

Supporting information

for

Cu-Catalyzed and Iodine Mediated Synthesis of Thioaurones via In-situ C-S Bond Generation using Xanthate as Sulfur Surrogate

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1. General information

All the reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm) and visualized by UV fluorescence quenching using an appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra Synthesis Pvt. Ltd. and used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the reactions were carried out in temperature-controlled IKA magnetic stirrers. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz (100 MHz and 125 MHz for ¹³C) instrument. ¹H NMR spectra were reported relative to residual TMS (δ 0 ppm) and DMSO-d₆ (δ 2.50 ppm). ¹³C NMR spectral data were reported relative to CDCl₃ (δ 77.16 ppm) and DMSO-d₆ (δ 39.51 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Coupling constants (*J*) are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and were corrected with benzoic acid as reference. Infrared spectra were recorded on an FTIR 4000 Series Spectrometer using a dry KBr pellet. The wavenumbers of recorded IR signals are quoted in cm⁻¹. High-resolution mass spectra (HRMS) were recorded on Q-Tof of a Micro mass spectrometer.

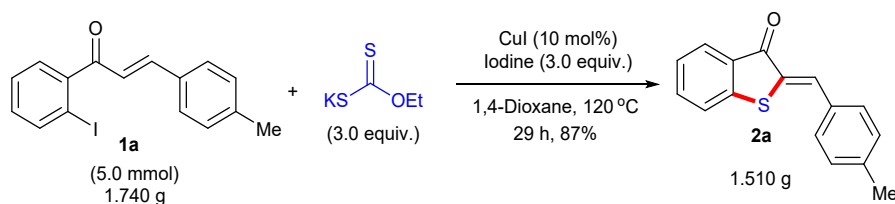
Solvents used for extraction and column chromatography were laboratory grade and used as received. Solvents for reactions were obtained from Fischer Scientific, India Pvt. Ltd. Various acetophenones were purchased from Alfa-aesar, Sigma-Aldrich Company, Avra synthesis, and Spectrochem Pvt Ltd. CuI, and iodine was purchased from Avra. Potassium ethyl xanthogenate was obtained from Sigma-Aldrich and used directly as received.

2.0. General procedure for the synthesis of benzo[*b*]thiophen-3(2*H*)-one derivative.

Under open atmosphere, (*E*)-2-iodochalcone (1.0 mmol), potassium ethyl xanthate (3.0 mmol), Iodine (3.0 mmol), and CuI (0.1 mmol) were successively added to an oven-dried long reaction tube (reaction tube length = 20-30 cm). Then, 1,4-dioxane (4 mL) was added and closed with a glass stopper and sealed with teflon. After that, the reaction tube was immersed in a 120 °C pre-heated oil bath. Then the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was brought to room temperature; saturated Na₂S₂O₃ solution was added and extracted with ethyl acetate (3×10 mL). Brine wash (1×20 mL) was given to the combined organic extractions and dried over anhydrous Na₂SO₄. Removal of solvent and silica gel column separation of the crude reaction mixture using hexanes and ethyl acetate mixture (90:10) afforded the corresponding (*Z*)-2-(4-methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2a): 92% yield (116 mg).

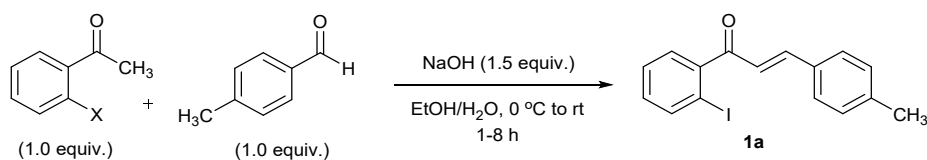
The same procedure was followed for the preparation of other benzo[*b*]thiophenone and thioindirubin 5.

2.1. General procedure for the scale-up synthesis.



Under open atmosphere, (*E*)-2-iodochalcone (5.0 mmol), potassium ethyl xanthate (15.0 mmol), iodine (15.0 mmol), and CuI (0.5 mmol) were successively added to an oven-dried round bottom flask. Then, 1,4-dioxane (20 mL) was added and connected with a reflux condenser. The round bottom flask was then immersed in a 120 °C pre-heated oil bath. Then the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was brought to room temperature; saturated Na₂S₂O₃ solution was added and extracted with ethyl acetate (3×50 mL). Brine wash (1×100 mL) was given to the combined organic extractions and dried over anhydrous Na₂SO₄. Removal of solvent and silica gel column separation of the crude reaction mixture using hexanes and ethyl acetate mixture (90:10) afforded the corresponding (*Z*)-2-(4-methylbenzylidene)benzo[*b*]thiophen-3(*2H*)-one (**2a**) in 87% yield (1.51 g).

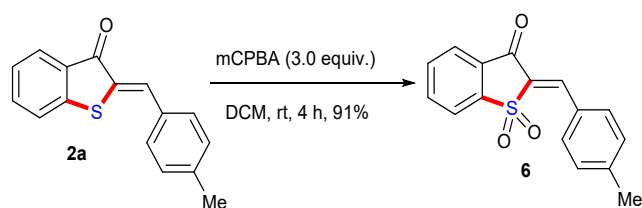
2.2. Typical procedure for the preparation of (*E*)-1-(2-iodophenyl)-3-(*p*-tolyl)-prop-2-en-1-one (**1a**). 2-Iodoacetophenone (**1a**) was synthesized using reported literature procedure.^{1,2}



A solution of NaOH (1.2 g, 30 mmol) in a mixture of water (6 mL) and ethanol (100 mL) was cooled to 0°C. 2-Iodoacetophenone (4.9g, 20 mmol) and benzaldehyde (2.04 mL, 20 mmol) were slowly added. The reaction mixture was allowed to warm to room temperature. After completion of the reaction, EtOH was removed under vacuum; water (100 mL) was added and extracted with EtOAc (3×25 mL). Organic extractions were combined and dried over anhydrous Na₂SO₄. The solvent was evaporated, and the crude material was purified by column chromatography (hexane/EtOAc 95:05 v/v) to yield the desired product. (*E*)-2-iodochalcone (**1a**): 91% yield; white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.48-7.42 (m, 3H), 7.41-7.38 (m, 1H), 7.38-7.35 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.19-7.13 (m, 1H), 7.03 (d, *J* = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 147.4, 145.0, 141.8, 140.1, 131.8, 131.3, 129.9, 128.8, 128.6, 128.1, 124.9, 92.3, 21.7.

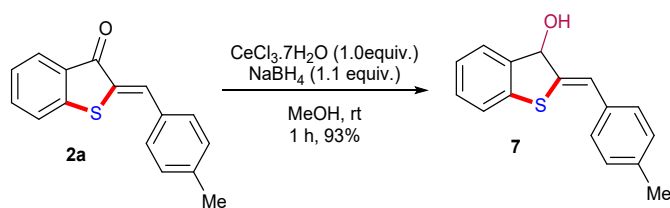
The same procedure was followed for the preparation of other 2-iodochalcones and 2-bromochalcones.

2.3. Preparation of (*Z*)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide (6).



(0.5 mmol) of **2a** was dissolved in dry DCM (3.5 mL) under an N₂ atmosphere in an oven-dried reaction tube with a pellet. To this mCPBA (1.5 mmol) was added and stirred at room temperature for 4h. After completion, the reaction mixture was diluted with DCM (10 mL) and washed with saturated NaHCO₃. The aqueous layer was extracted with DCM (10 mL) twice. Then combined organic layer was washed with brine solution and dried over anhydrous sodium sulfate, and concentrated in a vacuum. The residue was purified using column chromatography with hexanes/ethyl acetate (3:1 v/v) as eluent to afford the compound (**6**) in 89% yield. yellow solid; mp 182-184 °C; R_f = 0.53 (30% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, *J* = 7.6 Hz 1H), 8.09-8.04 (m, 3H), 8.03 (s, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 179.1, 145.6, 144.5, 136.6, 134.2, 134.0, 133.9, 132.5, 130.4, 130.0, 129, 125.0, 121.6, 22.1; FTIR (KBr) 2985, 2254, 1638, 1597, 1287, 734 cm⁻¹; HRMS (*m/z*) calculated for C₁₆H₁₃O₃S [M+H]⁺ : 285.0585; found: 285.0588.

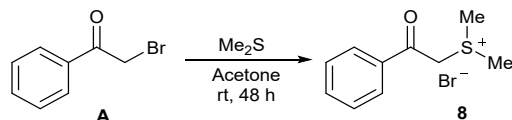
2.4. Preparation of (*Z*)-2-(4-methylbenzylidene)-2,3-dihydrobenzo[*b*]thiophen-3-ol (7).



To a stirred solution of α,β -unsaturated ketone **2a** (1.0 mmol) in methanol (5 mL) was added CeCl₃·7H₂O (373 mg, 1.0 mmol), the solution was cooled to 0 °C, and NaBH₄ (38 mg, 1.1 mmol) was added. The mixture was stirred at room temperature for 1 h before water was added and extracted with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄, and the solvents evaporated under a vacuum. Pure compound **7** was obtained in 93% yield after flash chromatography on silica gel. white solid ; mp 66-67 °C; R_f = 0.47 (20% ethyl acetate in hexanes); FTIR (KBr) 3397, 3055, 2921, 1655, 1613, 1456, 1306, 1250, 1157, 1117, 823, 750 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32-7.23 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.05 (s, 1H), 2.58 (s, 1H), 2.35 (s, 3H); ¹³C NMR

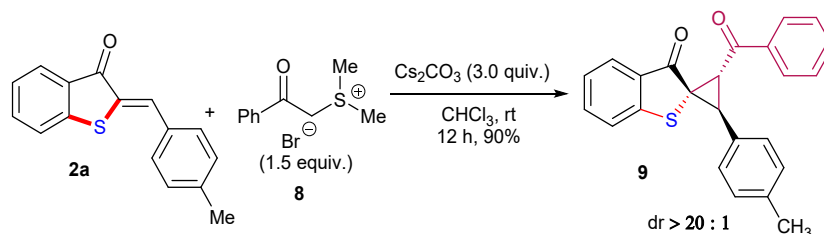
(CDCl₃, 125 MHz) δ 149.1, 140.0, 139.8, 139.6, 138.2, 129.4, 126.5, 124.4, 124.3, 123.7, 122.5, 121.2, 73.0, 21.3; HRMS (m/z) [M+NH₄]⁺ calculated for C₁₆H₁₈NOS : 272.1109; found: 272.1128.

2.5.1 Generation of α -keto-stabilized sulfonium ylide (**8**).³



To a 0.5 M solution of bromoketone **A** (5.0 mmol, 1.0 equiv.) in acetone dimethyl sulfide (440 μ L, 6.0 mmol, 1.2 equiv.) was added, and the mixture was stirred for 48 h at rt. Then, the precipitate of sulfonium salt **8** was separated from the solution, washed with acetone and dried under reduced pressure to give pure sulfonium salt **8**, which was readily converted to the corresponding sulfonium ylides. ¹H NMR (CDCl₃, 500 MHz) δ 8.03 (d, J = 7.5 Hz, 2H), 7.78 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.5 Hz, 2H), 5.64 (s, 2H), 3.03 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 191.4, 135.1, 133.9, 129.2, 128.7, 52.9, 24.6.

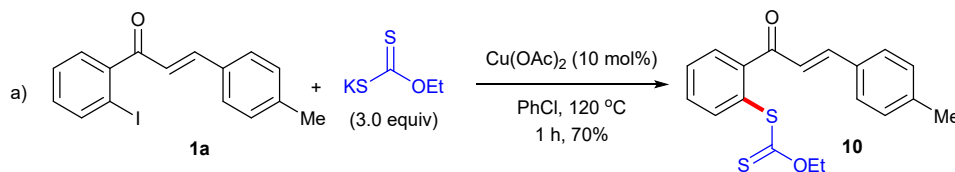
2.5.2 Preparation of (2*S*,2'*S*,3'*S*)-2'-benzoyl-3'-(*p*-tolyl)-3H-spiro[benzo[*b*]thiophene-2,1'-cyclopropan]-3-one (**9**).



General procedure for the synthesis of **9**. Under Ar atmosphere, to a solution of **2a** (0.5 mmol, 1.0 equiv.) in CHCl₃ 5 mL was added **8** (1.0 mmol, 1.5 equiv.), and Cs₂CO₃ (1.5 mmol, 3.0 equiv.). The reaction mixture was stirred at rt for 16 h. After the reaction was completed, the reaction mixture was extracted with CH₂Cl₂ (10 mL \times 3). The combined organic layer was dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether=1:5) to give the desired products **9** in 90% yield. Yellow solid ; mp 60-62 $^{\circ}$ C; R_f = 0.47 (10% ethyl acetate in hexanes); FTIR (KBr) 3060, 2923, 2856, 1670, 1592, 1450, 1287, 1216, 1014, 741, 714, 689, 543 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 8.15-8.09 (m, 2H), 7.69 (d, J = 7.5 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.56-7.50 (m, 3H), 7.45 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.21-7.17 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 4.41 (d, J = 16.0 Hz, 1H), 3.97 (d, J = 7.5 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 195.3, 194.7, 152.1, 137.6, 136.9, 135.1, 134.1, 130.9, 129.3, 129.2, 129.1, 129.0, 128.6,

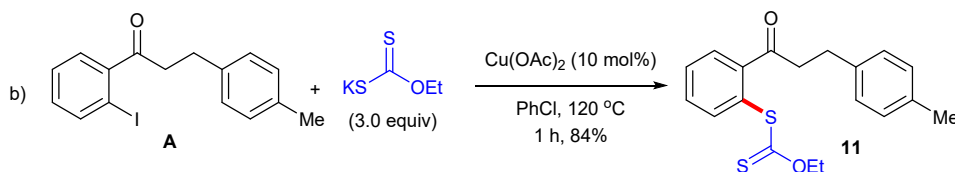
126.3, 124.8, 124.1, 51.3, 42.3, 37.6, 21.3; HRMS (m/z) [M+H]⁺ calculated for C₂₄H₁₉O₂S : 371.1093; found: 371.1106.

2.6. Preparation of (*E*)-*O*-Ethyl *S*-(2-(3-(*p*-tolyl)acryloyl)phenyl)carbonodithioate (**10**).



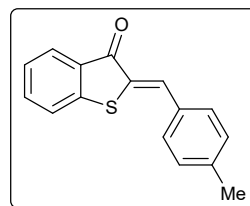
An oven-dried reaction tube was loaded with **1a** (0.5 mmol), potassium ethyl xanthate (1.0 mmol), and Cu(OAc)₂ (0.01 mmol), and then Chlorobenzene (2 mL) was added. The reaction tube was closed with a glass stopper and stirred at 120 °C for one hour. The reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with ethyl acetate, and the combined organic extractions were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by silica gel column using hexanes/ethyl acetate (85:15, v/v) mixture to afford the **10**.

The same procedure was followed for the preparation of Ethyl-*S*-(2-(3-(*p*-tolyl)propanoyl)phenyl) carbonodithioate **11**.

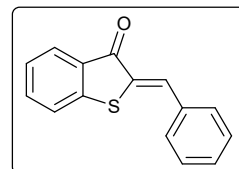


4.0. Experimental data.

(*Z*)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(*2H*)-one (2a**):**⁵ 92% yield (117 mg); bright yellow solid; mp 138-39 °C; *R*_f = 0.47 (5% ethyl acetate in hexanes); FTIR (KBr) 3001, 2912, 1678, 1593, 1273, 752 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.90-7.97 (m, 2H), 7.65-7.58 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.33-7.24 (m, 3H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 188.9, 146.2, 141.0, 135.3, 134.0, 131.7, 131.2, 130.7, 130.0, 129.4, 127.1, 125.7, 124.0, 21.8; HRMS (m/z) [M+Na]⁺ calculated for C₁₆H₁₂OSNa : 275.0507; found: 275.0505.

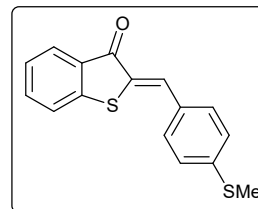


(*Z*)-2-Benzylidenebenzo[*b*]thiophen-3(*2H*)-one (2b**):**⁴ 70% yield (83 mg); bright yellow solid; mp 131-33 °C; *R*_f = 0.50 (5% ethyl acetate in hexanes); FTIR (KBr) 3057, 2985, 1681, 1566, 1264, 745 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.01-7.89 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.53-7.45 (m, 3H), 7.44-7.38

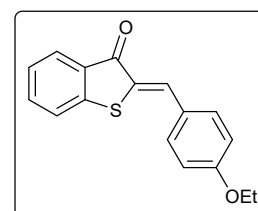


(m, 1H), 7.33-7.25 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.9, 146.3, 135.4, 134.4, 133.7, 131.1, 130.6, 130.4, 130.3, 129.2, 127.2, 125.8, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{10}\text{OSNa}$: 261.0350; found: 261.0345.

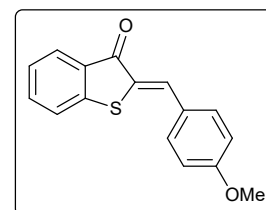
(Z)-2-(4-(Methylthio)benzylidene)benzo[*b*]thiophen-3(2H)-one (2c):⁶ 86% yield; (122 mg); bright yellow solid; mp 152-154 °C; R_f = 0.50 (10% ethyl acetate in hexanes); FTIR (KBr) 2993, 1678, 1585, 1273, 748 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.96-7.88 (m, 2H), 7.65-7.54 (m, 3H), 7.50 (d, J = 8.0 Hz, 1H), 7.34-7.25 (m, 3H), 2.53 (s, 3H); ^{13}C NMR, (CDCl_3 , 100 MHz) δ 188.8, 146.0, 142.6, 135.3, 133.4, 131.5, 130.7, 130.7, 129.3, 127.1, 126.0, 125.7, 124.0, 15.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{OS}_2\text{Na}$: 307.0227; found: 307.0220.



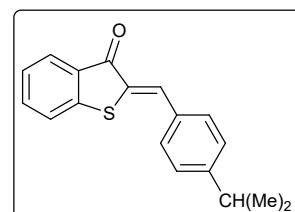
(Z)-2-(4-Ethoxybenzylidene)benzo[*b*]thiophen-3(2H)-one (2d): 89% yield (126 mg); bright yellow solid; mp 126-128 °C; R_f = 0.45 (15% ethyl acetate in hexanes); FTIR (KBr) 3026, 2980, 1674, 1592, 1262, 735 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (s, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.32-7.25 (m, 1H), 6.98 (d, J = 8.4 Hz, 2H), 4.10 (q, J = 6.8 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.7, 160.9, 146.1, 135.1, 134.0, 133.2, 130.9, 127.8, 127.1, 127.0, 125.6, 124.0, 115.2, 63.9, 14.8; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{SNa}$: 305.0611; found: 305.0612.



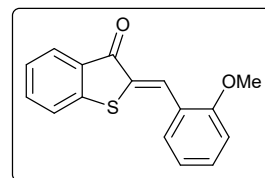
(Z)-2-(4-Methoxybenzylidene)benzo[*b*]thiophen-3(2H)-one (2e):⁴ 87% yield (117 mg); bright yellow solid; mp 153-54 °C; R_f = 0.42 (10% ethyl acetate in hexanes); FTIR (KBr) 3066, 2903, 1679, 1591, 1263, 733 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.99-7.88 (m, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.32-7.25 (m, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.8, 161.4, 146.1, 135.1, 133.9, 133.2, 130.9, 127.9, 127.1, 127.1, 125.6, 124.0, 114.8, 55.6; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{SNa}$: 291.0456; found: 291.0451.



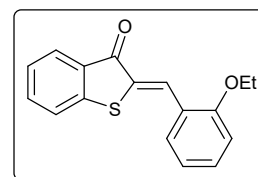
(Z)-2-(4-Isopropylbenzylidene)benzo[*b*]thiophen-3(2H)-one (2f): 56% yield (78 mg); bright yellow solid; mp 54-56 °C; R_f = 0.55 (5% ethyl acetate in hexanes); FTIR (KBr) 3025, 2961, 1678, 1593, 1282, 740 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.98-7.93 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 2.97 (hep, J = 6.8 Hz, 1H), 1.29 (d, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.9, 151.9, 146.3, 135.3, 134.0, 132.1, 131.4, 130.8, 129.5, 127.4, 127.2, 125.7, 124.1, 34.4, 23.9; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{16}\text{OSNa}$: 303.0820; found: 303.014.



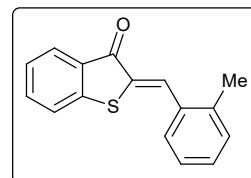
(Z)-2-(2-Methoxybenzylidene)benzo[b]thiophen-3(2H)-one (2g):⁴ 72% yield (97 mg); bright yellow solid; mp 153-54 °C; $R_f = 0.52$ (20% ethyl acetate in hexanes); FTIR (KBr) 3031, 2927, 1680, 1589, 1254, 733 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.43 (s, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 2H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.7, 159.3, 146.4, 135.2, 132.0, 130.9, 130.3, 130.0, 128.7, 127.1, 125.6, 124.0, 123.7, 120.9, 111.1, 55.7; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{SNa}$: 291.0456; found: 291.0457.



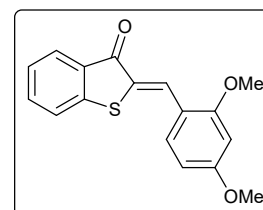
(Z)-2-(2-Ethoxybenzylidene)benzo[b]thiophen-3(2H)-one (2h): 71% yield (101 mg); bright yellow solid; mp 92-94 °C; $R_f = 0.52$ (10% ethyl acetate in hexanes); FTIR (KBr) 3021, 2990, 1680, 1588, 1248, 736 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.46 (s, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.32-7.25 (m, 1H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H) 4.13 (q, $J = 6.8$ Hz, 2H), 1.50 (t, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.8, 158.8, 146.4, 135.1, 131.9, 131.0, 130.2, 130.0, 129.0, 127.1, 125.5, 124.0, 123.8, 120.7, 112.0, 64.3, 14.9; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{SNa}$: 305.0612; found: 305.0603.



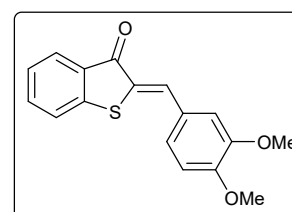
(Z)-2-(2-Methylbenzylidene)benzo[b]thiophen-3(2H)-one (2i):⁵ 94% yield (119mg); bright yellow solid; mp 120-122 °C; $R_f = 0.50$ (5% ethyl acetate in hexanes); FTIR (KBr) 3030, 2951, 1674, 1587, 1282, 734 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.20 (s, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.79-7.74 (m, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.34-7.25 (m, 4H), 2.50 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.6, 146.7, 139.8, 135.4, 133.4, 131.6, 131.4, 131.0, 130.9, 130.2, 128.9, 127.9, 126.5, 125.7, 124.1, 20.3; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{OSNa}$: 275.0506; found: 275.0498.



(Z)-2-(2,4-Dimethoxybenzylidene)benzo[b]thiophen-3(2H)-one (2j):⁶ 83% yield (124 mg); bright yellow solid; mp 168-170 °C; $R_f = 0.39$ (20% ethyl acetate in hexanes); FTIR (KBr) 3001, 2834, 1678, 1597, 1265, 752 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.40 (s, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.30-7.25 (m, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.48 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.6, 163.3, 161.0, 146.2, 134.8, 131.5, 131.3, 128.8, 127.8, 127.0, 125.4, 123.9, 116.9, 105.5, 98.5, 55.8, 55.7; ; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{SNa}$: 321.0561; found: 321.0553.



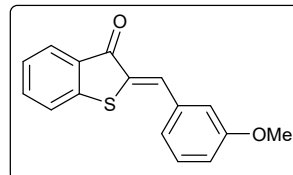
(Z)-2-(3,4-Dimethoxybenzylidene)benzo[b]thiophen-3(2H)-one (2k):⁷ 91% yield (135 mg); bright yellow solid; mp 155-157 °C; $R_f = 0.50$ (30% ethyl acetate in hexanes); FTIR (KBr) 3006, 2963, 1658, 1593, 1271, 745 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400



MHz) δ 7.96-7.90 (m, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.34-7.23 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.6, 151.2, 149.4, 146.0, 135.1, 134.1, 130.9, 128.1, 127.4, 127.1, 125.8, 125.7, 124.0, 113.2, 111.5, 56.2, 56.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{SNa}$: 321.0561; found: 321.0558.

(Z)-2-(3-Methoxybenzylidene)benzo[*b*]thiophen-3(2H)-one (2l): 81% yield (109 mg); bright yellow solid; mp 83-85 °C; R_f = 0.44 (10% ethyl acetate in hexanes); FTIR (KBr)

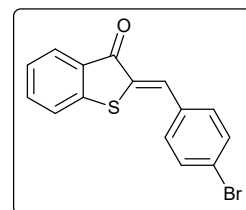
3064, 2960, 1676, 1592, 1273, 738 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.96-7.91 (m, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.33-7.27 (m, 2H), 7.24 (s, 1H), 6.98 (d, J = 8.0 Hz,



1H), 3.88 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.8, 160.1, 146.2, 135.7, 135.5, 133.7, 130.7, 130.6, 130.2, 127.2, 125.8, 124.0, 123.9, 116.5, 115.6, 55.5; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{SNa}$: 291.0456; found: 291.0456.

(Z)-2-(4-Bromobenzylidene)benzo[*b*]thiophen-3(2H)-one (2m):⁴ 95% yield (132 mg); bright yellow solid; mp 168-169 °C; R_f = 0.42 (10% ethyl acetate in hexanes); FTIR (KBr) 3001, 2956, 1684, 1594,

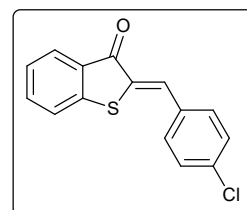
1282, 732 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.94 (d, J = 7.6 Hz, 1H), 7.87 (s, 1H), 7.64-7.53 (m, 5H), 7.50 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.7, 145.9, 135.6, 133.4, 132.5, 132.4, 132.2,



131.1, 130.4, 127.3, 126.0, 124.7, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{BrOSNa}$: 338.9455; found: 338.9440.

(Z)-2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3(2H)-one (2n):⁴ 88% yield (120 mg); bright yellow solid; mp 178-180 °C; R_f = 0.39 (5% ethyl acetate in hexanes); FTIR (KBr)

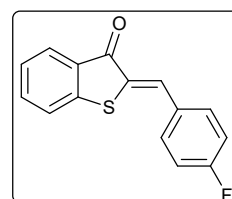
3065, 2932, 1684, 1579, 1282, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.92 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.63-7.55 (m, 3H), 7.48 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 8.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz)



δ 188.6, 145.9, 136.3, 135.6, 132.9, 132.2, 132.1, 130.9, 130.4, 129.5, 127.3, 125.9, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{ClOSNa}$: 273.0141; found: 273.0148.

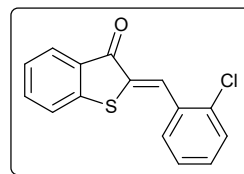
(Z)-2-(4-Fluorobenzylidene)benzo[*b*]thiophen-3(2H)-one (2o):⁴ 63% yield (80 mg); bright yellow solid; mp 166-168 °C; R_f = 0.52 (10% ethyl acetate in hexanes); FTIR (KBr) 3044, 1682, 1592, 1281,

737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.00-7.87 (m, 2H), 7.75-7.64 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 8.4 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.7, 163.6 (2C) (d, J = 251 Hz), 146.0, 135.5, 133.1(2C) (d, J = 8.0 Hz), 132.4, 130.7 (2C) (d, J = 3.0 Hz),

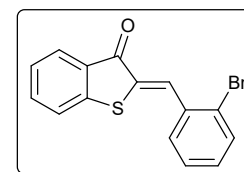


130.5, 130.0, 127.2, 125.9, 124.1, 116.5 (2C) (d, J = 22 Hz); HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{OFNa}$: 279.0256; found: 279.0261.

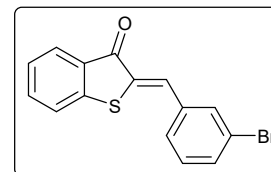
(Z)-2-(2-Chlorobenzylidene)benzo[b]thiophen-3(2H)-one (2p):⁴ 84% yield (114 mg); bright yellow solid; mp 147-149 °C; R_f = 0.56 (10% ethyl acetate in hexanes); FTIR (KBr) 3063, 2921, 1680, 1588, 1281, 735 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.32 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.41-7.28 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.4, 146.1, 136.7, 135.6, 133.0, 132.8, 131.0, 130.5, 130.5, 130.2, 129.4, 127.4, 127.2, 125.9, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{ClOSNa}$: 294.9960; found: 294.9950.



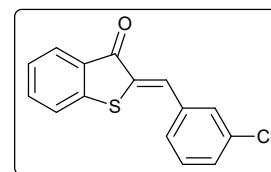
(Z)-2-(2-Bromobenzylidene)benzo[b]thiophen-3(2H)-one (2q): 61% yield (100 mg); bright yellow solid; mp 148-150 °C; R_f = 0.55 (10% ethyl acetate in hexanes); FTIR (KBr) 3060, 2922, 1678, 1591, 1278, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.25 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.27-7.22 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.3, 146.2, 135.6, 134.6, 133.8, 133.1, 132.1, 131.1, 130.6, 130.3, 127.8, 127.4, 127.1, 125.9, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{BrOSNa}$: 338.9455; found: 338.9453.



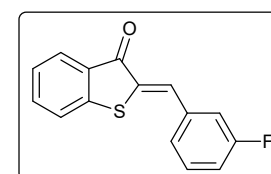
(Z)-2-(3-Bromobenzylidene)benzo[b]thiophen-3(2H)-one (2r):⁴ 65% yield (106 mg); bright yellow solid; mp 154-156 °C; R_f = 0.42 (5% ethyl acetate in hexanes); FTIR (KBr) 3054, 2921, 1682, 1585, 1281, 738 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (d, J = 7.6 Hz, 1H), 7.87-7.80 (m, 2H), 7.63-7.56 (m, 2H), 7.55-7.47 (m, 2H), 7.34 (t, J = 8.4 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.6, 146.0, 136.5, 135.7, 133.5, 133.0, 131.8, 131.6, 130.6, 130.3, 129.5, 127.3, 126.0, 124.1, 123.3; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{BrOSNa}$: 338.9455; found: 338.9441.



(Z)-2-(3-Chlorobenzylidene)benzo[b]thiophen-3(2H)-one (2s):⁵ 54% yield (73 mg); bright yellow solid; mp 161-163 °C; R_f = 0.55 (10% ethyl acetate in hexanes); FTIR (KBr) 3057, 3000, 1683, 1587, 1281, 738 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.92 (d, J = 7.6 Hz, 1H), 7.84 (s, 1H), 7.66 (s, 1H), 7.61-7.54 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.43-7.34 (m, 2H), 7.30 (t, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.6, 145.9, 136.2, 135.7, 135.2, 131.7, 130.6, 130.3, 130.3, 130.0, 129.1, 127.3, 127.3, 126.0, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{ClOSNa}$: 294.9960; found: 294.9952.



(Z)-2-(3-Fluorobenzylidene)benzo[b]thiophen-3(2H)-one (2t): 60% yield (76 mg); bright yellow solid; mp 119-121 °C; R_f = 0.47 (10% ethyl acetate in hexanes); FTIR (KBr) 3078, 2924, 1679, 1580, 1273, 735 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (d, J = 7.6 Hz, 1H), 7.88 (s, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.53-7.36 (m, 4H), 7.30 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.7, 163.1 (2C) (d, J = 245 Hz), 146.0, 136.6 (2C) (d, J = 8.0 Hz), 135.7, 132.0, 131.7, 130.7 (2C)

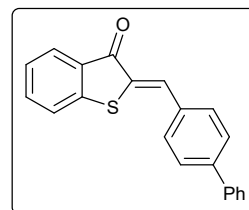


(d, $J = 8.0$ Hz), 130.3, 127.3, 127.0 (2C) (d, $J = 8.0$ Hz), 126.0, 124.1, 117.2 (2C) (d, $J = 7.0$ Hz), 117.0 (2C) (d, $J = 6.0$ Hz); HRMS (m/z) $[M+Na]^+$ calculated for $C_{15}H_9OFSNa$: 279.0256; found: 279.0252.

(Z)-2-([1,1-Biphenyl]-4-ylmethylene)benzo[*b*]thiophen-3(2H)-one (2u): 85% yield (134 mg); bright yellow solid; mp 155-157 °C; $R_f = 0.44$ (5% ethyl acetate in hexanes); FTIR

(KBr) 3028, 2954, 1673, 1587, 1286, 729 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (s, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 7.6$ Hz, 2H), 7.65 (d, $J = 7.6$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.55-7.44 (m, 3H), 7.40 (t, $J = 6.8$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz)

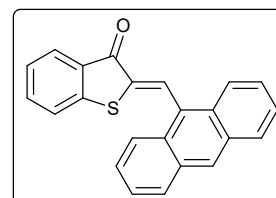
δ 188.8, 146.1, 142.9, 140.1, 135.4, 133.4, 133.3, 131.7, 130.6, 130.3, 129.1, 128.2, 127.8, 127.3, 127.2, 125.8, 124.1; HRMS (m/z) $[M+Na]^+$ calculated for $C_{21}H_{14}OSNa$: 337.0663; found: 337.0666.



(Z)-2-(Anthracen-9-methylene)benzo[*b*]thiophen-3(2H)-one (2v):⁴ 83% yield (141 mg); bright yellow solid; mp 156-158 °C; $R_f = 0.52$ (15% ethyl acetate in hexanes); FTIR

(KBr) 3001, 1670, 1558, 1265, 752 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 1H), 8.53 (s, 1H), 8.12-8.04 (m, 4H), 8.00 (d, $J = 7.6$ Hz, 1H) 7.56-7.50 (m, 5H), 7.30 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.8, 146.8,

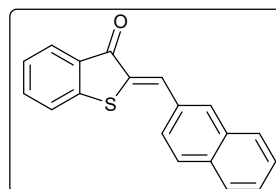
139.0, 135.7, 131.8, 131.4, 131.4, 129.1, 129.0, 128.9, 127.4, 126.6, 125.8, 125.7, 125.6, 124.1; HRMS (m/z) $[M+Na]^+$ calculated for $C_{23}H_{14}OSNa$: 361.0663; found: 361.0669.



(Z)-2-(Naphthalen-2-ylmethylene)benzo[*b*]thiophen-3(2H)-one (2w):⁴ 90% yield (130 mg); bright yellow solid; mp 106-108 °C; $R_f = 0.38$ (10% ethyl acetate in hexanes); FTIR

(KBr) 3060, 2957, 1676, 1586, 1269, 734 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 8.20 (s, 1H), 8.12 (s, 1H), 8.01-7.88 (m, 3H), 7.85 (d, $J = 6.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.62-7.51 (m, 4H), 7.31 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR

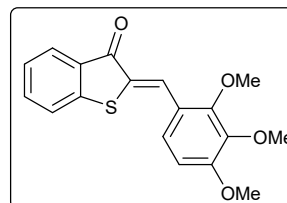
($CDCl_3$, 100 MHz) δ 188.8, 146.2, 135.4, 133.9, 133.9, 133.4, 132.1, 132.0, 130.7, 130.6, 129.0, 128.9, 128.9, 127.9, 127.9, 127.2, 127.0, 125.8, 124.1; HRMS (m/z) $[M+Na]^+$ calculated for $C_{19}H_{12}ONaSn$: 311.0507; found: 311.0500.



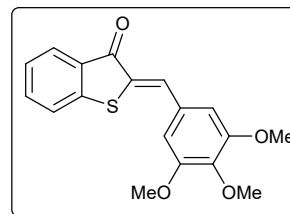
(Z)-2-(2,3,4-Trimethoxybenzylidene)benzo[*b*]thiophen-3(2H)-one (2x): 51% yield (84 mg); bright yellow solid; mp 132-134 °C; $R_f = 0.58$ (30% ethyl acetate in hexanes);

FTIR (KBr) 3002, 2940, 1673, 1586, 1282, 741 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 8.28 (s, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.56-7.46 (m, 3H), 7.31-7.25 (m, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H);

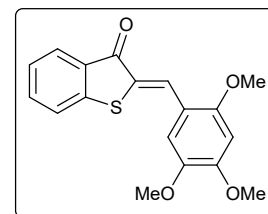
^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.6, 156.0, 154.6, 146.1, 142.5, 135.0, 131.0, 129.0, 128.6, 127.1, 125.5, 125.4, 123.9, 121.8, 107.6, 62.1, 61.1, 56.2; HRMS (m/z) $[M+Na]^+$ calculated for $C_{18}H_{16}O_4Sn$: 351.0667; found: 351.0674.



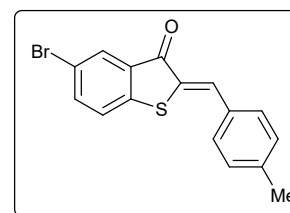
(Z)-2-(3,4,5-Trimethoxybenzylidene)benzo[b]thiophen-3(2H)-one (2y): 90% yield (148 mg); bright yellow solid; mp 142-144 °C; $R_f = 0.53$ (30% ethyl acetate in hexanes); FTIR (KBr) 3055, 2998, 1669, 1582, 1282, 778 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.88 (s, 1H), 7.61-7.55 (m, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 6.96 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.6, 153.6, 146.0, 140.2, 135.4, 134.0, 130.7, 129.9, 129.5, 127.2, 125.8, 124.0, 108.4, 61.2, 56.3; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{SNa}$: 351.0667; found: 351.0658.



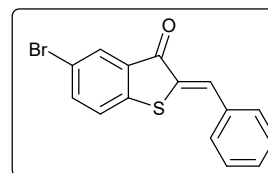
(Z)-2-(2,4,5-Trimethoxybenzylidene)benzo[b]thiophen-3(2H)-one (2z): 58% yield (96 mg); Orange solid; mp 154-156 °C; $R_f = 0.39$ (30% ethyl acetate in hexanes); FTIR (KBr) 3061, 2915, 1660, 1584.2, 1214, 721 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.41 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.33 (s, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 6.52 (s, 1H), 3.95 (s, 6H), 3.91 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 188.4, 155.6, 152.6, 145.8, 143.3, 134.8, 131.2, 128.8, 127.3, 127.0, 125.4, 123.8, 115.2, 112.4, 96.6, 56.6, 56.5, 56.2; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{SNa}$: 351.0667; found: 351.0672.



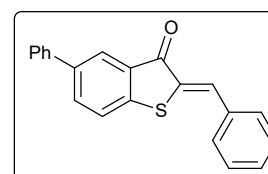
(Z)-5-Bromo-2-(4-methylbenzylidene)benzo[b]thiophen-3(2H)-one (2aa):⁸ 70% yield (116 mg); bright yellow solid; mp 210-212 °C; $R_f = 0.39$ (5% ethyl acetate in hexanes); FTIR (KBr) 3079, 2999, 1675, 1584, 1249, 727 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.03 (s, 1H), 7.94 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 1H), 7.31-7.25 (m, 2H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 187.5, 144.9, 141.5, 137.9, 135.0, 132.4, 131.4, 131.3, 130.1, 129.9, 129.1, 125.3, 119.3, 21.8; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{11}\text{BrOSNa}$: 352.9612; found: 352.9614.



(Z)-2-Benzylidene-5-bromobenzo[b]thiophen-3(2H)-one (2ab):⁸ 65% yield (103 mg); bright yellow solid; mp 156-160 °C; $R_f = 0.52$ (5% ethyl acetate in hexanes); FTIR (KBr) 3032, 2963, 1673, 1583, 1250, 747 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.04 (s, 1H), 7.96 (s, 1H), 7.70-7.64 (m, 3H), 7.52-7.42 (m, 3H), 7.38 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 187.5, 145.0, 138.0, 134.7, 134.1, 132.3, 131.2, 130.7, 130.1, 129.9, 129.3, 125.4, 119.6; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{BrOSNa}$: 338.9455; found: 338.9442.



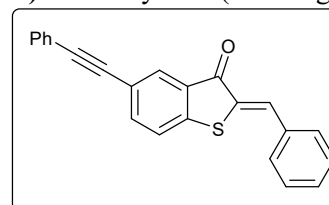
(Z)-2-Benzylidene-5-phenylbenzo[b]thiophen-3(2H)-one (2ac): 83% yield (130 mg); bright yellow solid; mp 136-138 °C; $R_f = 0.45$ (5% ethyl acetate in hexanes); FTIR (KBr) 3028, 2960, 1681, 1592, 1254, 762 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.17 (s, 1H), 8.00 (s, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.73



(d, $J = 7.2$ Hz, 2H), 7.63 (d, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.53-7.42 (m, 5H), 7.39 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.8, 145.1, 139.5, 139.2, 134.4, 134.3, 134.0, 131.2, 131.2, 130.8, 130.4, 129.2, 129.1, 128.0, 127.1, 125.4, 124.3; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{14}\text{OSNa}$: 337.0663; found:337.0652.

(Z)-2-Benzylidene-5-(phenylethynyl)benzo[b]thiophen-3(2H)-one (2ad): 74% yield (118 mg);

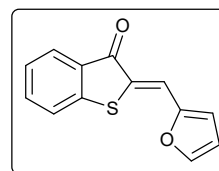
bright yellow solid; mp 132-134 °C; $R_f = 0.59$ (10% ethyl acetate in hexanes); FTIR (KBr) 3020, 2923, 1679, 1593, 1250, 758 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.08 (s, 1H), 7.98 (s, 1H), 7.70 (d, $J = 7.6$ Hz, 3H), 7.57-7.52 (m, 2H), 7.52-7.46 (m, 3H), 7.44 (d, $J = 7.2$ Hz, 1H),



7.39-7.34 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.1, 145.9, 138.0, 134.4, 134.2, 131.8, 131.2, 130.8, 130.5, 130.2, 130.1, 129.3, 128.7, 128.6, 124.0, 122.9, 121.2, 90.7, 88.1; HRMS (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{15}\text{OS}$: 339.0844; found:339.0822.

(Z)-2-(Furan-2-ylmethylene)benzo[b]thiophen-3(2H)-one (2ae):⁹ 86% yield (98 mg); bright yellow

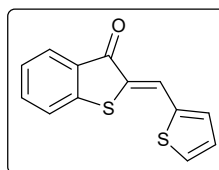
solid; mp 125-127 °C; $R_f = 0.58$ (20% ethyl acetate in hexanes); FTIR (KBr) 3066, 2964, 1675, 1597, 1292, 734 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.91 (d, $J = 8.0$ Hz, 1H), 7.75 (s, 1H), 7.72-7.66 (m, 1H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 3.6$ Hz, 1H), 6.66-6.55 (m, 1H);



^{13}C NMR (CDCl_3 , 100 MHz) δ 188.4, 151.2, 146.5, 146.2, 135.2, 130.9, 128.6, 126.9, 125.5, 124.0, 119.5, 118.0, 113.4; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_8\text{O}_2\text{SNa}$: 251.0143; found: 251.0124.

(Z)-2-(Thiophen-2-ylmethylene)benzo[b]thiophen-3(2H)-one (2af):⁴ 80% yield (98 mg); bright

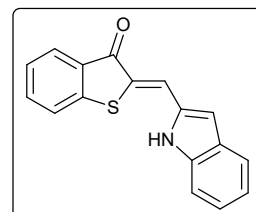
yellow solid; mp 169-170 °C; $R_f = 0.51$ (15% ethyl acetate in hexanes); FTIR (KBr) 3062, 2994, 1670, 1583, 1279, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.14 (s, 1H), 7.92 (d, $J = 7.6$ Hz, 1H), 7.65 (d, $J = 4.8$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.53-7.49 (m, 2H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 4.0$ Hz, 1H);



^{13}C NMR (CDCl_3 , 100 MHz) δ 188.4, 145.7, 139.3, 135.3, 133.8, 131.8, 131.1, 129.0, 128.8, 127.1, 126.1, 125.8, 124.2; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_8\text{OS}_2\text{Na}$: 266.9914; found:266.9899.

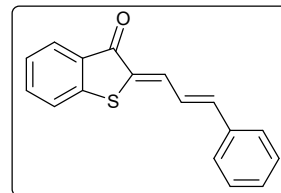
(Z)-2-((1H-Indol-2-yl)methylene)benzo[b]thiophen-3(2H)-one (2ag): 54% yield (75 mg); dark red

solid; mp 233-235 °C; $R_f = 0.38$ (30% ethyl acetate in hexanes); FTIR (KBr) 3057, 2925, 1617, 1587, 1282, 738 cm^{-1} ; ^1H NMR (DMSO-d_6 , 400 MHz) δ 12.25 (s, 1H), 8.24 (s, 1H), 7.98-7.92 (m, 2H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.28-7.18 (m, 2H); ^{13}C NMR (DMSO-d_6 , 100 MHz) δ 186.4,

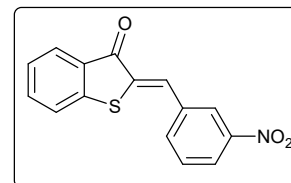


144.0, 136.5, 135.1, 131.2, 130.1, 127.2, 126.1, 125.8, 125.7, 124.4, 123.9, 123.3, 121.3, 118.5, 112.6, 111.6; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{11}\text{NOSNa}$: 300.0459; found: 300.0449.

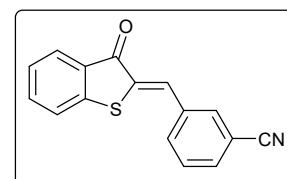
(Z)-2-((E)-3-Phenylallylidene)benzo[b]thiophen-3(2H)-one (2ah):¹⁰ 66% yield (87 mg); bright yellow solid; mp 122-124 °C; $R_f = 0.39$ (10% ethyl acetate in hexanes); FTIR (KBr) 3061, 2921, 1668, 1593, 1284, 734 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.90 (d, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 11.2$ Hz, 1H), 7.60-7.52 (m, 3H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.43-7.33 (m, 3H), 7.27 (d, $J = 9.2$ Hz, 1H), 7.11 (d, $J = 15.2$ Hz, 1H), 6.99 (dd, $J = 11.6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 188.1, 145.2, 143.7, 136.1, 135.2, 133.2, 133.1, 131.8, 129.8, 129.1, 127.7, 127.0, 125.5, 124.4, 124.1; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{12}\text{OSNa}$: 287.0507; found: 287.0495.



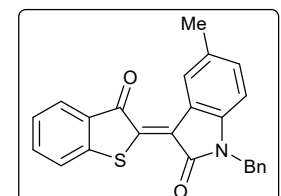
(Z)-2-(3-Nitrobenzylidene)benzo[b]thiophen-3(2H)-one (2ai):^{4, 11} 69% yield (98 mg); bright yellow solid; mp 228-230 °C; $R_f = 0.50$ (15% ethyl acetate in hexanes); FTIR (KBr) 3014, 2913, 1680, 1527, 1445, 1347, 1279, 735 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.57 (t, $J = 2.0$ Hz, 1H), 8.26 (d, $J = 8.0$ Hz, 1H), 8.00-7.94 (m, 3H), 7.69-7.61 (m, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 188.5, 148.9, 145.6, 136.4, 136.2, 136.1, 133.4, 130.2, 130.1, 130.1, 127.5, 126.3, 125.0, 124.3, 124.3; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_9\text{NO}_3\text{SNa}$: 306.0201; found: 306.0192.



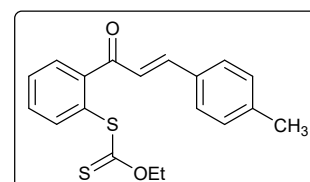
(Z)-3-((3-Oxobenzob[thiophen-2(3H)-ylidene)methyl]benzonitrile (2aj): 71% yield (94 mg); bright yellow solid; mp 256-258 °C; $R_f = 0.47$ (15% ethyl acetate in hexanes); FTIR (KBr) 3067, 2920, 2222, 1676, 1592, 1282, 782 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.00-7.93 (m, 2H), 7.90 (d, $J = 10.0$ Hz, 1H), 7.87 (s, 1H), 7.68 (d, $J = 9.5$ Hz, 1H), 7.65-7.57 (m, 2H), 7.53 (d, $J = 9.5$ Hz, 1H), 7.34 (t, $J = 9.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 188.5, 145.7, 136.0, 135.8, 134.8, 133.8, 133.0, 132.9, 130.1, 130.1, 127.5, 126.3, 124.2, 118.3, 113.7; HRMS (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{10}\text{NOS}$: 266.0483; found: 266.0477.



(E)-1-Benzyl-5-methyl-3-(3-oxobenzob[thiophen-2(3H)-ylidene) indolin-2-one (5): 83% yield (127 mg); dark red solid; mp 234-236 °C; $R_f = 0.39$ (15% ethyl acetate in hexanes); FTIR (KBr) 2983, 1672, 1587, 1271, 736 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.00 (s, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 1H), 7.34-7.25 (m, 6H), 6.63 (d, $J = 8.0$ Hz, 1H), 4.99 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 190.5, 168.8, 147.7, 141.7, 139.7, 136.0, 135.7, 132.7, 132.4, 129.7, 128.9, 127.8, 127.5, 127.4, 126.8, 126.0, 124.2, 121.2, 108.9, 44.1, 21.5; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{24}\text{H}_{17}\text{NO}_2\text{SNa}$: 406.0878; found: 406.0884.

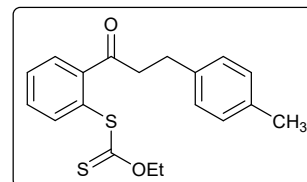


(E)-O-Ethyl S-(2-(3-(p-tolyl)acryloyl)phenyl)carbonodithioate (9): orange solid ; mp 54-56 °C; $R_f = 0.52$ (10% ethyl acetate in hexanes); FTIR (KBr) 3026, 2981, 1647, 1597, 1286, 766 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.63-7.53 (m, 4H), 7.46-



7.39 (m, 3H), 7.18 (d, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 16$ Hz, 1H), 4.52 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.27 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 212.2, 194.7, 146.4, 144.7, 141.5, 137.5, 131.9, 130.8, 130.4, 129.9, 129.8, 128.8, 128.7, 127.9, 125.5, 70.6, 21.7, 13.6; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{S}_2\text{Na}$: 365.0646; found: 365.0645.

Ethyl-S-(2-(3-(p-tolyl)propanoyl)phenyl) carbonodithioate (10) lime green liquid ; $R_f = 0.53$ (7% ethyl acetate in hexanes); FTIR (KBr) 3053, 2981, 2924, 1697, 1230, 1032, 810, 758 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.62-7.54 (m, 1H), 7.54-7.47 (m, 3H), 7.13-7.09 (m, 4H), 4.56 (q, $J = 7.2$ Hz, 2H), 3.20 (t, $J = 7.2$ Hz, 2H), 2.98 (t, $J = 7.6$ Hz, 2H), 2.31 (s, 3H), 1.30 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 212.0, 203.3, 144.7, 137.9, 137.5, 135.7, 131.1, 130.4, 129.3, 128.4, 128.1, 127.6, 70.7, 44.3, 30.0, 21.1, 13.7; HRMS (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}_2\text{Na}$: 367.0802; found: 367.0799.



3. References.

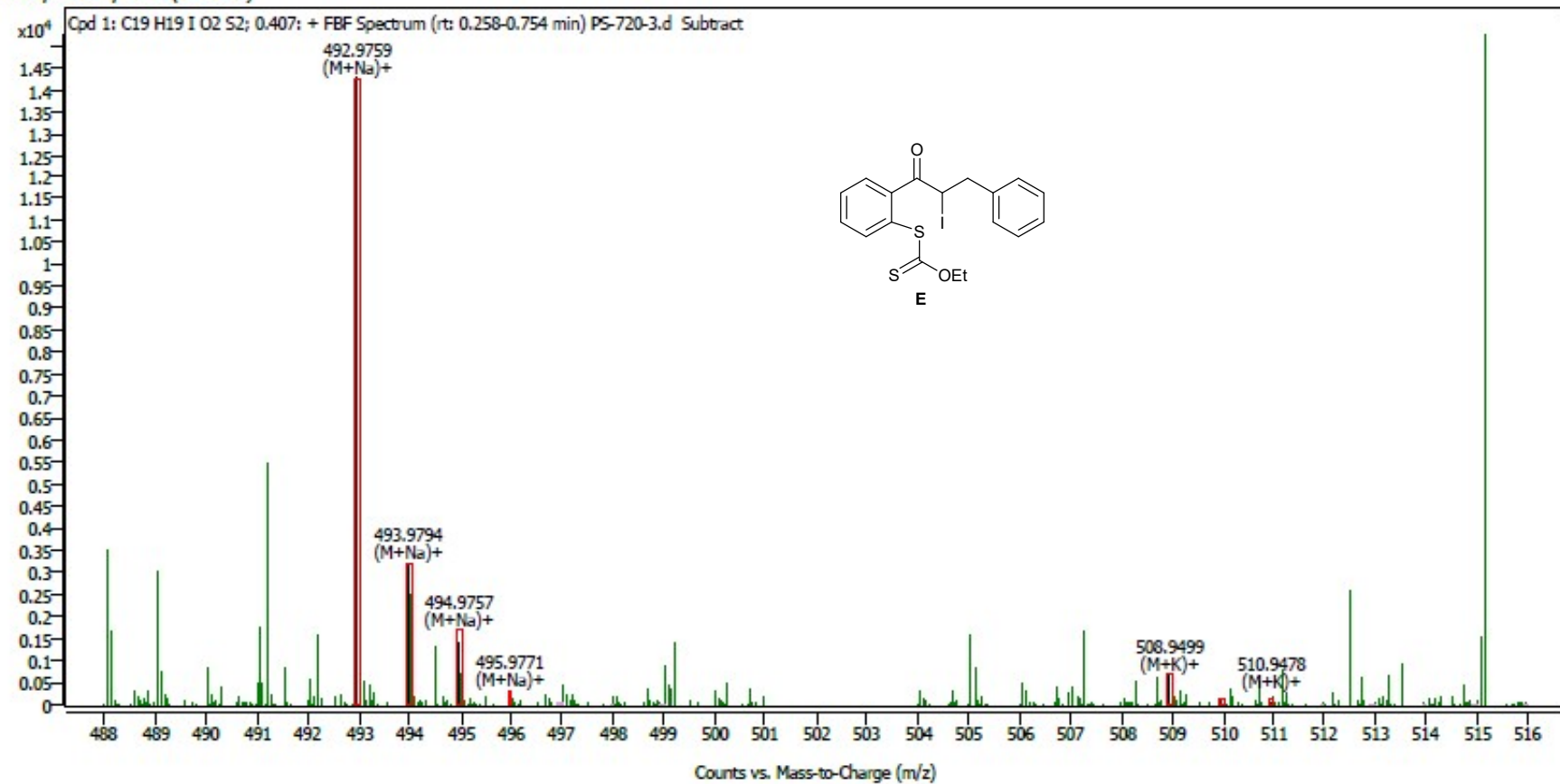
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5.0. HRMS data for compound E.

Compound Details

Cpd. 1: C₁₉H₁₉I O₂S₂

Compound Spectra (overlaid)

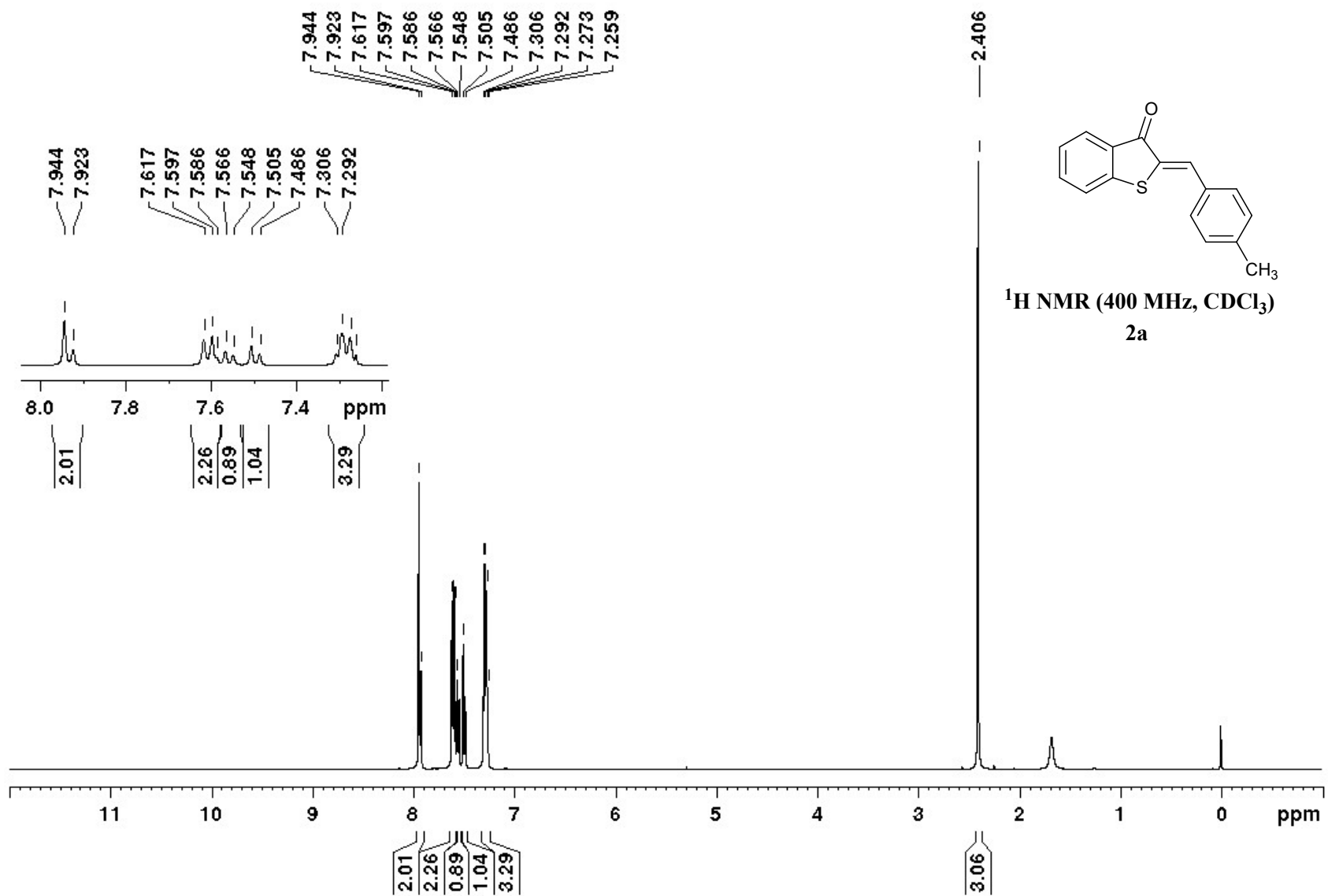


Compound ID Table

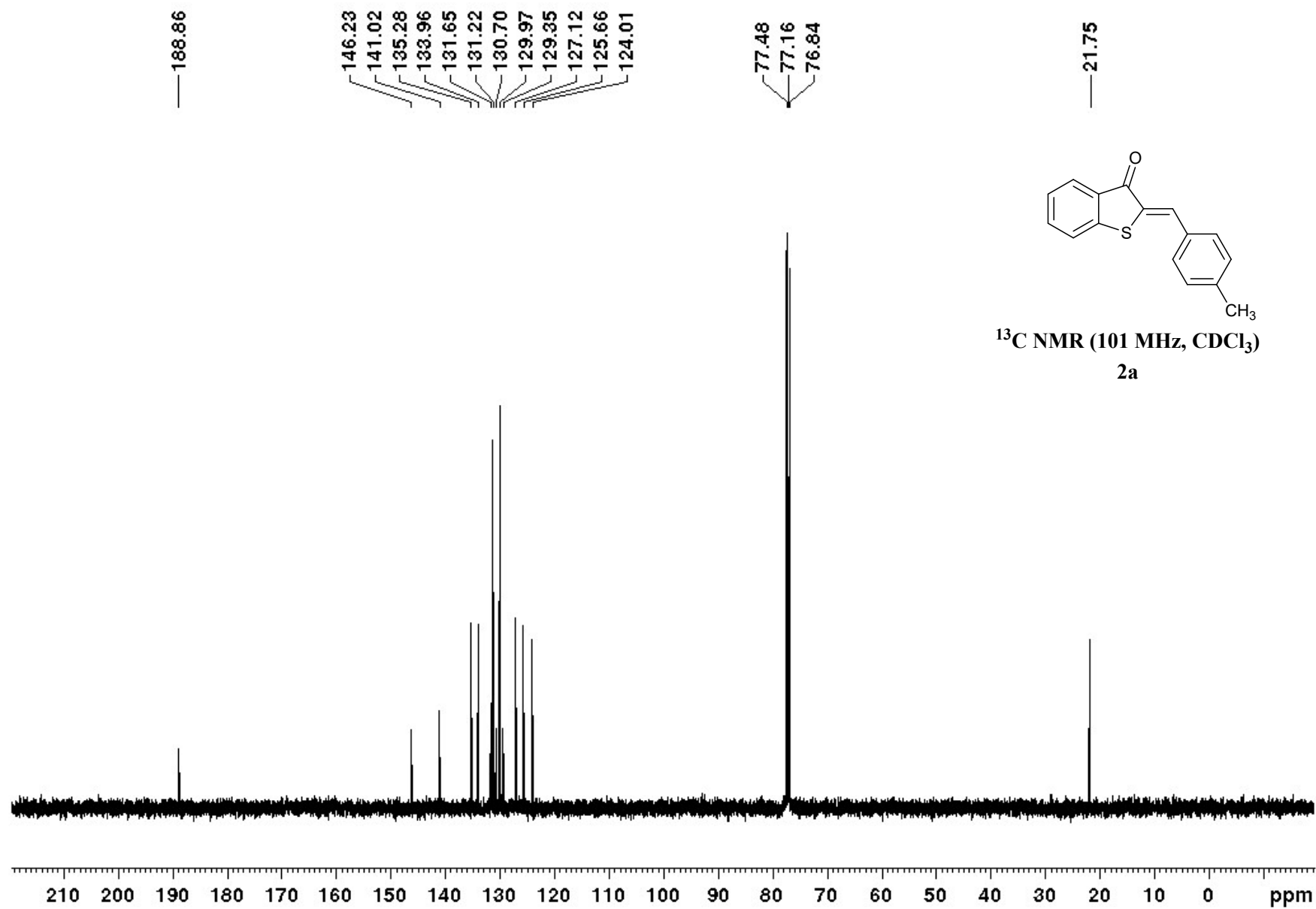
Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C ₁₉ H ₁₉ I O ₂ S ₂	469.9871	469.9869	492.9759	(M+Na)+	-0.43	-0.20
				508.9499	(M+K)+		

2.0. ^1H and ^{13}C spectra for all compounds.

^1H NMR spectrum of compound 2a

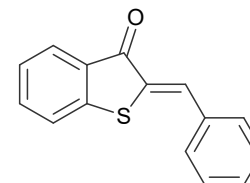


¹³C NMR spectrum of compound 2a

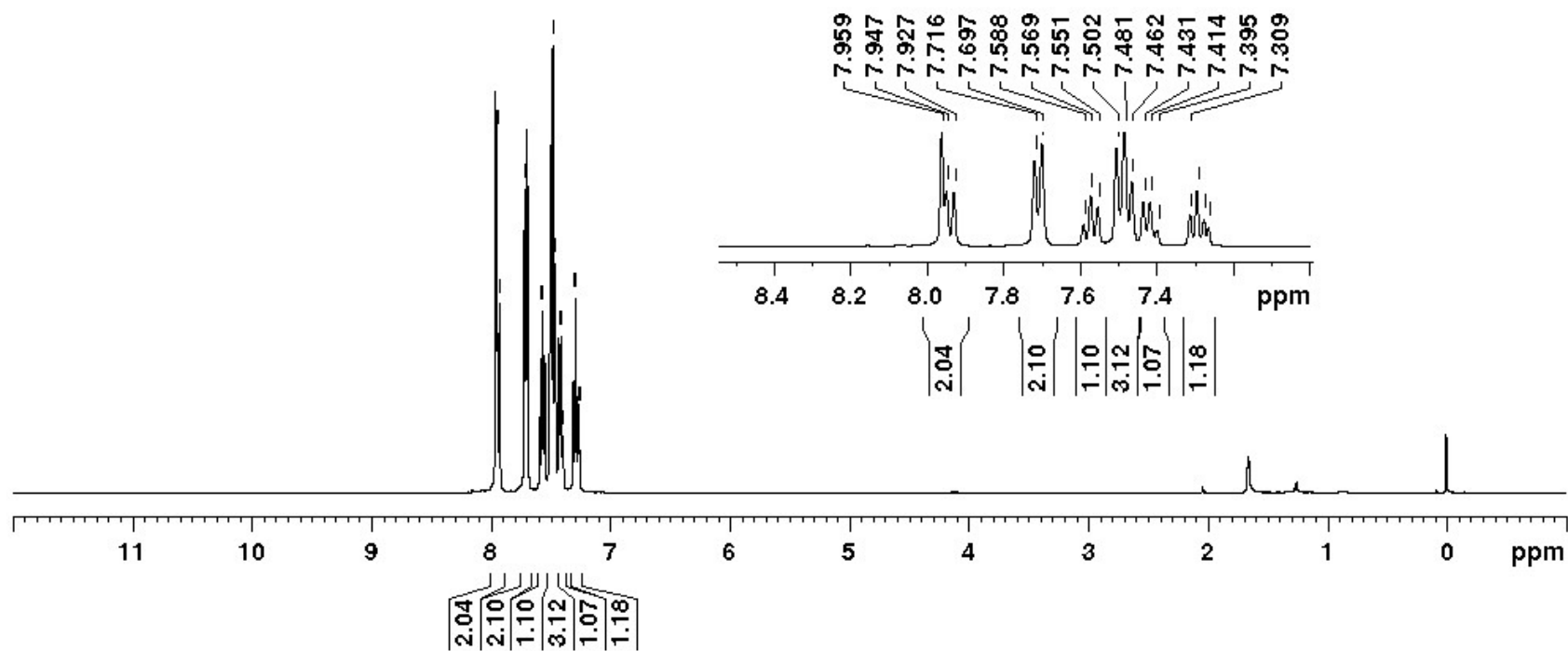


¹H NMR spectrum of compound 2b

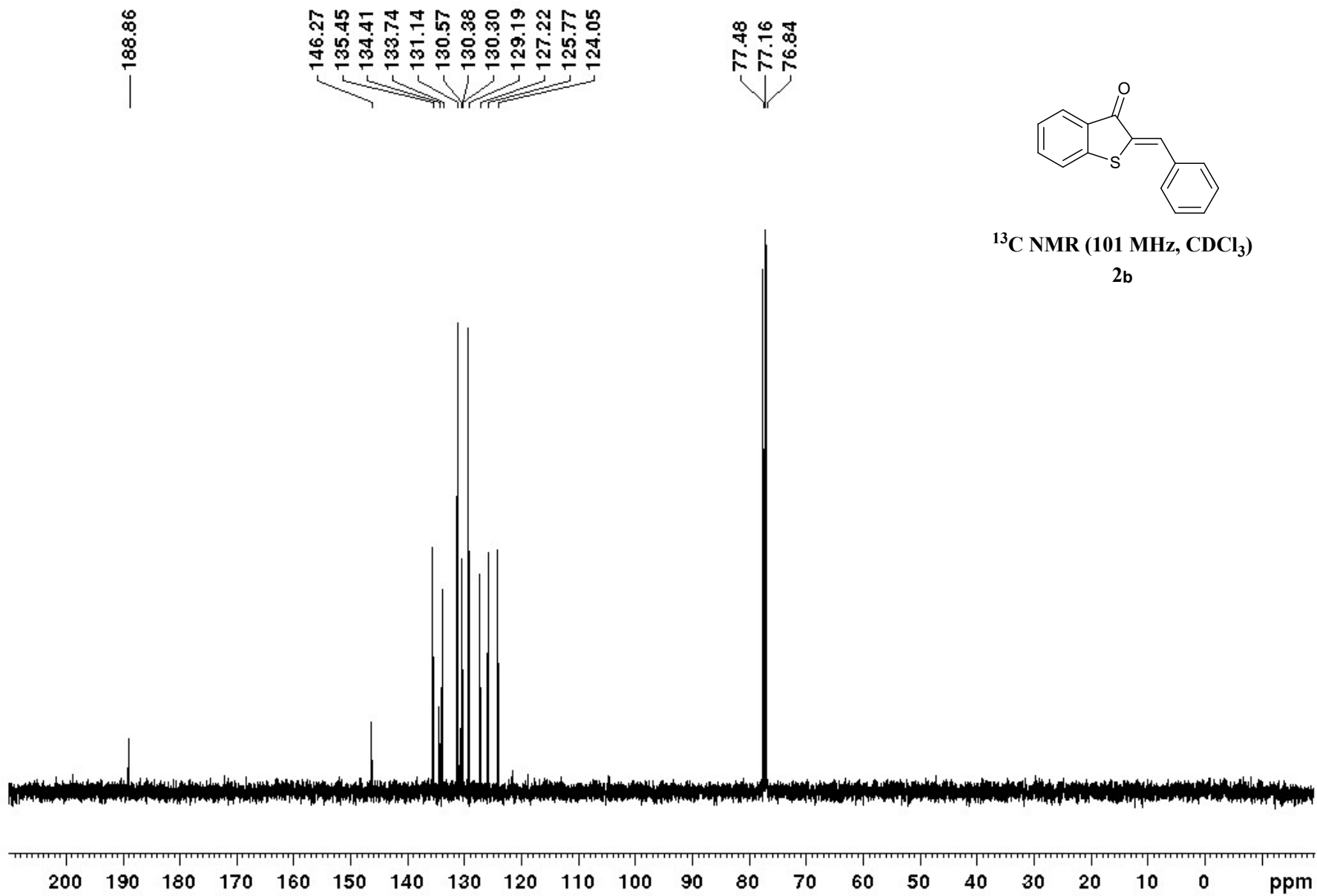
7.959
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7.481
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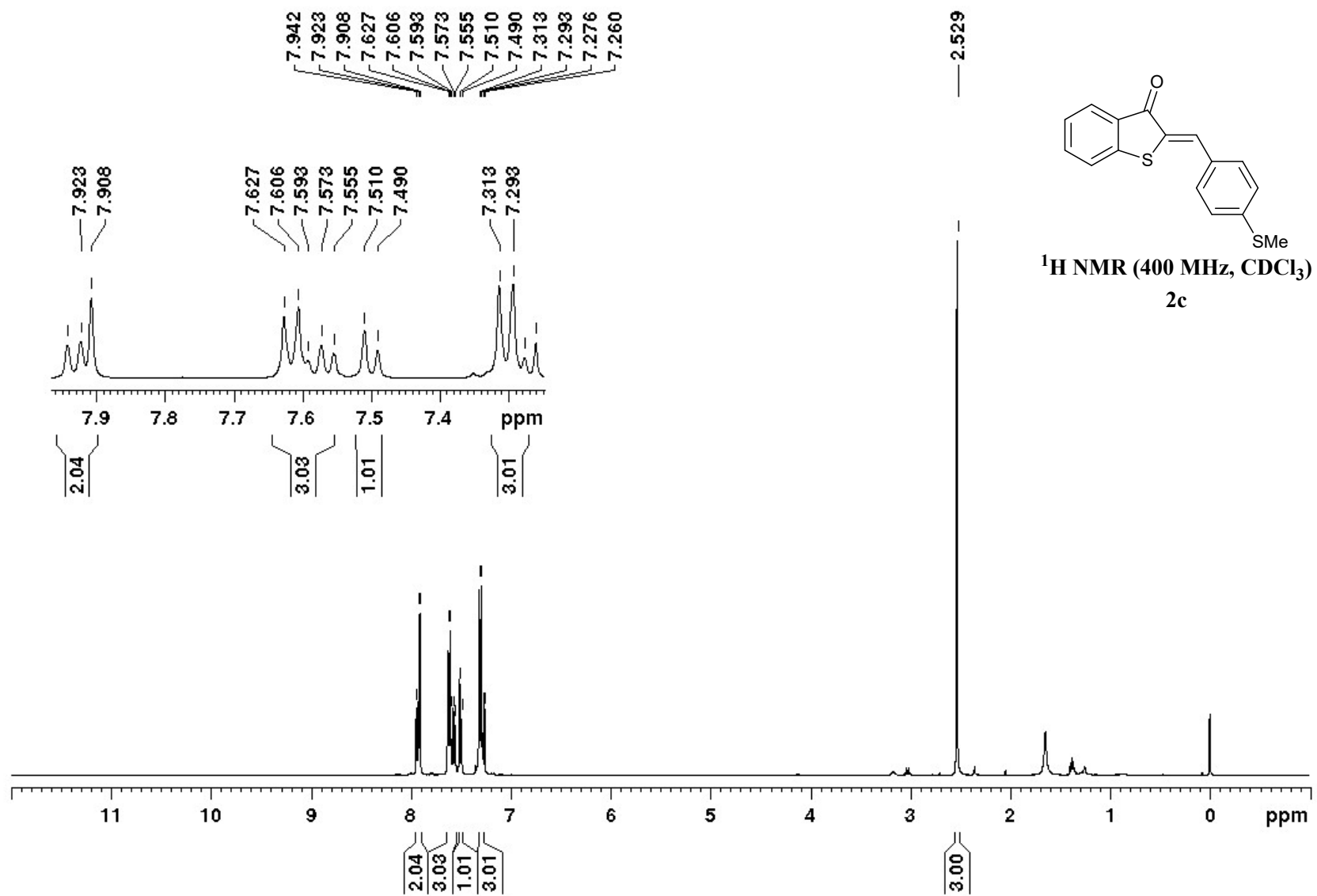
¹H NMR (400 MHz, CDCl₃)
2b



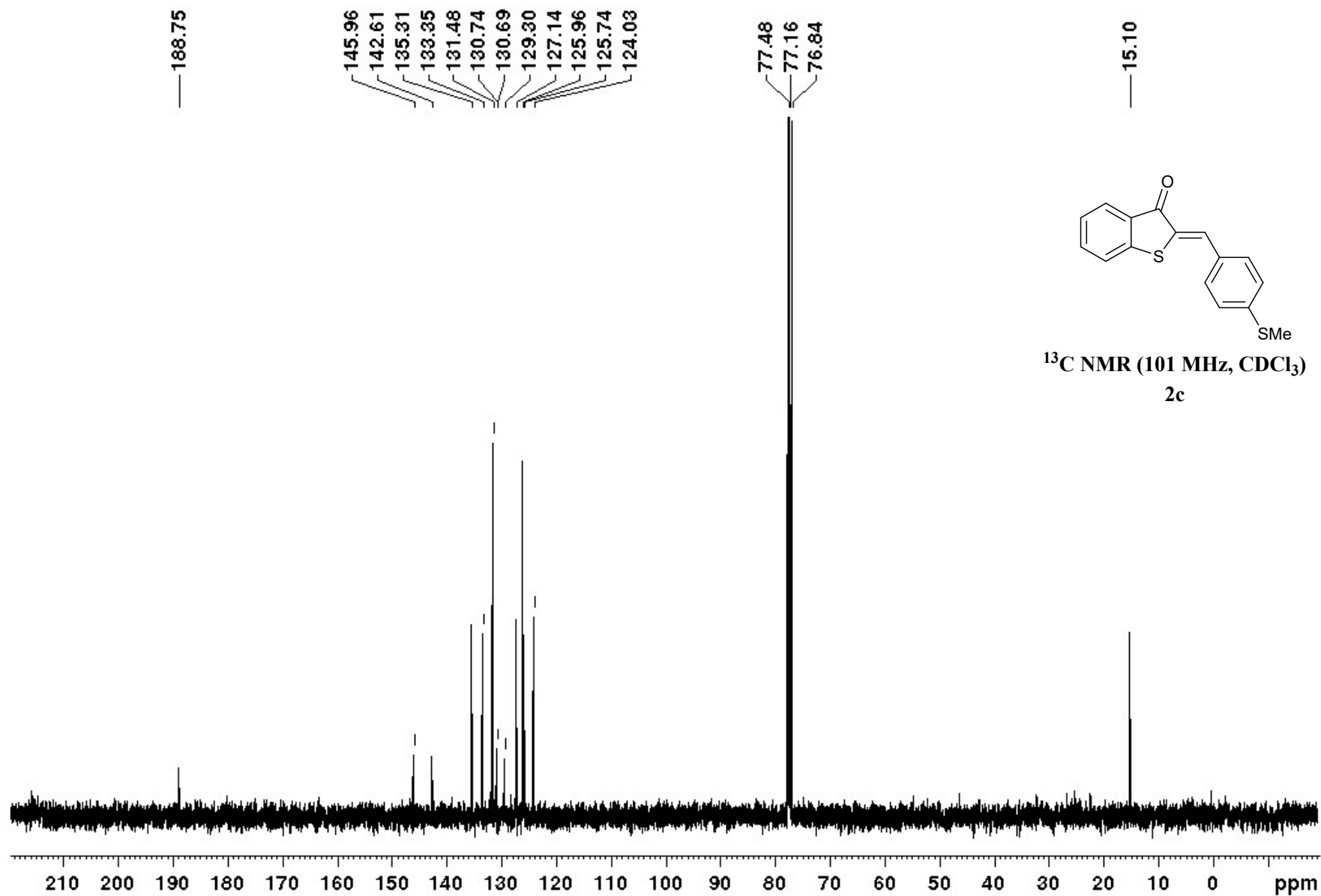
¹³C NMR spectrum of compound 2b



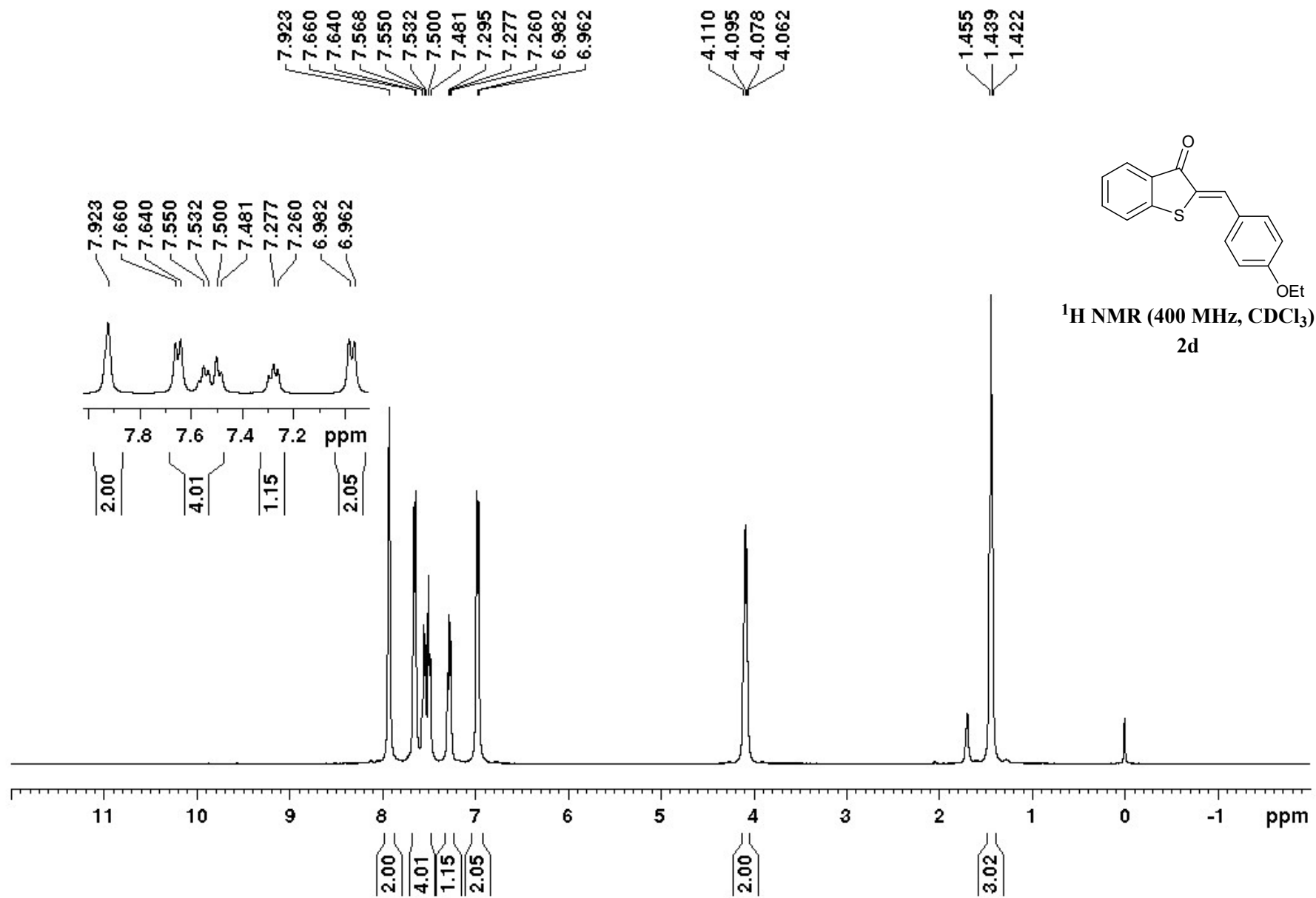
¹H NMR spectrum of compound 2c



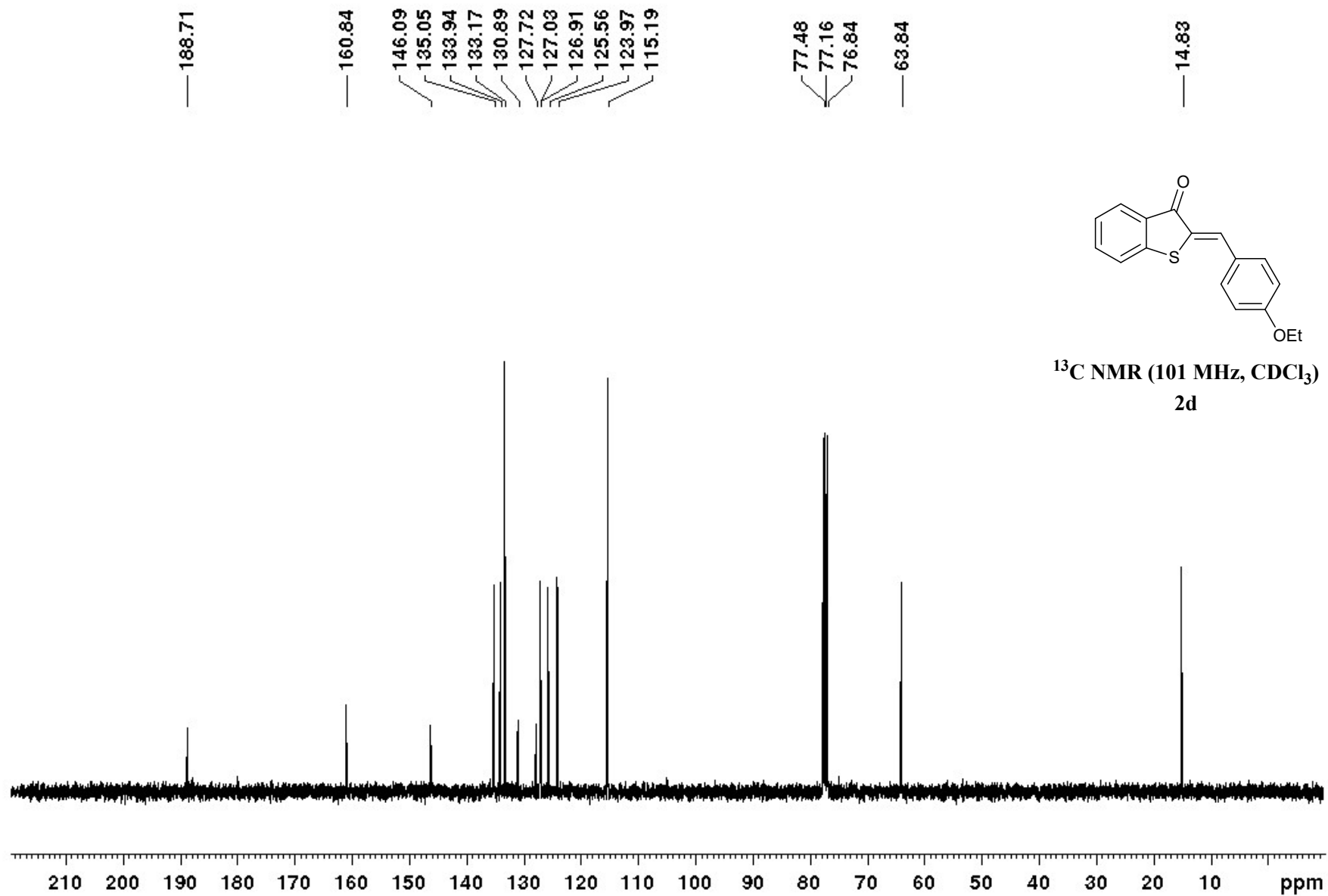
¹³C NMR spectrum of compound 2c



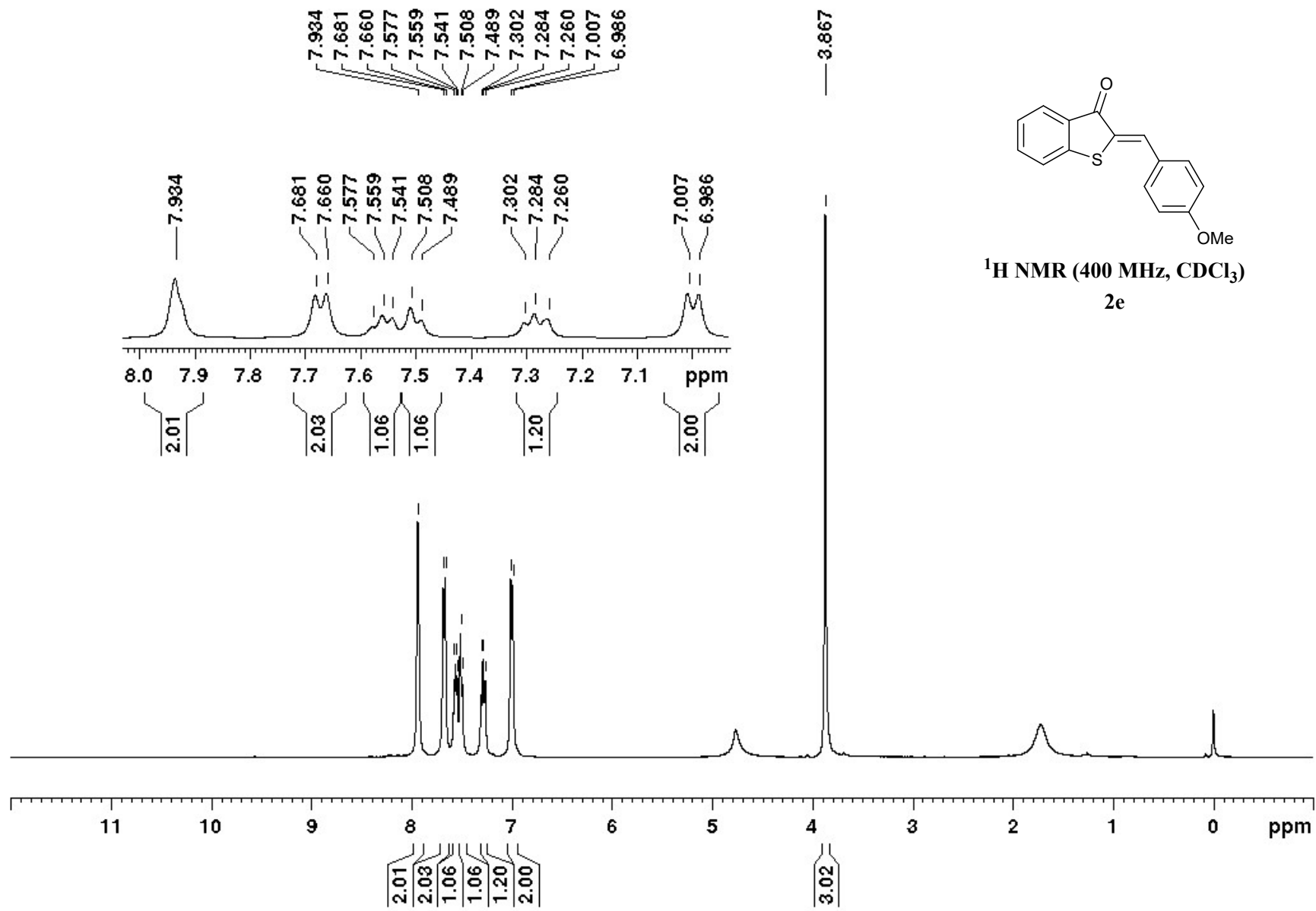
¹H NMR spectrum of compound 2d



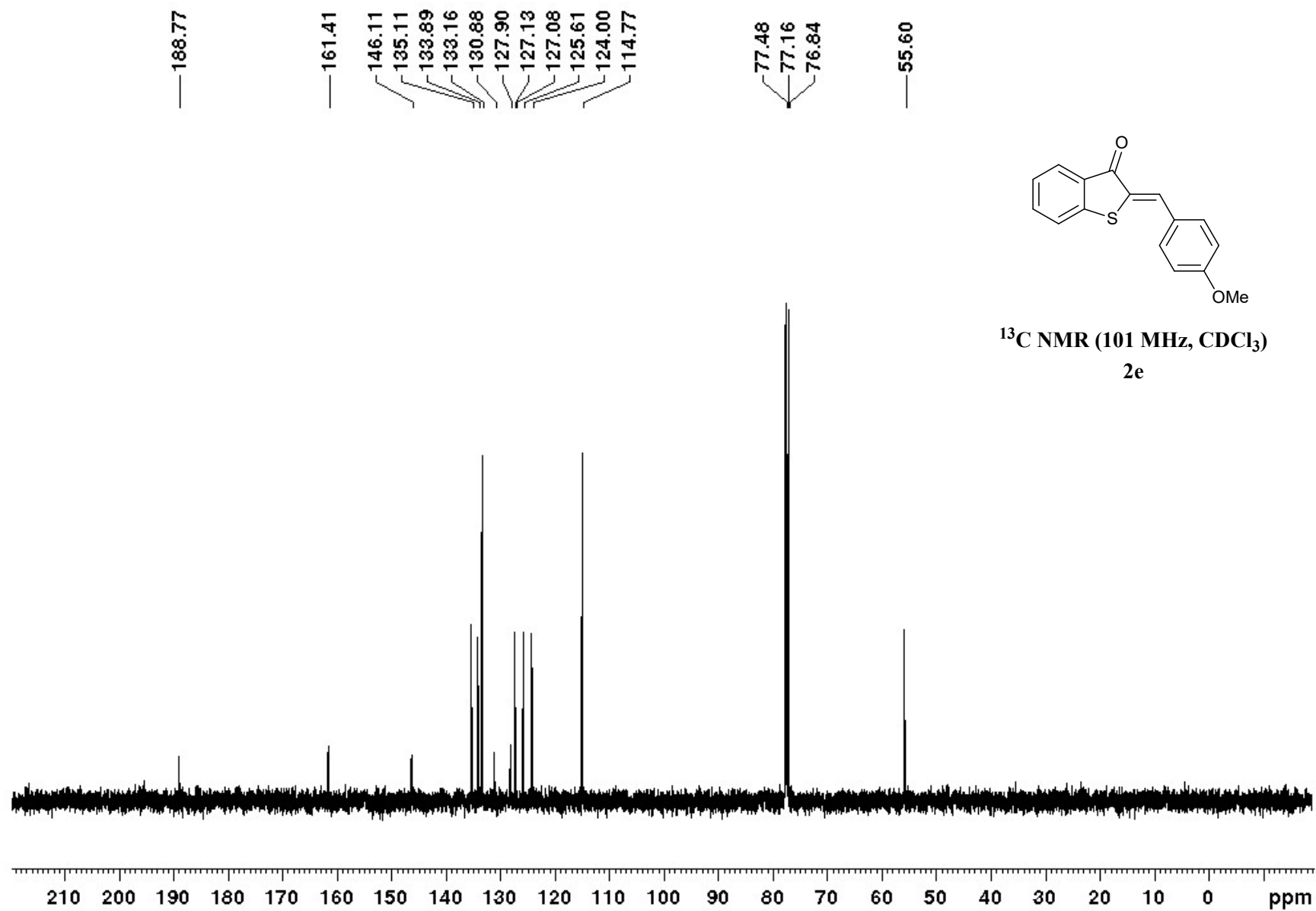
¹³C NMR spectrum of compound 2d



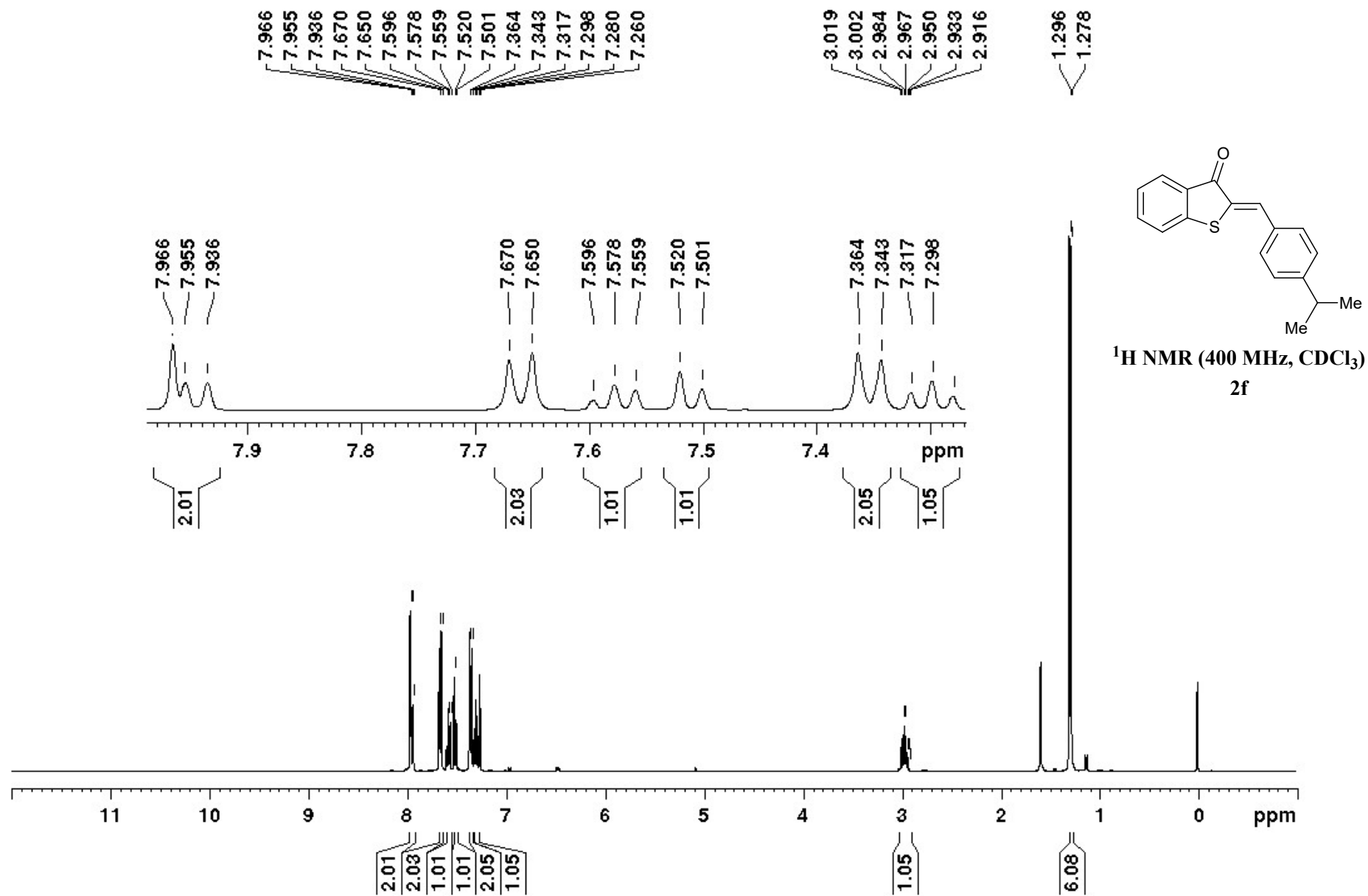
¹H NMR spectrum of compound 2e



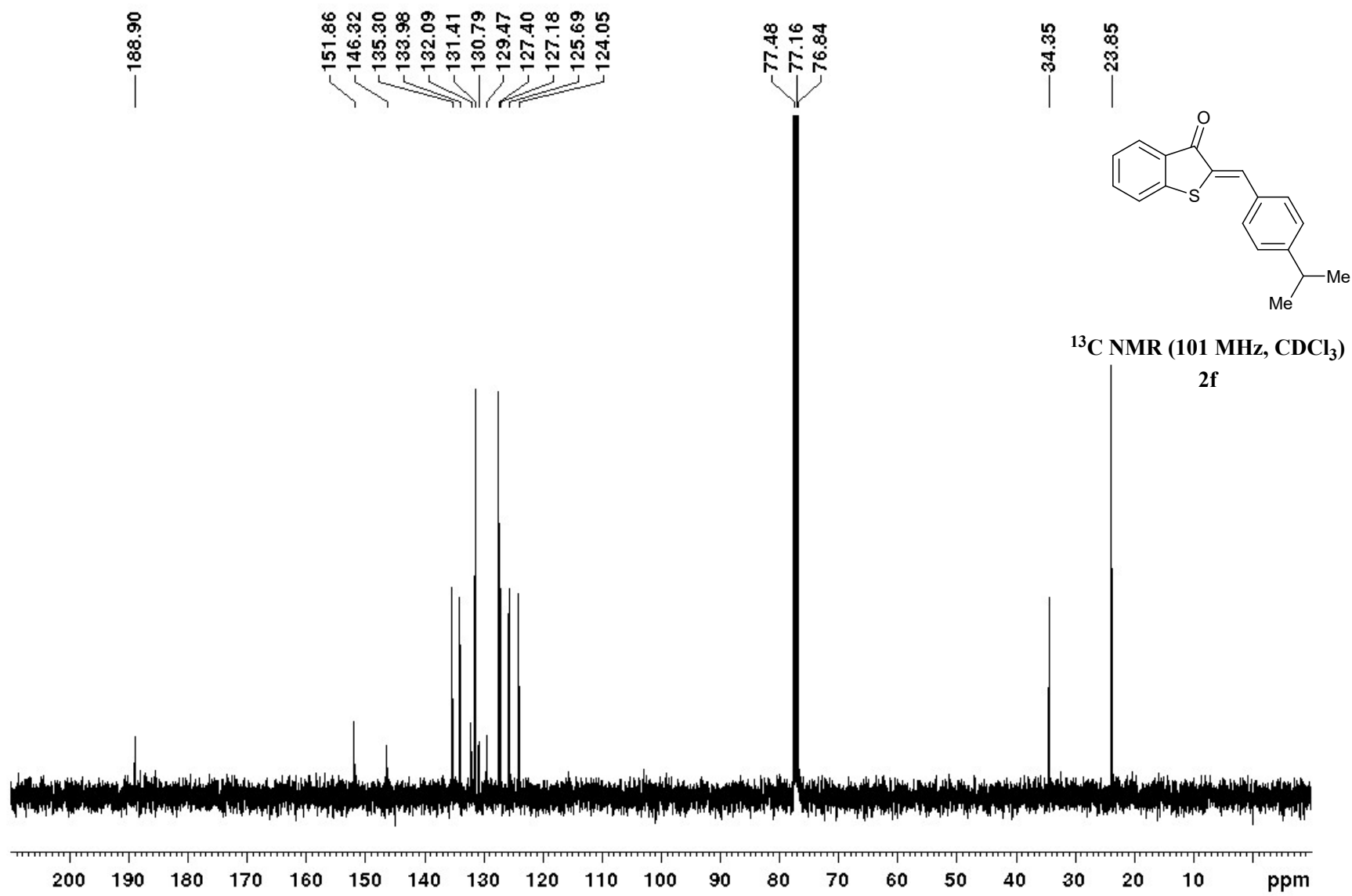
¹³C NMR spectrum of compound 2e



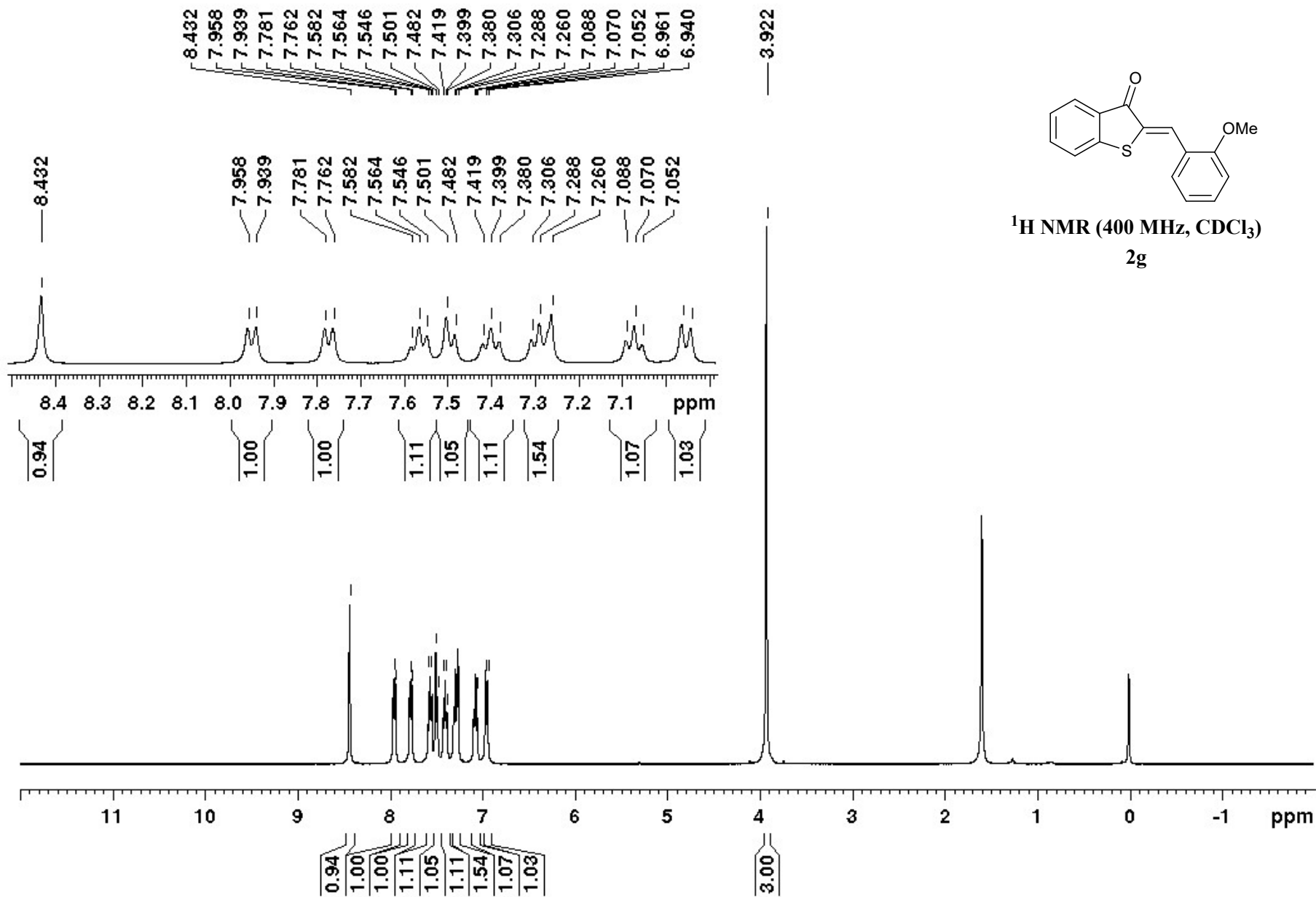
¹H NMR spectrum of compound 2f



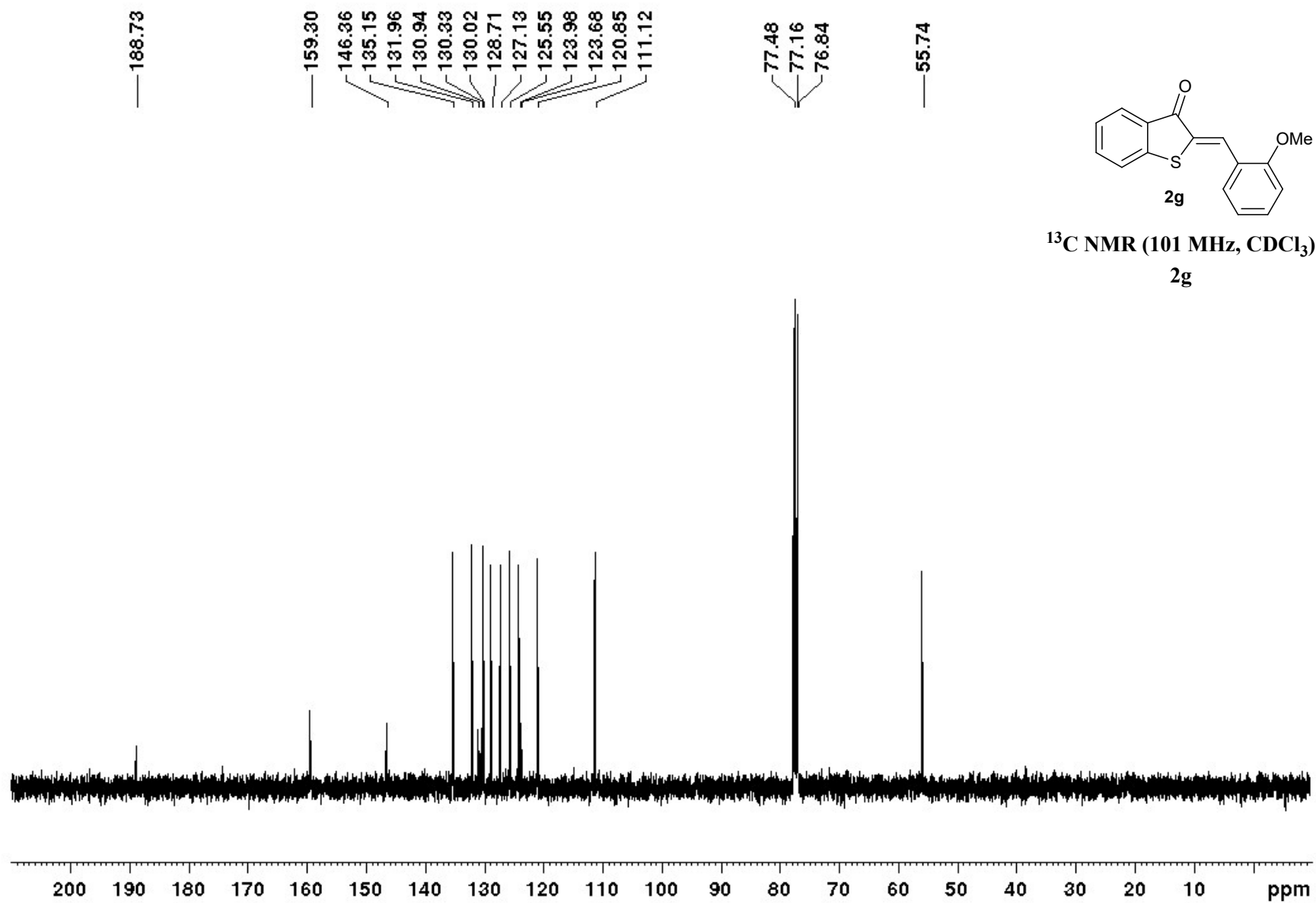
¹³C NMR spectrum of compound 2f



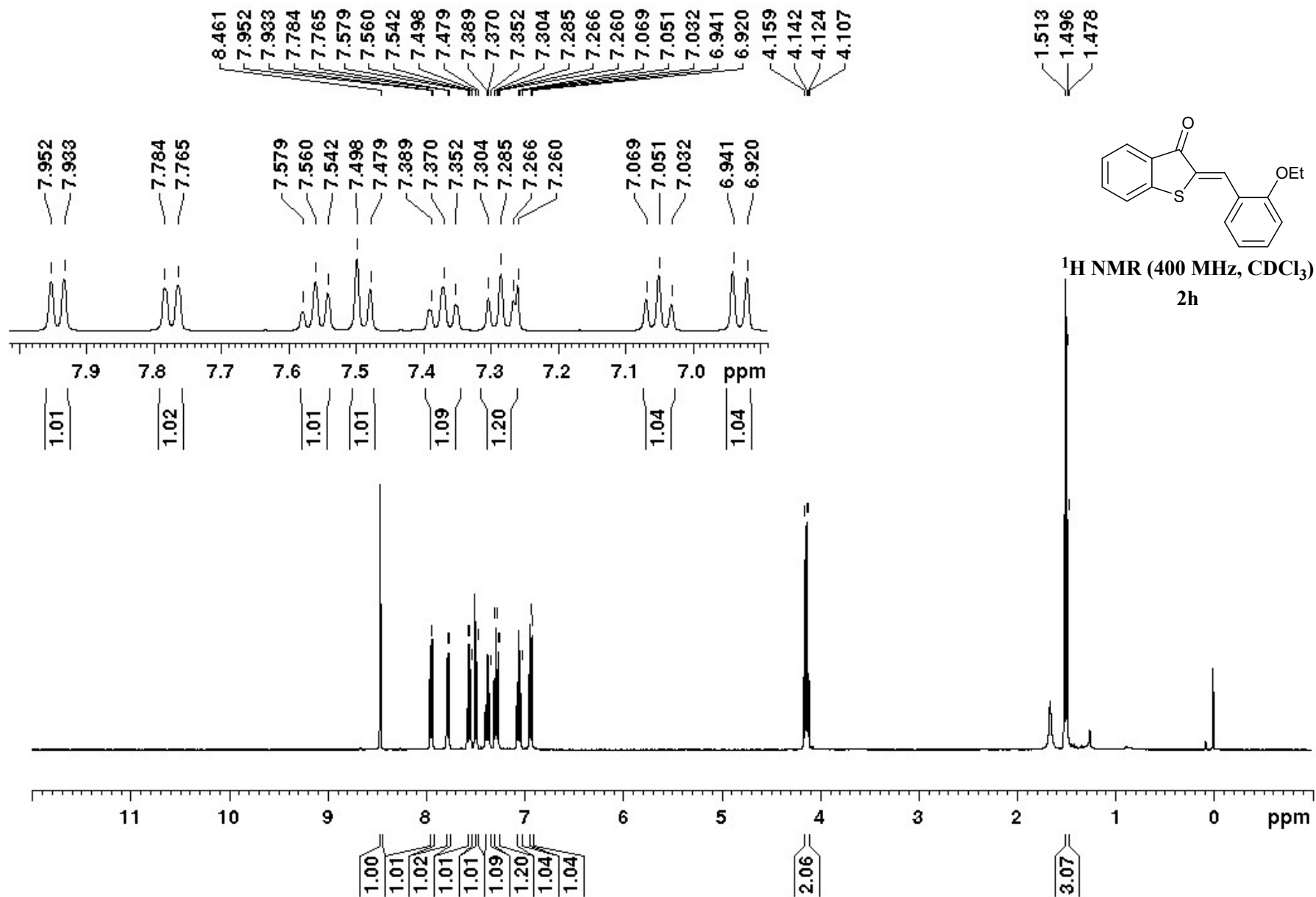
¹H NMR spectrum of compound 2g



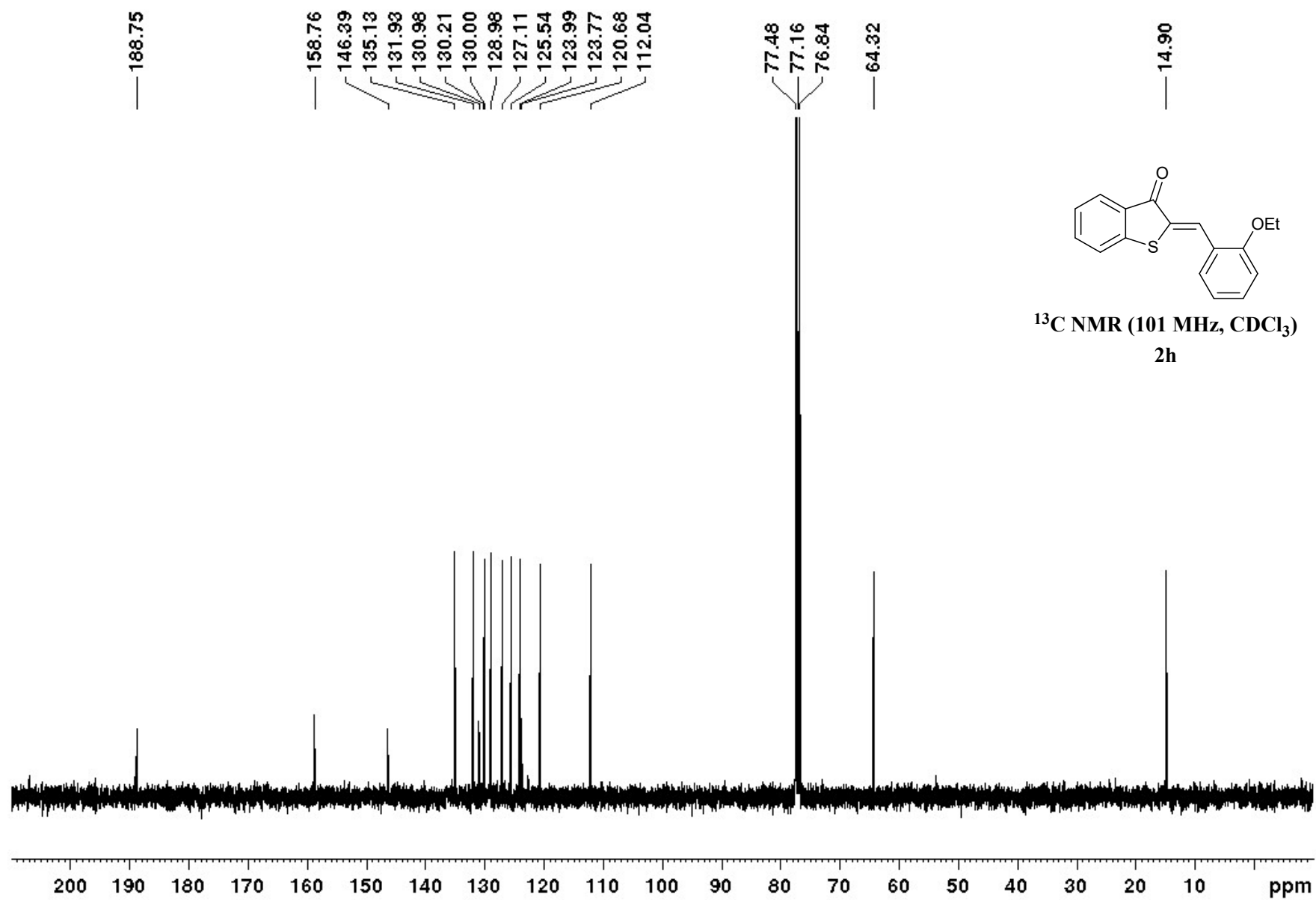
¹³C NMR spectrum of compound 2g



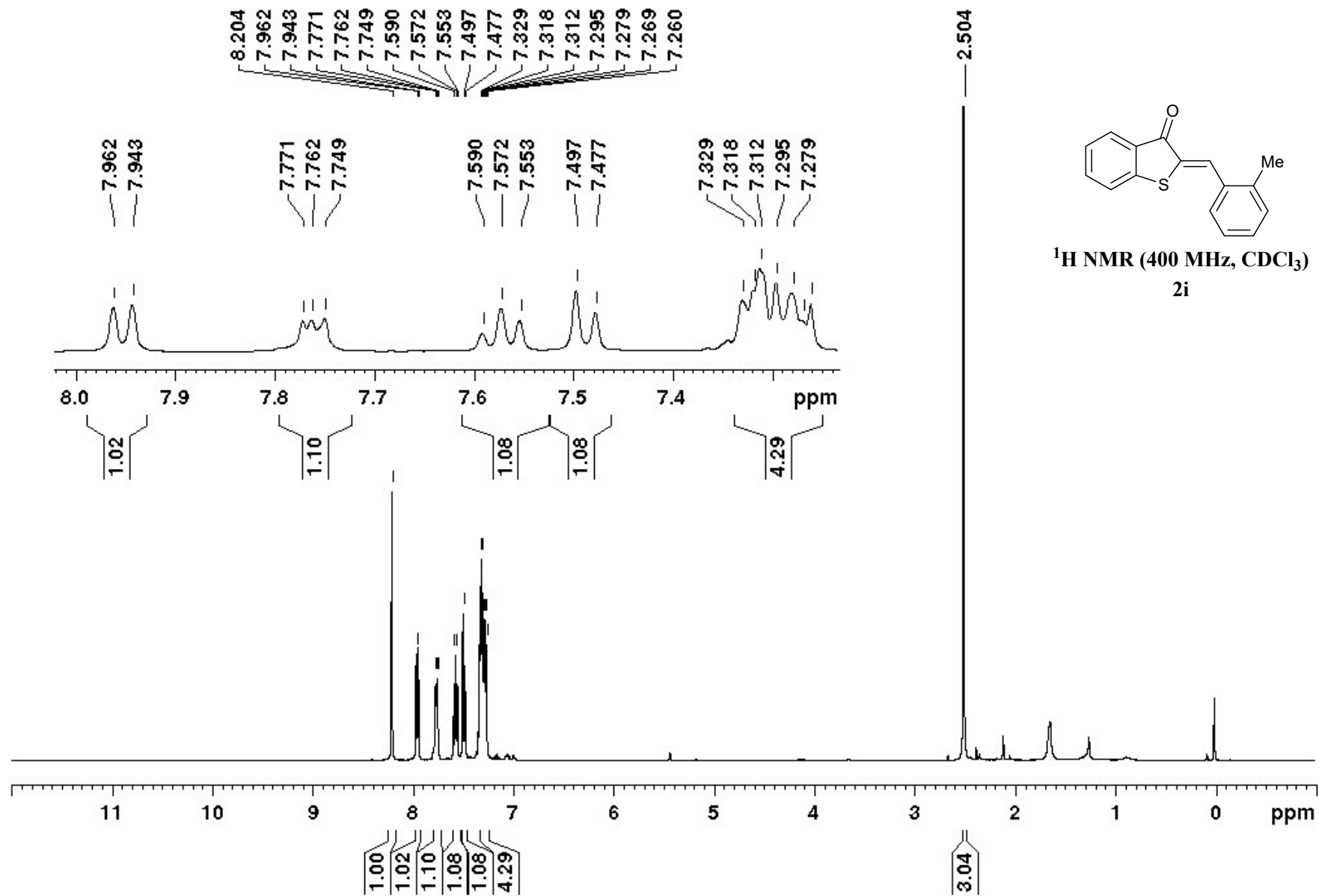
¹H NMR spectrum of compound 2h



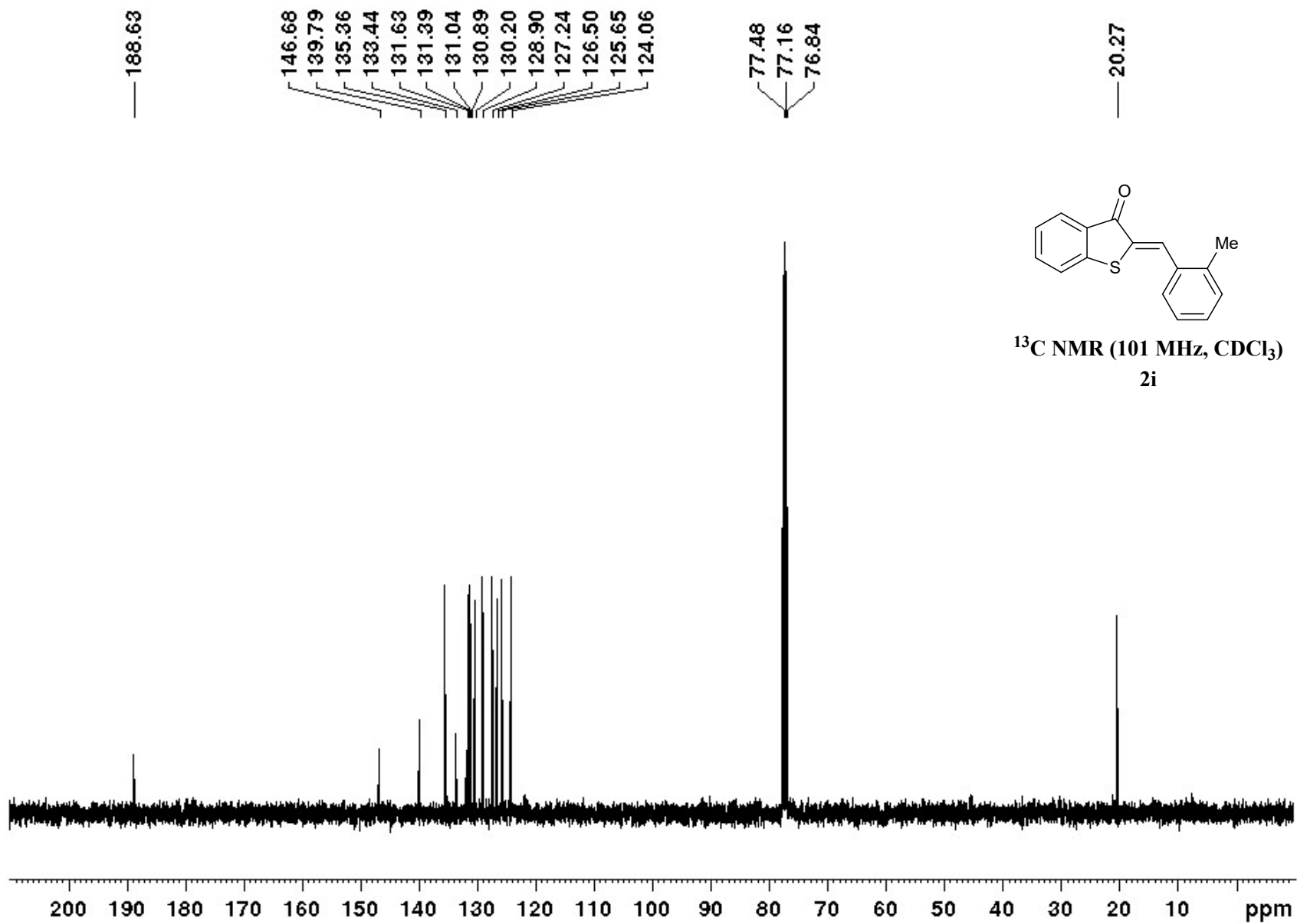
¹³C NMR spectrum of compound 2h



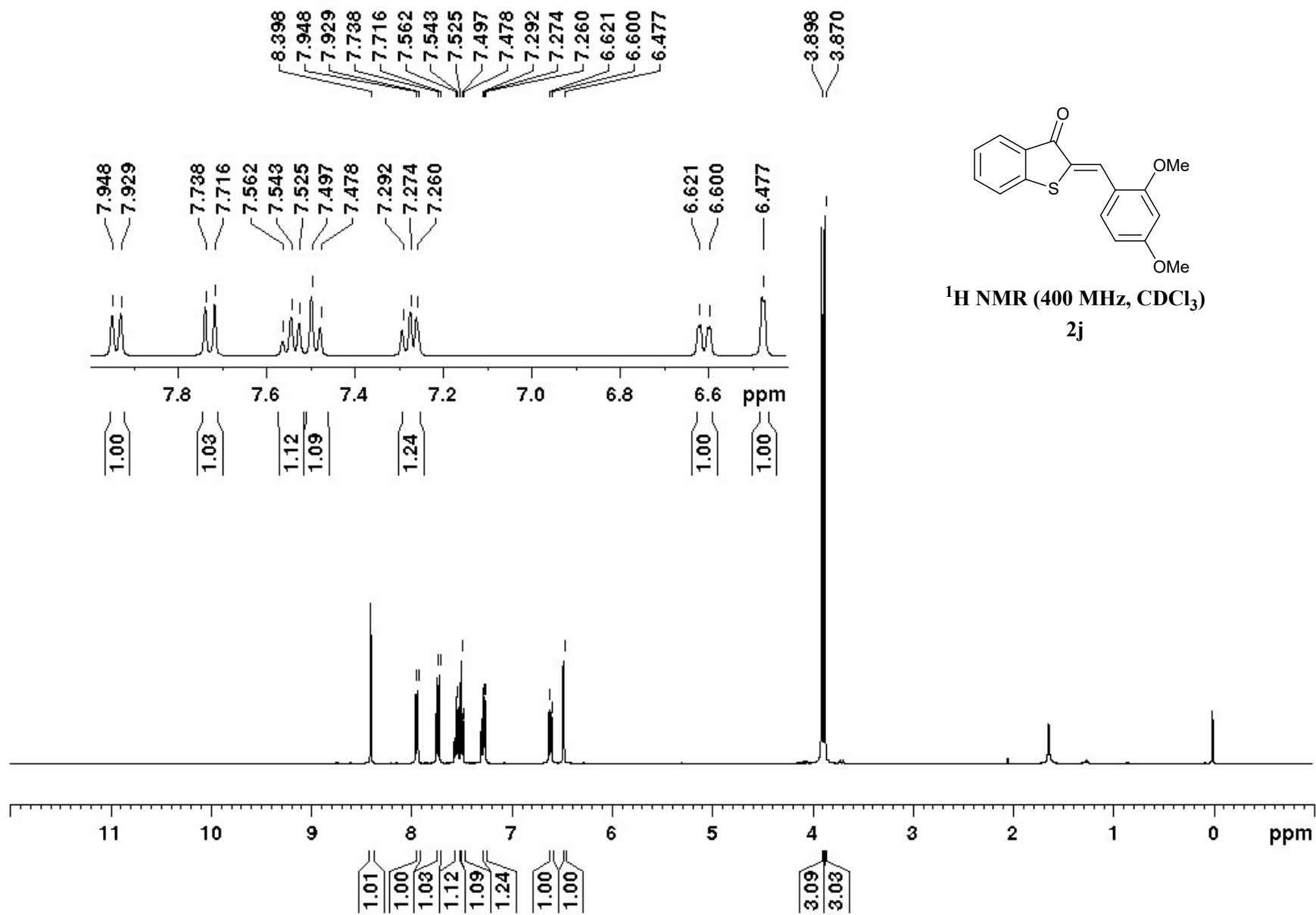
¹H NMR spectrum of compound 2i



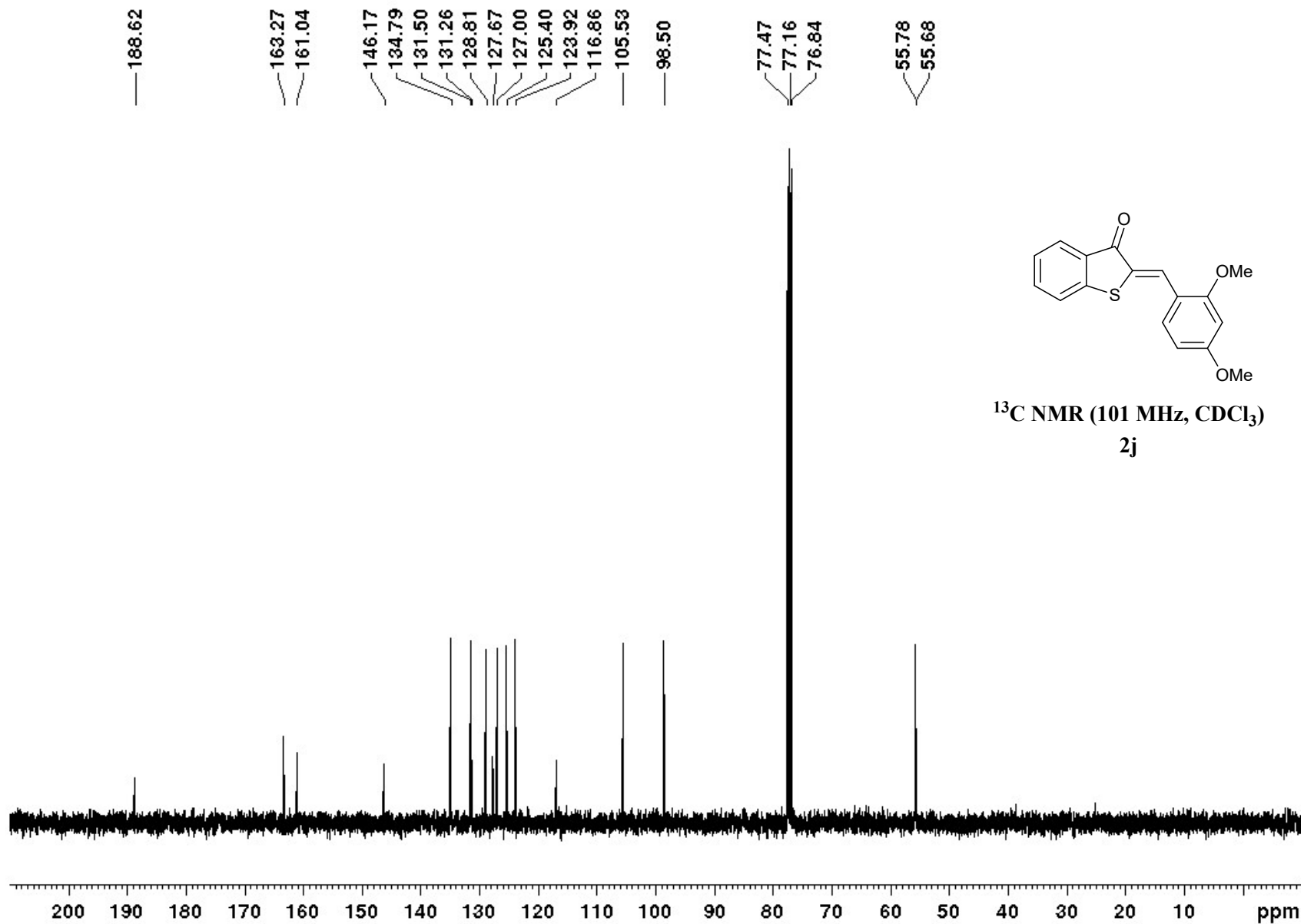
¹³C NMR spectrum of compound 2i



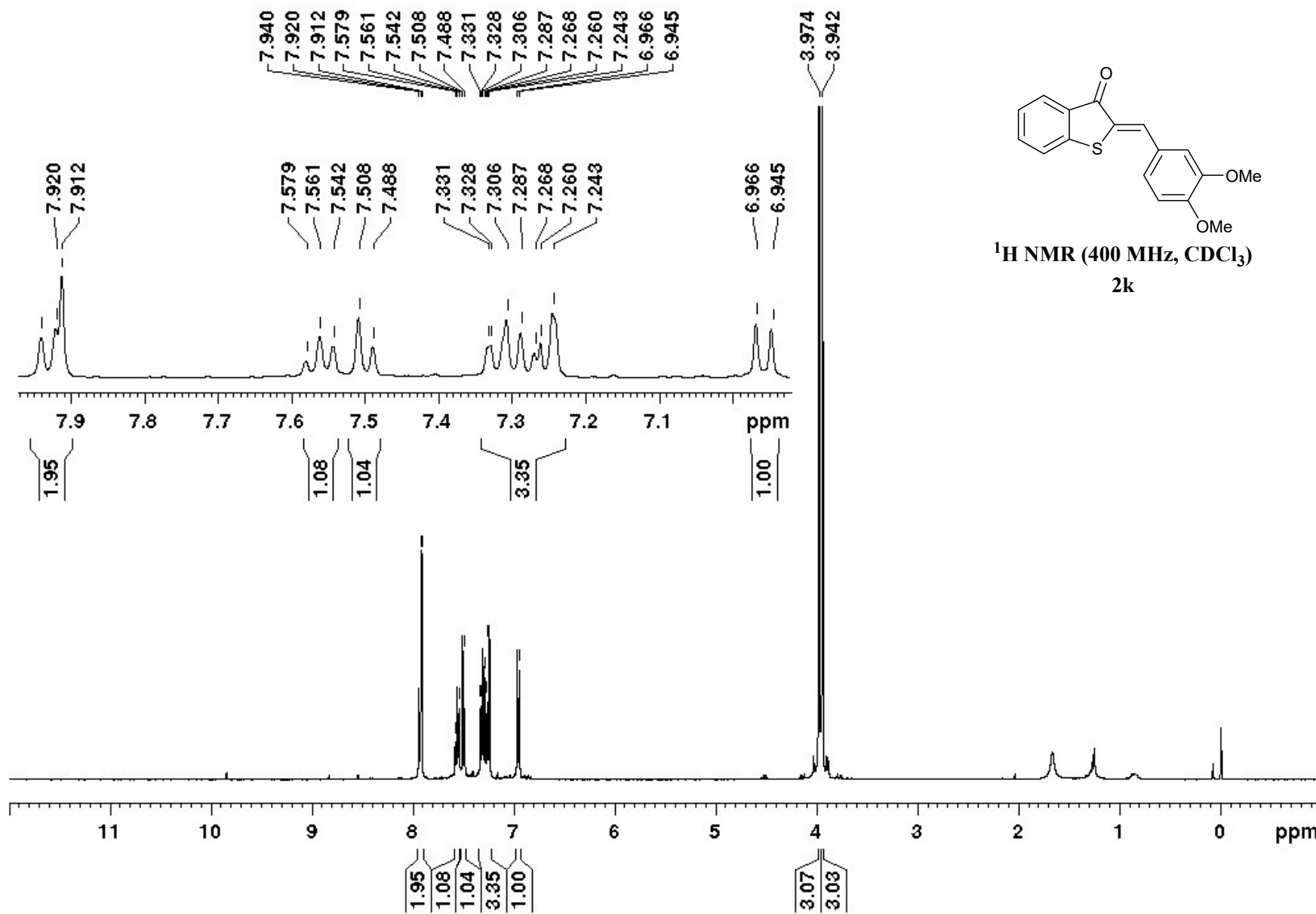
¹H NMR spectrum of compound 2j



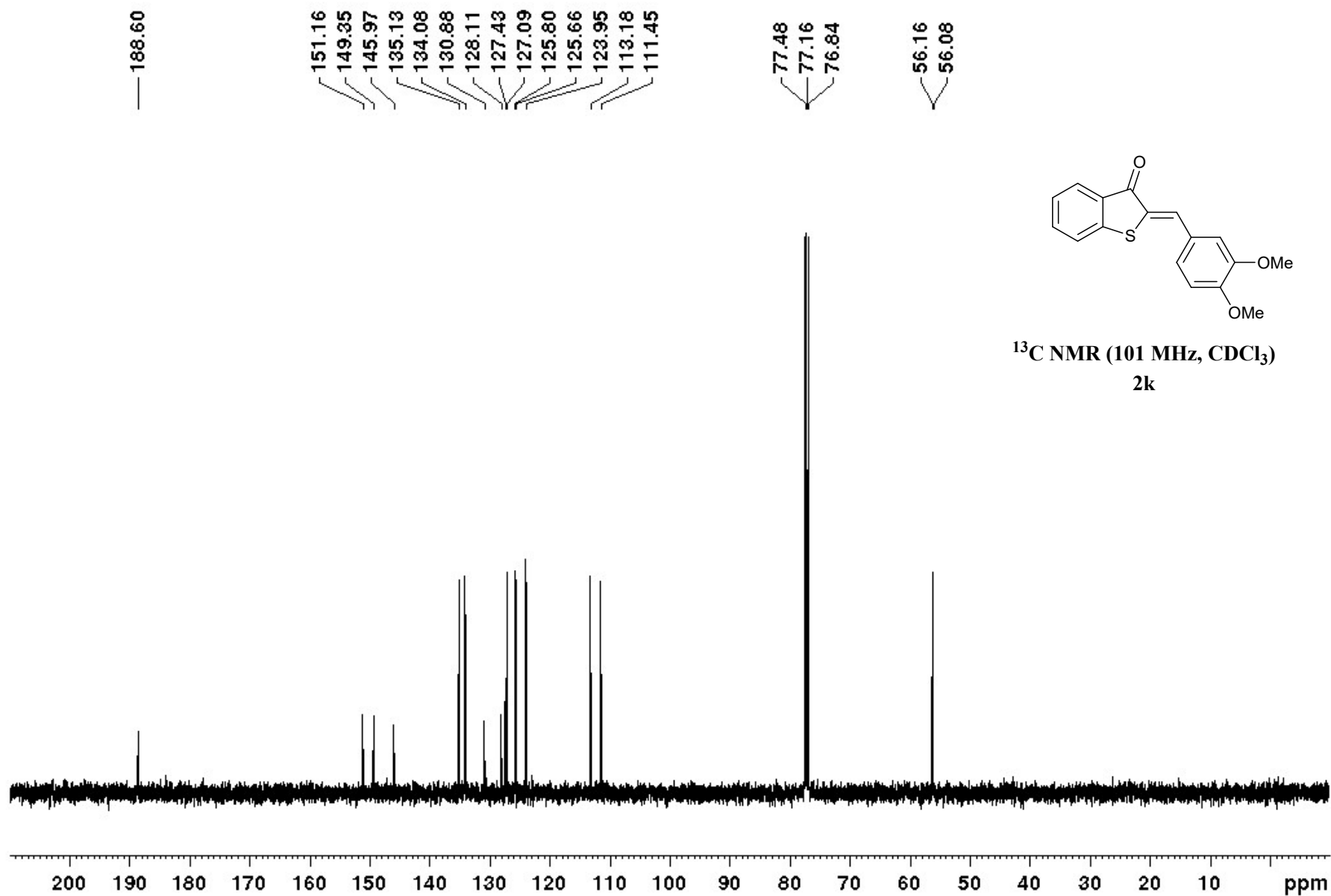
¹³C NMR spectrum of compound 2j



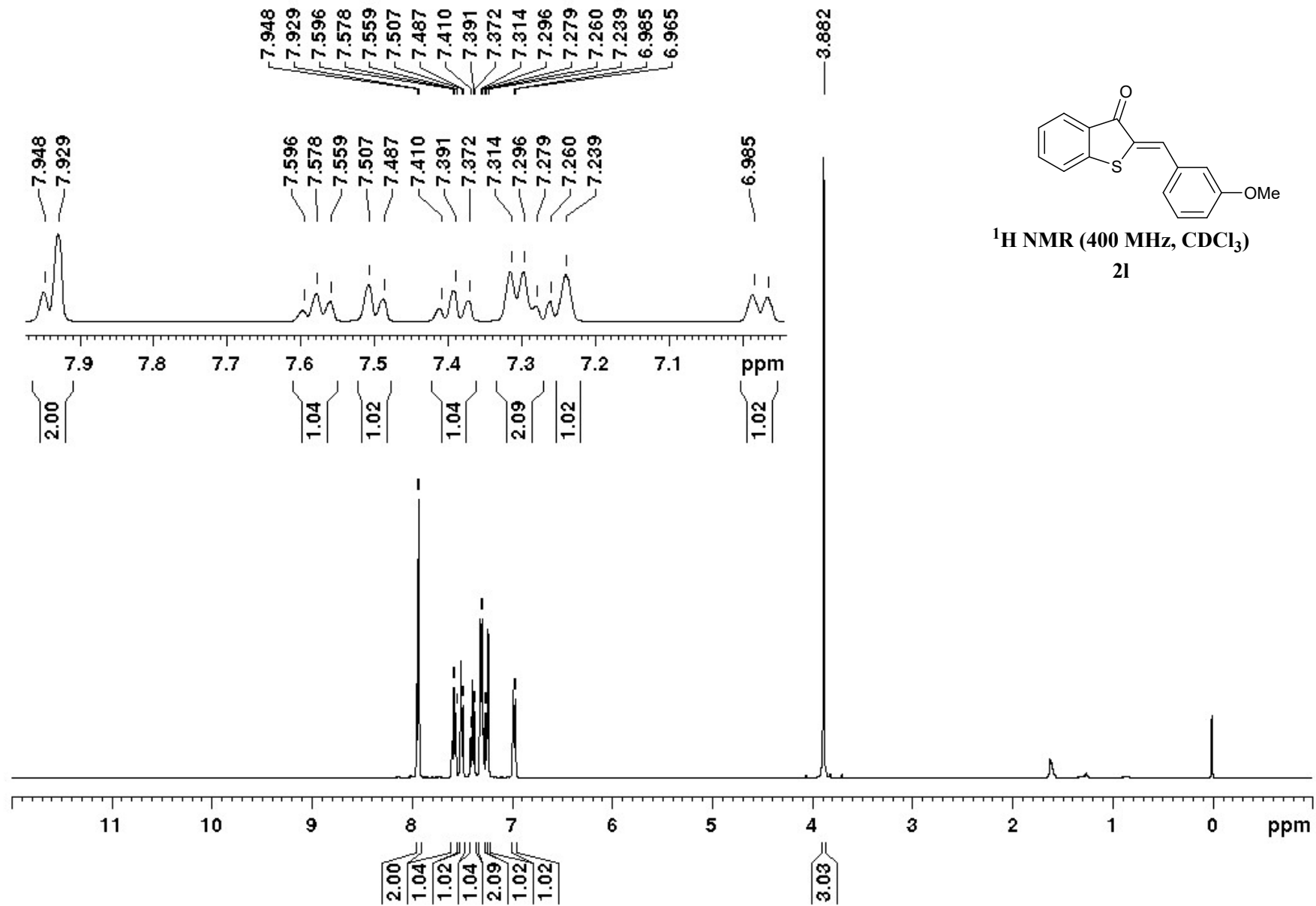
¹H NMR spectrum of compound 2k



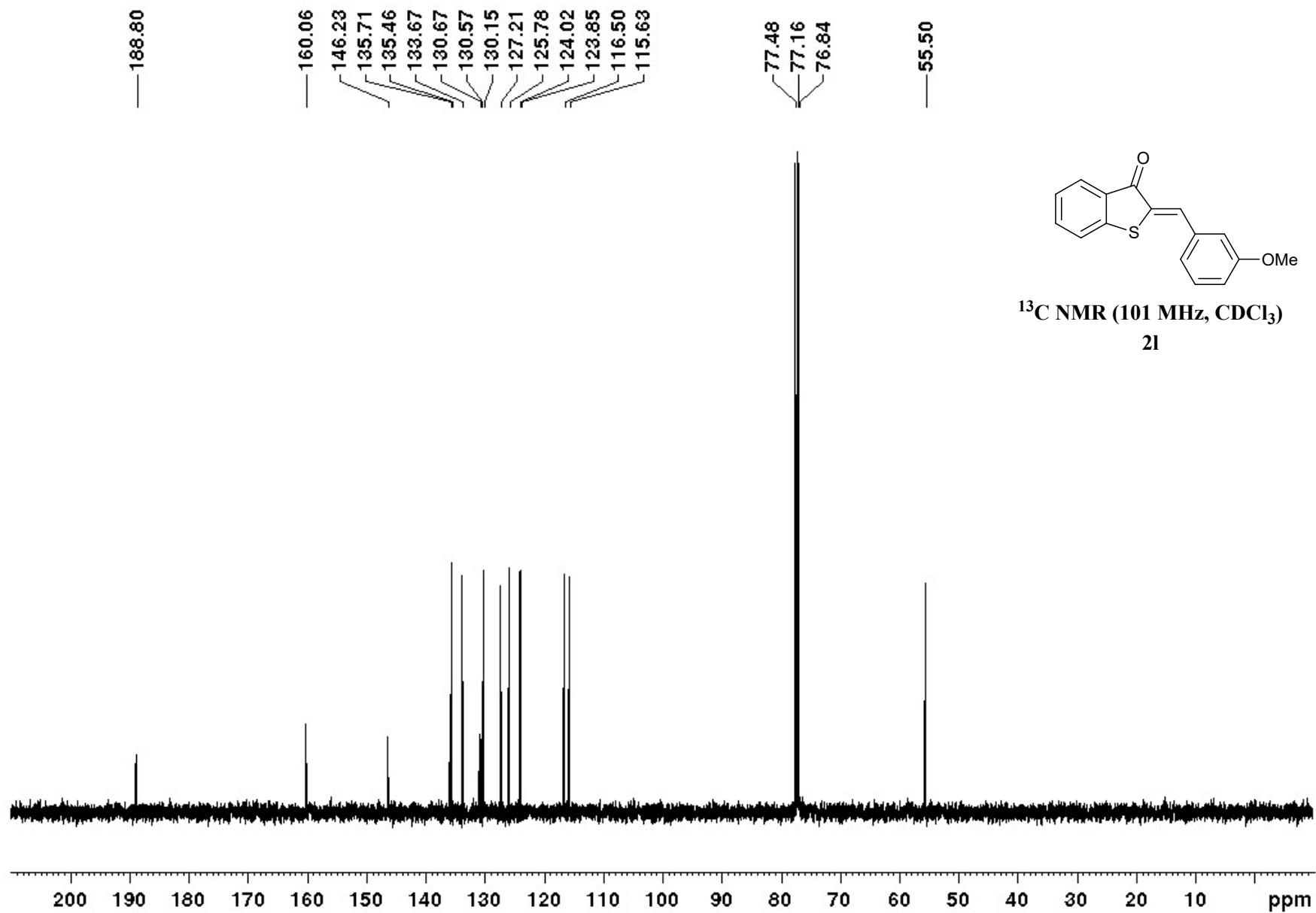
¹³C NMR spectrum of compound 2k



¹H NMR spectrum of compound 21

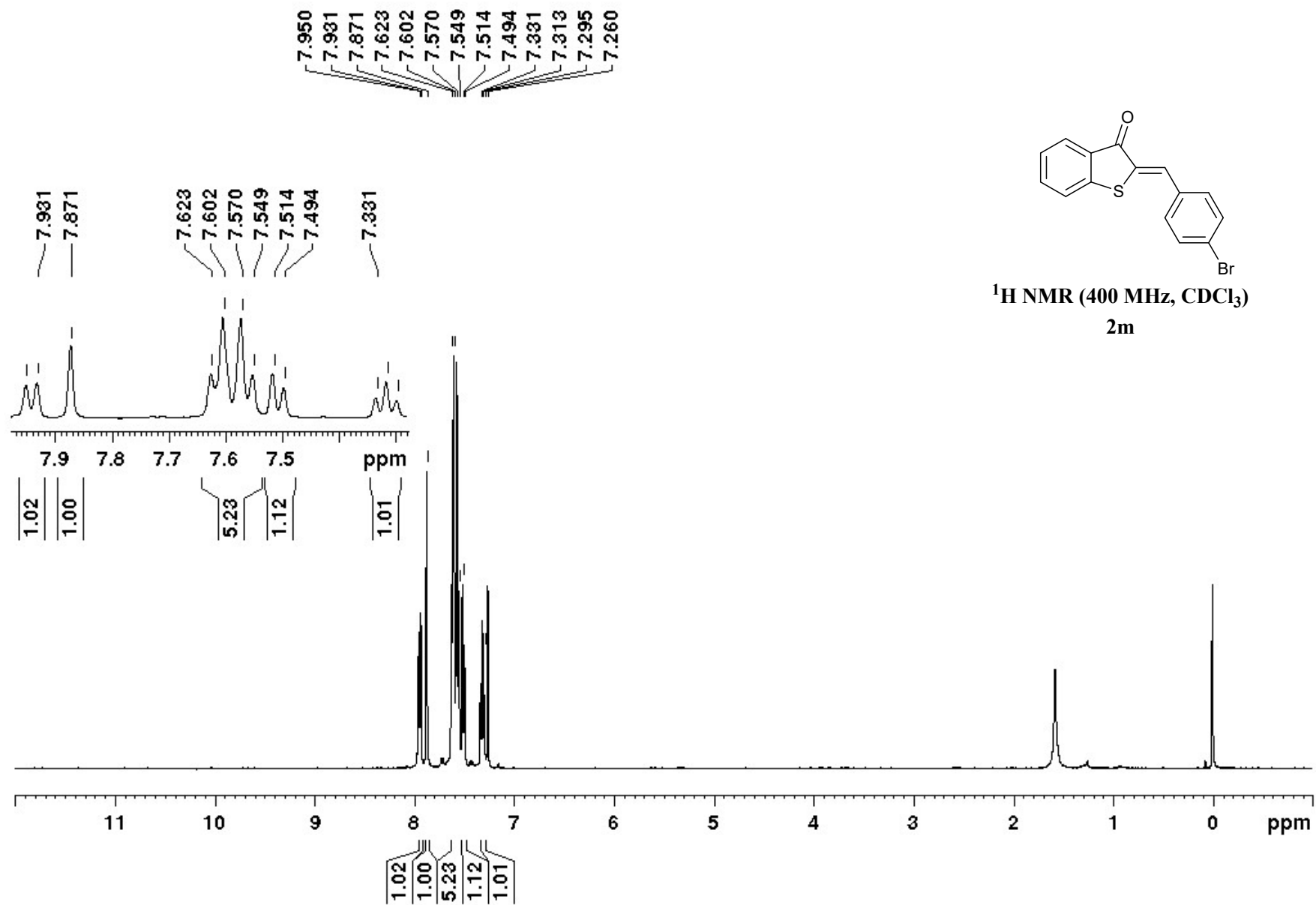


¹³C NMR spectrum of compound 21

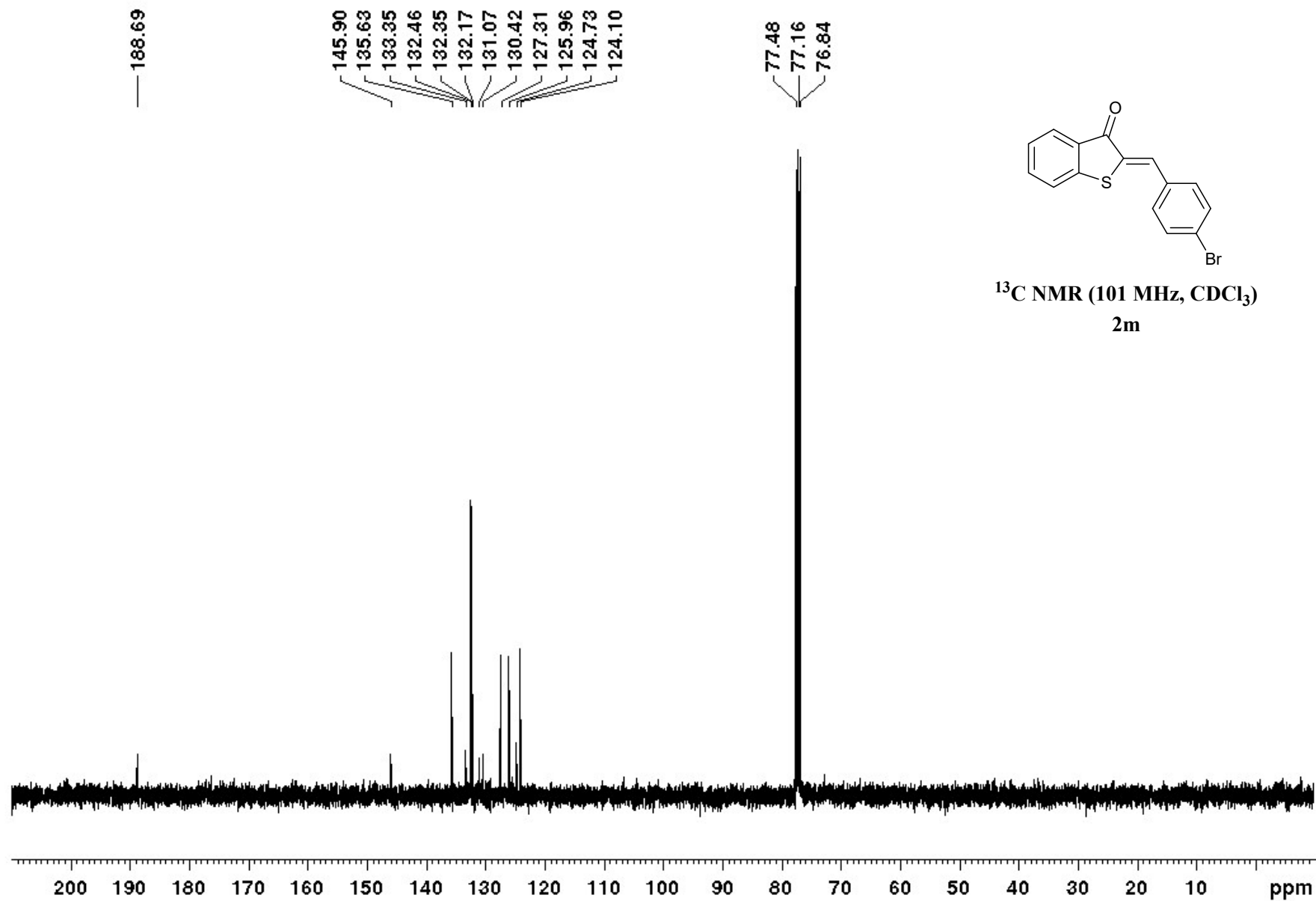


v

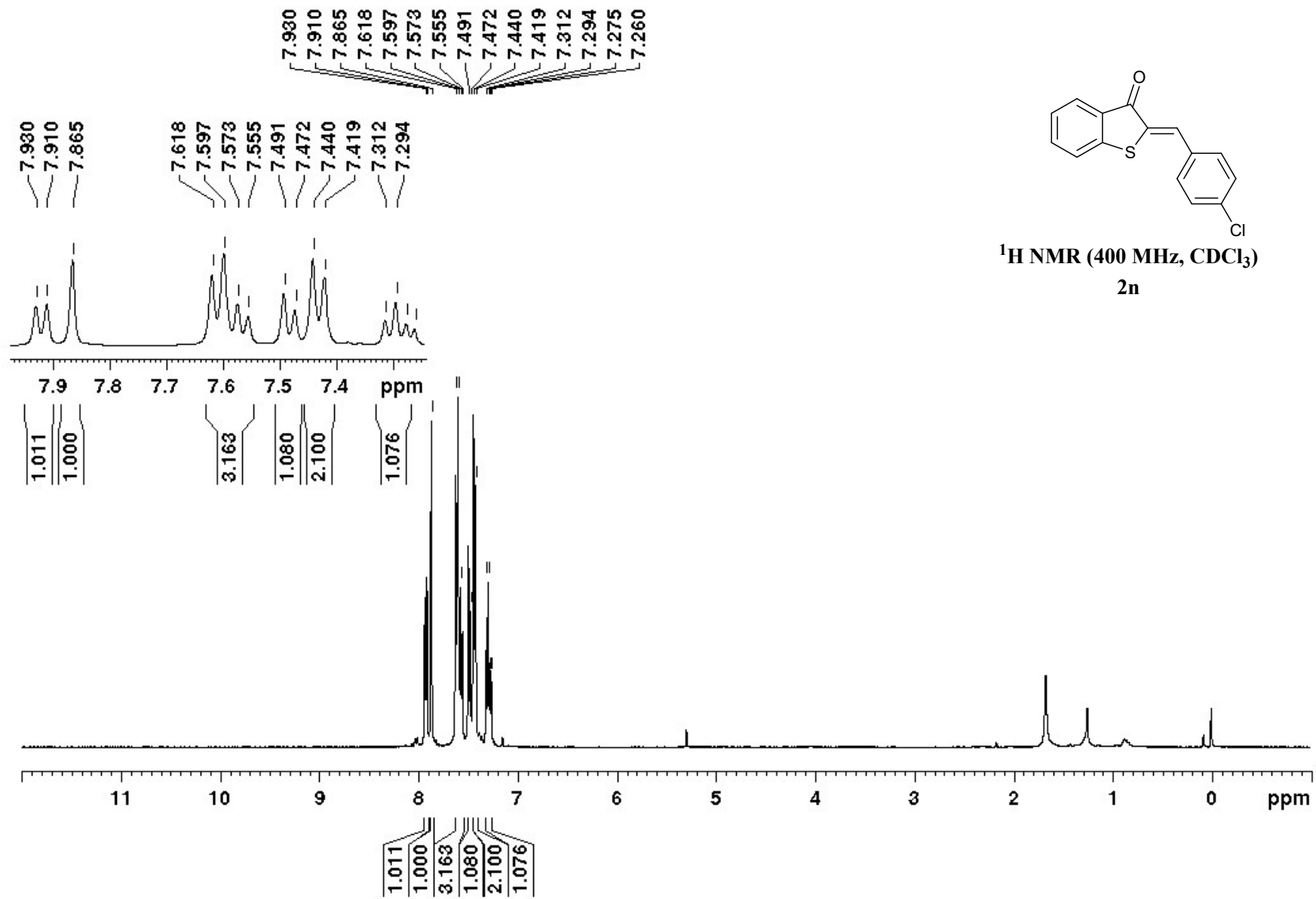
¹H NMR spectrum of compound 2m



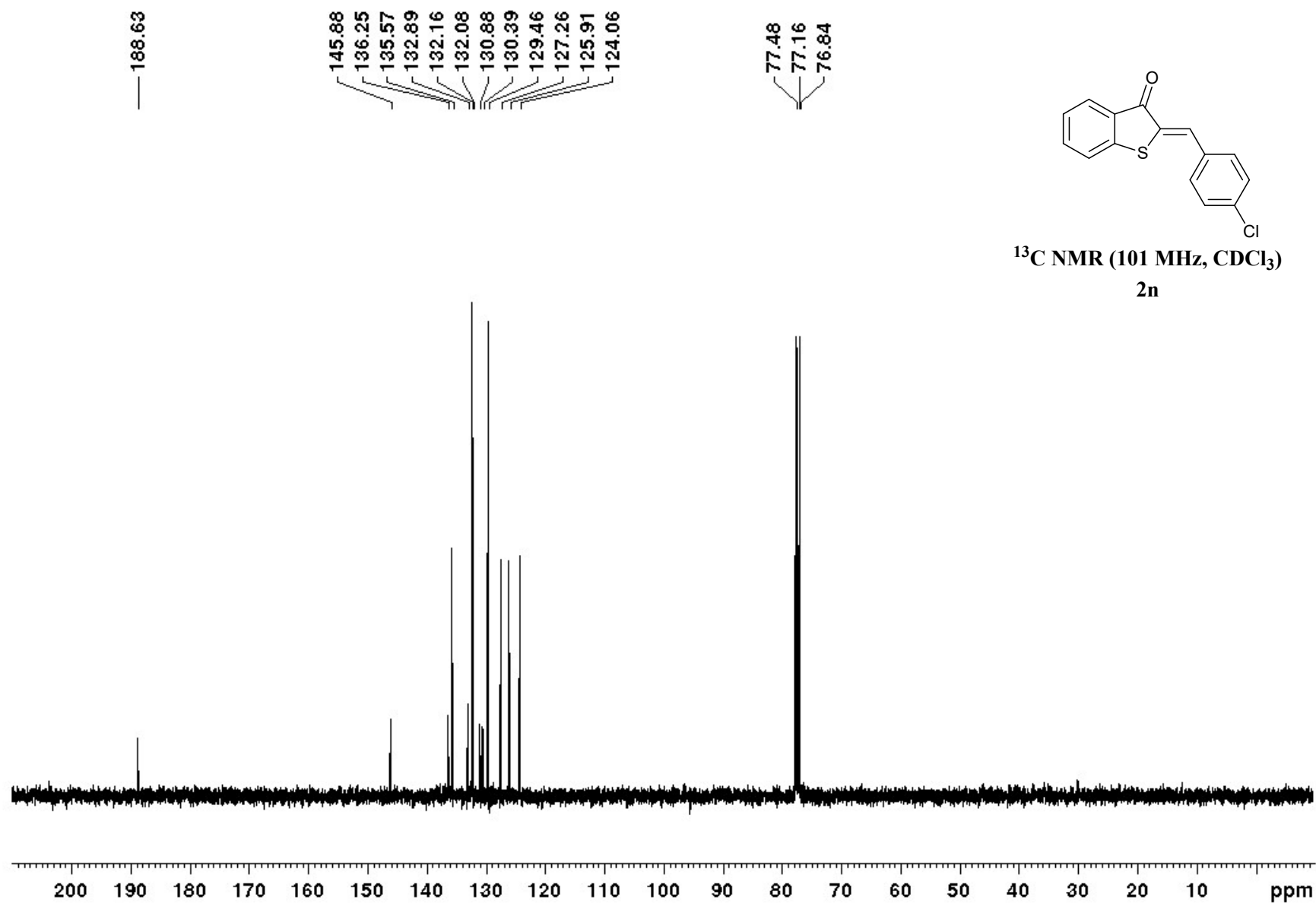
¹³C NMR spectrum of compound 2m



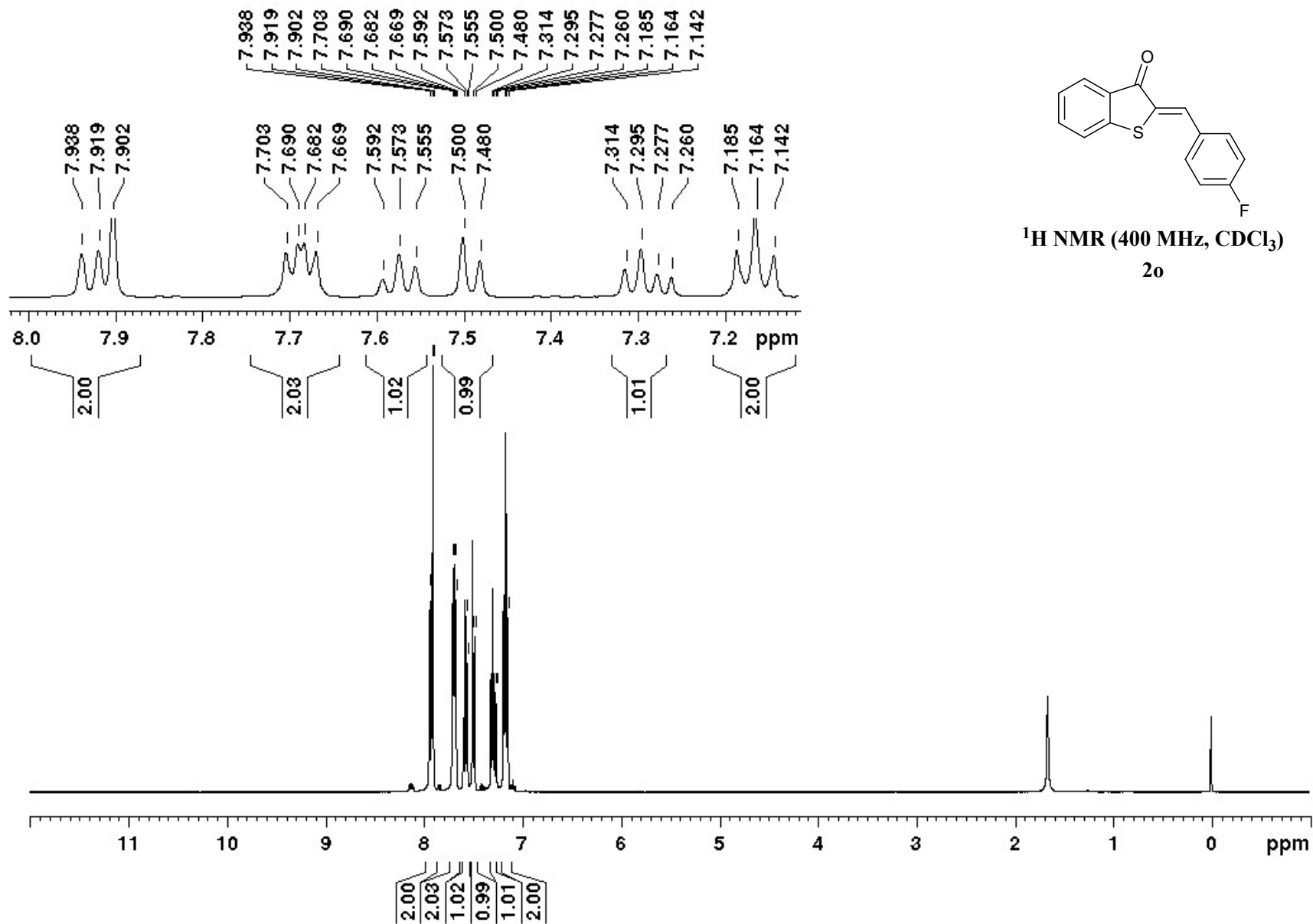
¹H NMR spectrum of compound 2n



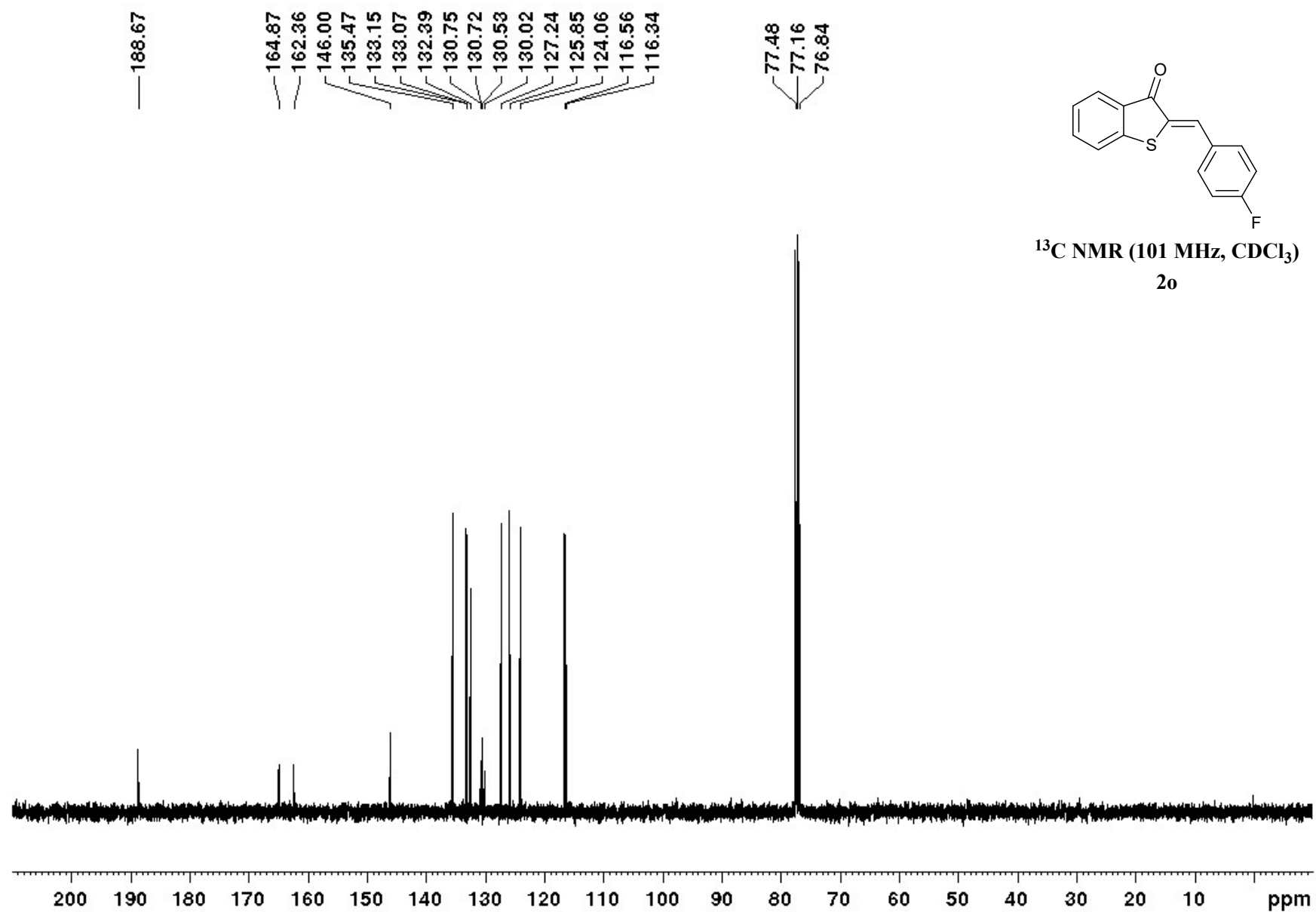
¹³C NMR spectrum of compound 2n



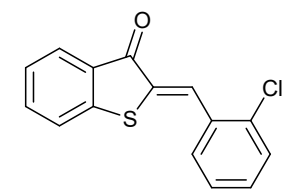
¹H NMR spectrum of compound 2o



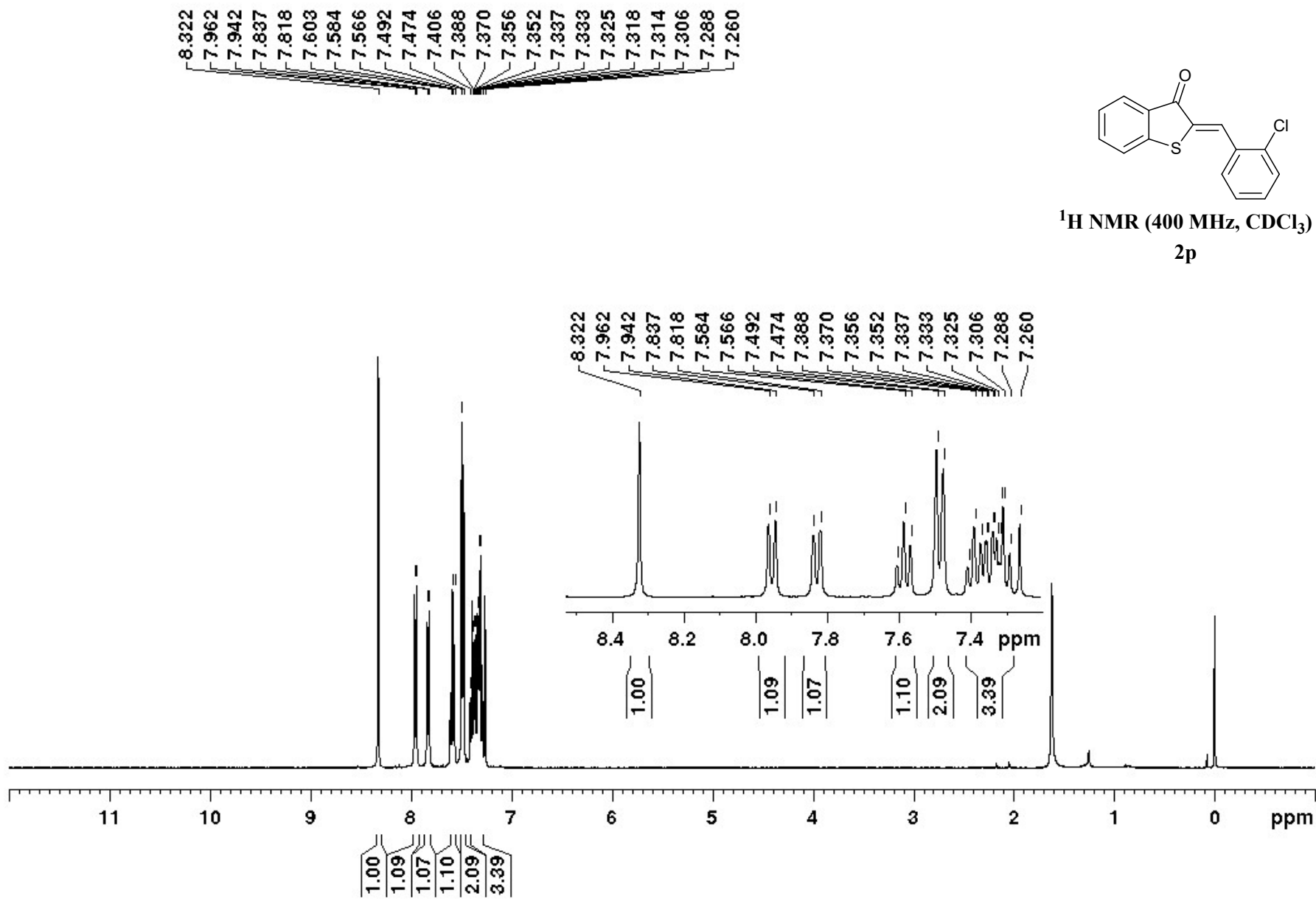
¹³C NMR spectrum of compound 2o



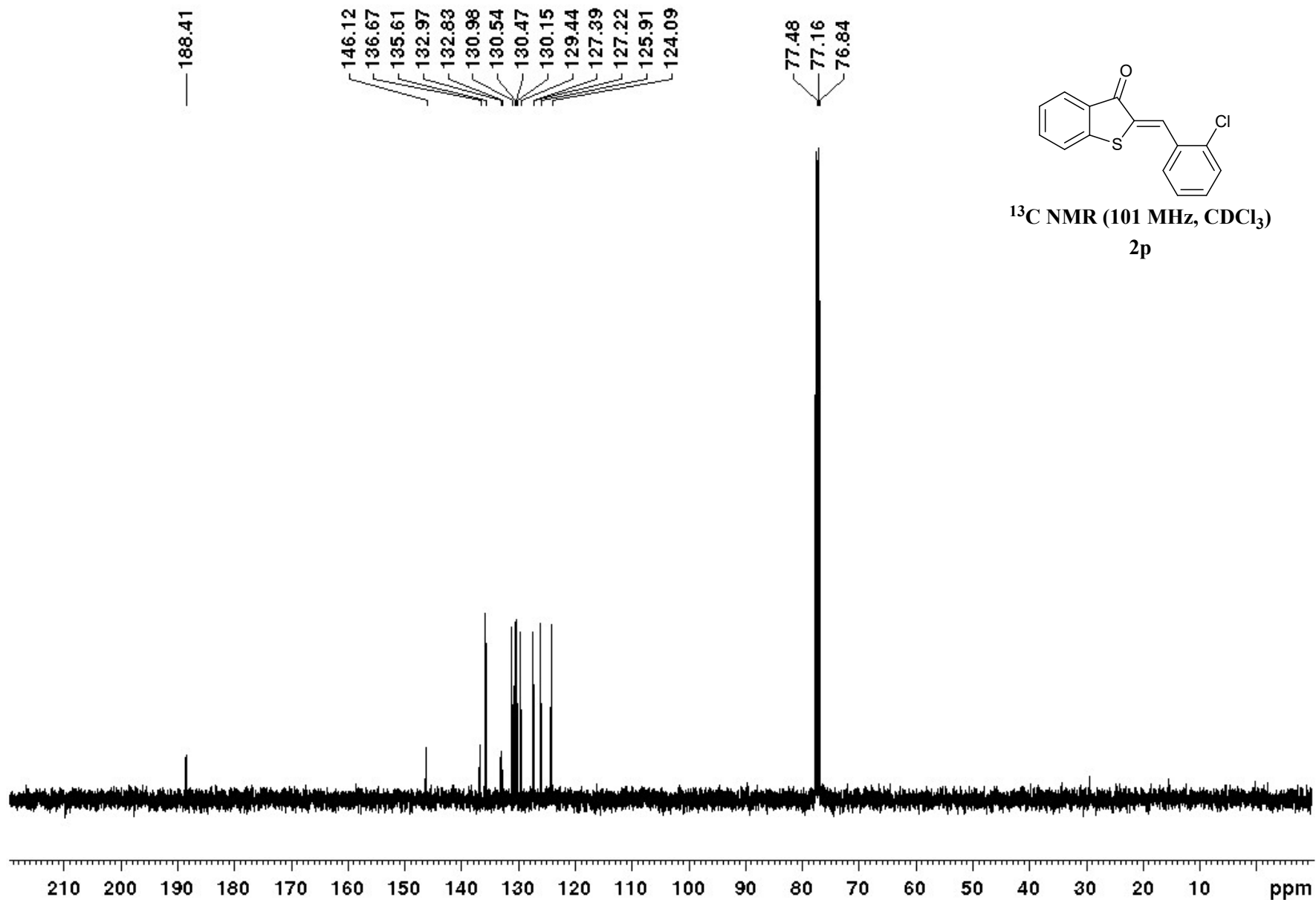
¹H NMR spectrum of compound 2p



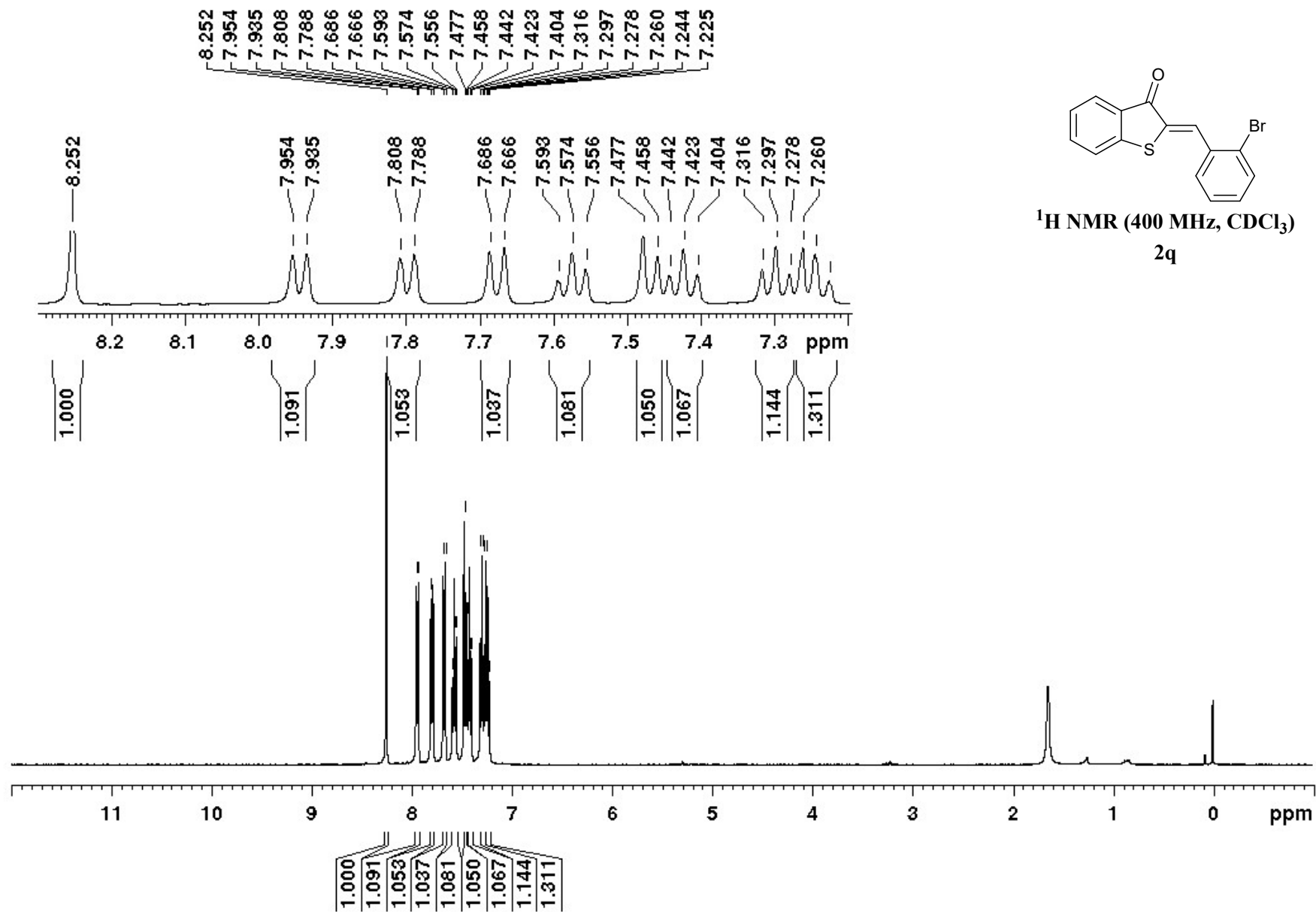
¹H NMR (400 MHz, CDCl₃)
2p



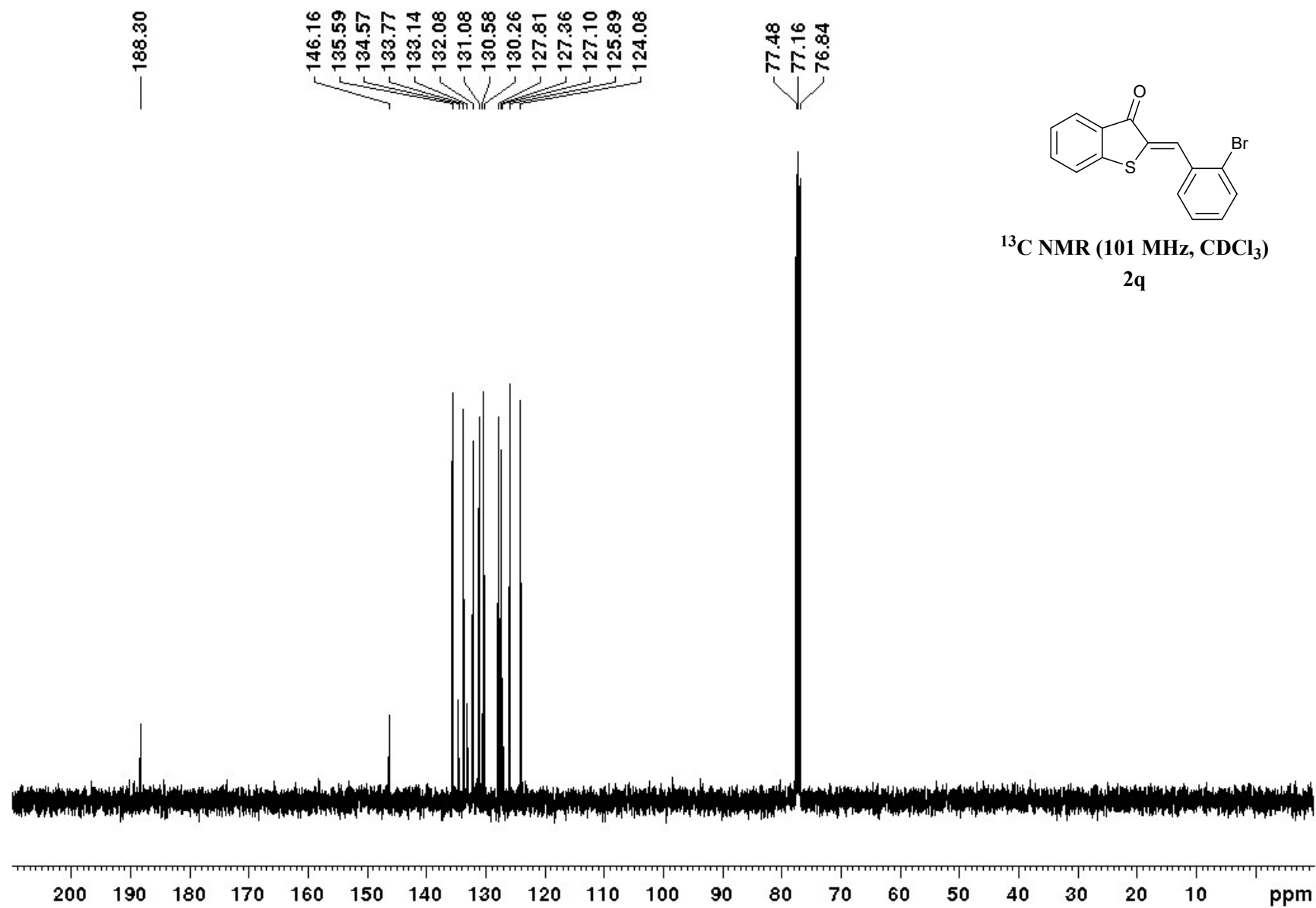
¹³C NMR spectrum of compound 2p



¹H NMR spectrum of compound 2q

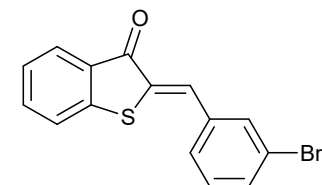


¹³C NMR spectrum of compound 2q



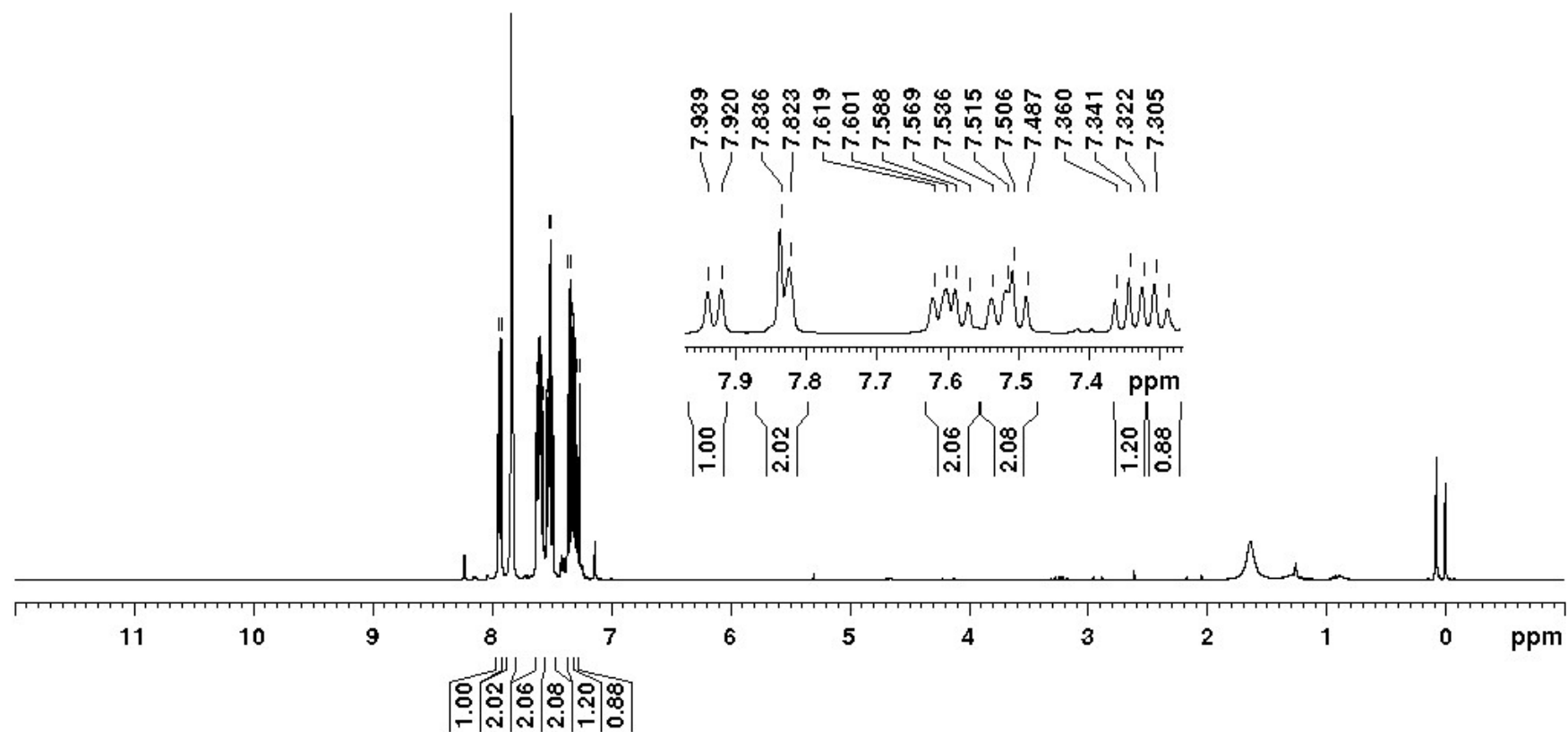
¹H NMR spectrum of compound 2r

7.939
7.920
7.836
7.823
7.619
7.601
7.588
7.569
7.536
7.515
7.506
7.487
7.360
7.341
7.322
7.305
7.286
7.260

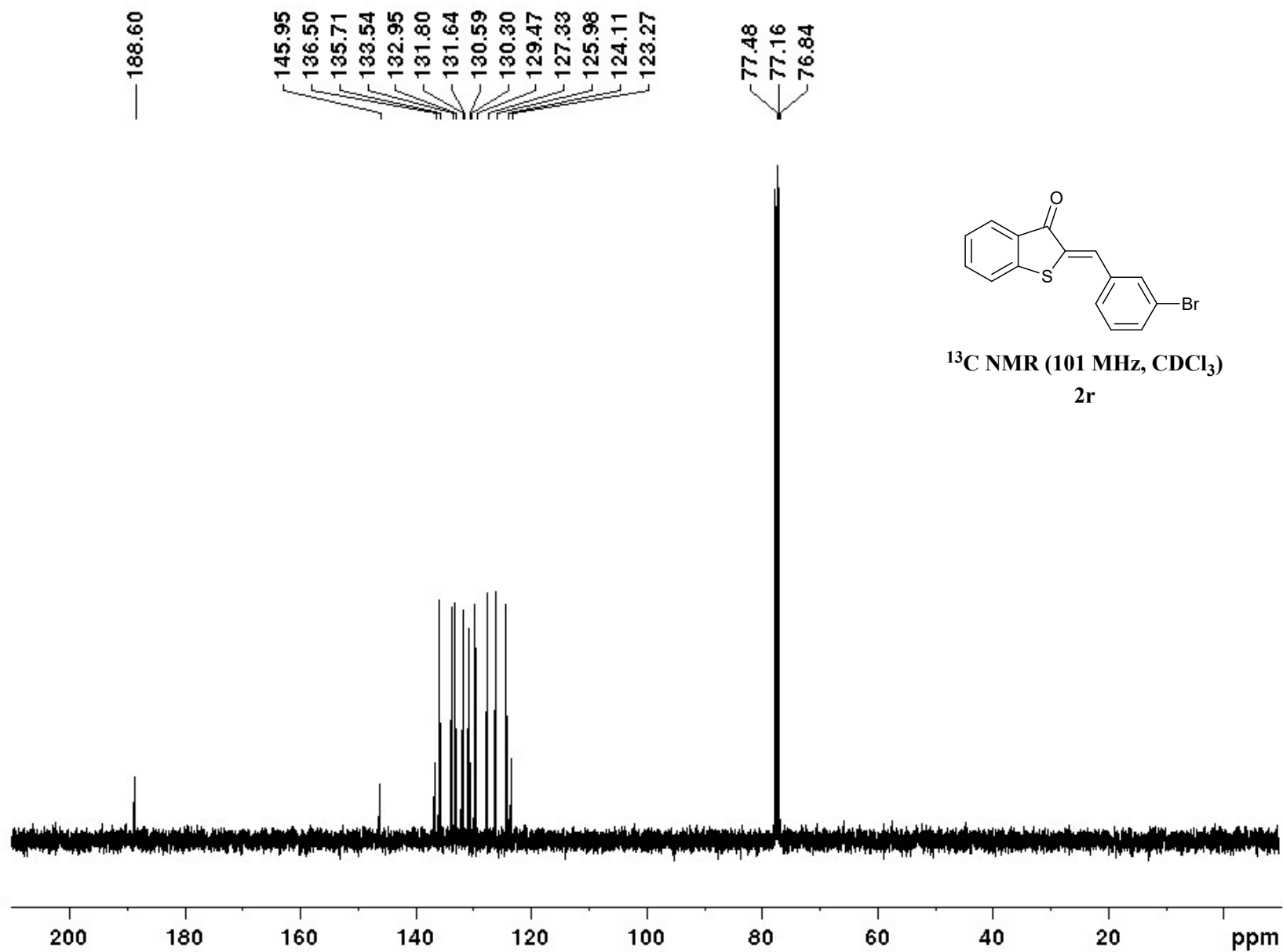


¹H NMR (400 MHz, CDCl₃)

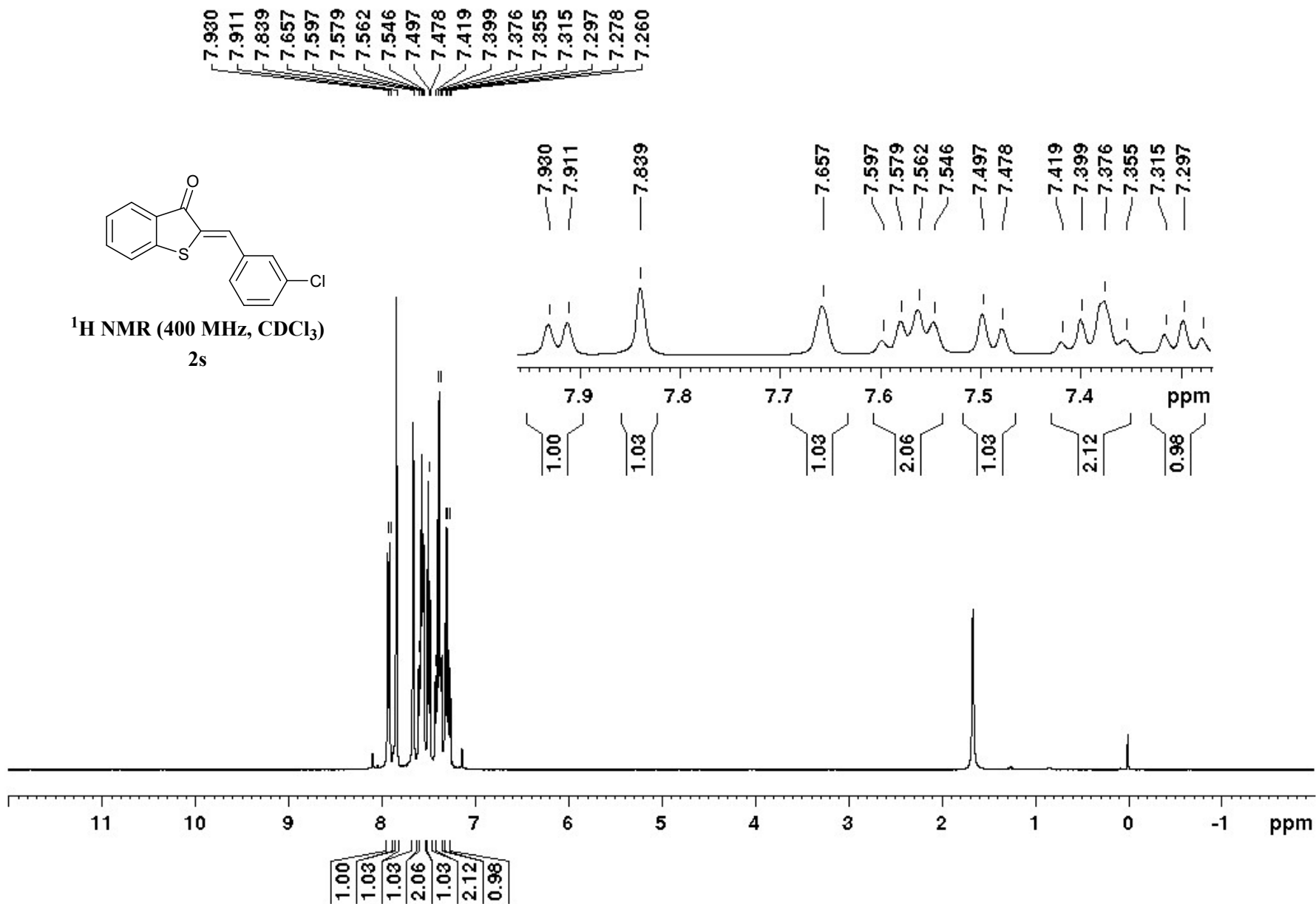
2r



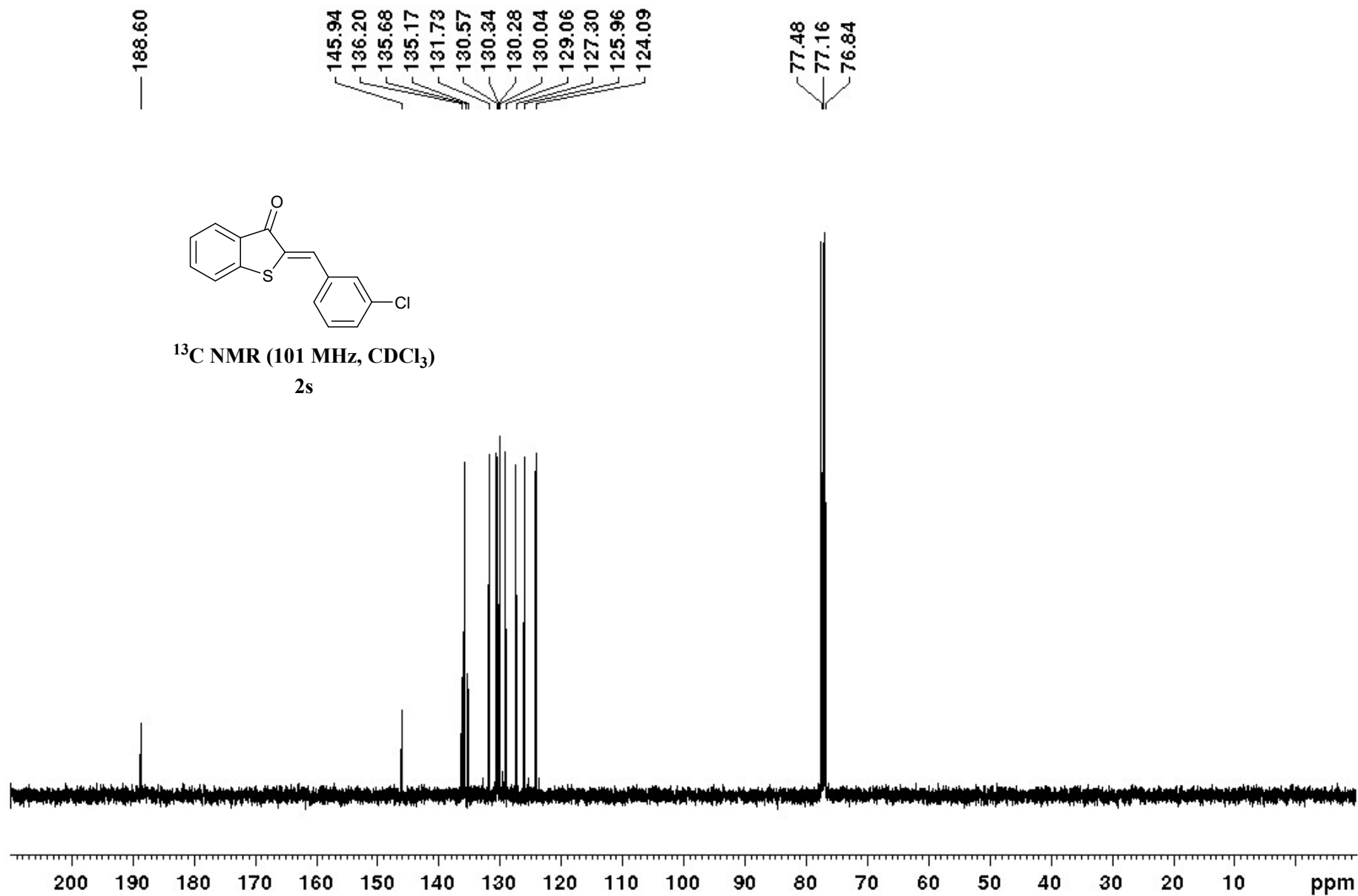
¹³C NMR spectrum of compound 2r



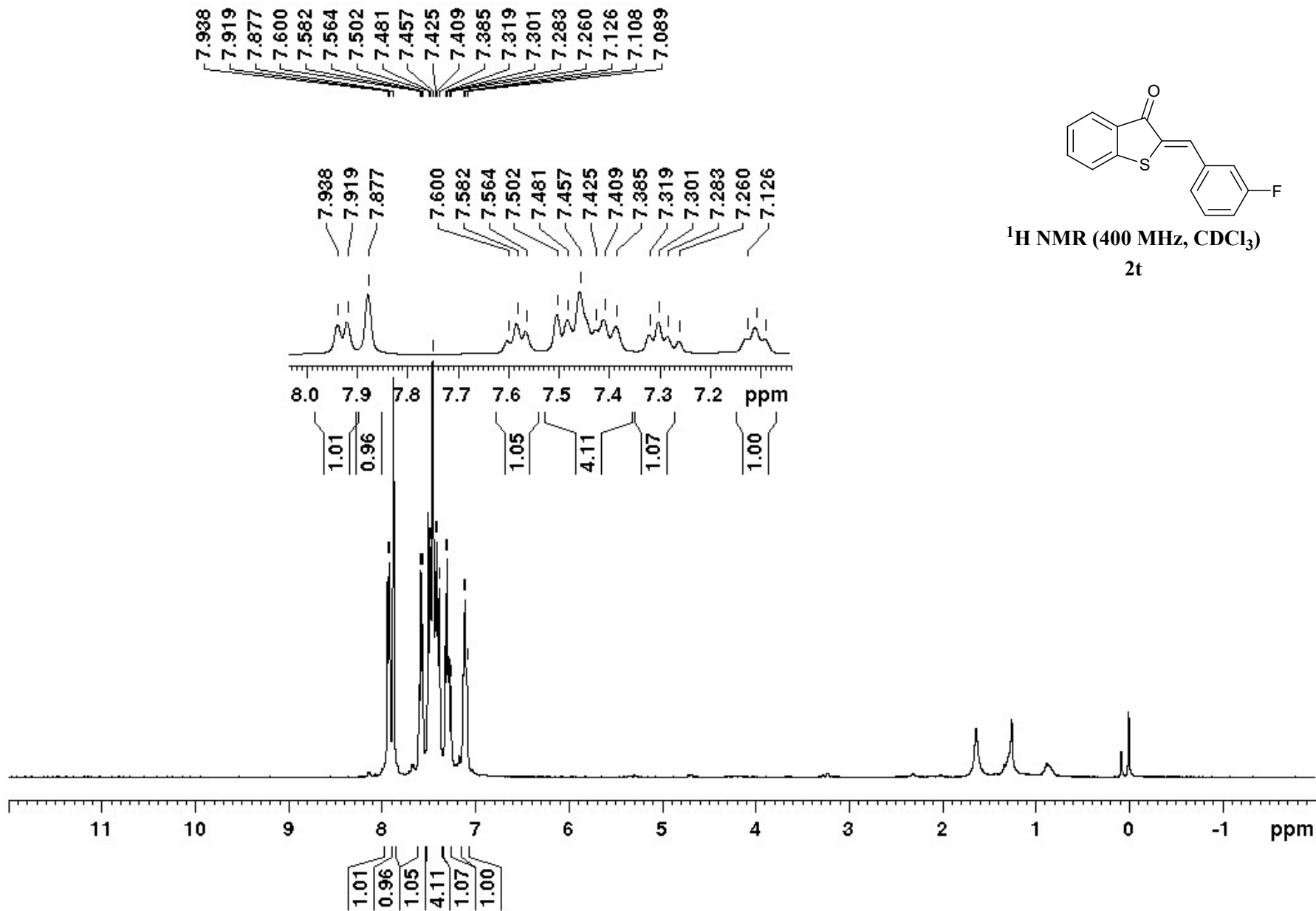
¹H NMR spectrum of compound 2s



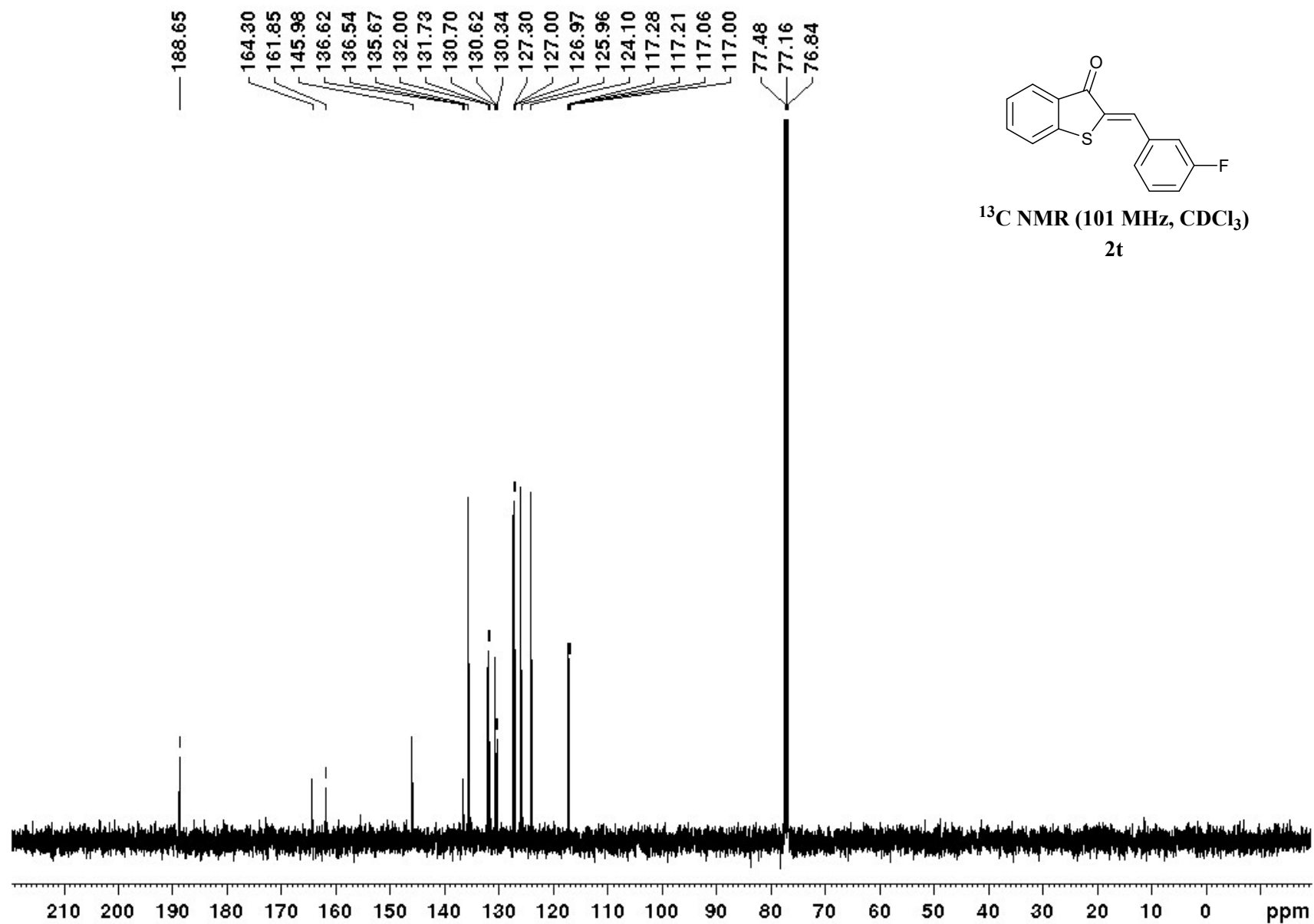
¹³C NMR spectrum of compound 2s



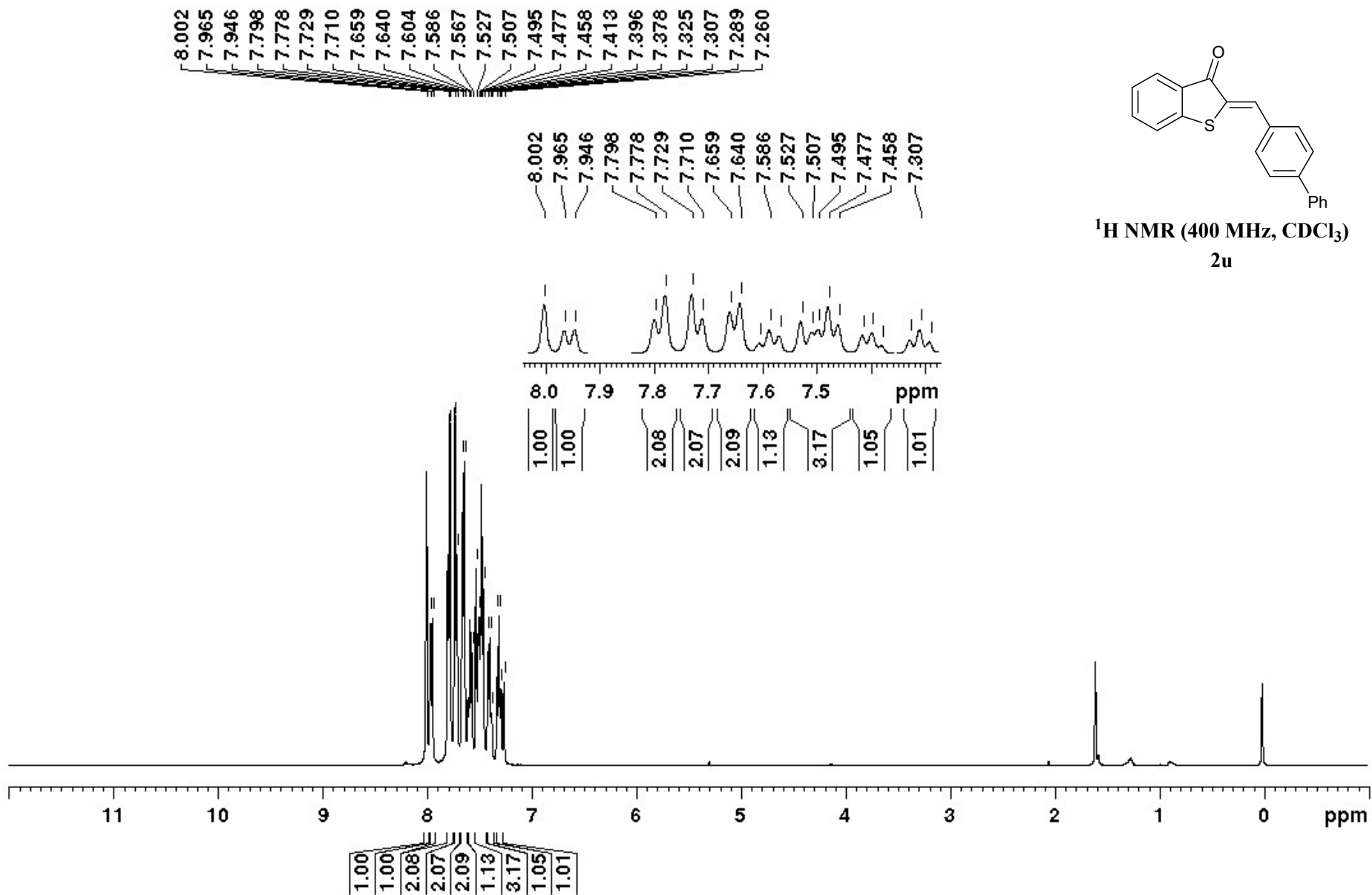
¹H NMR spectrum of compound 2t



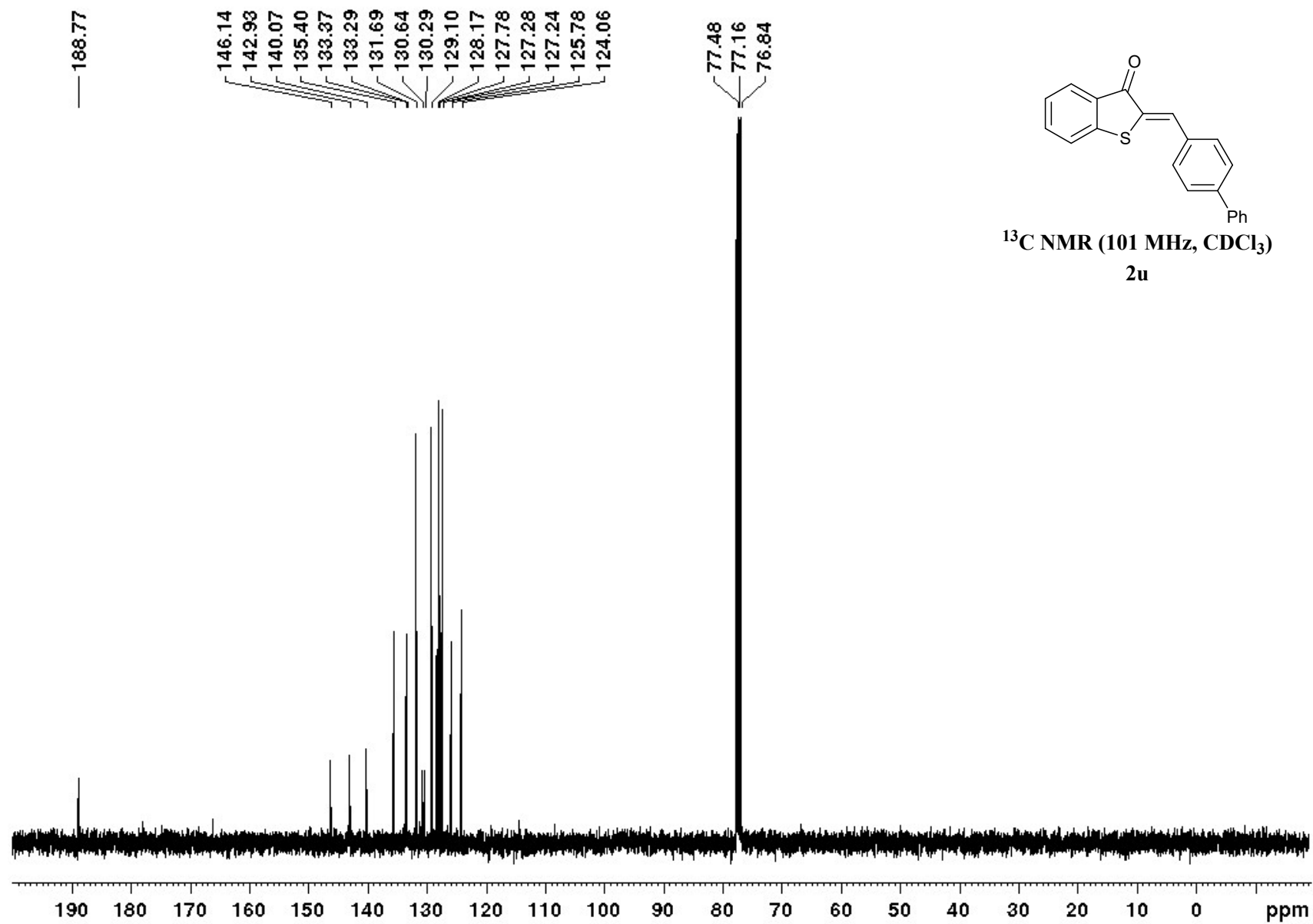
¹³C NMR spectrum of compound 2t



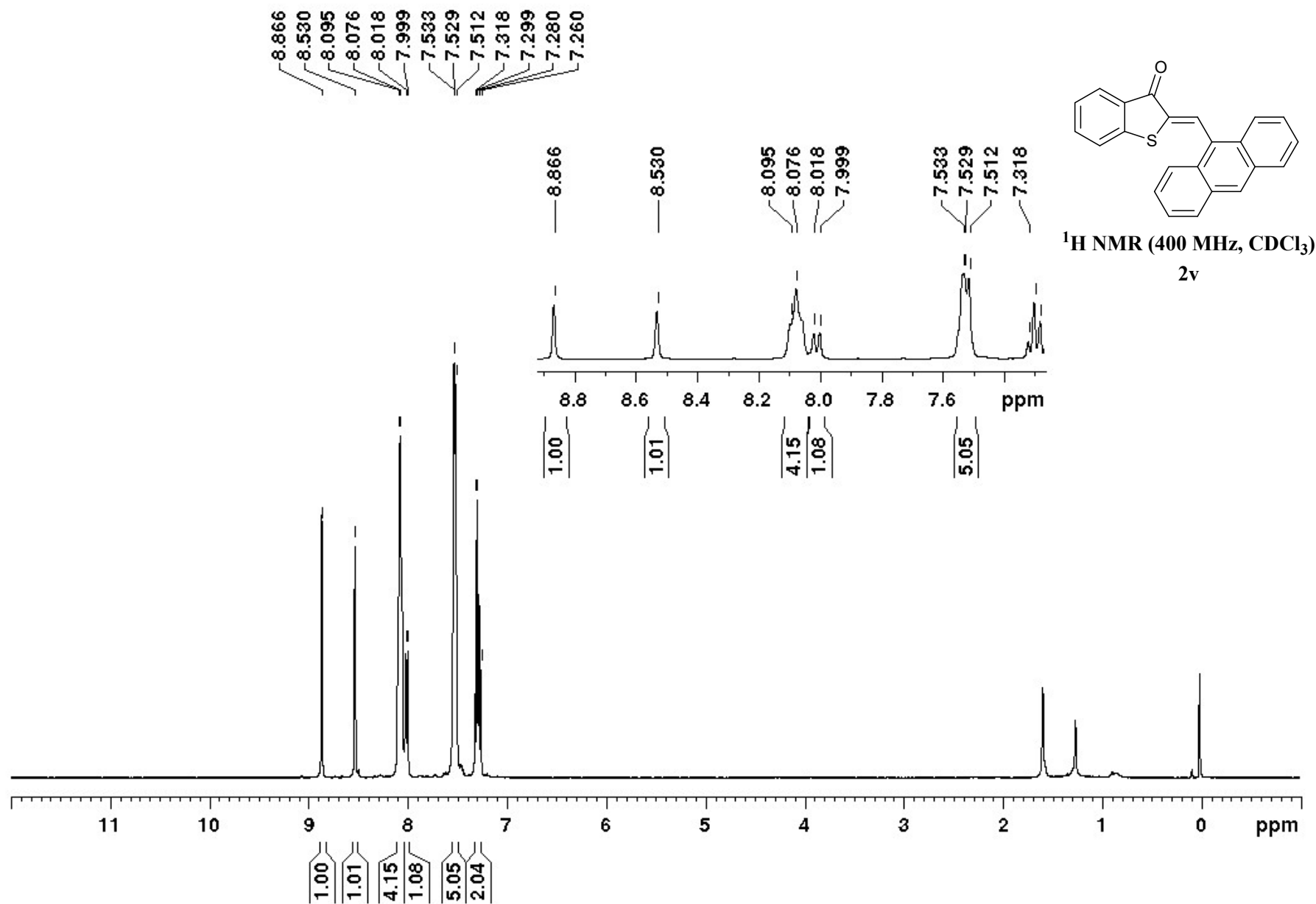
¹H NMR spectrum of compound 2u



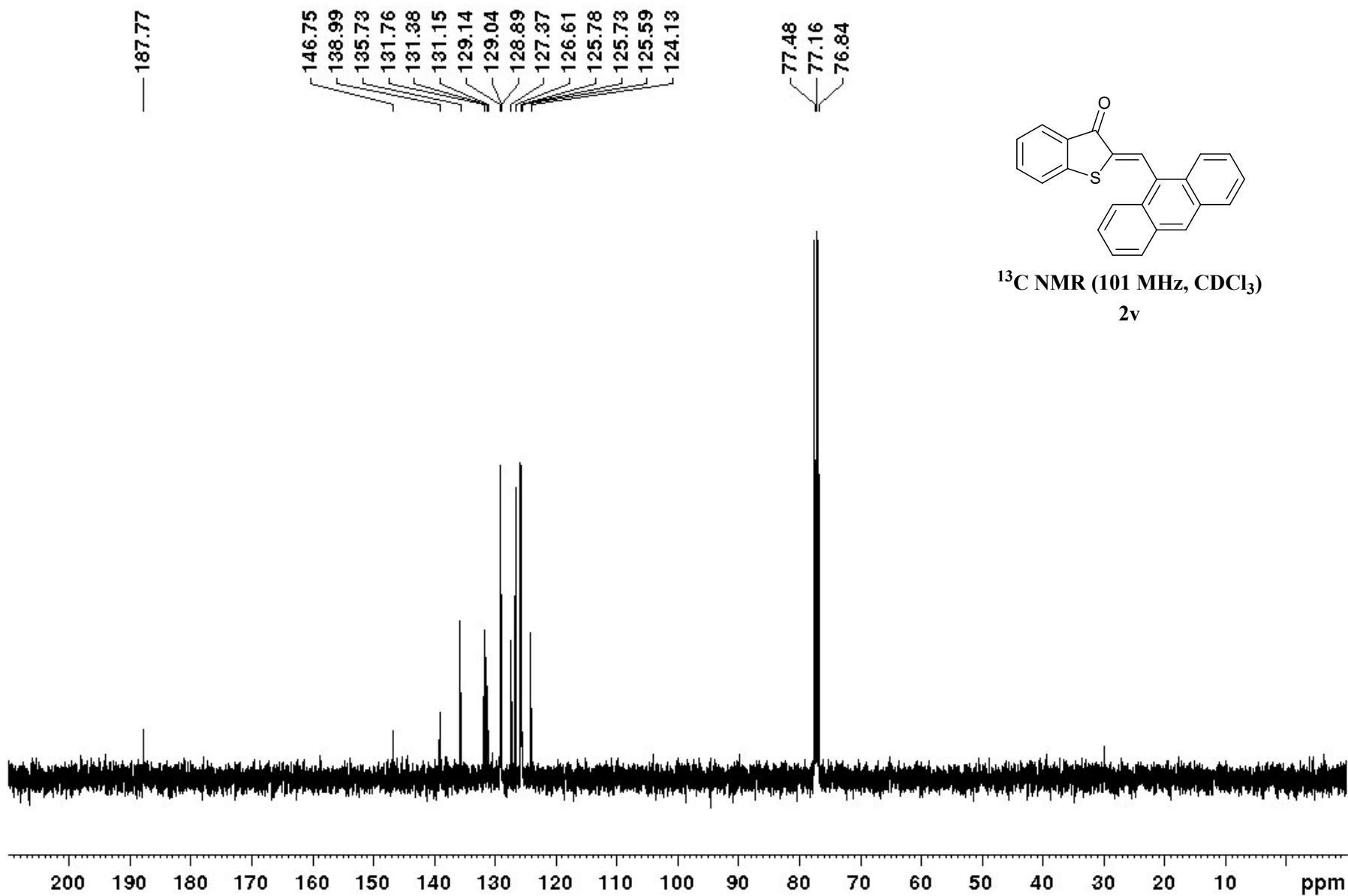
¹³C NMR spectrum of compound 2u



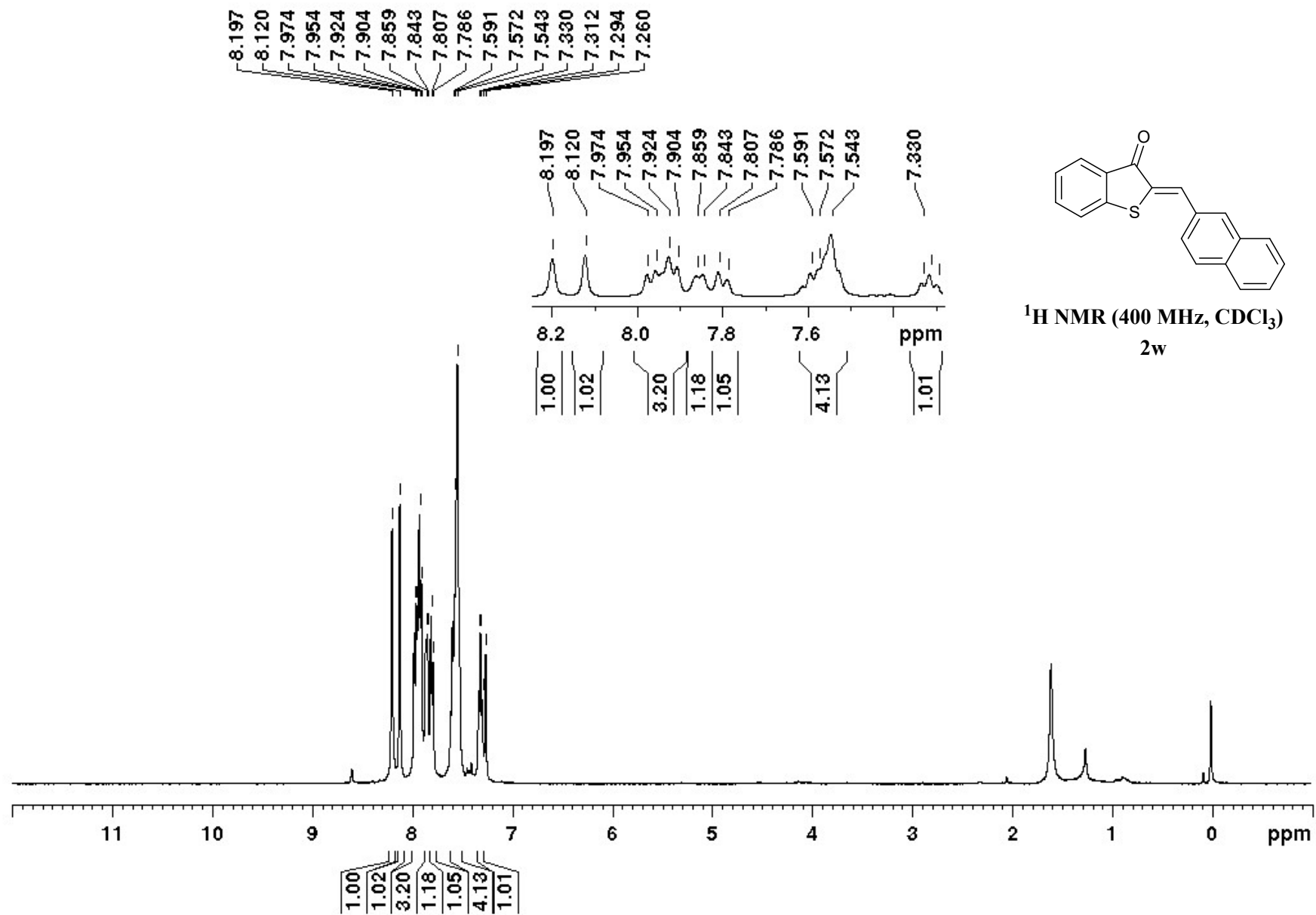
¹H NMR spectrum of compound 2v



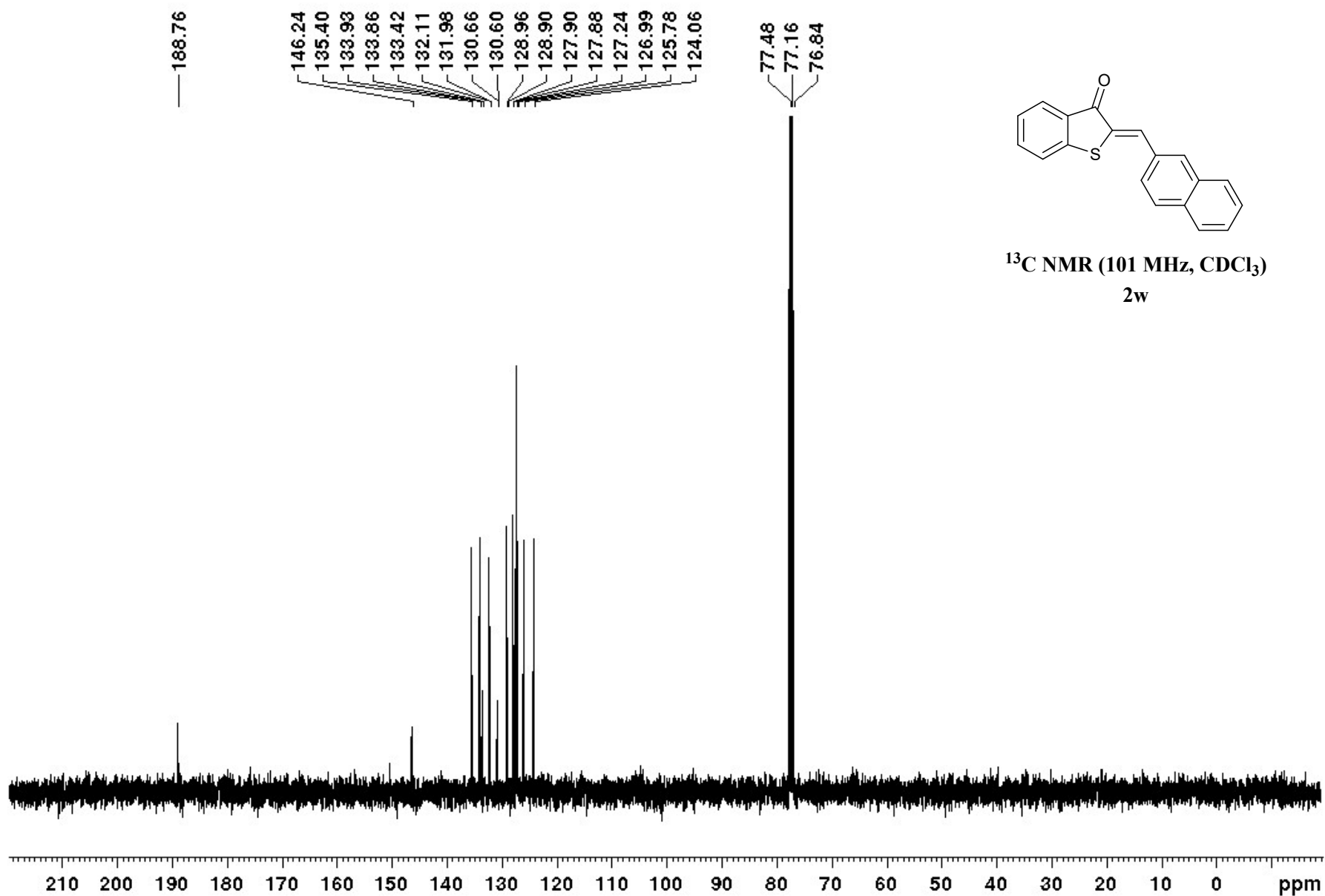
¹³C NMR spectrum of compound 2v



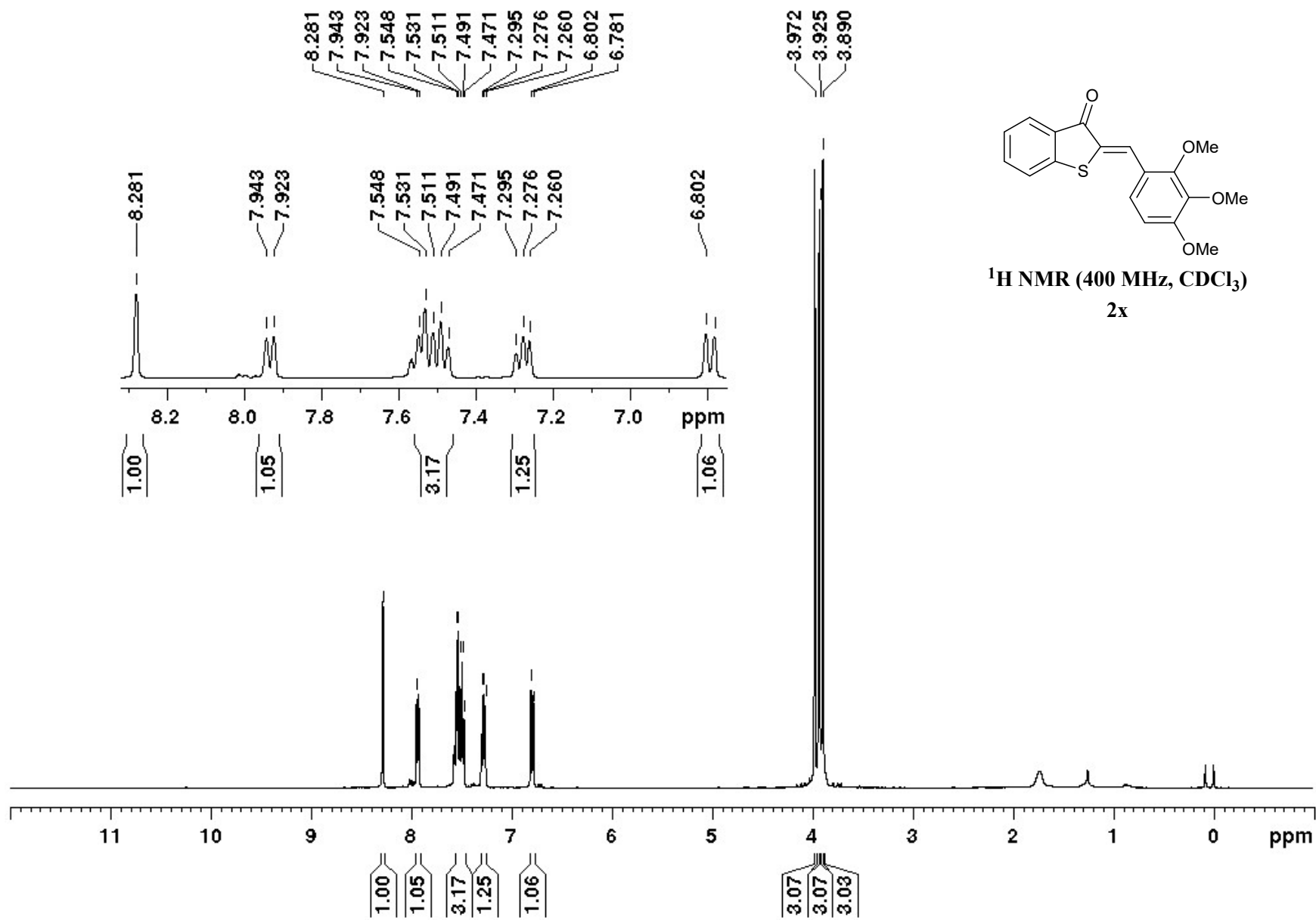
¹H NMR spectrum of compound 2w



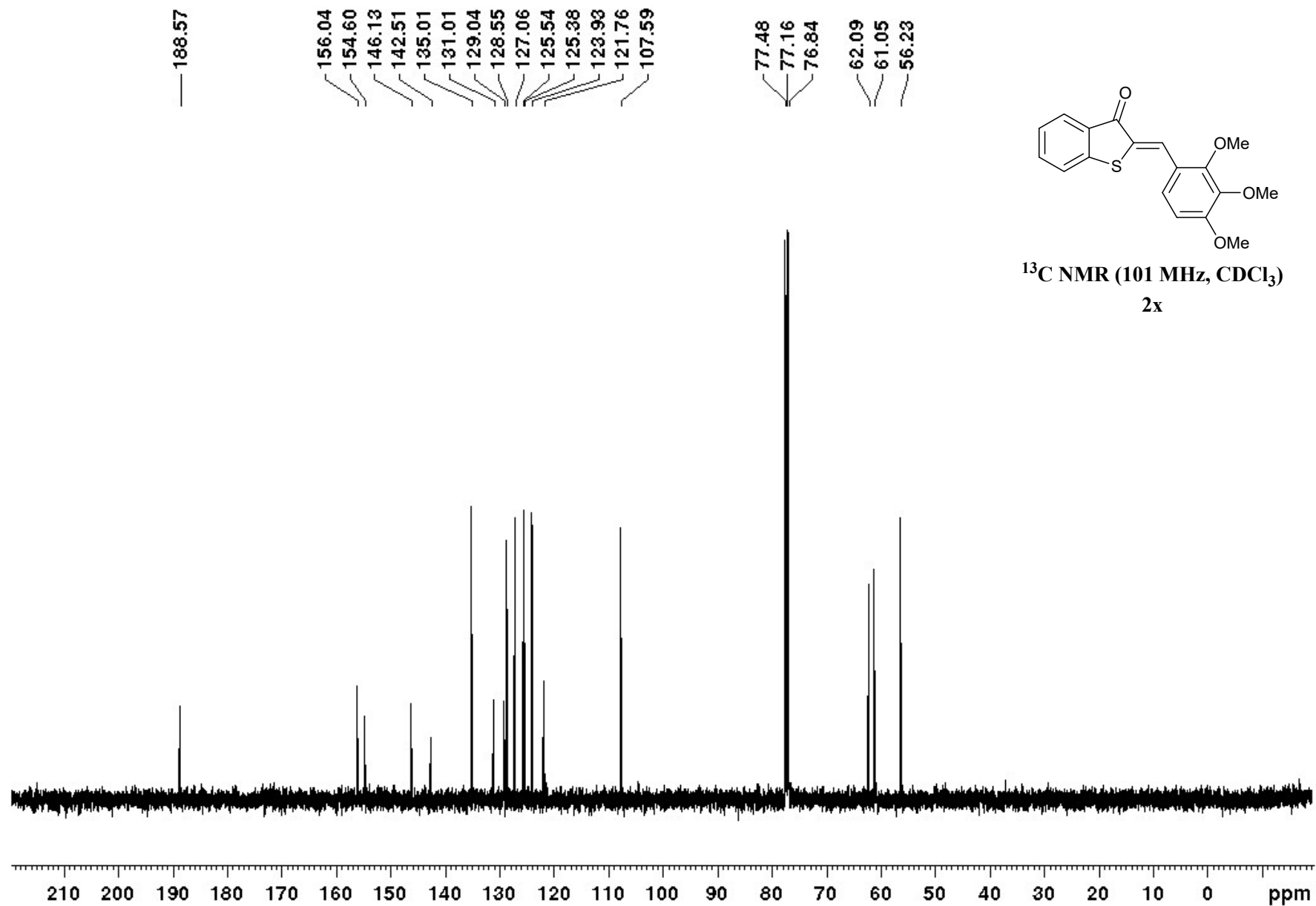
¹³C NMR spectrum of compound 2w



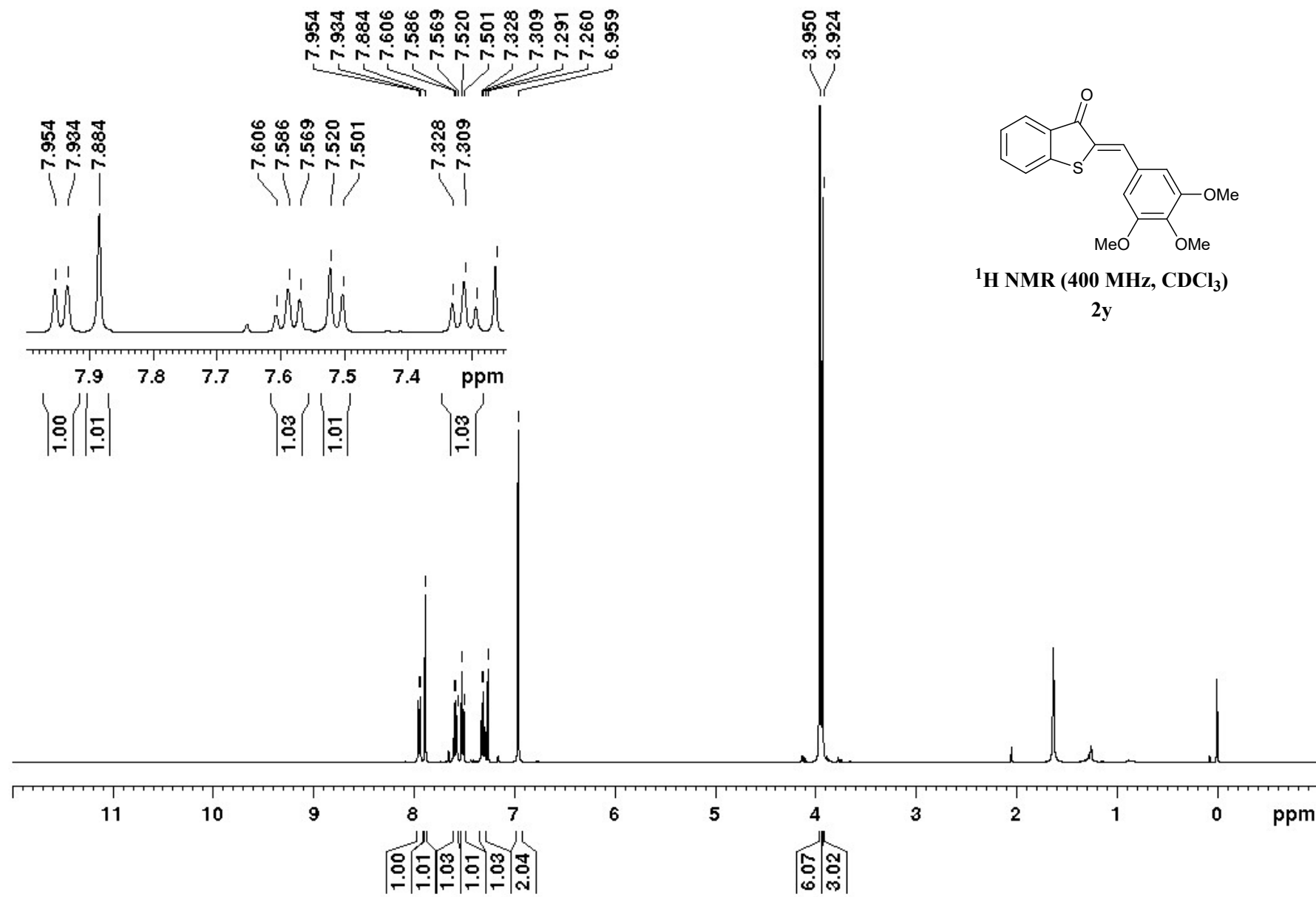
¹H NMR spectrum of compound 2x



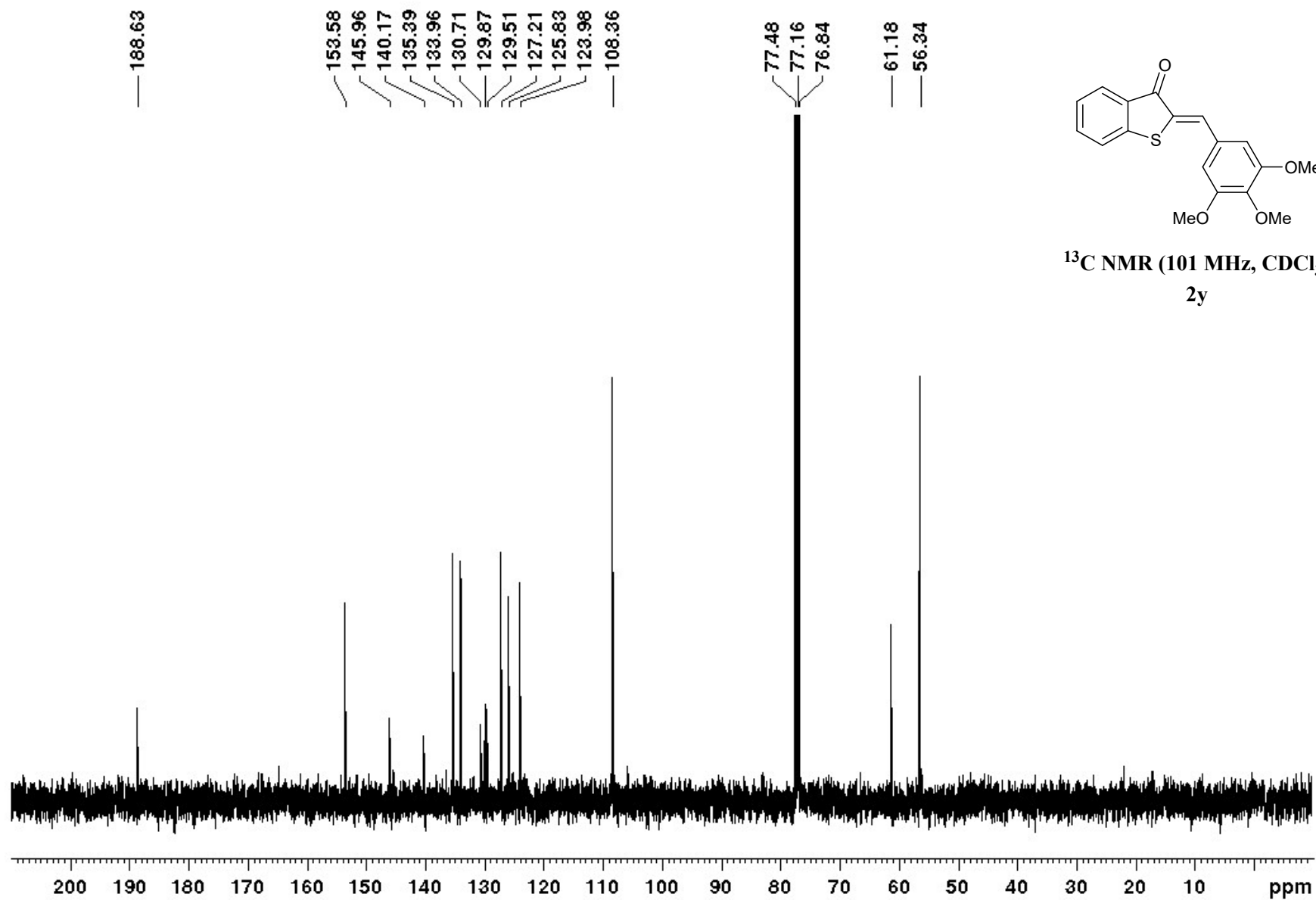
¹³C NMR spectrum of compound 2x



¹H NMR spectrum of compound 2y

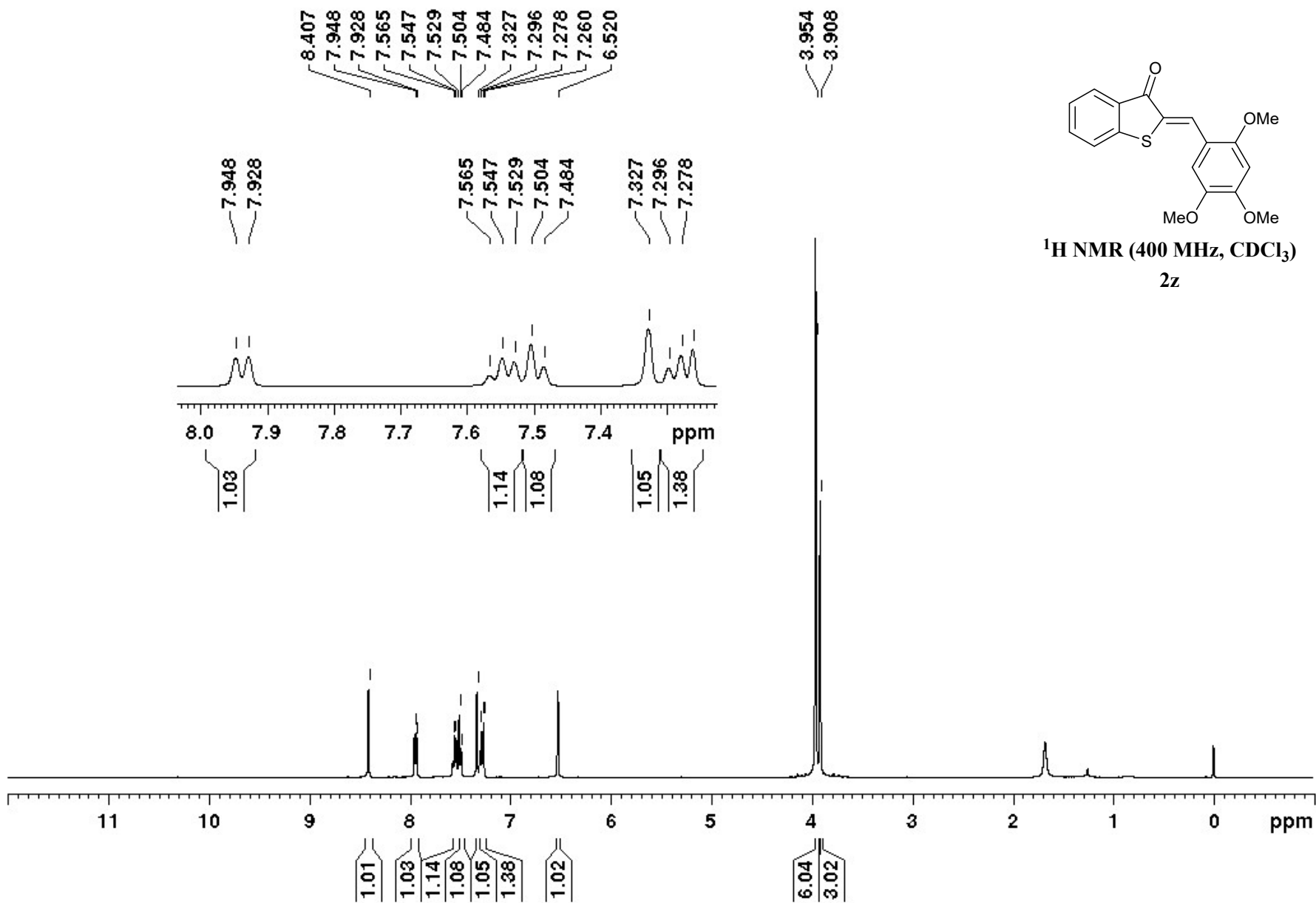


¹³C NMR spectrum of compound 2y

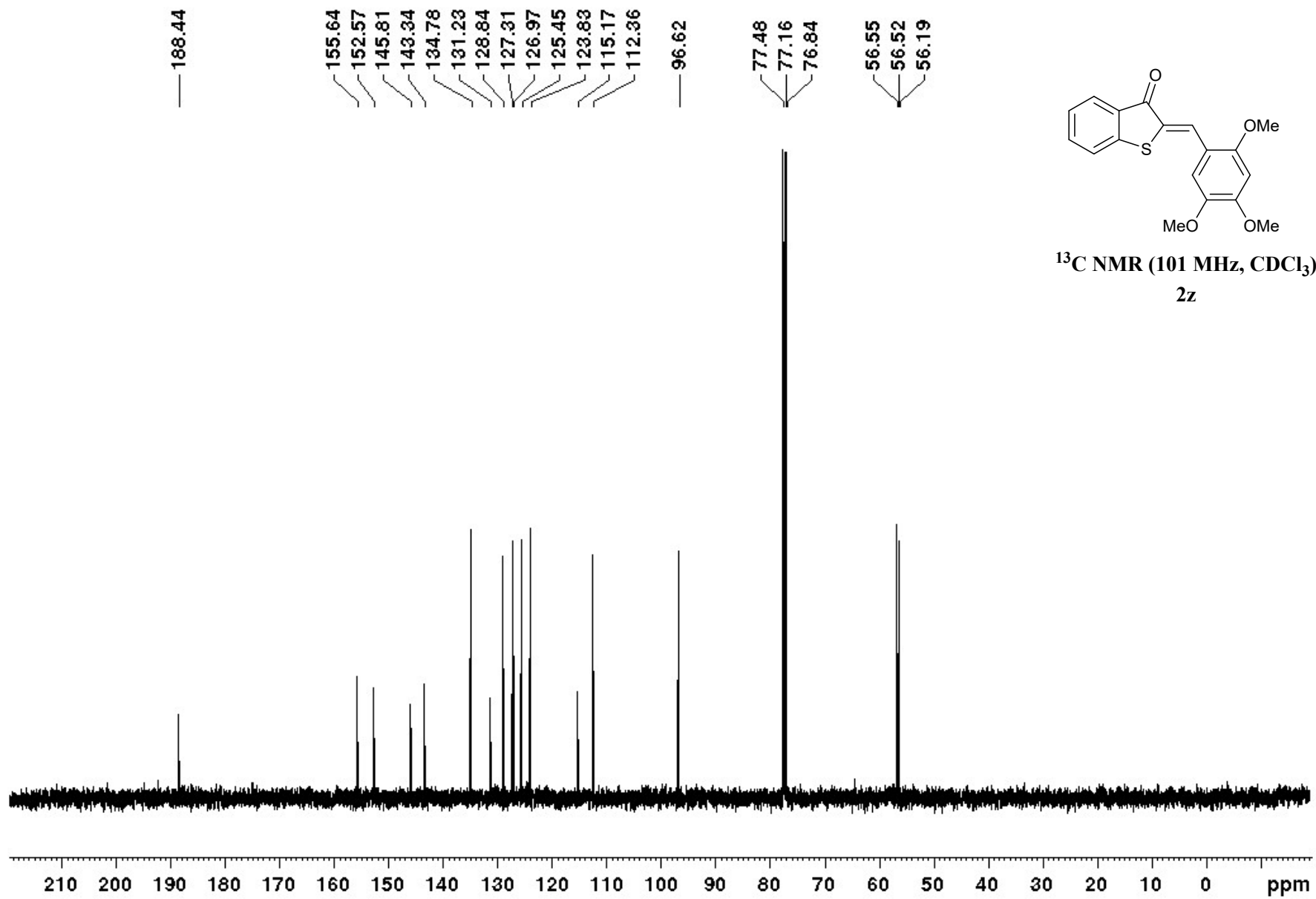


v

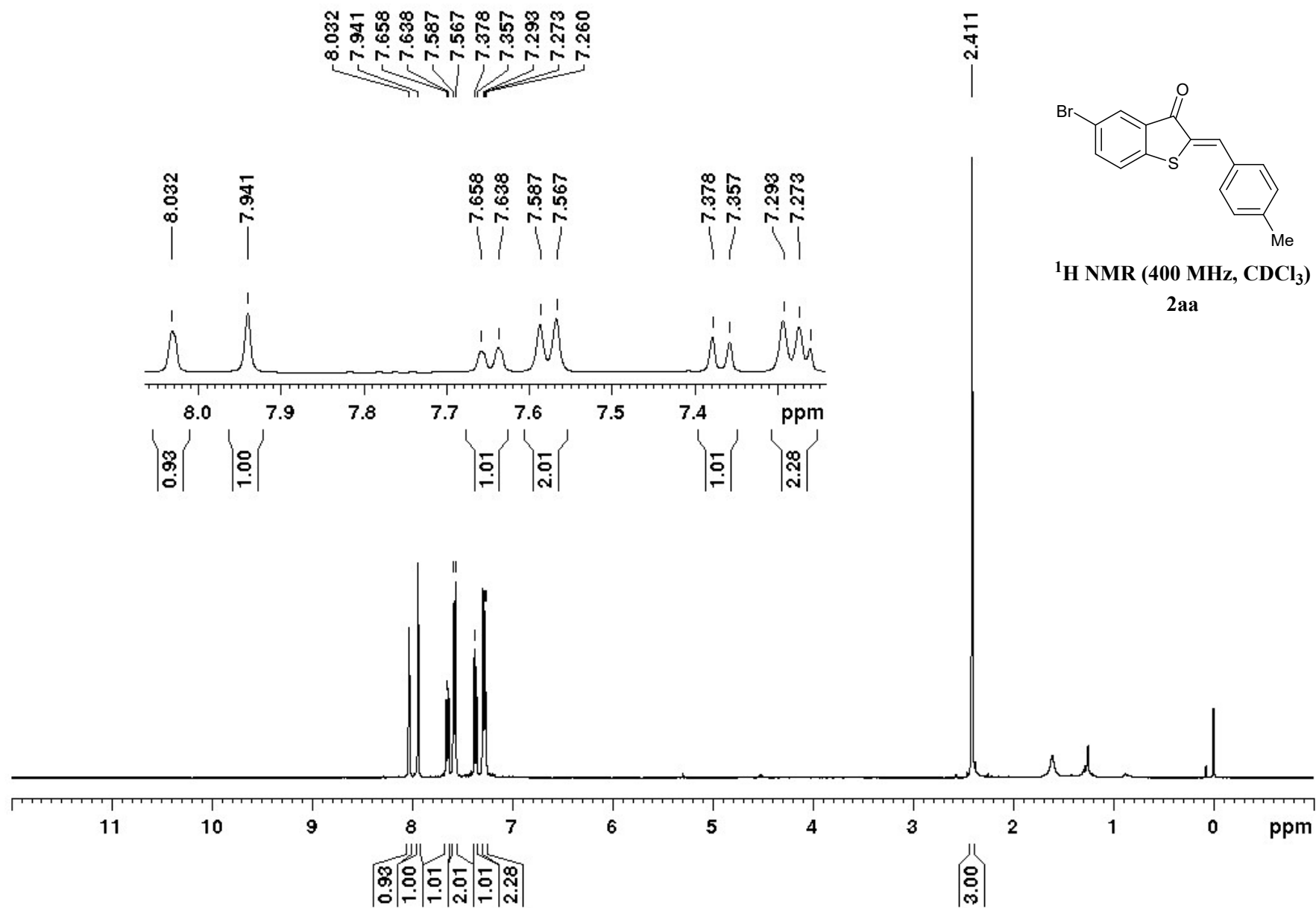
¹H NMR spectrum of compound 2z



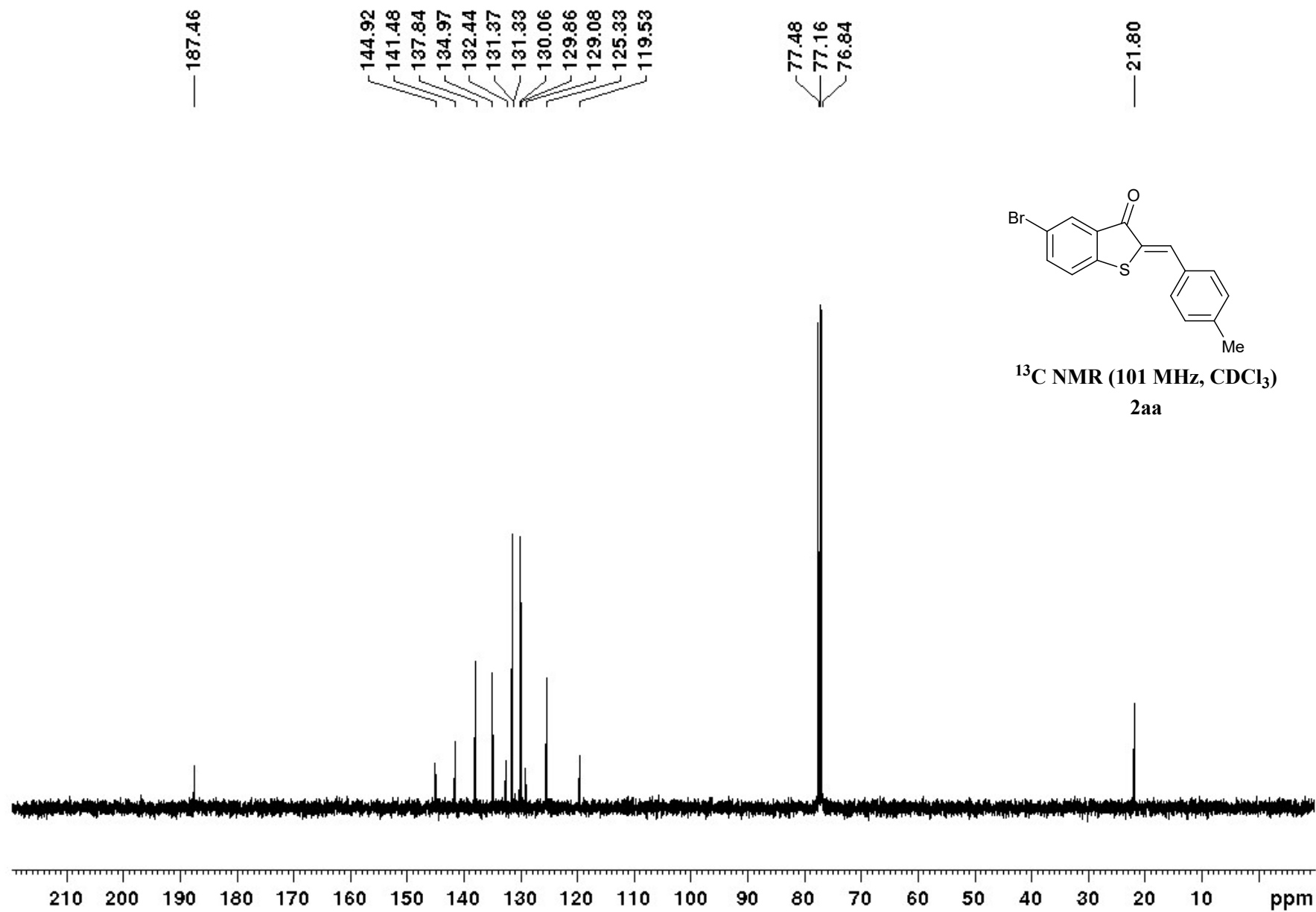
¹³C NMR spectrum of compound 2z



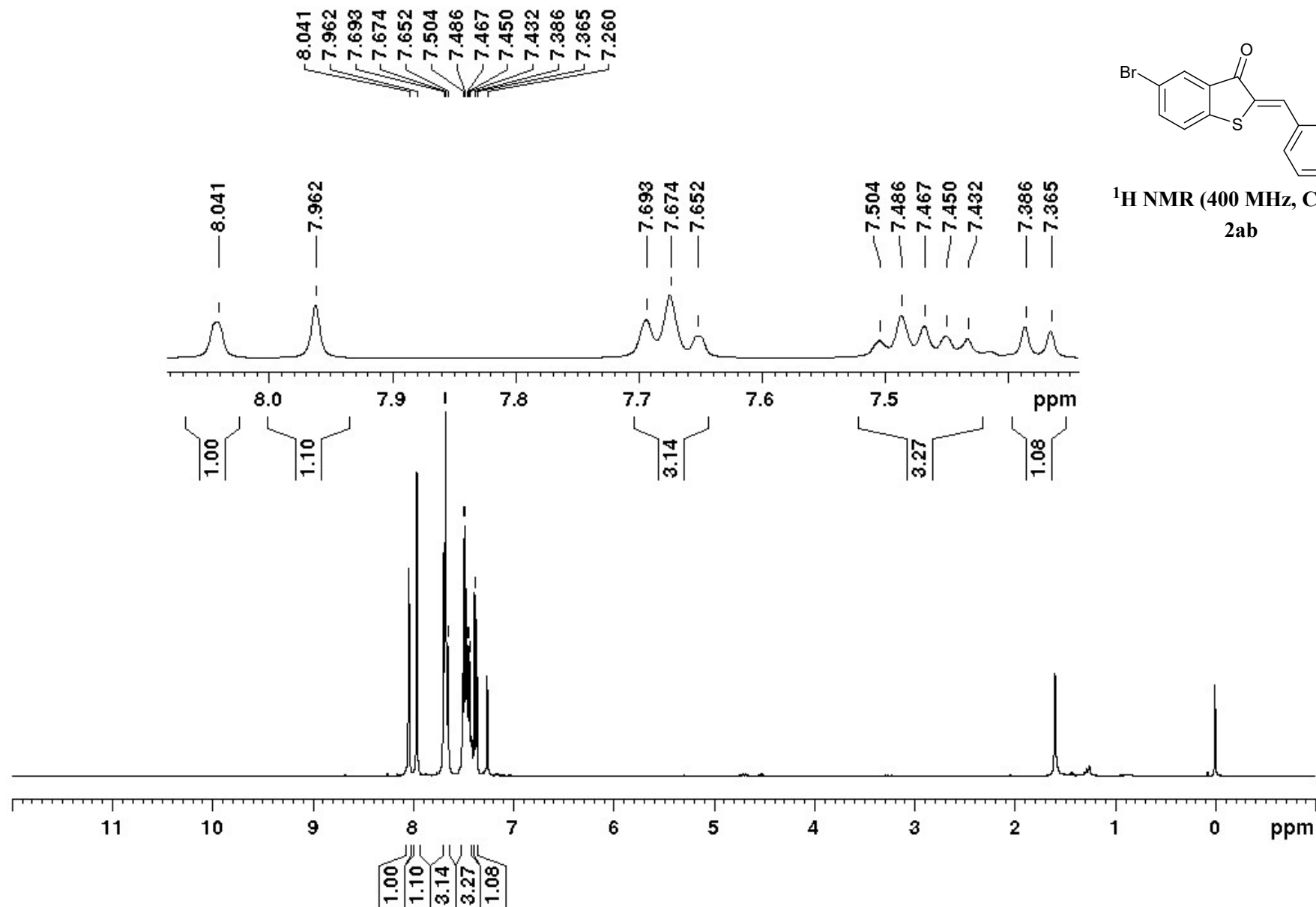
¹H NMR spectrum of compound 2aa



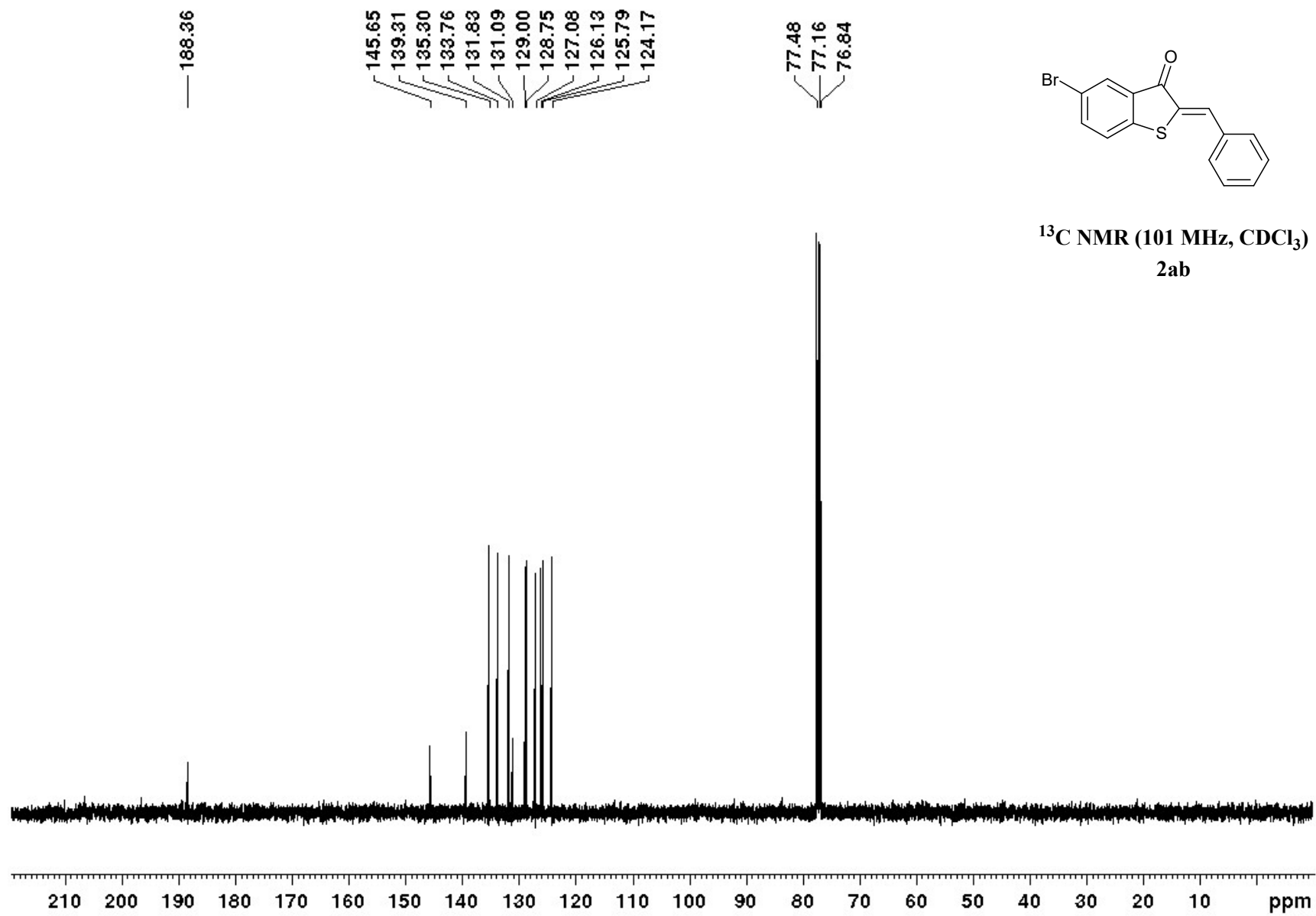
¹³C NMR spectrum of compound 2aa



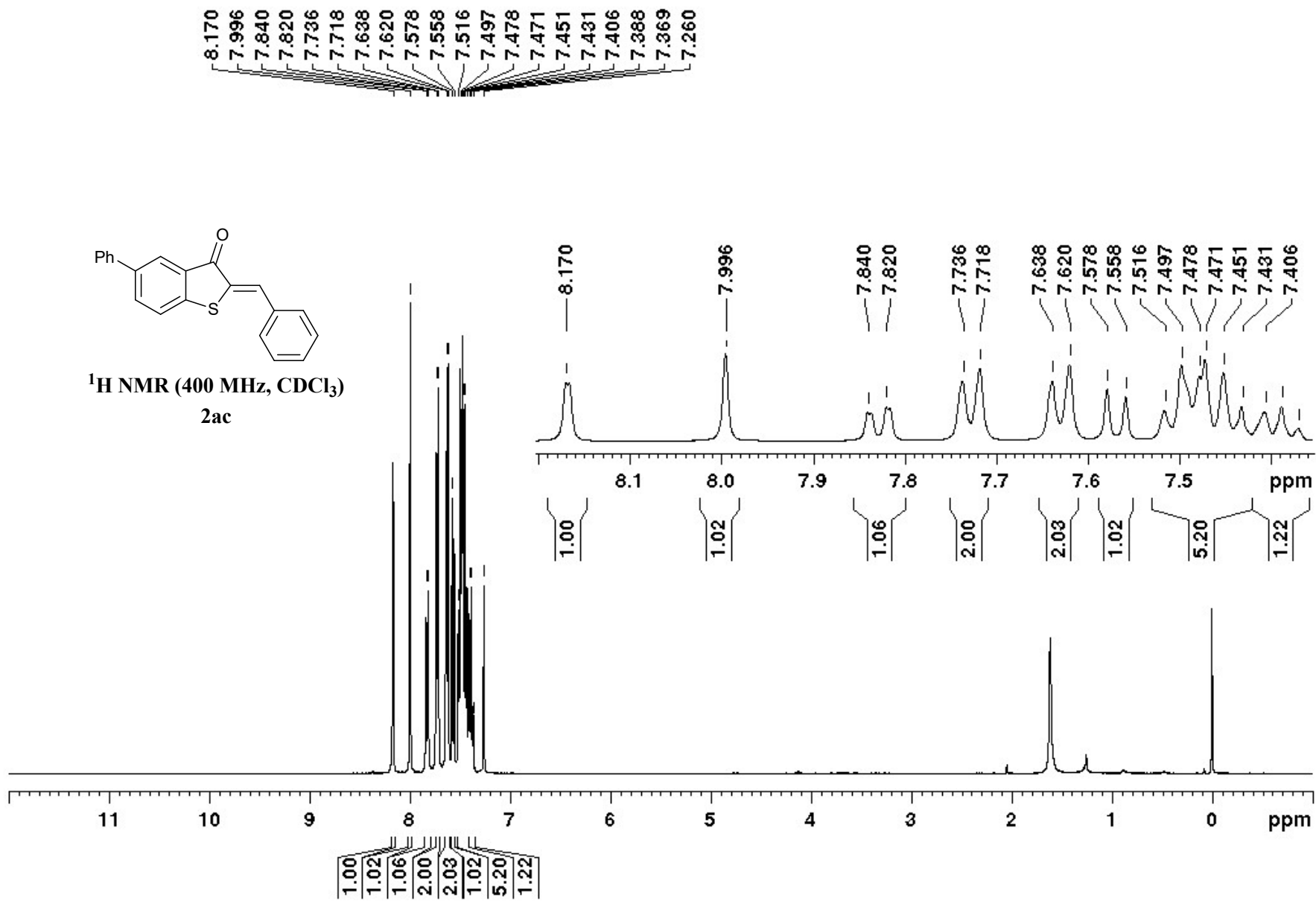
¹H NMR spectrum of compound 2ab



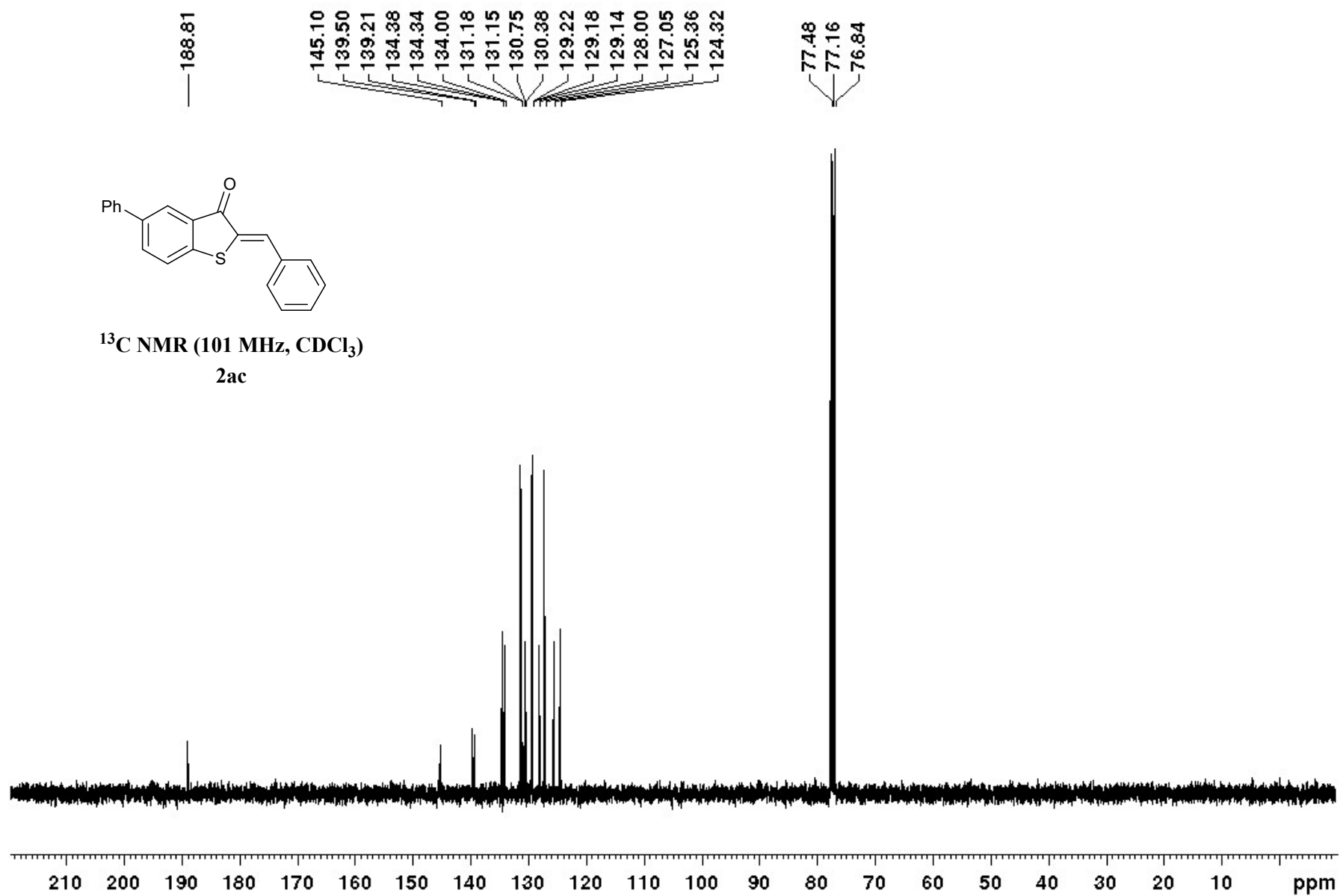
¹³C NMR spectrum of compound 2ab



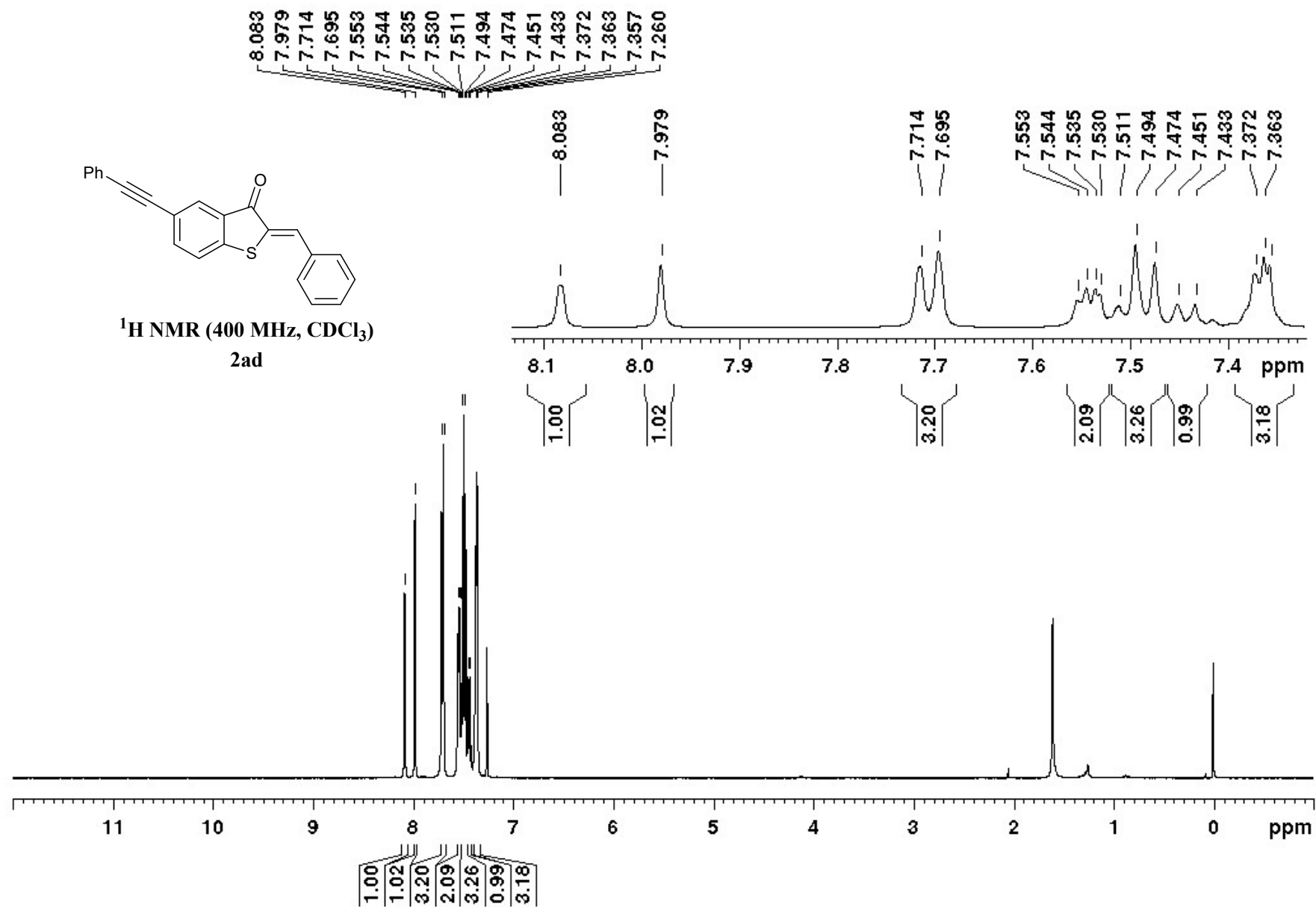
¹H NMR spectrum of compound 2ac



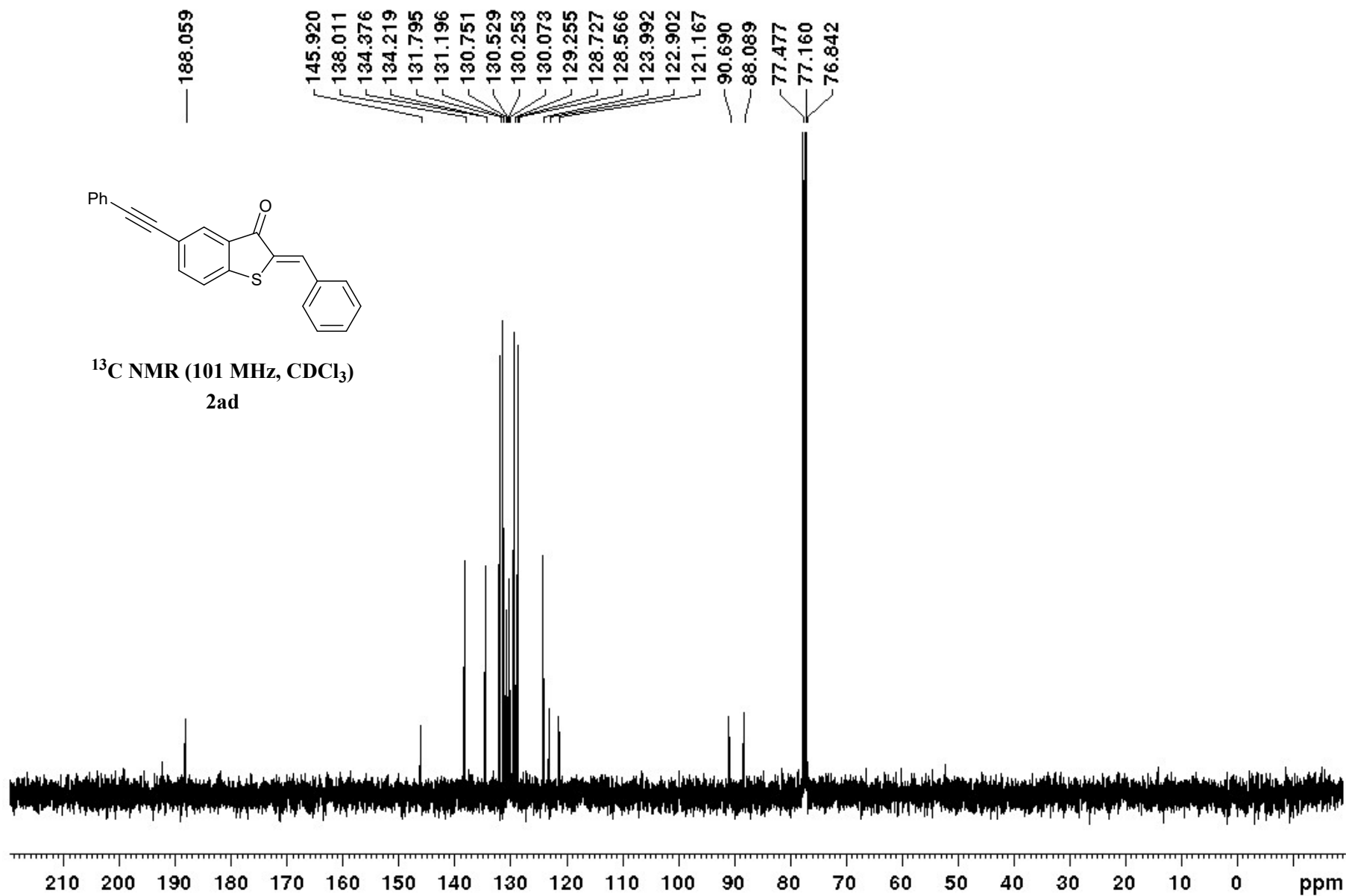
¹³C NMR spectrum of compound 2ac



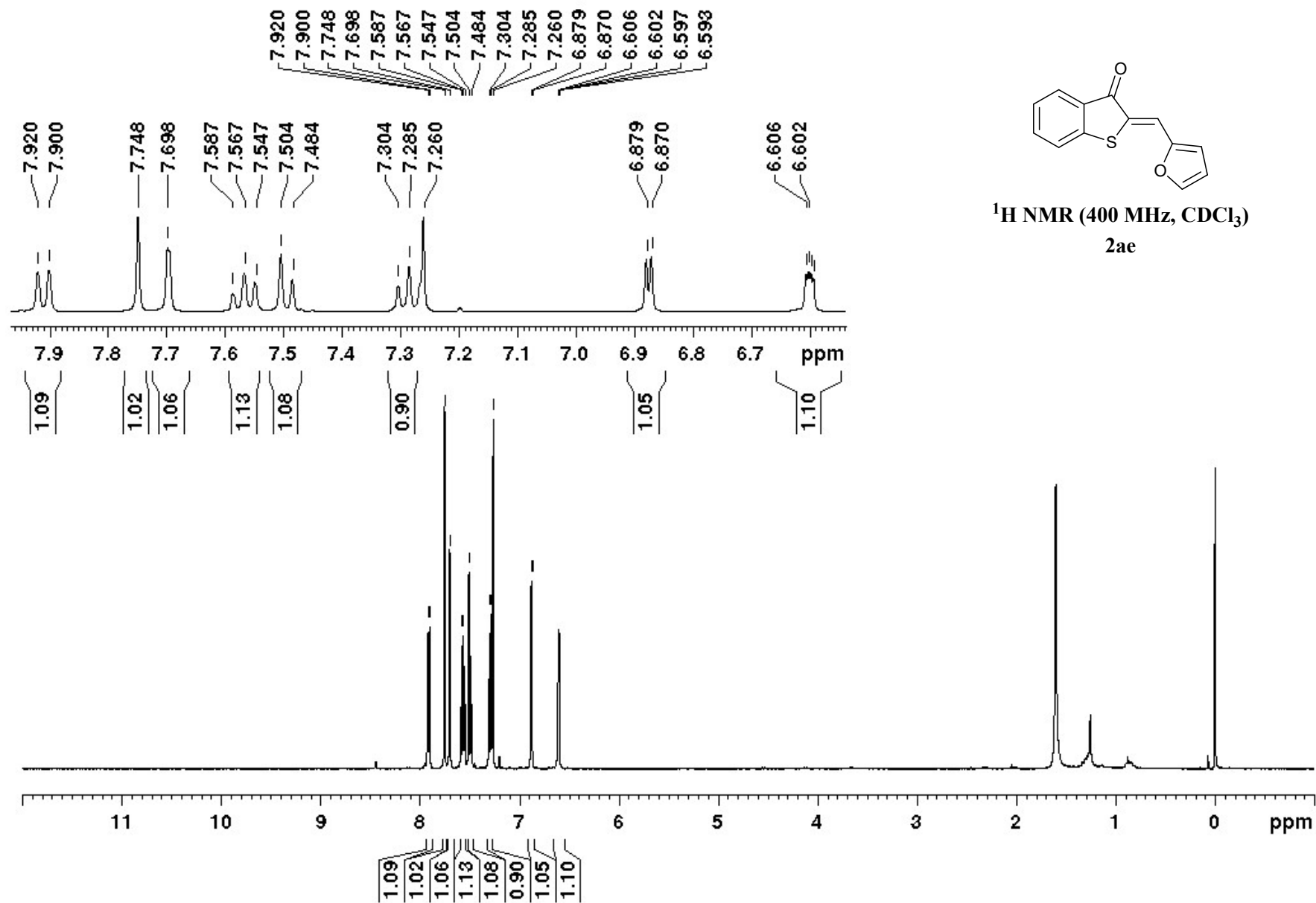
¹H NMR spectrum of compound 2ad



¹³C NMR spectrum of compound 2ad

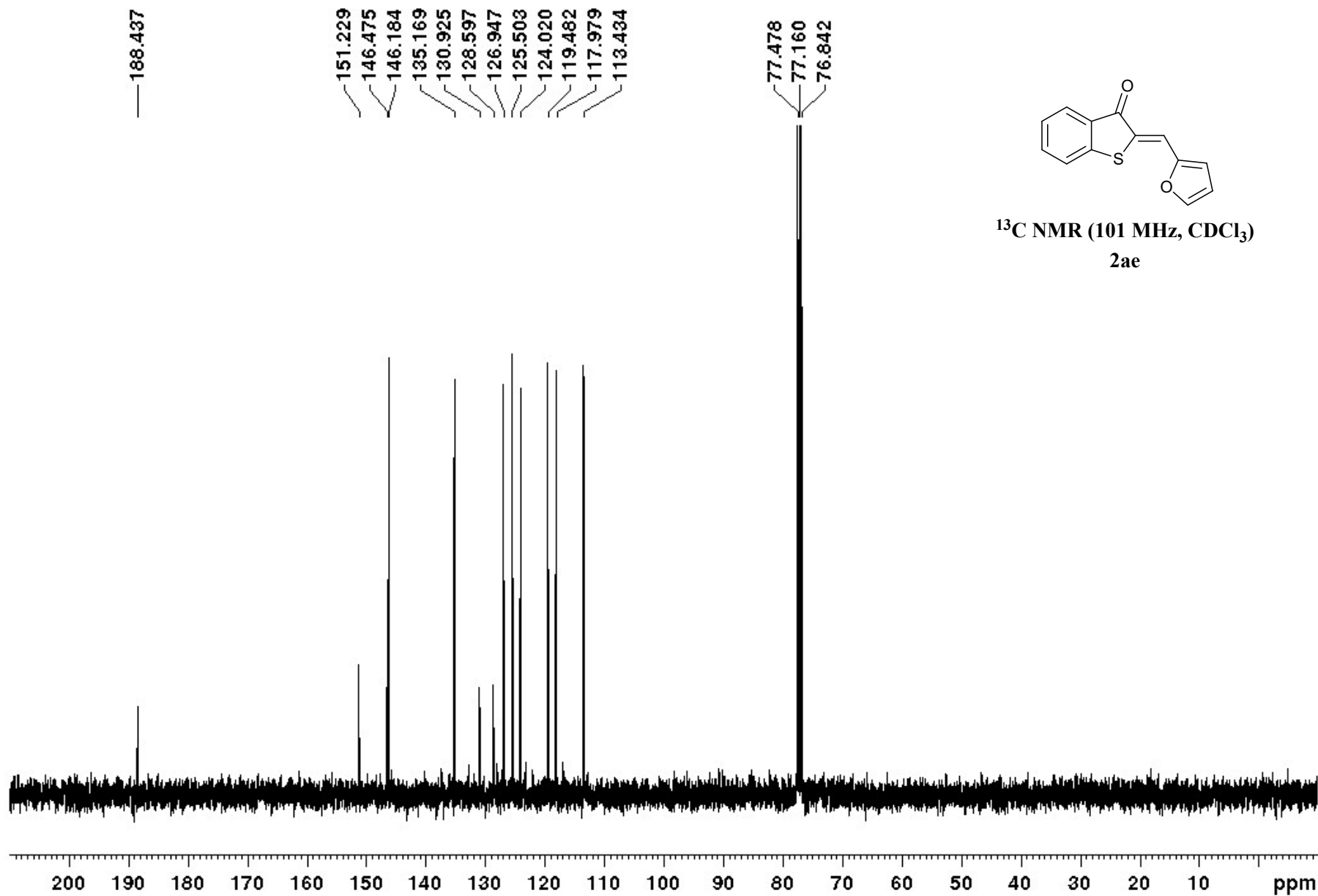


¹H NMR spectrum of compound 2ae



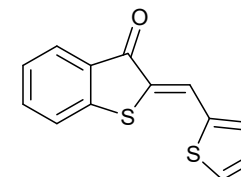
¹H NMR (400 MHz, CDCl₃)
2ae

¹³C NMR spectrum of compound 2ae

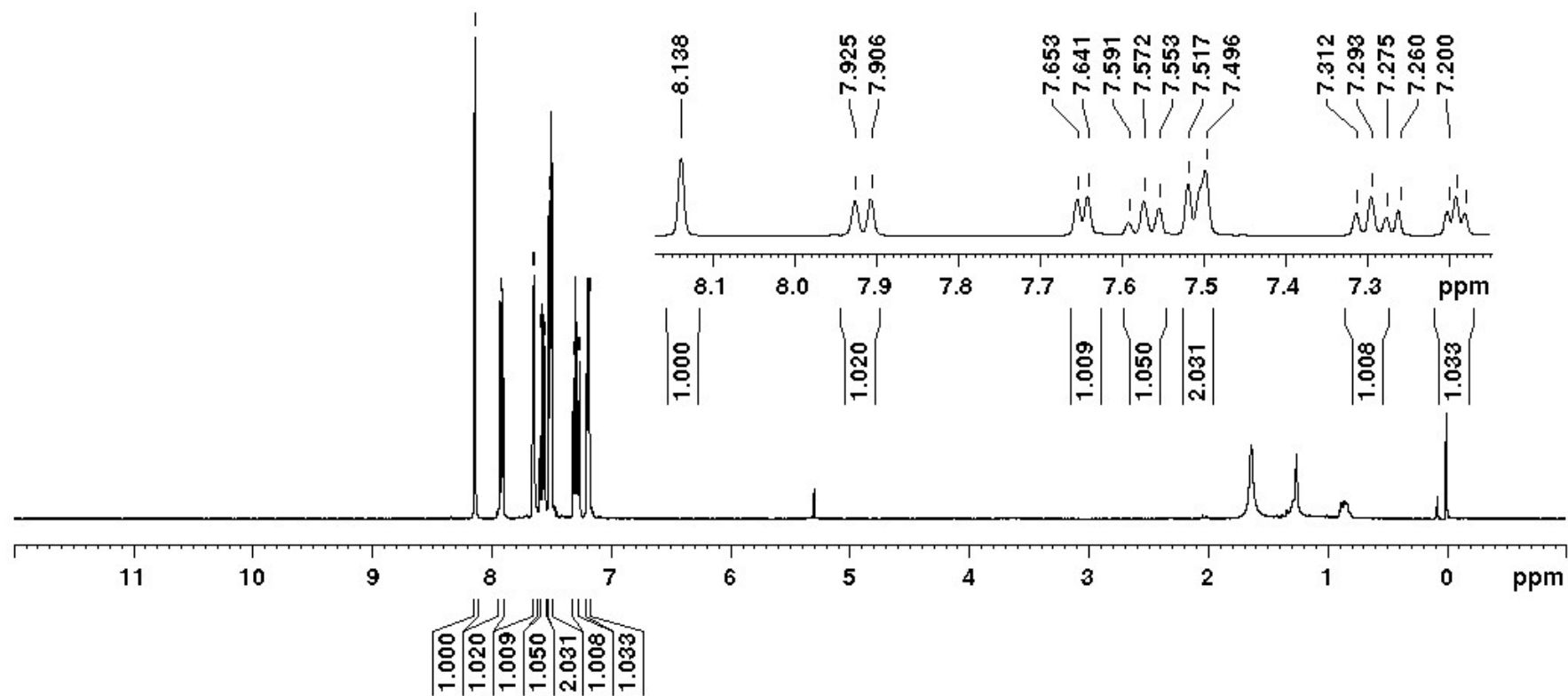


¹H NMR spectrum of compound 2af

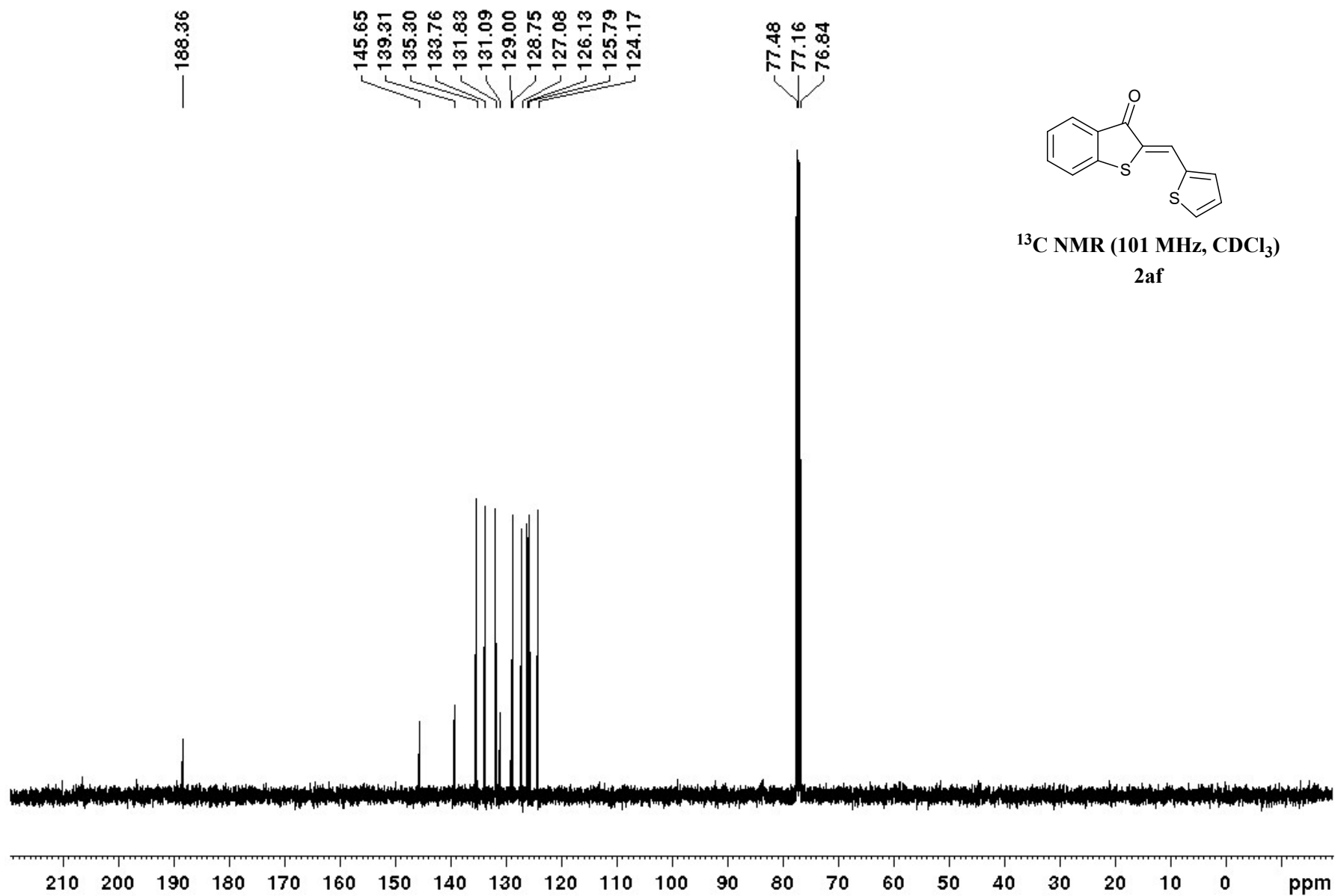
8.138
7.925
7.906
7.653
7.641
7.591
7.572
7.553
7.517
7.496
7.312
7.293
7.275
7.260
7.200
7.190
7.179



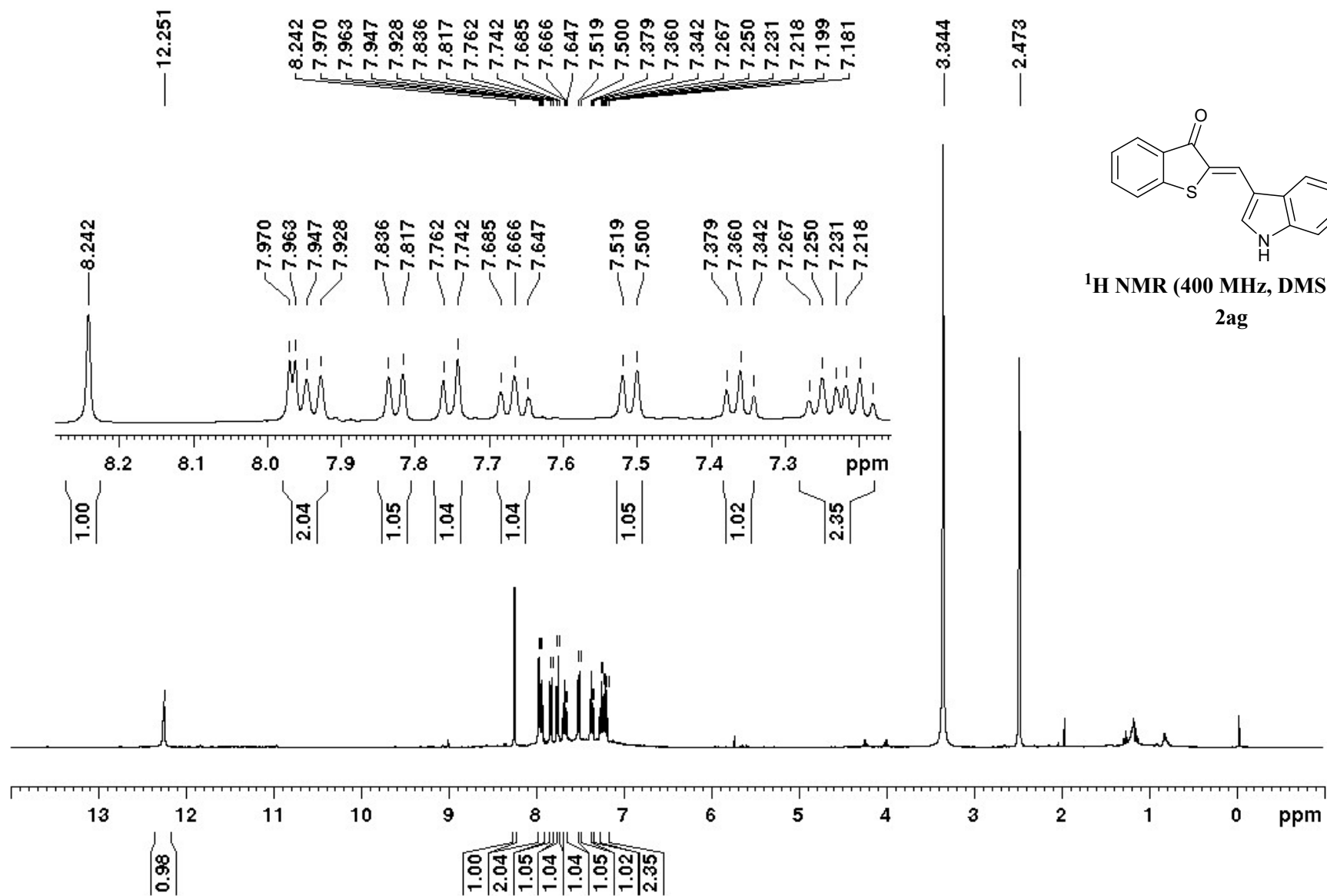
¹H NMR (400 MHz, CDCl₃)
2af



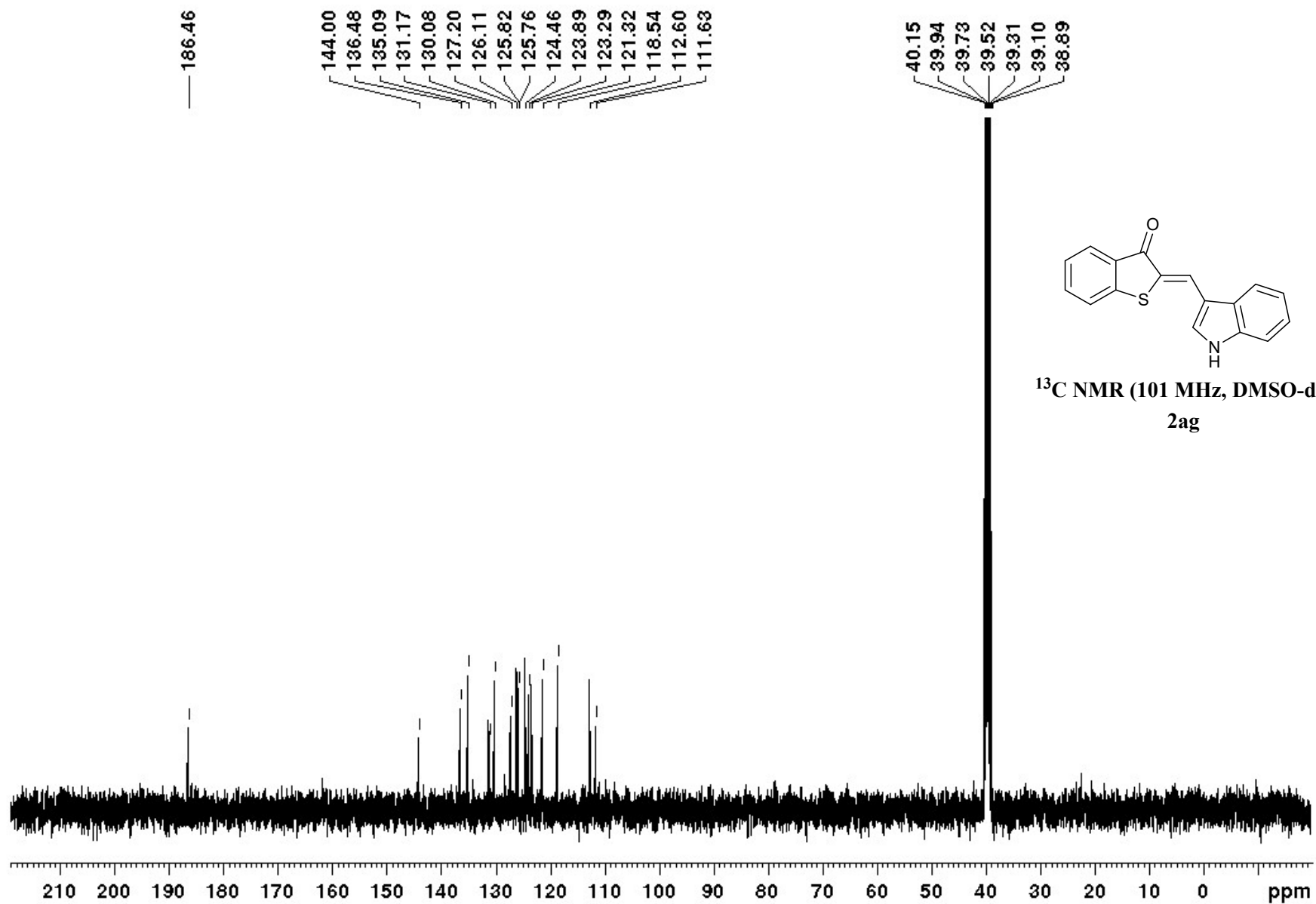
¹³C NMR spectrum of compound 2af



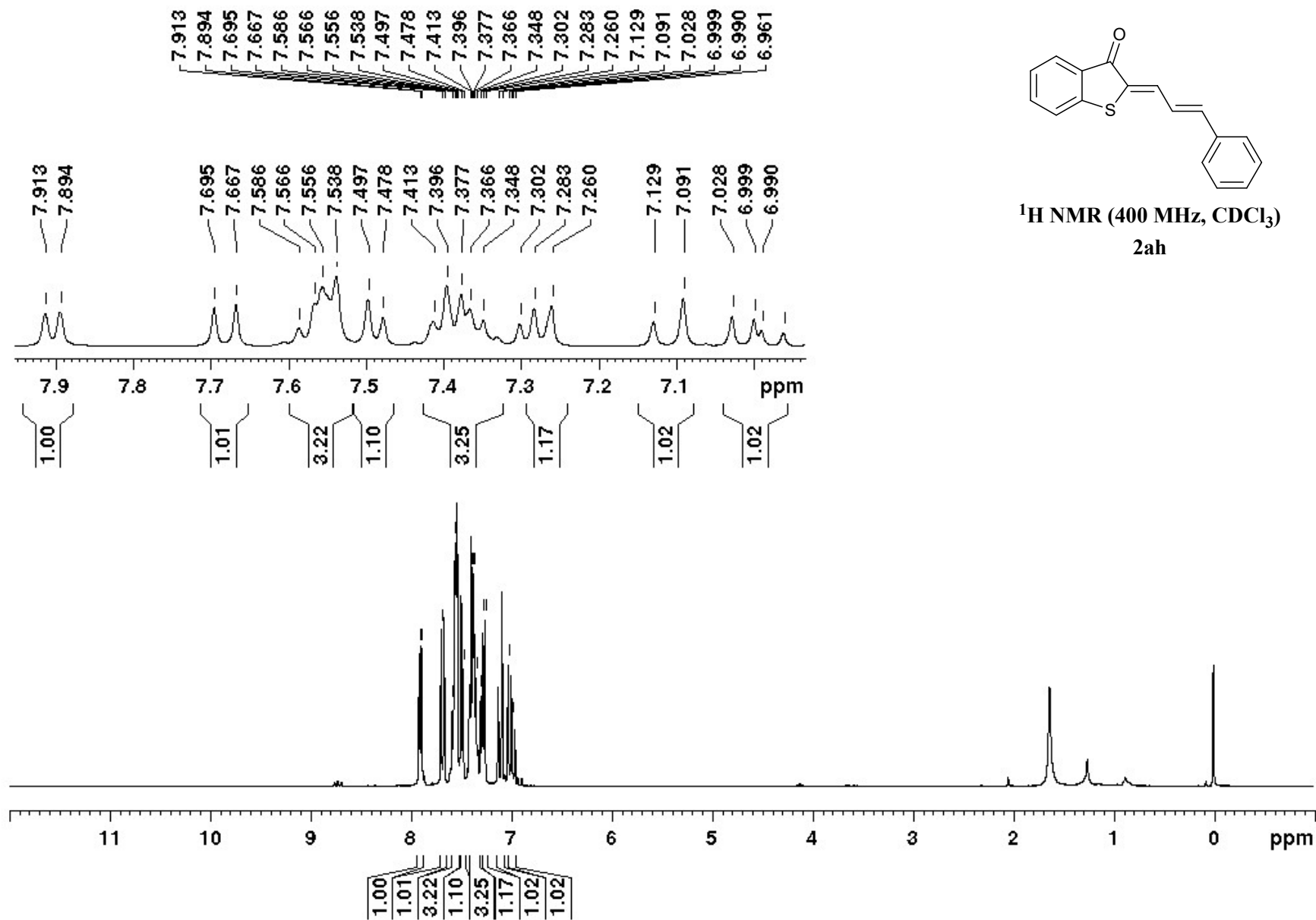
¹H NMR spectrum of compound 2ag



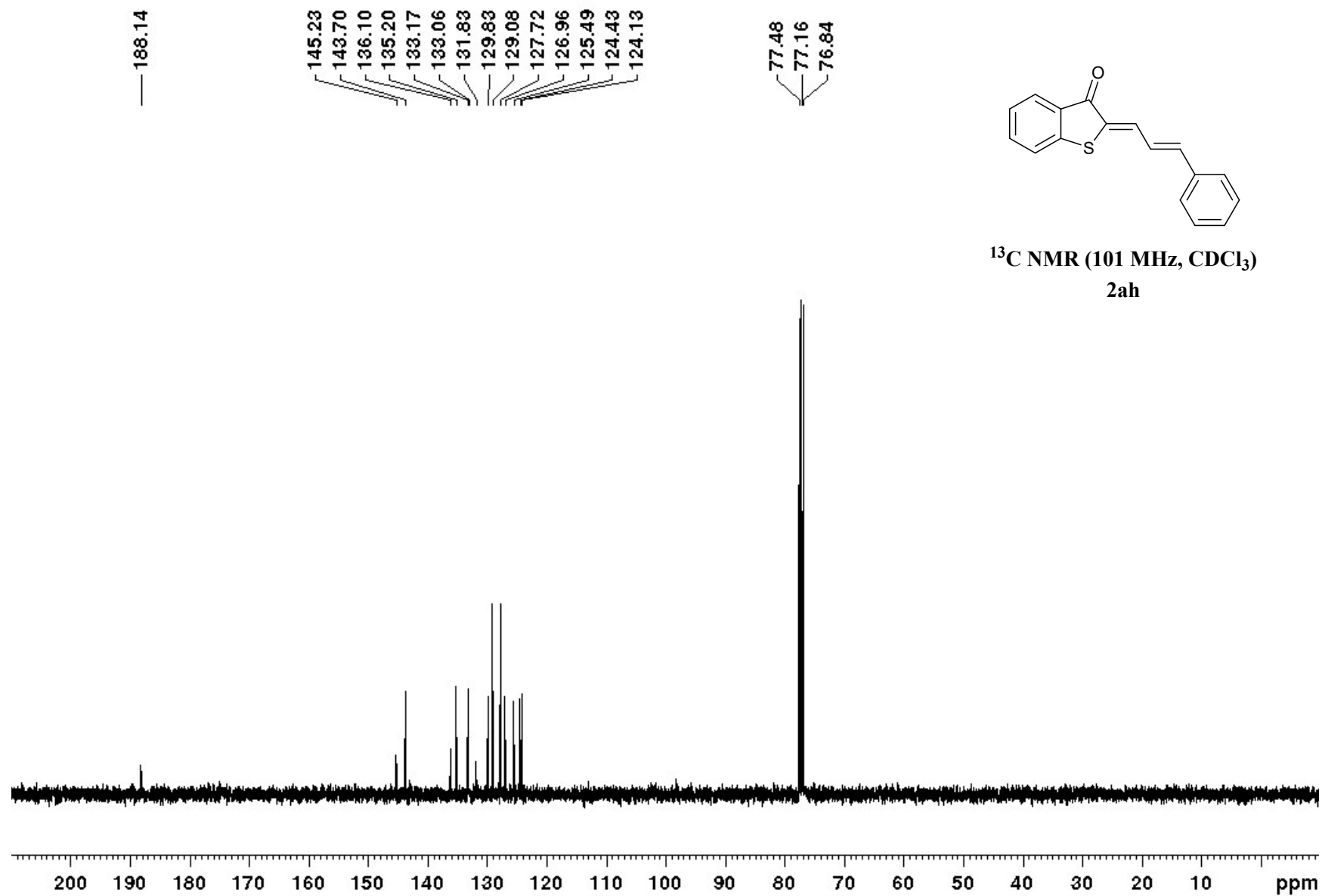
¹³C NMR spectrum of compound 2ag



¹H NMR spectrum of compound 2ah

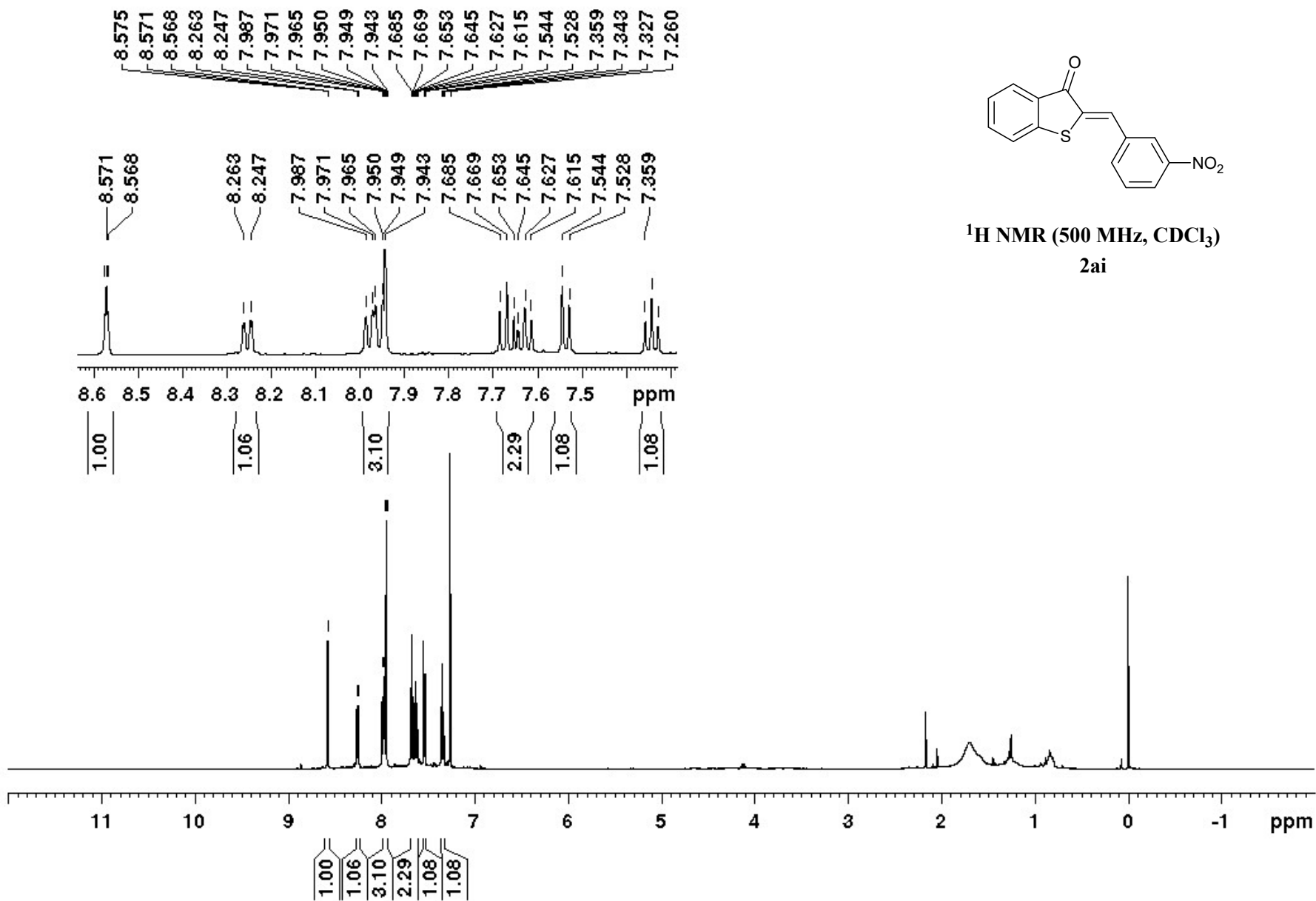


¹³C NMR spectrum of compound 2ah

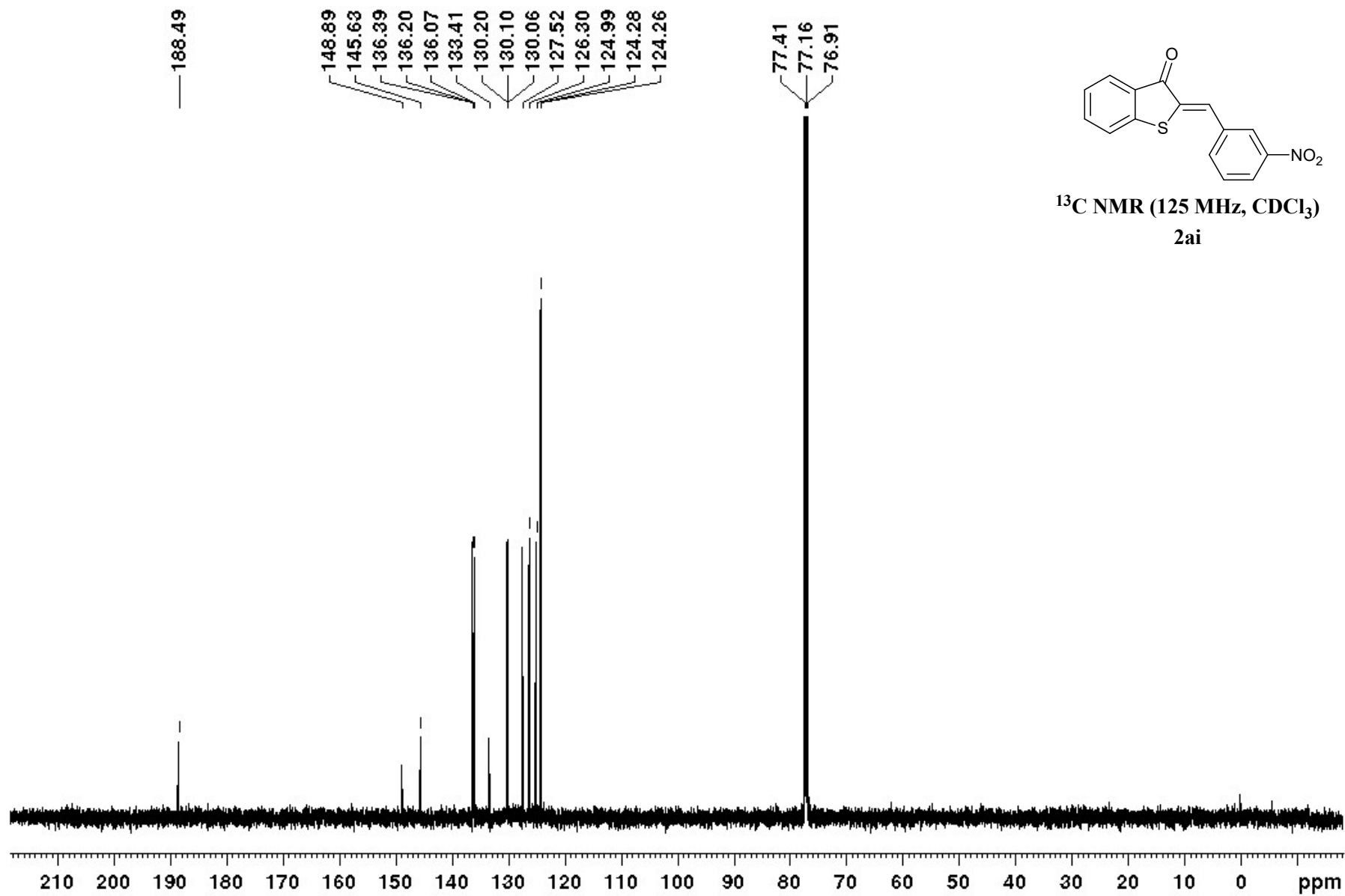


v

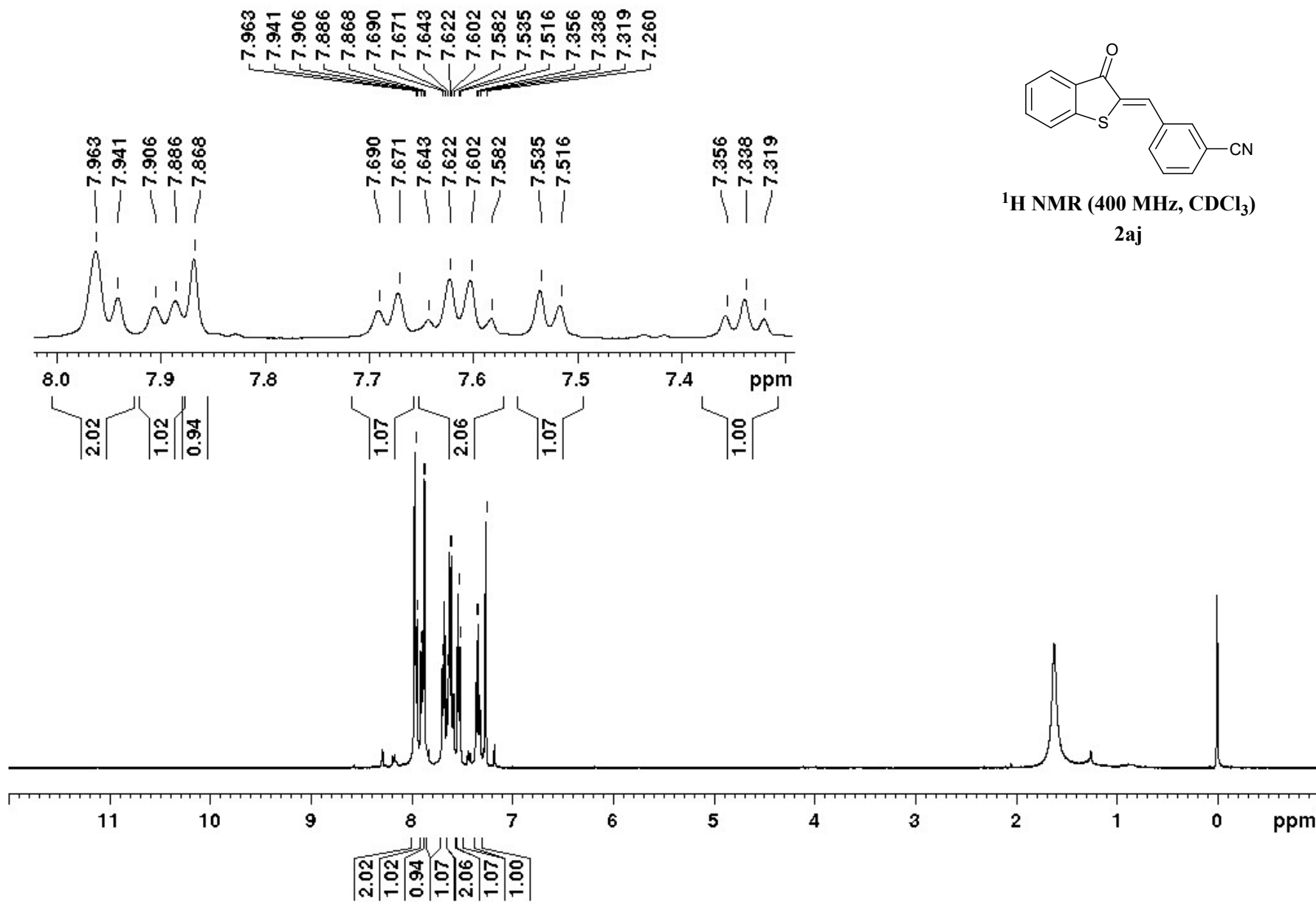
¹H NMR spectrum of compound 2ai



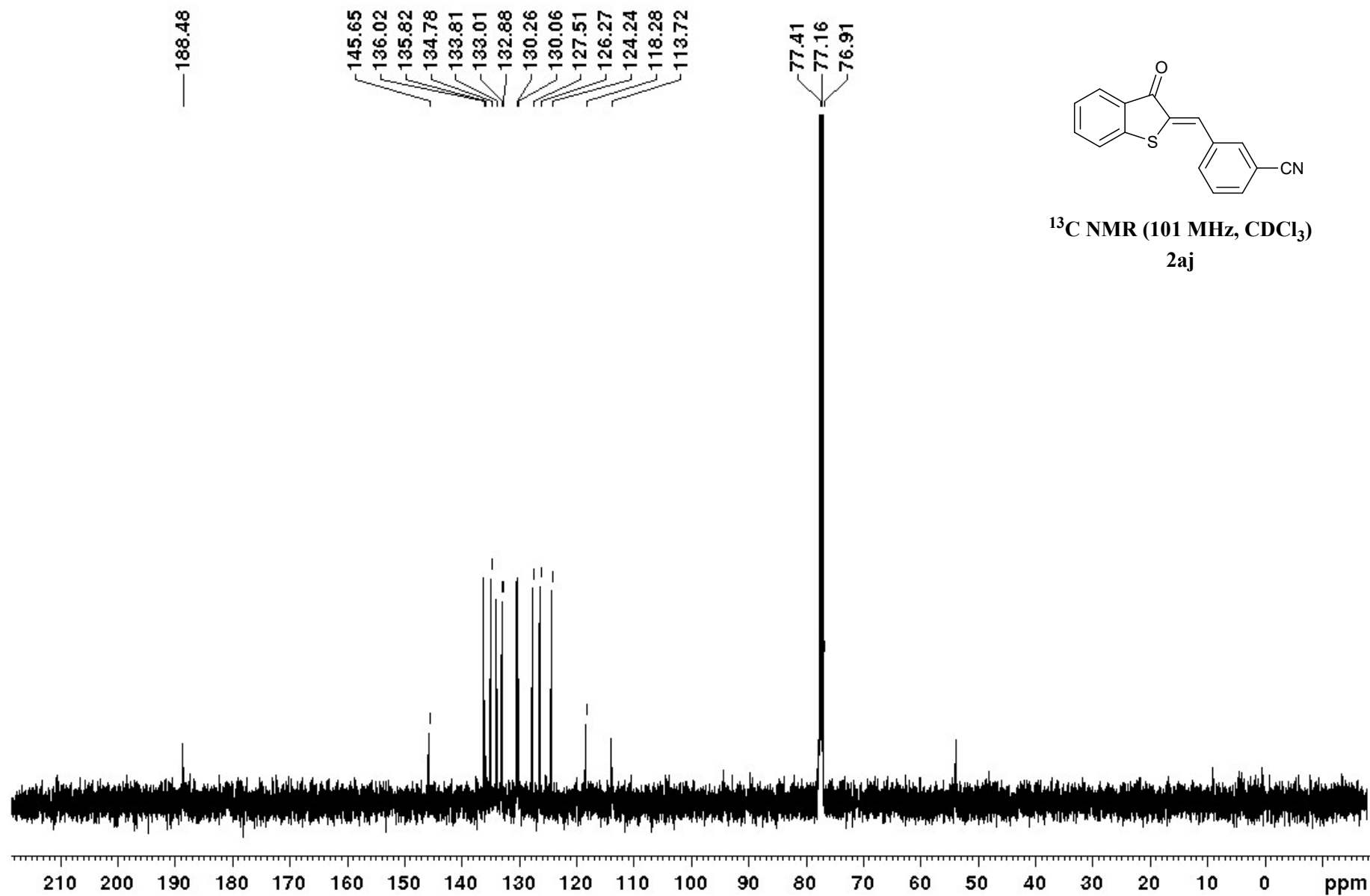
¹³C NMR spectrum of compound 2ai



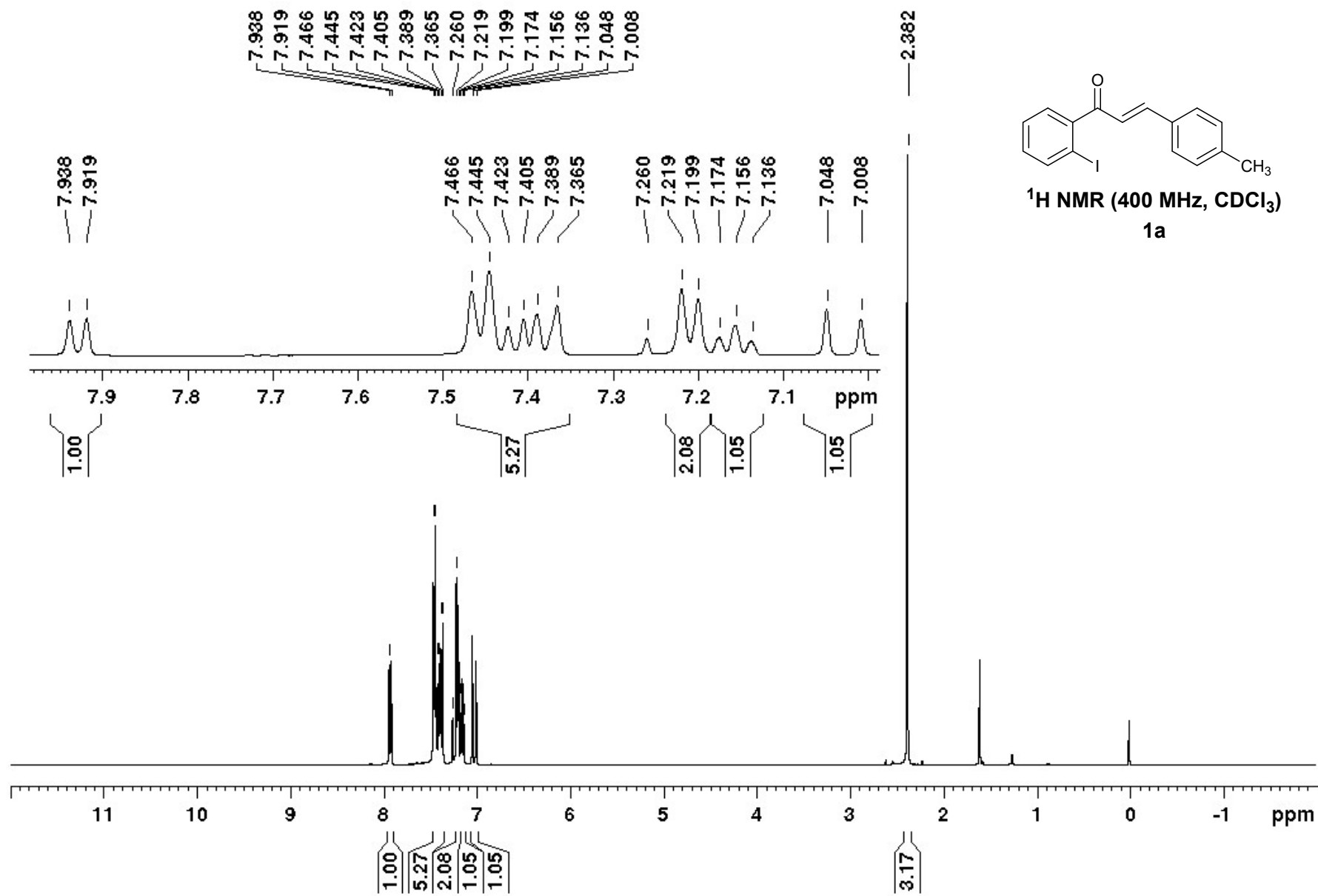
¹H NMR spectrum of compound 2aj



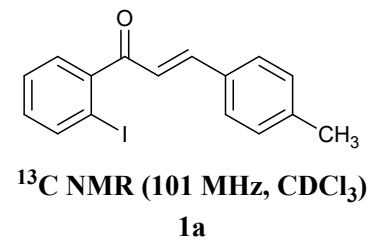
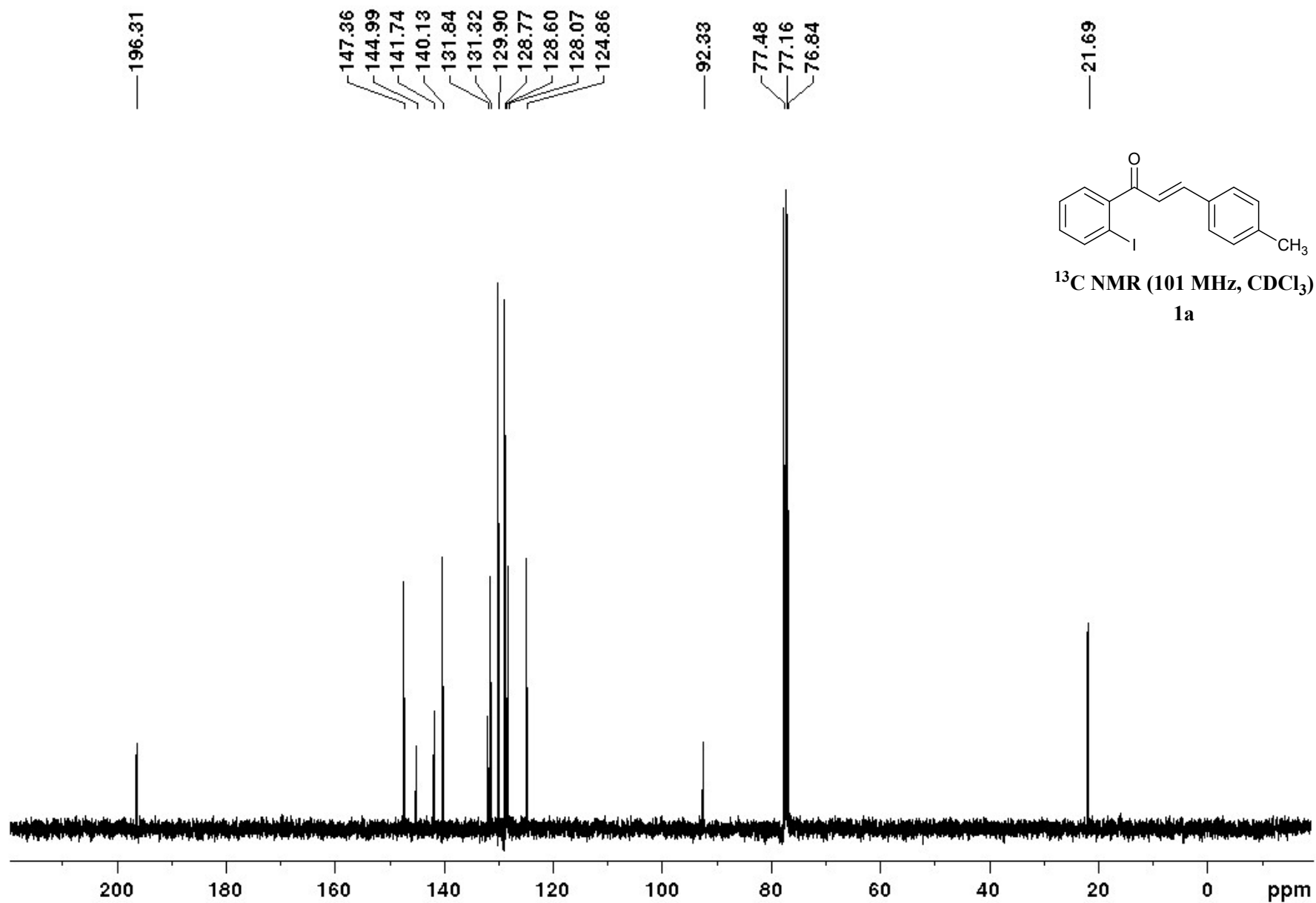
¹³C NMR spectrum of compound 2aj



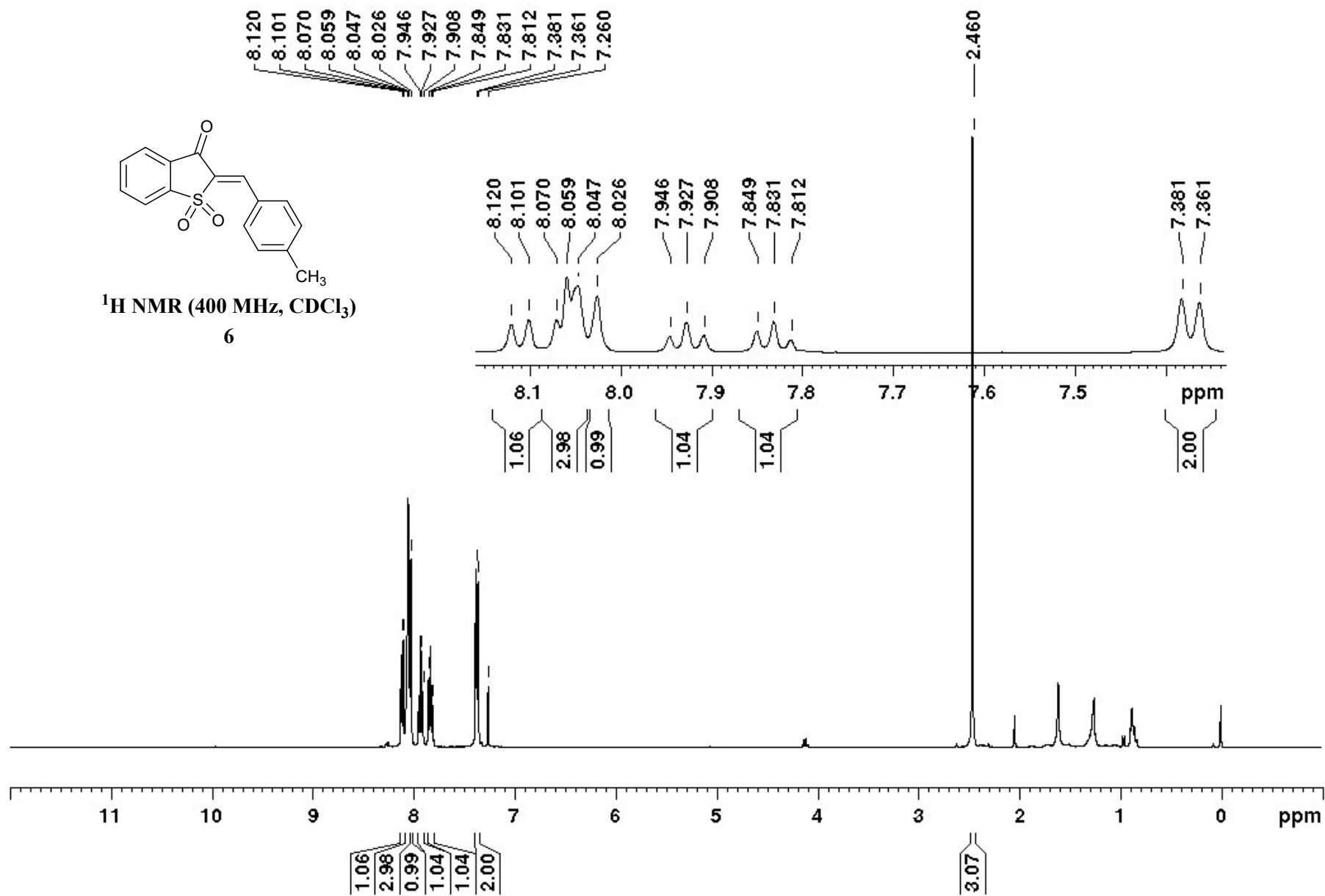
¹H NMR spectrum of compound 1a



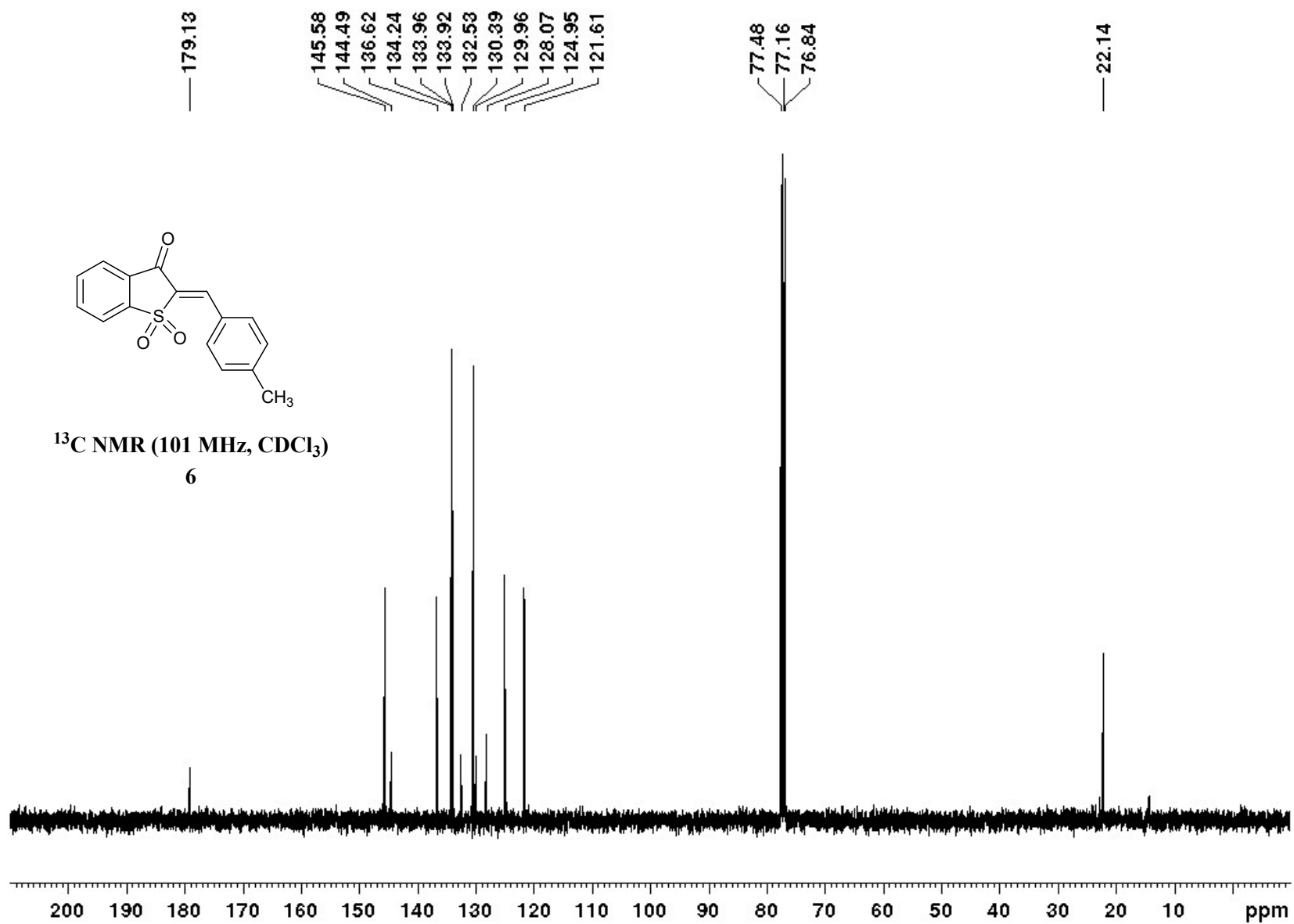
¹³C NMR spectrum of compound 1a



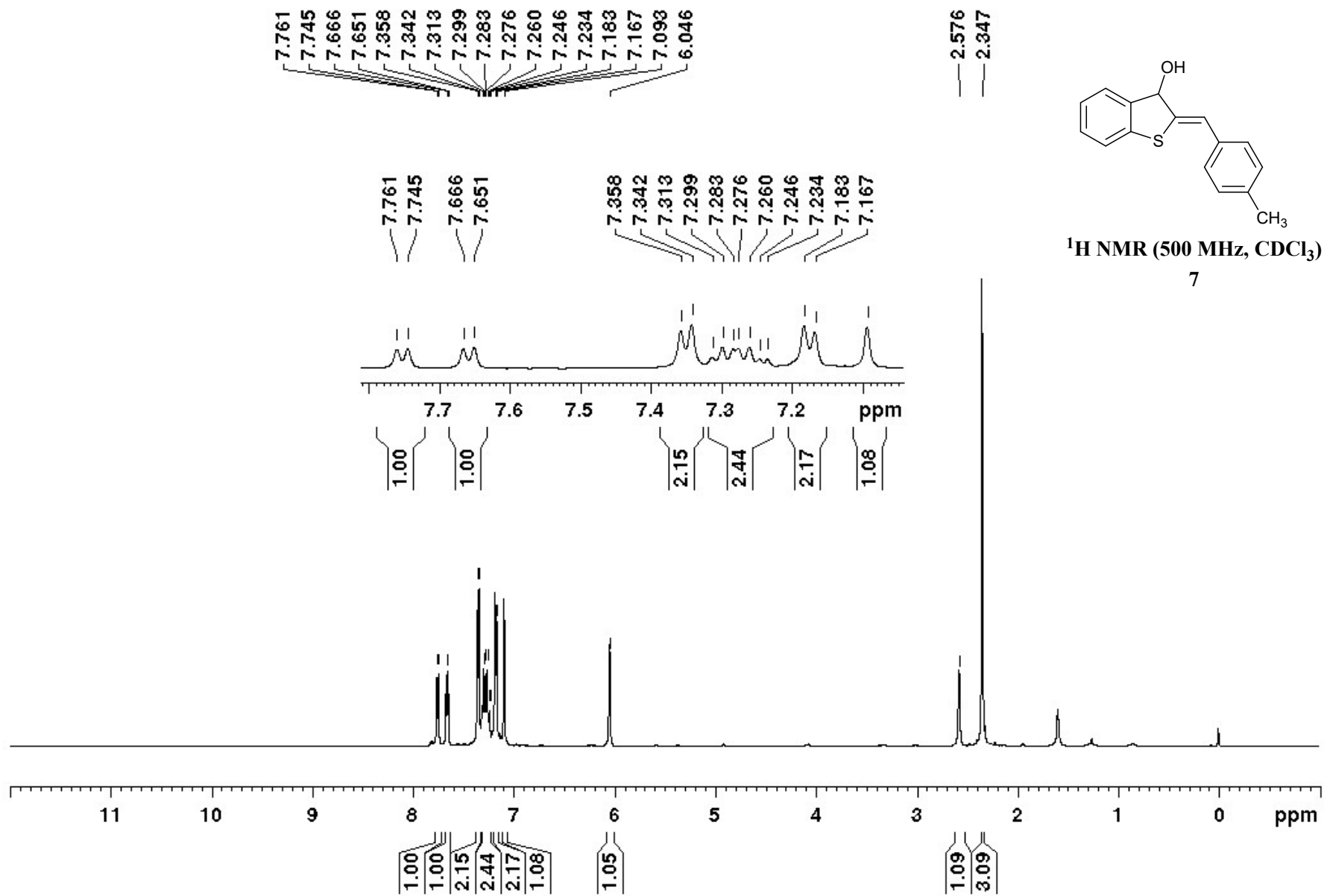
¹H NMR spectrum of compound 6



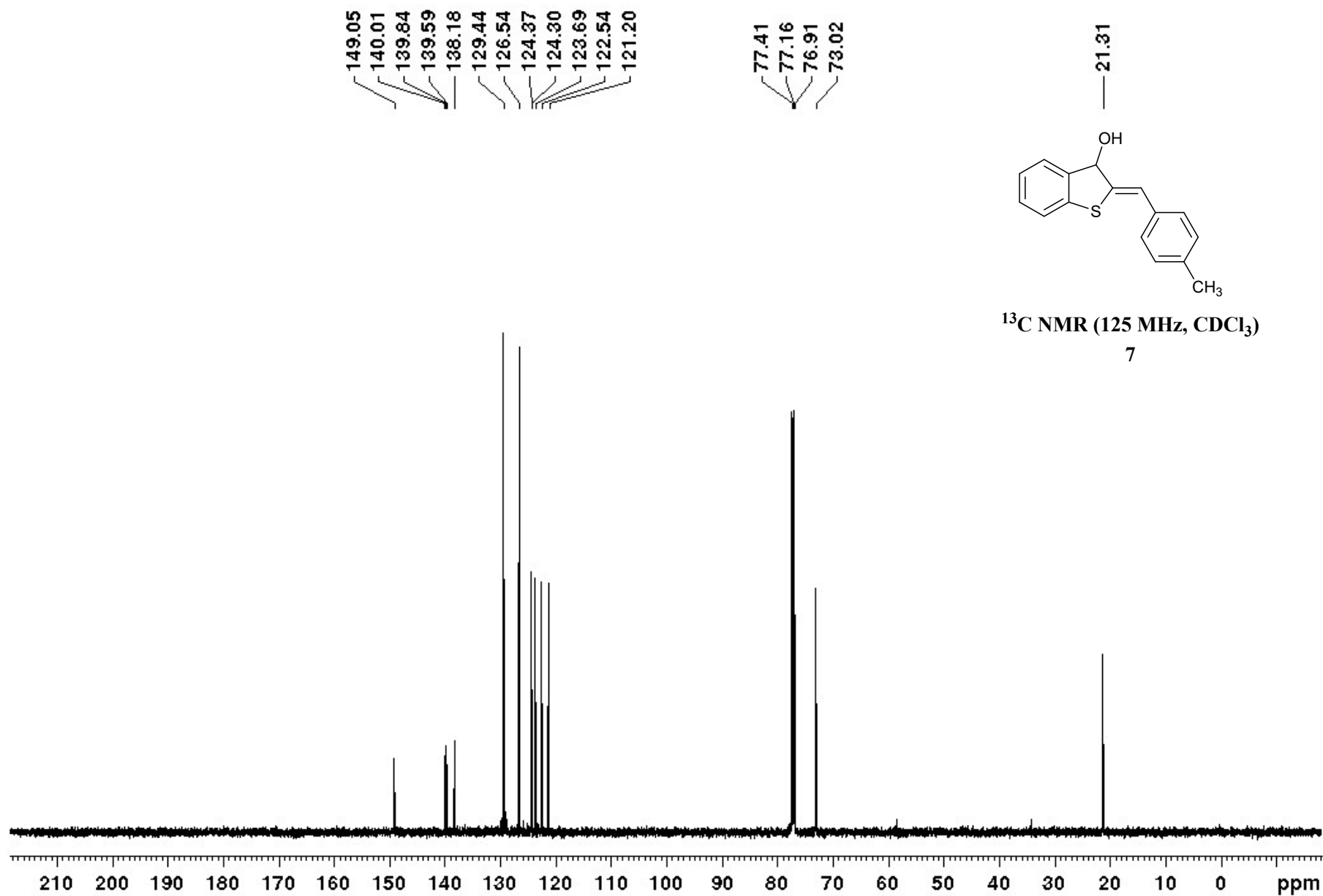
¹³C NMR spectrum of compound 6



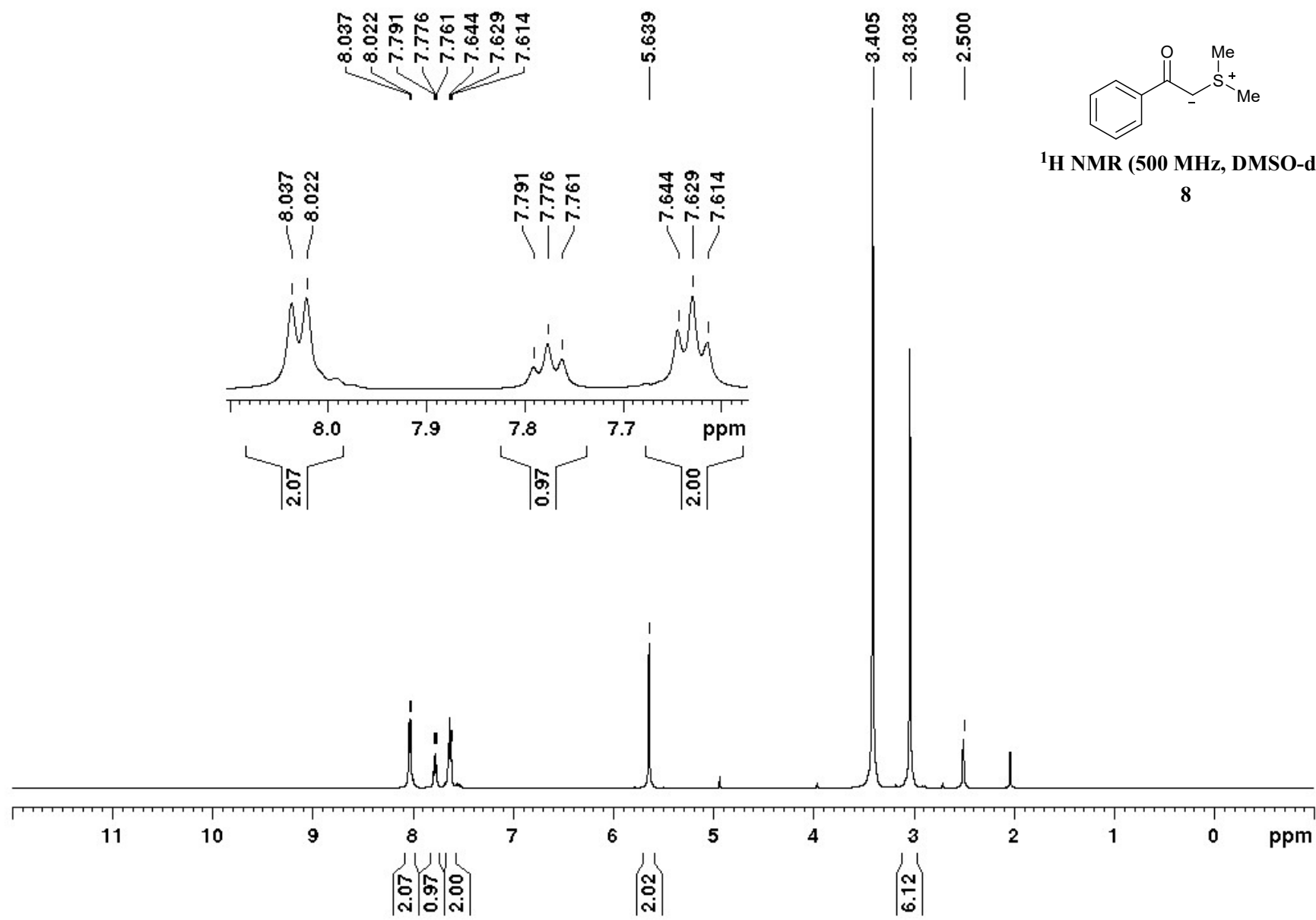
¹H NMR spectrum of compound 7



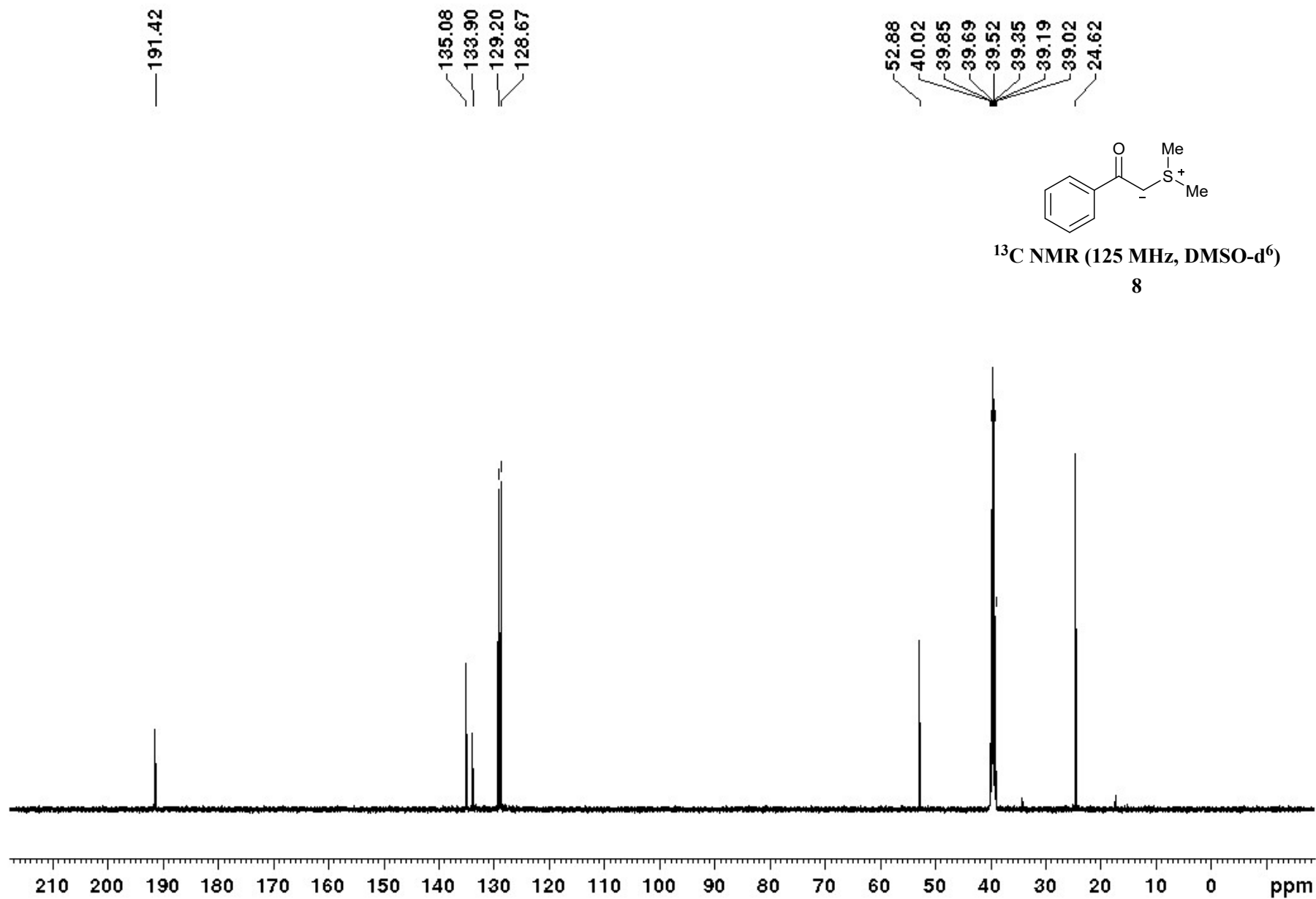
¹³C NMR spectrum of compound 7



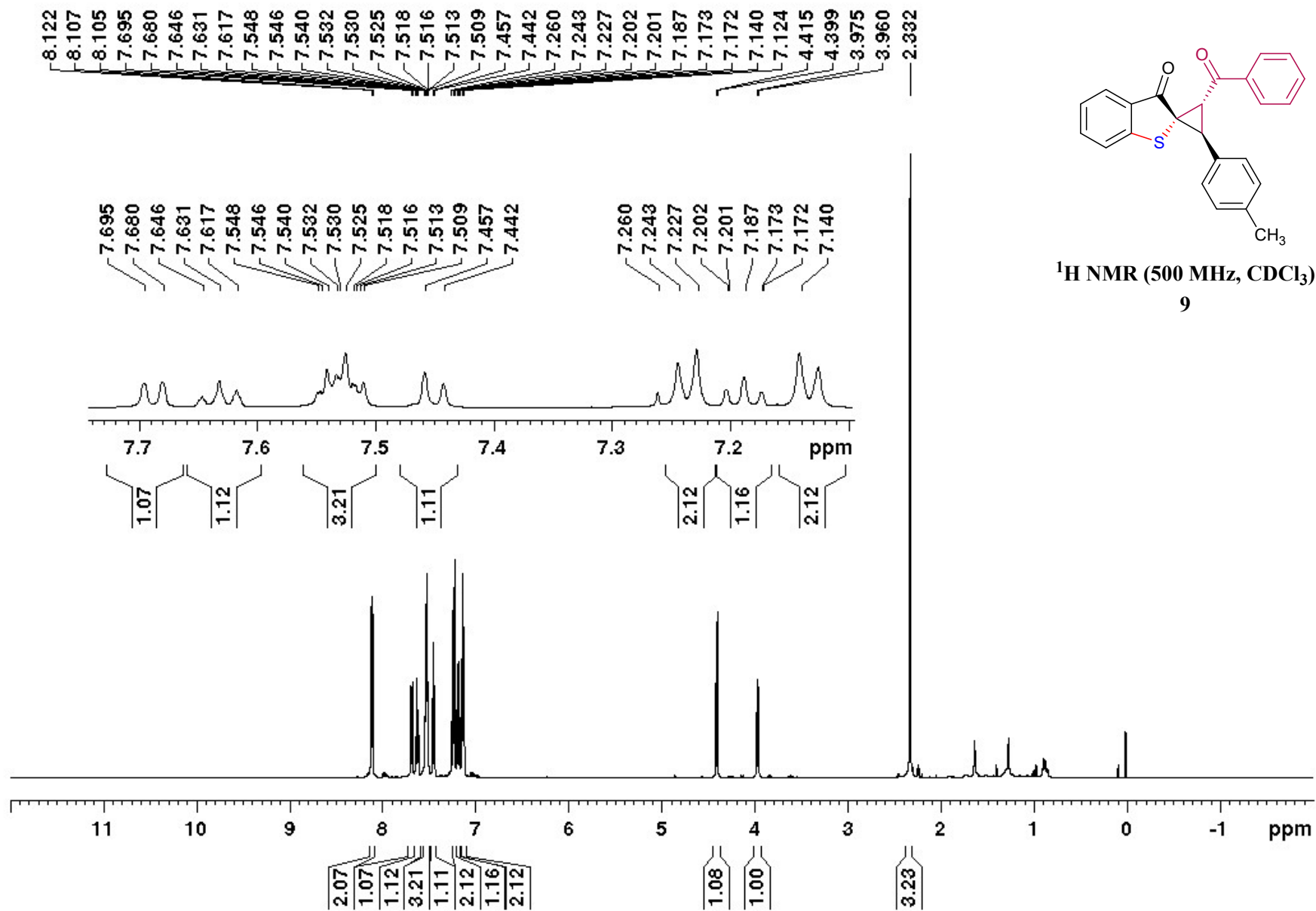
¹H NMR spectrum of compound 8



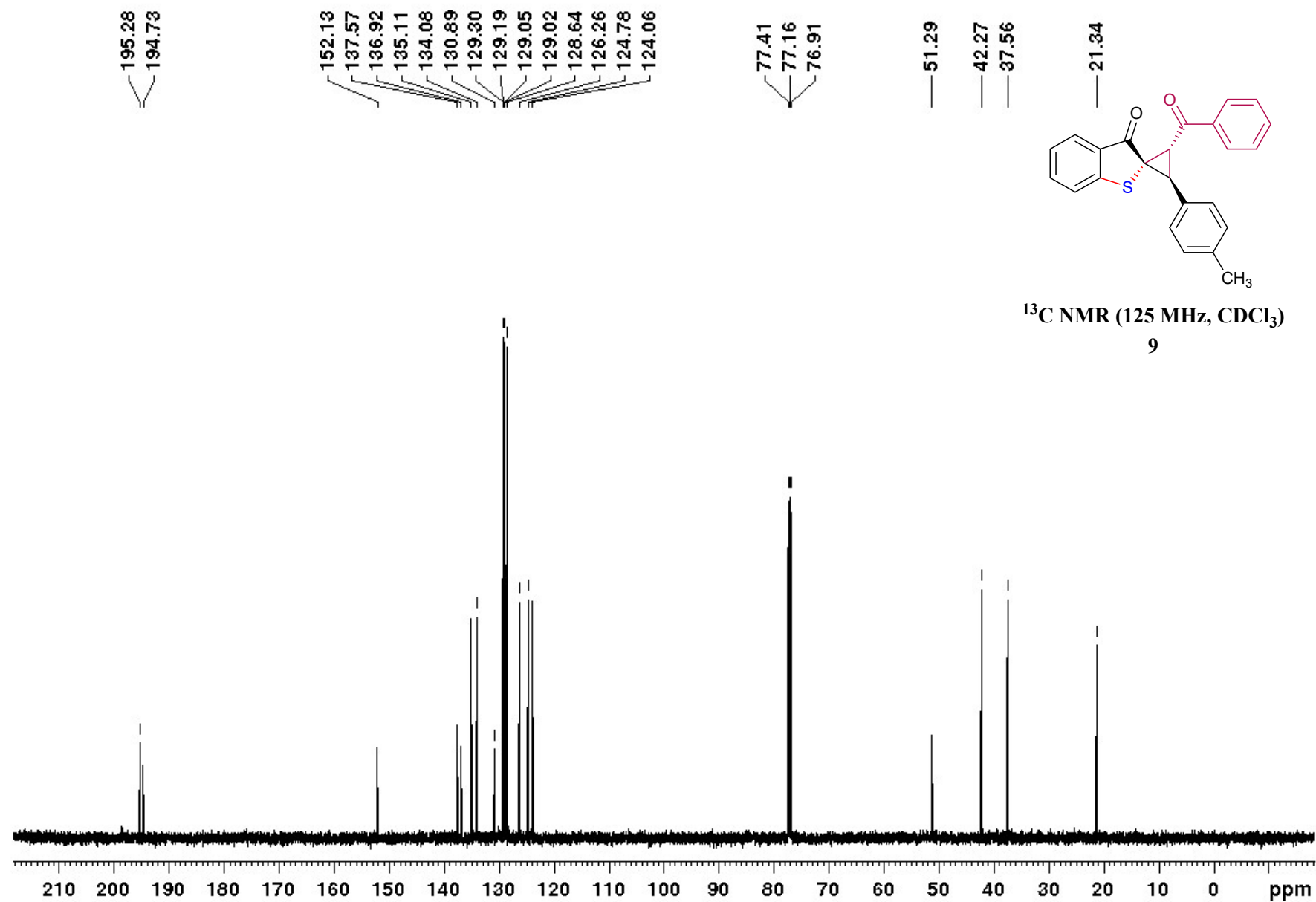
¹³C NMR spectrum of compound 8



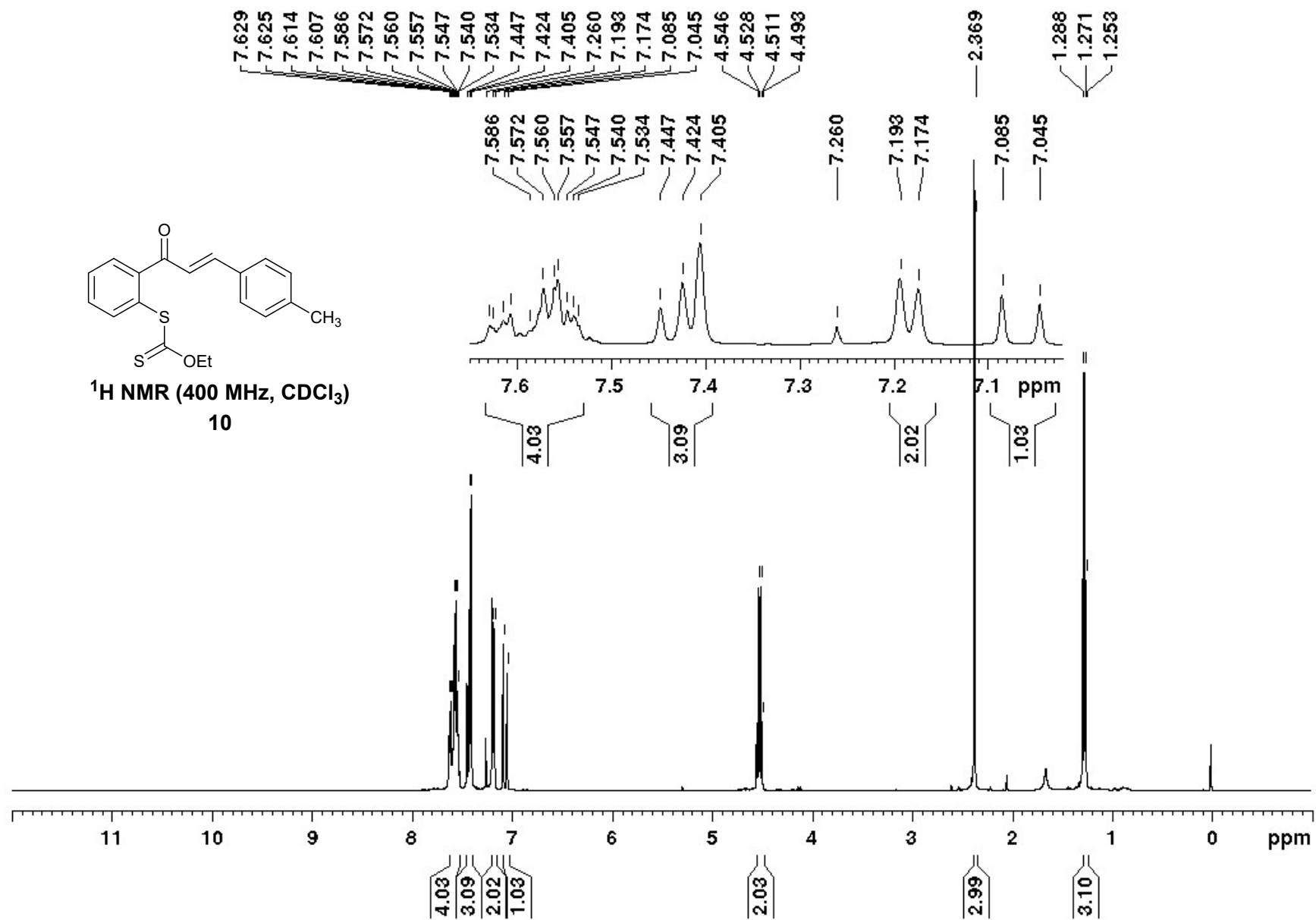
¹H NMR spectrum of compound 9



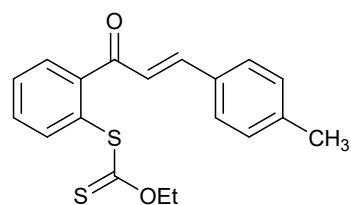
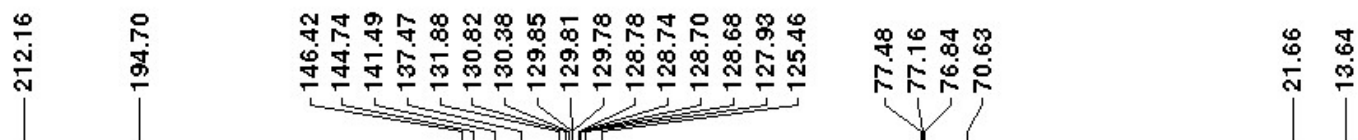
¹³C NMR spectrum of compound 9



¹H NMR spectrum of compound 10

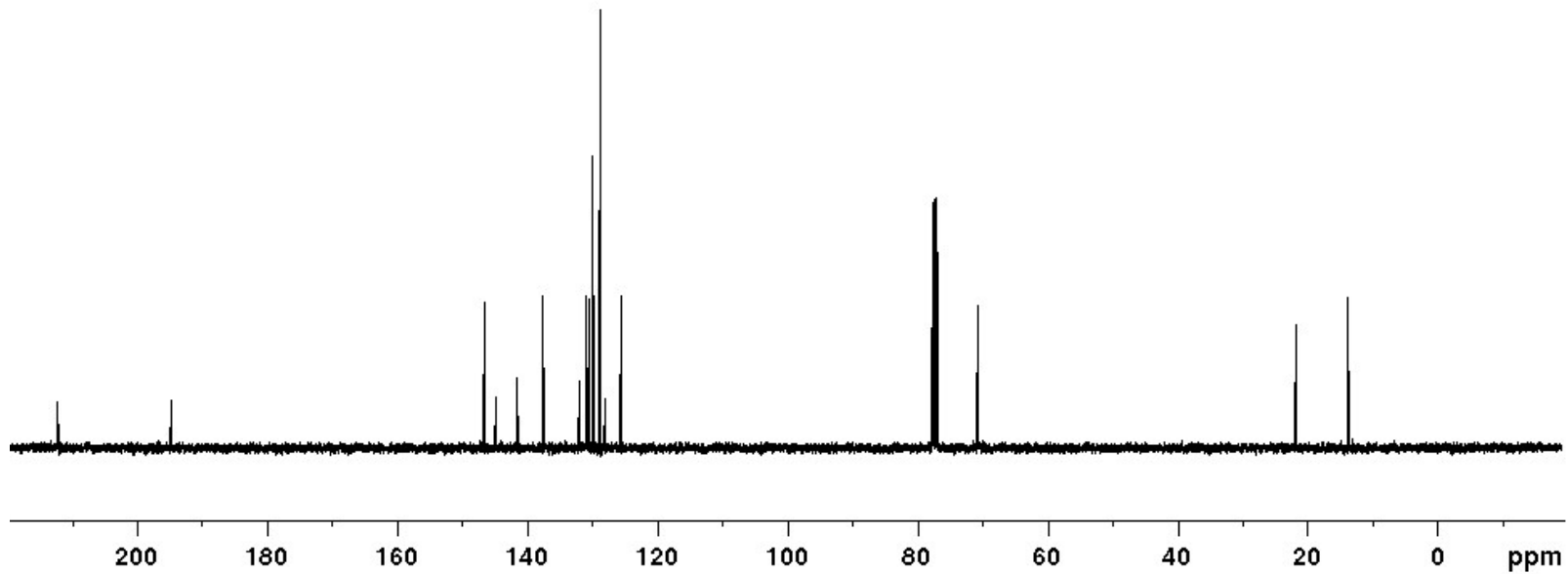


¹³C NMR spectrum of compound 10

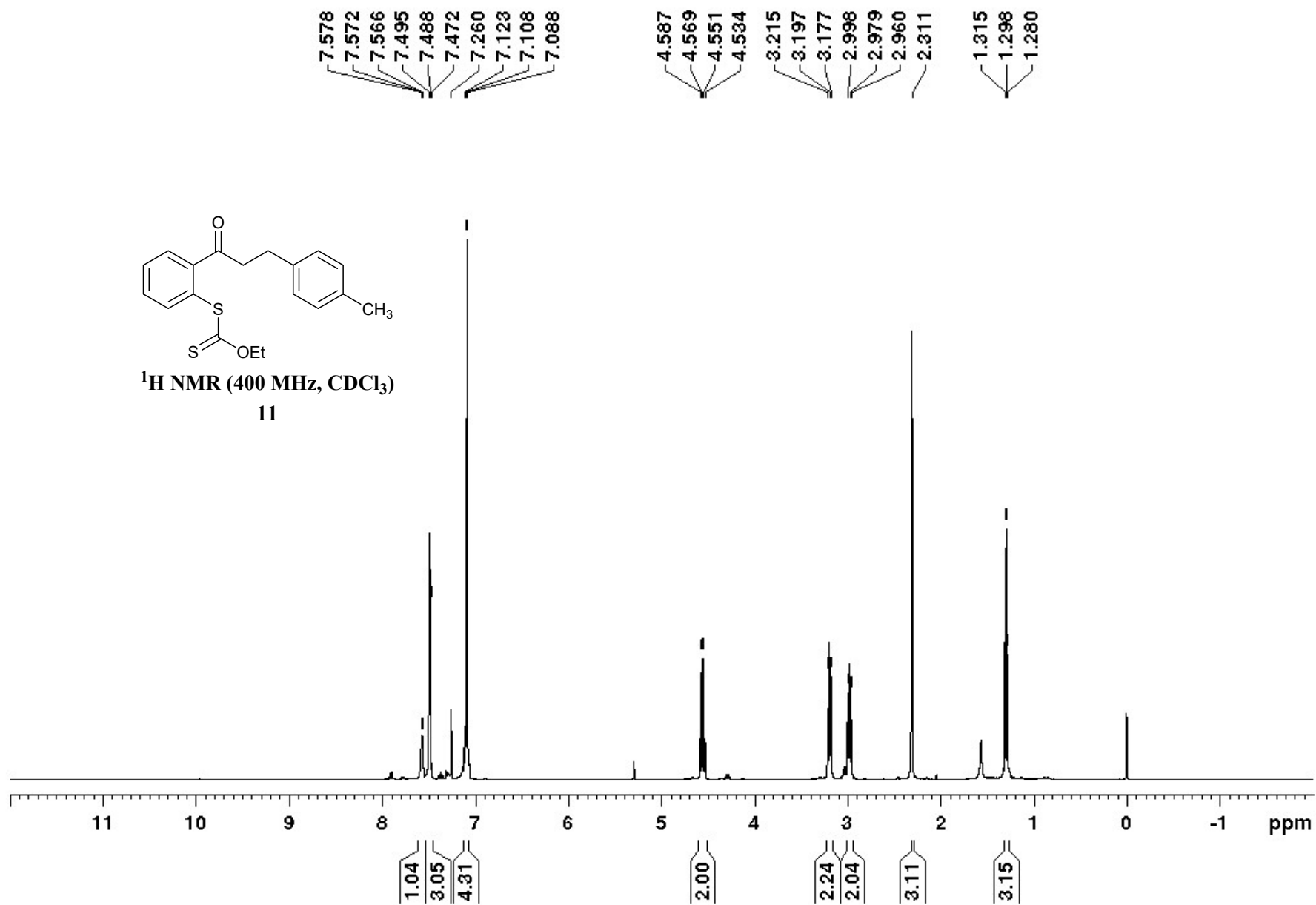


¹³C NMR (101 MHz, CDCl₃)

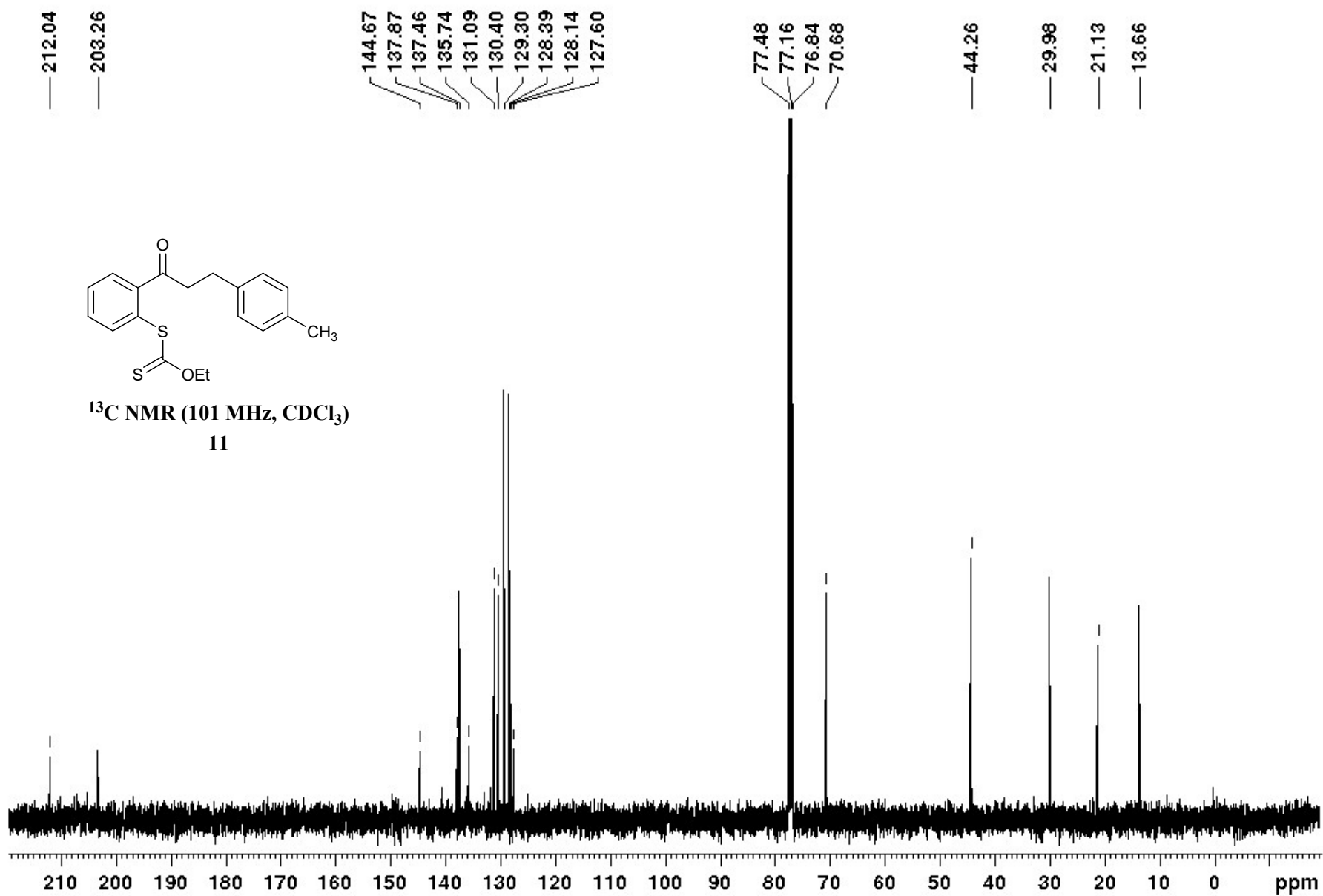
10



¹H NMR spectrum of compound 11



¹³C NMR spectrum of compound 11



6.0. Single crystal XRD data for Compound

Single crystals of (*Z*)-2-(2-methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one **2i** and (*Z*)-2-(2-chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-one **2p** and derivatives are suitable for X-ray analysis was obtained by slow evaporation of 0.01 M solution in 1:1 mixture of MeOH:DCM. Thermal ellipsoids are shown at the 50% probability level and hydrogens are omitted for clarity.

5.1 XRD Data for Compound **2i** (CCDC No. 2142524)

Bond precision:	C-C = 0.0057 Å	Wavelength=0.71073
Cell:	a=7.0327(12) b=7.7486(14) c=11.892(2)	
	alpha=84.539(9) beta=79.040(9) gamma=76.596(9)	
Temperature:	296 K	
	Calculated	Reported
Volume	618.00(19)	617.99(19)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₁₆ H ₁₂ O S	?
Sum formula	C ₁₆ H ₁₂ O S	C ₁₆ H ₁₂ O S
Mr	252.32	252.32
Dx, g cm ⁻³	1.356	1.356
Z	2	2
Mu (mm ⁻¹)	0.245	0.245
F000	264.0	264.0
F000'	264.35	
h,k,lmax	8,9,14	8,9,14
Nref	2176	2173
Tmin,Tmax	0.937,0.976	0.935,0.976
Tmin'	0.934	
Correction method=	# Reported T Limits: Tmin=0.935 Tmax=0.976	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.999	Theta(max)= 24.998
R(reflections)=	0.0792(1503)	wR2(reflections)= 0.2405(2173)
S =	1.013	Npar= 164

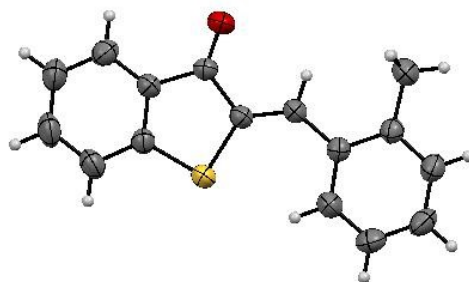


Figure S1. Single-crystal X-ray structure of compound **2i** (CCDC No. 2142524) Ellipsoids represent 50% probability level.

5.2 XRD Data for Compound **2p** (CCDC No. 2142521)

Bond precision:	C-C = 0.0054 Å	Wavelength=0.71073
Cell:	a=21.345(3) b=3.9444(5) c=14.7541(19)	
	alpha=90 beta=100.455(5) gamma=90	
Temperature:	296 K	
	Calculated	Reported
Volume	1221.6(3)	1221.6(3)
Space group	C c	C c
Hall group	C -2yc	C -2yc
Moiety formula	C ₁₅ H ₉ Cl O S?	
Sum formula	C ₁₅ H ₉ Cl O S	C ₁₅ H ₉ Cl O S
Mr	272.73	272.73
Dx, g cm ⁻³	1.483	1.483
Z	4	
Mu (mm ⁻¹)	0.465	0.465
F000	560.0	560.0
F000'	561.28	
h,k,lmax	24,4,17	24,4,17
Nref	2160 [1081]	1747
Tmin,Tmax	0.890,0.933	
Tmin'	0.890	
Correction method=	Not given	
Data completeness=	1.62/0.81	Theta(max)= 24.989
R(reflections)=	0.0278(1614)	wR2(reflections)= 0.0614(1747)
S =	1.041	Npar= 163

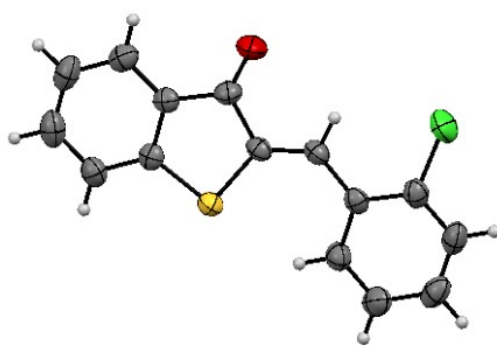


Figure S1. Single-crystal X-ray structure of compound **2i** (CCDC No. 2142521) Ellipsoids represent 50% probability level.