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Synthesis of new alkoxy/alkylthiovinylated oxazoles using tosylmethyl isocyanide

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Contents

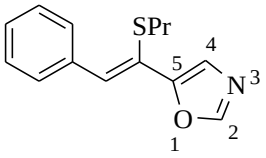
Experimental

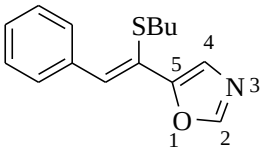
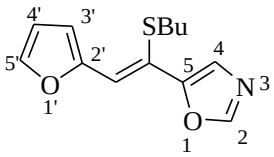
The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded in $CDCl_3$ solutions at room temperature on Bruker DPX-400 and AV-400 spectrometers (400.13, 100.61 and 40.56 MHz, respectively). ^{1}H, ^{13}C and ^{15}N Chemical shifts (δ in ppm) were measured with accuracy of 0.01, 0.02 and 0.1 ppm, respectively, and referred to TMS (^{1}H, ^{13}C) and nitromethane (^{15}N). The assignment of ^{1}H and ^{13}C signals in spectra was performed using 2D heteronuclear correlation HMBC-gp and HSQC-gp ^{13}C-^{1}H methods. The values of the δ ^{15}N were obtained through the 2D ^{1}H-^{15}N HMBC-gp experiment. Coupling constants (*J* in Hz) values approaches to 0.1 Hz. Chromato-mass spectrometry analysis was performed on an Agilent Technologies 5975C chromato-mass spectrometer (EI, 70 eV, mass-selective detector), AT-6890N chromatograph, Ultra-2 column (5% phenylmethylsilicone), evaporator temperature 250 °C, temperature of the column thermostat 70–280 °C, temperature rise rate 20 degree·min^{-1}. The IR spectra of the compounds were recorded on a Bruker IFC-25 instrument. Elemental analysis was performed on a Thermo Finning 1112ser automatic analyzer. Column chromatography was carried out on silica gel 60 (70–200 mesh; Merk).

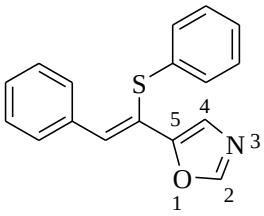
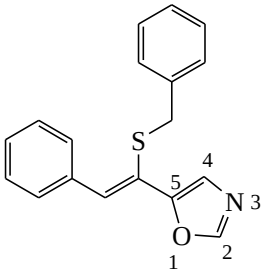
The starting aldehydes **1a-i** were synthesized according to the protocol.[1]

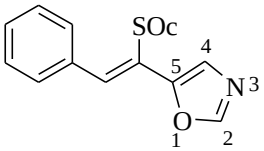
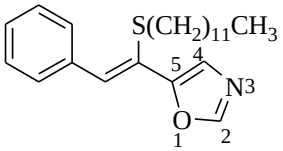
*General procedure for the synthesis of oxazoles **3a-i**.* To aldehydes (1 mmol) was added TosMIC (1.1 mmol) and K_2CO_3 (1.4 mmol) in a 6 ml of MeOH. The reaction mixture was stirred for 2 h at 55 °C. Then methanol was removed in vacuo, the residue was dissolved in ether and the precipitate was filtered off, then the ether was removed and the residue was purified by column chromatography (SiO_2, eluent-chloroform).

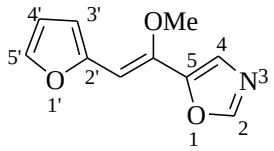
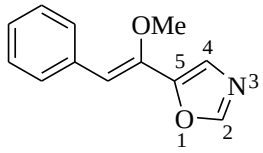
Characterization of synthesized compounds

	*5-[2-Phenyl-1-(propylsulfanyl)ethenyl]-1,3-oxazole* **3a**. Yellow oil (0.212 g, 89%). IR ν_{max} 2962, 2872, 1696, 1496, 1102, 968, 756, 694, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.87 (s, 1H, H-2), 7.83 (d, 2H, H-o (Ph), *J* 7.6 Hz), 7.38 (dd, 2H, H-m (Ph), ^{3}J 7.4 Hz, ^{3}J 7.6 Hz), 7.36 (s, 1H, H-4), 7.33 (s, 1H, =CH), 7.28 (t, 2H, H-p (Ph), ^{3}J 7.4 Hz), 2.63 (t, 2H, SCH_2 (Pr), *J* 7.3 Hz), 1.53 (m, 2H, $C\underline{H}_2CH_3$ (Pr)), 0.87 (t, 3H, CH_3 (Pr), *J* 7.4 Hz); ^{13}C NMR ($CDCl_3$): 152.23 (C-5), 150.77 (C-2), 135.65 (C-ipso), 133.70 (C-4), 130.01 (C-o), 128.30 (C-p), 128.21 (C-m), 125.23 (=CH), 121.42 (=C-S), 36.35 (SCH_2 (Pr)), 22.97 ($\underline{C}H_2CH_3$ (Pr)), 13.20 (CH_3 (Pr)); ^{15}N NMR ($CDCl_3$): -121.8;

	$^{2}J_{NH}$ 12.8 Hz. GC-MS, m/z (%): 245 $[M]^{+}$ (44), 230 (12), 214 (91), 207 (34), 187 (19), 174 (40), 165 (18), 147 (53), 129 (33), 115 (75), 103 (19), 91 (61), 73 (32), 68 (34), 44 (100), 41 (63), 35 (63). Found (%:) C, 68.52; H, 6.10; N, 5.68, S, 13.23. Calculated $C_{14}H_{15}NOS$ (%): C, 68.57; H, 6.12; N, 5.71, S, 13.06.
	*5-[2-Phenyl-1-(buthylsulfanyl)ethenyl]-1,3-oxazole* **3b**. Yellow oil (0.270 g, 87%). IR ν_{max} 2958, 2866, 1691, 1497, 1100, 967, 754, 694, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.82 (s, 1H, H-2), 7.78 (d, 2H, H-o (Ph), ^{3}J 8.0 Hz), 7.34 (dd, 2H H-m (Ph), ^{3}J 8.0 Hz, ^{3}J 7.2 Hz), 7.32 (s, 1H, H-4), 7.28 (s, 1H, =CH), 7.26 (t, 2H, H-p (Ph), ^{3}J 7.2 Hz), 2.62 (t, 2H, SCH_2 (Bu), J 7.3 Hz), 1.47 (m, 2H, $SCH_2C\underline{H}_2$ (Bu)), 1.26 (m, 2H, $C\underline{H}_2CH_3$ (Bu)), 0.77 (t, 3H, CH_3 (Bu), J 7.4 Hz); ^{13}C NMR ($CDCl_3$): 152.38 (C-5), 150.70 (C-2), 135.83 (C-ipso), 133.71 (C-4), 130.17 (C-o), 128.44 (C-p), 128.36 (C-m), 125.54 (=CH), 121.68 (=C-S), 34.18 SCH_2 (Bu), 31.80 $SCH_2\underline{C}H_2$ (Bu)), 21.92 ($\underline{C}H_2CH_3$ (Bu)), 13.76 (CH_3 (Bu)); ^{15}N NMR ($CDCl_3$): -118.8; $^{2}J_{NH}$ 13.3 Hz. GC-MS, m/z (%): 259 $[M]^{+}$ (12), 253 (11), 207 (100), 191 (13), 179 (19), 159 (7), 147 (16), 133 (11), 115 (12), 105 (12), 91 (29), 73 (19), 56 (13), 44 (59), 41 (23), 34 (7). Found (%:) C, 69.52; H, 6.56; N, 5.38, S, 12.33. Calculated $C_{15}H_{17}NOS$ (%): C, 69.50; H, 6.56; N, 5.40, S, 12.36.
	*5-[1-(Butylsulfanyl)-2-(2-furyl)ethenyl]-1,3-oxazole* **3c**. Dark brown oil (0.288 g, 81%). IR ν_{max} 2956, 2867, 1601, 1470, 1098, 1018, 969, 743, 639 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.85 (s, 1H, H-2), 7.47 (d, 1H, H-5', J 1.6 Hz), 7.29 (s, 1H, H-4), 7.26 (s, 1H, =CH), 7.25 (d, 1H, H-3', ^{3}J 3.7 Hz), 6.52 (dd, 1H, H-4', J 3.7 Hz, J 1.6 Hz), 2.75 (t, 2H, SCH_2 (Bu), J 7.5 Hz), 1.54 (m, 2H, $SCH_2C\underline{H}_2$ (Bu)), 1.37 (m, 2H, $C\underline{H}_2CH_3$ (Bu)), 0.85 (t, 3H, CH_3 (Bu), J 7.3 Hz); ^{13}C NMR ($CDCl_3$): 151.98 (C-5), 151.60 (C-2'), 150.75 (C-2), 142.81 (C-5'), 125.19 (C-4'), 122.25 (=CH), 118.43 (=C-S), 113.09 (C-3'), 112.25 (C-4'), 33.92 (SCH_2 (Bu)), 32.02 ($SCH_2\underline{C}H_2$ (Bu)), 21.88 ($\underline{C}H_2CH_3$ (Bu)), 13.61 (CH_3 (Bu)); ^{15}N NMR ($CDCl_3$): -119.5; $^{2}J_{NH}$ 12.6 Hz. GC-MS, m/z (%): 249 $[M]^{+}$ (100), 193 (35), 164 (84), 137 (22), 112 (29), 109 (13), 97 (8), 81 (93), 68 (27), 51 (21), 41 (30), 39 (19). Found (%:) C, 62.66; H, 6.00; N, 5.58; S, 12.67. Calculated

	$C_{13}H_{15}NO_2S$ (%): C, 62.65; H, 6.02; N, 5.62; S, 12.85.
	*5-[2-Phenyl-1-(phenylsulfanyl)ethenyl]-1,3-oxazole* **3d**. Yellow oil (0.109 g, 73%). IR ν_{max} 3132, 3059, 2925, 2854, 1581, 1482, 1443, 1253, 1100, 969, 829, 746, 693, 639 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.85 (s, 1H, H-2), 7.84 (d, 2H, H-o (SPh), *J* 7.6 Hz), 7.71 (s, 1H, =CH), 7.43-7.36 (m, 4H H-m, p (SPh)), 7.31-7.25 (m, 4H (Ph)), 7.16 (s, 1H, C-4); ^{13}C NMR ($CDCl_3$): 151.83 (C-5), 150.64 (C-2), 136.36 (C-4), 135.30 (C-ipso (SPh)), 135.25 (C-ipso (Ph)), 130.22 (C-o (Ph)), 129.42 (C-m (Ph)), 129.11 (C-p (Ph)), 128.55 (C-o (SPh)), 128.01 (C-m (SPh)), 126.51 (C-p (SPh)), 126.22 (CH), 119.09 (=C-S); ^{15}N NMR ($CDCl_3$): -119.8. $^2J_{NH}$ 12.8 Hz; GC-MS, m/z (%): 279 $[M]^+$ (59), 250 (5), 234 (4), 223 (3), 201 (2), 191 (4), 170 $[M\text{-}SPh]^+$ (11), 167 (39), 142 (14), 134 (3), 115 (100), 109 (4), 89 (11), 77 (9), 65 (12), 51 (15), 39 (11). Found (%:) C, 73.31; H, 5.00; N, 11.79; S, 5.21. Calculated $C_{17}H_{13}NOS$ (%): C, 73.12; H, 4.66; N, 11.47; S, 5.02
	*5-[1-(Benzylsulfanyl)-2-phenylethenyl]-1,3-oxazole* **3e**. Yellow oil (0.308 g, 87%). IR ν_{max} 3132, 3059, 3027, 2924, 2855, 1684, 1494, 1448, 1103, 967, 829, 755, 695, 637 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.87 (s, 1H, H-2), 7.70 (d, 2H, H-o (Ph), ^3J 7.6 Hz), 7.36 (t, 1H, H-p (Ph), ^3J 7.8 Hz); 7.34 (m, 2H, H-m (Ph)), 7.32 (s, 1H, H-4), 7.29 (s, 1H, =CH), 7.19 (m, 3H, H-m, p (SBn)), 7.10 (d, 2H, H-o (SBn), ^3J 7.6 Hz), 3.86 (s, 2H, SCH_2); ^{13}C NMR ($CDCl_3$): 152.17 (C-5), 150.87 (C-2), 137.13 (C-ipso (Ph)), 135.52 (C-ipso (SBn), 134.59 (C-4), 129.93 (C-o (Ph)), 128.93 (C-o (SBn), 128.45 (C-m,p (Ph)), 128.26 (C-m (SBn), 127.34 (C-p (SBn)), 125.48 (=CH), 120.72 (=C-S), 38.69 (SCH_2); ^{15}N ($CDCl_3$) δ: -120.1. $^2J_{NH}$ 12.8 Hz. GC-MS, m/z (%): 293 $[M]^+$ (6), 202 $[M\text{-}CH_2Ph]^+$ (22), 175 (5), 167 (1), 147 (14), 134 (3), 115 (6), 103 (4), 91 (100), 77 (6), 68 (23), 45 (11), 39 (11). Found (%:) C, 73.41; H, 5.15; N, 4.74; S, 10.78. Calculated $C_{18}H_{15}NOS$ (%): C, 73.72; H, 5.12; N, 4.78; S, 10.92

	*5-[1-(Octylsulfanyl)-2-phenylethenyl]-1,3-oxazole* **3f**. Yellow oil (0.155 g, 68%). IR ν_{max} 3128, 2925, 2855, 1694, 1549, 1497, 1455, 1101, 1076, 968, 755, 694, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.89 (s, 1H, H-2), 7.84 (d, 2H, *J* 7.7 Hz, H-o), 7.40 (dd, 3H, H-m, ^{3}J 7.7 Hz, ^{3}J 7.4 Hz), 7.34 (1H, H-4), 7.31 (t, 3H, H-p, ^{3}J 7.4 Hz), 2.66 (t, 2H, SCH_2, *J* 7.3 Hz), 1.54-1.47 (m, 4H, $SCH_2(\underline{CH_2})_2$), 1.28-1.19 (m, 8H $S(CH_2)_3(\underline{CH_2})_4CH_3$), 0.88 (t, 3H, CH_3, *J* 7.4 Hz); ^{13}C NMR ($CDCl_3$): 152.35 (C-5), 150.68 (C-2), 135.82 (C-ipso), 133.74 (C-4), 130.06 (C-o), 128.35 (C-p), 128.25 (C-m), 125.54 (=CH), 121.66 (=C-S), 34.42 ($S\underline{C}H_2$), 31.78 ($SCH_2\underline{C}H_2$), 29.56 ($S(CH_2)_2\underline{C}H_2$), 29.13 ($\underline{C}H_2(CH_2)_3CH_3$), 29.06 ($\underline{C}H_2(CH_2)_2CH_3$), 28.61 ($\underline{C}H_2CH_2CH_3$), 22.80 ($\underline{C}H_2CH_3$), 14.30 ($CH_3$); ^{15}N -120.3. $^{2}J_{NH}$ 13.0 Hz; GC-MS, m/z (%): 315 $[M]^+$ (68), 224 (10), 203 (100), 175 (16), 161 (4), 134 (8), 115 (62), 102 (7), 91 (31), 75 (18), 68 (33), 41 (45). Found (%:) C, 72.30; H, 8.01; N, 4.51; S, 10.21. Calculated $C_{19}H_{25}NOS$ (%): C, 72.38; H, 7.94; N, 4.44; S, 10.16
	*5-[1-(Dodecylsulfanyl)-2-phenylethenyl]-1,3-oxazole* **3g**. Dark orange oil (0.164g, 63%). IR ν_{max} 2924, 2853, 1661, 1551, 1496, 1350, 1101, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.89 (s, 1H, H-2), 7.84-7.82 (d, 2H, H-o, *J* 7.8 Hz), 7.41-7.39 (dd, 2H, H-m, *J* 7,5 7.8 Hz), 7.34 (s, 1H, H-4), 7.38 (s, 1H, =CH), 7.31 (t, 1H, H-p, *J* 7.5 Hz), 2.71-2.64 (m, 2H, SCH_2), 1.70-1.66 (m, 2H, $SCH_2\underline{CH_2}$), 1.51-1.47 (m, 2H, $S(CH_2)_2\underline{CH_2}$), 1.39-1.17 (m, 16H, $S(CH_2)_3(\underline{CH_2})_8$), 0.89 (t, 3H, CH_3, *J* 7.0 Hz); ^{13}C NMR ($CDCl_3$): 152.33 (C-5), 150.82 (C-2), 135.77 (C-ipso), 133.78 (C-4), 130.08 (C-o), 128.37 (C-p), 128.27 (C-m), 125.31 (=CH), 121.55 (=C-S), 39.30 ($S\underline{C}H_2$), 34.43 ($SCH_2\underline{C}H_2$), 29.74 ($S(CH_2)_2\underline{C}H_2$), 29.67 ($\underline{C}H_2(CH_2)_5CH_3$), 29.60 ($\underline{C}H_2(CH_2)_4CH_3$), 29.51 ($\underline{C}H_2(CH_2)_3CH_3$), 29.31 ($\underline{C}H_2(CH_2)_2CH_3$), 28.62 ($\underline{C}H_2CH_2CH_3$), 22.77 ($\underline{C}H_2CH_3$), 14.20 ($CH_3$); ^{15}N NMR ($CDCl_3$): -119.9. $^{2}J_{NH}$ 13.1 Hz. GC-MS, m/z (%): 371 $[M]^+$ (29), 203 (61), 175 (11), 147 (20), 115 (47), 112 (26), 91 (20), 71 (27), 68 (30), 43 (100). Found (%): C, 74, 39; H, 8.86; N, 3.72; S, 8.60. Calculated $C_{23}H_{33}NOS$ (%): C, 74.39; H, 8.89; N, 3.77; S, 8.63.

	*5-[2-(2-Furanyl)-1-methoxyethenyl]-1,3-oxazole* **3h**. Dark orange oil (0.189 g, 75%). IR ν_{max} 3130, 2937, 2851, 1689, 1527, 1481, 1348, 1268, 1197, 1076, 1015, 739, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.87 (s, 1H, H-2), 7.43 (d, 1H, *J* 1.7 Hz, H-5'), 7.19 (s, 1H, H-4), 6.71 (d, 1H, ^{3}J 3.7 Hz, H-3'), 6.49 (dd, 1H, *J* 3.7, *J* 1.7 Hz, H-4'), 6.41 (s, 1H, =CH), 3.81 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 150.81 (C-2), 149.97 (C-2'), 147.91 (C-5), 142.92 (=<u>C</u>OMe), 141.95 (C-5'), 124.00 (C-4), 112.12 (C-4'), 110.66 (C-3'), 104.42 (=CH), 59.45 (CH_3). ^{15}N NMR ($CDCl_3$): -120.3. $^{2}J_{NH}$ 14.3 Hz. GC-MS, m/z (%): 191 $[M]^+$ (100), 176 (21), 162 (2), 148 (65), 121 (17), 108 (4), 96 (36), 77 (8), 68 (32), 52 (21), 40 (20). Found (%): C, 63.00; H, 4.68; N, 7.47. Calculated $C_{10}H_9NO_3$ (%): C, 62.82; H, 4.71; N, 7.33.
	*5-[1-Methoxy-2-phenylethenyl]-1,3-oxazole* **3i**. Yellow oil (0.088 g, 86%). IR ν_{max} 2850, 1688, 1633, 1524, 1498, 1352, 1263, 1149, 1074, 1029 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.89 (s, 1H, H-2), 7.69 (d, 2H, H-o, *J* 7.7 Hz), 7.36-7.33 (dd, 2H, H-m, *J* 7.7, *J* 8.7 Hz), 7.28 (t, 1H, H-p, *J* 8.7 Hz), 7.21 (s, 1H, H-4), 6.37 (s, 1H, =CH), 3.76 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 150.81 (C-2), 148.45 (C-5), 144.91 (=C(OMe)-), 134.39 (C-ipso, Ph), 129.01 (C-o), 128.63 (C-m), 127.64 (C-p), 123.94 (N=<u>C</u>H-C), 114.47 (=CH), 59.36 (CH_3); ^{15}N NMR ($CDCl_3$): -122.6. $^{2}J_{NH}$ 10.0 Hz, $^{2}J_{NH}$ 13.9 Hz. GC-MS, m/z (%): 201$[M]^+$ (100), 186 (6), 173 (3), 158 (45), 145 (5), 131 (53), 115 (27), 103 (65), 89 (31), 77 (36), 68 (29), 63 (23), 62 (11), 51 (23), 40 (33), 39 (19). Found: C, 71.53; H, 5.2; N, 7.00. Calculated $C_{12}H_{11}O_2N$ (%): 71.56; H, 5.50; N, 6.96.

References

1. (*a*) N. A. Keiko, L. G. Stepanova, E. A. Verochkina and L. I. Larina, *ARKIVOC*, 2010, (**ii**), 49; (*b*) E. V. Kondrashov, A. R. Romanov, I. A. Ushakov and A. Yu. Rulev, *J. Sulfur Chem.*, 2016, **38** (1), 18.

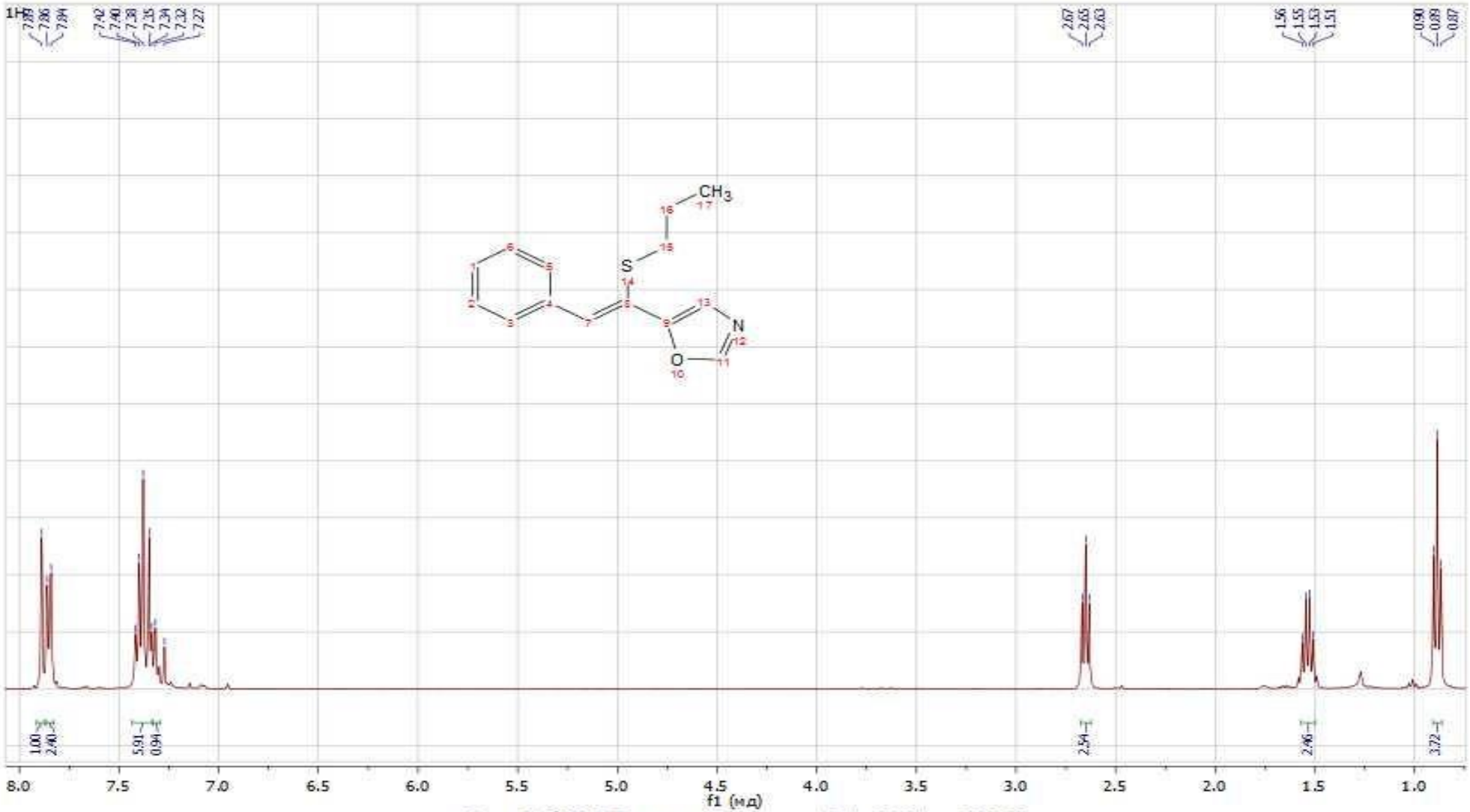


Figure S1. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$ at 400 MHz

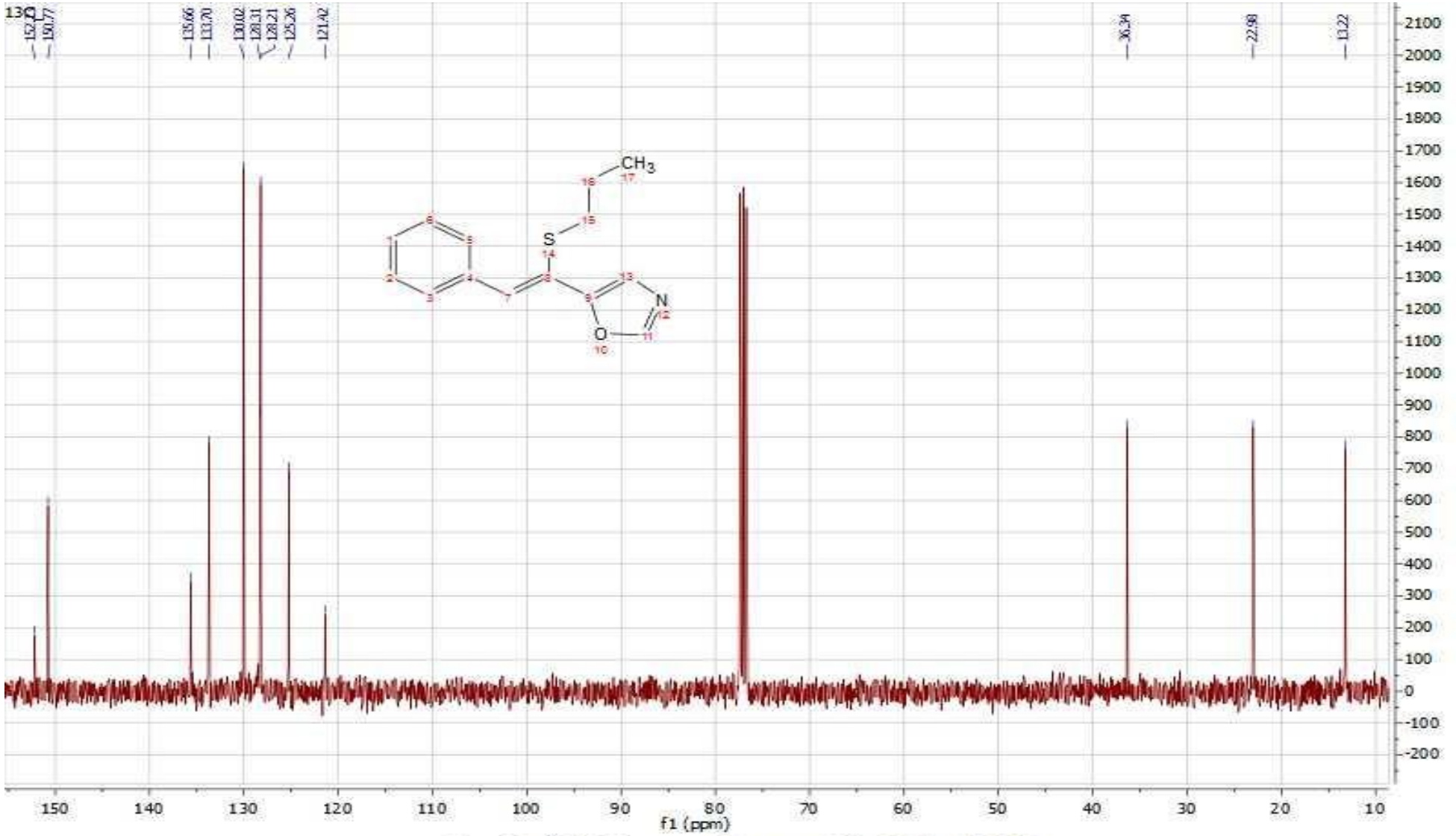


Figure S2. ^{13}C NMR spectrum of compound **3a** in $CDCl_3$ at 400 MHz

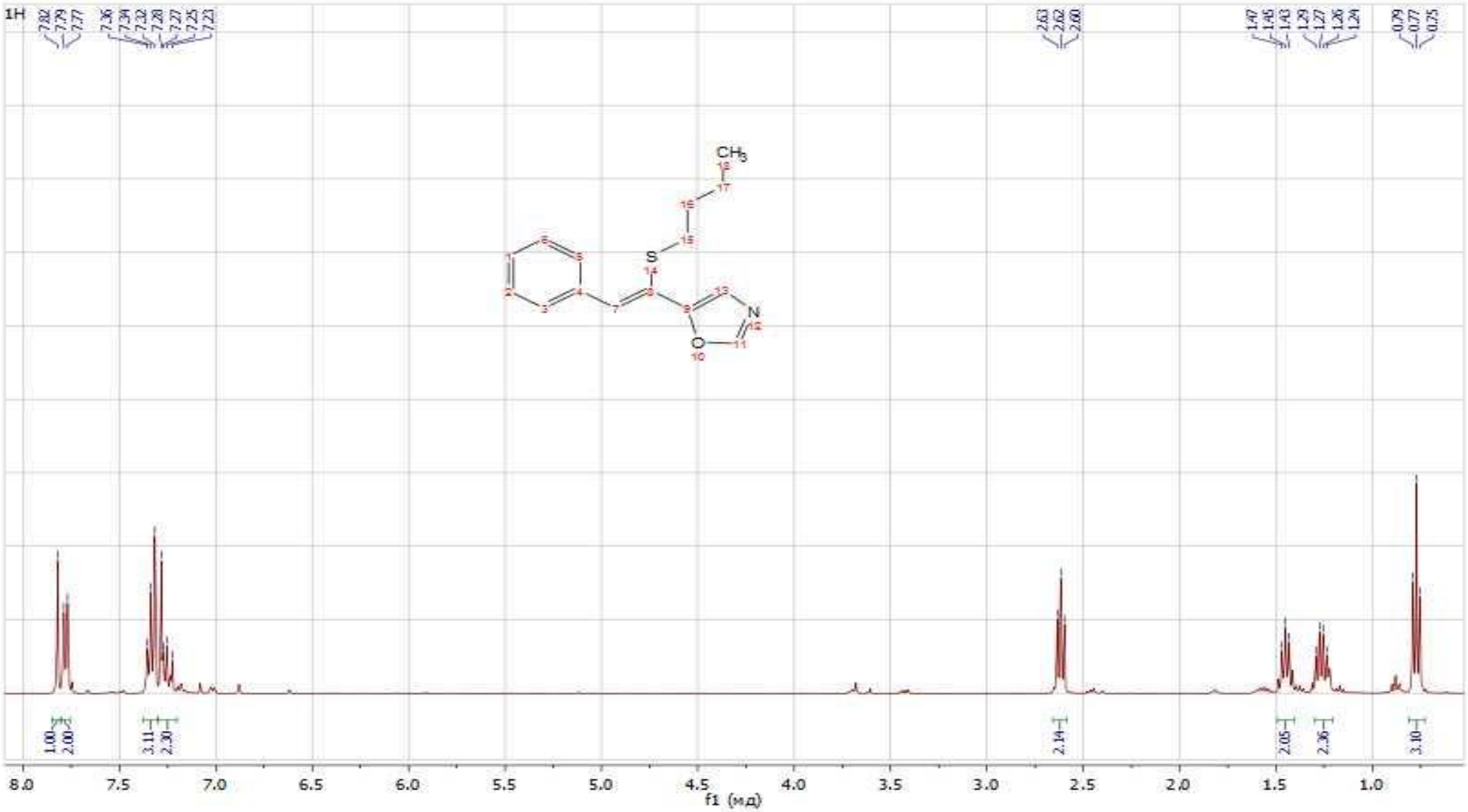


Figure S3. ^{1}H NMR spectrum of compound **3b** in $CDCl_3$ at 400 MHz

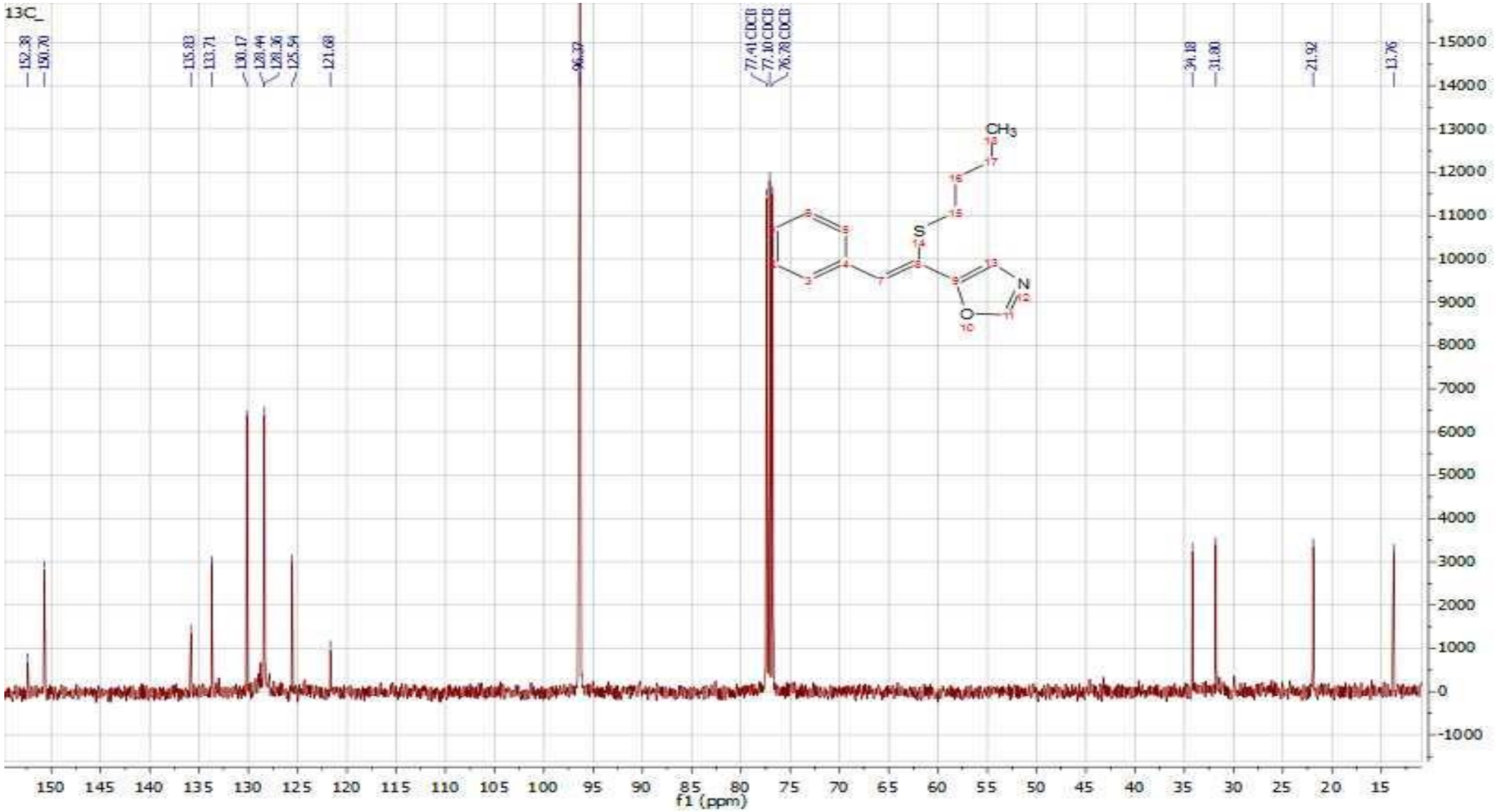


Figure S4. ^{13}C NMR spectrum of compound **3b** in $CDCl_3 + CCl_4$ at 400 MHz

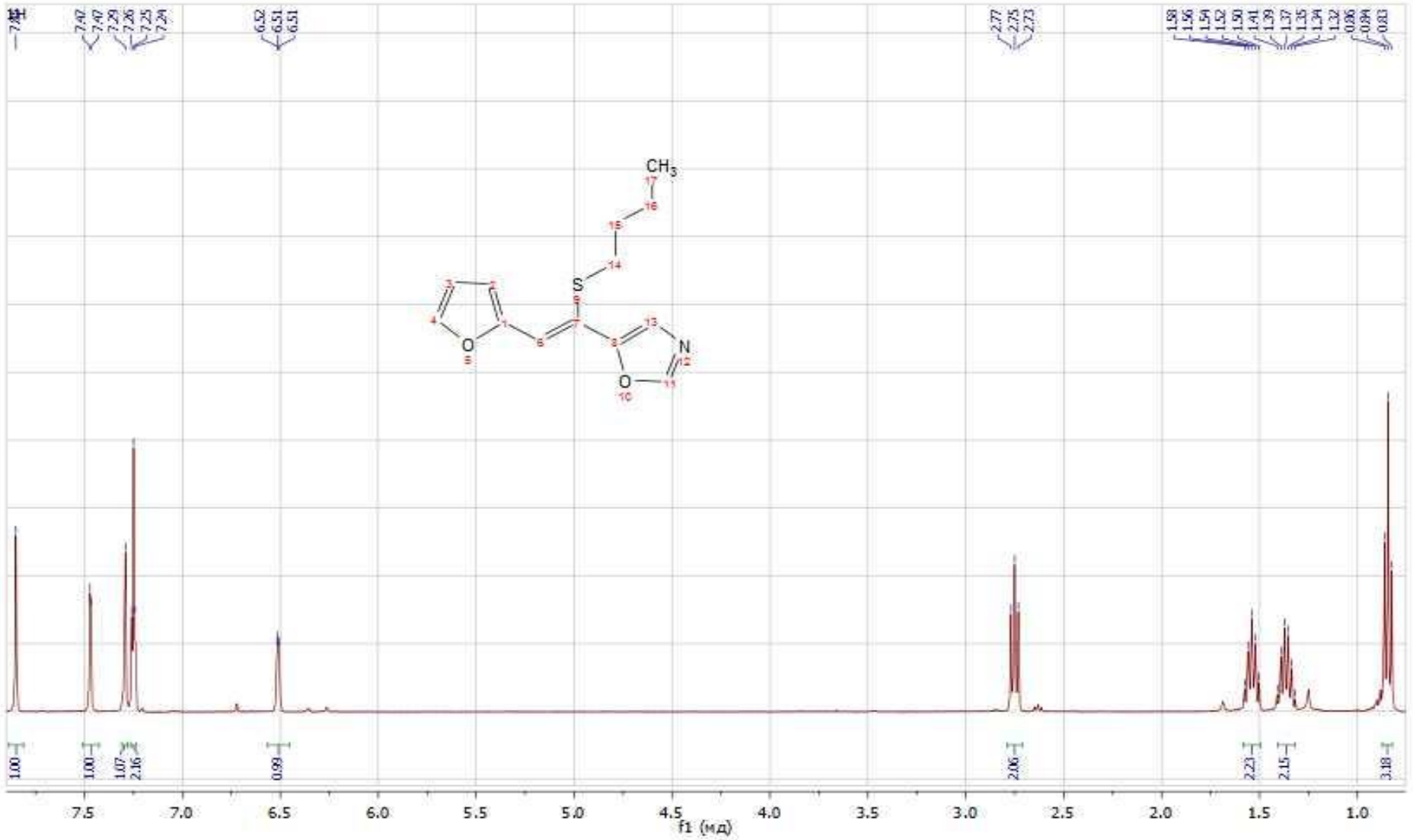


Figure S5. ^{1}H NMR spectrum of compound **3c** in $CDCl_3$ at 400 MHz

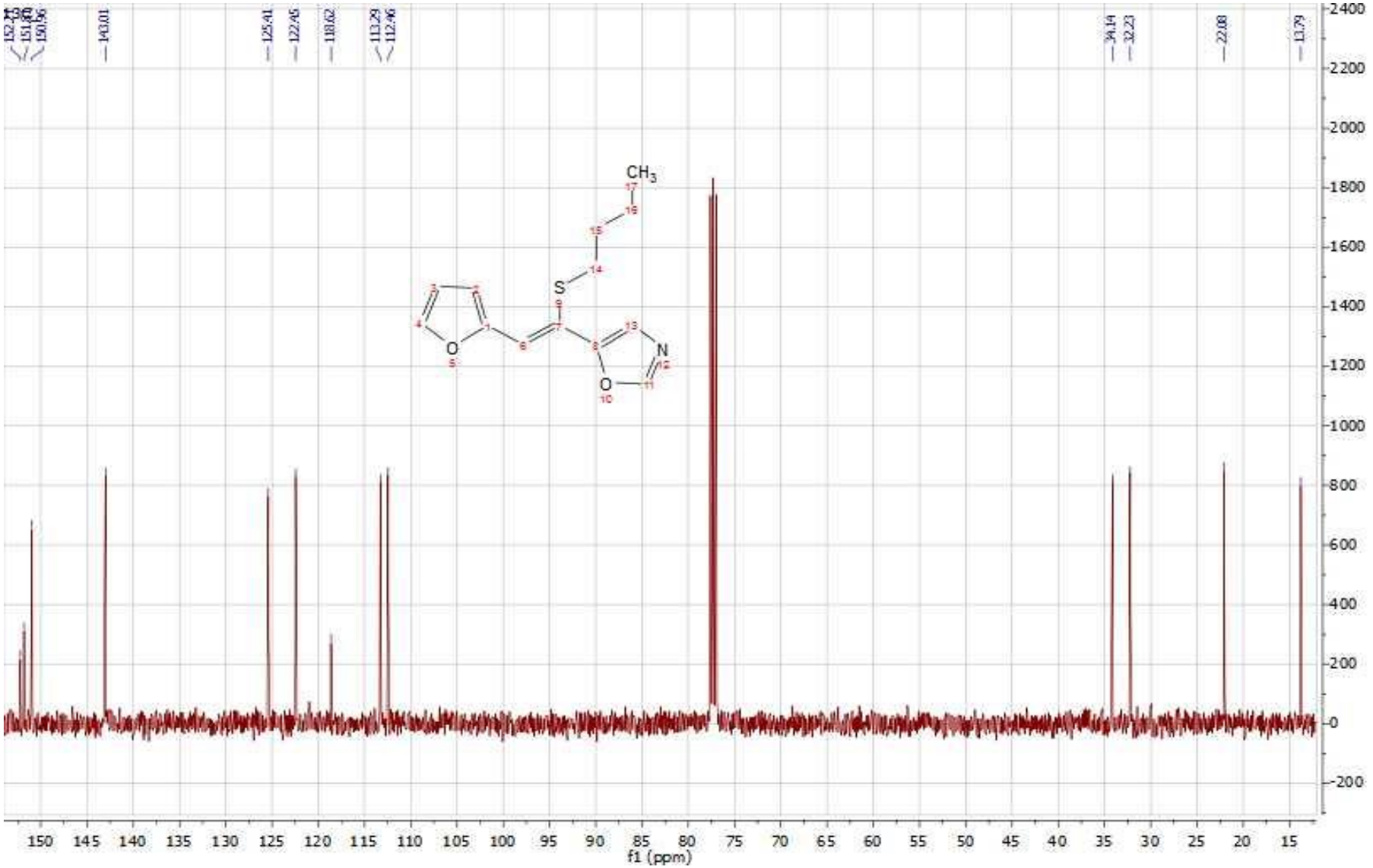


Figure S6. ^{13}C NMR spectrum of compound **3c** in $CDCl_3$ at 400 MHz

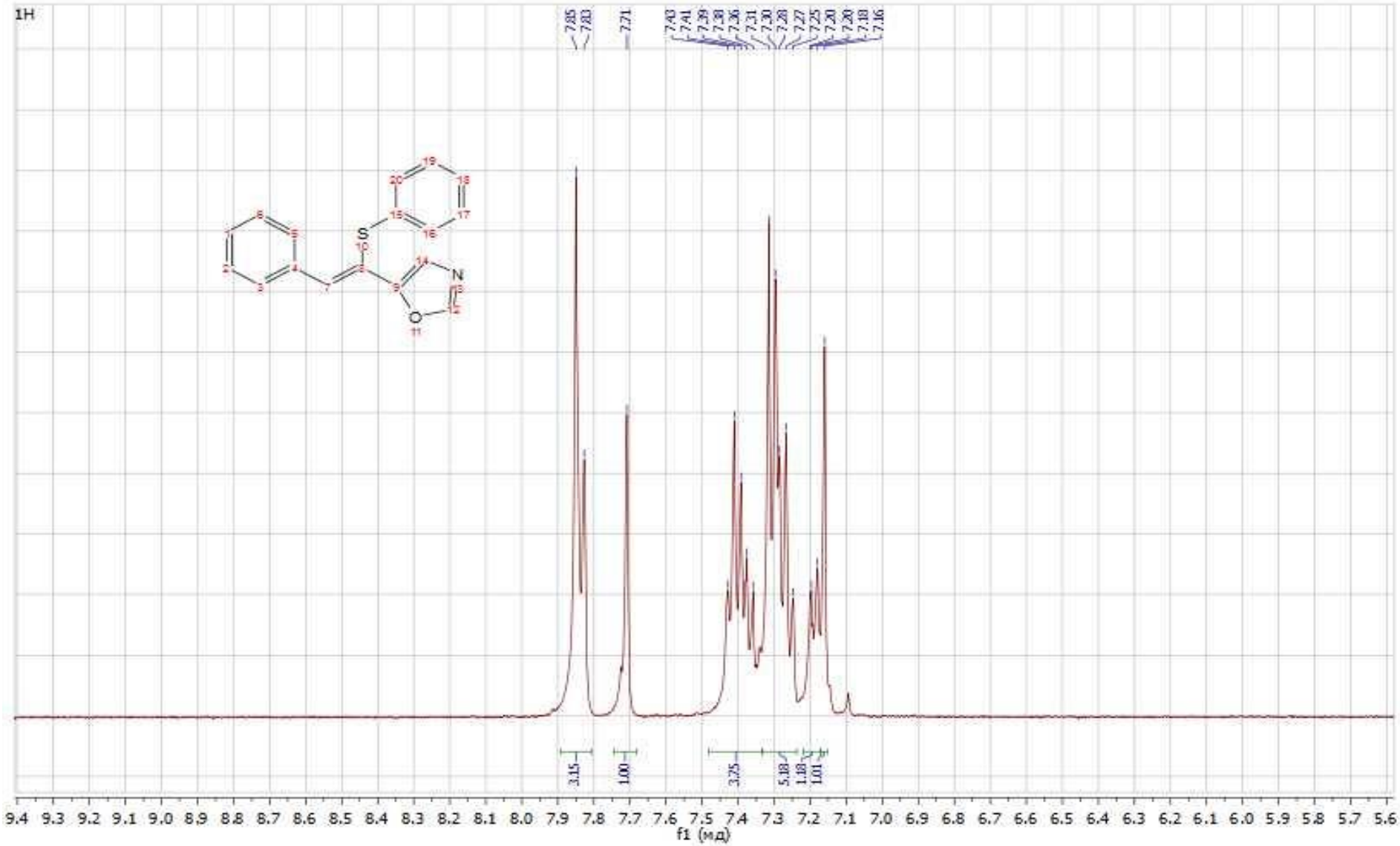


Figure S7. ^{1}H NMR spectrum of compound **3d** in CDCl3 at 400 MHz

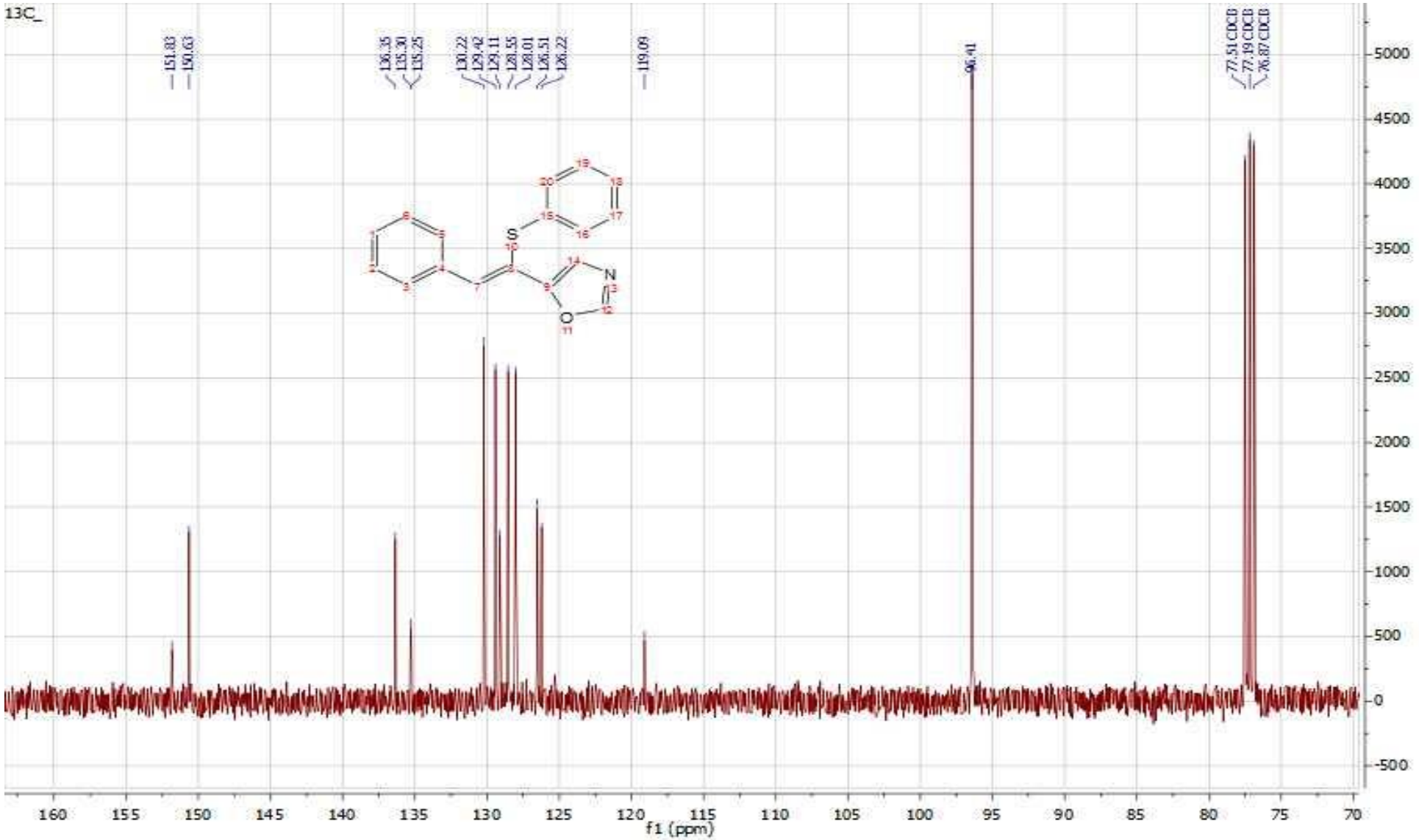


Figure S8. ^{13}C NMR spectrum of compound **3d** in $CDCl_3$ + CCl_4 at 400 MHz

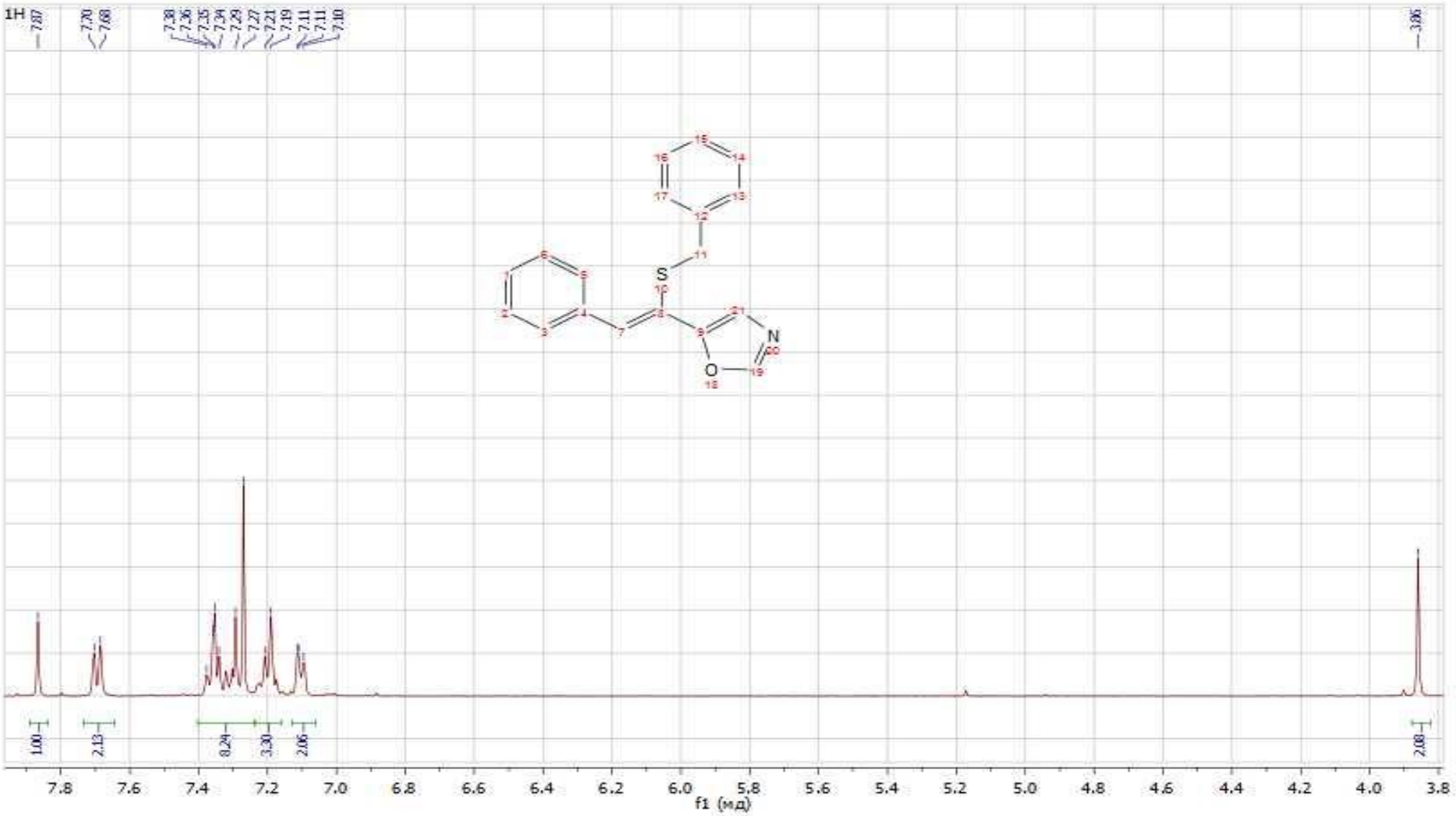


Figure S9. ^{1}H NMR spectrum of compound **3e** in $CDCl_3$ at 400 MHz

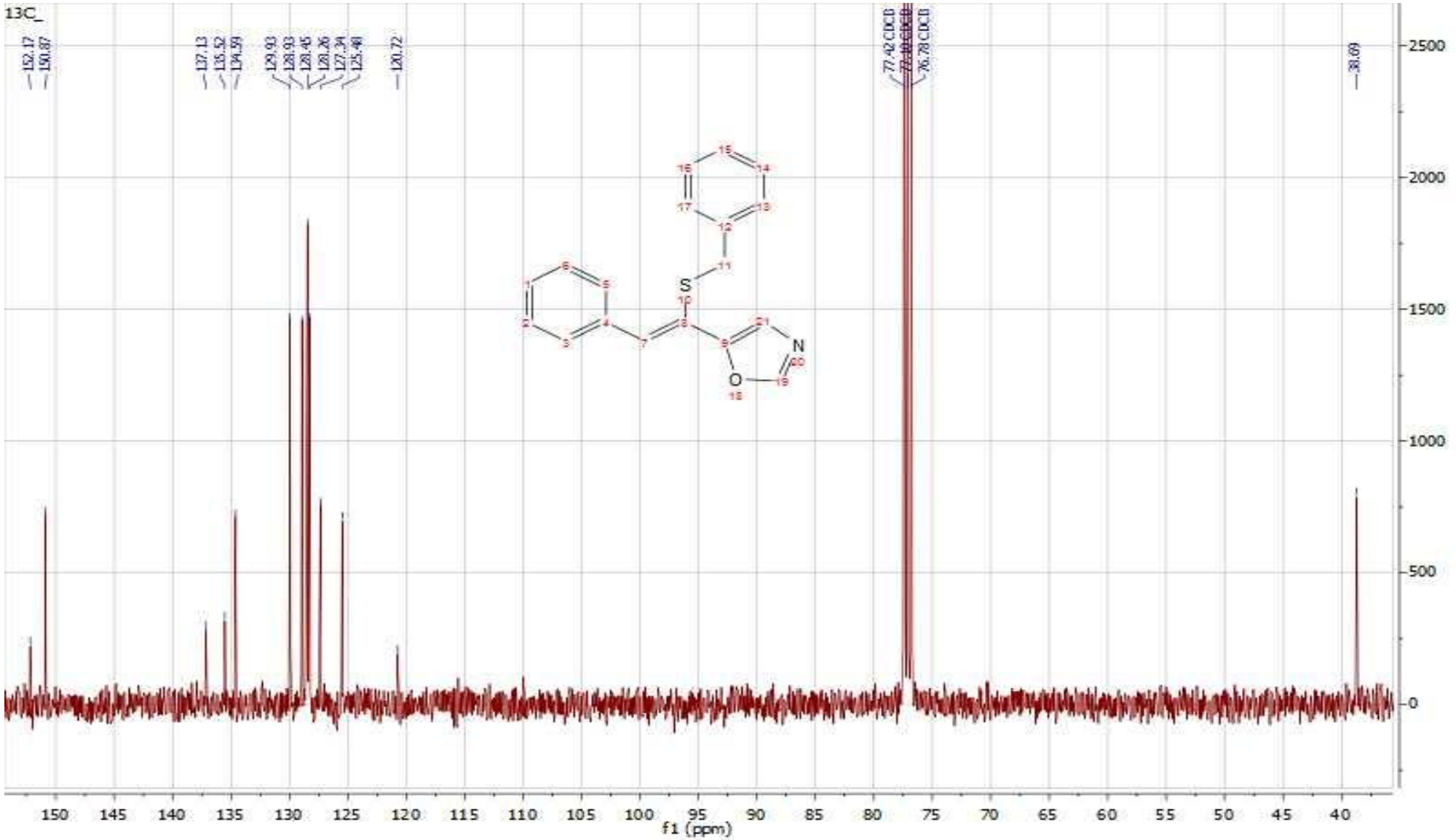


Figure S10. ^{13}C NMR spectrum of compound **3e** in $CDCl_3$ at 400 MHz

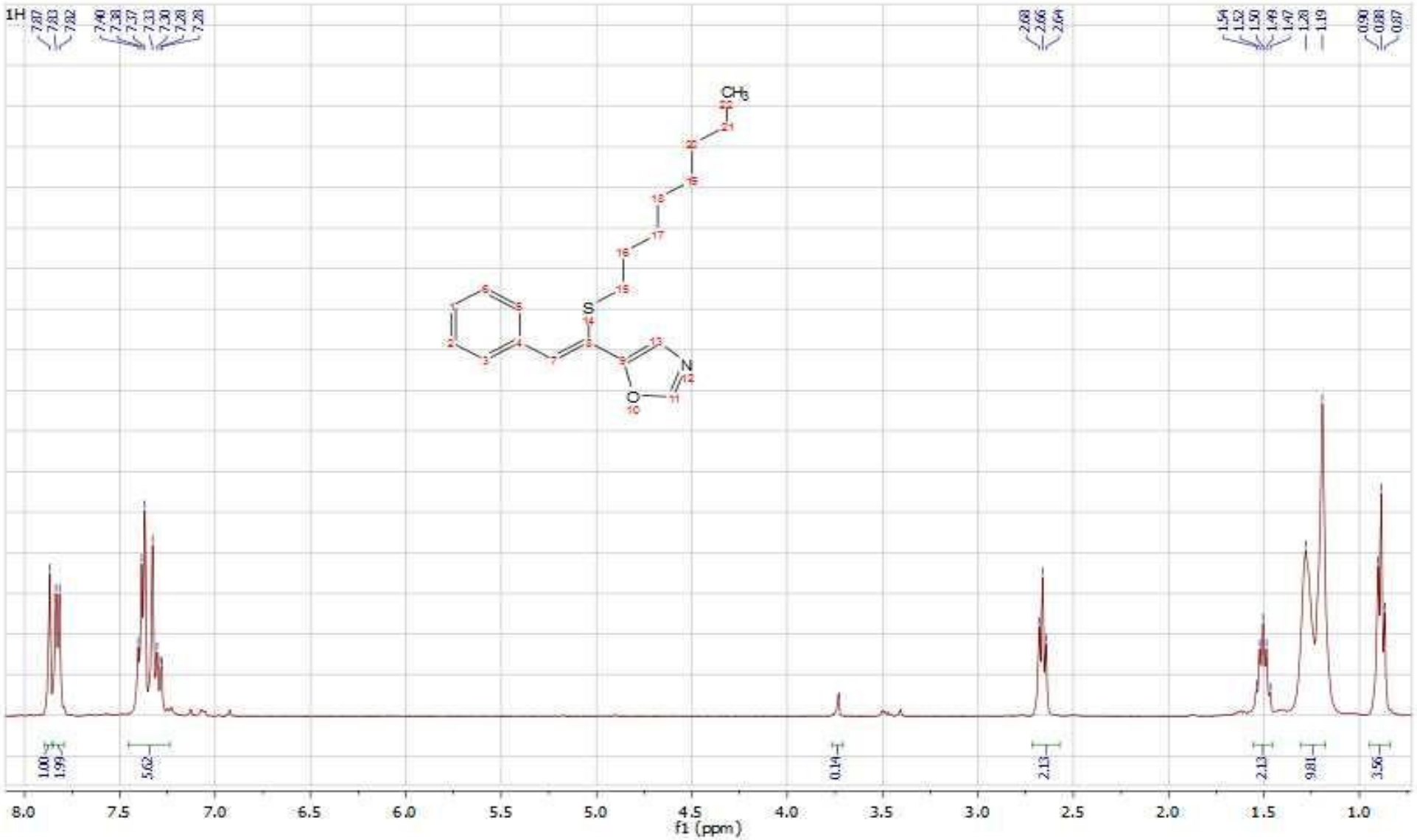


Figure S11. ^{1}H NMR spectrum of compound **3f** in $CDCl_3$ at 400 MHz

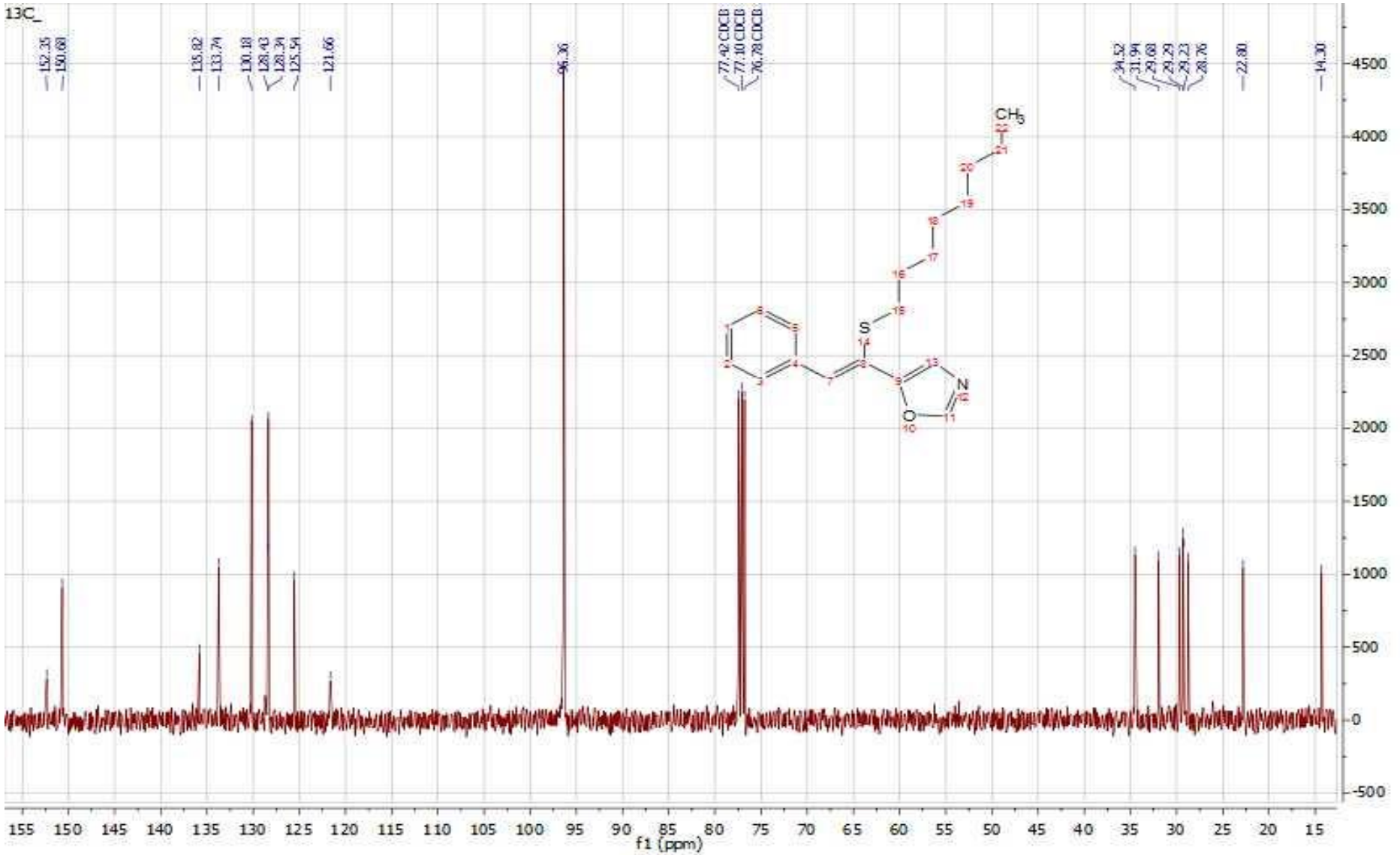


Figure S12. ^{13}C NMR spectrum of compound **3f** in $CDCl_3$+ CCl_4 at 400 MHz

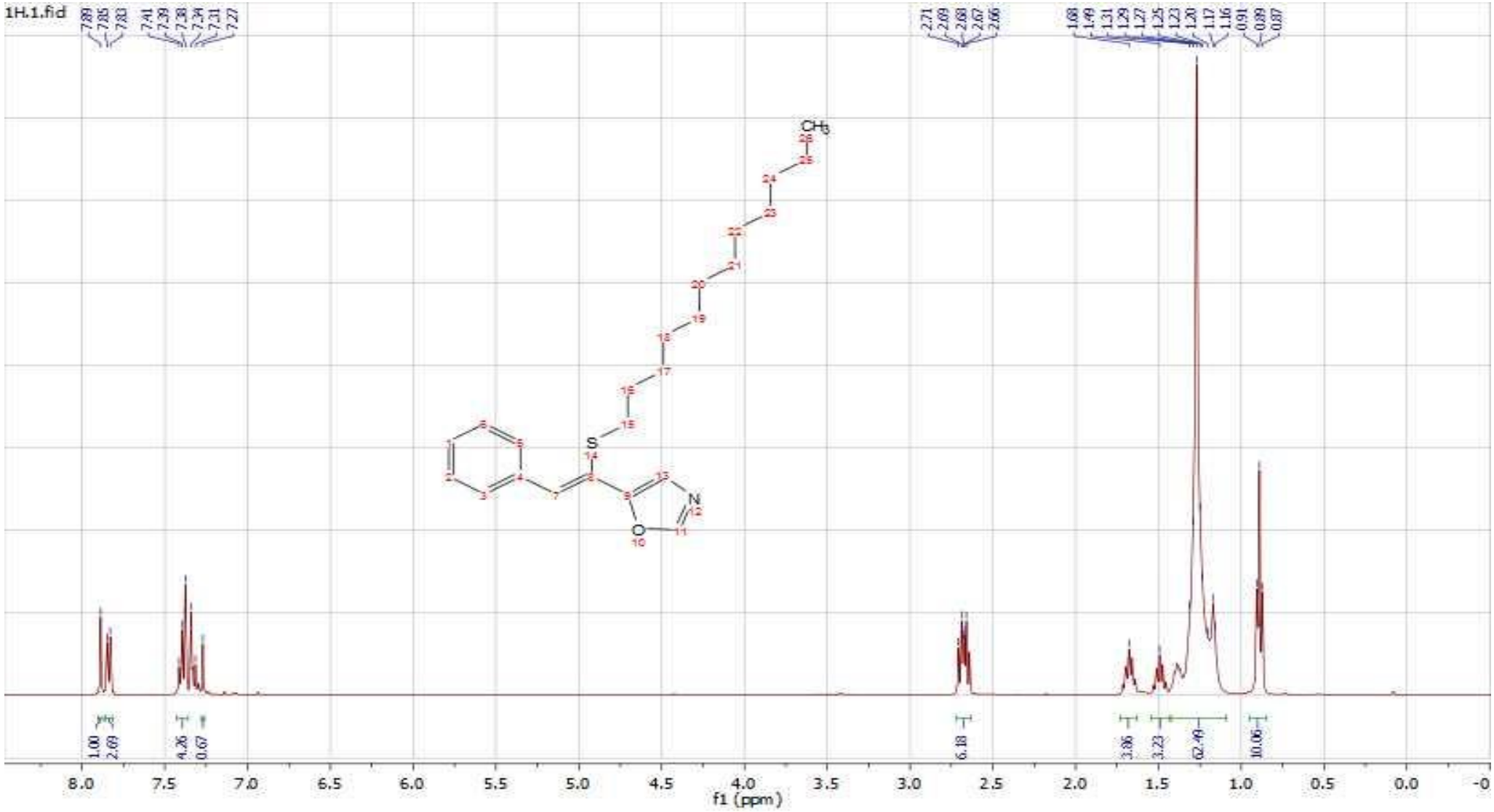


Figure S13. ^{1}H NMR spectrum of compound **3g** in $CDCl_3$ at 400 MHz

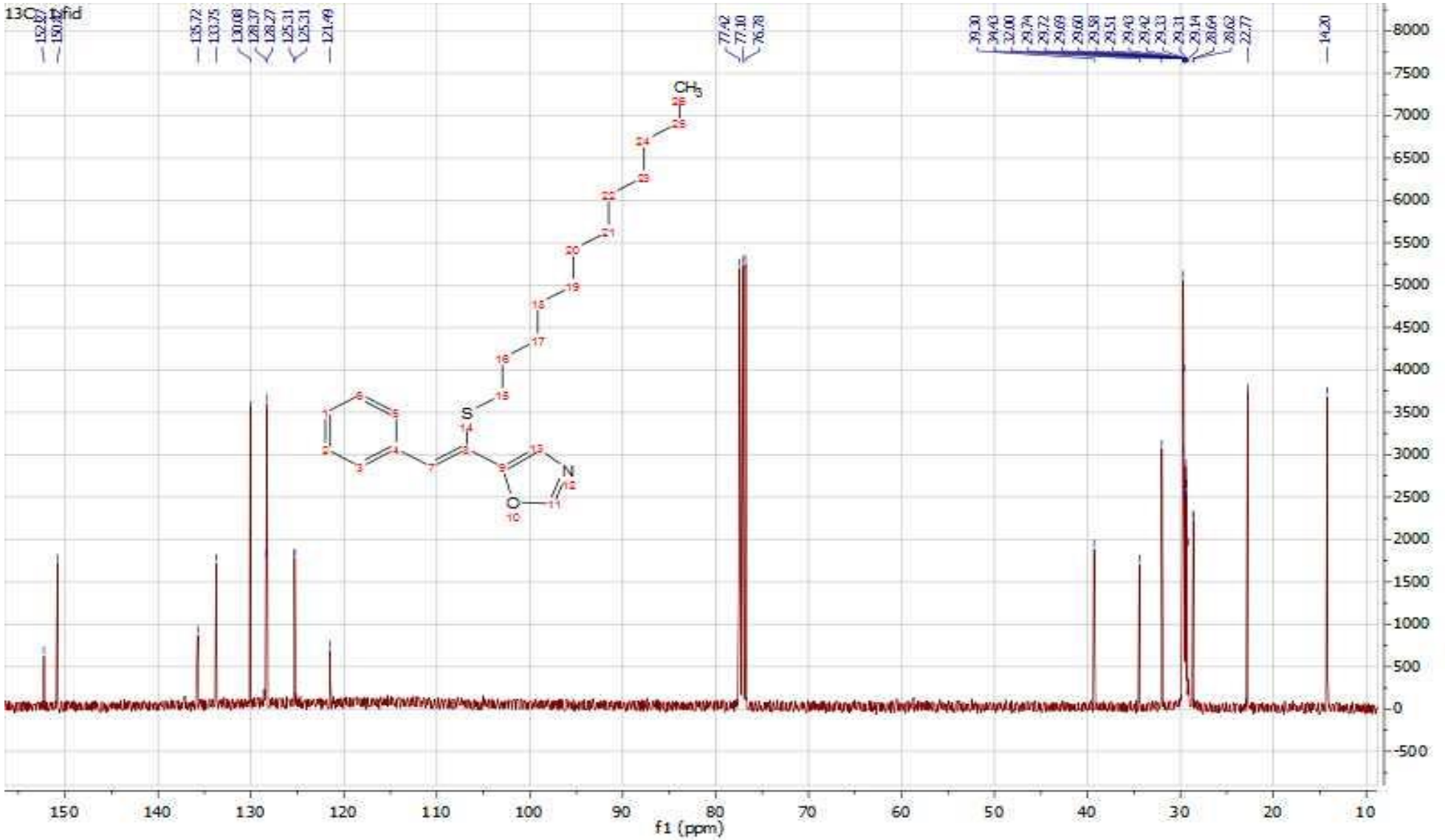


Figure S14. ^{13}C NMR spectrum of compound **3g** in $CDCl_3$ at 400 MHz

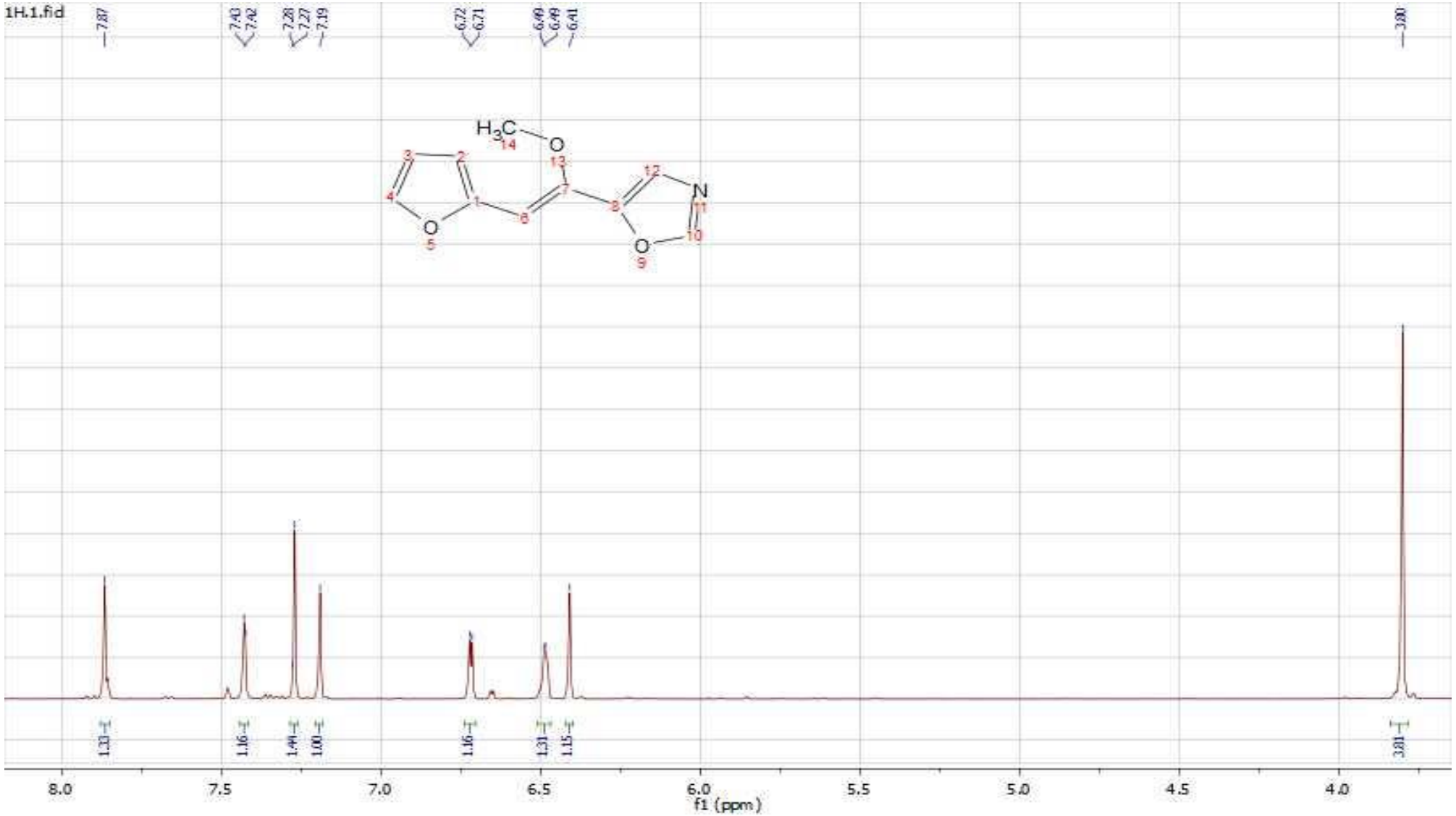


Figure S15. ^{1}H NMR spectrum of compound **3h** in $CDCl_3$ at 400 MHz

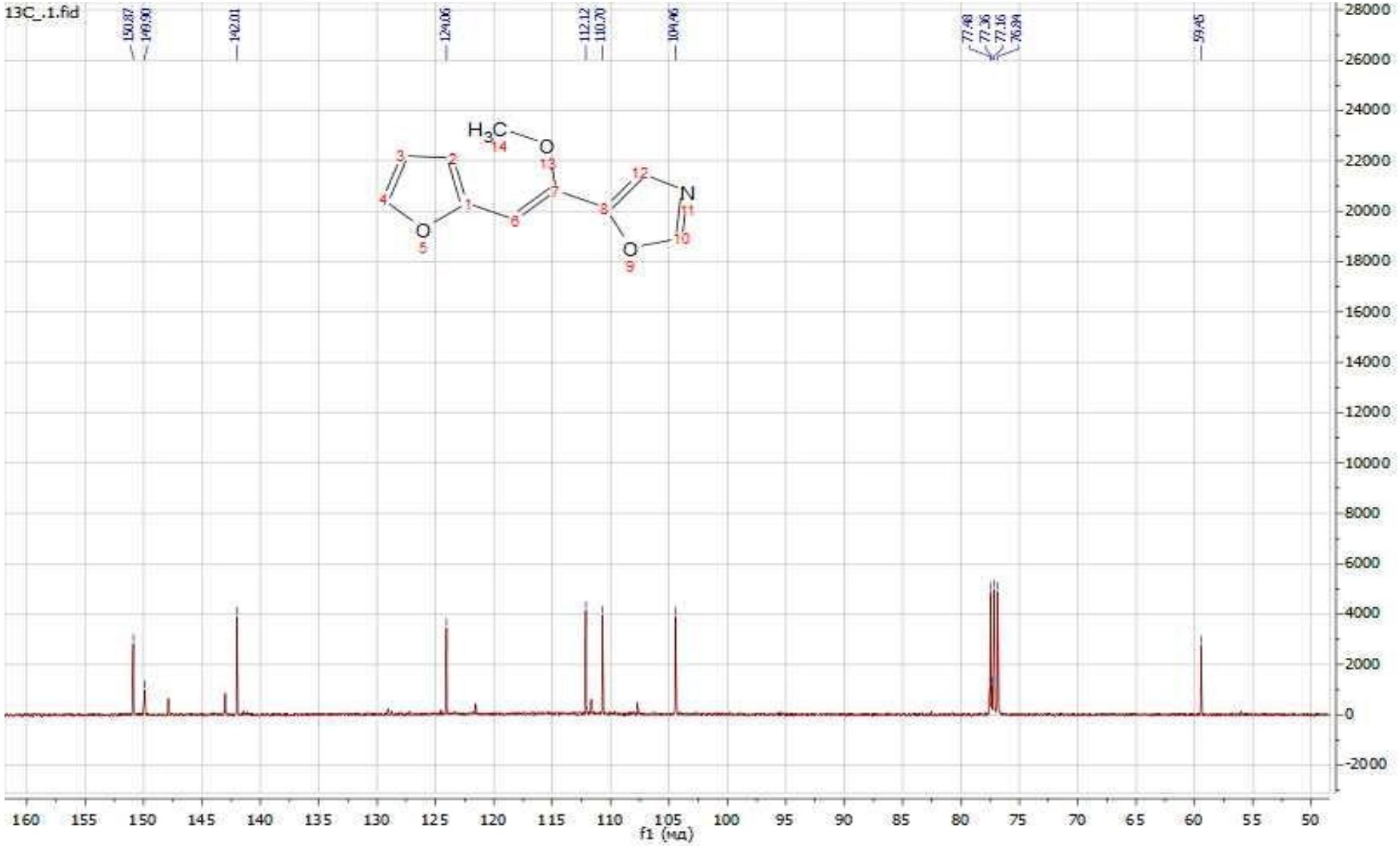


Figure S16. ^{13}C NMR spectrum of compound **3h** in $CDCl_3$ at 400 MHz

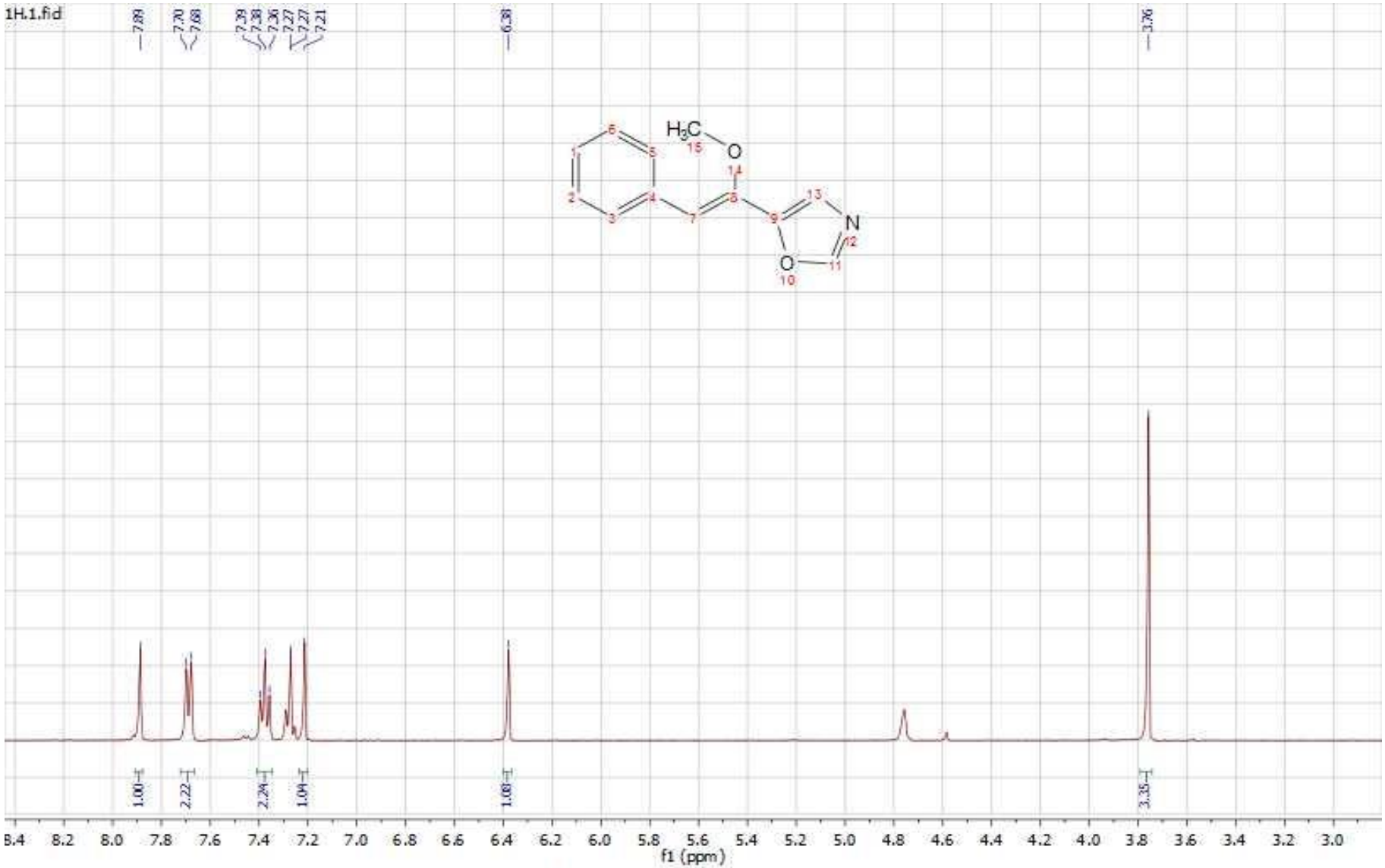


Figure S17. ^{1}H NMR spectrum of compound **3i** in $CDCl_3$ at 400 MHz

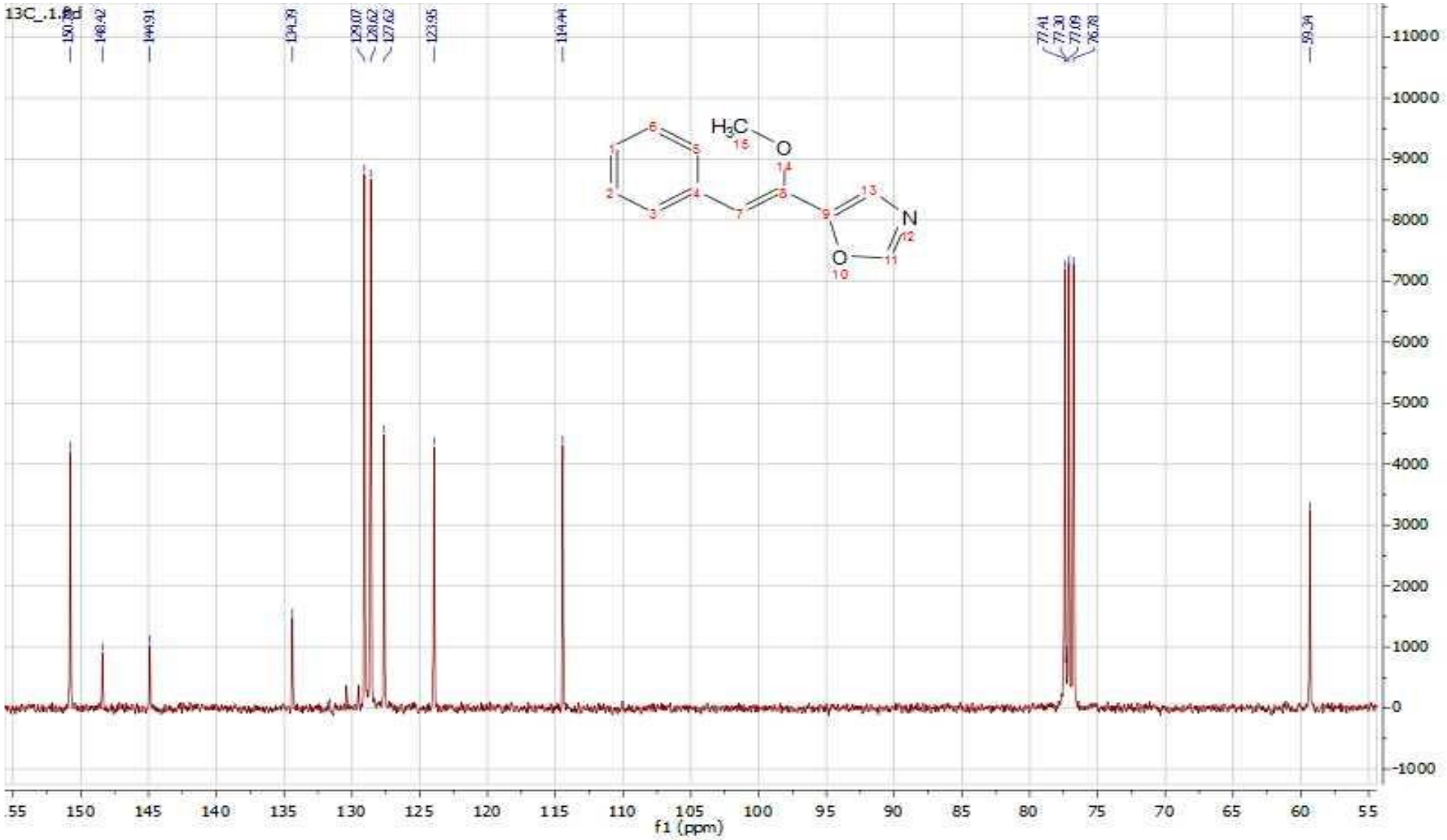


Figure S18. ^{13}C NMR spectrum of compound **3i** in $CDCl_3$ at 400 MHz