Transition Metal-Catalyzed Chemoselective Methylenation of Dicarbonyl Substrates.

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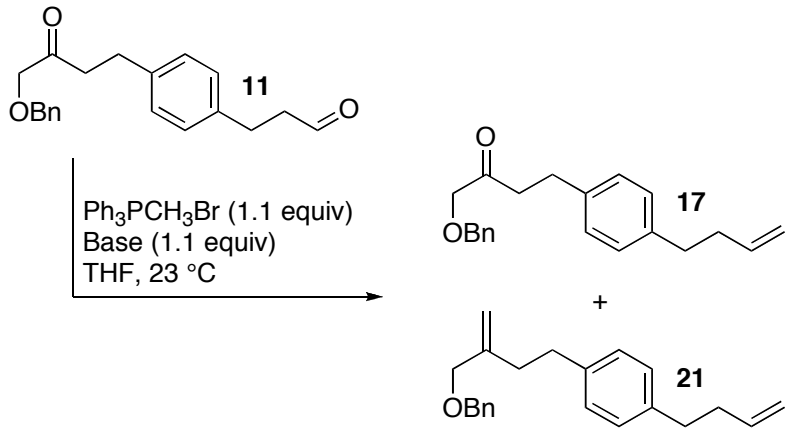
Supporting Information

Table S1. Chemoselective Wittig Methylenation of Ketoaldehyde 11 with Various Bases.



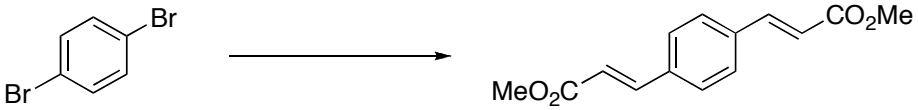
entry	Base	yield (%)[a] 17	21
1	*n*-BuLi[c]	46	31
2	LiHMDS	41	30
3	NaHMDS	56	31
4	KHMDS	56	14
5	Cs_2CO_3[b]	20	---

[a]Isolated yields. [b]Cs_2CO_3 (3 equiv), 0.1 M in THF/DMF (1:1) at reflux. [c] At -78 °C.

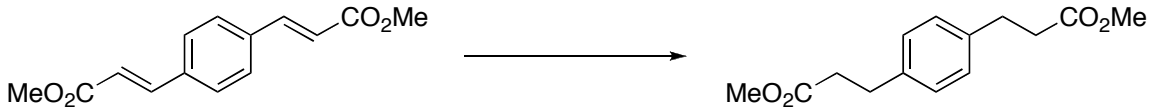
General Information

Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. The solvents were dried using standard methods prior to use. Dioxane and 2-propanol were distilled over calcium hydride. $RhCl(PPh_3)_3$ is commercially available, but was prepared from $RhCl_3 \bullet 3H_2O$ and 4 PPh_3 according to the literature.[1] CuCl was purchased from Strem and used without further purification. $TMSCHN_2$ is commercially available, but was prepared according to the literature.[2-3] Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Melting points are uncorrected. Infrared spectra are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^1H NMR spectra were recorded in $CDCl_3$, unless otherwise noted and chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of $CDCl_3$ (76.9 ppm) on the δ scale.

Synthesis of Dicarbonyl Substrates



(2*E*,2'*E*)-Dimethyl 3,3'-(1,4-phenylene)diprop-2-enoate. A solution of palladium acetate (670 mg, 3.00 mmol), IMes•HCl (1.97 g, 5.80 mmol) and potassium carbonate (40.6 g, 294 mmol) in DMF (75 mL) was stirred for 15 min. A solution of *p*-dibromobenzene (17.3 g, 73.4 mmol) in DMF (75 mL) was then added, followed by the addition of methyl acrylate (21.5 mL, 239 mmol). The resulting mixture was heated to 120 °C and stirred for 60 h. The mixture was cooled to rt, then added to water (150 mL). The mixture was washed with dichloromethane (3 x 150 mL), and the combined organic layers were washed with saturated aqueous $NaHCO_3$, then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (100% CH_2Cl_2) to give a black solid which is further purified by washing with ether to produce a white solid (17.4 g, 96% y.). R_f 0.45 (25% EtOAc/hexanes). IR (neat) 1724, 1433, 1166, 943, 842, 638 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16 Hz, 2H), 7.53 (s, 4H,), 6.47 (d, *J* = 16 Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 143.6, 136.1, 128.5, 118.9, 51.8. Elemental analysis calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73; Found: C, 68.31; H, 5.74.



Dimethyl 3,3'-(1,4-phenylene)dipropanoate. A solution of (2*E*,2'*E*)-dimethyl 3,3'-(1,4-phenylene)diprop-2-enoate (15.0 g, 60.8 mmol) and palladium 10% on carbon (3.36 g, 3.20 mmol) in methanol (600 mL) was stirred under an atmosphere of hydrogen for 6 h. The mixture was filtered

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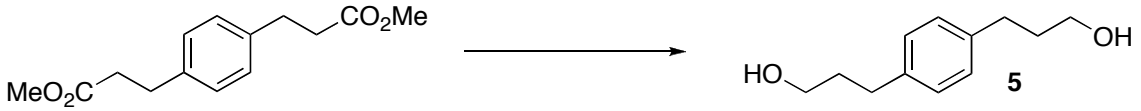
[1] Osborn J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77-79.

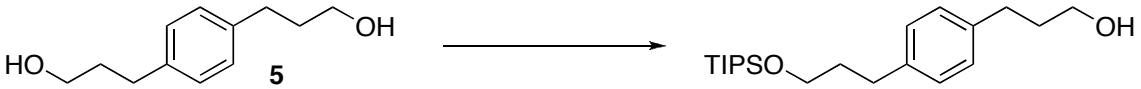
[2] Lebel, H.; Paquet, V. *J. Am. Chem. Soc.* **2004**, *126*, 320-328.

[3] As the quality of Aldrich's solution change from batch to batch, it is highly recommended to check the purity of commercial solution's (^1H NMR or GC-MS spectra) prior to use. For instance, we have experienced a batch that contain up to 50% of $TMSCH_2Cl$. See : Lebel, H.; Guay, D.; Paquet, V.; Huard, K. *Org. Lett.* **2004**, *6*, 3047-3050.

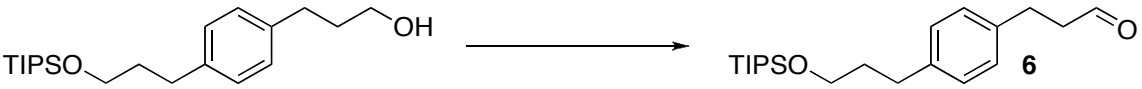
through Celite, washed with dichloromethane (2 L), and the solvent was removed under reduced pressure to provide the desired pur product as a white solid (15.2 g, 100% y.). R_f 0.35 (25% EtOAc/hexanes). IR (neat) 2956, 1727, 1433, 1301, 1178, 1148, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 3.66 (s, 6H), 2.91 (t, J = 8 Hz, 4H), 2.61 (t, J = 8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 138.3, 128.3, 51.5, 35.6, 30.4. Elemental analysis calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; Found: C, 67.26; H, 7.38.



3,3'-(1,4-Phenylene)dipropan-1-ol (5). To a solution of dimethyl 3,3'-(1,4-phenylene)dipropanoate (11.0 g, 44.0 mmol) in ether (600 mL) at 0 °C, was added $LiAlH_4$ (8.87 g, 222 mmol) in 4 portions. The resulting mixture was stirred for 12 h at rt. The reaction was poured into a mixture of saturated aqueous solution of Rochelle's salt (200 mL), dichloromethane (150 mL) and ice (~200 g) and stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with dichloromethane (3 x 100 mL). The combined organic layers were washed with aqueous 1N HCl (200 mL), water (200 mL), saturated aqueous $NaHCO_3$ (200 mL), saturated aqueous NaCl (200 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product **5** as a white solid (8.29 g, 97% y.). R_f 0.20 (50% EtOAc/hexanes). IR (neat) 3330, 3247, 2927, 2874, 1433, 1059, 1032, 907, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 3.67 (t, J = 6 Hz, 4H), 2.67 (t, J = 8 Hz, 4H), 1.91-1.84 (m, 4H), 1.51-1.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 128.4, 62.2, 34.2, 31.5. Elemental analysis calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; Found: C, 73.94; H, 9.66.

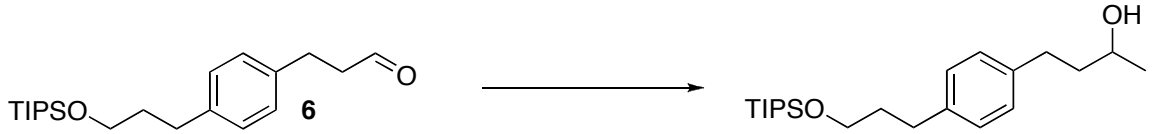


3-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)propan-1-ol. To a suspension of sodium hydride (0.41 g, 10.3 mmol) in THF (8 mL) was added a solution of **5** (2.00 g, 10.3 mmol) in THF (12 mL). The resulting mixture was stirred for 30 min, before the addition of triisopropylsilyl chloride (2.18 mL, 10.3 mmol). After vigorous stirring for 30 min, the mixture was poured into a 10% aqueous solution of potassium carbonate (200 mL). The aqueous layer was washed with dichloromethane (3 x 60 mL). The combined organic layers were washed with saturated aqueous NaCl (200 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography with a solvent gradient (10% EtOAc/hexanes, 25% EtOAc/hexanes et 8:1:1 CH_2Cl_2/EtOAc/MeOH) to give a colorless oil (2.03 g, 56% y.). R_f 0.30 (25% EtOAc/hexanes). IR (neat) 2941, 2865, 1464, 1105, 883 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 4H), 3.74 (t, J = 6 Hz, 2H), 3.67 (t, J = 6 Hz, 2H), 2.72-2.67 (m, 4H), 1.96 (s, 1H), 1.93-1.83 (m, 4H), 1.11-1.08 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 138.9, 128.4, 128.2, 62.5, 62.1, 34.6, 34.2, 31.6, 31.5, 17.9, 11.9. HMRS (CI) calcd for $C_{21}H_{39}O_2Si$ $[M+H]^+$: 351.2714. Found: 351.2704.

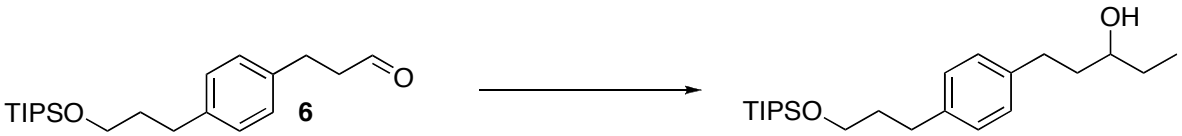


3-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)propanal (6). To a solution of 3-(4-(3-(triisopropyl-silyloxy)propyl)phenyl)propan-1-ol (3.00 g, 8.50 mmol) in dichloromethane (20 mL) at 0 °C, was added TEMPO (13 mg, 0.080 mmol), followed by potassium bromide (152 mg, 1.27 mmol). The resulting mixture was stirred at 0 °C for 15 min. A solution of buffered bleach (32.0 mL, 25.7 mmol, pH ~9 using saturated solution of $NaHCO_3$) was then added and the resulting mixture was vigorously

stirred for 1 h at room temperature. The two layers were separated and the aqueous layer was washed with dichloromethane (20 mL). The combined organic layers were washed with 10% aqueous hydrochloric acid containing 1.6 g (0.010 mol) of potassium iodide (50 mL), 10% aqueous sodium thiosulfate (20 mL), then water (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (10% EtOAc/hexanes) to give **6** as a colorless oil (2.98 g, 100% y.). R_f 0.55 (25% EtOAc/hexanes). IR (neat) 2943, 2866, 1713, 1464, 1104, 883, 680 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1 Hz, 1H), 7.16 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 3.73 (t, *J* = 6 Hz, 2H), 2.94 (t, *J* = 8 Hz, 2H), 2.79-2.67 (m, 4H), 1.91-1.81 (m, 2H), 1.13-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) 201.5, 140.2, 137.4, 128.6, 128.0, 62.4, 45.3, 34.6, 31.5, 27.6, 17.9, 11.9. HMRS (CI) calcd for $C_{21}H_{37}O_2Si$ $[M+H]^+$: 349.2557. Found: 349.2562.

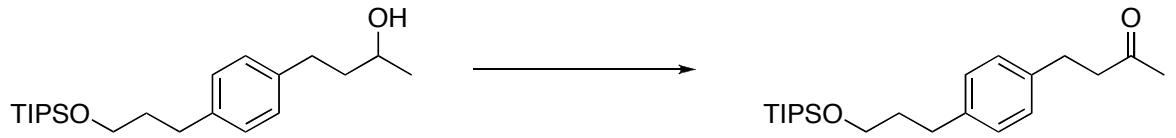


4-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)butan-2-ol. To a solution of **6** (9.96 g, 28.6 mmol) in ether (300 mL) at -78 °C, was added dropwise a solution of methylmagnesium iodide in ether (12.4 mL, 34.8 mmol) (internal temperature < 5 °C). The resulting mixture was warmed to 0 °C and stirred for 1 h. A saturated aqueous solution of NH_4Cl (50 mL) was added. The two layers were separated and the aqueous layer was washed with ether (3 x 60 mL). The combined organic layers were washed with water (100 mL), aqueous 1N HCl (100 mL), saturated aqueous $NaHCO_3$ (100 mL) and saturated aqueous NaCl (100 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (10% EtOAc/hexanes) to give a colorless oil (8.12 g, 78% y.). R_f 0.30 (25% EtOAc/hexanes). IR (neat) 3360, 2941, 2865, 1463, 1102, 882, 678 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 4H), 3.85-3.81 (m, 1H), 3.72 (t, *J* = 6 Hz, 2H), 2.77-2.61 (m, 4H), 1.89-1.82 (m, 2H), 1.80-1.73 (m, 2H), 1.58 (s, 1H), 1.23 (d, *J* = 6 Hz, 3H), 1.10-1.06 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.1, 128.4, 128.2, 67.4, 62.5, 40.8, 34.7, 31.6, 31.6, 23.5, 18.0, 11.9. HMRS (CI) calcd for $C_{22}H_{41}O_2Si$ $[M+H]^+$: 365.2870. Found: 365.2863.

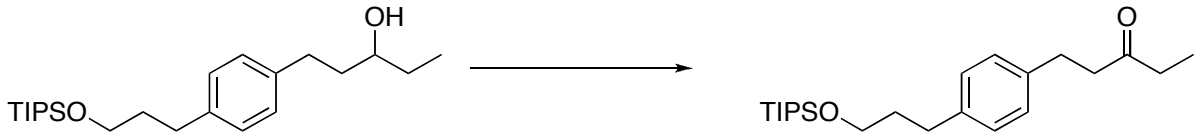


1-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)pentan-3-ol. To a solution of **6** (2.98 g, 8.54 mmol) in ether (90 mL) at -78 °C, was added dropwise a solution of ethylmagnesium iodide in ether (3.50 mL, 9.28 mmol) (internal temperature < 5 °C). The resulting mixture was warmed to 0 °C and stirred for 1 h. A saturated aqueous solution of NH_4Cl (20 mL) was added. The two layers were separated and the aqueous layer was washed with ether (3 x 50 mL). The combined organic layers were washed with water (50 mL), aqueous 1N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and saturated aqueous NaCl (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (15% EtOAc/hexanes) to give a colorless oil (2.45 g, 76% y.). R_f 0.45 (25% EtOAc/hexanes). IR (neat) 3328, 2940, 2865, 1463, 1106, 882, 681 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 3.71 (t, *J* = 6 Hz, 2H), 3.59-3.53 (m, 1H), 2.80-2.69 (m, 1H), 2.69-2.60 (m, 3H), 1.88-1.70 (m, 4H), 1.58-1.44 (m, 3H), 1.09-1.06 (m, 21H), 0.95 (t, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.3, 128.4, 128.2, 72.6, 62.6, 38.6, 34.7, 31.6, 31.6, 30.2, 18.0, 11.9, 9.8. HMRS (CI) calcd for $C_{23}H_{43}O_2Si$ $[M+H]^+$: 379.3027. Found: 379.3033.

1-Phenyl-3-(4-(3-(triisopropylsilyloxy)propyl)phenyl)propan-1-ol. To a solution of **6** (2.08 g, 6.00 mmol) in ether (60 mL) at -78 °C, was added dropwise a solution of phenylmagnesium bromide in ether (4.60 mL, 6.10 mmol) (internal temperature < 5 °C). The resulting mixture was warmed to 0 °C and stirred for 1 h. A saturated aqueous solution of NH_4Cl (30 mL) was added. The two layers were separated and the aqueous layer was washed with ether (3 x 50 mL). The combined organic layers were washed with water (40 mL), aqueous 1N HCl (40 mL), saturated aqueous $NaHCO_3$ (40 mL) and saturated aqueous NaCl (40 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (10% EtOAc/hexanes) to give a colorless oil (1.94 g, 76% y.). R_f 0.45 (25% EtOAc/hexanes). IR (neat) 2942, 2865, 1463, 1104, 1064, 883 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.16 (s, 4H), 4.73-4.71 (m, 1H), 3.76 (t, *J* = 6 Hz, 2H), 2.80-2.64 (m, 4H), 2.21-2.01 (m, 3H), 1.93-1.86 (m, 2H), 1.12 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 139.7, 138.8, 128.4, 128.2, 127.5, 125.8, 73.8, 62.5, 40.4, 34.6, 31.6, 31.5, 17.9, 11.9. HMRS (CI) calcd for $C_{27}H_{42}NaO_2Si$ $[M+H]^+$: 449.2846. Found: 449.2850.

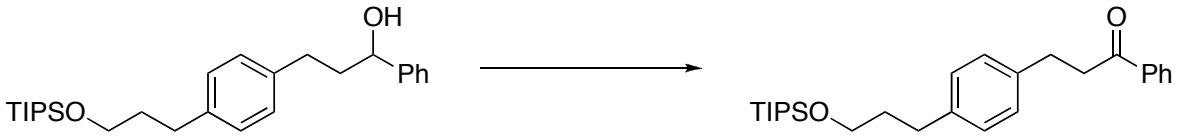


4-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)butan-2-one. To a suspension of [Pd(I*i*Pr)$(OAc)_2$•(H_2O)] (449 mg, 0.710 mmol), tetrabutylammonium acetate (412 mg, 1.37 mmol), powder molecular sieves 3Å (4.3 g), was added a solution of the alcohol (10.4 g, 28.6 mmol) in toluene (300 mL). The resulting mixture was stirred at 60 °C for 24 h under an atmosphere of oxygen. The mixture is filtered on silica gel and washed with pentane (3 x 70 mL), then with ether (3 x 100 mL) to recover the desired ketone. The solvent was removed under reduced pressure to provide the desired pur product as a yellow oil (10.2 g, 98% y.). R_f 0.65 (25% EtOAc/hexanes). IR (neat) 2944, 2866, 1720, 1105 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 3.71 (t, *J* = 6 Hz, 2H), 2.90-2.84 (m, 2H), 2.77-2.65 (m, 4H), 2.14 (s, 3H), 1.89-1.80 (m, 2H), 1.09-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 140.0, 138.0, 128.5, 128.0, 62.5, 45.2, 34.6, 31.5, 29.9, 29.2, 17.9, 11.9. Elemental analysis calcd for $C_{22}H_{38}O_2Si·H_2O$: C, 69.42; H, 10.59 Found: C, 69.13; H, 10.79.

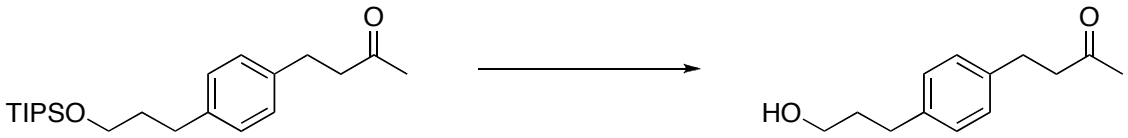


1-(4-(3-(Triisopropylsilyloxy)propyl)phenyl)pentan-3-one. To a suspension of [Pd(I*i*Pr)$(OAc)_2$•(H_2O)] (100 mg, 0.160 mmol), tetrabutylammonium acetate (103 mg, 0.34 mmol), powder molecular sieves 3Å (924 mg), was added a solution of the alcohol (2.33 g, 6.16 mmol) in toluene (65 mL). The resulting mixture was stirred at 60 °C for 24 h under an atmosphere of oxygen. The mixture is filtered on silica gel and washed with pentane (3 x 30 mL), then with ether (3 x 40 mL) to recover the desired ketone. The solvent was removed under reduced pressure to provide the desired pur product as a yellow oil (2.29 g, 99% y.). R_f 0.65 (25% EtOAc/hexanes). IR (neat) 2941, 2865, 1716, 1462, 1103, 882 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 9 Hz, 2H), 7.10 (d, *J* = 9 Hz, 2H), 3.72 (t, *J* = 6 Hz, 2H), 2.88 (t, *J* = 8 Hz, 2H), 2.74-2.65 (m, 4H), 2.41 (q, *J* = 7 Hz, 2H), 1.89-1.80 (m, 2H), 1.08-1.03 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 140.0, 138.2, 128.5, 128.1, 62.5,

43.9, 36.0, 34.6, 31.6, 29.4, 17.9, 11.9, 7.6. HMRS (CI) calcd for $C_{23}H_{40}NaO_2Si$ $[M+Na]^+$: 399.2690. Found: 399.2696.



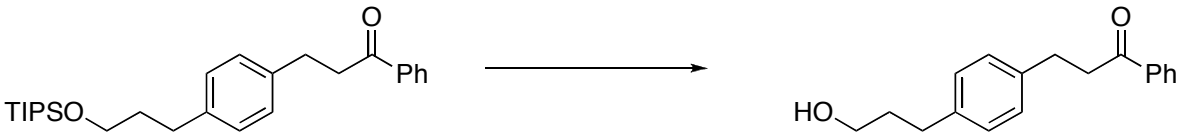
1-Phenyl-3-(4-(3-(triisopropylsilyloxy)propyl)phenyl)propan-1-one. To a suspension of [Pd(I*i*Pr)$(OAc)_2$•(H_2O)] (58 mg, 0.092 mmol), tetrabutylammonium acetate (75 mg, 0.070 mmol), powder molecular sieves 3Å (530 mg), was added a solution of the alcohol (1.50 g, 3.52 mmol) in toluene (35 mL). The resulting mixture was stirred at 60 °C for 24 h under an atmosphere of oxygen. The mixture is filtered on silica gel and washed with pentane (3 x 30 mL), then with ether (3 x 30 mL) to recover the desired ketone. The solvent was removed under reduced pressure to provide the desired pur product as a yellow oil (1.47 g, 98% y.). R_f 0.40 (25% EtOAc/hexanes). IR (neat) 2941, 2864, 1687, 1463, 1449, 1097, 882 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8,1 Hz, 2H), 7.59-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 3.72 (t, *J* = 6 Hz, 2H), 3.30 (t, *J* = 8 Hz, 2H), 3.05 (t, *J* = 8 Hz, 2H), 2.69 (t, *J* = 8 Hz, 2H), 1.90-1.81 (m, 2H), 1.10-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 140.1, 138.4, 136.8, 132.9, 128.5, 128.5, 128.2, 127.9, 62.5, 40.5, 34.7, 31.6, 29.6, 18.0, 11.9. HMRS (CI) calcd for $C_{27}H_{41}O_2Si$ $[M+H]^+$: 425.2870. Found: 425.2870.



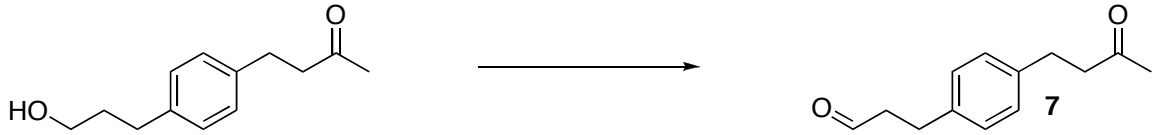
4-(4-(3-Hydroxypropyl)phenyl)butan-2-one. To a solution of the silyl ether (3.46 g, 9.54 mmol) in THF (50 mL), was added a solution of TBAF in THF (10.0 mL, 10.0 mmol). The resulting mixture was stirred at rt for 30 min. Aqueous 1N HCl (15 mL) was added, then the two layers were separated. The aqueous layer was washed with ether (3 x 40 mL). The combined organic layers were washed with water (75 mL), saturated aqueous $NaHCO_3$ (75 mL) and saturated aqueous NaCl (75 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give a colorless oil (1.93 g, 98% y.). R_f 0.10 (25% EtOAc/hexanes). IR (neat) 3387, 2935, 2864, 1710, 1515, 1363, 1055 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 3.65 (t, *J* = 6 Hz, 2H), 2.87 (t, *J* = 7 Hz, 2H), 2.74 (t, *J* = 7 Hz, 2H), 2.66 (t, *J* = 8 Hz, 2H), 2.13 (s, 3H), 1.90-1.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 139.5, 138.3, 128.4, 128.2, 62.1, 45.1, 34.1, 31.5, 30.0, 29.2. HMRS (CI) calcd for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1380. Found: 207.1371.

1-(4-(3-Hydroxypropyl)phenyl)pentan-3-one. To a solution of the silyl ether (2.29 g, 6.09 mmol) in THF (65 mL), was added a solution of TBAF in THF (6.10 mL, 6.10 mmol). The resulting mixture was stirred at rt for 45 min. Aqueous 1N HCl (10 mL) was added, then the two layers were separated. The aqueous layer was washed with ether (3 x 30 mL). The combined organic layers were washed with water (60 mL), saturated aqueous $NaHCO_3$ (60 mL) and saturated aqueous NaCl (60 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give a yellowish oil (1.16 g, 87% y.). R_f 0.10 (25%

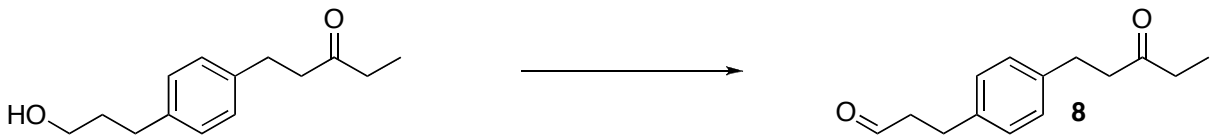
EtOAc/hexanes). IR (neat) 3387, 2937, 1708, 1412, 1375, 1112, 1057 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 3.62 (t, *J* = 6 Hz, 2H), 2.89, (s, 1H), 2.83 (t, *J* = 8 Hz, 2H), 2.70-2.62 (m, 4H), 2.38 (q, *J* = 7 Hz, 2H), 1.87-1.80 (m, 2H), 1.01 (t, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 139.4, 138.1, 128.2, 127.9, 61.6, 43.6, 35.7, 33.9, 31.3, 29.1, 7.4. HMRS (CI) calcd for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1536. Found: 221.1532.



3-(4-(3-Hydroxypropyl)phenyl)-1-phenylpropan-1-one. To a solution of the silyl ether (1.47 g, 3.45 mmol) in THF (35 mL), was added a solution of TBAF in THF (3.50 mL, 3.50 mmol). The resulting mixture was stirred at rt for 45 min. Aqueous 1N HCl (10 mL) was added, then the two layers were separated. The aqueous layer was washed with ethyl acetate (3 x 25 mL). The combined organic layers were washed with water (30 mL), saturated aqueous $NaHCO_3$ (30 mL) and saturated aqueous NaCl (30 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (30% EtOAc/hexanes) to give a brown oil (588 mg, 63% y.). R_f 0.10 (25% EtOAc/hexanes). IR (neat) 3378, 2941, 2864, 1684, 1449, 1056, 882, 837, 676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7 Hz, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.14 (d, *J* = 8 Hz, 2H), 3.67 (t, *J* = 6 Hz, 2H), 3.29 (t, *J* = 7 Hz, 2H), 3.04 (t, *J* = 7 Hz, 2H), 2.68 (t, *J* = 8 Hz, 2H), 2.01 (br s, 1H), 1.93-1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 139.5, 138.5, 136.6, 132.9, 128.5, 128.4, 128.3, 127.9, 62.1, 40.4, 34.1, 31.5, 29.6. HMRS (CI) calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$: 291.1355. Found: 291.1359.

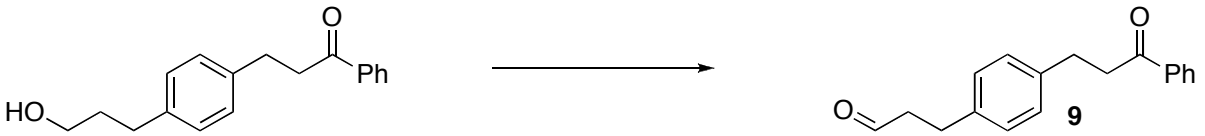


3-(4-(3-Oxobutyl)phenyl)propanal (7). To a solution of Dess Martin Periodinane (0.450 g, 1.07 mmol) in dichloromethane (4 mL), was added a solution of the alcohol (200 mg, 0.970 mmol) in dichloromethane (2 mL). The resulting mixture was stirred at rt for 60 min. Aqueous 10% $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (20 mL) and saturated aqueous NaCl (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product **7** as a colorless oil (198 mg, 100% y.). R_f 0.25 (25% EtOAc/hexanes). IR (neat) 2924, 1714, 1516, 1361, 1161 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.80, (s, 1H), 7.10 (s, 4H), 2.91 (t, *J* = 8 Hz, 2H), 2.85 (t, *J* = 8 Hz, 2H), 2.77-2.71 (m, 4H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 201.6, 138.8, 137.9, 128.4, 128.3, 45.2, 45.0, 30.0, 29.5, 27.5. HMRS (CI) calcd for $C_{13}H_{15}O_2$ $[M-H]^-$: 203.1077. Found: 203.1075.

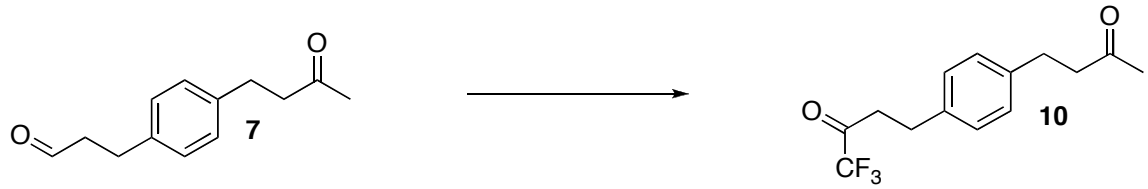


3-(4-(3-Oxopentyl)phenyl)propanal (8). To a solution of Dess Martin Periodinane (0.22 g, 0.50 mmol) in dichloromethane (5 mL), was added a solution of the alcohol (100 mg, 0.450 mmol) in dichloromethane (5 mL). The resulting mixture was stirred at rt for 60 min. Aqueous 10% $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL) were added, and the resulting mixture was stirred until the

two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (20 mL) and saturated aqueous NaCl (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product **8** as a colorless oil (98 mg, 100% y.). R_f 0.30 (25% EtOAc/hexanes). IR (neat) 2938, 1710, 1518, 1412, 1372, 1113, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.07 (s, 4H), 2.89-2.81 (m, 4H), 2.73-2.60 (m, 4H), 2.37 (q, J = 7 Hz, 2H), 1.00 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 201.4, 138.8, 137.7, 128.2, 128.1, 44.9, 43.5, 35.7, 29.0, 27.3, 7.4. HMRS (CI) calcd for $C_{14}H_{18}NaO_2$ $[M+Na]^+$: 235.1329. Found: 235.1327.

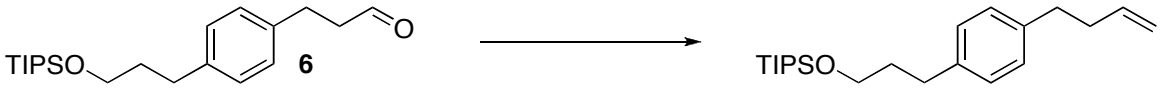


3-(4-(3-Oxo-3-phenylpropyl)phenyl)propanal (9). To a solution of Dess Martin Periodinane (173 mg, 0.410 mmol) in dichloromethane (5 mL), was added a solution of the alcohol (100 mg, 0.370 mmol) in dichloromethane (5 mL). The resulting mixture was stirred at rt for 60 min. Aqueous 10% $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (20 mL) and saturated aqueous NaCl (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product **9** as an amber oil (98 mg, 100% y.). R_f 0.25 (25% EtOAc/hexanes). IR (neat) 2926, 1720, 1682, 1448, 1203, 909, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.96 (d, J = 7 Hz, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 2H), 7.19 (d, J = 8 Hz, 2H), 7.13 (d, J = 8 Hz, 2H), 3.29 (t, J = 7 Hz, 2H), 3.04 (t, J = 8 Hz, 2H), 2.93 (t, J = 7 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 199.1, 139.1, 137.9, 136.6, 132.9, 128.5, 128.5, 128.3, 127.9, 45.2, 40.3, 29.5, 27.5. HMRS (CI) calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1380. Found: 267.1380.

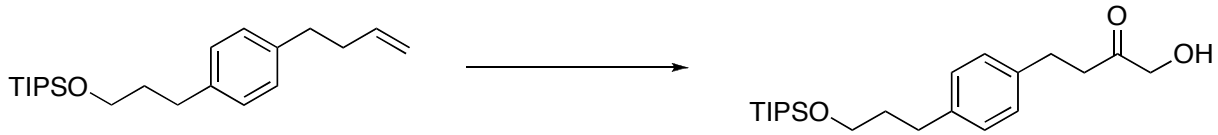


1,1,1-Trifluoro-4-(4-(3-oxobutyl)phenyl)butan-2-one (10). To a solution of aldehyde **7** (682 mg, 3.34 mmol) in THF (20 mL) was added $TMSCF_3$ (255 μL, 1.68 mmol). The resulting mixture was stirred for 1 h, before a second addition of $TMSCF_3$ (255 μL, 1.68 mmol), followed by a solution of TBAF in THF (57 μL, 0.057 mmol). The resulting mixture was stirred for another 2 h, then aqueous 1N HCl (2 mL) was added. After 30 min of stirring, the two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (10 mL), aqueous saturated solution of $NaHCO_3$ (10 mL) and saturated aqueous NaCl (10 mL), then dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was used directly in the next step. To a solution of Dess Martin Periodinane (4.72 g mg, 11.1 mmol) in dichloromethane (20 mL), was added a solution of the crude alcohol in dichloromethane (10 mL). The resulting mixture was stirred at rt for 60 min. Aqueous 10% $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 25 mL). The combined organic layers were washed with water (30 mL) and saturated aqueous NaCl (30 mL), then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give **10** as a colorless oil (405 mg, 47% y.). R_f 0.15 (10% EtOAc/hexanes). IR (neat) 3387, 2832, 1705, 1362, 1166, 1053 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 4H), 3.02 (t, J

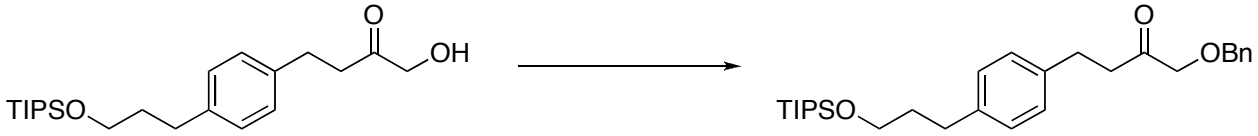
= 7 Hz, 2H), 2.94 (t, *J* = 7 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 190.6 (q, *J* = 35 Hz), 139.2, 136.9, 128.5, 128.2, 115.4 (q, *J* = 290 Hz), 44.9, 37.9, 29.9, 29.1, 27.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.6. HMRS (CI) calcd for $C_{14}H_{16}F_3O_2$ $[M+H]^+$: 273.1097. Found: 273.1102.



(3-(4-(But-3-enyl)phenyl)propoxy)triisopropylsilane. To a solution of chlorotris(triphenylphosphine)rhodium (67 mg, 0.072 mmol) and triphenylphosphine (829 mg, 3.16 mmol) in THF (20 mL), was added 2-propanol (250 μL, 3.26 mmol) followed by the aldehyde **6** (1.00 g, 2.88 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane in THF (1.20 mL, 4.15 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at room temperature. After 4 hours, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (2% EtOAc/hexanes) to give a colorless oil (847 mg, 85% y.). R_f 0.75 (10% EtOAc/hexanes). IR (neat) 2942, 2866, 1464, 1106, 882, 681 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 4H), 5.96 (ddt, *J* = 17, 10, 7, 1H), 5.13 (d, *J* = 17 Hz, 1H), 5.06 (d, *J* = 10 Hz, 1H), 3.79 (t, *J* = 6 Hz, 2H), 2.76 (t, *J* = 8 Hz, 4H), 2.47-2.40 (m, 2H), 1.97-1.88 (m, 2H), 1.16 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.0, 138.1, 128.3, 128.2, 114.7, 62.6, 35.6, 34.9, 34.7, 31.7, 18.0, 12.0. HMRS (CI) calcd for $C_{22}H_{39}OSi$ $[M+H]^+$: 347.2765. Found: 347.2766.

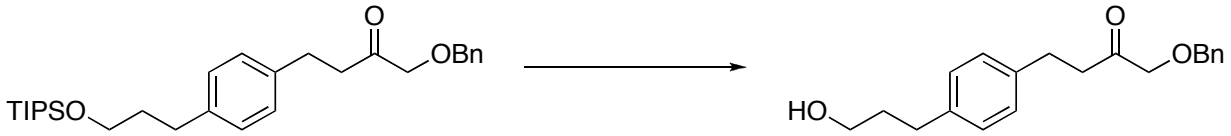


1-Hydroxy-4-(4-(3-(triisopropylsilyloxy)propyl)phenyl)butan-2-one. To a solution of olefin (4.00 g, 11.6 mmol) in acetone (95 mL), water (21 mL) and acetic acid (4.5 mL), was added dropwise a solution of $KMnO_4$ (2.92 g, 18.5 mmol) in acetone (35 mL) and water (12 mL). The resulting mixture was stirred at room temperature until completion (3 hours). EtOH was added until effervescence stopped. The mixture was filtered through a pad of Celite® and washed with ether. The solvent was removed under reduced pressure. The filtrate was diluted with ether and washed with saturated aqueous $NaHCO_3$ until pH = 8 and saturated aqueous NaCl (100 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give a colorless oil (3.01 g, 69% y.). R_f 0.30 (25% EtOAc/hexanes). IR (neat) 3442, 2941, 2865, 1720, 1563, 1102, 1067, 882, 679 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 4.19 (d, *J* = 4 Hz, 2H), 3.72 (t, *J* = 6 Hz, 2H), 3.17 (t, *J* = 4 Hz, 1H), 2.94 (t, *J* = 8 Hz, 2H), 2.74-2.67 (m, 4H), 1.89-1.81 (m, 2H), 1.11-1.07 (m, 21H);. ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 140.4, 137.2, 128.6, 128.0, 68.2, 62.4, 39.9, 34.5, 31.5, 29.1, 17.9, 11.9. HMRS (CI) calcd for $C_{22}H_{39}O_3Si$ $[M+H]^+$: 379.2663. Found: 379.2658.

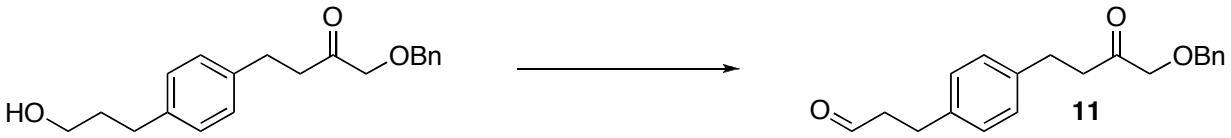


1-(Benzyloxy)-4-(4-(3-(triisopropylsilyloxy)propyl)phenyl)butan-2-one. To a solution of the alcohol (315 mg, 0.830 mmol) in mixture of cyclohexane (6.5 mL) and dichloromethane (3.5 mL), was added benzyl trichloroacetimidate (200 μL, 1.08 mmol), followed by freshly distilled triflic acid (15 μL, 0.17 mmol). The resulting mixture was stirred for 30 min. The mixture was then filtered and the filtrate was washed with ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure

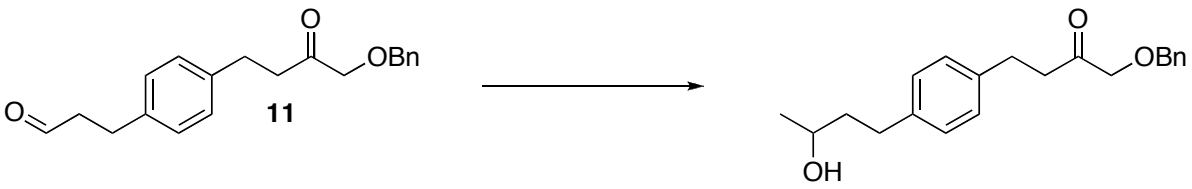
and the residue was purified by flash chromatography (8% EtOAc/hexanes) to give a colorless oil (206 mg, 53% y.). R_f 0.50 (25% EtOAc/hexanes). IR (neat) 2941, 2864, 1721, 1463, 1101, 910, 882, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 7.15 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 4.58 (s, 2H), 4.04 (s, 2H), 3.75 (t, *J* = 6 Hz, 2H), 2.92 (t, *J* = 7 Hz, 2H), 2.81 (t, *J* = 7 Hz, 2H), 2.71 (t, *J* = 8 Hz, 2H), 1.91-1.84 (m, 2H), 1.13-1.08 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 140.1, 137.9, 137.0, 128.5, 128.5, 128.3, 128.1, 127.8, 127.7, 75.0, 73.2, 62.4, 40.5, 34.6, 31.5, 28.8, 17.9, 11.9. HMRS (CI) calcd for $C_{29}H_{45}O_3Si$ $[M+H]^+$: 469.3132. Found: 469.3140.



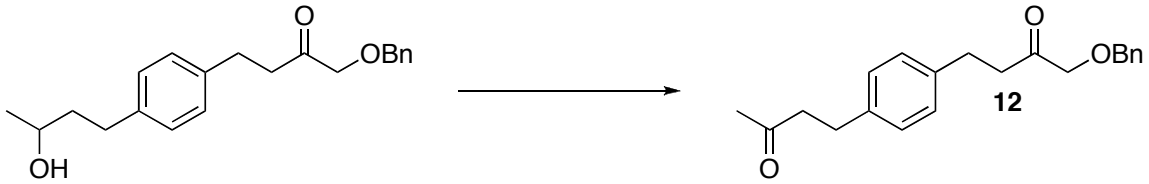
1-(Benzyloxy)-4-(4-(3-hydroxypropyl)phenyl)butan-2-one. To a solution of the silyl ether (2.62 g, 5.58 mmol) in MeCN (55 mL), was added a solution of HF (48% wt in H_2O) (2.00 mL, 55.6 mmol). The resulting mixture was stirred at rt for 60 min. Saturated aqueous $NaHCO_3$ (60 mL) was added, and the resulting mixture was stirred for 30 min. The two layers were then separated and the aqueous layer was washed with ether (3 x 35 mL). The combined organic layers were washed with water (35 mL), saturated aqueous $NaHCO_3$ (35 mL) and saturated aqueous NaCl (35 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give a yellowish oil (1.40 g, 81% y.). R_f 0.35 (25% EtOAc/hexanes). IR (neat) 3423, 2930, 2862, 1721, 1454, 1075, 738, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 7.14 (s, 4H), 4.58 (s, 2H), 4.06 (s, 2H), 3.67 (t, *J* = 6 Hz, 2H), 2.92 (t, *J* = 7 Hz, 2H), 2.81 (t, *J* = 7 Hz, 2H), 2.70 (t, *J* = 8 Hz, 2H), 2.39 (br s, 1H), 1.93-1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 139.5, 137.9, 136.9, 128.3, 128.2, 128.0, 127.7, 127.6, 74.8, 73.0, 61.7, 40.3, 33.9, 31.4, 28.6. HMRS (CI) calcd for $C_{20}H_{24}NaO_3$ $[M+Na]^+$: 335.1618. Found: 335.1611.



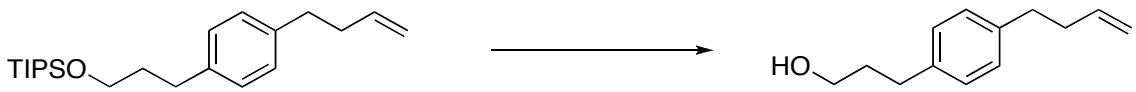
3-(4-(4-(Benzyloxy)-3-oxobutyl)phenyl)propanal (11). To a solution of Dess Martin Periodinane (601 mg, 1.42 mmol) in dichloromethane (5 mL), was added a solution of the alcohol (429 mg, 1.37 mmol) in dichloromethane (10 mL). The resulting mixture was stirred at rt for 60 min. Aqueous 10% $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 20 mL). The combined organic layers were washed with water (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and saturated aqueous NaCl (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product as a colorless oil (405 mg, 95% y.). R_f 0.20 (25% EtOAc/hexanes). IR (neat) 2922, 2856, 1718, 1454, 1076, 739, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1 Hz, 1H), 7.36-7.30 (m, 5H), 7.10 (s, 4H), 4.56 (s, 2H), 4.02 (s, 2H), 2.94-2.85 (m, 4H), 2.80-2.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 201.5, 138.7, 138.0, 137.0, 128.5, 128.4, 128.3, 127.9, 127.8, 75.0, 73.3, 45.1, 40.5, 28.7, 27.6. HMRS (CI) calcd for $C_{20}H_{22}NaO_3$ $[M+Na]^+$: 333.1461. Found: 333.1471.



1-(Benzyloxy)-4-(4-(3-hydroxybutyl)phenyl)butan-2-one. To a solution of **11** (730 mg, 2.35 mmol) in ether (30 mL) at -100 °C, was added dropwise a solution of methylmagnesium iodide in ether (900 μL, 2.52 mmol) (internal temperature < 5 °C). The resulting mixture was warmed to -78 °C and stirred for 30 min, before warming to -20 °C for 30 min. A saturated aqueous solution of NH_4Cl (10 mL) was added at -20 °C, then the mixture was allowed to warm to rt. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (15 mL), aqueous 1N HCl (15 mL), saturated aqueous $NaHCO_3$ (15 mL) and saturated aqueous NaCl (15 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (10% EtOAc/hexanes) to give a light yellow oil (208 mg, 27% y.). R_f 0.10 (25% EtOAc/hexanes). IR (neat) 3408, 2925, 2861, 1722, 1514, 1454, 1372, 1077, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 5H), 7.13-7.08 (m, 4H), 4.55 (s, 2H), 4.03 (s, 2H), 3.85-3.78 (m, 1H), 2.91-2.87 (m, 2H), 2.80-2.76 (m, 2H), 2.76-2.59 (m, 2H), 2.08 (br s, 1H), 1.78-1.71 (m, 2H), 1.22 (d, J = 6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 139.8, 138.0, 137.0, 128.4, 128.3, 128.2, 127.9, 127.8, 75.0, 73.2, 67.3, 40.7, 40.5, 31.5, 28.7, 23.5. HMRS (CI) calcd for $C_{21}H_{26}NaO_3$ $[M+Na]^+$: 349.1779. Found: 349.1774.

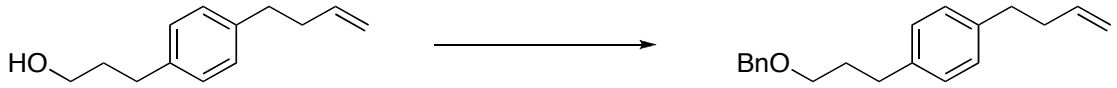


1-(Benzyloxy)-4-(4-(3-oxobutyl)phenyl)butan-2-one (12). To a solution of Dess Martin Periodinane (405 mg, 0.960 mmol) in dichloromethane (7 mL), was added a solution of the alcohol (208 mg, 0.640 mmol) in dichloromethane (3 mL). The resulting mixture was stirred at rt for 2 h. Aqueous 10% $Na_2S_2O_3$ (3 mL) and saturated aqueous $NaHCO_3$ (3 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and saturated aqueous NaCl (10 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product **12** as colorless oil (200 mg, 96% y.). R_f 0.20 (25% EtOAc/hexanes). IR (neat) 2923, 1715, 1516, 1366, 1159, 1077, 740, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 5H), 7.09 (s, 4H), 4.55 (s, 1H), 4.02 (s, 2H), 2.89-2.83 (m, 4H), 2.79-2.71 (m, 4H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9 (2C), 138.7, 138.5, 137.0, 128.4, 128.4, 128.3, 128.0, 127.8, 75.0, 73.3, 45.1, 40.5, 30.0, 29.2, 28.7. HMRS (CI) calcd for $C_{21}H_{24}NaO_3$ $[M+Na]^+$: 347.1616. Found: 347.1617.

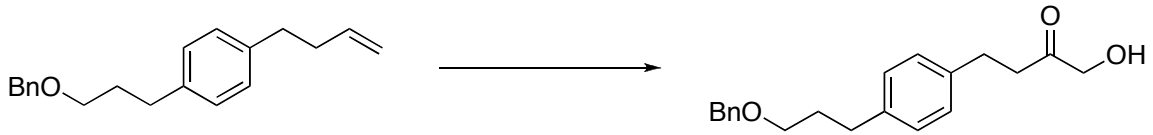


3-(4-(But-3-enyl)phenyl)propan-1-ol. To a solution of the silyl ether (8.11 g, 23.4 mmol) in THF (250 mL), was added a solution of TBAF in THF (24.0 mL, 24.0 mmol). The resulting mixture was stirred at rt for 60 min. Aqueous 1N HCl (30 mL) was added, then the two layers were separated. The aqueous layer was washed with ethyl acetate (3 x 75 mL). The combined organic layers were washed with water (80 mL), saturated aqueous $NaHCO_3$ (80 mL) and saturated aqueous NaCl (80 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by

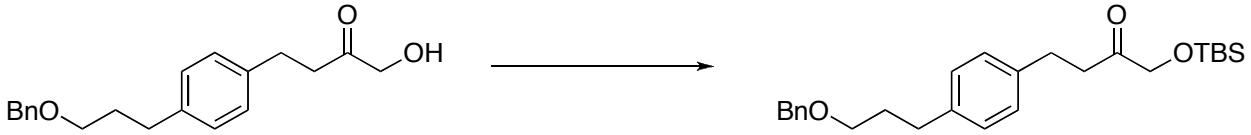
flash chromatography (25% EtOAc/hexanes) to give a colorless oil (4.10 g, 92% y.). R_f 0.25 (25% EtOAc/hexanes). IR 3325, 2927, 2857, 1514, 1438, 1042, 910, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 4H), 5.93 (ddt, *J* = 17, 10, 7, 1H), 5.11 (d, *J* = 17 Hz, 2H), 5.04 (d, *J* = 17 Hz, 2H), 3.69 (t, *J* = 6 Hz, 2H), 2.76-2.69 (m, 4H), 2.61 (br s, 1H), 2.46-2.38 (m, 2H), 1.97-1.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 139.1, 138.0, 128.2, 128.1, 114.7, 61.9, 35.4, 34.7, 34.0, 31.5. HRMS (CI) calcd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1425. Found: 191.1430.



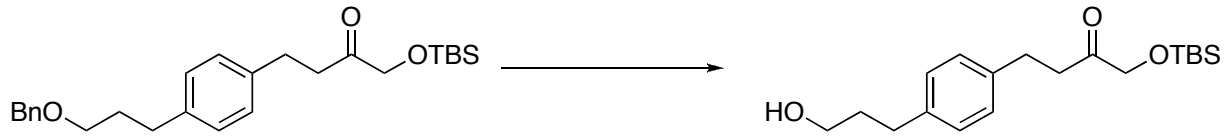
1-(3-(Benzyloxy)propyl)-4-(but-3-enyl)benzene. To a solution of sodium hydride (589 mg, 24.5 mmol) in THF (50 mL), was added a solution of the alcohol (4.02 g, 21.1 mmol) in THF (170 mL), followed by benzyl bromide (3.60 mL, 29.7 mmol), then tetrabutylammonium iodide (215 mg, 0.57 mmol). The resulting mixture was stirred at rt for 45 min. Aqueous 10% K_2CO_3 (50 mL) was added, then the two layers were separated. The aqueous layer was washed with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water (60 mL), saturated aqueous $NaHCO_3$ (60 mL) and saturated aqueous NaCl (60 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (5% EtOAc/hexanes) to give a yellow oil (5.69 g, 96% y.).R_f 0.75 (25% EtOAc/hexanes). IR (neat) 2925, 2854, 1453, 1100, 910, 734, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.11 (s, 4H), 5.88 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.09-4.97 (m, 2H), 4.52 (s, 2H), 3.50 (t, *J* = 6 Hz, 2H), 2.72-2.66 (m, 4H), 2.41-2.34 (m, 2H), 1.99-1.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.1, 138.5, 138.2, 128.3, 128.3, 128.3, 127.6, 127.4, 114.7, 72.8, 69.5, 35.5, 34.9, 31.9, 31.3. HMRS (CI) calcd for $C_{20}H_{25}O$ $[M+H]^+$: 281.1900. Found: 281.1892.



4-(4-(3-(Benzyloxy)propyl)phenyl)-1-hydroxybutan-2-one. To a solution of the alkene (4.00 g, 14.3 mmol) in acetone (120 mL), water (27 mL) and acetic acid (5.70 mL), was added dropwise a solution of $KMnO_4$ (3.60 g, 22.8 mmol) in acetone (45 mL) and water (60 mL). The resulting mixture was stirred at room temperature for 2 hours. EtOH was added until effervescence stopped. The mixture was filtered through a pad of Celite® and washed with ether. The solvent was removed under reduced pressure. The filtrate was diluted with ether and washed with saturated aqueous $NaHCO_3$ until pH = 8 and saturated aqueous NaCl (100 mL), then dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% EtOAc/hexanes) to give a colorless oil (3.20 g, 72% y.). R_f 0.10 (25% EtOAc/hexanes). IR (neat) 3424, 2928, 2856, 1717, 1453, 1364, 1099, 1068, 737, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 7.12 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 4.52 (s, 2H), 4.19 (s, 2H), 3.50 (t, *J* = 6 Hz, 2H), 3.21 (br s, 1H), 2.94 (t, *J* = 8 Hz, 2H), 2.73-2.68 (m, 4H), 1.97-1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 140.0, 138.4, 137.4, 128.6, 128.2, 128.0, 127.5, 127.4, 72.8, 69.3, 68.2, 39.8, 31.8, 31.2, 29.0. HMRS (CI) calcd for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798. Found: 313.1790.



4-(4-(3-(Benzyloxy)propyl)phenyl)-1-(tert-butyldimethylsilyloxy)butan-2-one. To a mixture of imidazole (751 mg, 10.9 mmol), 4-dimethylaminopyridine (57 mg, 0.47 mmol) and *t*-butyl-dimethylsilyl chloride (1.61 g, 10.4 mmol), was added a solution of the alcohol (2.27 g g, 7.27 mmol) in DMF (120 mL). The resulting mixture was stirred for 2 min at rt. Saturated aqueous ammonium chloride (40 mL) was then added and the two layers were separated. The aqueous layer was washed with ether (3 x 40 mL). The combined organic layers were washed with water (50 mL), saturated aqueous $NaHCO_3$ (50 mL), saturated aqueous NaCl (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product as yellowish oil (3.00 g, 97% y.). R_f 0.60 (25% EtOAc/hexanes). IR (neat) 2928, 2856, 1719, 1679, 1253, 1100, 836, 778 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 5H), 7.12 (s, 4H), 4.53 (s, 2H), 4.17 (s, 2H), 3.51 (t, *J* = 6 Hz, 2H), 2.95-2.89 (m, 2H), 2.85-2.81 (m, 2H), 2.71 (t, *J* = 8 Hz, 2H), 1.98-1.91 (m, 2H), 0.94 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 139.6, 138.4, 138.2, 128.5, 128.2, 128.1, 127.5, 127.4, 72.8, 69.4, 69.3, 39.8, 31.8, 31.3, 28.8, 25.7, 18.2, -5.5. HMRS (CI) calcd for $C_{26}H_{38}NaO_3Si$ $[M+Na]^+$: 449.2482. Found: 449.2478.



1-(tert-Butyldimethylsilyloxy)-4-(4-(3-hydroxypropyl)phenyl)butan-2-one. A solution of the benzyl ether (257 mg, 0.600 mmol) and palladium 10% on carbon (72 mg, 0.067mmol) in ethyl acetate (10 mL) was stirred under an atmosphere of hydrogen for 1 h. The mixture was filtered through Celite, and washed with ether (3 x 20 L). The solvent was removed under reduced pressure and the residue was purified by flash chromatography (15% EtOAc/hexanes) to give a colorless oil (174 mg, 86% y.). R_f 0.30 (25% EtOAc/hexanes). IR (neat) 2930,2858, 2252, 1716, 1256, 1105, 907, 839, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 4.18 (d, *J* = 4 Hz, 2H), 3.63 (t, *J* = 6 Hz, 2H), 3.23 (t, *J* = 5 Hz, 1H), 2.93 (t, *J* = 8 Hz, 2H), 2.71 (t, *J* = 8 Hz, 2H), 2.64 (t, *J* = 8 Hz, 2H), 1.85-1.78 (m, 2H), 0.91 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 140.2, 137.3, 128.5, 128.0, 68.2, 62.2, 39.8, 34.3, 31.5, 29.0, 25.8, 18.2, -5.37. HMRS (CI) calcd for $C_{19}H_{33}O_3Si$ $[M+H]^+$: 337.2193. Found: 337.2188.

3-(4-(4-(tert-butyldimethylsilyloxy)-3-oxobutyl)phenyl)propanal (13). To a solution of Dess Martin Periodinane (138 mg, 0.33 mmol) in dichloromethane (4 mL), was added a solution of the alcohol (109 mg, 0.32 mmol) in dichloromethane (2 mL). The resulting mixture was stirred at rt for 1 h. Aqueous 10% $Na_2S_2O_3$ (3 mL) and saturated aqueous $NaHCO_3$ (3 mL) were added, and the resulting mixture was stirred until the two layers were colorless. The two layers were separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic layers were washed with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and saturated aqueous NaCl (10 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure to provide the desired pur product as colorless oil (84 mg, 78% y.). R_f 0.40 (25% EtOAc/hexanes). IR (neat) 2928, 2856, 1719, 1258, 1102, 836, 779 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (t, *J* = 1 Hz, 1H), 7.10 (s, 4H), 4.13 (s, 2H), 2.93-2.85 (m, 4H), 2.82-2.72 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 201.5, 138.8, 137.9, 128.4, 128.3, 69.3, 45.1, 39.7, 28.7, 27.5, 25.6, 18.2, -5.60. HMRS (CI) calcd for $C_{19}H_{30}NaO_3Si$ $[M+Na]^+$: 357.1856. Found: 357.1854. Elemental analysis calcd for $C_{19}H_{30}O_3Si{\cdot}H_2O$: C, 64.73; H, 9.15; Found: C, 64.62; H, 9.08.

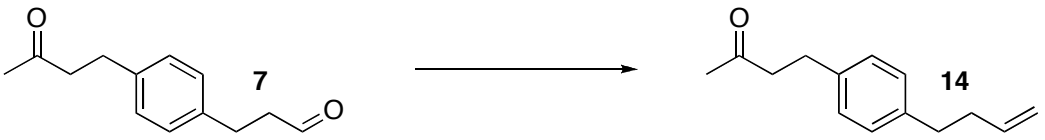
General Procedure for the Chemoselective Methylenation

Method A: Catalytic Methylenation using Wilkinson's Catalyst.
To a solution of chlorotris(triphenylphosphine)rhodium (23 mg, 0.025 mmol) and triphenylphosphine (288 mg, 1.10 mmol) in THF (10 mL), was added 2-propanol (75.0 μL, 1.00 mmol) followed by the aldehyde (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane in THF (0.82 mL, 1.40 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at room temperature. After 2 hours, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel.

Method B: Catalytic Methylenation using CuCl as Catalyst.
To a solution of CuCl (5 mg, 0.05 mmol) and triphenylphosphine (288 mg, 1.10 mmol) in THF (10 mL (0.1 M)) at 25 °C, was added 2-propanol (84 μL, 1.1 mmol) followed by the aldehyde (1.00 mmol) and the trimethylsilyldiazomethane ether solution (0.82 mL, 1.40 mmol). The resulting mixture was then heated at 60 °C and the reaction was stirred until the reaction showed completion by TLC analysis. Aqueous 3% H_2O_2 (10 mL) was added and the organic layer was washed with ether (3 x 20 mL). The combined organic layers were washed with brine (2 x 20 mL), then dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel.

Method C: Wittig Procedure for the Methylenation
To a solution of methyltriphenylphosphonium bromide (393 mg, 1.10 mmol) in THF (10 mL), was added sodium hexamethyldisilazide (202 mg, 1.10 mmol). The resulting yellow mixture was heated at 60 °C and stirred for 2 hours. After cooling to room temperature, the aldehyde (1.00 mmol) was then added and the solution was stirred at room temperature. After completion of the reaction, the solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel.

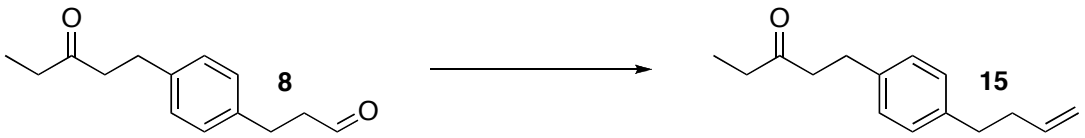
Characterization of Alkene Products



4-(4-(But-3-enyl)phenyl)butan-2-one (14). The title compound was prepared from 3-(4-(3-oxobutyl)phenyl)propanal (**7**) (106 mg, 0.52 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **14** (90 mg, 85%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.50 (25% EtOAc/hexanes). IR (neat) 2925, 1716, 1515, 1364, 160 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 5.86 (ddt, J = 17, 10, 7 Hz, 1H), 5.04 (d, J = 17 Hz, 1H), 4.98 (d, J = 10 Hz, 1H), 2.89-2.85 (m, 2H), 2.77-2.73 (m, 2H), 2.70-2.66 (m, 2H), 2.38-2.33 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 139.5, 138.3, 138.0, 128.4, 128.1, 114.8, 45.1, 35.4, 34.8, 30.0, 29.2. HRMS (CI) calc. for $C_{14}H_{18}NaO$ $[M+Na]^+$: 225.1251. Found: 225.1249.

4-(4-(But-3-enyl)phenyl)butan-2-one (14). The title compound was prepared from 3-(4-(3-oxobutyl)phenyl)propanal (**7**) (204 mg, 1 mmol) according to the general procedure **B** (reaction time 4 h). The desired alkene **14** (152 mg, 75%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes).

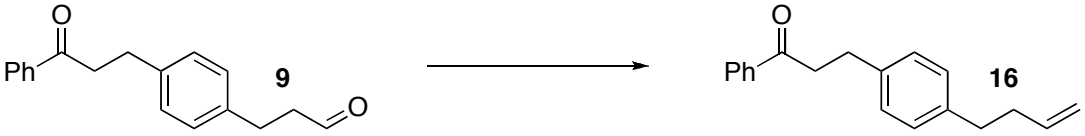
4-(4-(But-3-enyl)phenyl)butan-2-one (14). The title compound was prepared from 3-(4-(3-oxobutyl)phenyl)propanal (**7**) (121 mg, 0.59 mmol) according to the general procedure **C** (reaction time 16 h). The desired alkene **14** (92 mg, 77%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes).



1-(4-(But-3-enyl)phenyl)pentan-3-one (15). The title compound was prepared from 3-(4-(3-oxopentyl)phenyl)propanal (**8**) (105 mg, 0.48 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **15** (83 mg, 80 %) was obtained as a colorless oil after flash chromatography (2.5% EtOAc/hexanes). R_f 0.30 (10% EtOAc/hexanes). IR (neat) 2938, 1710, 1518, 1412, 1372, 1113, 823 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 4H), 5.86 (ddt, *J* = 18, 10, 7 Hz, 1H), 5.04 (d, *J* = 18 Hz, 1H), 4.98 (d, *J* = 10 Hz, 1H), 2.90-2.85 (m, 2H), 2.74-2.65 (m, 4H), 2.44-2.32 (m, 4H), 1.04 (t, *J* = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.7, 139.5, 138.5, 138.0, 128.4, 128.1, 114.8, 43.9, 36.0, 35.4, 34.8, 29.4, 7.70. HRMS (MAB) calc. for $C_{15}H_{20}O$ $[M]^+$: 216.1514. Found 216.1513.

1-(4-(But-3-enyl)phenyl)pentan-3-one (15). The title compound was prepared from 3-(4-(3-oxopentyl)phenyl)propanal (**8**) (109 mg, 0.50 mmol) according to the general procedure **B** (reaction time 16 h). The desired alkene **15** (86 mg, 80%) was obtained as a colorless oil after flash chromatography (2.5% EtOAc/hexanes).

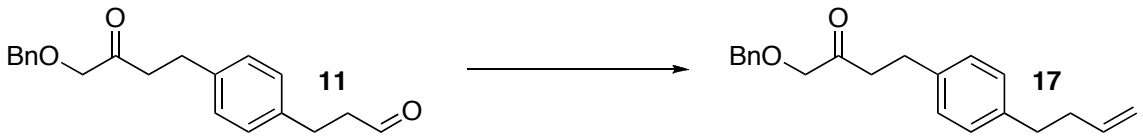
1-(4-(But-3-enyl)phenyl)pentan-3-one (15). The title compound was prepared from 3-(4-(3-oxopentyl)phenyl)propanal (**8**) (97 mg, 0.45 mmol) according to the general procedure **C** (reaction time 5 h). The desired alkene **15** (60 mg, 62%) was obtained as a colorless oil after flash chromatography (2.5% EtOAc/hexanes).



3-(4-But-3-enylphenyl)-1-phenylpropan-1-one (16). The title compound was prepared from 3-(4-(3-oxo-3-phenylpropyl)phenyl]propanal (**9**) (134 mg, 0.50 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **16** (110 mg, 83 %) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.35 (10% EtOAc/hexanes). IR (neat) 2924, 2854, 1684, 1448, 1202, 975, 911, 724, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7 Hz, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 5.86 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.04 (d, *J* = 17 Hz, 1H), 4.98 (d, *J* = 10 Hz, 1H), 3.32-3.27 (m, 2H), 3.06-3.01 (m, 2H), 2.71-2.65 (m, 2H), 2.39-2.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 139.6, 138.5, 138.0, 136.7, 133.0, 128.5, 128.5, 128.2, 127.9, 114.8, 40.4, 35.5, 34.8, 29.6. HRMS (CI) calc. for $C_{19}H_{21}O$ $[M+H]^+$: 265.1586. Found: 265.1585.

3-(4-But-3-enylphenyl)-1-phenylpropan-1-one (16). The title compound was prepared from 3-(4-(3-oxo-3-phenylpropyl)phenyl]propanal (**9**) (134 mg, 0.50 mmol) according to the general procedure **B** (reaction time 7 h). The desired alkene **16** (103 mg, 78 %) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes).

3-(4-But-3-enylphenyl)-1-phenylpropan-1-one (16). The title compound was prepared from 3-(4-(3-oxo-3-phenylpropyl)phenyl]propanal (**9**) (98 mg, 0.37 mmol) according to the general procedure **C** (reaction time 3 h). The desired alkene **16** (58 mg, 59 %) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes).



1-(Benzyloxy)-4-(4-(but-3-enyl)phenyl)butan-2-one (17). The title compound was prepared from 3-(4-(4-(benzyloxy)-3-oxobutyl)phenyl)propanal (**11**) (110 mg, 0.36 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **17** (81 mg, 74%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.35 (10% EtOAc/hexanes). IR (neat) 2925, 2856, 1723, 1437, 1102, 913 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.09 (s, 4H), 5.85 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.03 (d, *J* = 17 Hz, 1H), 4.97 (d, *J* = 10 Hz, 1H), 4.55 (s, 2H), 4.02 (s, 2H), 2.90-2.86 (m, 2H), 2.80-2.76 (m, 2H), 2.69-2.65 (m, 2H), 2.37-2.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.0, 139.6, 138.1, 138.0, 137.0, 128.5, 128.4, 128.2, 127.9, 127.8, 114.8, 75.1, 73.3, 40.6, 35.4, 34.8, 28.8. HRMS (CI) calc. for $C_{21}H_{24}NaO_2$ $[M+Na]^+$: 331.1668. Found: 331.1679.

1-(Benzyloxy)-4-(4-(but-3-enyl)phenyl)butan-2-one (17). The title compound was prepared from 3-(4-(4-(benzyloxy)-3-oxobutyl)phenyl)propanal (**11**) (120 mg, 0.39 mmol) according to the general procedure **B** (reaction time 16 h). The desired alkene **17** (86 mg, 72%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

1-(Benzyloxy)-4-(4-(but-3-enyl)phenyl)butan-2-one (17). The title compound was prepared from 3-(4-(4-(benzyloxy)-3-oxobutyl)phenyl)propanal (**11**) (20 mg, 0.060 mmol) according to the general procedure **C** (reaction time 2 h). The desired alkene **17** (11 mg, 56%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes).

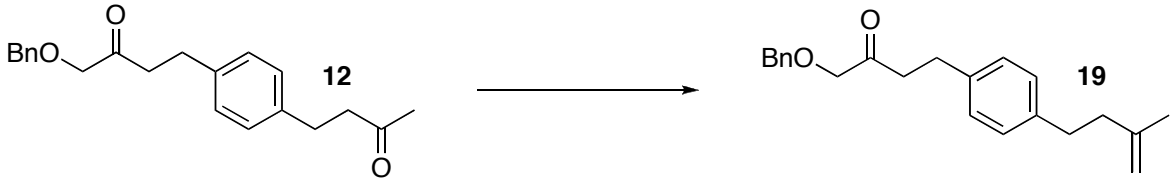
1-(3-((Benzyloxy)methyl)but-3-enyl)-4-(but-3-enyl)benzene (21). Diene **21** was also obtained in 31% yield. R_f 0.60 (10% EtOAc\Hexane). IR: 2926, 2854, 1640, 1514, 1453, 1095, 907, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 7.12 (s, 4H), 5.87 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.10-4.97 (m, 4H), 4.50 (s, 2H), 3.99 (s, 2H), 2.79-2.75 (m, 2H), 2.71-2.67 (m, 2H), 2.43-2.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.3, 139.2, 138.3, 138.1 (2C), 128.3, 128.2, 127.6, 127.5, 114.7, 112.1, 73.2, 71.9, 35.5, 34.9 (2C), 33.7. HRMS (CI) calc. for $C_{22}H_{27}O$ $[M+H]^+$: 307.2056. Found: 307.2051.

4-(4-(But-3-enyl)phenyl)-1-(*tert*-butyldimethylsilyloxy)butan-2-one (18). The title compound was prepared from 3-(4-(4-(*tert*-butyldimethylsilyl)-3-oxobutyl)phenyl)propanal (**13**) (103 mg, 0.21 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **18** (80 mg, 78%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.40 (10% EtOAc/hexanes). IR (neat) 2929, 2856, 1718, 1252, 1154, 1101, 845, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 4H), 5.86 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.04 (d, *J* = 17 Hz, 1H), 4.98 (d, *J* = 10 Hz, 1H), 4.14 (s, 2H), 2.92-2.78 (m, 4H), 2.70-2.65 (m, 2H), 2.39-2.32 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 139.5, 138.3, 138.1, 128.4, 128.2, 114.8, 69.4, 39.8, 35.5, 34.9, 28.8, 25.7, 18.2, -5.5. HRMS (CI) calc. for $C_{19}H_{31}O_3Si$ $[M+H]^+$: 357.1856. Found: 357.1854.

1-(*tert*-Butyldimethylsilyl)-4-(4-(but-3-enyl)phenyl)propanal (18). The title compound was prepared from 3-(4-(4-(*tert*-Butyldimethylsilyl)-3-oxobutyl)phenyl)propanal (**13**) (335 mg, 1.00 mmol) according to the general procedure **B** (reaction time 16 h). The desired alkene **18** (193 mg, 58%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

1-(*tert*-Butyldimethylsilyl)-4-(4-(but-3-enyl)phenyl)propanal (18). The title compound was prepared from 3-(4-(4-(*tert*-Butyldimethylsilyl)-3-oxobutyl)phenyl)propanal (**13**) (61 mg, 0.18 mmol) according to the general procedure **C** (reaction time 4 h). The desired alkene **18** (21 mg, 35%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).



4-(4-(3-((Benzyloxy)methyl)but-3-enyl)phenyl)butan-2-one (19). The title compound was prepared from 1-(benzyloxy)-(4-(3-oxobutyl)phenyl)butan-3-one (**12**) (94 mg, 0.29 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **19** (77 mg, 83%) was obtained as a colorless oil after flash chromatography (5% EtOAc/Hexanes). R_f 0.10 (10% EtOAc/hexanes). IR (neat) 2923, 2856, 1715, 1453, 1364, 1095, 738, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 7.11-7.10 (m, 4H), 5.08 (s, 1H), 4.97 (s, 1H), 4.49 (s, 2H), 3.98 (s, 2H), 2.88-2.84 (m, 2H), 2.76-2.72 (m, 2H), 2.40-2.36 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 145.5, 139.7, 138.3, 138.3, 128.4, 128.3, 128.2, 127.6, 127.5, 112.2, 73.1, 71.9, 45.2, 34.8, 33.6, 30.0, 29.3. HRMS (CI) calc. for $C_{22}H_{26}NaO_2$ $[M+Na]^+$: 345.1827. Found: 345.1825.

4-(4-(3-((Benzyloxy)methyl)but-3-enyl)phenyl)butan-2-one (19). The title compound was prepared from 1-(benzyloxy)-(4-(3-oxobutyl)phenyl)butan-3-one (**12**) (188 mg, 0.58 mmol) according to the general procedure **B** (reaction time 8 h). The desired alkene **19** (127 mg, 68%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes).

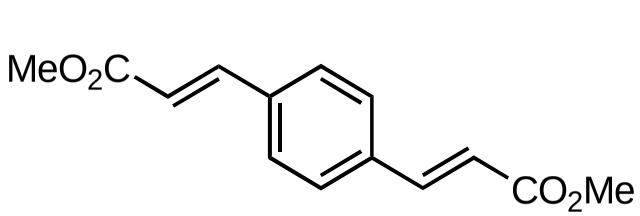
4-(4-(3-((Benzyloxy)methyl)but-3-enyl)phenyl)butan-2-one (19). The title compound was prepared from 1-(benzyloxy)-(4-(3-oxobutyl)phenyl)butan-3-one (**12**) (32 mg, 0.10 mmol) according to the general procedure **C** (reaction time 5 h). The desired alkene **19** (18 mg, 56%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes).

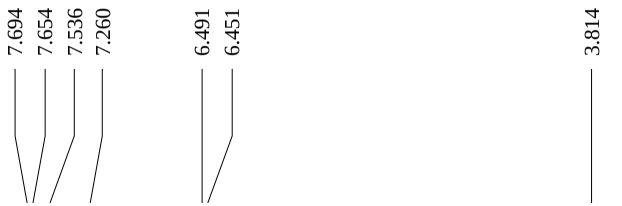
4-(4-(3-(Trifluoromethyl)but-3-enyl)phenyl)butan-2-one (20). The title compound was prepared from 1-(4-(4,4,4-trifluoro-3-oxobutyl)phenyl)butan-3-one (**10**) (67 mg, 0.25 mmol) according to the general procedure **A** (reaction time 2 h). The desired alkene **20** (52 mg, 79%) was obtained as a colorless oil after flash chromatography (3% EtOAc/hexanes). R_f 0.10 (10% EtOAc/hexanes). IR (neat) 2932, 1717, 1362, 1165, 1124 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 5.68 (s, 1H), 5.29 (s, 1H), 2.89-2.85 (m, 2H), 2.82-2.73 (m, 4H), 2.49 (t, J = 8 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz,

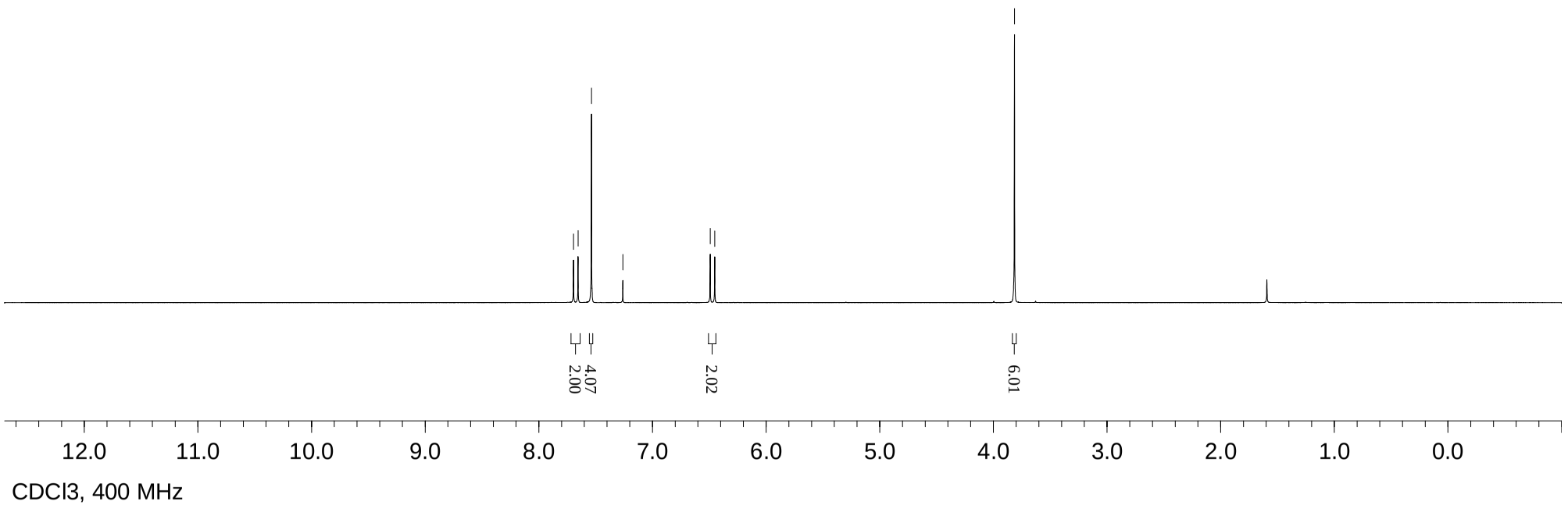
$CDCl_3$) δ 208.0, 138.8, 138.3, 137.6 (q, J = 29 Hz), 128.4, 128.3, 123.7 (q, J = 272 Hz), 118.1 (q, J = 6 Hz), 45.1, 33.2, 31.1, 30.0, 29.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -68.8. HRMS (CI) calc. for $C_{15}H_{18}F_3O$ $[M+H]^+$: 271.1304. Found: 271.1306.

4-(4-(3-(Trifluoromethyl)but-3-enyl)phenyl)butan-2-one (20). The title compound was prepared from 1-(4-(4,4,4-trifluoro-3-oxobutyl)phenyl)butan-3-one (**10**) (44 mg, 0.16 mmol) according to the general procedure **B** (reaction time 3 h). The desired alkene **20** (36 mg, 84%) was obtained as a colorless oil after flash chromatography (3% EtOAc/hexanes).

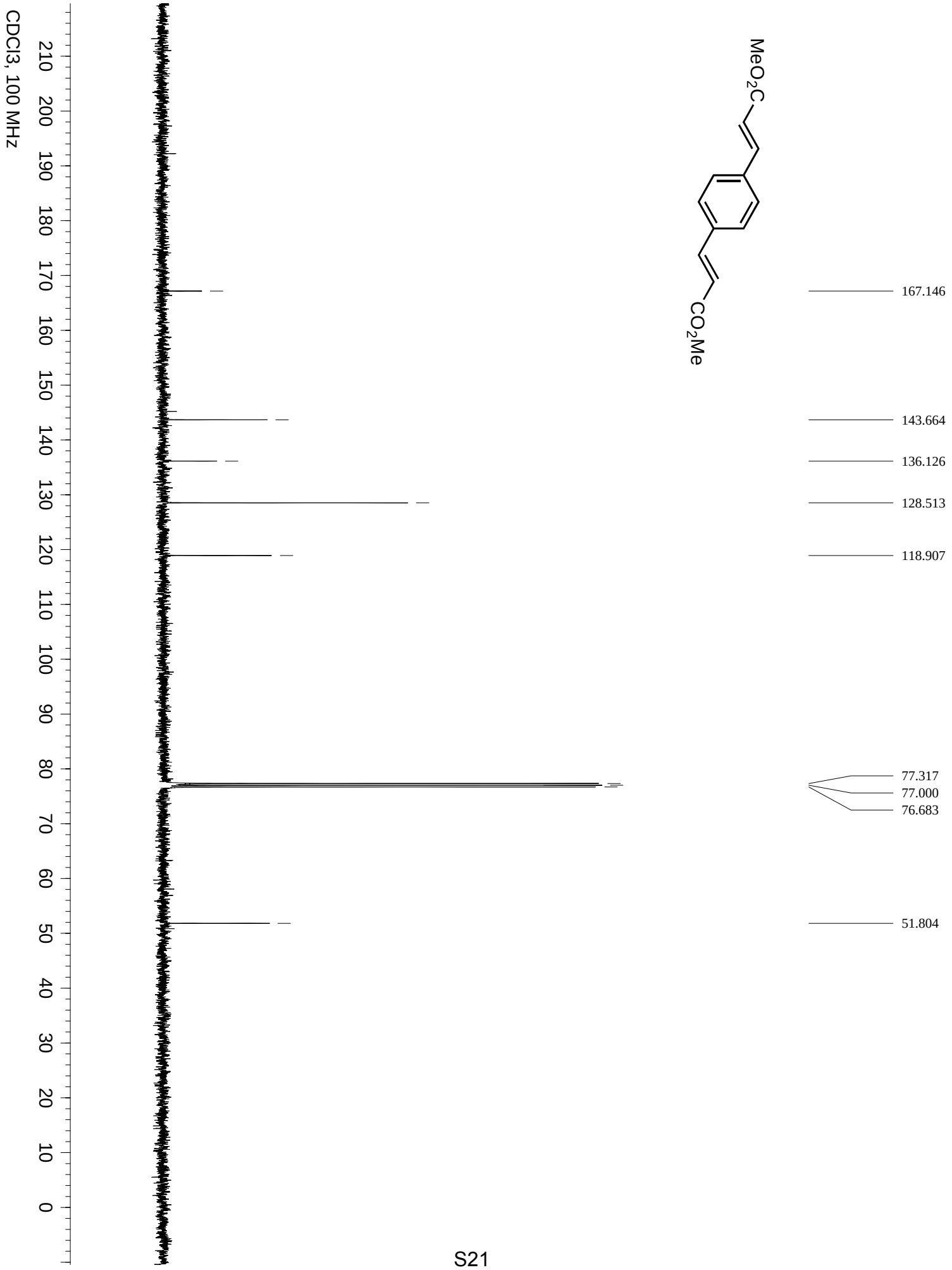
4-(4-(3-(Trifluoromethyl)but-3-enyl)phenyl)butan-2-one (20). The title compound was prepared from 1-(4-(4,4,4-trifluoro-3-oxobutyl)phenyl)butan-3-one (**10**) (44 mg, 0.16 mmol) according to the general procedure **C** (reaction time 1 h). The desired alkene **20** (40 mg, 93%) was obtained as a colorless oil after flash chromatography (3% EtOAc/hexanes).

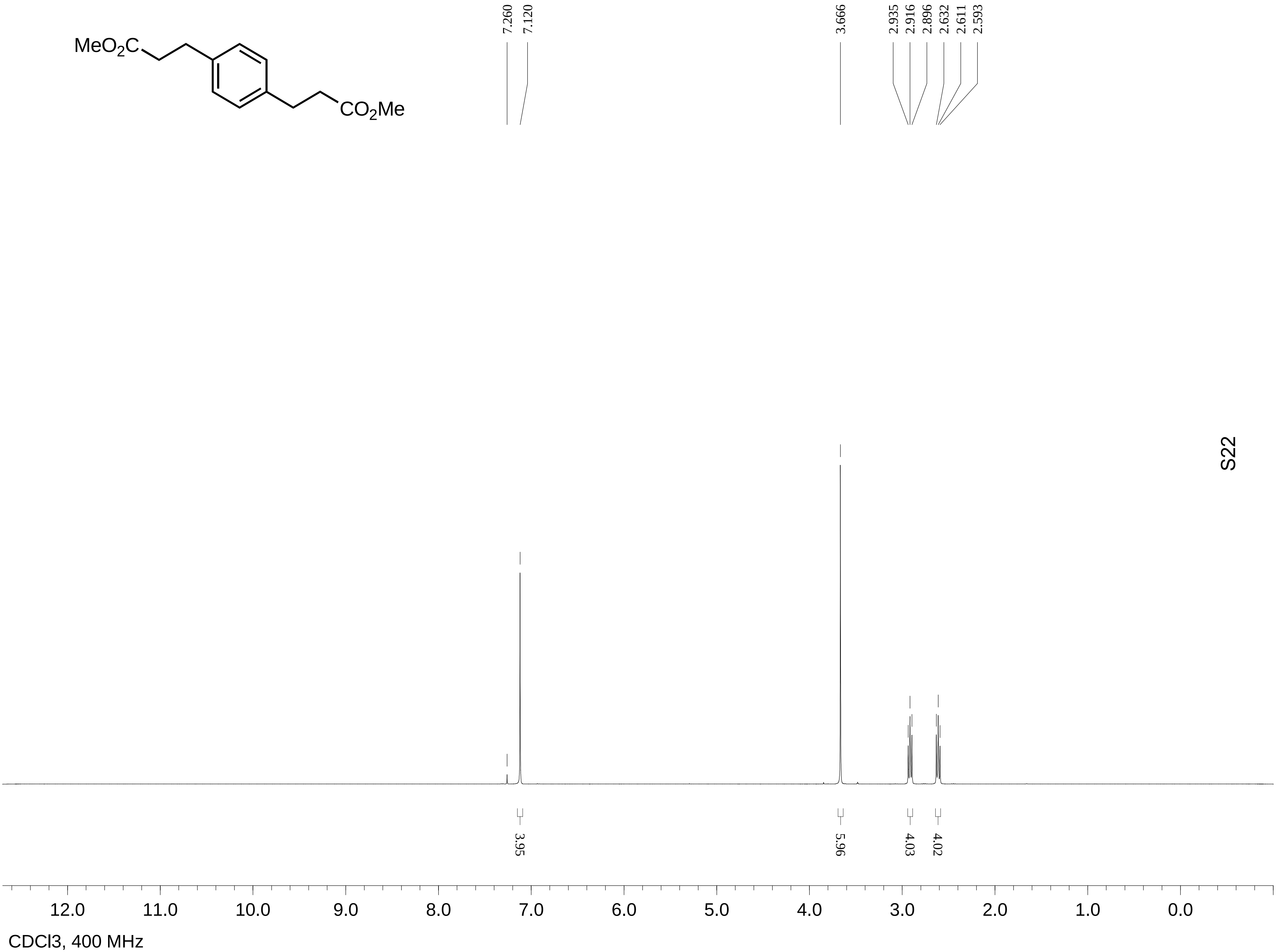






CDCl3, 400 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
MeO2C
CO2Me
167.146
143.664
136.126
128.513
118.907
77.317
77.000
76.683
51.804



MeO$_2$C
CO$_2$Me
7.260
7.120
3.666
2.935
2.916
2.896
2.632
2.611
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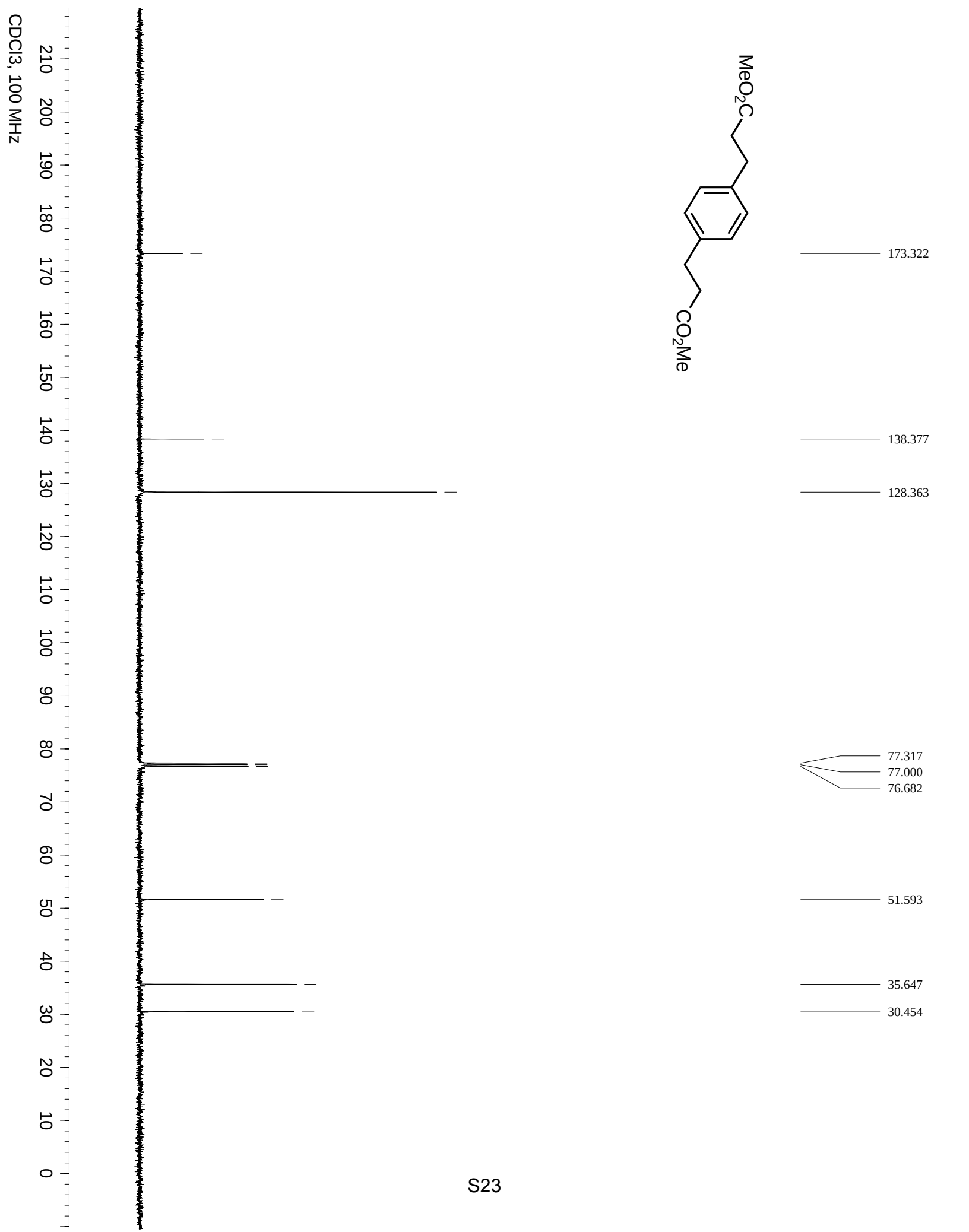
5.96
4.03
4.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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CO2Me
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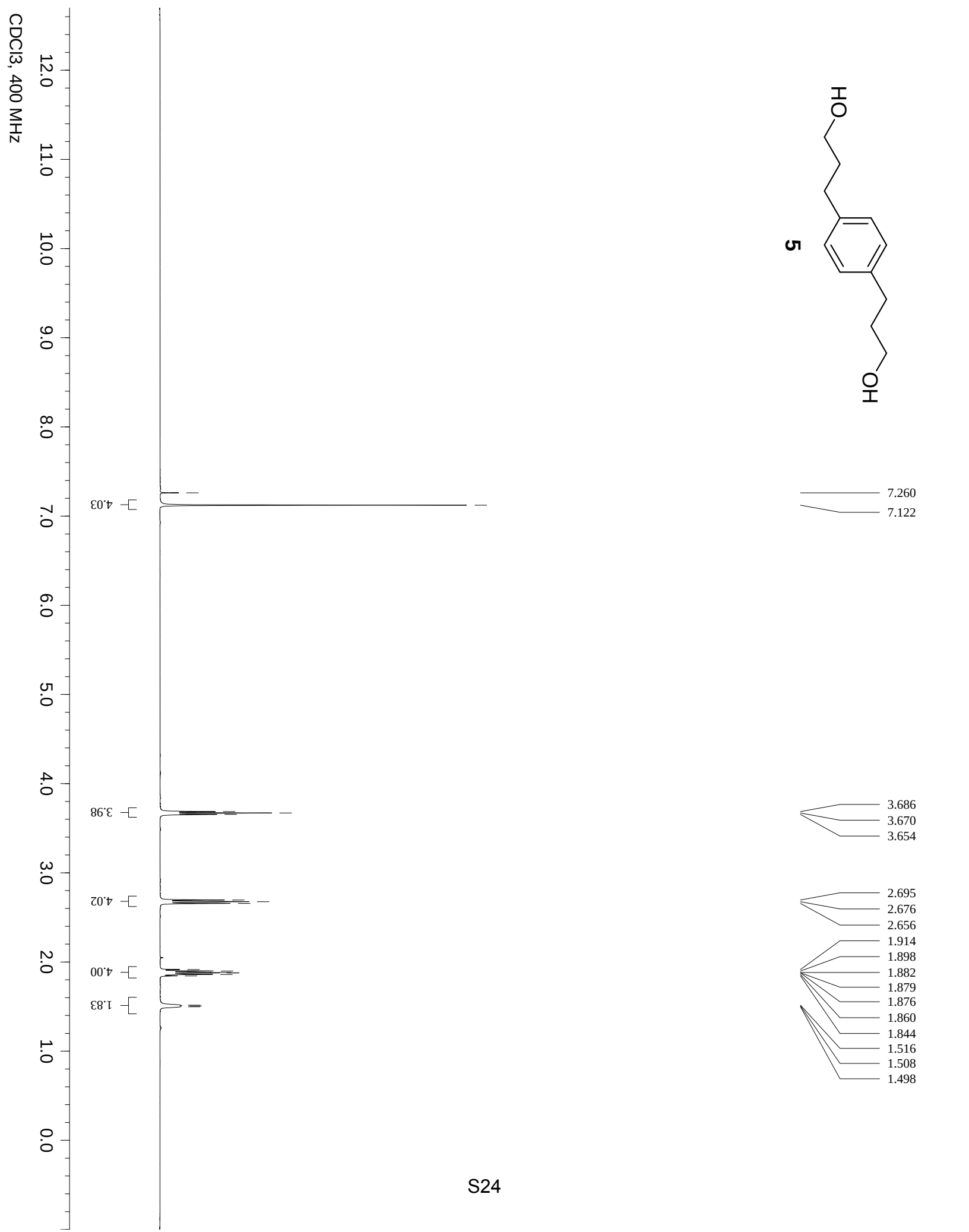
128.363
77.317
77.000
76.682
51.593
35.647
30.454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10.0
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7.0
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2.0
1.0
0.0
4.03
3.98
4.02
4.00
1.83
HO
OH
5
7.260
7.122
3.686
3.670
3.654
2.695
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1.860
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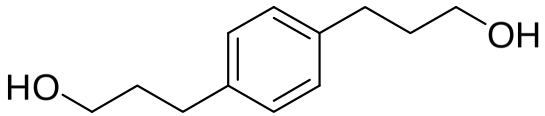
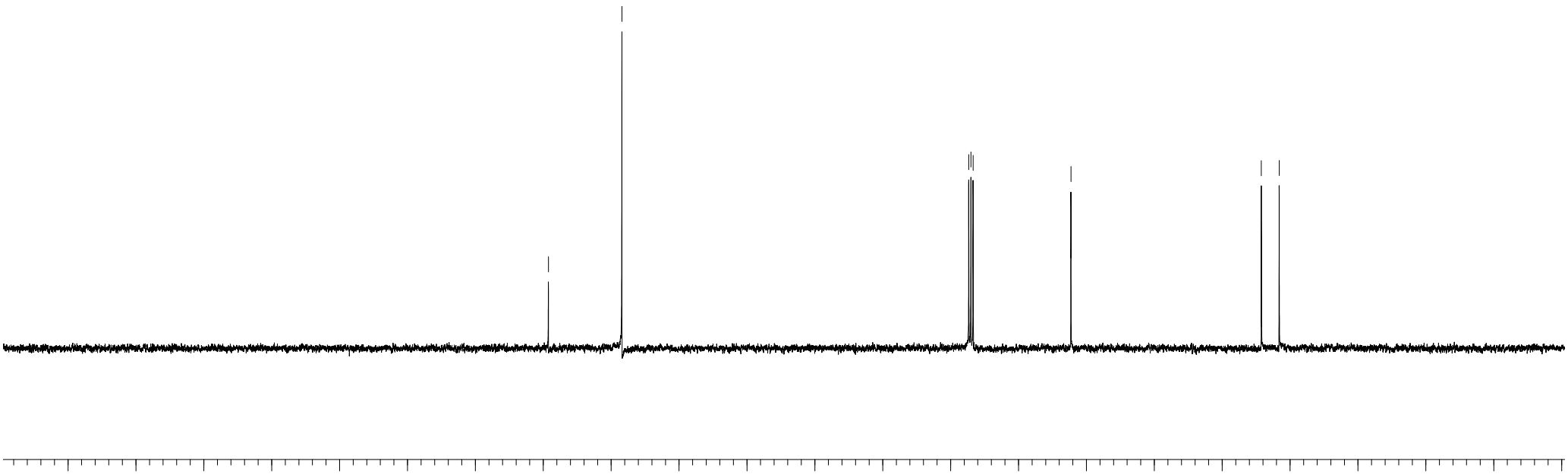
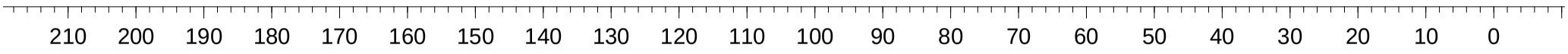
1.516
1.508
1.498



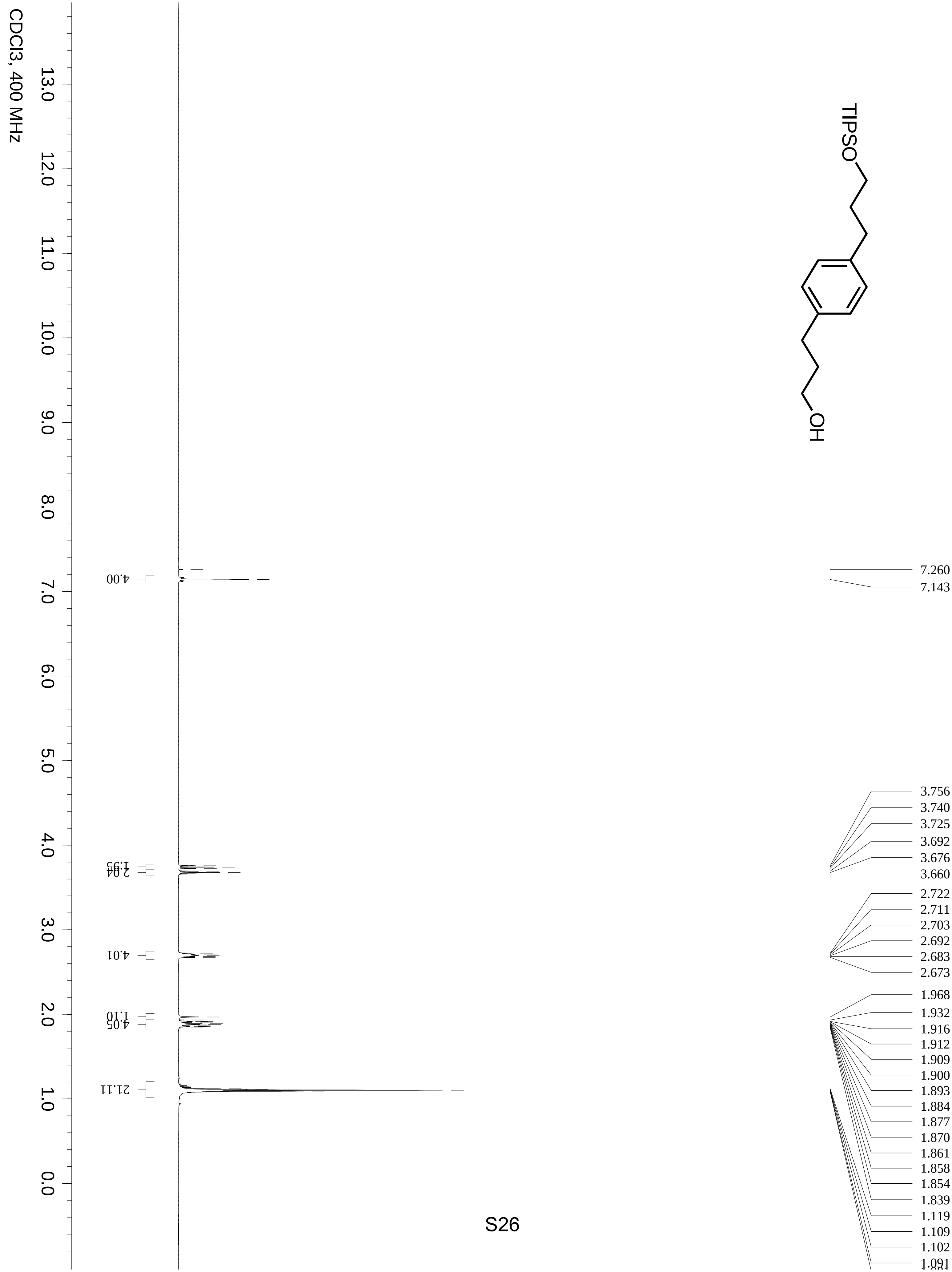
5

139.239
128.409
77.317
77.000
76.682
62.267
34.222
31.592





CDCl3, 100 MHz


CDCl3, 400 MHz
TIPSO
OH
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.00
1.95
2.04
4.01
1.10
4.05
21.11
7.260
7.143
3.756
3.740
3.725
3.692
3.676
3.660
2.722
2.711
2.703
2.692
2.683
2.673
1.968
1.932
1.916
1.912
1.909
1.900
1.893
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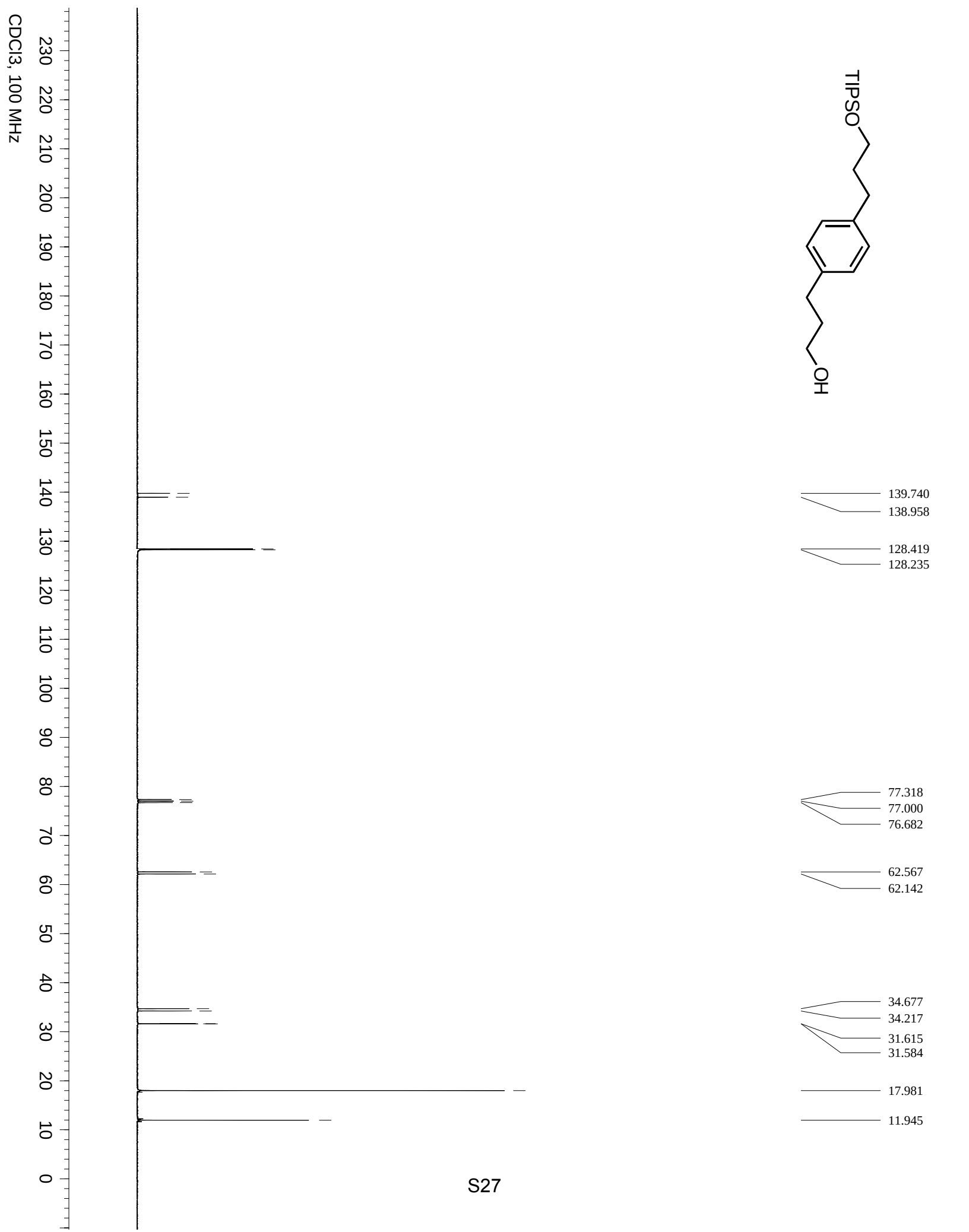
1.839
1.119
1.109
1.102
1.091


CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TIPSO
OH
139.740
138.958
128.419
128.235
77.318
77.000
76.682
62.567
62.142
34.677
34.217
31.615
31.584
17.981
11.945

CDCl3, 100 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.94
4.04
1.99
1.99
4.04
2.09
20.92
TIPSO
O
6
9.833
9.828
9.823
7.260
7.176
7.149
7.136
7.109
3.756
3.736
3.715
2.973
2.948
2.923
2.799
2.775
2.754
2.749
2.745
2.730
2.705
2.678
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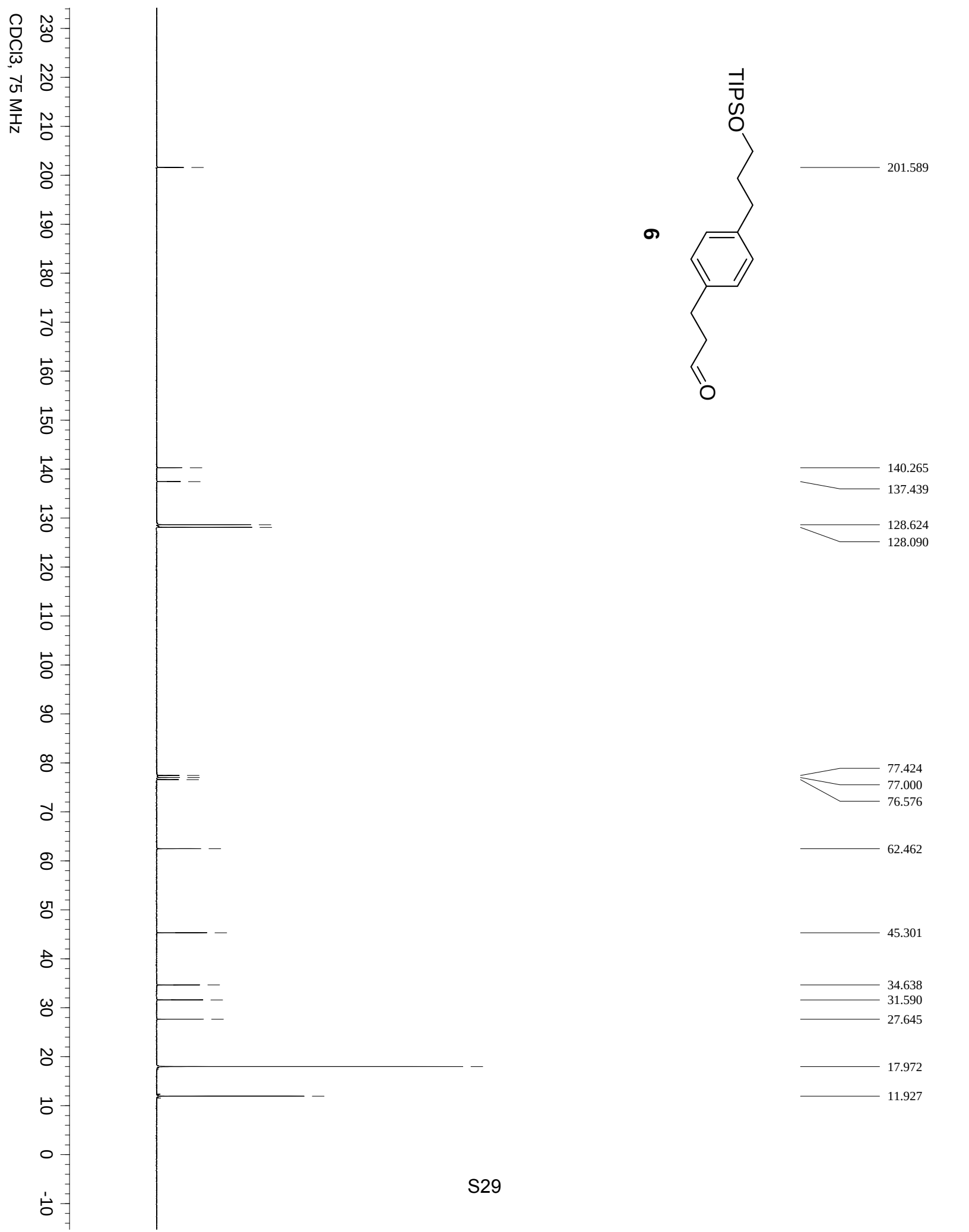
1.088
1.073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220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TIPSO
O
6
201.589
140.265
137.439
128.624
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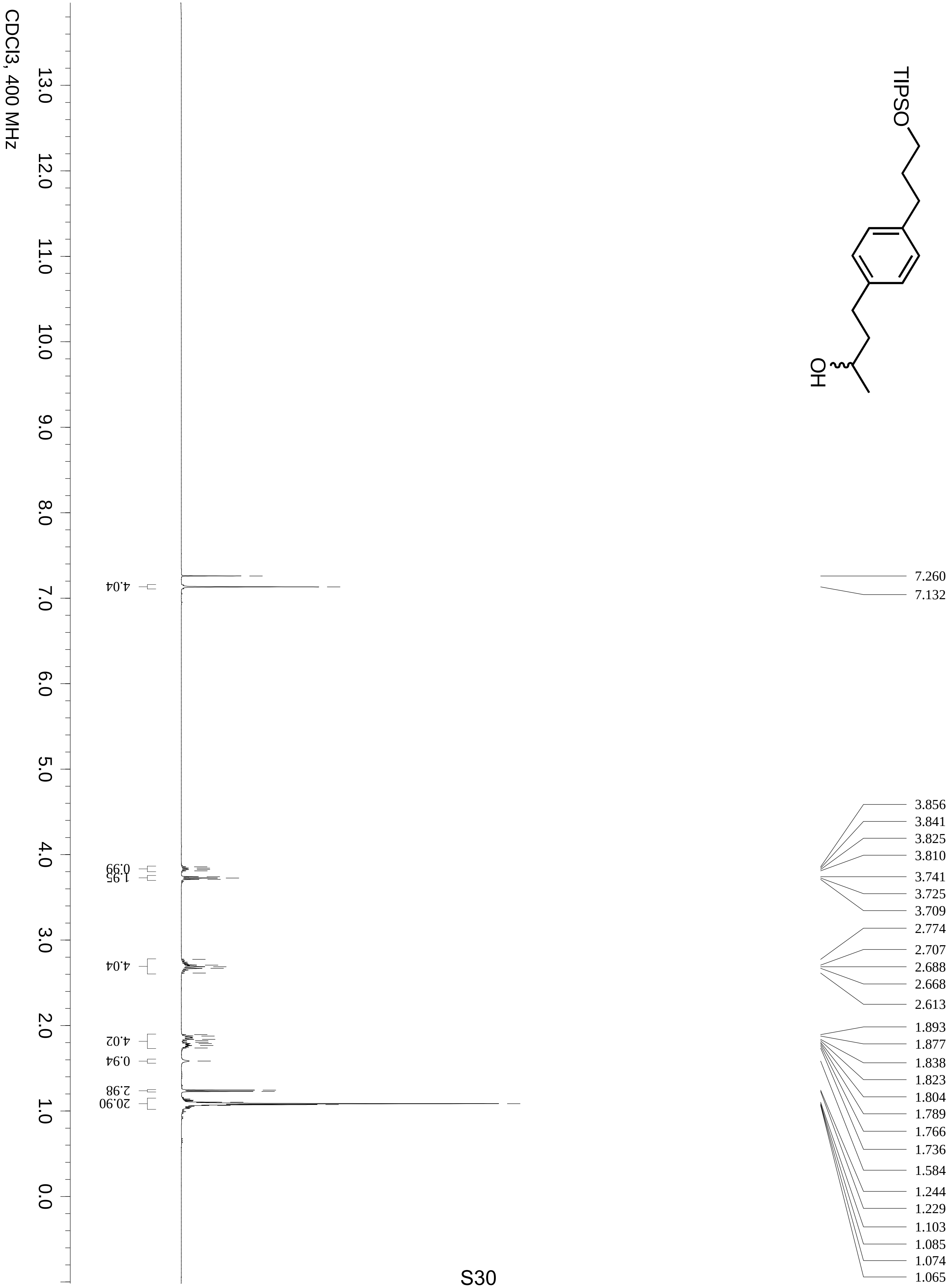
31.590
27.645
17.972
11.927


CDCl3, 400 MHz
TIPSO
OH
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3.856
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3.825
3.810
3.741
3.725
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2.707
2.688
2.668
2.613
1.893
1.877
1.838
1.823
1.804
1.789
1.766
1.736
1.584
1.244
1.229
1.103
1.085
1.074
1.065
4.04
0.99
1.95
4.04
4.02
0.94
2.98
20.90
13.0
12.0
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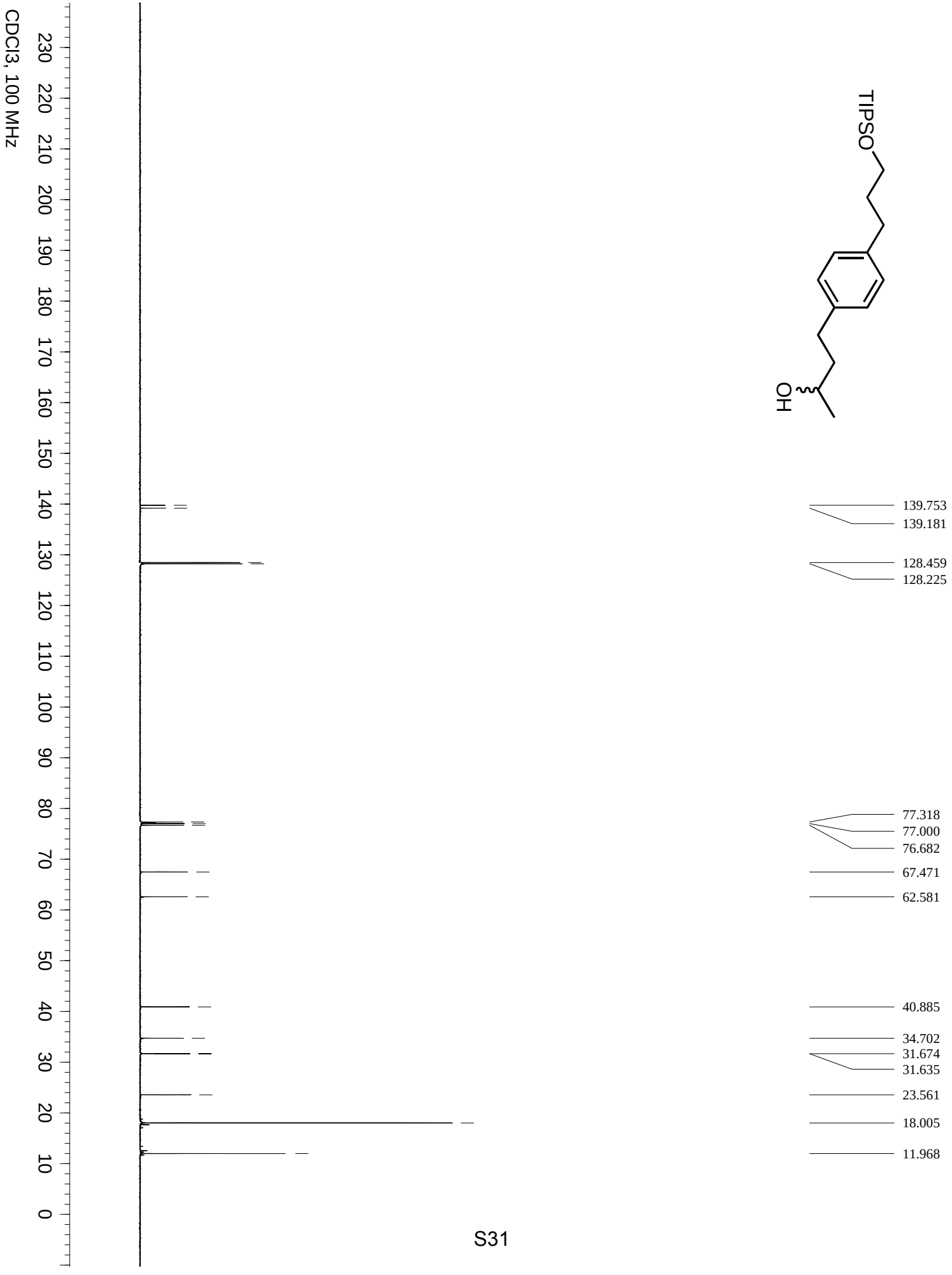
1.0
0.0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140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TIPSO
OH
139.753
139.181
128.459
128.225
77.318
77.000
76.682
67.471
62.581
40.885
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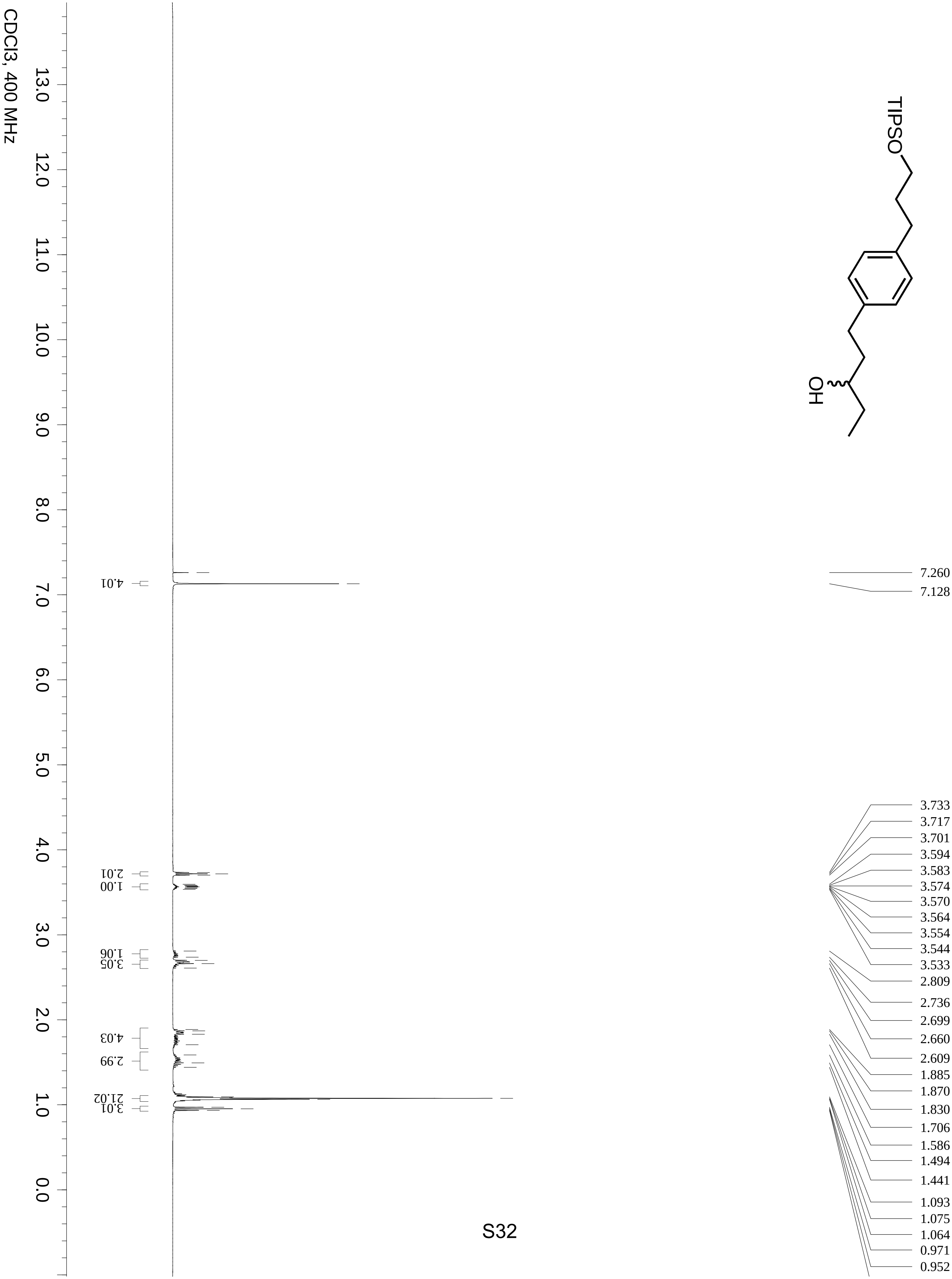
31.674
31.635
23.561
18.005
11.968


CDCl3, 400 MHz
TIPSO
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7.128
3.733
3.717
3.701
3.594
3.583
3.574
3.570
3.564
3.554
3.544
3.533
2.809
2.736
2.699
2.660
2.609
1.885
1.870
1.830
1.706
1.586
1.494
1.441
1.093
1.075
1.064
0.971
0.952
4.01
2.01
1.00
1.06
3.05
4.03
2.99
21.02
3.01
13.0
12.0
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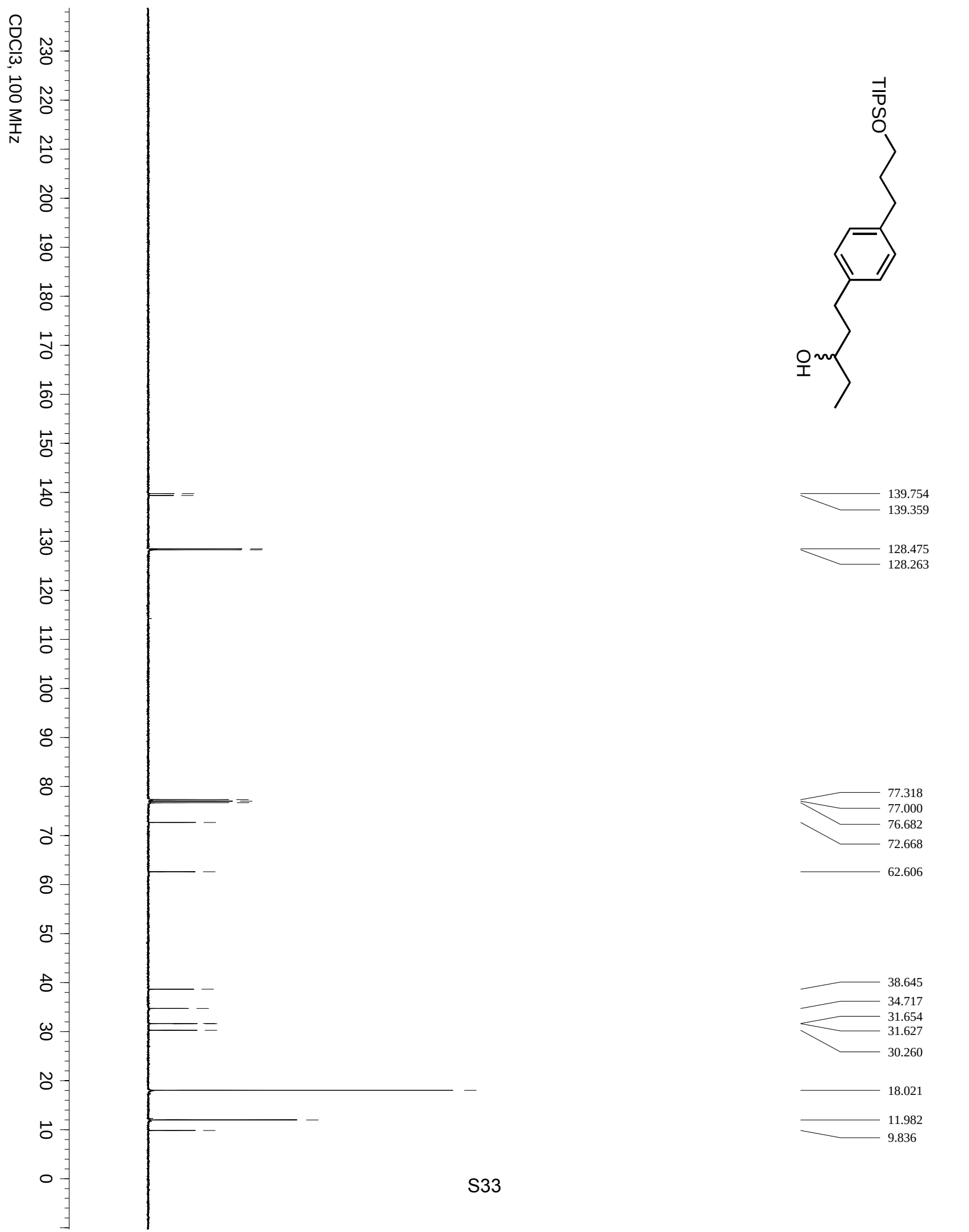
0.0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180
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130
120
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100
90
80
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60
50
40
30
20
10
0
TIPSO
OH
139.754
139.359
128.475
128.263
77.318
77.000
76.682
72.668
62.606
38.645
34.717
31.654
31.627
30.260
18.021
11.982
9.836


TIPSO
Ph
OH
7.404
7.393
7.349
7.339
7.316
7.287
7.165
4.735
4.723
4.710
3.780
3.764
3.749
2.803
2.747
2.729
2.708
2.646
2.214
2.160
2.070
2.019
1.934
1.899
1.864
1.128
4.97
4.00
0.96
1.96
3.98
2.95
2.01
20.95
11.0
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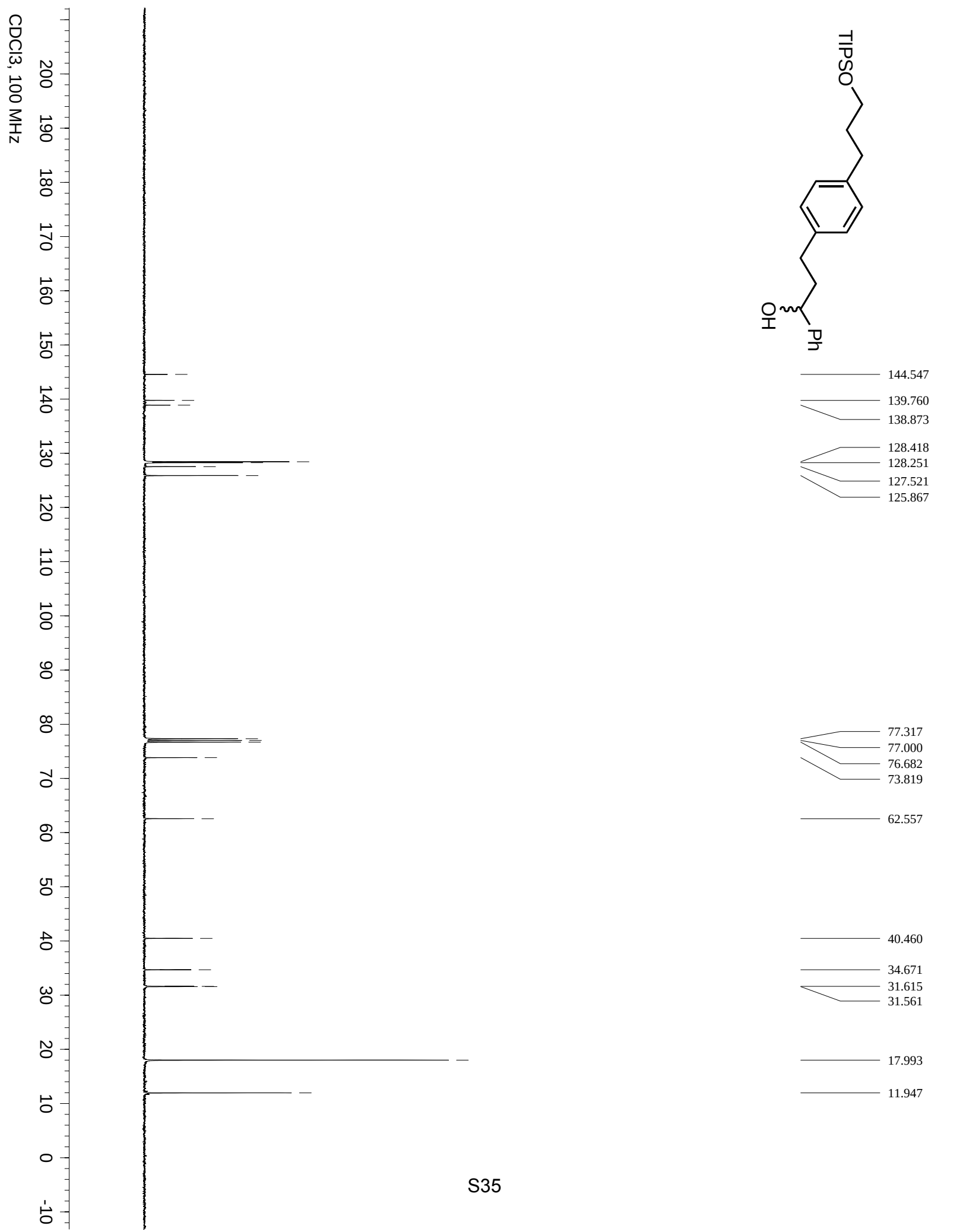
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz


CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TIPSO
OH
Ph
144.547
139.760
138.873
128.418
128.251
127.521
125.867
77.317
77.000
76.682
73.819
62.557
40.460
34.671
31.615
31.561
17.993
11.947

CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.05
2.03
2.01
4.00
3.00
2.04
21.03
TIPSO
O
7.260
7.149
7.121
7.111
7.083
3.739
3.718
3.697
2.902
2.897
2.874
2.851
2.846
2.779
2.773
2.750
2.727
2.722
2.708
2.683
2.677
2.656
2.143
1.894
1.873
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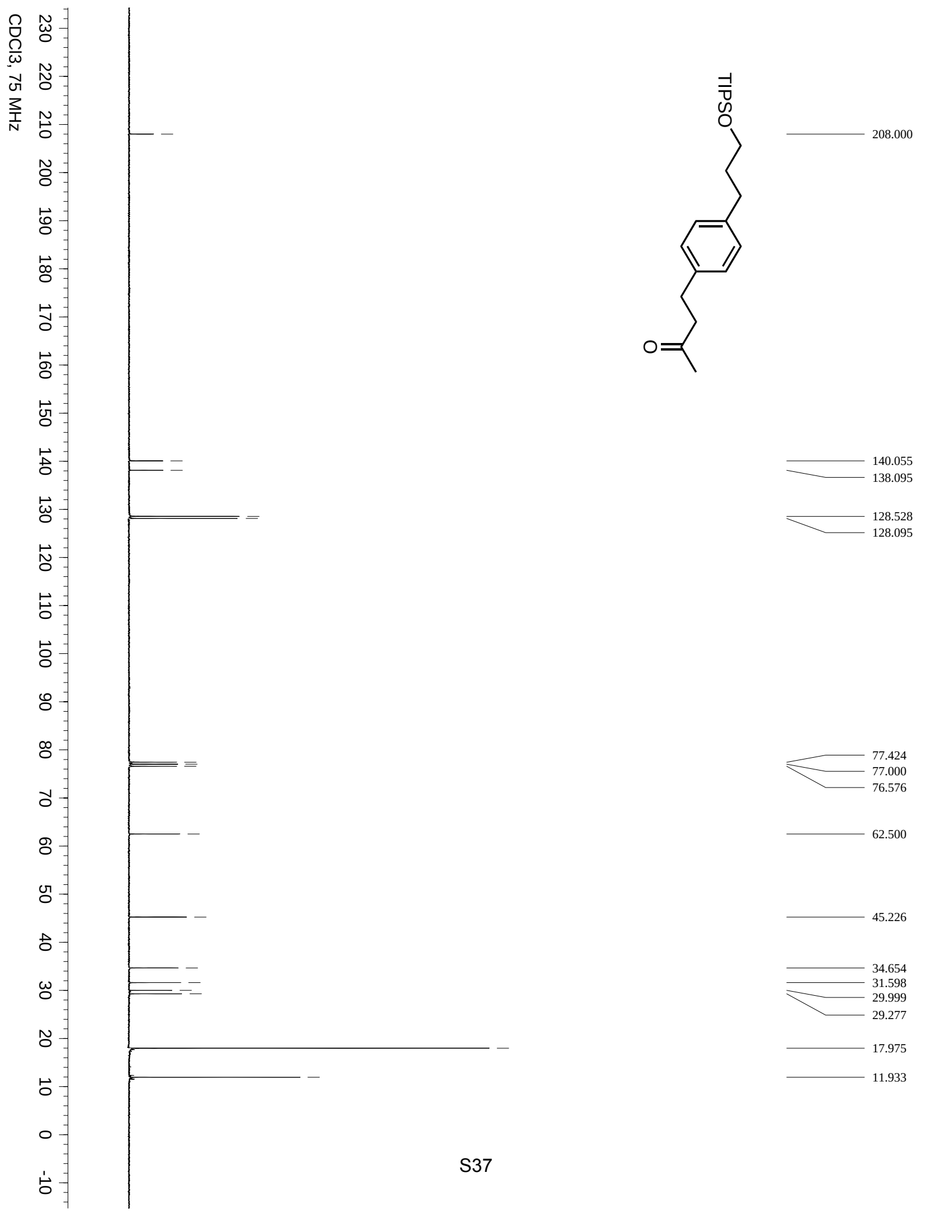
1.842
1.832
1.821
1.800
1.097
1.083
1.071


CDCl3, 75 MHz
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220
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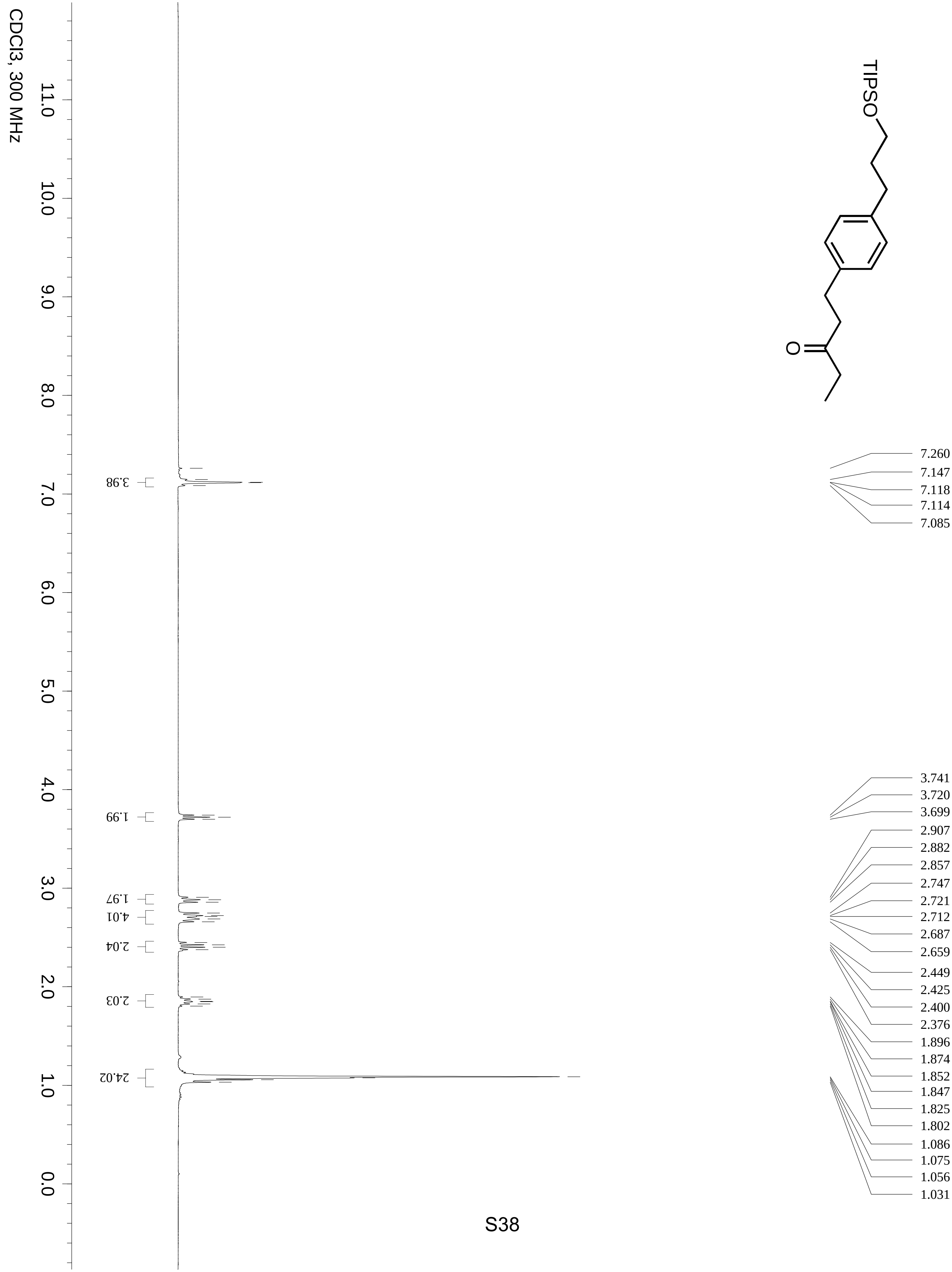
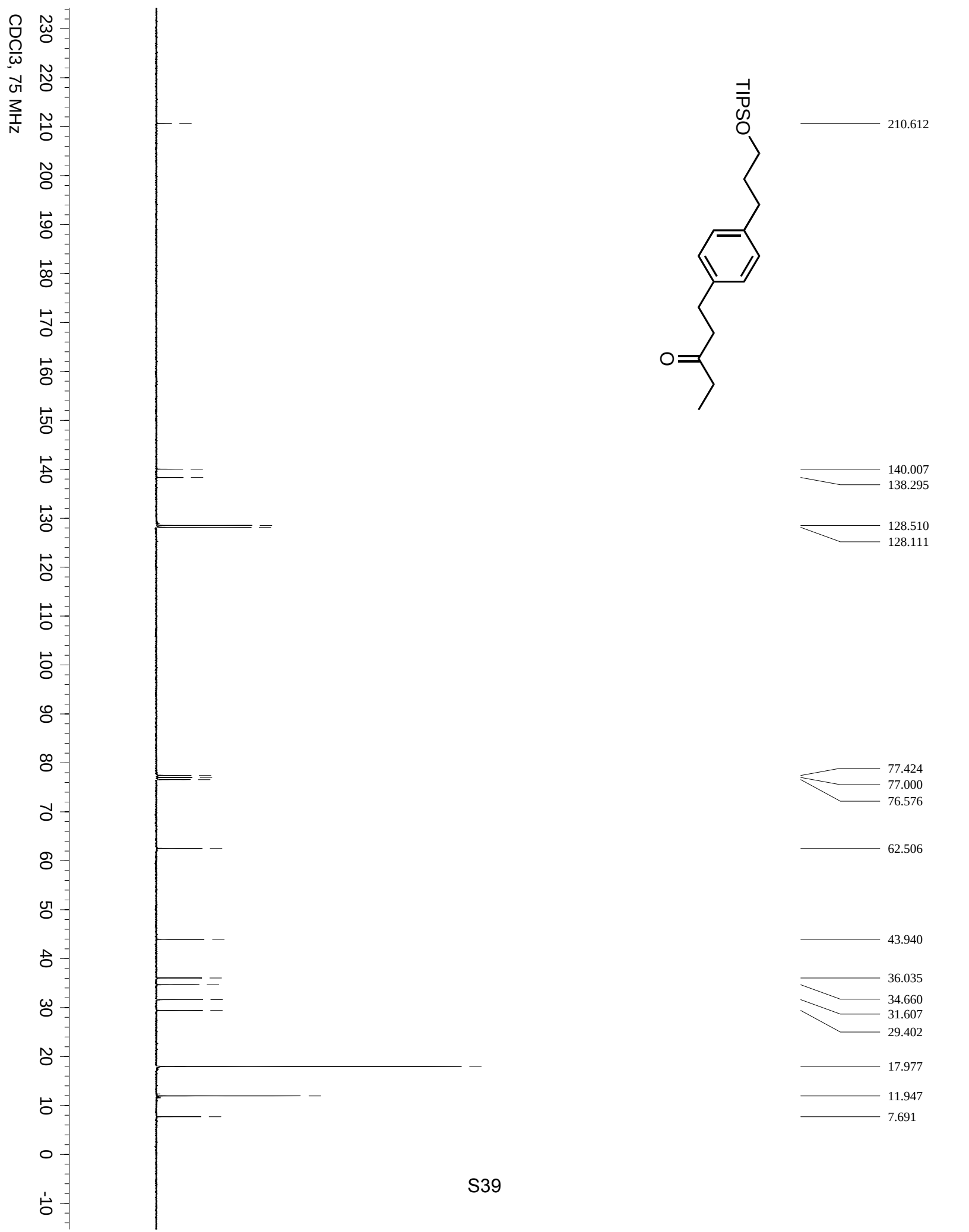
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TIPSO
O
208.000
140.055
138.095
128.528
128.095
77.424
77.000
76.576
62.500
45.226
34.654
31.598
29.999
29.277
17.975
11.933


CDCl3, 300 MHz
TIPSO
O
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.98
1.99
1.97
4.01
2.04
2.03
24.02
7.260
7.147
7.118
7.114
7.085
3.741
3.720
3.699
2.907
2.882
2.857
2.747
2.721
2.712
2.687
2.659
2.449
2.425
2.400
2.376
1.896
1.874
1.852
1.847
1.825
1.802
1.086
1.075
1.056
1.031


CDCl3, 75 MHz
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220
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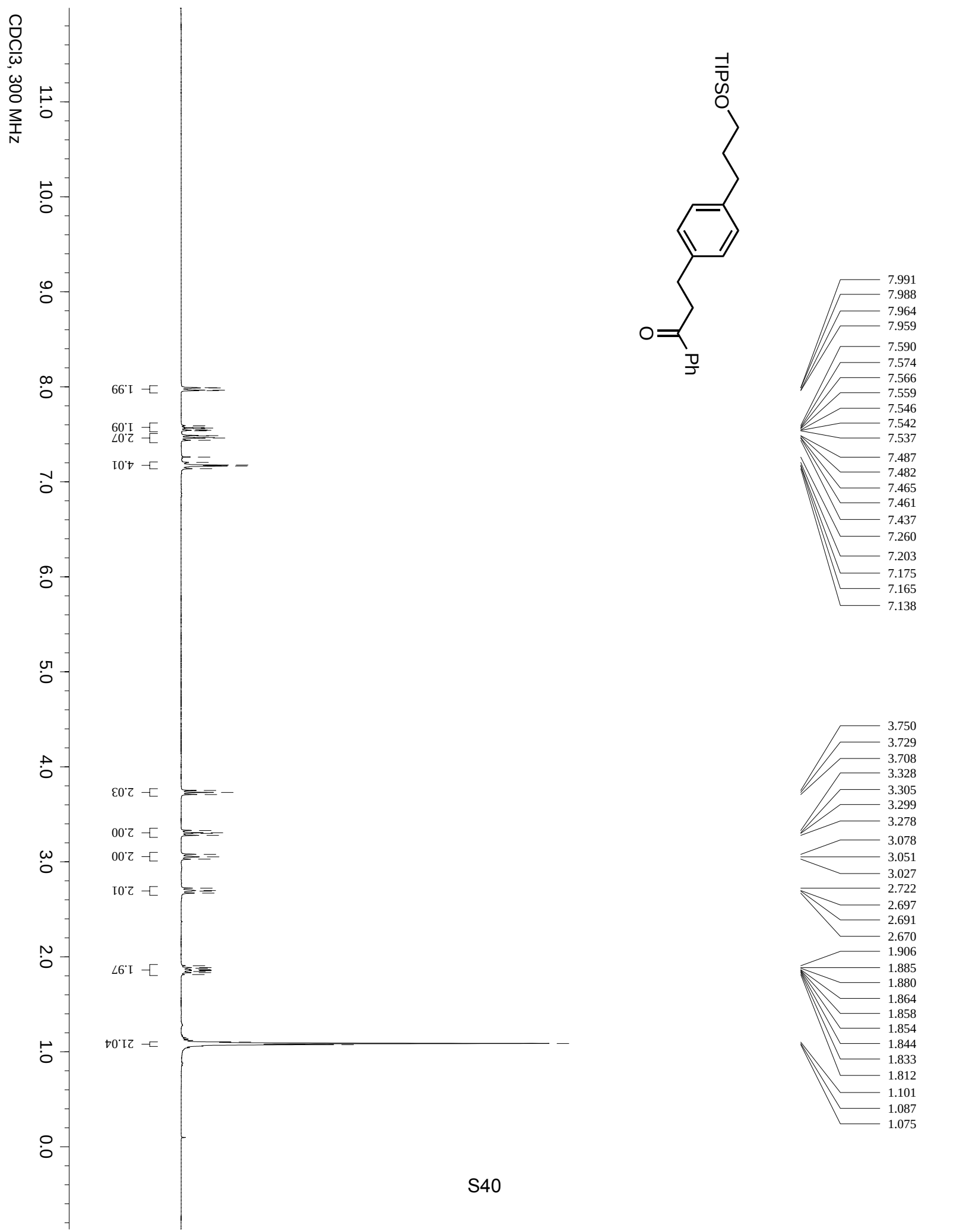
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TIPSO
O
210.612
140.007
138.295
128.510
128.111
77.424
77.000
76.576
62.506
43.940
36.035
34.660
31.607
29.402
17.977
11.947
7.691


CDCl3, 300 MHz
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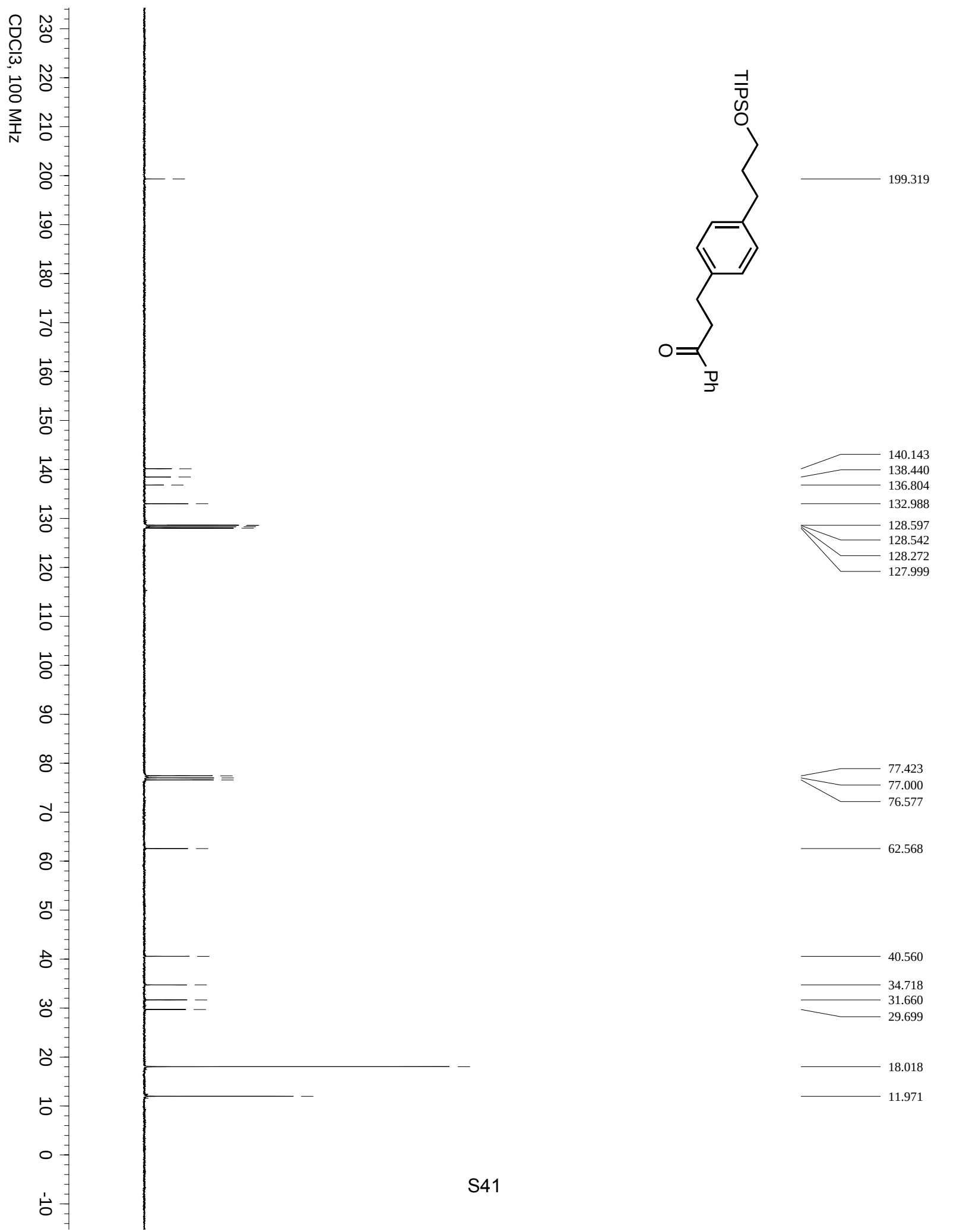
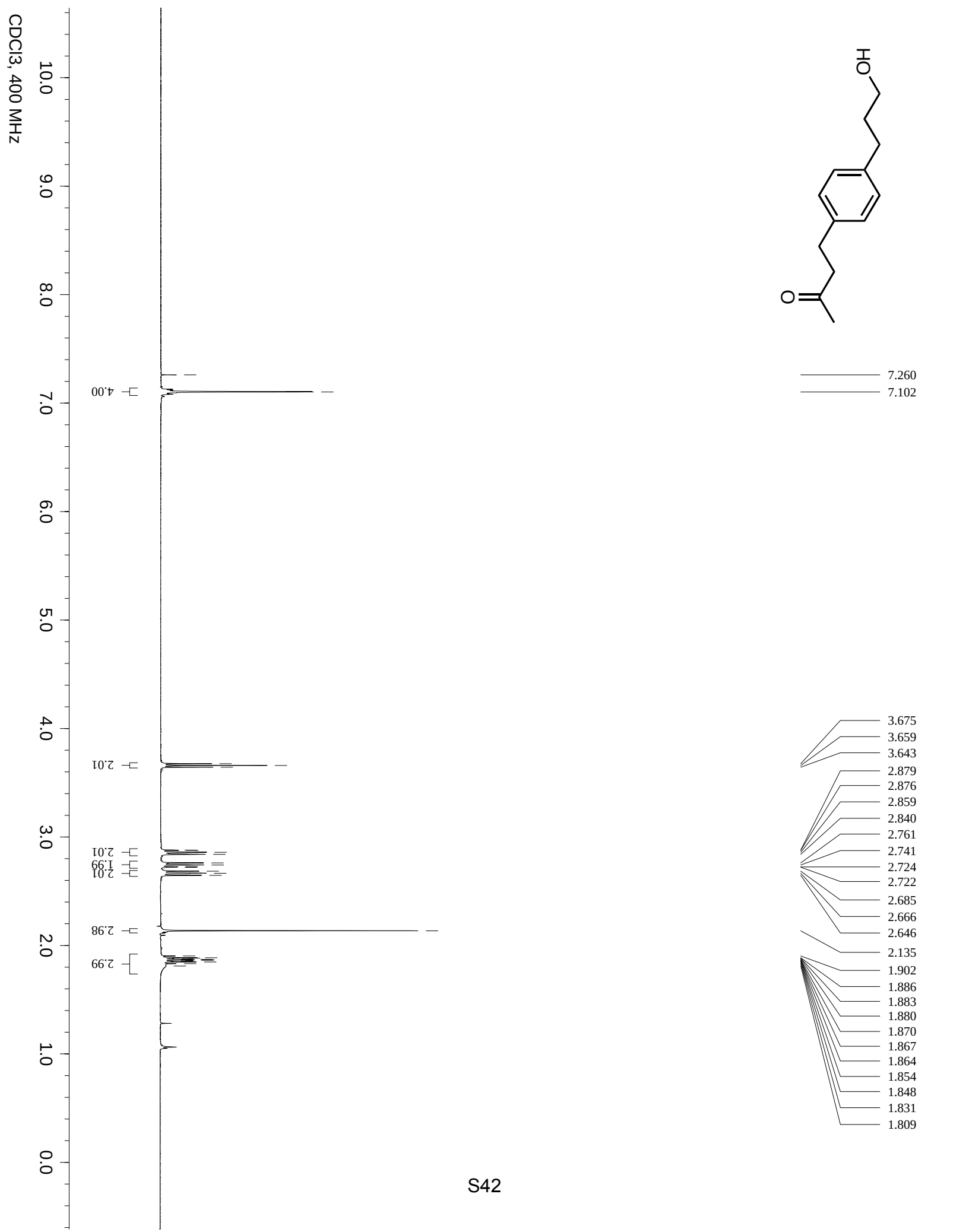
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.99
1.09
2.07
4.01
2.03
2.00
2.00
2.01
1.97
21.04
TIPSO
O
Ph
7.991
7.988
7.964
7.959
7.590
7.574
7.566
7.559
7.546
7.542
7.537
7.487
7.482
7.465
7.461
7.437
7.260
7.203
7.175
7.165
7.138
3.750
3.729
3.708
3.328
3.305
3.299
3.278
3.078
3.051
3.027
2.722
2.697
2.691
2.670
1.906
1.885
1.880
1.864
1.858
1.854
1.844
1.833
1.812
1.101
1.087
1.075


CDCl3, 100 MHz
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
TIPSO
O
Ph
199.319
140.143
138.440
136.804
132.988
128.597
128.542
128.272
127.999
77.423
77.000
76.577
62.568
40.560
34.718
31.660
29.699
18.018
11.971


CDCl3, 400 MHz
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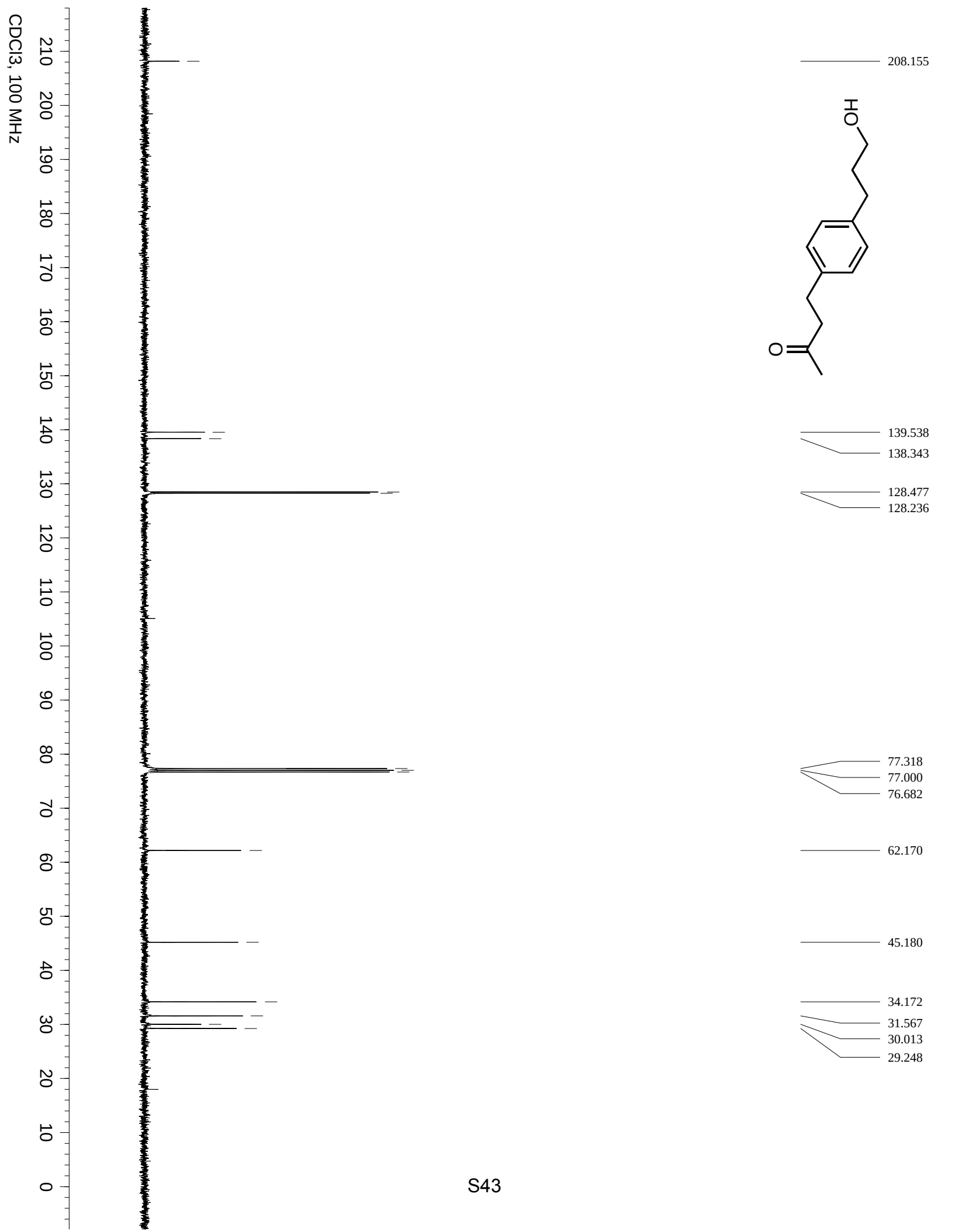
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.00
2.01
2.01
1.99
2.01
2.98
2.99
HO
O
7.260
7.102
3.675
3.659
3.643
2.879
2.876
2.859
2.840
2.761
2.741
2.724
2.722
2.685
2.666
2.646
2.135
1.902
1.886
1.883
1.880
1.870
1.867
1.864
1.854
1.848
1.831
1.809


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
208.155
OH
O
139.538
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128.477
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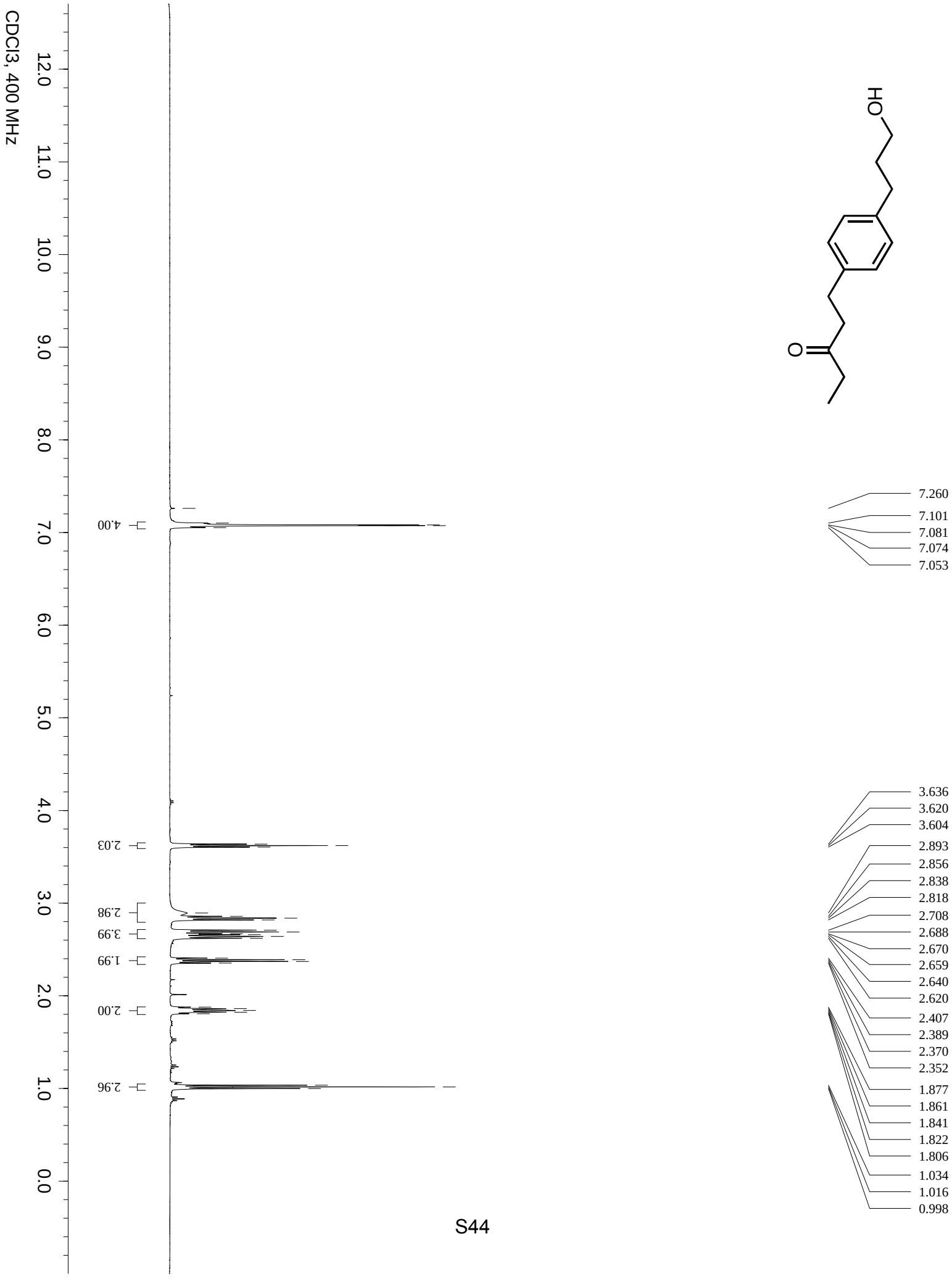
77.318
77.000
76.682
62.170
45.180
34.172
31.567
30.013
29.248


CDCl3, 400 MHz
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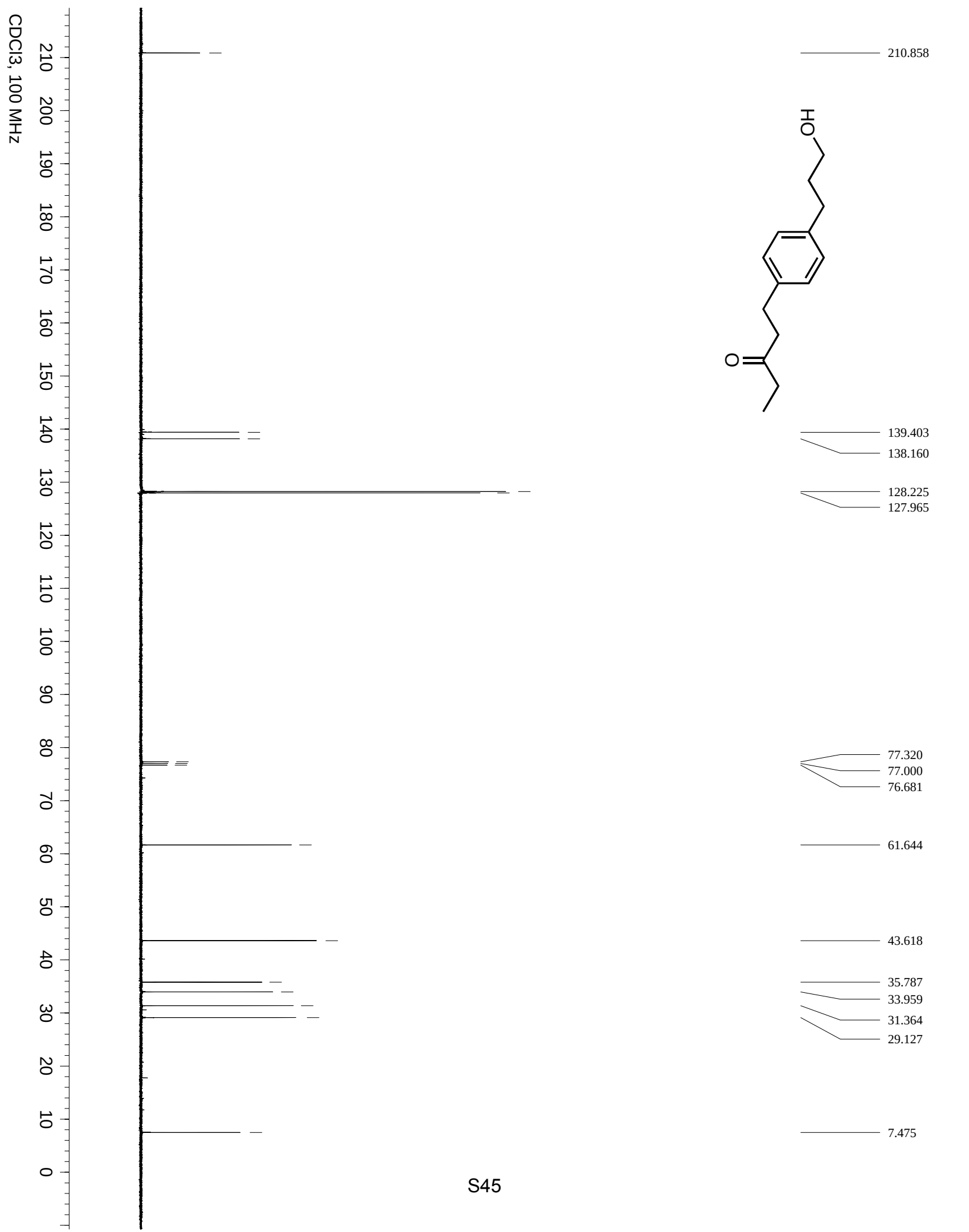
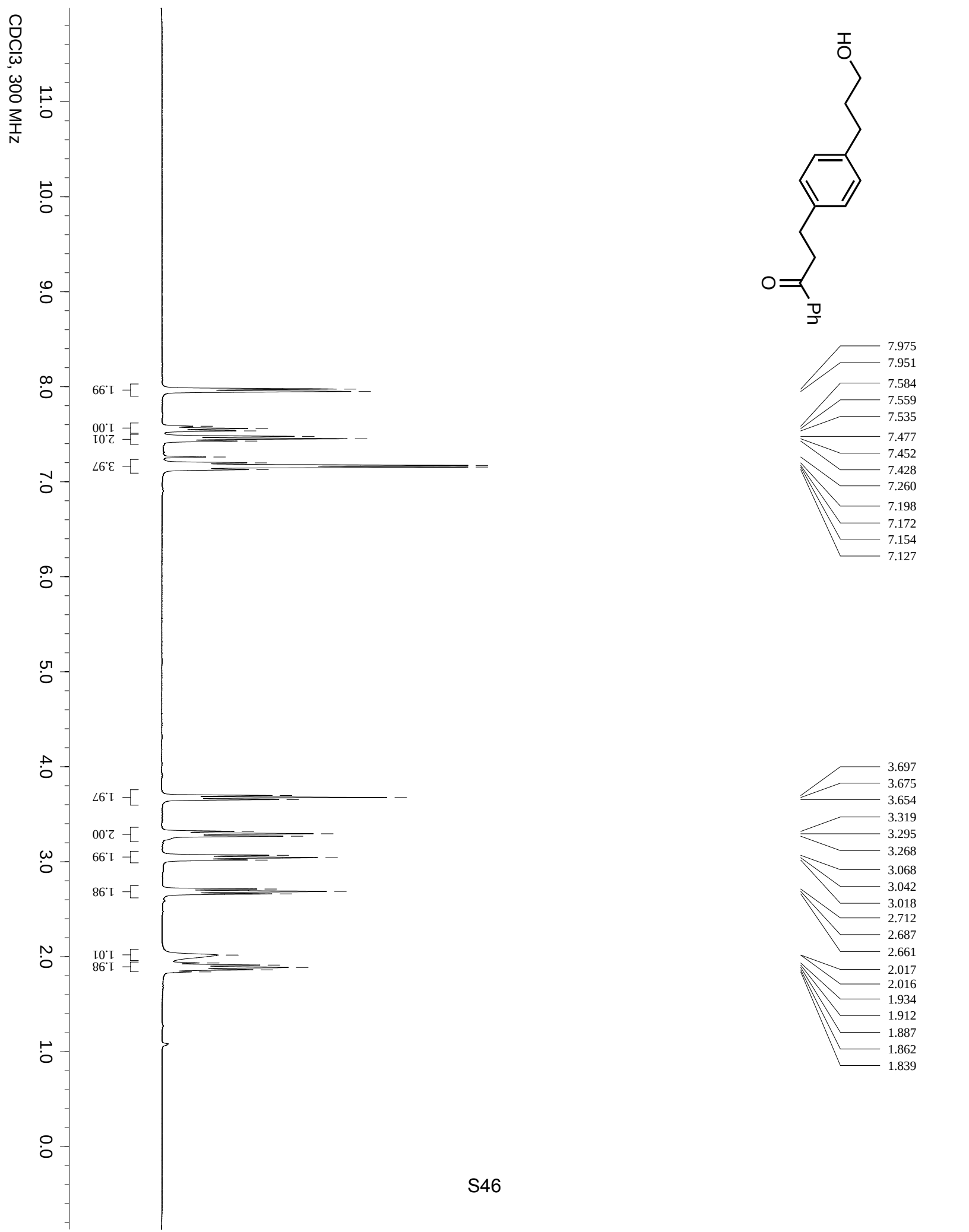
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.00
2.03
2.98
3.99
1.99
2.00
2.96
HO
O
7.260
7.101
7.081
7.074
7.053
3.636
3.620
3.604
2.893
2.856
2.838
2.818
2.708
2.688
2.670
2.659
2.640
2.620
2.407
2.389
2.370
2.352
1.877
1.861
1.841
1.822
1.806
1.034
1.016
0.998


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
HO
O
210.858
139.403
138.160
128.225
127.965
77.320
77.000
76.681
61.644
43.618
35.787
33.959
31.364
29.127
7.475


CDCl3, 300 MHz
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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.99
1.00
2.01
3.97
1.97
2.00
1.99
1.98
1.01
1.98
HO
O
Ph
7.975
7.951
7.584
7.559
7.535
7.477
7.452
7.428
7.260
7.198
7.172
7.154
7.127
3.697
3.675
3.654
3.319
3.295
3.268
3.068
3.042
3.018
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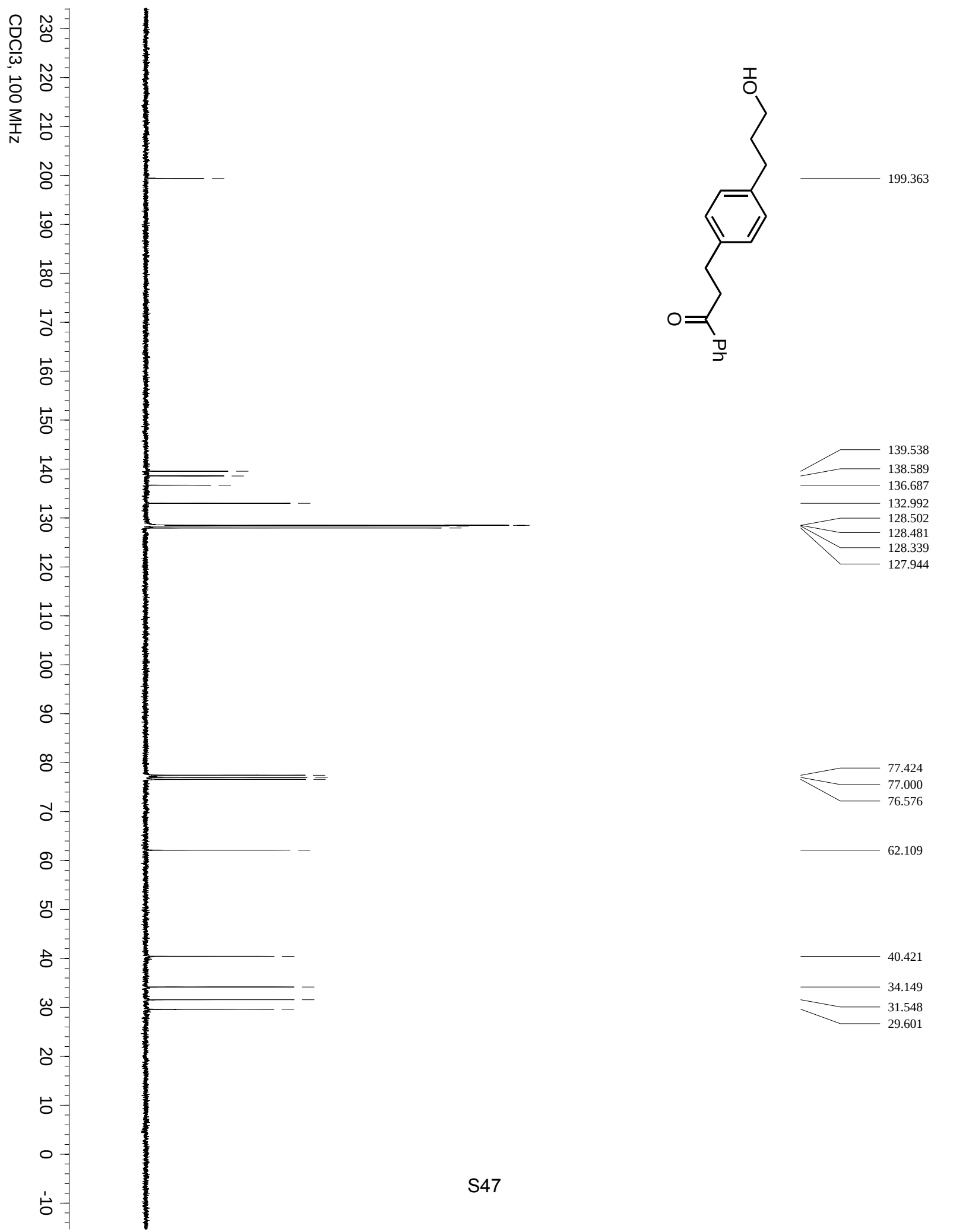
2.687
2.661
2.017
2.016
1.934
1.912
1.887
1.862
1.839


CDCl3, 100 MHz
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
HO
O
Ph
199.363
139.538
138.589
136.687
132.992
128.502
128.481
128.339
127.944
77.424
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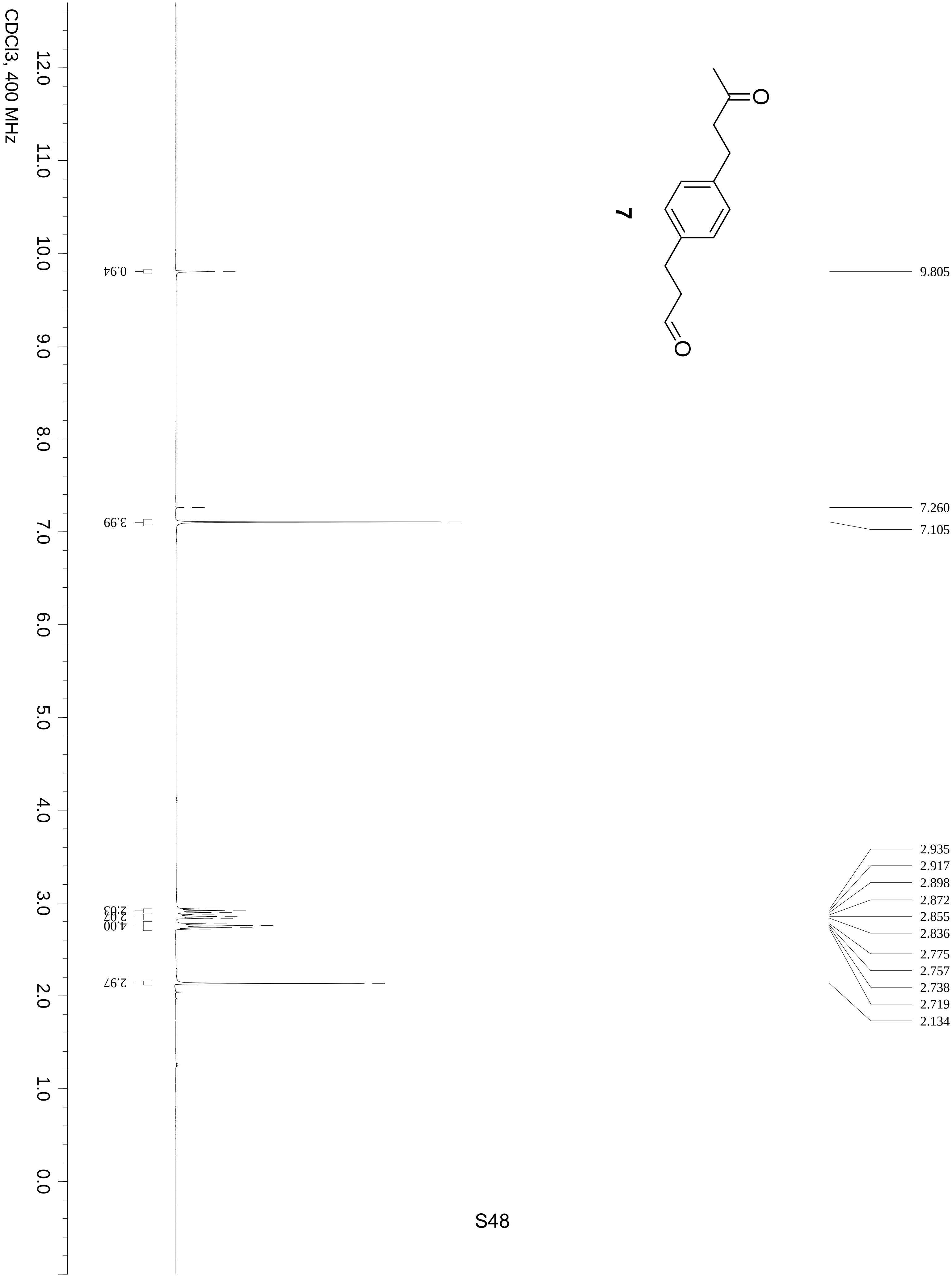
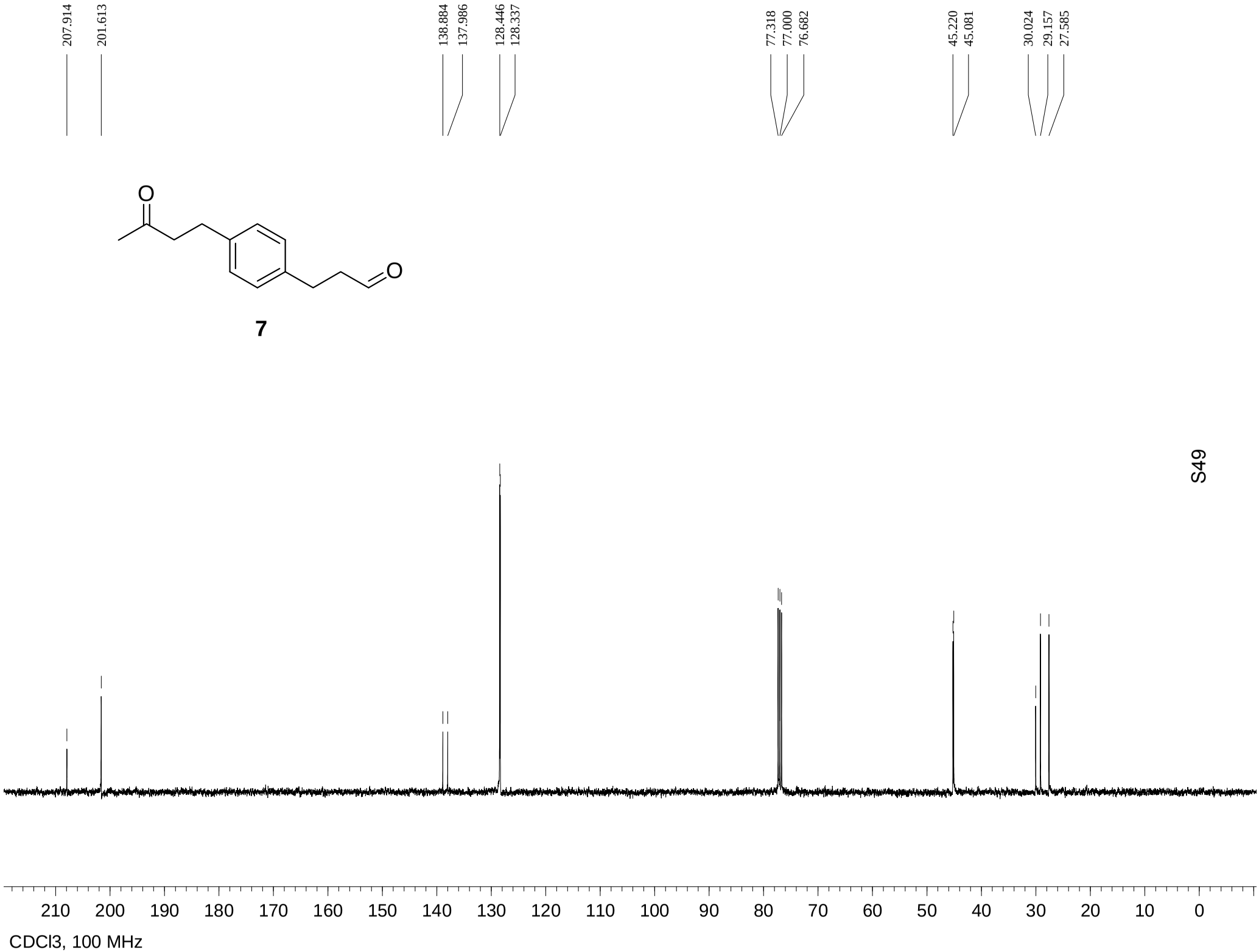
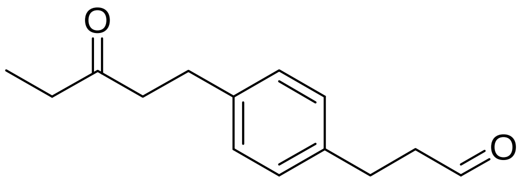
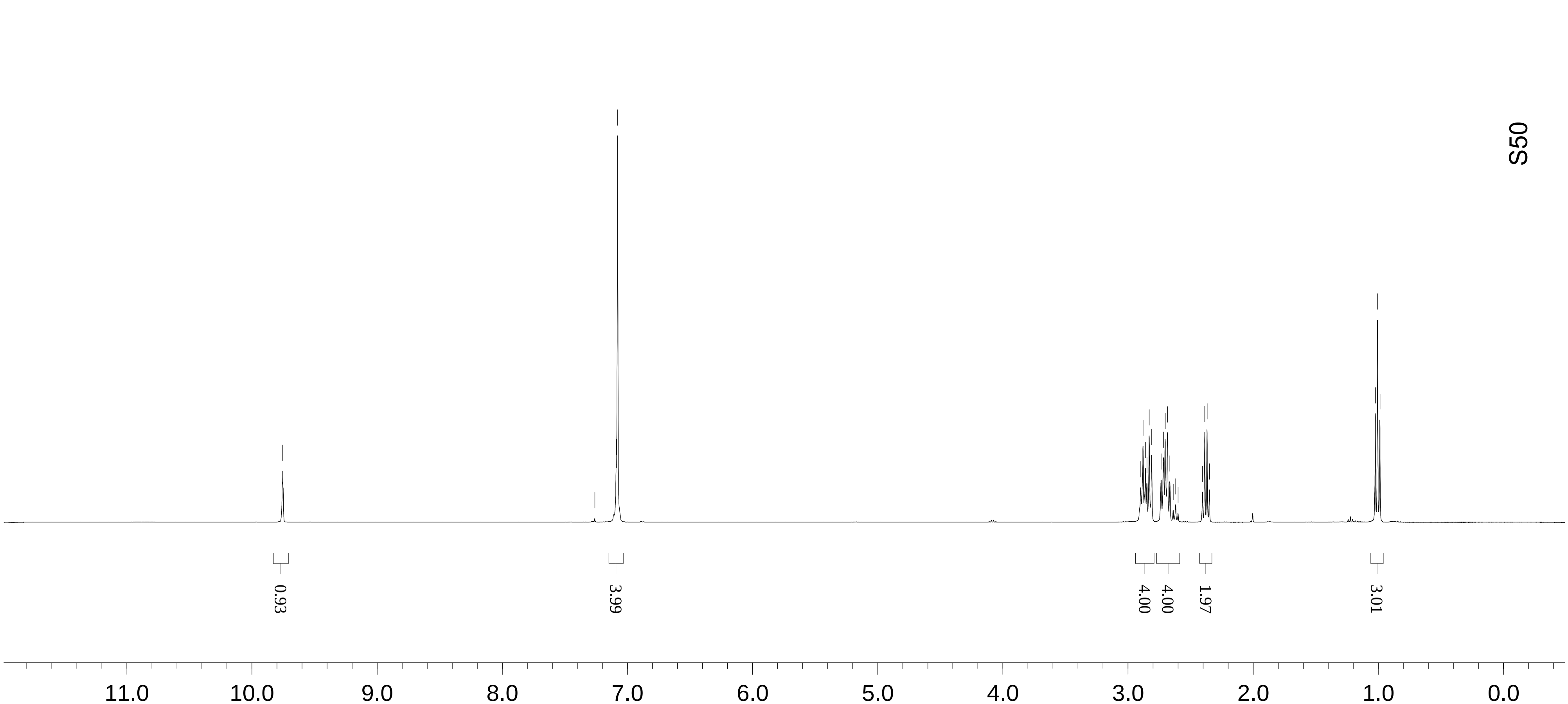
76.576
62.109
40.421
34.149
31.548
29.601


CDCl3, 400 MHz
7
9.805
7.260
7.105
2.935
2.917
2.898
2.872
2.855
2.836
2.775
2.757
2.738
2.719
2.134
0.94
3.99
2.03
2.02
4.00
2.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

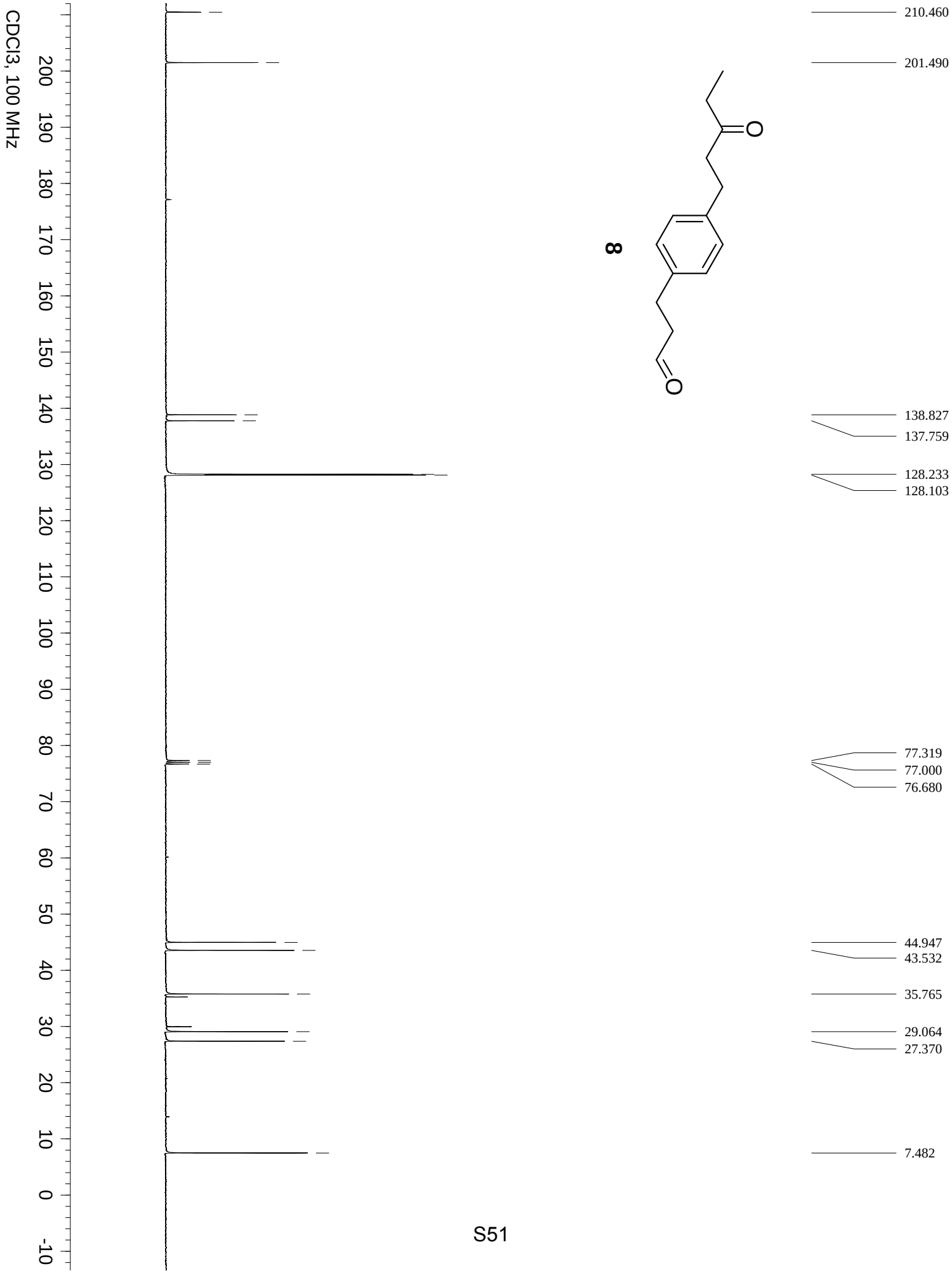

207.914
201.613
138.884
137.986
128.446
128.337
77.318
77.000
76.682
45.220
45.081
30.024
29.157
27.585
O
O
7
S49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
CDCl3, 100 MHz

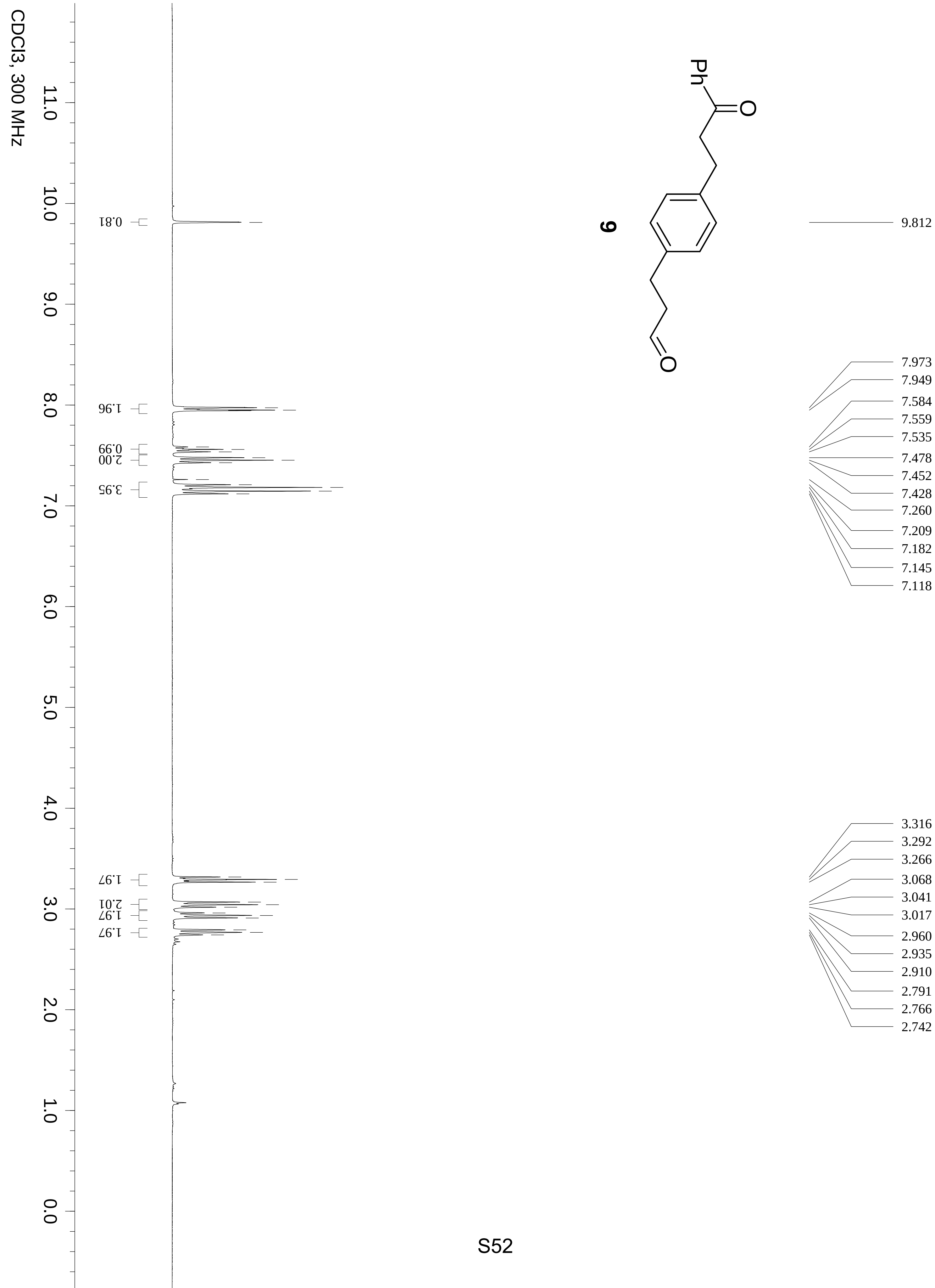


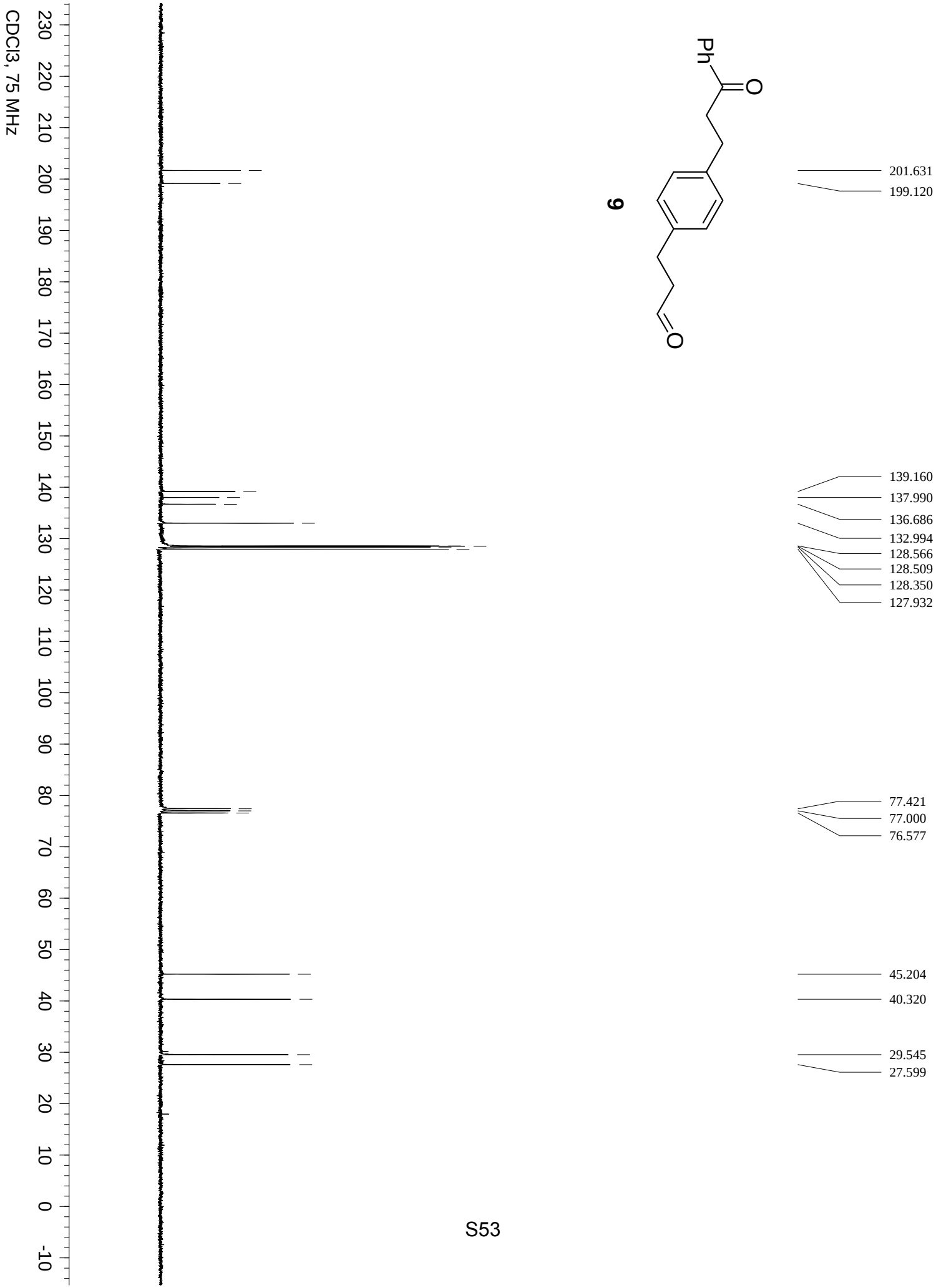
8



CDCl3, 400 MHz


CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
8
O
O
210.460
201.490
138.827
137.759
128.233
128.103
77.319
77.000
76.680
44.947
43.532
35.765
29.064
27.370
7.482


CDCl3, 300 MHz
9
Ph
O
9.812
7.973
7.949
7.584
7.559
7.535
7.478
7.452
7.428
7.260
7.209
7.182
7.145
7.118
3.316
3.292
3.266
3.068
3.041
3.017
2.960
2.935
2.910
2.791
2.766
2.742
0.81
1.96
0.99
2.00
3.95
1.97
2.01
1.97
1.97
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


CDCl3, 75 MHz
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
Ph
O
O
9
201.631
199.120
139.160
137.990
136.686
132.994
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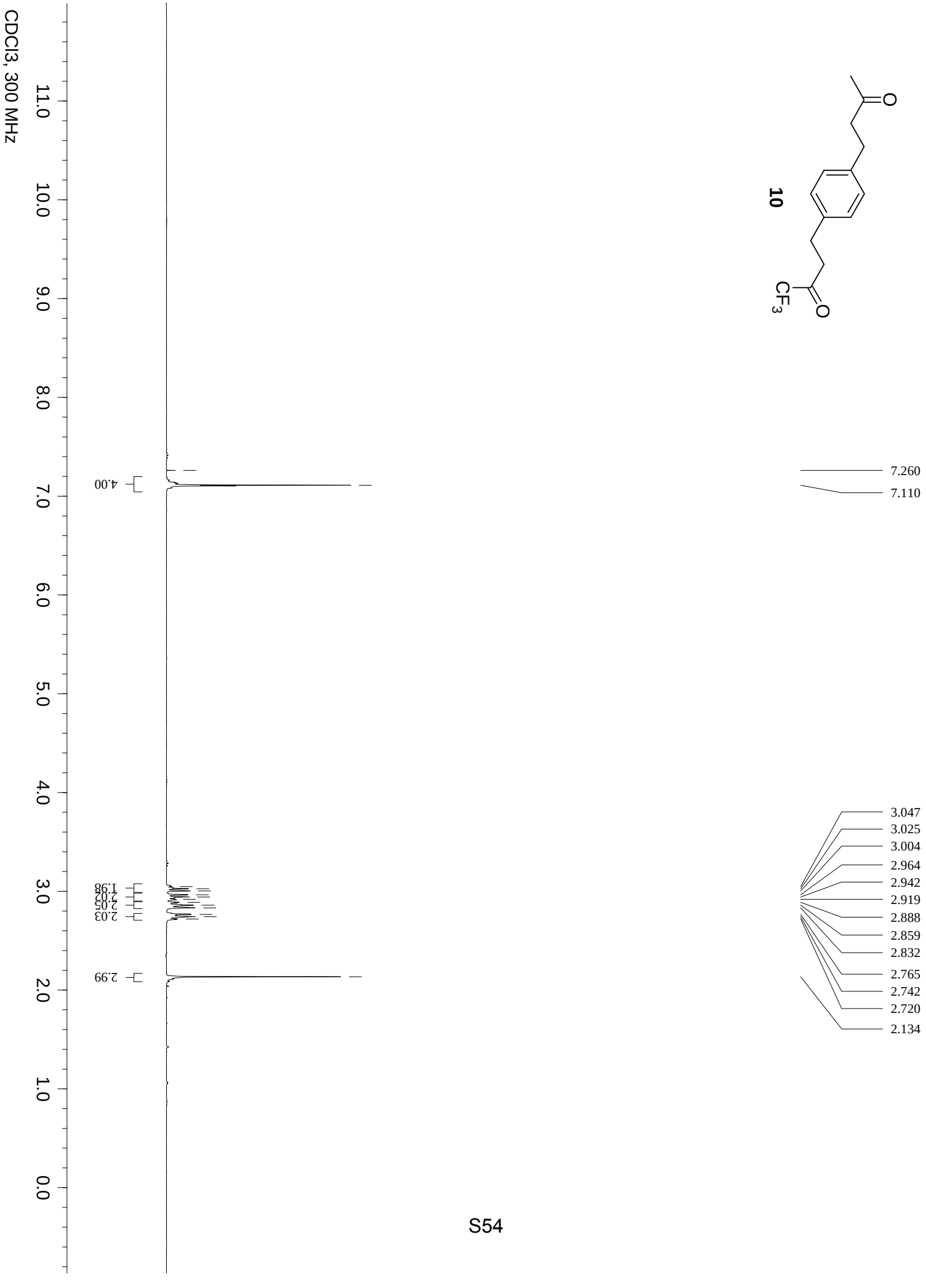
128.509
128.350
127.932
77.421
77.000
76.577
45.204
40.320
29.545
27.599


CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.00
1.98
2.02
2.05
2.03
2.99
10
O
O
CF3
7.260
7.110
3.047
3.025
3.004
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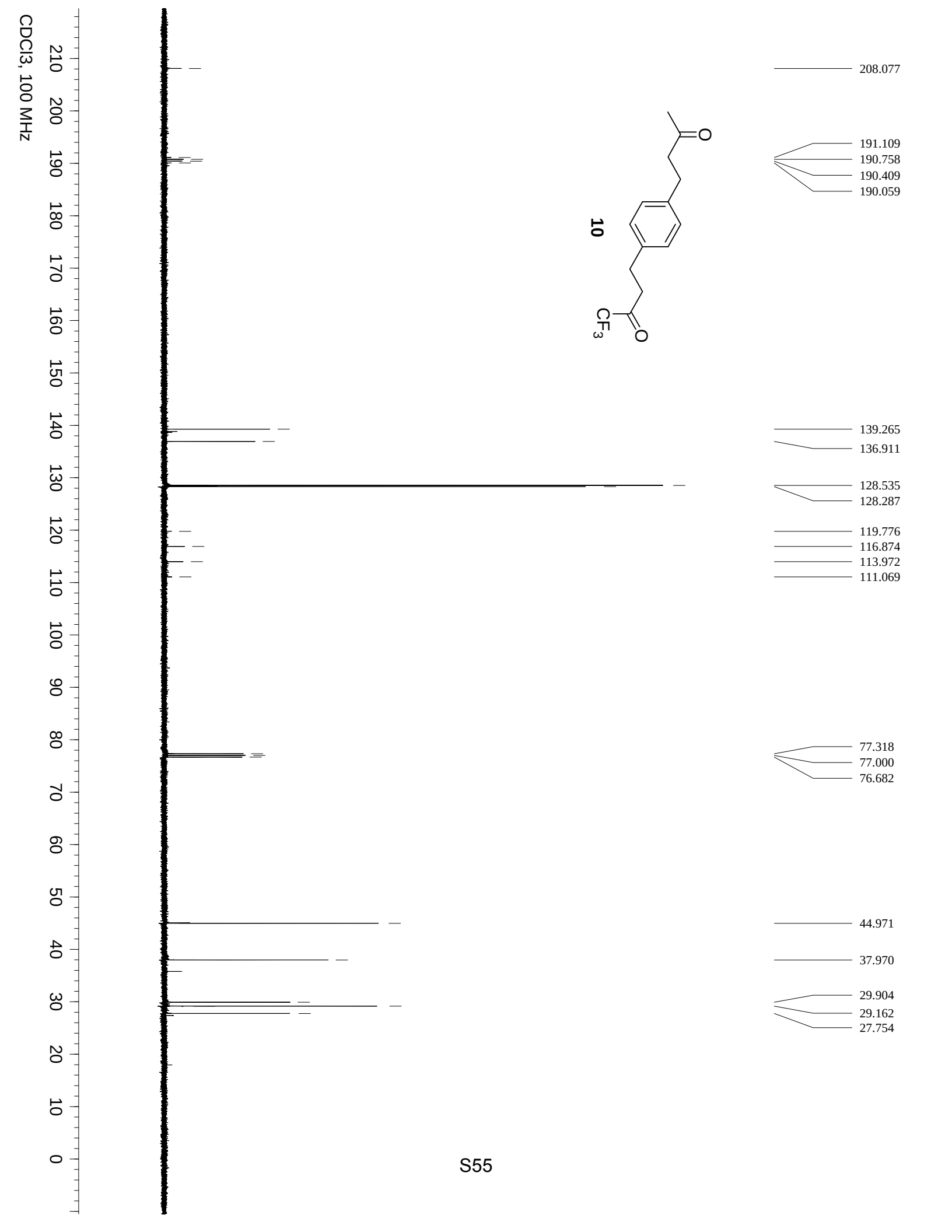
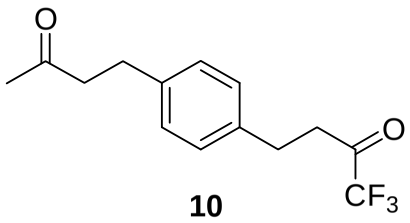
2.942
2.919
2.888
2.859
2.832
2.765
2.742
2.720
2.134


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
208.077
191.109
190.758
190.409
190.059
139.265
136.911
128.535
128.287
119.776
116.874
113.972
111.069
77.318
77.000
76.682
44.971
37.970
29.904
29.162
27.754
10
O
CF3
O

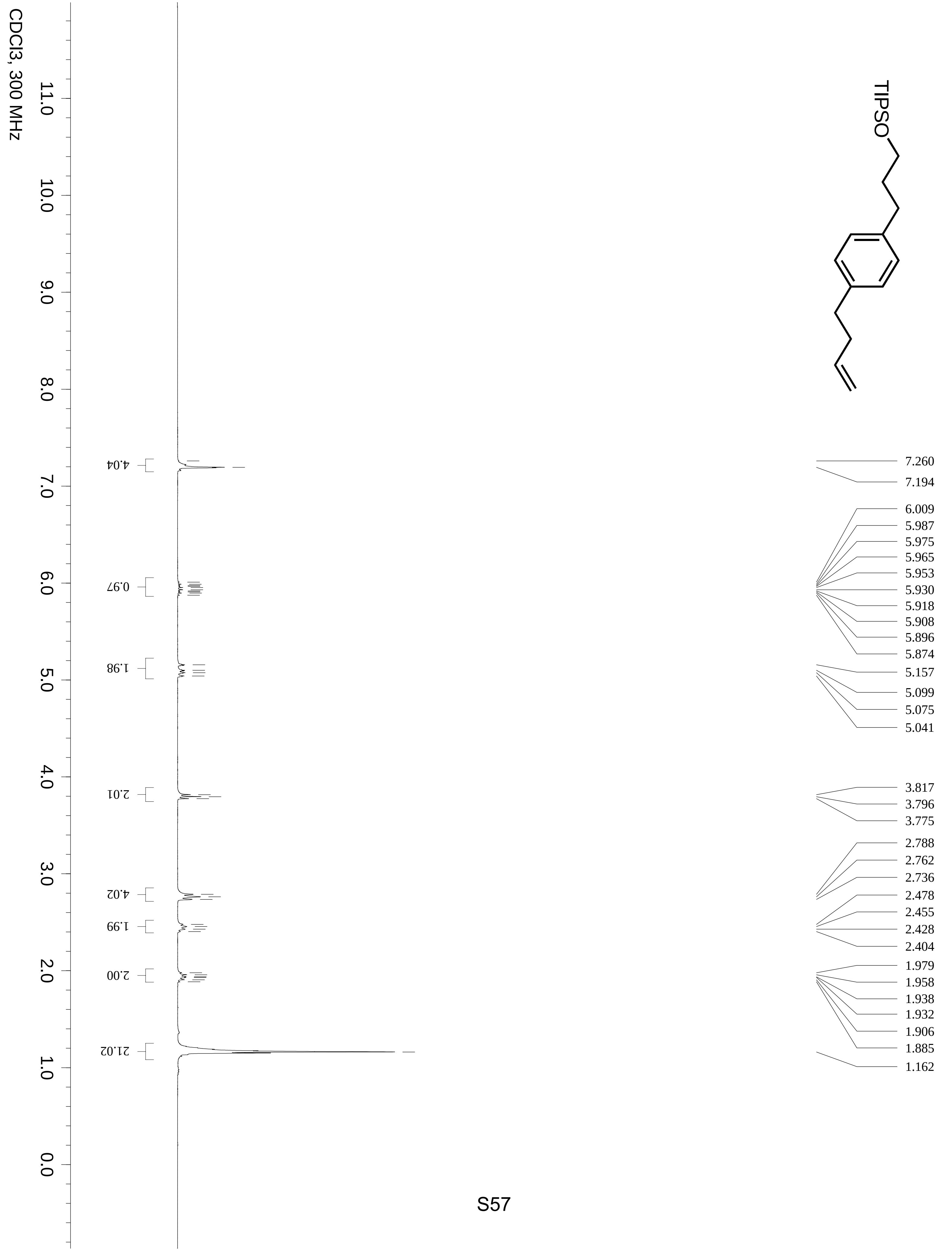


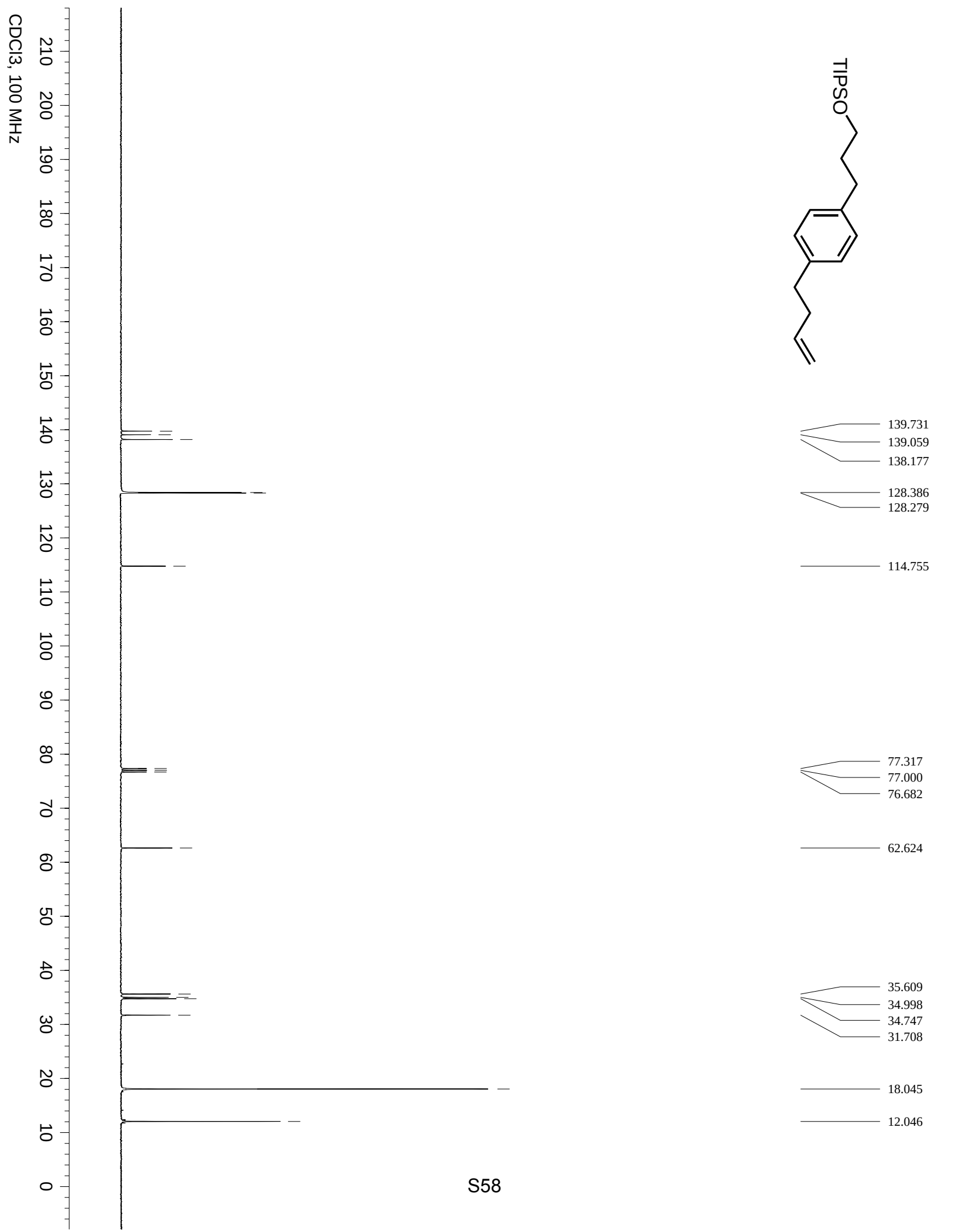
10

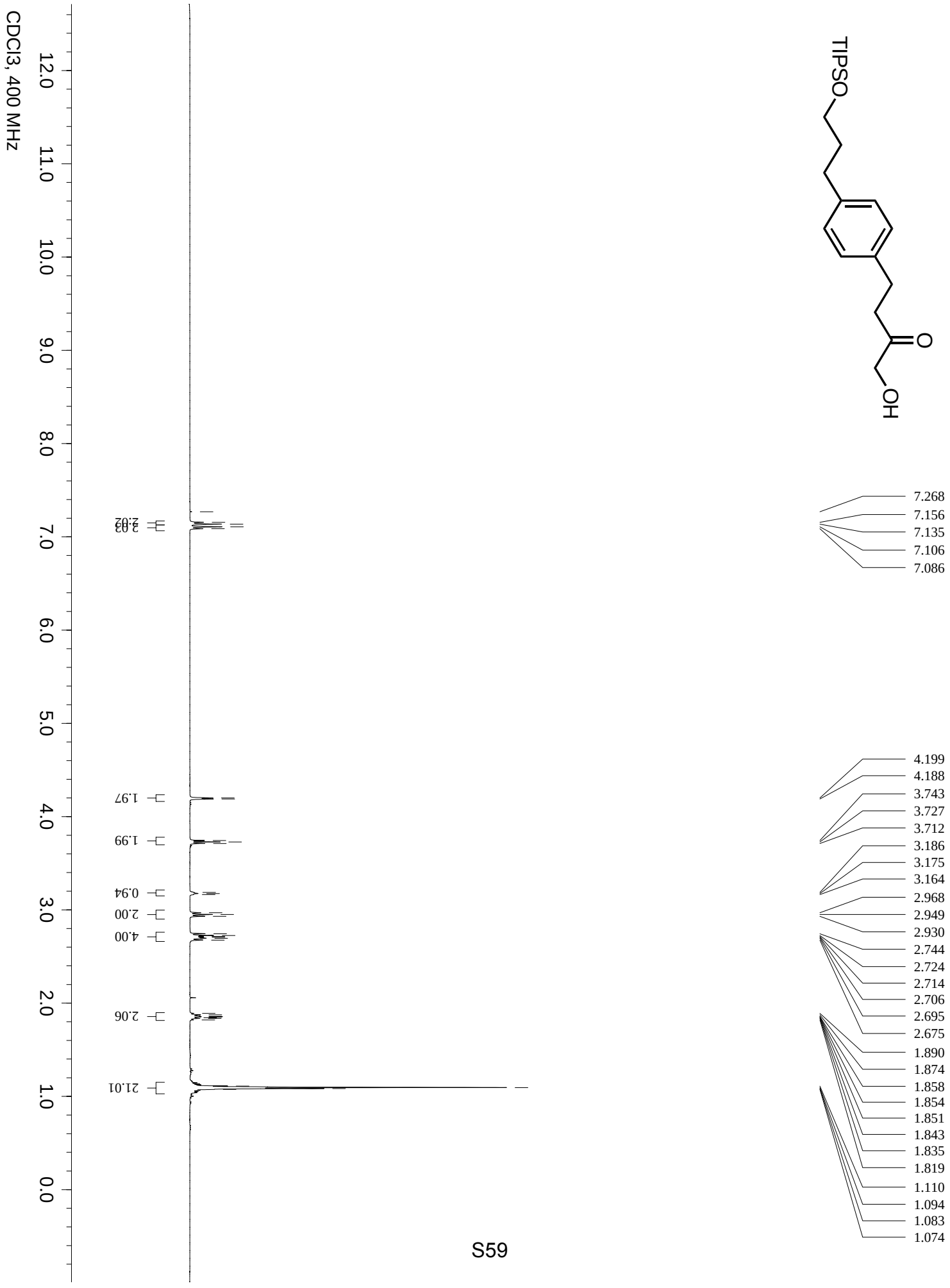
-79.661

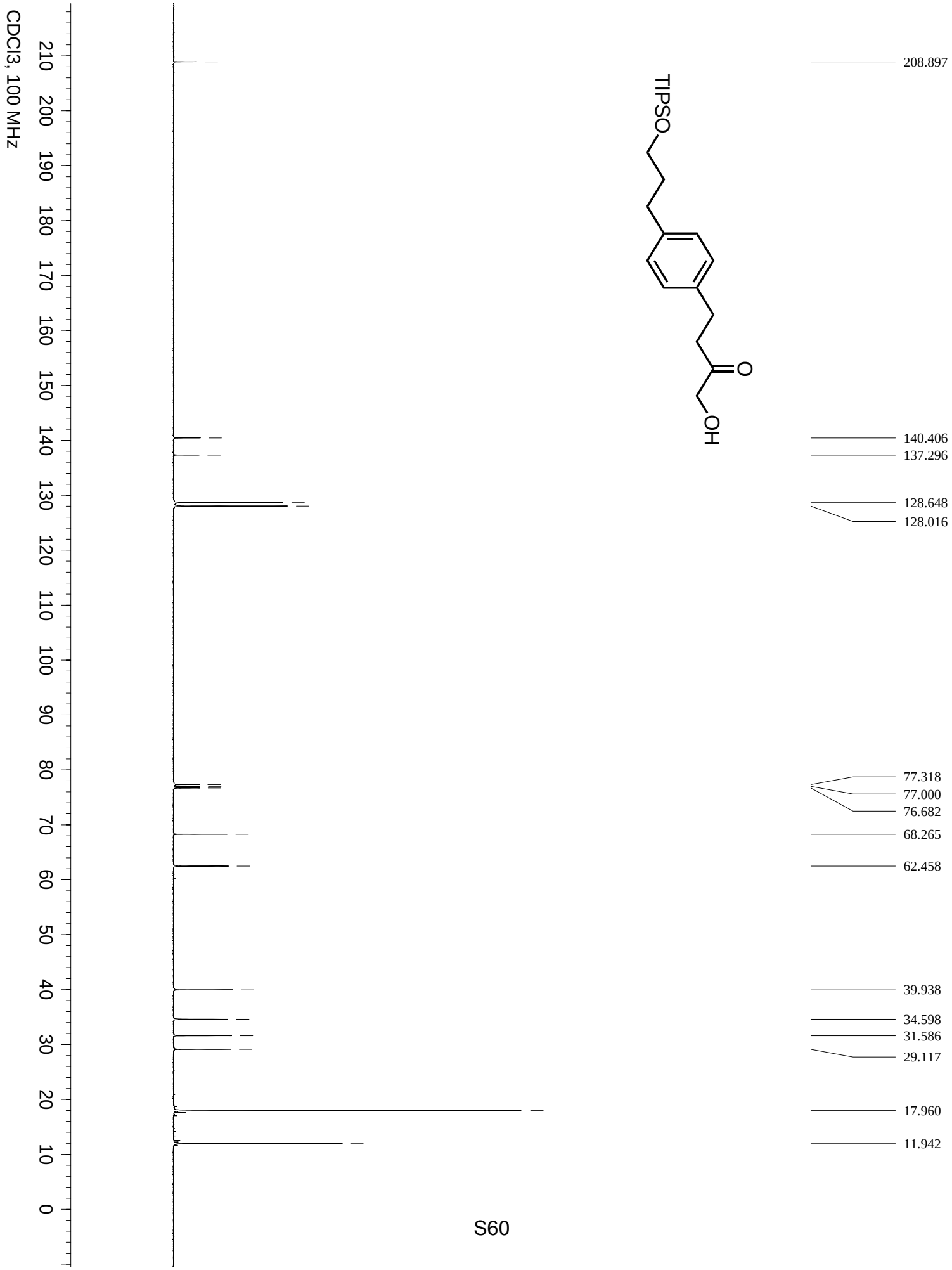
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180

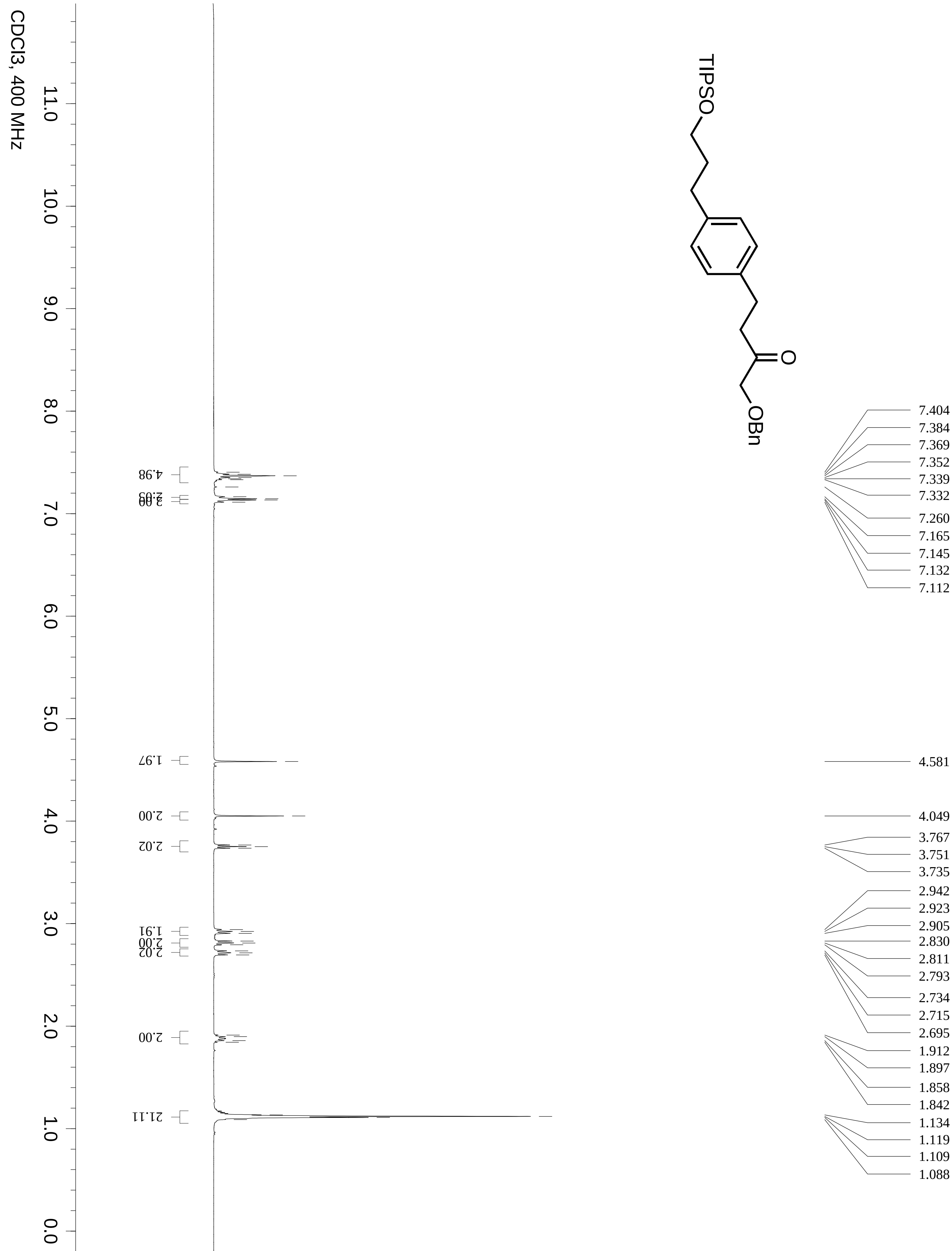
CDCl3, 282 MHz

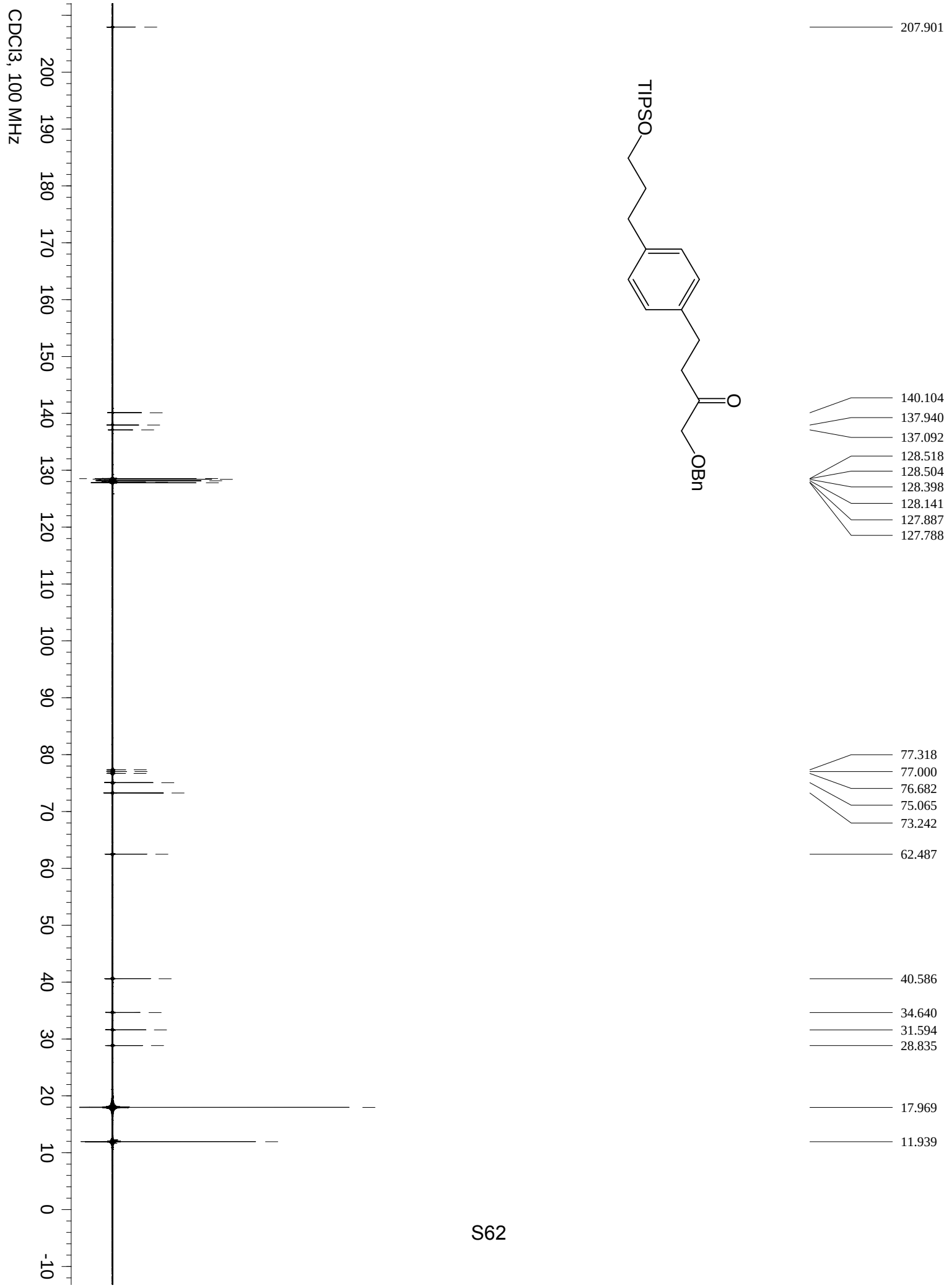

CDCl3, 300 MHz
TIPSO
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.04
0.97
1.98
2.01
4.02
1.99
2.00
21.02
7.260
7.194
6.009
5.987
5.975
5.965
5.953
5.930
5.918
5.908
5.896
5.874
5.157
5.099
5.075
5.041
3.817
3.796
3.775
2.788
2.762
2.736
2.478
2.455
2.428
2.404
1.979
1.958
1.938
1.932
1.906
1.885
1.162

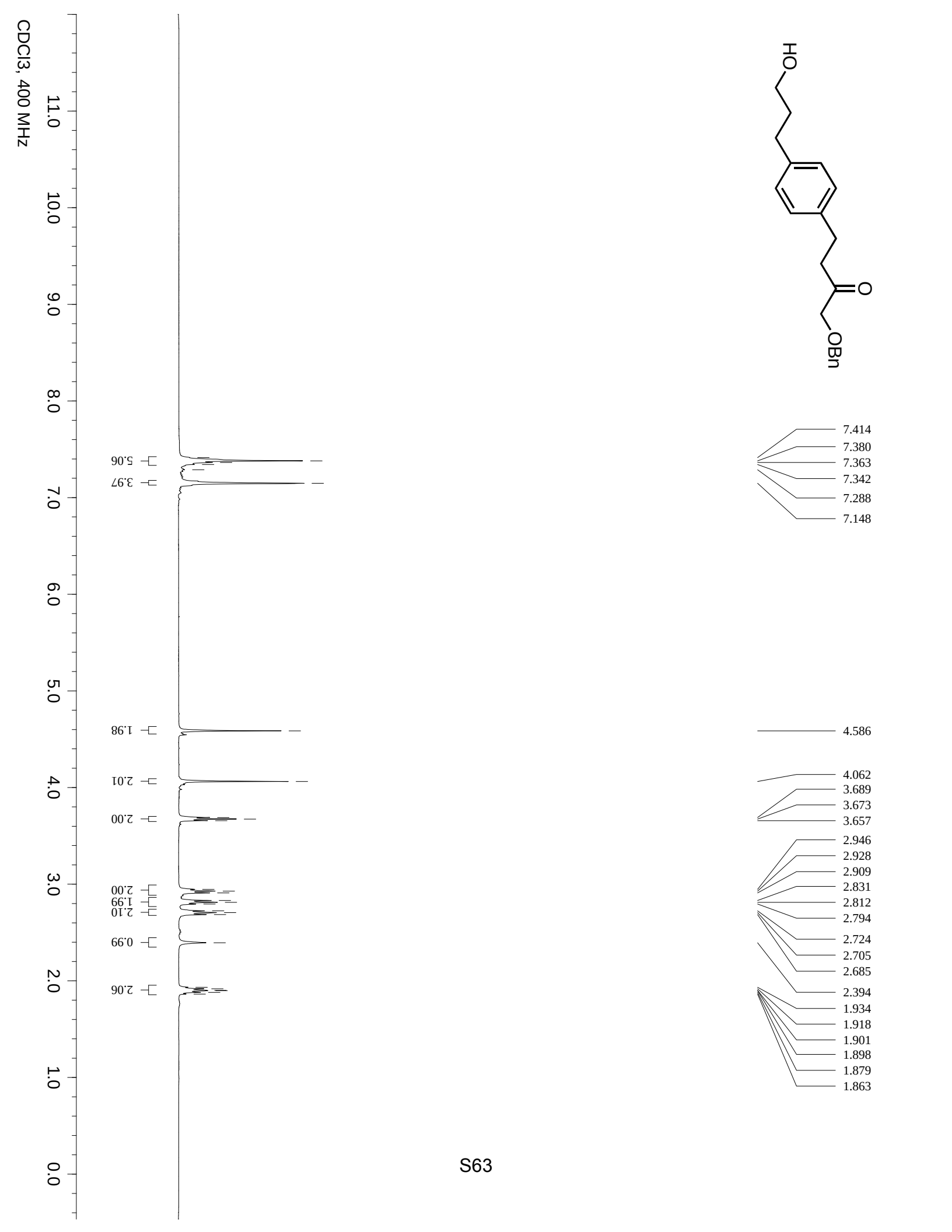

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TIPSO
139.731
139.059
138.177
128.386
128.279
114.755
77.317
77.000
76.682
62.624
35.609
34.998
34.747
31.708
18.045
12.046

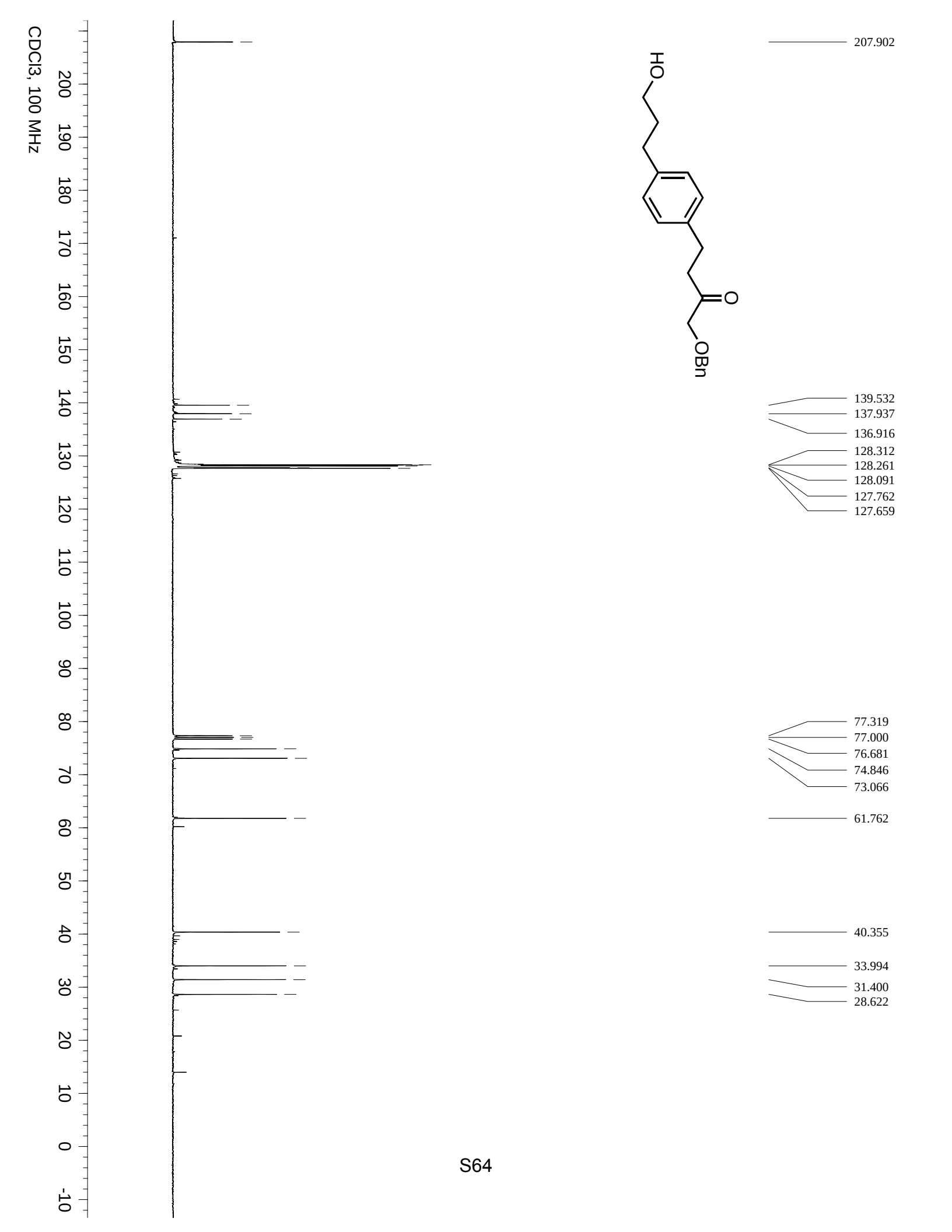

CDCl3, 400 MHz
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.03
2.02
1.97
1.99
0.94
2.00
4.00
2.06
21.01
TIPSO
O
OH
7.268
7.156
7.135
7.106
7.086
4.199
4.188
3.743
3.727
3.712
3.186
3.175
3.164
2.968
2.949
2.930
2.744
2.724
2.714
2.706
2.695
2.675
1.890
1.874
1.858
1.854
1.851
1.843
1.835
1.819
1.110
1.094
1.083
1.074

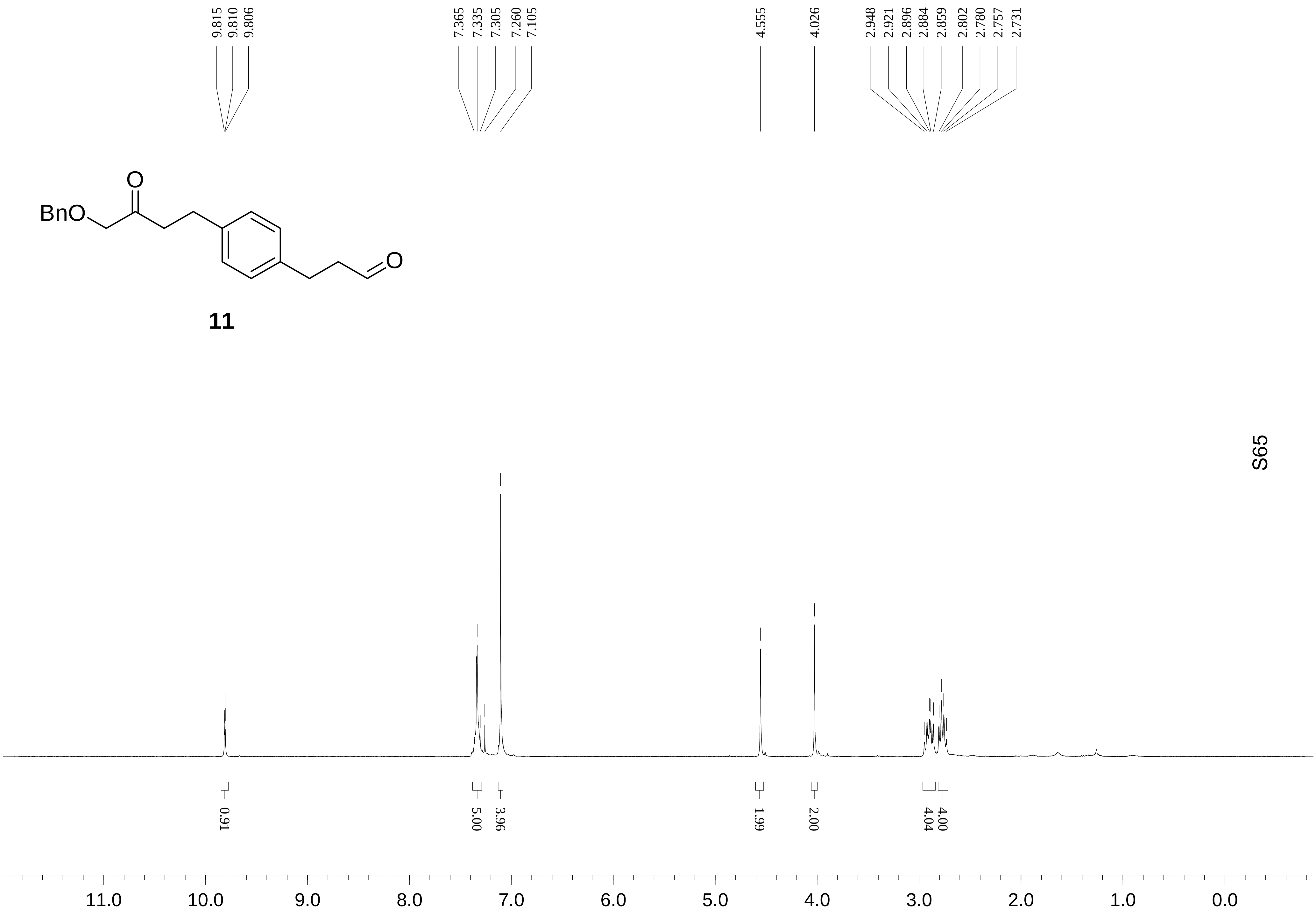

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TIPSO
O
OH
208.897
140.406
137.296
128.648
128.016
77.318
77.000
76.682
68.265
62.458
39.938
34.598
31.586
29.117
17.960
11.942


CDCl3, 400 MHz
TIPSO
OBn
O
7.404
7.384
7.369
7.352
7.339
7.332
7.260
7.165
7.145
7.132
7.112
4.581
4.049
3.767
3.751
3.735
2.942
2.923
2.905
2.830
2.811
2.793
2.734
2.715
2.695
1.912
1.897
1.858
1.842
1.134
1.119
1.109
1.088
4.98
2.02
2.00
1.97
2.00
2.02
1.91
2.00
2.02
2.00
21.11
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

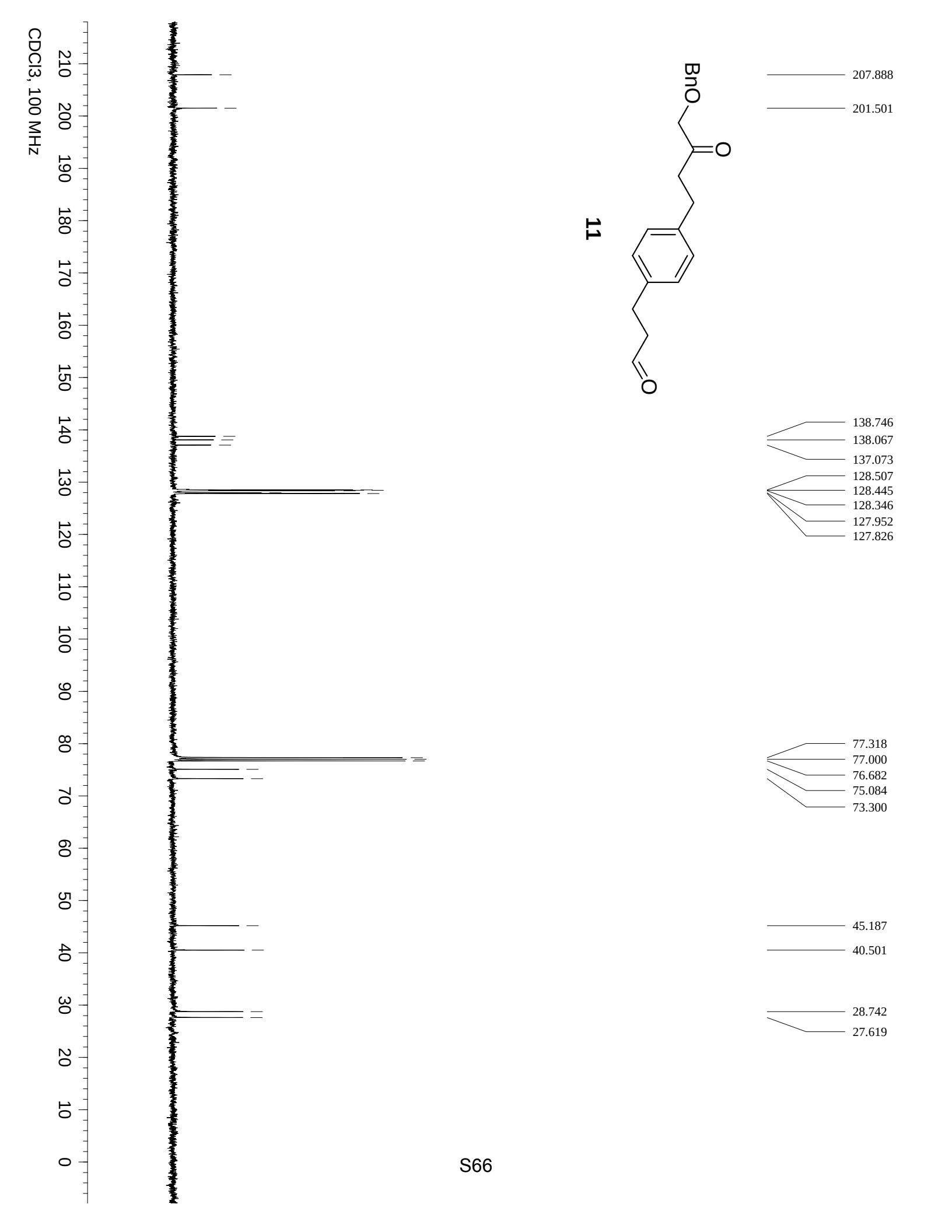

CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TIPSO
O
OBn
207.901
140.104
137.940
137.092
128.518
128.504
128.398
128.141
127.887
127.788
77.318
77.000
76.682
75.065
73.242
62.487
40.586
34.640
31.594
28.835
17.969
11.939

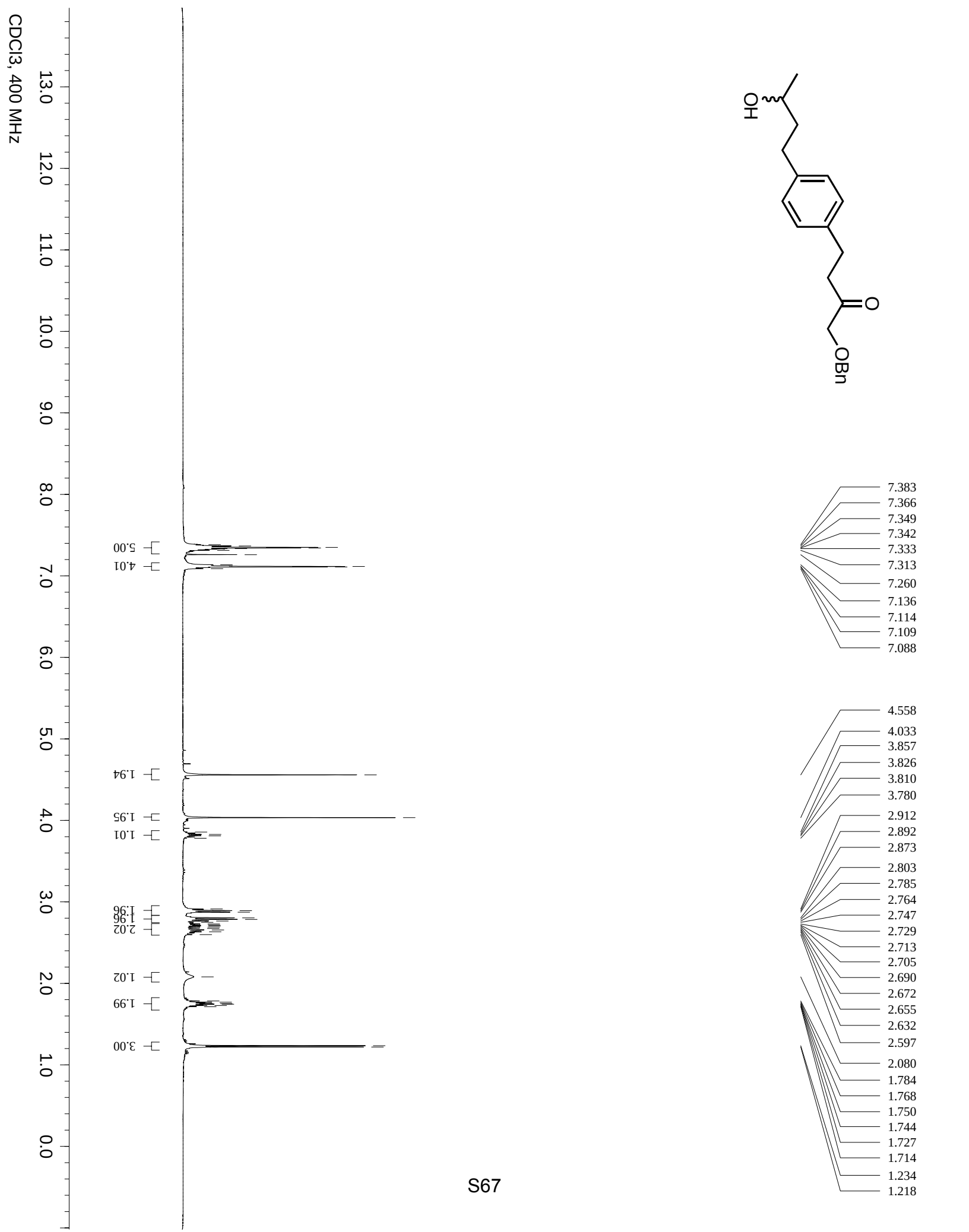

CDCl3, 400 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
5.06
3.97
1.98
2.01
2.00
2.00
1.99
2.10
0.99
2.06
HO
O
OBn
7.414
7.380
7.363
7.342
7.288
7.148
4.586
4.062
3.689
3.673
3.657
2.946
2.928
2.909
2.831
2.812
2.794
2.724
2.705
2.685
2.394
1.934
1.918
1.901
1.898
1.879
1.863

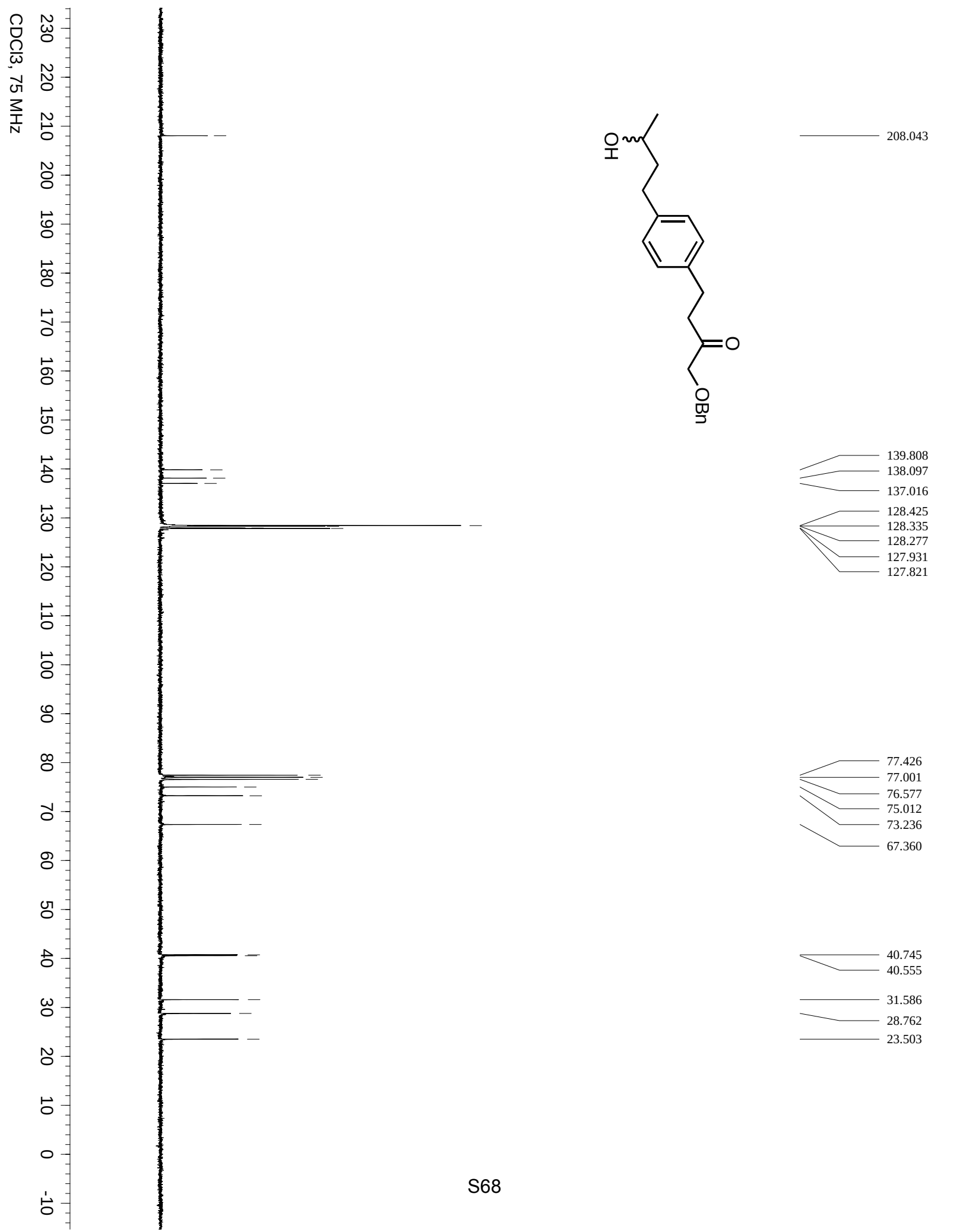

CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
HO
O
OBn
207.902
139.532
137.937
136.916
128.312
128.261
128.091
127.762
127.659
77.319
77.000
76.681
74.846
73.066
61.762
40.355
33.994
31.400
28.622

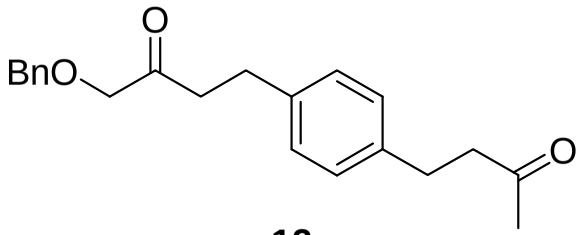


CDCl3, 300 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
BnO
O
O
11
207.888
201.501
138.746
138.067
137.073
128.507
128.445
128.346
127.952
127.826
77.318
77.000
76.682
75.084
73.300
45.187
40.501
28.742
27.619

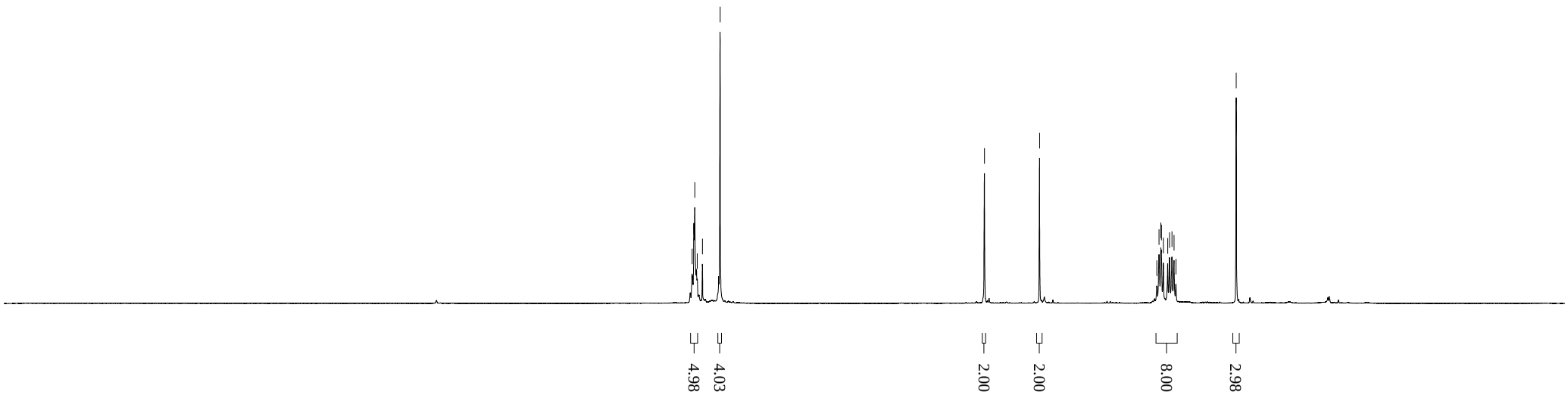

CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OH
O
OBn
7.383
7.366
7.349
7.342
7.333
7.313
7.260
7.136
7.114
7.109
7.088
4.558
4.033
3.857
3.826
3.810
3.780
2.912
2.892
2.873
2.803
2.785
2.764
2.747
2.729
2.713
2.705
2.690
2.672
2.655
2.632
2.597
2.080
1.784
1.768
1.750
1.744
1.727
1.714
1.234
1.218
5.00
4.01
1.94
1.95
1.01
1.96
1.96
2.02
1.02
1.99
3.00

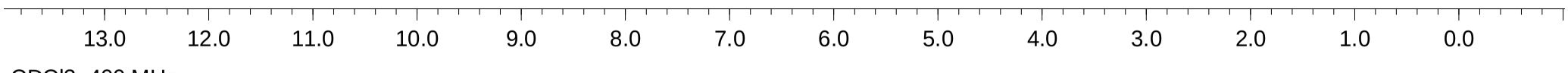

CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
OH
O
OBn
208.043
139.808
138.097
137.016
128.425
128.335
128.277
127.931
127.821
77.426
77.001
76.577
75.012
73.236
67.360
40.745
40.555
31.586
28.762
23.503



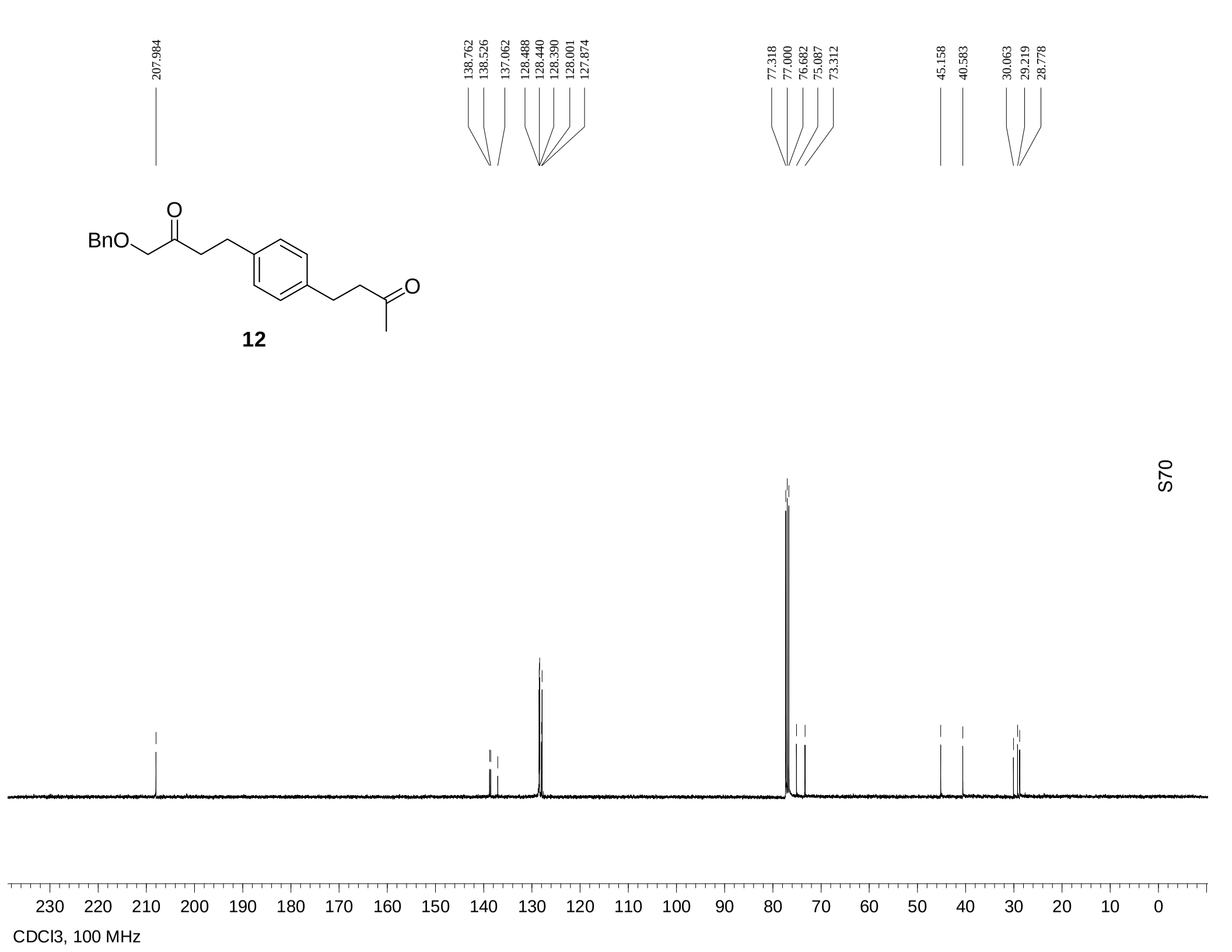
12

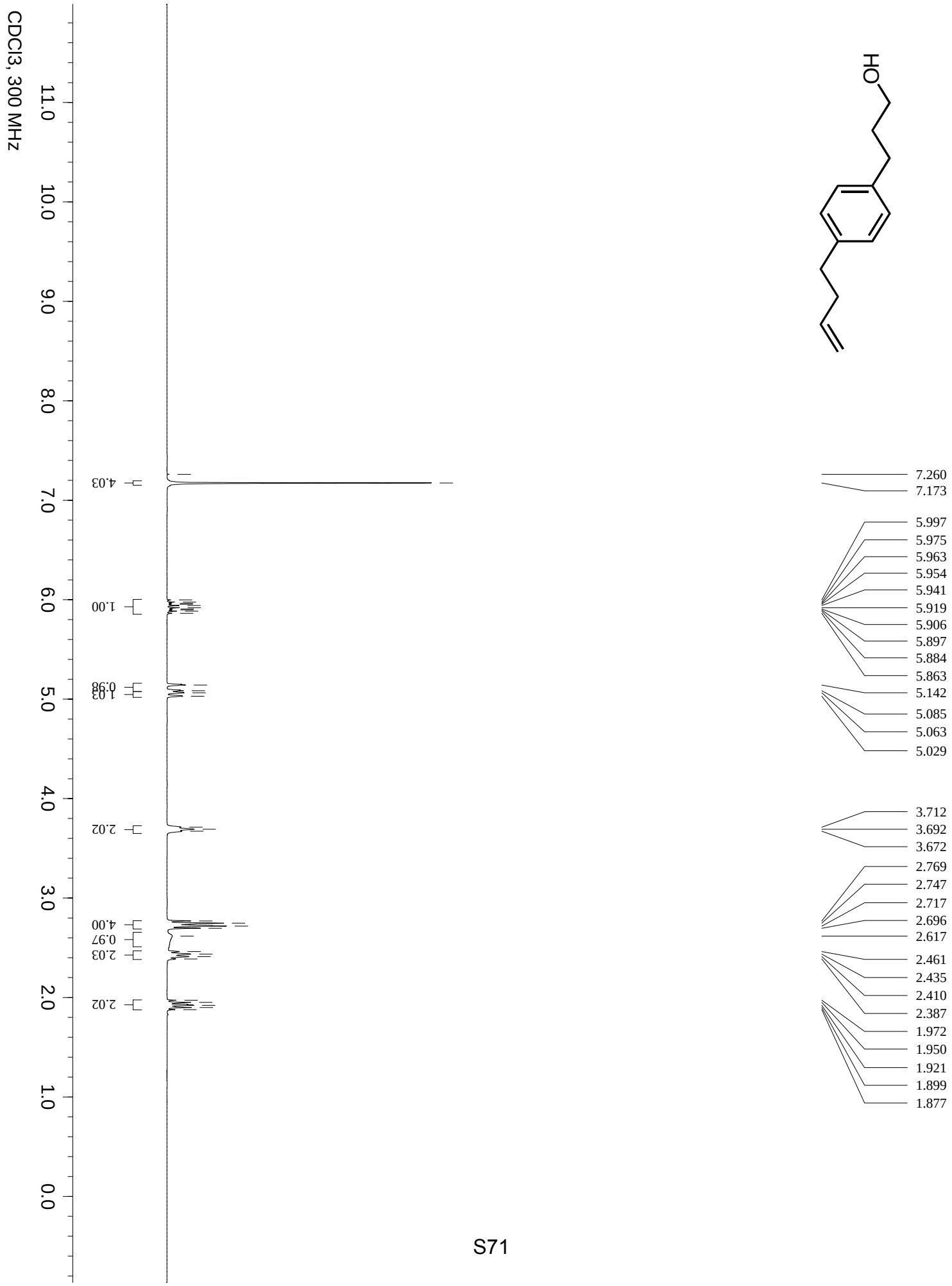
7.359
7.333
7.309
7.260
7.091
4.553
4.024
2.898
2.877
2.859
2.855
2.835
2.794
2.777
2.753
2.733
2.715
2.136

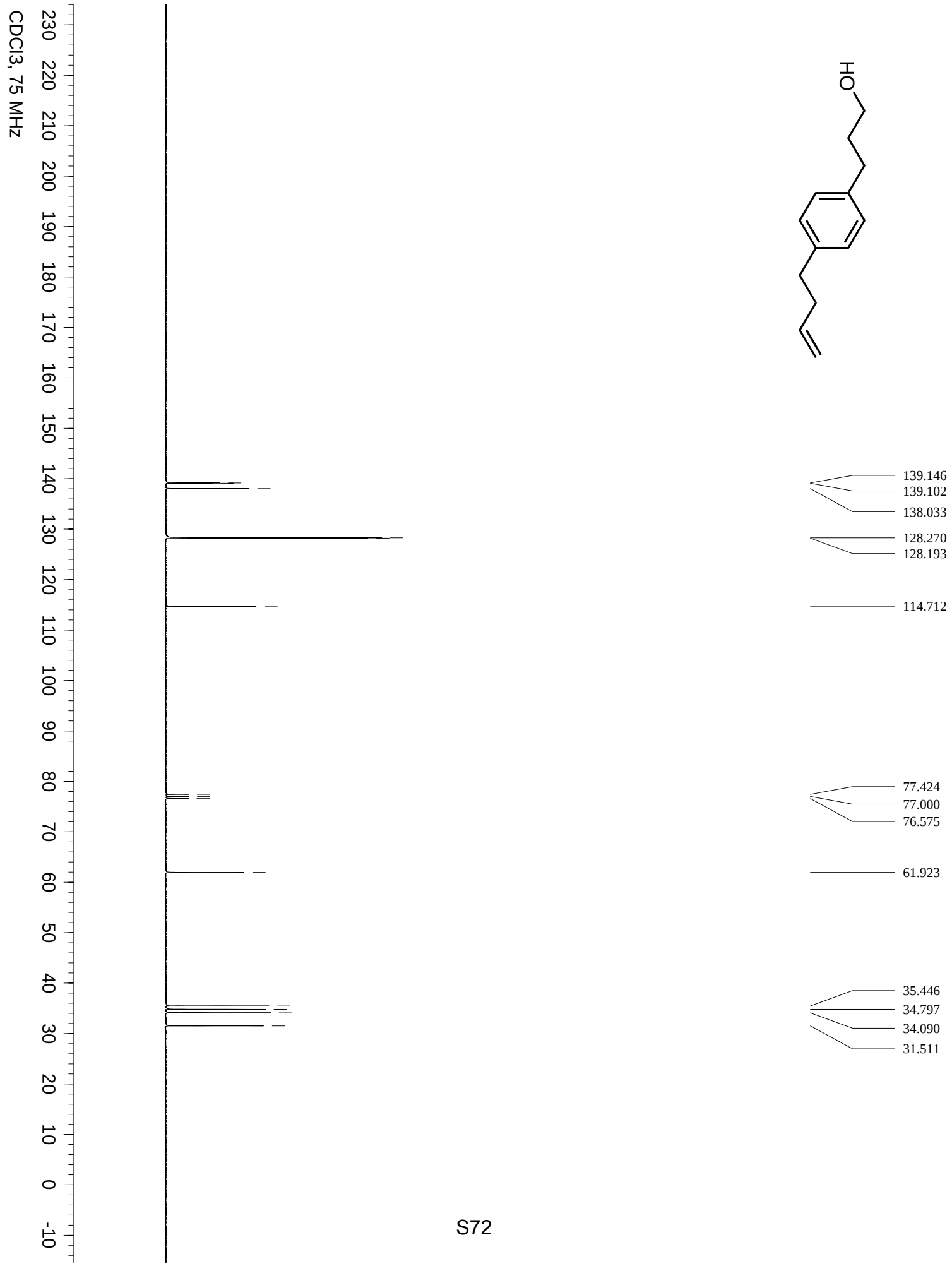


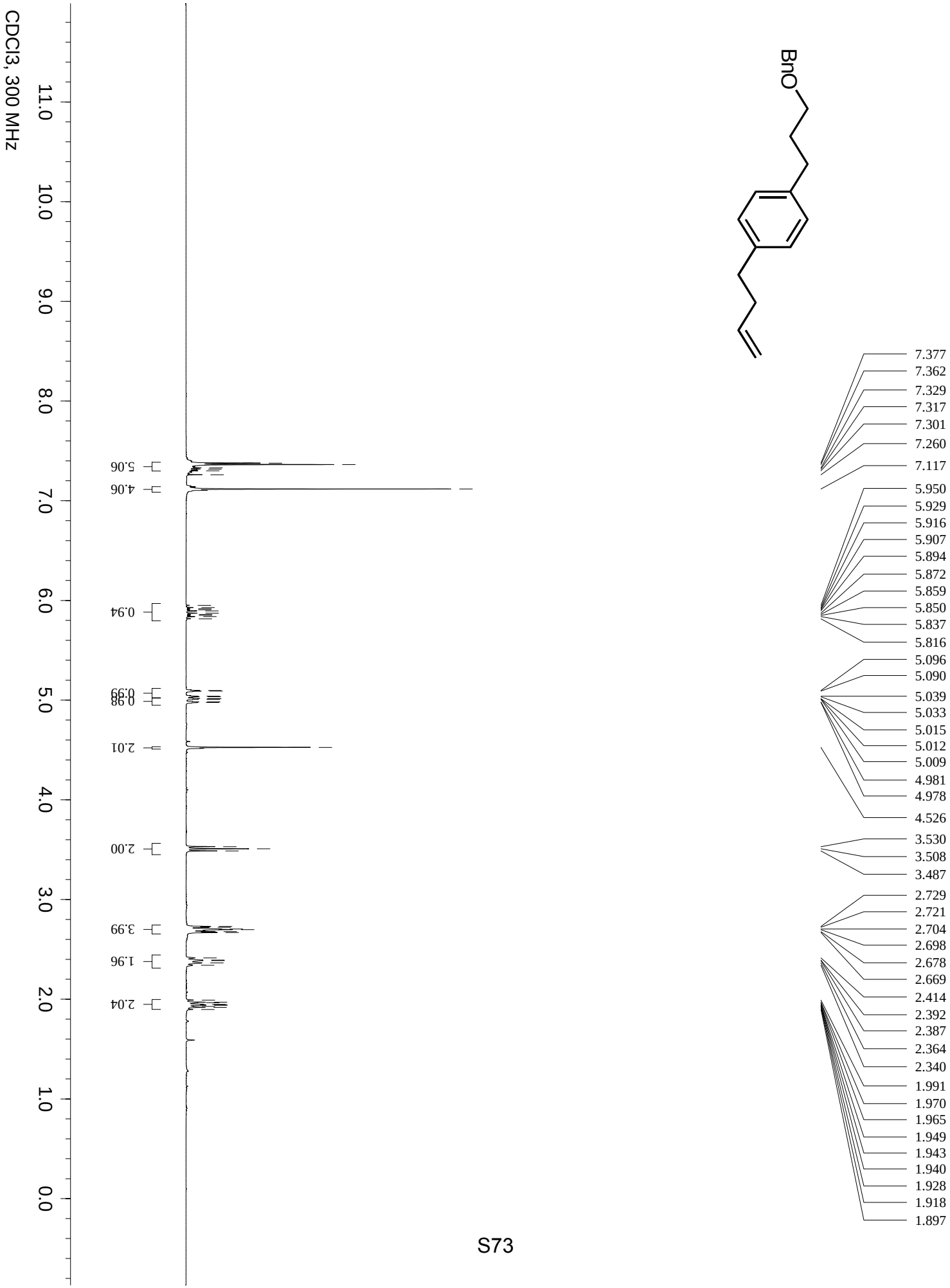


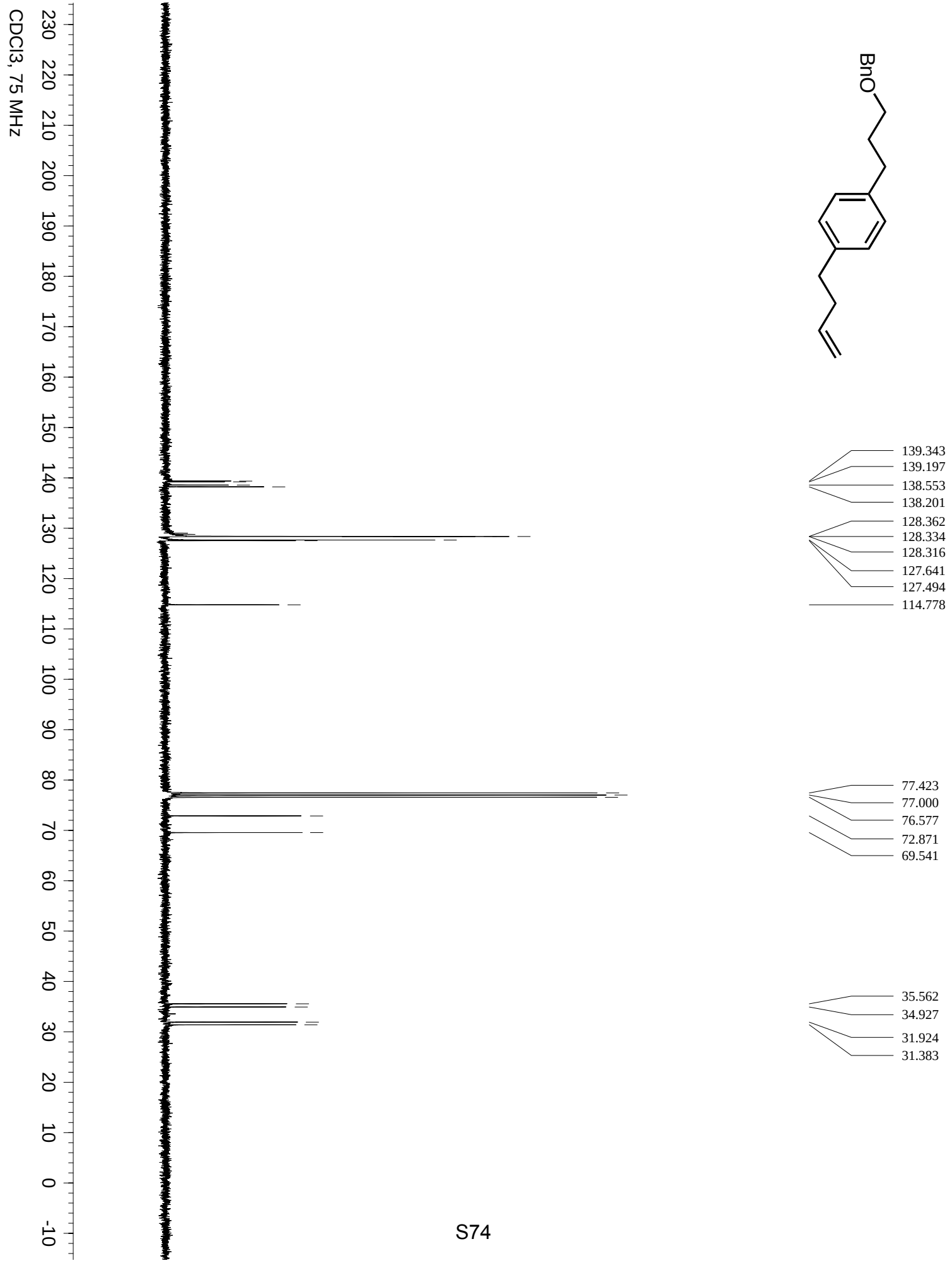
CDCl3, 400 MHz

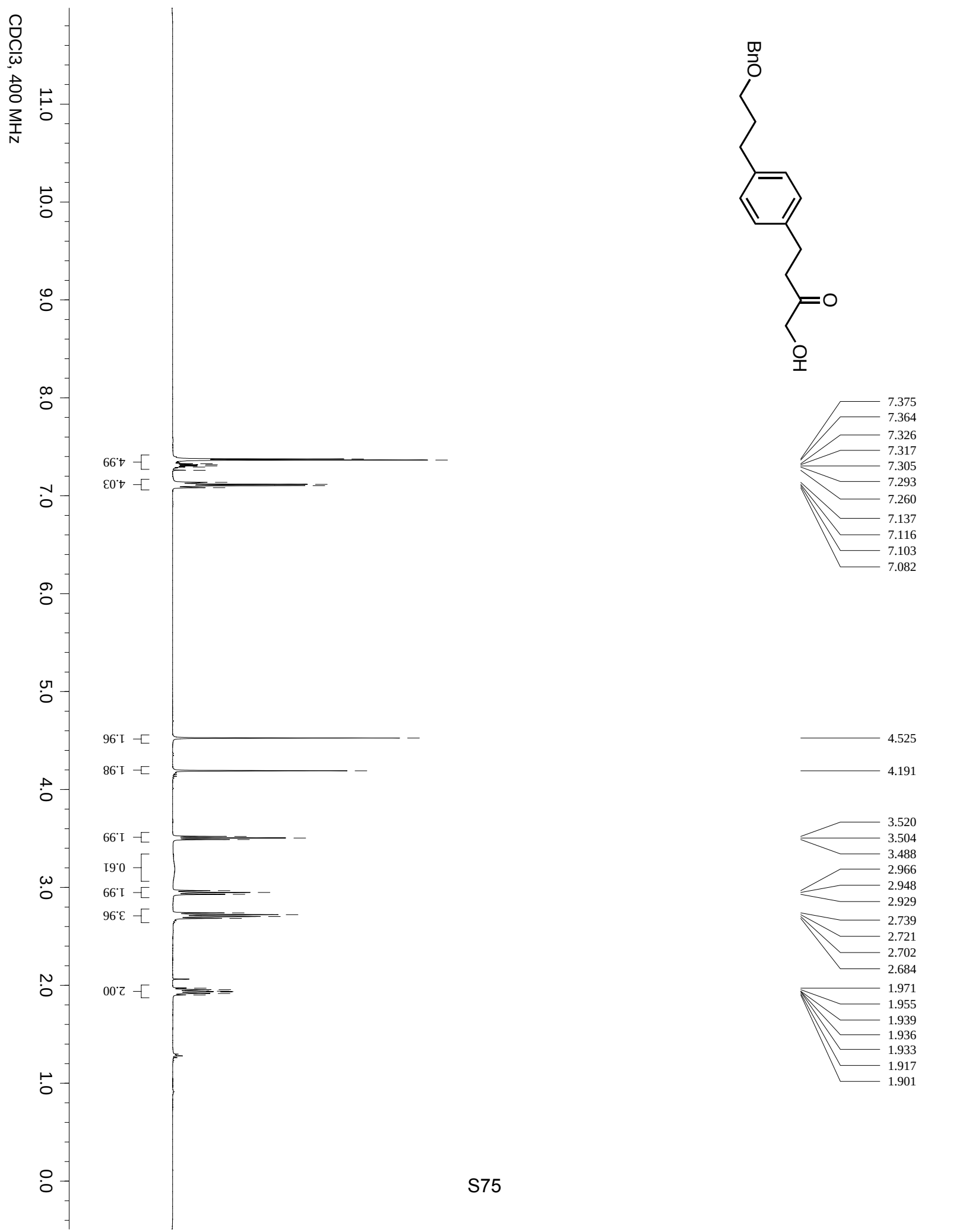

207.984
138.762
138.526
137.062
128.488
128.440
128.390
128.001
127.874
77.318
77.000
76.682
75.087
73.312
45.158
40.583
30.063
29.219
28.778
O
BnO
O
12
S70
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

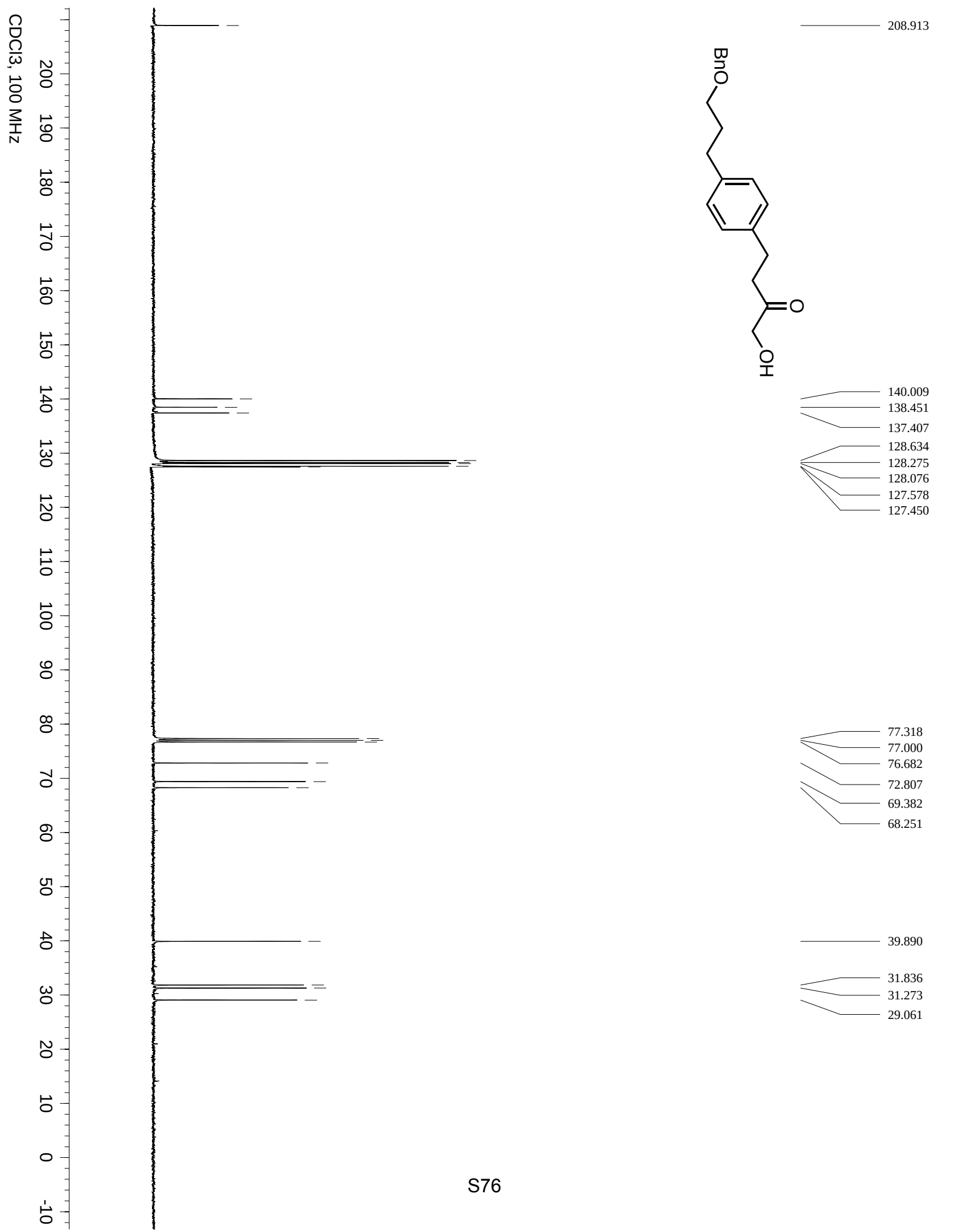

CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.03
1.00
1.03
0.98
2.02
4.00
0.97
2.03
2.02
OH
7.260
7.173
5.997
5.975
5.963
5.954
5.941
5.919
5.906
5.897
5.884
5.863
5.142
5.085
5.063
5.029
3.712
3.692
3.672
2.769
2.747
2.717
2.696
2.617
2.461
2.435
2.410
2.387
1.972
1.950
1.921
1.899
1.877

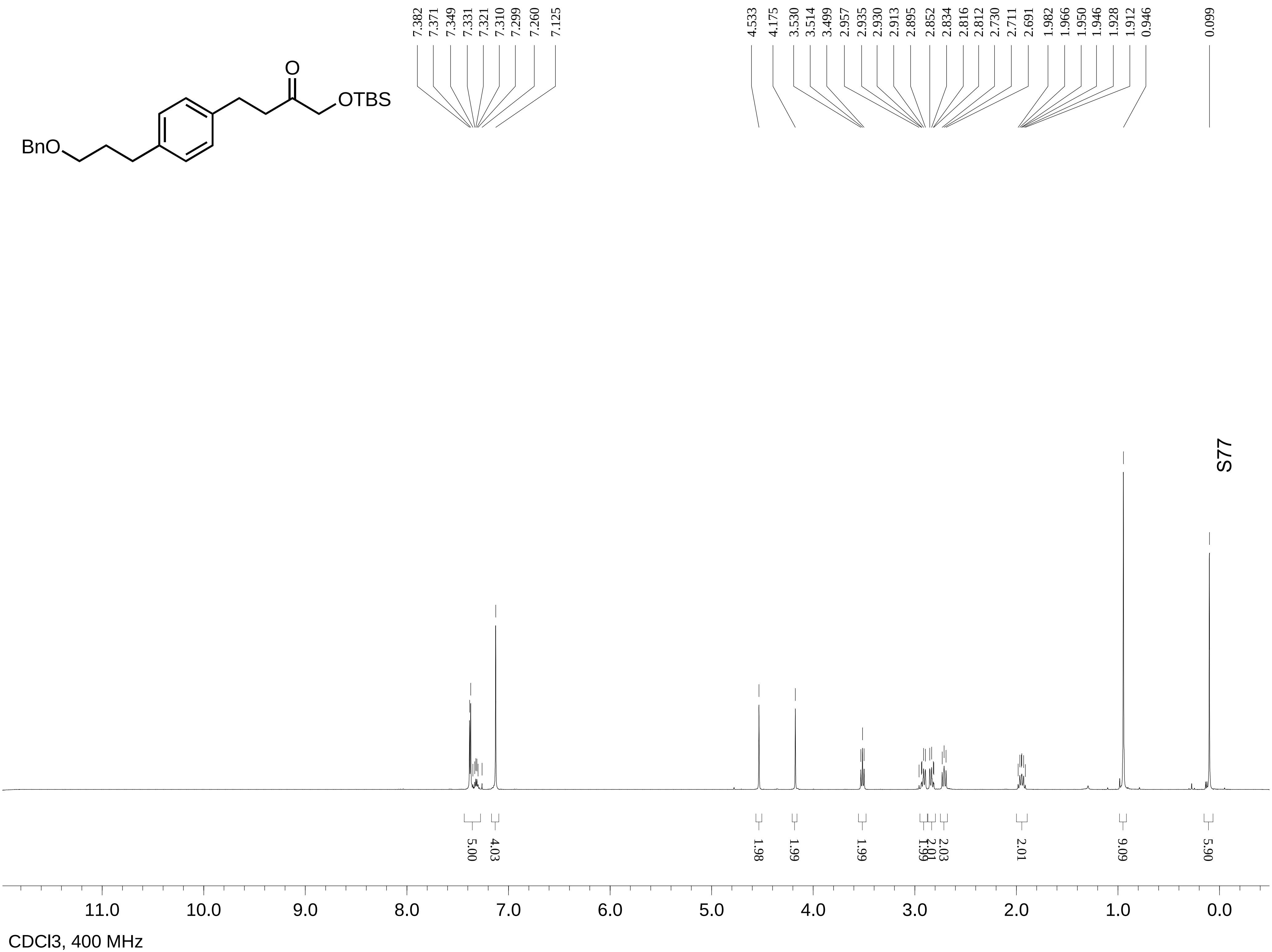

CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
OH
139.146
139.102
138.033
128.270
128.193
114.712
77.424
77.000
76.575
61.923
35.446
34.797
34.090
31.511

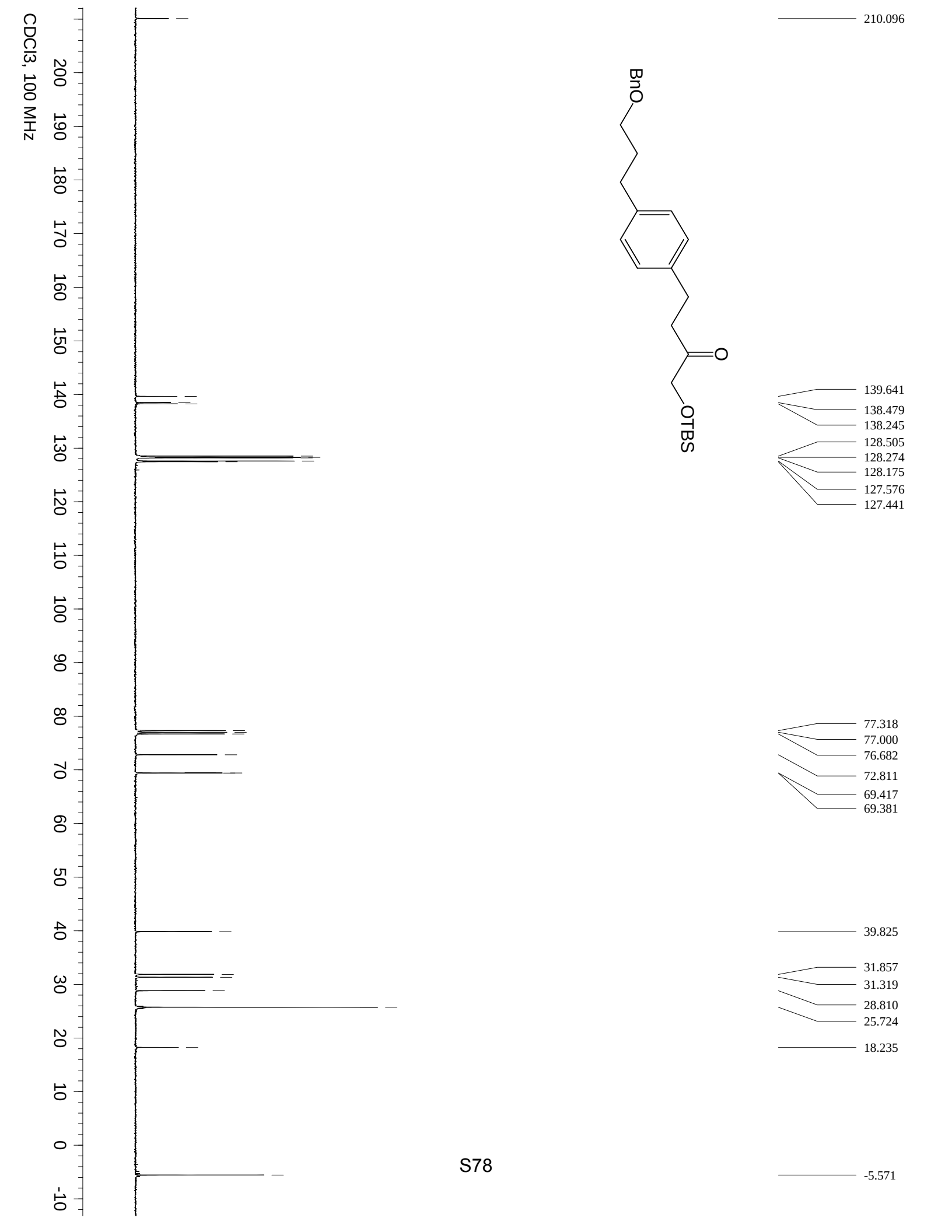

CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
5.06
4.06
0.94
0.99
0.98
2.01
2.00
3.99
1.96
2.04
BnO
7.377
7.362
7.329
7.317
7.301
7.260
7.117
5.950
5.929
5.916
5.907
5.894
5.872
5.859
5.850
5.837
5.816
5.096
5.090
5.039
5.033
5.015
5.012
5.009
4.981
4.978
4.526
3.530
3.508
3.487
2.729
2.721
2.704
2.698
2.678
2.669
2.414
2.392
2.387
2.364
2.340
1.991
1.970
1.965
1.949
1.943
1.940
1.928
1.918
1.897

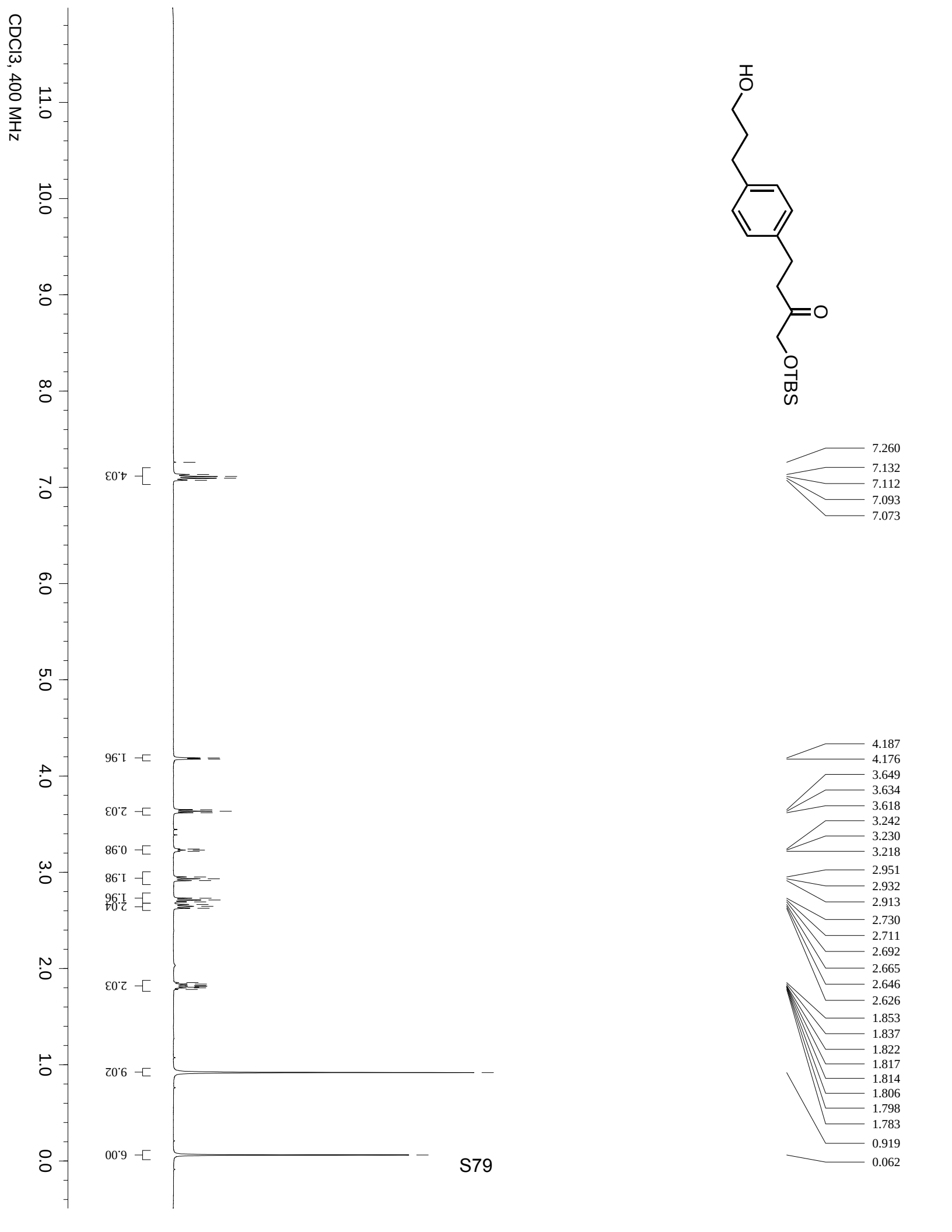

CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
BnO
139.343
139.197
138.553
138.201
128.362
128.334
128.316
127.641
127.494
114.778
77.423
77.000
76.577
72.871
69.541
35.562
34.927
31.924
31.383

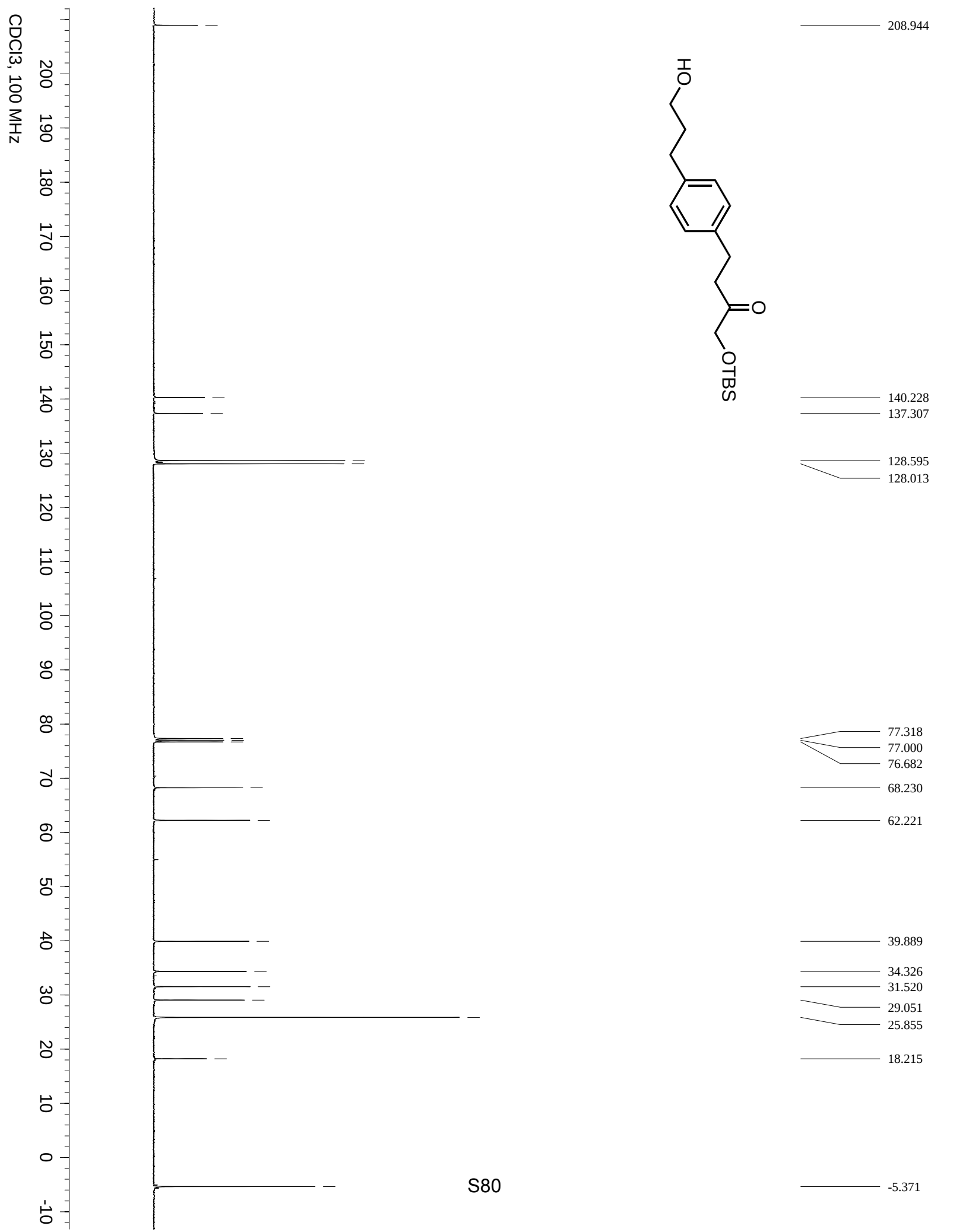

CDCl3, 400 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.99
4.03
1.96
1.98
1.99
0.61
1.99
3.96
2.00
BnO
O
OH
7.375
7.364
7.326
7.317
7.305
7.293
7.260
7.137
7.116
7.103
7.082
4.525
4.191
3.520
3.504
3.488
2.966
2.948
2.929
2.739
2.721
2.702
2.684
1.971
1.955
1.939
1.936
1.933
1.917
1.901

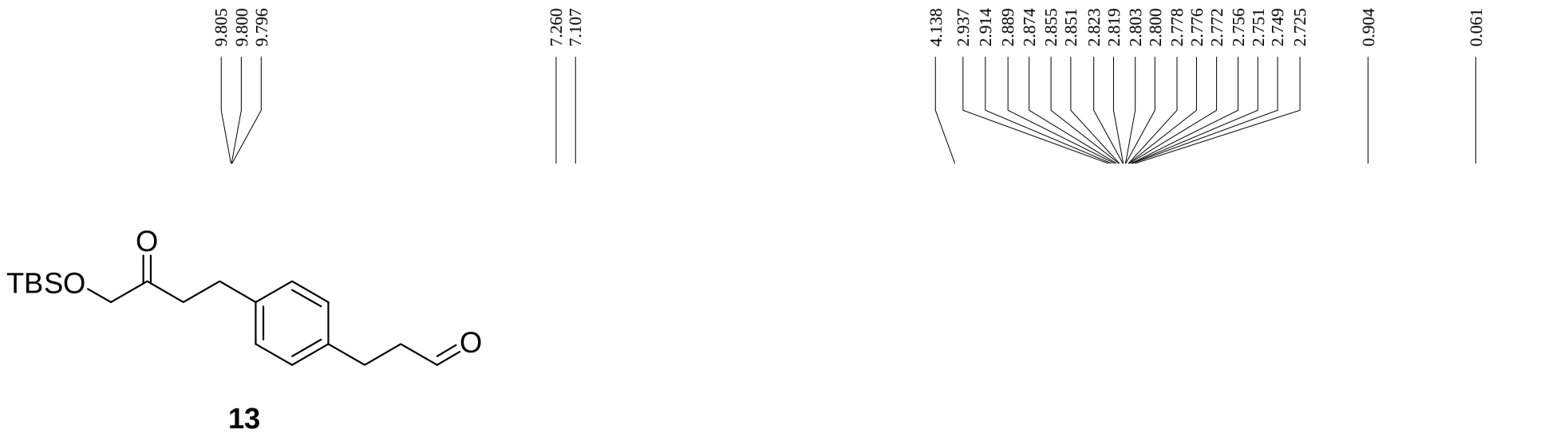

CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
BnO
O
OH
208.913
140.009
138.451
137.407
128.634
128.275
128.076
127.578
127.450
77.318
77.000
76.682
72.807
69.382
68.251
39.890
31.836
31.273
29.061


BnO
O
OTBS
7.382
7.371
7.349
7.331
7.321
7.310
7.299
7.260
7.125
4.533
4.175
3.530
3.514
3.499
2.957
2.935
2.930
2.913
2.895
2.852
2.834
2.816
2.812
2.730
2.711
2.691
1.982
1.966
1.950
1.946
1.928
1.912
0.946
0.099
5.00
4.03
1.98
1.99
1.99
1.99
2.01
2.03
2.01
9.09
5.90
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz

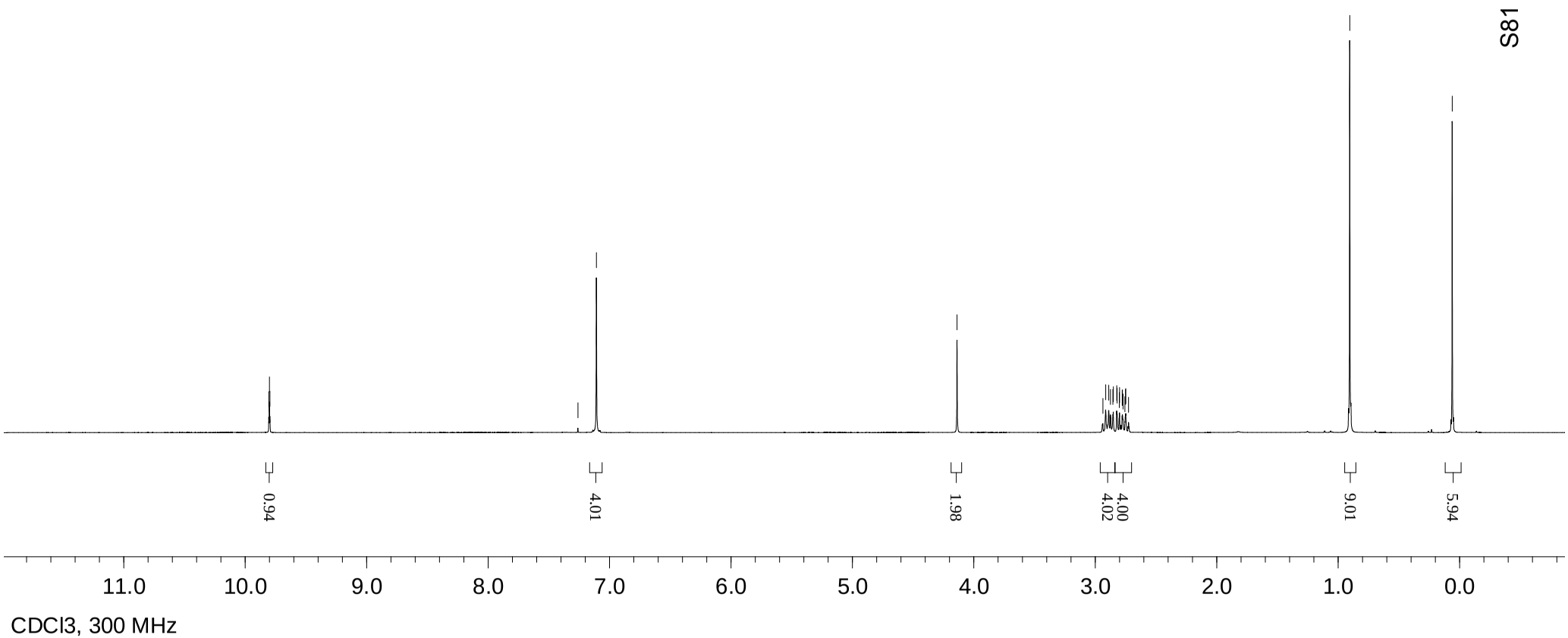

CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
BnO
O
OTBS
210.096
139.641
138.479
138.245
128.505
128.274
128.175
127.576
127.441
77.318
77.000
76.682
72.811
69.417
69.381
39.825
31.857
31.319
28.810
25.724
18.235
-5.571

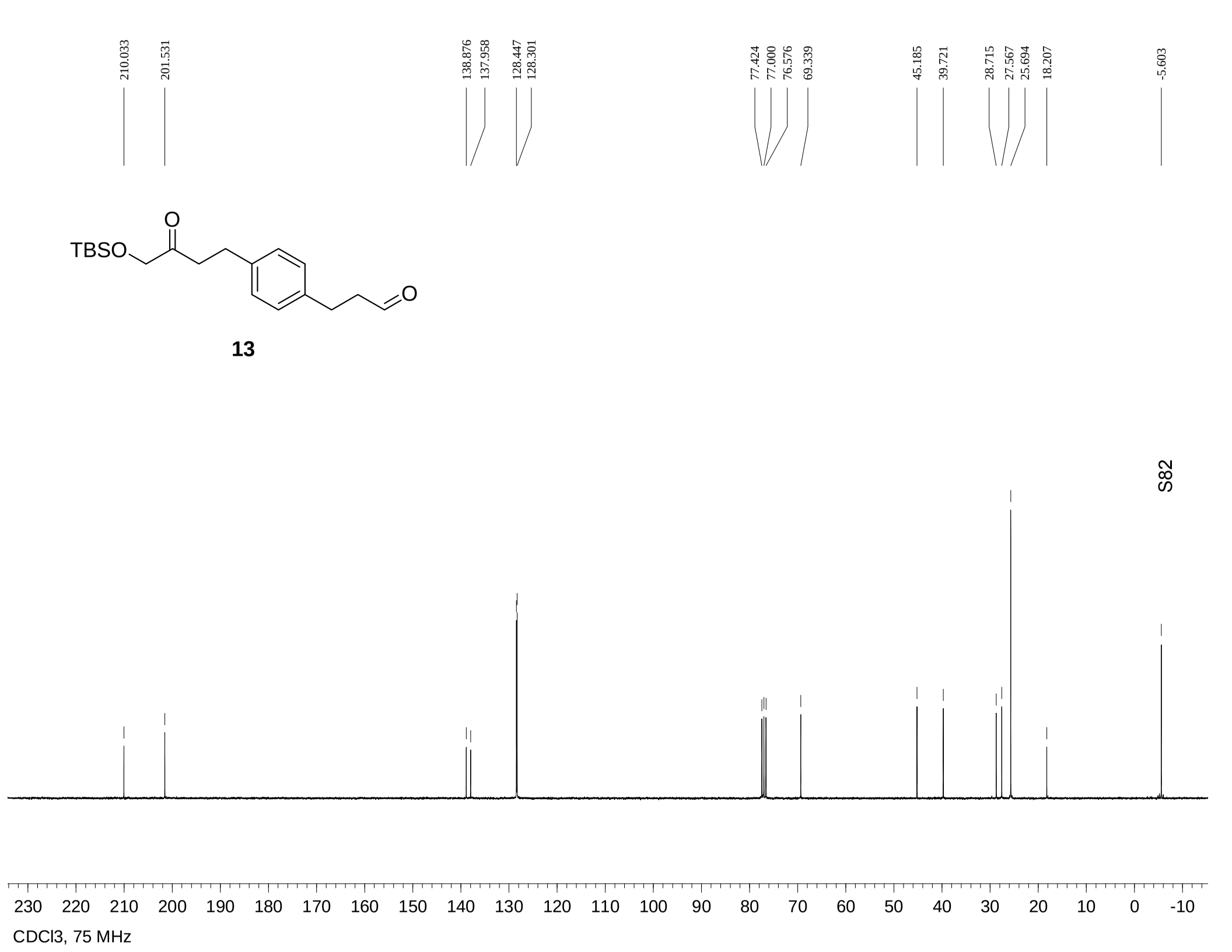

CDCl3, 400 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.03
1.96
2.03
0.98
1.98
1.96
2.04
2.03
9.02
6.00
HO
O
OTBS
7.260
7.132
7.112
7.093
7.073
4.187
4.176
3.649
3.634
3.618
3.242
3.230
3.218
2.951
2.932
2.913
2.730
2.711
2.692
2.665
2.646
2.626
1.853
1.837
1.822
1.817
1.814
1.806
1.798
1.783
0.919
0.062

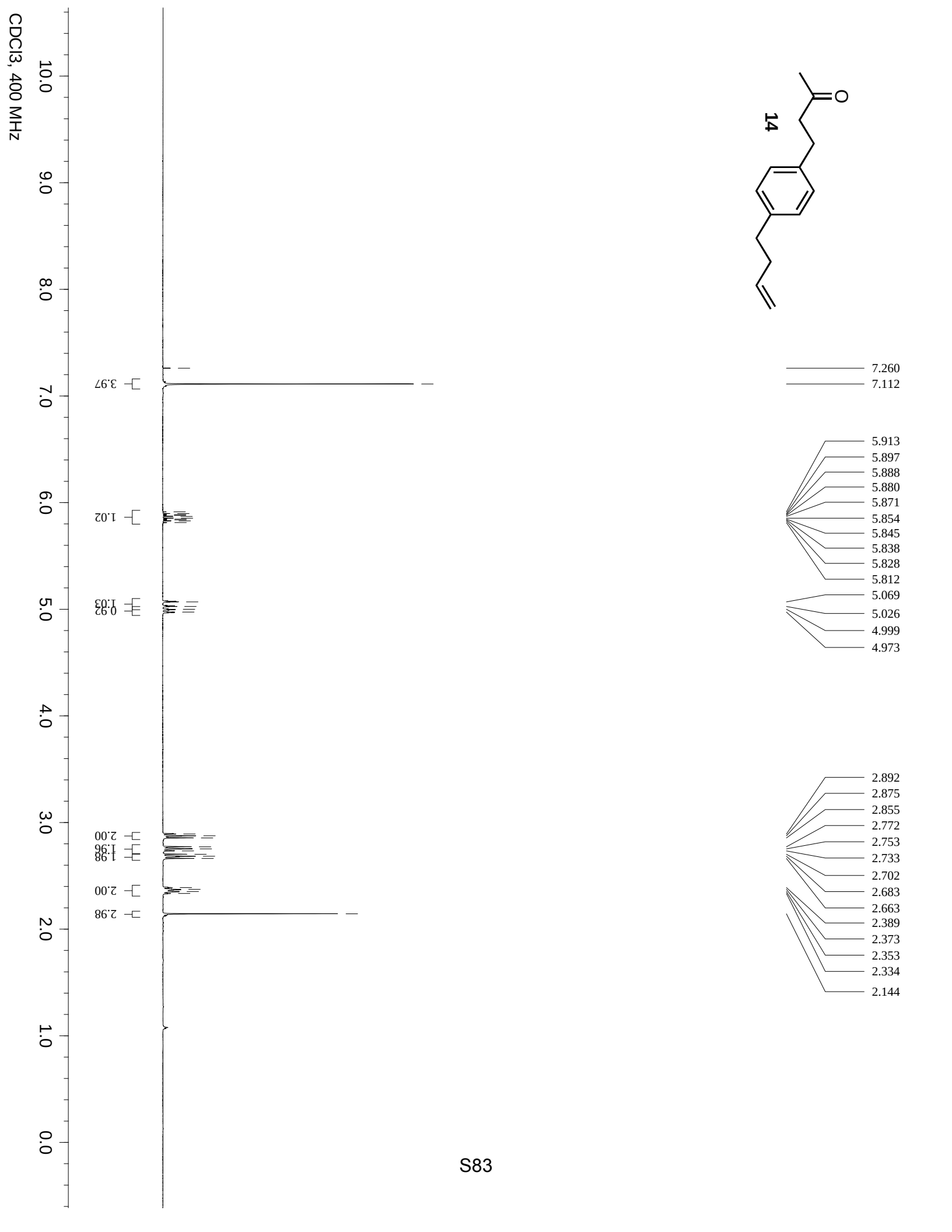

CDCl3, 100 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
HO
O
OTBS
208.944
140.228
137.307
128.595
128.013
77.318
77.000
76.682
68.230
62.221
39.889
34.326
31.520
29.051
25.855
18.215
-5.371

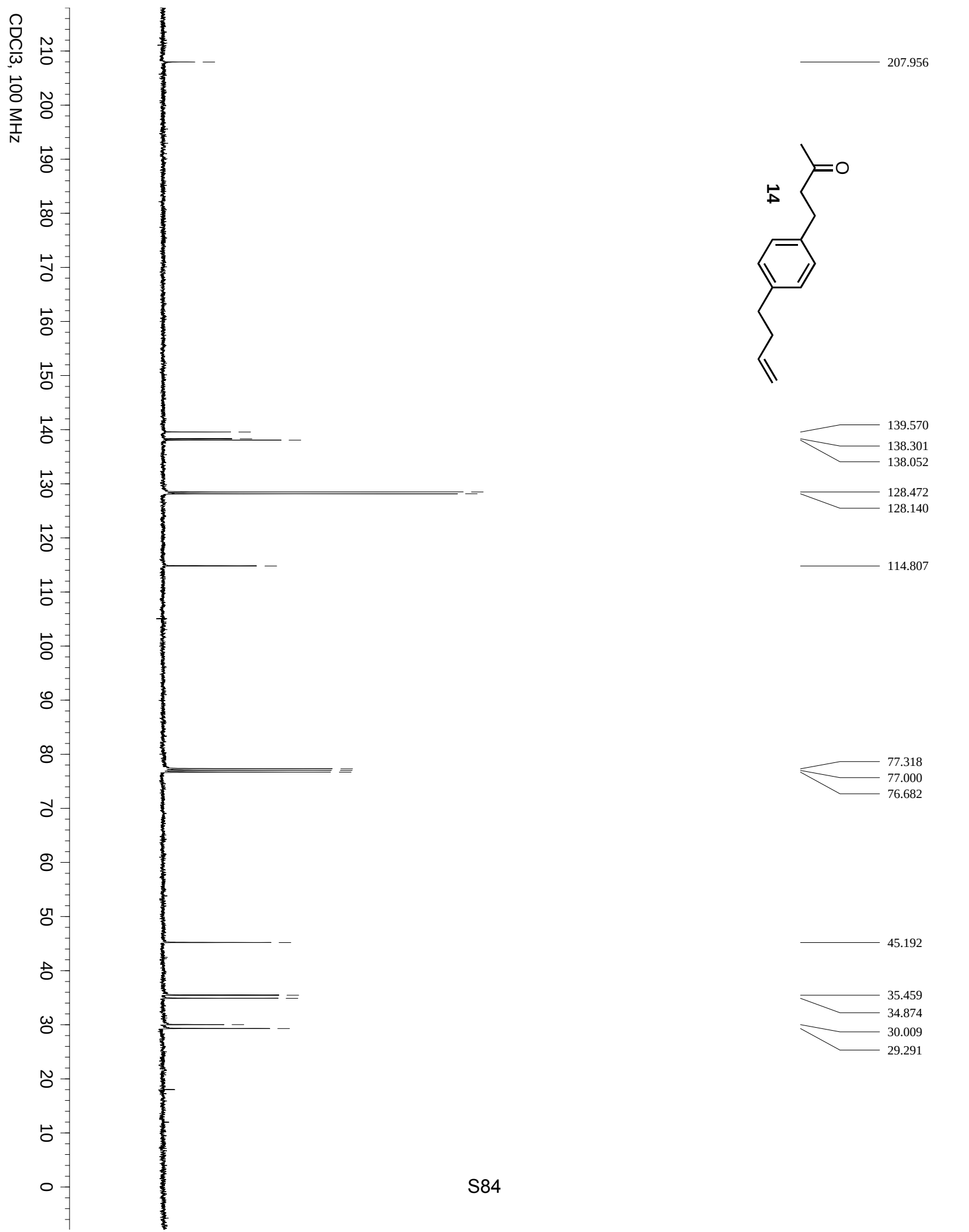

9.805
9.800
9.796
7.260
7.107
4.138
2.937
2.914
2.889
2.874
2.855
2.851
2.823
2.819
2.803
2.800
2.778
2.776
2.772
2.756
2.751
2.749
2.725
0.904
0.061
TBSO
O
O

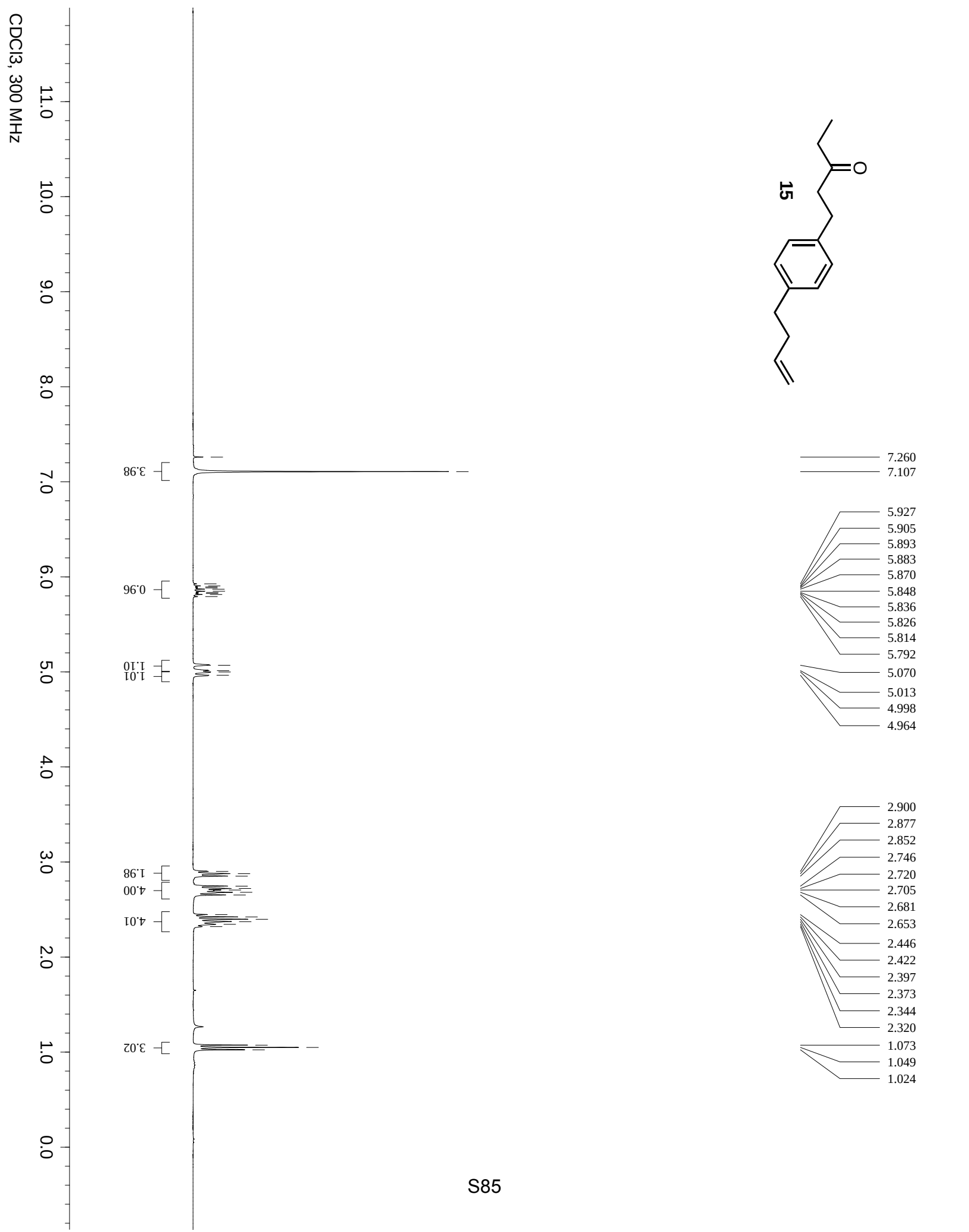
13

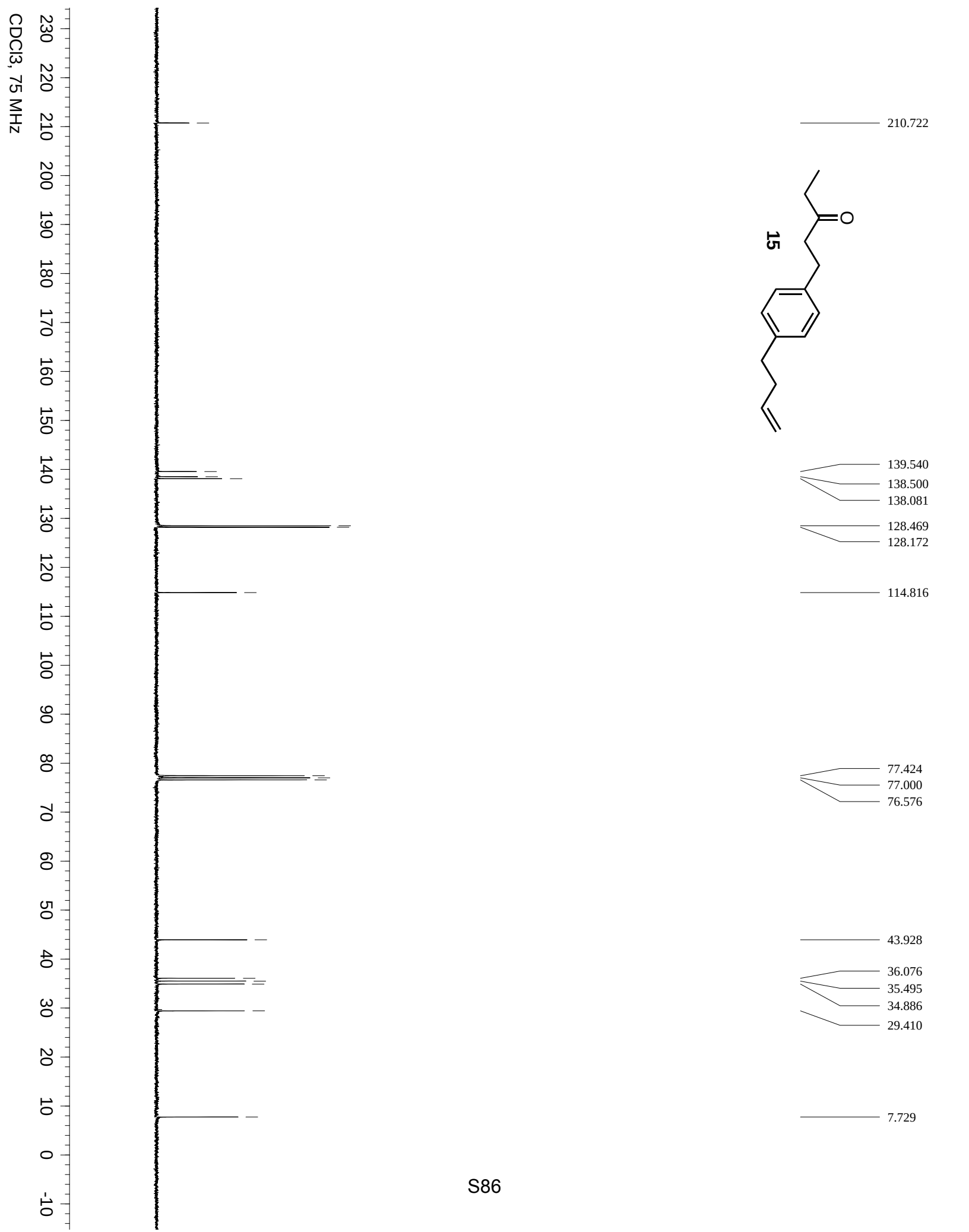

S81
0.94
4.01
1.98
4.02
4.00
9.01
5.94
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 300 MHz

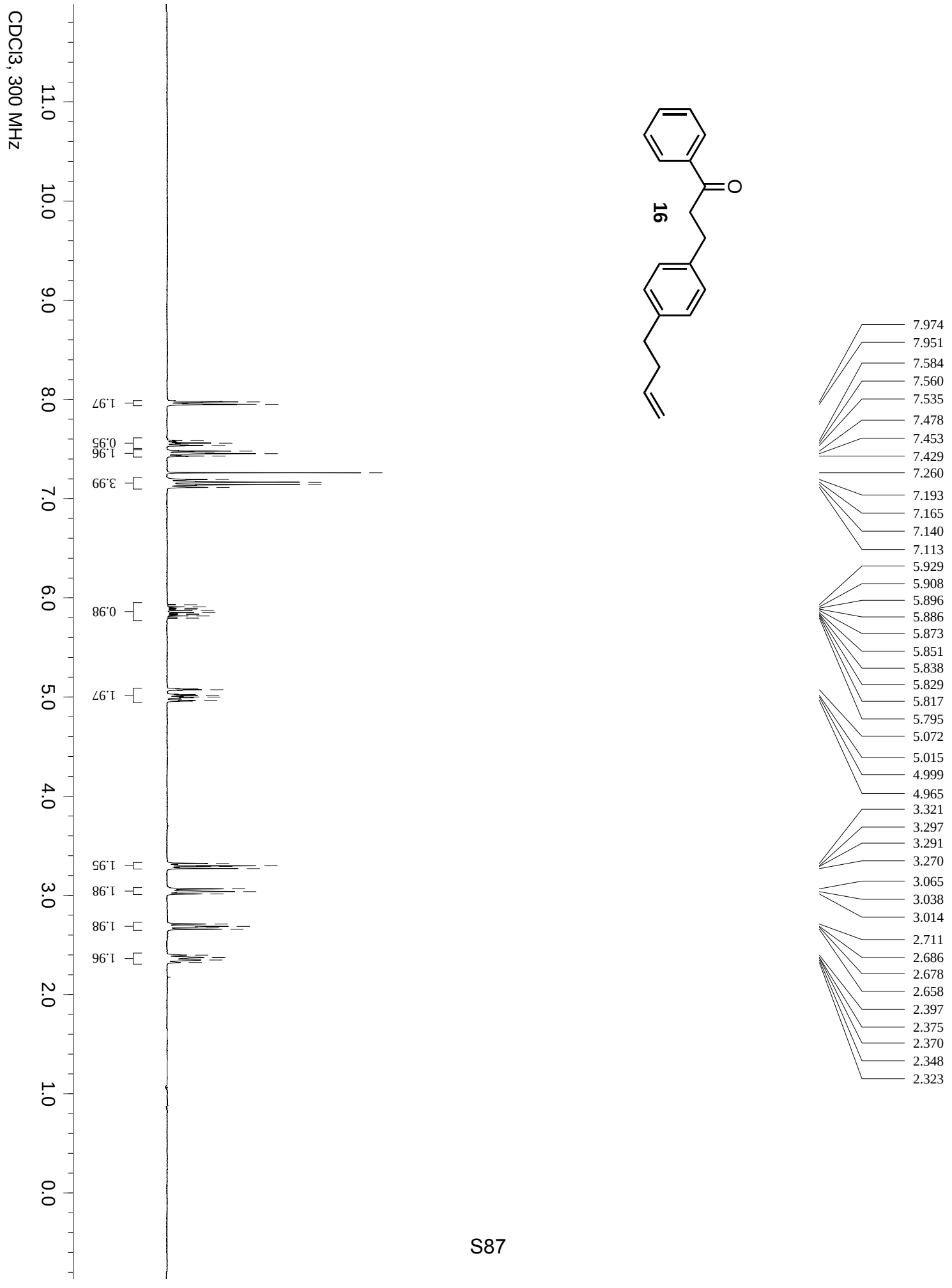

210.033
201.531
138.876
137.958
128.447
128.301
77.424
77.000
76.576
69.339
45.185
39.721
28.715
27.567
25.694
18.207
-5.603
TBSO
O
O
13
S82
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
CDCl3, 75 MHz

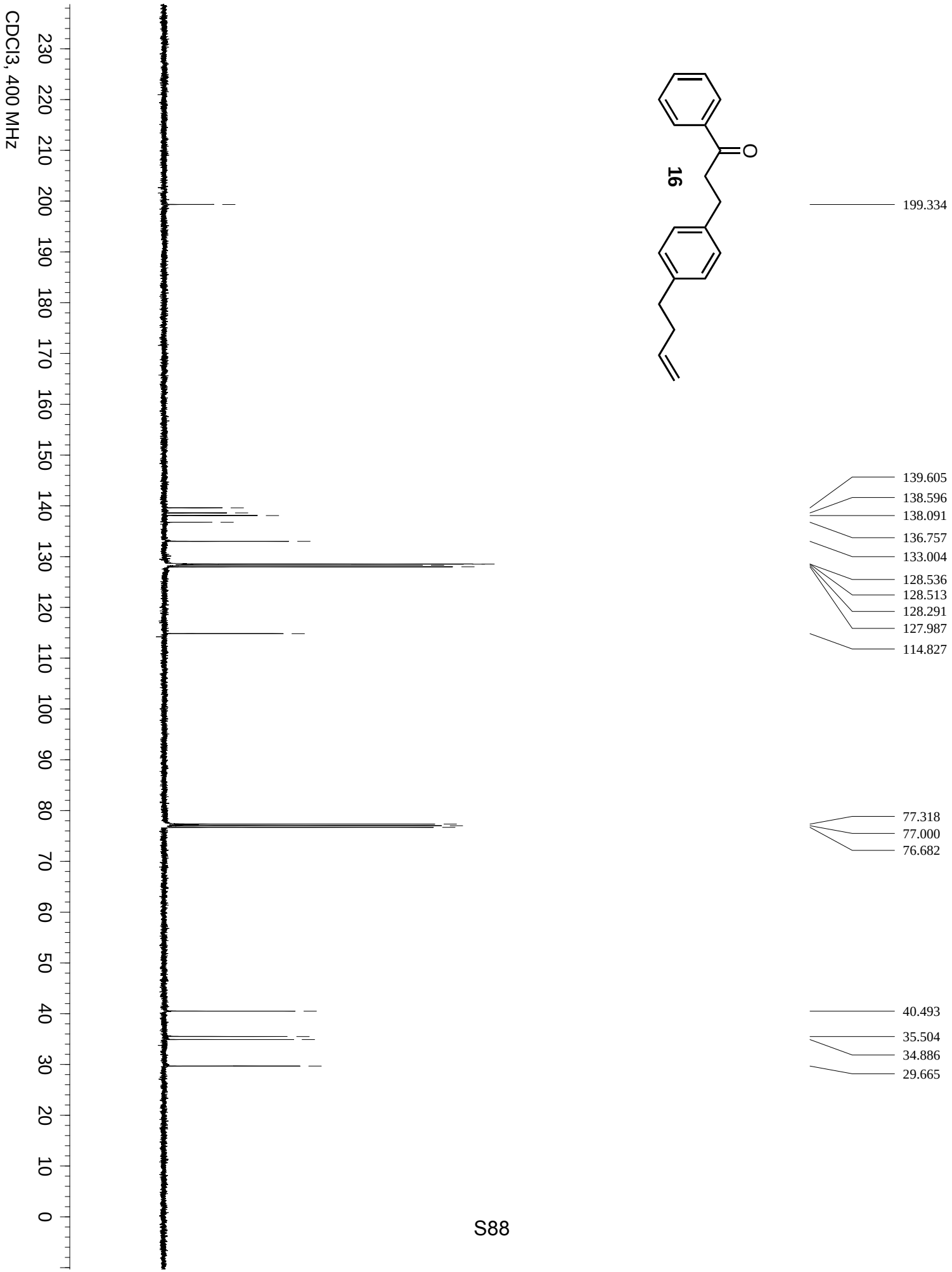

CDCl3, 400 MHz
14
O
7.260
7.112
5.913
5.897
5.888
5.880
5.871
5.854
5.845
5.838
5.828
5.812
5.069
5.026
4.999
4.973
2.892
2.875
2.855
2.772
2.753
2.733
2.702
2.683
2.663
2.389
2.373
2.353
2.334
2.144
3.97
1.02
0.92
1.03
2.00
1.96
1.98
2.00
2.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

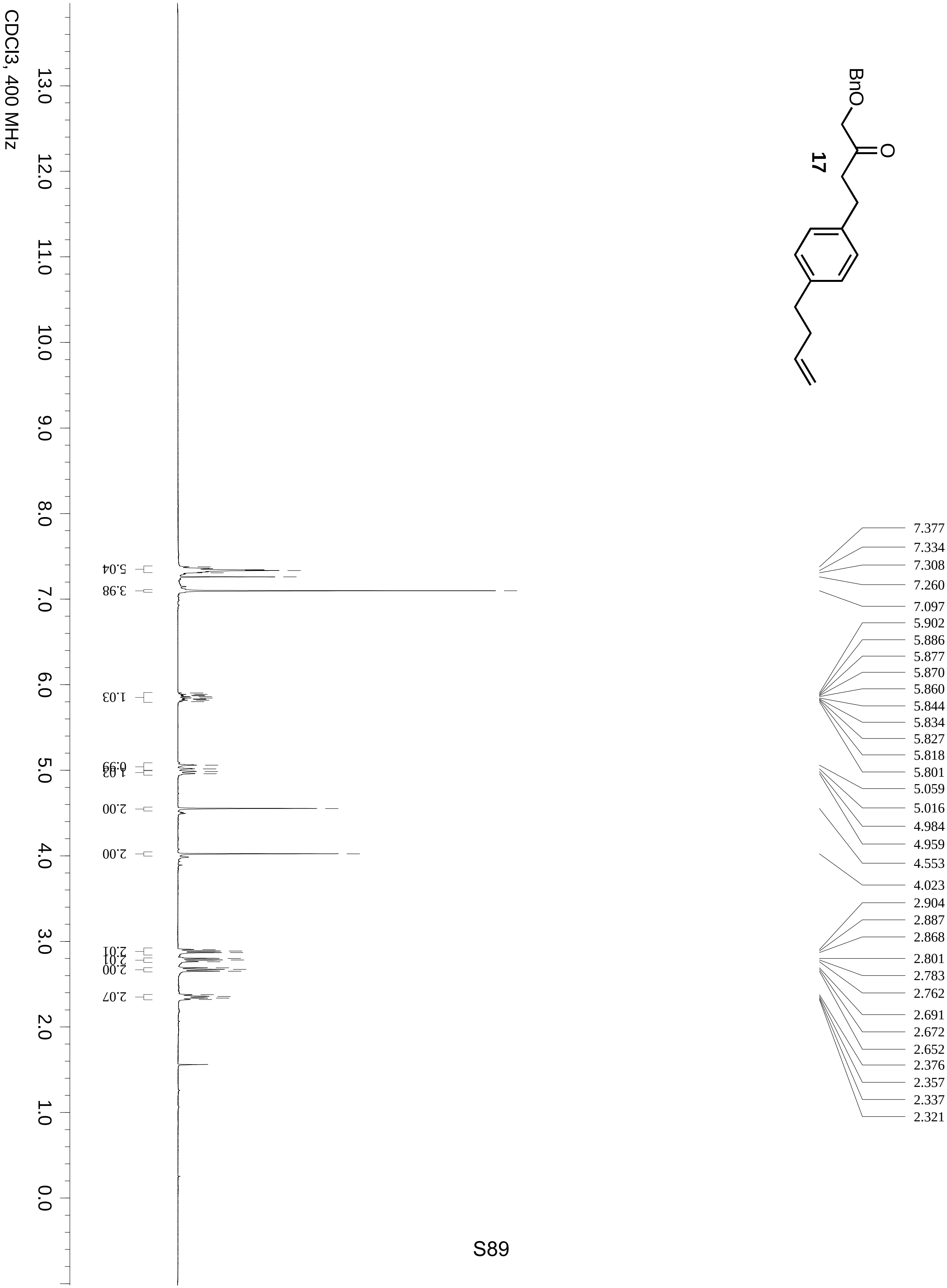

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
207.956
O
14
139.570
138.301
138.052
128.472
128.140
114.807
77.318
77.000
76.682
45.192
35.459
34.874
30.009
29.291

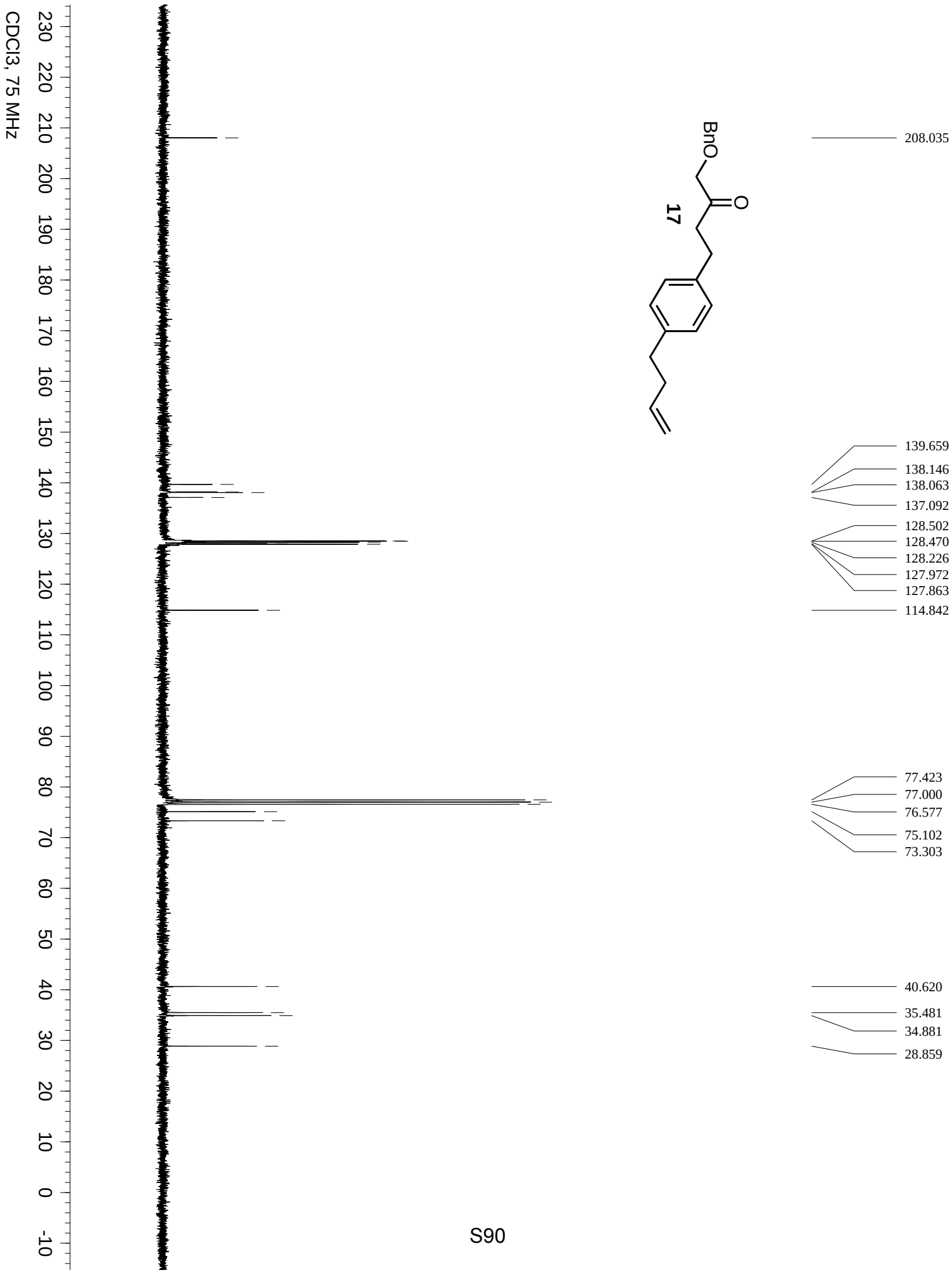

CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.98
0.96
1.10
1.01
1.98
4.00
4.01
3.02
15
O
7.260
7.107
5.927
5.905
5.893
5.883
5.870
5.848
5.836
5.826
5.814
5.792
5.070
5.013
4.998
4.964
2.900
2.877
2.852
2.746
2.720
2.705
2.681
2.653
2.446
2.422
2.397
2.373
2.344
2.320
1.073
1.049
1.024

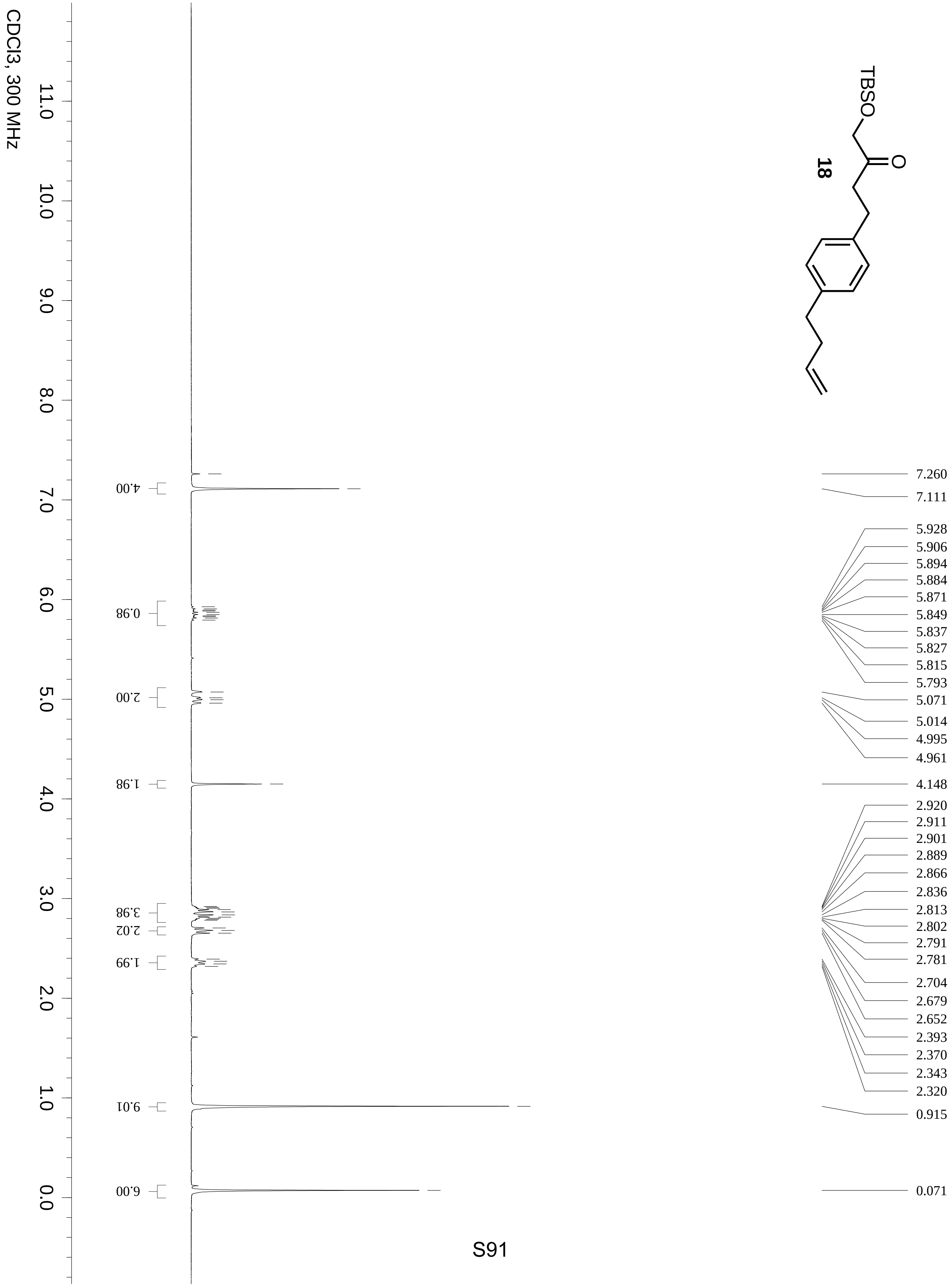

CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
15
O
210.722
139.540
138.500
138.081
128.469
128.172
114.816
77.424
77.000
76.576
43.928
36.076
35.495
34.886
29.410
7.729

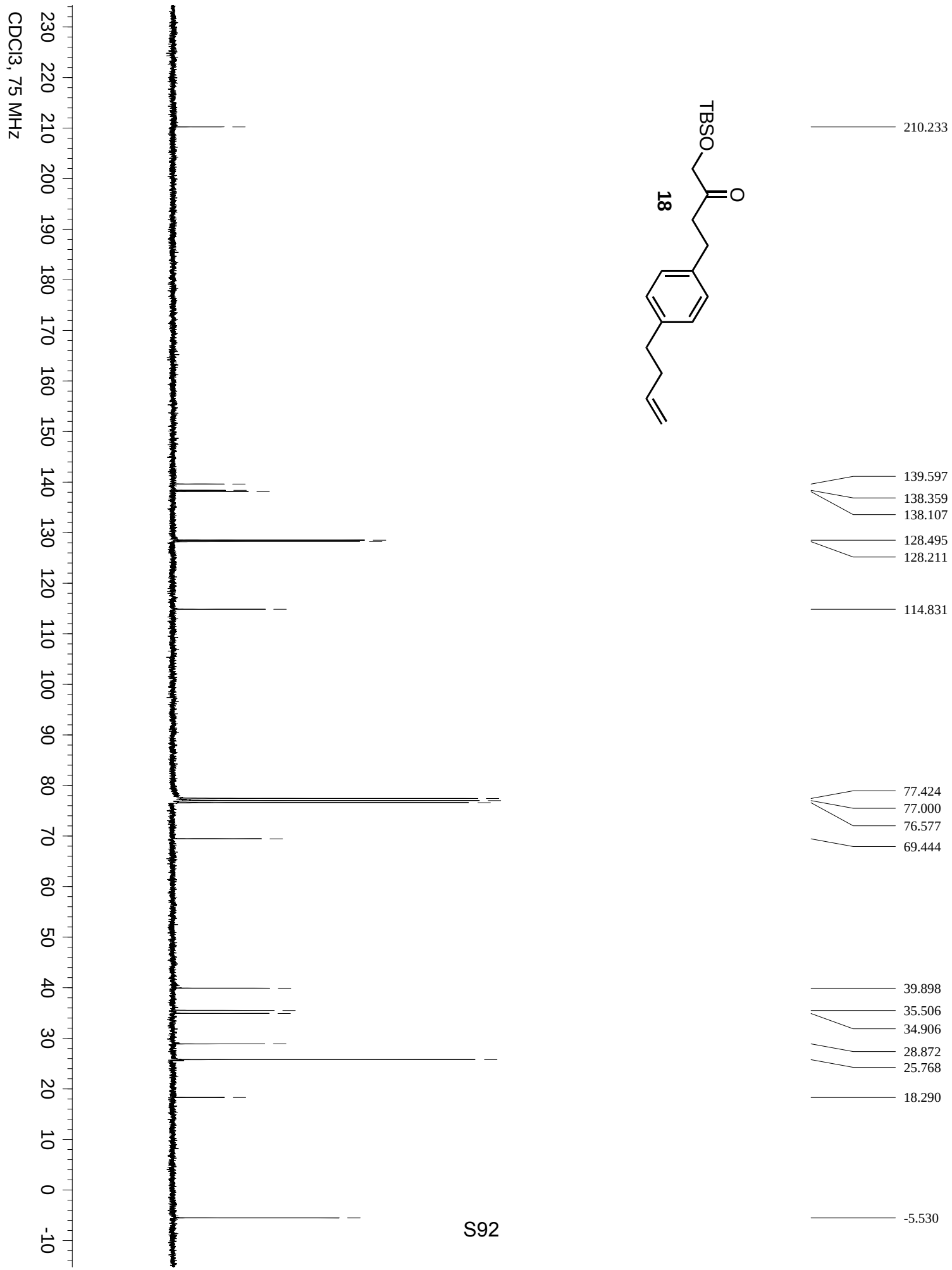

CDCl3, 300 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.97
0.95
1.96
3.99
0.98
1.97
1.95
1.98
1.98
1.96
16
O
7.974
7.951
7.584
7.560
7.535
7.478
7.453
7.429
7.260
7.193
7.165
7.140
7.113
5.929
5.908
5.896
5.886
5.873
5.851
5.838
5.829
5.817
5.795
5.072
5.015
4.999
4.965
3.321
3.297
3.291
3.270
3.065
3.038
3.014
2.711
2.686
2.678
2.658
2.397
2.375
2.370
2.348
2.323

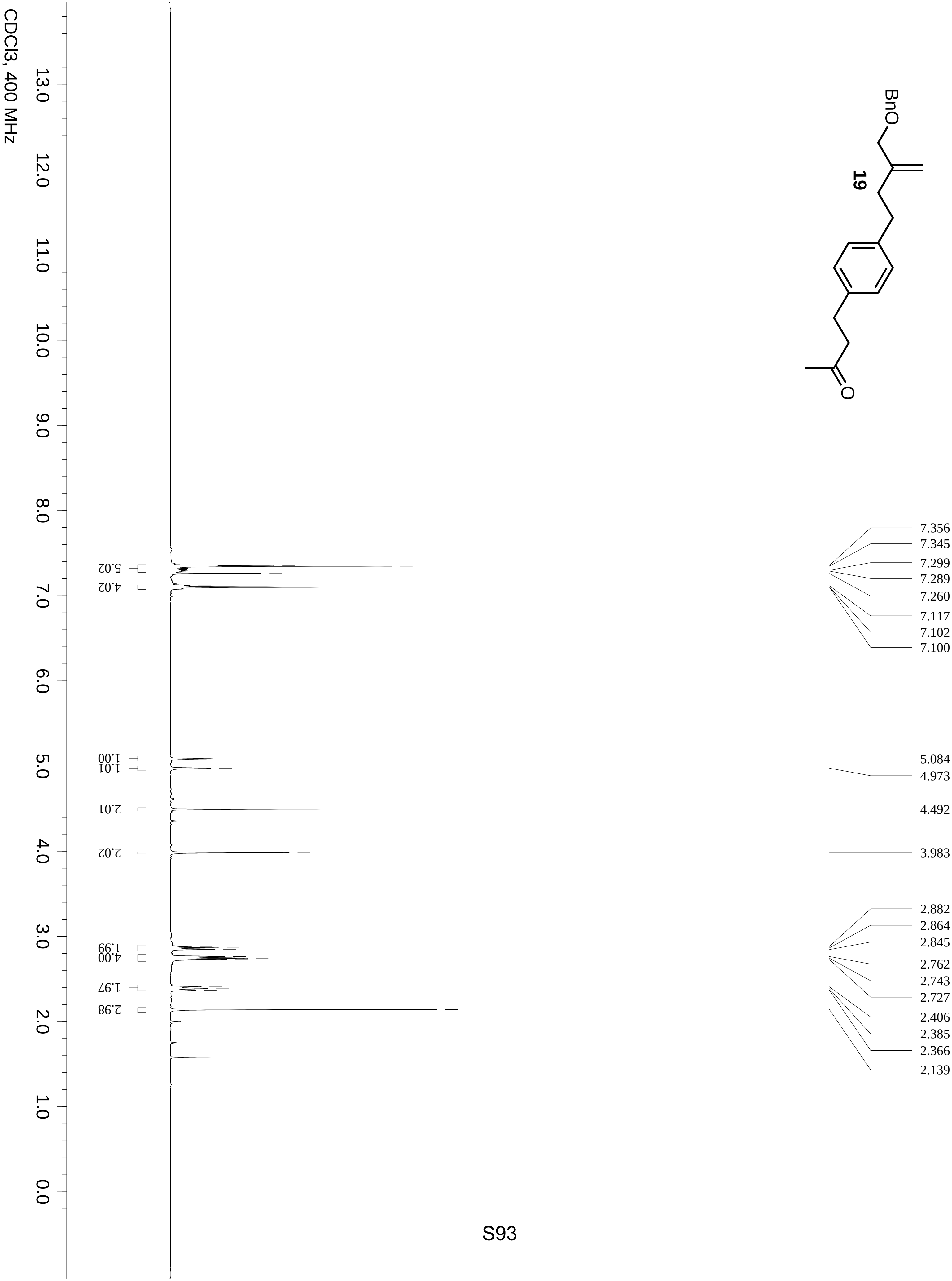

CDCl3, 400 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
16
199.334
139.605
138.596
138.091
136.757
133.004
128.536
128.513
128.291
127.987
114.827
77.318
77.000
76.682
40.493
35.504
34.886
29.665

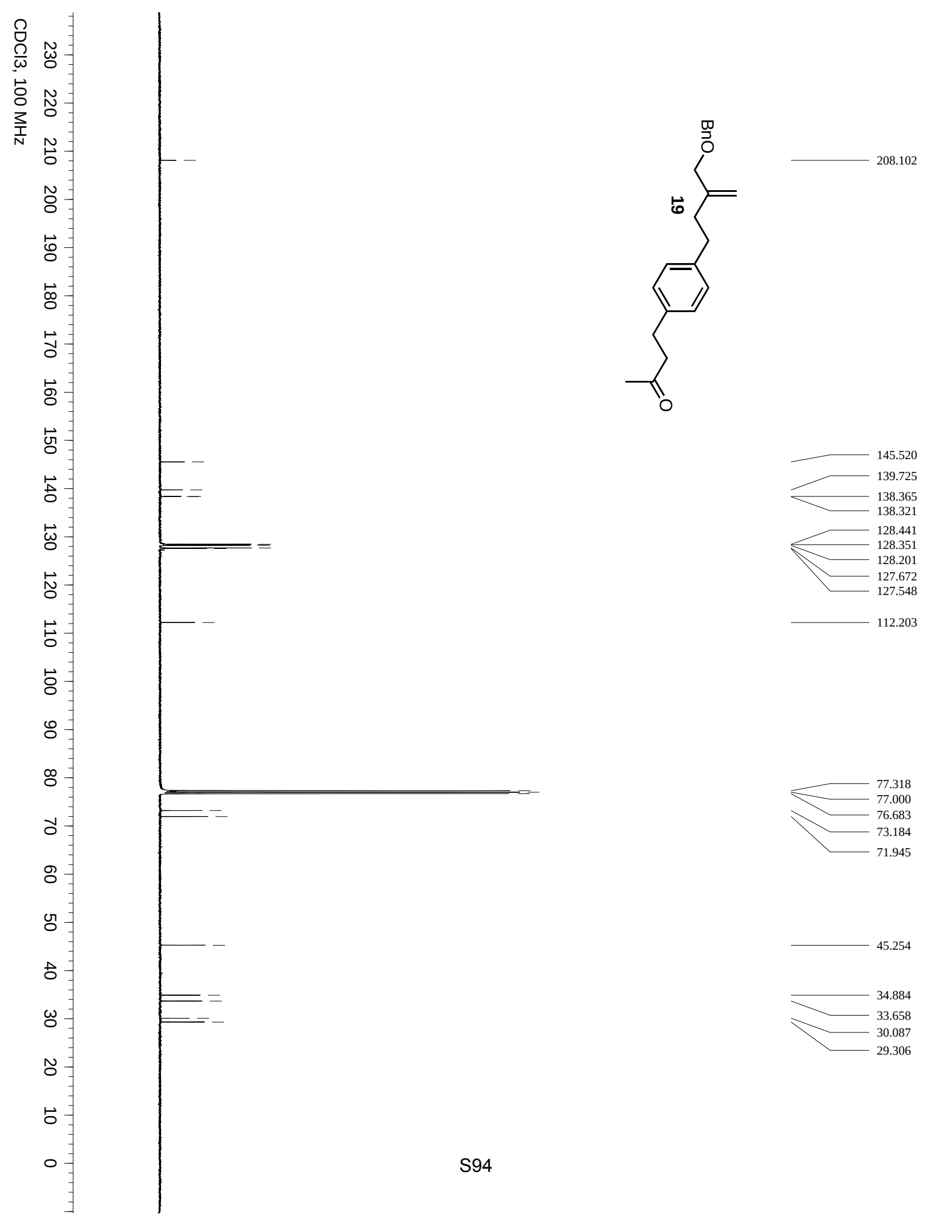

CDCl3, 400 MHz
BnO
O
17
7.377
7.334
7.308
7.260
7.097
5.902
5.886
5.877
5.870
5.860
5.844
5.834
5.827
5.818
5.801
5.059
5.016
4.984
4.959
4.553
4.023
2.904
2.887
2.868
2.801
2.783
2.762
2.691
2.672
2.652
2.376
2.357
2.337
2.321

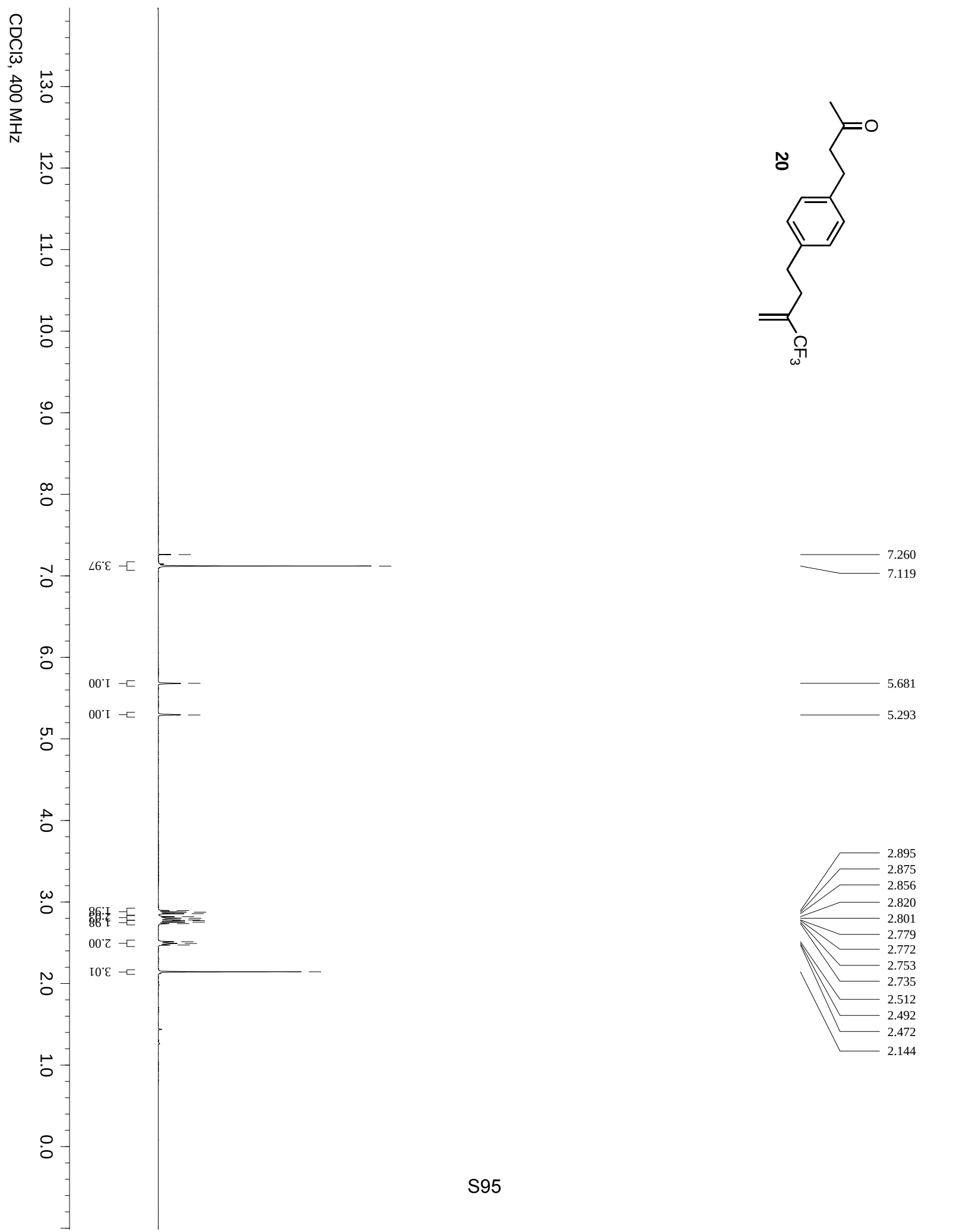

CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
BnO
O
17
208.035
139.659
138.146
138.063
137.092
128.502
128.470
128.226
127.972
127.863
114.842
77.423
77.000
76.577
75.102
73.303
40.620
35.481
34.881
28.859

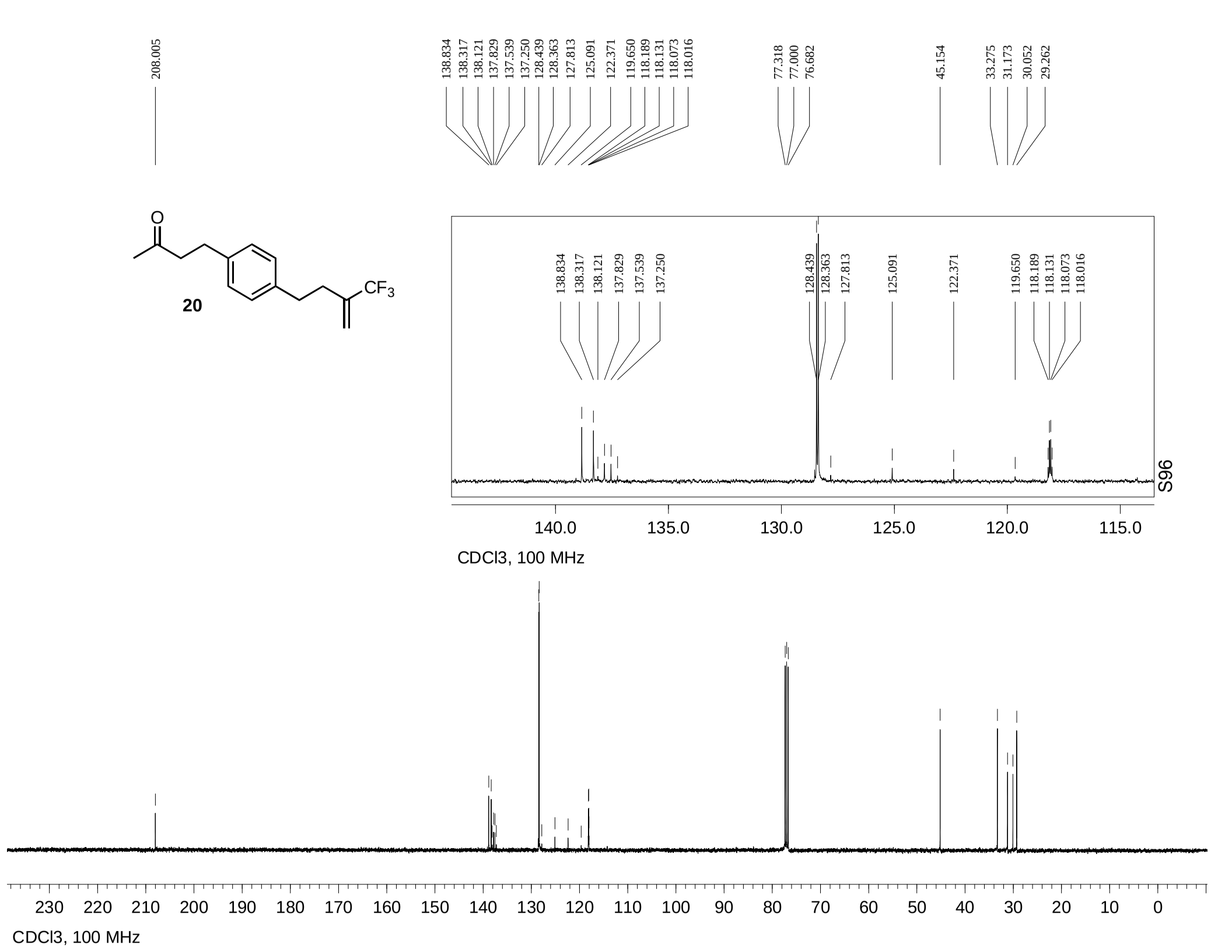

CDCl3, 300 MHz
TBSO
O
18
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.00
0.98
2.00
1.98
3.98
2.02
1.99
9.01
6.00
7.260
7.111
5.928
5.906
5.894
5.884
5.871
5.849
5.837
5.827
5.815
5.793
5.071
5.014
4.995
4.961
4.148
2.920
2.911
2.901
2.889
2.866
2.836
2.813
2.802
2.791
2.781
2.704
2.679
2.652
2.393
2.370
2.343
2.320
0.915
0.071

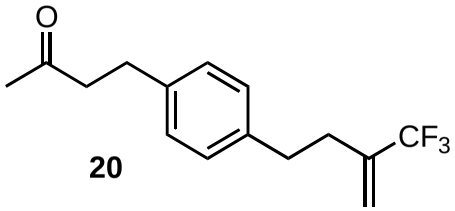

CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
TBSO
O
18
210.233
139.597
138.359
138.107
128.495
128.211
114.831
77.424
77.000
76.577
69.444
39.898
35.506
34.906
28.872
25.768
18.290
-5.530


CDCl3, 400 MHz
19
BnO
O
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
5.02
4.02
1.00
1.01
2.01
2.02
1.99
4.00
1.97
2.98
7.356
7.345
7.299
7.289
7.260
7.117
7.102
7.100
5.084
4.973
4.492
3.983
2.882
2.864
2.845
2.762
2.743
2.727
2.406
2.385
2.366
2.139


CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
BnO
19
O
208.102
145.520
139.725
138.365
138.321
128.441
128.351
128.201
127.672
127.548
112.203
77.318
77.000
76.683
73.184
71.945
45.254
34.884
33.658
30.087
29.306


CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.97
1.00
1.00
1.98
2.00
3.01
20
O
CF3
7.260
7.119
5.681
5.293
2.895
2.875
2.856
2.820
2.801
2.779
2.772
2.753
2.735
2.512
2.492
2.472
2.144


208.005
138.834
138.317
138.121
137.829
137.539
137.250
128.439
128.363
127.813
125.091
122.371
119.650
118.189
118.131
118.073
118.016
77.318
77.000
76.682
45.154
33.275
31.173
30.052
29.262
O
CF3
20
S96
140.0
135.0
130.0
125.0
120.0
115.0
CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
CDCl3, 100 MHz

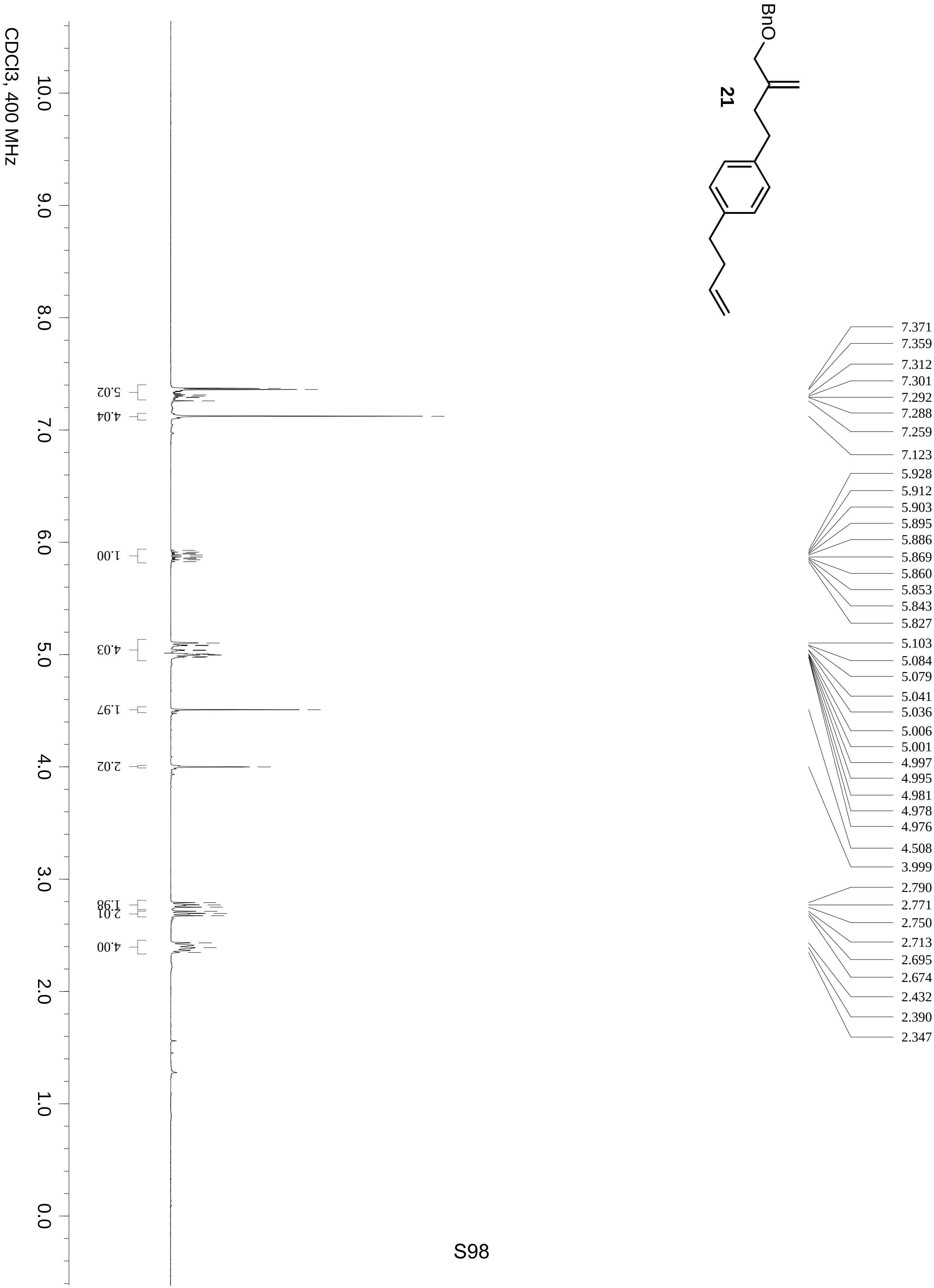


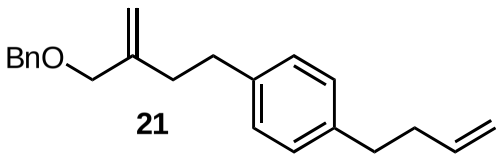
20

-68.892

-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120

CDCl3, 282 MHz


CDCl3, 400 MHz
21
BnO
7.371
7.359
7.312
7.301
7.292
7.288
7.259
7.123
5.928
5.912
5.903
5.895
5.886
5.869
5.860
5.853
5.843
5.827
5.103
5.084
5.079
5.041
5.036
5.006
5.001
4.997
4.995
4.981
4.978
4.976
4.508
3.999
2.790
2.771
2.750
2.713
2.695
2.674
2.432
2.390
2.347
5.02
4.04
1.00
4.03
1.97
2.02
1.98
2.01
4.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



21

145.627
139.357
139.287
138.364
138.184
128.326
128.233
127.667
127.526
114.787
112.119
77.317
77.000
76.683
73.210
71.961
35.551
34.944
33.739

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

CDCl3, 100 MHz