Supporting information

Debundling, Enrichment and Release of SWNTs Using Fluorene-Based Photocleavable Polymer

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1. Synthesis and characterization of polymers

1.1. General

All chemicals and solvents were commercially available and used as received unless otherwise stated. All chemical reactions were carried out in oven-dried glassware under nitrogen using standard Schlenck and syringe techniques. The synthesis of aldehyd **1**,[1] 2-bromo-7-iodo-fluorene,[2] 2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3] are described elsewhere. The synthesis of alcohol **2** is also described elsewhere, but full characterization was not published.[4] NMR spectra were recorded on a *Bruker DPX Avance 300 MHz* instrument or a *Bruker Avance III 500 MHz* instrument using deuterated solvents. Chemical shifts are reported relative to TMS ($\delta = 0.00$ ppm). Splitting patterns in ^1H NMR spectra are designated by s, singlet; d, doublet; t, triplet; m, multiplet; br, broad, and combinations thereof. Coupling constants *J* were given in Hz. IR spectra were recorded on a *Perkin Elmer spectrum GX* instrument. ESI-TOF mass spectra were recorded on a *Bruker MicrOTOF-Q* instrument and MALDI-TOF mass spectra were recorded on a PerSeptive Biosystems Voyager DE PRO time-of-flight instrument. Elemental analyses were recorded on a *Elementar vario Micro* instrument. Melting points were measured on a *Büchi Melting Point B-540* instrument using open capillaries and were uncorrected. Gel permeation chromatography measurements were performed on a Polymer Laboratories PL-GPC 50Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 x 7.5 mm) followed by the three PLgel 5 µm MixedC columns (300 x 7.5 mm) and a differential refractive index detector using THF as the eluent at 35°C with a flow rate of 1 $mL.min^{-1}$. The GPC system was calibrated using linear poly(styrene) standards ranging from 160 to 6×10^6 $g.mol^{-1}$. Calculation of the molecular weight proceeded via the Mark-Houwink parameters for polystyrene $K = 14.1\times10^{-5}$ $dL.g^{-1}$; alpha = 0.70.

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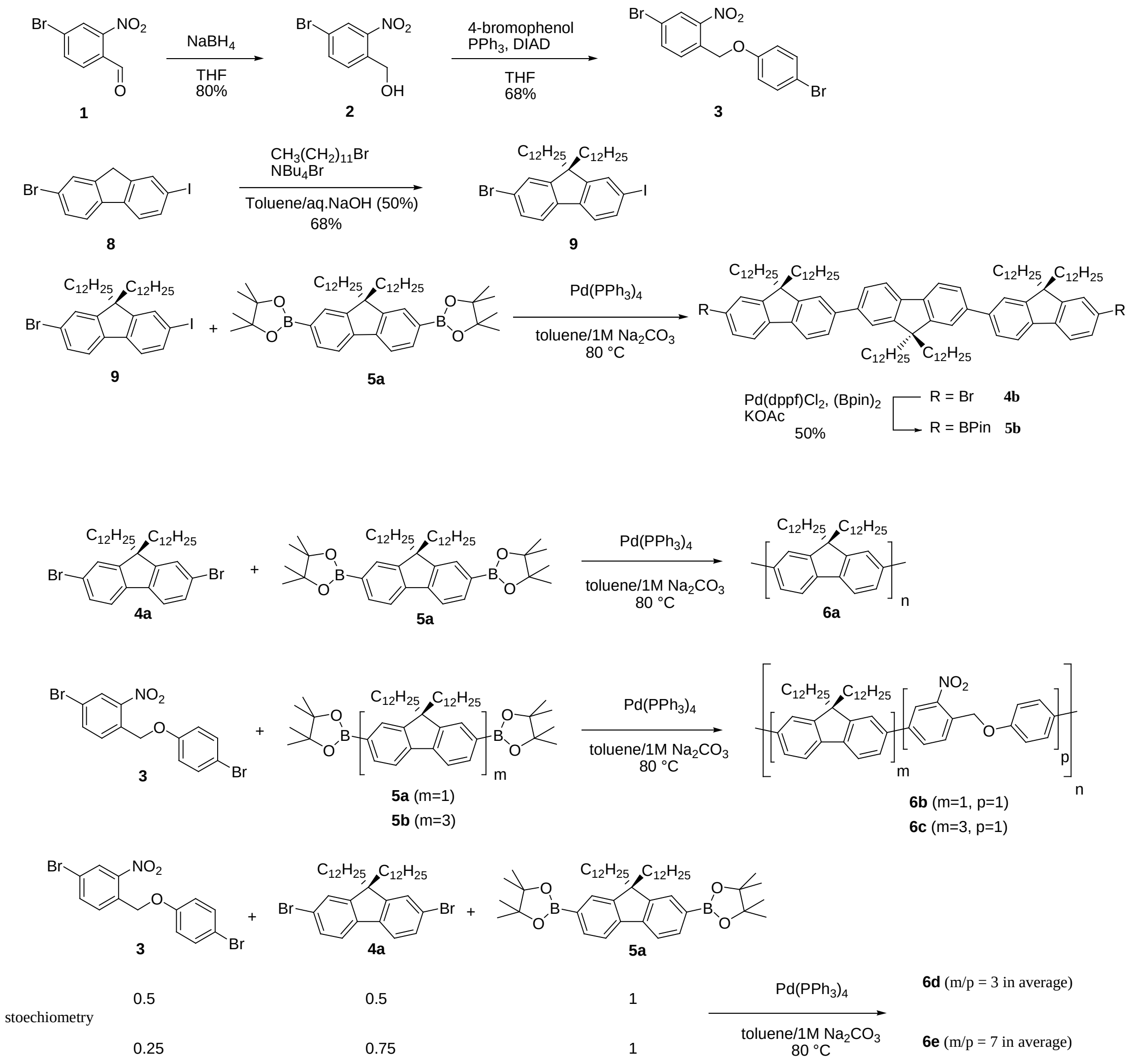
[1] G. Voß, H. Gerlach, *Chem. Ber.*, 1989, **122**, 1199.
[2] R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia, L.-S. Tan, *Chem. Mater.*, 2004, **16**, 185.
[3] H. Utsa, A. Facchetti, T. J. Marks, *Org. Lett.*, 2008, **10**, 1385.
[4] M. A. Gal'bershtam, Z. N. Budarina, *Zhurnal Organicheskoi Khimii*, 1969, **5**, 953.

1.2. Synthetic scheme



Scheme S1: Overall synthetic route for the synthesis of polymers **6a-e**.

1.3. Synthetic procedures

a) (4-Bromo-2-nitro)benzyl alcohol (2)

The reaction was performed according to a similar procedure.[5] Aldehyde **1** (1.25 g, 5.43 mmol) was dissolved in absolute THF (16 mL) and grinded $NaBH_4$ (400 mg, 10.57 mmol) was added by portions. After 15 min, a TLC analysis showed complete

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[5] E. Riguet, C. G. Bochet, *Org. Lett.*, 2007, **9**, 5453.

conversion of the starting aldehyde. The reaction mixture was cooled to 0 °C and quenched with 20% aq. NH_4Cl (15 mL) and extracted with Et_2O (3×20 mL). The organic phases were collected, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc: 2/1) to yield 1.02 g (80%) of the title compound as a light yellow powder. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.20$ (d, $J = 2.0$ Hz, 1H), 7.77 (dd, $J = 8.3$ Hz, $J = 2.0$ Hz, 1H), 7.64 (d, $J = 8.3$ Hz, 1H), 4.92 (s, 2H), 2.84 (br, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 147.8$ (C), 137.1 (CH), 136.0 (C), 131.1 (CH), 127.9 (CH), 121.6 (C), 61.9 (CH_2) ppm. Other analytical data are in accordance with the literature.

b) 4-Bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene (3):

This procedure was performed in the absence of light. Alcohol **2** (774 mg, 3.34 mmol), 4-bromophenol (693 mg, 4.0 mmol) and triphenylphosphine were dissolved in 25 mL absolute THF and the reaction mixture was cooled to 0 °C. Diisopropyl azodicarboxylate (860 μL, 4.0 mmol) was added to the reaction mixture within 15 min. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The next day, a TLC analysis showed complete conversion of the starting material and the reaction mixture was concentrated in vacuo. The remaining slurry was purified by column chromatography (hexane/EtOAc : 10/1) to yield the titled compound (877 mg, 68%) as a pale yellow solid. Mp: 110 °C. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.29$ (d, $J = 1.9$ Hz, 1H), 7.79 (dd, $J = 8.4$ Hz, $J = 1.9$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.36 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 157.0$ (C), 147.2 (C), 137.1 (CH), 132.62 (CH), 132.56 (C), 130.0 (CH), 128.1 (CH), 121.8 (C), 116.7 (CH), 114.1 (C), 66.7 (CH_2). IR (KBr, cm^{-1}): 3085 (m), 2926 (m), 2860 (m), 1592 (m), 1579 (m), 1525 (s), 1486 (s), 1340 (s), 1280 (m), 1240 (s), 1168 (m) 1039 (s). MS (EI, 70 eV): $m/z = 389$ [M^+ ($^{79}Br_2$)] (3), 387 [M^+ ($^{79}Br^{81}Br$)] (7), 385 [M^+ ($^{79}Br_2$)] (3), 216 (98), 214 (100), 158 (21), 156 (23). Elemental Analysis: $C_{13}H_9Br_2NO_3$ calcd for C 40.34, H 2.34, N 3.62; found: C 40.23, H 2.41, N 3.63.

c) 2-Bromo-7-iodo-9,9-didocedyl-fluorene (9)

2-bromo-7-iodo-fluorene **8** (4.0 g, 10.78 mmol), 1-bromododecane (6.72 g, 26.95 mmol) and NBu_4Br (650 mg, 2.0 mmol) were dissolved in toluene (35 mL), and 50% aq. NaOH (35 ml) were added. The reaction mixture was heated at 60 °C for 5 h and then cooled to room temperature. The mixture was extracted with hexane (3×50 mL), the organic phases were collected, washed successively with water, 1N HCl and water before drying over $MgSO_4$. The organic phase was filtered and concentrated in vacuo. The excess of reagent was distilled off using a Kugelrohr distillation setup. The sticky remaining oil was purified by column chromatography to yield the desired dialkylated fluorene **9** (5.20 g, 68%) as colorless oil which solidify on standing. M.p.: 43–44 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.65 (m, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.45 (m, 2H), 7.40 (d, *J* = 7.9 Hz, 1H), 1.90 (m, 4H), 0.99–1.34 (m, 36H), 0.87 (m, 6H), 0.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 152.9 (C), 152.5 (C), 139.8 (C), 139.3 (C), 136.2 (CH), 132.2 (CH), 130.3 (CH), 126.3 (CH), 121.8 (C), 121.6 (CH), 121.3 (CH), 93.1 (C), 55.8 (C), 40.3 (CH_2), 32.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.70 (CH_2), 29.68 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 14.3 (CH_3), (one aliphatic carbon signal overlapped). MS (EI, 70 eV): *m/z* = 709 (31), 708 [M^+ (^{81}Br)] (100), 707 (38), 706 [M^+ (^{81}Br)] (95), 582 (30), 580 (28), 413 (15), 412 (17), 411 (15), 410 (13), 371 (25), 369 (25), 332 (13), 245 (24), 243 (25), 178 (11).

d) 2,7''-Dibromo-9,9,9',9',9'',9''-hexa(dodecyl)-7,2';7',2''-terfluorene (4b)

A 3 necked 250 mL flask equipped with a condenser was charged with diboronic ester **5a** (1.317 g, 1.744 mmol) and fluorene **9** (3.21 g, 4.54 mmol) before being flushed with nitrogen. Degassed toluene (80 mL) and degassed 1M aq. Na_2CO_3 (80 mL) were added to the flask, followed by $Pd(PPh_3)_4$ (60 mg, 52 µmol). The reaction mixture was heated at 80 °C. After 42 h, the reaction mixture was allowed to cooled to room temperature and was transferred to a separating funnel to be extracted with CH_2Cl_2 (4×100 mL). The organic layers were collected, dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (hexane:CH_2Cl_2 : 99:1) afforded the desired compound (1.150 g, 40%)

as a colorless sticky oil which solidify on standing, and the excess of fluorene **9** (510 mg, 721 μmol). M.p.: 39–41 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.81 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.58–7.68 (m, 10H), 7.48 (m, 4H), 1.93–2.14 (m, 12H), 1.05–1.33 (m, 110H), 0.77–0.91 (m, 22H), 0.65–0.76 (m, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.4 (C), 152.0 (C), 151.3 (C), 141.1 (C), 140.5 (C), 140.2 (C), 140.0 (C), 139.4 (C), 130.1 (CH), 126.41 (CH), 126.37 (CH), 126.31 (CH), 121.64 (CH), 121.57 (CH), 121.2 (CH), 121.1 (C), 120.2 (CH), 55.7 (C), 55.5 (C), 40.46 (CH_2), 40.42 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 24.1 (CH_2), 23.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3) (several aliphatic carbon signals overlapped). MS (MALDI): [(M–H)$^+$] 1661.0. Elemental Analysis: $C_{111}H_{168}Br_2$ calcd for C 80.20, H 10.19; found: C 80.36, H 9.81.

e) 2,2'-(9,9,9',9',9'',9''-Hexadodecyl-9H,9'H,9''H-[2,2':7',2''-terfluorene]-7,7''-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5b)

An oven-dried 250 mL 3 necked flask equipped with a condenser was charged with dibromide **4b** (900 mg, 541 μmol), bis(pinacolato)diboron (316 mg, 1.25 mmol) and KOAc (308 mg, 3.13 mmol) and absolute dioxane (120 mL). The mixture was degassed during 30 min by bubbling nitrogen before Pd(dppf)Cl_2 (66 mg, 81 μmol) was added. The reaction mixture was heated at 80 °C overnight. The next day, the black crude mixture was diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (4×80 mL). The organic layers were collected, dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (hexane:EtOAc : 95:5) afforded the titled compound (474 mg, 50%) as a transparent amorphous sticky solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.79–7.88 (m, 8H), 7.76 (m, 2H), 7.62–7.70 (m, 8H), 2.09 (m, 12H), 1.42 (s, 24H), 1.05–1.32 (m, 110H), 0.80–0.90 (m, 22H), 0.72 (m, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 152.3 (C), 152.0 (C), 150.4 (C), 144.0 (C), 141.1 (C), 140.6 (C), 140.3 (C), 140.2 (C), 134.0 (CH), 129.1 (CH), 127.4 (C), 126.3 (CH), 126.2 (CH), 121.69 (CH), 121.66 (CH), 120.5 (CH), 120.1 (CH), 119.2 (CH), 83.9 (C), 55.5 (C), 55.4 (C), 40.5 (CH), 40.4 (CH), 32.1 (CH_2), 30.2 (CH_2), 29.78 (CH_2), 29.75 (CH_2), 29.5(CH_2), 29.4 (CH_2), 25.1 (CH_3), 24.1 (CH_2), 24.0

(CH_2), 22.8 (CH_2), 14.3 (CH_3) (several aliphatic carbon signals overlapped). MS (MALDI): [$(M–H)^+$] 1755.04. Elemental Analysis: $C_{123}H_{192}B_2O_4$ calcd for C 84.11, H 11.02; found: C 84.30, H 10.67.

1.4. General procedure for the synthesis of polymers via Suzuki coupling (GP)

A 2-necked round bottom flask equipped with a condenser was charged with diboronic ester (1.00 mmol) and the corresponding dibromid (1.00 mmol) or dibromids (1.00 mmol altogether). Toluene (20 mL) and 1 M Na_2CO_3 (20 mL) were added to the flask and the heterogeneous reaction mixture was degassed by passing a flow of nitrogen through the solution for 30 min. Then $Pd(PPh_3)_4$ (20 µmol) was added and the reaction mixture was heated at 85 °C for 3 days under vigorous stirring. The reaction mixture was cooled to room temperature, poured in MeOH (120 mL) and stir for 1 h. The precipitate was filtered, washed with MeOH and dried in vacuum. The polymer was purified by soxlet extraction for 14 h using toluene. Toluene was then evaporated to yield the corresponding polymer.

a) Poly(9,9-didodecyl-fluorene-2,7-diyl) (6a)

According to the GP, polyfluorene **6a** was prepared starting from 2,7-dibromo(9,9-didodecyl)fluorene **4a** (262.6 mg, 397.5 µmol), 2,2'-(9,9-didodecyl-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5a** (300.0 mg, 397.5 µmol) and $Pd(PPh_3)_4$ (18 mg, 16 µmol) in toluene (10mL) and 1M Na_2CO_3 (10 mL). Soxlet extraction yielded 395 mg (99%) of the titled polyfluorene. Mn = 12878, Mp = 35674, PDI = 4.2.

b) Poly(9,9-didodecyl-fluorene-2,7-diyl-*alt*-1-nitro-2(phenoxymethyl)benzene-5,4’-diyl) (6b)

This reaction was performed in the absence of light. According to the GP, the alternating copolymer **6b** was prepared starting from 4-bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene **3** (100 mg, 258 µmol), 2,2'-(9,9-didodecyl-fluorene-2,7-diyl)bis(4,4,5,5-

tetramethyl-1,3,2-dioxaborolane) **5a** (195 mg, 258 μmol) and Pd(PPh_3)$_4$ (12 mg, 10 μmol) in toluene (5mL) and 1M Na_2CO_3 (5 mL). Soxlet extraction 173 mg (92 %) of the titled copolymer **6b**. Mn = 6832, Mp = 18945, PDI = 2.77.

c) Poly(9,9,9',9',9'',9''-hexa(dodecyl)-7,2';7',2''-terfluorene-2,7’’-diyl-*alt*-1-nitro-2(phenoxymethyl)benzene-5,4’-diyl) (6c)

This reaction was performed in the absence of light. According to the GP, the alternating copolymer **6c** was prepared starting from 4-bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene **3** (19.6 mg, 50.7 μmol), diboric ester **5b** (89 mg, 50.7 μmol) and Pd(PPh_3)$_4$ (3 mg, 2 μmol) in toluene (8 mL) and 1M Na_2CO_3 (8 mL). Soxlet extraction yielded 84 mg (96%) of the titled alternating copolymer **6c**. Mn = 13500, Mp = 32600, PDI = 2.4.

d) Poly(9,9,-didodecylfluorene-2,7-diyl-*stat*-1-nitro-2(phenoxymethyl)benzene-5,4’-diyl) (75:25 mol%) (6d)

This reaction was performed in the absence of light. A 2-necked round bottom flask equipped with a condenser was charged with 2,2'-(9,9-didodecyl-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5a** (226.4 mg, 300 μmol), 2,7-dibromo(9,9-didodecyl)fluorene **4a** (99 mg, 150 μmol) and 4-bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene **3** (58 mg, 150 μmol). Toluene (12 mL) and 1 M Na_2CO_3 (12 mL) were added to the flask and the heterogeneous reaction mixture was degassed by passing a flow of nitrogen through the solution for 30 min. Then Pd(PPh_3)$_4$ (14 μmol, 12 μmol) was added and the reaction mixture was heated at 85 °C for 3 days under vigorous stirring. The reaction mixture was cooled to room temperature, poured in MeOH (120 mL) and stir for 1 h. The precipitate was filtered, washed with MeOH and dried in vacuum. The polymer was purified by soxlet extraction for 14 h using toluene to obtain 241 mg (93%) of the titled polymer. Mn = 4250, Mw = 8900, PDI = 2.1.

e) Poly(9,9,-didodecylfluorene-2,7-diyl-*stat*-1-nitro-2(phenoxymethyl)benzene-5,4’-diyl) (87.5:12.5 mol%) (6e)

This reaction was performed in the absence of light. A 2-necked round bottom flask equipped with a condenser was charged with 2,2'-(9,9-didodecyl-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5a** (226.4 mg, 300 μmol), 2,7-dibromo(9,9-didodecyl)fluorene **4a** (148.6 mg, 225 μmol) and 4-bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene **3** (29 mg, 75 μmol). Toluene (12 mL) and 1 M Na_2CO_3 (12 mL) were added to the flask and the heterogeneous reaction mixture was degassed by passing a flow of nitrogen through the solution for 30 min. Then $Pd(PPh_3)_4$ (14 μmol, 12 μmol) was added and the reaction mixture was heated at 85 °C for 3 days under vigorous stirring. The reaction mixture was cooled to room temperature, poured in MeOH (120 mL) and stir for 1 h. The precipitate was filtered, washed with MeOH and dried in vacuum. The polymer was purified by soxlet extraction for 14 h using toluene to obtain 249 mg (89%) of the title polymer. Mn = 4692, Mw = 9116, PDI = 1.95.

2. Dispersion of SWNTs

2.1. Preparation of SWNTs dispersions

Typically, ~1 mg of as-prepared HiPco SWNTs (purchased from Unidym) were dispersed for one hour in 15 ml toluene with ~50 mg of polymer using a ∅1/2” titanium sonotrode driven by a tip sonicator (Bandelin, 200 W maximum power, 20 kHz). In order to minimize potential damage of the SWNTs the most gentle adjustment of the device was chosen, namely the pulsed mode with 200 ms pulses at only 20% power. Dispersions were then filtered through a Toyopearl HW75F gel filtration medium (Tosoh Bioscience) in a glass column of ~2 cm length and 2 cm inner diameter to remove larger agglomerates. In order to avoid photocleavage of the polymers, all manipulations were performed as much as possible in shadowy light, and samples were stored in the dark.

2.2. Density Gradient Centrifugation (DGC)

DGC was explored for further purification of SWNT-polymer dispersions using an Optima Max-E centrifuge (Beckman-Coulter) equipped with a ML-80 fixed angle rotor similar to the procedure reported elsewhere.[6] In short 2 ml of the dispersion were overlaid onto 6 ml of chlorobenzene with 40 wt.% of 2,4,6-tribromotoluene (TBT) (Sigma) as the density gradient medium into 8 ml Quick-Seal polyallomer centrifuge tubes and then spun for 18–20 hours at 15°C and 45,000 rpm corresponding to centripetal accelerations of ~103,000 and ~140,000 g at the middle and bottom of the centrifuge tube, respectively. This resulted in a self-generated density gradient between 1.2 and 1.5 g/cm^{-3} for chlorobenzene/40 wt.% TBT. After centrifugation for 18-20 hours different coloured regions evolve within the density gradient whereas most of the SWNTs are in the first 1-2 ml of the lowermost region of the centrifuge tube. In the SWNT region fractions of ~100 μl were collected by carefully puncturing the tube at the top and bottom and applying a slight air overpressure via the top hole.

DGC was favored as purification step over classical centrifugation in order to provide a complete picture of all dispersed tubes and not to get rid of polymer/SWNT complexes with densities larger than the solvent (toluene). Note that considerable amounts of polymer/SWNTs complexes get lost by classical centrifugation as these complexes have densities slightly above 1g/ml (while toluene has a density of 0.87 g/ml). In order to collect all the polymer/SWNTs complexes, rather large eluent fractions were collected.

3. Irradiation procedure

The irradiation of suspensions **7b–e** was performed using the full spectral output of a 450W Xenon-lamp (Osram). The light was focused into a spot of ca. 1 cm diameter which corresponds to a measured irradiation intensity of 3W. The “photochemically active” part of this, corresponding to wavelengths from ~ 200 to 600 nm, was 0.6 W, which translates into 3.5×10^{-2} $W.cm^{-2}$.

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[6] N. Stürzl, F. Hennrich, S. Lebedkin, M. M. Kappes, *J. Phys Chem. C*, 2009, **113**, 14628.

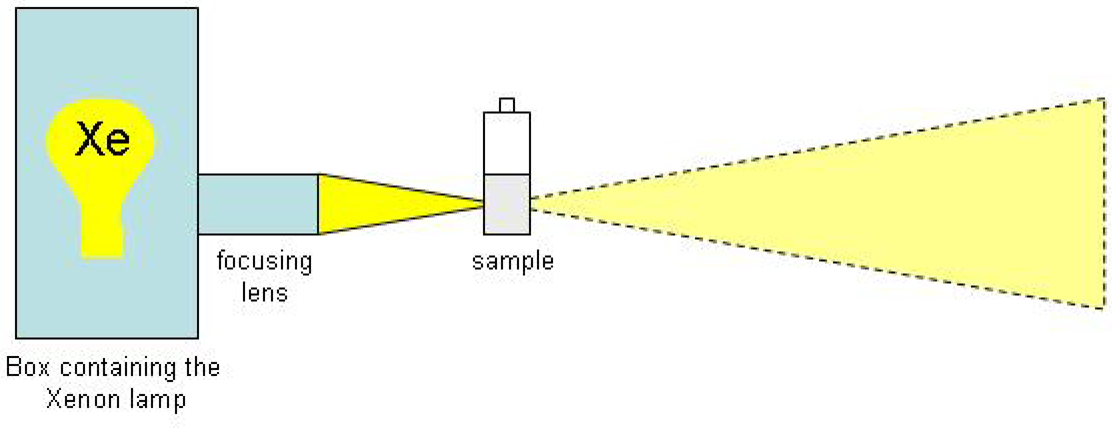

Figure S2: irradiation set-up used in this study, which comprises a Xenon lamp and a focusing lens.

The suspensions were filled in a quartz-cuvette and placed for approximately 2 min in the focused spot of the Xenon lamp at room temperature. During irradiation the temperature of the suspensions did not increase significantly.

4. Spectroscopic characterization of SWNTs dispersions

4.1. Photoluminescence spectroscopy

Photoluminescence (PLE) maps were measured in the emission range of ~900-1700 nm and excitation range of 500-950 nm (scanned in 3 nm steps) using an FTIR spectrometer (Bruker IFS66) equipped with a liquid-nitrogen-cooled Ge-photodiode and a monochromatized excitation light source as described elsewhere.[7] UV-vis-NIR absorption spectra of the fractions were recorded on a Varian Cary 500 spectrophotometer. For PLE and absorbance measurements, DGC fractions were diluted with toluene up to a 0.8 ml volume.

The relative distribution of (n,m) tubes present in a batch of raw SWNTs is estimated from PLE analysis of a sodium cholate dispersion. For a more accurate picture, the fluorescence efficiency of each SWNT should be taken into account.

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[7] S. Lebedkin, F. Hennrich, O. Kiowski, M. M. Kappes, *Phys. Rev. B*, 2008, **77**, 165429.

4.2. Raman spectra

The precipitated SWNTs were collected by centrifugation after irradiation of the suspension. The precipitate was re-suspended in toluene using an ultrasonic bath and a droplet of this sample was applied on glass slide and dried at room temperature to remove the organic solvent. The dried sample was then characterized with a confocal Raman microscope (WiTec) with a spectral resolution of 3.75 cm^{-1} using back-scattering configuration and a 10x objective excited with a HeNe laser with 632.8 nm excitation and with a power density of ~10^5 W/cm^2.

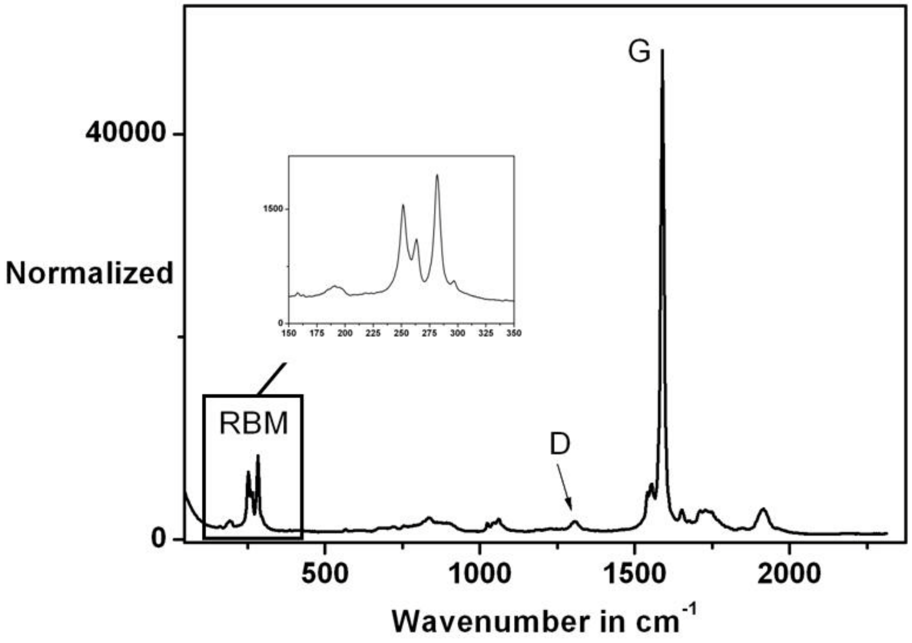

Figure S3: Raman spectrum of precipitated SWNTs from suspension **7b**.

Figure **S2** represents the Raman spectrum of precipitated SWNTs from suspension **7b**. The D peak is very small and the ratio D/G is around 0.05, which is close to the one found in pristine SWNTs.[8] It means that photoirradiation of the suspension **7b** did not induce any defect or covalent sidewall functionnalization to the SWNTs.

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[8] F. G. Brunetti, M. A. Herrero, J. d. M. Muñoz, A. Díaz-Ortiz, J. Alfonsi, M. Meneghetti, M. Prato, E. Vászquez *J. Amer. Chem. Soc.*, 2008, **130**, 8094.

4.3. Absorption spectra of suspensions 7b and 7c.

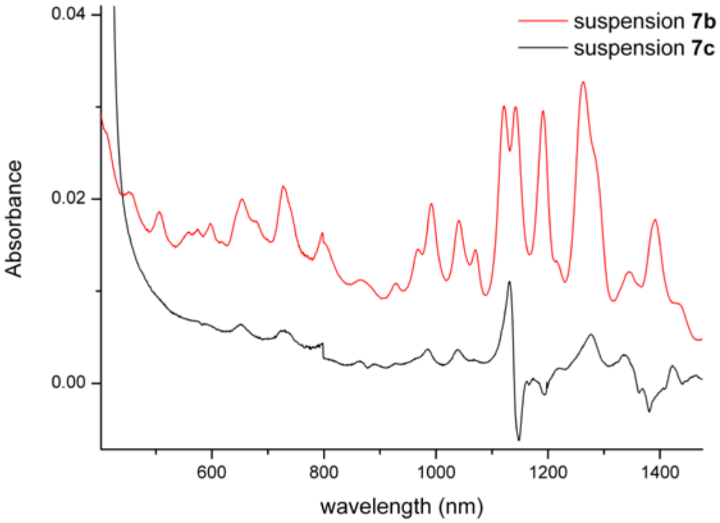


Figure S4: Absorption spectra of suspensions **7b** and **7c**.

5. Photo-cleavage of polymer 6c and suspension 7c

Suspension **7c** was filtered on a *Whatman* 0.2 μm pore size Nylon filter and redispersed in toluene to obtain a suspension of SWNTs/polymer **7c.** The filtration allowed the removal of traces of polymer **6c** (which were not removed completely by DGC) and the density gradient tribromotoluene dissolved in *o*-dichlorobenzene. However, in case of an equilibrium:

$$\text{SWNT/(polymer)}_a \leftrightarrows \text{SWNT/(polymer)}_{a-b} + \text{b(polymer)}$$

the redispersed SWNT will act as source for polymers species in solution. Thus, even after filtration there might be dissolved polymers remaining.

UV/VIS/NIR spectra were recorded from the dispersion **7c** before and after filtration and are presented in figure S5. The low concentration of the redispersed sample is due to the difficulty of washing out the SWNTs partially embedded on the filter.

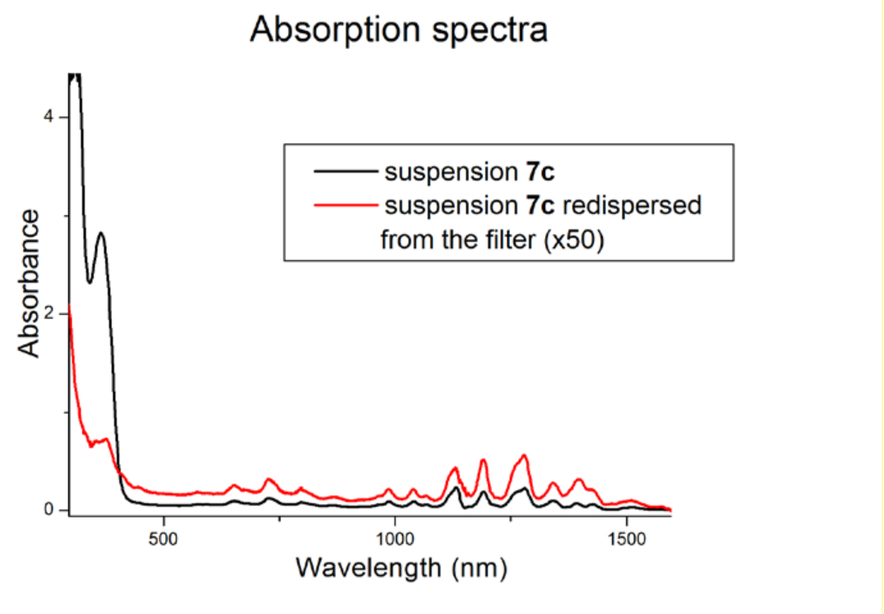


Figure S5: Absorption spectra of suspension **7c** before filtration (black line) and of the suspension **7c** redispersed from the filter (red line).

Fluorescence spectra were recorded from the redispersed SWNTs/polymer dispersion **7c** and from the polymer **6c** before and after light irradiation (figure S6).

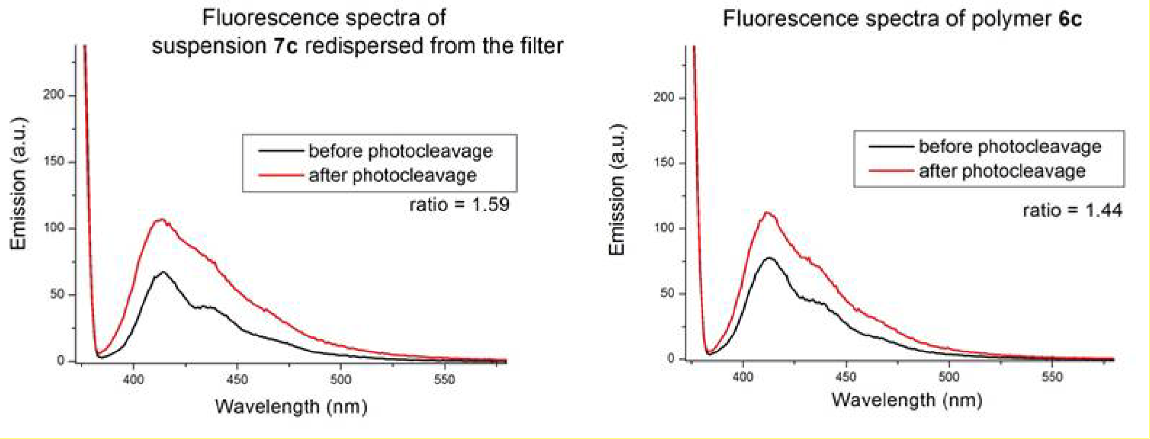


Figure S6: Fluorescence spectra of the redispersed SWNTs/polymer **7c** and polymer **6c** before and after photoirradition.

A comparable increase in fluorescence intensity is observed upon irradiation in both cases, pointing at a similar photo-cleavage mechanism for the dissolved polymer **6c** and for the polymer dispersing the SWNT **7c**.

We have performed GPC analysis of polymer **6c** before and after irradiation and the GPC traces are displayed in figure S7. As expected, a dramatic drop of the polymer length is observed after photoirradiation which confirms the expected degradation of the polymer to smaller chain length oligomers. Interestingly, the biggest peak after photo-cleavage has a molecular weight of about 1500 g/mol which corresponds to the one expected for the fluorene trimer released upon breaking of the *o*-nitrobenzyl ether subunits.

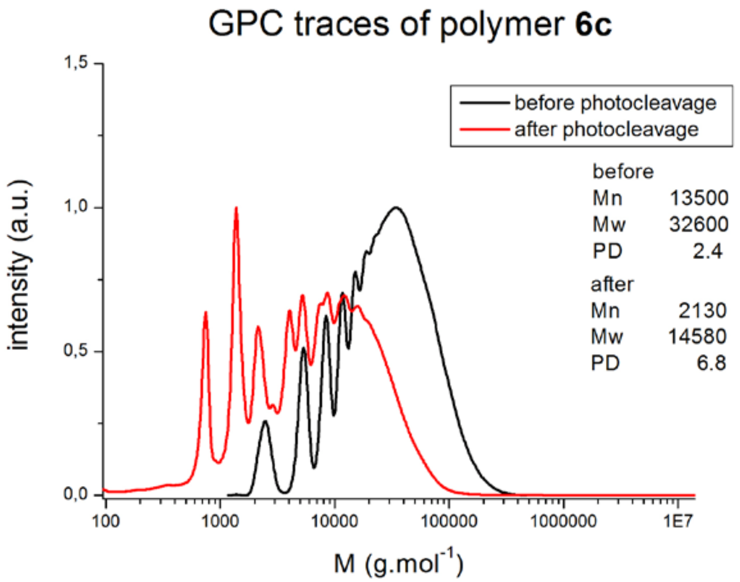


Figure S7: GPC analysis of the polymer **6c** before (black) and after (red) photo-cleavage.

Quantifications of the extent of photo-cleavage for the SWNT dispersion **7c** turned out to be difficult. Optical investigations are delicate due to the presence of optically active SWNTs and for alternative quantitative methods like TGA or GPC, the amount of available material is too little for serious investigations.

However, due to the similarity of the observed fluorescence spectra of the dissolved polymer **6c** and its SWNT dispersion **7c** (figure S6), we hypothesize comparable break down mechanisms and length distributions in both cases.

6. TEM images

The TEM investigations were performed in a Tecnai F20 ST operating at 200 kV using an extraction voltage for the field emission gun of 4.0 keV. The instrumental value of the beam current was 44μA. The point resolution of this microscope is about 0.235nm at Scherzer focus with an information limit of about 0.14 nm. The micrographs were taken with a 1K × 1K CCD camera.

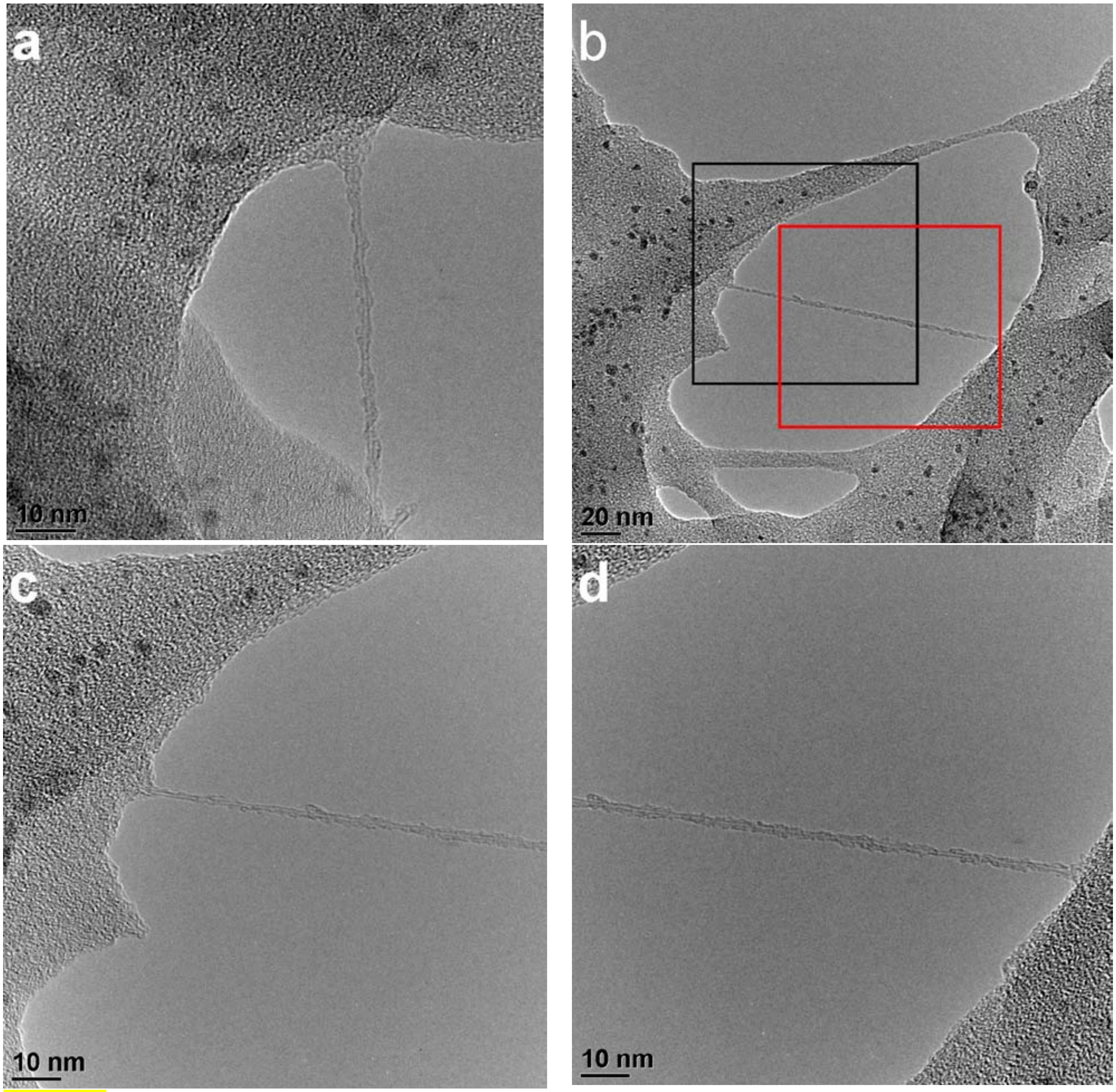
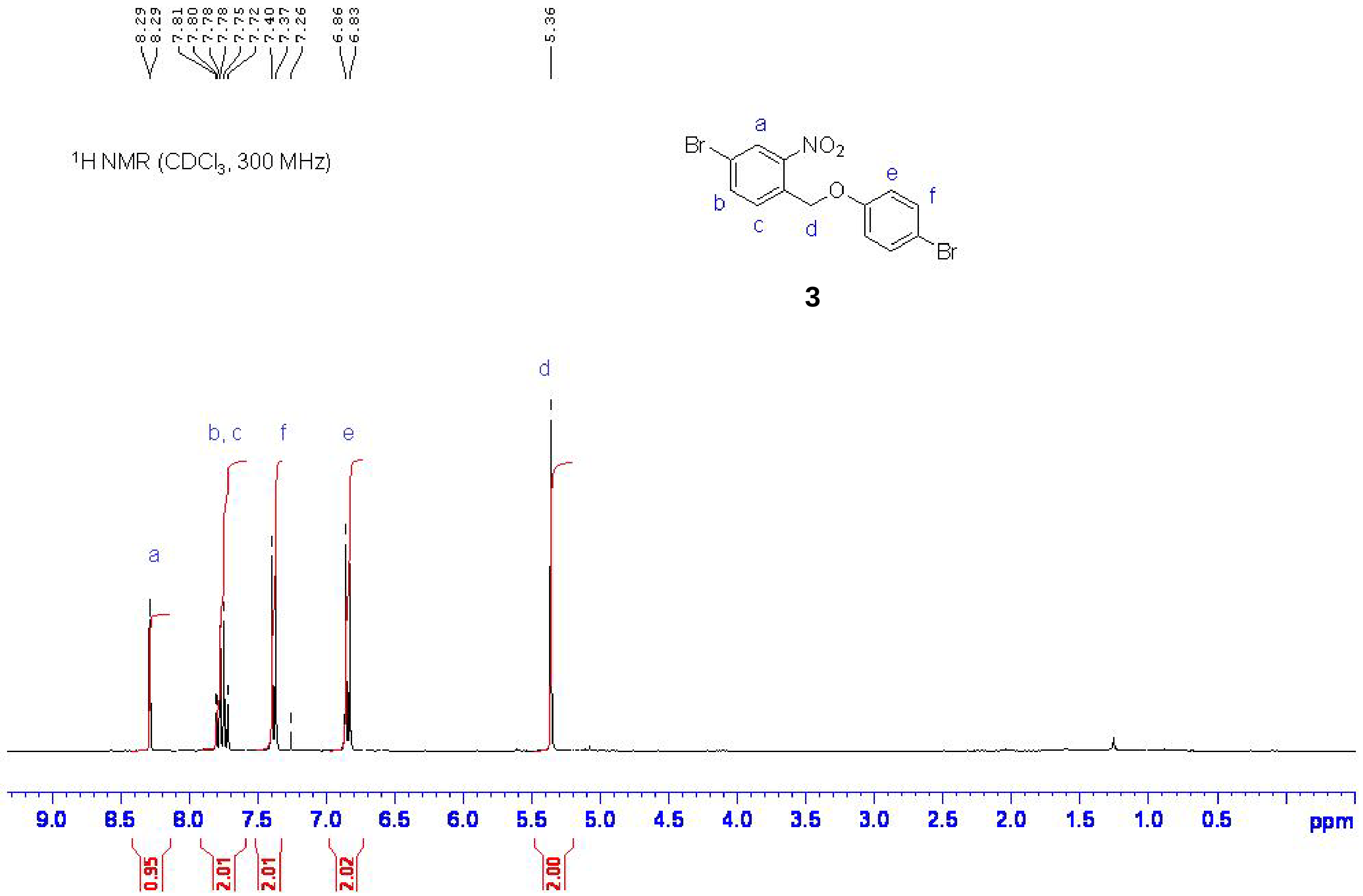


Figure S8: TEM images of precipitated SWNTs from suspension **7d**. Images c) and d) are the enhancement of the black and the red box of image b), respectively.

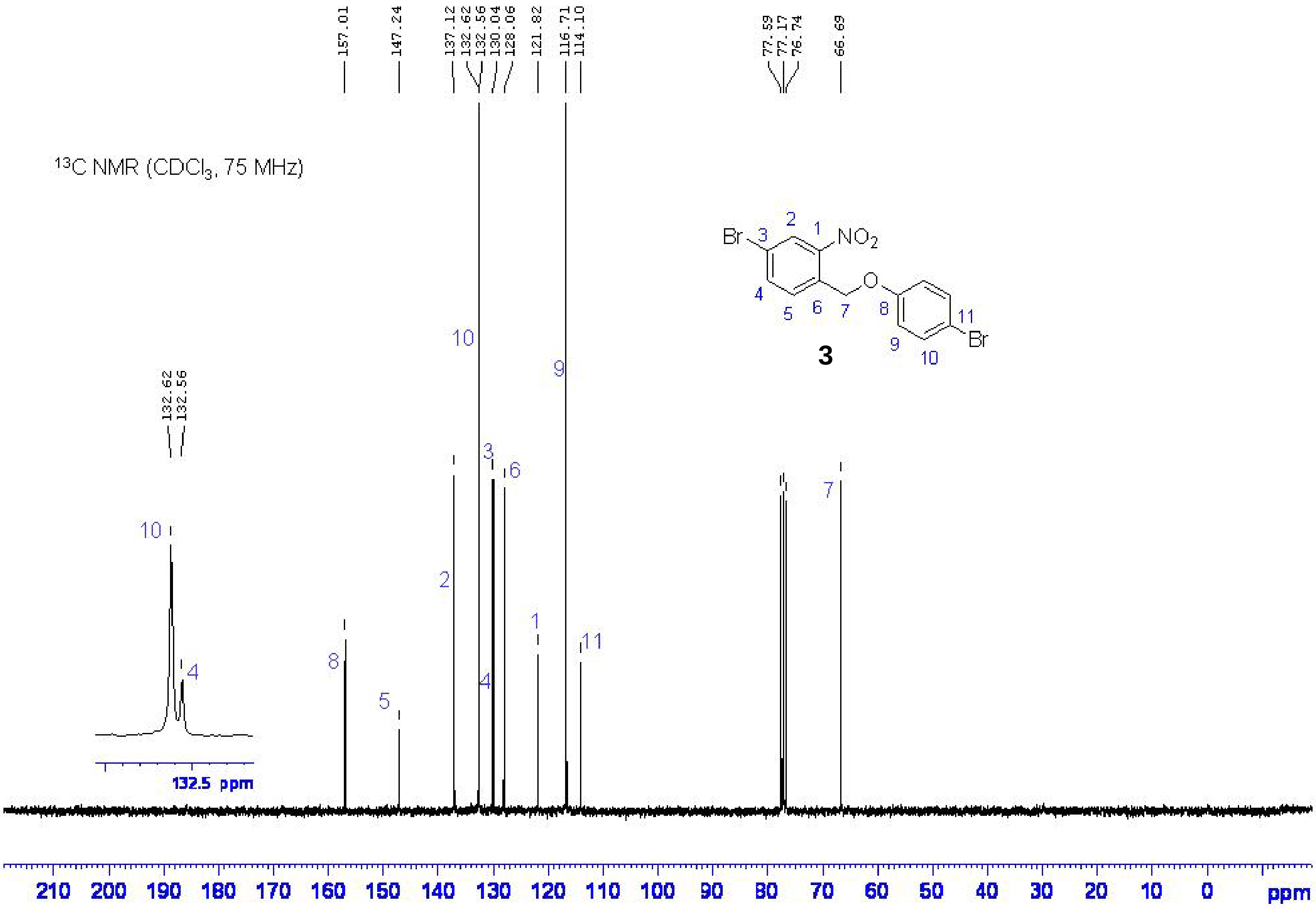
TEM images **S8a–d** show that after irradiation, the residues of polymer **7d** are still coating SWNTs. Moreover it is clear that the cleaved polymer adopts a wrapping conformation around the SWNT.

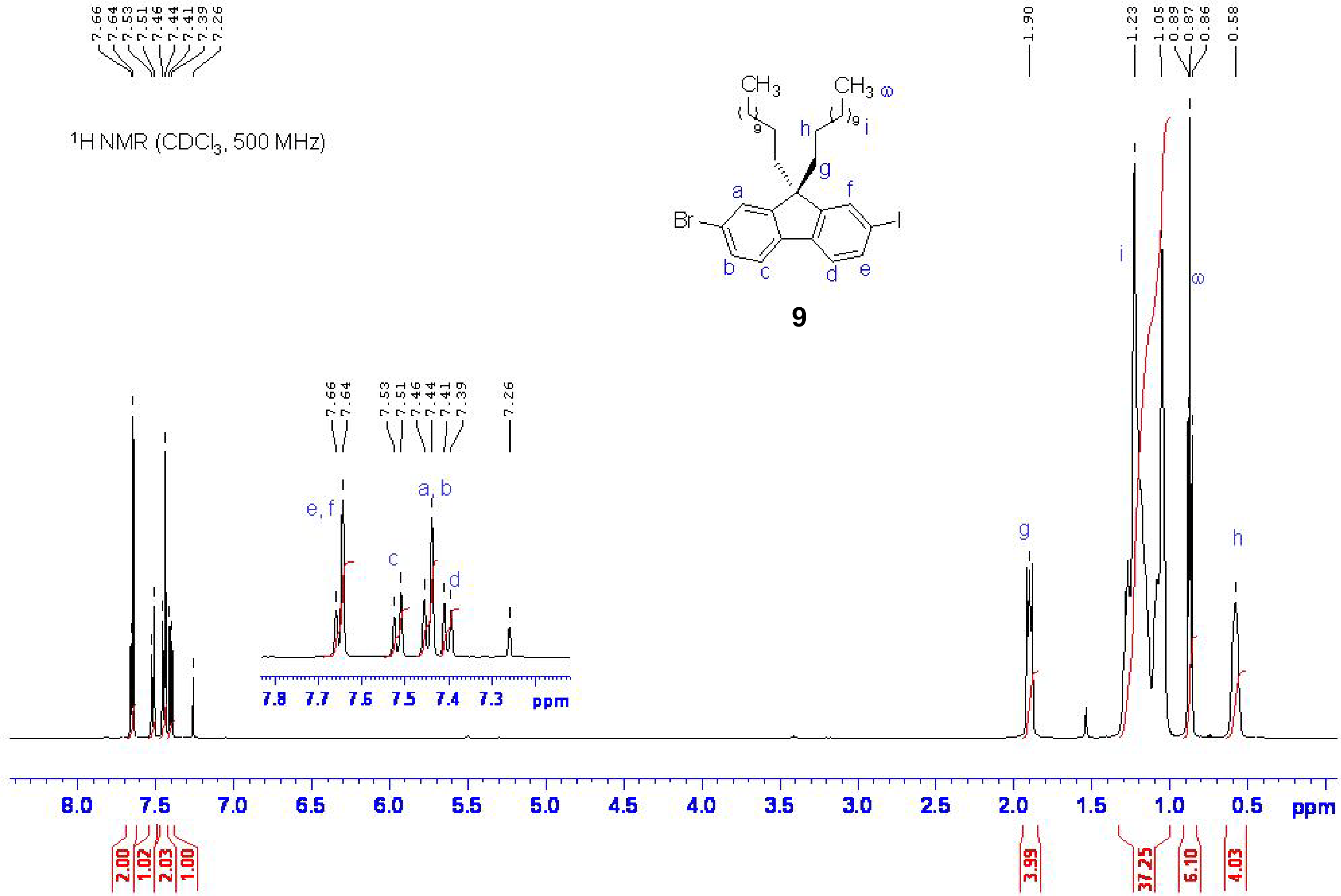
7. NMR spectra

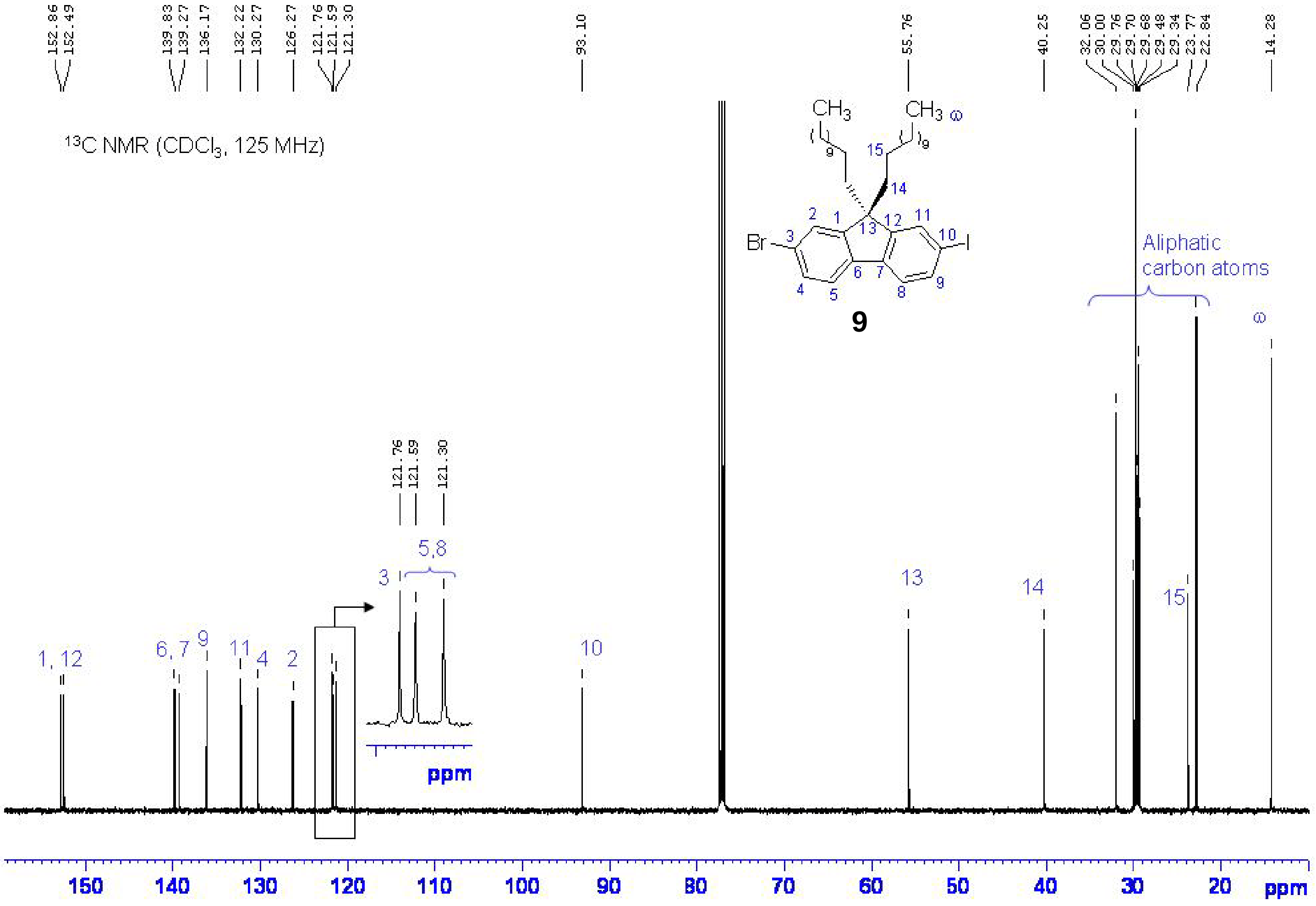


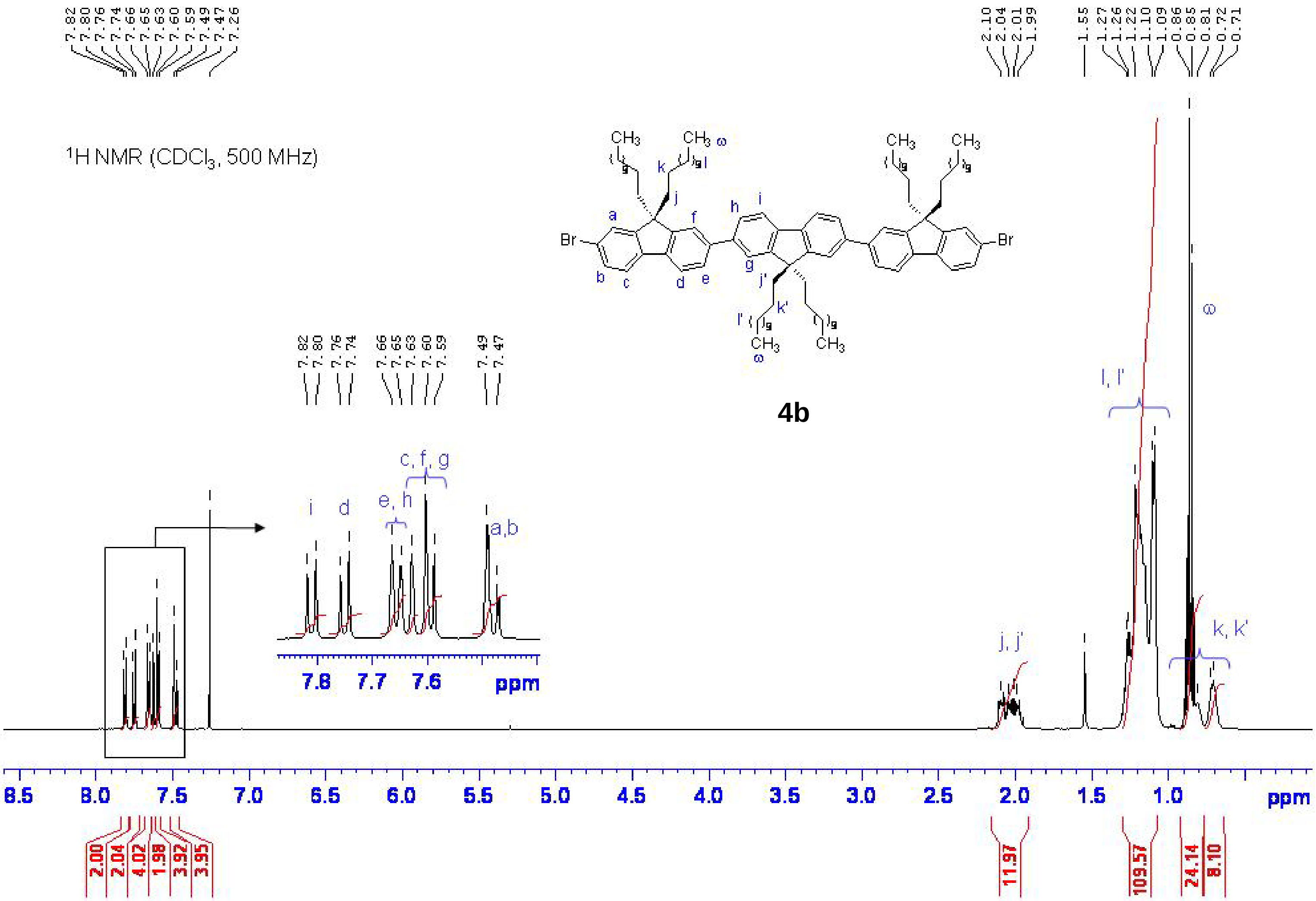
^{1}H NMR (CDCl$_3$, 300 MHz)

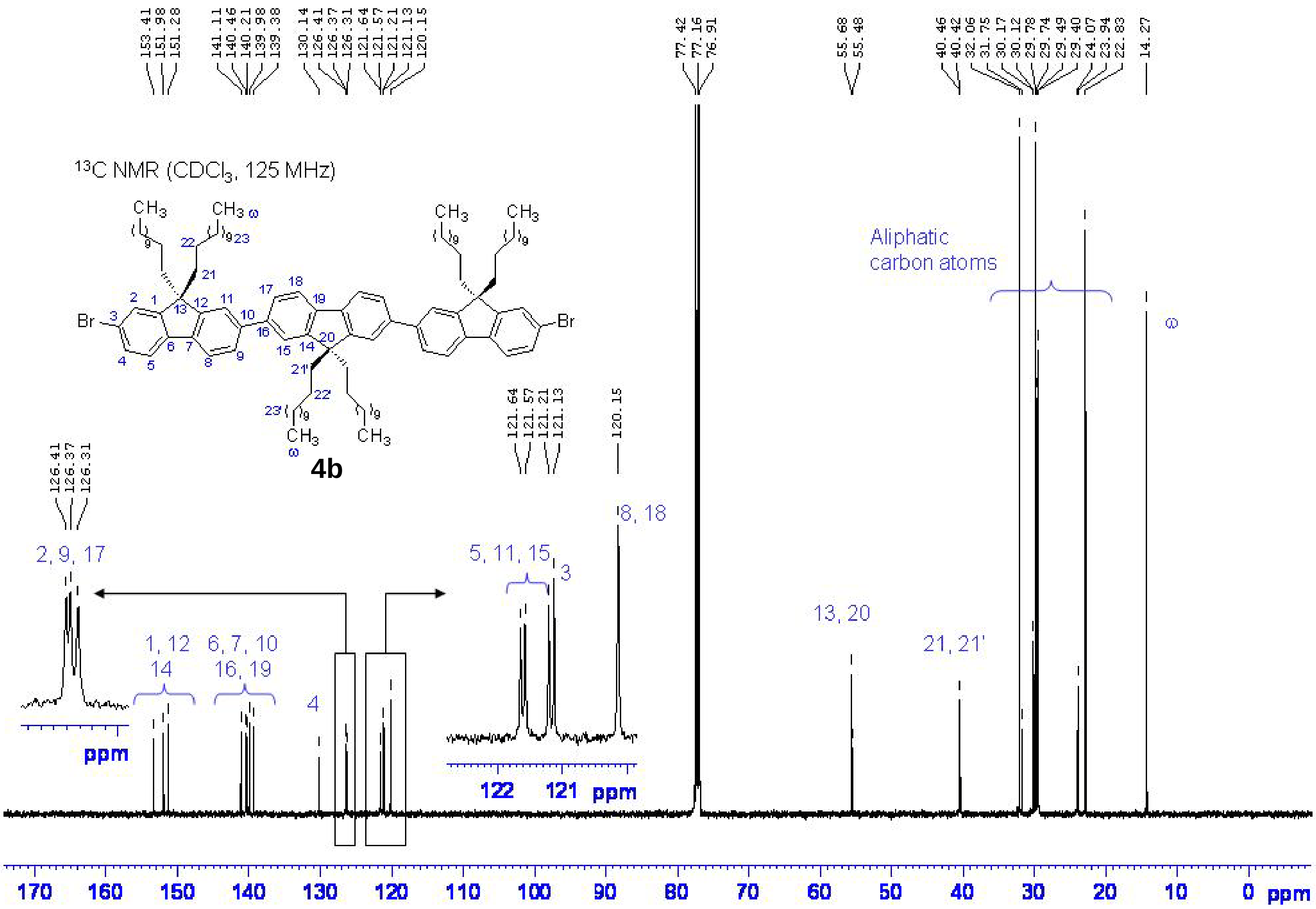
3

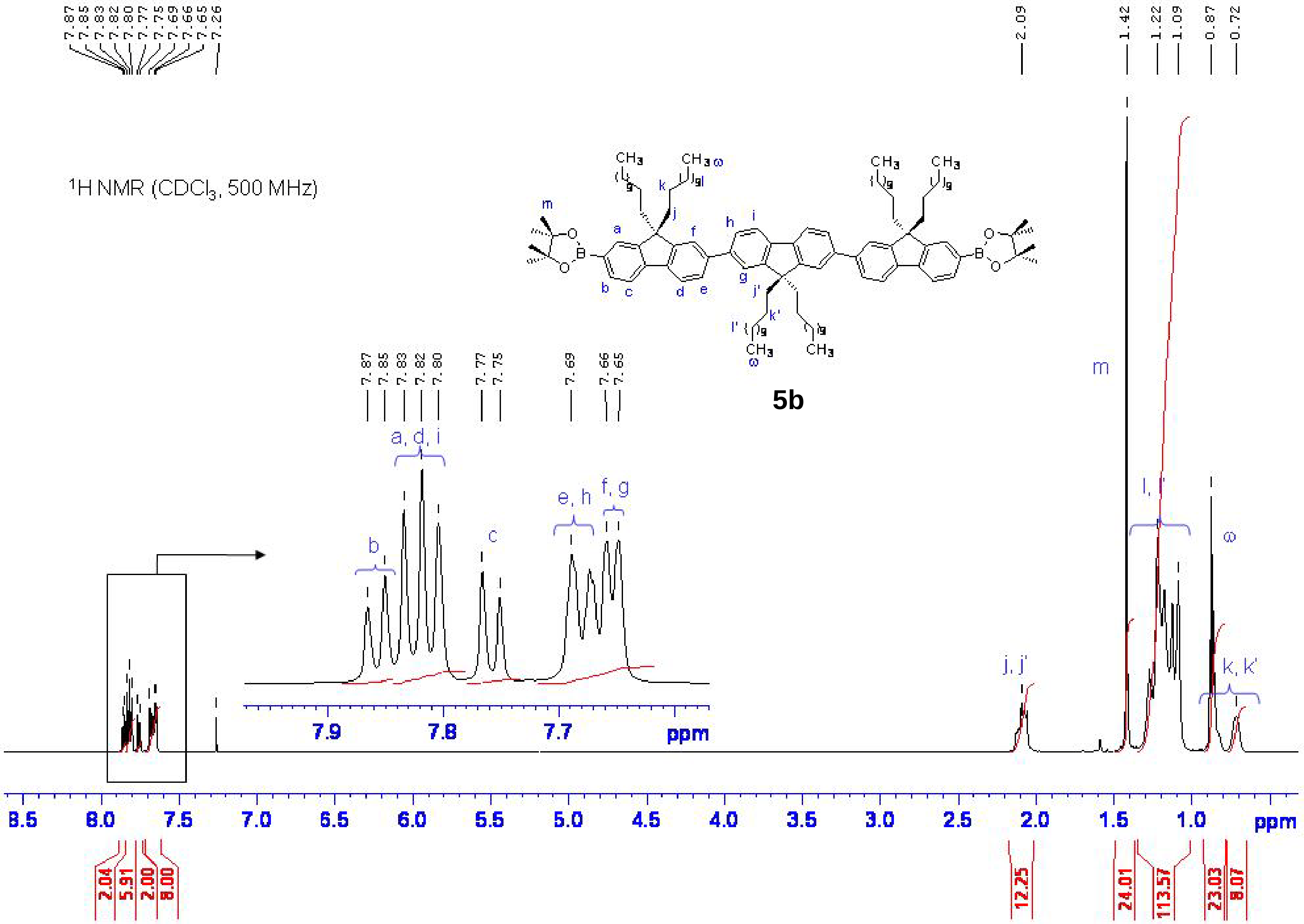

157.01
147.24
137.12
132.62
132.56
130.04
128.06
121.82
116.71
114.10
77.59
77.17
76.74
66.69
^{13}C NMR ($CDCl_3$, 75 MHz)
Br
NO_2
O
Br
1
2
3
4
5
6
7
8
9
10
11
3
132.62
132.56
10
4
132.5 ppm
10
9
3
6
2
7
8
4
5
1
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

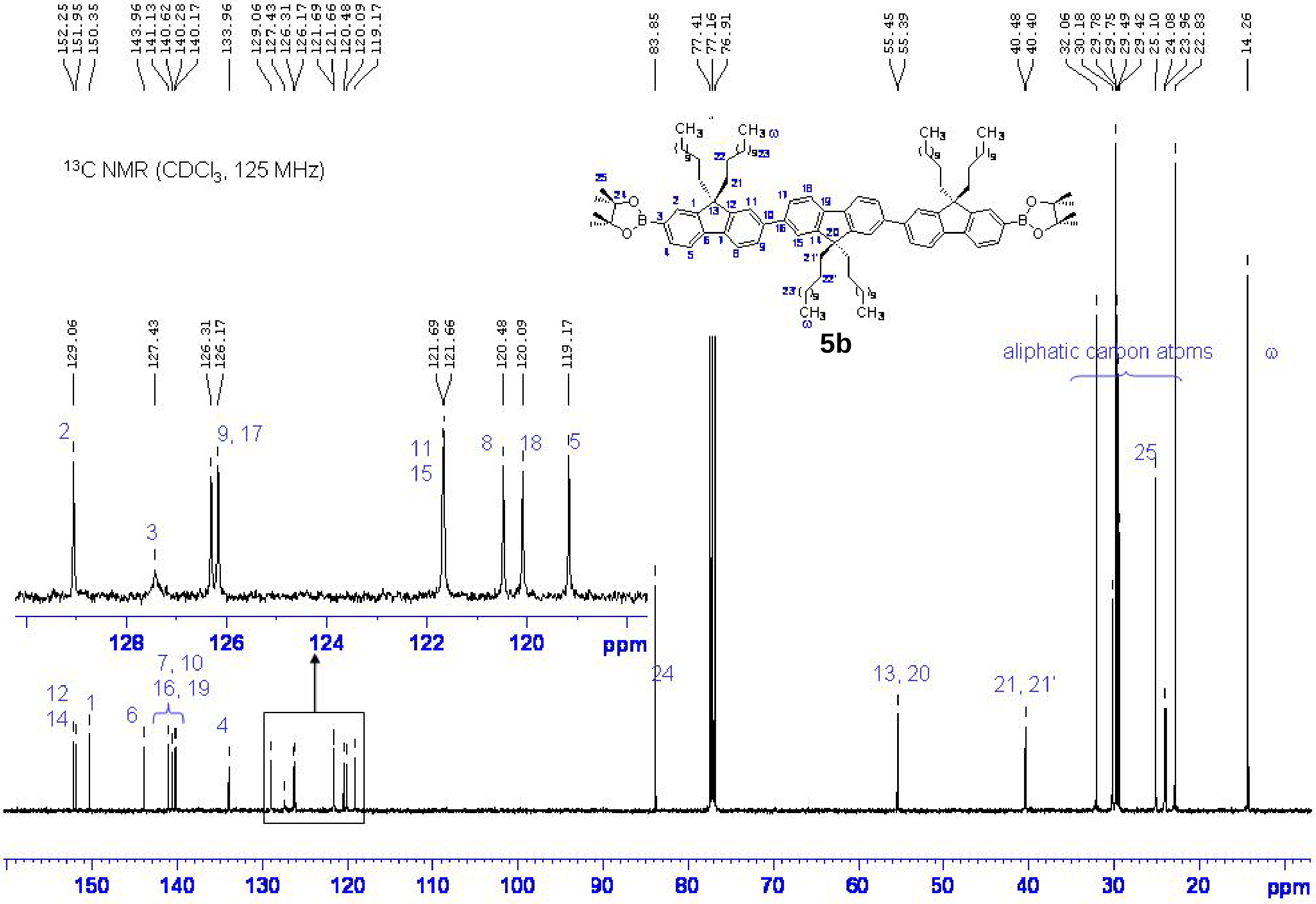

^{1}H NMR (CDCl$_3$, 500 MHz)
7.66
7.64
7.53
7.51
7.46
7.44
7.41
7.39
7.26
1.90
1.23
1.05
0.89
0.87
0.86
0.58
CH3
CH3 ω
9
9
h
i
g
a
f
Br
I
b
c
d
e
9
e, f
a, b
c
d
7.8
7.7
7.6
7.5
7.4
7.3
ppm
g
i
ω
h
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.02
2.03
1.00
3.99
37.25
6.10
4.03

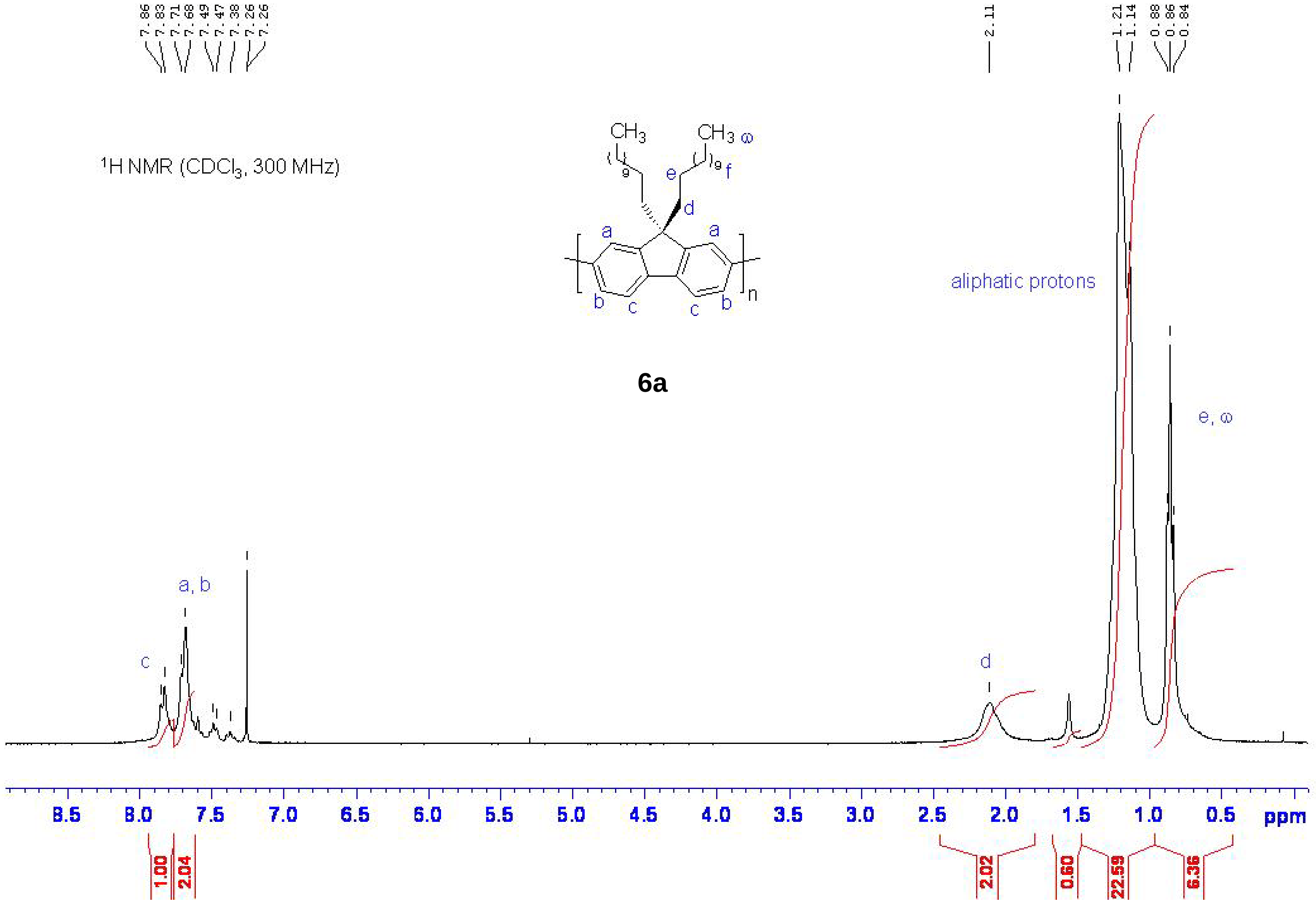

152.86
152.49
139.83
139.27
136.17
132.22
130.27
126.27
121.76
121.59
121.30
93.10
55.76
40.25
32.06
30.00
29.76
29.70
29.68
29.48
29.34
23.77
22.84
14.28
^{13}C NMR (CDCl$_3$, 125 MHz)
CH$_3$
CH$_3$ ω
9
9
15
14
Br
I
1
2
3
4
5
6
7
8
9
10
11
12
13
9
Aliphatic carbon atoms
ω
121.76
121.59
121.30
5,8
3
13
14
15
1, 12
6, 7
9
11
4
2
10
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

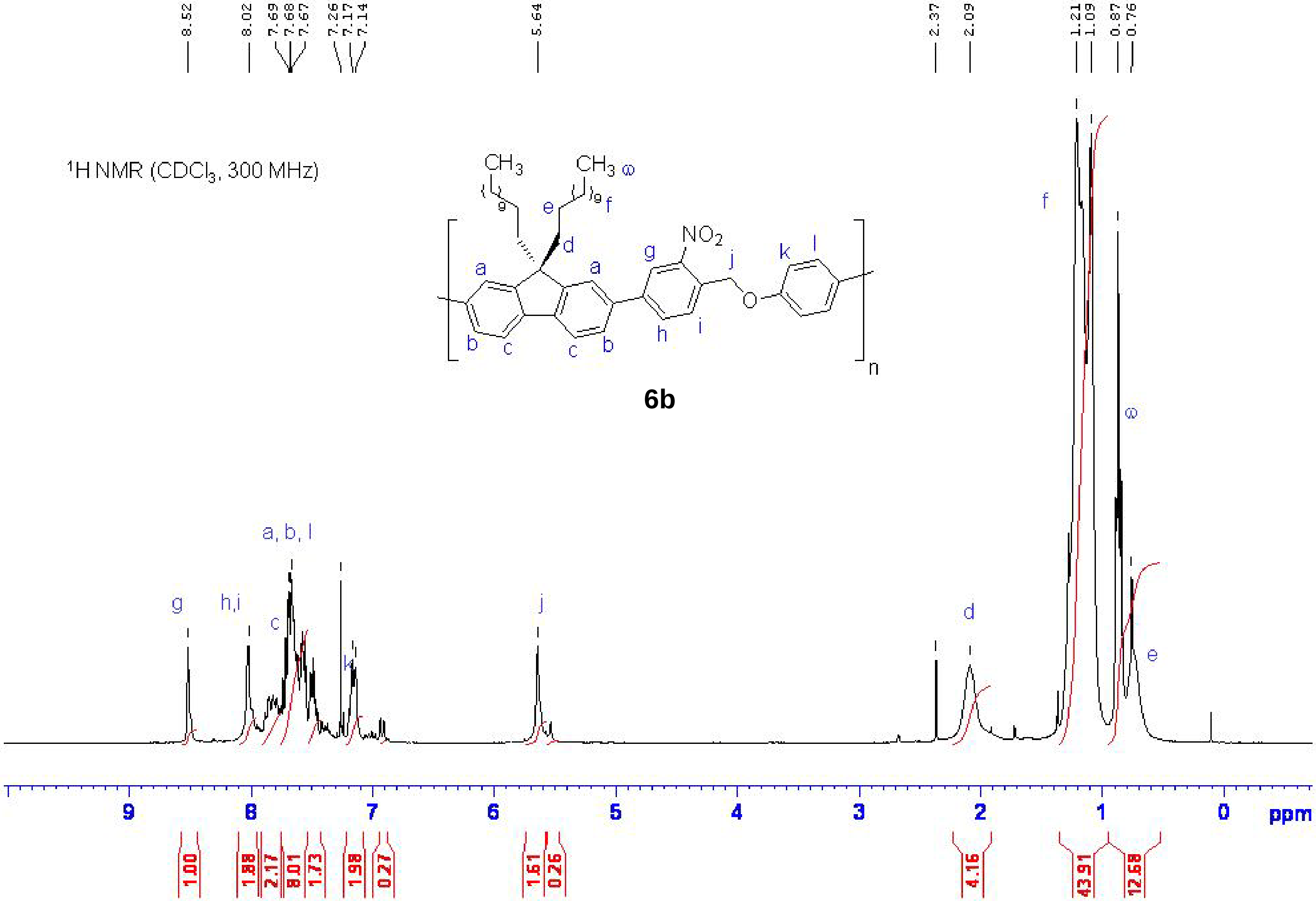

7.82 7.80 7.76 7.74 7.66 7.65 7.63 7.60 7.59 7.49 7.47 7.26
2.10 2.04 2.01 1.99
1.55 1.27 1.26 1.22 1.10 1.09 0.86 0.85 0.81 0.72 0.71
¹H NMR (CDCl₃, 500 MHz)
CH₃
ω
( )₉
l
k
j
a
f
h
i
Br
b
c
d
e
g
j'
k'
l'
4b
7.82 7.80 7.76 7.74 7.66 7.65 7.63 7.60 7.59 7.49 7.47
i
d
e, h
c, f, g
a,b
7.8
7.7
7.6
ppm
l, l'
j, j'
k, k'
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
ppm
2.00
2.04
4.02
1.98
3.92
3.95
11.97
109.57
24.14
8.10

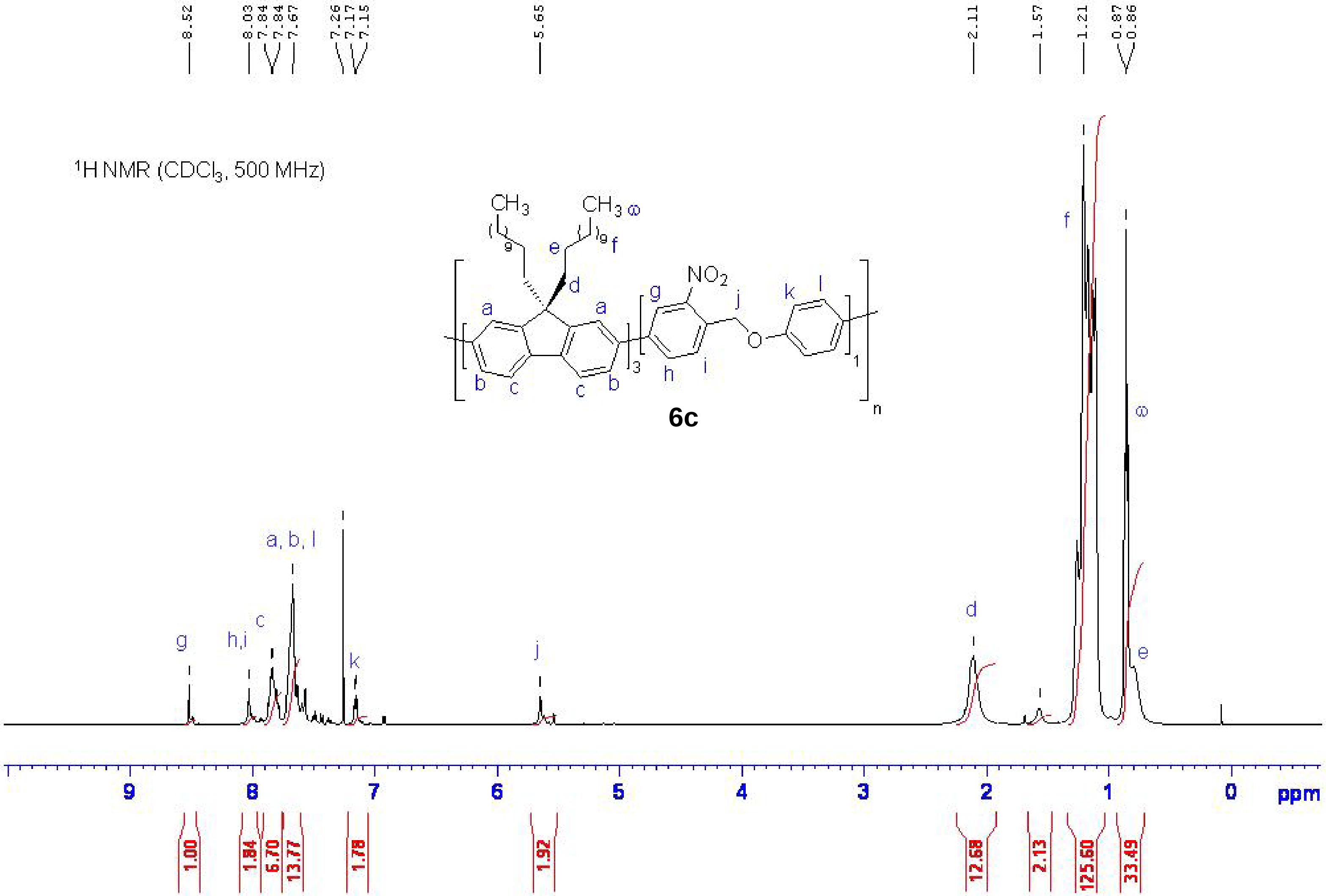

153.41
151.98
151.28
141.11
140.46
140.21
139.98
139.38
130.14
126.41
126.37
126.31
121.64
121.57
121.21
121.13
120.15
77.42
77.16
76.91
55.68
55.48
40.46
40.42
32.06
31.75
30.17
30.12
29.78
29.74
29.49
29.40
24.07
23.94
22.83
14.27
^{13}C NMR ($CDCl_3$, 125 MHz)
4b
Aliphatic carbon atoms
ω
126.41
126.37
126.31
2, 9, 17
ppm
1, 12
14
6, 7, 10
16, 19
4
121.64
121.57
121.21
121.13
120.15
5, 11, 15
3
8, 18
122
121
ppm
13, 20
21, 21'
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

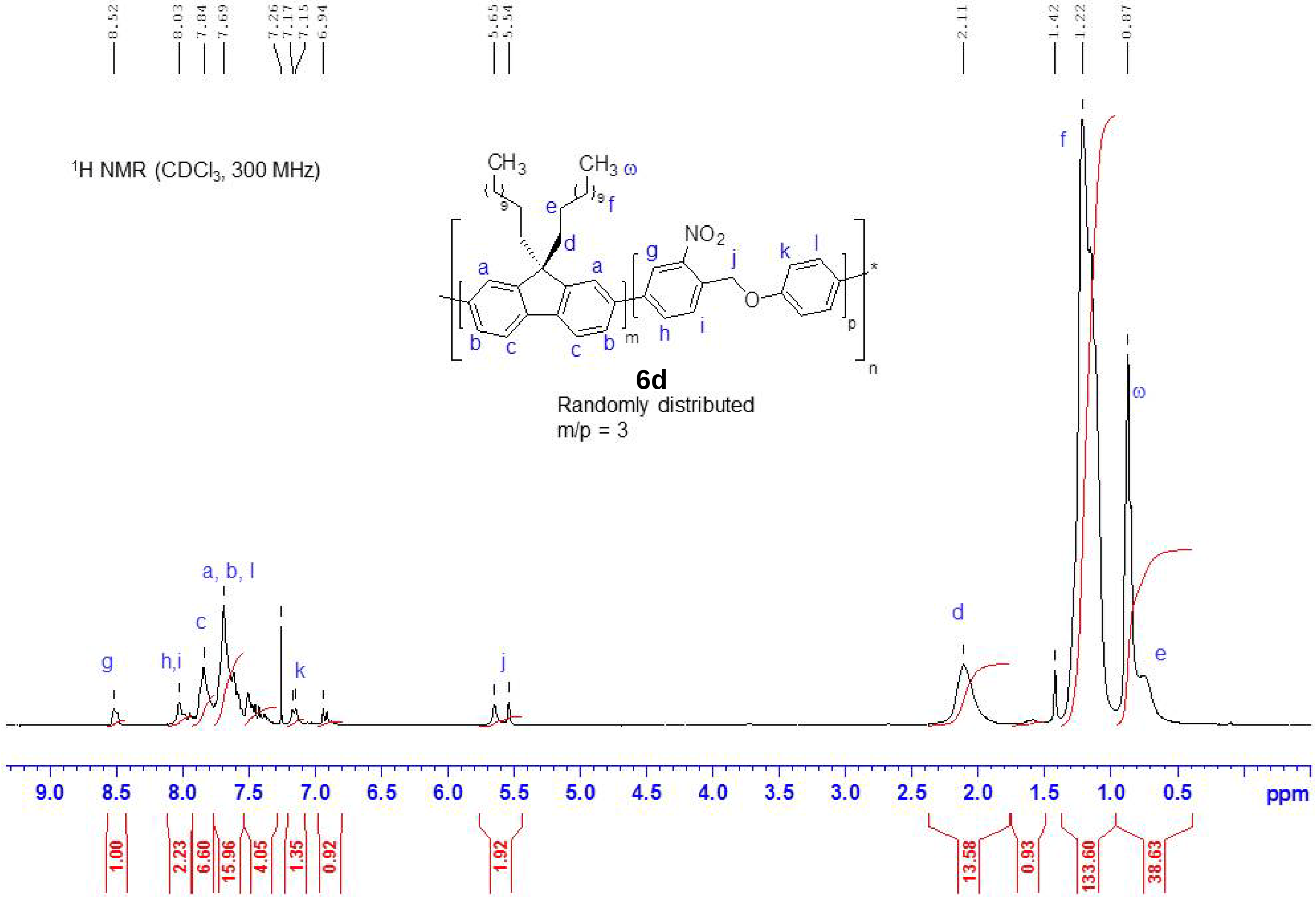

7.87 7.85 7.83 7.82 7.80 7.77 7.75 7.69 7.66 7.65 7.26
2.09
1.42 1.22 1.09 0.87 0.72
^{1}H NMR (CDCl$_3$, 500 MHz)
m
a
b
c
d
e
f
g
h
i
j
j'
k
k'
l'
CH$_3$
ω
5b
a, d, i
b
c
e, h
f, g
7.9
7.8
7.7
ppm
j, j'
l, l'
k, k'
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04 5.91 2.00 8.00
12.25
24.01
113.57
23.03 8.07

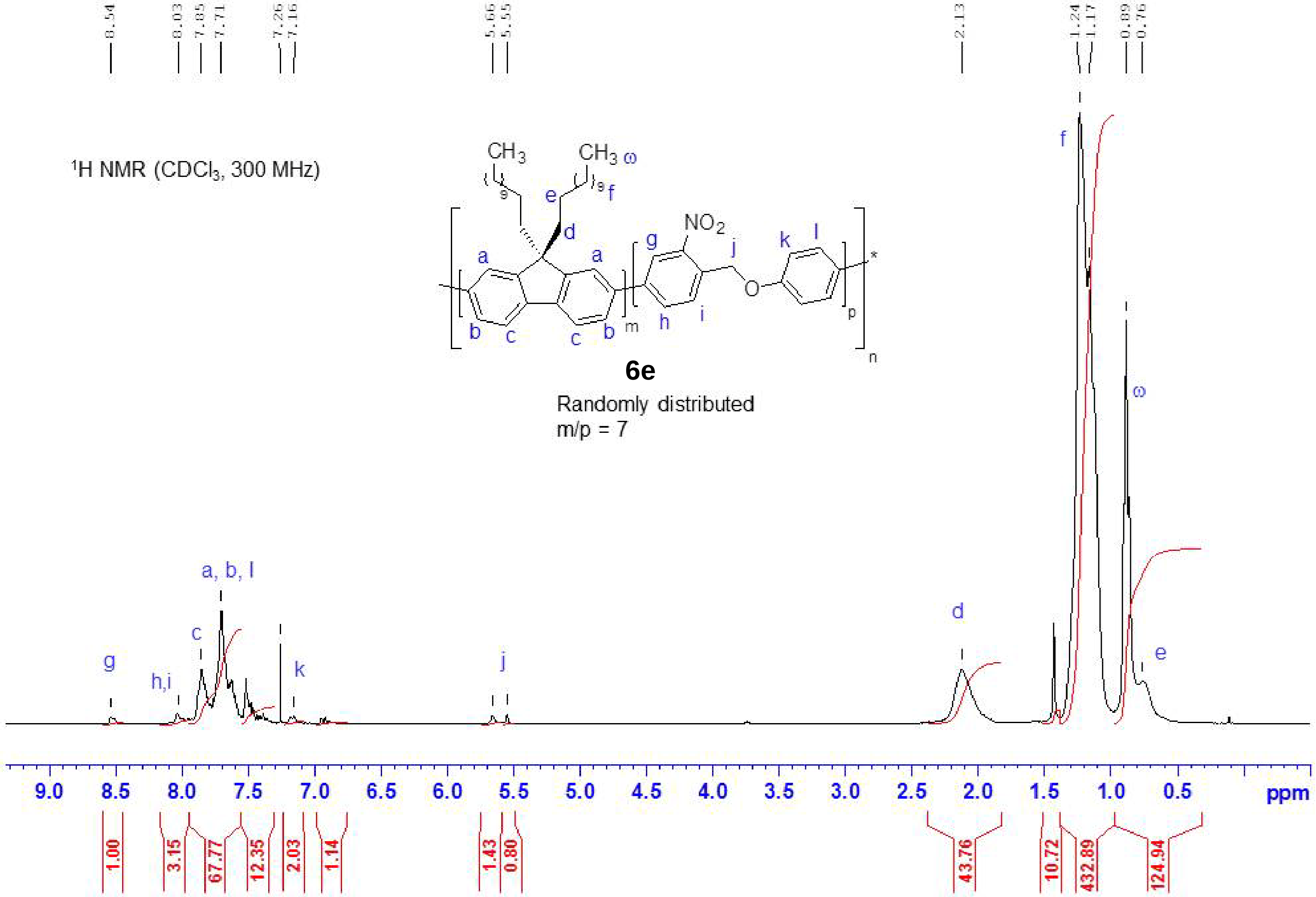

152.25
151.95
150.35
143.96
141.13
140.62
140.28
140.17
133.96
129.06
127.43
126.31
126.17
121.69
121.66
120.48
120.09
119.17
83.85
77.41
77.16
76.91
55.45
55.39
40.48
40.40
32.06
30.18
29.78
29.75
29.49
29.42
25.10
24.08
23.96
22.83
14.26
^{13}C NMR (CDCl$_3$, 125 MHz)
5b
aliphatic carbon atoms
ω
2
3
9, 17
11
15
8
18
5
25
128
126
124
122
120
ppm
24
13, 20
21, 21'
12
14
1
6
7, 10
16, 19
4
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.86
7.83
7.71
7.68
7.49
7.47
7.38
7.26
7.26
2.11
1.21
1.14
0.88
0.86
0.84
¹H NMR (CDCl₃, 300 MHz)
CH₃
CH₃ ω
9
e
9
f
d
a
a
b
c
c
b
n
6a
aliphatic protons
e, ω
a, b
c
d
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
ppm
1.00
2.04
2.02
0.60
22.59
6.36


^{1}H NMR (CDCl$_3$, 300 MHz)
8.52
8.02
7.69
7.68
7.67
7.26
7.17
7.14
5.64
2.37
2.09
1.21
1.09
0.87
0.76
CH$_3$
CH$_3$ ω
9
9
f
e
d
NO$_2$
g
j
k
l
a
a
O
b
c
c
b
h
i
n
6b
f
ω
a, b, l
g
h,i
c
k
j
d
e
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.88
2.17
8.01
1.73
1.98
0.27
1.61
0.26
4.16
43.91
12.58


8.52
8.03
7.84
7.84
7.67
7.26
7.17
7.15
5.65
2.11
1.57
1.21
0.87
0.86
^{1}H NMR (CDCl$_3$, 500 MHz)
CH$_3$
CH$_3$ ω
9
9
e
f
d
NO$_2$
g
j
k
l
a
a
b
c
c
b
3
h
i
1
n
6c
a, b, l
c
g
h,i
k
j
d
f
ω
e
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.84
6.70
13.77
1.78
1.92
12.68
2.13
125.60
33.49


8.52
8.03
7.84
7.69
7.26
7.17
7.15
6.94
5.65
5.54
2.11
1.42
1.22
0.87
¹H NMR (CDCl₃, 300 MHz)
CH₃
CH₃ ω
9
9
e
f
d
NO₂
g
j
k
l
a
a
b
c
c
b
m
h
i
p
n
*
6d
Randomly distributed
m/p = 3
f
ω
e
d
a, b, l
c
g
h,i
k
j
9.0
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
ppm
1.00
2.23
6.60
15.96
4.05
1.35
0.92
1.92
13.58
0.93
133.60
38.63


8.54
8.03
7.85
7.71
7.26
7.16
5.66
5.55
2.13
1.24
1.17
0.89
0.76
¹H NMR (CDCl₃, 300 MHz)
CH₃
CH₃ ω
9
9
e
f
d
NO₂
g
j
k
l
a
a
*
b
c
c
b
m
h
i
p
n
6e
Randomly distributed
m/p = 7
f
ω
a, b, l
c
g
h,i
k
j
d
e
9.0
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
ppm
1.00
3.15
67.77
12.35
2.03
1.14
1.43
0.80
43.76
10.72
432.89
124.94