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Supporting Information

Modular thiophene dendrons and dendrimers with peripheral functional groups

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Contents

Materials.

2-(6-bromohexyl)-thiophene,[1] and 4,7-dibromo-1,10-phenanthroline[2] were synthesized according to the literature procedure. 3,5,3',5'-Tetrabromo-[2,2']bithiophene was synthesized as reported earlier.[3] A second generation carbazole-terminated *Fréchet*-type polybenzylether dendrons (**4Cbz**) have been synthesized in our group.[4] CH_2Cl_2 for spectroscopic measurements was spectrophotometric grade. THF was freshly distilled from sodium benzophenone ketyl. All other commercially available reagents were purchased from Aldrich and used as received. Silica gel (60 Å, 32-63 μm, Standard Grade) was purchased from Sorbent Technologies, Inc. (Atlanta, GA).

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C nuclei. UV-vis spectra were recorded on an Agilent 8453 UV-visible Spectrometer and fluorescence spectra on a Perkin Elmer LS 45 Luminescence Spectrometer. High resolution mass spectra were recorded on a QSTAR XL MS/MS (quadrupole/TOF hybrid) mass spectrometer (Applied Biosystems/MDS Sciex, Foster City, CA, USA) at Mass Spectrometry Center, Department of Chemistry, University of Tennessee Knoxville. Elemental analyses were carried out by Galbraith Laboratories, Inc. (Knoxville, TN).

Synthesis.

Synthesis of 2-(6-Methoxyl-hexyl)-thiophene (1T6COMe). 70 mL of methanol was added dropwise to sodium (2.5 g, 108.7 mmol) at 0°C. After addition, it was warmed up to room temperature and stirred for 30 minutes. A solution of 2-(6-bromohexyl)-thiophene (14.8 g, 60 mmol) in 30 mL of methanol was added dropwise. After addition, the reaction mixture was heated up to refluxing overnight and then cooled to room temperature. Methanol was removed by rotary evaporation. The residue was

poured into 50 g of water-ice and extracted with CH_2Cl_2 (3×50 mL). The extract was dried over Na_2SO_4 and concentrated. The product was obtained as a colorless liquid by vacuum distillation (10.2 g, 85.7%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.11 (dd, J= 5.1 Hz, 1.2 Hz, 1H), 6.92 (dd, J= 5.1 Hz, 3.6 Hz, 1H), 6.79 (m, 1H), 3.38 (t, J= 6.6 Hz, 2H), 3.34 (s, 3H), 2.84 (t, J= 7.5 Hz, 2H), 1.71 (m, 2H), 1.59 (m, 2H), 1.40 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 145.57, 126.51, 123.80, 122.62, 72.70, 58.42, 31.59, 29.70, 29.41, 28.79, 25.74.

Synthesis of Tributyl-[5-(6-methoxy-hexyl)-thiophen-2-yl]-stannane (Sn1T6COMe). 25 mL of n-butyl lithium (2.5 M in hexane, 62.5 mmol) was added dropwise to a solution of 2-(6-methoxyl-hexyl)-thiophene (11.5 g, 58.0 mmol) in 50 mL of THF at -78°C under N_2. After 30 minutes of stirring upon addition, tributyltin chloride (20.5 g, 63.0 mmol) was added dropwise. The reaction was allowed to warm up to room temperature for 4 hours. THF was removed by rotary evaporation. The residue was poured into 100 mL of saturated $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2 (3×100 mL). The extract was dried over Na_2SO_4 and concentrated. The product was used directly for the next reaction without further purifications. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.01 (d, J= 2.7 Hz, 1H), 6.93 (d, J= 2.7 Hz, 1H), 3.39 (t, J= 6.3 Hz, 2H), 3.35 (s, 3H), 2.89 (t, J= 7.5 Hz, 2H), 1.73 (m, 2H), 1.60 (m, 8H), 1.38 (m, 10H), 1.11 (t, J= 8.1 Hz, 6H), 0.93 (t, J= 7.2 Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.28, 135.07, 133.61, 125.21, 72.75, 58.42, 31.65, 29.75, 29.48, 28.97, 28.89, 27.18, 25.81, 13.58, 10.61.

Synthesis of 5,5''-Bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophene (3T6COMe). In a one-necked flask was charged with 27.5 g of tributyl-[5-(6-methoxy-hexyl)-thiophen-2-yl]-stannane (56.4 mmol), 4.6 g of 2,3-dibromothiophene (19.0 mmol), 1.4 g of $Pd(PPh_3)_4$, and 100 mL of DMF. After three freeze-thaw cycles, the mixture was heated up to 110°C for 20 hours under nitrogen. After cooling to room temperature, DMF was removed by vacuum distillation and the residue was poured into water, extracted with CH_2Cl_2, and washed thoroughly with NaF solution to remove tributyltin chloride. The

organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography eluting with 3:1 hexane/diethyl ether to give the yellow oil product (7.9 g, 87.2%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.20 (d, J= 5.1 Hz, 1H), 7.11 (d, J= 5.1 Hz, 1H), 6.92 (d, J= 3.6 Hz, 1H), 6.85 (d, J= 3.3 Hz, 1H), 6.65 (m, 2H), 3.36 (t, J= 6.0 Hz, 4H), 3.23 (s, 6H), 2.78 (m, 4H), 1.67 (m, 4H), 1.56 (m, 4H), 1.37 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.43, 145.91, 135.14, 132.46, 132.18, 131.43, 129.74, 127.75, 126.04, 124.32, 124.18, 124.13, 72.95, 58.70, 31.65, 31.60, 30.20, 30.14, 29.68, 29.04, 26.00.

Synthesis of [5,5’’-Bis-(6-methoxy-hexyl)-[2,2’;3’,2’’]terthiophen-5’-yl]-tributyl-stannane (Sn3T6COMe). 4.0 mL of n-butyl lithium (2.5 M in hexane, 10.0 mmol) was added dropwise to a solution of 5,5’’-bis-(6-methoxy-hexyl)-[2,2’;3’,2’’]terthiophene (**3T6COMe**, 4.1 g, 8.6 mmol) in 30 mL of THF at -78°C under N_2. After 30 minutes of stirring upon addition, tributyltin chloride (3.3 g, 10.1 mmol) was added dropwise. The reaction was allowed to warm up to room temperature for 4 hours. THF was removed by rotary evaporation. The residue was poured into 40 mL of saturated $NaHCO_3$ aqueous solution extracted with CH_2Cl_2 (3×50 mL). The extract was dried over Na_2SO_4 and concentrated. The product was used directly for the next reaction without further purifications. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.10 (s, 1H), 6.90 (d, J= 3.6 Hz, 1H), 6.86 (d, J= 3.9 Hz, 1H), 6.65 (m, 2H), 3.36 (t, J= 6.9 Hz, 4H), 3.32 (s, 6H), 2.78 (m, 4H), 1.67 (m, 4H), 1.56 (m, 10H), 1.37 (m, 14H), 1.11 (m, 6H), 0.91 (dt, 9H, J= 7.2 Hz).

Synthesis of 2,3-Di(5,5''-di(6-methoxy-hexyl)-[2,2';3',2'']terthiophen-5'-yl)thiophene (7T6COMe). In a one-necked flask was charged with tributyl [5,5’’-bis-(6-methoxy-hexyl)-[2,2’;3’,2’’]terthiophene-5’-yl]stannane (**Sn3T6COMe**, 2.3 g, 3.0 mmol), 2,3-dibromothiophene (242 mg, 1.0 mmol), 75 mg of $Pd(PPh_3)_4$, and 50 mL of DMF. After three freeze-thaw cycles, the mixture was heated up to 110°C for 20 hours under nitrogen. After cooling to room temperature, the reaction

mixture was poured into water, extracted with CH_2Cl_2, and washed thoroughly with NaF solution to remove tributyltin chloride. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography eluting with 1:1 hexane/diethyl ether to give the yellow oil product (860 mg, 83.2%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.27 (d, J= 6.0 Hz, 1H), 7.22 (s, 1H), 7.18 (s, 1H), 7.17 (d, J= 6.0 Hz, 1H), 6.95 (d, J= 2.1 Hz, 1H), 6.94 (d, J= 1.8 Hz, 1H), 6.88 (d, J= 3.3 Hz, 1H), 6.86 (d, J= 3.0 Hz, 1H), 6.66 (m, 4H), 3.36 (t, J= 6.3 Hz, 8H), 3.32 (s, 12H), 2.77 (t, J= 7.5 Hz, 8H), 1.67 (m, 8H), 1.57 (m, 8H), 1.38 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.37, 147.16, 146.00, 145.83, 135.03, 134.76, 134.45, 132.83, 132.54, 132.16, 131.90, 131.79, 131.74, 131.61, 131.36, 131.03, 130.40, 129.62, 129.25, 127.53, 127.40, 126.30, 126.11, 124.84, 124.15, 124.13, 124.01, 72.74, 58.49, 31.47, 31.39, 30.01, 29.98, 29.50, 28.86, 28.84, 25.81.

Synthesis of 2,3-Di(5,5''-di(6-bromohexyl)-[2,2';3',2'']terthiophen-5'-yl)thiophene (7T6CBr). An emulsion of 2,3-di(5,5"-di(6-methoxy-hexyl)-[2,2';3',2"]terthiophen-5'-yl)thiophene (**7T6COMe**, 0.5 g, 0.48 mmol) in 20 mL HBr aqueous solution (47.0 ~ 49.0 wt%) was heated up to refluxing for 20 hours. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2. The extract was neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography eluting with 1:1 hexane/$CHCl_3$ to give the yellow oil product (360 mg, 60.5%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.29 (d, J= 5.1 Hz, 1H), 7.22 (s, 1H), 7.18 (s, 1H), 7.17 (d, J= 5.1 Hz, 1H), 6.95 (d, J= 1.8 Hz, 1H), 6.94 (d, J= 1.8 Hz, 1H), 6.88 (d, J= 3.6 Hz, 1H), 6.87 (d, J= 3.6 Hz, 1H), 6.66 (m, 4H), 3.40 (t, J= 6.9 Hz, 8H), 2.78 (t, J= 7.5 Hz, 8H), 1.86 (pentet, J= 6.9 Hz, 8H), 1.67 (pentet, J= 7.2 Hz, 8H), 1.43 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.18, 146.97, 145.81, 145.64, 135.16, 134.91, 134.59, 132.86, 132.66, 132.31, 132.04, 131.84, 131.78, 131.63, 131.42, 131.08, 130.45, 129.68, 129.29, 127.61, 127.46, 126.38, 126.19, 124.93, 124.32, 124.28, 124.13, 33.88, 32.63, 31.33, 31.26, 29.98, 29.94, 28.11, 27.84.

Synthesis of 14T6COMe. In a one-necked flask was charged with tributyl [5,5''-bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophene-5'-yl]stannane (2.3 g, 3.0 mmol), 3,5,3',5'-tetrabromo-[2,2']bithiophene (241 mg, 0.5 mmol), 75 mg of $Pd(PPh_3)_4$, and 50 mL of DMF. After three freeze-thaw cycles, the mixture was heated up to 110°C for 20 hours under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with CH_2Cl_2, and washed thoroughly with NaF solution to remove tributyltin chloride. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography eluting with 1:2 hexane/diethyl ether to give the yellow oil product (260 mg, 25.2%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.22 (s, 1H), 7.19 (s, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 7.12 (d, J= 3.6 Hz, 1H), 7.07 (d, J= 3.9 Hz, 1H), 6.95 (m, 4H), 6.89 (m, 4H), 6.67 (m, 8H), 3.37 (m, 16H), 3.34 (s, 24H), 2.77 (m, 16H), 1.67 (m, 16H), 1.58 (m, 16H), 1.39 (m, 32H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.41, 147.30, 147.21, 146.15, 146.03, 145.88, 137.81, 135.41, 134.59, 134.55, 134.49, 134.30, 134.19, 133.80, 133.31, 132.27, 132.03, 131.99, 131.92, 131.89, 131.69, 131.14, 130.74, 130.24, 129.50, 128.62, 127.44, 127.36, 126.59, 126.44, 126.36, 126.16, 125.99, 124.23, 124.18, 124.14, 124.07, 124.00, 72.69, 58.43, 31.44, 31.34, 29.97, 29.93, 29.46, 28.80, 25.77.

Synthesis of 14T6CBr. A solution of **14T6COMe** (100 mg, 0.05 mmol) in a mixture of acetic acid (30 mL) and HBr aqueous solution (47.0 ~ 49.0 wt%, 10 mL) was heated up to refluxing overnight. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2. The extract was neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography eluting with 2:1 hexane/$CHCl_3$ to give the yellow oil product (50 mg, 42.0%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.22 (s, 1H), 7.20 (s, 1H), 7.18 (s, 1H), 7.17 (s, 1H), 7.13 (d, J= 3.9 Hz, 1H), 7.09 (d, J= 4.2 Hz, 1H), 6.96 (m, 4H), 6.89 (m, 4H), 6.67 (m, 8H), 3.41 (m, 16H), 2.78 (m, 16H), 1.87 (m, 16H), 1.68 (m, 16H), 1.44 (m, 32H).

Synthesis of 3TCbz-2. To a solution of **4Cbz** (1.27 g, 1.0 mmol) in 1-methylpyrrolidone (NMP, 20 mL), To the suspension of NaH (60% dispersion in mineral oil, 80 mg, 2.0 mmol) in 1-methylpyrrolidone (NMP, 40 mL), **4Cbz** (1.27 g, 1.0 mmol) was added in portions, and after stirring for 30 min at room temperature, **3T6CBr** (230 mg, 0.4 mmol) in NMP (1 mL) was added dropwise to the reaction mixture and was heated up to 160 °C under N_2 for 2 days. After cooling to room temperature, NMP was removed under vacuum and water (~ 100 mL) was added. The mixture was neutralized with dilute hydrochloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by column chromatography eluting with 1:4 hexane/ CH_2Cl_2 to give the yellow solid product (360 mg, 30.5%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.08 (d, J= 7.8 Hz, 16H), 7.46~7.37 (m, 32H), 7.23~7.18 (m, 16H), 7.13 (d, J= 5.4 Hz, 1H), 7.05 (d, J= 5.4 Hz, 1H), 6.89 (d, J= 3.6 Hz, 1H), 6.82 (d, J= 3.6 Hz, 1H), 6.62~6.60 (m, 2H), 6.57 (d, J= 1.2 Hz, 4H), 6.53~6.45 (m, 10H), 6.29 (t, J= 2.1 Hz, 4H), 4.89 (s, 8H), 4.39 (s, 4H), 4.33 (t, J= 7.2 Hz, 16H), 3.85 (t, J= 6.3 Hz, 16H), 3.40 (t, J= 6.3 Hz, 4H), 2.71 (t, J= 7.2 Hz, 4H), 2.02 (m, 16H), 1.80 (m, 16H), 1.56 (m, 8H), 1.33 (m, 8H). Anal. Calcd $C_{194}H_{188}N_8O_{14}S_3$: C, 78.94; H, 6.42; N, 3.80; O, 7.59; S, 3.26; Found: C, 76.21; H, 6.41; N, 3.45; O, 7.82; S, 3.22.

Synthesis of 5,5''-Bis-(6-bromohexyl)-[2,2';3',2'']terthiophene (3T6CBr). An emulsion of 5,5''-bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophene (**3T6COMe**, 3.0 g, 6.3 mmol) in 40 mL HBr aqueous solution (47.0 ~ 49.0 wt%) was heated up to refluxing for 20 hours. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2. The extract was neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography eluting with 1:1 hexane/$CHCl_3$ to give the yellow solid product (2.85 g, 78.7%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.23 (d, J= 5.4 Hz, 1H), 7.17 (d, J= 5.4 Hz, 1H), 7.01 (d, J= 3.9 Hz, 1H), 6.94 (d, J= 3.3 Hz, 1H), 6.74 (d, J= 3.9 Hz, 1H), 6.72 (d, J= 3.3 Hz, 1H), 3.43 (t, J= 6.9 Hz, 4H), 2.83 (t, J= 7.5 Hz, 4H), 1.90 (pentet, J= 6.9 Hz, 4H), 1.73 (pentet, J= 7.5 Hz, 4H), 1.48 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.49,

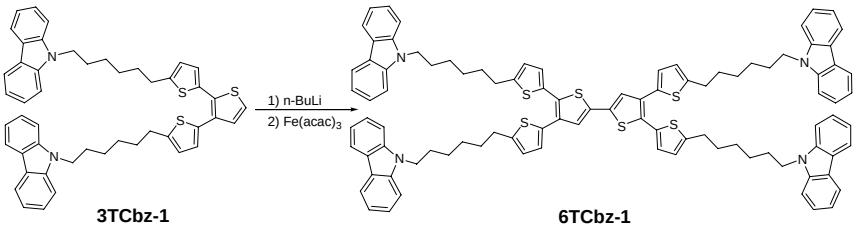
144.93, 134.57, 131.89, 131.59, 130.64, 129.11, 127.28, 125.54, 123.95, 123.79, 33.57, 32.30, 30.94, 30.88, 29.58, 29.54, 27.75, 27.48.

Synthesis of 5,5''-Bis-(6-carbazol-9-yl-hexyl)-[2,2';3',2'']terthiophene (3TCbz-1). To the suspension of NaH (60% dispersion in mineral oil, 400 mg, 10.0 mmol) in dry THF (50 mL), carbazole (1.5 g, 8.97 mmol) was added in portions, and after stirring for 30 min at room temperature, 5,5''-bis-(6-bromohexyl)-[2,2';3',2'']terthiophene (**3T6CBr**, 1.5 g, 2.61 mmol) in dry THF (10 mL) was added dropwise to the reaction mixture and refluxed overnight. After cooling to room temperature, THF was removed by rotary evaporation and water (~ 100 mL) was added. The mixture was neutralized with dilute hydrochloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by column chromatography eluting with 2:1 hexane/ CH_2Cl_2 to give the yellow solid product (1.65 g, 84.6%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.11 (d, J= 7.8 Hz, 4H), 7.43 (m, 8H), 7.22 (m, 5H), 7.11 (d, J= 4.8 Hz, 1H), 6.92 (d, J= 3.6 Hz, 1H), 6.85 (d, J= 3.6 Hz, 1H), 6.62 (d, J= 3.6 Hz, 1H), 6.59 (d, J= 3.6 Hz, 1H), 4.28 (t, J= 7.2 Hz, 4H), 2.70 (t, J= 7.2 Hz, 4H), 1.85 (m, 4H), 1.59 (m, 4H), 1.37 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.93, 145.43, 140.28, 134.98, 132.29, 131.96, 131.16, 129.53, 127.59, 125.89, 125.51, 125.54, 124.18, 124.02, 122.68, 120.25, 118.65, 108.55, 42.74, 31.19, 31.15, 29.86, 29.82, 28.71, 28.63, 26.82. HRMS *m/z* Calcd for $C_{48}H_{46}N_2S_3$ (M^+) 746.2823, Found 746.2784. Anal. Calcd $C_{48}H_{46}N_2S_3$: C, 77.17; H, 6.21; N, 3.75; S, 12.88; Found: C, 77.67; H, 6.22; N, 3.60; S, 11.84.

Synthesis of 6T6COMe. 0.5 mL of n-BuLi (2.5 M in hexane, 1.25 mmol) was added dropwise to a solution of 5,5''-bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophene (**3T6COMe**, 480 mg, 1.01 mmol) in dry THF at -78°C under N_2. After 30 min stirring upon addition, the mixture was transferred to another flask charged with $CuCl_2$ (0.41 g, 3.0 mmol) in 10 mL of dry THF at -78°C. The reaction mixture was warmed up to room temperature and reacted overnight. After normal workup, the residue was purified

by column chromatography eluting with 1:1 hexane/ ether to give the yellow oil product (310 mg, 65.2%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.16 (s, 2H), 6.95 (d, J= 3.6 Hz, 2H), 6.90 (d, J= 3.6 Hz, 2H), 6.67 (d, J= 3.6 Hz, 4H), 3.37 (t, J= 6.3 Hz, 8H), 3.33 (s, 12H), 2.78 (m, 8H), 1.68 (m, 8H), 1.58 (m, 8H), 1.39 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.24, 146.01, 134.27, 134.24, 132.18, 131.96, 130.64, 127.31, 126.32, 126.15, 124.16, 124.02, 72.65, 58.39, 31.40, 31.30, 29.93, 29.89, 29.43, 28.77, 25.75. HRMS *m/z* Calcd for $C_{52}H_{70}O_4S_6$ (M^+) 950.3598, Found 950.3662.

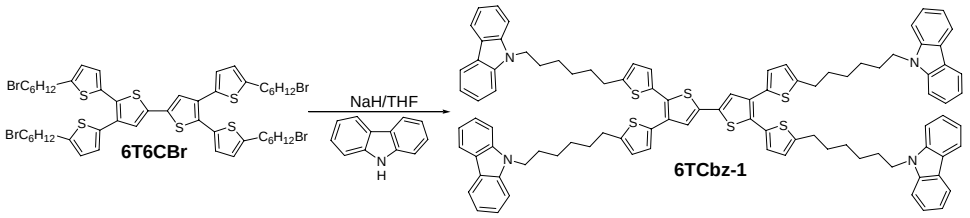
Synthesis of 6T6CBr. An emulsion of **6T6COMe** (1.0 g, 1.05 mmol) in 40 mL HBr aqueous solution (47.0 ~ 49.0 wt%) was heated up to refluxing for 20 hours. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2. The extract was neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography eluting with 2:1 hexane/$CHCl_3$ to give the yellow oil product (0.5 g, 41.5%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.16 (s, 2H), 6.95 (d, J= 3.3 Hz, 2H), 6.90 (d, J= 3.9 Hz, 2H), 6.68 (m, 4H), 3.41 (t, J= 6.3 Hz, 8H), 2.79 (m, 8H), 1.87 (pentet, J= 6.9 Hz, 8H), 1.68 (m, 8H), 1.45 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.16, 145.91, 134.47, 134.38, 132.27, 132.14, 130.77, 127.47, 126.46, 126.31, 124.37, 124.21, 33.86, 32.62, 31.33, 31.24, 29.95, 28.10, 27.83.



3TCbz-1 **6TCbz-1**

Synthesis of 6TCbz-1. n-BuLi (2.5 M in hexane, 0.8 mL, 2.0 mmol) was added to a 0 °C THF solution of **3TCbz-1** (1.49 g, 2.0 mmol), and the mixture was stirred at 0 °C for 0.5 h. This reaction mixture was then transferred at 0 °C into a refluxing THF solution containing $Fe(acac)_3$ (0.71 g, 2.0 mmol) and allowed to reflux overnight. The mixture was filtered, and the salts were washed with THF.

The filtrate was concentrated under reduced pressure to yield a red oil, which was purified by silica column chromatography (hexane/CH_2Cl_2, 3:2, v/v) to afford the desired product as a yellow solid (0.68, 45.6%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.09 (d, J= 7.8 Hz, 8H), 7.41 (m, 16H), 7.22 (m, 8H), 7.13 (s, 2H), 6.92 (dJ= 3.3 Hz, 2H,), 6.86 (d, J= 3.9 Hz, 2H), 6.60 (m, 4H), 4.28 (t, J= 7.2 Hz, 8H), 2.70 (m, 8H), 1.86 (m, 8H), 1.58 (m, 8H), 1.36 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.08, 145.83, 140.26, 134.28, 132.20, 131.98, 130.66, 127.39, 126.41, 126.23, 125.49, 124.27, 124.11, 122.67, 120.22, 118.64, 108.52, 42.73, 31.21, 31.12, 29.86, 29.83, 28.72, 28.63, 26.81. HRMS *m/z* Calcd for $C_{96}H_{90}N_4S_6$ (M^+) 1490.5490, Found 1490.5696. Anal. Calcd $C_{96}H_{90}N_4S_6$: C, 77.27; H, 6.08; S, 12.89; Found: C, 77.11; H, 6.25; S, 11.37.



Synthesis of 6TCbz-1. To the suspension of NaH (60% dispersion in mineral oil, 40 mg, 1.0 mmol) in dry THF (10 mL), carbazole (0.15 g, 0.90 mmol) was added in portions, and after stirring for 30 min at room temperature, **6T6CBr** (175 mg, 0.15 mmol) in dry THF (1 mL) was added dropwise to the reaction mixture and refluxed overnight. After cooling to room temperature, THF was removed by rotary evaporation and water (~ 50 mL) was added. The mixture was neutralized with dilute hydrochloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by column chromatography eluting with 3:2 hexane/ CH_2Cl_2 to give the yellow solid product (80.5 mg, 36.0%).

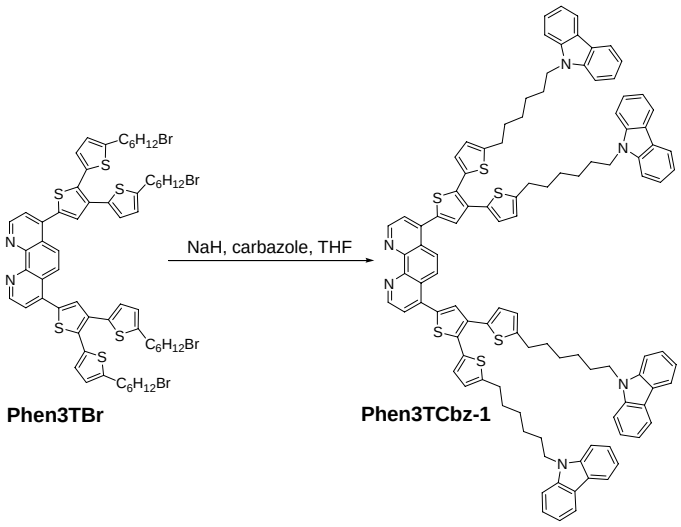
Synthesis of 4,7-Bis-[5,5''-bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophen-5'-yl]-1,10-phenanthroline (Phen3T). To a round-bottomed flask was charged 0.23 g of tributyl [5,5''-bis-(6-methoxy-hexyl)-[2,2';3',2'']terthiophene-5'-yl]stannane (**Sn3T6COMe**, 0.3 mmol), 33.8 mg of 4,7-dibromo-1,10-

phenanthroline (0.1 mmol), 75 mg of $Pd(PPh_3)_4$, and 10 mL of DMF. After three freeze-thaw cycles, the mixture was heated to 110 °C for 20 hours under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with CH_2Cl_2, and washed thoroughly with NaF solution to remove tributyltin chloride. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column using CH_2Cl_2/CH_3OH (20:1) as eluent. 96 mg of the pure product was obtained (yield: 85%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 9.22 (d, *J* =4.8 Hz, 2H), 8.46 (s, 2H), 7.73 (d, *J* =4.2 Hz, 2H), 7.42 (s, 2H), 7.05 (d, *J* =3.6 Hz, 2H), 6.98 (d, *J* =3.9 Hz, 2H), 6.71 (m, 4H), 3.36 (m, 20H), 2.81 (t, *J* =7.2 Hz, 8H), 1.69 (m, 8H), 1.58 (m, 8H), 1.40 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.4, 147.5, 146.6, 146.0, 139.7, 135.9, 133.8, 133.7, 132.2, 131.2, 131.1, 127.6, 126.3, 125.5, 124.1, 123.9, 123.7, 123.1, 72.4, 58.1, 31.1, 31.0, 29.7, 29.6, 29.2, 28.5, 25.5.

Synthesis of 4,7-Bis-[5,5''-bis-(6-bromo-hexyl)-[2,2';3',2'']terthiophen-5'-yl]-[1,10]-phenanthroline (Phen3TBr). An emulsion of **Phen3T** (226 mg, 0.2 mmol) in 20 mL HBr aqueous solution (47.0 ~ 49.0 wt%) was heated to reflux for 20 hours. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2. The extract was neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography eluting with 15:1 $CHCl_3$/EtOH to give the yellow oil product (108 mg, 41%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 9.20 (d, *J* =5.1 Hz, 2H), 8.44 (s, 2H), 7.71 (d, *J* =3.9 Hz, 2H), 7.42 (s, 2H), 7.04 (d, *J* =3.6 Hz, 2H), 6.97 (d, *J* =3.6 Hz, 2H), 6.71 (m, 4H), 3.40 (t, *J* =6.6 Hz, 4H), 3.39 (t, *J* =6.6 Hz, 4H), 2.80 (t, *J* =7.5 Hz, 8H), 1.84 (m, 8H), 1.69 (m, 8H), 1.43 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.8, 147.7, 147.0, 146.1, 140.1, 136.4, 134.2, 133.9, 132.5, 131.5, 131.4, 127.9, 126.6, 125.9, 124.5, 124.3, 124.1, 123.5, 33.8, 32.6, 31.3, 31.2, 29.9 (2), 29.6, 28.0, 27.8.

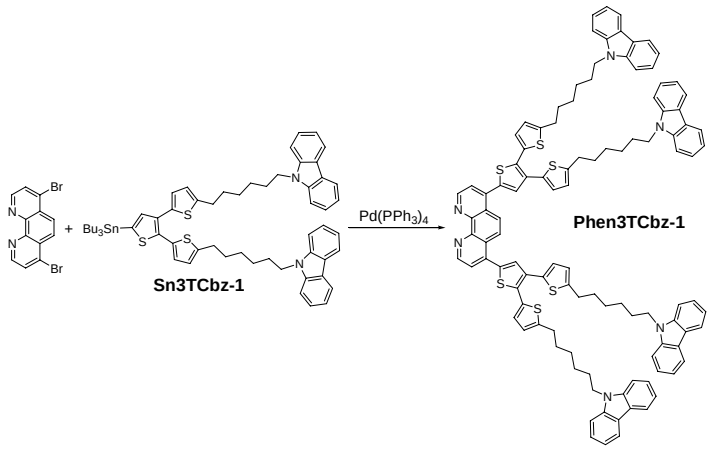
Synthesis of Sn3TCbz-1. About 0.5 mL of n-butyllithium (2.5 M in hexane, 1.3 mmol) was added dropwise to a solution of **3TCbz-1** (0.86 g, 1.2 mmol) in 20 mL of THF at -78 °C under N_2. After 30

minutes, 0.82 g of tributyltin chloride (0.42 g, 1.3 mmol) in 5.0 mL of anhydrous THF was added to the solution. The reaction mixture was then warmed to room temperature, stirred for another 3 hours, and poured into saturated $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent evaporated. The residue was used for the next reaction without further purification. ^1H NMR ($CDCl_3$, 300 MHz, δ): 8.09 (d, *J* = 7.8 Hz4H,), 7.43 (m, 8H), 7.22 (m, 4H), 7.09 (s, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 6.84 (d, *J* = 2.7 Hz, 1H), 6.59 (m, 2H), 4.27 (t, *J* = 7.2 Hz, 4H), 2.70 (m, 4H), 1.85 (m, 4H), 1.57 (m, 10H), 1.37 (m, 14H), 1.11 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 9H).



Synthesis of Phen3TCbz-1. To the suspension of NaH (60% dispersion in mineral oil, 40 mg, 1.0 mmol) in dry THF (10 mL), carbazole (0.15 g, 0.90 mmol) was added in portions, and after stirring for 30 min at room temperature, **Phen3TBr** (133 mg, 0.10 mmol) in dry THF (1 mL) was added dropwise to the reaction mixture and refluxed overnight. After cooling to room temperature, THF was removed by rotary evaporation and water (~ 50 mL) was added. The mixture was neutralized with dilute hydrochloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by column chromatography eluting with 20:1 CH_2Cl_2/ CH_3OH to give the product as yellow oil (128 mg, 77%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 9.22 (d, *J* =4.8 Hz, 2H), 8.44 (s, 2H), 8.09 (m, 8H), 7.72 (d, *J* =4.8 Hz, 2H), 7.49~7.35 (m, 18H), 7.25~7.18 (m, 8H), 7.05 (d, *J* =3.9 Hz, 2H), 6.97 (d, *J* =3.9

Hz, 2H), 6.65 (m, 4H), 4.27 (t, *J* =7.2 Hz, 4H), 4.25 (t, *J* =7.2 Hz, 4H), 2.72 (t, *J* =7.5 Hz, 8H), 1.84 (m, 8H), 1.61 (m, 8H), 1.36 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.76, 147.65, 146.90, 146.10, 140.27, 140.09, 136.42, 134.20, 133.94, 132.50, 131.52, 131.44, 127.89, 126.57, 125.92, 125.49, 124.45, 124.24, 124.09, 123.50, 122.69, 120.26, 118.65, 108.52, 42.81, 31.25, 31.18, 29.93, 29.87, 28.76, 28.66, 26.87.



Synthesis of Phen3TCbz-1 (Route a). To a round-bottomed flask was charged 0.31 g of **Sn3TCbz-1** (0.3 mmol), 33.8 mg of 4,7-dibromo-1,10-phenanthroline (0.1 mmol), 75 mg of $Pd(PPh_3)_4$, and 10 mL of DMF. After three freeze-thaw cycles, the mixture was heated to 110 °C for 20 hours under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with CH_2Cl_2, and washed thoroughly with NaF solution to remove tributyltin chloride. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column using CH_2Cl_2/CH_3OH (20:1) as eluent and 109 mg of pure product was obtained (yield: 65%).

Reference:

(1) Michalitsch, R.; ElKassmi, A.; Yassar, A.; Garnier, F. *J. Heterocycl. Chem.* **2001**, *38,* 649-653.

(2) Graf, G. I.; Hastreiter, D.; da Silva, L. E.; Rebelo, R. A.; Montalban, A. G.; McKillop, A. *Tetrahedron*, **2002**, *58,* 9095-9100.

(3) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett*. **2002**, *4*, 2067-2070.

(4) (a) Taranekar, P.; Park, J-Y.; Patton, D.; Fulghum, T.; Ramon, G. J.; Advincula, R. C. *Adv. Mater*. **2006**, *18*, 2461-2465. (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710-1715. (c) Taranekar, P.; Fulghum, T.; Patton, D.; Ponnapati, R.; Clyde, G.; Advincula, R. C. *J. Am. Chem. Soc.* **2007**, *129*, 12537-12548.

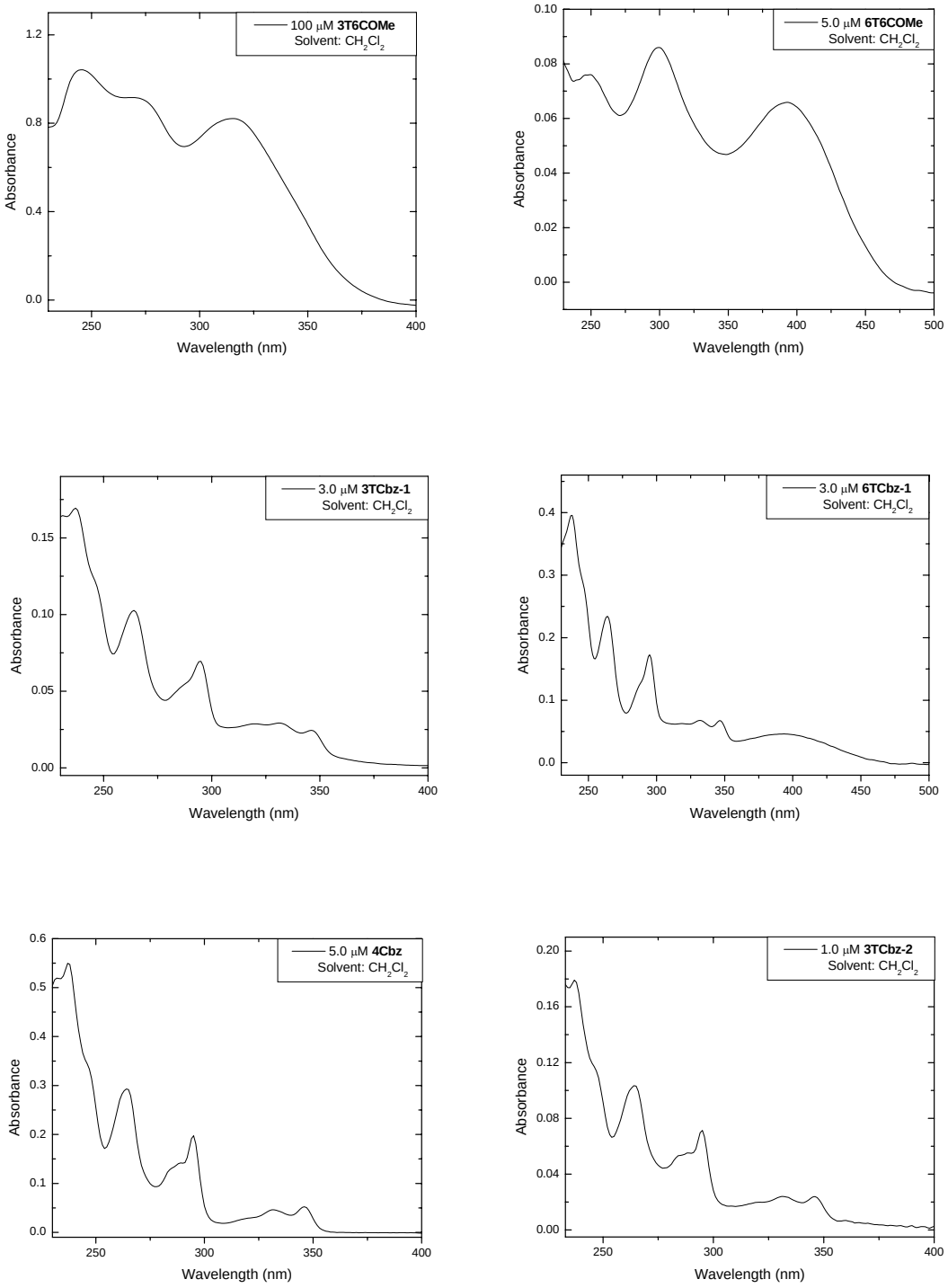


Figure S1. UV-vis spectra of dendritic molecules.

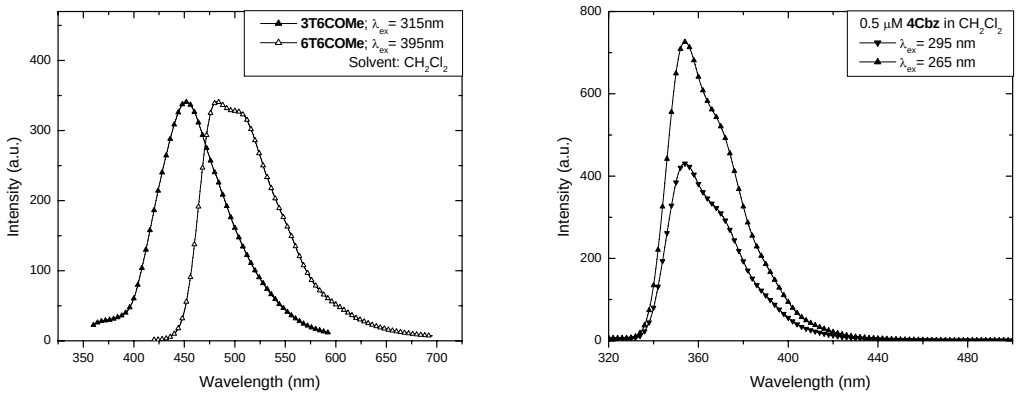
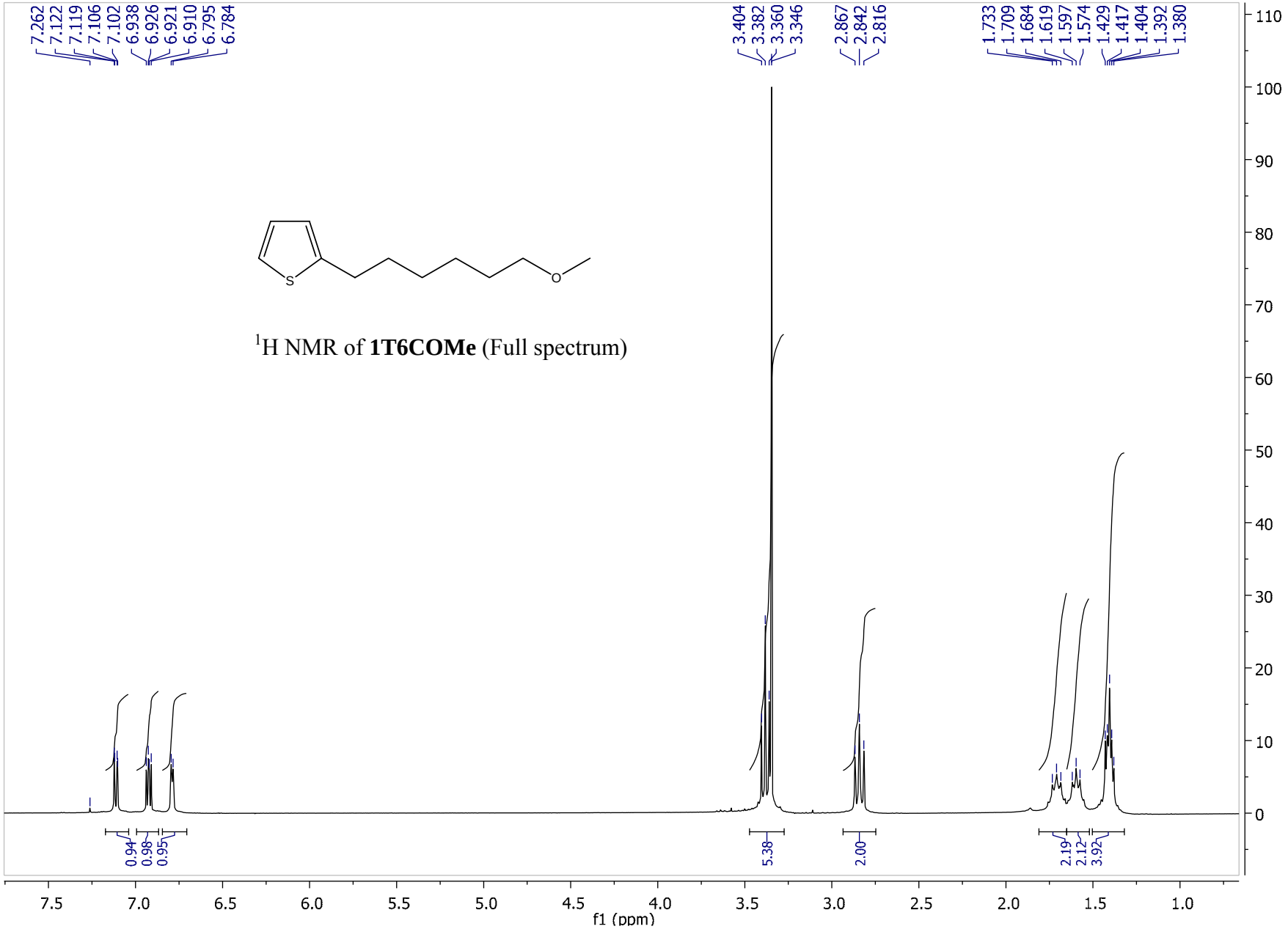


Figure S2. Emission spectra of dendritic molecules **3T6COMe**, **6T6COMe**, and **4Cbz**.

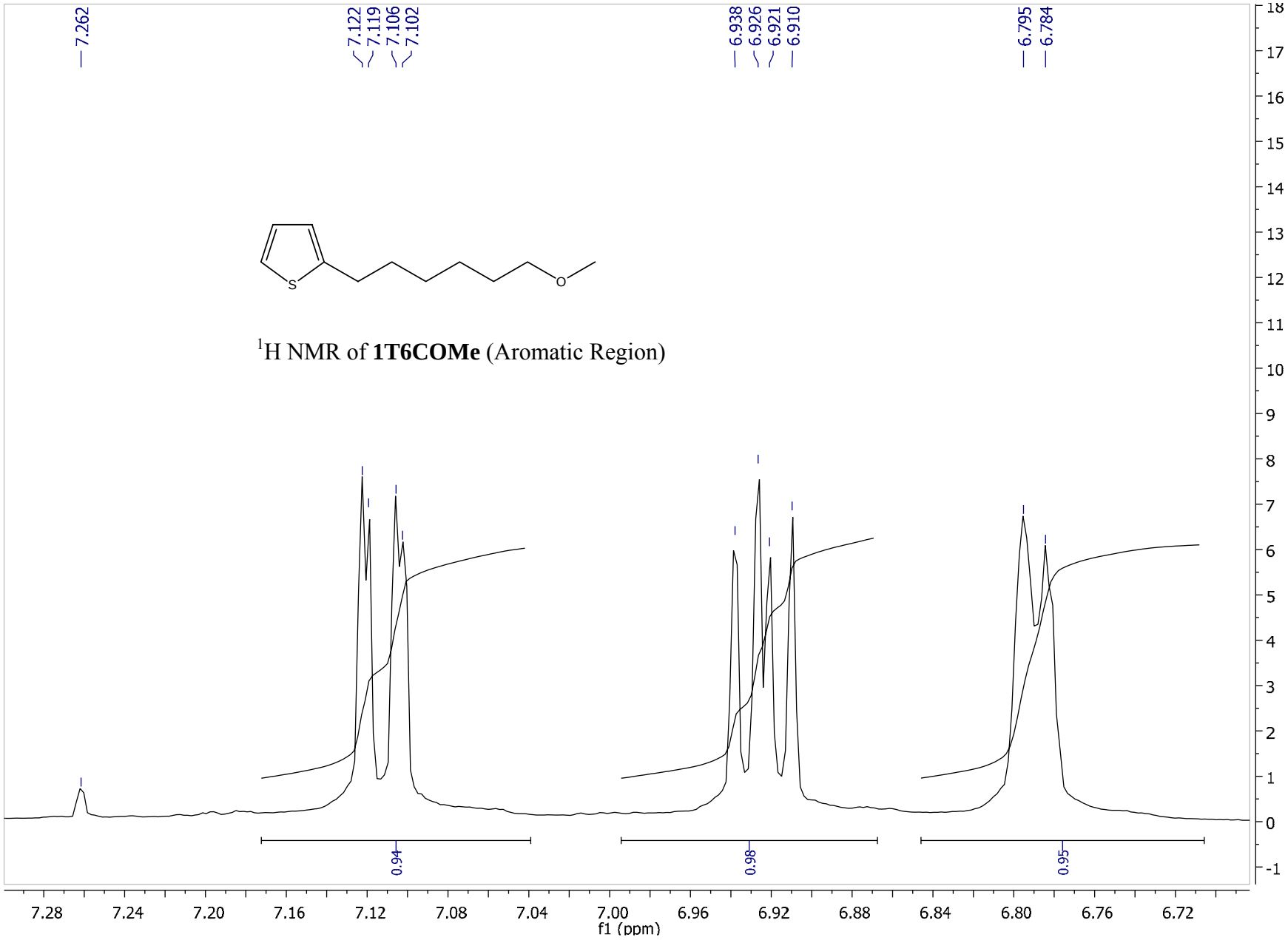
Table S1. Extinction coefficients, absorption, and fluorescence maxima of thiophene dendrons and dendrimers[a]

compd	λ^{abs}_{max}(nm) (ε)	λ^{fl}_{max}(nm)
3T6COMe	245(10418), 270sh(9131), 315(8213)	452[b]
6T6COMe	250(15204), 299(17207), 393(13181)	483, 505sh[c]
3TCbz-1	237(56453), 264(34209), 295(23162), 320(9573), 331(9751), 346(8167)	353, 370sh, 449[d]
6TCbz-1	238(131902), 264(78078), 295(57571), 332(22529), 346(22421), 393(15335)	353, 483, 505sh[d]
4Cbz	237(109958), 264(58601), 295(39474), 332(9218), 346(10490)	354, 370sh[d]
3TCbz-2	237(179065), 264(103393), 295(71400), 331(24037), 346(23935)	354, 370sh, 450[d]

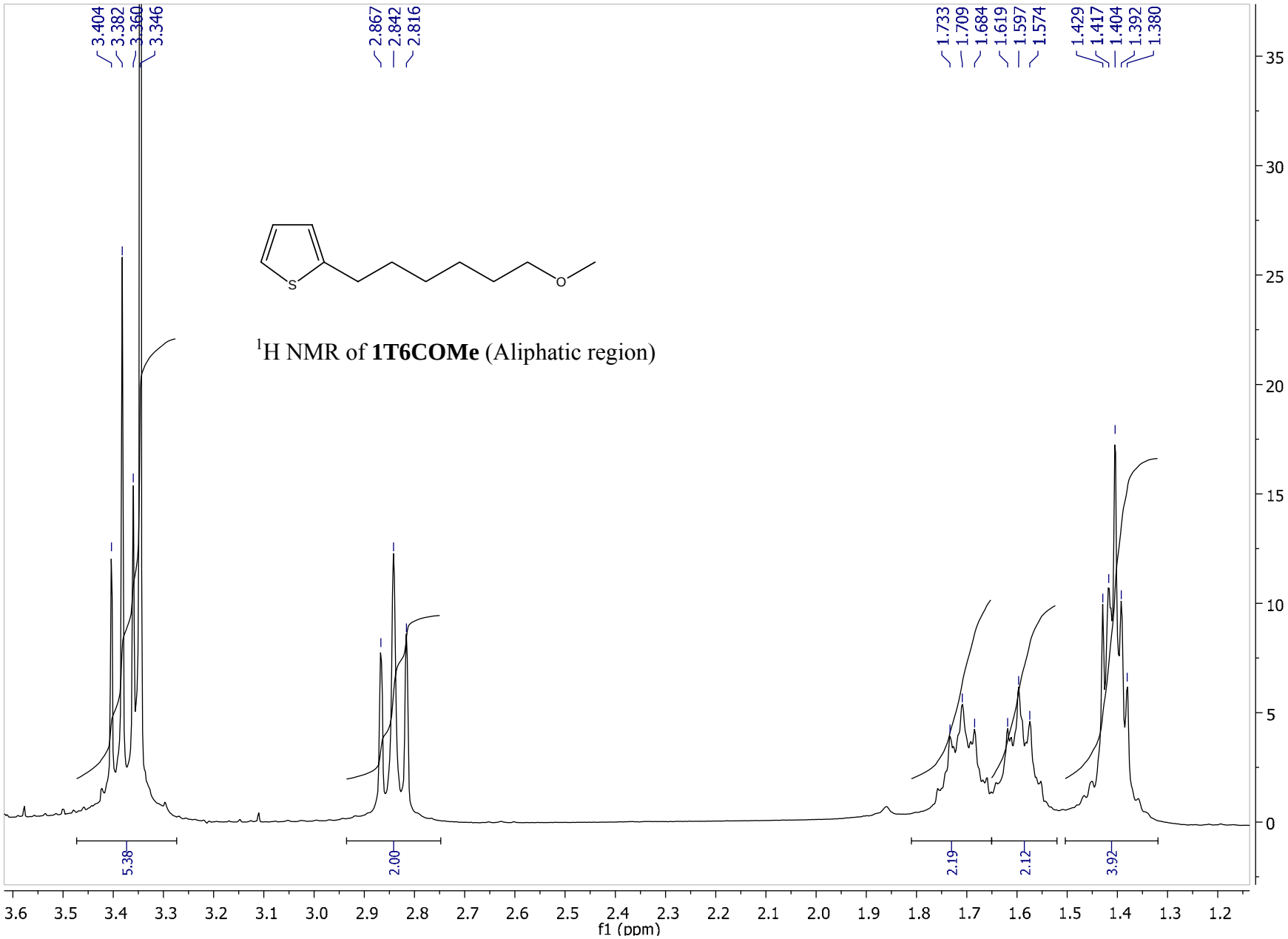
[a] For the absorption and fluorescence, the maxima (or shoulders) of the relevant bands are given. [b] λ_{ex}= 315 nm. [c] λ_{ex}= 395 nm. [d] λ_{ex}= 295 nm.



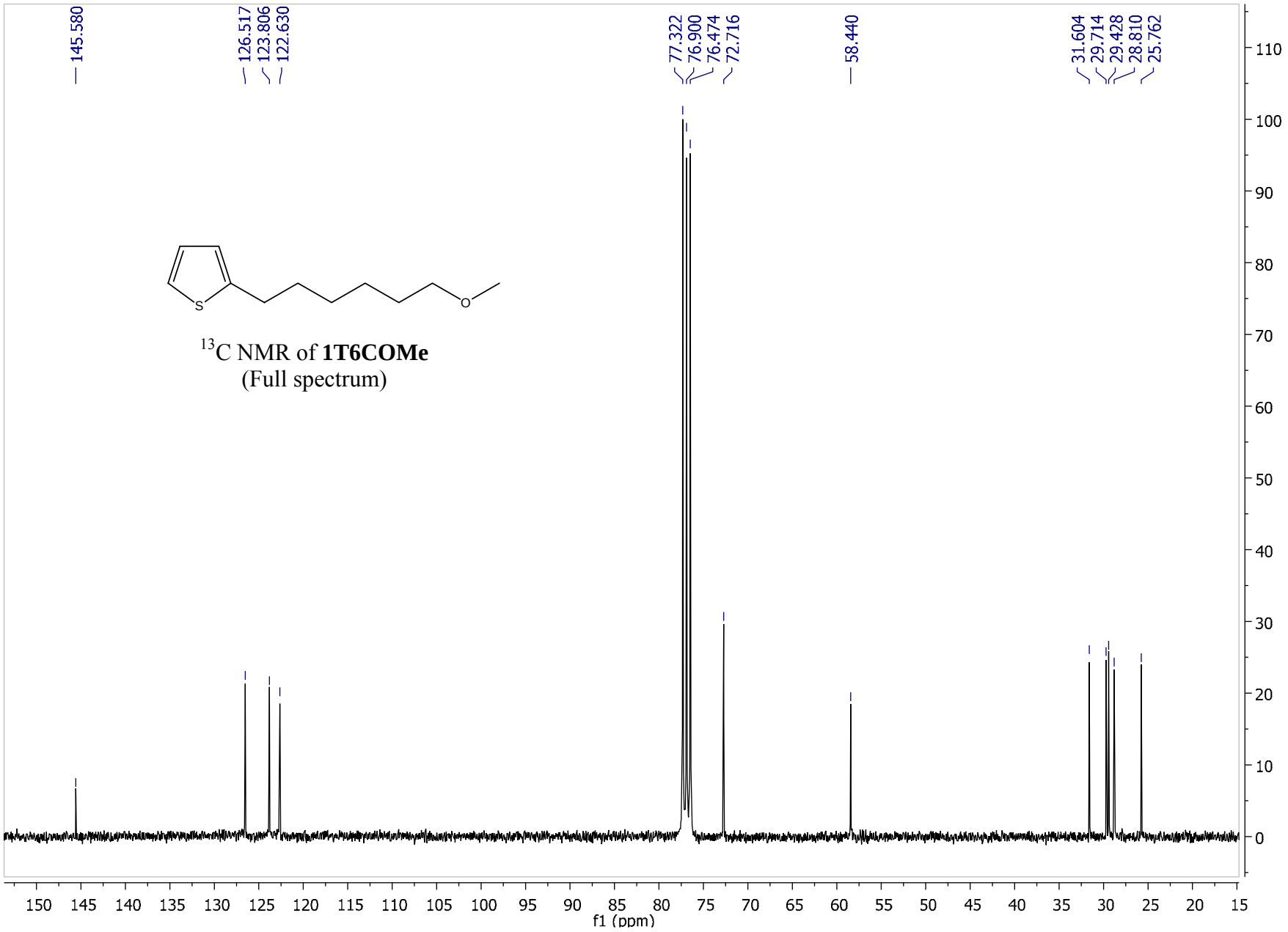
^{1}H NMR of **1T6COMe** (Full spectrum)



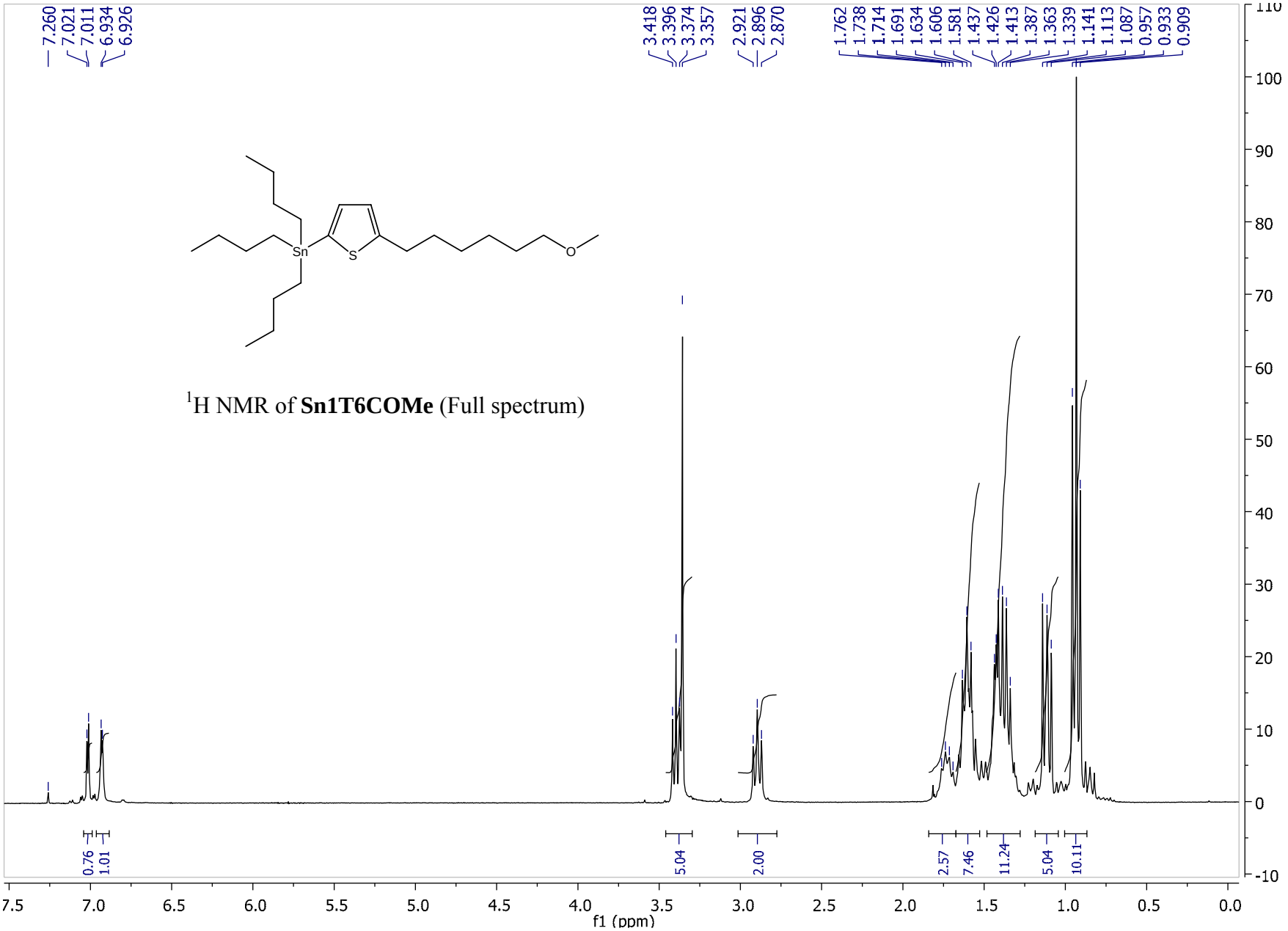
^{1}H NMR of **1T6COMe** (Aromatic Region)



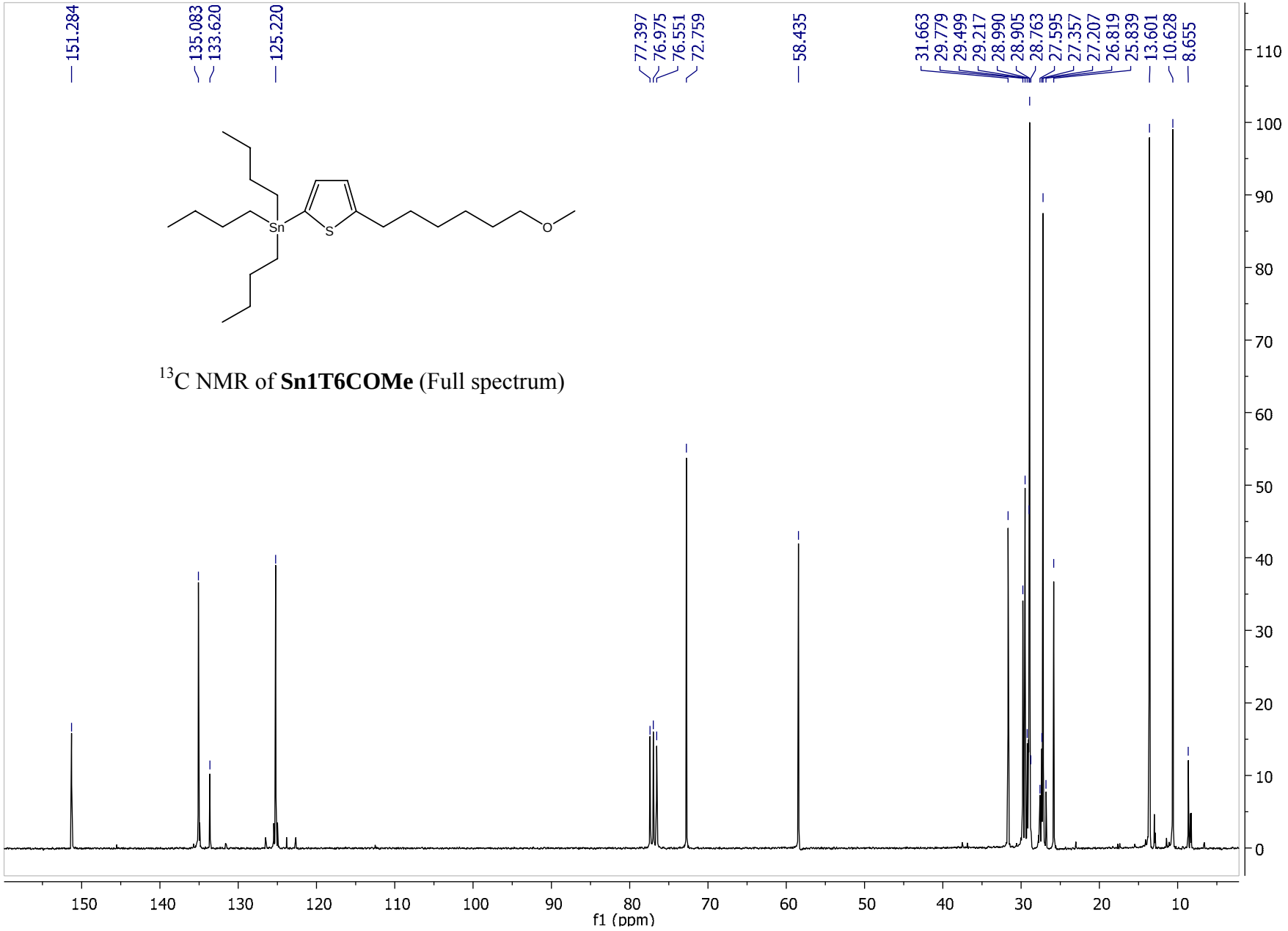
^{1}H NMR of **1T6COMe** (Aliphatic region)



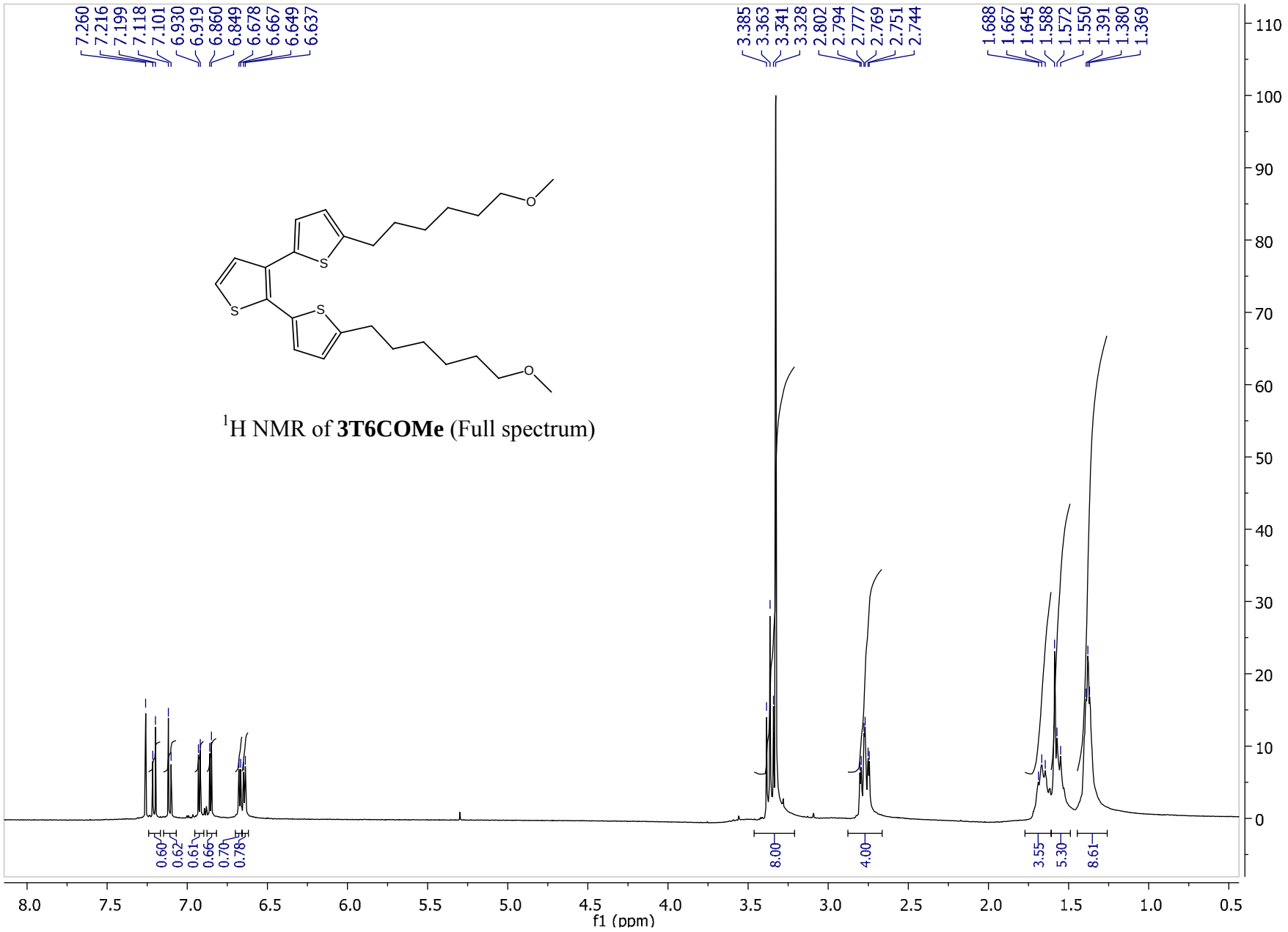
^{13}C NMR of **1T6COMe**
(Full spectrum)



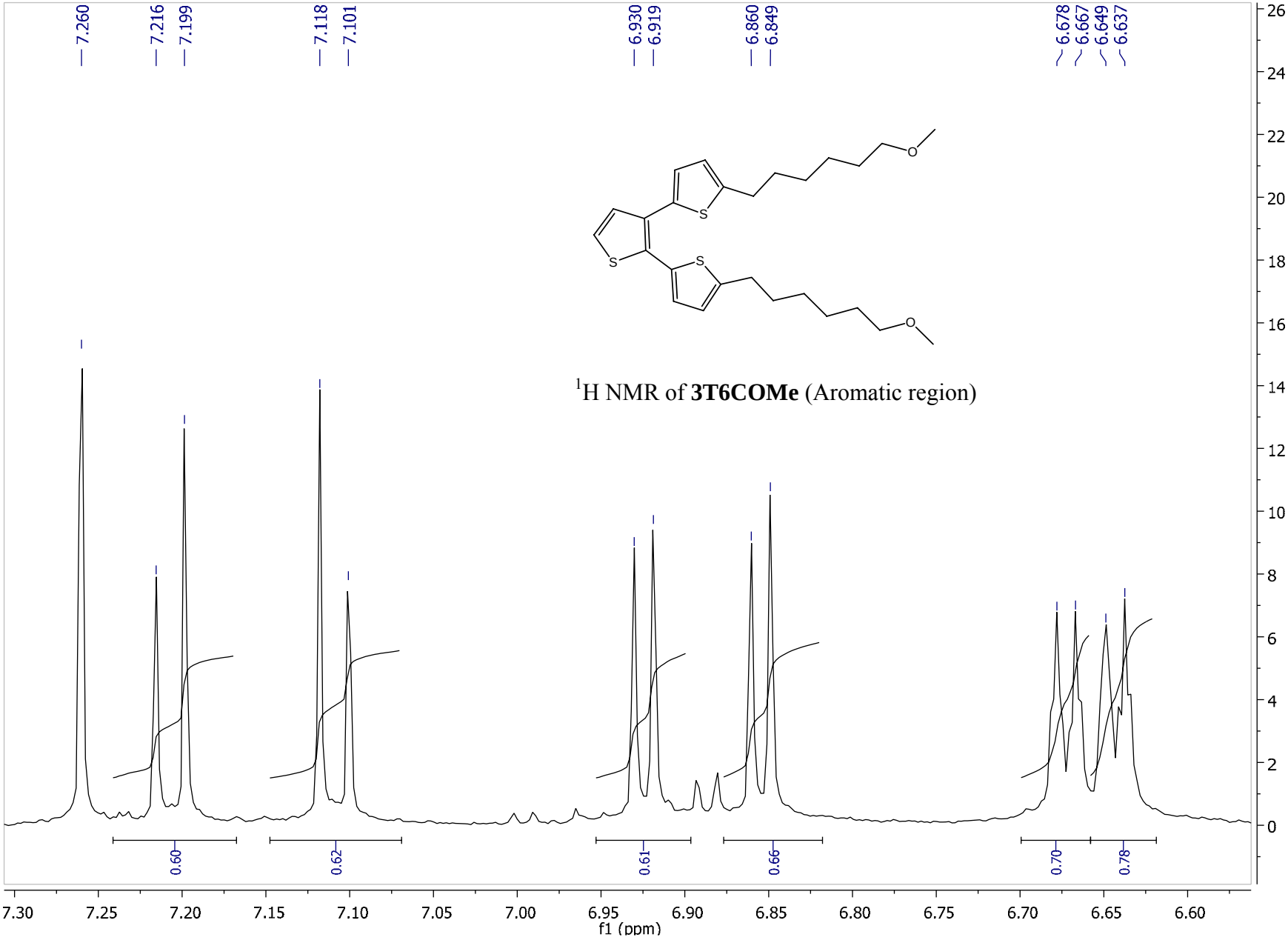
^{1}H NMR of **Sn1T6COMe** (Full spectrum)



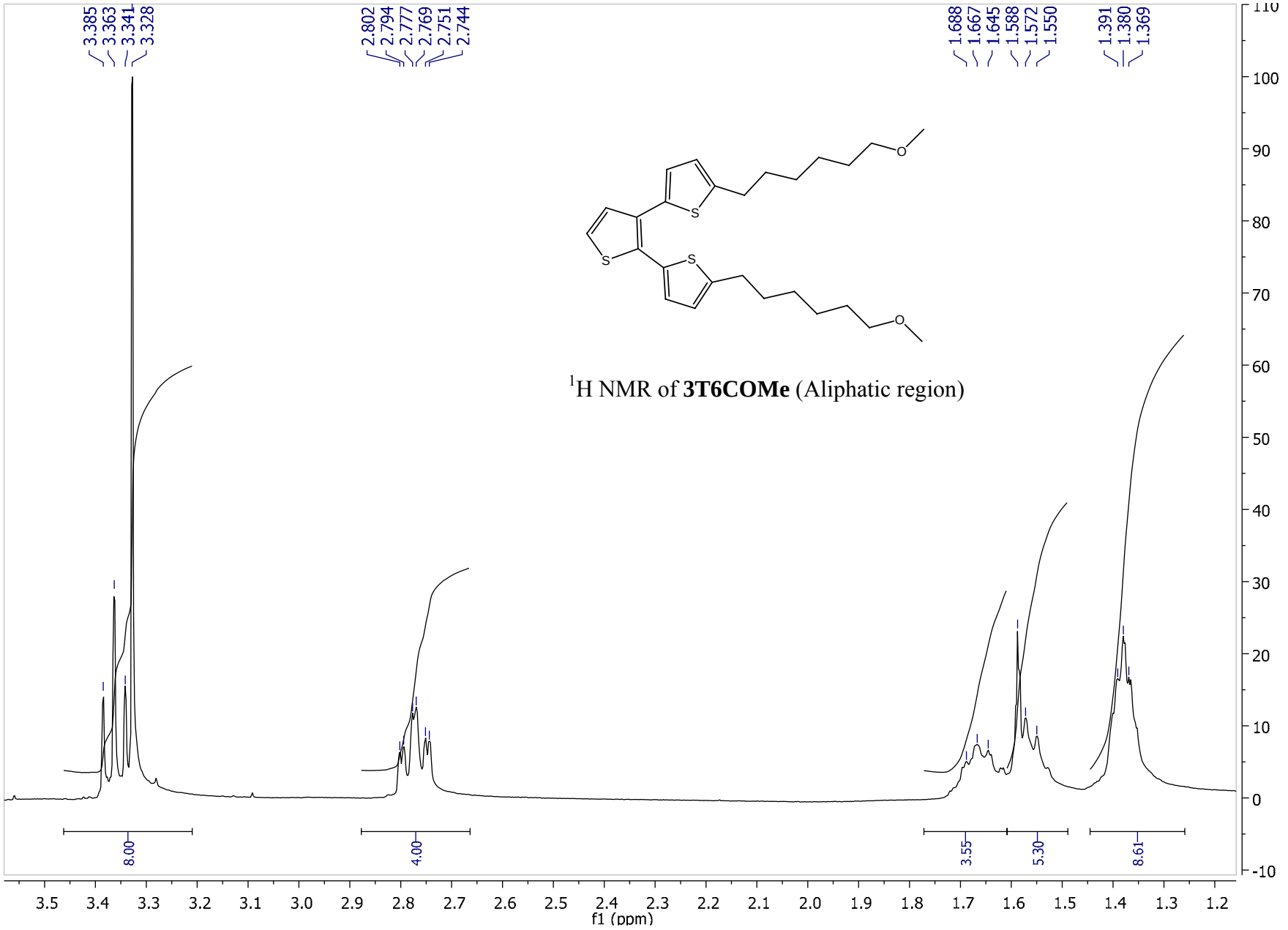
^{13}C NMR of **Sn1T6COMe** (Full spectrum)



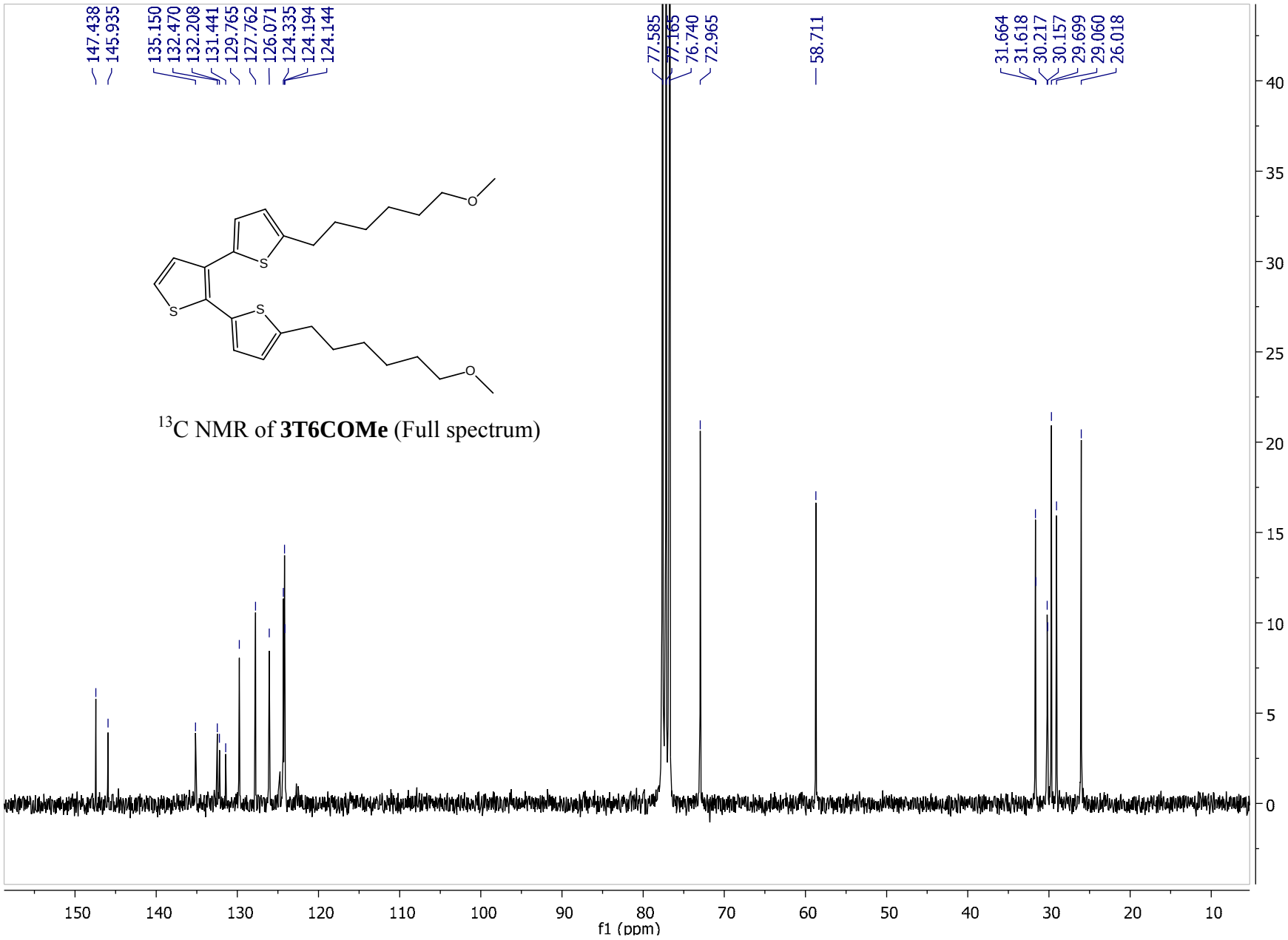
^{1}H NMR of **3T6COMe** (Full spectrum)



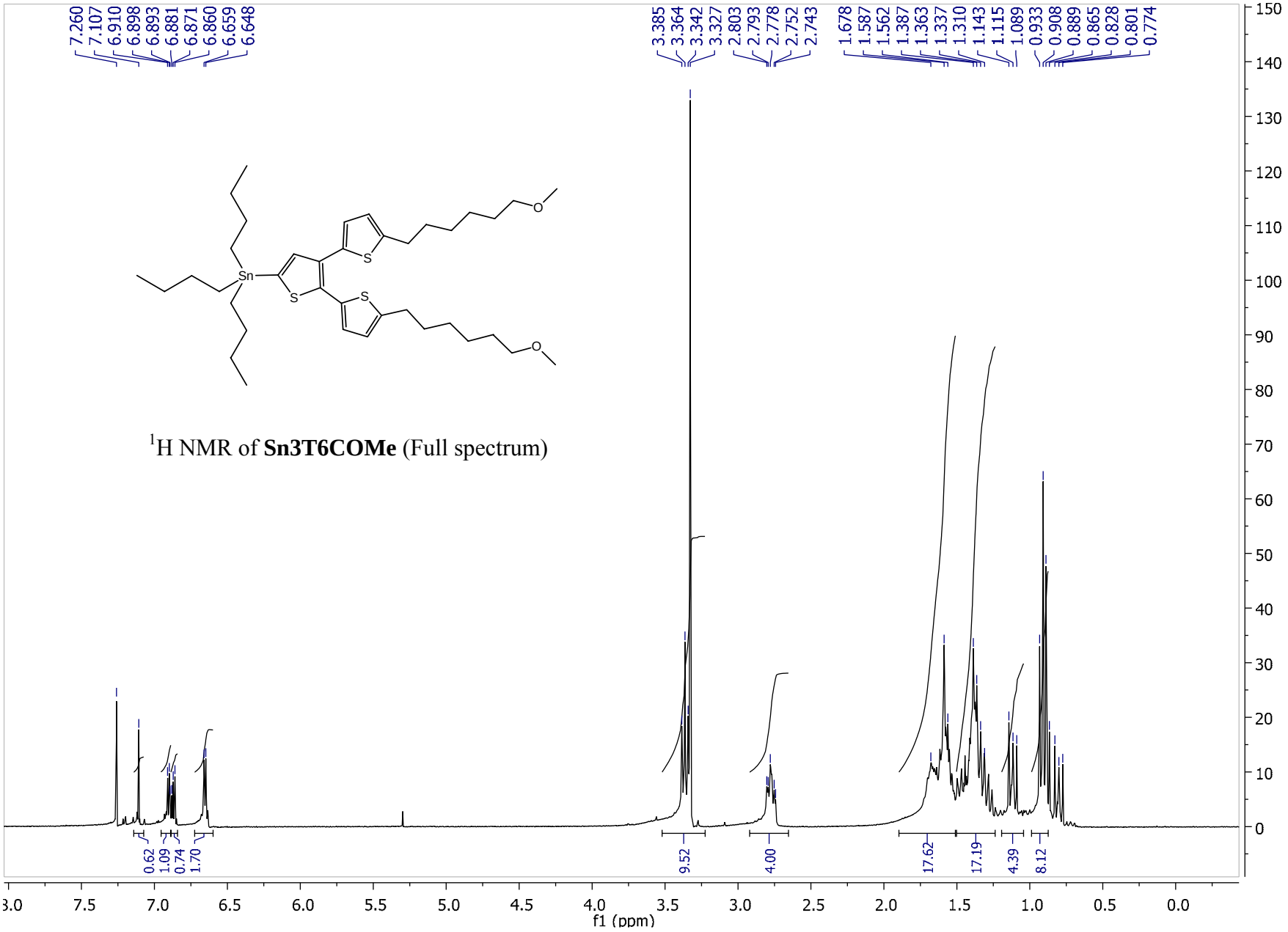
^{1}H NMR of **3T6COMe** (Aromatic region)



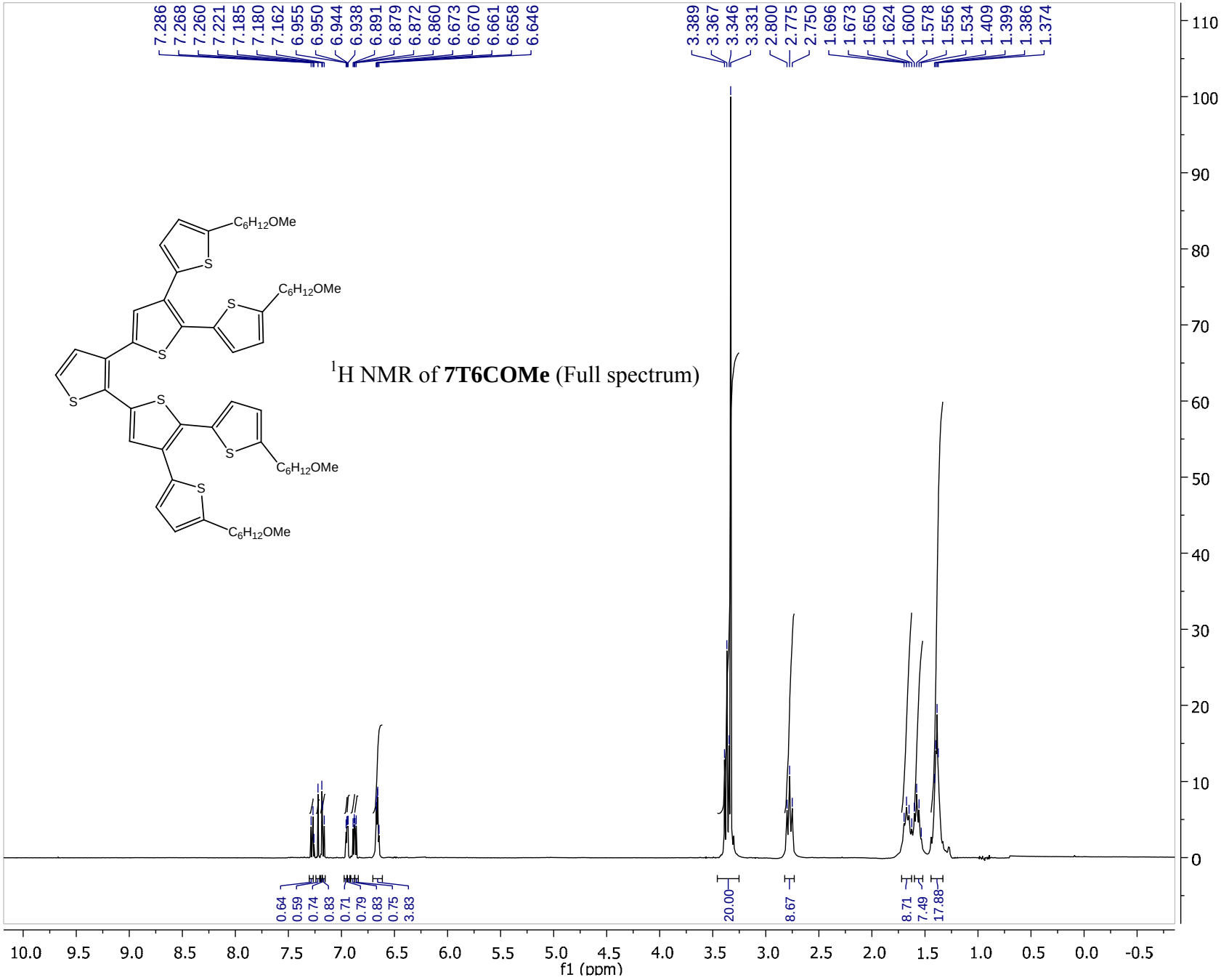
^{1}H NMR of **3T6COMe** (Aliphatic region)



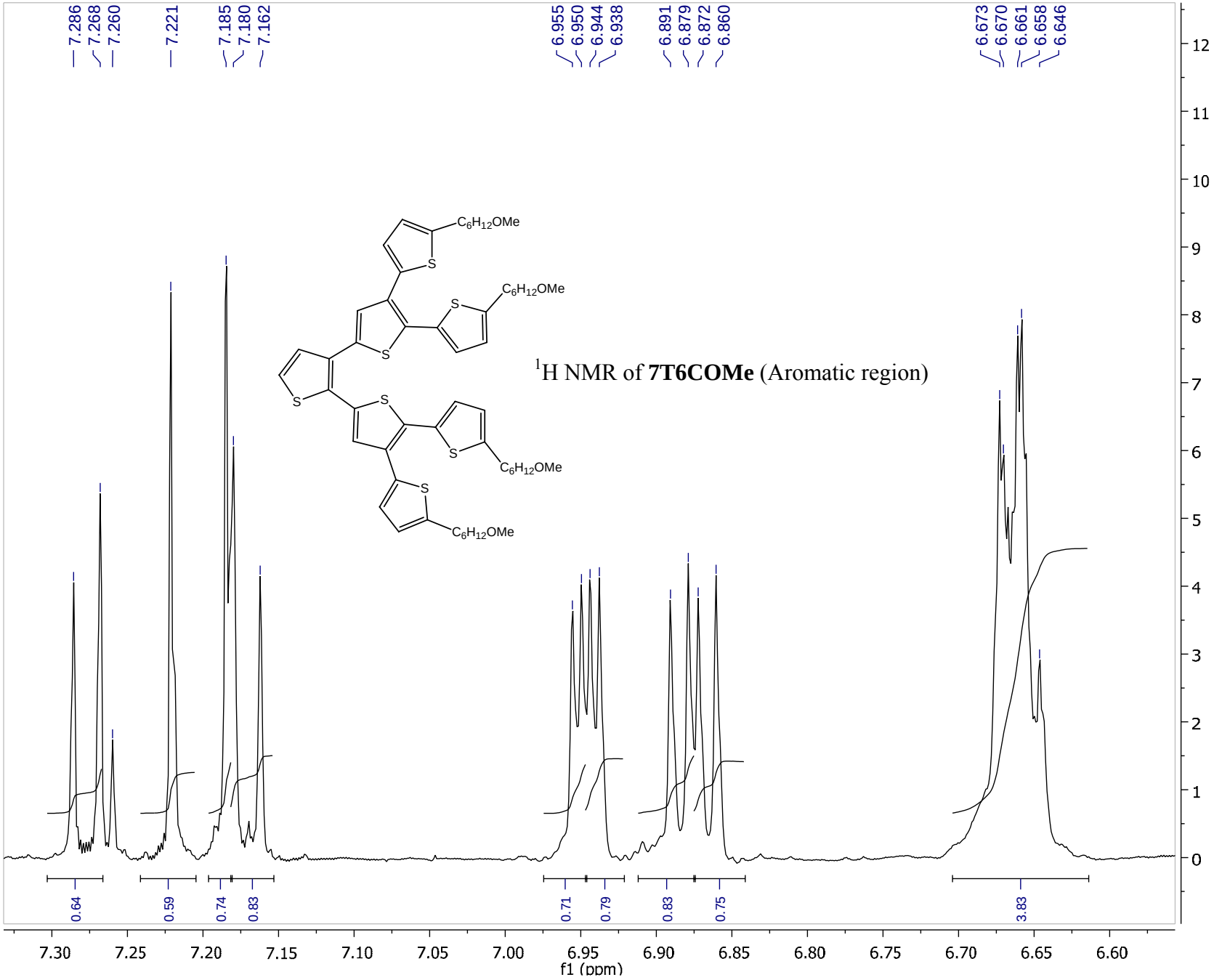
^{13}C NMR of **3T6COMe** (Full spectrum)



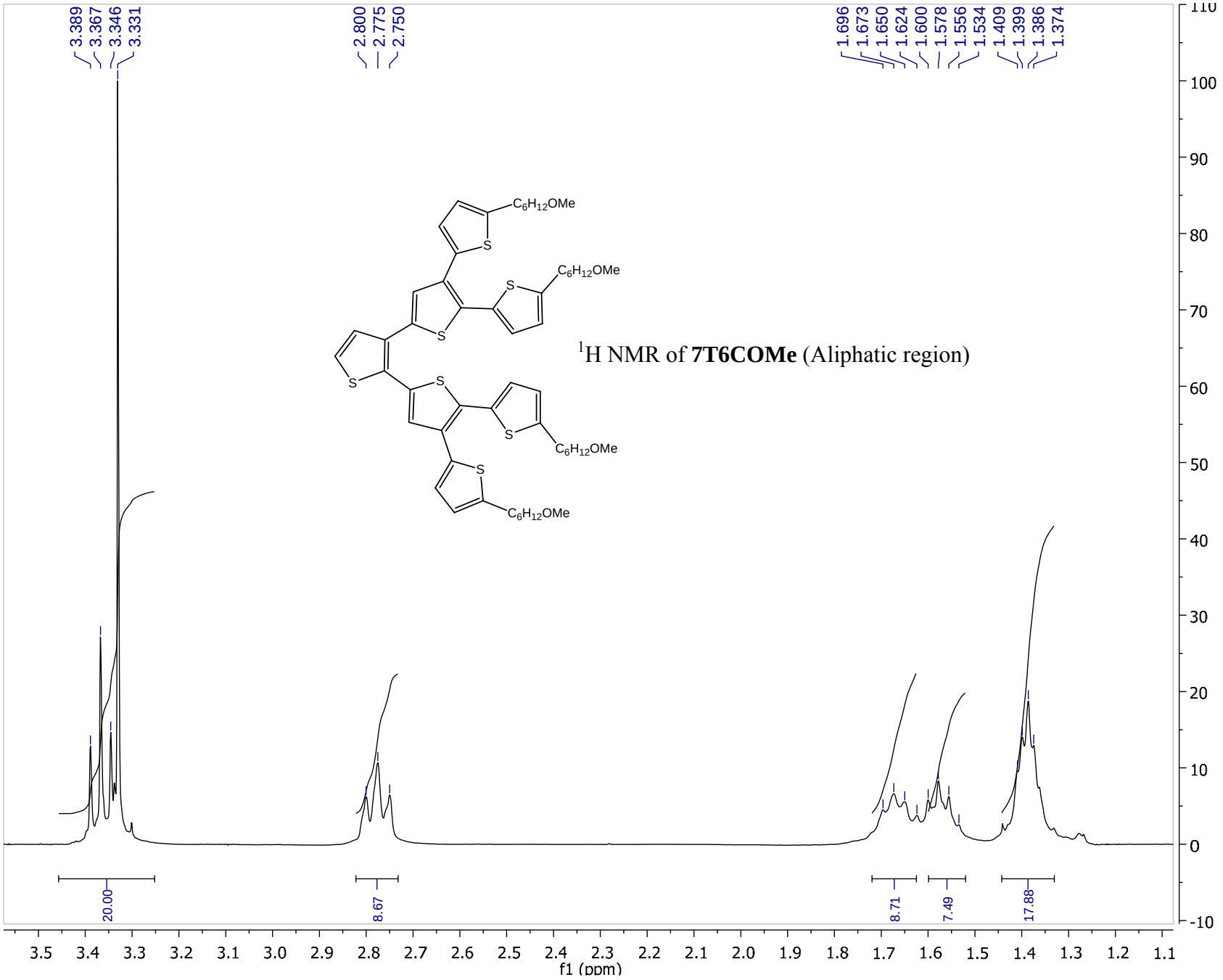
^{1}H NMR of **Sn3T6COMe** (Full spectrum)



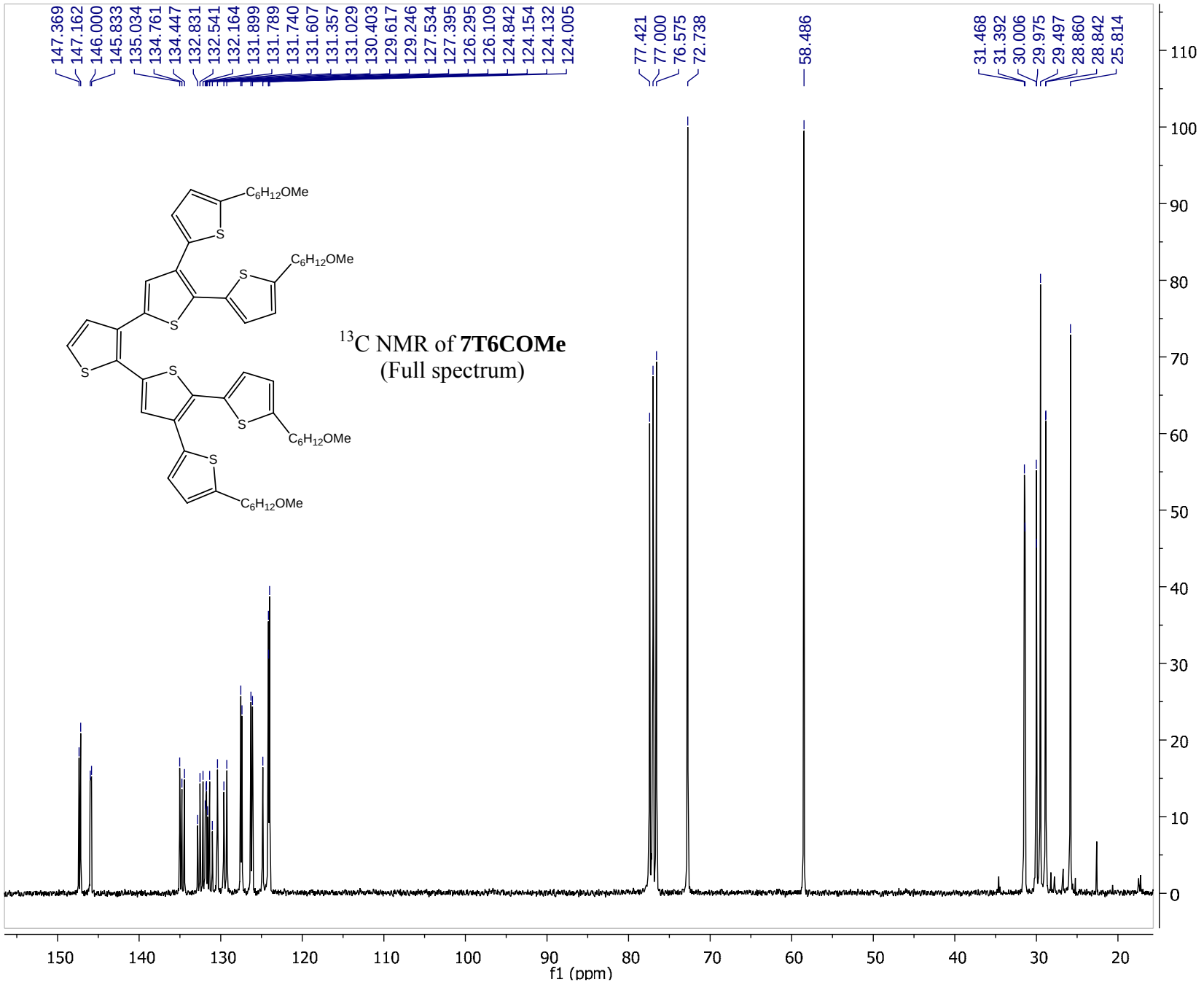
^{1}H NMR of **7T6COMe** (Full spectrum)

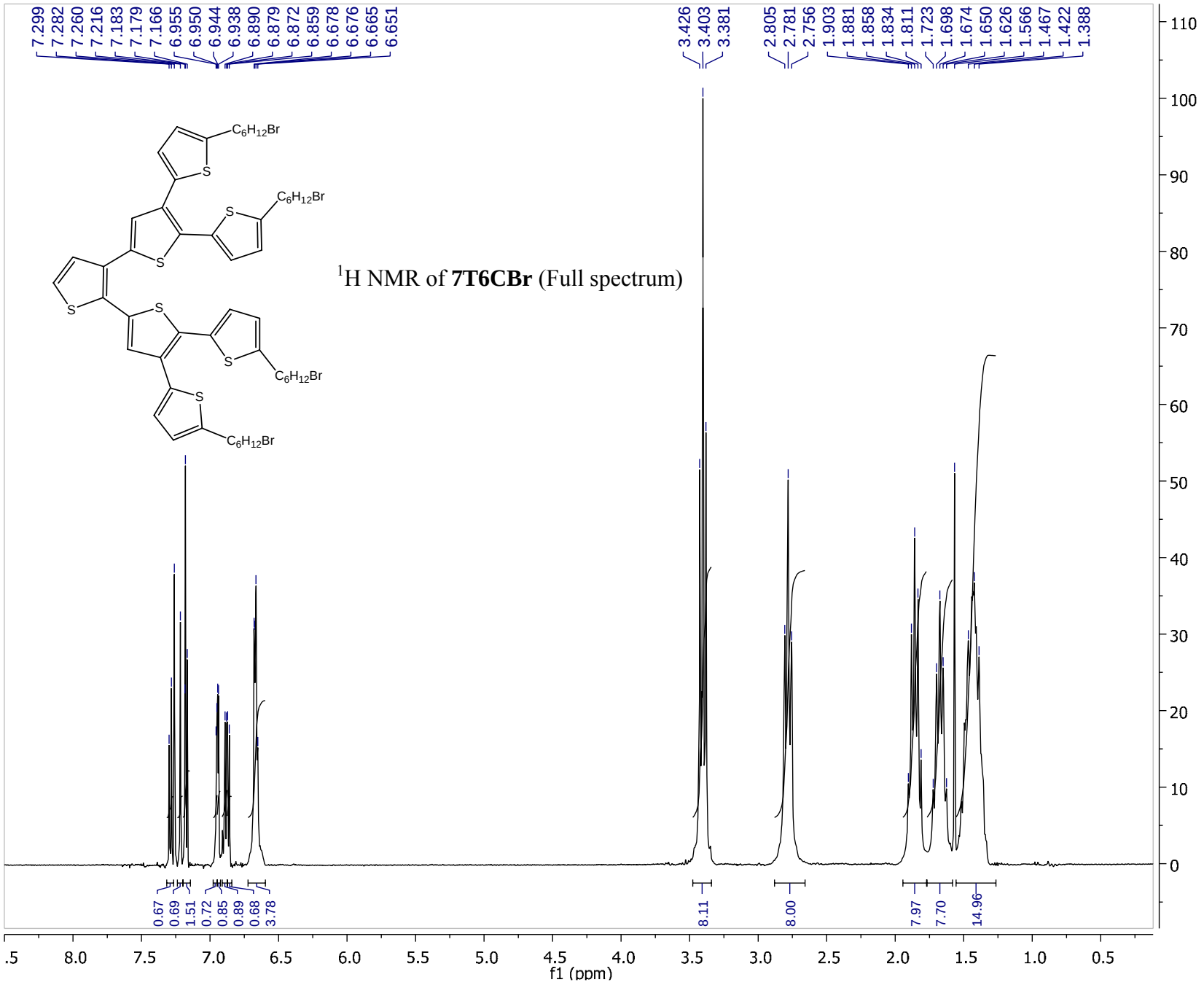


^{1}H NMR of **7T6COMe** (Aromatic region)

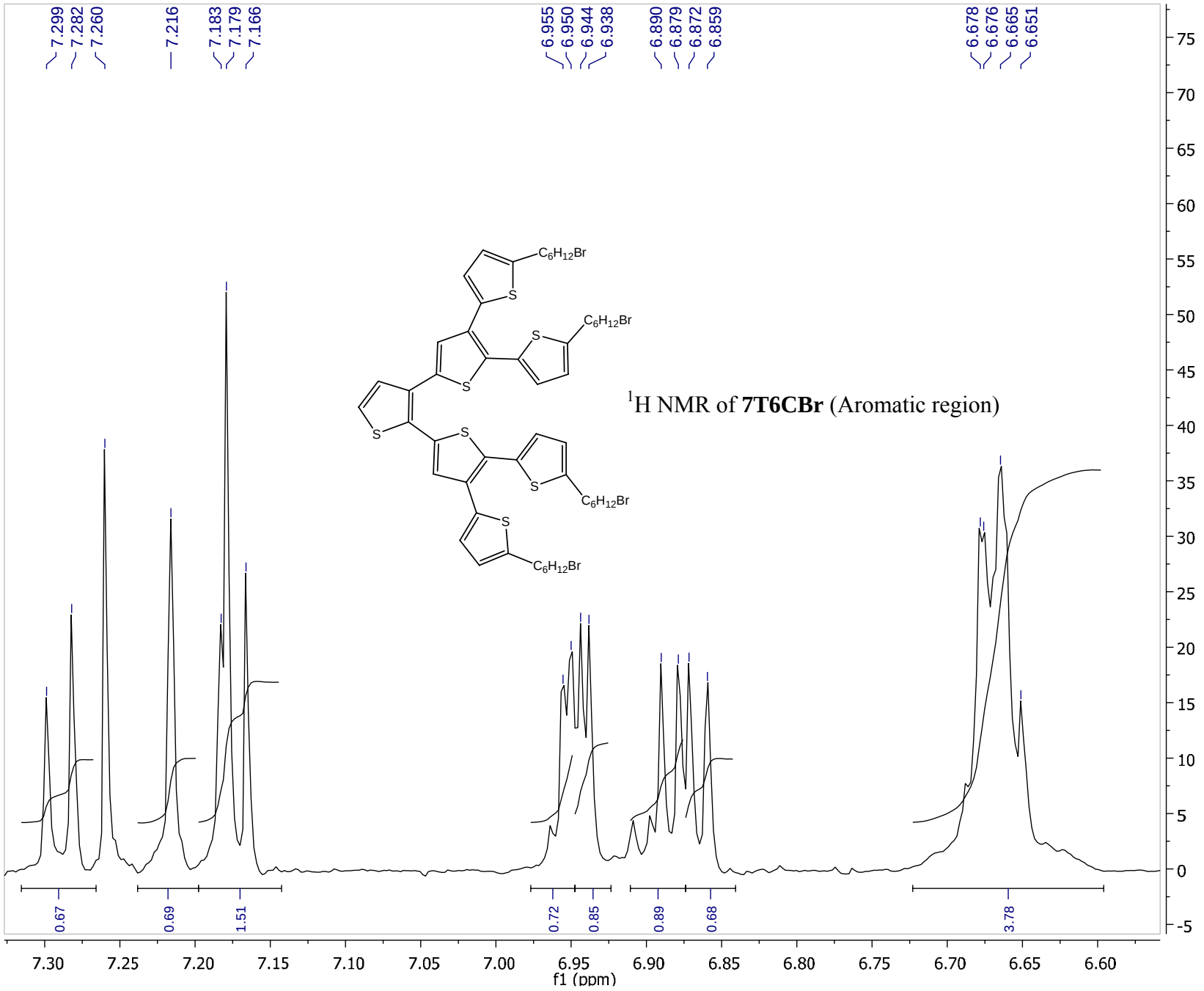


^{1}H NMR of **7T6COMe** (Aliphatic region)

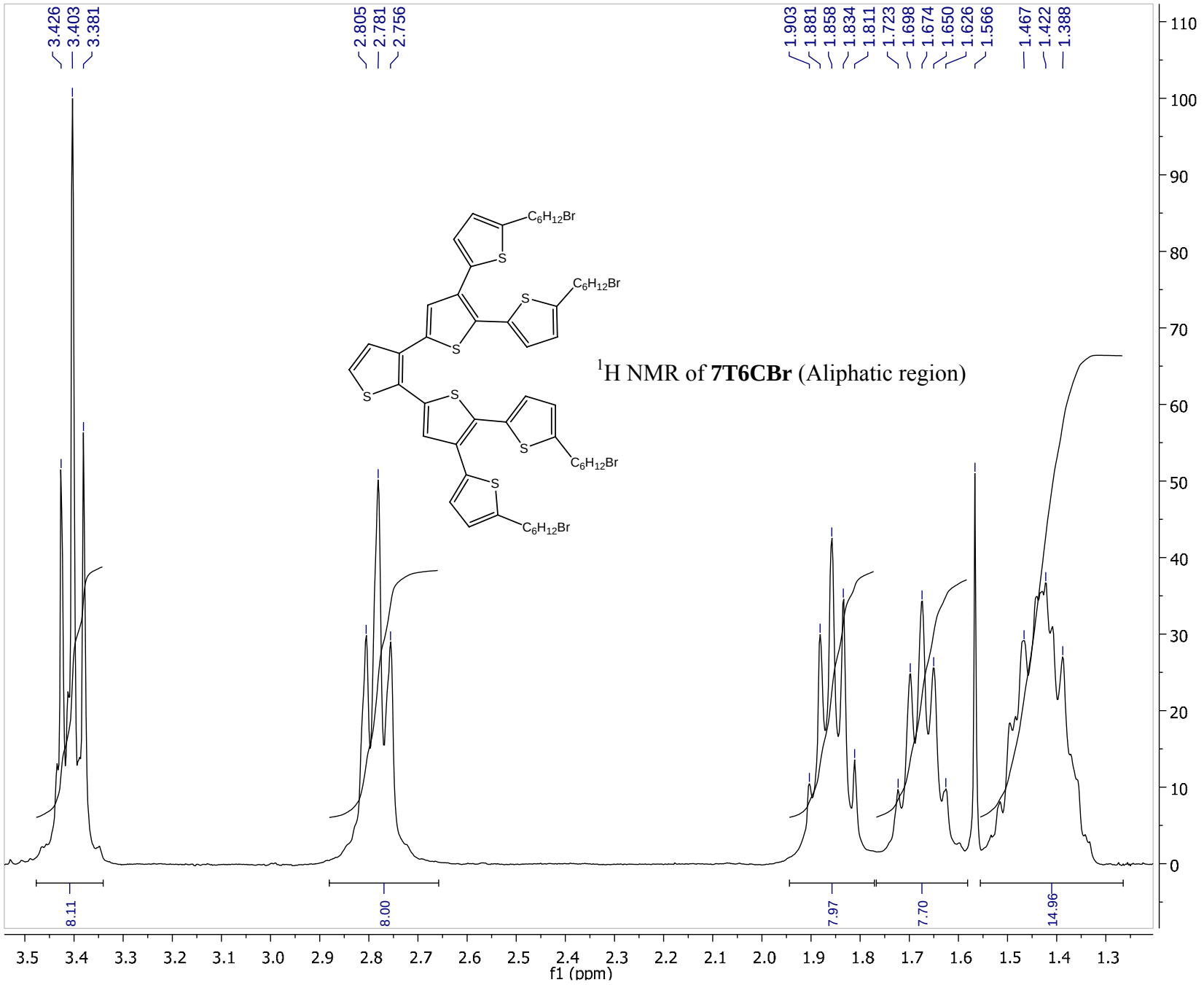




^{1}H NMR of **7T6CBr** (Full spectrum)



^{1}H NMR of **7T6CBr** (Aromatic region)



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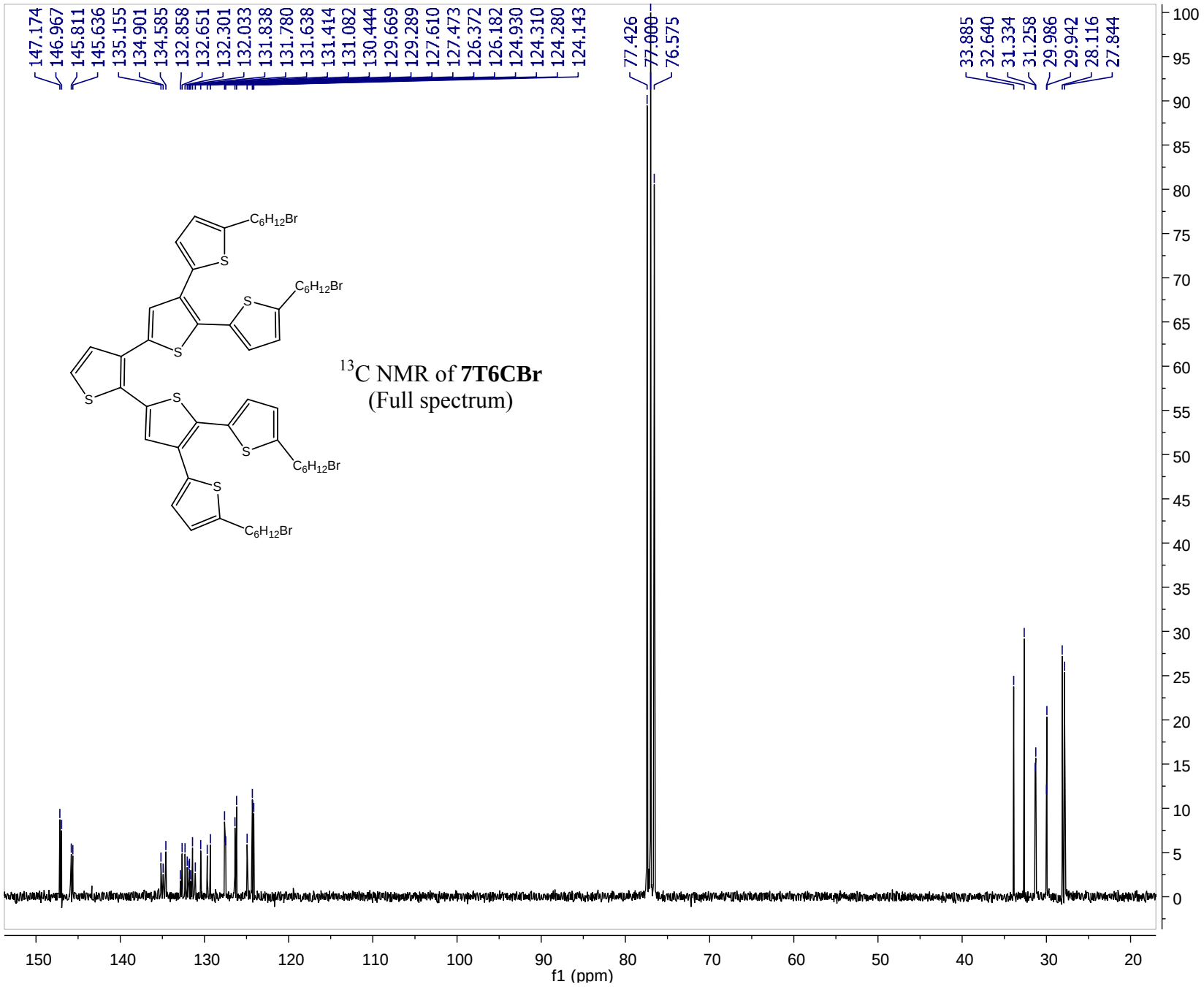
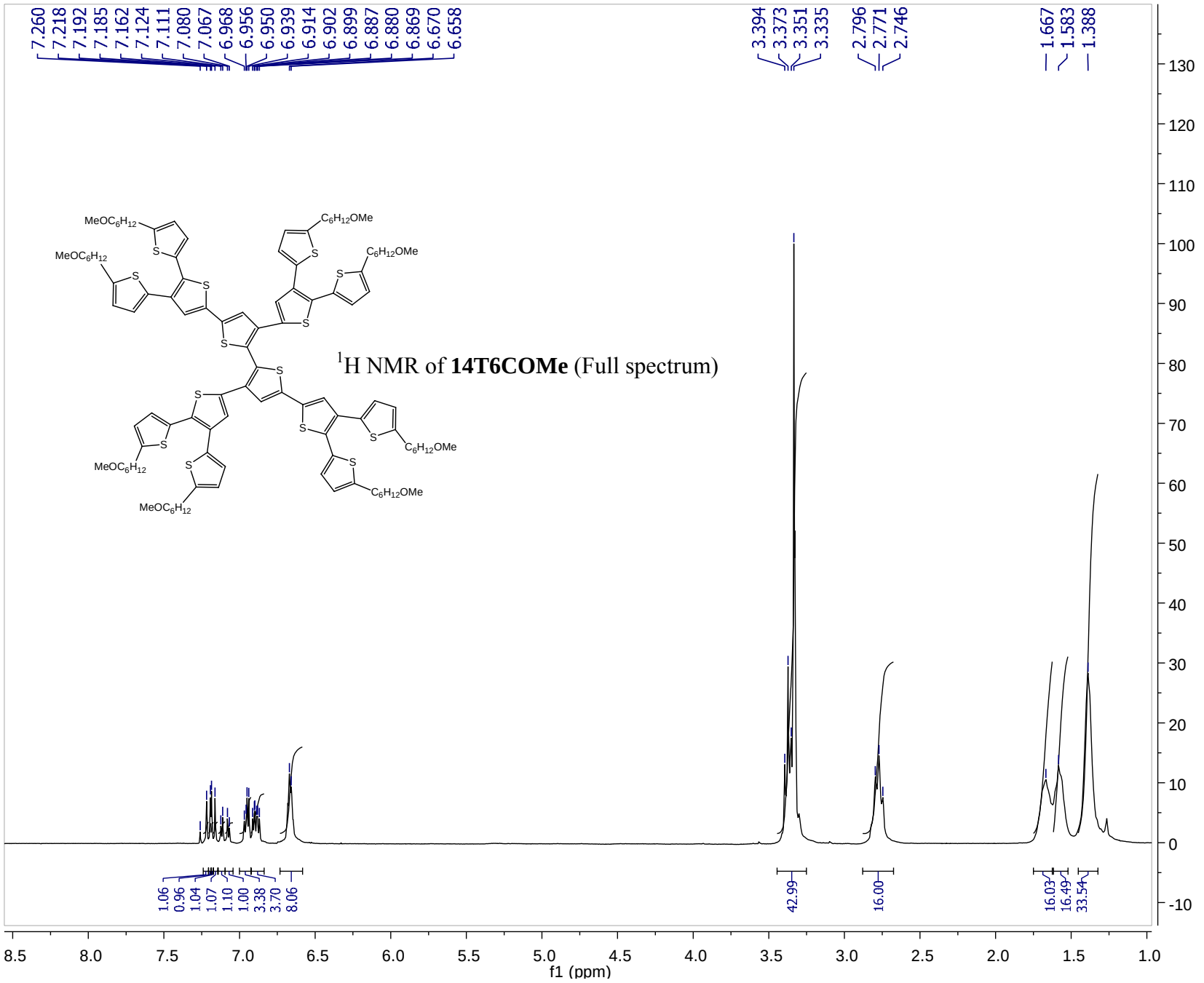
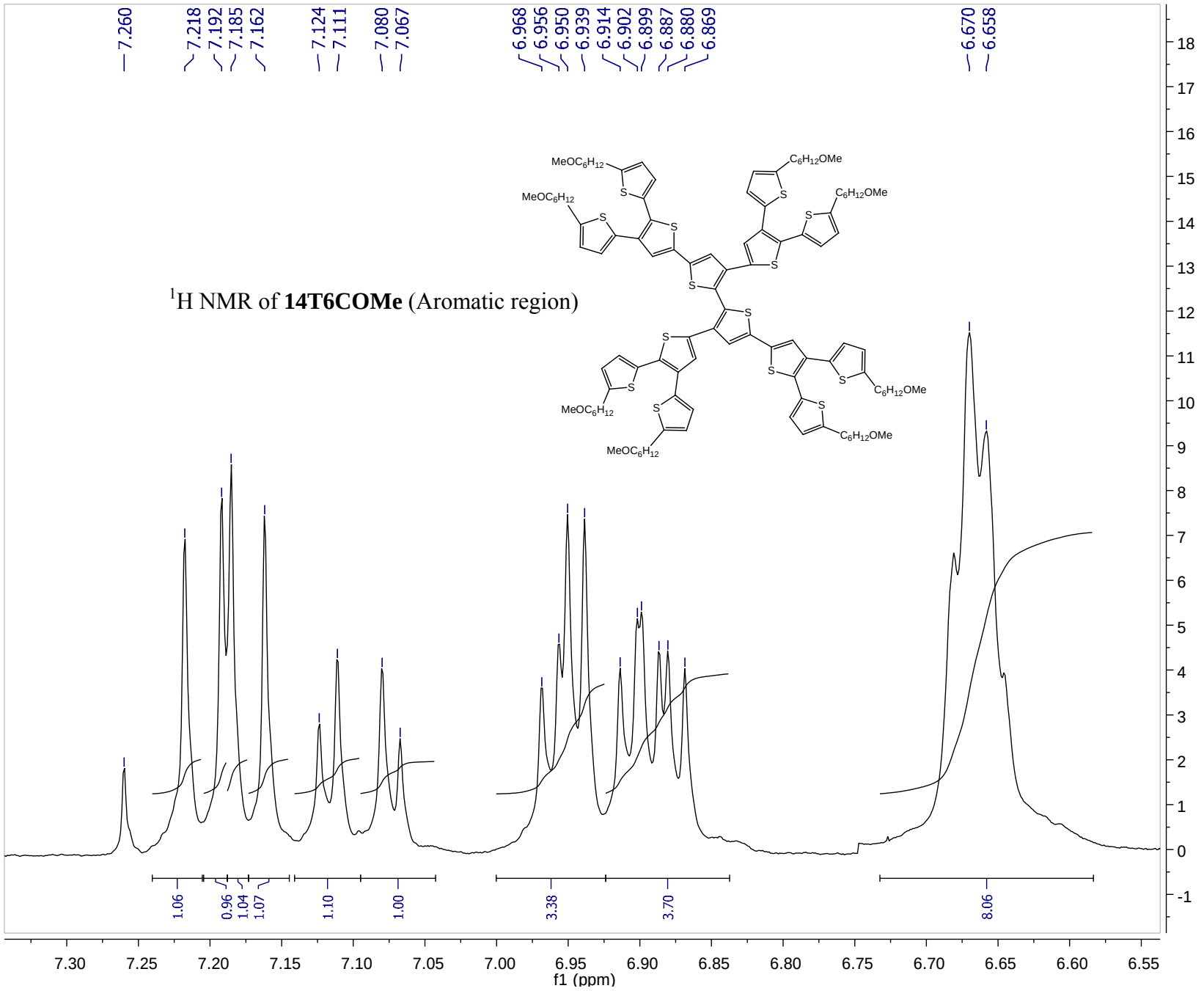
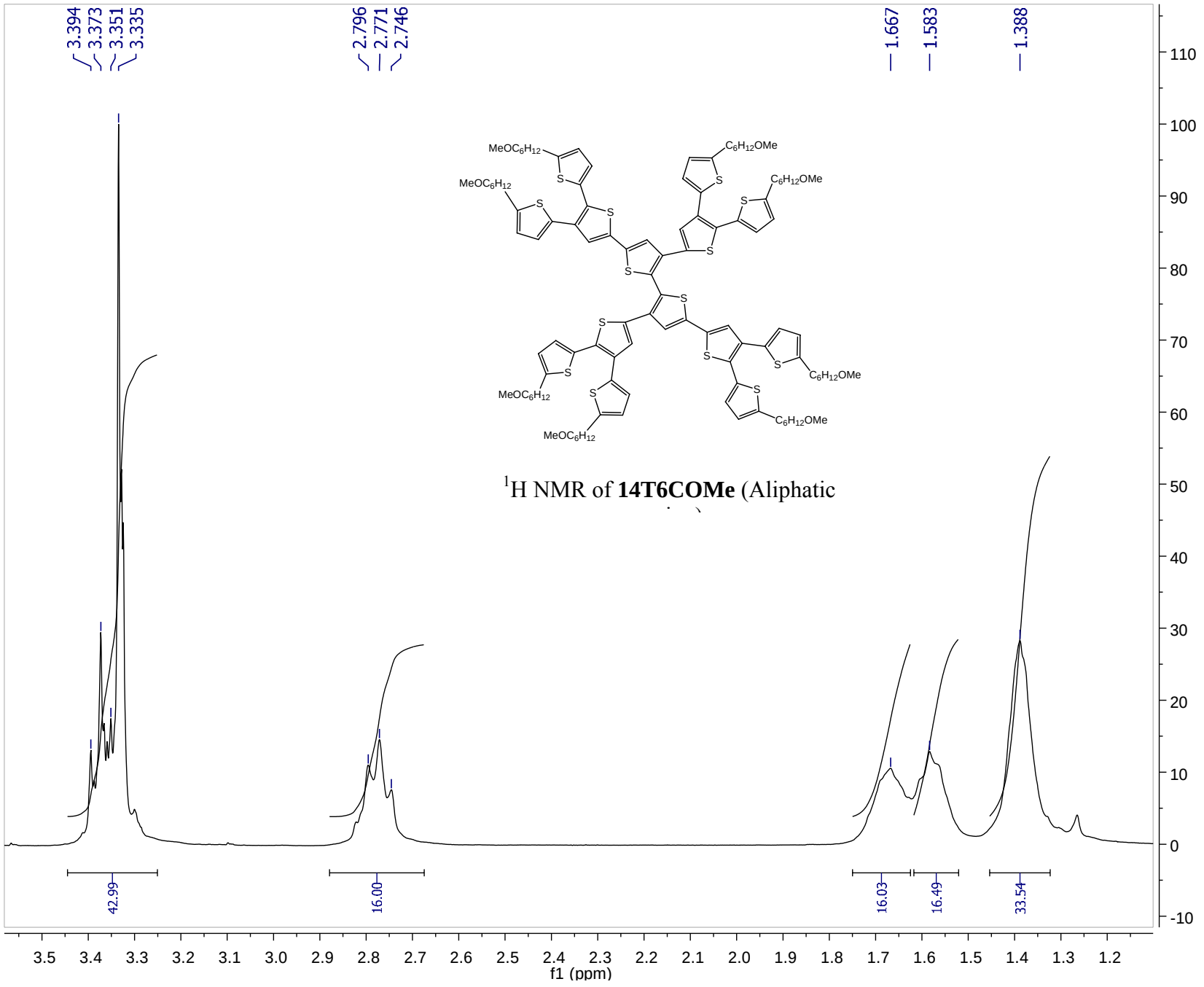


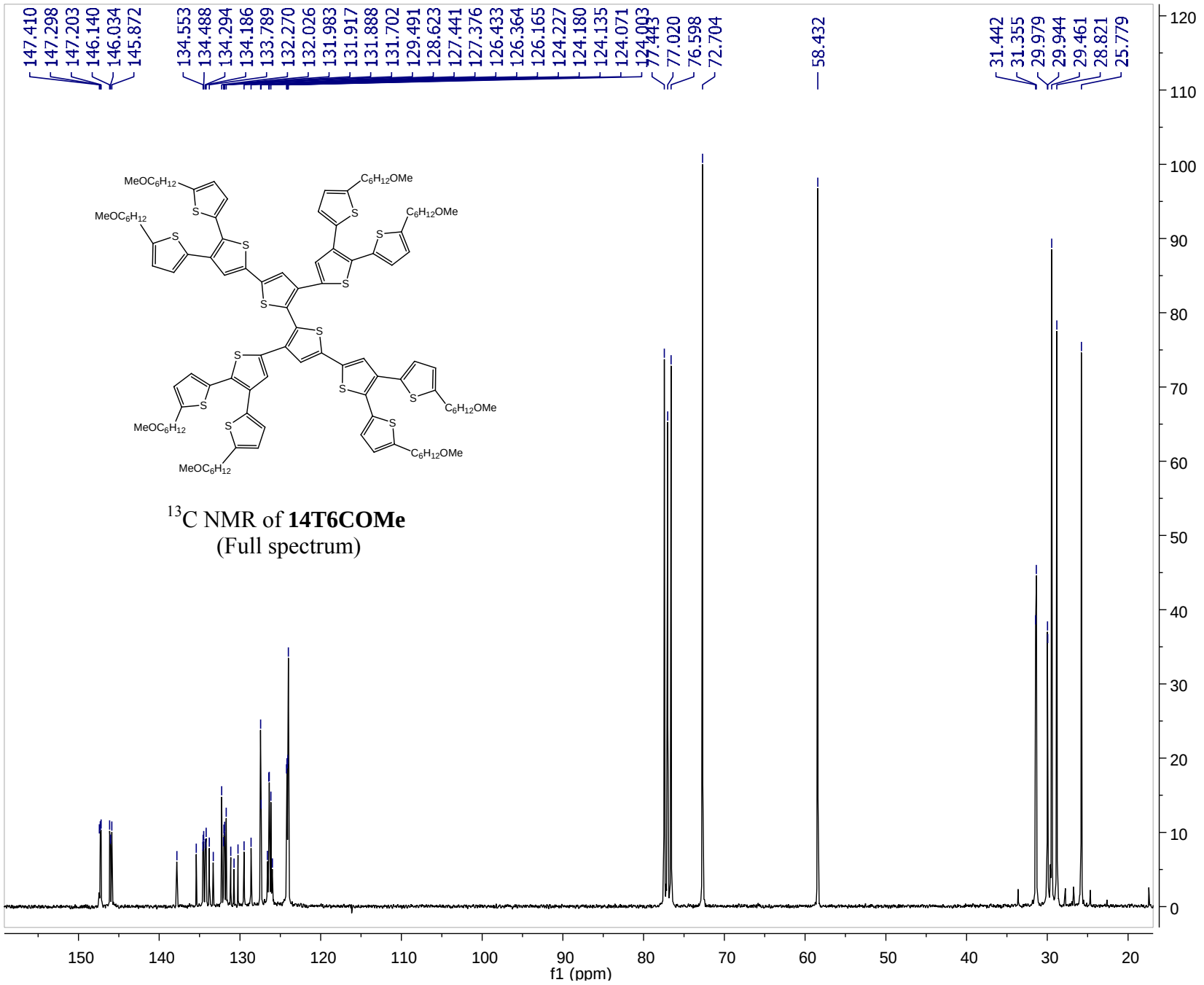




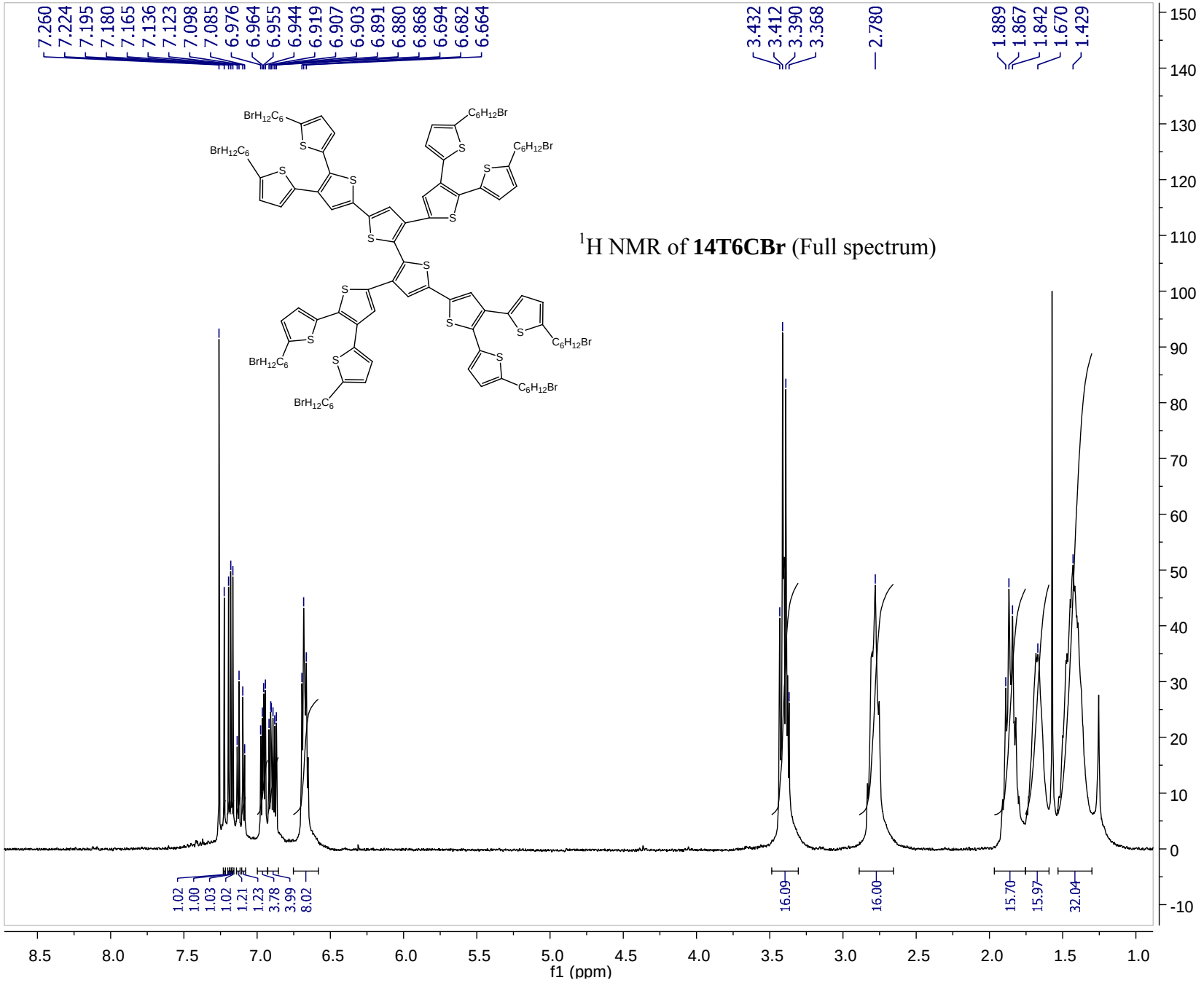
^{1}H NMR of **14T6COMe** (Aromatic region)

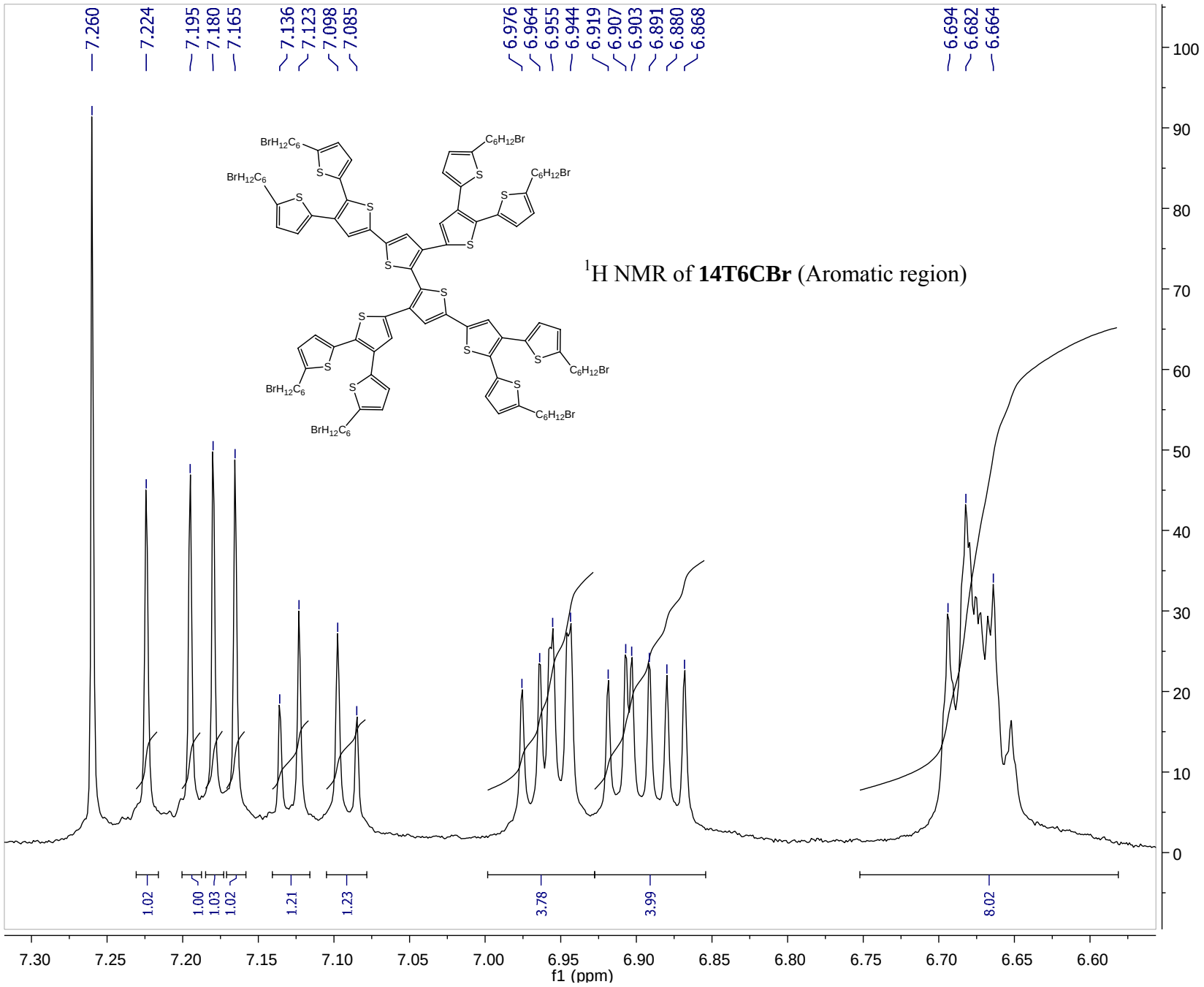


^{1}H NMR of **14T6COMe** (Aliphatic



^{13}C NMR of **14T6COMe**
(Full spectrum)





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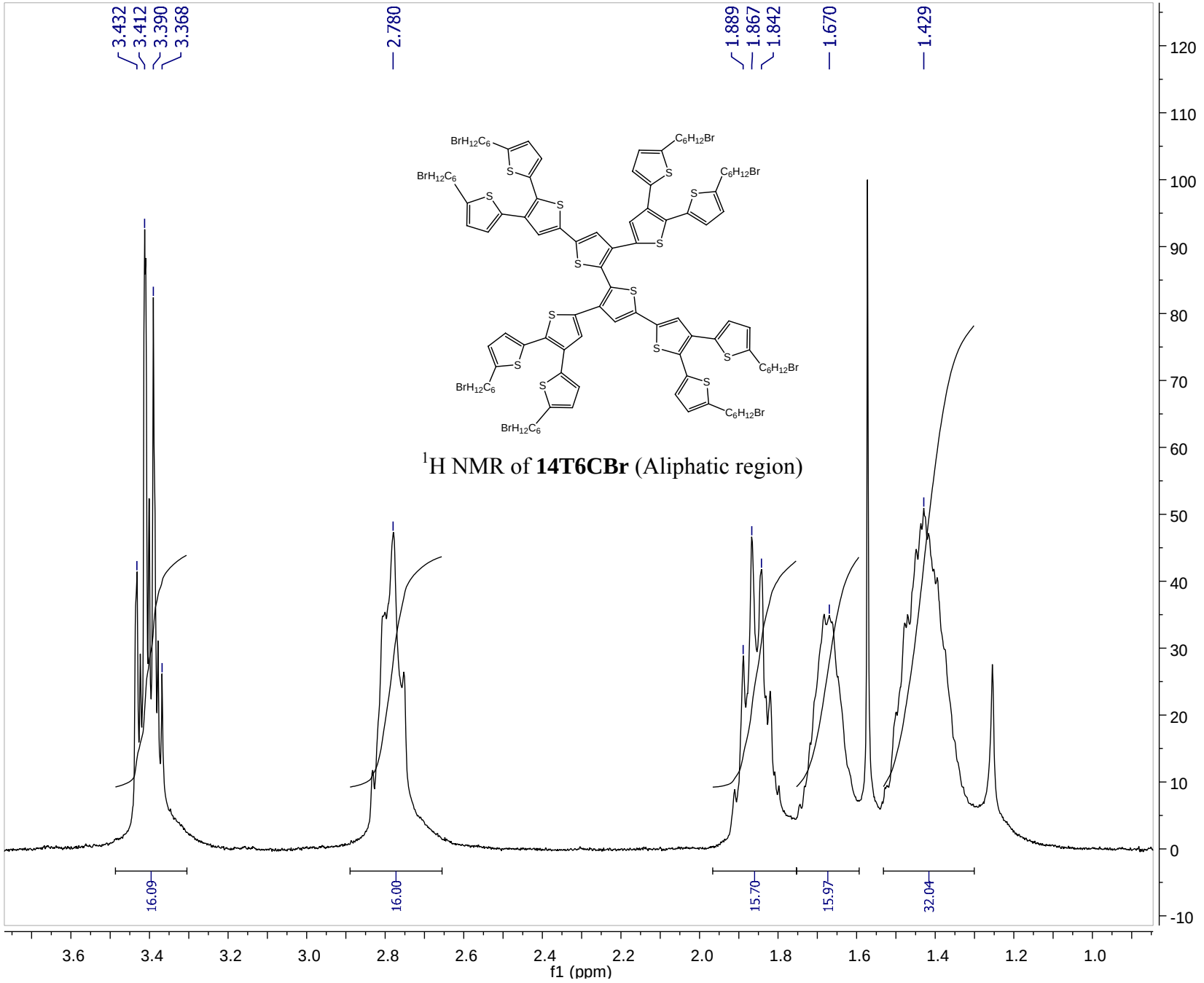

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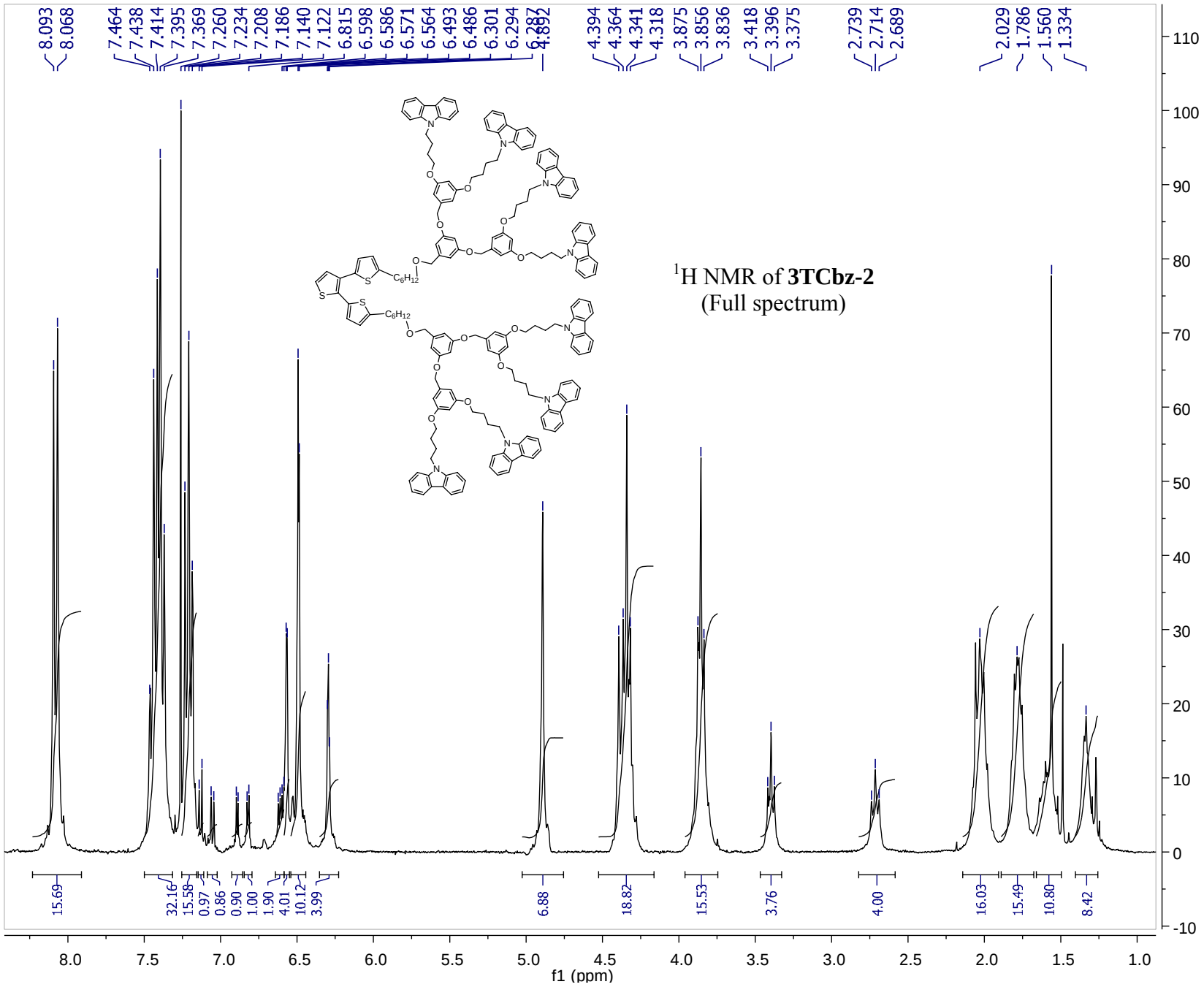
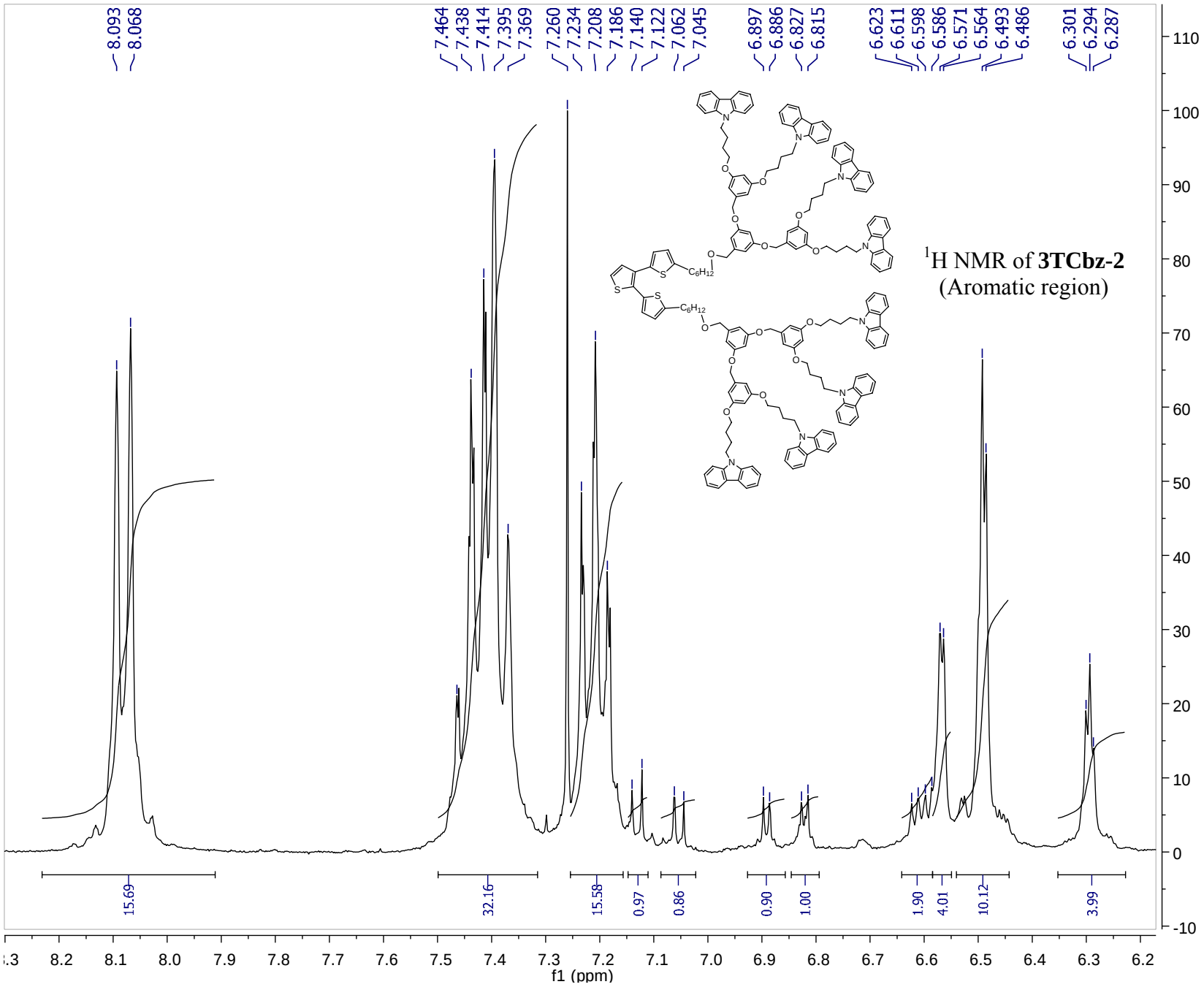
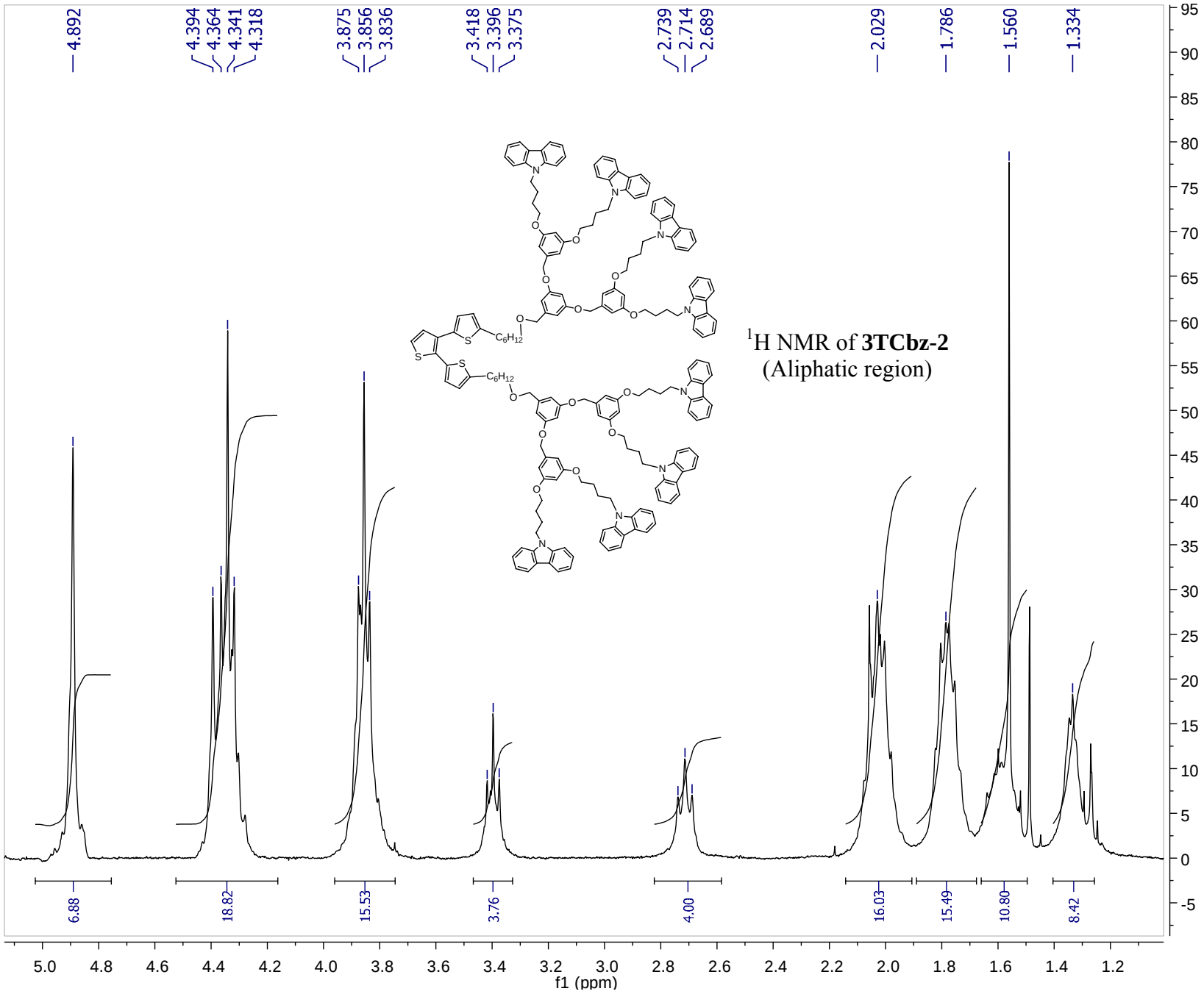


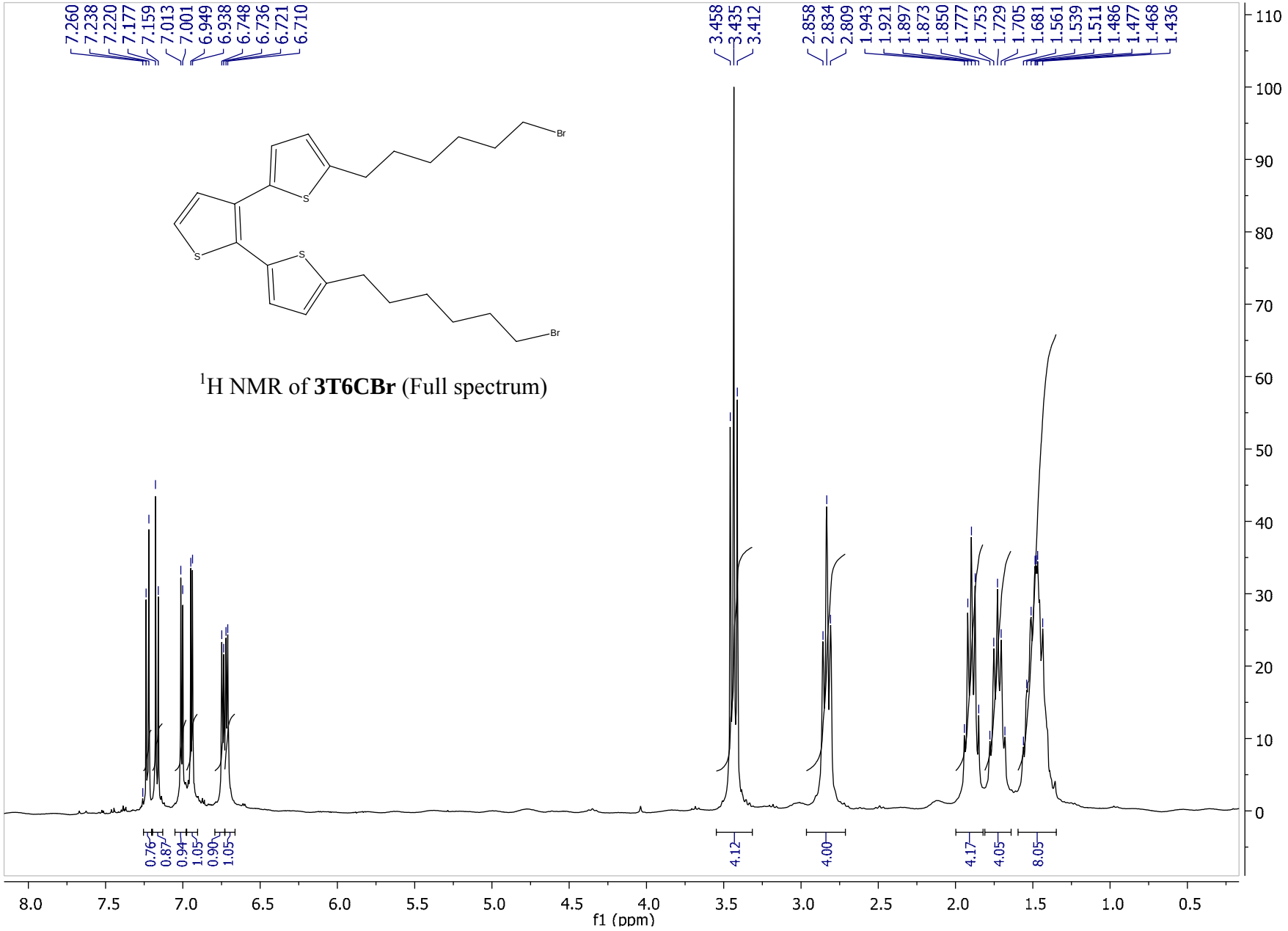
^{1}H NMR of **3TCbz-2**
(Full spectrum)



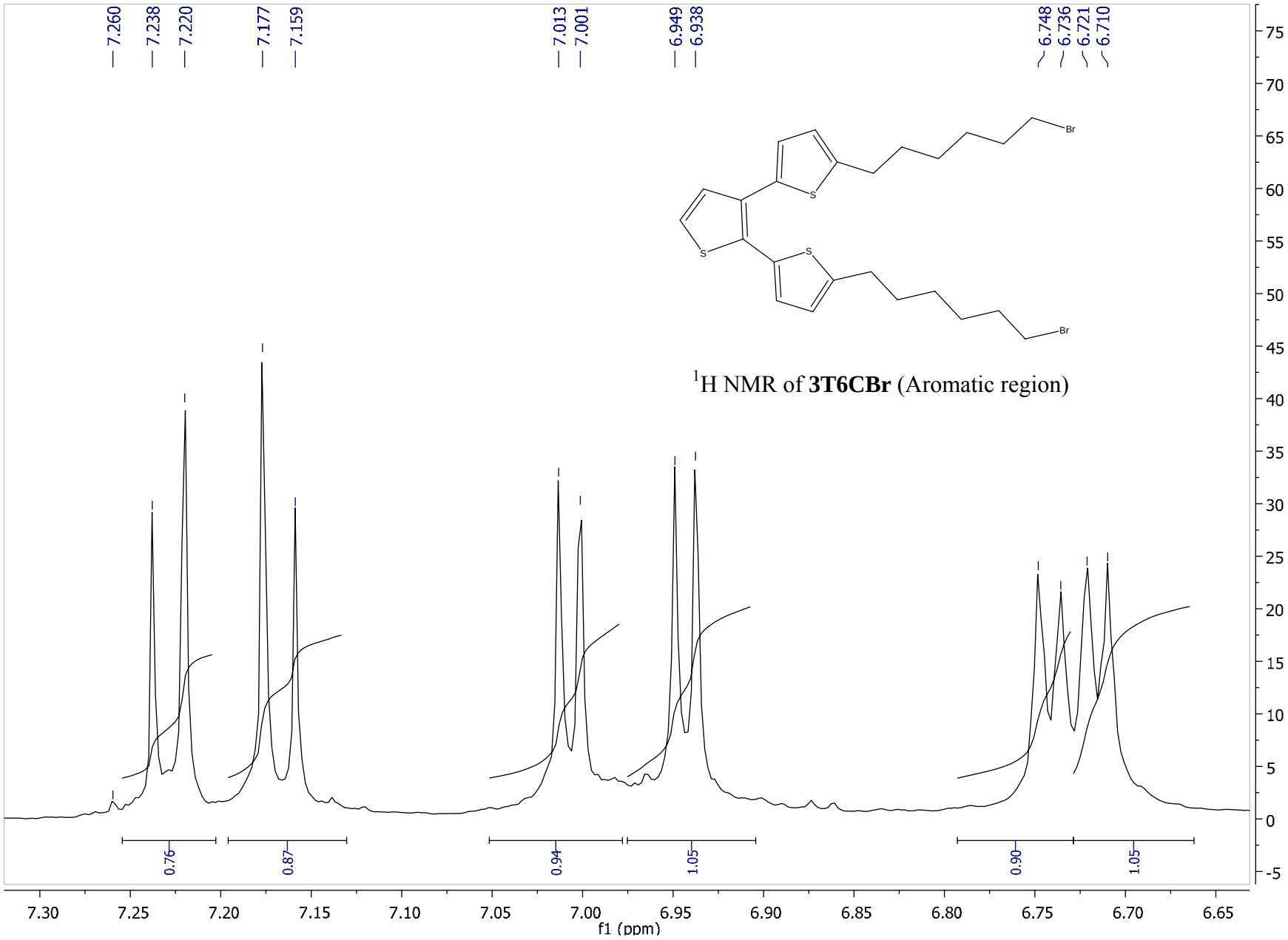
^{1}H NMR of **3TCbz-2**
(Aromatic region)



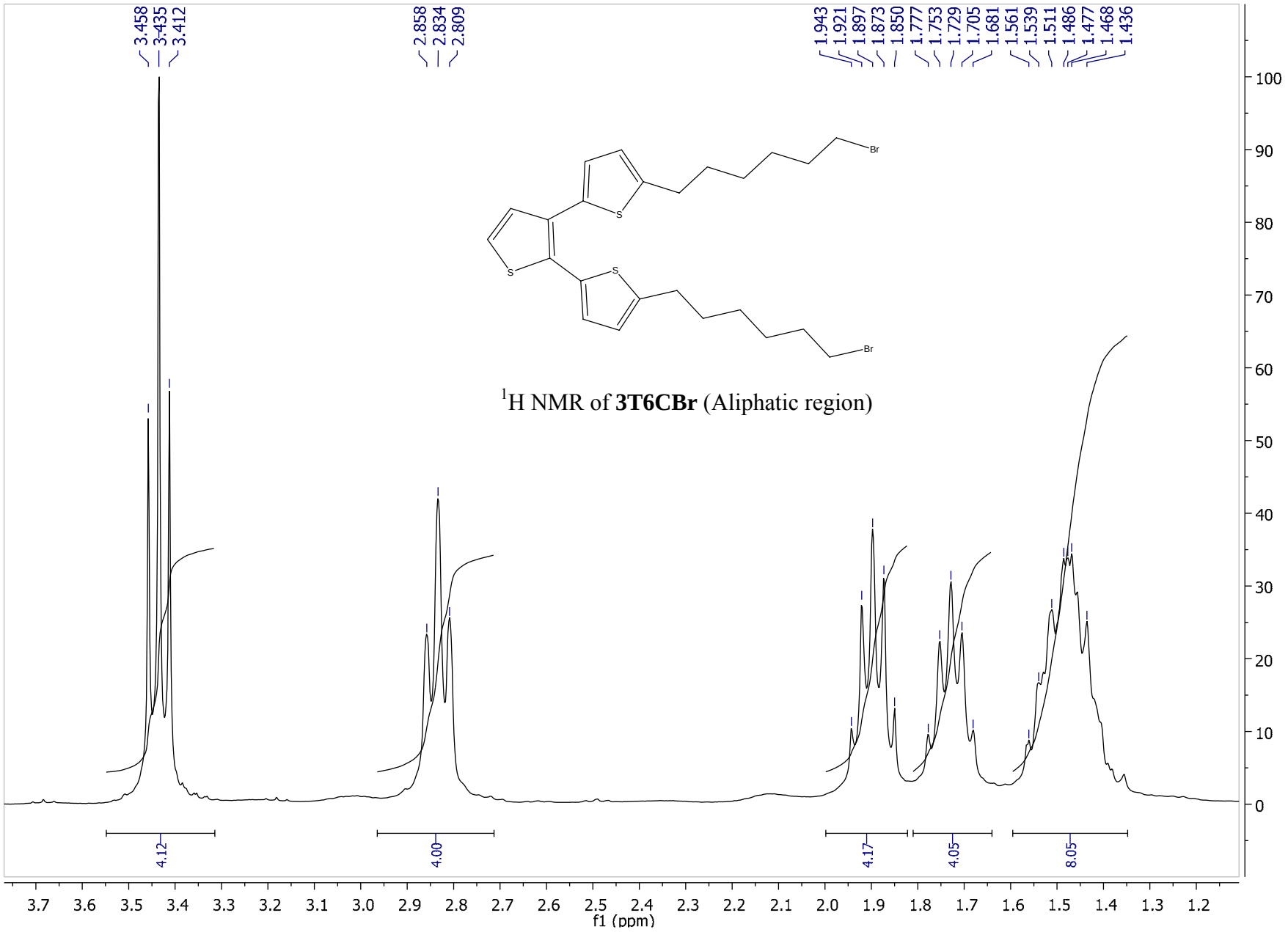
^{1}H NMR of **3TCbz-2**
(Aliphatic region)



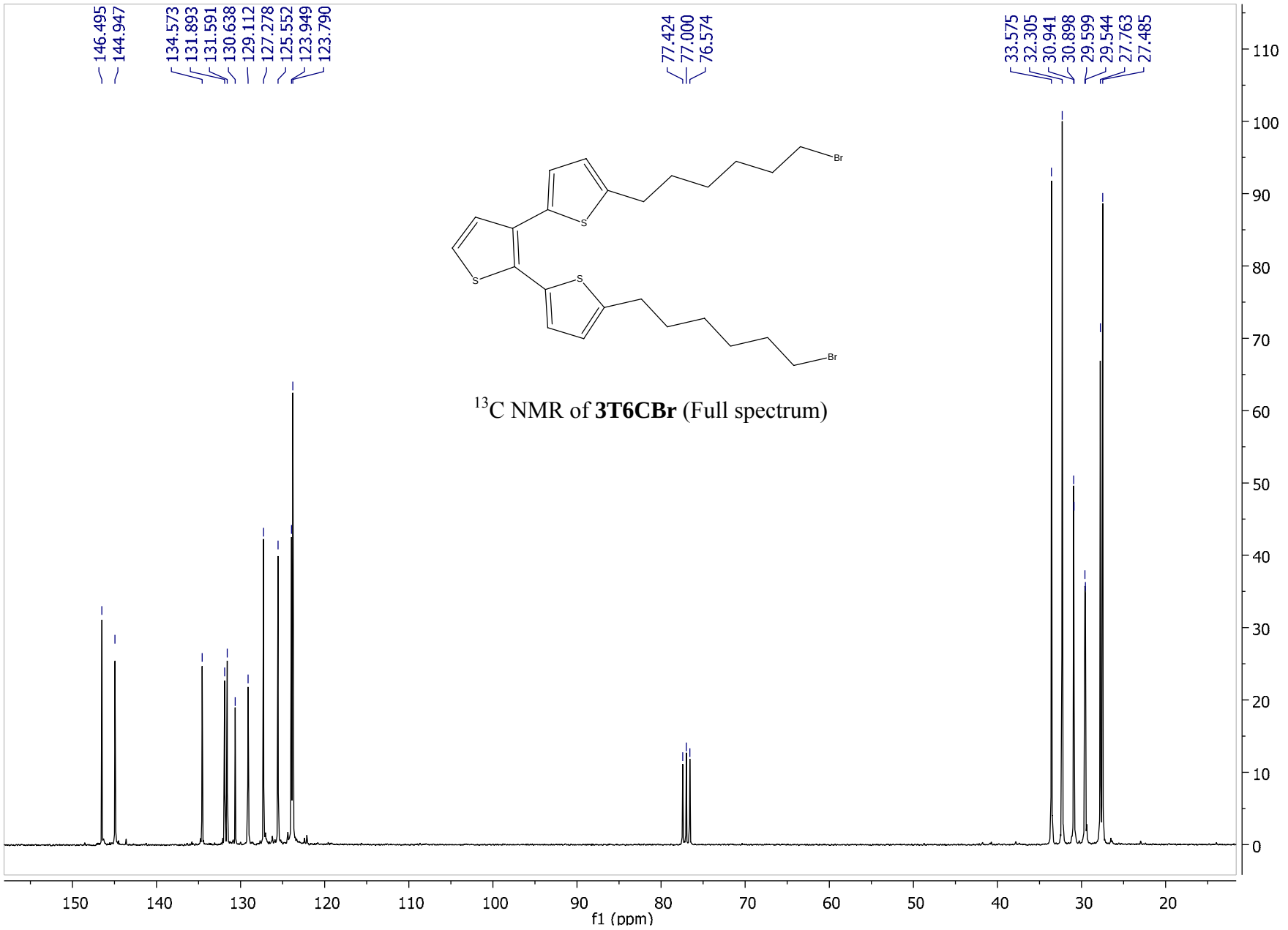
^{1}H NMR of **3T6CBr** (Full spectrum)



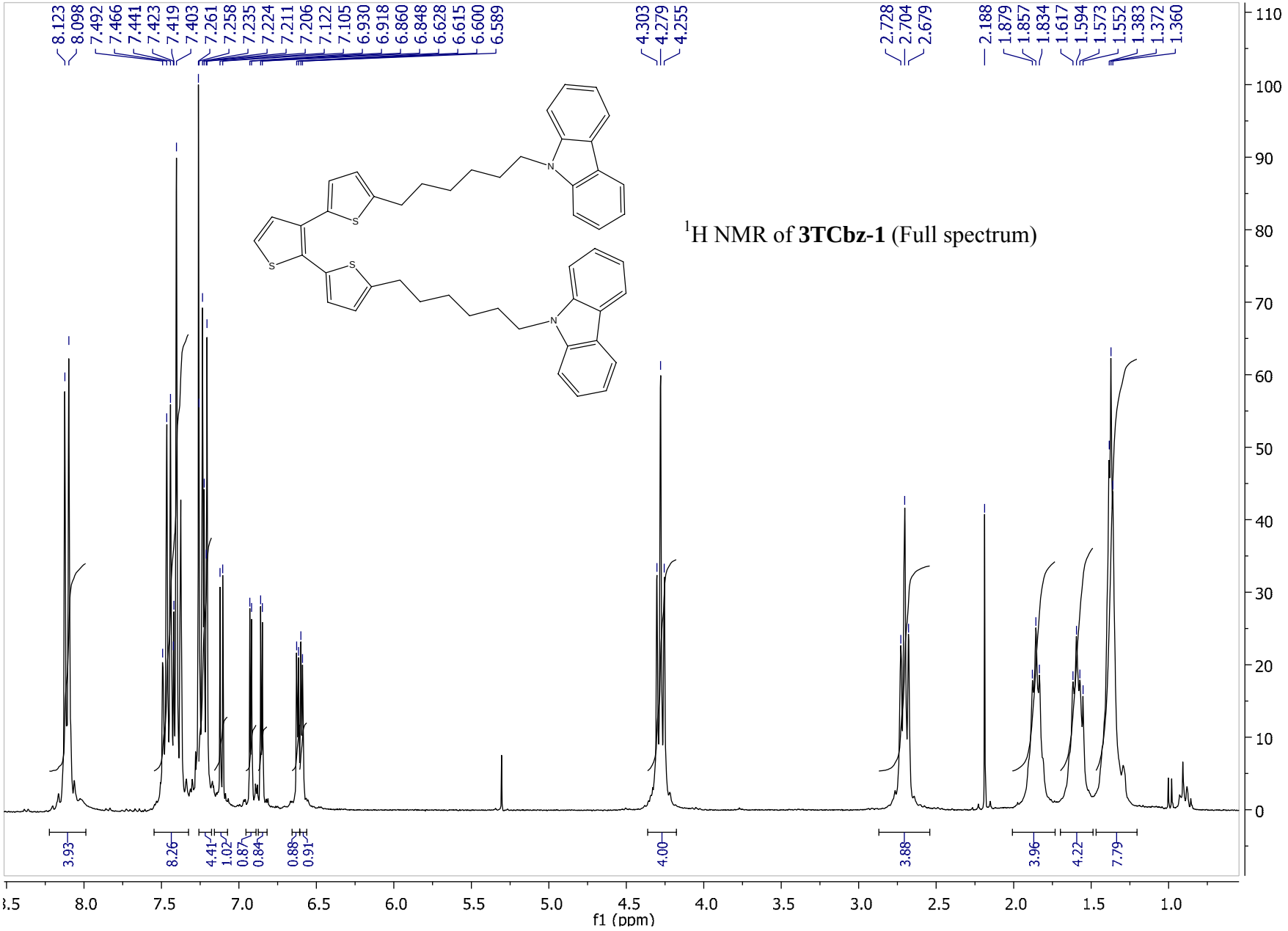
^{1}H NMR of **3T6CBr** (Aromatic region)



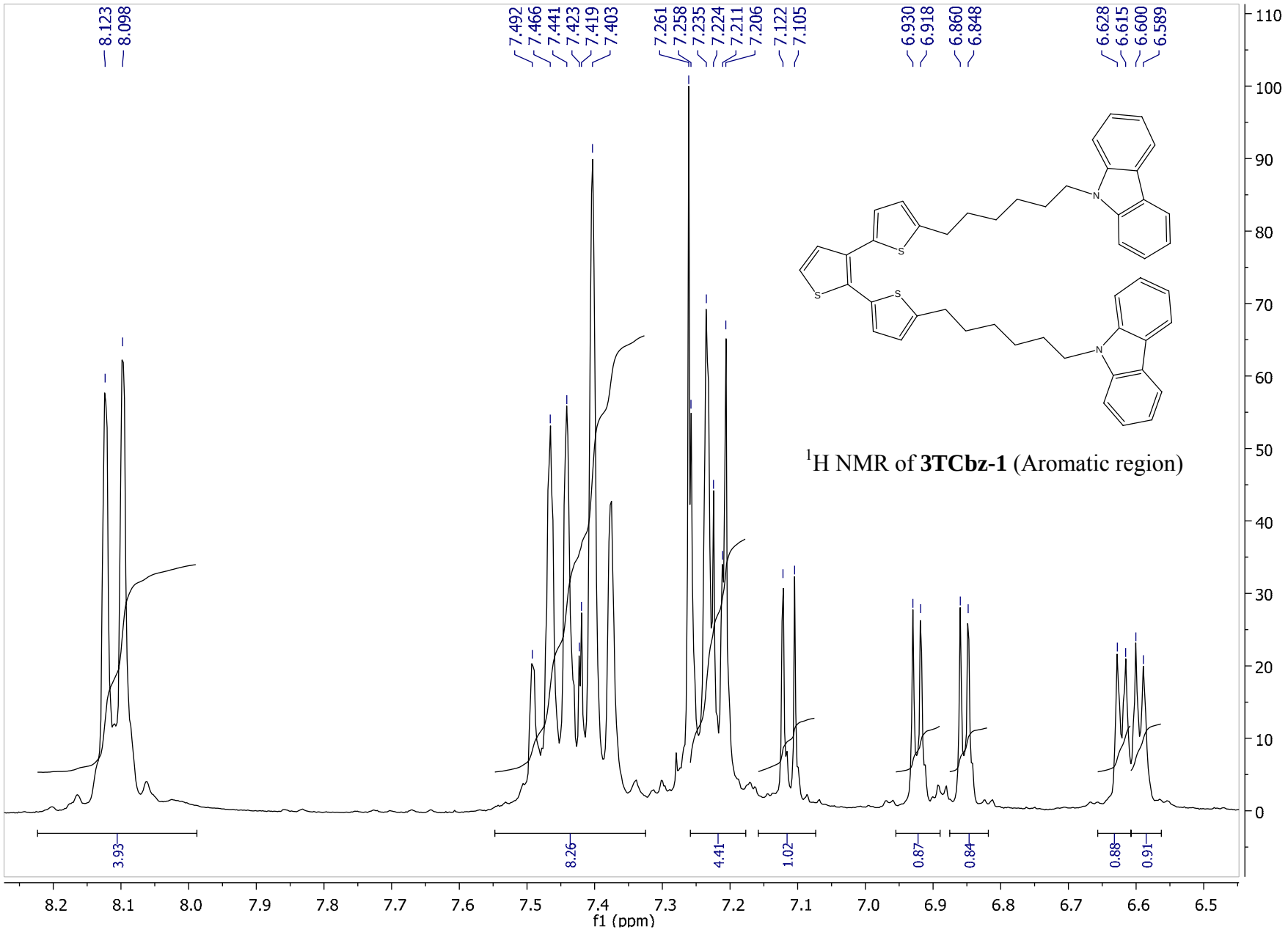
^{1}H NMR of **3T6CBr** (Aliphatic region)



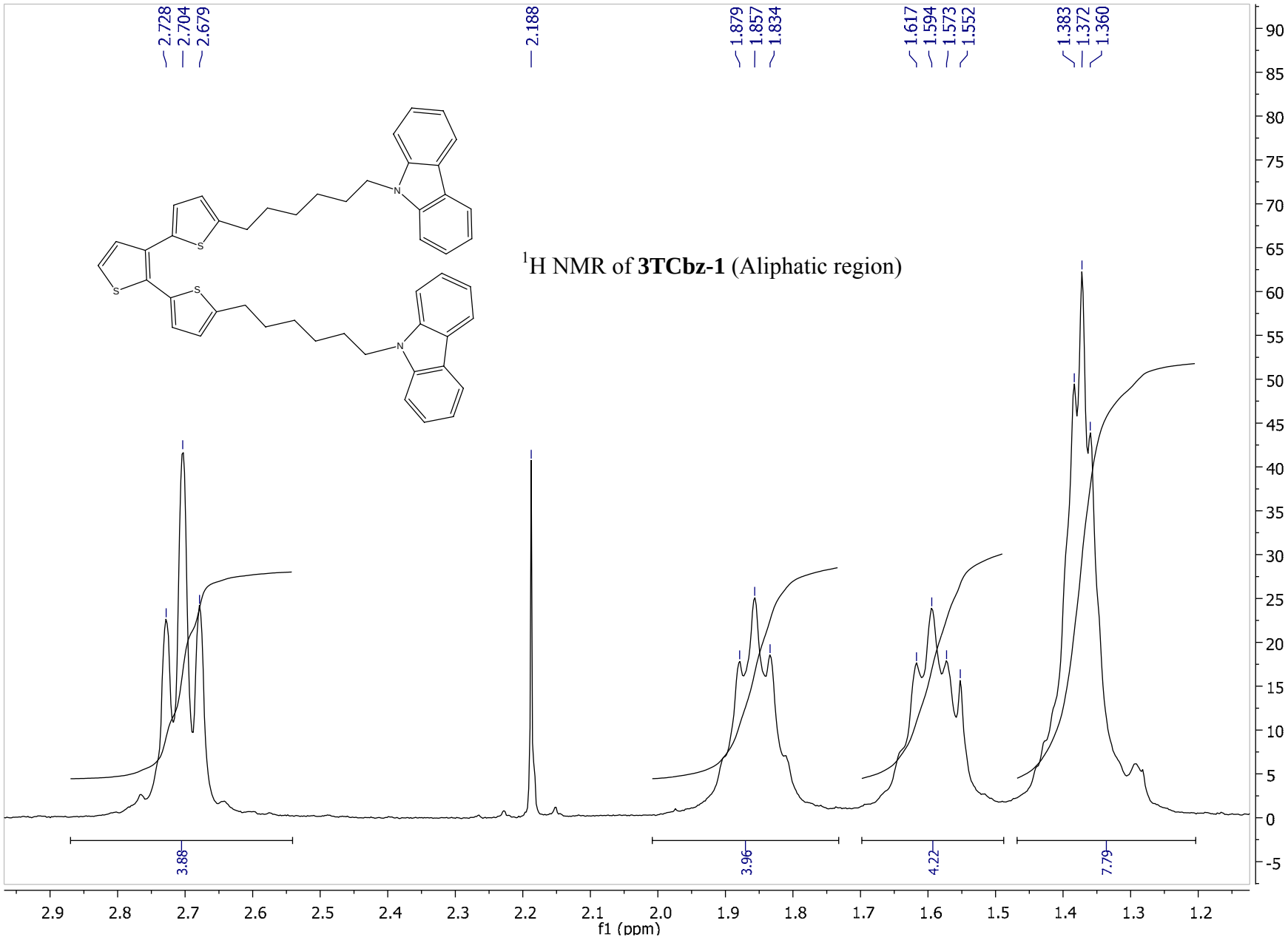
^{13}C NMR of **3T6CBr** (Full spectrum)

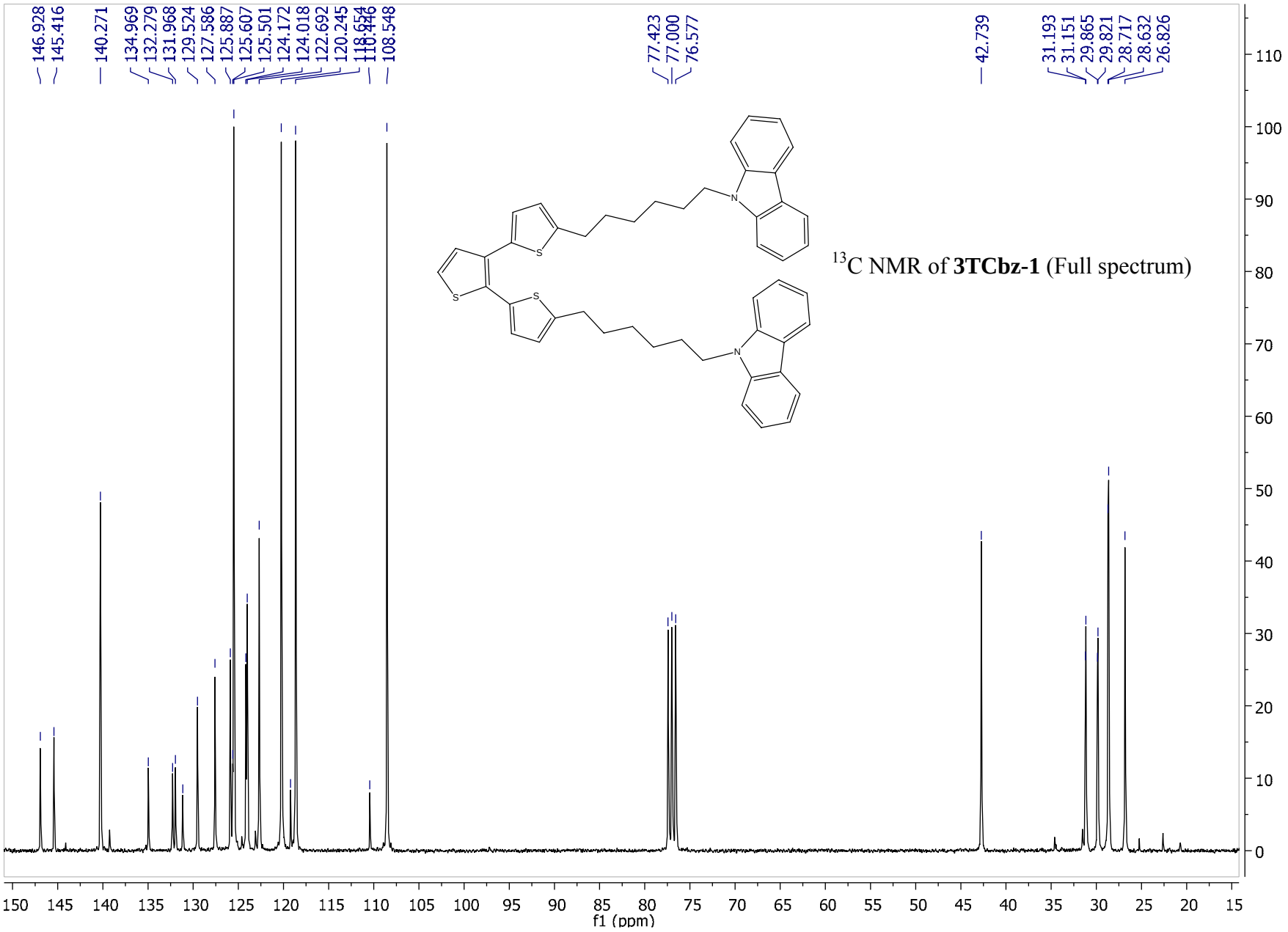


^{1}H NMR of **3TCbz-1** (Full spectrum)

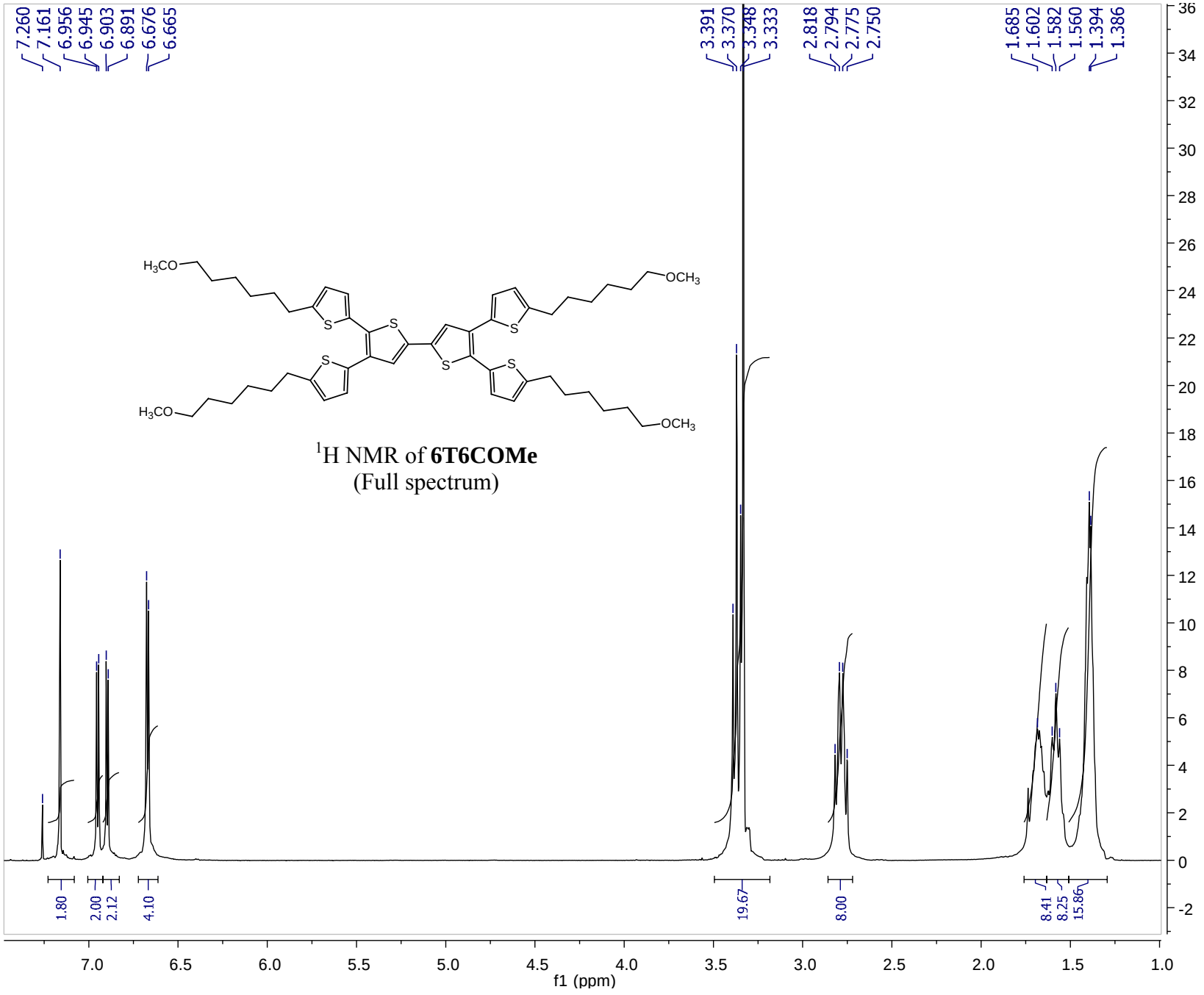


^{1}H NMR of **3TCbz-1** (Aromatic region)

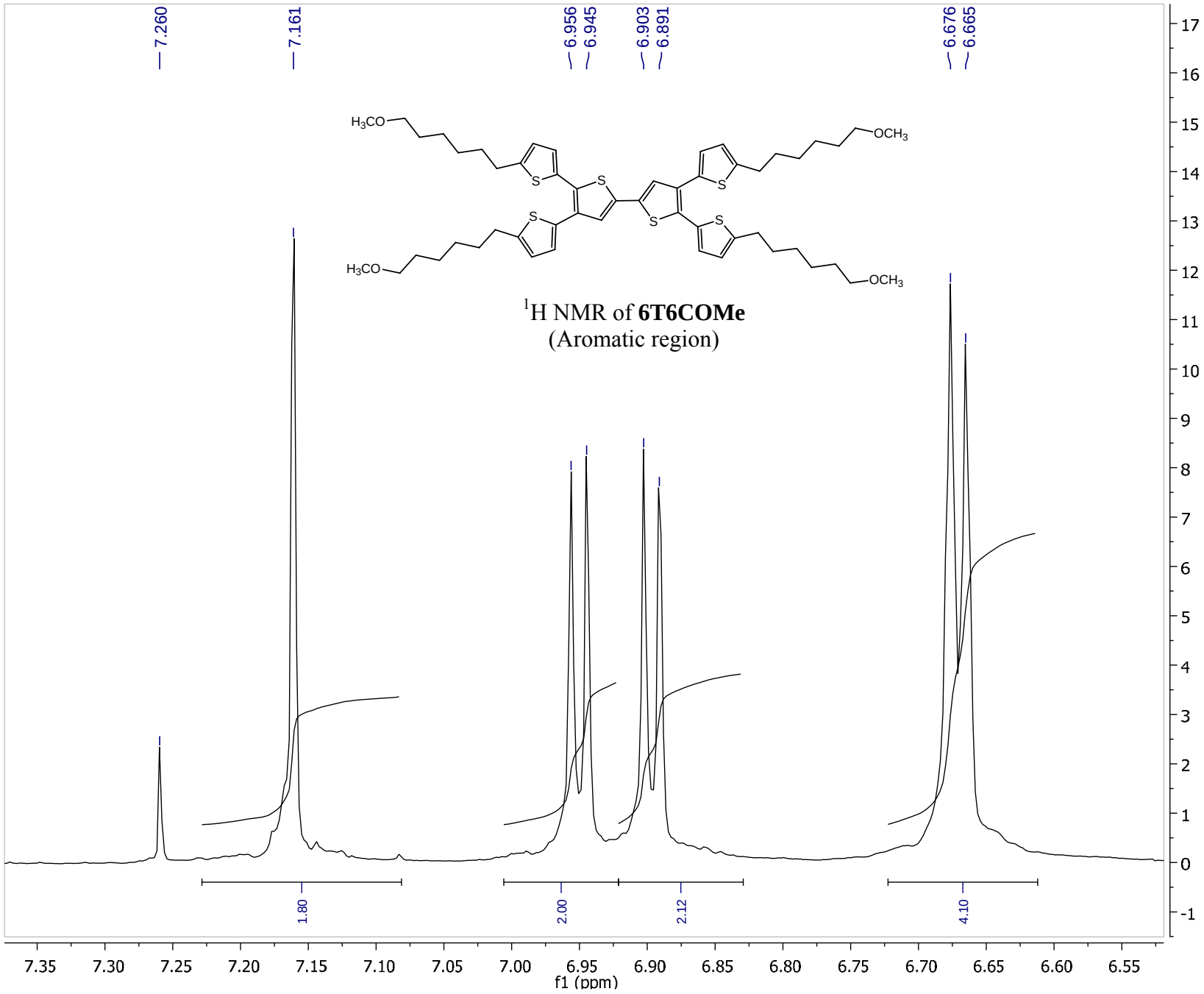




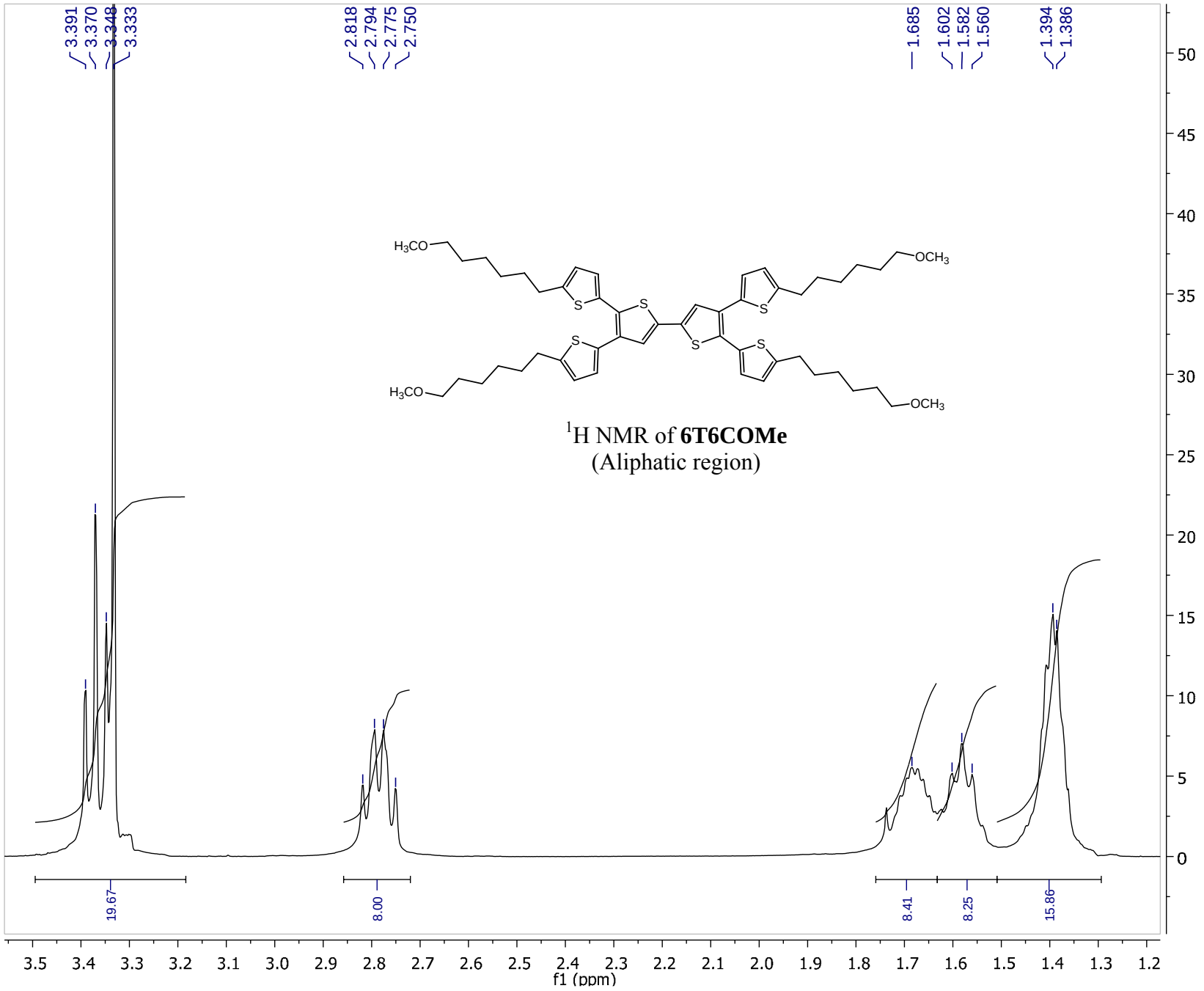
^{13}C NMR of **3TCbz-1** (Full spectrum)



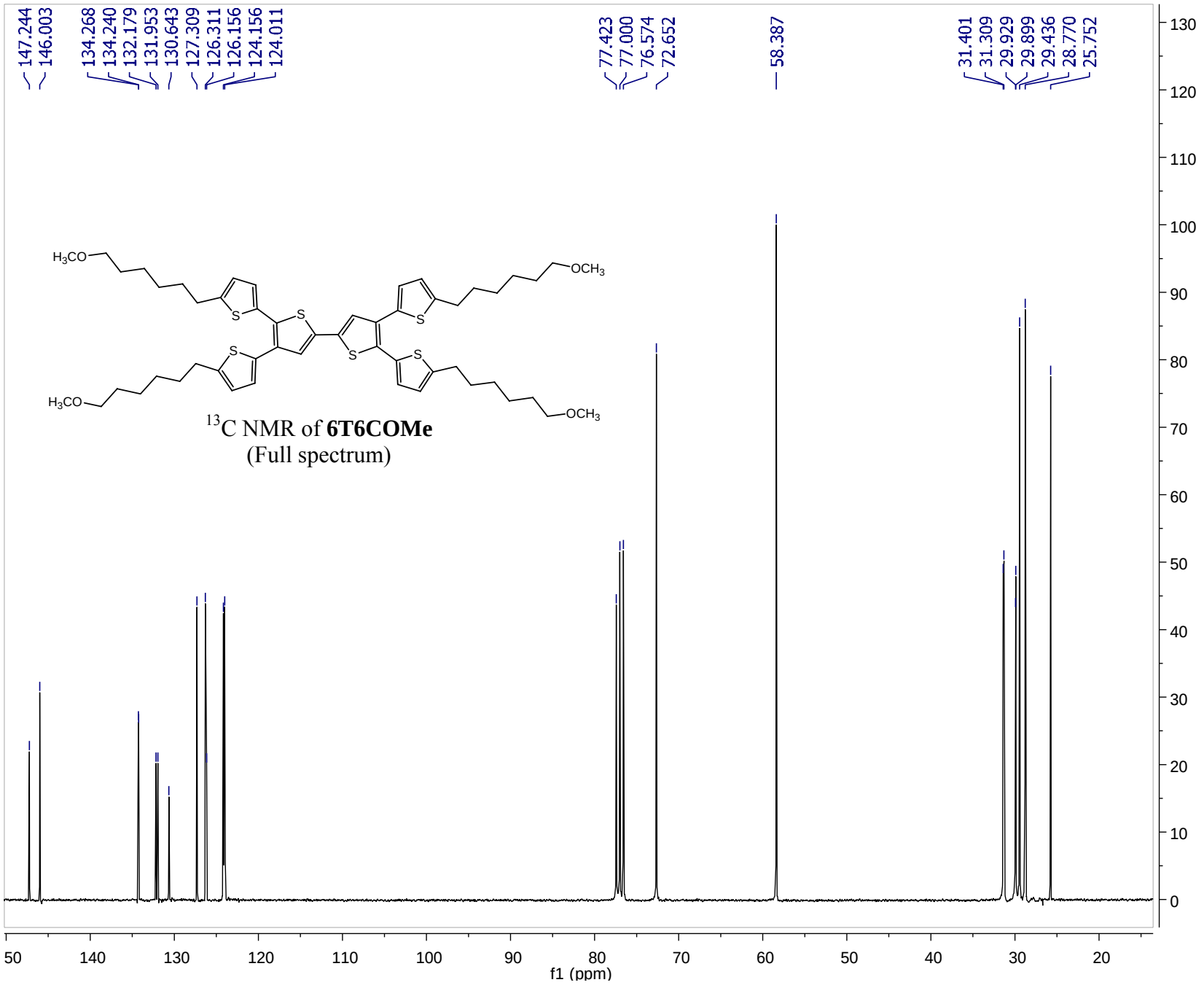
^{1}H NMR of **6T6COMe**
(Full spectrum)



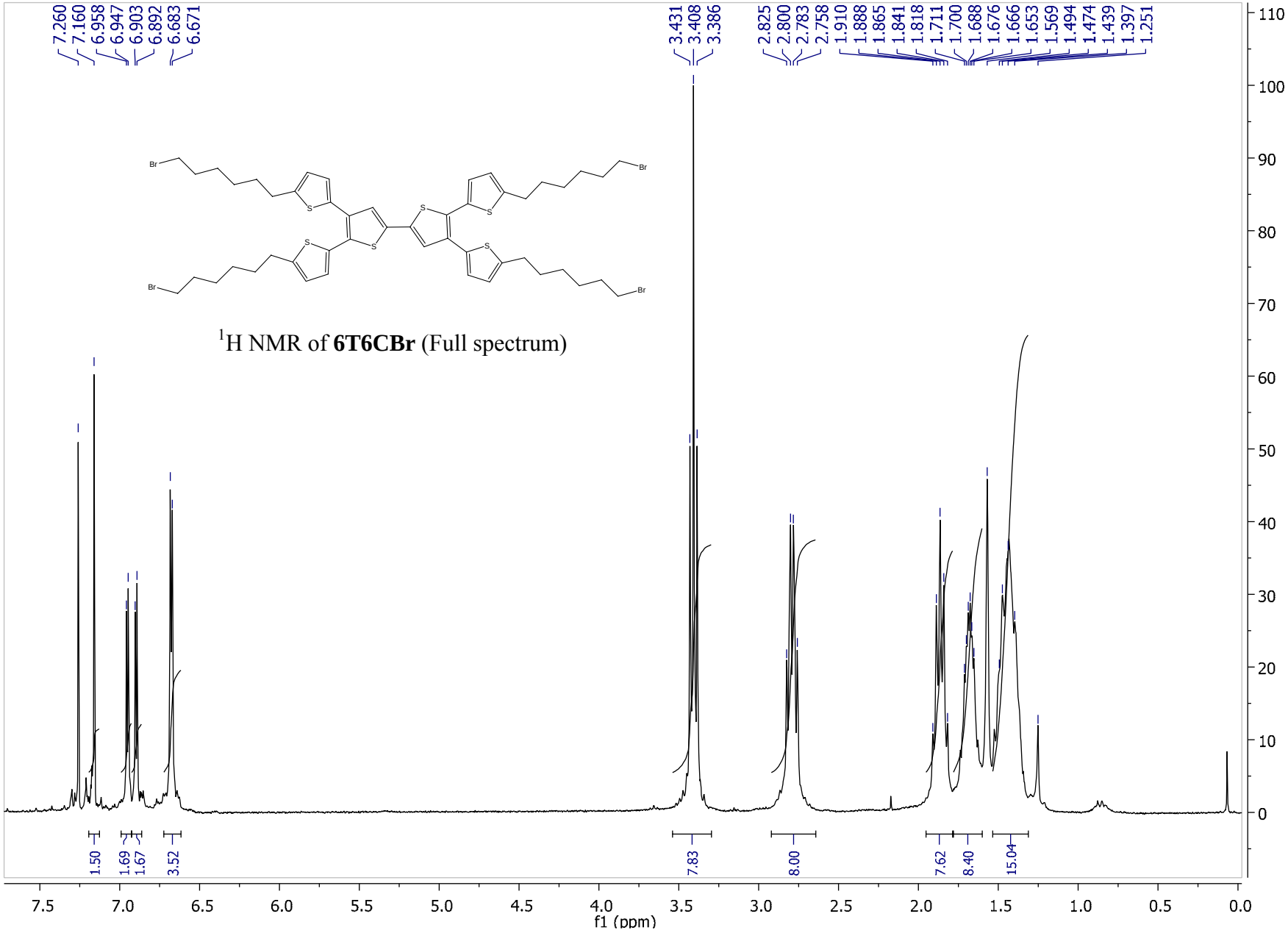
^{1}H NMR of **6T6COMe**
(Aromatic region)



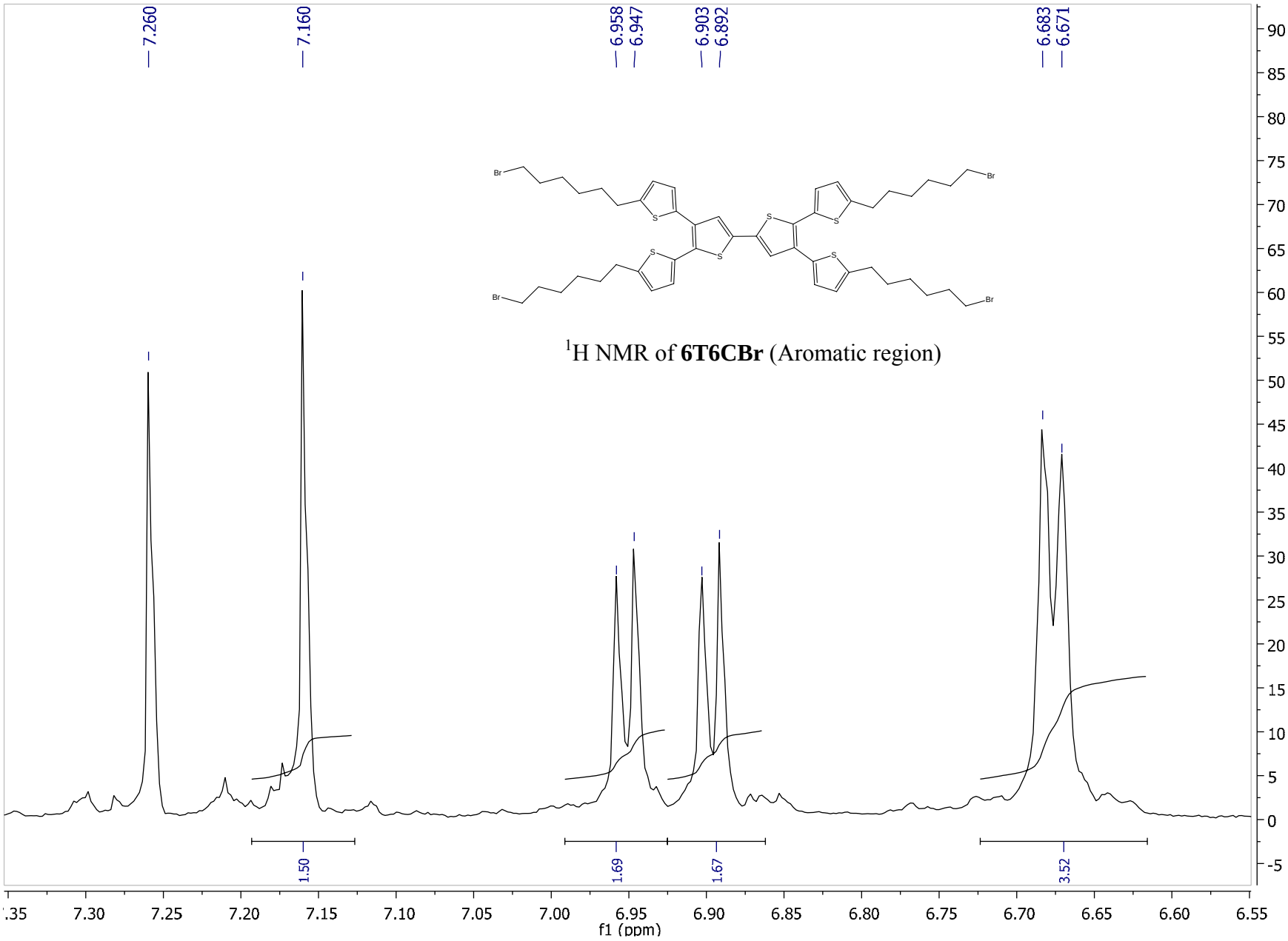
^{1}H NMR of **6T6COMe**
(Aliphatic region)



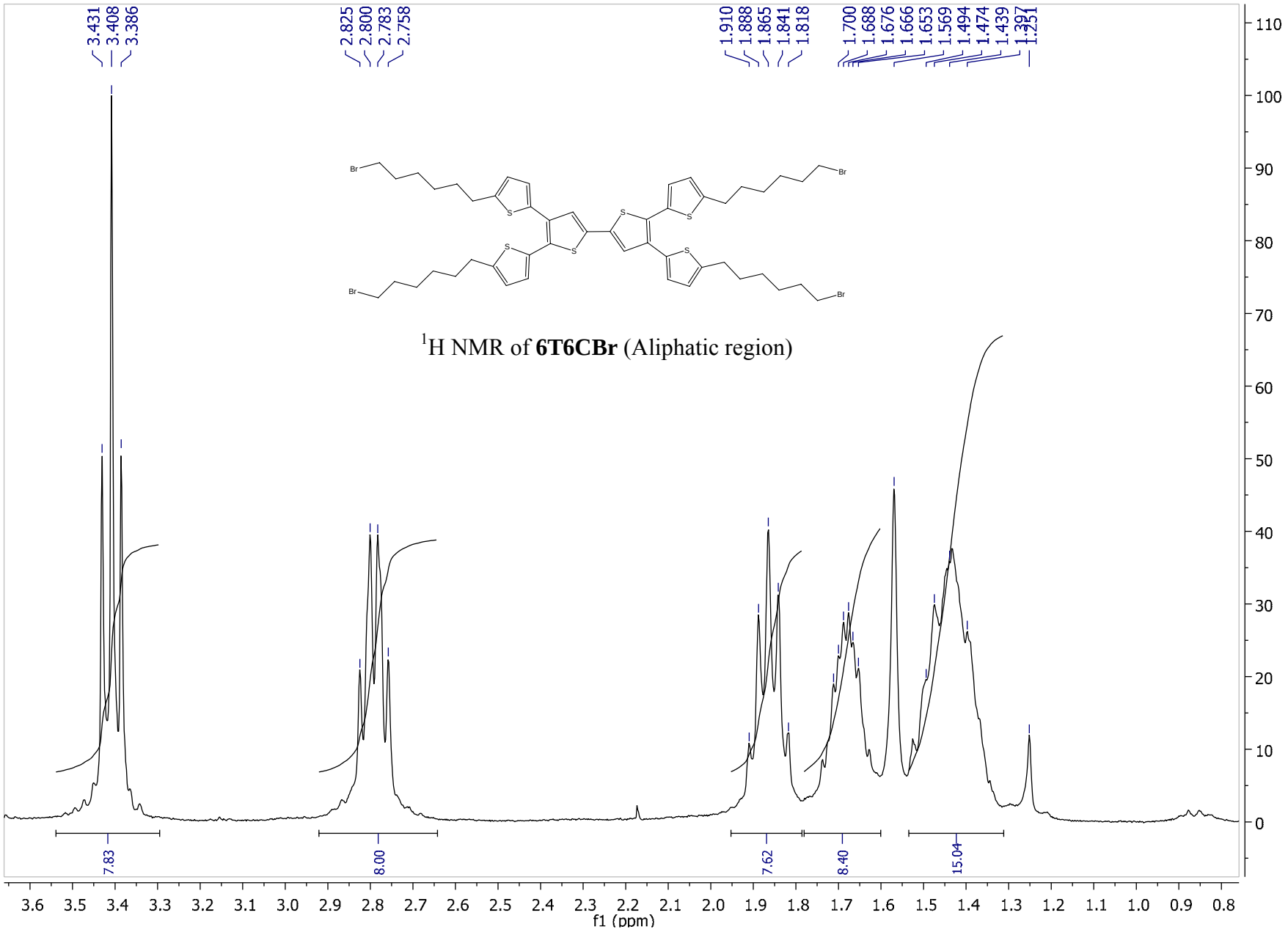
^{13}C NMR of **6T6COMe**
(Full spectrum)



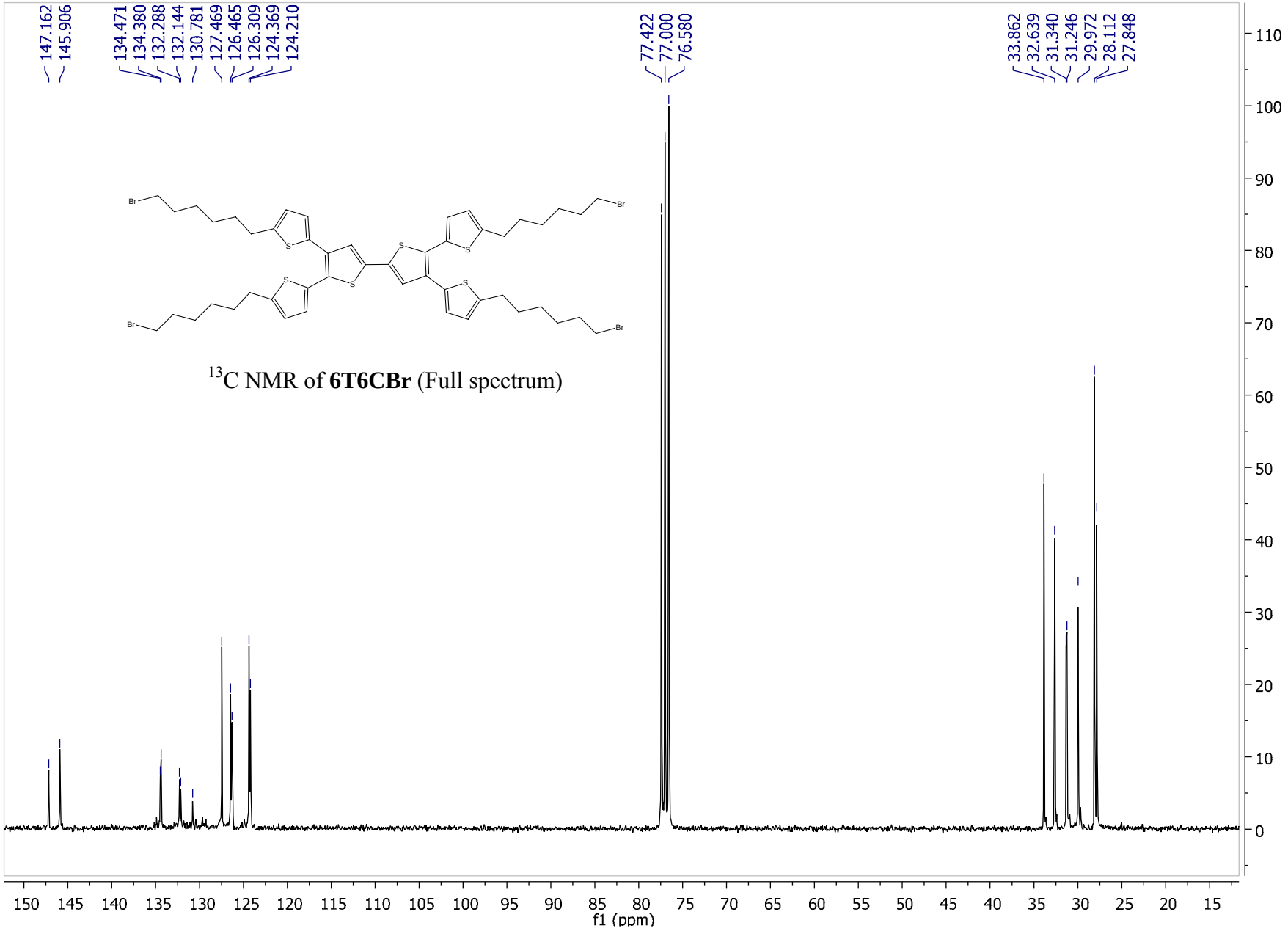
^{1}H NMR of **6T6CBr** (Full spectrum)



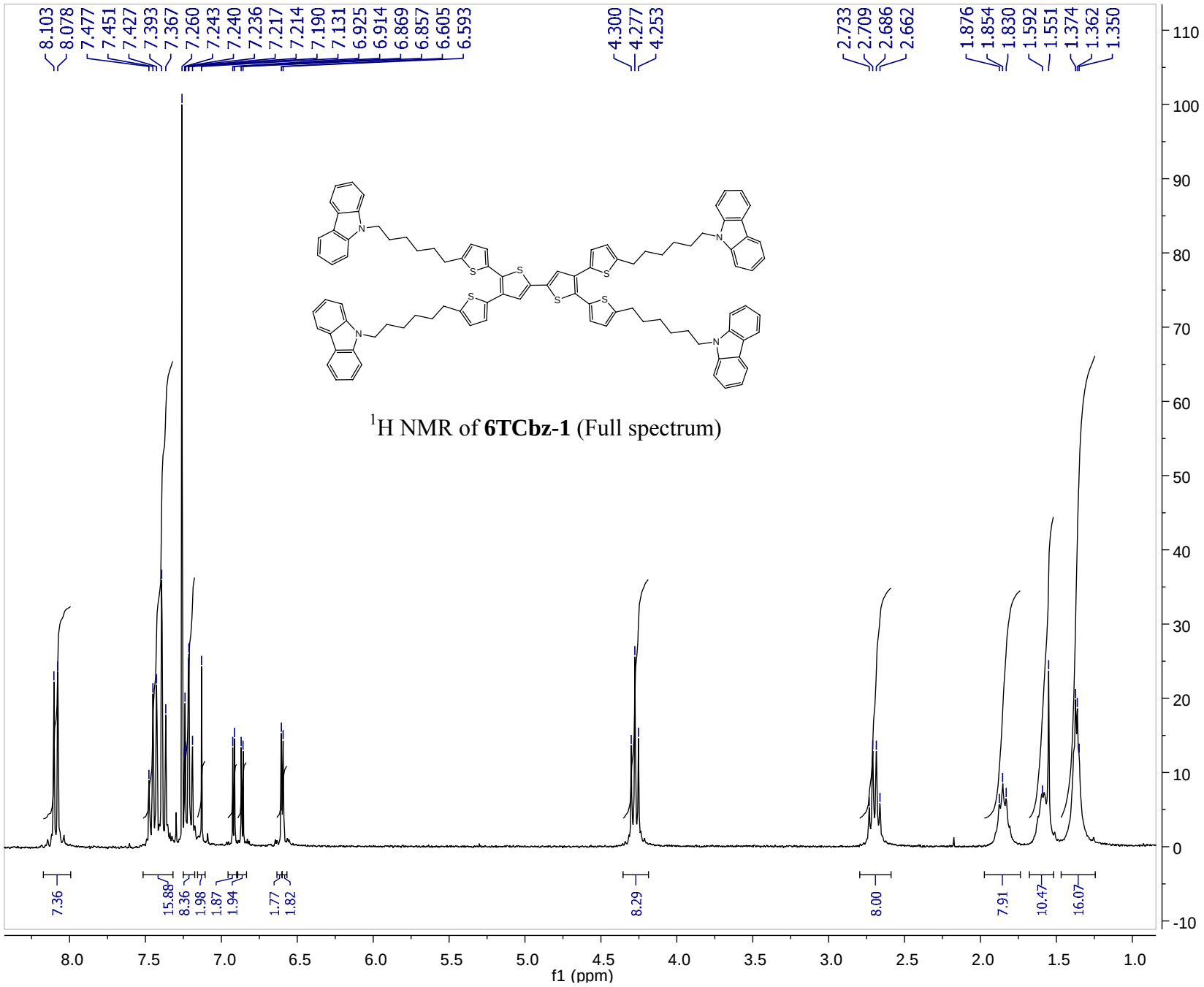
^{1}H NMR of **6T6CBr** (Aromatic region)



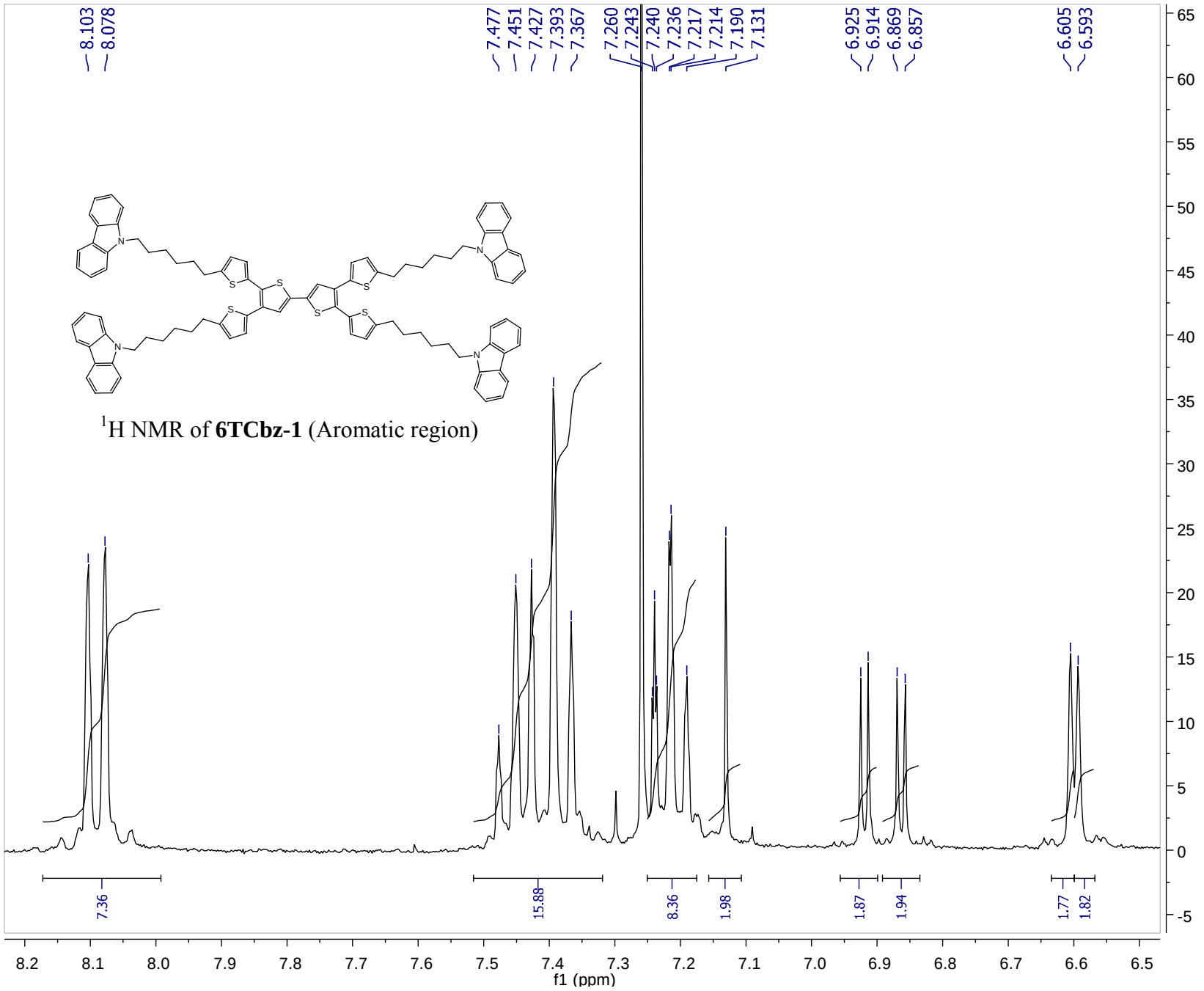
^{1}H NMR of **6T6CBr** (Aliphatic region)



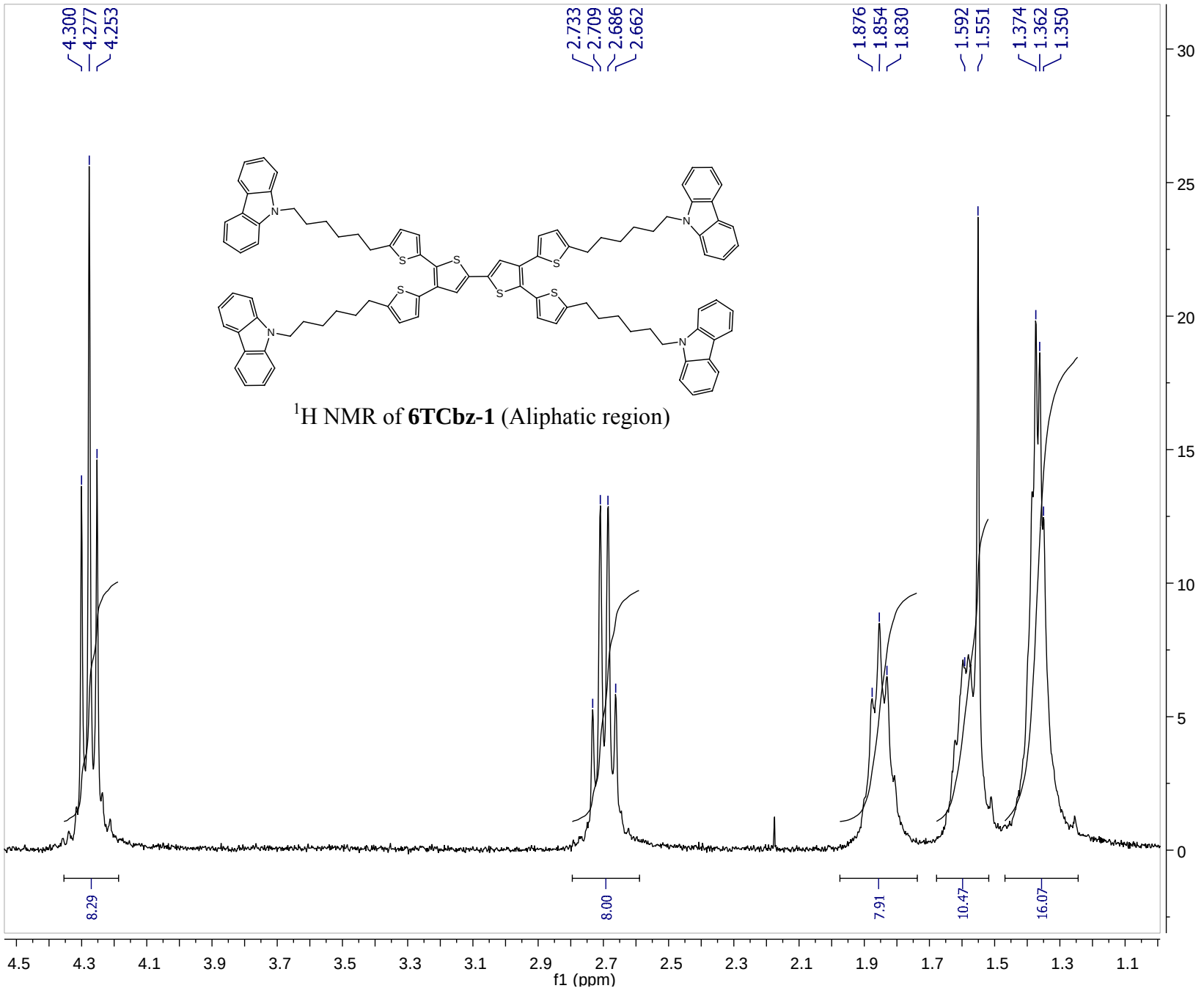
^{13}C NMR of **6T6CBr** (Full spectrum)



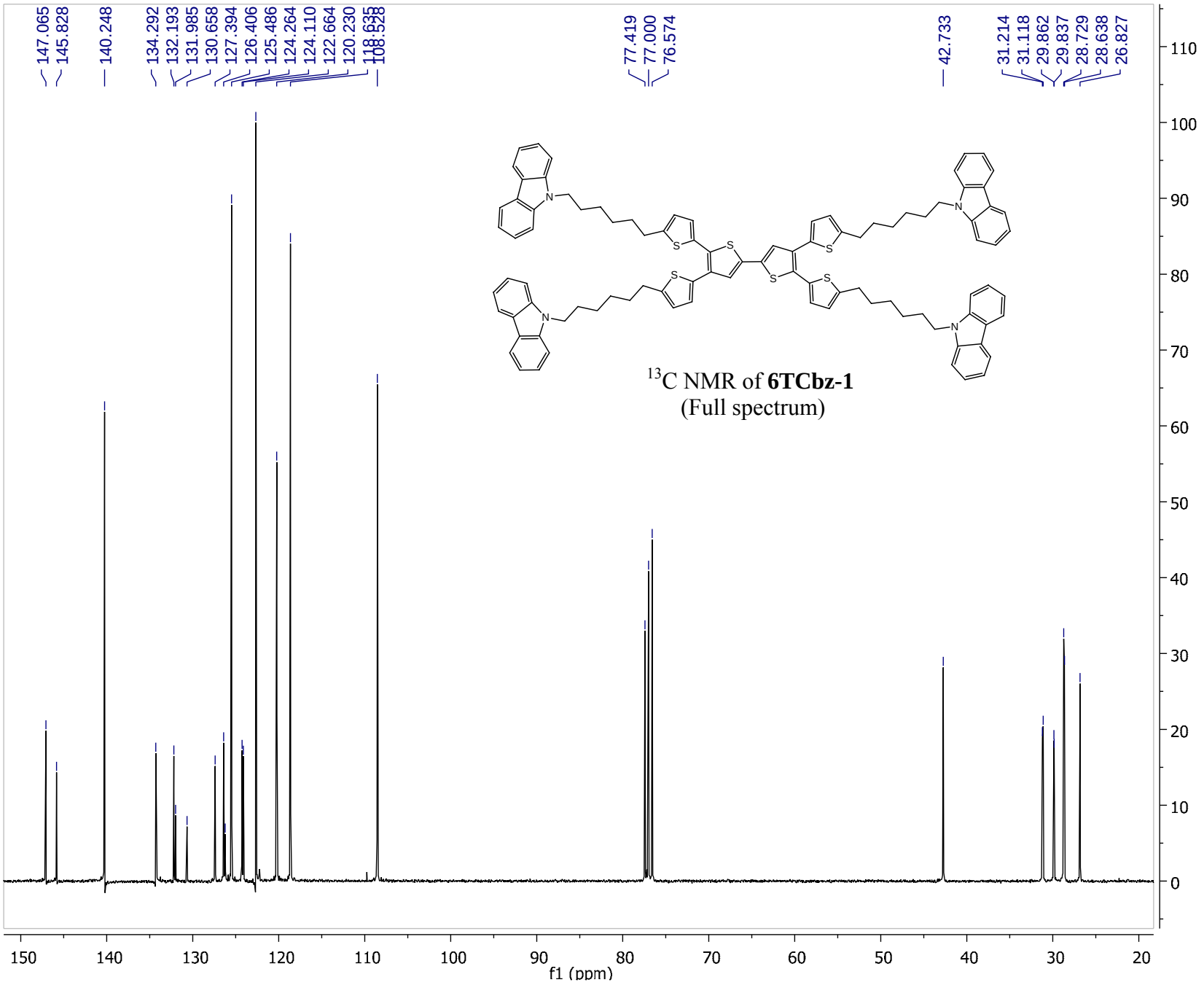
^{1}H NMR of **6TCbz-1** (Full spectrum)



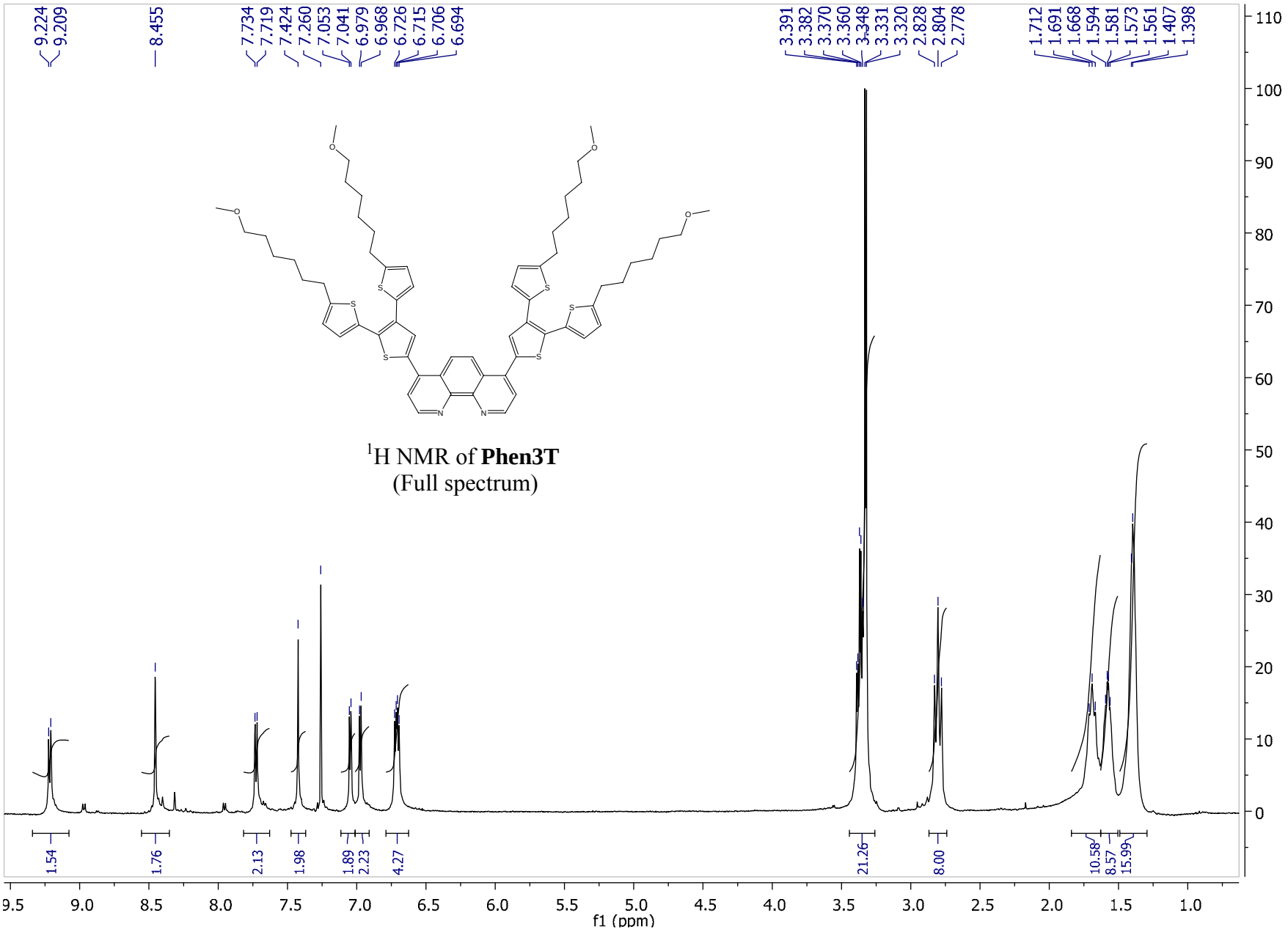
^{1}H NMR of **6TCbz-1** (Aromatic region)



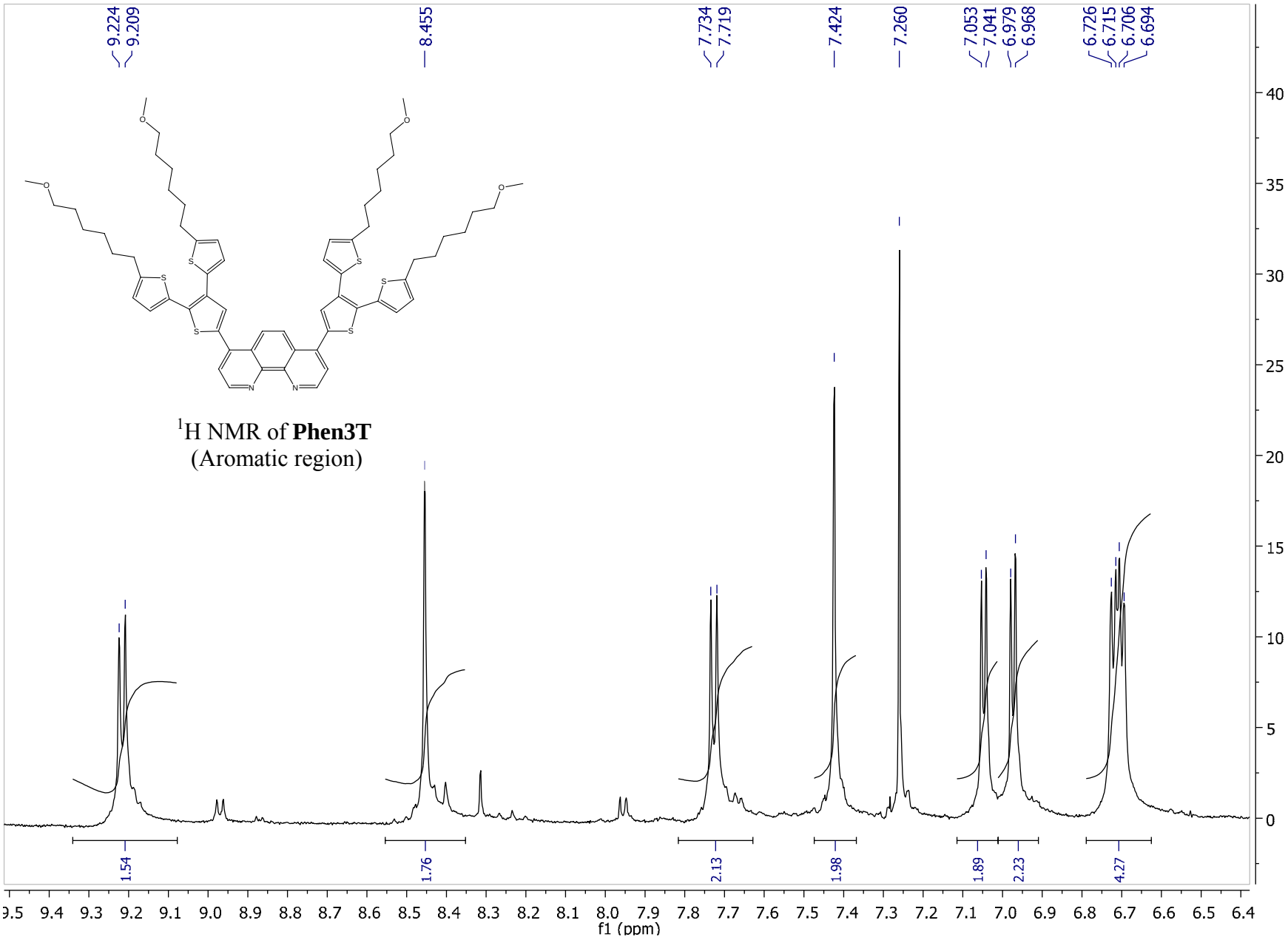
^{1}H NMR of **6TCbz-1** (Aliphatic region)



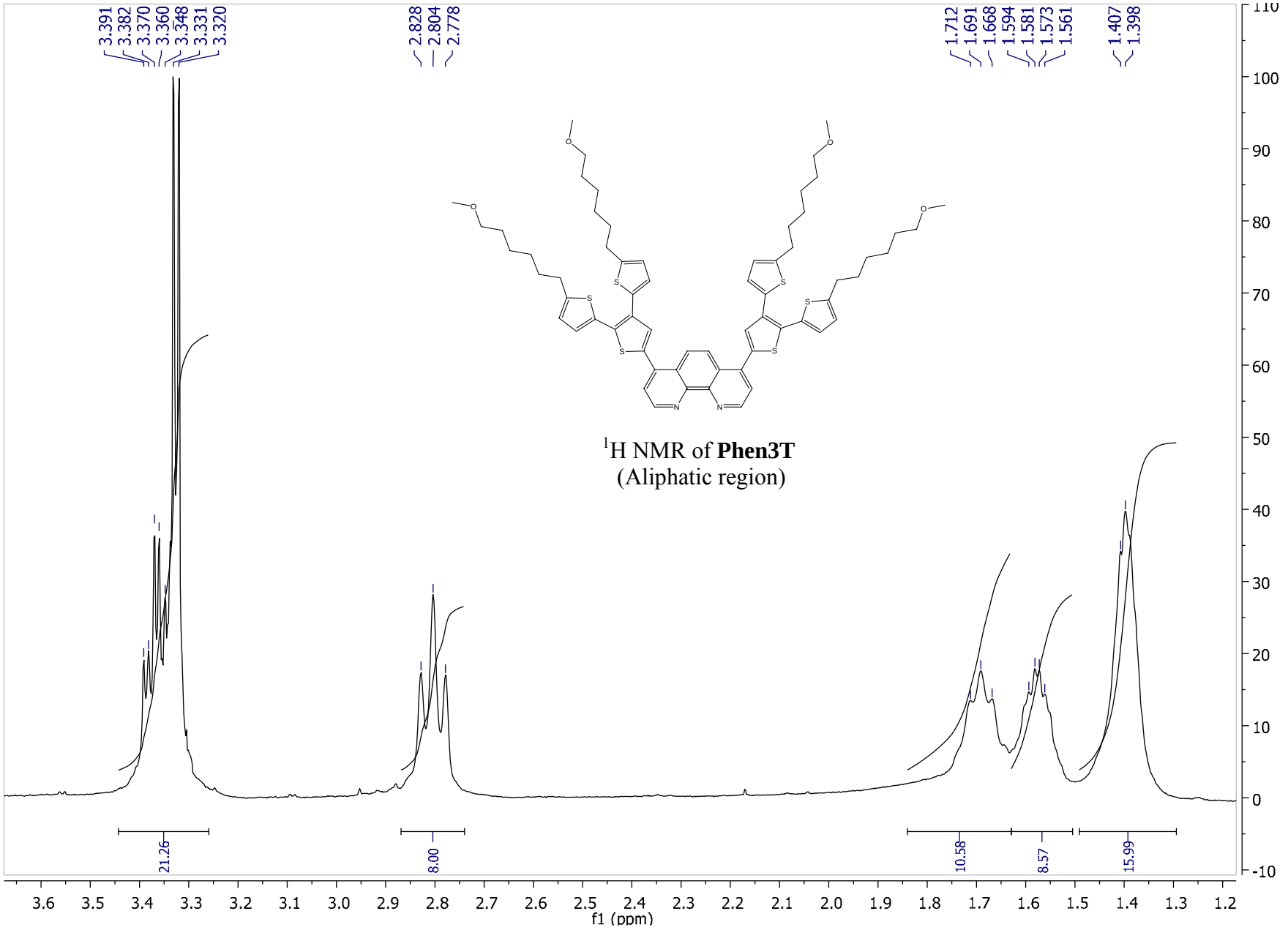
^{13}C NMR of **6TCbz-1**
(Full spectrum)



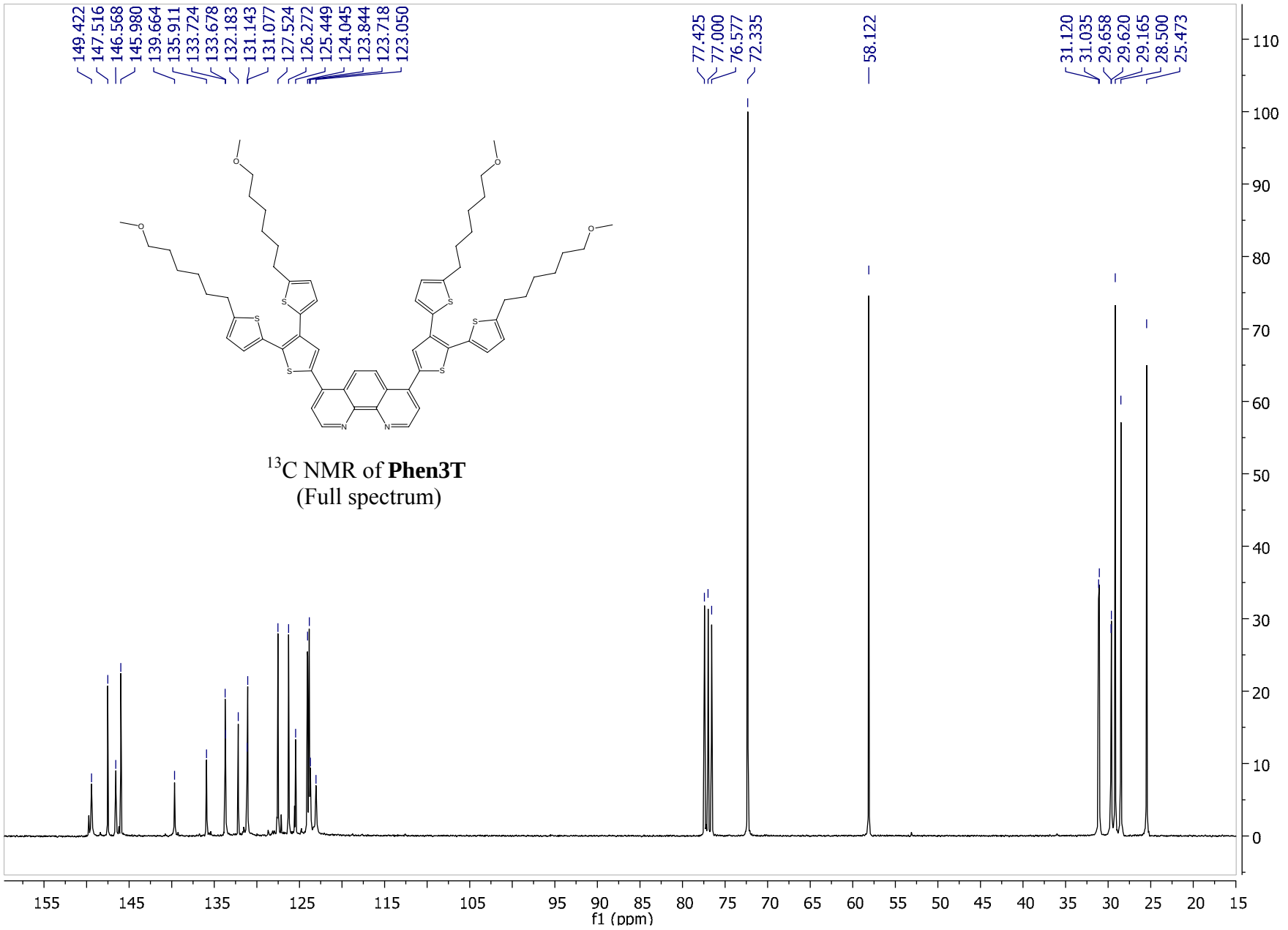
^{1}H NMR of **Phen3T**
(Full spectrum)



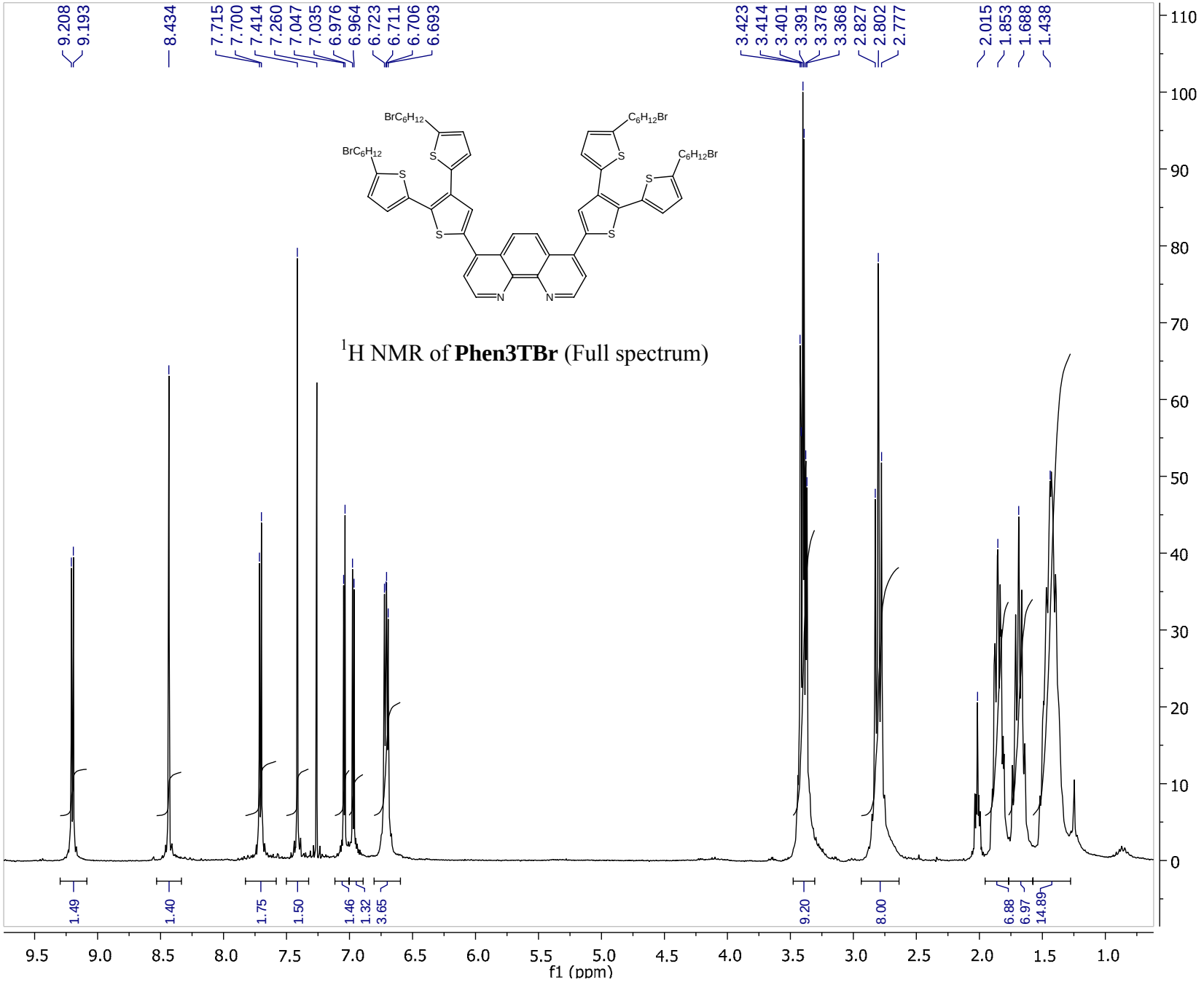
^{1}H NMR of **Phen3T**
(Aromatic region)



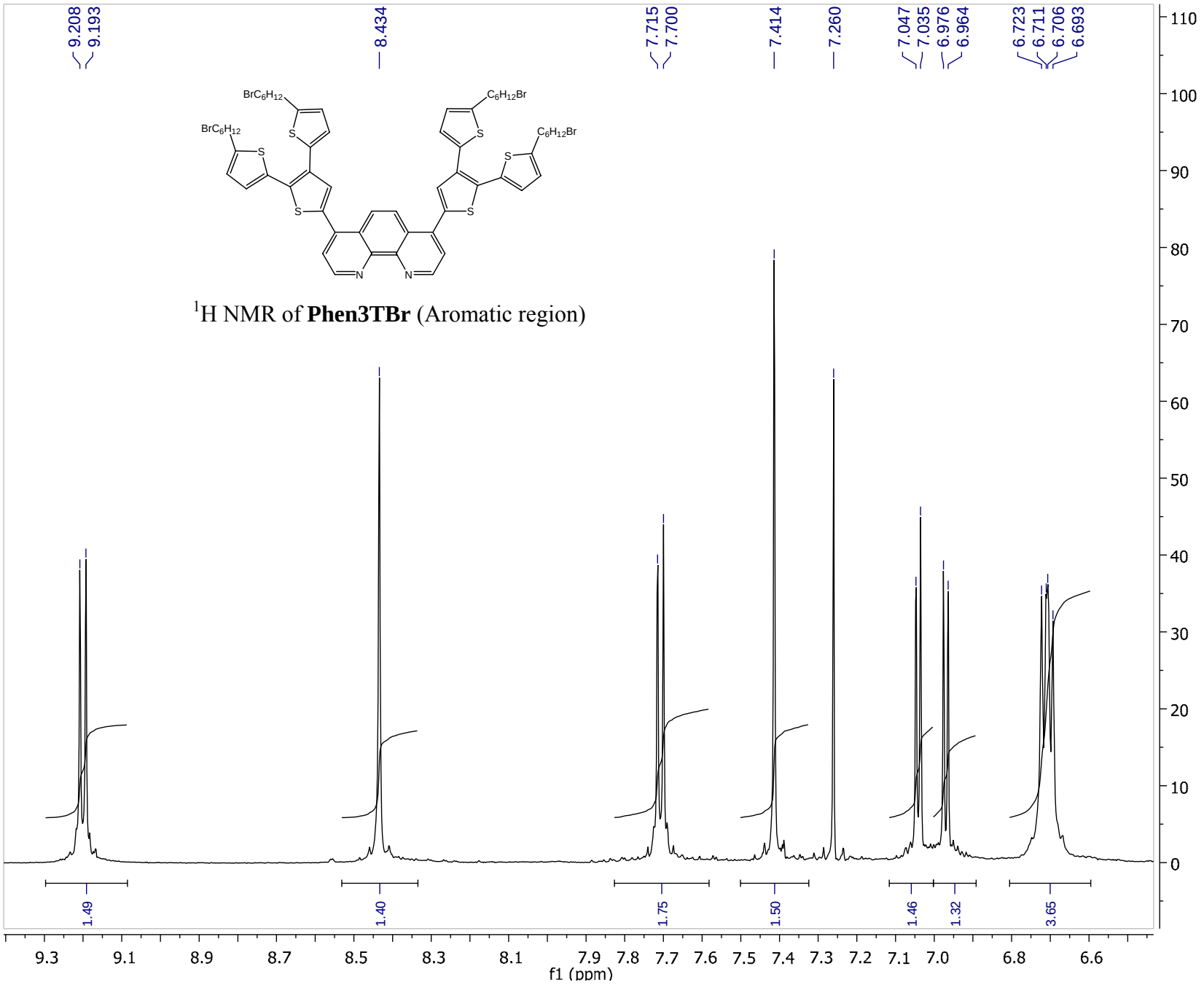
^{1}H NMR of **Phen3T**
(Aliphatic region)



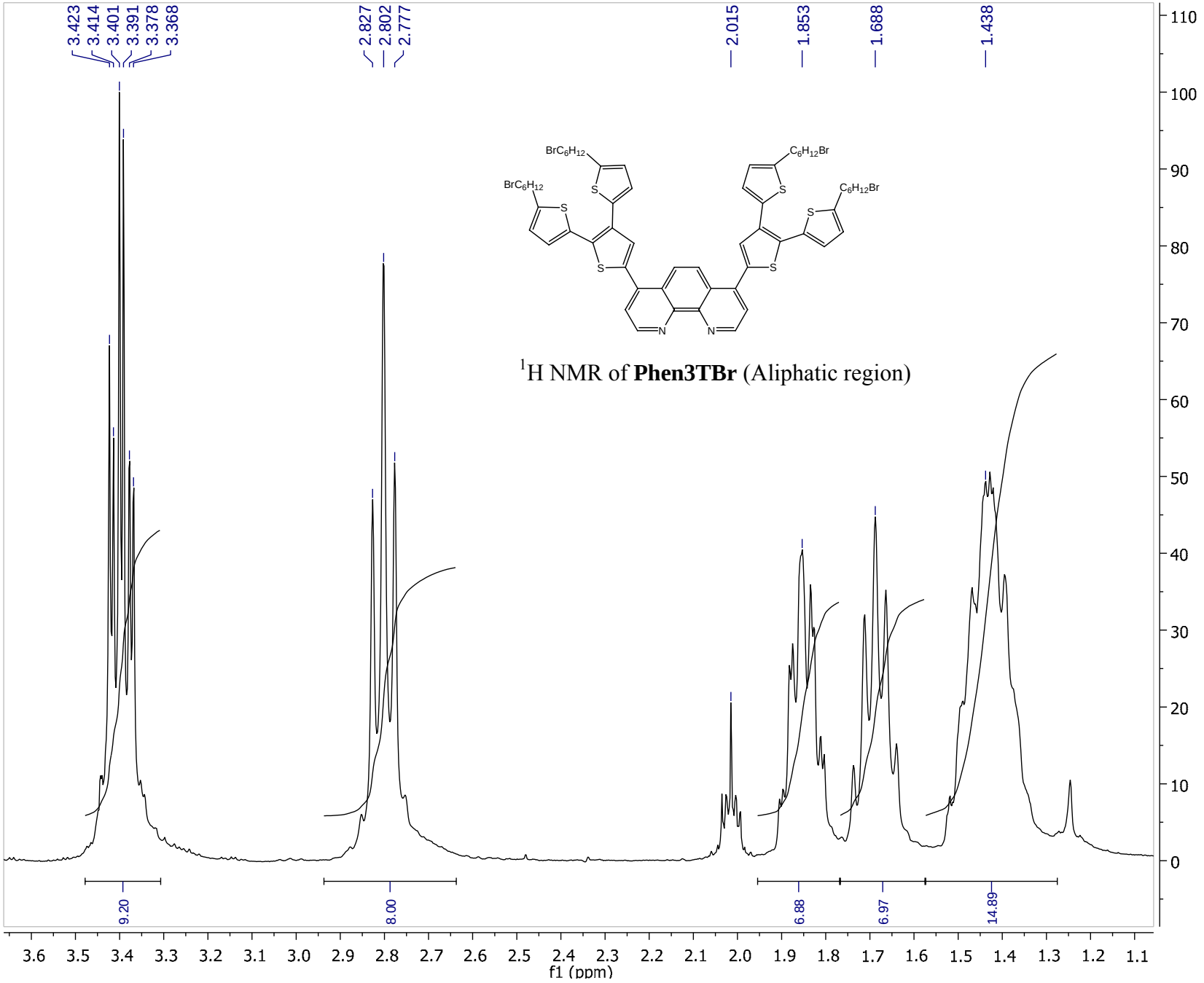
^{13}C NMR of **Phen3T**
(Full spectrum)



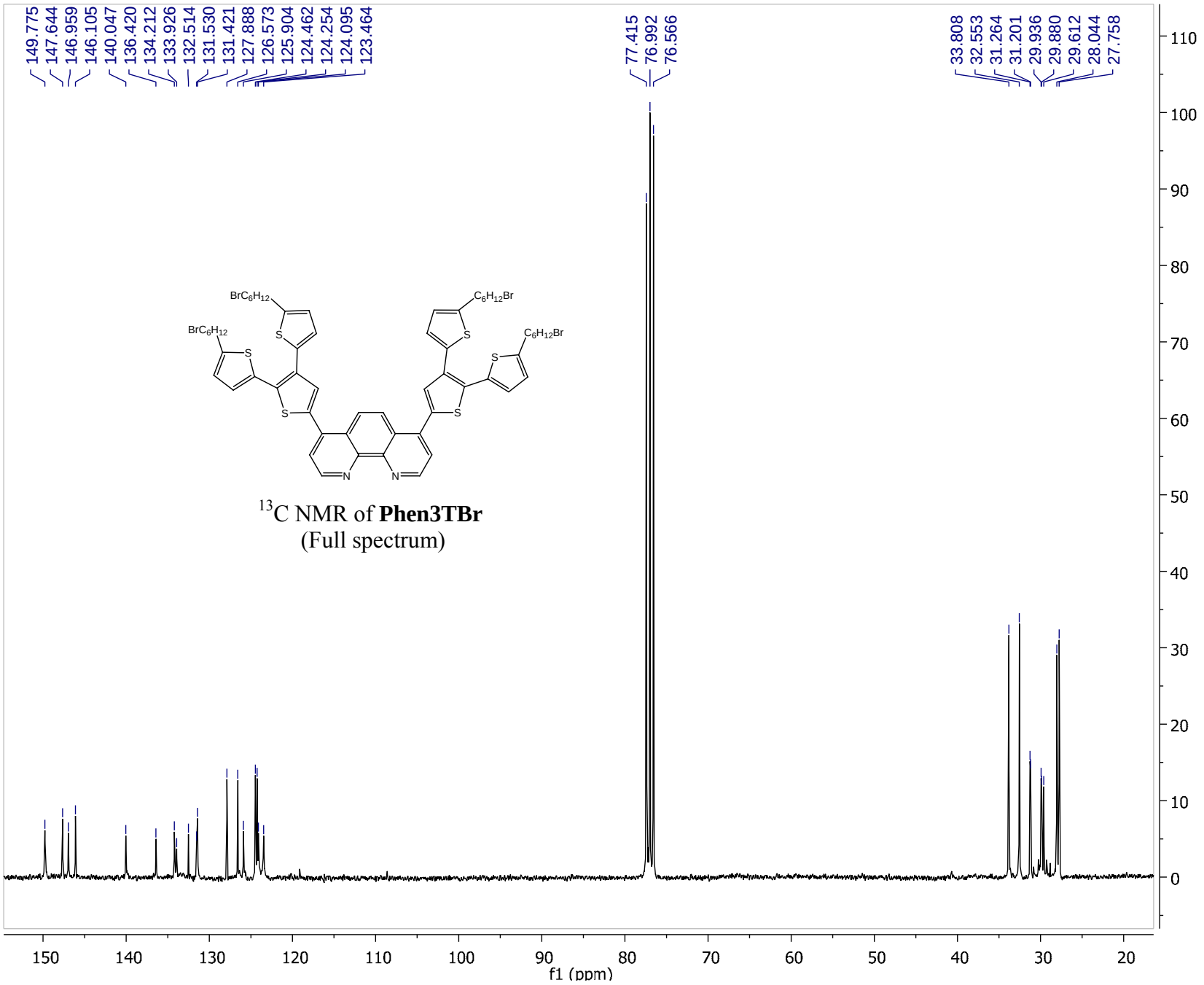
^{1}H NMR of **Phen3TBr** (Full spectrum)



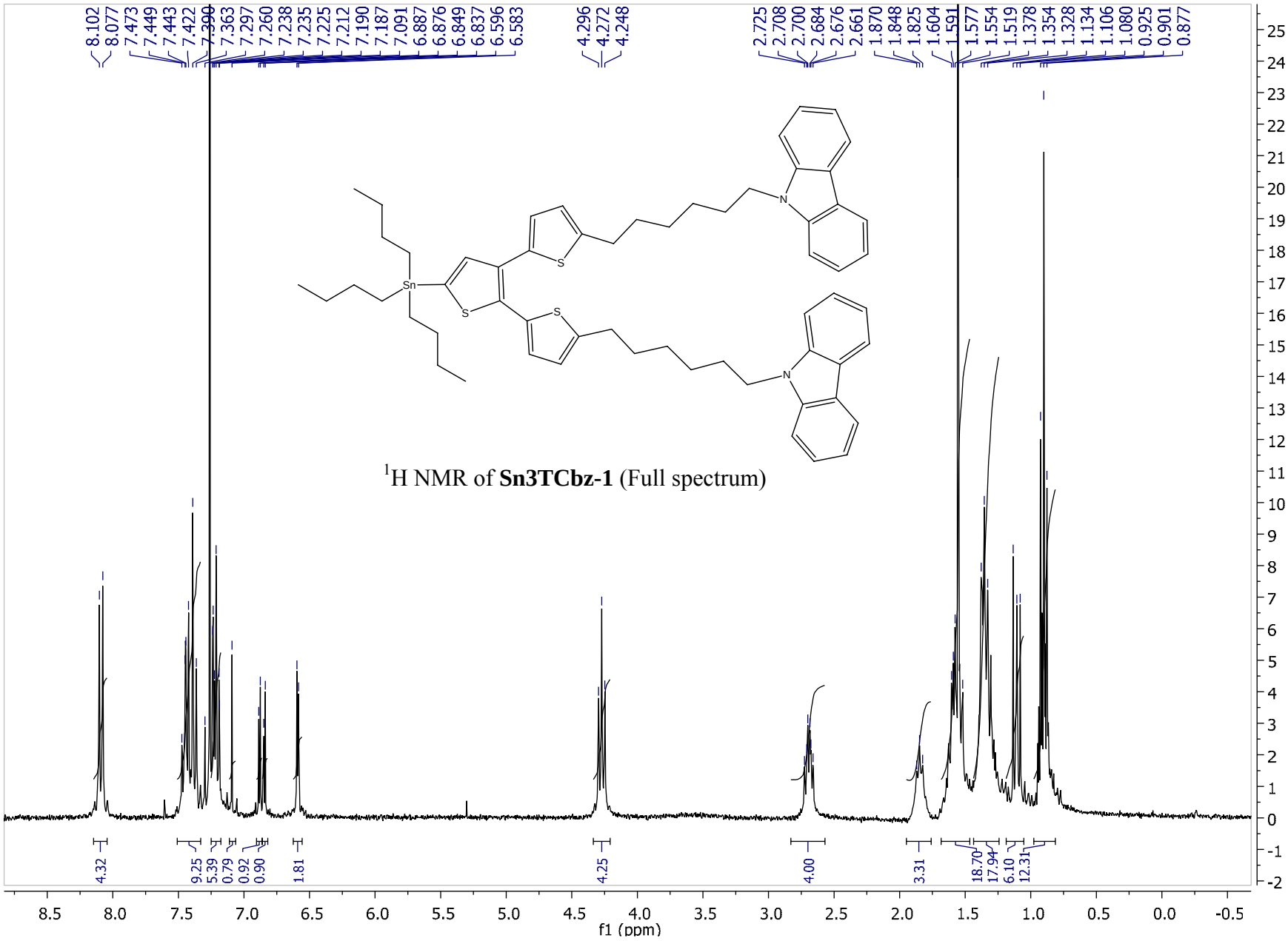
^{1}H NMR of **Phen3TBr** (Aromatic region)



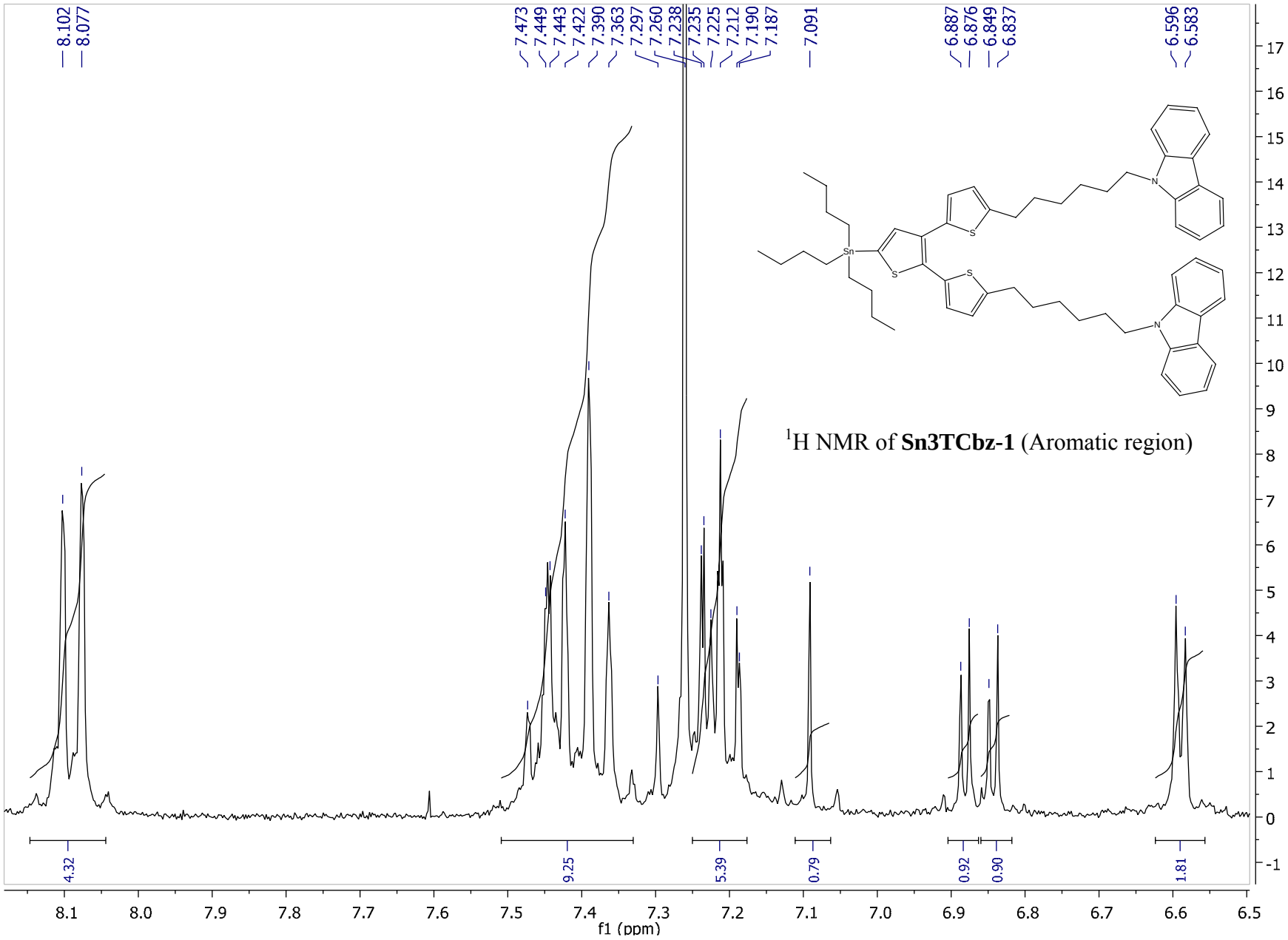
^{1}H NMR of **Phen3TBr** (Aliphatic region)



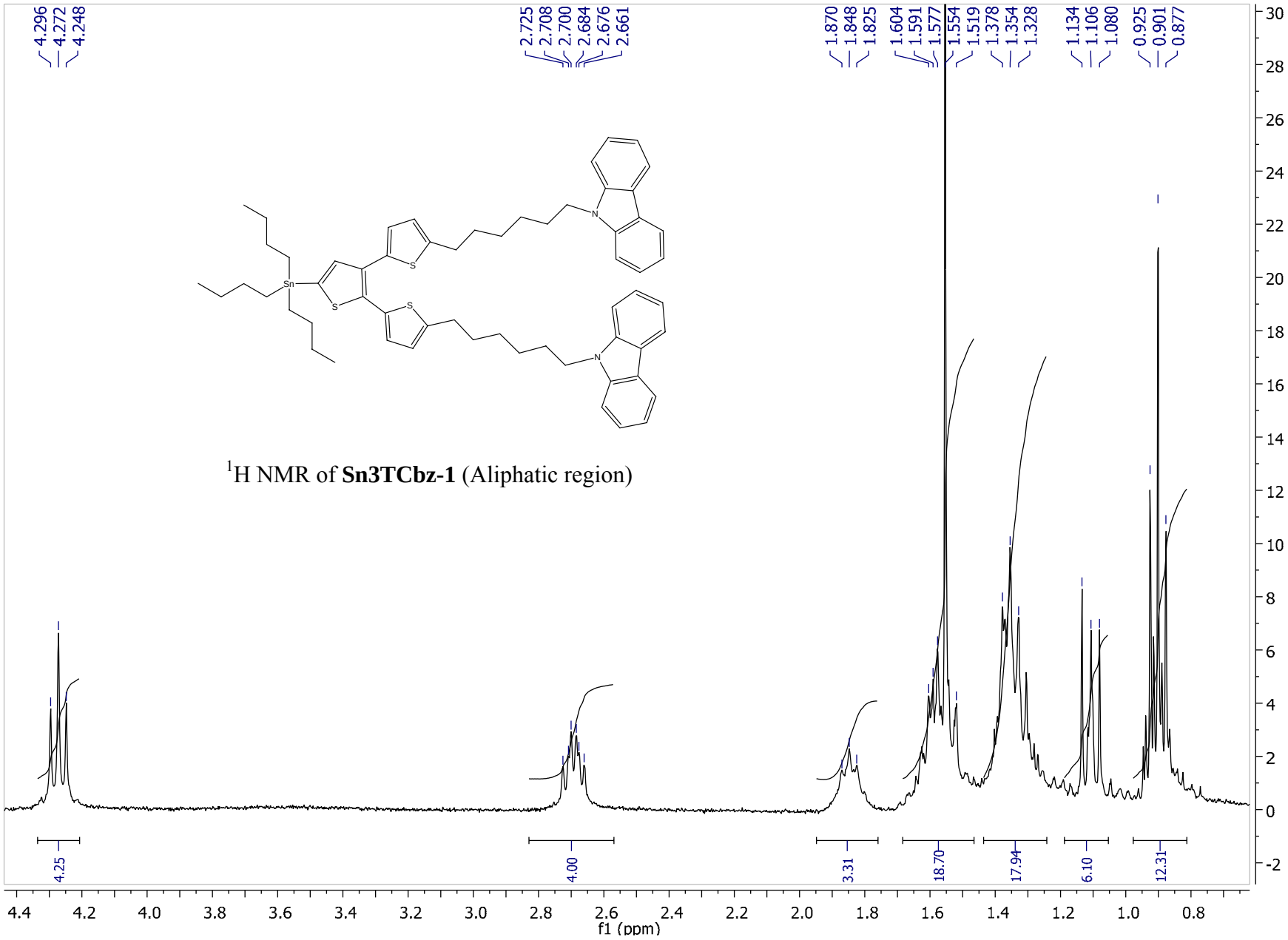
^{13}C NMR of **Phen3TBr**
(Full spectrum)



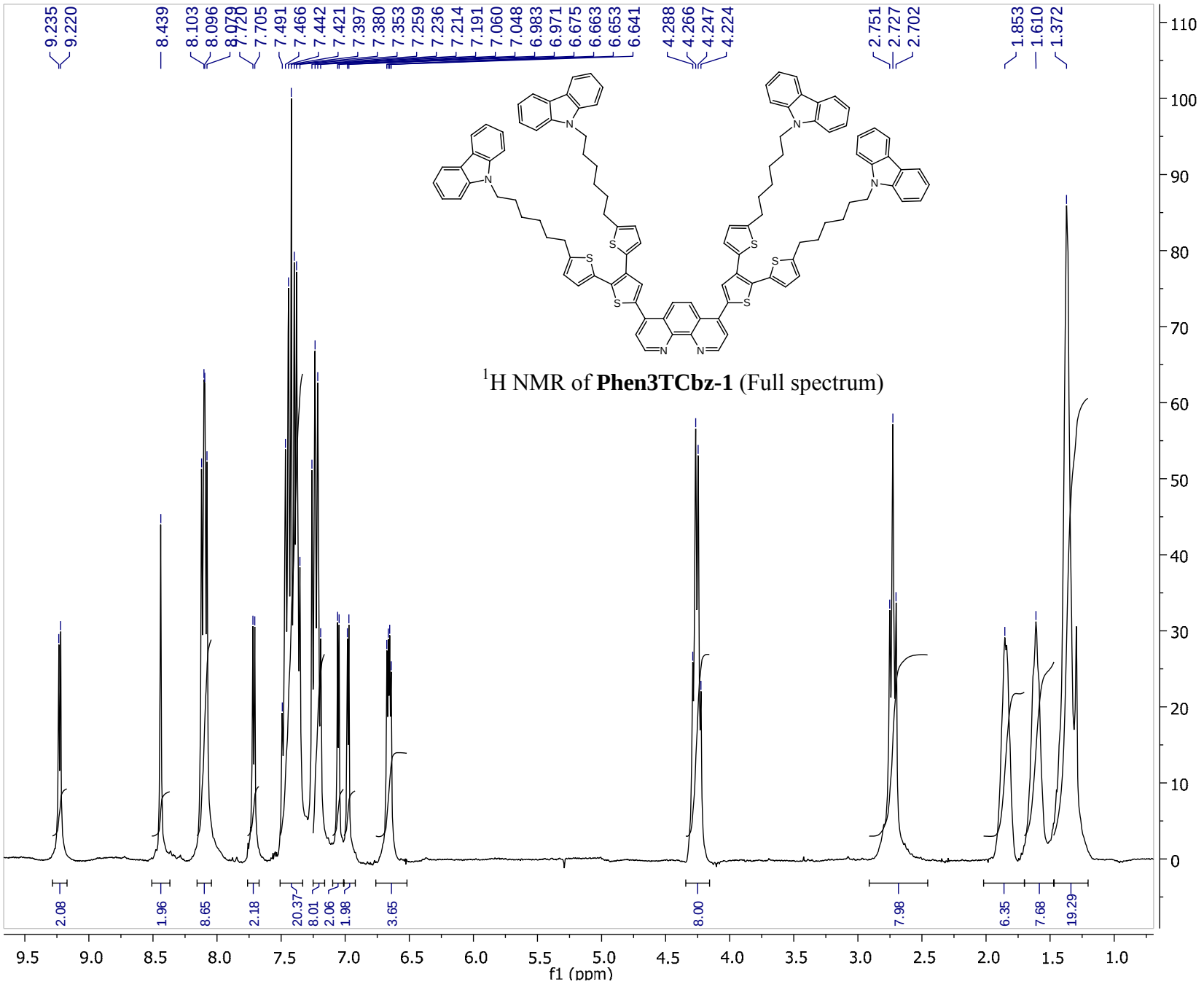
^{1}H NMR of **Sn3TCbz-1** (Full spectrum)



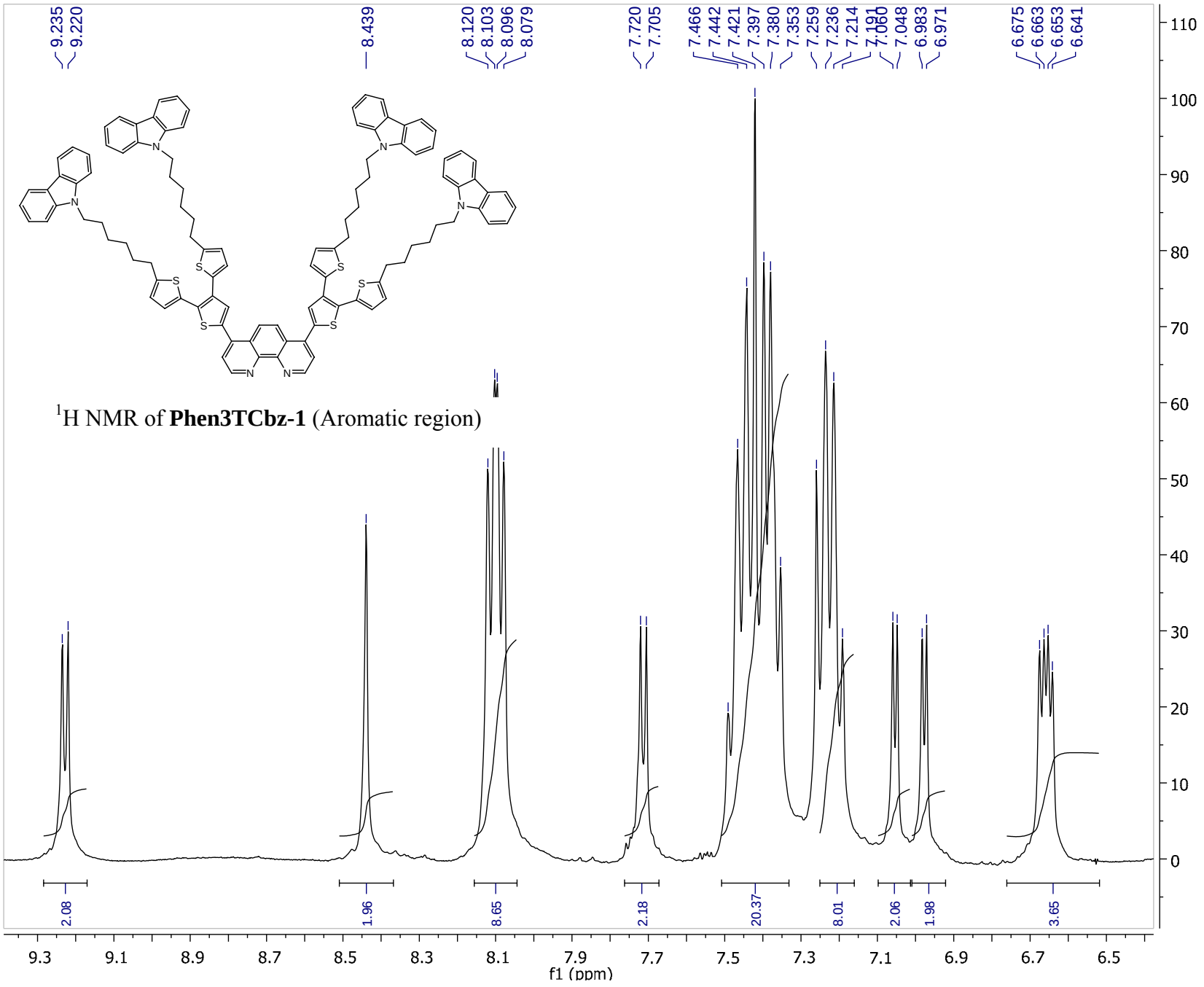
^{1}H NMR of **Sn3TCbz-1** (Aromatic region)



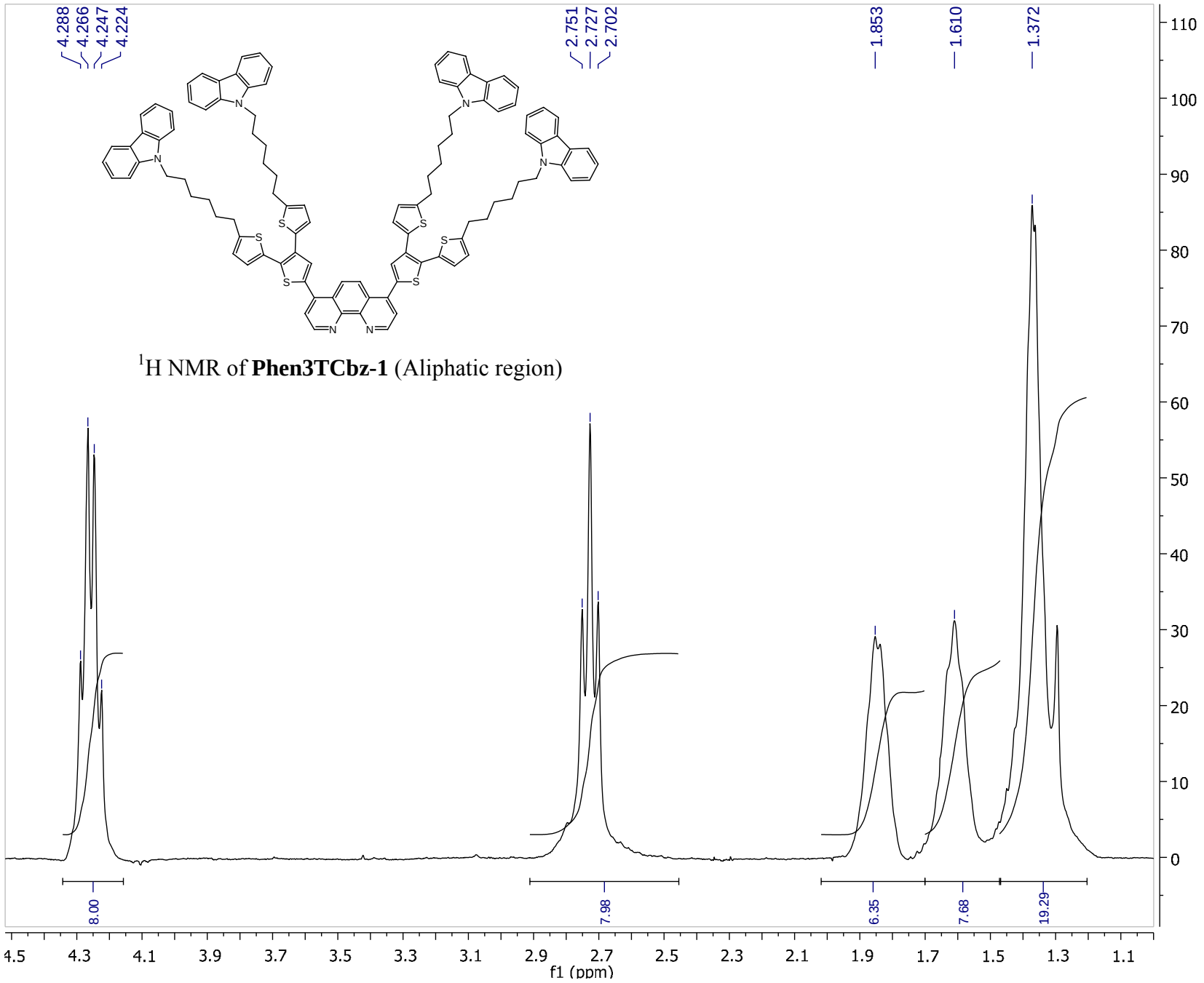
^{1}H NMR of **Sn3TCbz-1** (Aliphatic region)



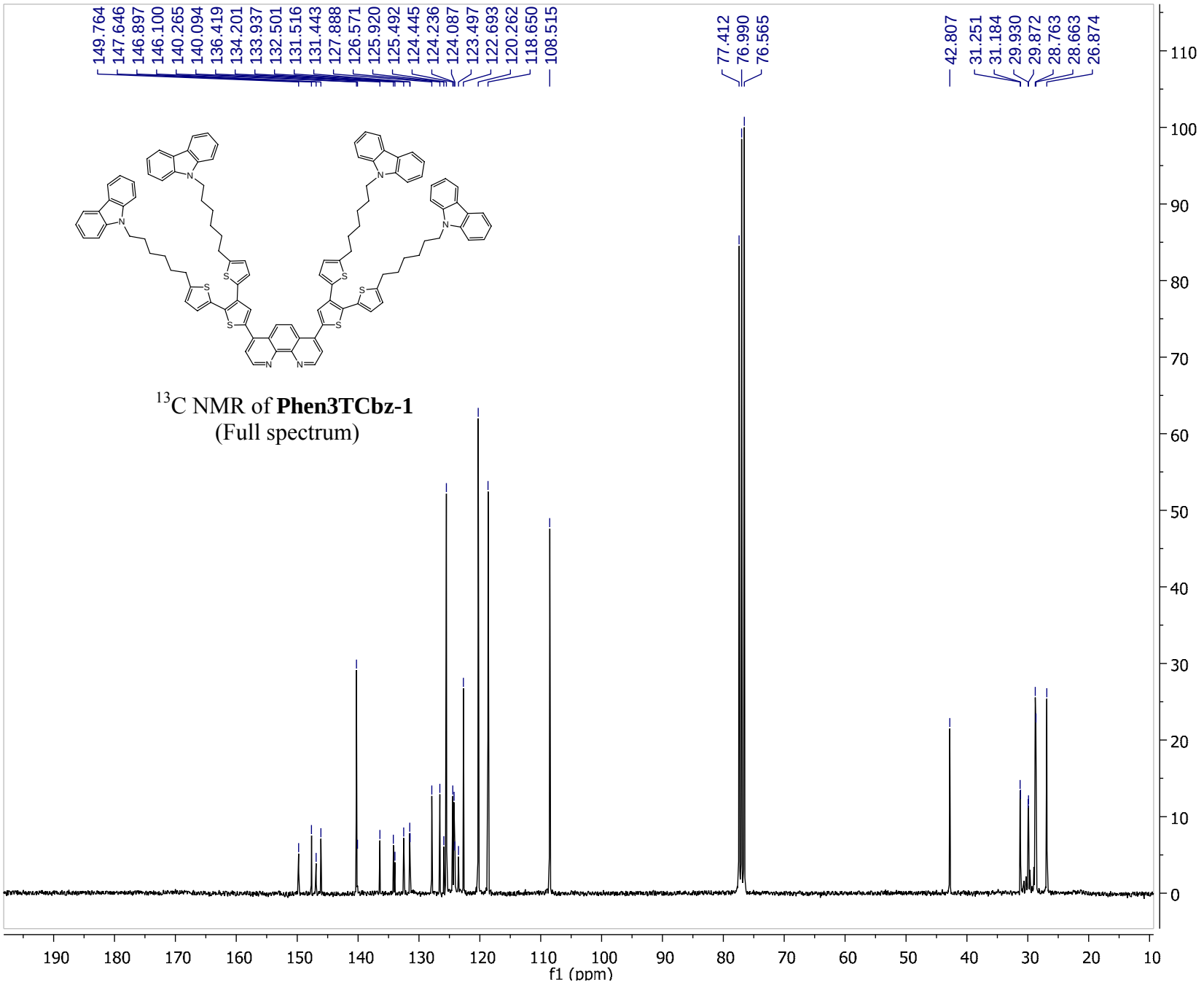
^{1}H NMR of **Phen3TCbz-1** (Full spectrum)



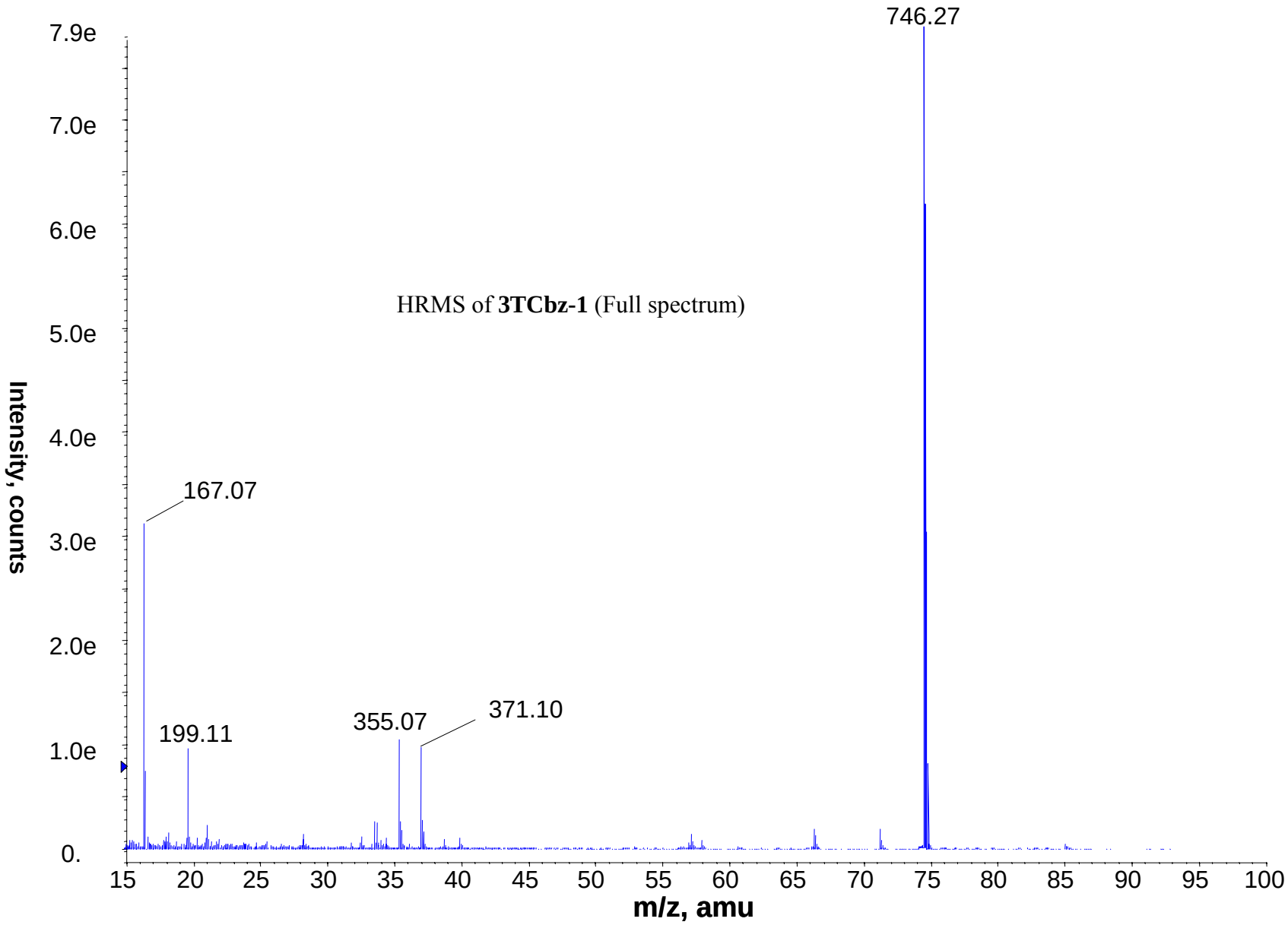
^{1}H NMR of **Phen3TCbz-1** (Aromatic region)

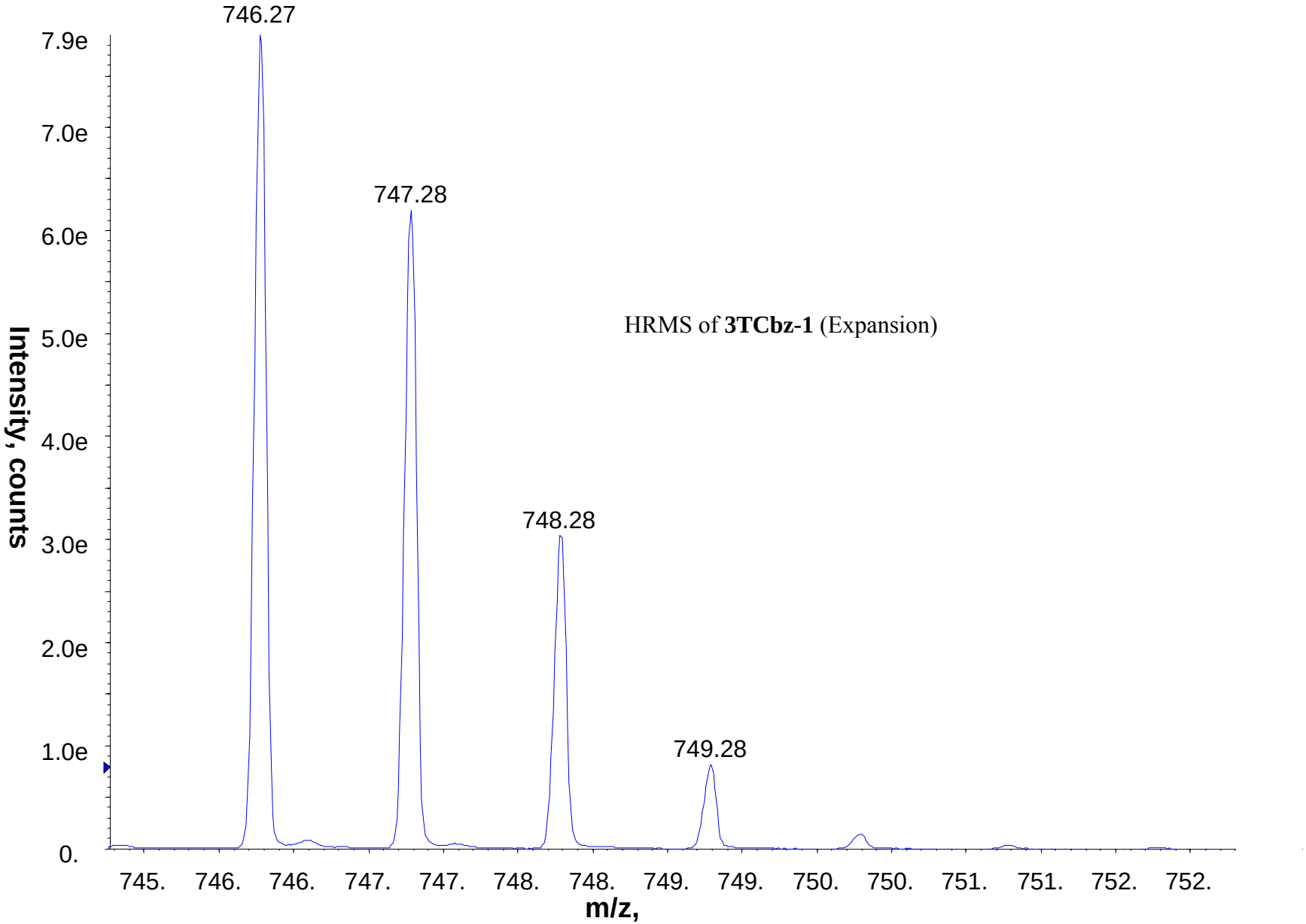


^{1}H NMR of **Phen3TCbz-1** (Aliphatic region)

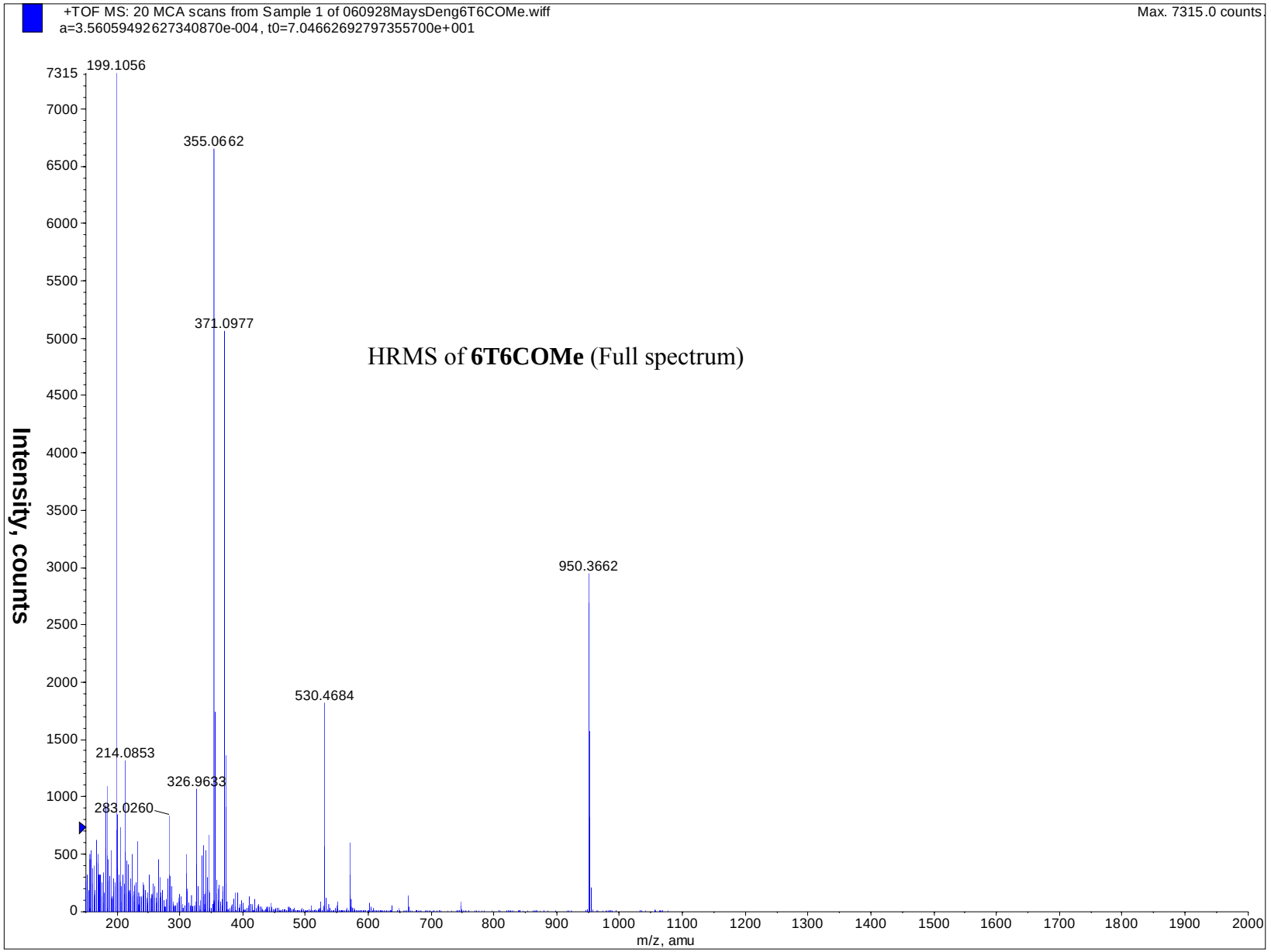


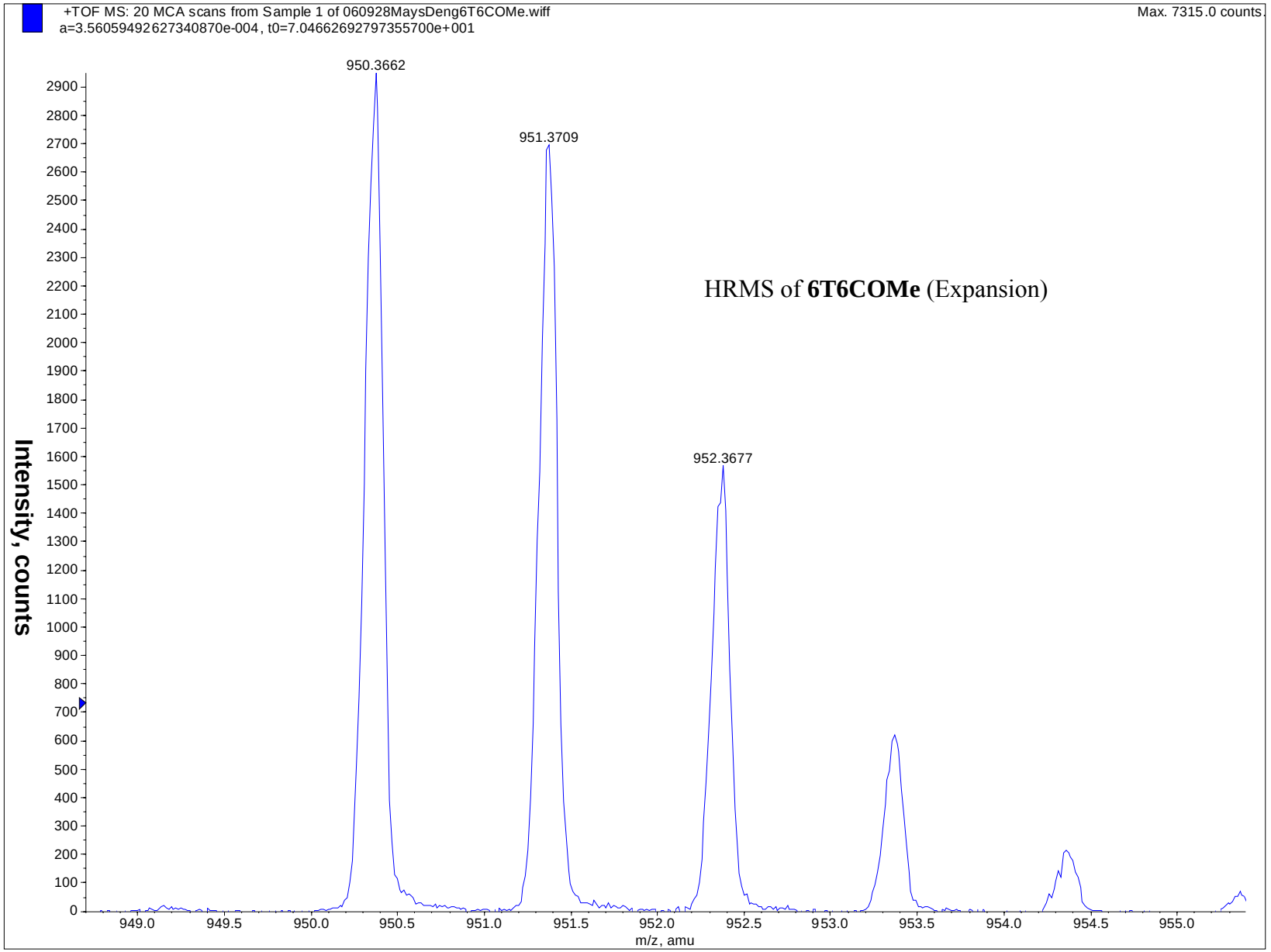
^{13}C NMR of **Phen3TCbz-1**
(Full spectrum)

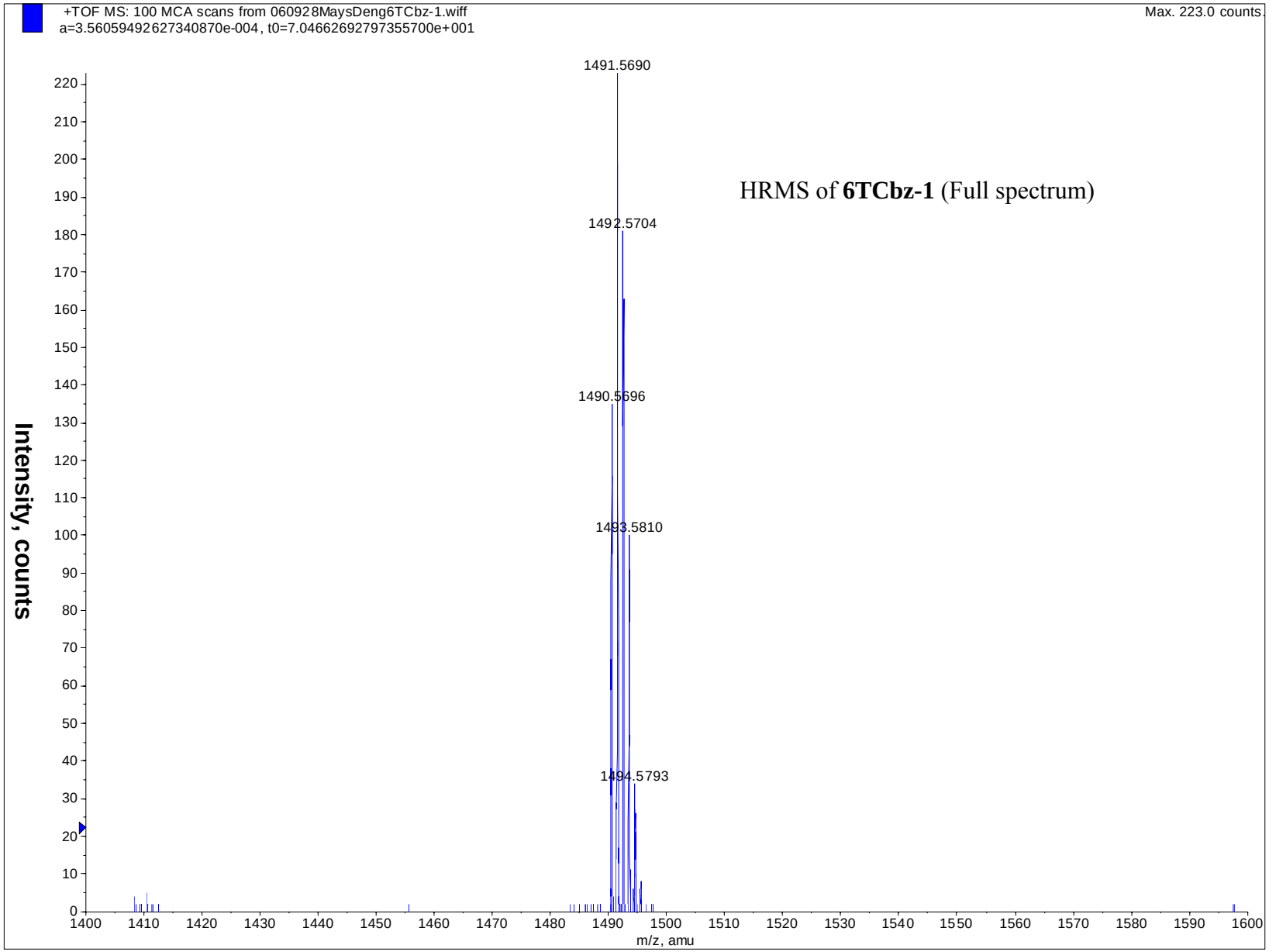




HRMS of **3TCbz-1** (Expansion)







HRMS of **6TCbz-1** (Full spectrum)