Supplementary Information for

Chirality Organization of Aniline Oligomers through Hydrogen Bonds of Amino Acid Moieties

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Table of Contents

General Methods.

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 Plus spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 or a JNM-ECS 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer. UV-vis. spectra were recorded using a HITACHI U-3500 spectrophotometer monitoring under argon atmosphere at 25 ^{o}C. Circular dichroism spectra were recorded using a JASCO J-720 or a JASCO J-820 spectropolalimeter. UV-vis. and circular dichroism measurements were conducted using 1-cm pathlength quartz cuvettes. Cyclic voltammograms were recorded on a BAS CV-50W voltammetry analyzer under argon atmosphere at 25 ^{o}C.

Syntheses of the Compounds.

Synthesis of Ethyl 2-(4-Aminophenylamino)benzoate. To a mixture of cesium carbonate (3.10 g, 9.5 mmol), palladium(II) acetate (89.8 mg, 0.40 mmol), (±)-BINAP (218 mg, 0.35 mmol), ethyl 2-bromobenzoate (454 mg, 2.0 mmol), and *p*-phenylenediamine (865 mg, 8.0 mmol) was added anhydrous toluene (40 mL). The mixture was stirred at 100 ^{o}C for 48 h under argon atmosphere. After cooling to ambient temperature, dichloromethane (30 mL) was added to the brown suspension and filtered. After evaporation of the solvent, a residue was purified by silica-gel column chromatography (from hexane to hexane/EtOAc = 4:1) to give the expected compound (62.0 mg, 0.24 mmol) as a brown-yellow solid, R_f = 0.64 (hexane/EtOAc = 5:2): yield 66%; mp 73 °C (uncorrected); IR (KBr) 3289, 3253, 3033, 2992, 2975, 1681, 1583, 1522, 1478, 1449 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 9.17 (s, 1H), 7.93 (dd, 1H, J = 7.8, 1.8 Hz), 7.23 (dt, 1H, J = 7.8, 1.8 Hz), 7.02 (dd, 2H, J = 6.4, 1.8 Hz), 6.89 (dd, 1H, J = 7.8, 0.9 Hz), 6.69 (dd, 2H, J = 6.4, 1.8 Hz), 6.62 (dt, 1H, J = 7.8, 0.9 Hz), 4.33 (q, 2H, J = 7.3 Hz), 3.69 (s, 2H), 1.38 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 168.9, 150.5, 144.5, 134.3, 131.8, 131.6, 126.7, 116.1, 116.0, 113.6, 111.2, 60.9, 14.6 ppm; HRMS (FAB) *m/z*: $[M]^+$ 256.1220, $C_{15}H_{16}N_2O_2$ (calc. 256.1212); Anal. Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found: C, 71.15; H, 5.91; N, 6.87.

*General Procedure for Synthesis of Tetraalanyl Derivative **1***. A mixture of **3** (73.0 mg 0.10 mmol) and sodium hydroxide (c.a. 180 mg) in tetrahydrofuran (10 mL) was refluxed for 27 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The dark brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained dark brown solid, 1-hydroxybenzotriazole (108 mg, 0.80 mmol), L/D-alanine methyl ester hydrochloride (112 mg, 0.80 mmol), and triethylamine (0.5 mL). The mixture was stirred at 0 ^{o}C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (154 mg, 0.80 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 25 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2),

water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from CH_2Cl_2 to CH_2Cl_2/EtOAc = 3:1) to give **1** as a yellow solid (**1-L**: 162 mg, 61%; **1-D**: 87.6 mg, 33%), R_f = 0.25 (CH_2Cl_2/EtOAc = 3:1).

1-L: mp 167-168 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H), 7.50 (d, 2H, J = 7.9 Hz), 7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint., 2H, J = 7.3 Hz), 4.64 (quint., 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 958.3864, $C_{50}H_{54}N_8O_{12}$ (calc. 958.3861) Anal. Calcd. for $C_{50}H_{54}N_8O_{12}$: C, 62.62; H, 5.68; N, 11.68. Found: C, 62.48; H, 5.41; N, 11.54.

1-D: mp 167-168 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H), 7.50 (d, 2H, J = 7.9 Hz), 7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint., 2H, J = 7.3 Hz), 4.64 (quint., 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 958.3858, $C_{50}H_{54}N_8O_{12}$ (calc. 958.3861).

*General Procedure for Synthesis of Dialanyl Derivative **2***. A mixture of **4** (58.6 mg, 0.10 mmol) and sodium hydroxide (c.a. 100 mg) in tetrahydrofuran (10 mL) was refluxed for 20 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The dark brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL)

was added to a mixture of the thus-obtained black solid, 1-hydroxybenzotriazole (27.0 mg, 0.20 mmol), L/D-alanine methyl ester hydrochloride (27.9 mg, 0.20 mmol), and triethylamine (0.5 mL). The mixture was stirred at 0 ^{o}C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (38.3 mg, 0.20 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 45 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to give **2** as a yellow solid (**2-L**: 29.2 mg, 42%; **2-D**: 18.9 mg, 27%), R_f = 0.63 (CH_2Cl_2/MeOH = 10:1).

2-L: mp 178-180 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H, J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quint., 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 700.2998, $C_{40}H_{40}N_6O_6$ (calc. 700.3009)

2-D: mp 178-180 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H, J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quint., 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 700.3022, $C_{40}H_{40}N_6O_6$ (calc. 700.3009)

Synthesis of ***3***. A solution of *p*-toluenesulfonate monohydrate (28.5 mg, 0.15 mmol) in ethanol (15 mL) was added to a mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (51.3 mg, 0.20 mmol) and ethyl 2-(4-aminophenylamino)benzoate (154 mg,

0.60 mmol). The mixture was stirred at reflux for 12 h under argon atmosphere. Once cooling to ambient temperature, the mixture was stirred at reflux for 32 h under oxygen atmosphere. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Aniline tetramer **3** (157 mg) was obtained as a red crystal by recrystallization from dichloromethane: yield 98%; mp 195-197 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3412, 3337, 3268, 3181, 3161, 1684, 1581, 1515, 1382, 1370, 1314 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.38 (s, 2H), 7.99 (s, 2H), 7.97 (d, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 8.0 Hz), 7.23-7.19 (m, 10H), 7.13 (d, 2H, J = 8.0 Hz), 6.70 (t, 2H, J = 8.0 Hz), 4.35 (q, 4H, J = 7.3 Hz), 4.33 (q, 4H, J = 7.3 Hz), 1.40 (t, 6H, J = 7.3 Hz), 1.34 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 167.7, 166.7, 148.1, 133.2, 130.8, 123.9, 123.8, 120.9, 120.3, 118.3, 117.4, 115.8, 115.7, 112.8, 110.9, 60.5, 59.9, 13.4, 13.2 ppm; HRMS (FAB) *m/z*: $[M]^+$ 730.2989, $C_{42}H_{42}N_4O_8$ (calc. 730.3003)

*Synthesis of **4***. A mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (256 mg, 1.0 mmol) and *p*-aminodiphenylamine (369 mg, 2.0 mmol) in acetic acid (15 mL) was stirred at 100 ^oC for 18 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Chloroform (15 mL) was added to the pink solid, which was refluxed for 10 h under oxygen atmosphere. After evaporation of the solvent, **4** (498 mg) was obtained as a red crystal by recrystallization from toluene: yield 85%; mp 211-213 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3416, 3361, 2926, 1686, 1599, 1513, 1103, 1020 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 8.63 (s, 2H), 7.89 (s, 2H), 7.24 (t, 4H, J = 7.8 Hz), 7.14 (d, 4H, J = 8.7 Hz), 7.10 (d, 4H, J = 8.7 Hz), 7.01 (d, 2H, J = 7.8 Hz), 6.86 (t, 2H, J = 7.8 Hz), 5.73 (s, 2H), 4.31 (q, 4H, J = 7.3 Hz), 1.33 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 167.9, 144.8, 138.9, 138.2, 136.7, 129.7, 122.4, 120.8, 120.4, 119.0, 118.1, 116.7, 61.6, 14.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 586.2582, $C_{36}H_{34}N_4O_4$ (calc. 586.2580)

General Procedures of UV-vis. and CD Measurements.

UV-vis. spectra of **1** and **2** were measured in a deaerated dichloromethane solution with the concentration 5.0 x 10^{-5} M under argon atmosphere at 25 ^{o}C. CD spectra of **1** and **2** were measured in an deaerated dichloromethane solution with the concentration 5.0 x 10^{-5} M under argon atmosphere at 25 ^{o}C.

General Procedures of Electrochemical Experiments.

The cyclic voltammetry was performed in a deaerated dichloromethane solution (5.0 x 10^{-4} M) containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at 25 ^{o}C with a three-electrode system consisting of a platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/Ag^{+} (0.01 M) reference electrode (BAS) at 100 mVs^{-1} scan rate. Redox potentials are given vs Fc/Fc^{+}.

X-ray Structure Analysis.

Measurements for **3** and **4** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. The structures of **3** and **4** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table S1. Hydrogen bonds are listed in Table S2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-772855 for **3**, CCDC-772856 for **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

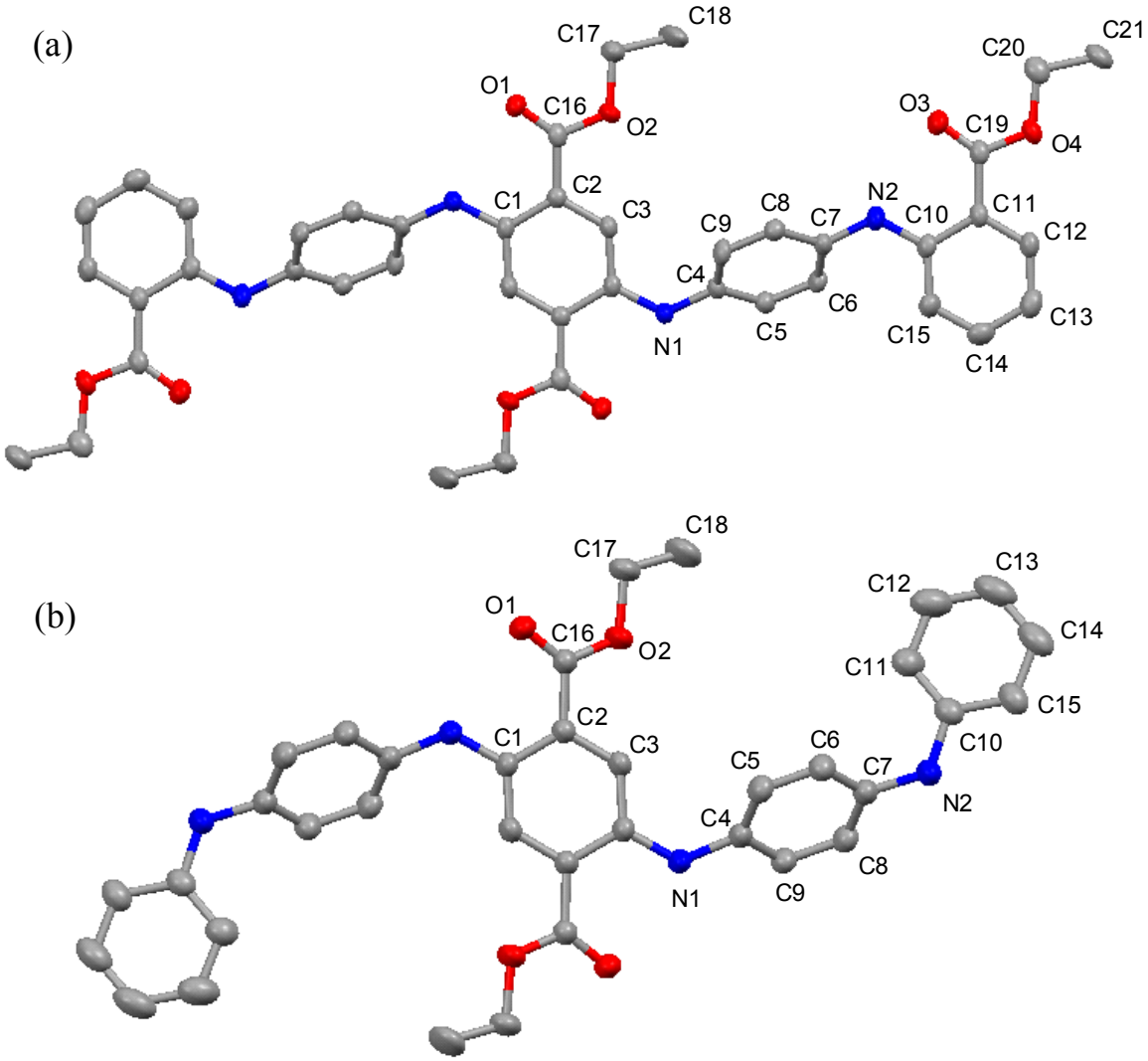

Figure S1. Crystal structures of (a) **3** and (b) **4** (50% probability ellipsoids).

Table S1. Crystallographic data for **3** and **4**.

	3	**4**
formula	$C_{44}H_{46}N_4O_8Cl_4$	$C_{36}H_{34}N_4O_4$
formula weight	900.68	586.69
crystal system	triclinic	triclinic
space group	*P*-1 (No. 2)	*P*-1 (No. 2)
a, Å	10.03528(18)	8.03011(17)
b, Å	10.64666(19)	10.2142(2)
c, Å	10.76910(19)	11.2028(2)
α, deg	101.5160(7)	62.5560(10)
β, deg	102.3520(7)	71.5440(12)
γ, deg	101.8180(7)	68.5560(11)
V, Å^3	1063.88(3)	748.25(3)
Z	1	1
D_{calcd}, g cm^{-3}	1.406	1.302
μ(Cu Kα), cm^{-1}	30.157	6.915
T, °C	-150	-150
λ(Cu Kα), Å	1.54187	1.54187
*R*1 [a]	0.0512	0.0378
*wR*2 [b]	0.2205	0.1106

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Intramolecular hydrogen bonds for **3** and **4**.

crystal	donor	acceptor	D • • • A (Å)	D–H • • • A (°)
3 [a]	N(1)	O(1*)	2.715(3)	130(3)
	N(1*)	O(1)	2.715(3)	130(3)
	N(2)	O(3)	2.697(3)	130(3)
	N(2*)	O(3*)	2.697(3)	130(3)
4 [a]	N(1)	O(1*)	2.7026(14)	155.9(18)
	N(1)	O(1)	2.7026(14)	155.9(18)

[a] The moleculars sits on an inversion center.

Table S3. Selected ^{1}H NMR Data for **1**-**4**.

		^{1}H NMR N-H (ppm) (5.0 x 10^{-3} M)		
		CD_2Cl_2	CD_2Cl_2/DMSO-d_6 (9:1)	CD_2Cl_2/DMSO-d_6 (1:1)
1-L	amide (central)	6.74	8.19	8.90
	amide (terminal)	6.69	7.73	8.65
	amine (central)	9.26	9.28	9.42
	amine (terminal)	8.02	8.27	8.53
2-L	amide (central)	6.85	8.17	8.85
	amine (central)	7.94	8.04	8.40
	amine (terminal)	5.70	6.48	7.63
3	amine (central)	9.40	9.41	
	amine (terminal)	8.75	8.75	
4	amine (central)	8.63	8.60	
	amine (terminal)	5.73	7.04	

Table S4. Selected Data of FT-IR data for **1**-**4**.[a]

compound	ν_{N-H} (cm^{-1})
1	3441, 3418, 3375, 3340
2	3411, 3337
3	3424, 3342
4	3416, 3360

[a] 5.0 x 10^{-3} M in CH_2Cl_2

Table S5. Redox potentials vs Fc / Fc^+ for **1-4**.[a]

compound	E^0_1 (V)	E^0_2 (V)	E^0_3 (V)
1-L	0.24	0.44	0.76
2-L	-0.06	0.09	0.48
3	0.31	0.60	0.79
4	0.04	0.24	0.53

[a] 5.0 x 10^{-3} M in CH_2Cl_2 containing 1.0 x 10^{-1} M Bu_4NClO_4

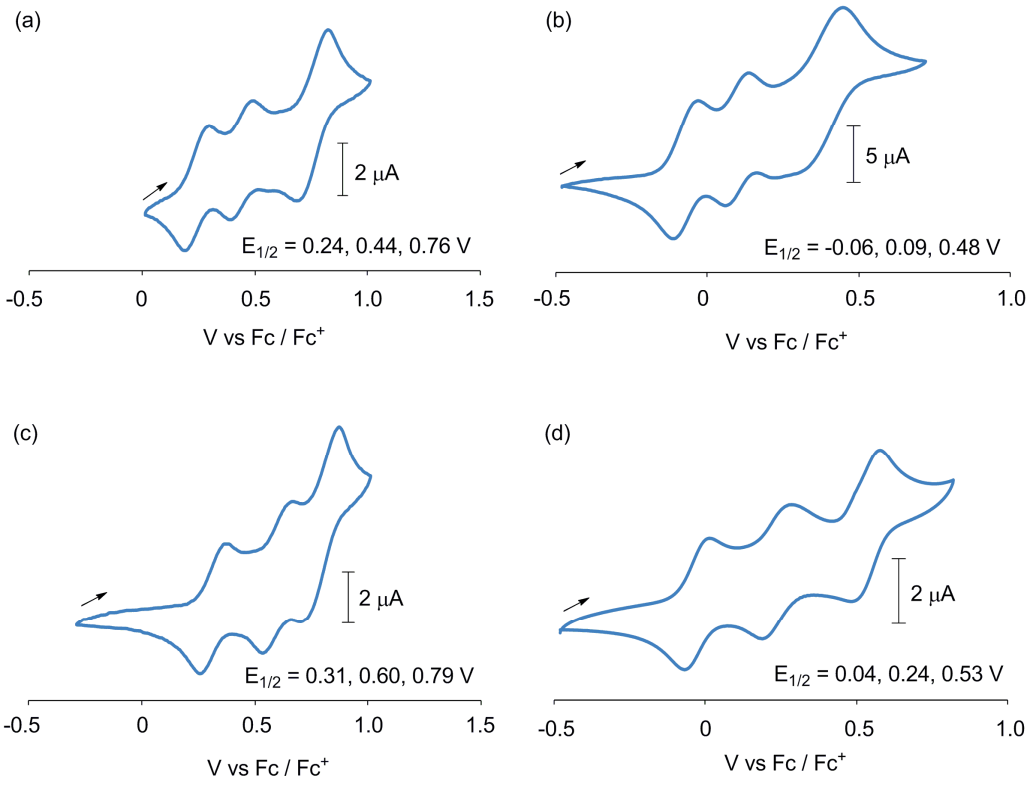

Figure S2. Cyclic voltammograms of (a) **1-L**, (b) **2-L**, (c) **3**, and (d) **4** in CH_2Cl_2 (5.0 x 10^{-4} M) containing 0.1 M Bu_4NClO_4 at a platinum working electrode with a scan rate 100 mV s^{-1} under argon atmosphere.

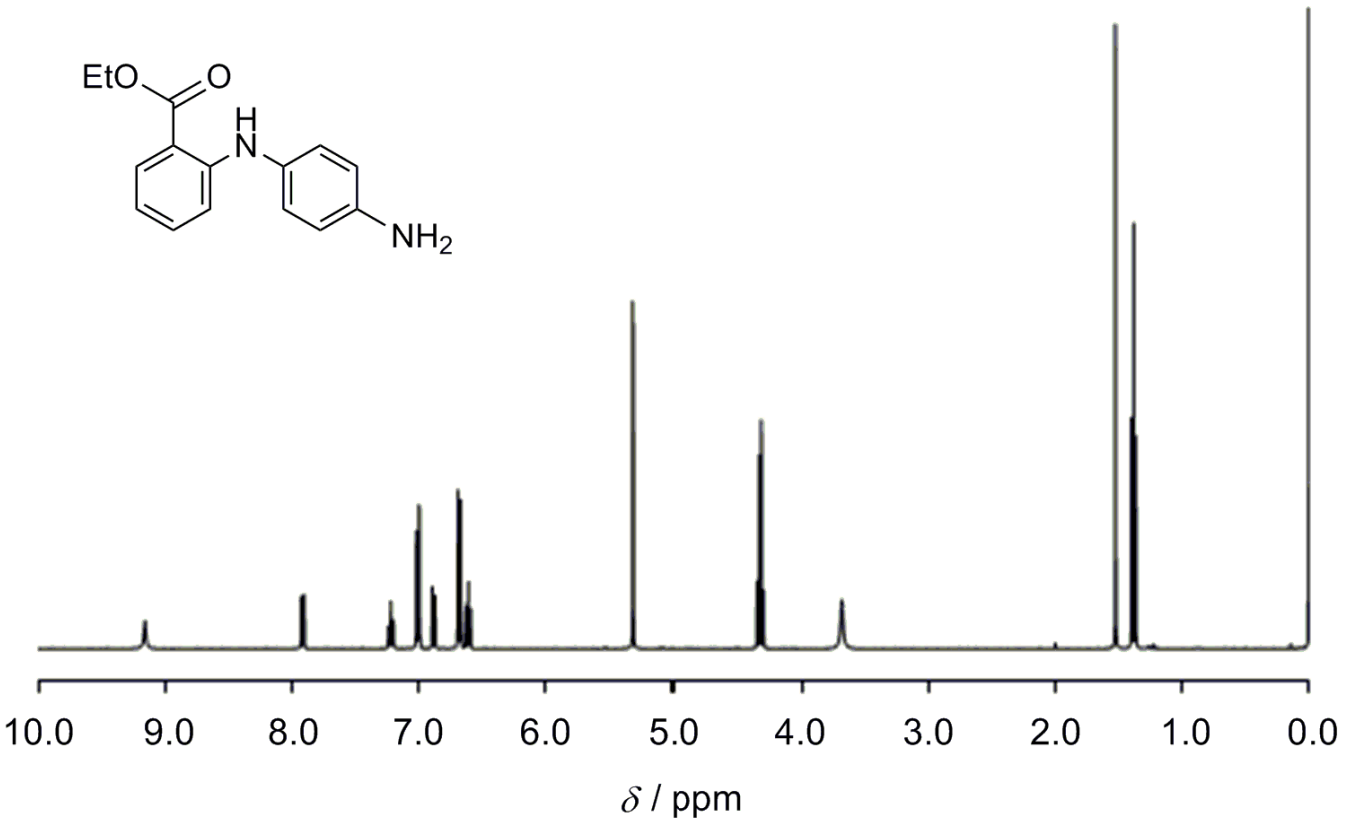

Figure S3. ^{1}H NMR spectrum of ethyl 2-(4-aminophenylamino)benzoate in CD_2Cl_2.

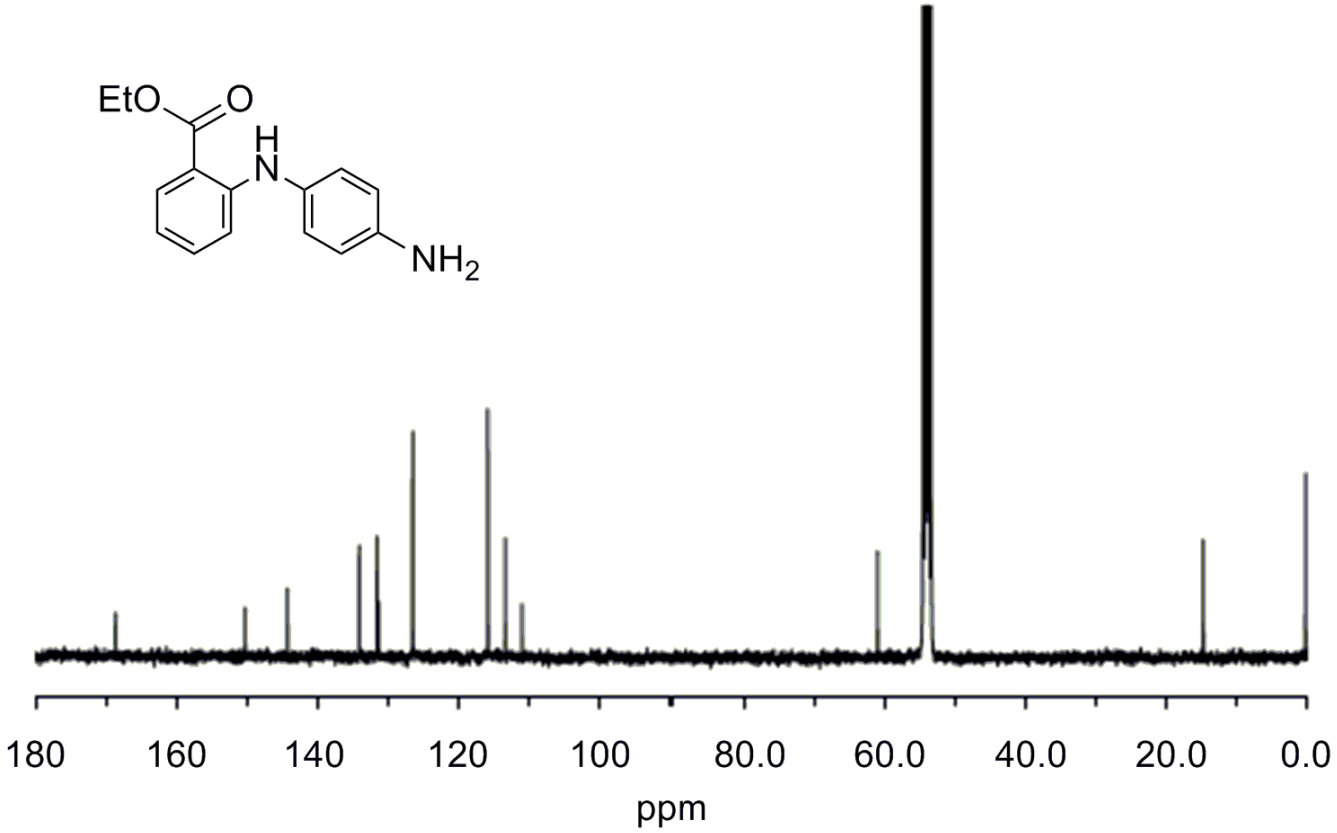

Figure S4. ^{13}C NMR spectrum of ethyl 2-(4-aminophenylamino)benzoate in CD_2Cl_2.

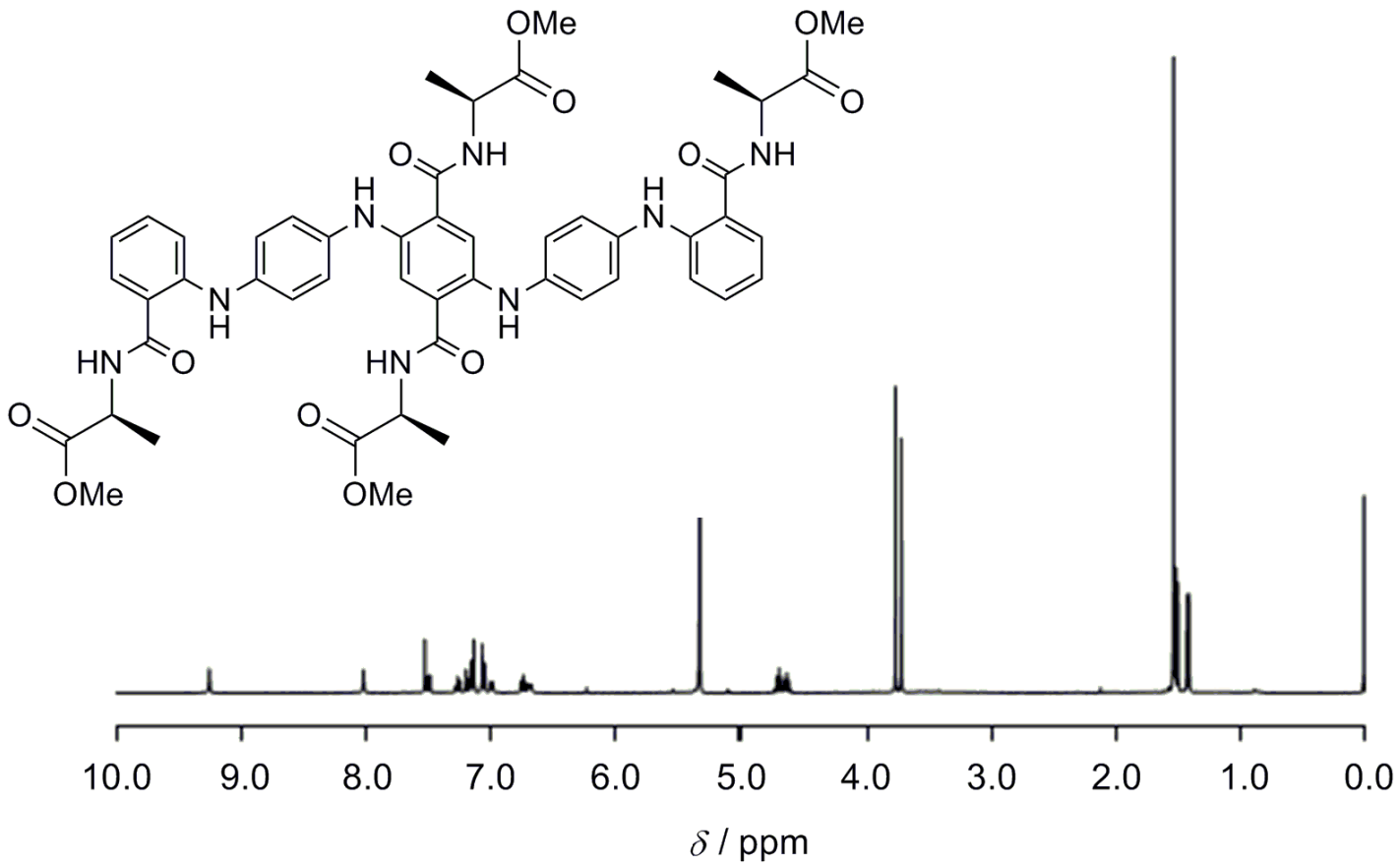

Figure S5. ^{1}H NMR spectrum of **1-L** in CD_2Cl_2.

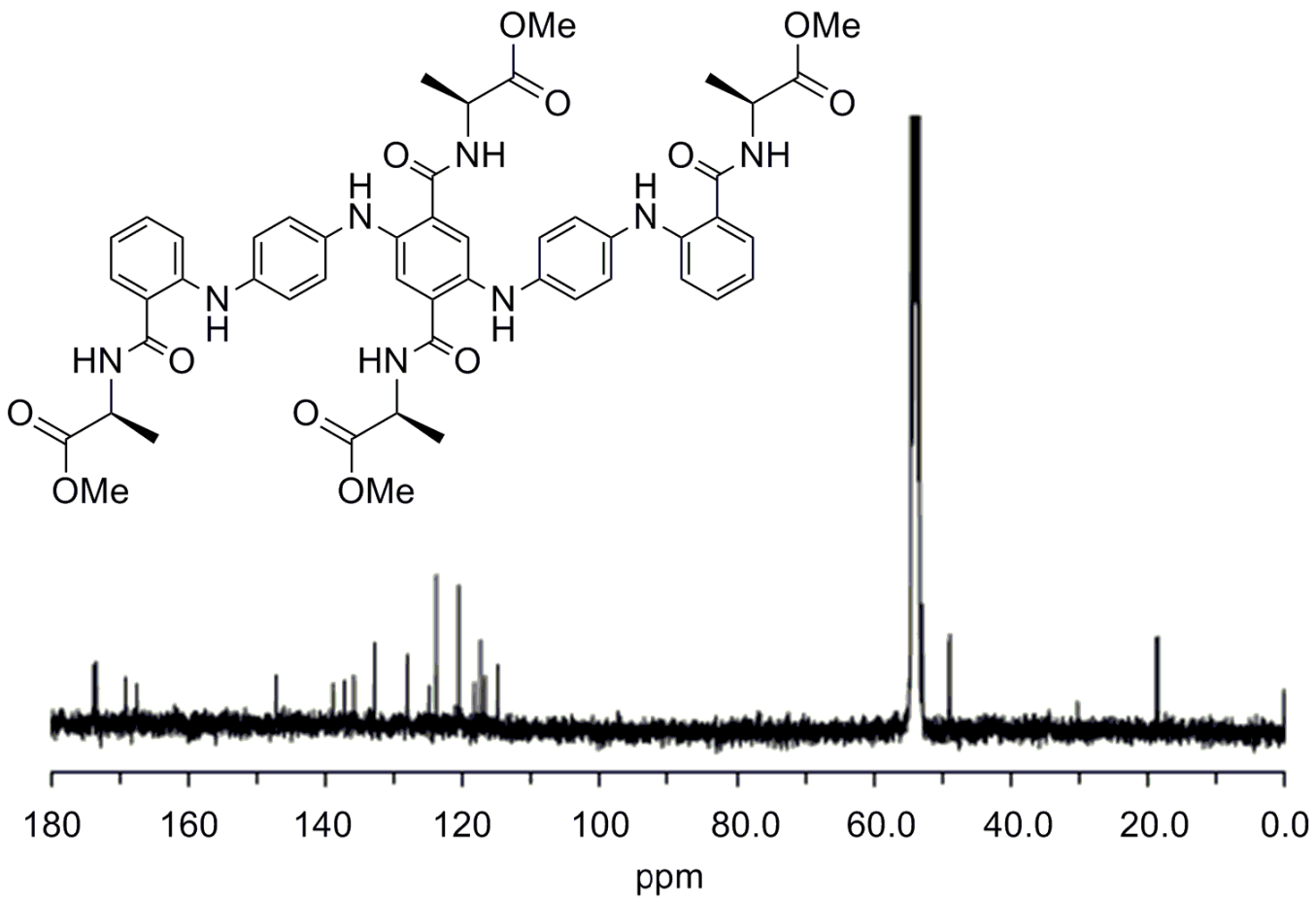

Figure S6. ^{13}C NMR spectrum of **1-L** in CD_2Cl_2.

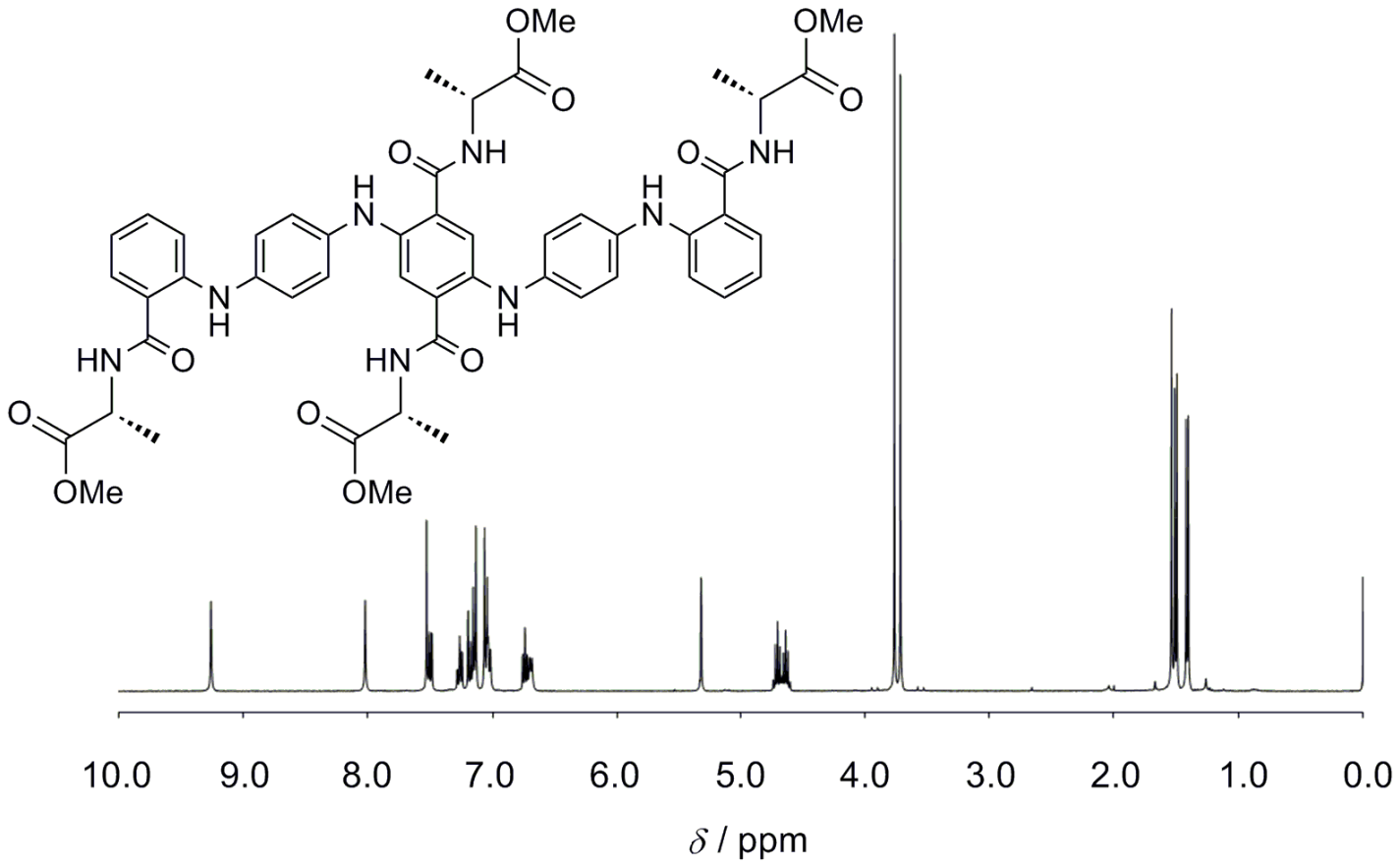

Figure S7. ^{1}H NMR spectrum of **1-D** in CD_2Cl_2.

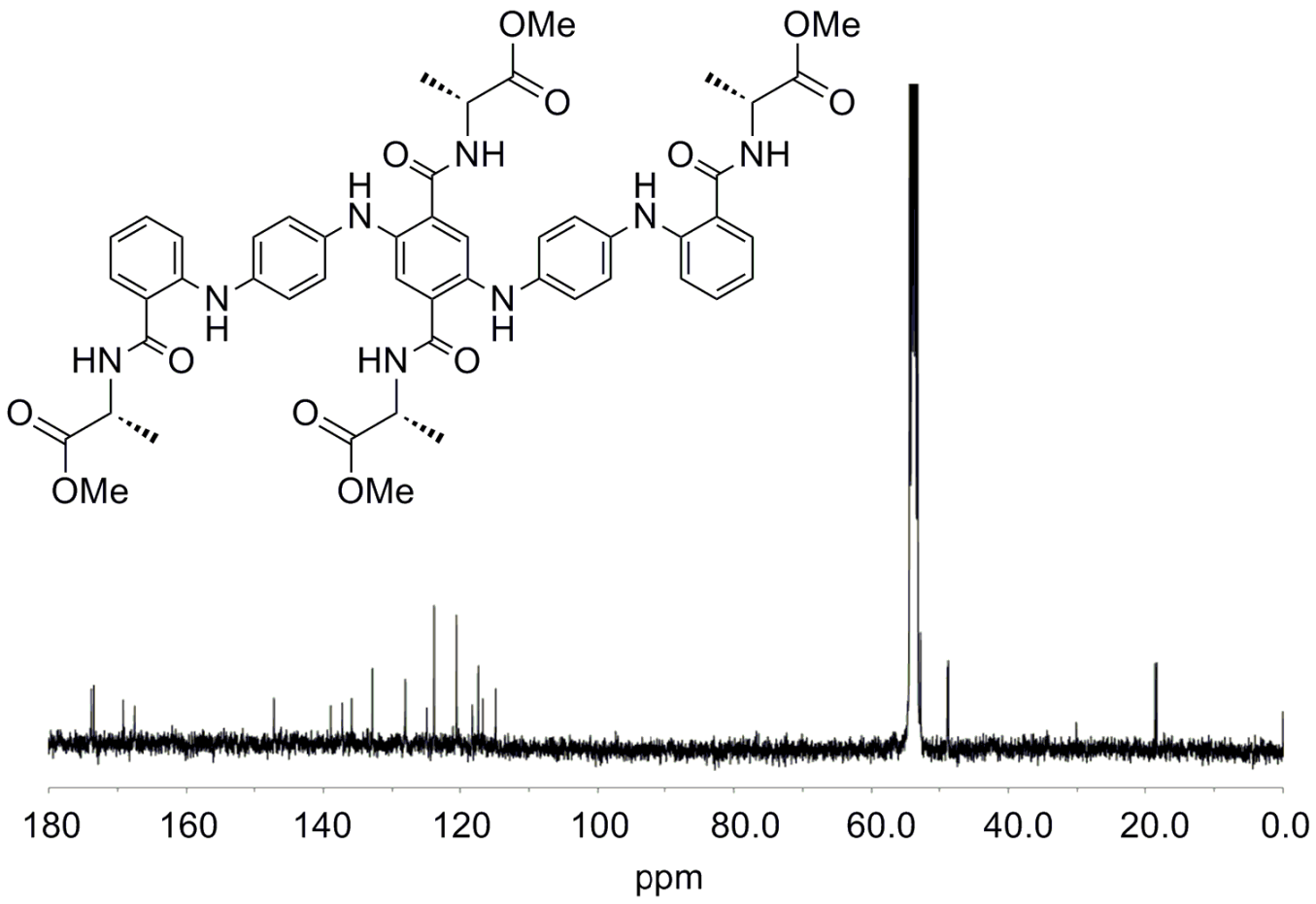

Figure S8. ^{13}C NMR spectrum of **1-D** in CD_2Cl_2.

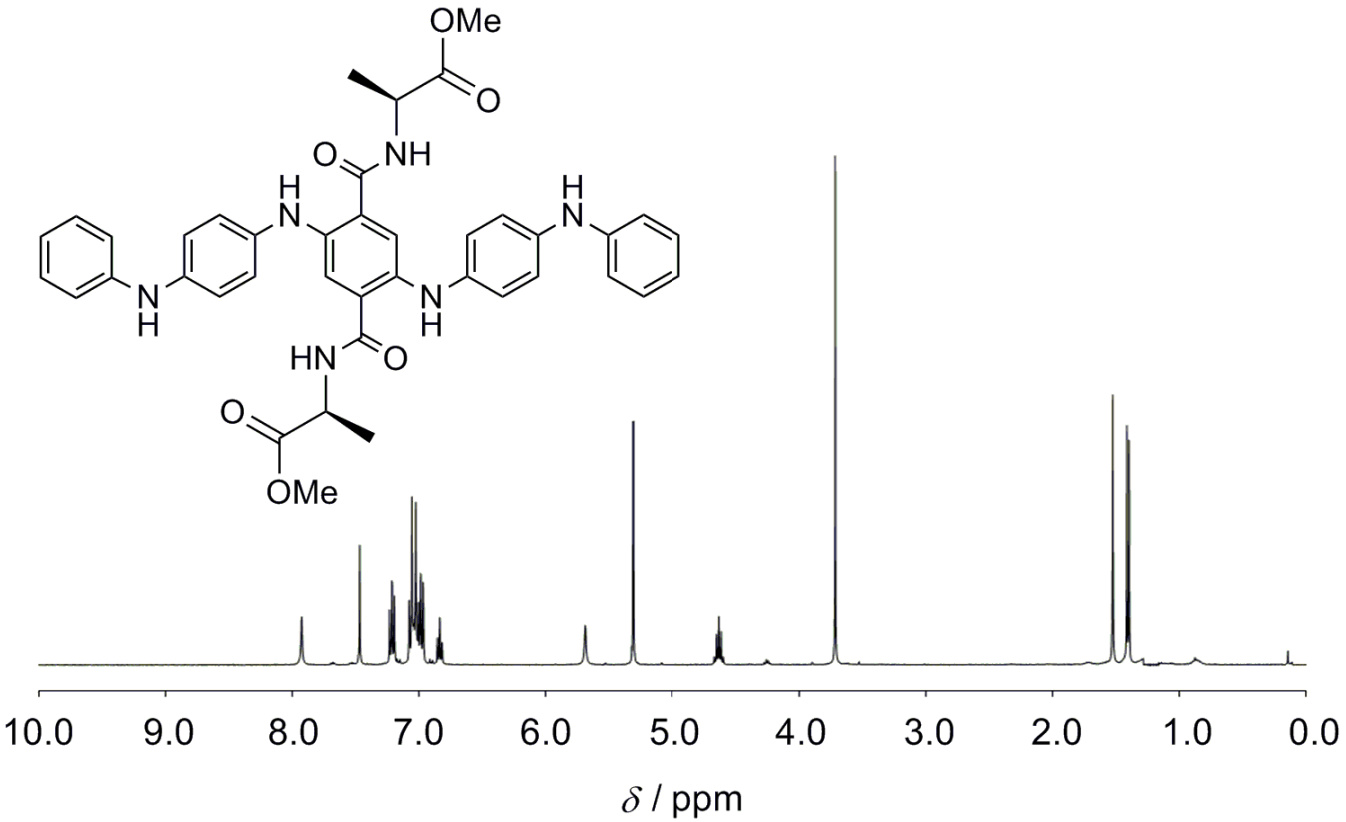

Figure S9. ^{1}H NMR spectrum of **2-L** in CD_2Cl_2.

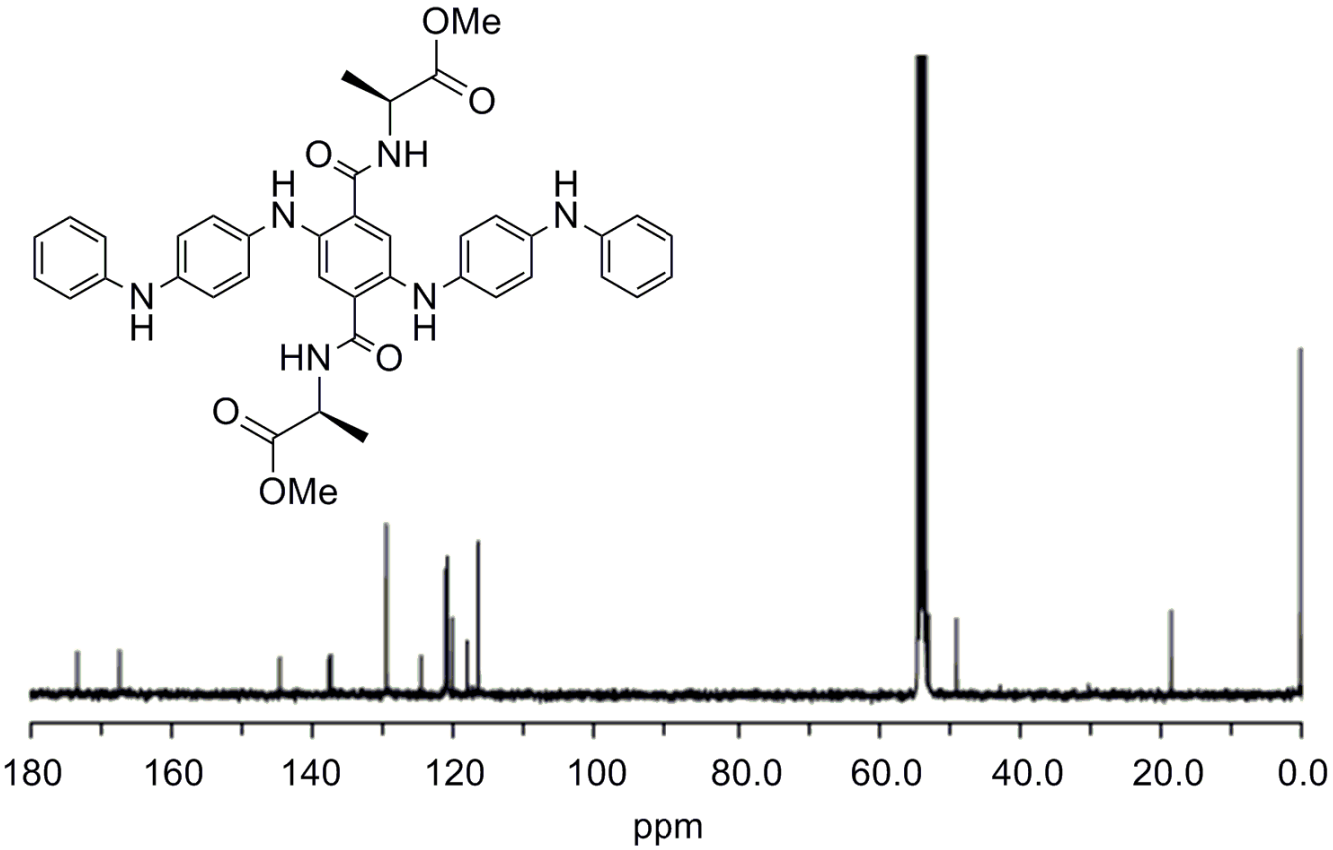

Figure S10. ^{13}C NMR spectrum of **2-L** in CD_2Cl_2.

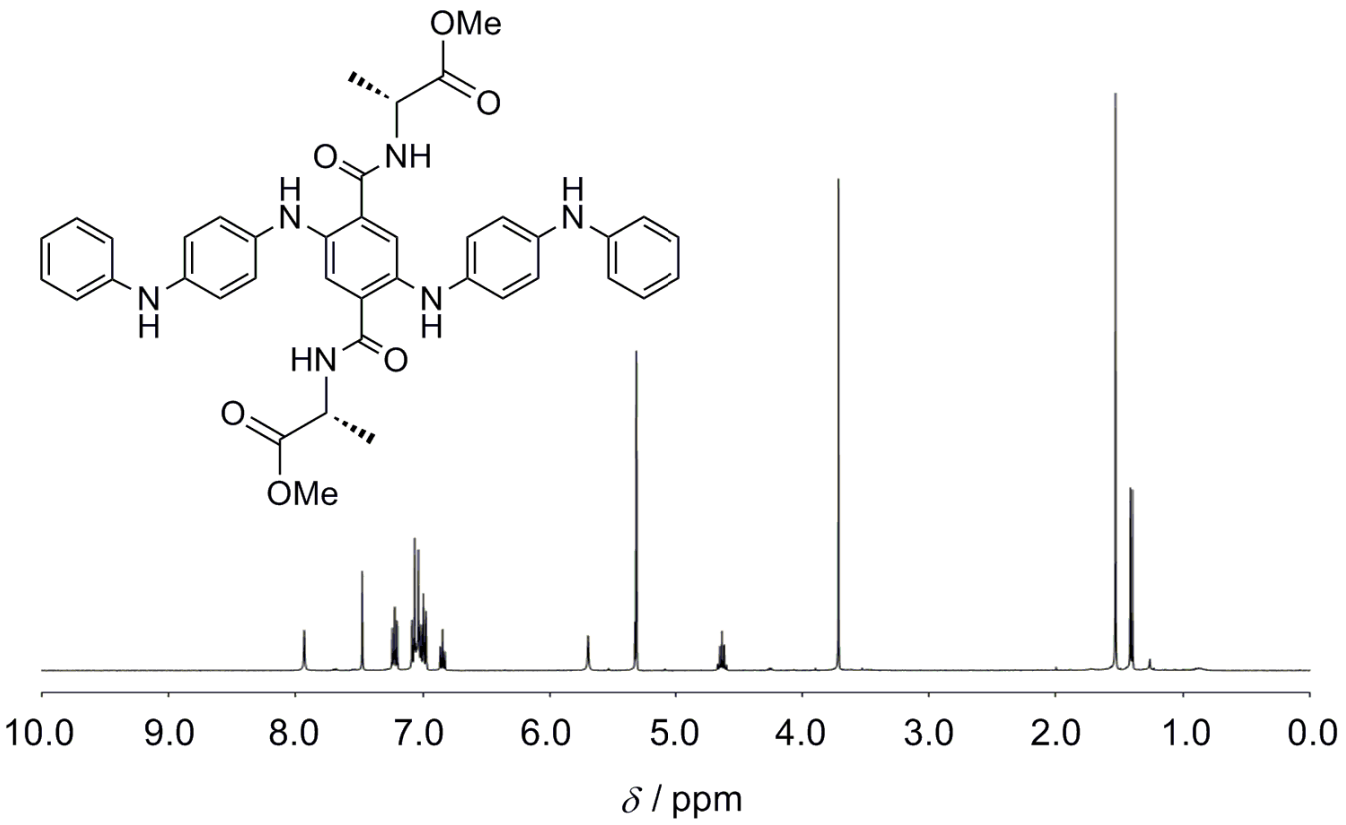

Figure S11. ^{1}H NMR spectrum of **2-D** in CD_2Cl_2.

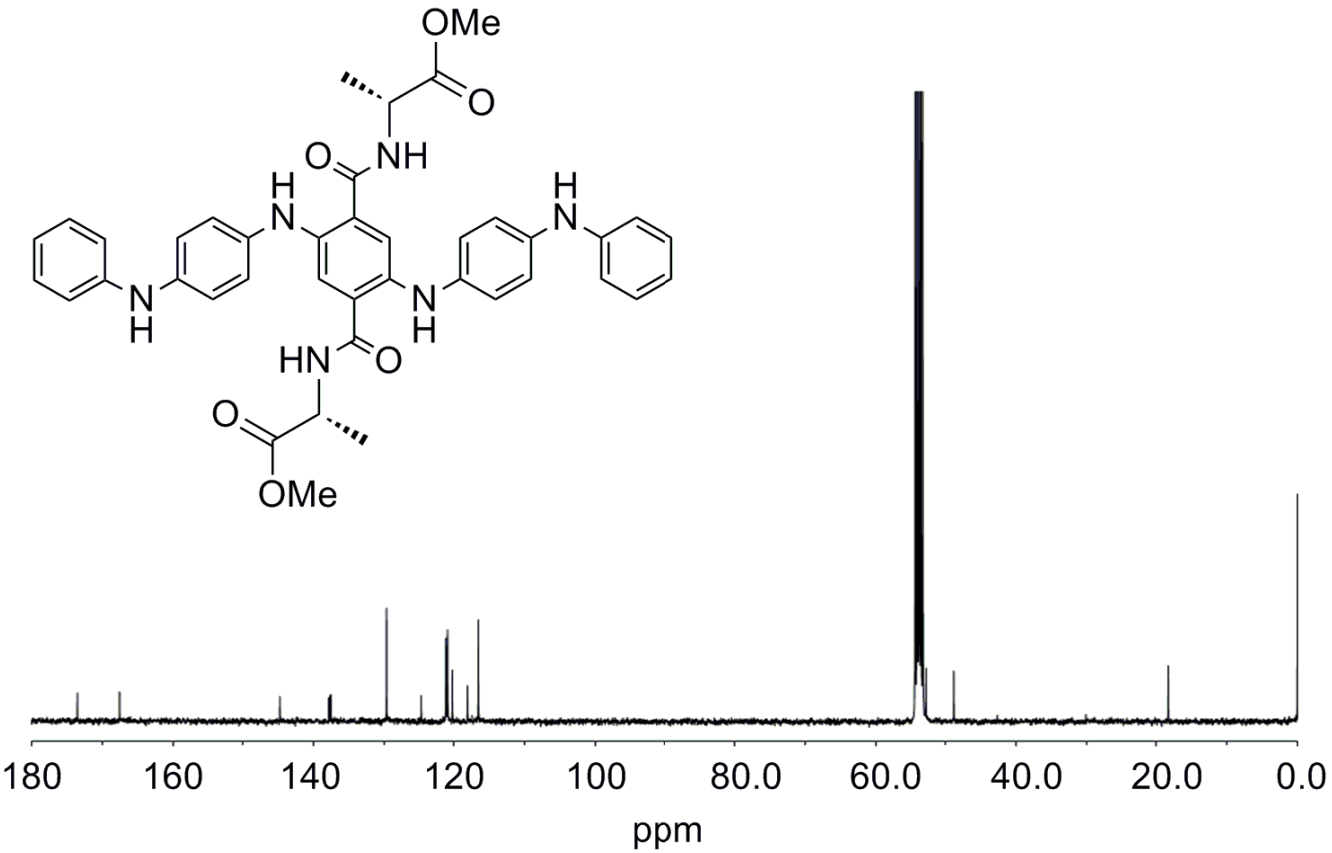

Figure S12. ^{13}C NMR spectrum of **2-D** in CD_2Cl_2.

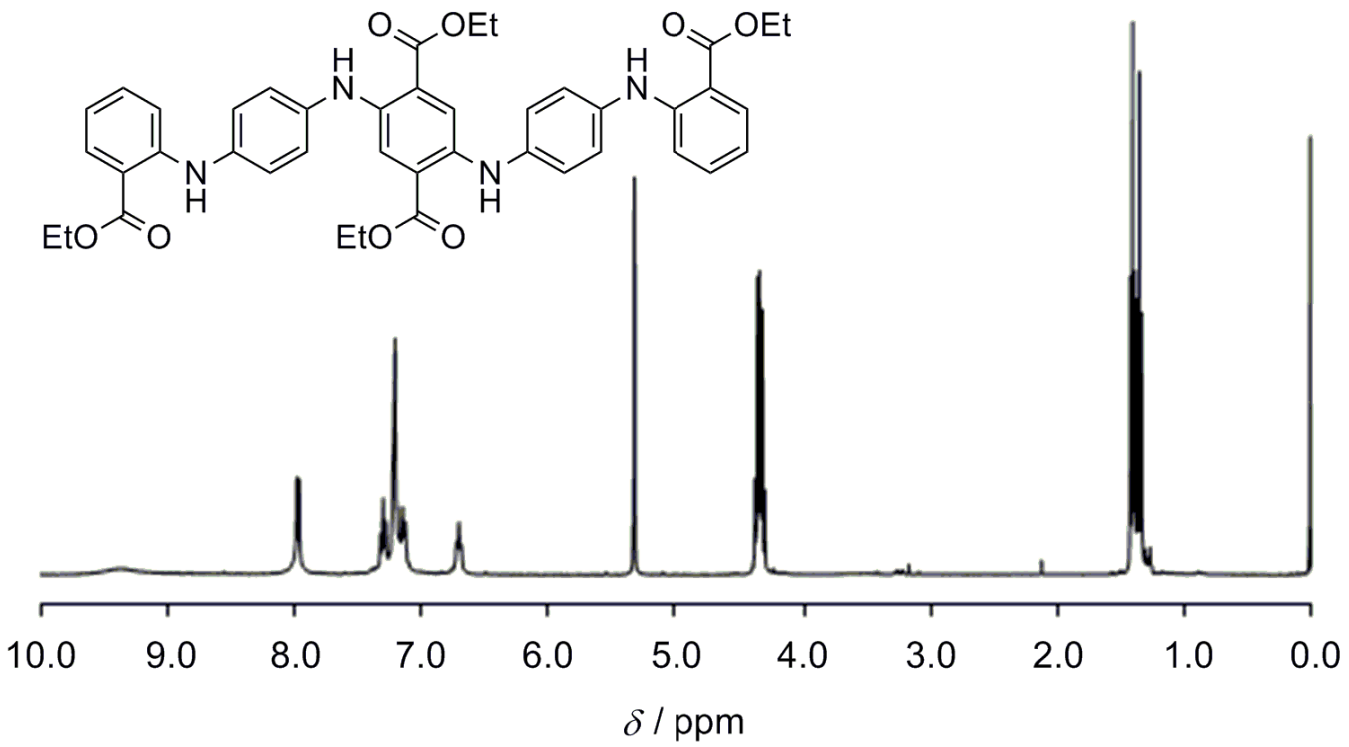

Figure S13. ^{1}H NMR spectrum of **3** in CD_2Cl_2.

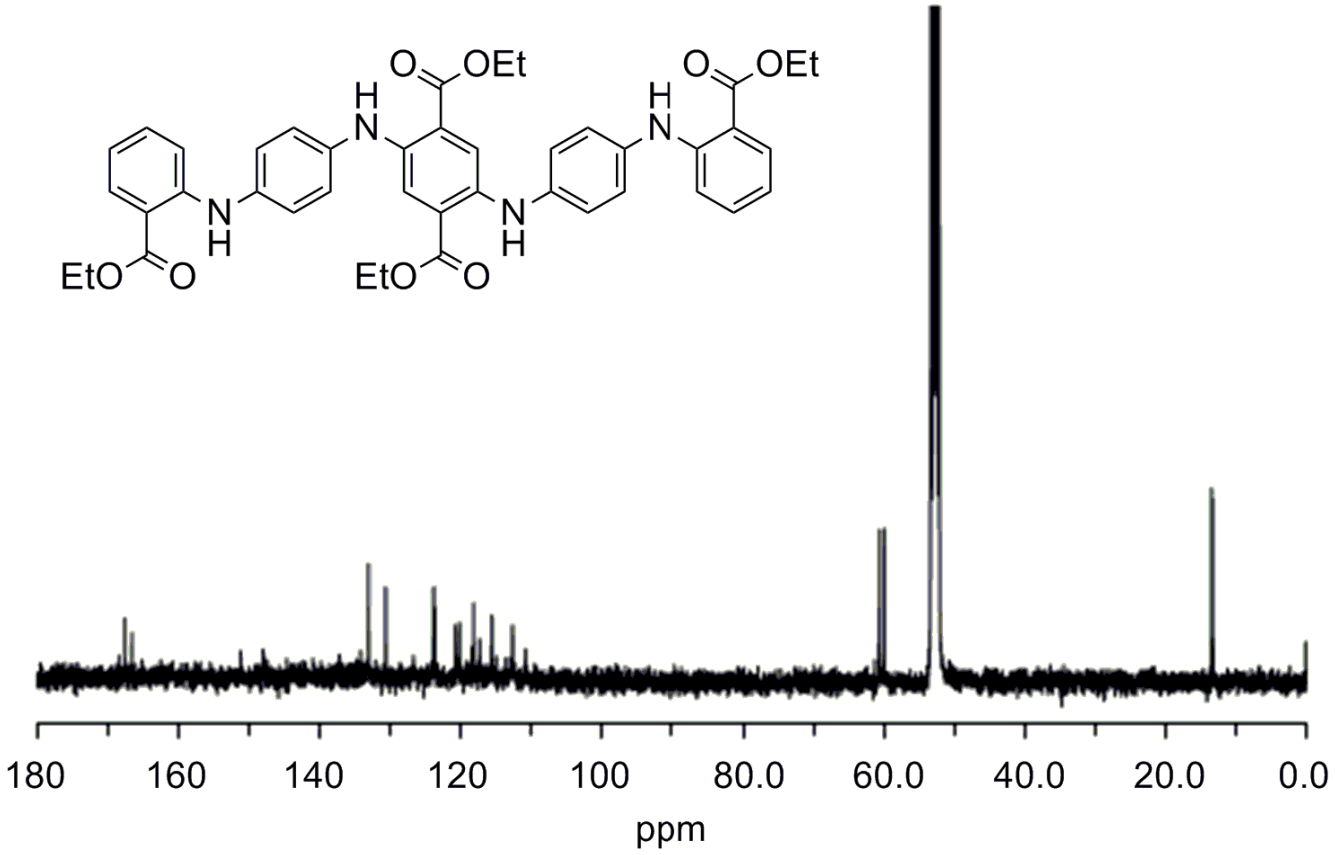

Figure S14. ^{13}C NMR spectrum of **3** in CD_2Cl_2.

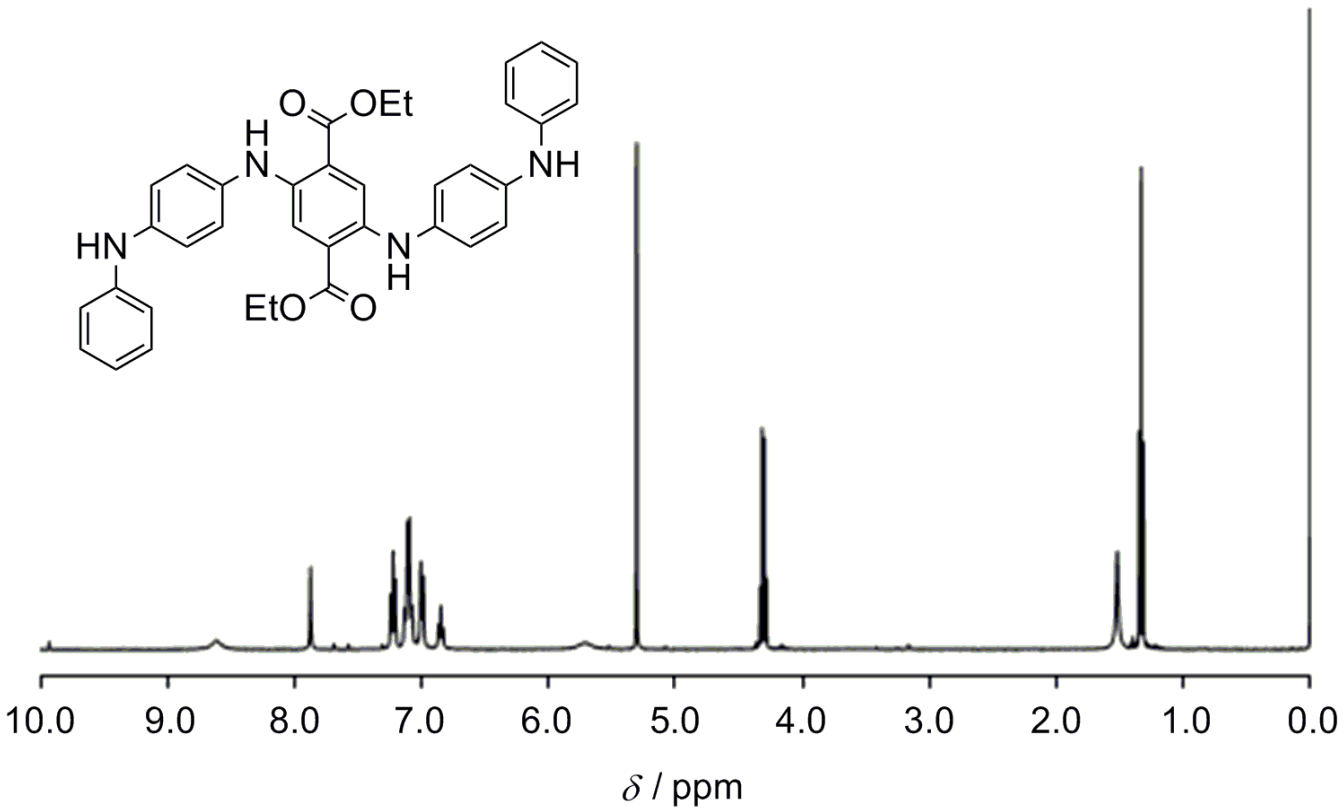

Figure S15. ^{1}H NMR spectrum of **4** in CD_2Cl_2.

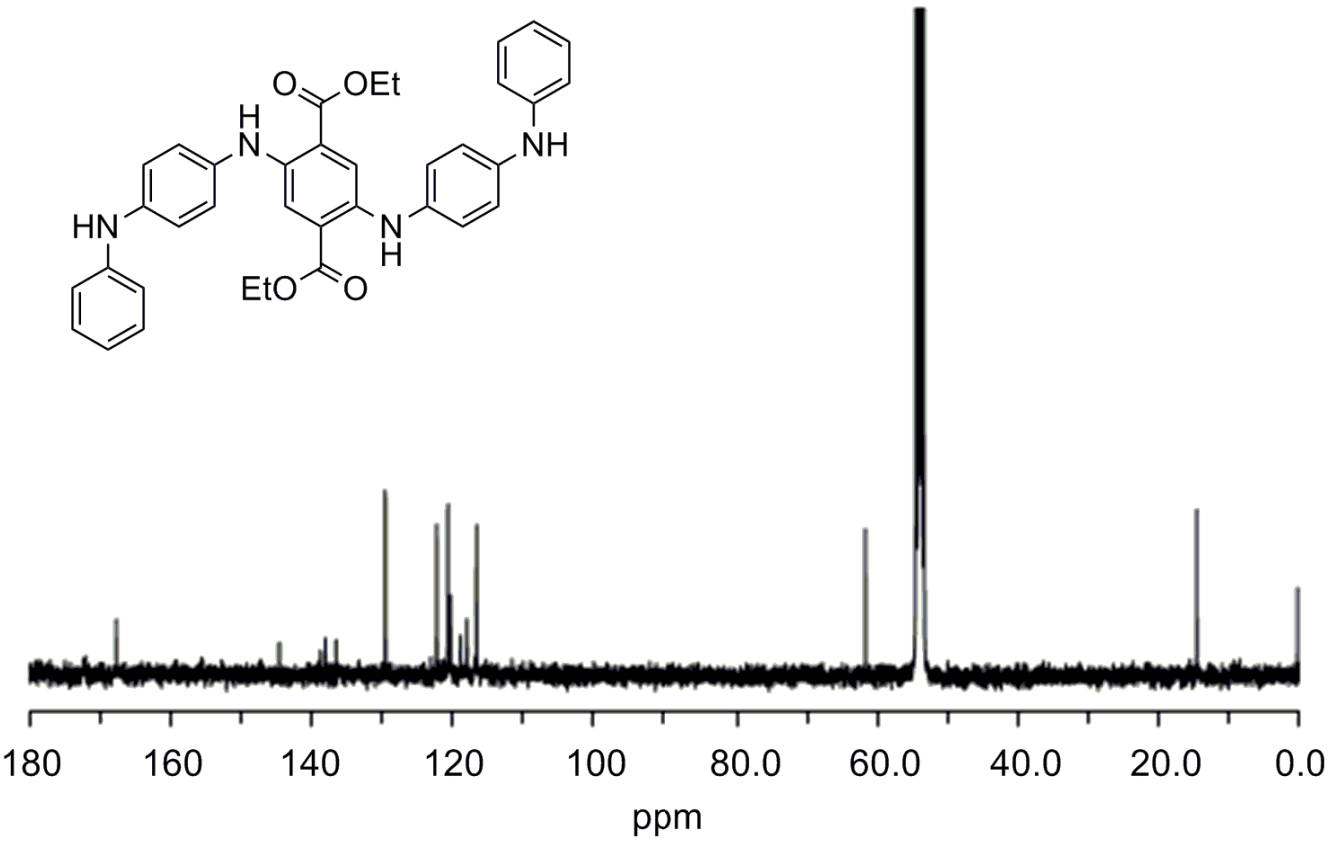

Figure S16. ^{13}C NMR spectrum of **4** in CD_2Cl_2.