

– Supporting Information –

**Photochromism of Amphiphilic Dithienylethenes
as Langmuir–Schaefer Films**

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Instrumentation

^1H and ^{13}C NMR spectra were recorded at 300.18 and 75.48 MHz, respectively, on a Varian Mercury plus spectrometer. Chemical shifts are referenced to solvent signals. ^{13}C NMR spectra were recorded with ^1H decoupling. High-resolution mass spectral analyses were carried out by the University of Saskatchewan on a API Qstar XL mass spectrometer or JEOL AccuTOF-GCv 4G mass spectrometer, using various ionization techniques (e.g., chemical ionization, electron ionization, electrospray ionization, or field desorption). HPLC analyses were performed on a HP 1090 Series II liquid chromatograph. A guard column containing SecurityGuard ULTRA pentafluorophenyl (PFP) cartridges, was connected to a Kinetex 2.6 μm PFP analytical column (150 mm \times 4.6 mm i.d.) from Phenomenex. An isocratic elution was run in which the mobile phase was 8:92 water/methanol with each solvent containing 0.1% trifluoroacetic acid. The flow rate was 1.4 mL min^{-1} , the injection volume was 5 μL , and signals were monitored at the isosbestic point at 368 nm. For the steady-state absorption studies in solution, absorption spectra were obtained at constant temperature (e.g., 21.0 ± 0.1 $^\circ\text{C}$) on a Cary 300 Bio UV–Vis spectrophotometer equipped with a dual cell Peltier circulator accessory. Absorption spectra were recorded at a scan rate, step size, and integration time of 300 nm min^{-1} , 0.5 nm, and 0.1 s, respectively. For quantum yield studies, all samples were irradiated with a 300 W xenon light source from Luzchem, measured in a 10 mm \times 4 mm quartz Suprasil fluorescence cell from Hellma and stirred. For ultraviolet irradiation, the xenon light source was filtered with a bandpass filter (Hoya U-340, $\lambda_c = 340 \pm 42$ nm) and an aqueous solution of potassium chromate ($\lambda_c = 313 \pm 7$ nm) circulated through a 50 mm \times 22 mm cylindrical cell from Hellma ($A_{313} = 0.040 \pm 0.005$). For visible irradiation, a bandpass

filter (Thorlabs FB530-10, $\lambda_c = 530 \pm 5$ nm) was used. For photoconversion, photostability studies and LS film studies, ultraviolet irradiation of all samples was performed with a 6 W UVA ($\lambda_c = 365$ nm) Ultra-Lum or UVP lamp. Visible irradiation in the photostability studies was carried out with a 300 W Osram EXR halogen lamp of a Kodak Ektagraphic III E Plus slide projector fitted with a longpass filter (Schott GG-495, $\lambda_c = 495 \pm 6$ nm). For the LS film studies, visible irradiation was carried out with an unfiltered 53 W halogen bulb. Surface-pressure–area isotherm measurements and LS film formation were performed on a KSV NIMA Technology 312D Langmuir trough at room temperature with ultrapure water as a subphase. For the steady-state absorption studies of LS films, absorption spectra were obtained at room temperature on a Shimadzu UV-2600 spectrophotometer. Spectra were recorded at a scan rate, step size, and integration time of 300 nm min^{-1} , 0.5 nm, and 0.1 s, respectively. Atomic force microscopy (AFM) measurements were performed at room temperature on a Bruker Icon AFM with FESPA probes in soft tapping mode. Nine AFM measurements were made for each sample with a scanning area $3.5 \mu\text{m} \times 3.5 \mu\text{m}$. Transmission electron microscopy (TEM) images were collected at room temperature on a Philips CM12 TEM operating at 120 kV ($\lambda = 0.0418$ Å) with a base pressure of 10^{-6} mbar. Calibrations were performed with a polycrystalline gold sample.

Materials

All reactants (99+%, Sigma-Aldrich), organic solvents (spectrophotometric grade, Sigma-Aldrich and Carl Roth), deuterated solvents (99.9 atom % D, Sigma-Aldrich), palladium catalysts (99.9+% Pd, Strem Chemicals), octafluorocyclopentene (99+%, SynQuest

Laboratories) were purchased and used as received. Dichloromethane, 1,4-dioxane and tetrahydrofuran were purified based on literature procedures.² Flash column chromatography was performed on silica gel (230-400 mesh, 60 Å, Sillicycle), neutral aluminum oxide (activated, 150 mesh, 58 Å, Sigma-Aldrich), and basic aluminum oxide (activated, 60 mesh, 58 Å, Alfa Aesar). Ultrapure water (18 MΩ•cm) was obtained from a Milli-Q Gradient A10 or an ELGA PURELAB Classic system.

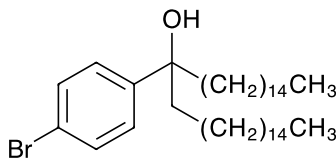
Quantum yield, photoconversion and photostability studies

The cyclization and cycloreversion quantum yields of **3** in ethyl acetate were determined using Aberchrome 540 as a chemical actinometer. The procedures used to determine the quantum yields of DTEs have been previously described in detail.³⁻⁴ The photoconversion of **3** from the open-ring to the closed-ring isomers in the photostationary state under irradiation with UV light was determined from HPLC studies. The integrated area for the peak representing the closed-ring isomer was divided by the sum of the integrated areas for the peaks representing both isomers and was calculated as a percentage. The photostability of **3** in ethyl acetate (0.1mM) was measured by UV-vis absorption spectroscopy over five ring-closing/ring-opening cycles in the presence of air. The absorbance was monitored at the 605 nm for the closed-ring isomer upon reaching the photostationary state or complete cycloreversion (i.e., 210 s of UV light followed by 75 s of visible light were used to complete one cycle).

Procedures for the synthesis of 3

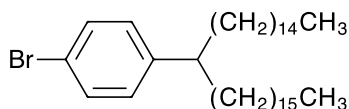
16-(4-Bromophenyl)dotriacontan-16-ol (4)

This method was based on a literature procedure.⁵ Hexadecylmagnesium bromide (11.9 mL of a 0.9 M solution in tetrahydrofuran, 10.7 mmol) was added dropwise to a stirred solution of 1-(4-bromophenyl)hexadecan-1-one (2.80 g, 7.08 mmol) in anhydrous tetrahydrofuran (30 mL) at room temperature under an atmosphere of argon. The starting ketone was synthesized following a reported procedure.⁶ After stirring at 50 °C for 10 h, the reaction mixture was allowed to cool to room temperature before an aqueous solution of ammonium chloride (20 mL, 0.5 M) was added. The mixture was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (25 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (5:1:0.1 petroleum ether/diethyl ether/triethylamine) gave pure **4** as a colorless solid (2.27 g, 52%). ¹H NMR (CDCl₃, δ): 0.88 (t, *J* = 7.2 Hz, 6H, CH₃), 0.90–1.38 (m, 54H, CH₂), 1.62–1.85 (m, 4H, CH₂), 7.20–7.28 (m, 2H, Ar H), 7.40–7.48 (m, 2H, Ar H). ¹³C NMR (CDCl₃, δ): 14.3, 22.9, 23.5, 29.5, 29.7, 29.8, 29.9, 32.1, 43.1, 120.3, 127.4, 131.2, 145.7. HRMS-CI (*m/z*): [M+CH₃CO₂]⁻ calcd for C₄₀H₇₂O₃⁸¹Br, 681.4650; found 681.4621.



1-Bromo-4-(1-pentadecylheptadecyl)benzene (5)

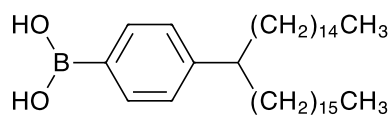
This method was based on a literature procedure.⁵ Methanesulfonic acid (0.63 mL, 9.70 mmol) was added dropwise to a stirred solution of **4** (1.50 g, 2.41 mmol) in anhydrous dichloromethane (28 mL) at $-5\text{ }^{\circ}\text{C}$. After stirring for 20 min, a solution of borane dimethyl sulfide complex (4.82 mL of a 1.0 M solution in dichloromethane, 4.82 mmol) was added dropwise to the reaction mixture at $-5\text{ }^{\circ}\text{C}$ and stirred for an additional 2 h. The reaction was quenched with aqueous solution of sodium bicarbonate (10 mL, 1M), diluted with deionized water (20 mL) and was extracted with diethyl ether ($3 \times 25\text{ mL}$). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (25 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (petroleum ether) gave a colorless solid (0.75 g, 51%). $^1\text{H NMR}$ (CDCl_3 , δ): 0.88 (t, $J = 7.2\text{ Hz}$, 6H, CH_3), 0.94–1.38 (m, 54H, CH_2), 1.38–1.68 (m, 4H, CH_2), 2.34–2.50 (m, 1H, CH), 6.90–7.10 (m, 2H, Ar H), 7.35–7.45 (m, 2H, Ar H). $^{13}\text{C NMR}$ (CDCl_3 , δ): 14.3, 22.9, 27.7, 29.5, 29.7, 29.8, 29.9, 32.1, 37.0, 45.7, 119.4, 129.6, 131.4, 145.6. HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{38}\text{H}_{69}^{81}\text{Br}$, 606.4562; found 606.4563.



4-(1-Pentadecylheptadecyl)phenylboronic acid

n-Butyllithium (0.285 mL of a 1.6 M solution in hexanes, 0.456 mmol) was added dropwise to a solution of **5** (0.250 g, 0.413 mmol) in tetrahydrofuran (5 mL) at $-78\text{ }^{\circ}\text{C}$ under an atmosphere of argon. After stirring for 1 h, trimethoxyborane (0.055 mL, 0.492

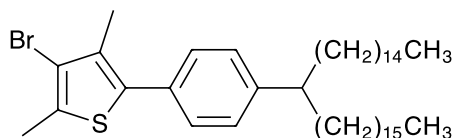
mmol) was added dropwise to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and then the mixture was allowed to warm to room temperature. After stirring for 14 h, aqueous hydrochloric acid (10 mL, 0.5 M) was added to give a biphasic mixture and then the mixture was extracted with chloroform ($4 \times 12\text{ mL}$). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The boronic acid was obtained as a colorless oil (0.217 g, 100%) and was used to prepare **6** without further purification.



4-Bromo-3,5-dimethyl-2-(4-(1-pentadecylheptadecyl)phenyl)thiophene (6)

Aqueous sodium carbonate (0.76 mL, 2 M) was added dropwise to a stirred mixture of 2,4-dibromo-3,5-dimethylthiophene (0.113 g, 0.419 mmol), 4-(1-pentadecylheptadecyl)-phenylboronic acid (0.217 g, 0.380 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.011 g, 0.010 mmol) in dioxane (5 mL) under an atmosphere of argon. The thiophene derivative was synthesized following a reported procedure.⁷ After stirring at $100\text{ }^{\circ}\text{C}$ for 4.5 h, the reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (15 mL) and poured into water (15 mL) to give a biphasic mixture. This mixture was extracted with diethyl ether ($3 \times 15\text{ mL}$). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride ($3 \times 15\text{ mL}$), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (1:10 diethyl ether/petroleum ether) gave pure **6** as a colorless solid (0.160 g, two step yield 54%). $^1\text{H NMR}$ (CDCl_3 , δ): 0.88 (t, $J = 7.2\text{ Hz}$, 6H, CH_3), 1.00–

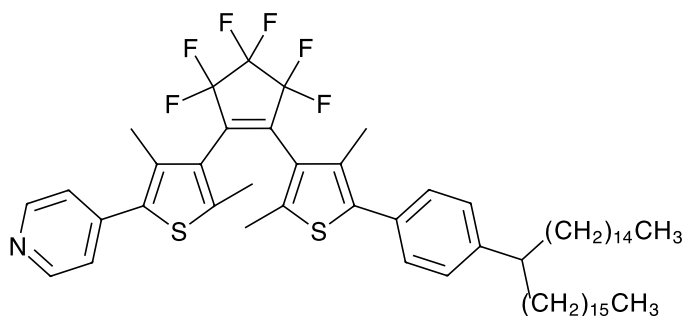
1.38 (m, 54H, CH₂), 1.40–1.75 (m, 4H, CH₂), 2.27 (s, 3H, CH₃), 2.43 (s, 3H), 2.43–2.60 (m, 1H, CH), 7.08–7.20 (m, 2H, Ar H), 7.26–7.34 (m, 2H, Ar H). ¹³C NMR (CDCl₃, δ): 14.3, 15.3, 15.8, 22.9, 27.8, 29.5, 29.7, 29.8, 29.9, 30.0, 32.1, 37.0, 45.9, 113.7, 128.0, 128.9, 132.0, 135.0, 146.2. HRMS-EI (*m/z*): [M]⁺ calcd for C₄₄H₇₅S⁸¹Br, 716.4752; found 716.4728.



4-(2-(2,4-Dimethyl-5-(4-pyridyl)-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl)-3,5-dimethyl-2-(4-(1-pentadecylheptadecyl)phenyl)thiophene (7)

n-Butyllithium (0.123 mL of a 1.6 M solution in hexanes, 0.197 mmol) was added dropwise to a solution of **6** (0.140 g, 0.196 mmol) in tetrahydrofuran (4 mL) at –78 °C under an atmosphere of argon. After stirring for 20 min, 4-(2,3,3,4,4,5,5-heptafluoro-1-cyclopenten-1-yl)-3,5-dimethyl-2-(4-pyridyl)thiophene (0.075 g, 0.196 mmol) in tetrahydrofuran (3 mL) was added dropwise via cannula to the reaction mixture. The thiophene derivative was synthesized following a reported procedure.⁸ After stirring at –78 °C for 3.5 h, the reaction mixture was allowed to warm to room temperature for 2 h, diluted with deionized water (8 mL), adjusted to pH 10 with a saturated aqueous solution of sodium bicarbonate and extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (2 × 15 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1 petroleum ether/ diethyl ether) gave pure **7** as a colorless oil (0.062 g, 31%). ¹H NMR

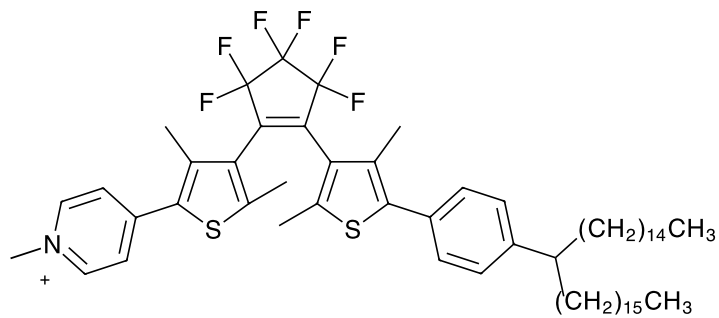
(CDCl₃, δ): 0.88 (t, *J* = 7.2 Hz, 6H, CH₃), 1.00–1.38 (m, 54H, CH₂), 1.44–1.80 (m, 4H, CH₂), 2.02–2.22 (m, 6H, CH₃), 2.30–2.40 (m, 6H, CH₃), 2.42–2.54 (m, 1H, CH), 7.05–7.36 (m, 6H, Ar H), 8.60 (s, 2H, Ar H). ¹³C NMR (CDCl₃, δ): 14.3, 15.2, 15.4, 22.8, 27.8, 29.5, 29.7, 29.8, 29.9, 30.5, 32.1, 37.0, 45.9, 66.0, 123.3, 125.7, 128.0, 128.9, 131.3, 133.4, 137.0, 141.8, 146.3, 150.2. HRMS-FD (*m/z*): [M]⁺ calcd for C₆₀H₈₅F₆NS₂, 997.6028; found 997.6059.



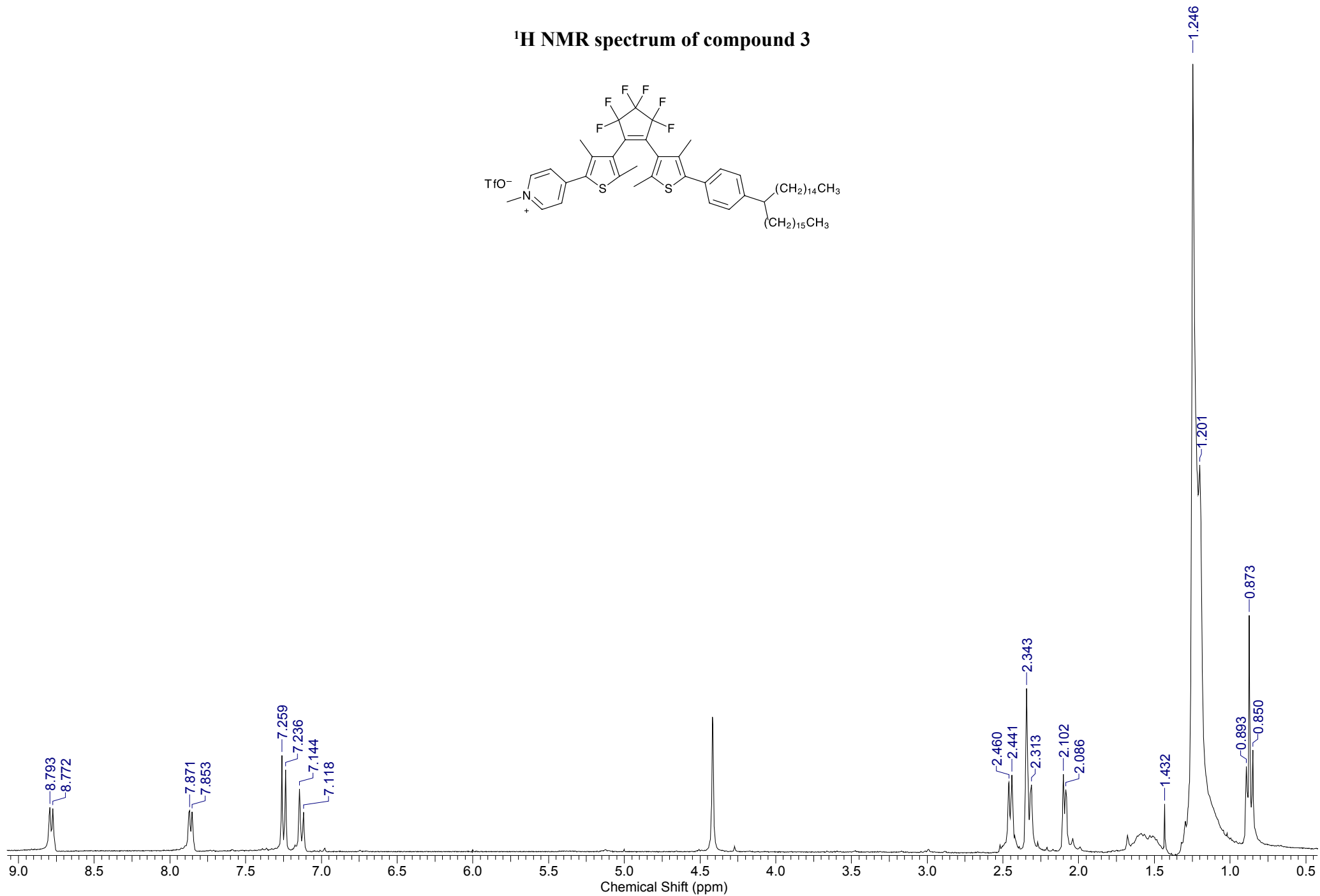
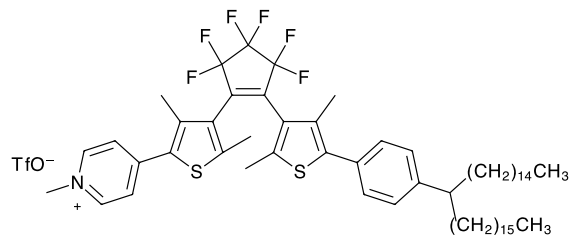
4-(4-(2-(2,4-Dimethyl-5-(4-(1-pentadecylheptadecyl)phenyl)-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl)-3,5-dimethyl-2-thienyl)-1-methylpyridinium trifluoromethanesulfonate (3)

A solution of methyl trifluoromethanesulfonate (12.3 μL, 0.112 mmol) in anhydrous dichloromethane (1.5 mL) was added dropwise to a solution of **7** (56.0 mg, 0.0561 mmol) in anhydrous dichloromethane (2 mL) under an atmosphere of argon. After stirring at room temperature for 2 h, the dichloromethane was removed under reduced pressure and the residue was washed with diethyl ether (2 × 3 mL). Recrystallization of the precipitate from dichloromethane/methanol gave pure **3** as off-white solid (45 mg, 69%). ¹H NMR (CDCl₃, δ): 0.88 (t, *J* = 7.2 Hz, 6H, CH₃), 1.00–1.38 (m, 54H, CH₂), 1.38–1.75 (m, 4H, CH₂), 2.02–2.22 (m, 3H, CH₃), 2.30–2.40 (m, 6H, CH₃), 2.42–2.54 (m, 4H, CH, CH₃),

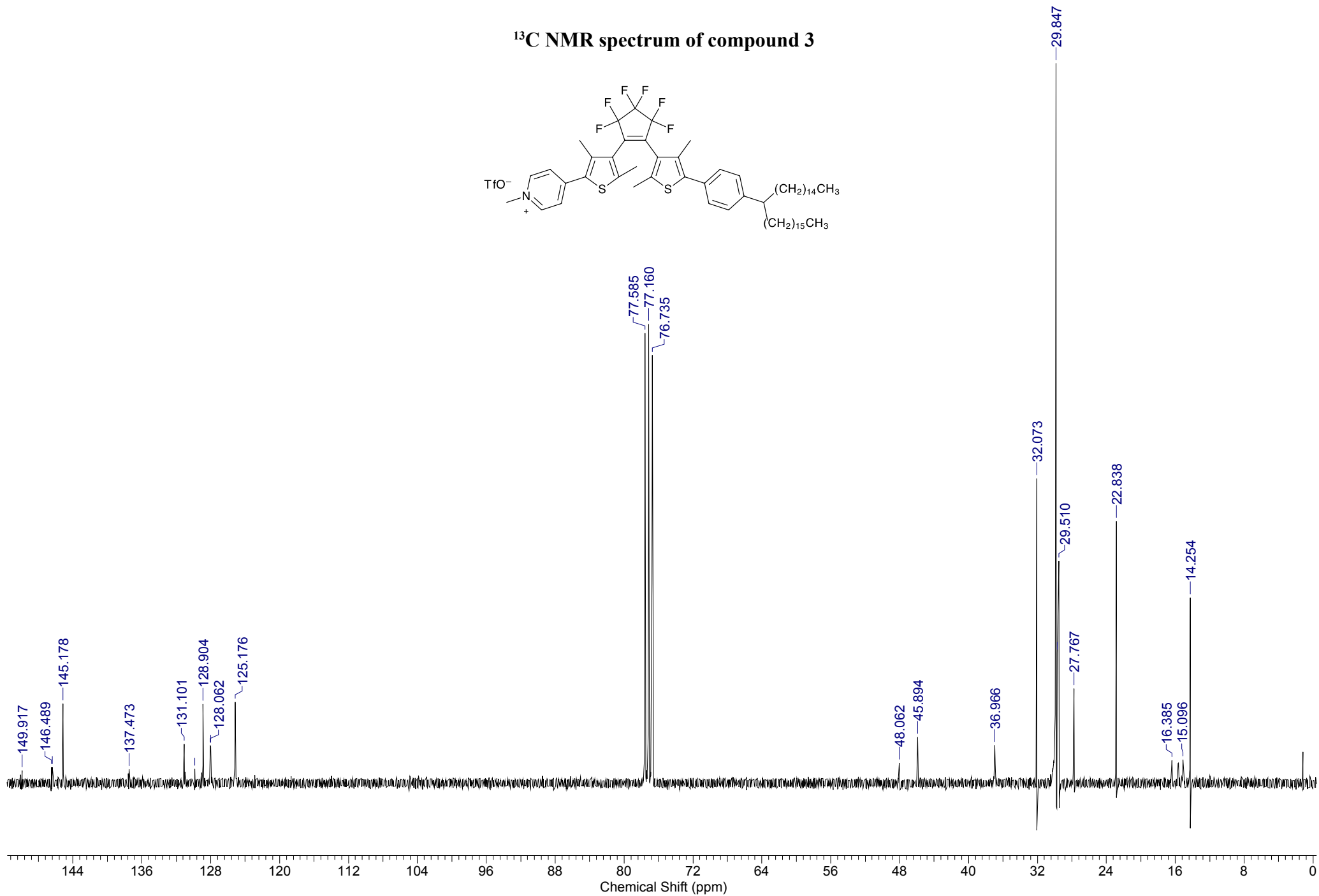
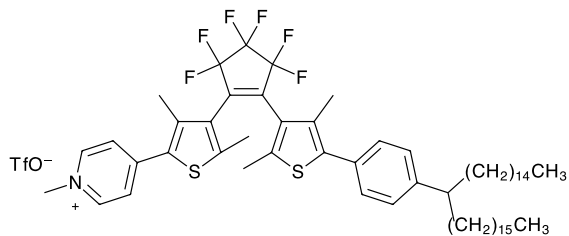
4.42 (s, 3H, CH₃), 7.05–7.36 (m, 4H, Ar H), 7.80–7.92 (m, 2H, Ar H), 8.75–8.87 (m, 2H, Ar H). ¹³C NMR (CDCl₃, δ): 14.3, 15.7, 22.9, 27.8, 29.5, 29.7, 29.8, 29.9, 32.1, 37.0, 37.1, 46.0, 48.1, 125.2, 128.0, 128.1, 128.9, 129.8, 131.0, 131.1, 137.5, 137.6, 145.2, 146.4, 146.5, 149.9, 150.1. HRMS-ESI (*m/z*): [M]⁺ calcd for C₆₁H₈₈NF₆S₂, 1012.6256; found 1012.6245.



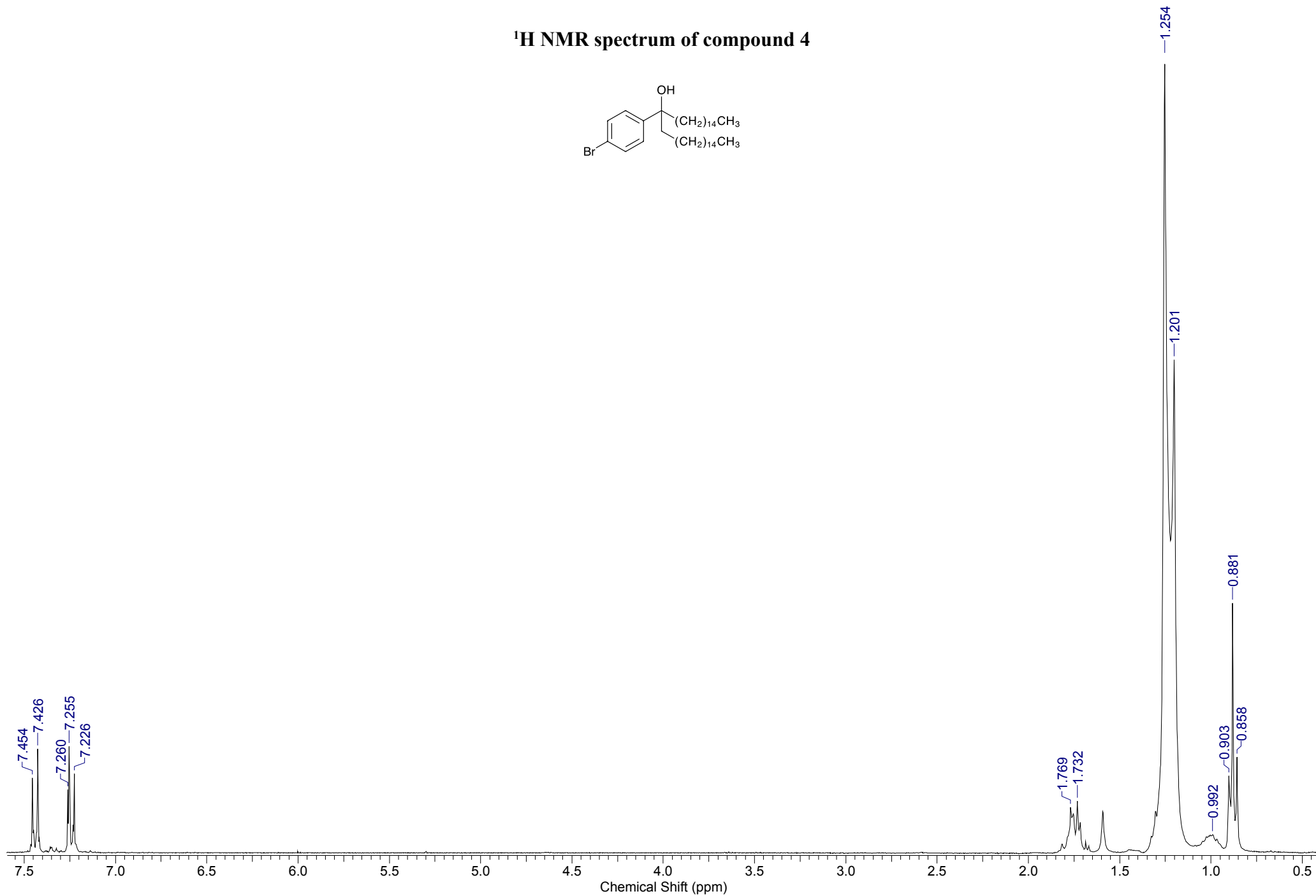
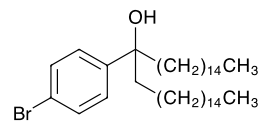
¹H NMR spectrum of compound 3



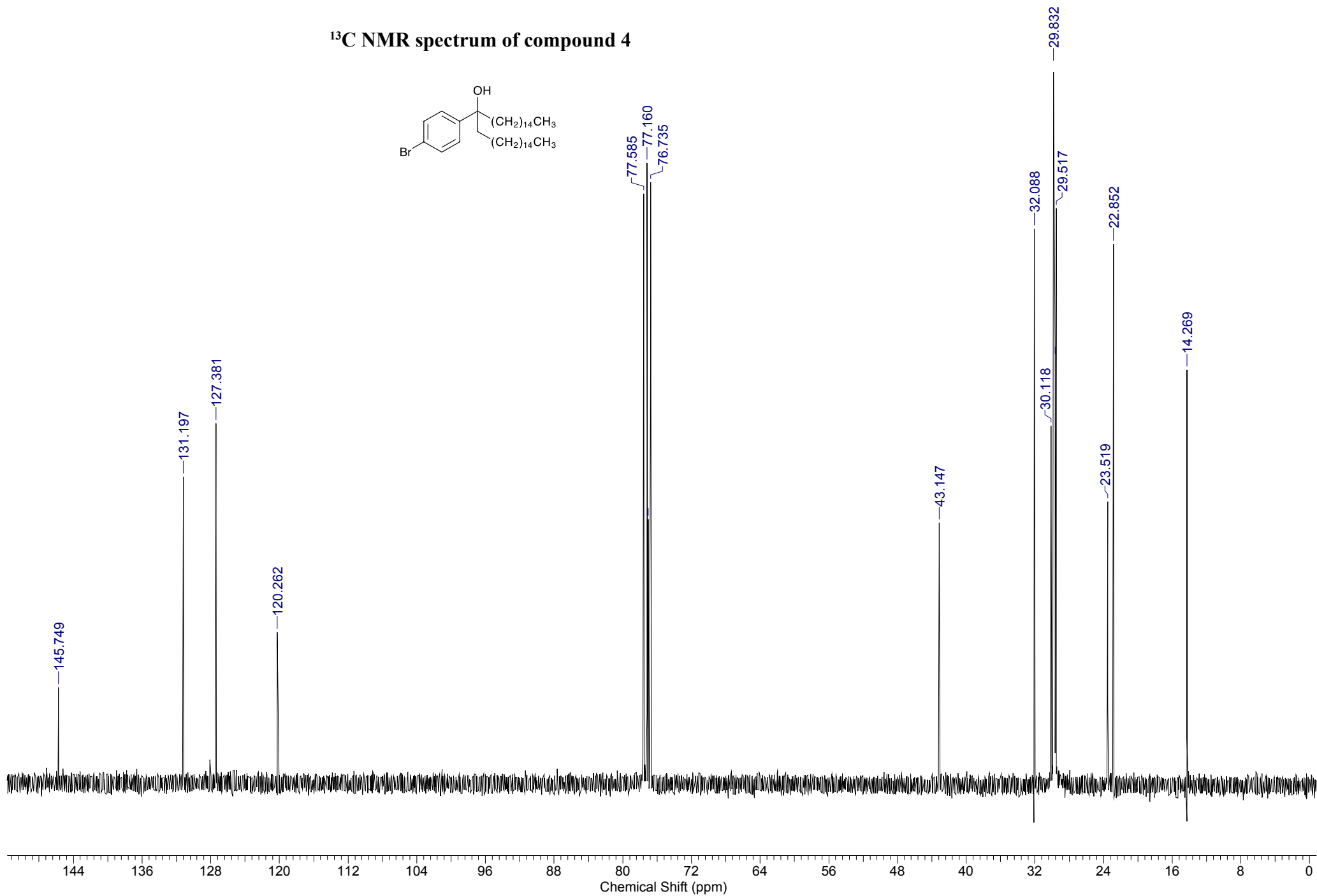
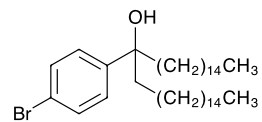
¹³C NMR spectrum of compound 3



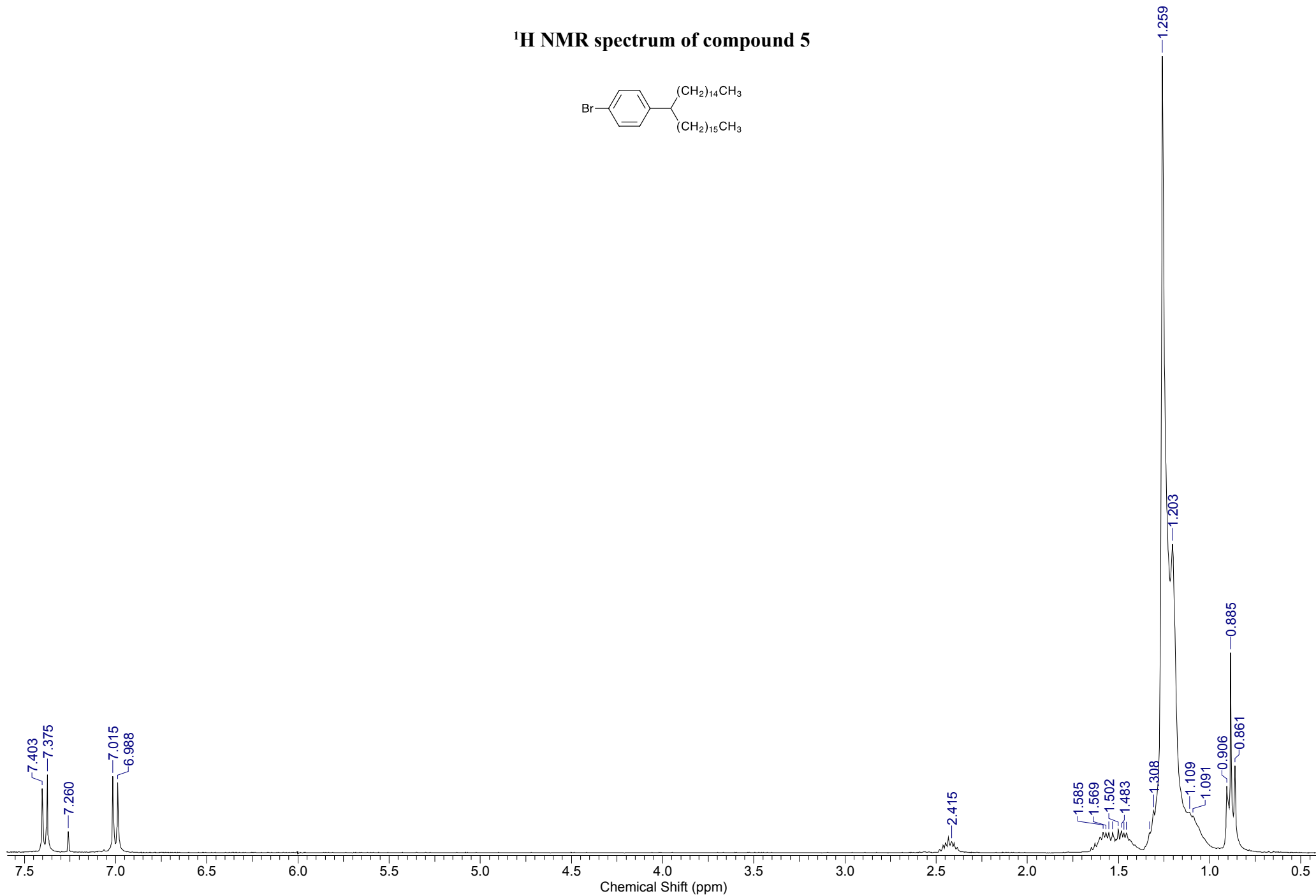
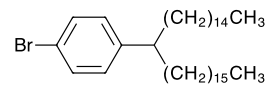
¹H NMR spectrum of compound 4



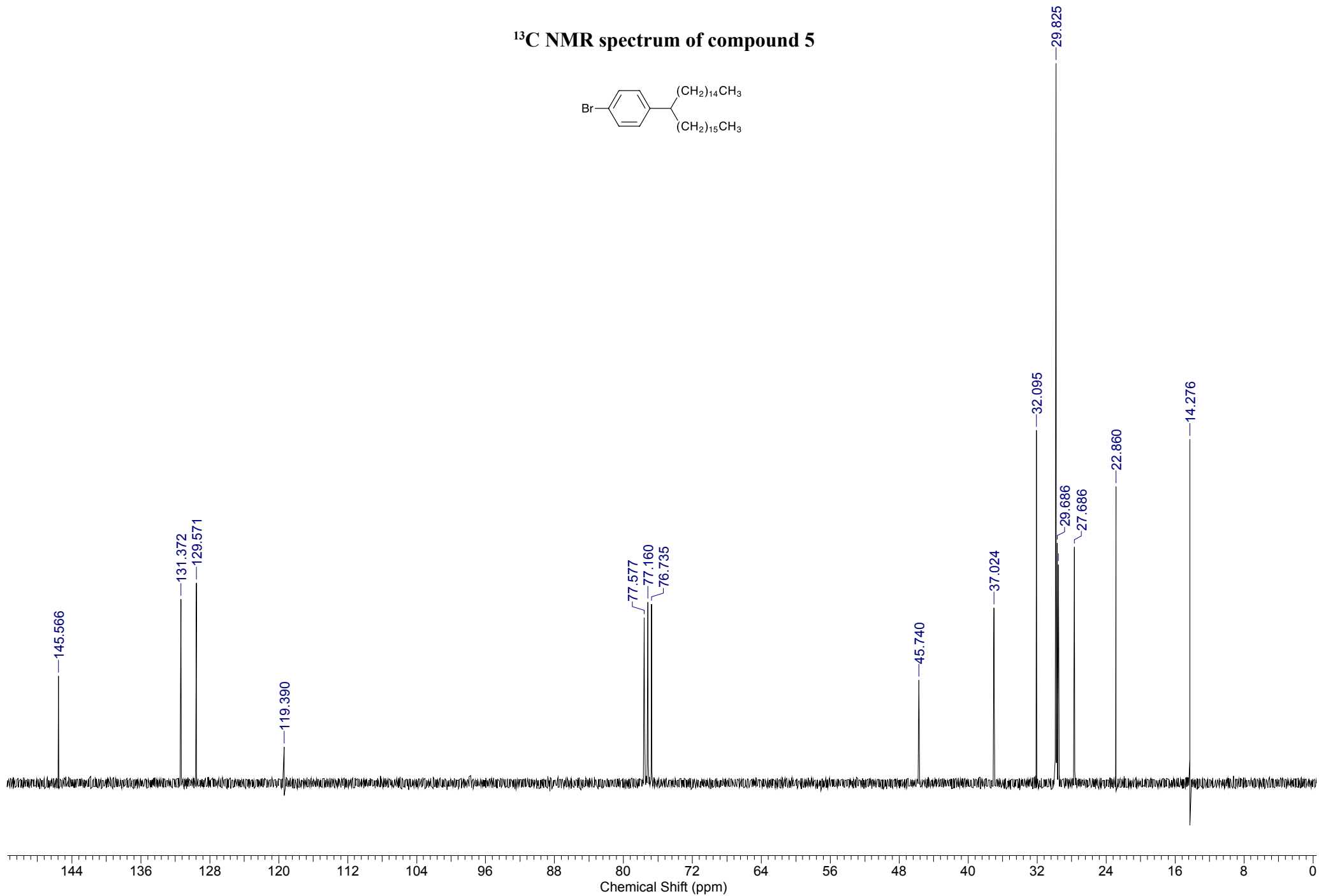
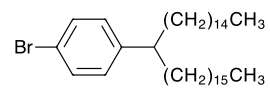
¹³C NMR spectrum of compound 4



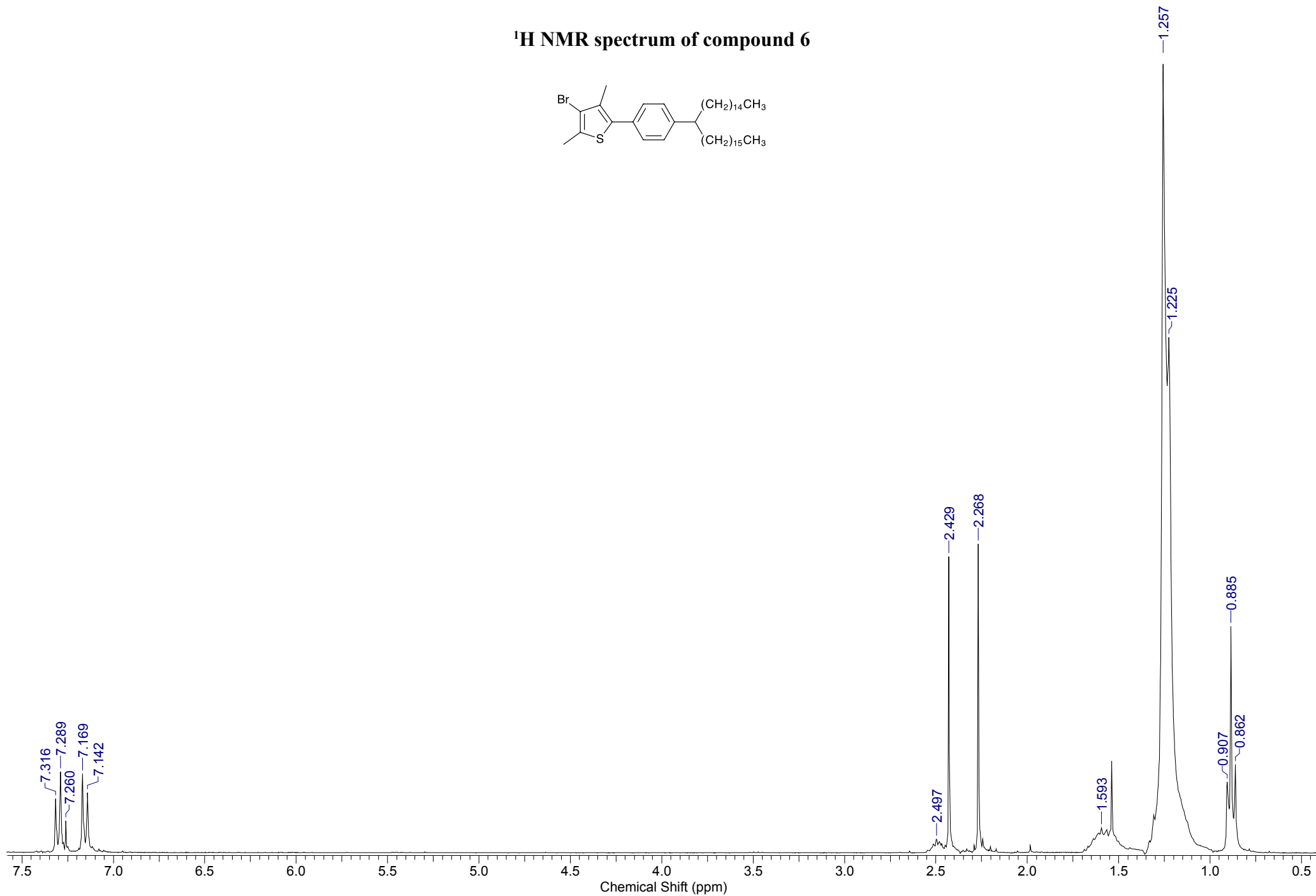
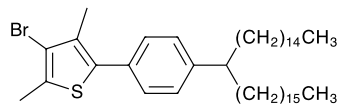
¹H NMR spectrum of compound 5



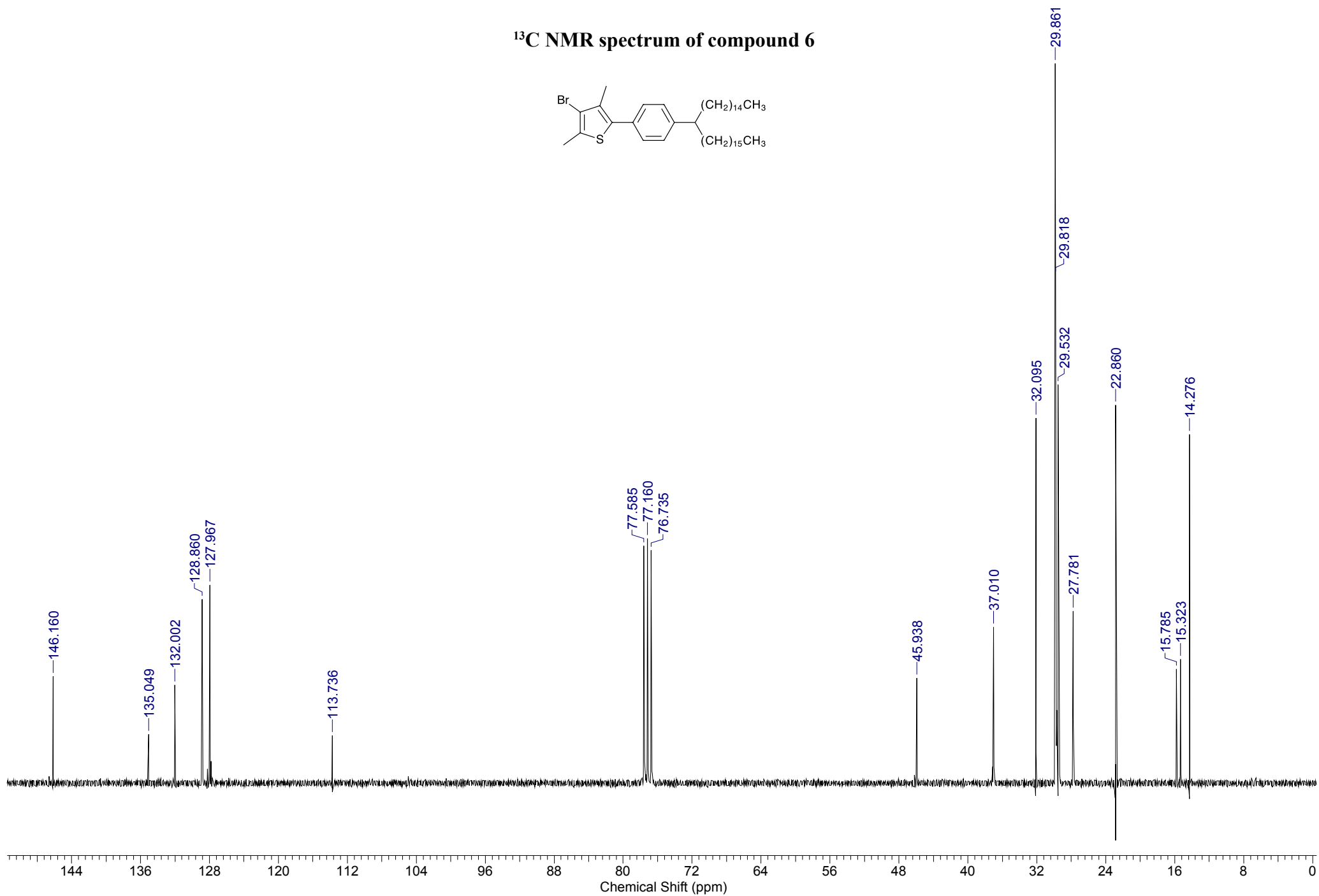
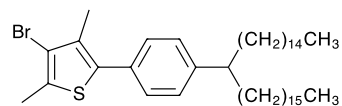
¹³C NMR spectrum of compound 5



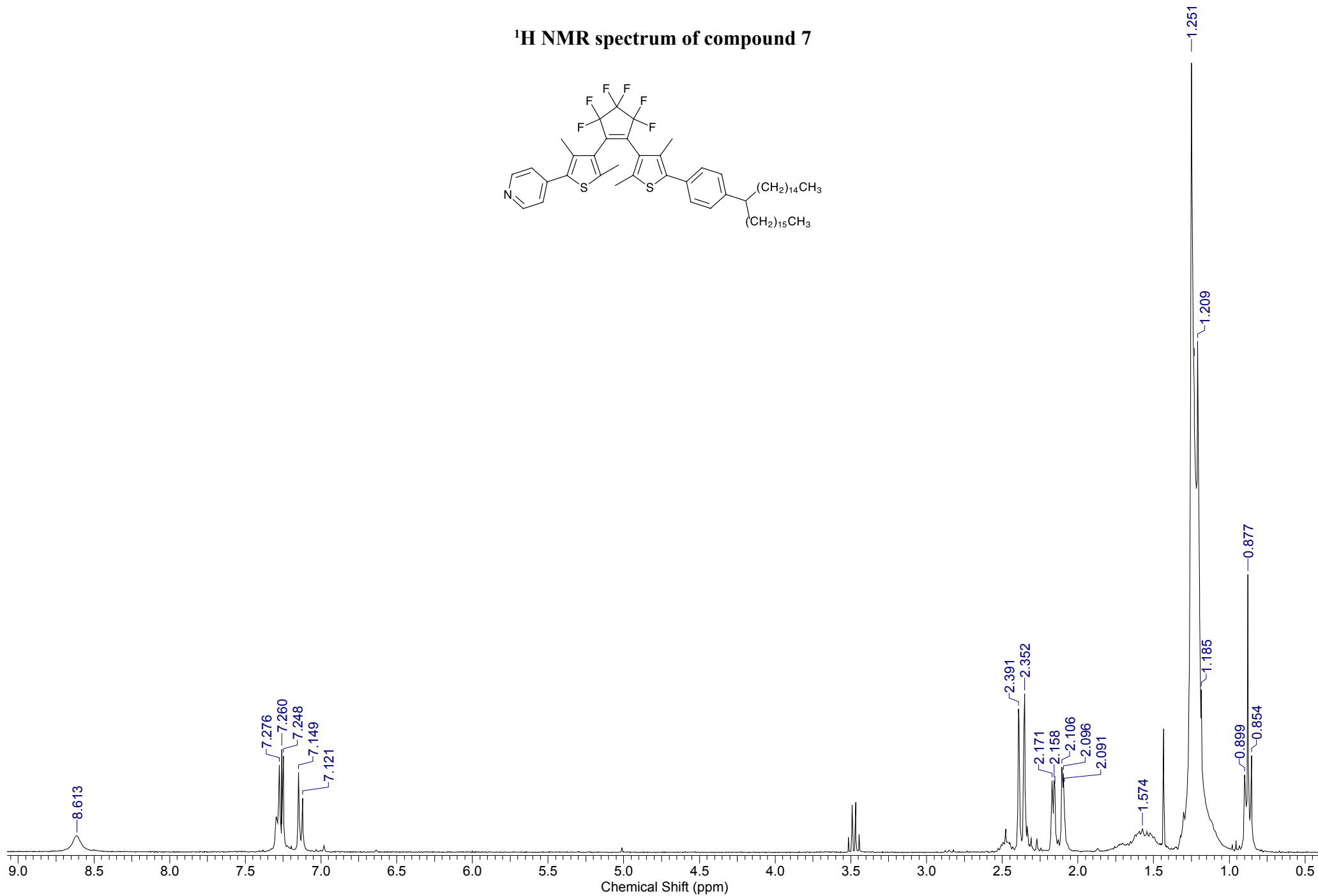
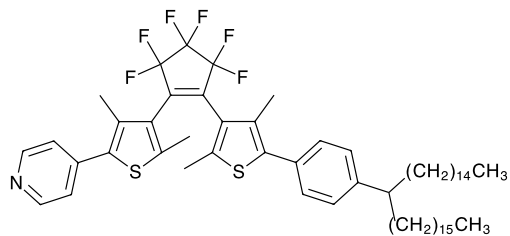
¹H NMR spectrum of compound 6



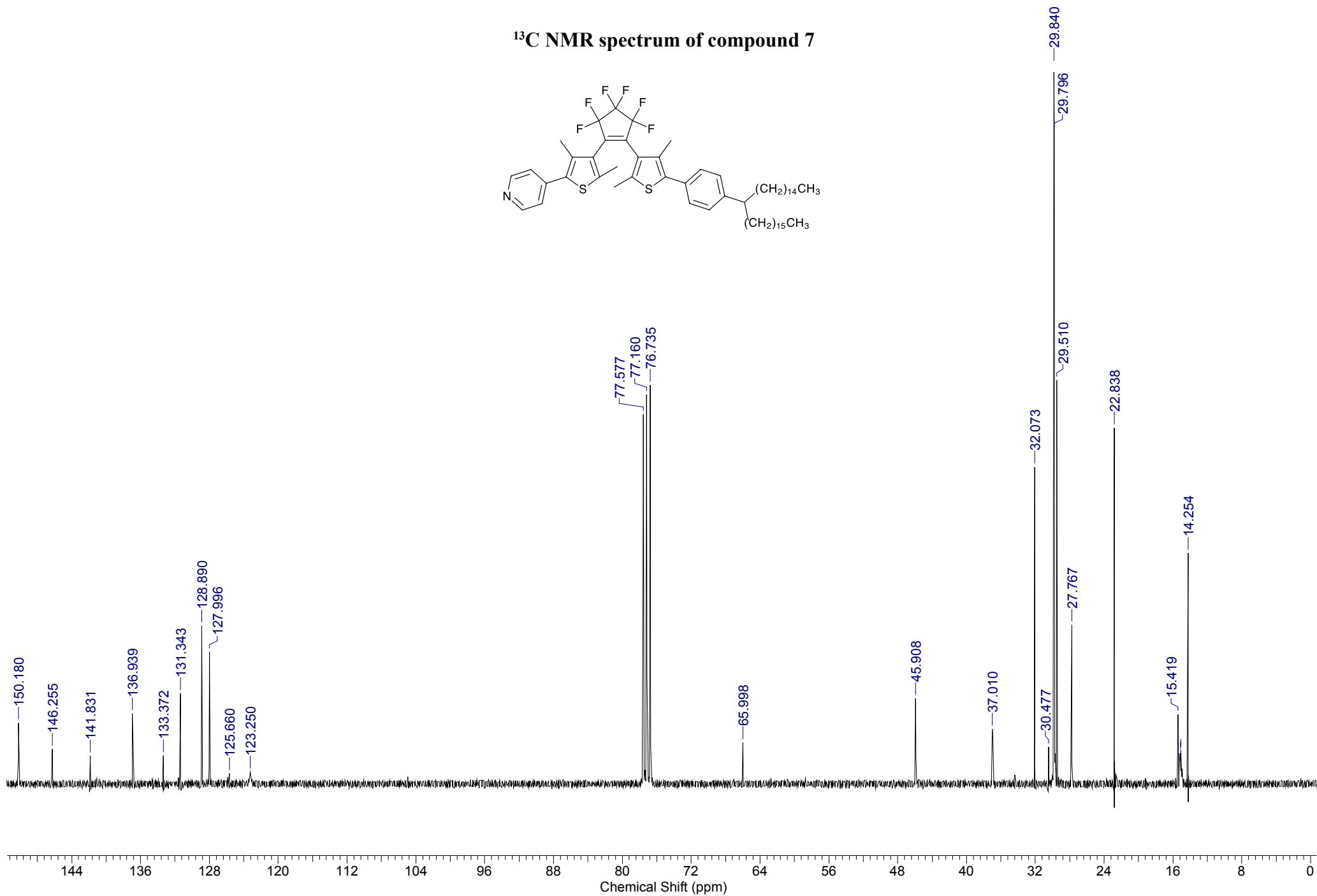
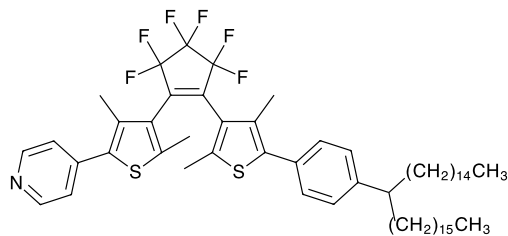
¹³C NMR spectrum of compound 6

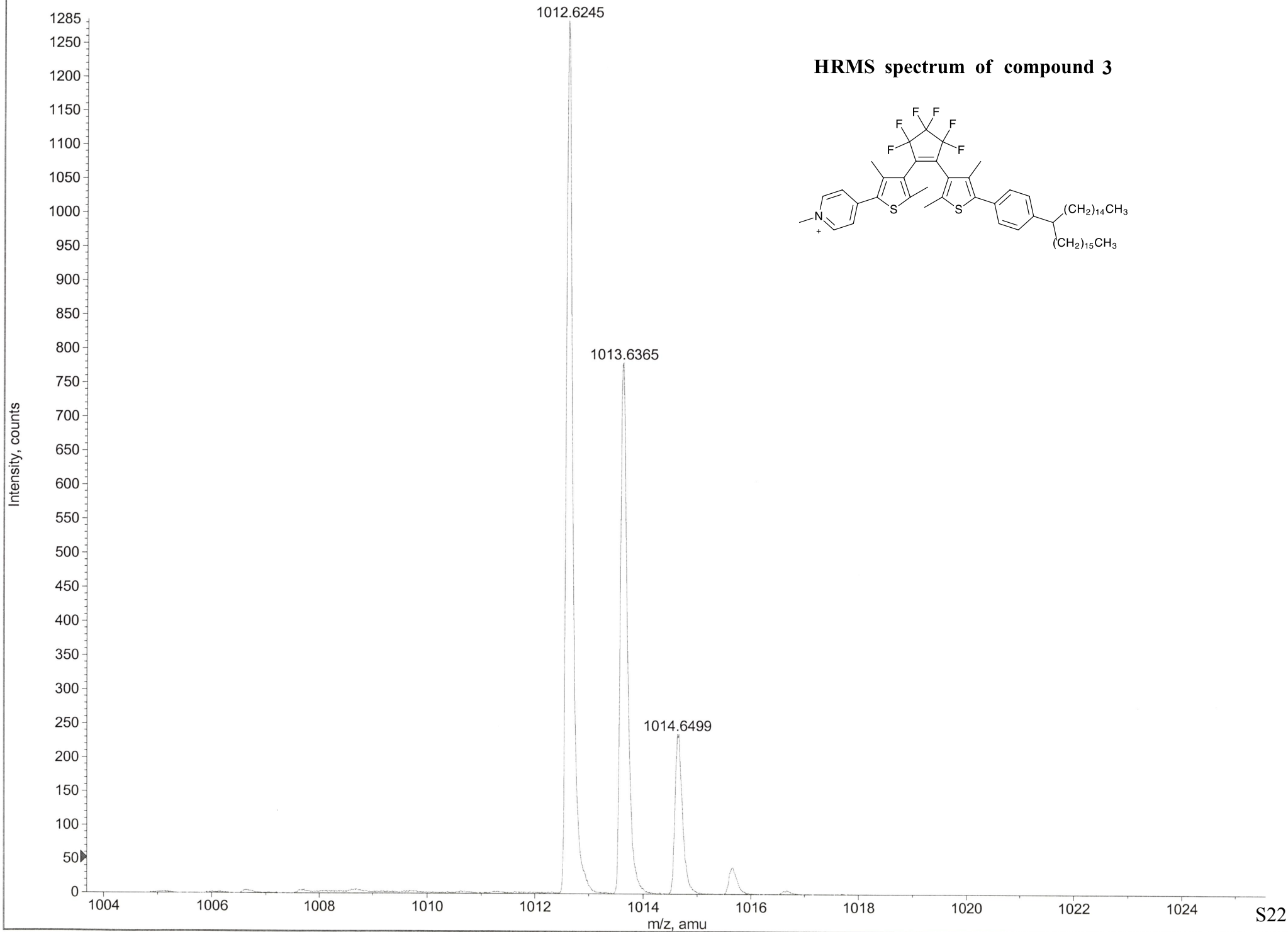


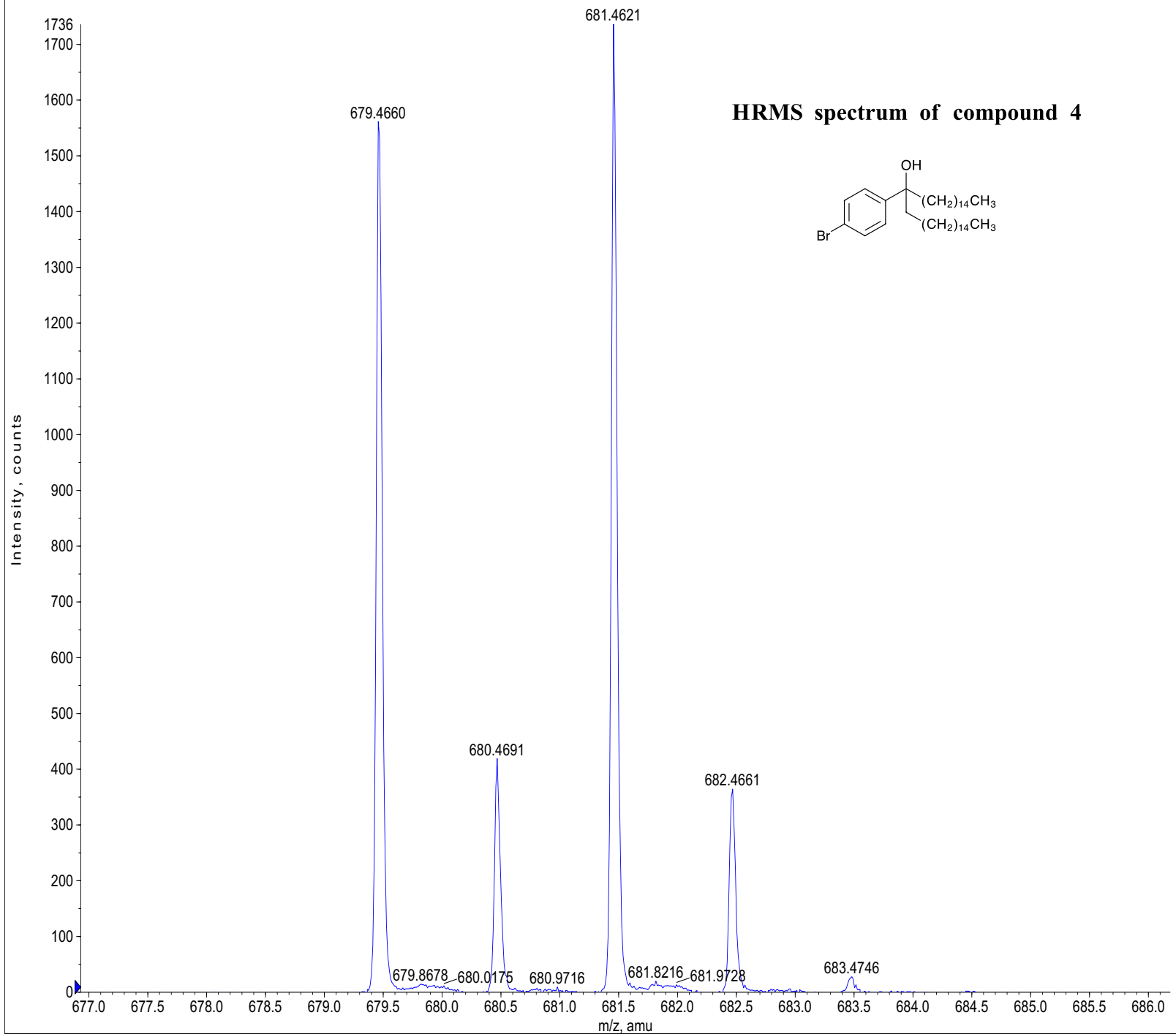
¹H NMR spectrum of compound 7



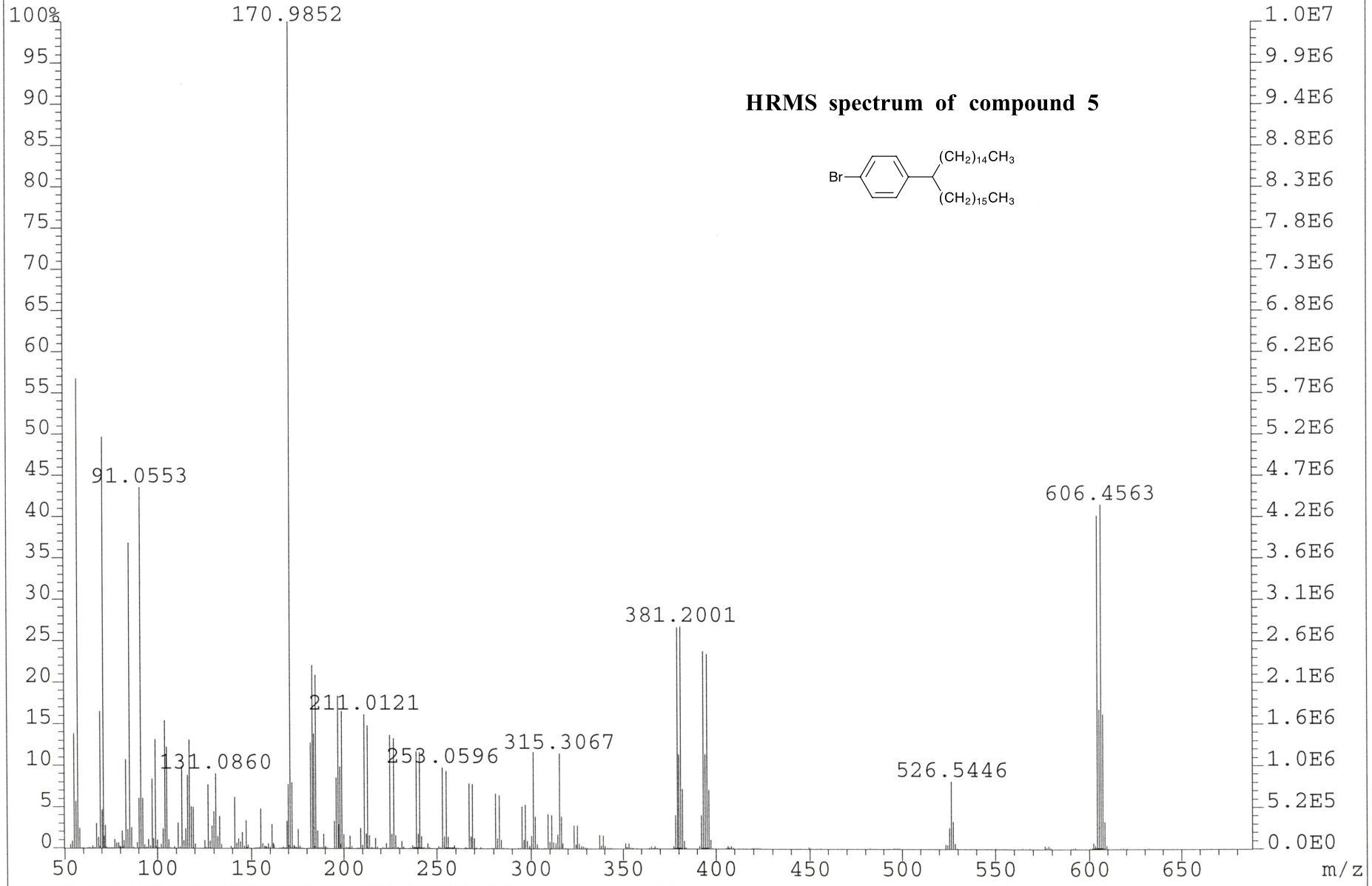
¹³C NMR spectrum of compound 7



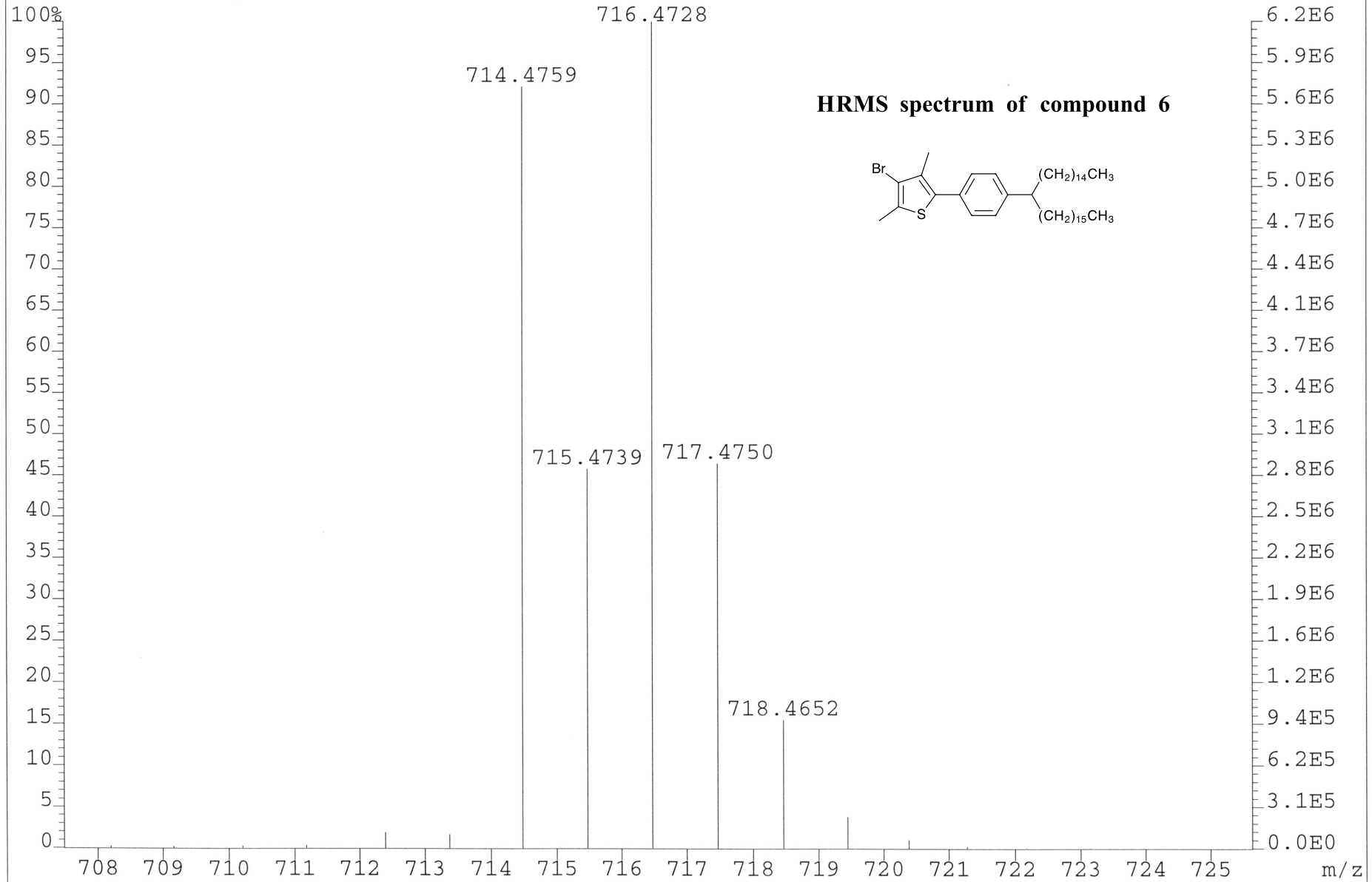




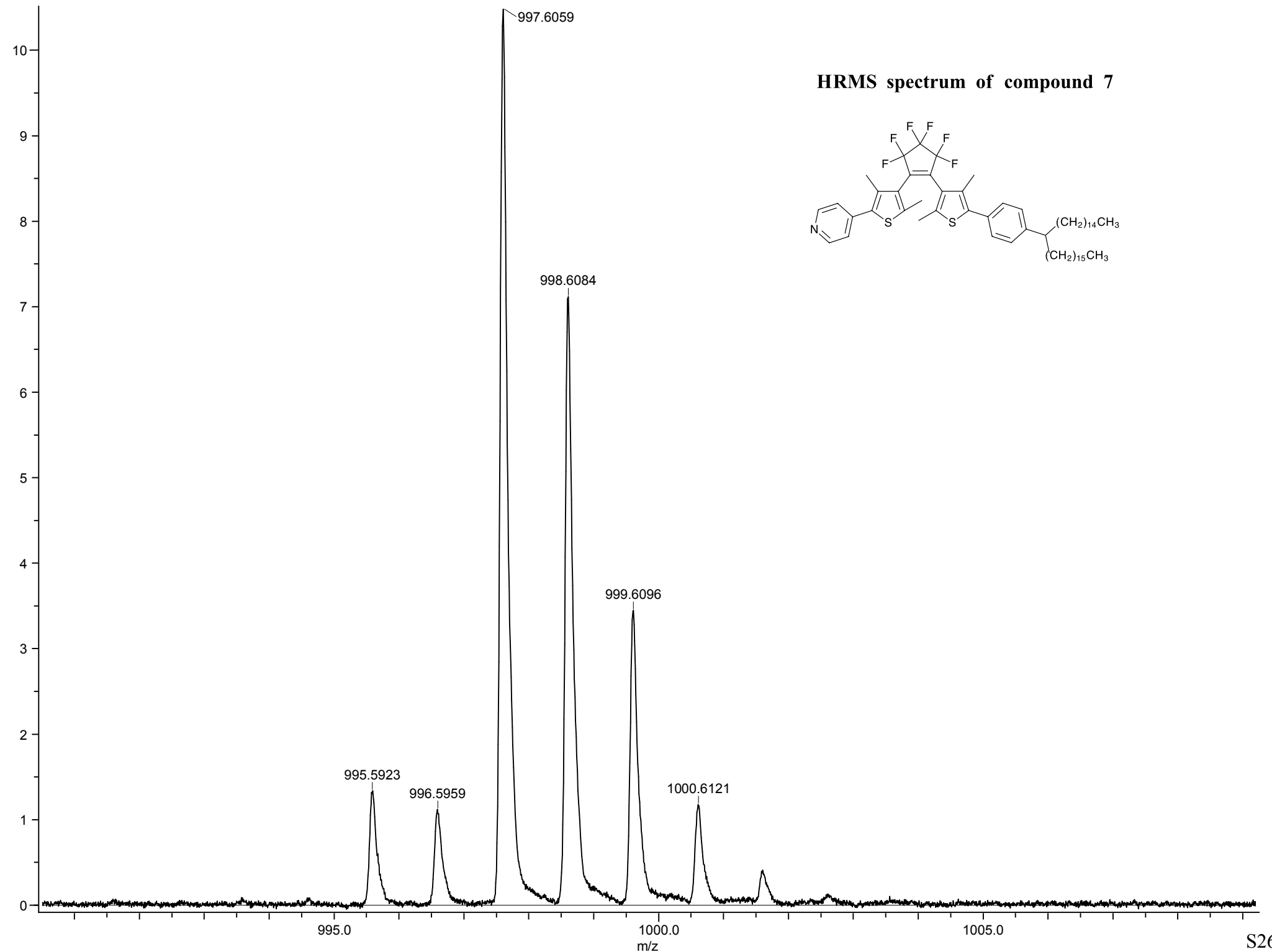
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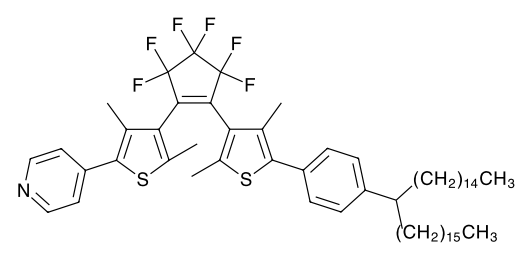
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$\times 10^3$ Intensity (10481)



HRMS spectrum of compound 7



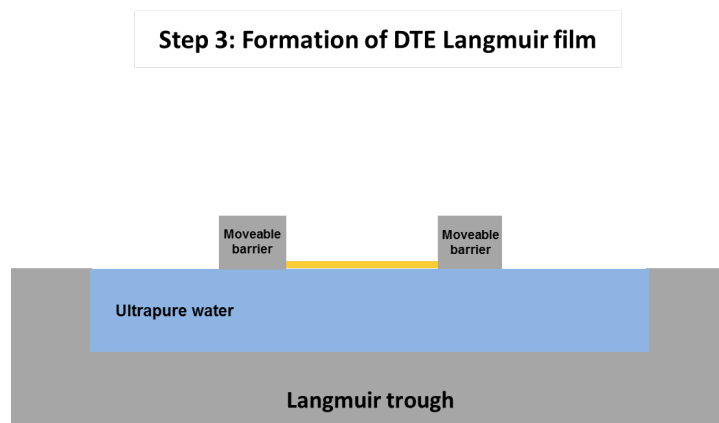
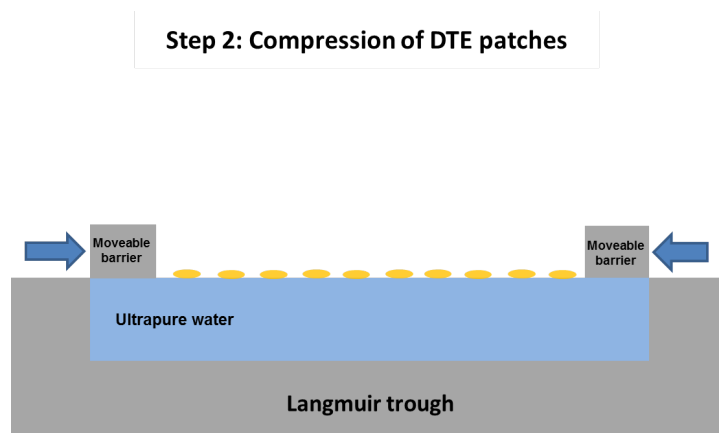
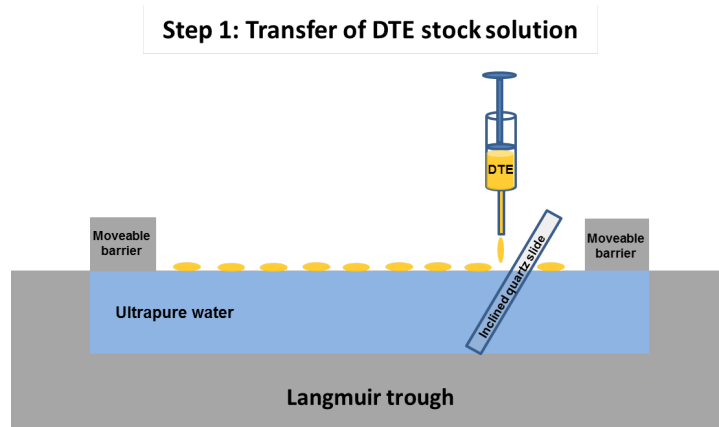


Chart S1. A schematic illustration for the preparation of a DTE Langmuir film.

A slight decrease in the maximum surface pressure is observed after five cycles, which suggests that the DTEs have some solubility in water (Figure S1). More specifically, **1** decreases by ca. 10%, **2** decreases by ca. 6%, and **3** decreases by ca. 4%. However, these changes are not significant. Therefore, Langmuir films of **1–3** are considered reversible and stable.

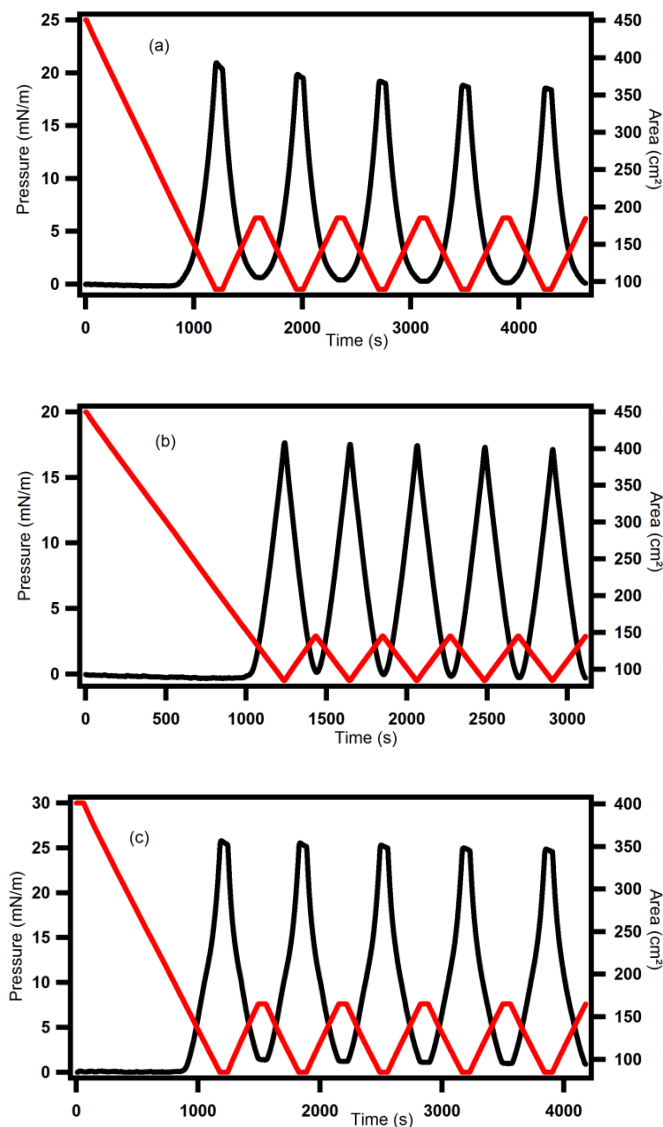


Fig. S1. Five consecutive compression–decompression cycles to assess the mechanical stability of Langmuir films of (a) **1**, (b) **2**, and (c) **3**. In all cases, the DTE concentration was 0.15 mg mL⁻¹ and the transferred volume was 150 μL.

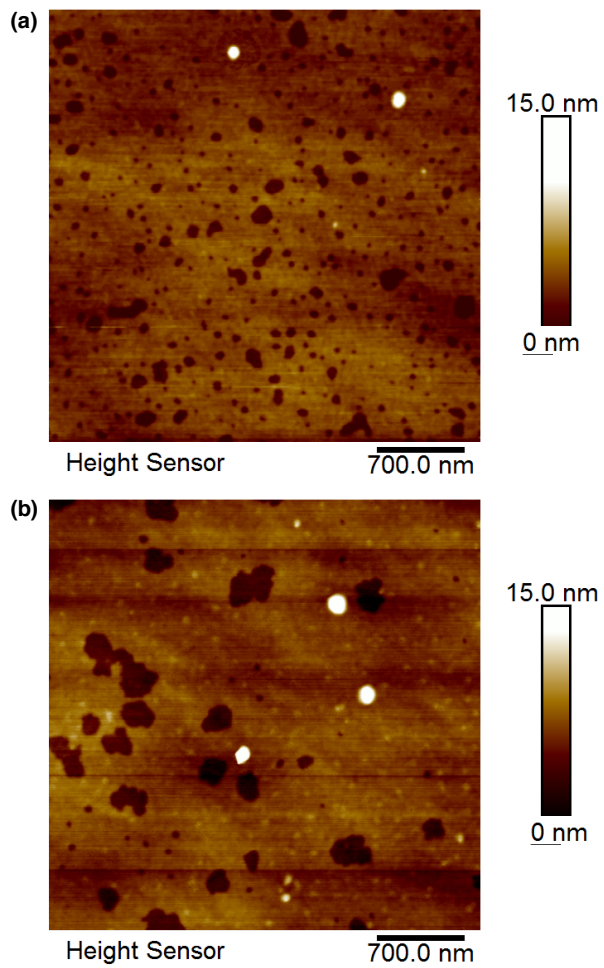


Fig. S2. AFM images of LS films of **1** prior to (a) and following (b) irradiation with UV light (6 W UVA lamp; $\lambda_c = 365$ nm; 6 min).

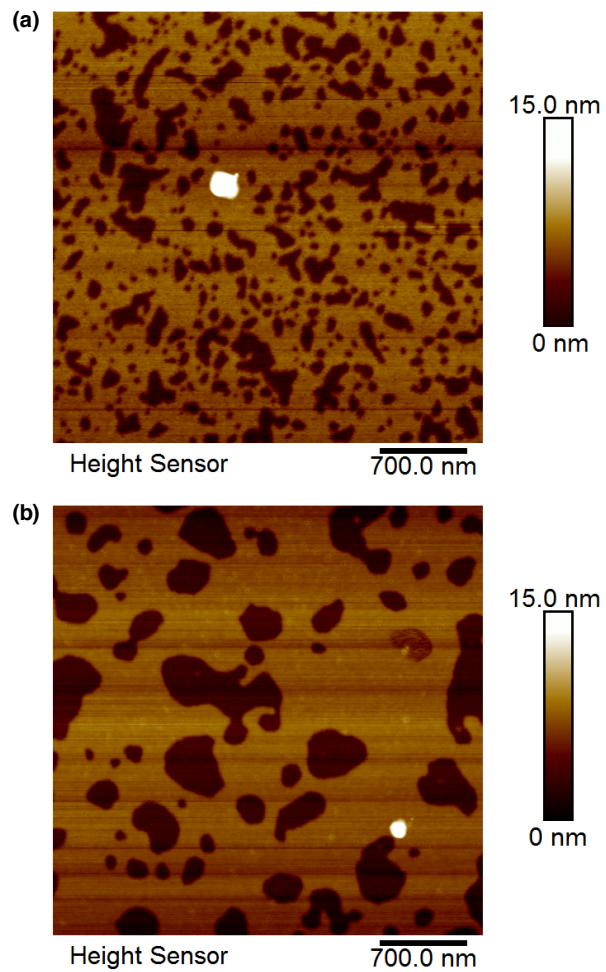


Fig. S3. AFM images of LS films of **2** prior to (a) and following (b) irradiation with UV light (6 W UVA lamp; $\lambda_c = 365$ nm; 6 min).

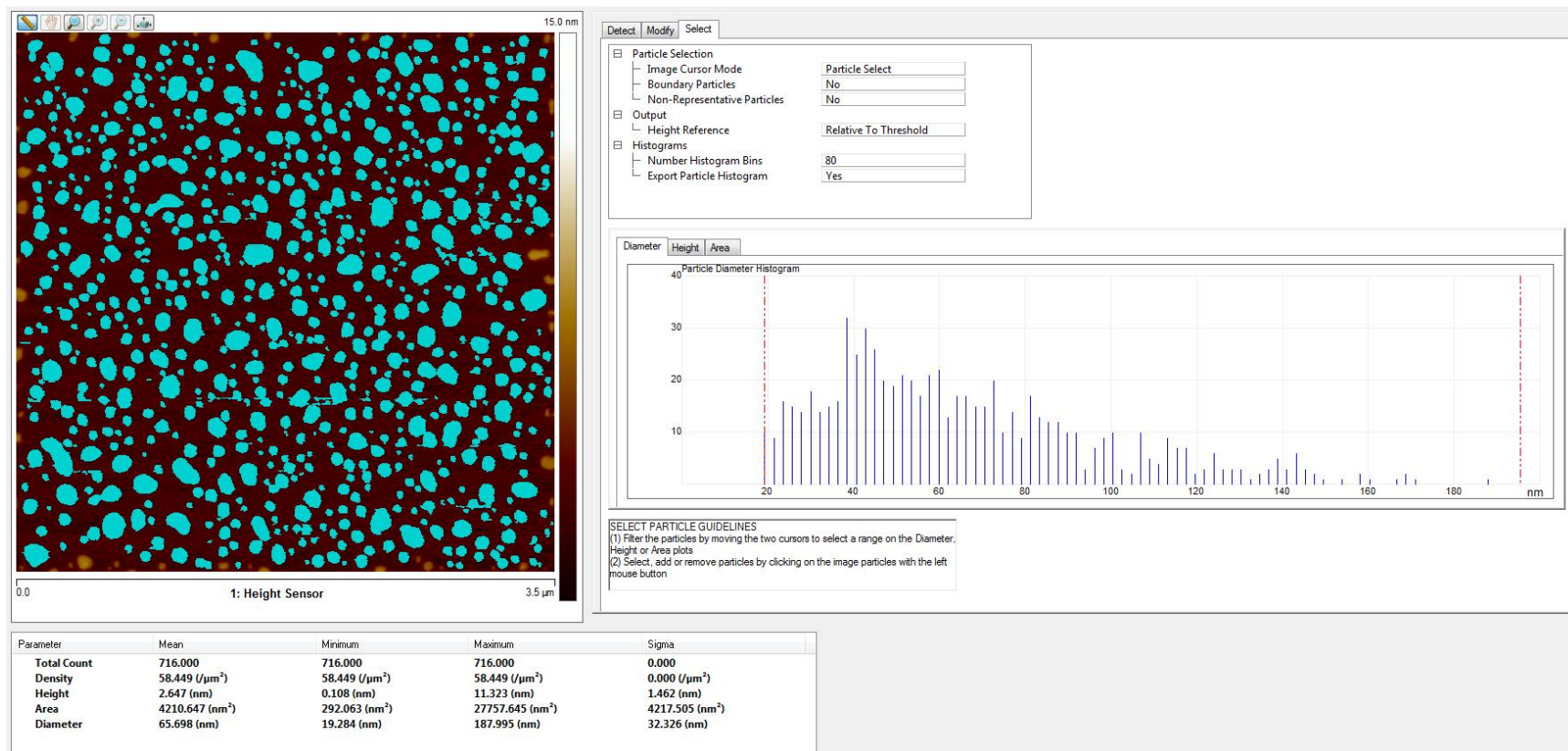


Fig. S4. AFM analysis of the diameter of the circular structures in a LS film of **3** prior to irradiation with UV light.

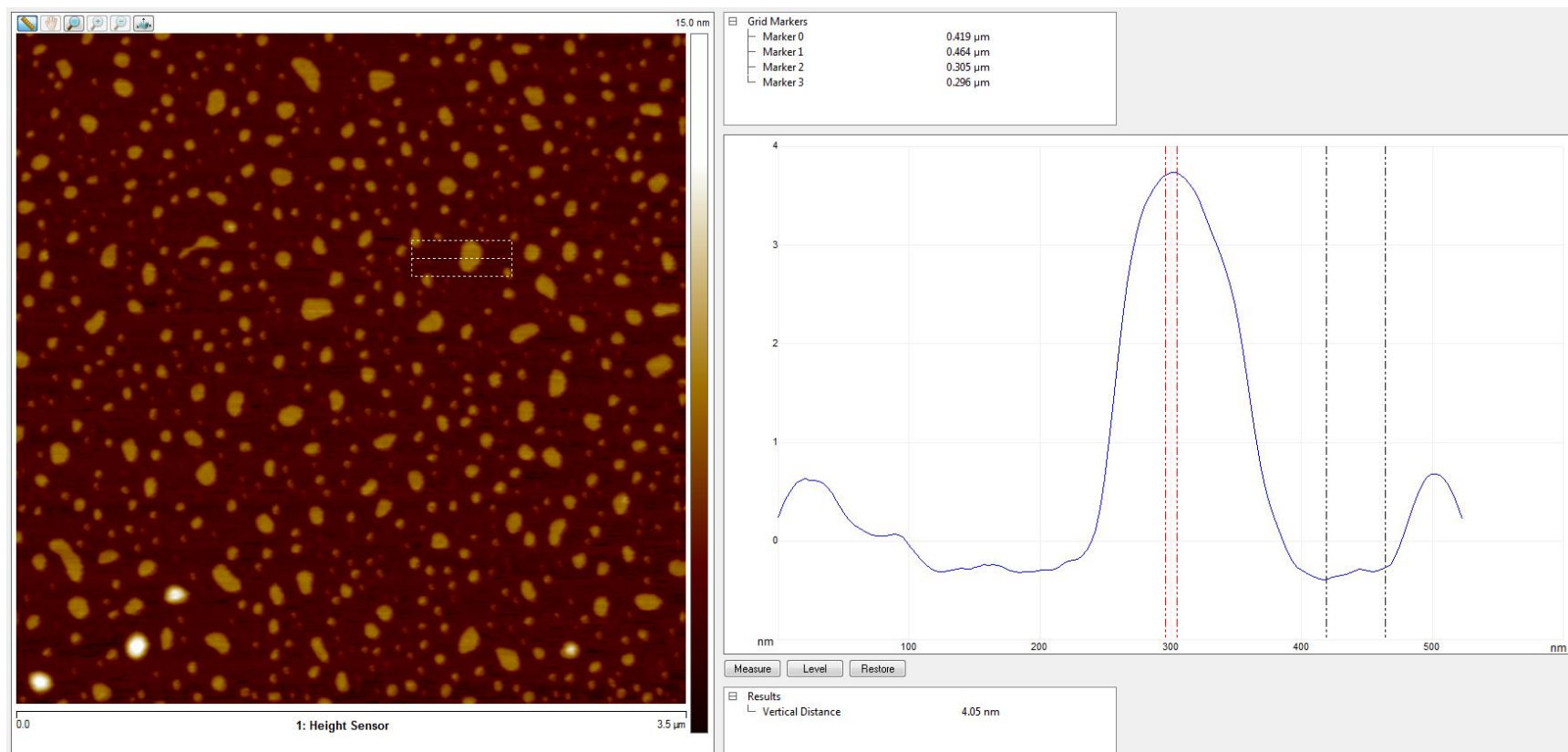


Fig. S5. AFM analysis of the thickness of a circular structure in a LS film of **3** prior to irradiation with UV light.

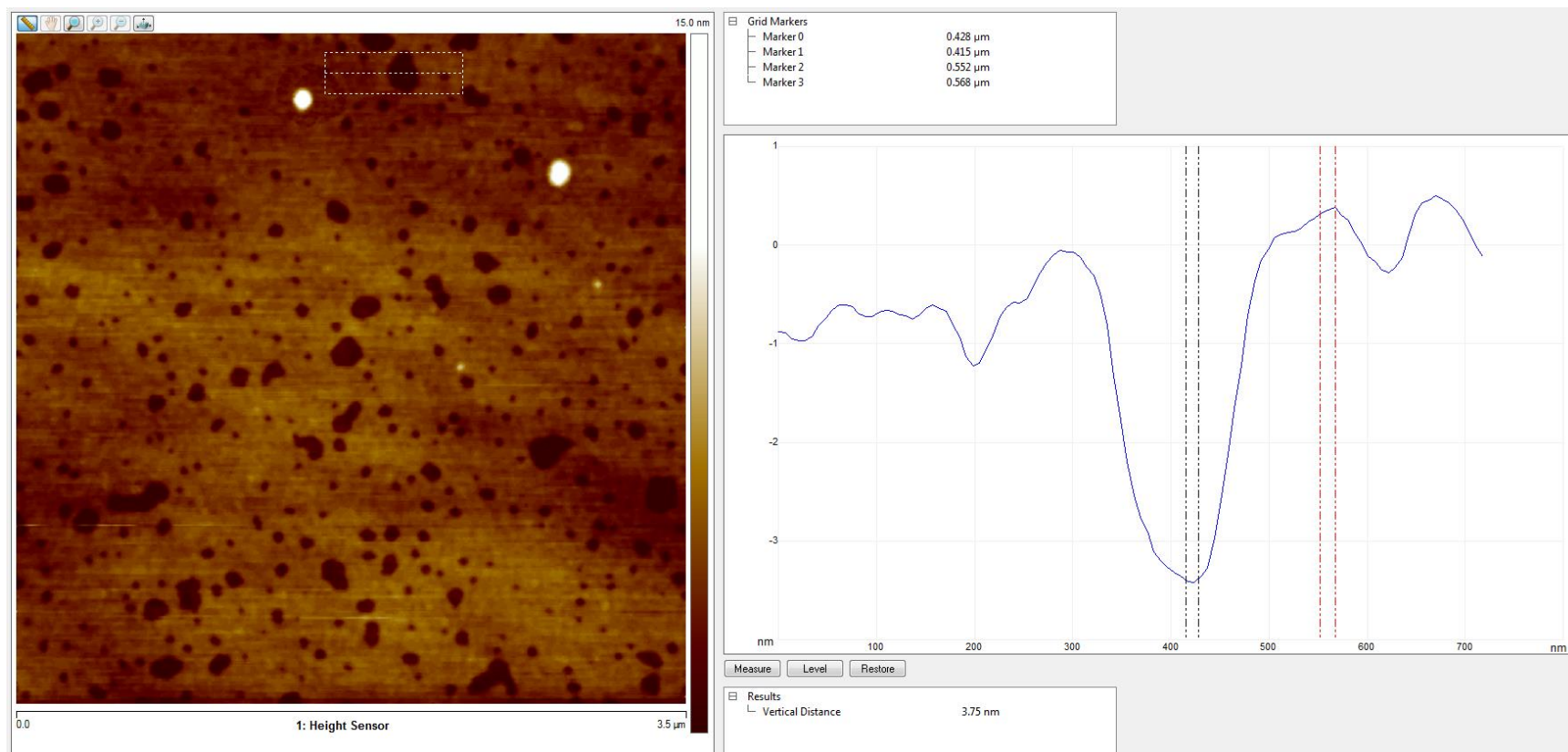


Fig. S6. AFM analysis of the thickness of a LS film of **1** prior to irradiation with UV light.

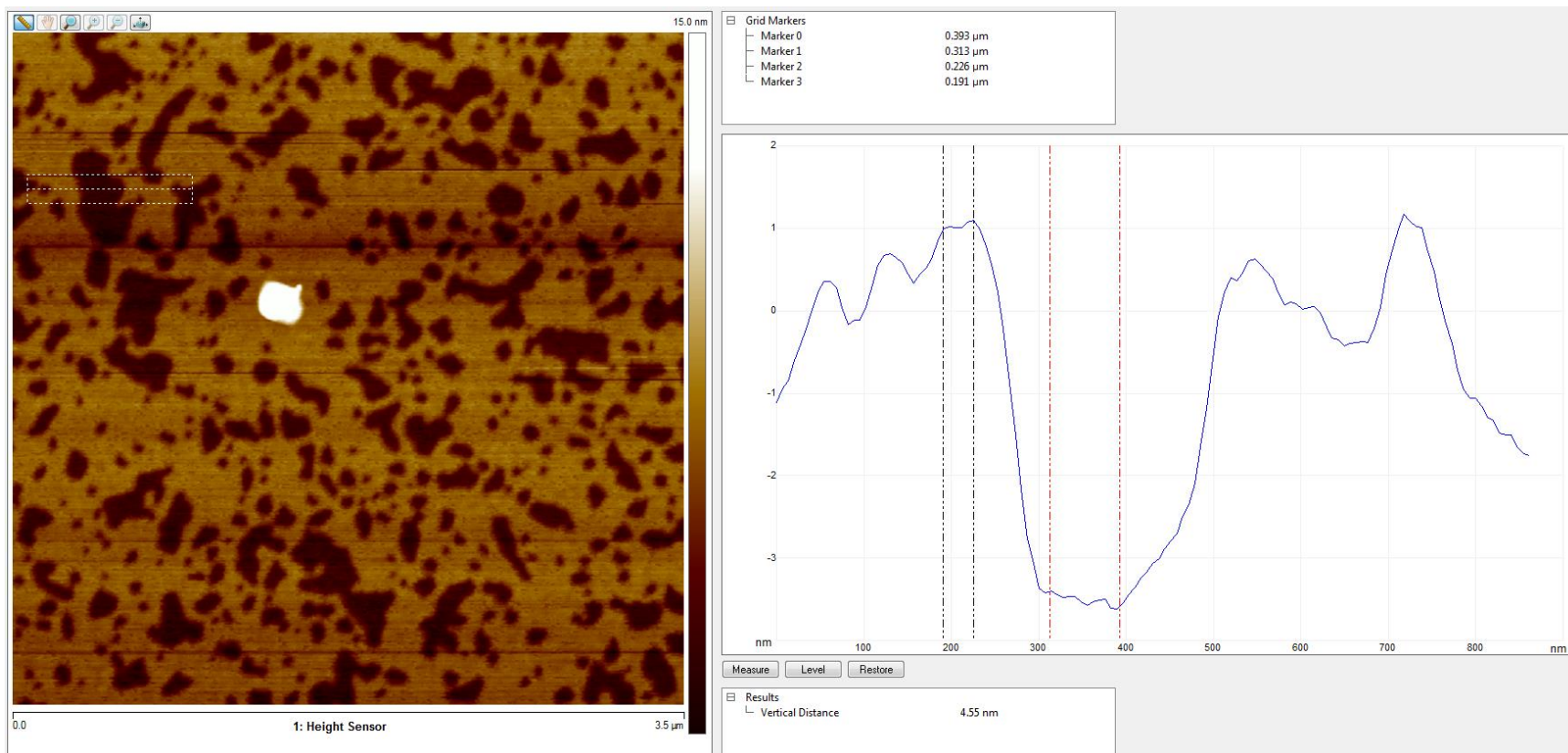


Fig. S7. AFM analysis of the thickness of a LS film of **2** prior to irradiation with UV light.

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