Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photocatalytic three-component annulation enabling stereoselective generation of (*Z*)-thiochromene 1,1-dioxides

Ke-Xian Song,[a] Xiao-Yan Qin,[a] Zi-Xuan Ma,[a] Fang-Zhou Geng,[a] Wen-Juan Hao,*[,a] Shu-Jiang Tu,[a] Bo Jiang*[,a]

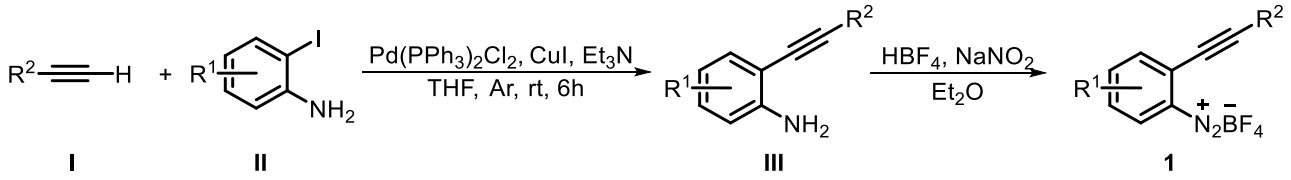
[a]School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, 221116, P. R. China; email: jiangchem@jsnu.edu.cn (BJ); wjhao@jsnu.edu.cn(WJH)

Contents

General Information

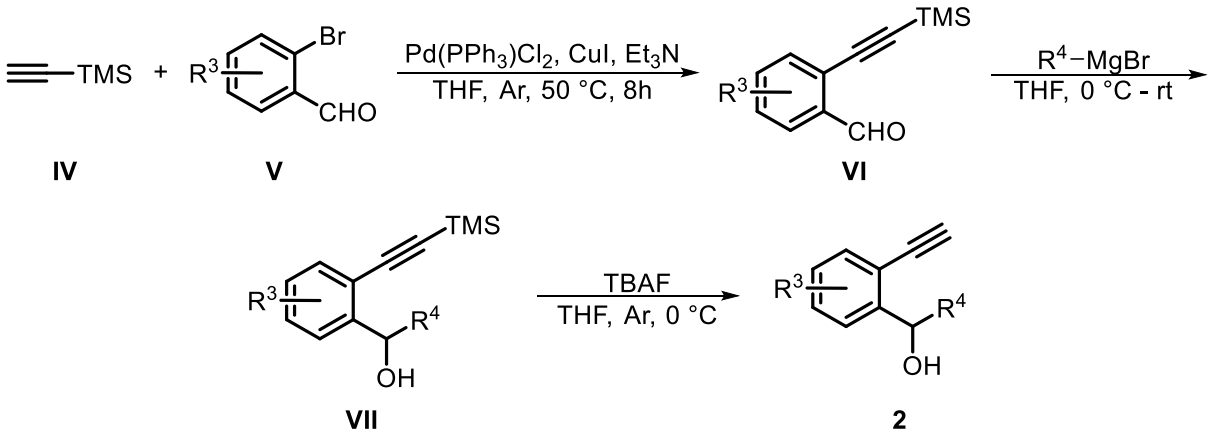
^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI and ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General Procedure for the Synthesis of Compounds 1



A mixture of $Pd(PPh_3)Cl_2$ (1 mol %, 0.1 mmol), CuI (2 mol %, 0.2 mmol), Et_3N (3.0 equiv, 30mmol) and *o*-iodoaniline (1.0 equiv, 10 mmol), dissolving in 20 mL anhydrous tetrahydrofuran (THF), were stirred for 15 minutes at room temperature under argon conditions. Then, terminal alkyne **I** (1.1 equiv, 11 mmol) was added to the reaction vial by drop wise and stirred for 6h. The reaction process was determined by TLC until the starting material consumed completely. The resulting mixture was extracted with 50 mL saturated NH_4Cl aqueous and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over Na_2SO_4. Then, the mixture was filtrated and the culture was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as the eluent to afford compound **III**. Then the mixture of HBF_4 (1.5 equiv, 15 mmol) and H_2O (3mL) was stirred at -10°C for 10 minutes before the ether solution of **III** was added dropwisely. Subsequently, an aqueous of $NaNO_2$ (1.1 equiv, 11 mmol) was added dropwise. After completion of the reaction, the mixture was filtered and the solid was washed with ether (5mL×3) to give the benzenediazonium tetrafluoroborate **1**.

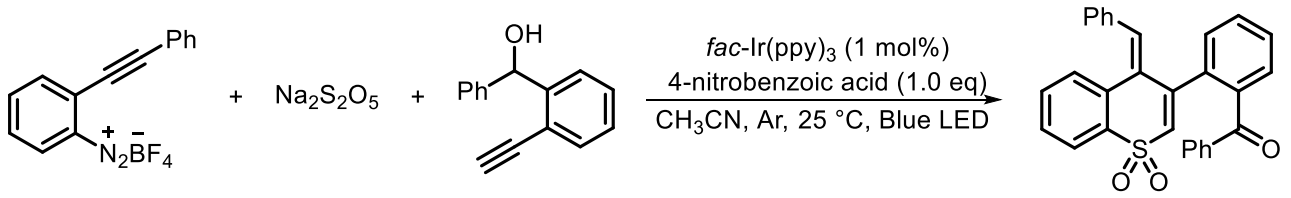
General Procedure for the Synthesis of Compounds 2



A mixture of $Pd(PPh_3)Cl_2$ (1 mol %, 0.1 mmol), CuI (2 mol %, 0.2 mmol), Et_3N (3.0 equiv, 30mmol) and 2-bromobenzaldehyde **V** (1.0 equiv, 10 mmol), dissolving in 20 mL anhydrous tetrahydrofuran (THF), were stirred for 15 minutes at room temperature under argon conditions. Then, terminal alkyne **IV** (1.1 equiv, 11 mmol) was added to the reaction vial by drop wise and stirred for 6h. The reaction process was determined by TLC until the starting material consumed completely. The resulting mixture was extracted with 50 mL saturated NH_4Cl aqueous and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried

over Na_2SO_4. Then, the mixture was filtrated and the culture was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as the eluent to afford compound **VI**. Compound **VI** (1.0 eq, 10 mmol)was dissolved in dry THF and stirred under argon atmosphere at 0 °C for 10 minutes before Grignard reagent (1.5 equiv, 15 mmol) was added drop wise. The reaction process was determined by TLC until the starting material consumed completely. The resulting mixture was extracted with 50 mL saturated NH_4Cl aqueous and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over Na_2SO_4. Then, the mixture was filtrated and the culture was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as the eluent to afford compound **VII**. Compound **VII** (1.0 eq, 10 mmol)was dissolved in dry THF and stirred under argon atmosphere at -10 °C for 10 minutes before TBAF (0.8 equiv, 8 mmol) was added drop wise. The resulting mixture was extracted with 50 mL saturated NH_4Cl aqueous and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over Na_2SO_4. Then, the mixture was filtrated and the culture was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to give the compound **2**.

General Procedure for the Synthesis of Products 3



1a **2a** **3a**

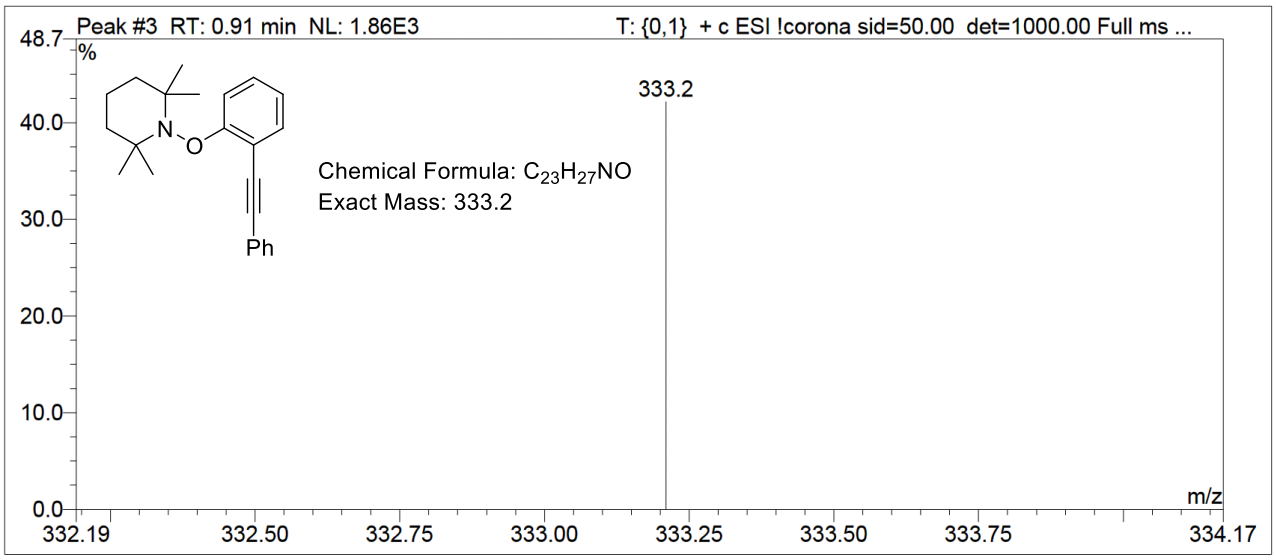
Example for the synthesis of **3a**:

$Na_2S_2O_5$ (3.0 equiv, 0.6 mmol, 114 mg), 2-(phenylethynyl)benzenediazonium tetrafluoroborate **1a** (3.0 equiv, 0.6 mmol, 175.2 mg), 4-nitrobenzoic acid (1.0 equiv, 0.2 mmol, 33.4 mg) and *fac*-Ir(ppy)$_3$ (1 mol %, 1.6 mg) was added to a Schlenk tube with a magnetic stir bar after the Schlenk tube was flamedried and subjected to evacuation/flushing with argon three times, then γ-hydroxyl terminal alkyne **2a** (1.0 equiv, 0.2 mmol, 41.6 mg) was dissolved in 1.0 mL dry CH_3CN and added to the tube. Then the mixture was stirred in photocatalytic parallel reactor at 25 °C under blue light (10W blue LEDs) irradiation until complete consumption of **2a** as monitored by TLC analysis. After the reaction was finished, the reaction mixture was filtered and the filtrate was washed with brine, extracted with EtOAc, concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 7:1) to afford the desired product **3a** as a white solid in 78% yield.

Mechanistic Investigations

Control Experiment with TEMPO

$Na_2S_2O_5$ (3.0 equiv, 0.6 mmol, 114 mg), 2-(phenylethynyl)benzenediazonium tetrafluoroborate **1a** (3.0 equiv, 0.6 mmol, 175.2 mg), 4-nitrobenzoic acid (1.0 equiv, 0.2 mmol, 33.4 mg), TEMPO (2.0 equiv, 0.2mmol, 31.2 mg) and *fac*-Ir(ppy)$_3$ (1 mol %, 1.6 mg) was added to a Schlenk tube with a magnetic stir bar after the Schlenk tube was flamedried and subjected to evacuation/flushing with argon three times, then γ-hydroxyl terminal alkyne **2a** (1.0 equiv, 0.2 mmol, 41.6 mg) was dissolved in 1.0 mL dry CH_3CN and added to the tube. Then the mixture was stirred in photocatalytic parallel reactor at 25 °C under blue light (blue LEDs) irradiation. The corresponding product was not detected according to TLC analysis. The product 2,2,6,6-tetramethyl-1-(2-(phenylethynyl)phenoxy)piperidine was detected by ESI-HRMS.



Luminescence Quenching Experiment

The luminescence quenching experiment was taken using a F-4600 Spectrophotometer (Hitachi, Japan). The excitation wavelength was 400 nm. The emission intensity was collected at 506 nm. The samples were prepared by mixing *fac*-Ir(ppy)$_3$ (1.0×10^{-4} mol/L) and different amount of quenchers (aryldiazonium tetrafluoroborate **1a**, $Na_2S_2O_5$ and γ-hydroxyl terminal alkyne **2a**) in CH_3CN (total volume = 2.0 mL) in a light path quartzfluorescence cuvette. The concentration of **1a** and **2a** stock solution both are 1.0×10-4 mol/L in CH_3CN. For each quenching experiment, each volume of quenchers (**1a**, $Na_2S_2O_5$ and **2a**) stock solution was titrated to a mixed solution of *fac*-Ir(ppy)$_3$ (20, 20, 20, 20, 20, 20, 20×10-3 mL, in a total volume = 2.0 mL). Then the emission intensity was collected and the results were presented in Figure S1-S3.

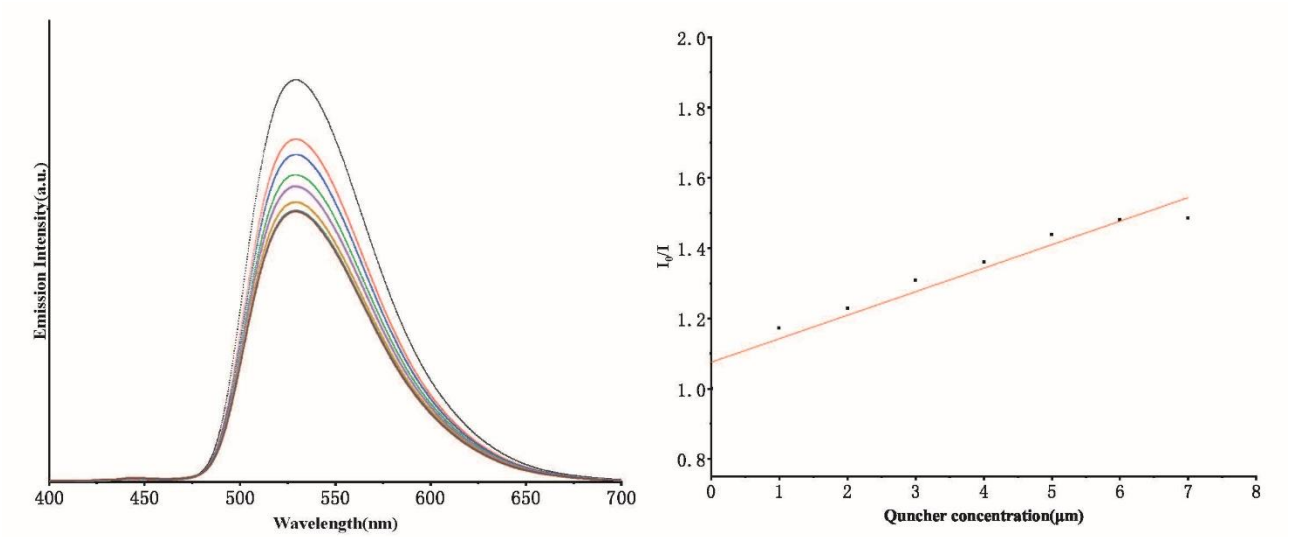


Figure S1. Luminescence quenching of *fac*-Ir(ppy)$_3$ with **1a**

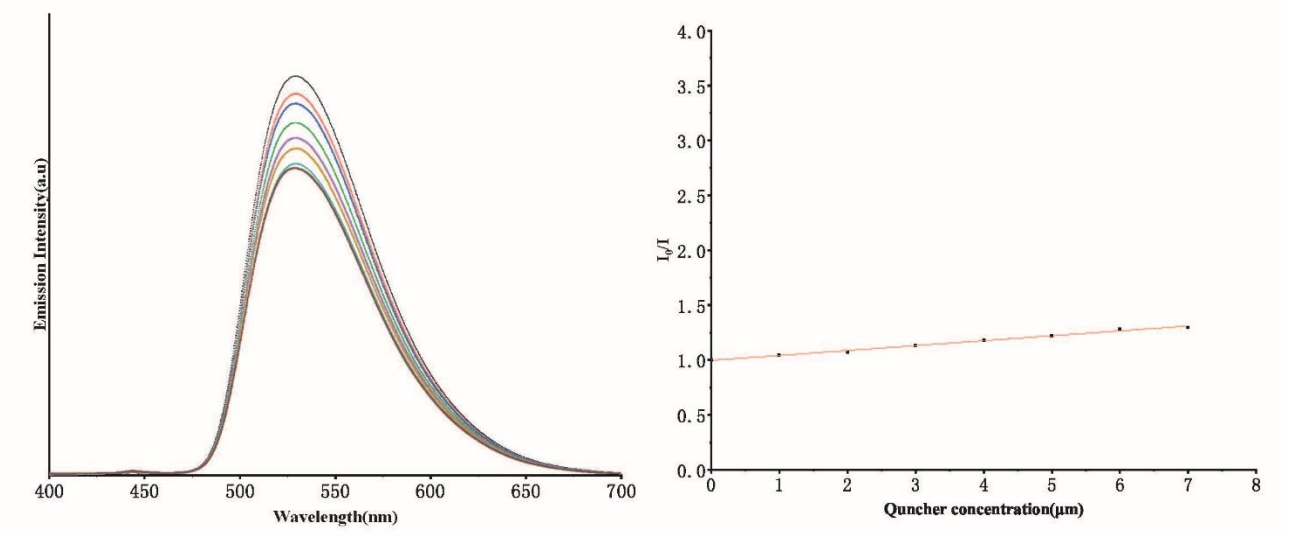


Figure S2. Luminescence quenching of *fac*-Ir(ppy)$_3$ with **2a**

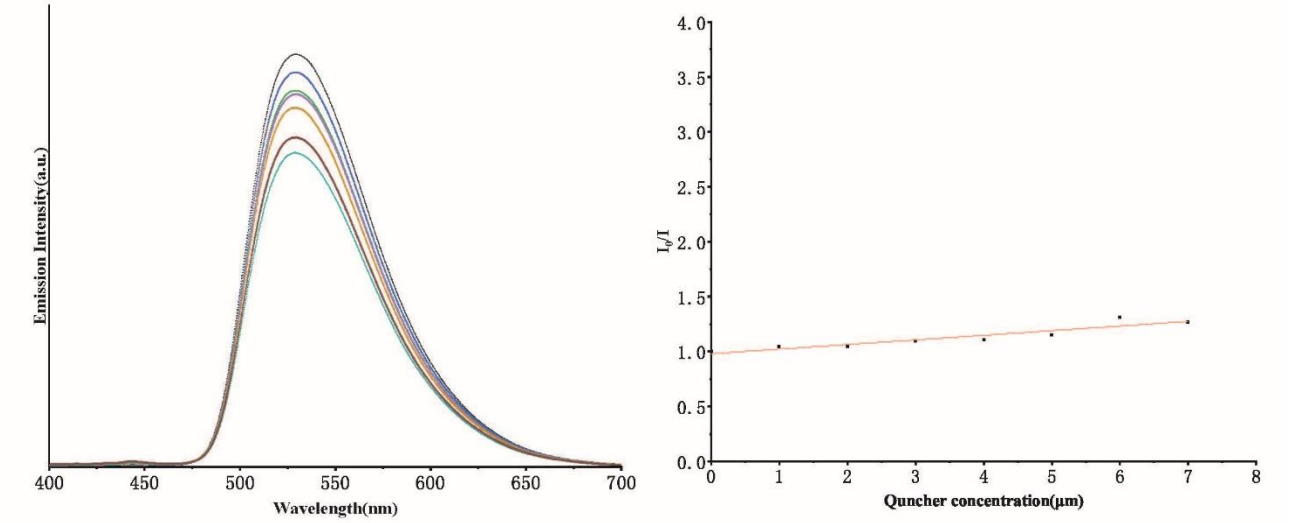
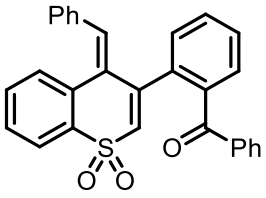


Figure S3. Luminescence quenching of *fac*-Ir(ppy)$_3$ with $Na_2S_2O_5$

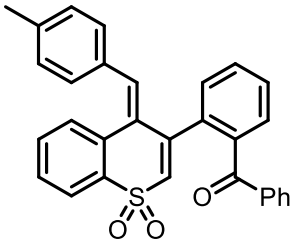
(*Z*)-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3a)



(*Z*/*E* > 19:1)

70 mg, 78%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.912 – 7.876 (d, *J* = 14.4 Hz, 1H), 7.714 – 7.639 (m, 6H), 7.376 – 7.304 (m, 2H), 7.245 – 7.165 (m, 3H), 7.152 – 7.062 (m, 3H), 7.006 – 6.964 (d, *J* = 16.8 Hz, 2H), 6.877 – 6.836 (d, *J* = 16.4 Hz, 1H), 6.719 (s, 1H), 6.686 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 153.8, 139.4, 139.3, 137.1, 136.5, 135.9, 134.8, 133.7, 133.4, 131.7, 131.6, 130.9, 130.3, 130.2, 130.1, 129.9, 129.8, 129.1, 128.5, 128.4, 128.3, 124.3, 122.8. IR (film, ν, cm^{-1}) 1664, 1577, 1440, 1305, 1121, 1023, 929, 846, 746, 699. HR-MS (ESI) m/z calcd for $C_{29}H_{19}O_3S$ $[M-H]^+$ 447.1055, found 447.1055.

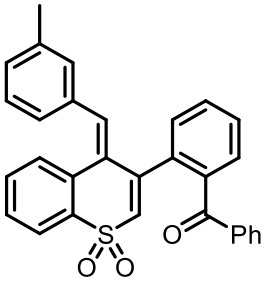
(*Z*)-(2-(4-(4-methylbenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3b)



(*Z*/*E* > 19:1)

42 mg, 45%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.918 – 7.862 (m, 1H), 7.718 – 7.621 (m, 6H), 7.388 – 7.283 (m, 2H), 7.243 – 7.177 (m, 2H), 7.127 – 7.063 (m, 1H), 6.967 – 6.872 (m, 5H), 6.714 – 6.634 (d, *J* = 32.0 Hz, 2H), 2.250 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 153.9, 139.6, 139.5, 139.5, 137.0, 136.5, 135.9, 133.9, 133.4, 131.8, 131.5, 130.9, 130.9, 130.2, 130.2, 130.0, 129.9, 129.8, 129.2, 128.3, 128.3, 124.0, 122.8, 21.4. IR (film, ν, cm^{-1}) 1664, 1595, 1507, 1449, 1295, 1126, 1070, 929, 769, 706. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1169.

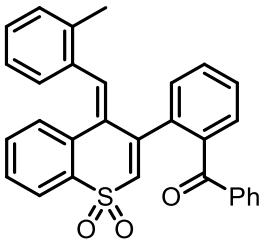
(*Z*)-(2-(4-(3-methylbenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3c)



(*Z*/*E* = 10:1)

68 mg, 74%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.925 – 7.874 (d, *J* = 20.4 Hz, 1H), 7.722 – 7.615 (m, 6H), 7.386 – 7.296 (m, 2H), 7.257 – 7.190 (m, 3H), 7.130 – 7.056 (m, 1H), 7.019 – 6.967 (d, *J* = 20.8 Hz, 2H), 6.790 (s, 2H), 6.725 – 6.642 (d, *J* = 33.2 Hz, 2H), 2.192 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 153.8, 139.6, 139.4, 138.2, 137.0, 136.6, 135.9, 134.7, 133.8, 133.4, 131.6, 131.4, 130.9, 130.7, 130.3, 130.3, 130.2, 130.1, 130.0, 129.9, 129.9, 128.4, 128.3, 128.2, 126.9, 124.2, 122.8, 122.3, 21.2. IR (film, ν, cm^{-1}) 1661, 1595, 1447, 1285, 1148, 1072, 925, 767, 700, 653. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1170.

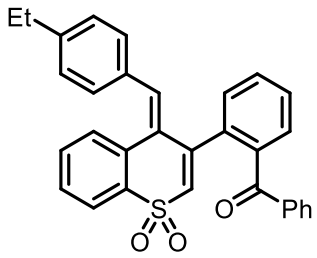
(*Z*)-(2-(4-(2-methylbenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3d)



(*Z*/*E* = 10:1)

81 mg, 88%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.843 – 7.792 (d, *J* = 20.4 Hz, 1H), 7.781 – 7.739 (m, 1H), 7.719 – 7.643 (m, 3H), 7.562 – 7.493 (m, 2H), 7.365 – 7.281 (m, 2H), 7.241 – 7.173 (d, *J* = 24.2 Hz, 1H), 7.157 – 7.039 (m, 5H), 7.007 – 6.915 (d, *J* = 36.8 Hz, 1H), 6.888 – 6.805 (m, 2H), 6.738 (s, 1H), 6.642 (s, 1H), 2.104 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 153.5, 139.6, 139.2, 137.3, 136.5, 136.5, 135.8, 134.4, 133.6, 133.2, 132.3, 131.7, 130.7, 130.5, 130.5, 130.2, 129.9, 129.7, 129.1, 128.3, 128.0, 125.8, 124.3, 122.5, 19.8. IR (film, ν, cm^{-1}) 1661, 1595, 1447, 1295, 1148, 1072, 925, 881, 753, 707. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1170.

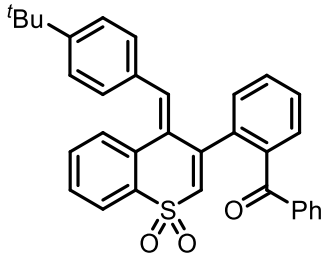
(*Z*)-(2-(4-(4-ethylbenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3e)



(*Z*/*E* = 2:1)

61 mg, 64%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.934 – 7.868 (m, 2H), 7.672 – 7.642 (m, 3H), 7.567 – 7.470 (m, 2H), 7.360 – 7.308 (m, 2H), 7.244 – 7.201 (d, *J* = 17.2 Hz, 2H), 7.127 – 7.099 (m, 1H), 6.965 – 6.924 (d, *J* = 16.4 Hz, 5H), 6.707 – 6.635 (d, *J* = 28.8 Hz, 2H), 2.599 – 2.532 (m, 2H), 1.197 – 1.148 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.5, 153.9, 145.8, 145.5, 139.7, 139.3, 137.8, 136.9, 136.5, 135.9, 135.4, 133.9, 133.4, 132.0, 131.6, 131.1, 130.9, 130.5, 130.2, 130.0, 129.4, 129.0, 128.3, 128.2, 128.0, 127.6, 127.0, 124.0, 122.8, 28.7, 15.1. IR (film, ν, cm^{-1}) 1654, 1507, 1457, 1295, 1214, 1123, 1070, 929, 829, 767. HR-MS (ESI) m/z calcd for $C_{31}H_{23}O_3S$ $[M-H]^+$ 475.1368, found 475.1370.

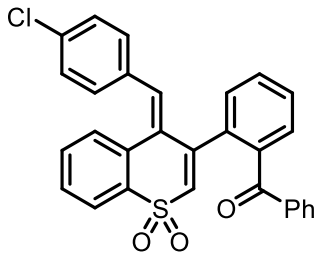
(*Z*)-(2-(4-(4-(tert-butyl)benzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3f)



(*Z*/*E* = 3.5:1)

88 mg, 87%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.905 – 7.877 (d, *J* = 11.2 Hz, 1H), 7.687 – 7.629 (m, 6H), 7.349 – 7.299 (m, 2H), 7.239 – 7.194 (d, *J* = 18.0 Hz, 2H), 7.146 – 7.101 (m, 3H), 6.985 – 6.926 (m, 3H), 6.703 – 6.624 (d, *J* = 31.6 Hz, 2H), 1.230 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.5, 154.0, 152.7, 139.5, 139.4, 139.4, 136.9, 136.5, 135.9, 133.9, 133.4, 133.3, 131.8, 131.7, 131.6, 131.5, 130.9, 130.9, 130.5, 130.2, 130.1, 129.9, 129.8, 128.4, 128.3, 128.3, 128.2, 125.4, 124.3, 123.9, 122.7, 34.8, 31.2. IR (film, ν, cm^{-1}) 1659, 1603, 1448, 1297, 1215, 1149, 1072, 930, 833, 767. HR-MS (ESI) m/z calcd for $C_{33}H_{27}O_3S$ $[M-H]^+$ 503.1681, found 503.1678.

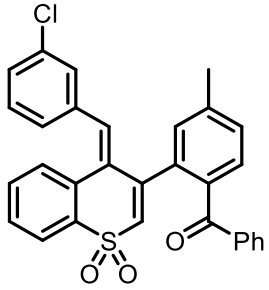
(*Z*)-(2-(4-(4-chlorobenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3g)



(*Z*/*E* > 19:1)

66 mg, 69%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.944 – 7.888 (m, 1H), 7.733 – 7.632 (m, 6H), 7.425 – 7.315 (m, 2H), 7.260 – 7.211 (d, *J* = 19.6 Hz, 2H), 7.162 – 7.081 (m, 3H), 6.934 – 6.880 (d, *J* = 21.6 Hz, 2H), 6.845 – 6.796 (d, *J* = 19.6 Hz, 1H), 6.761 – 6.594 (d, *J* = 66.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 153.8, 139.4, 137.6, 137.2, 136.3, 135.9, 135.1, 133.6, 133.5, 133.2, 132.3, 131.7, 131.2, 131.0, 130.5, 130.4, 130.3, 130.1, 129.8, 128.9, 128.7, 128.4, 124.7, 123.0. IR (film, ν, cm^{-1}) 1654, 1559, 1458, 1293, 1151, 1069, 929, 767, 705, 669. HR-MS (ESI) m/z calcd for $C_{29}H_{18}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0669.

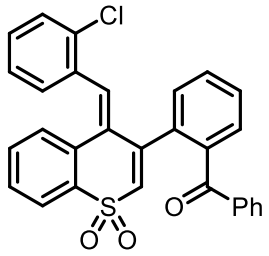
(*Z*)-(2-(4-(3-chlorobenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)-4-methylphenyl)(phenyl)methanone (3h)



(*Z*/*E* > 19:1)

67 mg, 68%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.951 – 7.904 (m, 1H), 7.743 – 7.639 (m, 6H), 7.423 – 7.370 (m, 2H), 7.292 (s, 2H), 7.175 – 7.106 (m, 2H), 7.063 – 6.998 (m, 1H), 6.894 – 6.861 (d, *J* = 13.2 Hz, 1H), 6.855 – 6.783 (m, 2H), 6.758 (s, 1H), 6.592 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 153.6, 139.3, 137.2, 136.9, 136.6, 136.3, 135.9, 134.5, 133.7, 133.3, 132.9, 131.7, 131.0, 130.5, 130.4, 130.0, 129.8, 129.7, 129.4, 129.0, 128.8, 128.5, 127.9, 124.9, 123.1. IR (film, ν, cm^{-1}) 1663, 1595, 1473, 1297, 1150, 1069, 926, 831, 767, 704. HR-MS (ESI) m/z calcd for $C_{29}H_{18}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0665.

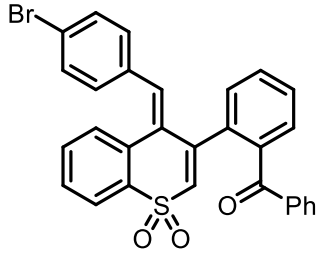
(*Z*)-(2-(4-(2-chlorobenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3i)



(*Z*/*E* > 19:1)

66 mg, 69%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.937 – 7.893 (m, 1H), 7.778 – 7.626 (m, 6H), 7.413 – 7.362 (m, 1H), 7.335 – 7.272 (d, *J* = 25.2 Hz, 2H), 7.239 – 7.190 (m, 2H), 7.175 – 7.096 (m, 2H), 6.991 – 6.910 (m, 2H), 6.872 – 6.825 (d, *J* = 18.8 Hz, 1H), 6.764 – 6.633 (d, *J* = 52.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.0, 153.6, 138.5, 137.0, 136.7, 136.4, 135.2, 134.4, 134.0, 133.8, 133.7, 133.1, 131.8, 131.7, 131.1, 131.0, 130.6, 130.5, 130.4, 130.2, 130.2, 129.7, 128.7, 128.1, 126.7, 124.8, 122.9. IR (film, ν, cm^{-1}) 1654, 1559, 1457, 1385, 1297, 1150, 1071, 910, 765, 704. HR-MS (ESI) m/z calcd for $C_{29}H_{18}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0667.

(*Z*)-(2-(4-(4-bromobenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3j)

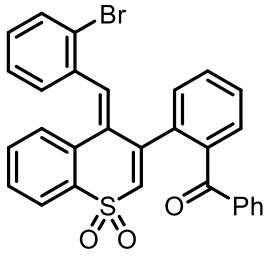


(*Z*/*E* = 12:1)

69 mg, 66%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.917 – 7.890 (m, 1H), 7.693 – 7.646 (m, 5H), 7.519 – 7.483 (m, 1H), 7.409 – 7.348 (m, 2H), 7.338 – 7.291 (d, *J* = 18.8 Hz, 1H), 7.239 (s, 2H), 7.153 – 7.101 (m, 1H), 6.930 – 6.866 (m, 1H), 6.860 – 6.784 (m, 3H), 6.746 (s, 1H), 6.582 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 196.4, 153.7, 139.3, 137.5, 137.1, 136.2, 133.6, 133.6,

133.4, 132.3, 131.7, 131.7, 131.6, 131.3, 130.9, 130.7, 130.5, 130.5, 130.4, 130.3, 130.0, 129.7, 128.7, 128.4, 128.3, 124.6, 123.4, 123.0. IR (film, ν, cm^{-1}) 1660, 1596, 1484, 1296, 1150, 1071, 930, 821, 703, 669. HR-MS (ESI) m/z calcd for $C_{29}H_{13}BrO_3S$ $[M-H]^+$ 525.0160, found 525.0162.

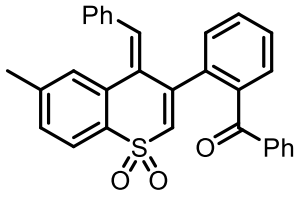
(*Z*)-(2-(4-(2-bromobenzylidene)-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3k)



(*Z*/*E* > 19:1)

54 mg, 51%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.930 – 7.877 (d, *J* = 21.2 Hz, 1H), 7.788 – 7.743 (d, *J* = 18.0 Hz, 1H), 7.732 – 7.606 (m, 5H), 7.531 – 7.478 (d, *J* = 21.2 Hz, 1H), 7.412 – 7.351 (m, 1H), 7.351 – 7.280 (m, 1H), 7.225 – 7.162 (m, 2H), 7.152 – 6.992 (m, 3H), 6.950 – 6.845 (m, 2H), 6.723 – 6.606 (d, *J* = 46.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 153.4, 138.6, 137.7, 137.0, 136.6, 136.5, 136.2, 133.5, 133.4, 133.1, 132.9, 132.0, 131.7, 131.2, 131.1, 130.7, 130.6, 130.4, 130.3, 130.2, 129.9, 128.7, 128.1, 127.4, 124.9, 124.5, 123.0, 122.4. IR (film, ν, cm^{-1}) 1659, 1596, 1457, 1296, 1149, 1071, 938, 768, 705, 669. HR-MS (ESI) m/z calcd for $C_{29}H_{13}BrO_3S$ $[M-H]^+$ 525.0160, found 525.0162.

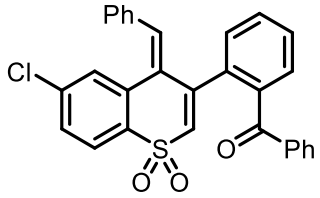
(*Z*)-(2-(4-benzylidene-6-methyl-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3n)



(*Z*/*E* > 19:1)

48 mg, 52%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.786 – 7.725 (d, *J* = 24.4 Hz, 1H), 7.705 – 7.606 (m, 6H), 7.308 – 7.262 (d, *J* = 18.4 Hz, 1H), 7.217 – 7.110 (m, 6H), 7.045 – 6.979 (d, *J* = 26.4 Hz, 2H), 6.733 – 6.570 (m, 3H), 2.058 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 153.6, 140.5, 139.5, 139.5, 136.4, 135.7, 134.8, 134.3, 133.4, 133.3, 131.6, 131.5, 130.8, 130.5, 130.4, 130.3, 130.2, 130.1, 129.7, 129.1, 129.0, 128.4, 128.1, 127.4, 124.6, 122.8, 21.3. IR (film, ν, cm^{-1}) 1666, 1599, 1445, 1295, 1132, 1072, 931, 840, 761, 639. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1171.

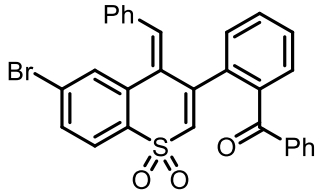
(*Z*)-(2-(4-benzylidene-6-chloro-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3o)



(*Z*/*E* > 19:1)

55 mg, 57%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.812 – 7.773 (d, *J* = 15.6 Hz, 1H), 7.724 – 7.669 (m, 4H), 7.666 – 7.621 (m, 2H), 7.320 – 7.270 (m, 3H), 7.252 – 7.168 (m, 5H), 7.039 – 6.984 (d, *J* = 22.0 Hz, 2H), 6.750 – 6.710 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 153.9, 140.9, 139.5, 136.5, 136.0, 135.6, 135.4, 135.3, 134.1, 133.6, 131.8, 130.8, 130.7, 130.3, 130.3, 129.9, 129.7, 128.8, 128.6, 128.3, 127.6, 124.4, 124.4. IR (film, ν, cm^{-1}) 1662, 1559, 1457, 1339, 1151, 1067, 930, 844, 756, 668. HR-MS (ESI) m/z calcd for $C_{29}H_{13}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0667.

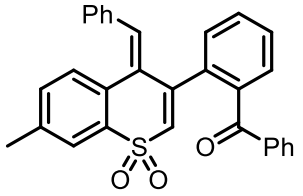
(*Z*)-(2-(4-benzylidene-6-bromo-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3p)



(*Z*/*E* > 19:1)

69 mg, 65%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.733 – 7.669 (m, 5H), 7.661 – 7.613 (m, 2H), 7.476 – 7.439 (m, 1H), 7.292 (s, 1H), 7.253 – 7.178 (m, 5H), 7.051 – 6.992 (d, *J* = 23.6 Hz, 2H), 6.894 – 6.867 (d, *J* = 10.8 Hz, 1H), 6.751 – 6.705 (d, *J* = 18.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 153.8, 141.0, 139.6, 135.9, 135.8, 135.5, 135.2, 134.0, 133.5, 132.8, 131.7, 131.4, 130.7, 130.3, 130.2, 130.1, 129.7, 128.7, 128.3, 124.8, 124.3, 124.3. IR (film, ν, cm^{-1}) 1661, 1576, 1444, 1299, 1131, 1082, 932, 844, 752, 697. HR-MS (ESI) m/z calcd for $C_{29}H_{13}BrO_3S$ $[M-H]^+$ 525.0160, found 525.0162.

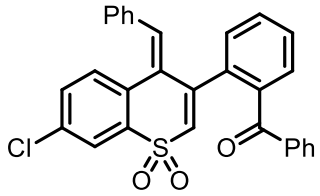
(*Z*)-(2-(4-benzylidene-7-methyl-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3q)



(*Z*/*E* = 10:1)

48 mg, 52%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.737 – 7.630 (m, 7H), 7.384 – 7.324 (d, *J* = 24.0 Hz, 2H), 7.199 – 7.095 (m, 4H), 6.999 – 6.952 (d, *J* = 18.8 Hz, 2H), 6.912 – 6.869 (d, *J* = 17.2 Hz, 1H), 6.770 – 6.726 (d, *J* = 17.6 Hz, 1H), 6.709 – 6.619 (d, *J* = 36.0 Hz, 2H), 2.362 (s, 3H). ^{13}C NMR (100 MHz, $CDDCl_3$) δ 196.5, 153.9, 139.4, 139.1, 138.5, 136.9, 136.7, 136.1, 135.0, 133.4, 131.8, 131.6, 131.3, 131.0, 130.9, 130.3, 130.2, 130.1, 129.8, 128.9, 128.5, 128.4, 127.5, 124.4, 122.9, 21.3. IR (film, ν, cm^{-1}) 1662, 1560, 1448, 1298, 1133, 1070, 929, 832, 755, 699. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1173.

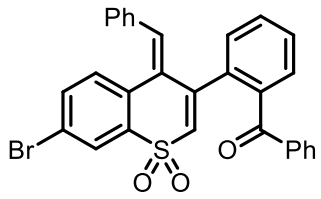
(*Z*)-(2-(4-benzylidene-7-chloro-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3r)



(*Z*/*E* = 2:1)

43 mg, 45%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.90 – 7.87 (d, J = 12.0 Hz, 1H), 7.68 – 7.63 (m, 3H), 7.57 – 7.46 (m, 3H), 7.41 – 7.36 (m, 2H), 7.23 – 7.19 (m, 2H), 7.05 – 7.02 (d, J = 12.0 Hz, 2H), 6.98 – 6.90 (m, 3H), 6.73 – 6.70 (d, J = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.3, 154.1, 139.5, 139.2, 138.7, 136.3, 135.9, 134.7, 134.4, 133.6, 133.6, 132.3, 132.1, 131.7, 131.2, 131.0, 130.6, 130.4, 130.3, 129.8, 129.3, 129.1, 128.6, 128.4, 127.5, 126.3, 124.0, 123.0, 122.5. IR (film, ν, cm^{-1}) 1655, 1540, 1448, 1300, 1215, 1134, 928, 828, 753, 697. HR-MS (ESI) m/z calcd for $C_{29}H_{13}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0669.

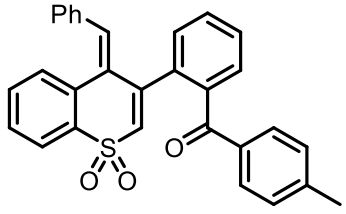
(*Z*)-(2-(4-benzylidene-7-bromo-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(phenyl)methanone (3s)



(*Z*/*E* = 4:1)

60 mg, 57%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (d, J = 12.0 Hz, 1H), 7.70 – 7.66 (d, J = 16.0 Hz, 4H), 7.52 – 7.45 (m, 3H), 7.34 – 7.29 (m, 3H), 7.22 – 7.18 (d, J = 16.0 Hz, 3H), 7.05 – 6.99 (d, J = 24.0 Hz, 3H), 6.75 – 6.69 (d, J = 24.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.4, 152.4, 139.6, 138.8, 135.1, 133.7, 133.5, 131.8, 131.6, 131.4, 131.0, 130.8, 130.7, 130.5, 130.3, 130.3, 129.8, 129.7, 129.4, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 127.6, 126.5, 125.9, 125.4. IR (film, ν, cm^{-1}) 1654, 1559, 1457, 1302, 1214, 1134, 1086, 929. 752, 699. HR-MS (ESI) m/z calcd for $C_{29}H_{13}BrO_3S$ $[M-H]^+$ 525.0160, found 525.0161.

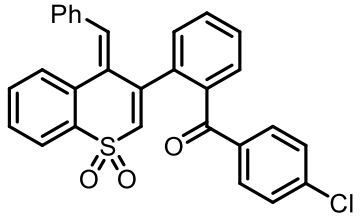
(*Z*)-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(p-tolyl)methanone (3t)



(*Z*/*E* > 19:1)

46 mg, 50%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.973 – 7.925 (m, 1H), 7.765 – 7.673 (m, 4H), 7.618 – 7.569 (d, *J* = 19.6 Hz, 2H), 7.408 (s, 1H), 7.262 – 7.164 (m, 3H), 7.156 – 7.104 (m, 1H), 7.073 – 7.010 (m, 4H), 6.921 – 6.874 (d, *J* = 18.8 Hz, 1H), 6.786 – 6.714 (d, *J* = 20.8 Hz, 2H), 2.264 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 154.1, 144.5, 139.7, 139.2, 137.0, 136.3, 134.8, 133.6, 133.4, 131.5, 131.4, 130.8, 130.4, 130.3, 130.1, 130.1, 129.8, 129.0, 128.9, 128.4, 128.2, 124.2, 122.7, 21.6. IR (film, ν, cm^{-1}) 1652, 1558, 1457, 1384, 1294, 1152, 1072, 933, 751, 669. HR-MS (ESI) m/z calcd for $C_{30}H_{22}NaO_3S$ $[M+Na]^+$ 485.1187, found 485.1169.

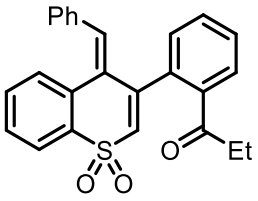
(*Z*)-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)phenyl)(4-chlorophenyl)methanone (3u)



(*Z*/*E* > 19:1)

41 mg, 43%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.949 – 7.901 (m, 1H), 7.728 – 7.646 (m, 4H), 7.602 – 7.552 (m, 2H), 7.421 – 7.375 (m, 1H), 7.226 – 7.071 (m, 6H), 7.046 – 6.988 (d, *J* = 23.2 Hz, 2H), 6.879 – 6.823 (d, *J* = 22.4 Hz, 1H), 6.730 (s, 1H), 6.662 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 153.8, 140.1, 139.5, 139.0, 137.0, 136.4, 134.7, 134.2, 133.4, 131.9, 131.5, 131.0, 130.5, 130.3, 130.2, 129.9, 129.8, 129.3, 128.6, 128.6, 124.6, 123.0. IR (film, ν, cm^{-1}) 1660, 1585, 1488, 1400, 1301, 1149, 1089, 932, 848, 749. HR-MS (ESI) m/z calcd for $C_{29}H_{18}ClO_3S$ $[M-H]^+$ 481.0665, found 481.0663.

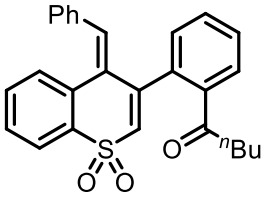
(*Z*)-1-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)phenyl)propan-1-one (3v)



(*Z*/*E* = 10:1)

40 mg, 49%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.119 – 8.075 (d, *J* = 17.6 Hz, 1H), 7.788 – 7.742 (m, 1H), 7.643 – 7.567 (m, 3H), 7.519 – 7.472 (m, 1H), 7.330 – 7.274 (d, *J* = 22.4 Hz, 2H), 7.227 – 7.175 (m, 2H), 7.163 – 7.120 (m, 2H), 7.031 – 6.968 (m, 1H), 6.684 – 6.532 (d, *J* = 60.8 Hz, 2H), 2.843 – 2.758 (m, 2H), 1.072 – 1.005 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ203.5, 154.6, 139.5, 137.6, 136.7, 135.9, 134.8, 134.7, 132.9, 131.9, 131.7, 130.9, 130.4, 130.1, 129.8, 129.2, 128.9, 128.8, 128.7, 123.5, 123.4, 34.7, 8.4. IR (film, ν, cm^{-1}) 1696, 1616, 1507, 1374, 1293, 1150, 1069, 927, 735, 694. HR-MS (ESI) m/z calcd for $C_{25}H_{19}O_3S$ $[M-H]^+$ 399.1055, found 399.1058.

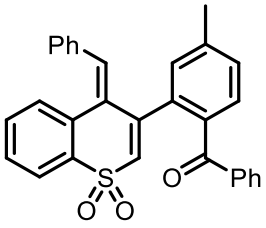
(*Z*)-1-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)phenyl)pentan-1-one (3w)



(*Z*/*E* = 4:1)

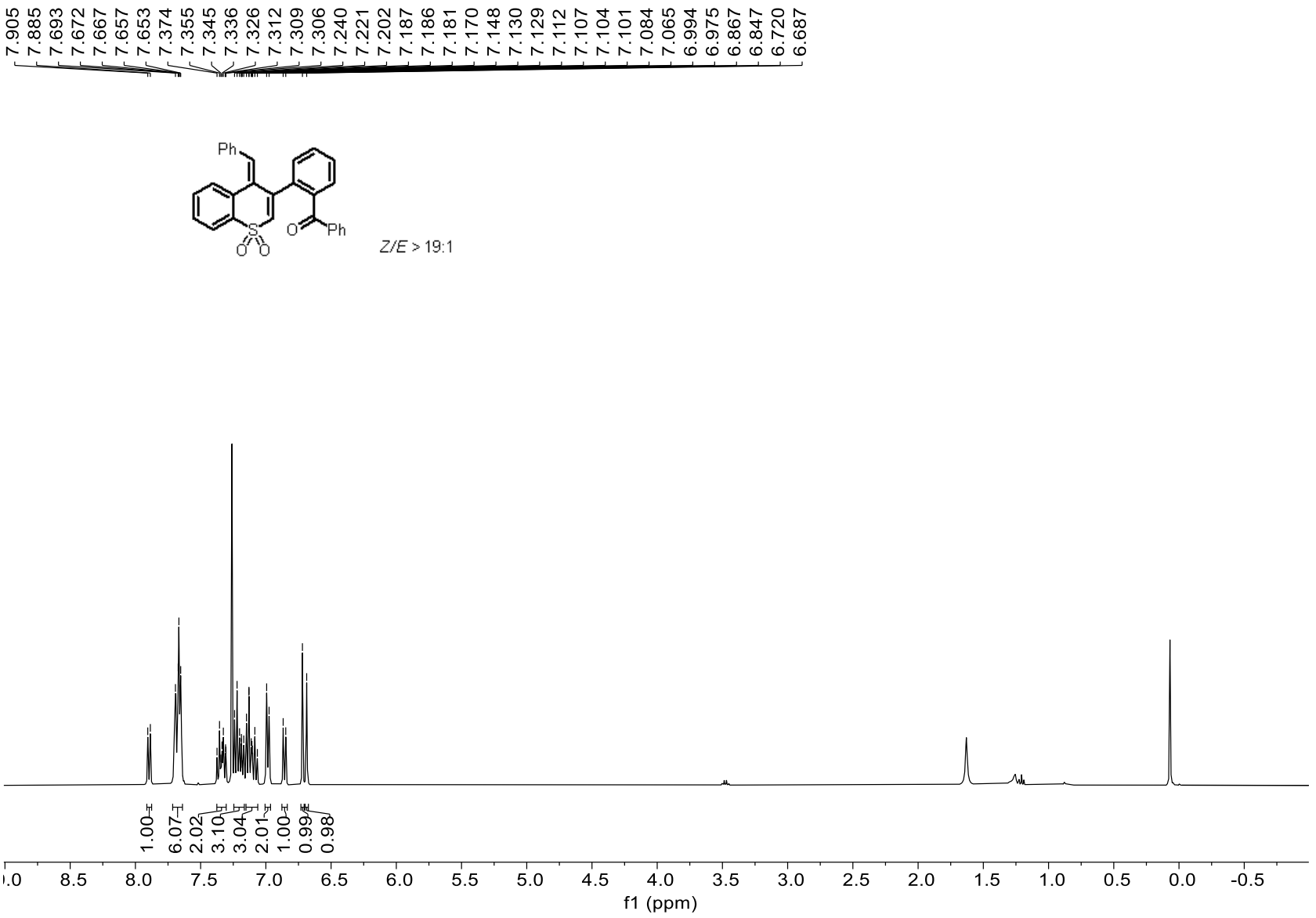
40 mg, 49%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.121 – 8.090 (d, *J* = 12.4 Hz, 1H), 7.807 – 7.753 (m, 1H), 7.627 – 7.584 (m, 2H), 7.528 – 7.479 (m, 1H), 7.295 – 7.269 (d, *J* = 10.4 Hz, 2H), 7.242 – 7.176 (m, 3H), 7.147 – 7.101 (d, *J* = 18.4 Hz, 2H), 7.029 – 6.954 (m, 1H), 6.674 – 6.517 (d, *J* = 62.8 Hz, 2H), 2.798 – 2.686 (m, 2H), 1.545 – 1.455 (m, 2H), 1.245 – 1.163 (m, 2H), 0.851 – 0.753 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ203.0, 154.7, 139.4, 137.6, 137.4, 136.8, 136.0, 134.9, 134.7, 132.8, 132.0, 131.7, 130.9, 130.4, 130.1, 129.8, 129.2, 129.1, 128.8, 128.6, 127.7, 123.4, 41.1, 26.5, 22.4, 14.0, 13.9. IR (film, ν, cm^{-1}) 1682, 1576, 1457, 1295, 1148, 1069, 928, 835, 746, 696. HR-MS (ESI) m/z calcd for $C_{27}H_{23}O_3S$ $[M-H]^+$ 427.1368, found 427.1369.

(*Z*)-(2-(4-benzylidene-1,1-dioxido-4H-thiochromen-3-yl)-4-methylphenyl)(phenyl)methanone (3x)

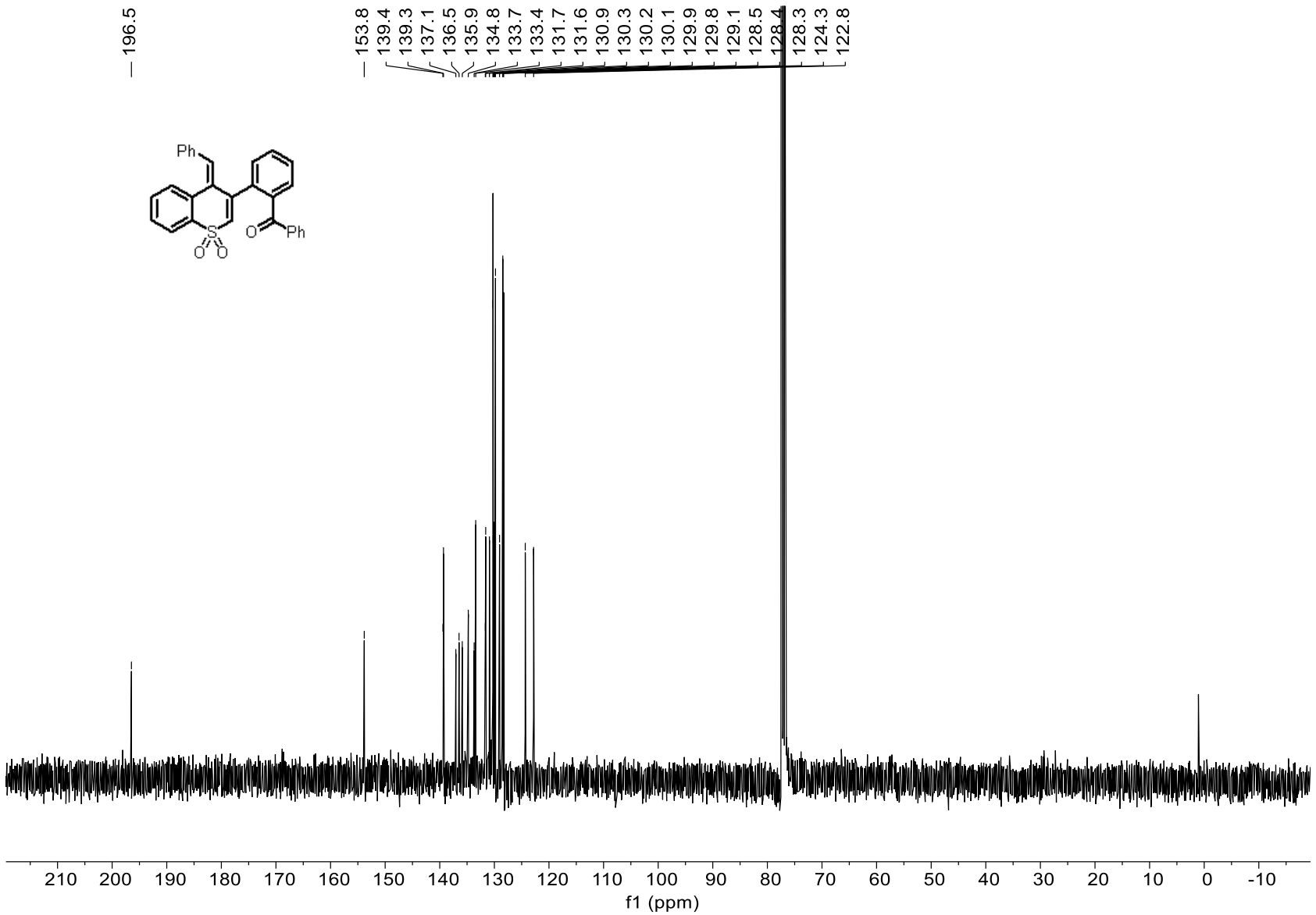


(*Z*/*E* > 19:1)

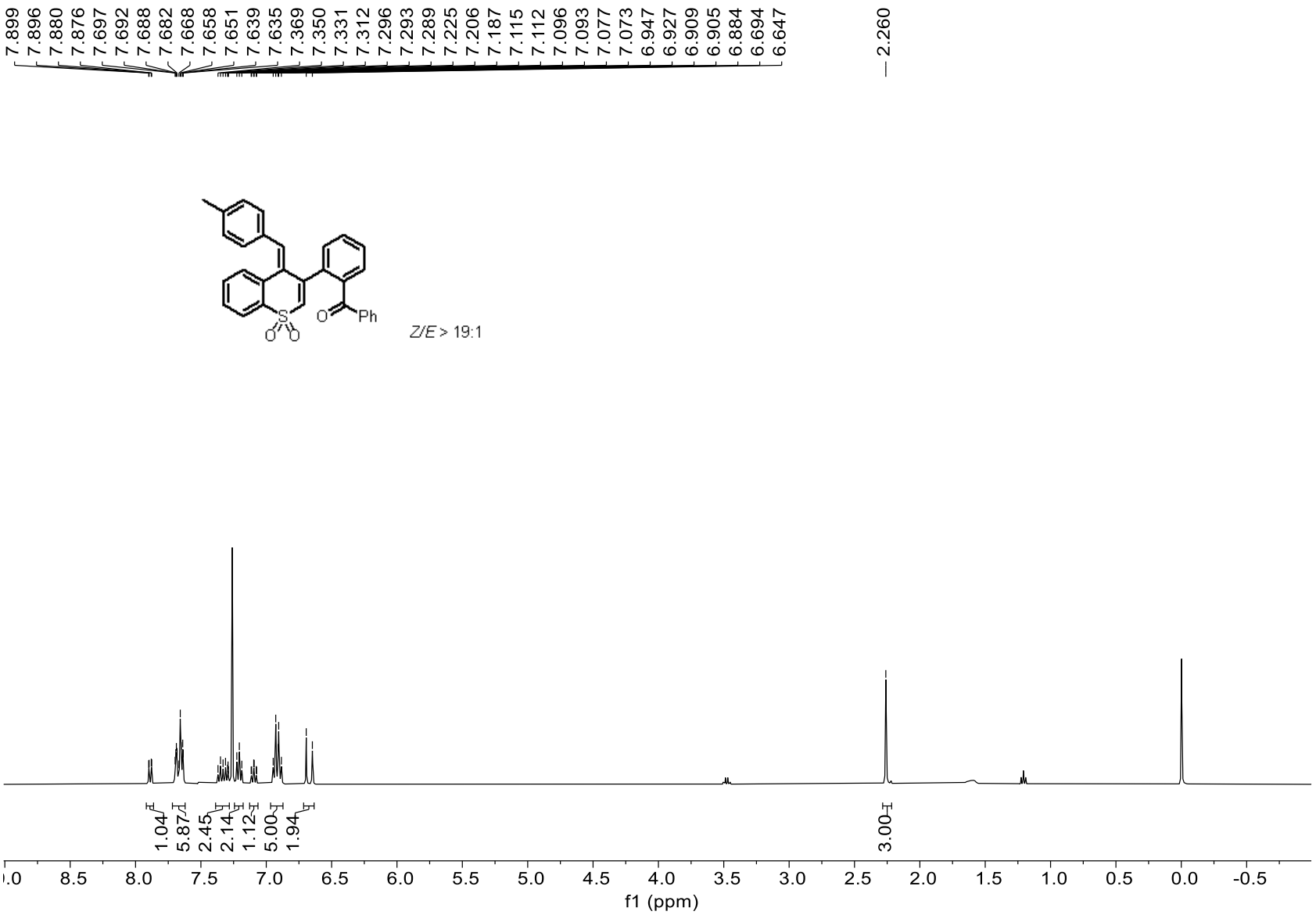
43 mg, 47%; white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.928 – 7.877 (d, *J* = 20.4 Hz, 1H), 7.682 – 7.631 (d, *J* = 20.4 Hz, 2H), 7.597 – 7.556 (d, *J* = 16.4 Hz, 1H), 7.508 (s, 1H), 7.469 – 7.420 (d, *J* = 19.6 Hz, 1H), 7.376 – 7.291 (m, 2H), 7.235 – 7.192 (d, *J* = 17.2 Hz, 2H), 7.168 – 7.119 (d, *J* = 19.6 Hz, 2H), 7.076 (s, 1H), 7.011 – 6.955 (d, *J* = 22.4 Hz, 2H), 6.864 (s, 1H), 6.729 – 6.668 (d, *J* = 24.4 Hz, 2H), 2.532 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 154.2, 142.3, 139.1, 137.1, 136.7, 136.3, 134.9, 133.8, 133.3, 131.9, 131.8, 130.8, 130.6, 130.5, 130.3, 130.0, 129.8, 129.0, 128.5, 128.4, 128.3, 127.3, 124.0, 122.8, 21.5. IR (film, ν, cm^{-1}) 1653, 1601, 1446, 1302, 1150, 1070, 933, 790, 694, 668. HR-MS (ESI) m/z calcd for $C_{30}H_{21}O_3S$ $[M-H]^+$ 461.1121, found 461.1122.



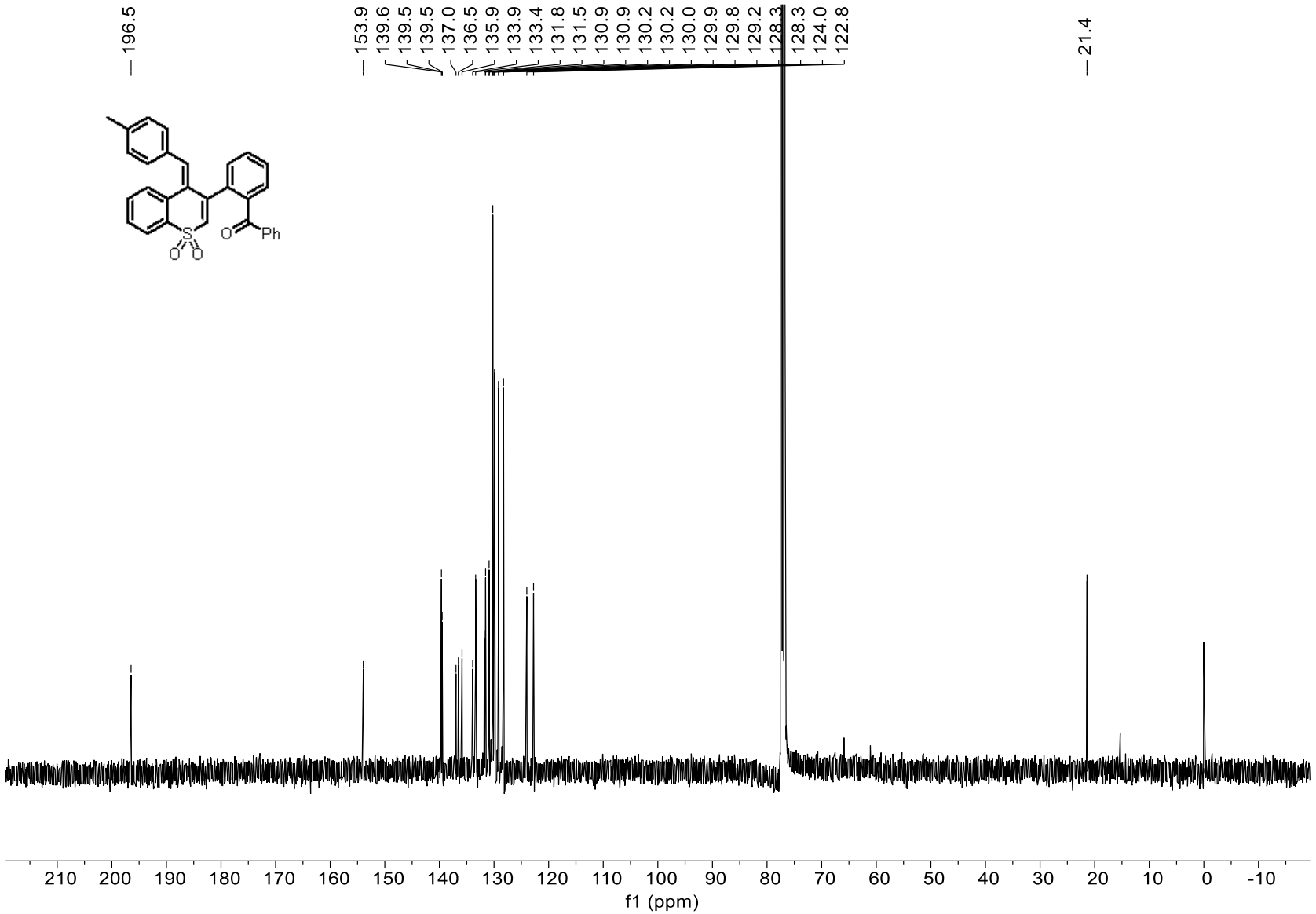
^{1}H NMR Spectrum of Compound **3a**



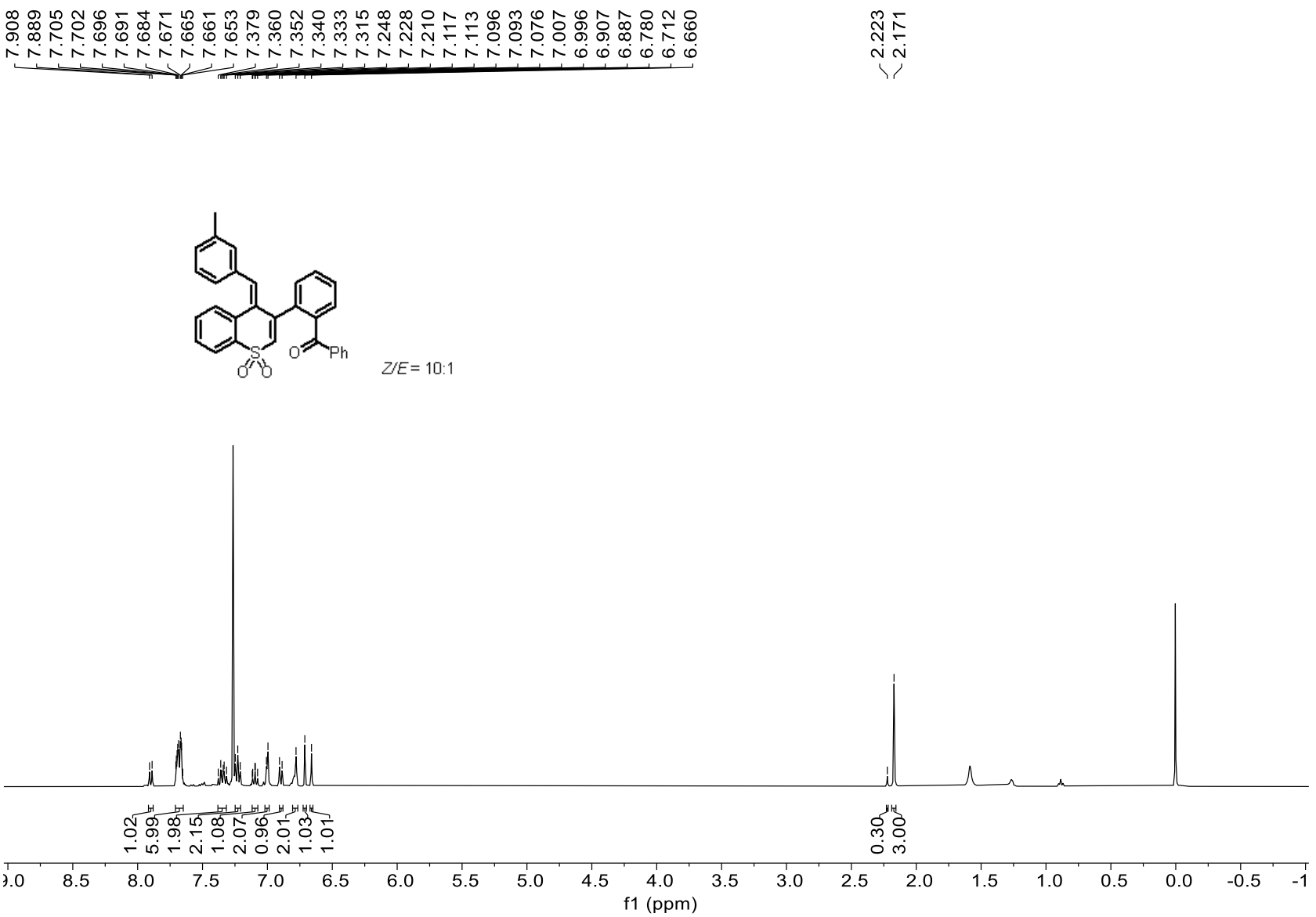
^{13}C NMR Spectrum of Compound **3a**



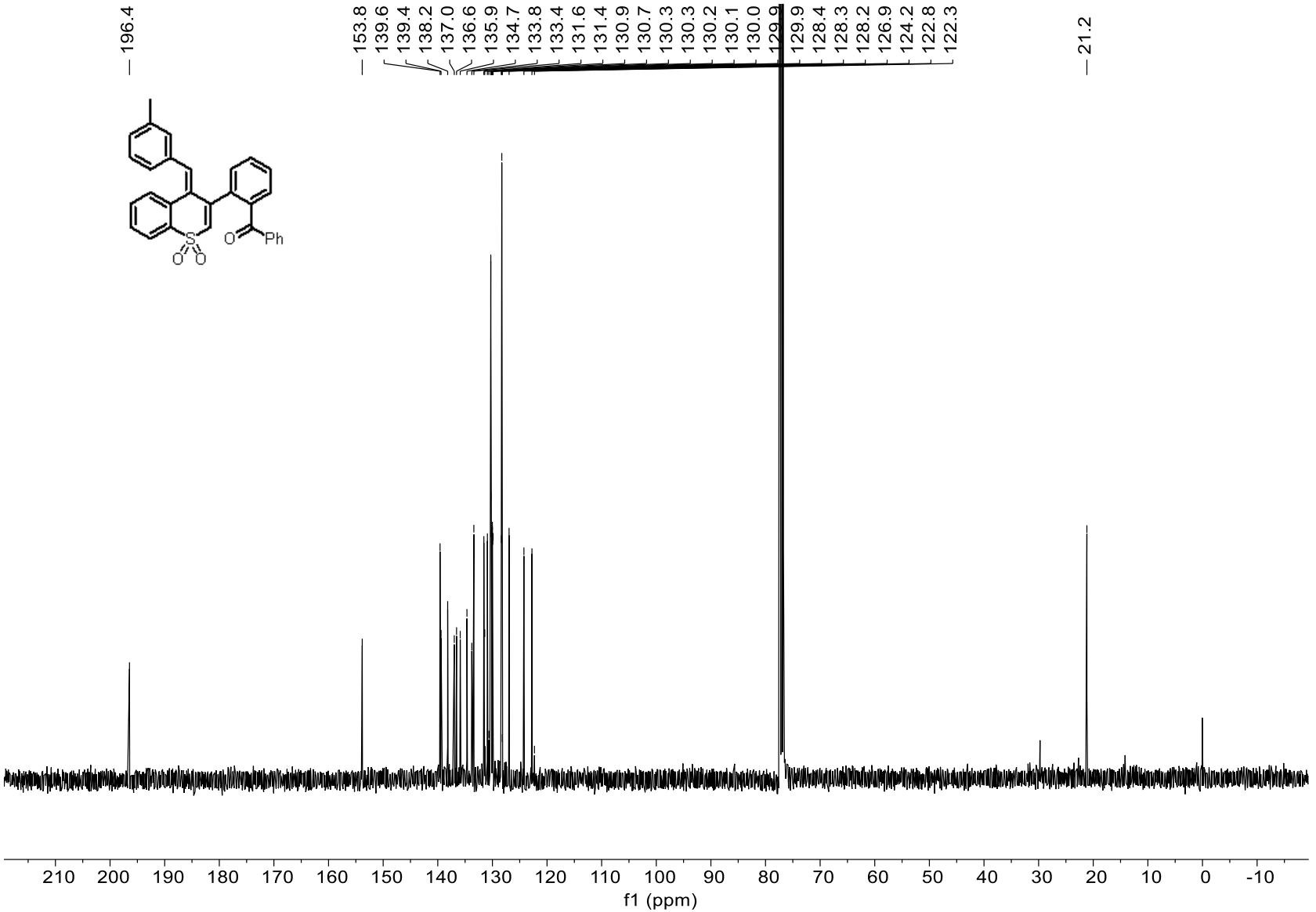
^{1}H NMR Spectrum of Compound **3b**



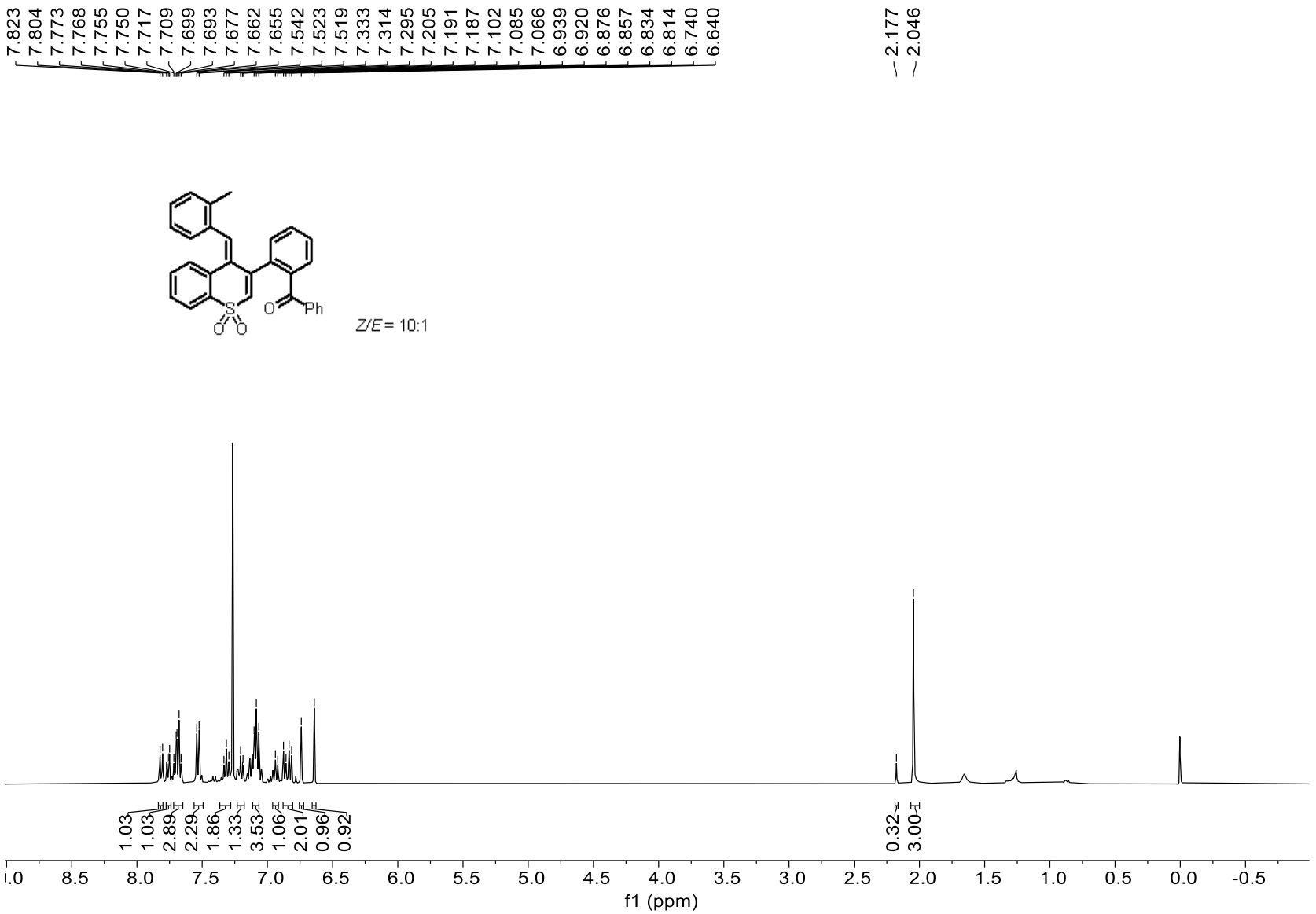
^{13}C NMR Spectrum of Compound **3b**



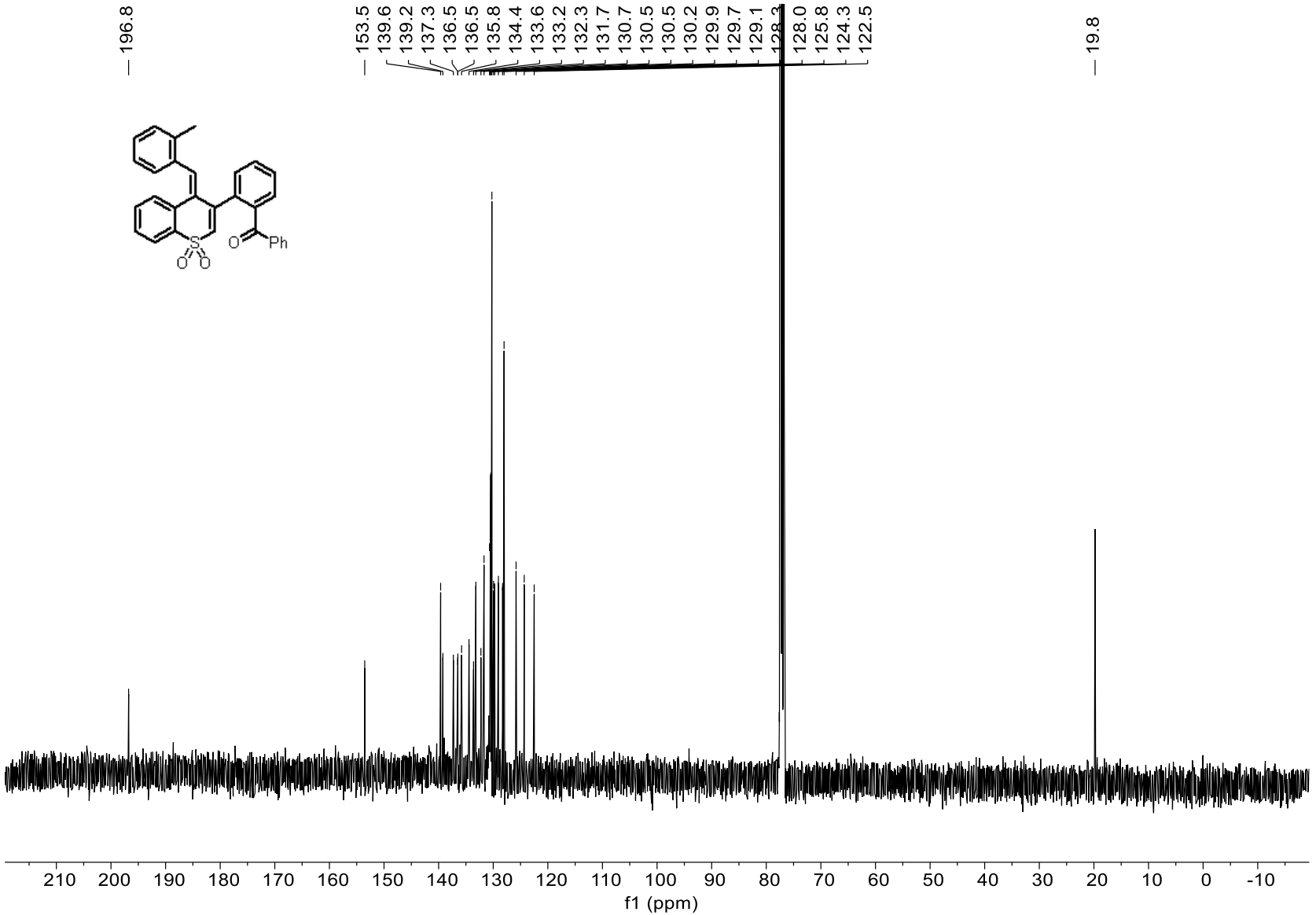
^{1}H NMR Spectrum of Compound **3c**



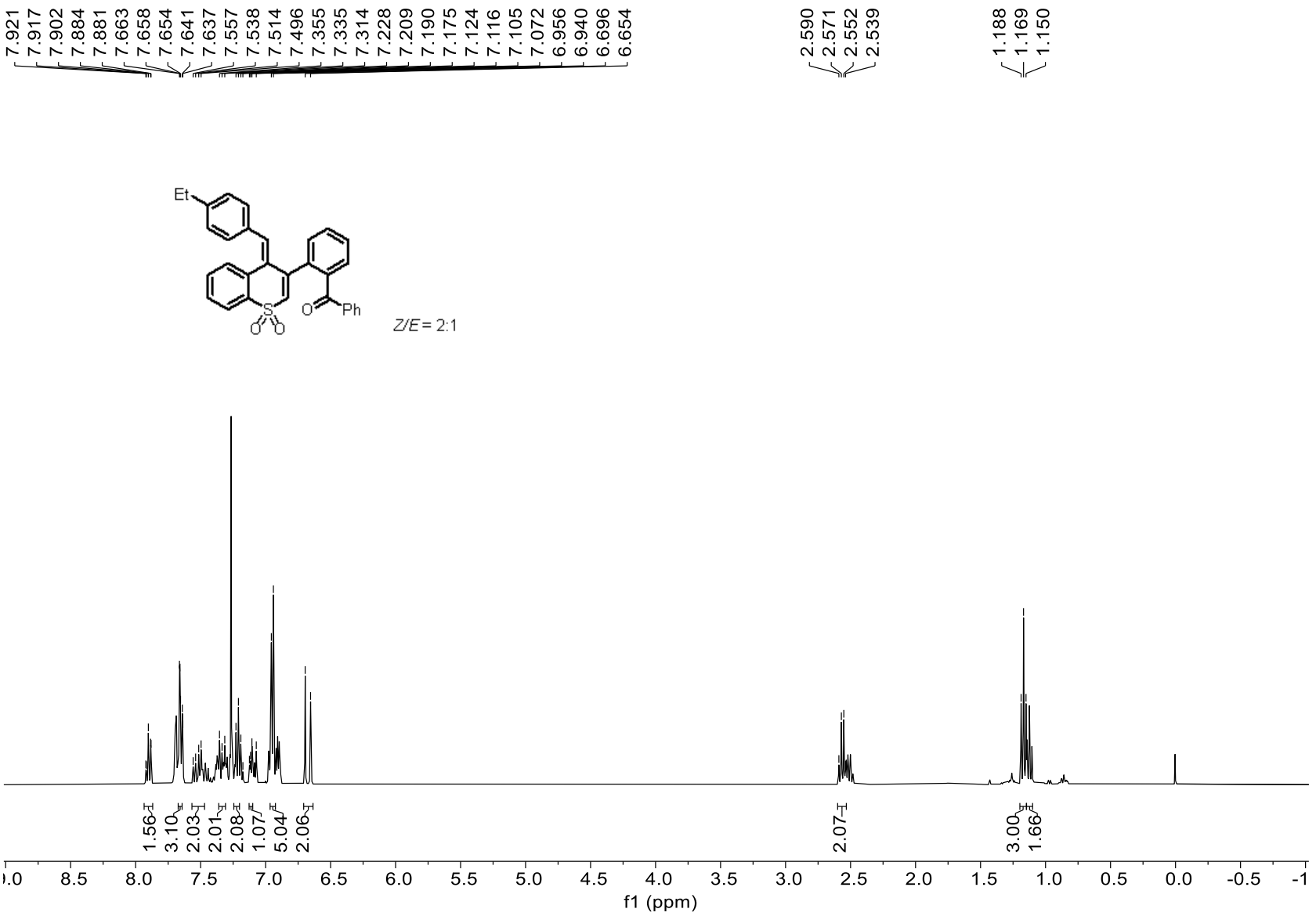
^{13}C NMR Spectrum of Compound **3c**



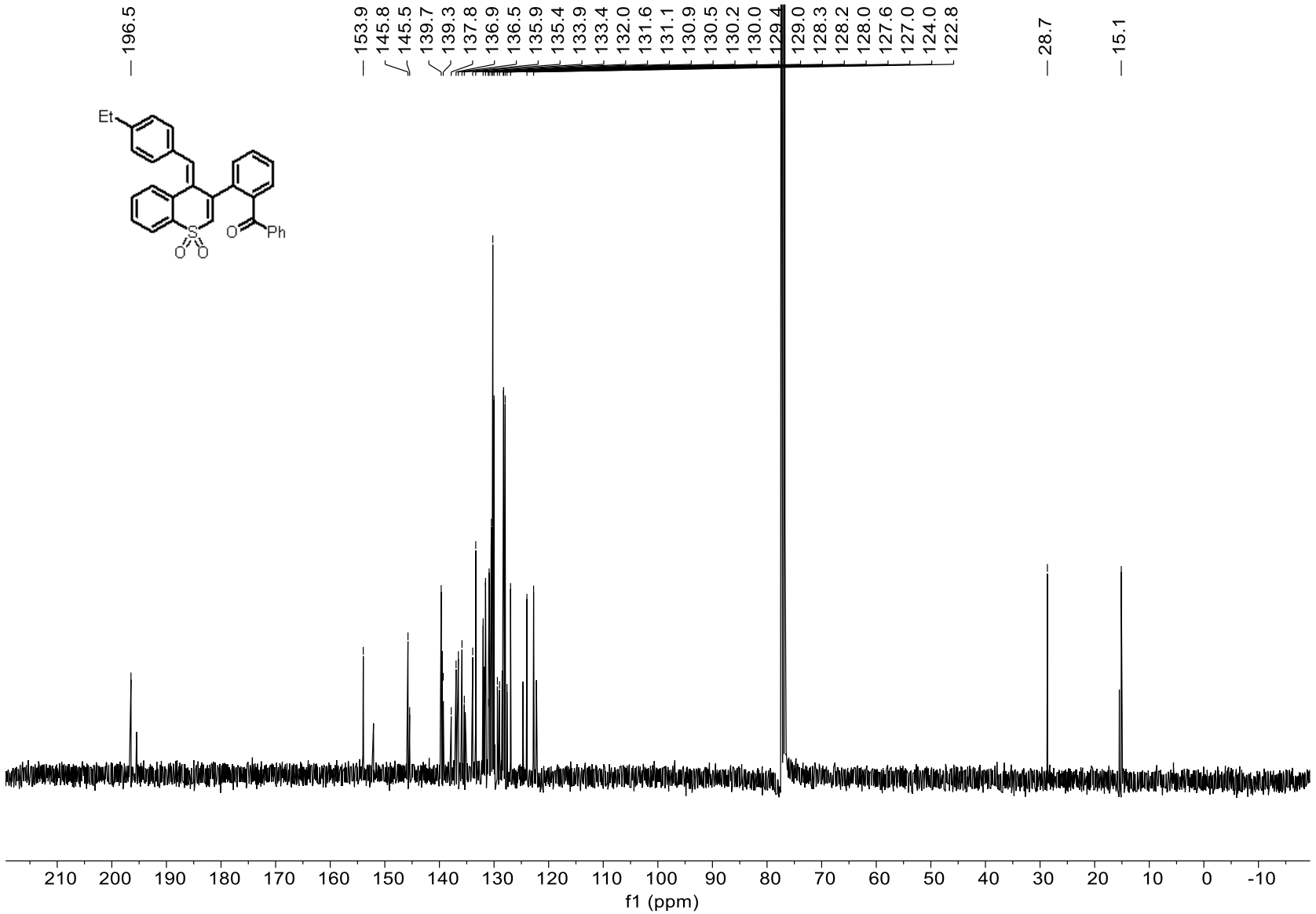
^{1}H NMR Spectrum of Compound **3d**



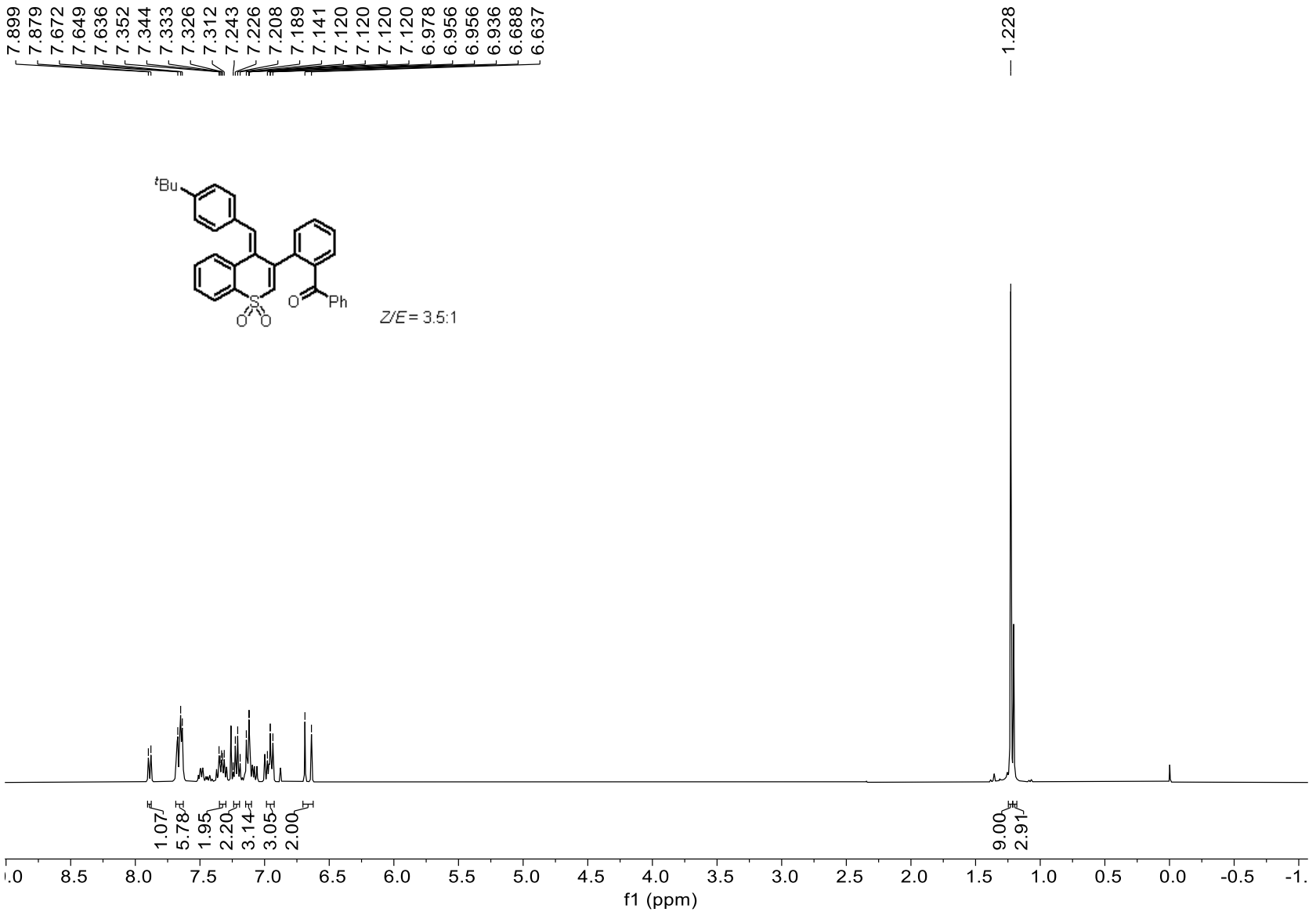
^{13}C NMR Spectrum of Compound **3d**



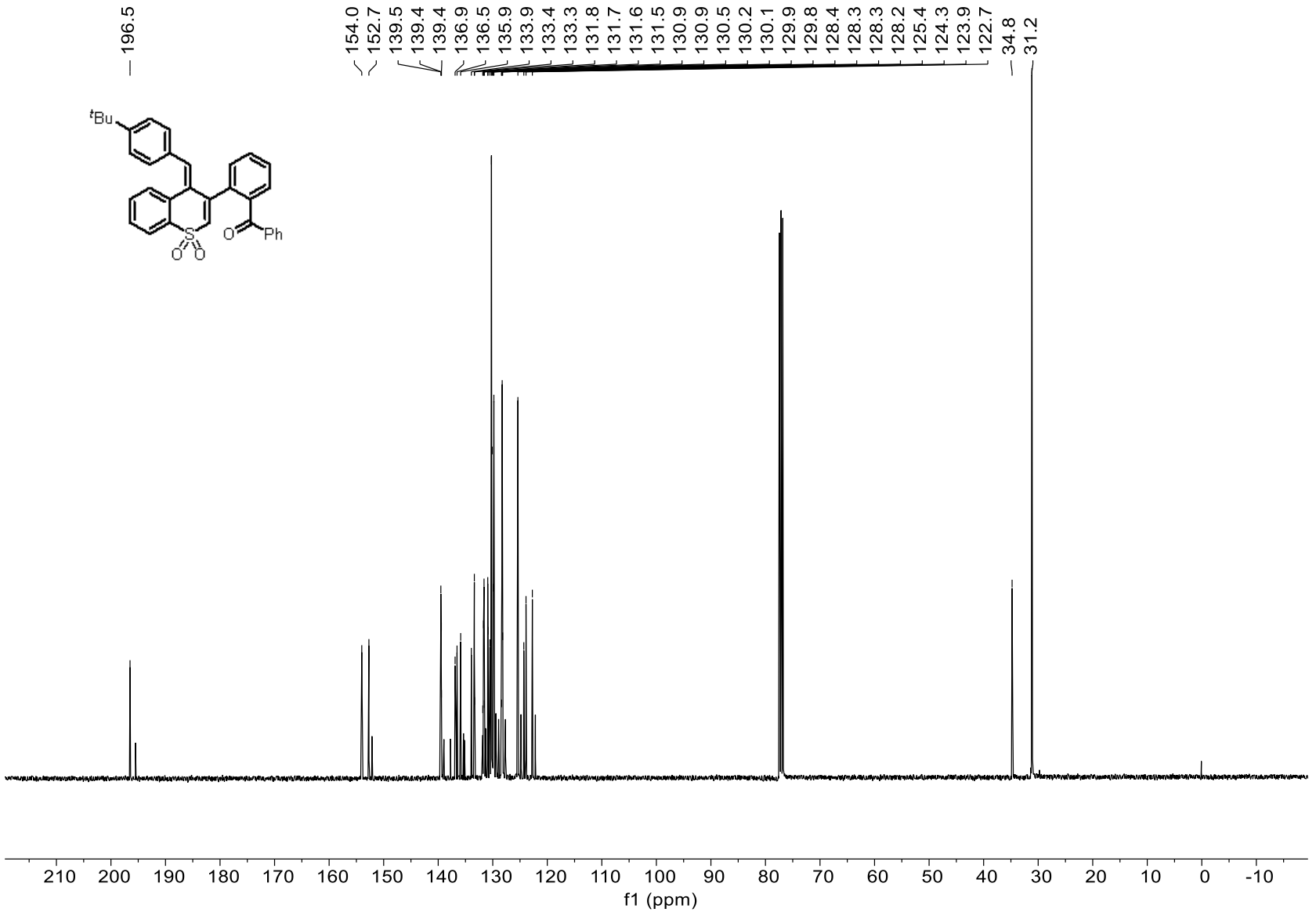
^{1}H NMR Spectrum of Compound **3e**



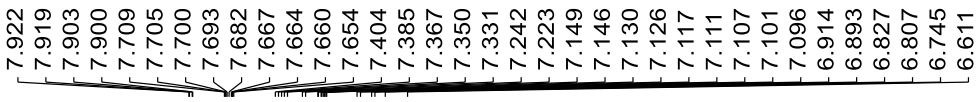
^{13}C NMR Spectrum of Compound **3e**

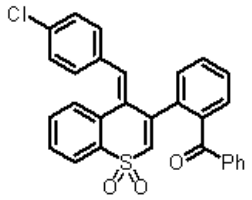


^{1}H NMR Spectrum of Compound **3f**

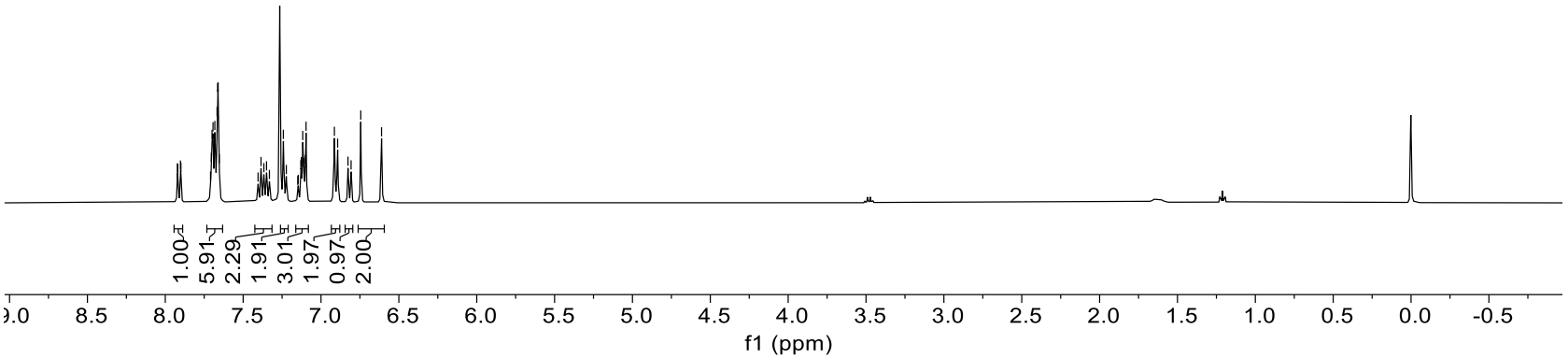


^{13}C NMR Spectrum of Compound **3f**

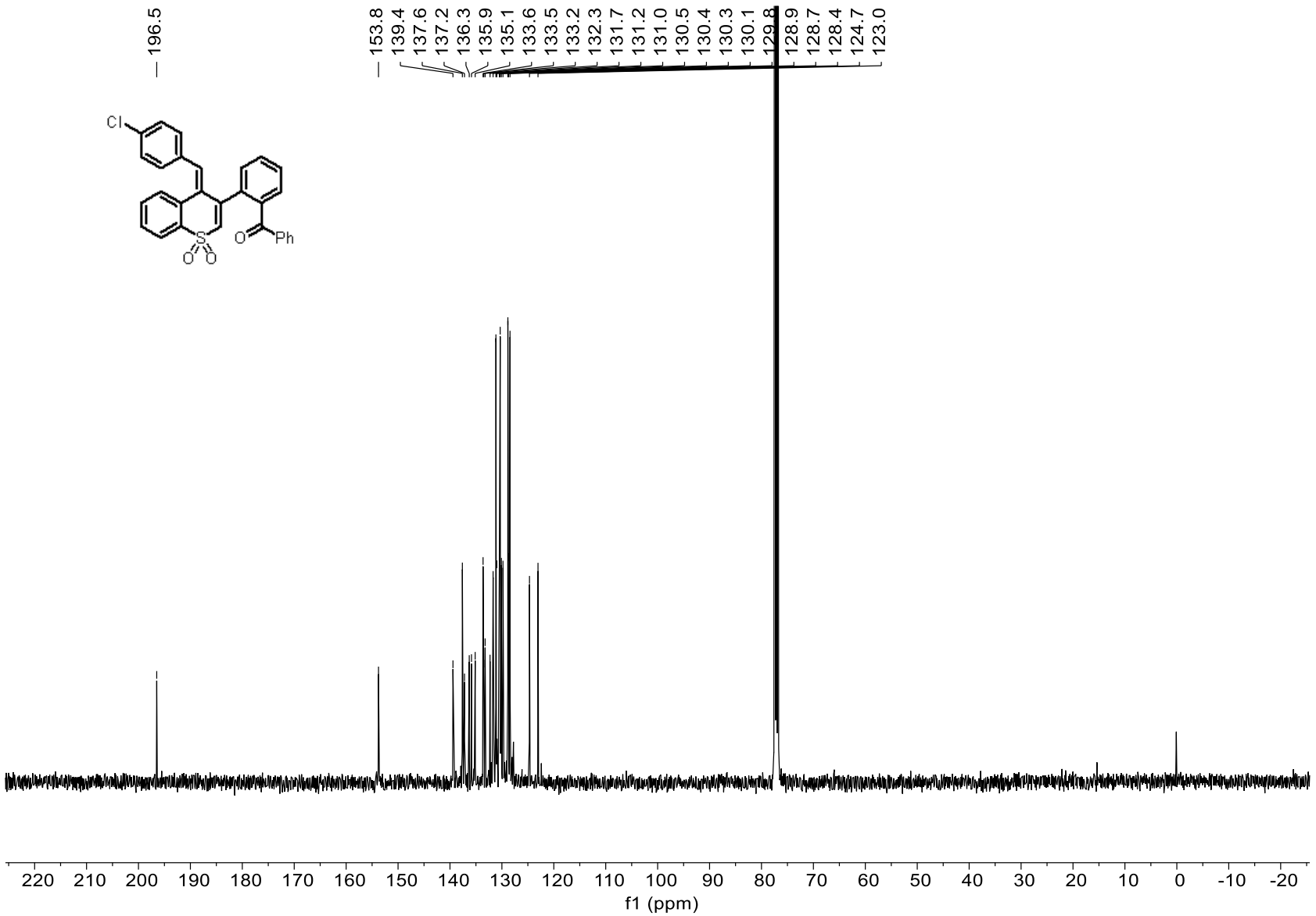




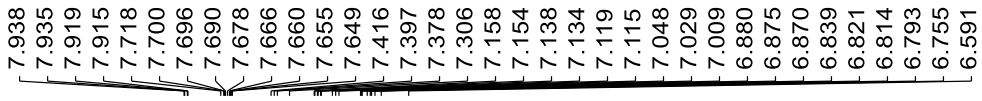
Z/*E* > 19:1

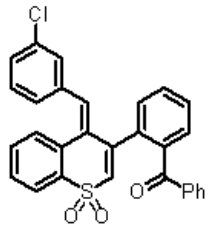


^{1}H NMR Spectrum of Compound **3g**

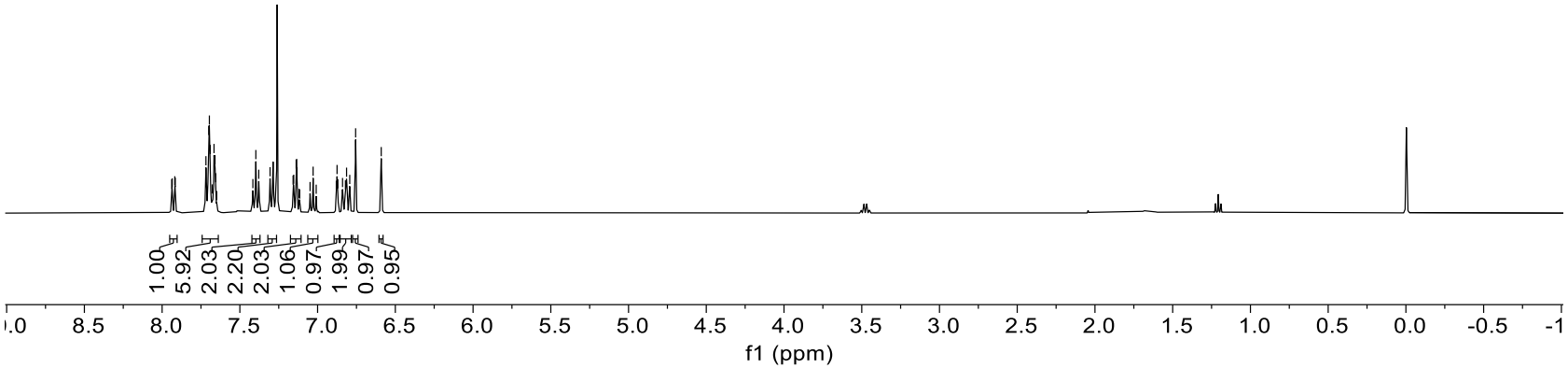


^{13}C NMR Spectrum of Compound **3g**

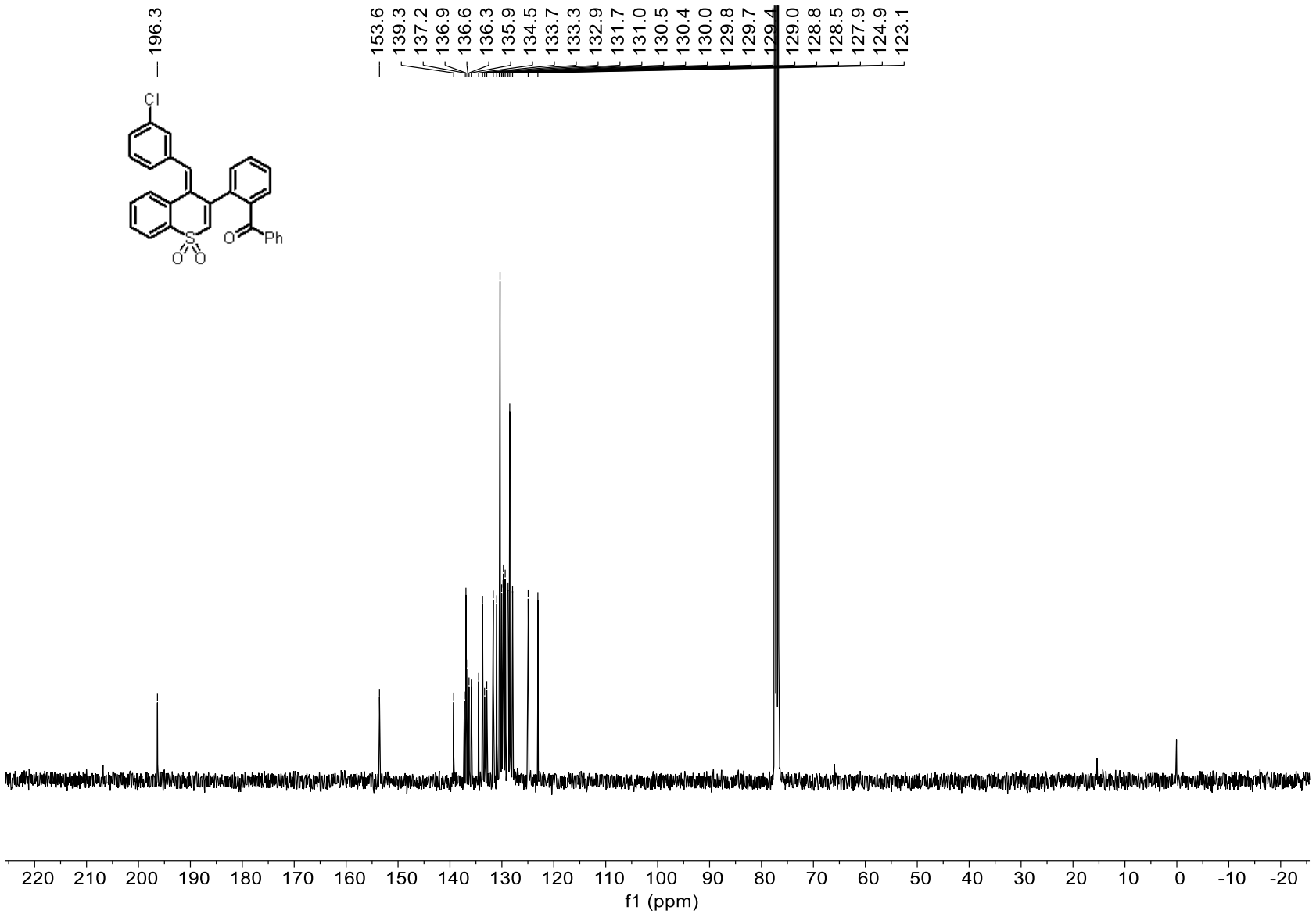




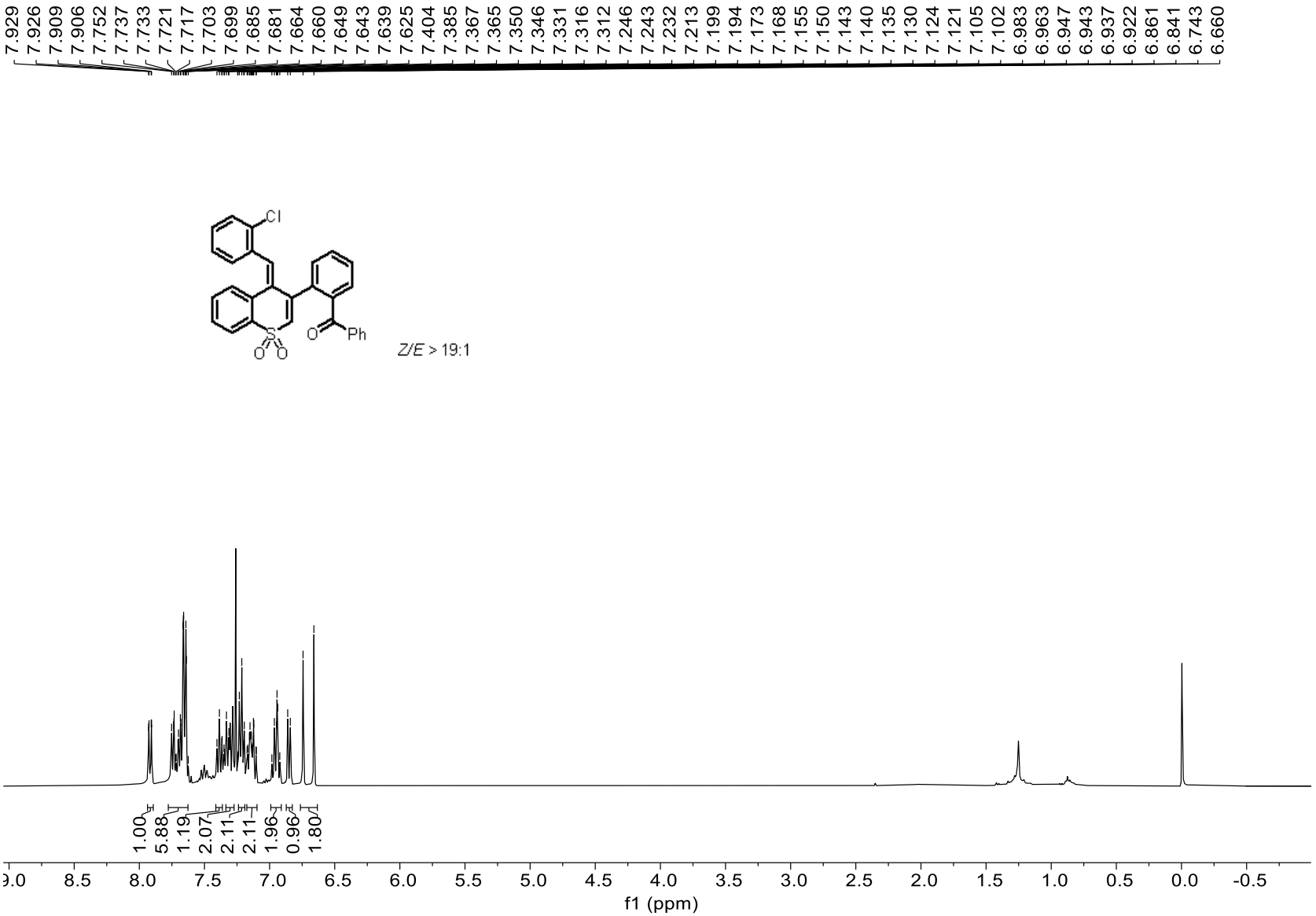
Z/*E* > 19:1



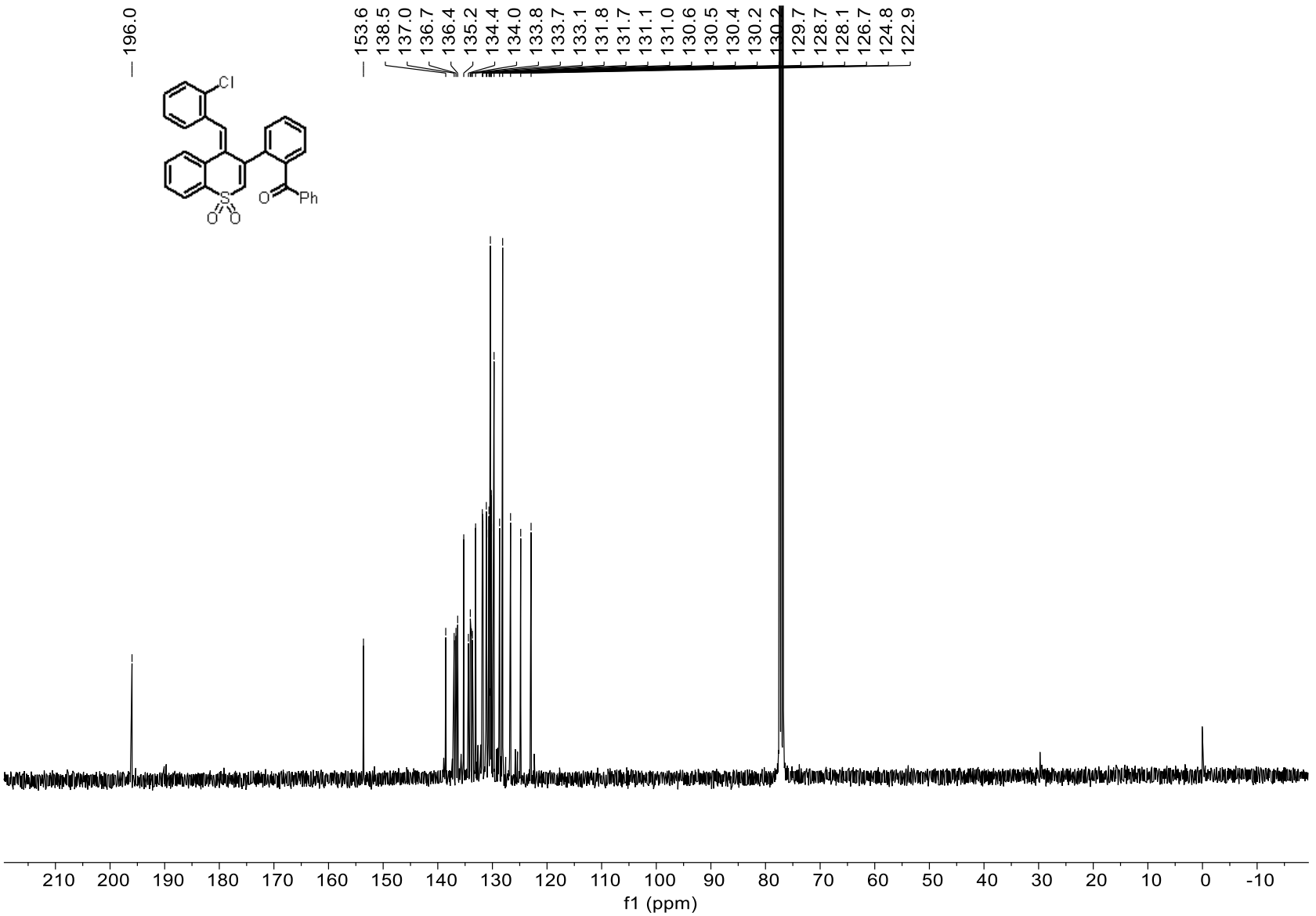
^{1}H NMR Spectrum of Compound **3h**



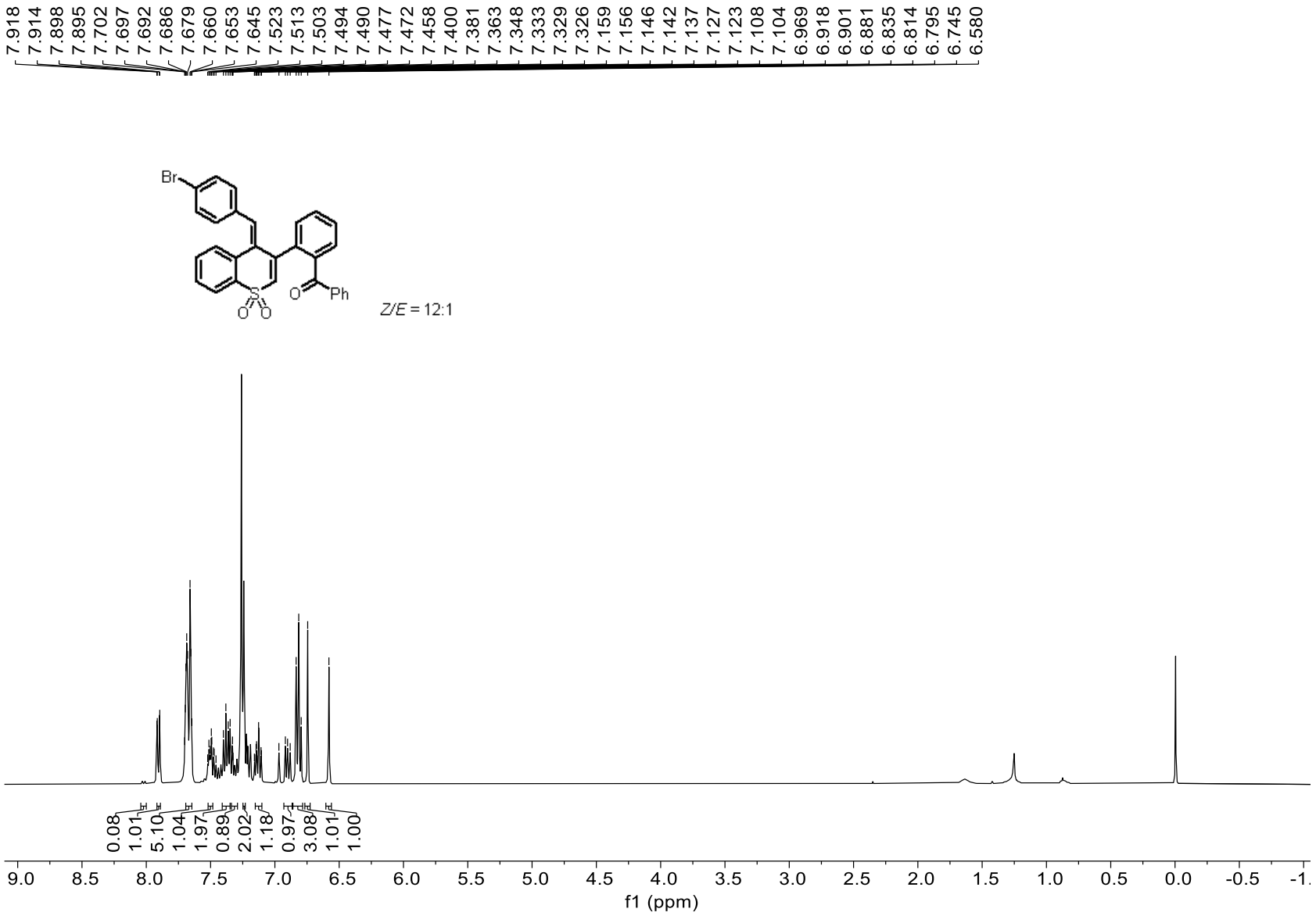
^{13}C NMR Spectrum of Compound **3h**



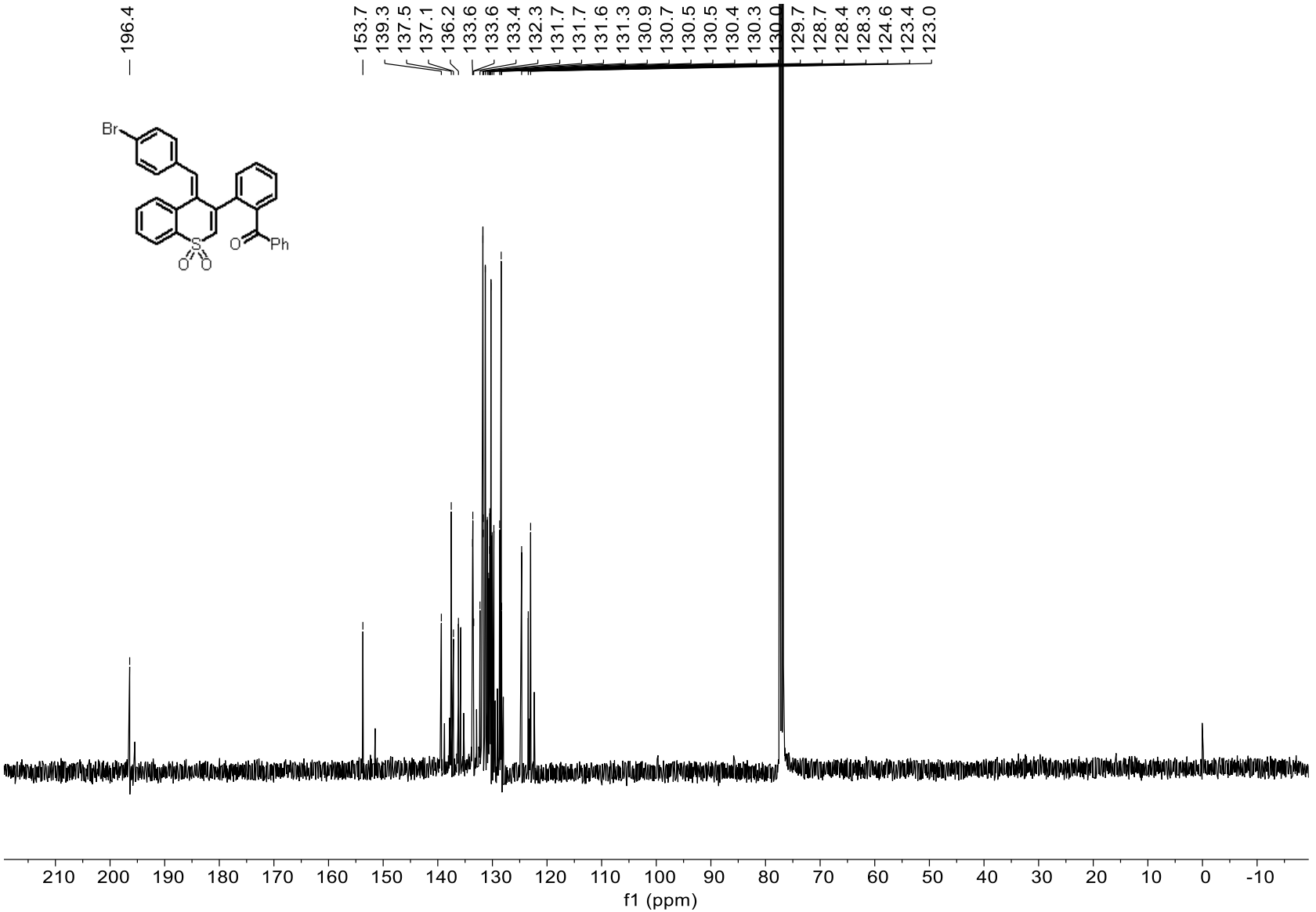
^{1}H NMR Spectrum of Compound **3i**



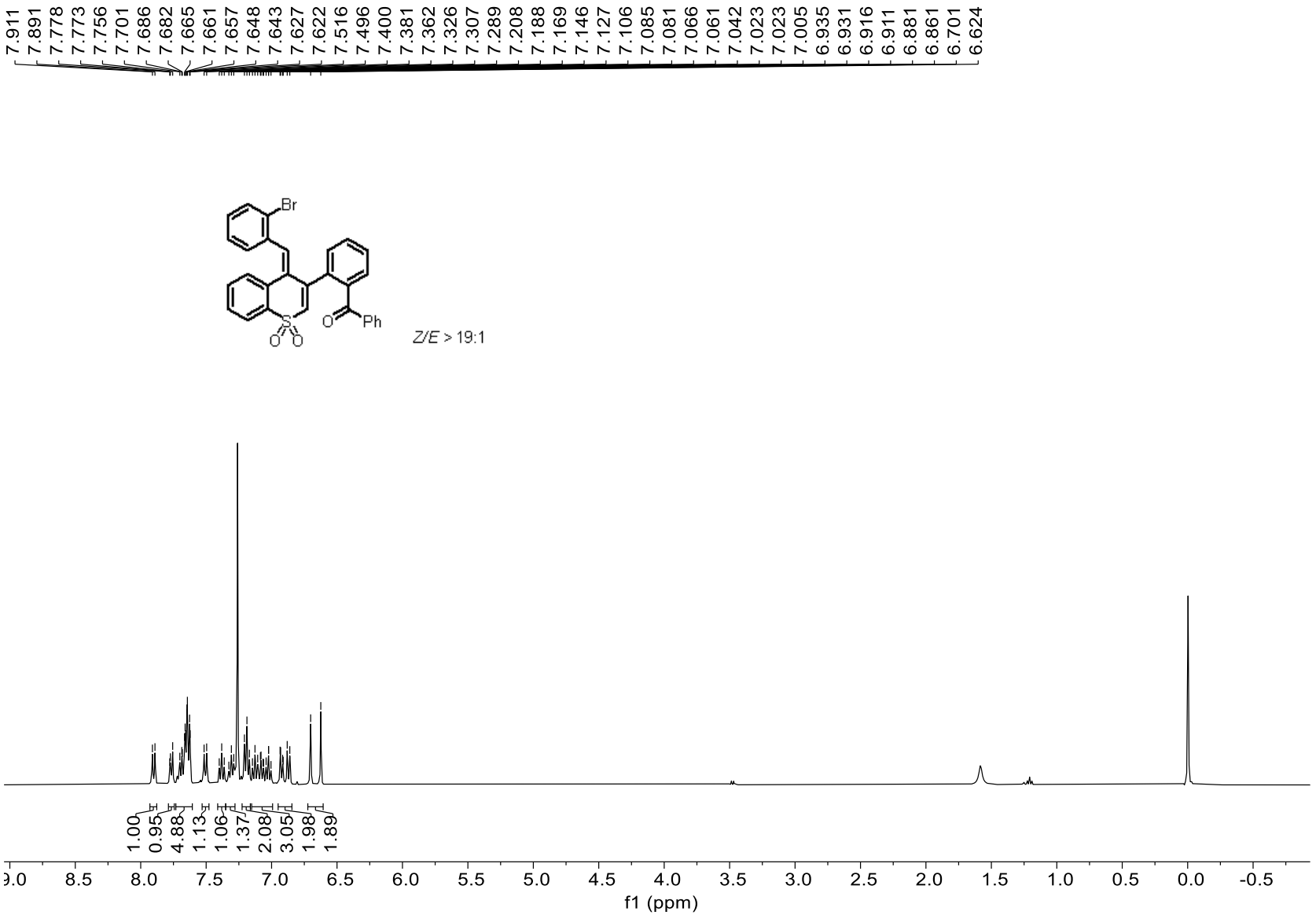
^{13}C NMR Spectrum of Compound **3i**



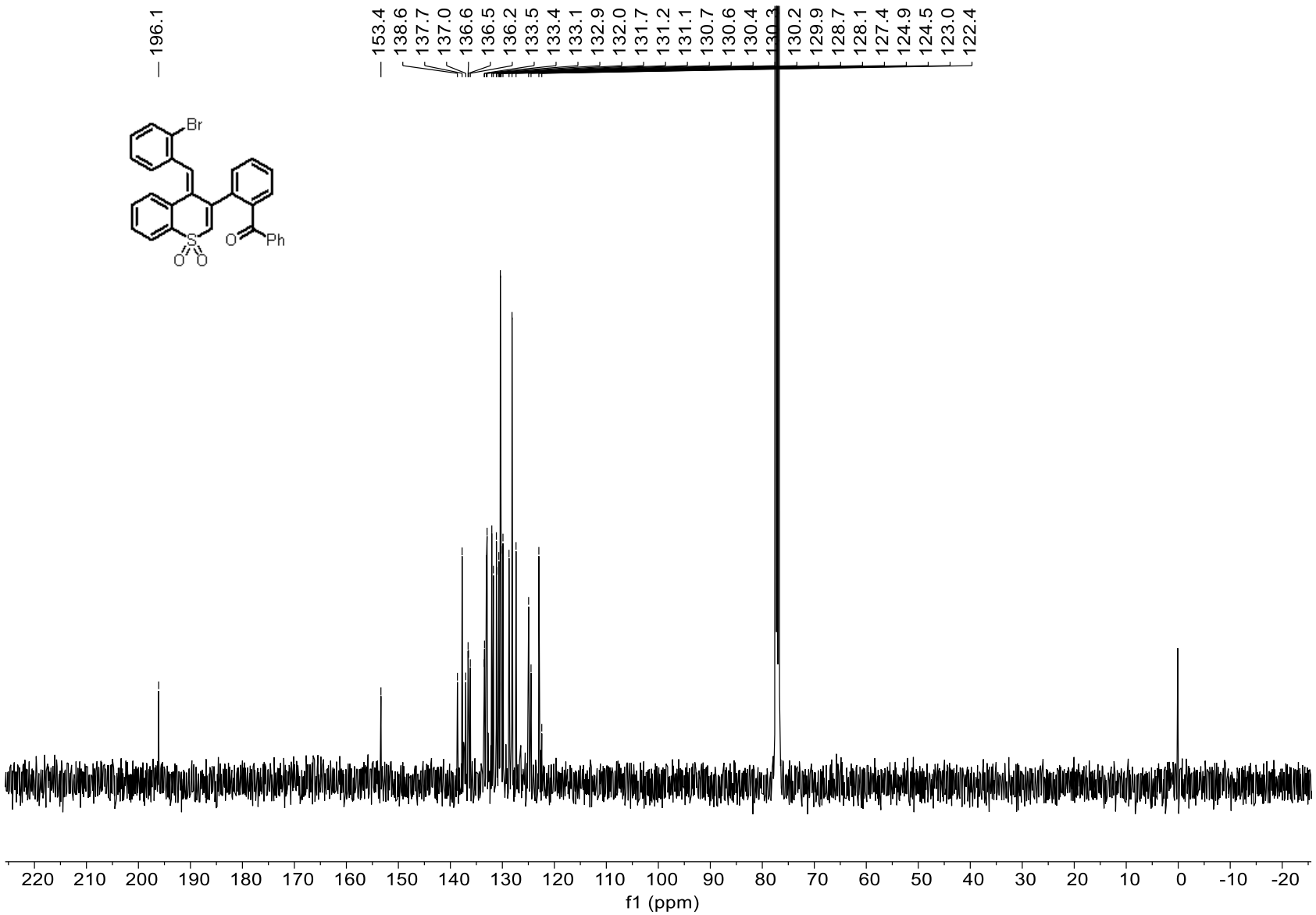
^{1}H NMR Spectrum of Compound **3j**



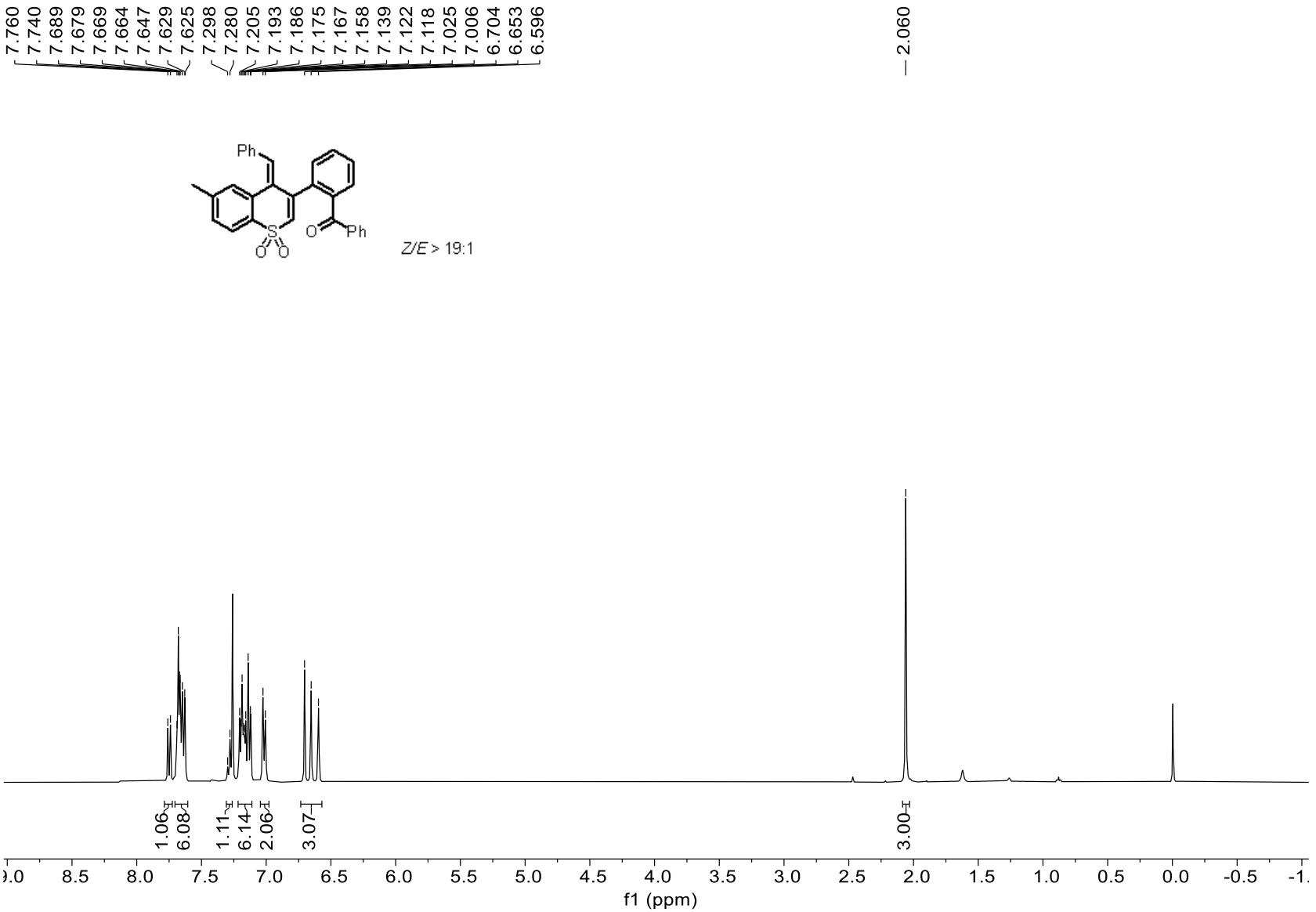
^{13}C NMR Spectrum of Compound **3j**



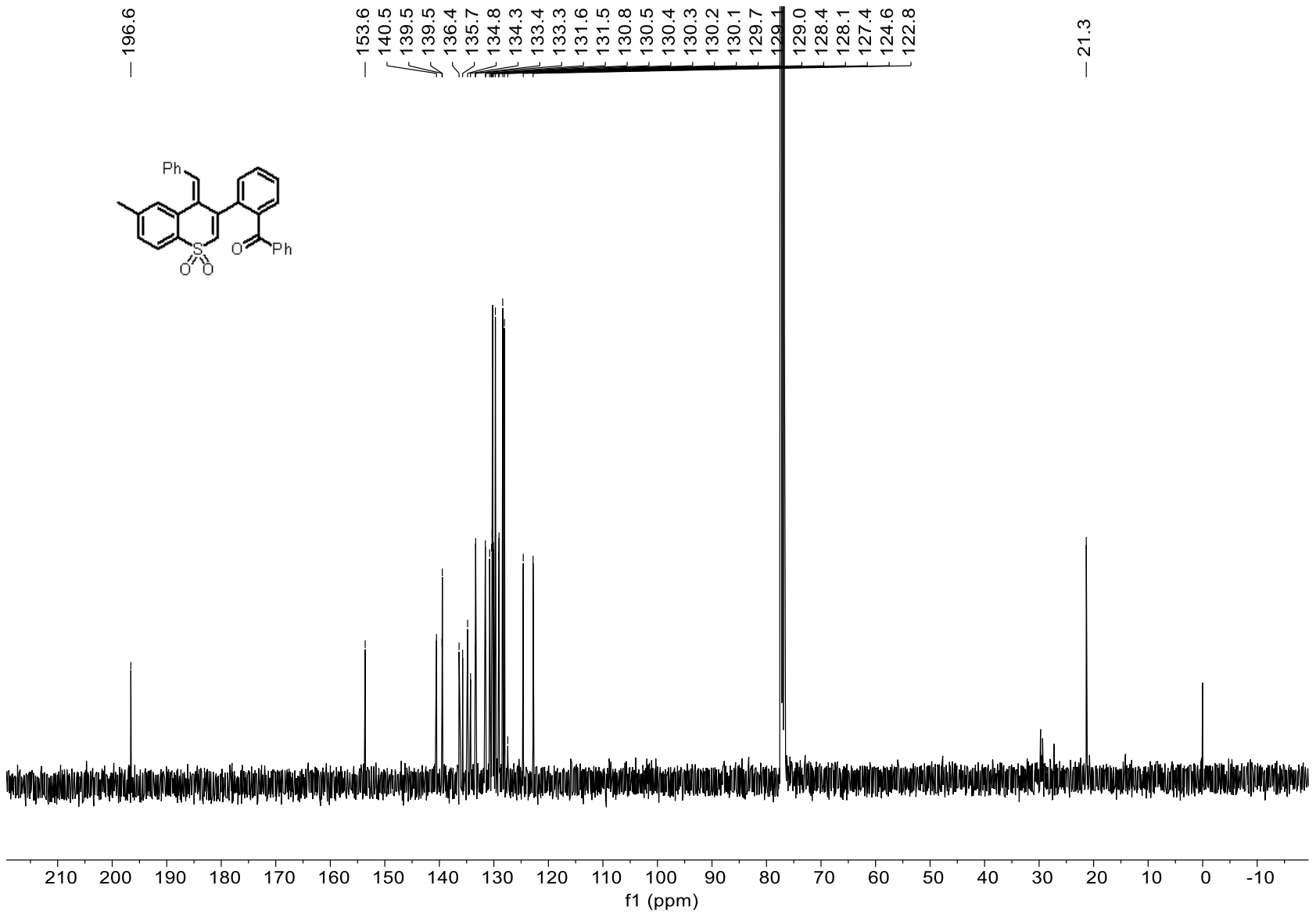
^{1}H NMR Spectrum of Compound **3k**



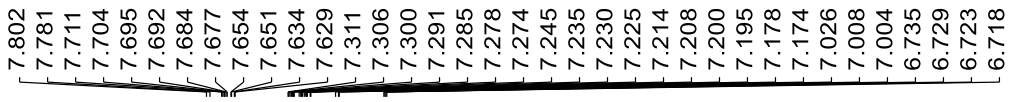
^{13}C NMR Spectrum of Compound **3k**

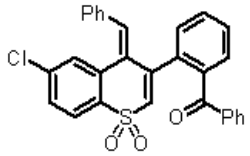


^{1}H NMR Spectrum of Compound **3n**

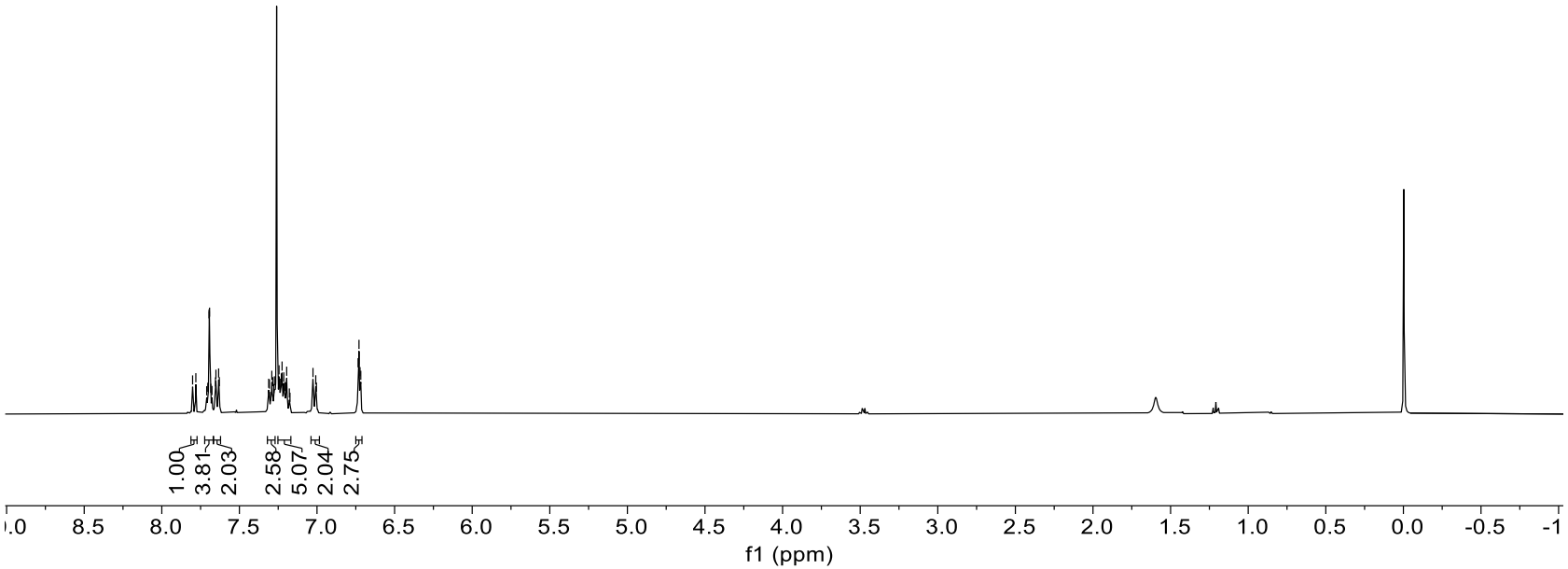


^{13}C NMR Spectrum of Compound **3n**

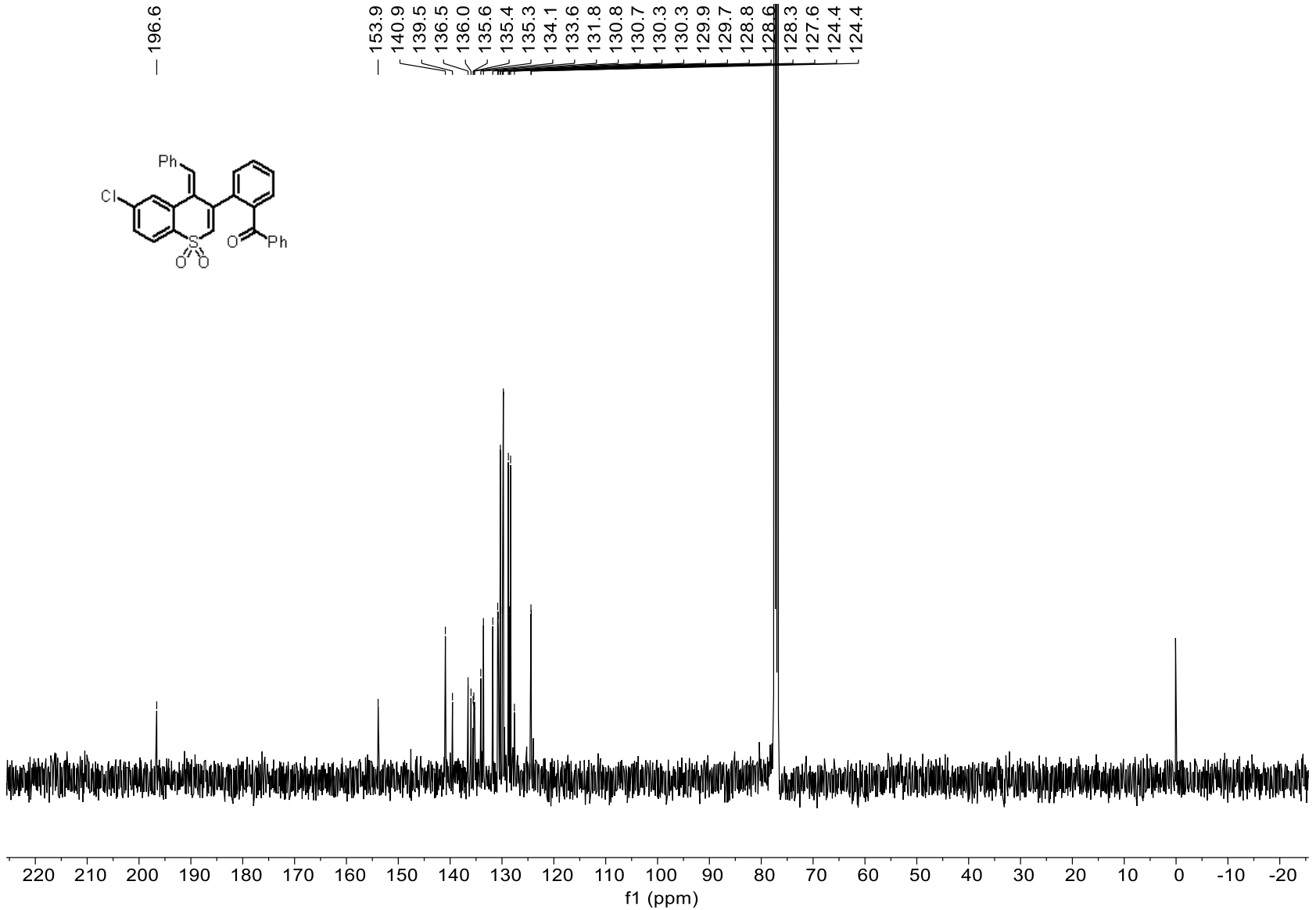




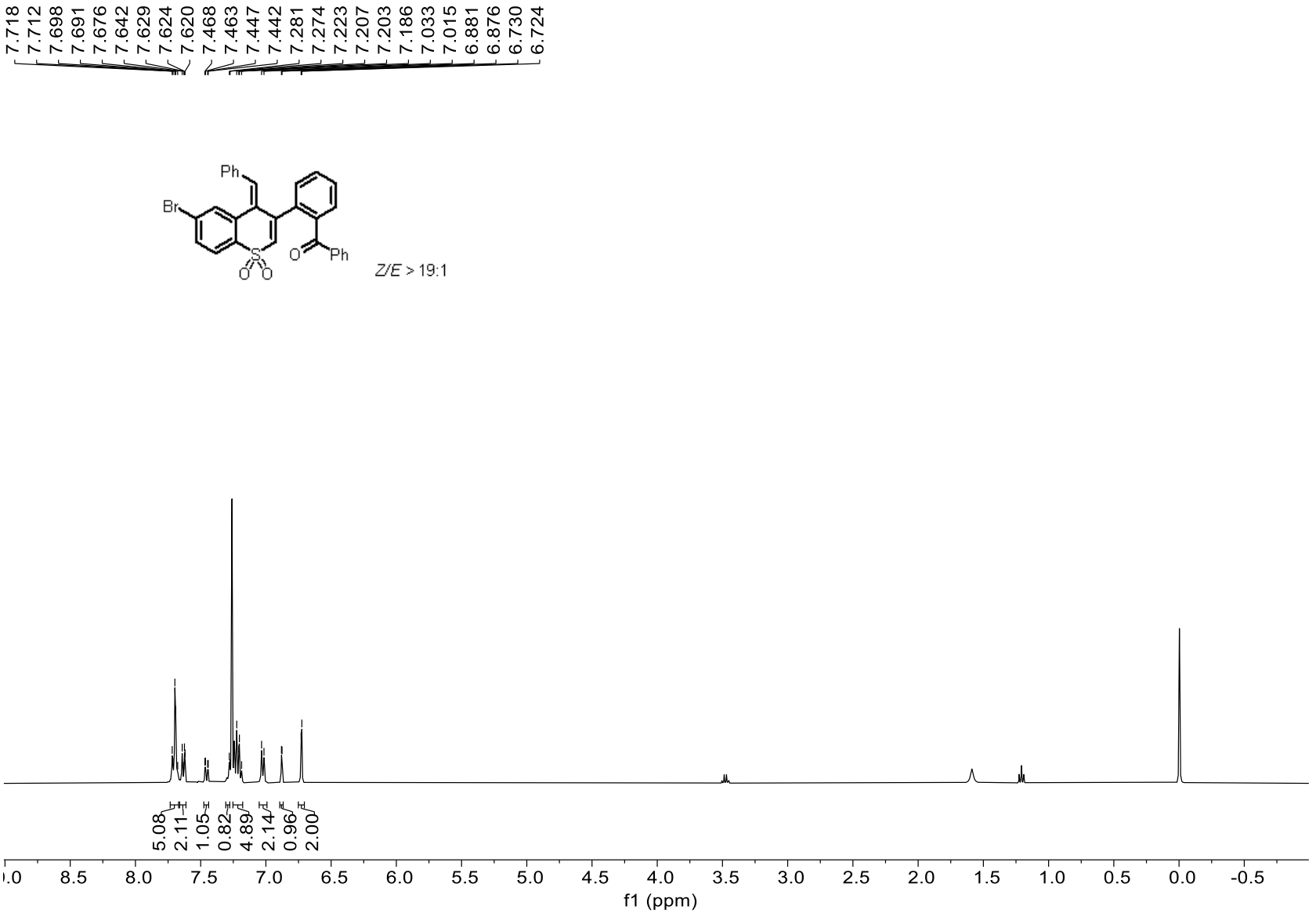
Z/*E* > 19:1



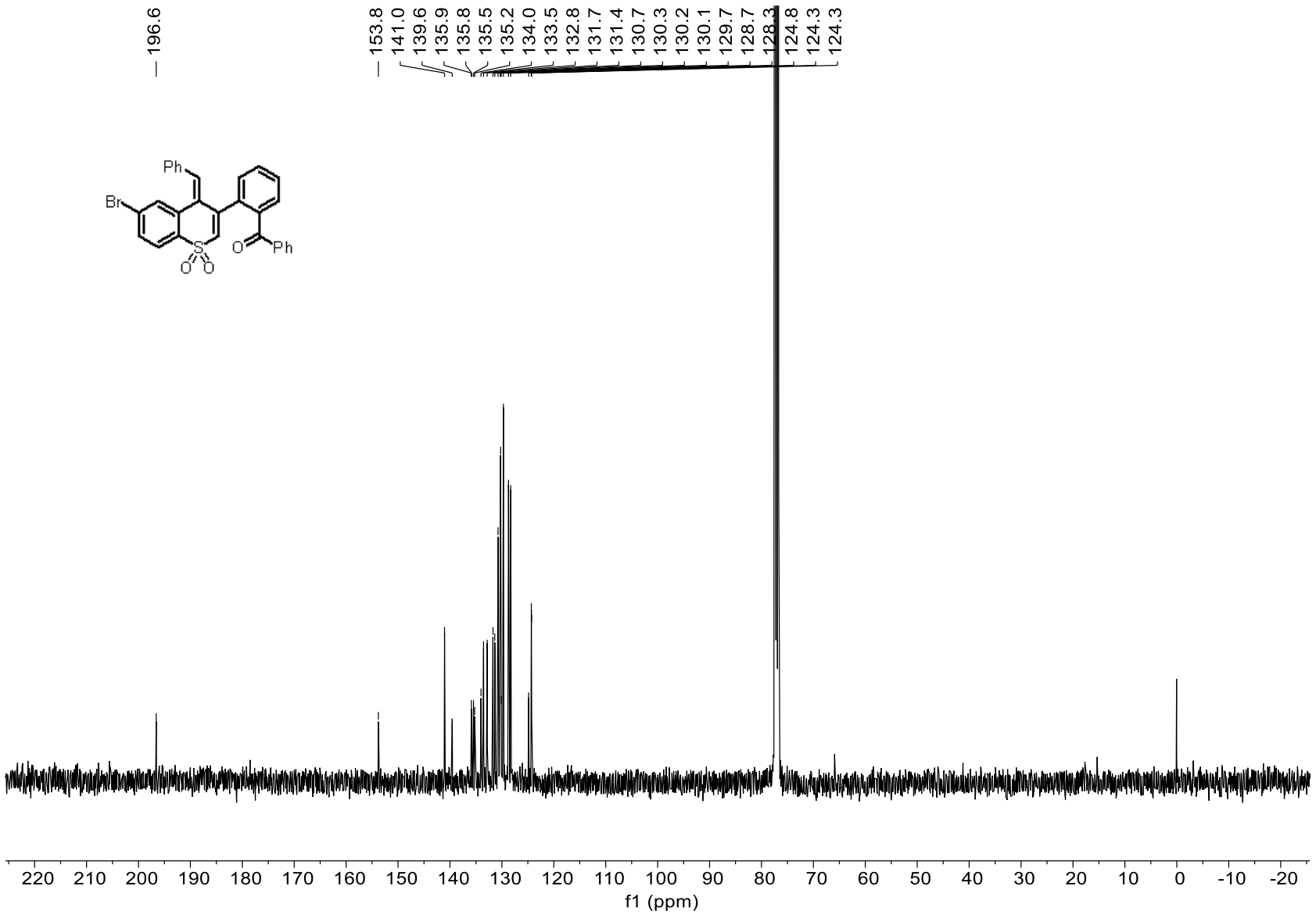
^{1}H NMR Spectrum of Compound **3o**



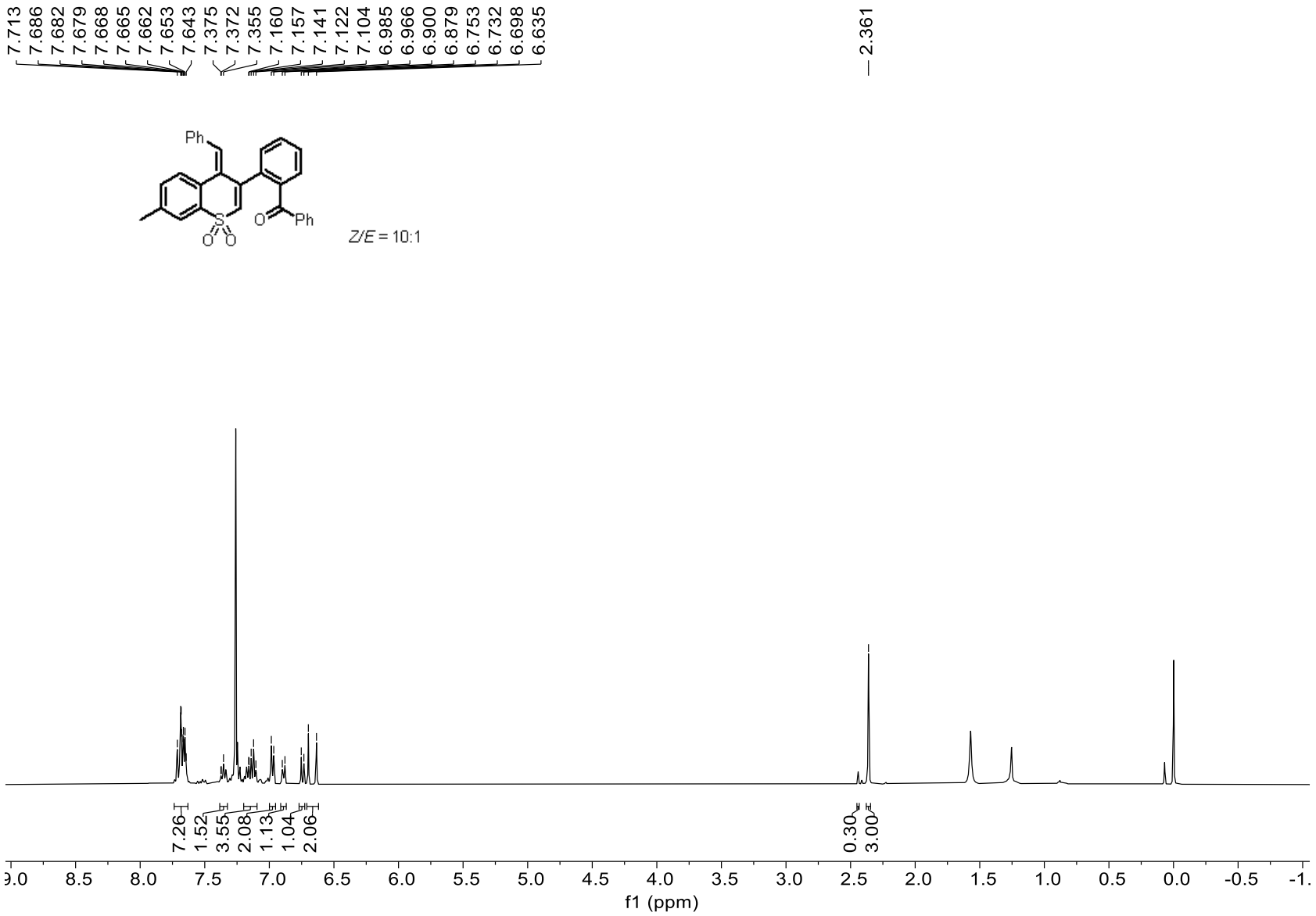
^{13}C NMR Spectrum of Compound **3o**



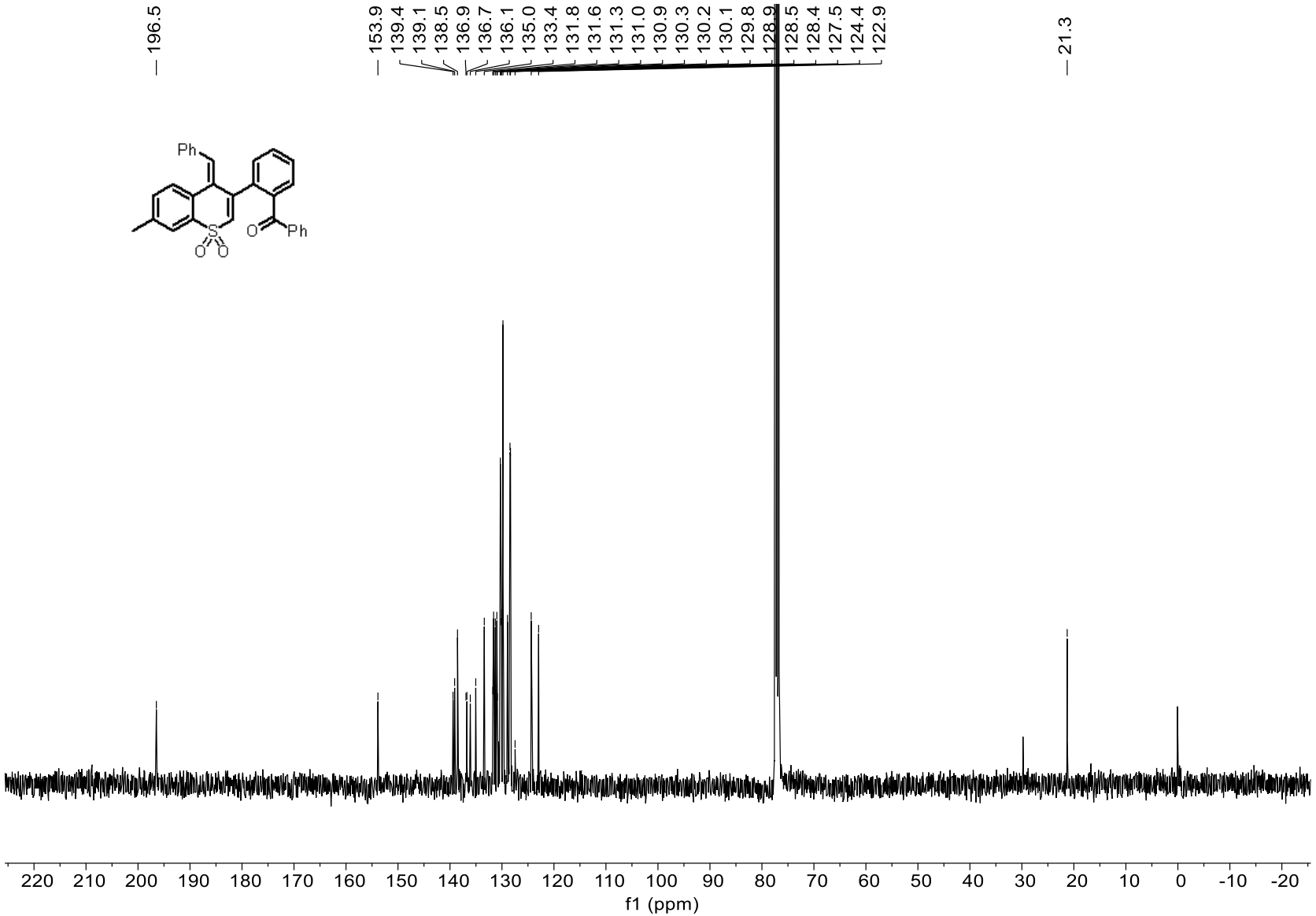
^{1}H NMR Spectrum of Compound **3p**



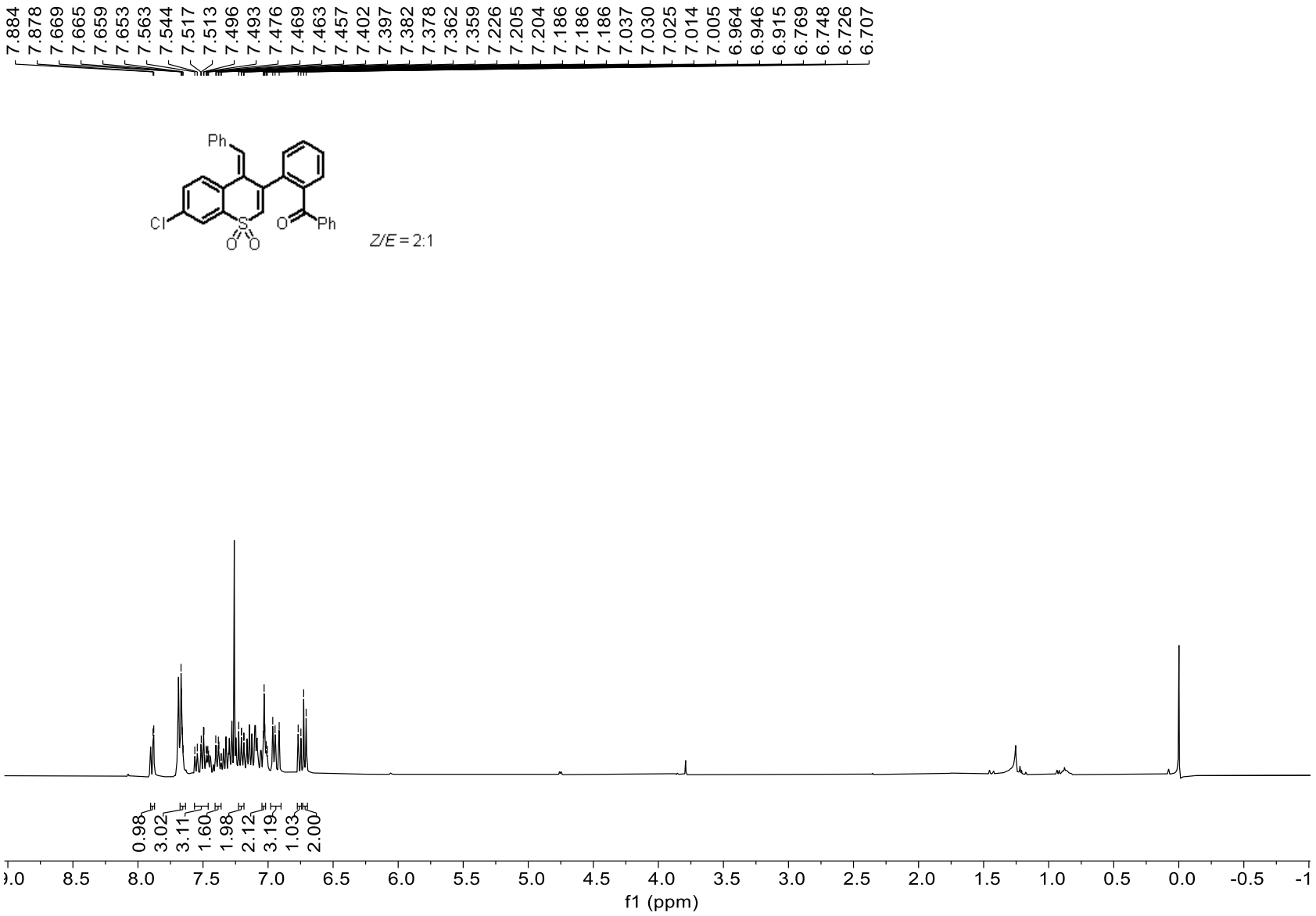
^{13}C NMR Spectrum of Compound **3p**



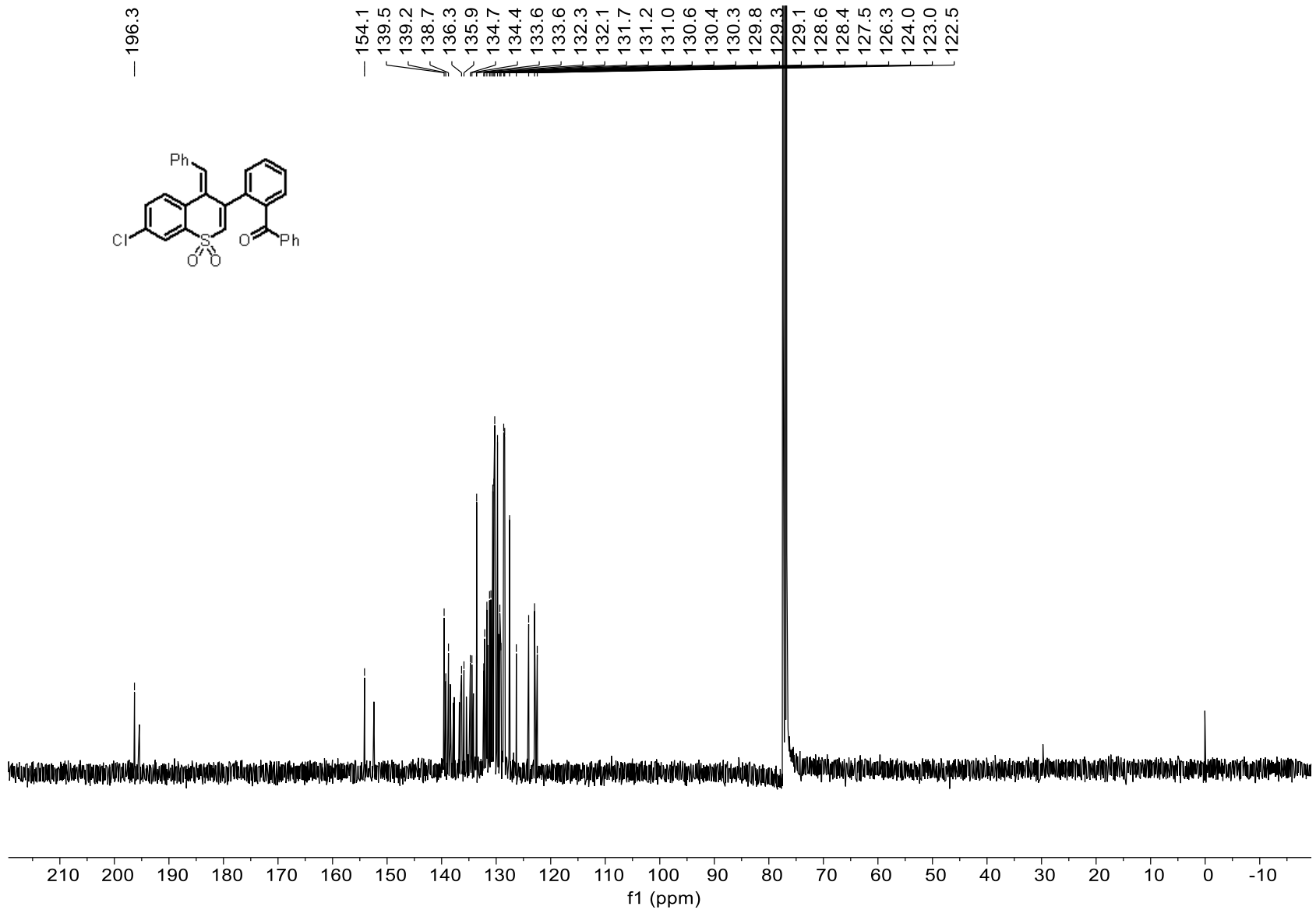
^{1}H NMR Spectrum of Compound **3q**



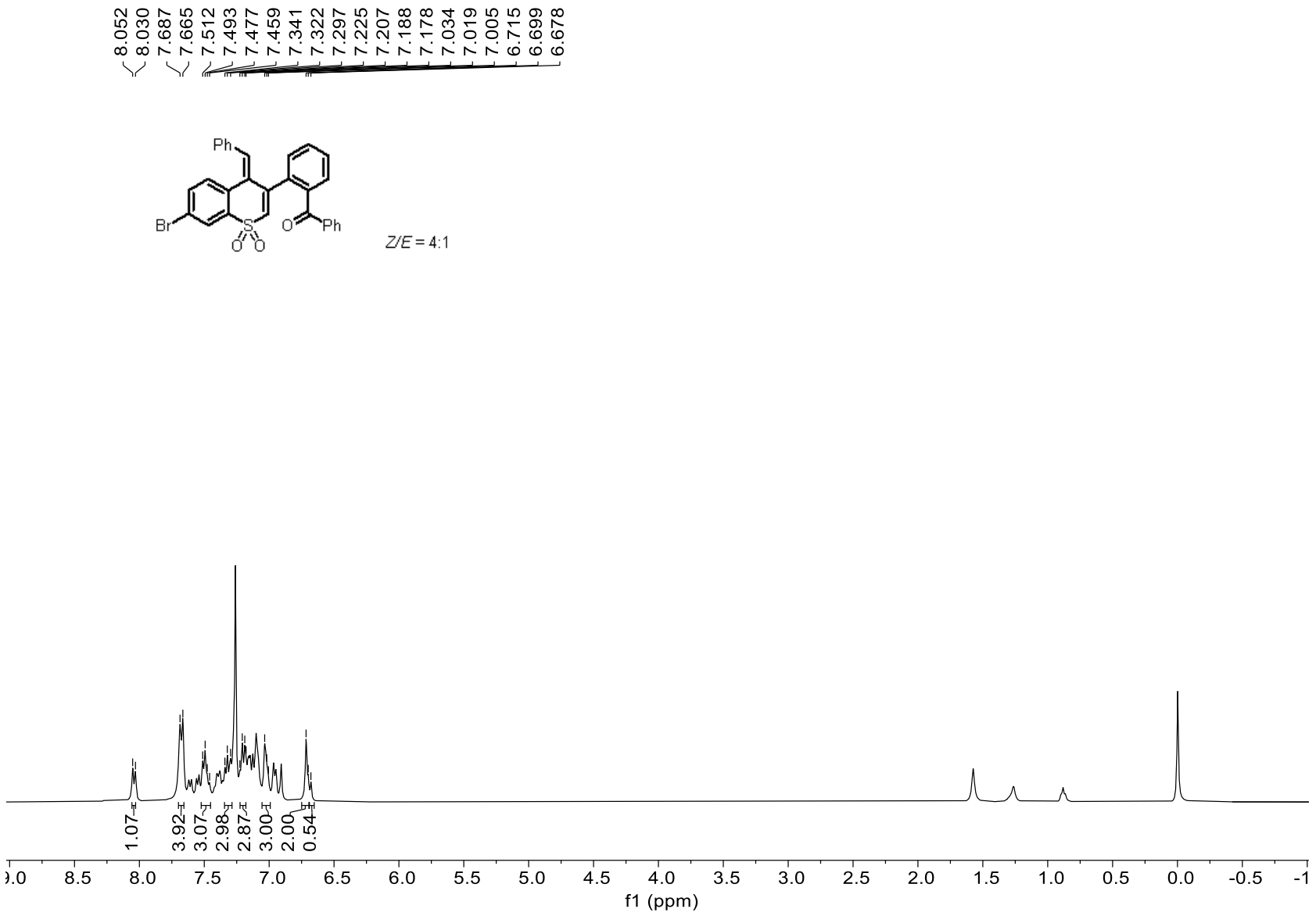
^{13}C NMR Spectrum of Compound **3q**



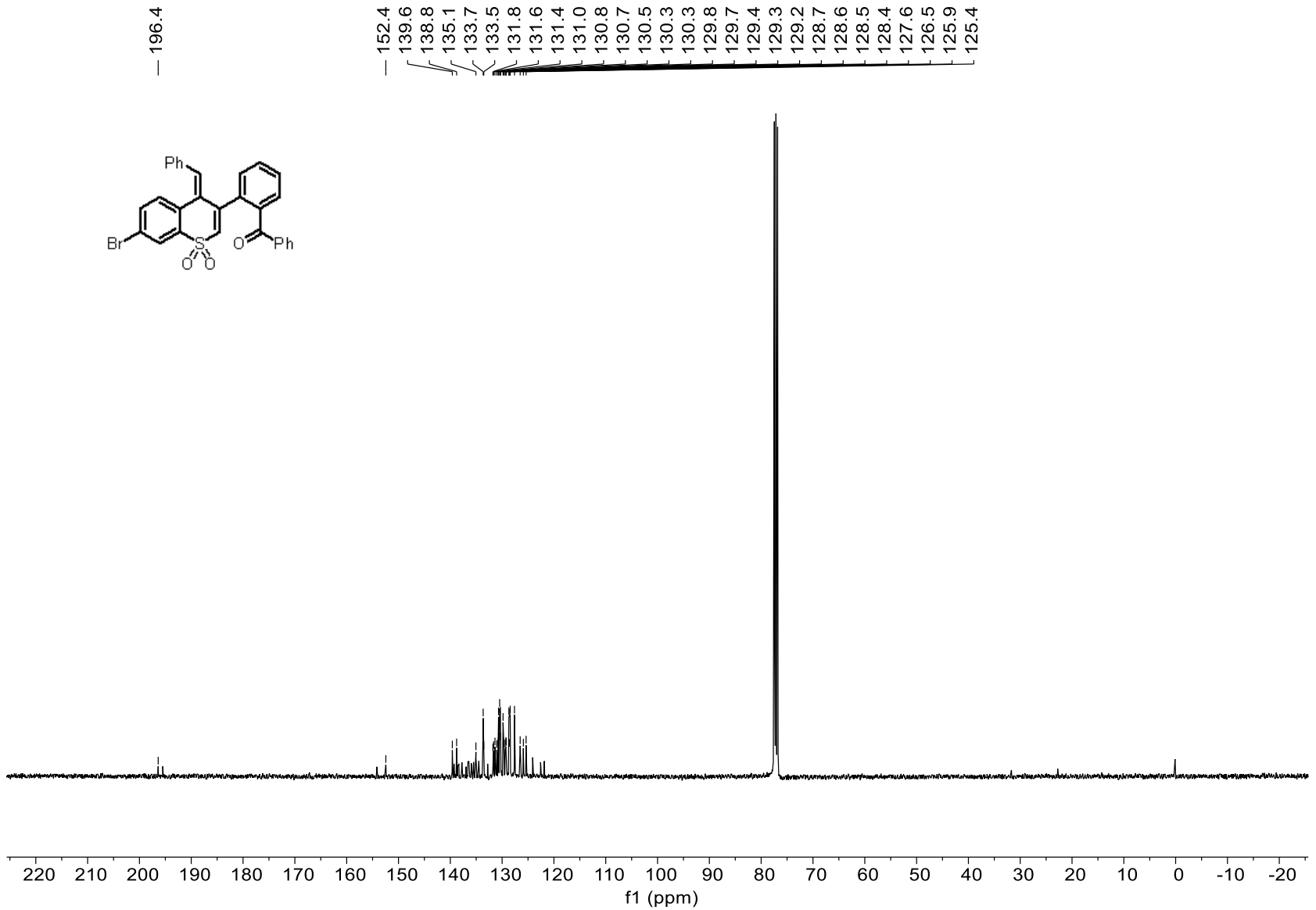
^{1}H NMR Spectrum of Compound **3r**



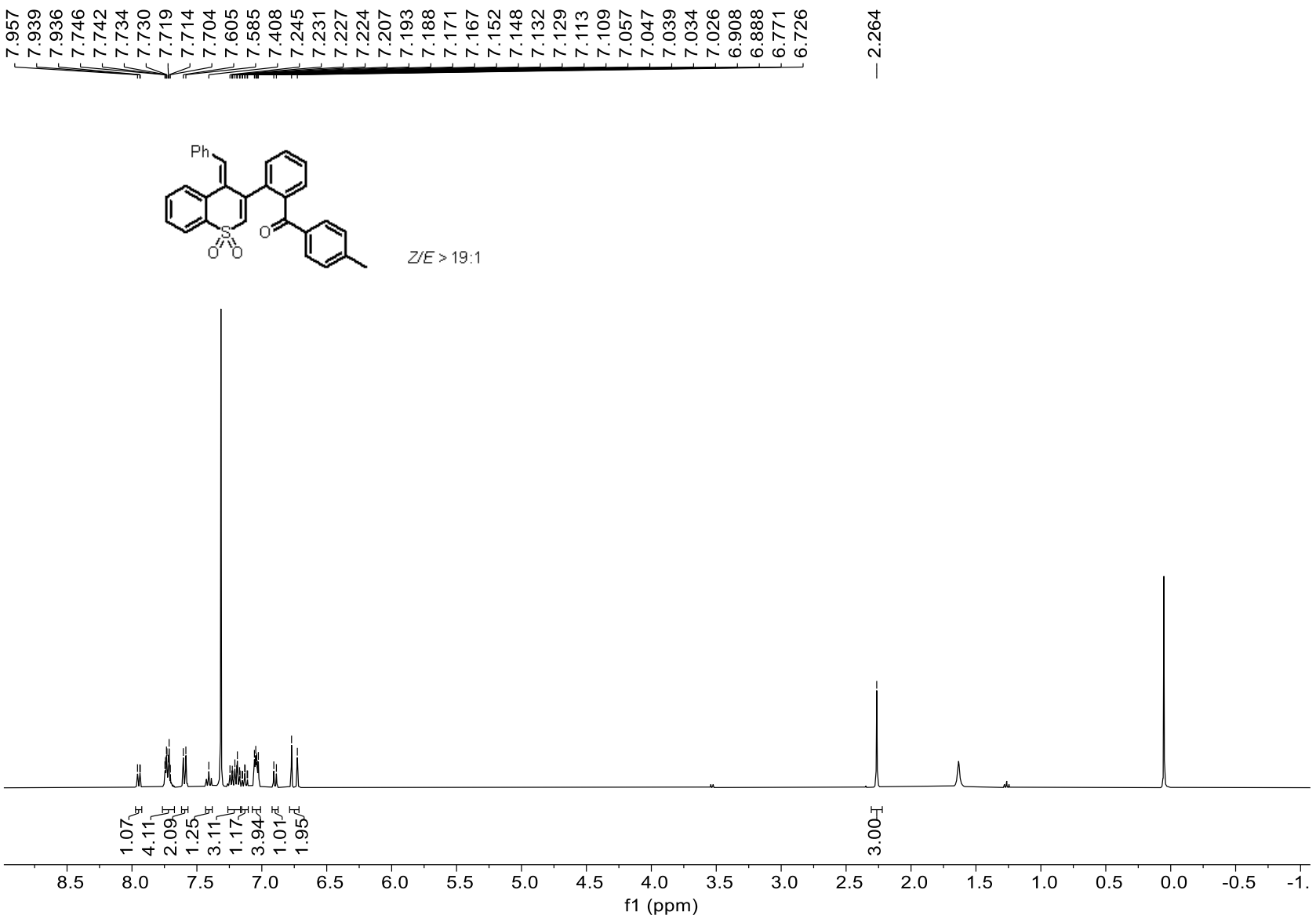
^{13}C NMR Spectrum of Compound **3r**



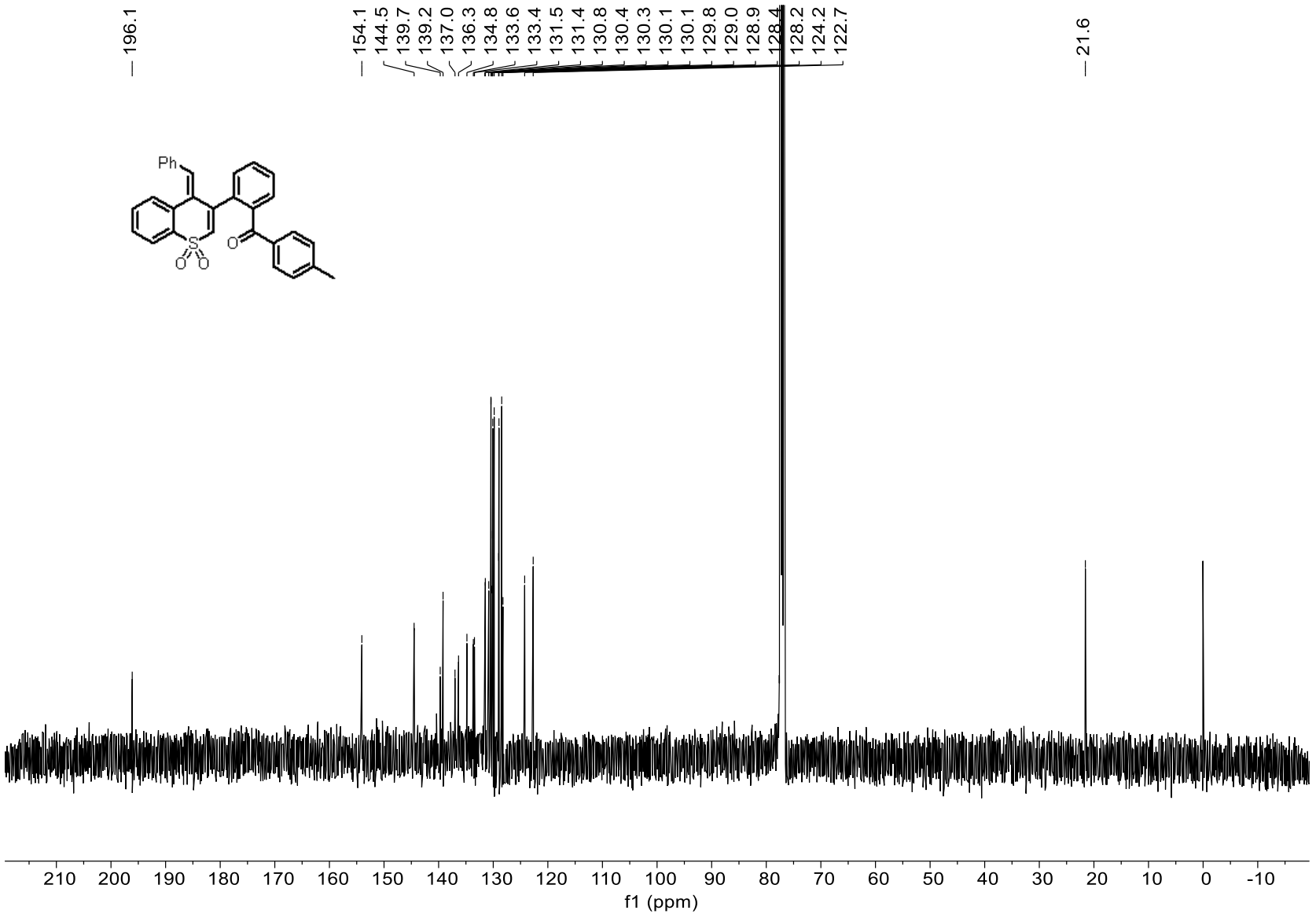
^{1}H NMR Spectrum of Compound **3s**



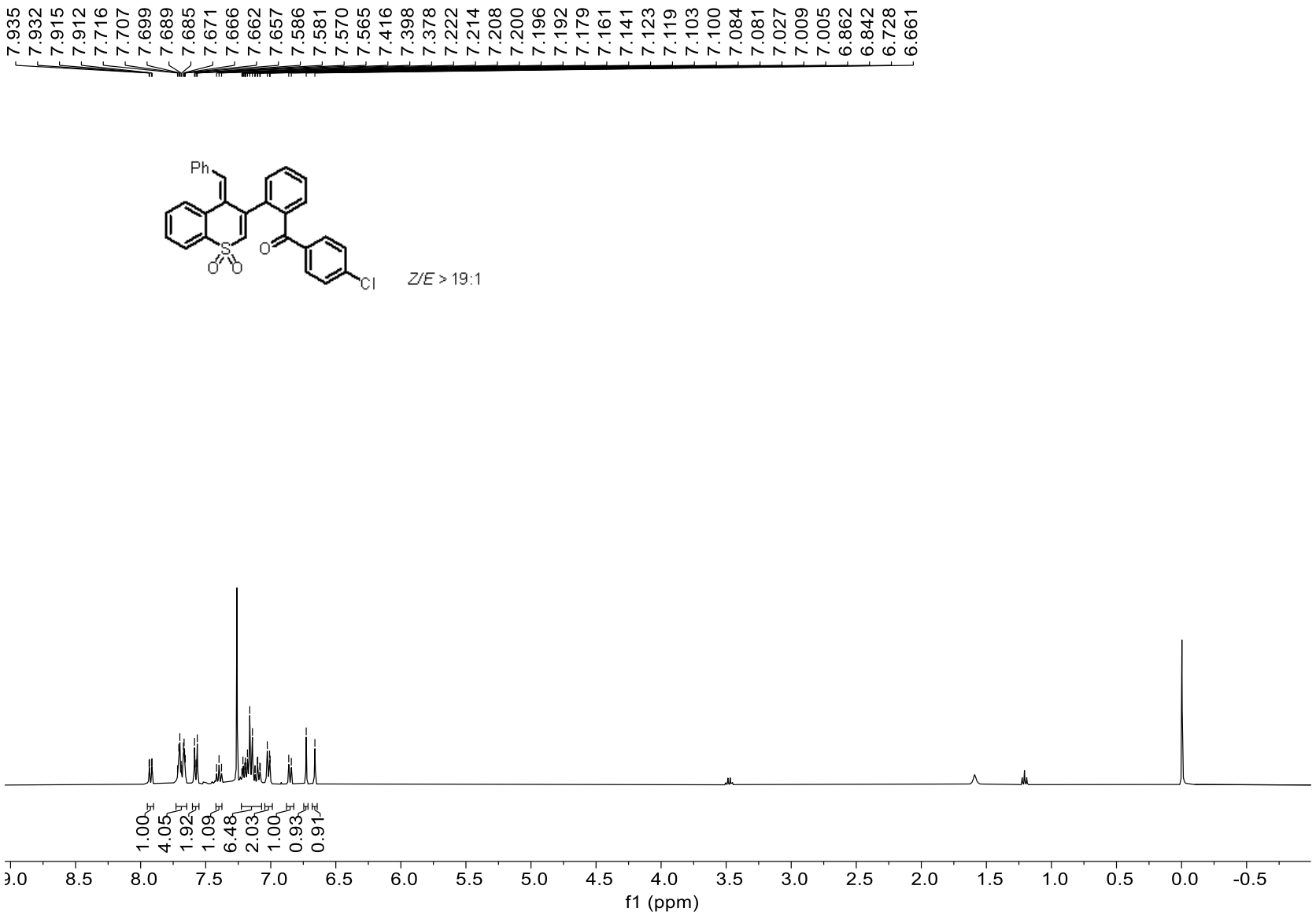
^{13}C NMR Spectrum of Compound **3s**



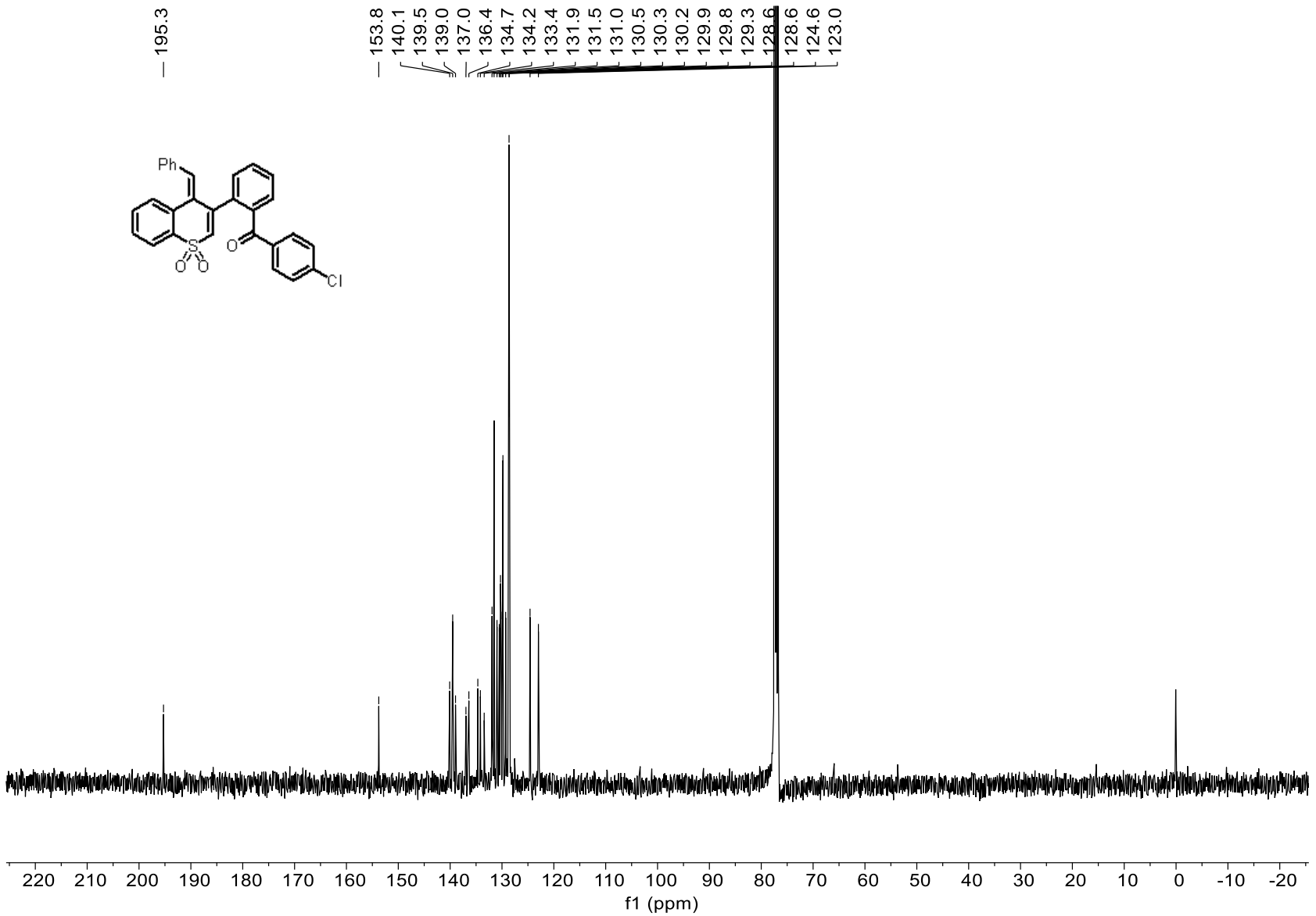
^{1}H NMR Spectrum of Compound **3t**



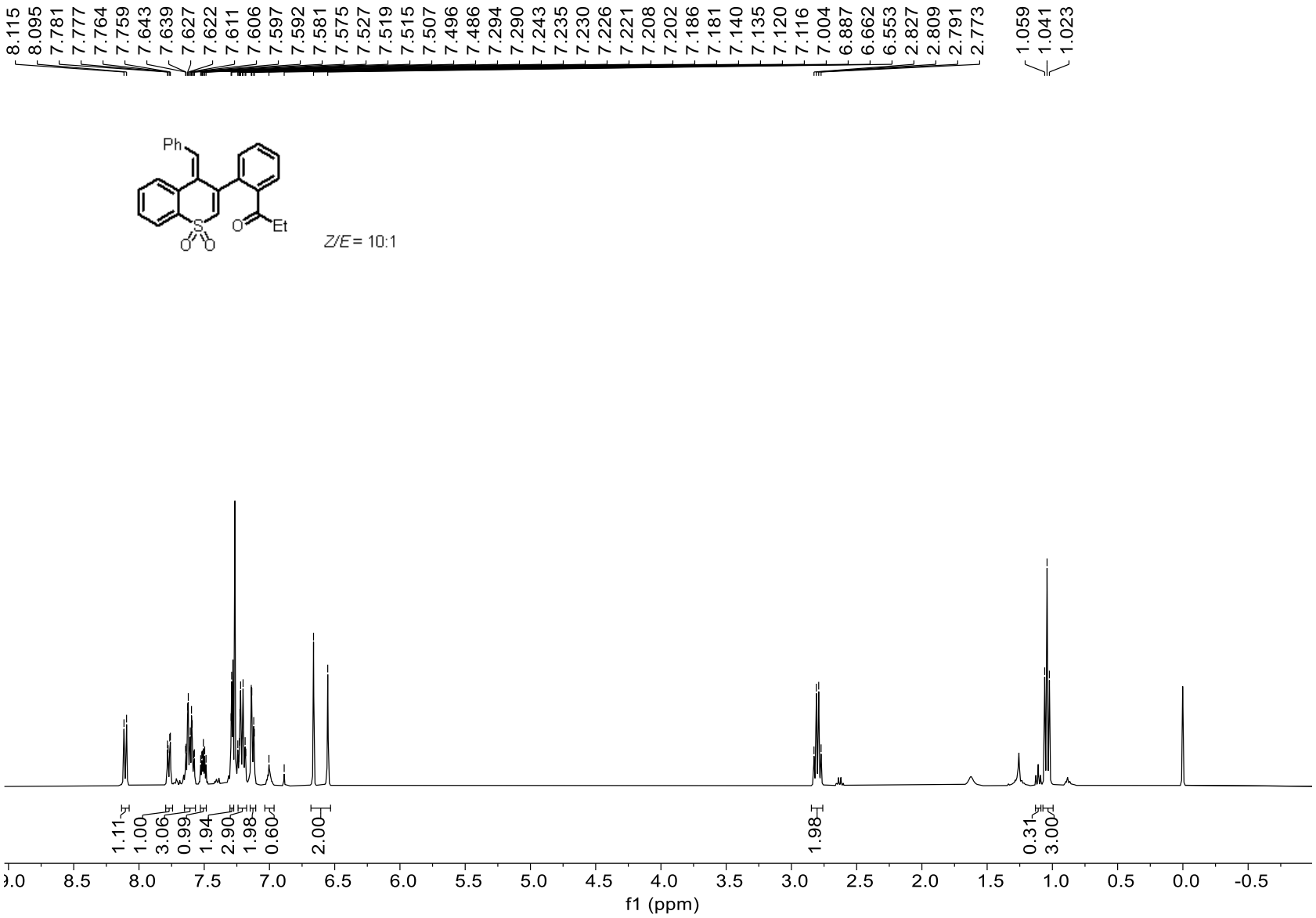
^{13}C NMR Spectrum of Compound **3t**



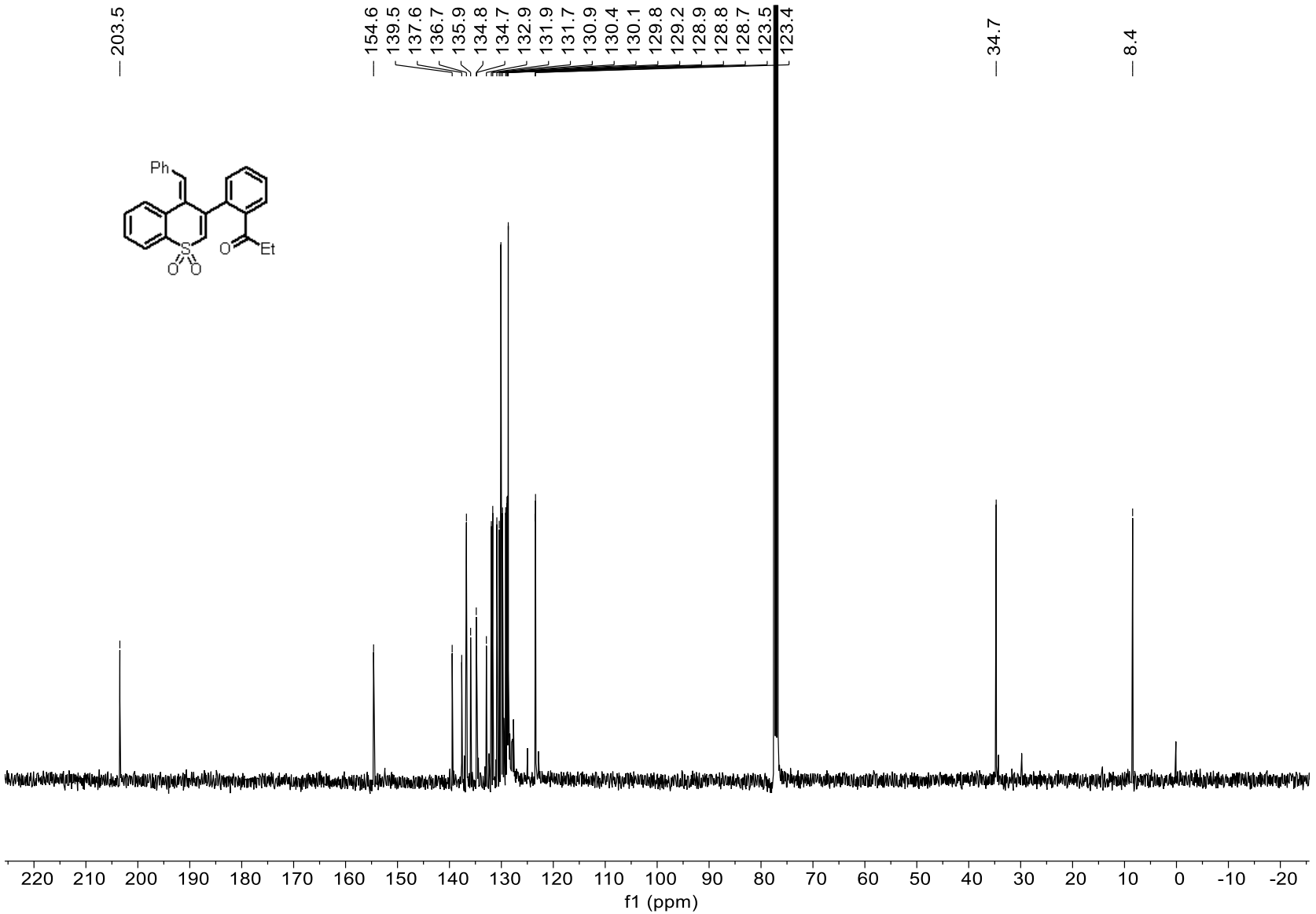
^{1}H NMR Spectrum of Compound **3u**



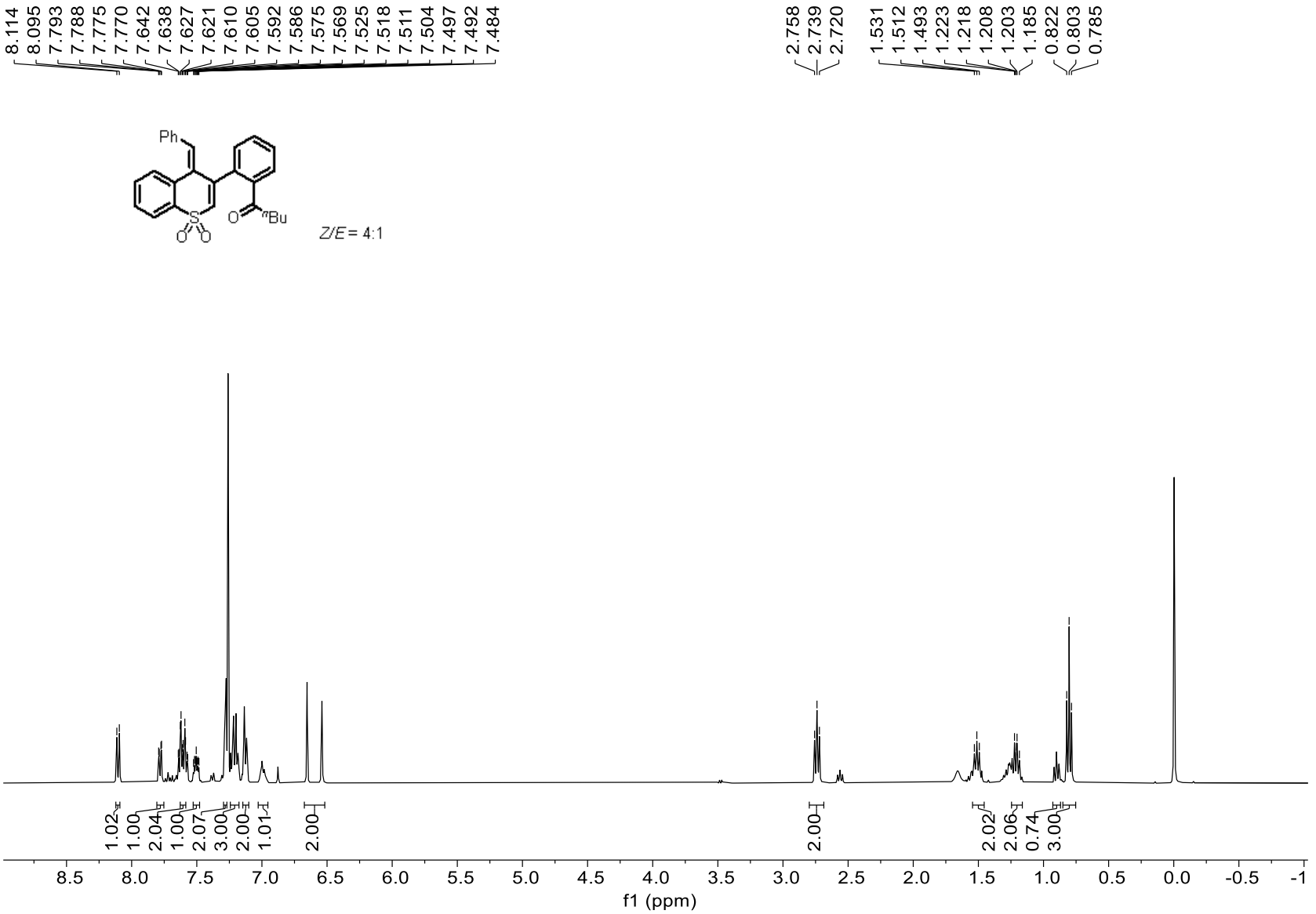
^{13}C NMR Spectrum of Compound **3u**



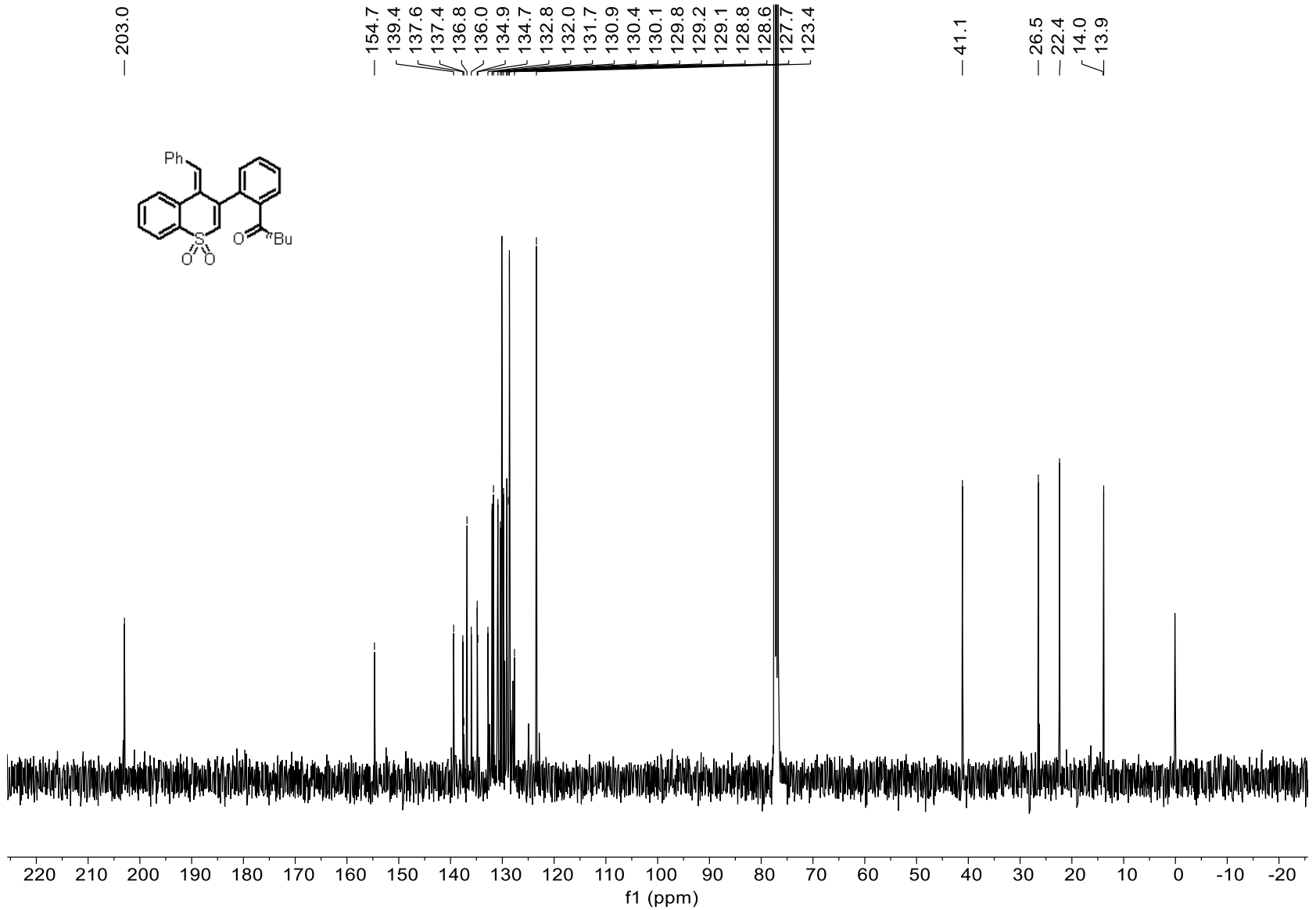
^{1}H NMR Spectrum of Compound **3v**



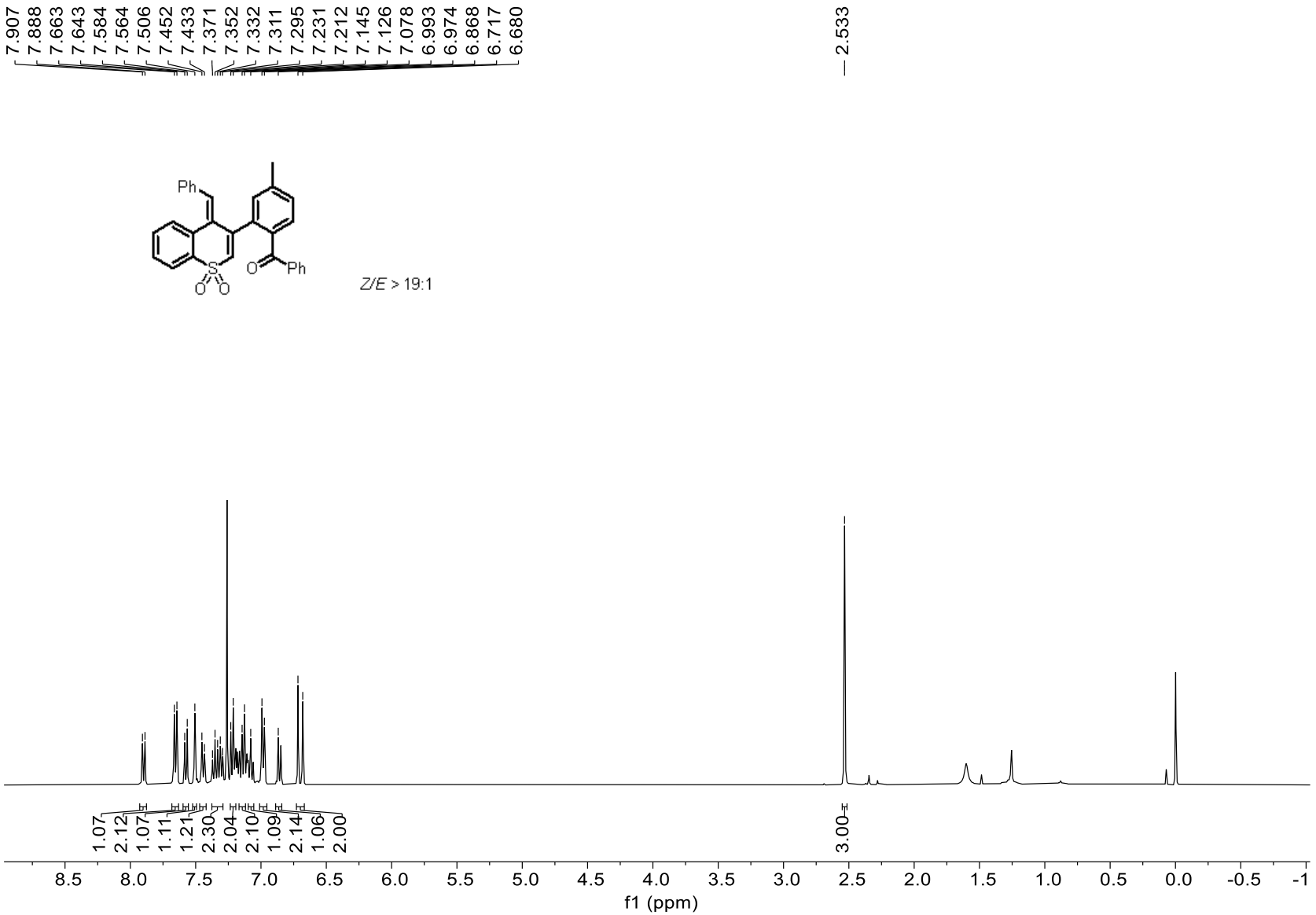
^{13}C NMR Spectrum of Compound **3v**



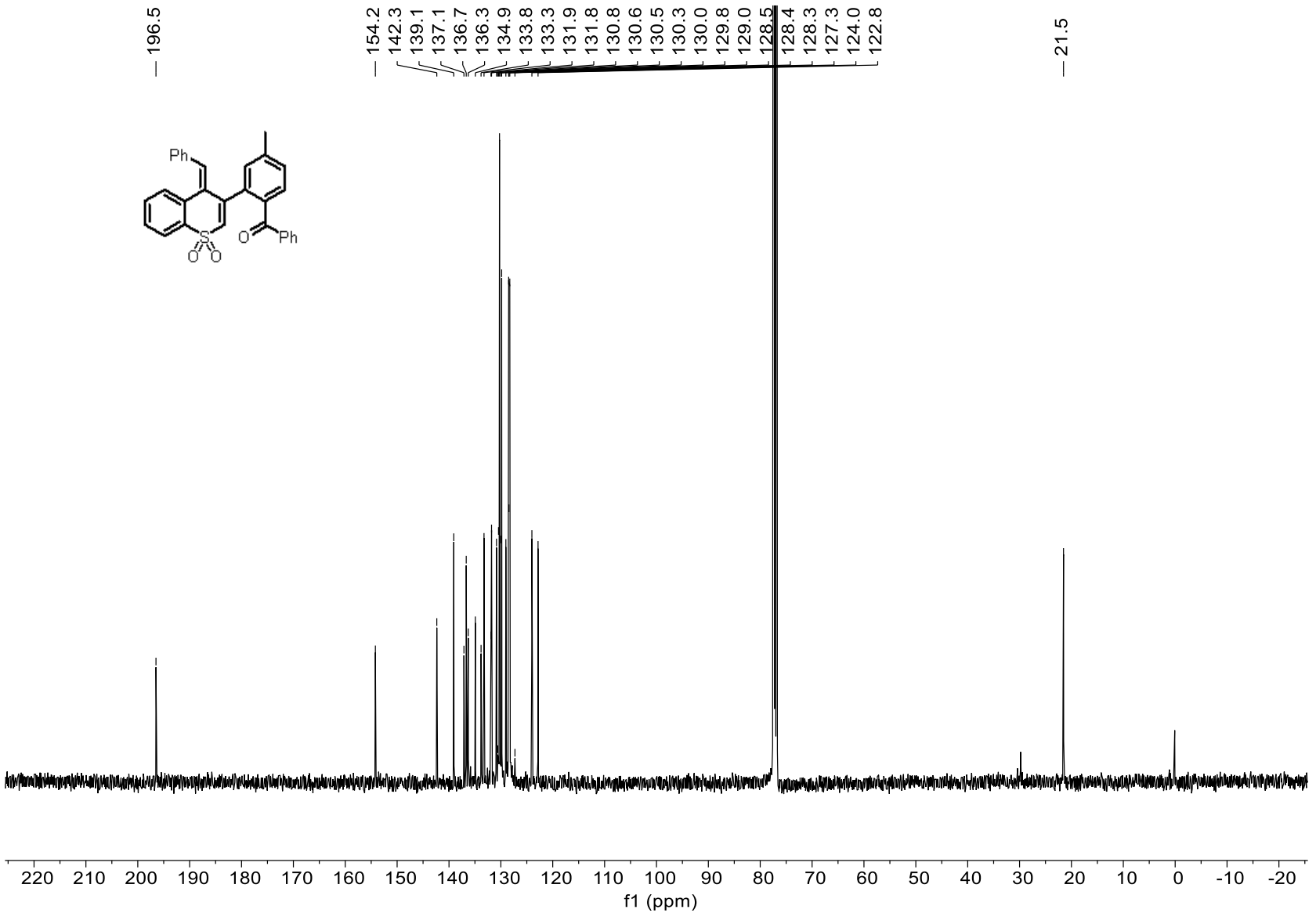
^{1}H NMR Spectrum of Compound **3w**



^{13}C NMR Spectrum of Compound **3w**



^{1}H NMR Spectrum of Compound **3x**



^{13}C NMR Spectrum of Compound **3x**