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Supporting Information

Saddle-shaped aza-nanographene with multiple odd-membered rings

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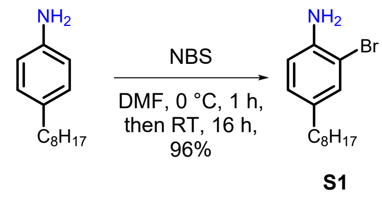
1. General remarks

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. 2-bromo-4-(*tert*-butyl)-6-chlorobenzaldehyde (**1**) was prepared according to the literature procedure.[1] Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. DMF was dried over magnesium sulfate, then distilled and stored under argon. For water-sensitive reactions solvents were dried using Solvent Purification System from MBraun (https://www.mbraun.com/us/). Transformations with moisture and oxygen sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin layer chromatography (TLC), which was performed on aluminium foil plates, covered with Silica gel 60 F_{254} (Merck) or Aluminium oxide 60 F_{254} (neutral, Merck). Products purification was done by means of column chromatography with Kieselgel 60 (Merck) or Aluminium oxide (Fluka). Occasionally, dry column vacuum chromatography (DCVC**)** for purification of products obtained was performed using Silica gel Type D 5F. The identity and purity of prepared compounds were proved by ^{1}H NMR and ^{13}C NMR spectrometry as well as by MS-spectrometry (*via* EI-MS or ESI-MS). NMR spectra were measured on Bruker AM 500 MHz, Bruker AM 600 MHz, Varian 600 MHz, Varian 400 MHz or Varian 200 MHz instruments with TMS as internal standard. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm), $CDCl_3$ (δ 7.26 ppm) or C_6D_6 (δ 7.16 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm) or C_6D_6 (δ 128.06 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constant (Hz), and integration. All melting points for crystalline products were measured with automated melting point apparatus EZ-MELT and were given without correction. A Shimadzu UV-3600i Plus spectrophotometer and an Edinburgh Instruments Spectrofluorometer FS5 equipped with Hamamatsu R13456 PMT were used to acquire the absorption and emission spectra. Spectrophotometric grade solvents were used without further purification.

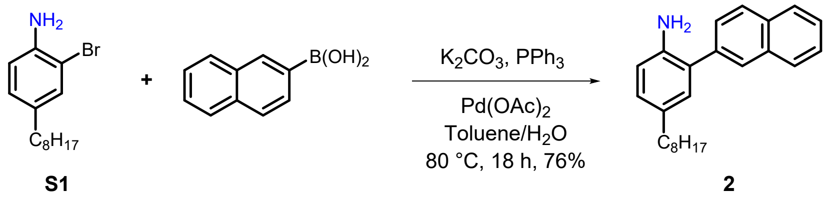
Linear optical measurements

All photophysical studies have been performed with freshly-prepared, air equilibrated solutions at room temperature (298 K). Steady-state fluorescence measurements were performed with dilute solutions (10^{-6} M, optical density < 0.1) contained in standard 1 cm quartz cuvettes at room temperature. Compounds were dissolved in dichloromethane (CH_2Cl_2) unless otherwise noted. Emission spectra were obtained under excitation at λ=430 nm, for compound **5** and **6**, and λ=460 nm for compounds **7** and **8**. Fluorescence quantum yields were measured by using coumarin 153 in ethanol (0.55) as a standard.

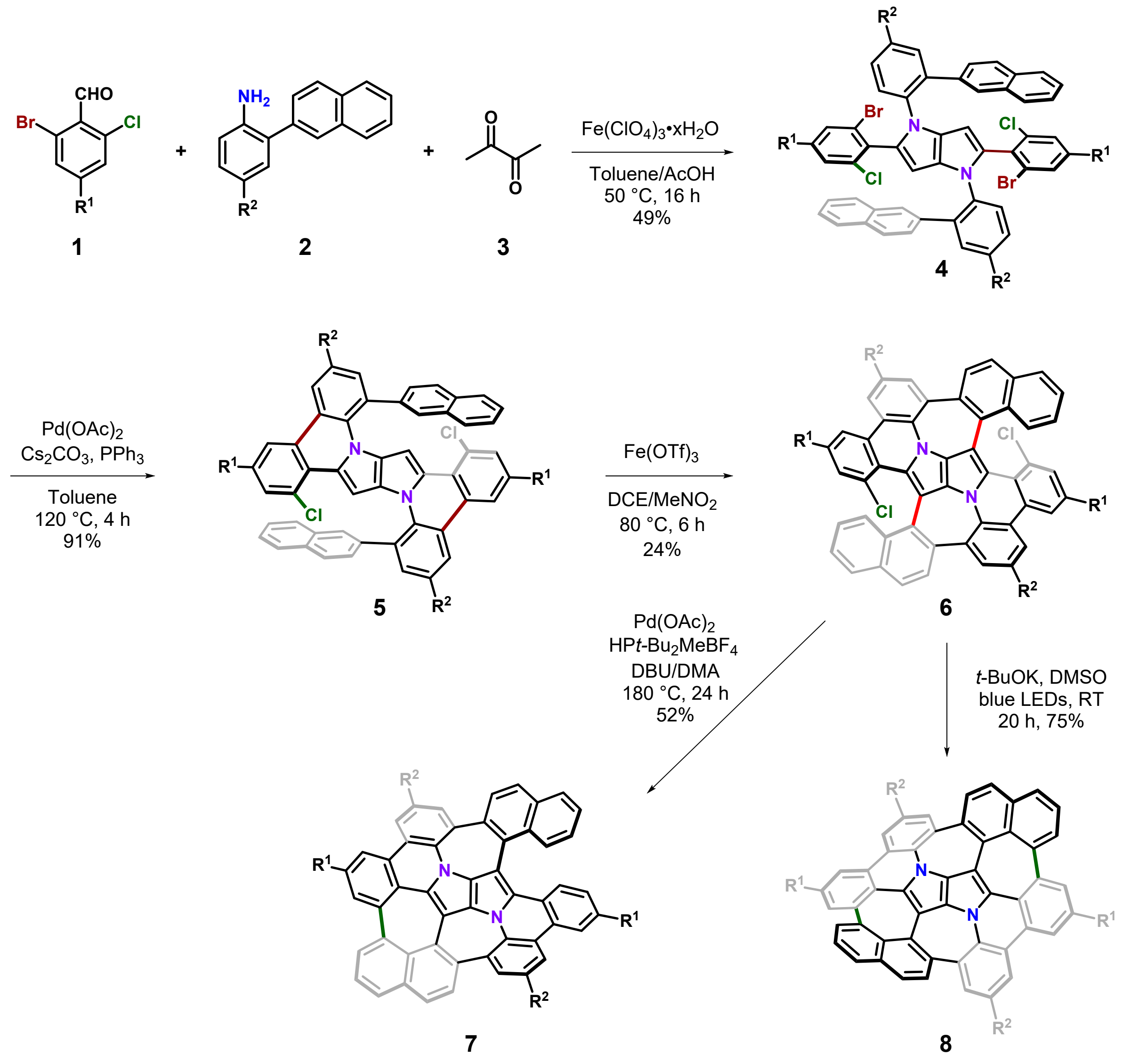
2. Experimental section



Scheme S1. Preparation of amine **S1**.

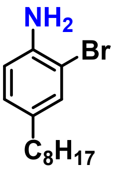


Scheme S2. Preparation of amine precursor **2**.



Scheme S3. Synthetic pathway towards the *N*-doped molecular saddle **8**. R^1 = *tert*-butyl; R^2 = n-C_8H_{17}.

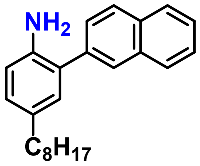
General procedure for the synthesis of 2-bromo-4-octylaniline (S1):



S1

N-Bromosuccinimide (9.34 g, 52.5 mmol) was dissolved in DMF (150 mL) and slowly added *via* a pressure equalizing dropping funnel into the 1L round-bottomed flask immersed in an ice-bath, containing a pre-cooled (0–5 °C) DMF solution (250 mL) of 4-*n*-octylaniline (10.27 g, 50.0 mmol). After addition was completed, the ice-bath was removed and the mixture was let to warm to RT and was stirred in the dark for 16 hours. Then, DMF was removed under reduced pressure. The residue was treated with diethyl ether (200 mL) and precipitated succinimide was filtered off. The filtrate was evaporated and purified by a column chromatography on silica gel (hexane/AcOEt, 95:5) affording **S1** (13.76 g, 96%) as a pale brown oil. R_f= 0.54 (SiO_2, hexane/CH_2Cl_2, 1:1). **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.24 (d, *J* = 1.7 Hz, 1H), 6.92 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.07 (bs, 2H), 2.51 – 2.44 (m, 2H), 1.59 – 1.49 (m, 2H), 1.34 – 1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 141.5, 134.9, 132.3, 128.5, 116.1, 109.7, 34.9, 32.0, 31.7, 29.6, 29.4, 29.3, 22.8, 14.2. **HRMS (ESI-TOF)** calcd for $C_{14}H_{23}BrN^+$: 284.1008 $[M+H]^+$, found: 284.1016.

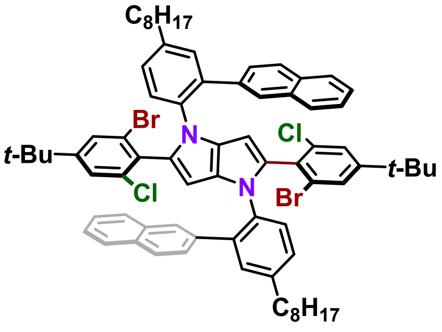
General procedure for the synthesis of 2-(naphthalen-2-yl)-4-octylaniline (2):



2

2-bromo-4-octylaniline (**S1**) (3.13 g, 11 mmol), 2-naphthylboronic acid (2.27 g, 13.2 mmol), K_2CO_3 (3.04 g, 22 mmol), PPh_3 (0.58 g, 2.2 mol) and $Pd(OAc)_2$ (0.25 g, 1.1 mol) were placed in a 100 mL Schlenk flask, which was flushed with argon prior to use. Then 50 mL of 1:1 v/v mixture of toluene and water was added, and the resulting mixture was stirred at 80 °C for 18 h. After cooling two layers were separated, water layer was extracted with ethyl acetate (3 × 20 mL). Organic layers were combined, solvents were evaporated and the crude product was purified by a column chromatography on silica gel (hexane/CH_2Cl_2, 1:1 to 2:3) affording **2** (2.76 g, 76%) as a brownish oil. R_f= 0.46 (SiO_2, hexane/CH_2Cl_2, 1:1). **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 7.93 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.08 (d, *J* = 1.9 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 4.43 (bs, 2H), 2.62 – 2.54 (m, 2H), 1.66 – 1.59 (m, 2H), 1.40 –1.24 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 137.0, 133.7, 132.6, 130.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 126.4, 126.1, 116.8, 35.3, 32.1, 31.9, 29.7, 29.53, 29.45, 22.8, 14.3. **HRMS (EI)** calcd for $C_{24}H_{29}N^{+\bullet}$: 331.2295 $[M]^{+\bullet}$, found: 331.2292.

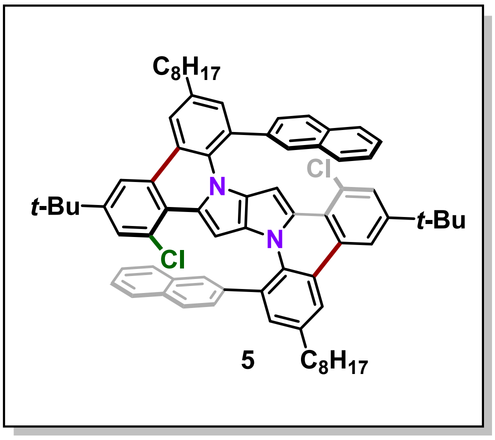
General procedure for the synthesis of 2,5-bis(2-bromo-4-(tert-butyl)-6-chlorophenyl)-1,4-bis(2-(naphthalen-2-yl)-4-octylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (4):



4

Glacial acetic acid (8 mL), toluene (8 mL), aldehyde (**1**) (2.21 g, 8.0 mmol), and aniline (**2**) (2.65 g, 8.0 mmol) were placed in a 25 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 50 °C for 30 minutes. After that time, $Fe(ClO_4)_3 \cdot x\ H_2O$ (85 mg, 0.24 mmol) was added, followed by diacetyl (**3**) (350 μL, 4 mmol). The resulting mixture was stirred at 50 °C in an open flask under air for 16 hours. Since no precipitate was formed, solvents were evaporated and crude product was purified by a column chromatography (hexane/CH_2Cl_2, 3:1). Collected product was triturated with methanol, filtered and dried affording **4** (2.42 g, 49%) as a white solid. M.p. = 228–230 °C. R_f= 0.54 (SiO_2, hexane/CH_2Cl_2, 6:1). **^{1}H NMR (600 MHz, CD_2Cl_2)** Complex mixture of atropisomers *δ* 7.80 – 7.02 (m, 74H), 6.99 (d, *J* = 1.9 Hz, 1H), 6.89 (d, *J* = 1.9 Hz, 1H), 5.96 (s, 1H), 5.87 (s, 0.7H), 5.76 (s, 1H), 5.68 (s, 0.6H), 5.67 (s, 1H), 5.58 (s, 1H), 5.55 (s, 0.6H), 2.64 (t, J = 7.4 Hz, 12H), 1.67 – 1.61 (m, 12H), 1.38 – 1.22 (m, 110H), 0.90 – 0.84 (m, 18H). **^{13}C NMR (151 MHz, CD_2Cl_2)** *δ* 154.30, 154.26, 154.17, 153.98, 153.96, 153.8, 142.42, 142.37, 142.35, 142.32, 142.21, 142.19, 138.1, 138.02, 137.98, 137.88, 137.86, 137.84, 137.78, 137.55, 137.51, 137.45, 137.38, 137.34, 137.26, 137.18, 137.08, 136.94, 136.89, 136.85, 136.53, 135.06, 134.99, 134.94, 134.92, 134.87, 134.81, 134.25, 134.18, 134.16, 134.11, 134.07, 134.00, 133.22, 133.21, 133.16, 133.10, 133.08, 133.05, 132.36, 132.26, 132.25, 132.16, 132.10, 132.05, 132.04, 132.00, 131.60, 131.55, 131.54, 131.45, 131.42, 131.29, 131.17, 131.12, 131.09, 130.99, 130.90, 130.81, 130.58, 130.55, 130.53, 130.51, 130.48, 130.27, 130.22, 130.20, 130.18, 129.52, 129.39, 129.32, 129.13, 129.10, 129.03, 129.00, 128.91, 128.81, 128.71, 128.67, 128.60, 128.58, 128.55, 128.54, 128.52, 128.49, 128.46, 128.43, 128.35, 128.21, 128.16, 128.15, 128.02, 127.95, 127.93, 127.92, 127.91, 127.89, 127.84, 127.81, 127.79, 127.76, 127.75, 127.66, 127.61, 127.58, 127.52, 127.48, 127.45, 127.40, 126.1, 126.04, 126.01, 125.96, 125.93, 125.91, 125.87, 125.81, 125.7, 125.6, 97.8, 97.67, 97.5, 35.83, 35.80, 35.06, 35.05, 35.04, 32.3, 31.7, 31.08, 31.07, 31.06, 31.04, 29.9, 29.69, 29.65, 23.1, 14.3. **HRMS (ESI-TOF)** calcd for $C_{74}H_{78}Br_2Cl_2N_2Na^+$: 1245.3801 [M+Na]$^+$, found: 1245.3818.

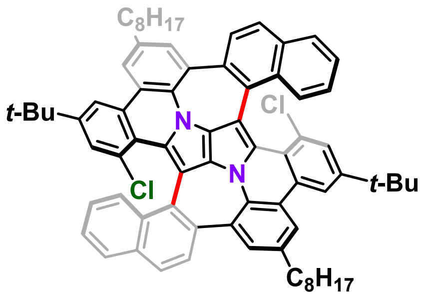
General procedure for the synthesis of (5):



5

A 20 mL pressure tube was equipped with a magnetic stir bar and was connected to an argon/vacuum line and the reaction setup was dried under vacuum (0.80 mmHg) by heating with a heat gun and allowed to cool to room temperature. Next, the reaction set-up was backfilled with argon and the tube was charged with **4** (613.1 mg, 0.5 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), Cs_2CO_3 (391.0 mg, 1.2 mmol) and PPh_3 (63.0 mg, 0.24 mmol) were added. Then 10 mL of dry toluene was added and the pressure tube was sealed. Reaction was conducted at 120 °C for 4 hours. Then, after cooling, 10 mL of water was added and resulting mixture was stirred for another 15 min. Reaction mixture was transferred to the separatory funnel, organic layer was separated, water layer was extracted with ethyl acetate (3 × 10 mL). Organic layers were combined and then filtered through celite. Solvents were then evaporated to give a glassy oil. The product was crushed out with cld methanol, and then pseudo-recrystallized from boiling methanol. Obtained yellow crystals were filtered and dried affording **5** (485 mg, 91%). M.p. = 176–178 °C. R_f= 0.55 (SiO_2, hexane/CH_2Cl_2, 6:1). **^{1}H NMR (500 MHz, C_6D_6)** *δ* 8.42 – 8.32 (m, 2H), 8.15 (s, 2H), 8.10 (s, 2H), 8.05 – 7.85 (m, 4H), 7.78 – 7.64 (m, 4H), 7.58 (s, 2H), 7.52 – 7.44 (m, 2H), 7.46 (s, 2H), 7.34 – 7.24 (m, 4H), 2.72 (t, *J* = 7.7 Hz, 4H), 1.79 – 1.67 (m, 4H), 1.43 – 1.36 (m, 4H), 1.36 – 1.22 (m, 16H), 1.19 – 1.14 (m, 16H), 0.90 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR (126 MHz, C_6D_6)** *δ* 148.1, 137.8, 133.4, 131.1, 130.5, 129.2, 128.6, 128.3, 128.2, 128.0, 126.6, 126.3, 124.6, 124.0, 122.3, 117.9, 36.2, 34.7, 32.3, 32.2, 31.1, 29.95, 29.90, 29.8, 23.1, 14.4. **HRMS (ESI-TOF)** calcd for $C_{74}H_{76}Cl_2N_2^+$: 1062.5380 [M]$^+$, found: 1062.5385.

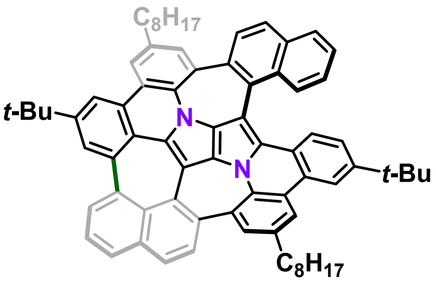
General procedure for the synthesis of (6):



6

A 50 mL round-bottom flask was equipped with a magnetic stir bar and was connected to an argon/vacuum line and the reaction set-up was dried under vacuum (0.80 mmHg) by heating with a heat gun and allowed to cool to room temperature. Next, the reaction set-up was backfilled with argon and the flask was charged with **5** (212.9 mg, 0.2 mmol) and equipped with septum. Then 24 mL of dry 1,2-dichloroethane (DCE) was poured *via* a syringe through a septum. Then, 90% iron(III) triflate (670.0 mg, 0.6 mmol) dissolved in 10 mL of dry nitromethane were added *via* a syringe through a septum. Reaction was conducted at 80 °C for 6 hours. Then 15 mL of water was added, and resulting mixture was stirred for another 15 min. Reaction mixture was transferred to the separatory funnel, organic layer was separated, water layer was extracted with CH_2Cl_2 (3 × 30 mL). Organic layers were combined. Solvents were evaporated and the crude product was purified by a column chromatography (hexane/CH_2Cl_2, 5:1). Collected product was treated with hot methanol, filtered and dried affording **6** (51 mg, 24%) as a yellow solid. Reaction was repeated to collect 102 mg of **6** in total. M.p. 353–355 °C. R_f= 0.58 (SiO_2, hexane/CH_2Cl_2, 6:1). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.06 (s, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.88 (s, 2H), 7.80 (s, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.25 (s, 2H), 7.22 – 7.18 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 2H), 2.71 – 2.57 (m, 4H), 1.68 – 1.60 (m, 4H), 1.43 – 1.25 (m, 20H), 1.22 (s, 18H), 0.92 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR (150 MHz, C_6D_6)** δ 151.0, 140.4, 138.5, 138.0, 135.4, 134.74, 134.70, 133.5, 133.1, 132.86, 132.82, 131.5, 130.8, 129.1, 128.5, 128.4, 128.2, 128.0, 127.8, 127.4, 126.7, 126.6, 125.5, 123.7, 121.9, 118.8, 113.3, 36.2, 35.0, 32.3, 32.1, 31.1, 29.94, 29.92, 29.8, 23.1, 14.4. **HRMS (ESI-TOF)** calcd for $C_{74}H_{72}Cl_2N_2^+$: 1058.5067 [M]$^+$, found: 1058.5067.

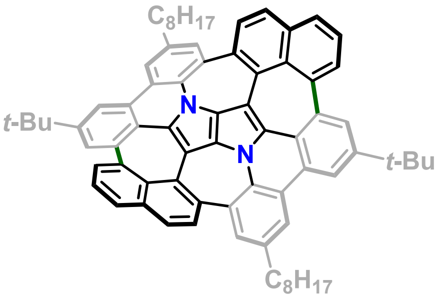
General procedure for the synthesis of (7):



7

A 20 mL pressure tube was equipped with a magnetic stir bar and was connected to an argon/vacuum line and the reaction set-up was dried under vacuum (0.80 mmHg) by heating with a heat gun and allowed to cool to room temperature. Next, the reaction set-up was backfilled with argon and the tube was charged with **6** (31.8 mg, 0.03 mmol), $Pd(OAc)_2$ (13.5 mg, 0.06 mmol), and [HP*t*-Bu_2Me][BF_4] (44.6 mg, 0.18 mmol). Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.72 mL) and *N*,*N*-dimethylacetamide (DMA, 3.0 mL) were added *via* a syringe, the tube was sealed and the solution was heated for 24 h at 180 °C. The color of the solution changed from yellow to red as the reaction progressed. The reddish crude solution was cooled to RT and toluene (6 mL) was poured into the tube. Then, a mixture was transfer to the separatory funnel and the organic layer was washed with degassed H_2O (3 × 6 mL). Organic layer was evaporated and the crude product was purified by a column chromatography (hexane/CH_2Cl_2, 5:1) affording **7** (15.4 mg, 52%) as a red solid. M.p. 179–181 °C. R_f= 0.45 (SiO_2, hexane/CH_2Cl_2, 6:1). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.60 (d, *J* = 8.9 Hz, 1H), 8.38 (d, *J* = 1.3 Hz, 1H), 8.23 (d, *J* = 0.8 Hz, 1H), 8.13 (s, 1H), 8.02 (d, *J* = 0.9 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.63 – 7.60 (m, 2H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 1.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.83 (dd, *J* = 8.7, 1.7 Hz, 1H), 2.70 – 2.55 (m, 4H), 1.72 – 1.61 (m, 4H), 1.39 – 1.35 (m, 4H), 1.34 (s, 9H), 1.30 – 1.23 (m, 16H), 1.22 (s, 9H), 0.88 – 0.84 (m, 6H). **^{13}C NMR (126 MHz, C_6D_6)** *δ* 151.3, 148.7, 142.4, 141.5, 139.9, 139.7, 139.4, 138.7, 138.3, 137.9, 137.5, 135.9, 135.7, 135.3, 134.8, 134.5, 134.4, 134.3, 134.2, 133.8, 133.2, 132.41, 132.38, 132.2, 131.4, 131.0, 130.9, 130.6, 129.9, 129.8, 128.8, 128.3, 128.0, 127.6, 127.2, 126.9, 126.8, 126.6, 126.54, 126.52, 126.3, 126.1, 125.2, 124.2, 123.4, 123.0, 122.2, 119.1, 118.9, 114.6, 104.0, 36.3, 36.2, 35.2, 34.9, 32.3, 32.20, 32.18, 31.4, 31.3, 29.92, 29.91, 29.8, 29.74, 29.72, 23.1, 14.3. **HRMS (ESI-TOF)** calcd for $C_{74}H_{73}N_2^+$: 989.5768 [M+H]$^+$, found: 989.5779.

General procedure for the synthesis of (8):



8

A 20 mL glass vial was equipped with a magnetic stir bar and was connected to an argon/vacuum line and the reaction set-up was dried under vacuum (0.80 mmHg) by heating with a heat gun and allowed to cool to room temperature. Next, the reaction set-up was backfilled with argon and the vial was charged with **6** (15.9 mg, 0.015 mmol) and *t*-BuOK (16.8 mg, 0.15 mmol). Then dry dimethylsulfoxide (DMSO, 8.0 mL) was added *via* a syringe, the vial was sealed and placed in a homemade photoreactor comprised of a 400 mL beaker with the inside covered with LED tape. A cooling fan with adjustable spin rate was used to maintain ambient temperature inside the photoreactor. The solution was irradiated with blue LED light (9 W, λ = 460 nm) for 20 h. The color of the solution changed from yellow to red as the reaction progressed. To the reddish crude solution, degassed H_2O (10 mL) was poured and transferred to separatory funnel. Then the water layer was extracted with CH_2Cl_2 (3 × 10 mL). Organic layer was evaporated and the crude product was dissolved in 5 mL of ethyl acetate, and filtered through a 0.45 mm filter syringe. Solvent was evaporated leaving minimal amount ~1 mL of ethyl acetate. Then 10 mL of iso-propanol was added inducing crystallization. Formed crystals were filtered and dried affording **8** (11.1 mg, 75%) as a red solid. M.p. 159–161 °C. R_f= 0.39 (SiO_2, hexane/CH_2Cl_2, 6:1, tailing, decomposition). **^{1}H NMR (500 MHz, C_6D_6)** *δ* 8.15 (s, 2H), 7.83 (s, 2H), 7.46 (s, 2H), 7.38 (d, *J* = 7.6 Hz, 4H), 7.18 (m, 2H, overlapped), 7.15 – 7.14 (m, 4H, overlapped), 7.05 (d, *J* = 8.5 Hz, 2H), 7.03 (s, 2H), 2.61 – 2.51 (m, 4H), 1.69 – 1.61 (m, 4H), 1.37 (s, 18H), 1.32 – 1.22 (m, 20H), 0.86 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, C_6D_6)** *δ* 150.1, 139.1, 138.8, 137.6, 136.9, 136.1, 135.4, 135.1, 134.8, 134.3, 133.6, 133.9, 132.1, 130.9, 130.1, 129.1, 128.7, 126.5, 125.9, 123.0, 122.0, 118.8, 111.8, 36.3, 35.1, 32.3, 32.2, 31.6, 29.9, 29.80, 29.78, 23.1, 14.3. **HRMS (APCI)** calcd for $C_{74}H_{71}N_2^+$: 987.5612 [M+H]$^+$, found: 987.5606.

3. X-Ray crystallography analysis

Experimental

Specimens suitable for the single crystal X-ray experiment were grown at room temperature from the acetone-methanol-tetrahydrofuran mixture with an approximate molar ratio yielding 1:2:10 during a slow evaporation process. Crystallization took roughly one week. As a result, relatively long (up to 5mm) and very thin (less than 0.05 mm), needle-shaped, yellow crystals grew.

The X-ray measurement of **6** was performed at 130.0(5) K on a Bruker D8 Venture PhotonII diffractometer equipped with a INCOATEC IµS micro-focus source (CuKα, λ = 1.54178 Å) and a mirror monochromator. A total of 5916 frames were collected with Bruker APEX3 program.[2] The frames were integrated with the Bruker SAINT software package[3] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 55710 reflections to a maximum θ angle of 59.18° (0.90 Å resolution), of which 8945 were independent (average redundancy 6.228, completeness = 99.6%, R_{int} = 6.90%, R_{sig} = 4.30%) and 7401 (82.74%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3693(8) Å, b = 16.4830(10) Å, c = 16.9960(11) Å, α = 98.522(4)°, β = 110.283(4)°, γ = 111.654(4)°, V = 3097.1(3) Å^3, are based upon the refinement of the XYZ-centroids of 9750 reflections above 20 $\sigma(I)$ with 5.844° < 2θ < 118.0°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[4] The ratio of minimum to maximum apparent transmission was 0.821. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.509 and 0.969.

The structure was solved and refined using SHELXTL Software Package[5,6] using the space group $P\bar{1}$, with Z = 2 for the formula unit, $C_{78}H_{80}Cl_2N_2O$. The final anisotropic full-matrix least-squares refinement on F^2 with 894 variables converged at $R1$ = 7.06%, for the observed data and $wR2$ = 18.59% for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was 0.530 e$^-$/Å^3 and the largest hole was -0.387 e$^-$/Å^3 with an RMS deviation of 0.050 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.214 g/cm^3 and $F(000)$, 1208 e$^-$. All the details concerning the crystal data and structural parameters of **6** are presented in Table S1.

The crystal, in the asymmetric part of the unit cell, contains two halves of centrosymmetric molecules of **6** denoted as A and B and disordered over two positions tetrahydrofuran (THF) moiety. The refined occupancy ratio of the THF molecule yields 0.684(7):0.316(7). Both intermediate product **6** molecules are disordered in their peripheral parts. In the molecule A the *tert*-butyl moiety is disordered over two sites with refined occupancy ratio yielding 0.897(7):0.103(7). In addition, whole the *n*-octyl chain is disordered over three alternative positions with refined occupancies equal to 0.645(3), 0.204(3) and 0.151(3) for the A, C and E variants respectively. In the molecule B the terminal 5-segment fragment of the *n*-octyl chain is disordered over four sites where the refined contributions yields 0.240(3), 0.326(3), 0.166(3) and 0.268(3) for B, D, F and H orientations respectively. Both the disorder and the relatively small size of the crystal result in limited scattering power up to 0.90 resolution, causing alert level B in the checkCIF report. To preserve reasonable bonds and angles values in the disordered fragments, a number of geometry restraints were used including restrains for atomic displacement parameters. All ordered non-hydrogen atoms and major component disordered moieties (occupancy greater than 0.5) were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. Their temperature factors were not refined and were set to be either 1.2 (C_{ar}-H, CH_2 moieties) or 1.5 (methyl groups) times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables.[7] Molecular graphics was prepared using program Mercury 4.1.[8] Thermal ellipsoids parameters are presented at 50% probability level in Figure S1 whereas packing of the molecules in the crystal lattice is given in Figure S2.

Table S1. Data collection and structure refinement for **6**.

Formula	$C_{78}H_{80}Cl_2N_2O$
M_x/ g·mol^{-1}	1132.34
T/ K	130.0(5)
λ/ Å	1.54178
Crystal size	0.024 × 0.100 × 0.598 mm
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.3693(8) Å α = 98.522(4)° b = 16.4830(10) Å β = 110.283(4)° c = 16.9960(11) Å γ = 111.654(4)°
V/ Å^3, Z	3097.1(3), 2
D_x/ g·cm^{-3}	1.214
μ/ mm^{-1}	1.304
F(000)	1208
θ_{min}, θ_{max}	2.92°, 59.18°
Index ranges (merged data)	$-14 \le h \le 14$, $-18 \le k \le 18$, $-18 \le l \le 18$
Reflections collected/ independent	55710/ 8945 R_{int} = 0.0690
Completeness	99.6%
Absorption correction	Multi-Scan
T_{max}, T_{min}	0.969, 0.509
Structure solution technique	direct methods
Refinement method	Full-matrix LSQ on F^2
Data / restraints / parameters	8945 / 218 / 894
GOF on F^2	1.082
Final R indices	7401 data; $I>2\sigma(I)$ $R1$ = 0.0706, $wR2$ = 0.1769 all data $R1$ = 0.0846, $wR2$ = 0.1859
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.530, -0.387 e·Å^{-3}

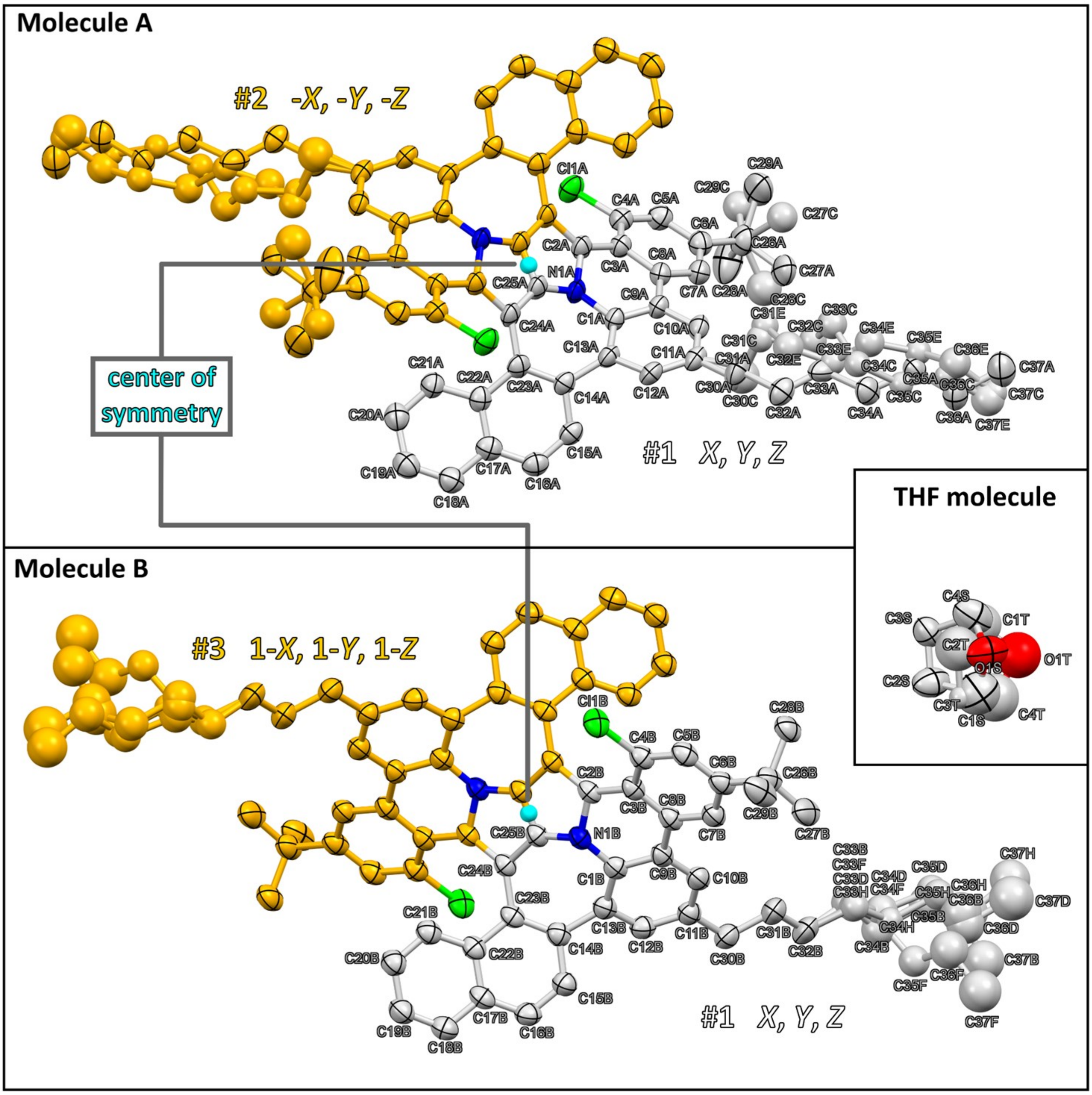


Figure S1. Thermal ellipsoid plot at 50% probability level together with numbering scheme of atoms in the structure of **6**. All separately displayed molecules in the same scale. Hydrogen atoms omitted for clarity. Numbering scheme applied for the atoms of the asymmetric unit only coloured in light grey except N, O and Cl atoms.

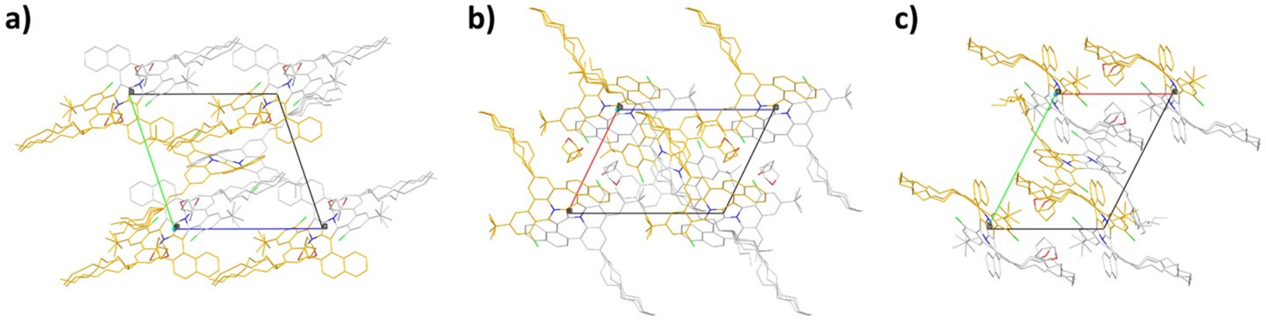


Figure S2. Packing diagram of **6**, view along [100] a), [010] b) and [001] c).

4. Photophysical properties

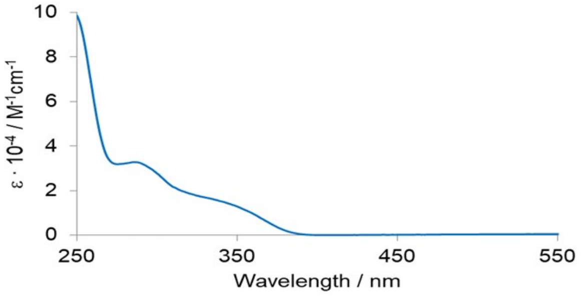


Figure S3. Absorption spectrum of **4** measured for CH_2Cl_2.

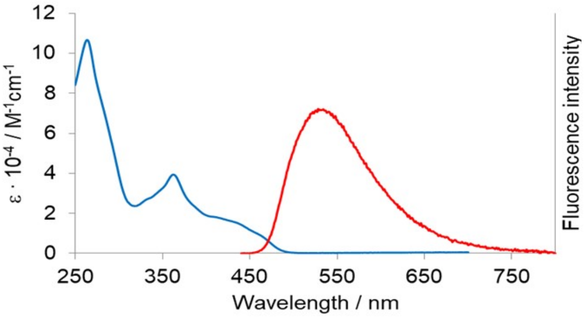


Figure S4. Absorption (blue) and emission (red) spectra of **5** measured for CH_2Cl_2.

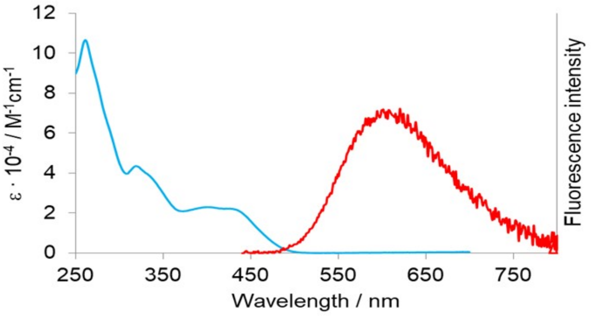


Figure S5. Absorption (blue) and emission (red) spectra of **6** measured for CH_2Cl_2.

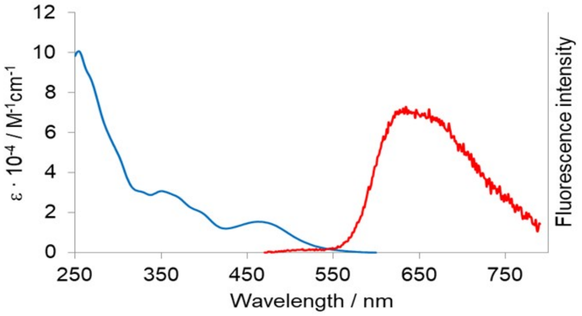


Figure S6. Absorption (blue) and emission (red) spectra of **7** measured for CH_2Cl_2.

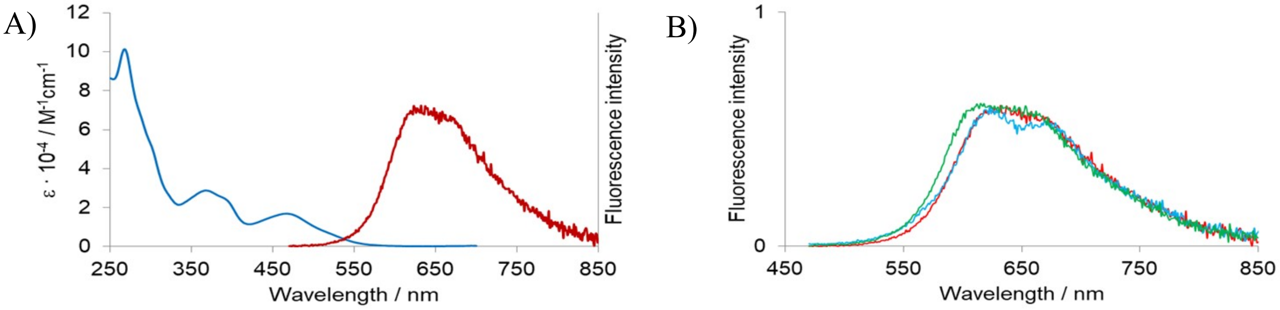


Figure S7. A) Absorption (blue) and emission (red) spectra of **8** measured for CH_2Cl_2. B) Comparison of emission spectra for solvents with various polarity: toluene (blue), tetrahydrofuran (green), CH_2Cl_2 (red).

5. Cyclic Voltammetry

The CV characteristics of compounds **4-8** are shown in Figures S8-S12 and summarized in Table S2.

Table S2. Summary of electrochemical properties of compounds **4-8**.[a]

Compound	Conc. [mmol/dm^3]	$E^{1/2}_{ox1}$ [V]	$E^{1/2}_{ox2}$ [V]	$E^{1/2}_{ox3}$ [V]	E_{ox1}^{onset} [V]	Ionic Potential [eV]
4	0.50	0.87	E_{pa}= 1.61 E_{pc}= —	—	0.79	-5.07
5	0.50	0.57	1.09	—	0.49	-4.77
6	0.50	0.70	1.06	—	0.62	-4.90
7	0.50	0.40	0.78	—	0.29	-4.57
8	0.50	0.14	0.42	0.87	0.05	-4.33

[a] Measurements conditions: electrolyte (NBu_4ClO_4, c = 0.1 M); solvent: dry, degassed dichloromethane; potential sweep rate: 100 mV/s; working electrode: GC; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl/$NaCl_{sat}$; all measurements were carried out at room temperature and under Ar atmosphere; b: calculated according to the equations: $IP(\mathrm{eV}) = -[E_{ox}^{onset} - E^{1/2}(Fc/Fc^+) + 4.8]$; $EA(\mathrm{eV}) = -[E_{red}^{onset} - E^{1/2}(Fc/Fc^+) + 4.8]$. $E^{1/2}(Fc/Fc^+)$ = 0.52 V under above-mentioned conditions.

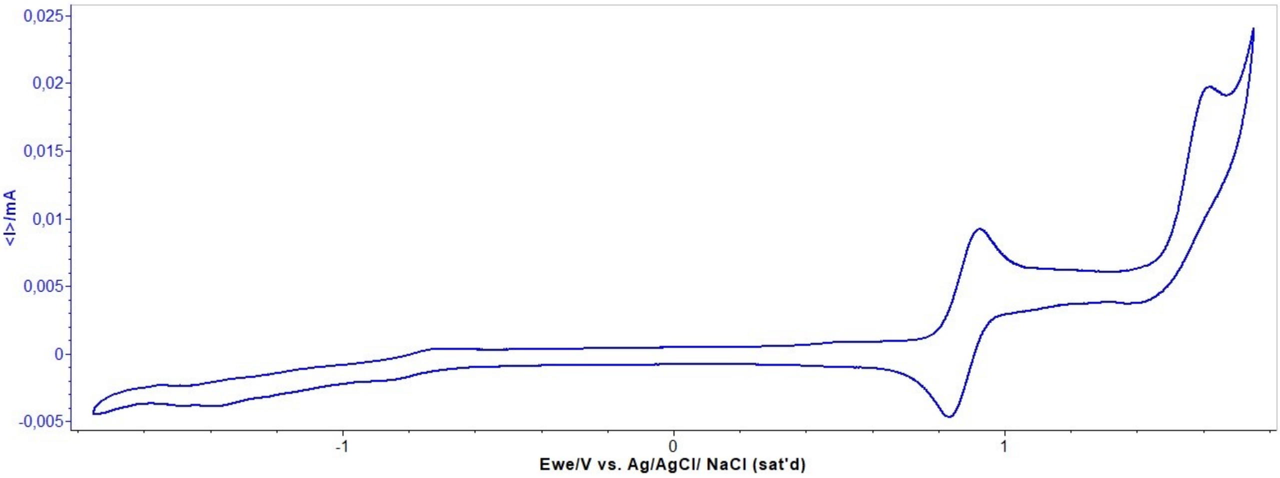


Figure S8a. Cyclic voltammograms of **4** measured for CH_2Cl_2. Potential window scanned: –1.75 to +1.75 V.

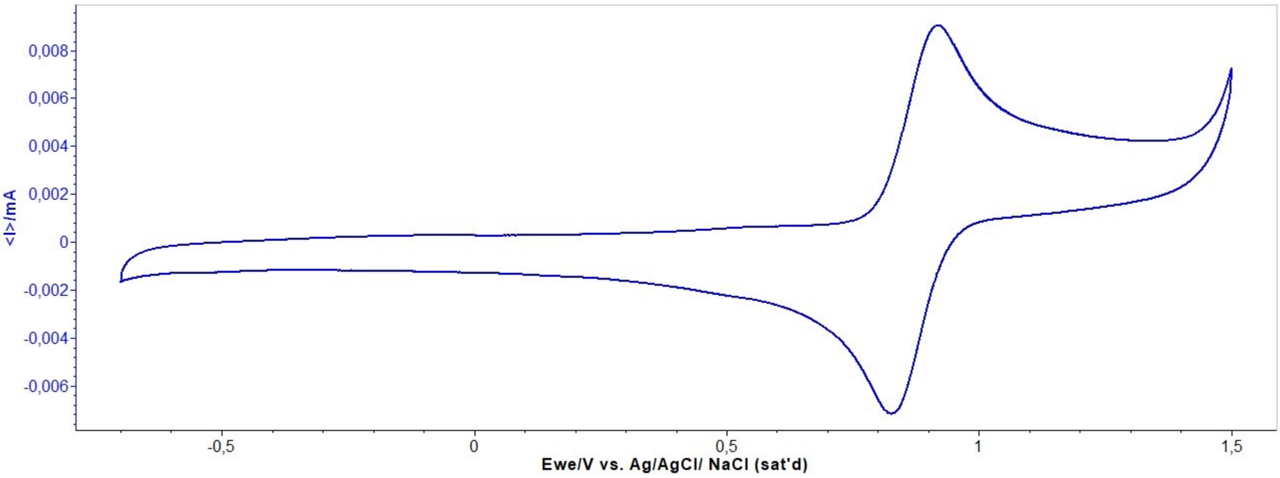


Figure S8b. Cyclic voltammograms of **4** measured for CH_2Cl_2. Potential window scanned: –0.7 to +1.5 V.

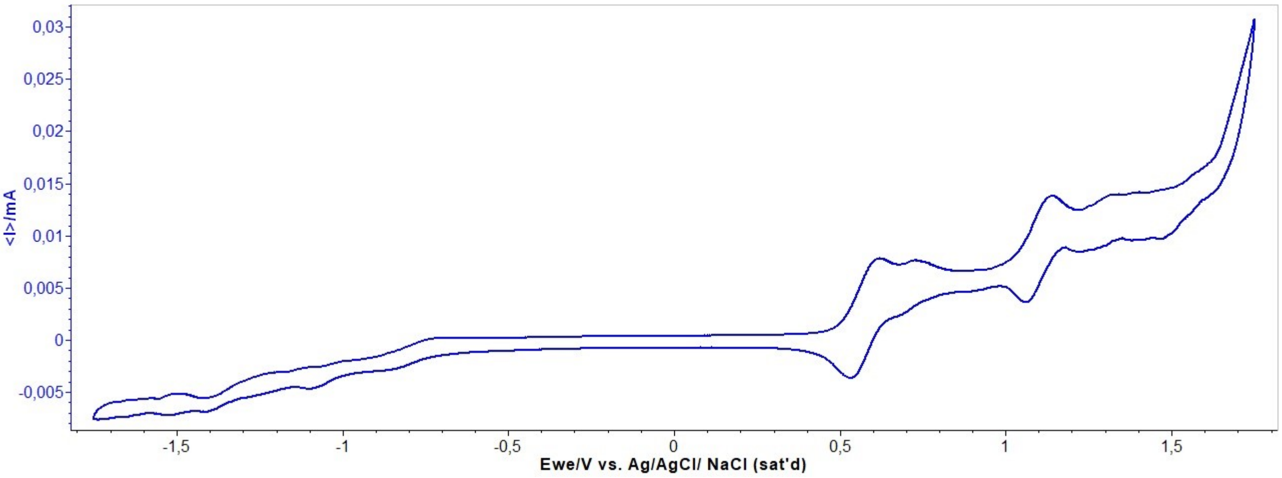


Figure S9a. Cyclic voltammograms of **5** measured for CH_2Cl_2. Potential window scanned: –1.75 to +1.75 V.

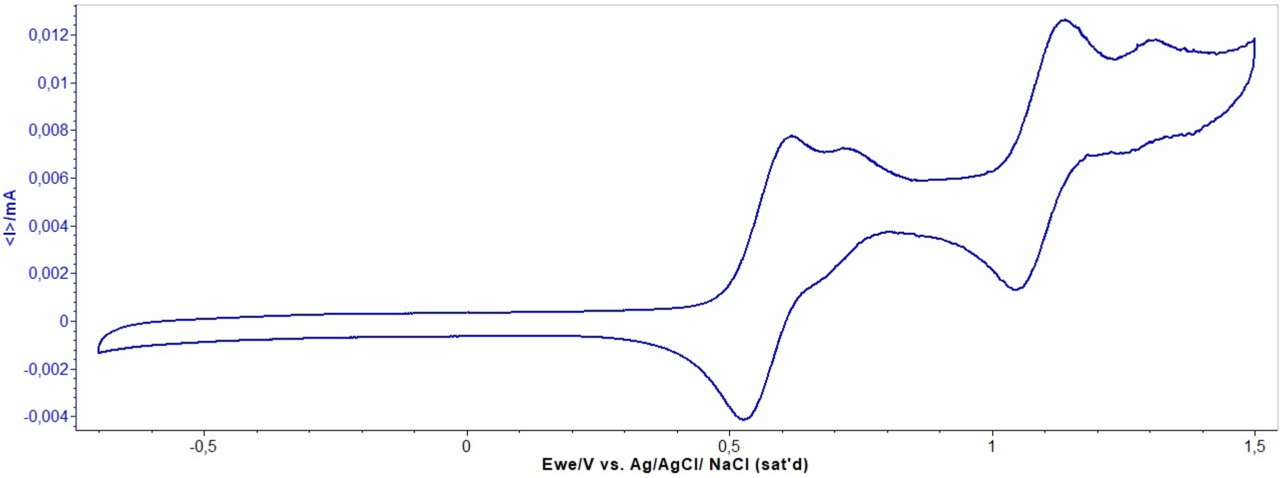


Figure S9b. Cyclic voltammograms of **5** measured for CH_2Cl_2. Potential window scanned: –0.7 to +1.5 V.

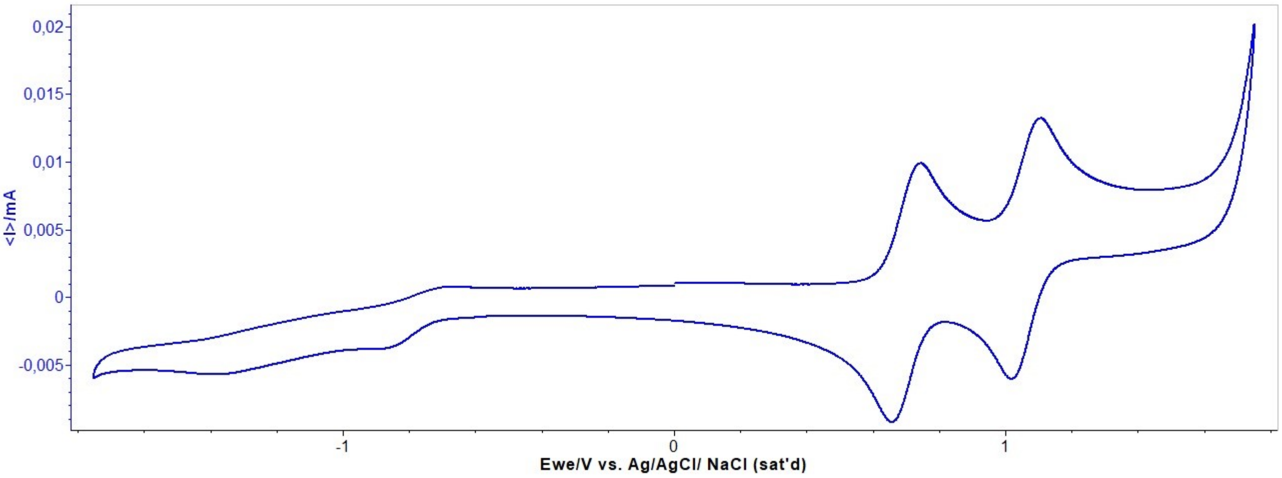


Figure S10a. Cyclic voltammograms of **6** measured for CH_2Cl_2. Potential window scanned: –1.75 to +1.75 V.

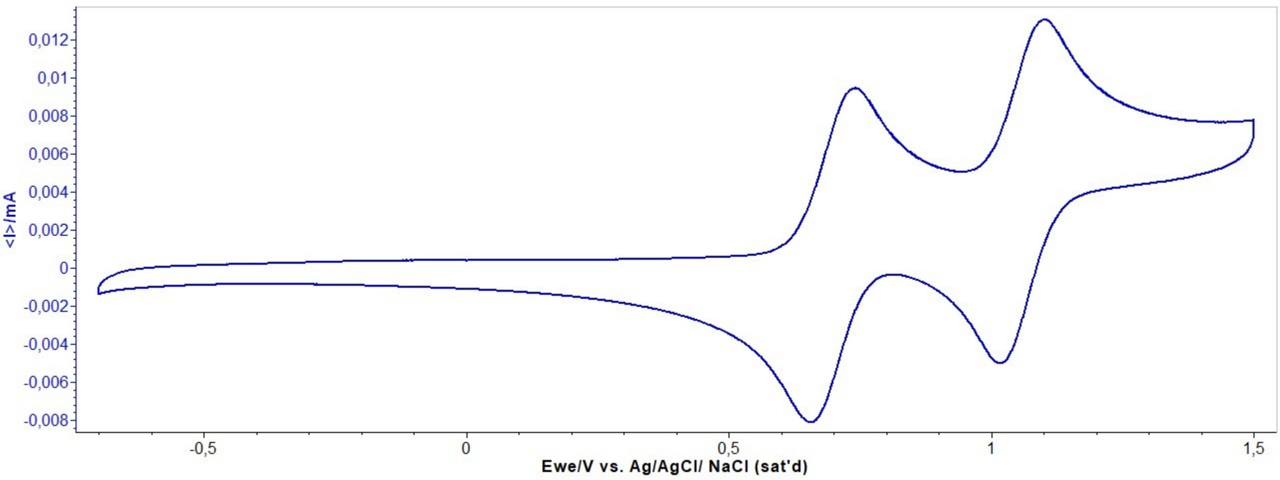


Figure S10b. Cyclic voltammograms of **6** measured for CH_2Cl_2. Potential window scanned: –0.7 to +1.5 V.

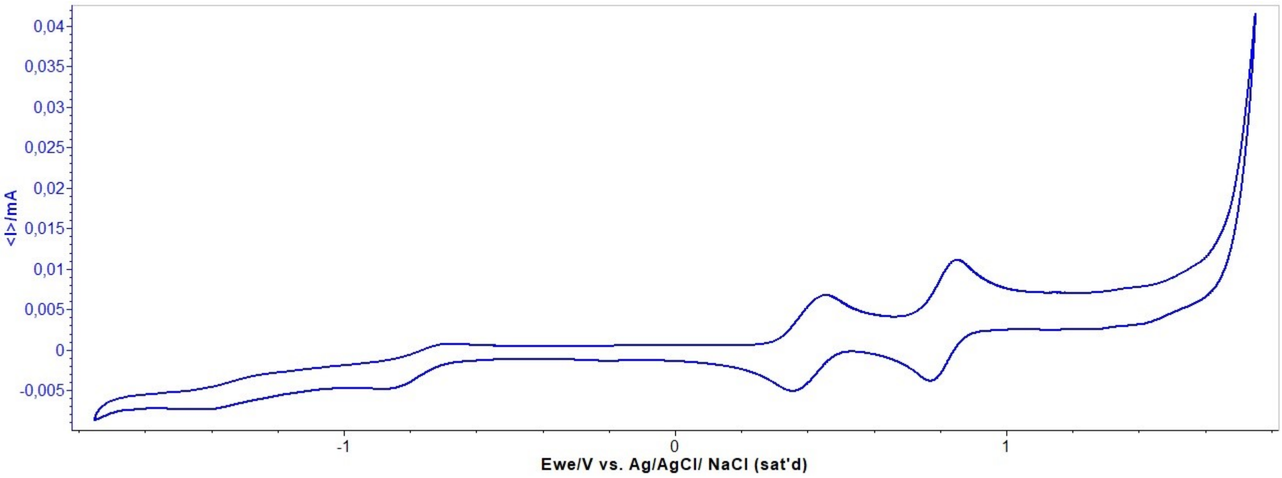


Figure S11a. Cyclic voltammograms of **7** measured for CH_2Cl_2. Potential window scanned: –1.75 to +1.75 V.

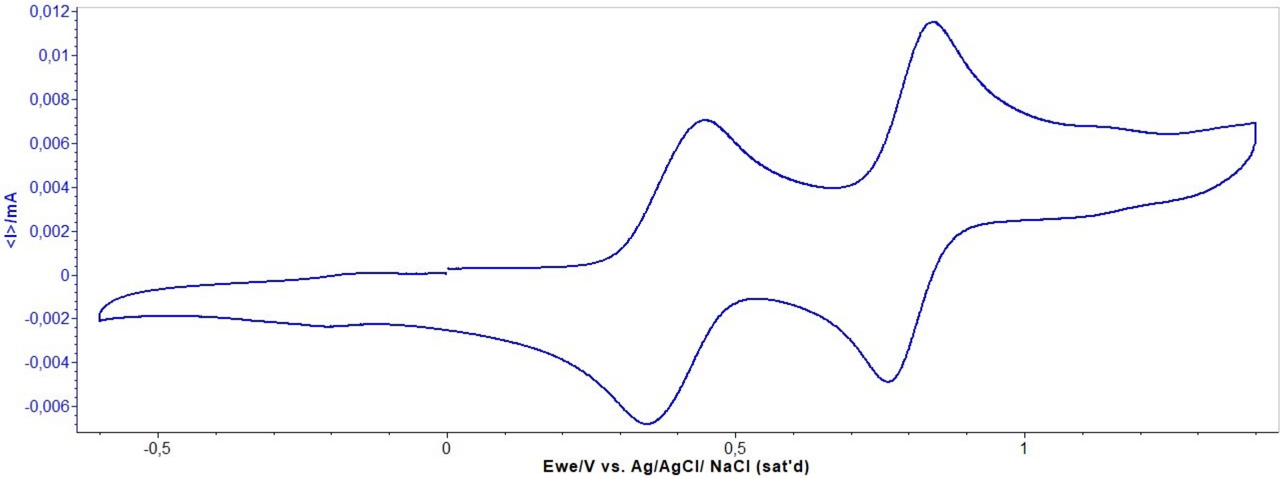


Figure S11b. Cyclic voltammograms of **7** measured for CH_2Cl_2. Potential window scanned: –0.6 to +1.4 V.

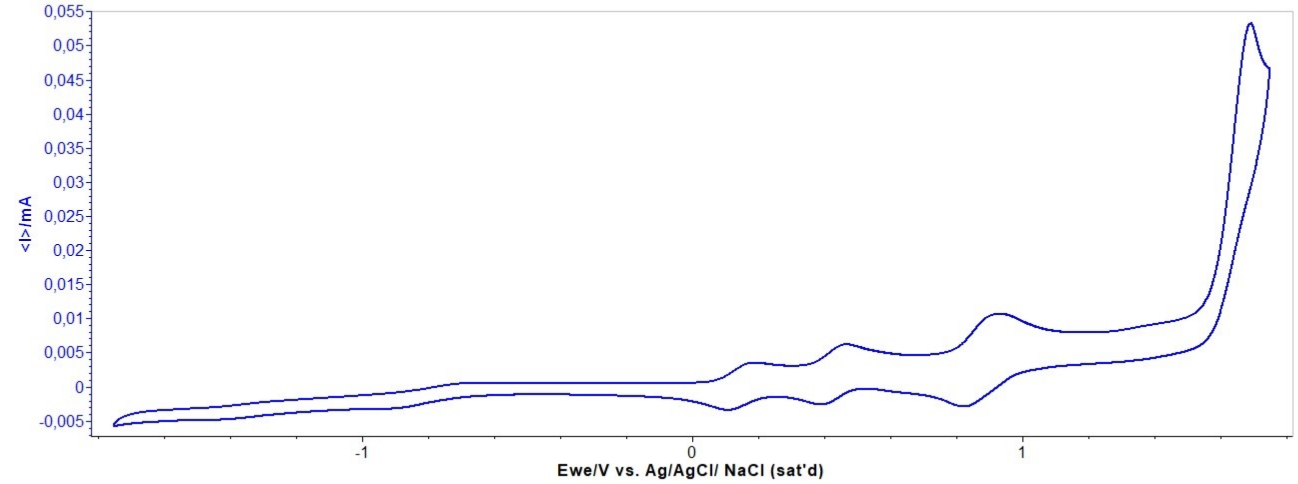


Figure S12a. Cyclic voltammograms of **8** measured for CH_2Cl_2. Potential window scanned: –1.75 to +1.75 V.

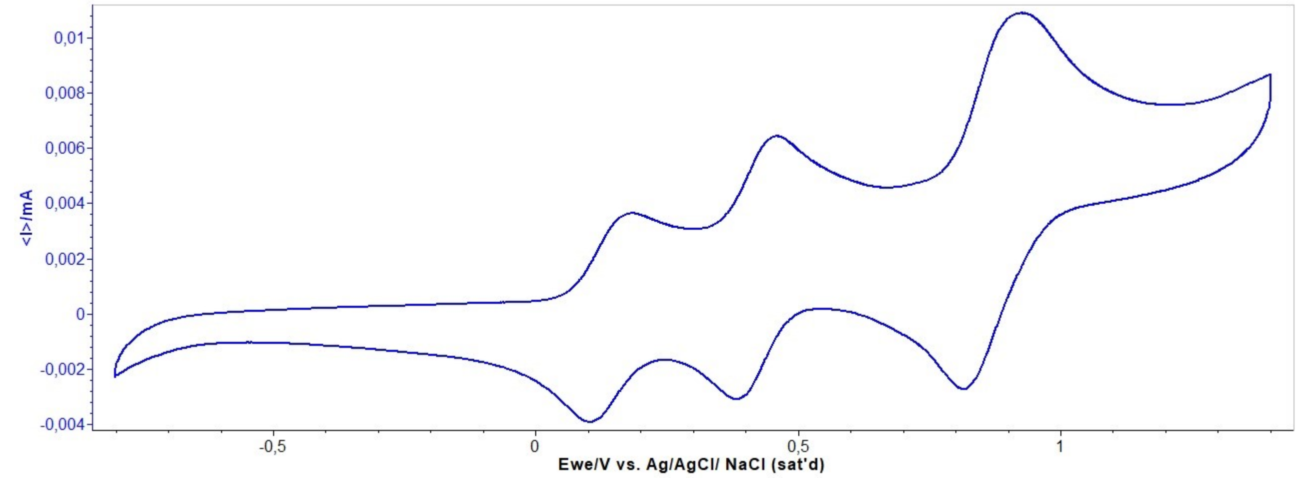


Figure S12b. Cyclic voltammograms of **8** measured for CH_2Cl_2. Potential window scanned: –0.8 to +1.4 V.

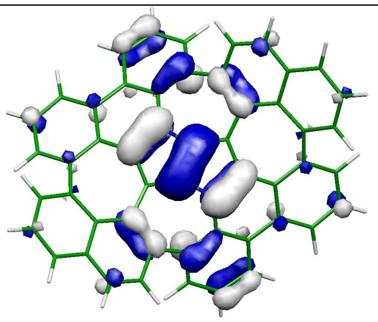
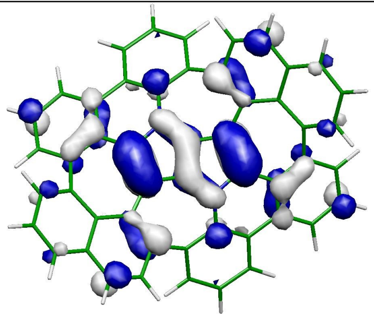
6. Computational investigation

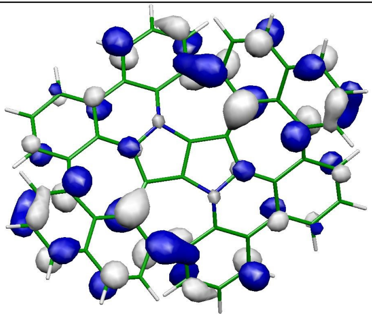
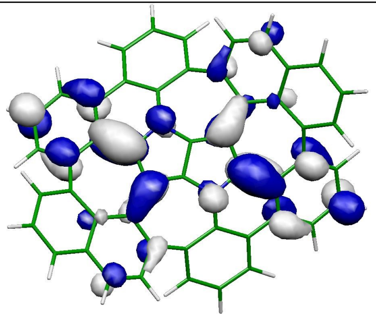
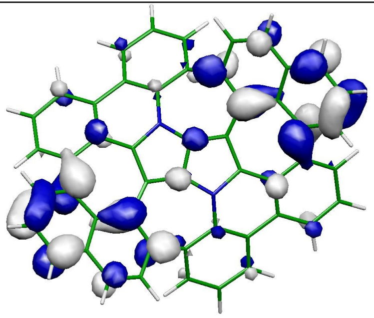
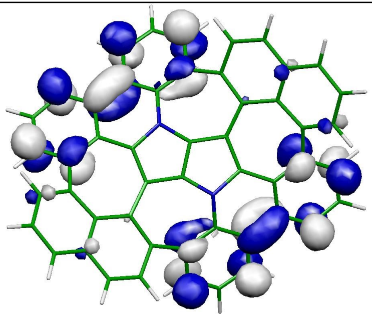
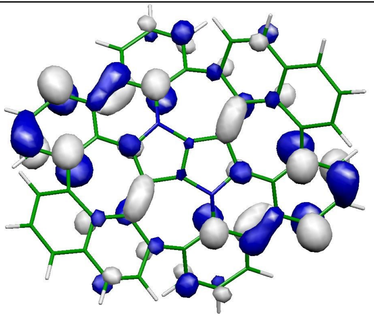
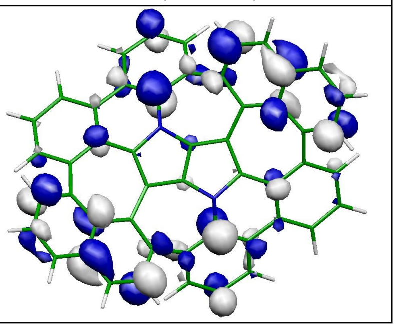
Quantum chemical calculations were performed for the aza-nanographene **8** structure with *tert*-butyls and *octyl*-chains replaced by hydrogen atoms (**8H**). The equilibrium geometries of the possible conformers of **8H** and the saddle-points between them in the closed-shell ground state (S_0) were determined with the MP2 method. Excitation energies, equilibrium geometries, and response properties of the lowest excited singlet states were calculated using the second-order algebraic diagrammatic construction ADC(2) method.[9–11] Additionally, geometry optimizations of all conformers of **8H** and the transient structures between them were performed at the DFT level of theory using B3-LYP functional[12] with Grimme dispersion (D3) correction.[13] Local minima and saddle-points were verified by computation of the Hessian at the DFT-optimized structures.

The correlation–consistent valence double zeta basis set with polarization functions on all atoms (cc-pVDZ) was used.[14] All calculations were performed with the TURBOMOLE 7.3[15] program package, making use of the resolution of the identity (RI) approximation for the evaluation of the electron-repulsion integrals.

Table S3. Vertical absorption energy (ΔE), oscillator strength (f), dipole moment (μ), leading electronic configurations and relevant Hartree-Fock orbitals (plotted with isovalue 0.03) of the lowest excited states of **8H** determined with the ADC(2)/cc-pVDZ method at the MP2/cc-pVDZ equilibrium geometry of the ground state.

State	ΔE/eV	f	μ/Debye	Electronic Configuration
S_0	0.0	-	0.82	$(85a)^2(83b)^2$
^1A	2.391	0.013	1.04	0.95(85a-86a)
^1B	2.611	0.053	0.90	0.79(85a-85b)-0.51(85a-84b)
^1B	2.727	0.251	1.92	0.78(85a-84b)+0.48(85a-85b)
^1B	2.865	0.057	2.00	0.91(85a-86b)
^1A	2.941	0.002	0.90	0.94(85a-87a)
^1B	3.301	0.293	1.26	0.64(85a-87b)+0.63(84a-84b)
^1A	3.210	0.004	1.61	0.91(84a-86a)
^1B	3.420	0.019	1.45	0.62(85a-87b)-0.62(84a-84b)

<table>
<tr><td colspan="6">HOMOs</td></tr>
<tr><td colspan="3">84a(-7.12eV)</td><td colspan="3">85a(-5.78eV)</td></tr>
<tr><td colspan="3"></td><td colspan="3"></td></tr>
<tr><td colspan="6">LUMOs</td></tr>
<tr><td colspan="2">86a(1.40eV)</td><td colspan="2">84b(1.51eV)</td><td colspan="2">85b(1.76eV)</td></tr>
</table>

		
86b(2.08eV)	87a(2.28eV)	87b(2.69eV)
		

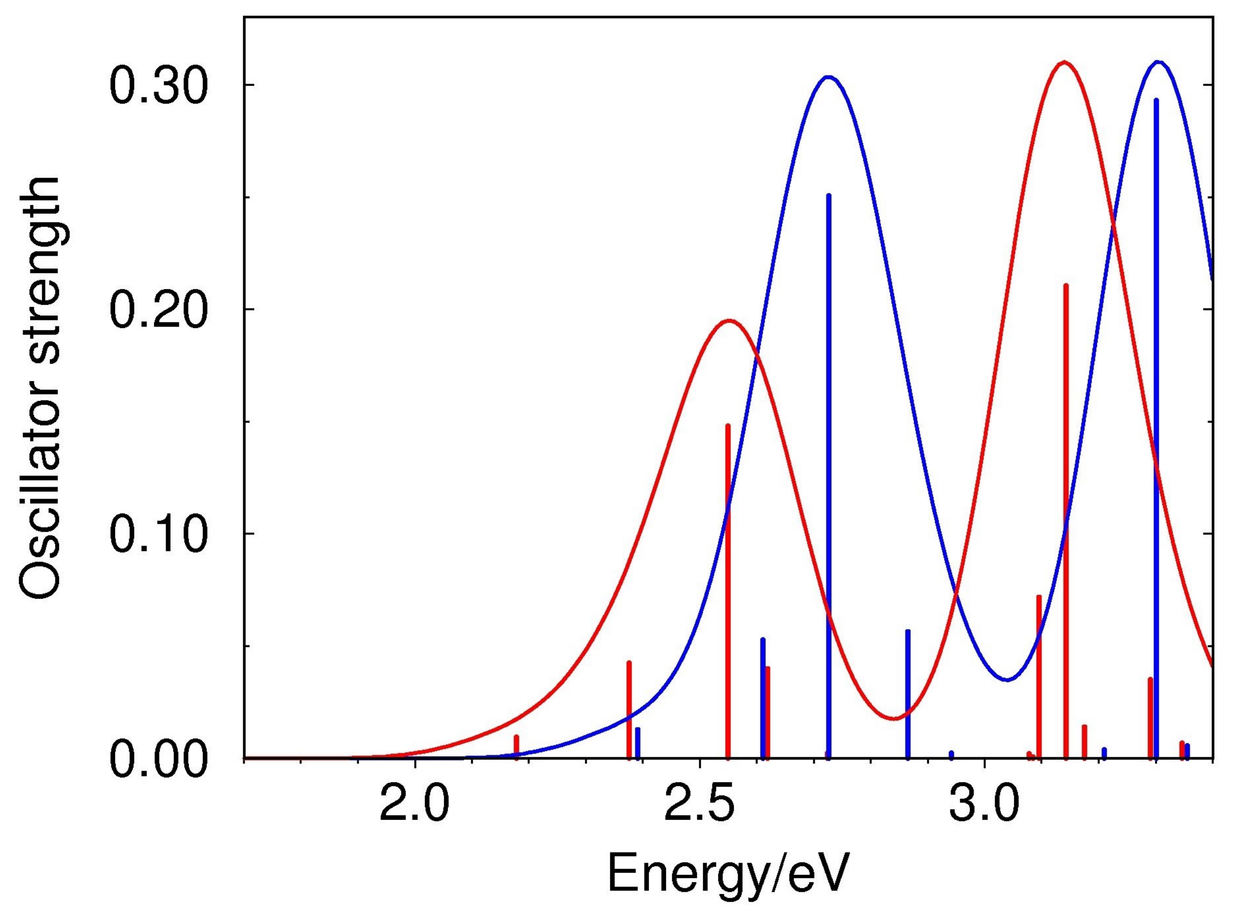


Figure S13. Simulated absorption spectra of **8H** computed with TD-DFT (red) and ADC(2) (blue) methods. The computed stick spectra were convoluted with Gaussian function of 0.25 eV FWHM.

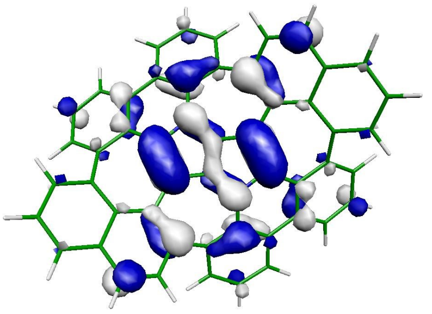
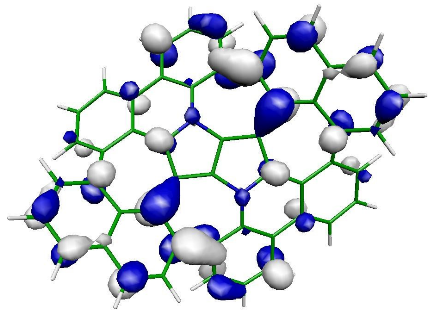
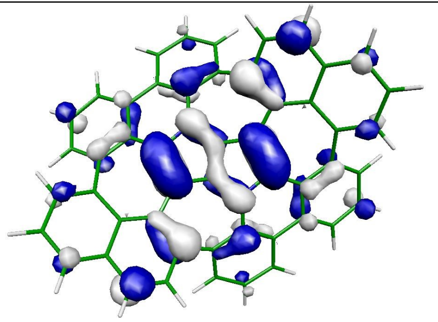
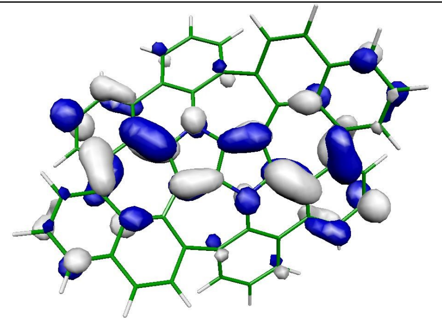
State	properties		hole	electron
^{1}A	E_{abo}	2.121		
	E_{fl}	1.926		
	f	0.010		
^{1}B	E_{abo}	2.339		
	E_{fl}	2.127		
	f	0.092		

Figure S14. Adiabatic (E_{abo}) and vertical fluorescence (E_{fl}) energies (in eV), oscillator strength (f), and natural transition orbitals (hole and electron) of the lowest excited singlet states of **8H** determined with the aid of the ADC(2)/cc-pVDZ method at their equilibrium geometry. Orbitals are plotted with isovalue 0.03.

Table S4. Cartesian geometries of **8H** (in Angstrom) optimized for racemization pathway determined with the aid of the MP2/cc-pVDZ method.

(*M*,*P*,*M*,*P*)-8H

FINAL HEAT OF FORMATION = -2022.105680

C	5.940689	2.027109	2.188113
C	4.734730	2.268334	1.473019
C	4.018727	1.185580	0.821826
C	4.656114	-0.118048	0.801666
C	5.815000	-0.304971	1.582852
C	6.450407	0.741842	2.285023
C	2.705852	1.472265	0.285589
C	2.242195	2.817812	0.185400
C	3.014235	3.855072	0.784761
C	4.199585	3.585755	1.446498
C	1.032861	3.315483	-0.567819
C	-0.318705	2.861240	-0.483621
C	-1.409567	3.569185	-1.064585
C	-1.117190	4.738925	-1.807320
C	0.202330	5.159072	-1.981916
C	1.255122	4.462212	-1.363185
N	-0.599030	1.611785	0.084177

C	-1.869827	1.004852	0.042320
C	-3.008681	1.799989	-0.277570
C	-2.788374	3.072323	-0.896747
C	-1.735697	-0.411385	0.086970
C	-0.338341	-0.610774	0.168463
C	0.338341	0.610774	0.168463
N	0.599030	-1.611785	0.084177
C	1.869827	-1.004852	0.042320
C	1.735697	0.411385	0.086970
C	3.008681	-1.799989	-0.277570
C	2.788374	-3.072323	-0.896747
C	1.409567	-3.569185	-1.064585
C	0.318705	-2.861240	-0.483621
C	-1.032861	-3.315483	-0.567819
C	-1.255122	-4.462212	-1.363185
C	-0.202330	-5.159072	-1.981916
C	1.117190	-4.738925	-1.807320
C	3.910603	-3.797415	-1.356957
C	5.195794	-3.252885	-1.259745
C	5.397912	-2.014439	-0.623869
C	4.323071	-1.286159	-0.069765
C	-3.910603	3.797415	-1.356957
C	-5.195794	3.252885	-1.259745
C	-5.397912	2.014439	-0.623869
C	-4.323071	1.286159	-0.069765
C	-2.242195	-2.817812	0.185400
C	-2.705852	-1.472265	0.285589
C	-4.018727	-1.185580	0.821826
C	-4.734730	-2.268334	1.473019
C	-4.199585	-3.585755	1.446498
C	-3.014235	-3.855072	0.784761
C	-5.940689	-2.027109	2.188113
C	-6.450407	-0.741842	2.285023
C	-5.815000	0.304971	1.582852
C	-4.656114	0.118048	0.801666
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TS1-8H

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C	-3.222700	3.723661	0.617121
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C	-4.645845	-0.312955	0.916749
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C	-6.469070	0.543534	2.365249
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H	-5.896443	-4.182958	-1.326500
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H	2.773002	-4.667852	1.362245
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H	0.653195	-6.346928	-1.850023
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H	7.077306	-2.901013	1.268869
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TS2-8H

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C	-6.025864	0.314676	0.979959
C	-4.439730	-3.571103	0.809850
C	-3.186409	-3.824966	0.289278
C	-2.338957	-2.773404	-0.168453
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(*M*,*M*,*P*,*P*)-8H

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C	1.859724	-1.050763	-0.199738
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C	5.109889	-3.788593	0.271609
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C	-1.760862	-0.366082	0.008393
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7. ^{1}H and ^{13}C NMR spectra for synthesized compounds

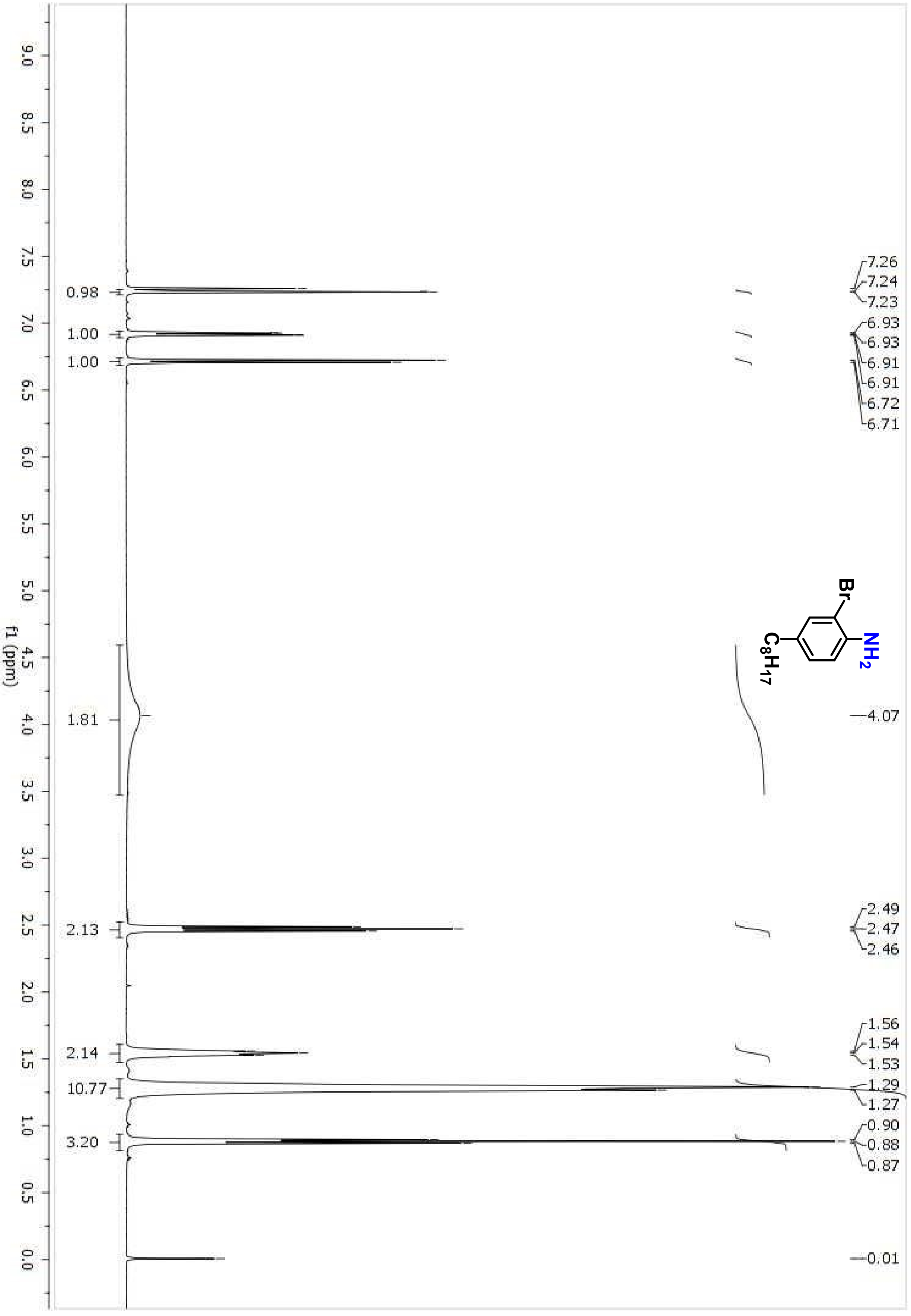

Figure S15. ^{1}H NMR spectrum of **S1** (500 MHz, $CDCl_3$).

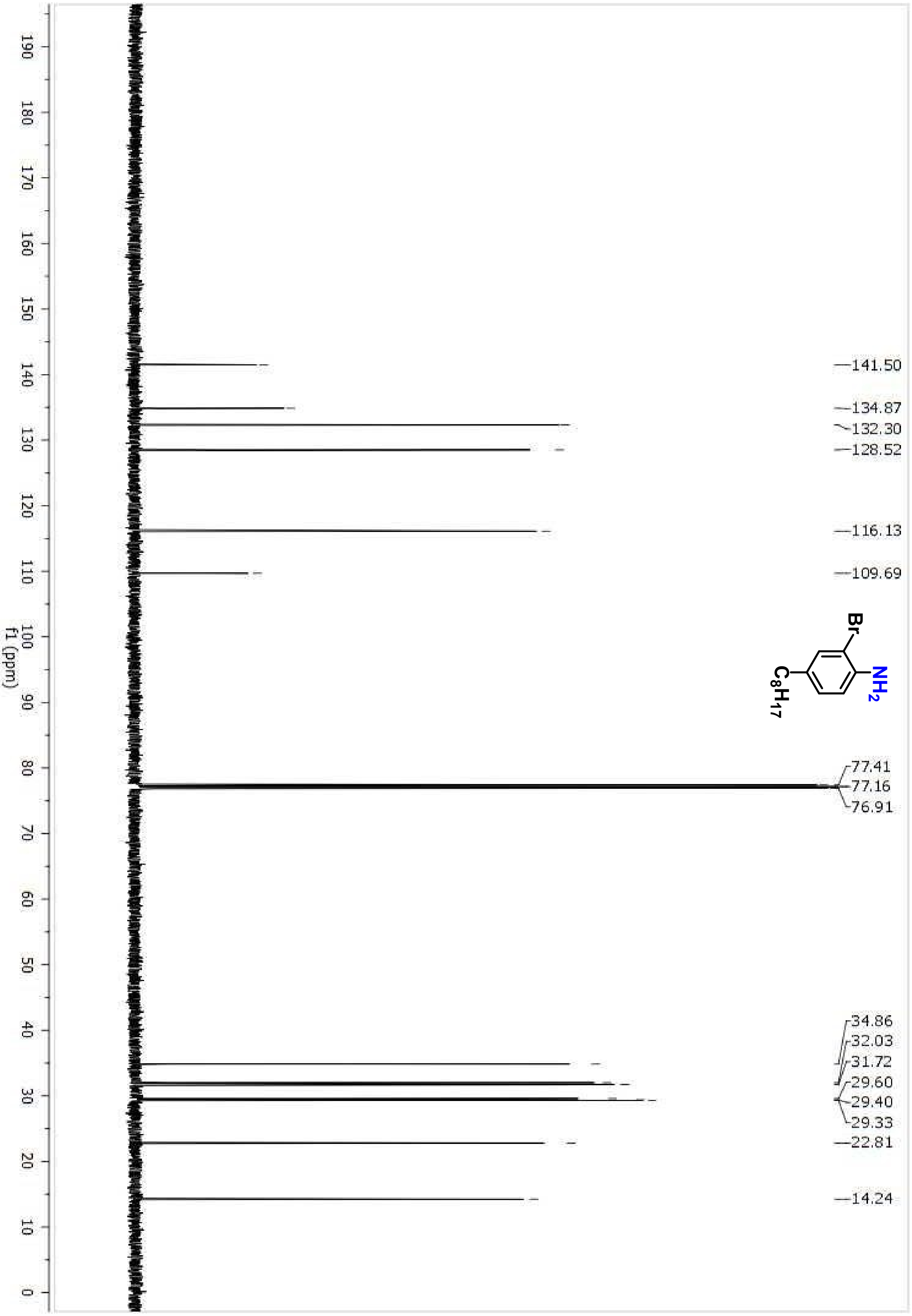

Figure S16. ^{13}C NMR spectrum of **S1** (126 MHz, CDCl$_3$).

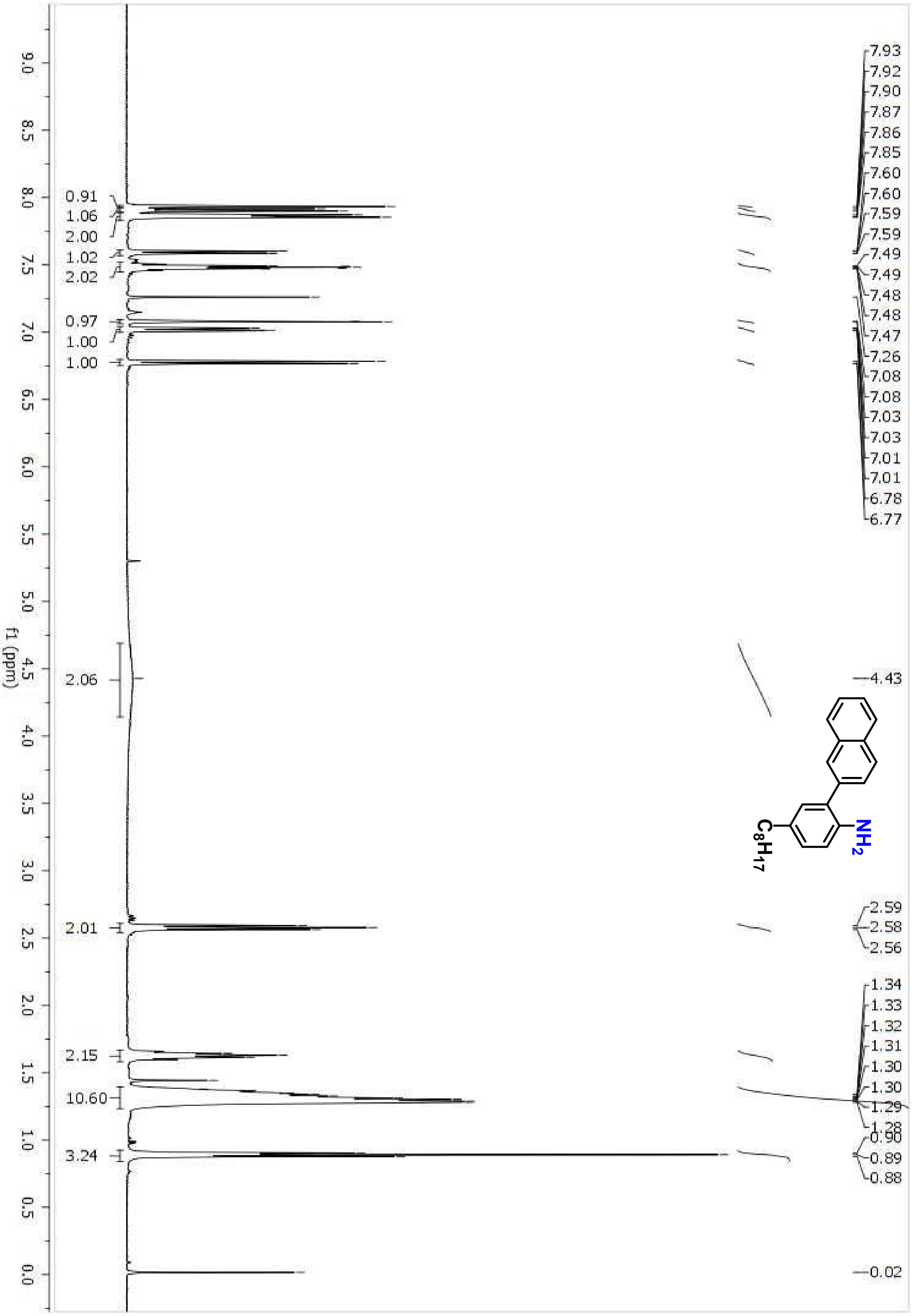

Figure S17. ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$).

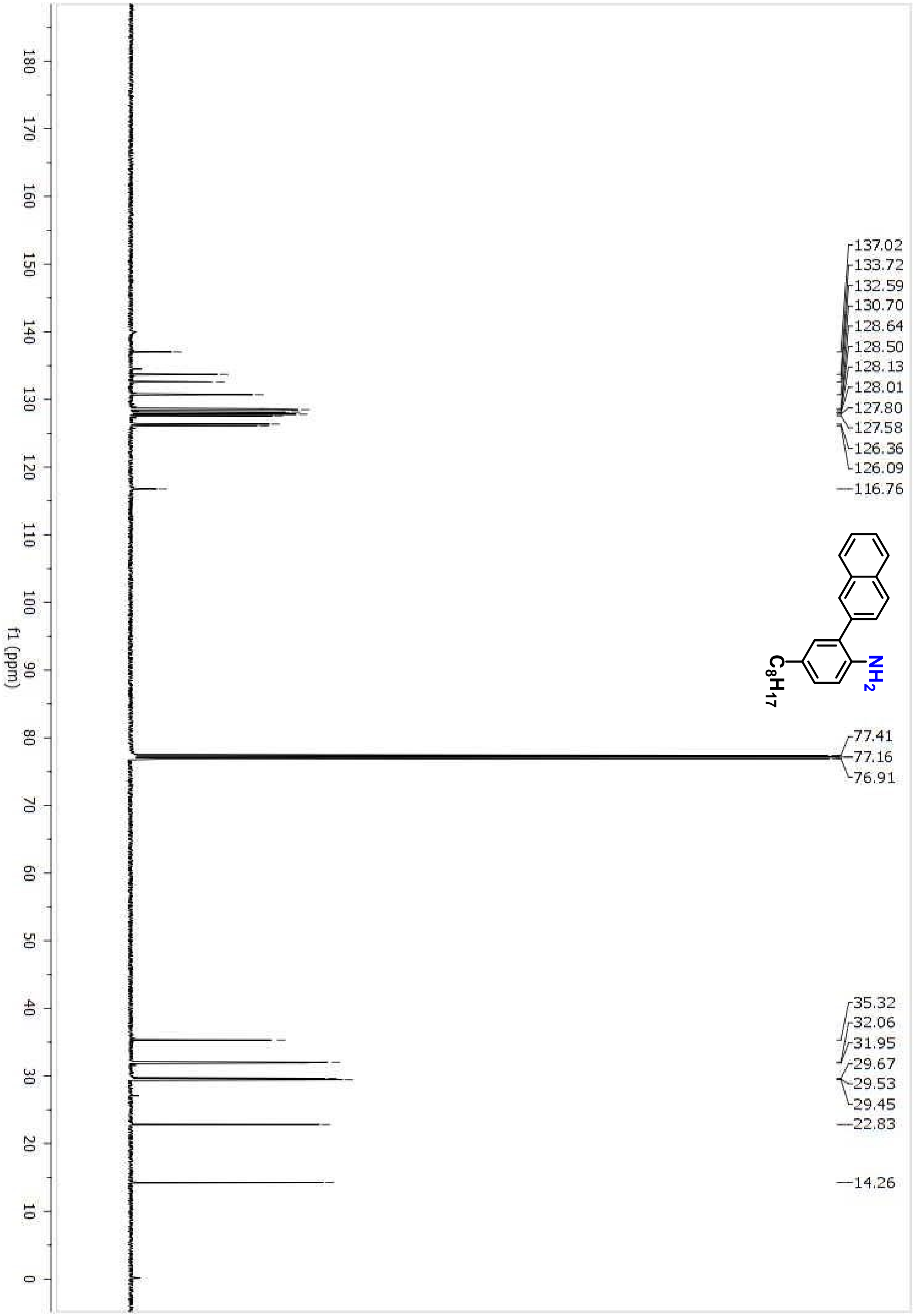

Figure S18. ^{13}C NMR spectrum of **2** (126 MHz, $CDCl_3$).

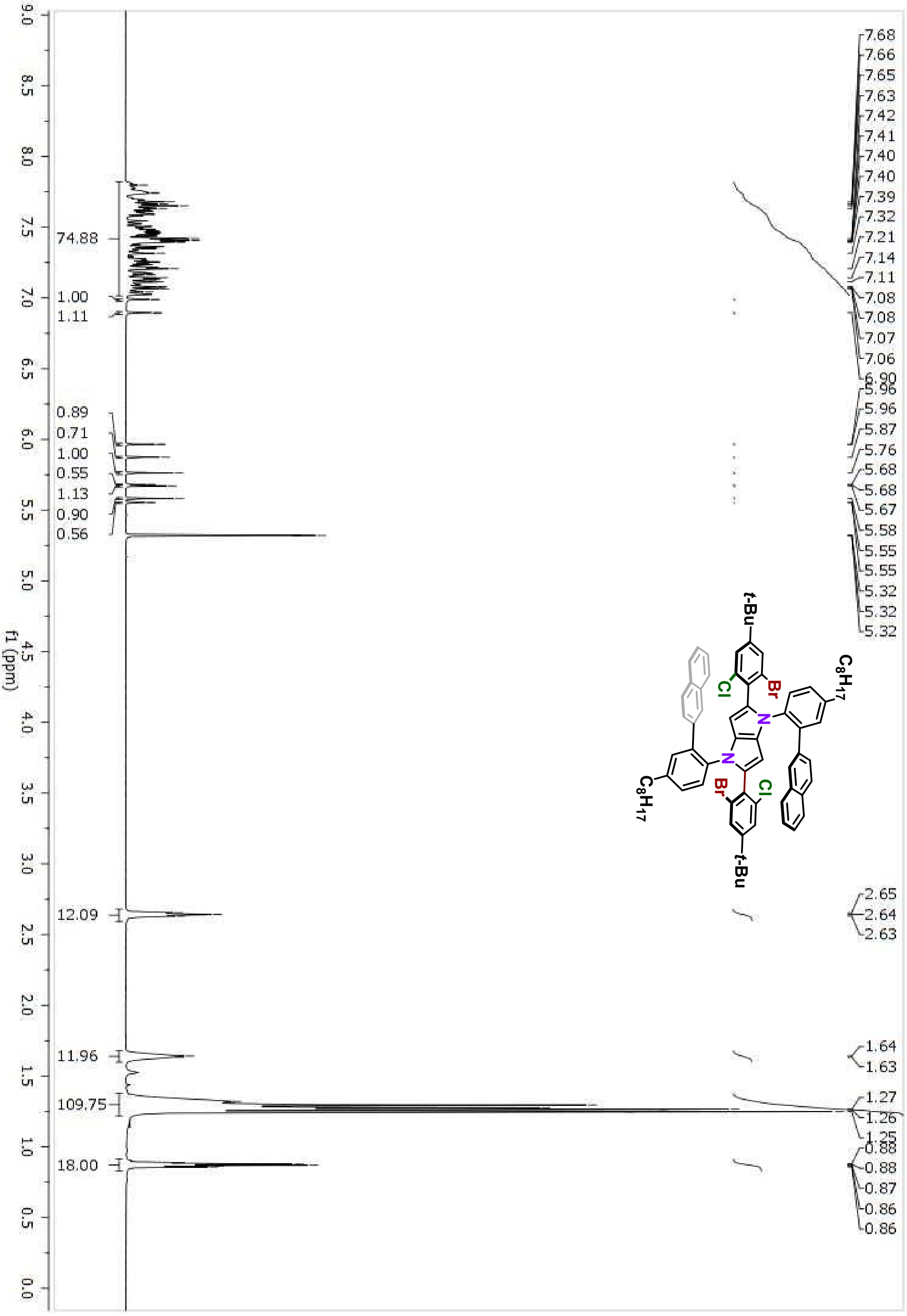

Figure S19. ^1H NMR spectrum of **4** (600 MHz, CD_2Cl_2).

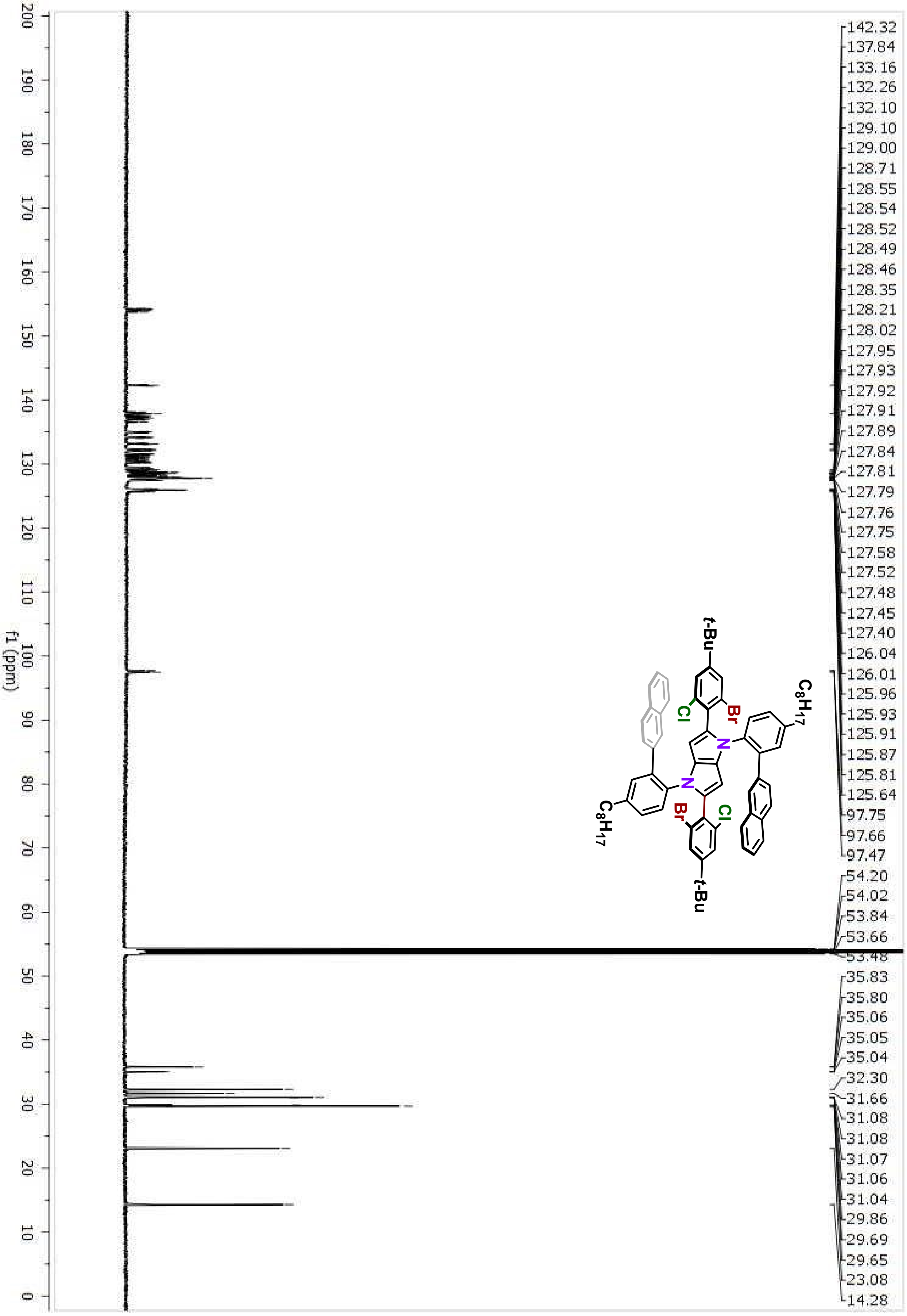

Figure S20. ^{13}C NMR spectrum of **4** (151 MHz, CD_2Cl_2).

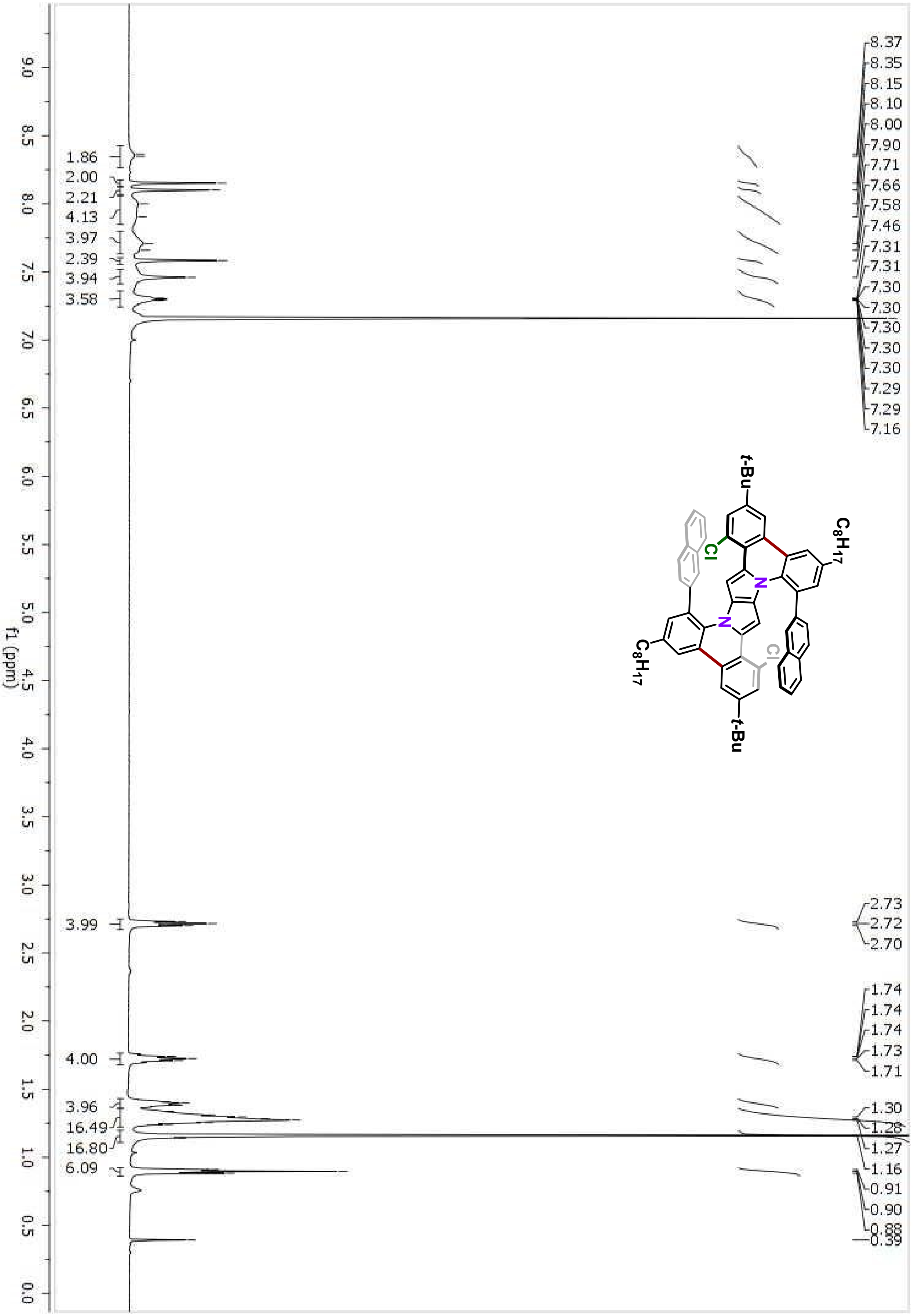

Figure S21. ^{1}H NMR spectrum of **5** (500 MHz, C_6D_6).

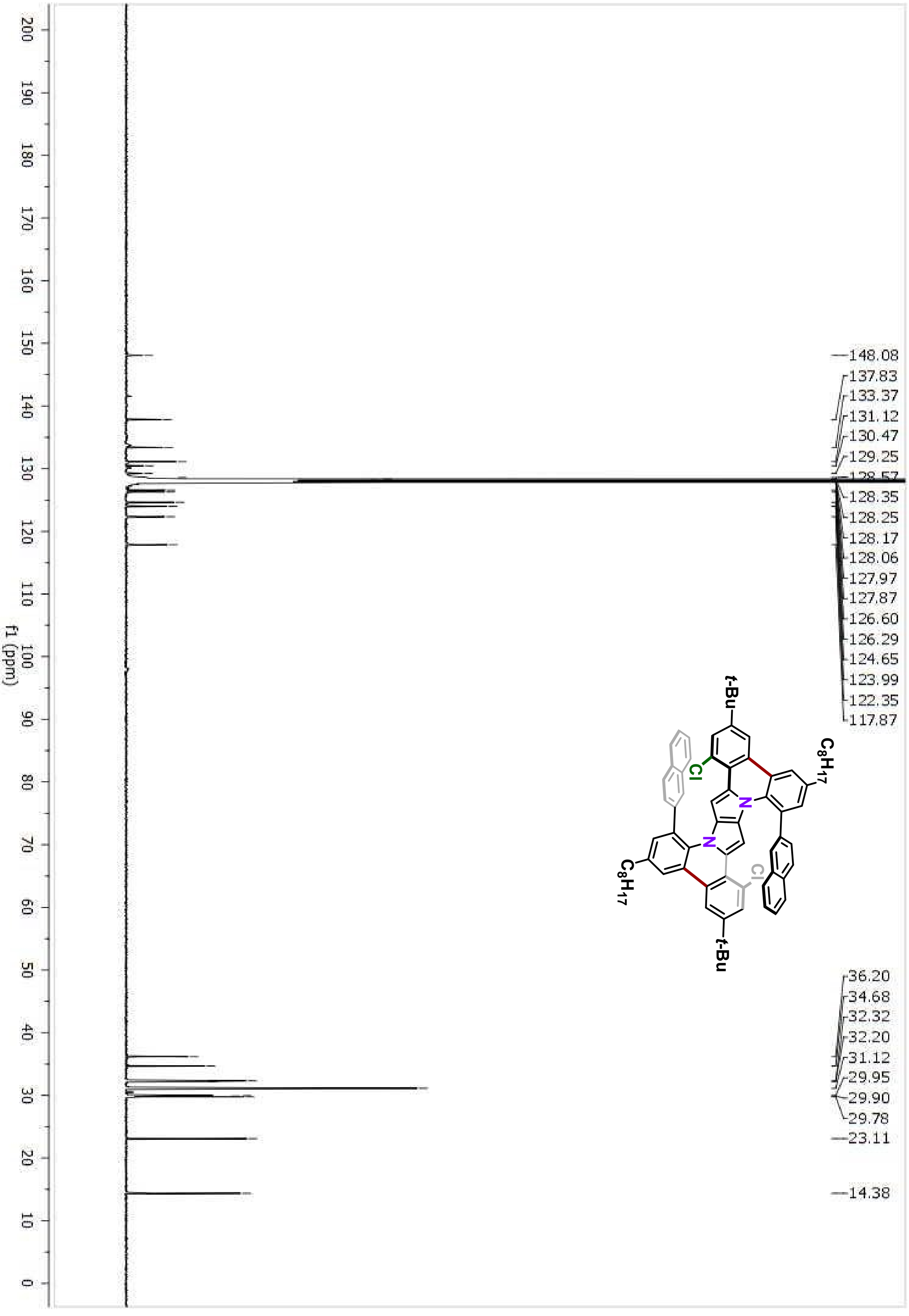

Figure S22. ^{13}C NMR spectrum of **5** (126 MHz, C_6D_6).

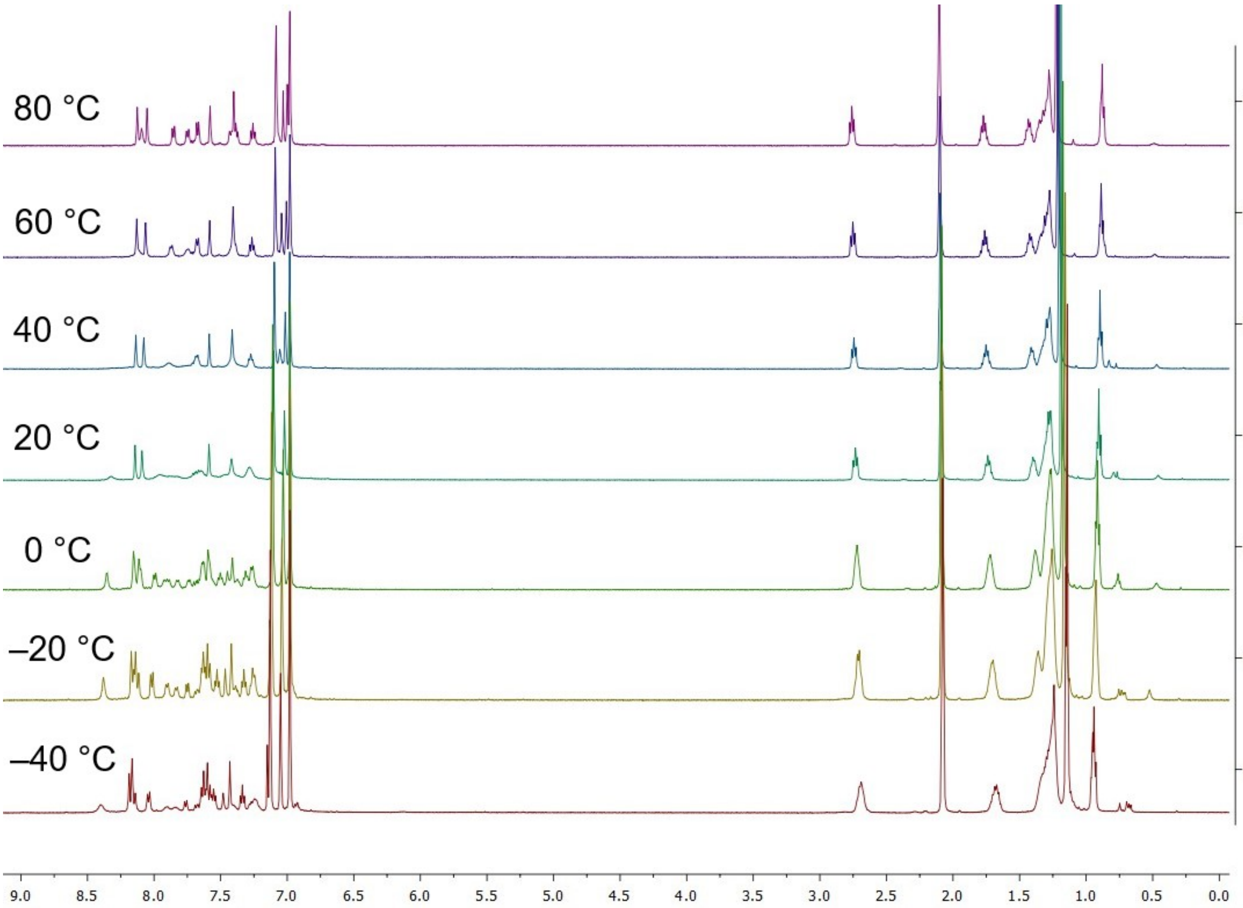

Figure S23. Variable temperature ^{1}H NMR spectra of **5** (500 MHz, toluene-d_8).

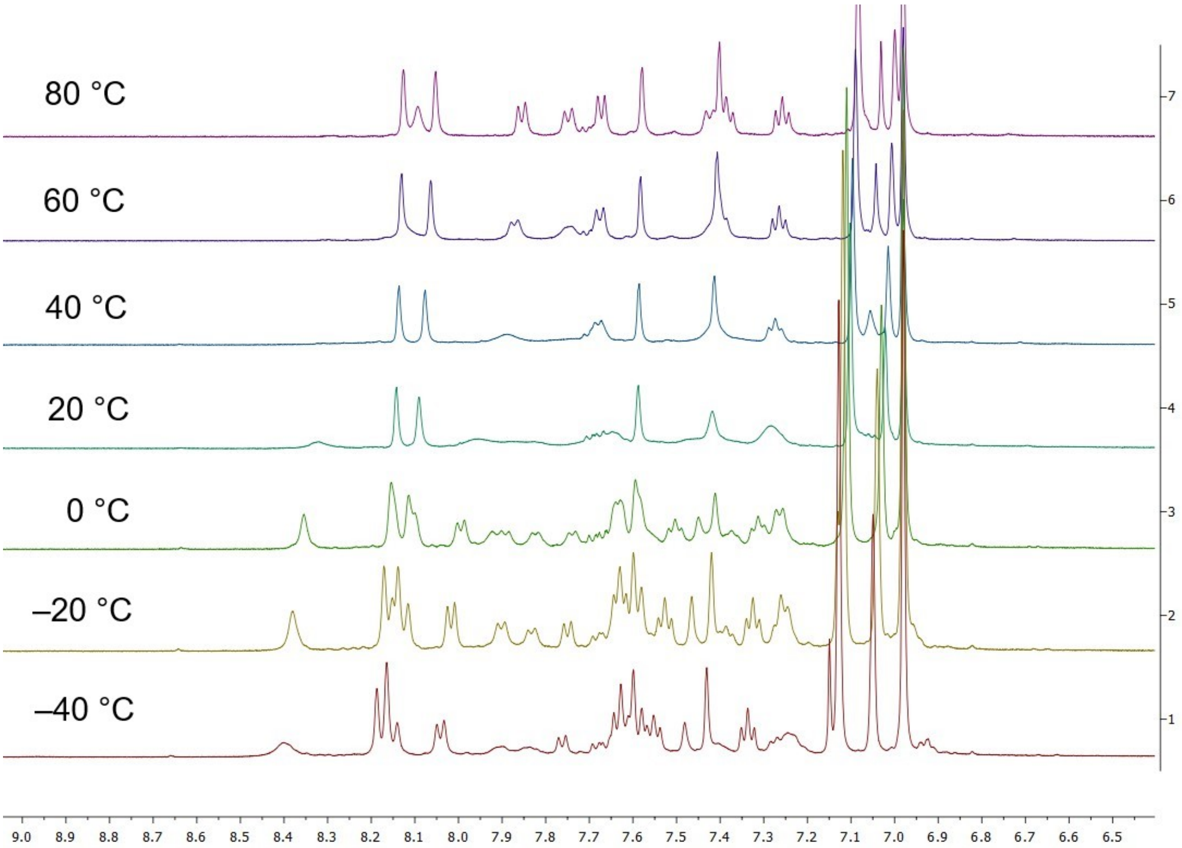

Figure S24. Zoomed-in aromatic region of variable temperature ^{1}H NMR spectra of **5** (500 MHz, toluene-d_8).

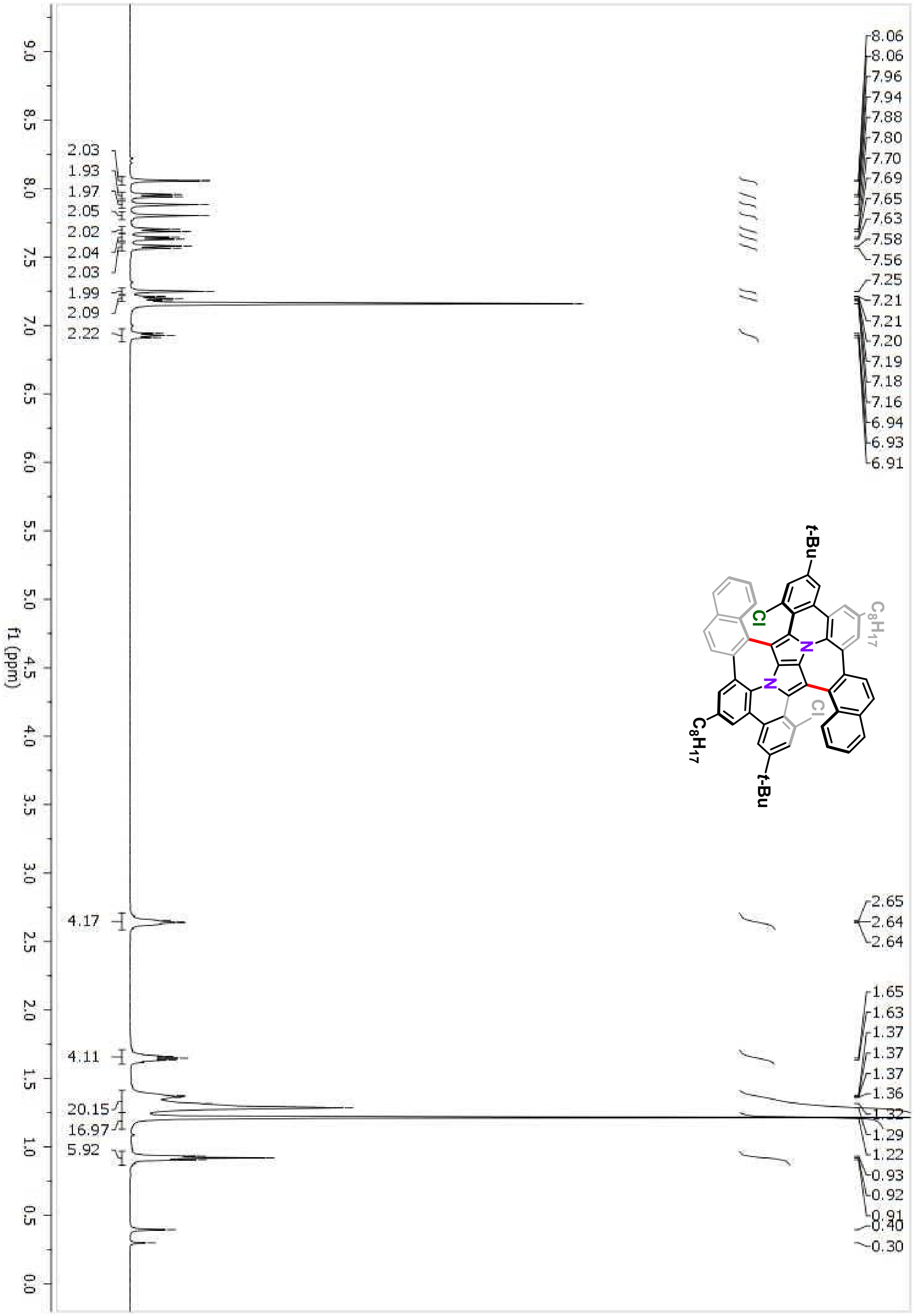

Figure S25. ^{1}H NMR spectrum of **6** (126 MHz, C_6D_6).

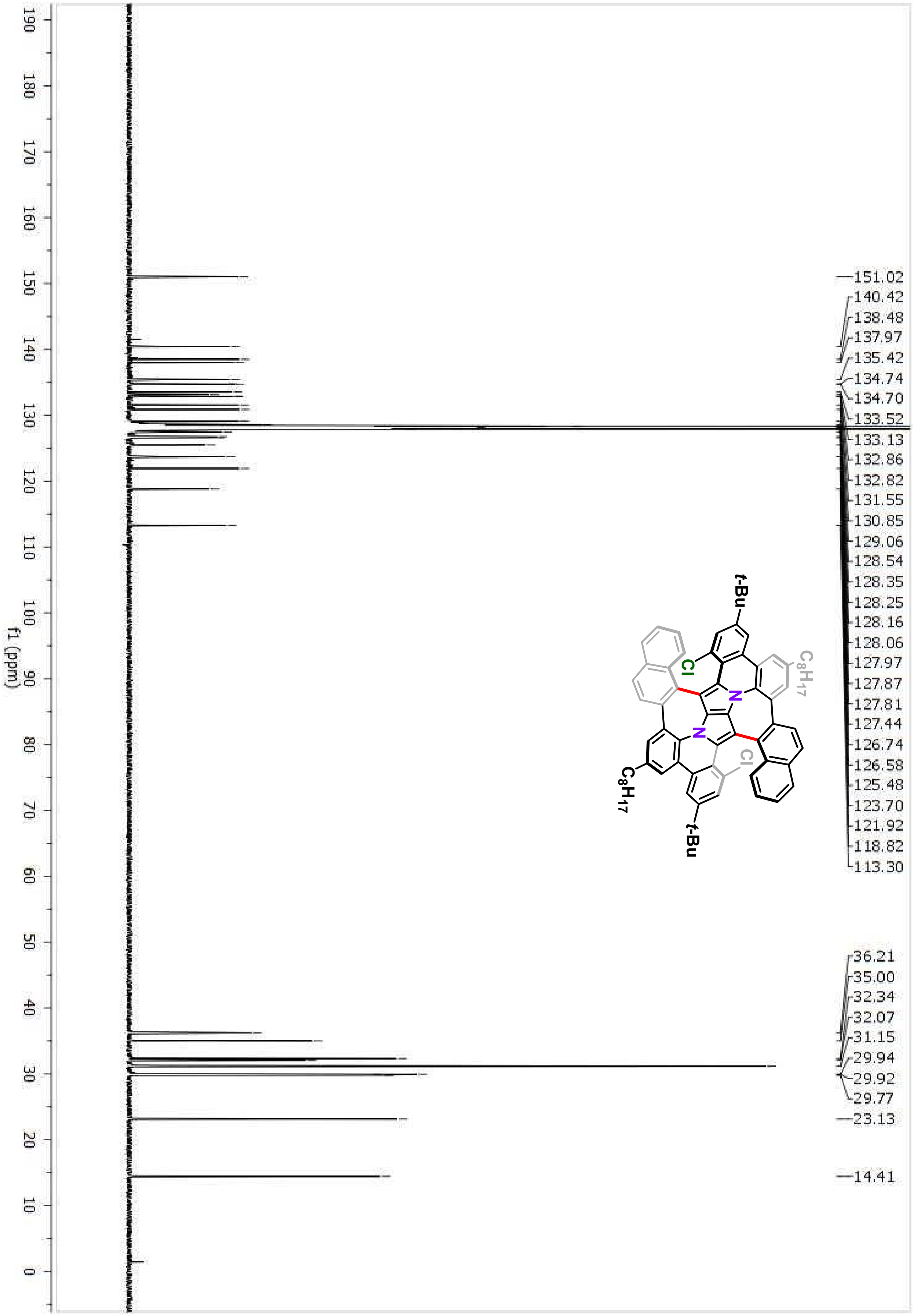

Figure S26. ^{13}C NMR spectrum of **6** (126 MHz, C_6D_6).

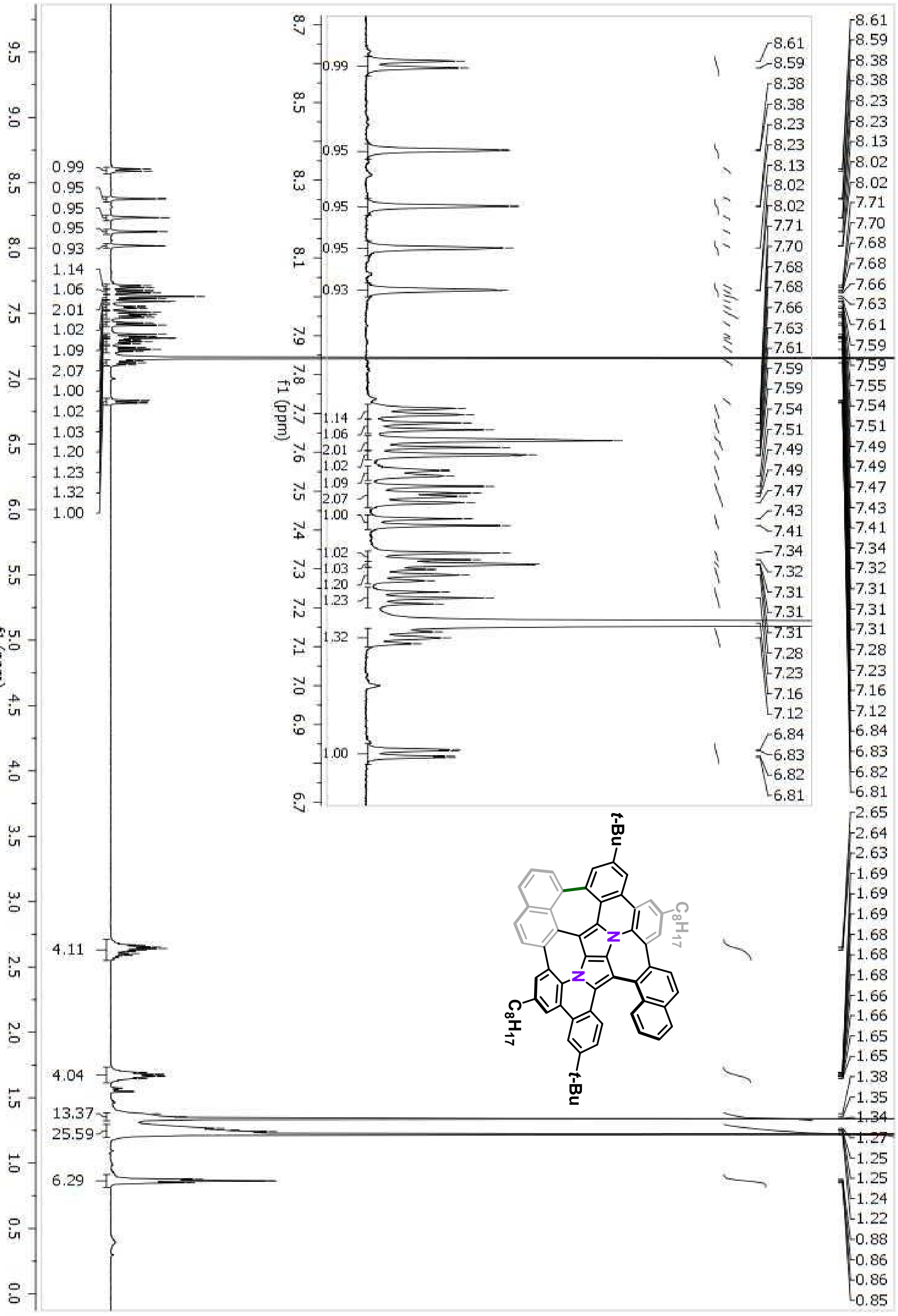

Figure S27. ^{1}H NMR spectrum of **7** (500 MHz, C_6D_6).

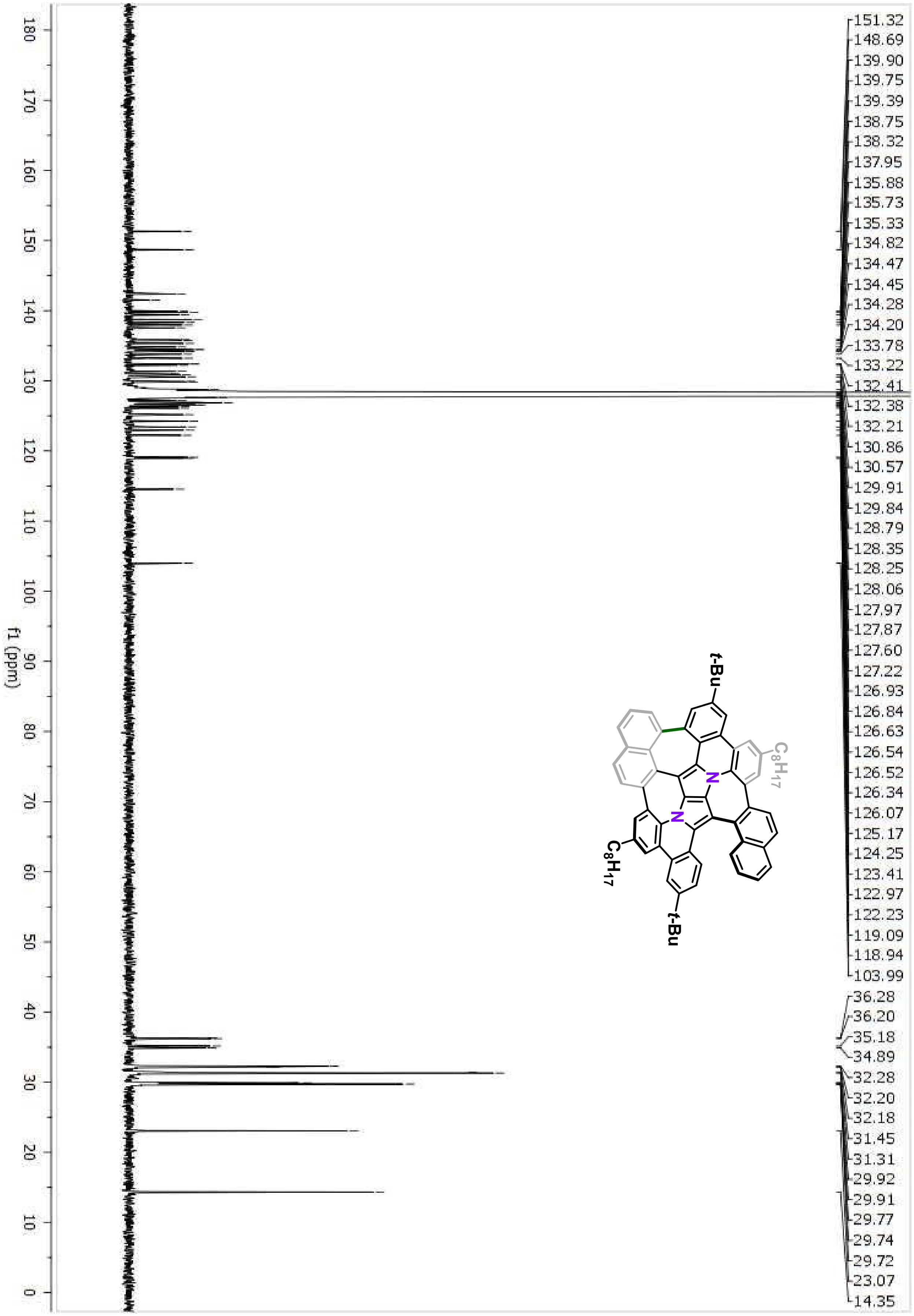

Figure S28. ^{13}C NMR spectrum of **7** (126 MHz, C_6D_6).

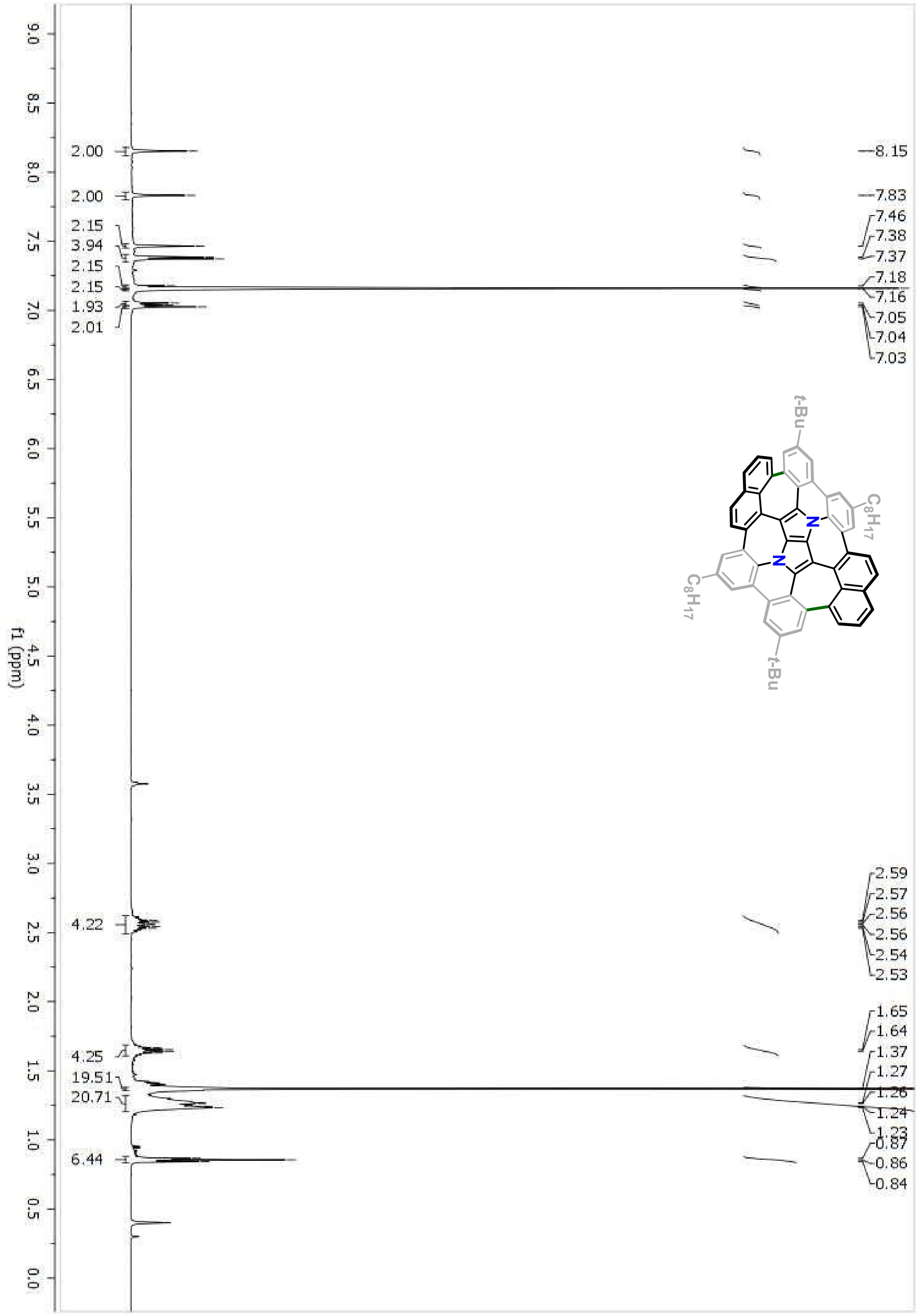

Figure S29. ^1H NMR spectrum of **8** (500 MHz, C_6D_6).

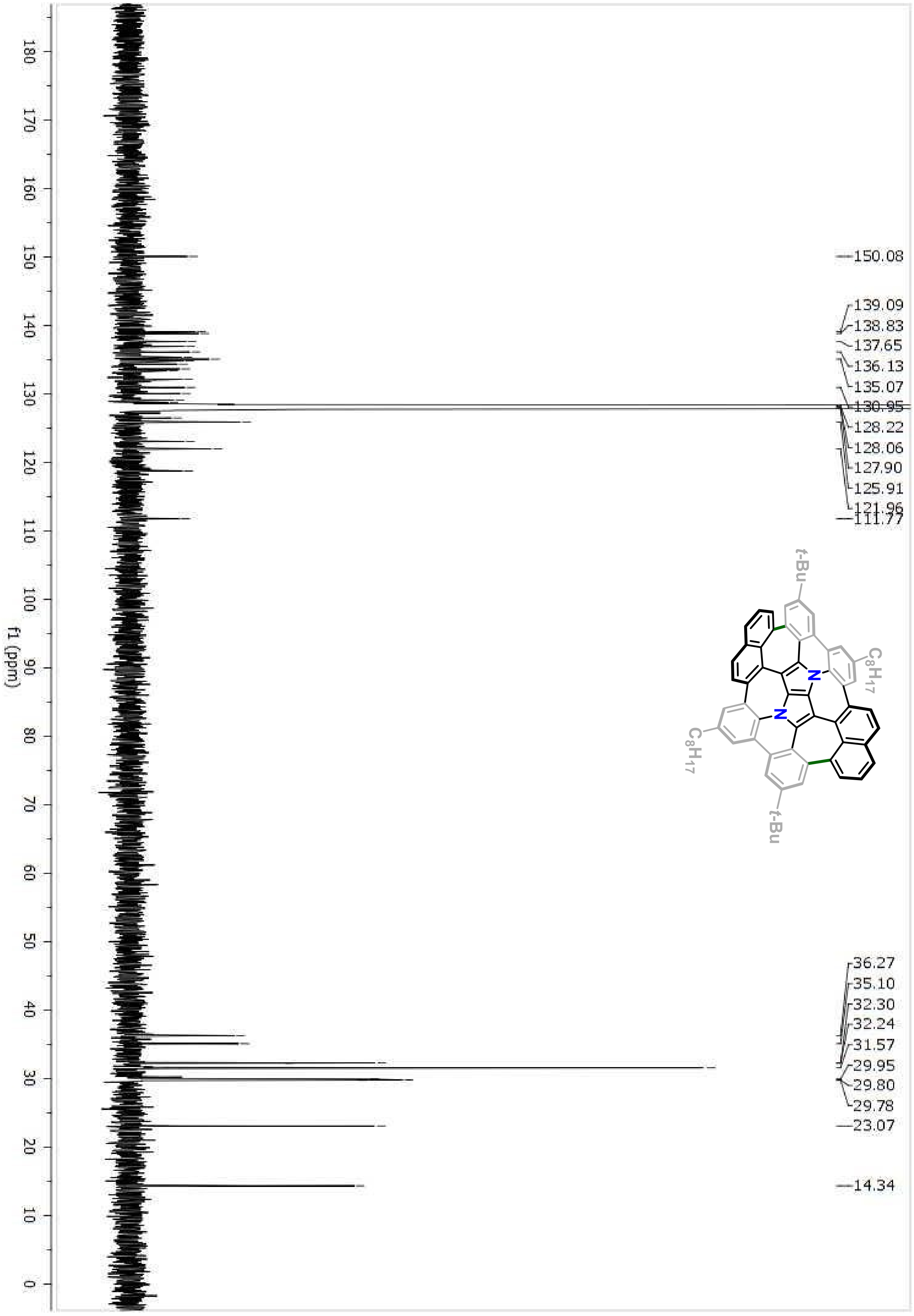

Figure S30. ^{13}C NMR spectrum of **8** (126 MHz, C_6D_6).

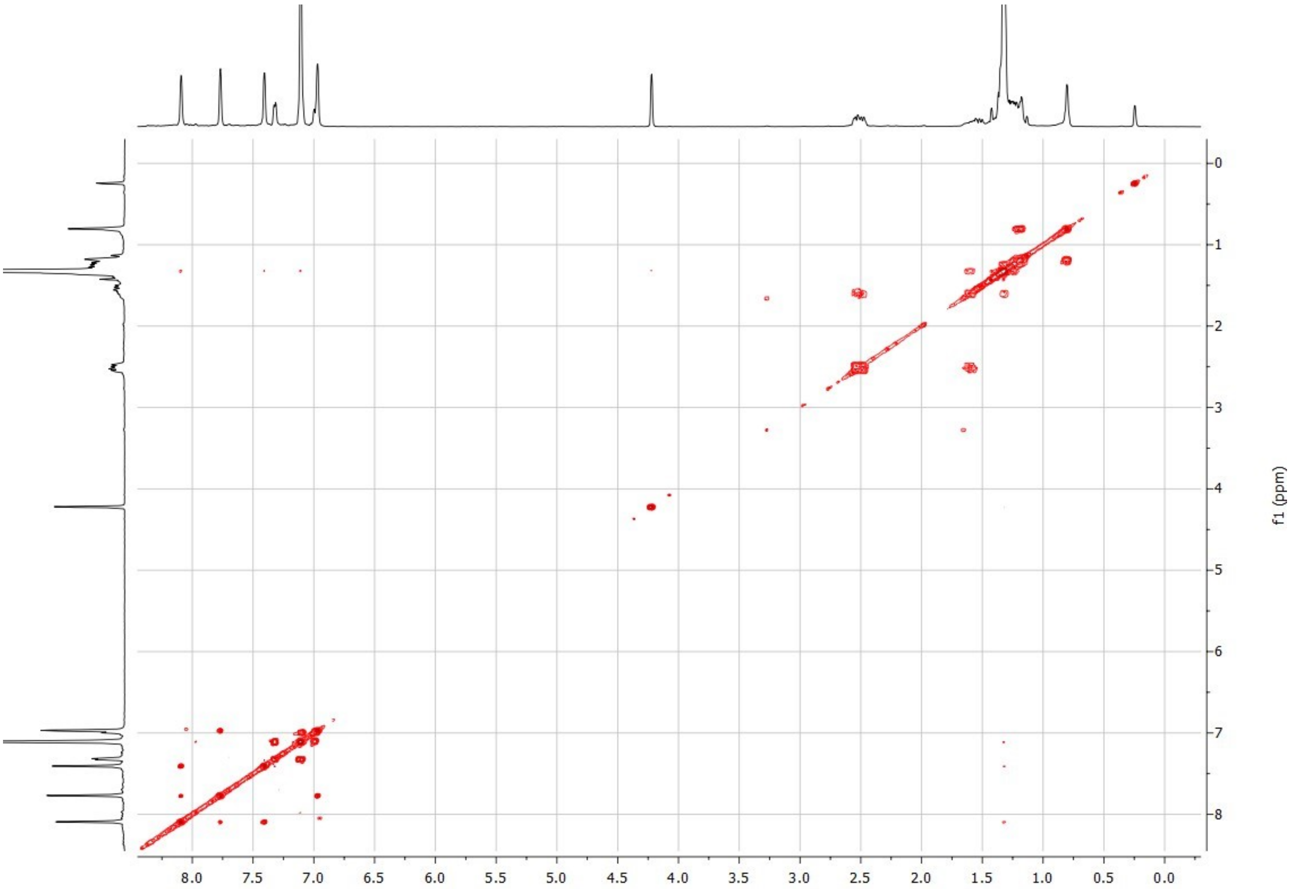

Figure S31. 2D H/H COSY spectrum of **8** (600 MHz, C_6D_6).

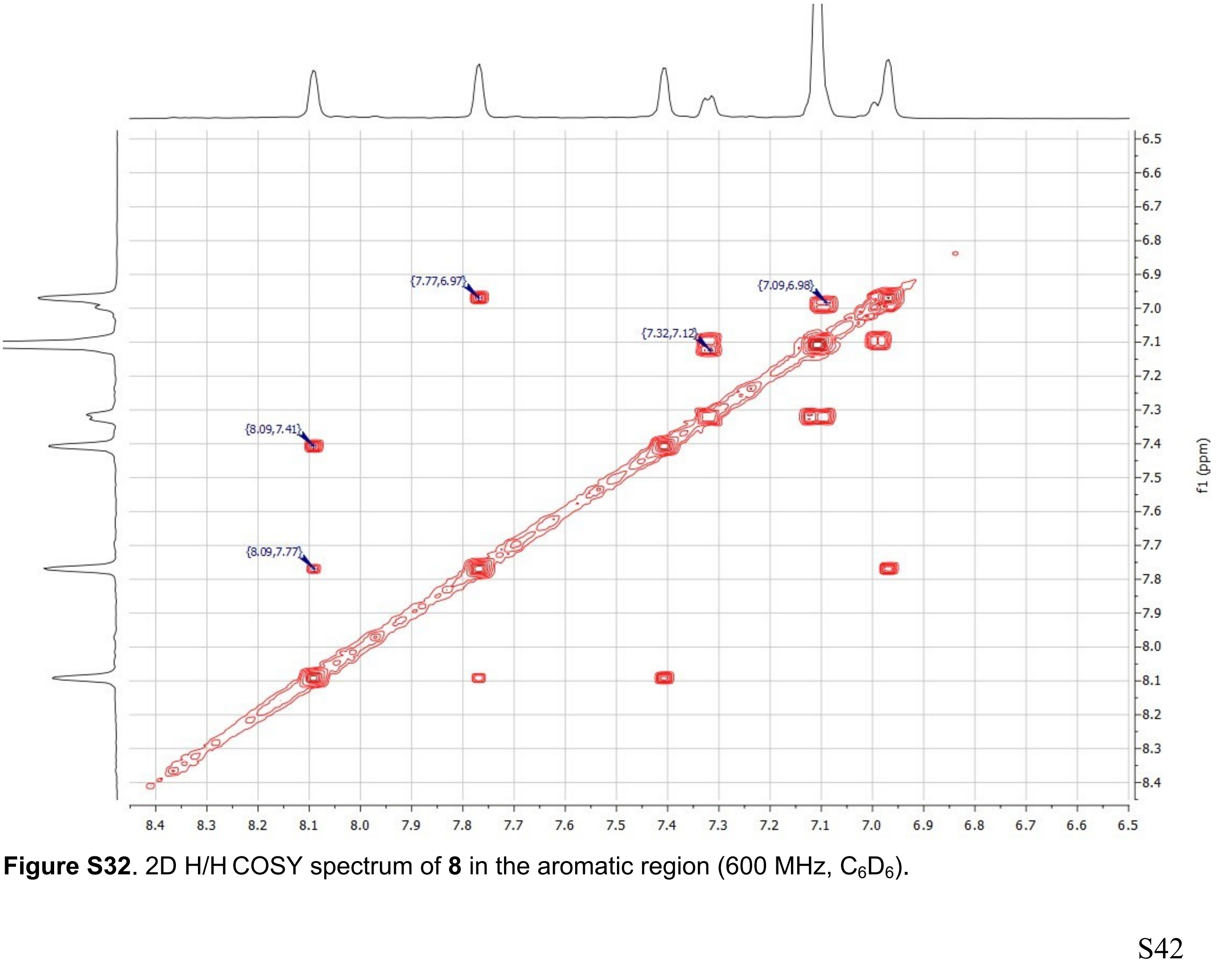

Figure S32. 2D H/H COSY spectrum of **8** in the aromatic region (600 MHz, C_6D_6).

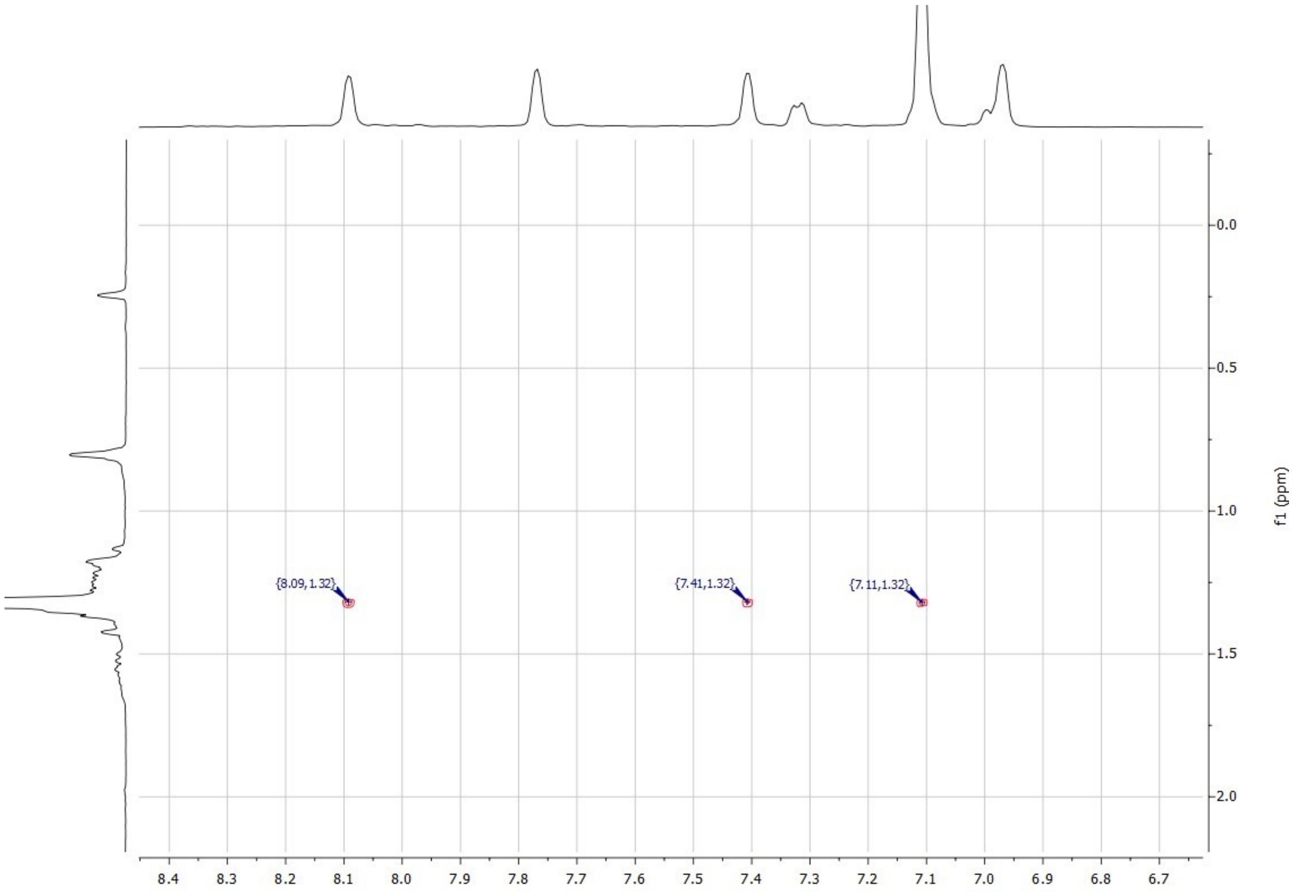

Figure S33. 2D H/H COSY spectrum of **8** in the aromatic vs aliphatic region (600 MHz, C_6D_6).

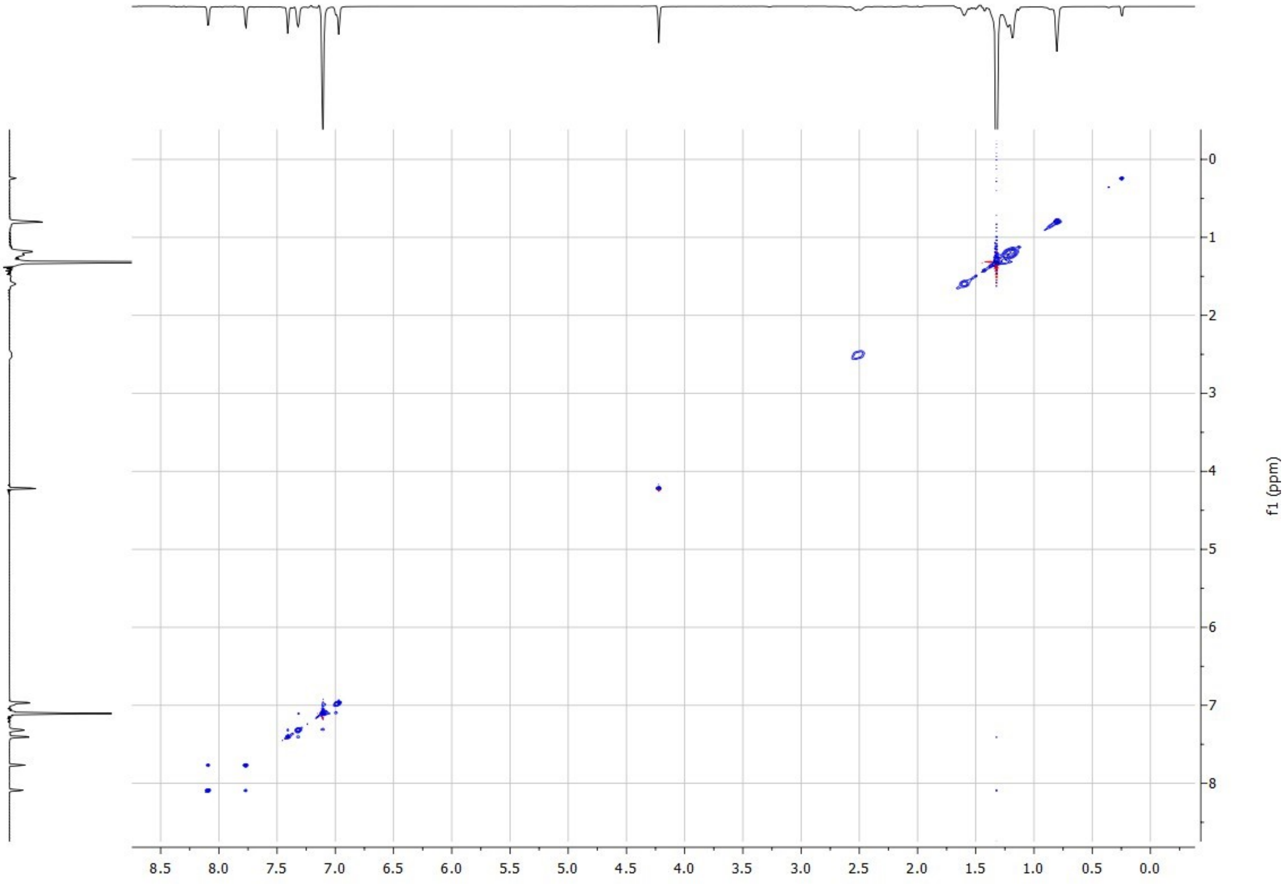

Figure S34. 2D H/H NOESY spectrum of **8** (600 MHz, C_6D_6).

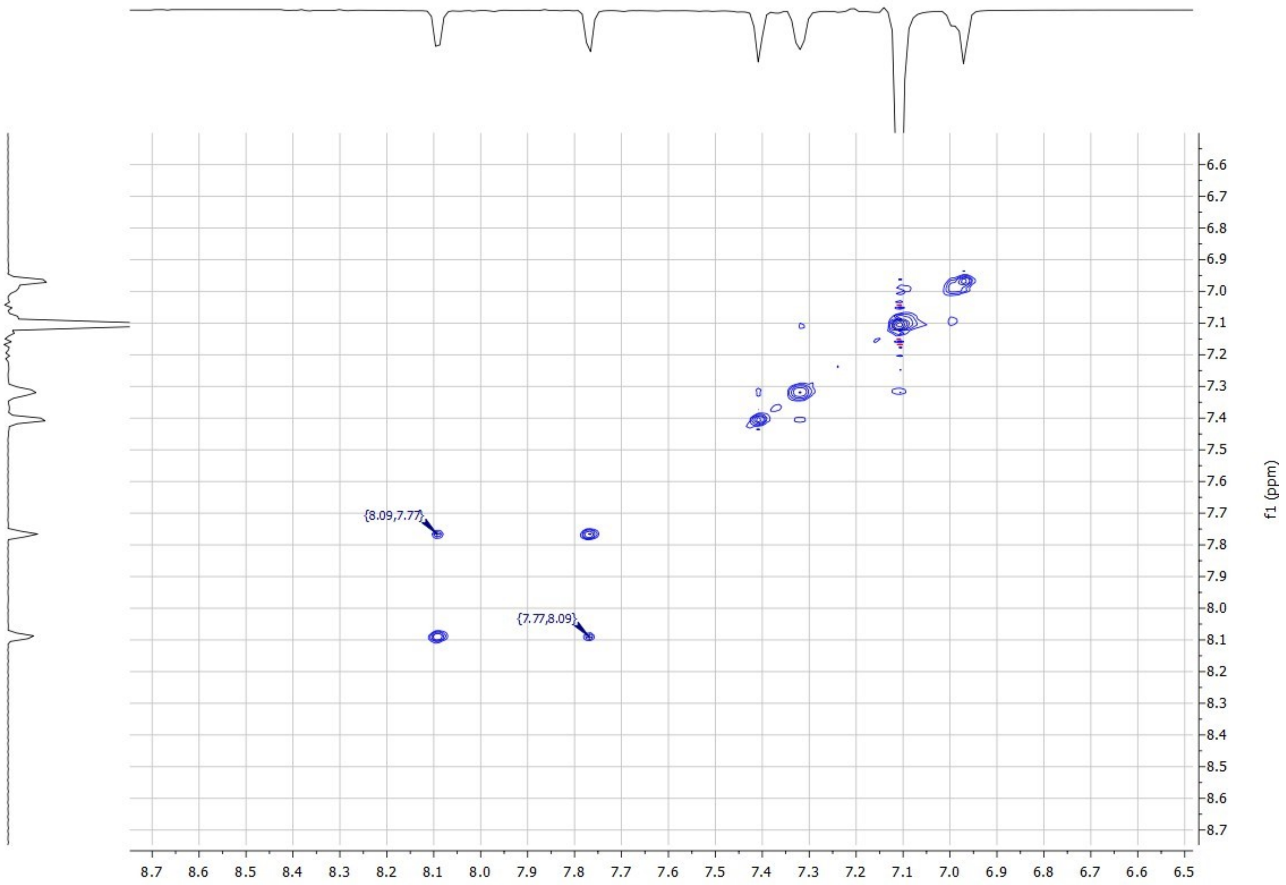

Figure S35. 2D H/H NOESY spectrum of **8** in the aromatic region (600 MHz, C_6D_6).

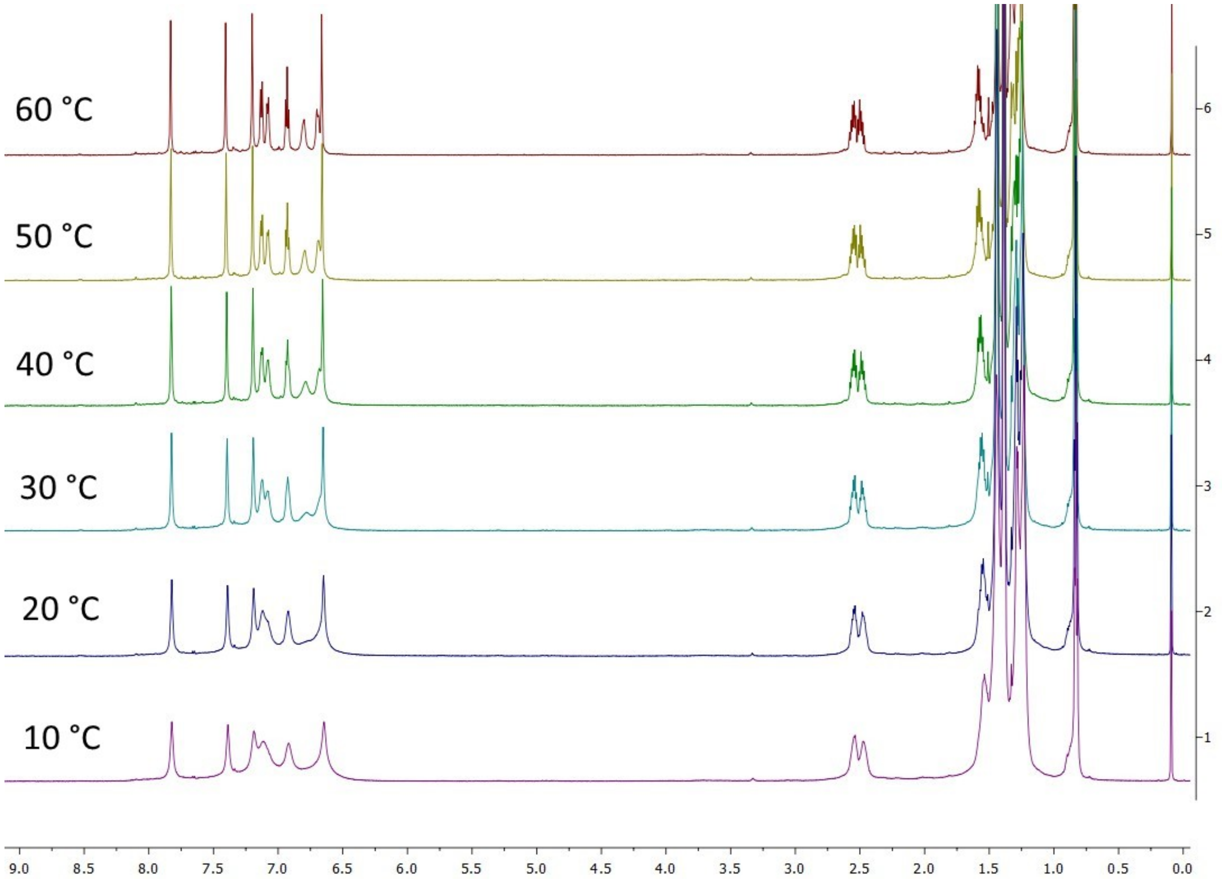

Figure S36. Variable temperature ^{1}H NMR spectra of **8** (600 MHz, cyclohexane-d_{12}).

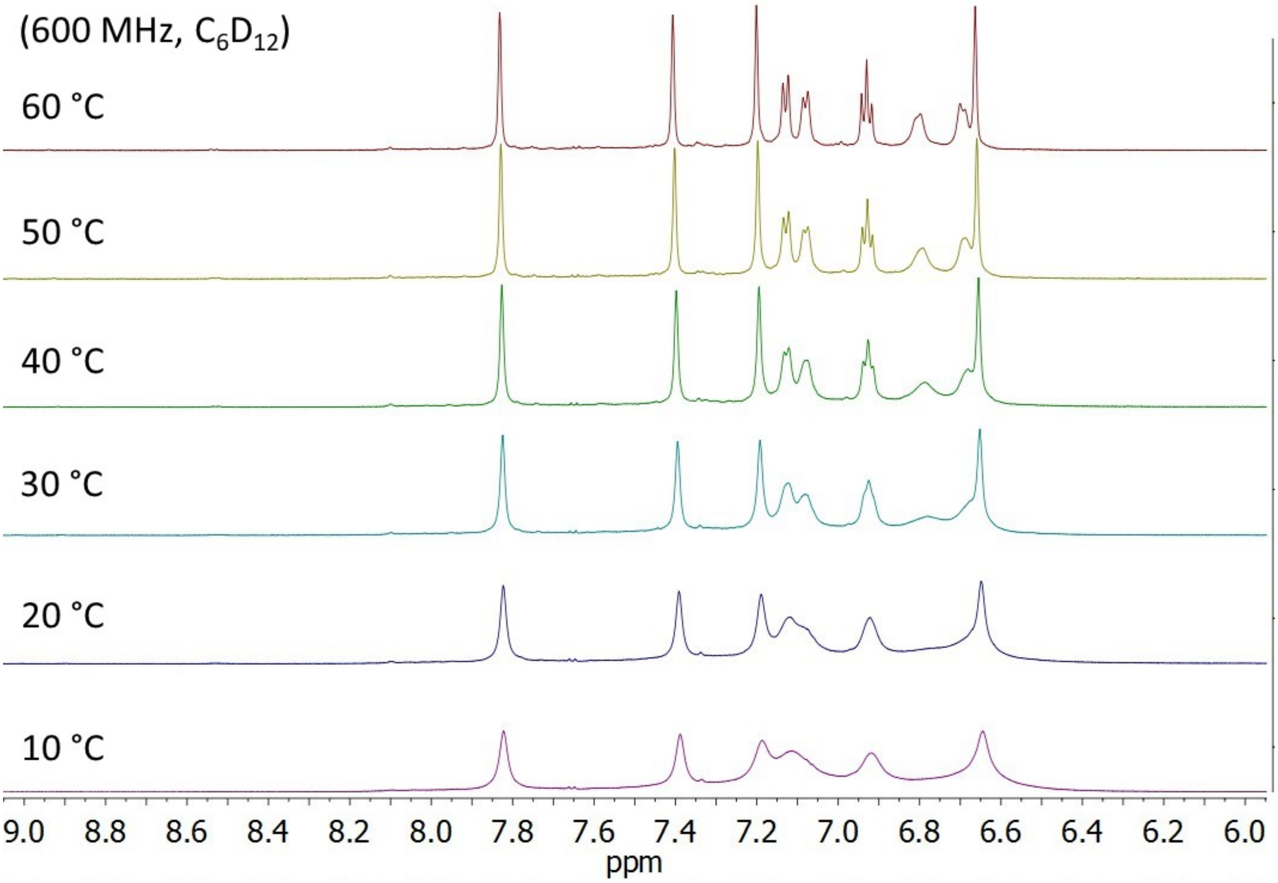

Figure S37. Zoomed-in aromatic region of variable temperature ^{1}H NMR spectra of **8** (600 MHz, cyclohexane-d_{12}).

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