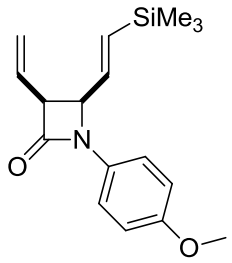
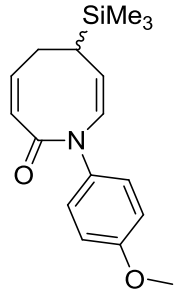
(3*S, 4*S**)-1-(4-Methoxyphenyl)-3-ethenyl-4-(*E*-2-(trimethylsilyl)ethenyl)azetidin-2-one 2**



Aldehyde **1**[1] (1.20 g, 9.38 mmol) and 4-methoxyaniline (1.15 g, 9.38 mmol) were dissolved in toluene (40 mL), the resulting mixture was stirred at room temperature for 2.5 hrs and $MgSO_4$ was added and stirred for further 10 mins, $MgSO_4$ was removed by filtration and the filtrate was transferred to a dry flask, triethylamine (1.56 mL, 11.3 mmol) was added and followed with dropwise addition of *trans*-crotonyl chloride (1.10 mL, 10 mmol), the resulting mixture was stirred at room temperature for 16 hrs. The reaction mixture was diluted with EtOAc (40 mL), washed with saturated aq. NH_4Cl (20 mL) and brine (3 x 10 mL) and the organic extract was dried with $MgSO_4$, filtered and concentrated, and then the residue was purified by column chromatography on silica gel using light petrol/EtOAc (4/1, v/v) as eluent to give product divinyl azetidinone **2** as a pale yellow oil (1.61 g, 57%). υ_{max}/ cm^{-1} 2958, 1737, 1513, 1249, 840; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 (2H, d, *J* = 9.2, Ar*H*), 6.87 (2H, d, *J* = 9.2, Ar*H*), 6.14 (1H, d, *J* = 18.8, 0.6 Hz SiC*H*=CH), 6.00 (1H, dd, *J* = 18.8, 6.9, SiCH=C*H*), 5.75 (1H, ddd, *J* 17.2, 10.3, 7.7, CH_2=C*H*), 5.43 (1H, app. dt, *J* = 17.2, 1.0, CH_aH$_b$=CH), 5.32 (1H, app. dt, *J* = 10.3, 1.0, CH$_a$*H*$_b$=CH), 4.61 (1H, app. td, *J* = 6.5, 1.0, NC*H*), 4.10 (1H, ddt, *J* = 7.7, 6.5, 1.0, COC*H*), 3.81 (3H, s, OCH_3), 0.10 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.6 (C), 155.9 (C), 140.6 (CH), 137.3 (CH), 131.7 (C), 129.0 (CH), 120.5 (CH_2), 118.2 (CH), 114.2 (CH), 59.5 (CH), 57.3 (CH), 55.4 (CH_3), -1.4 (CH_3); *m/z* (ESI) 324.1 (M + Na^+); HRMS calcd for $C_{17}H_{23}NNaO_2Si^+$ 324.1390, found 324.1389.

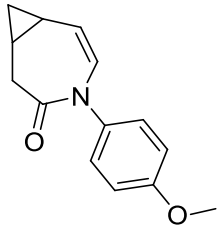
(3*Z*,7*Z*)-1-(4-Methoxyphenyl)-6-(trimethylsilyl)-5,6-dihydroazocin-2(1*H*)-one 3



(3S*, 4S*)-1-(4-Methoxyphenyl)-3-ethenyl-4-(*E*-2-(trimethylsilyl)ethenyl)azetidin-2-one **2** (270 mg, 0.89 mmol) in anhydrous toluene (5 mL) was heated in a sealed tube at 120 °C for 3 days. Concentration under vacuum afforded the crude product as a brown oil. Purification by column chromatography on silica gel eluting with petroleum ether: ethyl acetate 10:1 v:v afforded the title compound as pale yellow crystals (250 mg, 92%).

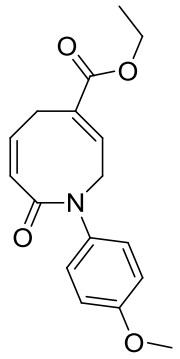
m.p: 93 – 95 °C (EtOAc); IR ($CHCl_3$) ν (cm^{-1}): 3011, 1657, 1618, 1509, 1249; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.20 (2H, d, *J* 9.0, Ar*H*), 6.91 (2H, d, *J* 9.0, Ar*H*), 6.29-5.89 (3H, br. m, CH=CH), 5.60-5.48 (1H, br. m, CH=CH), 3.79 (3H, s, OCH_3), 2.95-1.68 (3H, br. m, TMS*H* and TMSHCH_2), 0.08 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.4 (C), 158.1 (C), 132.7 (C), 132.3 (CH), 130.7 (CH), 127.2 (CH), 126.9 (CH), 123.8 (CH), 114.2 (CH), 55.4 (CH_3), 30.1 (CH_2), 21.8 (CH), -3.40 (CH_3); MS (ESI) m/z (M+H) expected: 302.1576, found: 302.1565, (M+Na) expected: 324.1396, found: 324.1390, (2M+Na) expected: 625.2894, found: 625.2871; (Found: C, 67.8; H, 7.9; N, 4.4. $C_{17}H_{23}NO_2Si$ requires C, 67.7; H, 7.7; N, 4.7%).

4-(4-Methoxyphenyl)-4-azabicyclo[5.1.0]oct-5-en-3-one 4



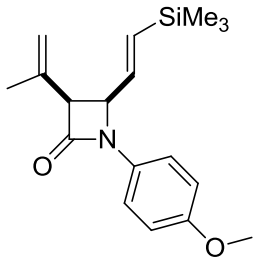
TBAF (1 M in THF, 0.52 mL. 0.53 mmol) was added to a solution of lactam **3** (80.0 mg, 0.13 mmol) in CH_2Cl_2 (10 mL), the reaction was stirred at room temperature for 16 hrs. The reaction mixture was concentrated. The residue was purified with column chromatography on silica gel using light petrol/EtOAc (1/2, v/v) as eluent to give product **4** as colourless solid (60.0 mg, 90%), mp 86 – 88 °C (EtOAc); υ_{max}/ cm^{-1} 3011, 2360, 1661, 1510, 1247; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.19 (2H, d, *J* = 6.8, Ar*H*), 6.92 (2H, d, *J* = 6.8, Ar*H*), 5.85 (1H, dd, *J* = 8.4, 1.2, NC*H*), 5.67 (1H, dd, *J* = 8.4, 3.6, NCH=C*H*), 3.83 (3H, s, CH_3), 2.93 (1H, dd, *J* = 12.8, 4.0, $COCH_aH_b$), 2.55 (1H, dd, *J* = 12.8, 9.6, $COCH_aH_b$), 1.77-1.66 (1H, m, $COCH_2CH$), 1.50-1.41 (1H, m, NCH=CHC*H*), 0.86 (1H, ddd, *J* = 9.6, 7.6, 4.8, $CHCH_aH_bCH$), 0.47 (1H, app. q, *J* = 4.8, $CHCH_aH_bCH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.1 (C), 158.3 (C), 134.1 (C), 129.1 (CH), 127.7 (CH), 119.3 (CH), 114.2 (CH), 55.5 (CH_3), 38.5 (CH_2), 18.8 (CH), 12.4 (CH), 8.1 (CH_2); *m/z* (ESI) 252.0 (29%, $M+Na^+$), 481.2 (100%, $2M+Na^+$); HRMS calcd for $C_{14}H_{15}NNaO_2^+$ 252.0995, found 252.0994. (Found: C, 73.4; H, 6.6; N, 6.1. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.7; N, 6.0%).

(3*E*, 6*Z*)-Ethyl-1-(4-methoxyphenyl)-8-oxo-1,2,5,8-tetrahydroazocine-4-carboxylate 7



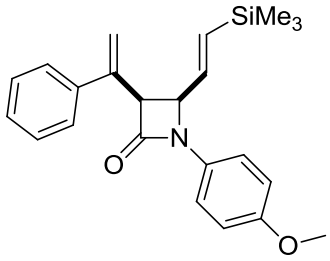
(2*Z*,6*Z*)-ethyl 1-(4-methoxyphenyl)-8-oxo-1,4,5,8-tetrahydroazocine-4-carboxylate **6** (50.0 mg, 1.66 mmol)[3] was dissolved in CH_2Cl_2 (5 mL) and followed with the dropwise addition of DBU (25 μL, 1.66 mmol) and stirred at room temperature for 16 hrs. The mixture was concentrated and the residue was purified by column chromatography on silica gel using light petrol/EtOAc (1/1, v/v) as eluent to give product as light yellow oil (46.0 mg, 92%). υ_{max}/ cm^{-1} 3007, 1707, 1655, 1511, 1248, 831; ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.21-7.17 (3H, m, NCH_2CH and Ar*H*), 6.90 (2H, d, *J* = 9.1, Ar*H*), 6.19 (1H, d, *J* = 9.2, COC*H*=CH), 6.14 (1H, d, *J* = 9.2, COCH=C*H*), 4.24 (2H, q, *J* = 7.2, CH_2CH_3), 3.79 (3H, s, OCH_3), 2.95-2.84 (4H, m, NCH_2 and COCH=CHCH_2), 1.32 (3H, t, *J* = 7.2, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.0 (C), 166.8 (C), 158.3 (C), 142.3 (CH), 132.5 (C), 129.7 (CH), 127.4 (CH), 125.3 (C), 118.1 (CH), 114.1 (CH), 61.2 (CH_2), 55.4 (CH_3), 31.1 (CH_2), 29.2 (CH_2), 14.2 (CH_3); *m/z* (ESI) 324.1 ($M+Na^+$); HRMS calcd for $C_{17}H_{19}NNaO_4^+$ 324.1206, found 324.1201.

1-(4-Methoxyphenyl)-3-(prop-1-en-2-yl)-4-((*E*)-2-(trimethylsilyl)ethenyl)azetidin-2-one 8



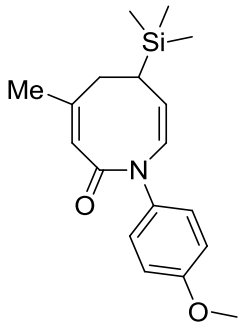
Method as **2:** Aldehyde **1**[1] (0.64 g, 5.00 mmol) and 3-methyl crotonoyl chloride (0.67 mL, 6.00 mmol) gave lactam **8** as a pale yellow oil (0.77 g, 49%). υ_{max}/ cm^{-1} 2958, 1735, 1513, 1249, 841; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 (2H, d, *J* = 9.1, Ar*H*), 6.85 (2H, d, *J* = 9.1, Ar*H*), 6.19 (1H, d, *J* = 18.8, SiC*H*=CH), 6.03 (1H, dd, *J* = 18.8, 7.2, SiCH=C*H*), 5.18 (1H, d, *J* = 0.8, CH_aH_b=C), 5.08 (1H, d, *J* = 0.8, CH_aH_b=C), 4.55 (1H, ddd, *J* = 7.6, 6.0, 1.0, NC*H*), 4.07 (1H, d, *J* = 6.0, COC*H*), 3.79 (3H, s, OCH_3), 1.69 (3H, s, CH_3), 0.07 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.6 (C), 156.0 (C), 140.7 (CH), 137.9 (CH), 136.8 (C), 131.9 (C), 118.2 (CH), 115.4 (CH_2), 114.2 (CH), 60.2 (CH), 59.6 (CH), 55.5 (CH_3), 22.4 (CH_3), -1.5 (CH_3); *m/z* (ESI) 338.1 ($M+Na^+$), 653.3 (2M+Na+); HRMS calcd for $C_{18}H_{25}NNaO_2Si^+$ 338.1547, found 338.1545.

(*E*)-1-(4-Methoxyphenyl)-3-(1-phenylethenyl)-4-((*E*)-2-(trimethylsilyl)ethenyl)azetidin-2-one 9



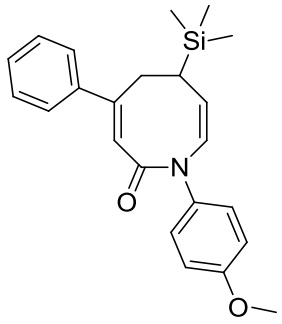
Method as **2:** Aldehyde **1**[1] (0.64 g, 5.00 mmol) and 3-phenylbut-2-enoyl chloride[4] (1.40 mL, 7.75 mmol) gave lactam **9** as pale yellow oil (0.78 g, 41%). υ_{max}/ cm^{-1} 3060, 3007, 1736, 1513, 1249, 839; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35 (2H, d, *J* = 9.2, Ar*H*), 7.30-7.20 (5H, m, Ar*H*), 6.81 (2H, d, *J* = 9.2, Ar*H*), 5.89 (1H, d, *J* = 18.7, 1.0, SiC*H*=CH), 5.71 (1H, dd, *J* = 18.7, 7.5, SiCH=C*H*), 5.64 (1H, s, C*H*H=C), 5.58 (1H, s, CH*H*=C), 4.67 (1H, d, *J* = 6.0 COC*H*), 4.60 (1H, d, *J* = 7.5, 6.0, NC*H*), 3.81 (3H, s, OCH_3), -0.19 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.5 (C), 156.0 (C), 139.7 (CH), 139.3 (C), 137.8 (CH), 131.8 (C), 128.3 (CH), 127.9 (CH), 125.6 (CH), 118.3 (CH), 115.9 (CH_2), 114.2 (CH), 60.1 (CH), 57.8 (CH), 55.5 (CH_3), -1.73 (CH_3); *m/z* (ESI) 400.1 ($M+Na^+$), 755.4 ($2M+H^+$), 777.4 ($2M+Na^+$), 1154.5 ($3M+Na^+$); HRMS calcd for $C_{23}H_{27}NNaO_2Si^+$ 400.1703, found 400.1706.

(3*Z*,7*Z*)-1-(4-Methoxyphenyl)-4-methyl-6-(trimethylsilyl)-5,6-dihydroazocin-2(1H)-one 10



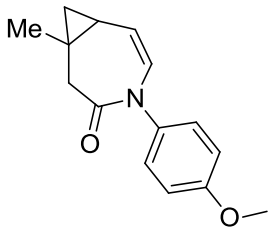
Method as **3**: lactam **8** (0.11 g, 3.49×10^{-1} mmol), column chromatography on silica gel using light petroleum/EtOAc ether (1/1, v/v) as eluent gave azocinone **10** as pale yellow oil (107 mg, 97%). υ_{max}/ cm^{-1} 3006, 1665, 1621, 1510, 1249, 1036, 835; NB: two equal populations of conformers apparent by spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.25-7.15 (4H, brm, Ar*H*), 6.91 (4H, d, *J* = 8.7, Ar*H*), 6.19-6.08 (1H, br m, CH=CH*), 5.95-5.85 (3H, brm, CH=CH, 2xC*H*=CCH$_3$), 5.50-5.35 (1H, brm, CH=CHCHSi*), 5.25-5.15 (1H, br m, CH=CHCHSi), 4.31 (6H, s, 2×OCH_3), 3.05 (1H, app. t, *J* = 13.5, CH_aH$_{b*}$), 2.55-2.40 (1H, m, CH_aH$_b$), 2.25-2.15 (1H, m, Me$_3$SiCH), 2.05-1.68 (9H, m, CH$_a$$H_b$, *2x*CHC$H_3$, Me$_3$SiC*H**) , 0.10 (18H, s, 2×Si(CH_3)$_3$); *m/z* (ESI) 316.2 (M+H$^+$), 338.1 (M+Na$^+$), 631.3 (2M+H$^+$), 653.3 (2M+Na$^+$), 968.5 (3M+Na$^+$); HRMS calcd for $C_{18}H_{25}NO_2Si^+$ 316.1733, found 316.1720.

(3*E*,7*Z*)-1-(4-Methoxyphenyl)-4-phenyl-6-(trimethylsilyl)-5,6-dihydroazocin-2(1H)-one 11



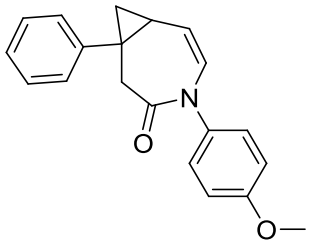
Method as **3**: lactam **9** (0.23 g, 0.61 mmol), column chromatography on silica gel using light petrol/EtOAc ether (2/1, v/v) as eluent gave azocinone **11** as pale yellow oil (201 mg, 87%). υ_{max}/ cm^{-1} 3006, 2958, 1646, 1604, 1352, 1249, 841; NB: two unequal populations of conformers apparent by spectroscopy, data for major conformer ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.51-7.20 (7H, m, Ar*H*), 6.96 (2H, d, *J* = 8.4, Ar*H*), 6.50 (1H, s, COC*H*=C), 6.02 (1H, d, *J* = 9.1, NC*H*=CH), 5.27 (1H, dd, *J* = 9.1, *J* = 7.0, NCH=C*H*), 3.85 (3H, s, OCH_3), 3.27 (1H, app. t, *J* = 14.0, CH_aH$_b$), 2.80 (1H, dd, *J* = 14.0, 2.8, CH$_a$$H_b$), 1.76 (1H, m, C*H*Si), 0.14 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.9 (C), 158.2 (C), 144.2 (C), 139.0 (C), 130.5 (C), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 124.5 (CH), 120.9 (CH), 114.5 (CH), 55.5 (CH_3), 30.5 (CH_2), 30.2 (CH), -2.64 (CH_3); *m/z* (ESI) 378.2 ($M+H^+$), 400.1 ($M+Na^+$), 755.4 ($2M+H^+$), 777.4 ($2M+Na^+$), 1154.5 ($3M+Na^+$); HRMS calcd for $C_{23}H_{27}NNaO_2Si^+$ 400.1703, found 400.1705.

4-(4-Methoxyphenyl)-1-methyl-4-azabicyclo[5.1.0]oct-5-en-3-one 12



Method as **4**: azocinone **10** (60.0 mgs, 0.19 mmol), column chromatography on silica gel using light petrol/EtOAc (2/1, v/v) as eluent gave product **12** as a light yellow oil (43 mgs, 93%). υ_{max}/ cm^{-1} 3007, 1658, 1609, 1247, 1034, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.18 (2H, d, J = 6.8, Ar*H*), 6.91 (2H, d, J = 6.8, Ar*H*), 5.81 (1H, d, J = 8.8, NC*H*=CH), 5.65 (1H, dd, J = 8.8, 4.8, NCH=C*H*), 3.82 (3H, s, OCH_3), 2.83 (1H, d, J = 12.4, COCH_aH$_b$), 2.65 (1H, d, J = 12.4, COCH$_a$$H_b$), 1.30 (3H, s, C$H_3$), 1.26-1.22 (1H, app. dt, J = 9.2, 4.8, NCH=CHC*H*), 0.76-0.78 (1H, m, MeCCH_aH$_b$), 0.73-0.69 (1H, dd, J = 9.2, 4.8, MeCCH$_a$$H_b$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.4 (C), 158.2 (C), 134.0 (C), 128.2 (CH), 127.6 (CH), 119.7 (CH), 114.2 (CH), 55.5 (CH_3), 43.9 (CH_2), 27.4 (C), 24.5 (CH_3), 20.7 (CH), 15.9 (CH_2); ES-MS 244.13 ($M+H^+$), 266.1 ($M+Na^+$); HRMS calcd for $C_{15}H_{17}NaO_2^+$ 266.1151, found 266.1167.

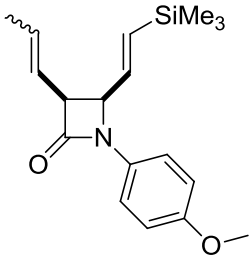
4-(4-Methoxyphenyl)-1-phenyl-4-azabicyclo[5.1.0]oct-5-en-3-one 13



Method as **4**: azocinone **11** (0.10 g, 0.27 mmol) in CH_2Cl_2 (10 mL), column chromatography on silica gel using light petrol/EtOAc (1/1, v/v) as eluent gave product **13** as a pale yellow oil (69.5 mg, 86%). υ_{max}/ cm^{-1} 3010, 1661, 1510, 1248, 1034, 834; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.37-7.28 (5H, m, Ar*H*), 7.20 (2H, d, *J* = 6.8, Ar*H*), 6.92 (2H, *J* = 6.8, Ar*H*), 5.92 (1H, d, *J* = 8.8, NC*H*=CH), 5.77 (1H, dd, *J* = 8.8, 5.2, NCH=C*H*), 3.82 (3H, s, OCH_3), 3.26 (1H, d, *J* = 12.8, COCH_aH$_b$), 2.96 (1H, d, *J* = 12.8, COCH$_a$$H_b$), 1.75 (1H, app. dt, *J* = 9.6, 5.2, NCH=CHC*H*), 1.33 (1H, dd, *J* = 9.6, 5.2, NCH=CHCHCH_aH$_b$), 1.35-1.25 (1H, m, NCH=CHCHCH$_a$$H_b$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 170.2 (C), 158.4 (C), 144.0 (C), 128.8 (CH), 128.3 (CH), 127.6 (CH), 127.4 (CH),126.7 (CH), 118.4 (CH), 114.2 (CH), 55.5 (CH_3), 44.1 (CH_2), 36.5 (C),[†] 22.1 (CH), 16.1 (CH_2); *m/z* (ESI) 328.1 ($M+Na^+$), 633.3 ($2M+Na^+$); HRMS calcd for $C_{15}H_{17}NNaO_2^+$ 328.1315, found 328.1313.

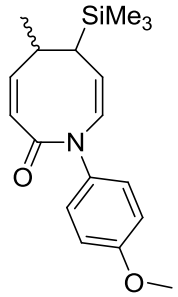
[†]- poor signal to noise, revealed by HMBC.

(3S*,4S*)-1-(4-Methoxyphenyl)-3-(prop-1-enyl)-4-((*E*)-2-(trimethylsilyl)ethenyl)azetidin-2-one 14



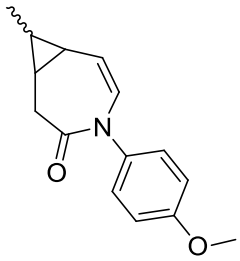
Method as **2:** Aldehyde **1**[1] (0.28 g, 10.0 mmol) and pent-2-enoyl chloride (1.42 g, 12 mmol), column chromatography on silica gel using light petrol/EtOAc (3/1, v/v) as eluent gave lactam **14** as a brown oil as *cis*/t*rans* (1/1) mixture (1.90 g, 63%). υ_{max}/ cm^{-1} 2958, 1735, 1513, 1388, 1248, 840; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35 (4H, d, *J* = 9.1, Ar*H,* Ar*H**), 6.85 (2H, d, *J* = 9.1, Ar*H*), 6.84 (2H, d, *J* = 9.1, ArH), 6.10 (1H, d, *J* = 18.8, Me_3SiCH=CH), 6.09 (1H, d, *J* = 18.8, Me_3SiCH=CH), 5.99 (1H, dd, *J* = 18.8, 6.5, Me_3SiCH=C*H*), 5.97 (1H. dd, *J* = 18.8, 6.5, Me_3SiCH=C*H*), 5.86-5.76 (2H, m, MeC*H*=CH), 5.47 (1H, ddq, *J* = 10.8, 9.0, 1.8, MeCH=C*H*), 5.39 (1H, ddq, J = 15.3, 8.2, 1.4, MeCH=C*H*) 4.62 (1H, app t, *J* = 6.5, NC*H*), 4.58 (1H, app t, *J* = 6.5, NC*H*), 4.39 (1H, dd(d), *J* = 9.0, 6.5, (0.7) COC*H*), 4.05 (1H, ddt, *J* = 8.2, 6.5, 1.0, COC*H*), 3.79 (6H, s, 2xOCH_3), 1.73 (3H, ddd, *J* = 6.9, 1.8, 1.0, CH_3CH=CH), 1.69 (3H, dd, *J* = 6.6, 1.4, CH_3CH=CH), 0.08 (9H, s, $Si(CH_3)_3$), 0.07 (9H, s, $Si(CH_3)_3$) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.8 (C), 155.9 (C), 141.1 (CH), 140.9 (CH*), 136.9 (CH), 136.8 (CH*), 131.9 (C), 131.8 (CH), 130.4 (CH*), 121.7 (CH), 120.4 (CH*), 118.2 (CH), 118/1 (CH*), 114.2 (CH), 59.8 (CH), 59.7 (CH*), 56.8 (CH), 55.4 (CH_3), 52.2 (CH*), 18.1 (CH_3), 13.8 (CH_3*), -1.4(CH_3); *m/z* (ESI) 338.1 ($M+Na^+$); HRMS calcd for $C_{18}H_{25}NNaO_2Si^+$ 338.1547, found 338.1540.

(3*Z*,7*Z*)-1-(4-Methoxyphenyl)-5-methyl-6-(trimethylsilyl)-5,6-dihydroazocin-2(1H)-one 15



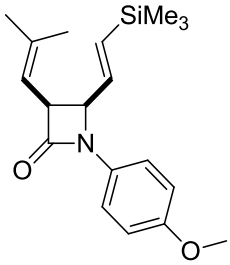
Method as **3**: Azetidinone **14** (1.00 g, 3.15 mmol), column chromatography on silica gel using light petrol/EtOAc ether (2/1, v/v) as eluent to give azocinone **15** as pale yellow oil as a ~1:1 mixture of diastereoisomers (0.54 g, 54%). υ_{max}/ cm^{-1} 3007, 2961, 1656, 1618, 1604, 1510, 1248; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.26-7.21 (2H, m, Ar*H*), 6.92 (2H, m, Ar*H*), 6.21 (1H, d, *J* = 7.5, NC*H*=CH), 5.98 (1H, dd, *J*=13.2, 2.3, COC*H*=CH), 5.63 (1H, dd, *J*= 13.2, 2.3, COCH=C*H*), 5.56 (1H, dd, *J*= 11.6, 7.5, NCH=C*H*), 3.81 (3H, s, OCH_3), 2.86-2.76 (1H, m, C*H*Si), 2.31 (1H, dd, *J* = 11.6, 3.2, C*H*Si) 1.15 (1H, d, *J* = 6.7, CH_3CH), 1.09 (1H, d, J = 7.5 CH_3CH*), 0.14 (9H, s, (CH_3)$_3$), 0.13 (9H, s, (CH_3)$_3$*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.1 (C), 158.0 (C), 139.3 (CH), 132.9 (C), 131.3 (CH), 127.2 (CH), 123.3 (CH), 122.0 (CH), 114.2 (CH), 55.4 (OCH_3), 36.0 (CH), 27.0 (CH), 20.9 (CH*C*H$_3$), 18.7 (CH*C*H$_3$*), -1.87 ($SiCH_3$); *m/z* (ESI) 316.1 $(M+H^+)$, 338.1 $(M+Na)^+$, 631.3 $(2M+H)^+$, 653.3 $(2M+Na)^+$. 968.5 $(3M+Na)^+$; HRMS calcd for $C_{18}H_{26}NO_2Si^+$ 316.1727, found 316.1728.

4-(4-Methoxyphenyl)-8-methyl-4-azabicyclo[5.1.0]oct-5-en-3-one 16



Method as **4**: azocinone **15** (0.30 g, 9.46×10^{-1} mmol), chromatography on silica gel using light petrol/EtOAc (1/1, v/v) as eluent gave the product **16** as a pale yellow oil as a mixture of two diastereoisomers (~2:1 ratio by ^{1}H NMR by relative integration) (0.21 g, 90%). υ_{max}/ cm^{-1} 3011, 1659, 1510, 1247, 1057, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.20 (2H, d, *J* = 8.9, Ar*H**), 7.15 (2H, d, *J* = 9.1, Ar*H*), 6.90 (2H, d, *J* = 8.9, Ar*H**), 6.89 (2H, d, *J* = 9.1, Ar*H*), 5.98 (1H, dd, *J* = 8.6, 2.2, NC*H*=CH*), 5.76 (1H, dd, *J* = 8.7, 0.6, NC*H*=CH**),** 5.65 (1H, dd, *J* = 8.9, 4.5, NCH=C*H*), 5.46 (1H, ddd, *J* = 8.6, 1.8, 0.8, NCH=C*H**), 3.81 (3H, s, OCH_3*), 3.80 (3H, s, OCH_3), 2.88 (1H, dd, *J* = 12.7, 3.4, CH_aH$_b$), 2.62 (1H, dd, *J* = 12.7, 9.0, CH$_a$*H*$_b$), 2.58 (1H, dd, *J* = 12.9, 6.4 CH_aH$_{b*}$), 2.55 (1H, dd, *J* = 12.9, 9.8, CH$_a$*H*$_{b*}$), 1.65-1.51 (2H, m, CH_2C*H** and CH=CHC*H**), 1.49-1.40 (1H, m, CH_2C*H*), 1.15-1.10 (1H, obs. m, CH=CHC*H*), 1.12 (3H, d, *J* = 6.1, CH_3*), 1.10 (3H, d, *J* = 6.9, CH_3), 0.95-0.80 (2H, m, C*H*CH_3, C*H*CH_3*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.2 (C=O*), 171.9 (C=O), 158.1 (C,C*), 134.2 (ArC*), 134.0 (ArC), 133.4 (NC*H*=CH*), 128.2 (NC*H*=CH), 127.8 (ArCH*), 127.6 (ArCH), 119.2 (NCH=*C*H), 116.9 (NCH=*C*H*), 114.2 (ArCH*), 114.1 (ArCH), 55.41 (CH_3, CH_3*), 38.0 (CH_2), 32.5 (CH_2*), 28.1 (CH), 21.0 (CH), 17.9 (CH_3), 17.0 (CH*), 15.9 (CH), 15.1 (CH*), 8.10 (CH_3*), 7.55 (CH*); *m/z* (ESI) 244.1 ($M+H^+$), 266.1 ($M+Na^+$), 509.2 ($2M+Na^+$); HRMS calcd for $C_{15}H_{17}NNaO_2^+$ 266.1151, found 266.1148.

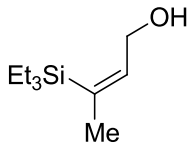
(3*S,4*S**)-1-(4-Methoxyphenyl)-3-((*E*)-3-methylbut-1-en-1-yl)-4-((*E*)-2-(trimethylsilyl)vinyl)azetidin-2-one 17**



Method as **2:** Aldehyde **1**[1] (325 mg, 2.50 mmol) and 4-methylpent-2-enoyl chloride,[4] column chromatography on silica gel eluting with petroleum ether: ethyl acetate 10:1 v:v afforded the title compound as a ~4 *syn* :1 *anti* mixture of diastereoisomers a yellow oil (167 mg, 20%).

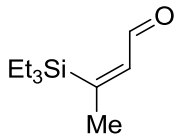
IR ($CHCl_3$) ν (cm^{-1}): 3009, 2959, 1733, 1513, 1248; for major diastereoisomer ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.36 (2H, d, *J* 9.2, Ar*H*), 6.87 (2H, d, *J* 9.2, Ar*H*), 6.06 (1H, d, *J* 18.8, TMSC*H*=CH), 5.96 (1H, dd, *J* 18.8, 6.6, THSCH=C*H*), 5.24 (1H, d, *J* 9.1, $(CH_3)_2$C=C*H*), 4.61 (1H, app. t, *J* 6.1, NC*H*), 4.30 (1H, dd, *J* 9.1, 6.1, COC*H*), 3.80 (3H, s, OCH_3), 1.77 (3H, s, CH_3), 1.68 (3H, s, CH_3), 0.08 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.4 (C), 155.8 (C), 141.4 (CH), 138.8 (C), 136.4 (CH), 132.0 (C), 118.1 (CH), 114.8 (CH), 114.2 (CH), 60.0 (CH), 55.4 (CH_3), 53.3 (CH), 25.6 (CH_3), 18.7 (CH_3), -1.3 (CH_3); MS (ESI) m/z (M+Na) expected: 352.1709, found: 352.1709, (2M+Na): expected: 681.3520, found: 681.3527.

(*Z*)-3-(Triethylsilyl)but-2-en-1-ol[5]



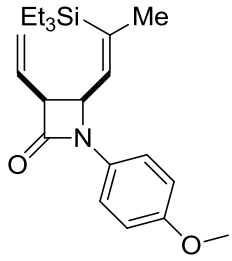
$[Cp^*Ru(CNCH_3)_3]^+PF_6^-$ (123 mg, 7.50×10^{-5} mol) was added to a solution of 2-butyn-1-ol (3.43 g, 48.9 mmol) and triethylsilane (6.83 g, 58.7 mmol) in acetone (50 mL) at 0 ºC, then warmed to room temperature. After stirring 30 mins, the mixture was concentrated and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (2/1, v/v) as eluent to give product as colourless oil (6.80 g, 75%) yield. υ_{max}/ cm^{-1} 3451, 2956, 1615, 982; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.21 (1H, tq, *J* = 6.8, 1.5, C=C*H*), 4.12 (2H, d, *J* = 6.8, CH_2OH), 1.80 (3H, d, *J* = 1.5, CH_3), 0.92 (9H, t, *J* = 7.9, Si(CH_3)$_3$), 0.65 (6H, q, *J* = 7.9, Si(CH_2)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 141.4 (CH), 136.9 (C), 62.1 (CH_2), 25.2 (CH_3), 7.4 (CH_3), 4.0 (CH_2); *m/z* (ESI) 209.1 ($M+Na^+$); HRMS calcd for $C_{10}H_{22}NaOSi^+$ 209.1332, found 209.1337.

(*Z*)-3-(Triethylsilyl)but-2-enal



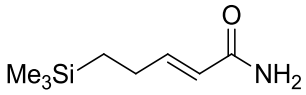
(*Z*)-3-(Triethylsilyl)but-2-enol (6.00 g, 32.3 mmol) and MnO_2 (56.1 g, 645 mmol) were dissolved in CH_2Cl_2 (120 mL). The resulting mixture was stirred at room temperature for 16 hrs. MnO_2 was then removed by filtrating the mixture from celite (6 cm pack) and the filtrate was reduce to give crude product as colourless oil (5.20 g, 88%). υ_{max}/ cm^{-1} 2959, 1681, 1663, 1166, 1006; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.80 (1H, d, *J*= 8.5, C*H*O), 6.58 (1H, dq, J_1= 8.5, 1.6, C=C*H*CHO), 2.11 (3H, d, J = 1.6, CH_3), 1.02-0.97 (9H, m, 3×CH_3Si), 0.80 (6H, dq, J_1= 8.0, 1.2, Si(CH_2)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 192.9 (CHO), 167.5 (C), 143.5 (CH), 26.9 (CH_3), 7.3 (CH_3), 4.6 (CH_2); *m/z* (ESI) 207.1 (M + Na^+); HRMS calcd for $C_{10}H_{20}NaOSi^+$ 207.1176, found 207.1188.

(3*S, 4*S**)-1-(4-Methoxyphenyl)-4-((*Z*)-2-(triethylsilyl)prop-1-enyl)-3-ethenylazetidin-2-one 18**



Method as **2:** (*Z*)-3-(Triethylsilyl)but-2-enal (0.92 g, 5.00 mmol), column chromatography on silica gel using light petrol/EtOAc (3/1, v/v) as eluent to give product as yellow oil (1.15 g, 64%). υ_{max}/ cm^{-1} 2957, 1735, 1513, 1387, 1247, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39 (2H, d, *J* = 9.2, Ar*H*), 6.85 (2H, d, *J* = 9.2, Ar*H*), 6.09 (1H, app. dq, *J*= 10.0, 1.5, C=C*H*), 5.81-5.77 (1H, ddd, *J*= 17.1, 10.4, 8.0, CH_2=C*H*), 5.32 (1H, dt, *J*= 17.1, 1.5, C$H_a$$H_b$=CH), 5.32 (1H, dt, *J*= 10.4, 1.5, C$H_a$$H_b$=CH), 4.81 (1H, dd, *J*= 10.0, 6.0, NC*H*), 4.07 (1H, ddt, *J*= 8.0, 6.0, 1.0 COC*H*), 3.80 (3H, s, OCH_3), 1.90 (3H, s, CH_3), 1.04-0.96 (9H, m, Si(CH_2CH_3)$_3$), 0.81-0.71 (6H, m, Si(C$H_2$$CH_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.8 (C), 156.0 (C), 141.8 (C), 139.2 (CH), 131.8 (C), 129.0 (CH), 120.5 (CH_2), 118.3 (CH), 114.2 (CH), 58.2 (CH), 56.4 (CH), 55.5 (CH_3), 25.7 (CH_3), 7.4 (CH_3), 3.8 (CH_2); *m/z* (ESI) 358.2 ($M+H^+$), 380.2 ($M+Na^+$), 715.4 ($2M+H^+$), 737.4 ($2M+Na^+$), 1094.6 ($3M+Na^+$); HRMS calcd for $C_{21}H_{31}NNaO_2Si^+$ 380.2016, found 380.2014.

(*E*)-5-(Trimethylsilyl)pent-2-enamide 22



Grubbs-Hoveyda II metathesis initiator (38.0 mg, 3 mol%) was added to a solution of acrylamide (142 mg, 2.00 mmol) and but-3-en-1-yltrimethylsilane[6] (0.70 mL, 4.00 mmol) in anhydrous dichloromethane (6 mL) and heated at reflux for 24 hours. The reaction was concentrated and purified column chromatography on silica gel eluting with petroleum ether: ethyl acetate 1:2 v:v to give the title compound as a clear glass (134 mg, 40%).

IR ($CHCl_3$) ν (cm^{-1}): 3530, 3414, 3008, 1681, 1642; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.95 (1H, dt, *J* 15.3, 6.5, COCH=C*H*), 5.86 (1H, d, *J* 15.3, COC*H*=CH), 5.72 (2H, br.s, NH_2), 2.23 (2H, ddd, *J* 17.0, 6.5, 1.6, CH=CHCH_2), 0.69 (2H, d, *J* 17.0, CH_2Si(CH_3)$_3$), -0.03 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 168.2 (C), 148.9 (CH), 121.3 (CH), 26.5 (CH_2), 15.0 (CH_2), -1.7 (CH_3); MS (ESI) m/z (M+Na) expected: 194.0972, found: 194.0968.

References:

(1) J. Robichaud and F. Tremblay, *Org. Lett.* 2006, **8**, 597-600.
(2) B. Alcaide, Y. Martín-Cantalejo, J. Pérez-Castells, J. Rodríguez-López and M. A. Sierra, *J. Org. Chem.* 1992, **57**, 5921-5931.
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(4) T. Yasuhiro, T. Akira, *Bull. Chem. Soc. Jpn.,* 1987, **60**, 3039-3040.
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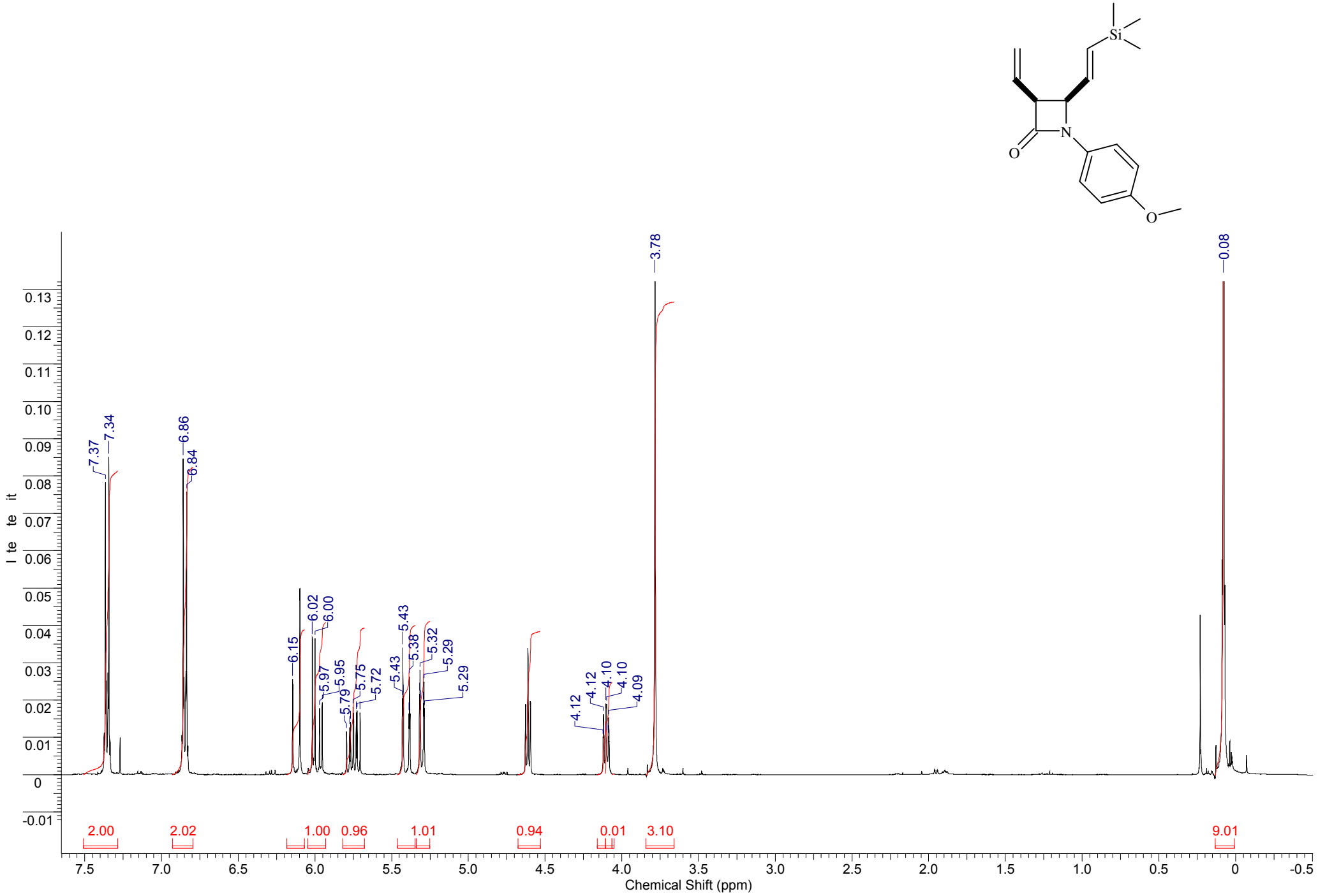
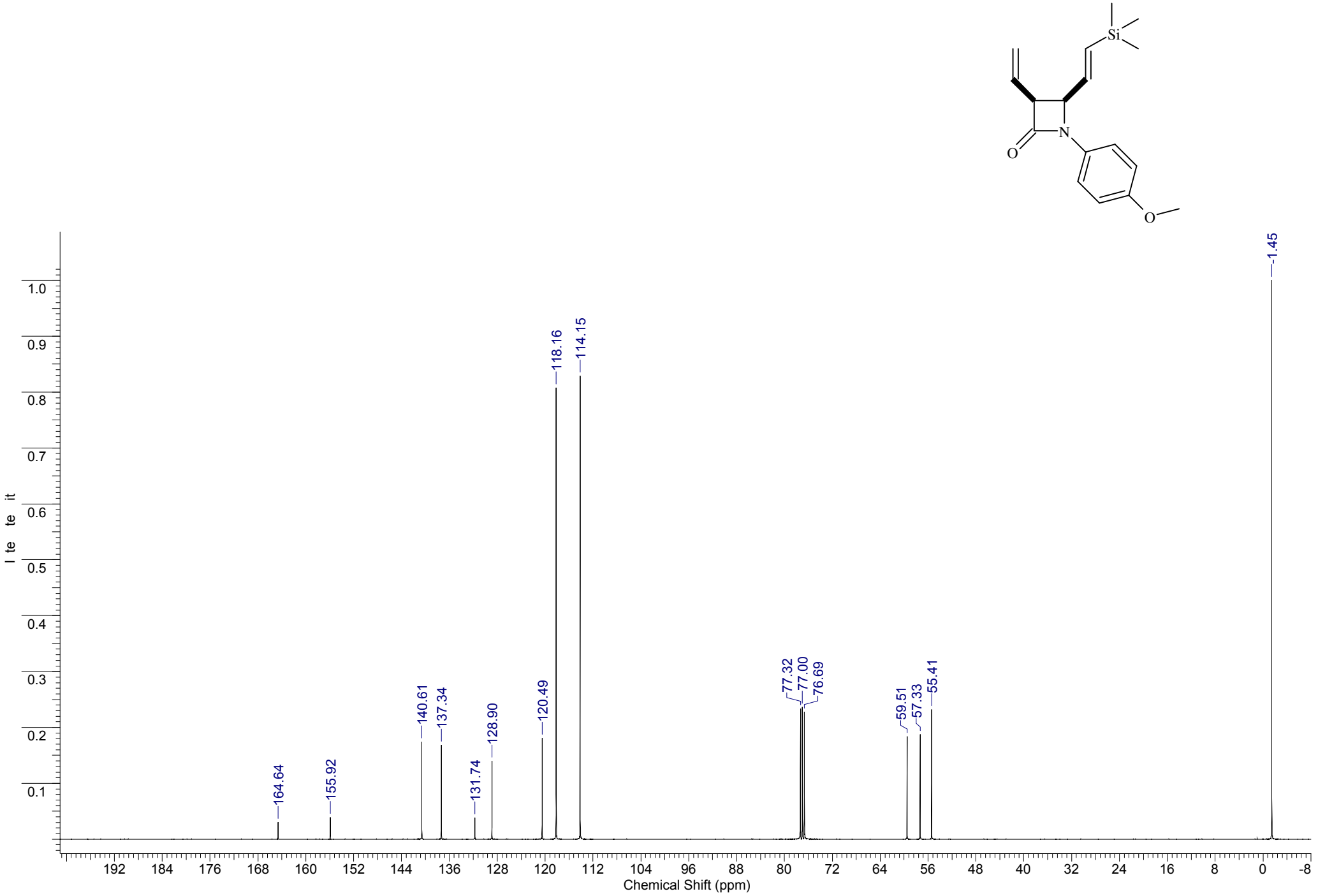
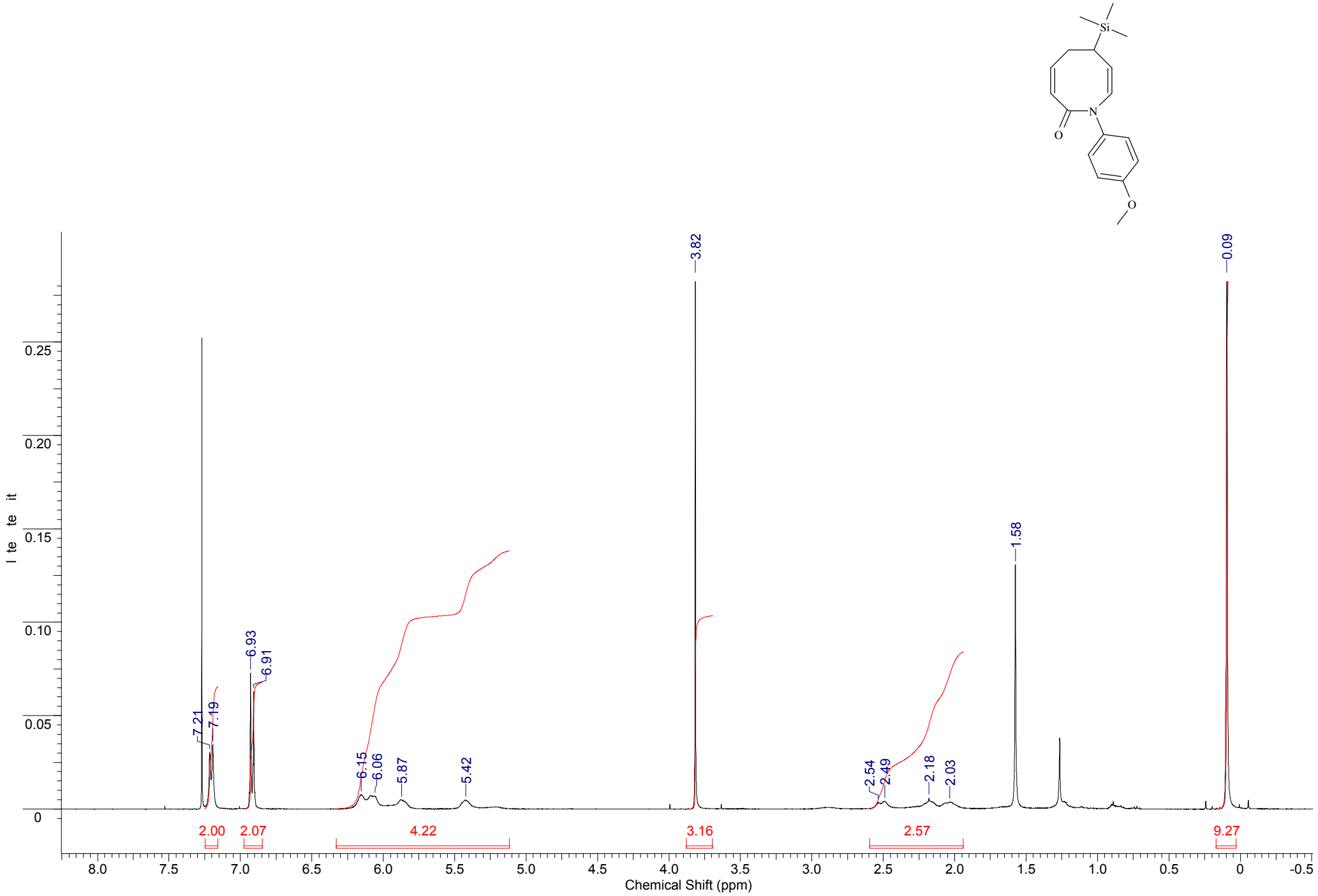
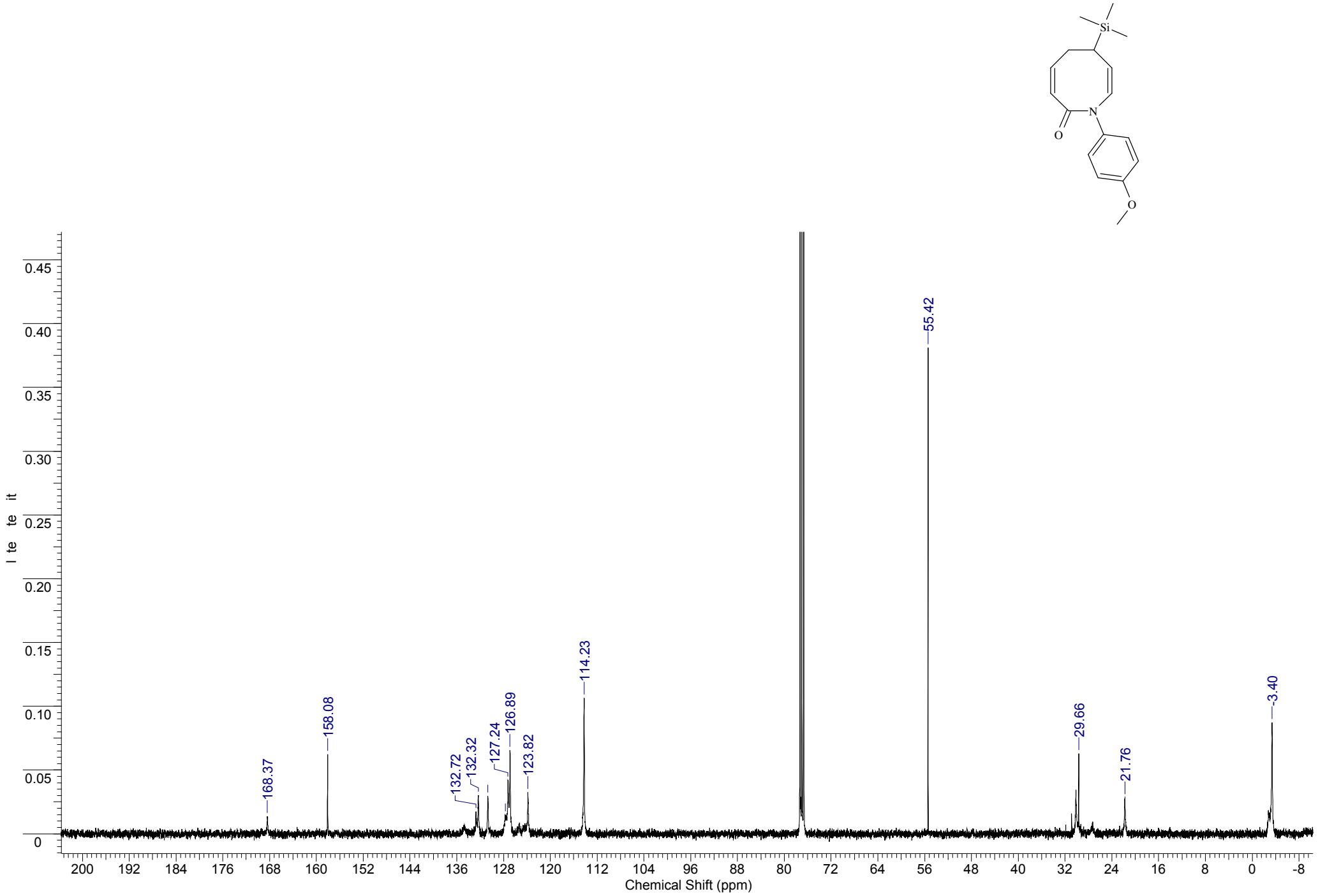
(6) S. H. Lipponen and J. V. Seppala, *Organometallics*, 2011, **30**, 528-33.









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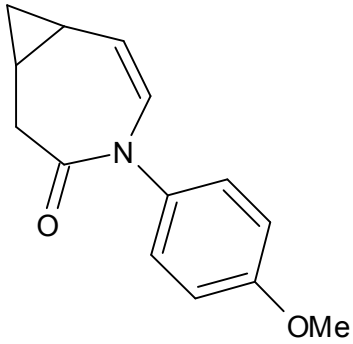

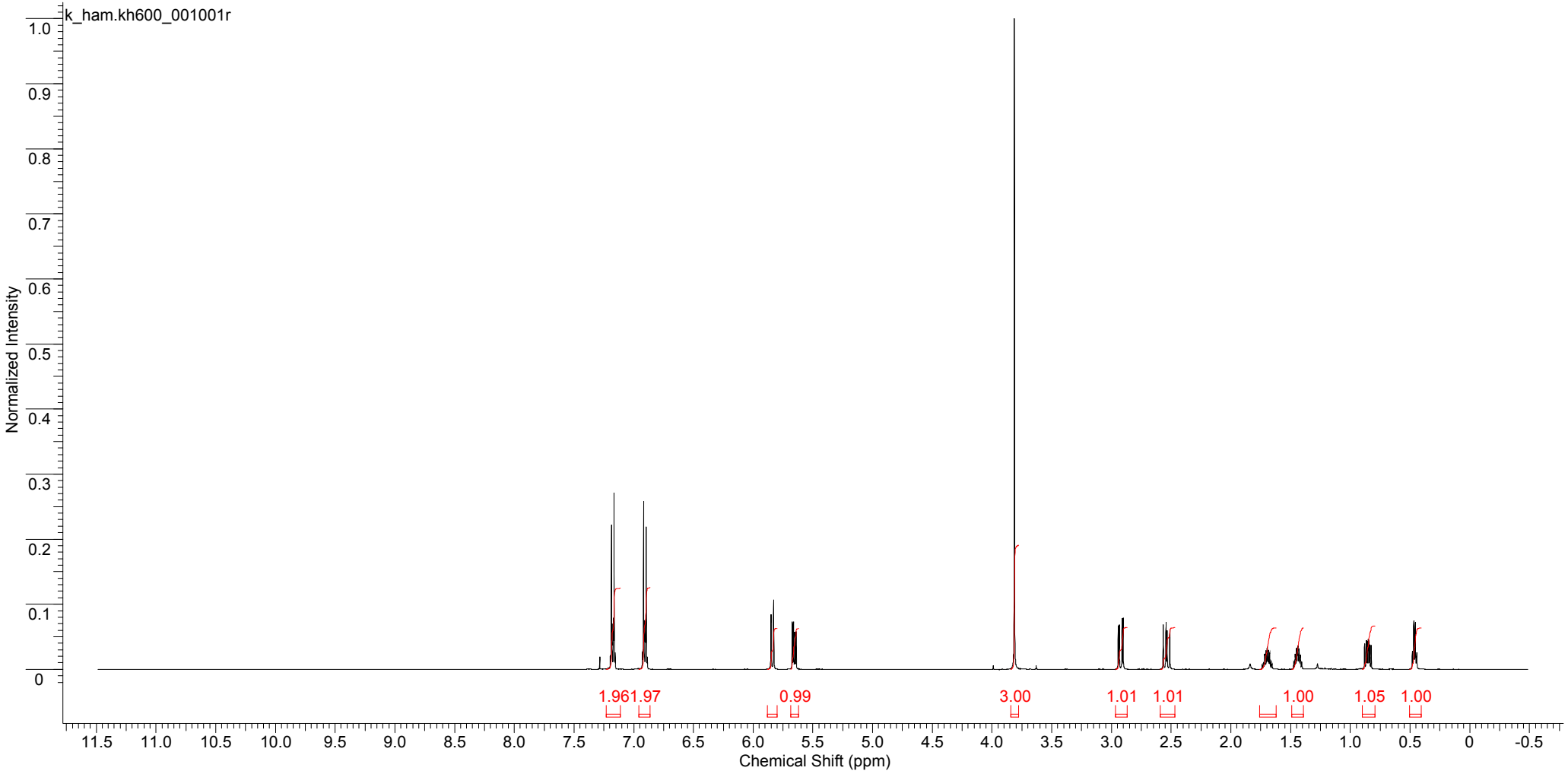

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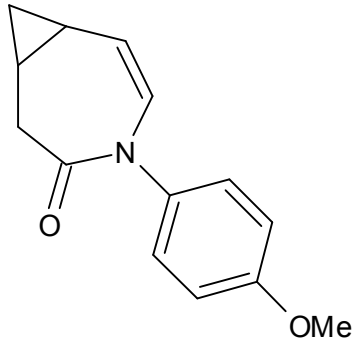

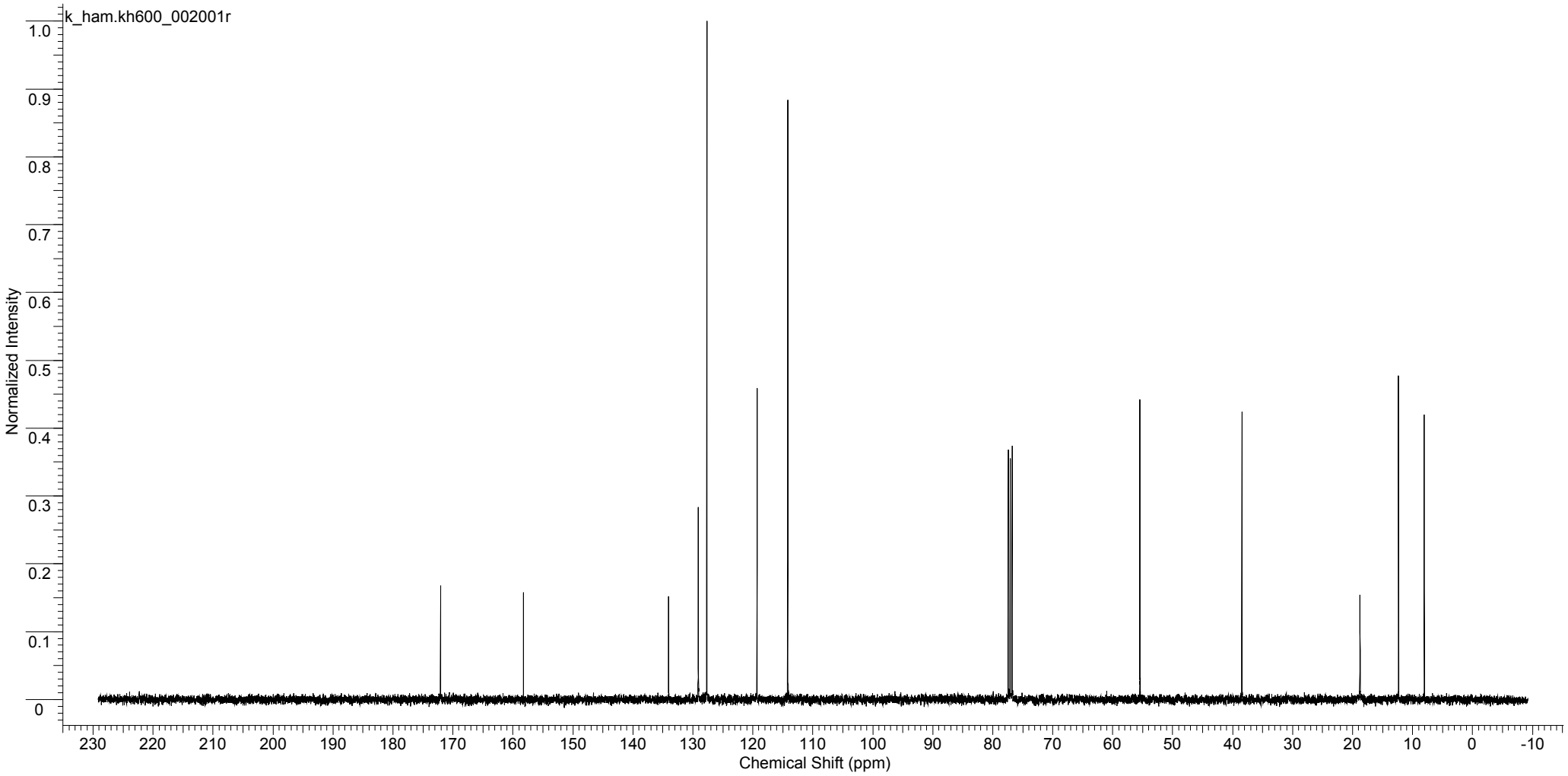

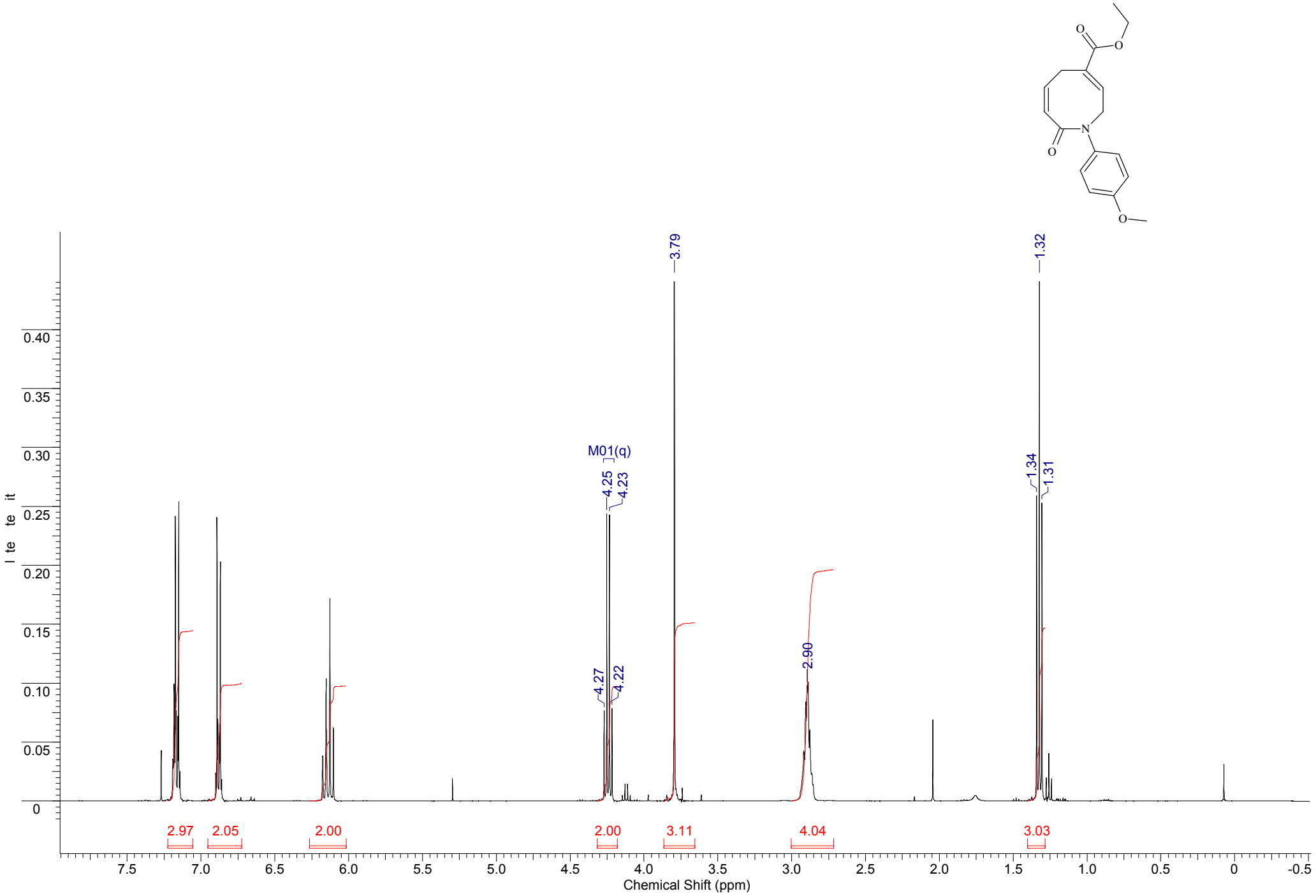

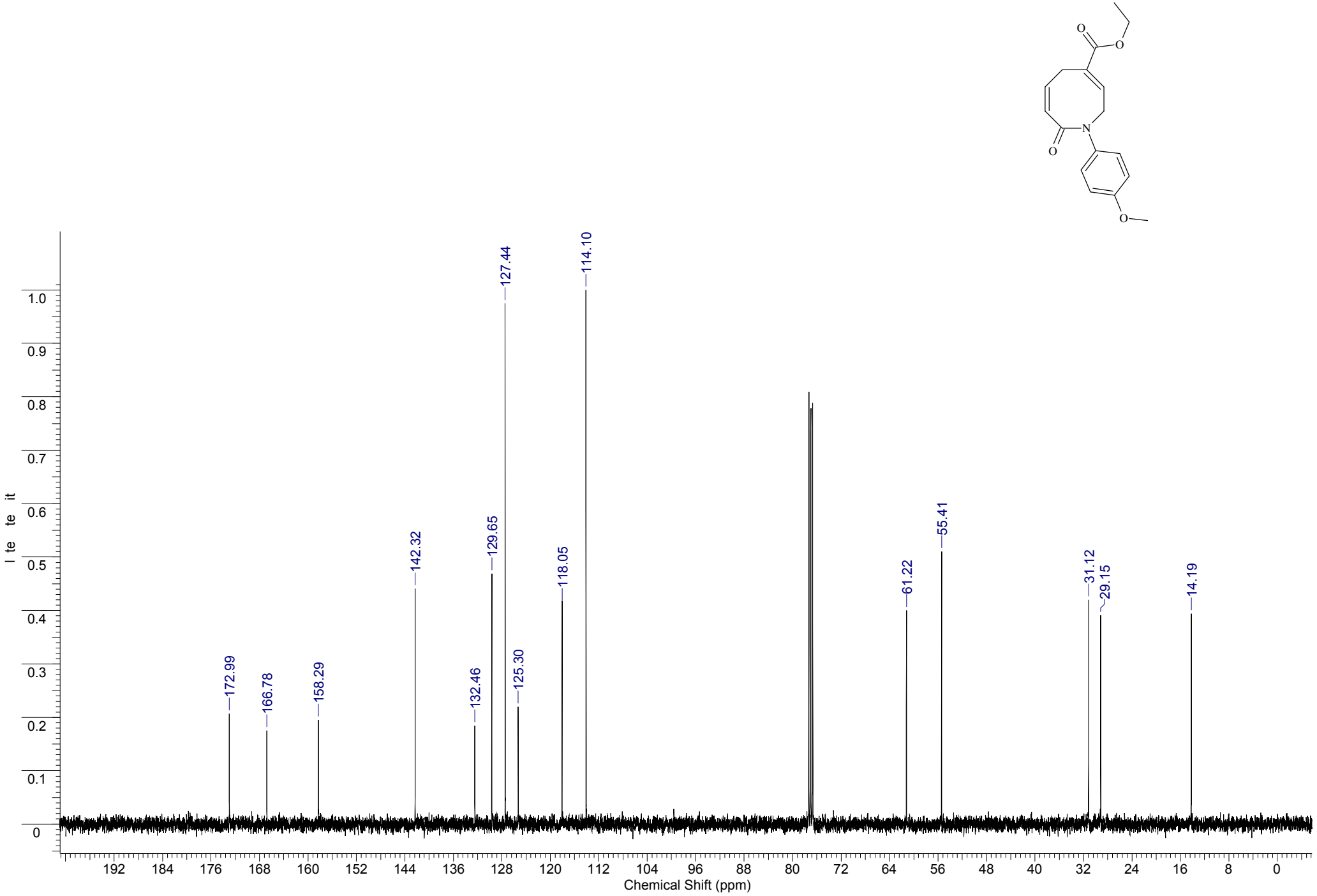

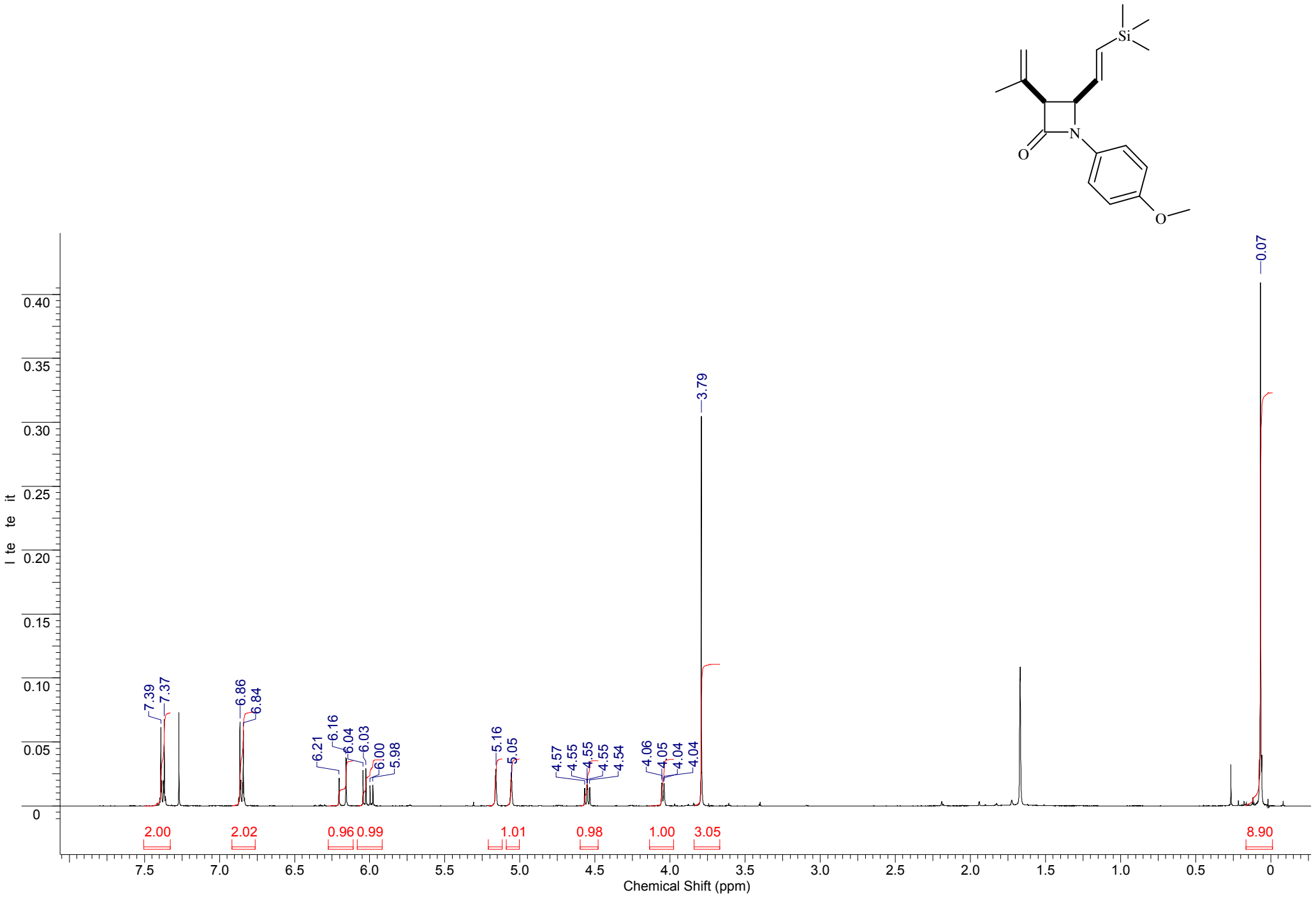

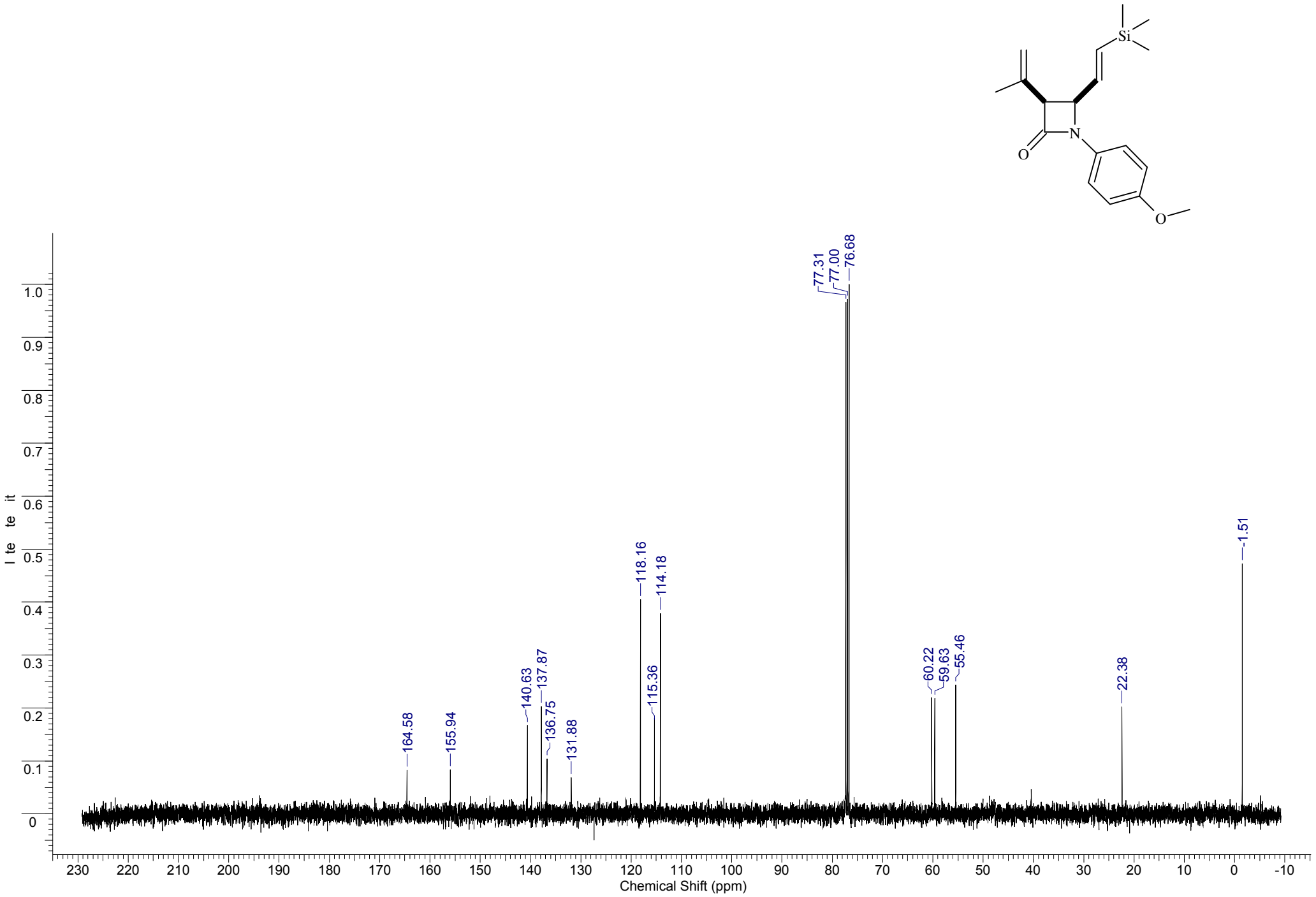

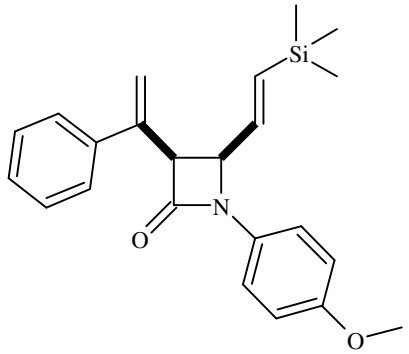

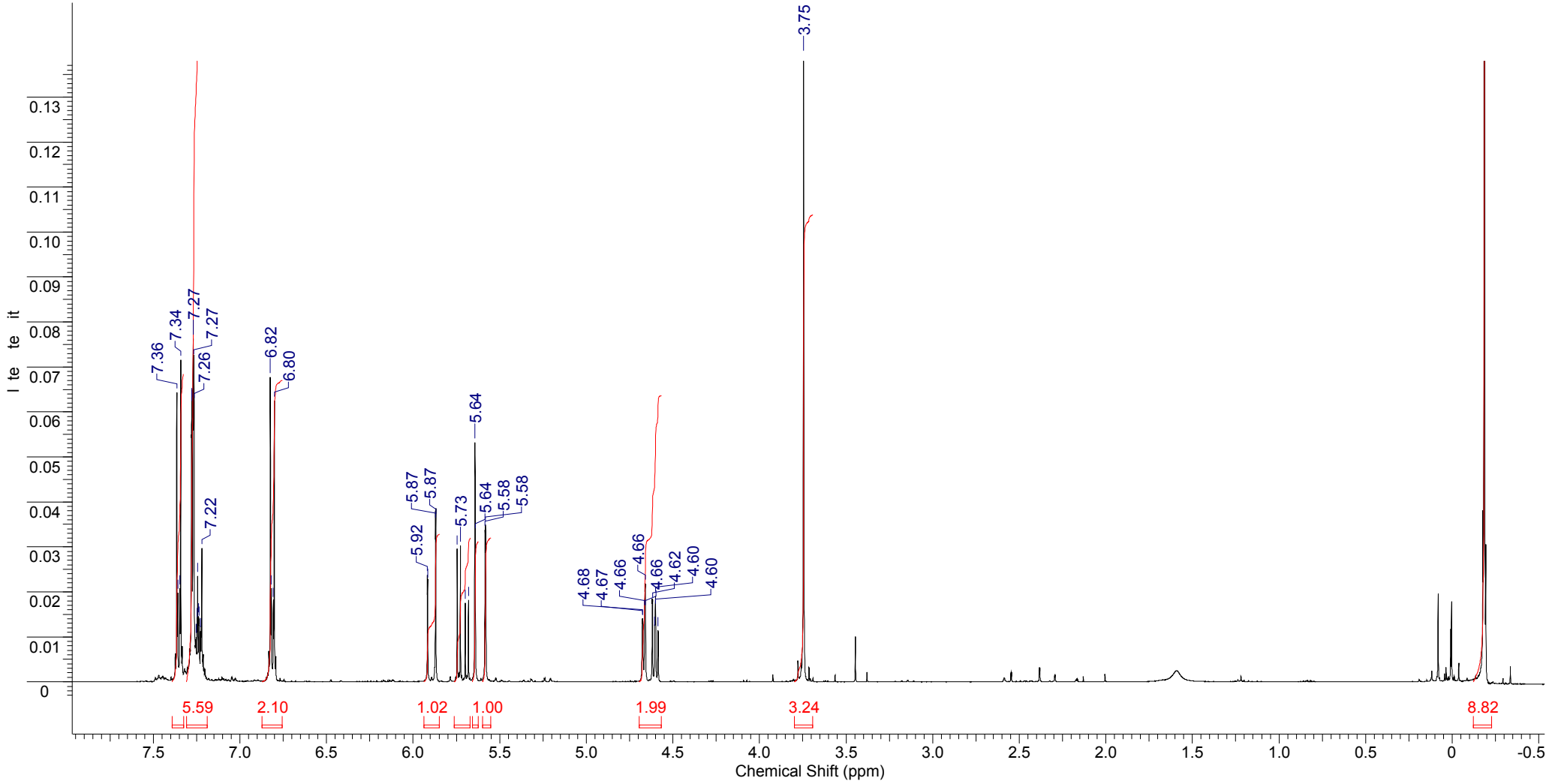

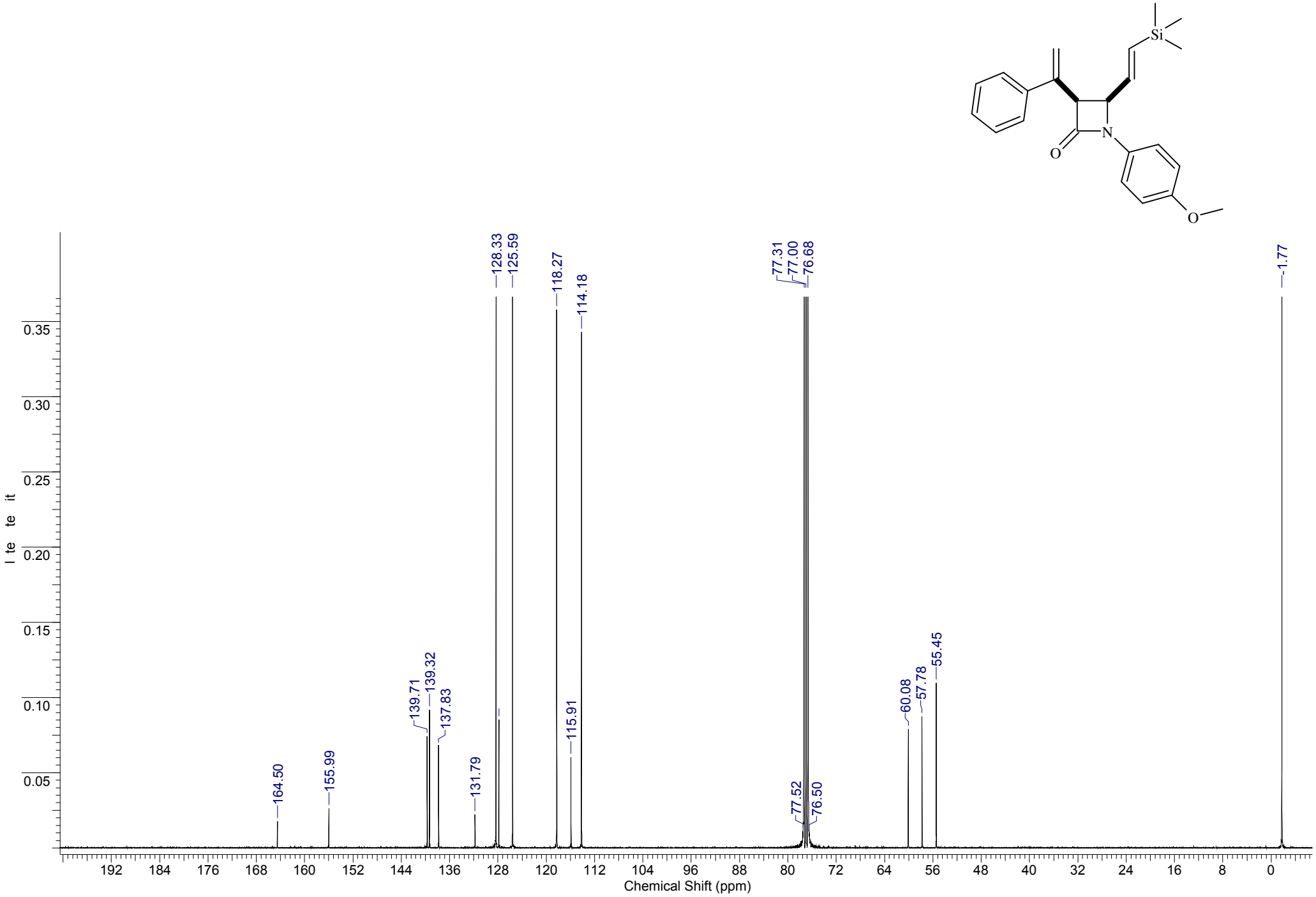

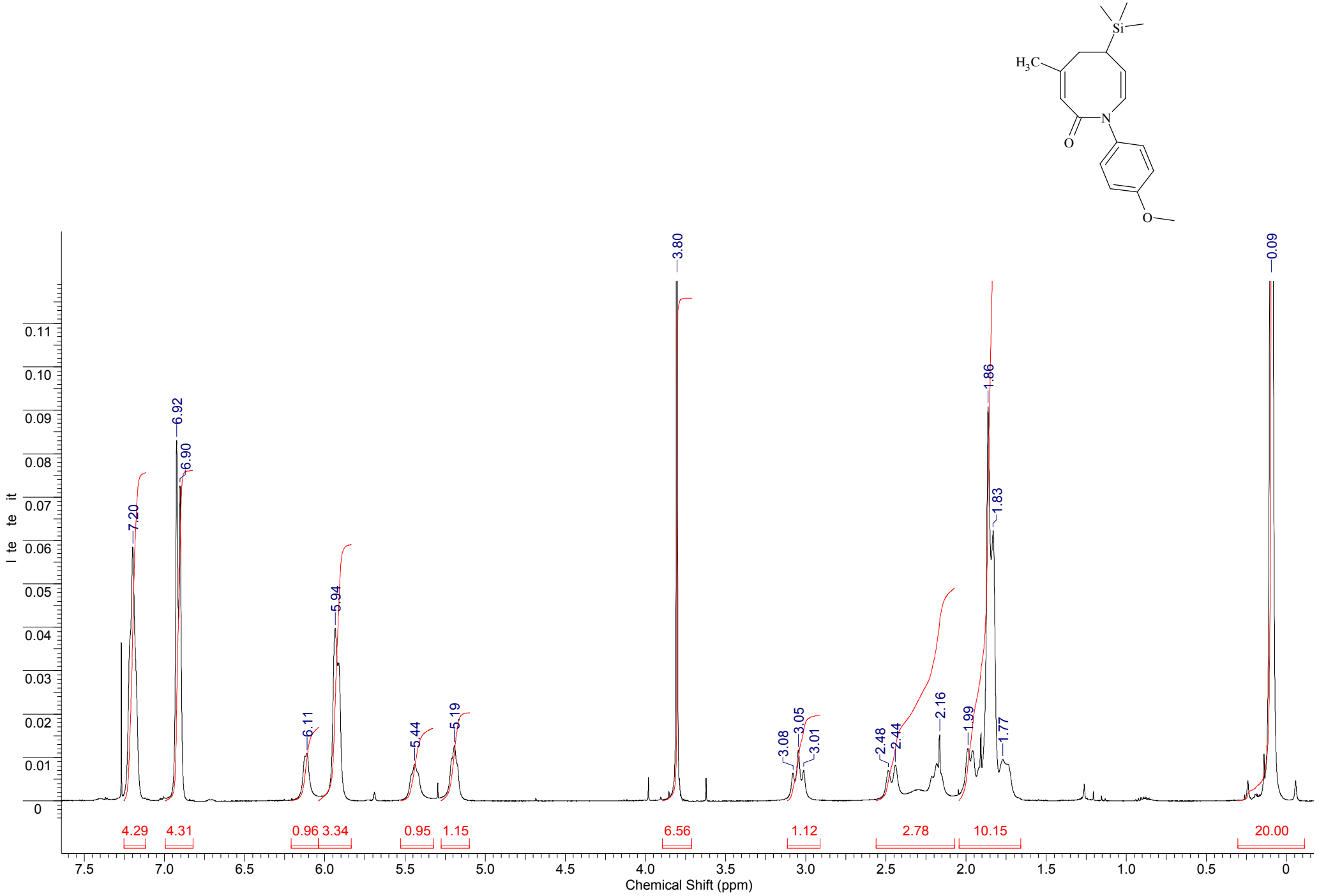

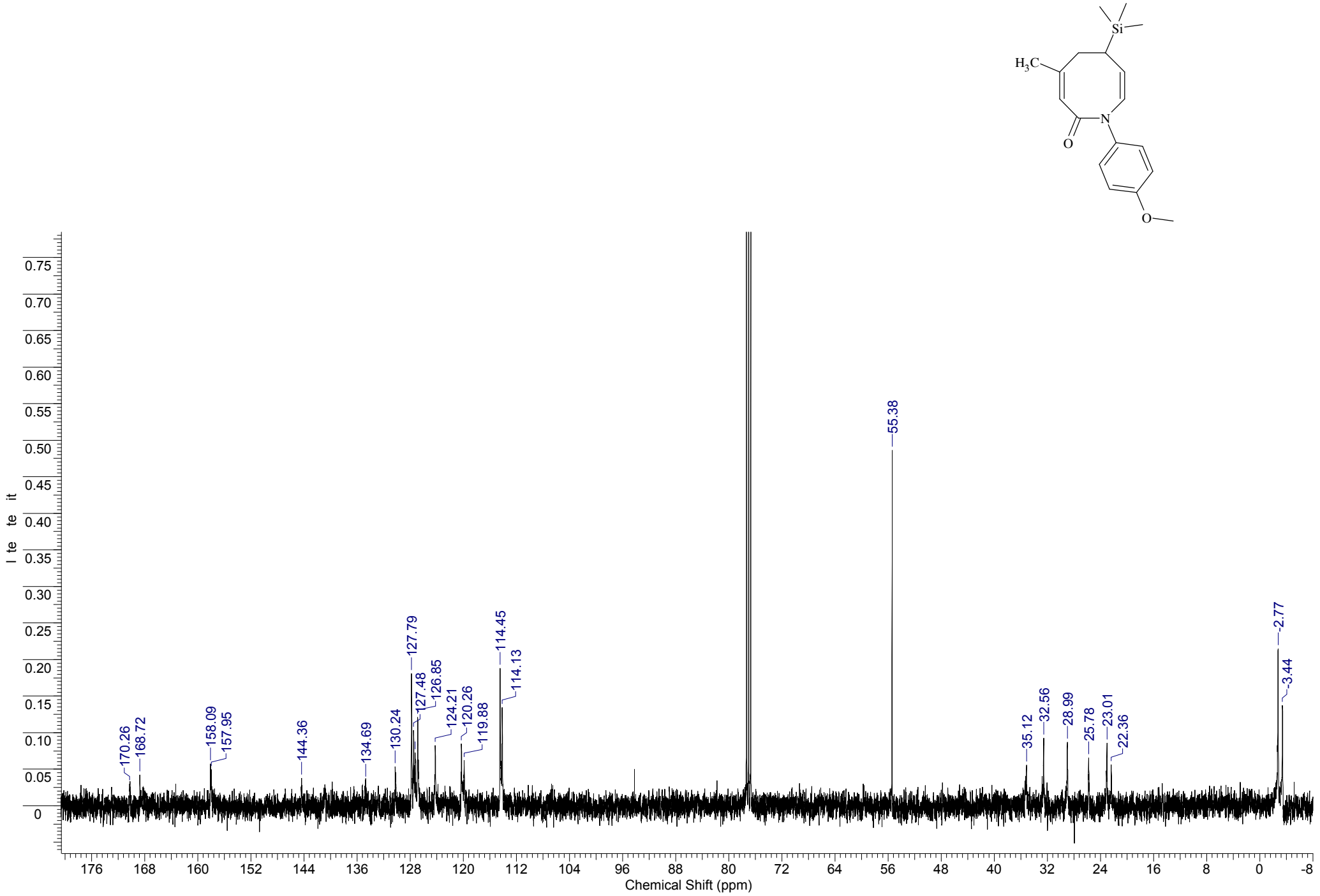

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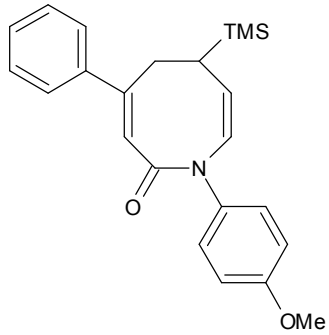


b_you.by614p_001001r

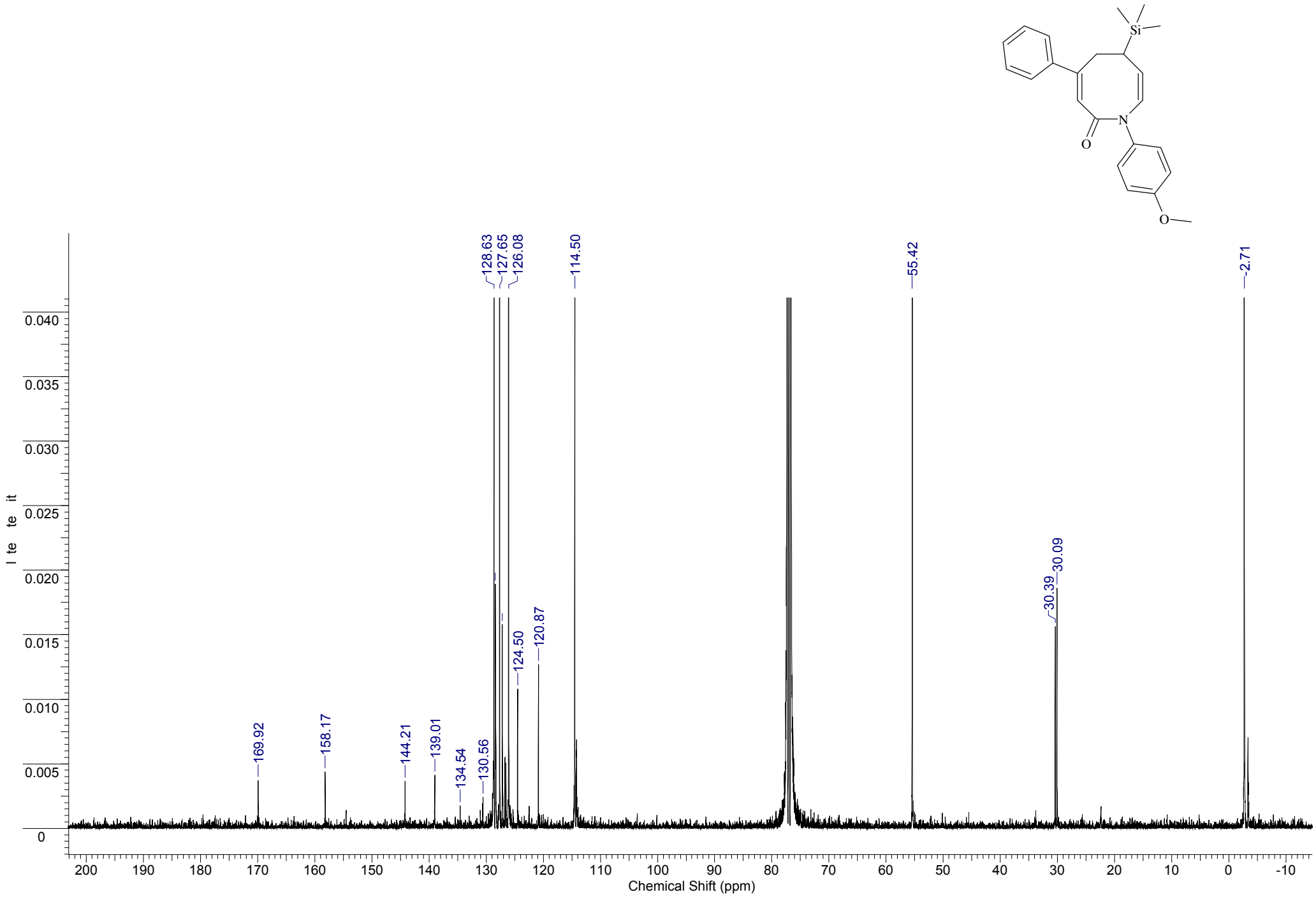
Absolute Intensity

0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0

7.14 1.95 0.65 0.66 0.66 3.00 0.65 0.66 0.67 8.81

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5

Chemical Shift (ppm)



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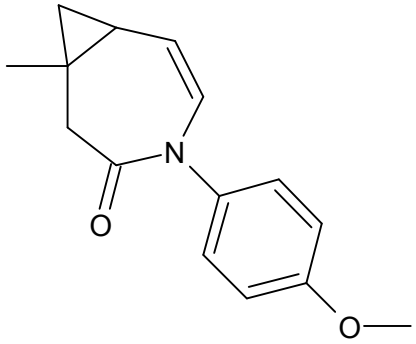

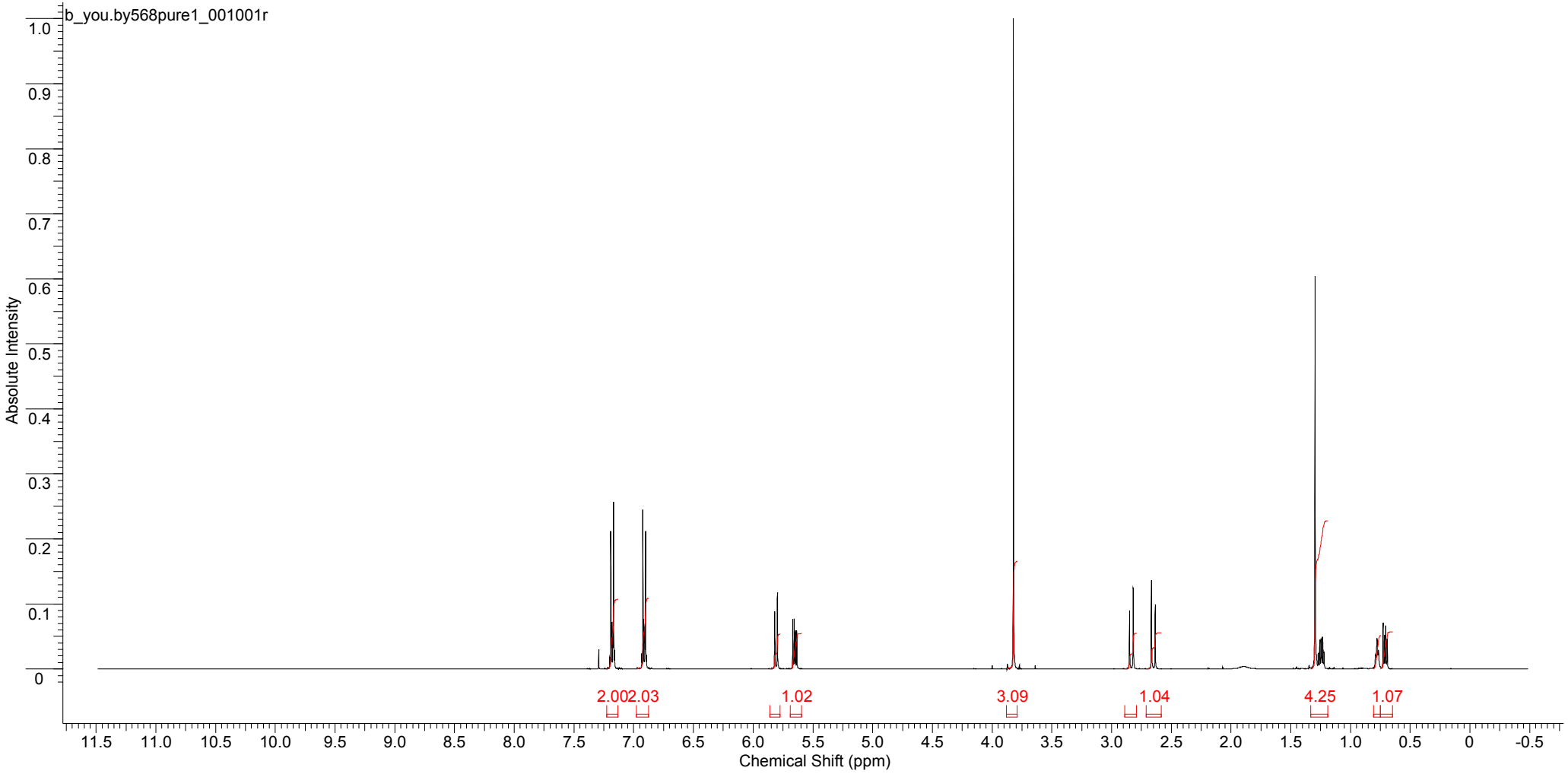

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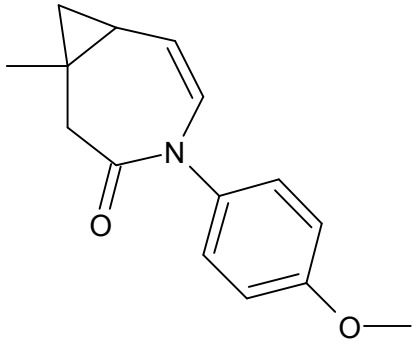


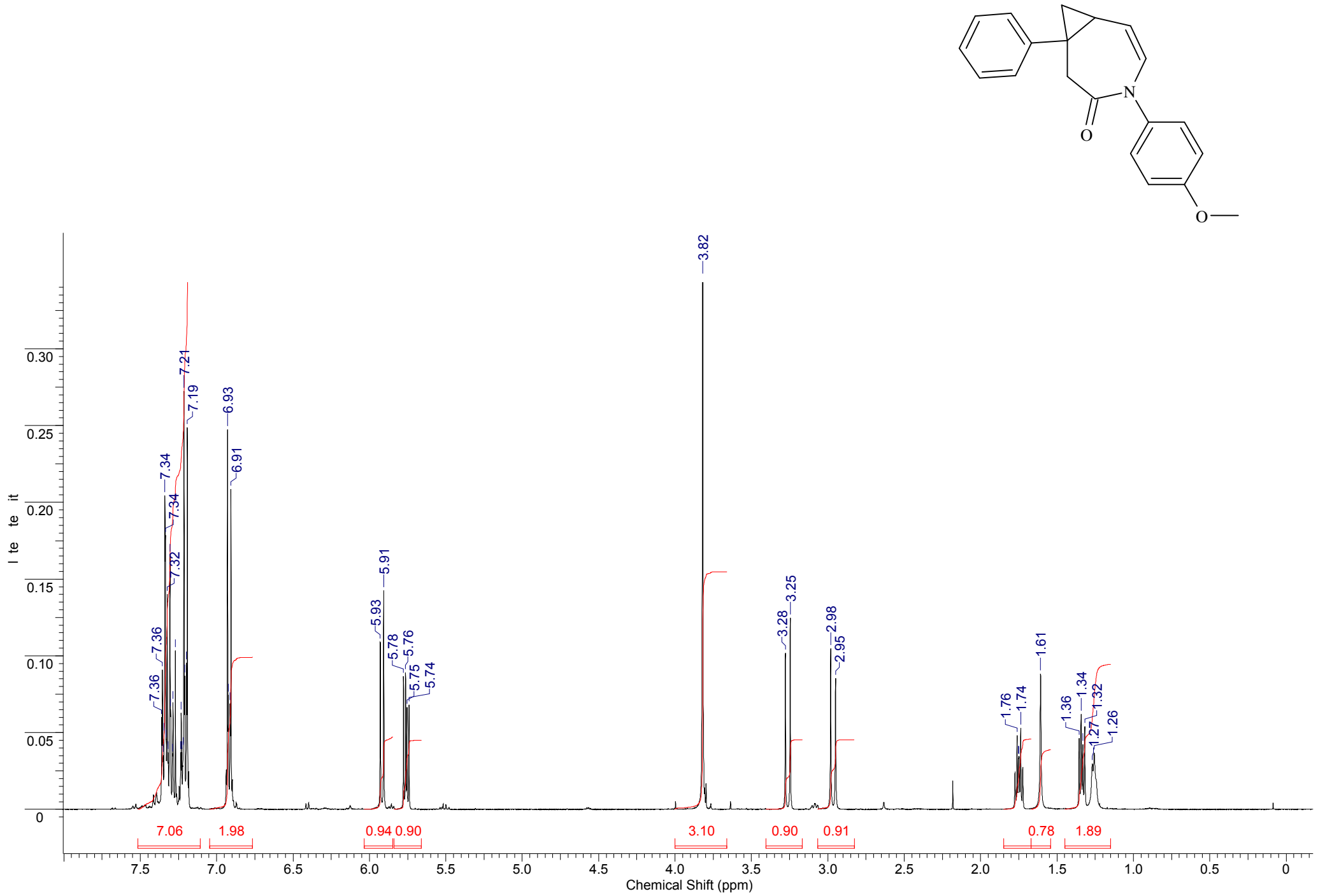
b_you.by568pure1_002001r

Absolute Intensity

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

Chemical Shift (ppm)



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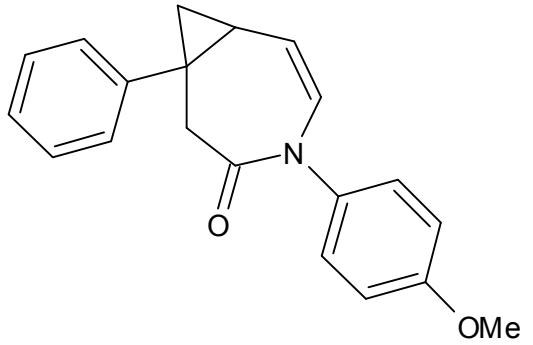
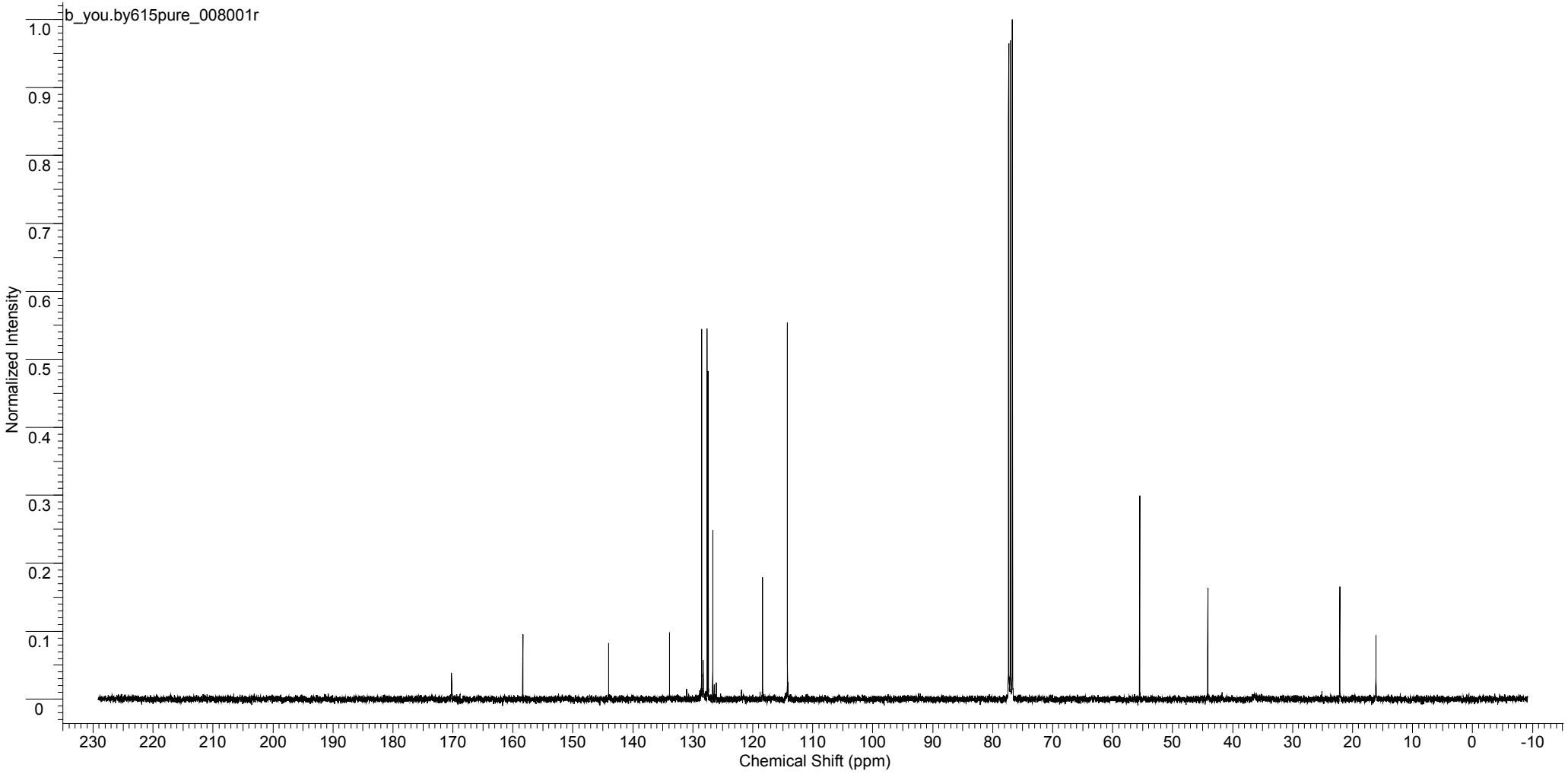
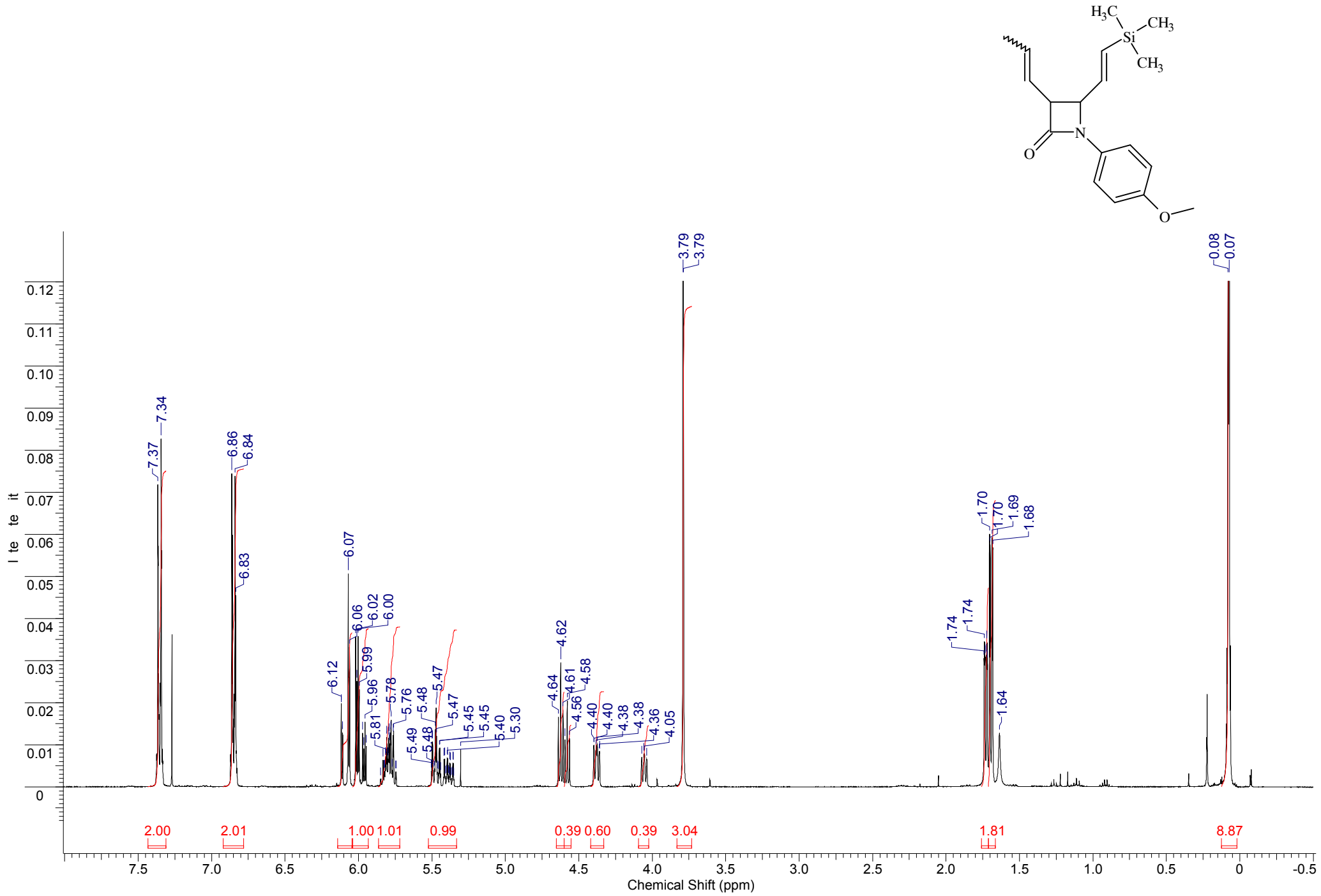
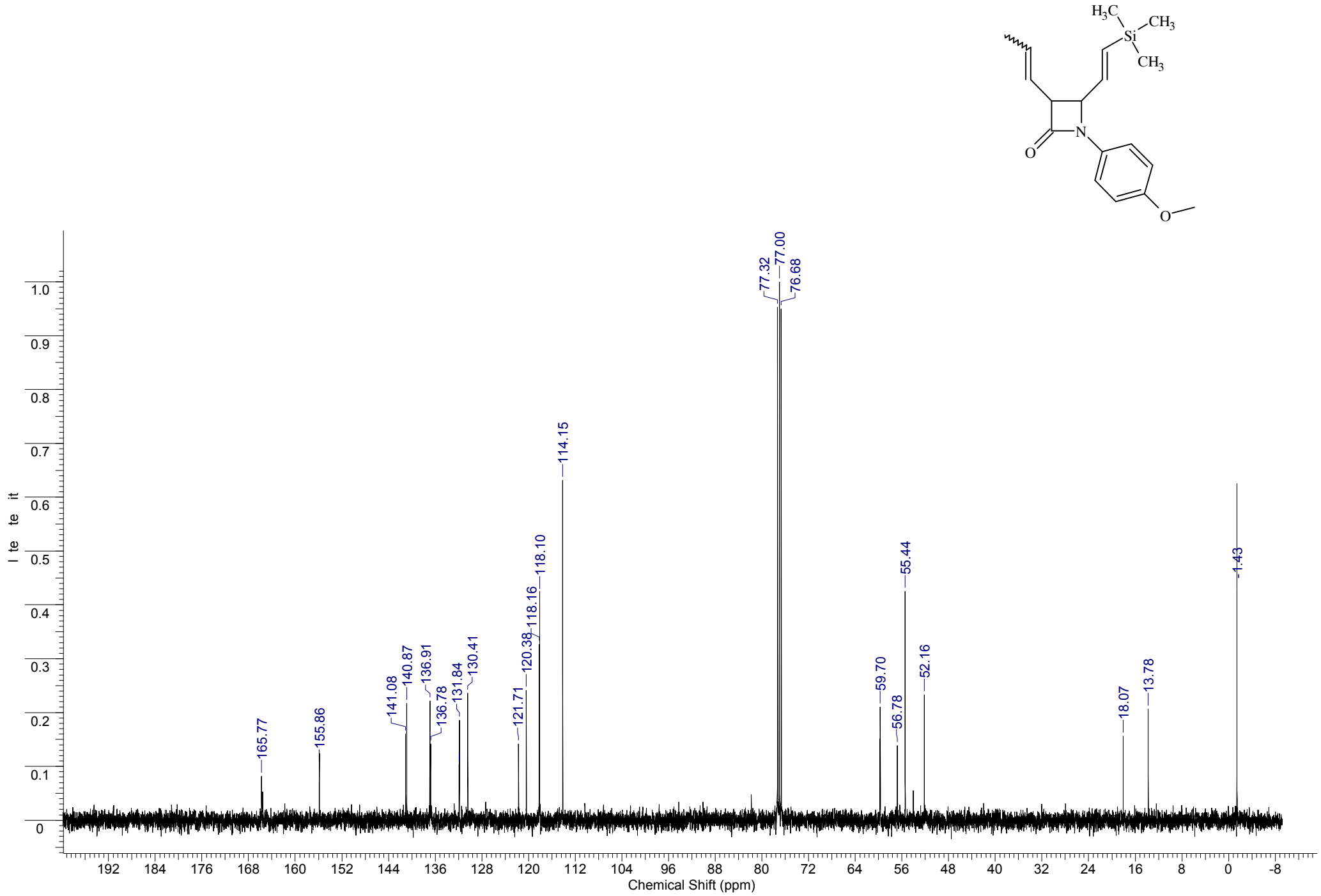
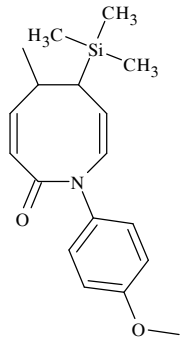


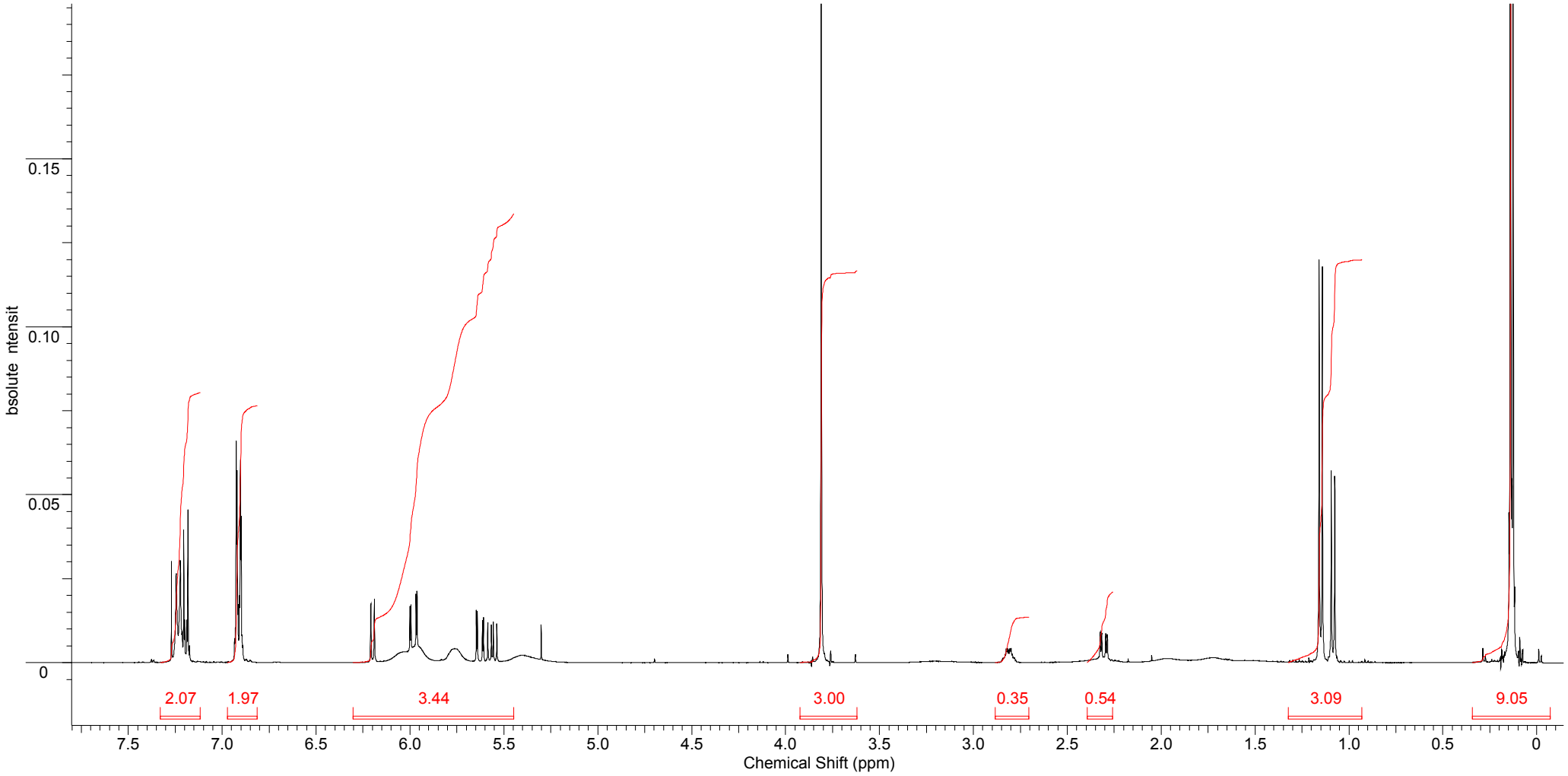


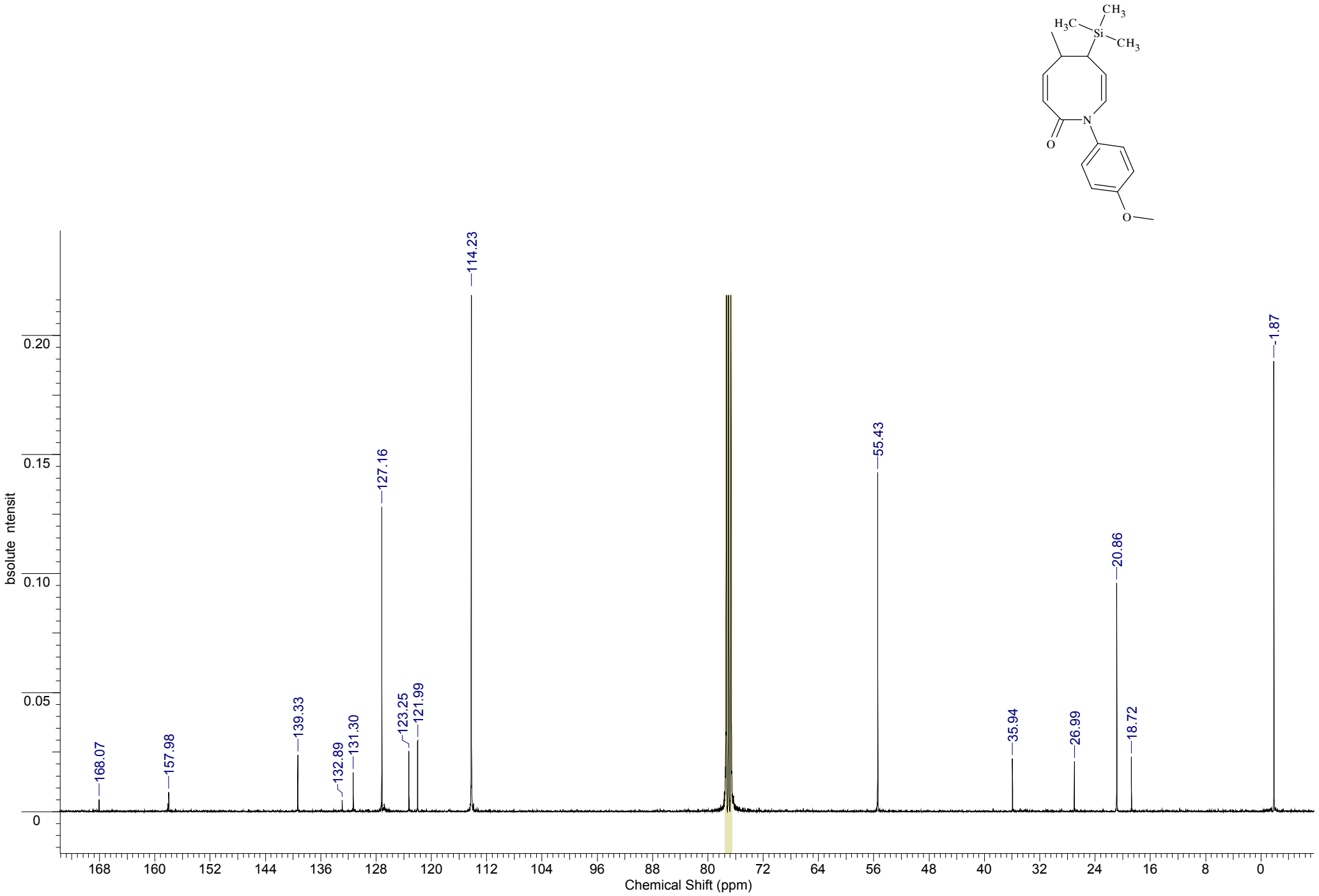


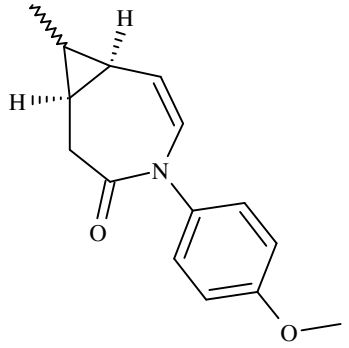


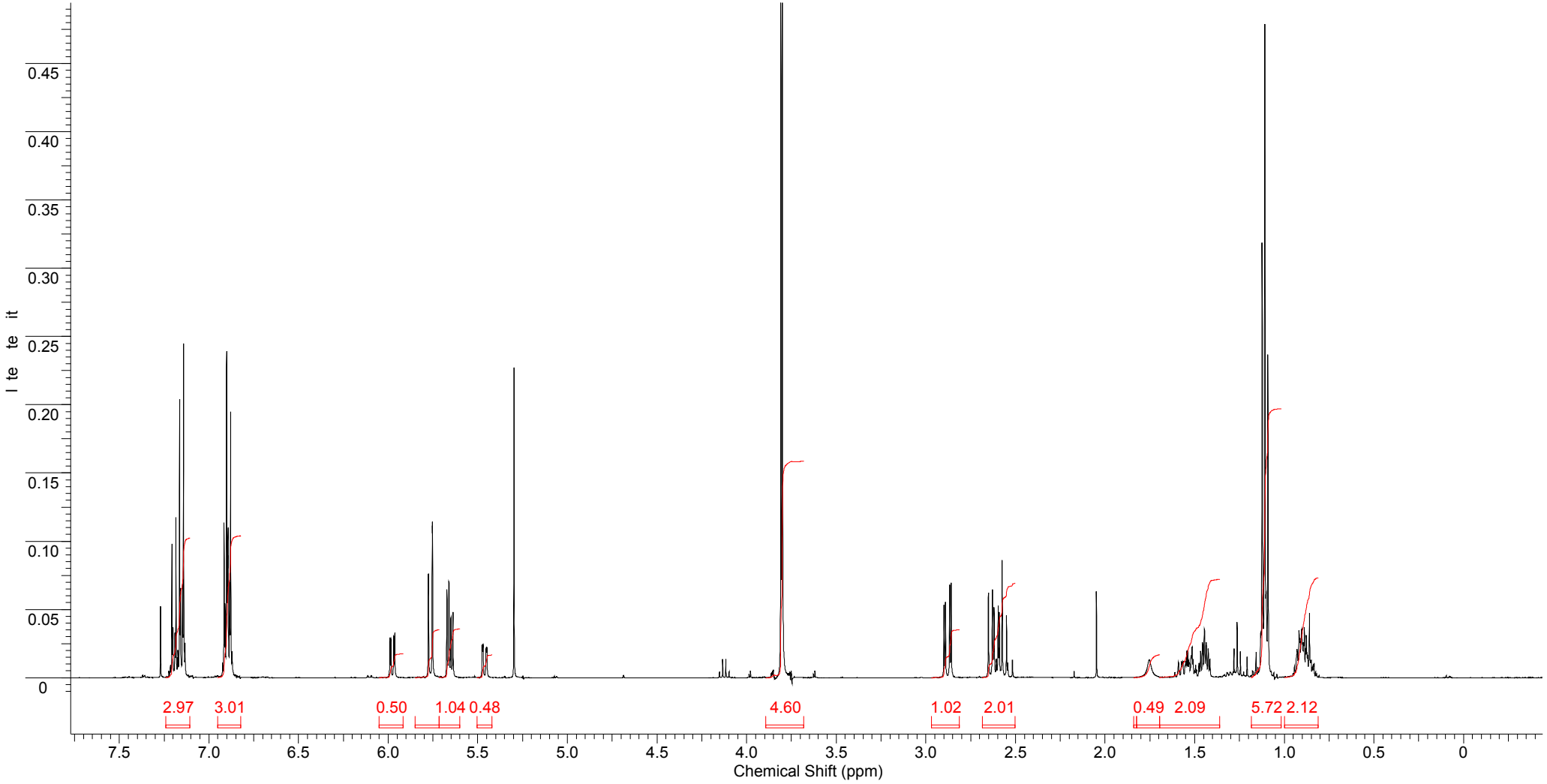
2 diastereoismers, broadening due to slow conformational exhange, rotamers











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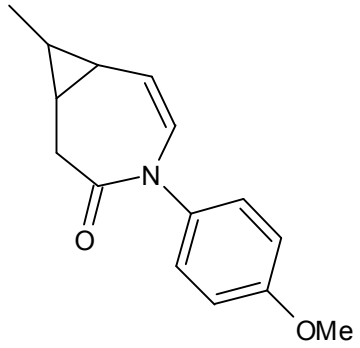

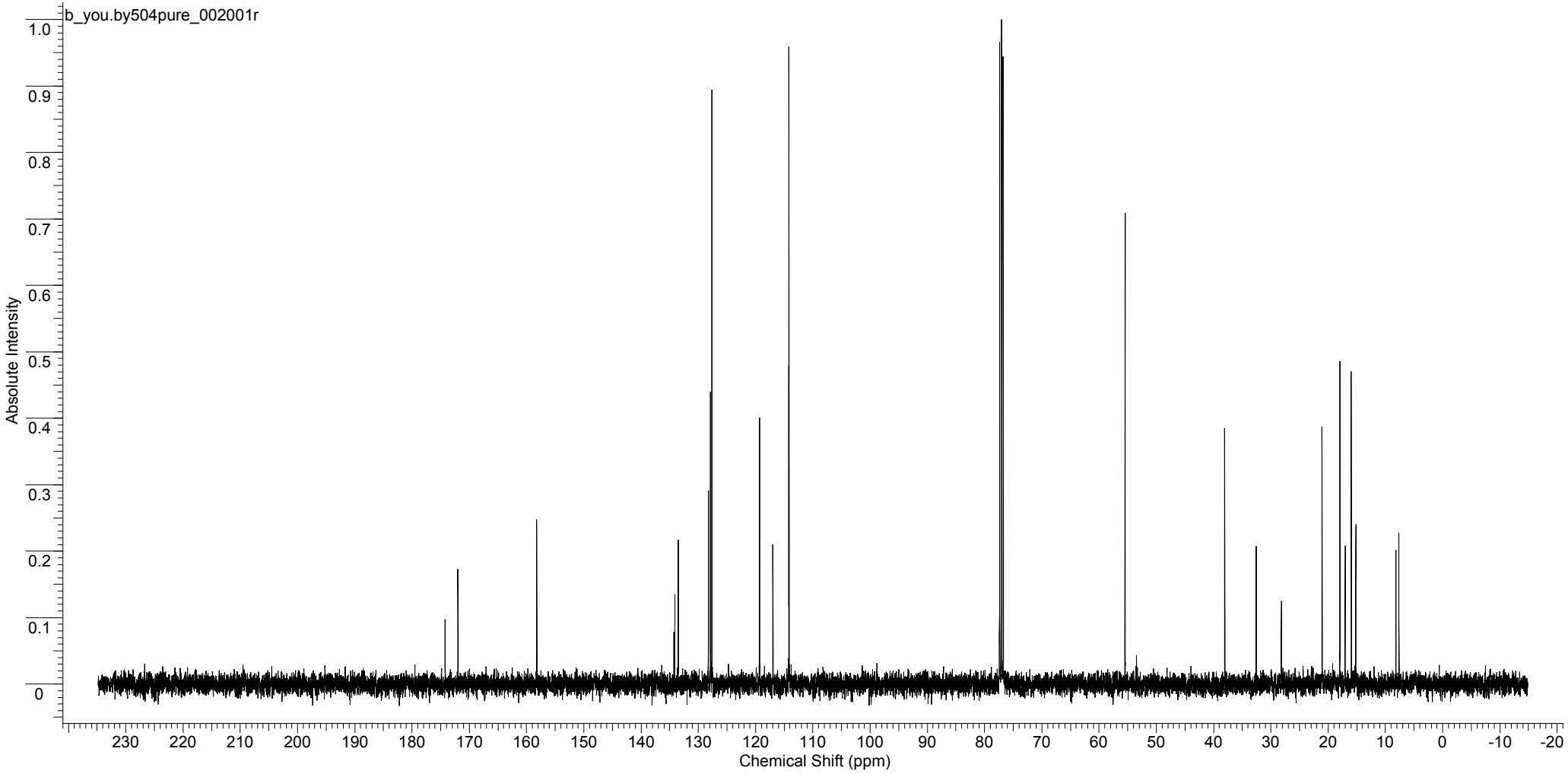

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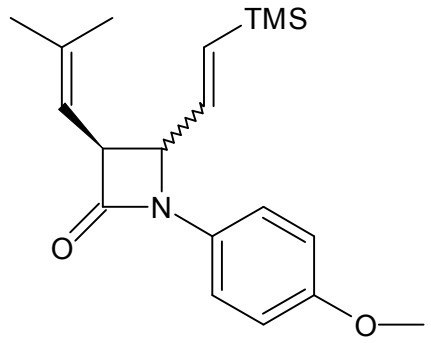


b_you.by593purere_001001r

Absolute Intensity

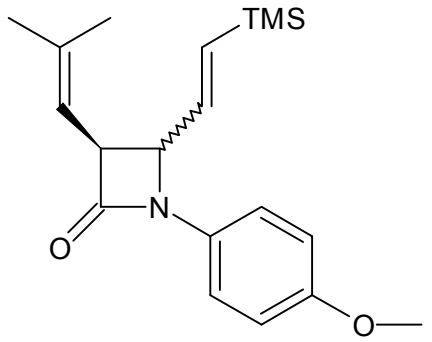
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0

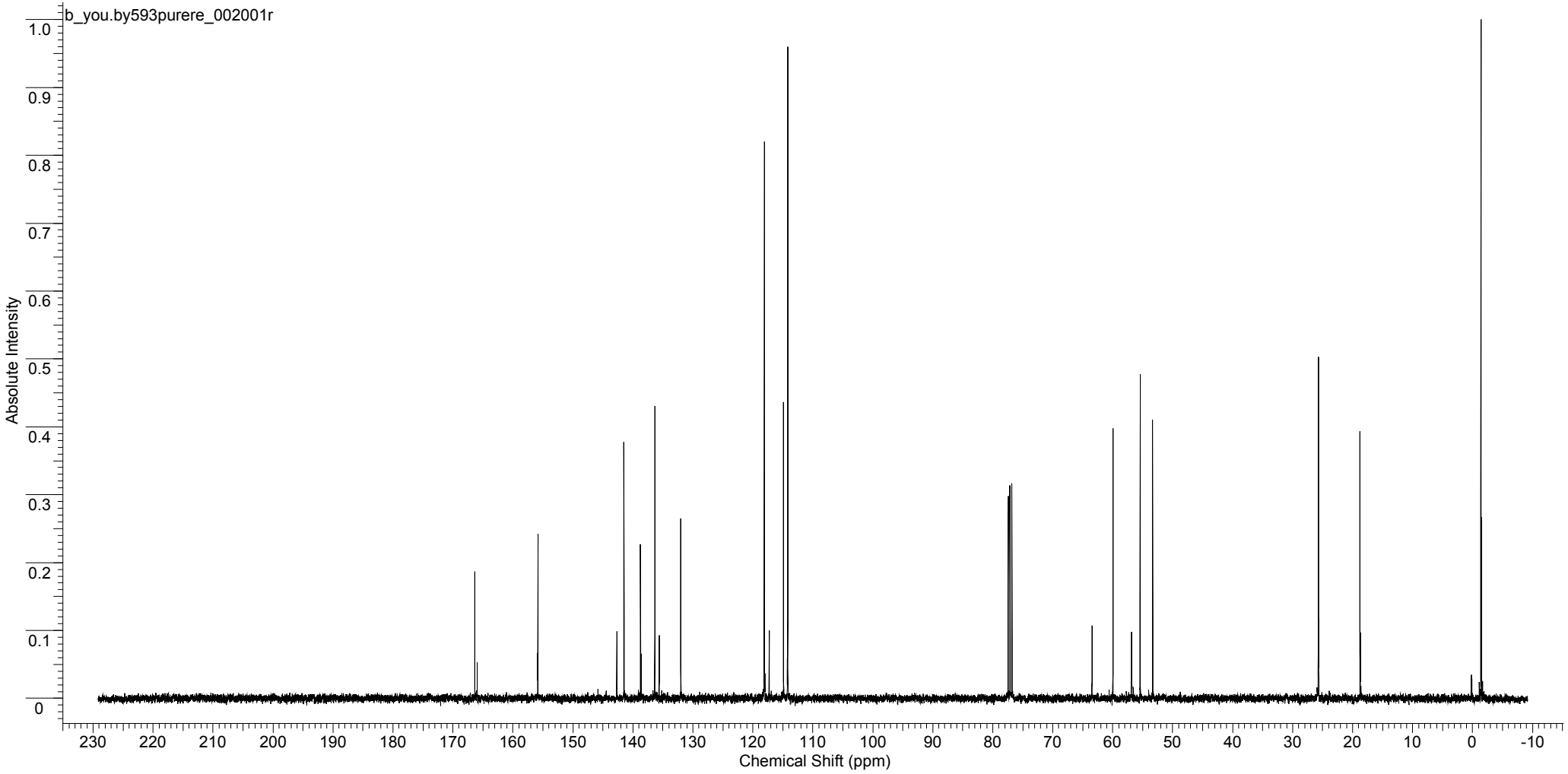
2.29 2.59 2.37 1.01 1.00 1.04 3.94 3.85 10.78

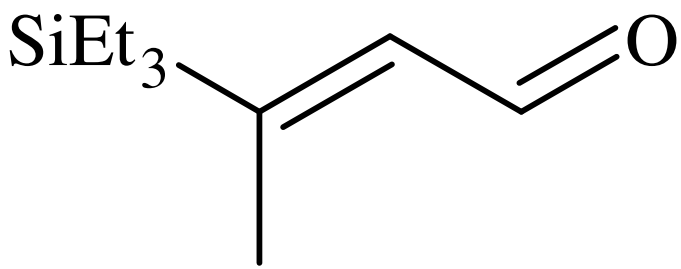
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5

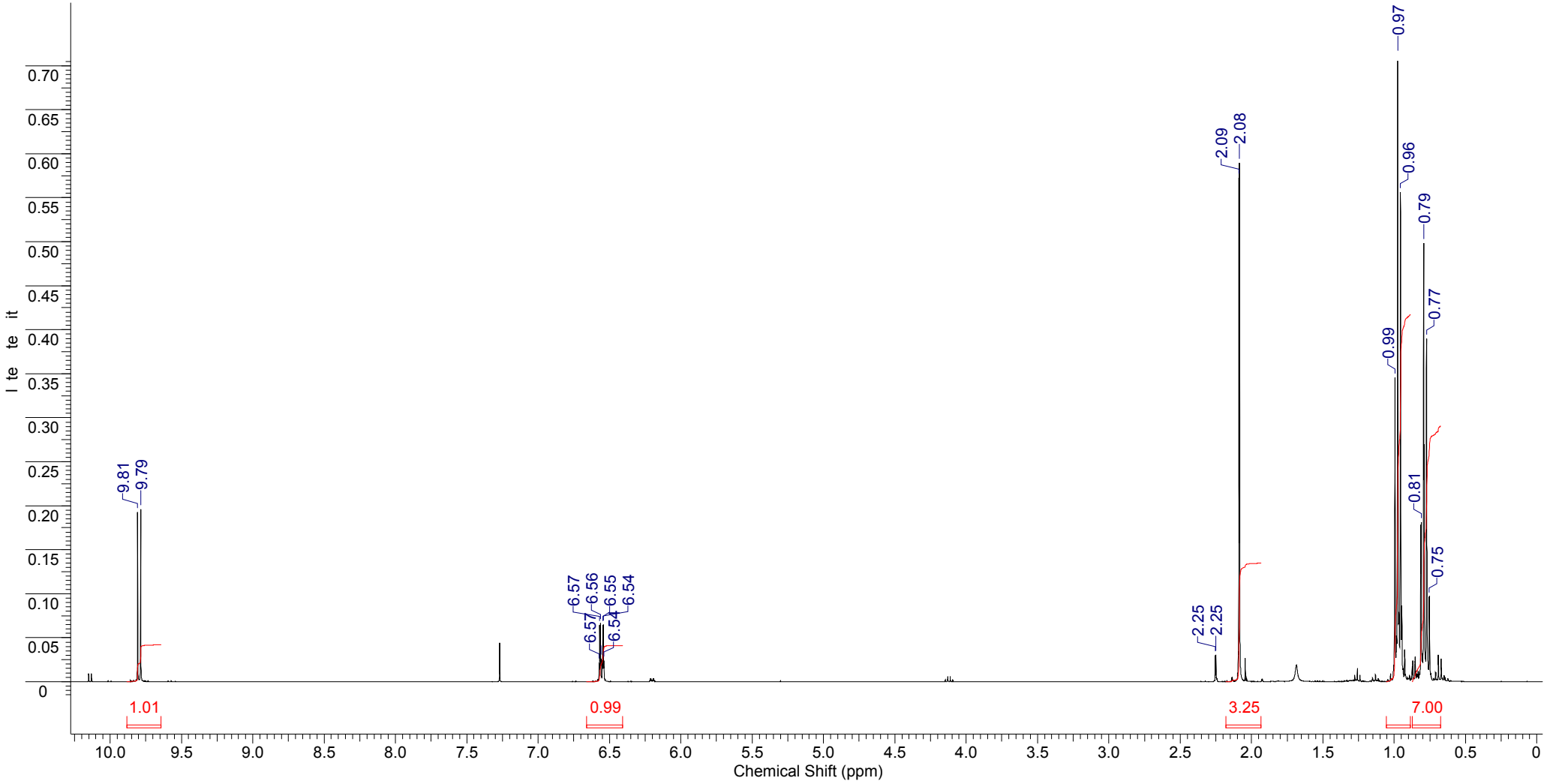
Chemical Shift (ppm)

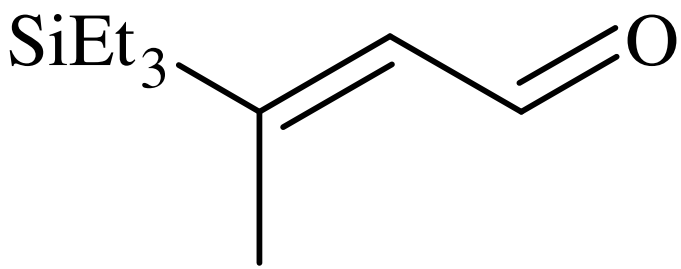
01/02/2011 13:48:32

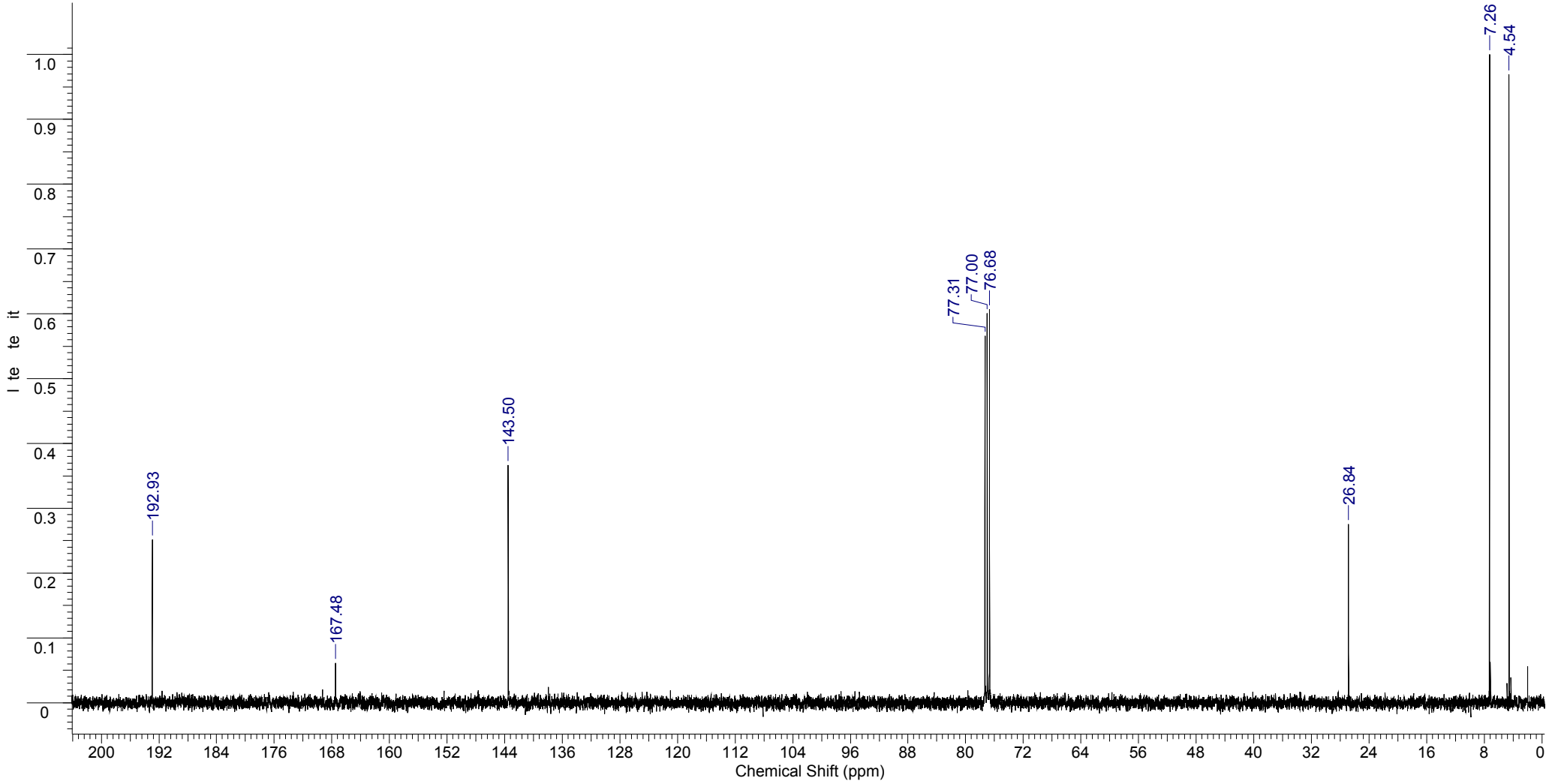


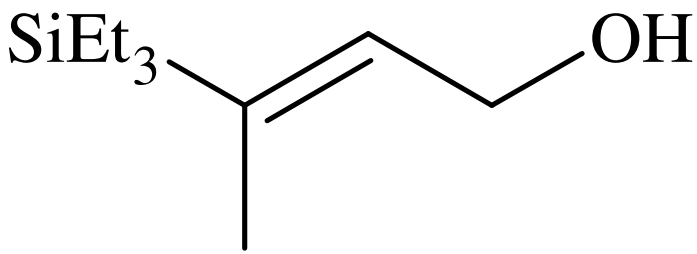


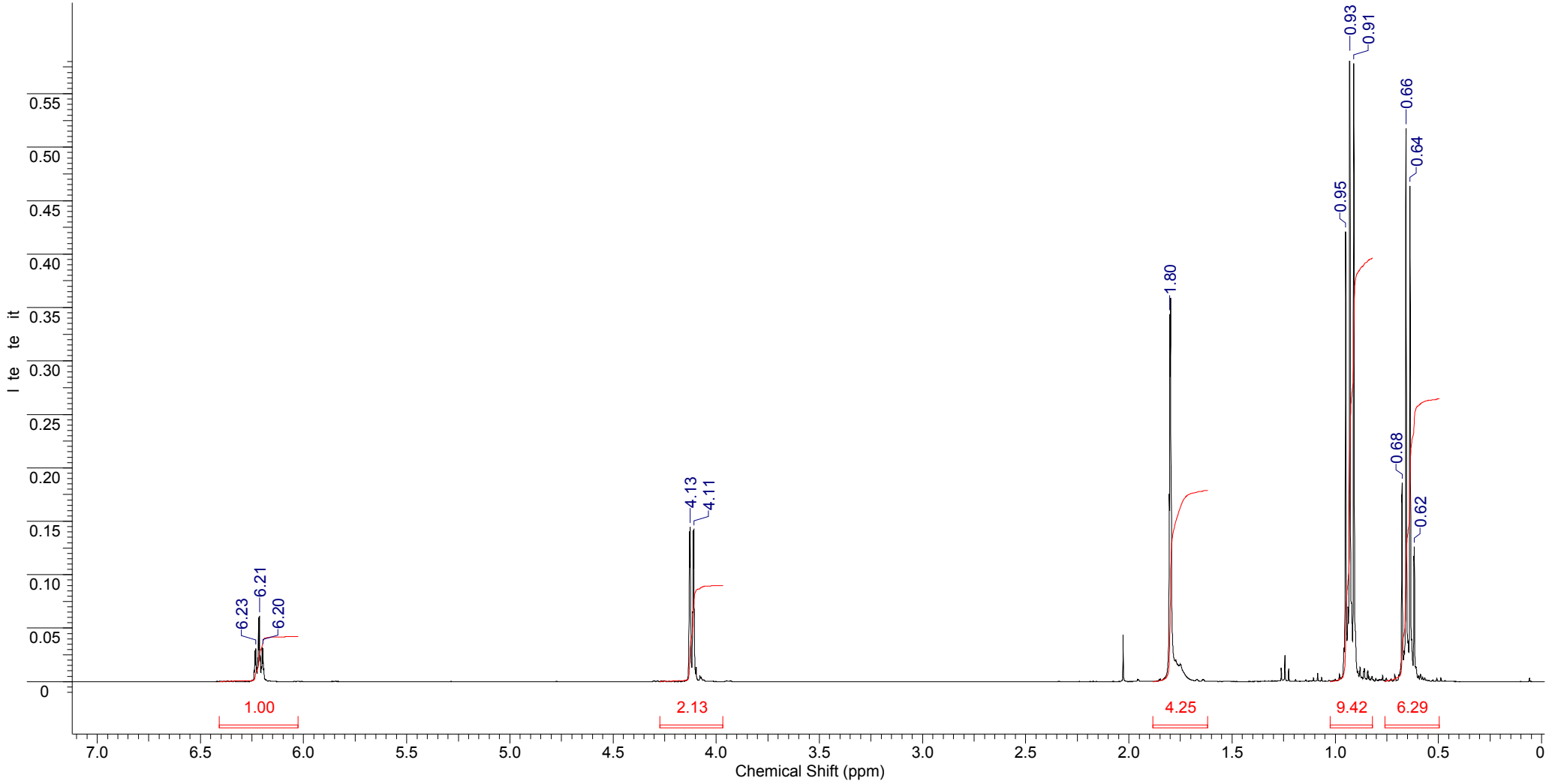


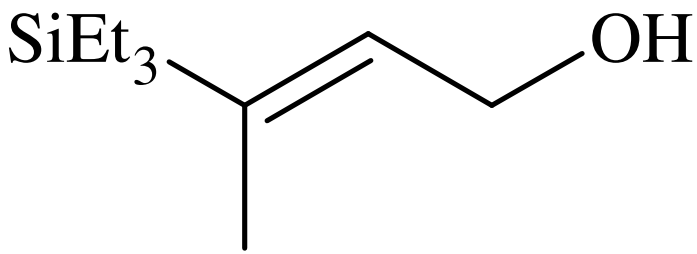


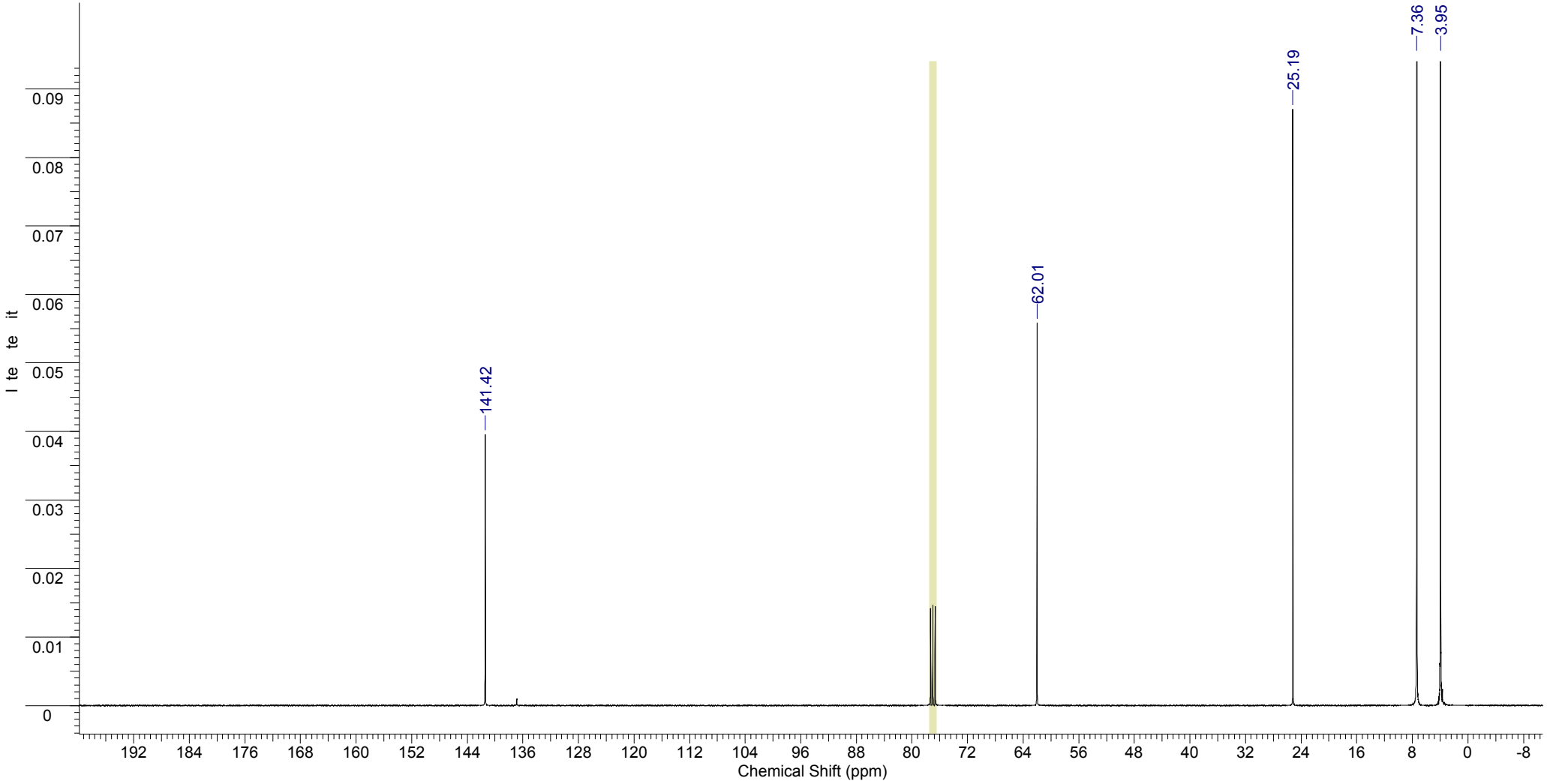


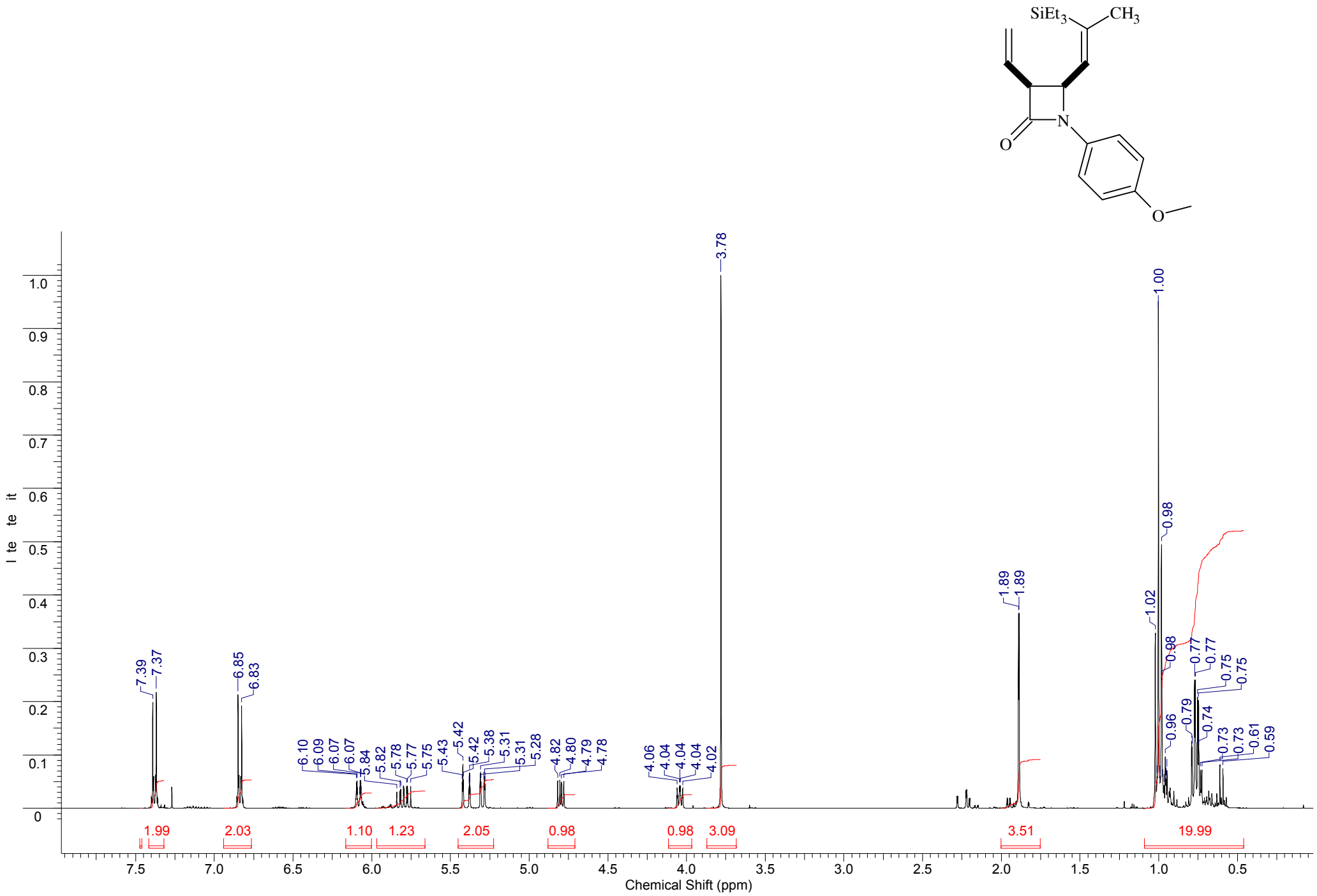


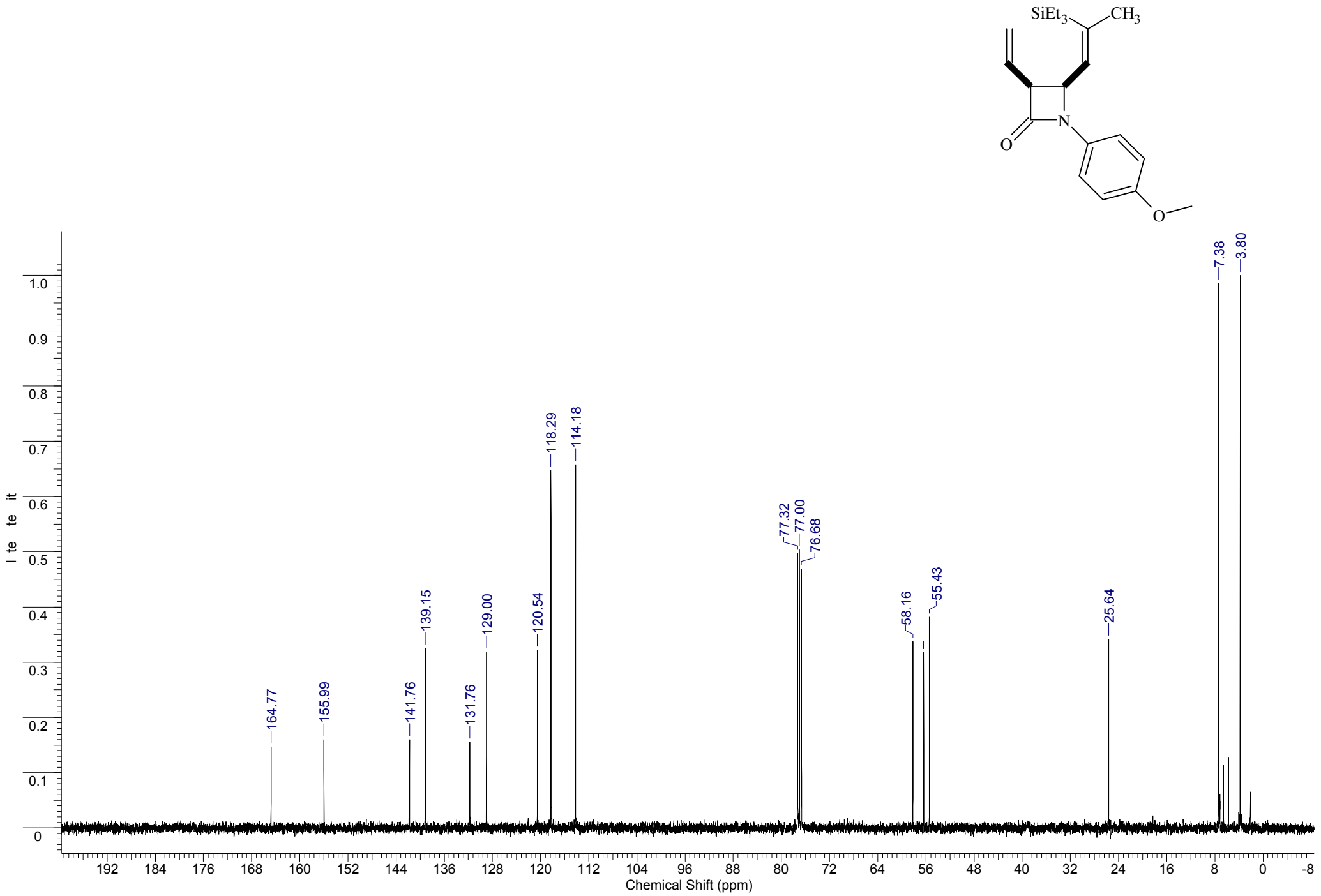












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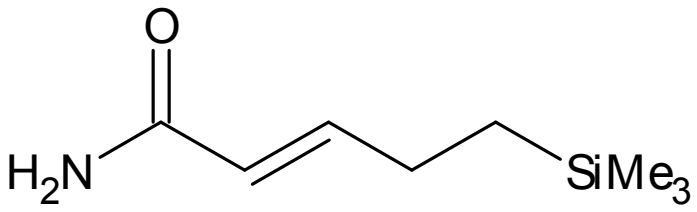

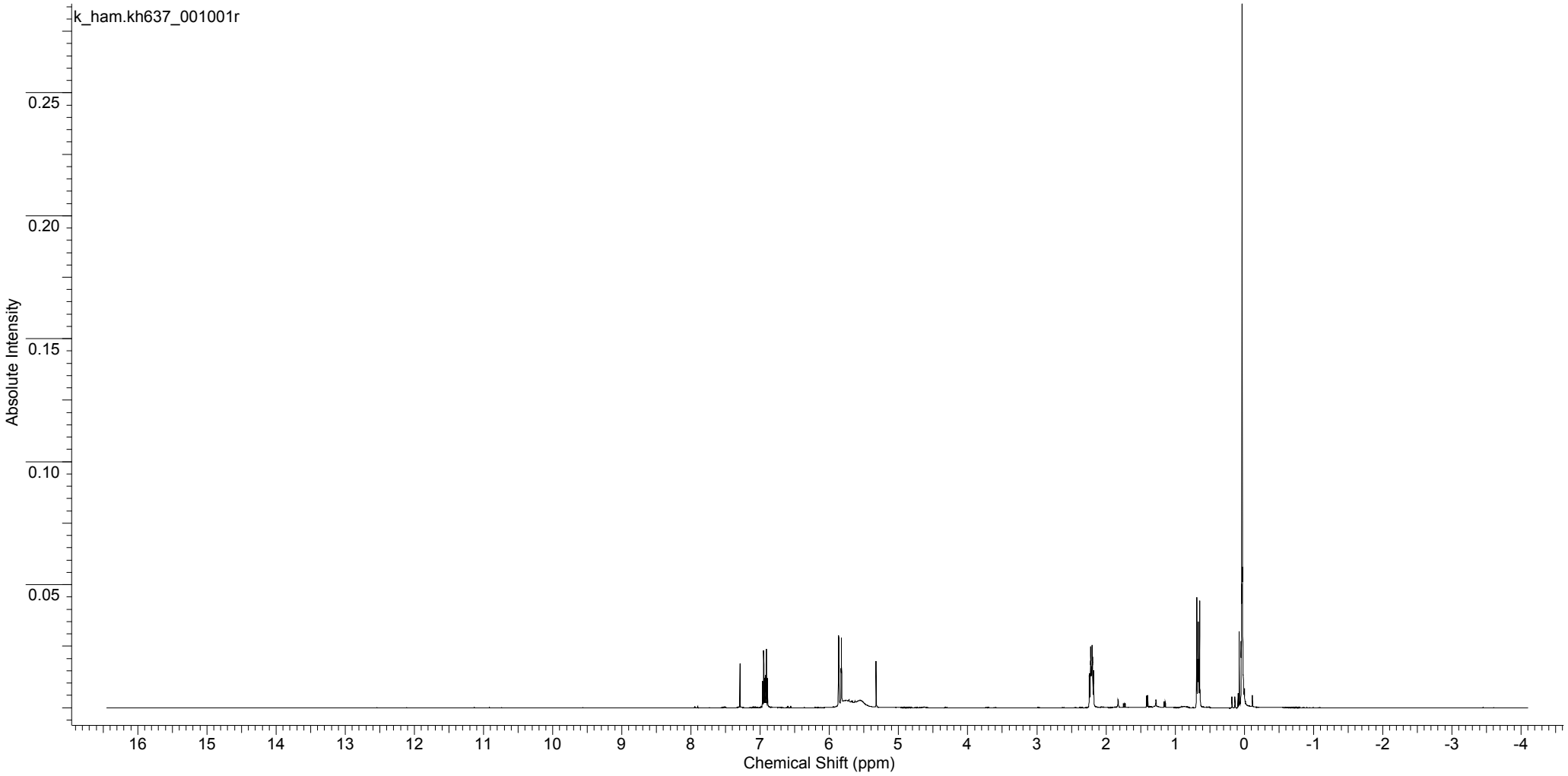

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