Supporting Information for

N-Heterocyclic Carbene-Catalyzed Formal Cross-Coupling Reaction of α-Haloenals with Thiols: Organocatalytic Construction of sp^2 Carbon–Sulfur Bonds

Lin He,* Hao Guo, Yuan-Zhen Li, Guang-Fen Du, Bin Dai*

Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region, 832000, China

Contents

1. General Methods & General experimental procedure ……..S1-S2

2. Spectroscopic data for all products ……...S3-S10

3. References……..……S10

3. Copies of ^{1}H NMR and ^{13}C NMR spectra…….S11-S31

4. ROESY spectra of **3a**…….…….....…S32

General Methods: Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in an oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F254. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra were recorded on 400 MHz spectrometer using deuterated chloroform as solvent, with tetramethylsilane as an internal standard and reported in ppm (δ). Infrared spectra were recorded on a FT/IR spectrophotometer and reported as wave number(cm^{-1}). EI mass spectra were measured on Agilent 7890A/5975C GC-MS and methanol or acetonitrile was used to dissolve the sample. High-resolution mass spectra (HRMS) were recorded on

FTICRMS. Thiols were obtained from commercial supplies and used without purification. α-Haloenals were synthesized according to literature.[1] Anhydrous THF and toluene were distilled from sodium and benzophenone. CH_2Cl_2 and CH_3CN were distilled from calcium hydride. Petroleum ether (PE), where used, has a boiling range of 60–90 °C.

Genera procedure for the synthesis α-thioenals: A suspension of potassium carbonate (110mg, 0.8mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH_2Cl_2 (2.0 mL) was stirred at ambient temperature for 0.5 h. Thiol (0.75mmol) and aldehyde (0.5mmol) were added subsequently and the solution was stirred at room temperature until full consume of the starting α-haloenal as indicated by TLC. The reaction mixture was then filtered through a short pad of silica gel and the silica gel was washed with 20 mL of 20% EtOAc in petroleum ether. After removal of the solvent under reduced pressure, the crude material was subjected to column chromatography (silica gel, PE-EtOAc, 10:1~100:1) to give the desired product.

procedure for the synthesis IV: A suspension of potassium carbonate (110mg, 0.8mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH_2Cl_2 (2.0 mL) was stirred at ambient temperature for 0.5 h. Lithium chloride (26mg, 0.6mmol), Thiol (1.5mmol) and aldehyde (0.5mmol) were added subsequently and the solution was stirred at room temperature until full consume of the starting α-haloenal as indicated by TLC. The crude material was purified by column chromatography (silica gel, PE-Et_2O, 30:1) to afford the desired product.

procedure for the Elimination of IV: A suspension of potassium carbonate (42mg, 0.3mmol) and IMes·HCl (9mg, 0.025mmol) in freshly distilled CH_2Cl_2 (2.0 mL) was stirred at ambient temperature for 0.5 h. Bisulfenylated aldehyde (**IV**) was then added and the solution was stirred at room temperature until full consume of the starting Bisulfenylated aldehyde as indicated by TLC. The crude material was subjected to column chromatography (silica gel, PE-EtOAc, 10:1~100:1) to give the desired product.

Experimental Data:

(*Z*)-2-(ethylthio)-3-phenylacrylaldehyde (3a)

Purified with ethyl acetate/petroleum ether (1/50), yielding 107 mg (90%) of **3a** as a yellow oil. R_f = 0.53 (1/15 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 1.20 (t, *J* = 7.42 Hz, 3H,), 2.98 (q, *J* = 7.41 Hz ,2H), 7.43-7.49 (m, 3H), 7.60 (s, 1H), 7.93-7.96 (m, 2H), 9.59 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 15.1, 26.7 128.6, 130.6, 131.3, 134.2, 135.9, 152.0, 191.7; IR (KBr) 2967.0, 2926.6, 1695.8, 1633.4, 1593.0, 1443.7, 1364.2, 1123.2, 756.1, 693.7, 527.3 cm^{-1}; GC-MS (EI): m/z 192.0 (M^+); HRMS calcd for $C_{11}H_{12}OS$ (EI): 192.0609; Found: 192.0611.

(*Z*)-3-phenyl-2-(propylthio)acrylaldehyde (3b)

Purified with ethyl acetate/petroleum ether (1/20), yielding 91 mg of **3b** (88%) as a yellow oil. R_f = 0.53 (1/10 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 0.93 (t, *J* = 7.34 Hz, 3H), 1.49-1.59 (m, 2H), 2.92 (t, *J* = 7.32 Hz, 2H), 7.43-7.48 (m, 3H), 7.59 (s, 1H), 7.95-7.98 (m, 2H), 9.56 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 13.2, 23.4, 34.4, 128.5, 130.6, 131.3, 134.3, 136.2, 151.9, 191.7; IR (KBr) 2976.7, 1699.2, 1583.3, 1449.4, 1355.4, 1117.5, 763.7, 689.7, 523.8 cm^{-1}; GC-MS (EI): m/z 206.0 (M^+); HRMS calcd for $C_{12}H_{14}OS$ (EI): 206.0765; Found: 206.0767.

(*Z*)-2-(butylthio)-3-phenylacrylaldehyde (3c)

Purified with ethyl acetate/petroleum ether (1/50), yielding 101 mg (90%) of **3c** as a yellow oil. R_f = 0.57 (1/10 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 0.85 (t, *J* = 7.32 Hz ,3H), 1.30-1.39 (m, 2H), 1.46-1.54 (m, 2H), 2.94 (t, *J* =7.42 Hz, 2H), 7.43-7.48 (m, 3H), 7.58 (s,1H), 9.58 (s,1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 13.57, 21.75, 32.06, 32.15, 128.51, 130.56, 131.24, 134.26, 136.26, 151.77, 191.73; IR (KBr) 2963.5, 2867.7, 1692.8, 1596.9, 1447.7, 1361.9, 1298.1, 1116.7, 758.6, 688.9, 529.3 cm^{-1}; GC-MS (EI): m/z 220.0 (M^+); HRMS calcd for $C_{13}H_{16}OS$ (EI): 220.0922; Found: 220.0925.

(*Z*)-2-(octadecylthio)-3-phenylacrylaldehyde (3d)

Purified with ethyl acetate/petroleum ether (1/100), yielding 142 mg (70%) of **3d** as a yellow solid. R_f = 0.63 (1/10 ethyl acetate/petroleum ether) ; m.p. 53.3-54.5℃; ^{1}H NMR (400 MHz $CDCl_3$) δ = 0.88 (t, *J* = 6.84 Hz, 3H), 1.20-1.29 (m, 30H), 1.46-1.56 (m, 2H), 2.93 (t, *J* = 7.42 Hz, 2H), 7.42-7.48 (m, 3H), 7.59 (s, 1H), 7.93-7.97 (m, 2H), 9.58 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 14.12, 22.69, 28.59, 28.80, 29.09, 29.36, 29.44, 29.52, 29.62, 29.65, 29.97, 31.92, 32.50, 128.49, 130.55, 131.24, 134.26, 136.27, 151.79, 191.72; IR (KBr) 2925.5, 2844.4, 1680.9, 1636.9, 1593.1, 1356.4, 1114.4, 727.4 cm^{-1}; HRMS calcd for $C_{27}H_{44}OS$ (EI): 416.3113; Found: 416.3113.

(*Z*)-2-(benzylthio)-3-phenylacrylaldehyde (3e)

Purified with ethyl acetate/petroleum ether (1/30), yielding 110 mg (86%) of **3l** as a yellow solid. R_f = 0.57 (1/5 ethyl acetate/petroleum ether) ; m.p. 36.8-38.7℃;^{1}H NMR (400 MHz $CDCl_3$) δ = 4.17 (s, 2H), 7.15-7.22 (m, 5H), 7.40-7.41 (m, 3H), 7.53 (s, 1H), 7.81-7.83 (m, 2H), 9.51 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 36.69, 127.17, 128.40, 128.45, 129.03, 130.65, 131.16, 134.04, 135.43, 137.42, 152.86, 191.66; IR (KBr) 3059.1, 2839.7, 1682.1, 1630.7, 1587.1, 1369.3, 1121.8, 757.8, 684.6, 516.6 cm^{-1}; GC-MS (EI): m/z 254.0 (M^+); HRMS calcd for $C_{16}H_{14}OS$ (EI): 254.0765; Found: 254.0763.

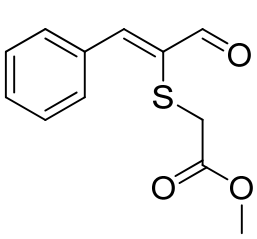
(*Z*)-2-(allylthio)-3-phenylacrylaldehyde(3f)

Purified with ethyl acetate/petroleum ether (1/50), yielding 61 mg (60%) of **3f** as a yellow oil. R_f = (ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 3.58-3.60 (m, 2H), 4.96-5.01 (m, 2H), 5.65-5.76 (m, 1H), 7.42-7.48 (m, 3H), 7.62 (s, 1H), 7.91-7.95 (m, 2H), 9.54 (s, 1H); ^{13}C NMR (100 MHz $CDCl_3$) δ = 35.29, 117.91, 128.57, 130.75, 131.32, 133.67, 134.15,

135.20, 152.87, 191.49; IR (KBr) 2837.4, 1698.4, 1626.7, 1583.1, 1559.7, 1488.1, 1371.2, 1123.4, 911.5, 691.8, 525.1; GC-MS (EI): m/z 203.9 (M^+); HRMS calcd for $C_{12}H_{12}OS$ (EI): 204.0609; Found: 204.0611.

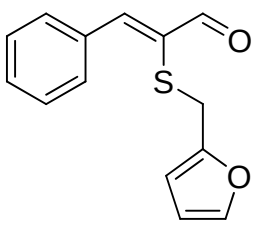
(*Z*)-methyl 2-((3-oxo-1-phenylprop-1-en-2-yl)thio)acetate(3g)

Purified with ethyl acetate/petroleum ether (1/10), yielding 93 mg (79%) of **3g** as a yellow oil. R_f = (ethyl acetate/petroleum ether) ; ^{1}H NMR (400MHz $CDCl_3$) δ = 3.61 (s, 3H), 3.75 (s, 2H), 7.44-7.48 (m, 3H), 7.64 (s, 1H), 7.92-7.94 (m, 2H), 9.57 (s, 1H); ^{13}C NMR (100 MHz $CDCl_3$) δ = 33.32, 52.40, 128.66, 130.99, 131.29, 133.77, 134.09, 153.24, 169.74, 191.16; IR (KBr) 2834.9, 1744.4, 1688.9, 1627.9, 1548.7, 1432.2, 1359.2, 1272.2, 756.4, 689.7; GC-MS (EI): m/z 236.0 (M^+); HRMS calcd for $C_{12}H_{12}O_3S$ (EI): 236.0507; Found: 236.0511。



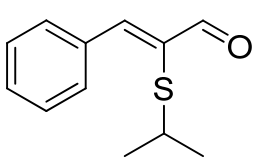
(*Z*)-2-((furan-2-ylmethyl)thio)-3-phenylacrylaldehyde(3h)

Purified with ethyl acetate/petroleum ether (1/10), yielding 116 mg (92%) of **3h** as a yellow solid. R_f = (ethyl acetate/petroleum ether) ; m.p.37.0-38.8℃; ^{1}H NMR (400 MHz DMSO) δ = 4.24 (s, 2H), 6.12-6.13 (m, 1H), 6.29-6.30 (m, 1H), 7.45-7.50 (m, 4H), 7.82-7.84 (m, 2H), 7.95 (s, 1H), 9.59 (s, 1H); ^{13}C NMR (100 MHz DMSO) δ = 27.61, 107.99, 110.48, 128.47, 130.60, 130.72, 133.77, 134.04, 142.62, 150.58, 153.09, 191.95; IR (KBr) 2834.4, 1684.7, 1630.3, 1595.1, 1361.3, 1127.6, 1011.4, 927.6, 742.4, 693.9; GC-MS (EI): m/z 243.9 (M^+); HRMS calcd for $C_{14}H_{12}O_2S$ (EI): 244.0558; Found: 244.0563.



(*Z*)-2-(isopropylthio)-3-phenylacrylaldehyde (3i)

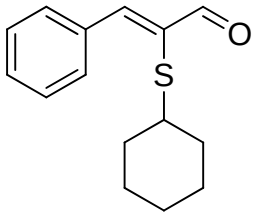
Purified with ethyl acetate/petroleum ether (1/50), yielding 67 mg (65%) of **3i** as a yellow oli. R_f = 0.48 (1/10 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 1.22 (d, 6H, *J* = 6.72 Hz), 3.78-3.85 (m, 1H), 7.43-7.48 (m, 3H), 7.64 (s,1H), 7.98-8.01 (m, 2H), 9.61 (s,1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 23.35, 36.22, 128.49, 130.67, 131.42, 134.28, 136.04, 152.63, 192.03; IR



(KBr) 2974.7, 2834.7, 1703.2, 1591.3, 1449.4, 1365.4, 1121.5, 767.7, 681.7, 523.8 cm^{-1}; GC-MS (EI): m/z 206.0 (M^+); HRMS calcd for $C_{12}H_{14}OS$ (EI): 206.0765; Found:206.0766.

(*Z*)-2-(cyclohexylthio)-3-phenylacrylaldehyde (3j)

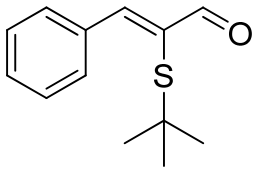
Purified with ethyl acetate/petroleum ether (1/20), yielding 110 mg (90%) of **3j** as a yellow solid. R_f = 0.56 (1/10 ethyl acetate/petroleum ether) ; m.p. 77.5-78.1℃; ^1H NMR



(400 MHz $CDCl_3$) δ = 1.18-1.35 (m, 5H), 1.55-1.59 (m,1H), 1.69-1.71 (m, 2H), 1.87-1.91 (m, 5H), 3.48-3.56 (m, 1H), 7.42-7.48 (m, 3H), 7.64 (s, 1H), 8.00-8.02 (m, 2H), 9.60 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 25.62, 25.84, 33.57, 44.36, 128.47, 130.64, 131.43, 134.33, 135.42, 152.72, 192.12; IR (KBr) 1938.7, 2834.7, 1693.2, 1637.3, 1571.3, 1365.4, 1121.5, 757.7, 691.7, 533.8 cm^{-1};GC-MS (EI): m/z 246.0 (M^+); HRMS calcd for $C_{15}H_{18}OS$ (EI): 246.1078; Found: 246.1080.

(*Z*)-2-(tert-butylthio)-3-phenylacrylaldehyde (3k)

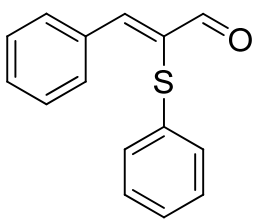
Purified with ethyl acetate/petroleum ether (1/50), yielding 58 mg (53%) of **3k** as a



colorless oil. R_f = 0.48 (1/10 ethyl acetate/petroleum ether) ; ^1H NMR (400 MHz $CDCl_3$) δ = 1.28 (s, 9H), 7.43-7.46 (m, 3H), 7.93 (s, 1H), 8.20-8.23 (m, 2H), 9.69 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 31.58, 49.92, 128.40, 131.24, 132.15, 133.28, 134.30, 155.80, 193.85; IR (KBr) 2966.7, 2824.7, 1703.2, 1627.3, 1591.3, 1365.4, 1093.5, 775.6, 663.7 cm^{-1}; GC-MS (EI): m/z 220.0 (M^+); HRMS calcd for $C_{13}H_{16}OS$ (EI): 220.0922; Found: 220.0923.

(*Z*)-3-phenyl-2-(phenylthio)acrylaldehyde (3l)[2]

Purified with ethyl acetate/petroleum ether (1/50), yielding 86 mg (90%) of **3l** as a green-



yellow oil. R_f = 0.51 (1/5 ethyl acetate/petroleum ether) ; ^1H NMR (400 MHz $CDCl_3$) δ = 7.14-7.18 (m, 1H), 7.20-7.26 (m, 3H), 7.26-7.28 (m, 1H), 7.87 (s, 1H), 7.93-7.98 (m, 2H), 9.54 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 126.7, 128.7, 129.0, 129.2, 131.2, 131.4, 133.1,

133.7 ,133.8, 151.2, 190.8; IR (KBr) 3053.7, 2827.2, 1696.5, 1589.1, 1480.4, 1450.1, 1353.4, 1116.5, 743.0, 688.1, 536.4 cm^{-1};GC-MS (EI): m/z 240.0 (M^+); HRMS calcd for $C_{15}H_{12}OS$ (EI): 240.0609; Found: 240.0611.

(*Z*)-2-(ethylthio)-3-(4-methoxyphenyl)acrylaldehyde (3m)

Purified with ethyl acetate/petroleum ether (1/20), yielding 92 mg (83%) of 3m as a yellow oil . R_f = 0.47 (1/5 ethyl acetate/petroleum ether) ; ^1H NMR (400 MHz $CDCl_3$) δ = 1.19 (t, *J* = 7.40 Hz, 3H), 2.95 (q, *J* = 7.40 Hz ,2H), 3.87 (s,3H), 6.95-6.99 (m, 2H), 7.56 (s, 1H), 8.00-8.03 (m, 2H), 9.54 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 15.05, 26.78, 55.44, 114.02, 127.09, 132.94, 133.59, 152.70, 161.64, 191.83; IR (KBr) 2963.8, 2926.1, 2834.6, 1684.8, 1604.7, 1513.3, 1455.0, 1417.3, 1363.6, 1305.3, 1251.6, 1181.9, 1128.1, 1026.4, 828.7, 770.4, 668.6, 534.9 cm^{-1}; GC-MS (EI): m/z 221.9 (M^+); HRMS calcd for $C_{12}H_{14}O_2S$ (EI): 222.0715; Found: 222.0713.

(*Z*)-3-(4-chlorophenyl)-2-(ethylthio)acrylaldehyde (3n)

Purified with ethyl acetate/petroleum ether (1/50), yielding 94 mg (83%) of **3n** as a yellow oil . R_f = 0.58 (1/10 ethyl acetate/petroleum ether) ; ^1H NMR (400 MHz $CDCl_3$) δ = 1.19 (t, *J* = 7.40 Hz, 3H), 2.99(q, *J* = 7.40 Hz, 2H), 7.41-7.44 (m, 2H), 7.54 (s, 1H), 7.88-7.92 (m, 2H), 9.58 (s,1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 15.10, 26.72, 128.81, 132.42, 132.66, 136.43, 136.52, 150.15, 191.38; IR (KBr) 2984.7, 2918.7, 2834.7, 1703.2, 1581.3, 1477.3, 1375.4, 1131.5, 1085.5, 991.6, 813.6, 747.7, 681.7, 523.8 cm^{-1}; GC-MS (EI): m/z 225.9 (M^+); HRMS calcd for $C_{11}H_{11}ClOS$ (EI): 226.0219; Found: 226.0217.

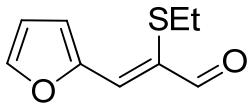
(*Z*)-2-(ethylthio)-3-(2-nitrophenyl)acrylaldehyde (3o)

Purified with ethyl acetate/petroleum ether (1/20), yielding 94 mg (76%) of **3o** as a brown-red oil . R_f = 0.46 (1/5 ethyl acetate/petroleum ether) ; ^1H NMR (400 MHz $CDCl_3$) δ = 1.12 (t, *J* = 7.42 Hz, 3H), 2.84 (q, *J* = 7.40 Hz, 2H),

7.57-7.66 (m, 2H), 7.70-7.74 (m, 1H), 8.02 (s,1H), 8.19-8.22(m, 1H), 9.70 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 14.86, 26.40, 124.91, 130.21 (d, 8.53 Hz), 131.59, 133.34, 138.88, 148.02, 190.73; IR (KBr) 2984.7, 2918.7, 2816.7, 1693.2, 1581.3, 1525.3, 1347.4, 1121.5, 859.6, 785.6, 747.7, 701.7, 673.7, 607.7, 513.8 cm^{-1}; GC-MS (EI): m/z 236.8 (M^+); HRMS calcd for $C_{11}H_{11}NO_3S$ (EI): 237.0460; Found: 237.0466.

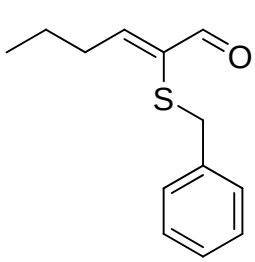
(*Z*)-2-(ethylthio)-3-(furan-2-yl)acrylaldehyde (3p)

Purified with ethyl acetate/petroleum ether (1/50), yielding 71 mg (78%) of **3p** as a brown solid. R_f = 0.49 (1/10 ethyl acetate/petroleum ether) ; m.p. 35.5-36.9℃; ^{1}H NMR (400 MHz $CDCl_3$) δ = 1.23 (t, *J* = 7.40 Hz, 3H), 3.06 (q, *J* = 7.40 Hz, 2H), 6.60-6.62 (m, 1H), 7.47 (s, 1H), 7.51 (d, *J* = 3.60 Hz, 1H), 7.63 (dd, *J* = 1.76 Hz, 0.6 Hz,1H), 9.51 (s,1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 15.36, 26.34, 113.16, 118.38, 131.98, 137.96, 145.49, 150.82, 190.29; IR (KBr) 3108.2, 2967.8, 2833.4, 1689.2, 1631.8, 1589.5, 1462.8, 1357.1, 1194.1, 1115.6, 1017.4, 946.5, 756.3, 656.6, 621.9, 508.7 cm^{-1}; GC-MS (EI): m/z 181.9 (M^+); HRMS calcd for $C_9H_{10}O_2S$ (EI): 182.0402; Found: 184.0404.



(*Z*)-2-(benzylthio)hex-2-enal (3q)

Purified with ethyl acetate/petroleum ether (1/50), yielding 70 mg (64%) of **3q** as a yellow solid. R_f = 0.49 (1/20 ethyl acetate/petroleum ether) ; m.p. 36.8-38.7℃;^{1}H NMR (400 MHz $CDCl_3$) δ = 1.23 (t, *J* = 7.40 Hz, 3H), 1.26-1.35 (m, 2H), 2.32-2.38 (m, 2H), 3.99 (s,2H), 6.93 (t, *J* = 7.34 Hz,1H,), 7.16-7.26 (m, 5H), 9.39 (s, 1H); ^{13}C NMR (100 MHz $CDCl_3$) δ = 13.72, 21.45, 32.61, 36.37, 126.97, 128.31, 128.90, 137.09, 138.15, 162.48, 191.21; IR (KBr) 3034.5, 2965.5, 2919.6, 1696.9, 1596.8, 1498.3, 1450.8, 1166.8, 1083.1, 753.3, 699.1 cm^{-1}; GC-MS (EI): m/z 220.0 (M^+); HRMS calcd for $C_{13}H_{16}OS$ (EI): 220.0922; Found: 220.0925.



2-(ethylthio)-3-phenylpropanal (3r)

Purified with ethyl acetate/petroleum ether (1/50), yielding 85 mg (80%) of **3r** as a colorless oil. R_f = 0.59 (1/20 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 1.21 (t, *J* =7.44 Hz, 3H), 2.36-2.49 (m, 2H), 2.88-2.93 (m,1H), 3.11-3.17 (m,1H), 3.39-3.44 (m,1H), 7.19-7.25 (m,3H), 7.28-7.32 (m,2H), 9.27 (s,1H), ^{13}C NMR (100 MHz $CDCl_3$) δ =14.42, 24.29, 34.34, 54.13, 126.94, 128,67, 128.96, 137.40, 192.81; IR (KBr) 2981.1, 2916.8, 2823.4, 1713.3, 1641.4, 1598.5, 1454.6, 1361.2, 1139.2, 759.4, 695.1; GC-MS (EI): m/z 194.0 (M^+); HRMS calcd for $C_{11}H_{14}OS$ (EI): 194.0765; Found: 194.0766.

2,2-bis(ethylthio)-3-phenylpropanal (3s)

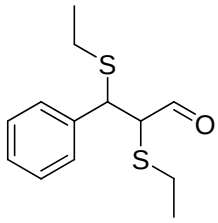
Purified with ethyl acetate/petroleum ether (1/100), yielding 79 mg (83%) of **3s** as a colorless oil. R_f = 0.41 (1/50 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ =1.20 (t, *J* = 7.52 Hz, 6H), 2.46-2.55 (m, 4H), 3.22 (s, 2H), 7.23-7.26 (m, 1H), 7.26-7.29 (m, 4H), 9.21 (s, 1H), ^{13}C NMR (100 MHz $CDCl_3$) δ = 13.88, 23.26, 39.58, 68.54, 127.27, 128.22, 130.44, 135.09, 188.89; IR (KBr) 3035.8, 2969.3, 2929.7, 2870.2, 1703.4, 1498.1, 1458.4, 1372.1, 1265.9, 1033.7, 974.2, 756.1, 696.7, 576.3 cm^{-1}; GC-MS (EI): m/z 254.0 (M^+); HRMS calcd for $C_{13}H_{18}OS_2$ (EI): 254.0799; Found: 254.0800.

(*Z*)-2-((2-(2-hydroxyethoxy)ethyl)thio)-3-phenylacrylaldehyde(3t)

Purified with ethyl acetate/petroleum ether (1/1), yielding 94 mg (76%) of **3t** as a yellow oil. R_f = 0.47 (1/4 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 2.58 (s, 1H), 3.14 (t, *J* = 6.24 Hz, 2H), 3.45-3.47 (m, 2H), 3.58-3.61 (m, 2H), 3.61-3.65 (m, 2H), 7.43-7.48 (m, 3H), 7.61 (s, 1H), 7.93-7.98 (m, 2H), 9.57 (s, 1H); ^{13}C NMR (100 MHz $CDCl_3$) δ = 31.98, 61.64, 70.30, 72.02, 128.62, 130.87, 131.34, 134.03, 135.42, 152.54, 191.79; IR (KBr) 3415.7, 2944.8, 2860.5, 1692.9, 1585.9, 1548.6, 1457.8, 1274.6, 1123.8, 1062.2, 758.9, 690.8, 538.4; GC-MS (EI): m/z 252.0 (M^+); HRMS calcd for $C_{13}H_{16}O_3S$ (EI): 252.0820 ; Found: 252.0816

2,3-bis(ethylthio)-3-phenylpropanal

Purified with diethyl ether/petroleum ether (1/30), yielding 33 mg (26%) of **IV** as a yellow oil. R_f = 0.40 (1/20 ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz $CDCl_3$) δ = 9.2034 (d, *J* = 5.72Hz, 1H), 7.2569-7.3764 (m, 5H), 3.9101 (d, *J* = 11.48Hz, 1H), 3.4625 (dd, J_1 = 11.52Hz, J_2 = 5.76Hz), 1.0789-1.2624 (m, 6H); ^{13}C NMR (100 MHz $CDCl_3$) δ = 189.18, 138.68, 128.81, 128.29, 127.94, 56.97, 47.09, 25.61, 25.10, 14.26, 14.05; GC-MS (EI): m/z 254.0 (M^+)

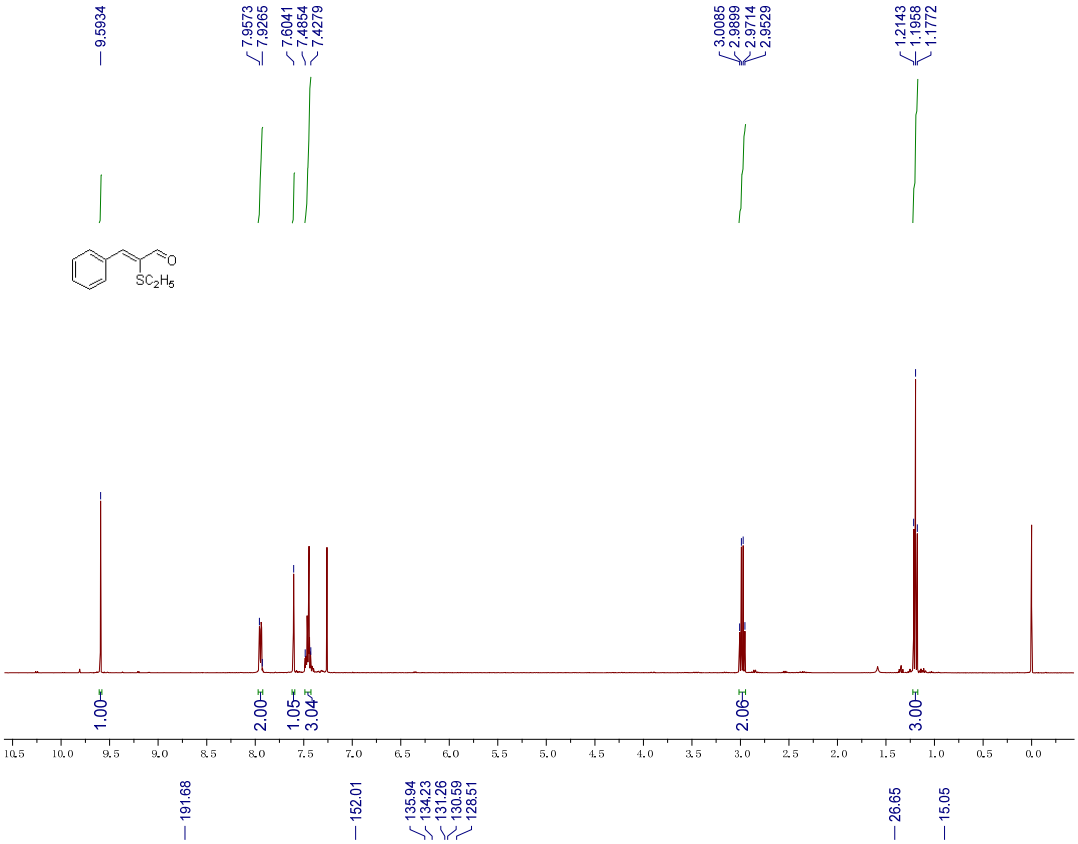


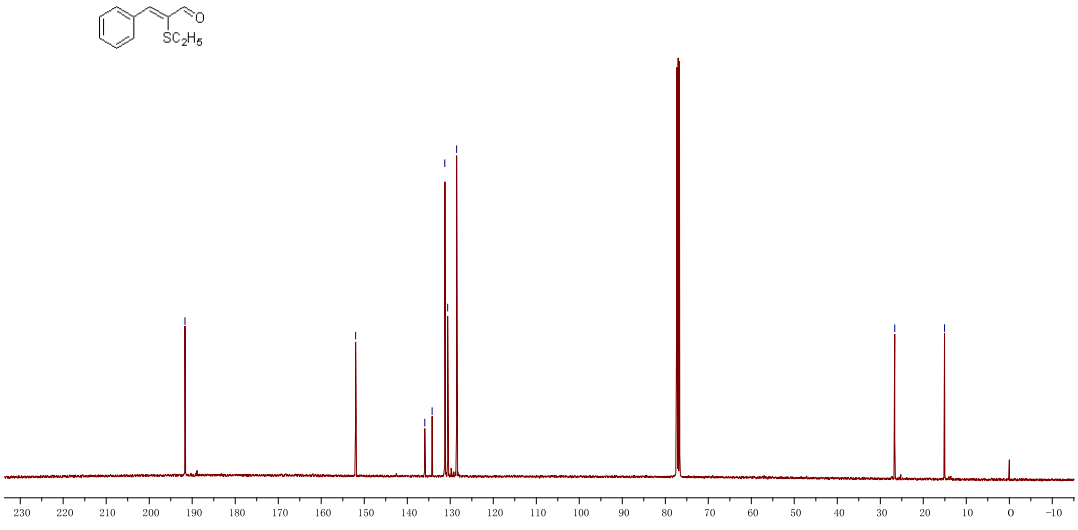
References

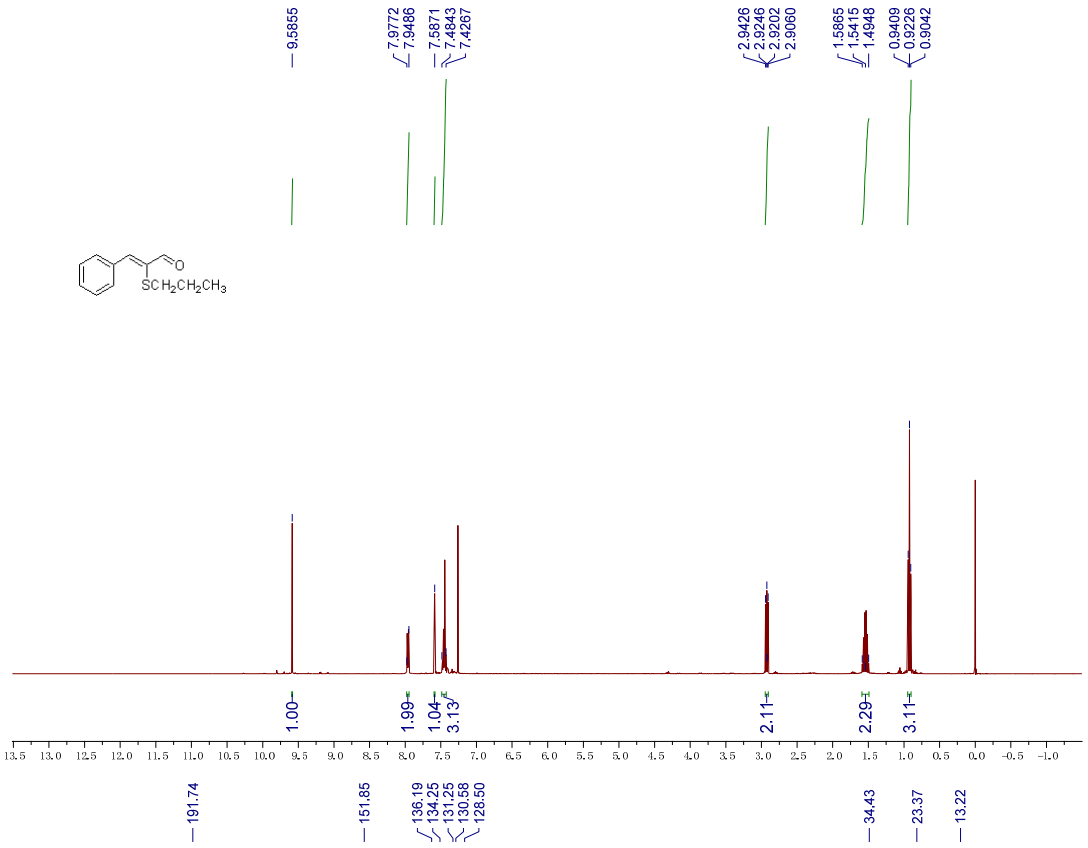
1. a) C. F. H. Allen, and C. O. Edens, *Organic Syntheses,* **1955**, 92; b) Deb K. Barma, Biao Lu, Rachid Baati, Charles Mioskowski, and J. R. Falck, *Tetrahedron Letters,* **2008**, 49, 4359-4361.

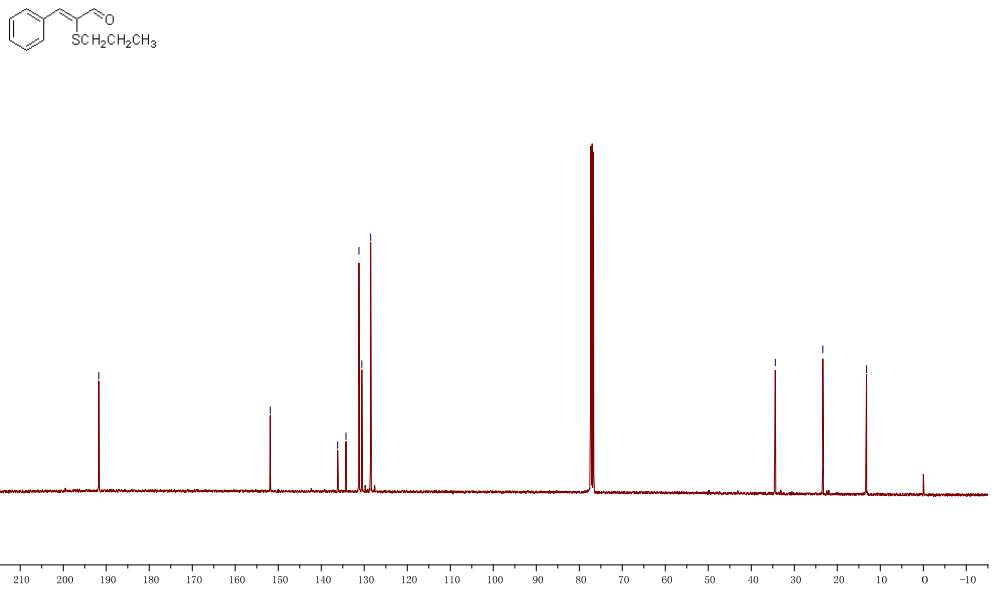
2. Claudio C. Silveira, Gelson Perin, Antonio L. Braga, Miguel J. Dabdoub, and Raquel G. Jacob, *Tetrahedron*, **1999**, 55, 7421-7432.

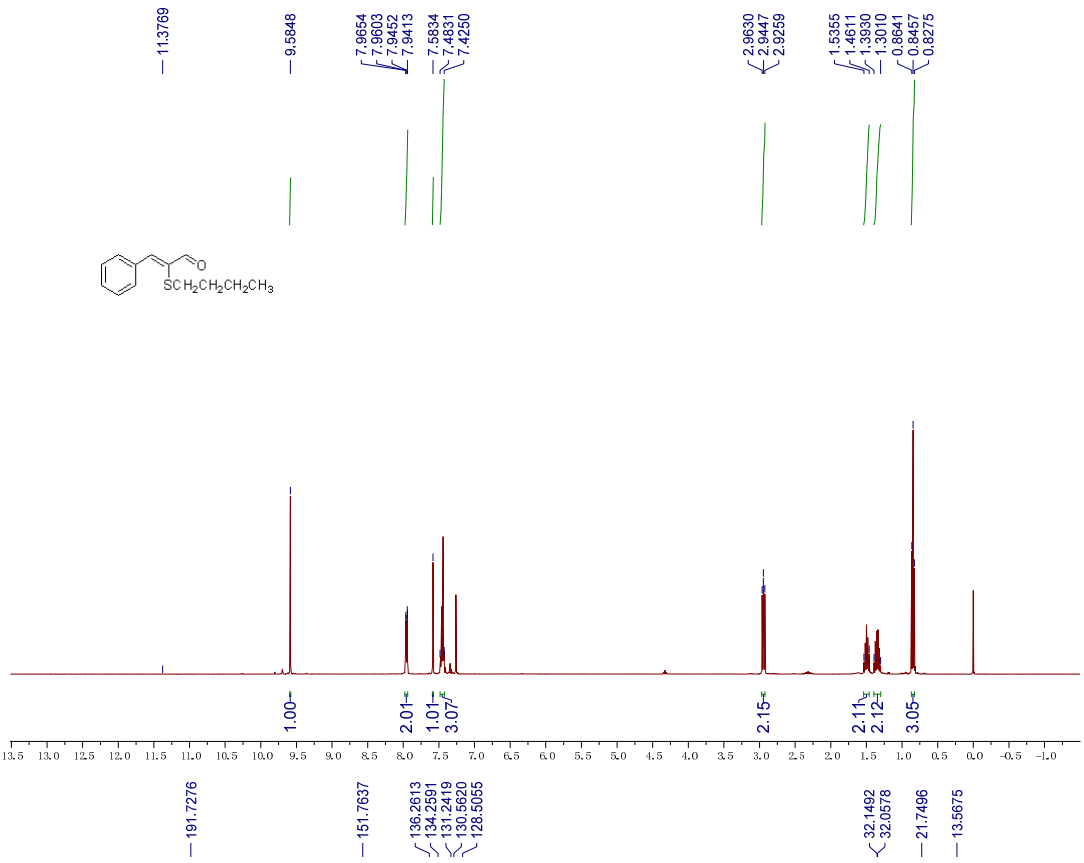
^{1}H and ^{13}C NMR Spectra of Products

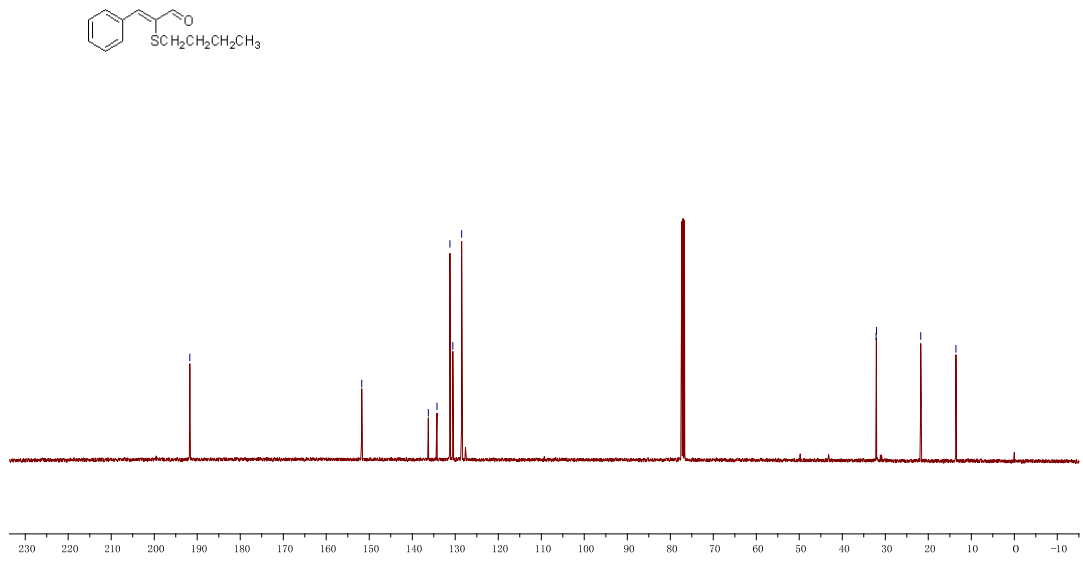




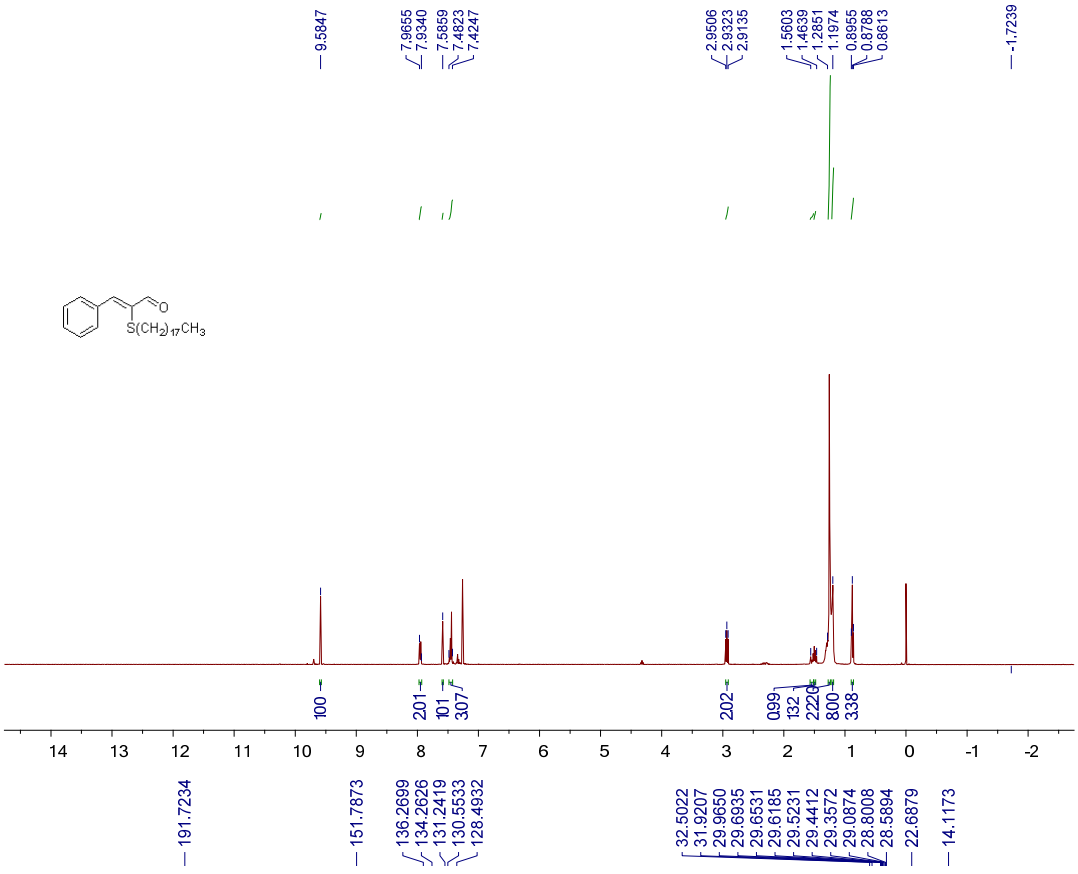

9.5855
7.9772
7.9486
7.5871
7.4843
7.4267
2.9426
2.9246
2.9202
2.9060
1.5865
1.5415
1.4948
0.9409
0.9226
0.9042
O
SCH2CH2CH3
1.00
1.99
1.04
3.13
2.11
2.29
3.11
191.74
151.85
136.19
134.25
131.25
130.58
128.50
34.43
23.37
13.22

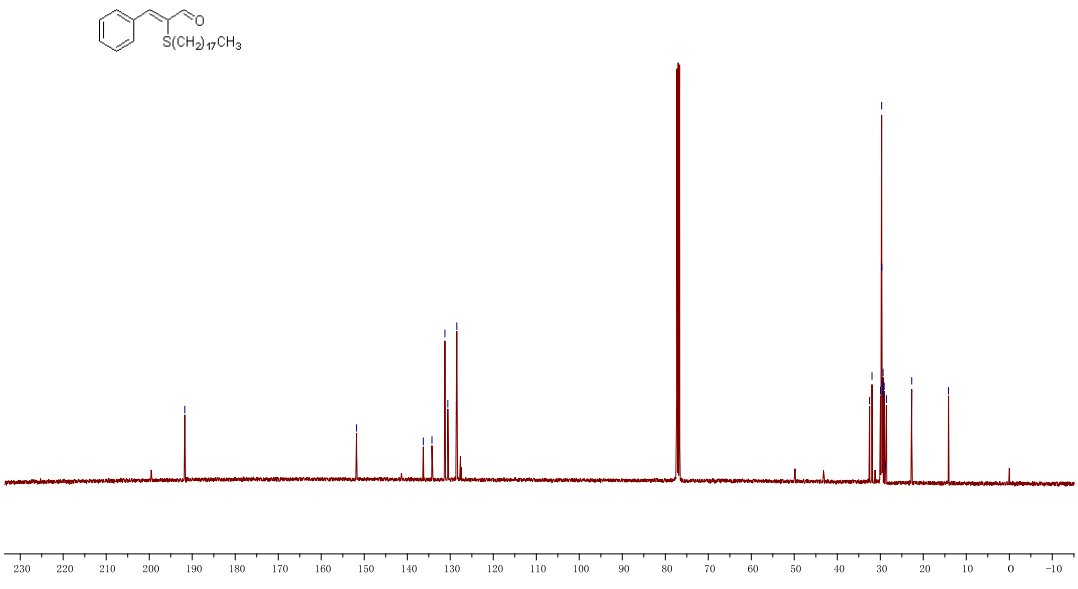

O
SCH2CH2CH3

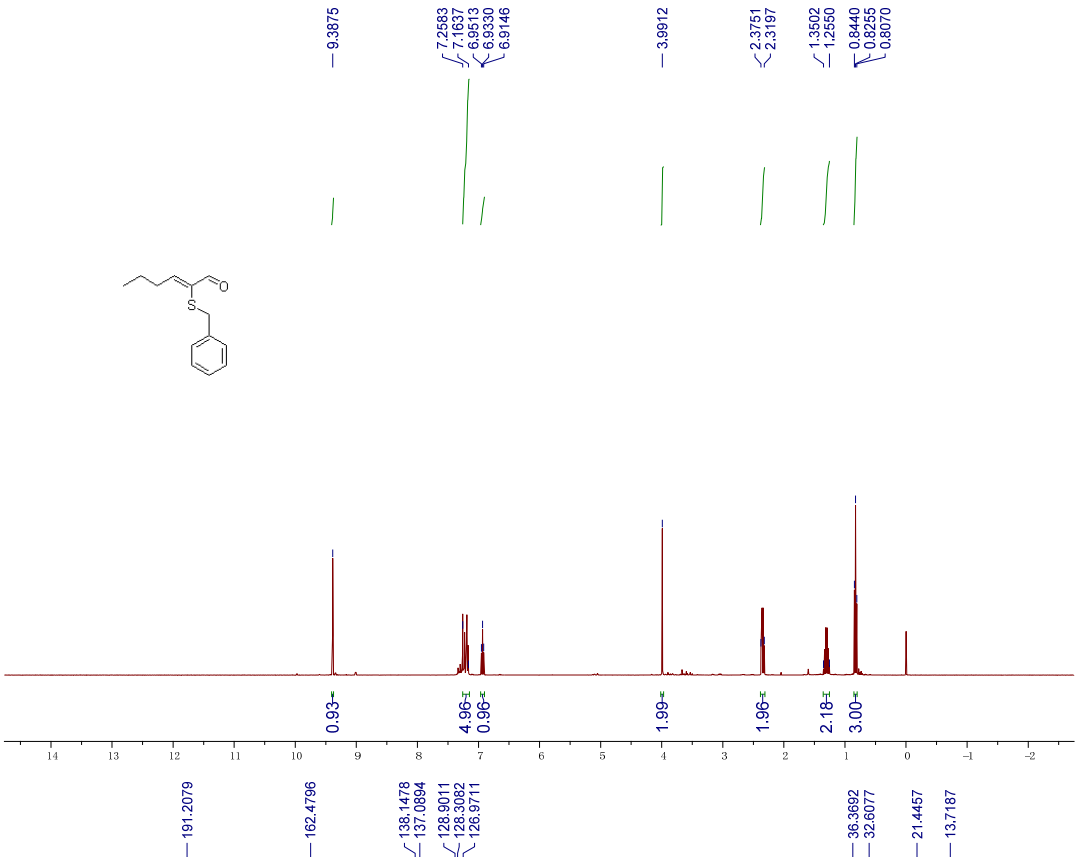

11.3769
9.5848
7.9654
7.9603
7.9452
7.9413
7.5834
7.4831
7.4250
2.9630
2.9447
2.9259
1.5355
1.4611
1.3930
1.3010
0.8641
0.8457
0.8275
O
SCH2CH2CH2CH3
1.00
2.01
1.01
3.07
2.15
2.11
2.12
3.05

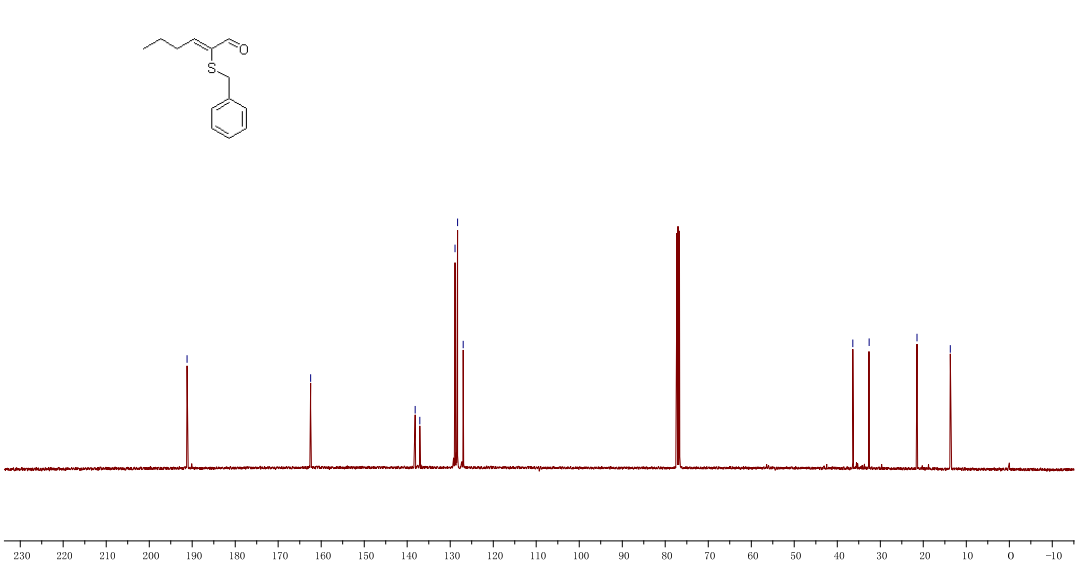

191.7276
151.7637
136.2613
134.2591
131.2419
130.5820
128.5055
32.1492
32.0578
21.7496
13.5675

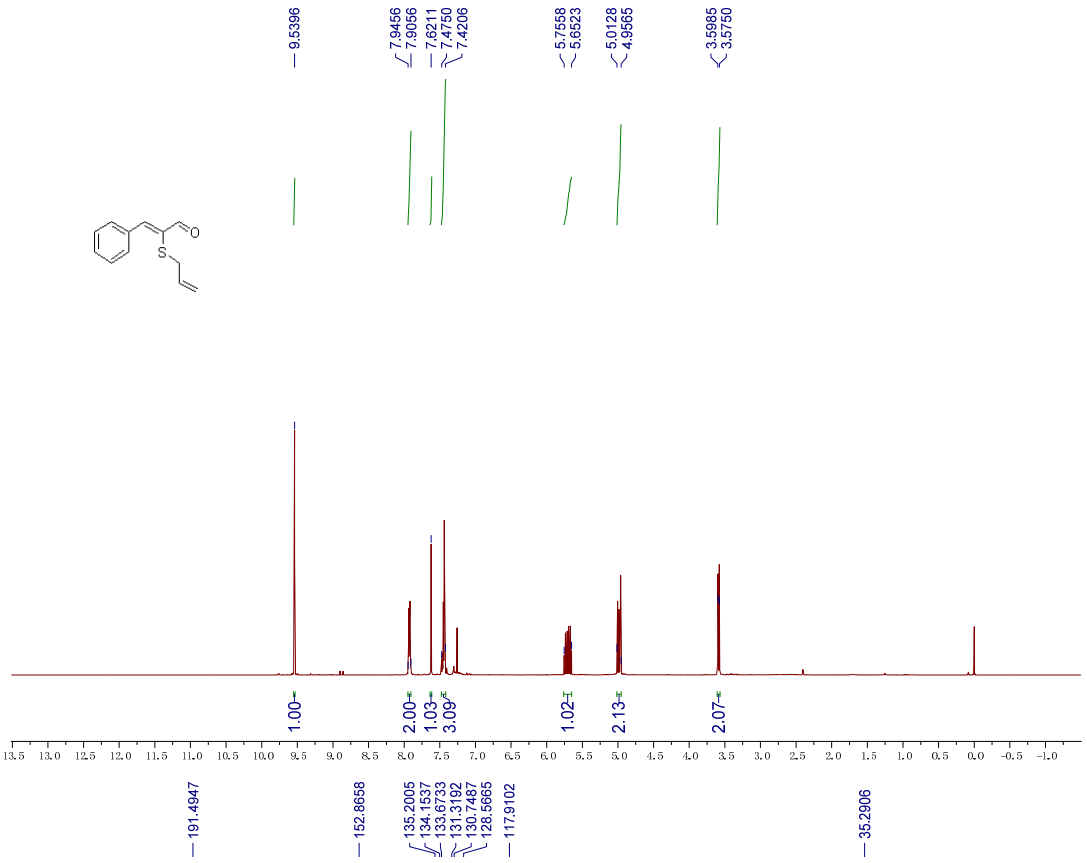
O
SCH2CH2CH2CH3

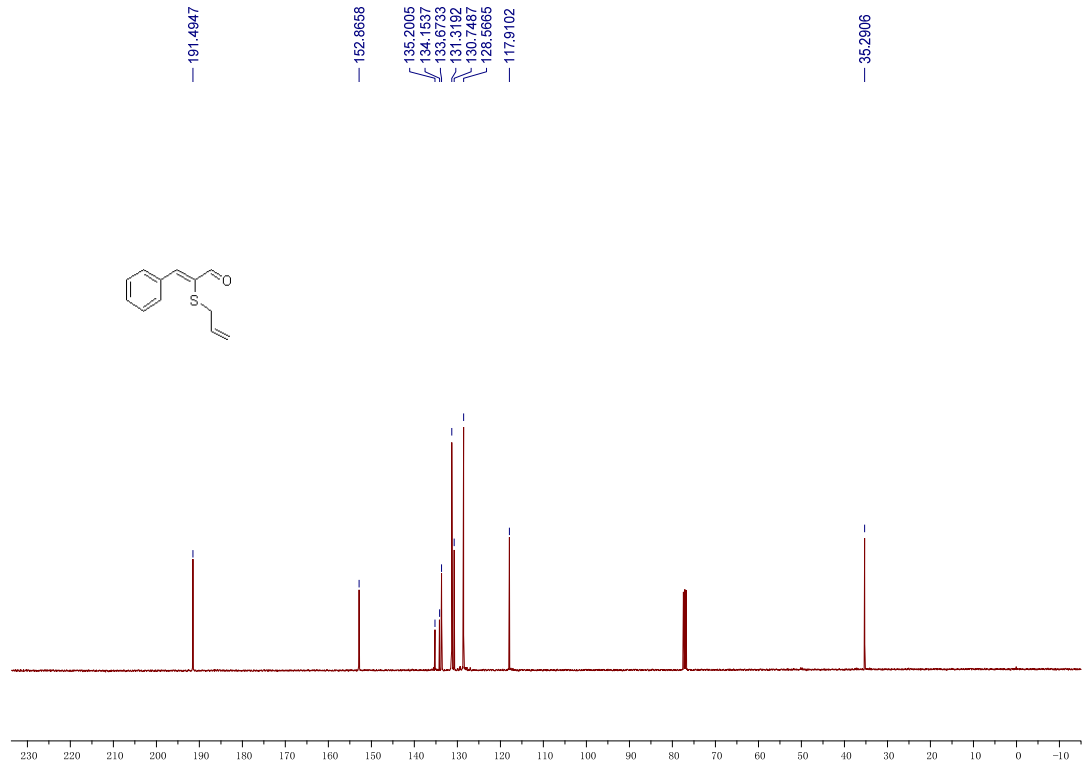

9.5847
7.9655
7.9340
7.5859
7.4823
7.4247
2.9506
2.9323
2.9135
1.5603
1.4639
1.2851
1.1974
0.8955
0.8788
0.8613
-1.7239
O
S(CH2)17CH3
100
201
101
307
202
099
132
222
800
338
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
191.7234
151.7873
136.2699
134.2626
131.2419
130.5533
128.4932
32.5022
31.9207
29.9650
29.6935
29.6531
29.6185
29.5231
29.4412
29.3572
29.0874
28.8008
28.5894
22.6879
14.1173

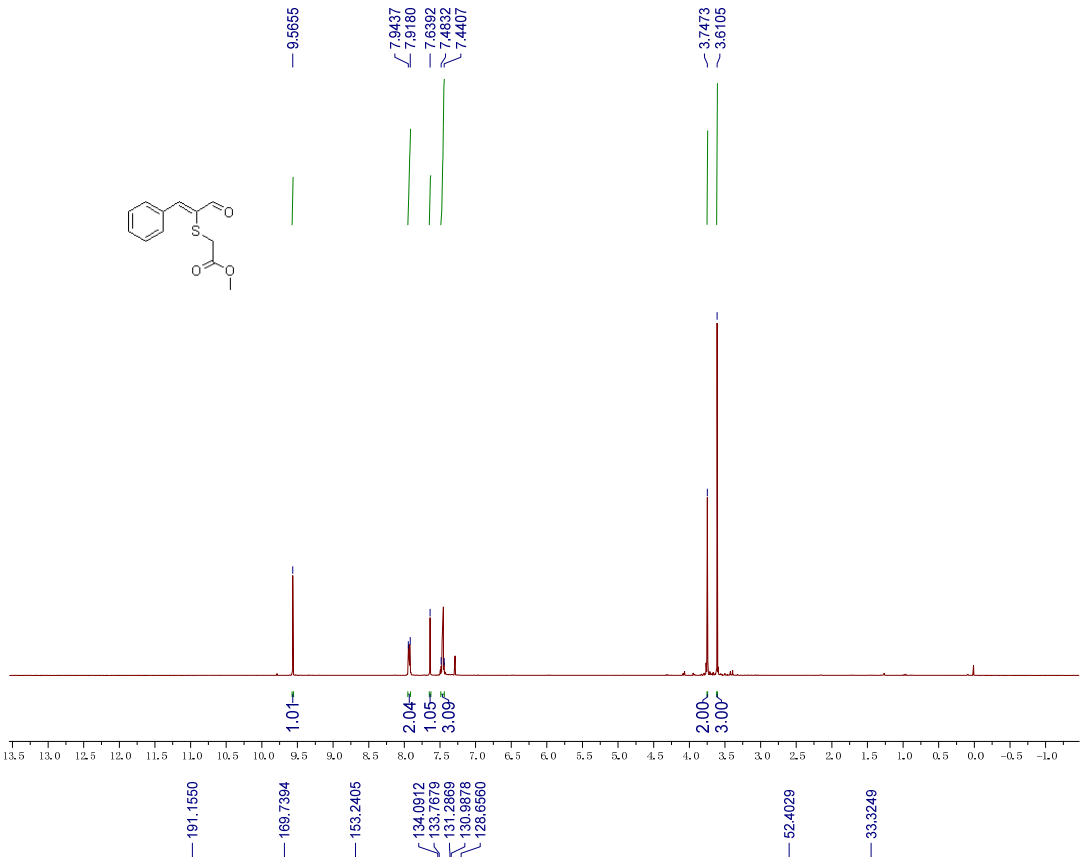

O
S(CH2)17CH3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

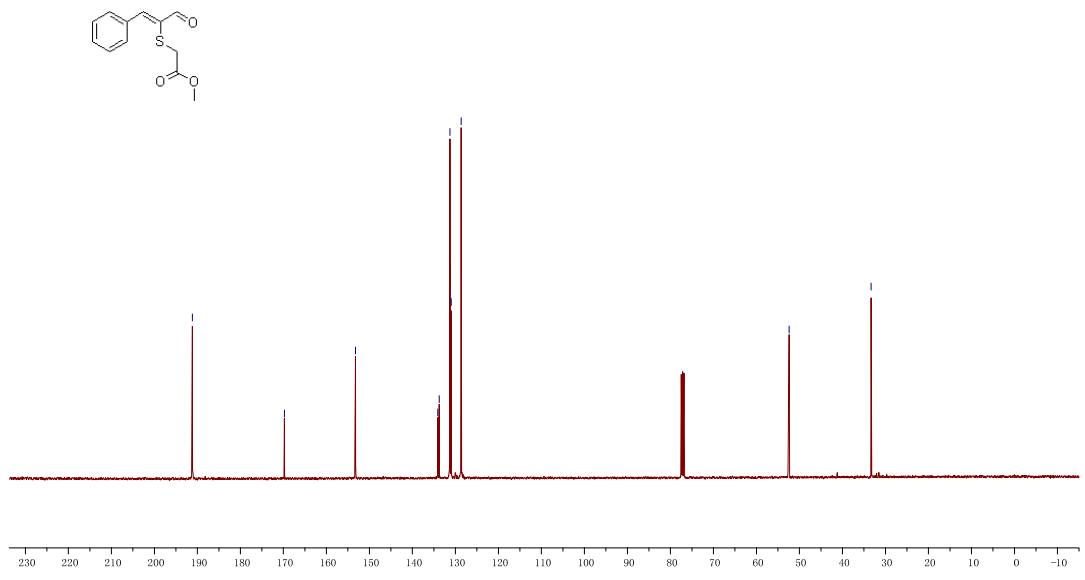

9.3875
7.2583
7.1637
6.9513
6.9330
6.9146
3.8912
2.3751
2.3197
1.3502
1.2550
0.8440
0.8255
0.8070
O
S
0.93
4.96
0.96
1.99
1.96
2.18
3.00

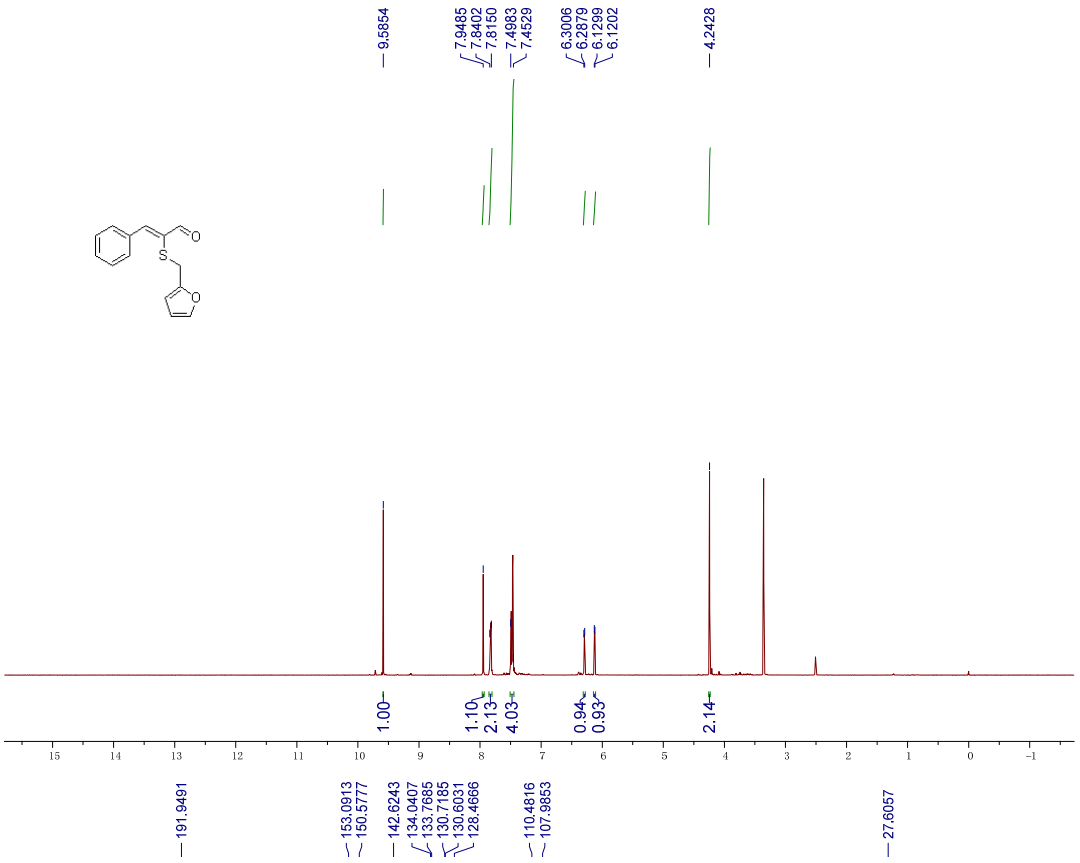

191.2079
162.4796
138.1478
137.0894
128.9011
128.3082
126.9711
36.3692
32.6077
21.4457
13.7187
O
S

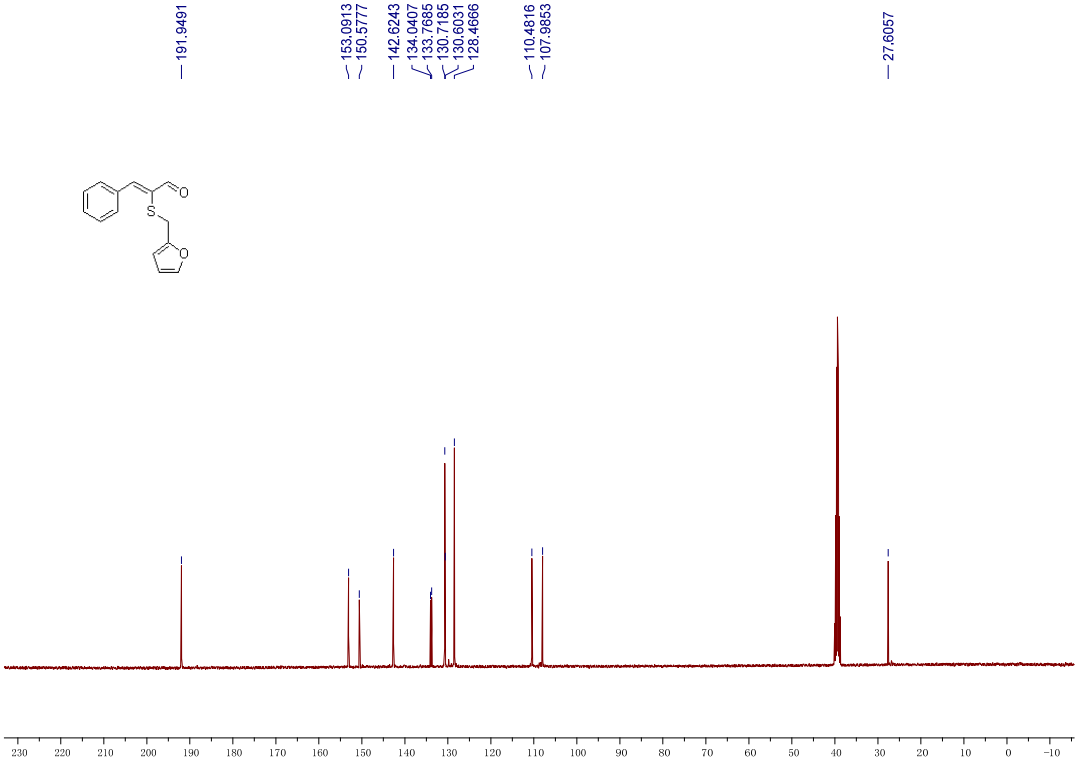

9.5396
7.9456
7.9056
7.6211
7.4750
7.4206
5.7558
5.6523
5.0128
4.9565
3.5985
3.5750
O
S
1.00
2.00
1.03
3.09
1.02
2.13
2.07

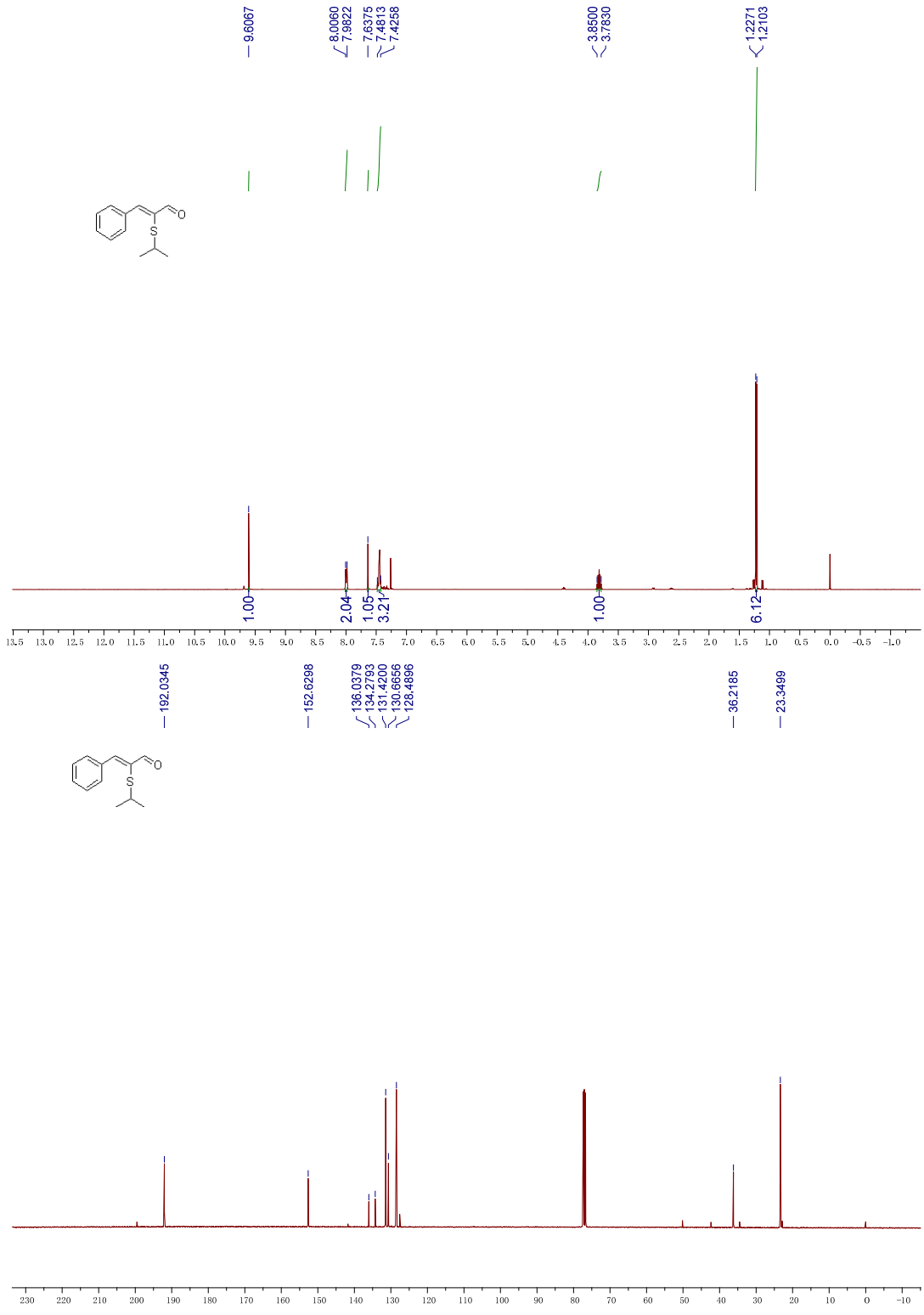

191.4947
152.8658
135.2005
134.1537
133.6733
131.3192
130.7487
128.5665
117.9102
35.2906
O
S

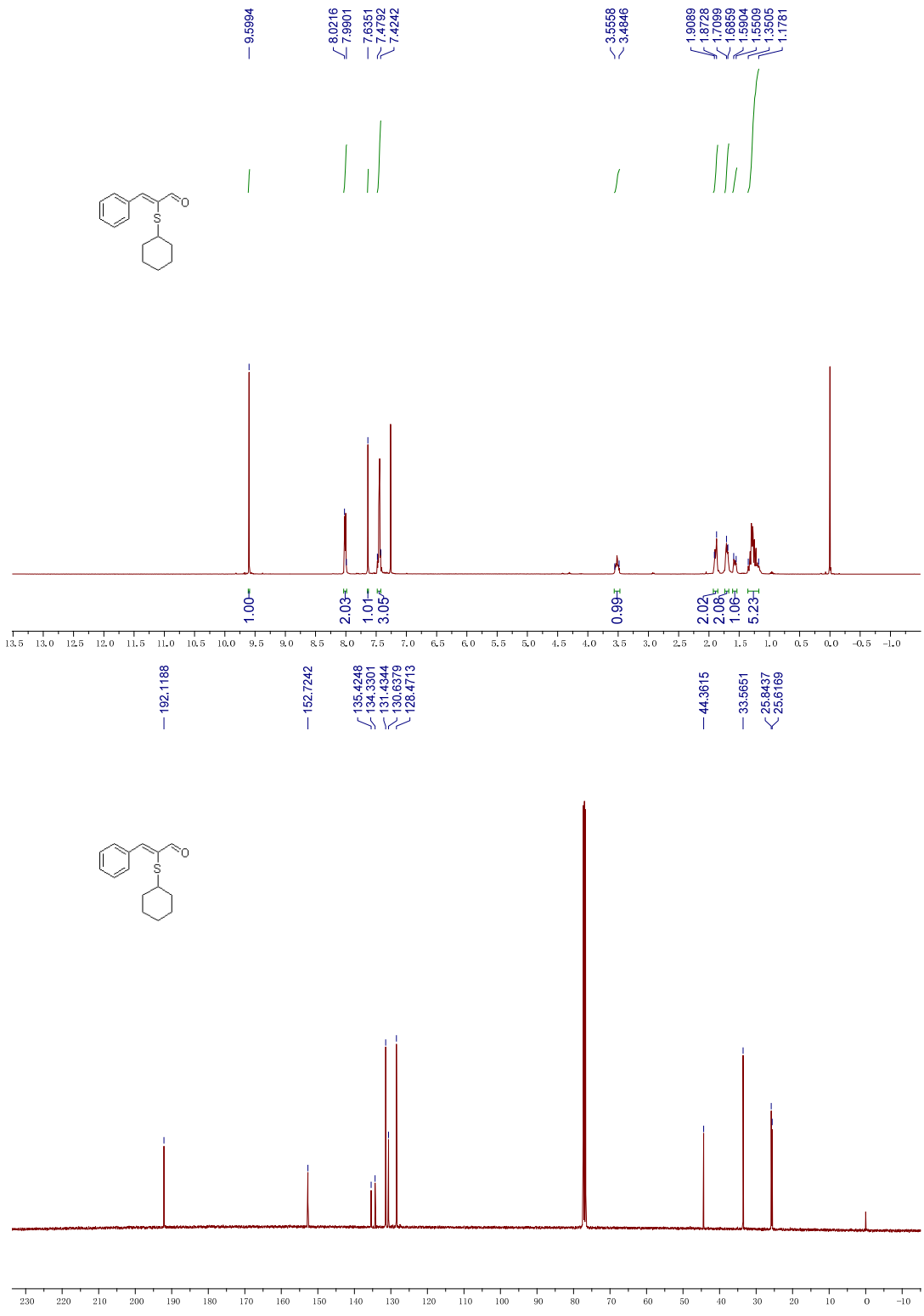

9.5655
7.9437
7.9180
7.6392
7.4832
7.4407
3.7473
3.6105
1.01
2.04
1.05
3.09
2.00
3.00

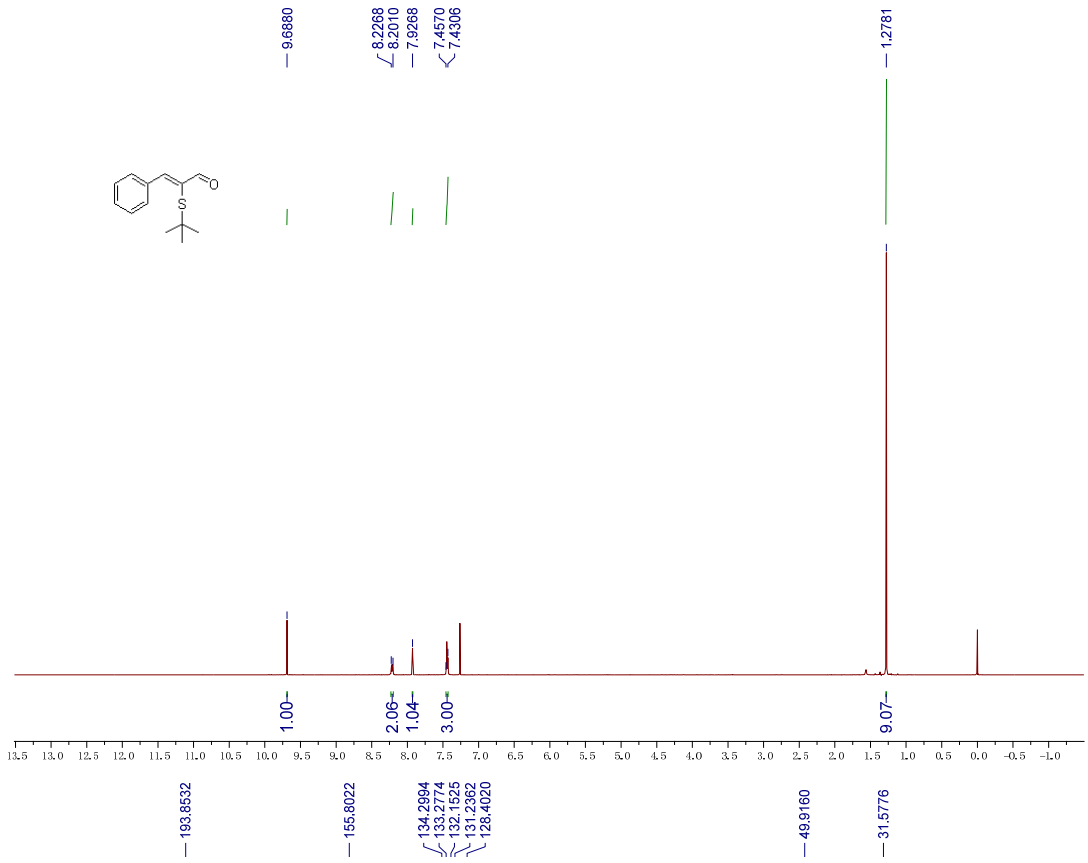

191.1550
169.7394
153.2405
134.0912
133.7679
131.2869
130.9878
128.6560
52.4029
33.3249

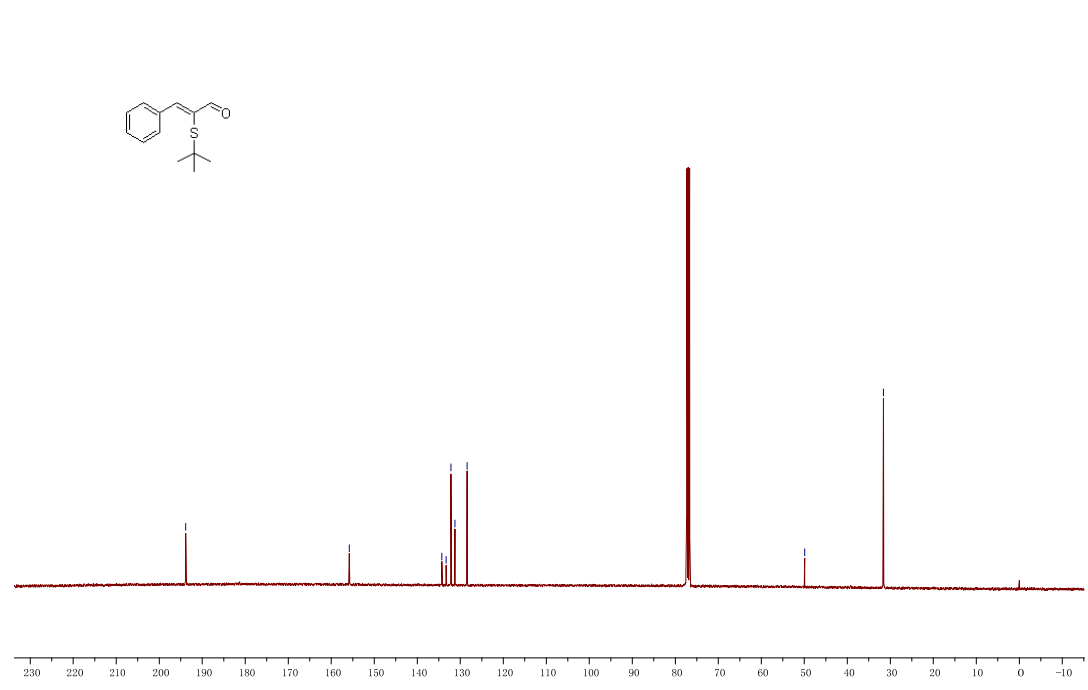

9.5854
7.9485
7.8402
7.8150
7.4983
7.4529
6.3006
6.2879
6.1299
6.1202
4.2428
1.00
1.10
2.13
4.03
0.94
0.93
2.14

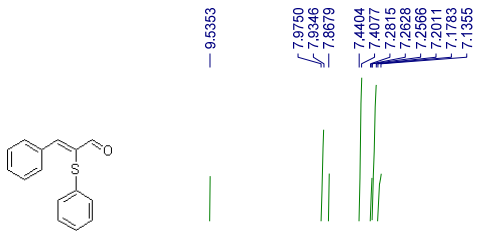

191.9491
153.0913
150.5777
142.6243
134.0407
133.7685
130.7185
130.6031
128.4666
110.4816
107.9853
27.6057

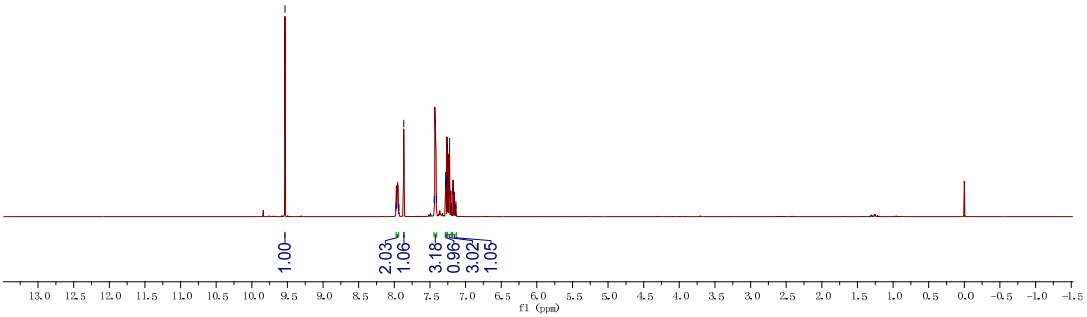

9.6067
8.0060
7.9822
7.6375
7.4813
7.4258
3.8500
3.7830
1.2271
1.2103
O
S
1.00
2.04
1.05
3.21
1.00
6.12
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
192.0345
152.6298
136.0379
134.2793
131.4200
130.6656
128.4896
36.2185
23.3499
O
S
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


9.5994
8.0216
7.9901
7.6351
7.4792
7.4242
3.5558
3.4846
1.9089
1.8728
1.7099
1.6859
1.5904
1.5509
1.3505
1.1781
O
S
1.00
2.03
1.01
3.05
0.99
2.02
2.08
1.06
5.23
192.1188
152.7242
135.4248
134.3301
131.4344
130.6379
128.4713
44.3615
33.5651
25.8437
25.6169

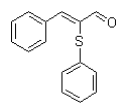

9.6880
8.2268
8.2010
7.9268
7.4570
7.4306
1.2781
O
S
1.00
2.06
1.04
3.00
9.07

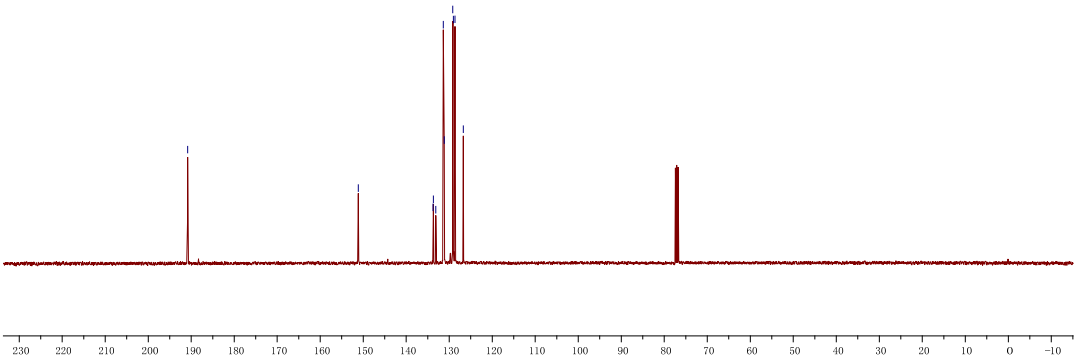

193.8532
155.8022
134.2994
133.2774
132.1525
131.2362
128.4020
49.9160
31.5776
O
S

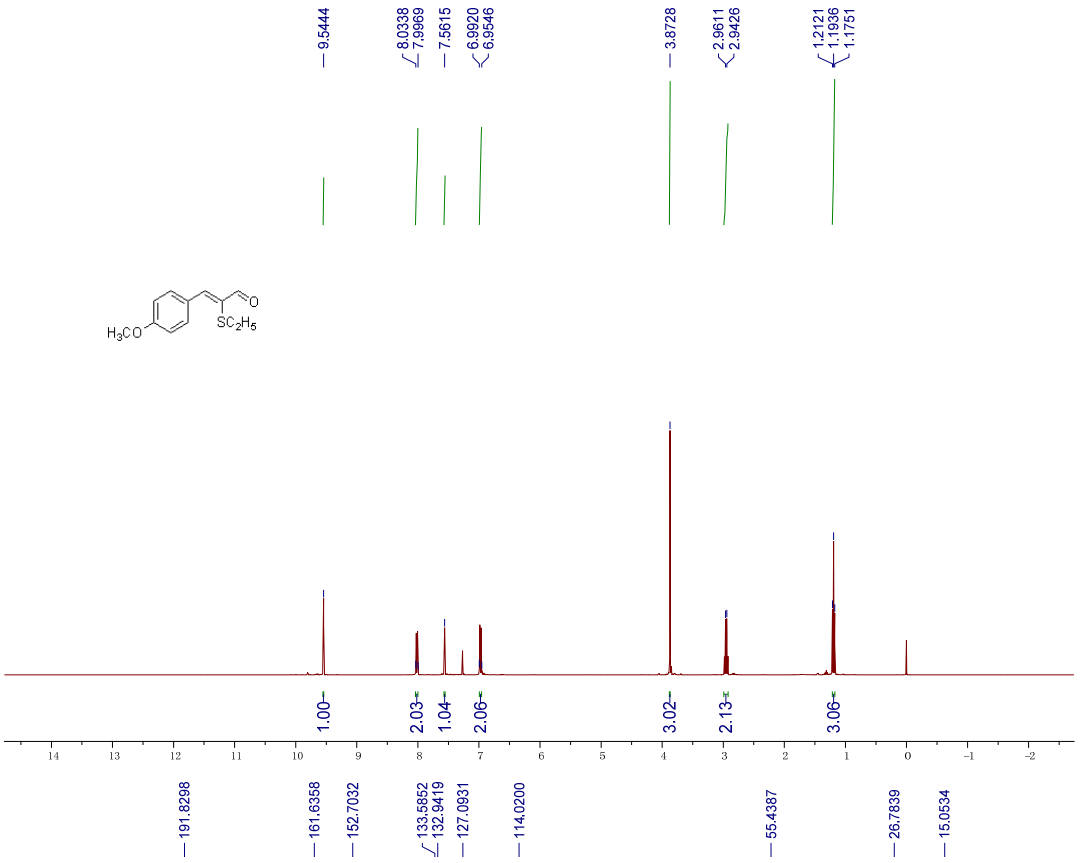

9.5353
7.9750
7.9346
7.8679
7.4404
7.4077
7.2815
7.2628
7.2566
7.2011
7.1783
7.1355
O
S

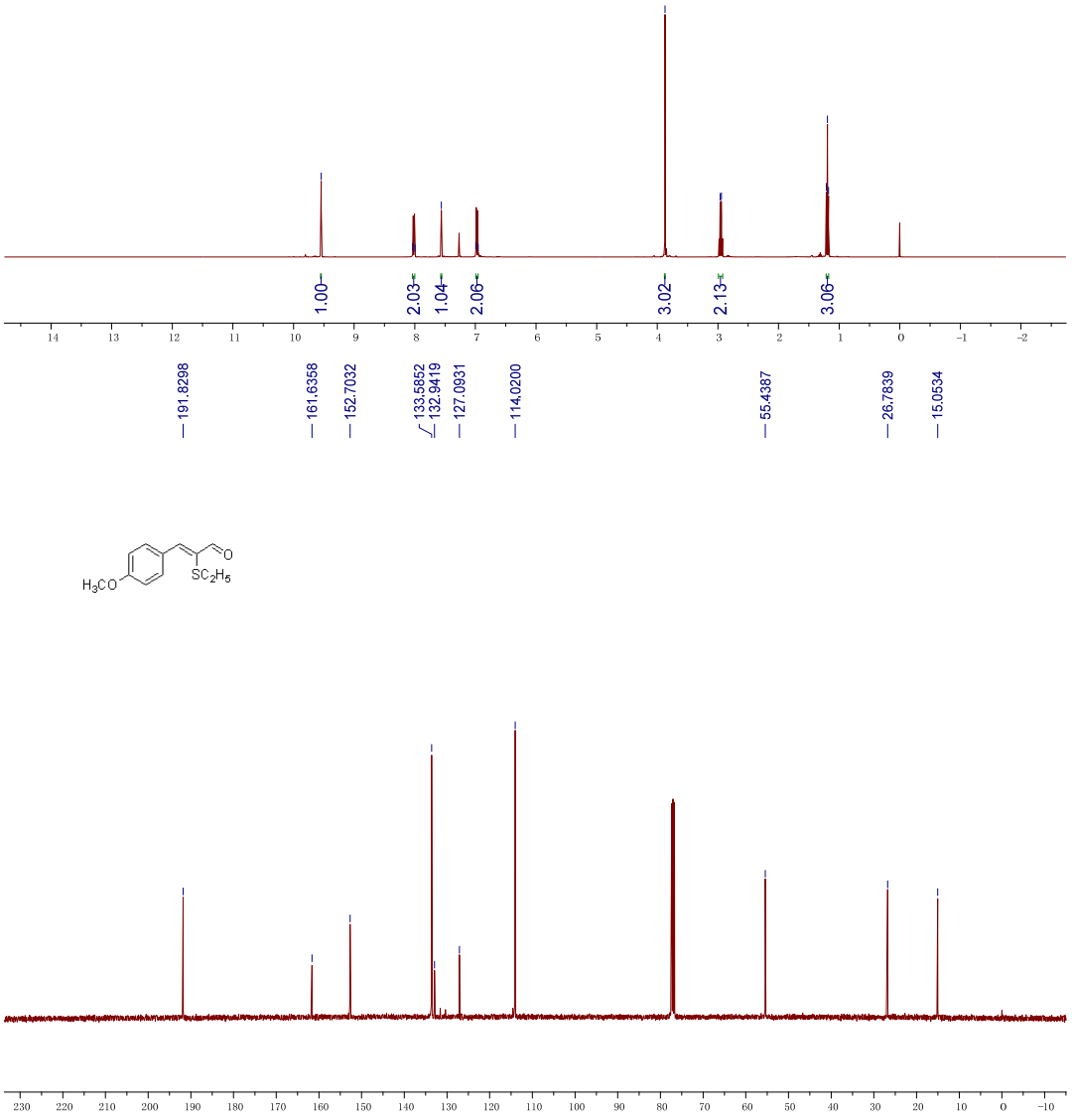

1.00
2.03
1.06
3.18
0.96
3.02
1.05
f1 (ppm)

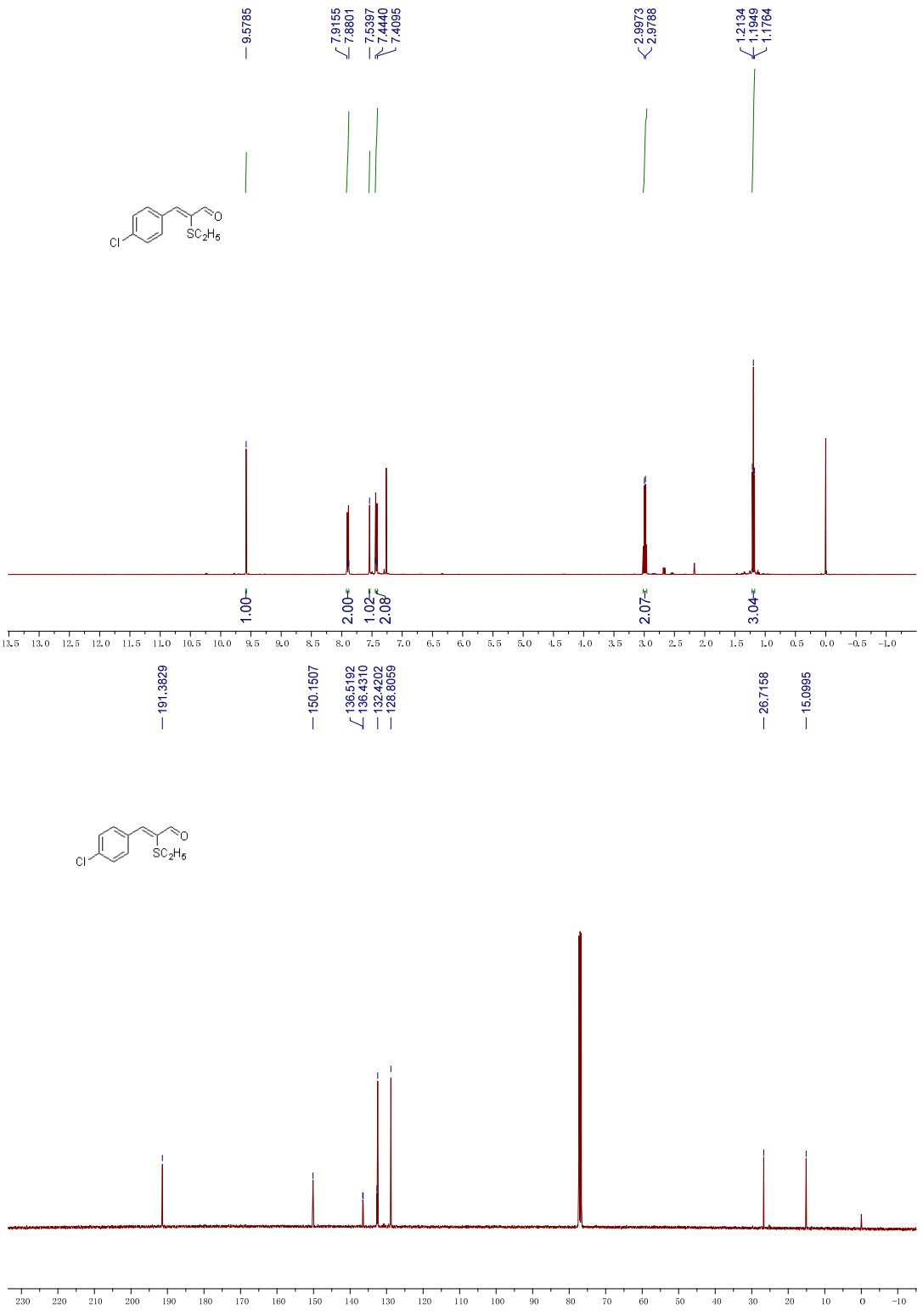

190.8438
151.1571
133.7639
133.6807
133.1127
131.3896
131.1652
129.1663
129.0209
128.6671
126.7278

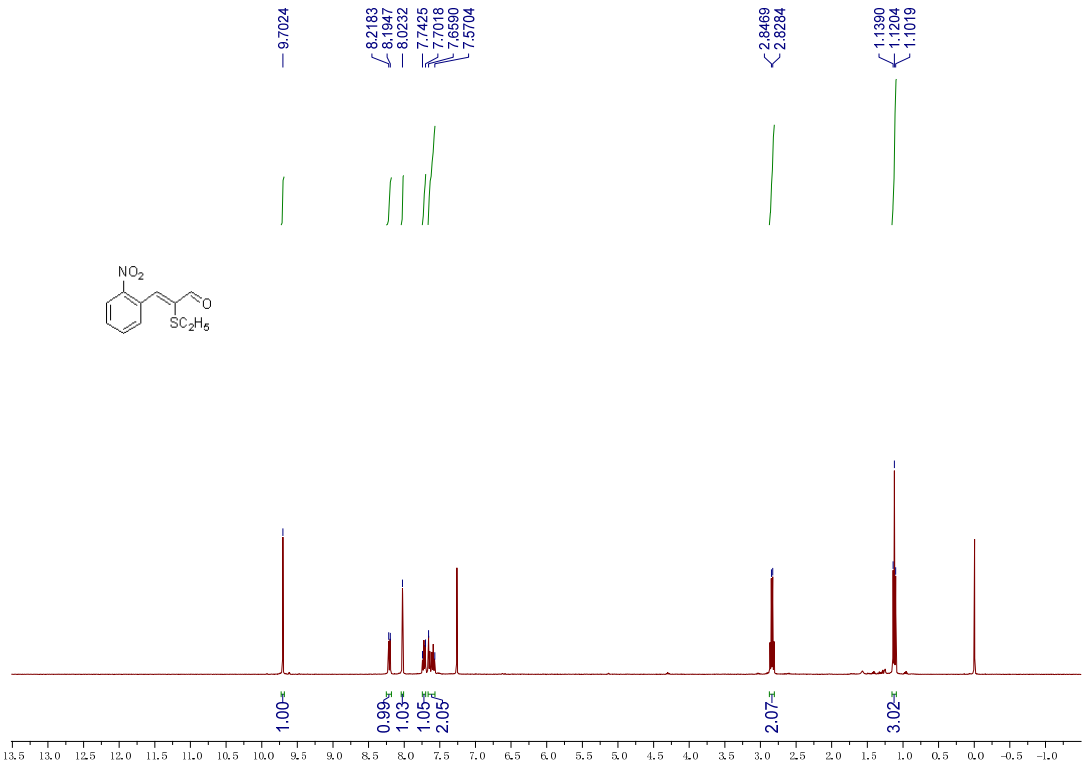

O
S

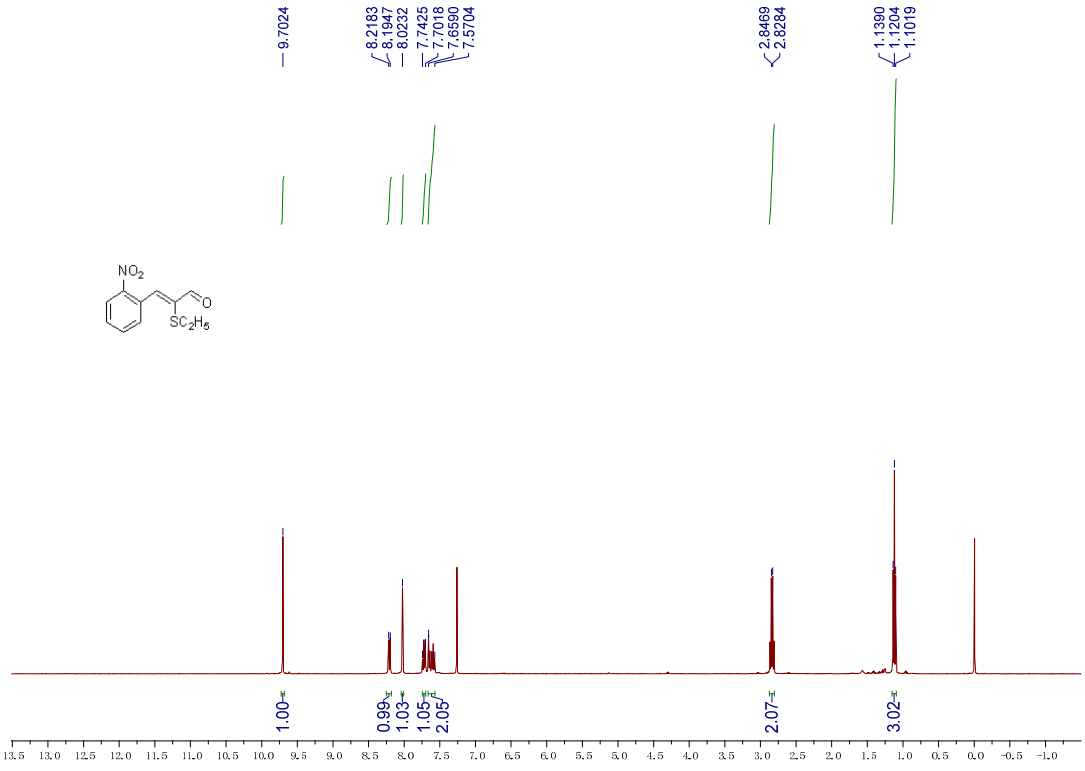


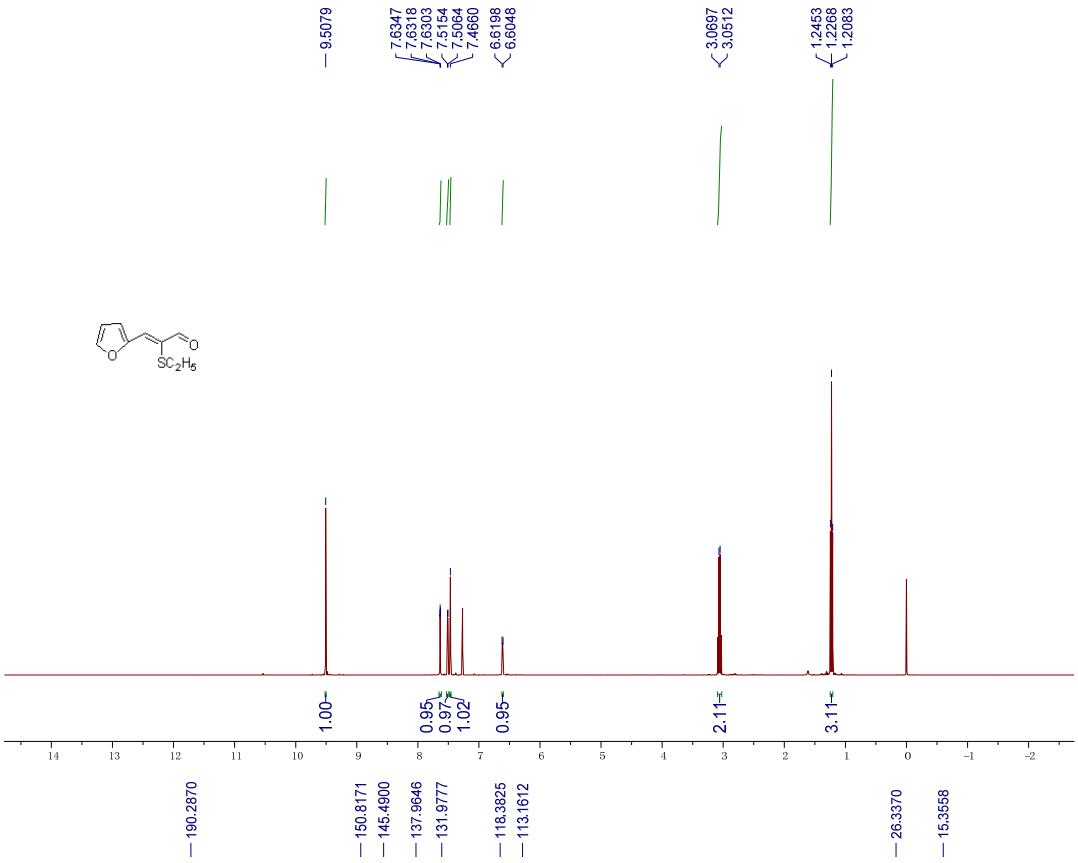

9.5444
8.0338
7.9969
7.5615
6.9920
6.9546
3.8728
2.9611
2.9426
1.2121
1.1936
1.1751
O
H3CO
SC2H5
1.00
2.03
1.04
2.06
3.02
2.13
3.06

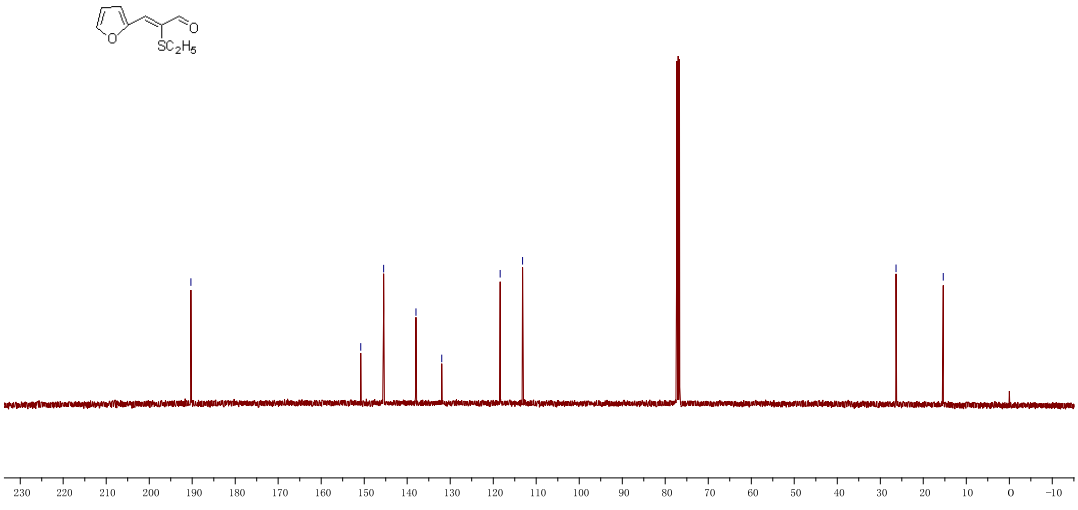

191.8298
161.6358
152.7032
133.5852
132.9419
127.0931
114.0200
55.4387
26.7839
15.0534
O
H3CO
SC2H5

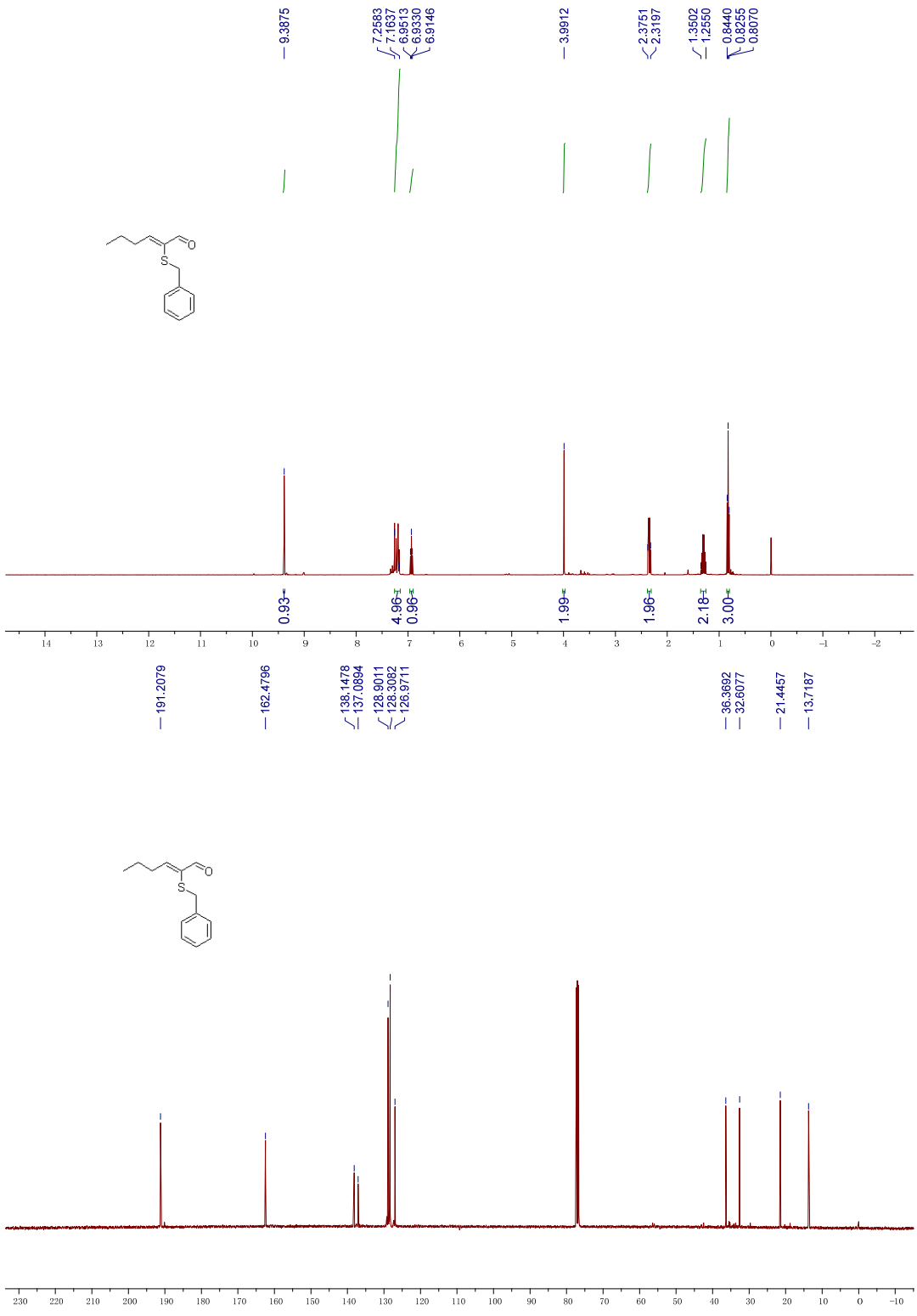

9.5785
7.9155
7.8801
7.5397
7.4440
7.4095
2.9973
2.9788
1.2134
1.1949
1.1764
Cl
O
SC2H5
1.00
2.00
1.02
2.08
2.07
3.04
191.3829
150.1507
136.5192
136.4310
132.4202
128.8059
26.7158
15.0995

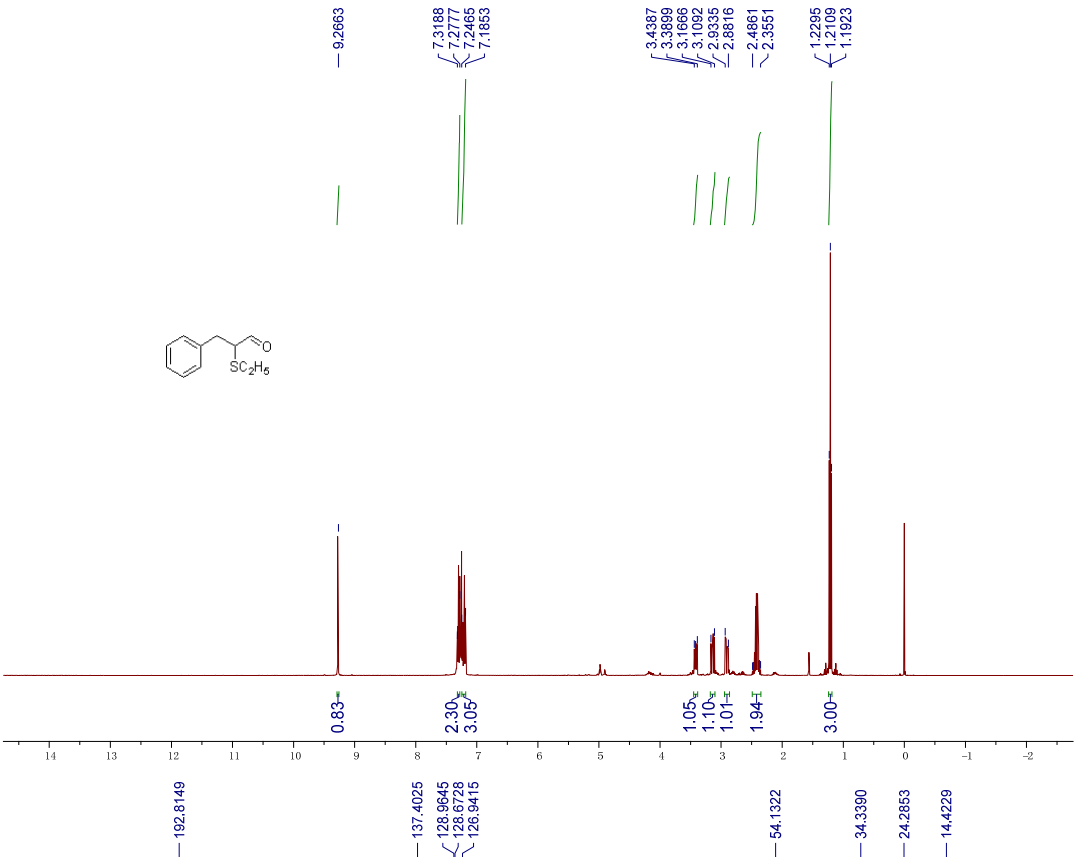

9.7024
8.2183
8.1947
8.0232
7.7425
7.7018
7.6590
7.5704
2.8469
2.8284
1.1390
1.1204
1.1019
NO2
O
SC2H5
1.00
0.99
1.03
1.05
2.05
2.07
3.02

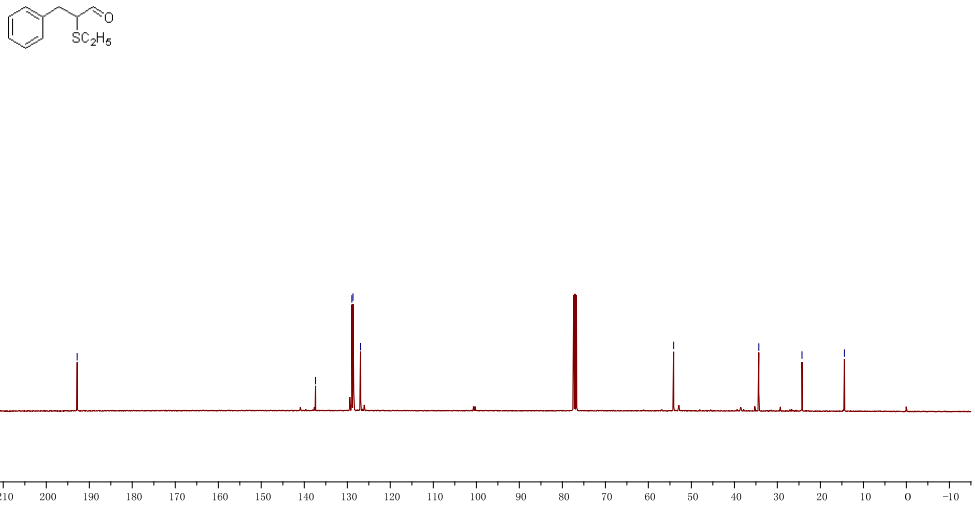

9.7024
8.2183
8.1947
8.0232
7.7425
7.7018
7.6590
7.5704
2.8469
2.8284
1.1390
1.1204
1.1019
NO2
O
SC2H5
1.00
0.99
1.03
1.05
2.05
2.07
3.02

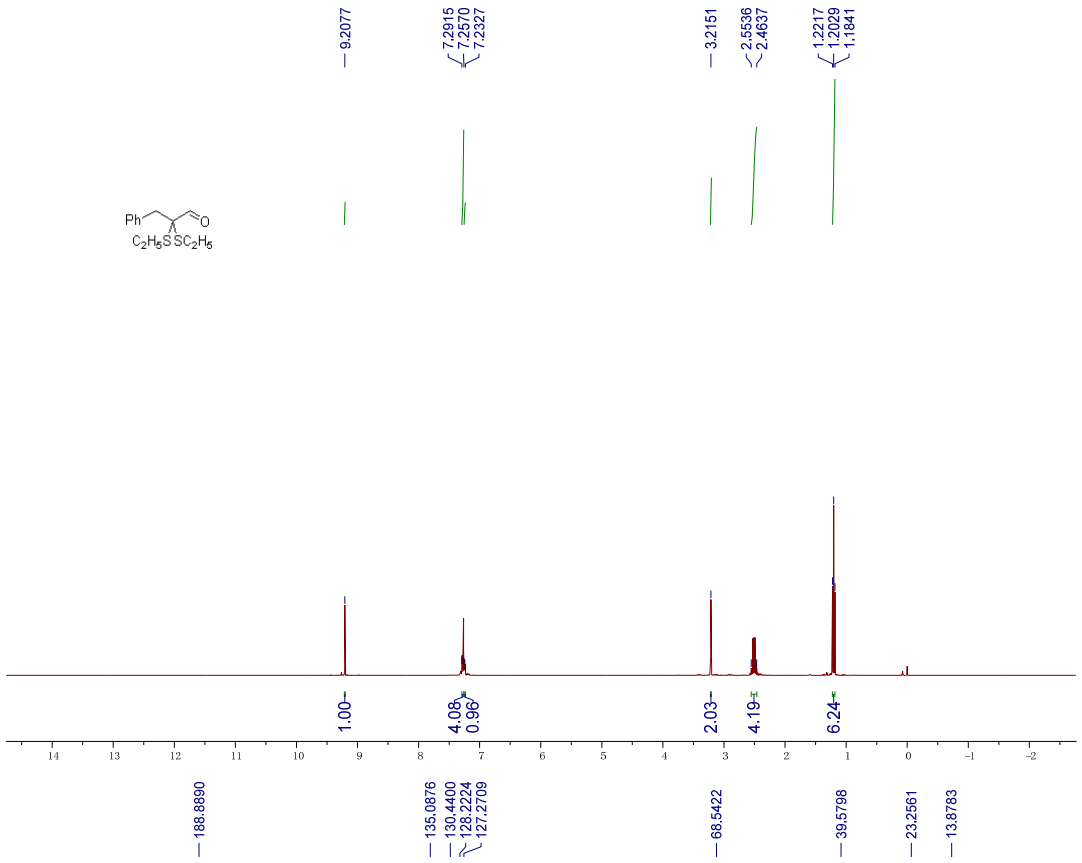

9.5079
7.6347
7.6318
7.6303
7.5154
7.5064
7.4660
6.6198
6.6048
3.0697
3.0512
1.2453
1.2268
1.2083
O
SC2H5
1.00
0.95
0.97
1.02
0.95
2.11
3.11

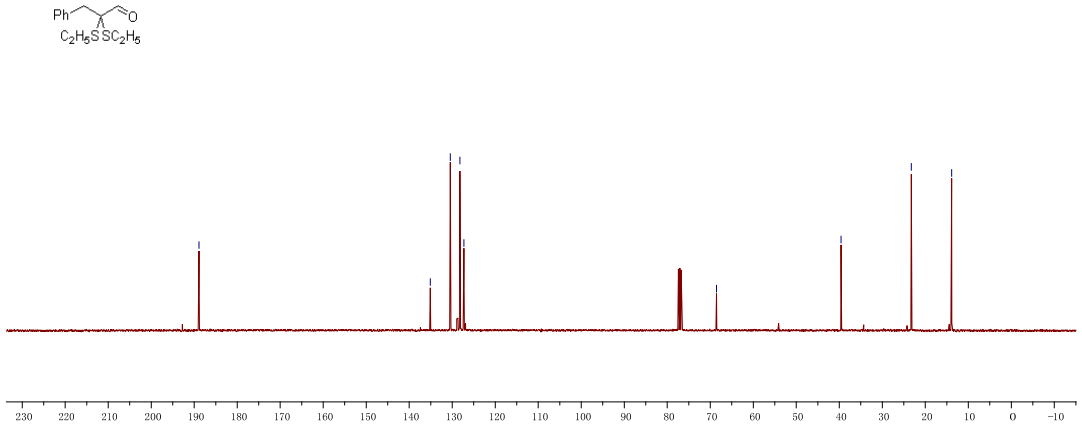

190.2870
150.8171
145.4900
137.9646
131.9777
118.3825
113.1612
26.3370
15.3558
O
SC2H5

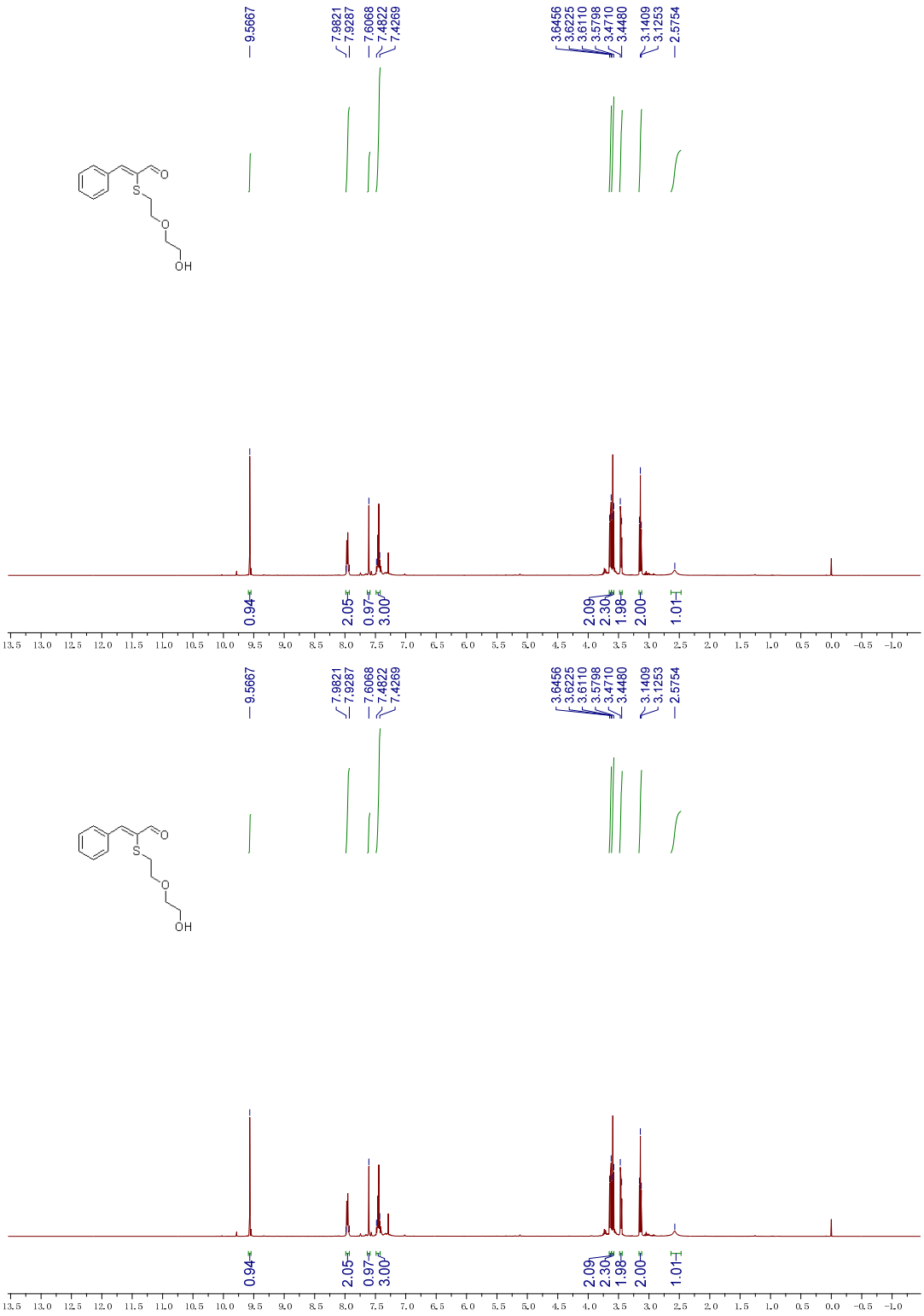

9.3875
7.2583
7.1637
6.9513
6.9330
6.9146
3.9912
2.3751
2.3197
1.3502
1.2550
0.8440
0.8255
0.8070
O
S
0.93
4.96
0.96
1.99
1.96
2.18
3.00
191.2079
162.4796
138.1478
137.0894
128.9011
128.3082
126.9711
36.3692
32.6077
21.4457
13.7187

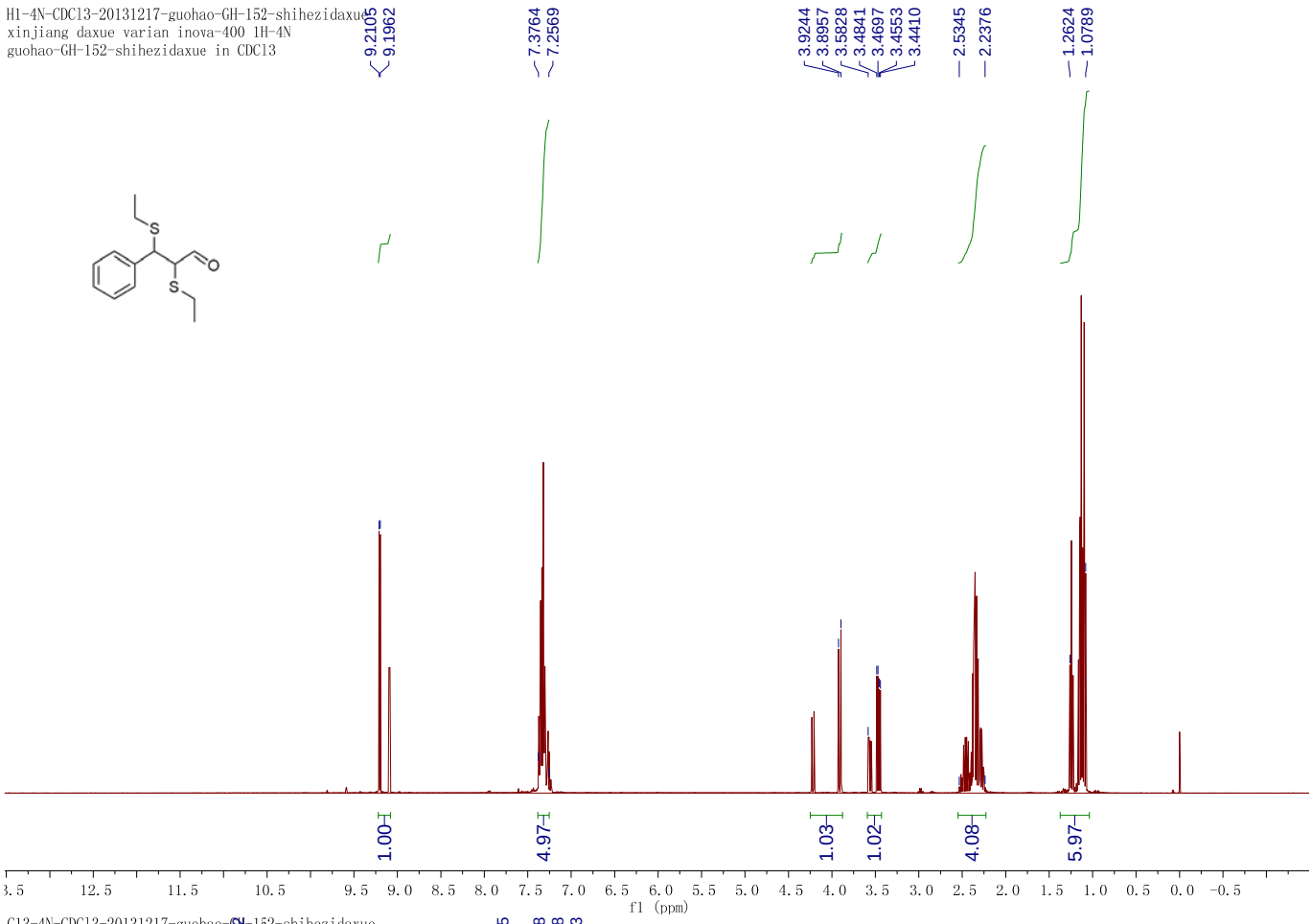

9.2663
7.3188
7.2777
7.2465
7.1853
3.4387
3.3899
3.1666
3.1092
2.9335
2.8816
2.4861
2.3551
1.2295
1.2109
1.1923
O
SC2H5
0.83
2.30
3.05
1.05
1.10
1.01
1.94
3.00
192.8149
137.4025
128.9645
128.6728
126.9415
54.1322
34.3390
24.2853
14.4229

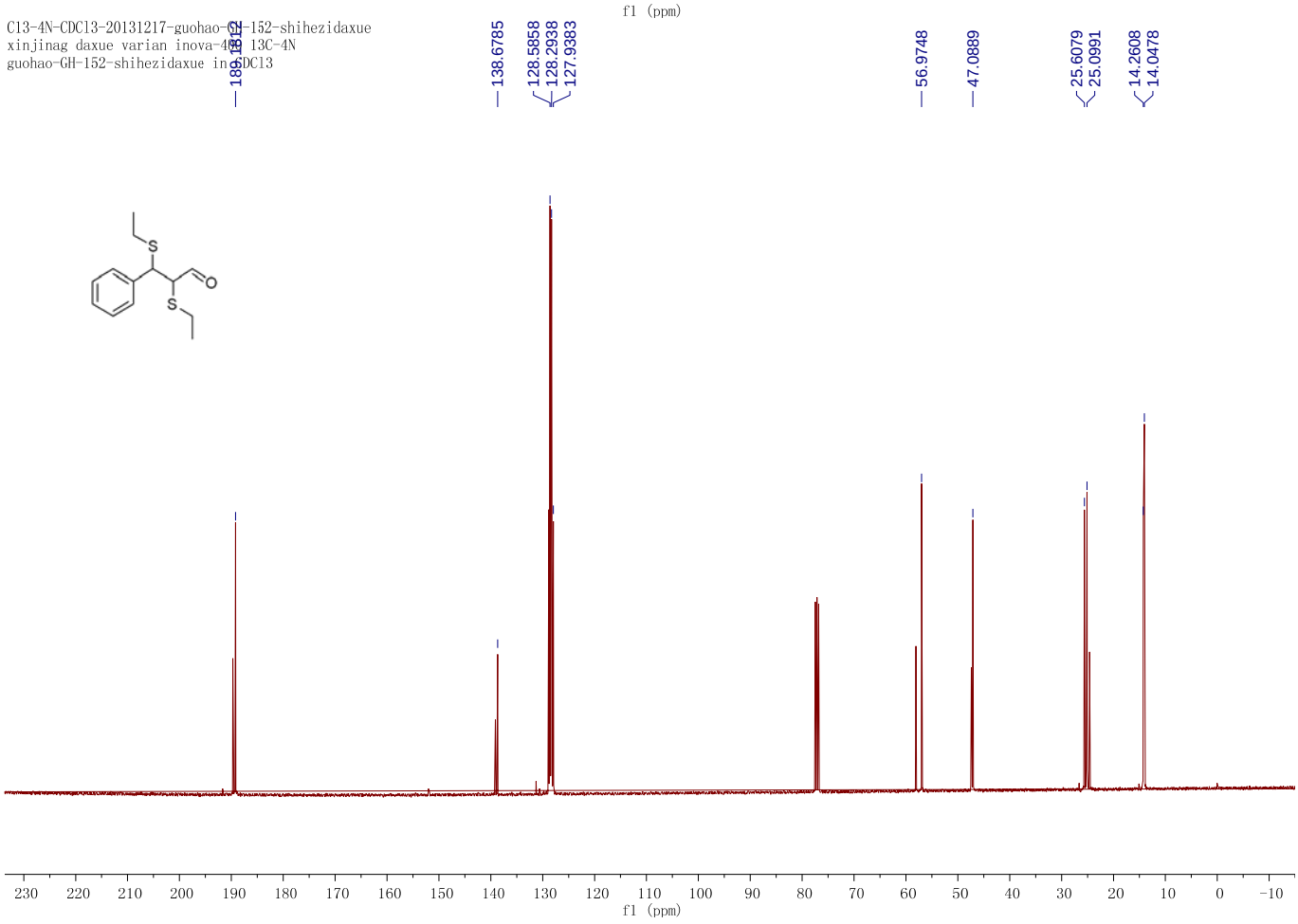

O
SC2H5


9.2077
7.2915
7.2570
7.2327
3.2151
2.5536
2.4637
1.2217
1.2029
1.1841
Ph
O
C2H5SSC2H5
1.00
4.08
0.96
2.03
4.19
6.24
188.8890
135.0876
130.4400
128.2224
127.2709
68.5422
39.5798
23.2561
13.8783

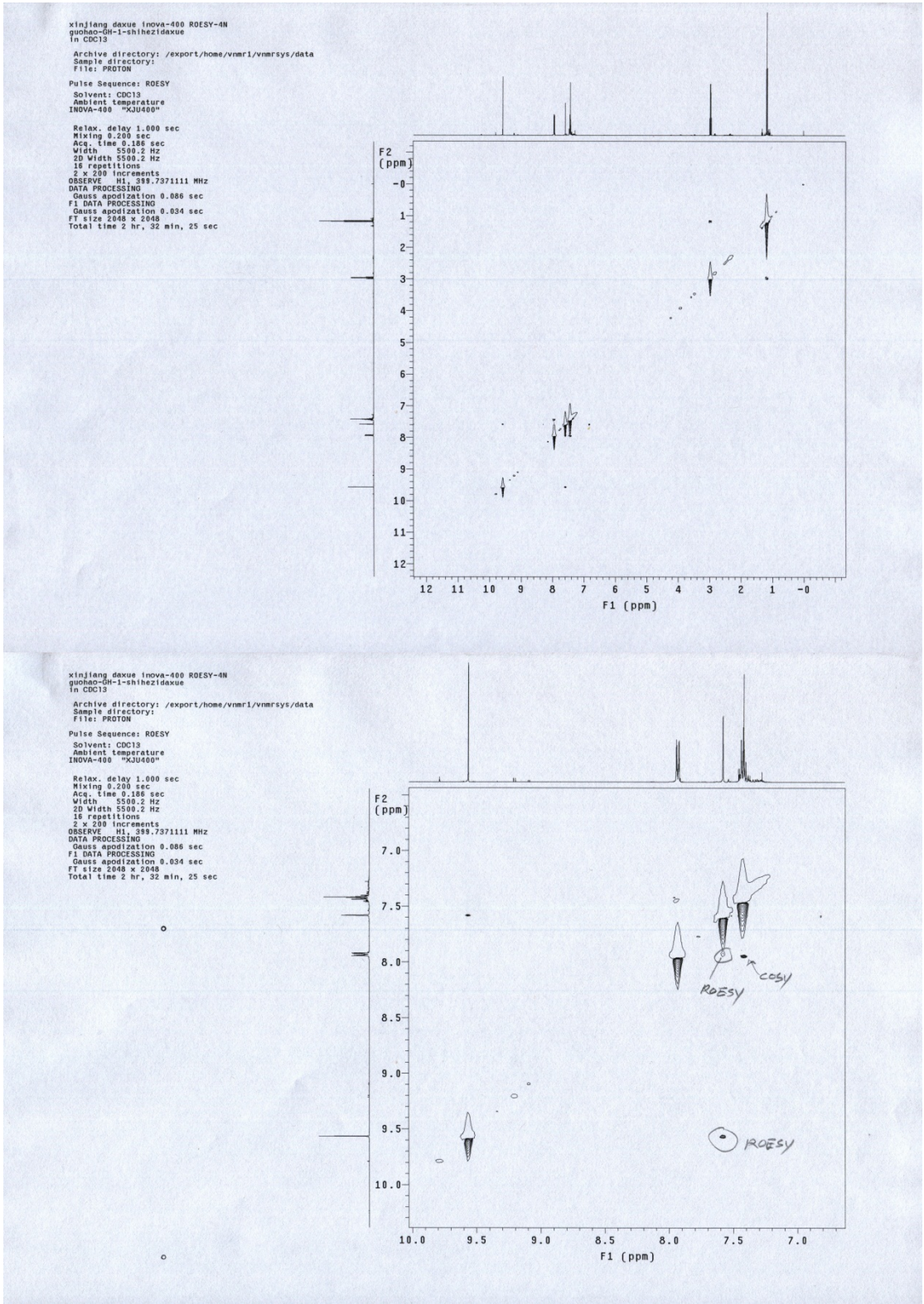

Ph
O
C2H5SSC2H5


9.5667
7.9821
7.9287
7.6068
7.4822
7.4269
3.6456
3.6225
3.6110
3.5798
3.4710
3.4480
3.1409
3.1253
2.5754
O
S
O
OH
0.94
2.05
0.97
3.00
2.09
2.30
1.98
2.00
1.01


H1-4N-CDCl3-20131217-guohao-GH-152-shihezidaxue
xinjiang daxue varian inova-400 1H-4N
guohao-GH-152-shihezidaxue in CDCl3
9.2105
9.1962
7.3764
7.2569
3.9244
3.8957
3.5828
3.4841
3.4697
3.4553
3.4410
2.5345
2.2376
1.2624
1.0789
1.00
4.97
1.03
1.02
4.08
5.97
f1 (ppm)


C13-4N-CDCl3-20131217-guohao-GH-152-shihezidaxue
xinjinag daxue varian inova-400 13C-4N
guohao-GH-152-shihezidaxue in CDCl3
189.1812
138.6785
128.5858
128.2938
127.9383
56.9748
47.0889
25.6079
25.0991
14.2608
14.0478
f1 (ppm)

ROESY of **3a**


xinjiang daxue inova-400 ROESY-4N
guohao-GH-1-shihezidaxue
in CDCl3
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: ROESY
Solvent: CDCl3
Ambient temperature
INOVA-400 "XJU400"
Relax. delay 1.000 sec
Mixing 0.200 sec
Acq. time 0.186 sec
Width 5500.2 Hz
2D Width 5500.2 Hz
16 repetitions
2 x 200 increments
OBSERVE H1, 399.7371111 MHz
DATA PROCESSING
Gauss apodization 0.086 sec
F1 DATA PROCESSING
Gauss apodization 0.034 sec
FT size 2048 x 2048
Total time 2 hr, 32 min, 25 sec
F2 (ppm)
F1 (ppm)
ROESY
COSY