Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Gold(III)Chloride Catalysed Synthesis of 5-Alkylidene-dihydrothiazoles

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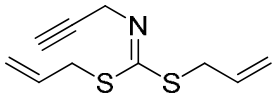
General procedure 1: synthesis of dithiocarboimidates 7a-7f

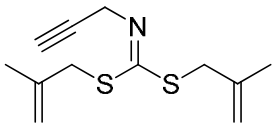
In a dry 50 ml flask 0,600 g (10,9 mmol, 1 equiv) propargylamine is dissolved in 30 ml of hexane. To this 11 g (109 mmol, 10 equiv) Et_3N is added. The flask is placed under inert atmosphere and is cooled to 0°C in order to buffer the exothermic reaction. Slowly 1,26 g (16,4 mmol, 1,5 equiv) carbondisulfide is added, using a syringe. The cooling baths is removed, and the reaction is allowed to stir at room temperature for one hour. A white suspension is formed. Subsequently, 8 equivalents of an allylic bromide are added and the reaction is stirred at room temperature during an overnight period. The extraction is performed from aqueous saturated $NaHCO_3$ by means of dichloromethane (3x). The combined organic phases are dried using $MgSO_4$ and the volatiles are removed by rotary evaporation. Further purification is performed by means of column chromatography when the allylic bromide could not be evaporated.

diallylprop-2-ynyl dithiocarboimidate 7a



^{1}H-NMR (300MHz, $CDCl_3$): δ 2.26 (1H, t, J=2.8Hz, C_q≡CH); 3.67 (2H, d, J=7.2Hz, SCH_2); 3.72 (2H, d, J=6.6Hz, SCH_2); 4.23 (2H, d, J=2.8Hz, NCH_2); 5.08 (1H, d, J=9.9Hz, CH=C$\underline{H}_E$H$_Z$); 5.15 (1H, d, J=9.9Hz, CH=C$\underline{H}_E$H$_Z$); 5.23 (1H, d, J=16.5Hz, CH=CH$_E\underline{H}_Z$); 5.28 (1H, d, J=15.7Hz, CH=CH$_E\underline{H}_Z$); 5.79-5.94 (2H, m, 2x C$\underline{H}$=CH$_2$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 34.5 (SCH_2); 35.5 (SCH_2); 42.3 ($C_q\underline{C}H_2$); 71.1 (C_q≡$\underline{C}$H); 81.6 ($\underline{C}_q$≡CH); 118.3 (CH=$\underline{C}H_2$); 119.0 (CH=$\underline{C}H_2$); 132.7 ($\underline{C}$H=CH$_2$); 133.0 ($\underline{C}$H=CH$_2$); 159.7 (NC_qS_2). **MS (ESI): m/z (%):** 212 (M + H$^+$, 100). **HRMS (ESI):** m/z calcd for $C_{10}H_{13}NS_2$+ H$^+$ = 212.0568, found =212.0571. **IR (cm^{-1}) vmax:** 1567 (N=CS_2); 1636 (CH=CH_2); 3296 (C≡CH). **Chromatography:** PE/EtOAc 95/5 Rf = 0.20. **Y:** 78%.

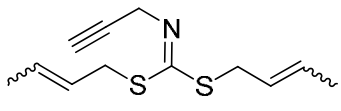
bis(2-methylallyl)prop-2-ynyl dithiocarboimidate 7b



^{1}H-NMR (300MHz, $CDCl_3$): δ 1.80 (3H, s, CH_3); 1.84 (3H, s, CH_3); 2.26 (1H, t, J=2.5Hz, HC≡C_q); 3.72 (2H, s, SCH_2); 3.74 (2H, s, SCH_2); 4.29 (2H, d, J=2.5Hz, NCH_2); 4.86 (1H, s, C_q=C$\underline{H}_aH_b$); 4.92 (1H, s, C_q=C$\underline{H}_aH_b$); 4.97 (1H, s, C_q=CH$_a\underline{H}_b$); 5.03 (1H, s, C_q=CH$_a\underline{H}_b$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 21.4 (CH_3); 21.6 (CH_3); 38.5 (SCH_2); 39.8 (SCH_2); 42.3 (NCH_2); 70.8 (H$\underline{C}$≡C_q); 81.1 (HC≡$\underline{C}_q$); 114.6 (H$_2\underline{C}$=C_q); 115.3 (H$_2\underline{C}$=C_q); 140.0 (H$_2$C=$\underline{C}_q$); 140.7 (H$_2$C=$\underline{C}_q$); 160.9 (NC_qS_2). **MS (ESI): m/z (%):** 240.3 (M + H$^+$, 100). **HRMS (ESI):** m/z calcd for $C_{12}H_{17}NS_2$ + H$^+$= 240.0881, found =240.0885. **IR (cm^{-1}) vmax:** 1568 (N=CS_2); 1649 (C=CH_2); 3298 (C≡CH). **Y:** 89%.

Di(but-2-enyl)prop-2-ynyl dithiocarboimidate 7c

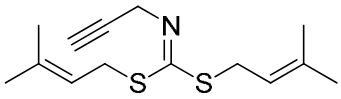
An inseparable mixture of EE, EZ and ZZ **7c** was characterised.



^{1}H-NMR (300MHz, $CDCl_3$): δ 1.70 (6H, m, 2x CH_3, EE of 2x CH_3, EZ of 2x CH_3, ZZ); 2.27 (1H, ~t, J=2.2Hz, C_q≡CH); 3.65 (2H, d, J=6.1Hz, $SC_{a,E}H_2$); 3.70 (2H, d, J=7.2Hz, $SC_{b,E}H_2$); 3.73 (2H, d, J=7.2Hz, $SC_{a,Z}H_2$); 3.78 (2H, d, J=7.7Hz, $SC_{b,Z}H_2$); 4.26 (2H, d, J=2.2Hz, $C_q\underline{C}H_2$); 5.47-5.57 (2H, m, 2x C$\underline{H}$CH$_3$); 5.60-5.79 (2H, m, 2x CH$_2$C$\underline{H}$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 13.0 (C_ZH_3); 17.9 (C_EH_3); 28.7 ($SC_{a,Z}H_2$); 29.3 ($SC_{b,Z}H_2$); 34.0 ($SC_{a,E}H_2$); 34.9 ($SC_{b,E}H_2$); 42.1 ($C_q\underline{C}H_2$); 70.9 (C_q≡$\underline{C}$H); 81.2 ($\underline{C}_q$≡CH); 124.2 (CH$_2\underline{C}_a$H, EZ); 124.3 (CH$_2\underline{C}_a$H, ZZ); 124.4 (CH$_2\underline{C}_b$H, EZ); 125.27 (CH$_2\underline{C}_a$H, EE); 125.35 (CH$_2\underline{C}_b$H, ZZ); 125.4 (CH$_2\underline{C}_b$H, EE); 128.5 ($\underline{C}_a$HCH$_3$, EZ); 128.6 ($\underline{C}_a$HCH$_3$, ZZ); 129.2 ($\underline{C}_b$HCH$_3$, EZ); 129.67 ($\underline{C}_a$HCH$_3$, EE); 129.71 ($\underline{C}_b$HCH$_3$, ZZ); 130.4 ($\underline{C}_b$HCH$_3$, EE); 160.6 (NC_qS_2, EE); 160.8 (NC_qS_2, EZ); 160.9 (NC_qS_2, ZZ). **MS (ESI): m/z (%):** 240 (M + H$^+$, 100).

HRMS (ESI): m/z calcd for $C_{12}H_{17}NS_2$ + H^+= 240.0880, found =240.0879. **IR (cm^{-1}) vmax:** 1561 ($N{=}CS_2$); 1698 (HC=CH); 3292 (C≡CH). **Y:** 79%.

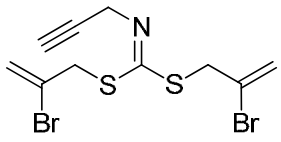
bis(3-methylbut-2-enyl)prop-2-ynyl dithiocarboimidate 7d



^{1}H-NMR (300MHz, $CDCl_3$): δ 1.70 (6H, s, 2x $C_qC_ZH_3$); 1.74 (6H, s, 2x $C_qC_EH_3$); 2.27 (1H, t, J=2.2Hz, C_q≡CH); 3.69 (2H, d, J=8.3Hz, SCH_2); 3.74 (2H, d, J=7.7Hz, SCH_2); 4.24 (2H, d, J=2.2Hz, C_qCH_2); 5.23-5.31 (2H, m, 2x $SCH_2C\underline{H}$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 17.9 (2x $C_q\underline{C}_ZH_3$); 25.8 (2x $C_q\underline{C}_EH_3$); 30.2 (SCH_2); 30.8 (SCH_2); 42.1 (NCH_2); 70.7 ($C_q{\equiv}\underline{C}H$); 81.3 ($\underline{C}_q{\equiv}CH$); 118.1 ($SCH_2\underline{C}H$); 118.2 ($SCH_2\underline{C}H$); 137.2 ($\underline{C}_q(CH_3)_2$); 138.0 ($\underline{C}_q(CH_3)_2$); 161.7 ($NCS_2$). **MS (ESI): m/z (%):** 268 (M + H^+, 100). **HRMS (ESI):** m/z calcd for $C_{14}H_{21}NS_2$+ H^+ = 268.1193, found =268.1201. **IR (cm^{-1}) vmax:** 1570 ($N{=}CS_2$); 1666 (HC=C); 3294 (C≡CH). **Chromatography:** Hex/EtOAc 95/5 Rf = 0.41. **Y:** 88%.

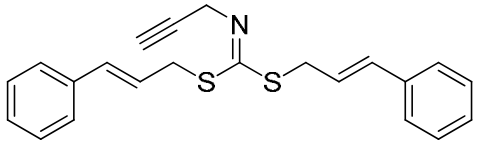
bis(2-bromo-allyl)prop-2-ynyl dithiocarboimidate 7e

Freshly destilled bromide must be used. The isolated product is to be used for ring closure immediately.



^{1}H-NMR (300MHz, $CDCl_3$): δ 2.28 (1H, t, J=2.8Hz, HC≡C_q); 4.06 (2H, s, SCH_2); 4.07 (2H, s, SCH_2); 4.34 (2H, d, J=2.8Hz, NCH_2); 5.51 (1H, d, J=1.4Hz, $C_q{=}CH_a\underline{H}_b$); 5.60 (1H, d, J=2.2Hz, $C_q{=}CH_a\underline{H}_b$); 5.90 (1H, ~d, J=1.4Hz, $C_q{=}C\underline{H}_aH_b$); 5.98 (1H, ~d, J=2.2Hz, $C_q{=}C\underline{H}_aH_b$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 41.4 (NCH_2); 42.67 (SCH_2); 42.71 (SCH_2); 71.3 ($\underline{C}H{\equiv}C_q$); 80.6 ($CH{\equiv}\underline{C}_q$); 120.6 (2x $C_q{=}\underline{C}H_2$); 127.6 (2x C_qBr); 157.9 (NCS_2). **MS (ESI): m/z (%):** 368 (M + H^+, 40); 370 (M + H^+, 100); 372 (M + H^+, 60). **HRMS (ESI):** m/z calcd for $C_{10}H_{11}Br_2NS_2$+ H^+ = 369.8757, found =369.8754. **IR (cm^{-1}) vmax:** 1576 ($N{=}CS_2$); 1623 ($C{=}CH_2$); 3295 (C≡CH). **Chromatography:** PE/EtOAc 95/5 Rf = 0.38. **Y:** 80%.

bis((Z)-3-fenylallyl)prop-2-ynyl dithiocarboimidate 7f

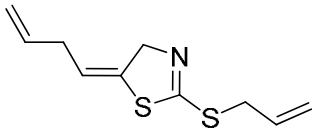


^{1}H-NMR (300MHz, $CDCl_3$): δ 2.27 (1H, t, J=2.5Hz, HC≡C_q); 3.89 (2H, d, J=7.2Hz, SCH_2); 3.92 (2H, d, J=7.2Hz, SCH_2); 4.31 (2H, d, J=2.5Hz, NCH_2); 6.23 (1H, dt, J=15.7Hz, J=7.2Hz, $SCH_2C\underline{H}$); 3.24 (1H, dt, J=15.7Hz, J=7.2Hz, $SCH_2C\underline{H}$); 6.60 (2H, ~d, J=15.7Hz, 2x $CH_2CH{=}C\underline{H}$); 7.26-7.38 (10H, m, 10x $CH_{arom.}$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 34.5 (SCH_2); 35.5 (SCH_2); 42.4 (NCH_2); 71.0 ($HC{\equiv}\underline{C}_q$); 81.2 ($HC{\equiv}\underline{C}_q$); 123.8 ($SCH_2\underline{C}H$); 124.2 ($SCH_2\underline{C}H$); 126.5 (2x $C_q\underline{C}H_{arom.\ ortho}$); 126.6 (2x $C_q\underline{C}H_{arom.\ ortho}$); 127.7 ($CH_{arom.\ para}$); 128.1 ($CH_{arom.\ para}$); 128.7 (2x $CH_{arom.\ meta}$); 128.7 (2x $CH_{arom.\ meta}$); 133.7 ($CH{=}\underline{C}HC_q$); 134.2 ($CH{=}\underline{C}HC_q$); 136.4 ($C_{q,\ arom.}$); 136.9 ($C_{q,\ arom.}$); 169.2 (NCS_2). **MS (ESI): m/z (%):** 364 (M + H^+, 100). **HRMS (ESI):** m/z calcd for $C_{22}H_{21}NS_2$ – H^+= 362.1037, found =362.1045. **IR (cm^{-1}) vmax:** 1566 ($N{=}CS_2$); 1672 ($CH_{arom.}$); 3288 (C≡CH). **Chromatography:** Hex/EtOAc 98/2 Rf = 0.20. **Y:** 81%.

General procedure 2: synthesis of dihydrothiazoles 9a-9f

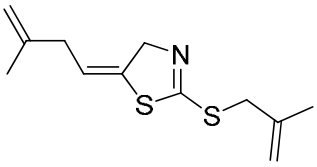
In a dry 25 ml flask under inert atmosphere, dithiocarboimidate **7** is dissolved in dry dichloromethane. Subsequently 0.05 equivalents of $AuCl_3$ is added and the reaction is stirred at room temperature for 15 minutes. The reaction mixture is filtered over a small plug of silica gel and after evaporation of the volatiles, dihydrothiazoles **9** are obtained.

(*E*)-2-(thioallyl)-5-(but-3-enylidene)-4,5-dihydrothiazole 9a



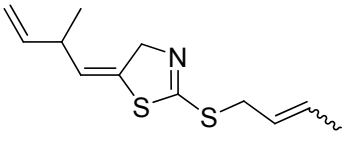
^{1}H-NMR (300MHz, $CDCl_3$): δ 2.76 (2H, dd, J=7.7Hz, J=6.1Hz, HCC$\underline{H}_2$CH); 3.76 (2H, d, J=6.6Hz, SCH_2); 4.83 (2H, ~d, J=3.0Hz, NCH_2); 5.01 (1H, ~dd, J=9.9Hz, J=1.1Hz, $CHCH_2CH=C\underline{H}_E\underline{H}_Z$); 5.06 (1H, ~dd, J=17.1Hz, J=1.1Hz, $CHCH_2CH=CH_E\underline{H}_Z$); 5.15 (1H, dd, J=9.9Hz, J=1.1Hz, $SCH_2CH=C\underline{H}_E\underline{H}_Z$); 5.28 (1H, dd, J=17.1, J=1.1Hz, $SCH_2CH=CH_E\underline{H}_Z$); 5.50 (1H, tt, J=7.7Hz, J=3.0Hz, C_q=CH); 5.76 (1H, ddt, J=17.1Hz, J=9.9Hz, J=6.1Hz, $C_qCHCH_2C\underline{H}$); 5.93 (1H, ddt, J=17.1Hz, J=9.9Hz, J=6.6Hz, $SCH_2C\underline{H}$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 34.3 ($HC\underline{C}H_2CH$); 34.7 (SCH_2); 67.1 (NCH_2); 115.6 ($CH=\underline{C}H_2$); 116.1 ($C_q=\underline{C}H$); 118.7 ($SCH_2CH=\underline{C}H_2$); 132.7 ($SCH_2\underline{C}H$); 135.0 ($HCCH_2\underline{C}H=CH_2$); 139.8 ($S\underline{C}_qCH_2$); 163.1 ($NC_qS_2$). **MS (ESI): m/z (%):** 212 ($M + H^+$, 100). **HRMS (ESI):** m/z calcd for $C_{10}H_{13}NS_2$+ H^+ = 212.0567, found =212.0564. **IR (cm^{-1}) vmax:** 1573 ($N=CS_2$); 1637 ($HC=CH_2$). **Y:** 92%.

(*E*)-2-(thio-2-methylallyl)-5-(3-methylbut-3-enylidene)-4,5-dihydrothiazole 9b



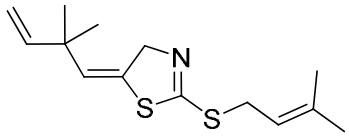
^{1}H-NMR (300MHz, $CDCl_3$): δ 1.73 (3H, s, CH_3); 1.84 (3H, s, CH_3); 2.71 (2H, d, J=7.7Hz, $CHC\underline{H}_2$); 3.79 (2H, s, SCH_2); 4.72 (1H, s, $CHCH_2C_q=CH_a\underline{H}_b$); 4.74 (1H, s, $CHCH_2C_q=C\underline{H}_aH_b$); 4.85 (2H, ~d, J=3.0Hz, NCH_2); 4.91 (1H, s, $SCH_2C_qCH_a\underline{H}_b$); 5.02 (1H, s, $SCH_2C_qC\underline{H}_aH_b$); 5.54 (1H, tt, J=7.7Hz, J=3.0Hz, SC_q=CH). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 21.5 (CH_3); 22.5 (CH_3); 38.6 ($CH\underline{C}H_2$); 38.8 (SCH_2); 66.9 (NCH_2); 111.1 ($C_q=\underline{C}H_2$); 114.9 ($C_q=\underline{C}H_2$); 116.6 ($C_q=\underline{C}HCH_2$); 139.7 ($\underline{C}_q=CH_2$); 140.2 ($\underline{C}_q=CH_2$); 143.1 ($S\underline{C}_q=CH$); 163.8 (NC_qS_2). **MS (ESI): m/z (%):** 240 ($M + H^+$, 100). **HRMS (ESI):** m/z calcd for $C_{12}H_{17}NS_2$+ H^+ = 240.0881, found =240.0875. **IR (cm^{-1}) vmax:** 1575 ($N=CS_2$); 1651 ($C=CH_2$). **Y:** 93%.

(5*E*)-2-(thiobut-2-enyl)-5-(2-methylbut-3-enylidene)-4,5-dihydrothiazole 9c



^{1}H-NMR (300MHz, $CDCl_3$): δ 1.10 (3H, d, J=6.6Hz, $CHC\underline{H}_3$); 1.69 (3H, 2x d, J=6.0Hz, $CH_2CH=CHC\underline{H}_3$, E and Z); 2.89 (1H, m, $C_q=CHC\underline{H}CH_3$); 3.72 (2H, d, J=6.6Hz, SCH_2, E); 3.80 (2H, d, J=7.7Hz, SCH_2, Z); 4.85 (2H, m, NCH_2); 5.34 (1H, dt, J=9.4Hz, J=3.0Hz, $C_q=C\underline{H}$); 5.50-5.75 (3H, m, $C\underline{H}=C\underline{H}$, $C\underline{H}=CH_2$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 13.0 ($CH_2CH=CH\underline{C}_ZH_3$); 17.9 ($CH_2CH=CH\underline{C}_EH_3$); 20.3 ($C_q=CHCH\underline{C}H_3$); 28.8 ($S\underline{C}H_2$, Z); 34.2 ($S\underline{C}H_2$, E); 39.3 ($C_q=CH\underline{C}HCH_3$); 66.9 ($NCH_2$); 113.2 ($CH=\underline{C}H_2$); 122.3 ($C_q=\underline{C}H$); 124.1 ($=C_{Z,a}H$); 125.2 ($=C_{E,a}H$); 129.1 ($=C_{Z,b}H$); 130.2 ($=C_{E,b}H$); 138.4 ($S\underline{C}_q=CH$); 140.8 ($\underline{C}H=CH_2$); 163.5 ($NC_qS_2$). **MS (ESI): m/z (%):** 240 ($M + H^+$, 100). **HRMS (ESI):** m/z calcd for $C_{12}H_{17}NS_2$+ H^+ = 240.0881, found =240.0889. **IR (cm^{-1}) vmax:** 1570 ($N=CS_2$); 1637, 1667 (C=C). **Y:** 91%.

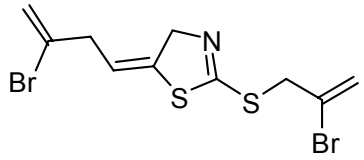
(*E*)-5-(2,2-dimethylbut-3-enylidene)-2-(thio-3-methylbut-2-enyl)-4,5-dihydrothiazole 9d



^{1}H-NMR (300MHz, $CDCl_3$): δ 1.16 (6H, s, $C_q(CH_3)_2$); 1.69 (3H, s, $HC=C_qC\underline{H}_3$); 1.73 (3H, s, $HC=C_qC\underline{H}_3$); 3.74 (2H, d, J=7.7Hz, SCH_2); 4.83 (2H, d, J=3.0Hz, NCH_2); 5.01 (1H, d, J=17.6Hz, $CH=CH_E\underline{H}_Z$); 5.05 (1H, d, J=9.9Hz, $CH=C\underline{H}_EH_Z$); 5.30 (1H, t, 7.7Hz, $SCH_2C\underline{H}$); 5.50 (1H, t, J=3.0Hz, $SC_q=C\underline{H}$); 5.82 (1H, dd, J=17.6Hz, J=9.9Hz; $C_qC\underline{H}=CH_2$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 17.9 ($HC=C_qC\underline{H}_3$); 25.8 ($HC=C_qC\underline{H}_3$); 27.6 ($HCC_q(C\underline{H}_3)_2$); 30.3 ($SCH_2$); 40.1 ($\underline{C}_q(CH)_2$); 66.4 ($NCH_2$); 111.4 ($HC=\underline{C}H_2$); 118.0 ($SCH_2\underline{C}H$); 126.6 ($SC_q=\underline{C}H$); 137.9 ($HC=\underline{C}_q(CH_3)_2$); 139.4 ($S\underline{C}_q=CH$); 145.2 ($H\underline{C}=CH_2$); 163.2 ($NC_qS_2$). **MS (ESI): m/z (%):** 268 ($M + H^+$, 100). **HRMS (ESI):** m/z calcd for $C_{14}H_{21}NS_2 + H^+$= 268.1194, found =268.1189. **IR (cm^{-1}) vmax:** 1572 ($N=CS_2$); 1633, 1670 (C=C). **Y:** 92%.

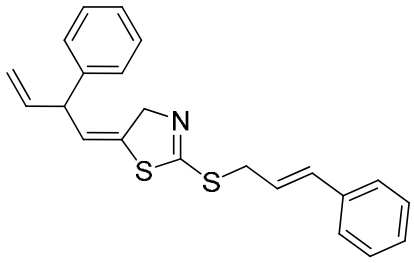
(E)-2-(thio-2-bromoallyl)-5-(3-bromo-but-3-enylidene)-4,5-dihydrothiazole 9e

An analytically pure sample can be obtained only through three consecutive chromatographic steps. In this case, yield drops considerably to 51%.

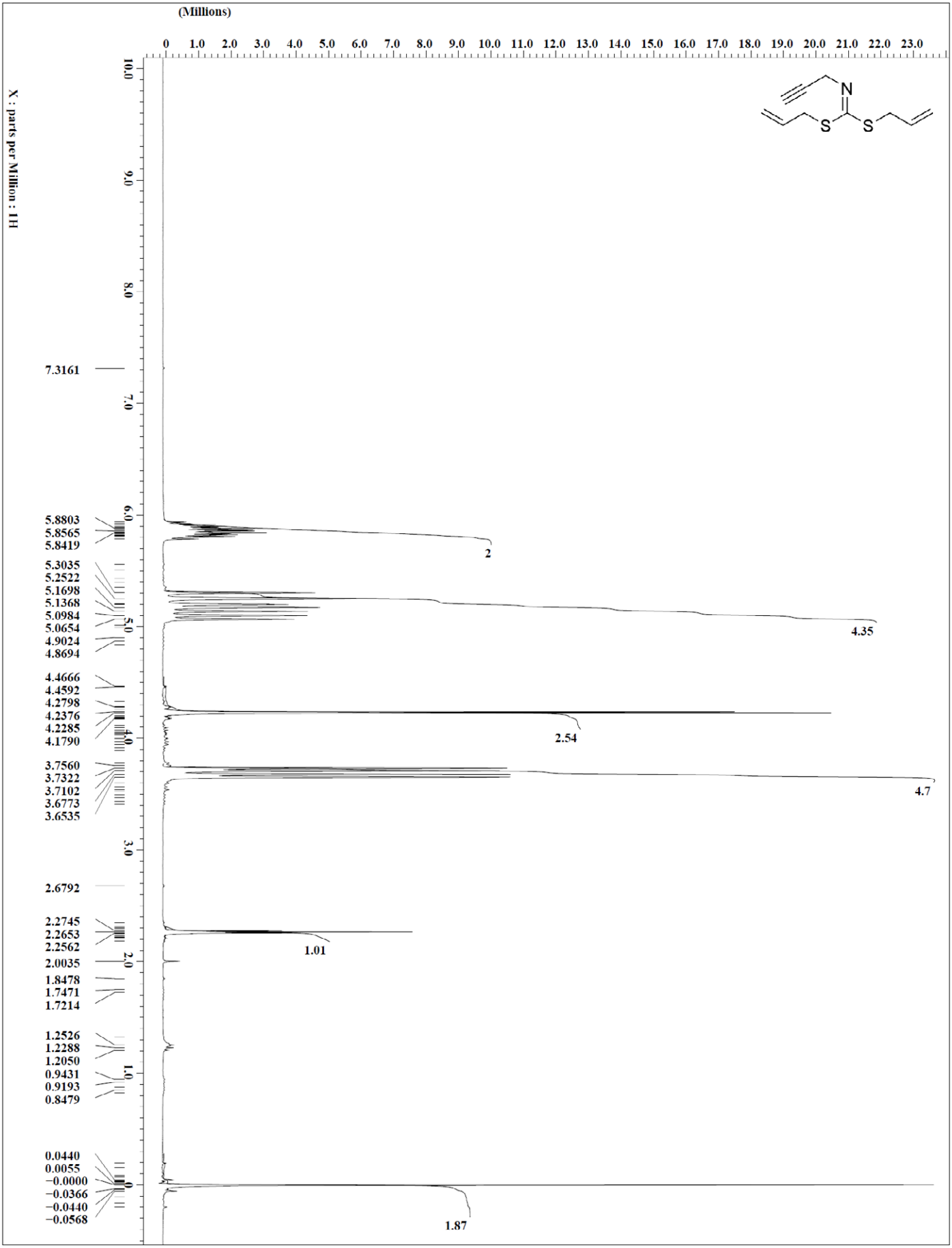


^{1}H-NMR (300MHz, $CDCl_3$): δ 3.15 (2H, d, J=7.7Hz, $CHC\underline{H}_2$); 4.12 (2H, s, SCH_2); 4.85 (2H, m, NCH_2); 5.43 (1H, d, J=1.8 Hz, $C_q=C\underline{H}_aH_b$); 5.51-5.55 (1H, m, $SC_q=CH$); 5.56 (1H, d, J=1.8 Hz, $C_q=C\underline{H}_aH_b$); 5.63 (1H, d, J=1.8 Hz, $C_q=CH_a\underline{H}_b$); 5.95 (1H, d, J=1.8 Hz, $C_q=CH_a\underline{H}_b$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 41.2 ($CH\underline{C}H_2$); 42.1 (SCH_2); 67.1 (NCH_2); 114.4 ($C_q=\underline{C}H_2$); 117.5 ($C_q=\underline{C}H_2$); 120.4 ($C_q=\underline{C}HCH_2$); 127.3 ($\underline{C}_q=CH_2$); 130.7 ($\underline{C}_q=CH_2$); 142.4 ($S\underline{C}_q=CH$); 162.1 (NC_qS_2). **MS (ESI): m/z (%):** 368 ($M + H^+$, 45); 370 ($M + H^+$, 100); 372 ($M + H^+$, 55). **HRMS (ESI):** m/z calcd for $C_{10}H_{11}Br_2NS_2 + H^+$ = 369.8757, found =369.8762. **IR (cm^{-1}) vmax:** 1570 ($N=CS_2$); 1631 ($C=CH_2$). **Chromatography:** PE/EtOAc 95/5 Rf = 0.21. **Y:** quant, purity 85%.

(E)-2-(cinnamylthio)-5-(2-fenylbut-3-enylidene)-4,5-dihydrothiazole 9f



^{1}H-NMR (300MHz, $CDCl_3$): δ 3.94 (2H, d, J=7.2Hz, SCH_2); 4.05 (1H, m, $CHC\underline{H}CH=CH_2$); 4.91 (2H, m, NCH_2); 5.13 (1H, d, J=17.6Hz, $CH=CH_E\underline{H}_Z$); 5.13 (1H, d, J=9.9Hz, $CH=C\underline{H}_EH_Z$); 5.70 (1H, dt, J=9.4Hz, J=3.0Hz, $SC_q=CH$); 5.94 (1H, ddd, J=17.6Hz, J=9.9Hz, J=6.6Hz, $CHC\underline{H}=CH_2$); 6.29 (1H, dt, J=15.6Hz, J=7.2Hz, $SCH_2C\underline{H}$); 6.60 (1H, d, 15.6Hz, $CH_2C\underline{H}=CH$); 7.20-7.38 (10H, m, $CH_{arom.}$). **^{13}C-NMR (75MHz, $CDCl_3$): δ** 34.6 (SCH_2); 50.5 ($CH_2=CH\underline{C}H$); 67.2 (NCH_2); 115.4 ($CHCH=\underline{C}H_2$); 120.0 ($SC_q\underline{C}H$); 123.9 ($SCH_2\underline{C}H$); 126.6 (2x $CH_{arom.\ ortho}$); 126.7 ($CH_{arom.\ para}$); 127.6 (2x $CH_{arom.\ meta}$); 128.0 ($CH_{arom.\ para}$); 128.7 (2x $CH_{arom.\ ortho}$); 128.9 (2x $CH_{arom.\ meta}$); 133.9 ($SCH_2CH=\underline{C}H$); 136.6 (C_q); 138.8 ($CH\underline{C}H=CH_2$); 139.9 (C_q); 142.2 (C_q); 163.4 (NC_qS_2). **MS (ESI): m/z (%):** 364 ($M + H^+$, 100). **HRMS (ESI):** m/z calcd for $C_{22}H_{21}NS_2 + H^+$= 364.1193, found =364.1185. **IR (cm^{-1}) vmax:** 1573 ($N=CS_2$); 1670 (C=C). **Chromatography:** PE/EtOAc 98/2 Rf = 0.29. **Y:** 74%.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5.8419
5.3035
5.2522
5.1698
5.1368
5.0984
5.0654
4.9024
4.8694
4.4666
4.4592
4.2798
4.2376
4.2285
4.1790
3.7560
3.7322
3.7102
3.6773
3.6535
2.6792
2.2745
2.2653
2.2562
2.0035
1.8478
1.7471
1.7214
1.2526
1.2288
1.2050
0.9431
0.9193
0.8479
0.0440
0.0055
−0.0000
−0.0366
−0.0440
−0.0568
2
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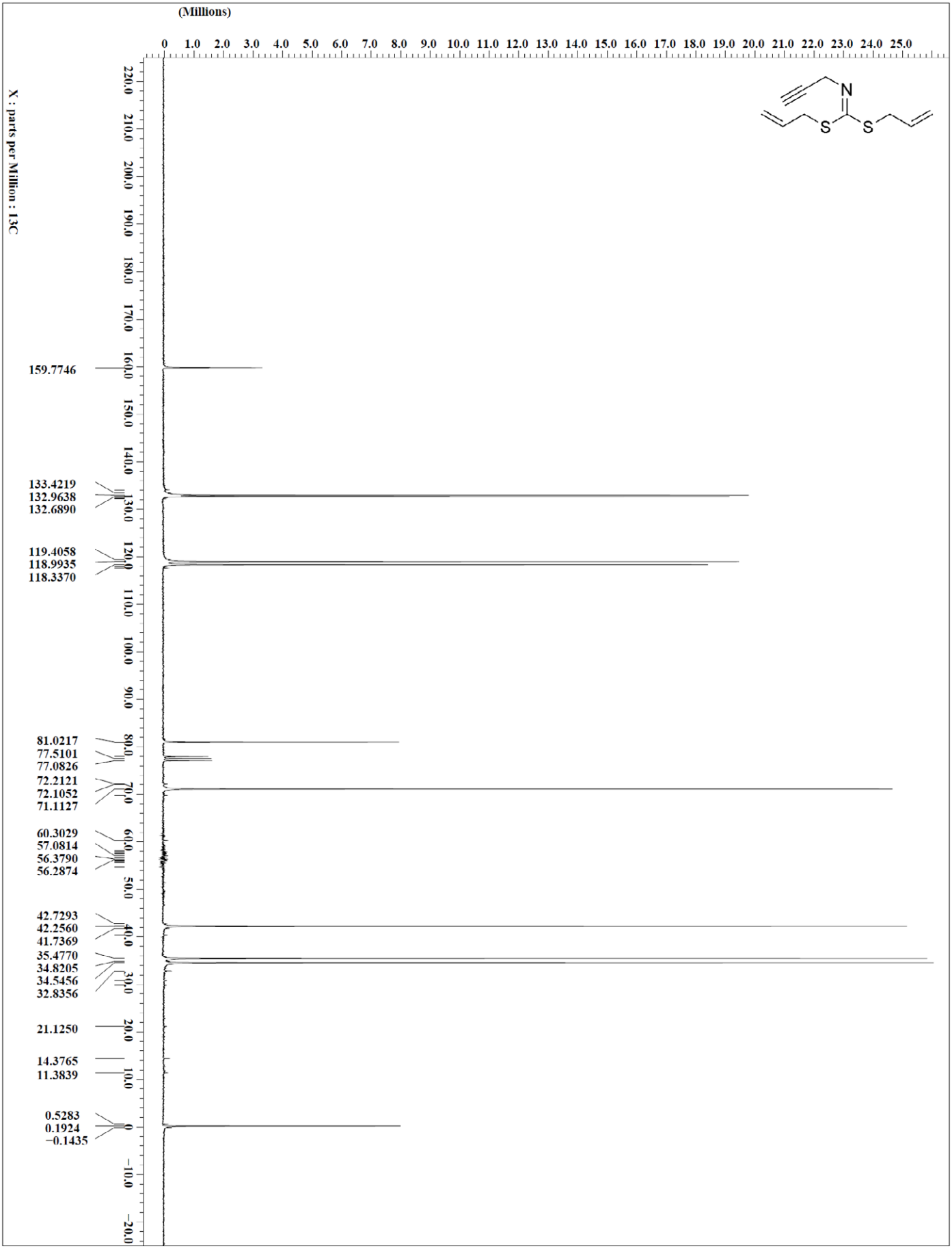
2.54
4.7
1.01
1.87
N
S
S


(Millions)
X : parts per Million : 13C
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118.9935
118.3370
81.0217
77.5101
77.0826
72.2121
72.1052
71.1127
60.3029
57.0814
56.3790
56.2874
42.7293
42.2560
41.7369
35.4770
34.8205
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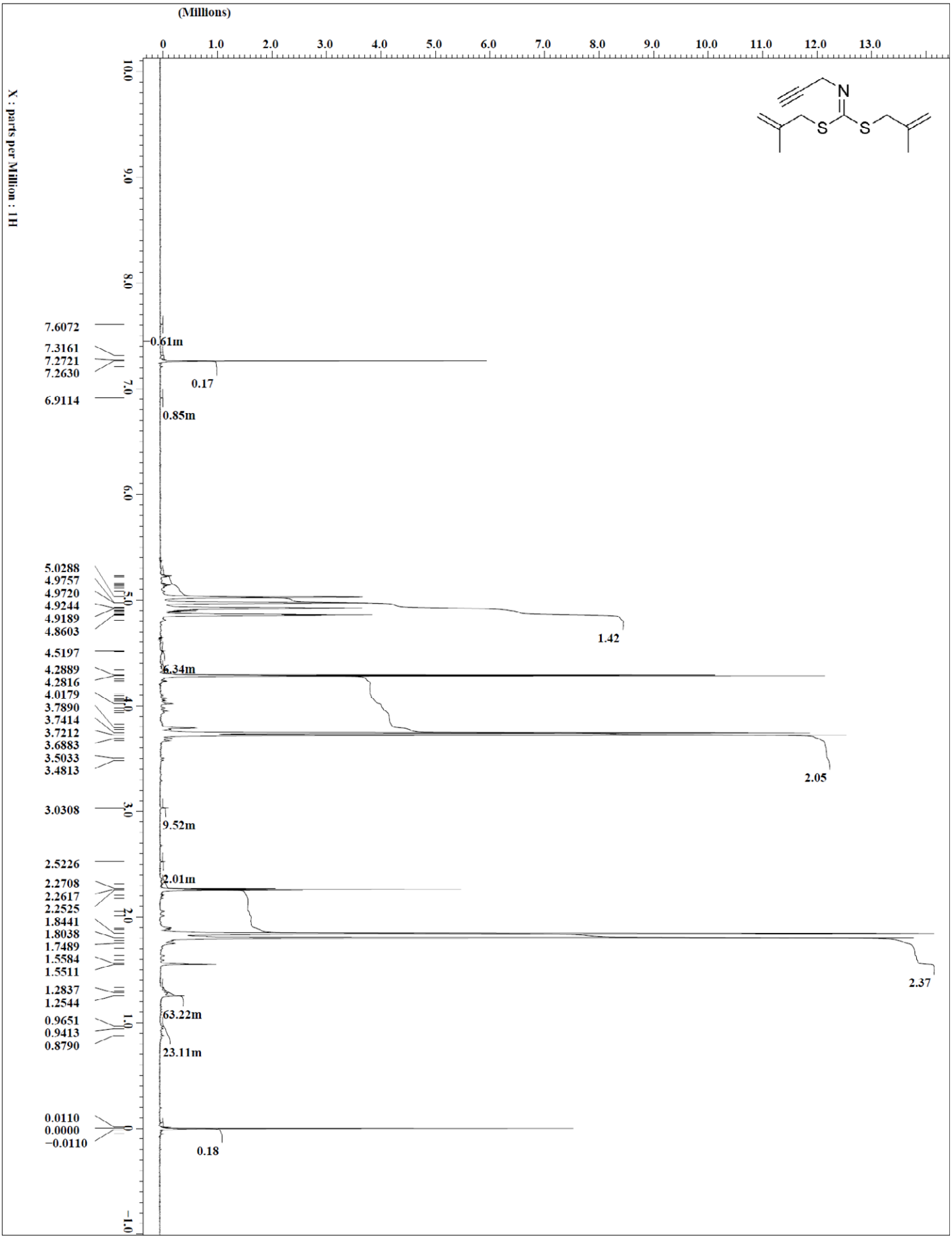
N
S
S


(Millions)
X : parts per Million : 1H
N
S
S
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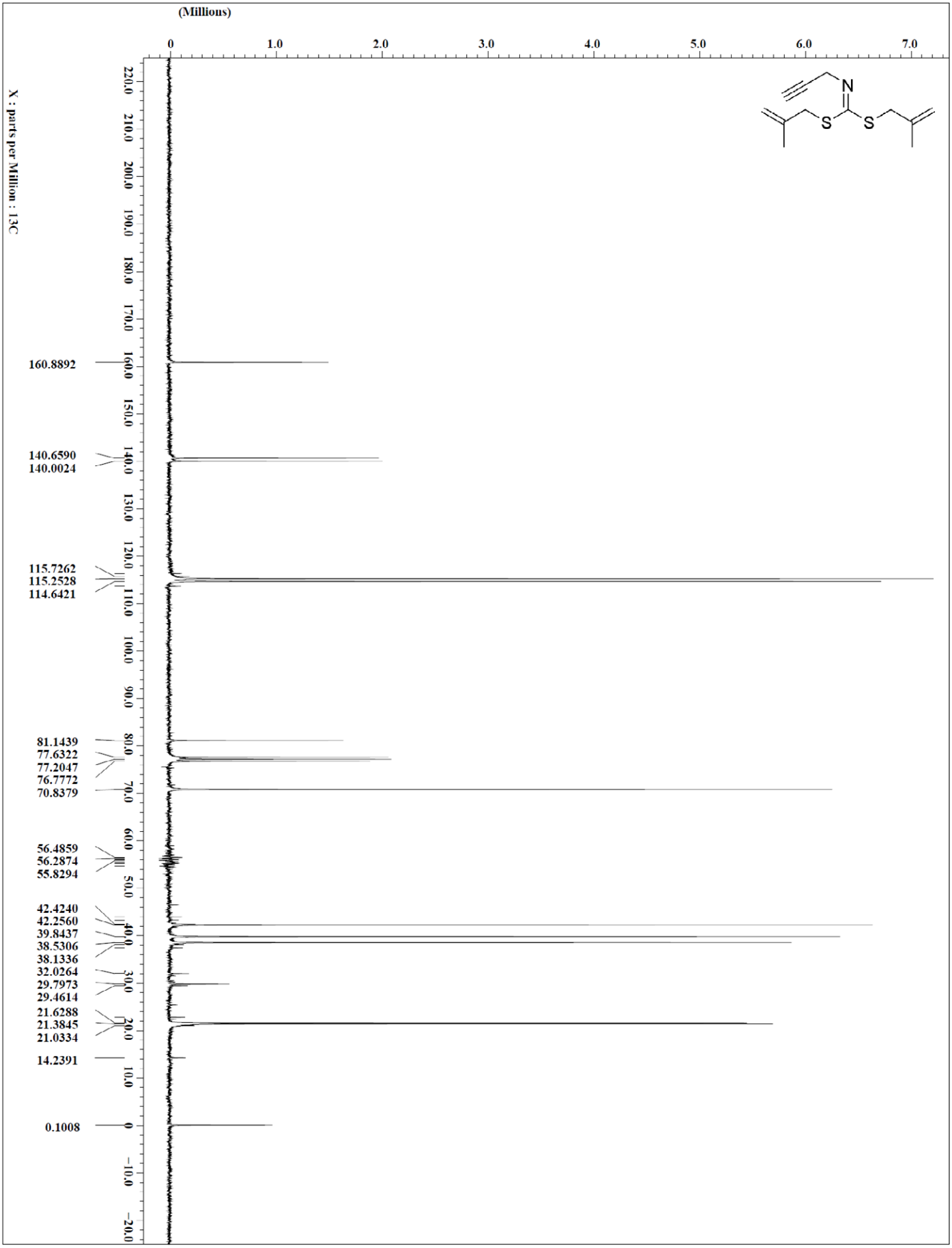
7.3161
7.2721
7.2630
6.9114
5.0288
4.9757
4.9720
4.9244
4.9189
4.8603
4.5197
4.2889
4.2816
4.0179
3.7890
3.7414
3.7212
3.6883
3.5033
3.4813
3.0308
2.5226
2.2708
2.2617
2.2525
1.8441
1.8038
1.7489
1.5584
1.5511
1.2837
1.2544
0.9651
0.9413
0.8790
0.0110
0.0000
−0.0110
0.61m
0.17
0.85m
1.42
6.34m
2.05
9.52m
2.01m
2.37
63.22m
23.11m
0.18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3.0
4.0
5.0
6.0
7.0
X : parts per Million : 13C
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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-20.0
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140.6590
140.0024
115.7262
115.2528
114.6421
81.1439
77.6322
77.2047
76.7772
70.8379
56.4859
56.2874
55.8294
42.4240
42.2560
39.8437
38.5306
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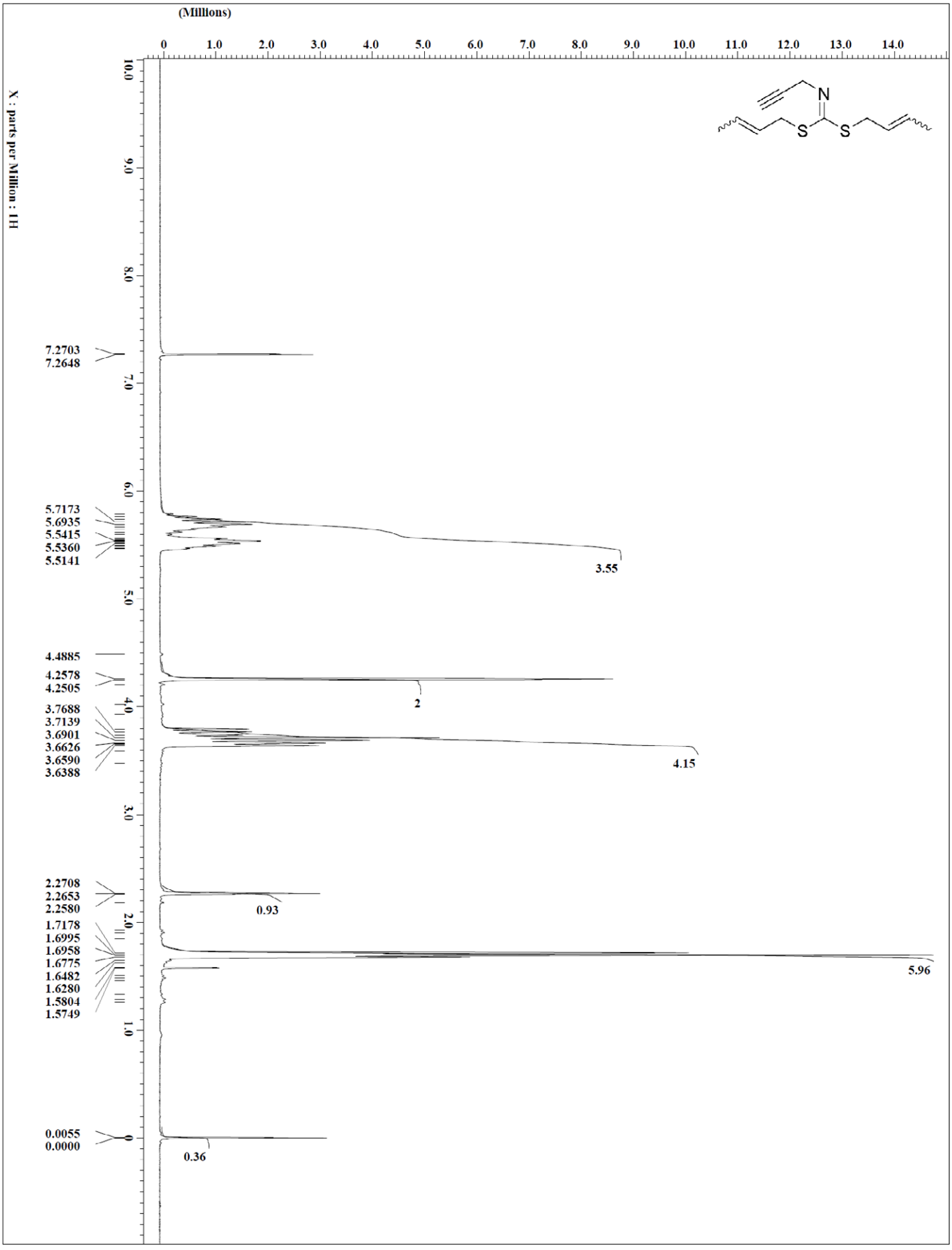
S
S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X : parts per Million : 1H
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5.5415
5.5360
5.5141
4.4885
4.2578
4.2505
3.7688
3.7139
3.6901
3.6626
3.6590
3.6388
2.2708
2.2653
2.2580
1.7178
1.6995
1.6958
1.6775
1.6482
1.6280
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0.93
5.96
0.36
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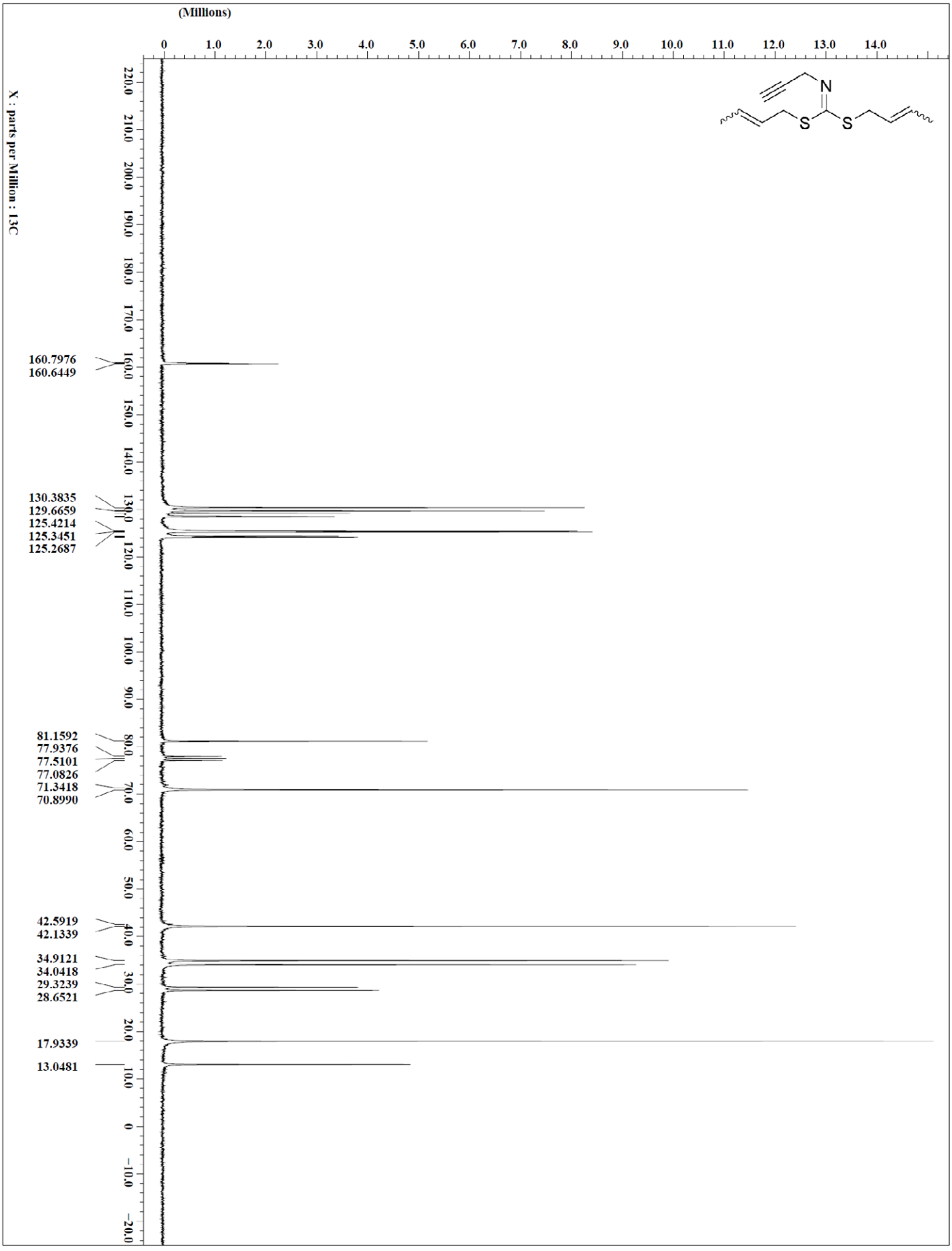
S
S


(Millions)
X : parts per Million : 13C
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77.9376
77.5101
77.0826
71.3418
70.8990
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29.3239
28.6521
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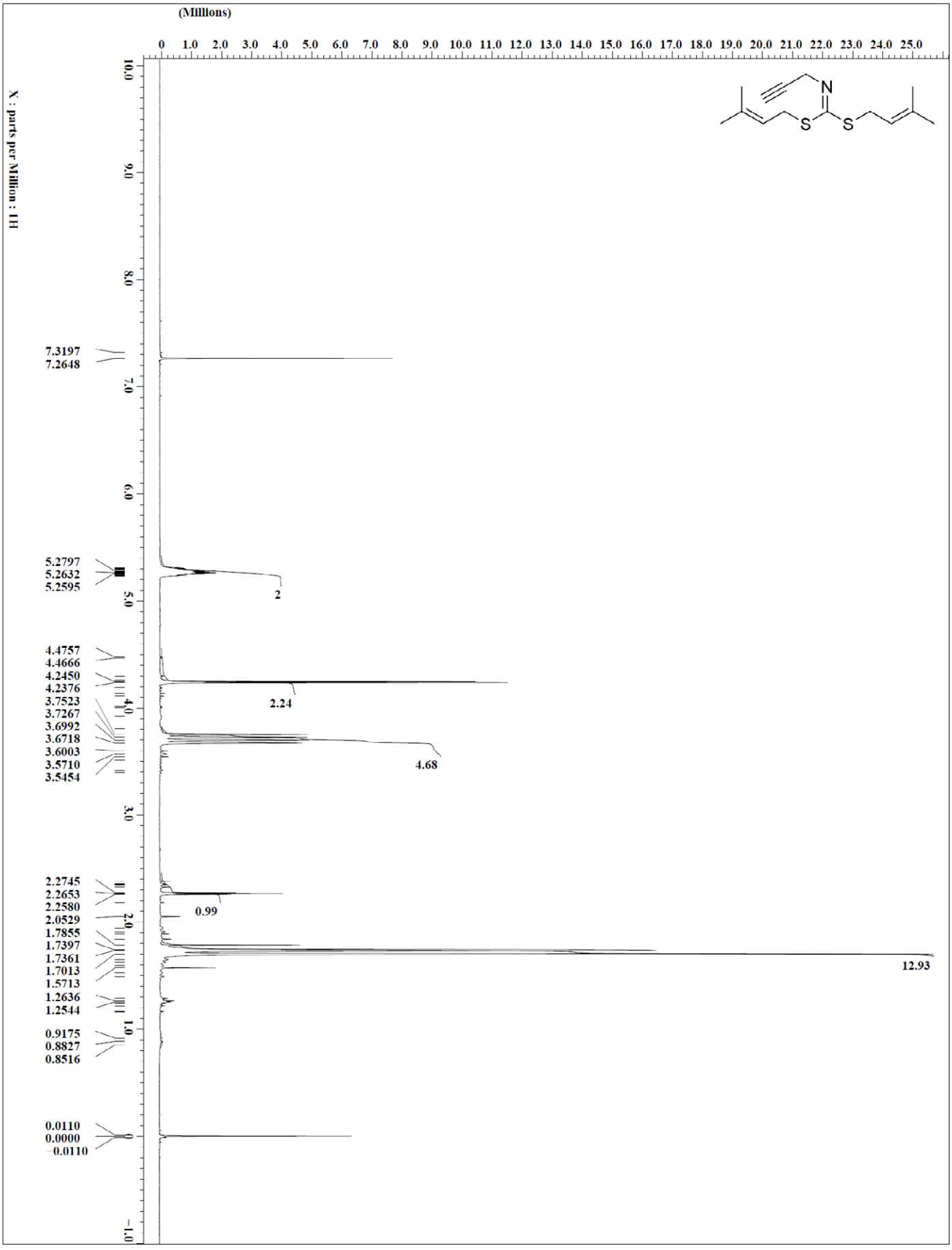
S
S


(Millions)
X : parts per Million : 1H
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4.2450
4.2376
3.7523
3.7267
3.6992
3.6718
3.6003
3.5710
3.5454
2.2745
2.2653
2.2580
2.0529
1.7855
1.7397
1.7361
1.7013
1.5713
1.2636
1.2544
0.9175
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0.0000
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4.68
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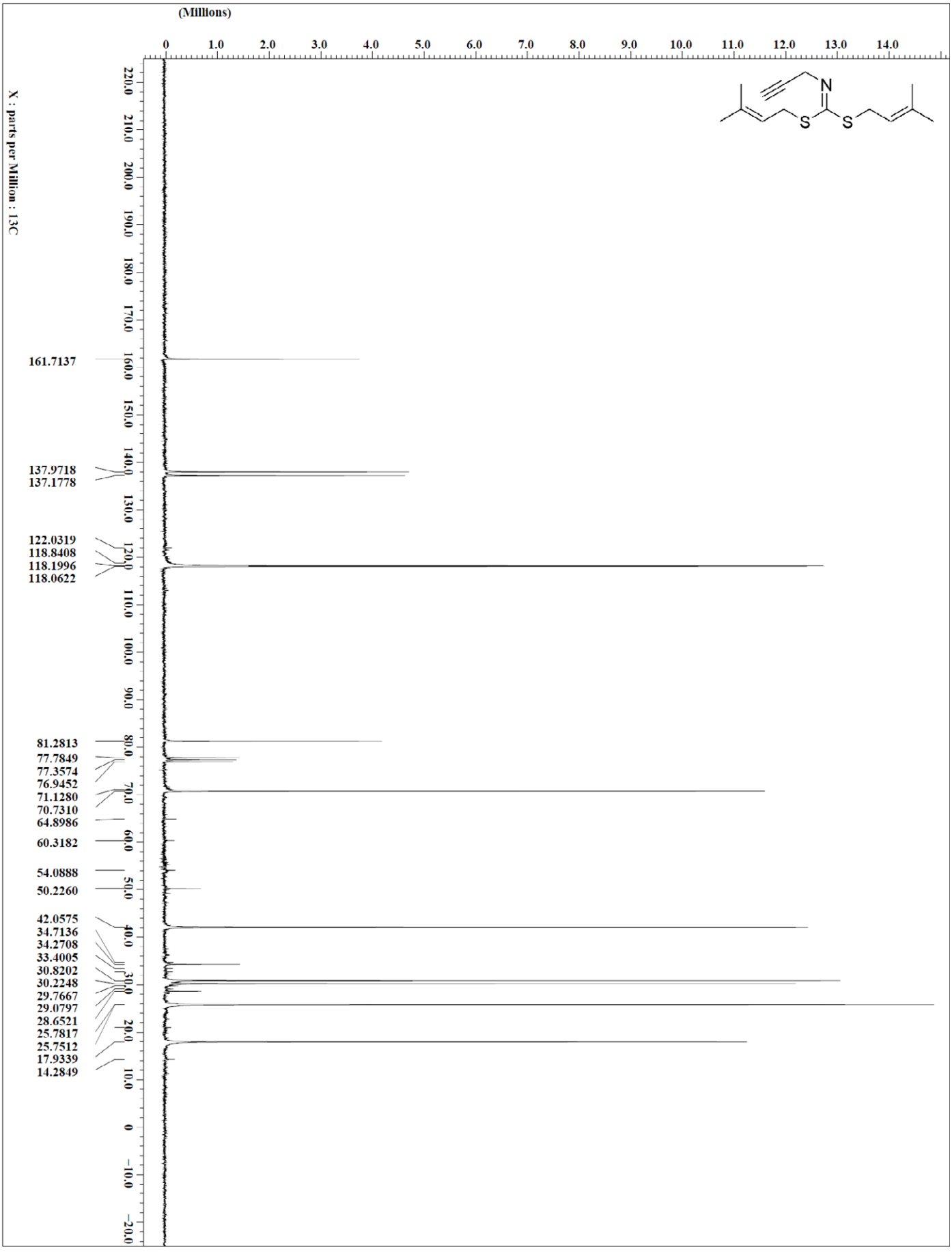
S
S


(Millions)
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137.1778
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118.1996
118.0622
81.2813
77.7849
77.3574
76.9452
71.1280
70.7310
64.8986
60.3182
54.0888
50.2260
42.0575
34.7136
34.2708
33.4005
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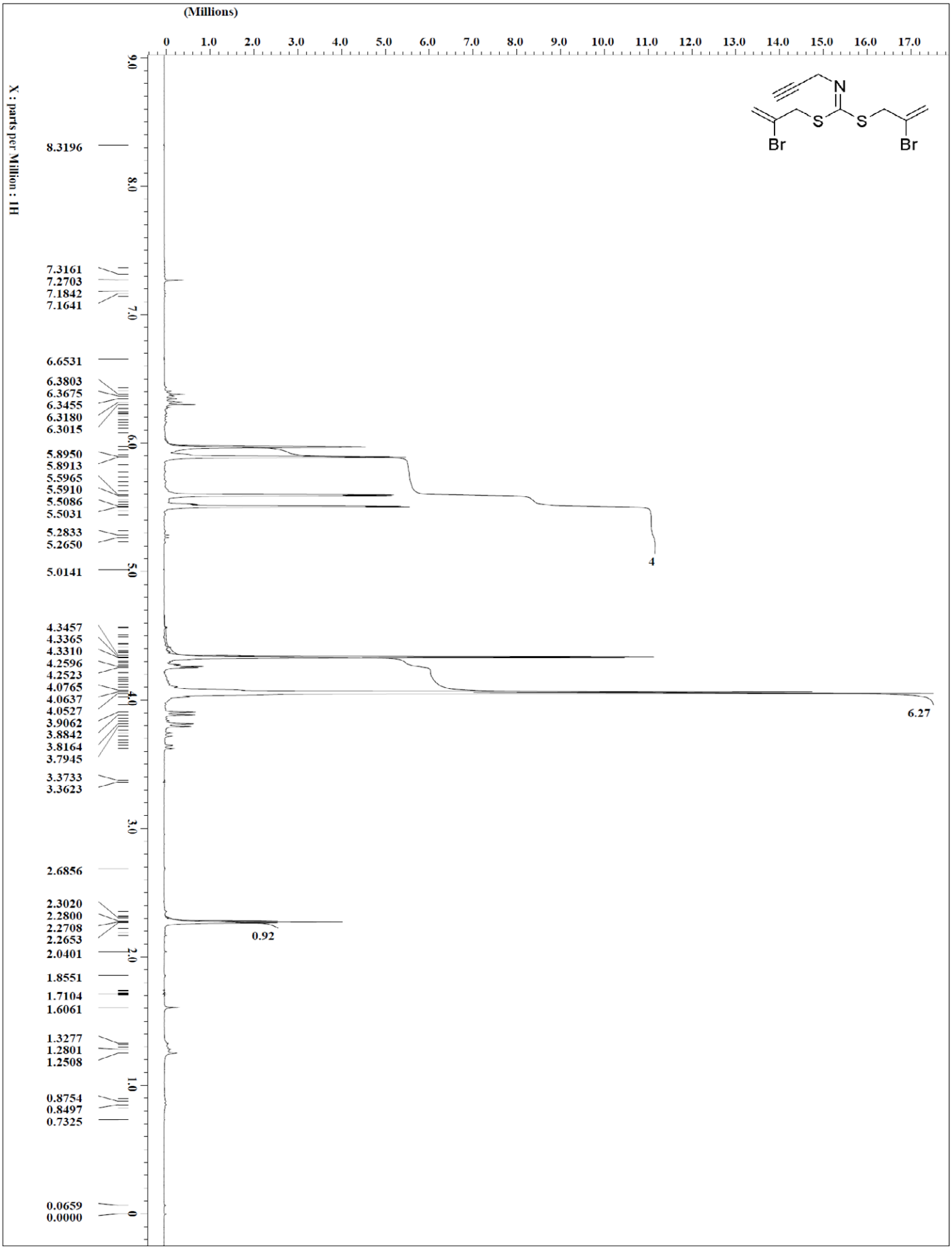
N
S
S


(Millions)
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6.3675
6.3455
6.3180
6.3015
5.8950
5.8913
5.5965
5.5910
5.5086
5.5031
5.2833
5.2650
5.0141
4.3457
4.3365
4.3310
4.2596
4.2523
4.0765
4.0637
4.0527
3.9062
3.8842
3.8164
3.7945
3.3733
3.3623
2.6856
2.3020
2.2800
2.2708
2.2653
2.0401
1.8551
1.7104
1.6061
1.3277
1.2801
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0.7325
0.0659
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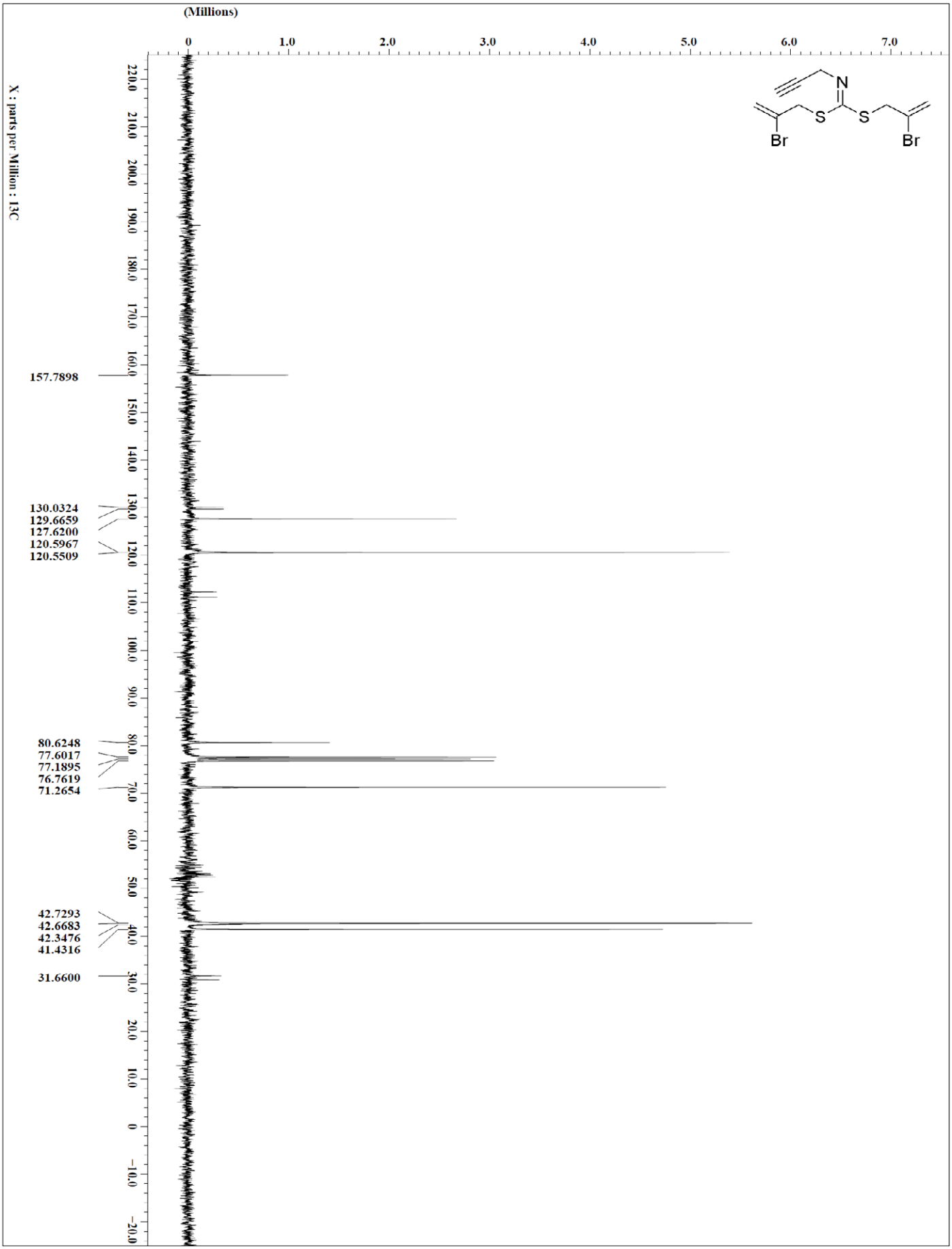
4
6.27
0.92
N
S
S
Br
Br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X : parts per Million : 13C
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150.0
140.0
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120.0
110.0
100.0
90.0
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70.0
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-20.0
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127.6200
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120.5509
80.6248
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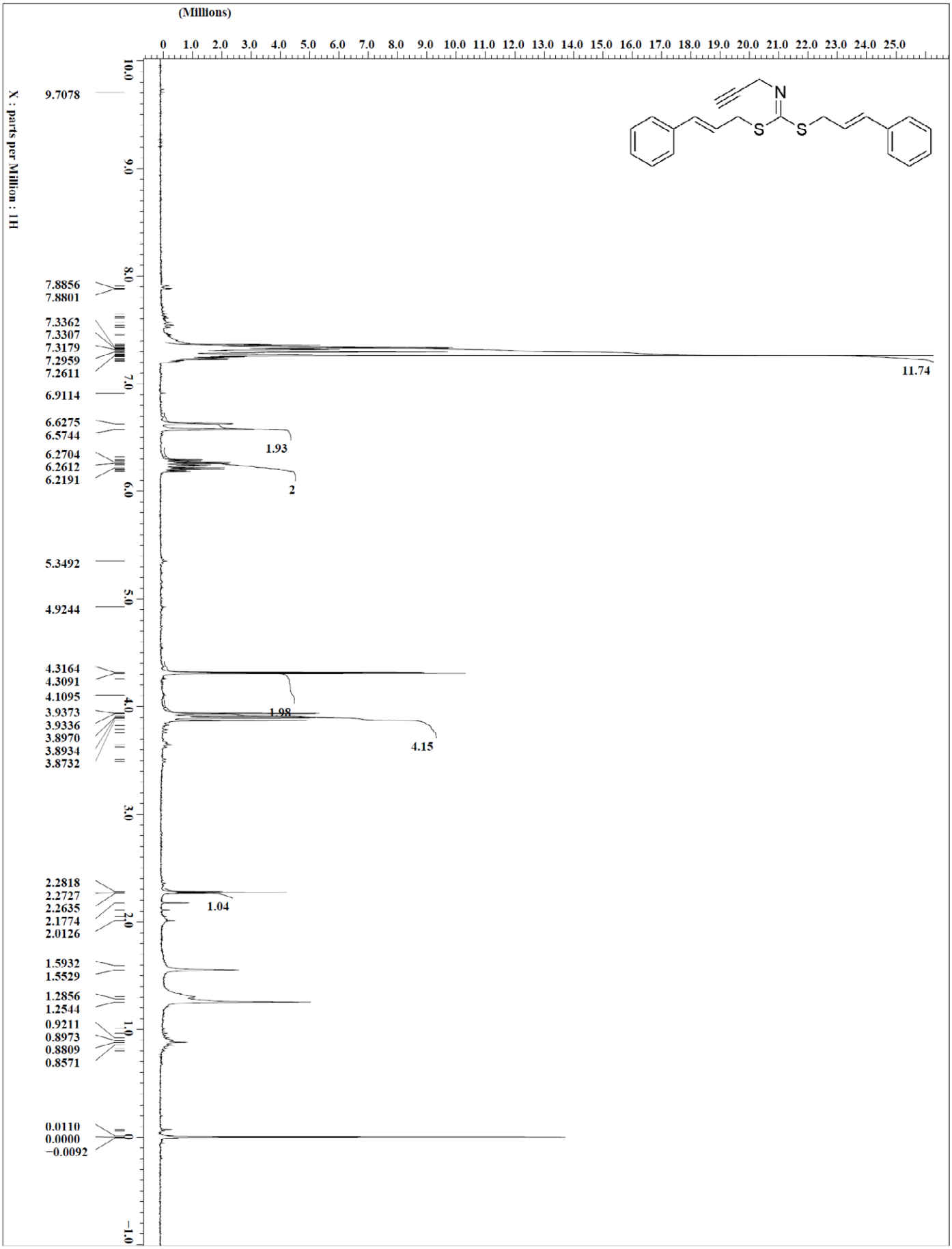
Br
Br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6.5744
6.2704
6.2612
6.2191
5.3492
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4.3164
4.3091
4.1095
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S
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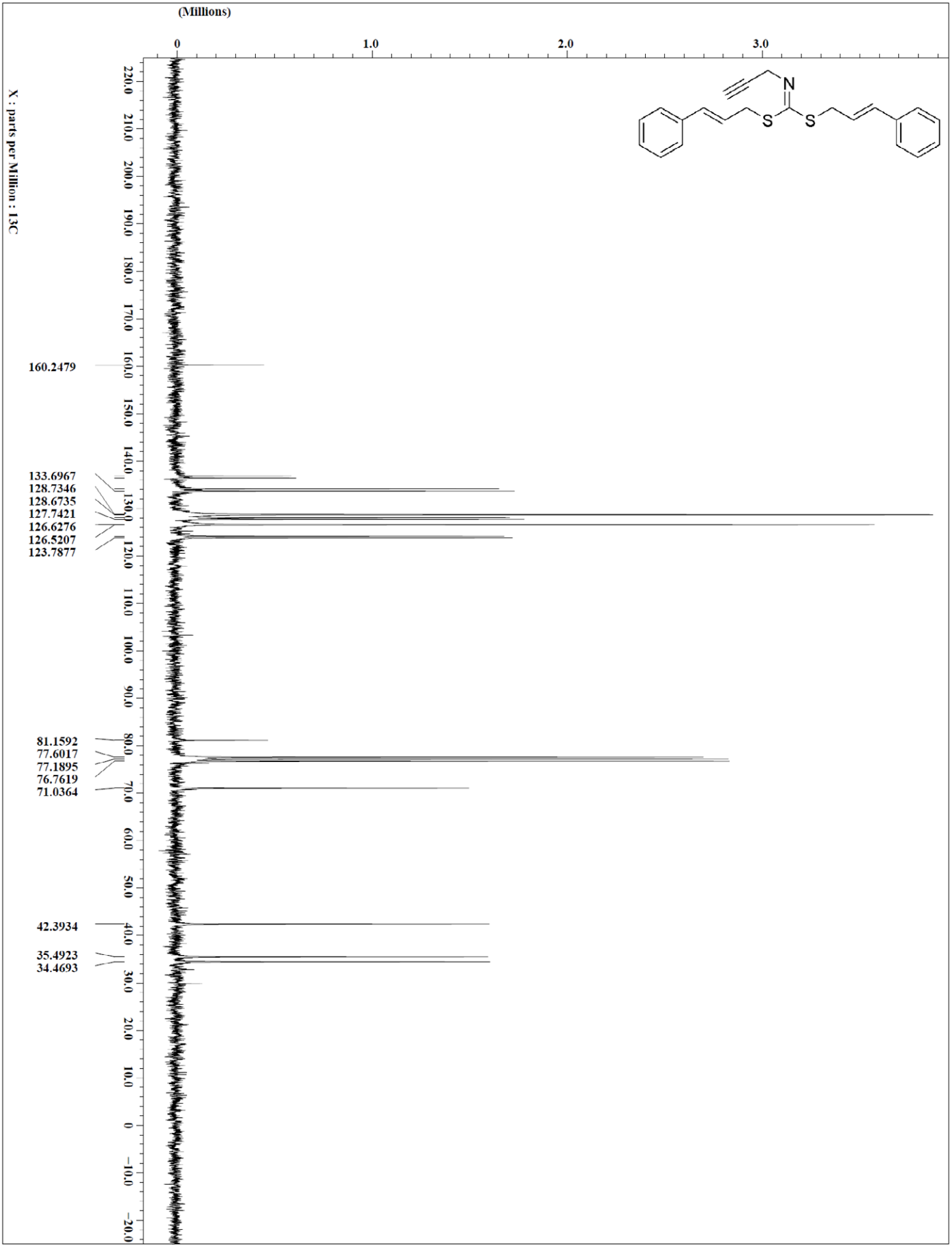
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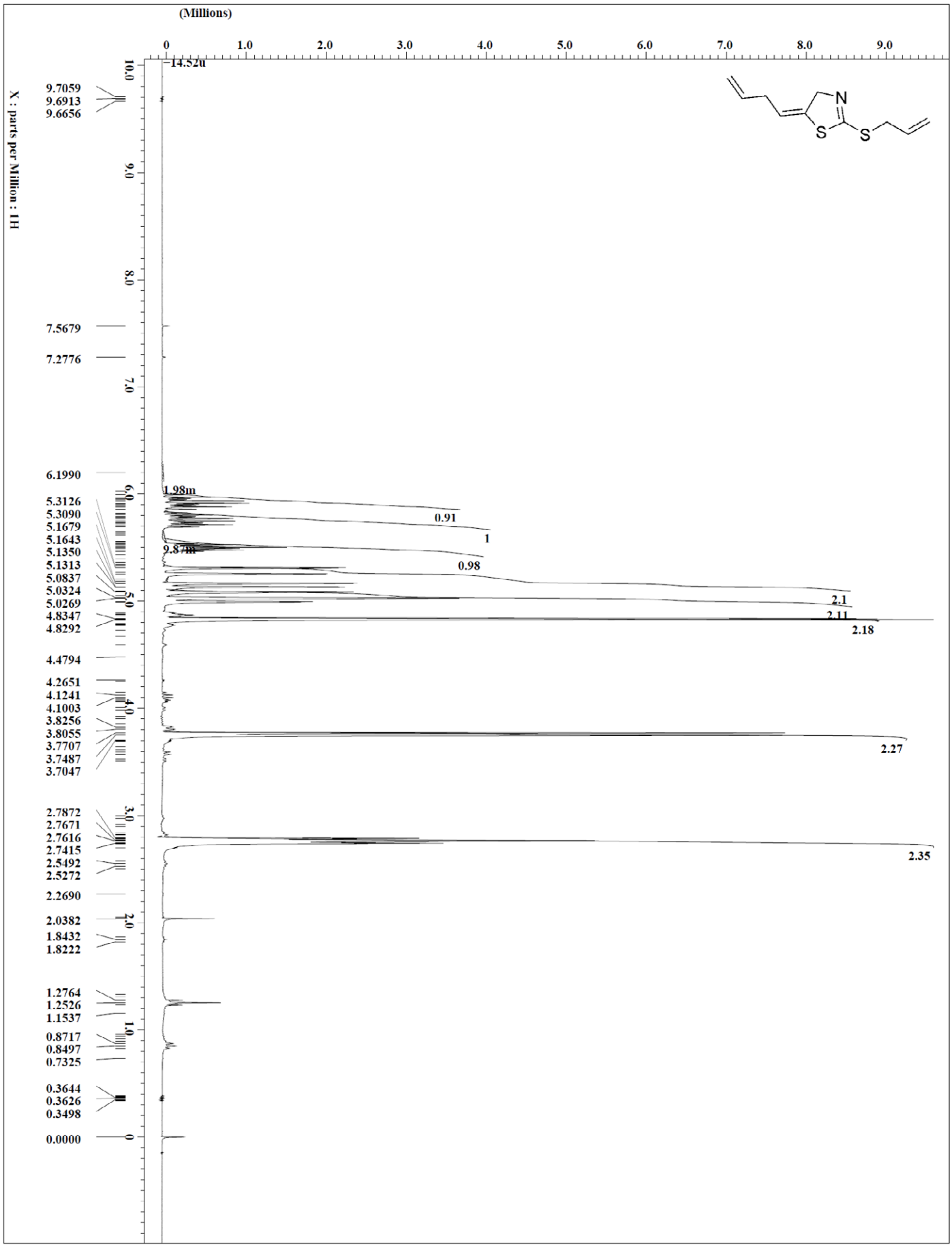
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5.1350
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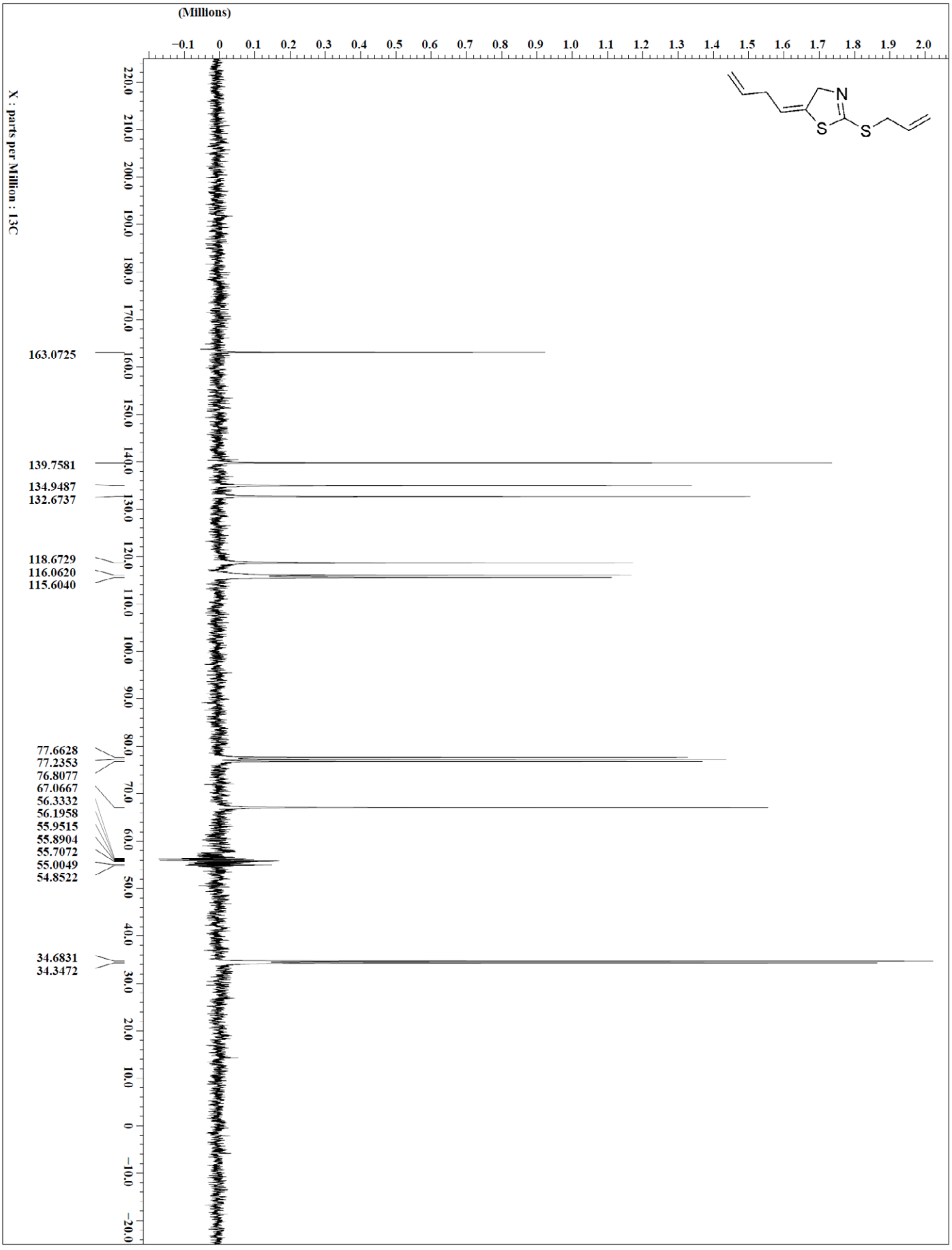
(Millions)
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67.0667
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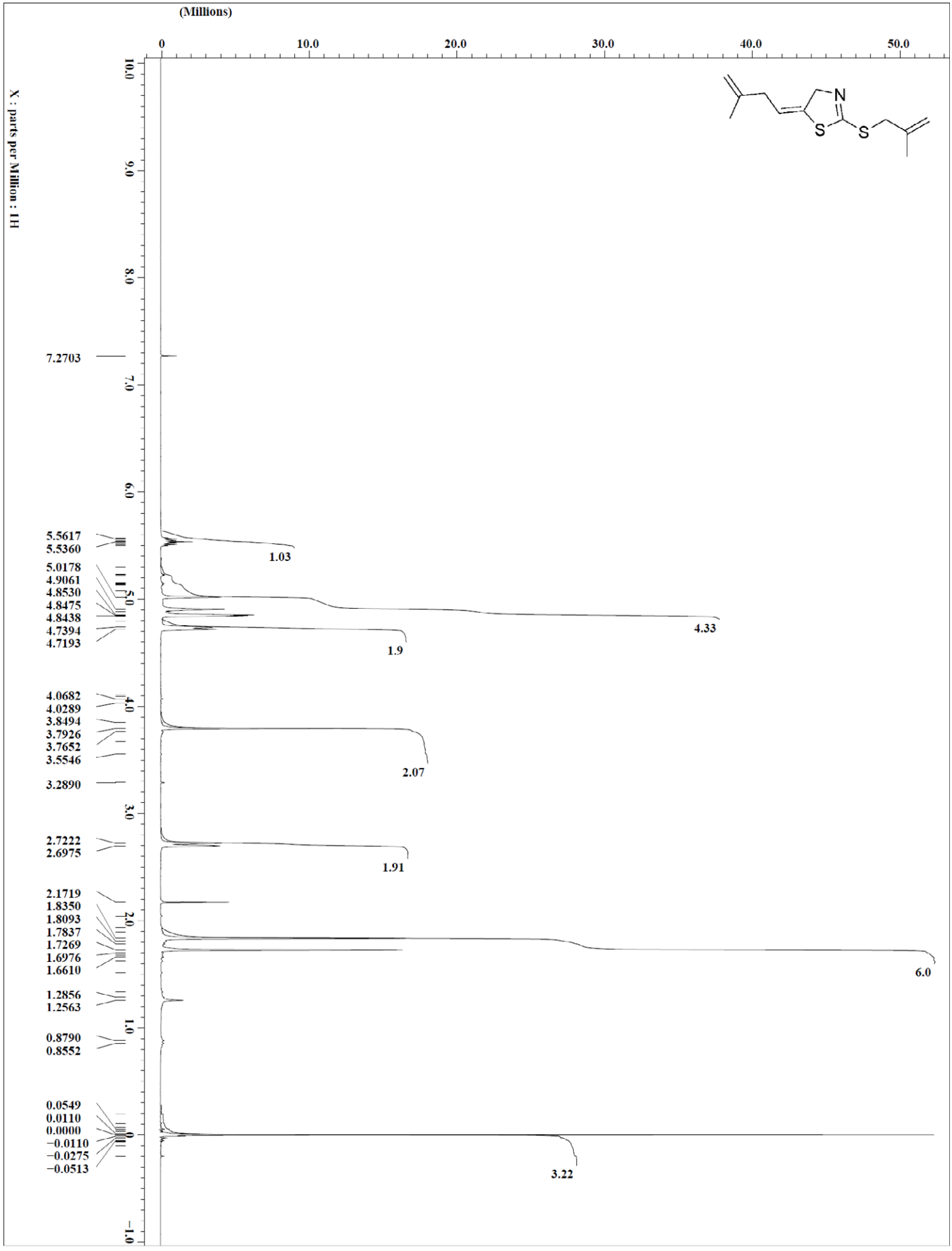
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1.2856
1.2563
0.8790
0.8552
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0.0110
0.0000
−0.0110
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S
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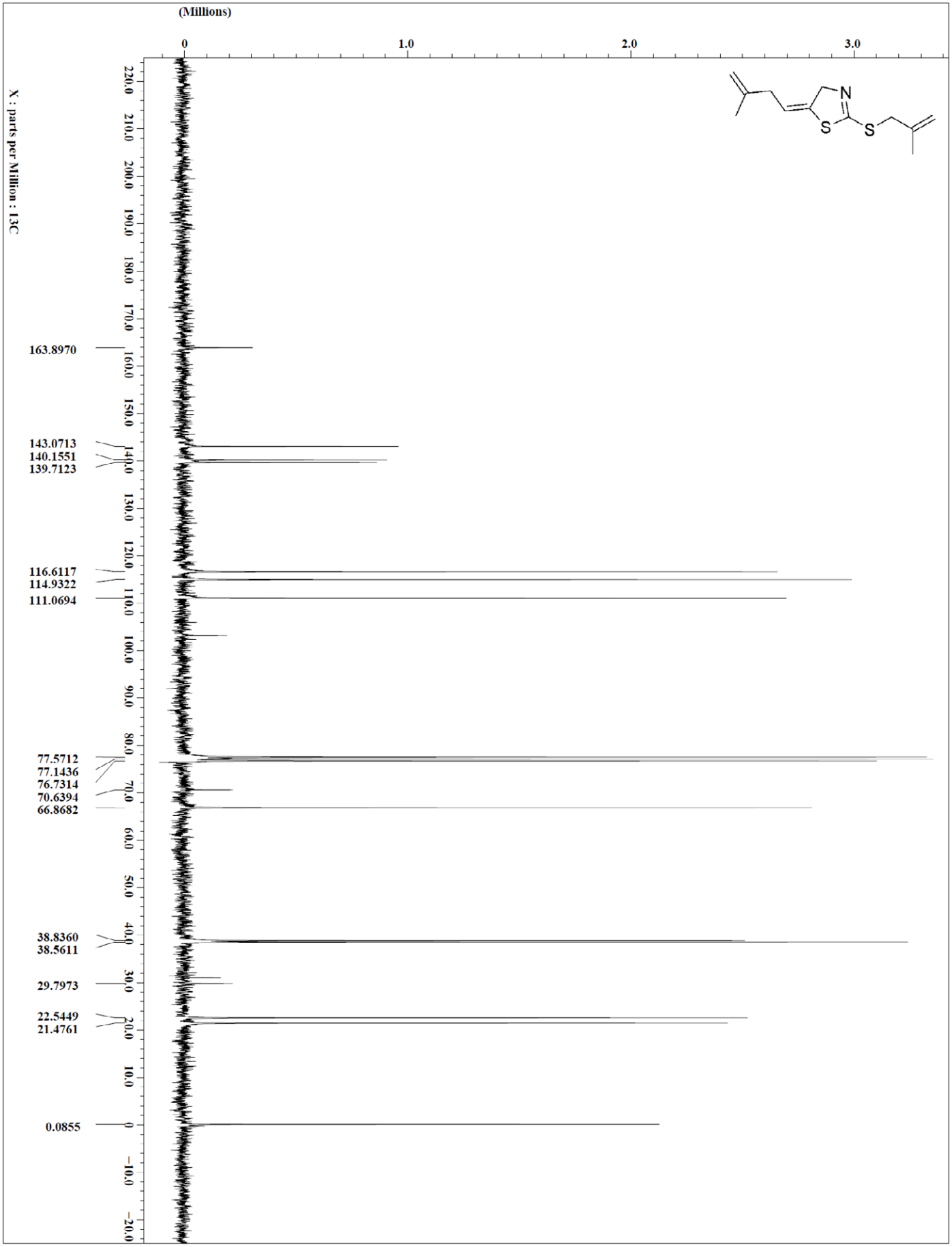
(Millions)
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X : parts per Million : 13C
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200.0
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140.0
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100.0
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80.0
70.0
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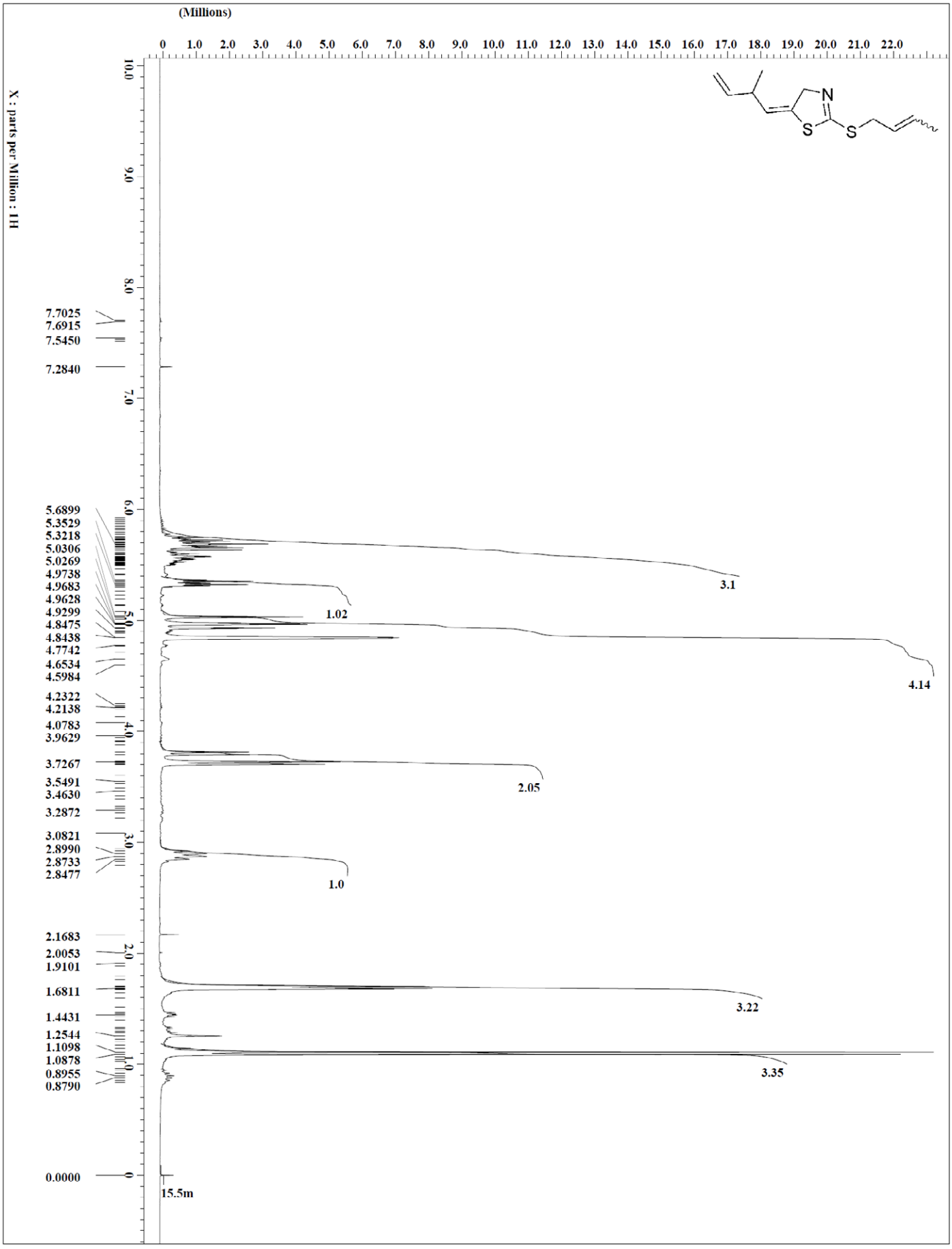
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5.0269
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4.8475
4.8438
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4.6534
4.5984
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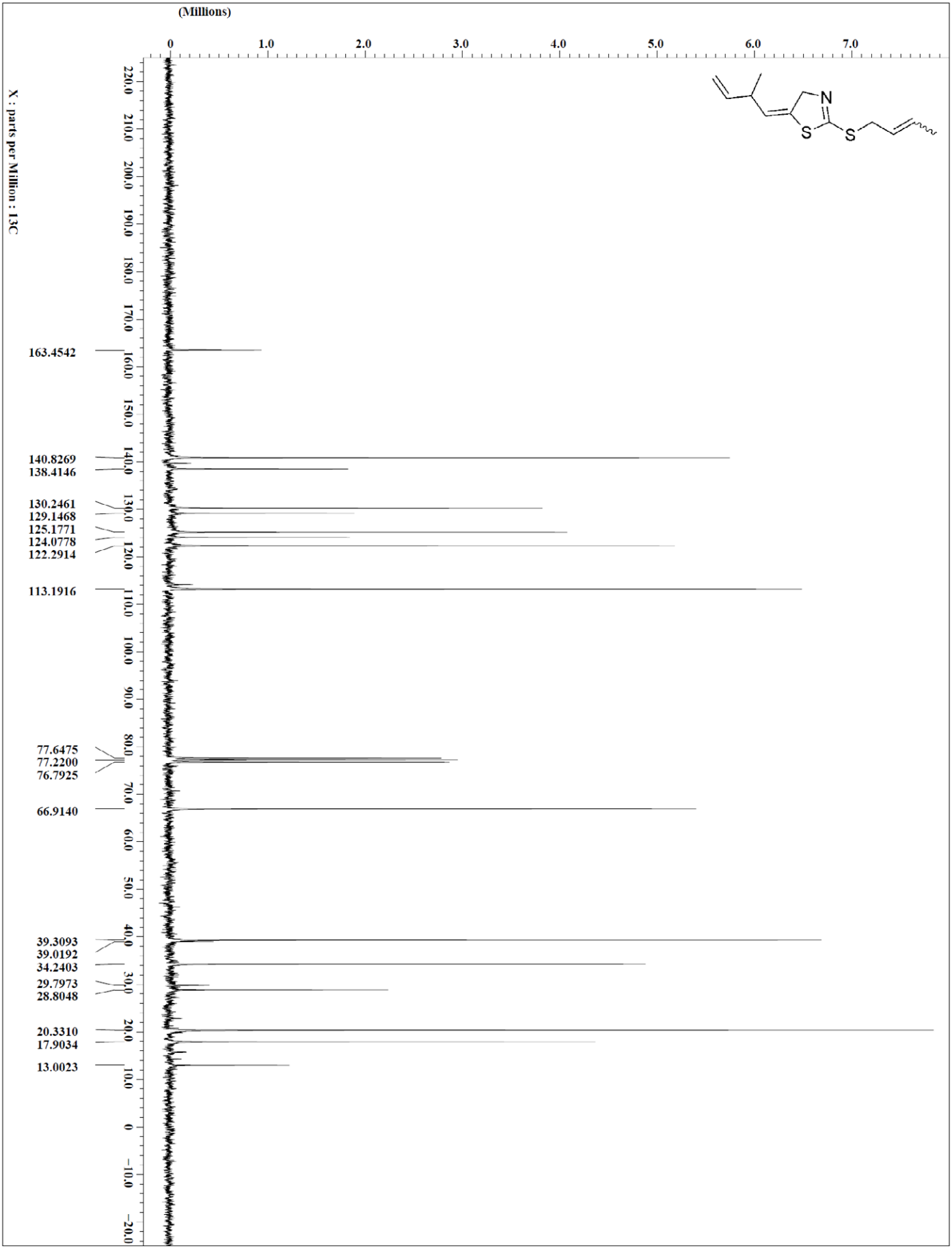
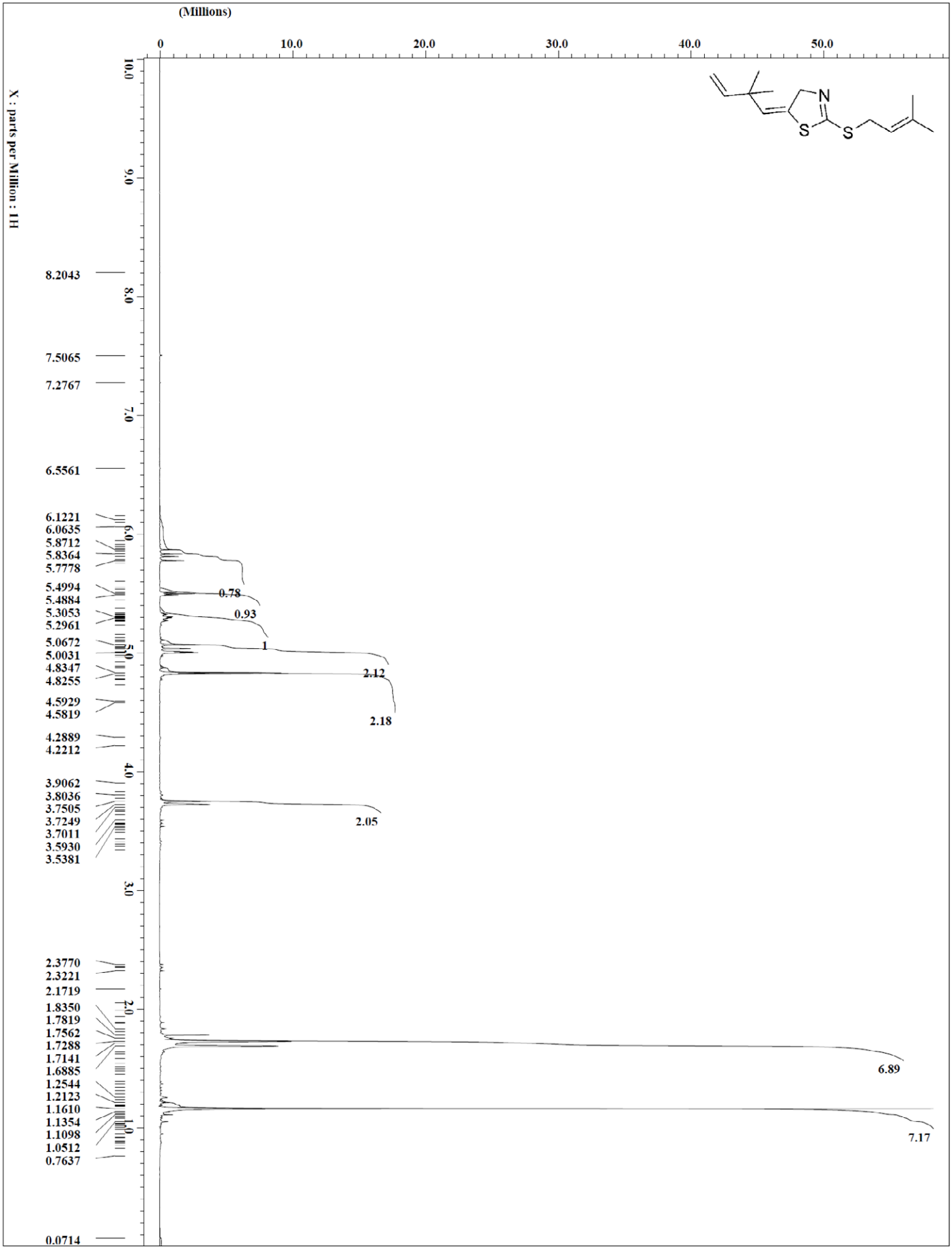
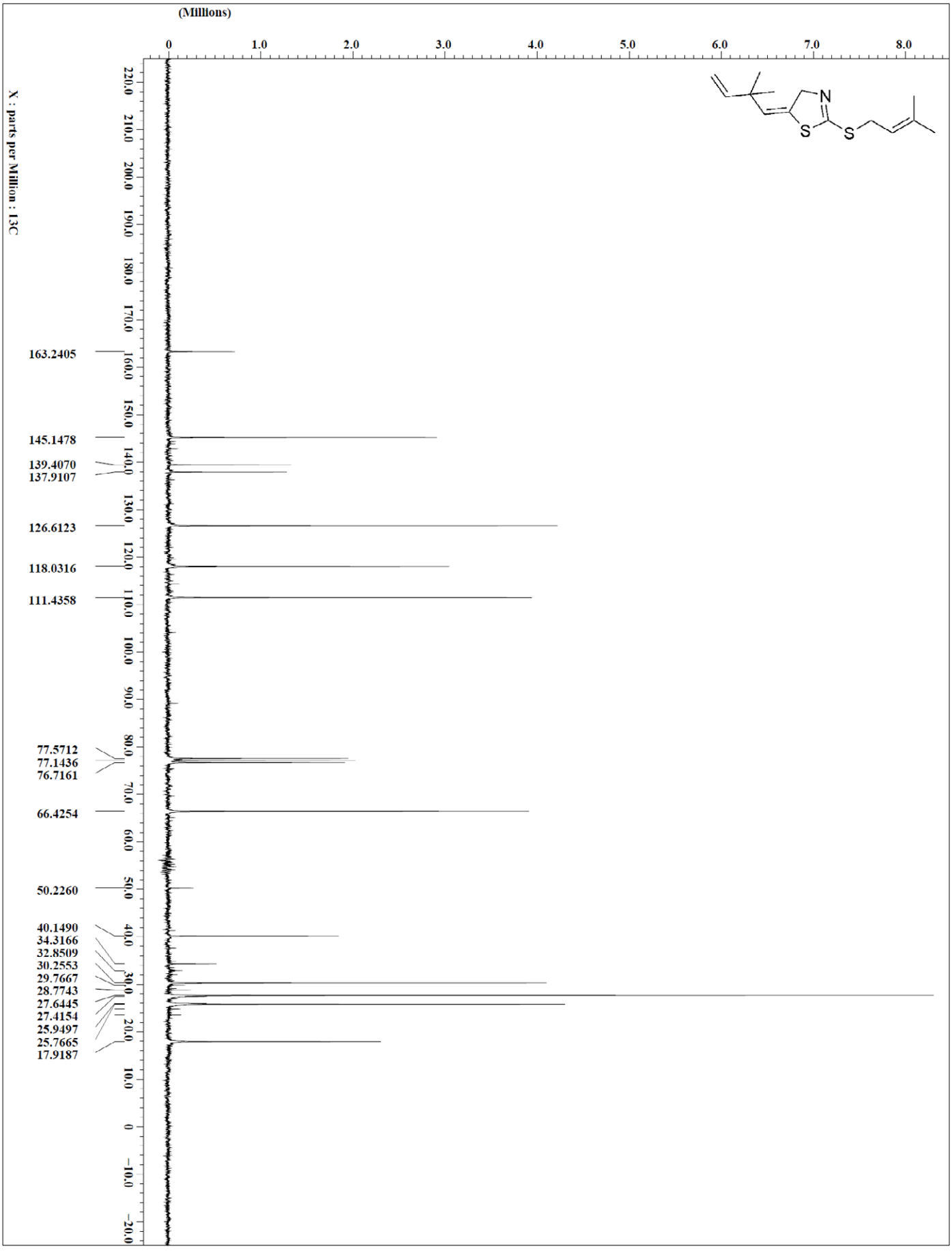
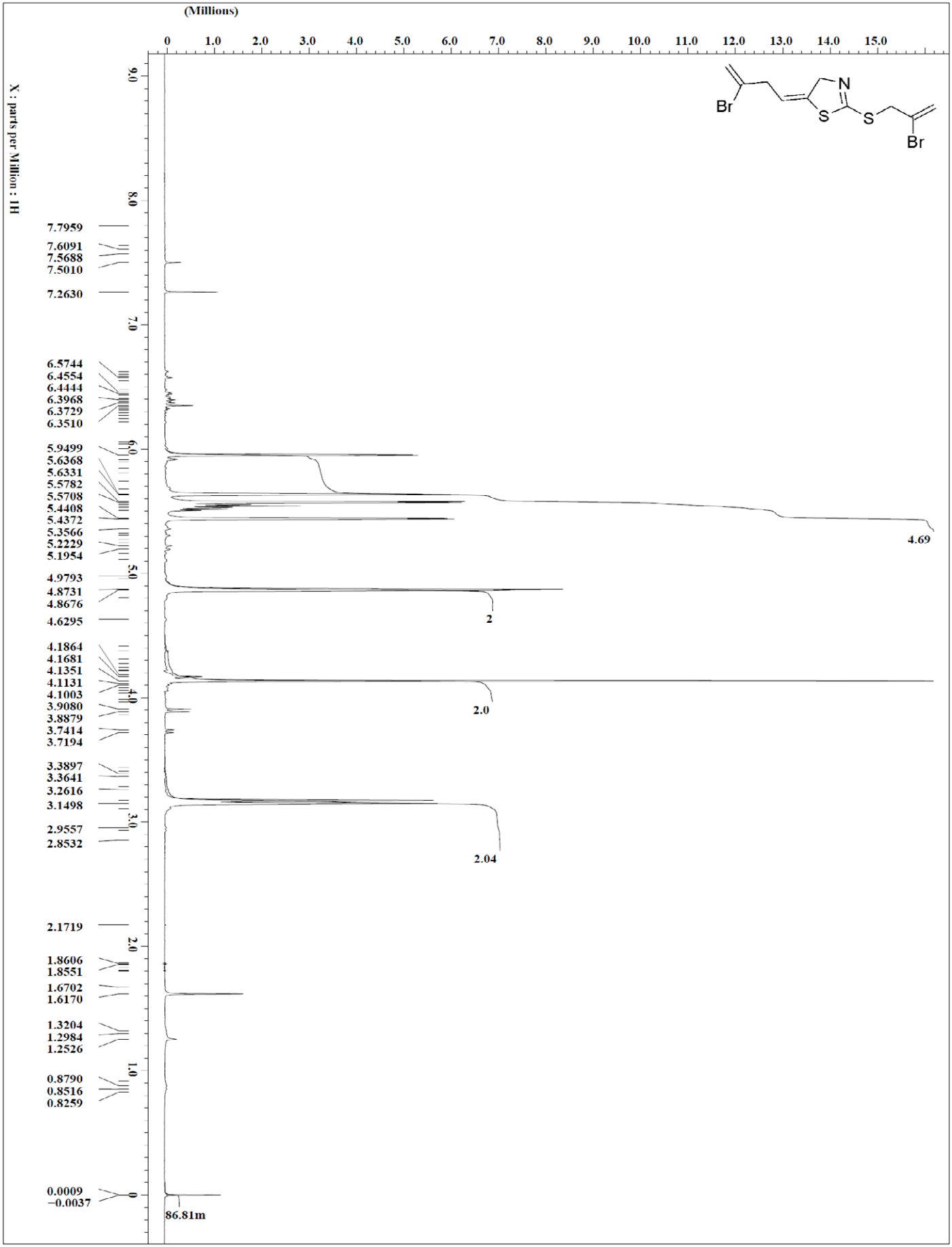
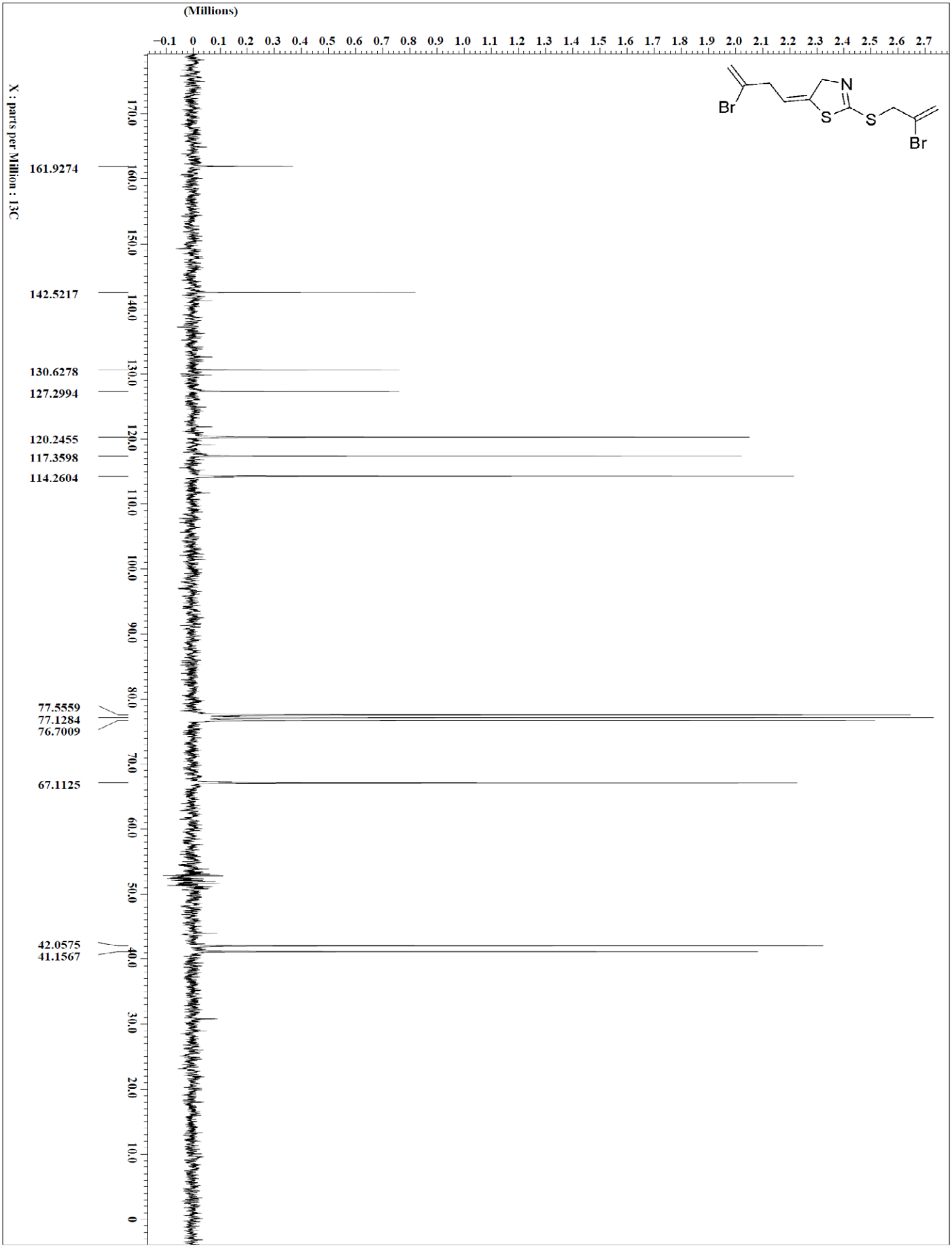
3.5491
3.4630
3.2872
3.0821
2.8990
2.8733
2.8477
2.1683
2.0053
1.9101
1.6811
1.4431
1.2544
1.1098
1.0878
0.8955
0.8790
0.0000
15.5m
3.1
1.02
4.14
2.05
1.0
3.22
3.35
N
S
S

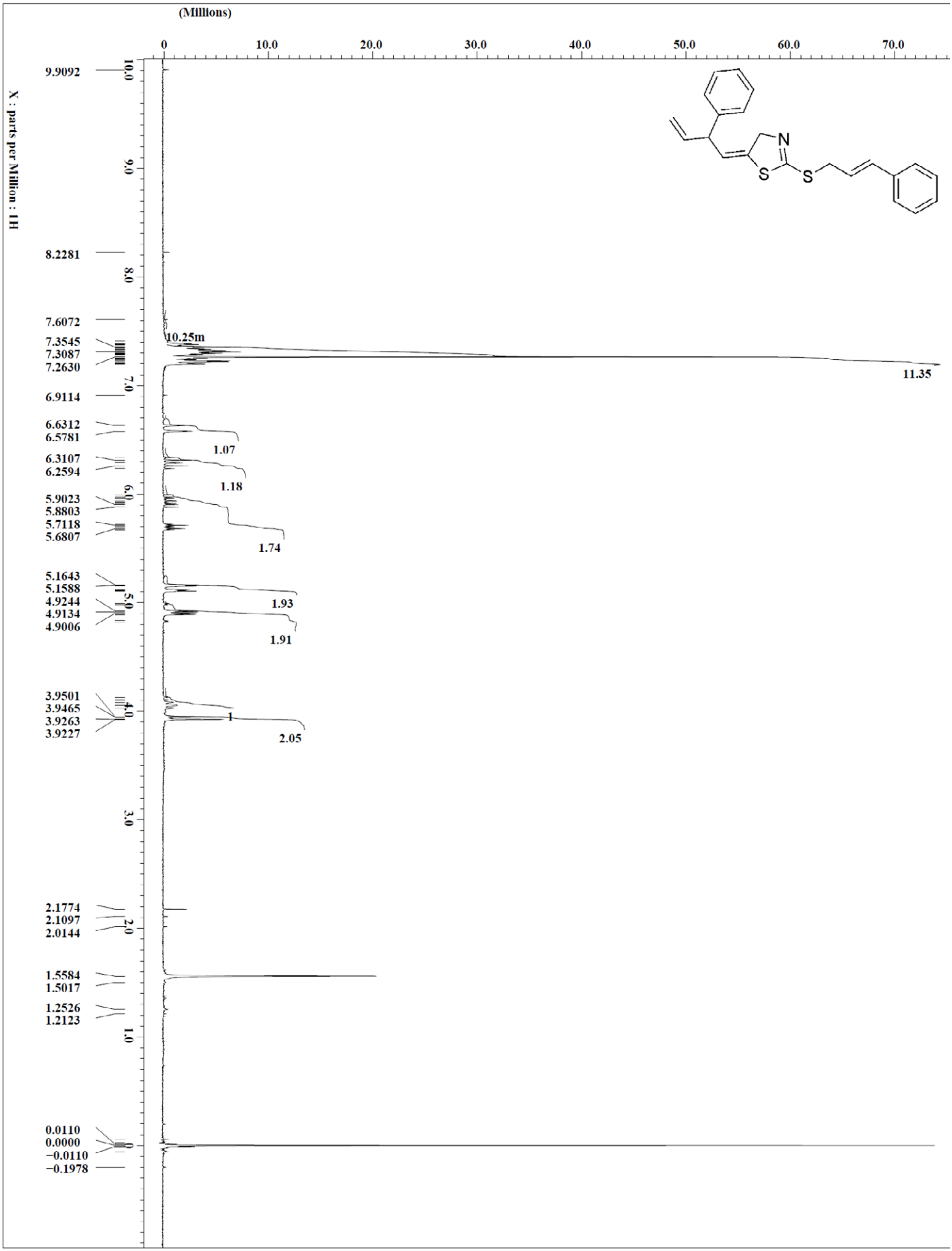

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
163.4542
140.8269
138.4146
130.2461
129.1468
125.1771
124.0778
122.2914
113.1916
77.6475
77.2200
76.7925
66.9140
39.3093
39.0192
34.2403
29.7973
28.8048
20.3310
17.9034
13.0023
N
S
S

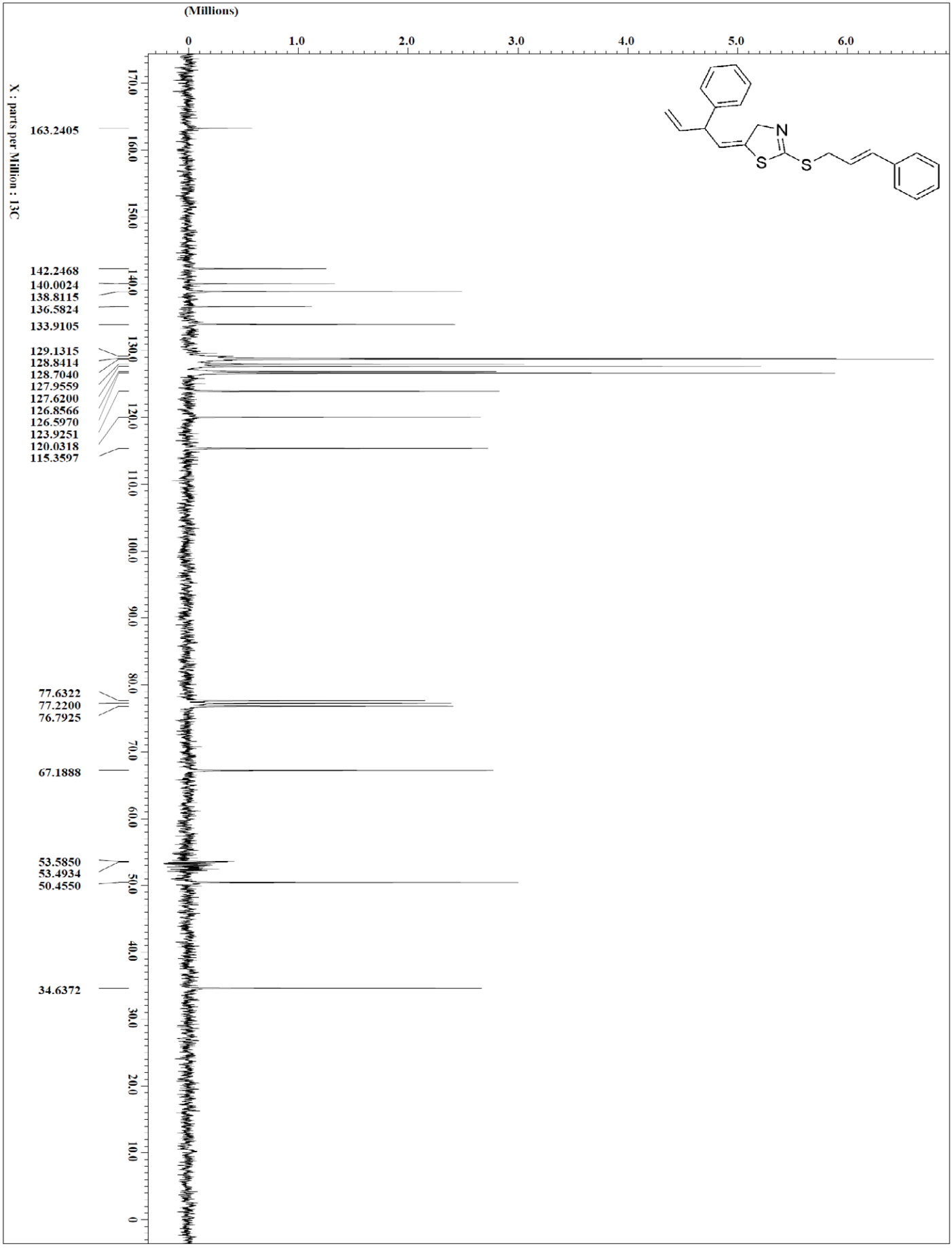

(Millions)
0
10.0
20.0
30.0
40.0
50.0
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.2043
7.5065
7.2767
6.5561
6.1221
6.0635
5.8712
5.8364
5.7778
5.4994
5.4884
5.3053
5.2961
5.0672
5.0031
4.8347
4.8255
4.5929
4.5819
4.2889
4.2212
3.9062
3.8036
3.7505
3.7249
3.7011
3.5930
3.5381
2.3770
2.3221
2.1719
1.8350
1.7819
1.7562
1.7288
1.7141
1.6885
1.2544
1.2123
1.1610
1.1354
1.1098
1.0512
0.7637
0.0714
0.78
0.93
1
2.12
2.18
2.05
6.89
7.17
N
S
S


(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
163.2405
145.1478
139.4070
137.9107
126.6123
118.0316
111.4358
77.5712
77.1436
76.7161
66.4254
50.2260
40.1490
34.3166
32.8509
30.2553
29.7667
28.7743
27.6445
27.4154
25.9497
25.7665
17.9187
N
S
S


(Millions)
X : parts per Million : 1H
Br
N
S
S
Br
7.7959
7.6091
7.5688
7.5010
7.2630
6.5744
6.4554
6.4444
6.3968
6.3729
6.3510
5.9499
5.6368
5.6331
5.5782
5.5708
5.4408
5.4372
5.3566
5.2229
5.1954
4.9793
4.8731
4.8676
4.6295
4.1864
4.1681
4.1351
4.1131
4.1003
3.9080
3.8879
3.7414
3.7194
3.3897
3.3641
3.2616
3.1498
2.9557
2.8532
2.1719
1.8606
1.8551
1.6702
1.6170
1.3204
1.2984
1.2526
0.8790
0.8516
0.8259
0.0009
−0.0037
4.69
2
2.0
2.04
86.81m


(Millions)
X : parts per Million : 13C
Br
N
S
S
Br
161.9274
142.5217
130.6278
127.2994
120.2455
117.3598
114.2604
77.5559
77.1284
76.7009
67.1125
42.0575
41.1567


(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
X : parts per Million : 1H
9.9092
8.2281
7.6072
7.3545
7.3087
7.2630
6.9114
6.6312
6.5781
6.3107
6.2594
5.9023
5.8803
5.7118
5.6807
5.1643
5.1588
4.9244
4.9134
4.9006
3.9501
3.9465
3.9263
3.9227
2.1774
2.1097
2.0144
1.5584
1.5017
1.2526
1.2123
0.0110
0.0000
−0.0110
−0.1978
10.25m
11.35
1.07
1.18
1.74
1.93
1.91
1
2.05
N
S
S


(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
X : parts per Million : 13C
163.2405
142.2468
140.0024
138.8115
136.5824
133.9105
129.1315
128.8414
128.7040
127.9559
127.6200
126.8566
126.5970
123.9251
120.0318
115.3597
77.6322
77.2200
76.7925
67.1888
53.5850
53.4934
50.4550
34.6372
N
S
S