Supporting Information

Lipophilic anilino squaraine dye as a new superfluorescent probe with efficient two photon transition and high photostability

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Table of contents

1. Structures and gels of previously reported dyes.

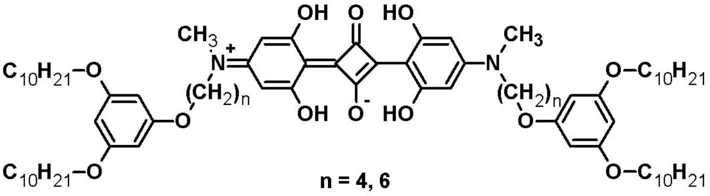


Figure S1. Previously reported by us dyes **P1** (n = 4) and **P2** (n = 6).

Figure S2. Dye **P2** (10 mg) solution and gels (T = 15°C): 1 – solution in benzene (0.3 ml), 2 – gel in hexane (1 ml), 3 – gel in cyclohexane (1 ml).

2. Materials, instruments and methods

Reagents and solvents. 2,6-Di-*tert*-butyl-4-methylphenol (DBPC), 1,4-dibromobutane, 1,6-dibromohexane, 1-bromodecane, 7-(bromomethyl)pentadecane and squaric acid were obtained from UOS Lab (Ukraine), phloroglucinol from Merck (Germany), triphenyl phosphine from Fluka (Switzeland), inorganic salts, acids and all solvents for synthesis were purchased from Macrochim (Ukraine). Benzene was dried by distillation over P_2O_5. Butanol was dried by distillation collecting the fractions with boiling point in the range 117-117.5°C.

Analytical methods and instruments. Thin layer chromatography (TLC) was carried out on Alugram Xtra Sil G/UV$_{254}$ plates (Macherey-Nagel, Germany) in following solvent systems: $CHCl_3$–*n*-hexane 1:1 (A), $CHCl_3$–*n*-hexane 2:1 (B), $CHCl_3$–MeOH 98:2 (C), $CHCl_3$–MeOH 96:4 (D), $CHCl_3$–MeOH 85:15 (E), EtOAc-*n*-hexane 15:85 (F). Column chromatography was performed on Silica 60M (0.04-0.063 mm, Macherey-Nagel, Germany).

^{1}H and ^{13}C NMR spectra were recorded on a Varian Agilent VNMRS instrument (400 and 100 MHz, respectively) with tetramethylsilane as an internal standard; chemical shifts are given in ppm. Mass-spectrometric analysis was carried out on Agilent 6224 Accurate-Mass TOF LC/MS (G6224A) instrument (Agilent Technologies, USA) using electrospray ionization (ESI) in positive ion detection mode. Compounds were dissolved in CH_2Cl_2 and the aliquots were injected in the flow of acetonitrile containing formic acid (0.1%). MALDI-TOF mass spectra were recorded on Autoflex II mass spectrometer (Bruker Daltonics Inc, Germany) equipped with a nitrogen laser. 9,10-Diphenylanthracene was used as a matrix.

3. Synthesis of the anilino squaraine dye

3-Decoxy-5-(2-hexyldecoxy)phenol (3). 5-Decoxybenzene-1,3-diol (**2**) (1.74 g, 6.54 mmol), 7-(bromomethyl)pentadecane (2.0 g, 6.56 mmol) and K_2CO_3 (1.37 g, 9.93 mmol) were suspended in DMF (30 ml). The reaction mixture was heated in inert atmosphere at 70-80°C (silicon oil bath). After ~5 hours, the mixture was diluted with water, acidified with HCl (10-15 %) and extracted with EtOAc. Organic phase was wahed with brine (5×), dried with Na_2SO_4 and evaporated to obtain a dark-brown oil (~3.21 g). It was dissolved in $CHCl_3$–*n*-hexane mixture (1:2, v/v) and purified by silica gel column chromatography. Compound **3** and unreacted **2** were isolated by step gradient elution with $CHCl_3$ in *n*-hexane (50–100%) and EtOAc in $CHCl_3$ (0.0–20%), respectively. Phenol **3** was obtained as a light-brown oil (0.92 g, yield 28%), whereas **2** was recovered as an oil that crystallized in a few hours to form a light-brown solid (0.78 g, unreacted 45%).

R_f 0.67 (C).^{1}H-NMR ($CDCl_3$) δ 6.06 (1H, m, 4-H), 5.99 (2H, m, 2-H, 6-H), 4.78 (1H, br s, OH), 3.89 (2H, t, J = 6.6 Hz, $OC\underline{H_2}$), 3.76 (2H, d, J = 5.62 Hz, $OC\underline{H_2}CH$), 1.75 (3H, m, $OCH_2C\underline{H_2}$,

$OCH_2C\underline{H}$), 1.48-1.20 (38H, m, $(C\underline{H_2})_7CH_3$, $(C\underline{H_2})_5CH_3$), 0.88 (9H, t, J = 6.72 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.5, 161.2, 157.2, 94.7, 94.5, 94.3, 71.1, 68.2, 38.0, 32.01, 32.00, 31.95, 31.47, 31.46, 30.1, 29.8, 29.69, 29.68, 29.66, 29.5, 29.43, 29.42, 29.3, 26.92, 26.89, 26.1, 22.8, 14.2. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{32}H_{59}O_3$ 491.4459; Found 491.4463.

1-(4-Bromobutoxy)-3-decoxy-5-(2-hexyldecoxy)benzene (4). Compound **3** (2.36 g, 4.82 mmol), 1,4-dibromobutane (5.25 g, 24.3 mmol) and K_2CO_3 (2.1 g, 15.2 mmol) were suspended in DMF (40 ml). The reaction mixture was heated in a silicon oil bath at 80-90°C in argon atmosphere. After ~2.5 hours, the mixture was dilued with water, neutralized with HCl (10-15%) and extracted with *n*-hexane. Organic phase was wahed with brine (5×) and dried with Na_2SO_4. Then the hexane solution was purified by silica gel column chromatography. The product was eluted with $CHCl_3$−*n*-hexane mixture (0-20% of $CHCl_3$). Transperrent colourless oil was obtained (1.64 g, yield 54%).
R_f 0.51 (A), 0.7 (B). ^1H-NMR ($CDCl_3$) δ 6.07 (1H, m, 4-H), 6.04 (2H, m, 2-H, 6-H), 3.95 (2H, t, J = 5.99 Hz, $OC\underline{H_2}(CH_2)_3Br$), 3.90 (2H, t, J = 6.60 Hz, OCH_2), 3.77 (2H, d, J = 5.62 Hz, $OC\underline{H_2}CH$), 3.48 (2H, t, J = 6.60 Hz, CH_2Br), 2.09-2.02 (2H, m, $CH_2C\underline{H_2}CH_2Br$ or $C\underline{H_2}CH_2CH_2Br$), 1.95-1.88 (2H, m, $CH_2C\underline{H_2}CH_2Br$ or $C\underline{H_2}CH_2CH_2Br$), 1.79-1.72 (3H, m, $OCH_2C\underline{H_2}$, $OCH_2C\underline{H}$), 1.46-1.20 (38H, m, $(C\underline{H_2})_7CH_3$, $(C\underline{H_2})_5CH_3$), 0.88 (9H, t, J = 6.48 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.4, 161.1, 160.7, 94.1, 93.9, 93.8, 71.0, 68.1, 66.9, 38.0, 33.5, 32.01, 32.00, 31.96, 31.49, 31.48, 30.1, 29.8, 29.69, 29.68, 29.66, 29.5, 29.43, 29.42, 29.36, 28.0, 26.92, 26.90, 26.2, 22.8, 14.2. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{36}H_{66}BrO_3$ 625.4190; Found 625.4197.

1-(6-azidohexoxy)-3,5-didecoxy-benzene (6). Compound **5** (1.21 g, 2.13 mmol) and NaN_3 (0.72 g, 10.6 mmol) were suspended in DMF (10 ml). The reaction mixture was heated in a silicon oil bath at ~80°C in argon atmosphere. After ~3 hours, the mixture was dilued with water and extracted with *n*-hexane. Organic phase was wahed with brine (4×) and dried with Na_2SO_4. Then hexane solution was purified by silica gel column chromatography. The product was eluted with $CHCl_3$−*n*-hexane mixture (20-50% of $CHCl_3$). Colourless oil was obtained (1.03 g, yield 91%).
R_f 0.38 (B), ^1H-NMR ($CDCl_3$) δ 6.05 (3H, m, 2-H, 4-H, 6-H), 3.92-3.88 (6H, m, OCH_2, $OC\underline{H_2}(CH_2)_5N_3$), 3.27 (2H, t, J = 6.85 Hz, CH_2N_3), 1.80-1.71 (6H, m, $OCH_2C\underline{H_2}$, $OCH_2C\underline{H_2}(CH_2)_4N_3$), 1.66-1.59 (2H, quint, J = 7.09 Hz, $C\underline{H_2}CH_2N_3$), 1.52-1.39 (8H, m, $O(CH_2)_2C\underline{H_2}$, $(C\underline{H_2})_2(CH_2)_2N_3$), 1.38-1.20 (24H, m, $(C\underline{H_2})_6CH_3$), 0.88 (6H, t, J = 6.85 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.0, 160.9, 93.9, 93.8, 68.0, 67.7, 51.4, 31.9, 29.60, 29.58, 29.4, 29.34, 29.28, 29.1, 28.8, 26.5, 26.1, 25.7, 22.7, 14.1. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{32}H_{58}N_3O_3$ 532.4473; Found 532.4451.

6-(3,5-Didecoxyphenoxy)hexan-1-amine (7). Azide derivative **6** (0.86 g, 1.62 mmol) was dissolved in dioxane (7 ml). Then triphenyl phosphine (0.52 g, 1.98 mmol) was added. The reaction precceded at room temperature for 3 hours and then a few drops of water were added. Next day, solvent was evaporated *in vacuo*. The residue was purified by column chromatograohy on silica gel. Product was eluted with MeOH in $CHCl_3$ (30%). After drying in high vacuum over P_2O_5 a light-yellow oil was obtained (0.57 g, yield 70%).

R_f 0.14 (E). ^{1}H-NMR ($CDCl_3$) δ 6.05 (3H, m, 2-H, 4-H, 6-H), 3.89 (6H, m, OCH_2, $OC\underline{H}_2(CH_2)_5N$), 2.72 (2H, t, J = 6.97 Hz, CH_2N), 2.03 (2H, br. s, NH_2), 1.80-1.71 (6H, m, $OCH_2C\underline{H}_2$, $OCH_2C\underline{H}_2(CH_2)_4N$), 1.53-1.20 (34H, m, $(C\underline{H}_2)_3CH_2N$, $(C\underline{H}_2)_7CH_3$), 0.88 (6H, t, J = 6.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.0, 160.9, 93.84, 93.80, 68.0, 67.8, 42.0, 33.3, 31.9, 29.60, 29.58, 29.4, 29.34, 29.28, 29.2, 26.7, 26.1, 26.0, 22.7, 14.1. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{32}H_{60}NO_3$ 506.4568; Found 506.4583.

N-[4-[3-decoxy-5-(2-hexyldecoxy)phenoxy]butyl]-6-(3,5-didecoxyphenoxy)hexan-1-amine (8). Amine derivative **7** (0.71g, 1.41 mmol), compound **4** (1.05 g, 1.68 mmol) and K_2CO_3 (0.39 g, 2.83 mmol) were suspended in dry benzene-DMSO mixture (5.6 and 4.2 ml, respectively). The reaction mixture was heated in a silicon oil bath at 35-45°C for ~22 hours with stirring. Then it was diluted with EtOAc, washed with aq. $NaHCO_3$ and NaCl (5×) solutions, dried with Na_2SO_4 and evaporated. Light-green oil was obtained (~1.8 g). Three amines (**7-9**) were seperated and purified by silica gel column chromatography. *tert*-Amine **9** was eluted with EtOAc in $CHCl_3$ (4-7%), target product **8** was eluted with EtOAc in $CHCl_3$ (7-13%) and then with MeOH (2-4%) in EtOAc-$CHCl_3$ (13% EtOAc) mixture, and unreacted **7** was eluted with MeOH in $CHCl_3$ (30%). Compounds **7-9** were dried for a few days in high vacuum over P_2O_5. Amine **9** was obtained as a colourless oil (0.24 g, yield 11%), product **8** was obtained as a light-yellow oil (0.87 g, yield 60%), while **7** was recovered as a yellow oil (70 mg, unreacted 10%).

R_f 0.32 (D).^{1}H-NMR ($CDCl_3$) δ 6.05 (6H, m, 2-H, 4-H, 6-H, 2'-H, 4'-H, 6'-H), 3.94-3.88 (10H, m, OCH_2, $OC\underline{H}_2CH$, $OC\underline{H}_2(CH_2)_5N$, $OC\underline{H}_2(CH_2)_3N$), 3.77 (2H, d, J = 5.87 Hz, $OC\underline{H}_2CH$), 2.72 (2H, t, J = 7.34 Hz, $O(CH_2)_3C\underline{H}_2N^*$), 2.67 (2H, t, J = 7.34 Hz, $O(CH_2)_5C\underline{H}_2N^*$), 1.84-1.68 (13H, m, $OCH_2C\underline{H}_2$, $OCH_2C\underline{H}$, $OCH_2C\underline{H}_2(CH_2)_4N$, $OCH_2(C\underline{H}_2)_2CH_2N$, NH), 1.58 (2H, quint, J = 7.09 Hz, $O(CH_2)_4C\underline{H}_2CH_2N$), 1.50-1.20 (70H, m, $(C\underline{H}_2)_7CH_3$, $(C\underline{H}_2)_5CH_3$, $O(CH_2)_2(C\underline{H}_2)_2(CH_2)_2N$), 0.88 (15H, t, J = 6.8 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.3, 161.0, 160.9, 160.7, 93.9, 93.81, 93.76, 93.7, 70.9, 68.0, 67.8, 67.6, 49.6, 49.4, 37.9, 31.93, 31.92, 31.88, 31.4 (br), 30.0, 29.7, 29.60, 29.58, 29.5 (br), 29.4, 29.35, 29.34, 29.29, 29.27, 29.2, 27.11, 27.08, 26.84, 26.81, 26.2 (br), 26.1, 26.0, 22.7, 14.1. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{68}H_{124}NO_6$ 1050.9423; Found. 1050.9420.

* – assignment of signals are based on integral intensities of corresponding signals of compound **9**.

N,N-bis[4-[3-decoxy-5-(2-hexyldecoxy)phenoxy]butyl]-6-(3,5-didecoxyphenoxy)hexan-1-amine (9). *tert*-Amine **9** was obtained as a side product during the synthesis of *sec*-amine **8** as described above.

R_f 0.43 (C), 0.8 (D). ^{1}H-NMR ($CDCl_3$) δ 6.05 (9H, m, 2-H, 4-H, 6-H, 2'-H, 4'-H, 6'-H), 3.93-3.87 (14H, m, OCH_2, $OC\underline{H}_2(CH_2)_5N$, $OC\underline{H}_2(CH_2)_3N$), 3.76 (4H, d, J = 5.67 Hz, $OC\underline{H}_2CH$), 2.46 (4H, t, J = 7.34 Hz, $O(CH_2)_3C\underline{H}_2N$), 2.41 (2H, t, J = 7.34 Hz, $O(CH_2)_5C\underline{H}_2N$), 1.74 (16H, m, $OCH_2C\underline{H}_2$, $OCH_2C\underline{H}$, $OCH_2C\underline{H}_2(CH_2)_4N$, $OCH_2C\underline{H}_2(CH_2)_2N$), 1.58 (4H, m, $O(CH_2)_2C\underline{H}_2CH_2N$, H_2O), 1.50-1.20 (110H, m, $(C\underline{H}_2)_7CH_3$, $(C\underline{H}_2)_5CH_3$, $O(CH_2)_2(C\underline{H}_2)_3CH_2N$), 0.88 (24H, m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 161.3, 161.04, 161.00, 160.94 (br), 93.90 (br), 93.88 (br), 93.85 (br), 93.75, 71.0, 68.1, 68.0 (br), 54.1 (br), 53.9 (br), 38.0, 32.00, 31.99, 31.95, 31.47, 31.45, 30.1, 29.8, 29.69, 29.67, 29.66, 29.50, 29.49, 29.42, 29.41, 29.37, 29.35, 27.4 (br), 27.2 (br), 26.91, 26.88, 26.16, 26.15, 23.8 (br), 22.8, 14.2. HRMS (ESI/Q-TOF): *m/z* $[M+H]^+$ Calcd for $C_{104}H_{188}NO_9$ 1595.4279; Found. 1595.4264.

2,4-Bis[4-[3-decoxy-5-(2-hexyldecoxy)phenoxy]butyl-[6-(3,5-didecoxyphenoxy)hexyl]amino]-2,6-dihydroxy-phenyl]squaraine (1).

5-[4-[3-decoxy-5-(2-hexyldecoxy)phenoxy]butyl-[6-(3,5-didecoxyphenoxy)hexyl]amino]benzene-1,3-diol (**10**). *sec*-Amine **8** (0.7 g, 0.666 mmol), phloroglucinol (0.17 g, 1.35 mmol), DBPC (59 mg, 0.268 mmol) and DIPEA (103 μl, 0.664 mmol) were dissolved in *n*-BuOH (2 ml) and heated in argon atmosphere in a silicon oil bath at 90-95^{o}C. After ~ 24 h, darck-red oil was obtained after solvent coevaporation with cyclohexane. Then it was purified by silica gel column chromatography. Product was eluted with EtOAc in $CHCl_3$ (4−13%). Compound **10** was obtained as a dark-brown oil (0.54 g, yield 71%).

R_f 0.51 (D).^{1}H-NMR ($CDCl_3$) δ 6.09-6.03 (6H, m, 2-H, 4-H, 6-H, 2'-H, 4'-H, 6'-H), 5.71 (2H, d, J = 1.71 Hz, 4-H, 5-H (phloramine)), 5.66 (1H, m, 2-H (phloramine)), 4.94 (2H, br., OH), 3.96-3.88 (10H, m, OCH_2, $OC\underline{H}_2(CH_2)_5N$, $OC\underline{H}_2(CH_2)_3N$), 3.77 (2H, d, J = 5.62 Hz, $OC\underline{H}_2CH$), 3.26 (2H, m, $O(CH_2)_3C\underline{H}_2N$*), 3.20 (2H, m, $O(CH_2)_5C\underline{H}_2N$*), 1.78-1.71 (13H, m, $OCH_2C\underline{H}_2$, $OCH_2C\underline{H}$, $OCH_2C\underline{H}_2(CH_2)_4N$, $OCH_2(C\underline{H}_2)_2CH_2N$), 1.62-1.55 (2H, m, $O(CH_2)_4C\underline{H}_2CH_2N$), 1.52-1.20 (70H, m, $(C\underline{H}_2)_7CH_3$, $(C\underline{H}_2)_5CH_3$, $O(CH_2)_2(C\underline{H}_2)_2(CH_2)_2N$), 0.88 (15H, t, J = 6.36 Hz, CH_3).

* – assignment of signals are based on integral intensities of corresponding signals of compound **9**.

2,4-Bis[4-[3-decoxy-5-(2-hexyldecoxy)phenoxy]butyl-[6-(3,5-didecoxyphenoxy)hexyl]amino]-2,6-dihydroxy-phenyl]squaraine (**1**). Compound **10** (0.25 g, 0.216 mmol) and squaric acid (12 mg, 0.105 mmol) were suspended in dry BuOH–benzene mixture (1:3, 45 ml) and heated in a silicon oil bath at 80-90^{o}C for ~4 h in argon atmosphere. The solvent was evaporated *in vacuo* with cyclohexane addition. The residue, a dark blue oil (~0.28 g), was purified by silica gel column chromatography. It was eluted with *n*-hexane-$CHCl_3$ mixture (3:7). Appropriate fractions were evaporated and then coevaporated three times with $CHCl_3$ and three times with CH_2Cl_2. Then the product was dried at room temperature in high vacuum over P_2O_5 for several days. Dark violet highly viscous oil was obtained (161 mg, yield 62%).

R_f 0.55 (F).^{1}H-NMR ($CDCl_3$) δ 11.0 (4H, s, OH), 6.08-6.05 (12H, m, 2-H, 4-H, 6-H, 2'-H, 4'-H, 6'-H), 5.80 (4H, s, squaraine core), 3.95 (4H, m, $OC\underline{H}_2(CH_2)_3N$), 3.92-3.88 (16H, m, OCH_2, $OC\underline{H}_2(CH_2)_5N$), 3.77 (4H, d, J = 5.87 Hz, $OC\underline{H}_2CH$), 3.42 (4H, m, $O(CH_2)_3C\underline{H}_2N$*), 3.36 (4H, m, $O(CH_2)_5C\underline{H}_2N$*), 1.87-1.61 (30H, m, $OCH_2C\underline{H}_2$, $OCH_2C\underline{H}$, $OCH_2C\underline{H}_2(CH_2)_2C\underline{H}_2CH_2N$, $OCH_2(C\underline{H}_2)_2CH_2N$), 1.55-1.20 (140H, m, $O(CH_2)_2(C\underline{H}_2)_2(CH_2)_2N$, $(C\underline{H}_2)_5CH_3$, $(C\underline{H}_2)_7CH_3$), 0.88 (30H, m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 181.4, 163.0, 161.5, 161.4, 161.09, 161.06, 160.9, 160.6, 157.9, 102.6, 94.2, 93.9, 93.8, 93.75, 93.70, 71.0, 68.13, 68.11, 67.7, 67.3, 51.6, 51.3, 38.0, 32.00, 31.99, 31.95, 31.46, 31.45, 30.1, 29.8, 29.69, 29.67, 29.65, 29.5, 29.42, 29.41, 29.36, 29.35, 29.3, 28.1 26.91, 26.89, 26.8, 26.7, 26.16, 26.15, 26.0, 25.0, 22.8, 14.20. MS (MALDI-TOF): *m/z* $[M]^{\bullet+}$ Calcd for $C_{152}H_{252}N_2O_{18}$ 2393.886; Found. 2394.017.

* – assignment of signals are based on integral intensities of corresponding signals of compound **9**.

4. NMR spectra of compounds

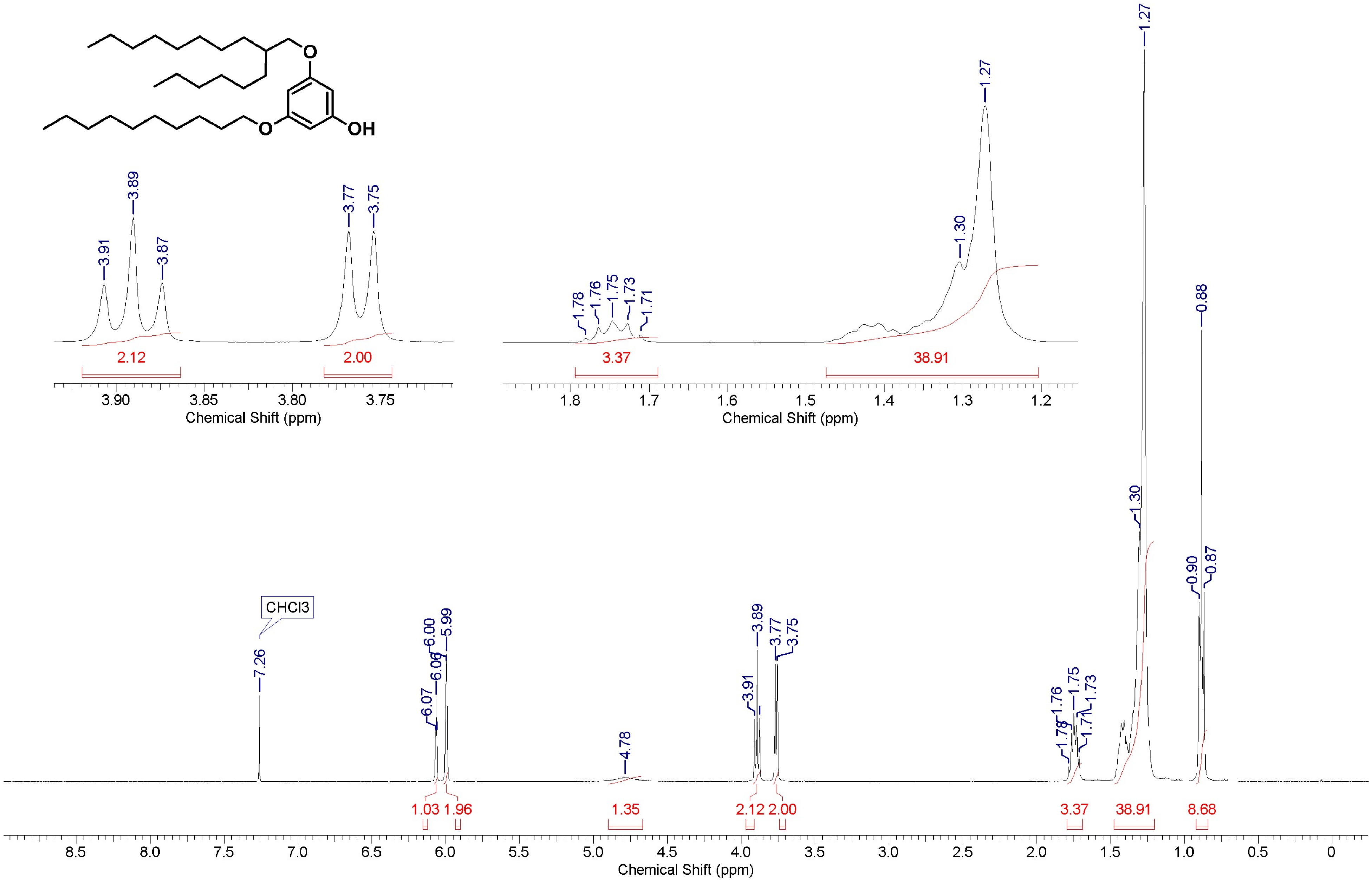


Figure S3. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

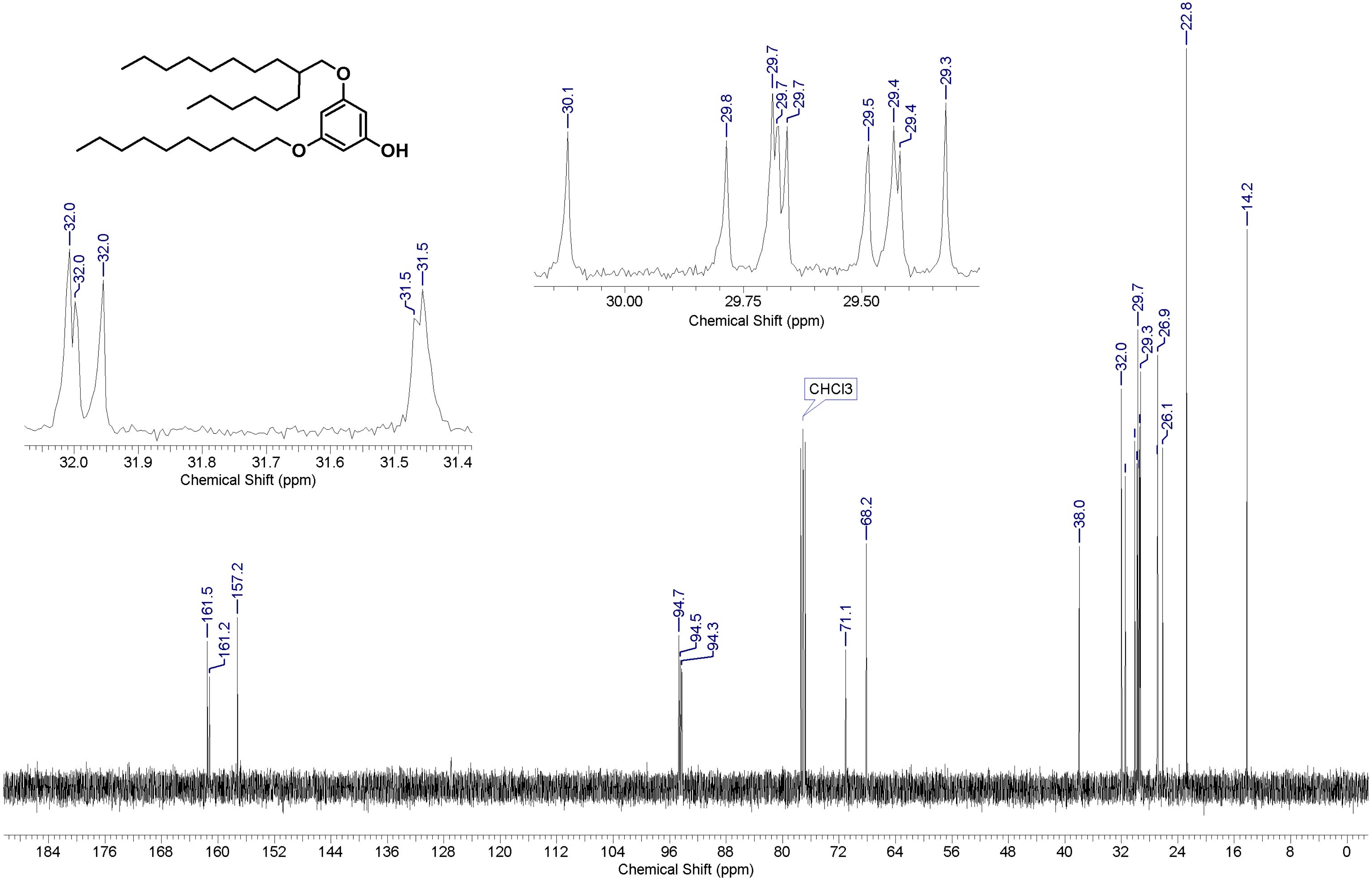


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$.

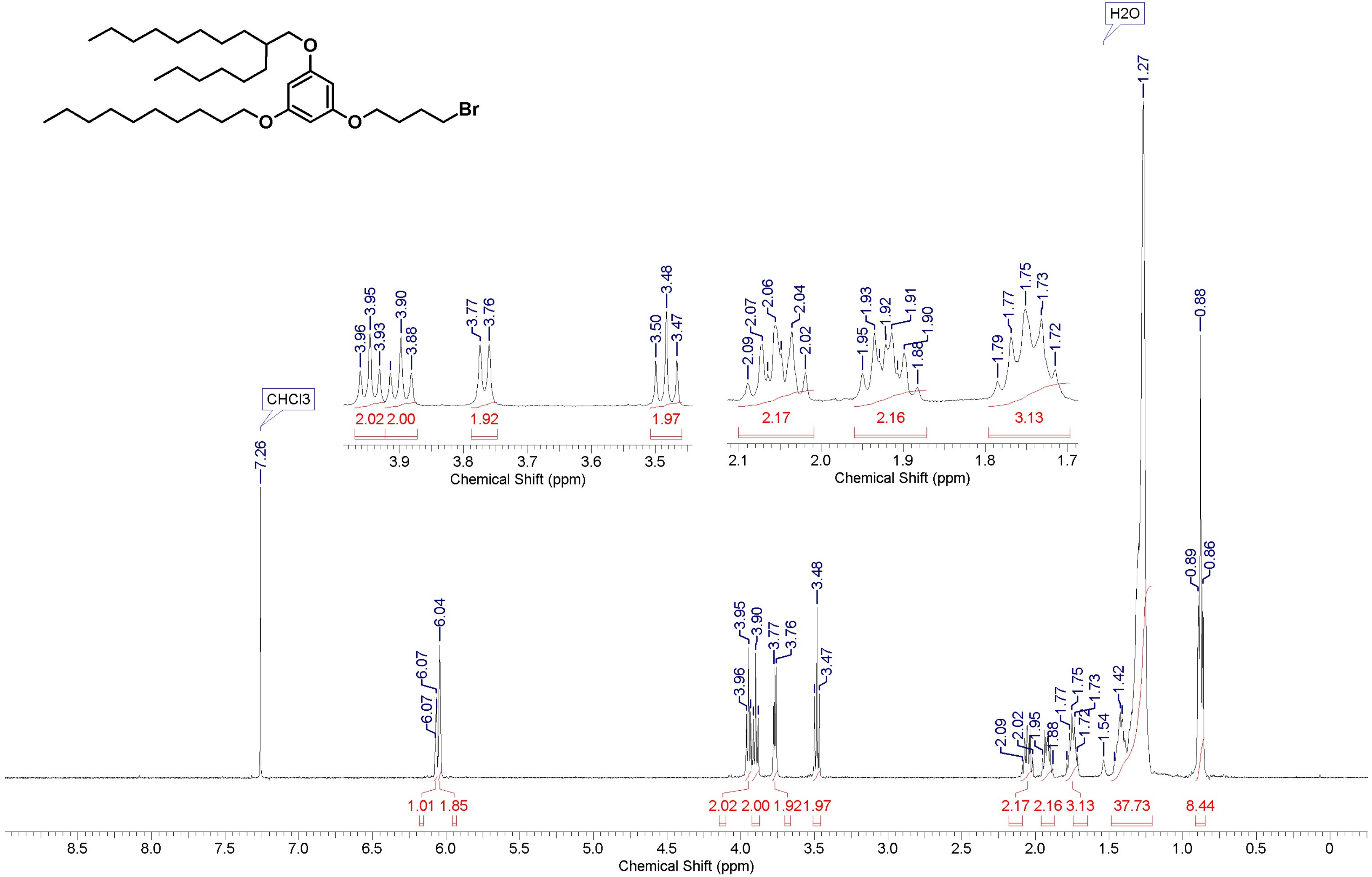


Figure S5. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

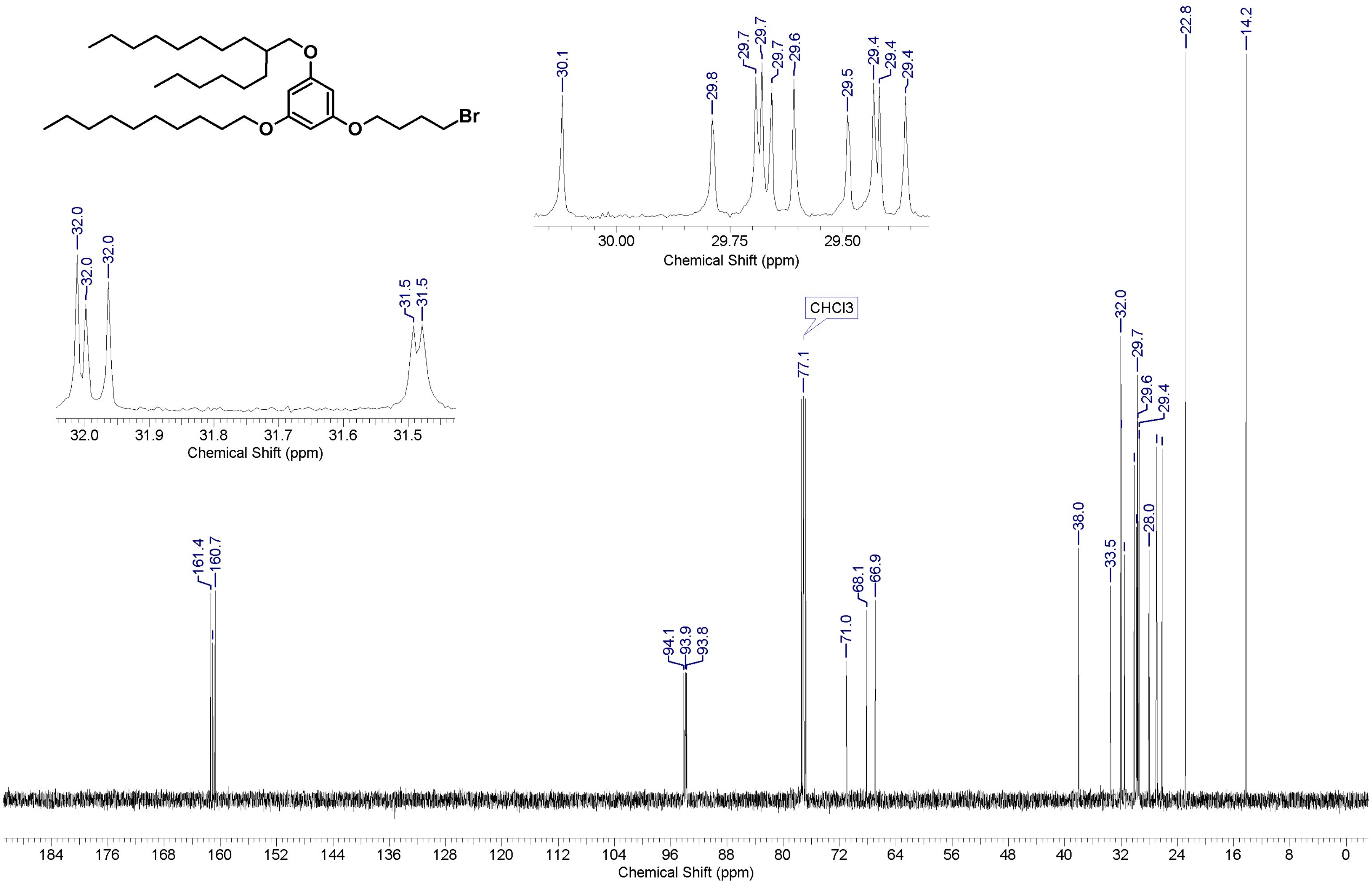


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of compound **4** in $CDCl_3$.

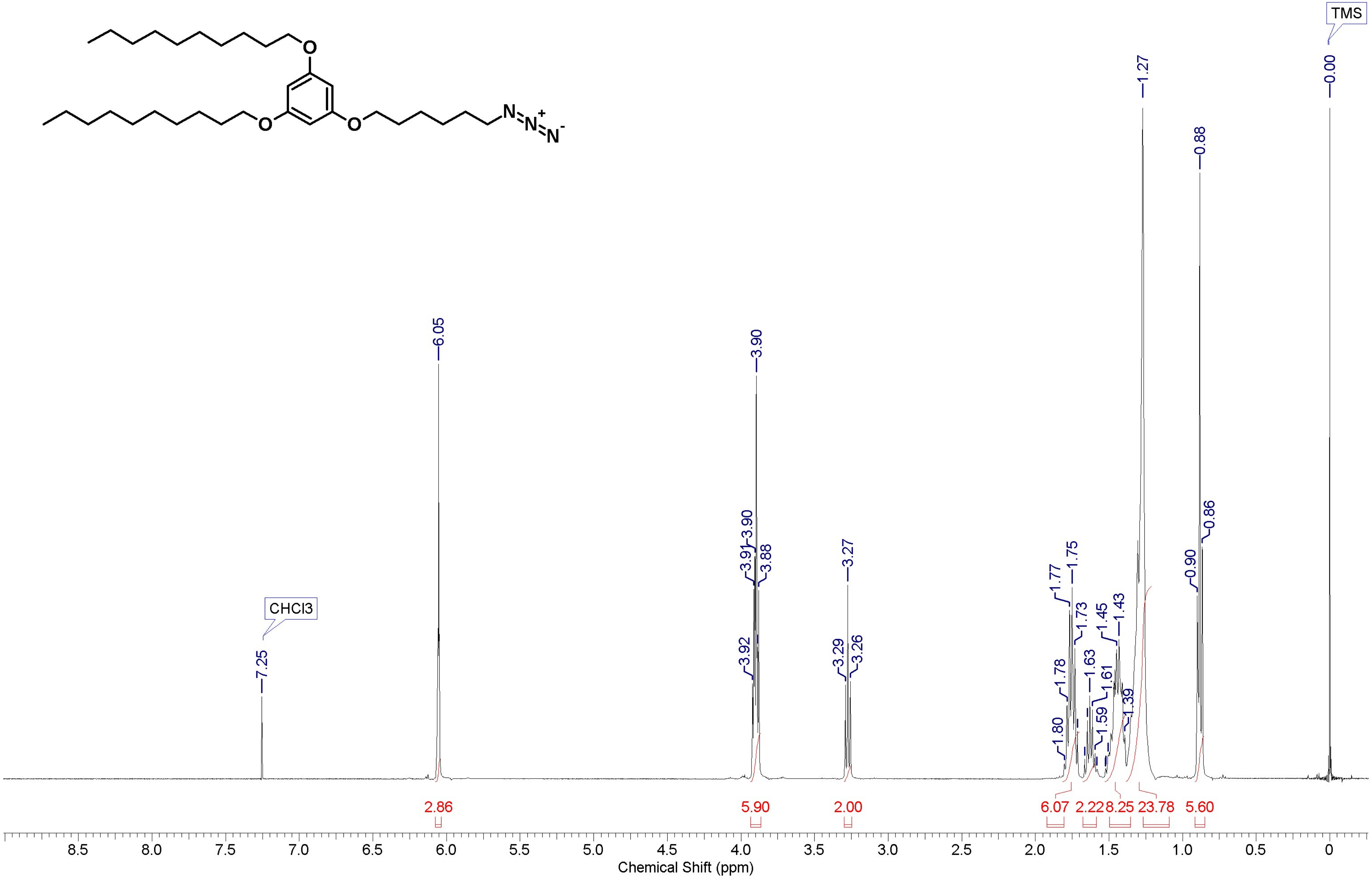


Figure S7. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

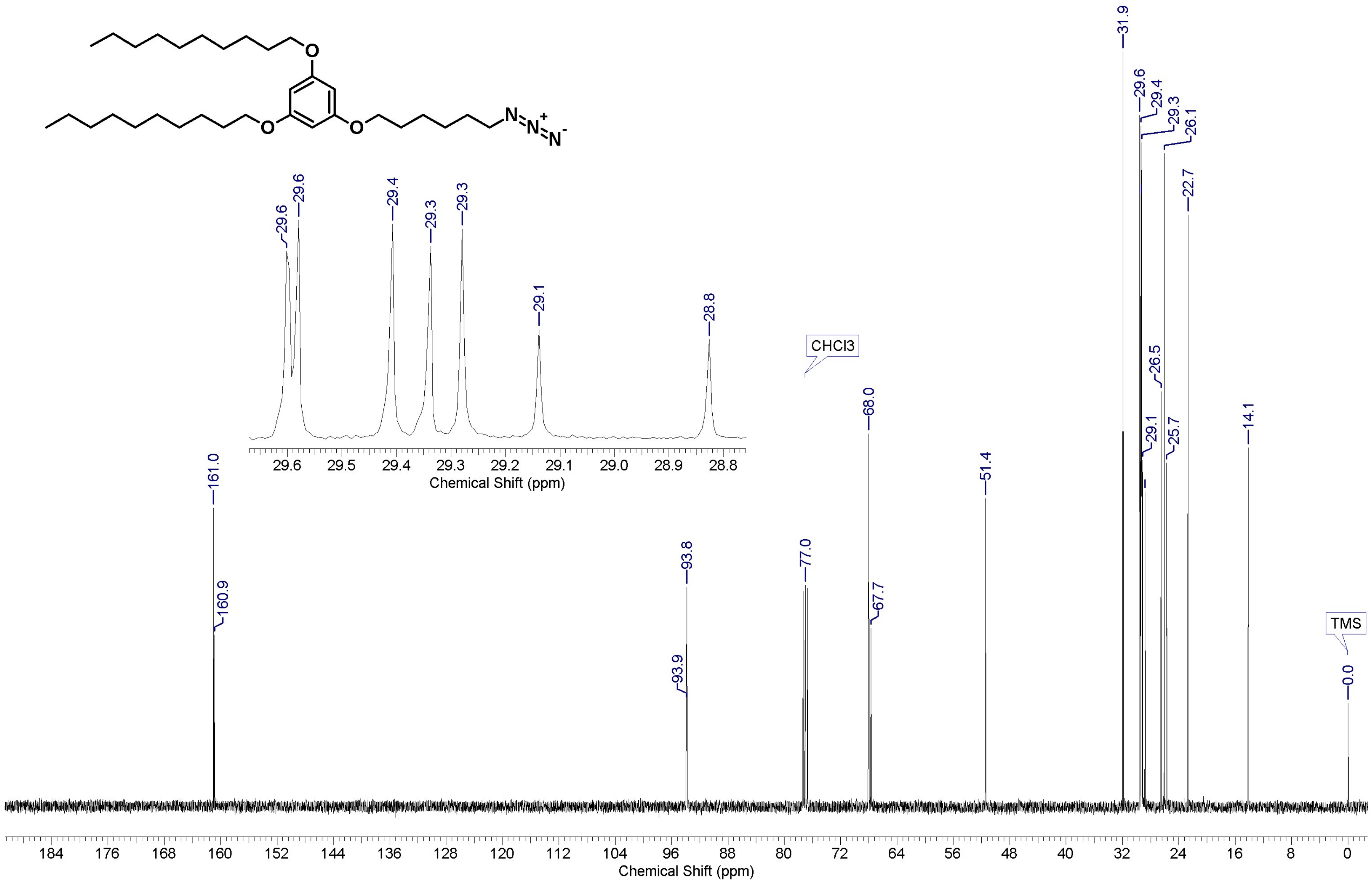


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of compound **6** in $CDCl_3$.

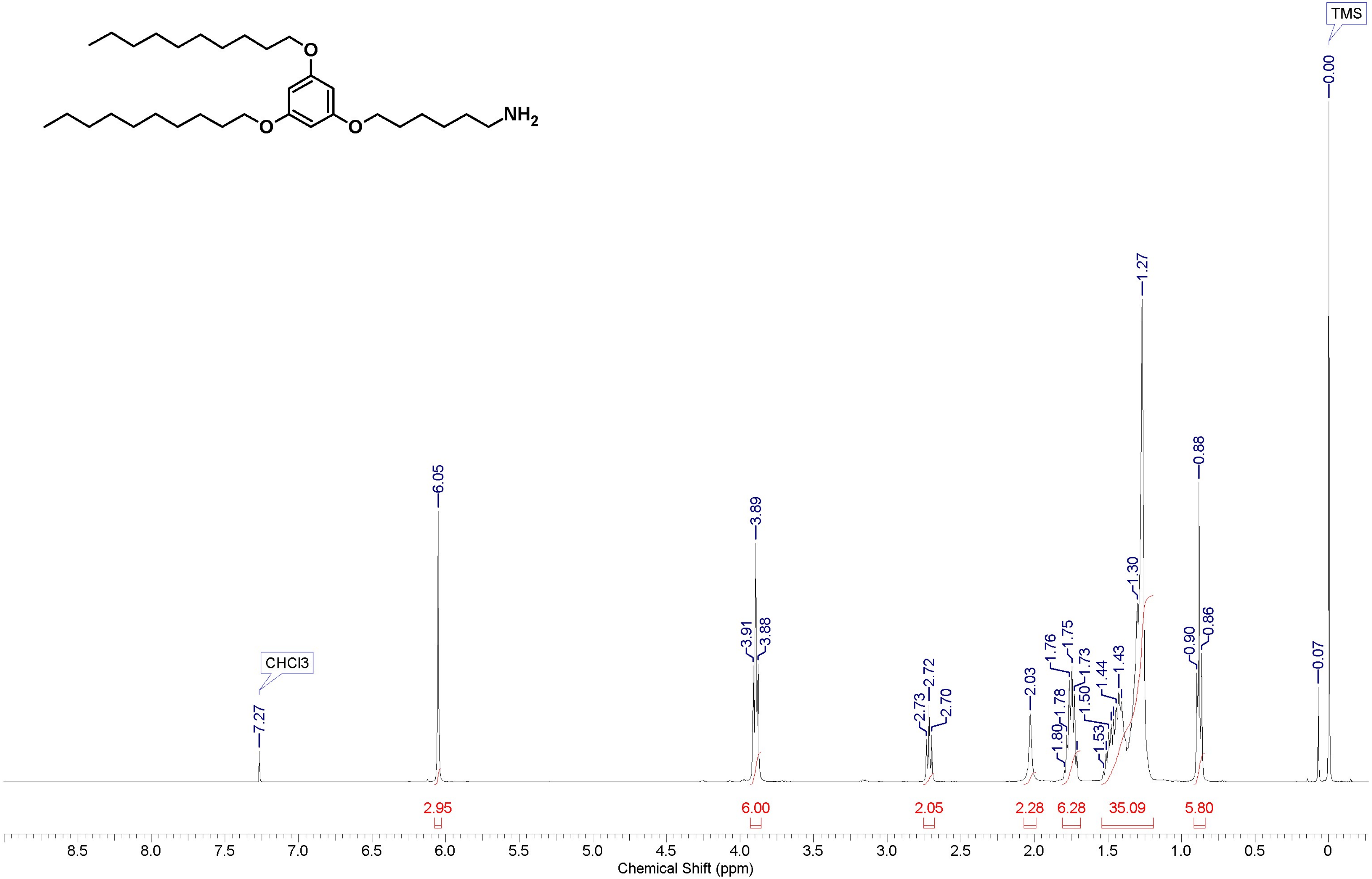
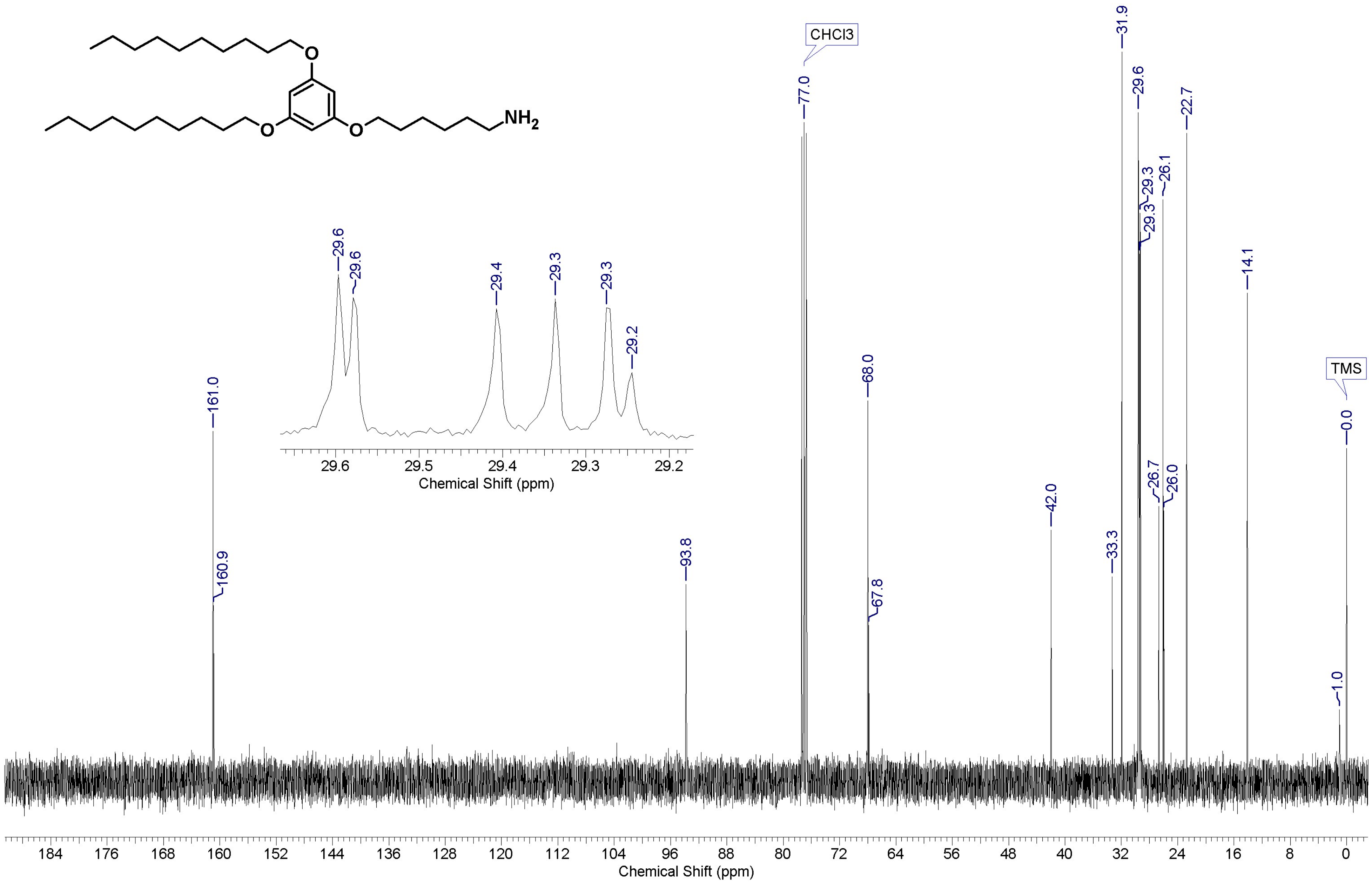


Figure S9. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.



.

Figure S10. ${}^{13}C\{{}^{1}H\}$ NMR spectrum of compound **7** in $CDCl_3$

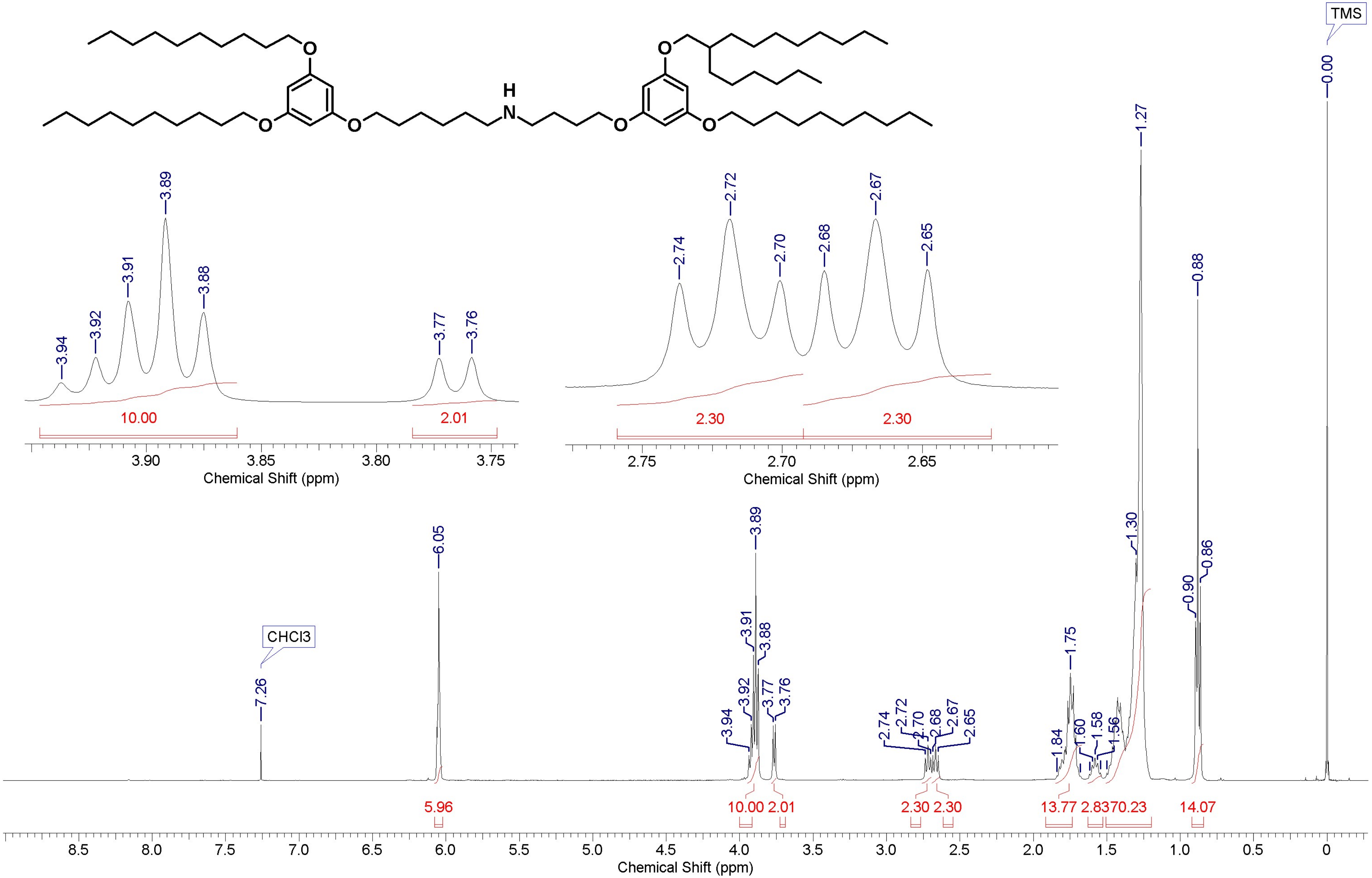


Figure S11. ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

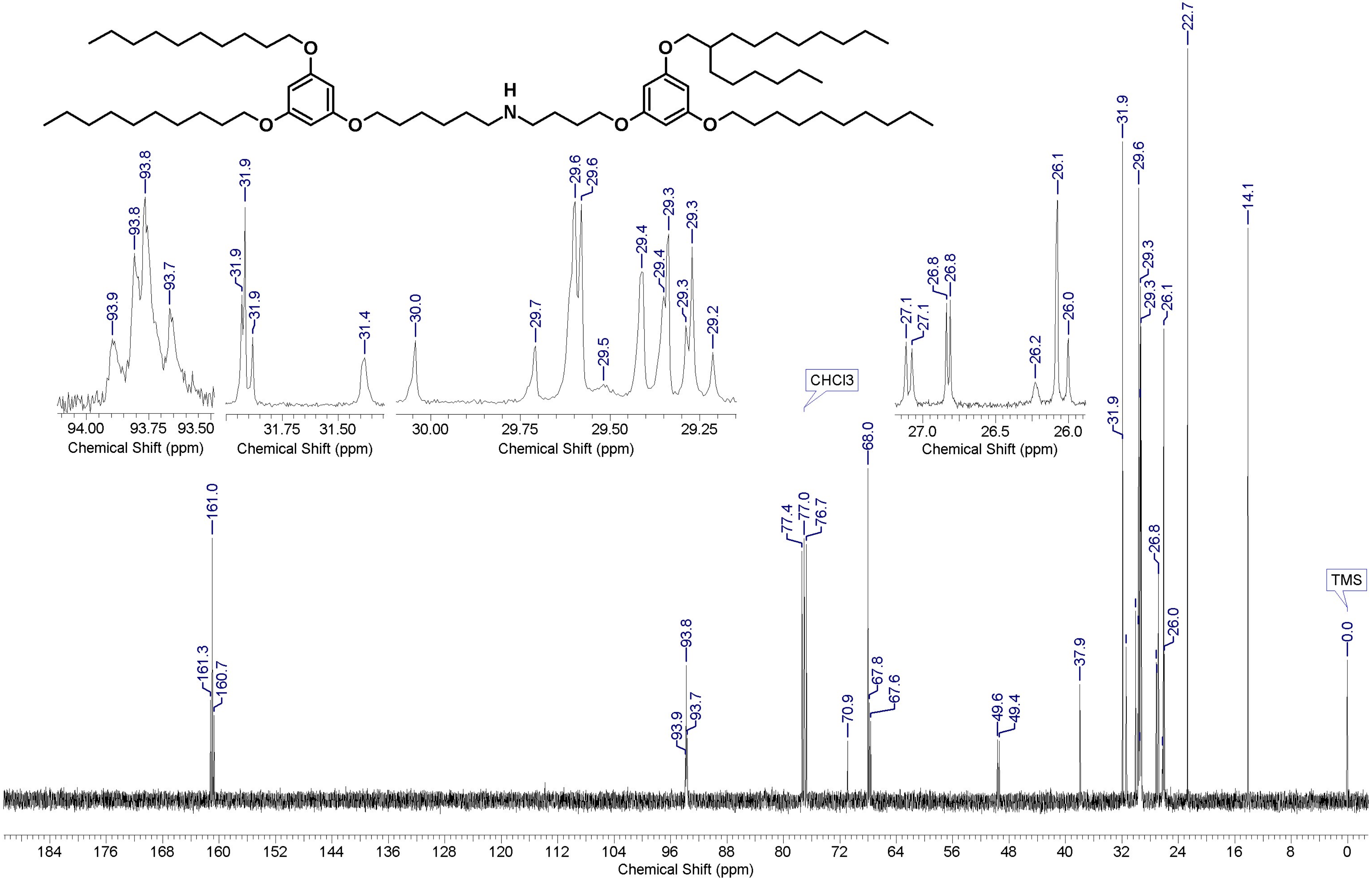


Figure S12. $^{13}C\{^1H\}$ NMR spectrum of compound **8** in $CDCl_3$.

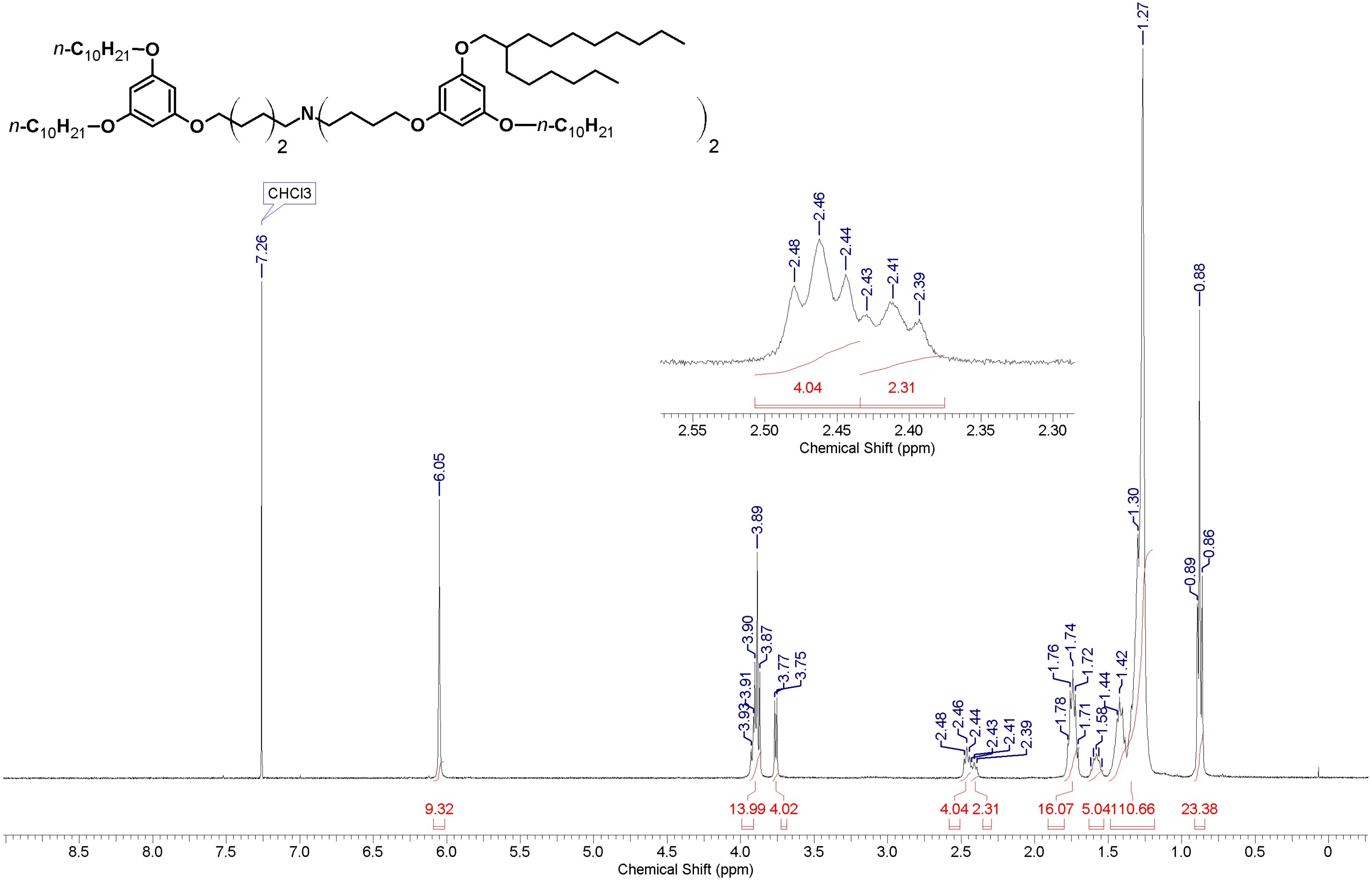


Figure S13. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

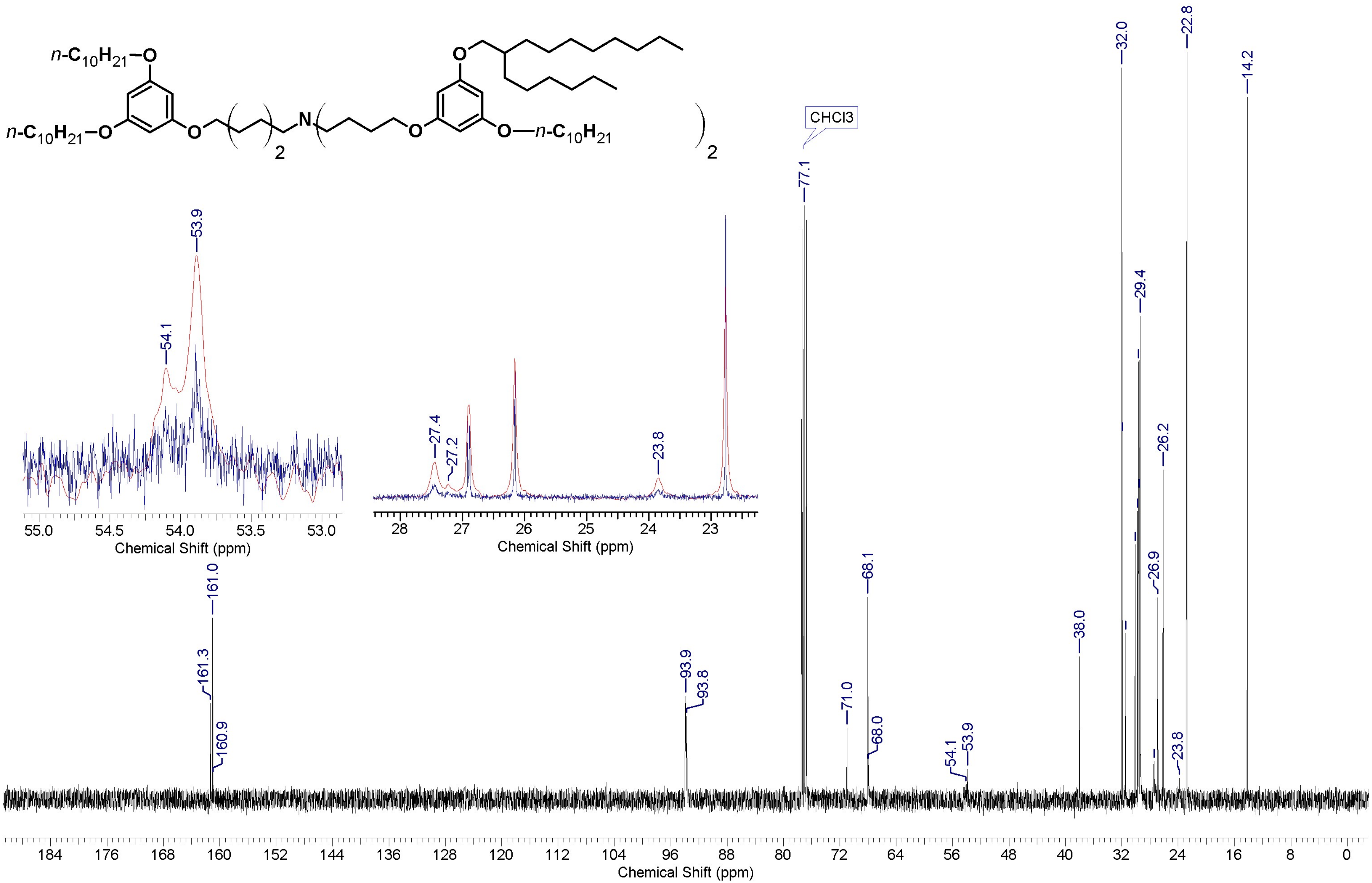


Figure S14. $^{13}C\{^1H\}$ NMR spectrum of compound **9** in $CDCl_3$.

Inserts: blue line – original spectrum, red line – spectrum with exponential line broadening parameter = 4

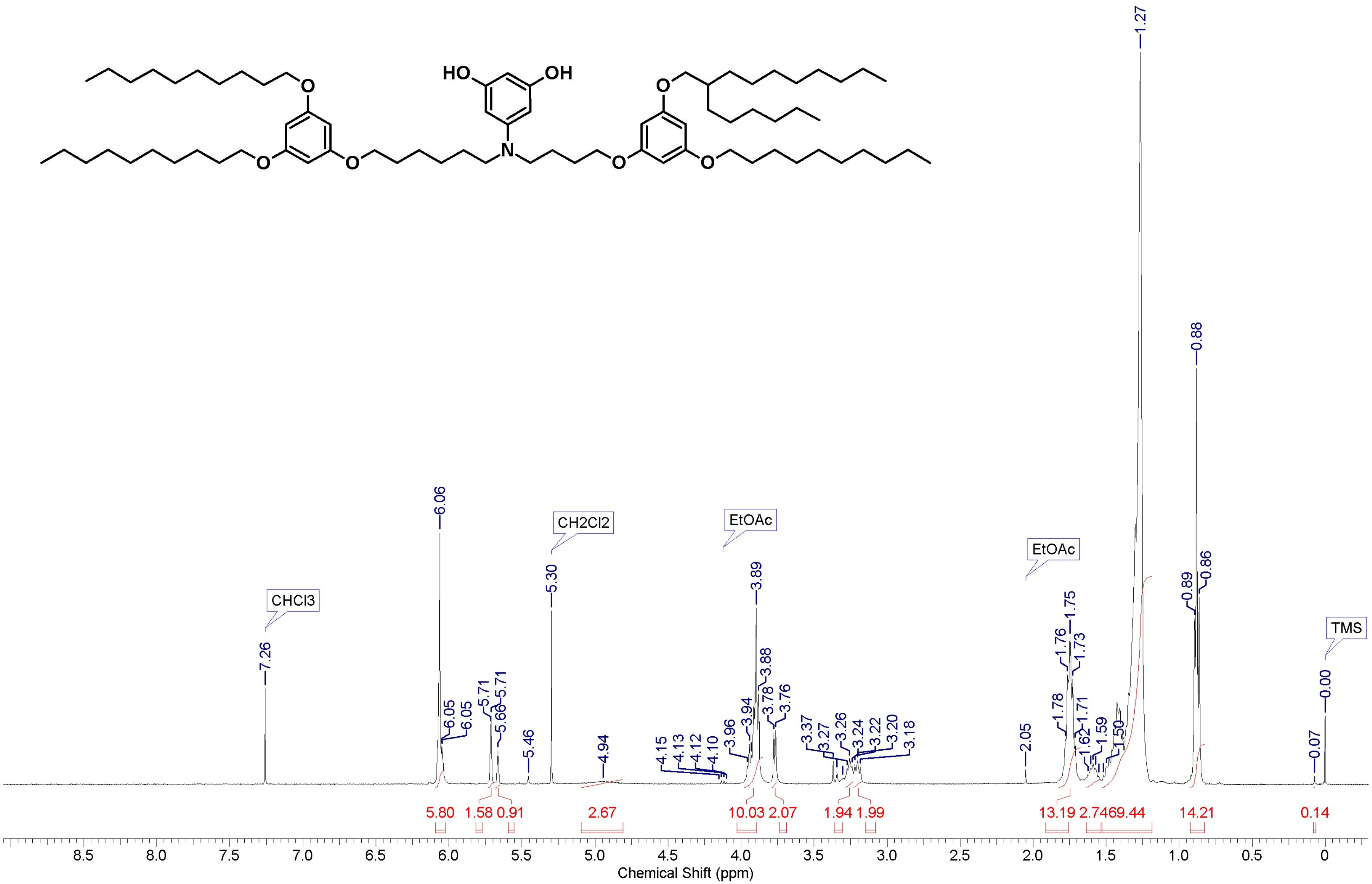


Figure S15. ^{1}H NMR spectrum of compound **10** in $CDCl_3$.

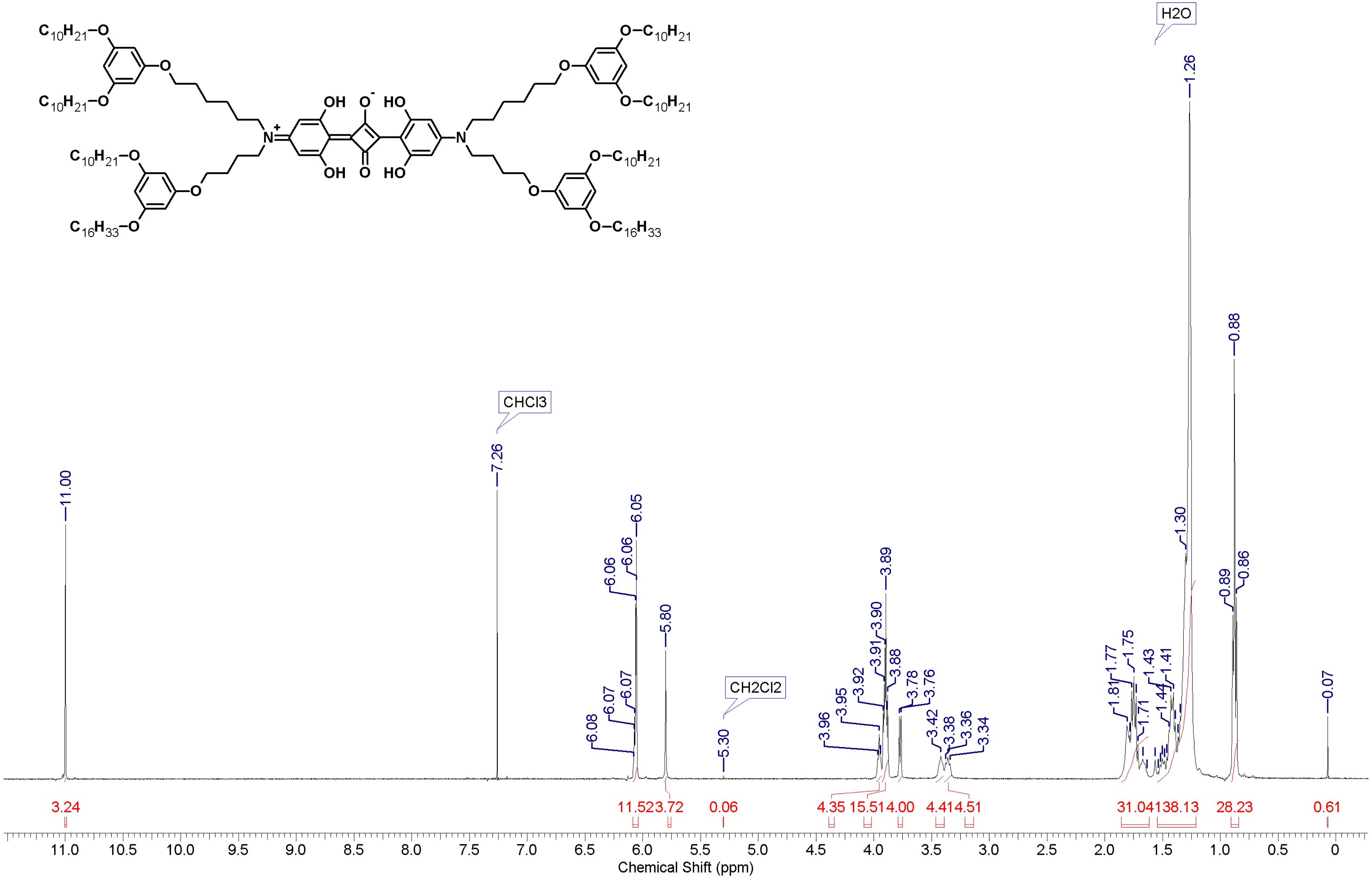


Figure S16. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.