Metal Free, Facile Sulfenylation of Ketene Dithioacetals Catalyzed By HBr-DMSO System

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MATERIALS AND METHODS

General Information. Unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification. PET refers to petroleum ether (bp. 60-90 °C) and EA refers to ethyl acetate, and all reaction solvents were freshly distilled prior to use. All reactions were carried out in oven-dried glassware. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points (M.P.) were determined on digital melting point apparatus and are uncorrected. Column chromatography was carried out using commercially available silica gel (100-200 mesh) under pressure. All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker-400 spectrometers, (^{1}H: 400 MHz, ^{13}C: 100 MHz), and were referenced to the residual peaks of $CDCl_3$ at 7.26 ppm (^{1}H NMR) and $CDCl_3$ at 77.23 ppm (^{13}C NMR). Chemical shifts (δ) are expressed in ppm, and Coupling constant (*J*) values are given in Hz. Data are reported as follows: Chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constant (Hz), and integration. Mass spectra were obtained with a Q-TOF Mass Spectrometer (HRMS). All starting materials were synthesized according to the previously reported protocols[1]. All the thiols and raw materials required for the preparation of ketene dithioacetals were purchased from Alfa Aesar and Sigma Aldrich.

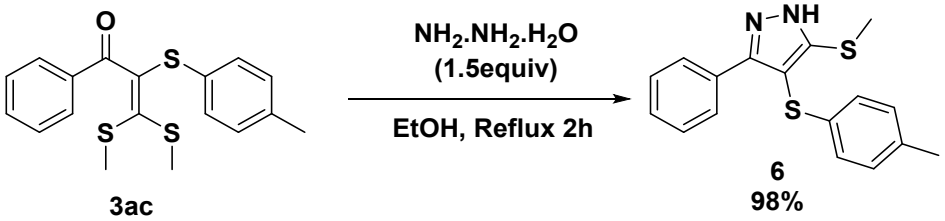
EXPERIMENTAL SECTION

General Procedure A: For the Synthesis of Sulfenylated Ketene Dithioacetals.

To a solution of ketene dithioacetal (0.44mmol), arylthiol **2a** (0.44mmol) in a mixture of DMSO:$CHCl_3$ (1:1, 3mL), was added 47% of aq. hydrobromic acid (HBr) (30mol%). The resulting mixture was stirred at 100 °C for 2h. Progress of the reaction was monitored by Thin Layer Chromatography (TLC). After completion of reaction, 5mL of water was added to the reaction mixture followed by extracted the product by ethyl acetate (3 × 10mL). The organic phases were combined and washed with a brine solution (1 × 10mL). Organic phases were dried over anhydrous Na_2SO_4 and evaporated the solvent under reduced pressure to obtain crude product. The resulting crude was then purified by column chromatography using petroleum ether and ethyl acetate (v/v = 92/8) to obtain the desired product in pure form.

The above procedure was also employed for sulfenylation of β-naphthol.

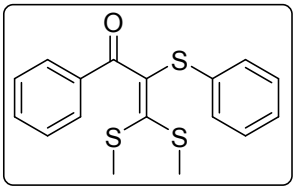
***General Procedure B: For Synthesis of 5-(Methylthio)-3-phenyl-4-(p-tolylthio)-1H-pyrazole (6)*:**



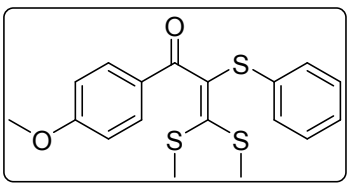
The starting material **3ac** was obtained by following the general procedure A. To a solution of **3ac** (0.29mmol) in ethanol (3mL), was added hydrazine hydrate (99%, 0.43mmol). The mixture was refluxed for 2h. Progress of the reaction was monitored by Thin Layer Chromatography (TLC). After the complettion of reaction, the reaction mixture was cooled to room temperature and concentrated under reduced pressure to get residue. The resulting residue was dissolved in dichloromethane (CH_2Cl_2) (5mL) and washed with water (5mL) and brine (5mL). The organic phase was dried over anhydrous Na_2SO_4. Organic phase was subjected to evaporation under reduced pressure to afford crude product. The crude product was washed by Et_2O (10mL) to afford pure solid product **6** (88 mg, 98% yield).

Characteristic Data for the compounds:

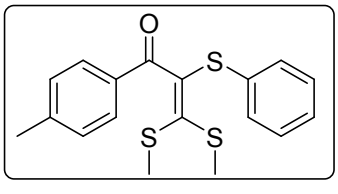
3,3-Bis(methylthio)-1-phenyl-2-(phenylthio)prop-2-en-1-one (3aa): Yield 99% (147mg), R_f 0.6 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.49 (s, 3H), 7.11 – 7.17 (m, 3H), 7.27 – 7.30 (m, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.46 – 7.51 (m, 1H), 7.72 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.4, 128.3, 128.3, 128.7, 129.2, 130.9, 133.1, 133.6, 135.3, 136.2, 138.7, 190.9. **HRMS (ESI)**: calcd for $C_{17}H_{17}OS_3$ [M+H] 333.0442, found 333.0441.



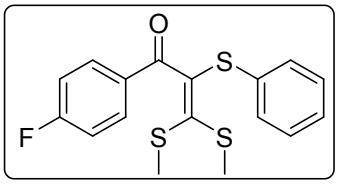
1-(4-Methoxyphenyl)-3,3-bis(methylthio)-2-(phenylthio)prop-2-en-1-one (3ba): Yield 99% (141mg), as yellow oil, R_f 0.5 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.48 (s, 3H), 3.83 (s, 3H), 6.84 (d, J = 8.8 Hz, 2H), 7.10 – 7.18 (m, 3H), 7.27 – 7.32 (m, 2H), 7.71 (d, J = 9.2 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.5, 55.4, 113.7, 128.4, 128.7, 129.2, 129.4, 131.0, 131.6, 133.8, 139.4, 163.7, 189.6; **HRMS (ESI)**: calcd for $C_{18}H_{19}O_2S_3$ [M+H] 363.0547, found 363.0543.



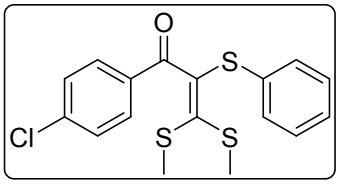
***3,3-Bis(methylthio)-2-(phenylthio)-1-(p-tolyl)prop-2-en-1-one (3ca)*:** Yield 99% (144mg), as yellow oil, R_f 0.65 in (10%, EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.37 (s, 3H), 2.48 (s, 3H), 7.10 – 7.19 (m, 5H), 7.29 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.5, 21.7, 127.5, 128.3, 128.7, 129.1, 129.4, 129.5, 131.0, 133.6, 139.0, 144.1, 190.5; **HRMS (ESI)**: calcd for $C_{18}H_{19}OS_3$ [M+H] 347.0598, found 347.0600.



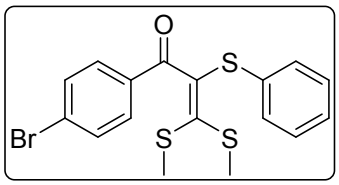
1-(4-Fluorophenyl)-3,3-bis(methylthio)-2-(phenylthio)prop-2-en-1-one (3da): Yield 98% (142mg), as yellow oil, R_f 0.57 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 2.49 (s, 3H), 7.02 (t, *J* = 8.4 Hz, 2H), 7.11 – 7.20 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.74 (dd, J_1 = 5.6 Hz, J_2 = 8.8 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.5, 115.57 (d, *J* = 21.9 Hz), 128.69 (d, *J* = 29.8 Hz), 130.8, 131.6, 131.8, 131.9, 132.6, 133.8, 135.3, 138.4, 167.77 (d, *J* = 253.8 Hz), 189.4; **HRMS (ESI)**: calcd for $C_{17}H_{16}FOS_3$ [M+H] 351.0347, found 351.0347.



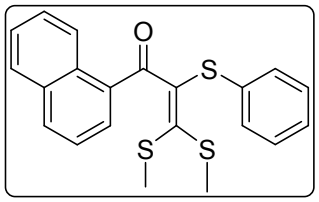
1-(4-Chlorophenyl)-3,3-bis(methylthio)-2-(phenylthio)prop-2-en-1-one (3ea): Yield 99% (141mg), as yellow oil, R_f 0.7 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.49 (s, 3H), 7.12 – 7.19 (m, 3H), 7.25 -7.29 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.5, 127.5, 128.5, 128.7, 128.8, 130.5, 133.7, 134.6, 136.6, 138.0, 139.6, 189.7; **HRMS (ESI)**: calcd for $C_{17}H_{15}ClNaOS_3$ [M+Na] 388.9871, found 388.9874.



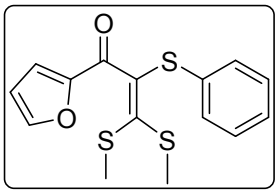
1-(4-Bromophenyl)-3,3-bis(methylthio)-2(phenylthio)prop-2-en-1-one (3fa): Yield 99% (135mg), as yellow oil, R_f 0.5 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.49 (s, 3H), 7.12 – 7.18 (m, 3H), 7.25 – 7.30 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 16.5, 18.5, 128.3, 128.5, 128.9, 130.6, 130.7, 131.7, 133.7, 135.0, 136.1, 138.0, 189.9; **HRMS (ESI)**: calcd for $C_{17}H1_6BrOS_3$ [M+H] 410.9547, found 410.9543.



3,3-Bis(methylthio)-1-(naphthalen-1-yl)-2-(phenylthio)prop-2-en-1-one (3ga): Yield 99% (138mg), as yellow viscous liquid, R_f 0.62 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.13 (s, 3H), 2.49 (s, 3H), 7.02 -7.07 (m, 3H), 7.24 - 7.30 (m, 2H), 7.40 -7.45 (m, 3H), 7.75 - 7.78 (m, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.9 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 5.6 Hz, 1H); **^{13}CNMR** (100 MHz): 16.7, 18.5, 113.7, 123.9, 125.8, 1626.2, 127.8, 128.1, 128.1, 128.7, 130.5, 130.8, 131.5, 133.4, 133.5, 133.7, 138.6, 139.8, 192.5; **HRMS (ESI)**: calcd for $C_{21}H_{19}O\ S_3$ [M+H] 383.0598, found 383.0595.

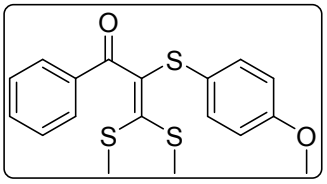


1-(Furan-2-yl)-3,3-bis(methylthio)-2-(phenylthio)prop-2-en-1-one (3ha): Yield 98% (147mg), as yellow oil, R_f 0.48 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.48 (s, 3H), 6.46 (dd, J_1 = 1.6 Hz, J_2 = 3.2 Hz, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 7.18 (t, *J* = 3.2 Hz, 3H), 7.33 - 7.37 (m, 2H), 7.53 (s, 1H); **^{13}CNMR** (100 MHz): 16.5, 18.7, 112.3, 119.2, 128.1, 128.8, 131.5, 132.7,

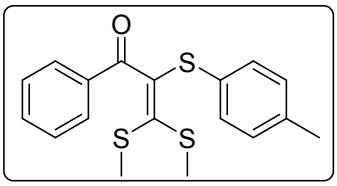


136.2, 139.5, 146.9, 152.2, 179.0; **HRMS (ESI)**: calcd for $C_{15}H_{15}O_2S_3$ [M+H] 323.0234, found 323.0232.

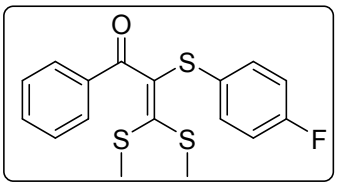
2-(4-Methoxyphenyl)thio-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3ab): Yield 99% (162mg), as pale yellow oil, R_f 0.63 in 10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.14 (s, 3H), 2.48 (s, 3H), 3.69 (s, 3H), 6.62 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H); **^{13}CNMR** (100 MHz): 16.3, 18.2, 55.2, 114.3, 120.4, 128.3, 129.2, 130.2, 133.2, 136.2, 136.7, 141.7, 160.3, 191.0; **HRMS (ESI)**: calcd for $C_{18}H_{19}O_2S_3$ [M+H] 363.0547, found 363.0548.



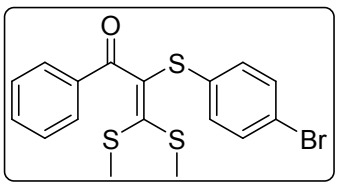
3,3-Bis(methylthio)-1-phenyl-2-(p-tolylthio)prop-2-en-1-one (3ac)[2]: Yield 99% (153mg), as yellow liquid, R_f 0.6 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.22 (s, 3H), 2.49 (s, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H).



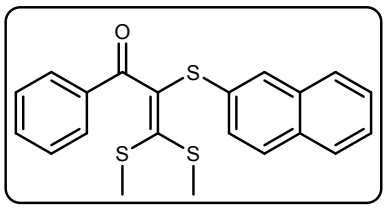
2-(4-Fluorophenyl)thio-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3ad): Yield 99% (155mg), as yellow liquid, R_f 0.55 in 10% (EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.49 (s, 3H), 6.81 (t, *J* = 8.4 Hz, 2H), 7.25 (dd, J_1 = 5.2 Hz, J_2 = 8.8 Hz, 2H); 7.37 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H); **^{13}CNMR** (100 MHz): 16.4, 18.3,115.94 (d, *J* = 21.9 Hz), 128.81 (d, *J* = 3.1 Hz), 128.4, 129.2, 133.3, 133.6, 136.1, 136.4, 136.5, 139.3, 163.03 (d, *J* = 248.1 Hz), 190.8; **HRMS (ESI)**: calcd for $C_{17}H_{16}FOS_3$ [M+H] 351.0347, found 351.0347.



2-(4-Bromophenyl)thio-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3ae): Yield 99% (179mg), as pale yellow oil, R_f 0.71 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.49 (s, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H); **^{13}CNMR** (100 MHz): 16.5, 18.5, 128.5, 129.2, 130.4, 130.5, 131.9, 133.4, 134.6, 136.0, 136.9, 137.9, 190.8; **HRMS (ESI)**: calcd for $C_{17}H_{16}BrOS_3$ [M+H] 410.9547, found 410.9545.

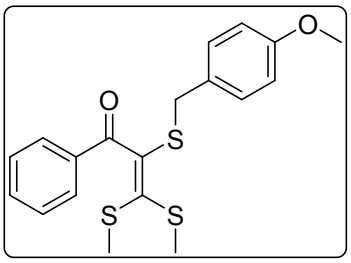


3,3-Bis(methylthio)-2-(naphthalen-2-ylthio)-1-phenylprop-2-en-1-one (3af): Yield 97% (165mg), as yellow oil, R_f 0.58 in (10% EA/PET):): **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.52 (s, 3H), 7.30 – 7.39 (m, 3H), 7.40 – 7.44 (m, 2H), 7.46

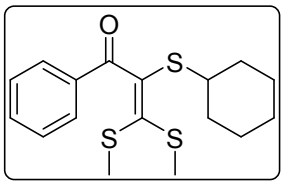


(t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.75 (m, 3H), 7.77 (s, 1H); **^{13}CNMR** (100 MHz): 16.5, 18.5, 126.3, 126.6, 126.6, 127.6, 128.3, 128.3, 128.4, 129.2, 130.1, 132.6, 133.1, 133.3, 133.4, 136.1, 136.4, 138.1, 190.9; **HRMS (ESI)**: calcd for $C_{21}H_{19}OS_3$ [M+H] 383.0598, found 383.0600.

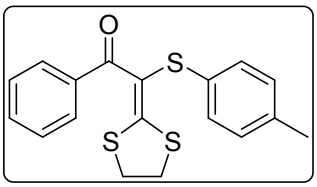
2-(4-Methoxybenzyl)thio-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3ag): Yield 97% (163mg), as yellow oil, R_f 0.46 in (10% EA/PET): **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.36 (s, 3H), 3.79 (s, 3H), 3.81 (s, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.52 - 7.61 (m, 1H), 7.88 (d, *J* = 7.6 Hz, 2H); **^{13}CNMR** (100 MHz): 16.2, 18.19, 37.5, 55.2, 113.8, 128.1, 128.2, 128.6, 129.3, 130.3, 133.4, 136.1, 139.3, 158.8, 191.3; **HRMS (ESI)**: calcd for $C_{19}H_{21}O_2S_3$ [M+H] 377.0704, found 377.0702.



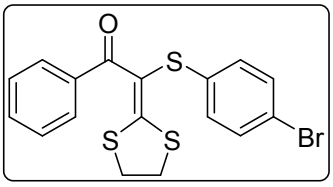
2-(Cyclohexylthio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3ah): Yield 99% (149mg), as yellow oil, R_f 0.59 in (10% EA/PET): **^{1}HNMR** (400 MHz, $CDCl_3$): δ 1.16 - 1.28 (m, 3H), 1.30 -1.40 (m, 2H), 1.48 -1.57 (m, 1H), 1.66 – 1.73 (m, 2H), 1.90 (d, *J* = 12.8 Hz, 2H), 2.09 (s, 3H), 2.44 (s, 3H), 2.83 – 2.92 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.90 – 7.98 (m, 2H); **^{13}CNMR** (100 MHz): 16.2, 18.4, 25.4, 25.8, 33.7, 46.7, 128.6, 129.4, 129.8, 133.3, 135.9, 138.2, 191.3; **HRMS (ESI)**: calcd for $C_{17}H_{23}OS_3$ [M+H] 339.0911, found 339.0908.



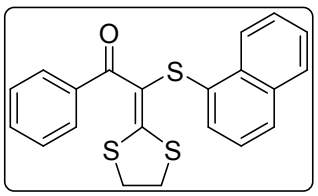
2-(1,3-Dithiolan-2-ylidene)-1-phenyl-2-(p-tolylthio)ethan-1-one (3ic): Yield 99% (153mg), as pale yellow soild, M.P. 182-184^{o}C. R_f 0.62 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.25 (s, 3H), 3.34 (t, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 2H); **^{13}CNMR** (100 MHz): 20.9, 35.4, 40.9, 112.3, 126.5, 127.4, 128.4, 129.7, 130.7, 132.8, 135.6, 138.8, 180.0, 192.1; **HRMS (ESI)**: calcd for $C_{18}H_{17}OS_3$ [M+H] 345.0442, found 345.0440.



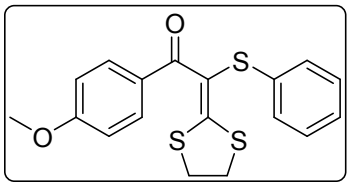
2-(4-Bromophenyl)thio-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (3ie): Yield 99% (181mg), as pale yellow soild, M.P. 177-179^{o}C, R_f 0.61 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.38 (t, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.32 (m, 4H); 7.39 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H); **^{13}CNMR** (100 MHz): 35.6, 41.0, 111.1, 119.4, 127.5, 127.8, 128.3, 130.9, 132.0, 135.8, 138.6, 181.1, 191.9; **HRMS (ESI)**: calcd for $C_{17}H_{14}BrOS_3$ [M+H] 408.9390, found 408.9388.



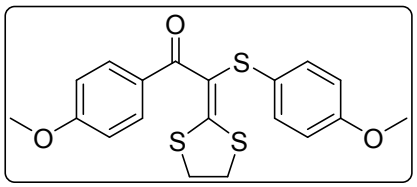
2-(1,3-Dithiolan-2-ylidene)-2-(naphthalen-1-ylthio)-1-phenylethan-1-one (3if): Yield 98% (167mg), pale yellow soild, M.P. 190-192°C, R_f 0.59 (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.34 (t, *J* = 7.2 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 7.16 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.21 - 7.26 (m, 2H), 7.32 -7.44 (m, 4H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.64 - 7.68 (m, 2H), 7.72 (d, *J* = 5.6 Hz, 1H); **^{13}CNMR** (100 MHz): 35.5, 41.0, 111.4, 124.0, 124.6, 125.4, 126.5, 127.1, 127.4, 127.7, 128.3, 128.6, 130.7, 131.6, 133.7, 134.0, 138.8, 181.0, 192.1; **HRMS (ESI)**: calcd for $C_{21}H_{17}OS_3$ [M+H] 381.0442, found 381.0440.



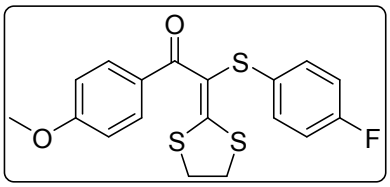
2-(1,3-Dithiolan-2-ylidene)-1-(4-methoxyphenyl)-2-(phenylthio)ethan-1-one (3ja): Yield 99% (141mg), as pale yellow solid, M.P. 168-170°C, R_f 0.49 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.35 (t, *J* = 6.8 Hz, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 6.78 – 6.82 (m, 2H), 7.05 – 7.12 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.69 – 7.73 (m, 2H); **^{13}CNMR** (100 MHz): 35.5, 40.7, 55.3, 112.8, 125.6, 126.1, 129.0, 130.0, 130.9, 131.1, 136.5, 162.0, 178.9, 190.8; **HRMS (ESI)**: calcd for $C_{18}H_{17}O_2S_3$ [M+H] 361.0391, found 361.0388.



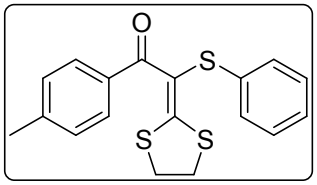
2-(1,3-Dithiolan-2-ylidene)-1-(4-methoxyphenyl)-2-(4-methoxyphenyl)thioethan-1-one (3jb): Yield 99% (153mg), as yellow semi solid, R_f 0.65 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.36 (t, *J* = 7.2 Hz, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 3.73 (s, 3H), 3.82 (s, 3H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H); **^{13}CNMR** (100 MHz): 35.5, 40.6, 55.3, 55.3, 112.8, 114.6, 126.9, 129.3, 130.0 131.0, 131.2, 158.4, 162.0, 176.5, 190.8; **HRMS (ESI)**: calcd for $C_{19}H_{19}O_3S_3$ [M+H] 391.0496, found 391.0497.



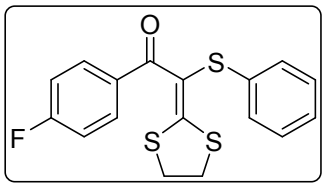
2-(1,3-Dithiolan-2-ylidene)-2-(4-fluorophenyl)thio)-1-(4-methoxyphenylethan-1-one (3jf): Yield 99% (148mg), as semi yellow solid, R_f 0.74 in (EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.37 (t, *J* = 7.2 Hz, 2H), 3.57 (t, *J* = 6.0 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.81 (t, *J* = 8.8 Hz, 2H), 7.02 (dd, J_1 = 5.2 Hz, J_2 = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H); **^{13}CNMR** (100 MHz): 35.6, 40.7, 55.3, 112.8, 116.07 (d, *J* = 22.0 Hz), 128.80 (d, *J* = 7.9 Hz), 130.8, 131.1, 131.4, 131.5, 161.41 (d, *J* = 245 Hz), 162.1, 177.9, 190.7; **HRMS (ESI)**: calcd for $C_{18}H_{16}FO_2S_3$ [M+H] 379.0296, found 379.0294.



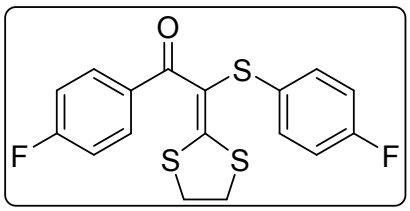
2-(1,3-Dithiolan-2-ylidene)-2-(phenylthio)-1-(p-tolyl)ethan-1-one (3ka): Yield 99% (144mg), as yellow solid, M.P. 165-167°C, R_f 0.65 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.30 (s, 3H), 3.34 (t, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 7.03 – 7.12 (m, 5H), 7.54 (t, *J* = 8.0 Hz, 2H); **^{13}CNMR** (100 MHz): 21.5, 35.5, 40.8, 111.7, 125.6, 126.1, 128.1, 128.7, 128.9, 135.8, 136.6, 141.4, 179.9, 191.9; **HRMS (ESI)**: calcd for $C_{18}H_{17}OS_3$ [M+H] 345.0442, found 345.0439.



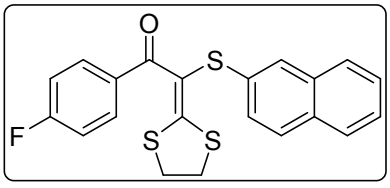
2-(1,3-Dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-(phenylthio)ethan-1-one (3la): Yield 99% (143mg), as yellow solid, M.P. 158-160°C, R_f 0.58 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.31 (t, *J* = 6.8 Hz, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.62 (dd, J_1 = 5.2 Hz, J_2 = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 35.4, 40.9, 111.2, 114.45 (d, J = 21.6 Hz), 125.7, 126.1, 129.0, 130.90(d, J = 8.7 Hz), 134.7, 134.7, 136.2, 164.14 (d, J = 249.4 Hz), 181.0, 190.5; **HRMS (ESI)**: calcd for $C_{17}H_{14}FOS_3$ [M+H] 349.0191, found 349.0190.



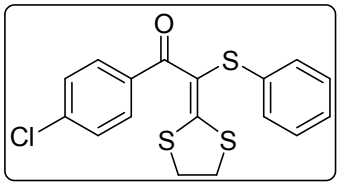
2-(1,3-Dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-((4-fluorophenyl)thio)ethan-1-one (3ld): Yield 99% (151mg), as yellow solid, M.P. 189-191°C, R_f 0.72 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.39 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.0 Hz, 2H), 6.87 (t, *J* = 8.8 Hz, 2H), 6.94 – 7.00 (m, 4H), 7.62 (dd, J_1 = 5.6 Hz, J_2 = 8.8 Hz, 2H); **^{13}CNMR** (100 MHz): 35.5, 40.9, 112.3, 114.59 (d, *J* = 21.8 Hz), 116.16 (d, *J* = 22.0 Hz), 128.84 (d, *J* = 8.25 Hz), 131.01 (d, *J* = 8.95 Hz), 131.26 (d, *J* = 3.1 Hz), 134.76 (d, *J* = 3.13 Hz), 161.67 (d, *J* = 278 Hz), 164.31 (d, *J* = 250 Hz), 180.1, 190.5; **HRMS (ESI)**: calcd for $C_{17}H_{13}F_2OS_3$ [M+H] 367.0097, found 367.0096.



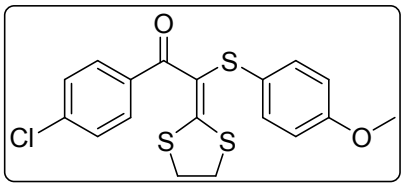
2-(1,3-Dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-(naphthalen-2-ylthio)ethan-1-one (3lf): Yield 99% (164mg), as yellow semi solid, R_f 0.63 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.37 (t, *J* = 6.8 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 6.9 (t, *J* = 8.8 Hz, 2H), 7.15 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.36 - 7.46 (m, 3H), 7.64 -7.69 (m, 4H), 7.73 (d, *J* = 7.6 Hz, 1H); **^{13}CNMR** (100 MHz): 35.5, 41.0, 111.2, 114.57 (d, *J* = 21.7 Hz), 124.29 (d, *J* =56.8 Hz), 125.6, 126.6, 127.1, 127.7, 128.8, 130.9, 131.38 (d, J = 69.9 Hz), 133.8, 134.8, 134.8, 164.30 (d, *J* = 250.01Hz), 181.4, 190.7; **HRMS (ESI)**: calcd for $C_{21}H_{16}FOS_3$ [M+H] 399.0347, found 399.0348.



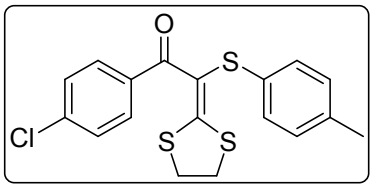
1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(phenylthio)ethan-1-one (3ma): Yield 99% (141mg), as yellow gum, R_f 0.70 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.36 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.0 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 35.5, 41.0, 117.3, 125.8, 126.2, 127.7, 129.0, 129.8, 136.2, 136.8, 137.1, 181.5, 190.8; **HRMS (ESI)**: calcd for $C_{17}H_{14}ClOS_3$ [M+H] 364.9895, found 364.9892.



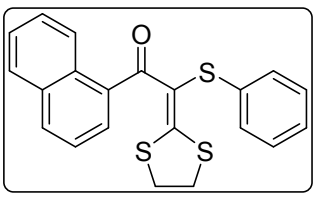
1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(4-methoxyphenyl)thio-ethan-1-one (3mb): Yield 99% (153mg), as yellow semi solid, R_f 0.63 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.38 (t, *J* = 7.2 Hz, 2H), 3.59 (t, *J* = 6.4 Hz, 2H), 3.73 (s, 3H), 6.71 (d, *J* = 8.8Hz, 2H), 6.94 (d, *J* = 8.8Hz, 2H), 7.26 (d, *J* =8.0 Hz, 2H), 7.54 (d, *J* = 8.4Hz, 2H); **^{13}CNMR** (100 MHz): 35.4, 40.9, 55.3, 113.4, 114.7, 126.7, 127.7, 129.3, 129.9, 136.8, 137.2, 158.5, 179.4, 190.8; **HRMS (ESI)**: calcd for $C_{18}H_{16}ClO_2S_3$ [M+H] 395.0001, found 395.0000.



1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-(p-tolylthio)ethan-1-one (3mc): Yield 99% (147mg), as yellow solid, M.P. 187-189^{o}C, R_f 0.76 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.37 (t, *J* = 5.6 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.00 Hz, 2H), 7.25 (d, *J* = 7.20 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 20.9, 35.9, 41.0, 111.9, 126.4, 127.7, 129.8, 129.9, 132.6, 135.8, 136.8, 137.1, 190.8; **HRMS (ESI)**: calcd for $C_{18}H_{16}ClOS_3$ [M+H] 379.0052, found 379.0050.

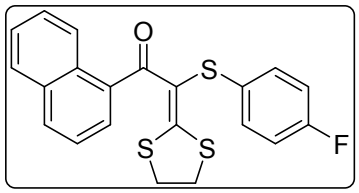


2-(1,3-Dithiolan-2-ylidene)-1-(naphthalen-1-yl)-2-(phenylthio)ethan-1-one (3na): Yield 97% (135mg), as pale yellow semi solid, R_f 0.81 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.39 (t, *J* = 7.2 Hz, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.23 – 7.27 (m, 1H), 7.28 – 7.31 (m, 1H), 7.35 – 7.45 (m, 2H), 7.72 (d, *J* = 12.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H); **^{13}CNMR** (100 MHz): 35.3, 41.2, 113.8, 124.2, 124.5, 125.1, 125.7, 125.8, 126.4, 126.6, 128.1, 128.7, 129.4, 130.2, 133.1, 136.5, 137.6, 180.9, 193.9; **HRMS (ESI)**: calcd for $C_{21}H_{17}OS_3$ [M+H] 381.0442, found 381.0442.

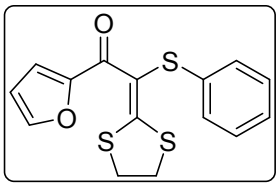


2-(1,3-Dithiolan-2-ylidene)-2-((4-fluorophenyl)thio)-1-(naphthalen-1-yl)ethan-1-one (3nd): Yield 98% (143mg), as yellow solid, M.P. 168-170^{o}C, R_f 0.83 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.42 (t, *J* = 7.2 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 6.73 (t, *J* = 8.4 Hz, 1H), 6.80 – 6.85 (m,

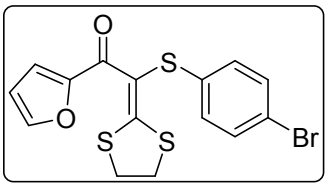
1H); 7.00 (t, J = 8.8 Hz, 1H), 7.25 (d, J = 4.4 Hz, 1H), 7.30 – 7.39 (m, 2H), 7.40 – 7.55 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 7.6 Hz, 2H); **^{13}CNMR** (100 MHz): 35.4, 41.2, 112.5, 115.77 (d, J = 22.3 Hz), 124.46 (d, J = 41.2 Hz), 125.1, 125.9, 126.2, 126.4, 126.6, 128.1, 129.5, 129.6, 130.2, 131.3, 133.1, 137.6, 162.7 (d, J = 246.0 Hz), 180.2, 193.8; **HRMS (ESI)**: calcd for $C_{21}H_{16}FOS_3$ [M+H] 399.0347, found 399.0347.



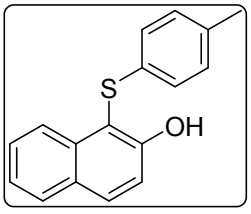
2-(1,3-Dithiolan-2-ylidene)-1-(furan-2-yl)-2-(phenylthio)ethan-1-one (3oa): Yield 99% (150mg), as yellow gum, R_f 0.76 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.31 (t, J = 6.8 Hz, 2H), 3.58 (t, J = 6.0 Hz, 2H), 6.40 (dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, 1H), 7.11 – 7.18 (m, 3H), 7.23 (d, J = 7.6 Hz, 2H), 7.54 – 7.56 (m, 1H), 7.62 (d, J = 3.6 Hz, 1H); **^{13}CNMR** (100 MHz): 35.0, 41.0, 109.1, 111.8, 119.7, 125.6, 129.2, 136.4, 146.2, 151.1, 176.6, 183.2; **HRMS (ESI)**: calcd for $C_{15}H_{13}O_2S_3$ [M+H] 321.0078, found 321.0077.



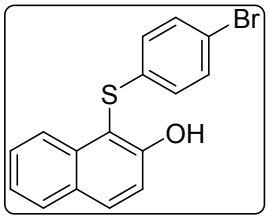
2-(4-Bromophenyl)thio-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one (3oe): Yield 98% (184mg), as yellow gum, R_f 0.85 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 3.33 (t, J = 7.2 Hz, 2H), 3.59 (t, J = 6.4 Hz, 2H), 6.40 – 6.43 (m, 1H); 7.02 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.50 – 7.59 (m, 2H); **^{13}CNMR** (100 MHz): 35.0, 41.0, 108.4, 111.9, 119.3, 119.6, 127.1, 131.2, 135.7, 146.4, 151.0, 176.3, 183.7; **HRMS (ESI)**: calcd for $C_{15}H_{12}BrO_2S_3$ [M+H] 398.9183, found 398.9181.



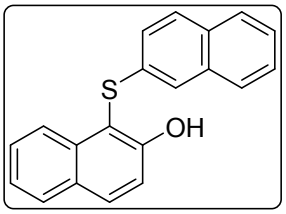
1-(p-Tolylthio)naphthalen-2-ol (5ac)[3]: Yield 99% (183mg), as yellow solid, M.P. 79-81^{o}C (lit [4] 78-79^{o}C); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.92 – 7.00 (m, 4H), 7.20 (s, 1H), 7.30 – 7.37 (m, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H).



1-(4-Bromophenyl)thionaphthalen-2-ol (5ae)[3]: Yield 98% (224mg), as brown solid; M.P: 104–106^{o}C (Lit [4] 103–105^{o}C); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 6.88 (d, J = 8.4Hz, 2H), 7.08 (s, 1H), 7.25 – 7.31 (m, 2H), 7.32 – 7.42 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H).

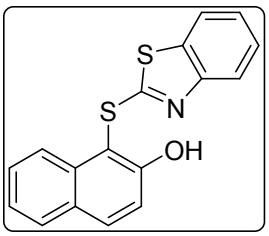


1-(Naphthalen-2-ylthio)naphthalen-2-ol (5af)[3]: Yield 99% (208mg), as white solid; M.P 92–94^{o}C (lit[3] 94-95^{o}C); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 7.16

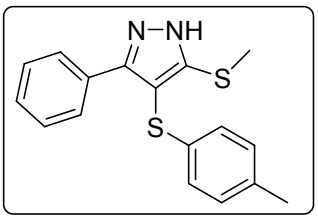


- 7.24 (m, 2H), 7.35 – 7.44 (m, 5H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.59 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.74 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H).

1-(Benzo[d]thiazol-2-ylthio)naphthalen-2-ol (5ag): Yield 99% (212mg), as yellow oil, R_f 0.75 in (10% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.52 – 7.57 (m, 2H), 7.71 – 7.75 (m, 4H), 7.92 (d, *J* = 8.4 Hz, 2H); **^{13}CNMR** (100 MHz): 86.1, 109.4, 116.4, 117.7, 123.5, 124.1, 126.3, 126.4, 127.7, 128.1, 128.2, 129.6, 129.8, 130.2, 130.5, 134.8, 153.7; **HRMS (ESI)**: calcd for $C_{17}H_{12}NOS_2$ [M+H] 310.0360, found 310.0361.



5-(Methylthio)-3-phenyl-4-(p-tolylthio)-1H-pyrazole (6): Yield 98% (88 mg), as yellow solid, M.P. 142-144^{o}C, R_f 0.42 in (30% EA/PET); **^{1}HNMR** (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.51 (s, 3H), 6.80 – 7.50 (m, 4H), 7.38 – 7.43 (m, 3H), 7.66 – 7.71 (m, 2H), 10.64 (sb, 1H, NH); **^{13}CNMR** (100 MHz): 14.9, 20.9, 125.5, 126.2, 127.3, 128.5, 128.8, 128.9, 129.3, 129.7, 133.8, 135.1; **HRMS (ESI)**: calcd for $C_{17}H_{17}N_2S_2$ [M+H] 313.0833, found 313.0834.



Refences

1. (a) P. Dhanalakshmi, S. Thimmarayaperumal and S. Shanmugam, *RSC Adv.,* 2014, **4**, 12028; (b) L. Zhu, H. Yu, Q. Guo, Q. Chen, Z. Xu, and R. Wang, *Org. Lett.* 2015, **17**, 1978; (c) H. Yuan, M. Wang, Y. Liu, L.Wang, J. Liu, and Q. Liu, *Chem. Eur. J.* 2010, **16**, 13450; (d) D. Liang, M.Wang, B. Bekturhun, B. Xiong, and Q, Liua, *adv. Synth. Catal.* 2010, **352**, 1593.
2. L. Deng and Y. Liu, *ACS Omega*, 2018, **3**, 11890.
3. S. K. R. Parumala, and R. K. Peddinti, *Green Chem.*, 2015, **17**, 4068.
4. X. Kang, R. Yan, G. Yu, X. Pang, X. Liu, X. Li, L. Xiang, G. Huang, *J. Org. Chem.* 2014, **79**, 10605.

COPIES OF ^{1}H NMR AND ^{13}C NMR

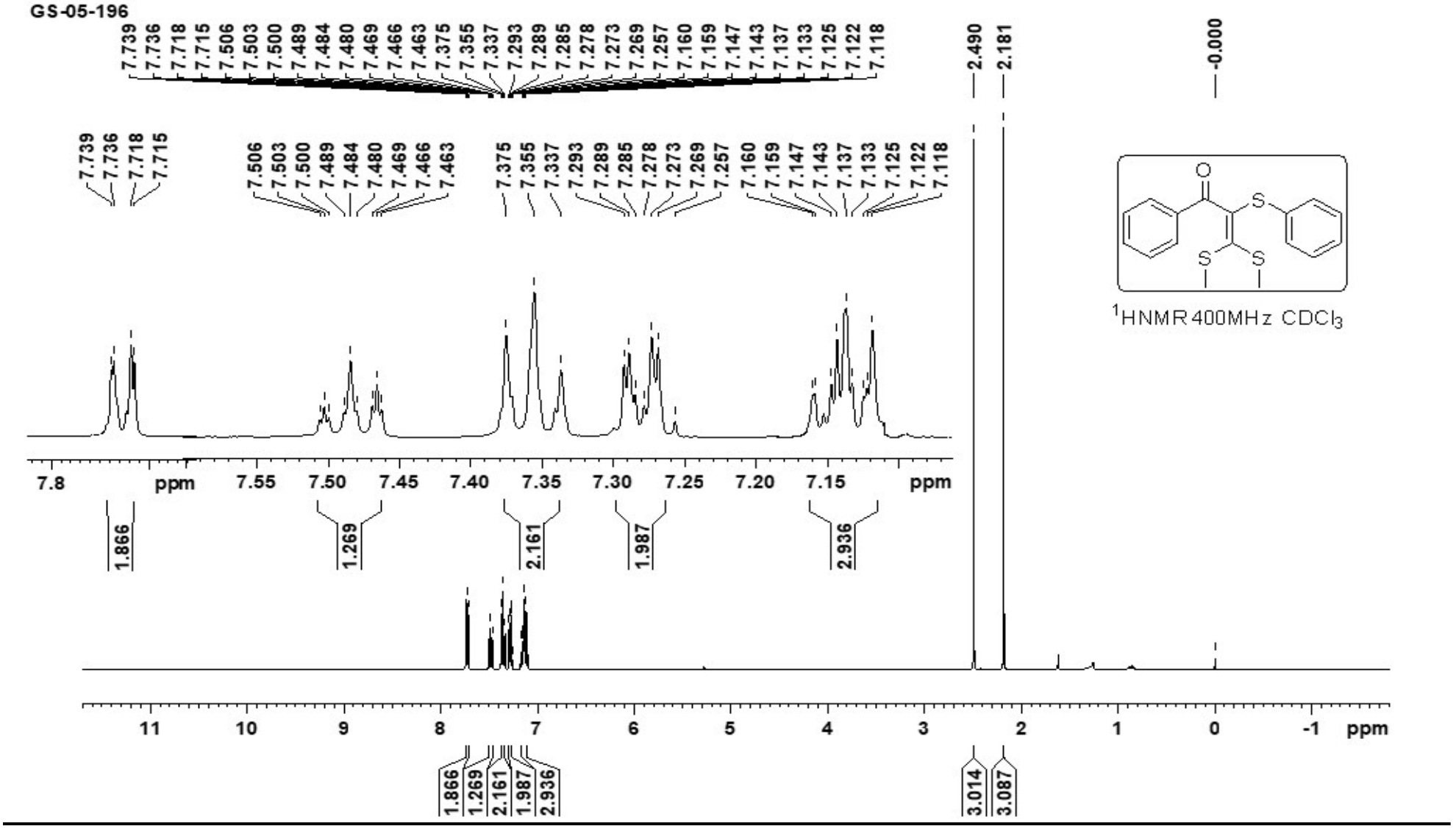


Fig.1. ^{1}H NMR Spectrum of 3aa

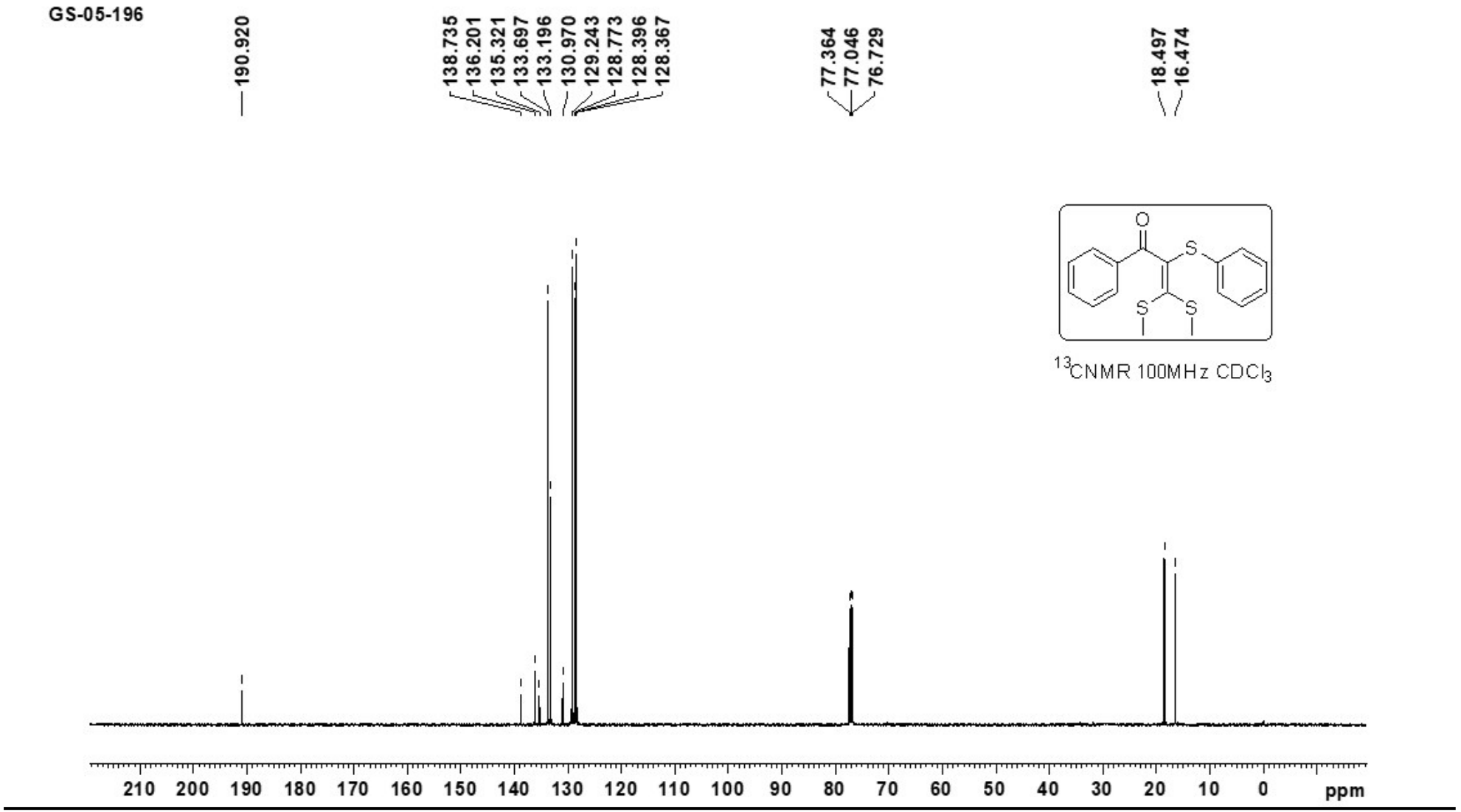


Fig.2. ^{13}C NMR Spectrum of 3aa

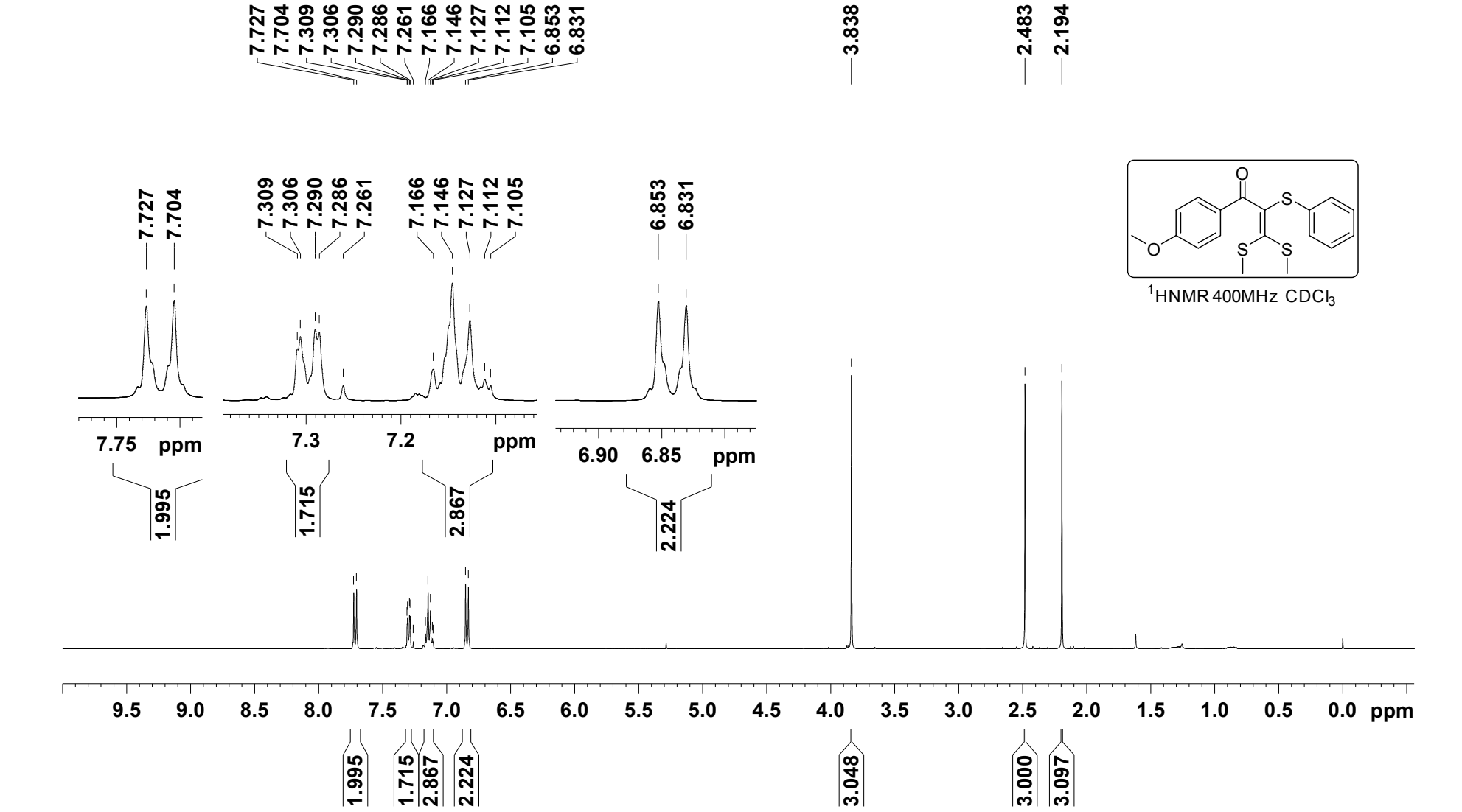


Fig.3. ^{1}H NMR Spectrum of 3ba

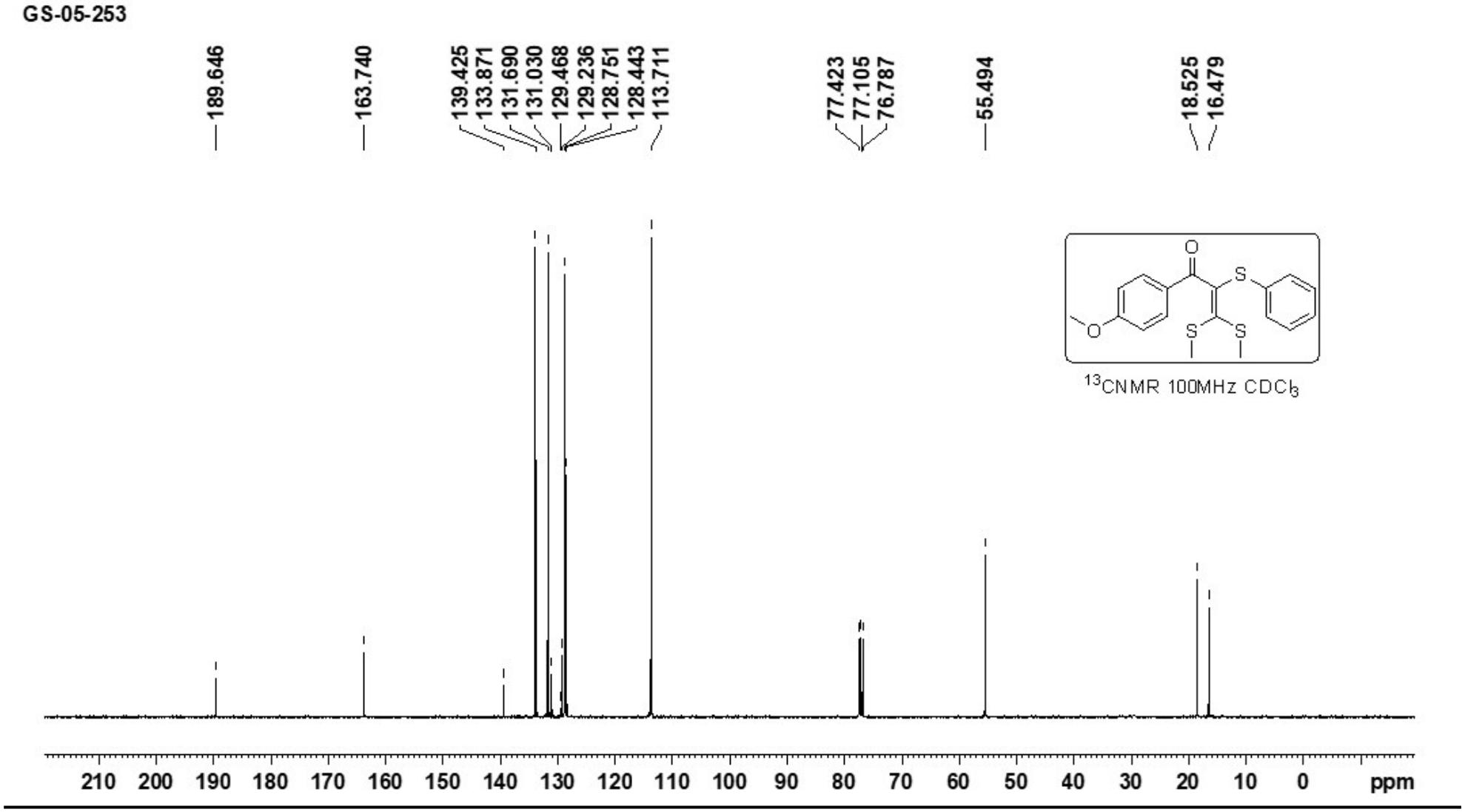


Fig.4. ^{13}C NMR Spectrum of 3ba

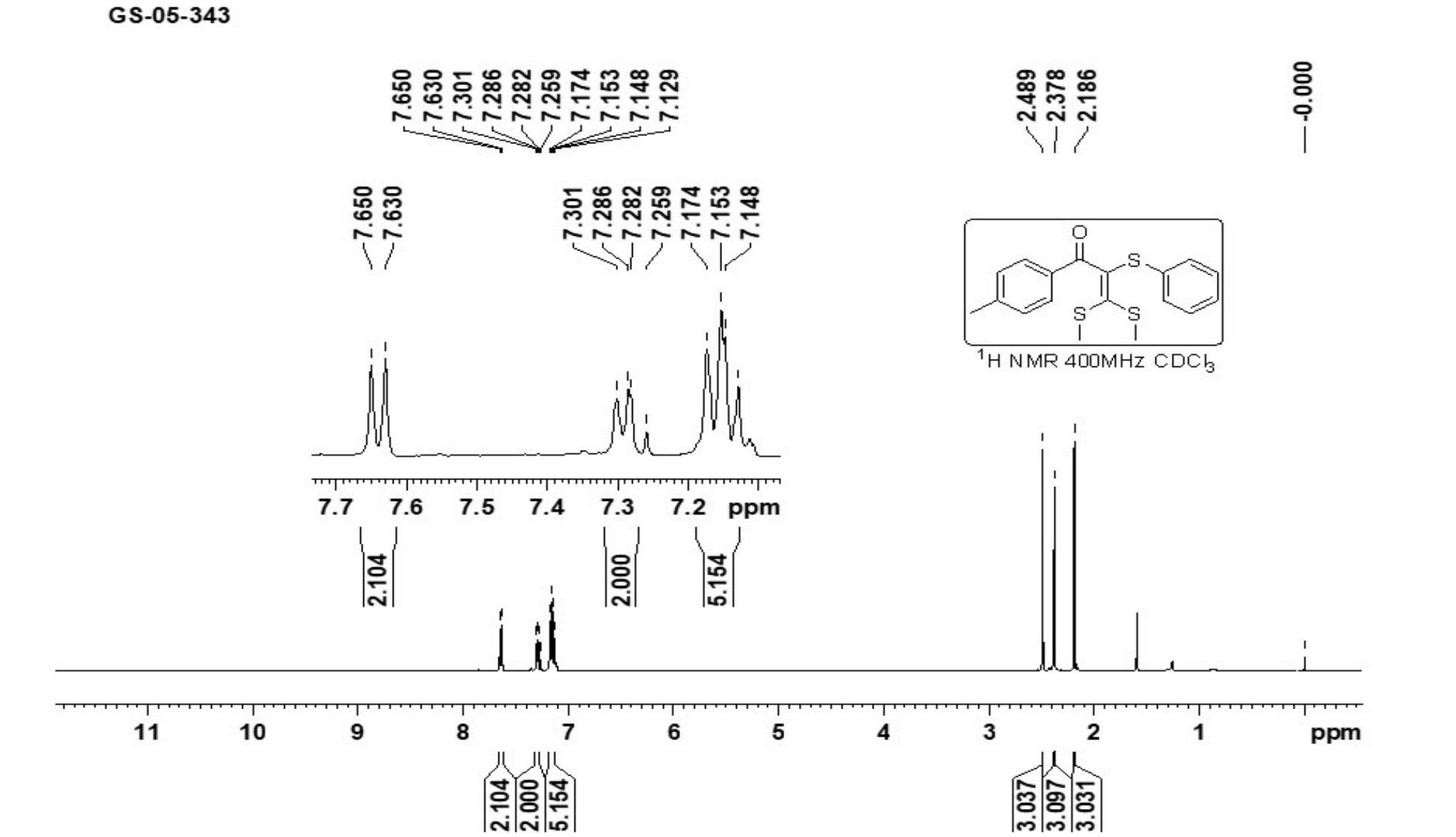


Fig.5. ^{1}H NMR Spectrum of 3ca

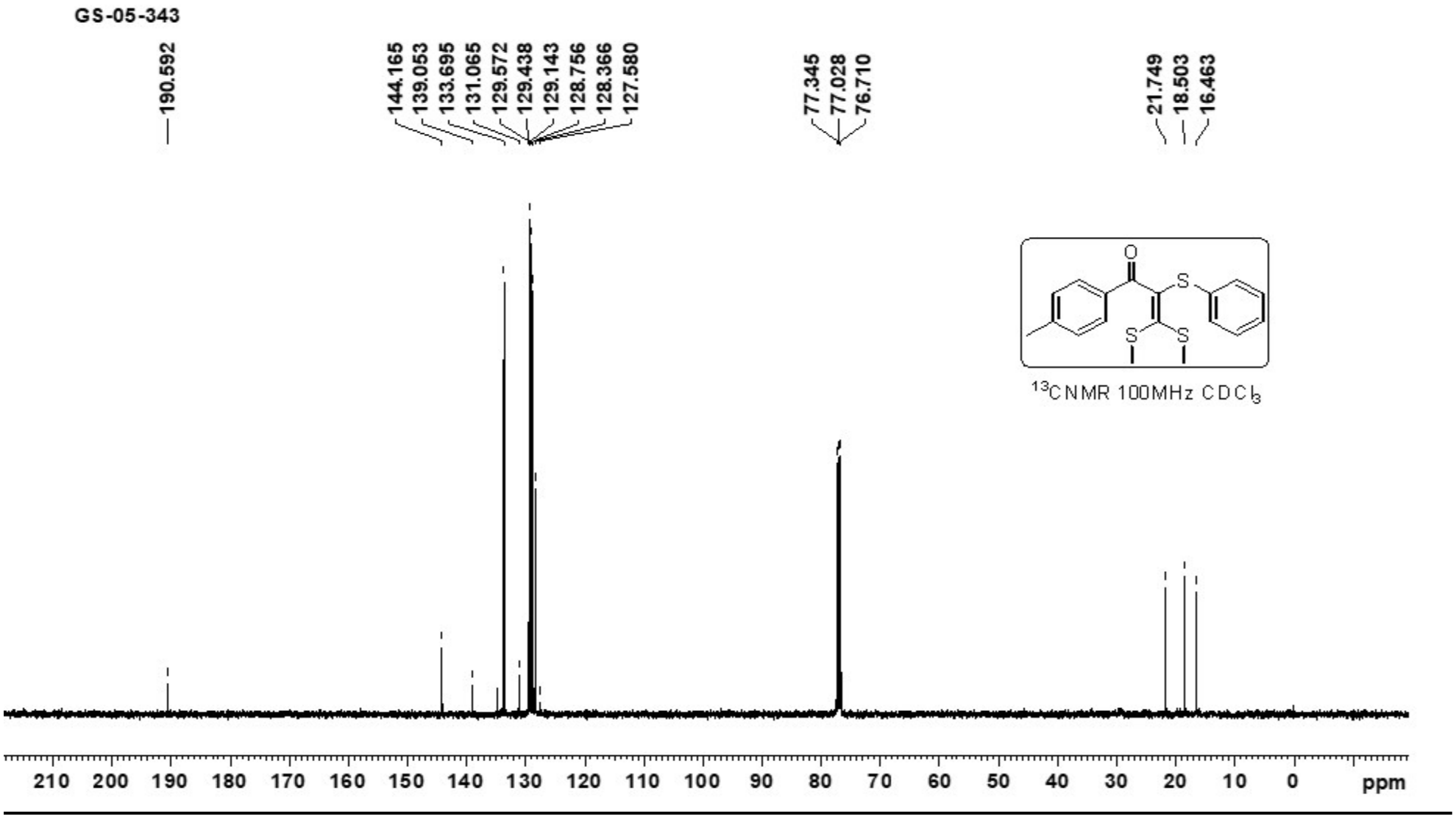


Fig.6. ^{13}C NMR Spectrum of 3ca

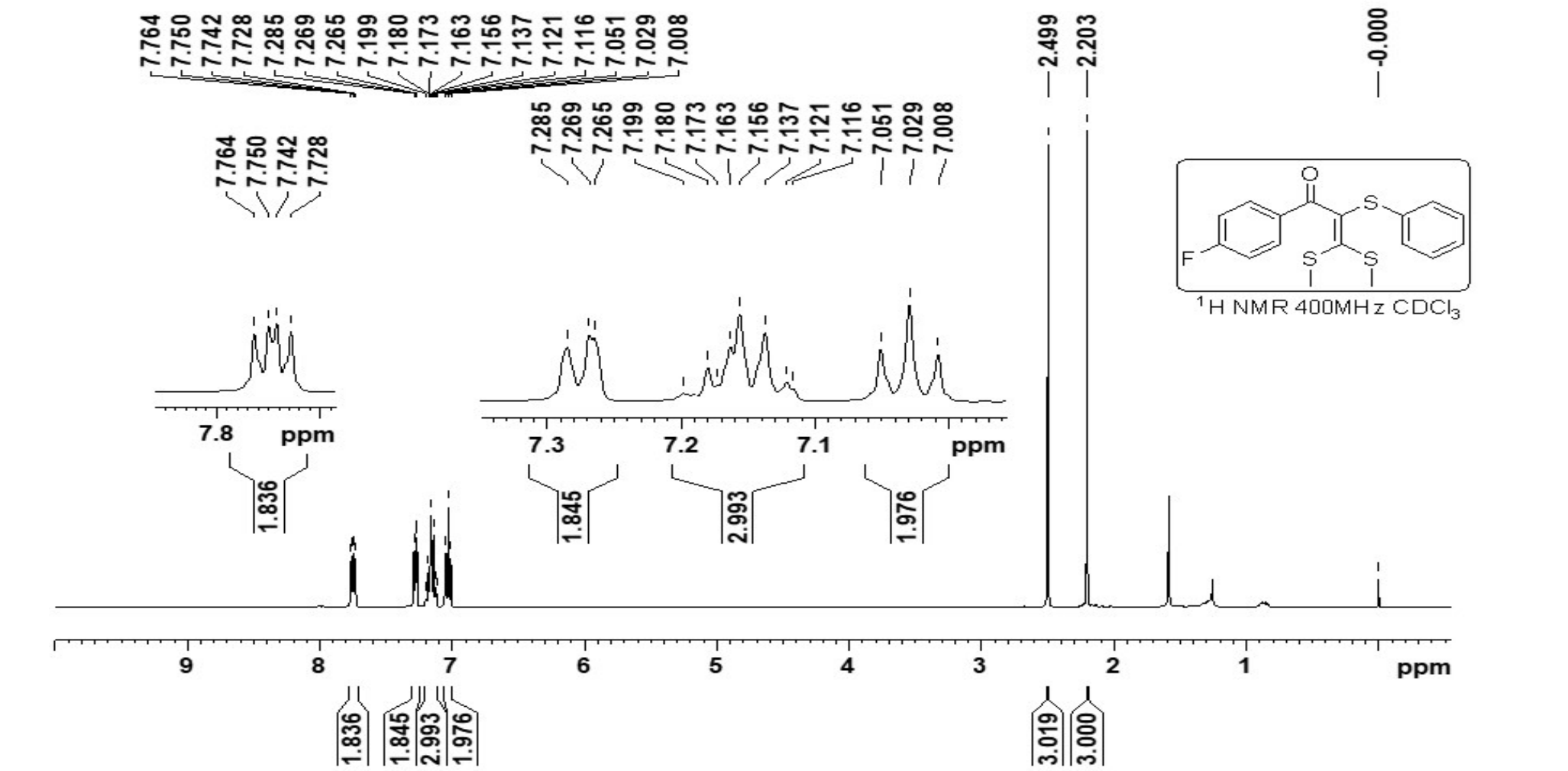


Fig. 7. [1]H NMR Spectrum of 3da

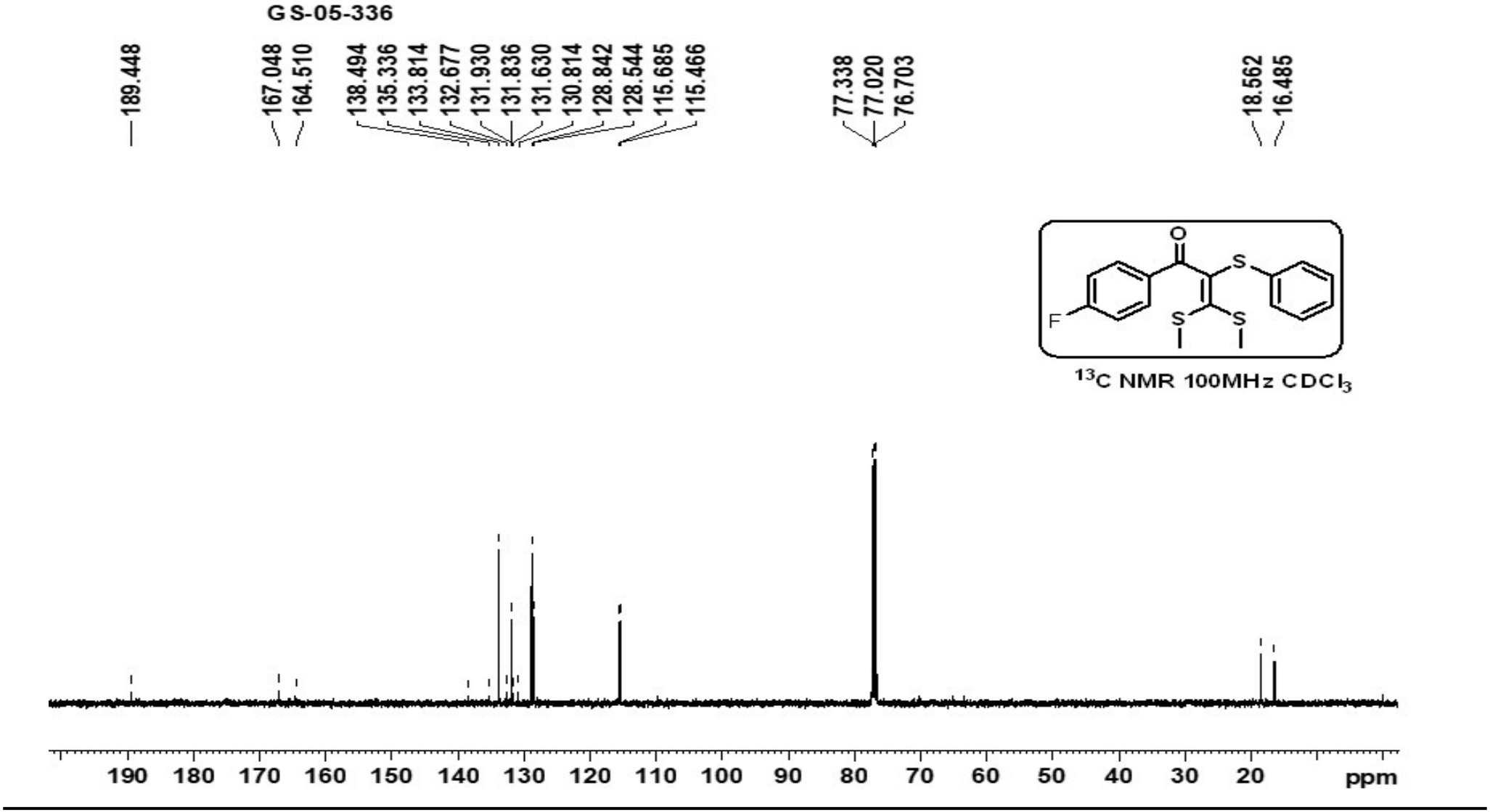


Fig. 8. ^{13}C NMR Spectrum of 3da

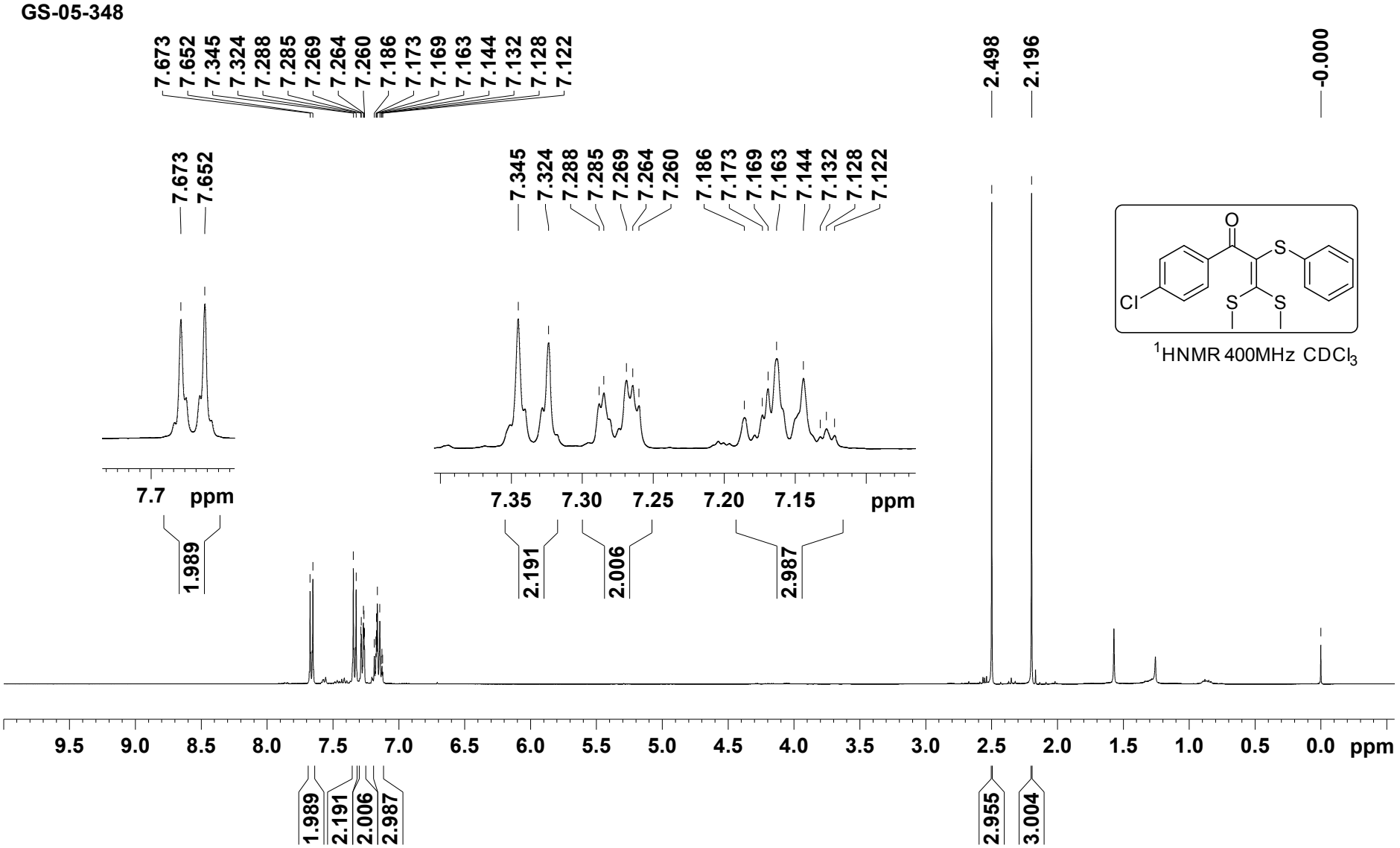


Fig. 9. ^{1}H NMR Spectrum of 3ea

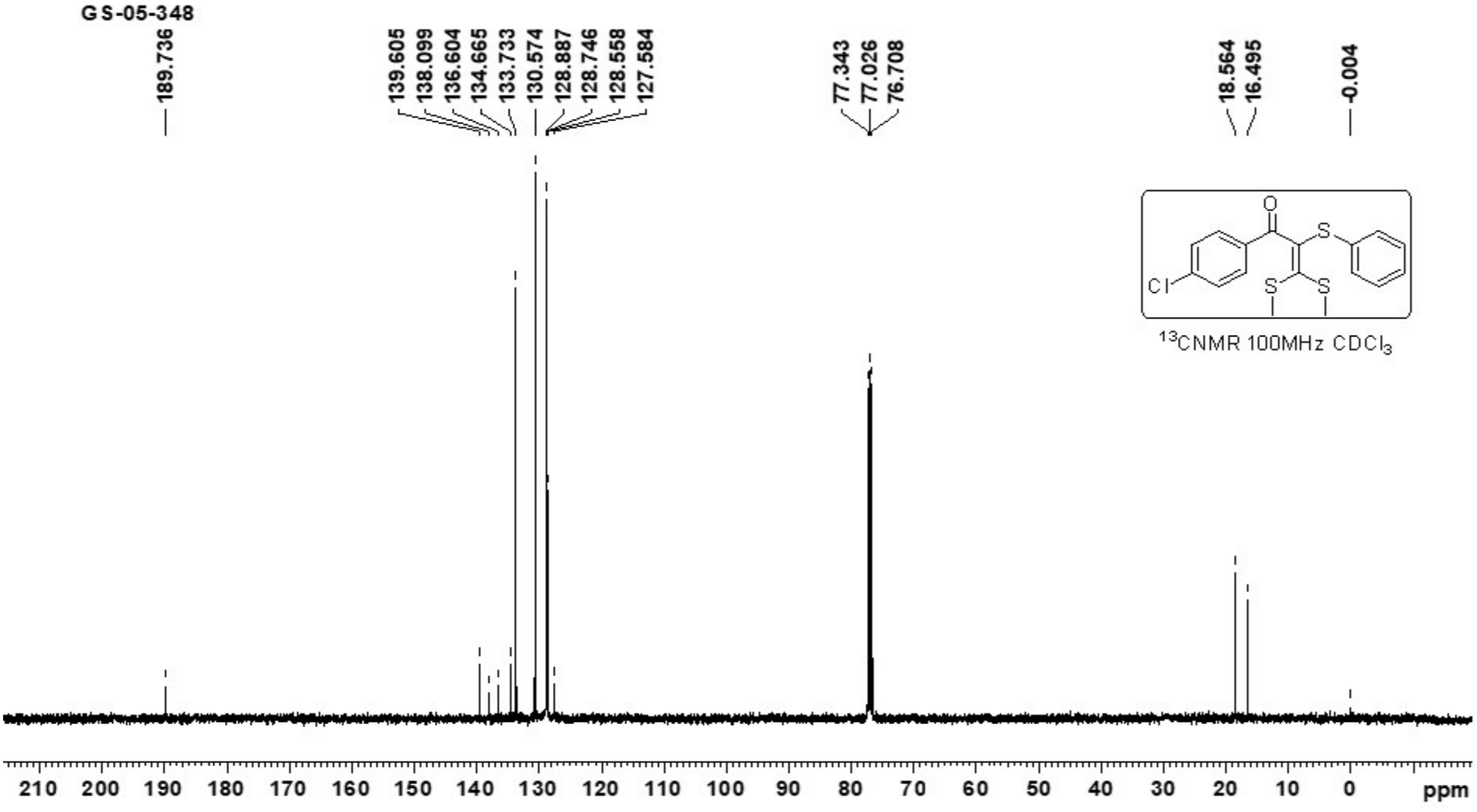


Fig. 10. ^{13}C NMR Spectrum of 3ea

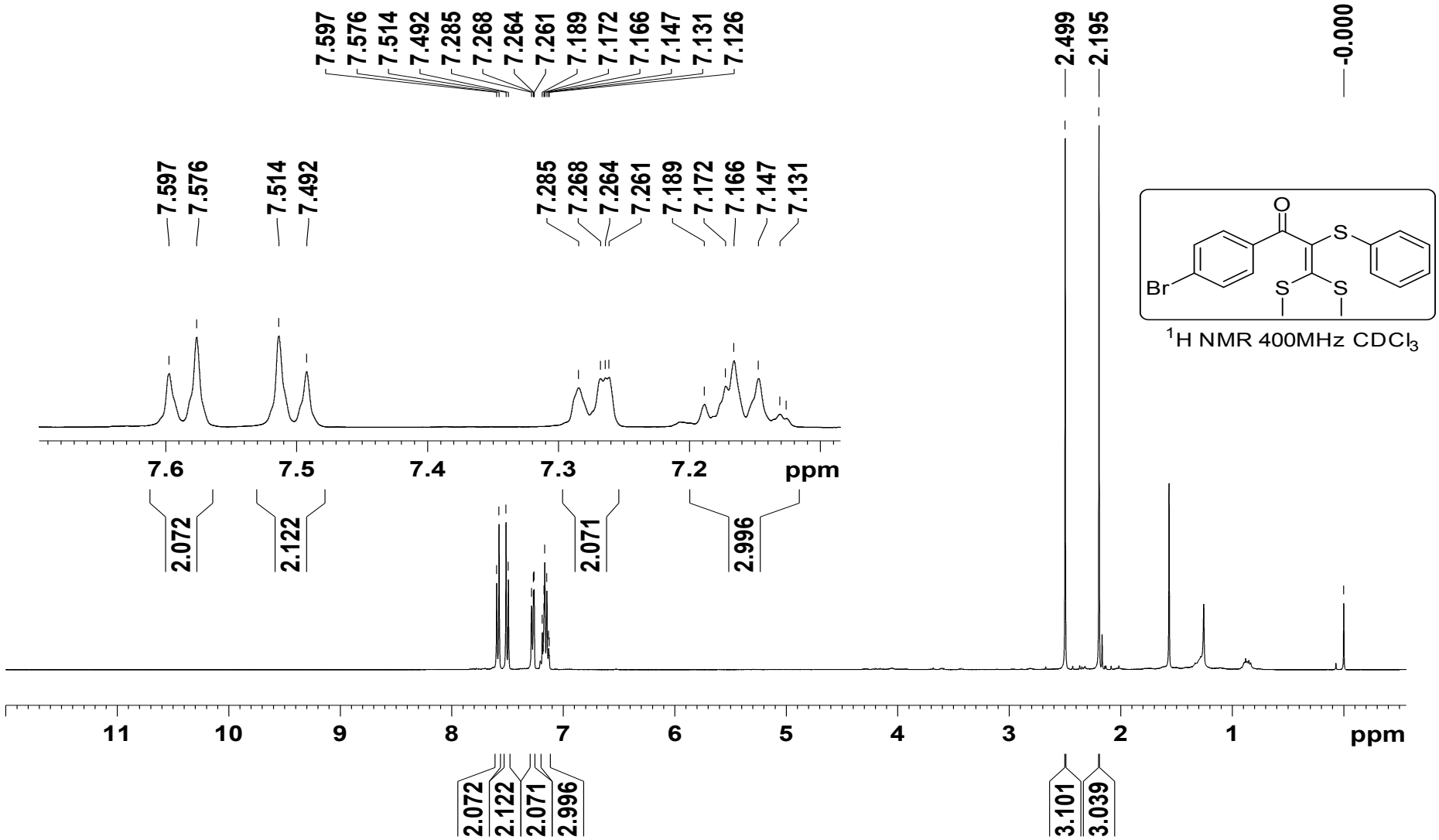


Fig. 11. ^{1}H NMR Spectrum of 3fa

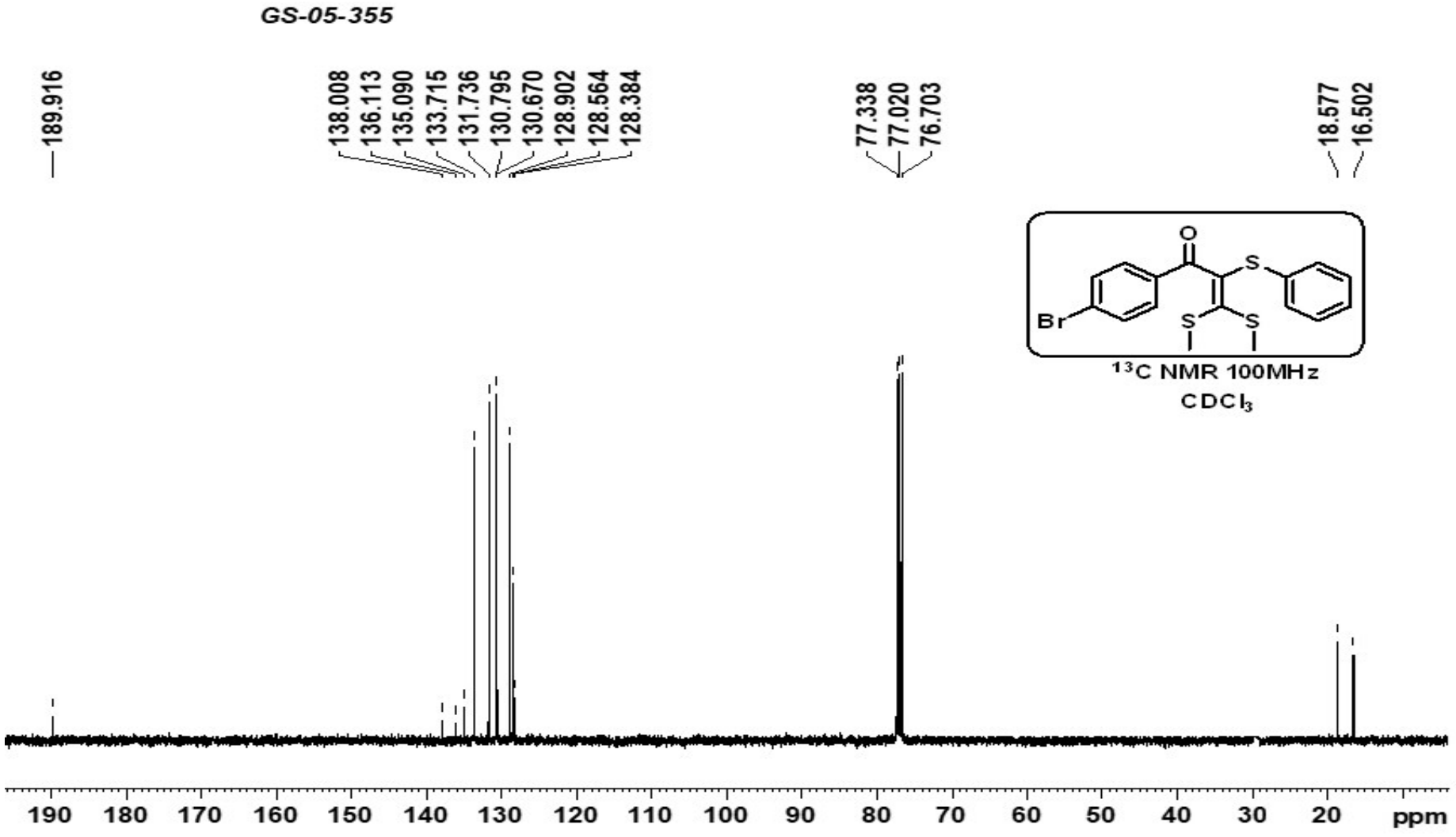


Fig. 12. ^{13}C NMR Spectrum of 3fa

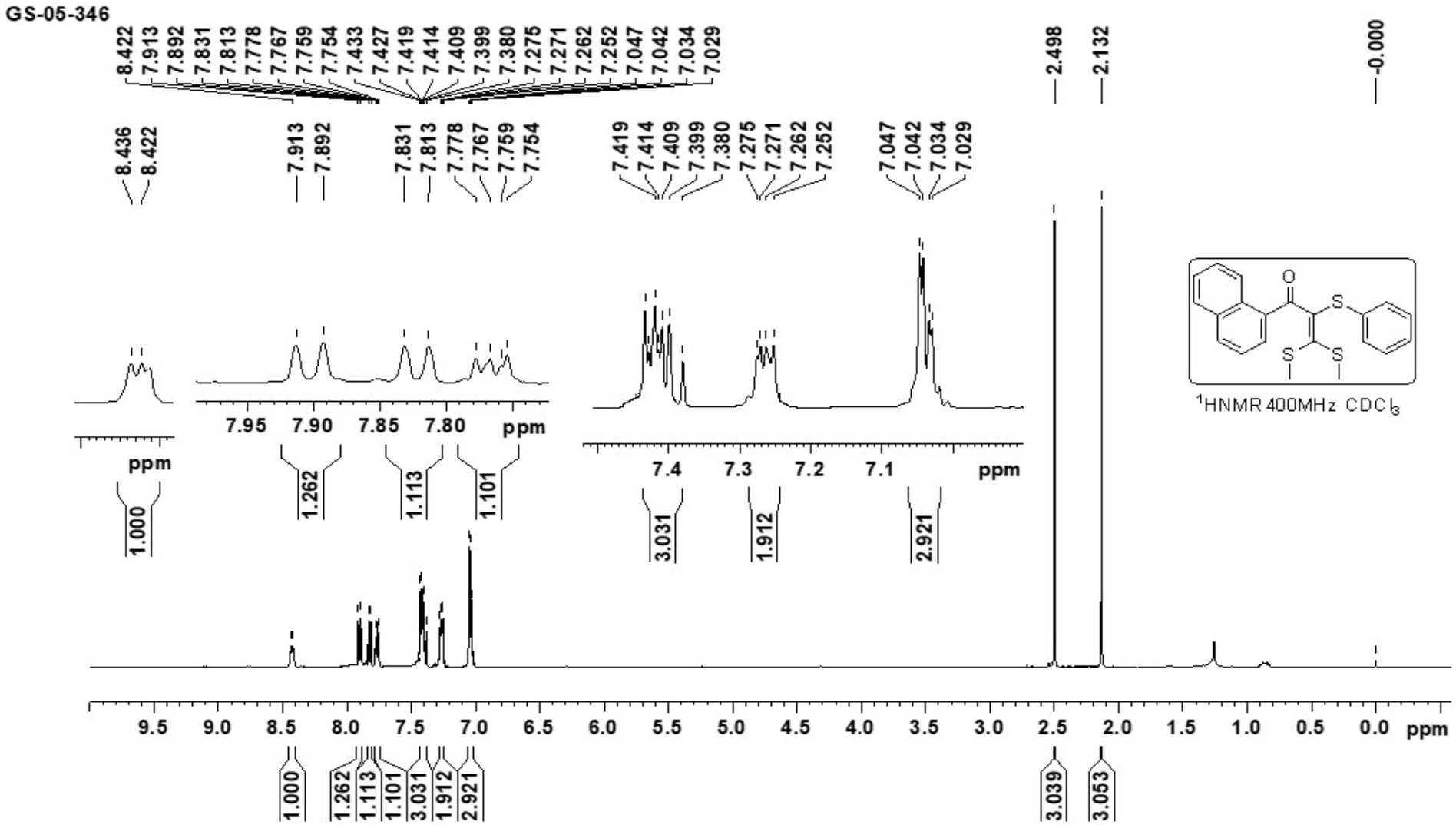


Fig. 13. ^{1}H NMR Spectrum of 3ga

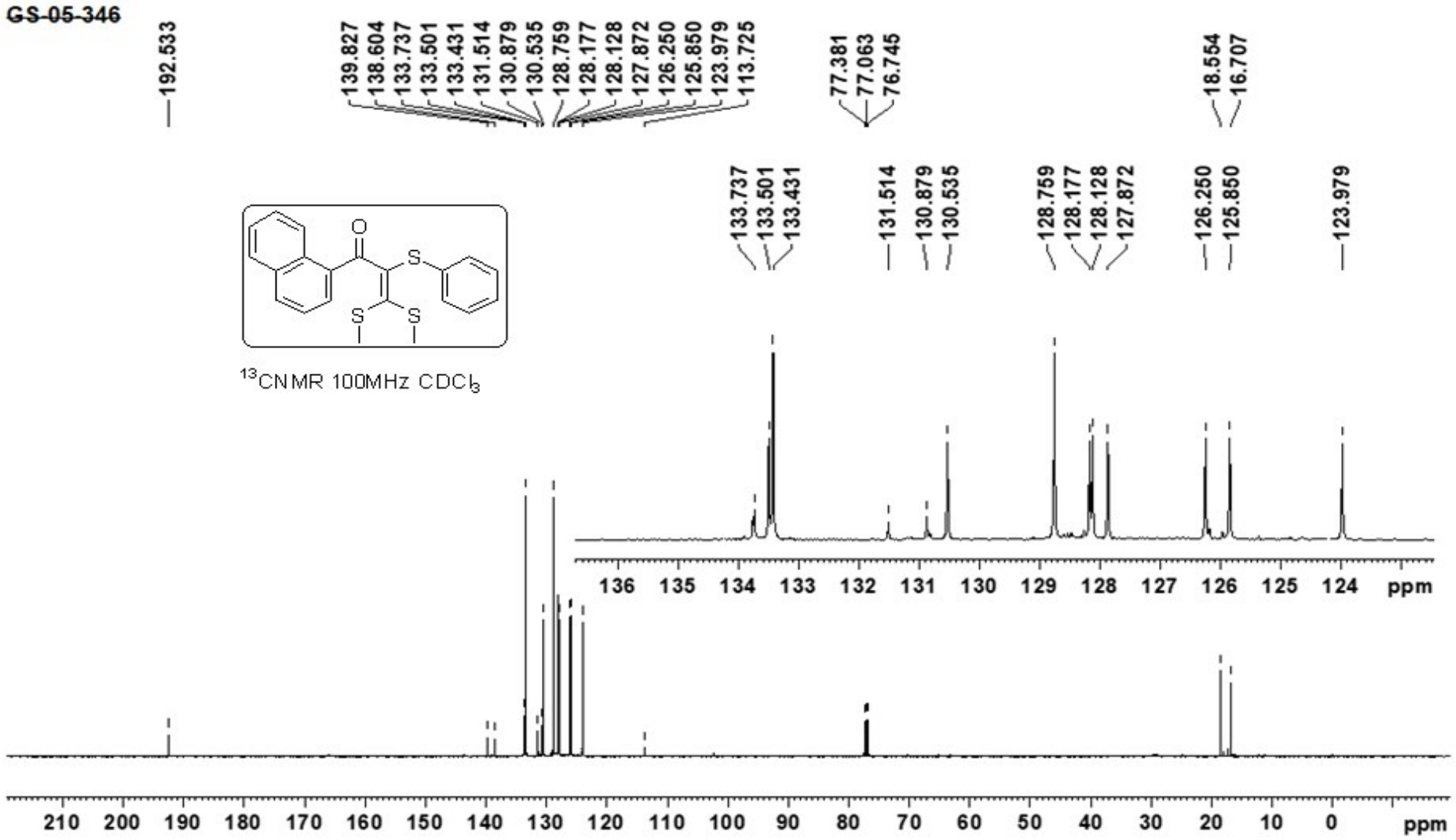


Fig. 14. ^{13}C NMR Spectrum of 3ga

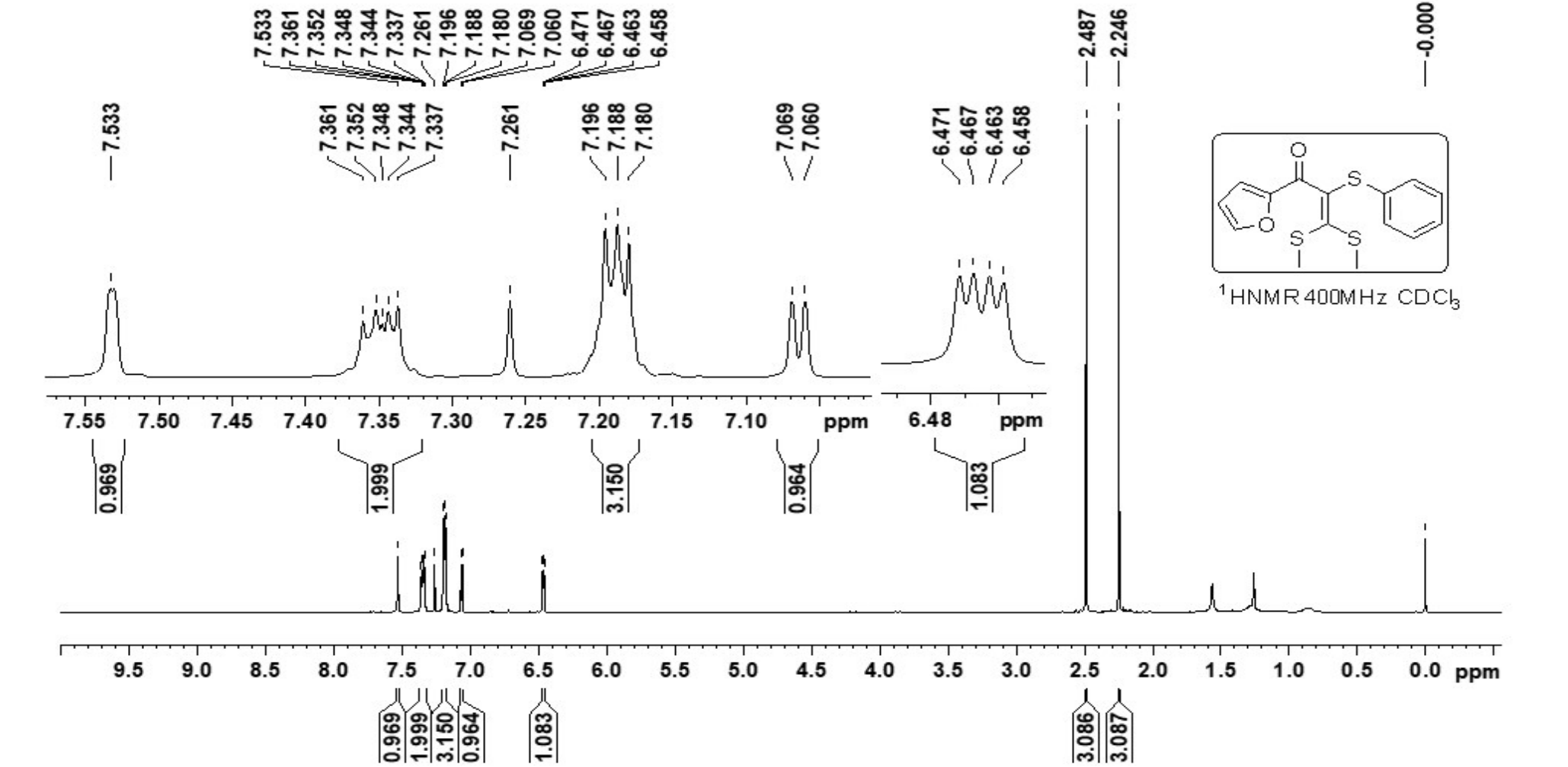


Fig. 15. ^{1}H NMR Spectrum of 3ha

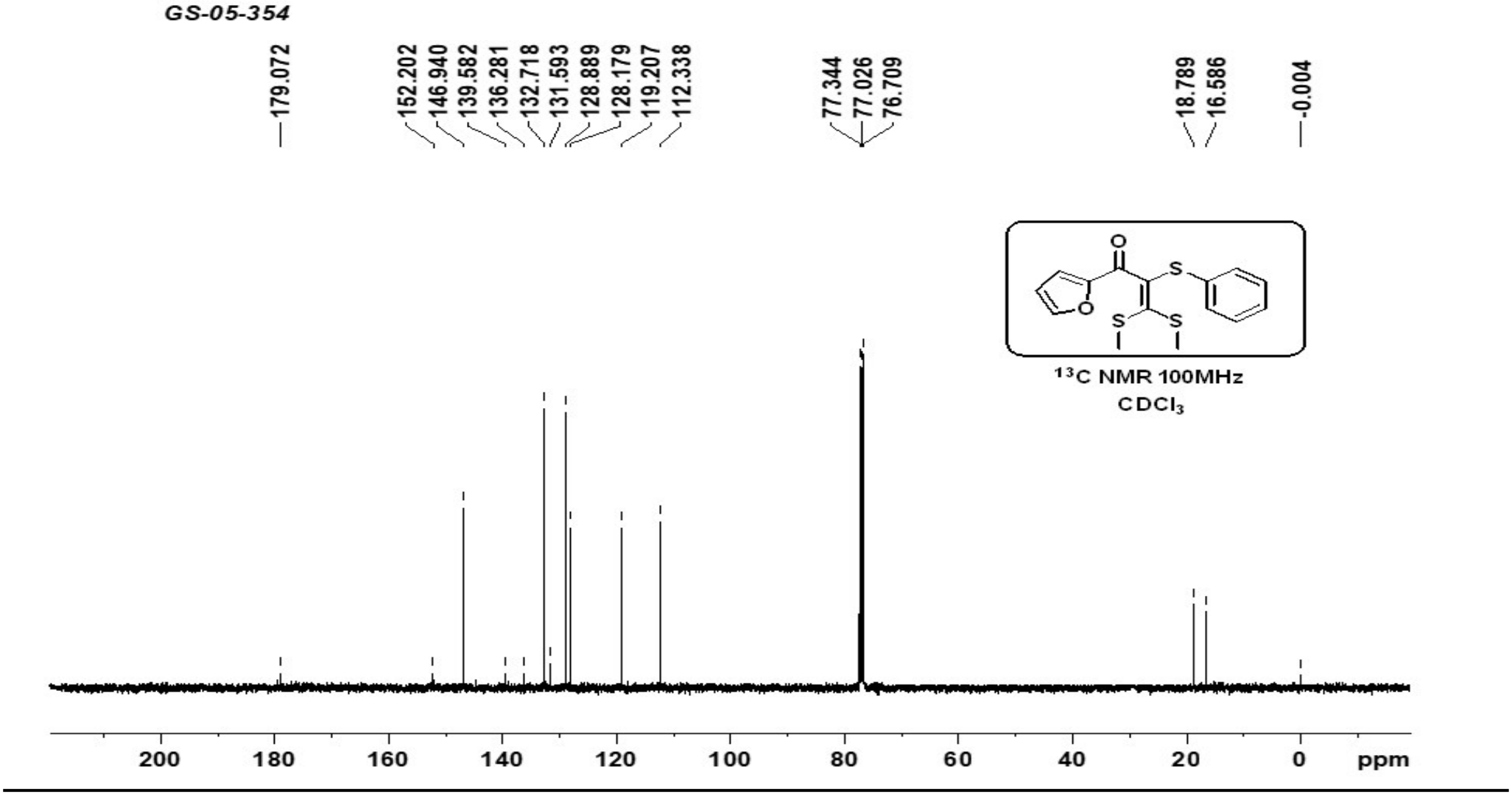


Fig. 16. ^{13}C NMR Spectrum of 3ha

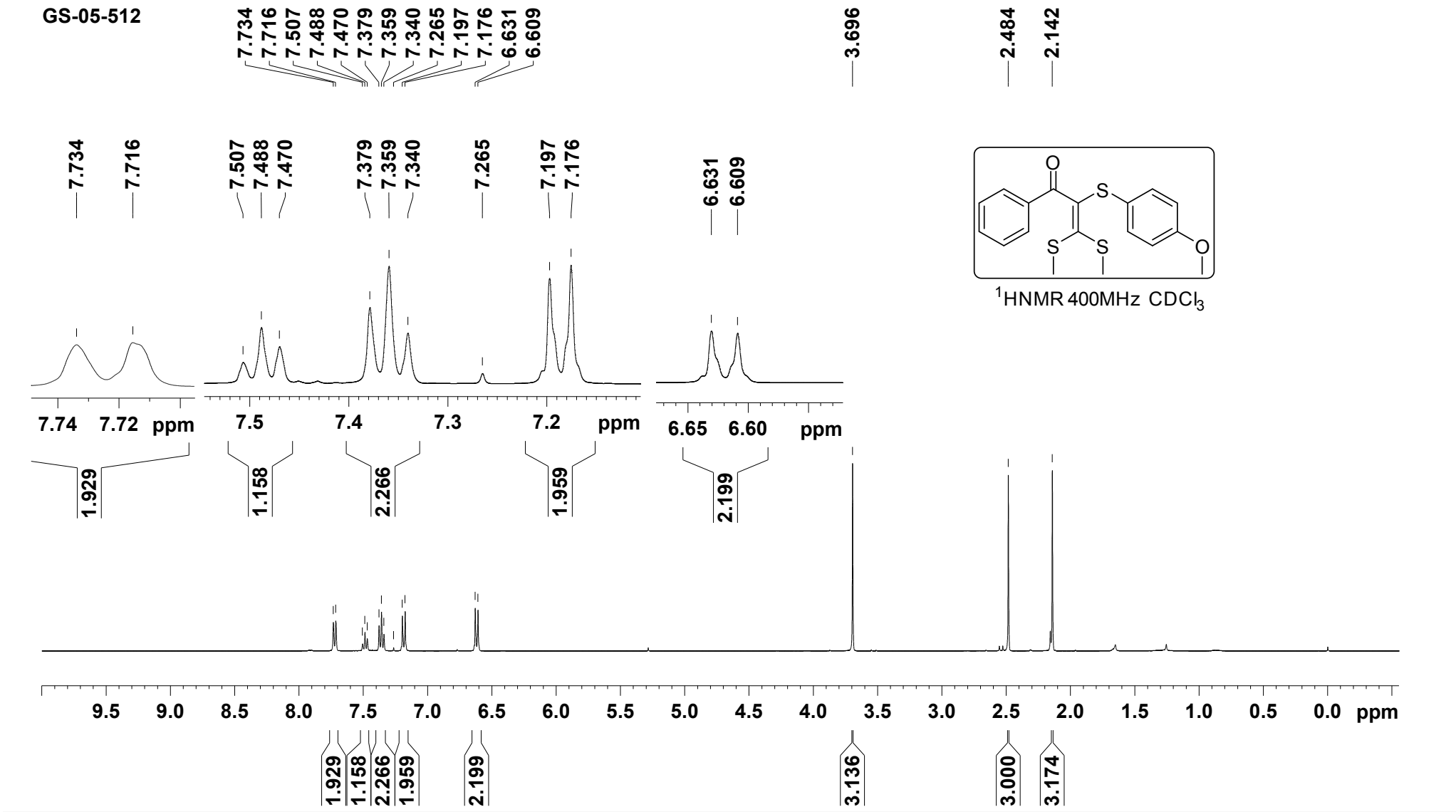


Fig. 17. [1]H NMR Spectrum of 3ab

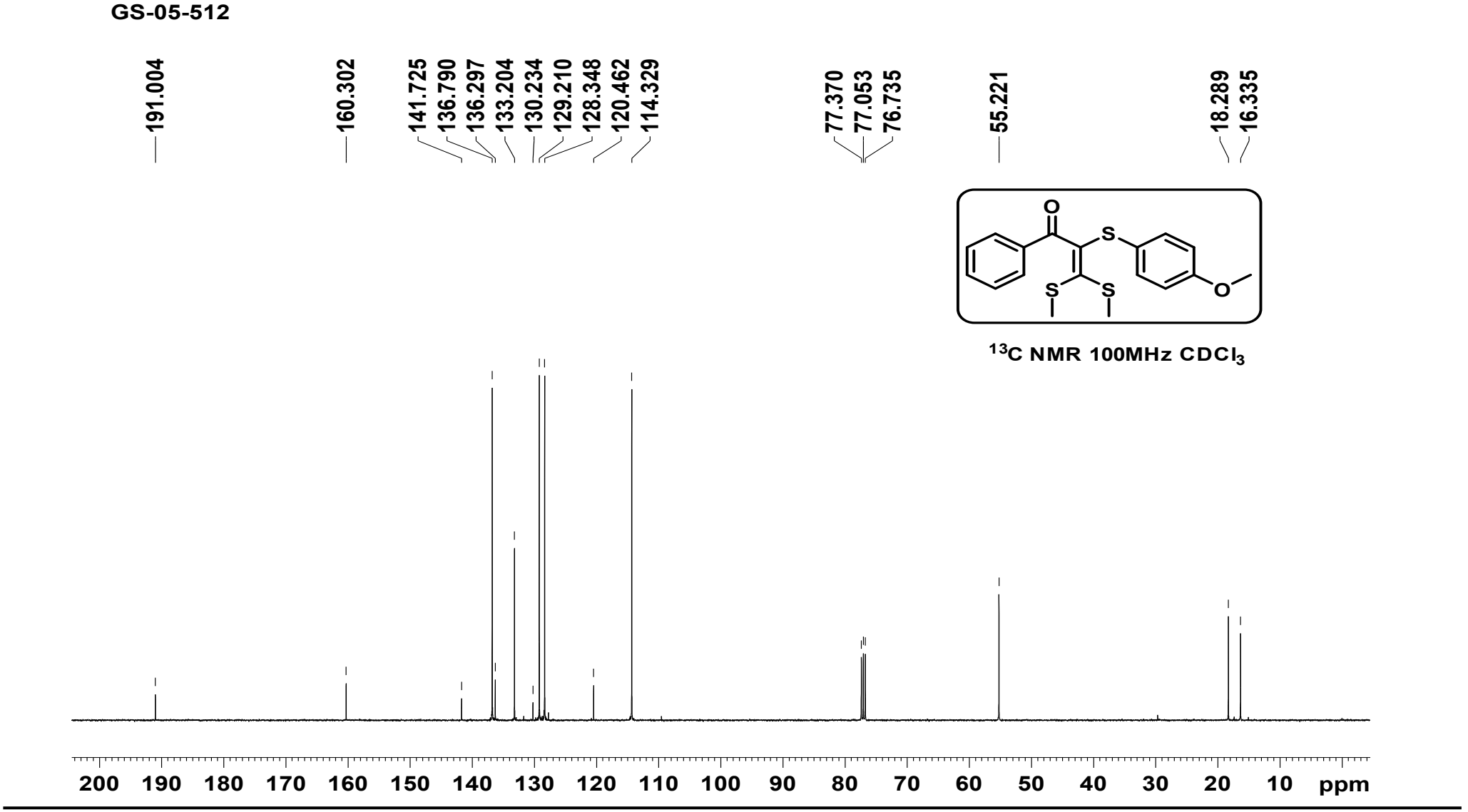


Fig. 18. ^{13}C NMR Spectrum of 3ab

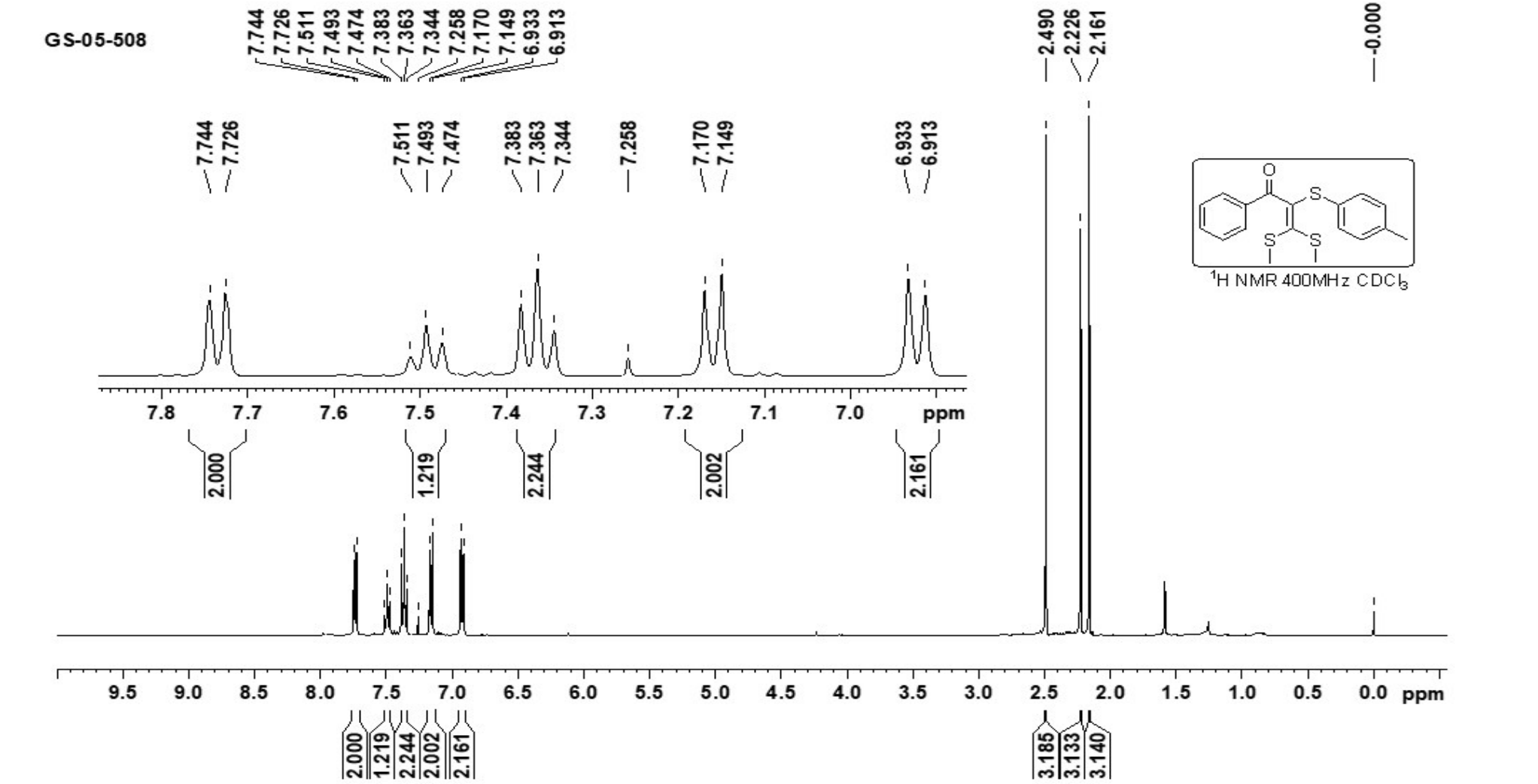


Fig. 19. ^{1}H NMR Spectrum of 3ac

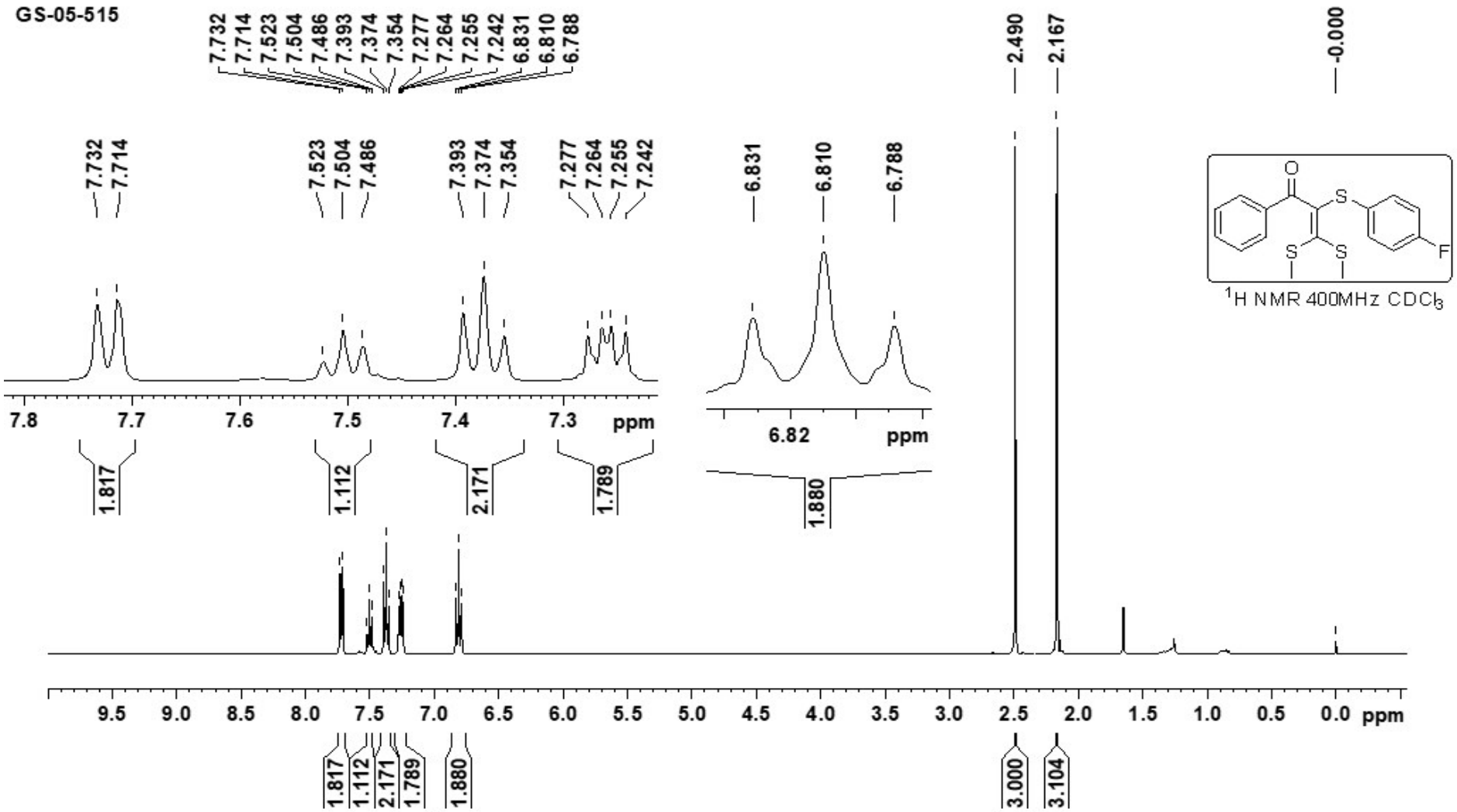


Fig. 20. ^{1}H NMR Spectrum of 3ad

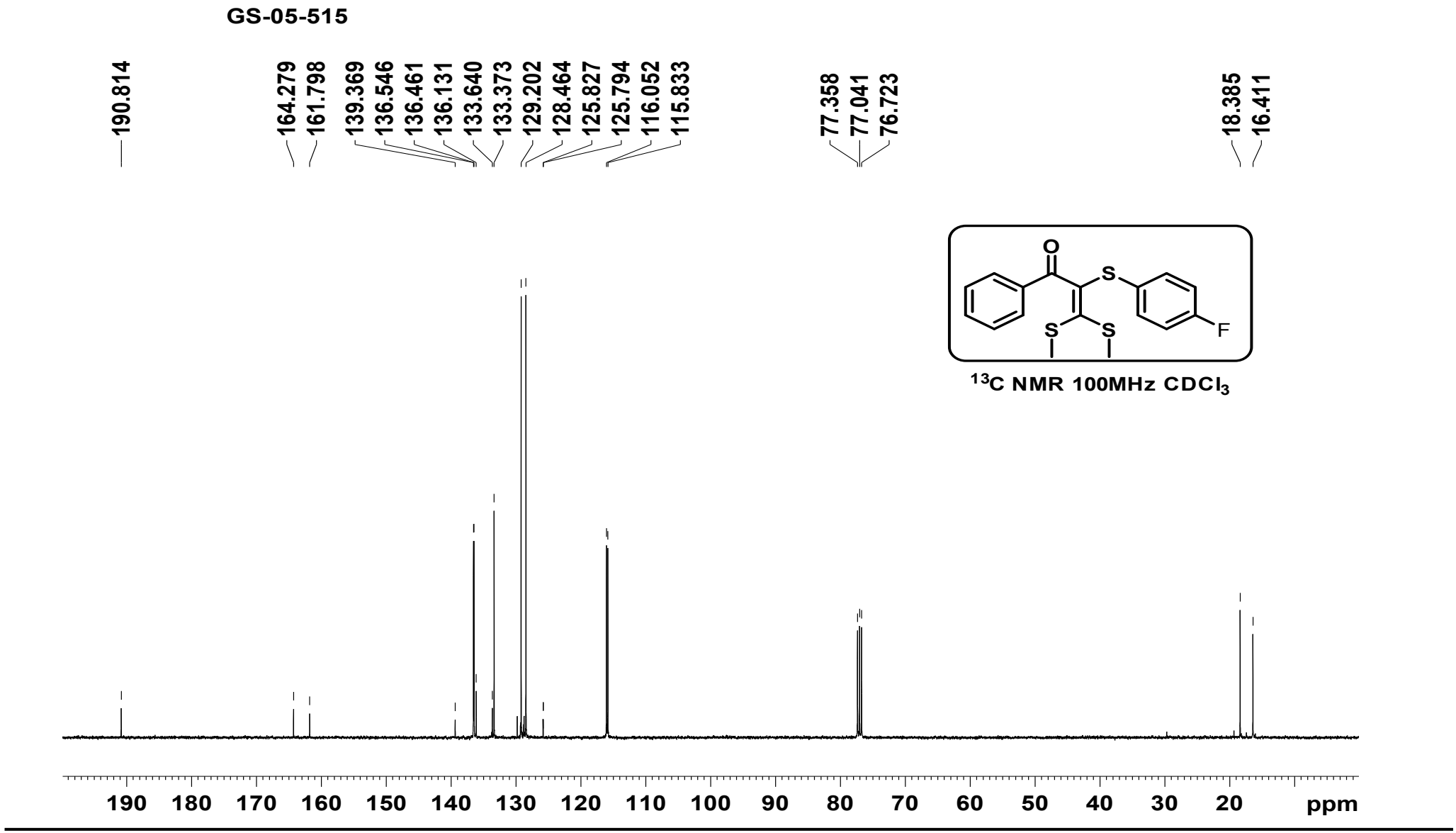


Fig. 21. ^{13}C NMR Spectrum of 3ad

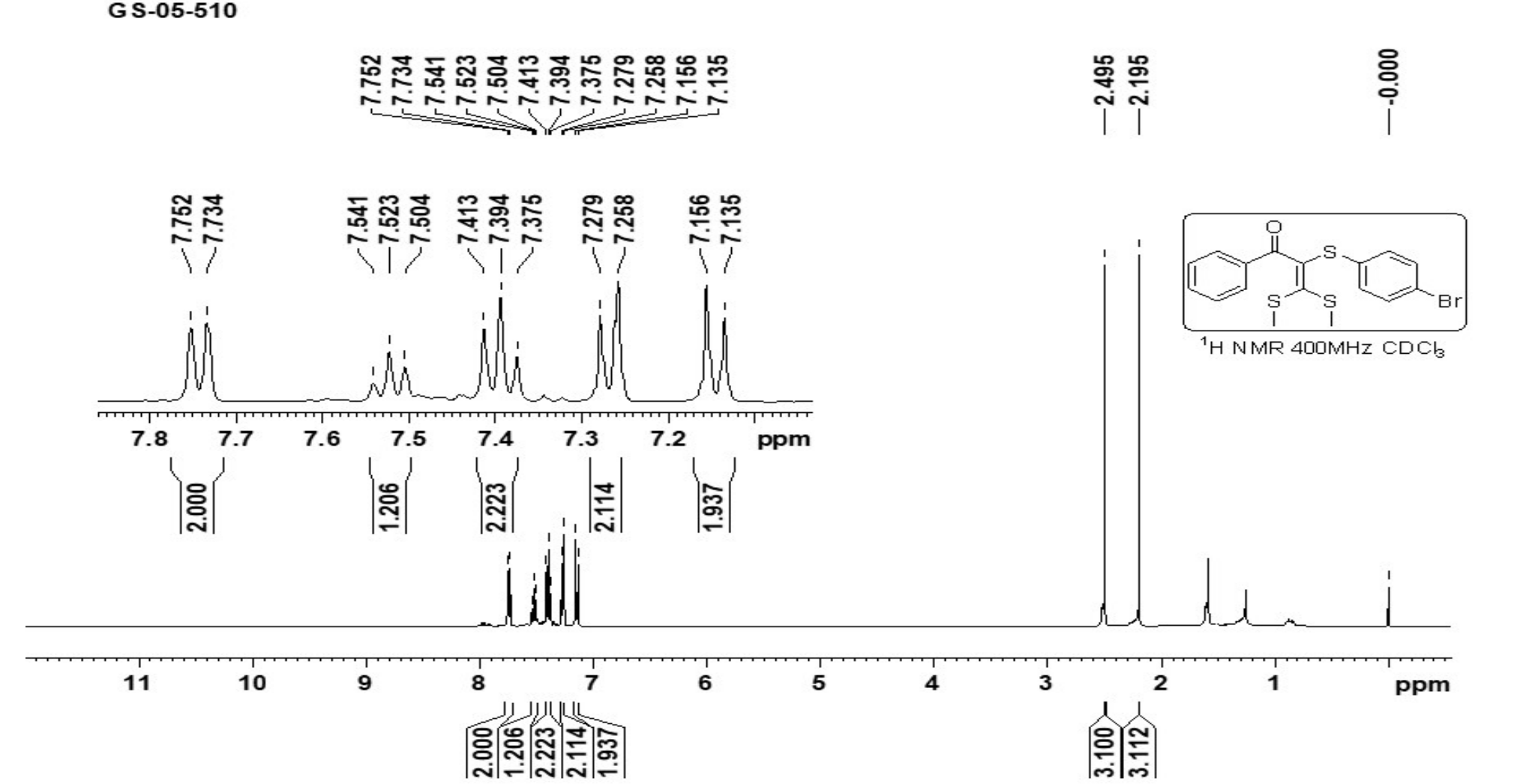


Fig. 22. ^{1}H NMR Spectrum of 3ae

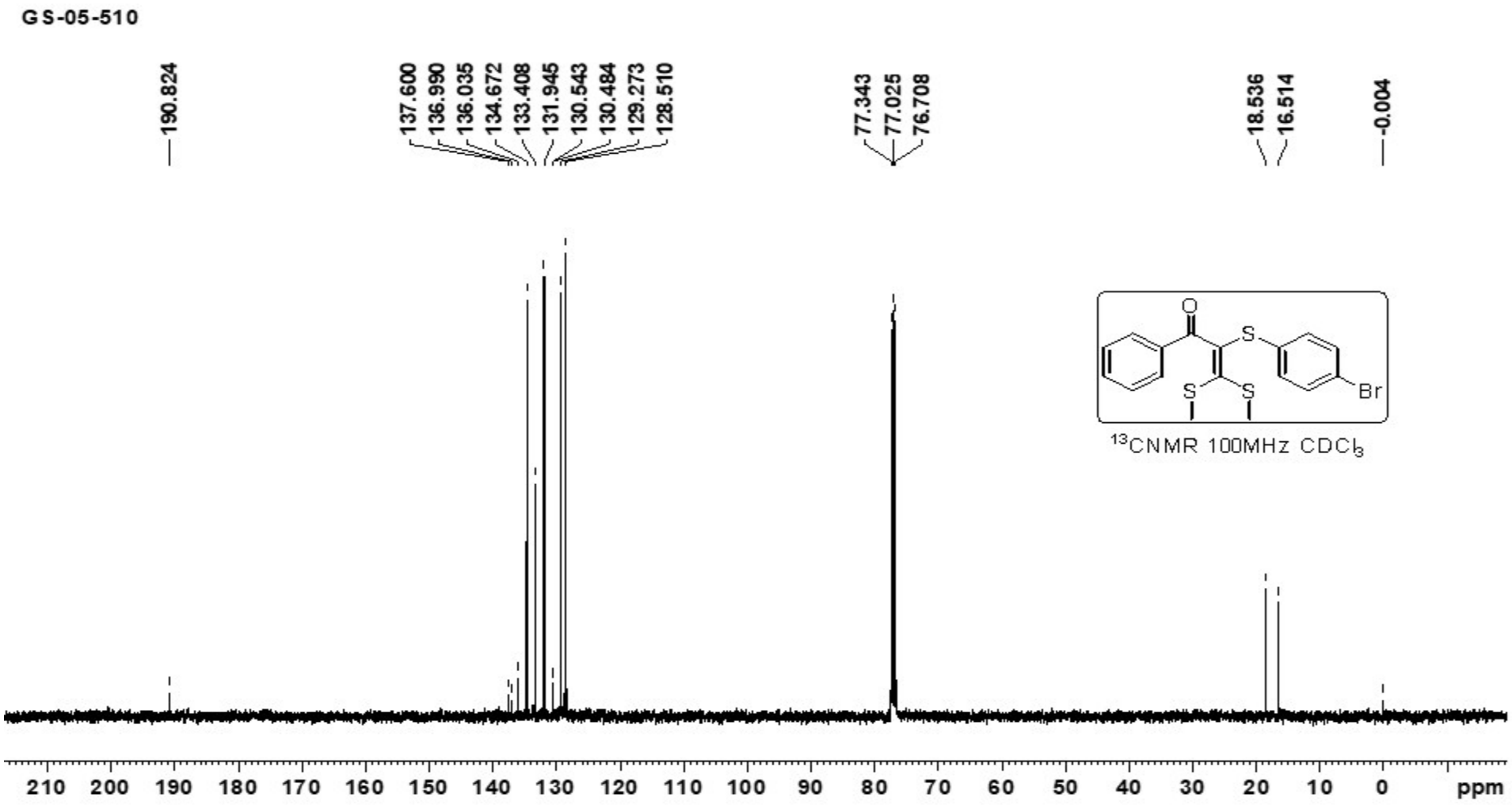


Fig. 23. ^{13}C NMR Spectrum of 3ae

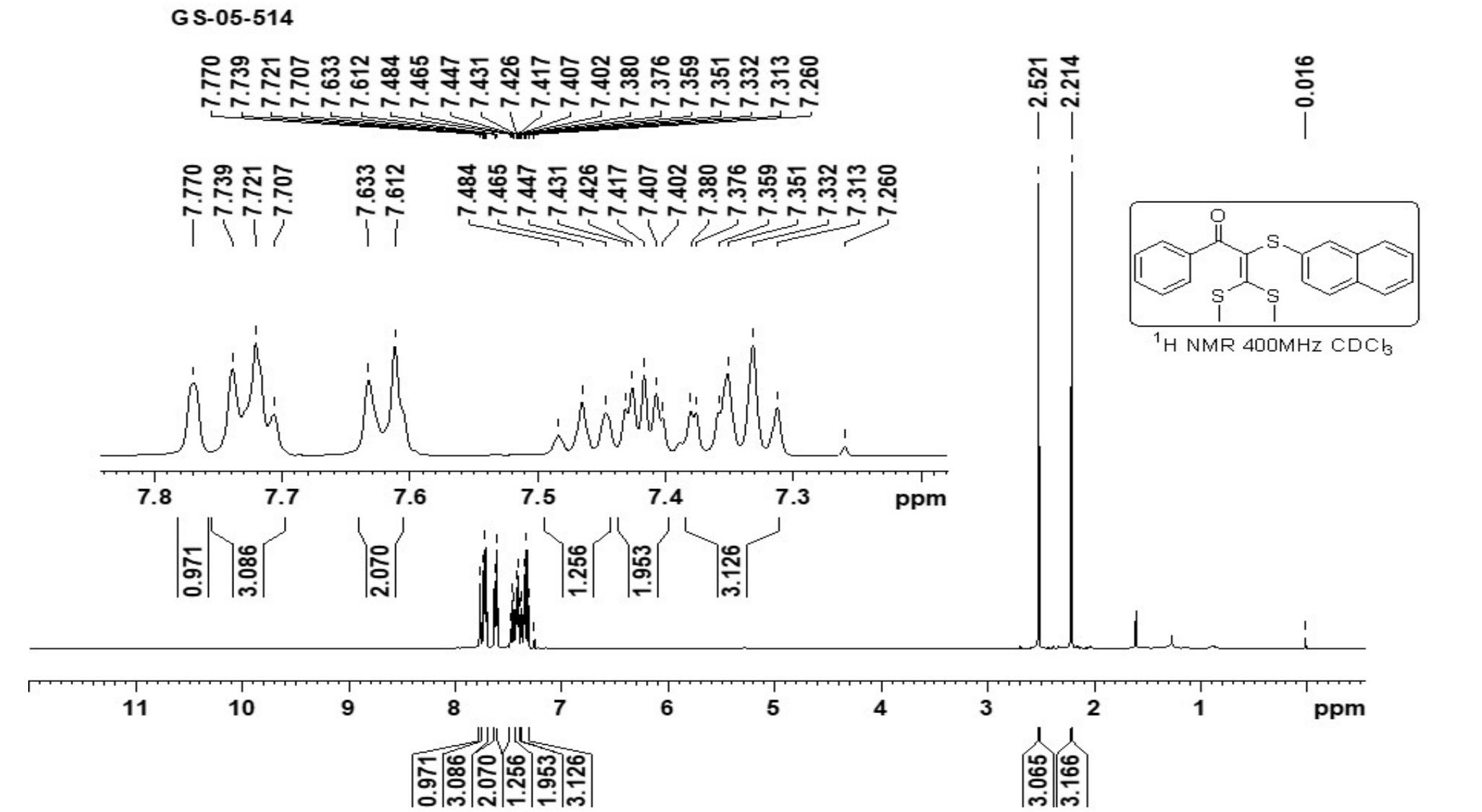


Fig. 24. ^{1}H NMR Spectrum of 3af

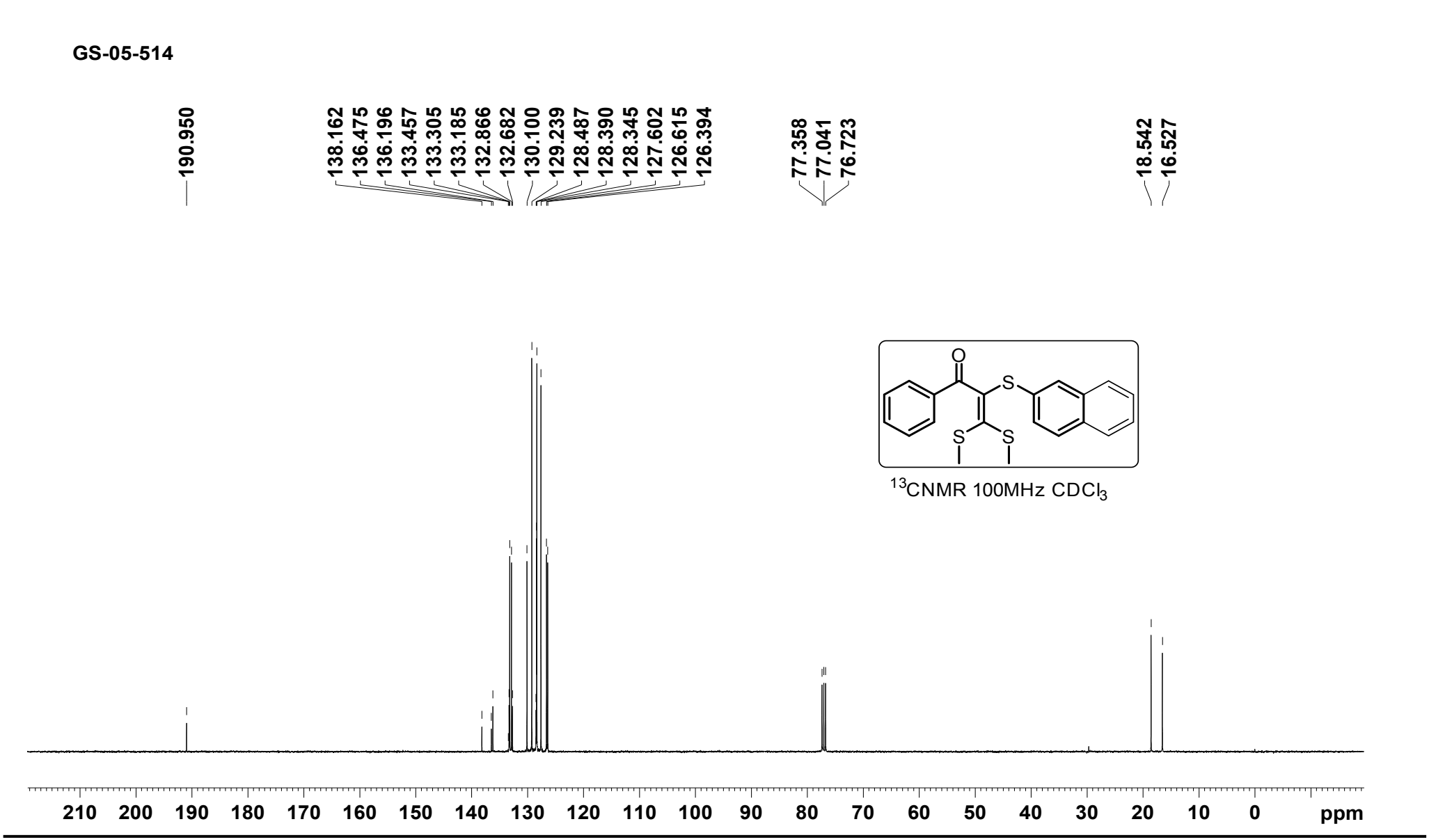


Fig. 25. ^{13}C NMR Spectrum of 3af

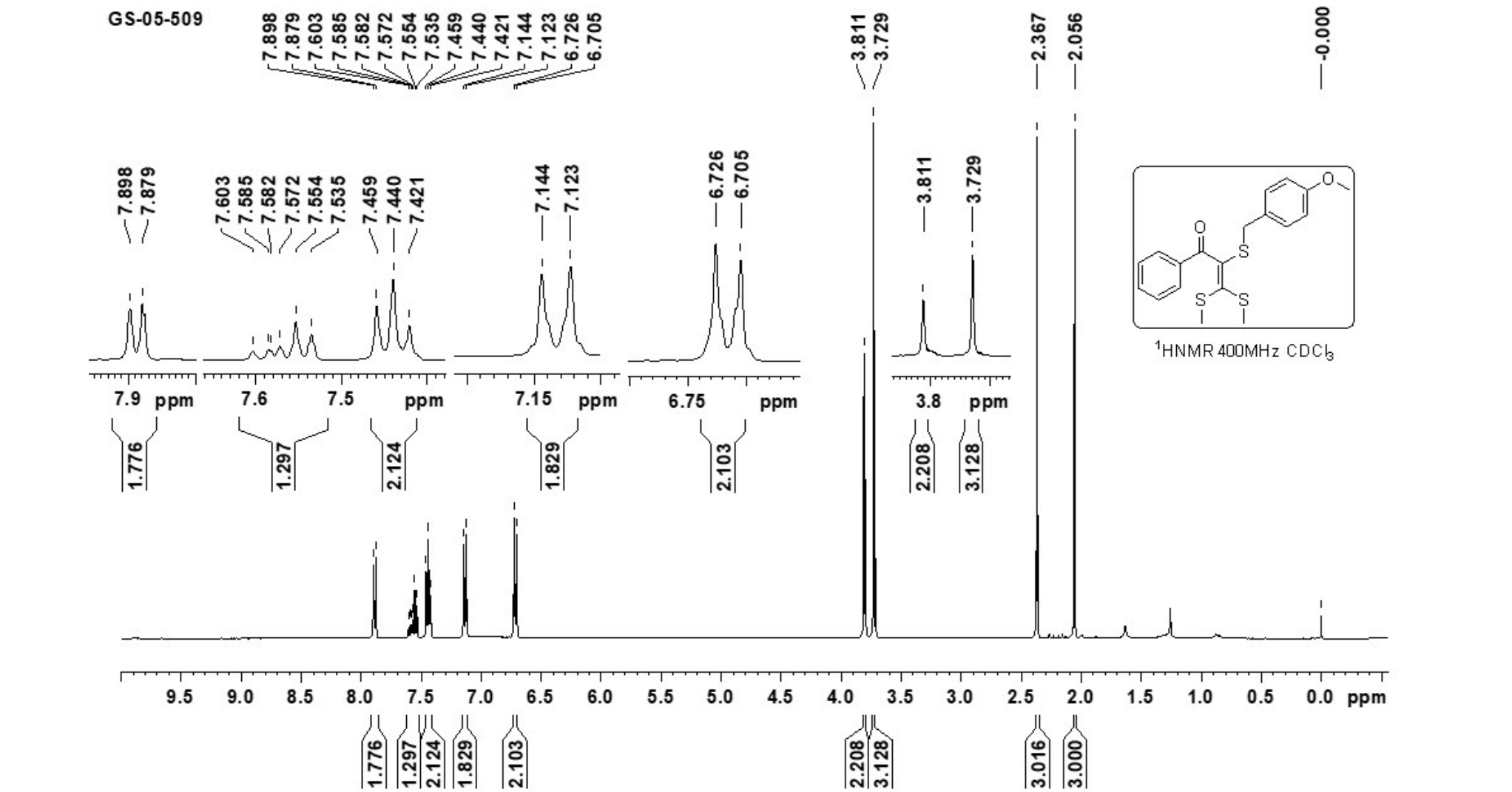


Fig. 26. ^{1}H NMR Spectrum of 3ag

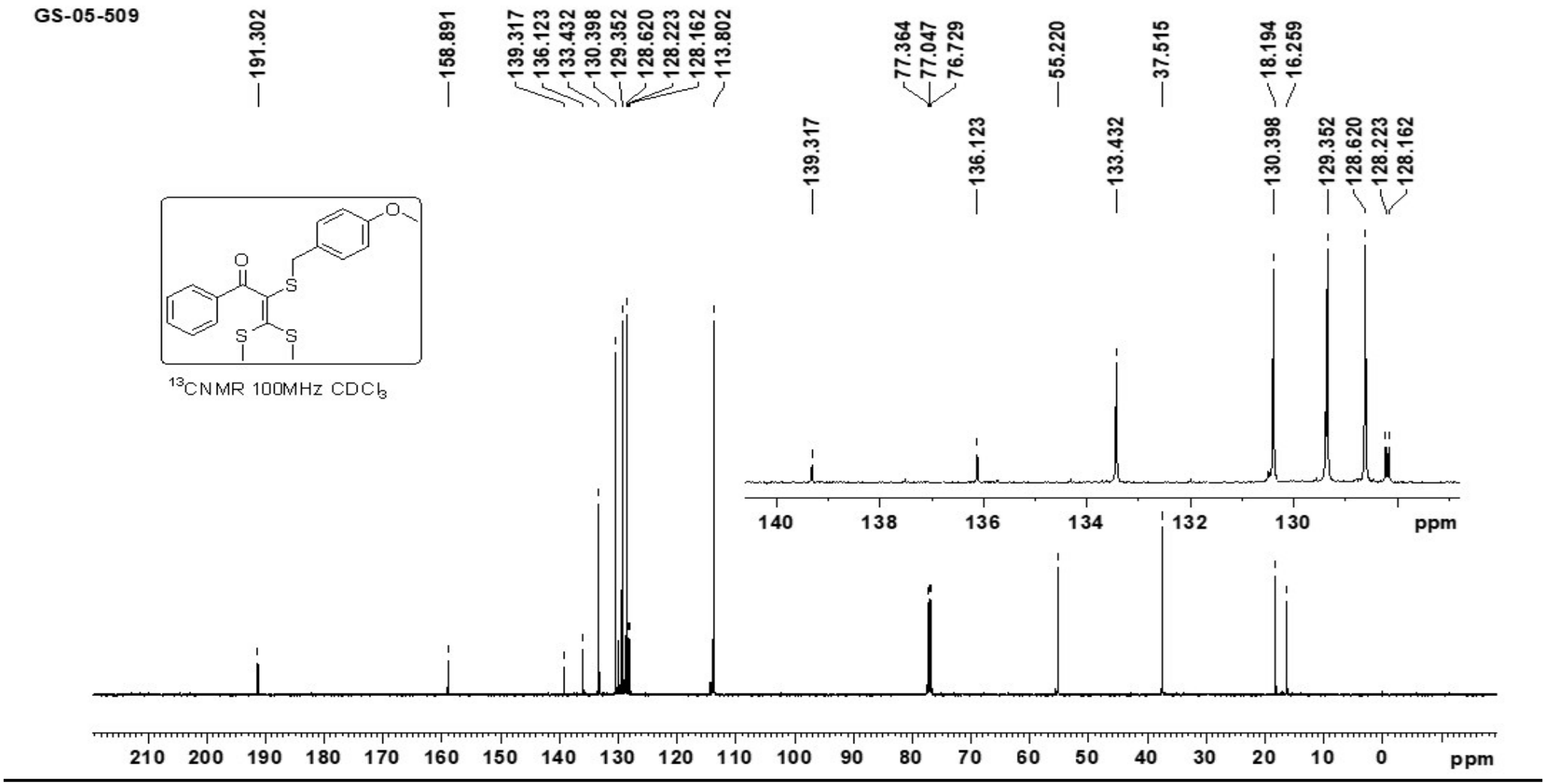


Fig. 27. ^{13}C NMR Spectrum of 3ag

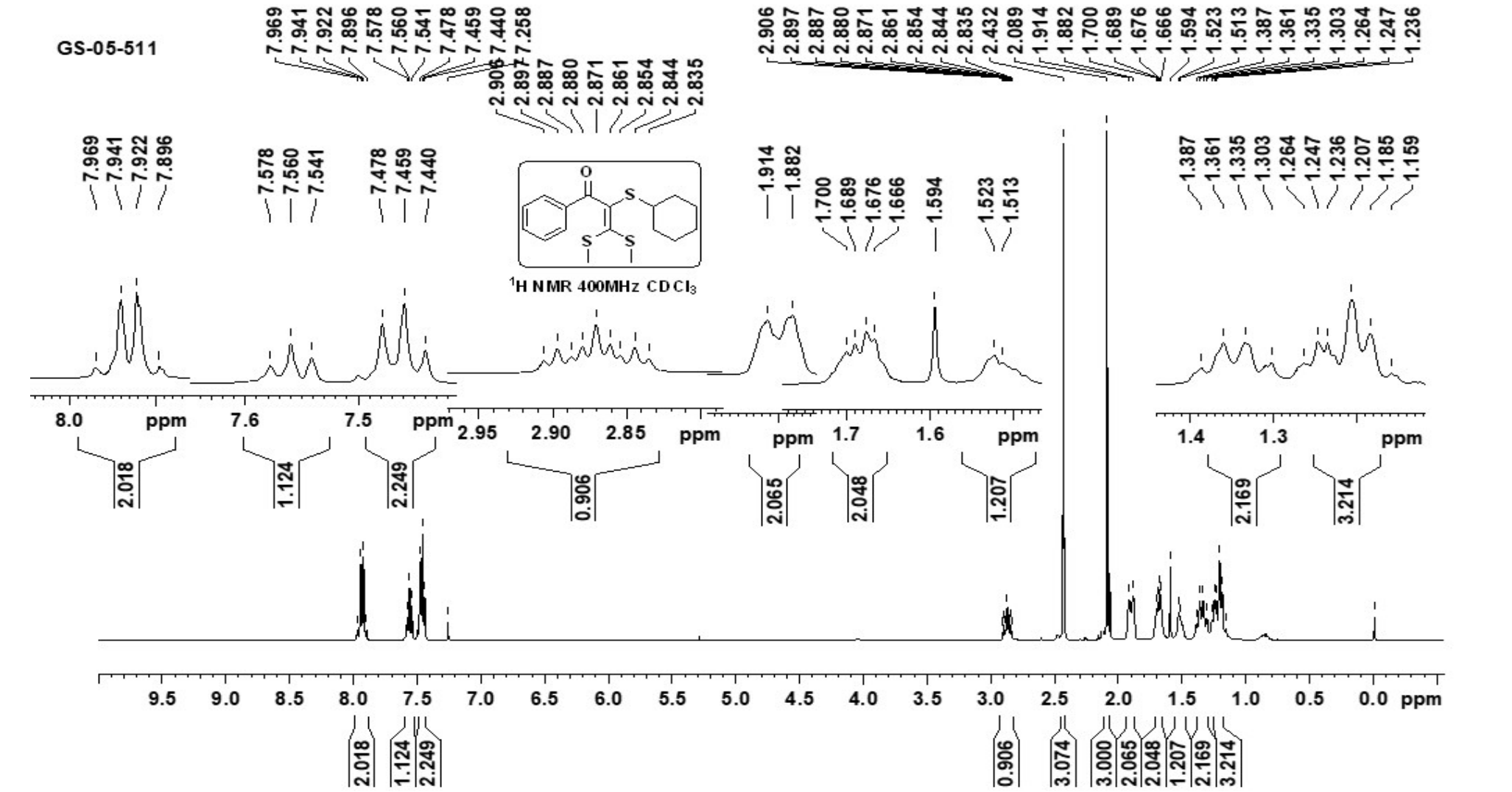


Fig. 28. ^{1}H NMR Spectrum of 3ah

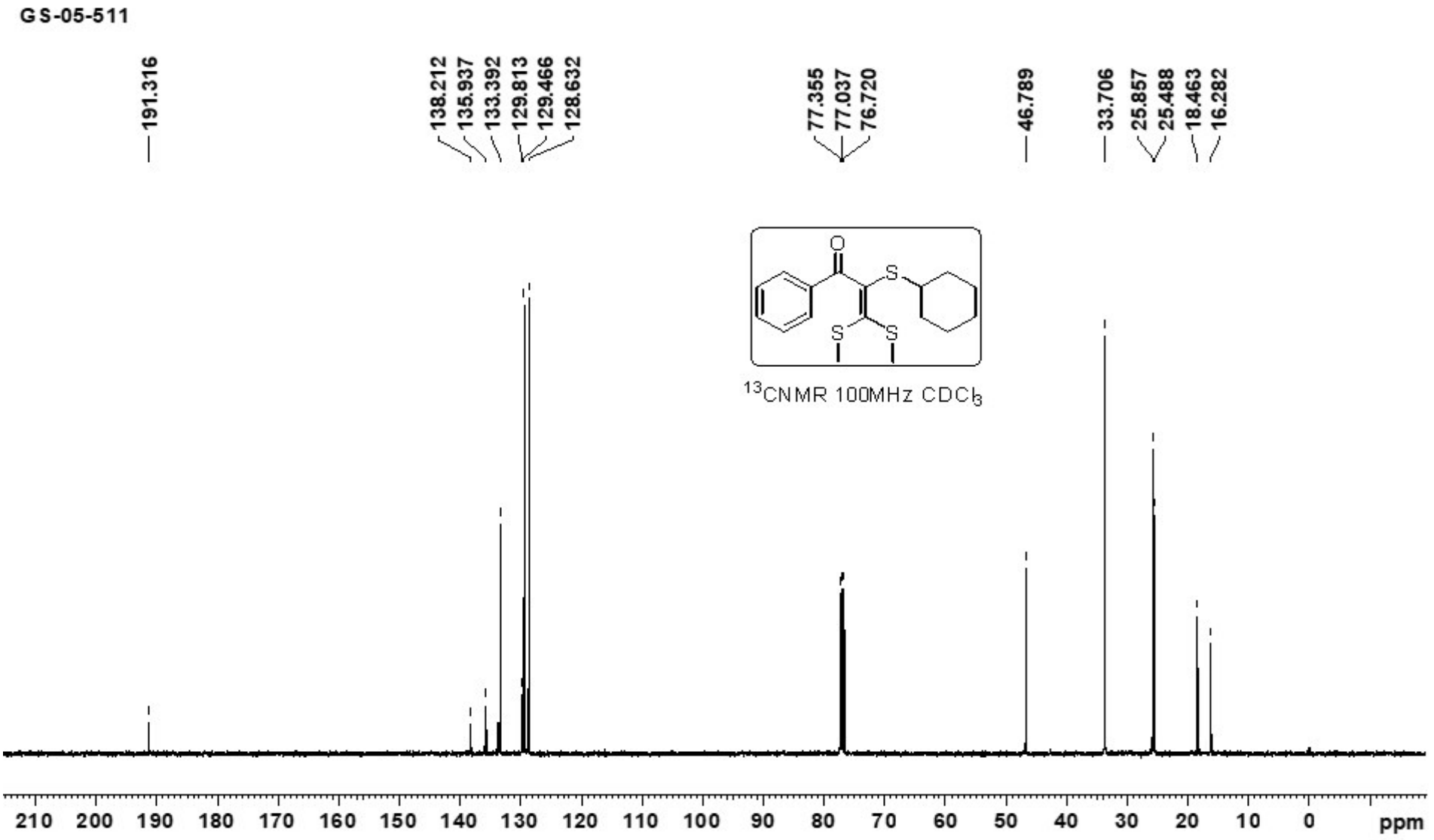


Fig. 29. ^{13}C NMR Spectrum of 3ah

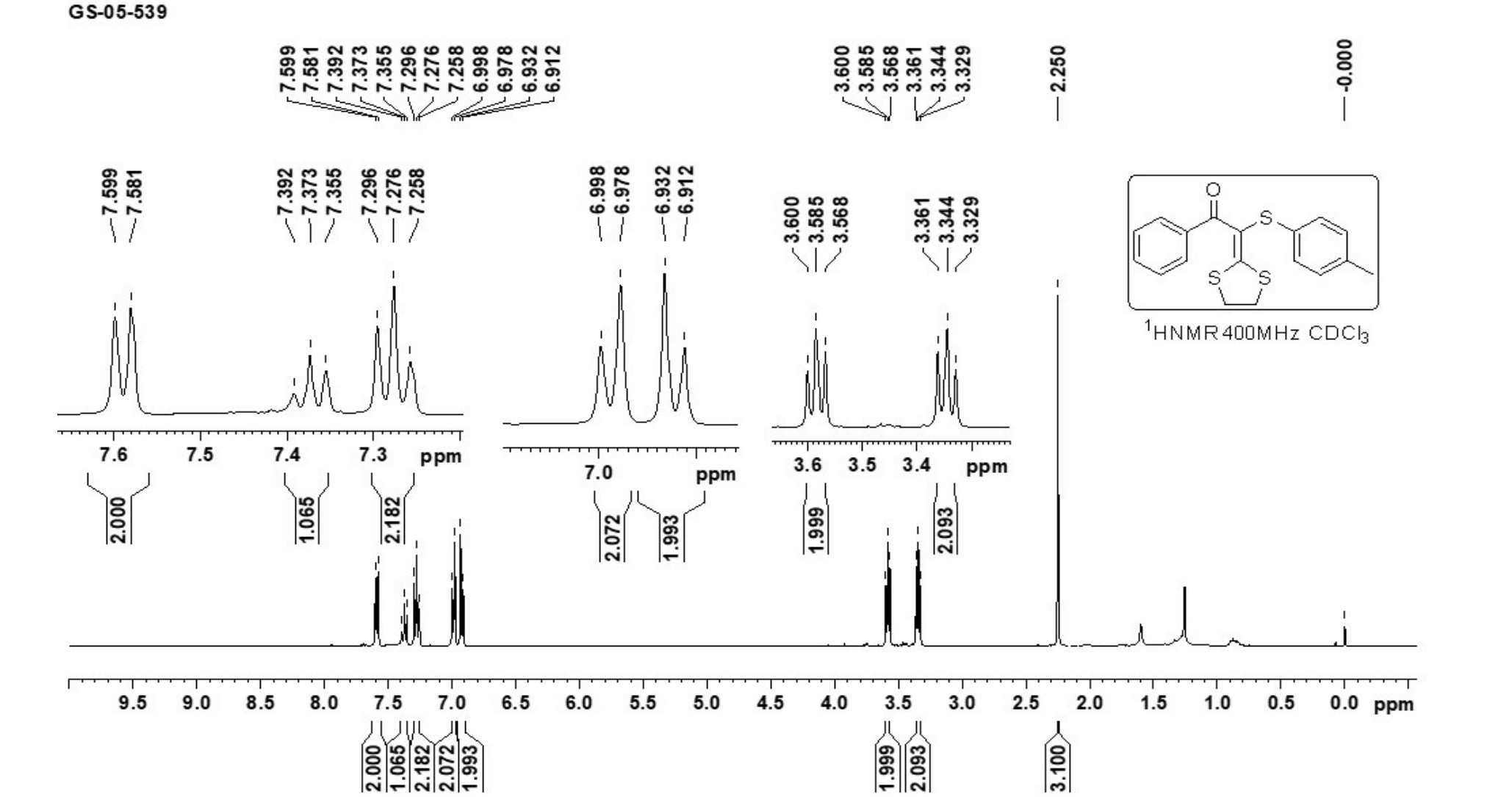


Fig. 30. ^{1}H NMR Spectrum of 3ic

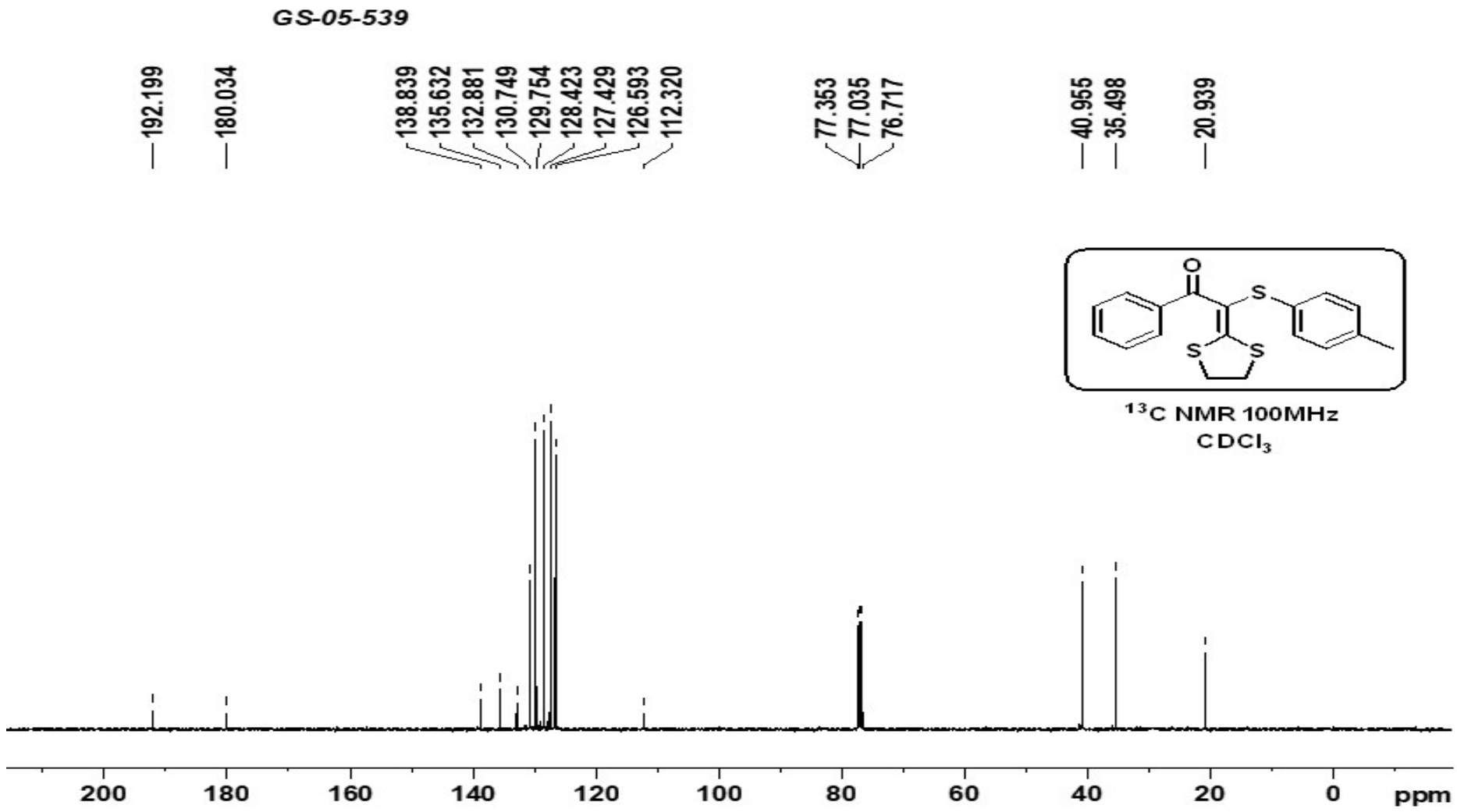


Fig. 31. ^{13}C NMR Spectrum of 3ic

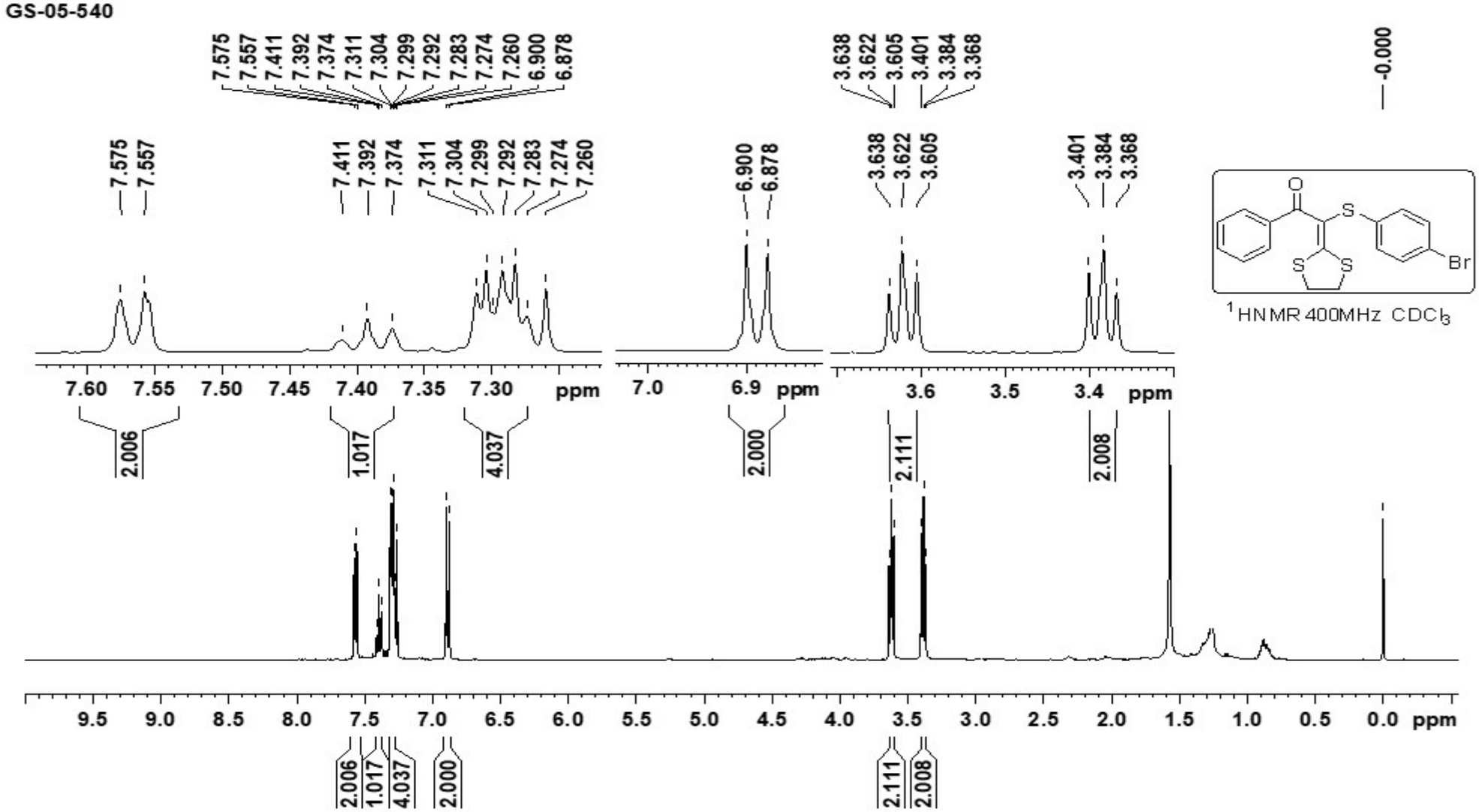


Fig. 32. ^{1}H NMR Spectrum of 3ie

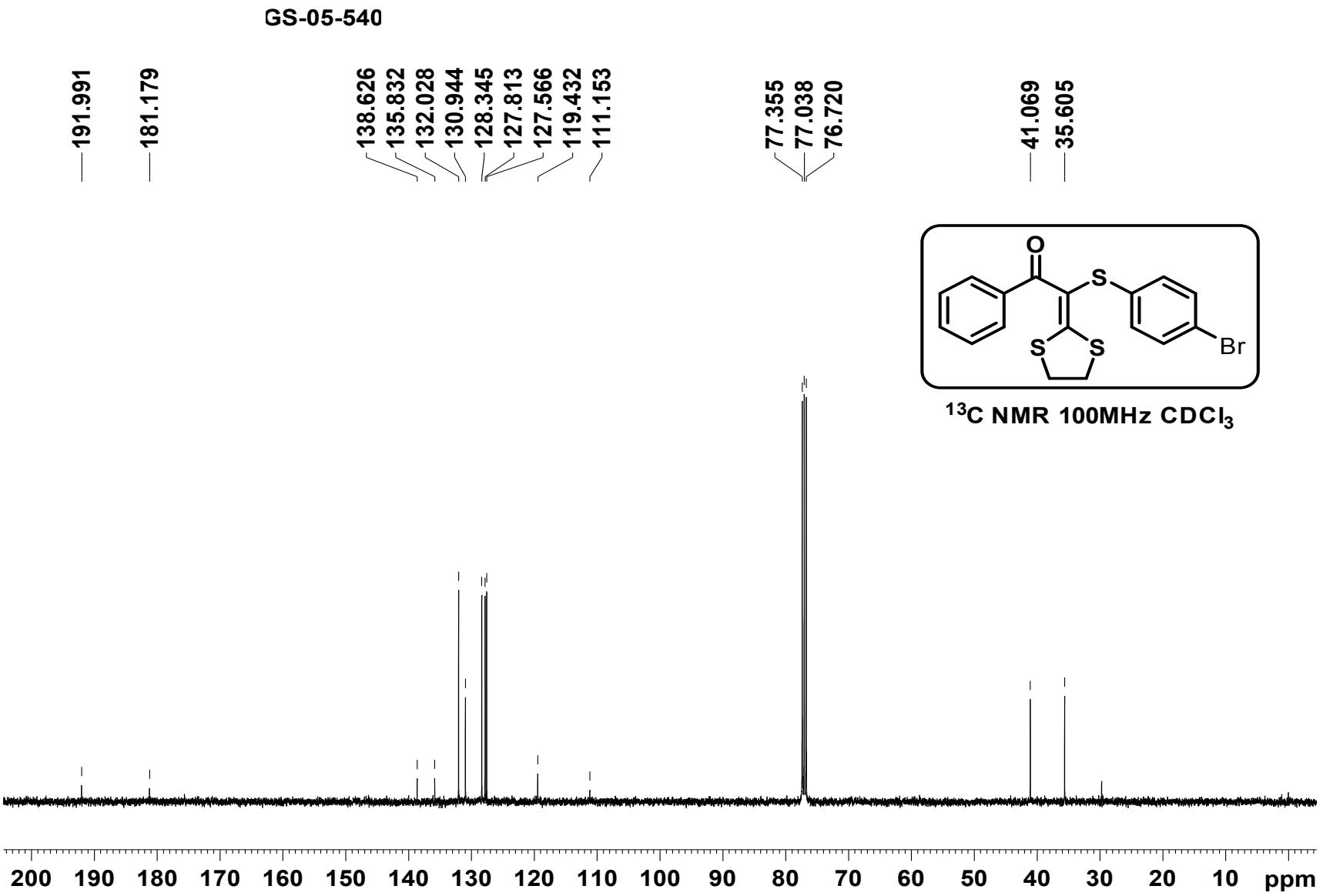


Fig. 33. ^{13}C NMR Spectrum of 3ie

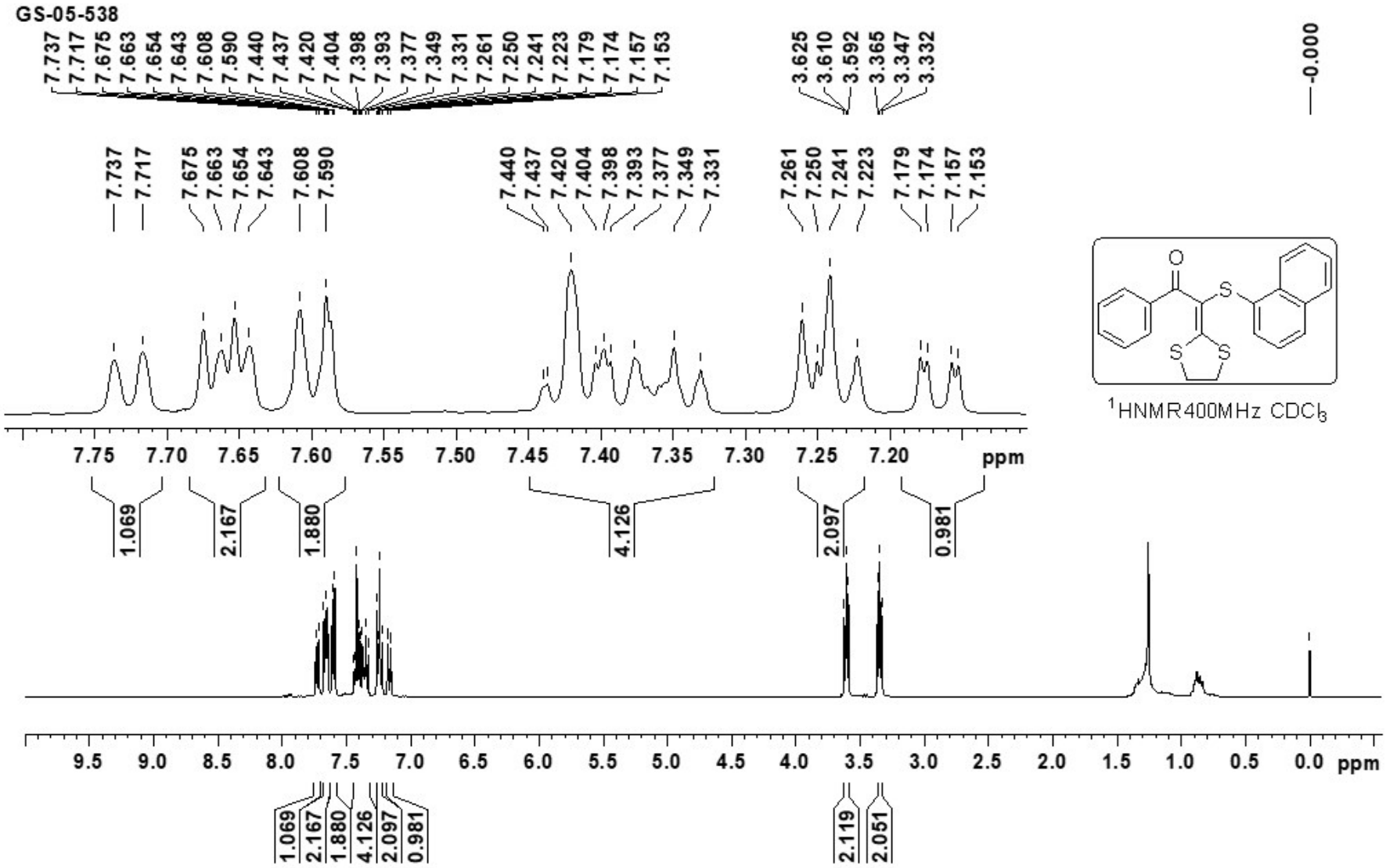


Fig. 34. ^{1}H NMR Spectrum of 3if

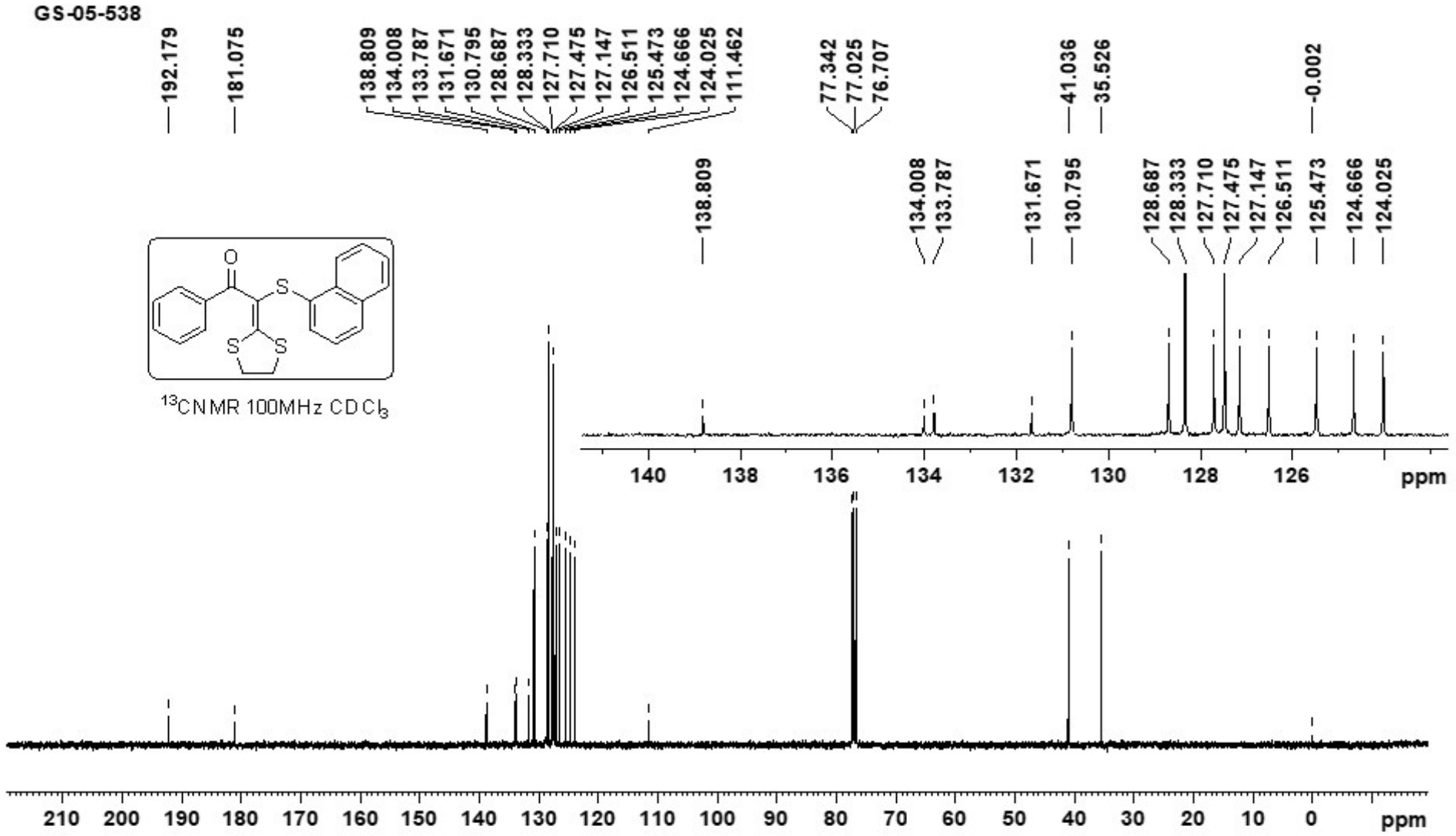


Fig. 35. ^{13}C NMR Spectrum of 3if

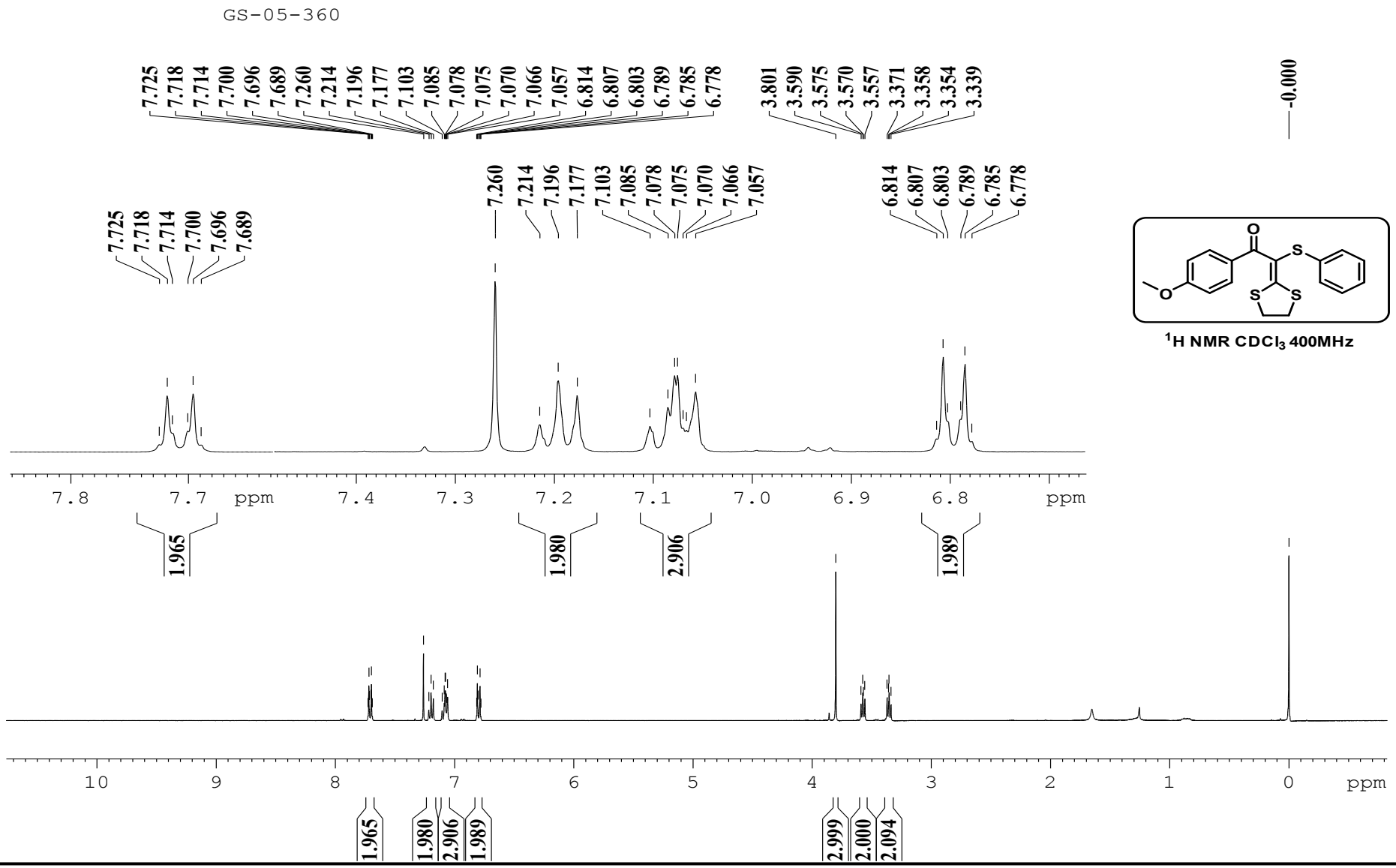


Fig. 36. ^{1}H NMR Spectrum of 3ja

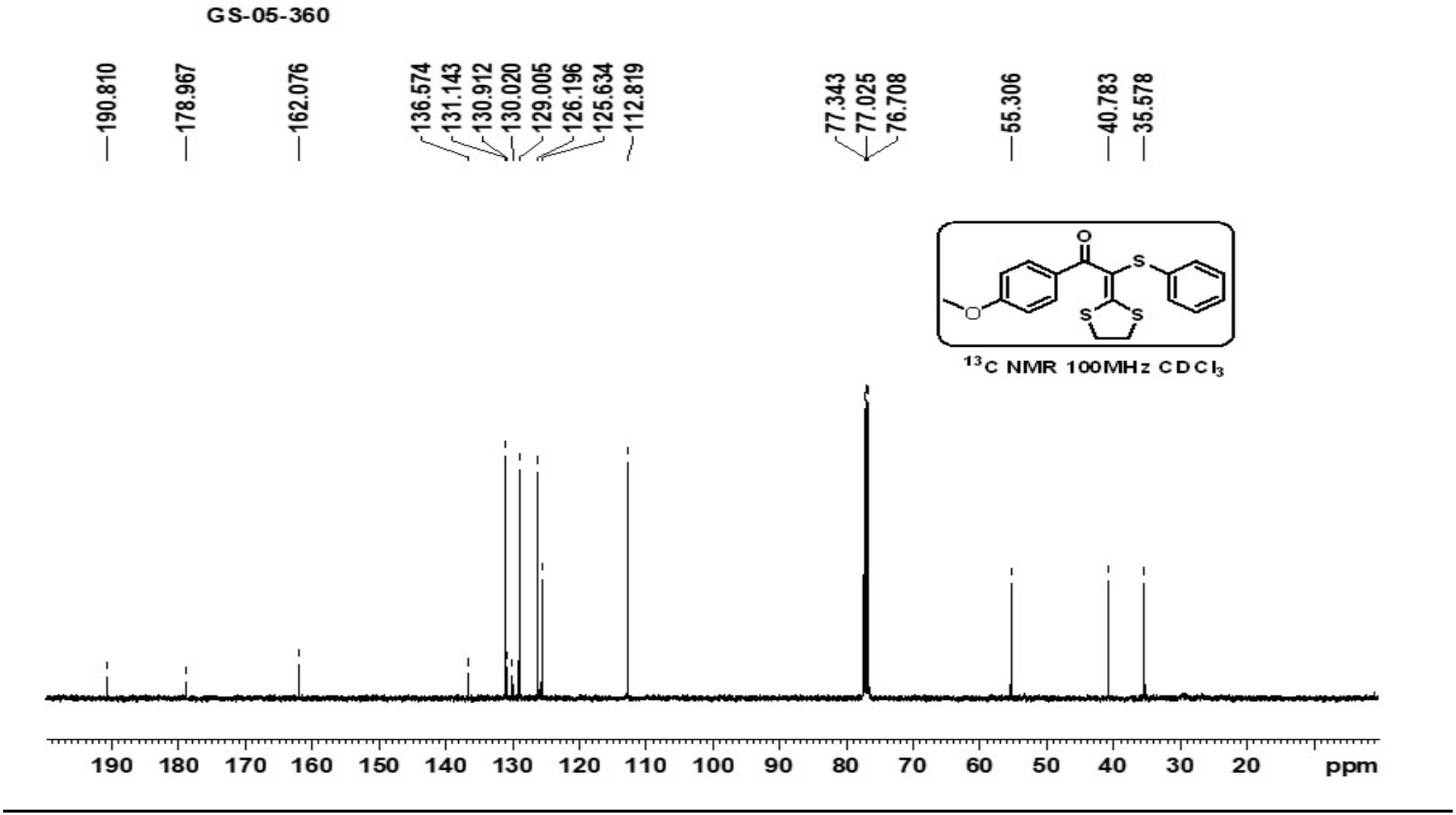


Fig. 37. ^{13}C NMR Spectrum of 3ja

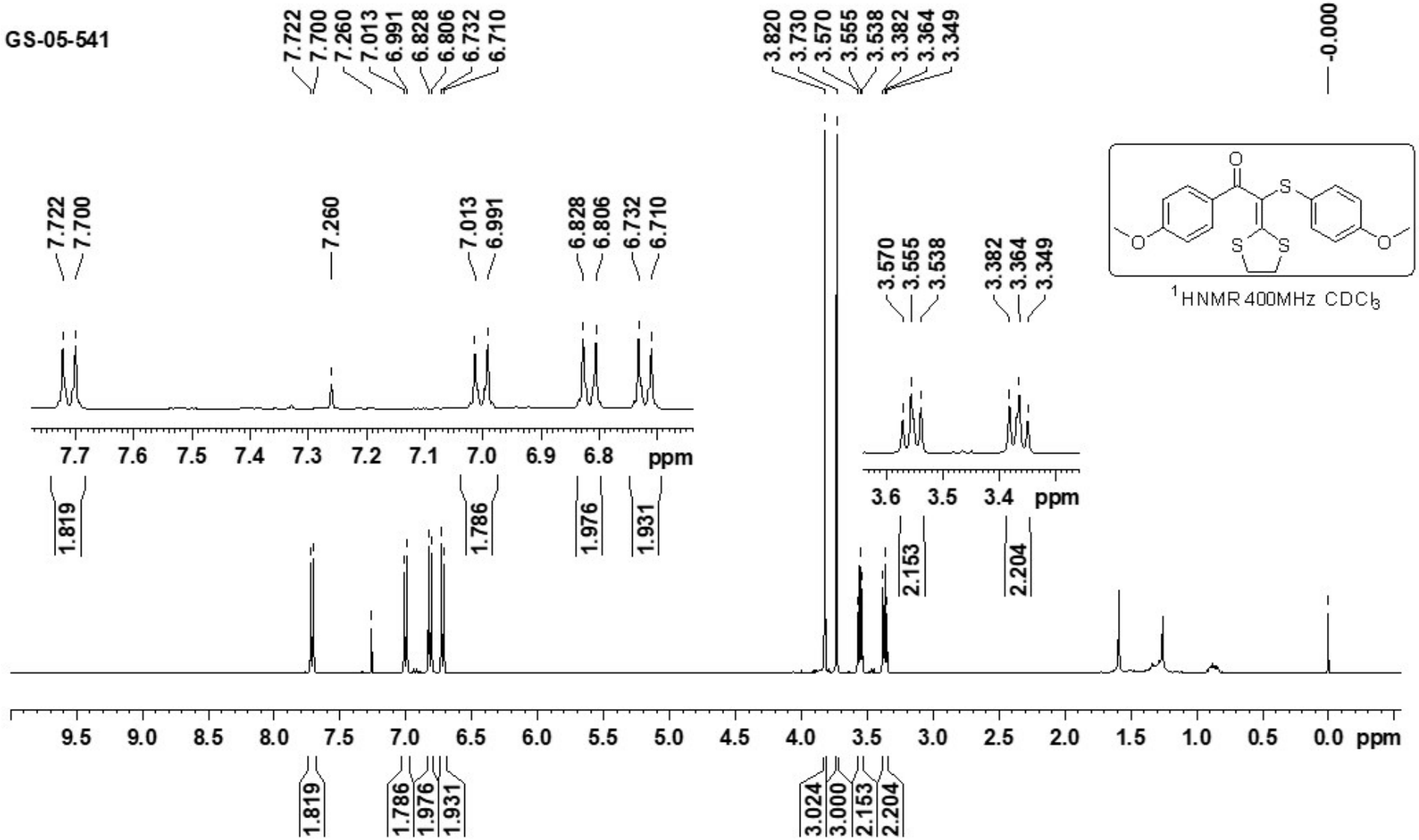


Fig. 38. ^{1}H NMR Spectrum of 3jb

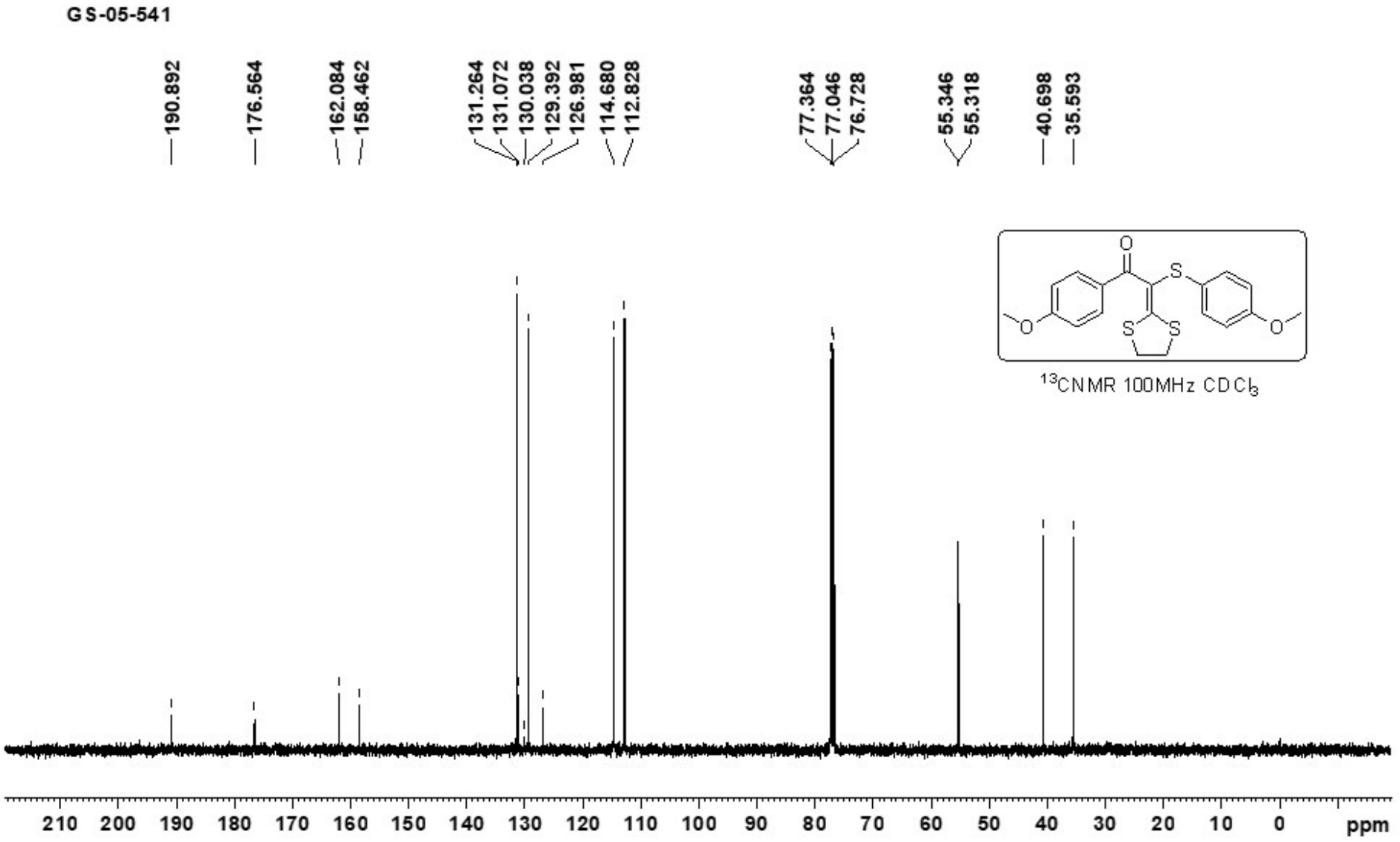


Fig. 39. ^{13}C NMR Spectrum of 3jb

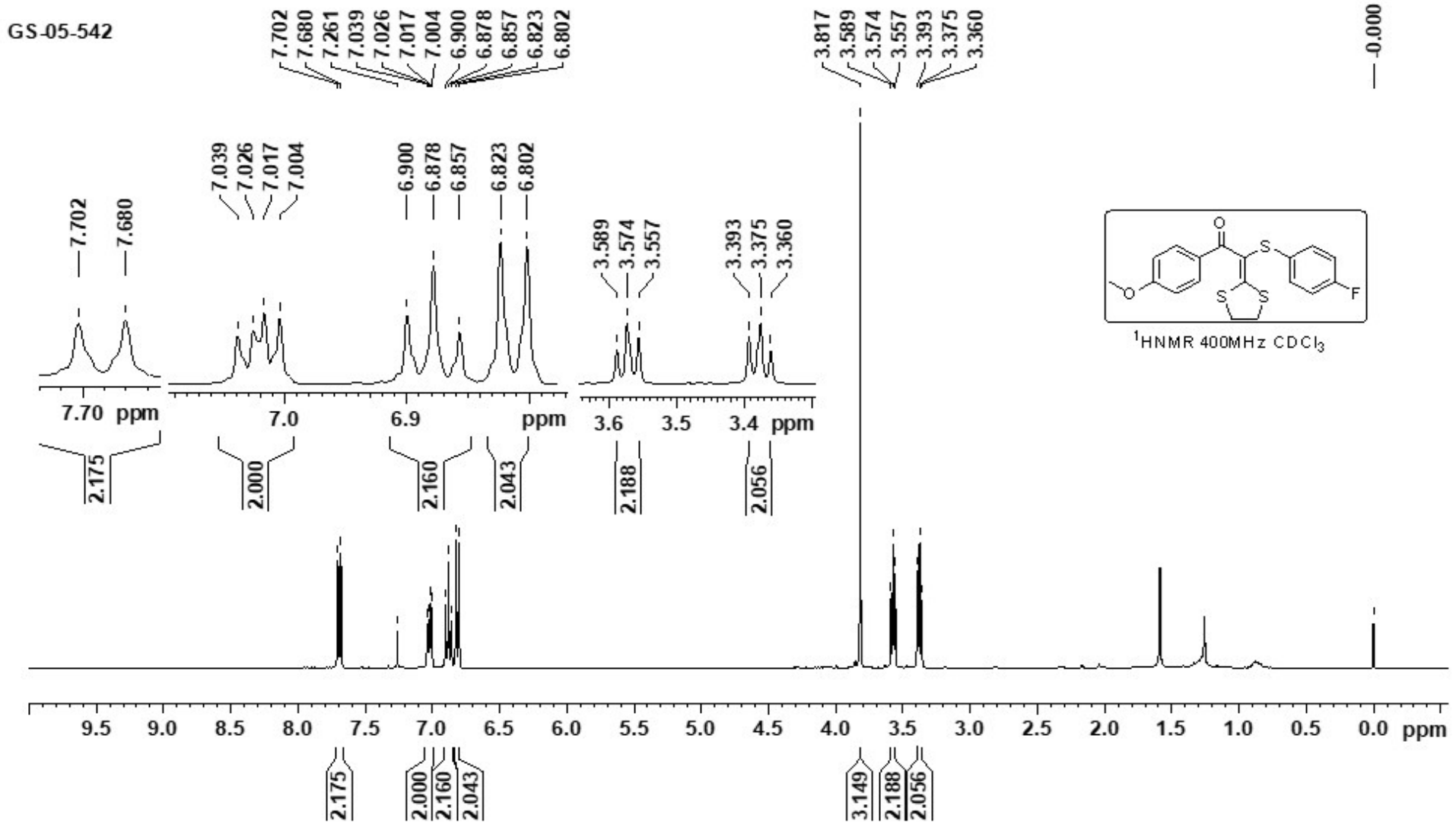


Fig. 40. ^{1}H NMR Spectrum of 3jf

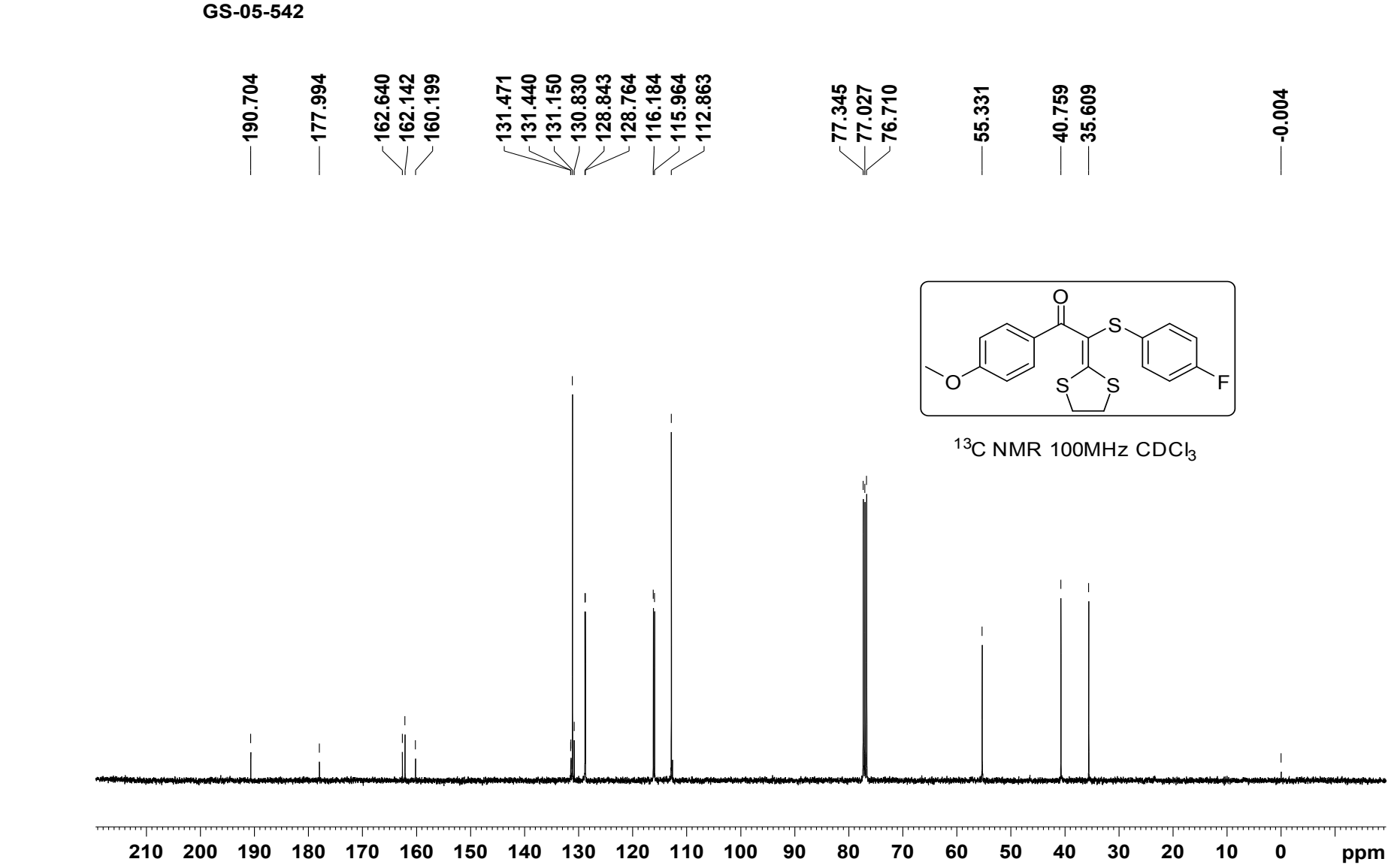


Fig. 41. ^{13}C NMR Spectrum of 3jf

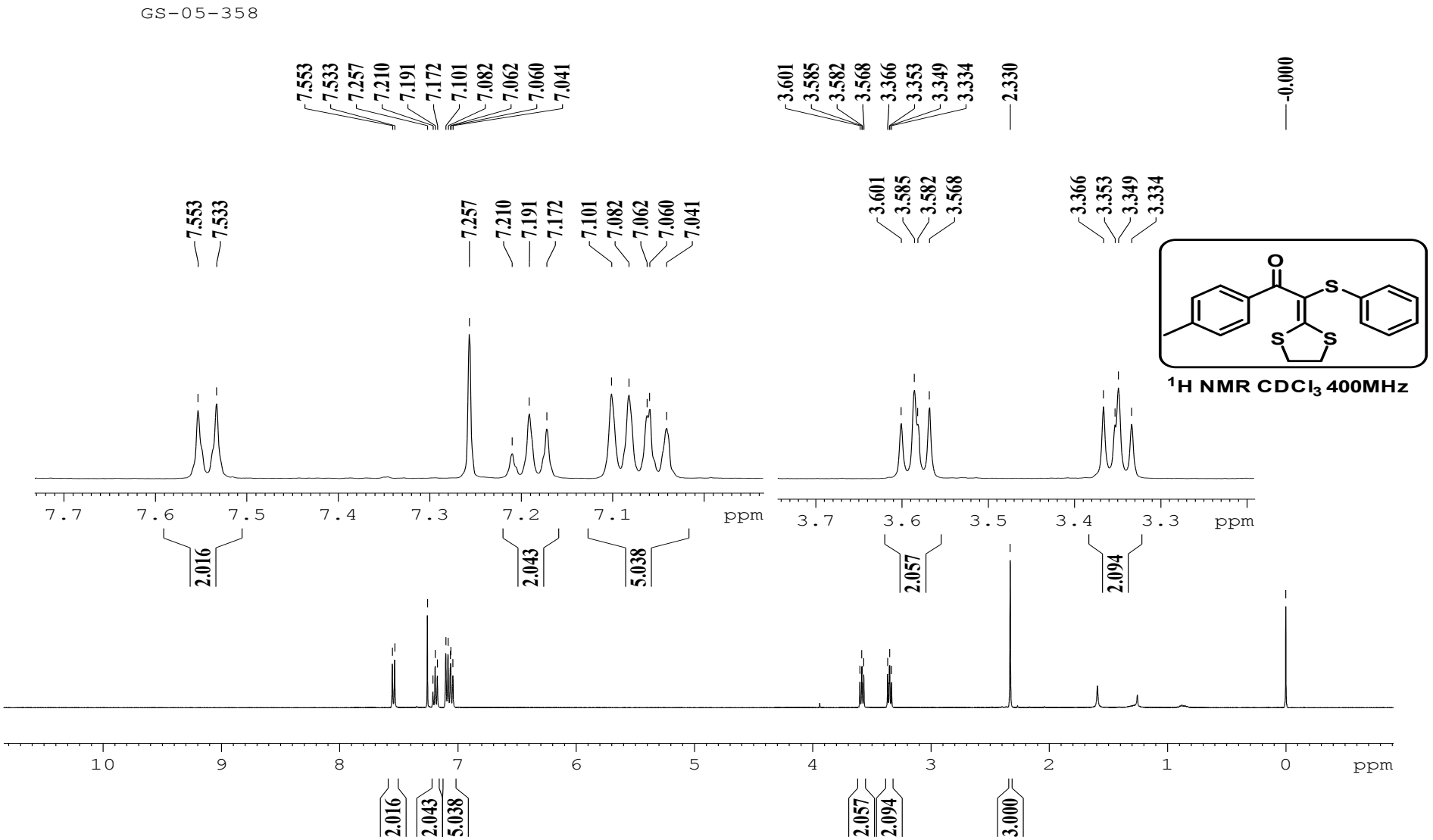


Fig. 42. ^{1}H NMR Spectrum of 3ka

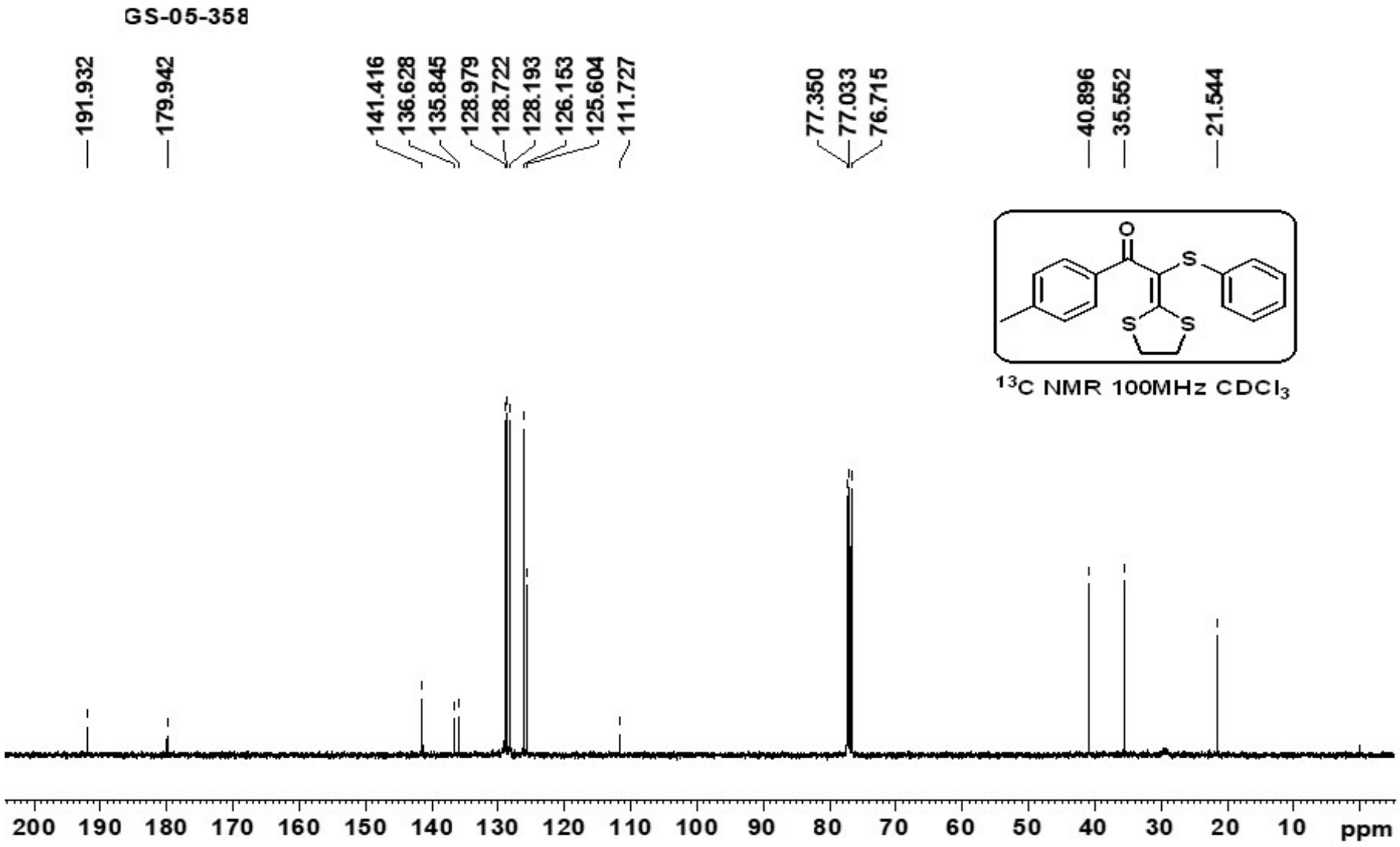


Fig. 43. ^{13}C NMR Spectrum of 3ka

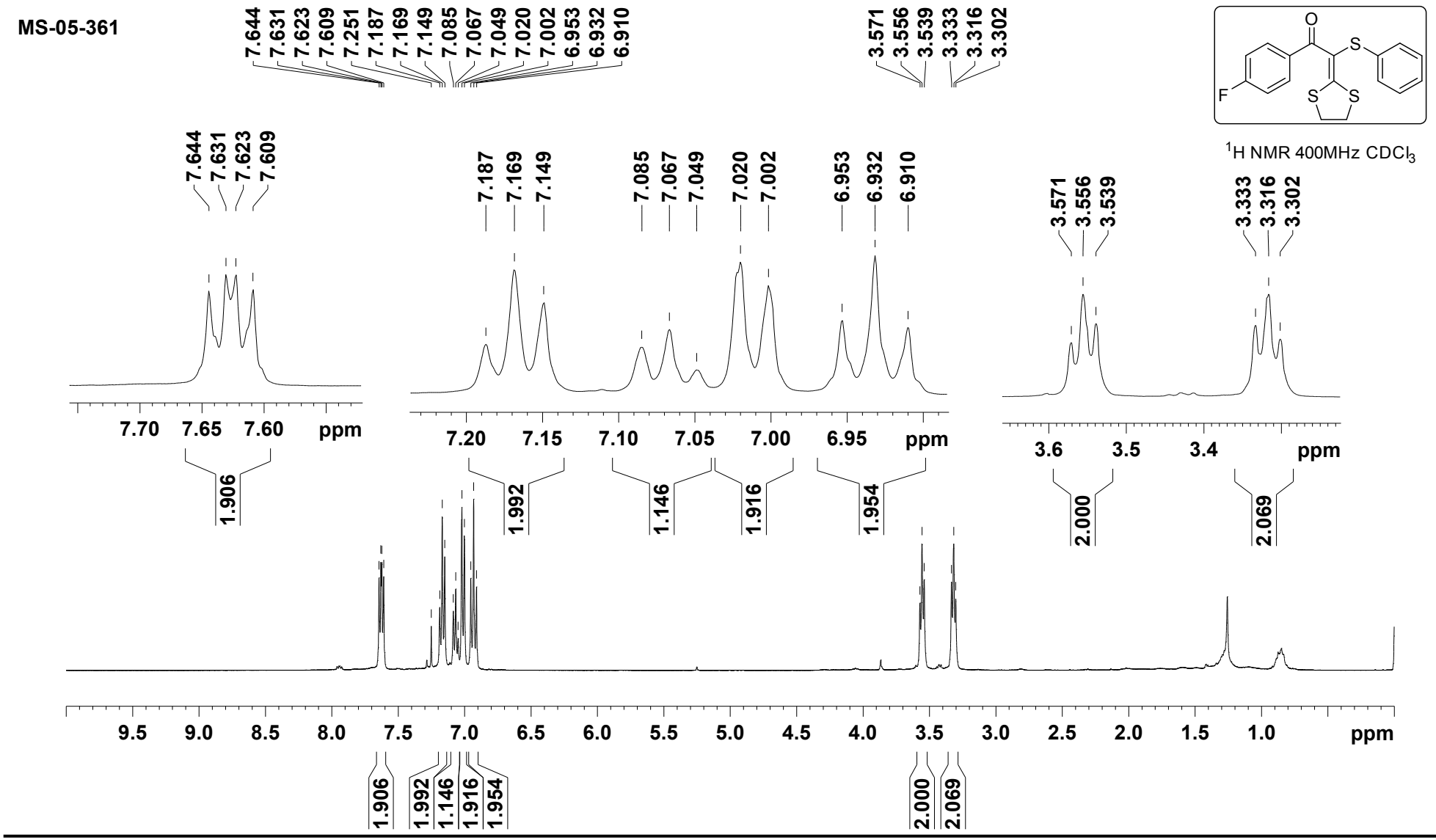


Fig. 44. [1]H NMR Spectrum of 3la

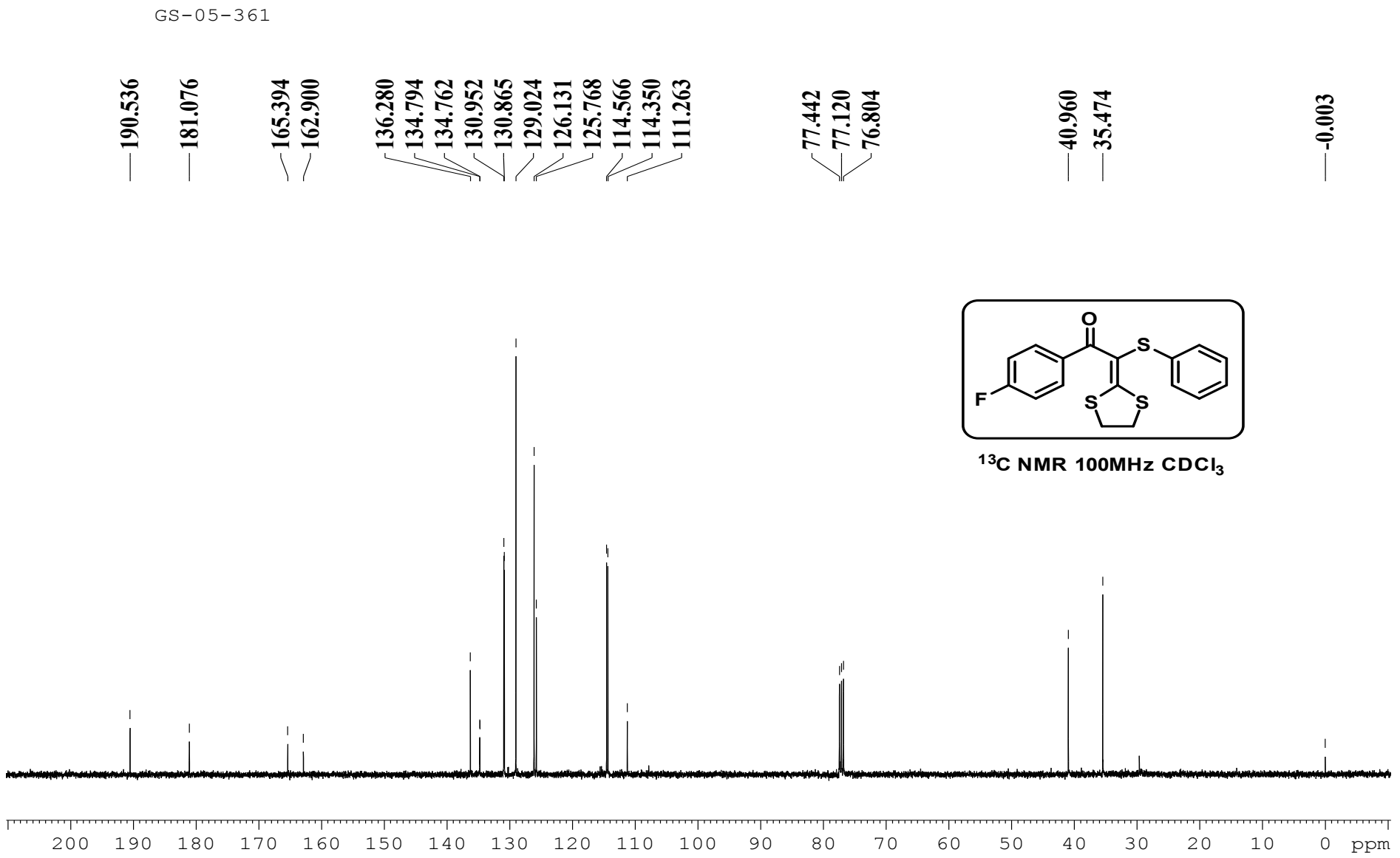


Fig. 45. ^{13}C NMR Spectrum of 3la

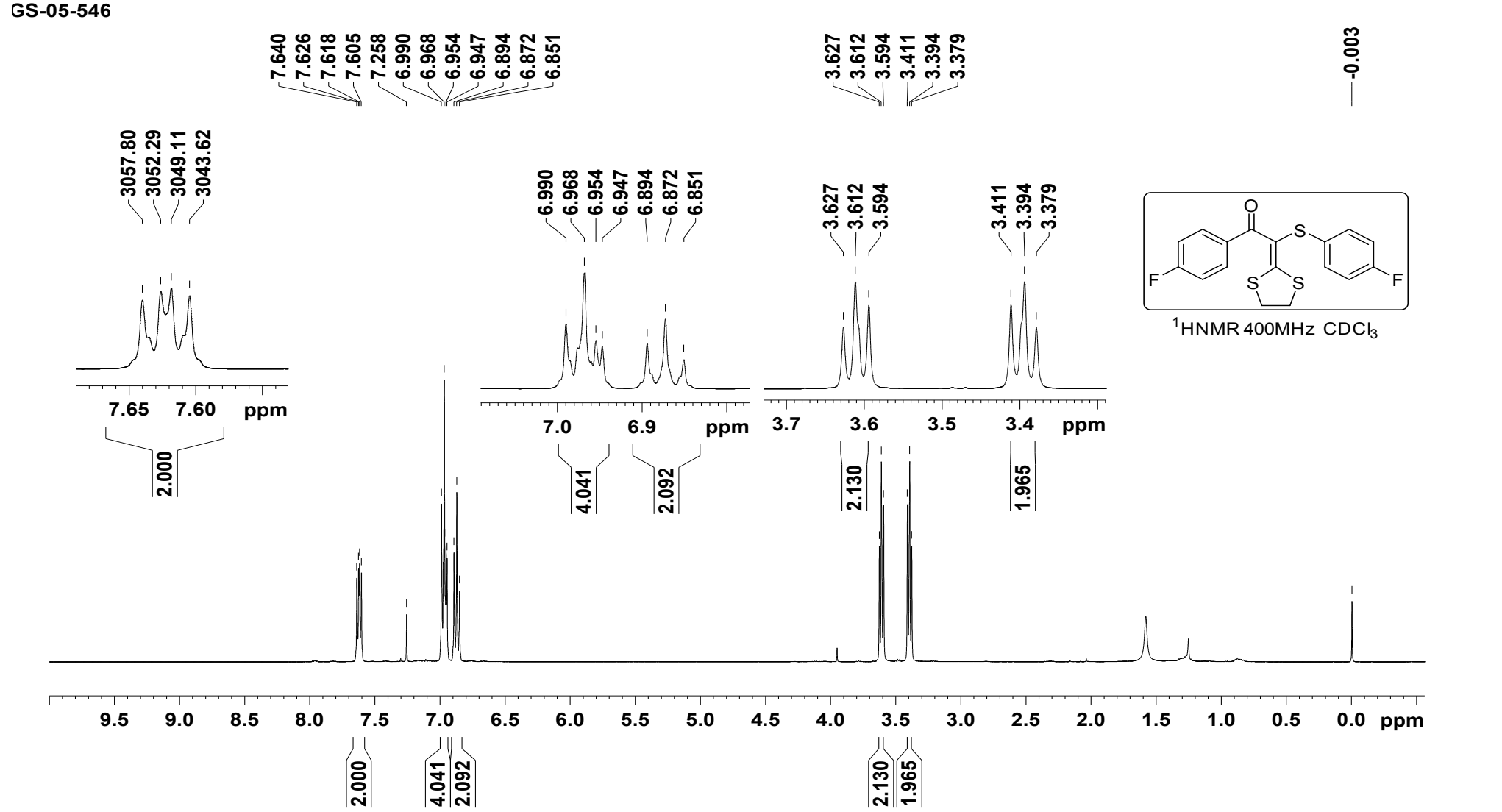


Fig. 46. ^{1}H NMR Spectrum of 3ld

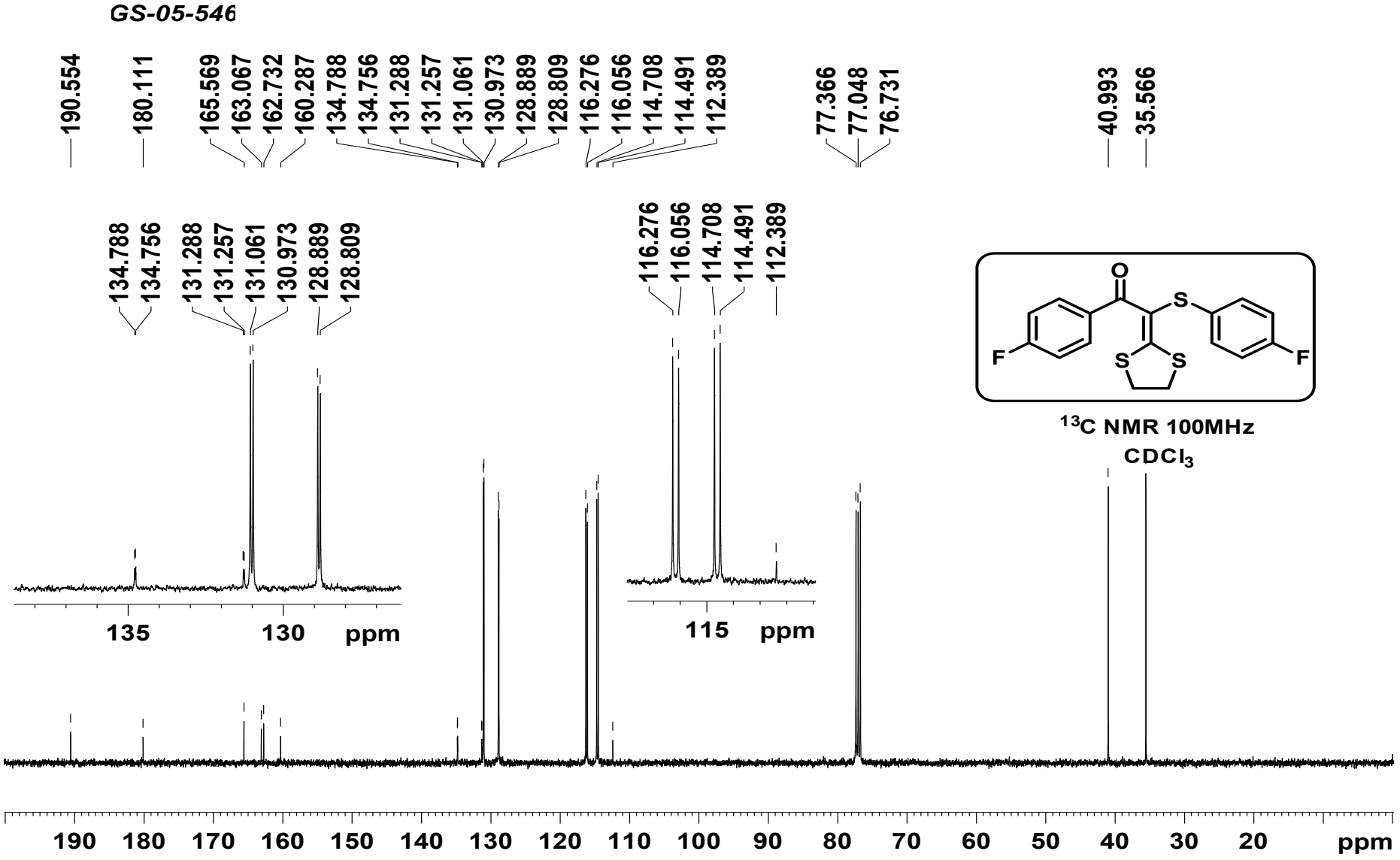


Fig. 47. ^{13}C NMR Spectrum of 3ld

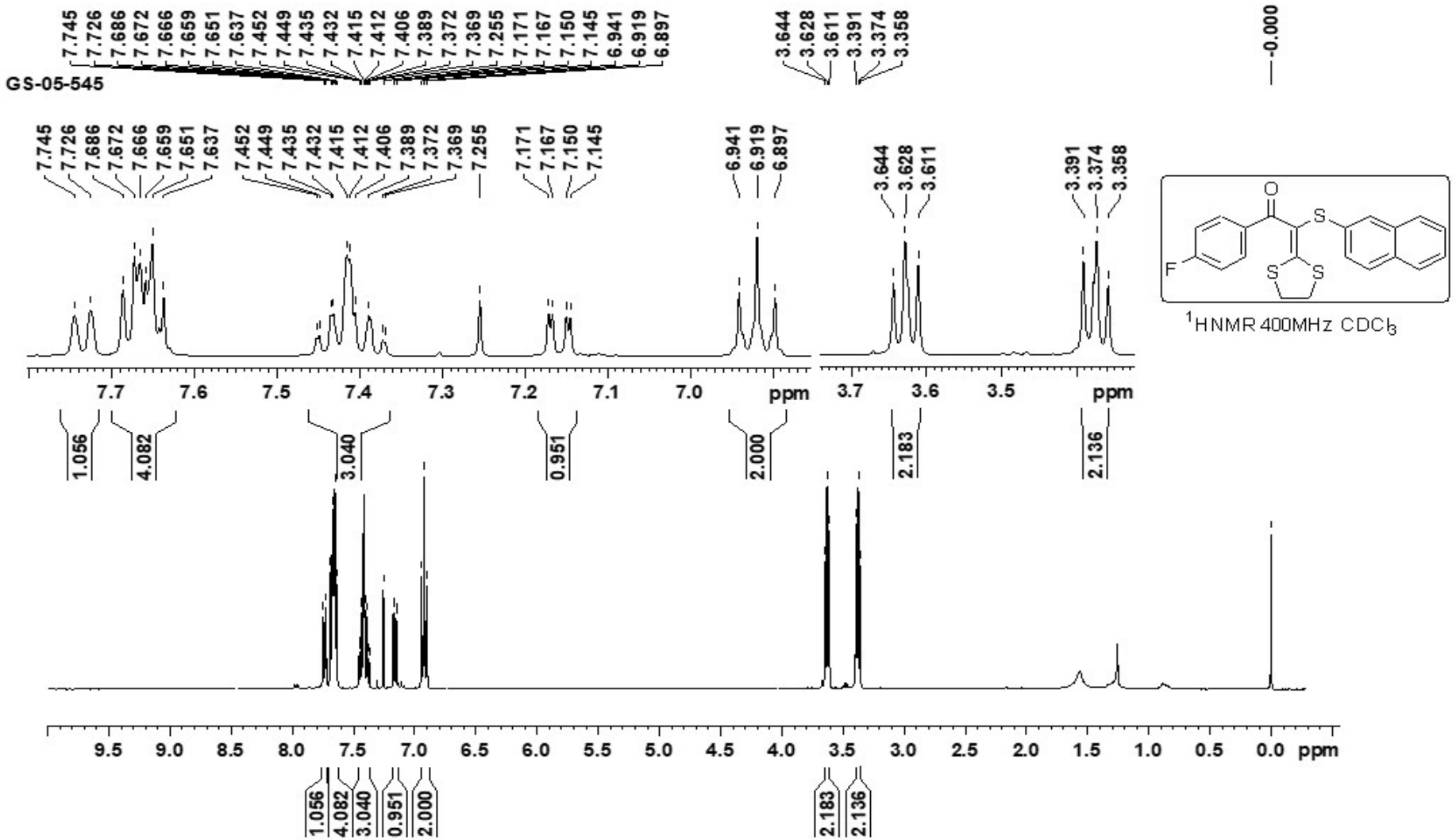


Fig. 48. ^{1}H NMR Spectrum of 3lf

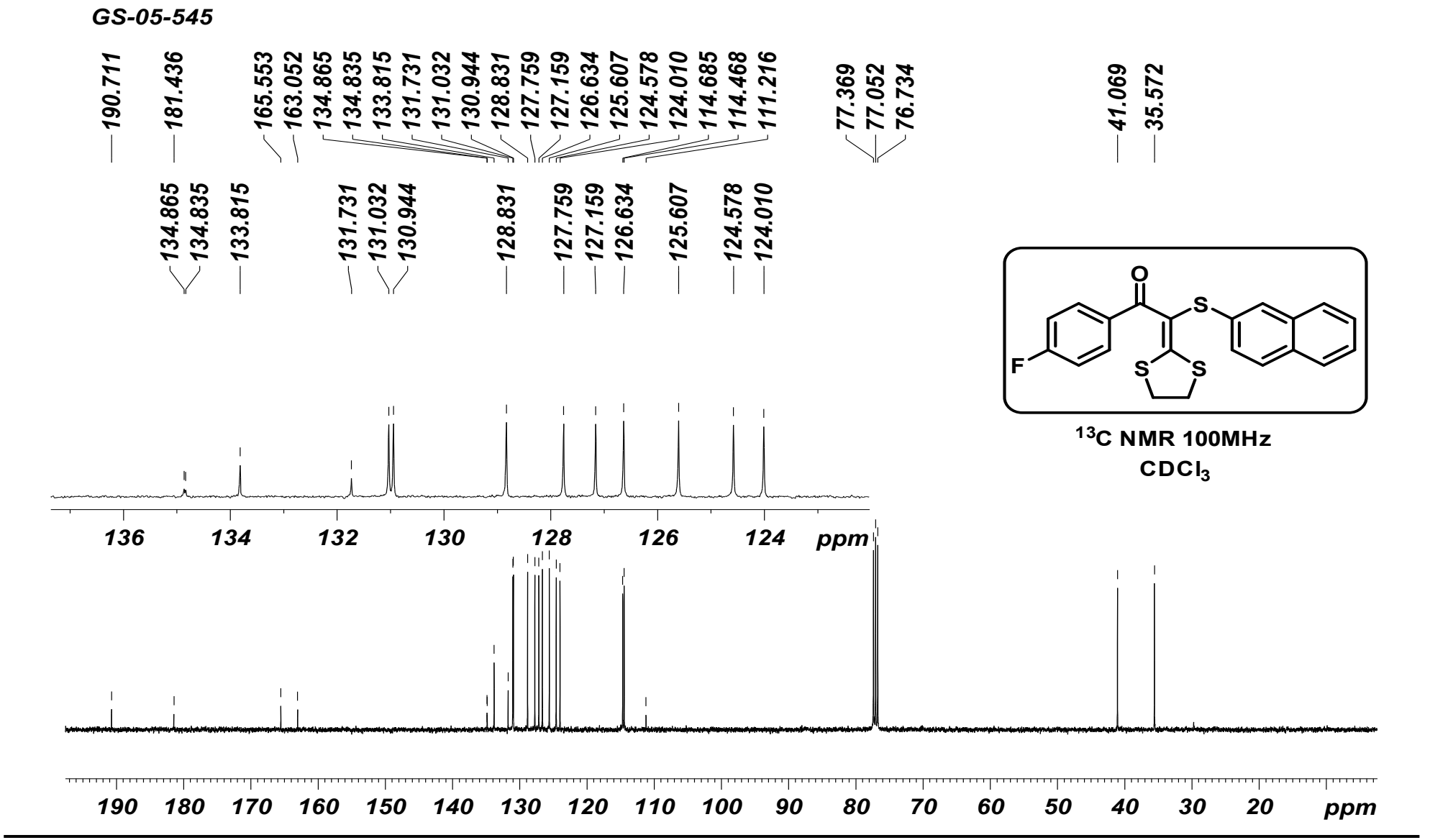


Fig. 49. ^{13}C NMR Spectrum of 3lf

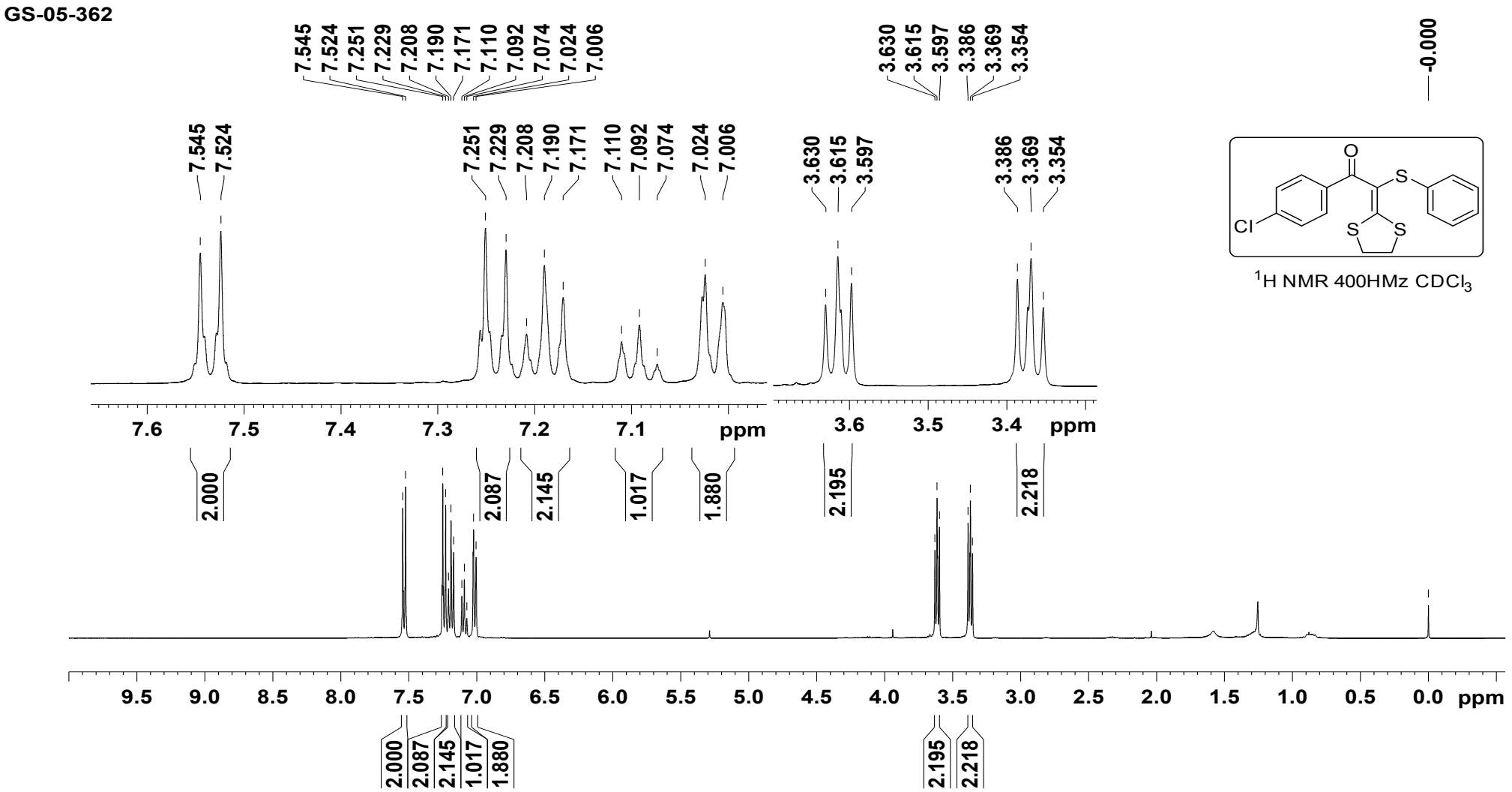


Fig. 50. ^{1}H NMR Spectrum of 3ma

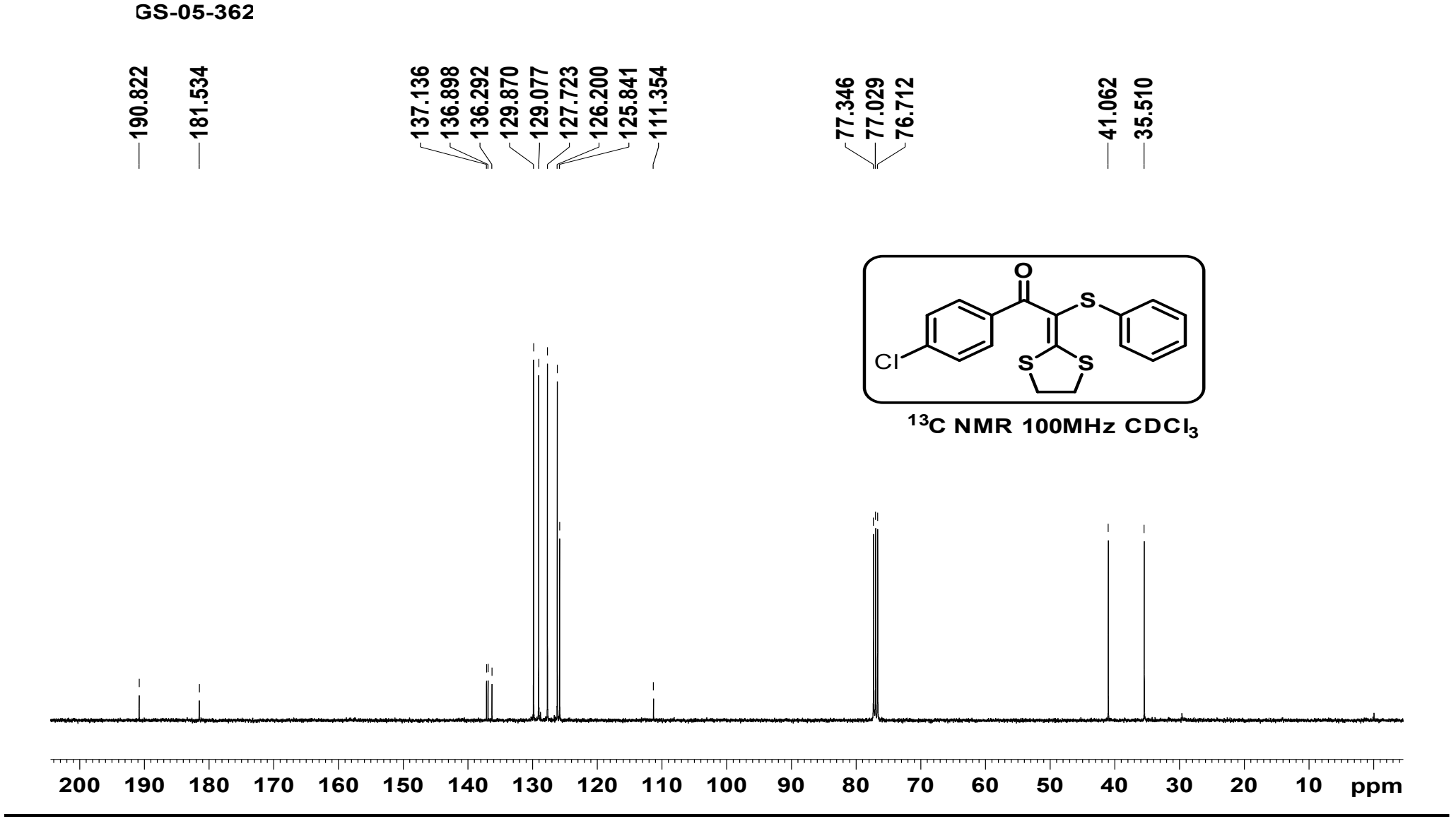


Fig. 51. ^{13}C NMR Spectrum of 3ma

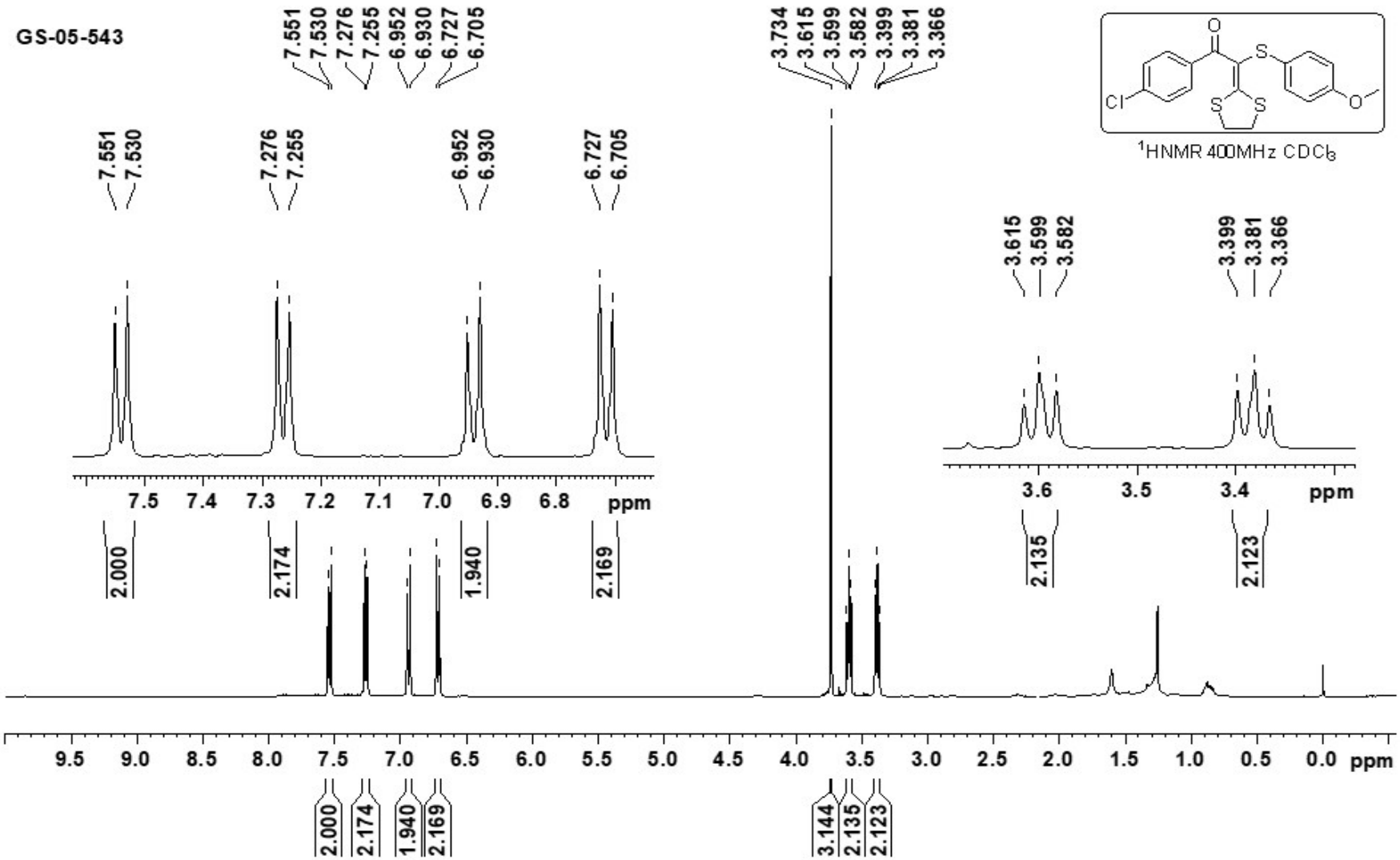


Fig. 52. [1]H NMR Spectrum of 3mb

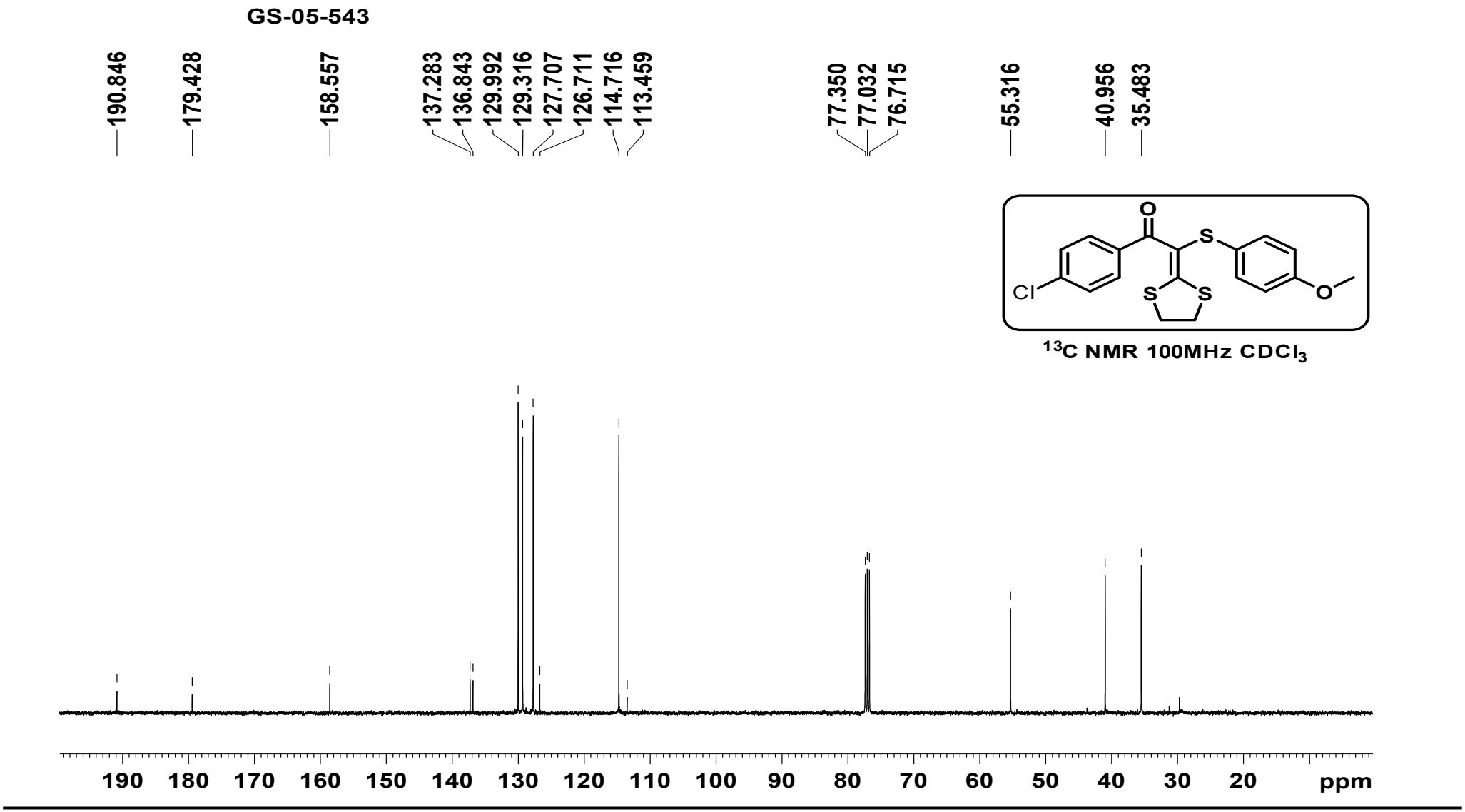


Fig. 53. ^{13}C NMR Spectrum of 3mb

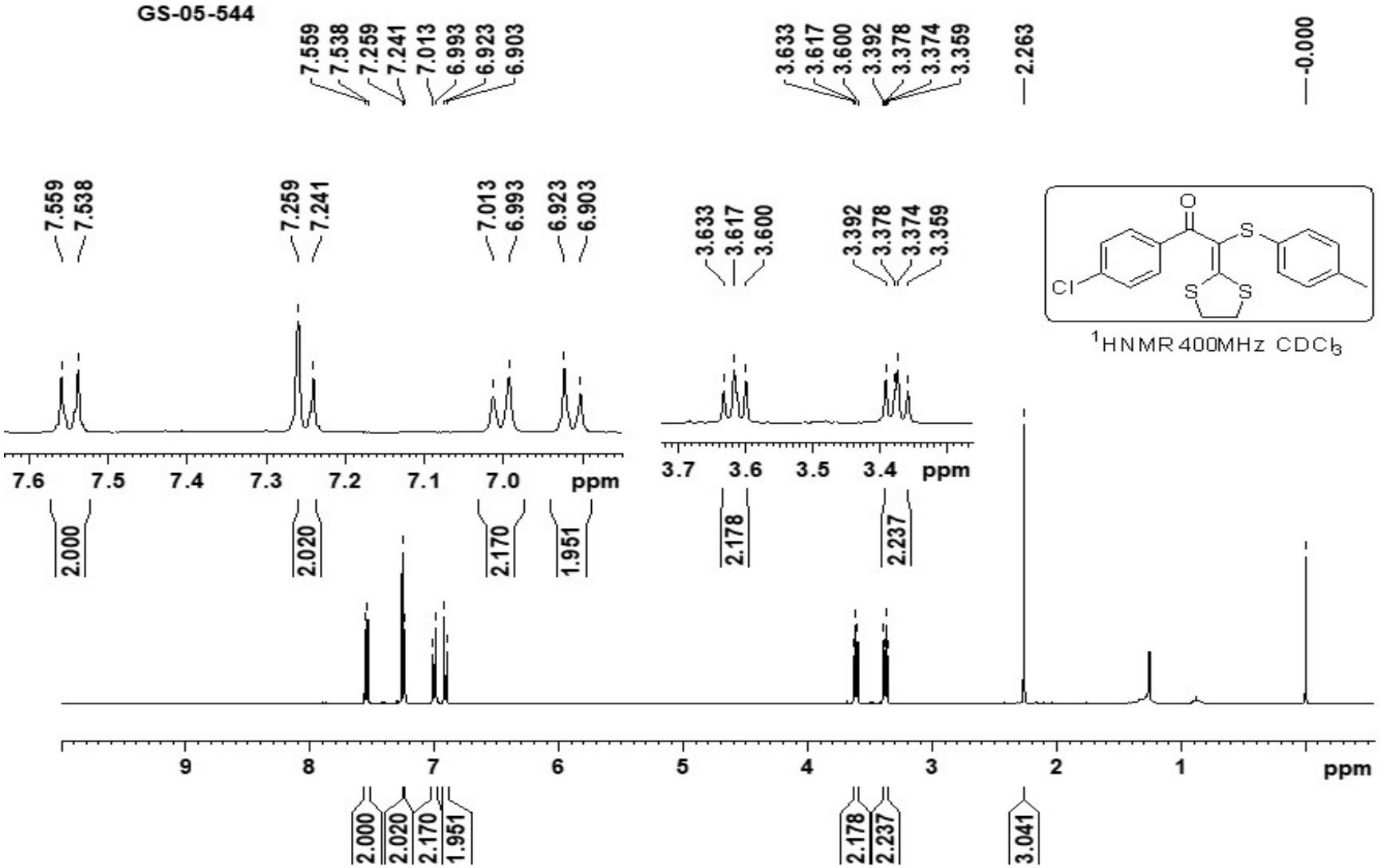


Fig. 54. ^{1}H NMR Spectrum of 3mc

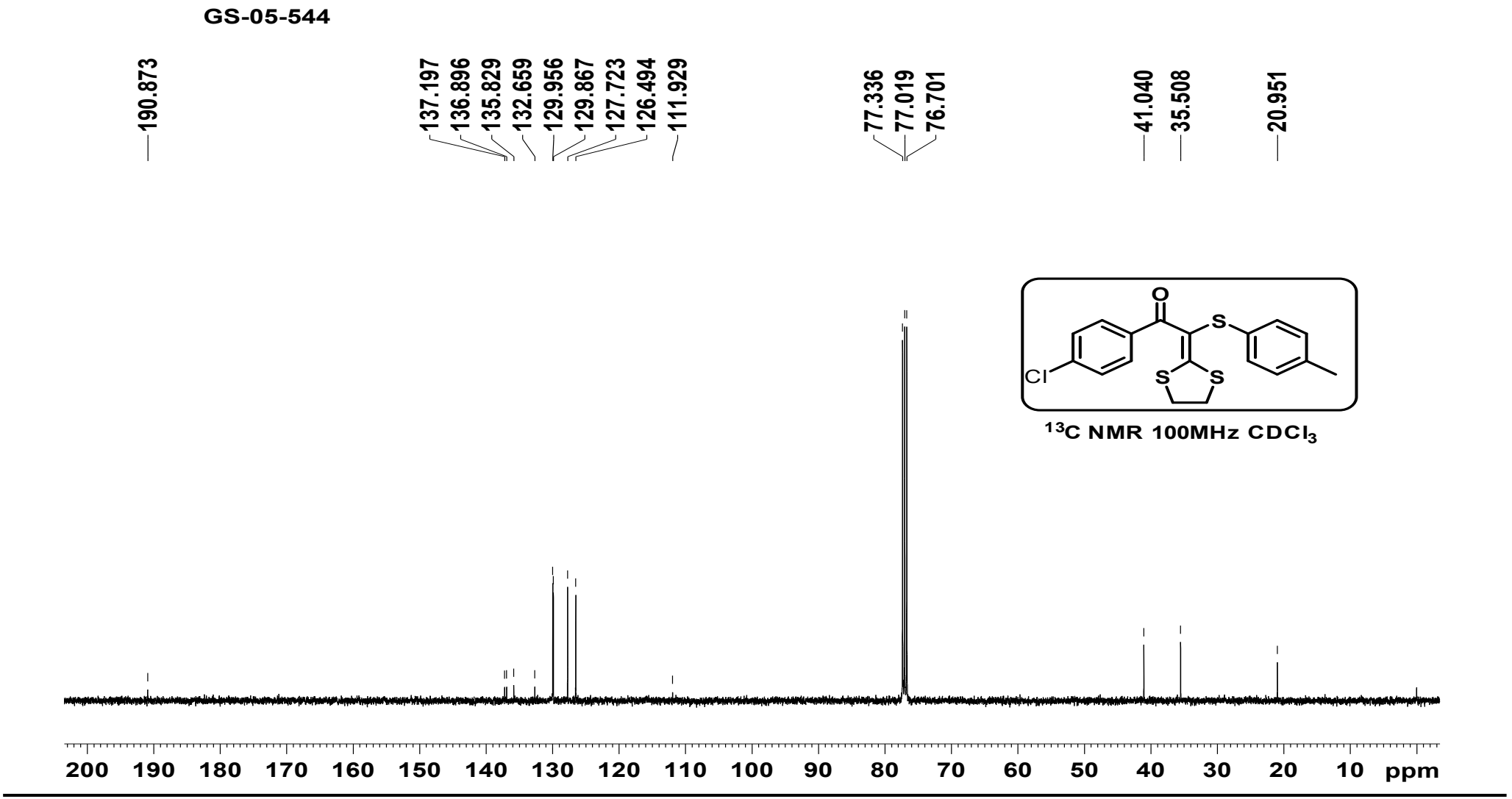


Fig. 55. ^{13}C NMR Spectrum of 3mc

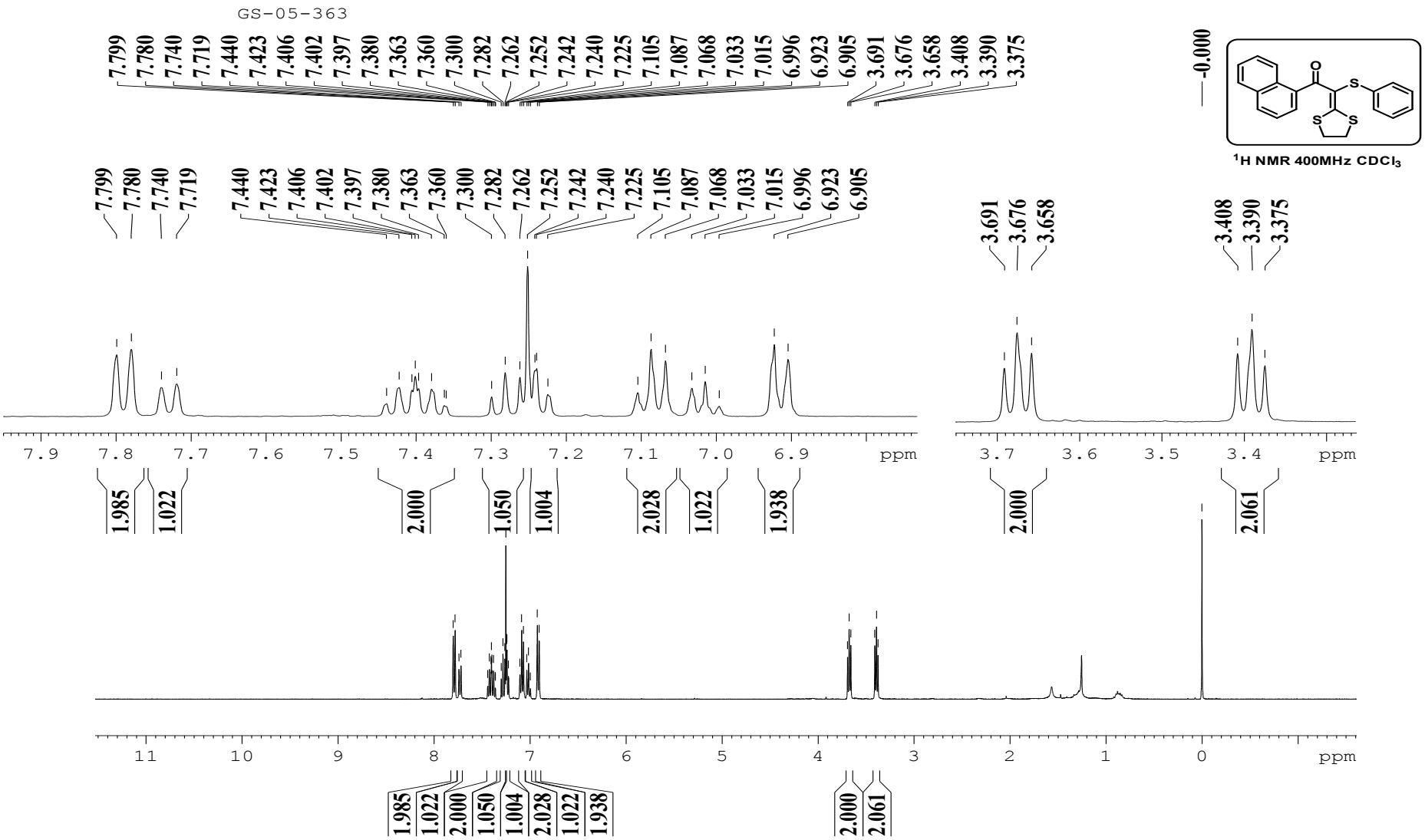


Fig. 56. ^{1}H NMR Spectrum of 3na

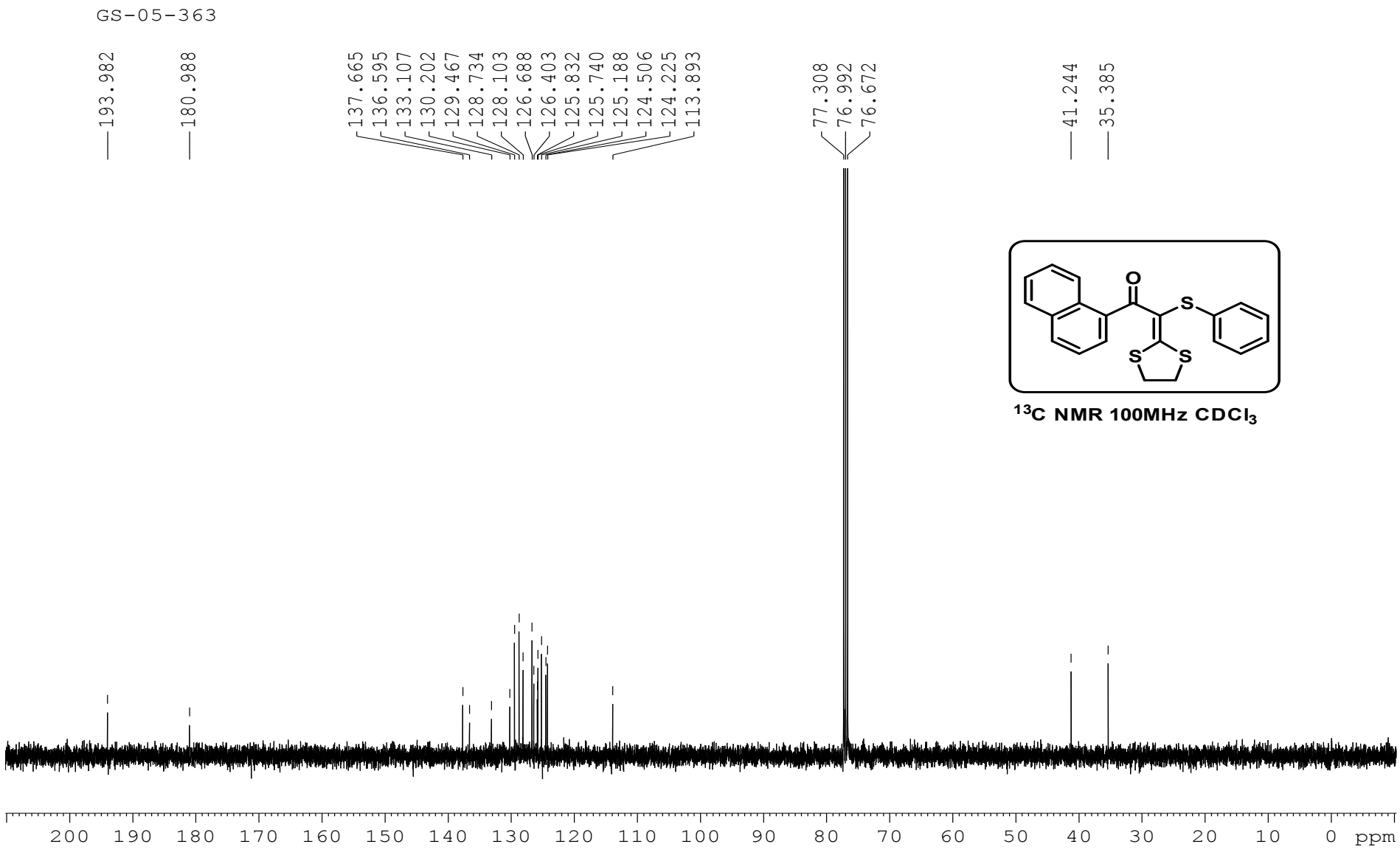


Fig. 57. ^{13}C NMR Spectrum of 3na

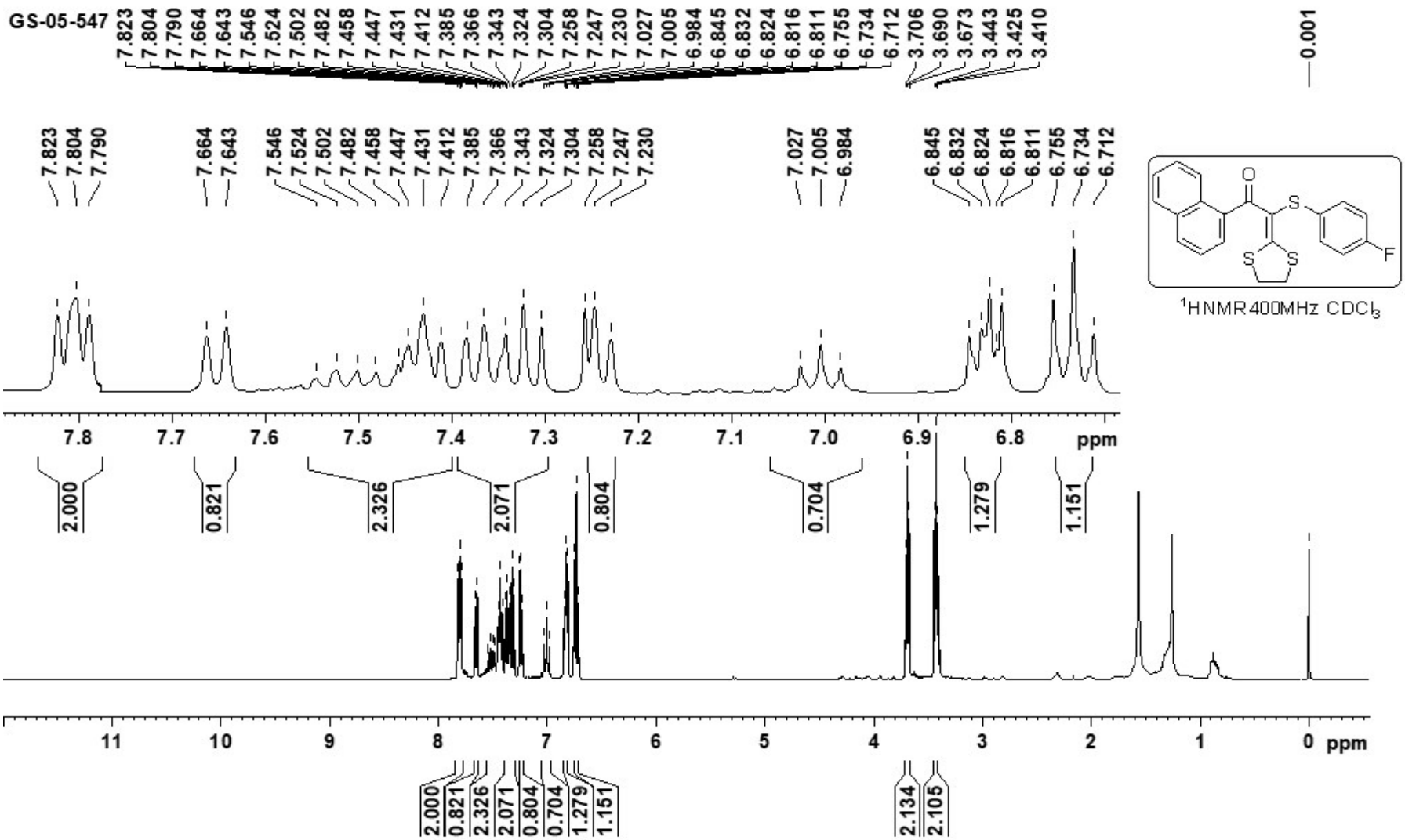


Fig. 58. ^{1}H NMR Spectrum of 3nd

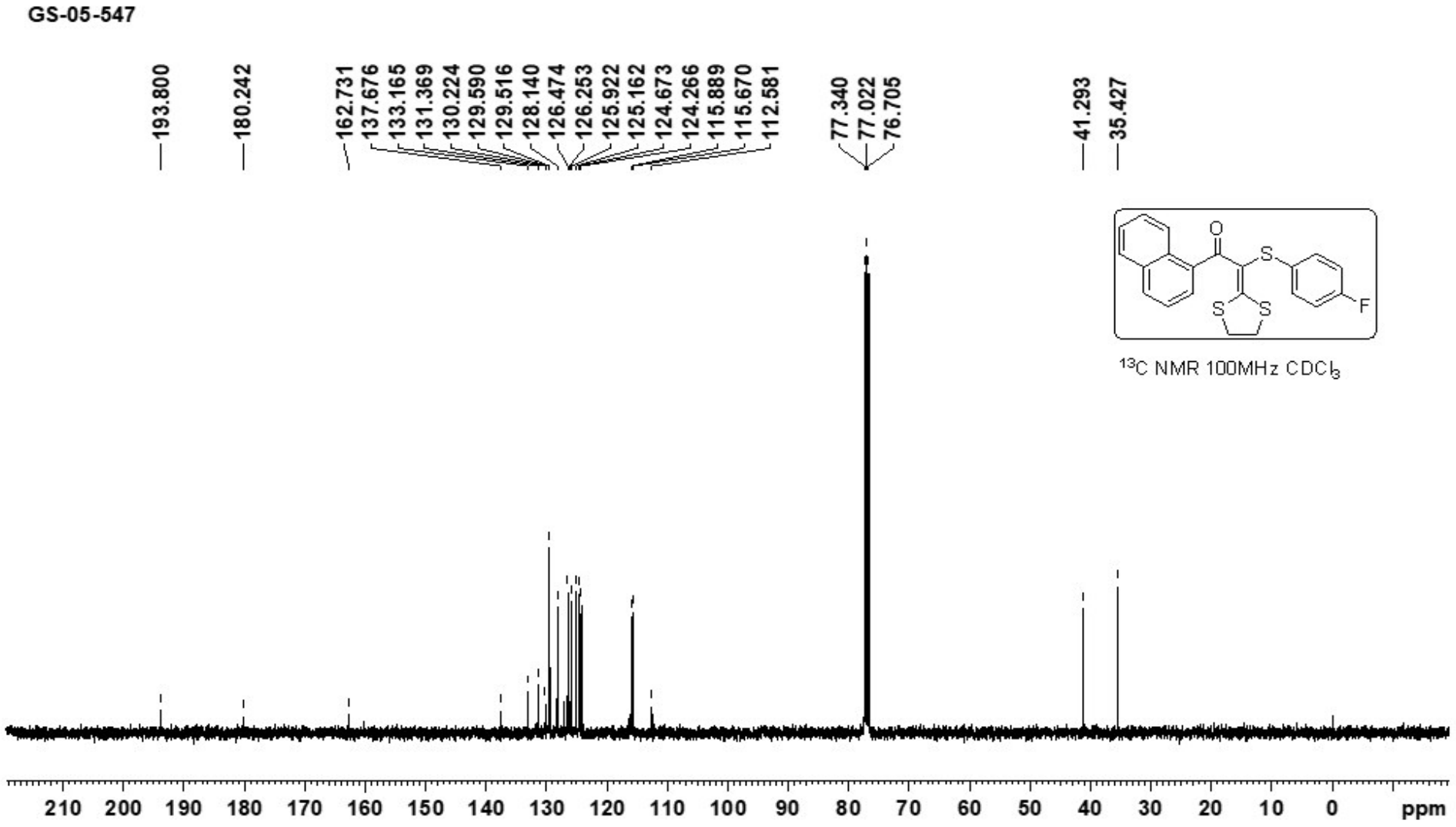


Fig. 59. ^{13}C NMR Spectrum of 3nd

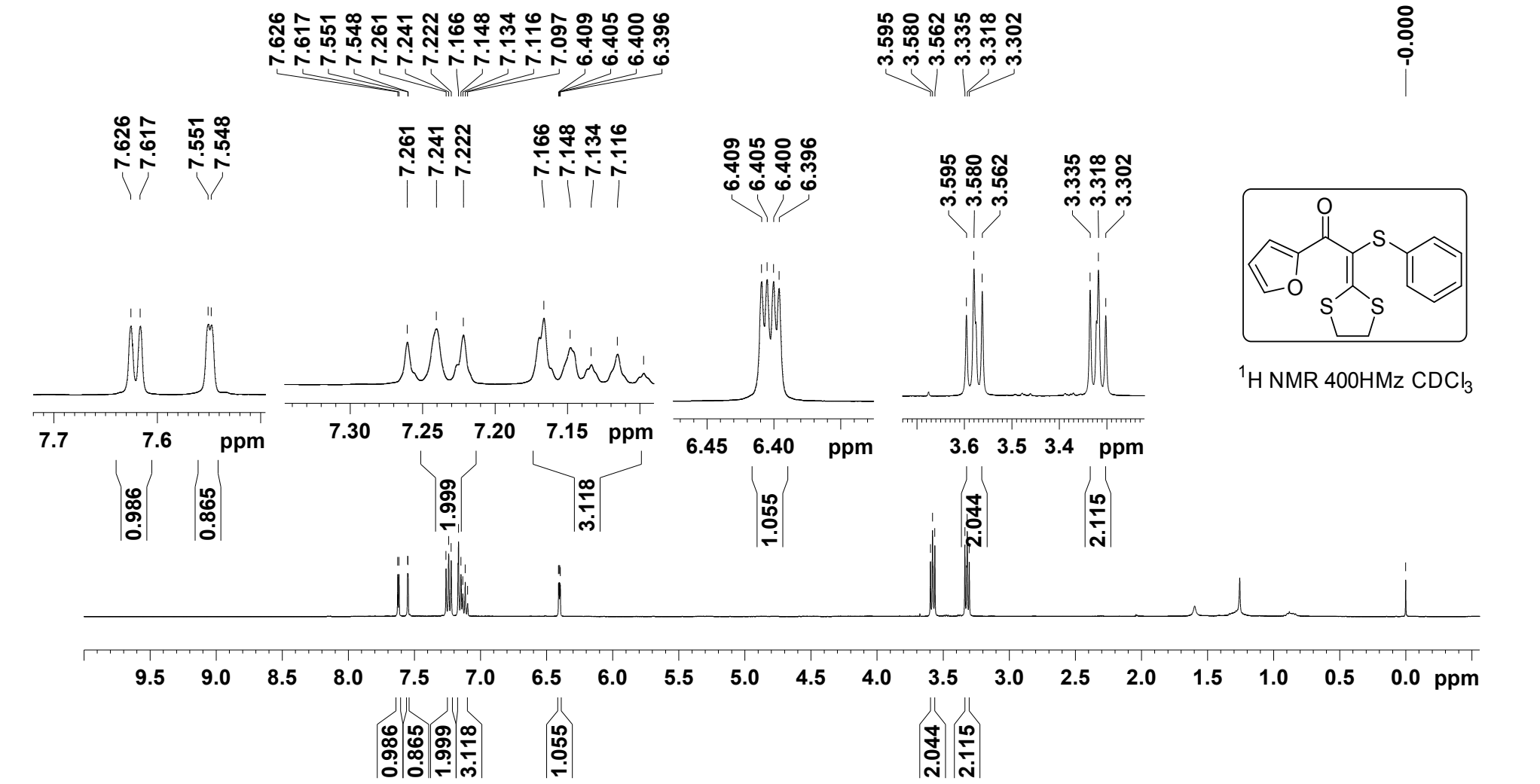


Fig. 60. ^{1}H NMR Spectrum of 3oa

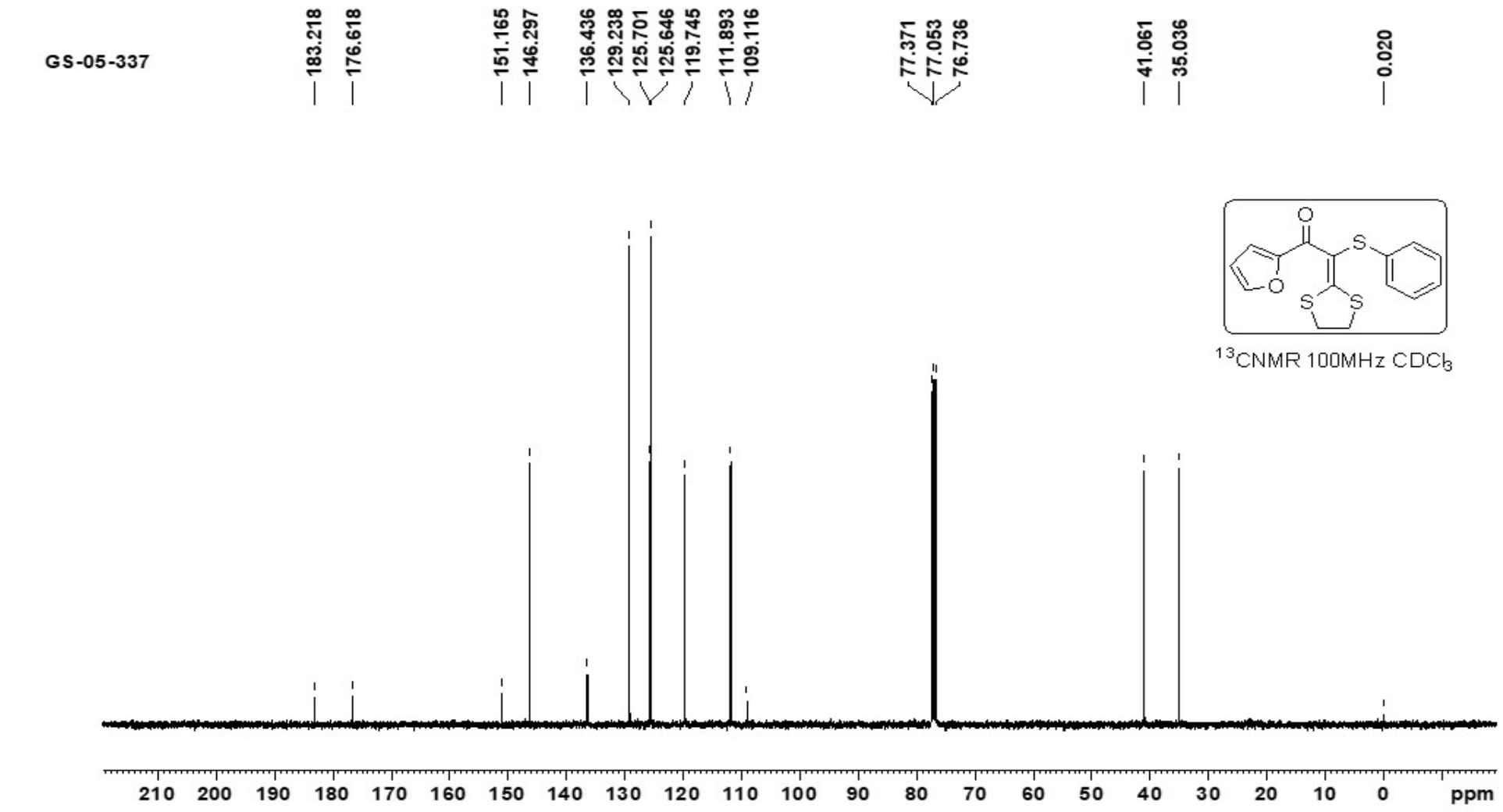


Fig. 61. ^{13}C NMR Spectrum of 3oa

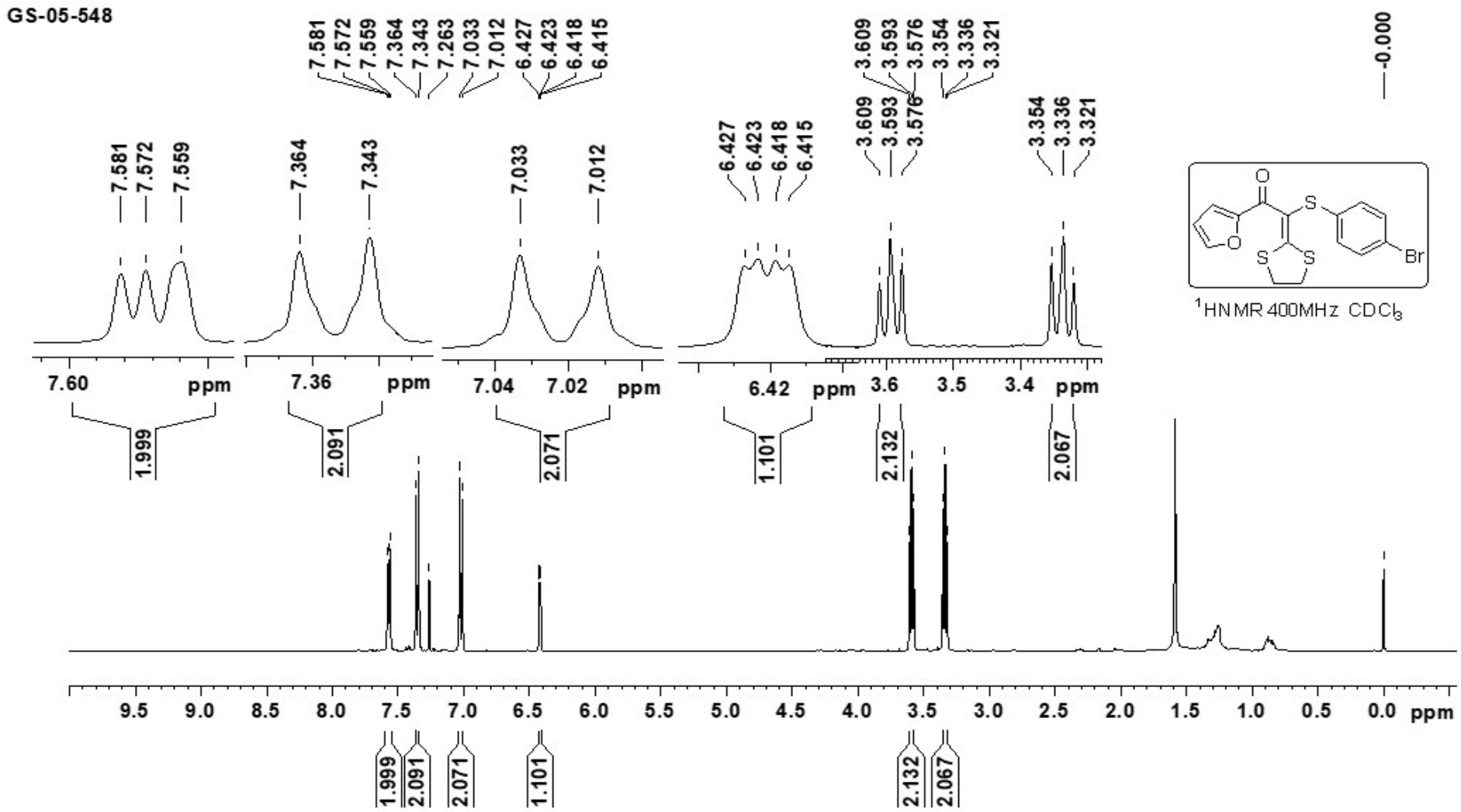


Fig. 62. ^{1}H NMR Spectrum of 3oe

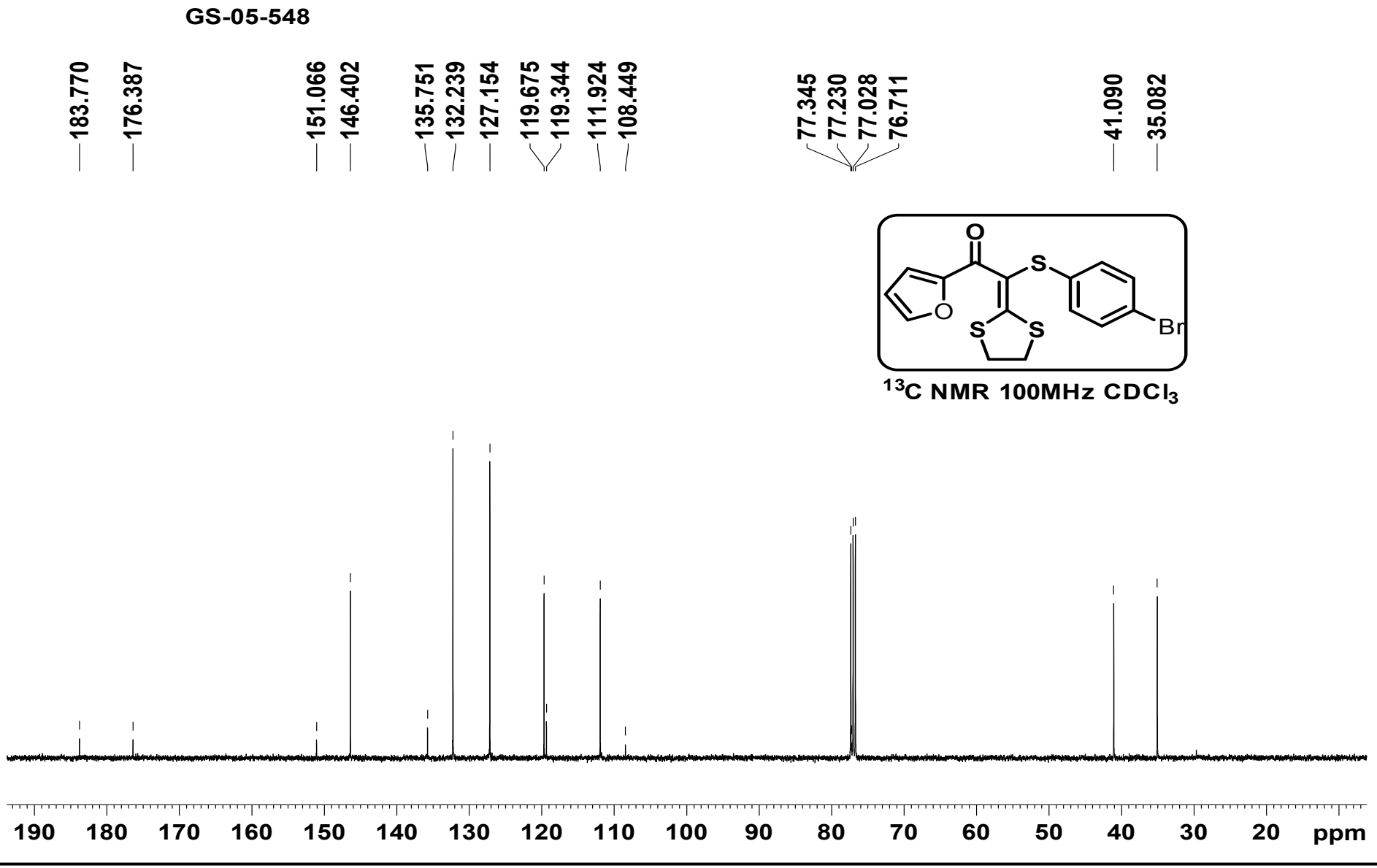


Fig. 63. ^{13}C NMR Spectrum of 3oe

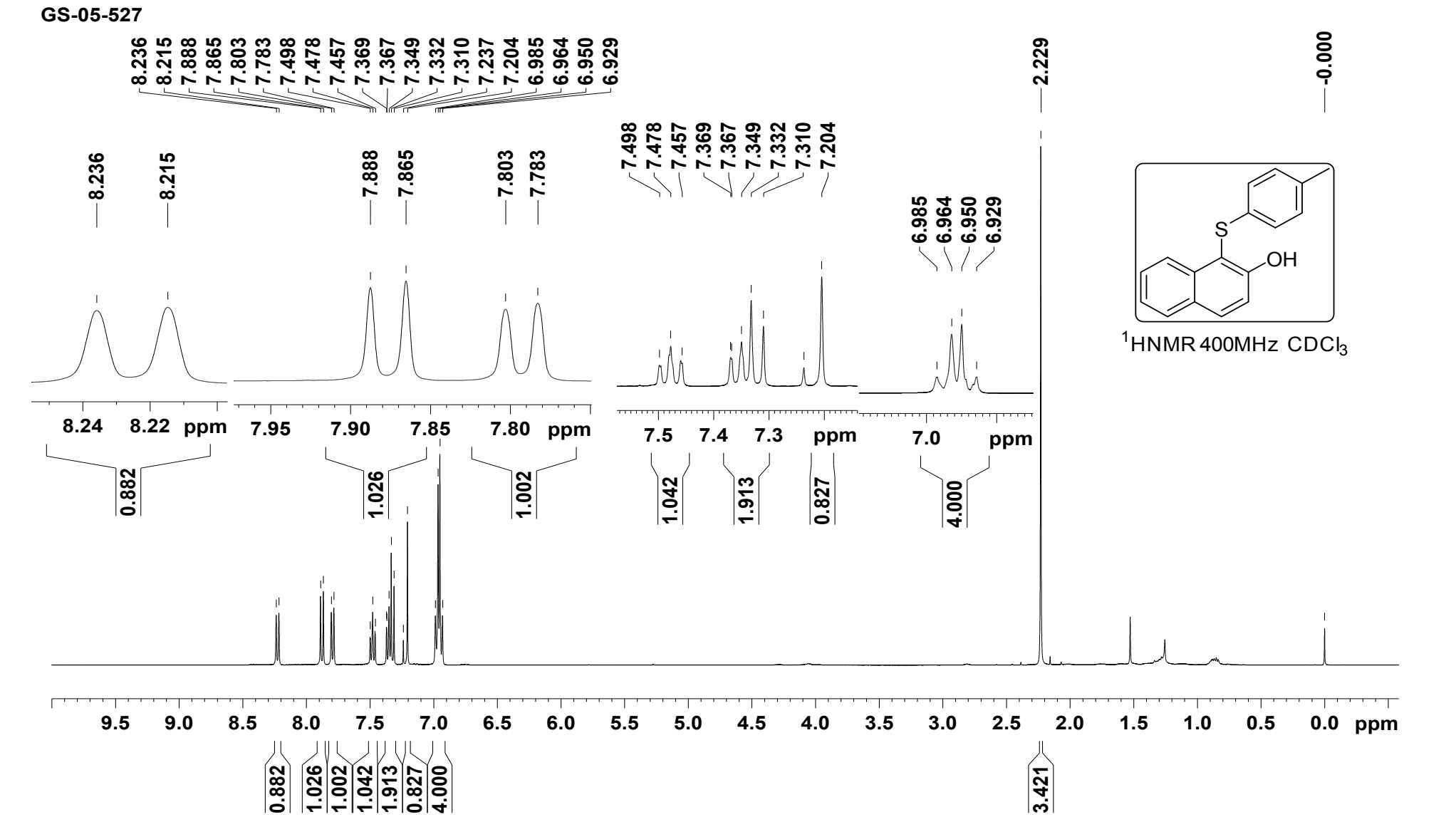


Fig. 64. ^{1}H NMR Spectrum of 5ac

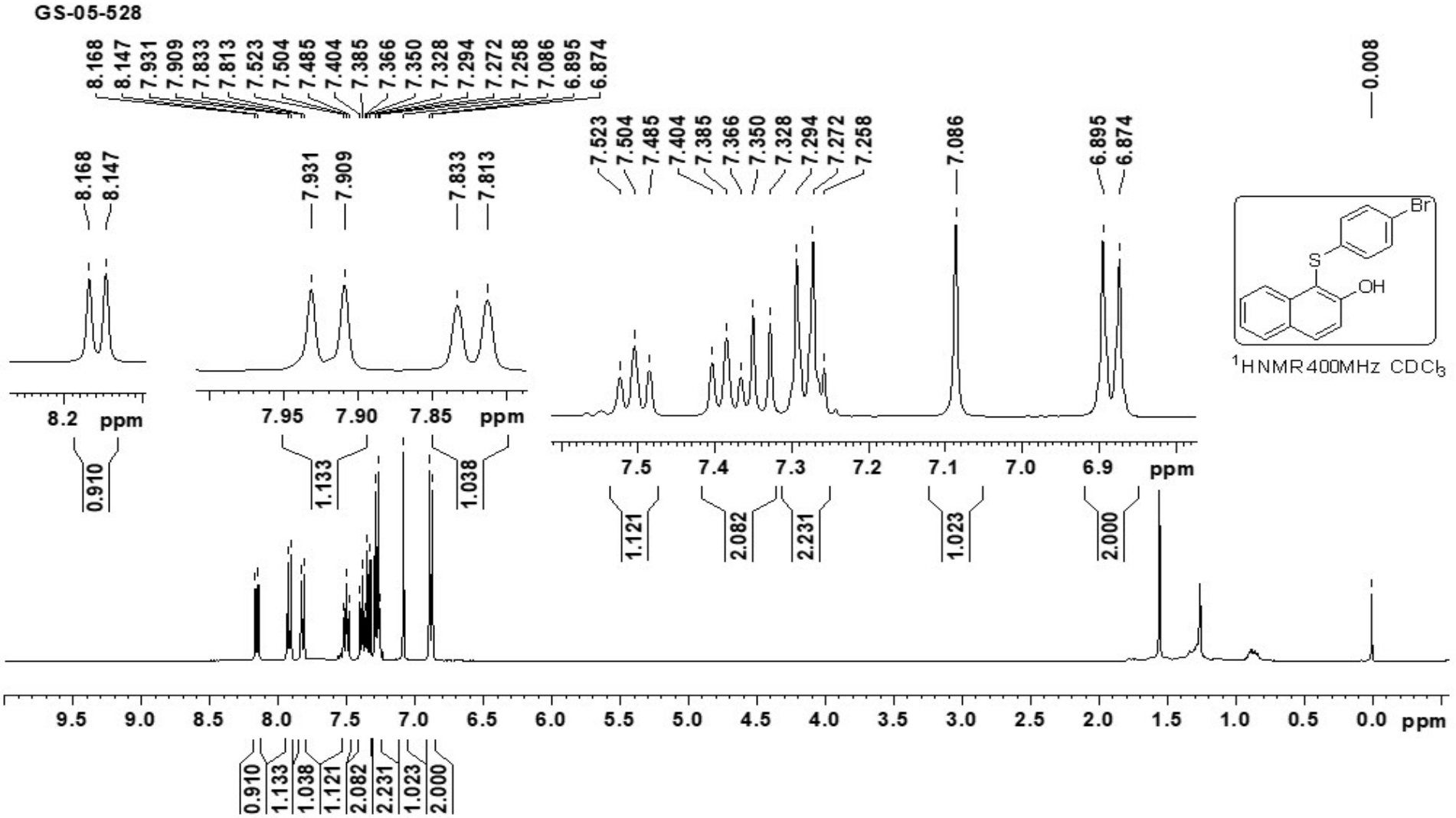


Fig. 65. ^{1}H NMR Spectrum of 5ae

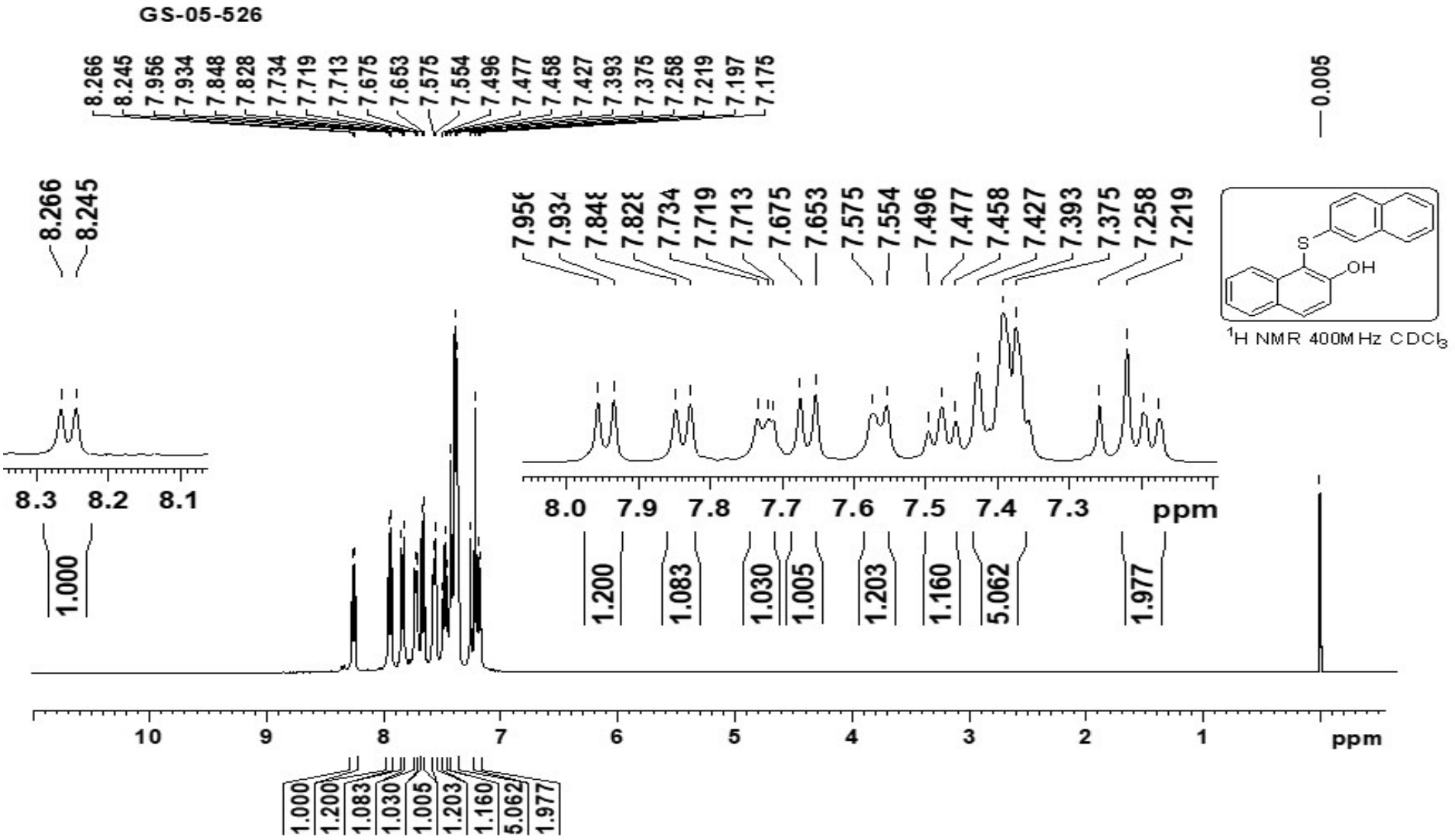


Fig. 66. ^{1}H NMR Spectrum of 5af

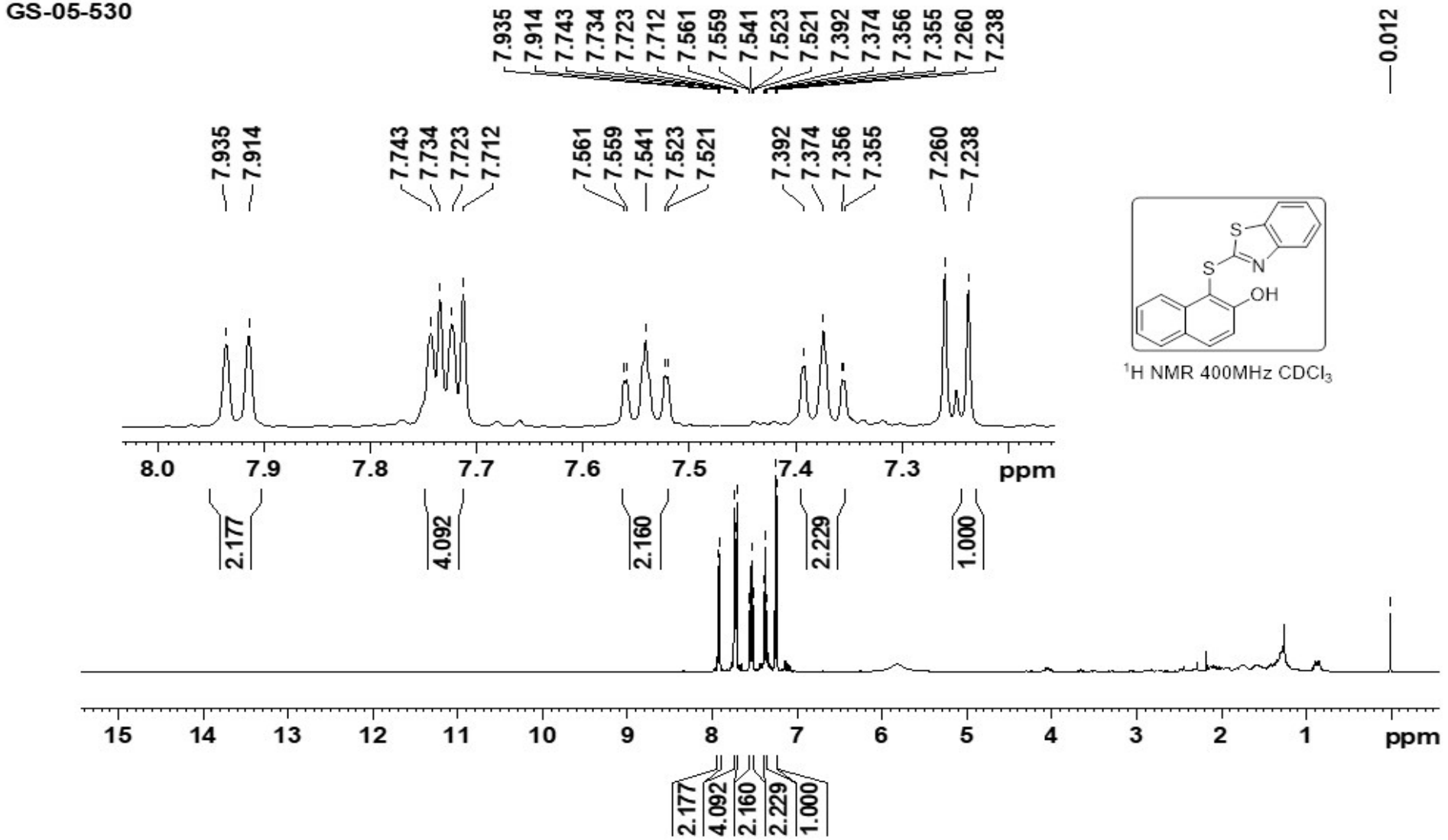


Fig. 67. ^{1}H NMR Spectrum of 5ag

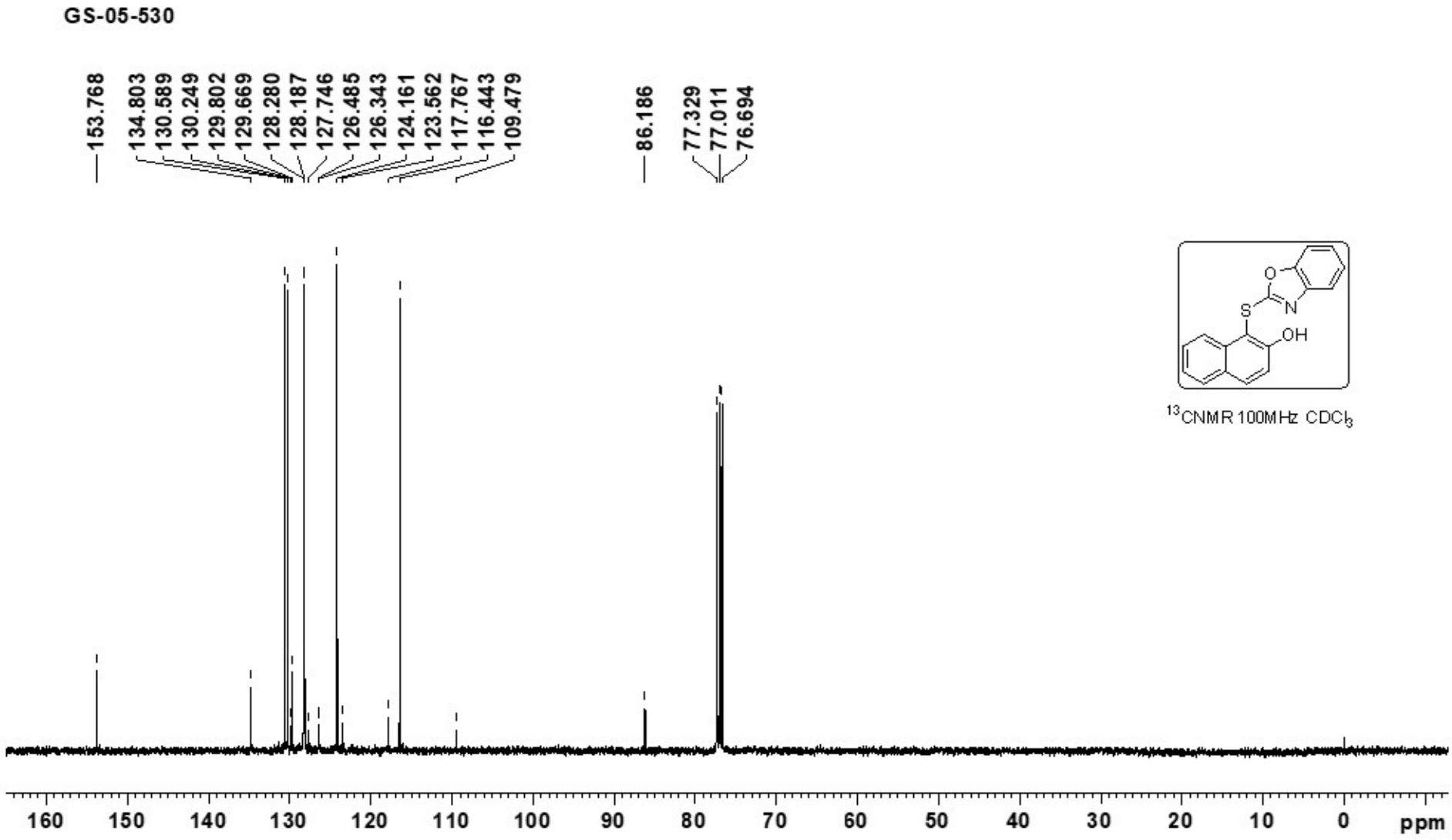


Fig. 68. ^{13}C NMR Spectrum of 5ag

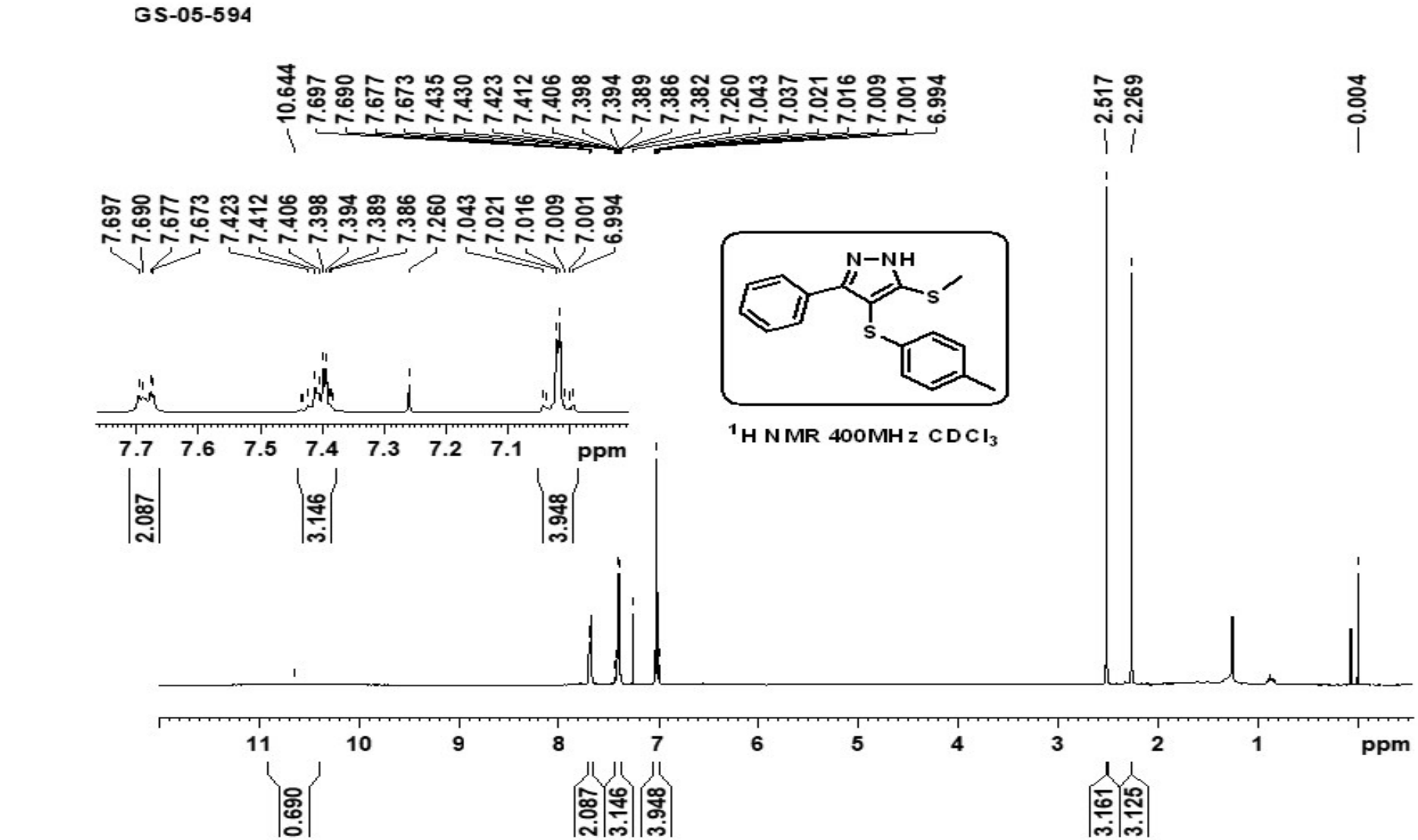


Fig. 69. ^{1}H NMR Spectrum of 6

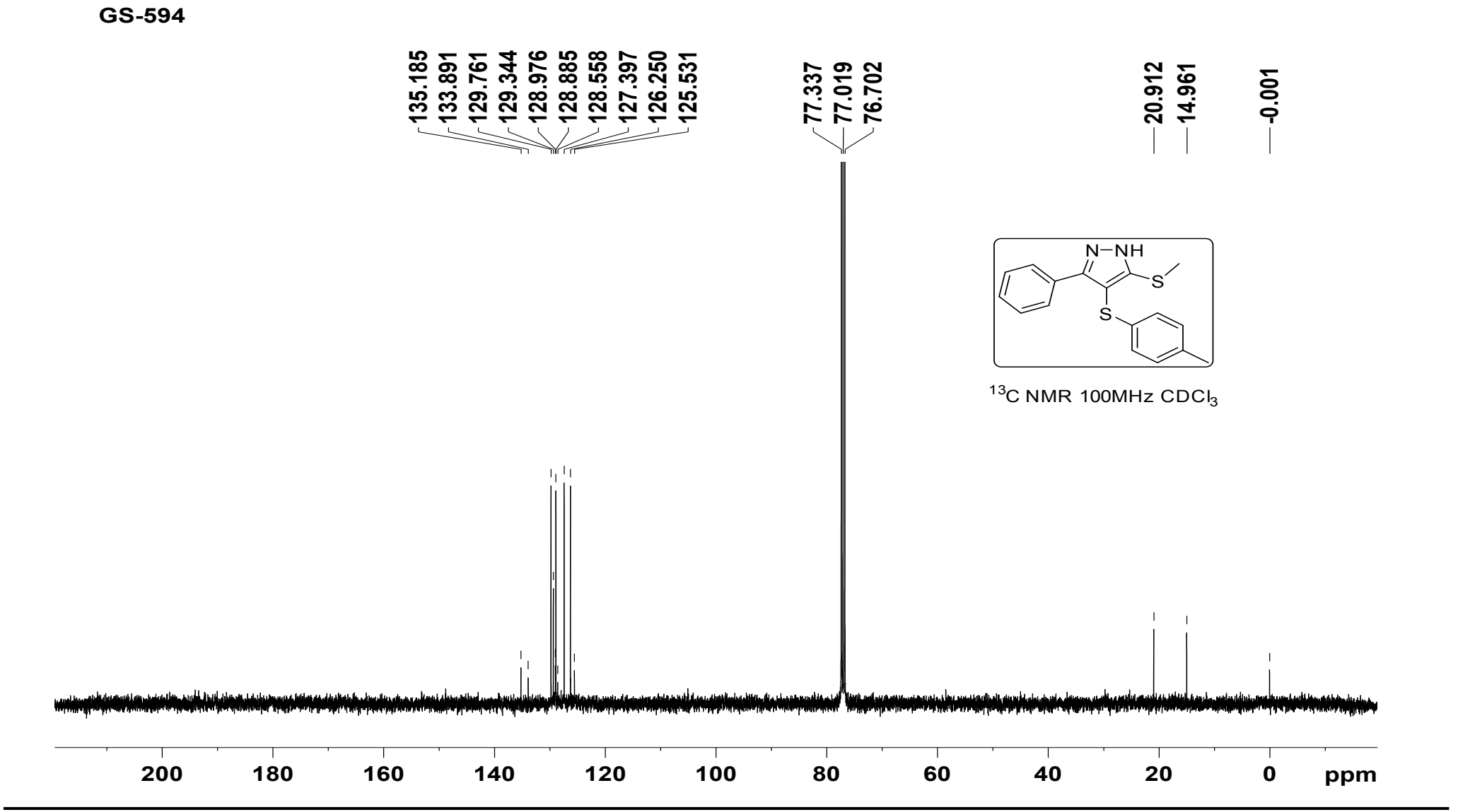


Fig. 70. ^{13}C NMR Spectrum of 6