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Transition metal free, green and facile halogenation of ketene dithioacetals using KX-Oxidant system

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Supporting Information

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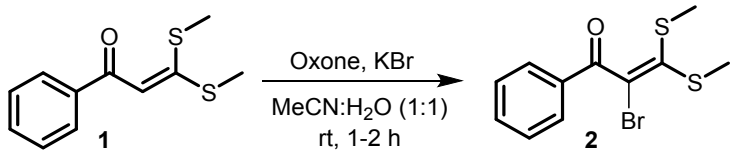
Material and Methods General Information:

All reactions were carried out in oven-dried glassware, all compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on JEOL -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 *J* values are given in Hz. Data are reported as follows: Chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, db = doublet broad, m = multiplet), coupling constant (Hz), and integration. 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. Mass measurement was performed on Agilent QTOF mass spectrometer with electron spray ionization (ESI) as the ion source. Column chromatography was carried out using commercially available silica gel (230-400 mesh) under pressure. Materials Unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification. PE refers to Petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, and all reaction solvents were freshly distilled prior to use.

All the Ketene dithioacetals starting materials were synthesized using the procedure given in literature[1].

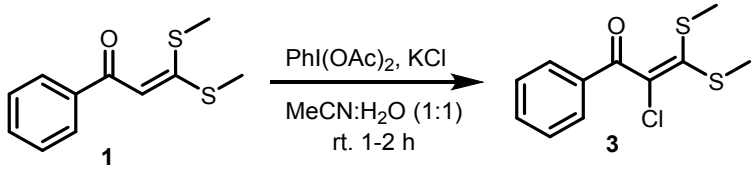
General experimental procedures:

Scheme 1: Bromination of ketene dithioacetals



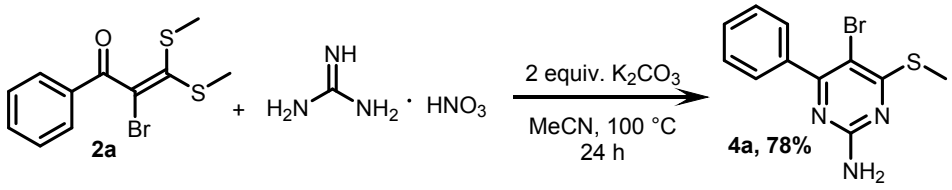
To a 25 ml reaction flask, was added ketene dithioacetal (100 mg, 0.44 mmol), oxone (301.9 mg 0.49 mmol), KBr (58.4 mg, 0.49 mmol) followed by MeCN:H_2O (1:1, 2 ml). The mixture was stirred at room temperature for 1-2 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the mixture was quenched with water, extracted with ethyl acetate. The organic layer was dried over sodium sulphate, concentrated in vacuo and purified by column chromatography to afford product **2**.

Scheme 2: Chlorination of ketene dithioacetals



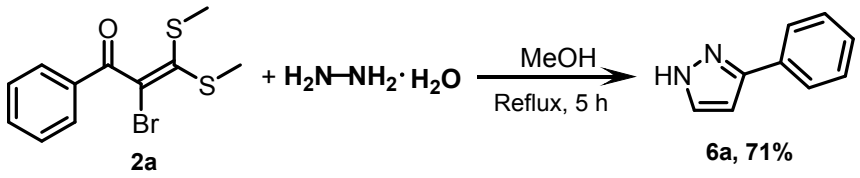
To a 25 ml reaction flask, was added ketene dithioacetal (100 mg, 0.44 mmol), diacetoxyiodobenzene (157.9 mg 0.49 mmol), KCl (36.5 mg, 0.49 mmol) followed by MeCN:H_2O (1:1, 2 ml). The mixture was stirred at room temperature for 1-2 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the mixture was quenched with water, extracted with ethyl acetate. The organic layer was dried over sodium sulphate, concentrated in vacuo and purified by column chromatography to afford product **3**.

Scheme 3: Reaction of 2a with guanidine



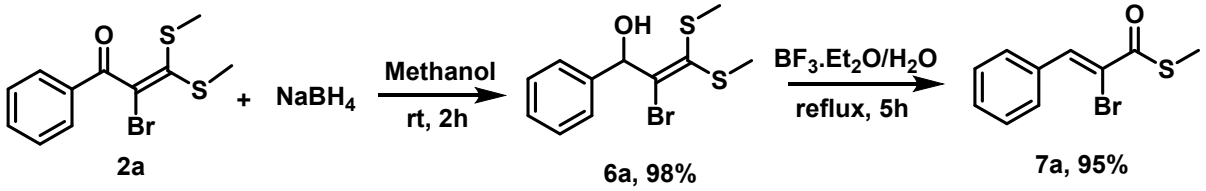
A mixture of **2a** (100 mg, 0.32 mmol), guanidine nitrate (40.2 mg, 0.32mol), and K_2CO_3 (91.1 mg, 0.65 mmol) in CH_3CN (5 mL) was stirred at 100 ℃ for 24 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography to obtain the desired product as pale yellow semi solid (77 mg).

Scheme 4: Reaction of 2a with hydrazine hydrate[2]



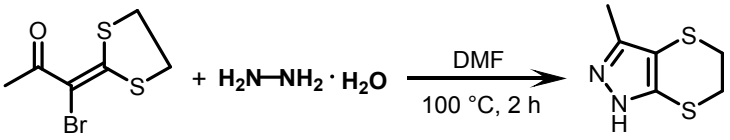
A mixture of **2a** (100 mg, 0.32 mmol) and hydrazine hydrate (30.72 mg, 0.96 mmol), in methanol (5 mL) was refluxed for 5 h. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography to obtain the desired product as pale yellow solid (30 mg, m.p. 74 ^{0}C.)

Scheme 5: Reaction of 2a with $NaBH_4$ and $BF_3(OEt)_2$[3]



A mixture of **2a** (100 mg, 0.32 mmol) and sodium borohydride (60.5 mg, 1.6 mmol), in methanol (5 mL) was stirred at room temperature for 2 h. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4, and evaporated under vacuum to give the carbinol **6a** (97 mg, 98%) as an undistillable, thick viscous liquid. To the crude carbinol **6a** was added 0.335 mg of boron trifluoride etherate, and the reaction mixture was stirred at room temperature for 5 min. It was then diluted with 5mL of water, and the solution was refluxed for 5h. The cooled reaction mixture was poured over water and extracted with ethylacetate. The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography to obtain the desired product **7a** as pale-yellow liquid (78 mg, 95%).

Scheme 6: Reaction of 2x with hydrazine hydrate[4].



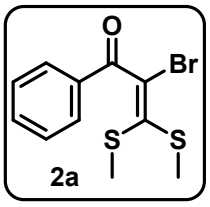
2x **8a, 72%**

A mixture of **2x** (100 mg, 0.41 mmol) and hydrazine hydrate (66.9 mg, 2.09 mmol), in DMF (5 mL) was stirred at 100 ℃ for 2 h. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography to obtain the desired product as pale yellow solid (56 mg, m.p. 110 ^{0}C.)

1) H. Yuan, M. Wang, Y. Liu, L. Wang, L. Liu and J. Liu, Q. *Chem. Eur. J.,* 2010, **16**, 13450; (b) C. Xu, J. Liu, W. Ming, Y. Liu, J. Liu, M. Wang and Q. Liu, *Chem. Eur. J.,* 2013, **19**, 9104; (c) Z. Fu, M. Wang, Y. Ma, Q. Liu and J. Liu, *J. Org. Chem.,* 2008, **73**, 7625; (d) Y. Yin, M. Wang, Q. Liu, J. Hu, S. Sun, J. Kang, *Tetrahedron Lett.,* 2005, **46**, 4399.
2) G. Singh, H. Ila and H. Junjappa, *J. Chem. Soc.Perkin. Trans. I,* 1987, 1945.
3) B. Myrboh, H. Ila and H. Junjappa, *J. Org. Chem.* 1983, **48**, 5327.
4) X. Y. Meng, Z. X. Fang, B. D. Barry, P. Q. Liao and X. H. Bi, *Chin Sci Bull.*, 2012, **57**, 2361.

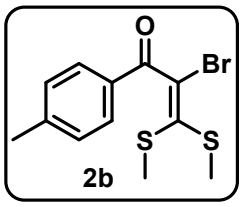
Spectroscopic Data

2-Bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (2a):



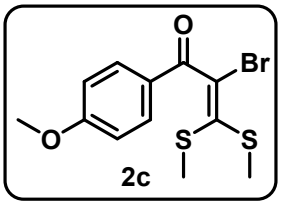
Red oil; Yield – 90% (121 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.33 (s, 3H), 2.79 (s, 3H), 7.50-7.56 (m, 2H), 7.63-7.69 (m, 1H), 7.90-7.94 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.3, 38.6, 126.4, 129.0, 129.7, 132.7, 134.7, 145.2, 186.8; MS (ESI): m/z calcd for $C_{11}H_{11}BrOS_2$ 301.94, found 302.97 [M+H], 304.97 [M+H+2].

2-Bromo-3,3-bis(methylthio)-1-(p-tolyl) prop-2-en-1-one (2b):



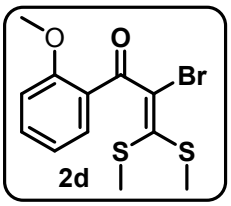
Yellow oil; Yield – 92% (122 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.35 (s, 3H), 2.45 (s, 3H), 2.79 (s, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.4, 21.9, 38.7, 126.8, 129.9, 130.0, 130.2, 144.9, 146.2, 186.5; MS (ESI): m/z calcd for $C_{12}H_{13}BrOS_2$ 315.96, found 316.99 [M+H], 318.97 [M+H+2].

2-Bromo-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (2c):



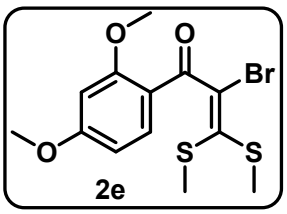
Yellow oil; Yield – 91% (119 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.34 (s, 3H), 2.76 (s, 3H), 3.87 (s, 3H), 6.95-6.99 (m, 2H), 7.85-7.89 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.4, 38.6, 55.6, 114.4, 125.4, 126.9, 132.2, 144.6, 164.8, 185.5; MS (ESI): m/z calcd for $C_{12}H_{13}BrO_2S_2$ 331.95, found 332.98 [M+H], 334.99 [M+H+2].

***2-Bromo-1-(2-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (2d)*:**



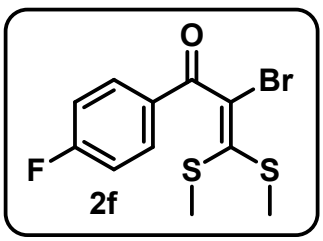
Yellow oil; Yield – 92% (121 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.42 (s, 3H), 3.84 (s, 3H), 6.92-7.02 (m, 2H), 7.44-7.50 (m, 1H), 7.72-7.54 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 16.4, 18.4, 55.8, 111.8, 120.5, 121.9, 125.6, 131.9, 134.4, 137.4, 159.1, 188.2; MS (ESI): m/z calcd for $C_{12}H_{13}BrO_2S_2$ 331.95, found 332.98 [M+H], 334.98 [M+H+2].

2-Bromo-1-(3,4-dimethoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (2e):



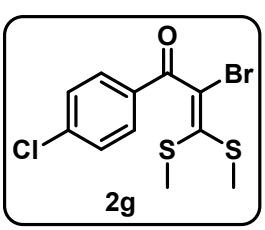
Colourless oil; Yield – 95% (121 mg); R_f = 0.6 (30% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3H), 2.45 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, J_1 = 8.4, J_2 = 2.1 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 16.2, 18.9, 55.9, 56.1, 110.0, 110.8, 117.9, 125.3, 127.4, 137.4, 149.4, 154.0, 188.0; MS (ESI): m/z calcd for $C_{13}H_{15}BrO_3S_2$ 361.96, found 362.97 [M+H], 364.99 [M+H+2].

2-Bromo-1-(4-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2f):



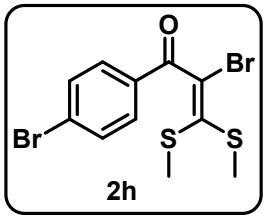
Yellow solid; M.p. 106-108 ℃; Yield – 86% (114 mg); R_f = 0.5 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.35 (s, 3H), 2.79 (s, 3H), 7.18-7.24 (m, 2H), 7.93-7.98 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.4, 38.7, 116.5 (d, *J* = 22.6 Hz), 125.9, (d, *J* = 9.6 Hz), 129.2, 132.5, 145.6, 166.7 (d, *J* = 250.6 MHz), 185.3; MS (ESI): m/z calcd for $C_{11}H_{10}BrFOS_2$ 319.93, found 320.94 [M+H], 322.96 [M+H+2].

2-Bromo-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2g):



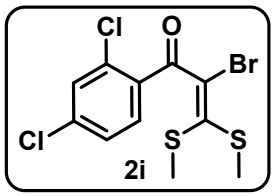
Yellow liquid; Yield – 90% (117 mg); R_f = 0.5 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.35 (s, 3H), 2.79 (s, 3H), 7.48-7.53 (m, 2H), 7.83 -7.89 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.6, 38.7, 125.5, 129.7, 131.0, 131.1, 141.7, 145.6, 185.5; MS (ESI): m/z calcd for $C_{11}H_{10}BrClOS_2$ 335.90, found 336.93 [M+H], 338.97 [M+H+2], 340.97 [M+H+4].

2-Bromo-1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2h):



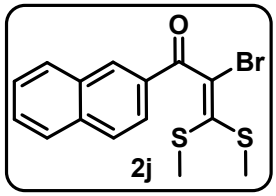
Orange liquid; Yield – 90% (113 mg); R_f = 0.32 (20% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.34 (s, 3H), 2.78 (s, 3H), 7.64-7.68 (m, 2H), 7.75-7.79 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.3, 38.7, 125.6, 130.3, 131.0, 131.5, 132.5, 145.8, 185.8; MS (ESI): m/z calcd for $C_{11}H_{10}BrClOS_2$ 379.85, found 380.86 [M+H], 382.86 [M+H+2], 384.88 [M+H+4].

2-Bromo-1-(2,4-dichlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2i):



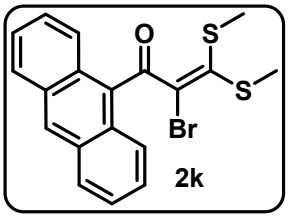
Yellow liquid; Yield - 93% (118 mg); R_f = 0.5 (20% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.09 (s, 3H), 2.48 (s, 3H), 7.28-7.33 (m, 1H), 7.42-7.46 (m, 1H), 7.53-7.57 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 16.9, 18.8, 118.9, 127.0, 130.5, 131.8, 133.6, 135.6, 137.8, 145.9, 186.9; MS (ESI): m/z calcd for $C_{11}H_9BrCl_2OS_2$ 369.87, found 370.88 [M+H], 372.87 [M+H+2], 374.89 [M+H+4], 376.88 [M+H+6].

2-Bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl) prop-2-en-1-one (2j):



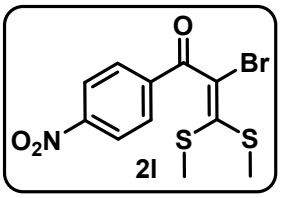
Yellow oil; Yield – 91% (117 mg); R_f = 0.4 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.18 (s, 3H), 2.81 (s, 3H), 7.54 (t, *J* = 7.20 Hz, 1H), 7.59-7.65 (m, 1H), 7.69-7.75 (m, 1H), 7.91-7.99 (m, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 9.03 (d, *J* = 8.40 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.1, 38.3, 124.0, 125.8, 127.1, 128.5, 128.7, 129.2, 129.9, 131.1, 132.1, 134.1, 135.5, 145.8, 188.0; MS (ESI): m/z calcd for $C_{15}H_{13}BrOS_2$ 351.96, found 352.97 [M+H], 354.97 [M+H+2].

1-(anthracen-9-yl)-2-bromo-3,3-bis(methylthio)prop-2-en-1-one (2k):



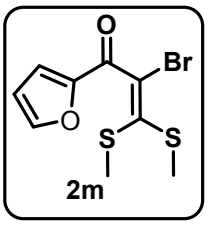
Colourless oil; Yield – 78% (97 mg); R_f = 0.5 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1. 56 (s, 3H), 2.45 (s, 3H), 7.45-7.52 (m, 4H), 7.89-7.94 (m, 2H), 7.98-8.03 (m, 2H), 8.48 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 17.9, 19.1, 124.8, 125.2, 125.4, 126.1, 126.6, 128.6, 128.8, 130.9, 135.4, 154.6, 191.2; MS (ESI): m/z calcd for $C_{19}H_{15}BrOS_2$ 401.97, found 402.97 [M+H], 404.99 [M+H+2].

2-Bromo-3,3-bis(methylthio)-1-(4-nitrophenyl)prop-2-en-1-one (2l):



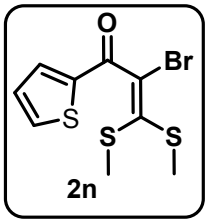
Yellow oil; Yield – 82% (106 mg); R_f = 0.5 (50% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.34 (s, 3H), 2.82 (s, 3H), 8.07–8.13 (m, 2H), 8.34–8.40 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.3, 38.8, 124.2, 124.6, 130.6, 137.6, 147.1, 151.0, 185.1; MS (ESI): m/z calcd for $C_{11}H_{10}BrNO_3S_2$ 346.93, found 347.94 [M+H], 349.94 [M+H+2].

2-Bromo-1-(furan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (2m):



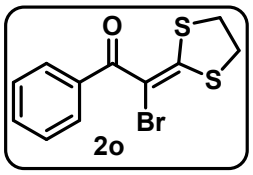
Colourless oil; Yield – 95% (130 mg); R_f = 0.4(10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.41 (s, 3H), 2.77 (s, 3H), 6.64 (dd, J_1 = 3.60, J_2 = 1.60 Hz, 1H), 7.32 (dd, J_1 = 3.60, J_2 = 0.40 Hz, 1H), 7.71 (dd, J_1 = 2.0, J_2 = 0.80 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 20.5, 38.7, 113.3, 121.4, 124.5, 146.9, 148.7, 149.2, 174.7; MS (ESI): m/z calcd for $C_9H_9BrO_2S_2$ 291.92, found 292.93 [M+H], 294.93 [M+H+2].

2-Bromo-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (2n):



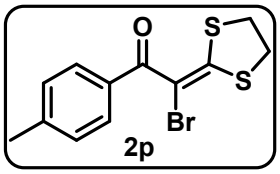
Orange liquid; Yield – 96% (129 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 2.47 (s, 3H), 7.12-7.16 (m, 1H), 7.65 (dd, J_1 = 1.2 Hz, J_2 = 4.0 Hz, 1H), 7.72 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 16.3, 19.1, 116.8, 128.2, 134.6, 135.4, 138.9, 141.6, 181.8; MS (ESI): m/z calcd for $C_9H_9BrOS_3$ 307.90, found 308.90 [M+H], 309.90 [M+H+2].

2-Bromo-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (2o):



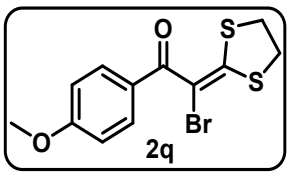
Yellow oil; Yield – 96% (130 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 3.42-3.47 (m, 2H), 3.59-3.64 (m, 2H), 7.37-7.43 (m, 2H), 7.44-7.50 (m, 1H), 7.68-7.73 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.1, 40.9, 100.3, 127.6, 128.7, 131.3, 138.2, 165.5, 188.5; MS (ESI): m/z calcd for $C_{11}H_9BrOS_2$ 299.93, found 300.93 [M+H], 302.94 [M+H+2].

2-Bromo-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (2p):



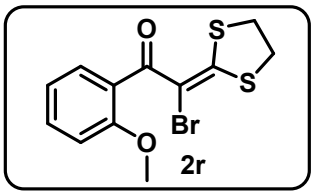
Yellow oil; Yield – 96% (128 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.40 (s, 3H), 3.44-3.48 (m, 2H), 3.59-3.64 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 21.6, 36.2, 40.9, 100.5, 108.4, 129.1, 135.3, 142.1, 164.5, 188.3; MS (ESI): m/z calcd for $C_{12}H_{11}BrOS_2$ 313.94, found 314.95 [M+H], 316.96 [M+H+2].

2-Bromo-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (2q):



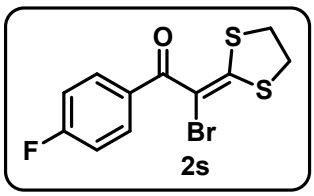
Colourless oil; Yield – 90% (118 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.43-3.48 (m, 2H), 3.58-3.62 (m, 2H), 3.85 (s, 3H), 6.88-6.92 (m, 2H), 7.76-7.81 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.2, 40.7, 55.3, 100.4, 113.0, 130.2, 131.5, 162.0, 163.4, 187.4; MS (ESI): m/z calcd for $C_{12}H_{11}BrO_2S_2$ 329.94, found 330.94 [M+H], 332.95 [M+H+2].

2-Bromo-2-(1,3-dithiolan-2-ylidene)-1-(2-methoxyphenyl)ethan-1-one (2r):



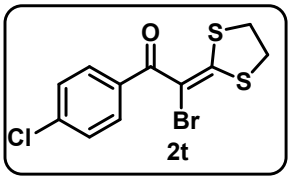
Colourless oil; Yield – 91% (119 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.32–3.37 (m, 2H), 3.55–3.59 (m, 2H), 3.75 (s, 3H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.90 (t, *J* = 7.60 Hz, 1H), 7.14-7.20 (m, 1H), 7.28-7.34 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 35.8, 41.1, 103.3, 110.8, 120.2, 128.2, 129.3, 131.2, 156.3, 164.5, 188.9; MS (ESI): m/z calcd for $C_{12}H_{11}BrO_2S_2$ 329.94, found 330.94 [M+H], 332.94 [M+H+2].

2-Bromo-2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)ethan-1-one (2s):



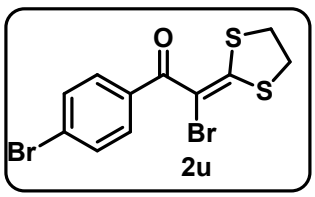
Yellow solid; M.p. 110-112 ℃; Yield – 90% (120 mg); R_f = 0.7 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.45-3.50 (m, 2H), 3.61-3.66 (m, 2H), 7.06-7.12 (m, 2H), 7.74-7.80 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.2, 40.9, 100.0, 114.8 (d, *J* = 22 Hz), 131.4 (d, *J* = 8.6 Hz), 134.2 (d, *J* = 2.9 Hz), 164.5 (d, *J* = 245.4 Hz), 165.8, 186.9; MS (ESI): m/z calcd for $C_{11}H_8BrFOS_2$ 317.92, found 318.92 [M+H], 320.93 [M+H+2].

2-Bromo-1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (2t):



Yellow solid; M.p. 114-116 ℃; Yield – 86% (112 mg); R_f = 0.6 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.44-3.49 (m, 2H), 3.61-3.66 (m, 2H), 7.36-7.40 (m, 2H), 7.64-7.68 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.2, 41.0, 99.8, 128.0, 130.3, 136.5, 137.5, 166.5, 187.3; MS (ESI): m/z calcd for $C_{11}H_8BrClOS_2$ 333.89, found 334.89 [M+H], 336.90 [M+H+2], 338.90 [M+H+4].

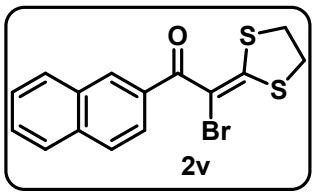
2-Bromo-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (2u):



Yellow solid; M.p. 110-112 ℃; Yield – 90% (114 mg); R_f = 0.6 (5% EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.44-3.49 (m, 2H), 3.61-3.66 (m, 2H), 7.52-7.61 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.2, 41.0, 99.8, 126.0, 130.4, 131.0, 137.0, 166.6, 187.4; MS (ESI): m/z calcd for

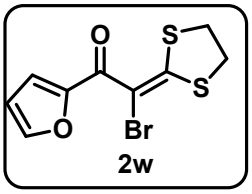
$C_{11}H_8Br_2OS_2$ 377.84, found 378.85 [M+H], 380.85 [M+H+2], 382.86 [M+H+4].

2-Bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one (2v):



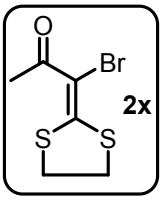
Yellow solid; M.p. 162-164 ℃; Yield – 90% (116 mg); R_f = 0.5 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.43-3.49 (m, 2H), 3.65-3.70 (m, 2H), 7.46-7.56 (m, 4H), 7.84-7.93 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.1, 41.4, 103.0, 124.5, 125.3, 125.4, 126.2, 126.8, 128.3, 130.0, 130.1, 133.3, 137.1, 166.5, 190.0; MS (ESI): m/z calcd for $C_{15}H_{11}BrOS_2$ 349.94, found 350.94 [M+H], 352.94 [M+H+2].

2-Bromo-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one (2w):



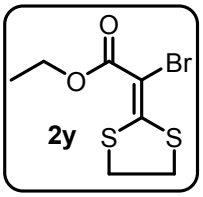
Yellow oil; Yield – 90% (123 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.34-3.39 (m, 2H), 3.51-3.56 (m, 2H), 6.44-6.47 (m, 1H), 7.52-7.58 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 35.7, 40.7, 97.7, 111.8, 120.2, 146.5, 150.7, 166.8, 173.4; MS (ESI): m/z calcd for $C_9H_7BrO_2S_2$ 289.91, found 290.91 [M+H], 292.92 [M+H+2].

1-bromo-1-(1,3-dithiolan-2-ylidene)propan-2-one (2x):



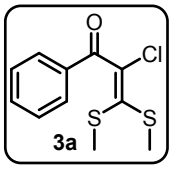
White solid; M.p. 114-116 ℃; Yield – 97% (145 mg); R_f = 0.4 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.46 (s, 3H), 3.36-3.41 (m, 2H), 3.58-3.63 (m, H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 28.5, 35.8, 41.2, 102.3, 163.2, 191.4; MS (ESI): m/z calcd for $C_6H_7BrOS_2$ 237.91, found 238.92.97 [M+H], 240.92 [M+H+2].

ethyl 2-bromo-2-(1,3-dithiolan-2-ylidene)acetate (2y):



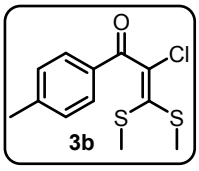
Yellow solid; M.p. 118-120 ℃; Yield – 95% (134 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.32 (t, *J* = 3.6 Hz, 3H), 3.40-3.45 (m, 2H), 3.62-3.66 (m, 2H), 4.26 (q, J_1 = 7.2 Hz, J_2 = 14.4Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 14.2, 36.7, 41.2, 62.1, 92.8, 162.2, 162.7; MS (ESI): m/z calcd for $C_7H_9BrO_2S_2$ 267.92, found 268.97 [M+H], 270.98 [M+H+2].

2-chloro-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3a):



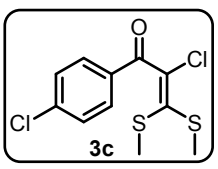
Red oil; Yield – 80% (92 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.14 (s, 3H), 2.48 (s, 3H), 7.47-7.52 (m, 2H), 7.57-7.64 (m, 1H), 7.88-7.92 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 43.0, 45.5, 125.1, 129.4, 130.4, 133.8, 141.2, 176.7, 185.9; MS (ESI): m/z calcd for $C_{11}H_{11}ClOS_2$ 257.99, found 258.99 [M+H], 260.98 [M+H+2].

2-chloro-3,3-bis(methylthio)-1-(p-tolyl)prop-2-en-1-one (3b):



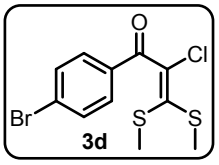
Yellow oil; Yield – 82% (94 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.15 (s, 3H), 2.43 (s, 3H), 2.47 (s, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.79-7.82 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.8, 18.5, 21.8,127.4, 129.4, 129.7, 130.2, 137.4, 145.0, 188.7; MS (ESI): m/z calcd for $C_{12}H_{13}ClOS_2$ 272.00, found 273.00 [M+H], 275.00 [M+H+2].

2-chloro-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (3c):



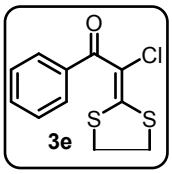
Yellow liquid; Yield – 81% (92 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.15 (s, 3H), 2.47 (s, 3H), 7.43-749. (m, 2H), 7.81-7.87 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.8, 18.5, 127.4, 129.1, 130.2, 130.8, 137.4, 140.3, 187.8; MS (ESI): m/z calcd for $C_{11}H_{10}Cl_2OS_2$ 291.95, found 292.96 [M+H], 294.97 [M+H+2], 296.98 [M+H+4].

1-(4-bromophenyl)-2-chloro-3,3-bis(methylthio)prop-2-en-1-one (3d):



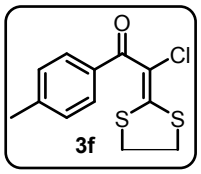
Orange oil; Yield – 90% (100 mg); R_f = 0.3 (% EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.18 (s, 3H), 2.47 (s, 3H), 7.61-7.66 (m, 2H), 7.73-7.78 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.8, 18.5, 126.3, 129.1, 130.9, 132.1, 133.8, 137.8, 188.0; MS (ESI): m/z calcd for $C_{11}H_{10}BrClOS_2$ 335.90, found 336.90 [M+H], 338.90 [M+H+2], 340.90 [M+H+4].

2-chloro-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (3e):



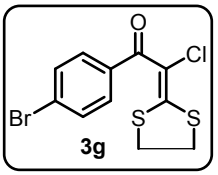
Yellow oil; Yield – 76% (88 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.41-3.48 (m, 2H), 3.54-3.59 (m, 2H), 7.39-7.44 (m, 2H), 7.46-7.52 (m, 1H), 7.72-7.76 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.2, 40.6, 112.4, 127.7, 128.7, 131.3, 137.5, 163.9, 187.6; MS (ESI): m/z calcd for $C_{11}H_9ClOS_2$ 255.97, found 256.99 [M+H], 257.99 [M+H+2].

2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(p-tolyl)ethan-1-one (3f):



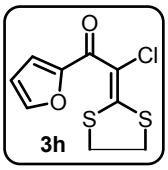
Yellow solid; M.p. 118-120 °C; Yield – 78% (89 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.39 (s, 3H), 3.42-3.47 (m, 2H), 3.52-3.57 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 21.5, 36.2, 40.6, 112.5, 128.4, 129.0, 134.7, 142.0, 163.2, 187.4; MS (ESI): m/z calcd for $C_{12}H_{11}ClOS_2$ 269.99, found 270.99 [M+H], 372.99 [M+H+2].

1-(4-bromophenyl)-2-chloro-2-(1,3-dithiolan-2-ylidene)ethan-1-one (3g):



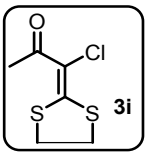
Pale yellow solid; M.p. 119-120 °C; Yield – 70% (78 mg); R_f = 0.4 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.44-3.49 (m, 2H), 3.54-3.60 (m, 2H), 7.53-7.57 (m, 2H), 7.59-7.64 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 36.3, 40.7, 111.9, 126.1, 130.4, 131.0, 136.3, 165.0, 186.4; MS (ESI): m/z calcd for $C_{11}H_8BrClOS_2$ 335.98, found 336.99 [M+H], 338.97 [M+H+2], 340.97 [M+H+4].

2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one (3h):



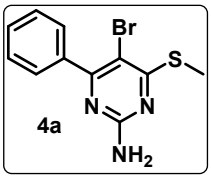
White solid; M.p. 98-100 °C; Yield – 70% (81 mg); R_f = 0.6 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 3.40-3.46 (m, 2H), 3.52-3.57 (m, 2H), 6.52-6.55 (m, 1H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.64-7.66 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 35.9, 40.6, 110.6, 111.9, 119.9, 146.7, 150.4, 165.1, 172.5; MS (ESI): m/z calcd for $C_9H_7ClOS_2$ 315.96, found 245.95 [M+H], 246.97 [M+H+2].

1-chloro-1-(1,3-dithiolan-2-ylidene)propan-2-one (3i):



Yellow solid; M.p. 116-118 °C; Yield – 82% (100 mg); R_f = 0.5 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.35 (3H), 3.36-3.41 (m, 2H), 3.50-3.56 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 27.2, 36.0, 40.9, 113.7, 160.7, 191.1; MS (ESI): m/z calcd for $C_6H_7ClOS_2$ 193.96, found 194.99 [M+H], 318.97 [M+H+2].

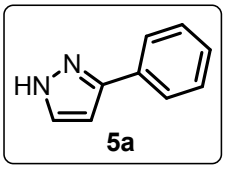
5-bromo-4-(methylthio)-6-phenylpyrimidin-2-amine (4a):



Pale yellow semi solid; Yield – 78% (77 mg); R_f = 0.3 (50% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.53 (s, 3H), 5.18 (s, 2H), 7.42-7.47 (m, 2H), 7.58-7.63 (m, 1H), 7.91-7.95 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.4, 104.8, 126.9, 128.6,

130.3, 137.2, 162.4, 163.4, 171.7; MS (ESI): m/z calcd for $C_{11}H_{10}BrN_3S$ 294.97, found 295.97 [M+H], 297.98 [M+H+2].

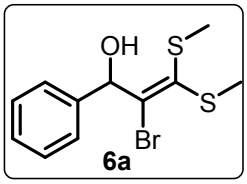
3-phenyl-1H-pyrazole (5a):



5a

Pale yellow semi solid; M.p. 74-76 ⍰C; Yield – 71% (30 mg); R_f = 0.7 (50% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 6.61 (d, *J* = 1.9 Hz, 1H), 7.30-7.36 (m, 1H), 7.39-7.45 (m, 2H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.76-7.78 (m, 2H), 8.45 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 102.6, 125.7, 128.0, 128.7, 132.0, 133.2, 148.9; MS (ESI): m/z calcd for $C_9H_8N_2$ 144.07, found 145.08 [M+H], 297.98.

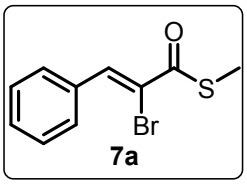
2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-ol (6a):



6a

Colourless liqiud; Yield – 98% (97 mg); R_f = 0.3 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.36 (s, 3H), 2.45 (s, 3H), 2.57 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 7.29-7.42 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.4, 104.8, 126.9, 128.6, 130.3, 137.2, 162.4, 163.4, 171.7; MS (ESI): m/z calcd for $C_{11}H_{13}BrOS_2$ 303.96, found 304.97 [M+H], 305.97 [M+H+2].

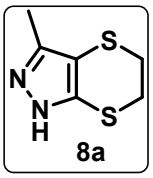
5-bromo-4-(methylthio)-6-phenylpyrimidin-2-amine (7a):



7a

Yellow liquid; Yield – 95% (78 mg); R_f = 0.8 (5% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.42 (s, 3H), 7.42-7.46 (m, 3H), 7.83-7.87 (m, 2H), 8.15 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.4, 104.8, 126.9, 128.6, 130.3, 137.2, 162.4, 163.4, 171.7; MS (ESI): m/z calcd for $C_{10}H_9BrOS$ 255.96, found 256.97 [M+H], 257.97 [M+H+2].

S-methyl-2-bromo-3-phenylprop-2-enethioate (8a):



8a

Yellow solid; M.p. 108-110 ⍰C; Yield – 72% (56 mg); R_f = 0.5 (10% in EtOAc/PE); ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.46 (s, 1H), 3.35-3.41 (m, 2H), 3.58-3.63 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 28.5, 35.8, 41.2, 102.2, 163.2, 191.3; MS (ESI): m/z calcd for $C_6H_8N_2S_2$ 172.01, found 173.02 [M+H].

^{1}H and ^{13}C NMR spectra

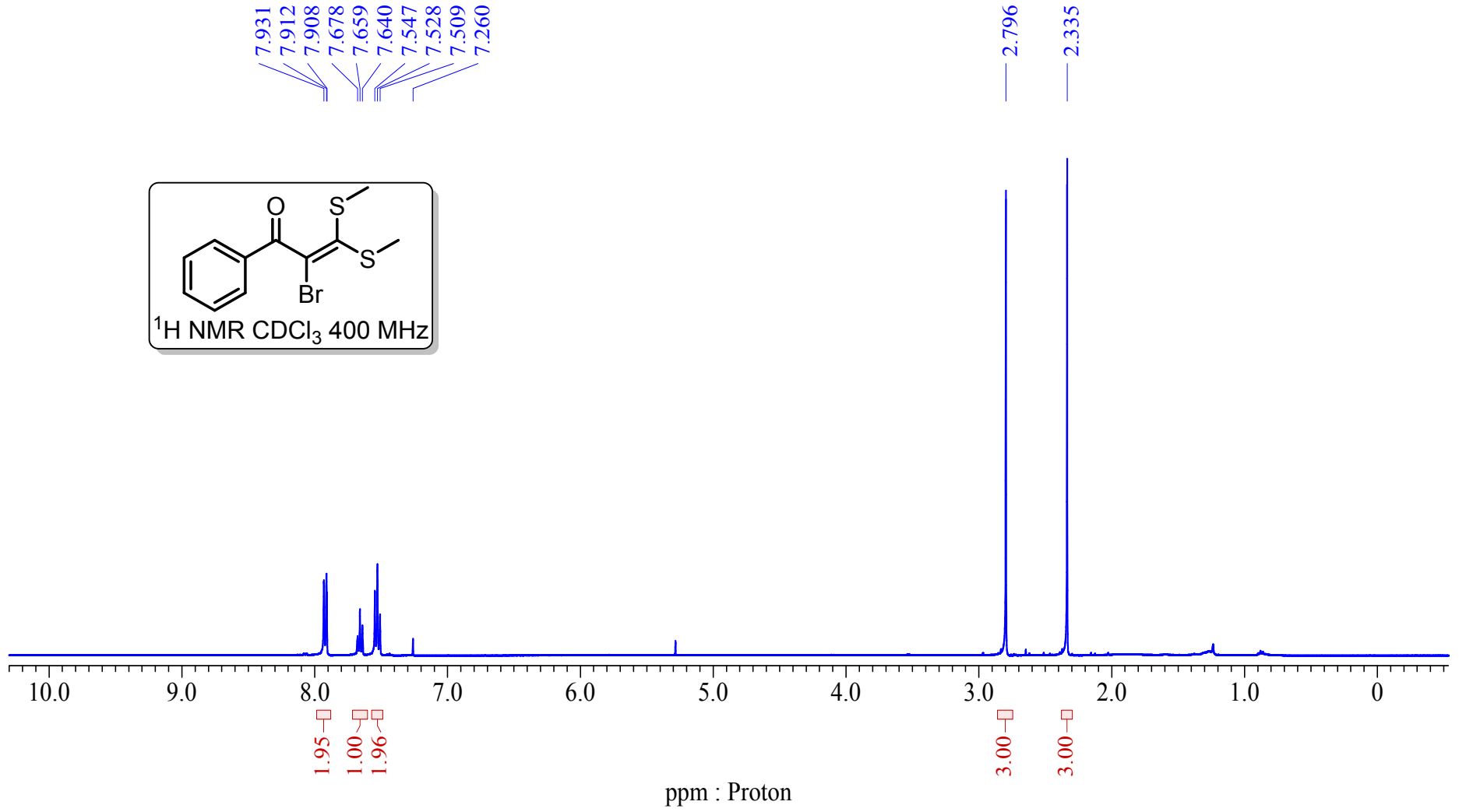


Fig. 1: ^{1}H NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**2a**)*

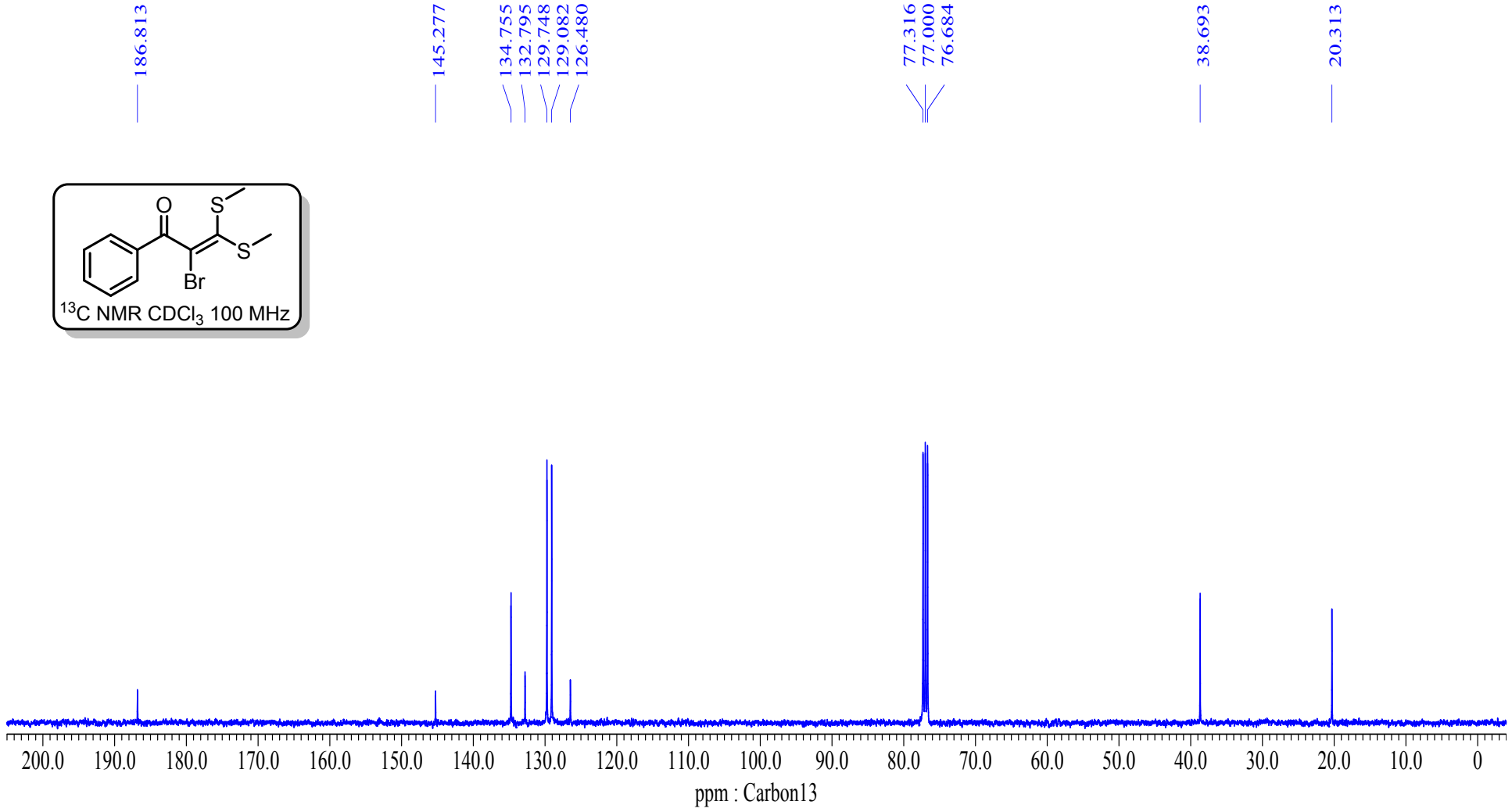


Fig. 2: ^{13}C NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one* (**2a**)

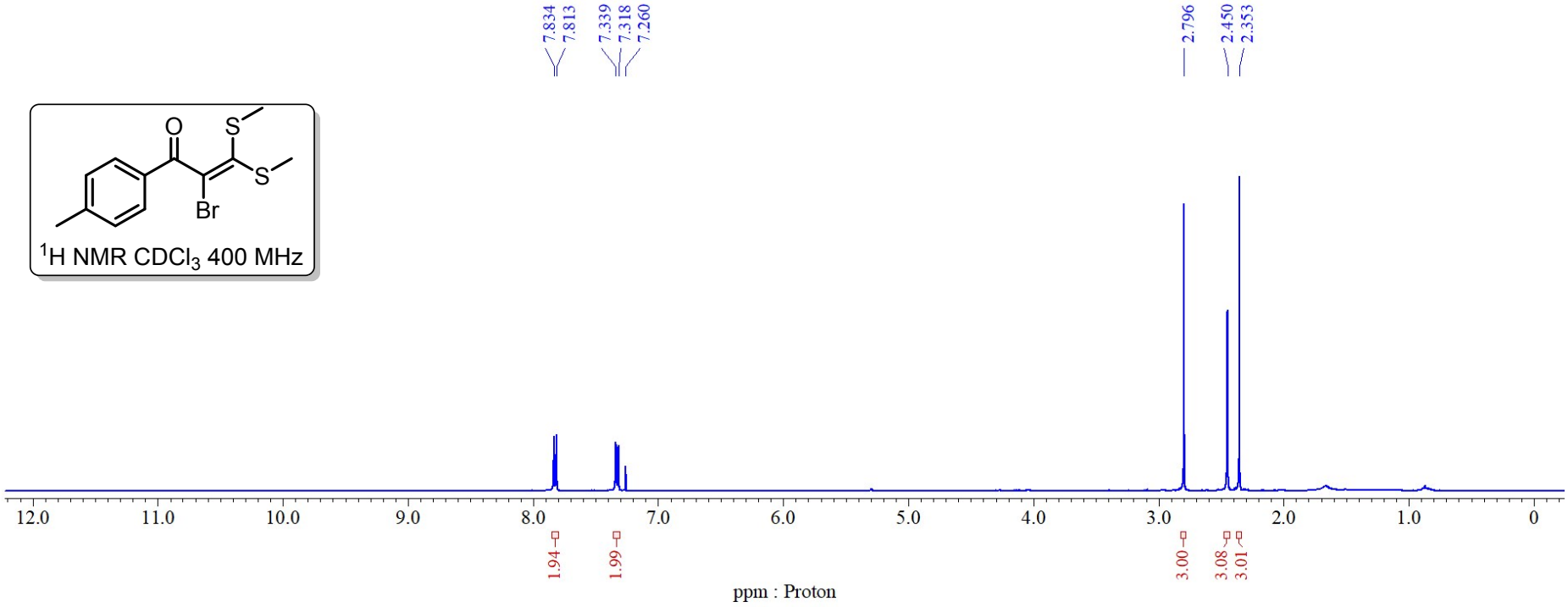


Fig. 3: ^{1}H-NMR of *2-bromo-3,3-bis(methylthio)-1-(p-tolyl) prop-2-en-1-one (**2b**)*

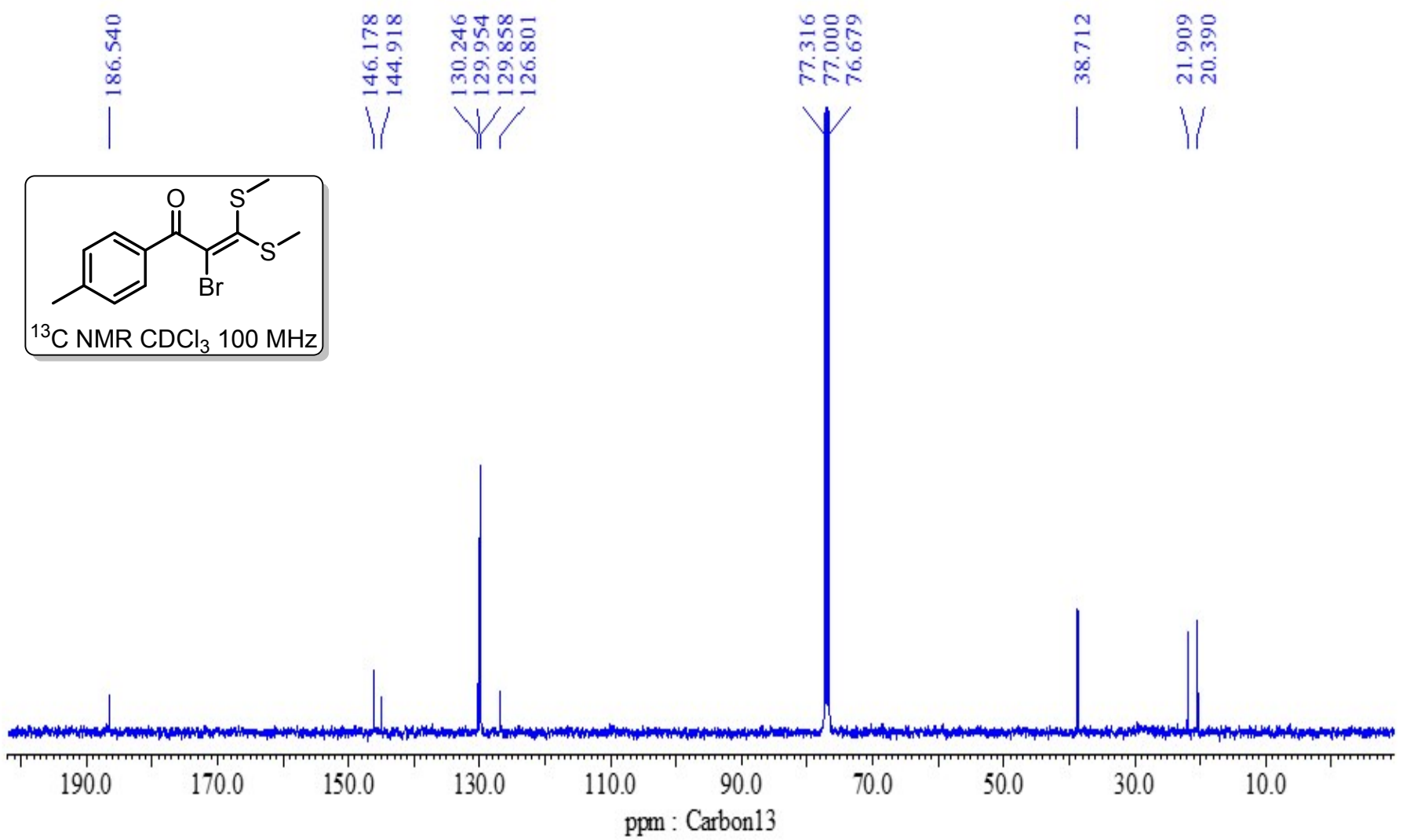


Fig. 4: ^{13}C-NMR of *2-bromo-3,3-bis(methylthio)-1-(p-tolyl) prop-2-en-1-one (**2b**)*

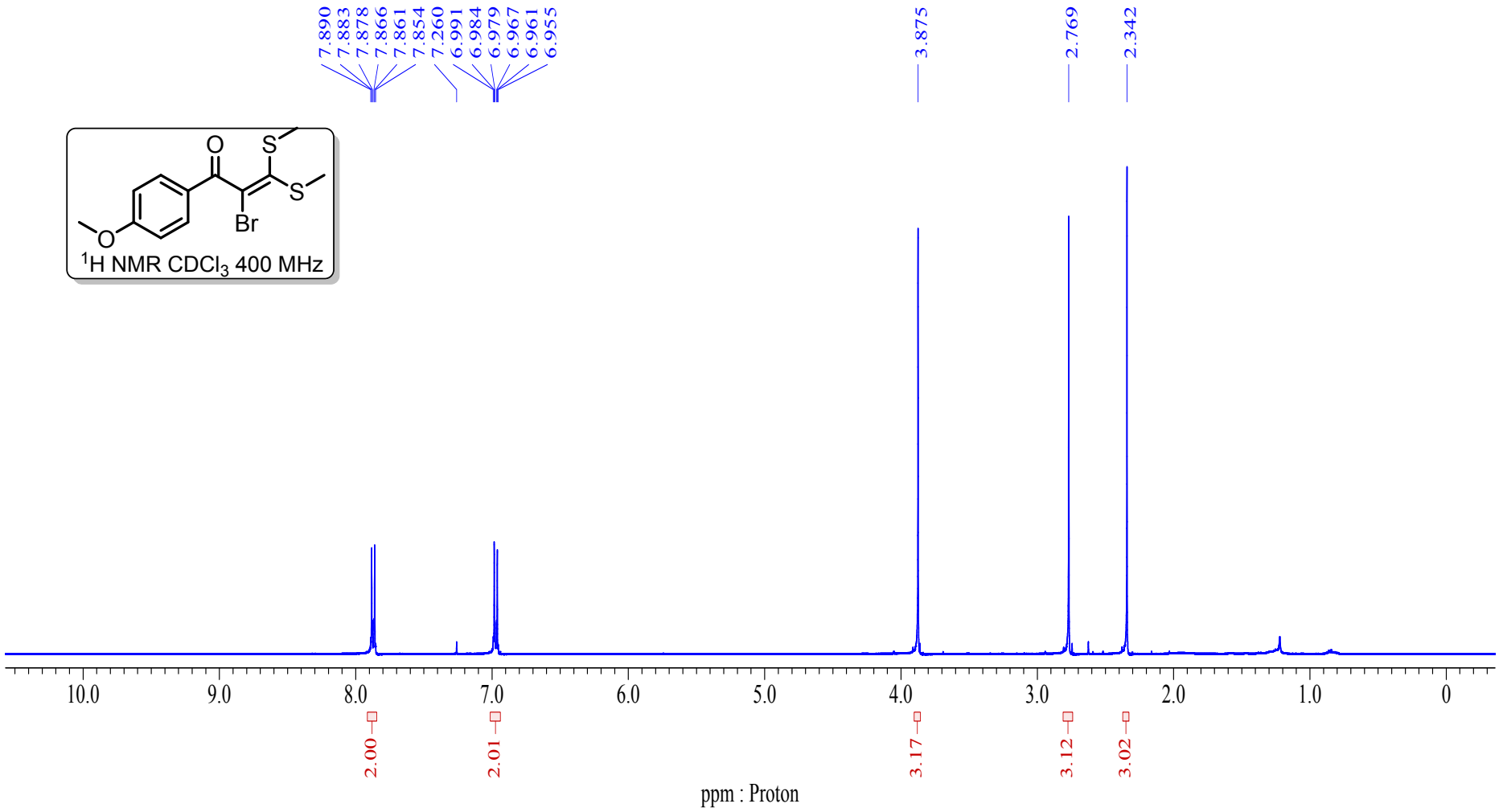


Fig. 5: ^{1}H-NMR spectrum of *2-bromo-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one* (***2c***)

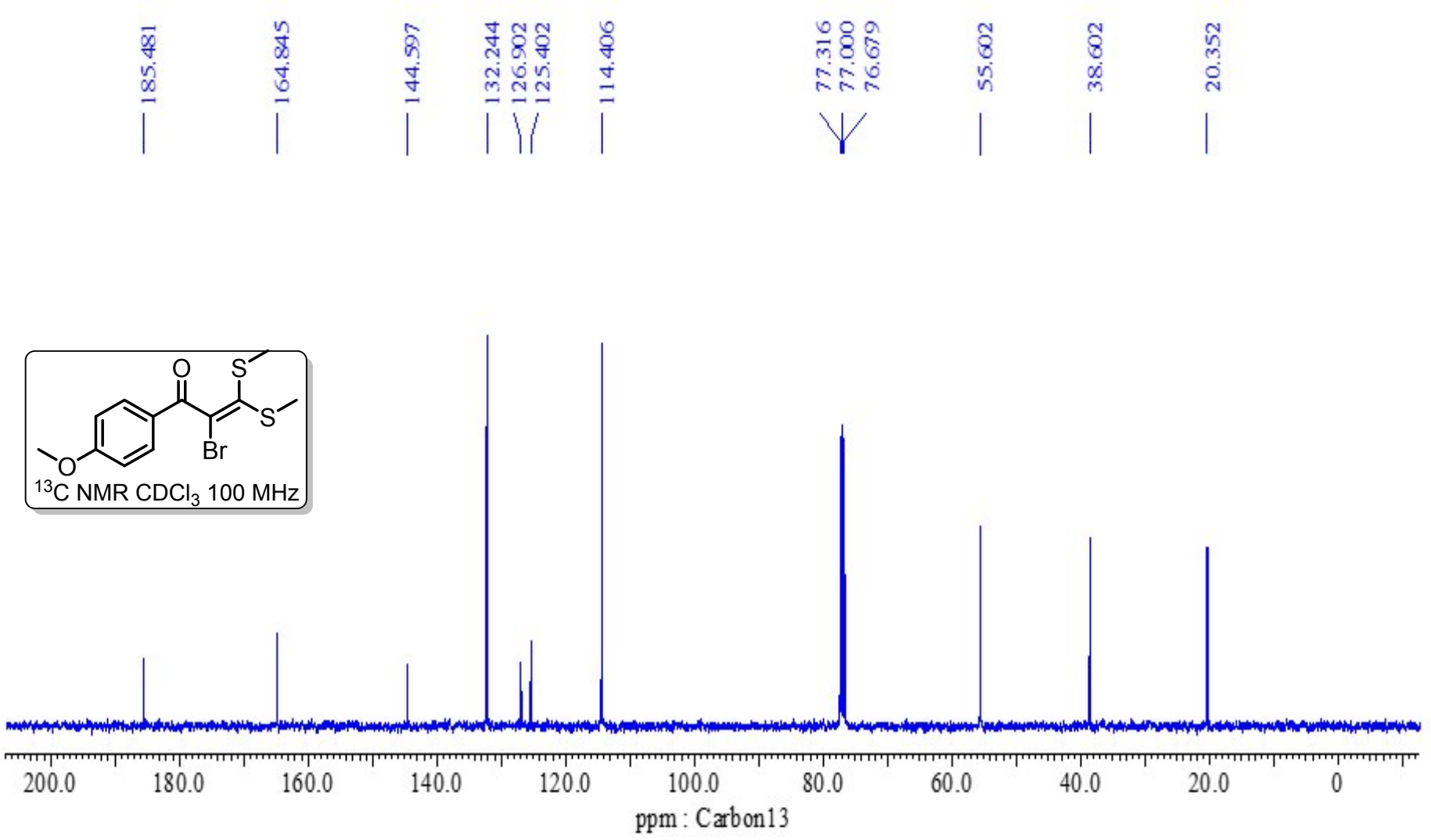


Fig. 6: ^{13}C-NMR spectrum of *2-bromo-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2c**)*

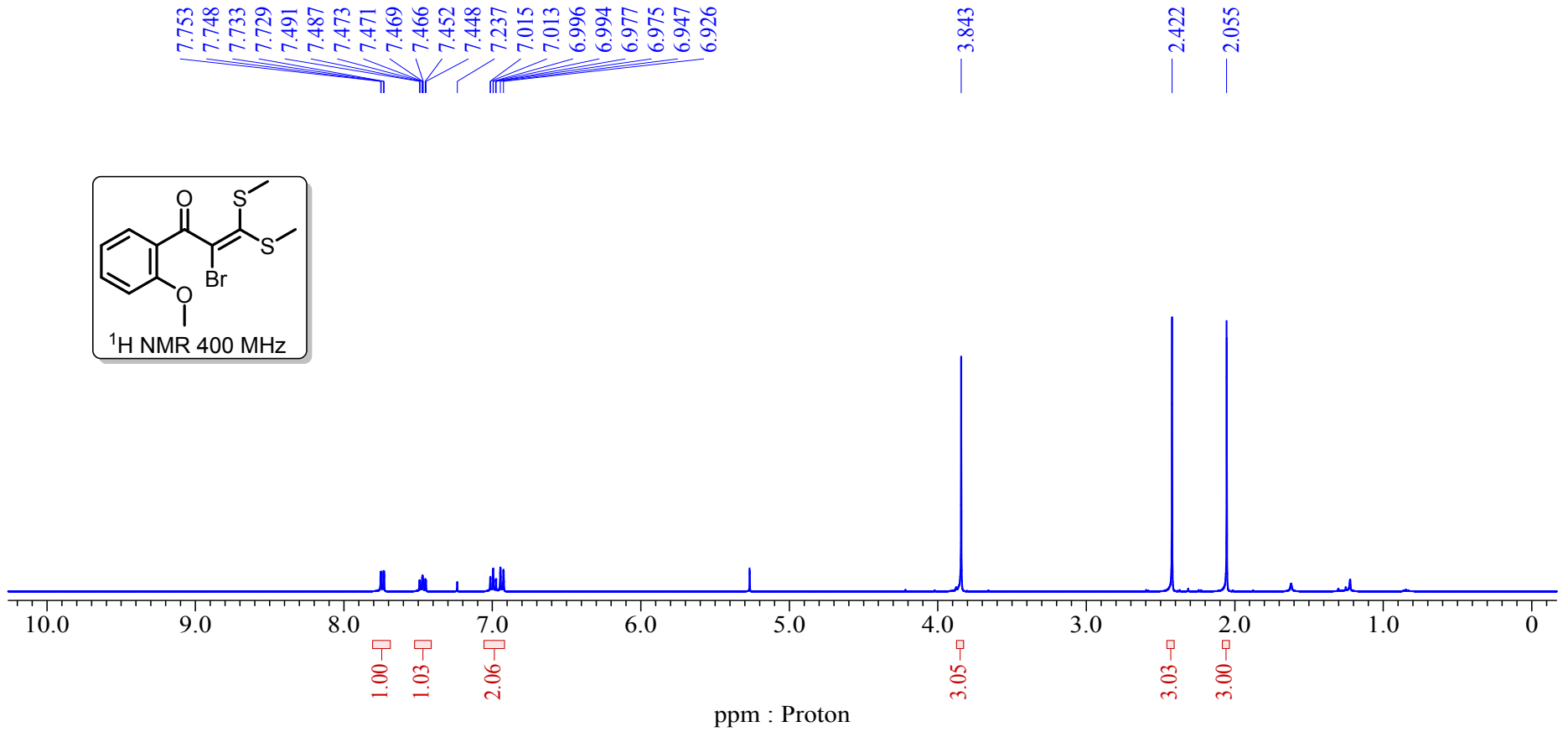


Fig. 7: ^{1}H-NMR spectrum of 2-bromo-1-(2-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2d**)

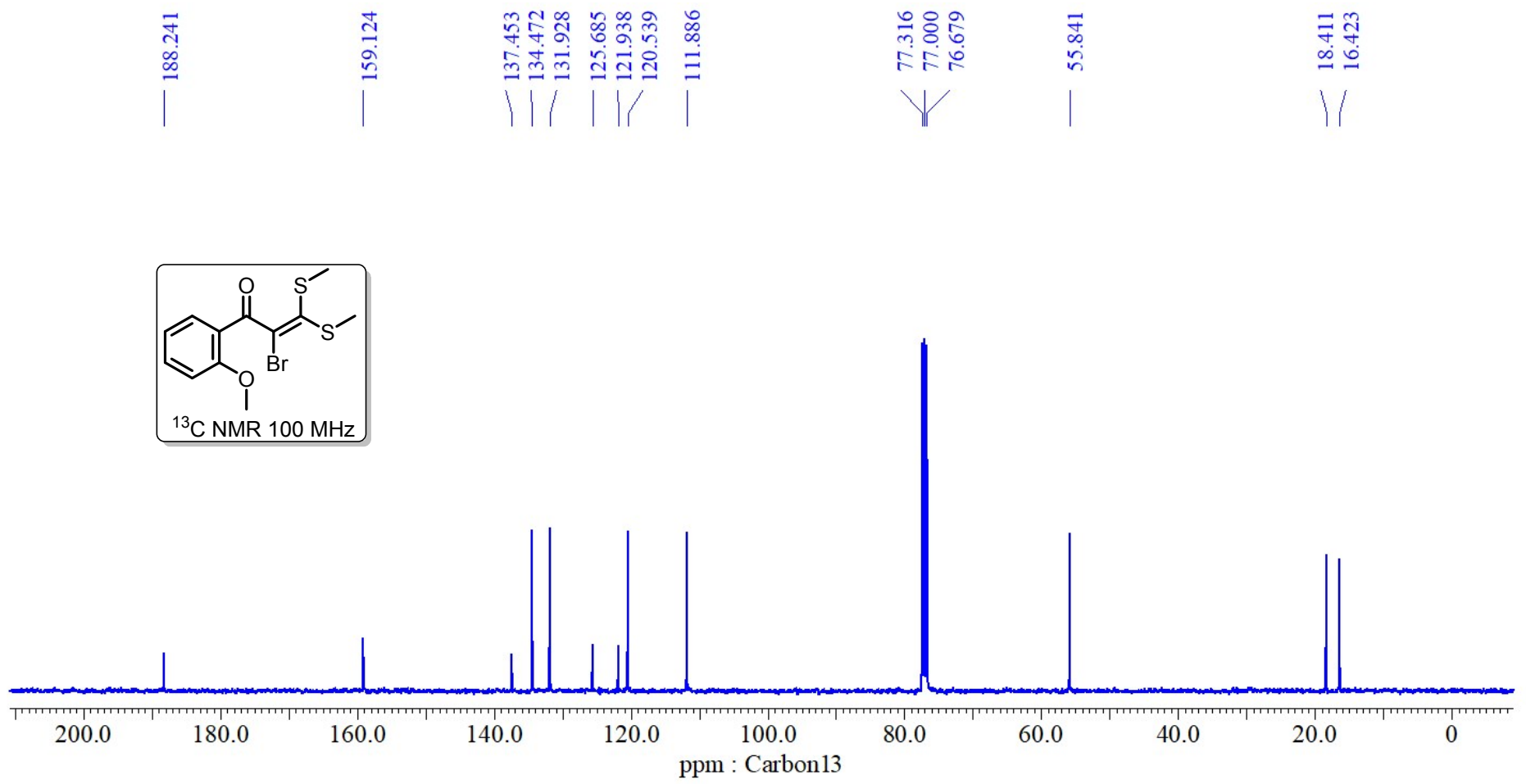


Fig. 8: ^{13}C-NMR spectrum of 2-bromo-1-(2-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2d**)

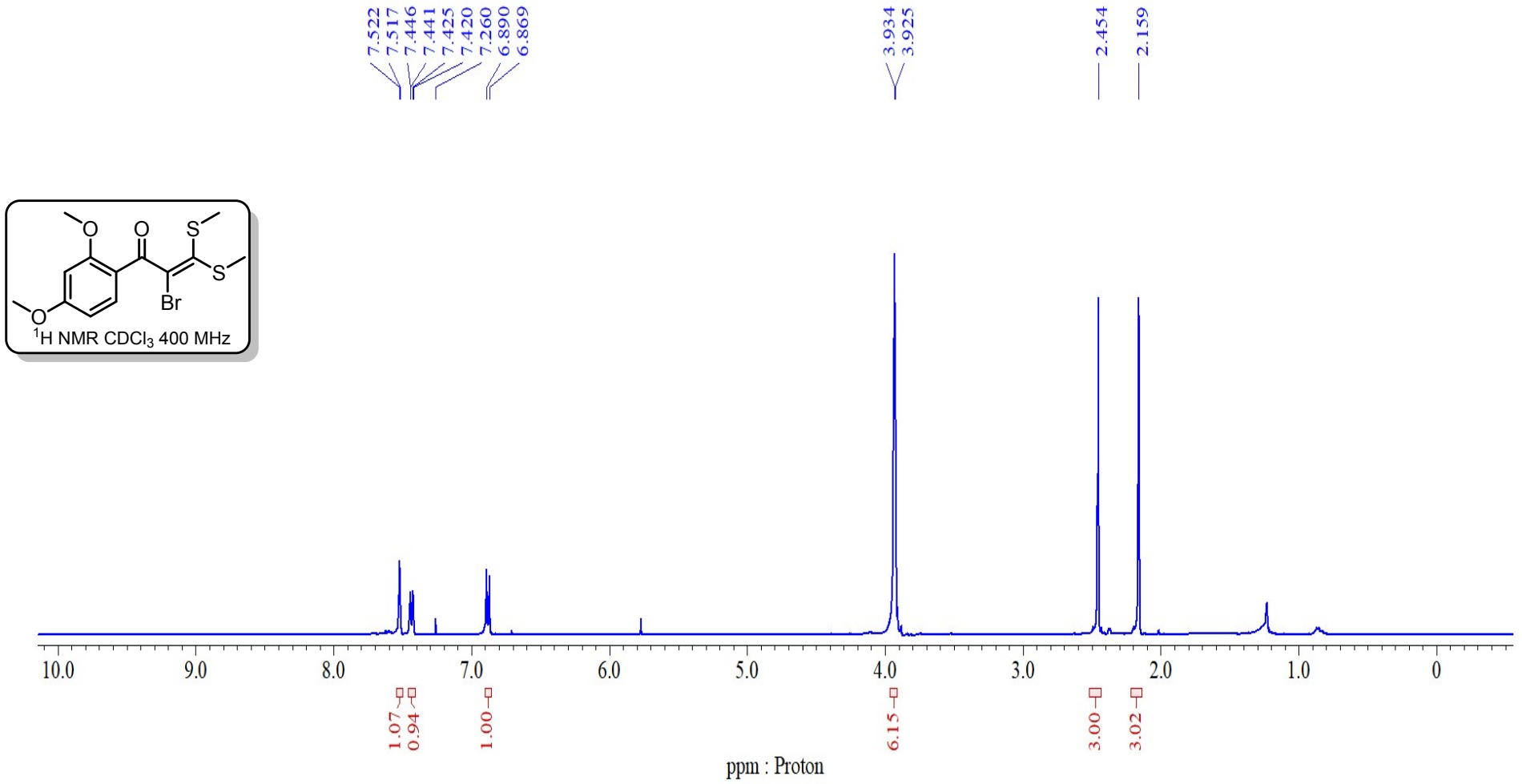


Fig. 9: ^{1}H-NMR spectrum of *2-bromo-1-(3,4-dimethoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2e**)*

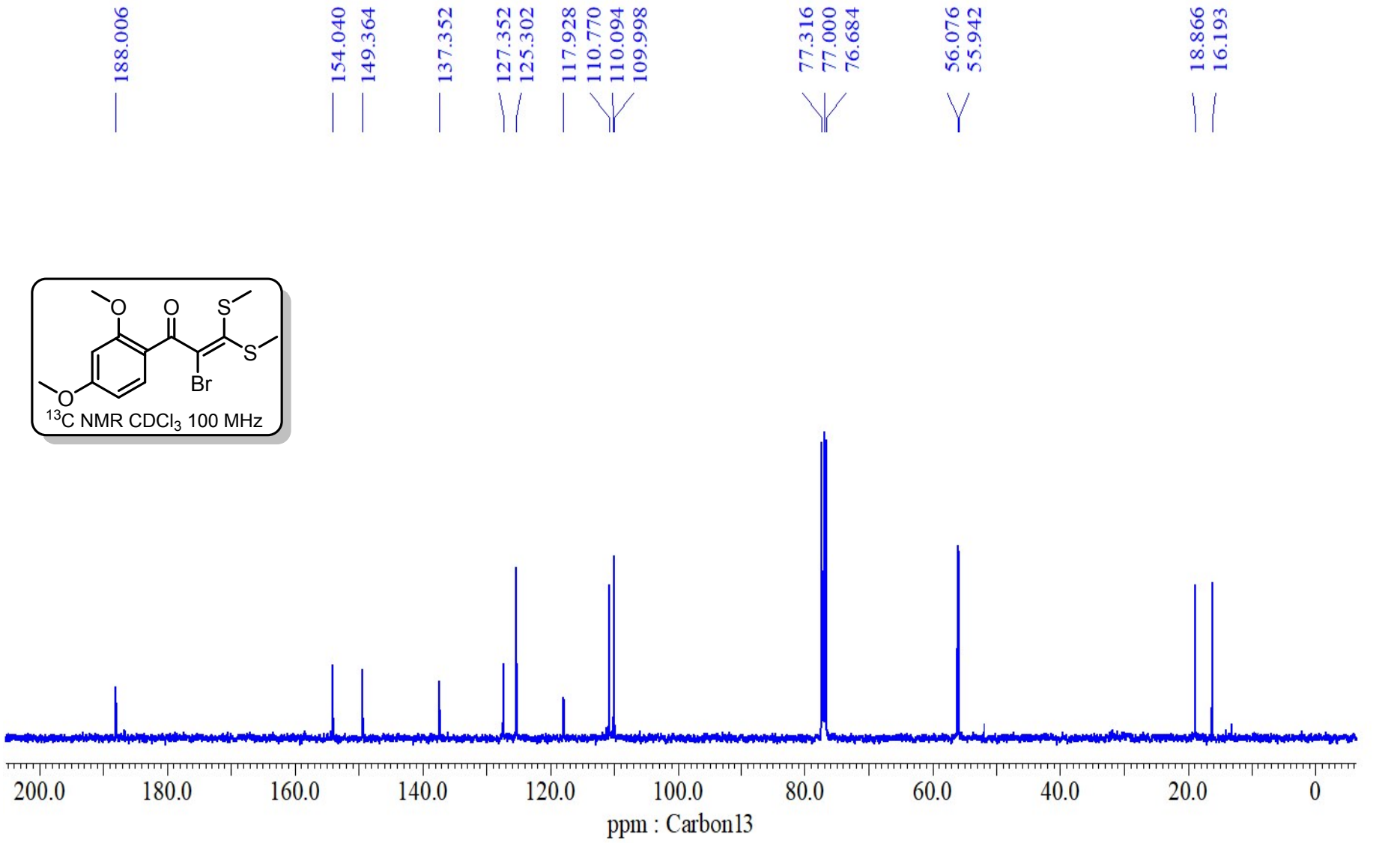


Fig. 10: ^{13}C-NMR spectrum of *2-bromo-1-(3,4-dimethoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2e**)*

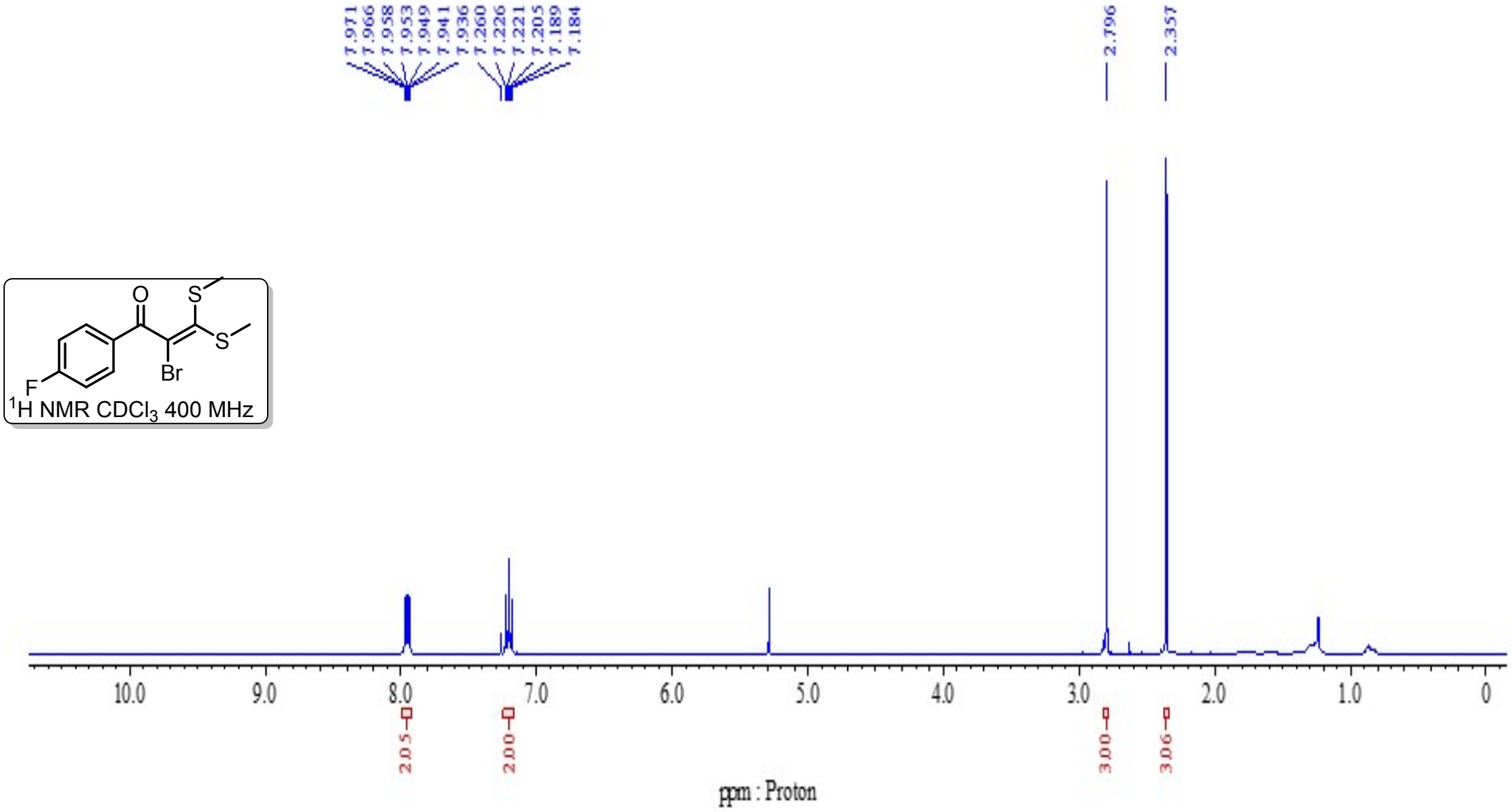


Fig. 11: ^{1}H-NMR spectrum of *2-bromo-1-(4-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2f**)*

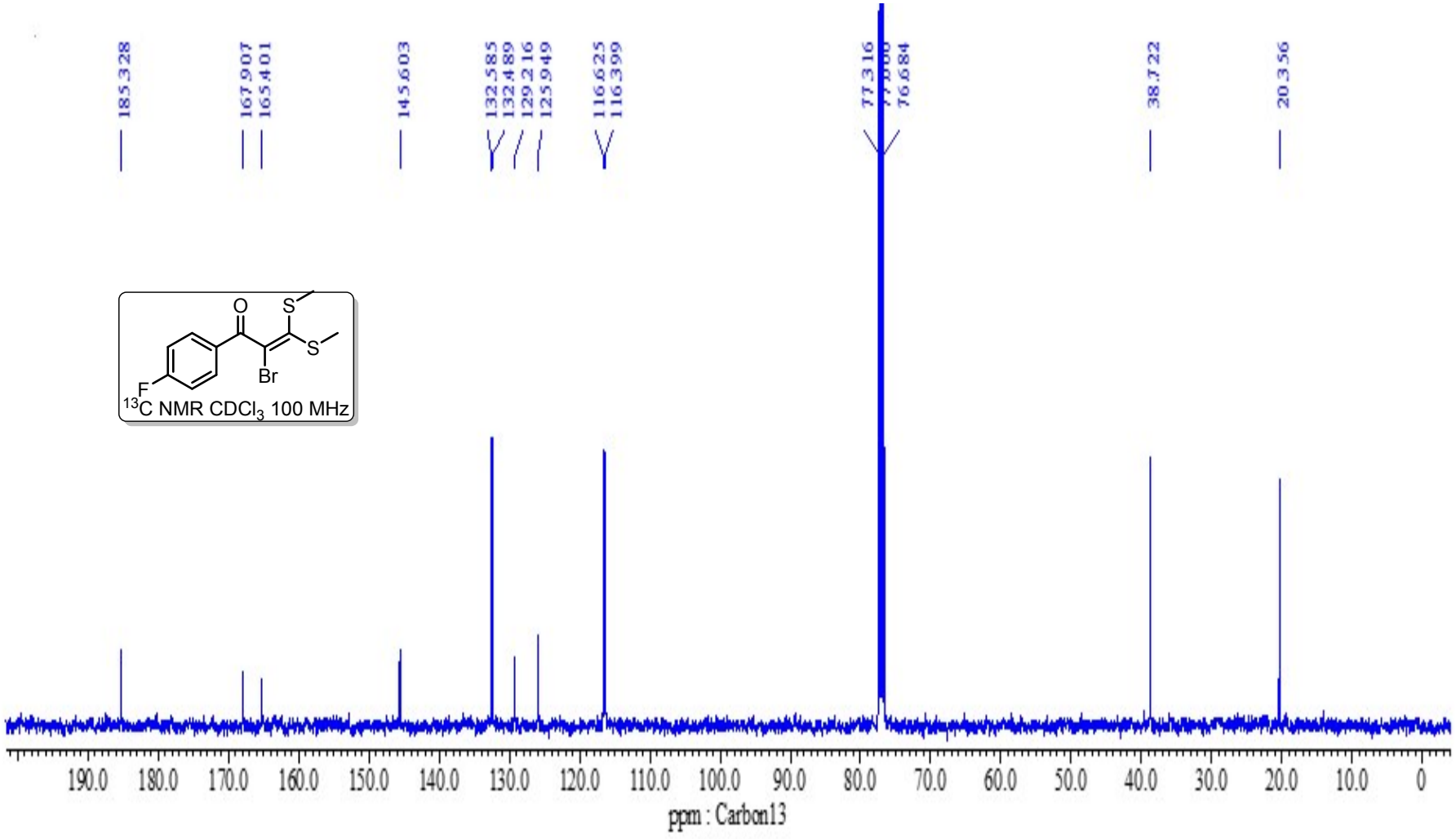


Fig. 12:[13]C-NMR spectrum of *2-bromo-1-(4-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2f**)*

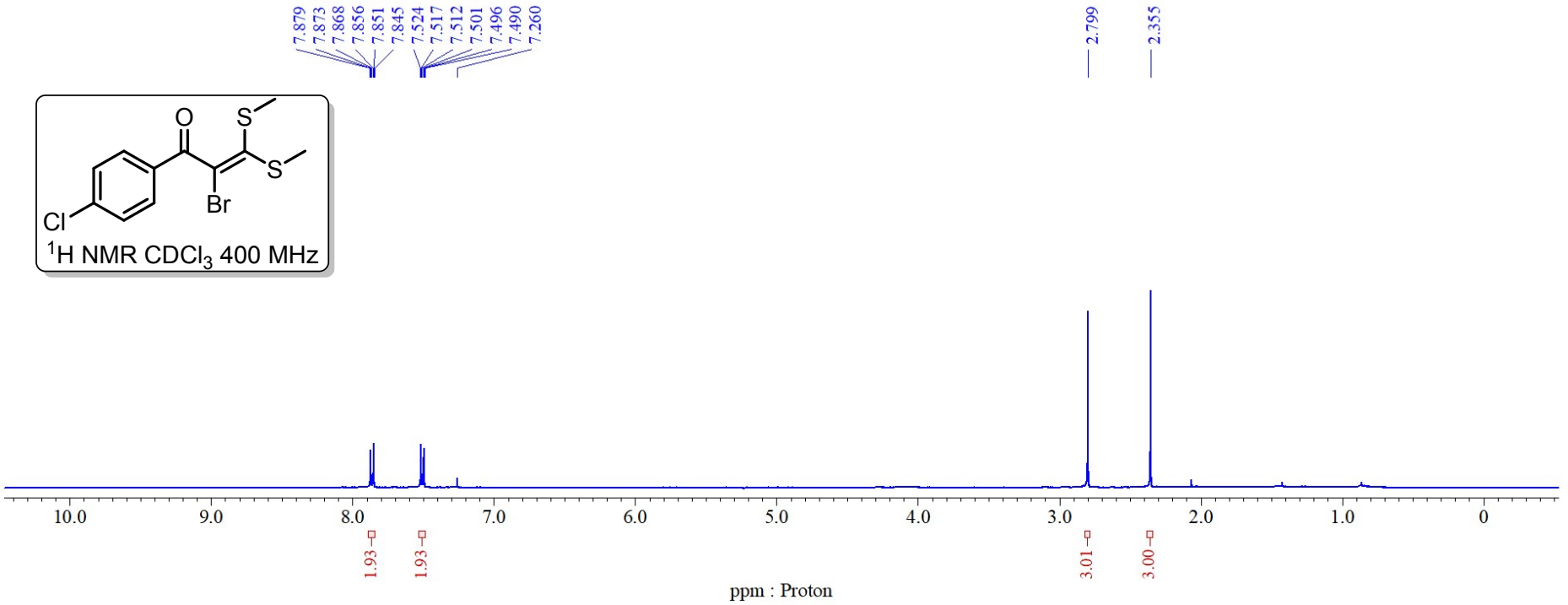


Fig. 13: ^{1}H-NMR spectrum of *2-bromo-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2g**)*

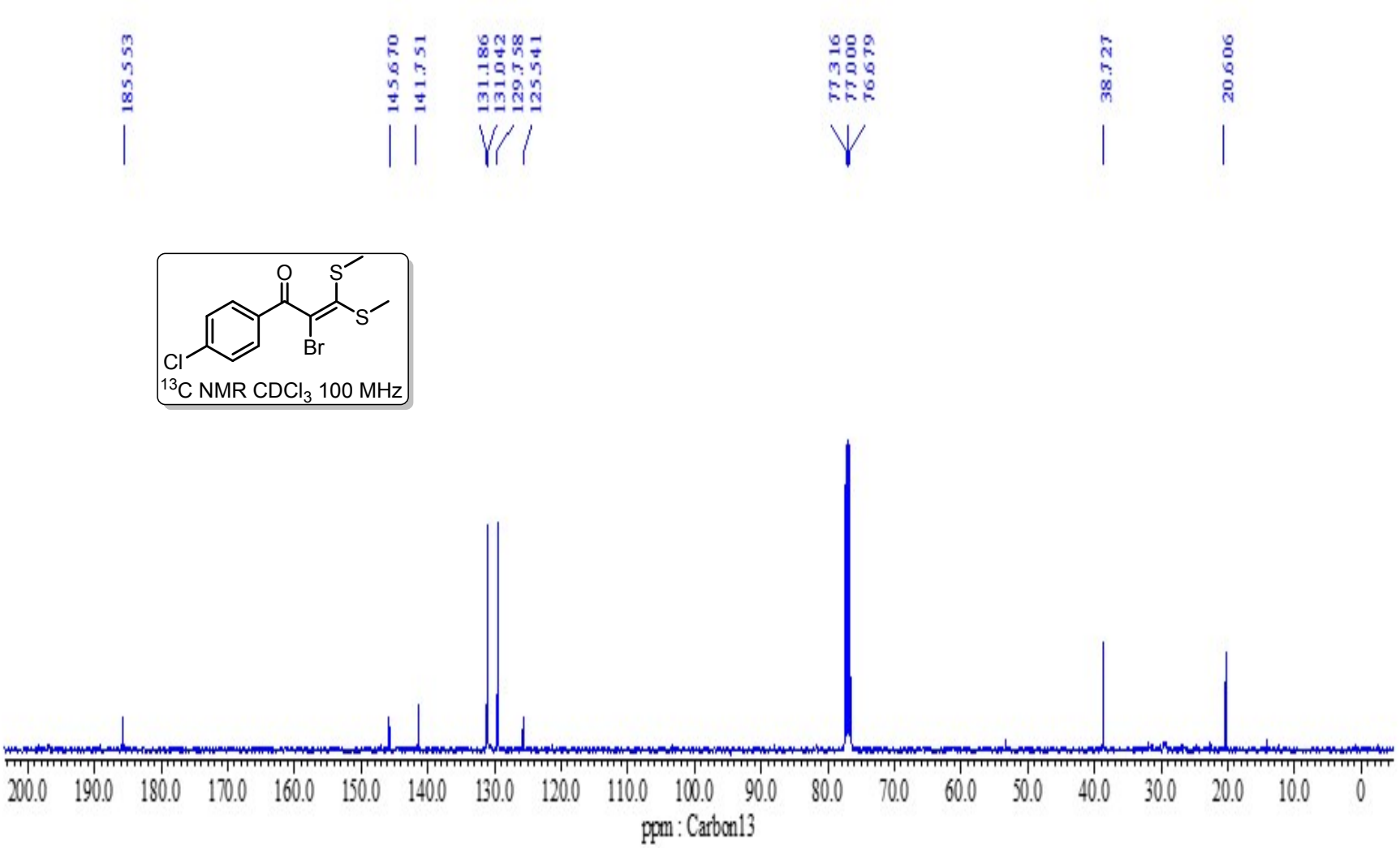


Fig.14: ^{13}C-NMR spectrum of *2-bromo-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2g**)*

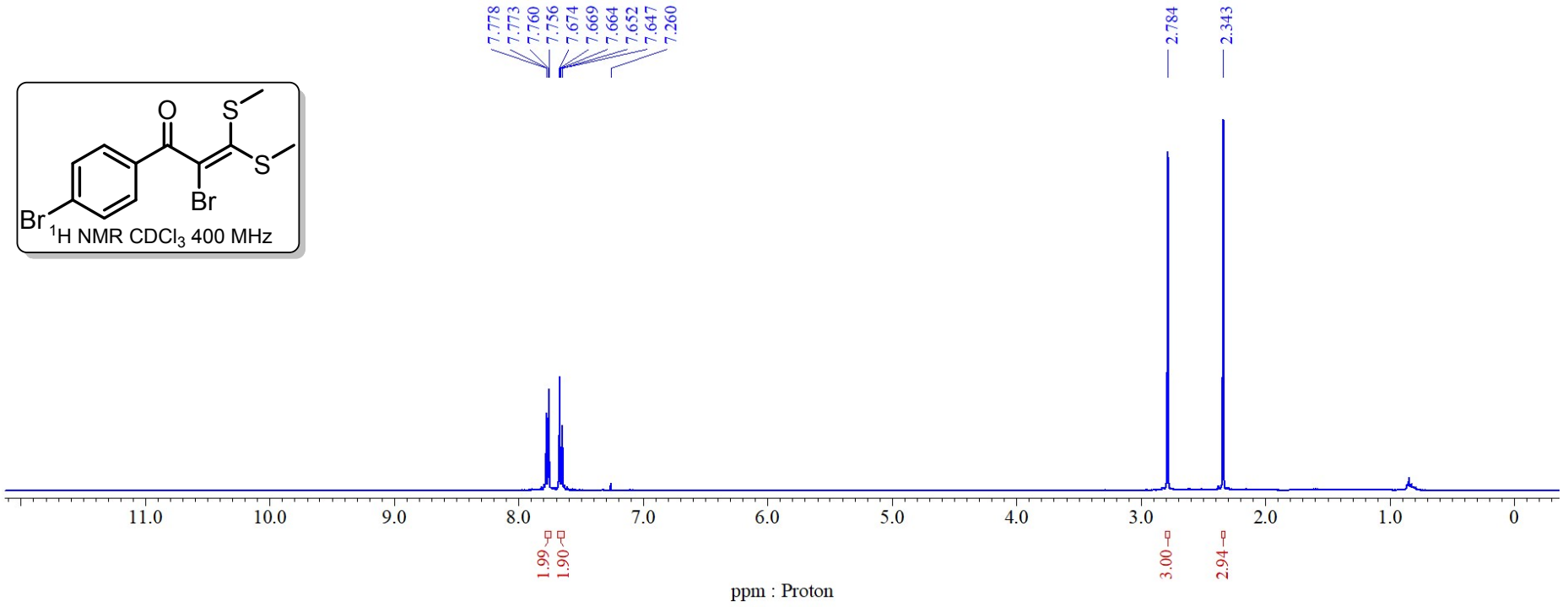


Fig. 15: ^{1}H-NMR spectrum of *2-bromo-1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2h**)*

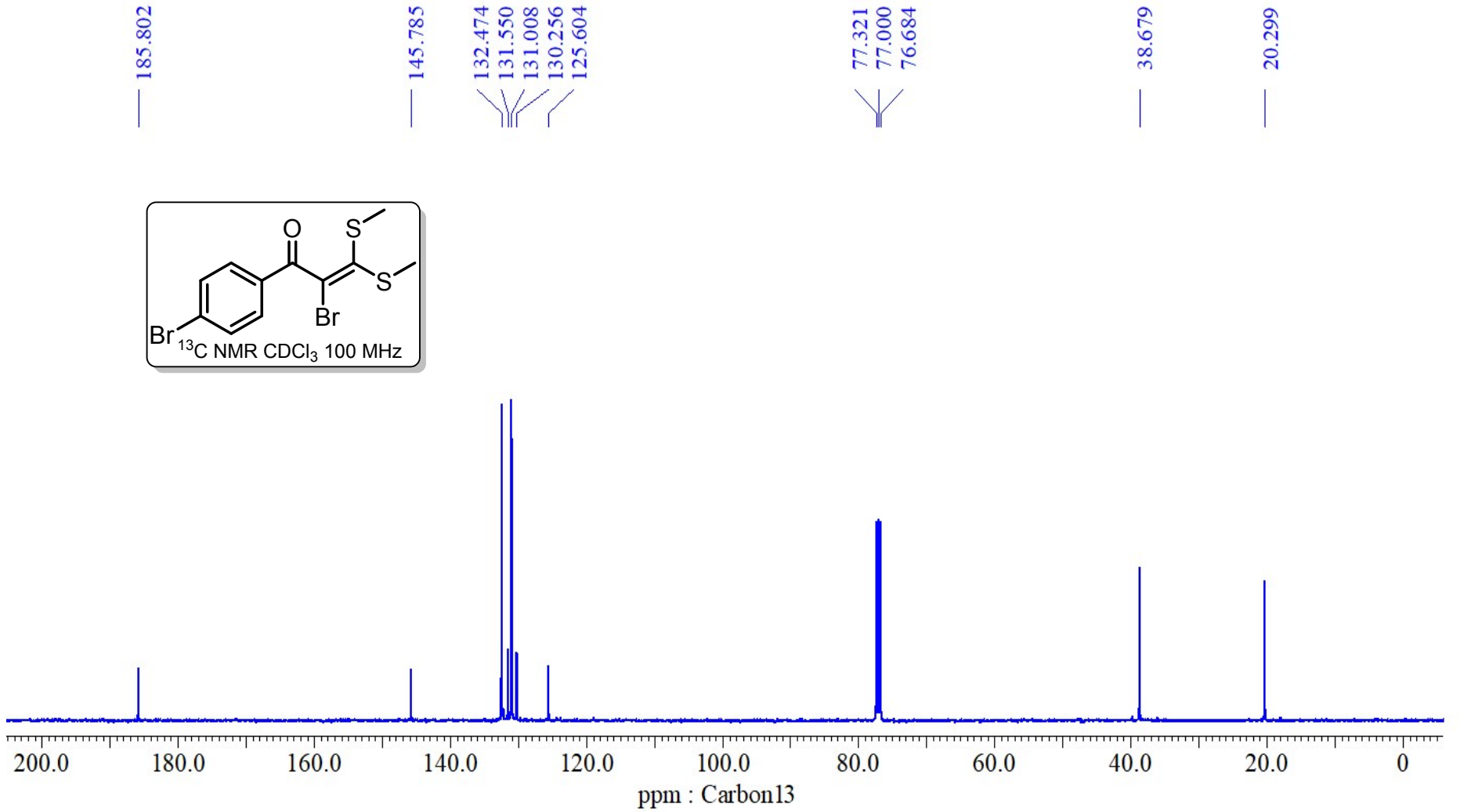


Fig. 16: ^{13}C-NMR spectrum of *2-bromo-1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2h**)*

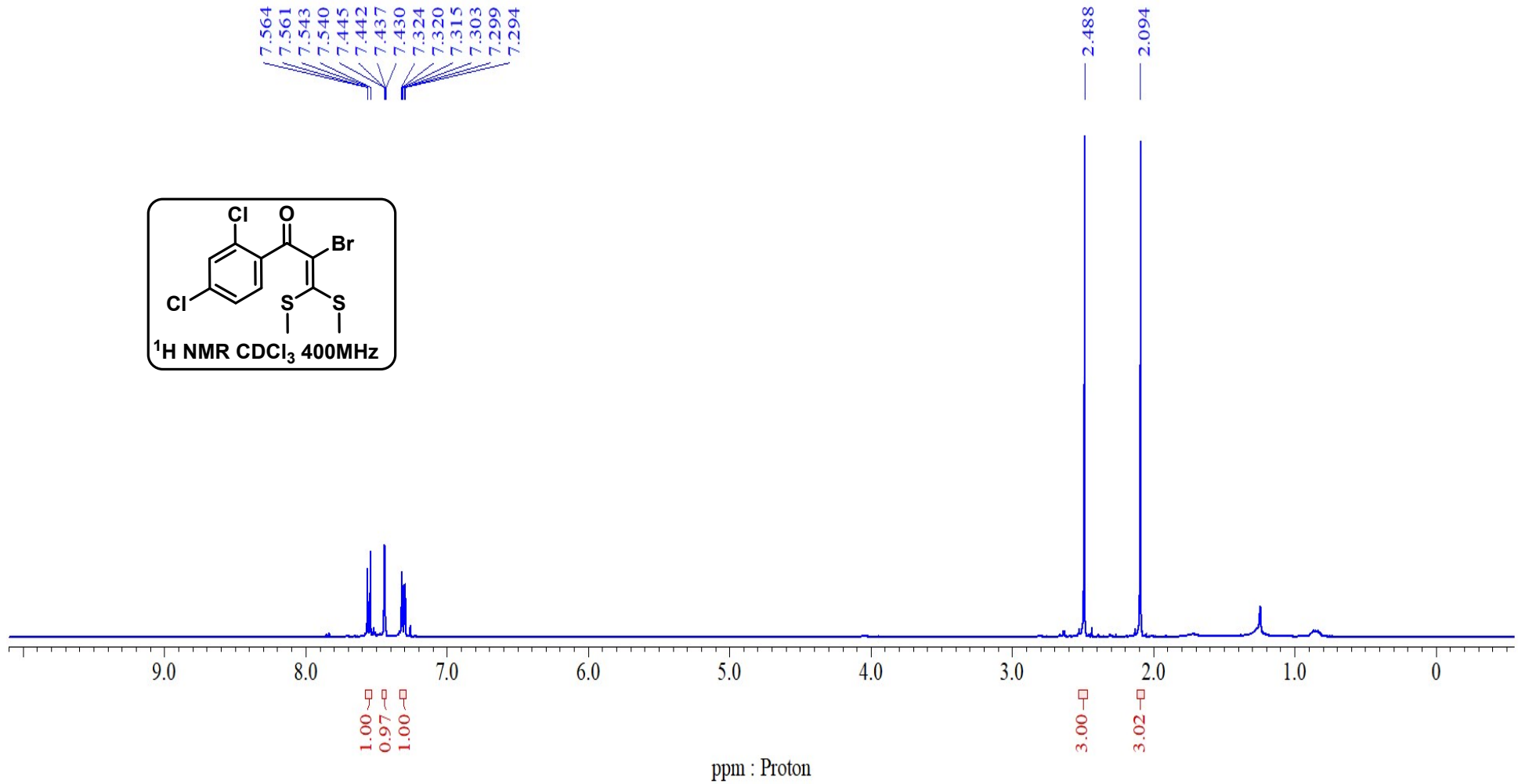


Fig. 17: ^{1}H-NMR spectrum of *2-bromo-1-(2,4-dichlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2i**)*

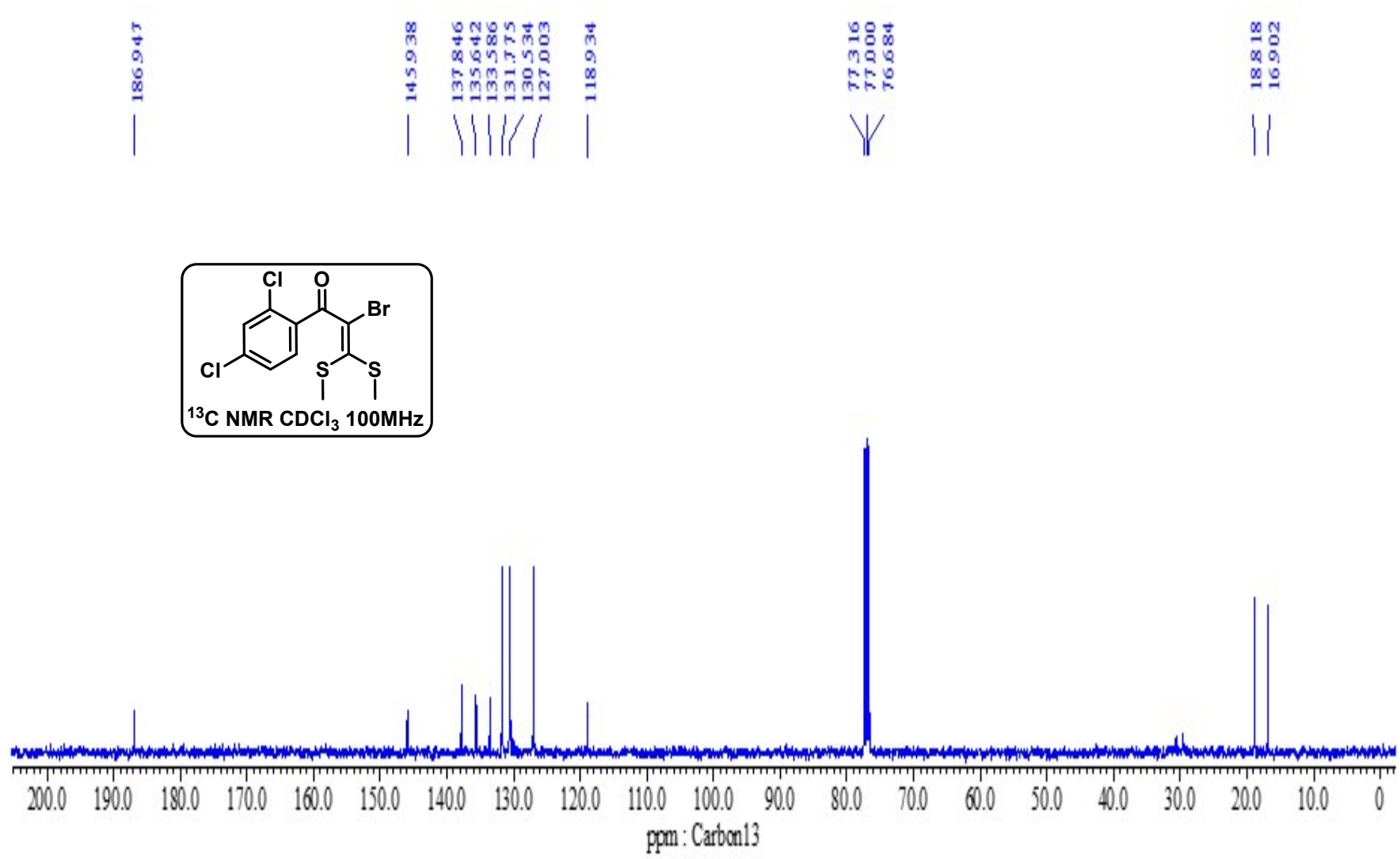


Fig. 18: ^{13}C-NMR spectrum of *2-bromo-1-(2,4-dichlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2i**)*

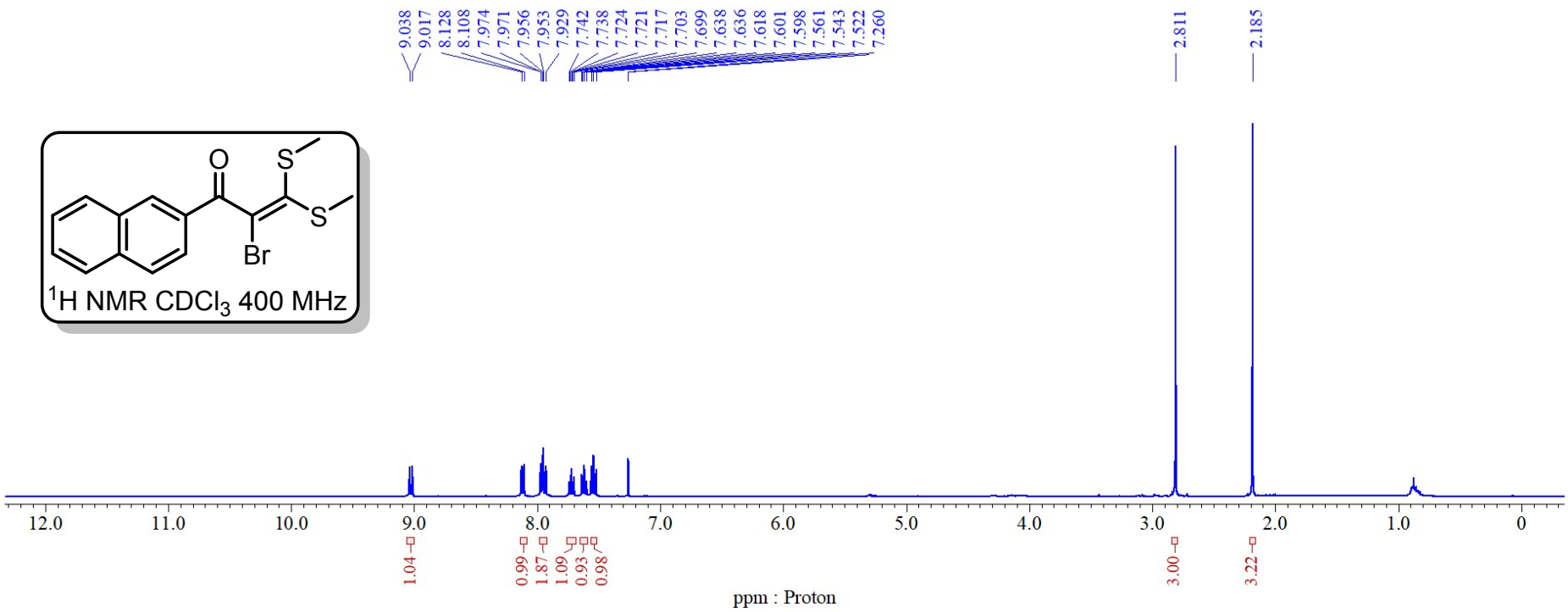


Fig. 19: ^{1}H NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl) prop-2-en-1-one* (***2j***)

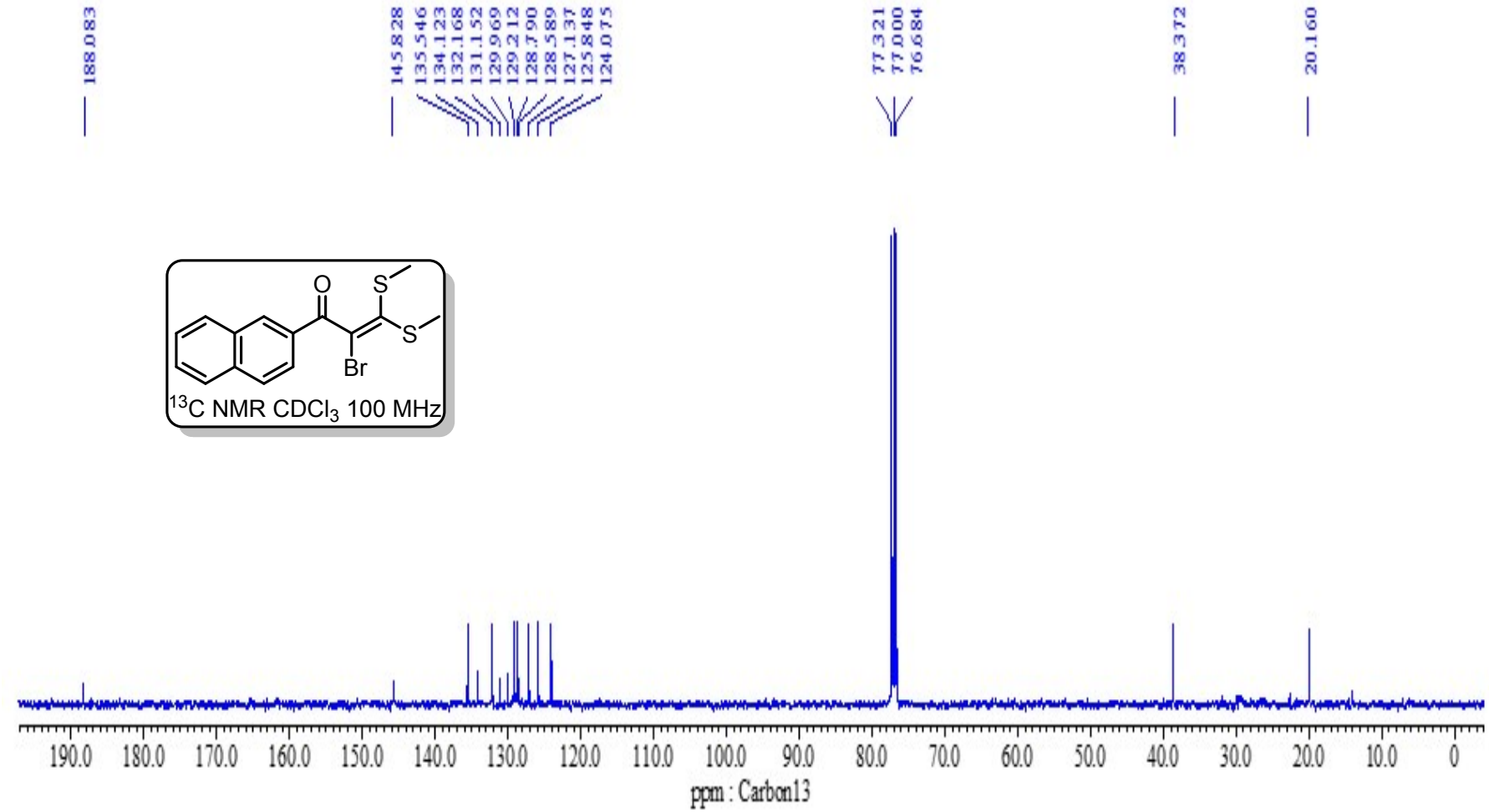


Fig. 20: ^{13}C NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl) prop-2-en-1-one (**2j**)*

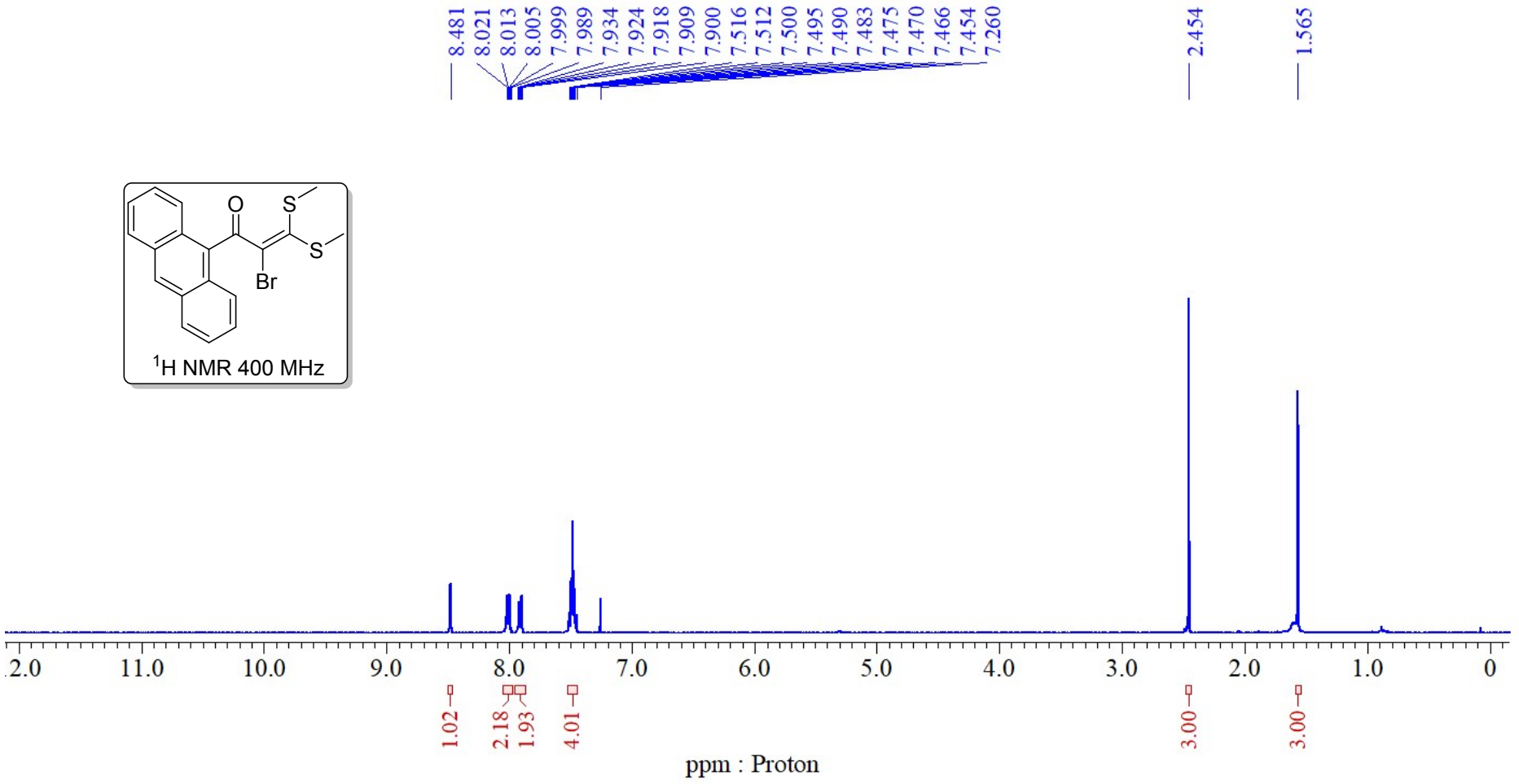


Fig. 21: ^{1}H NMR spectrum 1-(anthracen-9-yl)-2-bromo-3,3-bis(methylthio)prop-2-en-1-one (**2k**)

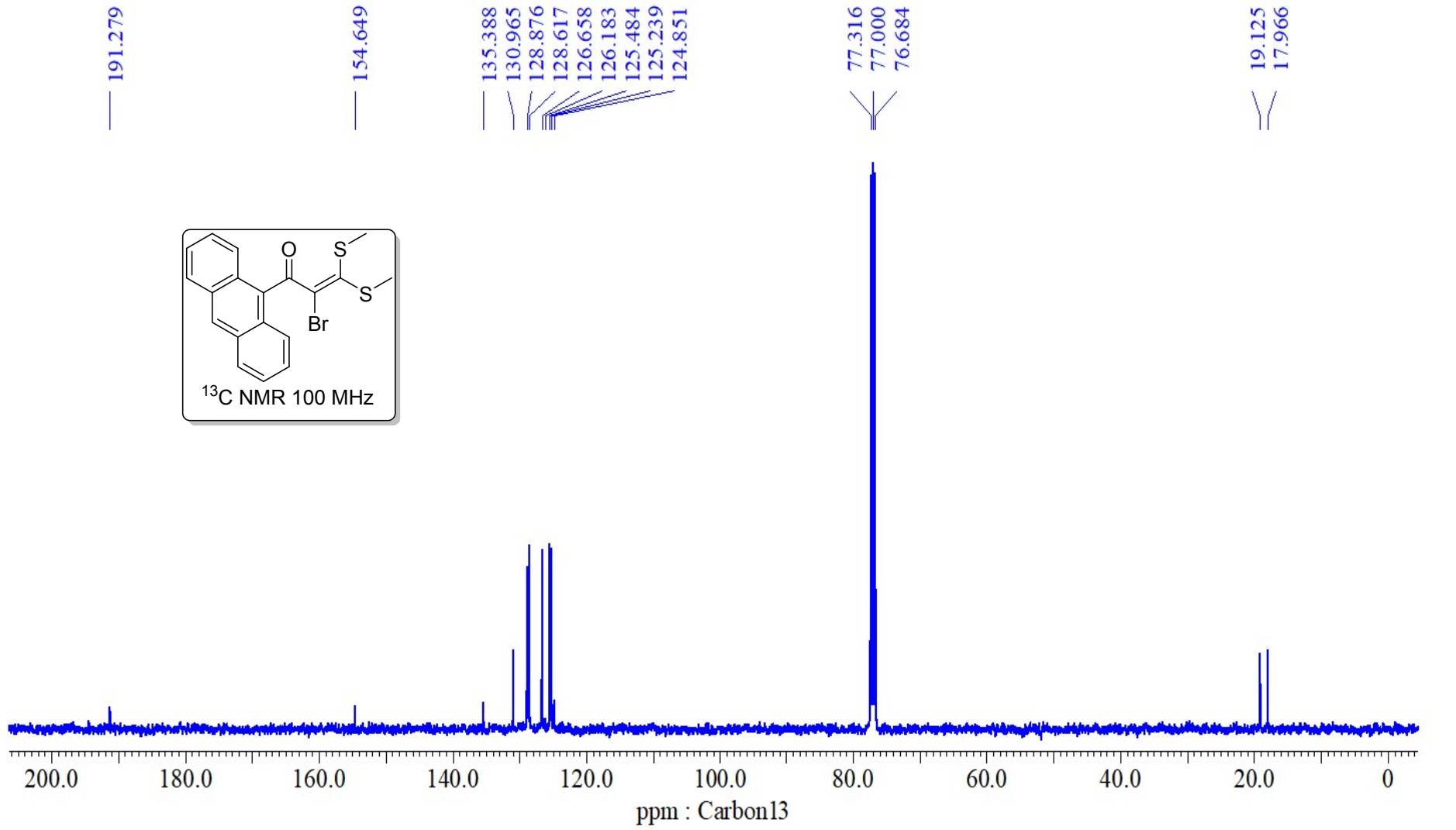


Fig. 22: ^{13}C NMR spectrum of 1-(anthracen-9-yl)-2-bromo-3,3-bis(methylthio)prop-2-en-1-one (**2k**)

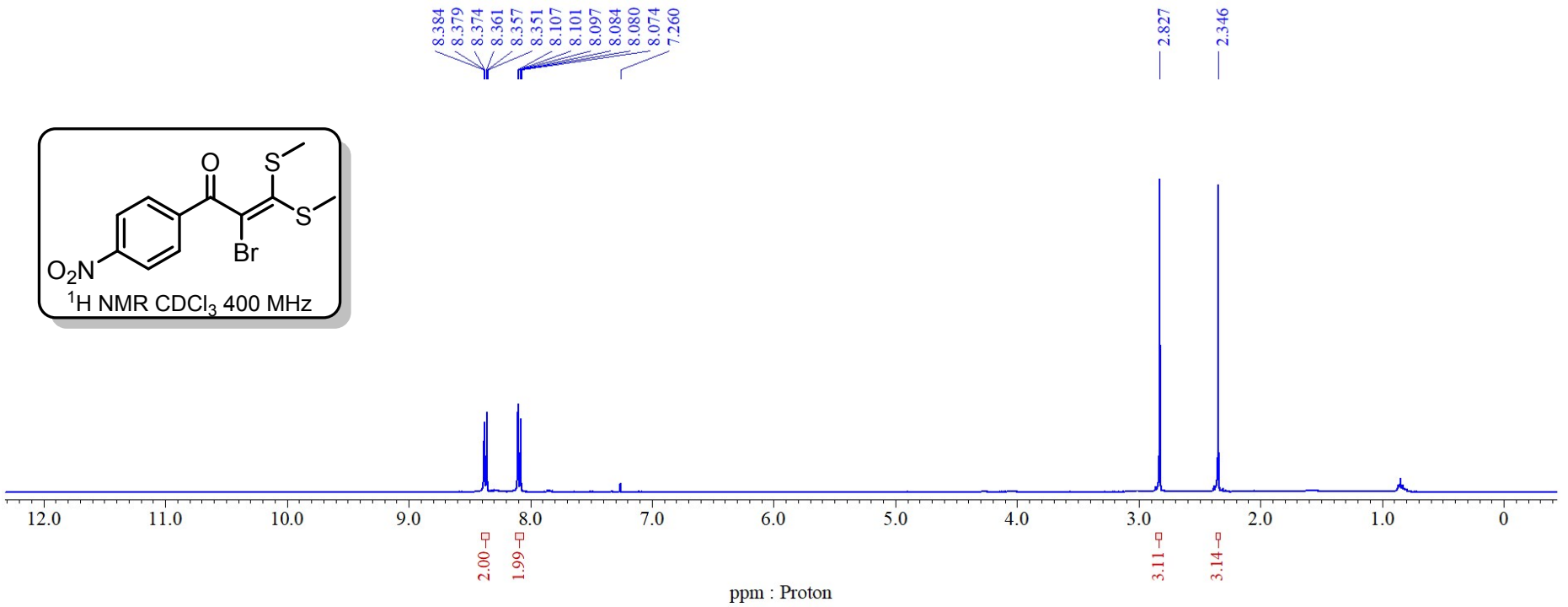


Fig. 23: ^{1}H NMR spectrum *2-bromo-3,3-bis(methylthio)-1-(4-nitrophenyl)prop-2-en-1-one (**2l**)*

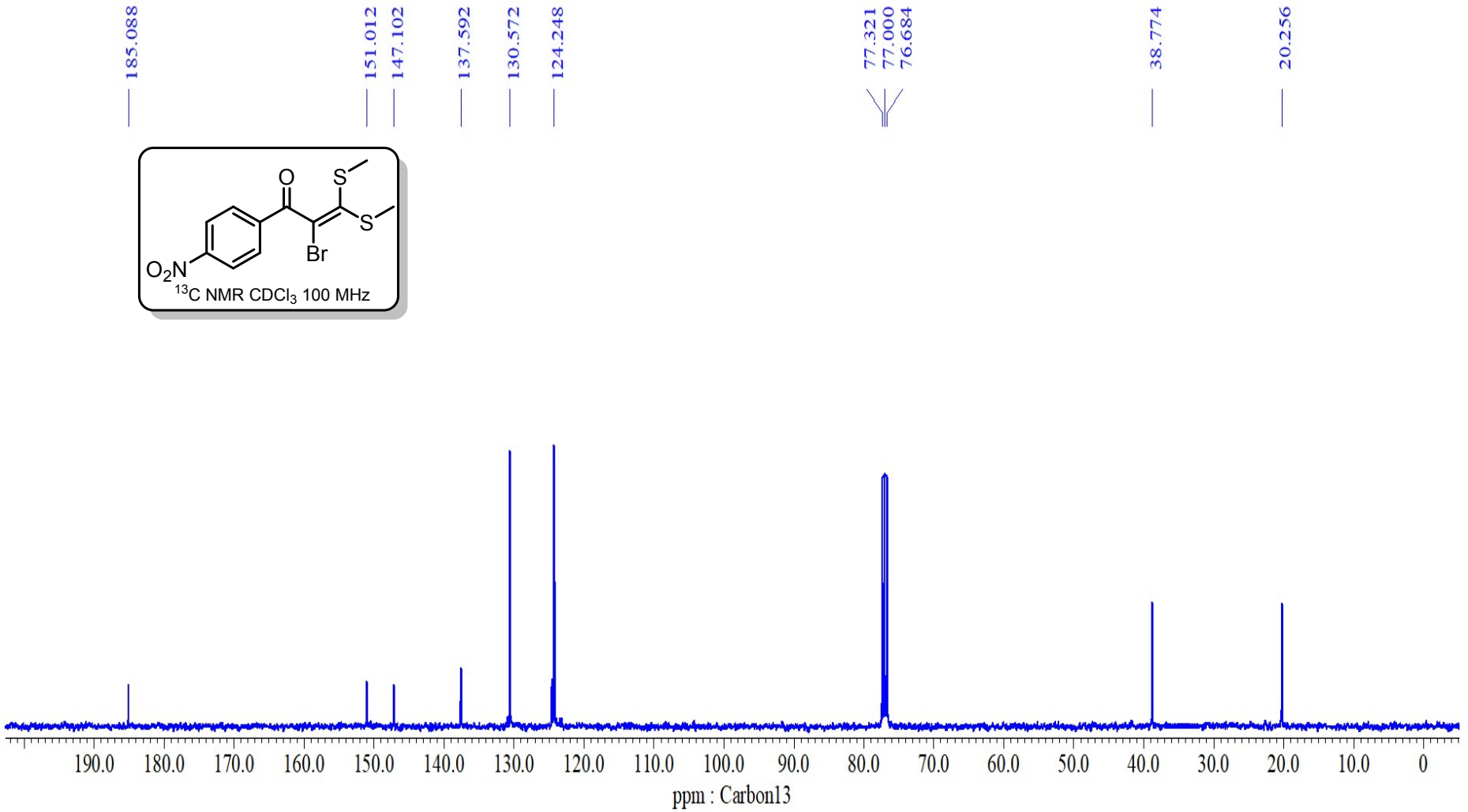


Fig. 24: ^{13}C-NMR spectrum *2-bromo-3,3-bis(methylthio)-1-(4-nitrophenyl)prop-2-en-1-one (**2l**)*

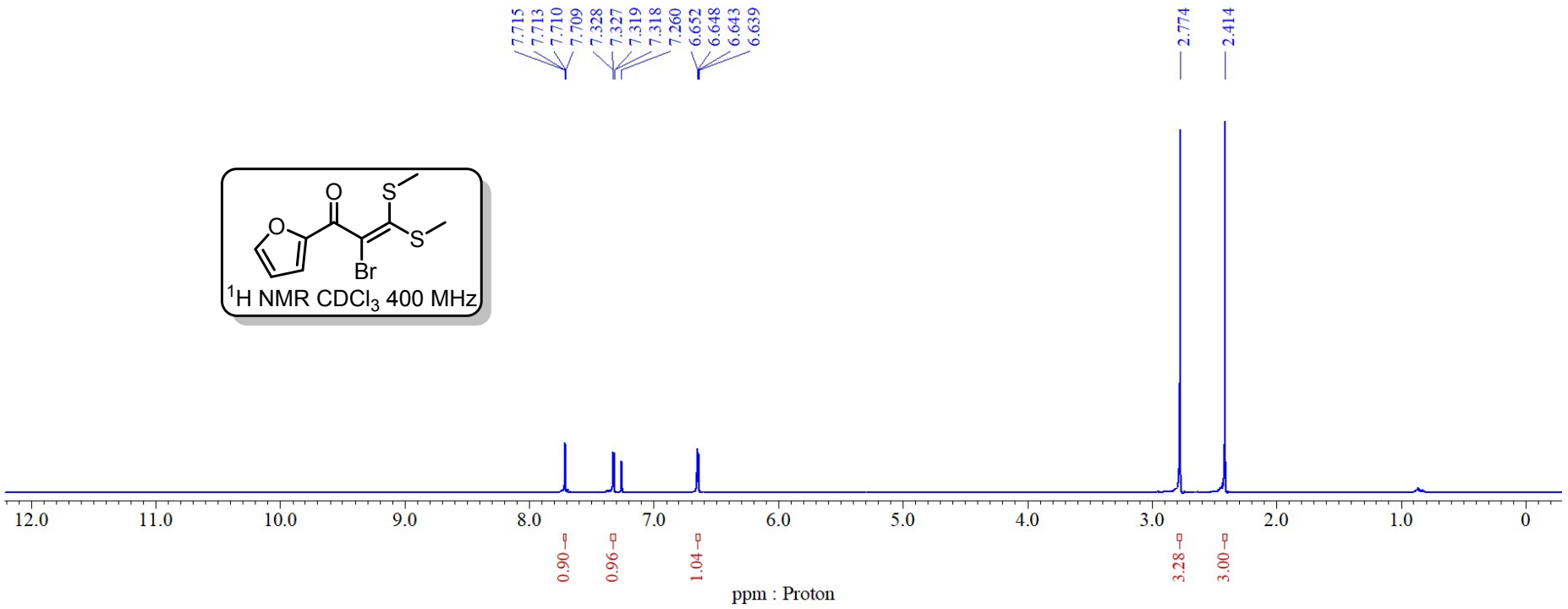


Fig. 25: ^{1}H-NMR spectrum of *2-bromo-1-(furan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (**2m**)*

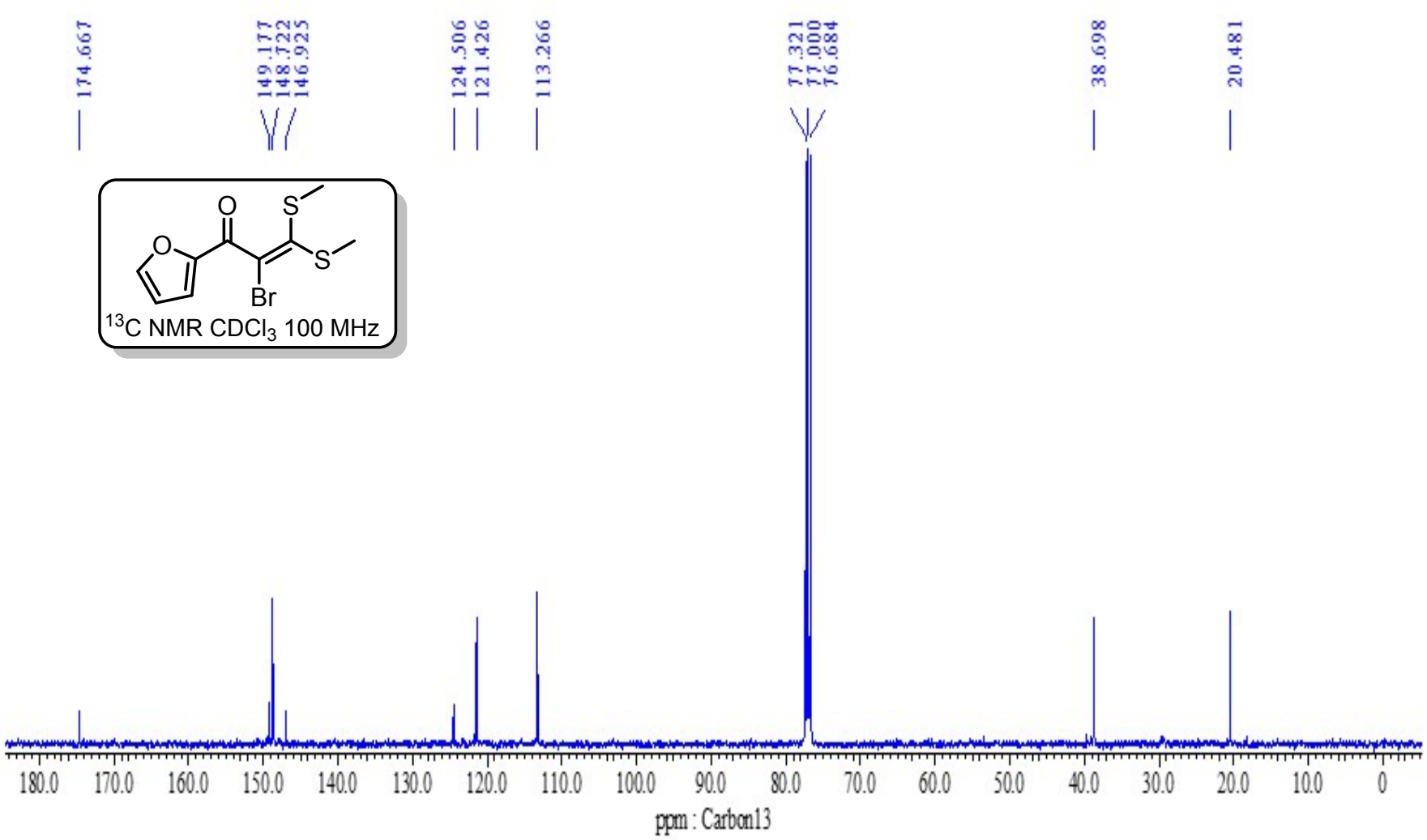


Fig. 26: ^{13}C-NMR spectrum of *2-bromo-1-(furan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (**2m**)*

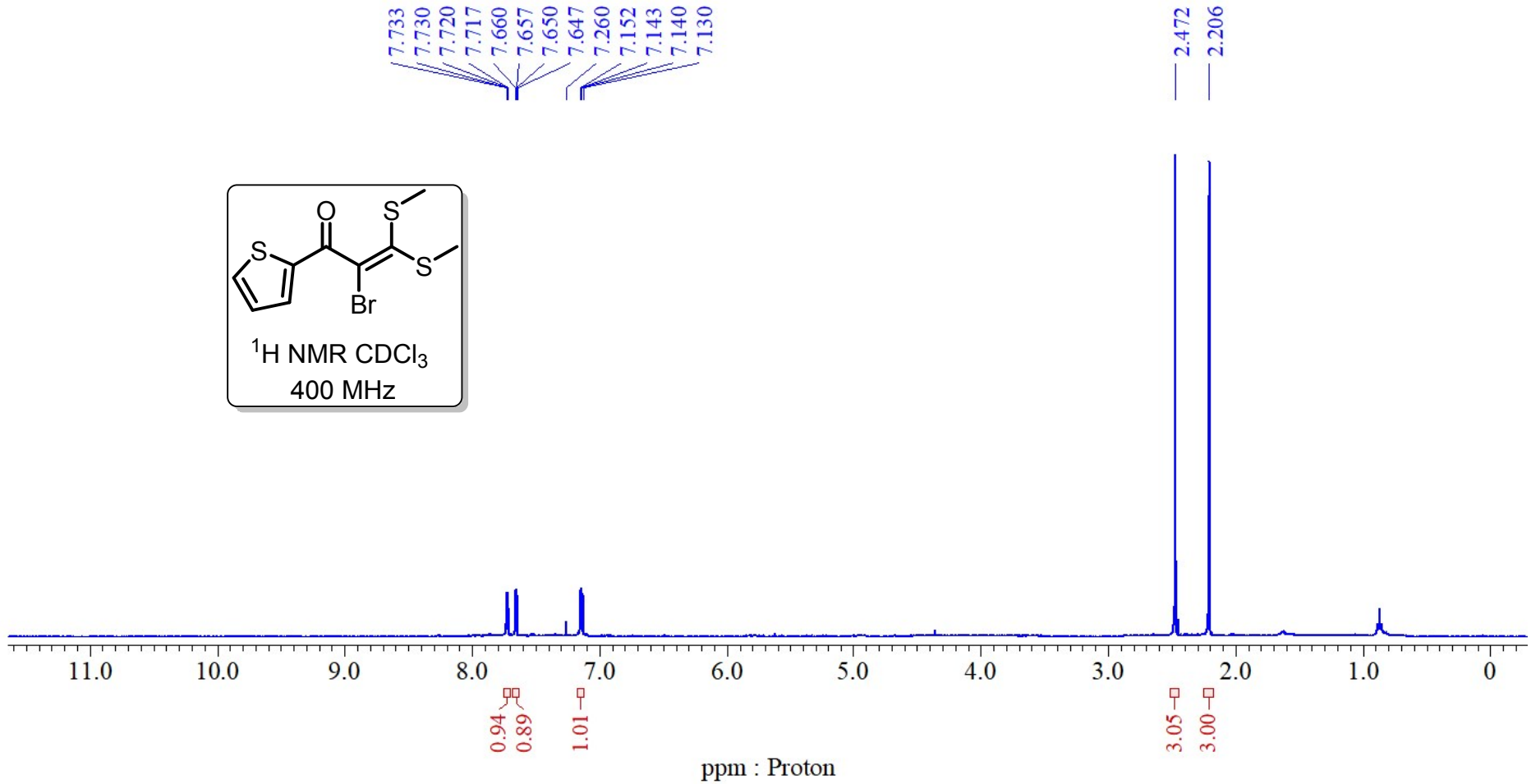


Fig. 27: ^{1}H-NMR spectrum of 2-bromo-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (**2n**)

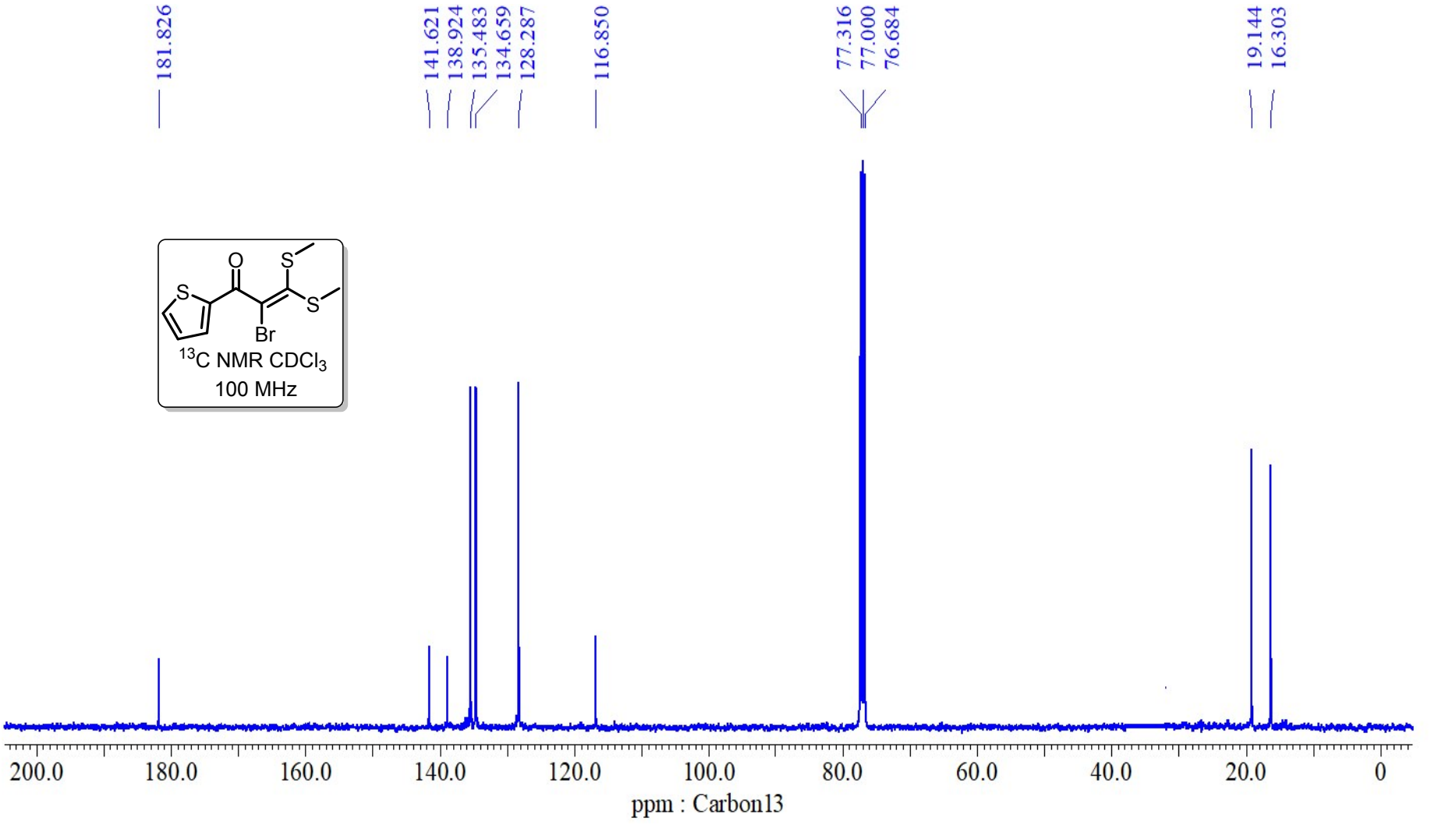


Fig. 28: ^{13}C-NMR spectrum 2-bromo-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (**2n**)

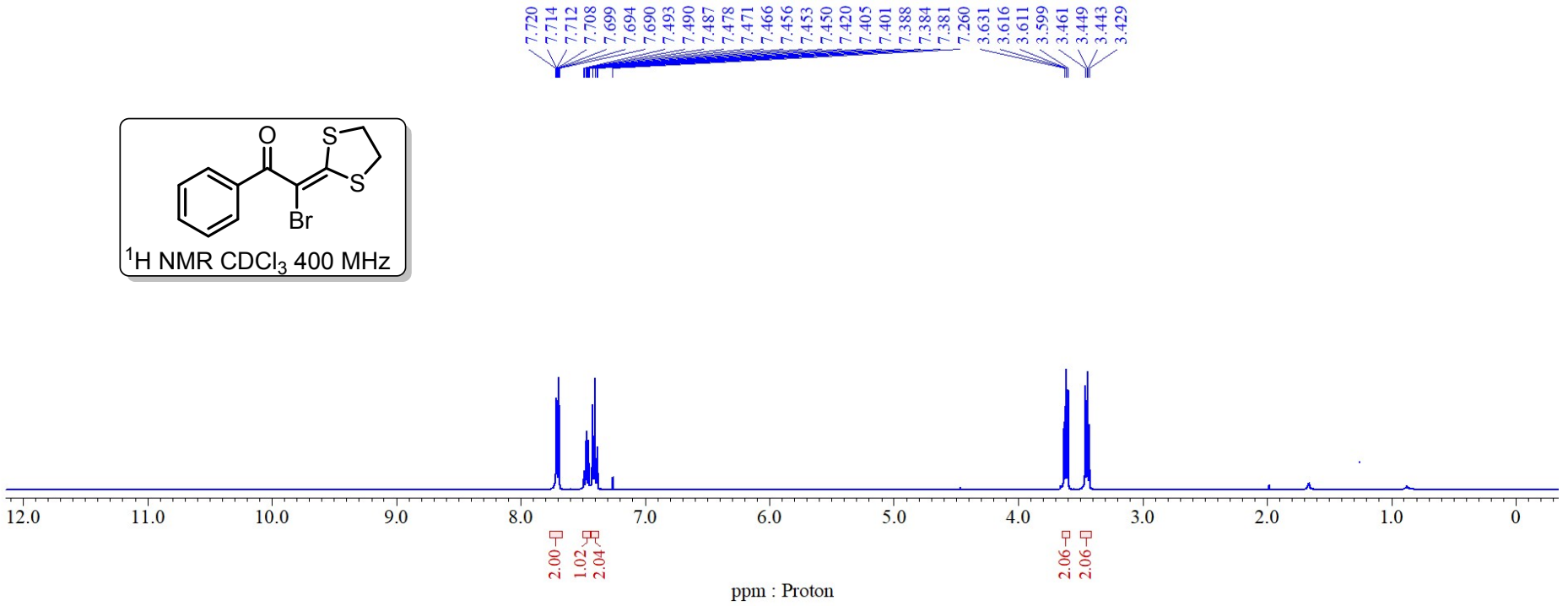


Fig. 29: ^{1}H-NMR spectrum of 2-bromo-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (**2o**)

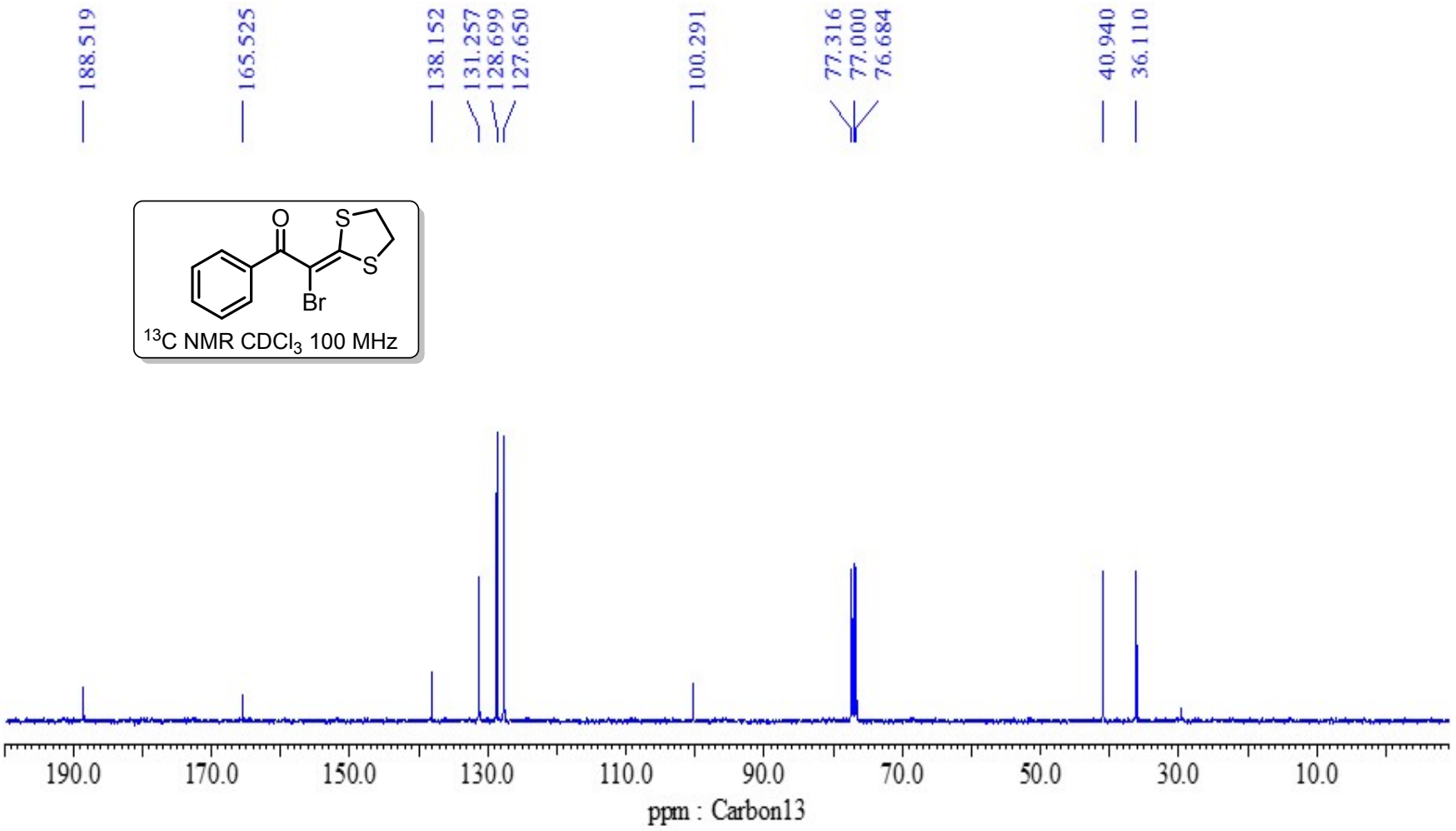


Fig. 30: ^{13}C-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (**2o**)*

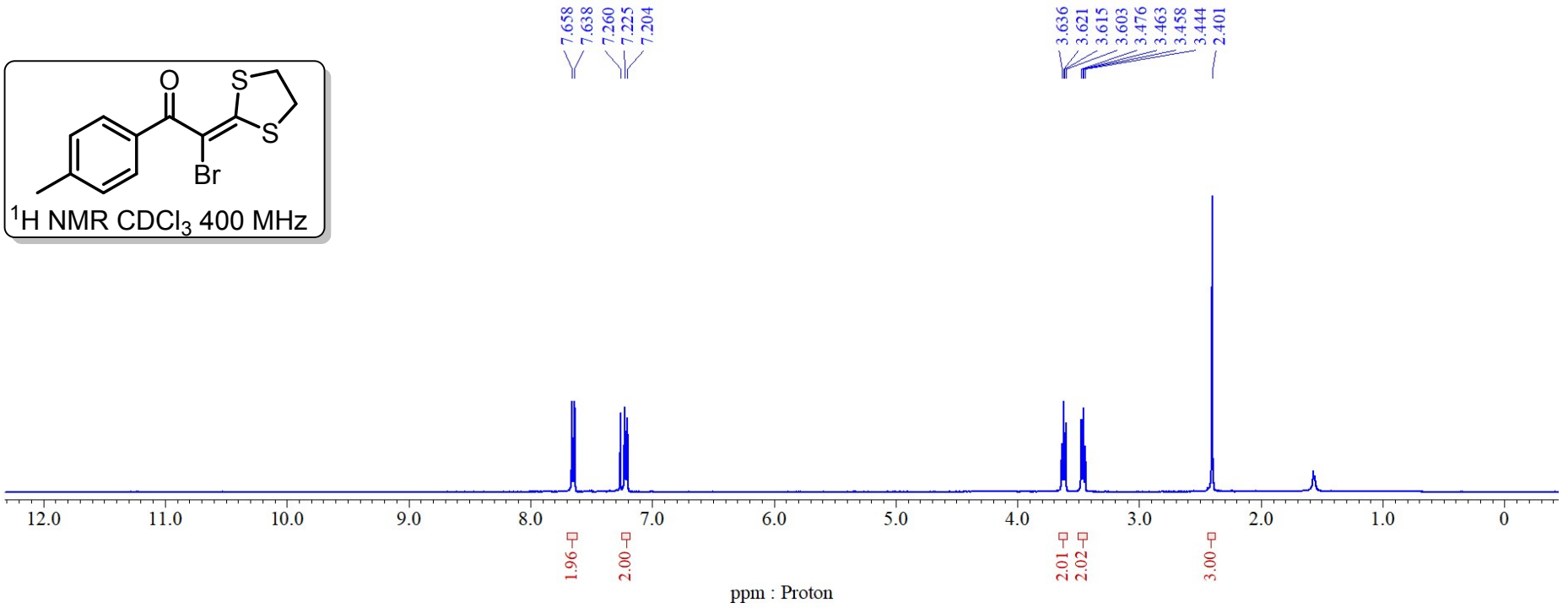


Fig. 31: ^{1}H-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (**2p**)*

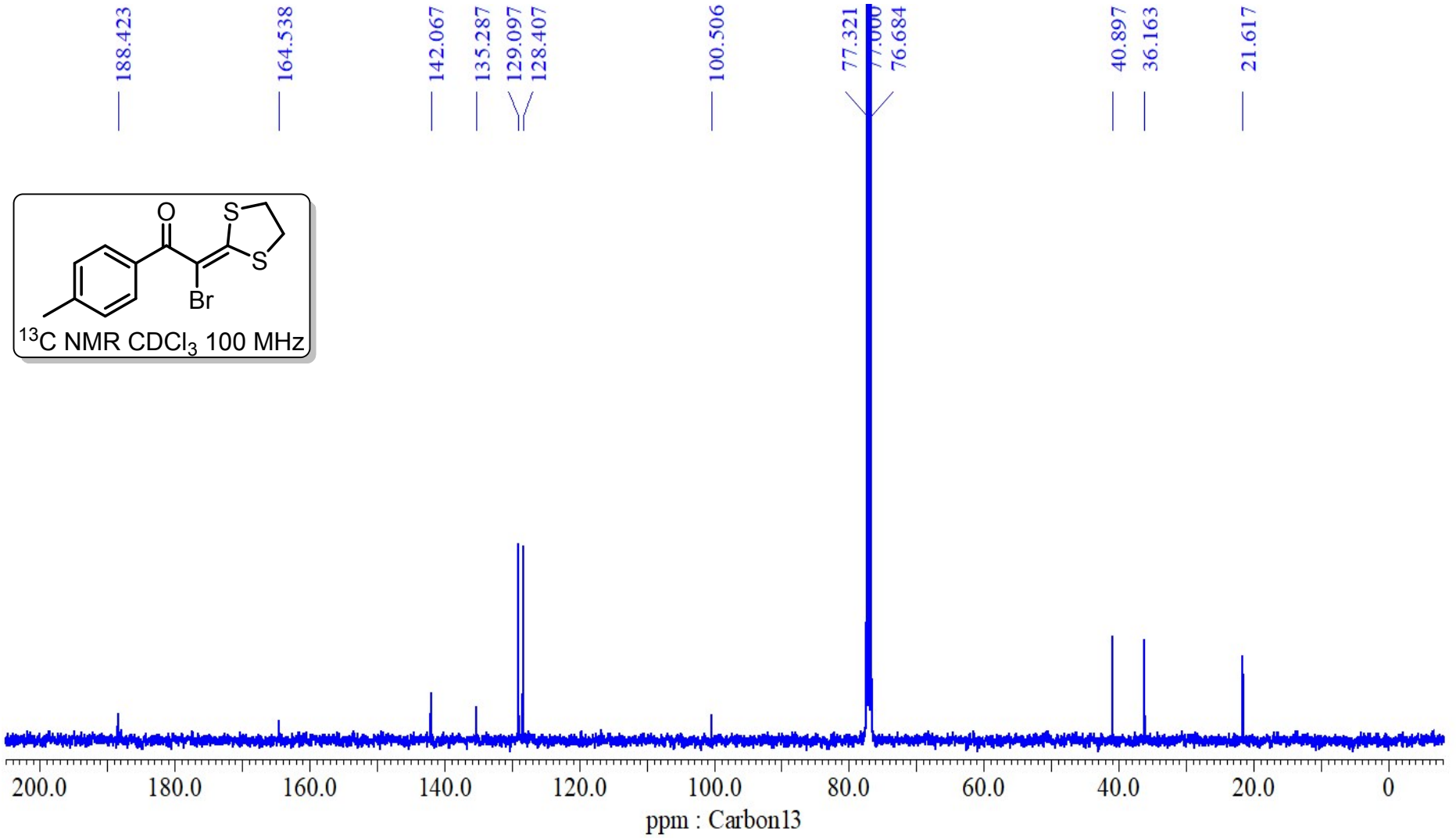


Fig. 32: ^{13}C-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(p-tolyl) ethan-1-one (**2p**)*

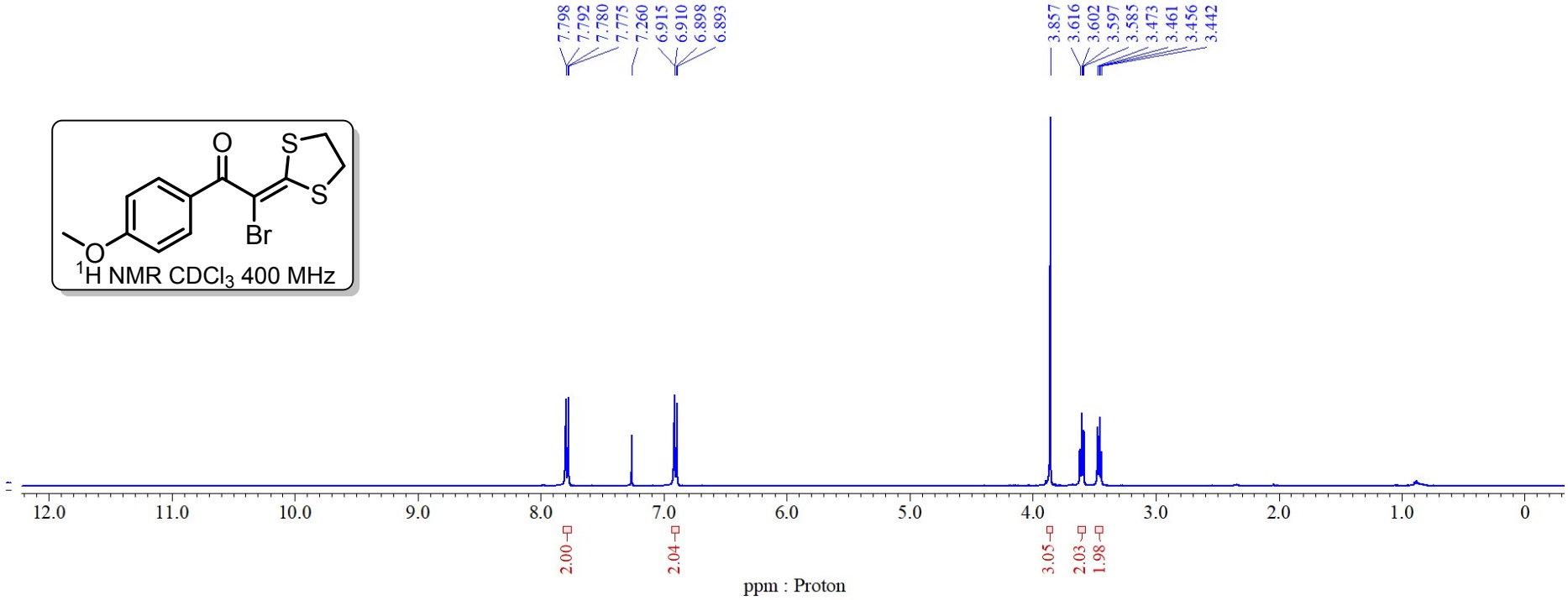


Fig. 33: ^{1}H-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one (**2q**)*

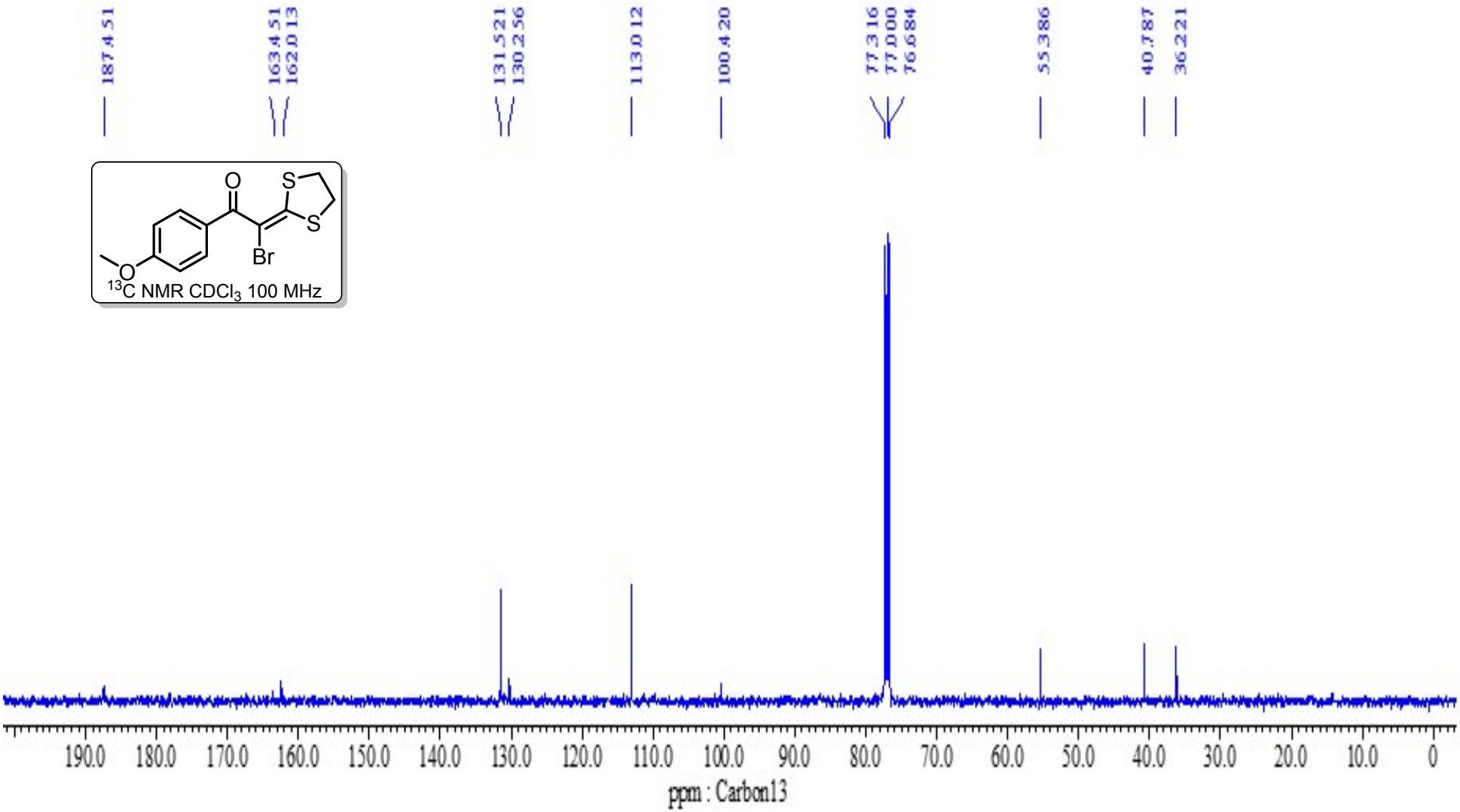


Fig. 34: ^{13}C-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one* (***2q***)

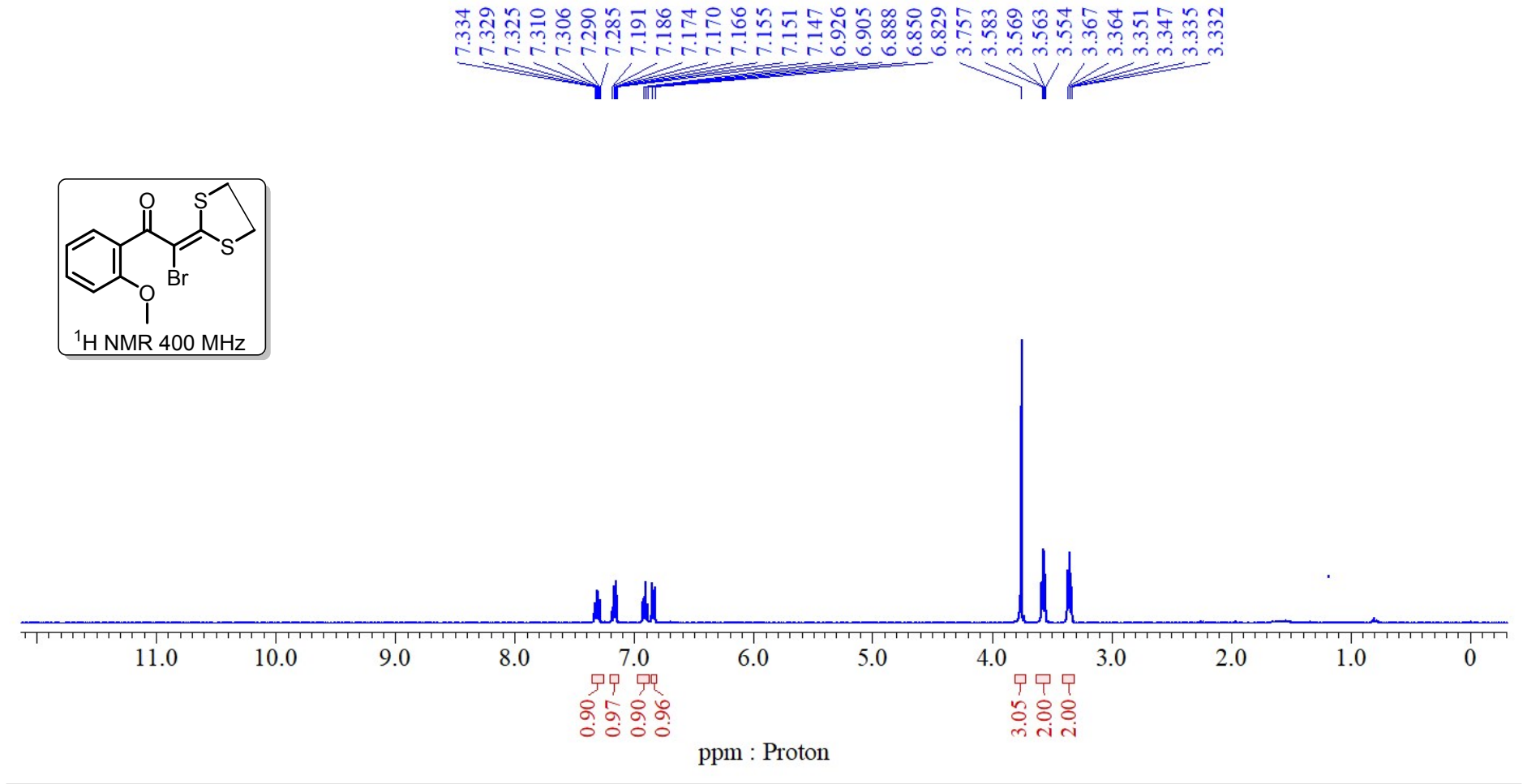


Fig. 35: ^{1}H-NMR spectrum of 2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(2-methoxyphenyl)ethan-1-one (**2r**)

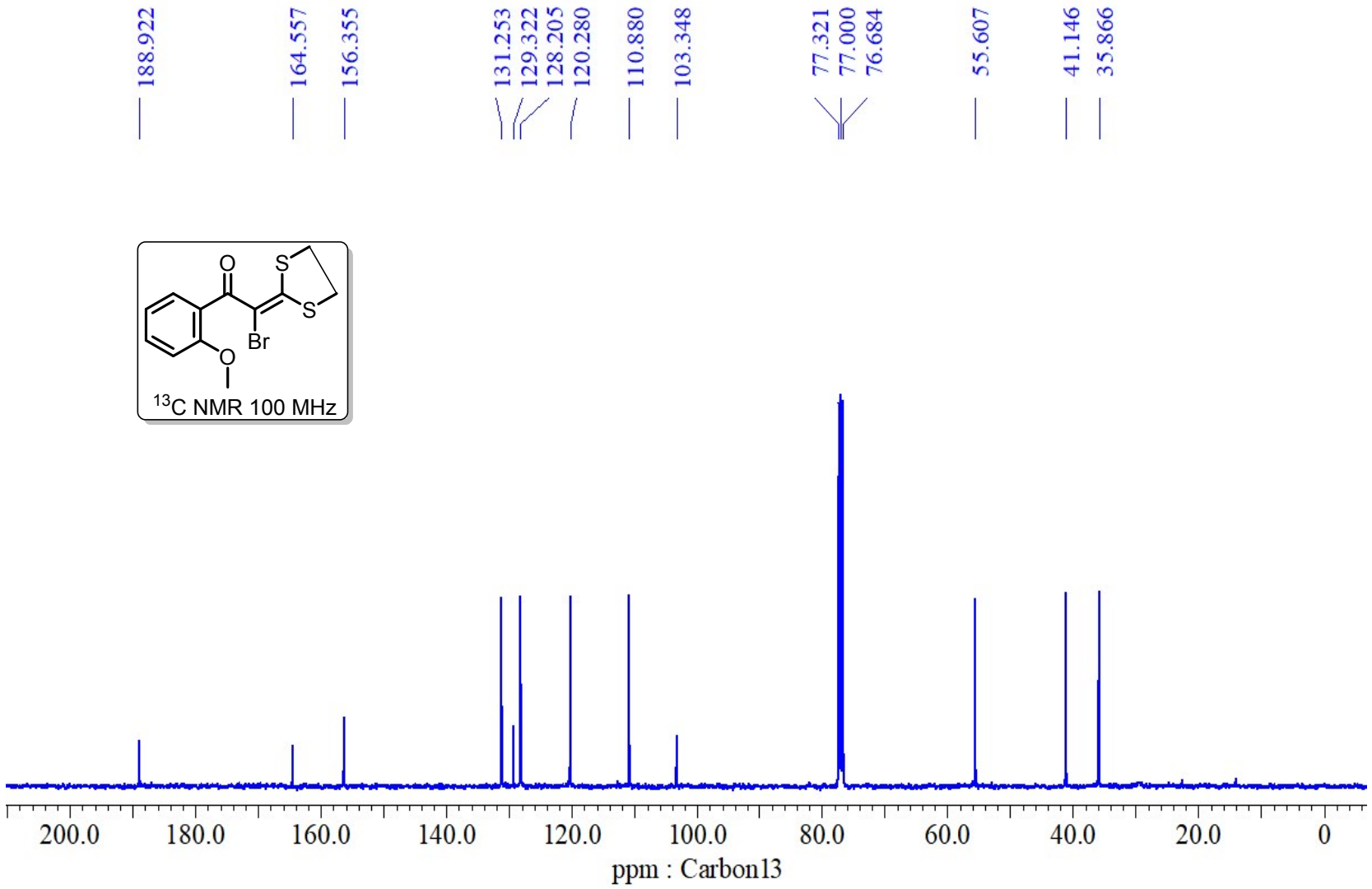


Fig. 36: ^{13}C-NMR spectrum of 2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(2-methoxyphenyl)ethan-1-one (***2r***)

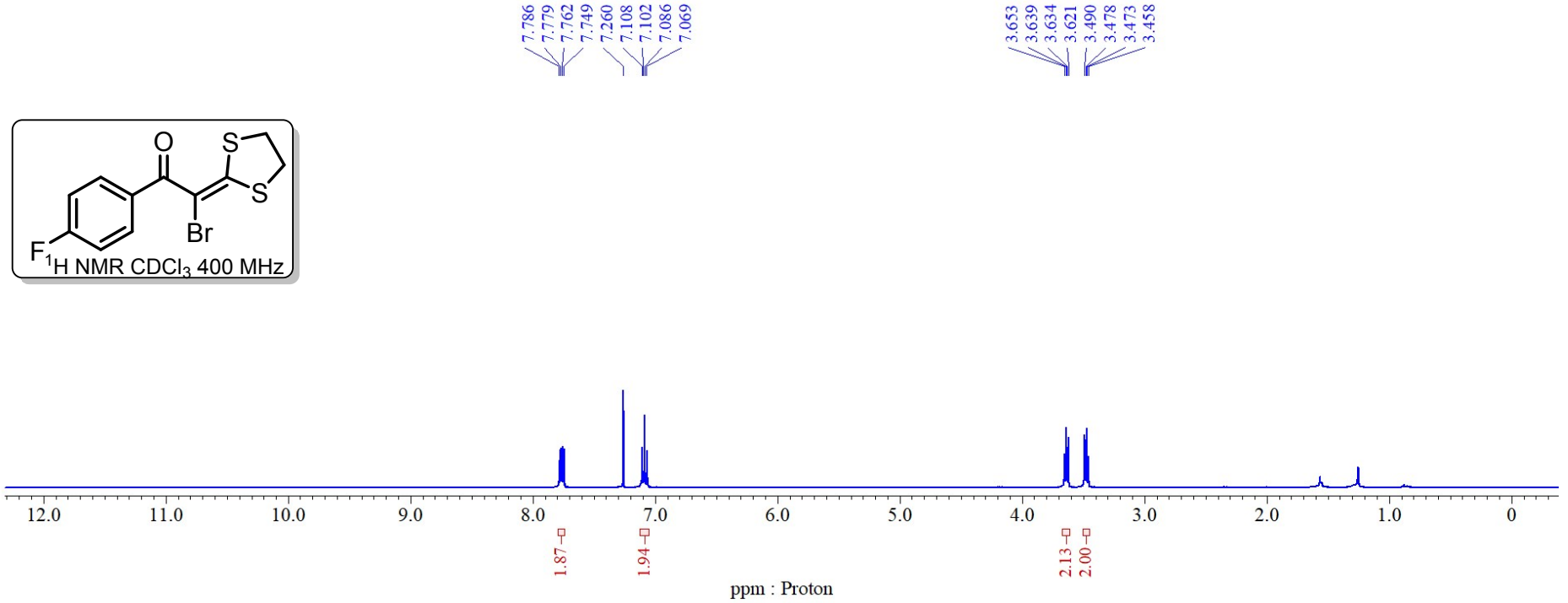


Fig. 37: ^{1}H-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)ethan-1-one (**2s**)*

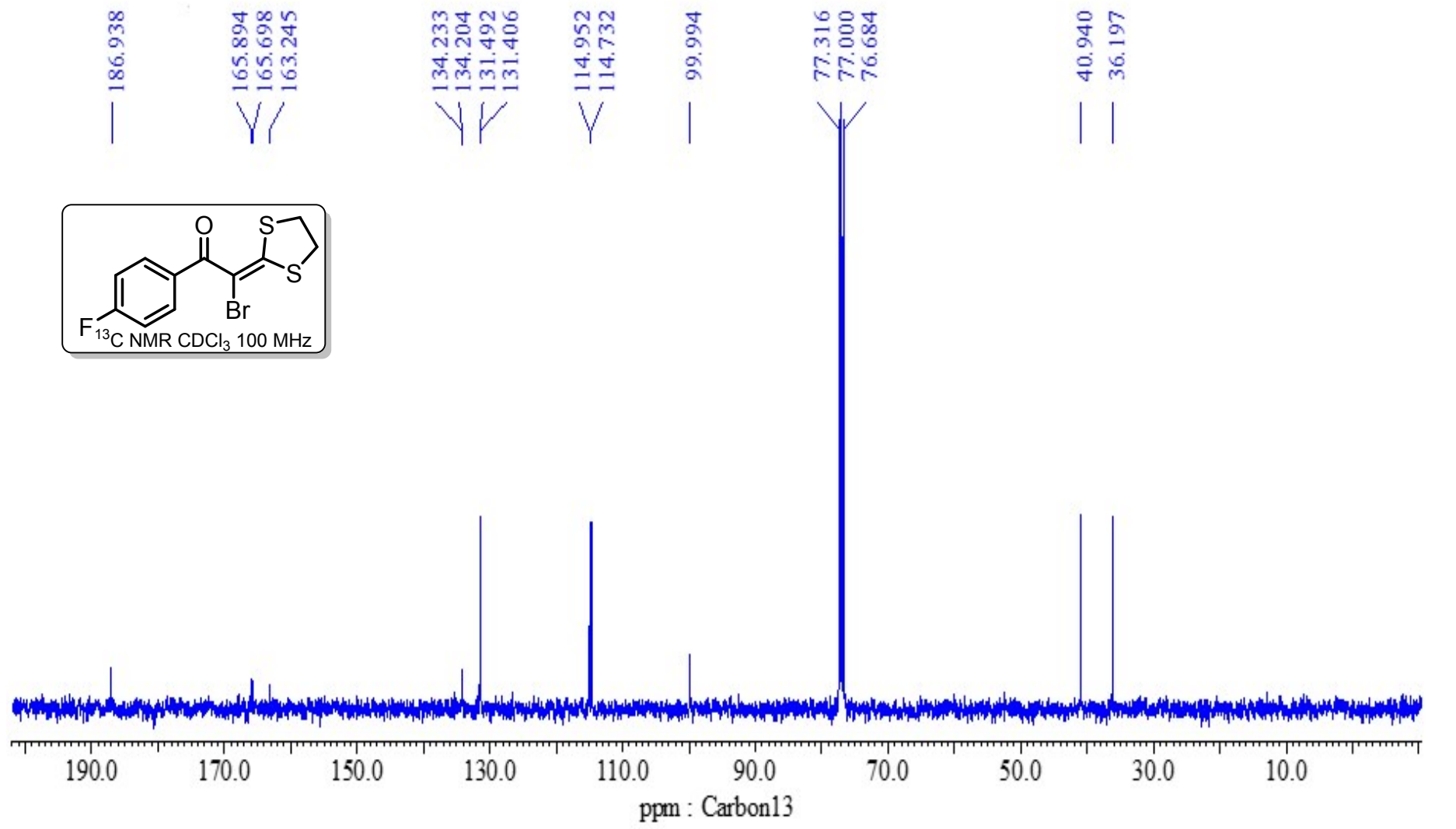


Fig. 38: ^{13}C-NMR of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)ethan-1-one* (***2s***)

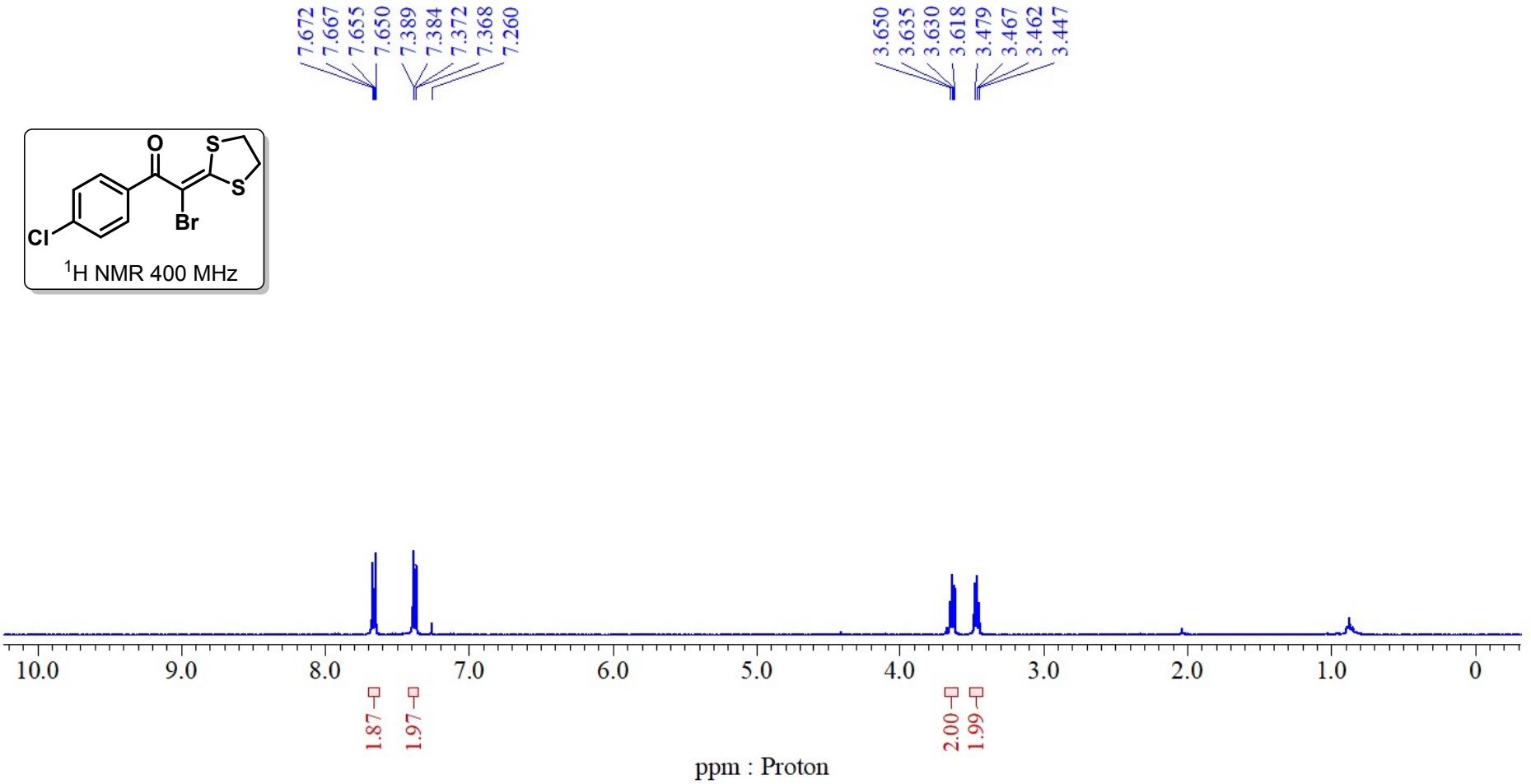


Fig.39: ^{1}H-NMR spectrum of 2-bromo-1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**2t**)

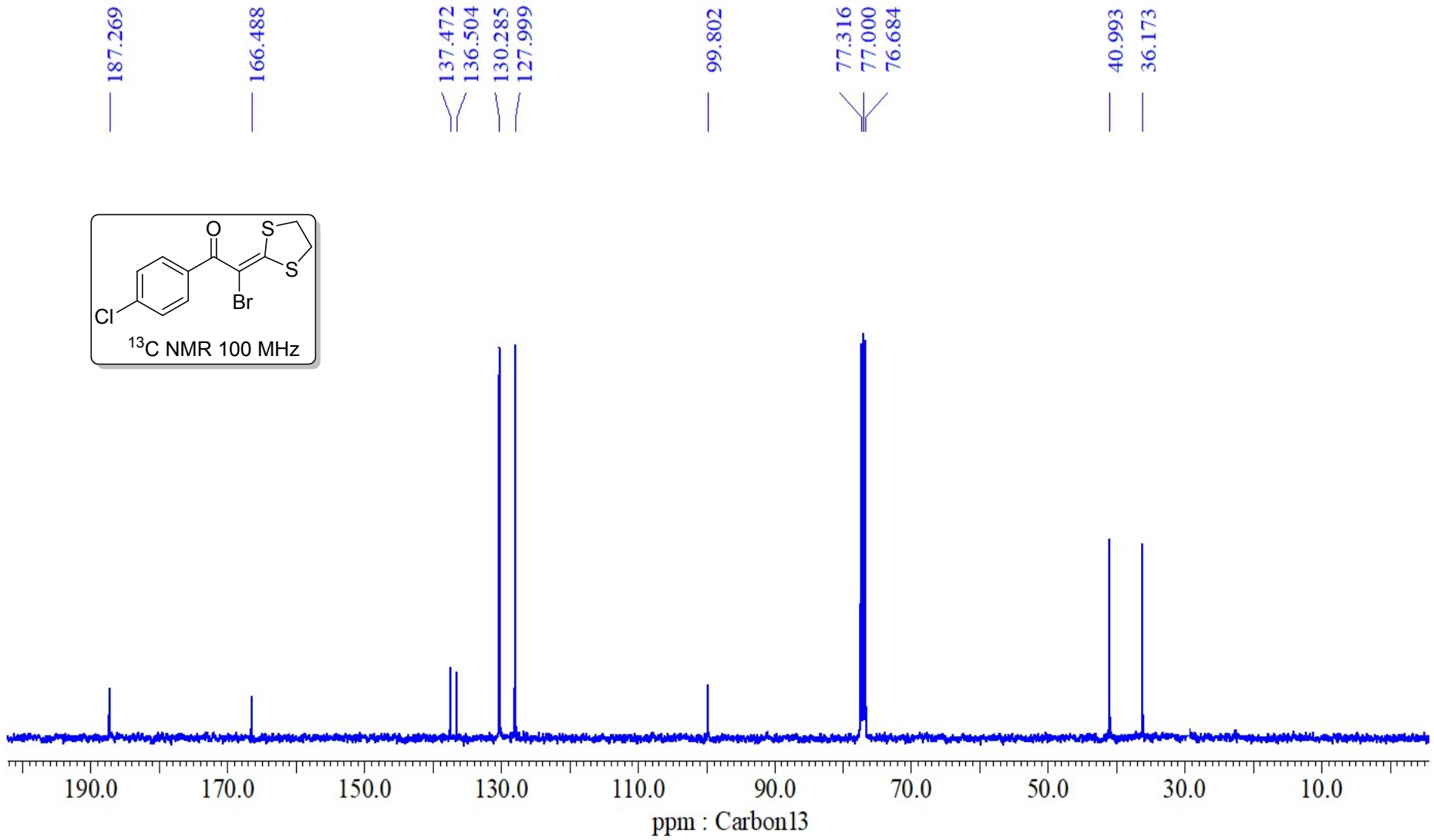


Fig.40: ^{13}C-NMR spectrum of 2-bromo-1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**2t**)

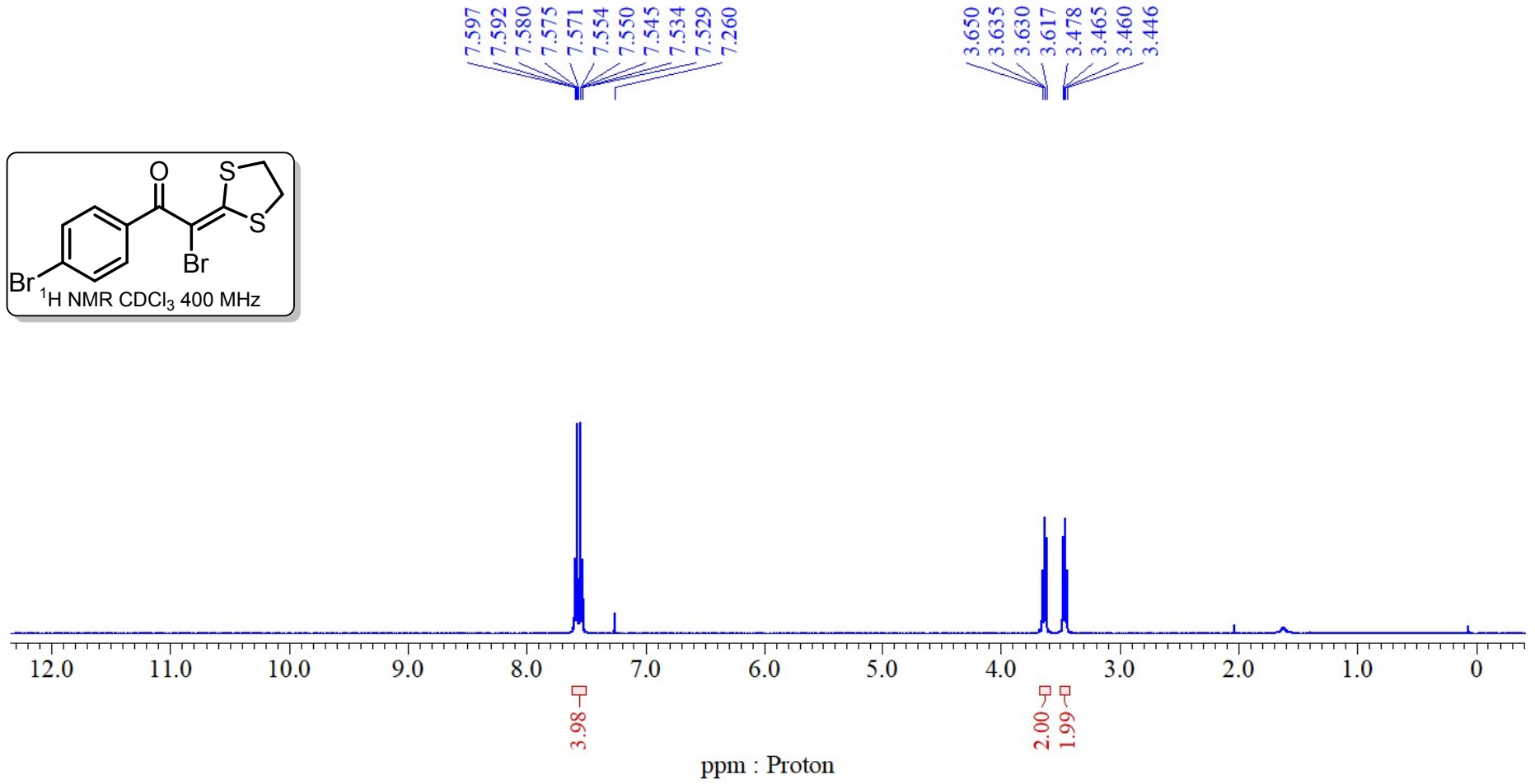


Fig. 41: ^{1}H-NMR spectrum of *2-bromo-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**2u**)*

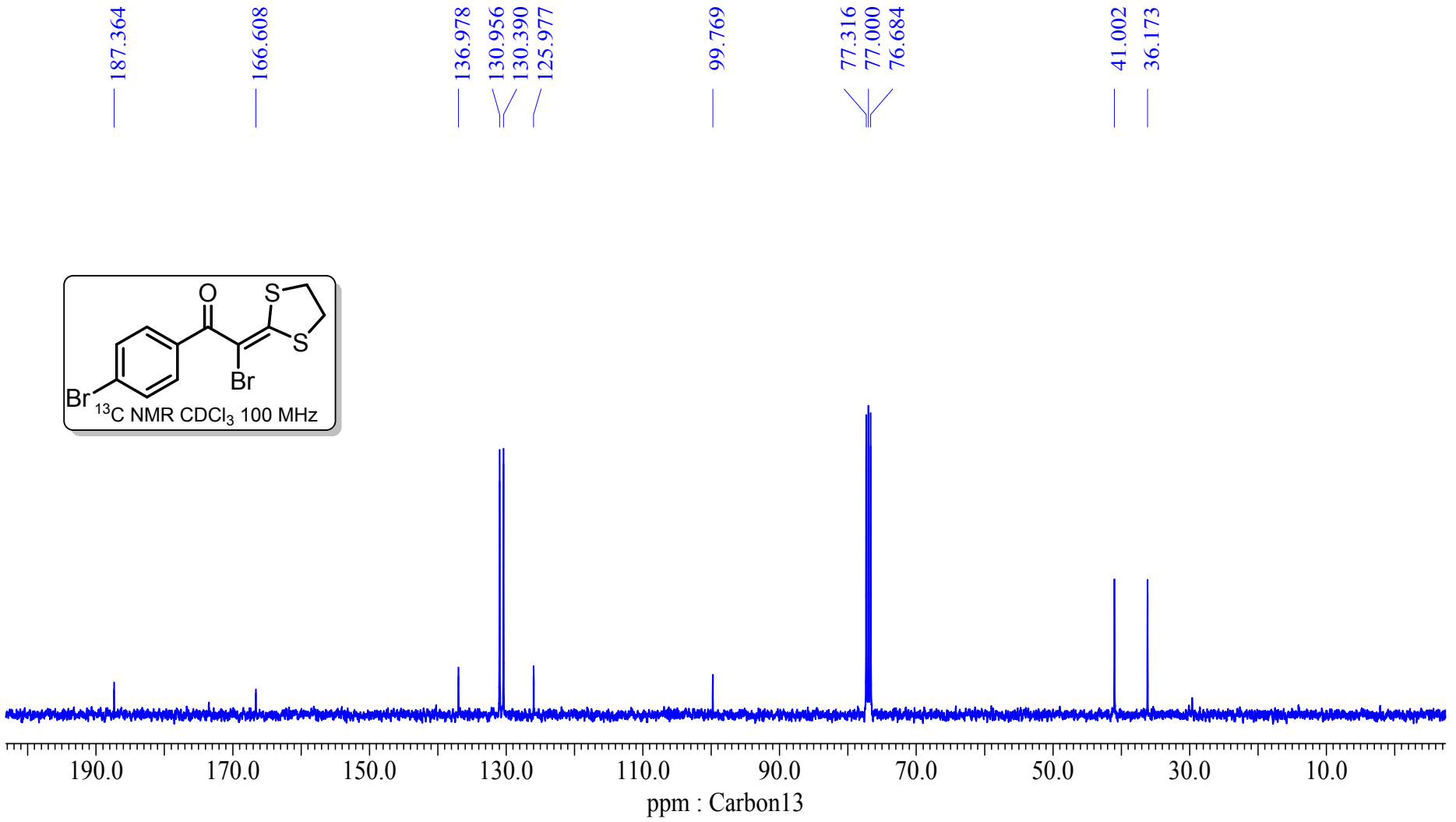


Fig. 42: ^{13}C-NMR spectrum of *2-bromo-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**2u**)*

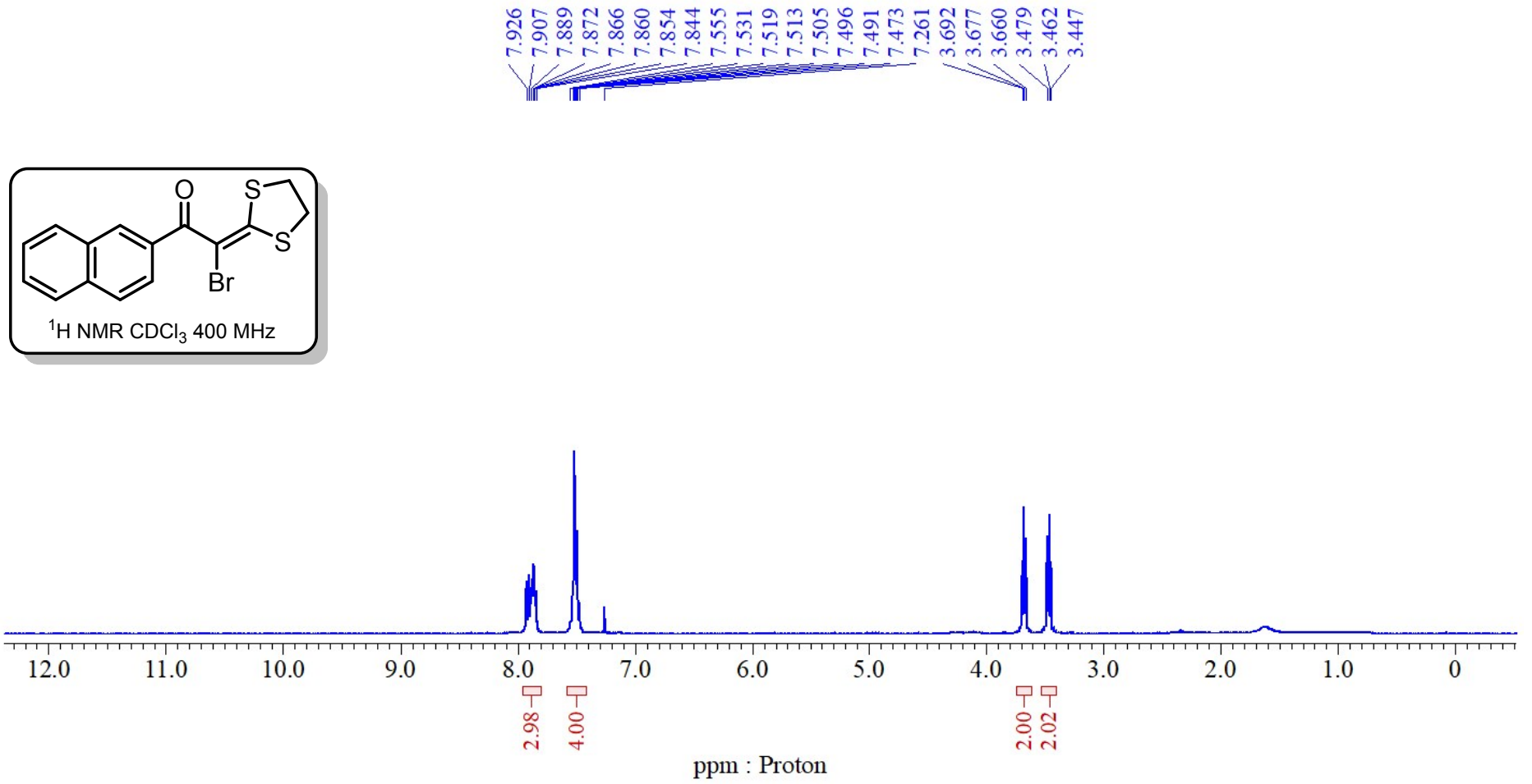


Fig. 43: ^{1}H-NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one (**2v**)*

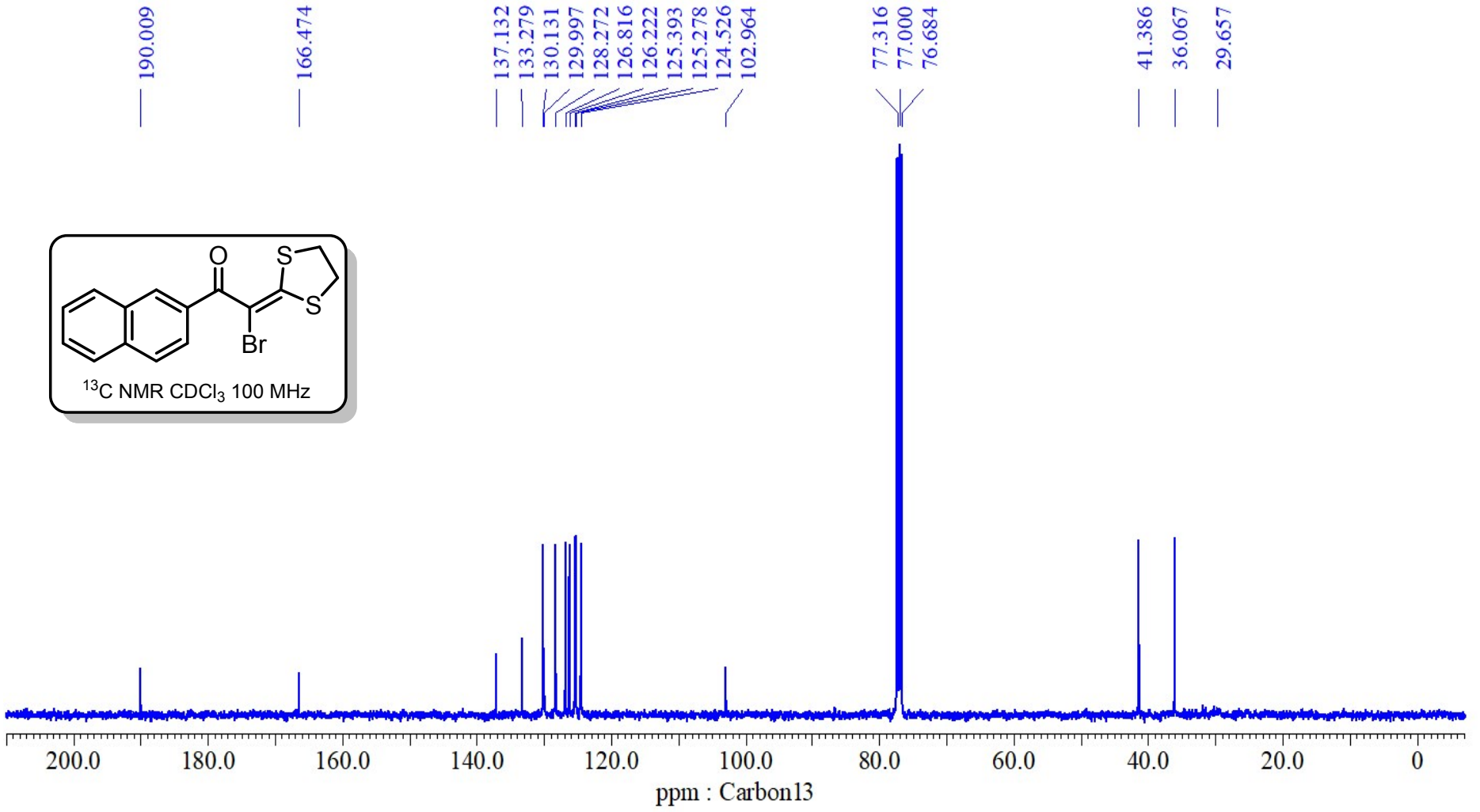


Fig. 44: ^{13}C-NMR spectrum of *2-bromo-3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one (**2v**)*

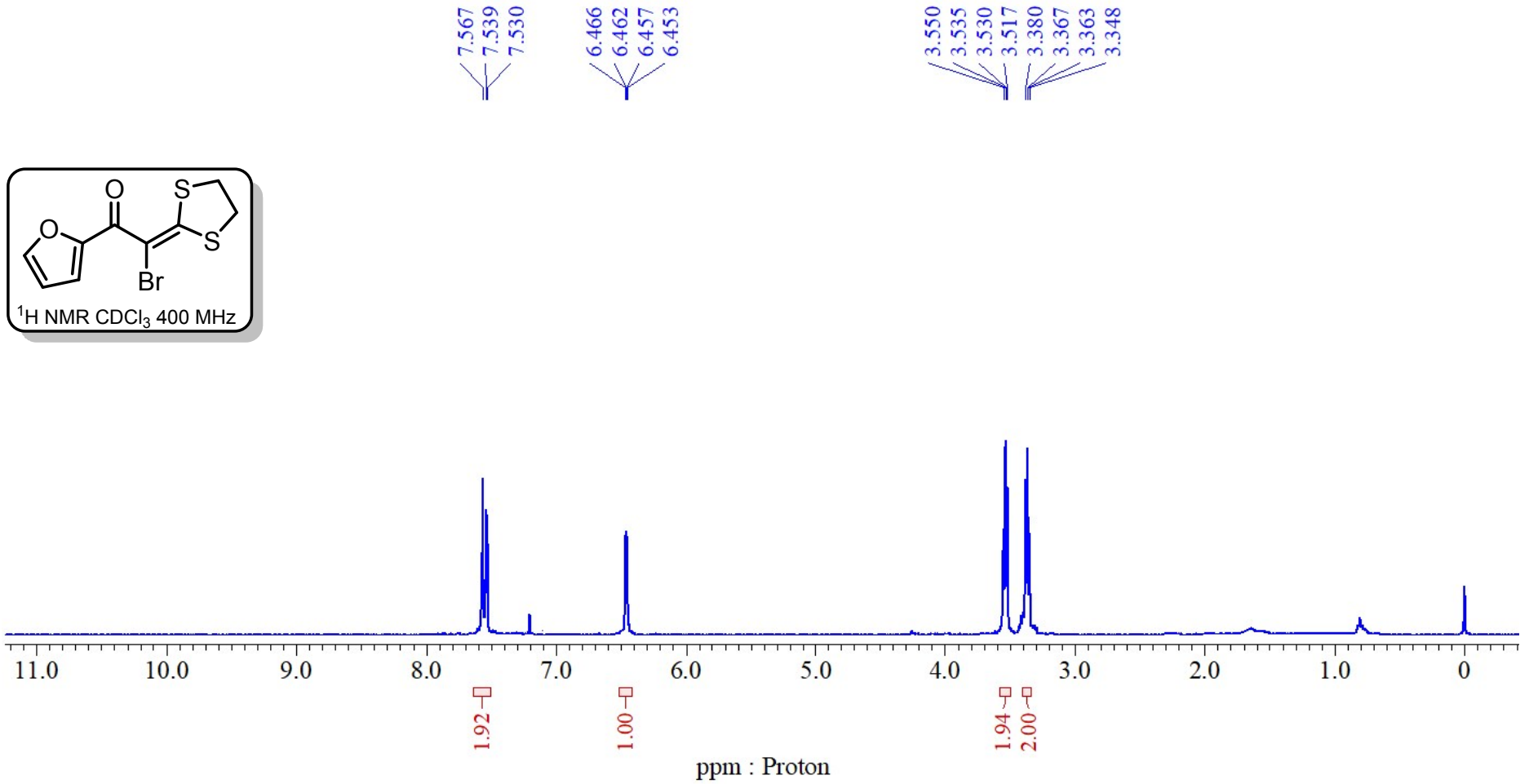


Fig. 45: ^{1}H-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one* (***2w***)

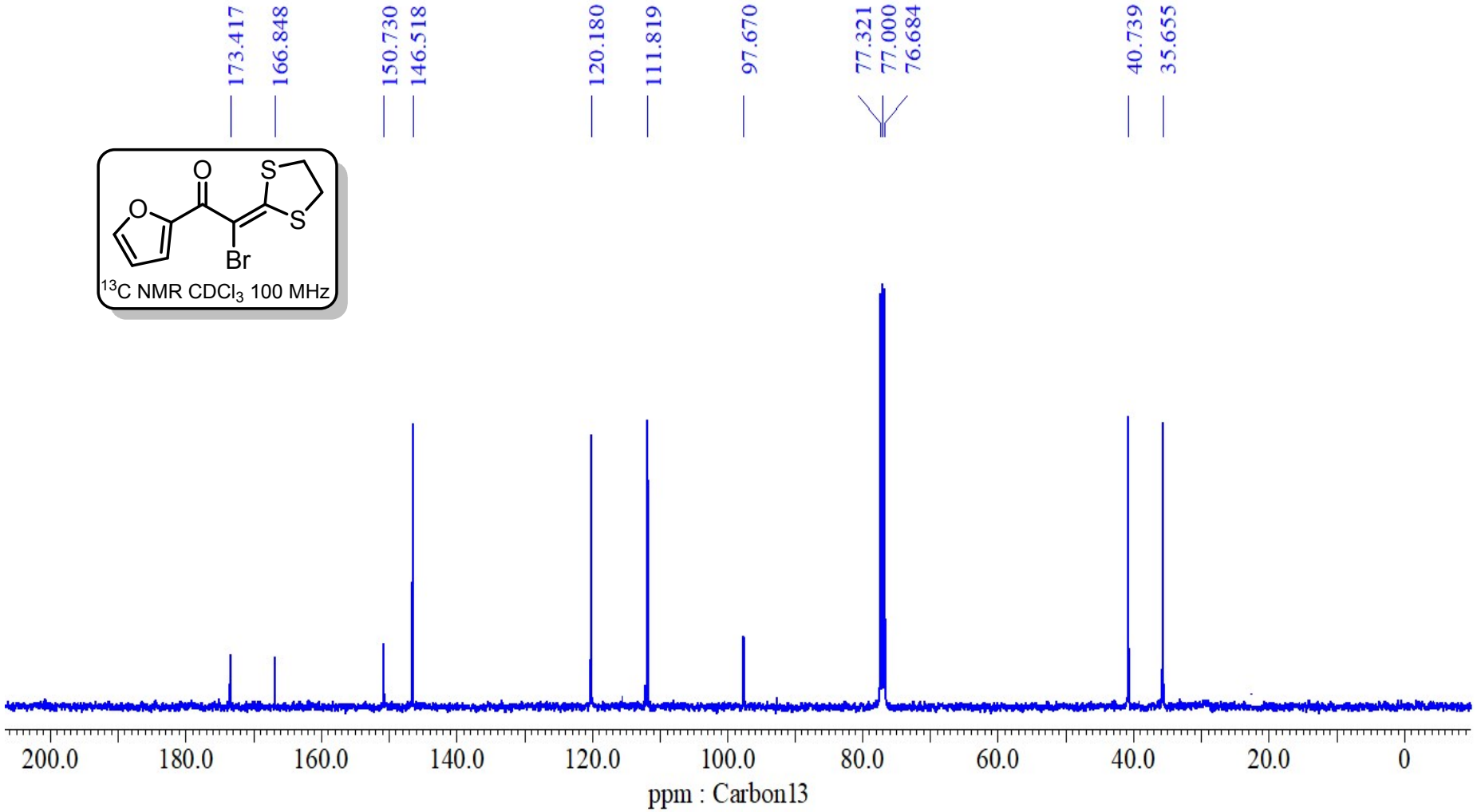


Fig. 46: ^{13}C-NMR spectrum of *2-bromo-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one (**2w**)*

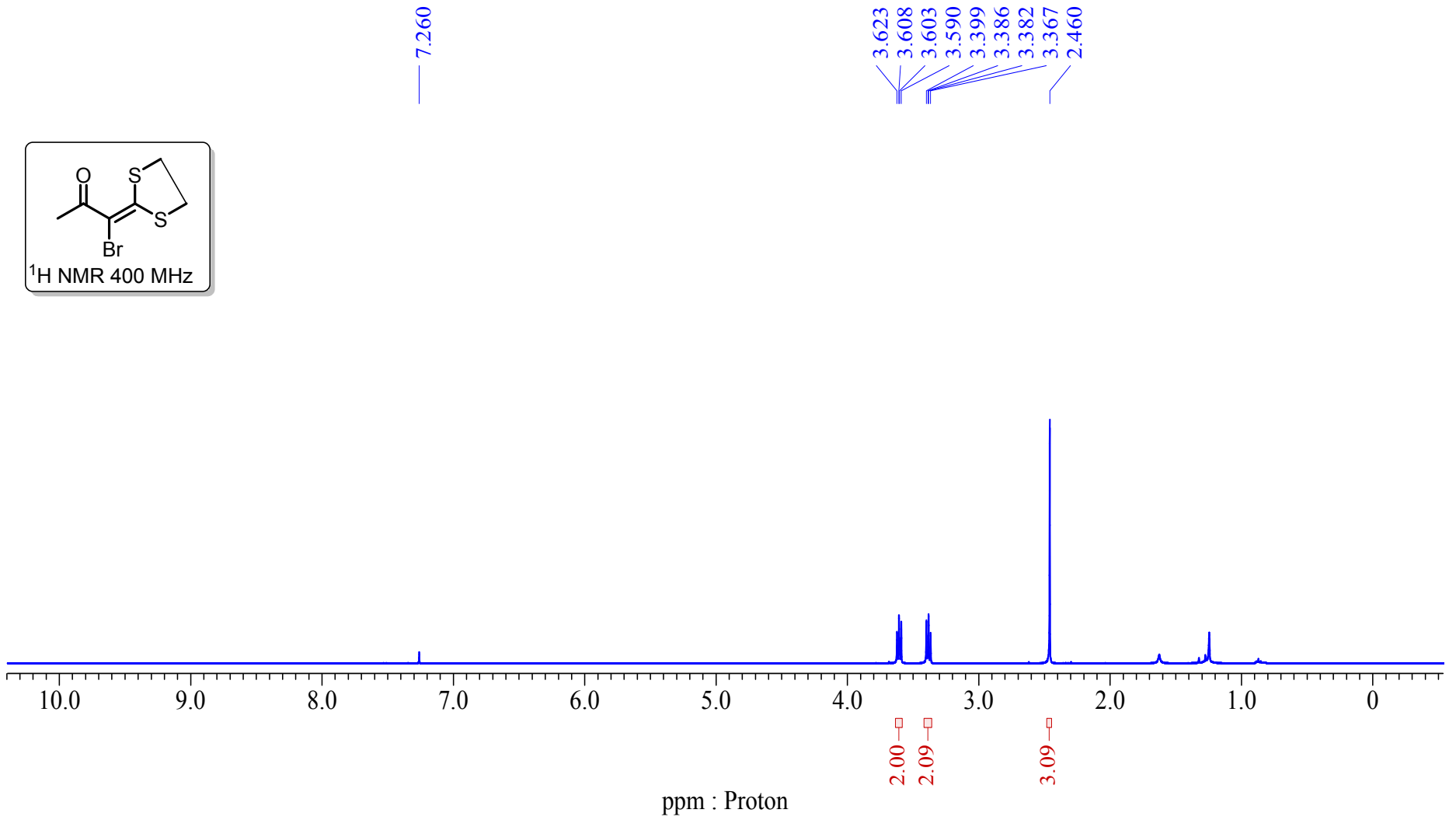


Fig.47: ^{1}H-NMR spectrum of *1-bromo-1-(1,3-dithiolan-2-ylidene)propan-2-one* (***2x***)

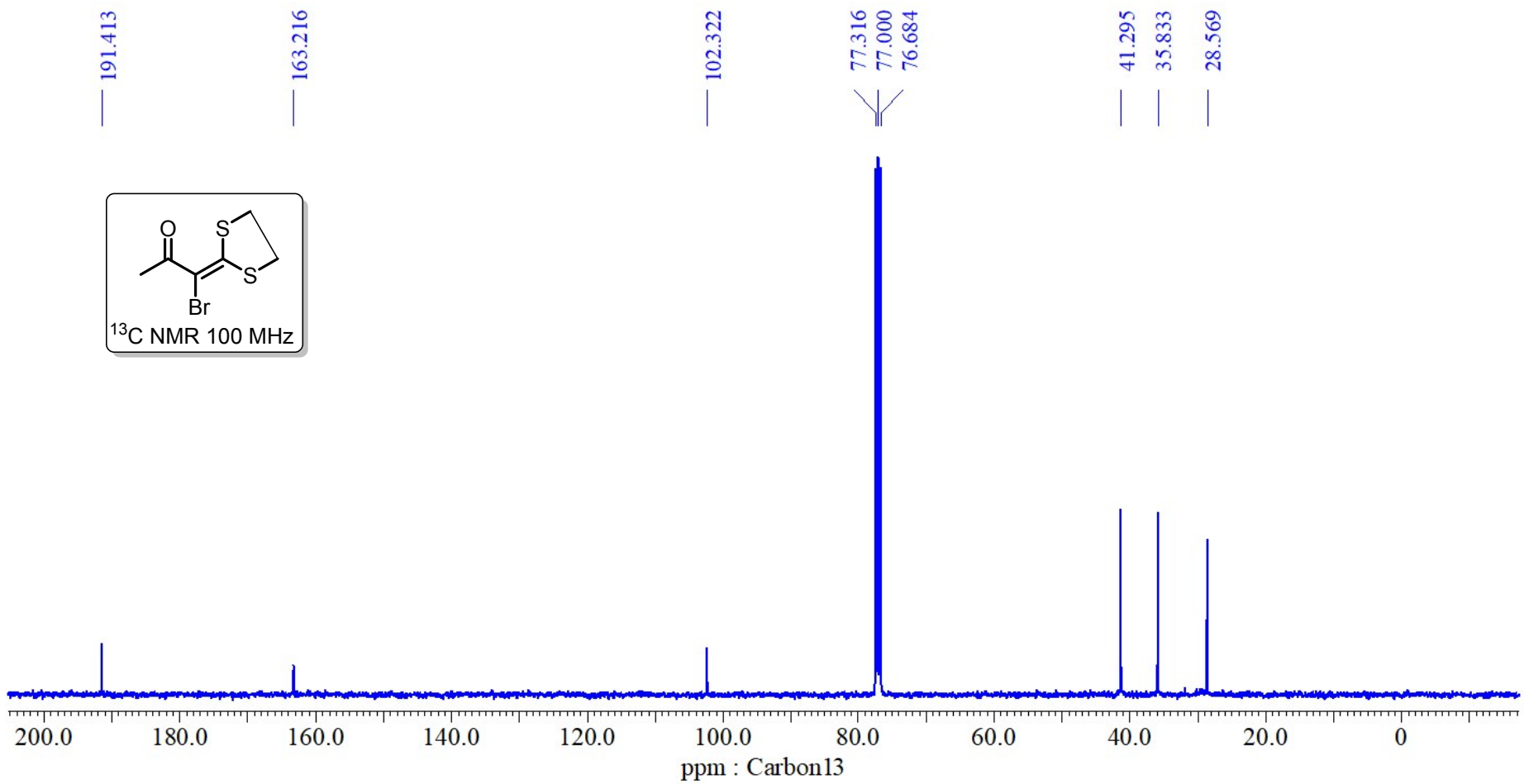


Fig.48: ^{13}C-NMR spectrum of *1-bromo-1-(1,3-dithiolan-2-ylidene)propan-2-one (**2x**)*

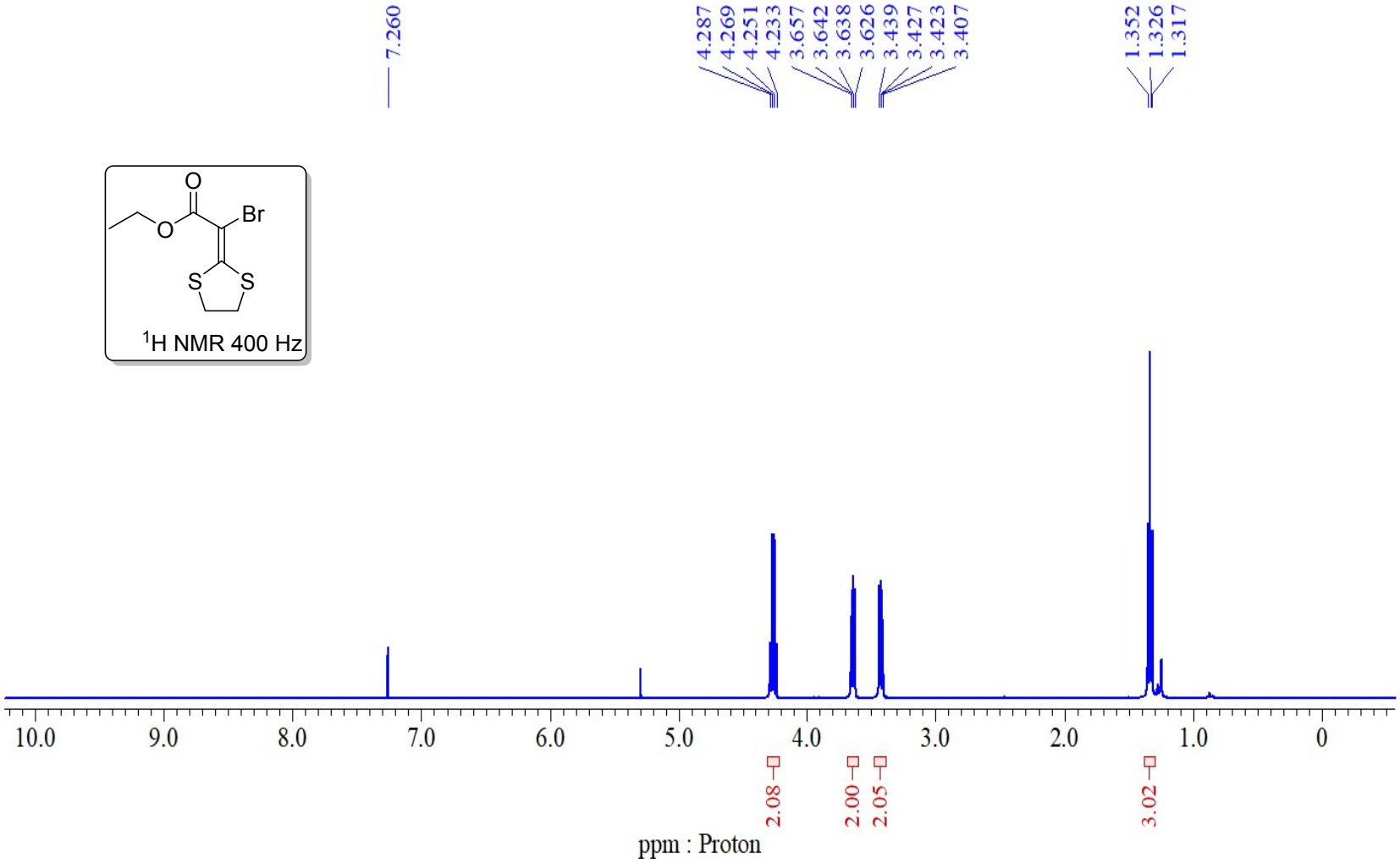

7.260
4.287
4.269
4.251
4.233
3.657
3.642
3.638
3.626
3.439
3.427
3.423
3.407
1.352
1.326
1.317
O
O
Br
S
S
1H NMR 400 Hz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.08
2.00
2.05
3.02
ppm : Proton

Fig.49: ^{1}H-NMR spectrum of *ethyl 2-bromo-2-(1,3-dithiolan-2-ylidene)acetate (**2y**)*

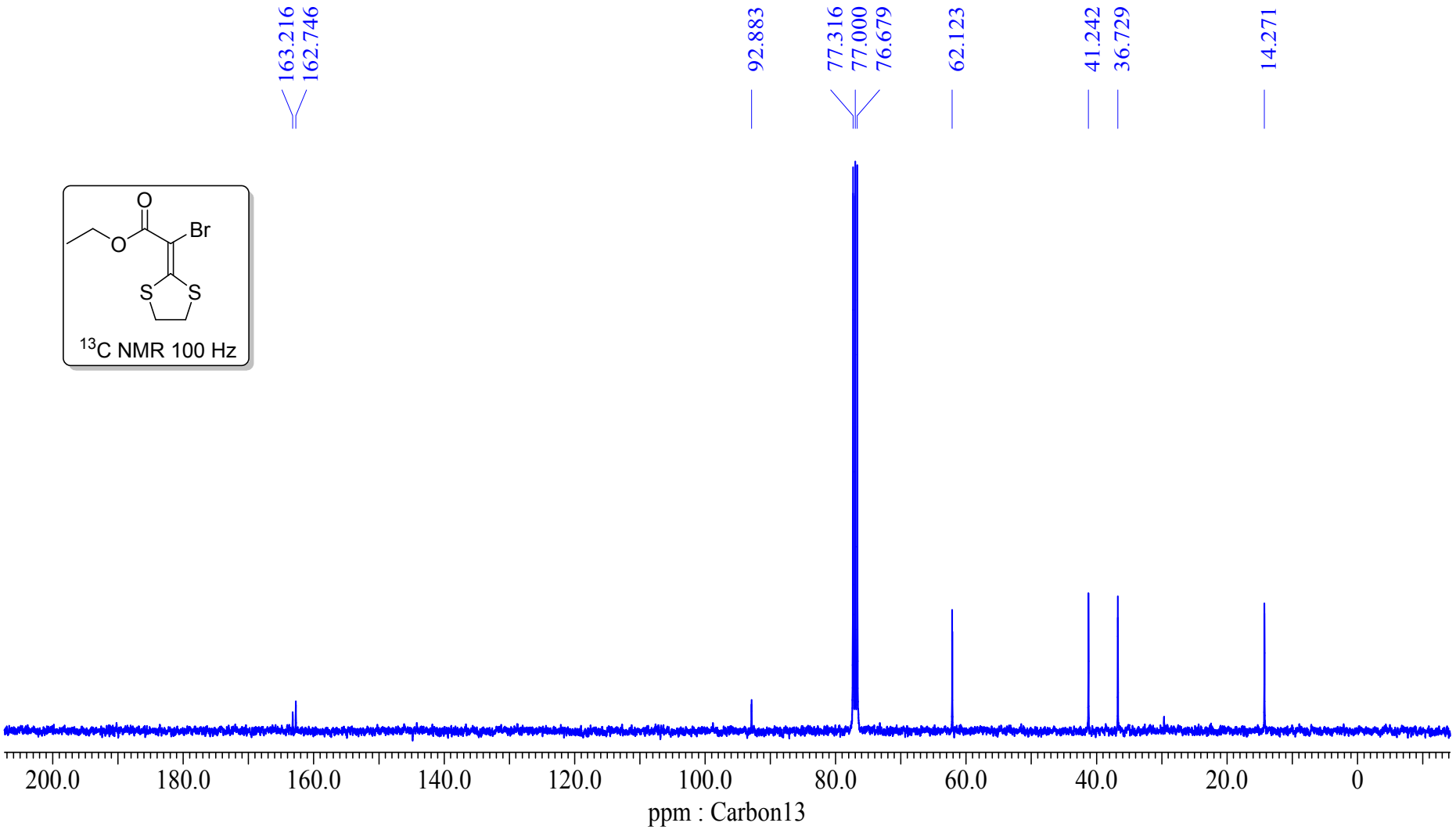


Fig.50: ^{13}C-NMR of spectrum of *ethyl 2-bromo-2-(1,3-dithiolan-2-ylidene)acetate (**2y**)*

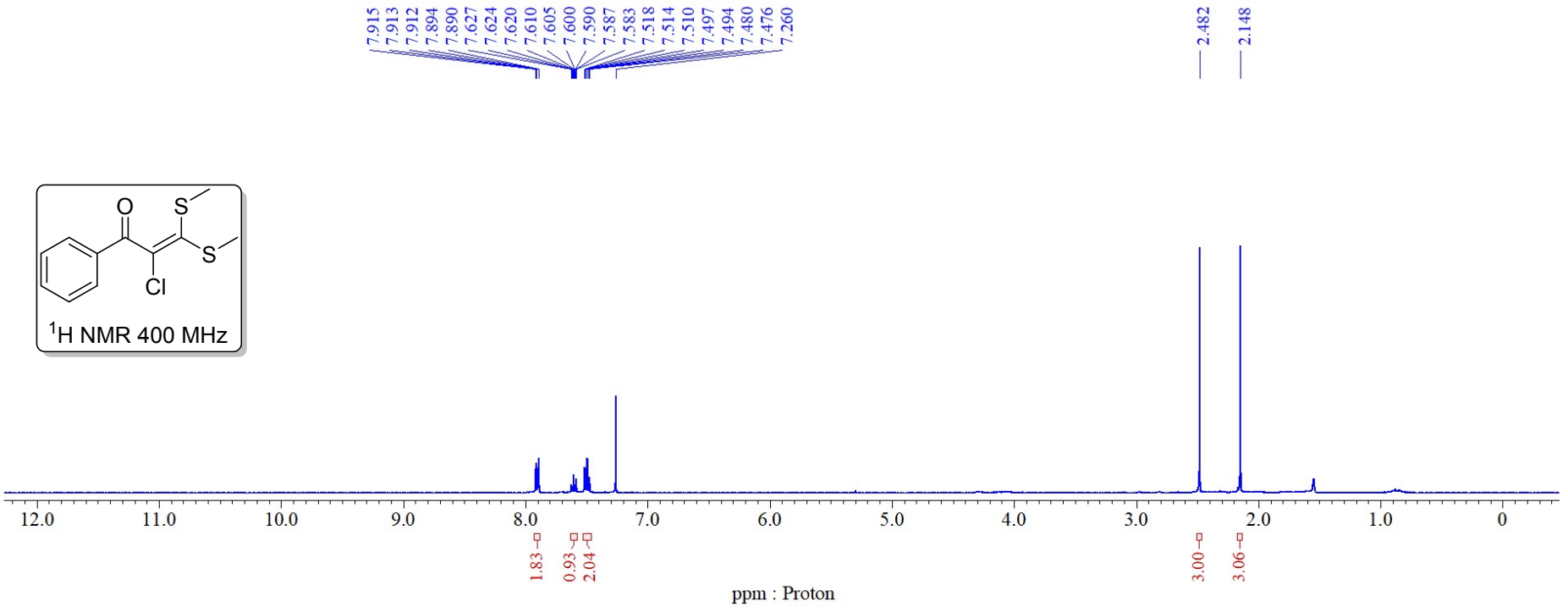


Fig.51: ^{1}H-NMR of spectrum of *2-chloro-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**3a**)*

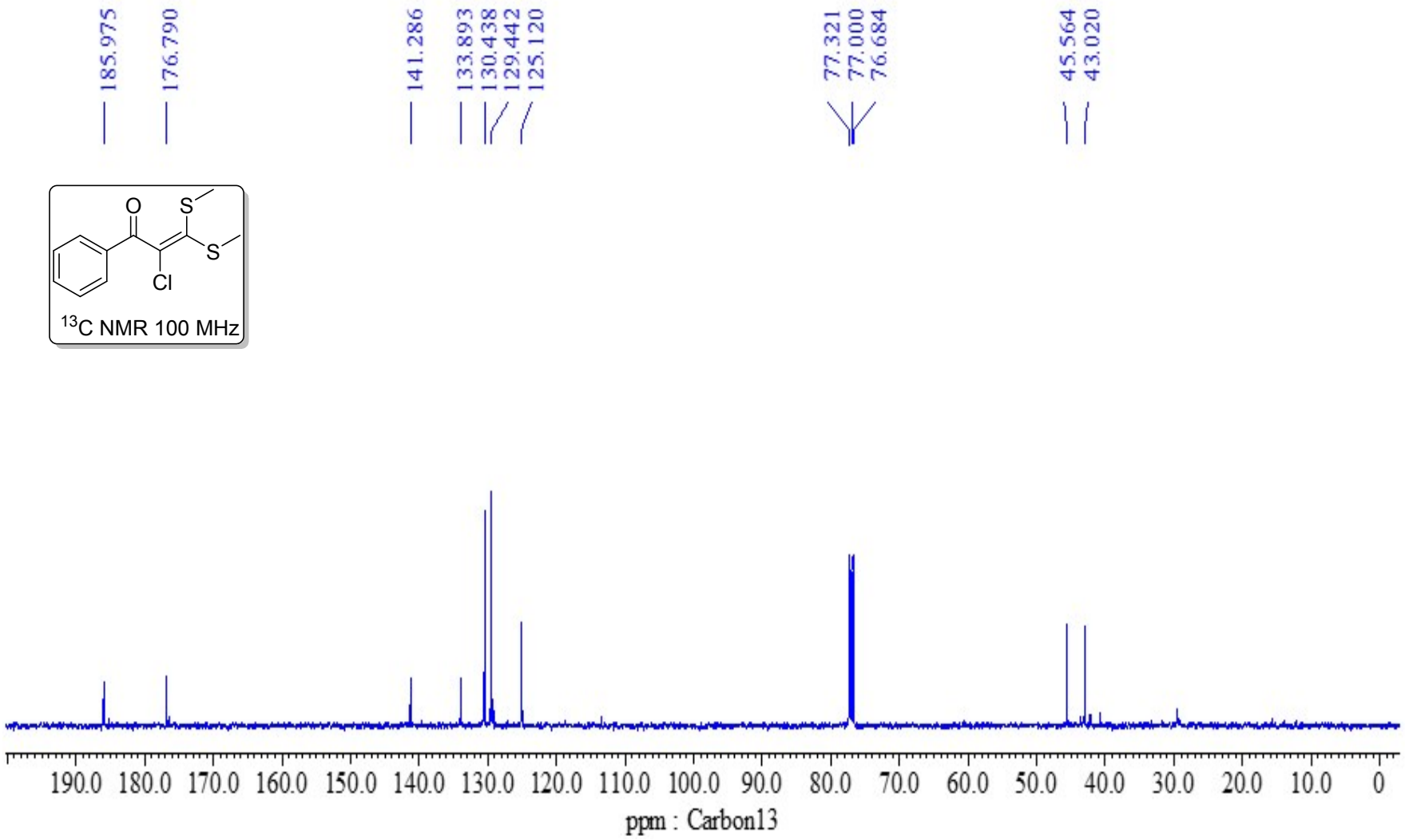
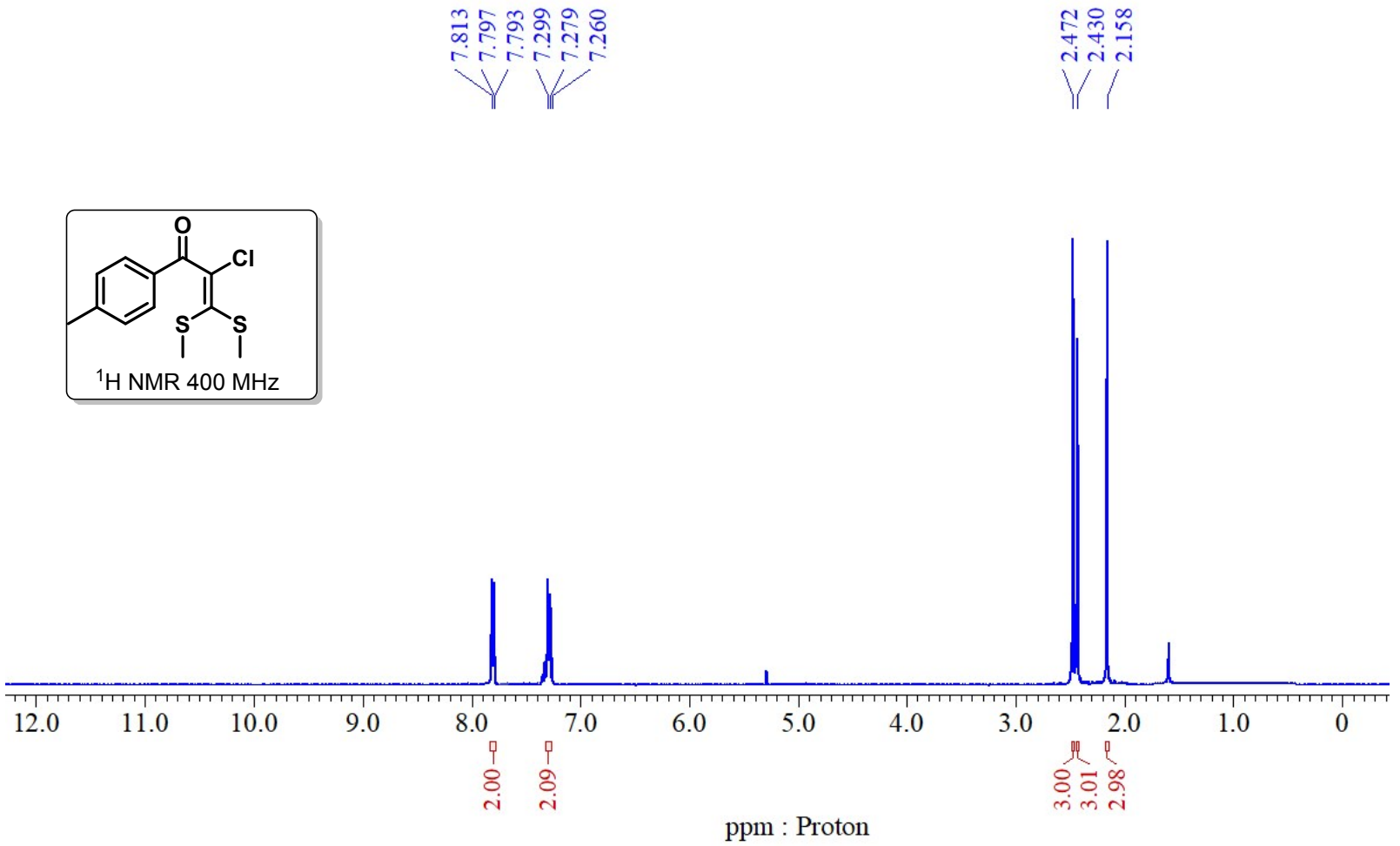


Fig.52: ^{13}C-NMR of spectrum of *2-chloro-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**3a**)*



p

Fig.53: ^{1}H-NMR spectrum of *2-chloro-3,3-bis(methylthio)-1-(p-tolyl)prop-2-en-1-one (**3b**)*

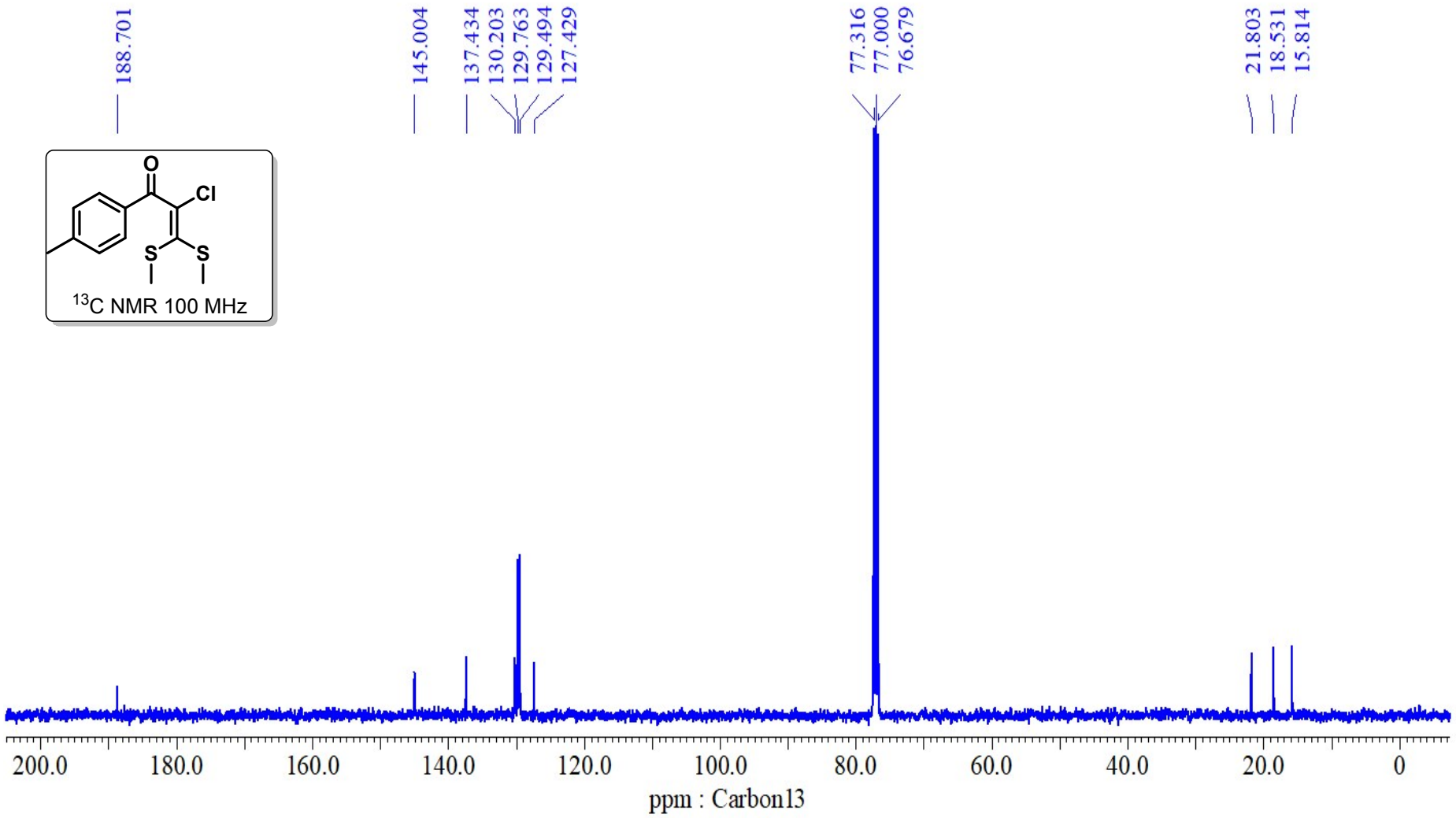


Fig.54: ^{13}C-NMR spectrum of *2-chloro-3,3-bis(methylthio)-1-(p-tolyl)prop-2-en-1-one (**3b**)*

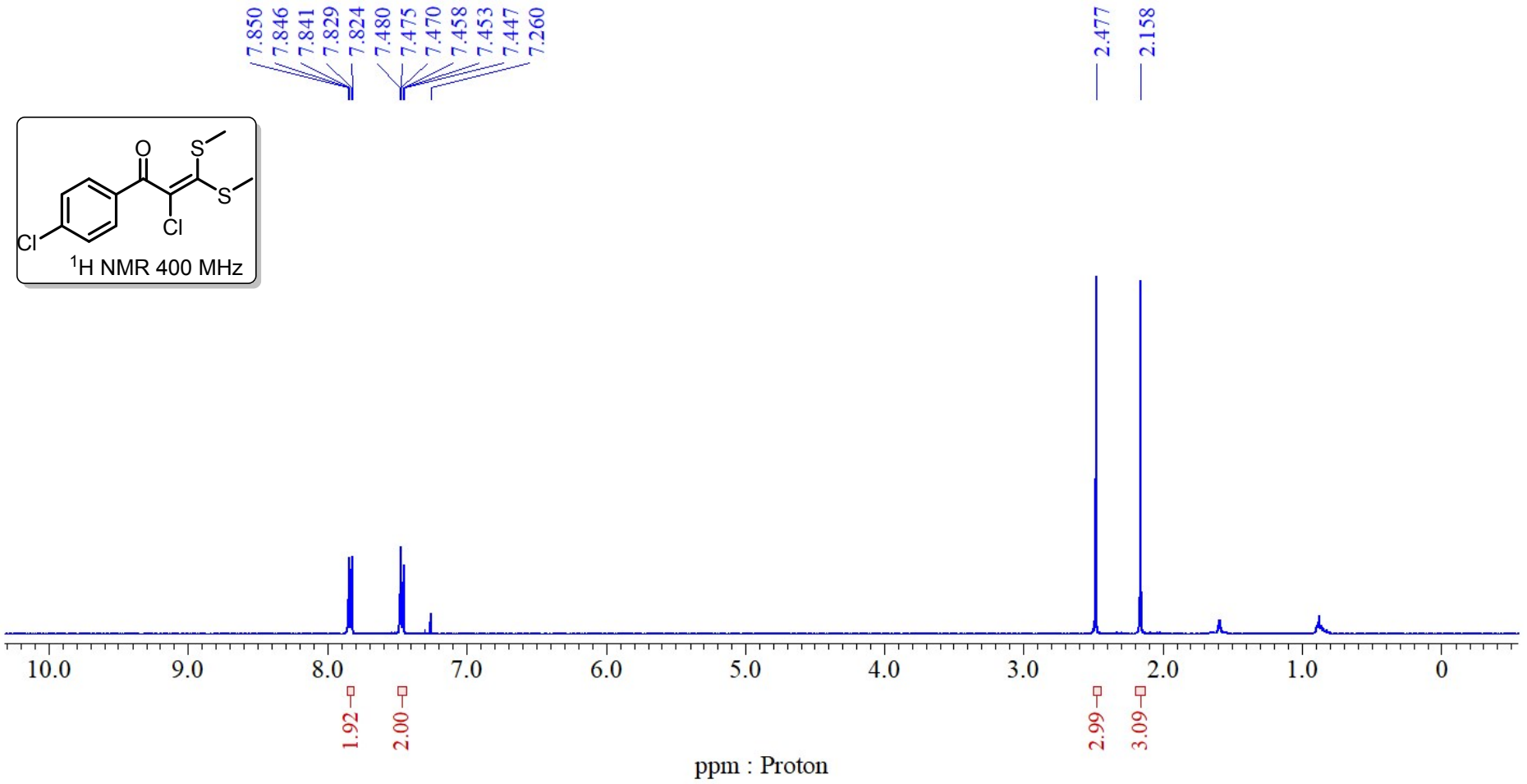


Fig.55: ^{1}H-NMR spectrum of *2-chloro-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**3c**)*

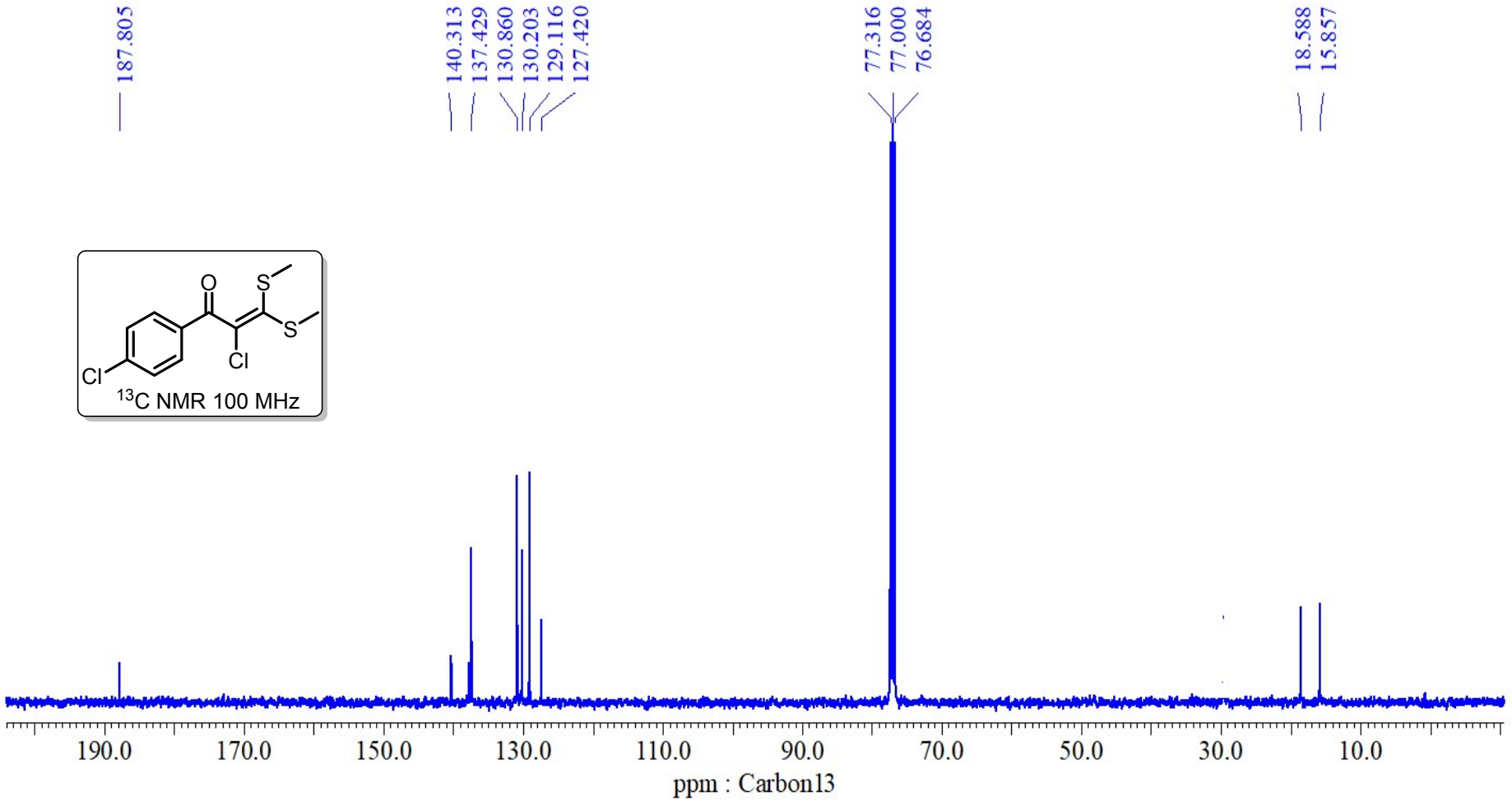


Fig.56: ^{13}C-NMR spectrum of *2-chloro-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**3c**)*

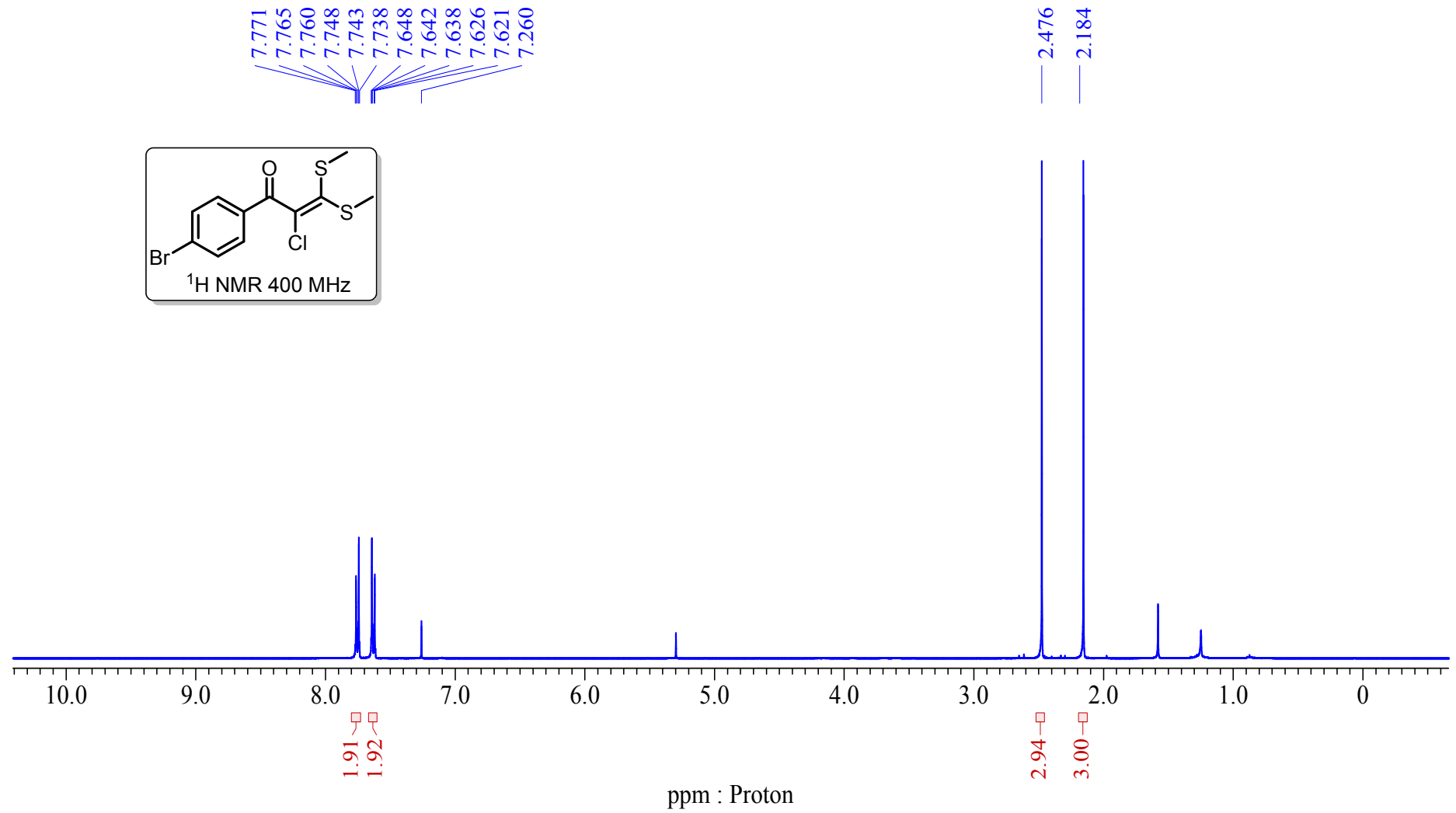


Fig.57: ^{1}H-NMR spectrum of *1-(4-bromophenyl)-2-chloro-3,3-bis(methylthio)prop-2-en-1-one (**3d**)*

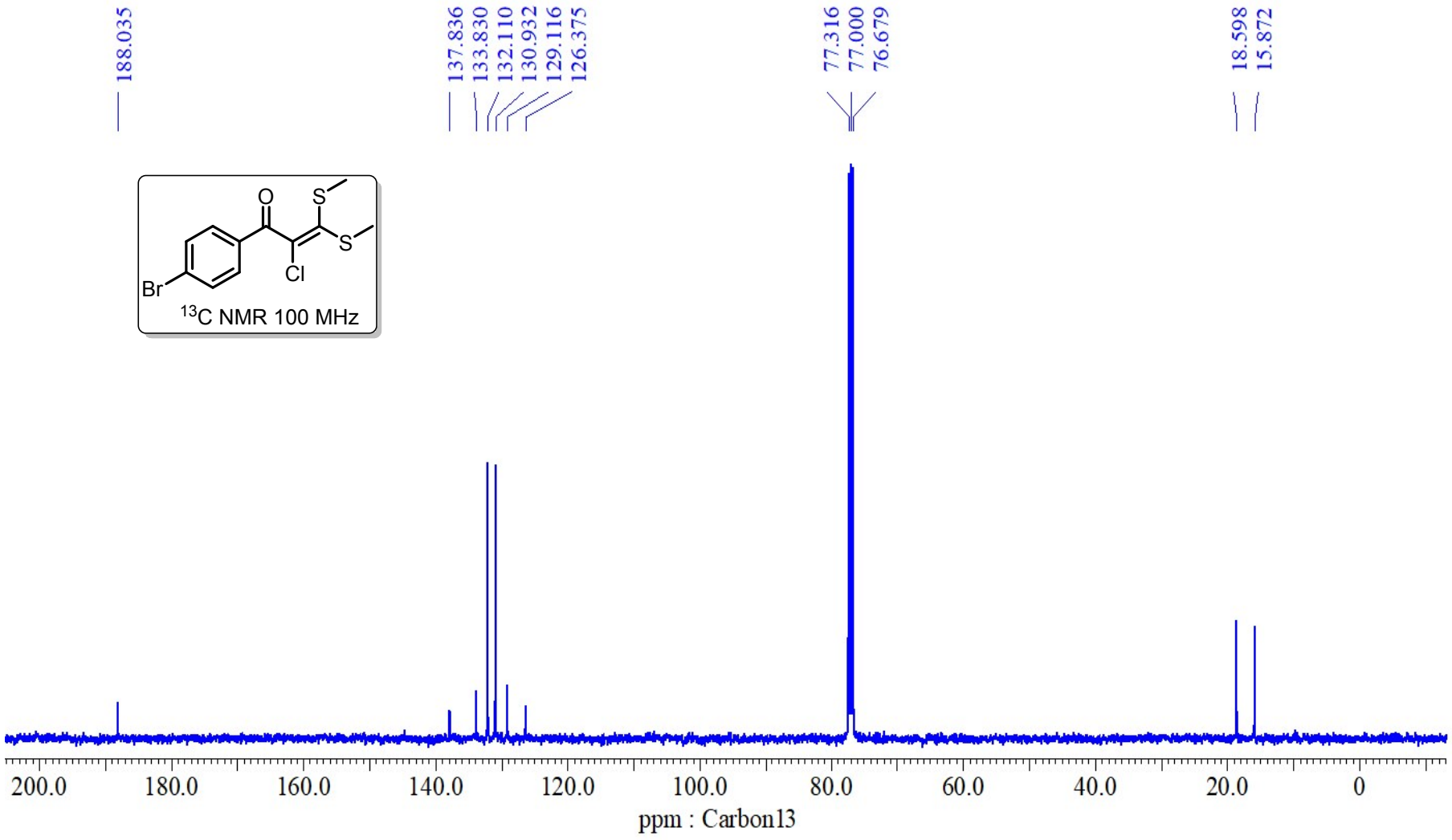


Fig.58: ^{13}C spectrum of *1-(4-bromophenyl)-2-chloro-3,3-bis(methylthio)prop-2-en-1-one (**3d**)*

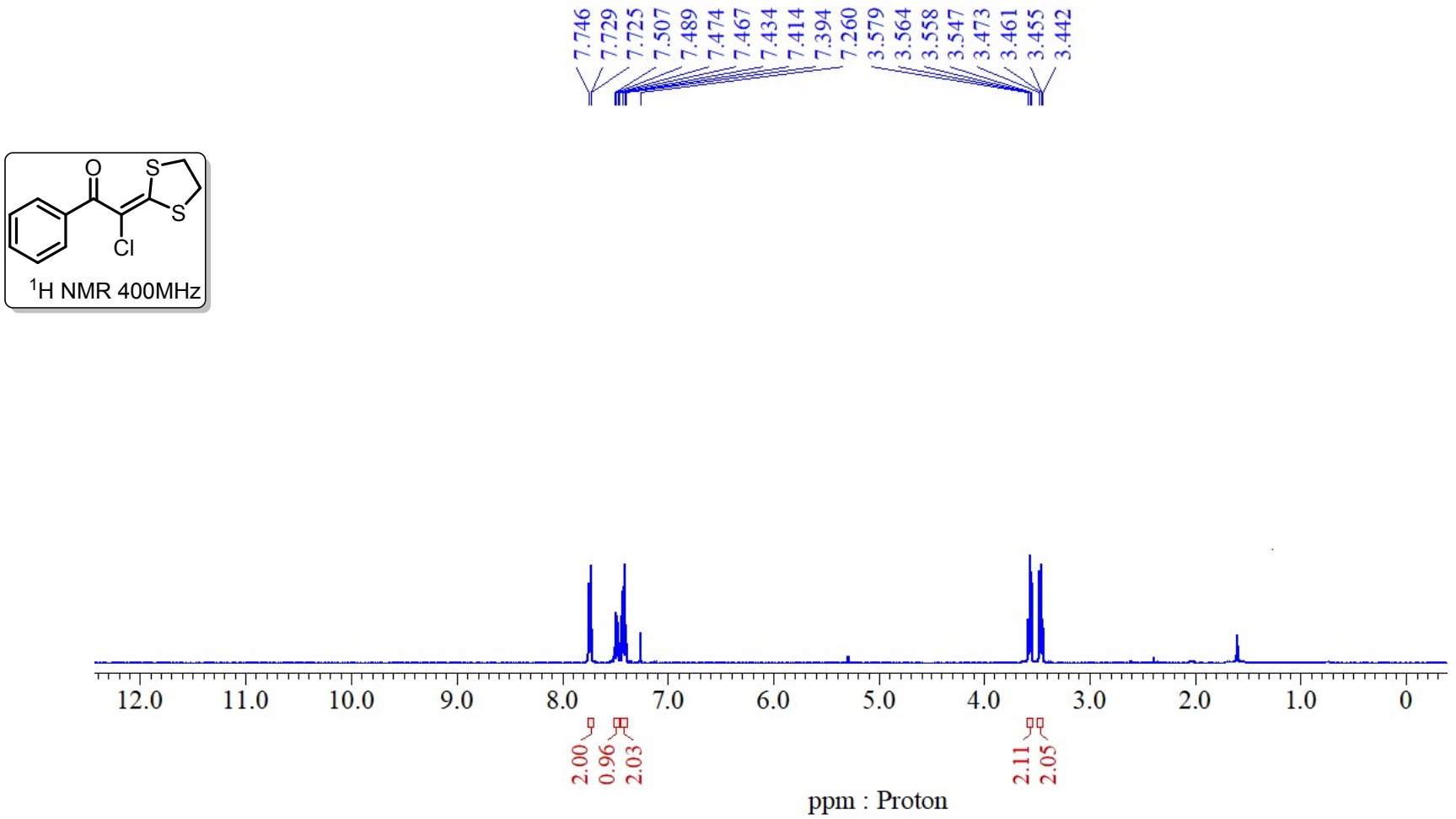


Fig.59: ^{1}H-NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one* (***3e***)

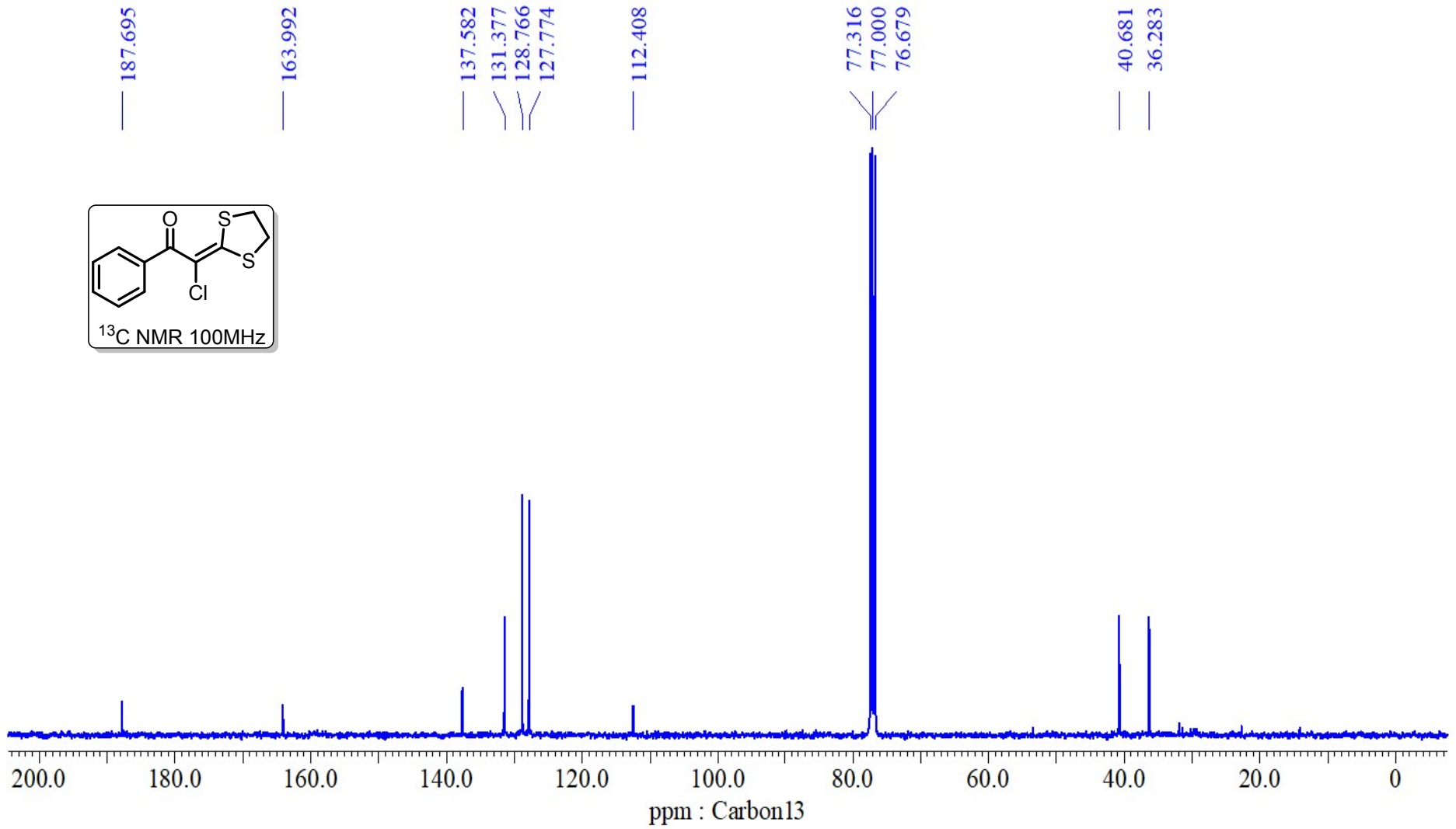


Fig.60: ^{13}C-NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-phenylethan-1-one (**3e**)*

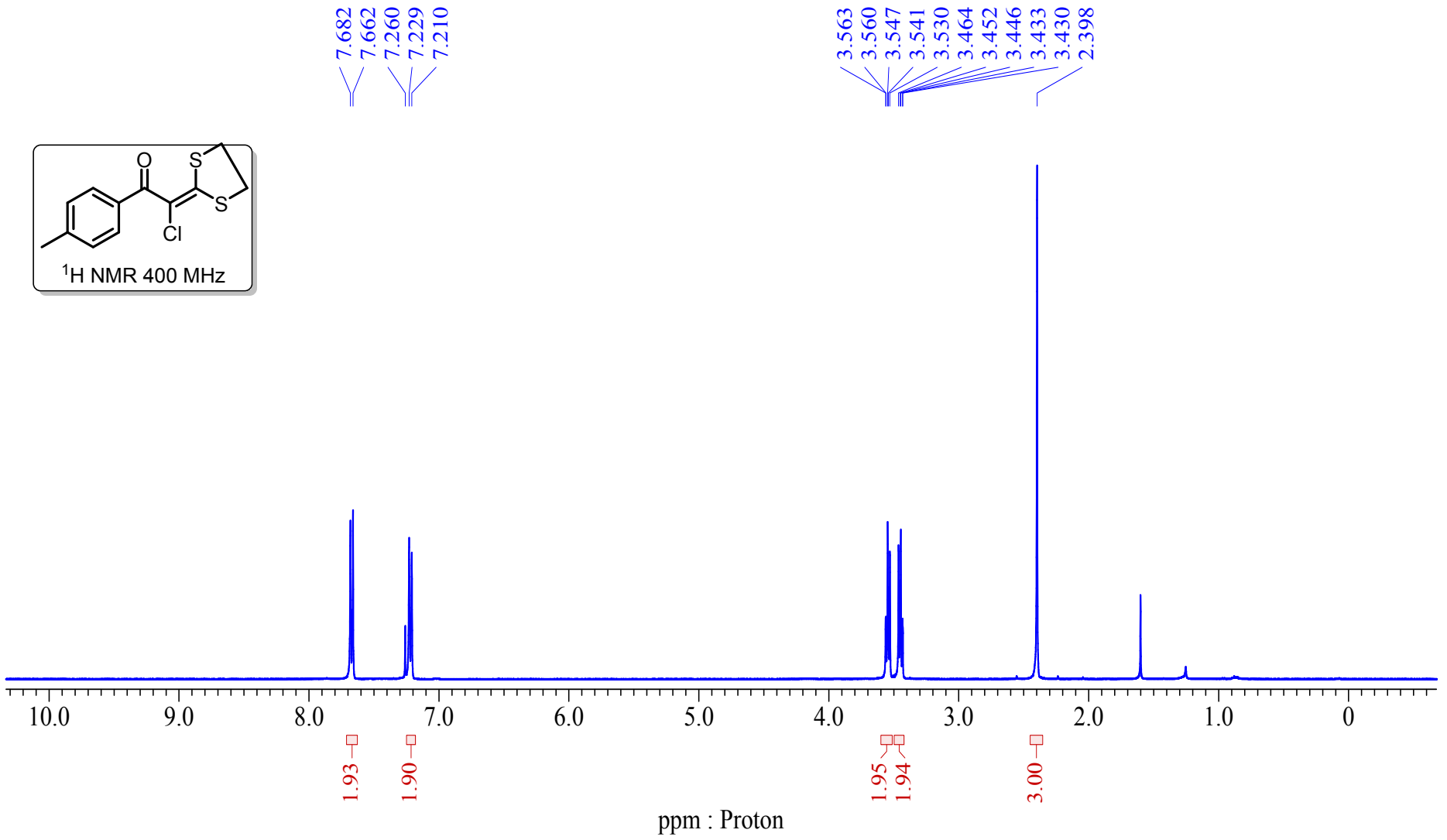


Fig.61: ^{1}H NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(p-tolyl)ethan-1-one* ***(3f)***

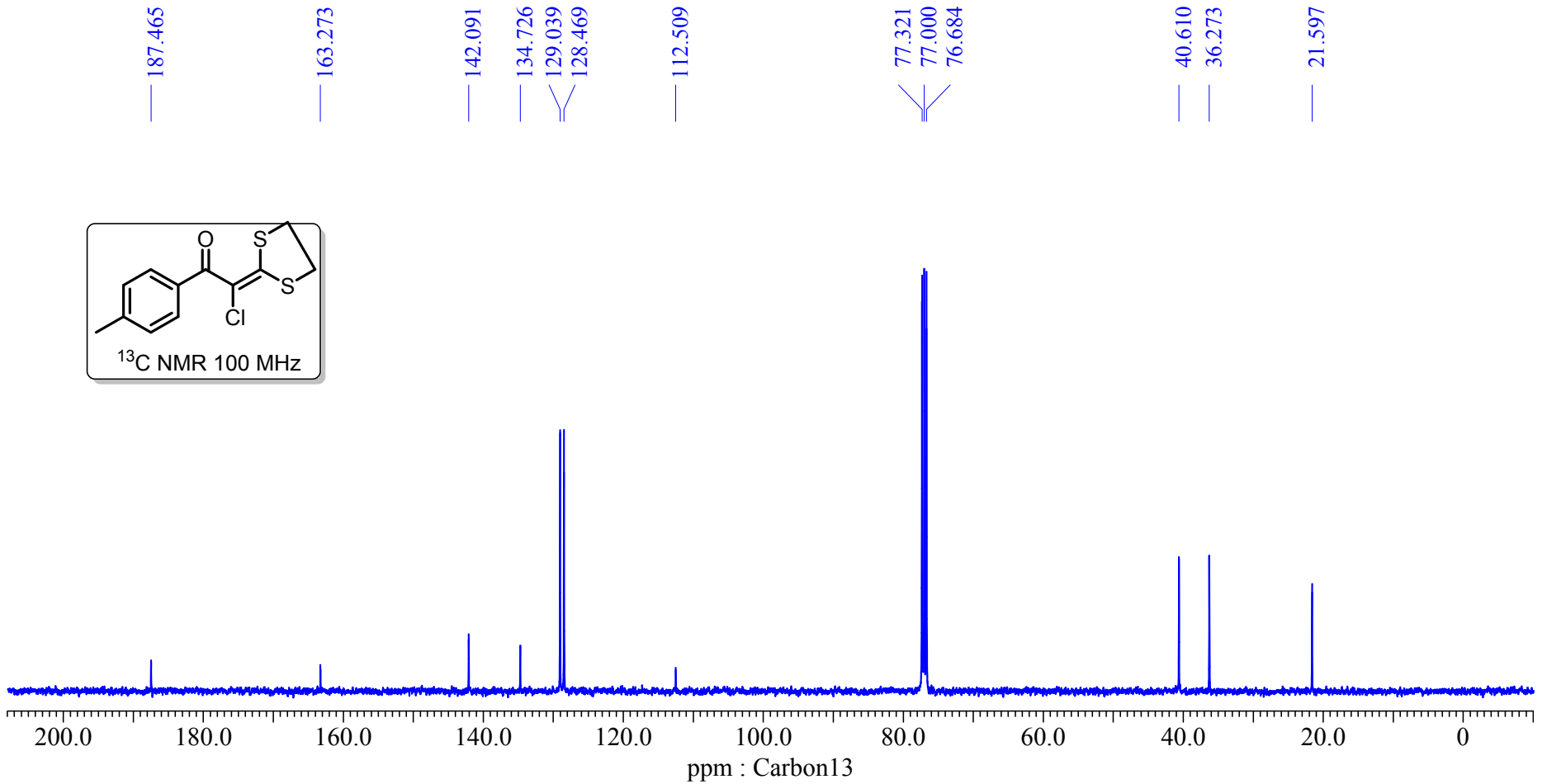


Fig.62: ^{13}C-NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(p-tolyl)ethan-1-one* ***(3f)***

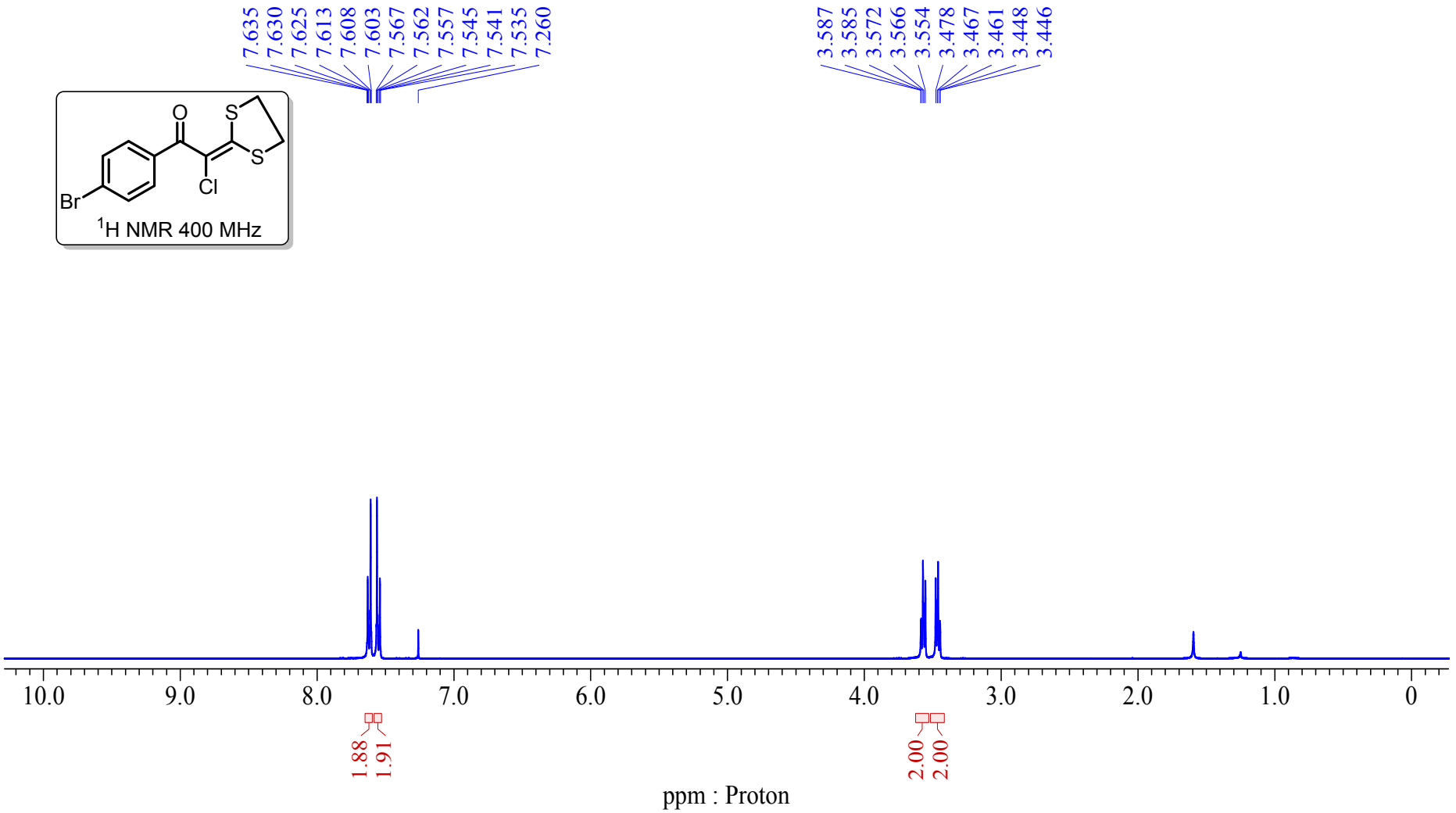


Fig.63: ^{1}H-NMR spectrum of *1-(4-bromophenyl)-2-chloro-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**3g**)*

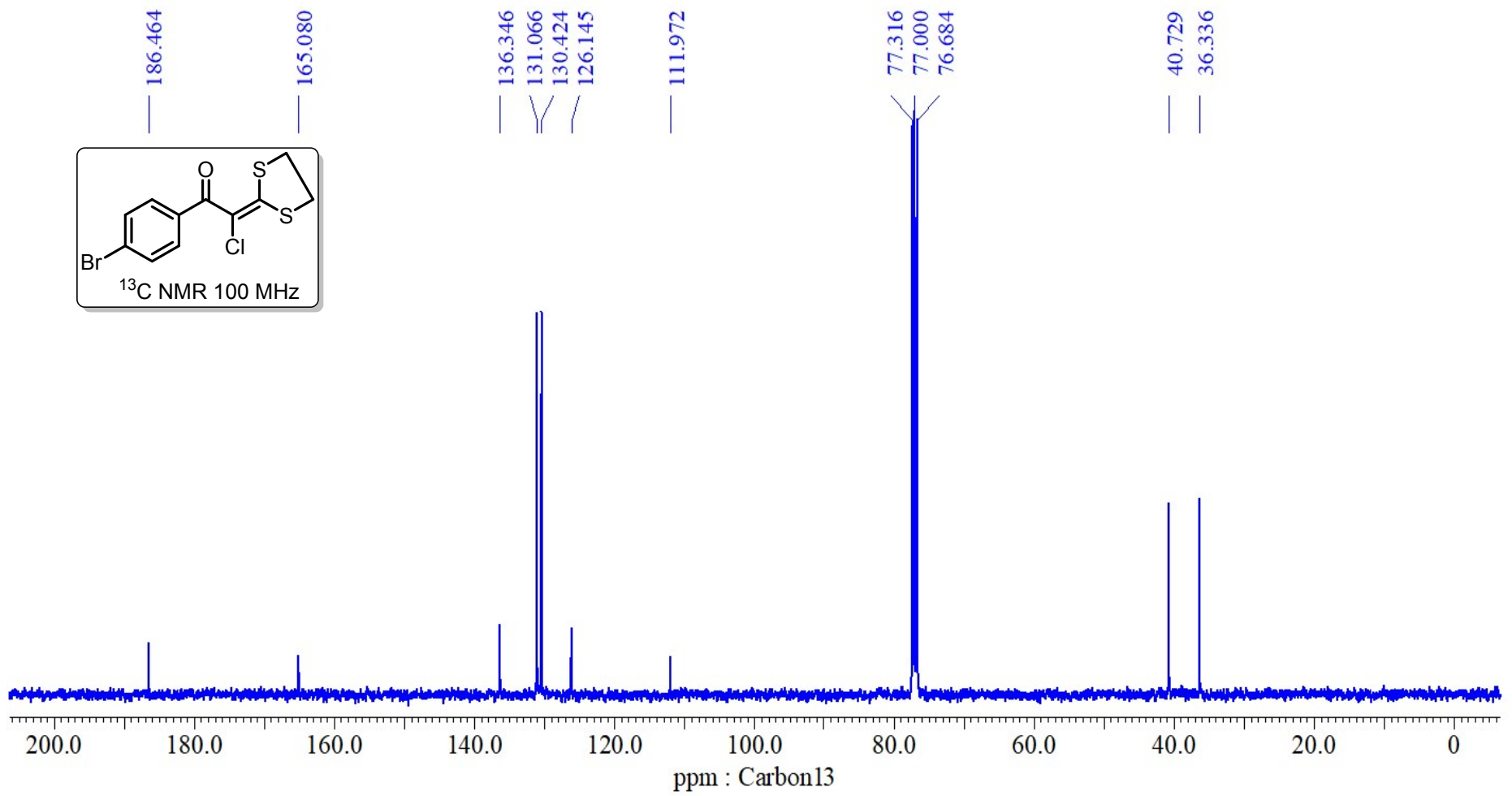


Fig.64: ^{13}C-NMR spectrum of *1-(4-bromophenyl)-2-chloro-2-(1,3-dithiolan-2-ylidene)ethan-1-one (**3g**)*

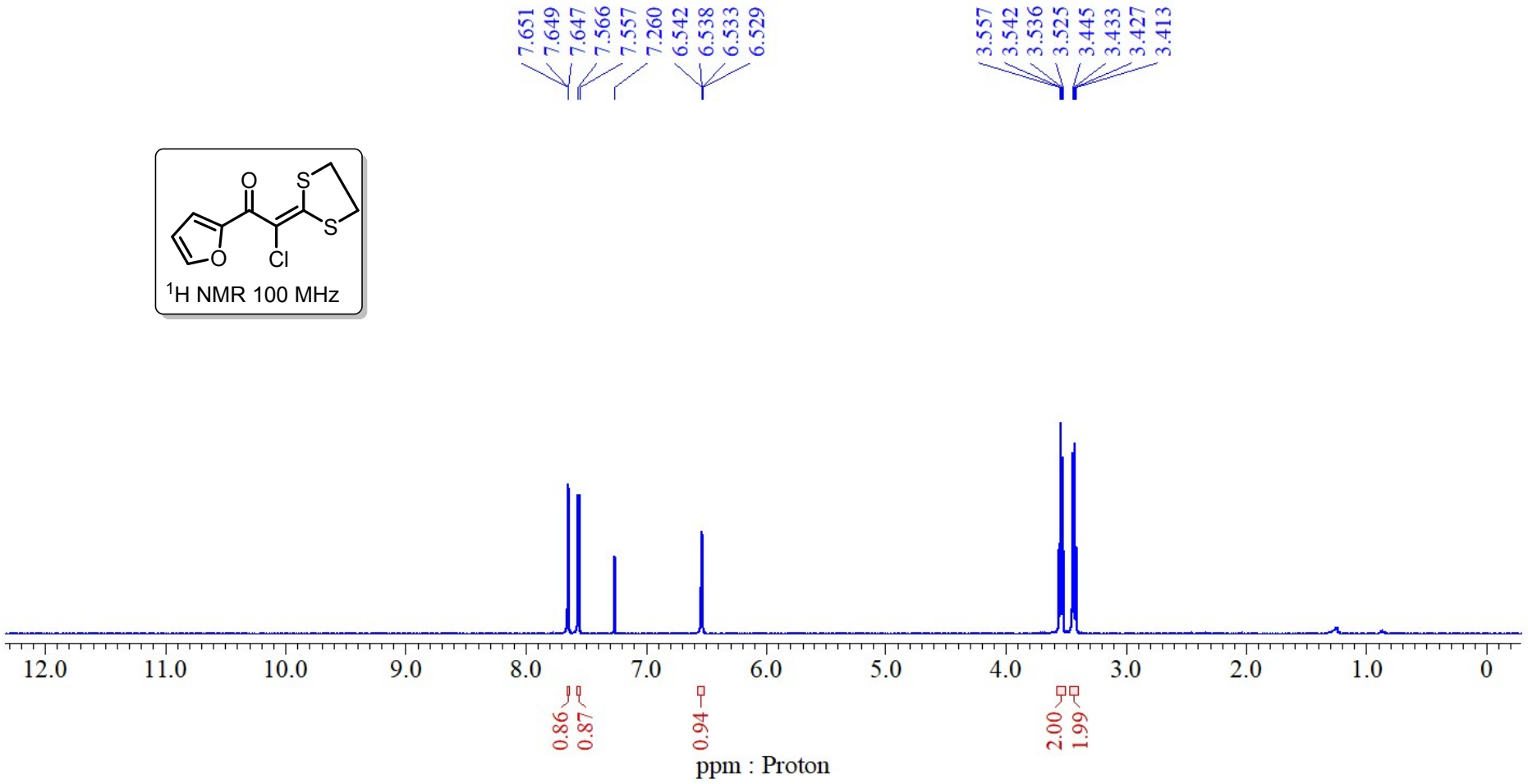


Fig.65: ^{1}H-NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-one* (***3h***)

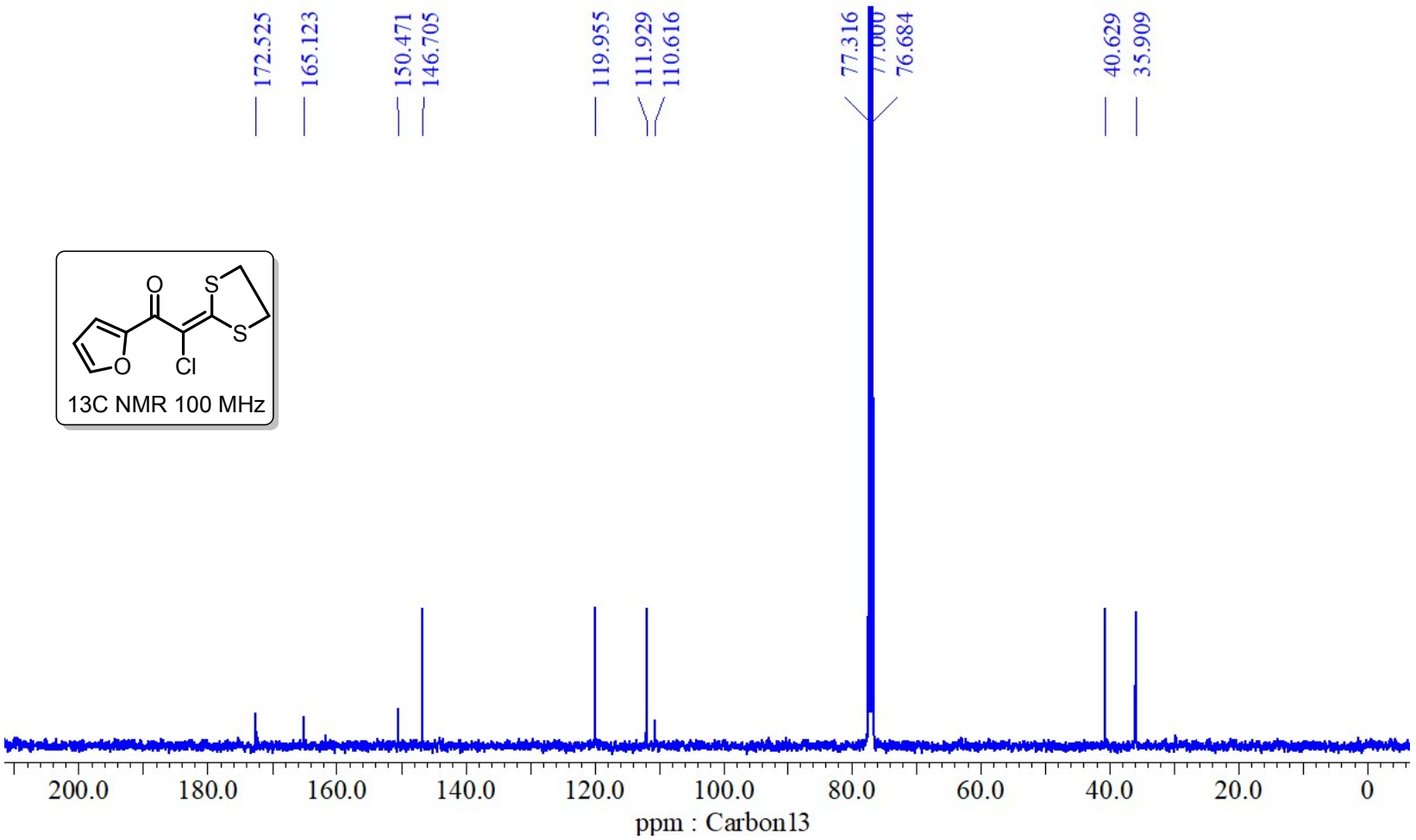


Fig.66: ^{13}C-NMR spectrum of *2-chloro-2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)ethan-1-on* (***3h***)

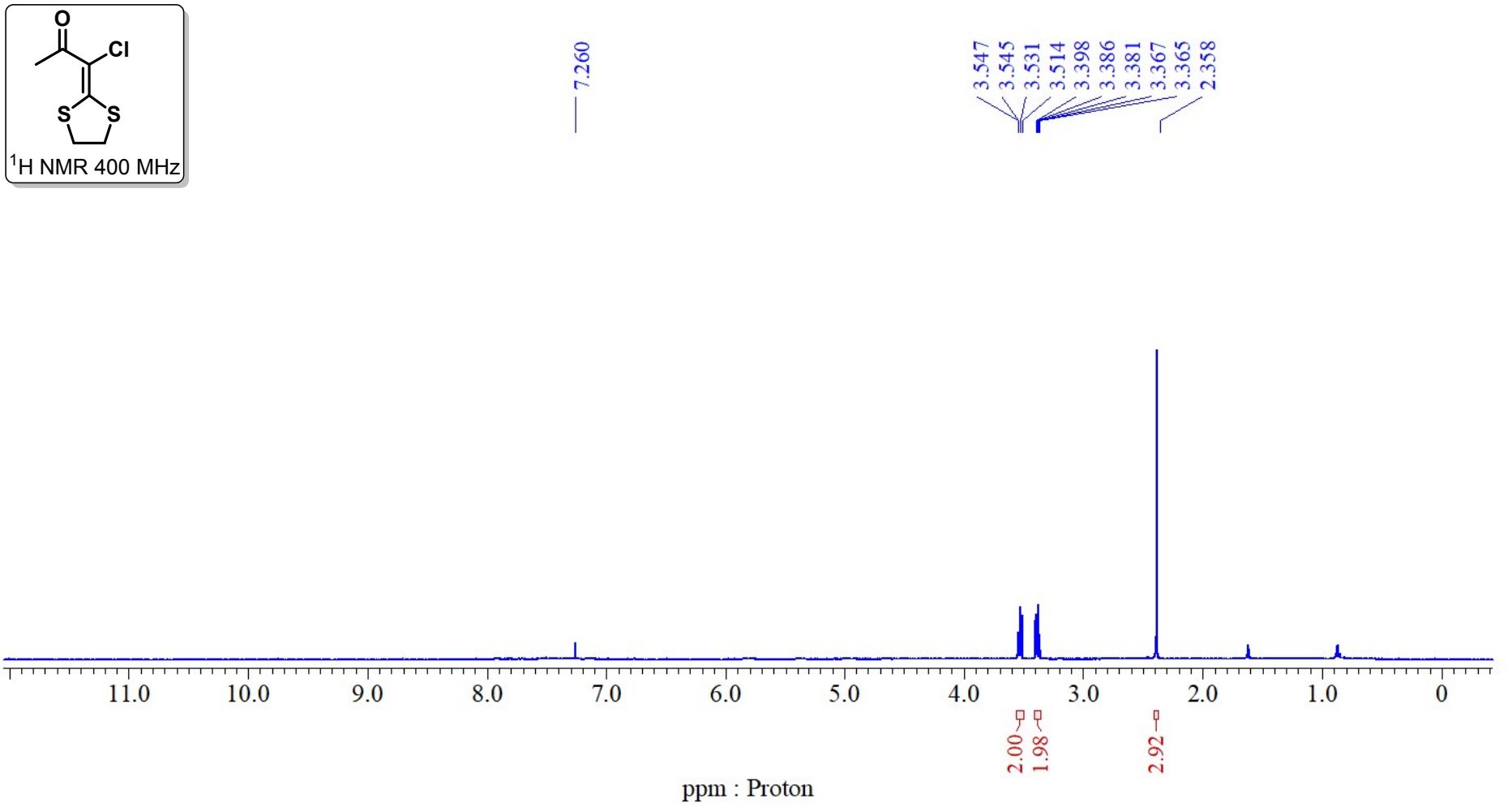


Fig.67: ^{1}H NMR spectrum of *1-chloro-1-(1,3-dithiolan-2-ylidene)propan-2-one (**3i**)*

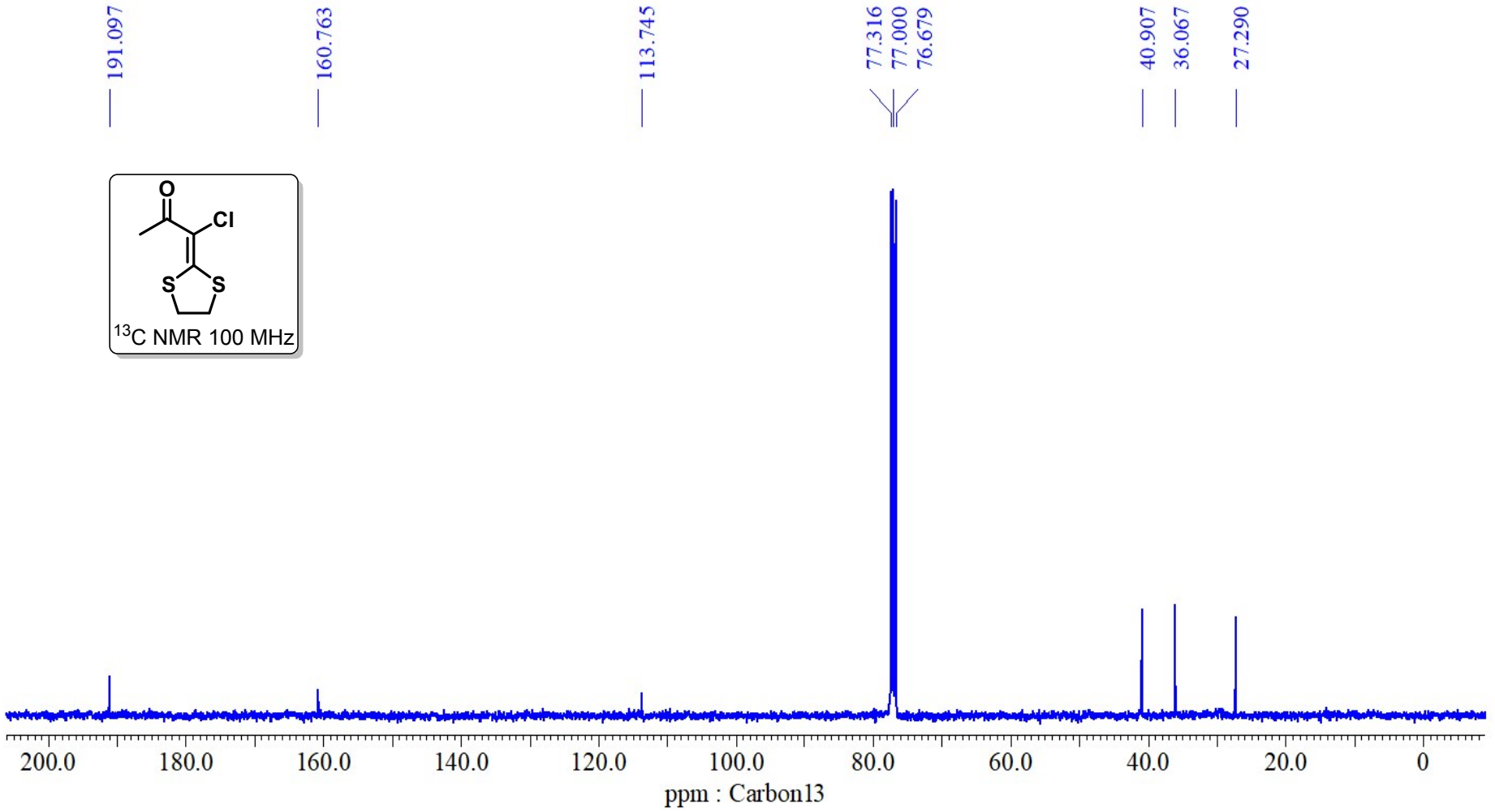


Fig.68: ^{13}C-NMR spectrum of *1-chloro-1-(1,3-dithiolan-2-ylidene)propan-2-one (**3i**)*

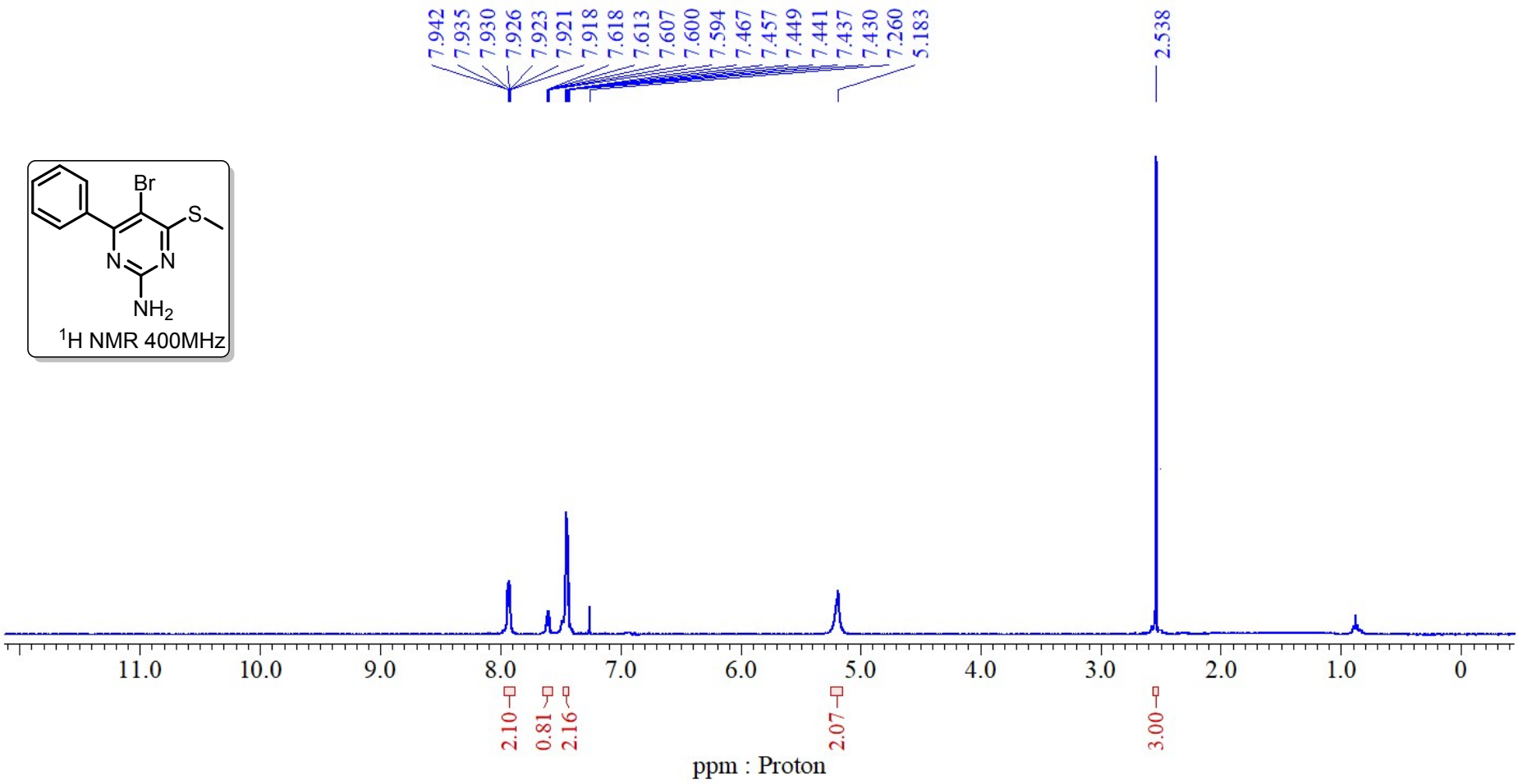


Fig.69: ^{1}H NMR spectrum of *5-bromo-4-(methylthio)-6-phenylpyrimidin-2-amine (**4a**)*

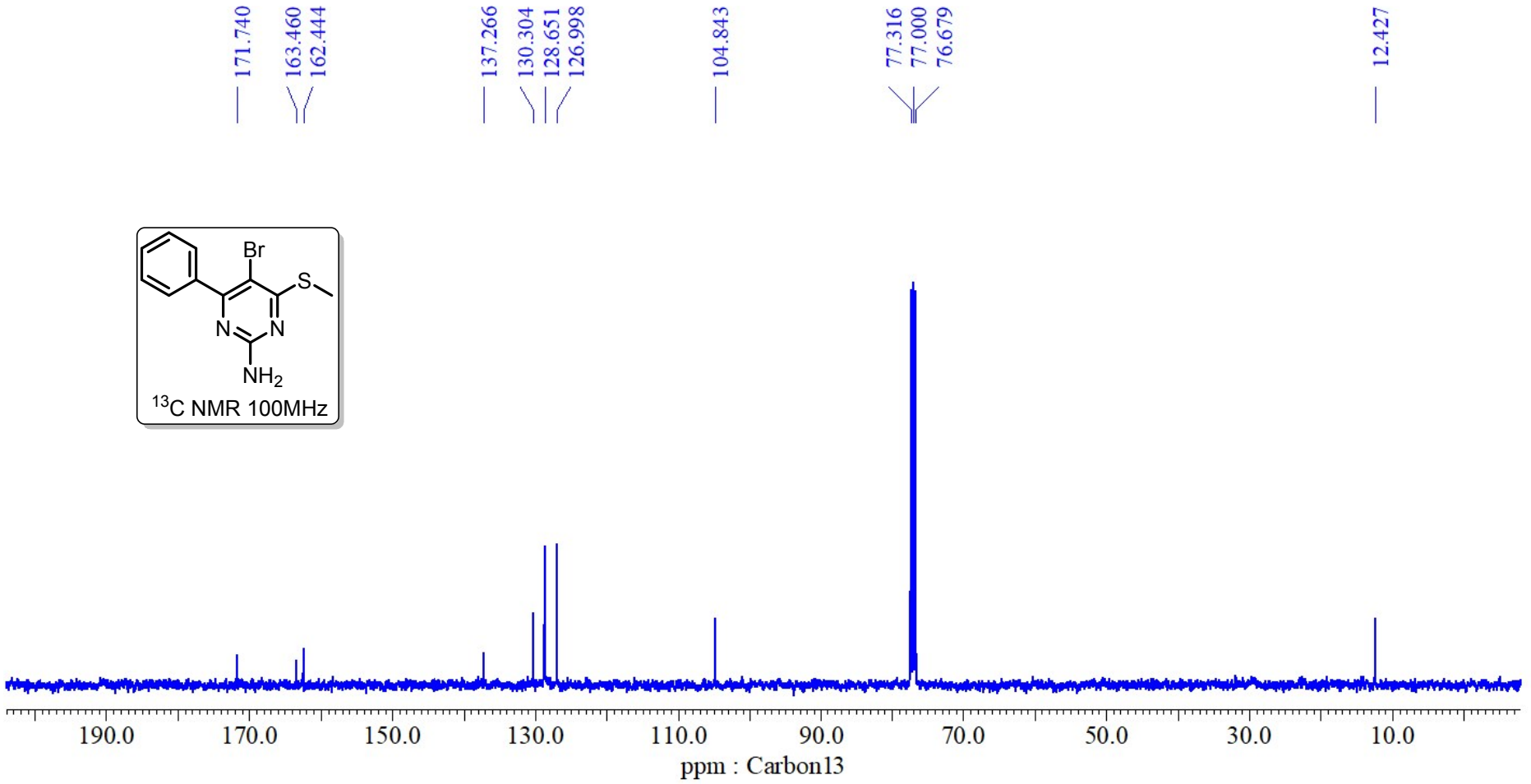


Fig.70: ^{13}C NMR spectrum of *5-bromo-4-(methylthio)-6-phenylpyrimidin-2-amine (**4a**)*

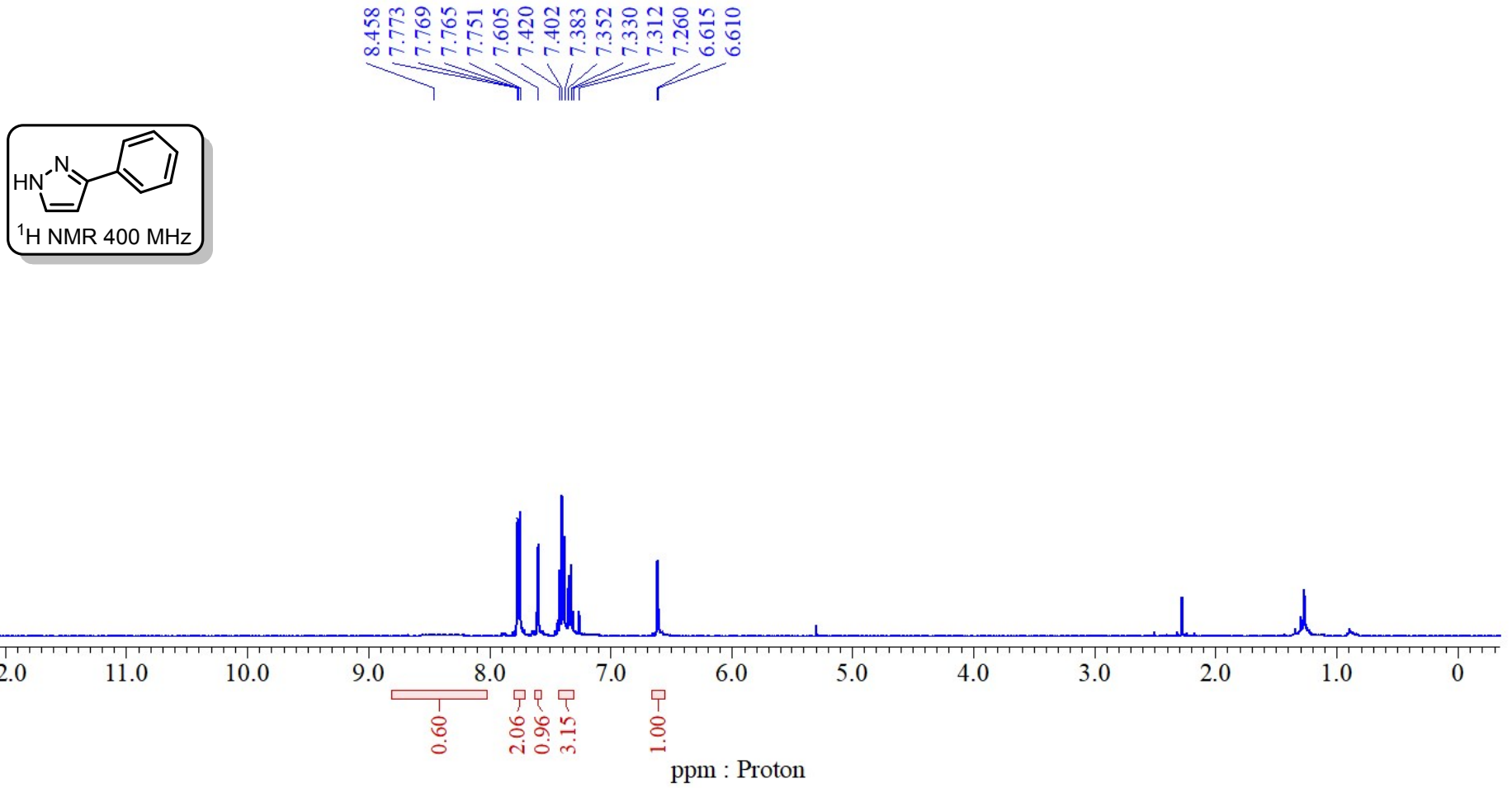


Fig.71: ^{1}H NMR spectrum of 3-phenyl-1H-pyrazole (***5a***)

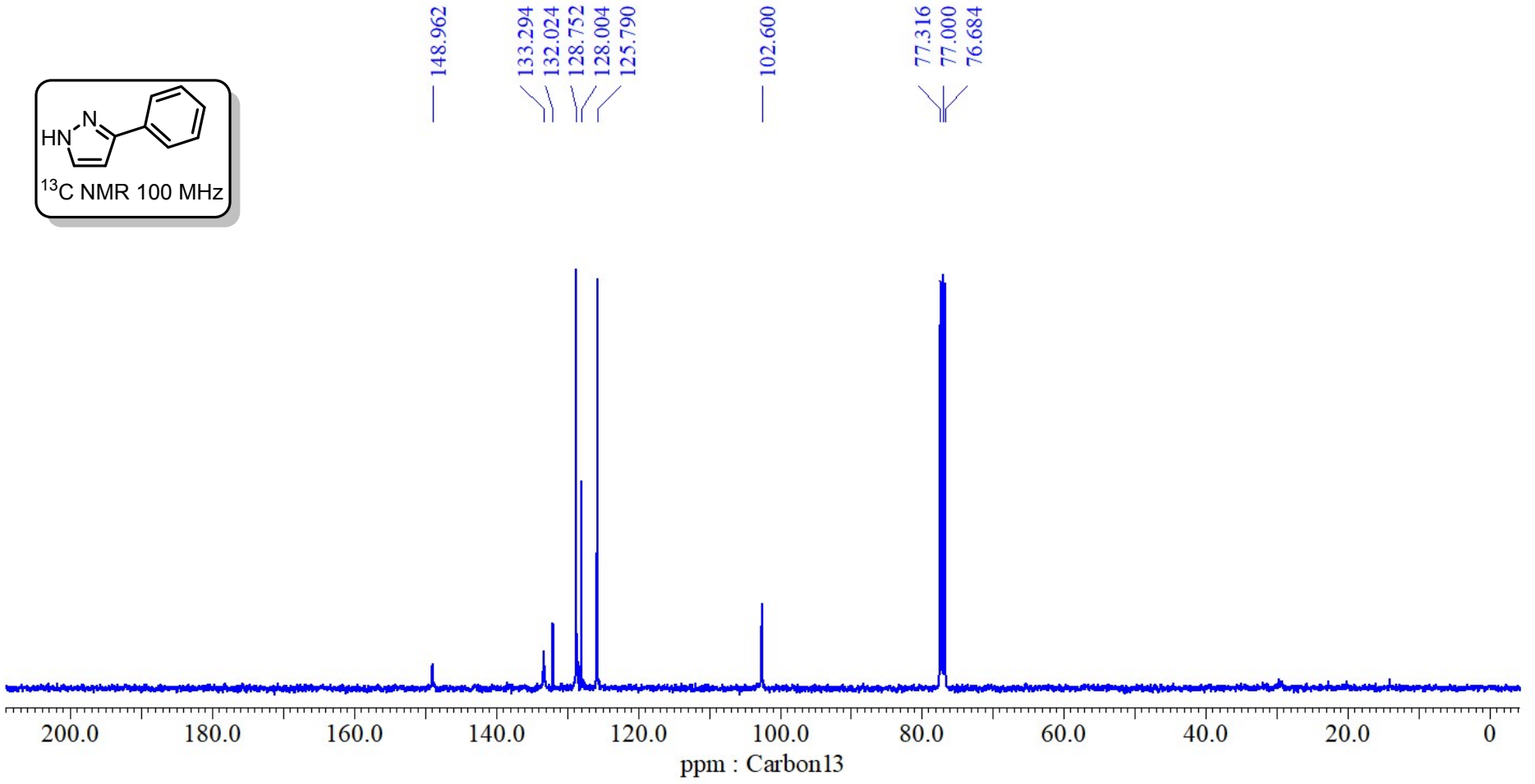


Fig.72: ^{13}C NMR spectrum of 3-phenyl-1H-pyrazole **(*5a*)**

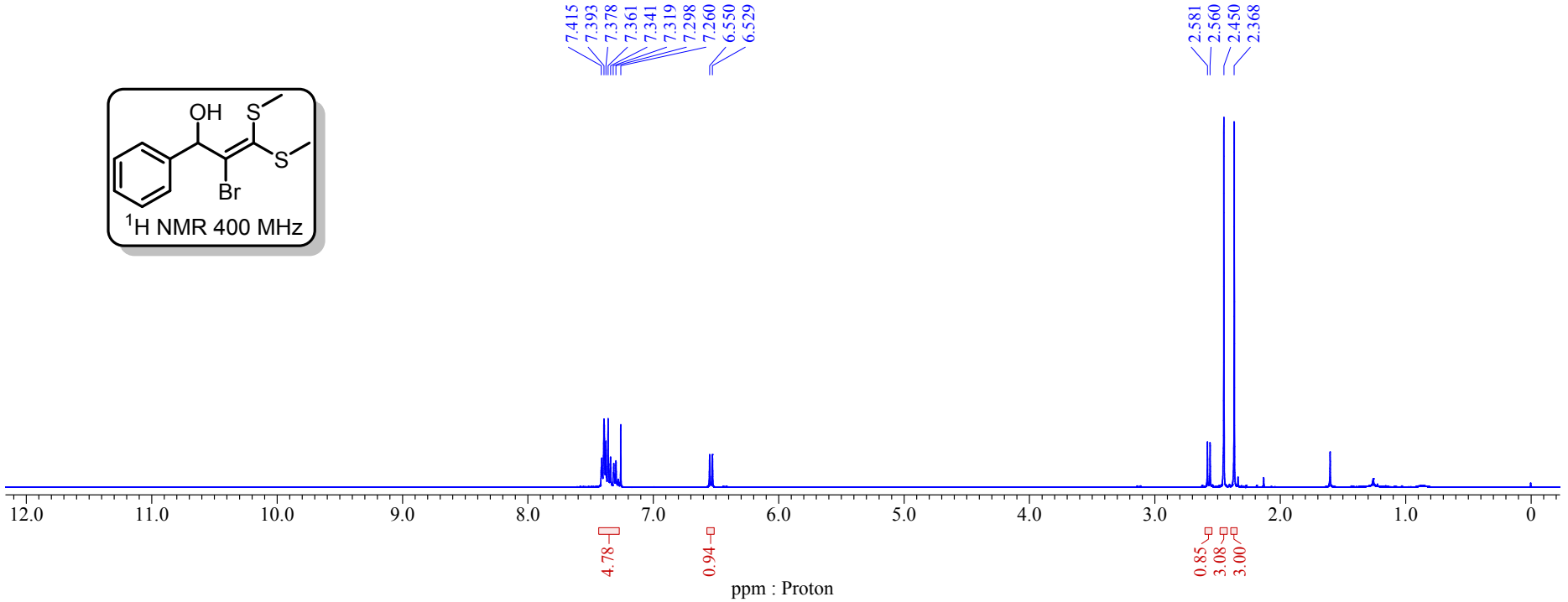


Fig.73: ^{1}H NMR spectrum of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-ol ***(6a)***

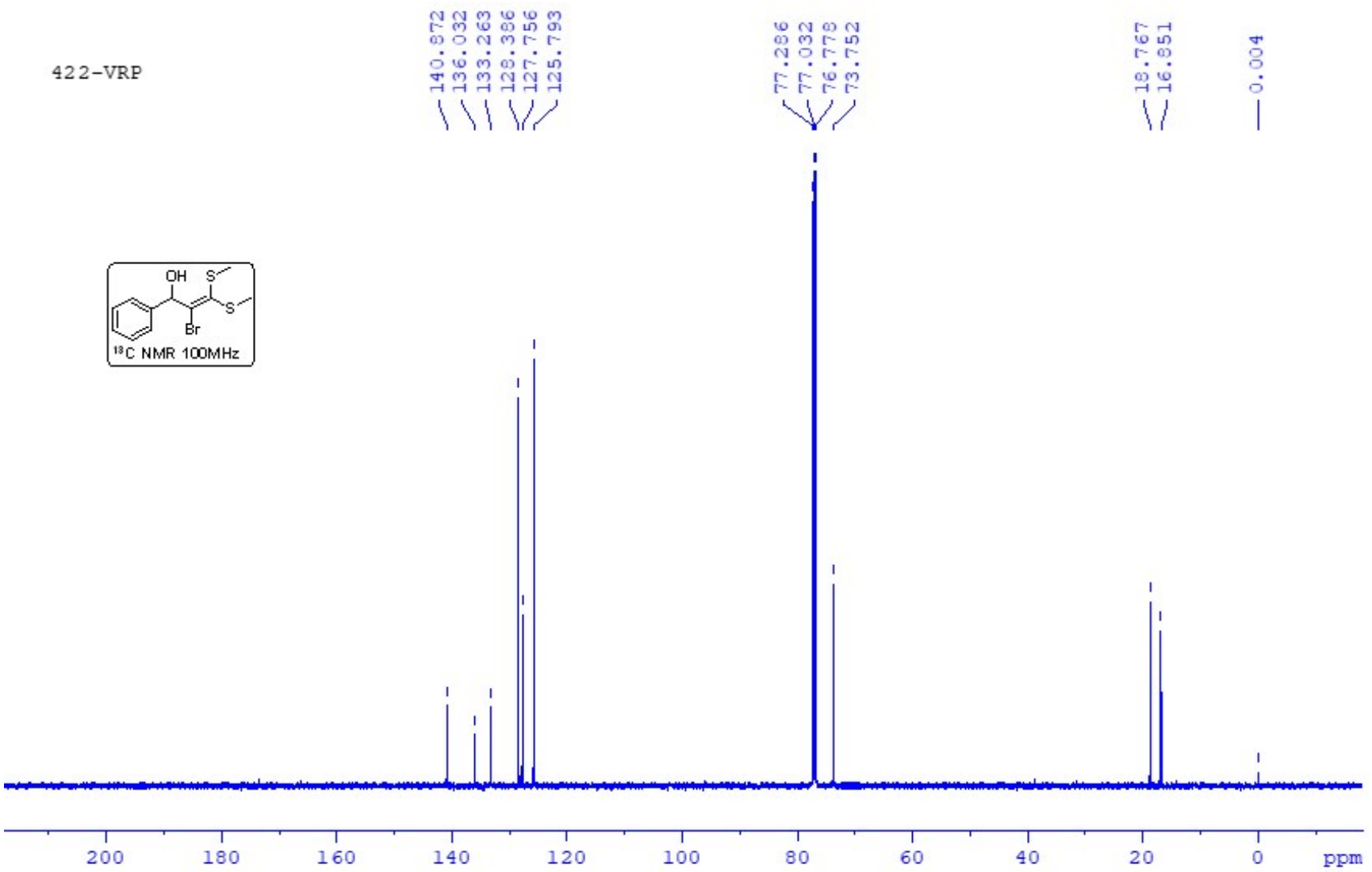


Fig.74: ^{13}C NMR spectrum of 2-bromo-3,3-bis(methylthio)-1-phenylprop-2-en-1-ol ***(6a)***

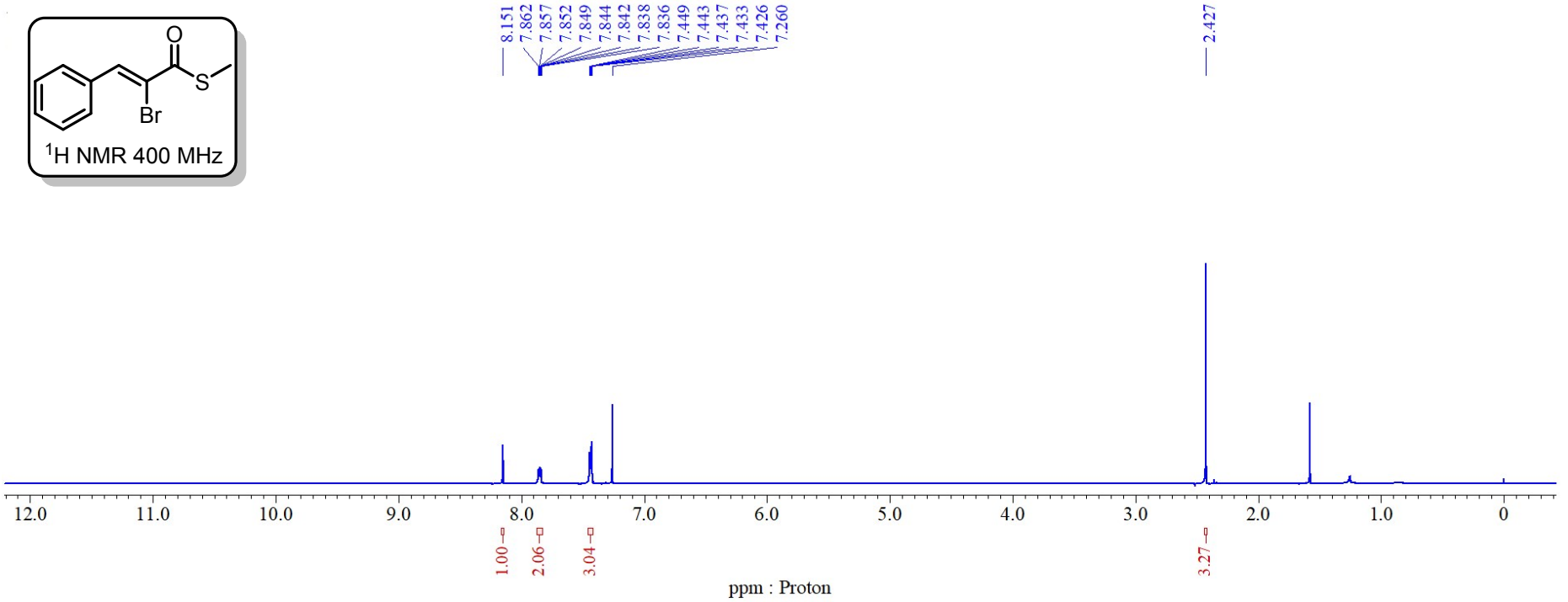


Fig.75: ^{1}H NMR spectrum of S-methyl-2-bromo-3-phenylprop-2-enethioate **(*7a*)**

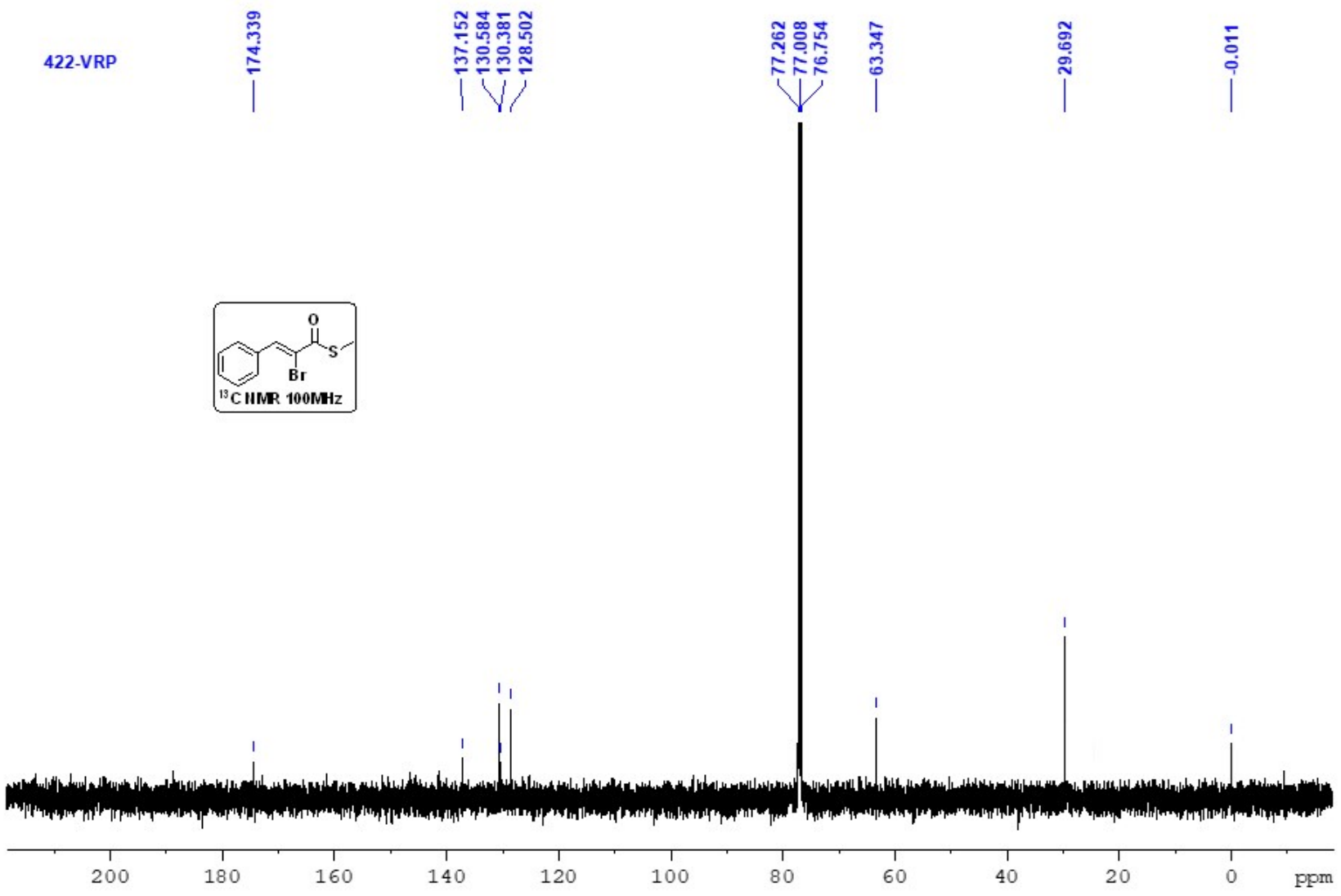


Fig.76: ^{13}C NMR spectrum of S-methyl-2-bromo-3-phenylprop-2-enethioate **(*7a*)**

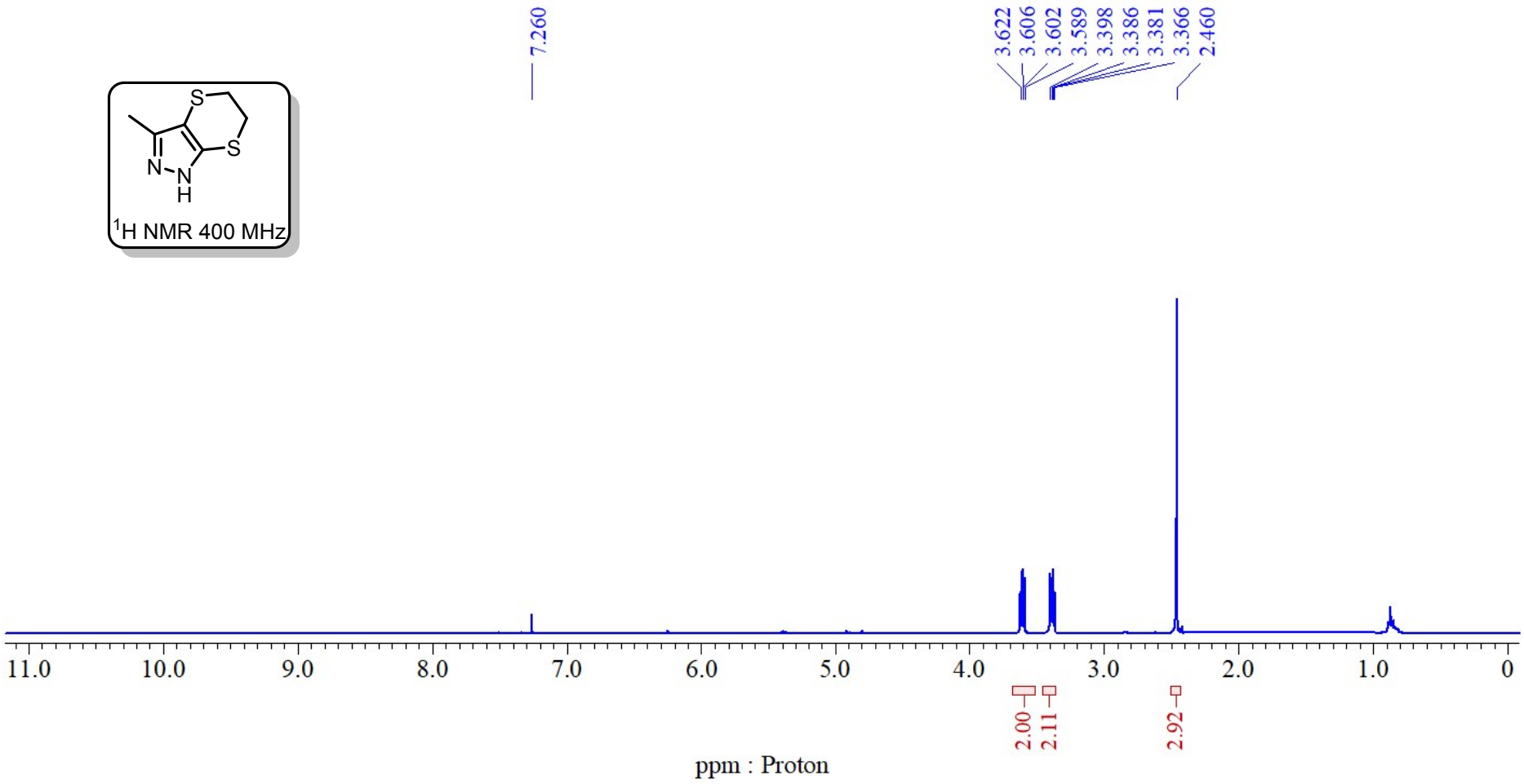


Fig.77: ^{1}H-NMR spectrum of *3-methyl-5,6-dihydro-1H-[1,4]dithiino[2,3-c]pyrazole (**8a**)*

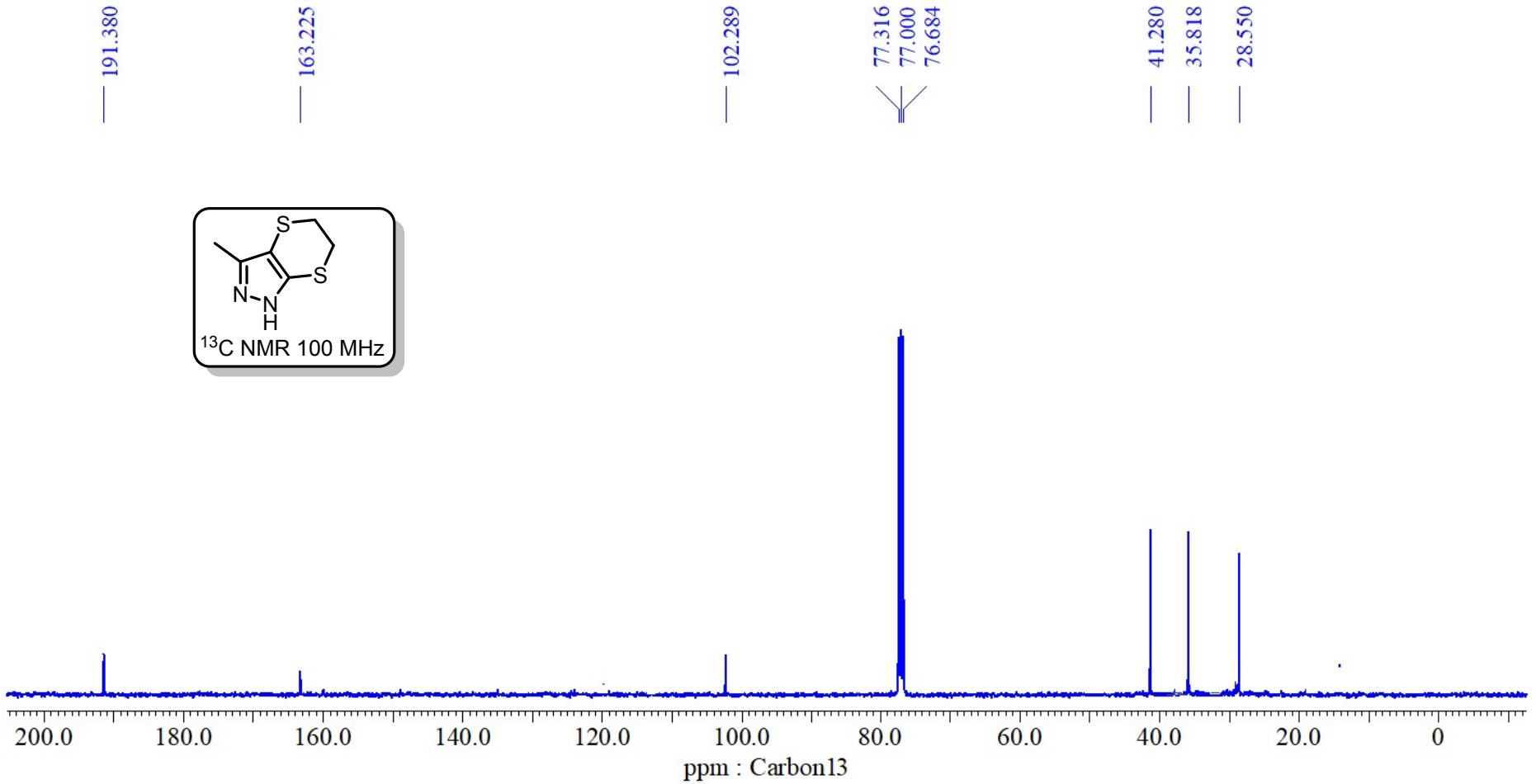


Fig.78: ^{13}C-NMR spectrum of *3-methyl-5,6-dihydro-1H-[1,4]dithiino[2,3-c]pyrazole (**8a**)*