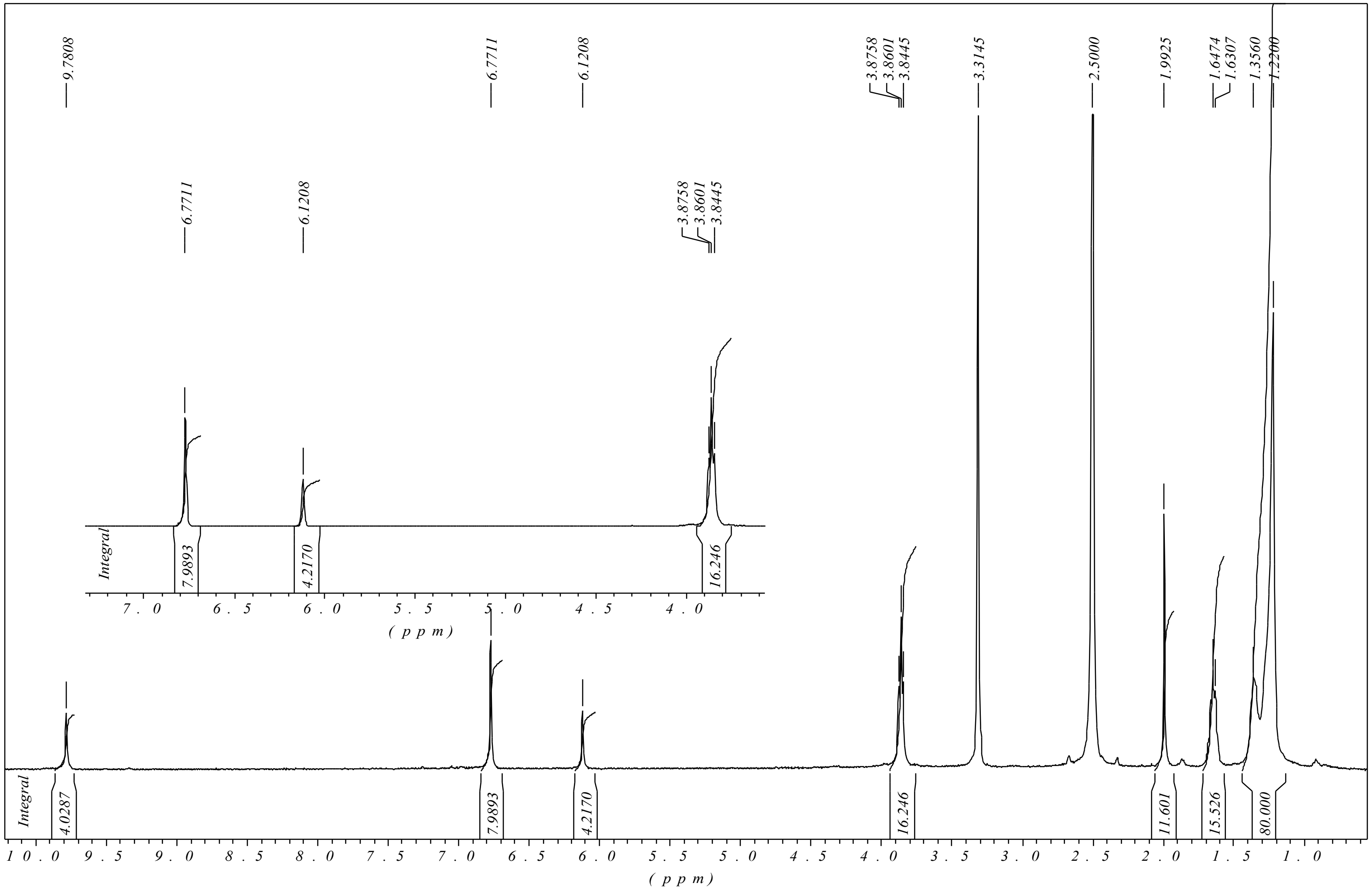

Figure S5. ^{1}H NMR spectrum of **7** (m = 14, 400 MHz, dmso-d_6, 25 °C).

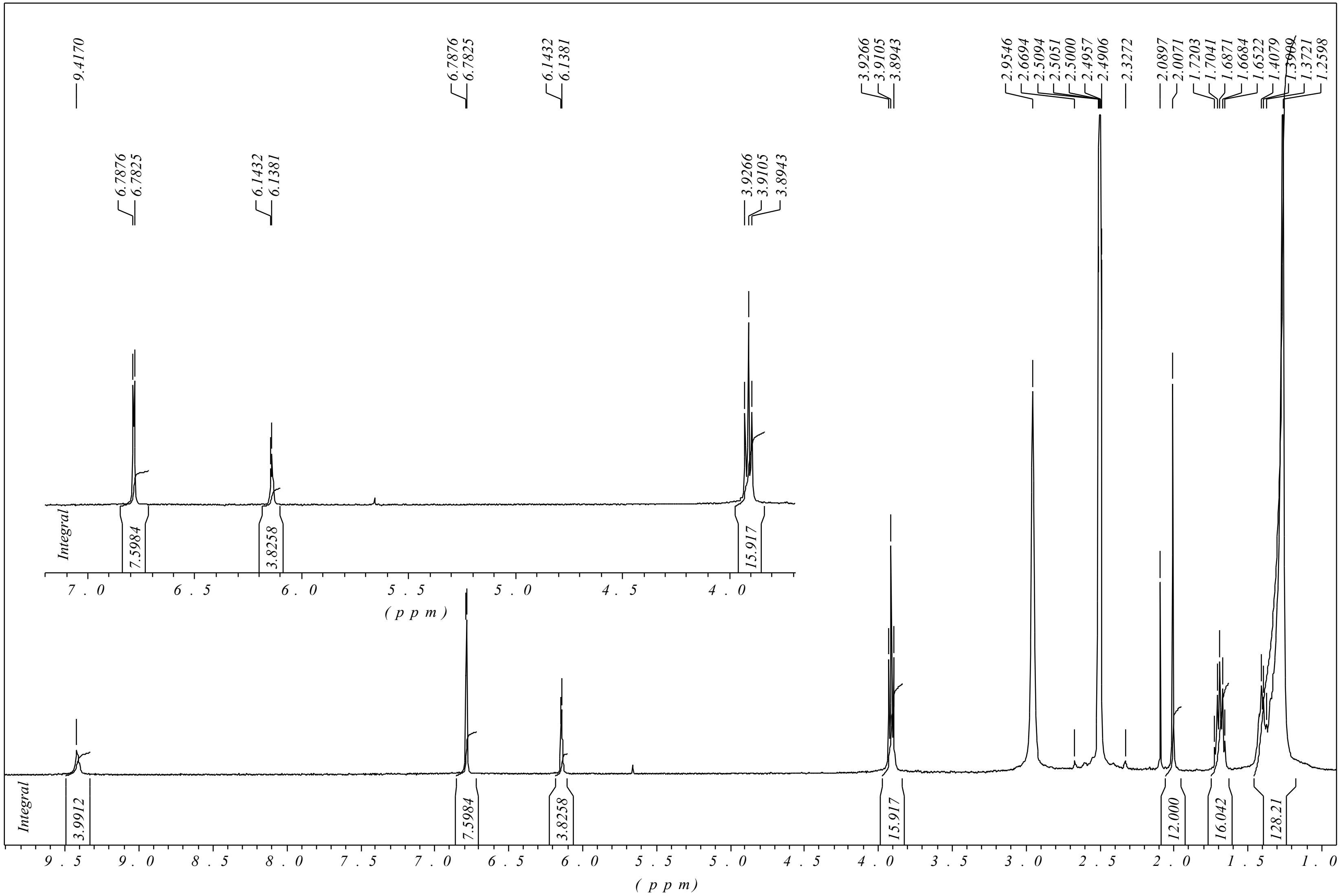

Figure S6. ^{1}H NMR spectrum of **7** (m = 20, 400 MHz, dmso-d_6, 80 °C).

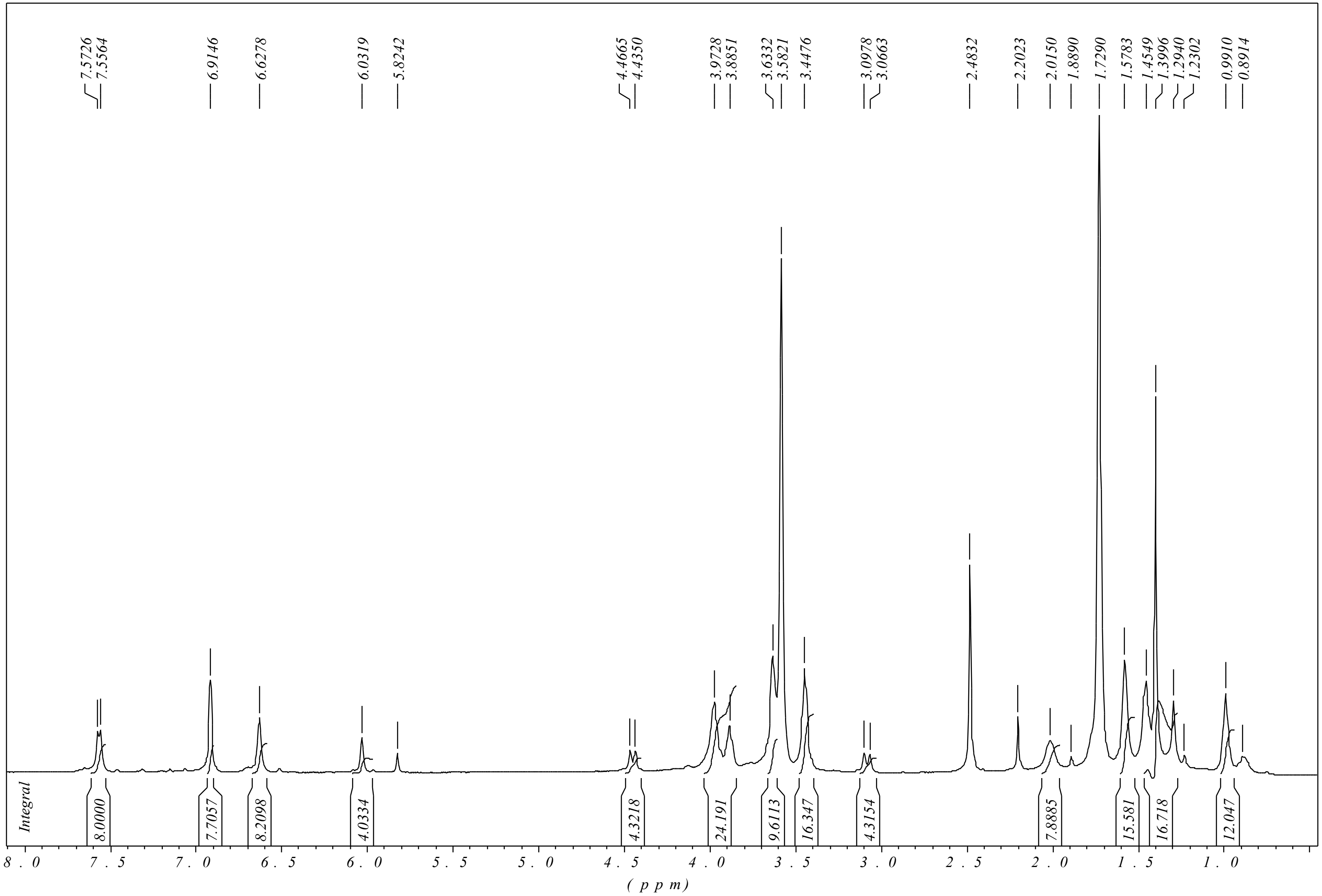

Figure S7. ^{1}H NMR spectrum of **10** (n = 1, 400 MHz, THF-d_8, 25 °C).

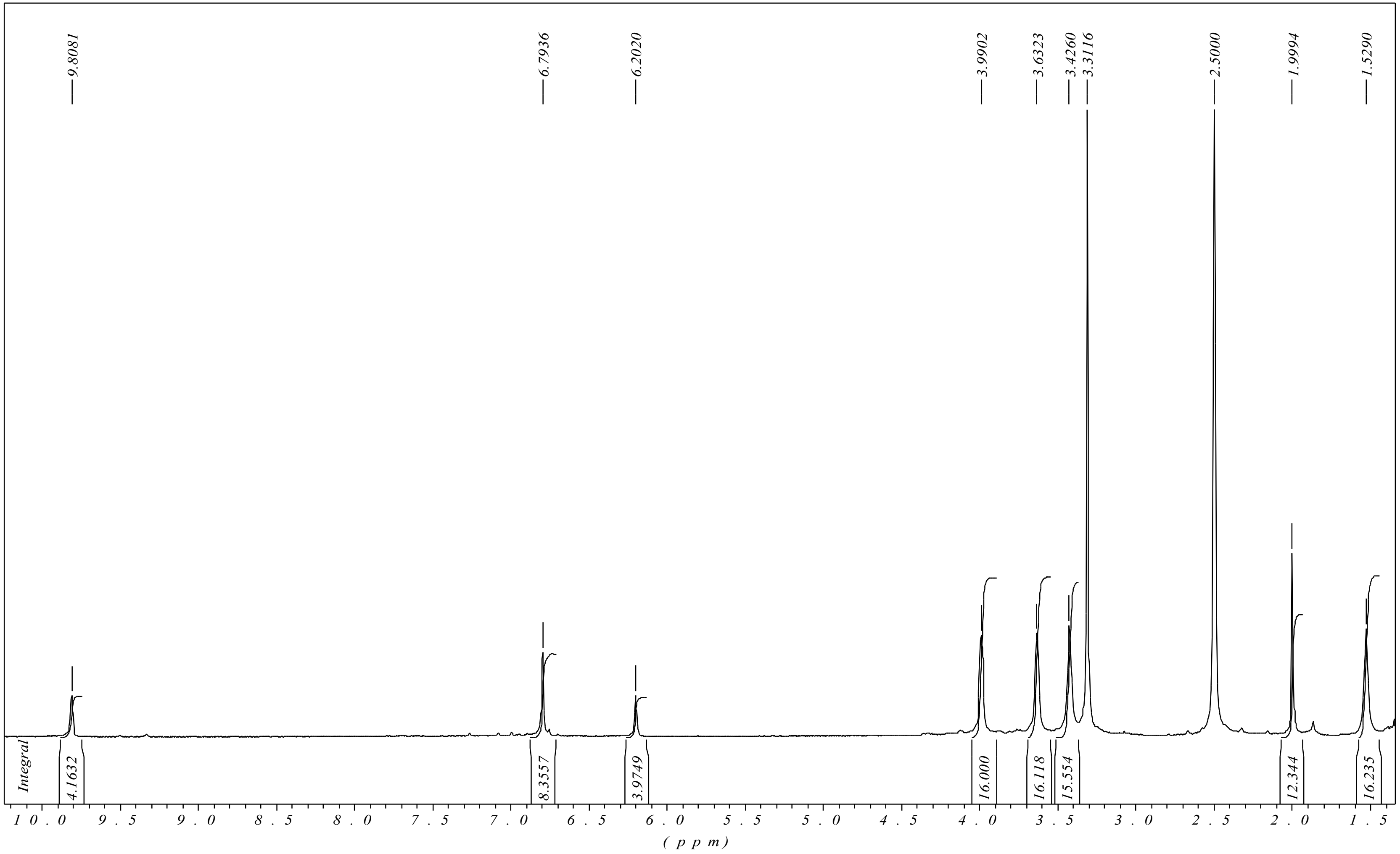

Figure S8. ^{1}H NMR spectrum of **11** (n = 1, 400 MHz, dmso-d_6, 25 °C).