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Supplementary information

Arylation of benzazoles at the 4 positions by activation of their 2-methylsulfinyl groups

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Instrumentation and Chemicals:

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{19}F NMR (594 MHz) spectra were recorded on a JEOL ECZ-600 spectrometer. Chemical shifts in ^{1}H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to residual $CHCl_3$ (δ = 7.26 ppm), CD_2HCN (δ = 1.94 ppm), or CD_3COCD_2H (δ = 2.05 ppm). Chemical shifts in ^{13}C NMR spectra were referenced to $CDCl_3$ (δ = 77.16 ppm), CD_3CN (δ = 118.26 ppm), or $(CD_3)_2CO$ (δ = 206.26 ppm). Chemical shifts in ^{19}F NMR spectra were reference to C_6H_5F (δ = –113.5 ppm), as an external standard. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using "LC/MS tuning mix, for APCI, low concentration" (Agilent Technologies, Inc.) as the internal standard. All non-aqueous reactions were carried out under an inert atmosphere of N_2 gas in oven-dried glassware unless otherwise noted. All reagents were commercially available and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F_{254}. Preparative flash chromatography was performed using Silica Gel (Silica Gel 60N, spherical neutral, particle size 100-210 μm, purchased from Kanto Chemical Co., Inc.) or monolithic silica column.[1] Aryl sulfoxides **1a** and **4** were prepared according to the reported procedures.[2,3]

Preparation of Substrates

General procedure for oxidation of benzazolyl sulfides to sulfoxides (GP1)

To a solution of a benzazolyl sulfoxide (0.33 M in CH_2Cl_2) was added *m*-chloroperbenzoic acid (contains ca. 30 wt% H_2O, 1.0 eq) portionwise at 0 °C. The resulting solution was allowed to warm to room temperature and stirred. Progress of the oxidation was checked by TLC. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with EtOAc. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/1) to give the corresponding benzazolyl sulfoxide.

Preparation of 5-chloro-2-(methylsulfinyl)benzo[*d*]thiazole (1b)

A 200-mL round bottom flask was charged with 5-chlorobenzo[*d*]thiazole-2-thiol (3.03 g, 15.0 mmol), potassium carbonate (2.49 g, 18.0 mmol), and acetone (45 mL). To the solution was added iodomethane (1.10 mL, 17.7 mmol), and the resulting mixture was stirred at room temperature for 5 h. After the reaction, the mixture was concentrated under reduced pressure.

Water was added to the residue, and organic components were extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 5-chloro-2-(methylsulfanyl)benzo[*d*]thiazole with some impurities. Subsequent oxidation in accordance with GP1 provided 5-chloro-2-(methylsulfinyl)benzo[*d*]thiazole (**1b**, 3.08 g, 13.3 mmol, 89%) as a white solid.

Preparation of 5-bromo-2-(methylsulfinyl)benzo[*d*]thiazole (1c)

A 100-mL two-necked flask was charged with 5-bromo-2-fluoroaniline (2.75 g, 14.5 mmol), potassium ethylxanthate (4.80 g, 29.9 mmol), and NMP (21 mL). The mixture was warmed to 140 °C and stirred for 3 h. After the reaction was cooled to room temperature, saturated aqueous NH_4Cl was added. The resulting mixture was filtrated to afford 5-bromobenzo[*d*]thiazole-2-thiol with some impurities. In a 50-mL round bottom flask, obtained 5-bromobenzo[*d*]thiazole-2-thiol was dissolved in acetone (20 mL). Potassium carbonate (1.22 g, 8.83 mmol) and iodomethane (0.55 mL, 8.83 mmol) were added to the solution and the mixture was stirred for 2 h. After the reaction, the mixture was concentrated under reduced pressure. Water was added to the residue, and the resulting mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford 5-bromo-2-(methylsulfanyl)benzo[*d*]thiazole. Subsequent oxidation in accordance with GP1 provided 5-bromo-2-(methylsulfinyl)benzo[*d*]thiazole (**1c**, 1.04 g, 3.76 mmol, 25%) as a white solid.

Preparation of 2-(isopropylsulfinyl)benzo[*d*]thiazole (1d)

A 100-mL round bottom flask was charged with benzo[*d*]thiazole-2-thiol (1.68 g, 10.0 mmol), potassium carbonate (1.63 g, 11.8 mmol), and acetone (30 mL). 2-Bromopropane (1.20 mL, 12.8 mmol) was added to the mixture and the resulting mixture was stirred at room temperature for 19 h. After the reaction, the mixture was concentrated under reduced pressure. Water was added to the residue, and the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 2-(isopropylsulfanyl)benzo[*d*]thiazole. Subsequent oxidation in accordance with GP1 provided 2-(isopropylsulfinyl)benzo[*d*]thiazole (**1d**, 1.54 g, 6.85 mmol, 69%) as a white solid.

Preparation of 2-(phenylsulfinyl)benzo[*d*]thiazole (1e)

A 100-mL two-necked flask was added with 2,2'-dibenzothiazolyl disulfide (3.33 g, 10.0 mmol) and THF (20 mL). The resulting solution was cooled to 0 °C and added with phenylmagnesium

bromide (1.0 M in THF, 11 mL, 11 mmol). The resulting mixture was stirred for 4 h at room temperature. After the reaction, 2 M HCl aq was added and the resulting biphasic solution was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford 2-(phenylsulfanyl)benzo[*d*]thiazole. Subsequent oxidation in accordance with GP1 provided 2-(phenylsulfinyl)benzo[*d*]thiazole (**1e**, 1.99 g, 7.68 mmol, 77%) as a white solid.

Preparation of 2-methylsulfinyl-1-tosyl-1*H*-benzo[*d*]imidazole (5)

A 100-mL two-necked flask was charged with 2-methylsulfanyl-1*H*-benzo[*d*]imidazole (1.31 g, 8.00 mmol) and THF (32 mL). To the solution was added NaH (482 mg, 20.1 mmol), and the resulting mixture was stirred at room temperature. After 30 min, *p*-toluenesulfonyl chloride (2.29 g, 12.0 mmol) was added and the resulting solution was stirred for an additional 14 h. After the reaction, saturated aqueous NH_4Cl was added, and the resulting biphasic solution was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 2-methylsulfanyl-1-tosyl-1*H*-benzo[*d*]imidazole with some impurities. Subsequent oxidation in accordance with GP1 provided 2-methylsulfinyl-1-tosyl-1*H*-benzo[*d*]imidazole (**5**, 1.53g, 4.58 mmol, 57%) as a white solid.

Preparation of 2,6-bis((2-ethylhexyl)sulfinyl)benzo[1,2-*d*:4,5-*d*']bis(thiazole) (8)

The procedure reported by Shi, Marks and Huang[4] was modified as follows: A 500-mL two-necked flask was charged with benzo[1,2-*d*:4,5-*d'*]bis(thiazole) (963 mg, 5.01 mmol) and THF (200 mL), and the resulting solution was cooled to –78 °C. *n*-BuLi (1.6 M in hexane, 7.2 mL, 12 mmol) was added slowly, and the resulting solution was stirred at –78 °C for 1 h. Di(2-ethylhexyl) disulfide (3.54 g, 12.2 mmol) was added and the resulting solution was stirred at room temperature for 4 h. After the reaction, water was added, and the resulting biphasic solution was concentrated under reduced pressure. The residue was extracted with EtOAc (60 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 50/1) to give 2,6-bis((2-ethylhexyl)sulfanyl)benzo[1,2-*d*:4,5-*d*']bis(thiazole) with some impurities. Subsequent oxidation in accordance with GP1 (2.0 eq *m*CPBA was used) provided 2,6-bis((2-ethylhexyl)sulfinyl)benzo[1,2-*d*:4,5-*d*']bis(thiazole) (**8**, 794 mg, 1.55 mmol, 31%) as a yellow solid.

Experimental Procedures

General Procedure for C4 Arylation of Benzazoles

Synthesis of **3aa** is representative. A 20-mL Schlenk tube was charged with 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.8 mg, 0.501 mmol), phenol (**2a**, 98.0 mg, 1.04 mmol), and DCE (5 mL), and the resulting solution was cooled to –20 °C. To the tube was added trifluoromethanesulfonic anhydride (160 μL, 0.975 mmol), and the resulting mixture was stirred at –20 °C. After 3 h, the mixture was warmed to 0 °C and stirred for an additional 1 h. After the reaction, saturated aqueous $NaHCO_3$ (2 mL) was added and the resulting biphasic solution was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to provide **3aa** (95.7 mg, 0.350 mmol, 70%) as a white solid.

Procedure for synthesis of tetracyclic aromatic system 10

The procedure reported by Yorimitsu[5] was modified as follows: A 50-mL two-necked flask was charged with 4-(5-chloro-2-(methylthio)benzo[*d*]thiazol-4-yl)benzene-1,3-diol (**3bj**, 65.0 mg, 0.201 mmol), cesium carbonate (99.7 mg, 0.306 mmol), and DMSO (20 mL). The resulting mixture was stirred at 130 °C for 12 h. After the reaction, saturated aqueous NH_4Cl was added, and the resulting biphasic solution was extracted with hexane/EtOAc = 1/1 (20 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **10** (16.1 mg, 0.0560 mmol, 28%) as a white solid.

Procedure for reductive removal of SMe group

The procedure reported by Martin[6] was modified as follows: A 20-mL greaseless Schlenk tube was charged with **3aa** (54.7 mg, 0.200 mmol), $Ni(cod)_2$ (11.0 mg, 0.0400 mmol), triethylsilane (0.16 mL, 1.0 mmol), and toluene (0.8 mL). The resulting mixture was stirred at 130 °C for 12 h. After the reaction, the mixture was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in MeOH (4 mL). 1 M HCl aq. (2 mL) was added to the solution and the resulting mixture was stirred at room temperature for 2 h. After deprotection of the triethylsilyl group, the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue

was purified by column chromatograph on silica gel (hexane/EtOAc = 10/1) to give **11** (18.4 mg, 0.0810 mmol, 40%) as a white solid.

Procedure for synthesis of benzothiazolinone

A 20-mL round bottom flask was charged with **3aa** (55.0 mg, 0.201 mmol) and CH_2Cl_2 (2 mL). To the tube was added with *m*CPBA (contains ca. 30 wt% H_2O, 101 mg, 0.408 mmol) and the resulting mixture was stirred for 10 h. After the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was added to another 20-mL round bottom flask. The flask was charged with H_2O (4 mL) and the resulting mixture was added with KOH (83.6 mg, 1.49 mmol). The mixture was stirred at 80 °C for 11 h. After the reaction, 2 M aqueous HCl was added to the solution. The resulting mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **12** (28.6 mg, 0.118 mmol, 59%) as a white solid.

Procedure for synthesis of 13

A 20-mL Schlenk tube was charged with **3aa** (272 mg, 0.996 mmol), imidazole (135 mg, 1.98 mmol), and DMF (5 mL). To the tube was added *t*BuMe$_2$SiCl (180 mg, 1.19 mmol) and the resulting mixture was stirred for 17 h. After the reaction, water was added and the resulting mixture was extracted with Et_2O (20 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was added to a 100-mL round bottom flask and dissolved in CH_2Cl_2 (10 mL). The resulting solution was cooled to 0 °C. *m*CPBA (contains ca 30 wt% H_2O, 494 mg, 2.00 mmol) was added to the flask and the resulting mixture was stirred at room temperature for 12 h. After the reaction, saturated aqueous $NaHCO_3$ was added and the resulting biphasic solution was extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5/1) to give **13** (392 mg, 0.933 mmol, 93%) as a white solid.

Procedure for synthesis of 14

A 10-mL Schlenk tube was charged with carbazole (30.4 mg, 0.182 mmol) and DMF (1 mL). NaH (ca 60 wt% in paraffin oil, 7.2 mg, 0.18 mmol) was added and the resulting mixture was

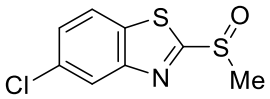
stirred at room temperature. After 1 h, **13** (42.4 mg, 0.101 mmol) was added to the mixture. After the reaction mixture was stirred for an additional 13 h, water was added and the resulting solution was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **14** (20.6 mg, 0.0525 mmol, 52%) as a white solid.

Procedure for synthesis of 15

A 20-mL Schlenk tube was charged with 2-phenylthiophene (35.1 mg, 0.219 mmol) and THF (1 mL), and the resulting solution was cooled to –78 °C. *n*BuLi (1.6 M in hexane, 0.13 mL) was added and the resulting solution was stirred at –78 °C. After 1 h, **13** (83.9 mg, 0.200 mmol) was added and the resulting mixture was stirred at room temperature for an additional 1 h. After the reaction, H_2O was added and the resulting biphasic solution was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 100/1) to give **15** (33.7 mg, 0.0674 mmol, 34%) as a yellow sticky solid.

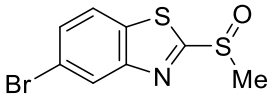
Characterization Data

5-chloro-2-(methylsulfinyl)benzo[*d*]thiazole (1b)



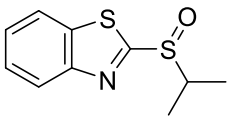
White solid (3.08 g, 13.3 mmol, 89%) from 5-chlorobenzo[*d*]thiazole-2-thiol (3.03 g, 15.0 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/1). ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 1.6 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 8.8, 1.6 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 180.9, 154.7, 134.4, 133.3, 127.0, 123.9, 123.2, 43.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_8H_7S_2N_1O_1{}^{35}Cl$ 231.9652; Found 231.9657. IR (ATR, cm^{-1}) 3086, 3059, 2997, 2910, 1431, 1296, 1058, 967, 890, 805. mp: 146.3 °C (decomp.).

5-bromo-2-(methylsulfinyl)benzo[*d*]thiazole (1c)



White solid (1.04 g, 3.76 mmol, 25%) from 5-bromo-2-fluoroaniline (2.75 g, 14.5 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/1). ^{1}H NMR ($CDCl_3$) δ 8.22 (d, J = 1.9 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.8, 1.9 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 180.7, 155.0, 134.9, 129.6, 126.9, 123.5, 120.8, 43.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_8H_7S_2N_1O_1{}^{81}Br$ 277.9126; Found 277.9130. IR (ATR, cm^{-1}) 3083, 3053, 2989, 2907, 2119, 1474, 1427, 1300, 1053, 802. mp: 171.7 °C–173.6 °C.

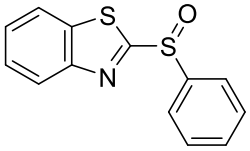
2-(isopropylsulfinyl)benzo[*d*]thiazole (1d)



White solid (1.54 g, 6.85 mmol, 69%) from benzo[*d*]thiazole-2-thiol (1.68 g, 10.0 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 3.36 (sep, J =6.9 Hz, 1H), 1.46 (d, J = 6.9 Hz, 3H), 1.30 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 177.0, 154.1, 136.0, 126.9, 126.2, 124.0, 122.3, 56.3, 16.3, 13.8; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{10}H_{13}S_2N_1O_1$ 226.0355; Found 226.0346. IR

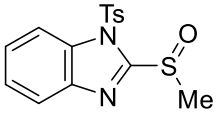
(ATR, cm^{-1}) 3060, 2868, 2086, 1470, 1421, 1315, 1233, 1063, 1022, 999, 758. mp: 88.7 °C–90.5 °C.

2-(phenylsulfinyl)benzo[*d*]thiazole (1e)



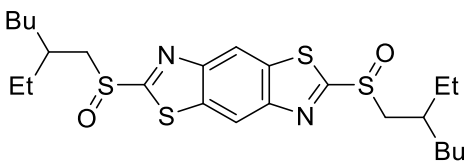
White solid (1.99 g, 7.68 mmol, 77%) from 2,2'-dibenzothiazolyl disulfide (3.33 g, 10.0 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.90 (dd, J = 7.8, 1.8 Hz, 2H), 7.55–7.51 (m, 4H), 7.45 (td, J = 7.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 178.4, 153.8, 143.1, 135.9, 132.1, 129.7, 126.9, 126.5, 124.7, 124.3, 122.4; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{13}H_{10}S_2N_1O_1$ 260.0198; Found 260.0193. IR (ATR, cm^{-1}) 3069, 2946, 2658, 2371, 2122, 1474, 1443, 1315, 1086, 1050, 992, 752. mp: 116.3 °C–118.0 °C.

2-methylsulfinyl-1-tosyl-1*H*-benzo[*d*]imidazole (5)



White solid (1.53 g, 4.58 mmol, 57%) from 2-methylsulfanyl-1*H*-benzo[*d*]imidazole (1.31 g, 8.00 mmol). Purification was done by chromatography on silica gel (hexane/EtOAc = 1/1). ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 3.26 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.3, 147.2, 142.2, 133.8, 133.7, 130.6, 127.7, 127.1, 125.7, 121.9, 113.2, 42.7, 21.8; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{15}H_{15}S_2N_2O_3$ 335.0519; Found 335.0516. IR (ATR, cm^{-1}) 3092, 3000, 2919, 2853, 1735, 1594, 1478, 1437, 1372, 1229, 1185, 1164, 1122, 1084, 1036, 965, 812, 766, 752. mp: 99.0 °C (decomp.).

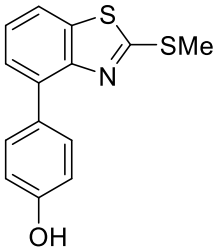
2,6-bis((2-ethylhexyl)sulfinyl)benzo[1,2-*d*:4,5-*d′*]bis(thiazole) (8)



Yellow solid (794 mg, 1.55 mmol, 31%, mixture of diastereomers) from benzo[1,2-*d*:4,5-*d′*]bis(thiazole) (963 mg, 5.01 mmol). Purification was done by chromatography on silica gel

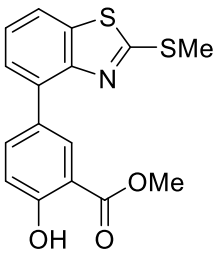
(hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 2H), 3.23–3.13 (m, 4H), 2.17–2.10 (m, 2H), 1.75–1.25 (m, 16H), 0.99–0.84 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 181.6, 181.5, 152.1, 135.5, 135.5, 117.3, 63.0, 62.8, 62.7, 34.5, 34.4, 32.7, 32.3, 28.5, 28.4, 26.2, 25.5, 23.0, 22.9, 14.1, 14.1, 10.6, 10.4; HRMS (APCI-MS, positive): *m*/*z* $[M]^+$ Calcd for $C_{24}H_{36}S_4N_2O_2$ 512.1654; Found 512.1652. IR (ATR, cm^{-1}) 2957, 2925, 2859, 1489, 1459, 1393, 1312, 1061, 1047, 1001, 830. mp: 81.6 °C (decomp.).

4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (3aa)



White solid (95.7 mg, 0.350 mmol, 70%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.8 mg, 0.501 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 4.88 (s, 1H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.6, 155.5, 150.8, 136.3, 134.5, 131.4, 131.0, 126.1, 124.5, 119.6, 115.4, 16.2; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{14}H_{12}S_2N_1O_1$ 274.0355; Found 274.0345. IR (ATR, cm^{-1}) 3057, 2995, 2920, 2110, 1611, 1513, 1426, 1226, 1077, 1032, 968, 796, 752. mp: 143.8 °C–145.5 °C.

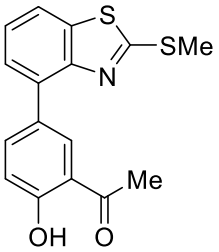
methyl 2-hydroxy-5-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)benzoate (3ab)



White solid (90.8 mg, 0.274 mmol, 55%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.7 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 100/1). ^{1}H NMR ($CDCl_3$) δ 10.82 (s, 1H), 8.50 (d, J = 2.1 Hz, 1H), 8.03 (dd, J = 8.8, 2.1 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 3.98 (s, 3H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.9, 167.3, 161.2, 150.6, 137.0, 136.7, 133.0, 131.2, 130.0, 125.6, 124.5, 120.0, 117.4, 112.2, 52.4, 15.9; HRMS

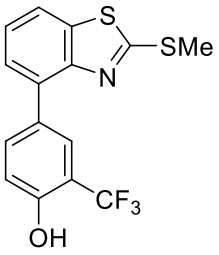
(APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{16}H_{14}S_2O_3N_1$ 332.0410; Found 334.0412. IR (ATR, cm^{-1}) 3152, 3031, 2959, 2921, 1671, 1459, 1436, 1213, 1198, 1093, 1017, 965, 747. mp: 139.5 °C–146.7 °C.

1-(2-hydroxy-5-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenyl)ethan-1-one (3ac)



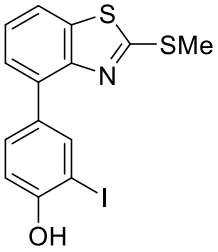
White solid (60.6 mg, 0.192 mmol, 38%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.6 mg, 0.500 mmol). Purification was done by recrystallization from hexane. ^{1}H NMR ($CDCl_3$) δ 12.32 (s, 1H), 8.41 (d, J = 2.4 Hz, 1H), 7.97 (dd, J = 8.2, 2.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 2.78 (s, 3H), 2.70 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 204.8, 167.7, 162.1, 150.7, 137.7, 136.7, 133.0, 132.2, 129.8, 125.6, 124.5, 120.2, 119.6, 118.3, 26.9, 16.0; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{16}H_{14}S_2N_1O_2$ 316.0460; Found 316.0452. IR (ATR, cm^{-1}) 3056, 2961, 2919, 2126, 1643, 1448, 1033, 962. mp: 126.4 °C–130.0 °C.

4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)-2-(trifluoromethyl)phenol (3ad)



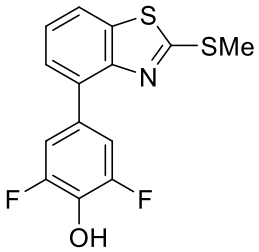
White solid (98.6 mg, 0.289 mmol, 58%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.8 mg, 0.500 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$) δ 8.21 (d, J = 2.3 Hz, 1H), 7.94 (dd, J = 8.6, 2.3 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 5.68 (d, J = 1.4 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 168.3, 156.0, 151.1, 137.3, 135.1, 133.3, 130.7, 128.9 (q, J = 4.4 Hz), 126.4, 125.5, 125.2 (q, J = 272.1 Hz), 121.2, 117.6, 117.0 (q, J = 30.4 Hz), 15.8; ^{19}F NMR ($CDCl_3$) δ –61.1; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{15}H_{10}S_2F_3N_1O_1$ 341,0150; Found 341.0154. IR (ATR, cm^{-1}) 3058, 2923, 2659, 1619, 1514, 1421, 1109, 1038, 969. mp: 145.4 °C–157.5 °C.

2-iodo-4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (3ae)



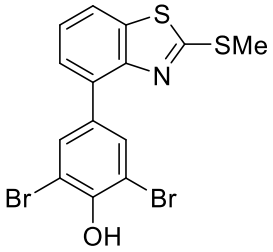
White solid (102 mg, 0.256 mmol, 51%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.7 mg, 0.500 mmol). Purification was done by washing with $CHCl_3$. ^{1}H NMR ($CDCl_3$) δ 8.31 (d, J = 2.1 Hz, 1H), 7.77 (dd, J = 8.2, 2.1 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 5.35 (s, 1H), 2.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.5, 154.5, 150.6, 139.5, 136.6, 133.4, 132.4, 131.5, 125.7, 124.5, 120.2, 114.7, 85.6, 16.1; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_{10}I_1S_2N_1O_1$ 398.9243; Found 398.9230. IR (ATR, cm^{-1}) 3014, 2912, 1425, 1382, 1330, 1276, 1196, 1041, 967. mp: 130.2 °C (decomp.).

2,6-difluoro-4-(2-(methylthio)benzo[*d*]thiazol-4-yl)phenol (3af)



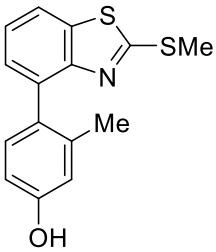
Pale brown solid (96.5 mg, 0.312 mmol, 62%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.8 mg, 0.501 mmol).Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($(CD_3)_2CO$) δ 7.96 (dd, J = 7.5, 1.8 Hz 1H), 7.67–7.63 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 168.7, 152.9 (dd, J = 240.1, 7.1 Hz), 150.9, 137.2, 134.1 (t, J = 16.0 Hz), 132.2, 130.4 (t, J = 8.6 Hz), 126.4, 125.3, 121.5, 113.4 (dd, J = 17.3, 5.7 Hz), 15.8; ^{19}F NMR ($(CD_3)_2CO$) δ –136.0; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_9S_2N_1O_1F_2$ 309.0088; Found 309.0086. IR (ATR, cm^{-1}) 3082, 1604, 1571, 1528, 158, 1390, 1246, 1075, 1016, 930, 782, 751. mp: 151.5 °C (decomp.).

2,6-dibromo-4-(2-(methylthio)benzo[*d*]thiazol-4-yl)phenol (3ag)



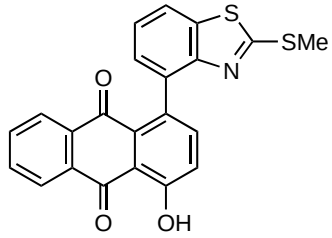
White solid (61.8 mg, 0.143 mmol, 29%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.4 mg, 0.499 mmol). Purification was done by washing with $CHCl_3$. ^{1}H NMR ($(CD_3)_2CO$) δ 8.19 (s, 2H), 7.97 (dd, J = 7.7, 1.3 Hz, 1H), 7.65 (dd, J = 7.7, 1.3 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 2.85 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 206.3, 169.0, 151.1, 137.5, 134.1, 134.0, 133.4, 131.7, 126.7, 125.7, 121.9, 111.2, 16.0; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{14}H_{10}S_2N_1O_1{}^{81}Br_2$ 433.8524; Found 433.8540. IR (ATR, cm^{-1}) 3061, 2985, 2087, 1437, 1282, 1223, 1165, 1044, 971, 873, 755. mp: 115.2 °C (decomp.).

3-methyl-4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (3ah)



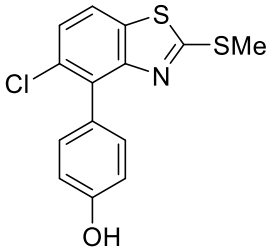
White solid (75.4 mg, 0.262 mmol, 52%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 98.3 mg, 0.498 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$) δ 7.74 (dd, J = 8.2, 1.2 Hz, 1H), 7.32 (t, J = 8.2 Hz, 1H), 7.27–7.26 (overlapped with $CHCl_3$, 1H), 7.18 (d, J = 8.2 Hz, 1H), 6.74 (d, J = 2.7 Hz, 1H), 6.71 (dd, J = 8.2, 2.7 Hz, 1H), 5.09 (s, 1H), 2.69 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.9, 155.4, 152.0, 138.3, 135.5, 135.3, 131.8, 131.5, 127.9, 124.1, 119.8, 117.0, 112.7, 20.8, 16.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{15}H_{14}S_2N_1O_1$ 288.0511; Found 288.0518. IR (ATR, cm^{-1}) 3156, 3063, 3018, 2957, 2918, 2123, 1609, 1435, 1291, 1230, 1026, 965, 860, 860, 805, 788. mp: 121.8 °C (decomp.).

1-hydroxy-4-(2-(methylthio)benzo[*d*]thiazol-4-yl)anthracene-9,10-dione (3ai)



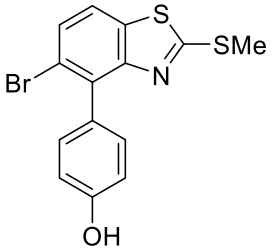
Red solid (85.4 mg, 0.212 mmol, 42%) from 2-(methylsulfinyl)benzo[*d*]thiazole (**1a**, 99.0 mg, 0.502 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 20/1). ^{1}H NMR ($(CD_3)_2CO$) δ 8.33 (d, J = 7.2 Hz, 1H), 7.97–7.90 (m, 4H), 7.74 (d, J = 8.7 Hz, 1H), 7.49–7.45 (m, 2H), 7.42 (d, J = 8.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 184.2 (2C), 167.9, 151.9, 141.9, 138.1, 136.0 (2C), 135.5, 134.8, 133.6, 133.1, 128.0, 127.8, 127.7, 127.4, 126.6, 125.6, 123.8, 121.3, 117.4, 15.5; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{22}H_{14}S_2N_1O_3$ 404.0410; Found 404.0418. IR (ATR, cm^{-1}) 3064, 205, 1735, 1672, 1636, 1591, 1448, 1349, 1225, 1057, 1035, 771, 750. mp: 202.8 °C (decomp.).

4-(5-chloro-2-(methylthio)benzo[*d*]thiazol-4-yl)phenol (3ba)



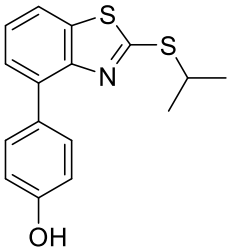
White solid (84.0 mg, 0.273 mmol, 55%) from 5-chloro-2-(methylsulfinyl)benzo[*d*]thiazole (**1b**, 116 mg, 0.501mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$) δ 7.63 (d, J = 8.9 Hz, 1H), 7.42–7.40 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 5.06 (s, 1H), 2.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.0, 155.7, 153.4, 133.9, 133.6, 131.9, 131.4, 128.3, 125.7, 120.2, 115.2, 16.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{14}H_{11}S_2N_1O_1{}^{35}Cl_1$ 307.9965; Found 307.9961. IR (ATR, cm^{-1}) 3261, 3006, 2922, 2121, 1513, 1421, 1377, 1208, 1168, 912, 827, 800. mp: 159.5 °C (decomp.).

4-(5-bromo-2-(methylthio)benzo[*d*]thiazol-4-yl)phenol (3ca)



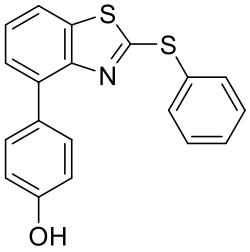
White solid (100 mg, 0.284 mmol, 57%) from 5-bromo-2-(methylsulfinyl)benzo[*d*]thiazole (**1c**, 138 mg, 0.501 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($(CD_3)_2CO$) δ 8.53 (s, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 2.70 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 169.5, 157.9, 154.3, 136.4, 135.5, 132.5, 130.0, 129.2, 121.9, 121.7, 115.2, 15.8; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_{10}S_2N_1O_1{}^{81}Br_1$ 352.9361; Found 352.9376. IR (ATR, cm^{-1}) 3162, 3015, 2918, 1610, 1512, 1419, 1382, 1223, 1100, 1073, 1033, 795. m.p. 178.0 °C (decomp.).

4-(2-(isopropylthio)benzo[*d*]thiazol-4-yl)phenol (3da)



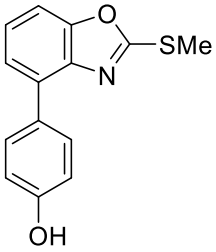
Colorless oil (87.9 mg, 0.292 mmol, 58%) from 2-(isopropylsulfinyl)benzo[*d*]thiazole (**1d**, 112 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 20/1)). ^{1}H NMR ($(CD_3)_2CO$) δ 8.50 (s, 1H), 7.87 (dd, J = 7.5, 1.4 Hz, 1H), 7.78 (d, J = 9.0 Hz, 2H), 7.54 (dd, J = 7.5, 1.4 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 9.0 Hz, 2H), 4.08 (sep, J = 6.9 Hz, 1H), 1.51 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($(CD_3)_2CO$) δ 165.7, 158.0, 151.3, 137.0, 135.2, 131.6, 130.9, 126.4, 125.5, 120.3, 115.7, 40.1, 23.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{16}H_{16}S_2N_1O_1$ 302.0668; Found 302.0667. IR (ATR, cm^{-1}) 3266, 3058, 3023, 2963, 2924, 2864, 2118, 1609, 1515, 1438, 1237, 996, 834, 780.

4-(2-(phenylthio)benzo[*d*]thiazol-4-yl)phenol (3ea)



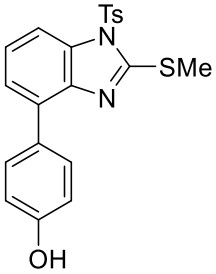
White solid (85.7 mg, 0.256 mmol, 51%) from 2-(phenylsulfinyl)benzo[*d*]thiazole (**1e**, 130 mg, 0.502 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($(CD_3)_2CO$) δ 8.50 (s, 1H), 7.84–7.80 (m, 3H), 7.74 (d, J = 9.0 Hz, 2H), 7.64–7.58 (m, 3H), 7.53 (dd, J = 7.5, 1.4 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($(CD_3)_2CO$) δ 168.6, 158.0, 151.9, 137.4, 136.1, 135.4, 131.6, 131.4, 130.9, 130.7, 130.4, 126.4, 125.5, 120.2, 115.7; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{19}H_{14}S_2N_1O_1$ 335.0433; Found 335.0434. IR (ATR, cm^{-1}) 3056, 1508, 1438, 1389, 1219, 1009, 832, 779. mp: 80.3 °C (decomp.).

4-(2-(methylsulfanyl)benzo[*d*]oxazol-4-yl)phenol (6)



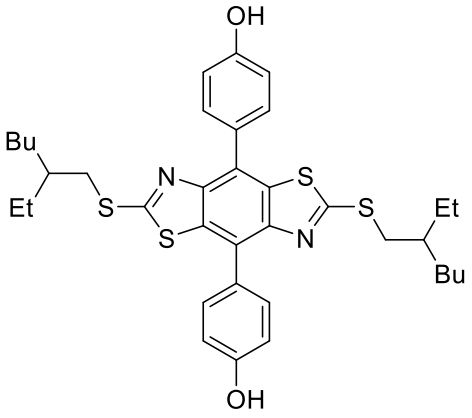
White solid (41.7 mg, 0.162 mmol, 32%) from 2-(methylsulfinyl)benzo[*d*]oxazole (**4**, 90.8 mg, 0.501 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 20/1), then recrystallization from hexane/EtOAc = 10/1. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 5.00 (s, 1H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.5, 155.7, 152.6, 139.4, 131.6, 130.2, 129.7, 124.1, 123.2, 115.8, 108.2, 14.7; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_{11}S_1N_1O_2$ 257.0505; Found 257.0495. IR (ATR, cm^{-1}) 3304, 2931, 1609, 1436, 1190, 1093, 1046, 833, 788, 751. mp: 129.2 °C–130.6 °C.

4-(2-(methylsulfanyl)-1-tosyl-1*H*-benzo[*d*]imidazol-4-yl)phenol (7)



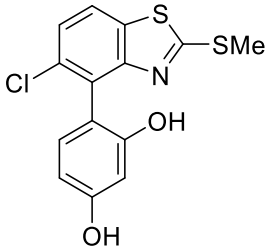
White solid (106 mg, 0.259 mmol, 52%) from 2-(methylsulfinyl)-1-tosyl-1*H*-benzo[*d*]imidazole (**5**, 168 mg, 0.501 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.1 Hz, 2H), 4.81 (d, J = 2.1 Hz, 1H), 2.71 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 155.3, 153.6, 146.2, 140.6, 134.8, 134.7, 130.9, 130.7, 130.2, 130.1, 127.5, 124.2, 123.6, 115.4, 111.4, 21.8, 15.5; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{21}H_{19}S_2N_2O_3$ 411.0832; Found 411.0818. IR (ATR, cm^{-1}) 3067, 2921, 1610, 1518, 1438, 1371, 1259, 1154, 1037, 971, 787, 752. mp: 74.8 °C (decomp.).

4,4'-(2,6-bis((2-ethylhexyl)sulfanyl)benzo[1,2-*d*:4,5-*d*']bis(thiazole)-4,8-diyl)diphenol (9)



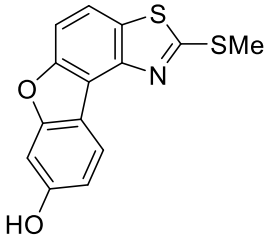
White solid (31.0 mg, 0.0466 mmol, 23%, mixture of diastereomers) from 2,6-bis((2-ethylhexyl)sulfinyl)benzo[1,2-*d*:4,5-*d*']bis(thiazole) (**8**, 103 mg, 0.200 mmol). Purification was done by washing with $CHCl_3$ then PTLC (hexane/EtOAc = 5/1). ^{1}H NMR ($(CD_3)_2CO$) δ 8.73 (s, 2H), 7.69 (d, J = 9.0 Hz, 4H), 7.02 (d, J = 9.0 Hz, 4H), 3.36 (dd, J = 6.2, 1.4 Hz, 4H), 1.80–1.76 (m, 2H), 1.49–1.40 (m, 8H), 1.31–1.28 (m, 8H), 0.90–0.86 (m, 12H); ^{13}C NMR ($(CD_3)_2CO$) δ 167.5, 158.5, 148.6, 136.2, 131.7, 130.2, 127.0, 116.0, 40.0, 37.9, 32.9, 29.3, 26.2, 23.6, 14.3, 11.0; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{36}H_{44}S_4N_2O_2$ 664.2280; Found 664.2296. IR (ATR, cm^{-1}) 3179, 2956, 2922, 2853, 2116, 1611, 1522, 1430, 1334, 1215, 1170, 1005, 826, 742. mp: 203.9 °C–204.8 °C.

4-(5-chloro-2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)benzene-1,3-diol (3bj)



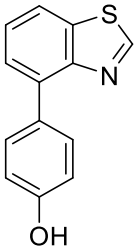
White solid (192 mg, 0.591 mmol, 39%) from 5-chloro-2-(methylsulfinyl)benzo[*d*]thiazole (**1b**, 348 mg, 1.50 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 6.61 (d, J = 2.4 Hz, 1H), 6.56 (dd, J = 8.2, 2.4 Hz, 1H), 6.49 (s, 1H), 5.04 (s, 1H), 2.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.3, 157.3, 155.0, 152.4, 133.5, 133.5, 132.5, 129.3, 126.7, 120.7, 116.6, 108.4, 105.5, 16.3; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_{10}{}^{35}Cl_1S_2N_1O_2$ 322.9836; Found 322.9840. IR (ATR, cm^{-1}) 3352, 3035, 2831, 1618, 1522, 1421, 1387, 1294, 1178, 1072, 796. mp: 90.0 °C (decomp.).

2-(methylsulfanyl)benzo[2,3]benzofuro[4,5-*d*]thiazol-8-ol (10)



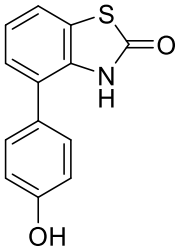
White solid (16.1 mg, 0.0560 mmol, 28%) from 4-(5-chloro-2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)benzene-1,3-diol (**3bj**, 65.0 mg, 0.201 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$) δ 8.28 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 6.94 (dd, J = 8.2, 2.1 Hz, 1H), 5.01 (s, 1H), 2.91 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 171.1, 159.0, 158.5, 156.3, 147.8, 130.8, 124.1, 118.6, 117.7, 116.3, 113.2, 109.3, 99.1, 16.1; HRMS (APCI-MS, positive): m/z $[M]^+$ Calcd for $C_{14}H_9S_2N_1O_1$ 287.0069; Found 287.0058. IR (ATR, cm^{-1}) 3254, 3084, 2920, 2855, 1632, 1599, 1393, 1283, 1118, 791. mp: 162.4 °C (decomp.).

4-(benzo[*d*]thiazol-4-yl)phenol (11)



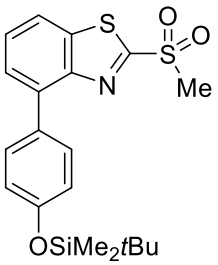
White solid (18.4 mg, 0.0810 mmol, 40%) from 4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (**3aa**, 54.7 mmol, 0.200 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR (CD_3CN) δ 9.12 (s, 1H), 8.01 (d, J = 7.4 Hz, 1H), 7.72 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.13 (s, 1H), 6.93 (d, J = 9.0 Hz, 2H); ^{13}C NMR (CD_3CN) δ 157.7, 155.0, 151.7, 137.1, 135.8, 131.9, 131.8, 131.4, 126.6, 121.5, 115.9; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{13}H_{10}S_1N_1O_1$ 228.0478; Found 228.0486. IR (ATR, cm^{-1}) 3159, 3067, 2930, 2801, 2127, 1610, 1514, 1453, 1226, 879, 779. mp: 143.8 °C (decomp.).

4-(4-hydroxyphenyl)benzo[*d*]thiazol-2(3*H*)-one (12)



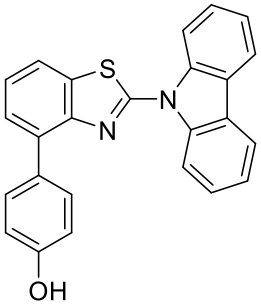
White solid (28.6 mg, 0.118 mmol, 59%) from 4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (**3aa**, 55.0 mg, 0.201 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 5/1). ^{1}H NMR ($(CD_3)_2CO$) δ 10.18 (s, 1H), 8.57 (s, 1H), 7.48 (dd, J = 6.6, 2.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.22–7.18 (m, 2H), 6.94 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($(CD_3)_2CO$) δ 170.4, 158.3, 134.8, 130.8, 129.9, 128.2, 127.4, 125.0, 123.8, 122.0, 116.7; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{13}H_{10}S_1N_1O_2$ 244.0427; Found 244.0430. IR (ATR, cm^{-1}) 3236, 3194, 2793, 1655, 1516, 1263, 1215, 1175, 839, 778. mp: 150.1 °C (decomp.).

4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(methylsulfonyl)benzo[*d*]thiazole (13)



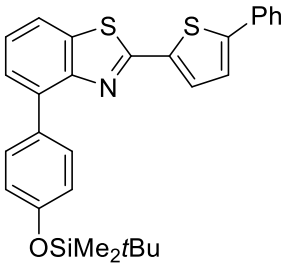
White solid (392 mg, 0.933 mmol, 93%) from 4-(2-(methylsulfanyl)benzo[*d*]thiazol-4-yl)phenol (**3aa**, 272 mg, 0.996 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$) δ 7.94 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 3.40 (s, 3H), 1.02 (s, 9H), 0.27 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 165.5, 156.2, 150.0, 138.4, 137.8, 131.0, 130.7, 128.4, 127.3, 120.7, 120.1, 42.2, 25.8, 18.4, –4.2; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{20}H_{26}S_2N_1O_3Si_1$ 420.1118; Found 420.1126. IR (ATR, cm^{-1}) 3057, 3012, 2952, 2927, 2855, 1924, 1605, 1512, 1464, 1317, 1271, 1153, 918, 781, 751. mp: 144.8 °C–149.4 °C.

4-(2-(9*H*-carbazol-9-yl)benzo[*d*]thiazol-4-yl)phenol (14)



White solid (20.6 mg, 0.0525 mmol, 52%) from 4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(methylsulfonyl)benzo[*d*]thiazole (**13**, 42.4 mg, 0.101 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 10/1). ^{1}H NMR (CD_3CN) δ 8.54 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 7.5 Hz, 2H), 7.97 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 8.9 Hz, 2H), 7.62–7.58 (m, 3H), 7.50–7.44 (m, 3H), 7.17 (s, 1H), 7.02 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CD_3CN) δ 158.2, 157.7, 148.2, 140.0, 135.6, 133.5, 131.7, 131.6, 128.2, 127.2, 126.1, 125.9, 123.9, 121.2, 120.9, 116.0, 114.6; HRMS (APCI-MS, positive): *m*/*z* $[M+H]^+$ Calcd for $C_{25}H_{17}S_1N_2O_1$ 393.1056; Found 393.1065. IR (ATR, cm^{-1}) 3365, 3115, 3058, 3027, 1595, 1512, 1444, 1337, 1210, 821, 768, 754. mp: 225.1 °C–229.6 °C.

4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(5-phenylthiophen-2-yl)benzo[*d*]thiazole (15)



Yellow oil (33.7 mg, 0.0674 mmol, 34%) from 4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(methylsulfonyl)benzo[*d*]thiazole (**13**, 83.9 mg, 0.200 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 100/1). ^{1}H NMR (CD_3CN) δ 7.87 (dd, J = 8.2, 1.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 4.1 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.44–7.41 (m, 4H), 7.37–7.36 (m, 1H), 6.99 (d, J = 9.0 Hz, 2H), 1.02 (s, 9H), 0.26 (s, 6H); ^{13}C NMR (CD_3CN) δ 161.1, 156.4, 151.8, 148.7, 137.2, 136.8, 136.0, 134.2, 132.9, 131.8, 130.9, 130.1, 129.5, 127.1, 126.7, 126.6, 125.4, 121.4, 120.6, 26.0, 18.8, –4.3; HRMS (APCI-MS, positive): m/z $[M+H]^+$ Calcd for $C_{29}H_{30}S_2N_1O_1Si_1$ 500.1533; Found 500.1536. IR (ATR, cm^{-1}) 3061, 3034, 2951, 2928, 2884, 2856, 1603, 1508, 1252, 1172, 905, 780.

X-ray Crystallography

Tables S1 summarizes crystallographic data for **3aa**. A suitable crystal for X-ray analysis was placed on the end of a micro-mount coated with NVH oil. The X-ray intensity data collection was carried out on a Rigaku XTALAB P200 with a photon-counting detector at –180 °C using Cu-Kα radiation (λ = 1.5418 Å). Equivalent reflections were merged and the collected images were processed by a Rigaku CrysAlisPro program. The initial structure was determined by SHELXT.[7] The further structure determination was performed by Fourier transform method and refined by least squares method on SHELXL.[8] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with the exception of the OH groups were refined using riding models. Two crystallographically independent but chemically equivalent molecules of **3aa** are present in the asymmetric unit. Data validation of the crystallographic data was done by the IUCR's CheckCIF routine.

Table S1. Crystallographic data for **3aa**.

Compound	**3aa**
Formula	$C_{14}H_{11}N_1O_1S_2$
Formula weight	273.36
Crystal system	*Triclinic*
Space group	*P*–1 (#2)
a / Å	9.6697(4)
b / Å	10.5598(4)
c / Å	13.8151(4)
α / °	93.577(2)
β / °	100.035(3)
γ / °	113.048(3)
V / Å^3	1264.84(9)
Z	4
μ mm^{-1}	3.695
$D_{calcd.}$ / g·cm^{-3}	1.435
Refl./restr./param.	4911/0/335
Completeness	0.976
GOF	1.050
R_1 ($I > 2\sigma(I)$)	0.0297
wR_2 ($I > 2\sigma(I)$)	0.0783
R_1 (all data)	0.0323
wR_2 (all data)	0.0797
Largest diff. peak and hole /e·Å^{-3}	0.434, –0.294
CCDC number	2349724

Computational Study

Density functional calculations were carried out using the Gaussian16 program.[9] Geometrical optimization of the structures was performed from model structures built on GaussView. The optimized structures were considered true minima if no imaginary vibration mode was obtained. Transition states were located to have a single imaginary vibration mode, which corresponds to the reaction process. IRC calculations were also performed to confirm whether the transition states are connected to the corresponding intermediates. Structural optimizations by DFT methods were performed at B3LYP-D3(BJ) level using 6-31+G(d,p) basis set for all atoms. The reported values of free energy were evaluated by single point calculations on each optimized geometry with a solvation effect of dichloromethane modeled by the SMD method at 298.150 K.

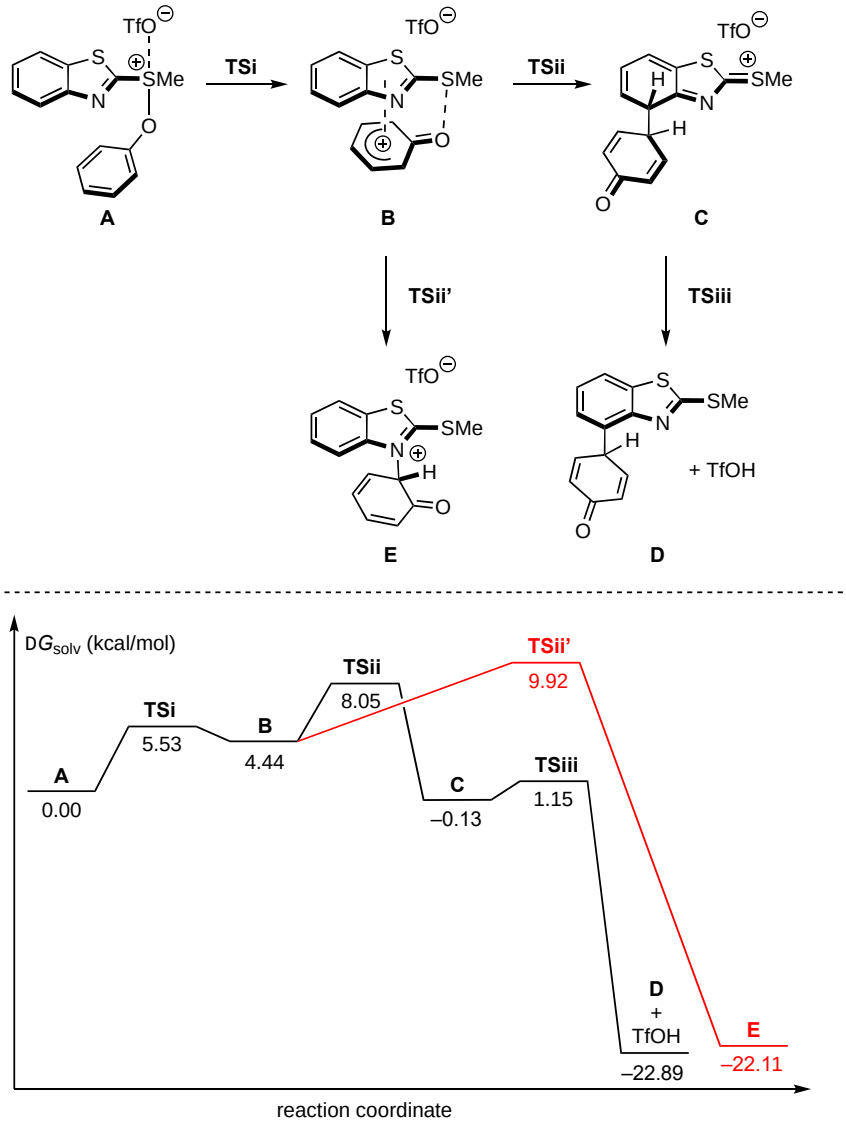


Fig. S1. Reaction profiles of stepwise rearrangement of **A** to **C** via **B** and deprotonation of **C** to form **D** (black) and N–C bond formation from **B** to form **E** (red).

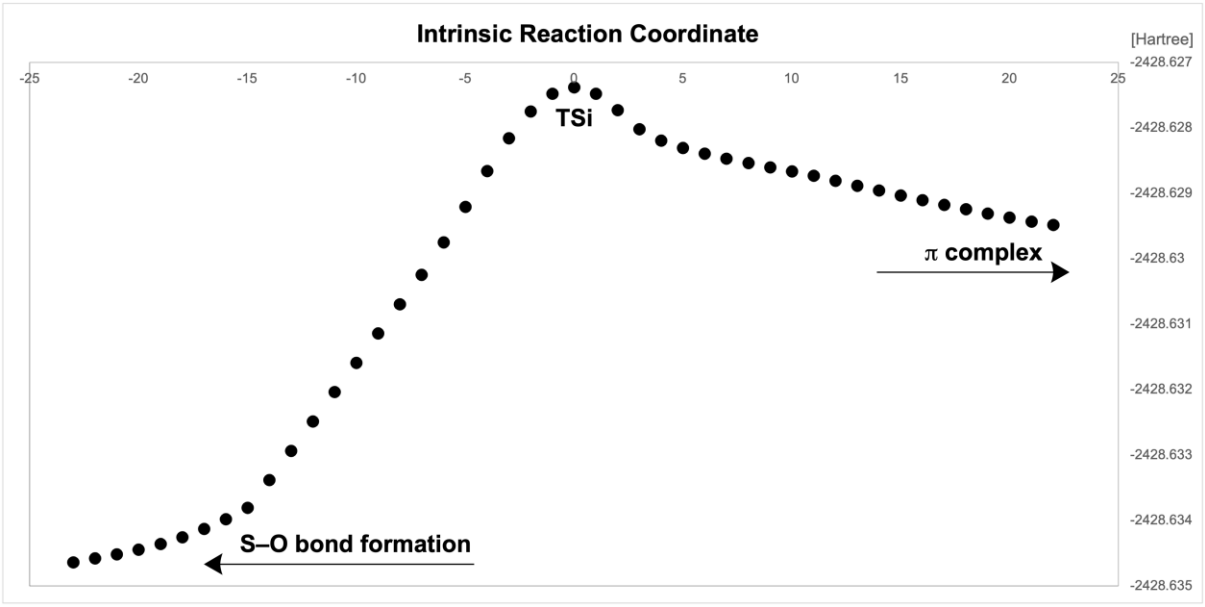


Fig. S2. IRC pathway from **TSi**.

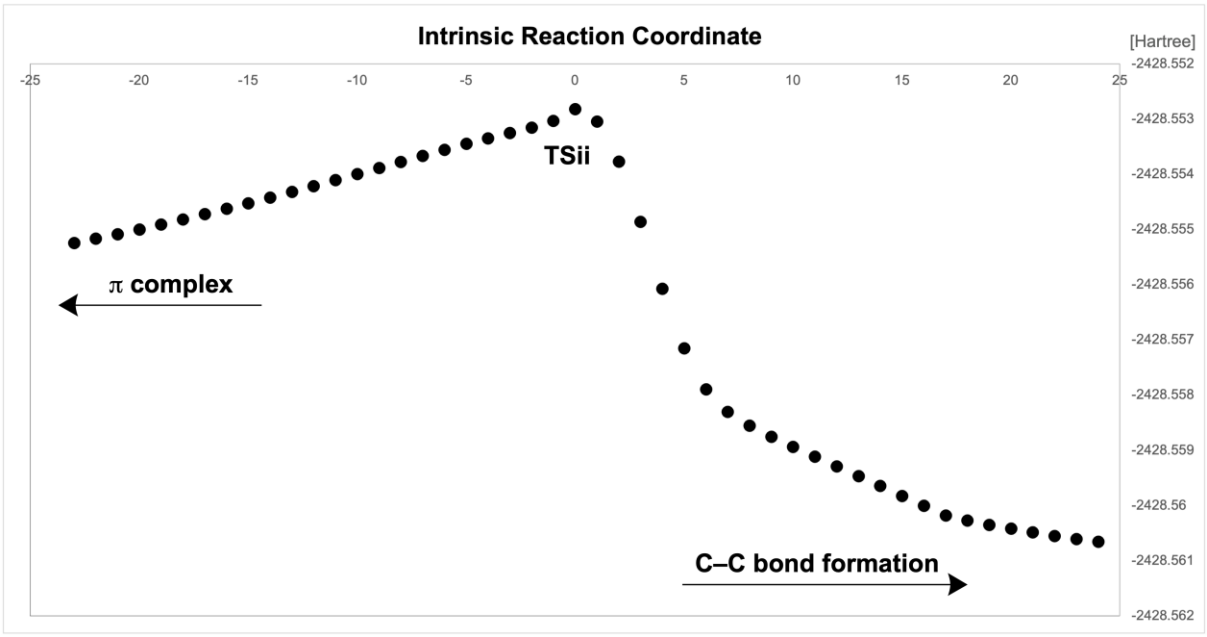


Fig. S3. IRC from **TSii**.

Table S2. Cartesian Coordinates of the Optimized Geometries in the XYZ Format (in Å).

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A

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C	-3.661000	-3.457200	-1.587000
C	-2.168900	-1.804800	-0.696400
C	-2.107200	-2.535400	0.519600
C	-2.812500	-3.729600	0.691400
C	-3.588400	-4.175700	-0.375400
H	-4.276200	-3.839000	-2.395100
H	-2.762200	-4.288500	1.619300
H	-4.149300	-5.098900	-0.269500
S	-1.053300	-1.714000	1.655900
N	-1.410300	-0.648900	-0.714100
C	1.065300	0.733600	2.149100
H	0.366100	0.613900	2.978200
H	1.692900	-0.141500	1.998200
H	1.678200	1.625800	2.284400
C	-0.795900	-0.495200	0.414700
C	-4.364400	2.392200	-0.134000
C	-2.847200	4.064500	-1.019500
C	-3.335800	1.864900	0.650700
H	-5.351500	1.942400	-0.096200
C	-1.811100	3.553500	-0.234700
H	-2.657900	4.914700	-1.667000
C	-2.079200	2.462800	0.589600
H	-3.497700	1.010600	1.299300
H	-0.818100	3.990700	-0.258700
C	-4.120500	3.486700	-0.969200
H	-4.921200	3.889100	-1.581900
C	-2.957100	-2.273500	-1.760000
H	-2.999800	-1.709900	-2.685800
O	-1.070500	1.951500	1.429600
S	0.112600	1.012500	0.638100
O	1.898500	-0.434600	-0.455500
S	3.080200	0.371600	-0.907300
O	3.423200	0.218300	-2.331900
O	3.093300	1.745500	-0.358600
C	4.495100	-0.474800	-0.011800
F	4.588200	-1.769400	-0.366800
F	4.313700	-0.421500	1.324300
F	5.666300	0.123700	-0.295900

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TSi

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C	2.430900	3.389700	-0.836200
C	1.311200	1.320600	-0.357100
C	1.434700	1.590600	1.038400
C	2.038300	2.762300	1.499500
C	2.533100	3.650800	0.547500
H	2.831200	4.108900	-1.543100
H	2.121800	2.976600	2.559300
H	3.009900	4.567200	0.880900
S	0.731700	0.290200	1.963600
N	0.682400	0.145100	-0.661600
S	-0.318300	-2.064400	0.237900
C	-0.454900	-2.706100	1.920700
H	0.502600	-2.620500	2.436300
H	-1.254900	-2.163600	2.427400
H	-0.727700	-3.757600	1.812100
C	0.327100	-0.489500	0.434000
C	1.827400	2.232100	-1.300000
H	1.733500	2.015600	-2.358300
C	4.215200	-0.598900	0.313000
C	3.684800	-0.765900	-2.068600
C	3.272900	-1.570300	0.602500
H	4.795900	-0.146300	1.110000
C	2.718800	-1.718800	-1.792900
H	3.850900	-0.435900	-3.088700
C	2.506000	-2.150400	-0.449900
H	3.099400	-1.908900	1.618100
H	2.099500	-2.145600	-2.574900
C	4.412900	-0.187000	-1.017400
H	5.141400	0.588200	-1.233200
O	1.576800	-3.031900	-0.178100
O	-2.775800	-0.866900	1.086300
S	-3.177400	0.475700	0.578500
O	-4.471100	0.968900	1.097400
O	-2.082300	1.467400	0.516000
C	-3.539300	0.128800	-1.230700
F	-4.517800	-0.789600	-1.365500
F	-2.444000	-0.342000	-1.863600
F	-3.933000	1.249100	-1.869300

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B

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C	-2.373400	3.335000	0.847200
C	-1.394800	1.170500	0.433300
C	-1.315400	1.492000	-0.958300
C	-1.745600	2.723600	-1.441200
C	-2.272700	3.637400	-0.523400
H	-2.786700	4.071600	1.527900
H	-1.667000	2.977100	-2.492700
H	-2.608300	4.605700	-0.881000
S	-0.587100	0.170500	-1.832000
N	-0.909600	-0.053900	0.774200
S	0.195700	-2.261200	-0.088200
C	0.543600	-2.793000	-1.787600
H	-0.374600	-2.805200	-2.378200
H	1.305400	-2.139500	-2.216700
H	0.935400	-3.808600	-1.702400
C	-0.445000	-0.692800	-0.292500
C	-1.950100	2.107200	1.337500
H	-2.000900	1.862000	2.392100
C	-4.104100	-0.143100	-0.547100
C	-3.911300	-0.406900	1.901300
C	-3.438800	-1.325800	-0.746200
H	-4.461200	0.441200	-1.387900
C	-3.192200	-1.563300	1.728900
H	-4.109700	-0.020300	2.894800
C	-2.944700	-2.089300	0.389700
H	-3.263900	-1.727800	-1.738000
H	-2.797500	-2.127300	2.567500
C	-4.327200	0.329000	0.770900
H	-4.861400	1.262200	0.912200
O	-2.294000	-3.151100	0.221100
O	4.084500	1.552100	-1.054200
S	3.068100	0.641900	-0.478100
O	1.876000	1.301700	0.101500
O	2.787500	-0.576000	-1.278600

C	3.932200	-0.055400	1.036300
F	4.288100	0.927100	1.891000
F	5.052100	-0.728100	0.695800
F	3.130400	-0.909800	1.707100

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TSii

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C	-0.345000	-3.169200	0.208000
C	-0.750800	-0.768400	-0.065100
C	-0.512200	-0.614400	1.330100
C	-0.159400	-1.685500	2.127400
C	-0.077300	-2.975700	1.546300
H	-0.261600	-4.158100	-0.229700
H	0.061900	-1.552500	3.181200
H	0.221400	-3.811600	2.169100
S	-0.720900	1.068100	1.771600
N	-1.083300	0.354400	-0.733000
S	-1.527800	2.947500	-0.536600
C	-1.421900	4.011500	0.938500
H	-2.146500	3.700500	1.694500
H	-0.404800	4.019400	1.337000
H	-1.677800	5.014800	0.591400
C	-1.113000	1.400600	0.088200
C	-0.747600	-2.084100	-0.633100
H	-0.661100	-2.187800	-1.708000
C	-3.380000	-1.765200	0.560300
C	-3.199600	-1.671700	-1.929700
C	-3.949400	-0.537200	0.576000
H	-3.230400	-2.326000	1.476800
C	-3.747500	-0.432900	-1.928600
H	-2.926800	-2.161700	-2.858800
C	-4.140300	0.225200	-0.669000
H	-4.283100	-0.071600	1.497700
H	-3.942200	0.108900	-2.848600
C	-2.921200	-2.352800	-0.687000
H	-2.796900	-3.428800	-0.721800
O	-4.622400	1.366000	-0.662800
O	3.050400	-0.375000	1.491100
S	2.747700	-0.112000	0.064200
O	2.280900	-1.288000	-0.709100
O	2.018900	1.148800	-0.206500
C	4.444400	0.220400	-0.670600
F	5.264200	-0.841200	-0.513400
F	5.034100	1.282400	-0.081000
F	4.362800	0.480800	-1.993200

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C

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C	1.968900	0.892000	-2.335500
C	0.454400	1.552100	-0.484900
C	-0.245600	2.360100	-1.417900
C	0.151900	2.450700	-2.735900
C	1.268600	1.692600	-3.191300
H	2.800200	0.303200	-2.707200
H	-0.379700	3.088600	-3.435300
H	1.553200	1.762100	-4.235100
S	-1.579200	3.159400	-0.603000
N	-0.010000	1.565100	0.770700
S	-1.996900	2.523800	2.322400
C	-1.154700	1.323100	3.412200
H	-0.118300	1.621400	3.572400
H	-1.706900	1.360700	4.353700
H	-1.223500	0.330100	2.965900
C	-1.089800	2.335400	0.872100
C	2.378000	-0.492400	1.173900
C	4.084800	0.380800	-0.447900
C	3.216400	-1.483600	1.520500
H	1.396900	-0.416800	1.629700
C	4.924300	-0.604700	-0.090100
H	4.400000	1.125600	-1.174000
C	4.547500	-1.618900	0.911200
H	2.935600	-2.227300	2.260500
H	5.919300	-0.685400	-0.518100
C	2.724800	0.554500	0.155300
H	2.741100	1.523700	0.677800
C	1.574800	0.694600	-0.922400
H	1.074500	-0.312800	-0.962000
O	5.322700	-2.532000	1.227200
O	-2.166500	-0.185600	-0.771800
S	-1.605700	-1.334300	-0.025200
O	-0.225800	-1.722400	-0.429100
O	-1.854900	-1.332500	1.433900
C	-2.627200	-2.786800	-0.632700
F	-2.502100	-2.942900	-1.966700
F	-3.934700	-2.602800	-0.359800
F	-2.238900	-3.935200	-0.043800

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TSiii

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C	1.041800	0.403600	2.469000
C	-0.172300	-1.150400	0.998800
C	-1.334800	-0.889400	1.765800
C	-1.309700	-0.039900	2.860300
C	-0.103000	0.605000	3.208100
H	1.947600	0.941900	2.724600
H	-2.204400	0.135800	3.449400
H	-0.086000	1.268500	4.065300
S	-2.666600	-1.841000	1.136200
N	-0.306400	-2.063000	0.008600
S	-2.115900	-3.666000	-1.210600
C	-0.626900	-3.876700	-2.246300
H	0.201100	-4.257200	-1.647700
H	-0.908100	-4.608800	-3.006300
H	-0.364000	-2.929400	-2.718100
C	-1.546200	-2.505500	-0.057900
C	2.474500	-0.702700	-0.815800
C	3.579500	-0.570900	1.434200
C	3.574700	-0.185200	-1.386900
H	1.609900	-0.959500	-1.419600
C	4.680700	-0.059600	0.859400
H	3.559900	-0.753400	2.505600
C	4.757800	0.178700	-0.593000
H	3.626900	-0.007700	-2.457100
H	5.562700	0.187700	1.443300
C	2.361500	-0.967400	0.659000
H	2.261000	-2.059500	0.776200
C	1.038800	-0.384900	1.245200
O	5.775500	0.653800	-1.115900
H	0.769500	0.576200	0.555600
O	-1.420500	0.490100	-1.257200
S	-0.722000	1.788000	-1.233800
O	0.487800	1.807000	-0.331100
O	-0.507800	2.465600	-2.522400
C	-1.902100	2.917500	-0.312800

F	-2.161700	2.433300	0.917800
F	-3.067900	3.020700	-0.976100
F	-1.384300	4.151000	-0.176300

D

C	1.235000	1.991200	0.011800
C	-0.713800	0.587200	0.007900
C	-1.520900	1.751400	-0.008200
C	-0.968500	3.031500	-0.014200
C	0.424100	3.135600	-0.003900
H	2.315400	2.101600	0.018900
H	-1.594300	3.917600	-0.026200
H	0.885200	4.118300	-0.008400
S	-3.217800	1.284400	-0.018700
N	-1.411100	-0.616000	0.011200
S	-3.919700	-1.672300	-0.002700
C	-2.865800	-3.161900	0.024300
H	-2.255900	-3.180400	0.928600
H	-3.556800	-4.008100	0.023400
H	-2.233400	-3.197000	-0.863900
C	-2.692900	-0.418700	-0.001300
C	2.368100	-0.636700	-1.236500
C	2.417000	-0.580300	1.272100
C	3.708000	-0.749600	-1.259800
H	1.799900	-0.609300	-2.163100
C	3.756800	-0.694200	1.248300
H	1.885700	-0.510200	2.218200
C	4.500100	-0.782300	-0.019400
H	4.258000	-0.820100	-2.194000
H	4.342800	-0.724000	2.162500
C	1.575200	-0.535000	0.032300
H	0.891400	-1.397000	0.064300
C	0.685800	0.707600	0.018700
O	5.736300	-0.881100	-0.041300

TfOH

H	1.386700	1.957300	-0.118100
O	1.251100	-0.047100	1.460000
S	0.863600	-0.141500	0.059600
O	1.271200	1.201800	-0.735100
O	1.230300	-1.258700	-0.790500
C	-1.011600	0.008100	-0.002800
F	-1.384100	1.152600	0.577300
F	-1.539900	-1.022800	0.658800
F	-1.426500	-0.008600	-1.268800

TSii'

C	1.235000	1.991200	0.011800
C	-0.713800	0.587200	0.007900
C	-1.520900	1.751400	-0.008200
C	-0.968500	3.031500	-0.014200
C	0.424100	3.135600	-0.003900
H	2.315400	2.101600	0.018900
H	-1.594300	3.917600	-0.026200
H	0.885200	4.118300	-0.008400
S	-3.217800	1.284400	-0.018700
N	-1.411100	-0.616000	0.011200
S	-3.919700	-1.672300	-0.002700
C	-2.865800	-3.161900	0.024300
H	-2.255900	-3.180400	0.928600
H	-3.556800	-4.008100	0.023400
H	-2.233400	-3.197000	-0.863900
C	-2.692900	-0.418700	-0.001300
C	2.368100	-0.636700	-1.236500
C	2.417000	-0.580300	1.272100
C	3.708000	-0.749600	-1.259800
H	1.799900	-0.609300	-2.163100
C	3.756800	-0.694200	1.248300
H	1.885700	-0.510200	2.218200
C	4.500100	-0.782300	-0.019400
H	4.258000	-0.820100	-2.194000
H	4.342800	-0.724000	2.162500
C	1.575200	-0.535000	0.032300
H	0.891400	-1.397000	0.064300
C	0.685800	0.707600	0.018700
O	5.736300	-0.881100	-0.041300

E

C	-3.263100	-1.454500	-2.335300
C	-1.867200	-0.907500	-0.479400
C	-1.536200	-2.261600	-0.335700
C	-2.051100	-3.232700	-1.194200
C	-2.918300	-2.809800	-2.199700
H	-3.945800	-1.151800	-3.122000
H	-1.784900	-4.278000	-1.082100
H	-3.334800	-3.540900	-2.884700
S	-0.443800	-2.490100	1.020400
N	-1.219300	-0.109500	0.476700
S	0.382900	-0.032300	2.641400
C	1.389700	-1.410300	3.286100
H	0.755200	-2.188000	3.715800
H	2.040300	-1.782100	2.493500
H	1.993400	-0.962300	4.078300
C	-0.456700	-0.791400	1.339300
C	-2.664800	3.657800	-0.518100
C	-0.918100	1.983300	-0.803600
C	-3.243600	3.042100	0.546700
H	-3.098400	4.580100	-0.895100
C	-1.357500	1.348800	0.485400
H	-0.072600	1.528200	-1.307800
C	-2.737700	1.768000	1.034700
H	-4.146000	3.428500	1.009400
H	-0.661800	1.740900	1.243100
C	-1.513700	3.114200	-1.221400
H	-1.156100	3.627900	-2.107700
C	-2.745800	-0.485100	-1.479400
H	-3.020400	0.556200	-1.593000
O	-3.308200	1.062400	1.861500
O	3.495900	-0.987400	-1.986700
S	2.603100	-0.579000	-0.880000
O	1.167800	-0.455200	-1.233400
O	2.868100	-1.228700	0.426000
C	3.101800	1.205600	-0.570700
F	2.936300	1.955800	-1.681000
F	4.395800	1.295500	-0.202200
F	2.356300	1.759700	0.409800

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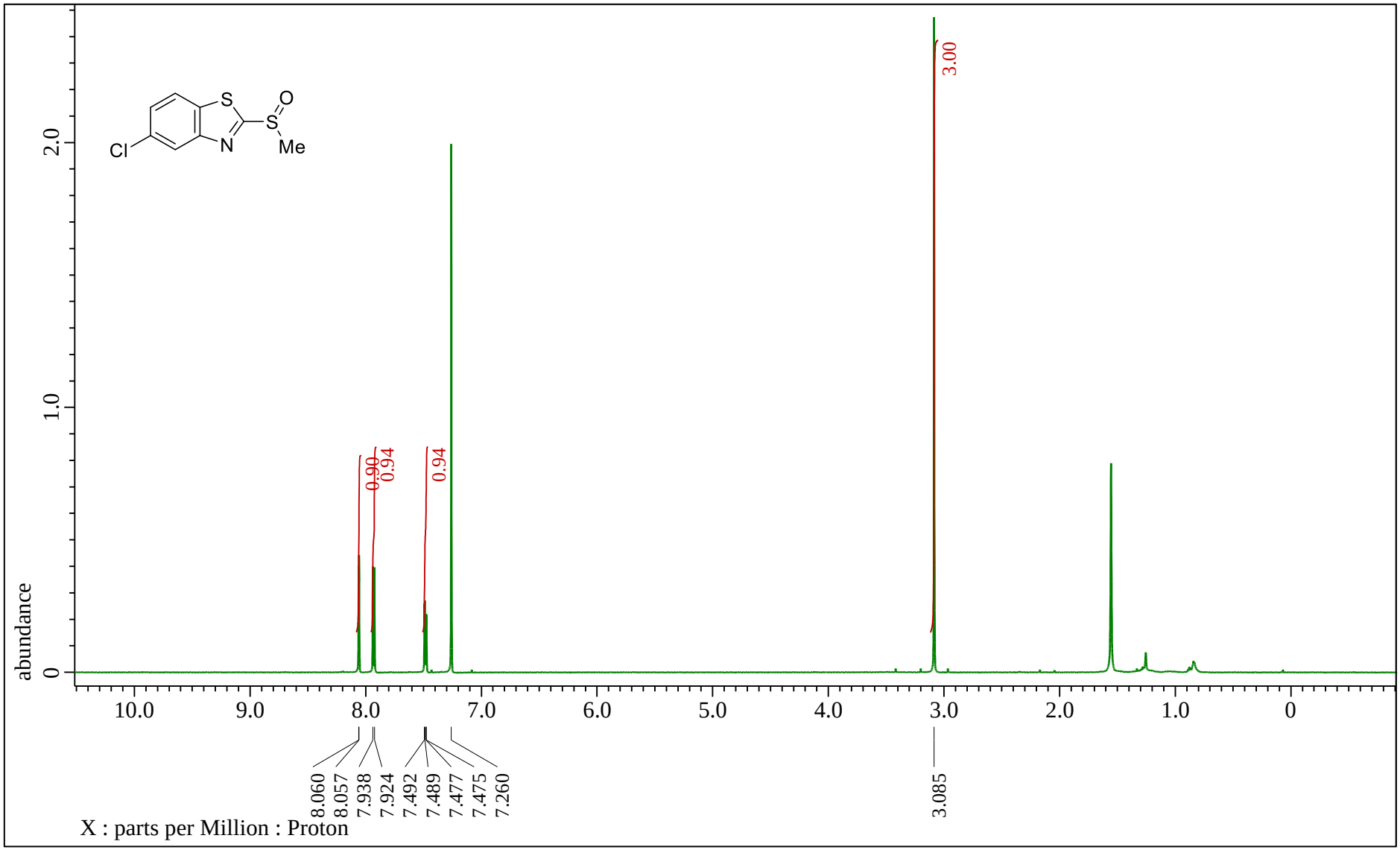

Fig. S4. ^{1}H NMR ($CDCl_3$) spectrum of **1b**.

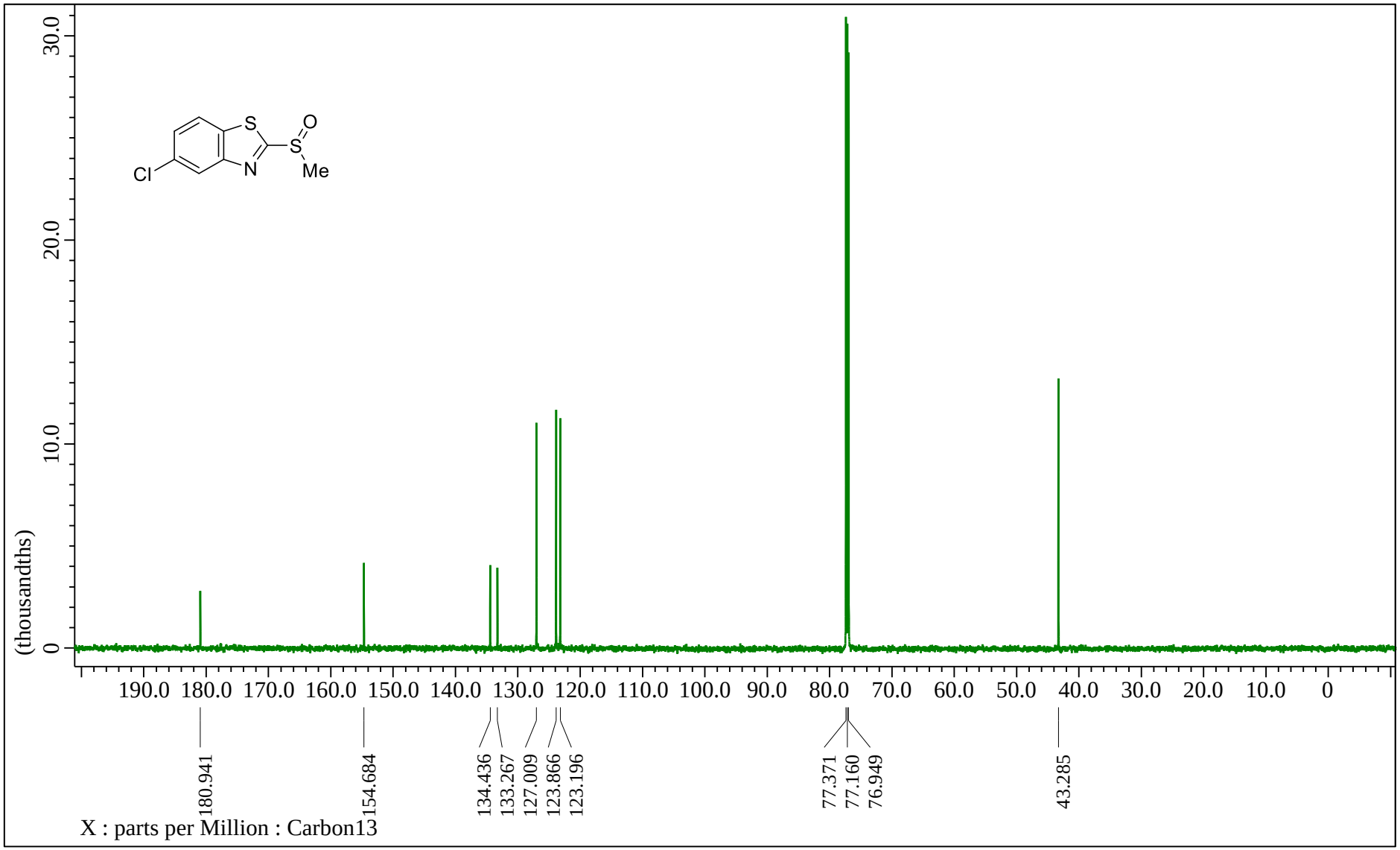

Fig. S5. ^{13}C NMR ($CDCl_3$) spectrum of **1b**.

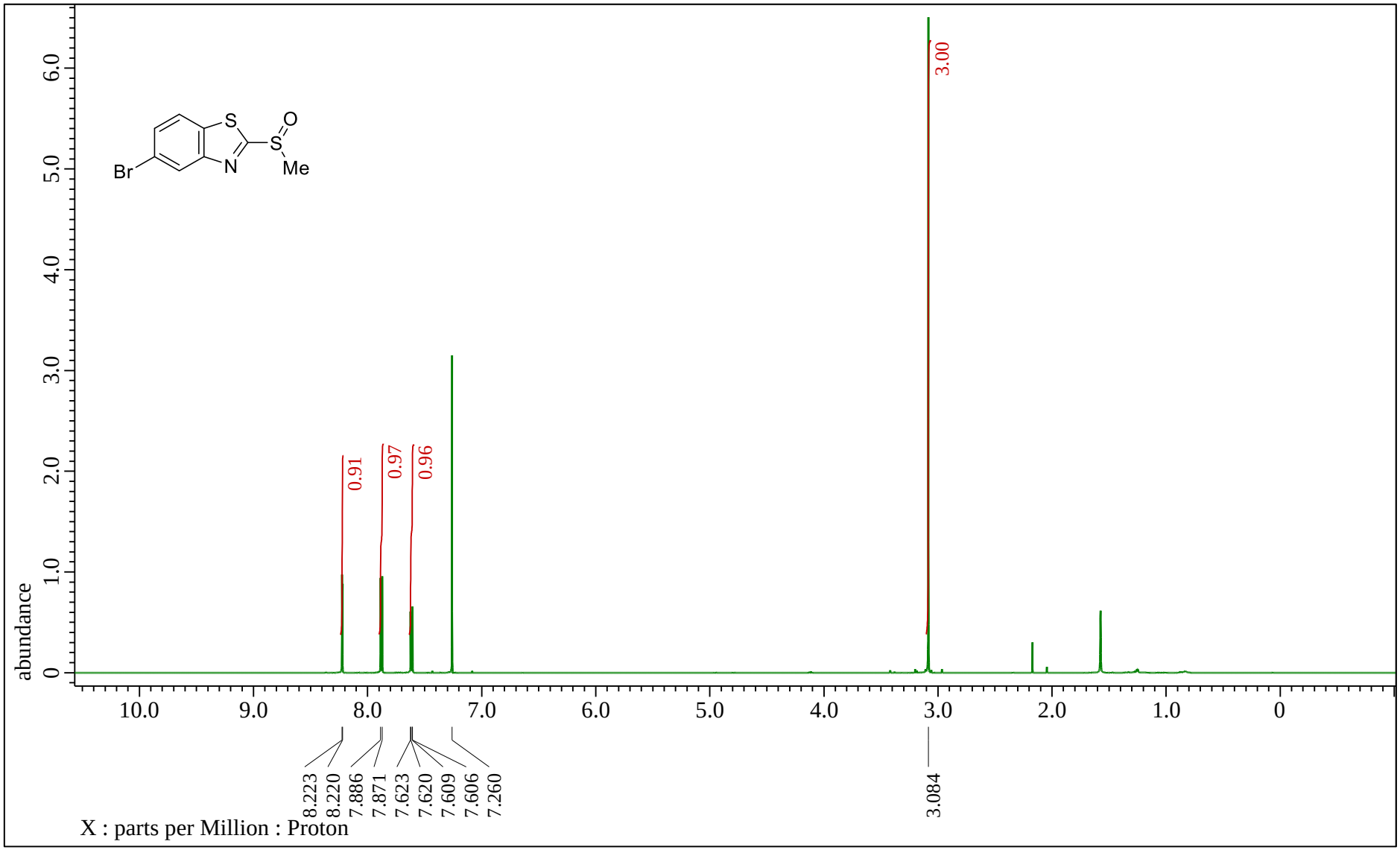

Fig. S6. ^{1}H NMR ($CDCl_3$) spectrum of **1c**.

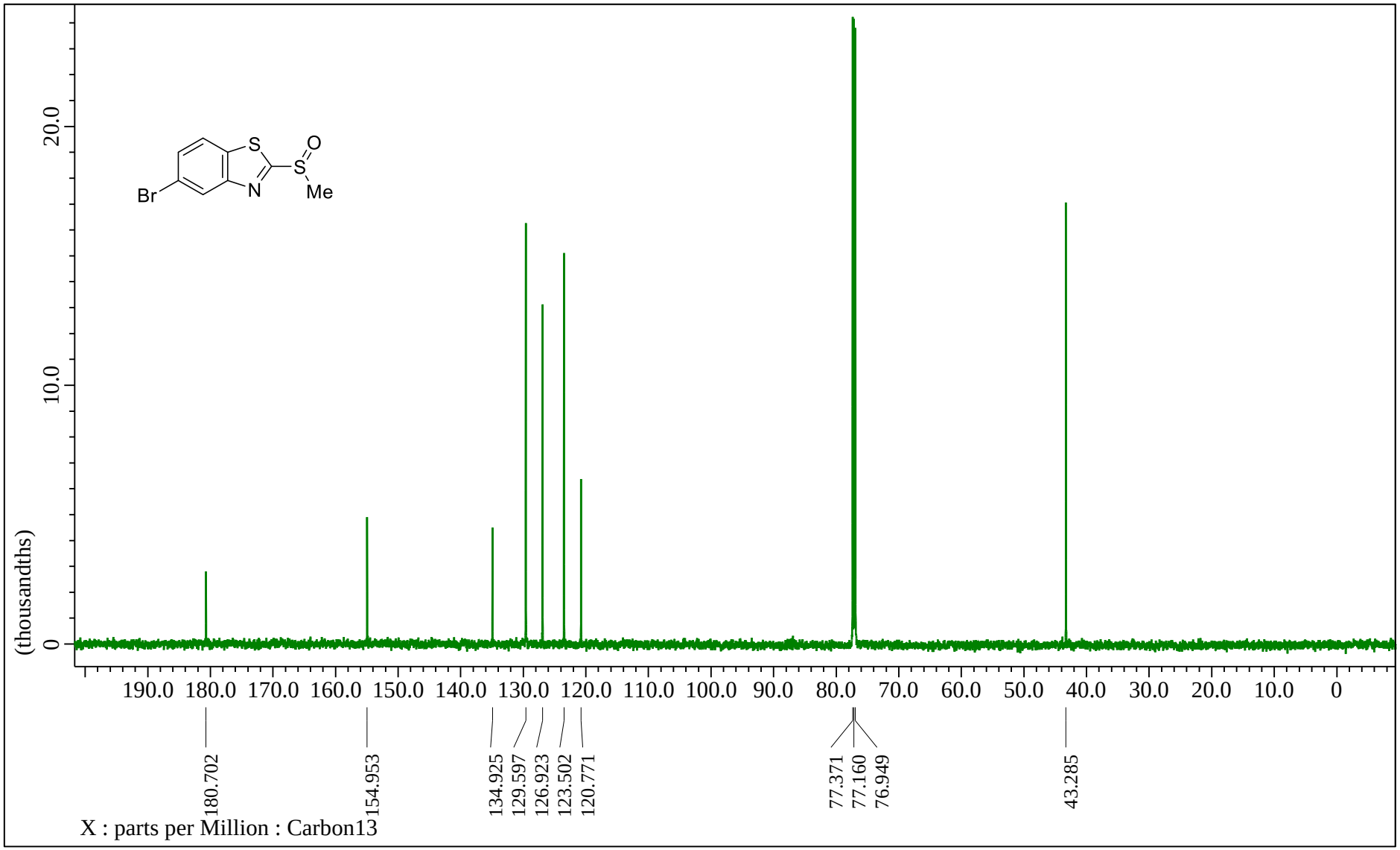

Fig. S7. ^{13}C NMR ($CDCl_3$) spectrum of **1c**.

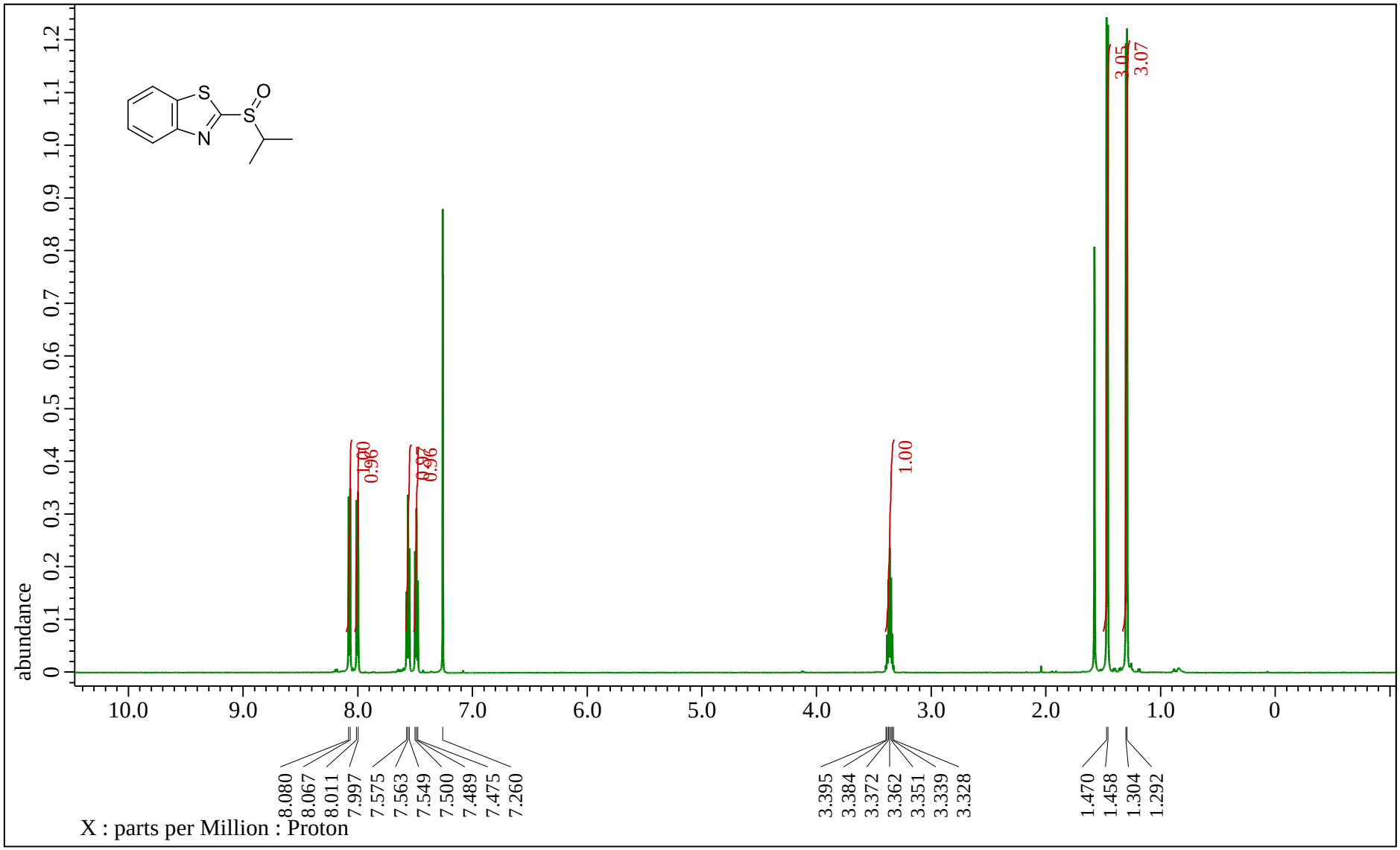

Fig. S8. ^{1}H NMR ($CDCl_3$) spectrum of **1d**.

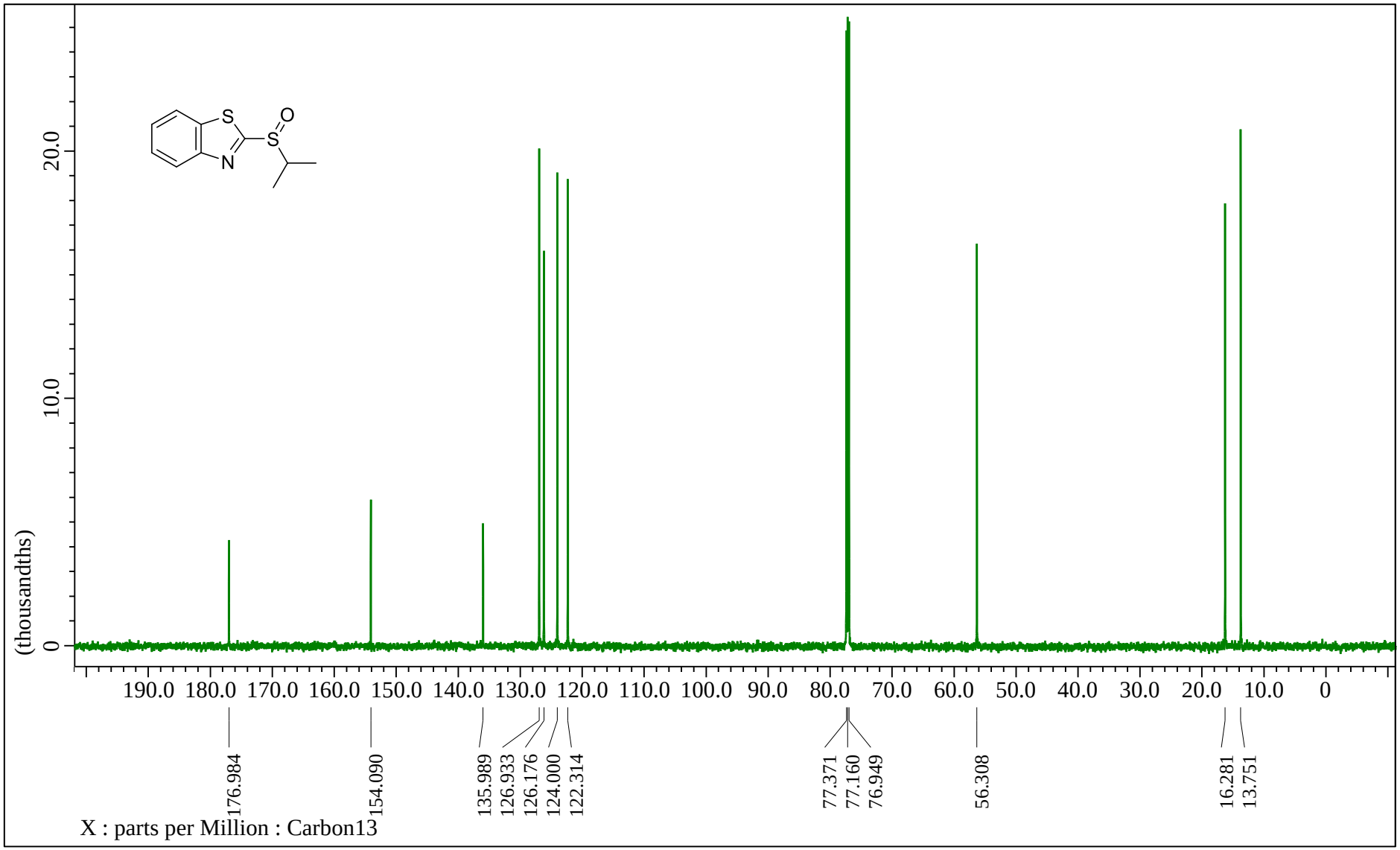

Fig. S9. ^{13}C NMR ($CDCl_3$) spectrum of **1d**.

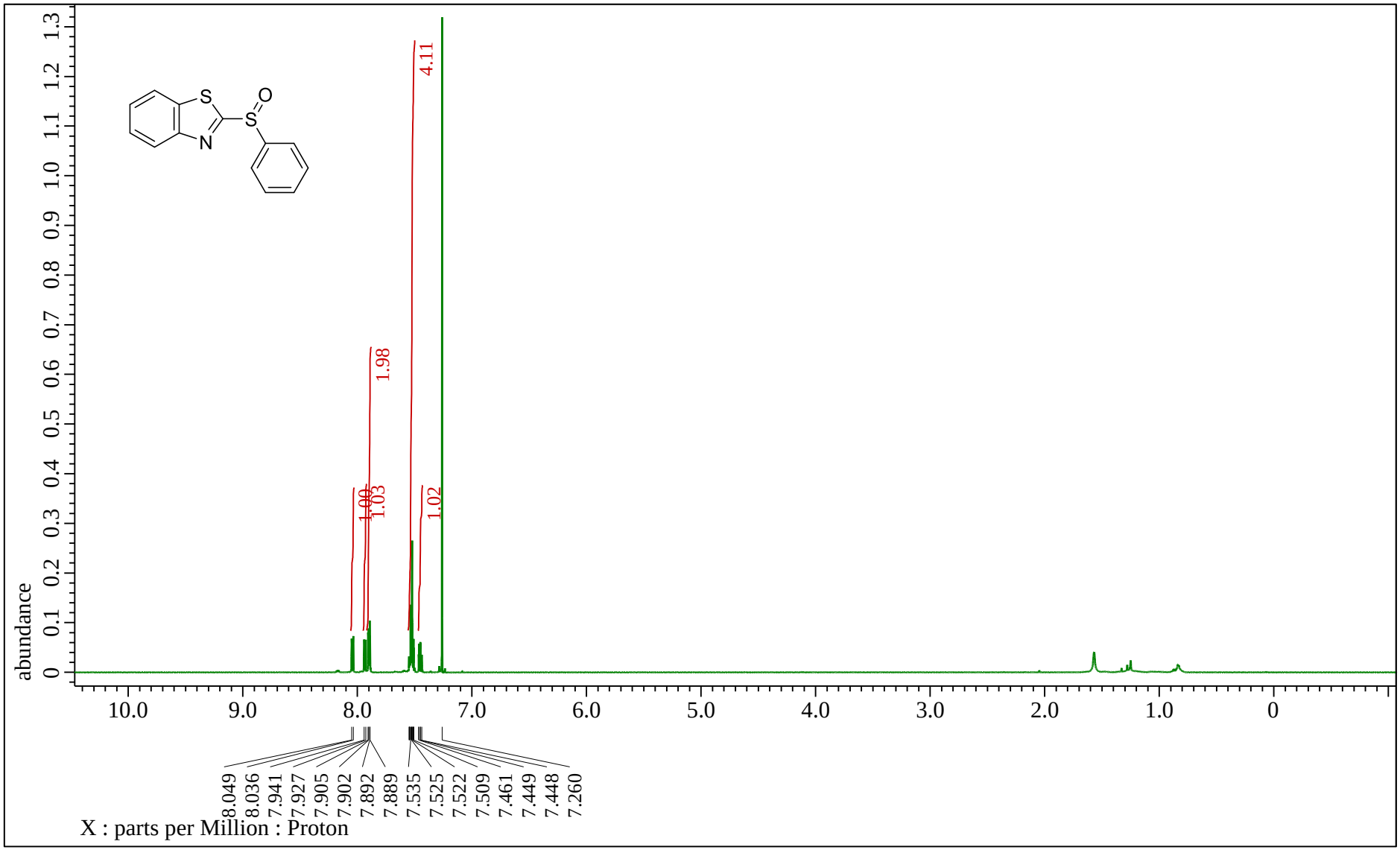

Fig. S10. ^{1}H NMR ($CDCl_3$) spectrum of **1e**.

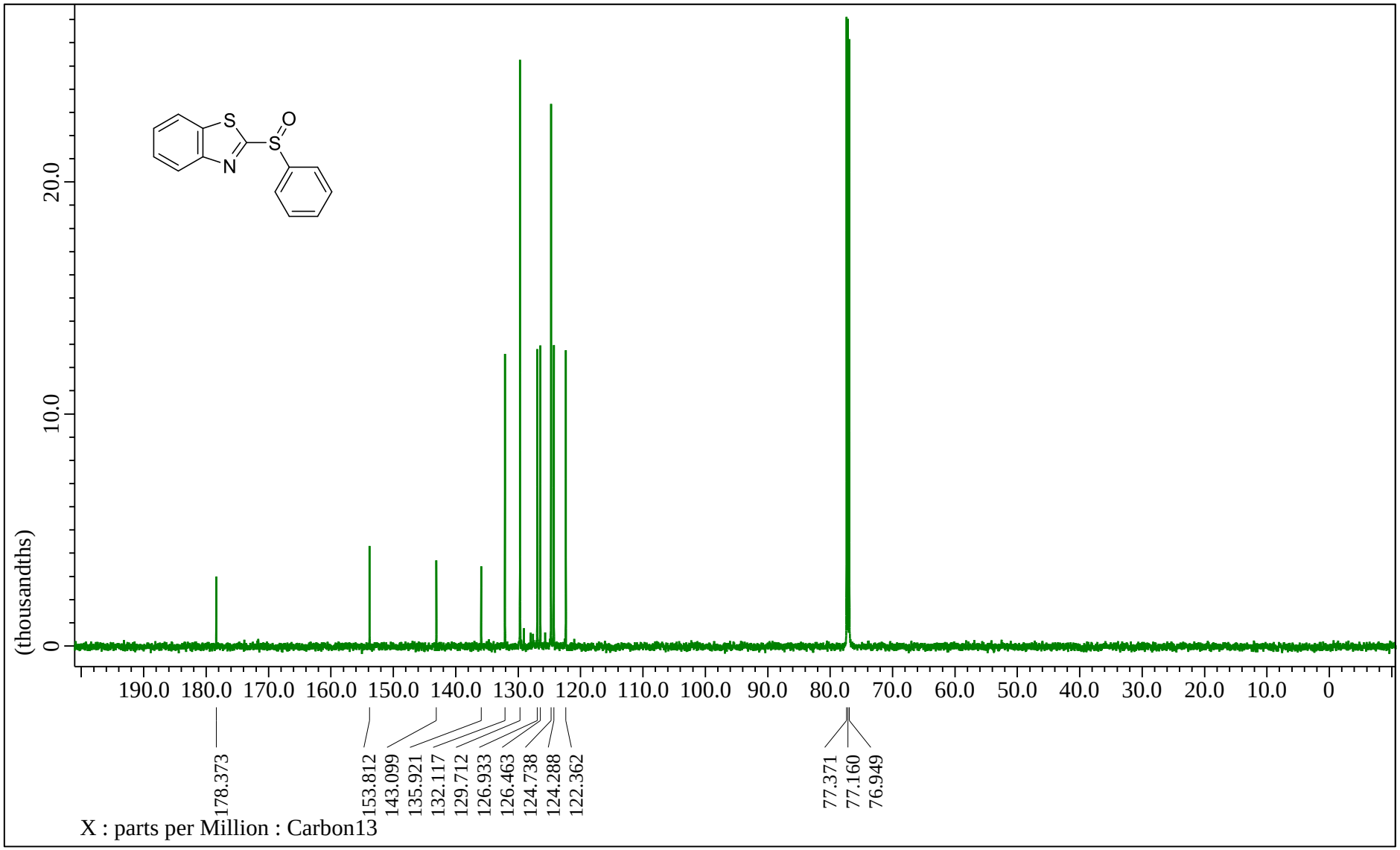

Fig. S11. ^{13}C NMR ($CDCl_3$) spectrum of **1e**.

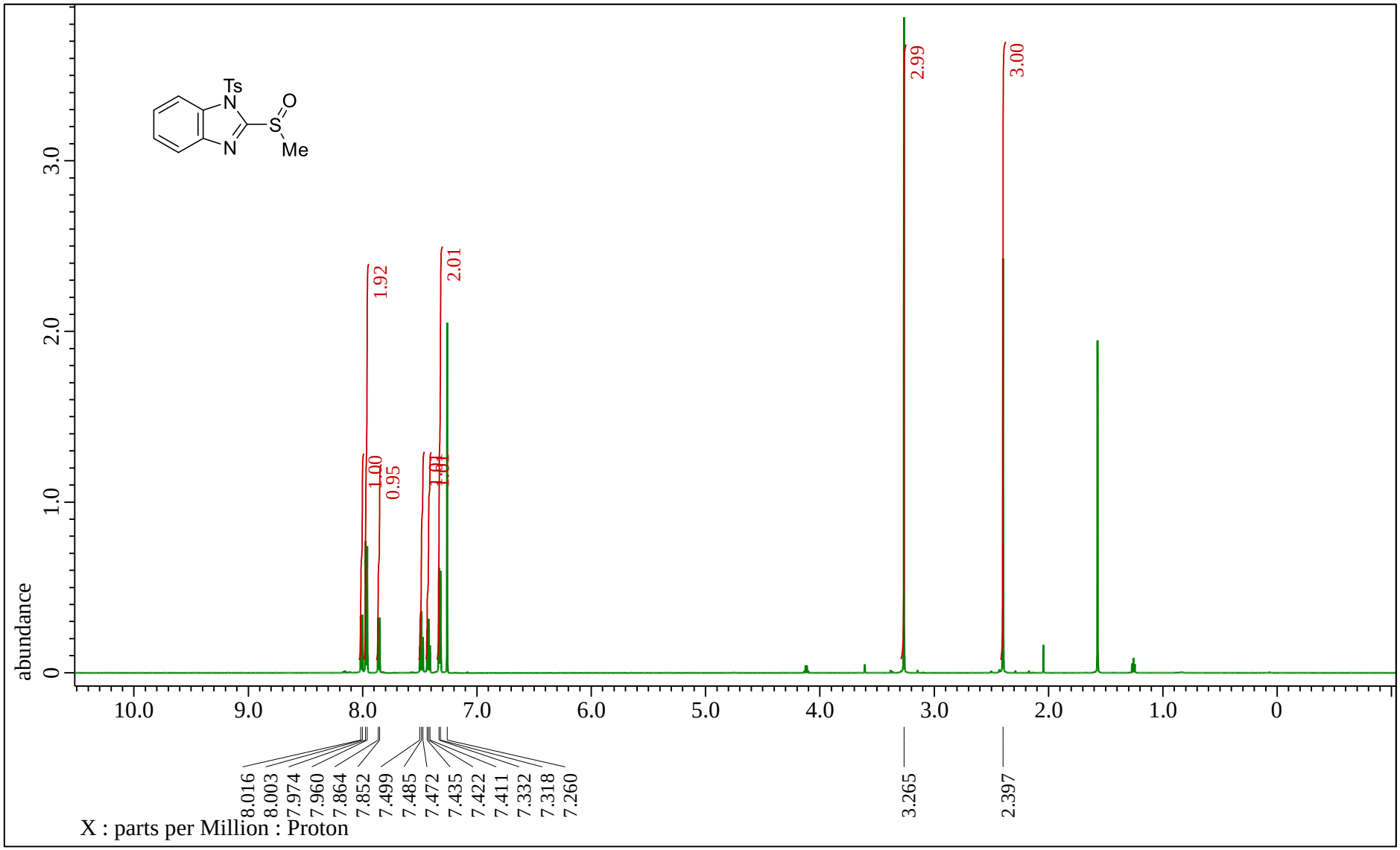

Fig. S12. ^{1}H NMR ($CDCl_3$) spectrum of **5**.

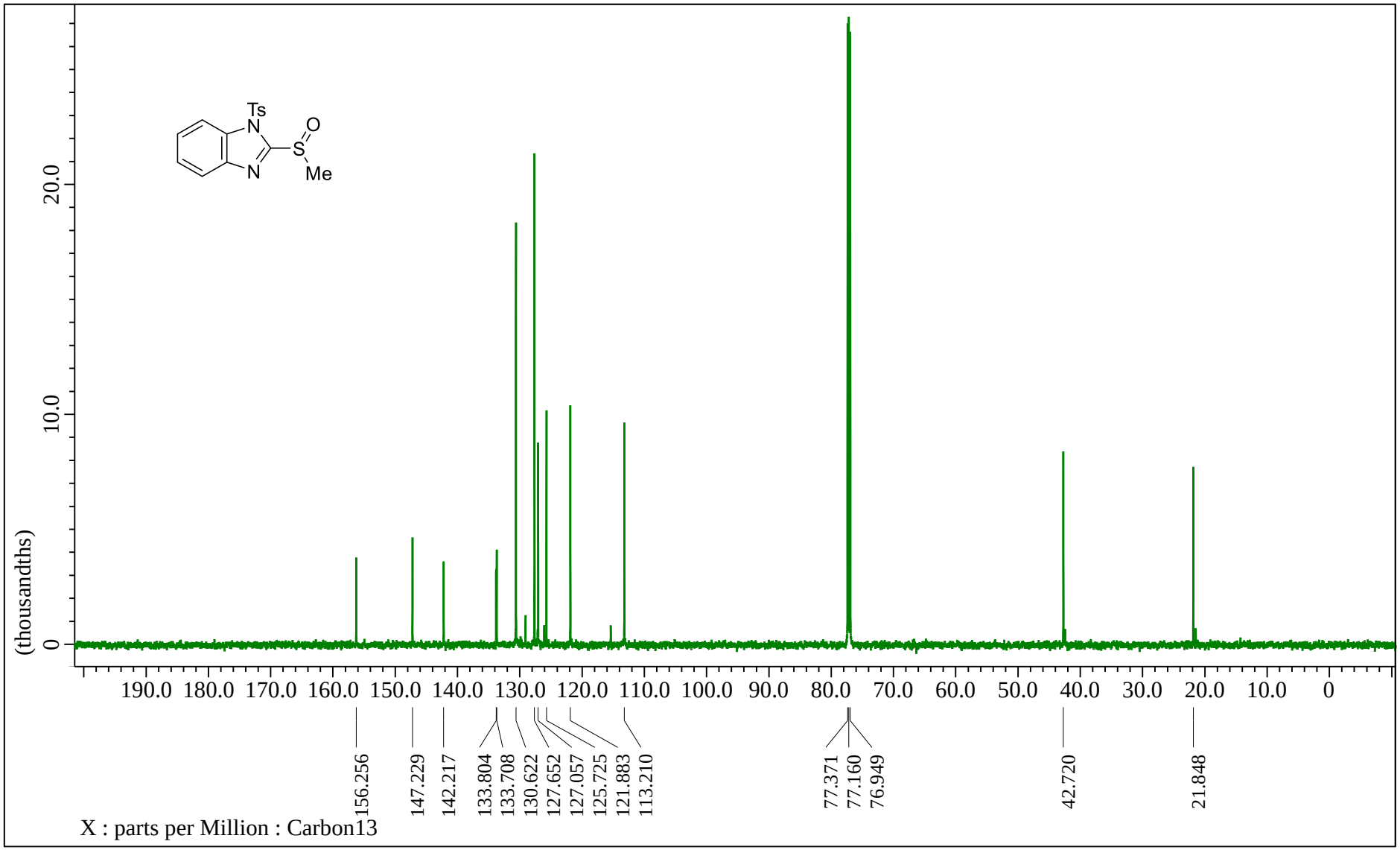

Fig. S13. ^{13}C NMR ($CDCl_3$) spectrum of **5**.

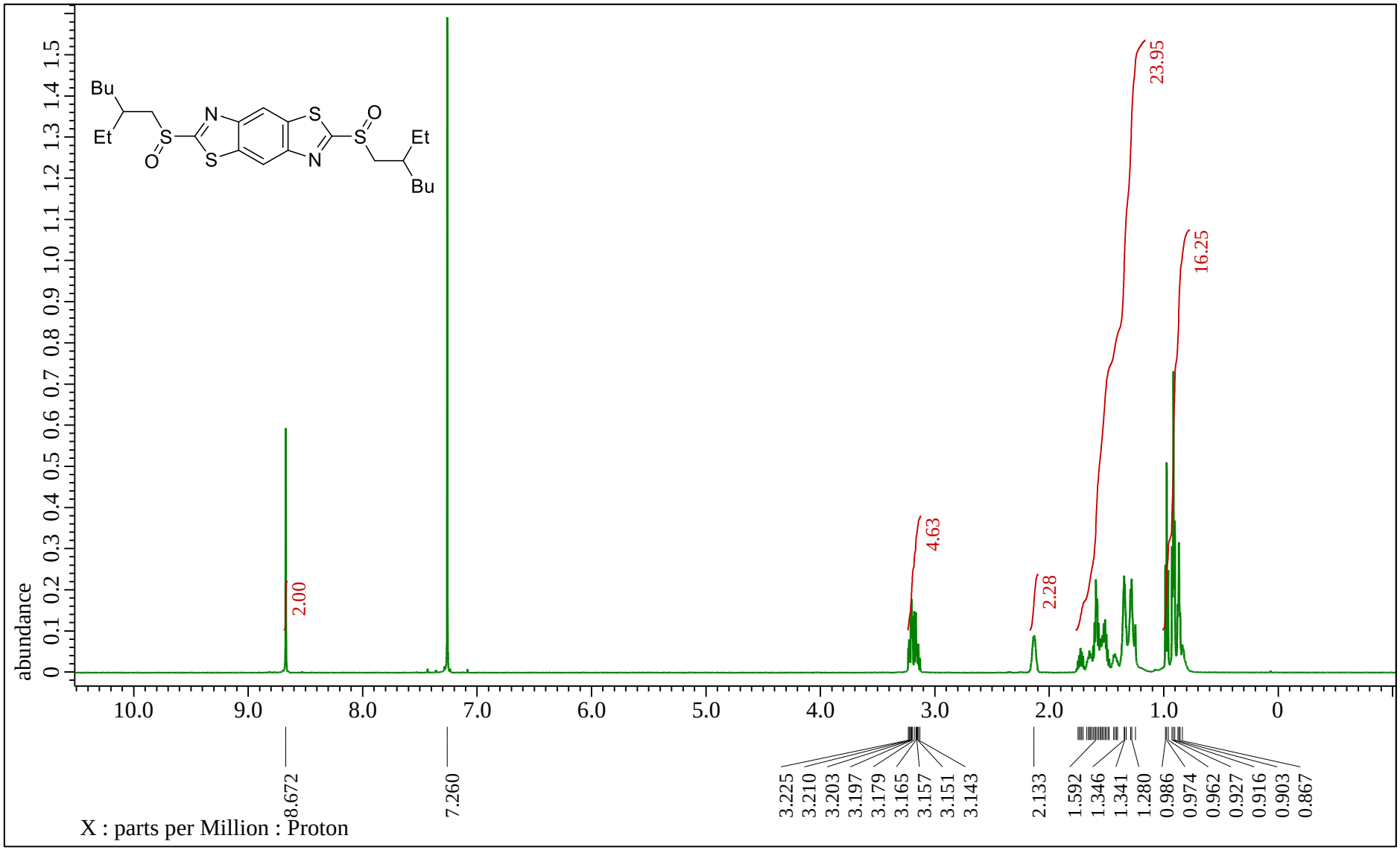

Fig. S14. ^{1}H NMR ($CDCl_3$) spectrum of **8**.

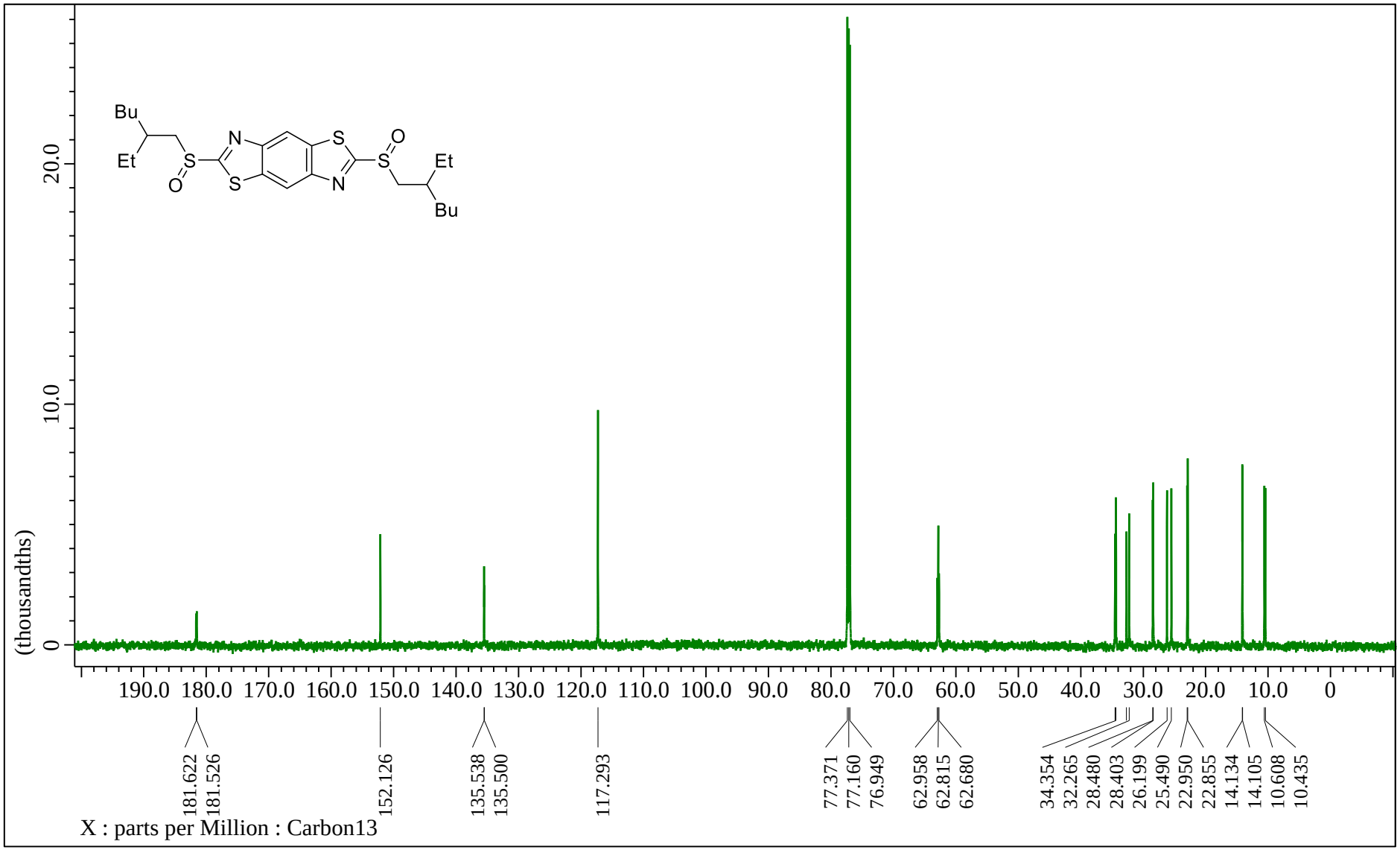

Fig. S15. ^{13}C NMR ($CDCl_3$) spectrum of **8**.

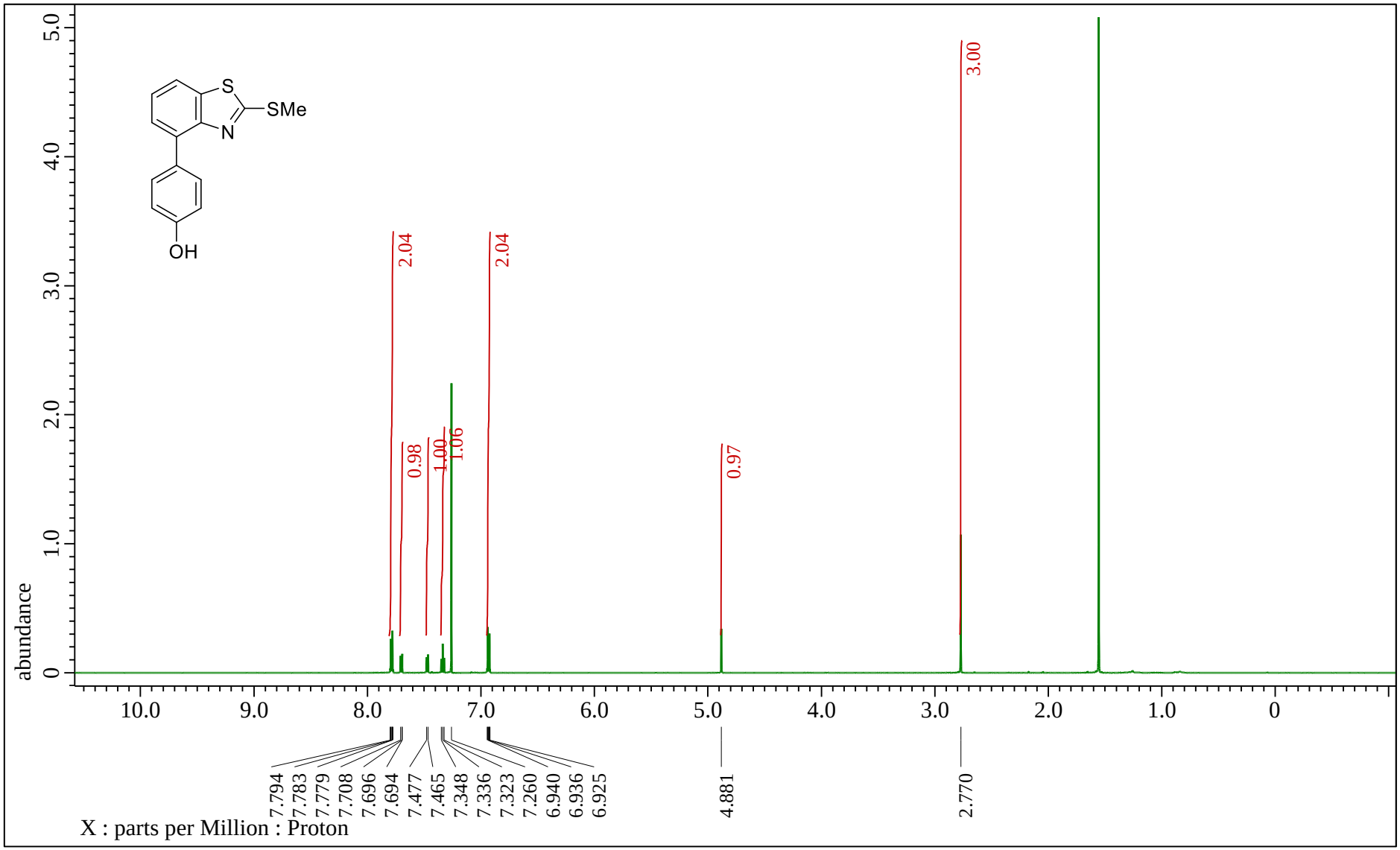

Fig. S16. ^{1}H NMR ($CDCl_3$) spectrum of **3aa**.

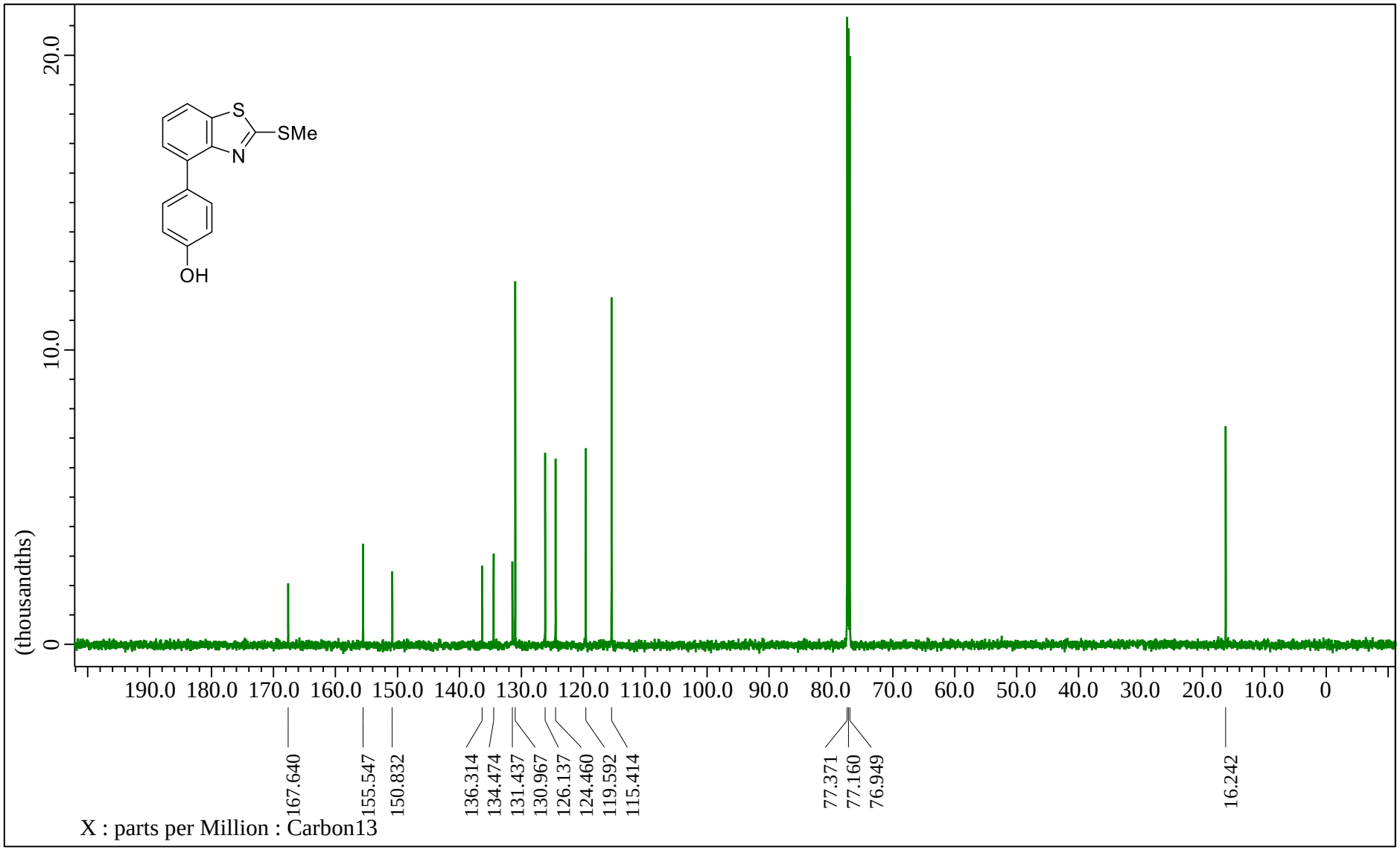

Fig. S17. ^{13}C NMR ($CDCl_3$) spectrum of **3aa**.

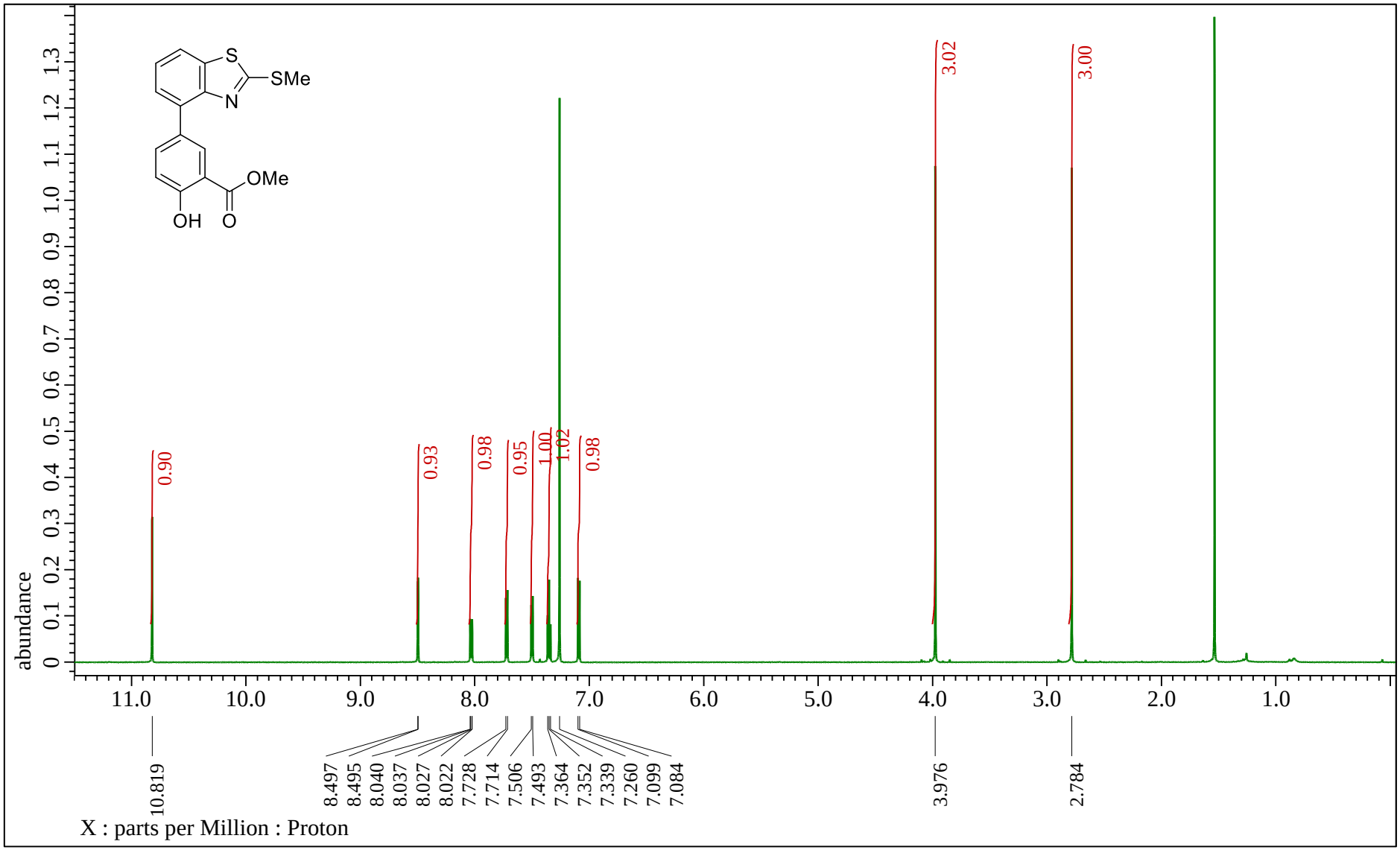

Fig. S18. ^{1}H NMR ($CDCl_3$) spectrum of **3ab.**

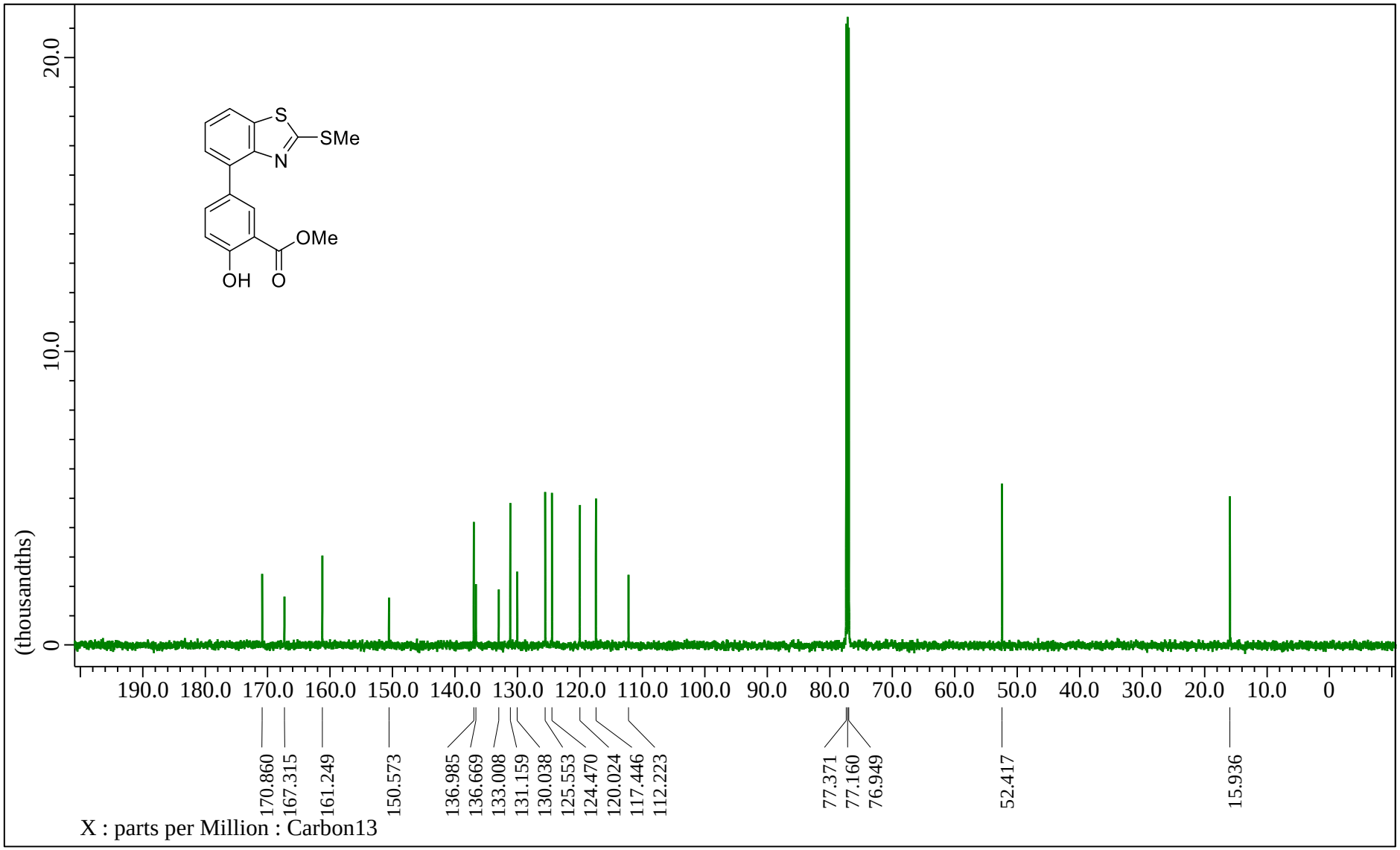

Fig. S19. ^{13}C NMR ($CDCl_3$) spectrum of **3ab**.

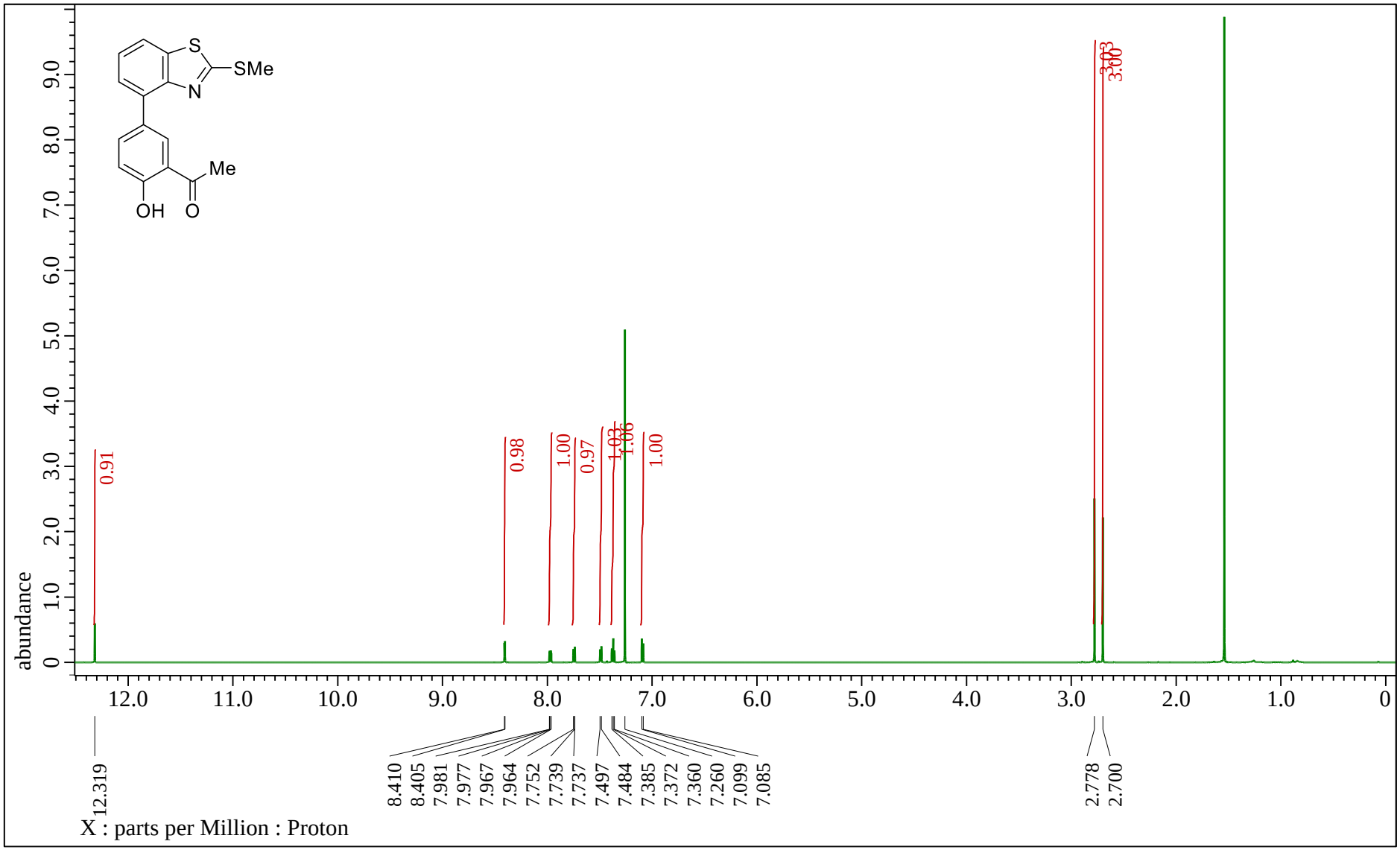

Fig. S20. ^{1}H NMR ($CDCl_3$) spectrum of **3ac**.

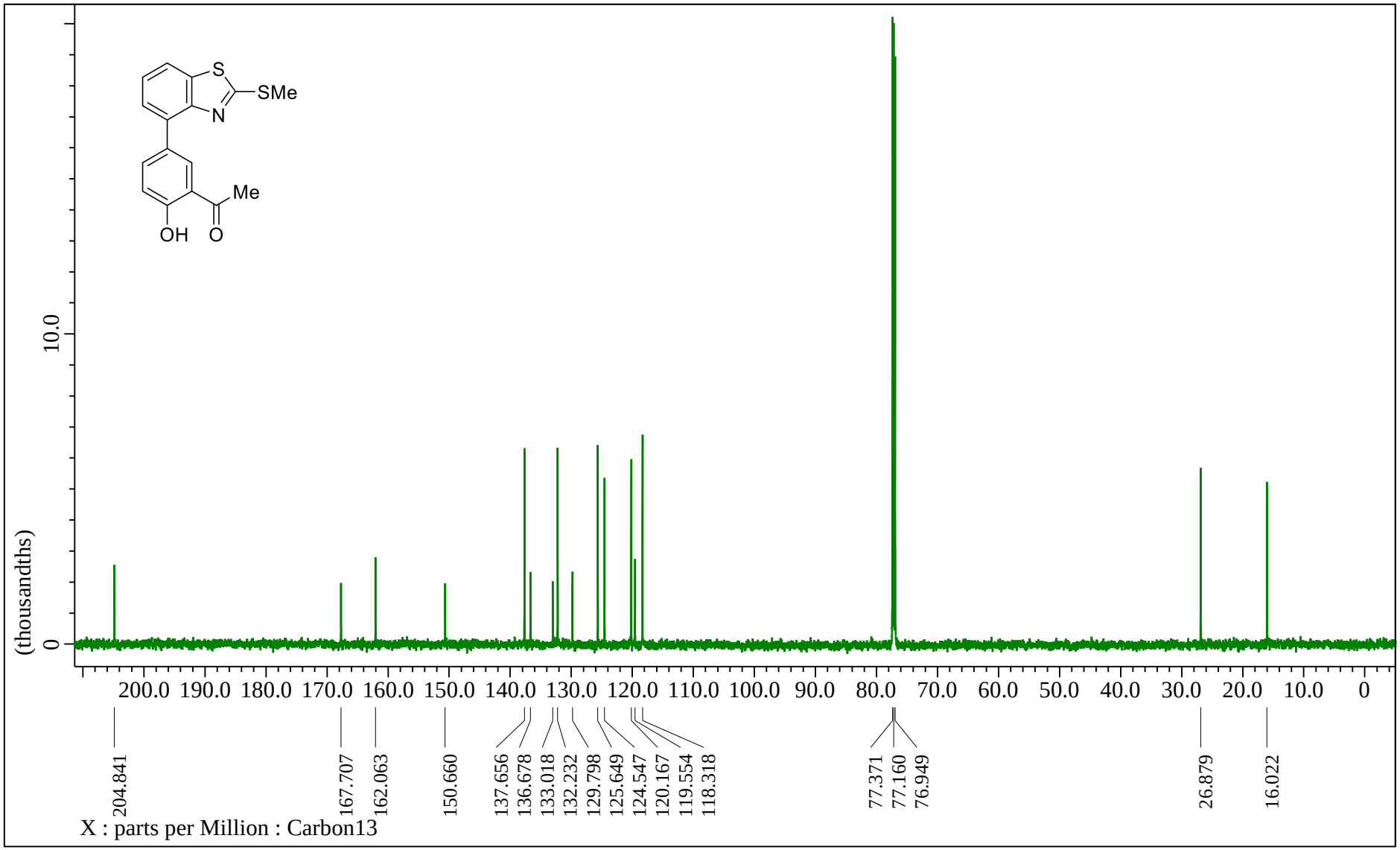

Fig. S21. ^{13}C NMR ($CDCl_3$) spectrum of **3ac**.

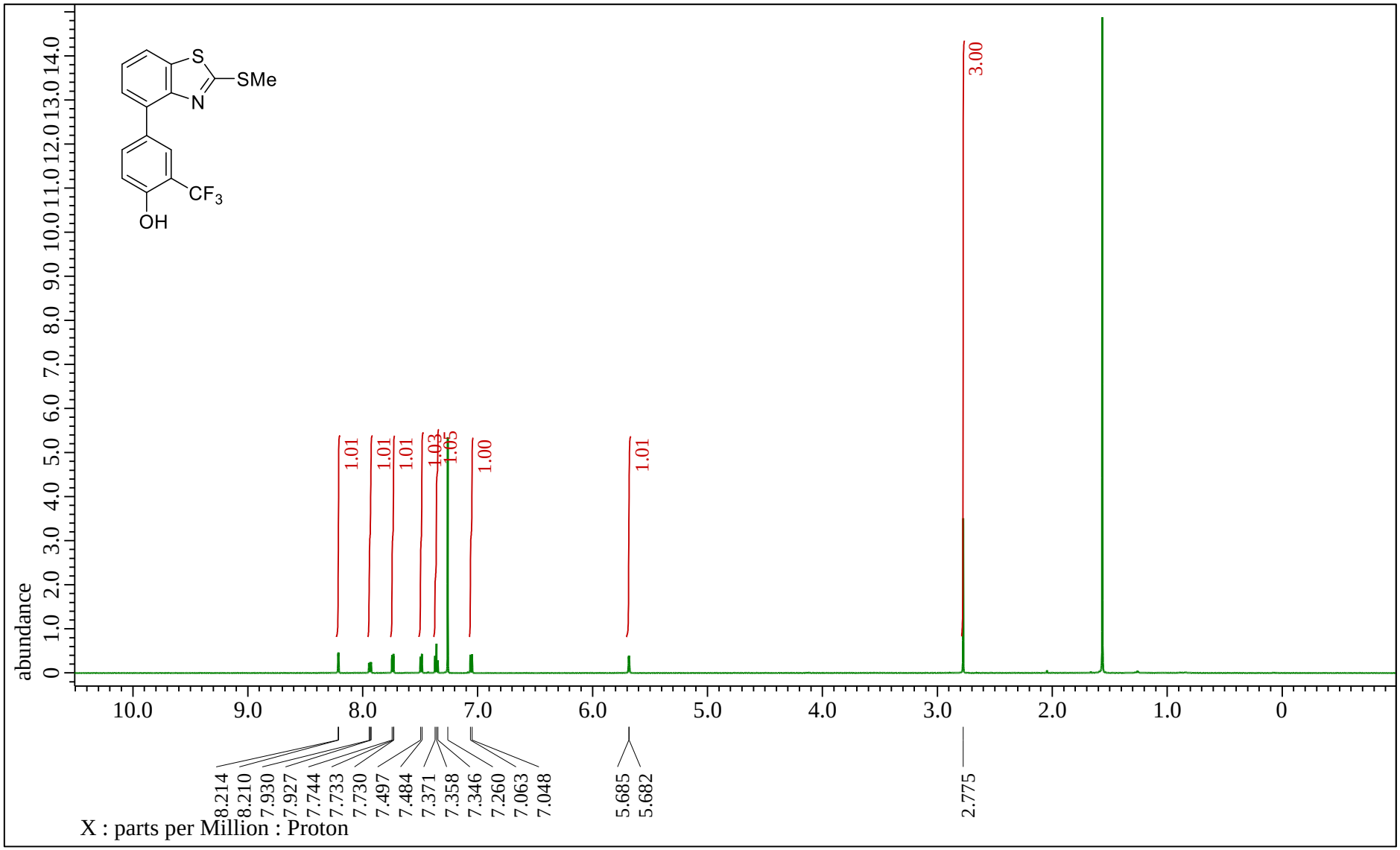

Fig. S22. ^{1}H NMR ($CDCl_3$) spectrum of **3ad**.

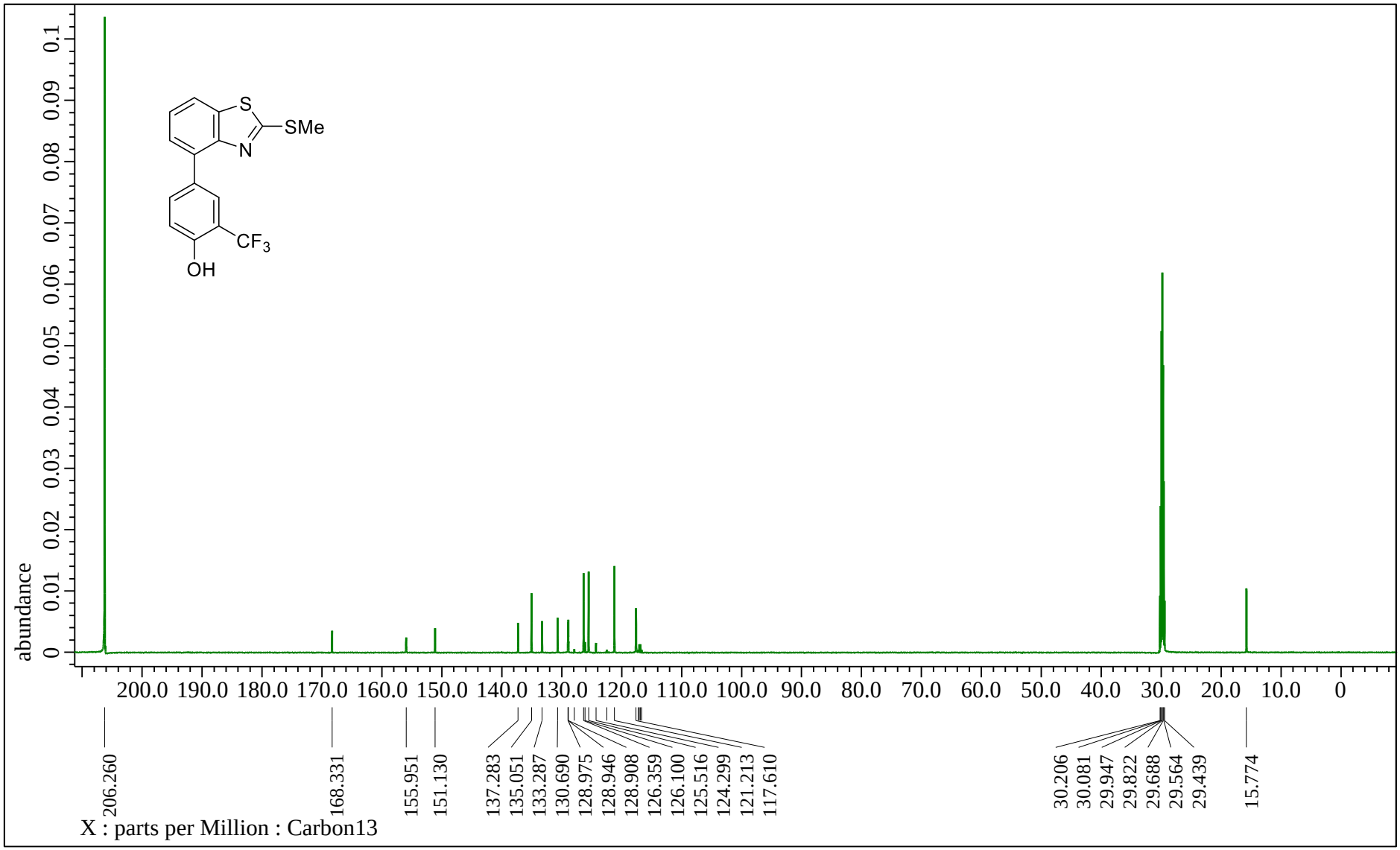

Fig. S23. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3ad**.

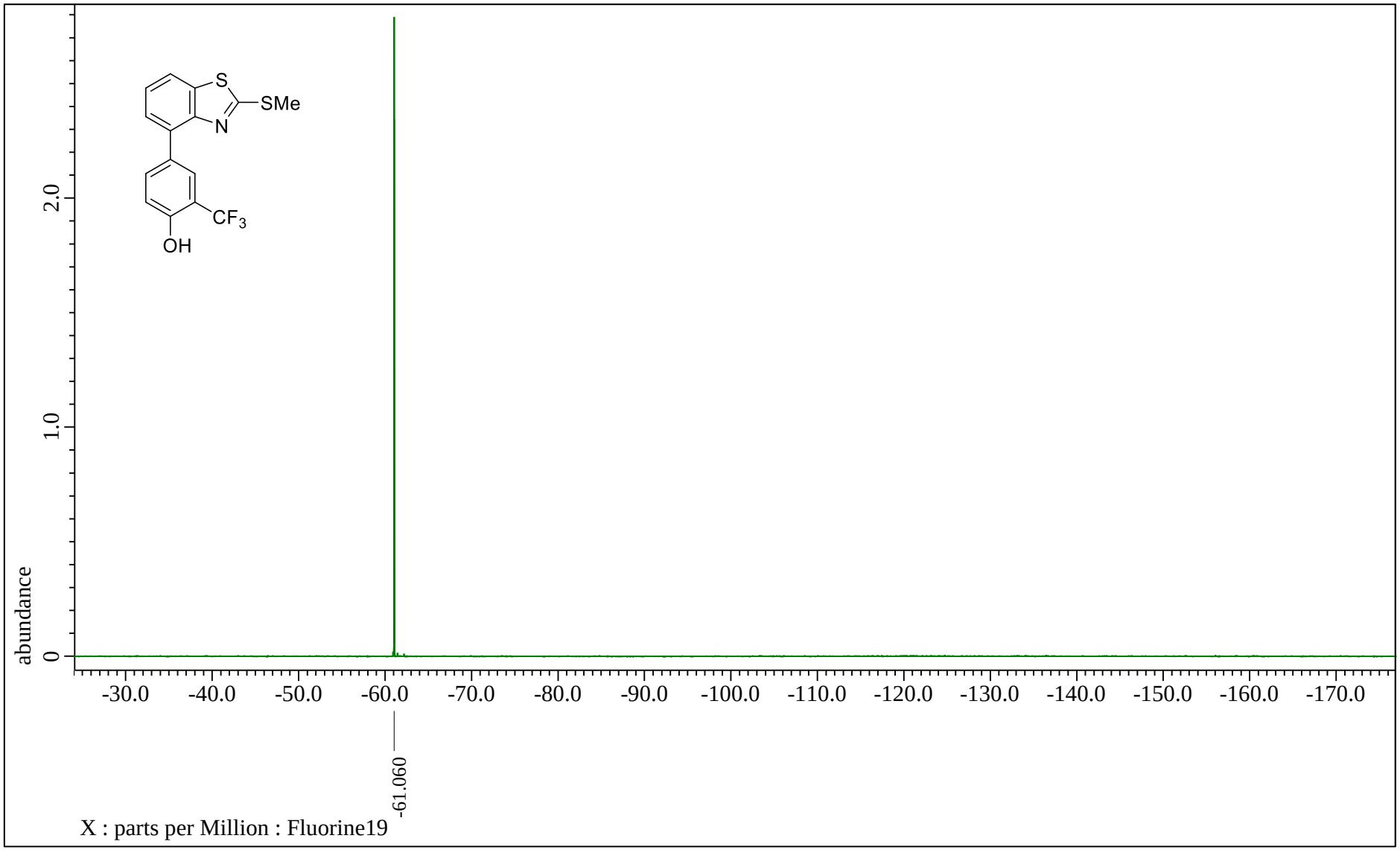

Fig. S24. ^{19}F NMR ($CDCl_3$) spectrum of **3ad**.

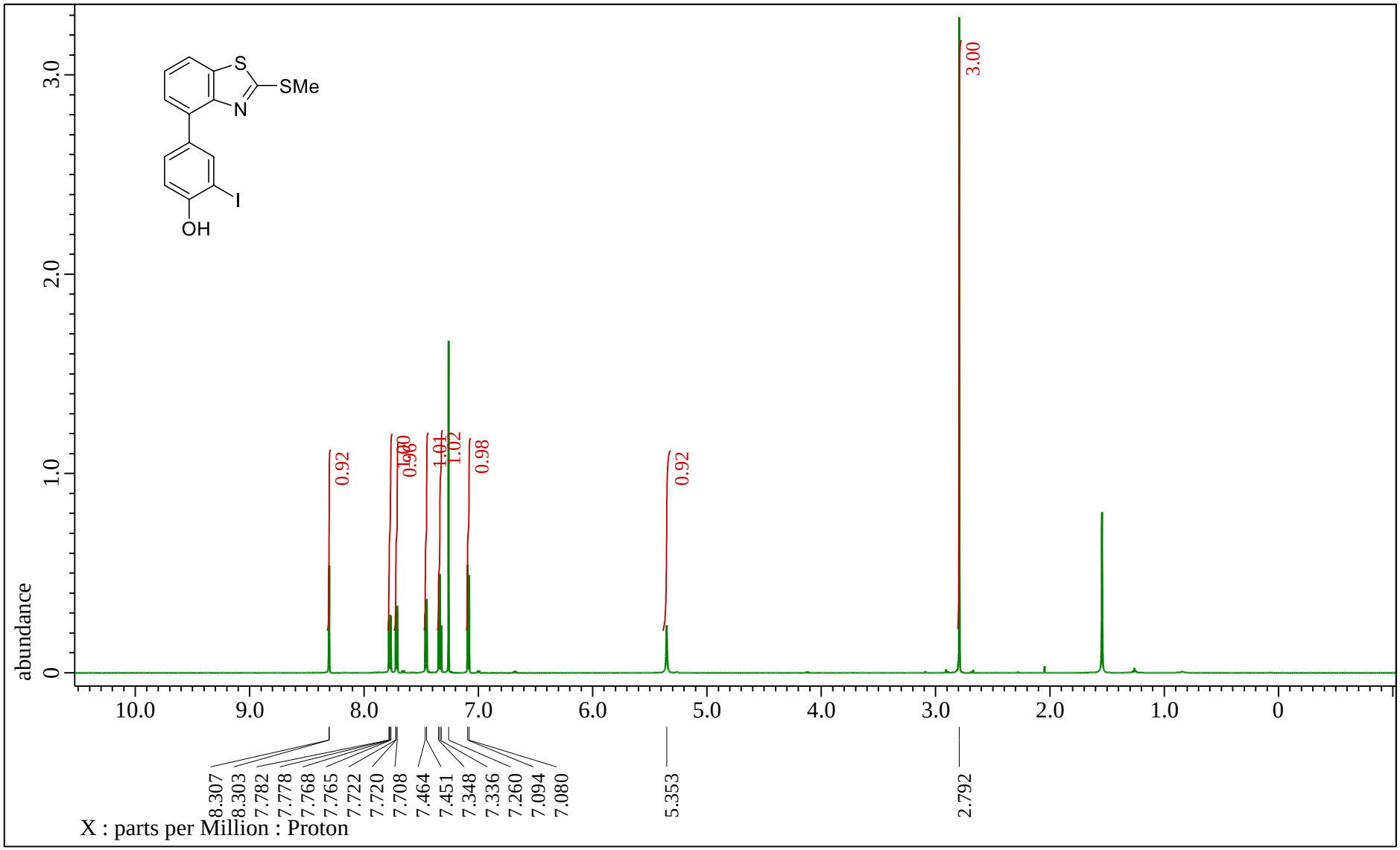

Fig. S25. ^{1}H NMR ($CDCl_3$) spectrum of **3ae**.

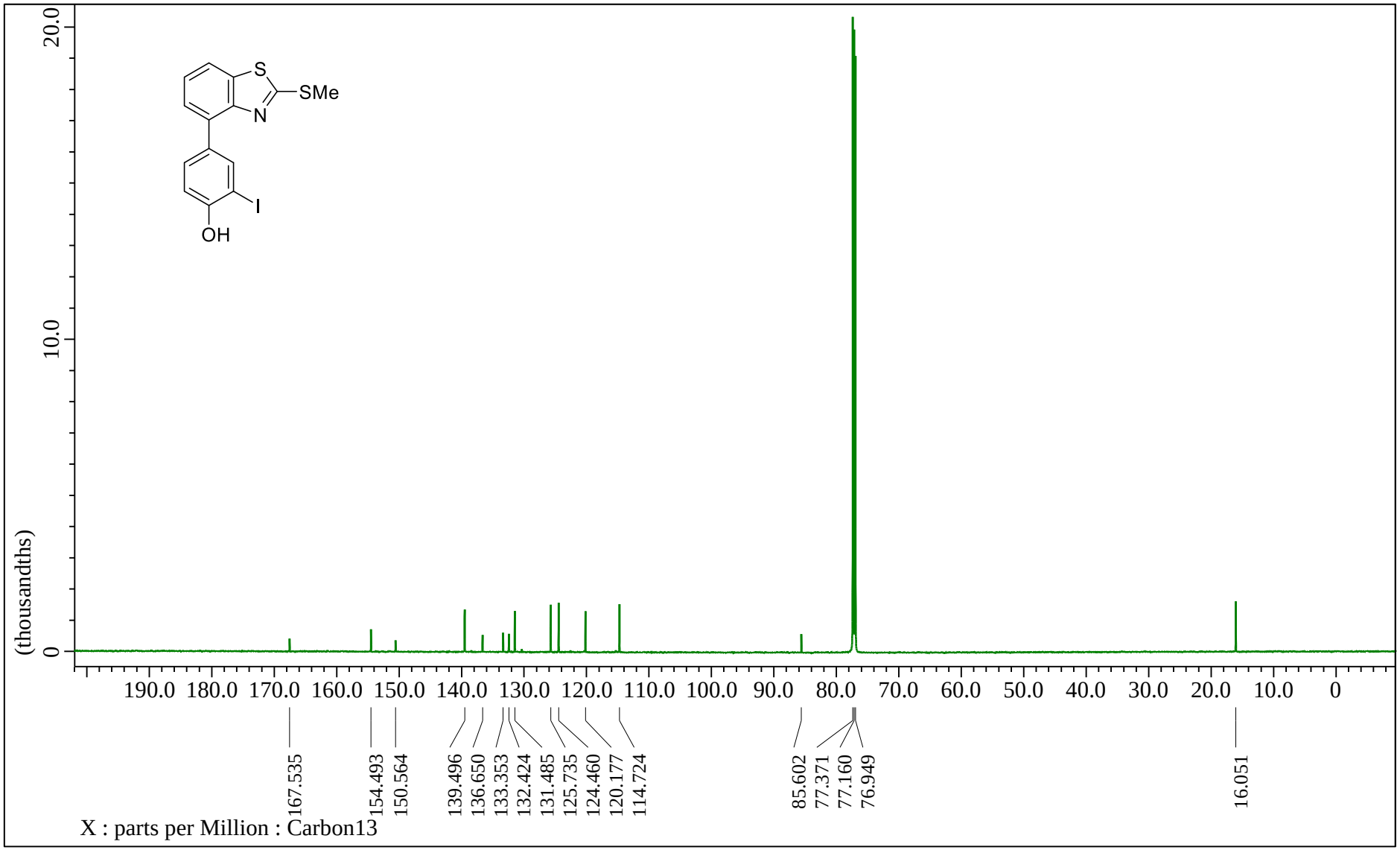

Fig. S26. ^{13}C NMR ($CDCl_3$) spectrum of **3ae**.

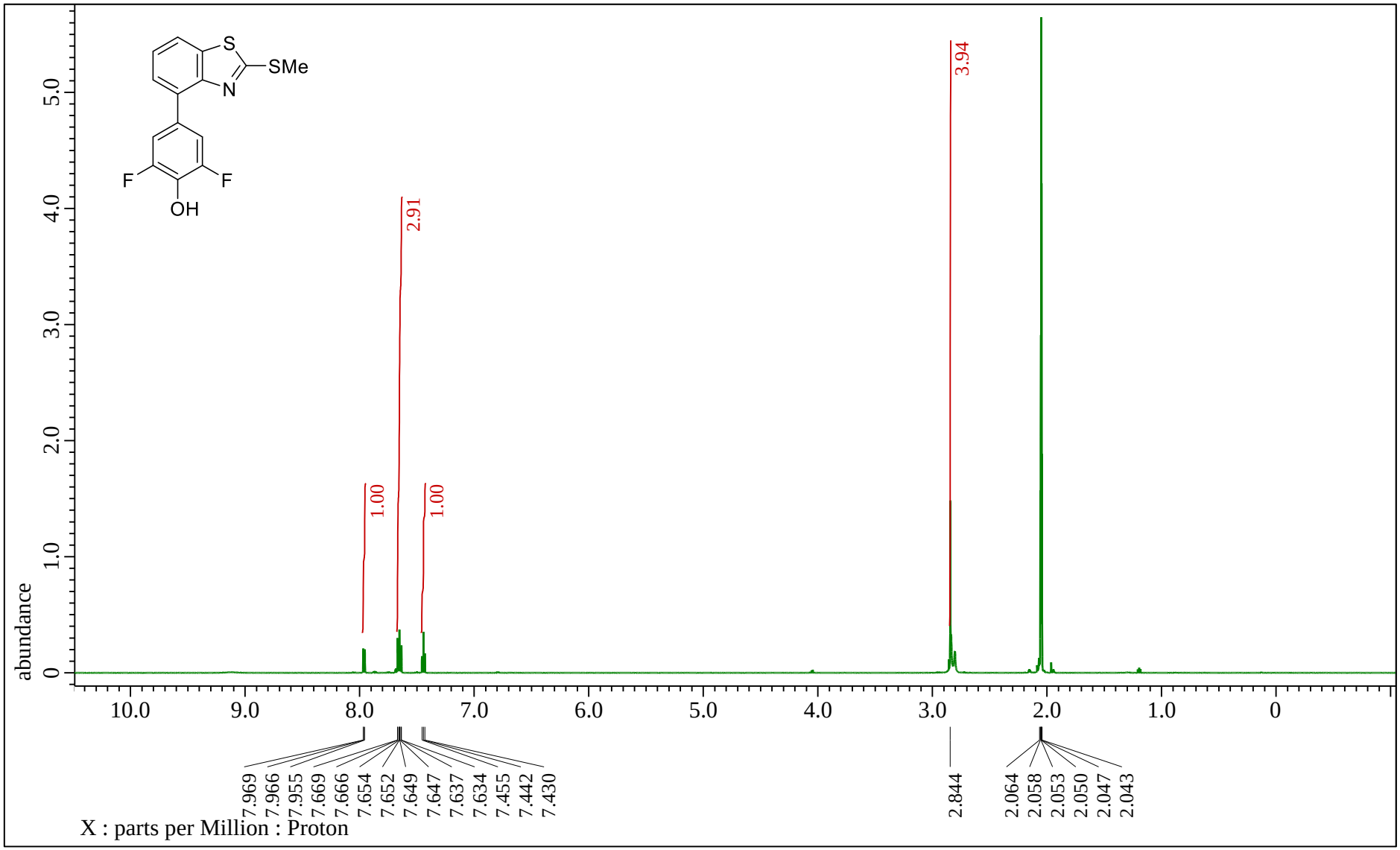

Fig. S27. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3af.**

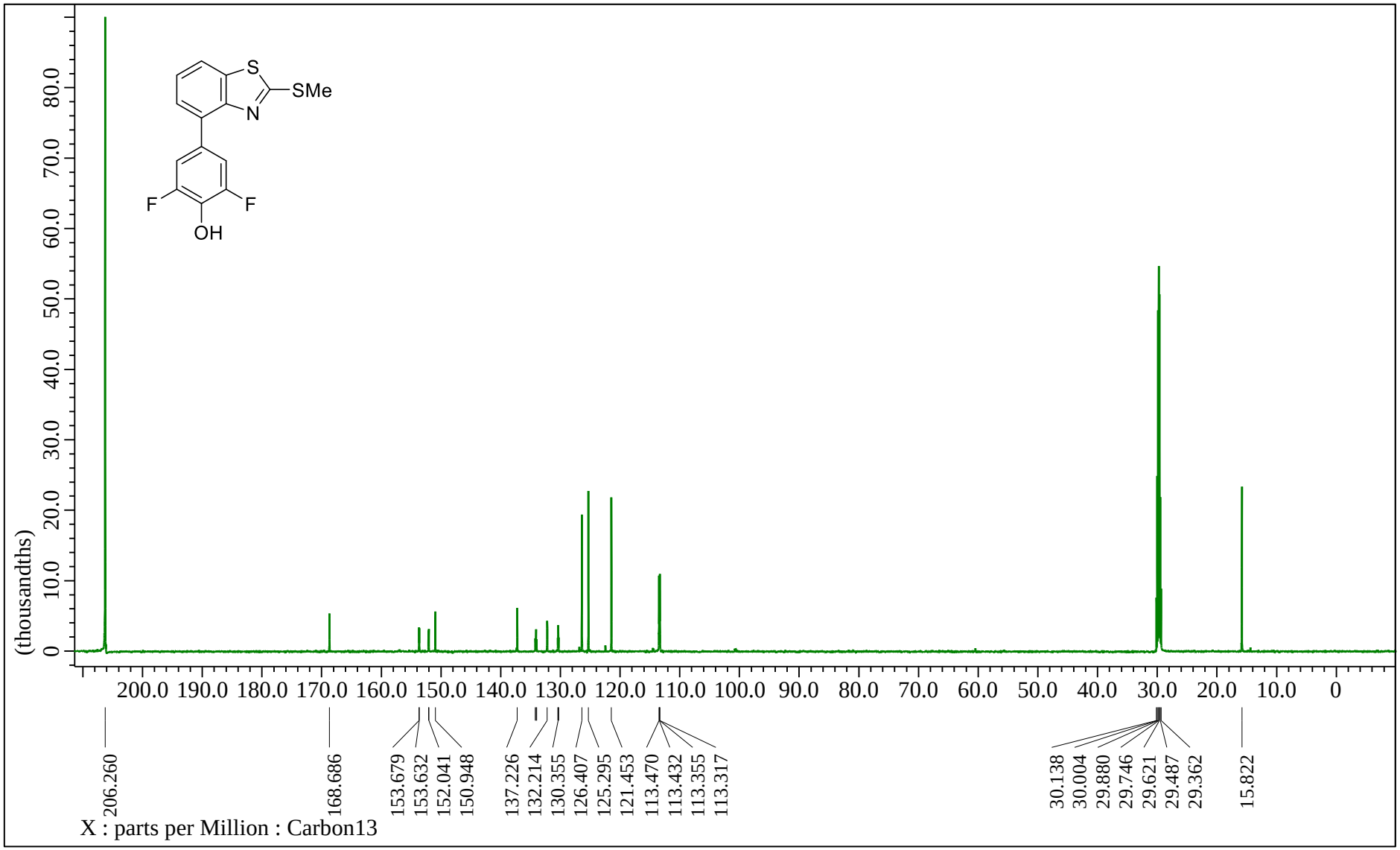

Fig. S28. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3af.**

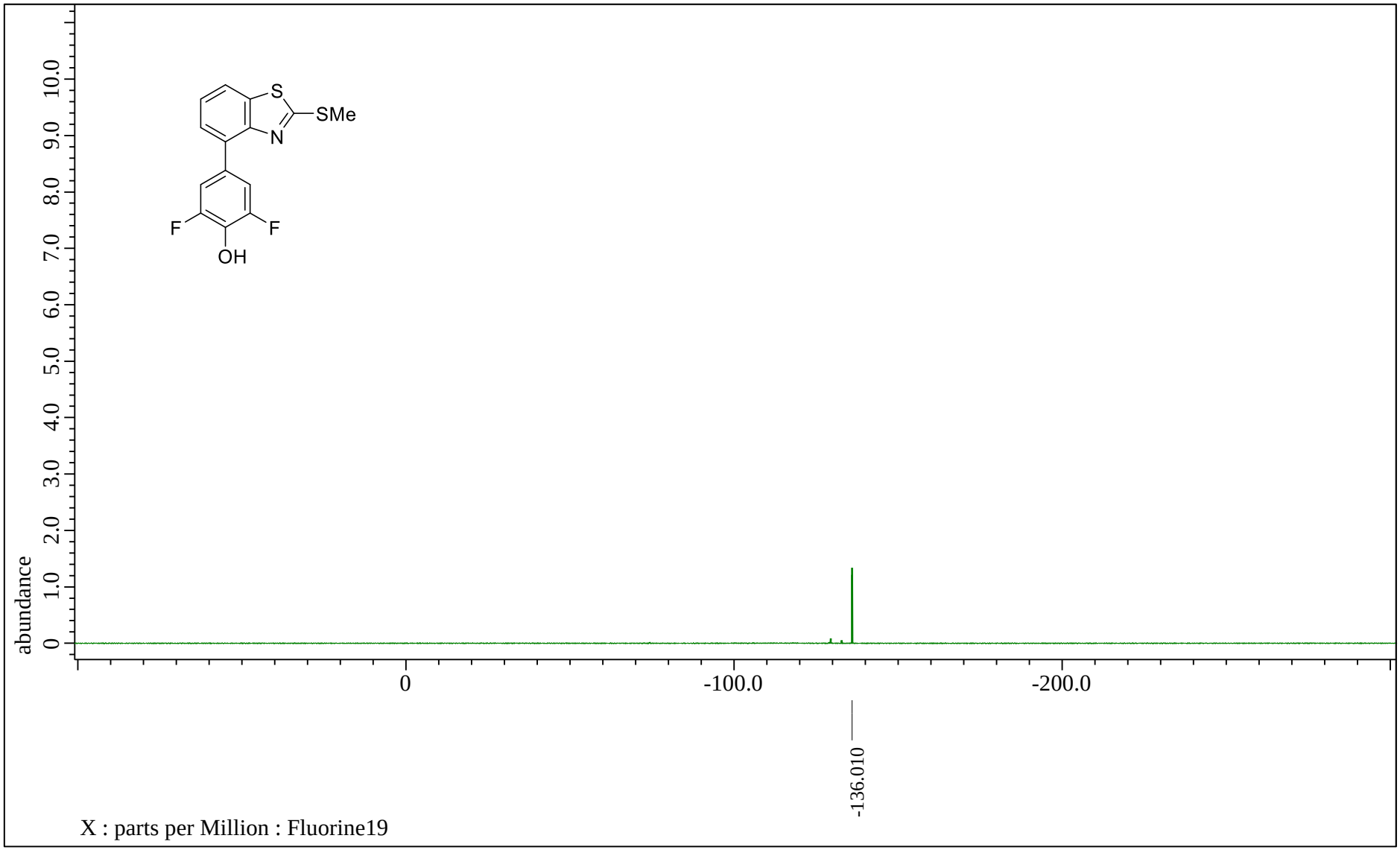

Fig. S29. ^{19}F NMR ($(CD_3)_2CO$) spectrum of **3af.**

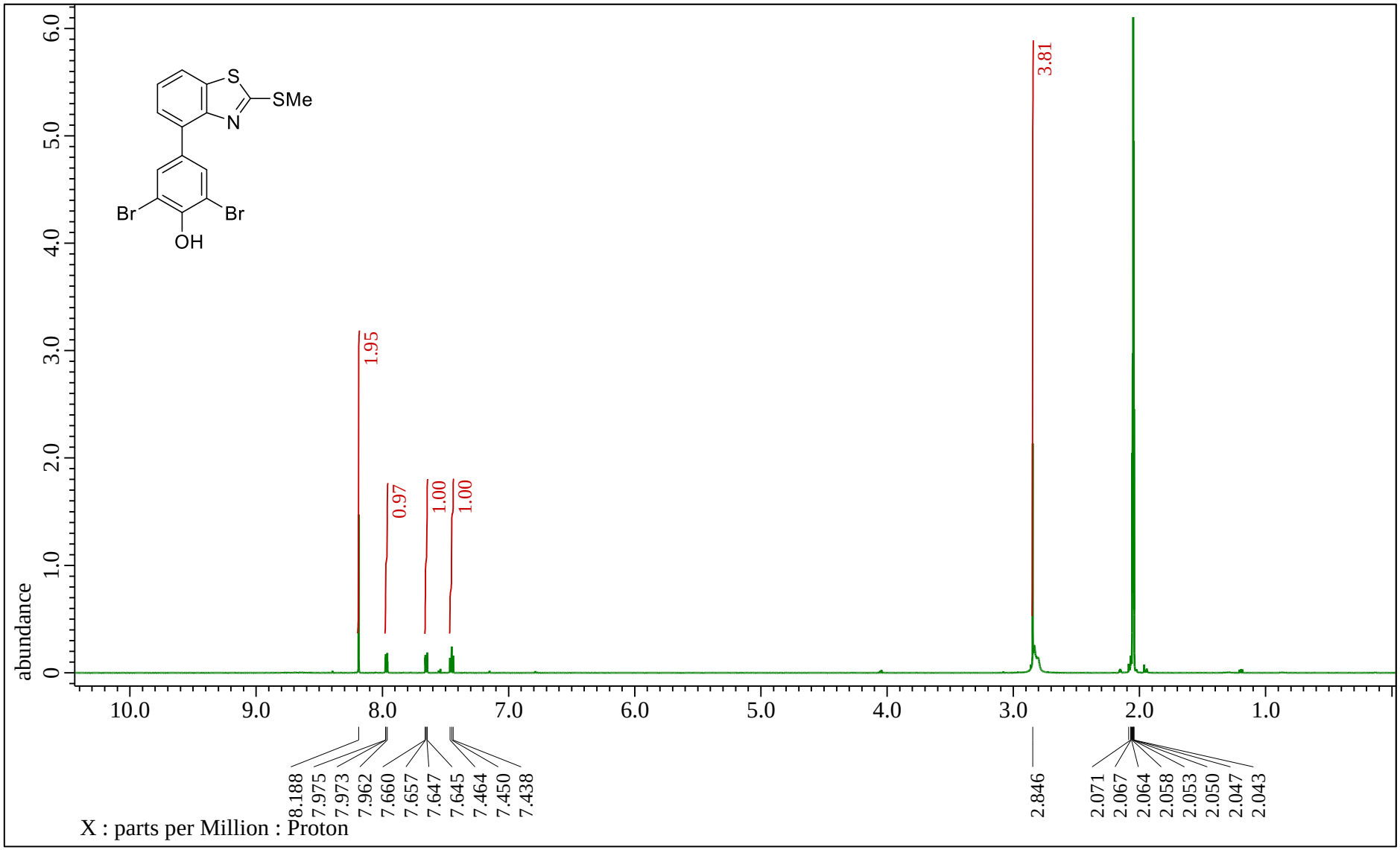

Fig. S30. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3ag.**

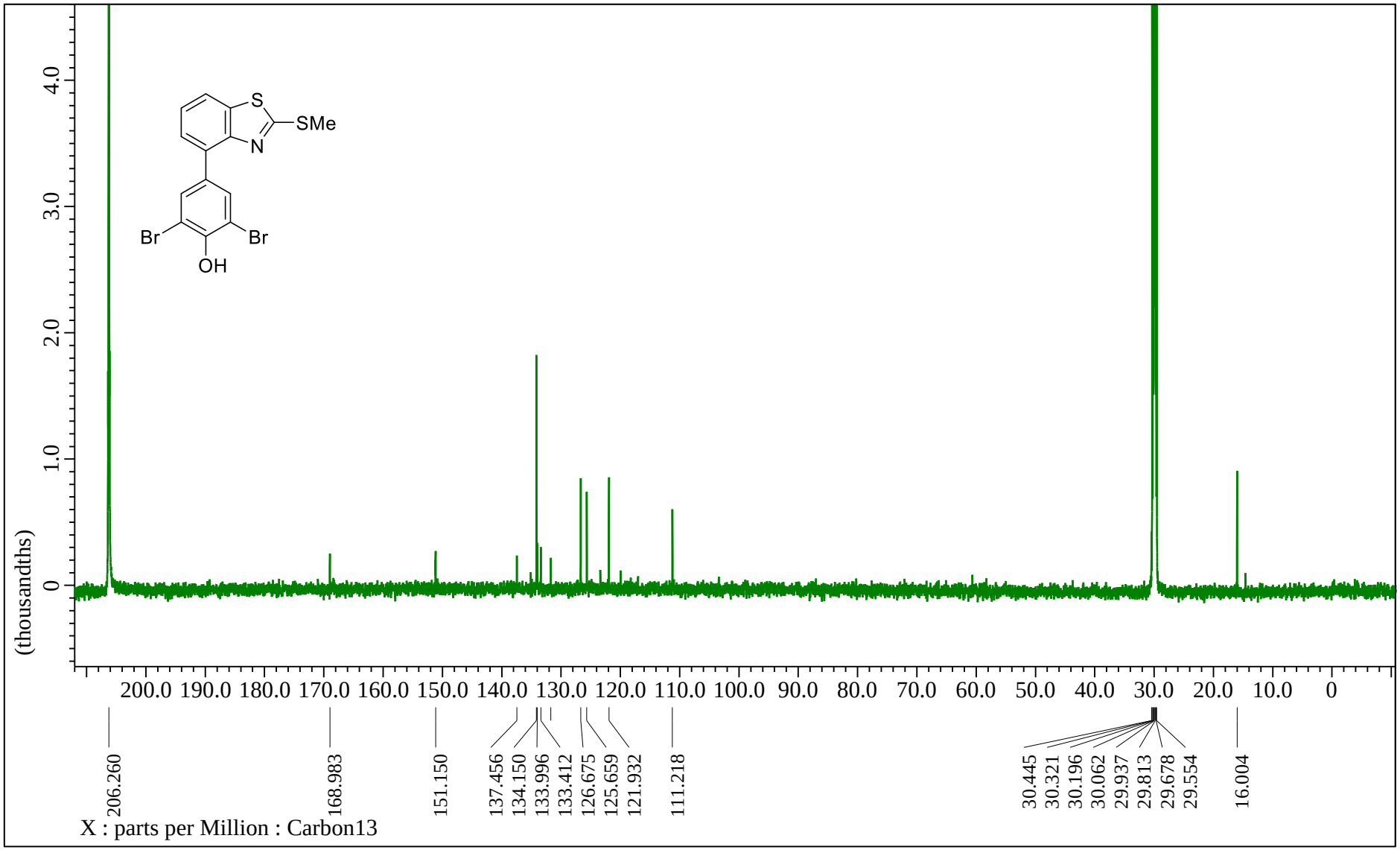

Fig. S31. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3ag**.

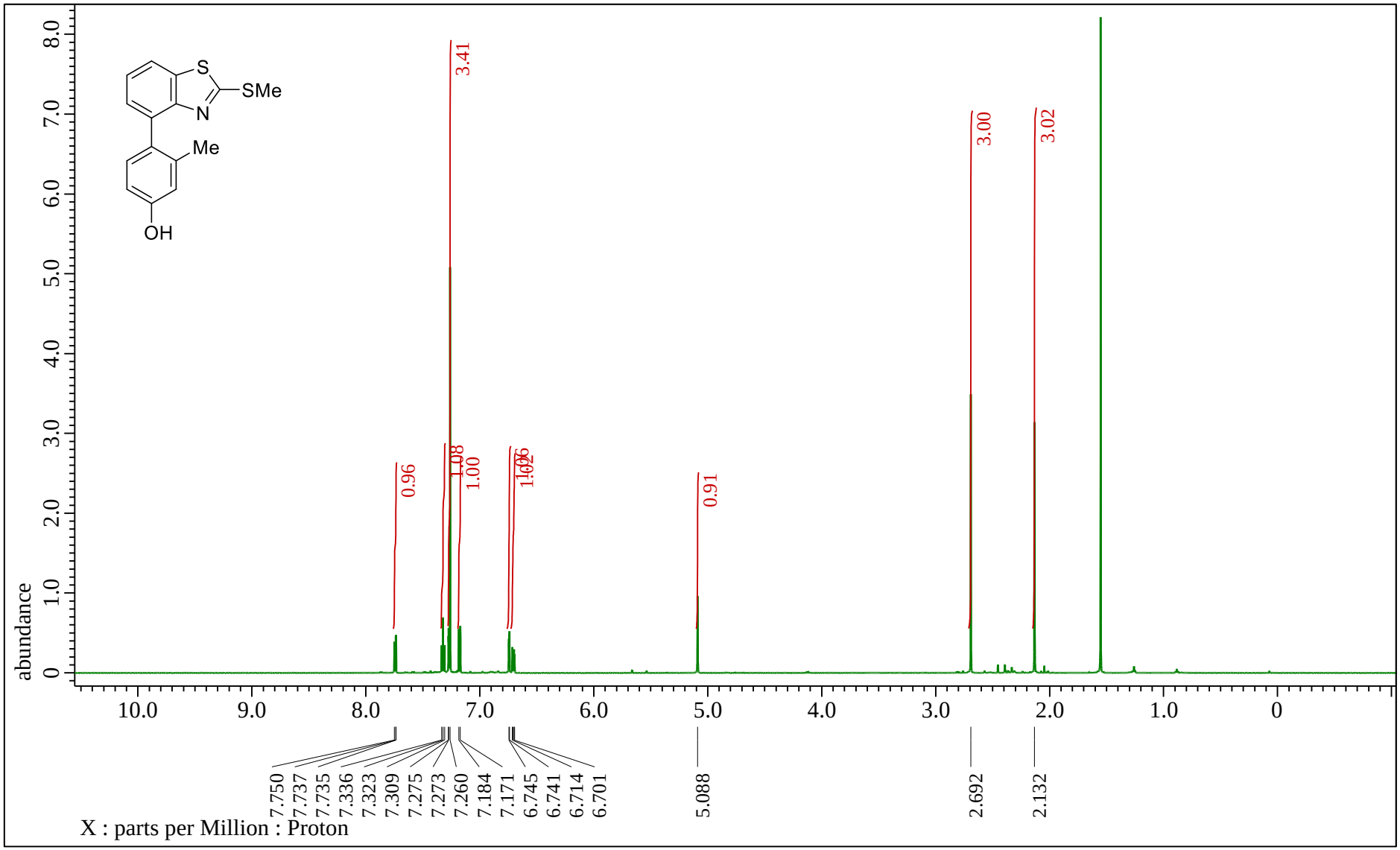

Fig. S32. ^{1}H NMR ($CDCl_3$) spectrum of **3ah**.

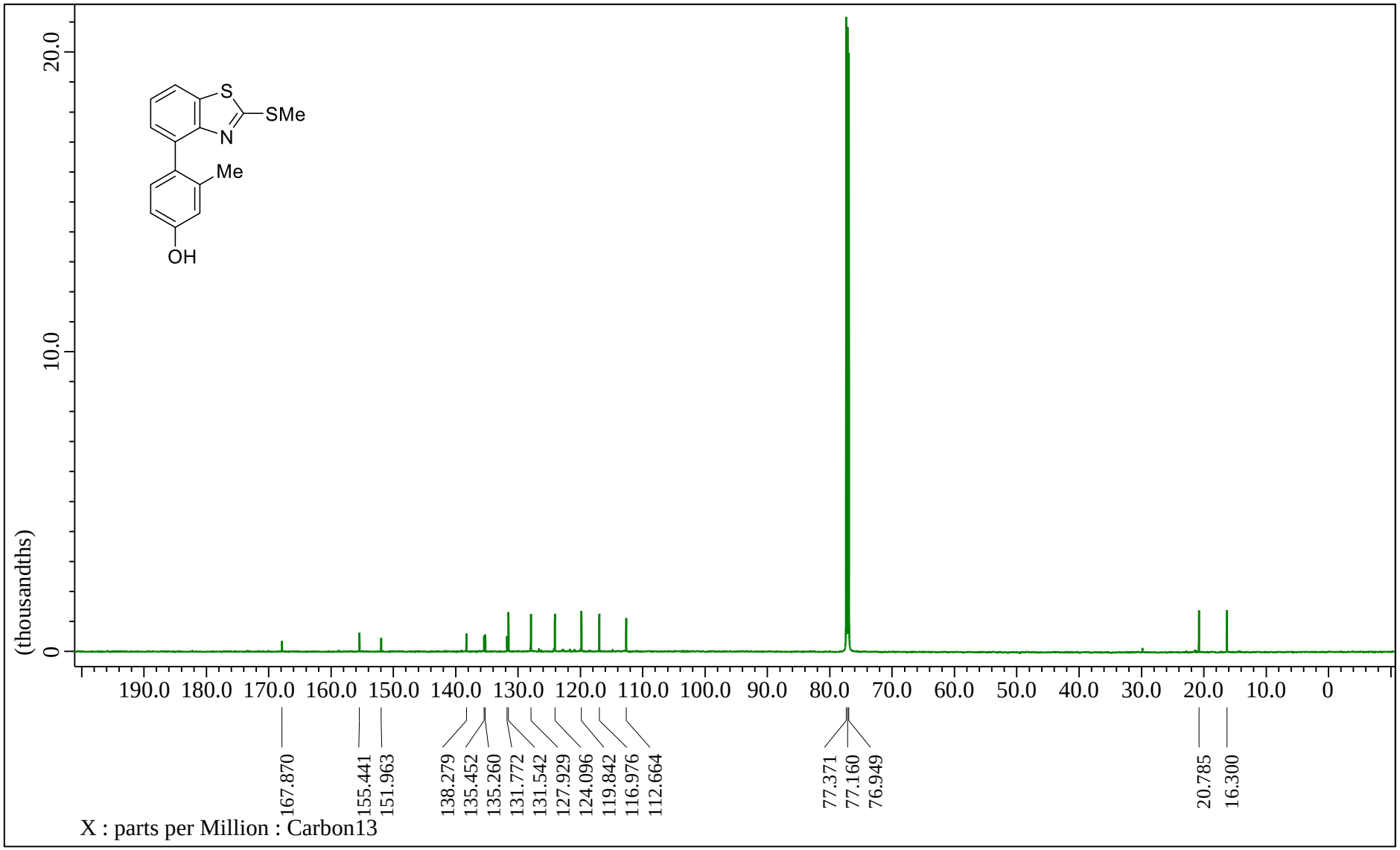

Fig. S33. ^{13}C NMR ($CDCl_3$) spectrum of **3ah**.

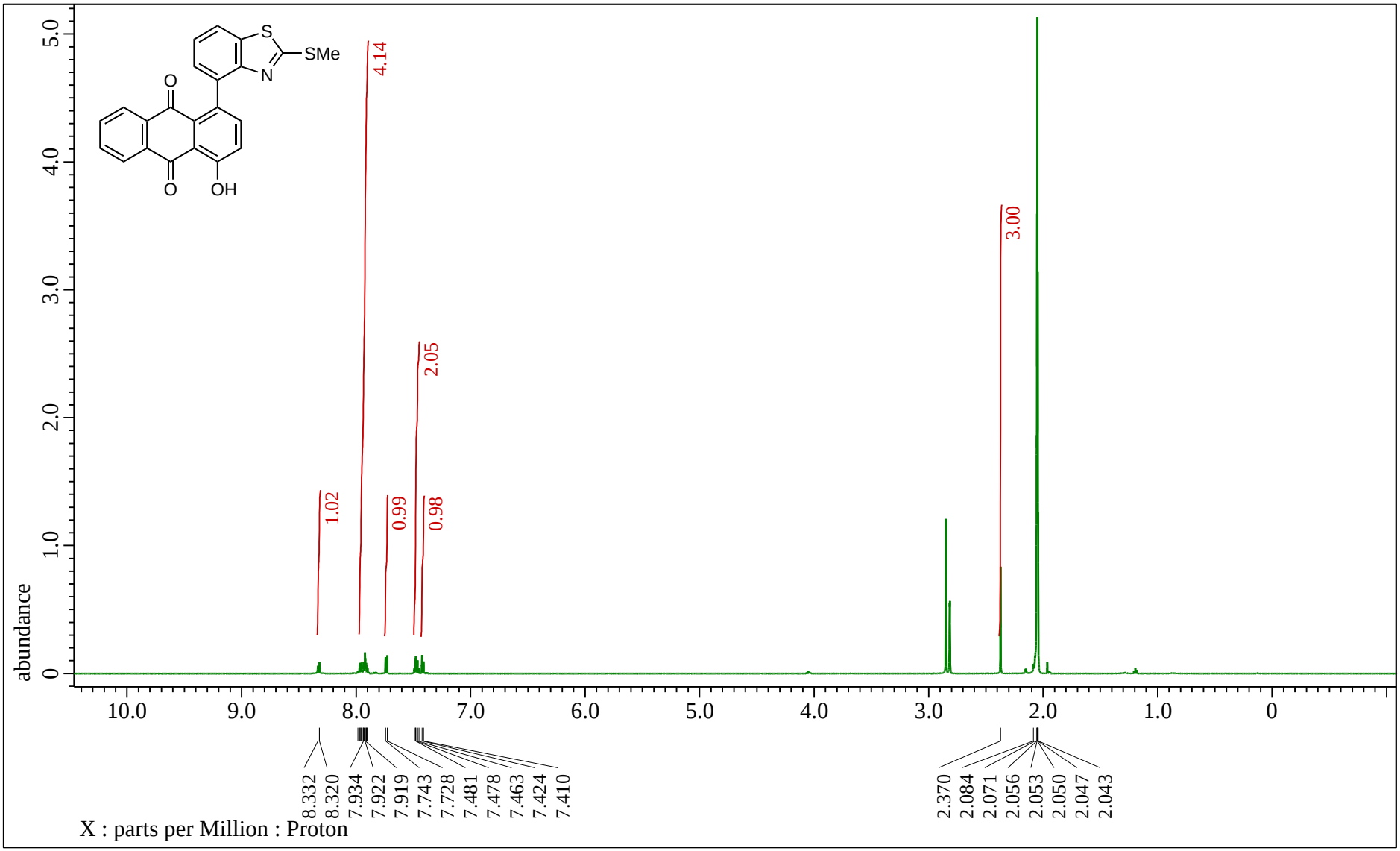

Fig. S34. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3ai**.

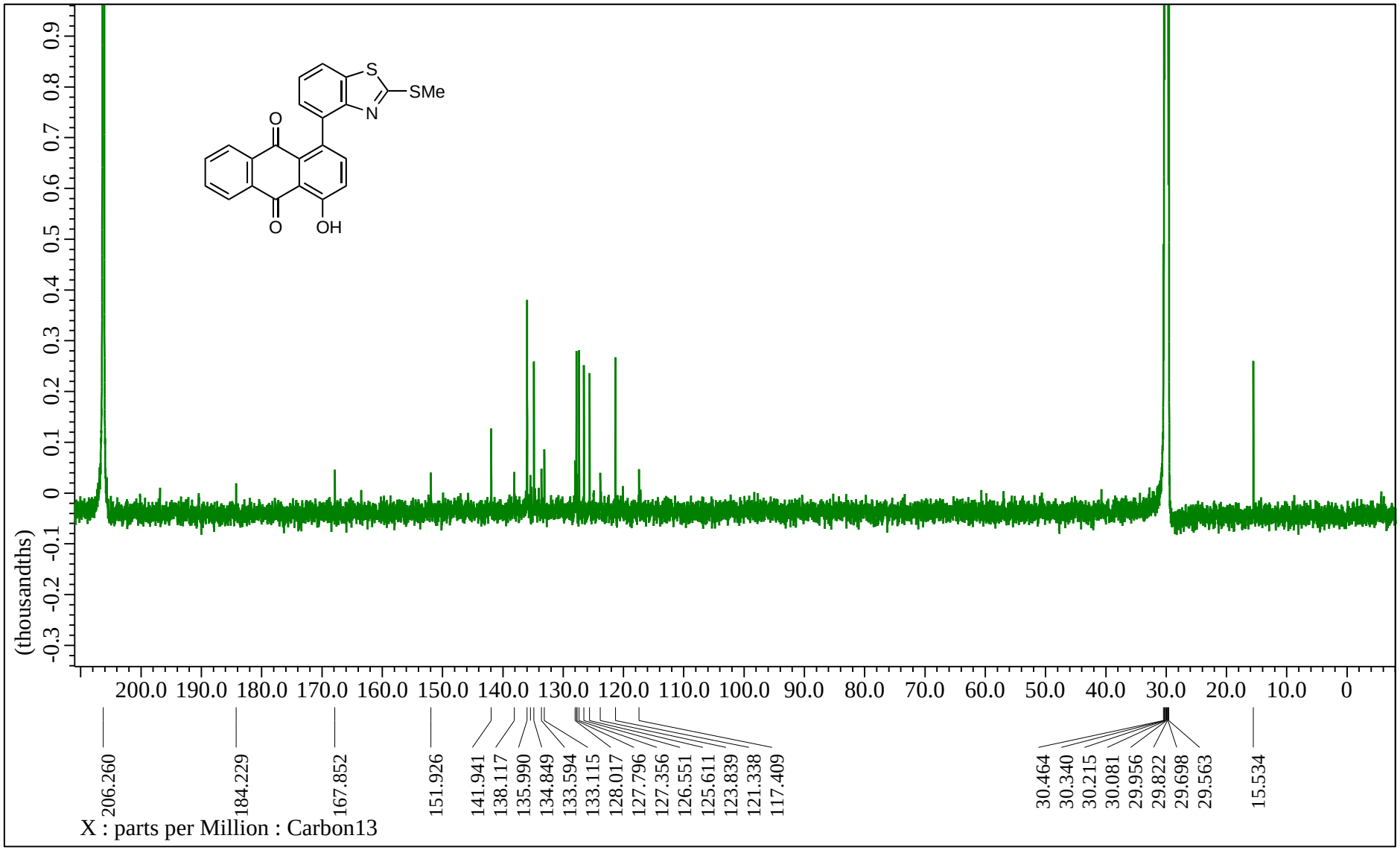

Fig. S35. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3ai**.

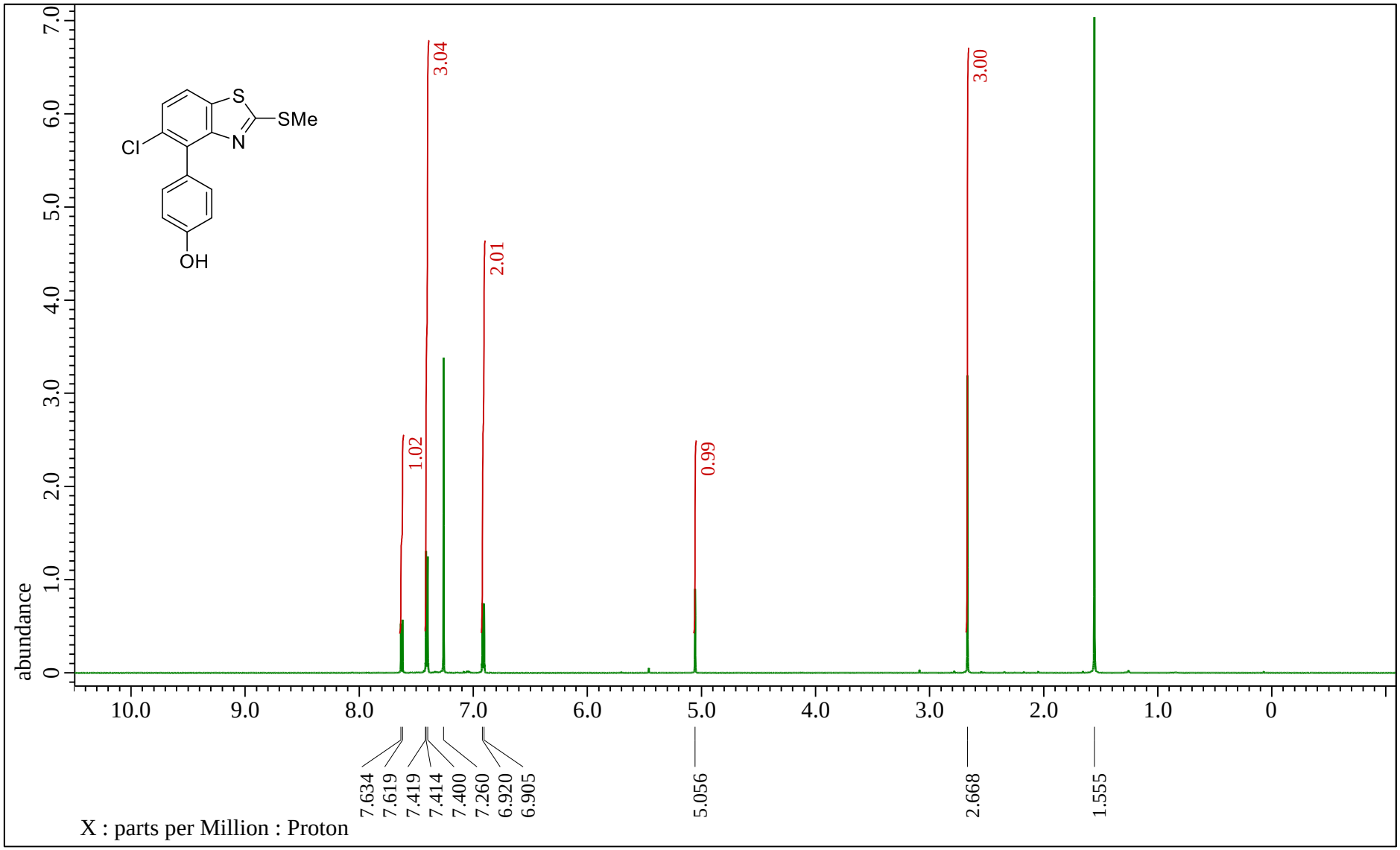

Fig. S36. ^{1}H NMR ($CDCl_3$) spectrum of **3ba**.

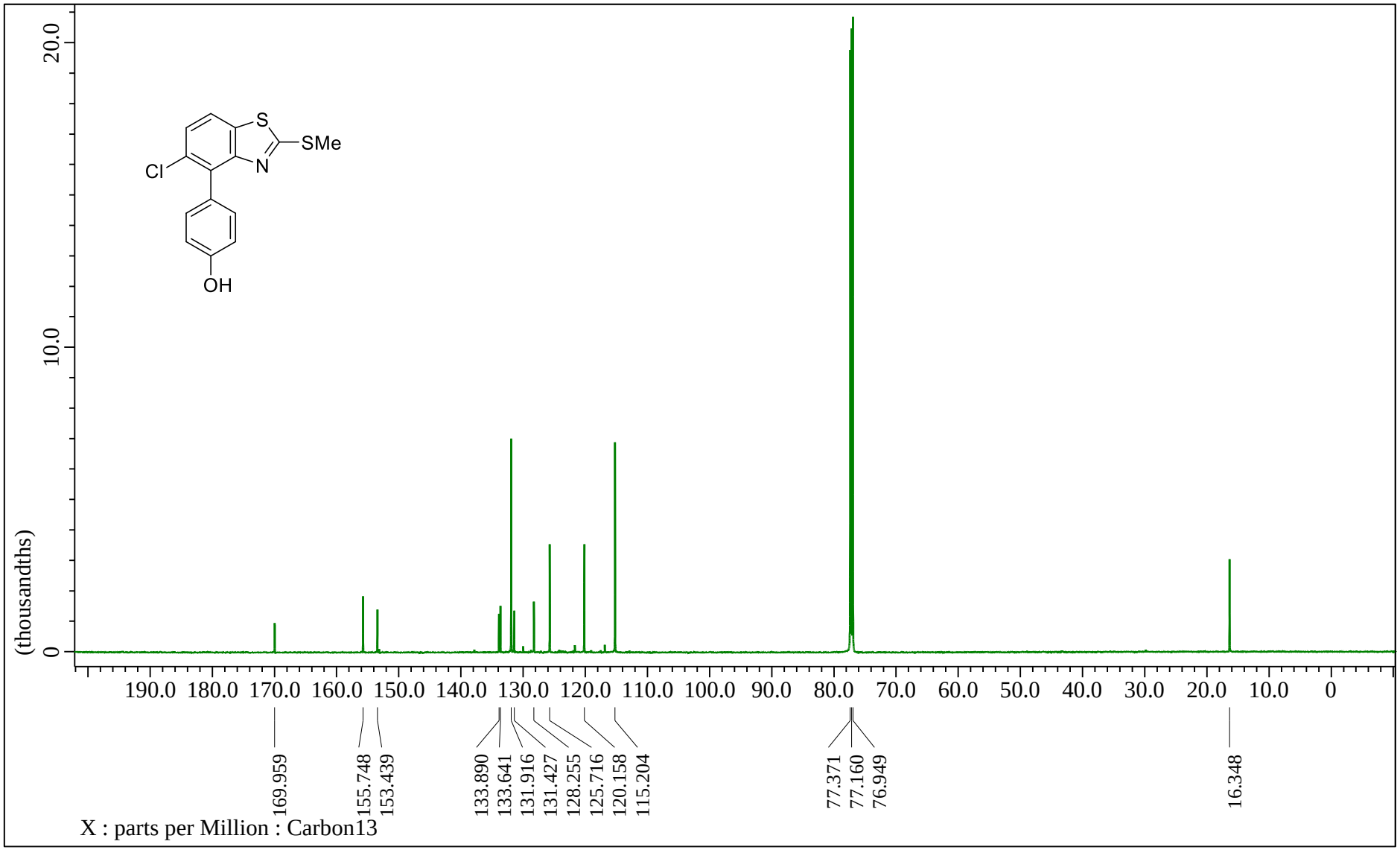

Fig. S37. ^{13}C NMR ($CDCl_3$) spectrum of **3ba**.

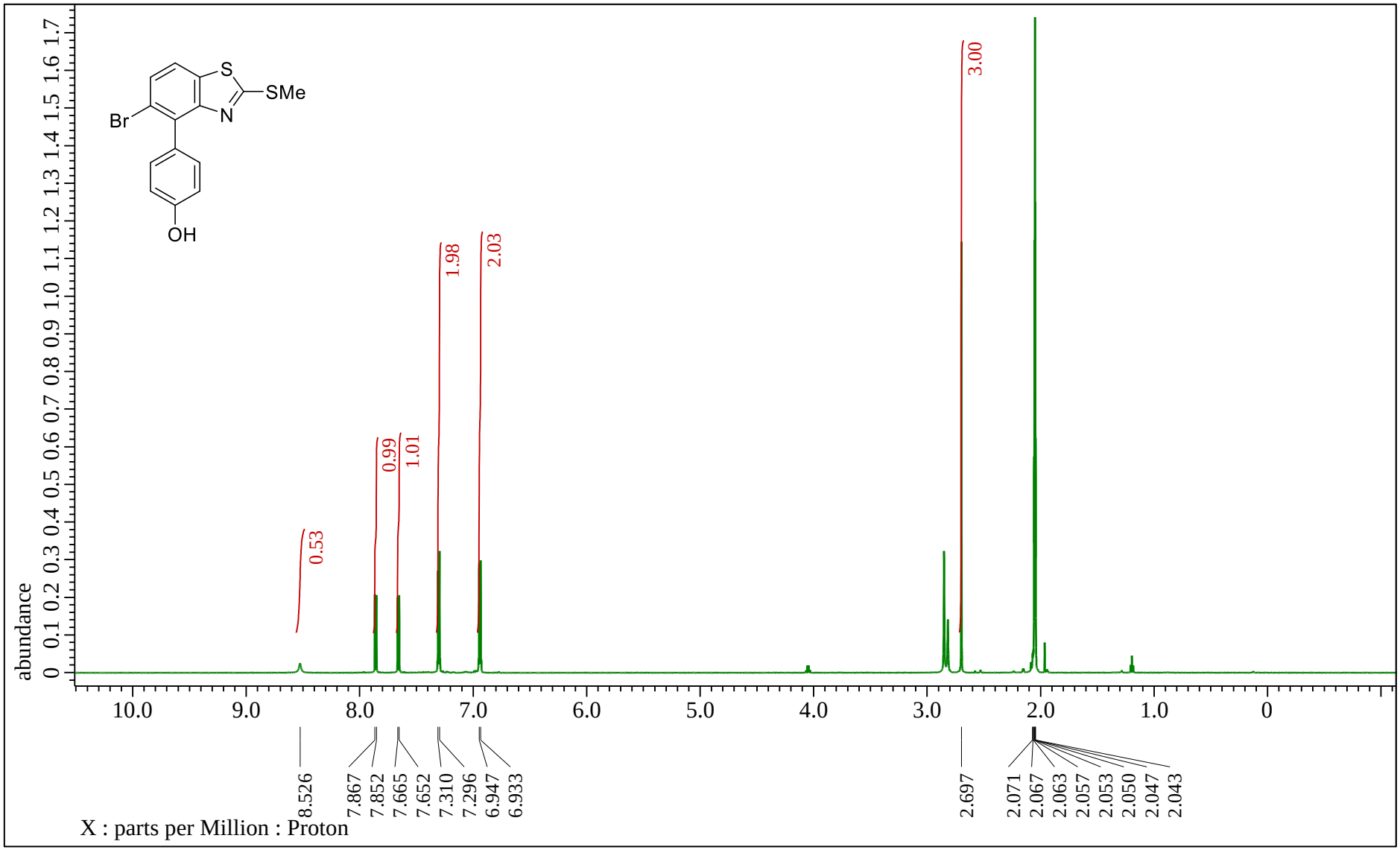

Fig. S38. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3ca**.

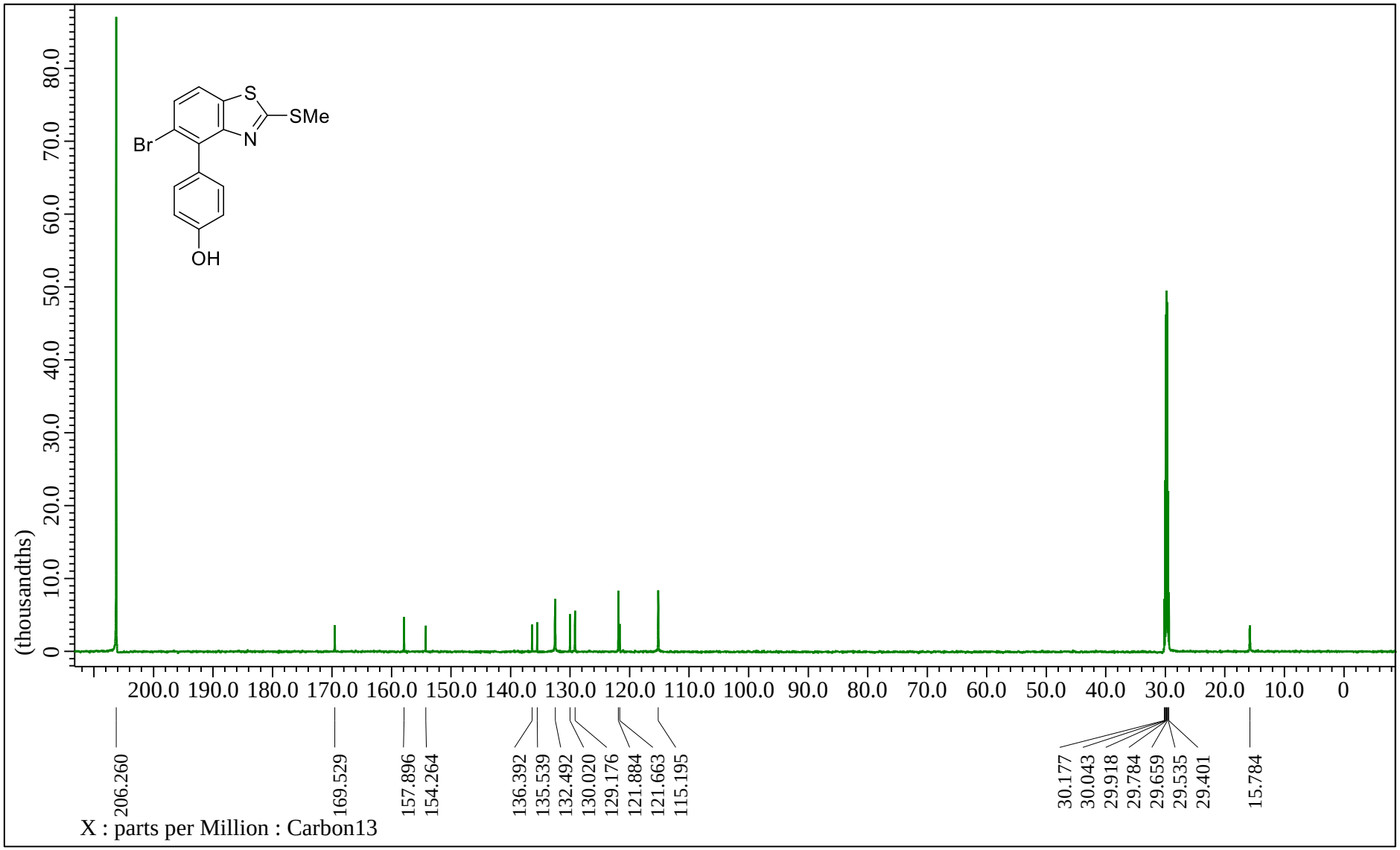

Fig. S39. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3ca**.

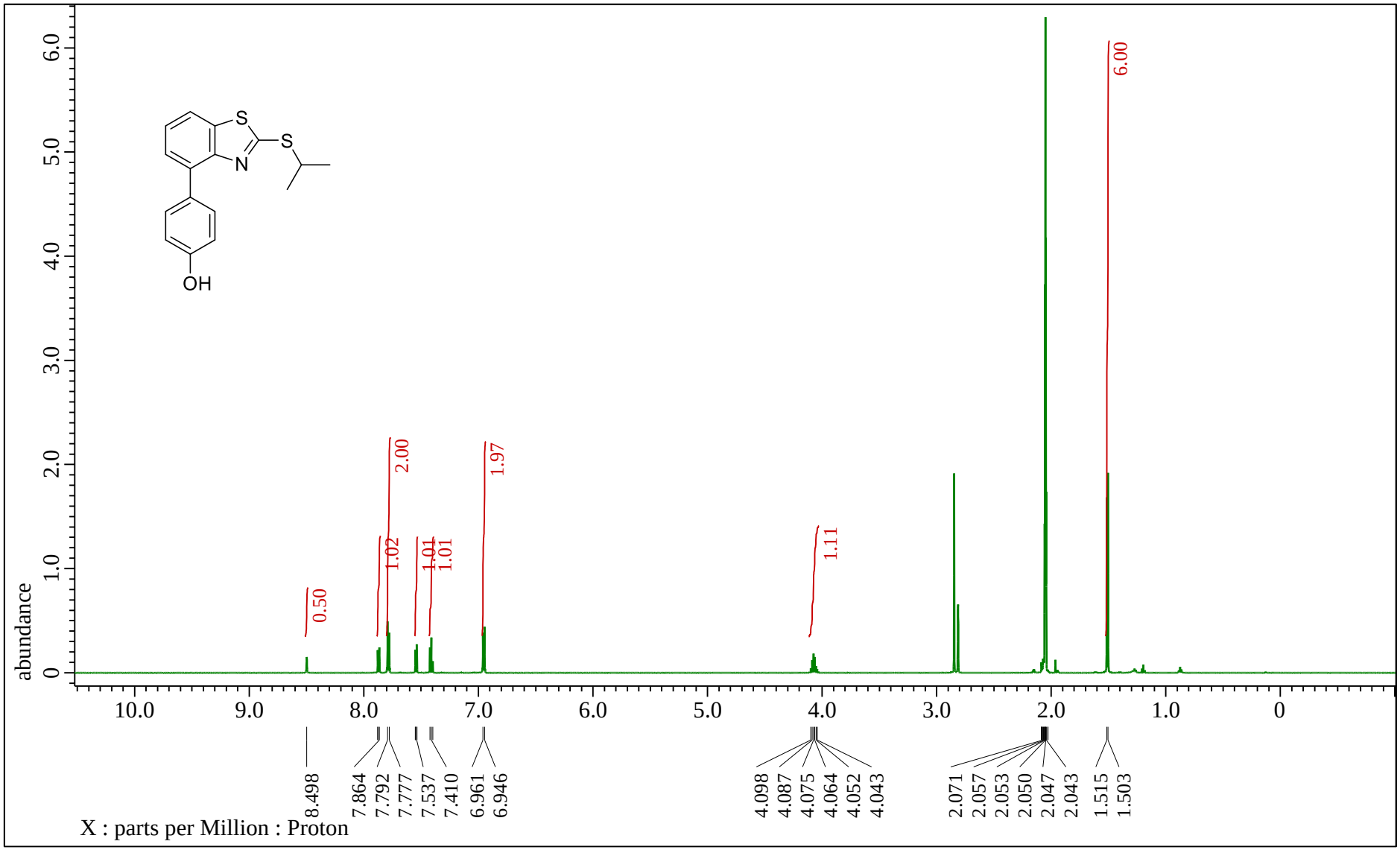

Fig. S40. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3da**.

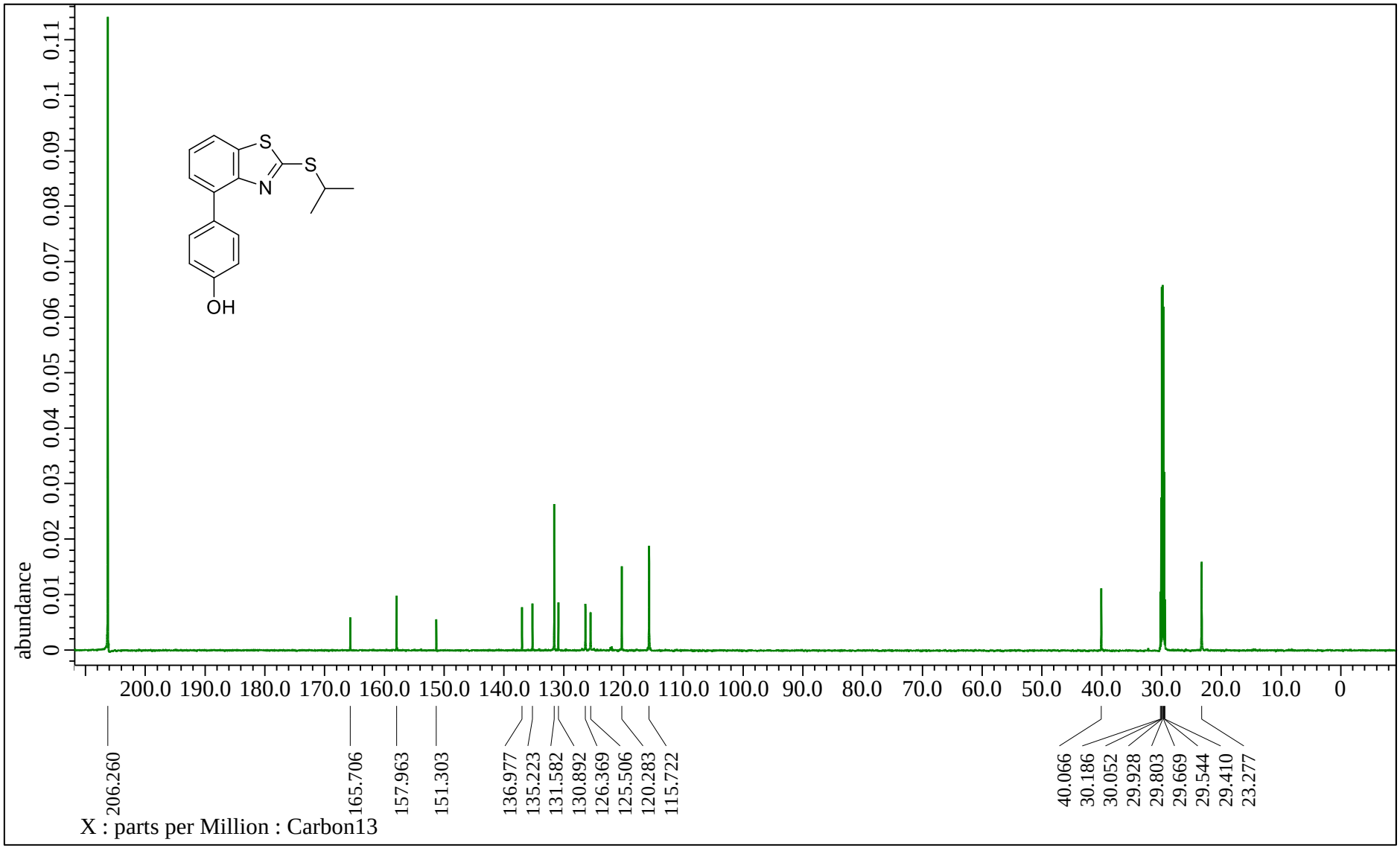

Fig. S41. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3da**.

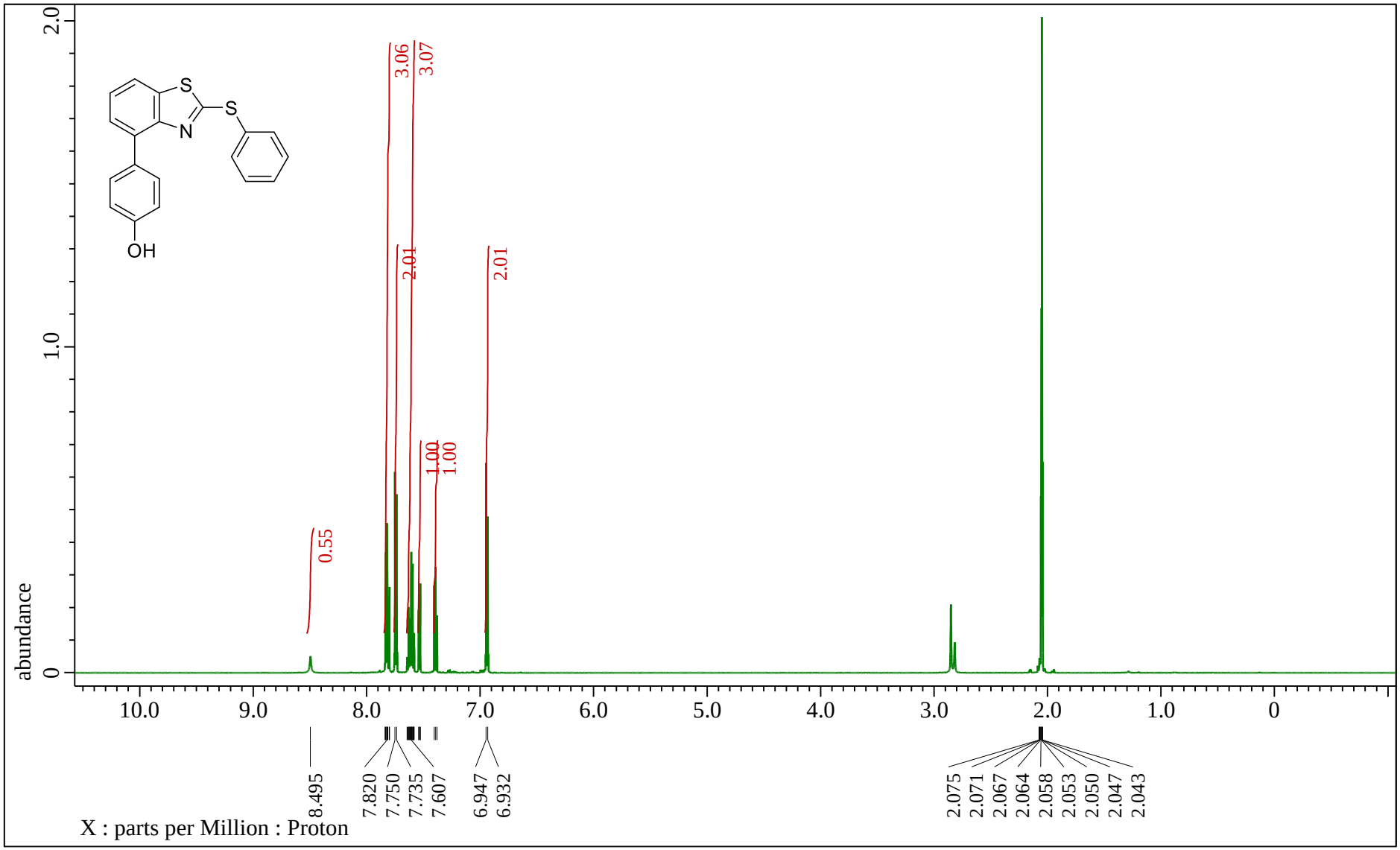

Fig. S42. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **3ea**.

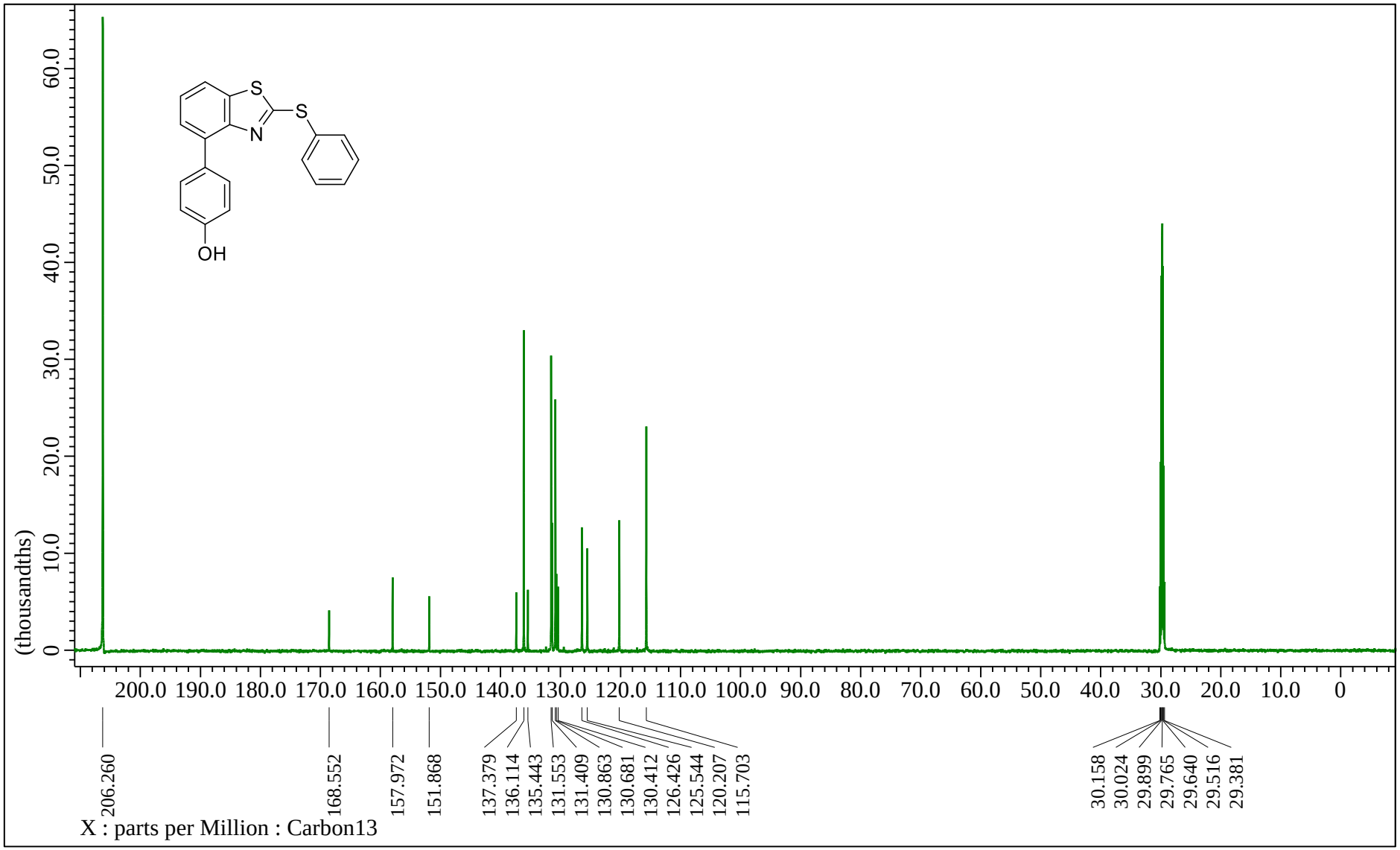

Fig. S43. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **3ea**.

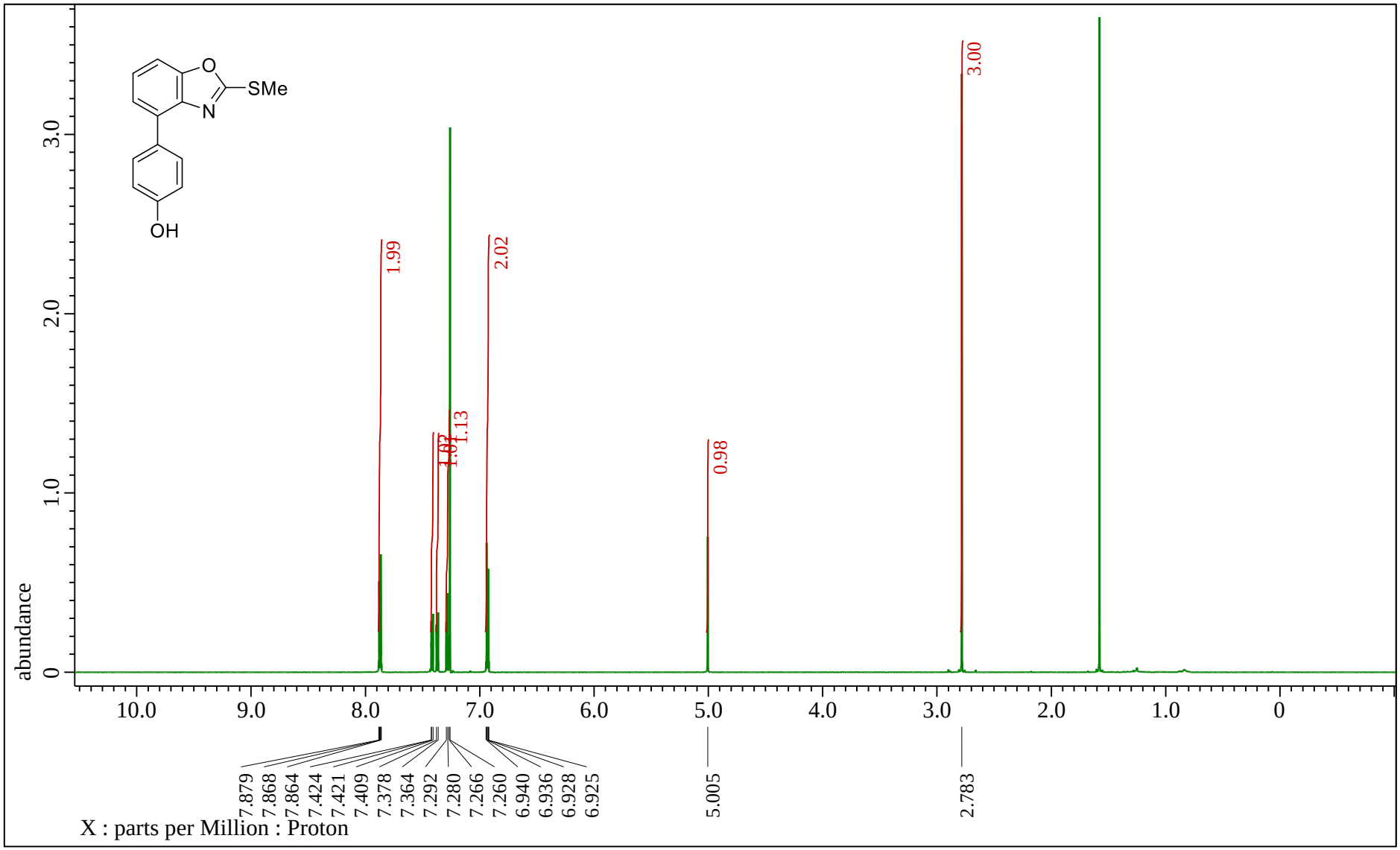

Fig. S44. ^{1}H NMR ($CDCl_3$) spectrum of **6**.

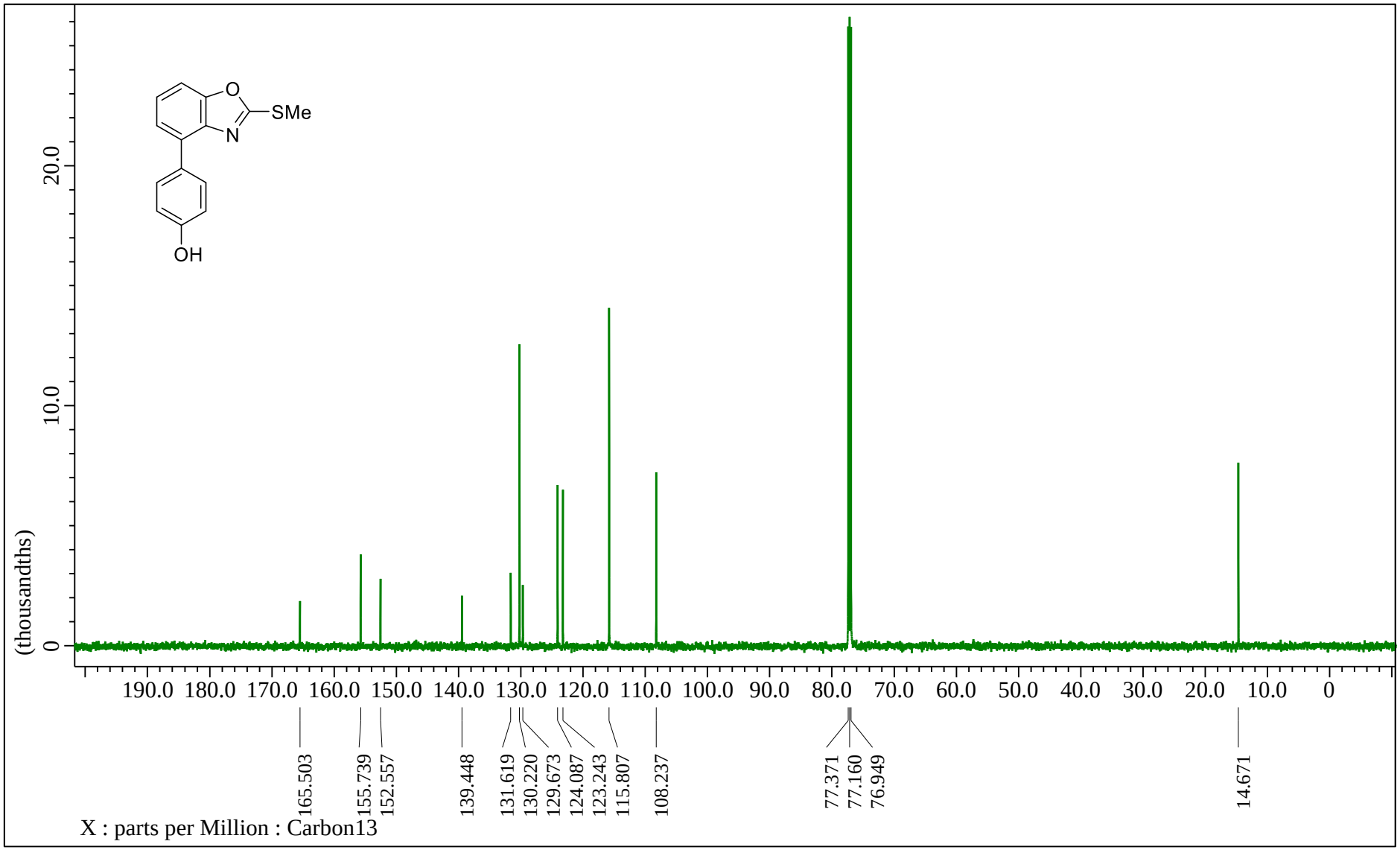

Fig. S45. ^{13}C NMR ($CDCl_3$) spectrum of **6**.

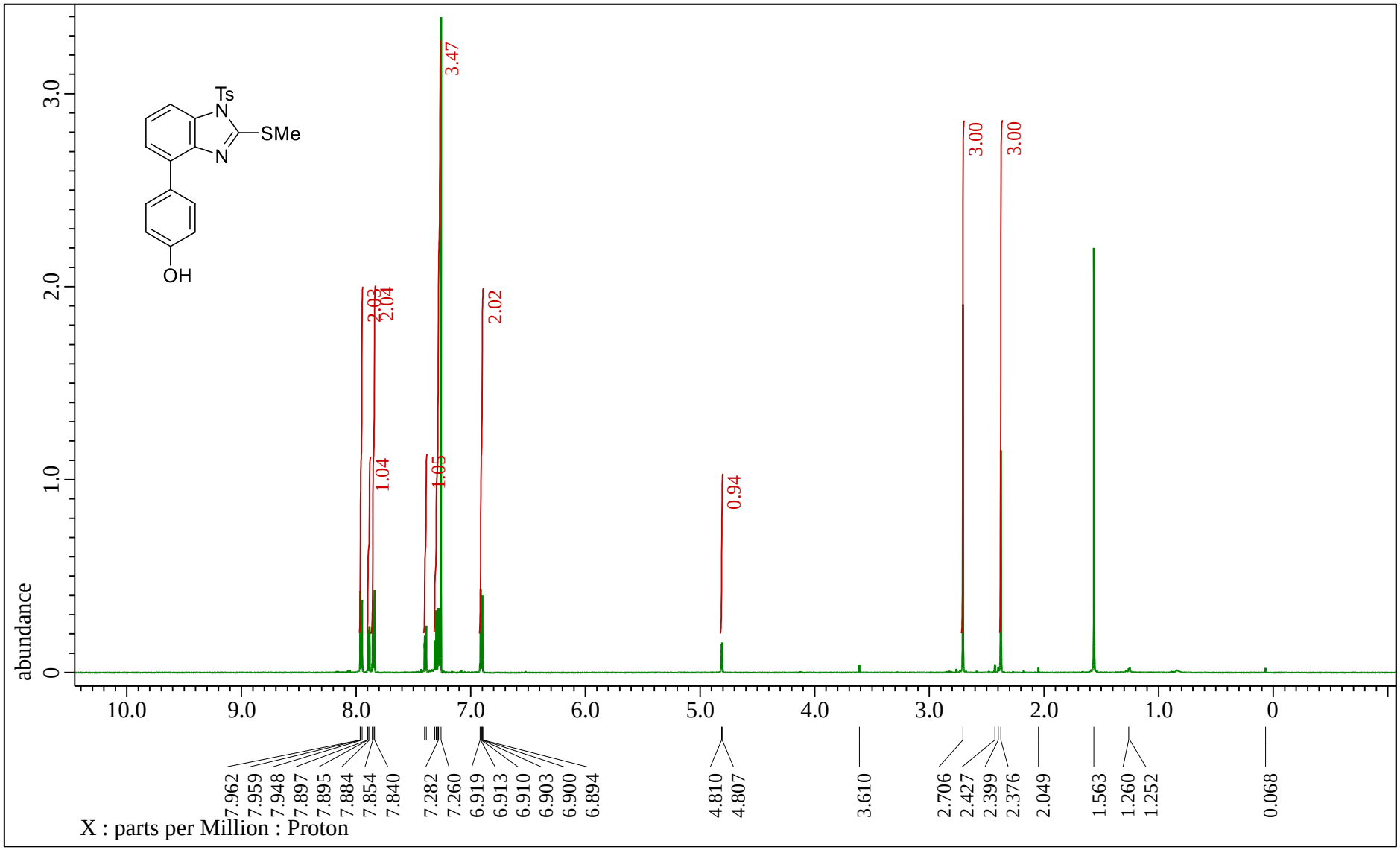

Fig. S46. ^{1}H NMR ($CDCl_3$) spectrum of **7**.

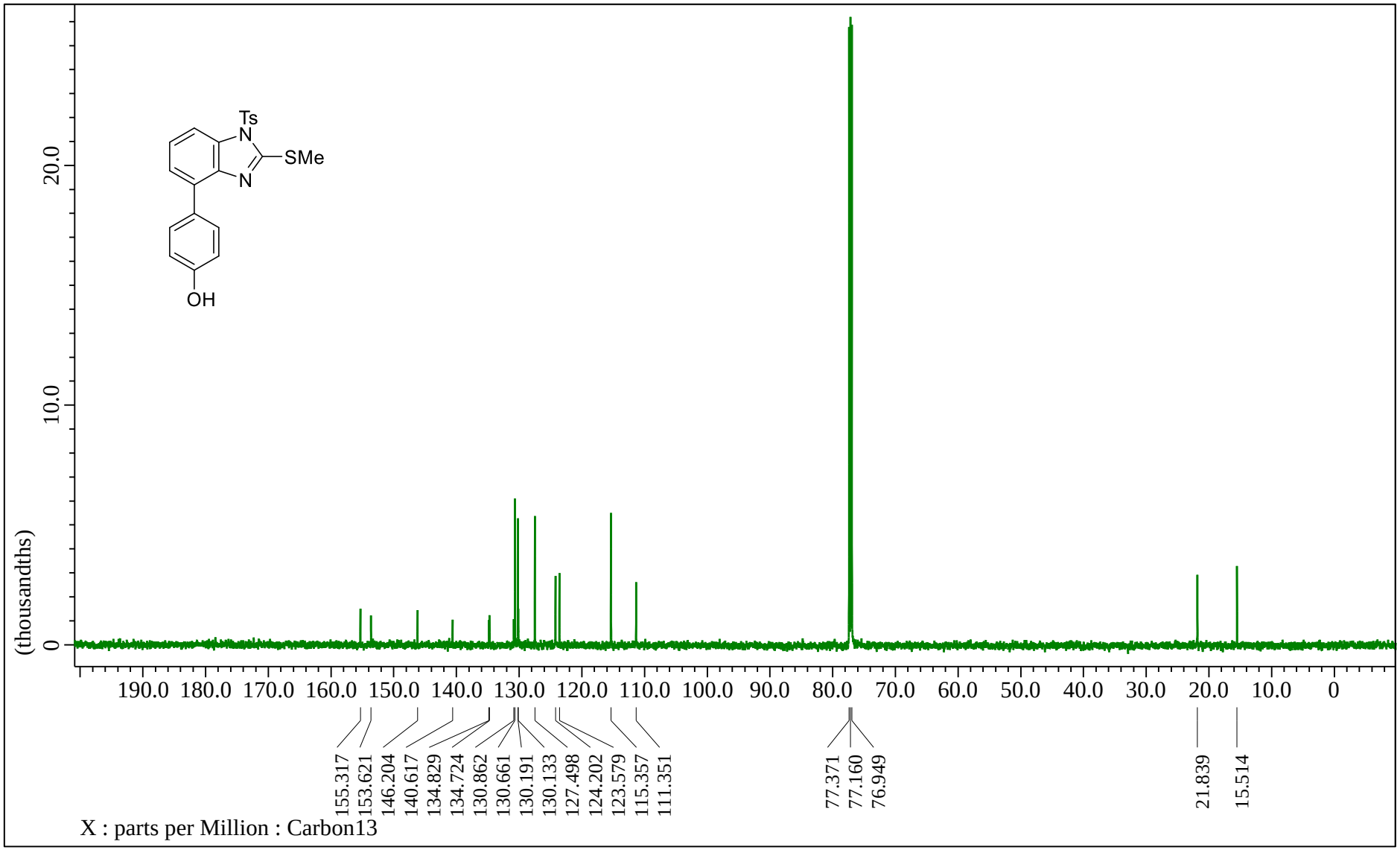

Fig. S47. ^{13}C NMR ($CDCl_3$) spectrum of **7**.

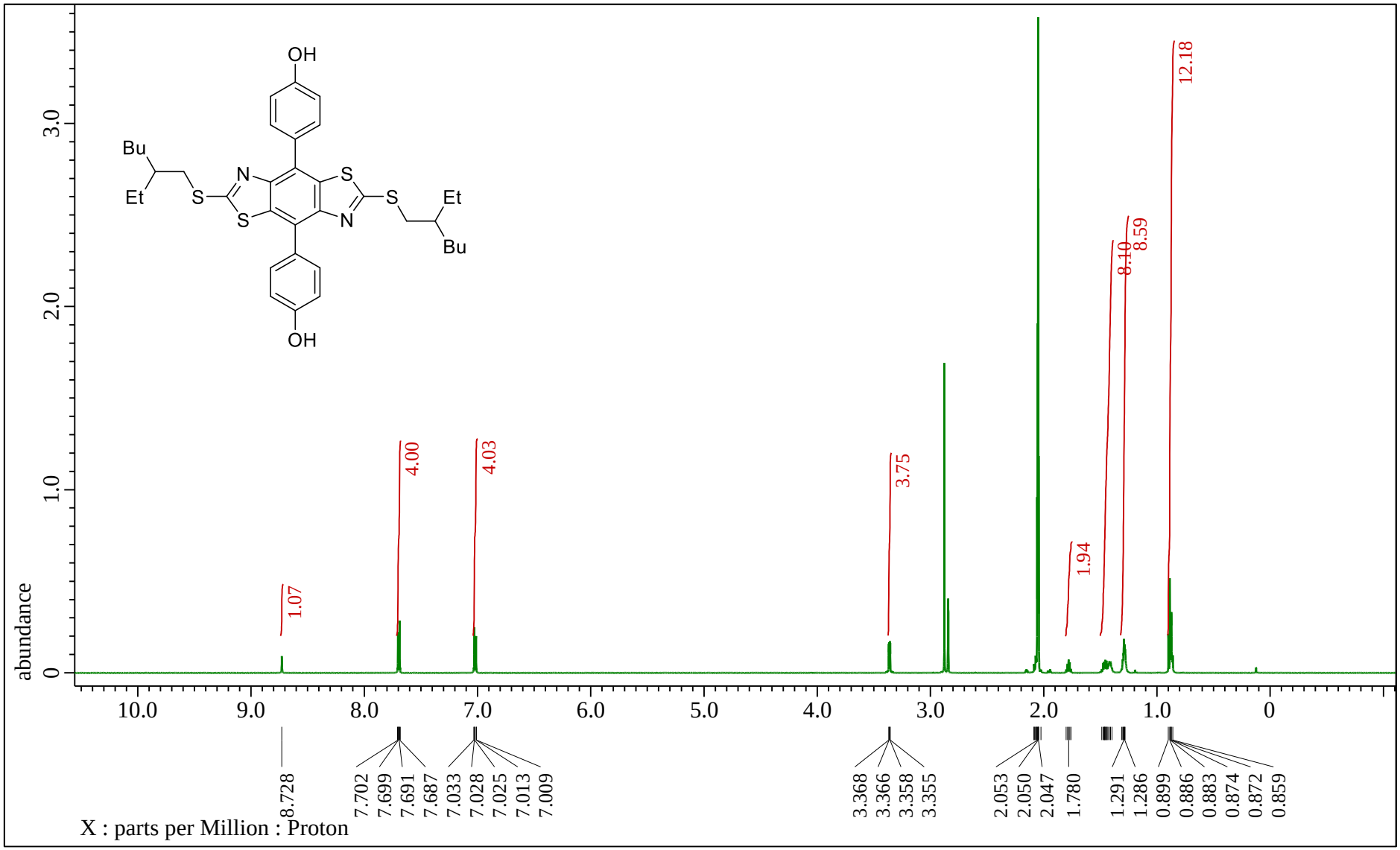

Fig. S48. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **9**.

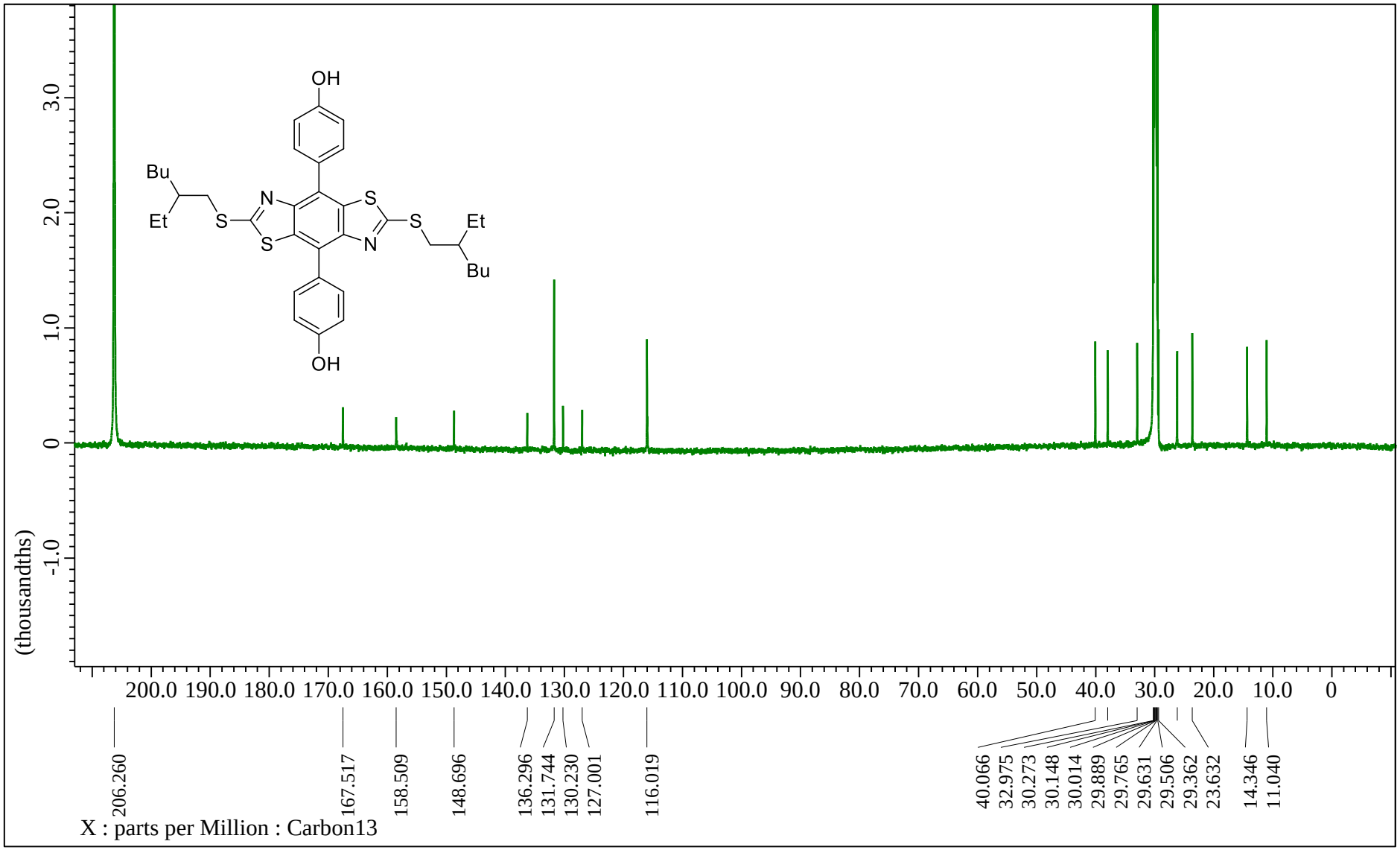

Fig. S49. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **9**.

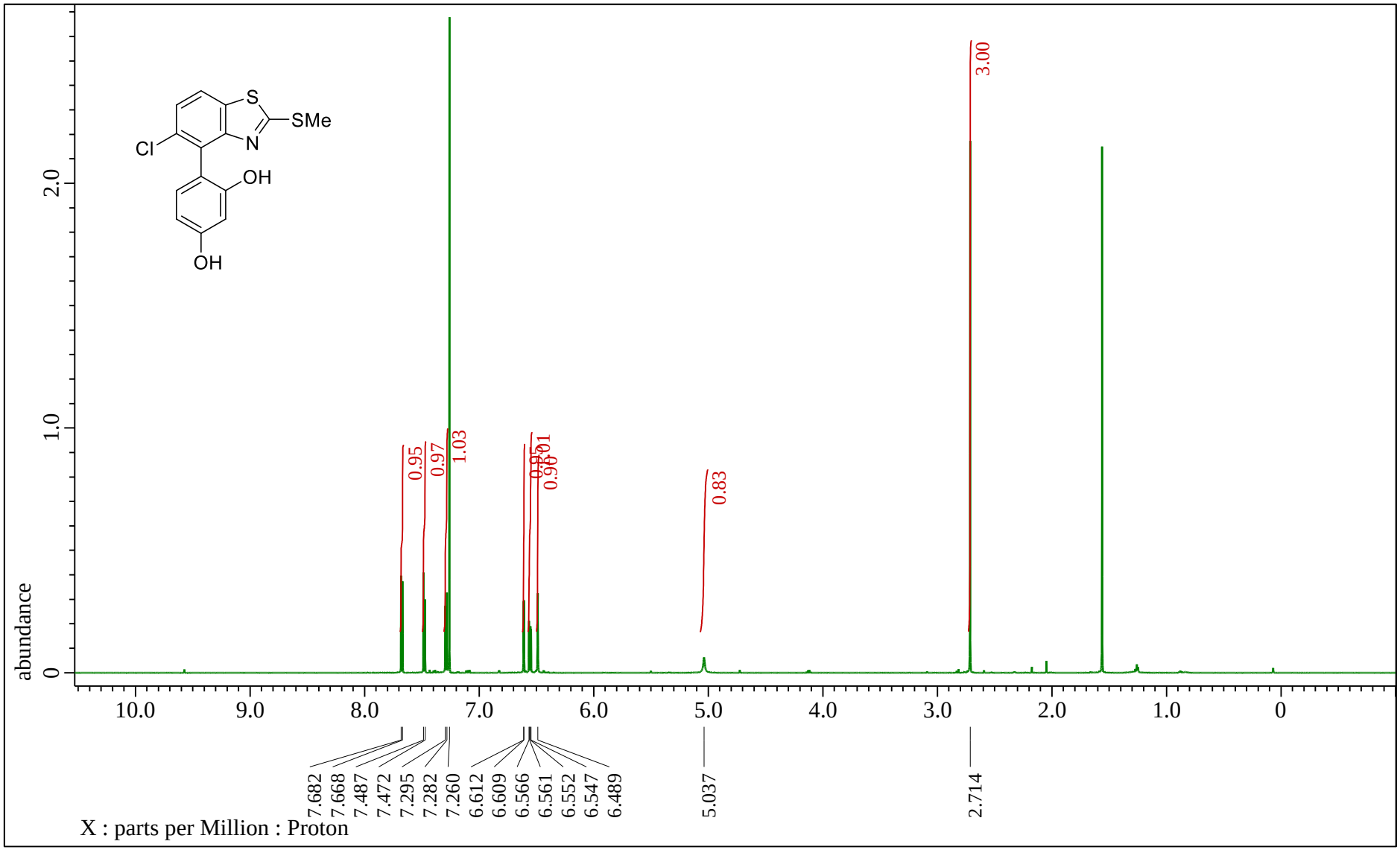

Fig. S50. ^{1}H NMR ($CDCl_3$) spectrum of **3bj**.

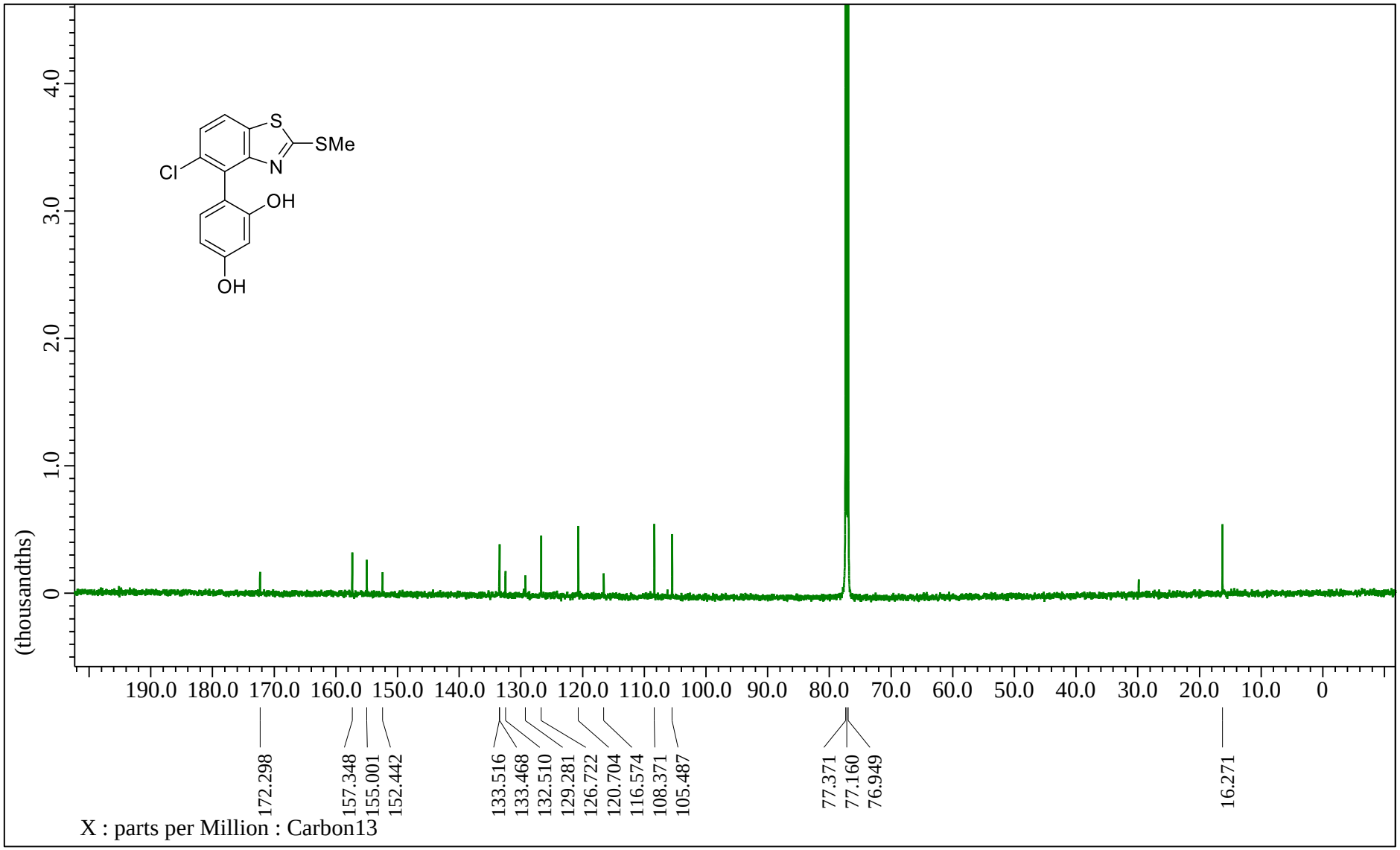

Fig. S51. ^{13}C NMR ($CDCl_3$) spectrum of **3bj.**

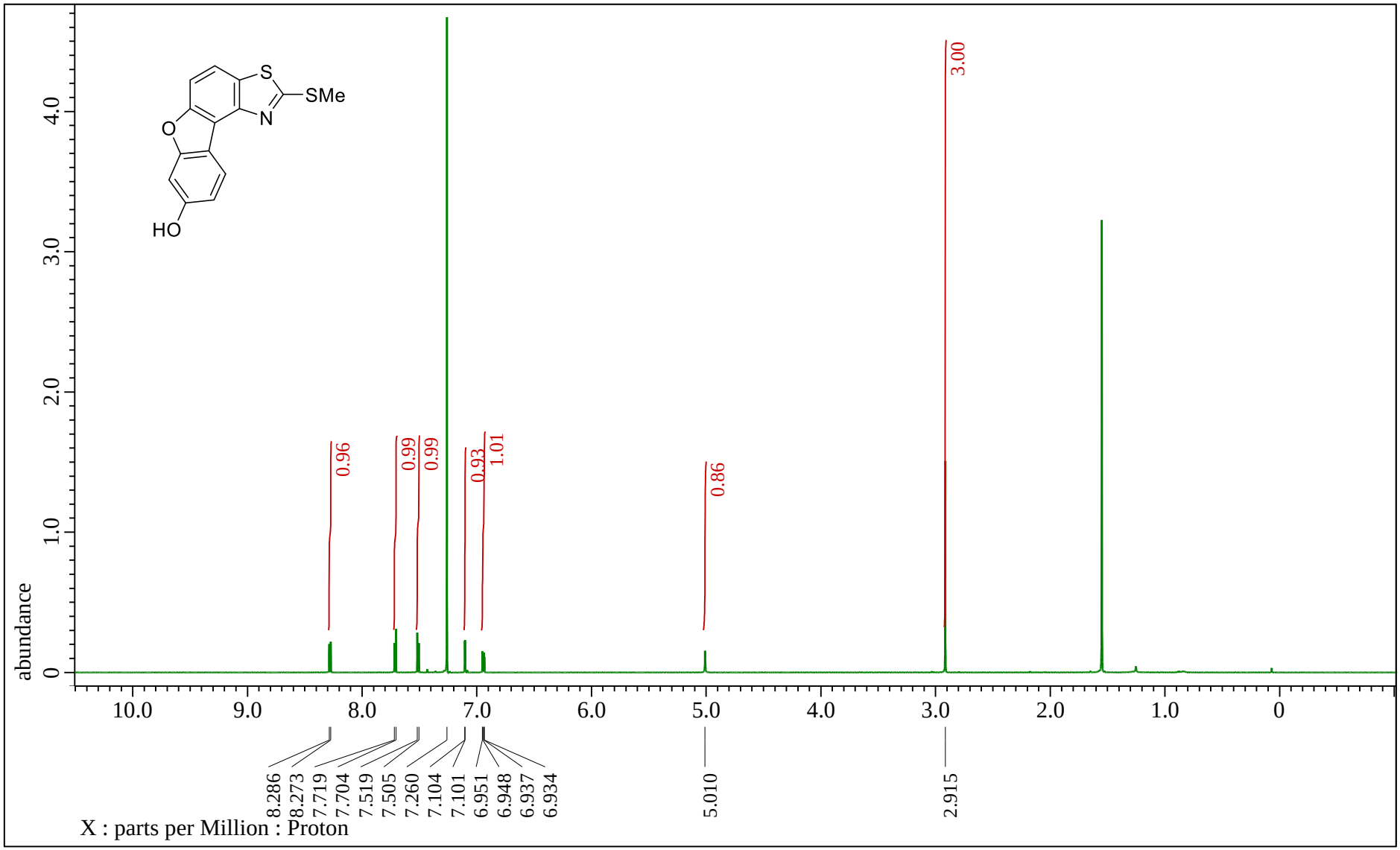

Fig. S52. ^{1}H NMR ($CDCl_3$) spectrum of **10**.

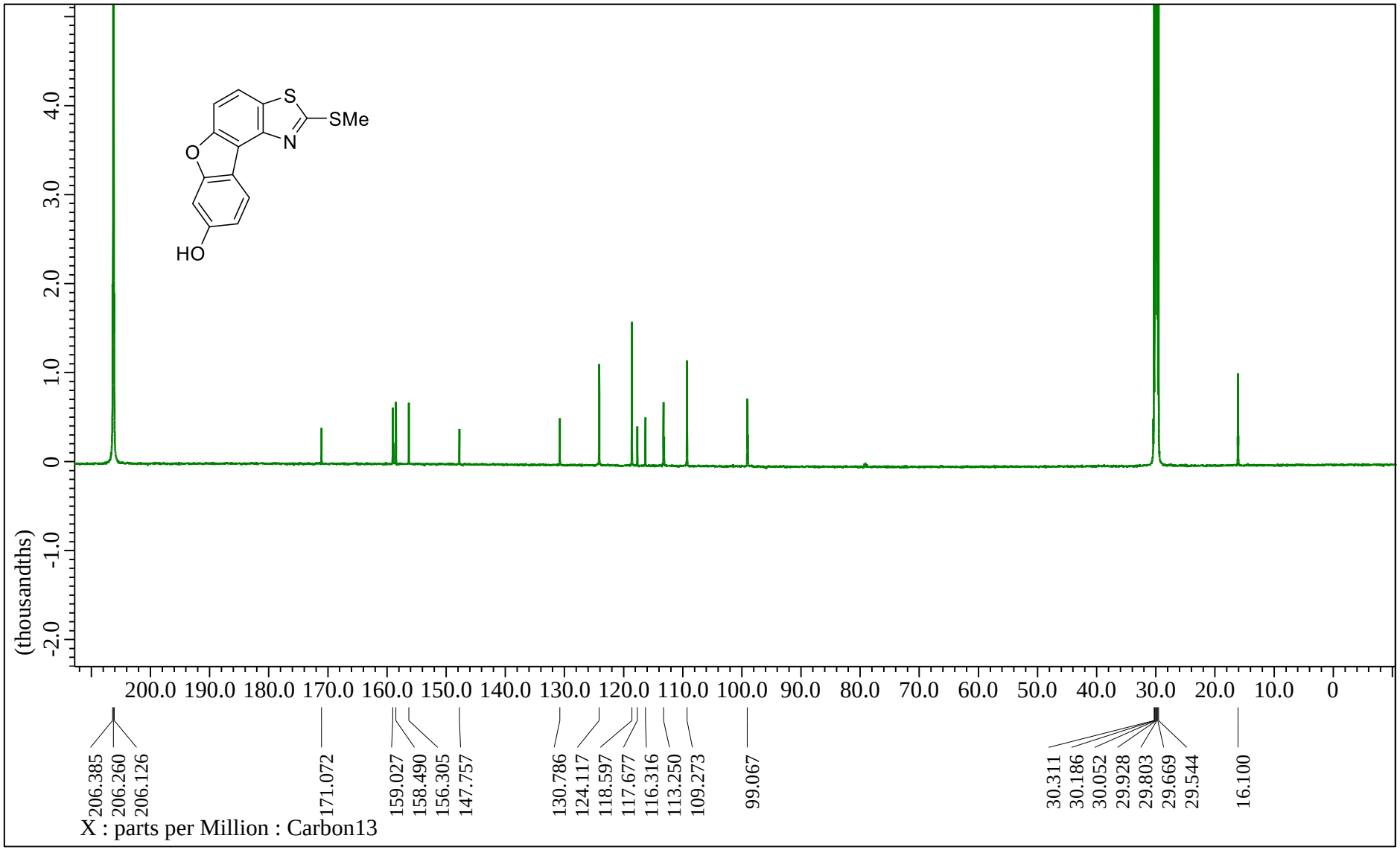

Fig. S53. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **10**.

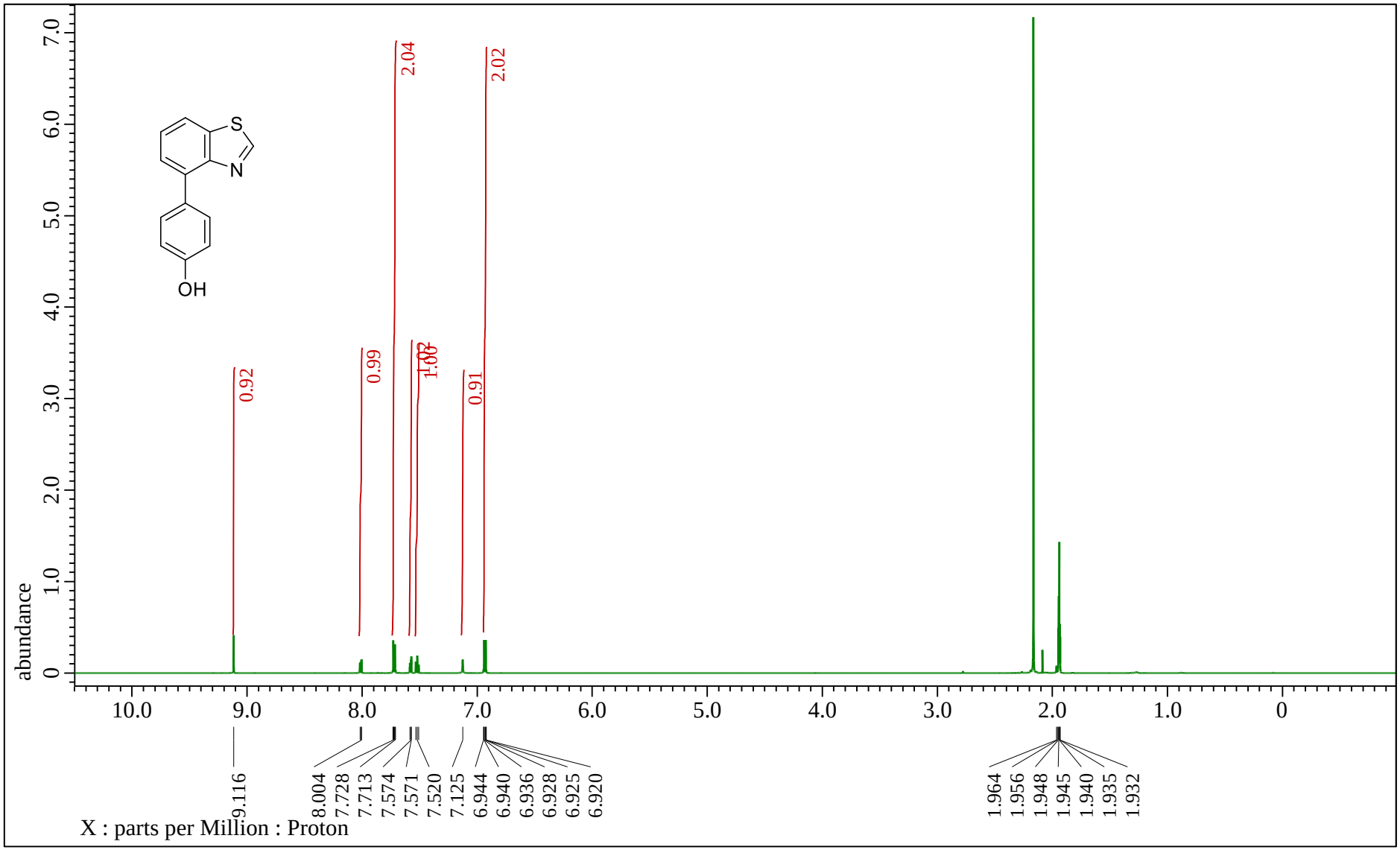

Fig. S54. ^{1}H NMR (CD_3CN) spectrum of **11**.

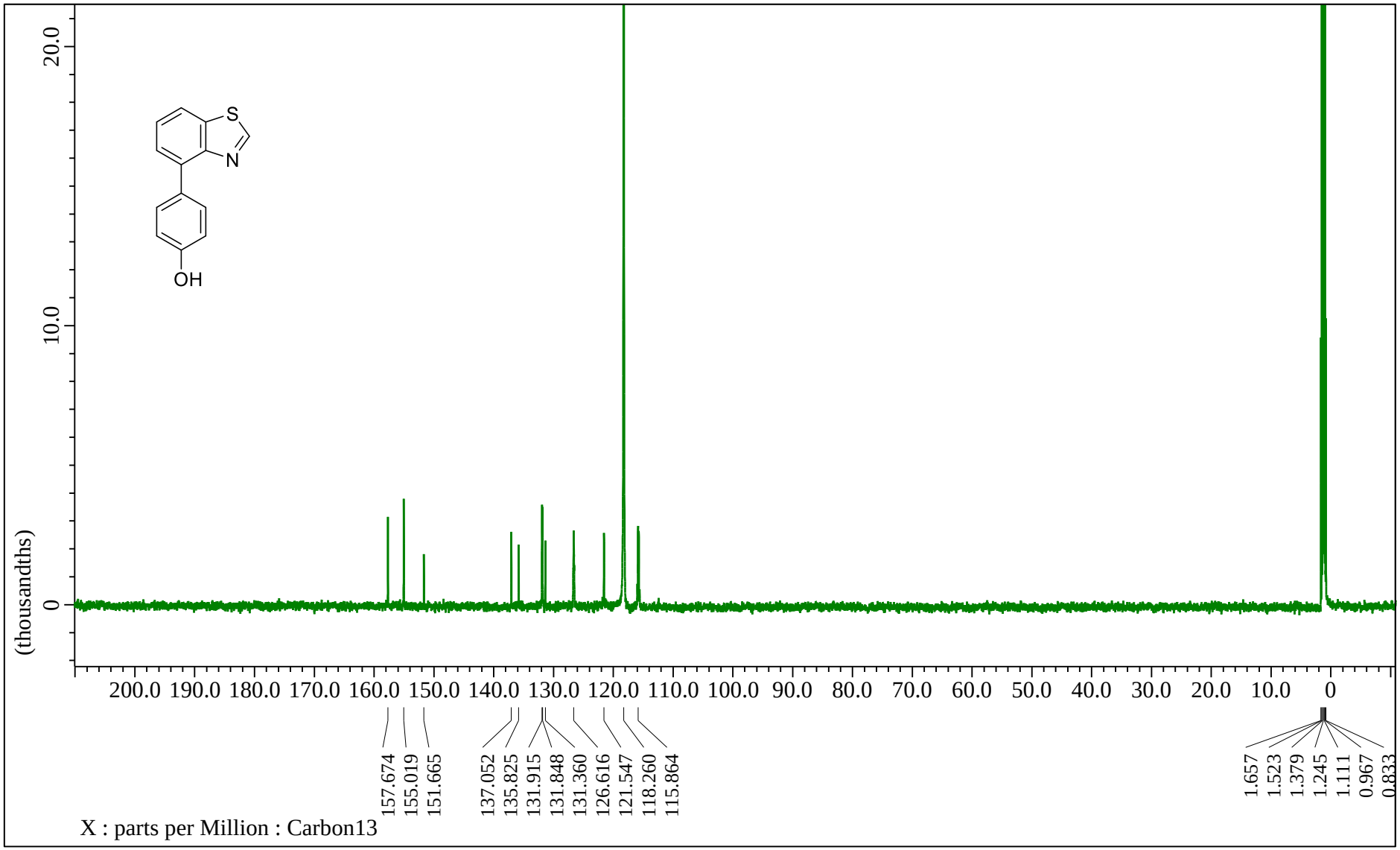

Fig. S55. ^{13}C NMR (CD_3CN) spectrum of **11**.

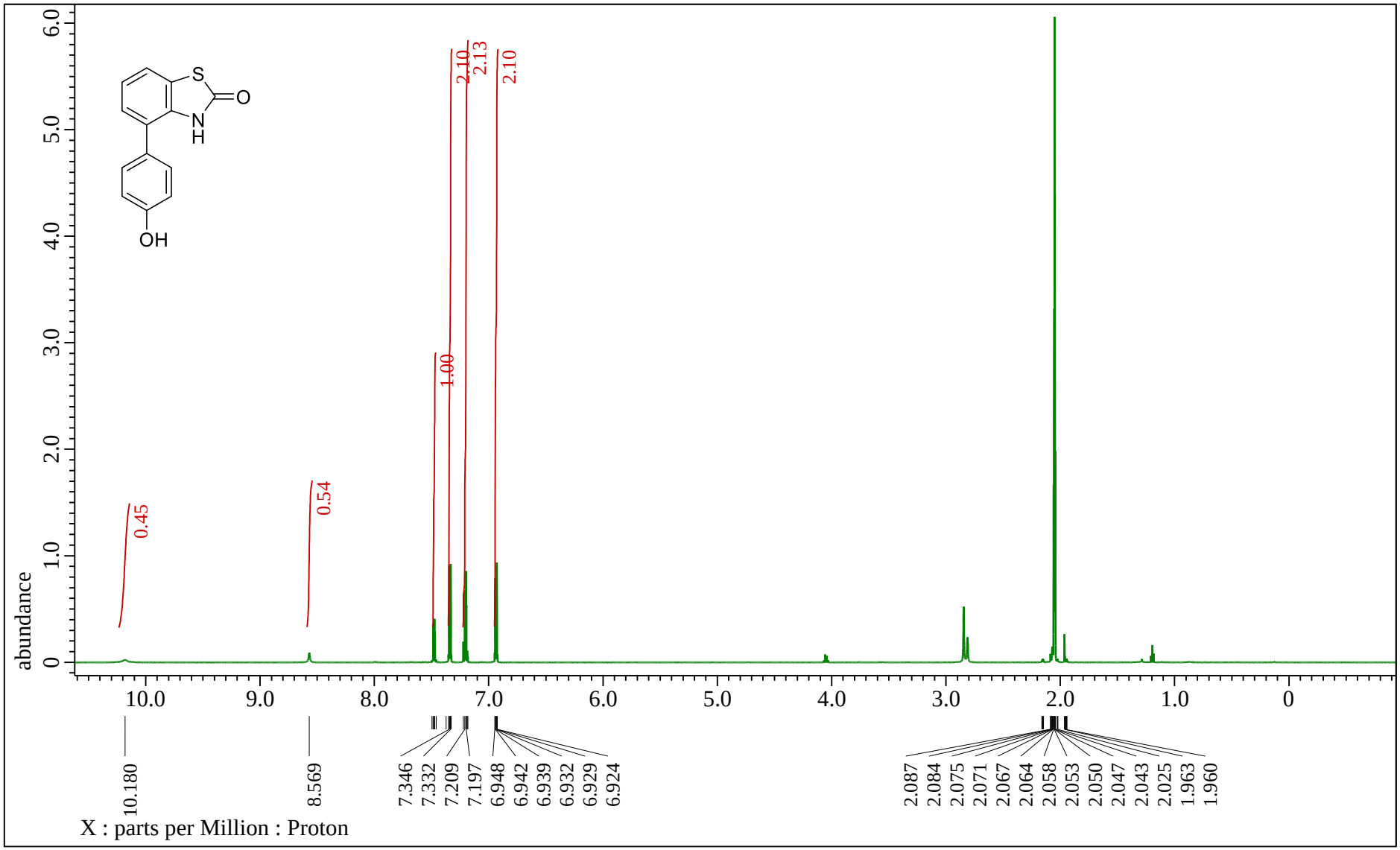

Fig. S56. ^{1}H NMR ($(CD_3)_2CO$) spectrum of **12**.

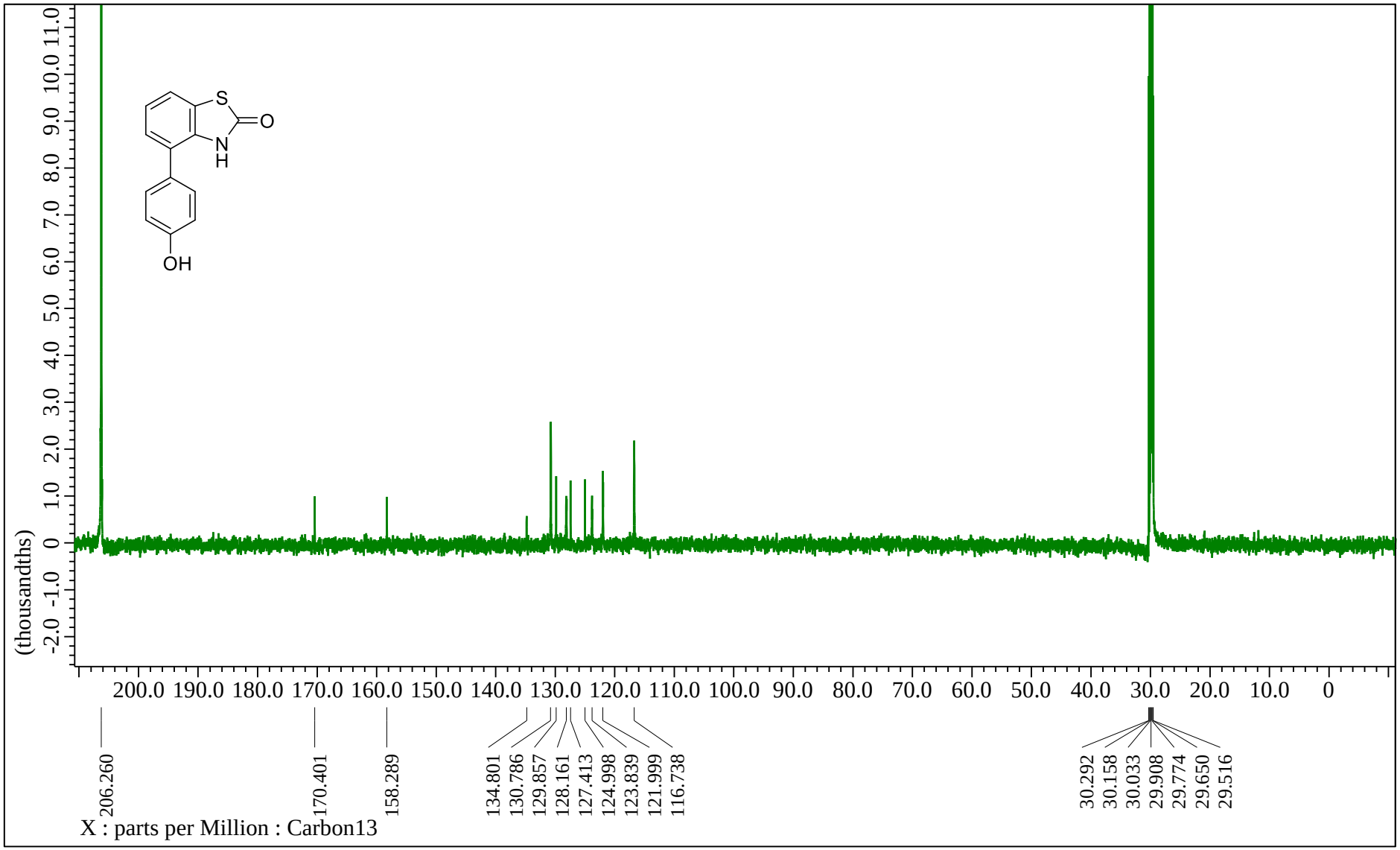

Fig. S57. ^{13}C NMR ($(CD_3)_2CO$) spectrum of **12**.

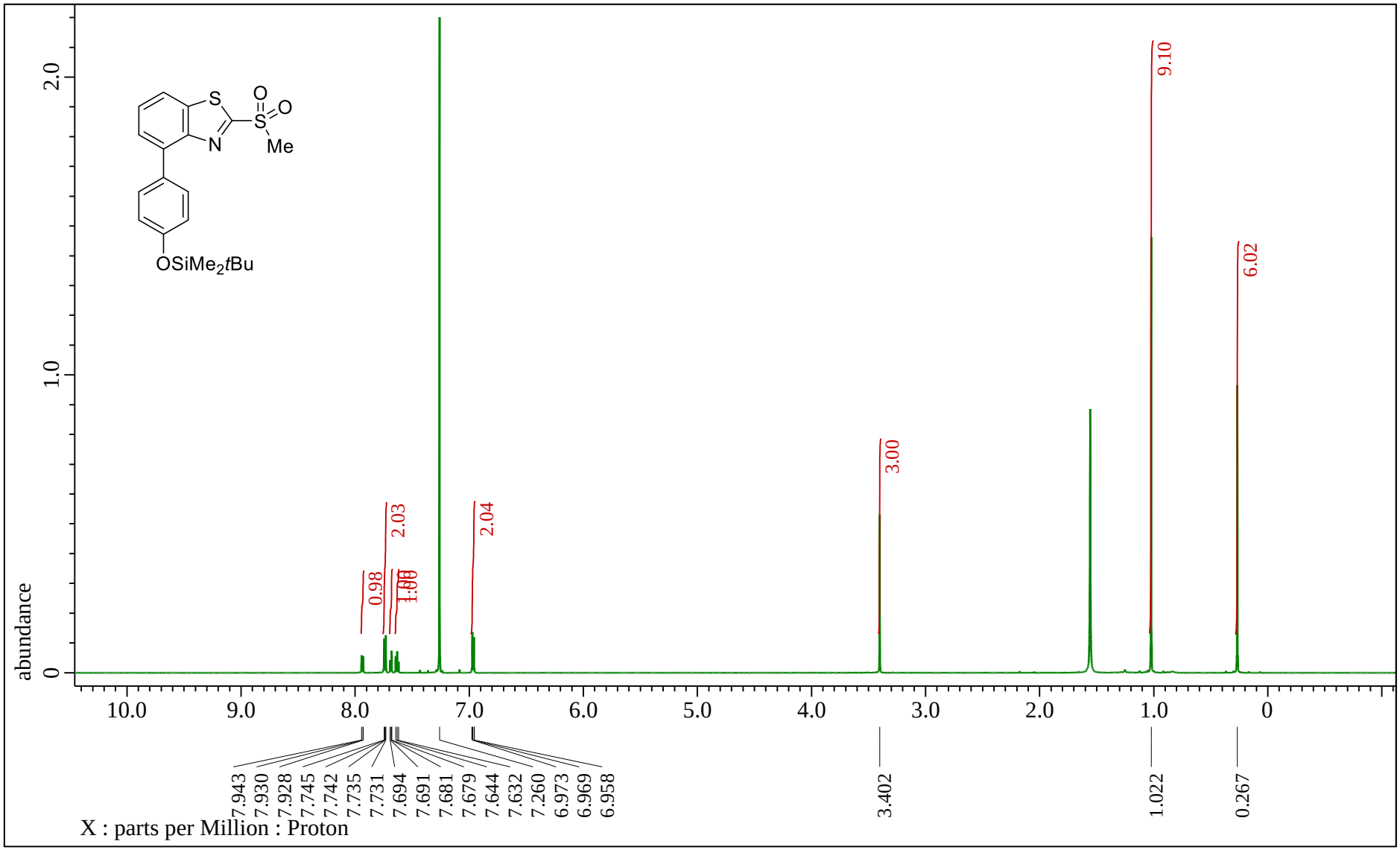

Fig. S58. ^{1}H NMR ($CDCl_3$) spectrum of **13**.

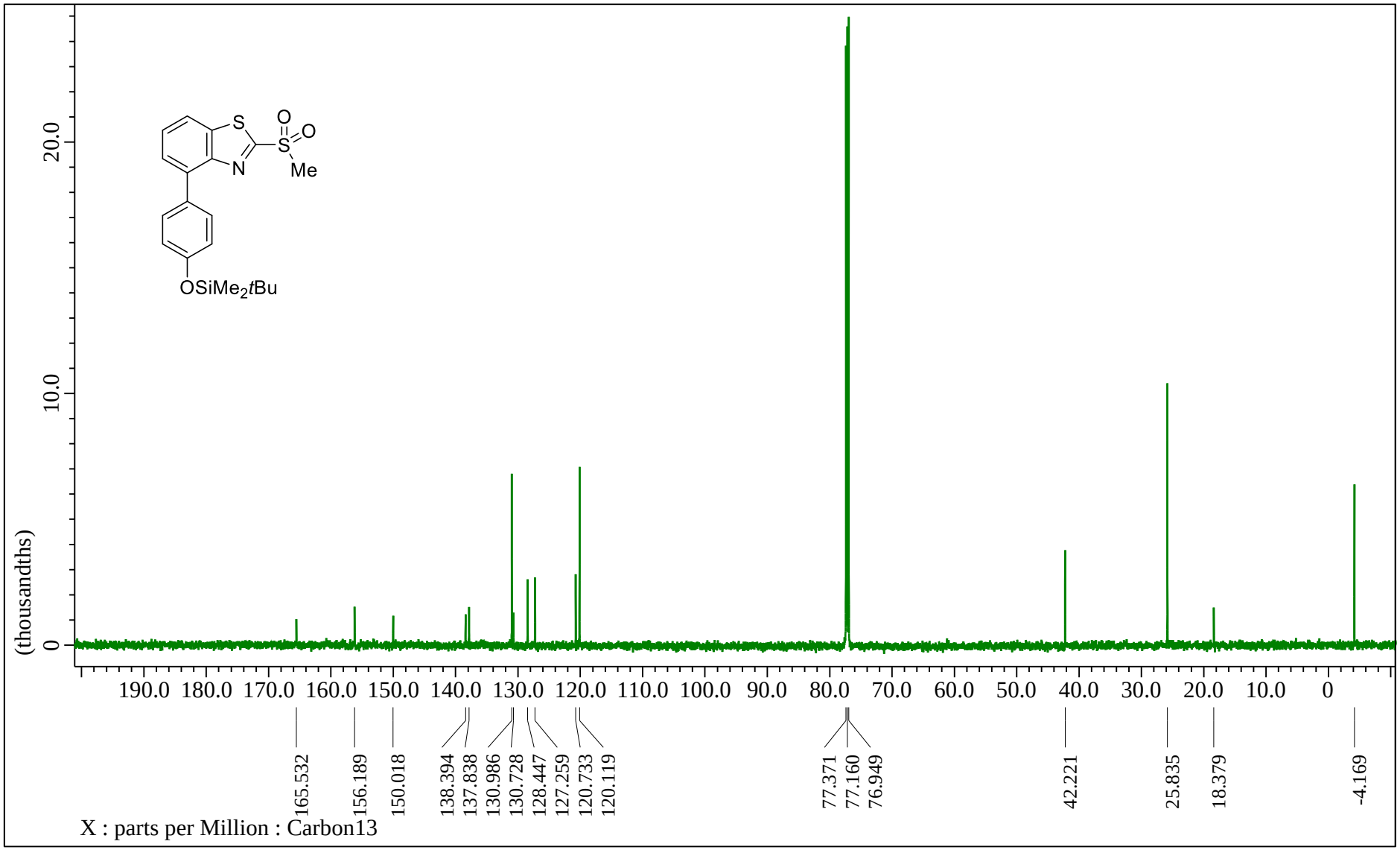

Fig. S59. ^{13}C NMR ($CDCl_3$) spectrum of **13**.

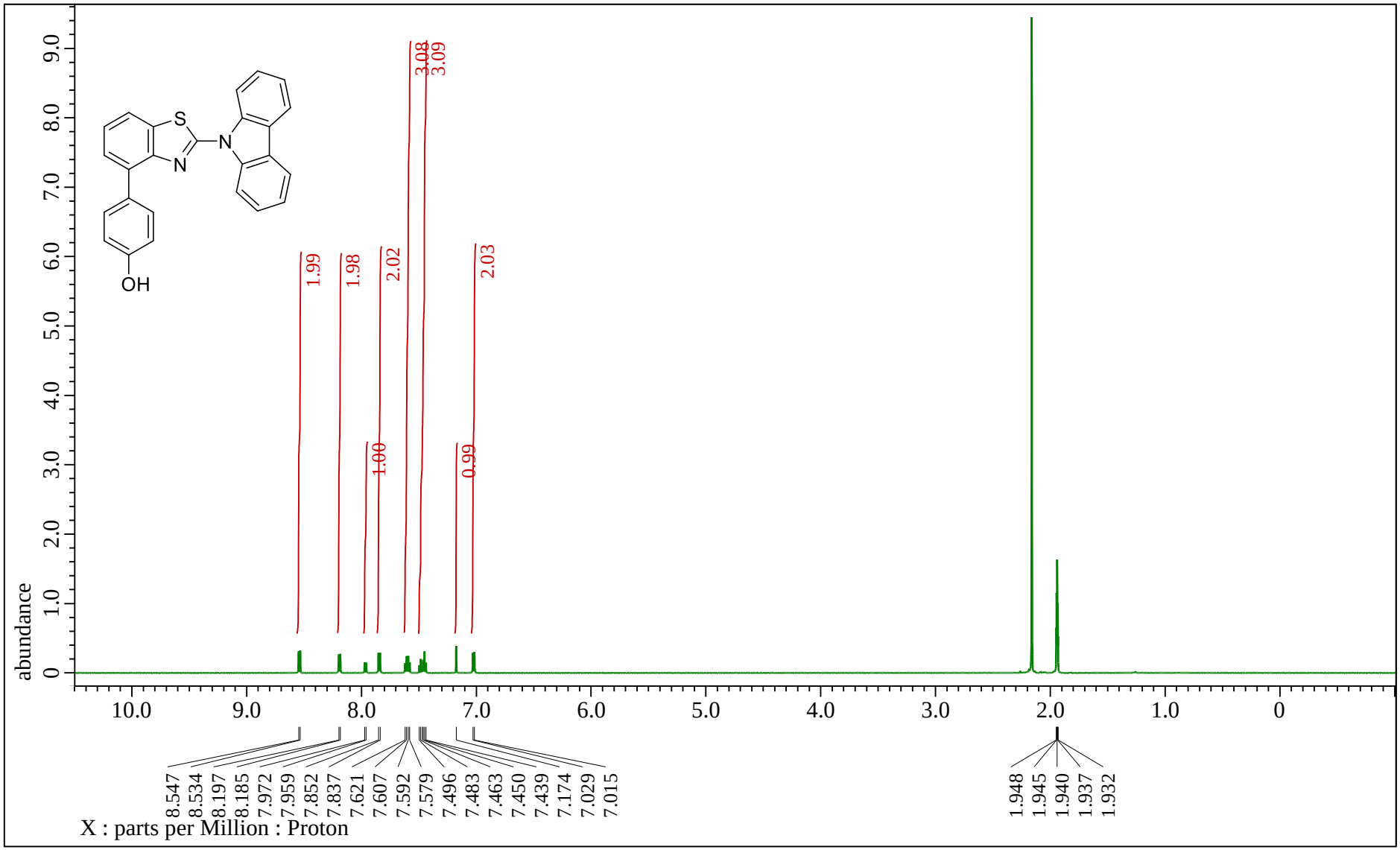

Fig. S60. ^{1}H NMR (CD_3CN) spectrum of **14**.

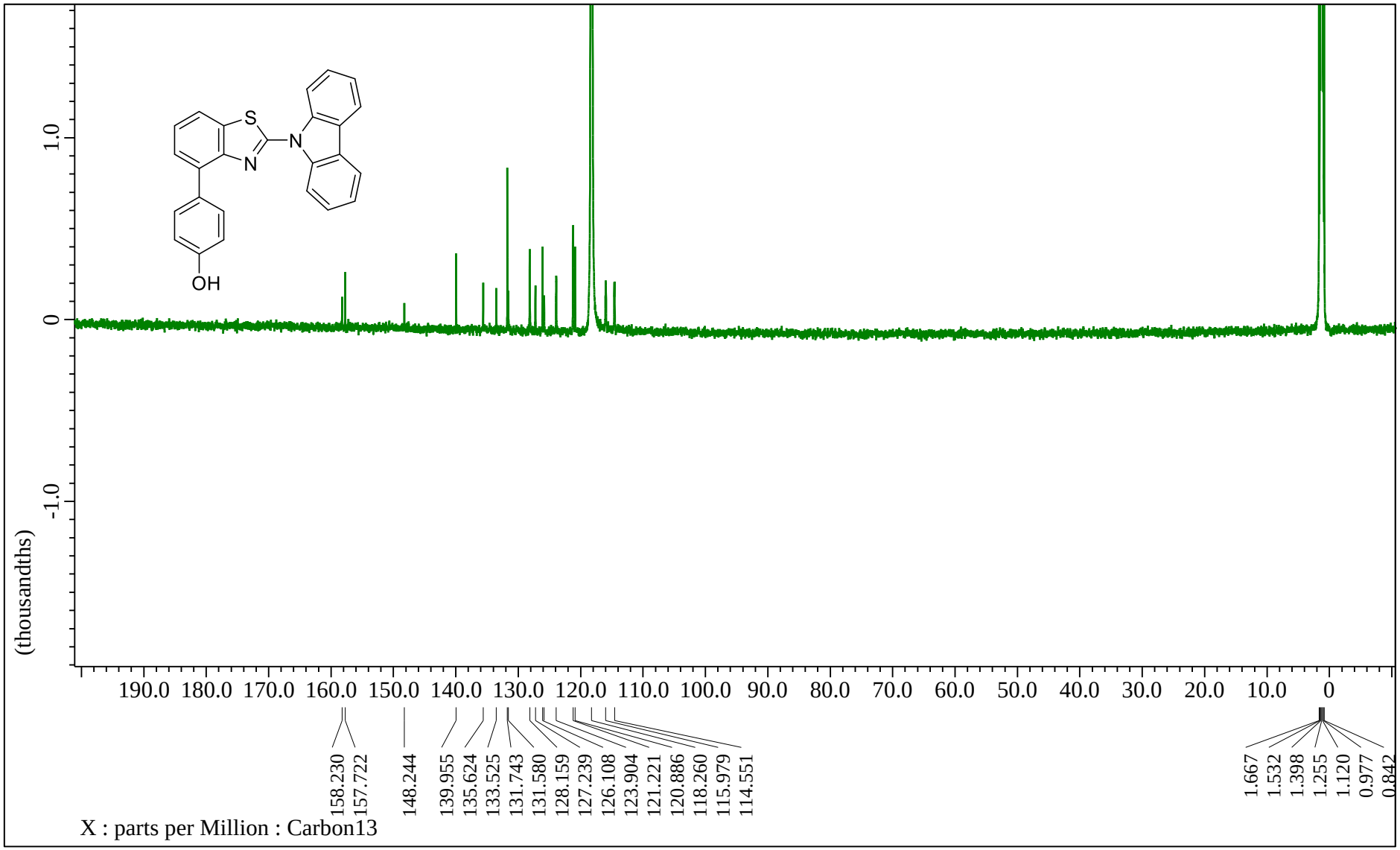

Fig. S61. ^{13}C NMR (CD_3CN) spectrum of **14**.

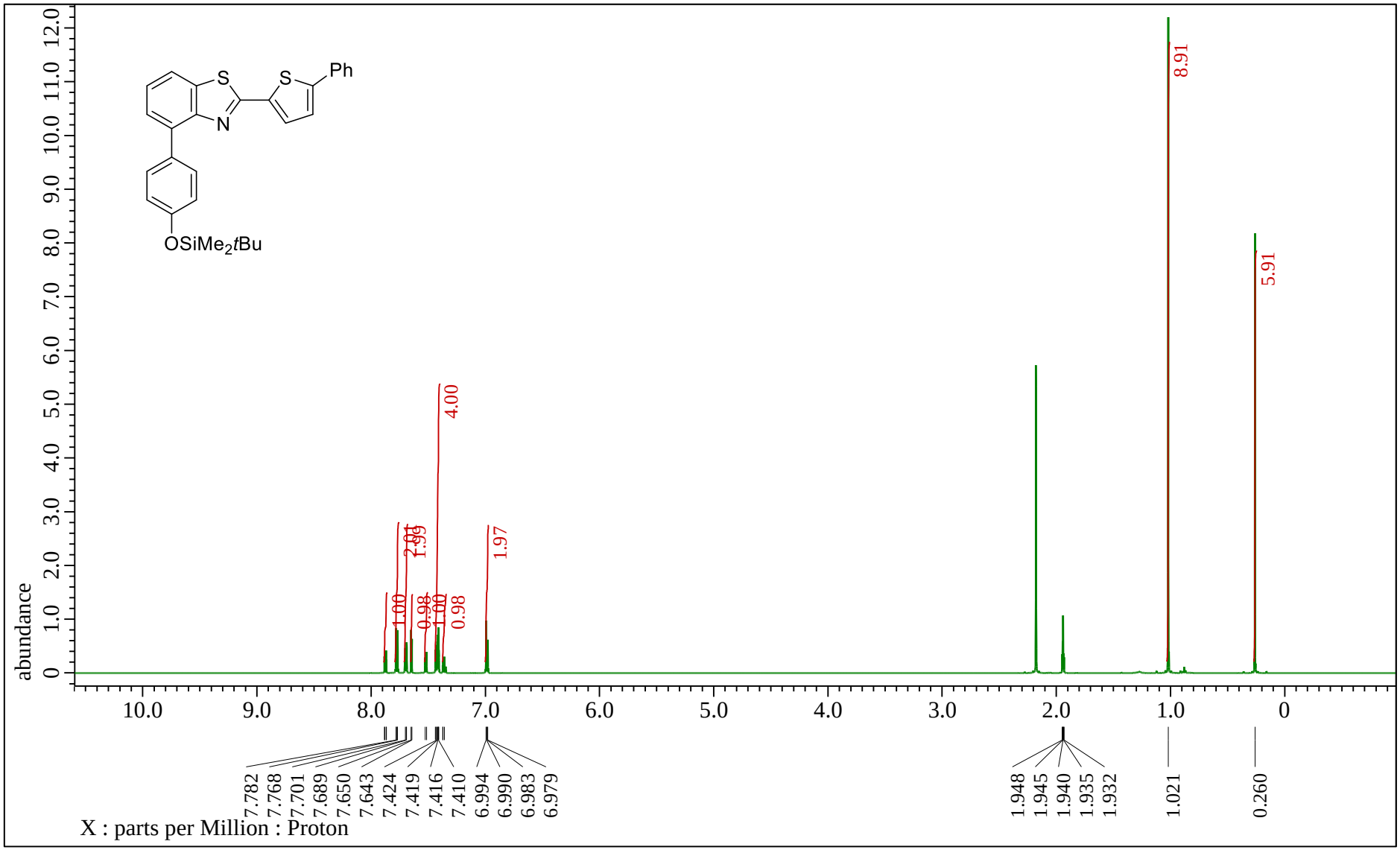

Fig. S62. ^{1}H NMR (CD_3CN) spectrum of **15**.

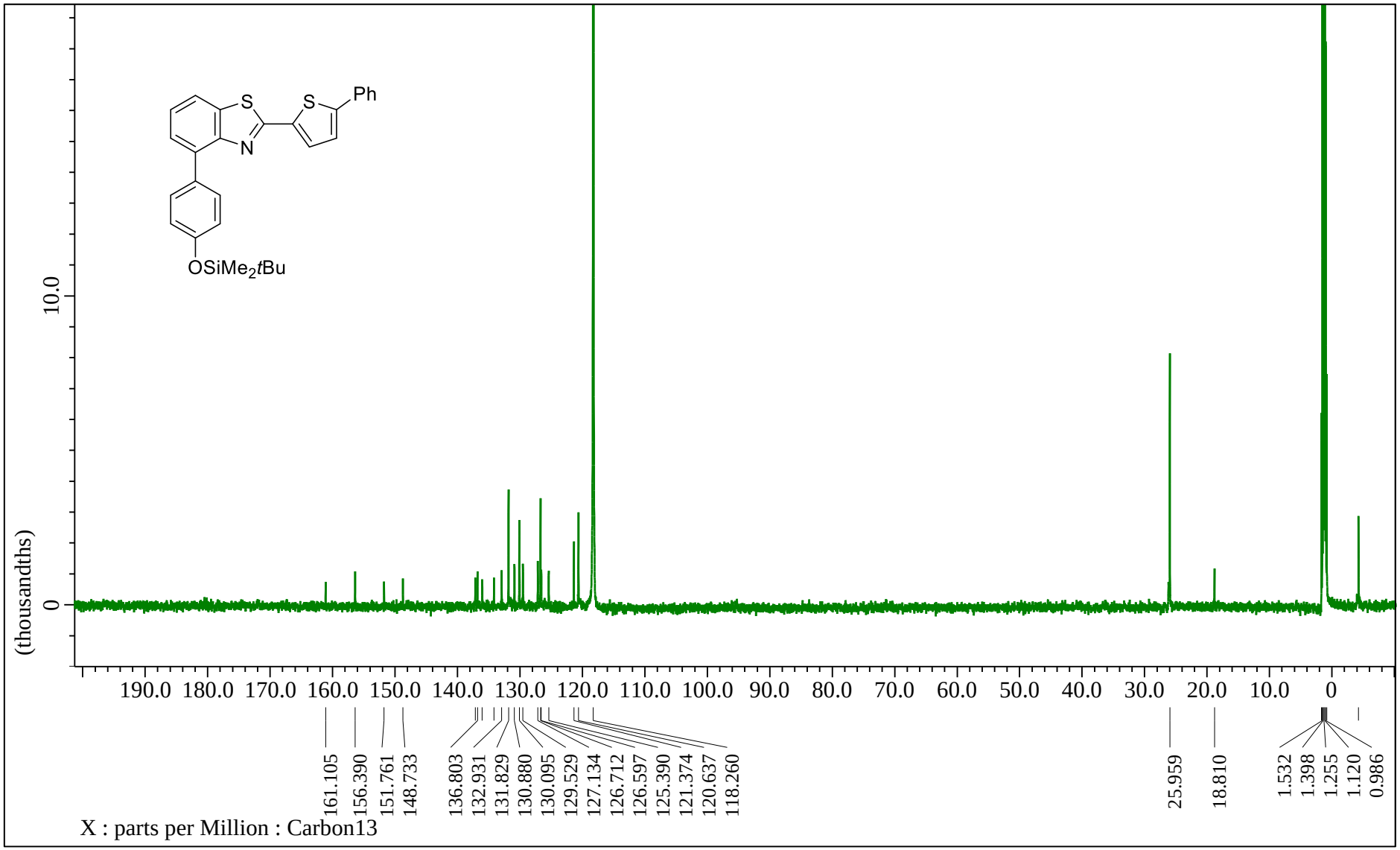

Fig. S63. ^{13}C NMR (CD_3CN) spectrum of **15**.