Palladium Catalyzed Oxidative Coupling of α-Enolic Dithioesters: A New Entry to 3,4,5-Trisubstituted 1,2-Dithioles via Double Activation Strategy

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Electronic Supplementary Information

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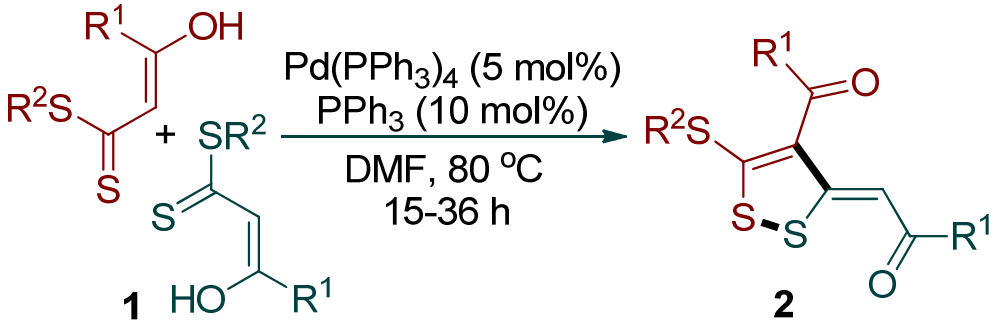
General Method:

All the chemicals except α-enolic dithioesters are commercially available and were used as received without any further purification. α-Enolic dithioesters were prepared following the literature procedure.[1] Thin-layer chromatography (TLC) was performed using silica gel 60 F_{254} precoated plates. Column chromatography was performed with 100-200 mesh silica gel. Infrared (IR) spectra were measured in KBr, and wavelengths (ν) are reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on NMR spectrometers operating at 300, 400, 500 and 75.5, 100, 125 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. Coupling constant (*J*) values are given in Hz. Mass spectra were recorded using electrospray ionization (ESI) mass spectrometry. The melting points are uncorrected.

1) Samuel, R.; Asokan, C. V.; Suma, S.; Chandran, P.; Retnamma, S.; Anabha, E. R. *Tetrahedron Lett*. **2007**, *48*, 8376.

General procedure for the synthesis of 4-acyl-3-acetylidene-5-alkylsulfanyl-[1,2]dithioles 2:

To a 5 mL DMF solution of α-enolic dithioester (1.0 mmol) tetrakis(triphenyl-phosphine)palladium(0) (5 mol%) and triphenylphosphine (10 mol%) were added and it was stirred under argon atmosphere at 80 °C for the stipulated period of time. After the completion of the reaction (monitored by TLC) it was worked up with dilute HCl followed by brine and extracted with ethyl acetate (2x10mL). The organic layer was dried over anhydrous Na_2SO_4 and was evaporated under vacuo. The crude reaction mixture was then purified by column chromatography using increasing amount of ethylacetate in ^{n}hexane as eluting solvent to afford pure 4-acyl-3-acetylidene-5-alkylsulfanyl-[1,2]dithioles **2**.



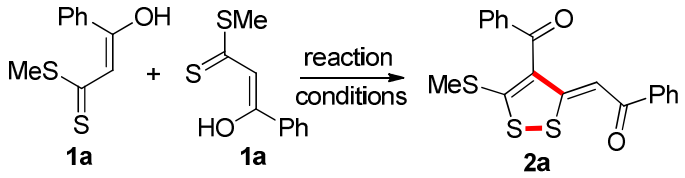
Optimization of model raction:

Initially, to a solution of methyl 3-hydroxy-3-phenylprop-2-enedithioate **1a** (1.0 mmol) in dry CH_3CN (10 ml), $Pd(PPh_3)_4$ (5 mol %) was added and the mixture was refluxed. Notably, the envisioned product 4-benzoyl-(Z)-3-(1-phenylacetylidene)-5-methylsulfanyl-1,2-dithiole **2a** was obtained in 30% yield after 24 h (Table 1, entry 1). Smelling a first-rate methodological essence in the above observation, we focussed on exploring the optimal reaction conditions for the synthesis of 1,2-dithiole **2a**. Several reaction parameters such as solvent, catalyst loading, additional ligands and temperature were examined (Table 1). The initial change of the solvent from CH_3CN to DMF effectively improved the yield of our desired product from 30% to 75% (Table 1, entry 2). Further, the use of solvents with different polarities like toluene, DCE, and THF could not improve the yield (Table 1, entries 3-5). Next, replacement of palladium(0) with Pd(II) catalysts such as $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ resulted in poor yields (Table 1, entries 6-7). However, the use of additional ligands such as PPh_3 and AgOAc improved the yield significantly (Table 1, entry 8) suggesting that the catalytic efficiency of Pd(0) species was superior to Pd(II) species.

Keeping in mind that the ligand PPh_3 may accelerate the reaction, we used 10 mol % of additional PPh_3 with 5 mol % of $Pd(PPh_3)_4$. To our delight, the desired product **2a** was obtained in 85% yield within 18 h (Table 1, entry 9). After the selection of suitable catalytic system, we moved toward its loading percentage. Use of 2 mol % of $Pd(PPh_3)_4$ decreased the yield to 75%, whereas the use of 10 mol % of catalyst led to

the generation of some additional undesired very close spots on TLC plate (Table 1, entries 10 and 11). Further, increasing the amount of ligand PPh_3 did not improve the result (Table 1, entry 12). The ideal temperature for the reaction was recognized to be 80 °C (Table 1, entries 13 and 14). Encouraged by the above result, we further checked the other transition metal catalysts like $Ru(PPh_3)_3Cl_2$ and $Rh(PPh_3)_3Cl$, which were found to be less efficient than palladium (Table 1, entries 15 and 16). Control experiment verified that the reaction did not proceed in the absence of catalyst (Table 1, entry 17). Thus the optimized condition was chosen to be 5 mol % of $Pd(PPh_3)_4$ in presence of 10 mol % PPh_3 in DMF at 80 °C (Table 1, entry 9).

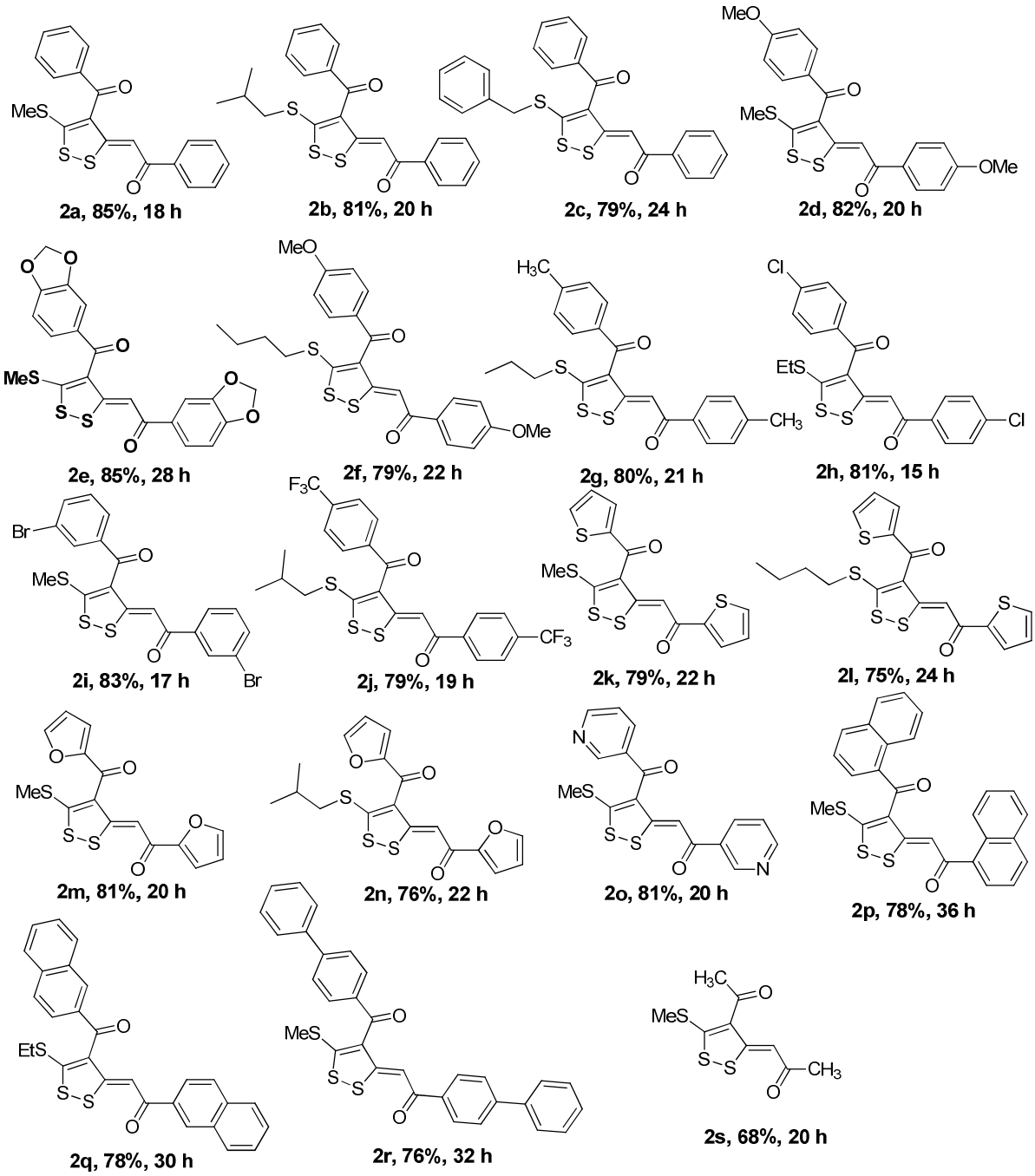
Table 1: Optimization of reaction condition for the model reaction:



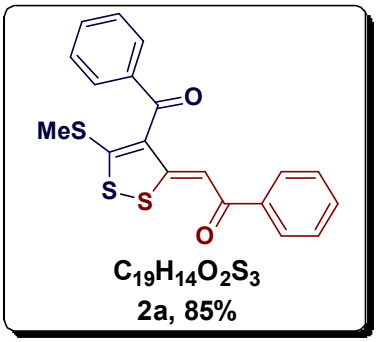
Entry	Catalyst [mol %]	Solvent	Temp [°C]	Time [h]	Yield [%][a]
1	$Pd(PPh_3)_4$ (5)	CH_3CN	reflux	24	30
2	$Pd(PPh_3)_4$ (5)	DMF	80	24	75
3	$Pd(PPh_3)_4$ (5)	Toluene	80	24	45
4	$Pd(PPh_3)_4$ (5)	DCE	reflux	24	15
5	$Pd(PPh_3)_4$ (5)	THF	reflux	24	20
6	$Pd(PPh_3)_2Cl_2$ (5)	DMF	80	24	20
7	$Pd(OAc)_2$(5)	DMF	80	24	30
8	$Pd(OAc)_2$(5), AgOAc (1eq) and PPh_3 (10)	DMF	80	24	70
9	**$Pd(PPh_3)_4$ (5); PPh_3(10)**	**DMF**	**80**	**18**	**85**
10	$Pd(PPh_3)_4$ (2); PPh_3(10)	DMF	80	18	75
11	$Pd(PPh_3)_4$ (10), PPh_3(10)	DMF	80	18	82
12	$Pd(PPh_3)_4$ (5); PPh_3(20)	DMF	80	18	82
13	$Pd(PPh_3)_4$ (5); PPh_3(10)	DMF	70	20	83
14	$Pd(PPh_3)_4$ (5); PPh_3(10)	DMF	100	16	80
15	$Ru(PPh_3)_3Cl_2$	DMF	80	24	40
16	$Rh(PPh_3)_3Cl$	DMF	80	24	45
17	none	DMF	80	48	NR

[a] Isolated pure yields.

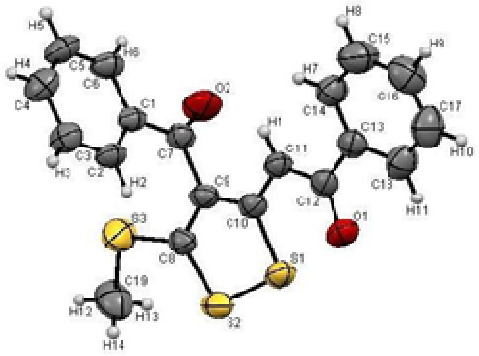
Table 2. Exploration of the substrate scope for the synthesis of **2**



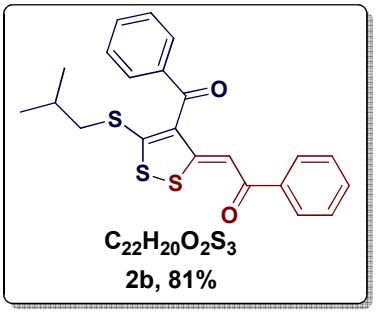
Characterization data and ortep diagrams for the isolated compounds



4-Benzoyl-3-(1-phenylacetylidene)-5-methylsulfanyl-[1,2]dithiole (2a): Yellow solid; M.p.- 151 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.81 (d, *J* = 7.2 Hz, 2H, Ar), 7.67 (d, *J* = 7.2 Hz, 2H, Ar), 7.56-7.18 (m, 6H, Ar), 6.89 (s, 1H, CH), 2.55 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 192.0 (C=O), 183.4 (C=O), 171.0, 136.2, 135.8, 134.2, 132.0, 131.6, 129.8, 129.0, 128.5, 127.4, 106.3, 18.2 (SMe); IR (KBr, ν_{max}, cm^{-1}): 3055, 1664, 1524, 1447, 1382, 1231, 742, 691; MS: HRMS: *m/z* = 371.0229 $[M+H]^+$. Found: 371.0237.

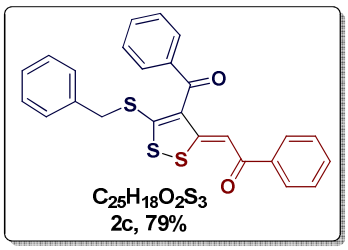


Crystal structure of 2a: CCDC 903331

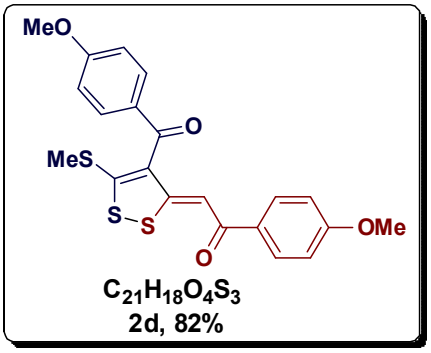


4-Benzoyl-3-(1-phenylacetylidene)-5-isobutylsulfanyl-[1,2]dithiole (2b): Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.90 (d, *J* = 7.2 Hz, 2H, Ar), 7.77 (d, *J* = 6.6 Hz, 2H, Ar), 7.63-7.36 (m, 6H, Ar), 6.97 (s, 1H, CH), 2.97 (d, *J* = 6.6 Hz, 2H, CH_2 of isobutyl), 2.01-1.92 (m, 1H, CH of isobutyl), 0.98

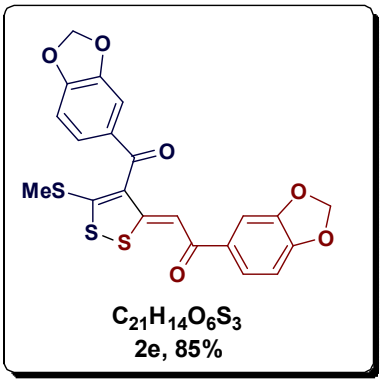
(d, *J* = 6.6 Hz, 6H, 2 CH_3 of isobutyl); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.3 (C=O), 183.8 (C=O), 166.6, 134.3, 132.3, 131.7, 131.6, 129.8, 129.0, 128.6, 128.5, 127.6, 127.4, 106.4, 44.7 (CH of isobutyl), 32.0 (CH_2 of isobutyl), 21.7 (2 CH_3 of isobutyl).



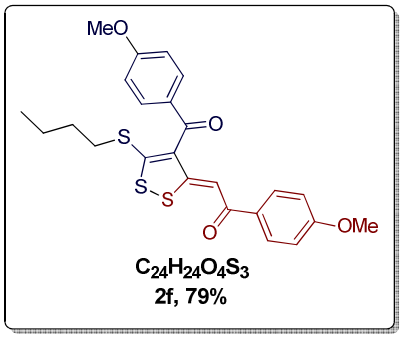
4-Benzoyl-3-(1-phenylacetylidene)-5-benzylsulfanyl-[1,2]dithiole (2c): Yellow sticky solid; ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.84-7.59 (m, 5H, Ar), 7.48-7.25 (m, 10H, Ar), 6.96 (s, 1H, CH), 4.27 (s, 2H, CH_2 of benzyl); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 189.6 (C=O), 183.6 (C=O), 170.2, 136.0, 134.3, 132.2, 132.1, 131.7, 129.8, 129.4, 129.0, 128.7, 128.5, 128.3, 128.1, 127.7, 127.4, 106.8, 40.3 (CH_2 of benzyl).



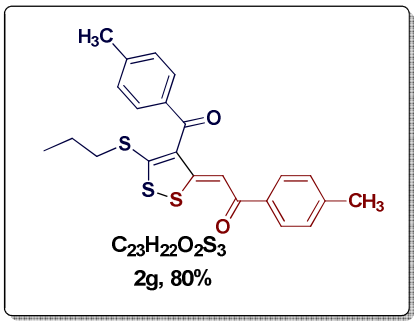
4-Methoxybenzoyl-3-(1-(4-methoxyphenyl) acetylidene)-5-methylsulfanyl-[1,2]dithiole (2d): Yellow solid; M.p.- 165 °C; ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.88 (d, *J* = 8.4 Hz, 2H, Ar), 7.77 (d, *J* = 8.7 Hz, 2H, Ar), 6.96 (d, *J* = 7.8 Hz, 3H, 2 Ar + CH), 6.86 (d, *J* = 8.7 Hz, 2H, Ar), 3.88 (s, 3H, OMe), 3.82 (s, 3H, OMe), 2.61 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.8 (C=O), 182.9 (C=O), 170.2, 164.6, 164.3, 162.5, 132.5, 129.5, 128.9, 128.9, 128.6, 114.3, 113.8, 106.0, 55.5 (OMe), 55.3 (OMe), 18.1 (SMe); IR (KBr, ν_{max}, cm^{-1}): 2928, 2837, 1598, 1507, 1419, 1370, 1169, 1023, 837, 606.



1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(4-(benzo[*d*][1,3]dioxole -5-carbonyl)-5-(methylthio)-3H-1,2-dithiol-3-ylidene) ethanone (2e): Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.43-7.31 (m, 4H, Ar), 6.87-6.75 (m, 3H, 2 Ar + CH), 6.07-5.98 (m, 4H, 2 CH_2), 2.61 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.3 (C=O), 182.5 (C=O), 167.3, 153.2, 150.7, 148.7, 148.0, 133.9, 130.7, 130.5, 127.5, 123.0, 108.8, 108.4, 108.1, 107.6, 105.9, 102.2 (CH_2), 101.6 (CH_2), 18.1 (SMe).

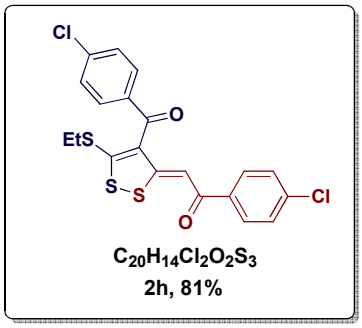


4-Methoxybenzoyl-3-(1-(4-methoxyphenyl) acetylidene)-5-butylsulfanyl-[1,2]dithiole (2f): Yellow solid; M.p.- 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.89 (d, *J* = 8.7 Hz, 2H, Ar), 7.78 (d, *J* = 8.7 Hz, 2H, Ar), 6.95 (d, *J* = 9.0 Hz, 3H, 2 Ar + CH), 6.86 (d, *J* = 9.0 Hz, 2H, Ar), 3.88 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.07 (t, *J* = 7.2 Hz, 2H, CH_2 of SBu), 1.70-1.62 (m, 2H, CH_2 of SBu), 1.41-1.33 (m, 2H, CH_2 of SBu), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3 of SBu); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.9 (C=O), 183.0 (C=O), 172.2, 169.8, 167.9, 164.7, 162.3, 155.4, 151.4, 132.5, 129.5, 114.3, 113.8, 106.2, 55.6 (OMe), 55.3 (OMe), 35.6, 31.2, 21.7, 13.4; IR (KBr, ν_{max}, cm^{-1}): 2924, 2852, 1649, 1599, 1425, 1371, 1262, 1228, 1167, 1029, 847, 638.

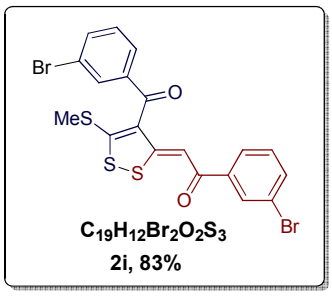


4-Methylbenzoyl-3-(1-(4-methylphenyl)acetylidene) -5-propylsulfanyl-[1,2]dithiole (2g): Yellow solid; M.p.- 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.80 (d, *J* = 8.1 Hz, 2H, Ar), 7.69 (d, *J* = 7.8 Hz, 2H, Ar), 7.28 (d, *J* = 8.1

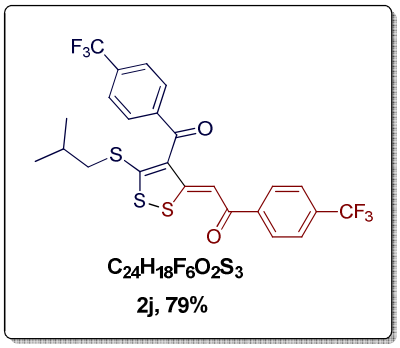
Hz, 2H, Ar), 7.16 (d, J = 8.1 Hz, 2H, Ar), 6.96 (s, 1H, CH), 3.05 (t, J = 7.2 Hz, 2H, CH_2 of SPr), 2.43 (s, 3H, p-CH_3), 2.35 (s, 3H, p-CH_3), 1.76-1.69 (m, 2H, CH_2 of SPr), 0.98 (t, J = 7.5 Hz, 3H, CH_3 of SPr); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 192.0 (C=O), 183.5 (C=O), 170.2, 145.6, 142.3, 133.5, 133.3, 130.0, 129.9, 129.8, 129.7, 129.2, 127.5, 106.4, 37.8, 22.7, 21.8, 21.5, 13.2; IR (KBr, ν_{max}, cm^{-1}): 2922, 1662, 1601, 1526, 1412, 1372, 1229, 1006, 856, 756, 695.



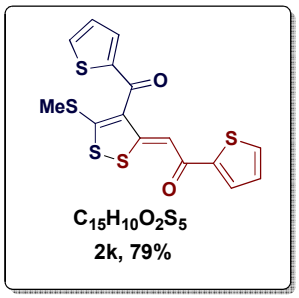
4-Chlorobenzoyl-3-(1-(4-chlorophenyl)acetylidene)-5-ethylsulfanyl-[1,2]dithiole (2h): Yellow solid; M.p.- 178 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.83 (d, J = 8.5 Hz, 2H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.47 (d, J = 8.6 Hz, 2H, Ar), 7.35 (d, J = 8.5 Hz, 2H, Ar), 6.92 (s, 1H, CH), 3.12 (q, J = 7.0 Hz, 2H, CH_2 of SEt), 1.37 (t, J = 7.0 Hz, 3H, CH_3 of SEt); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 191.1 (C=O), 182.4 (C=O), 170.9, 141.2, 138.1, 134.4, 134.3, 132.6, 131.3, 129.6, 128.9, 128.9, 106.0, 30.4 (CH_2 of SEt), 14.3 (CH_3 of SEt).



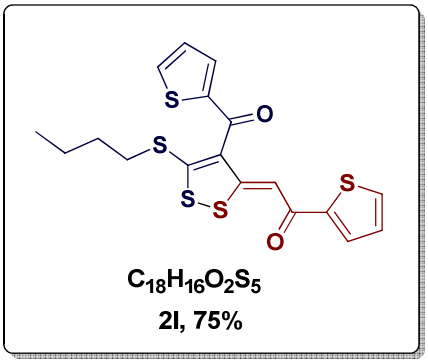
3-Bromobenzoyl-3-(1-(3-bromophenyl)acetylidene)-5-methylsulfanyl-[1,2]dithiole (2i): Yellow solid; M.p.- 183 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.04 (s, 1H, Ar), 7.92 (s, 1H, Ar), 7.76 (d, J = 7.8 Hz, 2H, Ar), 7.68 (d, J = 7.5 Hz, 1H, Ar), 7.56 (d, J = 7.8 Hz, 1H, Ar), 7.38 (t, J = 8.1 Hz, 1H, Ar), 7.25 (t, J = 7.8 Hz, 1H, Ar), 6.91 (s, 1H, CH), 2.66 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.5 (C=O), 182.9 (C=O), 172.9, 152.3, 139.2, 137.1, 134.5, 133.4, 132.3, 130.6, 130.5, 130.1, 128.4, 125.9, 125.8, 123.1, 122.8, 105.8, 18.3 (SMe); IR (KBr, ν_{max}, cm^{-1}): 2924, 2853, 1654, 1523, 1465, 1422, 1357, 1230, 775, 670; MS: HRMS: m/z = 526.8439 $[M+H]^+$. Found: 526.8448.



4-Trifluoromethylbenzoyl-3-(1-(4-trifluoromethyl phenyl) acetylidene)-5-isobutyl sulfanyl-[1,2] dithiole (2j): Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.00 (d, *J* = 8.1 Hz, 2H, Ar), 7.86 (d, *J* = 8.1 Hz, 2H, Ar), 7.79-7.62 (m, 2H, Ar), 7.51-7.44 (m, 2H, Ar), 6.94 (s, 1H, CH), 3.00 (d, *J* = 6.9 Hz, 2H, CH_2 of isobutyl), 2.00-1.96 (m, 1H, CH of isobutyl), 0.99 (d, *J* = 6.6 Hz, 6H, 2 CH_3 of isobutyl); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 191.0 (C=O), 182.0 (C=O), 171.4, 138.9, 132.3, 132.1, 131.5, 131.5, 130.0, 128.5, 128.4, 127.7, 126.1, 125.6, 125.5, 105.8, 44.8 (CH of isobutyl), 28.7 (CH_2 of isobutyl), 21.7 (2 CH_3 of isobutyl).

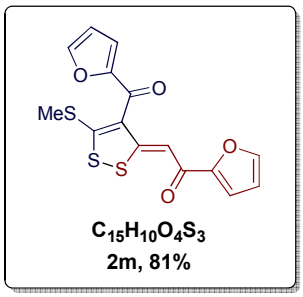


2-Thienoyl-3-(1-(2-thienyl)acetylidene)-5-methylsulfanyl-[1,2] dithiole (2k): Yellow solid; M.p.- 155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.84 (d, *J* = 4.0 Hz, 1H, Ar), 7.68 (t, *J* = 2.0 Hz, 1H, Ar), 7.57-7.54 (m, 2H, Ar), 7.17 (br, 1H, Ar), 7.08 (br, 1H, Ar), 6.97 (s, 1H, CH), 2.67 (s, 3H, SMe); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 184.5 (C=O), 178.1 (C=O), 169.8, 143.2, 142.8, 136.9, 136.3, 132.0, 129.8, 129.1, 128.7, 128.5, 106.5 18.6 (SMe).



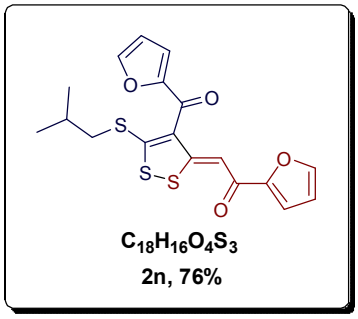
2-Thienoyl-3-(1-(2-thienyl)acetylidene)-5-butyl sulfanyl-[1,2] dithiole (2l): Yellow solid; M.p.- 143 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.80 (d, *J* = 1.0 Hz, 1H, Ar), 7.62 (d, *J* = 5.0 Hz, 1H, Ar), 7.53-7.50 (m, 2H, Ar), 7.13 (t, *J* = 5.5 Hz, 1H, Ar), 7.04 (t, *J* = 5.5 Hz, 1H, Ar), 6.92 (s, 1H, CH), 3.07 (t, *J* = 7.2 Hz, 2H, CH_2 of SBu), 1.72-1.64 (m, 2H, CH_2 of SBu), 1.42-1.34 (m, 2H, CH_2 of SBu), 0.90 (t, *J* = 9.0 Hz, 3H, CH_3 of SBu); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm):

184.1 (C=O), 177.8 (C=O), 169.2, 163.4, 142.6, 136.6, 136.0, 131.7, 129.5, 128.8, 128.2, 106.2, 35.9, 31.2, 21.8, 13.5; IR (KBr, ν_{max}, cm^{-1}): 2960, 1630, 1539, 1395, 1234, 1068, 718.



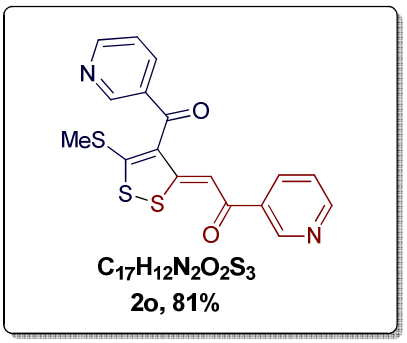
$C_{15}H_{10}O_4S_3$
2m, 81%

2-Furoyl-3-(1-(2-furyl)acetylidene)-5-methylsulfanyl-[1,2] dithiole (2m): Yellow solid; M.p.- 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.73 (br, 1H, Ar), 7.52 (br, 1H, Ar), 7.30-7.28 (m, 1H, Ar), 7.12 (d, *J* = 4.0 Hz, 1H, Ar), 6.99 (s, 1H, CH), 6.65-6.63 (m, 1H, Ar), 6.52-6.51 (m, 1H, Ar), 2.67 (s, 3H, SMe); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 178.7 (C=O), 174.2 (C=O), 170.3, 152.7, 148.5, 145.6, 122.3, 115.1, 113.4, 113.1, 112.8, 112.7, 106.2, 18.6 (SMe).

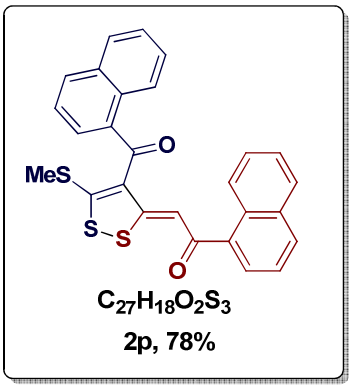


$C_{18}H_{16}O_4S_3$
2n, 76%

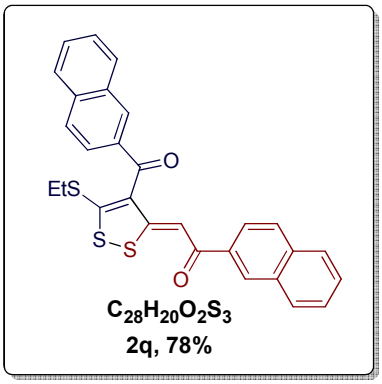
2-Furoyl-3-(1-(2-furyl)acetylidene)-5-isobutylsulfanyl-[1,2] dithiole (2n): Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.70 (br, 1H, Ar), 7.49 (br, 1H, Ar), 7.24 (br, 1H, Ar), 7.09 (d, *J* = 2.7 Hz, 1H, Ar), 6.96 (s, 1H, CH), 6.60 (br, 1H, Ar), 6.48 (br, 1H, Ar), 2.98 (d, *J* = 6.6 Hz, 2H, CH_2 of isobutyl), 2.04-1.93 (m, 1H, CH of isobutyl), 1.00 (d, *J* = 6.6 Hz, 6H, 2 CH_3 of isobutyl); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 178.6 (C=O), 174.0 (C=O), 169.2, 164.4, 151.8, 148.4, 145.2, 139.2, 121.9, 114.7, 114.0, 113.0, 112.3, 105.8, 44.7 (CH of isobutyl), 33.8 (CH_2 of isobutyl), 21.7 (2 CH_3 of isobutyl); MS: HRMS: *m/z* = 393.0283 $[M+H]^+$. Found: 393.0289.



3-Pyridoyl-3-(1-(3-pyridinyl)acetylidene)-5-methyl sulfanyl-[1,2] dithiole (2o): Yellow sticky solid; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.02 (s, 1H, Ar), 8.92 (s, 1H, Ar), 8.84 (d, *J* = 4.5 Hz, 1H, Ar), 8.66 (d, *J* = 4.0 Hz, 1H, Ar), 8.19 (d, *J* = 8.0 Hz, 1H, Ar), 8.08 (d, *J* = 8.0 Hz, 1H, Ar), 7.49-7.46 (m, 1H, Ar), 7.35-7.32 (m, 1H, Ar), 6.96 (s, 1H, CH), 2.67 (s, 3H, SMe); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 190.3 (C=O), 181.4 (C=O), 171.7, 170.8, 154.5, 152.2, 151.2, 148.7, 137.0, 135.0, 131.9, 131.5, 130.8, 124.0, 123.6, 105.8, 18.4 (SMe).

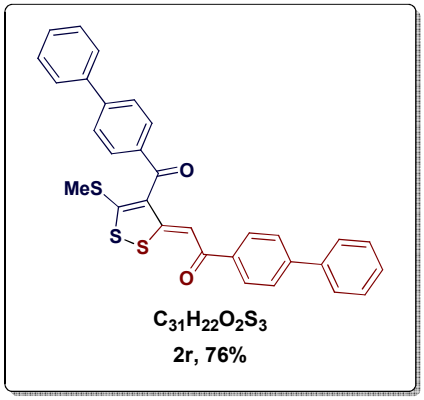


1-Naphthoyl-3-(1-(1-naphthyl)acetylidene)-5-methyl sulfanyl -[1,2] dithiole (2p): Yellow solid; M.p.- 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.67 (d, *J* = 8.1 Hz, 1H, Ar), 8.33 (d, *J* = 8.1 Hz, 1H, Ar), 8.05-7.75 (m, 5H, Ar), 7.64-7.24 (m, 7H, Ar), 6.94 (s, 1H, CH), 2.60 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 192.5 (C=O), 186.6 (C=O), 171.0, 134.6, 134.5, 134.0, 133.9, 133.6, 133.0, 131.2, 130.7, 130.5, 130.2, 128.6, 128.2, 127.2, 127.0, 126.8, 126.6, 126.2, 126.0, 125.5, 125.3, 124.8, 124.6, 110.8, 18.4 (SMe).

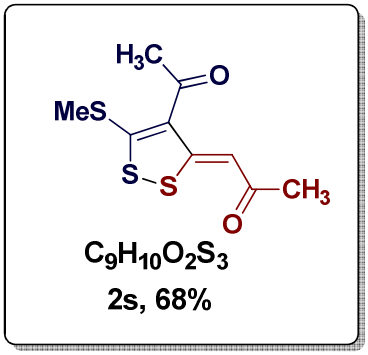


2-Naphthoyl-3-(1-(2-naphthyl)acetylidene)-5-ethyl sulfanyl-[1,2] dithiole (2q): Yellow solid; M.p.- 179 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.38 (s, 1H, Ar), 8.26 (s, 1H, Ar), 8.08-7.77 (m, 8H, Ar), 7.66-7.44 (m, 4H, Ar), 7.21 (s, 1H, CH), 3.12 (q, *J* = 7.2 Hz, 2H, CH_2 of SEt), 1.41-1.33 (m, 3H, CH_3 of SEt); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 192.5 (C=O), 183.7

(C=O), 170.8, 164.4, 136.3, 135.0, 133.6, 133.3, 132.8, 132.8, 132.7, 130.0, 129.3, 129.3, 129.2, 128.4, 128.4, 128.0, 127.8, 127.7, 127.1, 126.6, 124.6, 124.0, 106.9, 30.4 (CH_2 of SEt), 14.4 (CH_3 of SEt); IR (KBr, ν_{max}, cm^{-1}): 2924, 2852, 1651, 1508, 1437, 1390, 1223, 1126, 816, 793, 758, 471; MS: HRMS: *m/z* = 485.0704 $[M+H]^+$. Found: 485.0708.

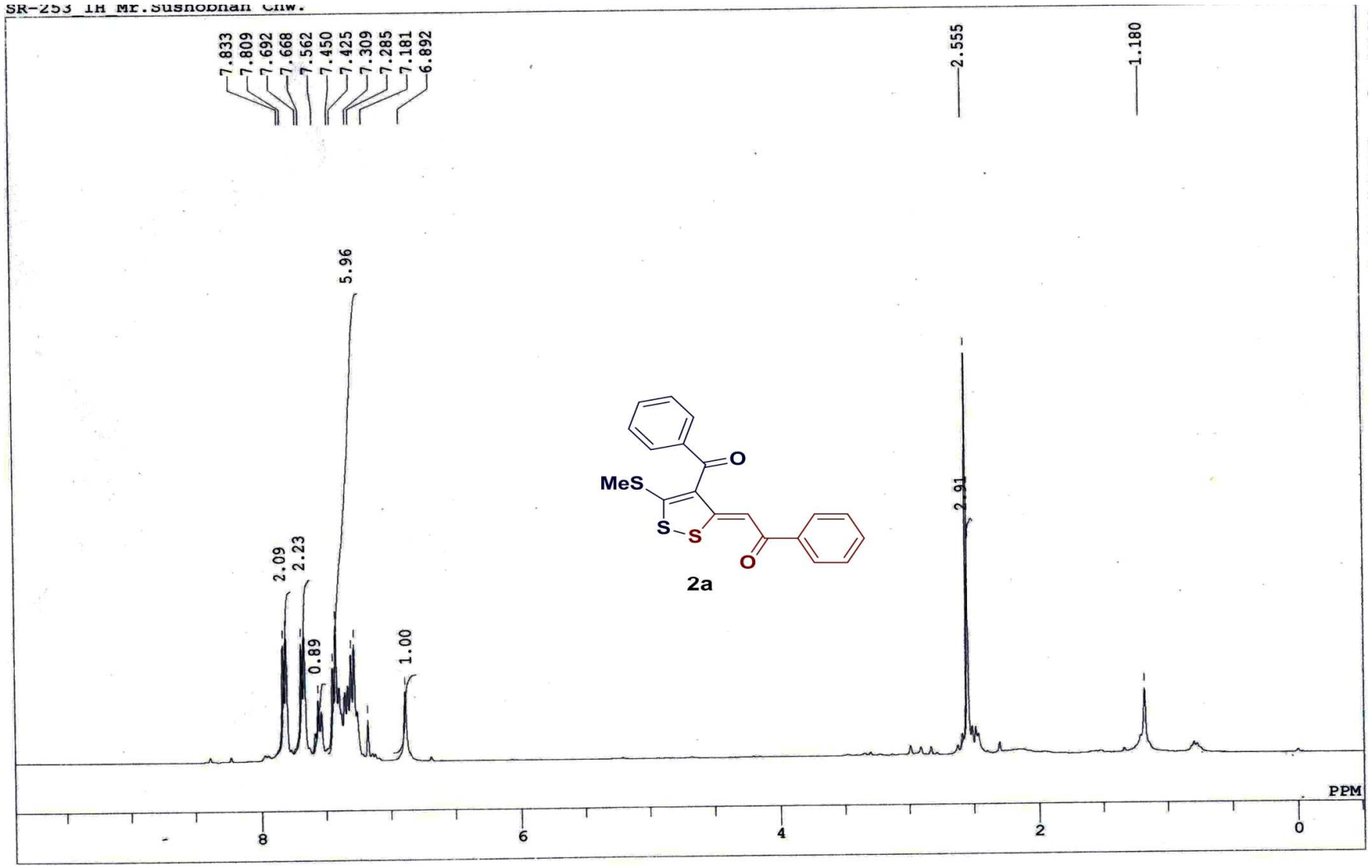


(4-Phenyl)benzoyl-3-(1-((4-Phenyl)phenyl) acetylidene)-5-methylsulfanyl-[1,2] dithiole (2r): Yellow solid; M.p.- 166 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.99 (d, *J* = 8.1 Hz, 2H, Ar), 7.86 (d, *J* = 8.4 Hz, 2H, Ar), 7.74-7.55 (m, 9H, Ar), 7.48-7.34 (m, 5H, Ar), 7.06 (s, 1H, CH), 2.65 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 191.7 (C=O), 183.0 (C=O), 170.9, 166.7, 147.0, 144.3, 140.0, 139.5, 134.8, 134.6, 132.2, 130.5, 129.0, 128.8, 128.5, 128.0, 127.9, 127.6, 127.2, 127.1, 127.1, 106.4, 18.2 (SMe); MS: HRMS: *m/z* = 523.0855 $[M+H]^+$. Found: 523.0867.

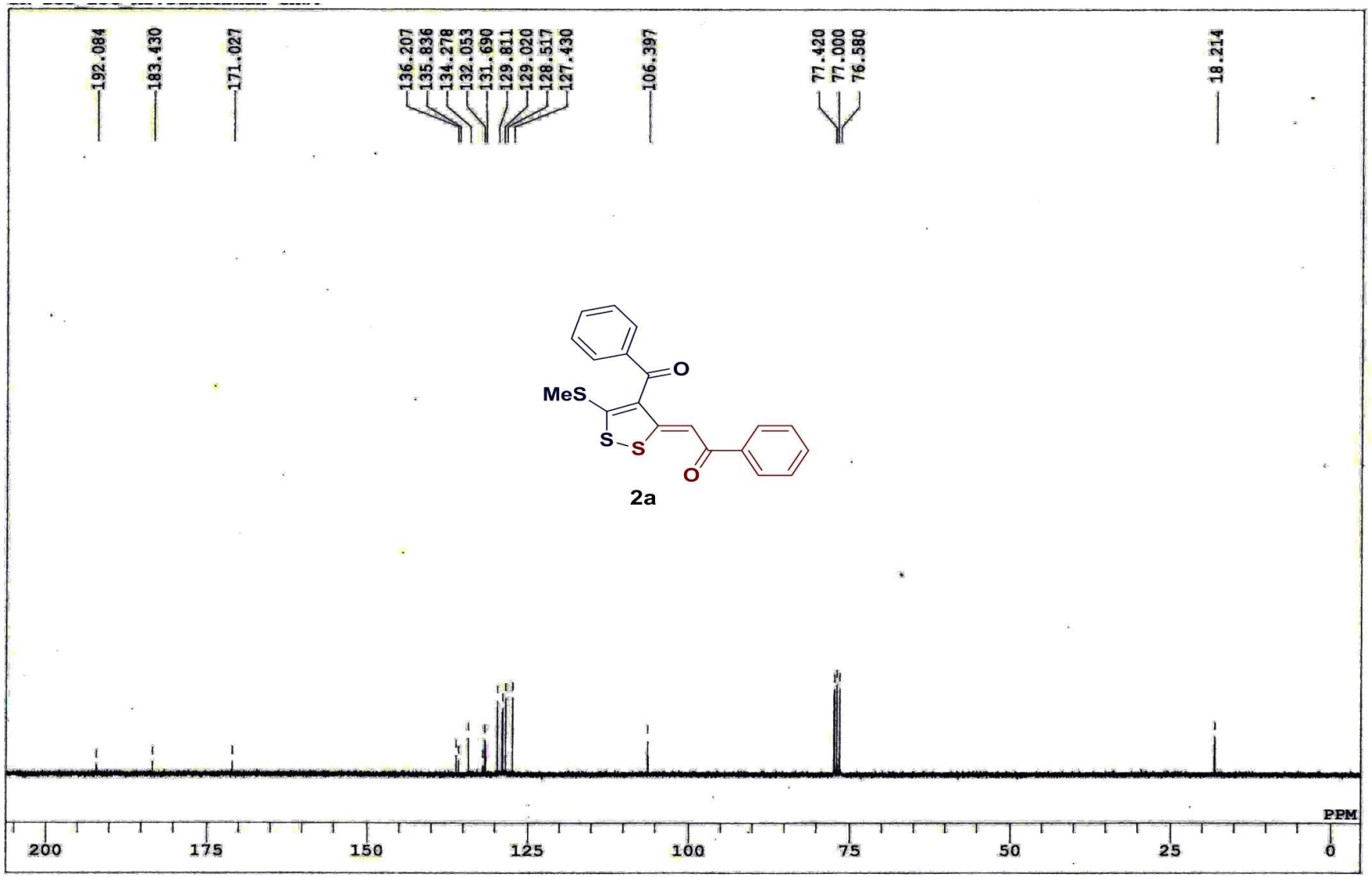


4-Acetyl-3-(methylacetylidene)-5-methylsulfanyl-[1,2] dithiole (2s): Yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 6.74 (s, 1H, CH), 2.66 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.31 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 189.7 (C=O), 182.5 (C=O), 168.5, 131.2, 126.5, 100.2, 36.4 (CH_3), 36.3 (CH_3), 18.4 (SMe).

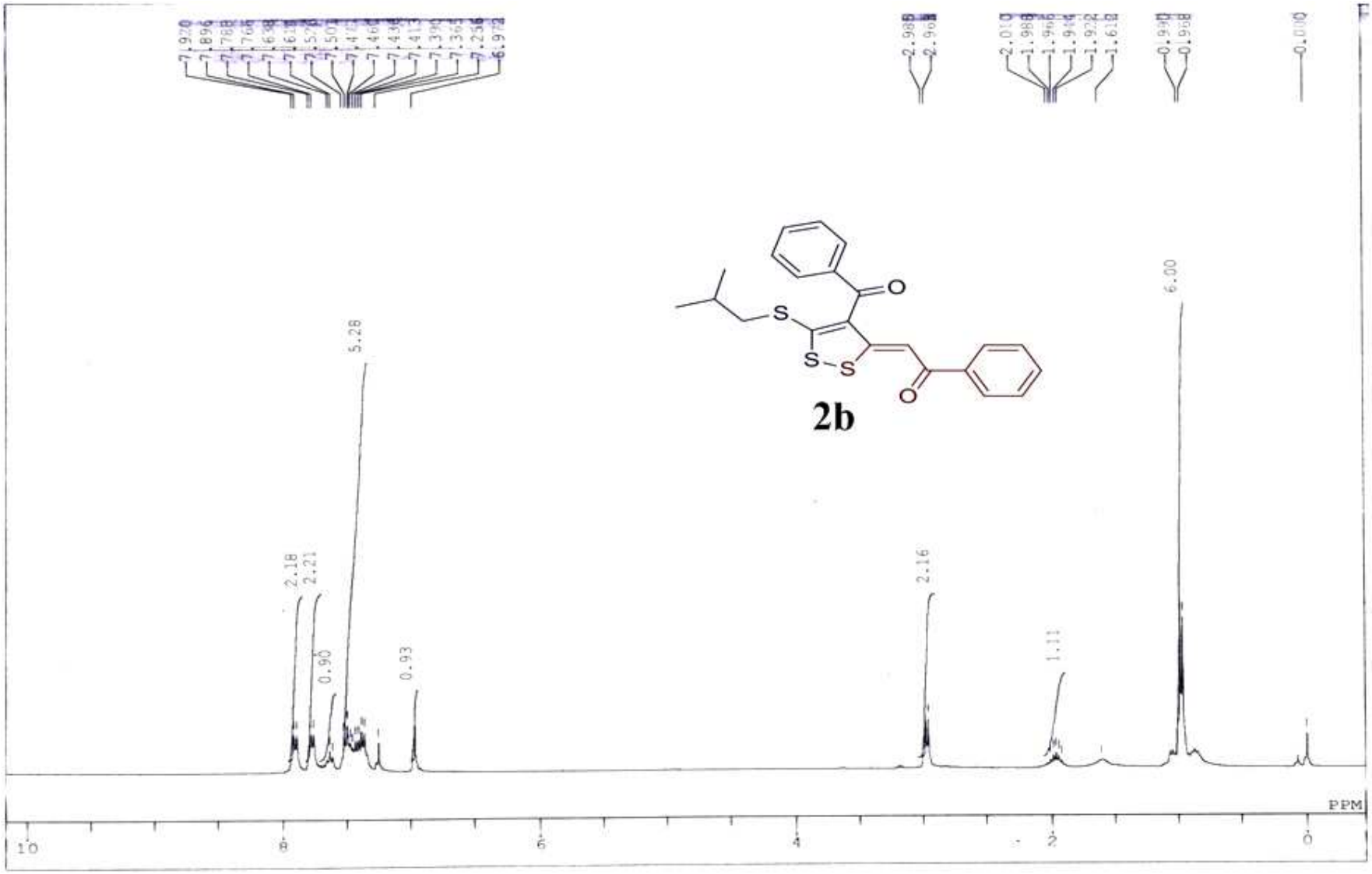
^{1}H spectrum of 2a:



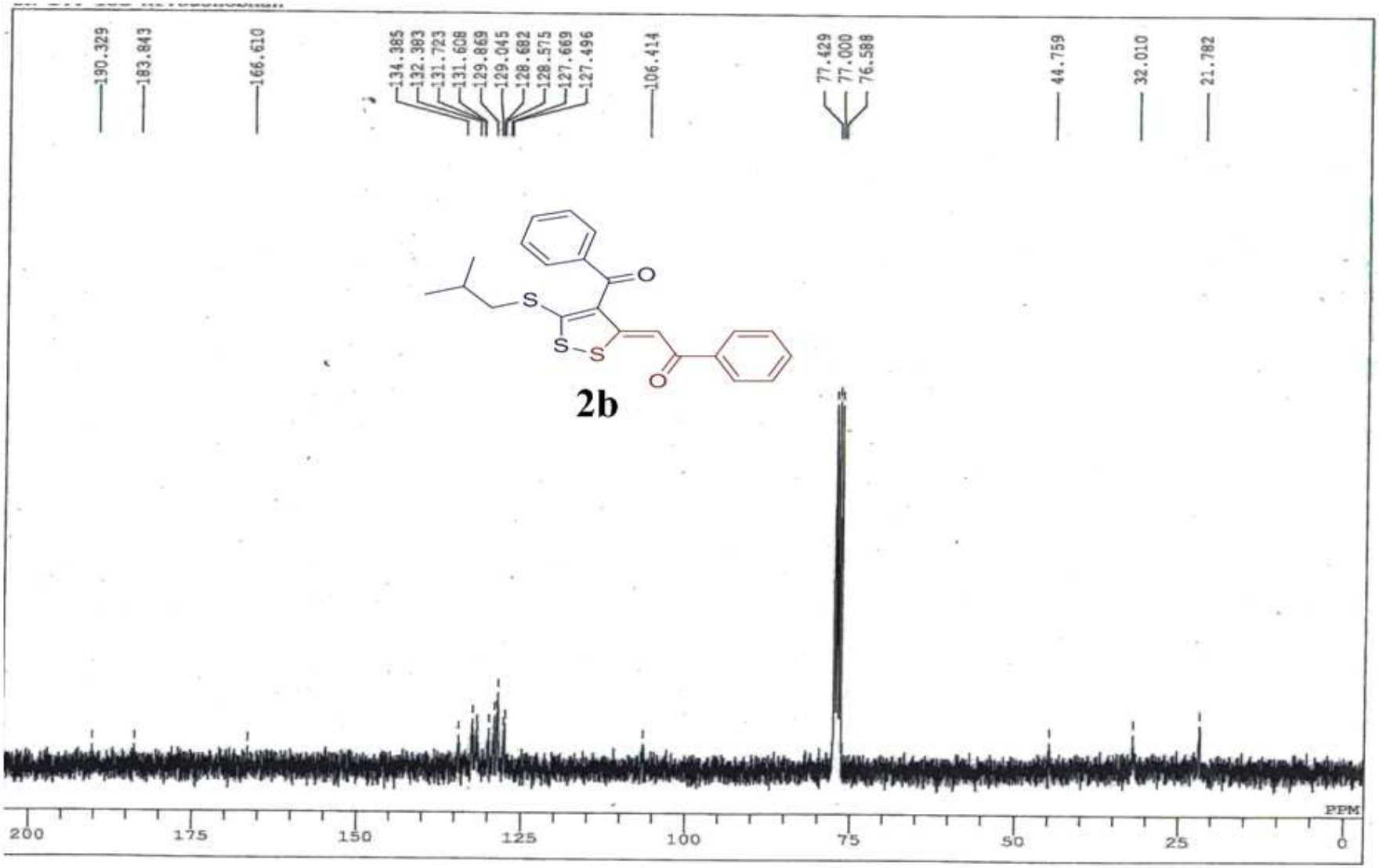
^{13}C spectrum of 2a:



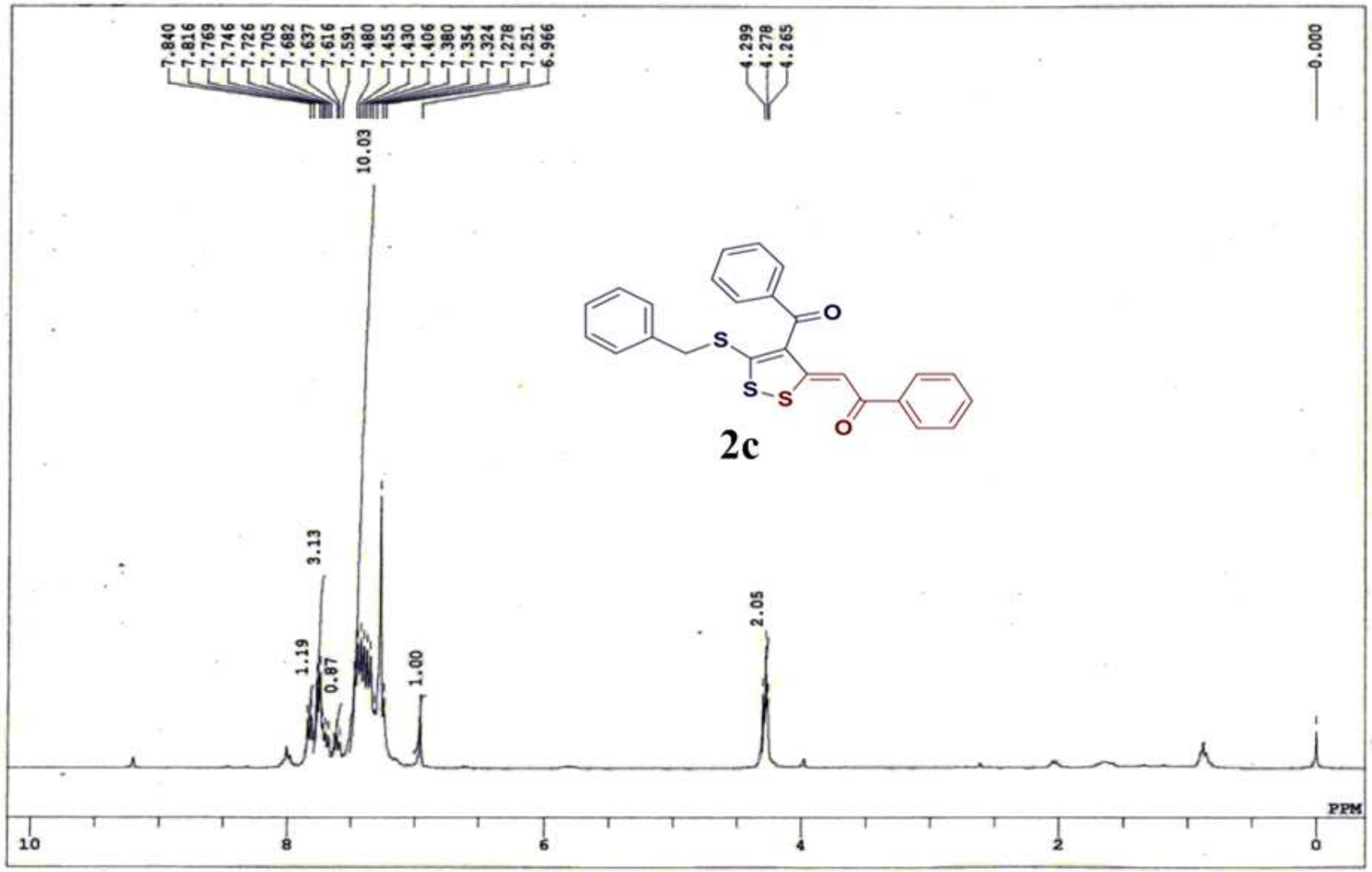
^{1}H spectrum of 2b:



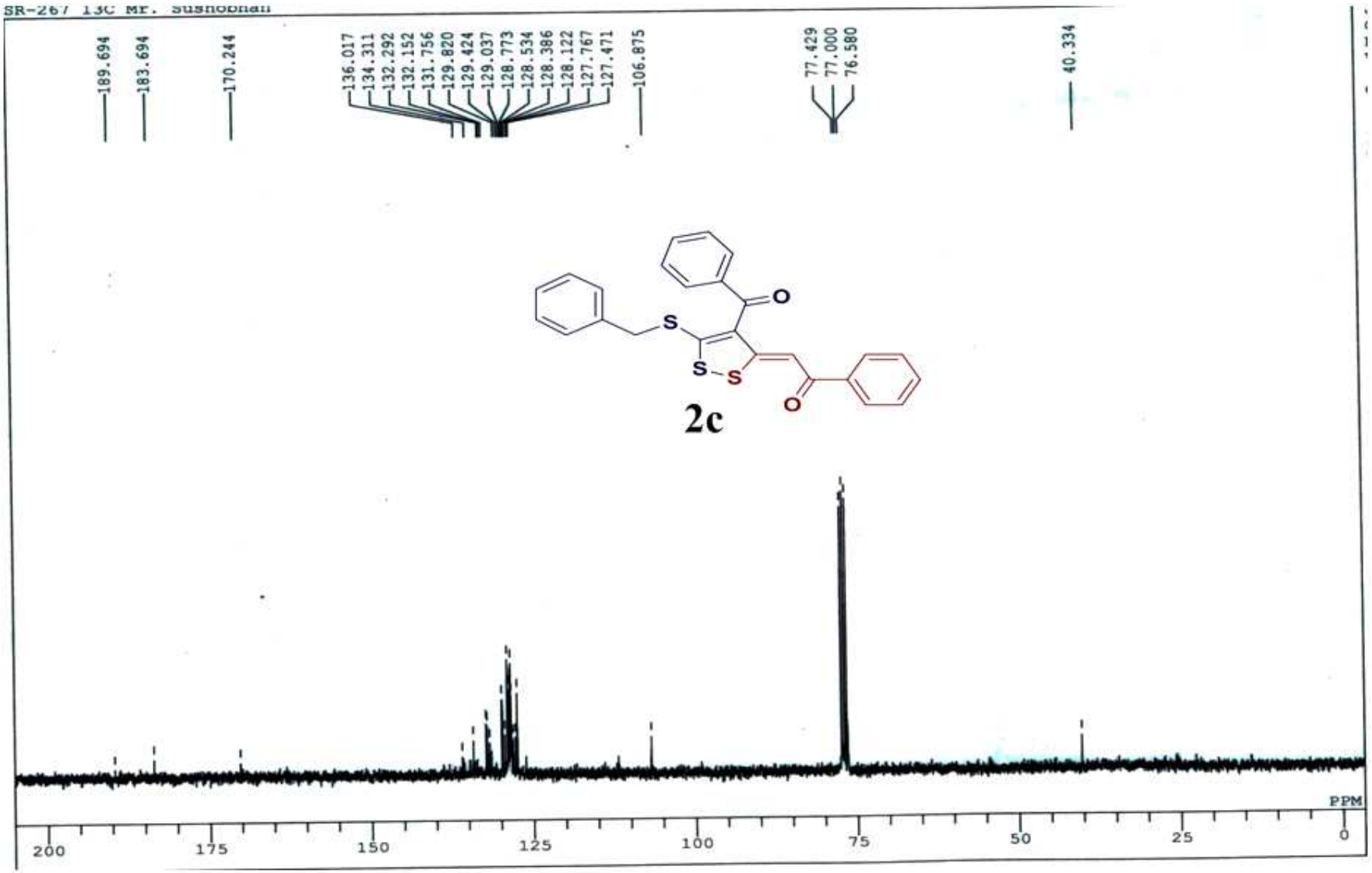
^{13}C spectrum of 2b:



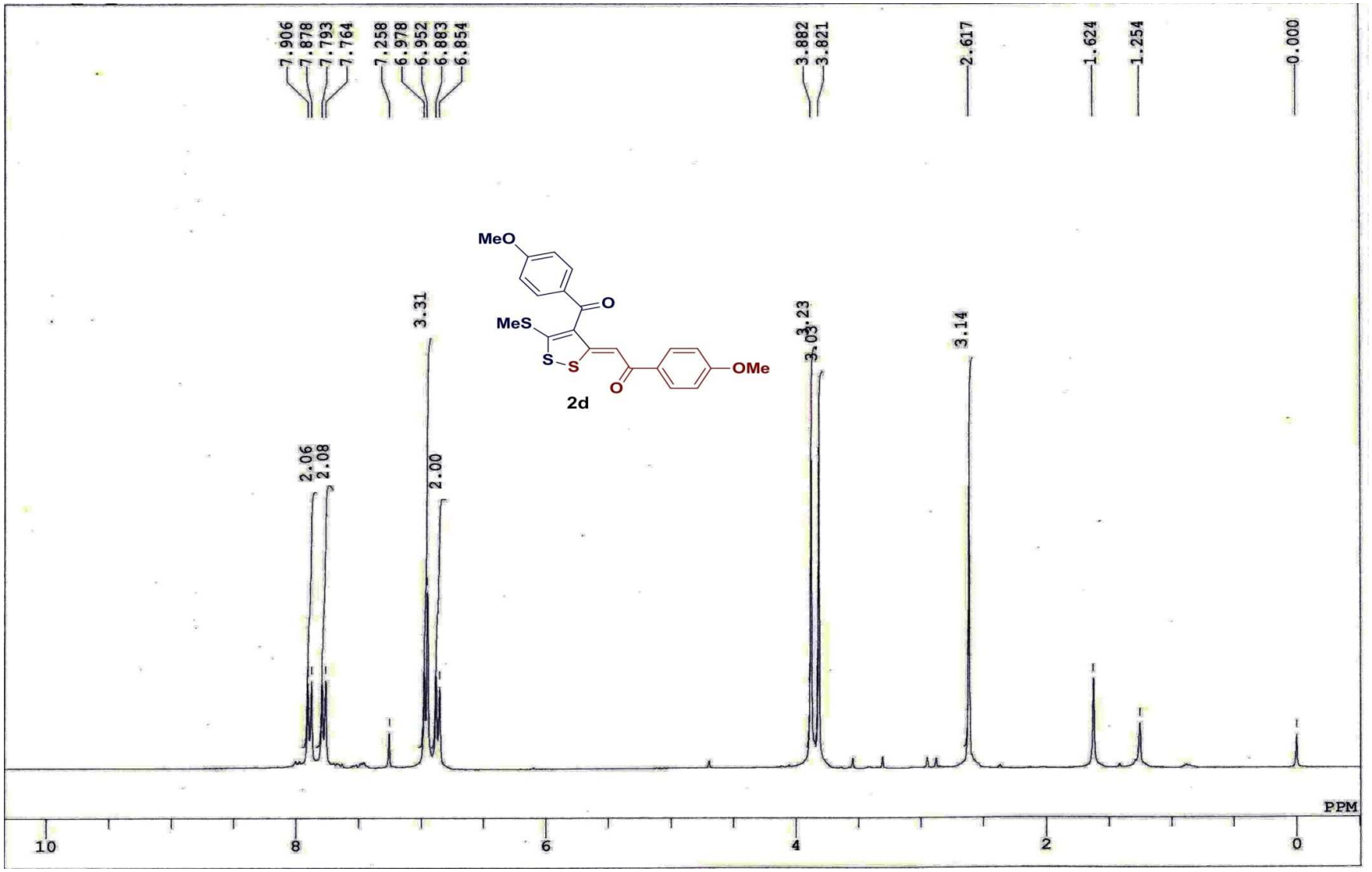
^{1}H spectrum of 2c:



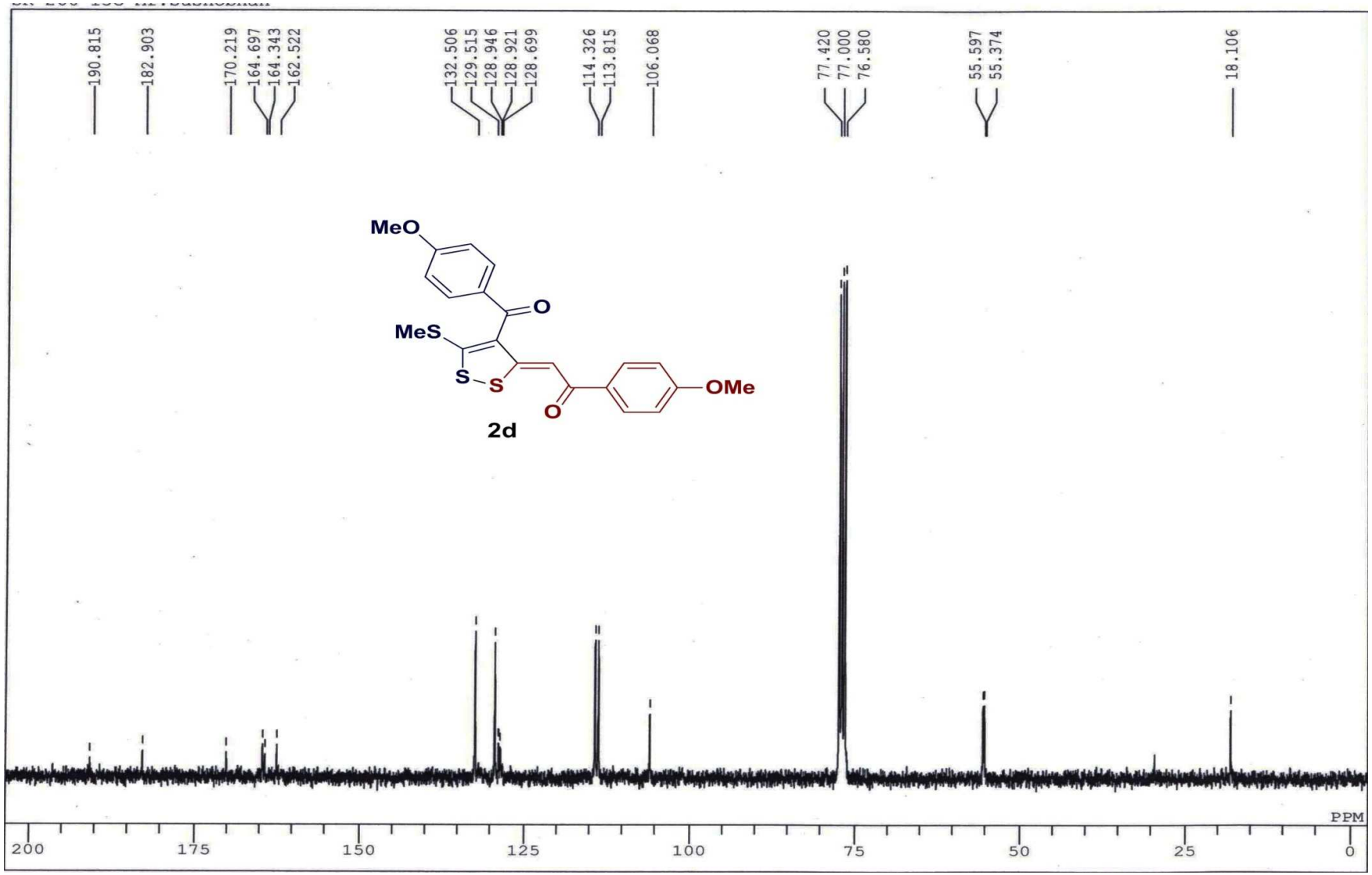
^{13}C spectrum of 2c:



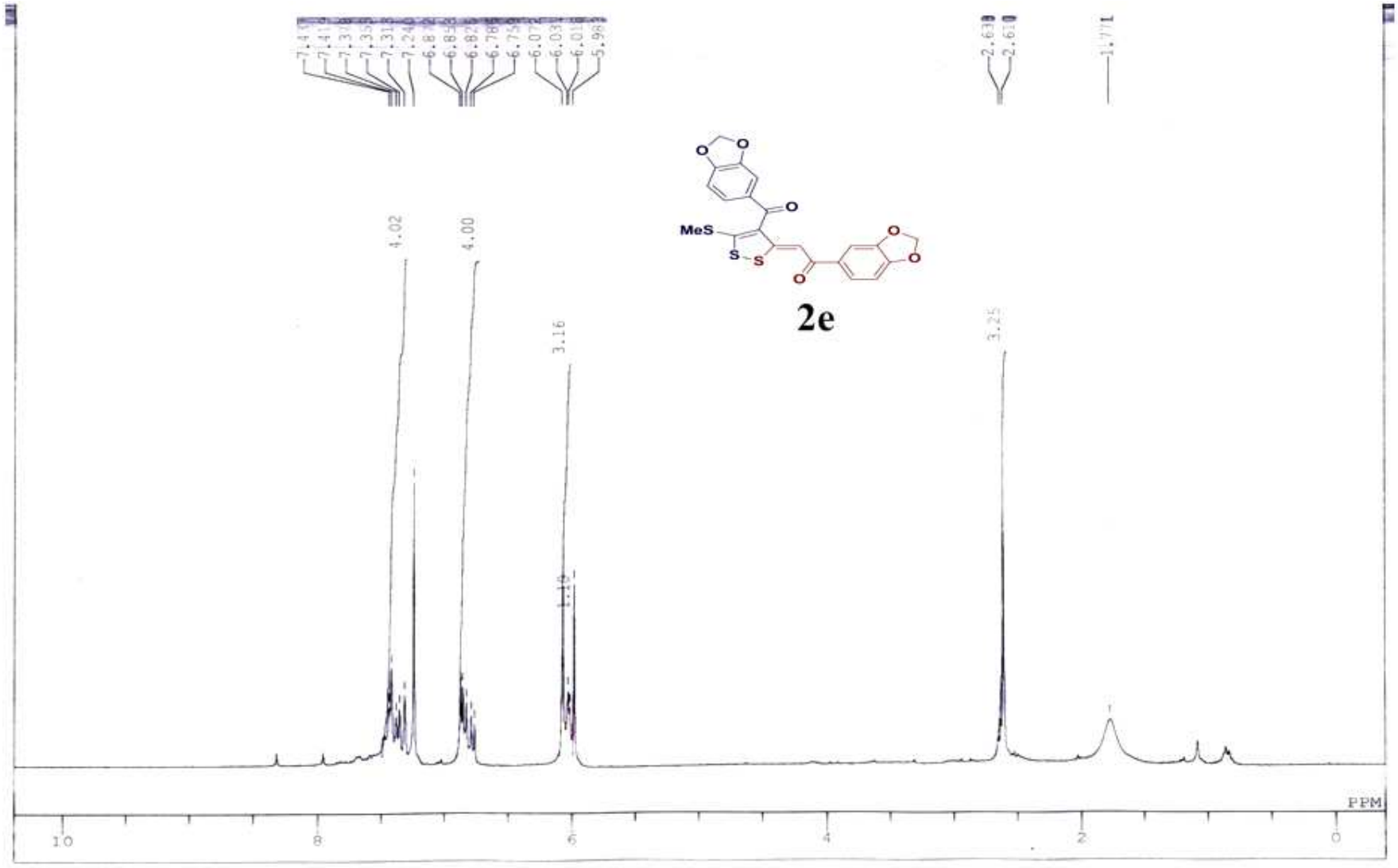
^{1}H spectrum of 2d:



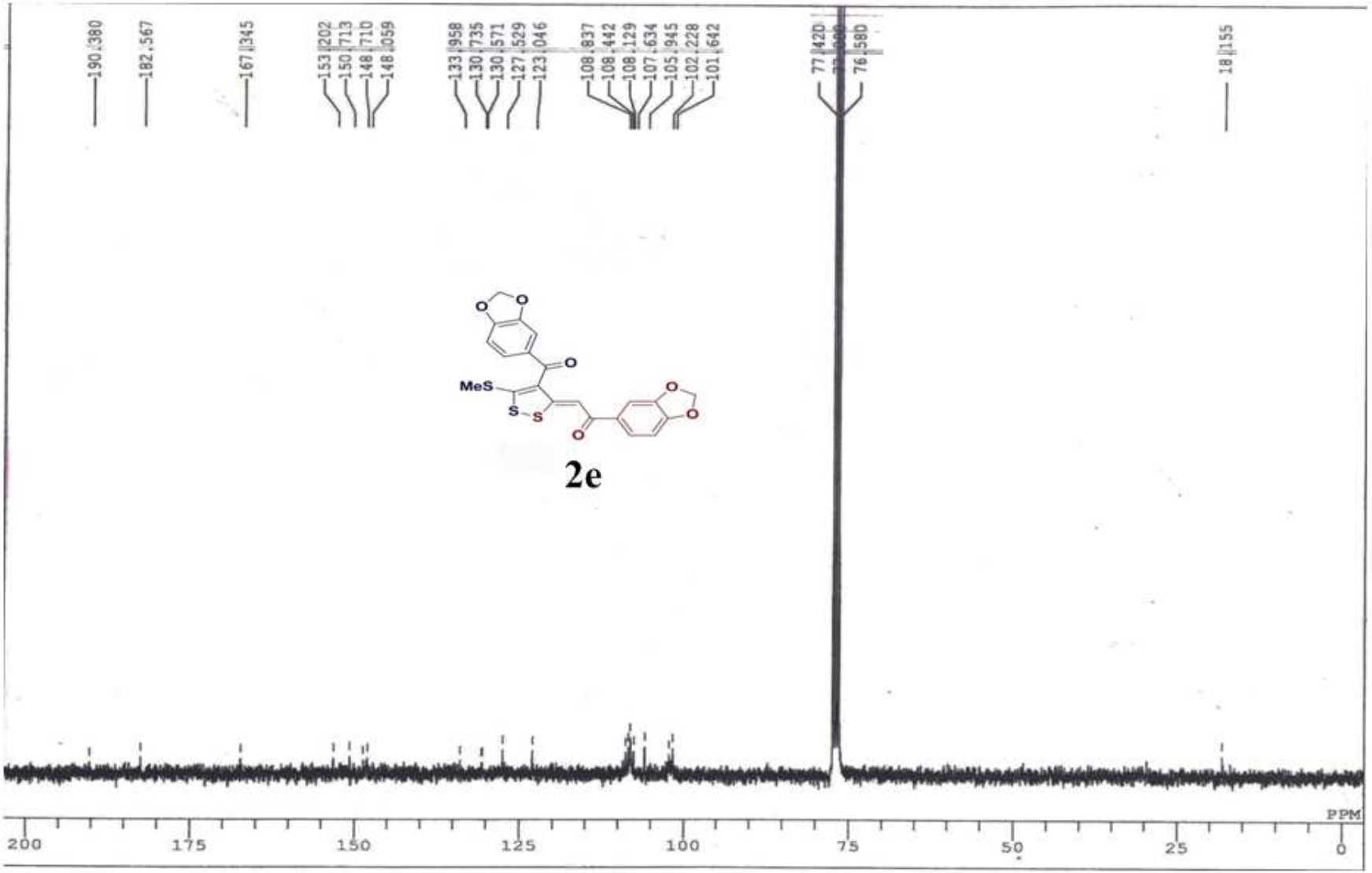
^{13}C spectrum of 2d:



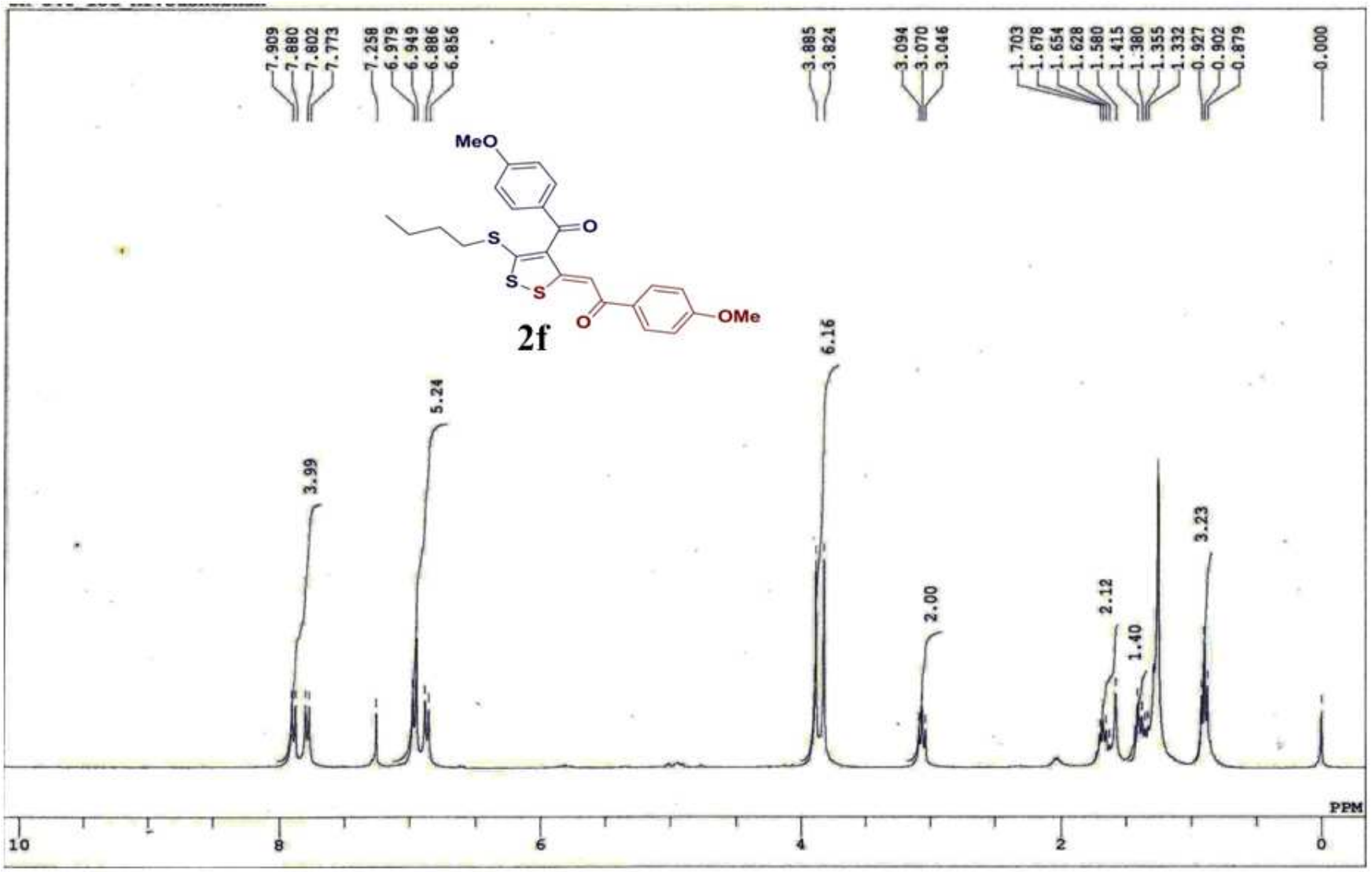
^{1}H spectrum of 2e:



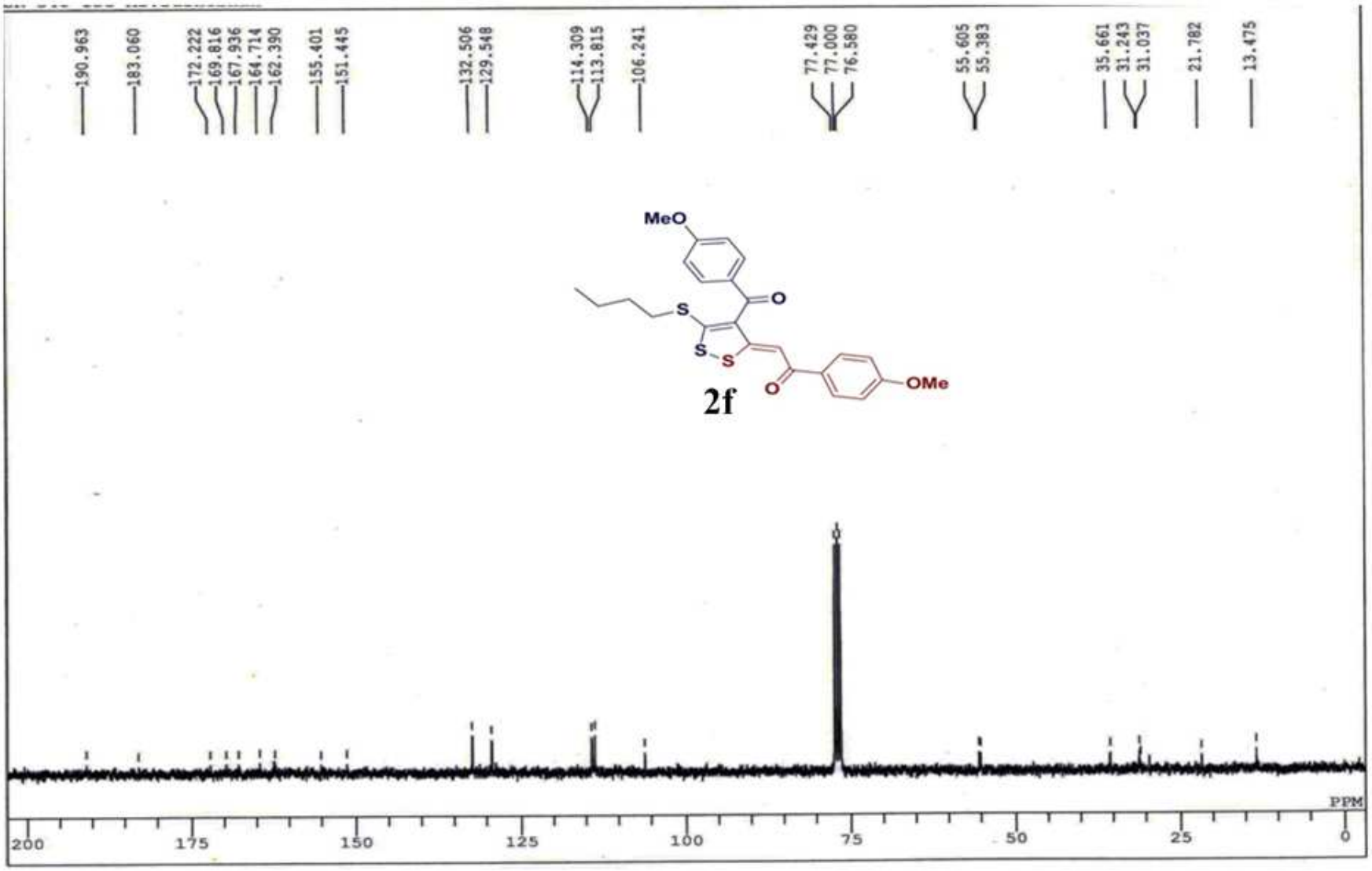
^{13}C spectrum of 2e:



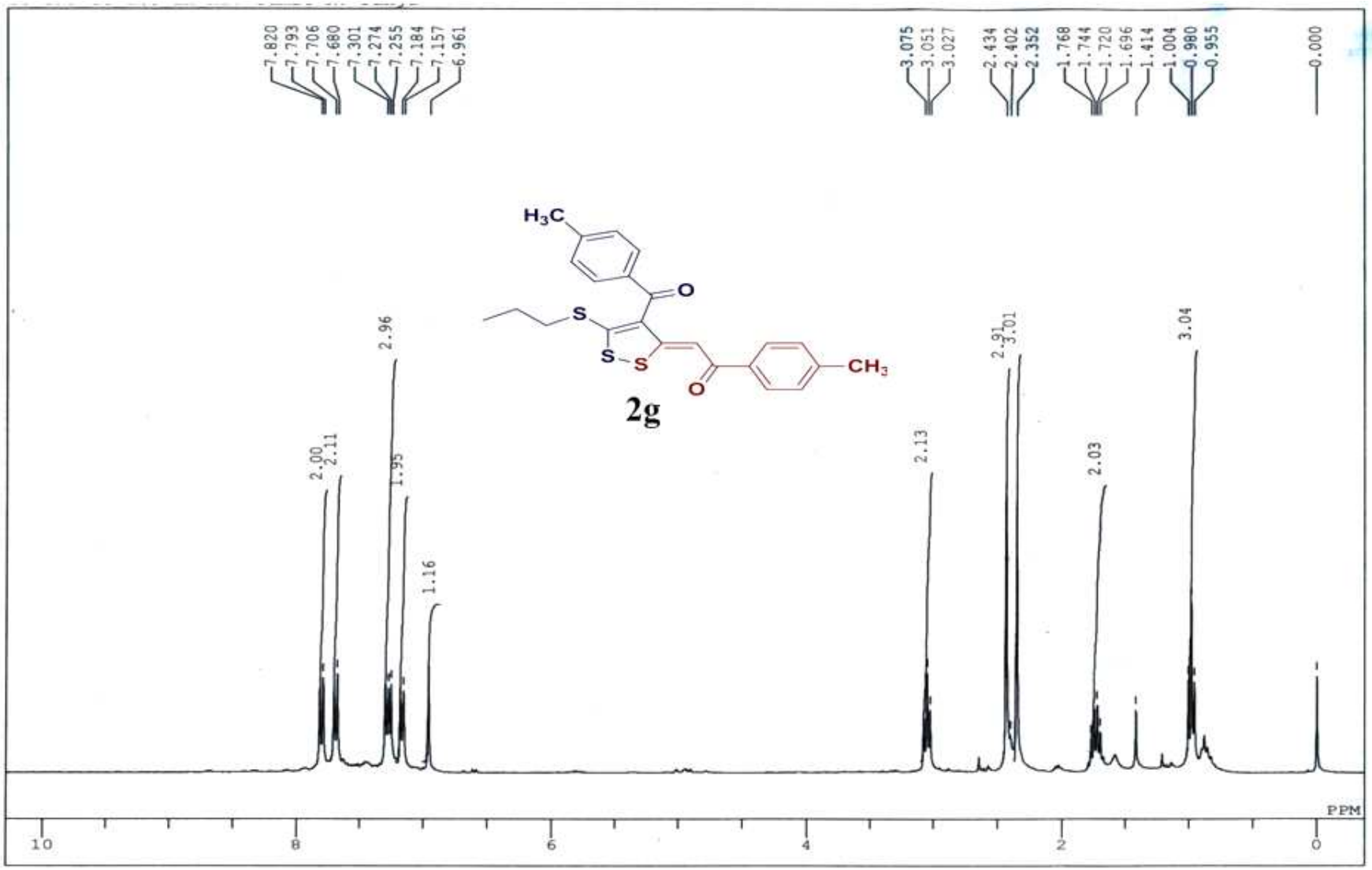
^{1}H spectrum of 2f:



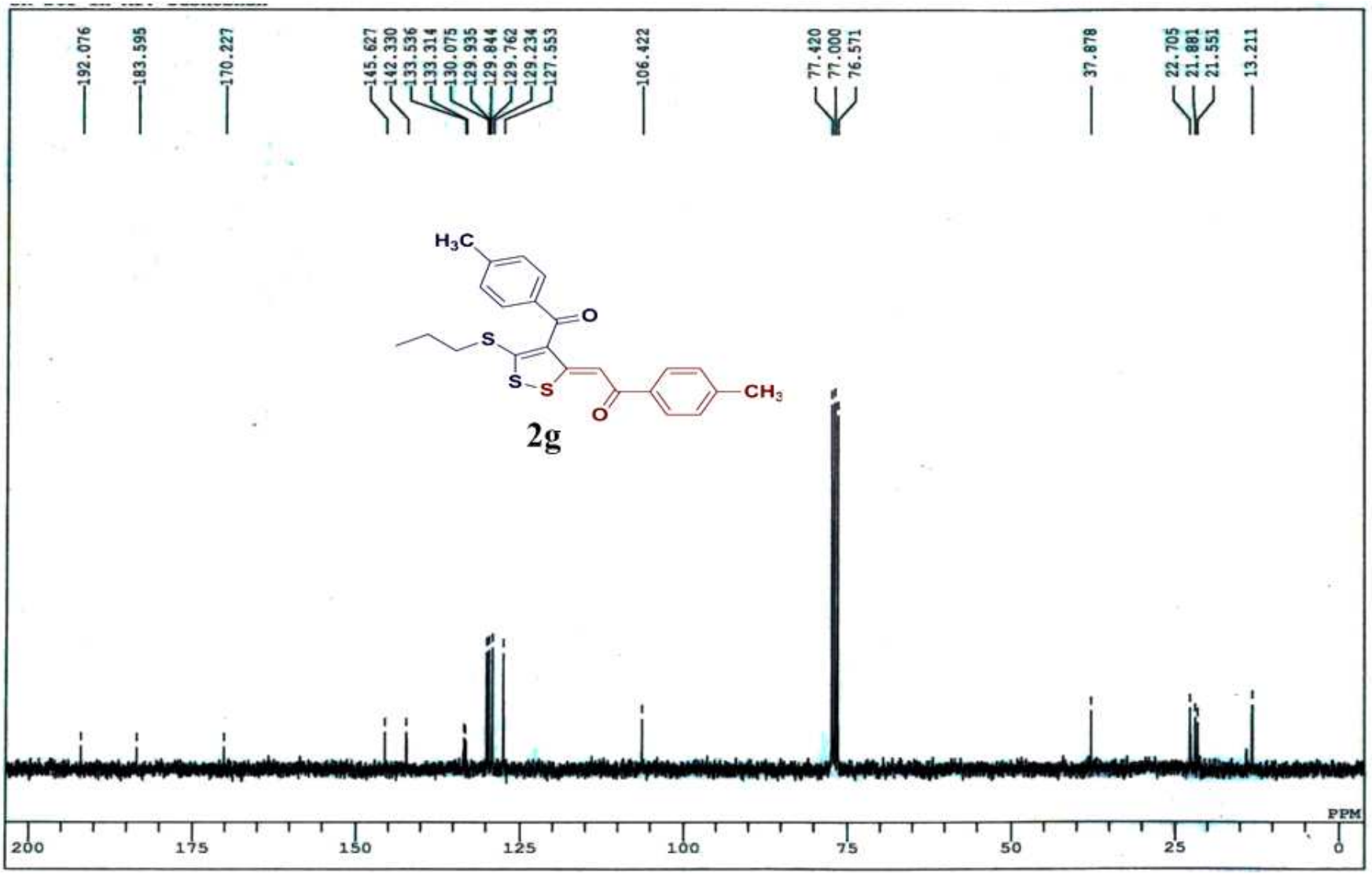
^{13}C spectrum of 2f:



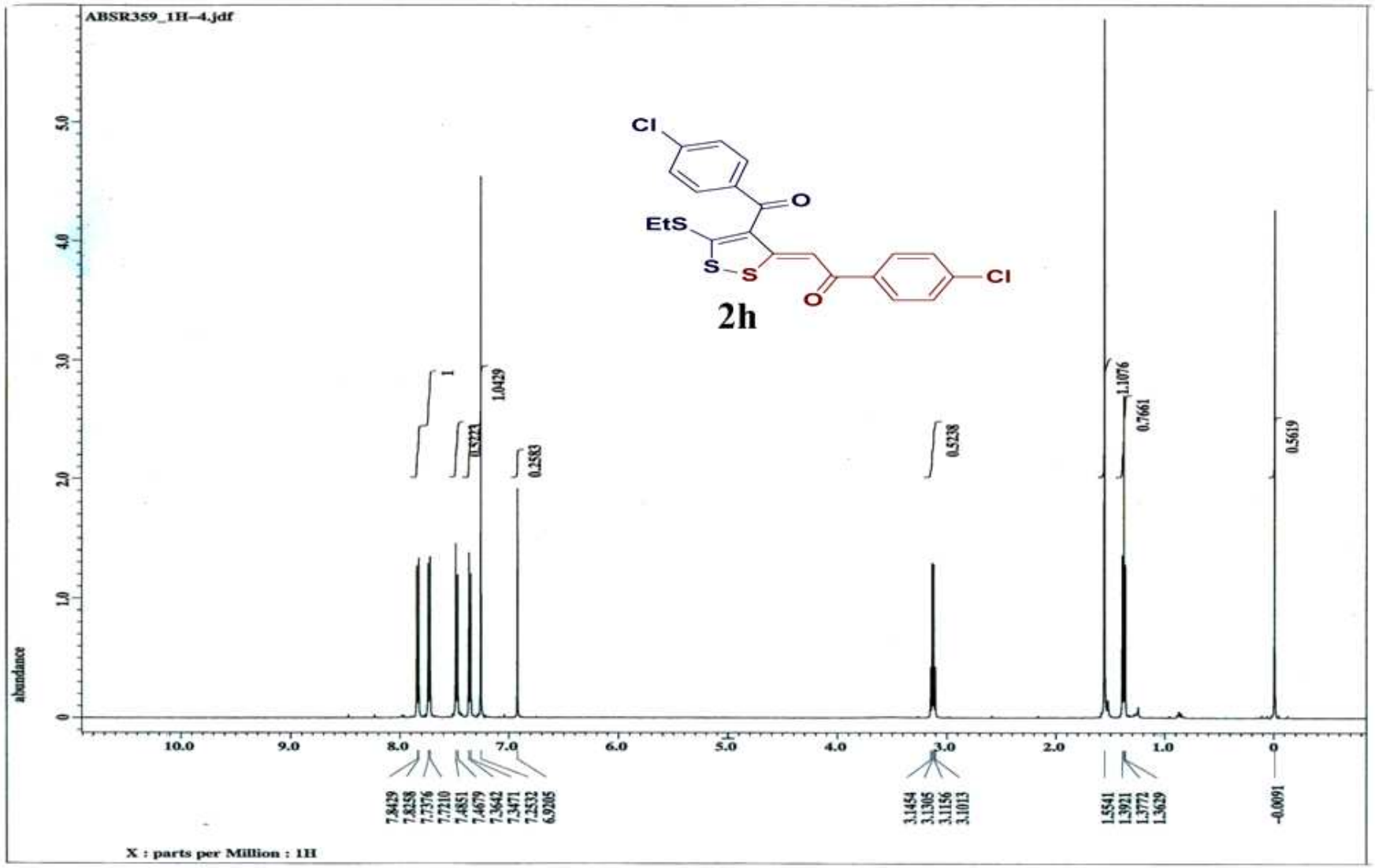
^{1}H spectrum of 2g:



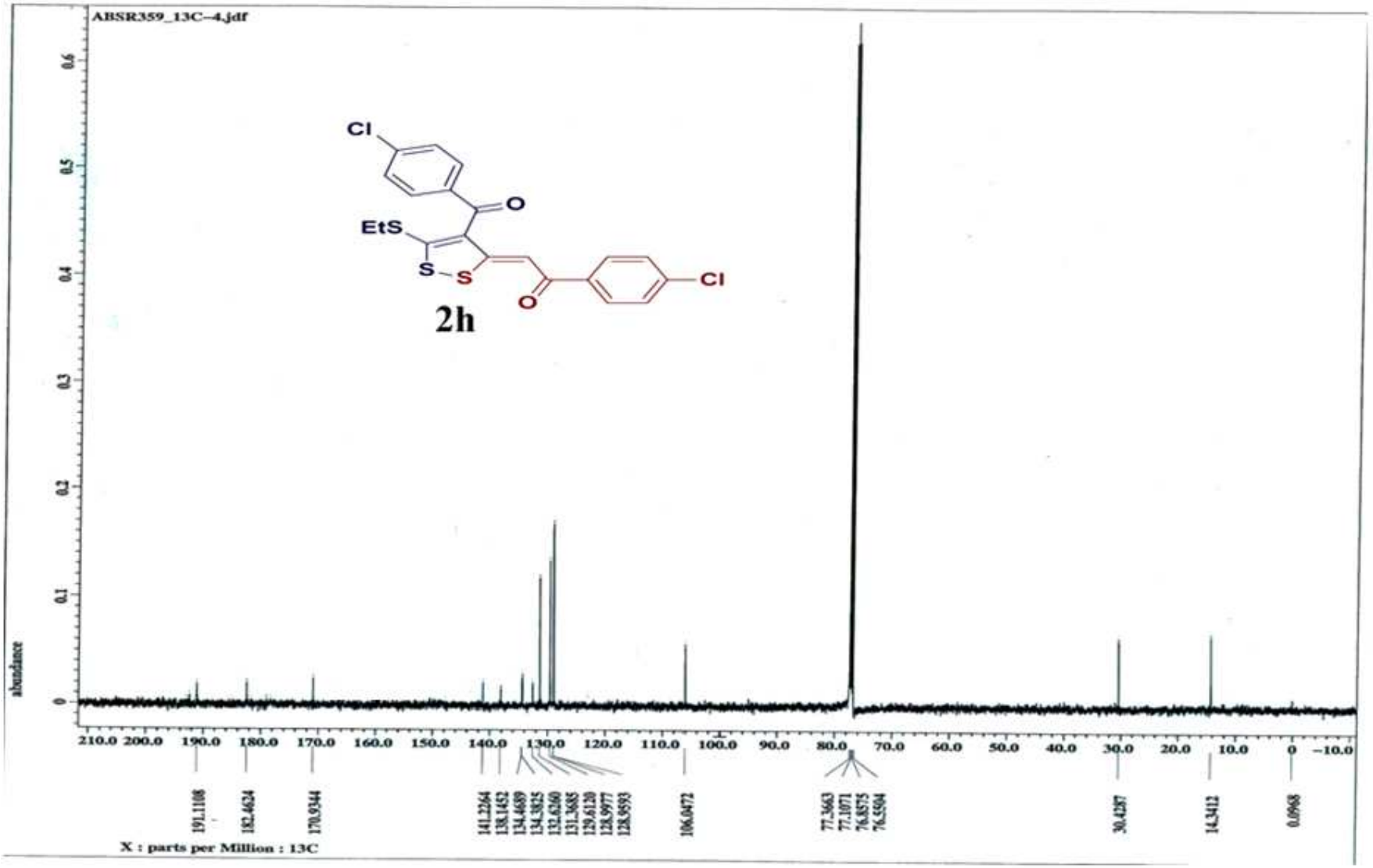
^{13}C spectrum of 2g:



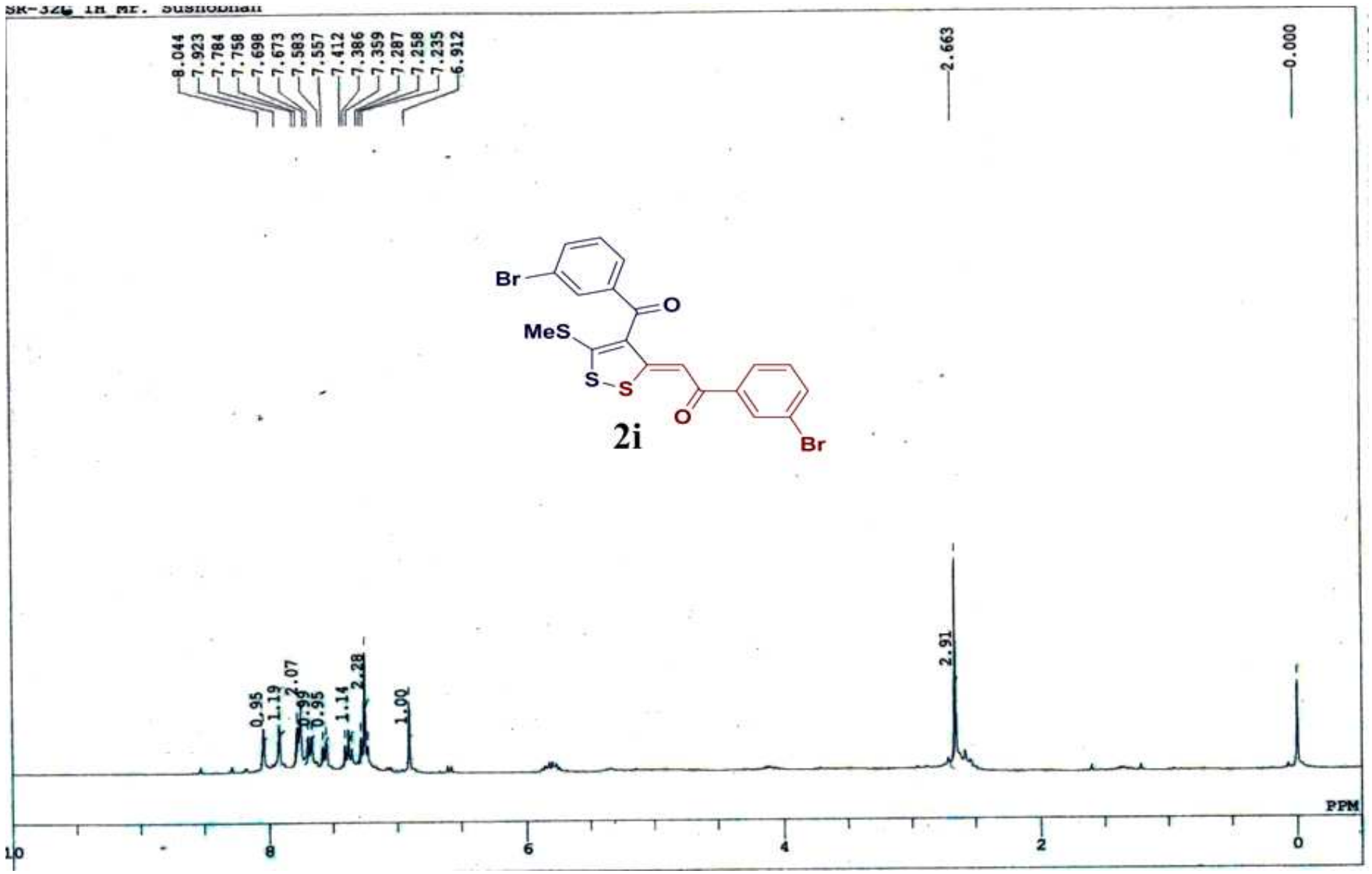
^{1}H spectrum of 2h:



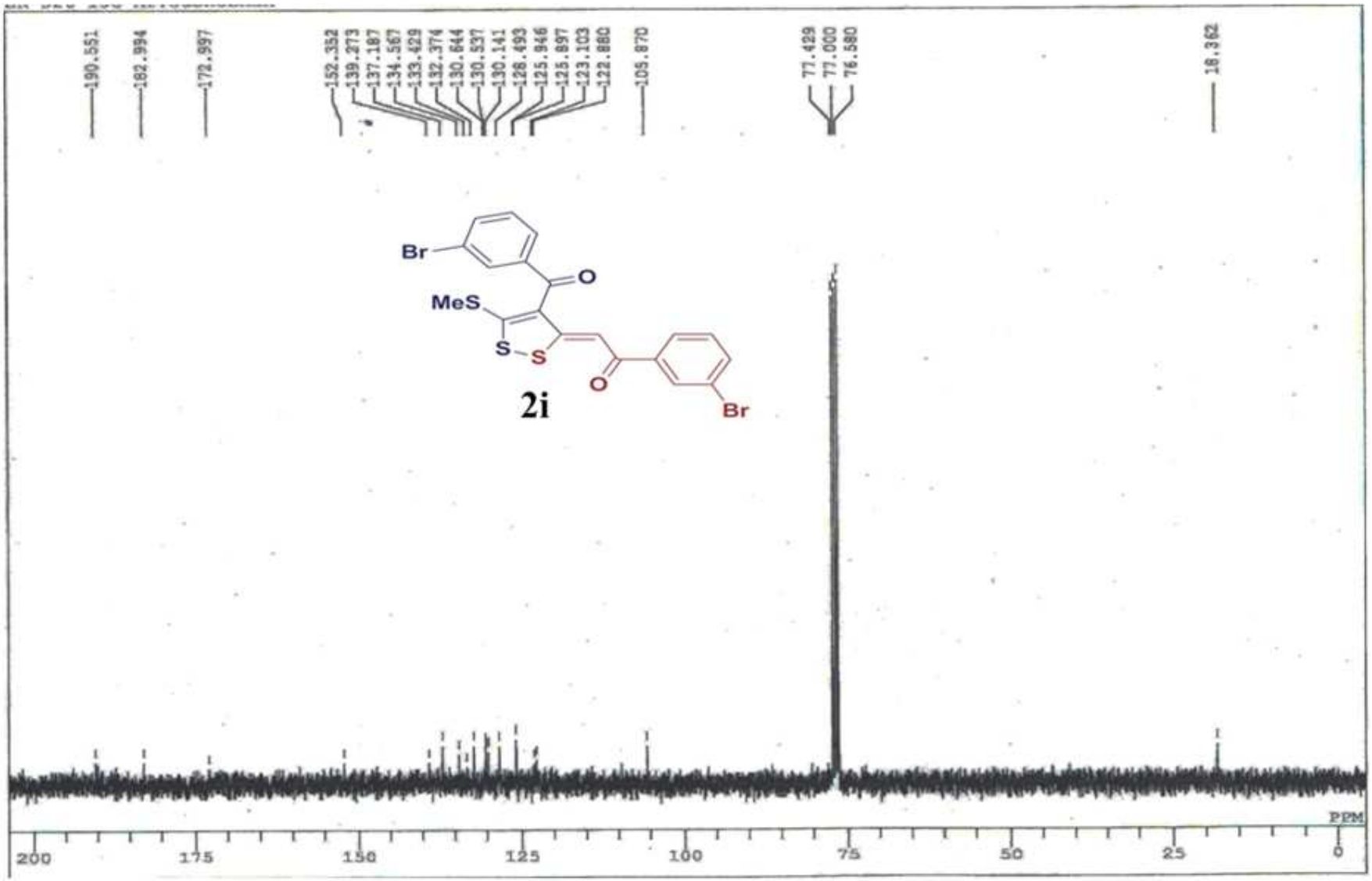
^{13}C spectrum of 2h:



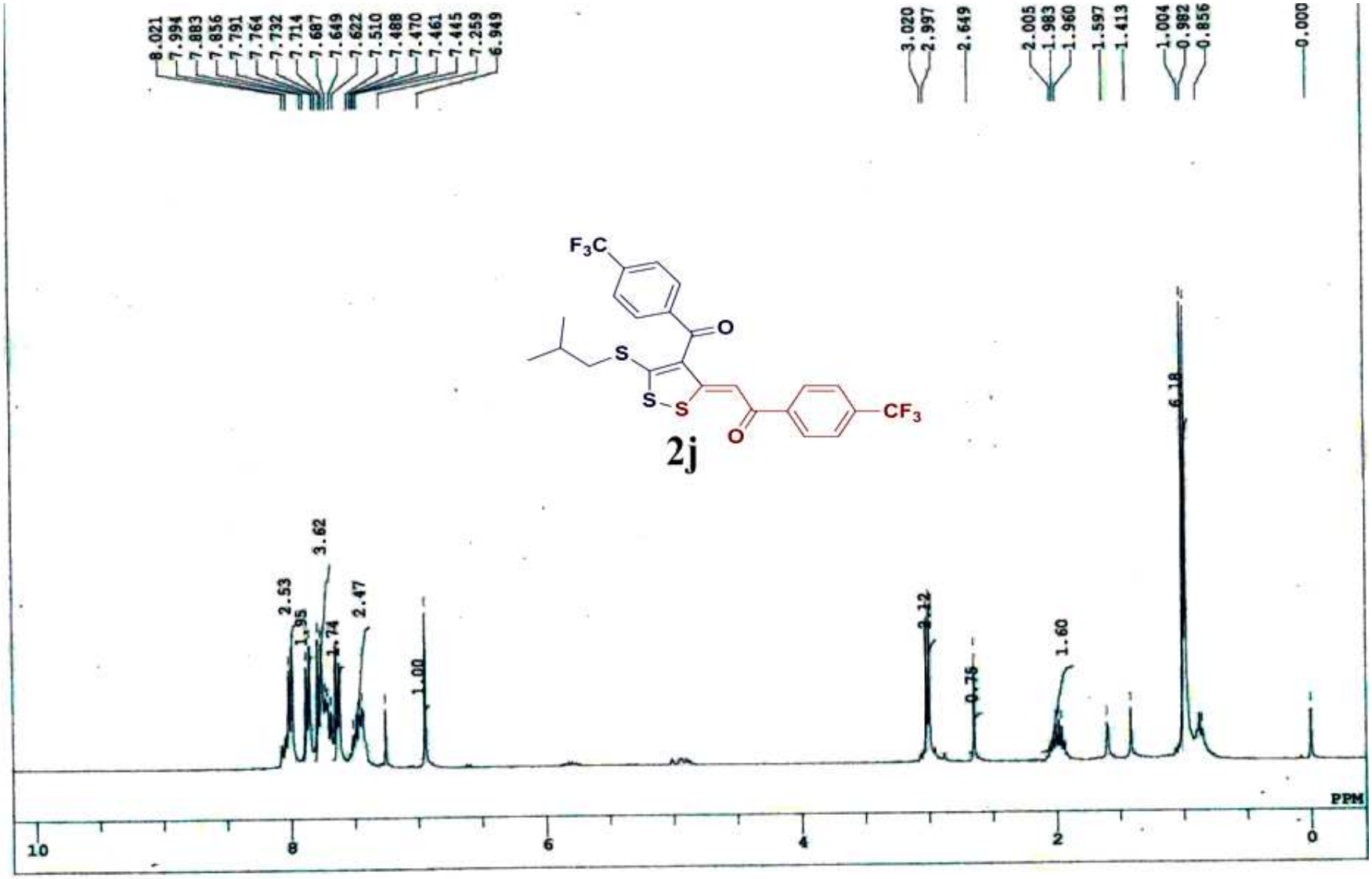
^{1}H spectrum of 2i:



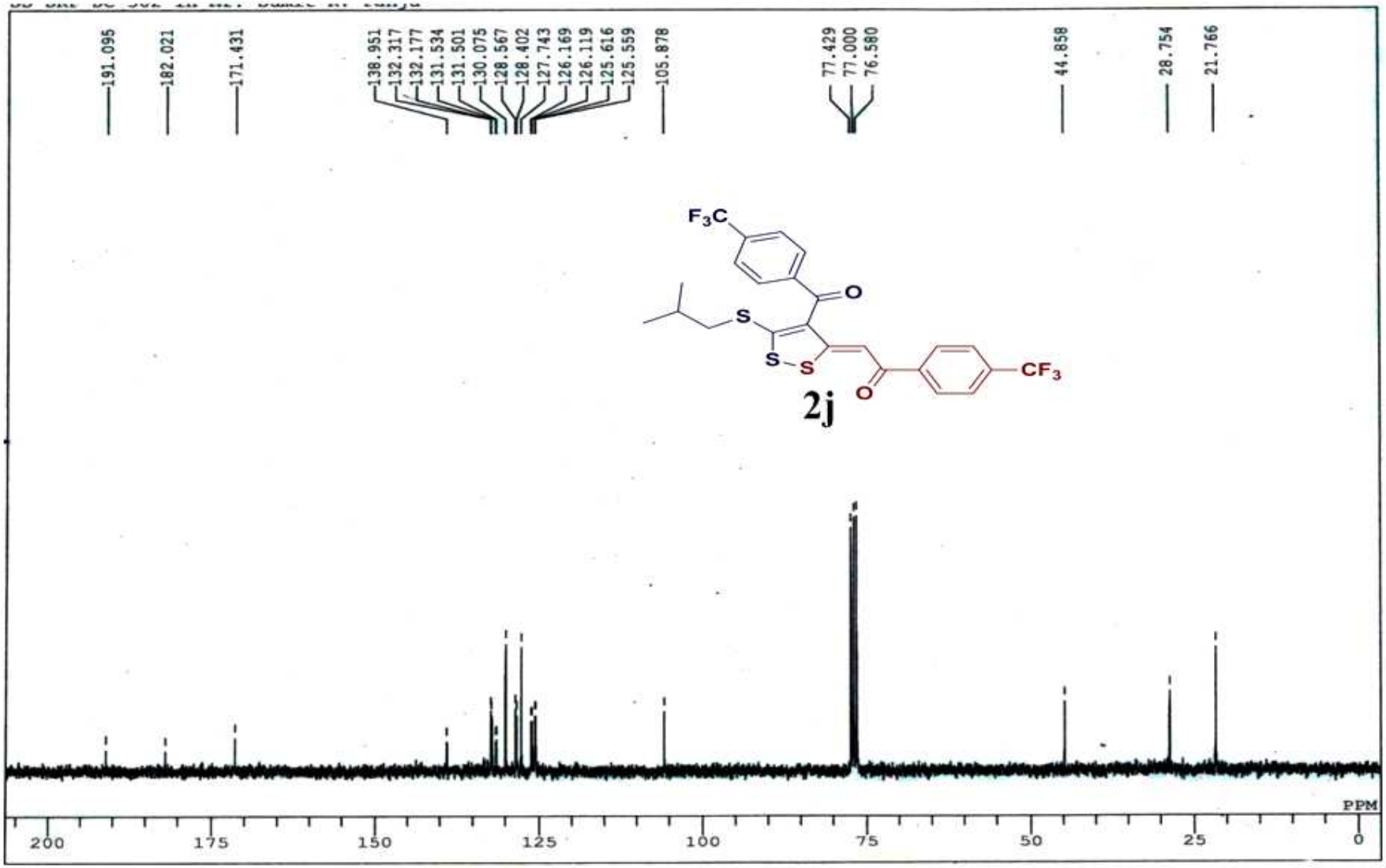
^{13}C spectrum of 2i:



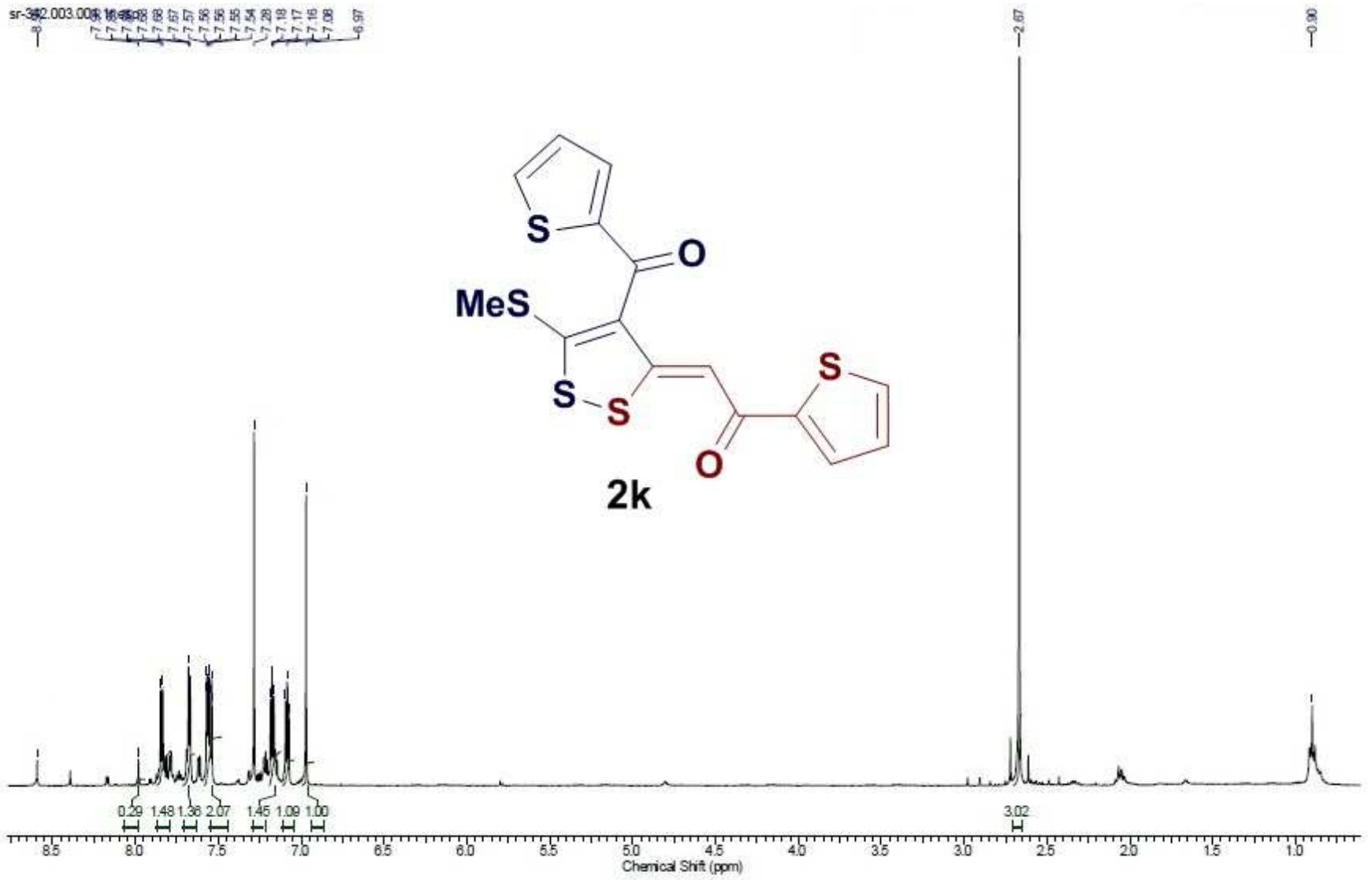
^{1}H spectrum of 2j:



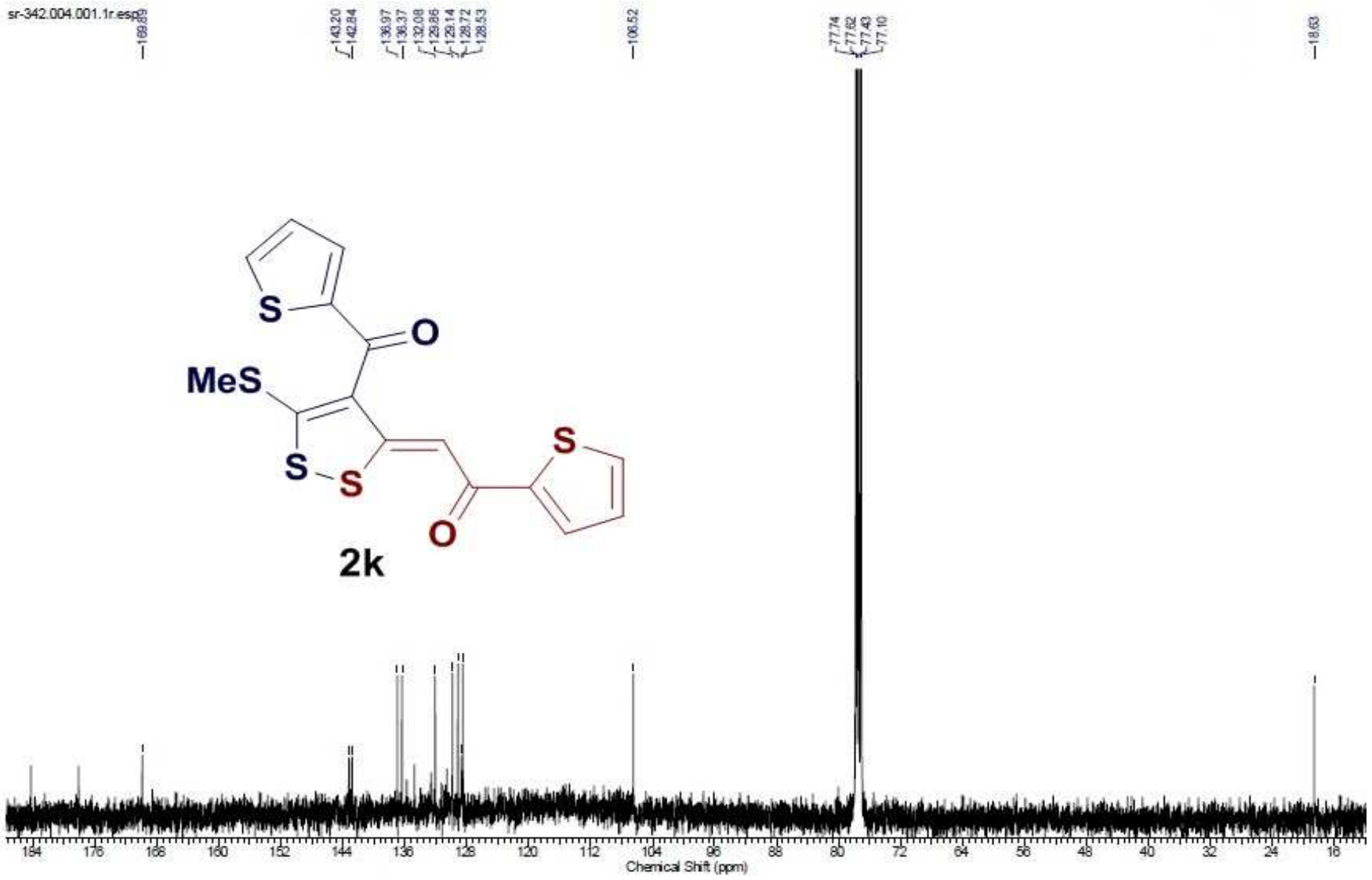
^{13}C spectrum of 2j:



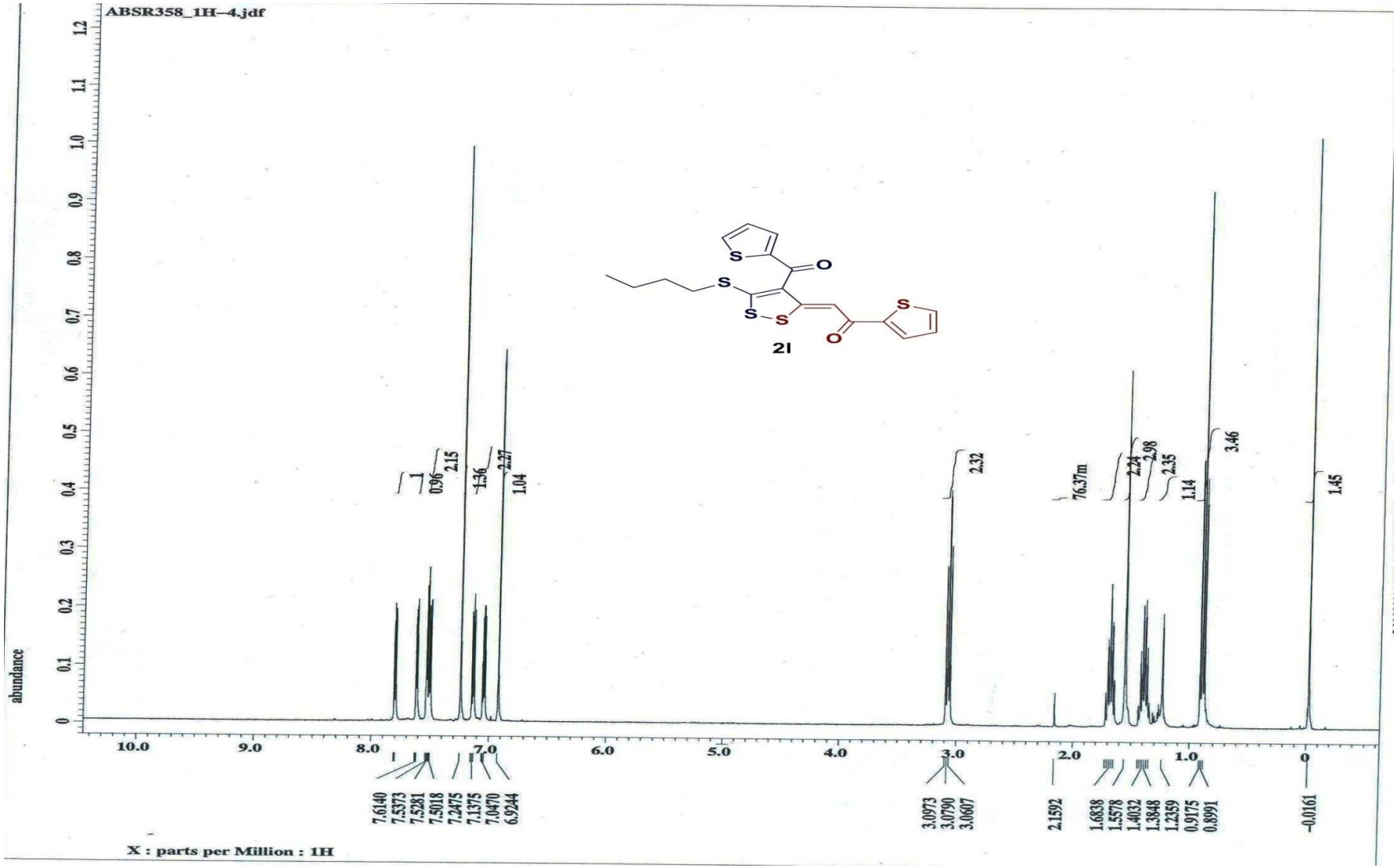
^{1}H spectrum of 2k:



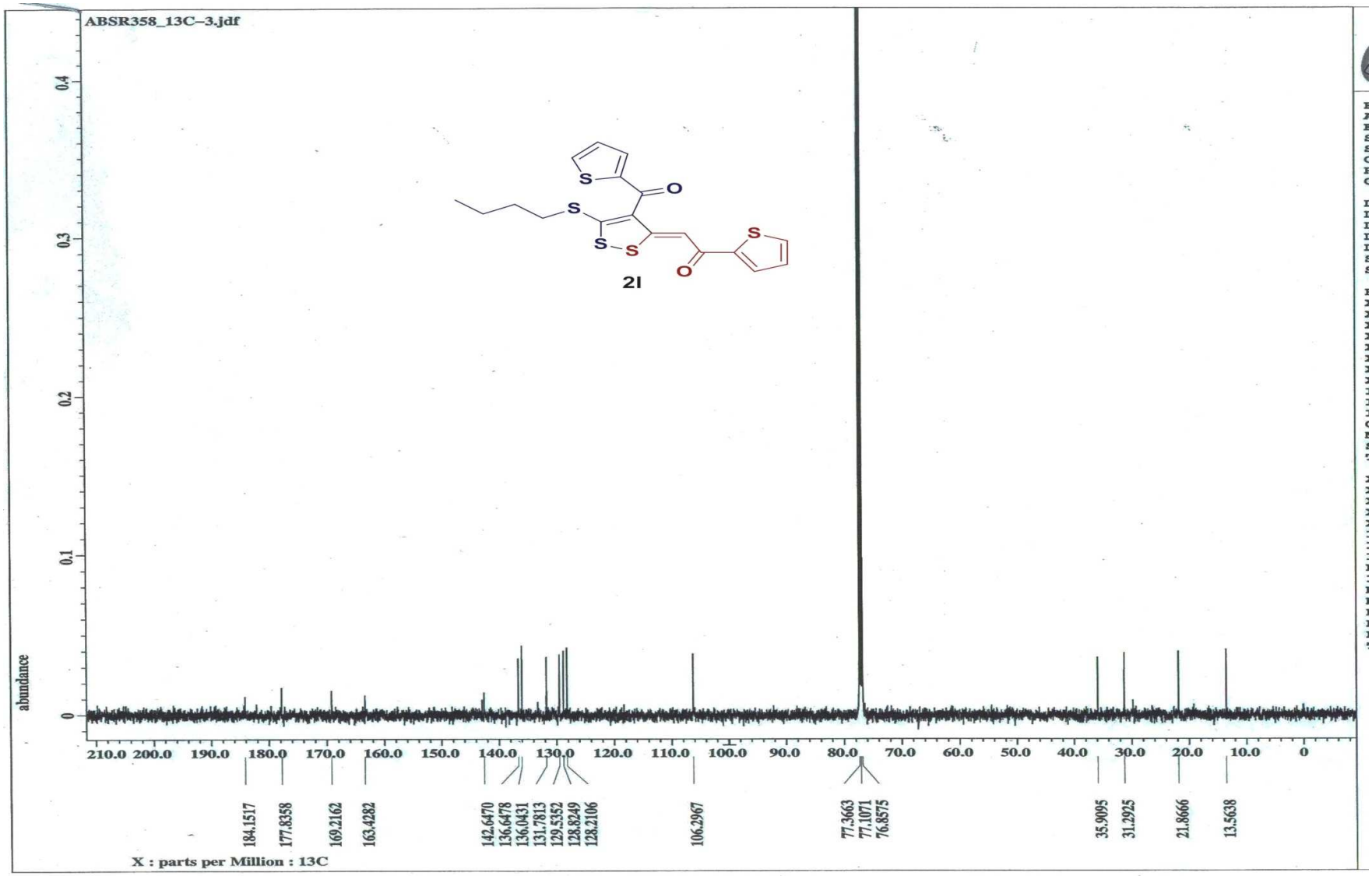
^{13}C spectrum of 2k:



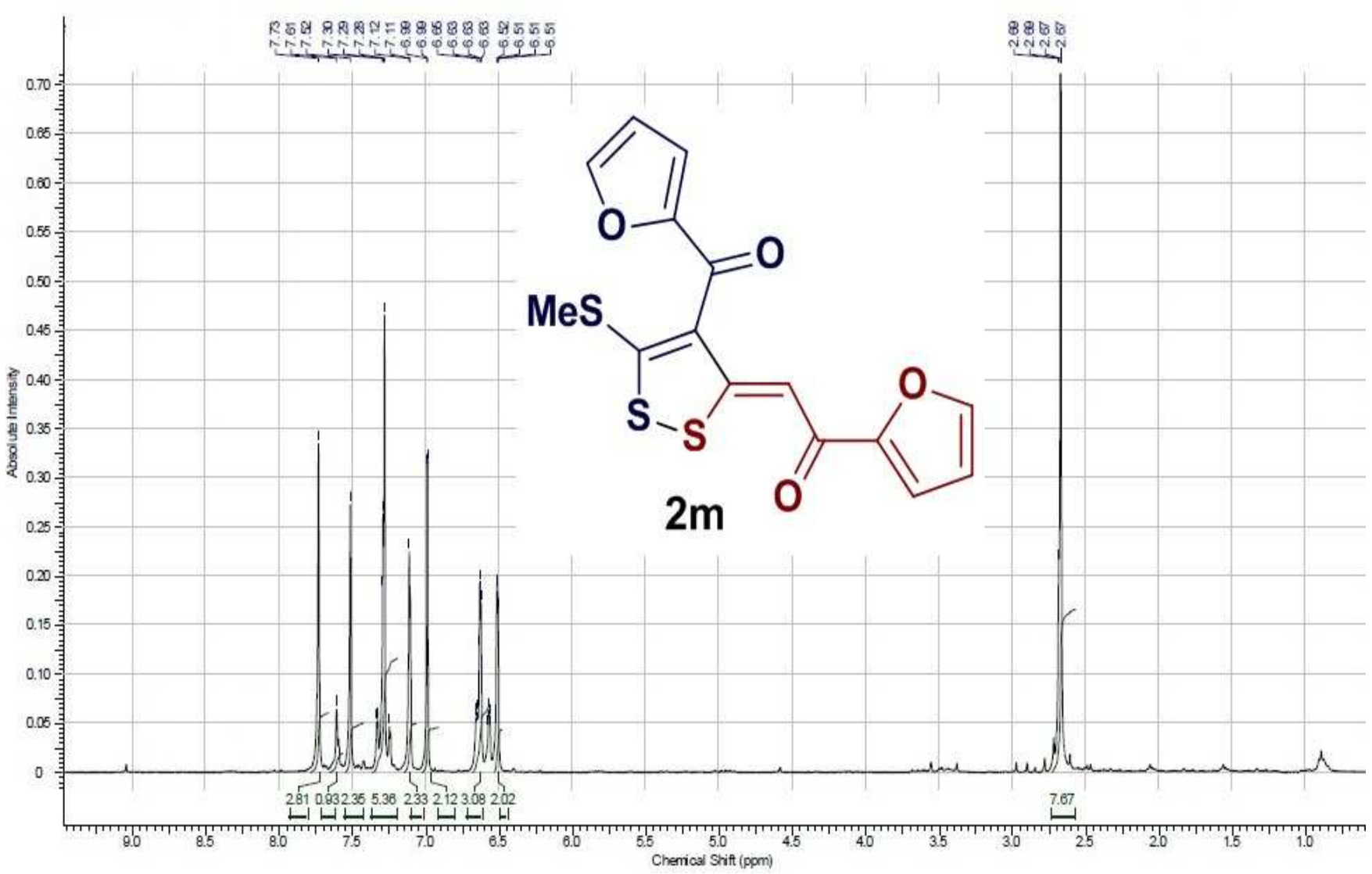
^{1}H spectrum of 2l:



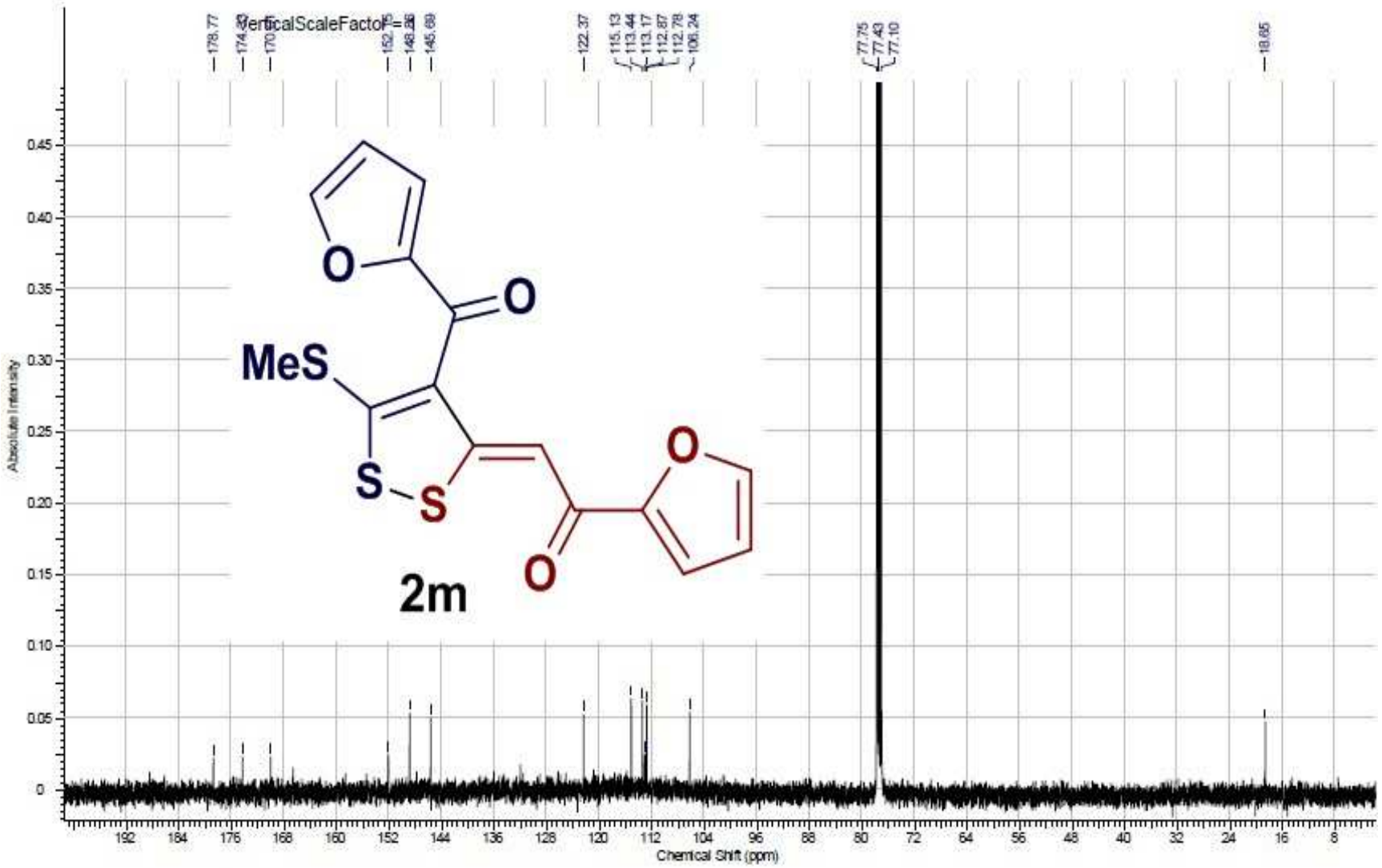
^{13}C spectrum of 2l:



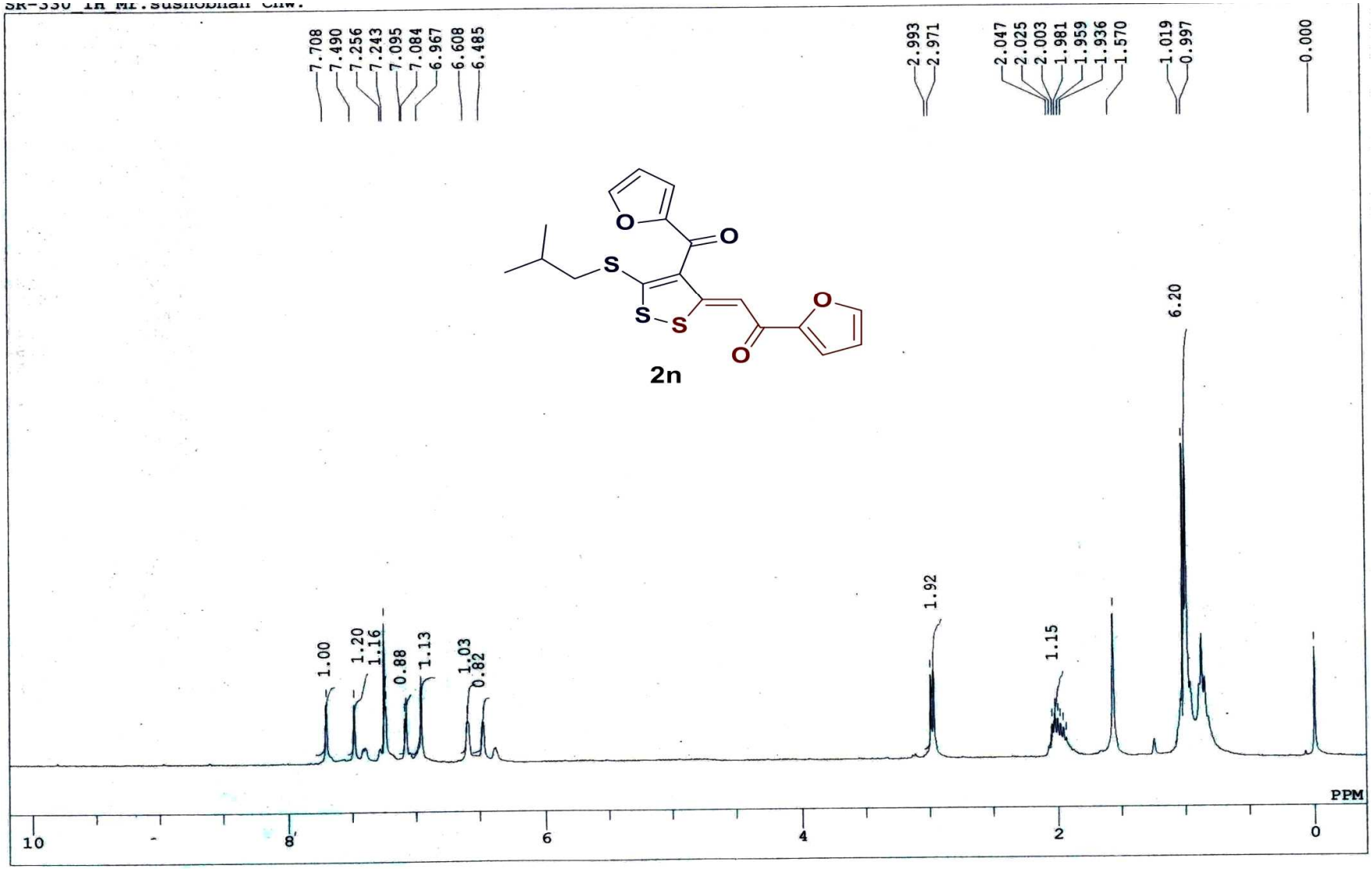
^{1}H spectrum of 2m:



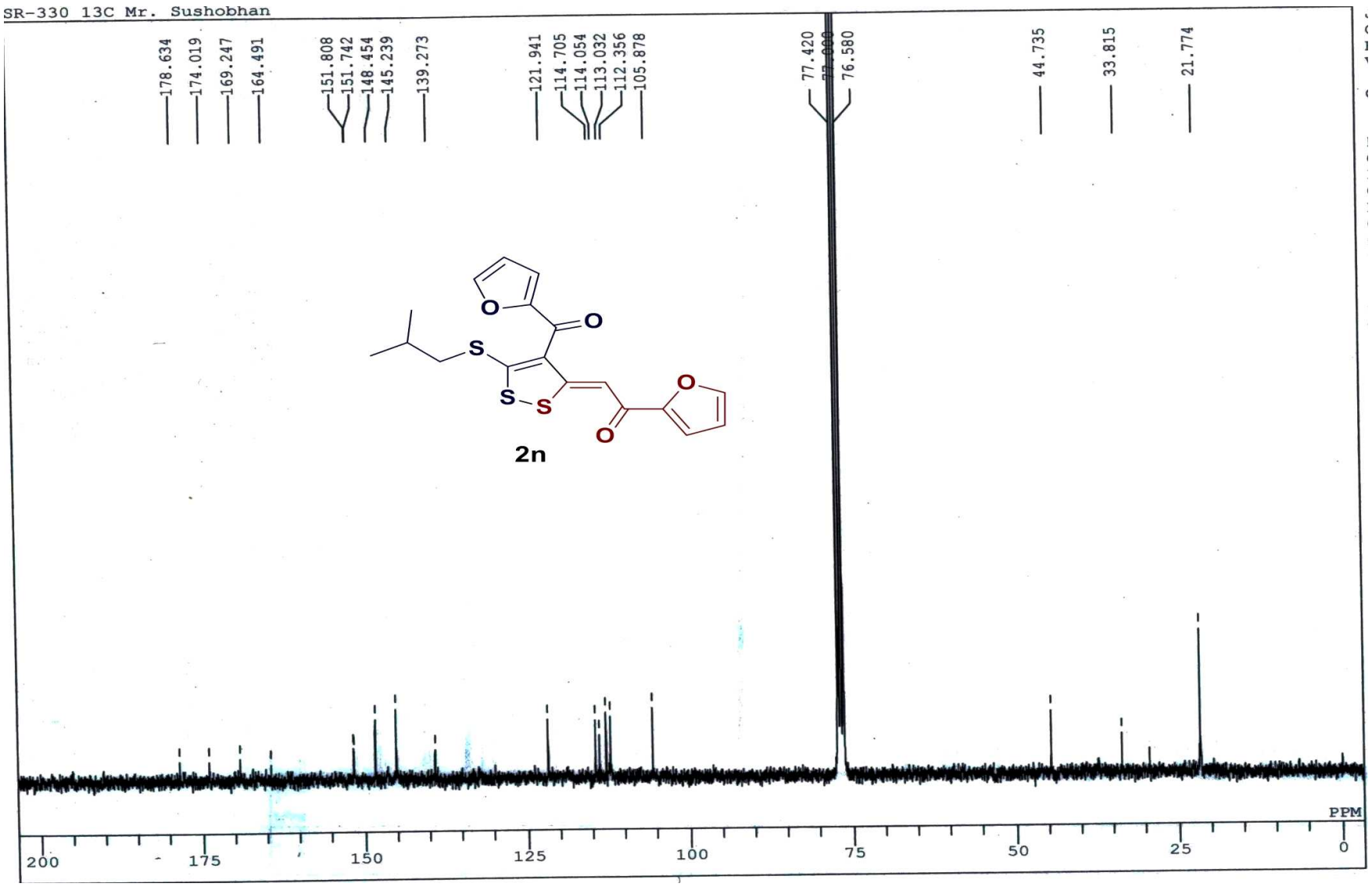
^{13}C spectrum of 2m:



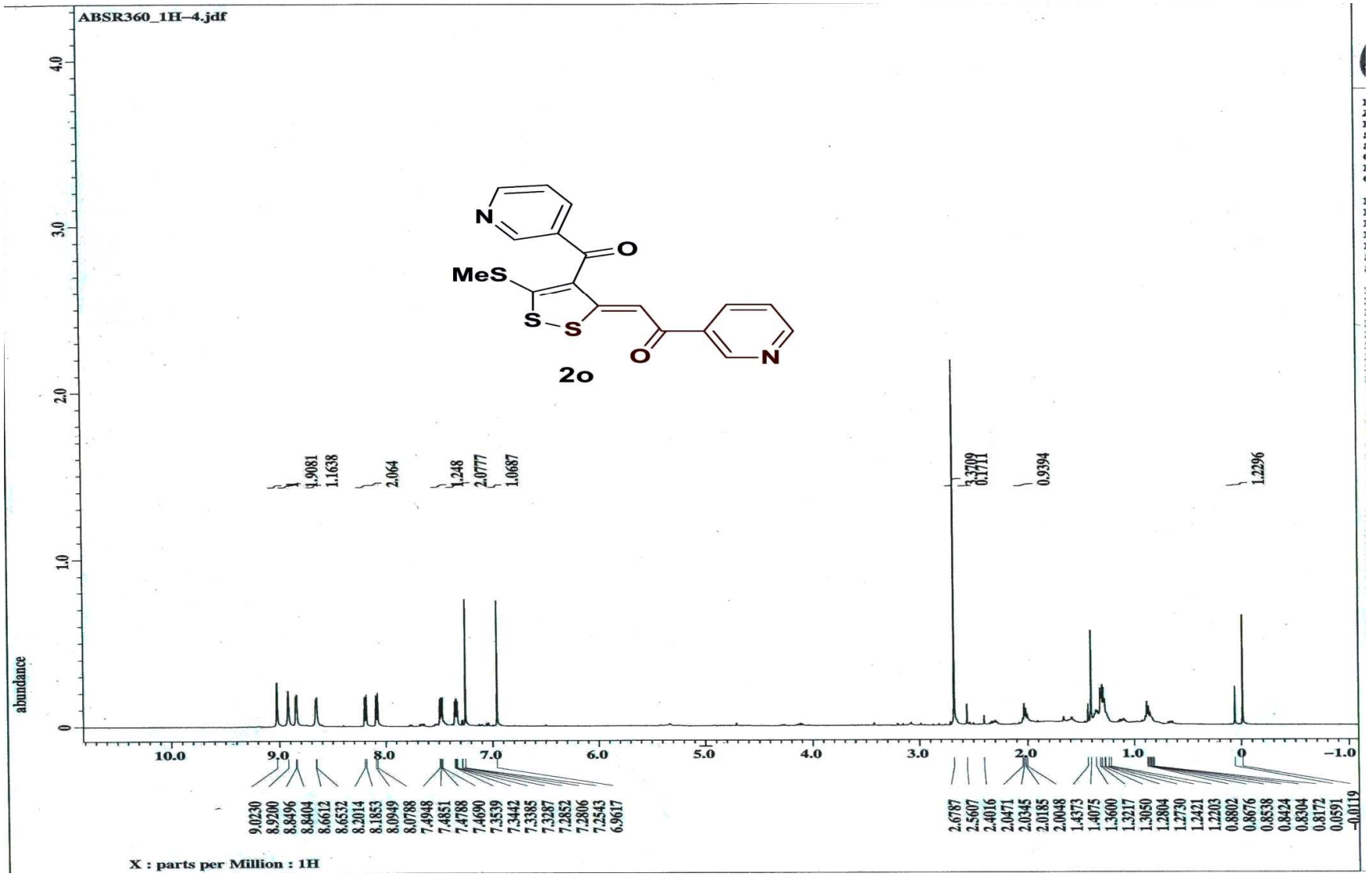
^{1}H spectrum of 2n:



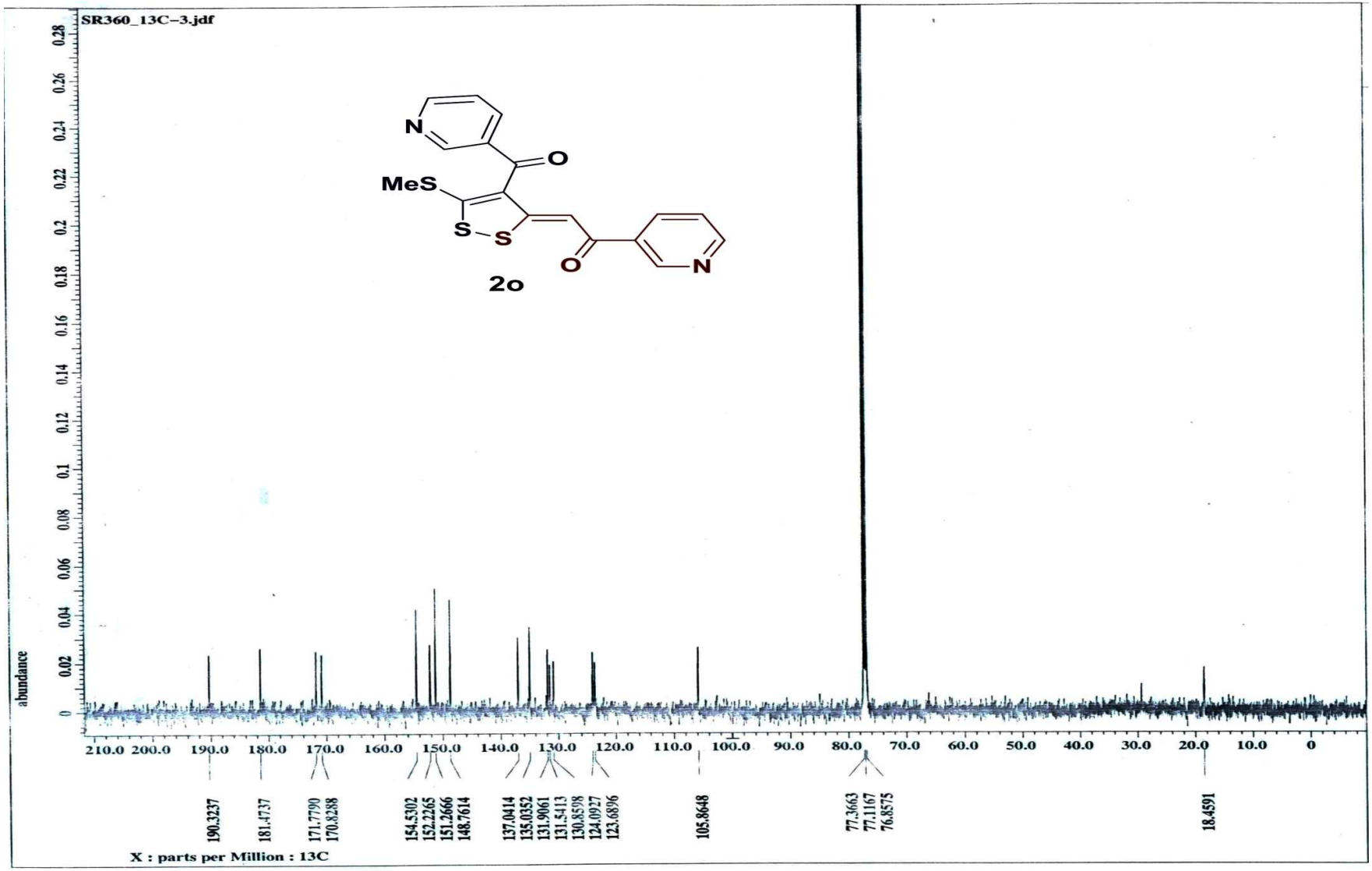
^{13}C spectrum of 2n:



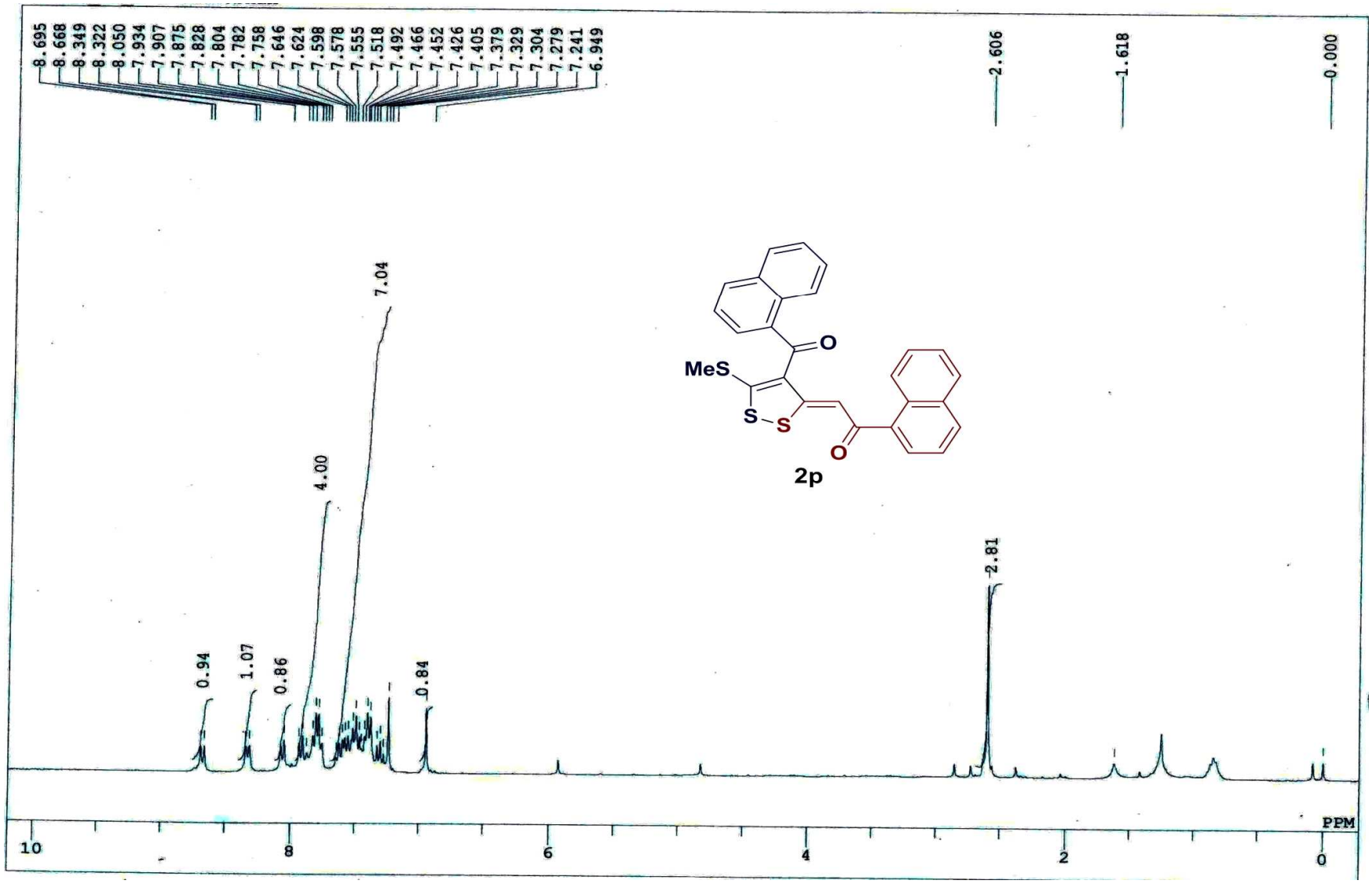
^{1}H spectrum of 2o:



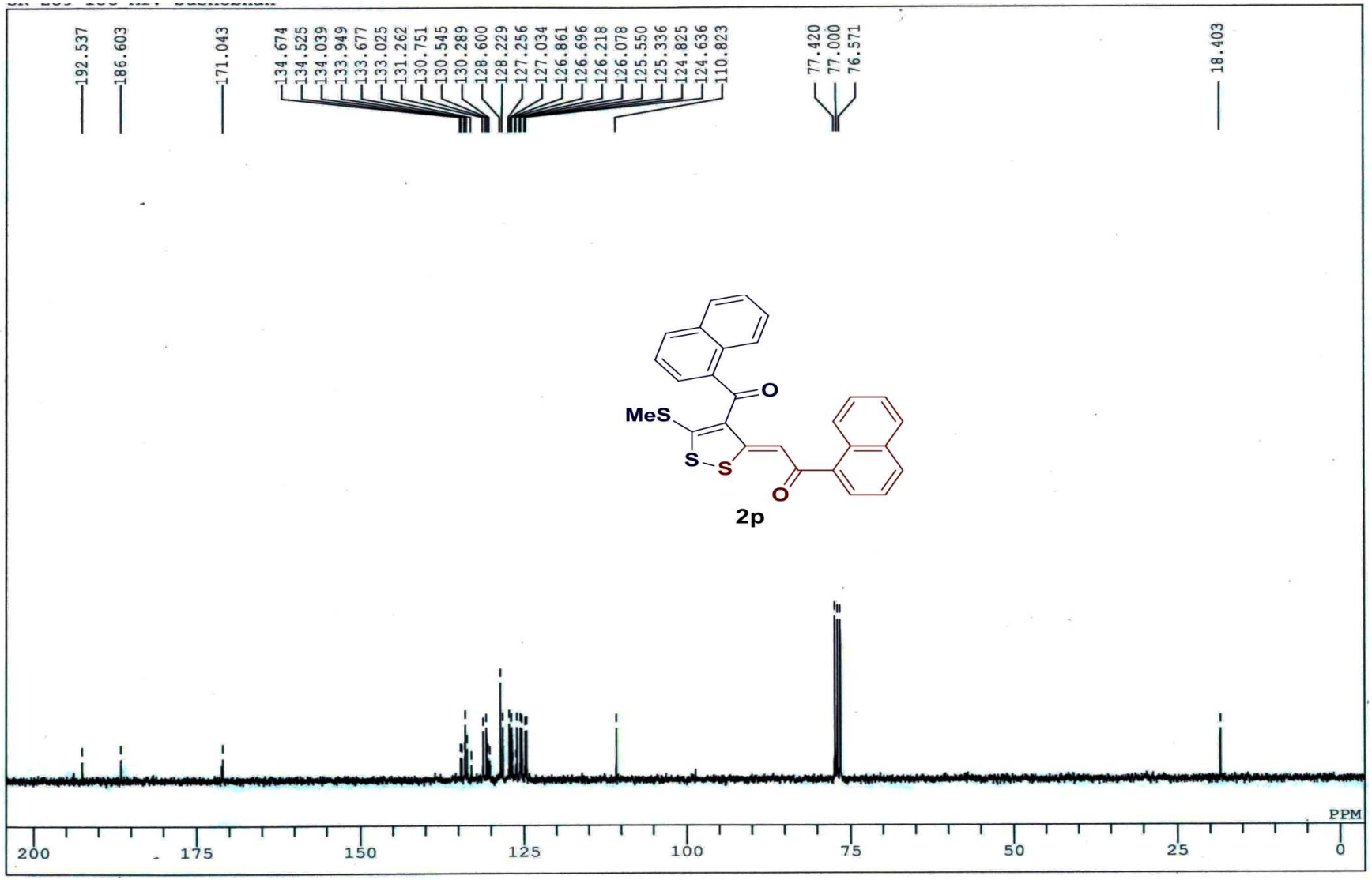
^{13}C spectrum of 2o:



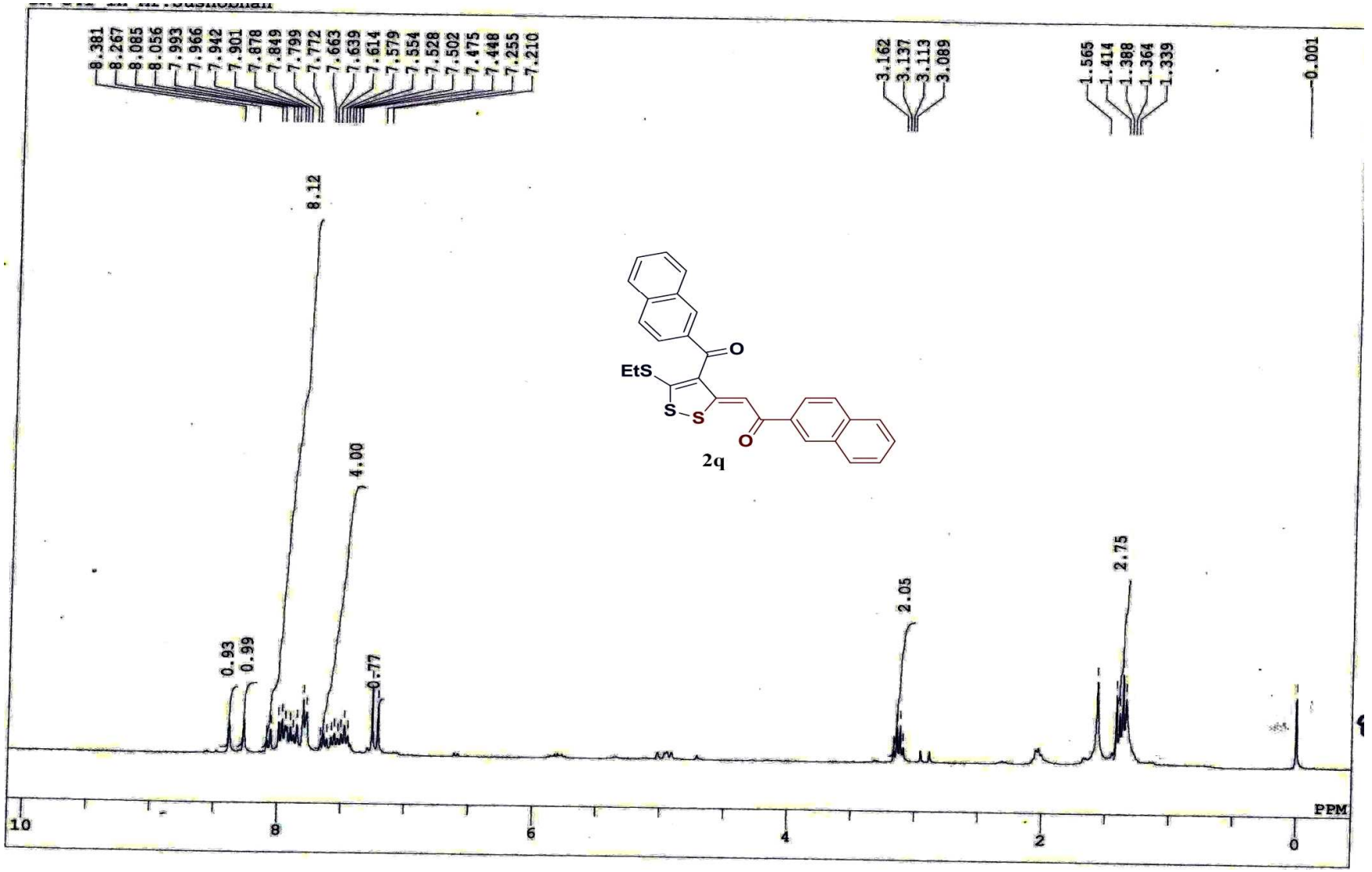
^{1}H spectrum of 2p:



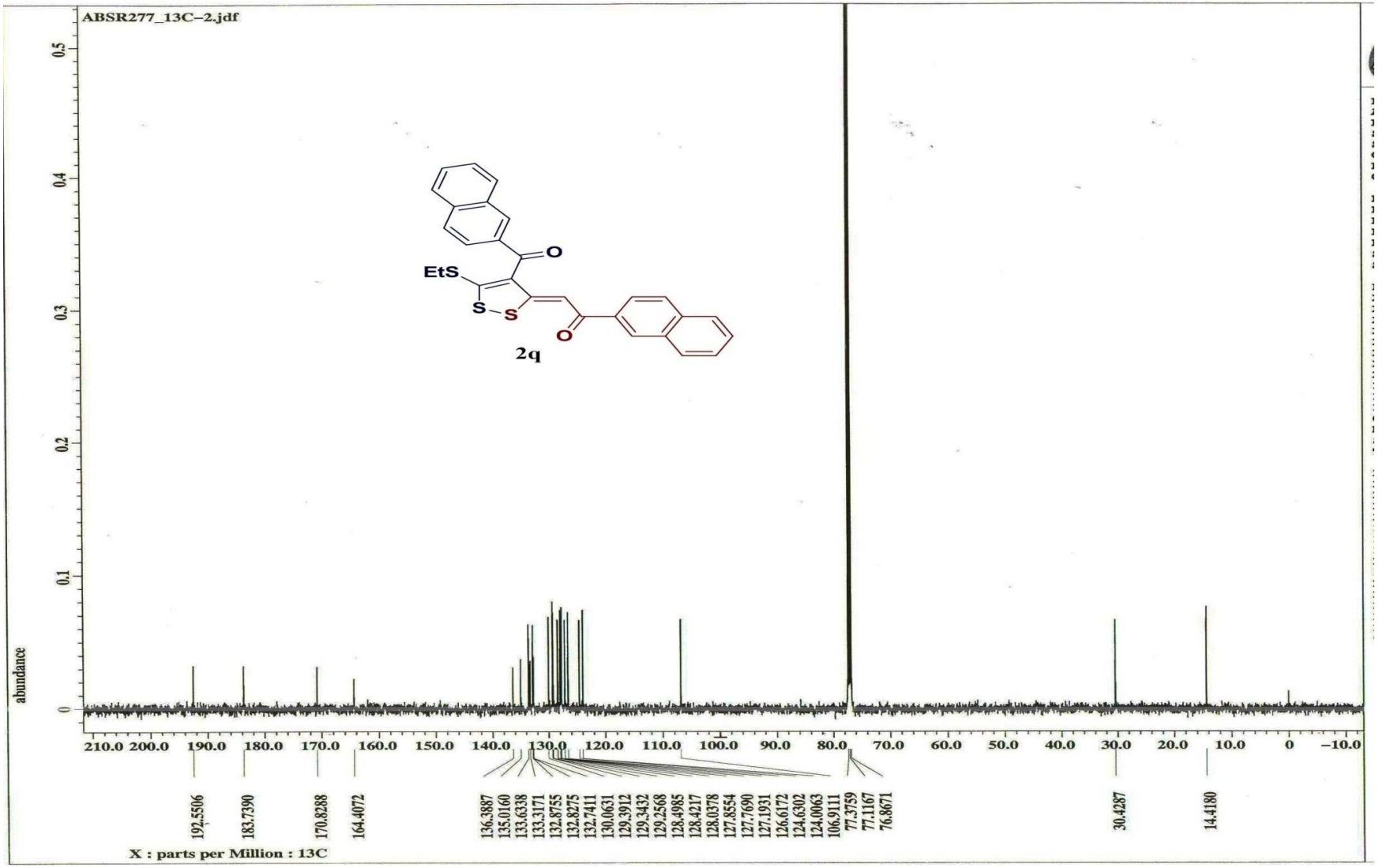
^{13}C spectrum of 2p:



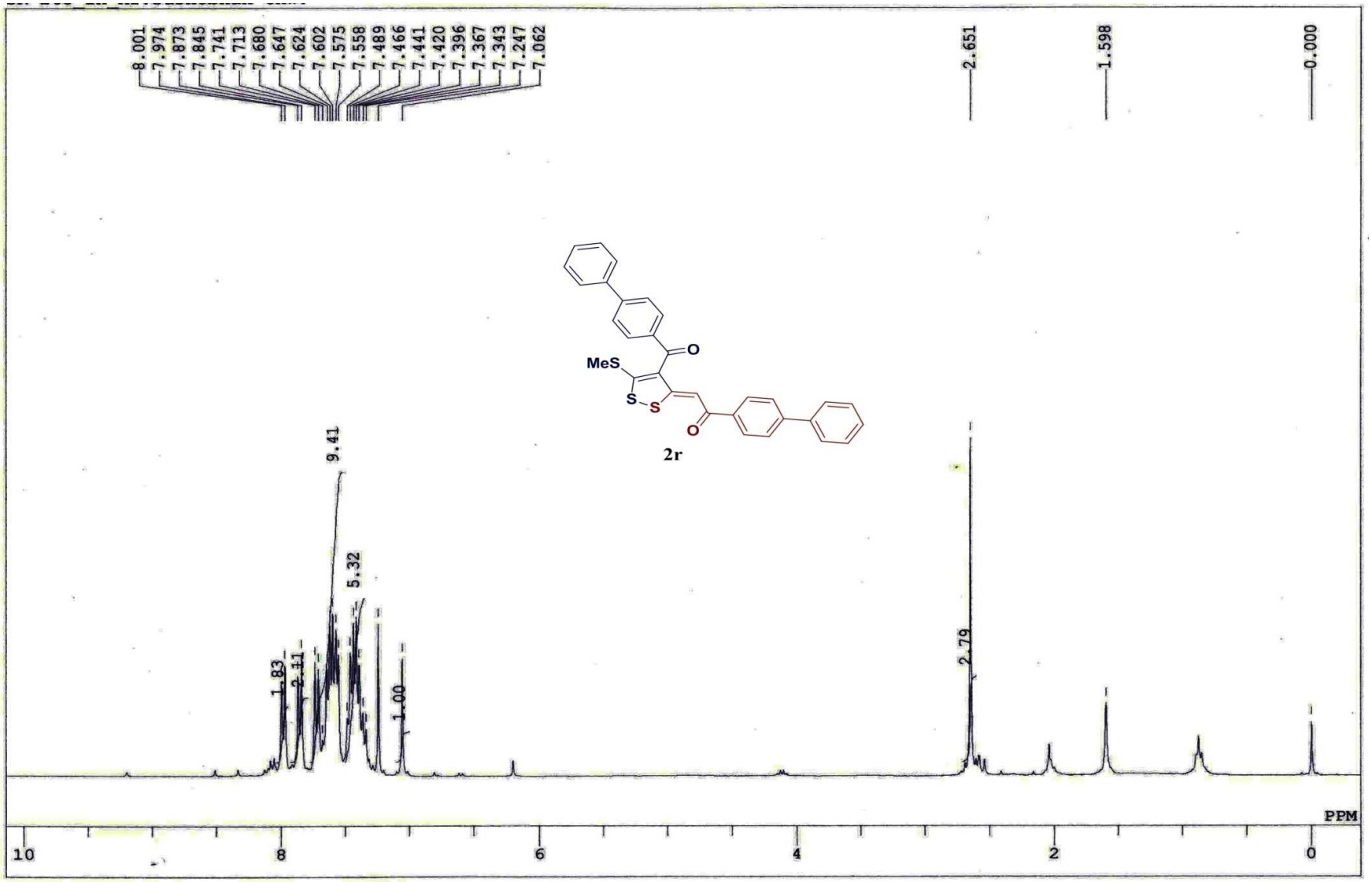
^{1}H spectrum of 2q:



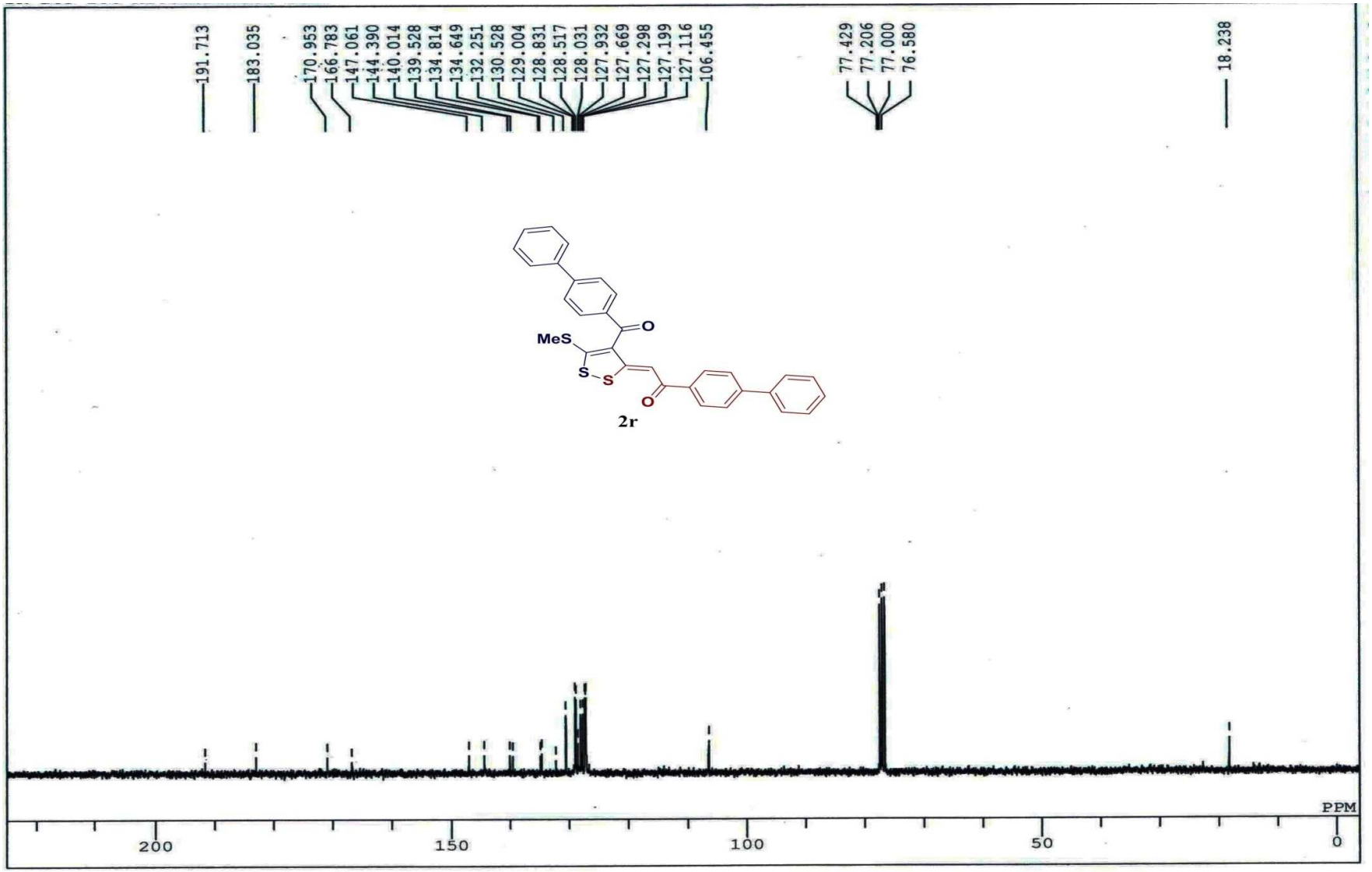
^{13}C spectrum of 2q:



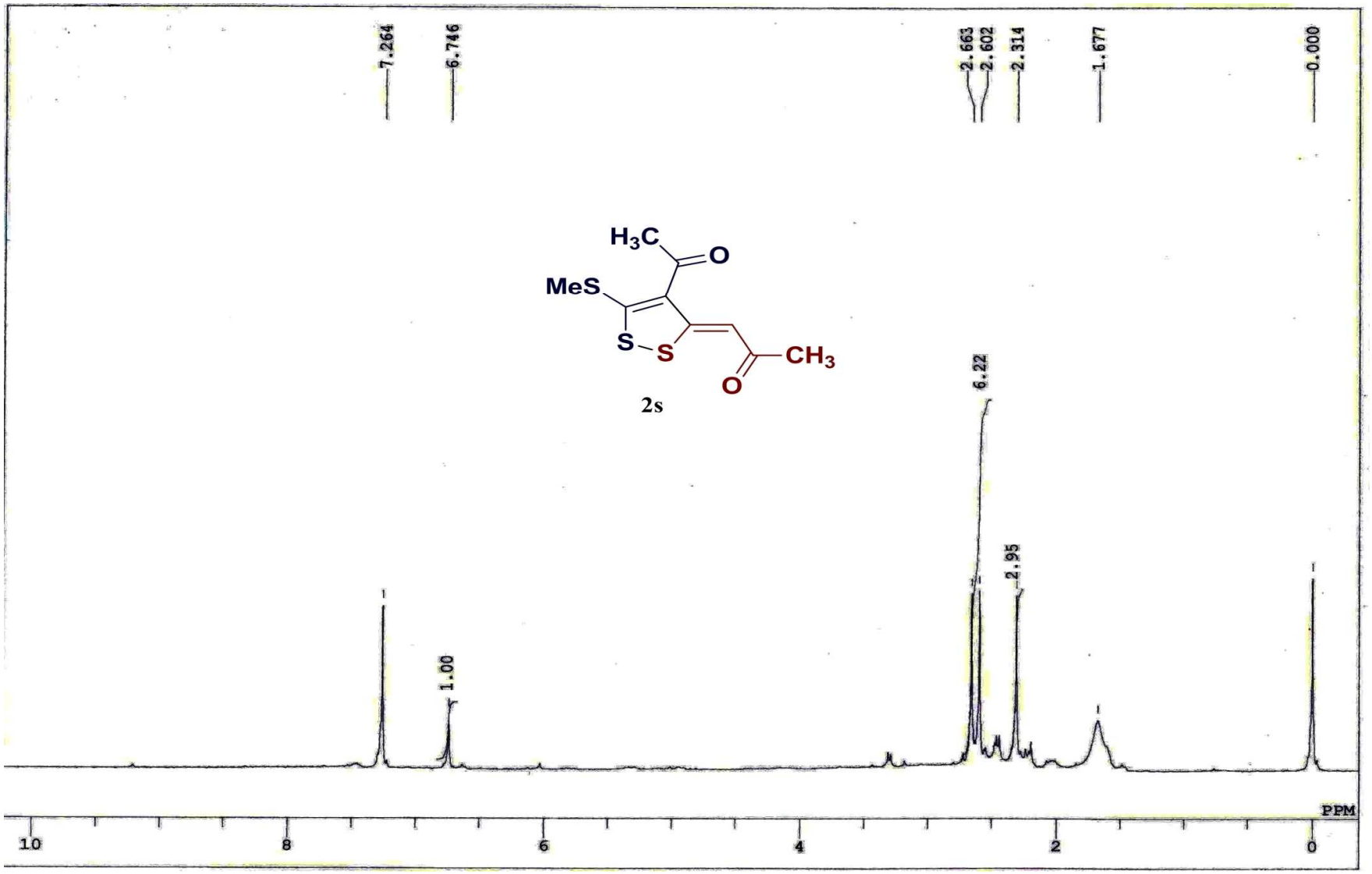
^{1}H spectrum of 2r:



^{13}C spectrum of 2r:



^{1}H spectrum of 2s:



^{13}C spectrum of 2s: