Electronic Supplementary Material (ESI) for Polymer Chemistry.

Suppressing Aggregation Induced Quenching in Anthracene Based Conjugated Polymers

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Experimental Section

General

^{1}H NMR spectra were recorded on a 400 MHz Avance III HD Spectrometer, 400 MHz Smart Probe Spectrometer or a 500 MHz DCH Cryoprobe Spectrometer in the stated solvent using residual protic solvent as the internal standard. ^{1}H NMR chemical shifts are reported to the nearest 0.01 ppm. The coupling constants (*J*) are measured in Hertz. ^{13}C NMR spectra were recorded on the 500 MHz DCH Cryoprobe Spectrometer in the stated solvent using the residual protic solvent as the internal standard. ^{13}C NMR chemical shifts are reported to the nearest 0.1 ppm. Mass spectra were obtained using a Waters LCT, Finnigan MAT 900XP or Waters MALDI micro MX spectrometer at the Department of Chemistry, University of Cambridge. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. Thin layer chromatography (TLC) was carried out on silica gel and visualized using UV light (254, 365 nm). Flash chromatography was carried out on a Biotage® Isolera automated flash chromatography machine on 60 micron silica gel cartridges purchased from Biotage®. Number-average (M_n) and weight-average (M_w) molecular weights were determined against a polystyrene standard using an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C.

Chemicals

Benzoquinone was purchased from Sigma Aldrich and recrystallised from ethanol before use. All other commercial chemicals were of ≥95% purity and were used as received without further purification. Anhydrous solvents were purchased from Sigma Aldrich or Acros Organics and used as received.

Sample Preparation

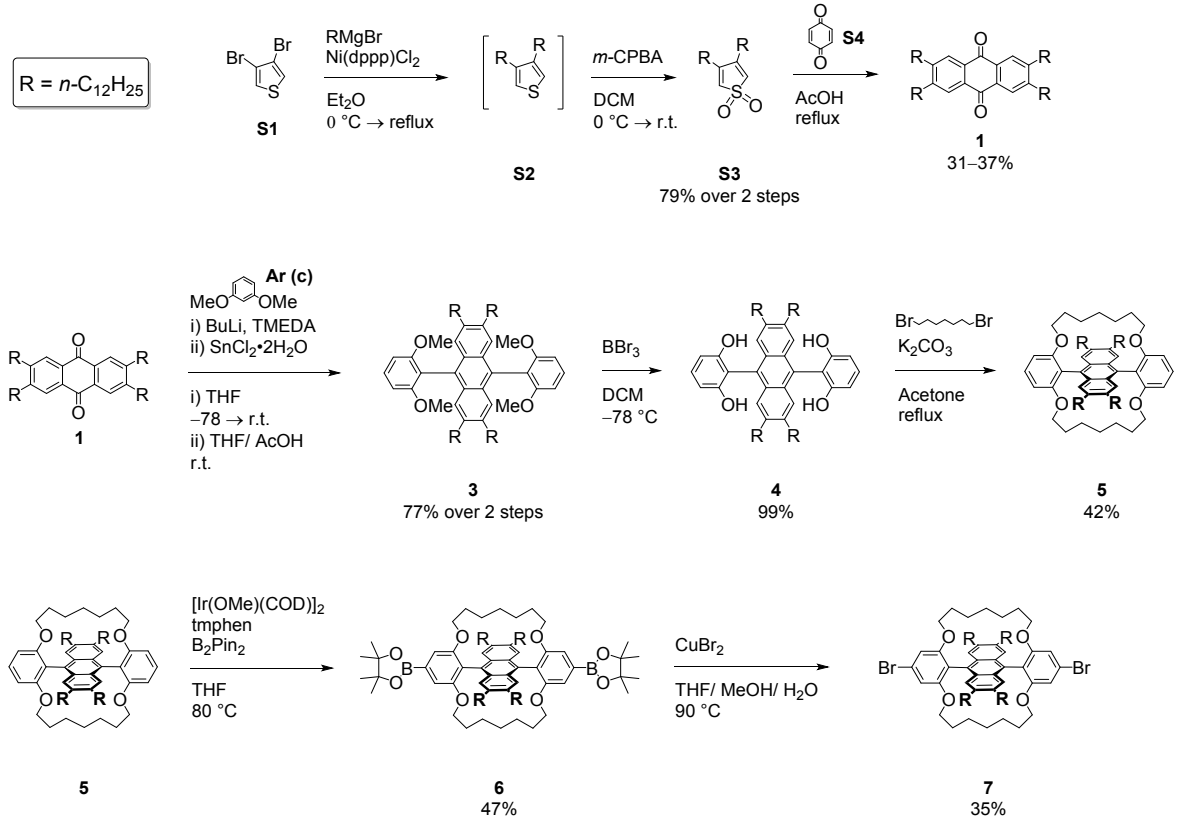
Solutions of the polymers at 0.2 mg/ml in toluene or dichlorobenzene were prepared in a N_2 glovebox.

Films of the polymers were prepared on fused silica substrates (JGS1, 13 mm diameter, supplied by Foctek) by spincoating in a N_2 glovebox. Solutions of the polymers (10 mg/ml) were dropped on the substrate and excess material was removed by spinning the substrate at 2000 rpm for 45 s. Samples were left to dry in the glovebox before measurements.

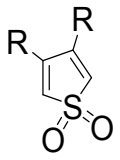
Photophysics

Absorption of all samples was measured using a Shimadzu UV-3600 Plus spectrophotometer. The steady-state photoluminescence was measured using an Edinburgh Instruments FLS980 Spectrometer, comprising a 450 W Xe1 xenon arc lamp focused into a monochromator to excite the samples between 360 – 370 nm and an R928P PMT to detect emission between 375 – 700 nm. Fluorescence lifetimes of samples excited using a PicoQuant pulsed 375 nm laser (repetition rate 10 – 100 MHz) were measured using a time-correlated single photon counting (TCSPC) setup comprising an Edinburgh Instruments Lifespec-ps spectrometer with a TCC900 PC card and a Hamamatsu-R3809U-50 microchannel plate photomultiplier tube. Solid state PLQYs were recorded on a Horiba Jobin Yvon SPEX Fluorolog 3 using a calibrated Quanta-Φ integrating sphere. Solid state PLQY data were obtained in triplicate from three samples that were prepared in parallel.

Synthesis of DPA monomers



Scheme S1. Synthesis of the polymer precursors **6** and **7**.



S3
R = *n*-$C_{12}H_{25}$

3,4-Bis(*n*-dodecyl)thiophene-*S*,*S*-dioxide (S3). Prepared based on a literature procedure for an analogue.[1]

Scale: *ca.* 9 g of product

Kumada coupling

A solution of 3,4-dibromothiophene (**S1**) (6 g, 24.8 mmol, 1.00 eq.) in dry Et_2O (250 mL) was cooled to to 0 °C in an ice bath and degassed for 30 min. Bis(diphenylphosphinopropane)nickel(II) chloride (270 mg, 0.50 mmol, 0.02 eq.) was then added, and the resulting red solution was degassed for a further 10 min. It was then stirred at 0 °C under argon while a degassed solution of dodecylmagnesium bromide (1 M in Et_2O) (58.3 mL, 58.3 mmol, 2.35 eq.) was added over *ca.* 30 min via dropping funnel. During the addition the colour of the mixture slowly changed from red to yellow to orange. Once addition of the Grignard reagent was complete, the mixture was allowed to warm to room temperature. The exothermic nature of the reaction caused the mixture to reflux for a few minutes, during which it turned dark brown. It was stirred at room temperature for a further 2 h, and then

heated to reflux overnight. The mixture was cooled to room temperature and poured onto a mixture of conc. HCl (10 mL) and ice. Water was added until the total volume of the mixture was *ca.* 1 L and the layers were separated. The aqueous layer was further extracted with Et_2O (2 × 100 mL) and the organic extracts were combined, dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was passed through a plug of silica gel (eluent: *n*-hexane) to afford the intermediate 3,4-bis(*n*-dodecyl)thiophene (**S2**) as a clear oil that was typically free of any aromatic impurities. ^{1}H NMR data were in accordance with those reported in the literature.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.91 (s, 2H), 2.55 – 2.49 (m, 4H), 1.63 (dt, *J* = 15.3, 7.5 Hz, 4H), 1.43 – 1.23 (m, 36H), 0.91 (t, *J* = 6.8 Hz, 6H). It was used immediately without further purification.

Oxidation

The previously obtained 3,4-bis(*n*-dodecyl)thiophene (**S2**) was dissolved in DCM (220 mL) and cooled to 0 °C in an ice bath under air. A solution of 3-chloroperbenzoic acid (15 g, ≤ 77% pure, ≤ 87 mmol, ≤ 3.5 eq. based on 3,4-dibromothiophene (**S1**)) in DCM (200 mL) was then added dropwise over *ca.* 30 min. The resulting white suspension was warmed to room temperature overnight. It was then washed sequentially with 1 M $NaHSO_3$ (3 × 100 mL), saturated K_2CO_3 (5 × 100 mL), brine (1 × 100 mL) and water (1 × 100 mL). The organic layer was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: *n*-hexane to remove any unreacted 3,4-bis(*n*-dodecyl)thiophene (**S2**), then 95:5 *n*-hexane/ EtOAc v/v). 3,4-Bis(*n*-dodecyl)thiophene-*S*,*S*-dioxide (**S3**) was isolated as a white waxy solid (8.85 g, 19.6 mmol, 79% based on 3,4-dibromothiophene (**S1**). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.23 (s, 2H), 2.29 (t, *J* = 7.3 Hz, 4H), 1.61 – 1.48 (m, 4H), 1.42 – 1.19 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.5, 124.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 27.9, 27.1, 22.7, 14.1; HRMS (ESI): *m/z* 453.3781 [M–H$^+$]. Calcd. for $C_{28}H_{53}O_2S^+$: 453.3766.

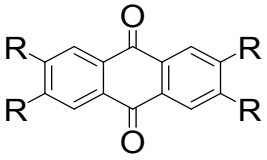
Scale: *ca.* 56 g of product

Kumada coupling

The reaction was carried out analogously to on smaller scale at the same dilution with 3,4-dibromothiophene (**S1**) (40 g, 165 mmol, 1.0 eq.), bis(diphenylphosphinopropane)nickel(II) chloride (1.80 g, 3.33 mmol, 0.02 eq.) and dodecylmagnesium bromide (1 M in Et_2O) (400 mL, 400 mmol, 2.42 eq.) in Et_2O (1700 mL). The same work up procedure was followed, but on a larger scale. *Caution should be taken when quenching such a large amount of Grignard reagent.*

Oxidation

The reaction was carried out analogously to on smaller scale at the same dilution with solutions of 3,4-bis(*n*-dodecyl)thiophene (**S2**) in DCM (1500 mL) and 3-chloroperbenzoic acid (100 g, ≤ 77% pure, ≤ 580 mmol, ≤ 3.5 eq. based on 3,4-dibromothiophene (**S1**)) in DCM (1300 mL). After stirring at room temperature overnight the solvent was removed under reduced pressure and the residue stirred in a large volume of *n*-hexane (*ca.* 1500 mL). The resulting suspension was the filtered through celite, and the celite washed with further *n*-hexane (*ca.* 1500 mL). The solvent was removed under reduced pressure and the residue was passed through a thick plug of silica gel (eluent: *n*-hexane to remove any unreacted 3,4-bis(*n*-dodecyl)thiophene (**S2**), then 95:5 *n*-hexane/ EtOAc v/v) to afford 3,4-bis(*n*-dodecyl)thiophene-*S*,*S*-dioxide (**S3**) (56 g, 124 mmol, 75% based on 3,4-dibromothiophene (**S1**)).



1

R = *n*-$C_{12}H_{25}$

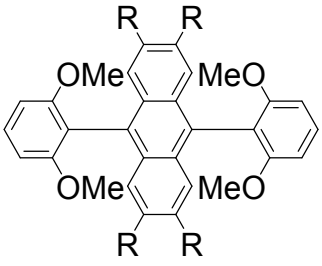
2,3,6,7-Tetrakis(*n*-dodecyl)anthracene-9,10-dione (1). Prepared based on a literature procedure for an analogue.[3]

Scale: *ca.* 2 g of product

Degassed acetic acid (145 mL) was added to 3,4-bis(*n*-dodecyl)thiophene-*S*,*S*-dioxide (**S3**) (6.60 g, 14.6 mmol, 2.20 eq.) and *p*-benzoquinone (**S4**) (706 mg, 6.53 mmol, 1.00 eq.) and the resulting mixture was heated to reflux under argon for 40 h. The mixture was cooled to r.t. A precipitate formed which was isolated via filtration and washed sequentially with acetic acid (3 × 10 mL) and copious methanol. It was then suspended in methanol (200 mL), heated to reflux for 30 min, and cooled to room temperature. The precipitate was isolated via filtration, washed with methanol (3 × 50 mL) and dried under high vacuum to obtain 2,3,6,7-tetrakis(*n*-dodecyl)anthracene-9,10-dione (**S5**) as a powder (1.78–2.15 g, 2.02–2.44 mmol, 31–37%). While the colour of the material obtained via this procedure varies from white to light red, ^{1}H NMR spectra free of impurities are consistently obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.04 (s, 4H), 2.77 – 2.71 (m, 8H), 1.69 – 1.60 (m, 8H), 1.46 – 1.21 (m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 183.6, 147.8, 131.6, 127.7, 33.0, 31.9, 30.8, 29.7, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1; HRMS (ESI): *m/z* 881.8115 [M–H$^+$]. Calcd. for $C_{62}H_{105}O_2^+$: 881.8109.

Scale: *ca.* 14 g of product

The reaction was carried out analogously to on smaller scale at the same dilution with 3,4-bis(*n*-dodecyl)thiophene-*S*,*S*-dioxide (**S3**) (56.0 g, 124 mmol, 2.20 eq.) and *p*-benzoquinone (**S4**) (6.09 g, 56.3 mmol, 1.00 eq.) in acetic acid (1480 mL). 2,3,6,7-Tetrakis(*n*-dodecyl)anthracene-9,10-dione (**S5**) was obtained as a light red powder (14.33 g, 16.3 mmol, 29%)



3

R = *n*-$C_{12}H_{25}$

9,10-Bis(2,6-dimethoxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (3). Prepared based on a modified literature procedure for an analogue.[4]

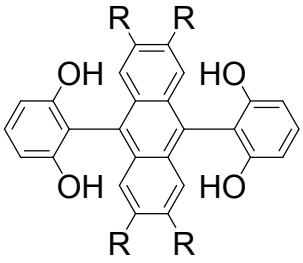
Scale: *ca.* 1 g of product

1,3-Dimethoxybenzene (**Ar (c)**) (1.46 g, 10.6 mmol, 8.20 eq.) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (1.54 mL, 10.3 mmol, 8.00 eq.) were dissolved in dry THF (25 mL) under argon and cooled to 0 °C. *n*–BuLi (1.6 M in hexane, 6.45 mL, 10.3 mmol, 8.00 eq.) was added dropwise

over 2 min, and the resulting mixture was stirred at room temperature for 30 min. In a separate flask, 2,3,6,7-tetrakis(*n*-dodecyl)anthracene-9,10-dione (**1**) (1.14 g, 1.29 mmol, 1.00 eq.) was added to dry THF (100 mL) under argon and the resulting suspension was cooled to –78 °C. The previously prepared solution of 2,6-dimethoxyphenyllithium was added over *ca.* 5 min, and the mixture was allowed to warm to room temperature overnight to afford a dark orange solution. The reaction mixture was quenched with satd. aqueous NH_4Cl solution (100 mL) and extracted with $CHCl_3$ (3 × 50 mL). The organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to obtain the crude intermediate diol (**2c**). It was dissolved in THF (50 mL) to give a near colourless solution and stirred under air at room temperature. To this, a solution of $SnCl_2 \bullet 2H_2O$ (1.22 g, 6.45 mmol, 5.00 eq.) in 6:1 v/v THF/ AcOH (105 mL) was added dropwise over 1 h. The reaction mixture turned a dark red and was stirred overnight at room temperature. The resulting near colourless solution was evaporated under reduced pressure (toluene was added to co-evaporate AcOH). The residue was then added to a mixture of DCM (100 mL) and 1 M HCl (100 mL). The layers were separated and the aqueous layer was extracted further with DCM (2 × 100 mL). The organic extracts were combined, washed with 1 M HCl (50 mL), dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: firstly 5:95 DCM/ *n*–hexane v/v to elute residual 2,6-dimethoxybenzene (**S6**), followed by a gradient to 17:83 DCM/ *n*–hexane v/v) to obtain a light brown oil. It was dissolved in minimal DCM (*ca.* 2 mL) and methanol (*ca.* 30 mL) was added to produce a precipitate. 9,10-Bis(2,6-dimethoxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**3**) was obtained as an off-white solid which was isolated via filtration and washed with methanol (1.11 g, 0.99 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (t, *J* = 8.4 Hz, 2H), 7.27 (s, 4H), 6.81 (d, *J* = 8.4 Hz, 4H), 3.57 (s, 12H), 2.62 – 2.56 (m, 8H), 1.56 – 1.46 (m, 8H), 1.36 – 1.20 (m, 72H), 0.89 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.3, 137.8, 129.3, 129.1, 127.3, 125.3, 116.9, 104.3, 56.0, 33.1, 32.1, 31.0, 29.9, 29.9, 29.8, 29.8, 29.8, 29.8, 29.5, 22.9, 14.3; HRMS (ESI): *m/z* 1145.9225 [M–Na$^+$]. Calcd. for $C_{78}H_{122}O_4Na^+$: 1145.9235.

Scale: *ca.* 23 g of product

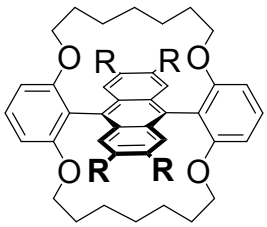
The reaction was carried out based on the smaller scale procedure. The suspension of 2,3,6,7-tetrakis(*n*-dodecyl)anthracene-9,10-dione (**1**) (22.9 g, 26.0 mmol, 1.00 eq.) was prepared in dry THF (2000 mL). The lithiated solution of **Ar (c)** (29.43 g, 213 mmol, 8.20 eq.) was prepared in dry THF (500 mL) with *N*,*N*,*N*',*N*'-tetramethylethylenediamine (24.2 g, 208 mmol, 8.00 eq.) and *n*–BuLi (1.6 M in hexane, 130 mL, 208 mmol, 8.00 eq.). The crude diol (**2c**) was obtained via the same work up procedure as on the smaller scale, but scaled up accordingly. For the aromatization step **2c** was dissolved in THF (500 mL) and treated with $SnCl_2 \bullet 2H_2O$ (24.6 g, 130 mmol, 5.00 eq.) dissolved in a mixture of THF (600 mL) and AcOH (50 mL). For work up, the solvent was removed under reduced pressure (toluene was added to co-evaporate AcOH). The residue was stirred in hot hexane (*ca.* 1500 mL) and the resulting suspension filtered through celite. The celite was then washed with further hot hexane (*ca.* 1500 mL). The solvent was removed under reduced pressure and the residue was passed through a thick plug of silica gel packed with *n*-hexane (eluent: 5:95 DCM/ *n*-hexane v/v until the fluorescent blue band began to elute, then 1:1 DCM/ *n*-hexane v/v). The residue was stirred in methanol overnight and filtered to afford 9,10-bis(2,6-dimethoxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**3**) as a light yellow solid (23.2 g, 20.6 mmol, 79%).



4

R = *n*-$C_{12}H_{25}$

9,10-Bis(2,6-dihydroxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (4). In our hands this procedure is successful in quantitative yield between 200 mg – 20 g of starting material. A representative procedure is outlined here on 10 g scale. A solution of 9,10-bis(2,6-dimethoxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**3**) (10.0 g, 8.90 mmol, 1.00 eq.) in dry DCM (1000 mL) was cooled to –78 °C in a dry ice/ acetone bath under argon. BBr_3 (1 M in DCM, 53.4 mL, 53.4 mmol, 6.00 eq.) was added dropwise and the resulting mixture was allowed to warm to room temperature overnight. It was stirred at room temperature for a further 24 h, and the reaction progress was monitored by ^{1}H NMR. The resulting dark solution was then cooled in an ice bath, quenched with satd. $NaHCO_3$ (200 mL) and the layers separated. The aqueous layer was further extracted with DCM (2 × 100 mL) and the organic extracts combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient 5:95–1:1 DCM/ *n*-hexane v/v) to obtain 9,10-bis(2,6-dihydroxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**4**) as a brown oil (9.40 g, 8.80 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.48 (s, 4H), 7.42 (t, J = 8.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 4H), 4.51 (bs, 4H), 2.71 – 2.64 (m, 8H), 1.59 – 1.46 (m, 8H), 1.38 – 1.20 (m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 154.5, 141.9, 130.5, 130.3, 124.4, 123.3, 111.2, 107.9, 33.0, 31.9, 30.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 22.7, 14.1; HRMS (ASAP): *m/z* 1067.8776 [M–H$^+$]. Calcd. for $C_{78}H_{115}O_4^+$: 1067.8795.



5

R = *n*-$C_{12}H_{25}$

(5).

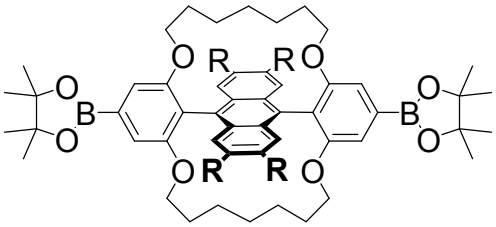
Scale: *ca.* 10 g of product

9,10-Bis(2,6-dihydroxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**4**) (21.4 g, 20.0 mmol, 1.00 eq.) and 1,7-dibromoheptane (10.4 g, 40.0 mmol, 2.00 eq.) were dissolved in dry acetone (500 mL) under argon. Two suspensions of K_2CO_3 (9.70 g, 70.2 mmol, 3.50 eq.) in dry acetone (2.3 ltr) were also prepared under argon and heated to reflux. The aforementioned solution of **4** and 1,7-dibromoheptane was then divided into two equal portions which were added dropwise to the K_2CO_3 suspensions over 1.5 h. The resulting mixtures were then heated to reflux for 3 days. The solvent from both reactions was evaporated under reduced pressure before the residues were combined and partitioned between DCM (500 mL) and water (500 mL). The aqueous layer was acidified with 6 M HCl

and the layers were separated. The aqueous layer was further extracted with DCM (4 × 100 mL) and the organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient 0:1–12:98 DCM/ *n*-hexane v/v) to obtain **5** as a light oil which solidified to a yellow-white solid after either drying under high vacuum or trituration with methanol (10.7 g, 8.47 mmol, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.42 (t, *J* = 8.2 Hz, 2H), 7.27 (s, 4H), 6.81 (d, *J* = 8.2 Hz, 4H), 3.72 (t, *J* = 5.3 Hz, 8H), 2.64 – 2.56 (m, 8H), 1.54 – 1.45 (m, 8H), 1.35 – 1.20 (m, 80H), 1.08 (td, *J* = 10.9, 5.5 Hz, 8H), 0.88 (t, *J* = 6.8 Hz, 12H), 0.62 – 0.54 (m, 4H), 0.49 – 0.39 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 159.2, 137.1, 129.2, 128.7, 127.5, 125.5, 120.2, 107.9, 69.7, 33.0, 32.0, 31.3, 29.7, 29.7, 29.7, 29.7, 29.7, 29.6, 29.4, 29.1, 27.9, 24.9, 22.7, 14.13; HRMS (ASAP): *m/z* 1260.0695 [M–H$^+$]. Calcd. for $C_{88}H_{139}O_4^+$: 1260.0673.

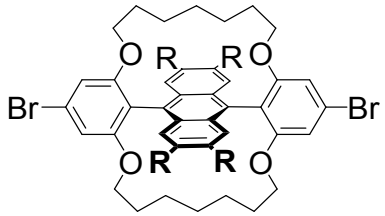
Scale: *ca.* 100 mg of product

A similar procedure was followed in a single flask starting from 9,10-bis(2,6-dihydroxyphenyl)-2,3,6,7-tetrakis(*n*-dodecyl)anthracene (**4**) (200 g, 0.19 mmol, 1.00 eq.), 1,7-dibromoheptane (103 mg, 0.40 mmol, 2.12 eq.) and K_2CO_3 (129 mg, 0.94 mmol, 5.00 eq.) in dry acetone (10 mL for tetrol, 40 mL for alkyl halide). The same work up and purification procedure was followed as on large scale. **5** was obtained as a white solid (87 mg, 0.07 mmol, 37%).



6
R = *n*-$C_{12}H_{25}$

(6). In a nitrogen glovebox, (**5**) (600 mg, 0.48 mmol, 1.00 eq.), bis(pinacolato)diboron (282 mg, 1.11 mmol, 2.33 eq.), $[Ir(OMe)(COD)]_2$ (23.8 µmol, 0.05 eq.), and 3,4,7,8-tetramethyl-1,10-phenanthroline (47.6 µmol, 0.10 eq.) were added to a 20 mL oven dried microwave vial. The vial was sealed with a crimped septum cap and removed from the glovebox. Dry THF (11 mL) was added and the mixture was stirred in a preheated 80 °C oil bath protected from light for 16 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: 15:85 DCM/ *n*-hexane v/v to remove trace unreacted **5**, followed by 1:3 DCM/ *n*-hexane v/v to elute any mono-borylated intermediate and 30:70 DCM/ *n*-hexane v/v to elute **6**) to obtain **6** as a pale viscous oil which solidified to a yellow-white solid after trituration with methanol and drying under high vacuum (340 mg, 0.23 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.23 (bs, 8H), 3.78 (t, *J* = 5.3 Hz, 8H), 2.61 – 2.53 (m, 8H), 1.52 – 1.40 (m, 32H), 1.36 – 1.19 (m, 80H), 1.08 (td, *J* = 10.7, 5.5 Hz, 8H), 0.87 (t, *J* = 6.8 Hz, 12H), 0.57 (dd, *J* = 13.4, 6.6 Hz, 4H), 0.47 – 0.37 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.7, 137.2, 129.0, 127.6, 125.7, 123.5, 113.5, 83.88, 69.51, 33.21, 31.94, 31.68, 29.79 – 29.63 (5C), 29.38, 29.20, 28.00, 25.02, 24.97, 22.70, 14.12; HRMS (ASAP): *m/z* 1511.2333 [M$^+$]. Calcd. for $C_{100}H_{160}B_2O_8^+$: 1511.2299; Anal. Calcd. for $C_{100}H_{160}{}^{11}B_2O_8$: C, 79.44; H, 10.67. Found: C, 79.54; H, 10.60 (average of two runs). The C–B carbon environment was not detected by ^{13}C NMR because of signal broadening due to the quadrupolar relaxation of ^{11}B. Some aliphatic signals heavily overlap in the ^{13}C NMR spectrum and so are reported as a range.

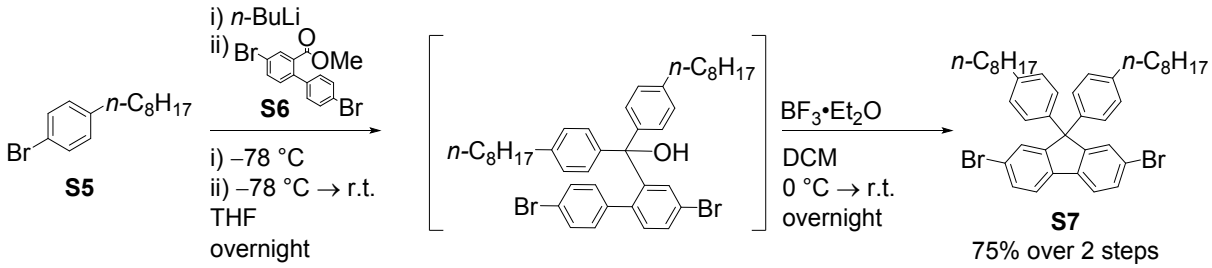


7

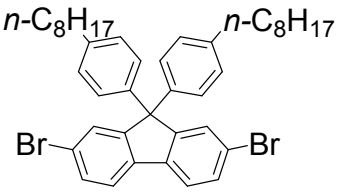
R = *n*-$C_{12}H_{25}$

(7). *While the yield of this procedure is reproducible, the required reaction time appears to be heavily dependent on the purity of the starting material. Using even slightly discoloured* **6** *(otherwise pure by* ^{1}*H NMR) can increase the required reaction time to 1 week.* **6** (300 mg, 0.20 mmol, 1.00 eq.) was dissolved in a mixture of degassed THF (25.5 mL) and methanol (17 mL) in a pressure tube. A degassed solution of $CuBr_2$ (253 mg, 1.13 mmol, 5.70 eq.) in water (17 mL) was added and the tube was sealed under argon. It was then submerged in a preheated 100 °C oil bath and stirred protected from light (min. 28 h, max 1 week). The solvents were evaporated and the residue was partitioned between DCM (25 mL) and 1M HCl (25 mL). The layers were separated and the aqueous layer was further extracted with DCM (4 × 25 mL). The organic layers were combined, washed with 1 M HCl (20 mL), dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient 0:1–1:9 DCM/ *n*-hexane v/v) and the first luminescent blue band to elute was collected. The residue was dried under high vacuum to afford **7** as a yellow-white solid (98 mg, 69 µmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.23 (s, 4H), 6.95 (s, 4H), 3.71 (t, *J* = 5.3 Hz, 8H), 2.66 – 2.58 (m, 8H), 1.53 – 1.45 (m, 8H), 1.37 – 1.19 (m, 80H), 1.08 (td, *J* = 10.7, 5.5 Hz, 8H), 0.88 (t, *J* = 6.8 Hz, 12H), 0.61 – 0.52 (m, 4H), 0.44 – 0.34 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.4, 137.6, 129.0, 126.6, 125.3, 121.6, 118.9, 111.4, 69.7, 33.0, 32.0, 31.4, 29.8 – 29.7 (6C), 29.4, 29.0, 27.9, 24.9, 22.7, 14.13; HRMS (ASAP): *m/z* 1415.8824 [M–H$^+$]. Calcd. for $C_{88}H_{137}{}^{79}Br_2O_4^+$: 1415.8884; Anal. Calcd. for $C_{88}H_{136}Br_2O_4$: C, 74.55; H, 9.67. Found: C, 74.32; H, 9.57 (average of two runs). Some aliphatic signals heavily overlap in the ^{13}C NMR spectrum and so are reported as a range.

Synthesis of 9,9-diarylfluorene monomer



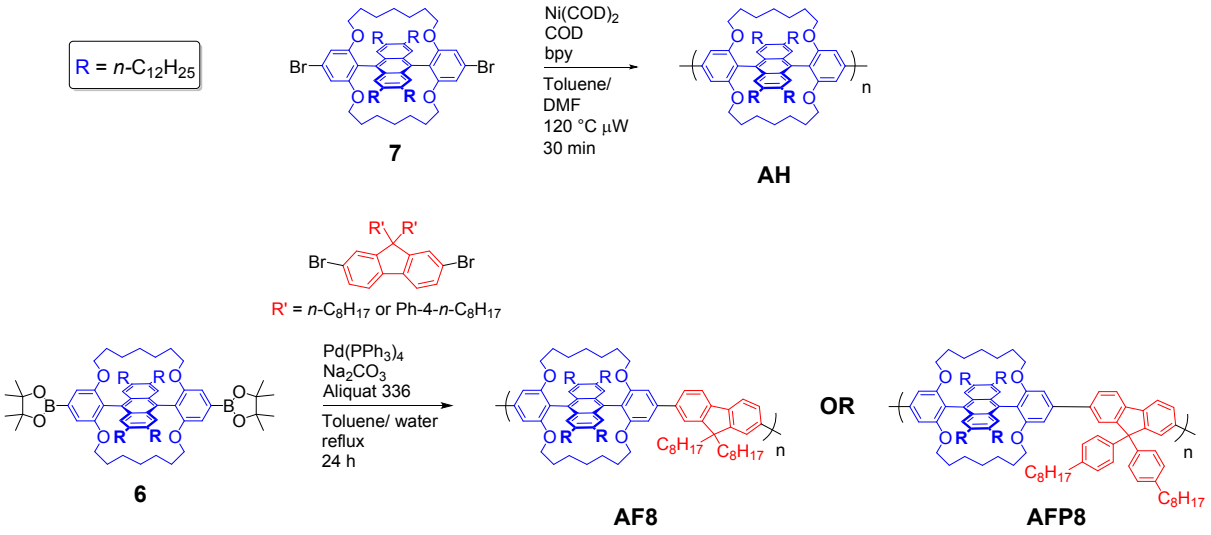
Scheme S2. Synthesis of the polymer precursor **S7**.



S7

2,7-Dibromo-9,9-bis(4-*n*-octylphenyl)fluorene (**S7**). *While poly(9,9-bis(4-n-octylphenyl)fluorene has been previously studied,*[5] *to the best of our knowledge the synthesis and full characterisation of this monomer have not been reported in the academic literature prior to this study*. A solution of 4-*n*-octylbromobenzene (**S5**) (5.00 g, 18.6 mmol, 2.33 eq.) in dry THF (200 mL) was cooled to −78 °C in a dry ice bath under argon. *n*-BuLi (1.6 M in *n*-hexane, 11.6 mL, 18.6 mmol, 2.33 eq.) was added dropwise and the resulting mixture was stirred at −78 °C for 3 h. A solution of methyl-4,4'-dibromobiphenyl-2-carboxylate (**S6**)[6] (2.96 g, 8.00 mmol, 1.00 eq.) in dry THF (50 mL) was then added dropwise to the lithiated solution, and the resulting mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with satd. aqueous NH_4Cl solution (500 mL) and extracted with $CHCl_3$ (3 × 100 mL). The organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to obtain the crude intermediate tertiary alcohol as a yellow oil. It was dissolved in dry DCM (200 mL) under argon and the resulting solution was cooled to 0 °C in an ice bath. BF_3 diethyl etherate (2.81 mL, 22.8 mmol, 2.85 eq.) was added dropwise and the mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with ice water (*ca.* 300 mL) and the layers were separated. The organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified twice by flash chromatography on silica gel (eluent: *n*-hexane) to obtain 2,7-dibromo-9,9-bis(4-*n*-octylphenyl)fluorene (**S7**) as a viscous colourless oil (4.20 g, 6.00 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 (d, J = 8.1 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.08 – 7.00 (m, 8H), 2.59 – 2.51 (m, 4H), 1.63 – 1.55 (m, 4H), 1.37 – 1.20 (m, 20H), 0.91 – 0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 153.6, 142.0, 141.8, 138.2, 130.9, 129.6, 128.6, 128.0, 121.9, 121.6, 65.3, 35.7, 32.0, 31.5, 29.6, 29.6, 29.4, 22.8, 14.3; HRMS (ASAP): *m/z* 699.2170 [M–H$^+$]. Calcd. for $C_{41}H_{49}{}^{79}Br_2{}^+$: 699.2201; Anal. Calcd. for $C_{41}H_{48}Br_2$: C, 70.29; H, 6.91. Found: C, 70.43; H, 7.06 (average of two runs).

Synthesis of Polymers



Scheme S3. Synthesis of the conjugated polymers.

Suzuki polycondensation general procedure. The diboronic acid bis(pinacol) ester **6** (85.0 mg, 56.2 µmol, 1.00 eq.), dibromoarylene monomer (56.2 µmol, 1.00 eq.) and $Pd(PPh_3)_4$ (0.6 mg, 0.6 µmol, 1 mol%.) were combined in a 5 mL crimp cap microwave vial under argon. Degassed toluene (2 mL w/ 1 drop Aliquat 336) and degassed 2 M aqueous Na_2CO_3 (0.25 mL) were then added sequentially to the reaction vessel. The resulting mixture was degassed with argon for 5 min and then submerged in a preheated 115 °C oil bath overnight (minimum 16 h) protected from light. The reaction mixture was cooled to room temperature and then added dropwise into vigorously stirring methanol (200 mL) to precipitate the crude polymer which was filtered into a Soxhlet thimble. It was washed sequentially in a Soxhlet apparatus with acetone (2 h) and *n*-hexane (overnight, minimum 16 h) before it was extracted with chloroform (1 h) The solvent volume was reduced to *ca.* 2 mL and the residue added dropwise into vigorously stirring methanol (200 mL) to precipitate the desired polymers, which were isolated via filtration and washed copiously with acetone.

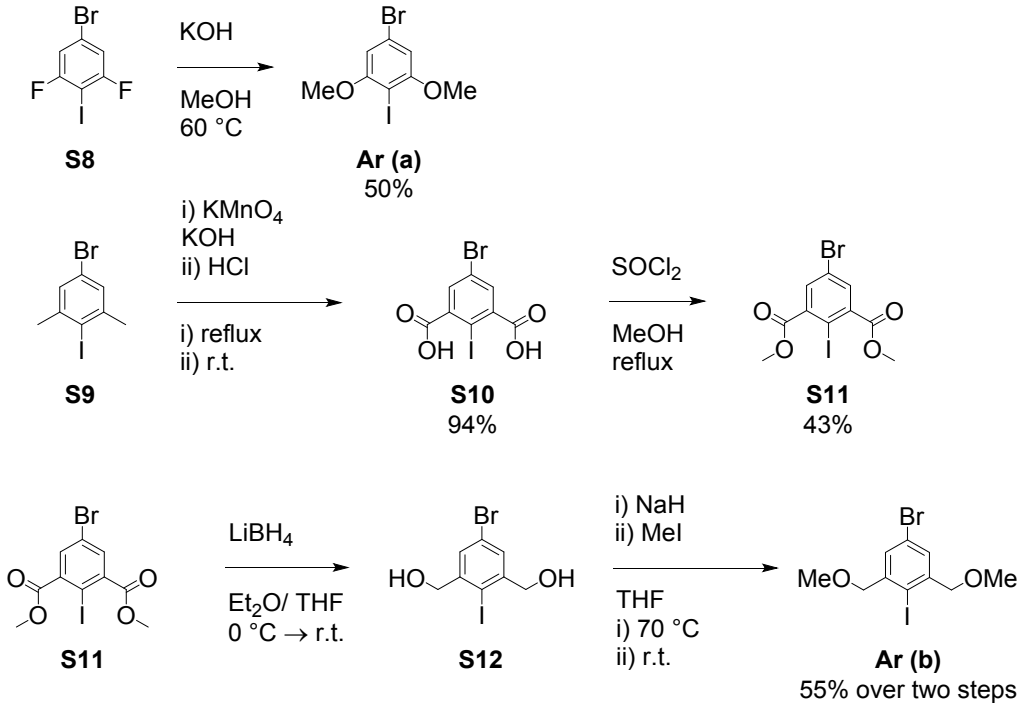
AF8 Yellow film (38 mg, 23 µmol, 41%). GPC (chlorobenzene) M_n = 35,000, M_w = 56,000, PDI = 1.6.

AFP8 Dark yellow film (43 mg, 24 µmol, 43%). GPC (chlorobenzene) M_n = 31,000, M_w = 46,000, PDI = 1.5

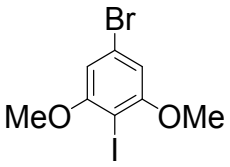
AH. In a nitrogen glovebox, $Ni(COD)_2$ (66.0 mg, 0.24 mmol, 2.50 eq.) and 2,2'-bipyridine (27.7 mg, 0.24 mmol, 2.50 eq.) were added to a 5 mL oven dried microwave vial. The vial was sealed with a crimped septum cap and removed from the glovebox. The vial was flushed with argon via a syringe needle for 5 mins before a solution of 1,5-cyclooctadiene (30 µL, 0.24 mmol, 2.50 eq.) in dry, degassed *N*,*N*-dimethylformamide (970 µL) was added. The resulting mixture was briefly sonicated and then stirred in a 60 °C oil bath for 10 min to afford a blue/purple mixture. A solution of **7** (137 mg, 96.6 µmol, 1.00 eq.) in dry, degassed toluene (5 mL) was added and the reaction mixture was heated in a microwave reactor at 120 °C for 30 min. The reaction mixture was cooled to room temperature and then added

dropwise into a vigorously stirred mixture of methanol (200 mL) and conc. HCl (10 mL) to precipitate the crude polymer which was filtered into a Soxhlet thimble. It was washed sequentially in a Soxhlet apparatus with acetone (1 h) and *n*-hexane (overnight, minimum 16 h) before it was extracted with chloroform (1 h). The solvent was evaporated under reduced pressure and the residue was dissolved in minimal chlorobenzene (< 3 mL). The concentrated solution was then added dropwise into vigorously stirring methanol (200 mL) and the precipitated polymer fibres were isolated via filtration and washed copiously with acetone. Light yellow fibres (60 mg, 48 μmol, 50%). GPC (chlorobenzene) M_n = 66,000, M_w = 110,000, PDI = 1.7.

Synthesis of intermediates for the unsuccessful route

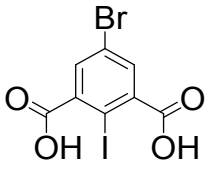


Scheme S4. Synthesis of synthetic intermediates.



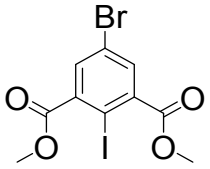
Ar (a)

4-Bromo-2,6-dimethoxyiodobenzene (Ar (a)).[7] A methanolic solution of potassium hydroxide was prepared by through portionwise addition of KOH (10 × 2.93 g, 522 mmol, 11.1 eq.) to dry methanol (338 mL) under argon at 5 °C over 30 min. This solution was added dropwise over 30 min to a solution of 4-bromo-2,6-difluoroiodobenzene (**S8**) (15.0 g, 47.0 mmol, 1.00 eq.) in dry methanol (9 mL) at 60 °C over 30 min. The resulting mixture was heated to 60 °C for a week. It was then cooled to room temperature and concentrated under reduced pressure. The residue was partitioned between ethyl acetate (100 mL) and water (250 mL) and the layers were separated. The aqueous layer was further extracted (3 × 50 mL) and the organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to obtain a white solid (9.29 g, 27.1 mmol, 58%). It was heated to reflux in hexane (200 mL) and ethanol was added until full dissolution was observed. The resulting solution was cooled to room temperature overnight and then to −15 °C for 24 h to obtain 4-bromo-2,6-dimethoxyiodobenzene (**Ar (a)**) as colourless crystals (7.99 g, 23.3 mmol, 50%). ^{1}H NMR data were in accordance with those reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.65 (s, 2H), 3.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =160.0, 123.6, 108.0, 76.4, 57.0.



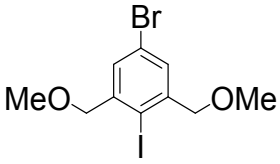
S10

5-Bromo-2-iodoisophthalic acid (S10). 5-Bromo-2-iodo-*meta*-xylene (**S9**) (100 g, 321 mmol, 1.00 eq.) was added to celite (200 g) in t-BuOH/ H_2O (1:1 v/v, 1000 mL) and the resulting mixture heated in a 110 °C oil bath. KOH was added (ca. 5 g) followed by portionwise addition of $KMnO_4$ (264 g, 1.67 mol, 5.20 eq.) over *ca.* 5 h. The oil bath temperature was reduced to 90 °C and stirring continued for a further 60 h. Unreacted $KMnO_4$ was quenched by addition of ethanol (100 mL) and the reaction mixture was filtered hot through a pad of celite, which was subsequently washed with 1 M NaOH (1000 mL). The mixture was concentrated under reduced pressure (*ca.* 1000 mL), cooled in an ice bath and acidified with conc. HCl (*ca.* pH 1) to precipitate a white powder. It was isolated by filtration, washed with ice cold water (3 × 100 mL) and dried under suction to obtain crude 5-bromo-2-iodoisophthalic acid (**S10**) (111.8 g, 301 mmol, 94%) which was used directly in the next step. ^{1}H NMR data were in accordance with those reported in the literature.[8] ^{1}H NMR (400 MHz, DMSO) δ (ppm) = 7.80 (s, 2H).



S11

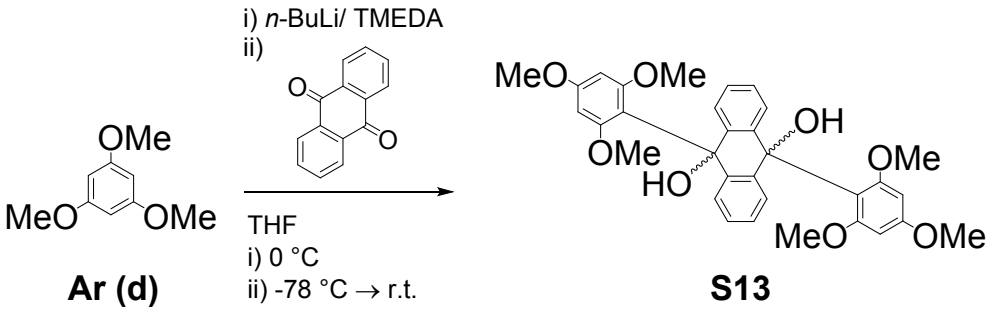
Dimethyl 5-bromo-2-iodoisophthalate (S11). 5-Bromo-2-iodoisophthalic acid (**S10**) (111.8 g, 301 mmol, 1.00 eq.) was added to methanol (510 mL) under argon and the reaction mixture cooled in a salt ice bath. Thionyl chloride (61 mL, 835 mmol, 2.78 eq.) was added dropwise and the resulting mixture heated to reflux overnight. The reaction mixture was cooled to room temperature and white solid precipitated. It was isolated via filtration and washed with ice cold methanol of afford dimethyl 5-bromo-2-iodoisophthalate (**S11**) as a white powder (51 g, 128 mmol, 43%). ^{1}H NMR data were in accordance with those reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.74 (s, 1H), 3.94 (s, 3H). A higher yield has been reported for this procedure in the literature, but after aqueous workup and purification by flash chromatography.[8]



Ar (b)

4-Bromo-2,6-bis(methoxymethyl)iodobenzene (Ar (b)). To a solution of dimethyl 5-bromo-2-iodoisophthalate (**S11**) (23.5 g, 58.9 mmol, 1.00 eq.) in dry diethyl ether (500 mL) was added a mixture of $LiBH_4$ (2.82 g, 129 mmol, 2.20 eq.) in dry THF (170 mL) dropwise under argon. The resulting mixture was warmed to room temperature overnight and then carefully quenched with 1 M HCl (100 mL). It was then extracted with diethyl ether (3 × 100 mL) and the organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was triturated with *n*-hexane and filtered to obtain the intermediate 4-bromo-2,6-bis(hydroxymethyl)iodobenzene (**S12**) (19.2 g, 56 mmol, 95%) which was used as obtained. A solution of the intermediate (19.1 g, 55.7

mmol, 1.00 eq.) in dry THF (200 mL) was added dropwise to a suspension of NaH (60% suspension in mineral oil, 5.8 g, 144.6 mmol, 2.60 eq.) in dry THF (300 mL) cooled in a salt ice bath under argon. The resulting mixture was warmed to room temperature and then refluxed for 1.5 h. It was then cooled to room temperature and methyl iodide (13.87 mL, 223 mmol, 4.00 eq.) was added. Stirring was continued overnight before quenching the reaction mixture with satd. NH_4Cl (100 mL). It was then extracted with diethyl ether (1 × 200 mL, 2 × 100 mL) and the organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was firstly purified by flash chromatography on silica gel (eluent: gradient 0:1 → 5:95 EtOAc/ *n*-hexane v/v) and then by recrystallisation from *n*-hexane (100 mL, reflux → −15 °C) to obtain 4-bromo-2,6-bis(methoxymethyl)iodobenzene (**Ar (b)**) as white crystals (12.1 g, 32.6 mmol, 55% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 (s, 2H), 4.43 (s, 4H), 3.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.9, 130.3, 123.2, 98.2, 78.4, 58.9; HRMS (ASAP): *m/z* 369.9067 [M^+]. Calcd. for $C_{10}H_{12}O_2$ $^{79}Br^{127}I^+$: 369.9065.



Scheme S5. Synthesis of **S13**.

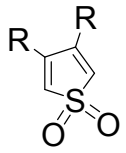
(S13). 1,3,5-Trimethoxybenzene (**Ar (d)**) (640 mg, 3.80 mmol, 3.95 eq.) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (0.56 mL, 3.74 mmol, 3.90 eq.) were dissolved in dry THF (5 mL) under argon and cooled to 0 °C. *n*–BuLi (1.6 M in hexane, 2.34 mL, 3.74 mmol, 3.90 eq.) was added dropwise over 2 min, and the resulting mixture was stirred at room temperature for 1 h. In a separate flask, anthraquinone (200 mg, 0.96 mmol, 1.00 eq.) was added to dry THF (20 mL) under argon and the resulting suspension was cooled to –78 °C. The previously prepared solution of 1,3,5-trimethoxyphenyllithium was added over *ca.* 5 min, and the mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with methanol (80 mL) and filtered to obtained crude **S13** as a white powder that was washed with further methanol (3 × 10 mL) (434 mg, 0.80 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.36 – 7.32 (m, 4H), 7.16 (s, 2H), 7.12 – 7.08 (m, 4H), 6.15 (bs, 4H), 3.77 (s, 6H), 3.59 (bs, 12H).

X-Ray Crystallography

Single-crystal X-ray diffraction data were collected for **6** on a Bruker D8-QUEST instrument, fitted with an Incoatec IμS Cu microsource and PHOTON-100 CMOS detector. The structure was solved using SHELXT[9] and refined using SHELXL.[10] The diffraction pattern showed a rapid drop-off in intensity at higher diffraction angle, with $I/\sigma(I)$ falling below 3.0 around 1.10 Å resolution. This is not unexpected for this large molecule, particularly with the dodecyl chains. The data are truncated at 1.00 angstrom for the refinement and the precision of the result is correspondingly restricted. The molecules are situated on crystallographic inversion centres, and the core of the molecule is well resolved. The dodecyl chains are also quite well resolved until about the last three C atoms in each chain, which have large displacement ellipsoids. The C-C and 1,3-C···C distances are restrained along the chain (using one free variable) and the displacement parameters are restrained with a tight ISOR restraint. The geometry towards the end of the dodecyl chains, and especially the geometically-placed H atoms, is highly uncertain, and some usually short intermolecular contacts should not be over-interpreted.

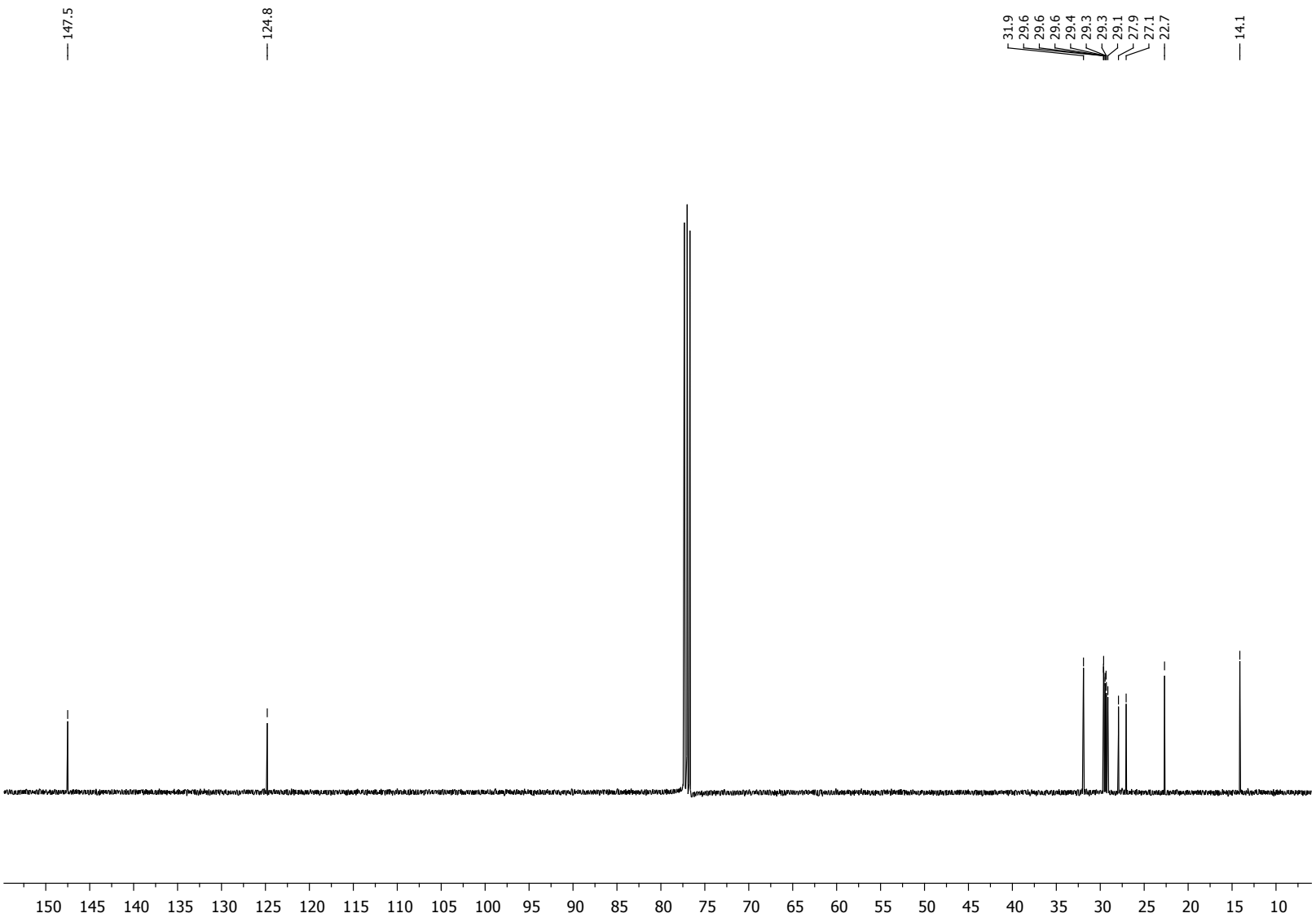
CCDC number	2024118
Cambridge data number	HB_B1_0007
Chemical formula	$C_{100}H_{160}B_2O_8$
Formula weight	1511.89
Temperature / K	180(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a / angstrom	19.2620(7)
b / angstrom	12.5345(5)
c / angstrom	21.0985(8)
alpha / degrees	90
beta / degrees	110.846(2)
gamma / degrees	90
Unit-cell volume / angstrom^3	4760.6(3)
Z	2
Calc. density / g cm^{-3}	1.055
F(000)	1668
Radiation type	CuKα
Absorption coefficient / mm^{-1}	0.488
Crystal size / mm3	0.22 x 0.20 x 0.03
2-Theta range / degrees	4.91-100.86
Completeness to max 2-theta	1.000
No. of reflections measured	37058
No. of independent reflections	4996
R_{int}	0.089
No. parameters / restraints	497 / 342
Final R1 values (I > 2σ(I))	0.098
Final wR(F^2) values (all data)	0.152
Goodness-of-fit on F^2	1.033
Largest difference peak & hole / e angstrom^{-3}	0.594, -0.284

NMR spectra

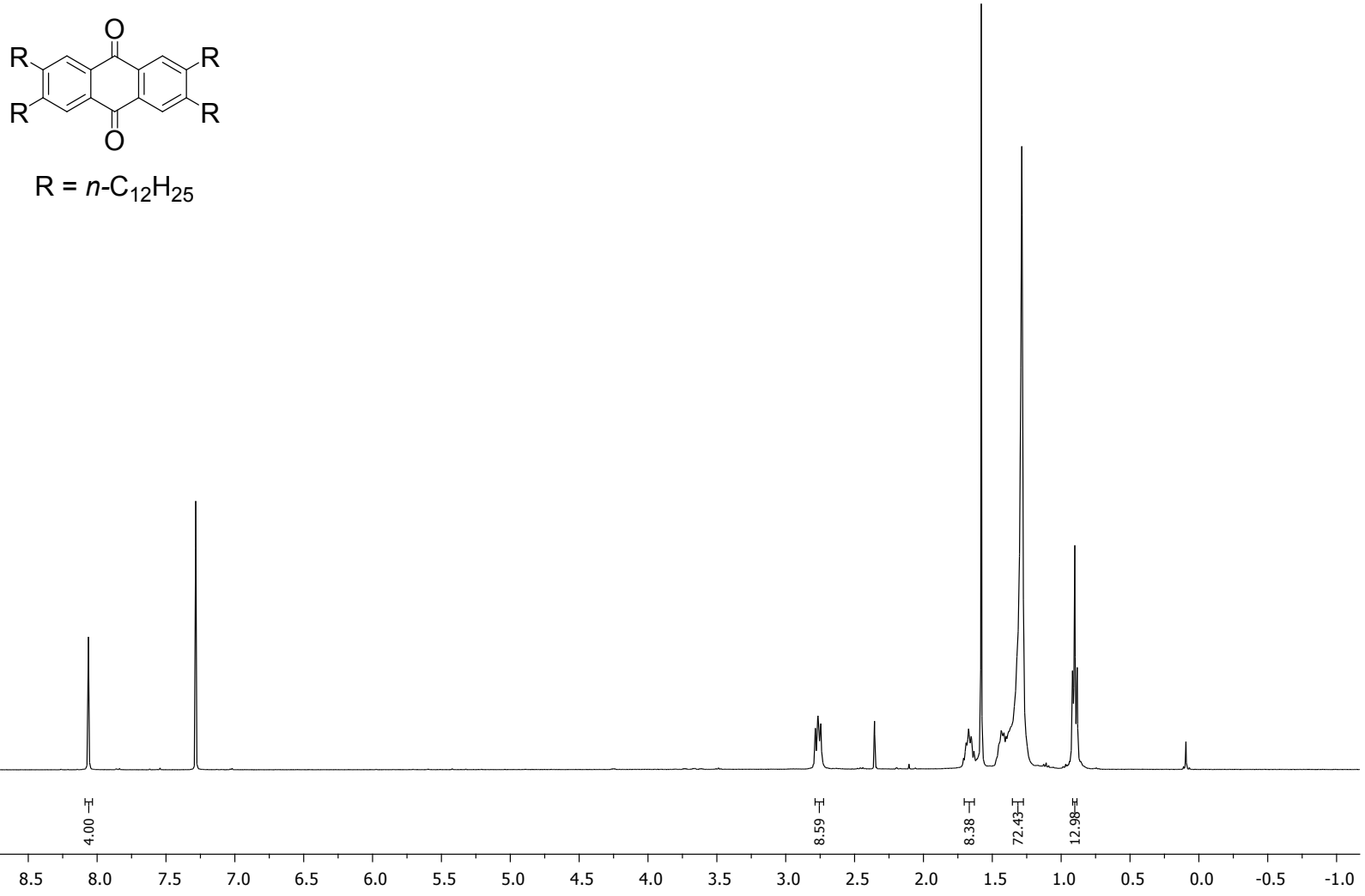


R = *n*-$C_{12}H_{25}$

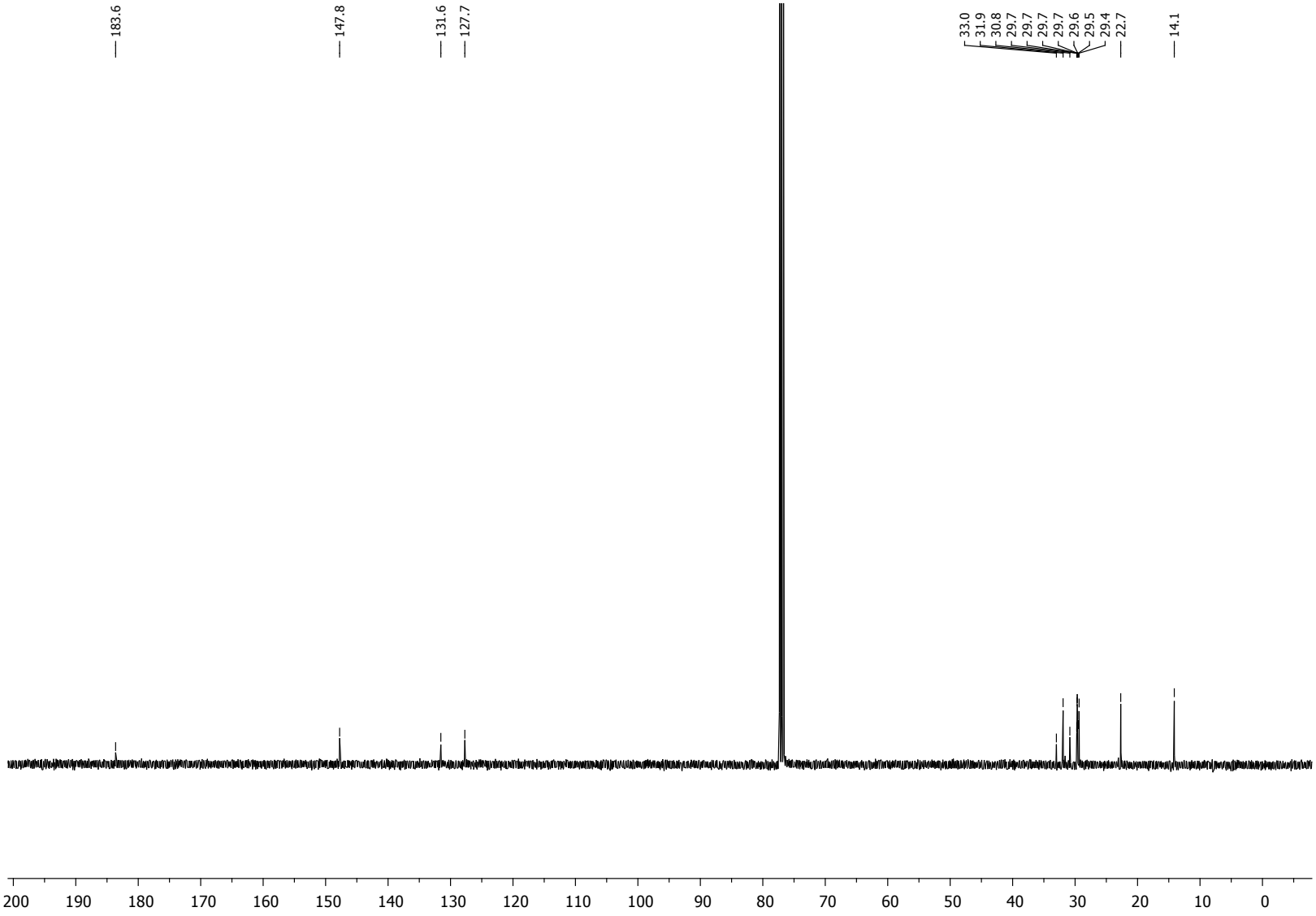
Spectrum S1. ^{1}H NMR spectrum of **S3** in $CDCl_3$.



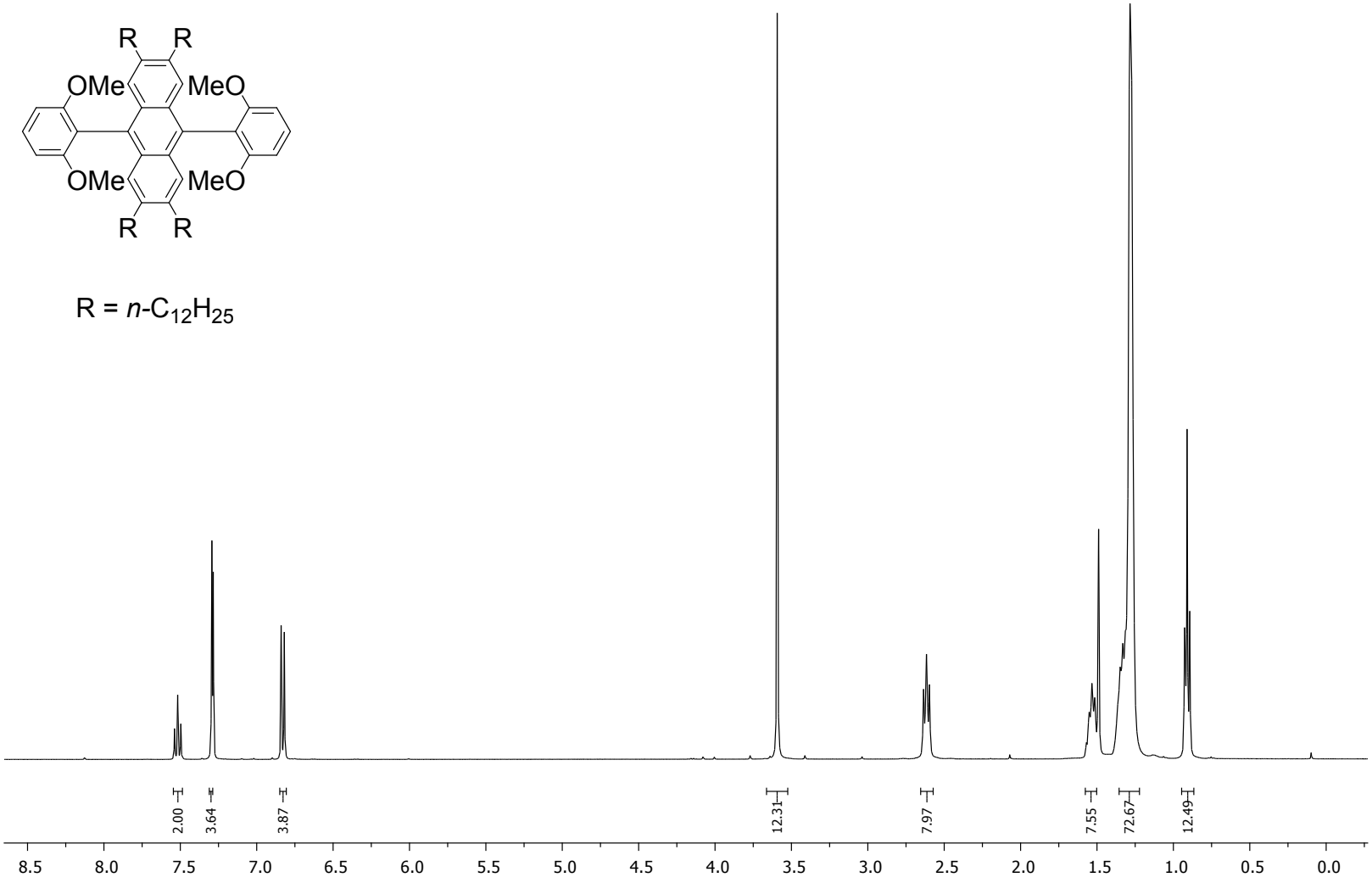
Spectrum S2. ^{13}C NMR spectrum of **S3** in $CDCl_3$.


O
R
R
R
R
O
R = n-C12H25
4.00
8.59
8.38
72.43
12.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

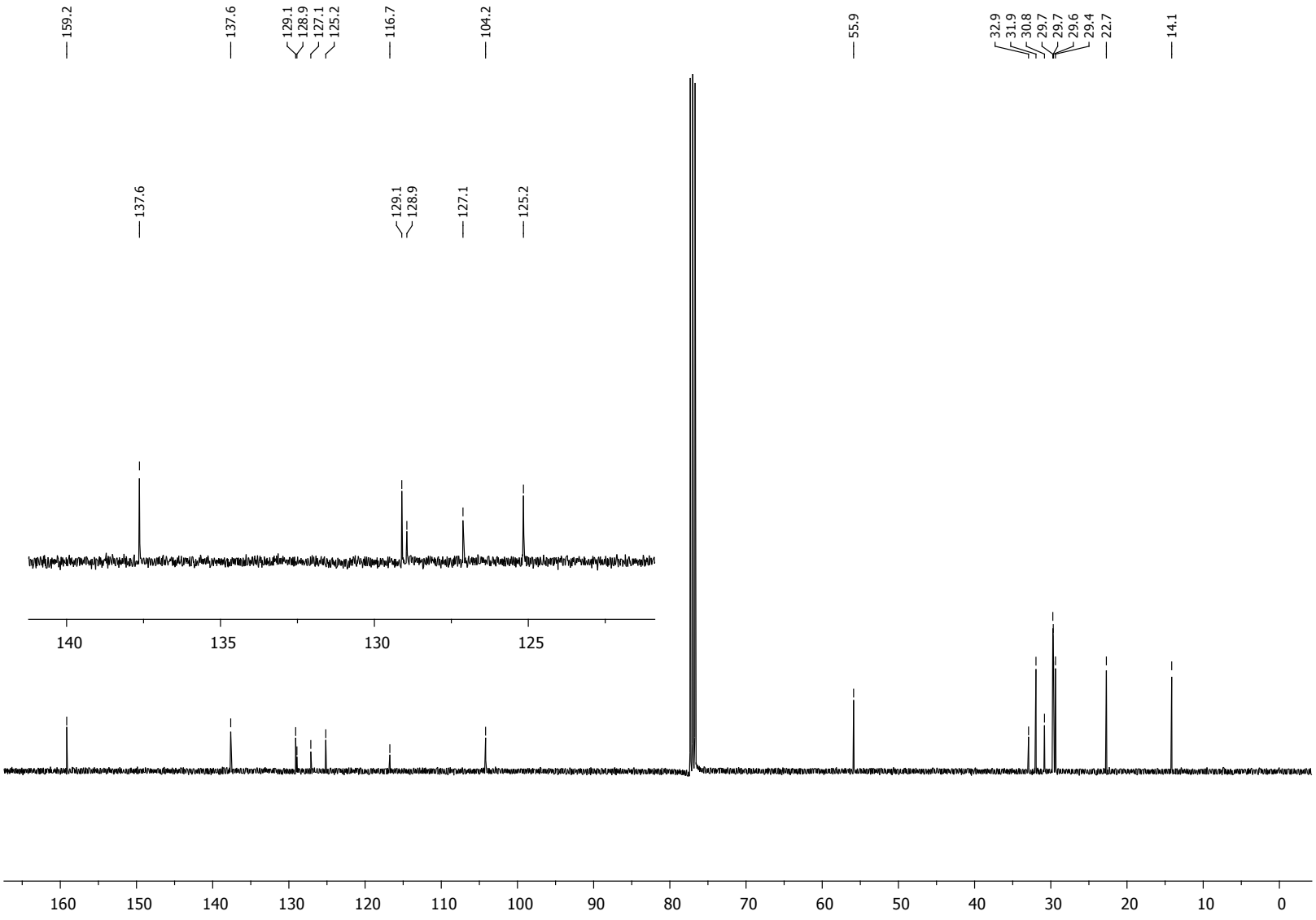
Spectrum S3. ^{1}H NMR spectrum of **1** in $CDCl_3$.



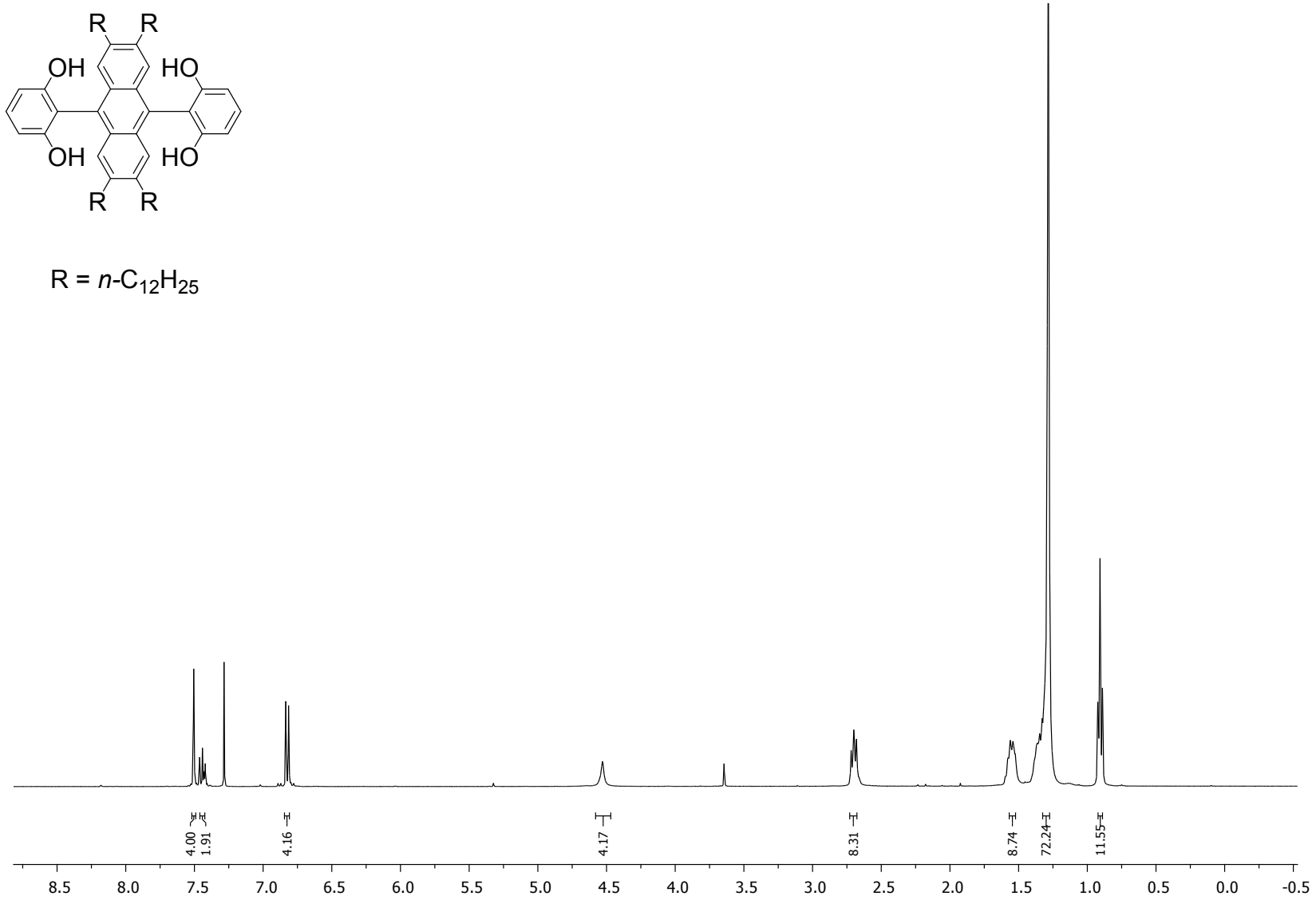
Spectrum S4. ^{13}C NMR spectrum of **1** in $CDCl_3$.



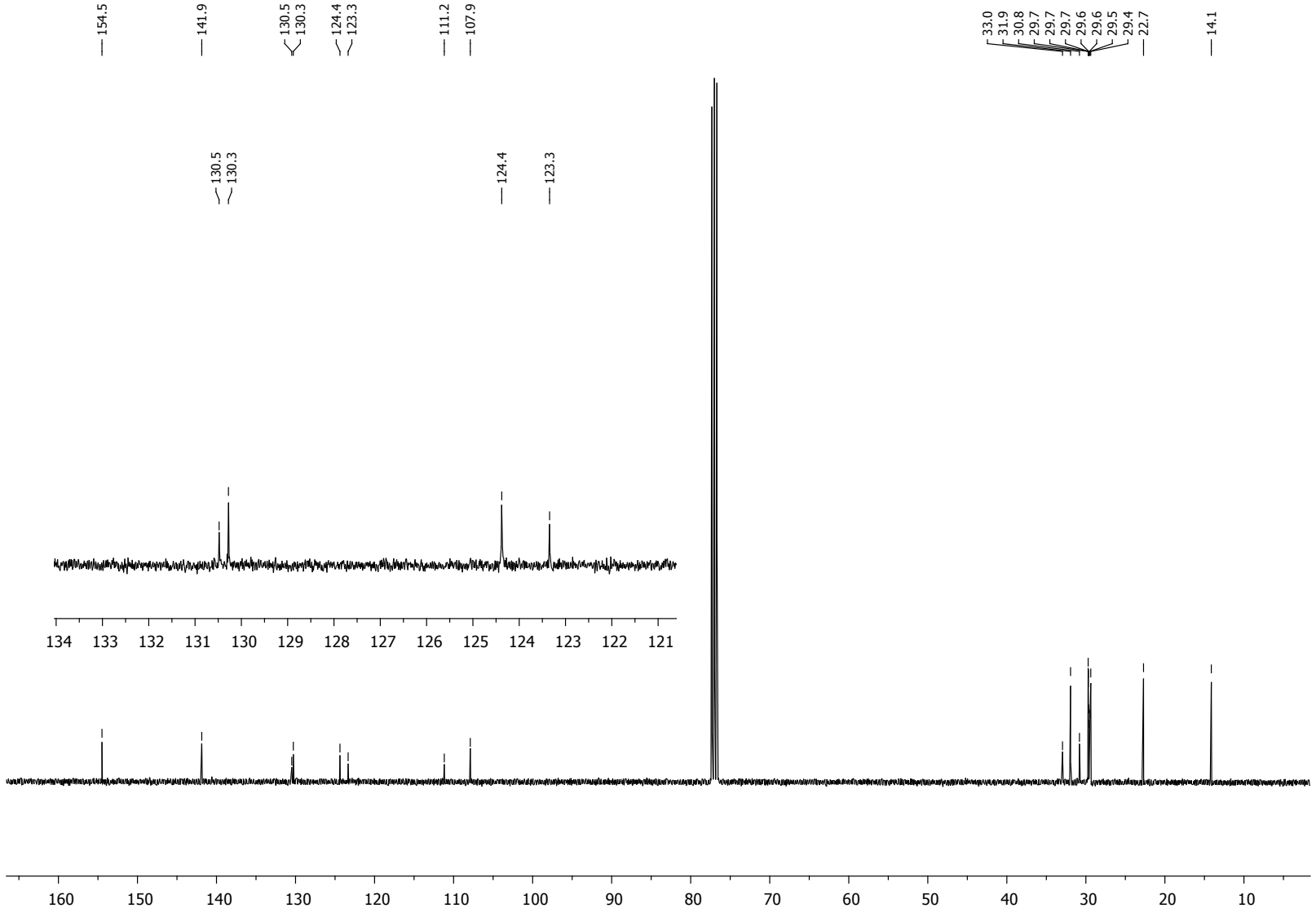
Spectrum S5. ^{1}H NMR spectrum of **3** in $CDCl_3$.



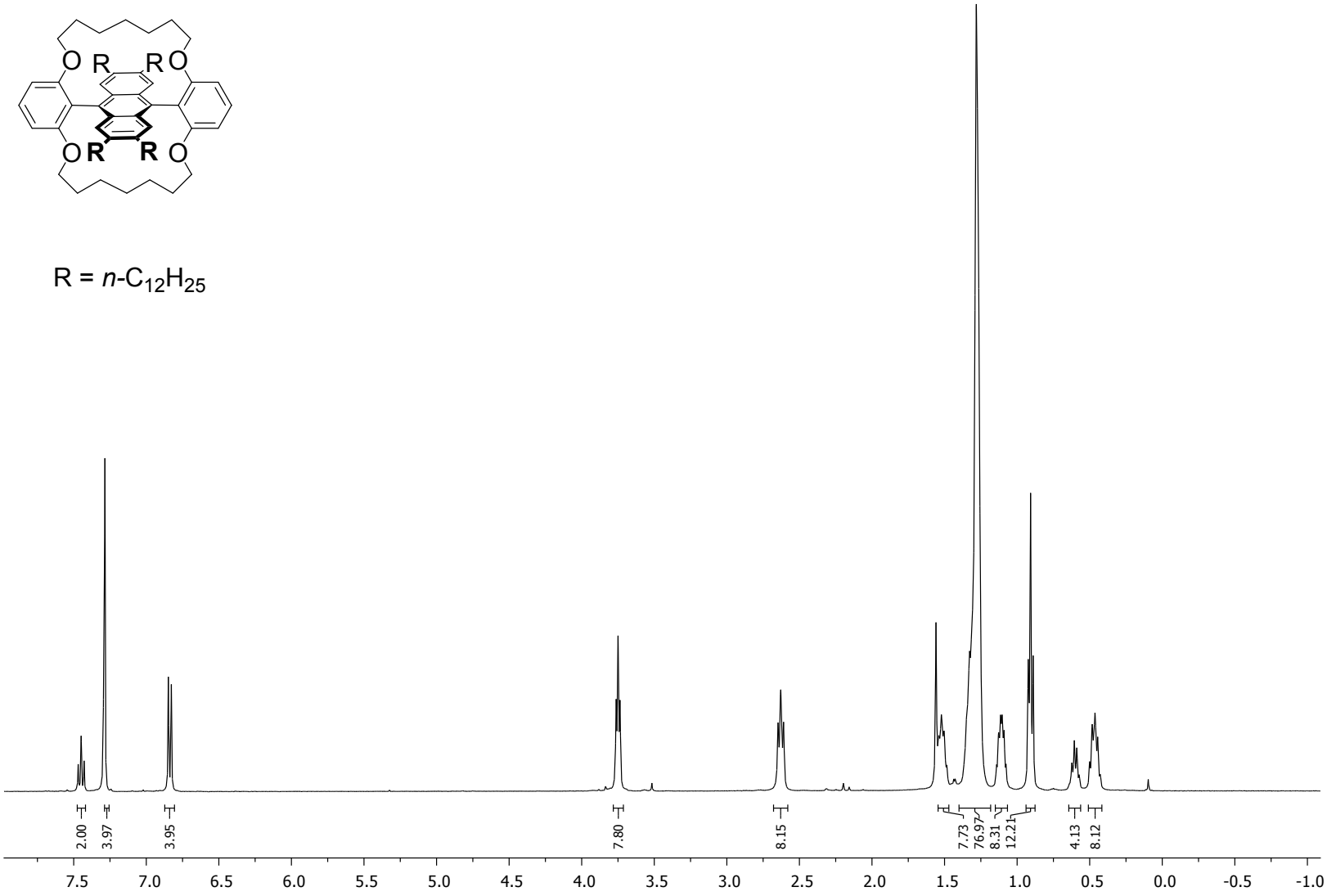
Spectrum S6. ^{13}C NMR spectrum of **3** in $CDCl_3$.



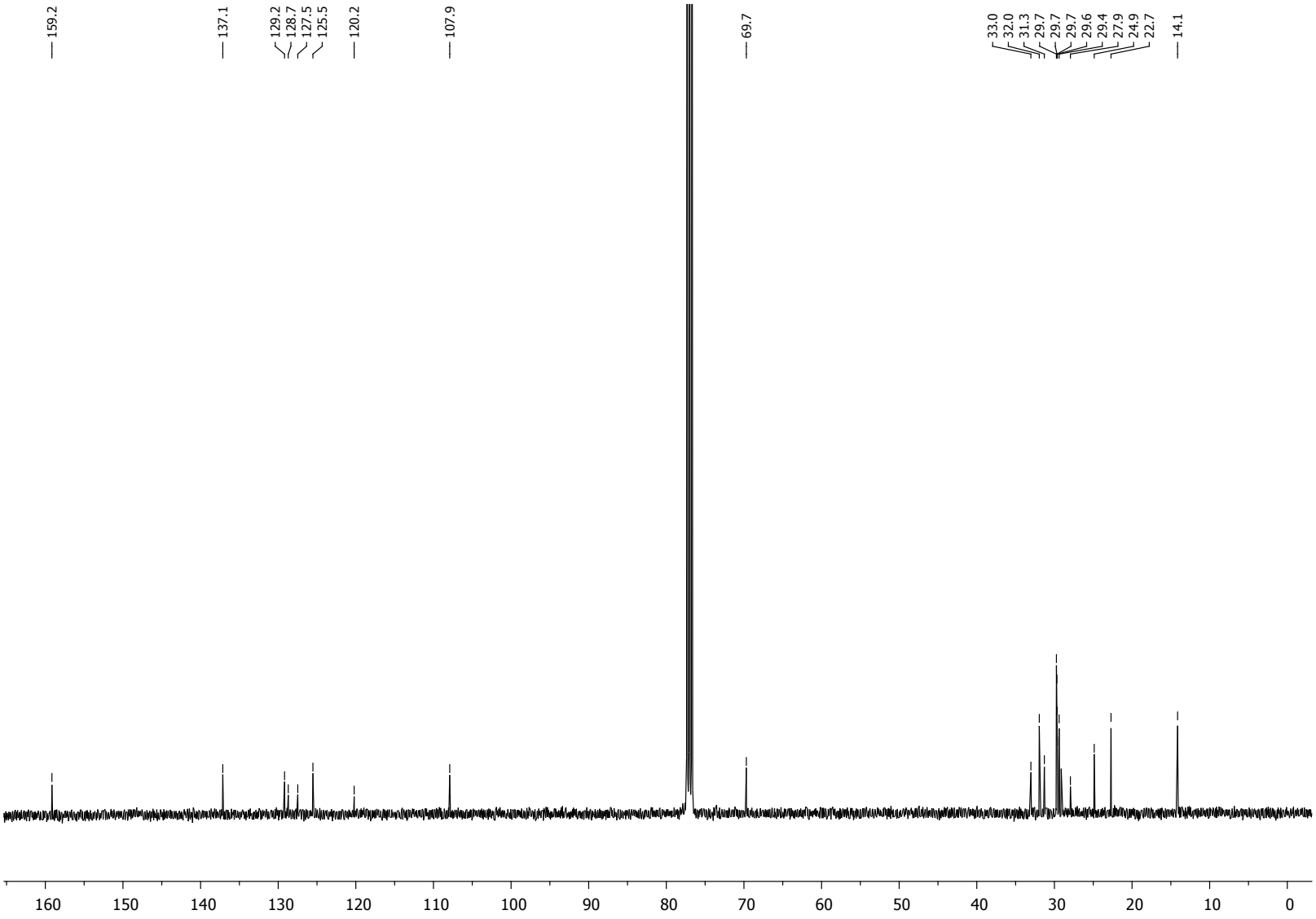
Spectrum S7. ^{1}H NMR spectrum of **4** in $CDCl_3$.



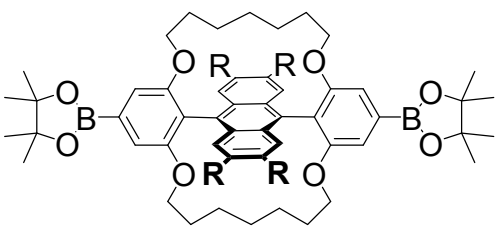
Spectrum S8. ^{13}C NMR spectrum of **4** in $CDCl_3$.



Spectrum S9. ^{1}H NMR spectrum of **5** in $CDCl_3$.

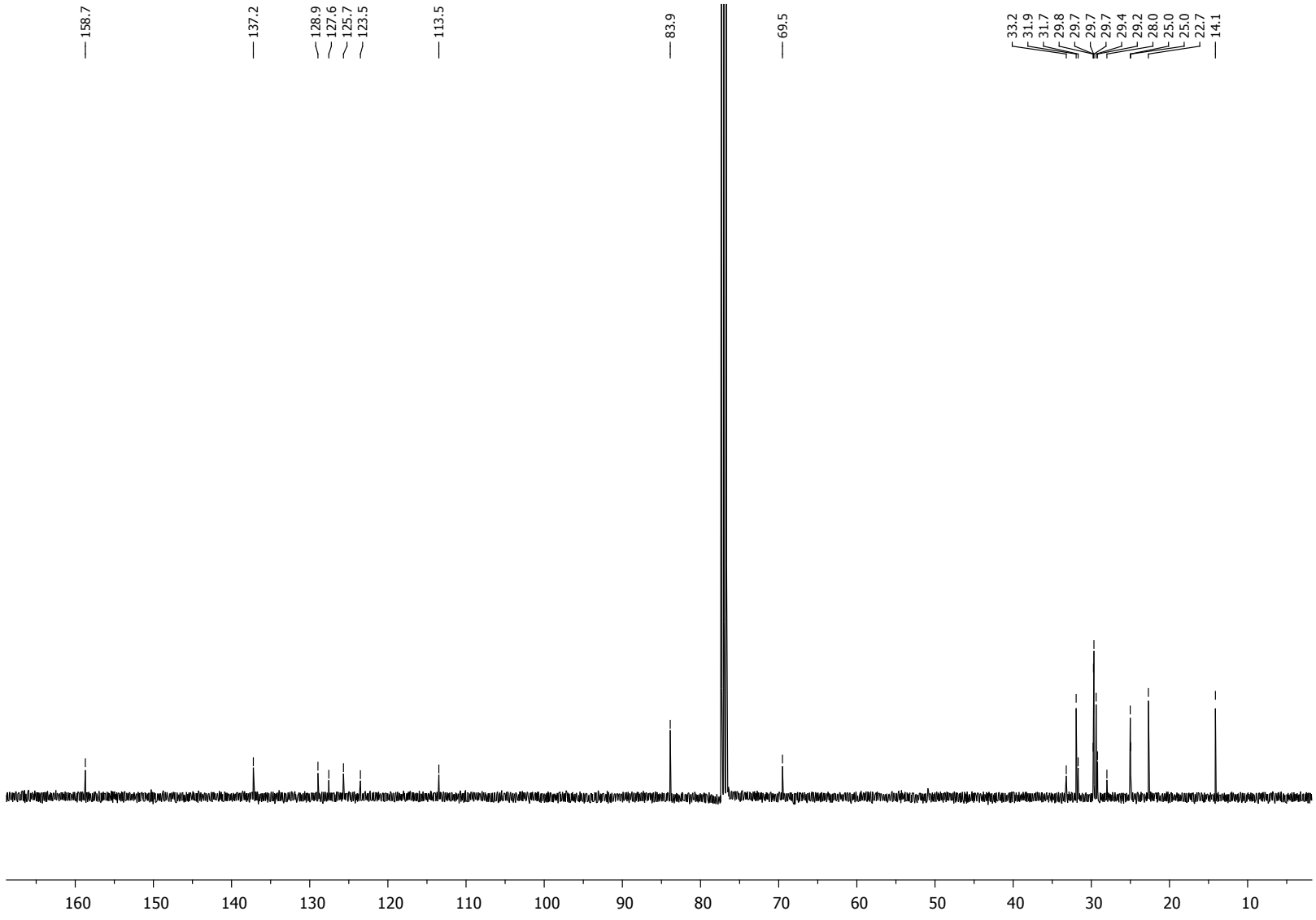


Spectrum S10. ^{13}C NMR spectrum of **5** in $CDCl_3$.

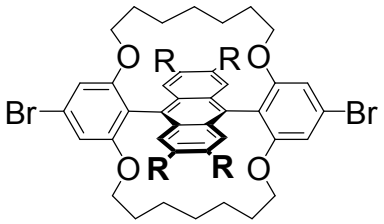


R = *n*-$C_{12}H_{25}$

Spectrum S11. ^{1}H NMR spectrum of **6** in $CDCl_3$.

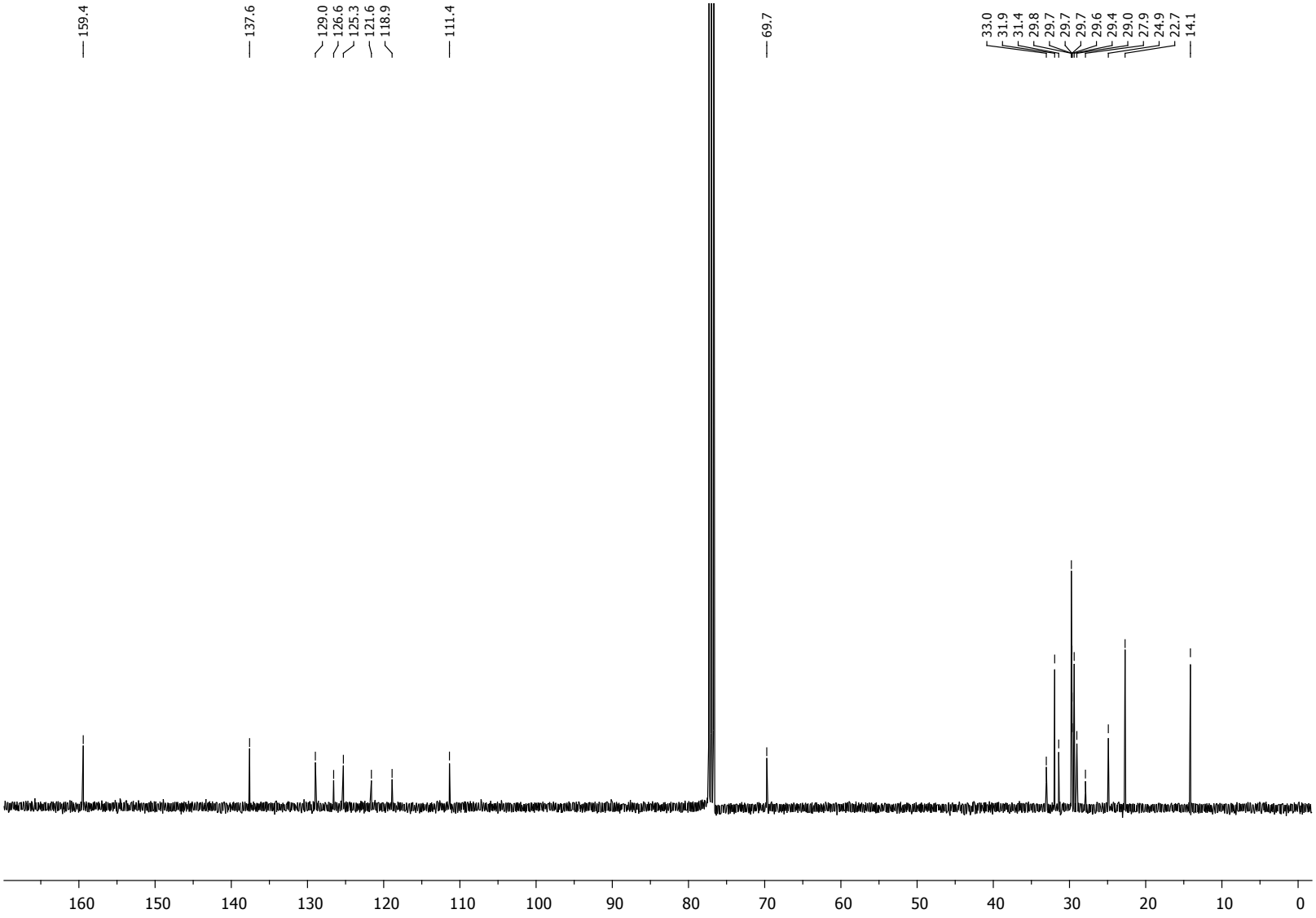


Spectrum S12. ^{13}C NMR spectrum of **6** in $CDCl_3$.

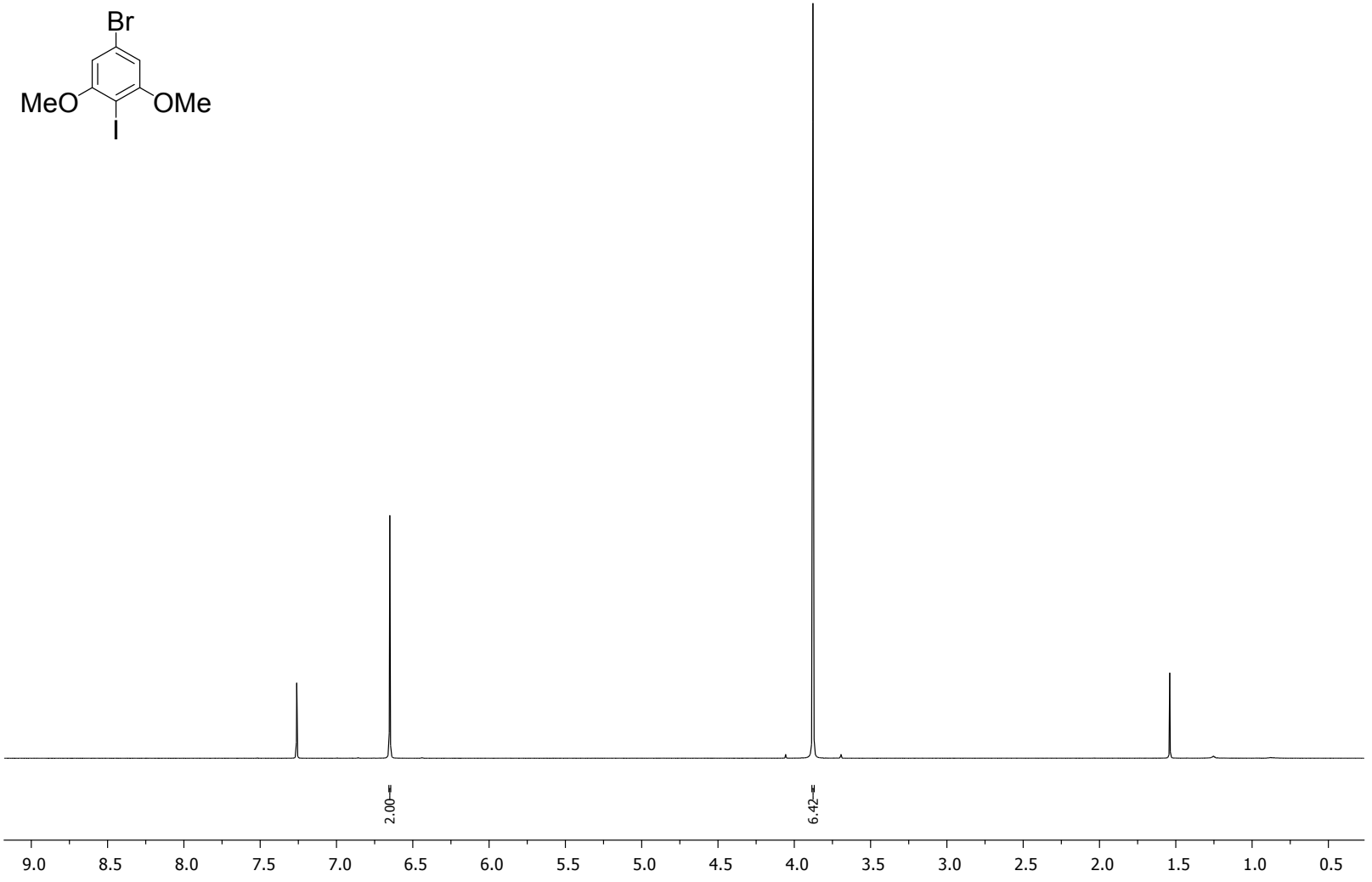


R = *n*-$C_{12}H_{25}$

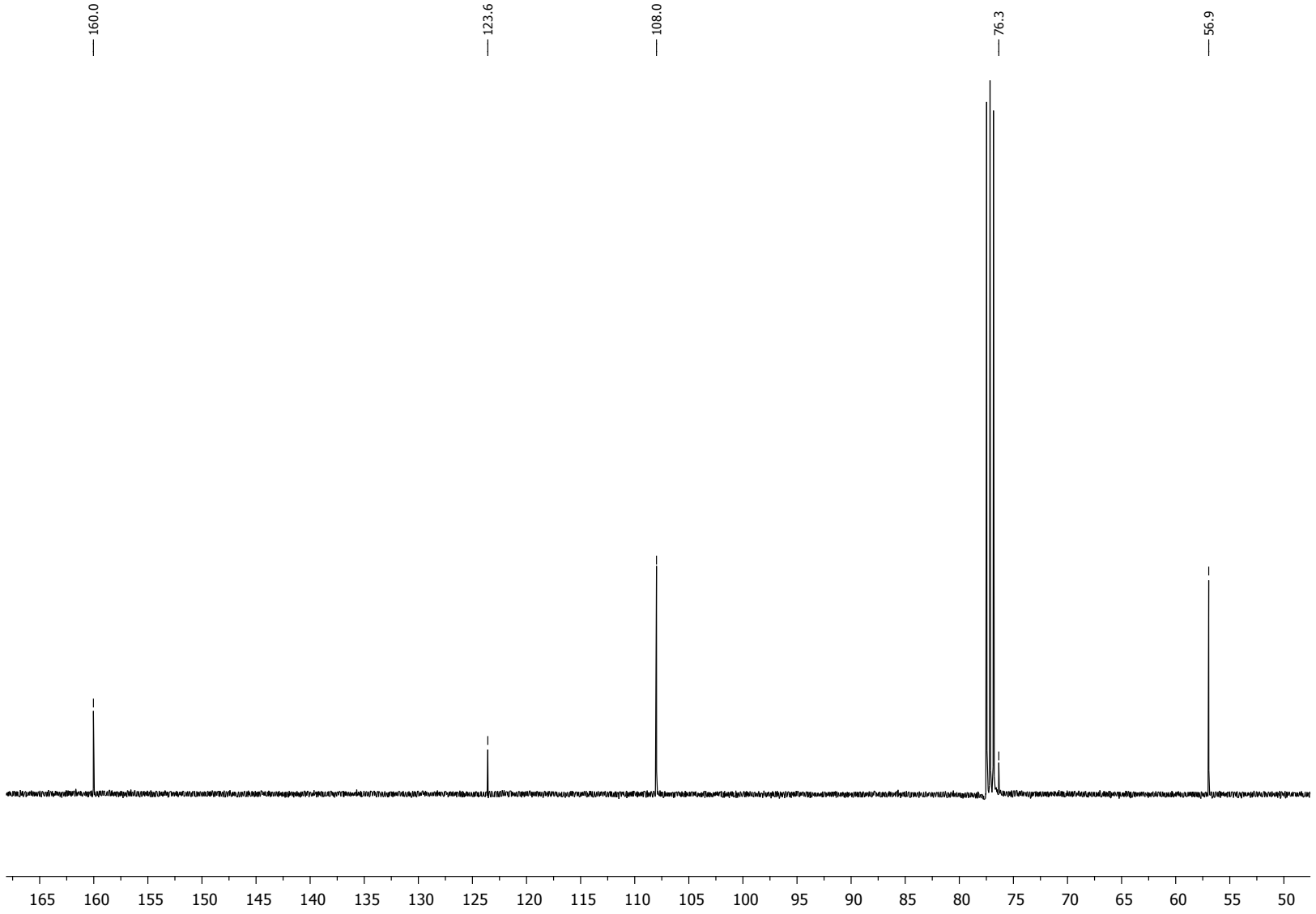
Spectrum S13. ^{1}H NMR spectrum of **7** in $CDCl_3$.



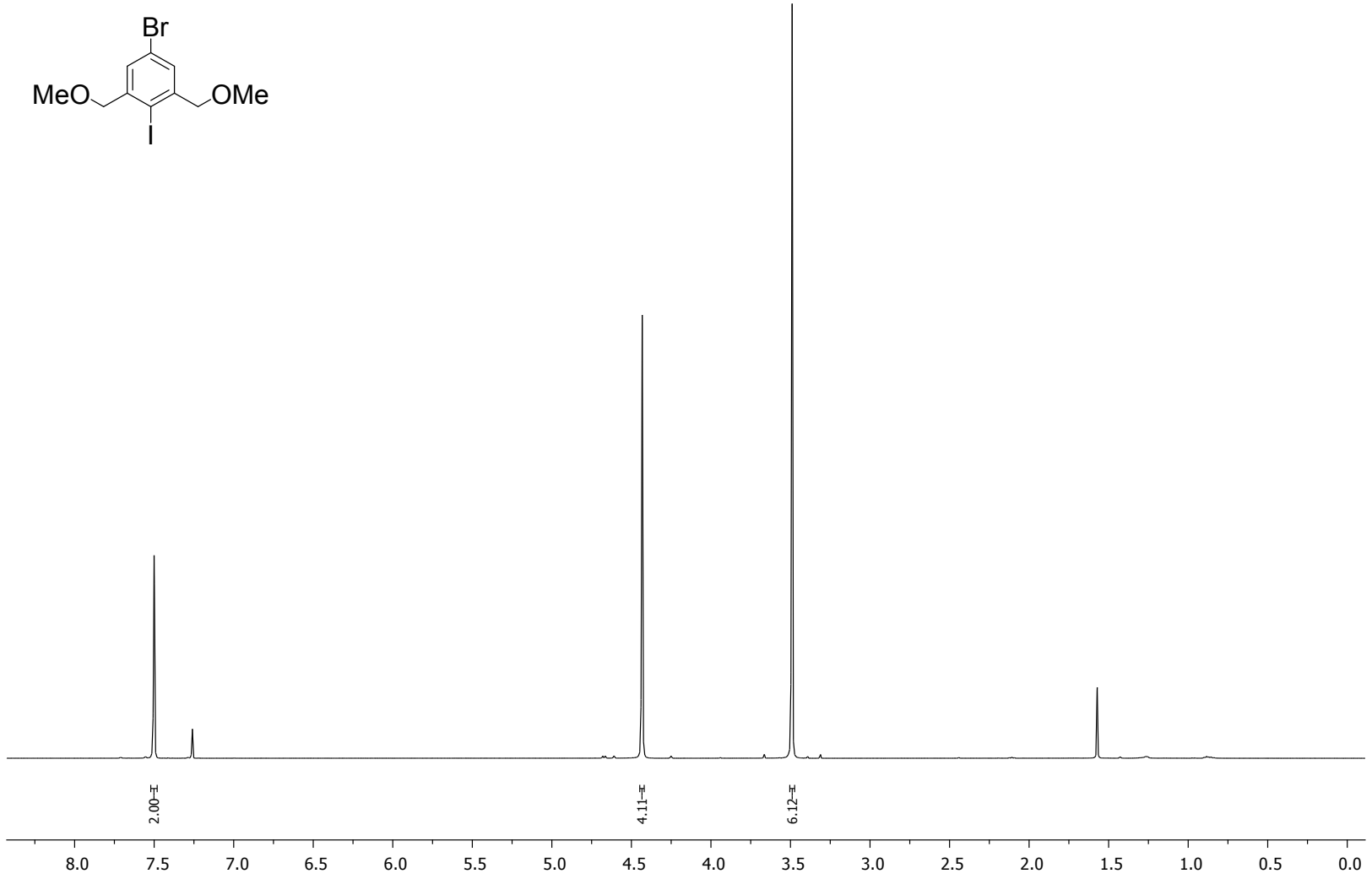
Spectrum S14. ^{13}C NMR spectrum of **7** in $CDCl_3$.



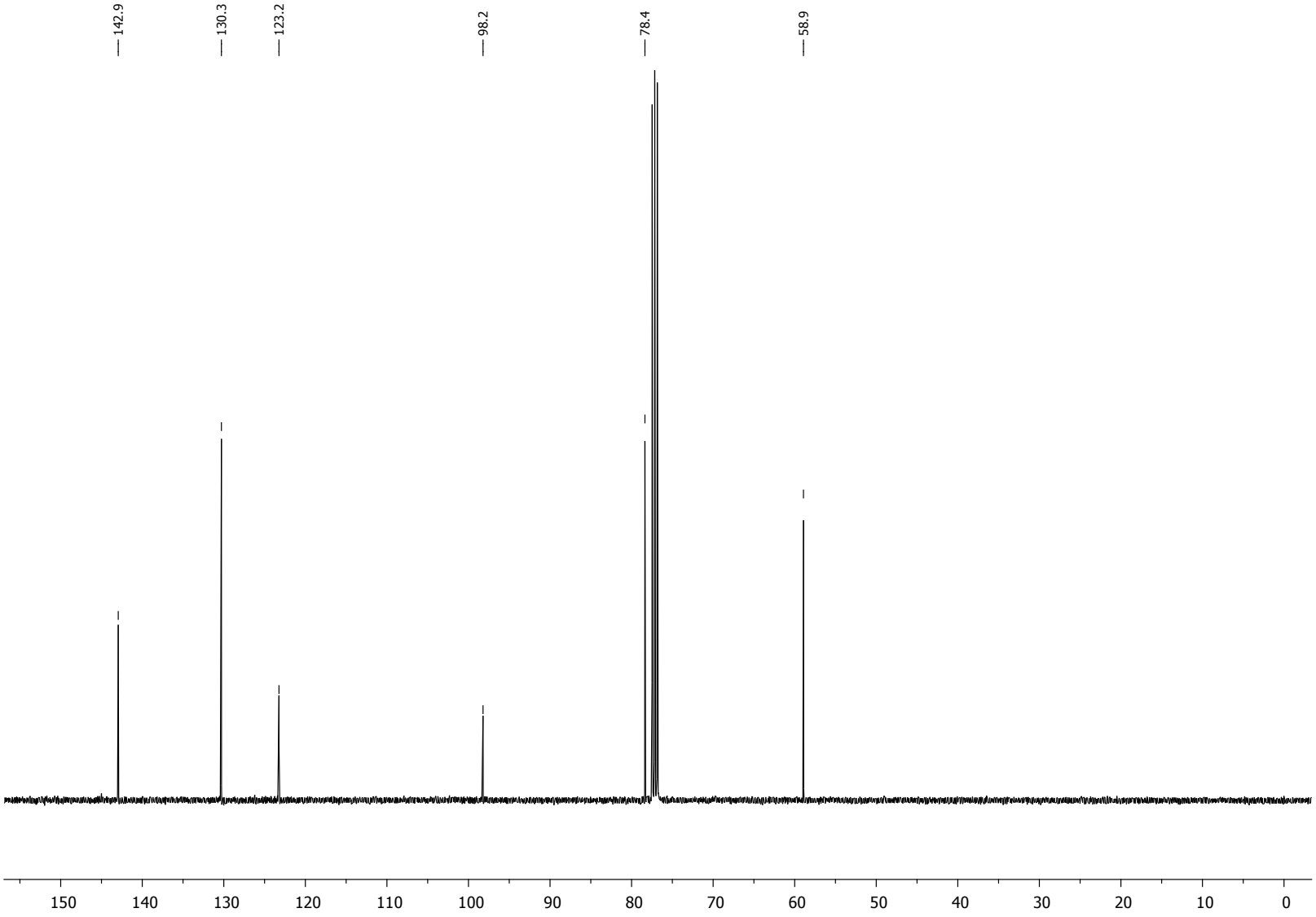
Spectrum S15. ^{1}H NMR spectrum of **Ar (a)** in $CDCl_3$.



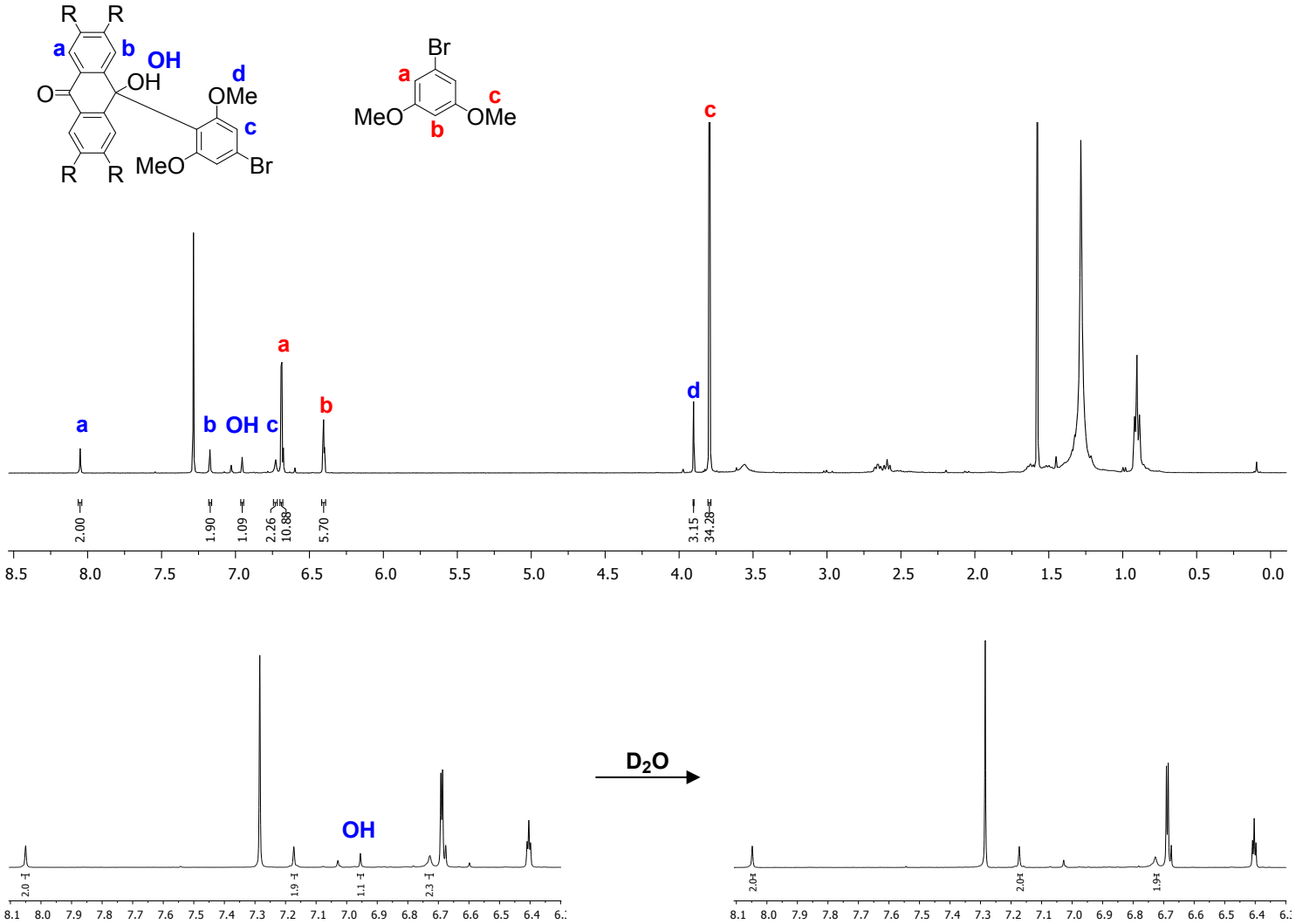
Spectrum S16. ^{13}C NMR spectrum of **Ar (a)** in $CDCl_3$.



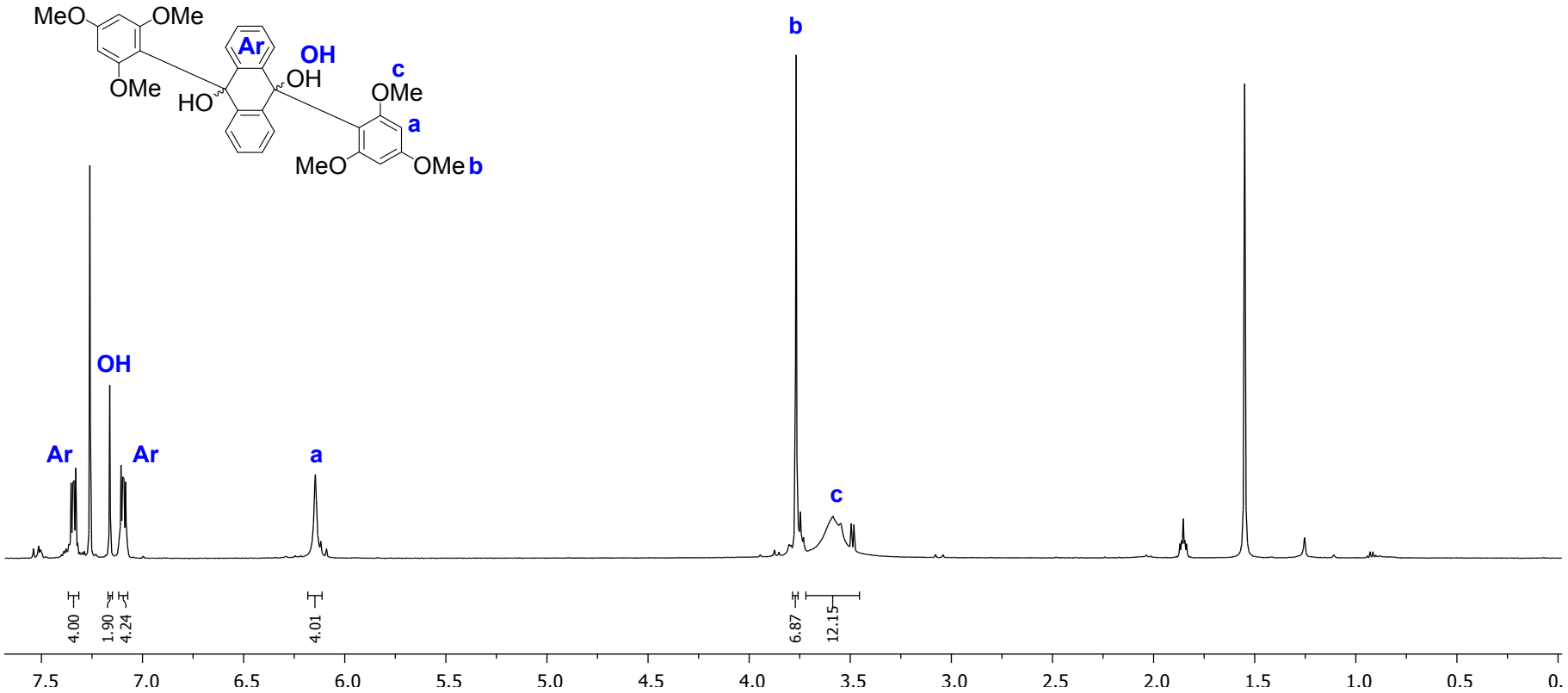
Spectrum S17. ^{1}H NMR spectrum of **Ar (b)** in $CDCl_3$.



Spectrum S18. ^{13}C NMR spectrum of **Ar (b)** in $CDCl_3$.

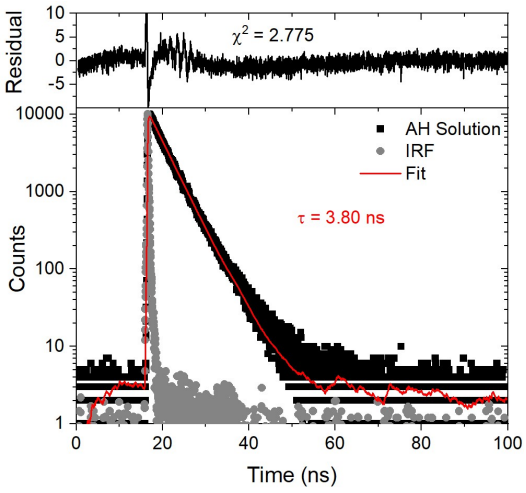


Spectrum S19. (Top) ^{1}H NMR spectrum in $CDCl_3$ of the crude reaction mixture obtained after treatment of **1** with 4.5 eq of the Grignard reagent of **Ar (a)** in THF at room temperature. It contains the product of mono-addition (**2b**) and dehalogenated **Ar (a)**. (Bottom) D_2O shake to confirm assignment of the tertiary alcohol peak.



Spectrum S20. ^{1}H NMR spectrum in $CDCl_3$ of **S13**.

Photophysics



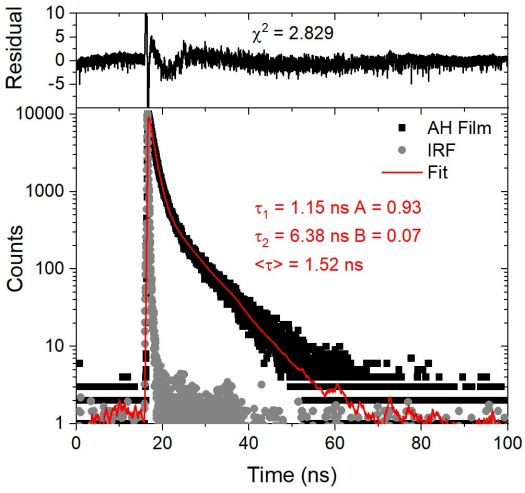


Figure S1. PL decays for **AH**. (left) toluene solution; (right) spin coated film.

Figure S2. PL decays for **AF8**. (left) toluene solution; (right) spin coated film.

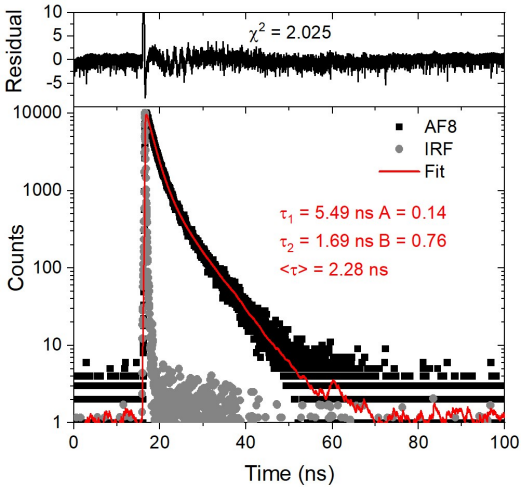
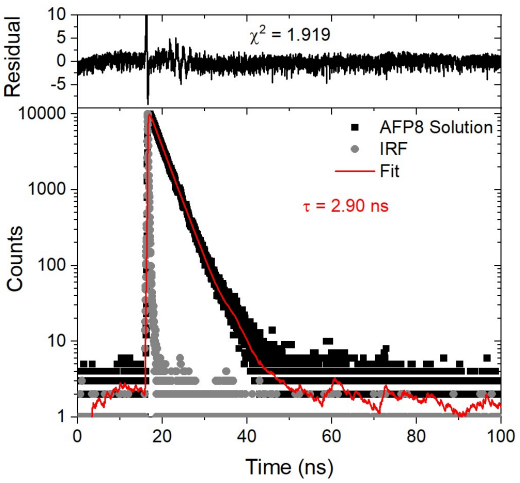
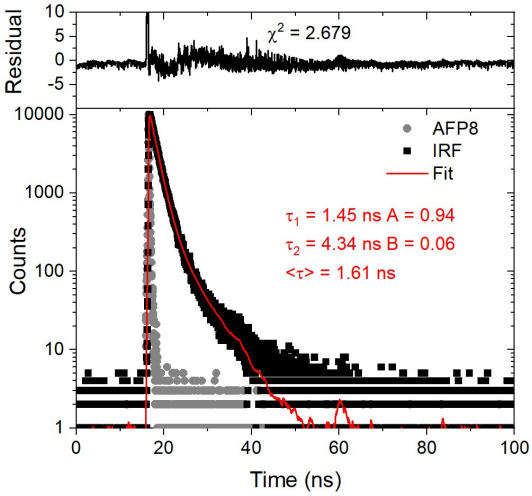


Figure S3. PL decays for **AFP8**. (left) toluene solution; (right) spin coated film.

Table S1. PL decay data for the polymers.





Polymer	Solution			Film			
	A	τ /ns	A_1	τ_1 /ns	A_2	τ_2 /ns	<τ> /ns
AH	1	3.80	0.93	1.15	0.07	6.38	1.52

AF8	1	2.94	0.76	1.69	0.14	5.49	2.28
AFP8	1	2.90	0.94	1.45	0.06	4.34	1.61

The amplitude weighted average lifetime ($<\tau>$) is proportional to the steady-state intensity and the relative quantum yield ($<\tau>$) is calculated according to Equation 1[11],

$$<\tau> = \frac{\left(\sum_i A_i \tau_i\right)}{\sum_i A_i} \quad (1)$$

Where A_i is the amplitude for the *i*ths exponential component and τ_i is the corresponding lifetime.

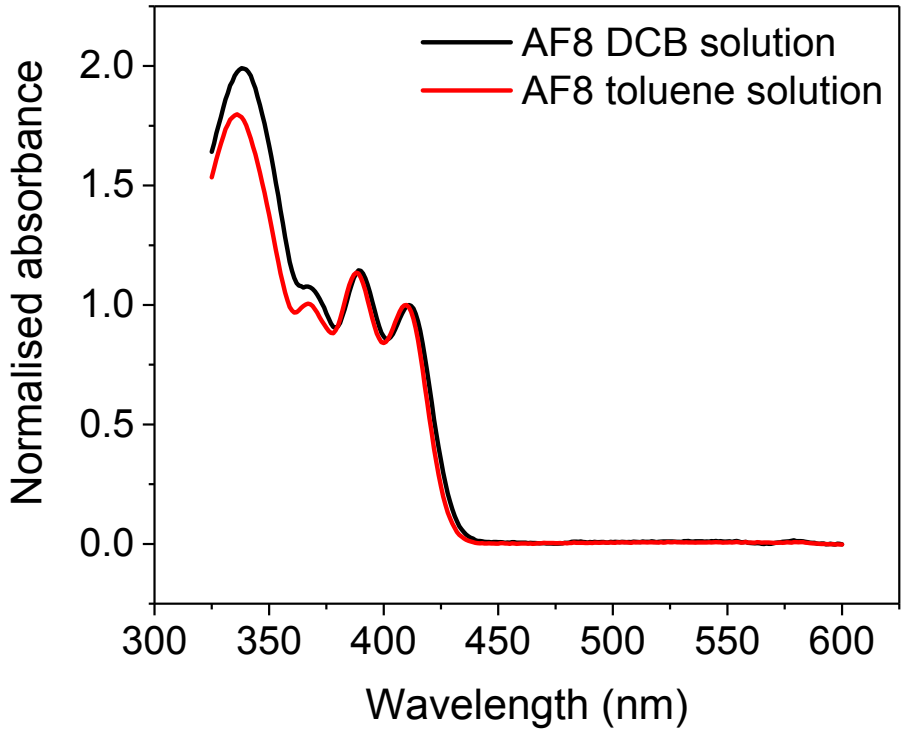


Figure S4. Absorption spectra of AF8 in DCB and toluene.

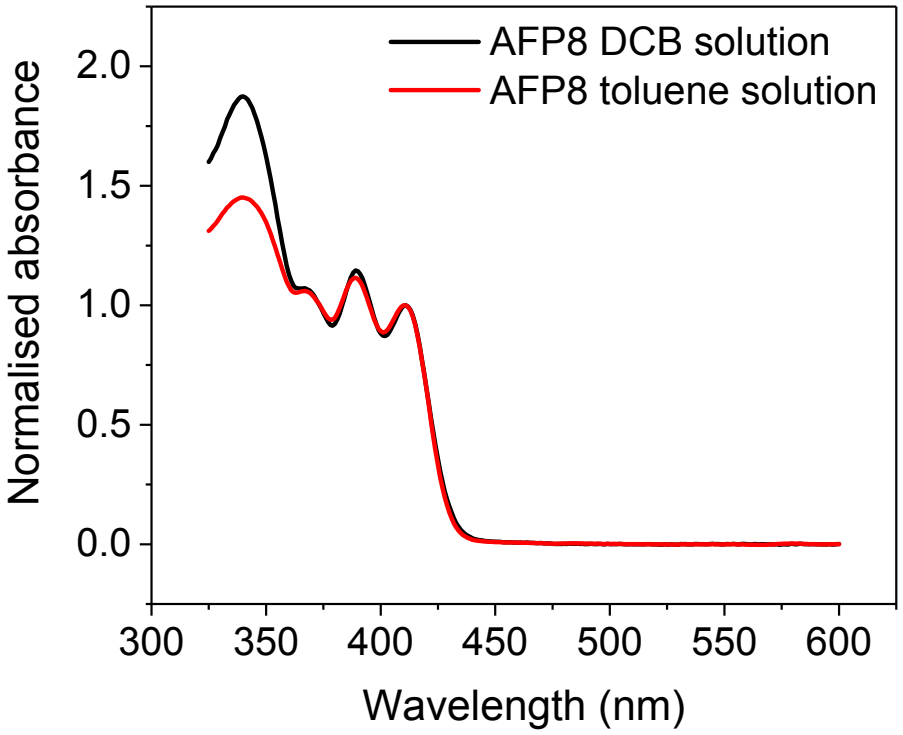


Figure S5. Absorption spectra of AFP8 in DCB and toluene.

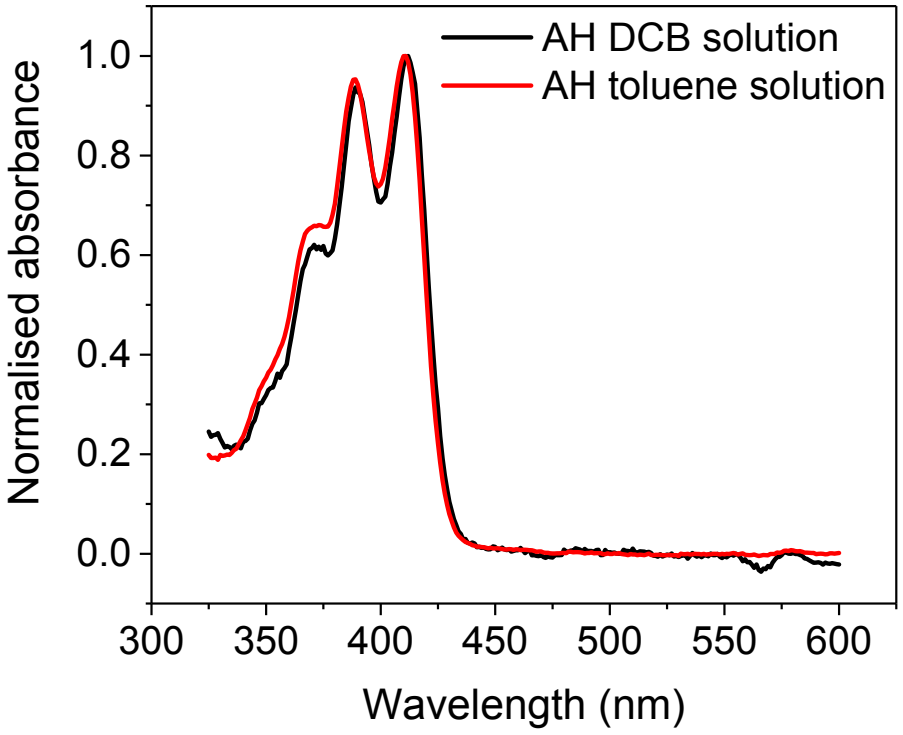


Figure S6. Absorption spectra of AH in DCB and toluene.

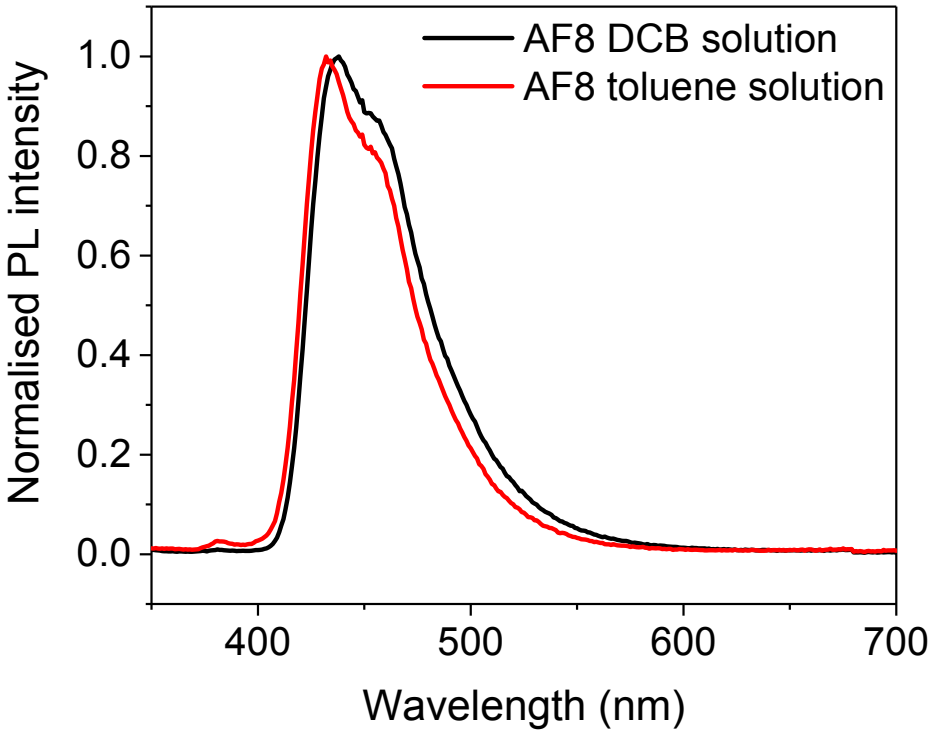


Figure S7. PL spectra of AF8 in DCB and toluene (λ_{exc} = 340 nm).

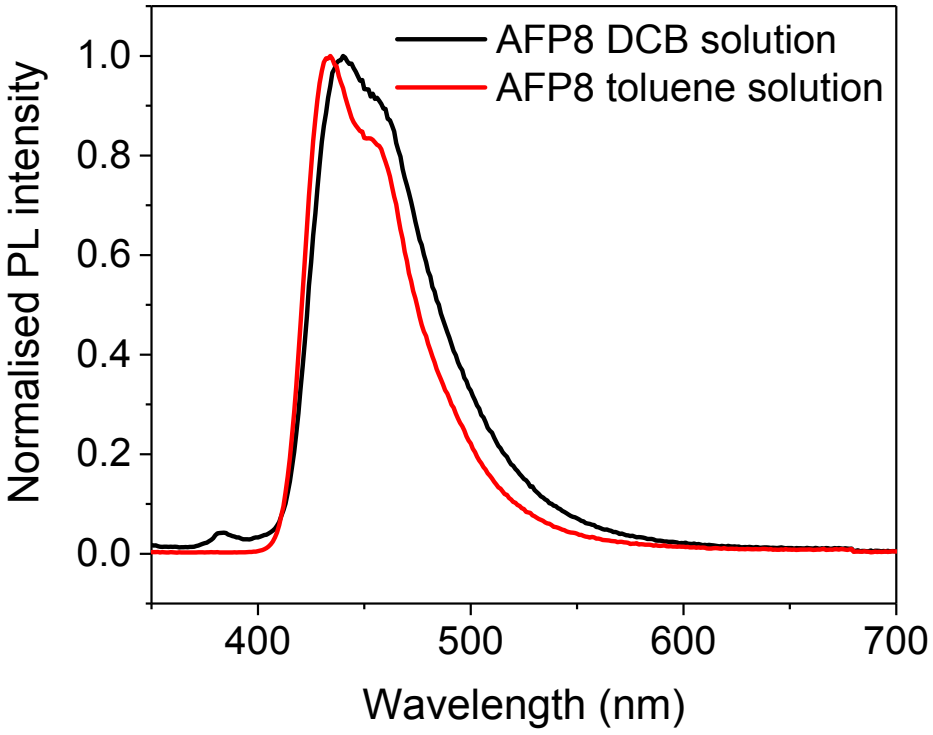


Figure S8. PL spectra of AFP8 in DCB and toluene (λ_{exc} = 340 nm).

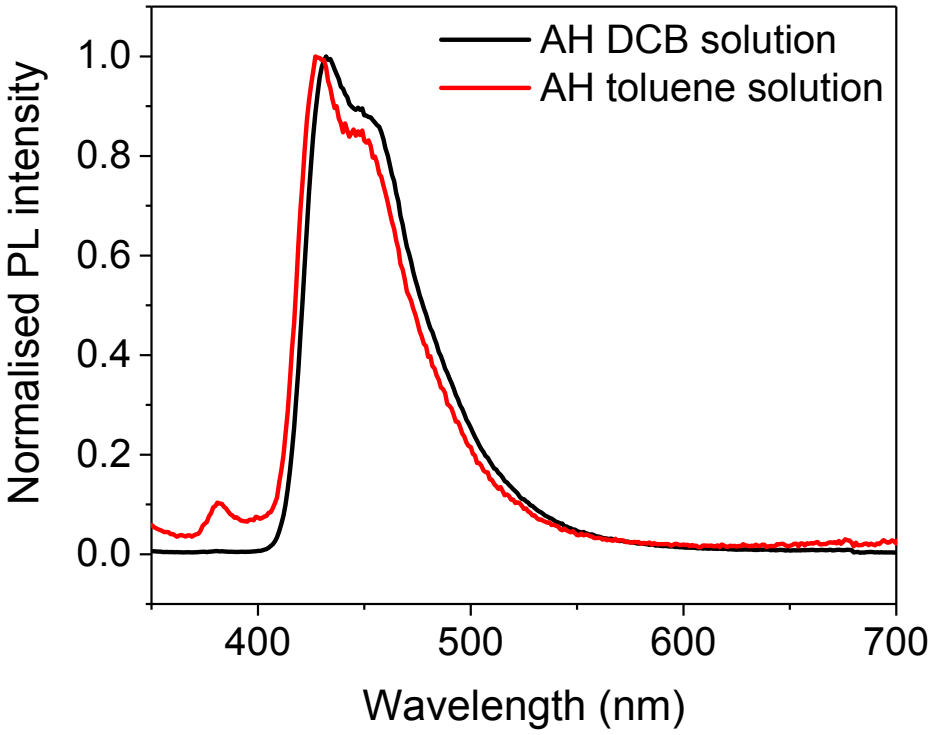
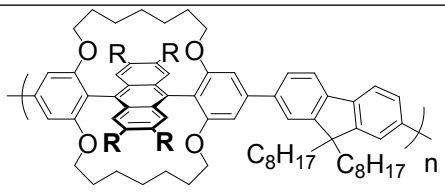
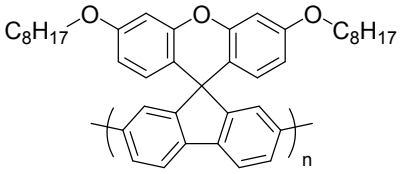
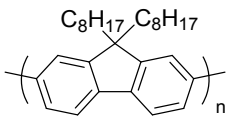
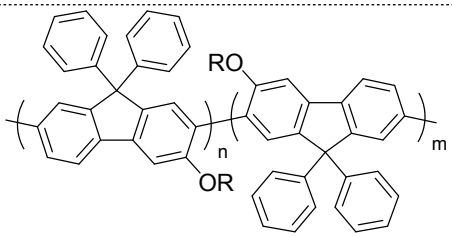
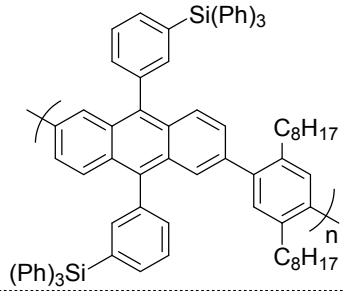
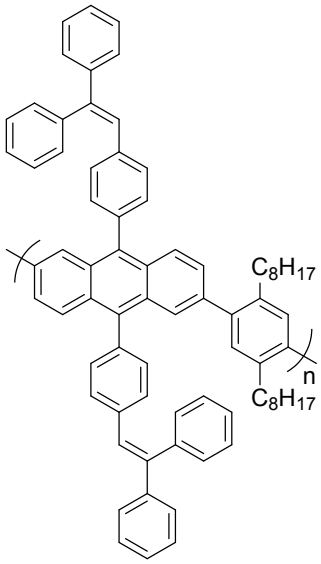
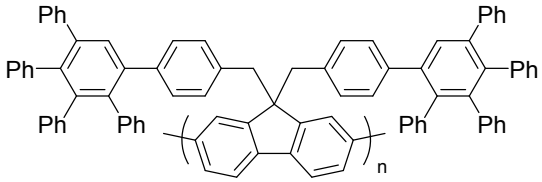
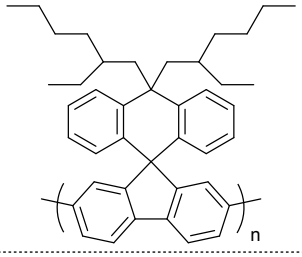


Figure S9. PL spectra of AH in DCB and toluene (λ_{exc} = 340 nm).

Literature comparison

Table S2. Comparison of **AF8** (entry 1) with literature blue-emitting polymers.

Entry	Structure	Δ PL 0–0 (sol/ film)	Φ_R	Reference
1	 R = *n*-$C_{12}H_{25}$	**0 nm**	**1**	**This work**
2		8 nm	0.94	*Macromolecules* **2005**, 38, 10055–10060.
3		19 nm	0.66	*Appl. Phys. Lett.* **1998**, 73, 629

4	 R = -C_6H_{12}-Cz	4 nm	0.71	*Adv. Mater.* **2019**, 31, 1804811
5		0 nm	0.72	*Macromolecules* ***2010,*** 3613–3623.
6		6 nm	0.24	*Macromolecules* ***2010,*** 3613–3623.
7		8 nm	n.a.	*J. Am. Chem. Soc.* **2001**, 123, 946–953
8		5 nm	n.a.	*J. Mater. Chem.* **2004**, 14, 1342–1346

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