(Electronic Supplementary Information)

Novel Chemoselective Tosylation of the Alcoholic Hydroxyl Group of Syn-α,β-Disubstituted β-Hydroxy Carboxylic Acids.

Yikang Wu and Ya-Ping Sun*

State Key Laboratory of Bio-organic and Natural Products Chemistry,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032, China
E-mail address: yikangwu@mail.sioc.ac.cn

Table of Contents of ESI

General information[1]. The starting β-hydroxy acids were prepared by treating corresponding Crimmins *syn*-aldols (prepared from appropriate *N*-acylthiazolidinethiones and aldehydes by $TiCl_4$-mediated asymmetric aldolization under the conditions reported[2] by Crimmins and co-workers) with $LiOH/H_2O_2$ following the standard procedure[3] of Evans in good to excellent yields. The THF used in the reaction was freshly distilled over Na/benzophenone under argon. The MeLi was purchased from Acros (solution in diethyl ether, containing LiBr). The ^1H NMR spectra were recorded at 300 MHz in $CDCl_3$ with $SiMe_4$ as the internal reference.

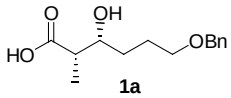
References

1 For compound **1c** and **1h**, see (a) Y. Wu, Y.-P. Sun, Y.-Q. Yang, Q. Hu, Q.; Zhang, *J. Org. Chem.* 2004, **69**, 6141-614, and (b) L. M. Dollinger, A. R. Howell, *J. Org. Chem.* 1996, **61**, 7248-7249, respectively.

2 See, e.g.: (a) M. T. Crmmins, B. W. King, E. A. Tabet, K. Chaudhary, K. *J. Org. Chem.* **2001**, *66*, 894-902. (b) M. T. Crimmins, K. Chaudhary, *Org. Lett.* **2000**, *2*, 775-778.

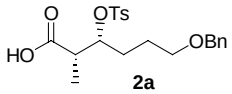
3 D. A. Evans, T. C. Britton, J. A. Ellman, *Tetrahedron Lett.* **1987**, *28*, 6141-6144.

The physical and spectroscopic data for all the new compounds



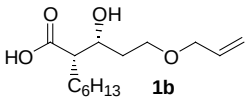
1a

Compound **1a**: A colorless oil. $[\alpha]^{27}_D$ +17.7 (*c* 3.1, $CHCl_3$). ^1H NMR δ 7.38-7.26 (m, 5H), 4.53 (s, 2H), 3.89 (dt, *J* = 9.7, 3.3 Hz, 1H), 3.61-3.47 (m, 2H), 2.63 (dq, *J* = 3.9, 7.2 Hz, 1H), 1.82-1.63 (m, 3H), 1.55-1.43 (m, 1H), 1.19 (d, *J* = 7.1 Hz, 3H); FT-IR (film) 3700-2700 (lump, centered around 3405), 1651, 1020, 703 cm^{-1}; ESI-MS m/z 253.05 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{14}H_{20}O_4Na$ ($[M+Na]^+$): 275.1254. Found: 275.1265.



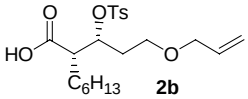
2a

Compound **2a**: A colorless oil. $[\alpha]^{26}_D$ +23.0 (*c* 0.6, $CHCl_3$). ^1H NMR δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.37-7.26 (m, 7H), 4.90 (q, *J* = 5.8 Hz, 2H), 3.41 and 3.42 (two triplets, *J* = 6.1 Hz, 2H altogether), 2.76 (dq, *J* = 4.8, 7.3 Hz, 1H), 2.41 (s, 3H), 1.85-1.77 (m, 2H), 1.65-1.54 (m, 2H), 1.16 (d, *J* = 7.3 Hz, 3H); FT-IR (film) 3600-2200 (lump), 1712, 1599, 1498, 1455, 1363, 1189, 1098, 925 cm^{-1}; ESI-MS m/z 424.1 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{21}H_{26}O_6SNa$ ($[M+Na]^+$): 429.1342. Found: 429.1359.



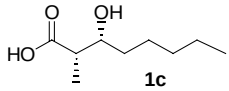
1b

Compound **1b**: A colorless oil. $[\alpha]^{27}_{D}$ +14.3 (*c* 3.1, $CHCl_3$). ^{1}H NMR δ 5.89 (ddt, *J* = 10.5, 17.3, 5.6 Hz, 1H), 5.27 (br d, *J* = 17.4 Hz, 2H), 5.21 (br d, *J* = 10.2 Hz, 1H), 4.07-3.97 (m, 3H), 3.74 (dt, *J* = 4.9, 7.2 Hz, 1H), 3.64 (dt, *J* = 4.0, 9.0 Hz, 1H), 2.53 (dt, *J* = 5.2, 9.1 Hz, 1H), 1.90-1.28 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H); FT-IR (film) 3600-2300 (lump), 3360, 1709, 1459, 1205, 1118, 991, 927 cm^{-1}; ESI-MS m/z 281.2 ($[M+Na]^+$), 259.2 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{14}H_{26}O_4Na$ ($[M+Na]^+$): 281.1723. Found: 281.1729.



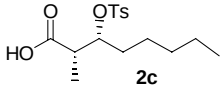
2b

Compound **2b**: A colorless oil. $[\alpha]^{26}_{D}$ +16.2 (*c* 0.8, $CHCl_3$). ^{1}H NMR δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.85 (ddt, *J* = 10.6, 17.5, 5.1 Hz 1H), 5.23 (br d, *J* = 17.2 Hz, 1H), 5.17 (br d, *J* = 10.1 Hz, 1H), 4.88 (q, *J* = 5.8 Hz, 1H), 3.84 (d, *J* = 5.5 Hz, 1H), 3.51-3.44 (m, 1H), 3.36-3.26 (m, 1H), 2.79 (dt, *J* = 5.0, 7.7 Hz, 1H), 2.44 (s, 3H), 1.99 (q, *J* = 5.8 Hz, 2H), 1.55-1.11 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); FT-IR (film) 3600-2300 (lump), 1712, 1599, 1456, 1369, 1177, 1097, 920 cm^{-1}; ESI-MS m/z 435.20 ($[M+Na]^+$). ESI-HRMS: Calcd for $C_{21}H_{32}O_6SNa$ ($[M+Na]^+$): 435.1812. Found: 435.1818.



1c

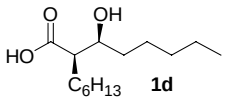
Compound **1c**: A colorless oil: $[\alpha]^{23}_{D}$ +8.13 (*c* 0.55, $CHCl_3$). ^{1}H NMR δ 6.20-5.40 (very br lump, 1H), 3.97 (m, 1H), 2.61 (dq, *J* = 7.1, 3.2 Hz, 1H), 1.49-1.31 (m, 8H), 1.20 (d, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.4 Hz, 3H). FT-IR (film) 3445, 1736, 1460, 1379, 1181 cm^{-1}. ESI-MS m/z: 197.1 ($[M+Na]^+$), 192.1($[M+NH_4]^+$). EI-HRMS calcd for $C_9H_{18}O_3$ (M^+) 174.1256; found 174.1243.



2c

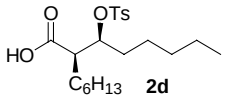
Compound **2c**: A colorless oil. $[\alpha]^{25}_{D}$ +10.9 (*c* 0.65, $CHCl_3$). ^{1}H NMR δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J*

= 8.1 Hz, 2H), 4.85 (dt, *J* = 10.2, 3.9 Hz 1H), 2.75 (dq, *J* = 7.1, 6.4 Hz, 1H), 2.45 (s, 3H), 1.76-1.70 (m, 1H), 1.64-1.56 (m, 1H), 1.33-1.16 (m, 9H), 0.83 (t, *J* = 6.6 Hz, 3H); FT-IR (film) 3600-2300 (lump), 1717, 1601, 1497, 1364, 1188, 1096, 908 cm^{-1}; ESI-MS m/z 346.2 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{16}H_{24}O_5SNa$ ($[M+Na]^+$): 351.1237. Found: 351.1237.



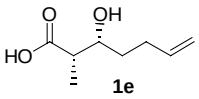
1d

Compound **1d**: A colorless oil. $[\alpha]^{27}_D$ –10.4 (*c* 2.7, $CHCl_3$). ^{1}H NMR δ 3.88-3.85 (m, 1H), 2.48 (dt, *J* = 10.0, 4.3 Hz, 1H), 1.73-1.24 (m, 15H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 6.4 Hz, 3H); FT-IR (film) 3700-2700 (lump), 3254, 1704, 1456, 1219, 701 cm^{-1}; ESI-MS m/z 262.4 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{14}H_{28}O_3Na$ ($[M+Na]^+$): 267.1931. Found: 267.1940.



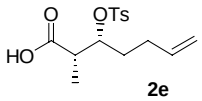
2d

Compound **2d**: A colorless oil. $[\alpha]^{25}_D$ –3.5 (*c* 0.4, $CHCl_3$). ^{1}H NMR δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.72 (dt, *J* = 4.5, 6.6 Hz, 1H), 2.69 (ddd, *J* = 4.1, 6.3, 10.1 Hz, 1H), 2.44 (s, 3H), 1.63-1.39 (m, 3H), 1.29-1.16 (m, 15H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); FT-IR (film) 3500-2400 (lump), 1710, 1599, 1460, 1364, 1188, 1072, 913 cm^{-1}; ESI-MS m/z 416.4 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{21}H_{34}O_5SNa$ ($[M+Na]^+$): 421.2019. Found: 421.2015.



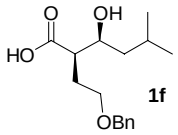
1e

Compound **1e**: A colorless oil. $[\alpha]^{26}_D$ +7.4 (*c* 1.05, $CHCl_3$). ^{1}H NMR δ 5.84 (ddt, *J* = 10.2, 16.9, 6.8 Hz, 1H), 5.07 (br d, *J* = 17.2 Hz, 1H), 5.00 (br d, *J* = 10.2 Hz, 1H), 3.96 (dt, *J* = 9.1, 3.8 Hz, 1H), 2.61 (dq, *J* = 3.6, 7.2 Hz, 1H), 2.33-2.10 (m, 2H), 1.69-1.47 (m, 2H), 1.22 (d, *J* = 7.6 Hz, 3H); FT-IR (film) 3600-2700 (lump), 3393, 1712, 1642, 1460, 1207, 916 cm^{-1}; ESI-MS m/z 181.2 ($[M+Na]^+$), 176.2 ($[M+NH_4]^+$). MALDI-HRMS: Calcd for $C_8H_{14}O_3Na$ ($[M+Na]^+$): 181.0835. Found: 181.0846.



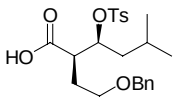
2e

Compound **2e**: A colorless oil. $[\alpha]^{25}_{D}$ +8.2 (*c* 0.95, $CHCl_3$). ^{1}H NMR δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 5.70 (ddt, *J* = 9.9, 17.8, 6.3 Hz, 1H), 5.03 (br d, *J* = 17.1 Hz, 1H), 4.97 (br d, *J* = 11.8 Hz, 1H), 4.88 (dt, *J* = 7.2, 5.1 Hz, 1H), 2.76 (dq, *J* = 5.2, 6.9 Hz, 1H), 2.45 (s, 3H), 2.08-1.72 (m, 4H), 1.17 (d, *J* = 6.9 Hz, 3H); FT-IR (film) 3700-2300 (lump), 1713, 1645, 1598, 1456, 1363, 1177, 1077, 918 cm^{-1}; ESI-MS m/z 330.1 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{15}H_{20}O_5SNa$ ($[M+Na]^+$): 335.0924. Found: 335.0937.



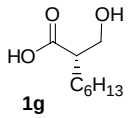
1f

Compound **1f**: A colorless oil. $[\alpha]^{27}_{D}$ –7.0 (*c* 3.34, $CHCl_3$). ^{1}H NMR δ 7.38-7.26 (m, 5H), 4.25 (s, 2H), 4.03-3.98 (m, 1H), 3.63-3.56 (m, 2H), 2.64 (dt, *J* = 8.0, 4.0 Hz, 1H), 2.12-2.00 (m, 1H), 1.95-1.88 (m, 1H), 1.84-1.76 (m, 1H), 1.49 (ddd, *J* = 4.2, 9.9, 13.9 Hz, 1H), 1.26-1.15 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H); FT-IR (film) 3700-2300 (lump), 3419, 1707, 1499, 1455, 1367, 1177, 1079, 738, 698 cm^{-1}; ESI-MS m/z 303.1 ($[M+Na]^+$), 281.2 ($[M+H]^+$), 176.2 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{16}H_{24}O_4Na$ ($[M+Na]^+$): 303.1567. Found: 303.1554.



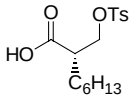
2f

Compound **2f**: A colorless oil. $[\alpha]^{27}_{D}$ –12.0 (*c* 0.6, $CHCl_3$). ^{1}H NMR δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.36-7.27 (m, 7H), 4.96 (dt, *J* = 8.7, 4.2 Hz, 1H), 4.46 (s, 2H), 3.55-3.46 (m, 2H), 2.92 (dt, *J* = 9.6, 4.5 Hz, 1H), 2.41 (s, 3H), 1.98-1.93 (m, 1H), 1.83-1.57 (m, 3H), 1.44-1.38 (m, 1H), 0.87 (d, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 7.5 Hz, 3H); FT-IR (film) 3600-2300 (lump), 1712, 1599, 1499, 1454, 1360, 1176, 1097, 925, 888 cm^{-1}; ESI-MS m/z 452.1 ($[M+NH_4]^+$), 435.1 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{23}H_{30}O_6SNa$ ($[M+Na]^+$): 457.1655. Found: 457.1668.



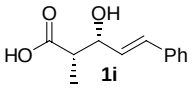
1g

Compound **1g**: A colorless oil. $[\alpha]^{27}_{D}$ +3.0 (*c* 2.28, $CHCl_3$). ^{1}H NMR δ 6.80-6.20 (lump, 2H), 3.79 (d, *J* = 6.2 Hz, 2H), 2.62 (br quint, *J* = 6.2 Hz, 1H), 1.86-60 (m, 1H), 1.60-1.44 (m, 1H), 1.44-1.20 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H); FT-IR (film) 3700-2300 (lump), 3369, 1710, 1467, 1199, 1032 cm^{-1}; ESI-MS m/z 192.3 ($[M+NH_4]^+$). MALDI-HRMS: Calcd for $C_9H_{18}O_3Na$ ($[M+Na]^+$): 197.1148. Found: 197.1160.



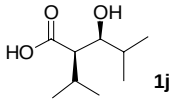
2g

Compound **2g**: A colorless oil. $[\alpha]^{26}_{D}$ +3.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 7H), 4.17 (dd, *J* = 9.6, 7.8 Hz, 1 H), 2.74 (quint, *J* = 6.7 Hz, 1H), 2.46 (s, 3H), 1.60-1.47 (m, 2H), 1.28-1.24 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); FT-IR (film) 3700-2300 (lump), 1713, 1599, 1498, 1463, 1366, 1177, 1097, 974, 815 cm^{-1}; ESI-MS m/z 346.2 ($[M+NH_4]^+$), 435.1 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{16}H_{24}O_5SNa$ ($[M+Na]^+$): 351.1237. Found: 351.1246.



1i

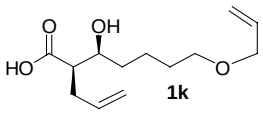
Compound **1i**: A colorless oil. $[\alpha]^{27}_{D}$ +2.8 (*c* 0.2, $CHCl_3$). ^{1}H NMR δ 7.41-7.25 (m, 5H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.21 (dd, *J* = 6.0, 16.0 Hz, 1H), 5.8-4.8 (lump, 2H, 2OH's), 4.66-4.63 (m, 1H), 2.81 (dq, *J* = 3.9, 7.3 Hz, 2H), 1.26 (d, *J* = 7.1 Hz, 3H); FT-IR (film) 3700-2300 (lump), 3400, 1705, 1498, 1207, 967 cm^{-1}; ESI-MS m/z 229.1 ($[M+Na]^+$). MALDI-HRMS: Calcd for $C_{12}H_{14}O_3Na$ ($[M+Na]^+$): 229.0835. Found: 229.0844.



1j

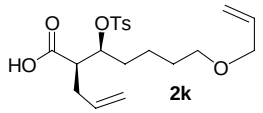
Compound **1j**: A colorless oil. $[\alpha]^{27}_{D}$ +7.7 (*c* 0.55, $CHCl_3$). ^{1}H NMR δ 3.43 (dd, *J* = 8.6, 3.5 Hz, 1H), 2.31 (dd, *J* = 3.5, 9.4 Hz, 1H), 2.21-2.09 (m, 1H) 1.69-1.58 (m, 1H), 1.10-0.92 (several doublets stemming from different conformers with an average *J* = 6.8 Hz, 12H altogether); FT-IR (film of conc. solution in CH_2Cl_2)

3299, 1679, 1290, 1007 cm^{-1}; ESI-MS m/z 197.2 ($[M+Na]^+$), 192.3 ($[M+NH_4]^+$). MALDI-HRMS: Calcd for $C_9H_{18}O_3Na$ ($[M+Na]^+$): 197.1148. Found: 197.1161.



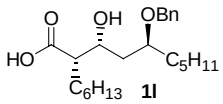
1k

Compound **1k**: A colorless oil. $[\alpha]^{25}_D$ –7.9 (*c* 0.4, $CHCl_3$). ^1H NMR δ 5.89 (ddt, *J* = 10.2, 17.3, 5.6 Hz, 1H), 5.83 (ddt, *J* = 10.1, 17.0, 6.9 Hz, 1H), 5.28 (br d, *J* = 17.5 Hz, 1H), 5.19 (br d, *J* = 10.4 Hz, 1H), 5.12 (br d, *J* = 16.9 Hz, 1H), 5.06 (br d, *J* = 10.3 Hz, 1H), 3.97 (br d, *J* = 5.8 Hz, 2H), 3.90 (q, *J* = 5.3 Hz, 1H), 3.46 (br t, *J* = 6.2 Hz, 2H), 2.26 (dt, *J* = 4.9, 6.8 Hz, 1H), 2.55-2.44 (m, 1H), 2.41-2.33 (m, 1H), 1.67-1.42 (m, 6H); FT-IR (film) 3600-2300 (lump), 3402, 1709, 1642, 1460, 1082, 917 cm^{-1}; ESI-MS m/z 265.2 ($[M+Na]^+$), 243.3 ($[M+H]^+$). MALDI-HRMS: Calcd for $C_{13}H_{22}O_4Na$ ($[M+Na]^+$): 265.1410. Found: 265.1422.



2k

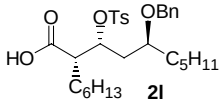
Compound **2k**: A colorless oil. $[\alpha]^{25}_D$ –10.7 (*c* 0.3, $CHCl_3$). ^1H NMR δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 7H), 5.89 (ddt, *J* = 11.4, 17.4, 5.1 Hz, 1 H), 5.69 (ddt, *J* = 10.5, 17.1, 6.6 Hz, 1H), 5.25 (br d, *J* = 17.1 Hz, 1H), 5.20 (br d, *J* = 10 Hz, 1H), 5.18 (br d, *J* = 17 Hz, 1H), 5.04 (br d, *J* = 10 Hz, 1H), 4.78 (dt, *J* = 4.5, 6.6 Hz, 1H), 3.93 (dt, *J* = 5.7, 1.2 Hz, 1H), 3.33 (t, *J* = 6.5 Hz, 2H), 2.83 (dt, *J* = 9.4, 5.9 Hz, 1H), 2.45 (s, 3H), 2.40-1.27 (m, 2H), 1.73-1.62 (m, 3H), 1.50-1.42 (m, 3H); FT-IR (film) 3600-2300 (lump), 1712, 1639, 1459, 1370, 1237, 1177, 917 cm^{-1}; ESI-MS m/z 414.1 ($[M+NH_4]^+$), 397.2 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{20}H_{28}O_6SNa$ ($[M+Na]^+$): 419.1499. Found: 419.1506.



1l

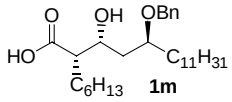
Compound **1l**: A colorless oil. $[\alpha]^{27}_D$ +11.6 (*c* 3.1, $CHCl_3$). ^1H NMR δ 7.44-7.26 (m, 5H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.20-4.10 (m, 1H), 3.77-3.73 (m, 1H), 2.50 (dt, *J* = 4.7, 7.3 Hz, 1H),

1.87-1.29 (m, 20H), 0.88 (t, *J* = 6.4 Hz, 3H); FT-IR (film) 3600-2300 (lump), 3419, 1705, 1445, 1207, 734, 698 cm^{-1}; ESI-MS m/z 379.2 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{23}H_{38}O_4Na$ ($[M+Na]^+$): 401.2662. Found: 401.2653.



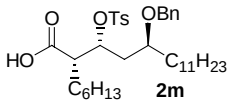
2l

Compound **2l**: A colorless oil. $[\alpha]^{27}_D$ +22.4 (*c* 2.0, $CHCl_3$). ^1H NMR δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 7H), 7.32-7.26 (m, 5H), 5.07 (ddd, *J* = 2.7, 4.8, 7.4 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.29 (d, *J* = 10.9 Hz, 1H), 3.50-3.45 (m, 1H), 2.76 (dt, *J* = 4.9, 7.2 Hz, 1H), 2.41 (s, 3H), 1.90-1.81 (m, 2H), 1.59-1.19 (m, 18H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); FT-IR (film) 3600-2300 (lump), 1709, 1600, 1499, 1455, 1367, 1177, 906 cm^{-1}; ESI-MS m/z 550.2 ($[M+NH_4]^+$), 397.2 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{30}H_{44}O_6SNa$ ($[M+Na]^+$): 555.2751. Found: 555.2732.



1m

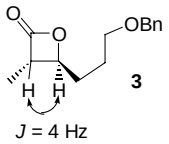
Compound **1m**: A colorless oil. $[\alpha]^{28}_D$ +12.3 (*c* 0.15, $CHCl_3$). ^1H NMR δ 7.38-7.24 (m, 5H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.18-4.13 (m, 1H), 3.79-3.74 (m, 1H), 2.49 (br dt, *J* = 9.2, 4.8 Hz, 1H), 1.86-1.02 (m, 32H), 0.88 (not fully resolved t, *J* = 5 Hz, 3H); FT-IR (film) 3600-2400 (lump), 3448, 1707, 1458, 1206, 1069, 733, 697 cm^{-1}; ESI-MS m/z 463.0 ($[M+H]^+$). MALDI -HRMS: Calcd for $C_{29}H_{50}O_4Na$ ($[M+Na]^+$): 485.3601. Found: 485.3599.



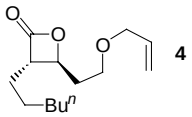
2m

Compound **2m**: A colorless oil. $[\alpha]^{27}_D$ +18.9 (*c* 0.9, $CHCl_3$). ^1H NMR δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.37-7.27 (m, 7H), 5.08 (ddd, *J* = 2.3, 4.6, 7.1 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.30 (d, *J* = 11.2 Hz, 1H), 3.50-3.46 (m, 1H), 2.77 (dt, *J* = 4.7, 7.1 Hz, 1H), 2.42 (s, 3H), 1.85-1.73 (m, 2H), 1.70-1.10 (m, 30H), 0.89 (t, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H); FT-IR (film) 3600-2300 (lump), 1712, 1599, 1498, 1455, 1366, 1178, 1097, 996, 906, 766 cm^{-1}; ESI-MS m/z 639.55 ($[M+Na]^+$). ESI-HRMS: Calcd for $C_{36}H_{56}O_6SNa$ ($[M+Na]^+$):

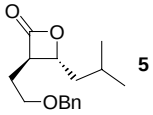
639.3690. Found: 639.3696.



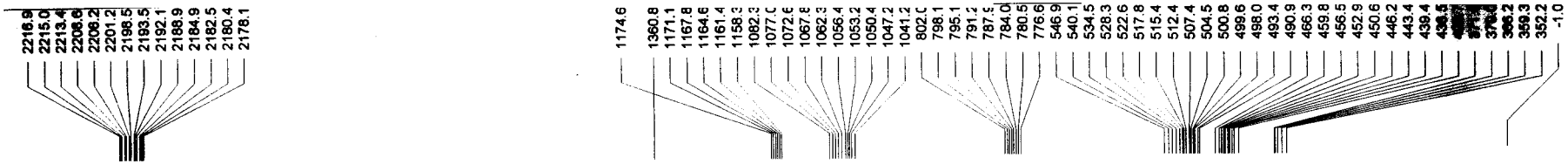
Compound **3**: A colorless oil. $[\alpha]^{24}_{D}$ –14.5 (*c* 0.25, $CHCl_3$). ^{1}H NMR δ 7.38-7.26 (m, 5H), 4.51 (s, 2H), 4.21 (dt, *J* = 3.9, 6.5 Hz, 1H), 3.60-3.45 (m, 2H), 3.23 (dq, *J* = 4.0, 7.5 Hz, 1H), 1.93 (br q, *J* = 7.3 Hz, 2H), 1.89-1.66 (m, 2H), 1.36 (d, *J* = 7.6 Hz, 3H); FT-IR (film) 1823, 1598, 1495, 1455, 1362, 1178, 993 cm^{-1}; ESI-MS m/z 235.1 ($[M+H]^+$). ESI-HRMS: Calcd for $C_{14}H_{18}O_3Na$ ($[M+Na]^+$): 257.1148. Found: 257.1138.

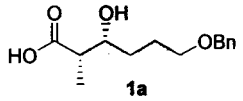


Compound **4**: A colorless oil. $[\alpha]^{26}_{D}$ –15.9 (*c* 0.4, $CHCl_3$). ^{1}H NMR δ 5.90 (ddt, *J* = 10.6, 17.3, 5.4 Hz, 1H), 5.28 (br d, *J* = 16.8 Hz, 1H), 5.20 (br d, *J* = 10.9 Hz, 1H), 4.42 (dt, *J* = 4.0, 6.5 Hz, 1H), 3.98 (d, *J* = 5.7 Hz, 2H), 3.62-3.51 (m, 2H), 3.31 (ddd, *J* = 4.1, 7.1, 8.4 Hz, 1H), 2.13-2.04 (m, 2H), 1.85-1.72 (m, 2H), 1.47-1.26 (m, 8H), 0.89 (t, *J* = 6.1 Hz, 3H); FT-IR (film) 1824, 1649, 1465, 1119 cm^{-1}; ESI-MS m/z 258.2 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{14}H_{24}O_3Na$ ($[M+Na]^+$): 263.1618. Found: 263.1611.

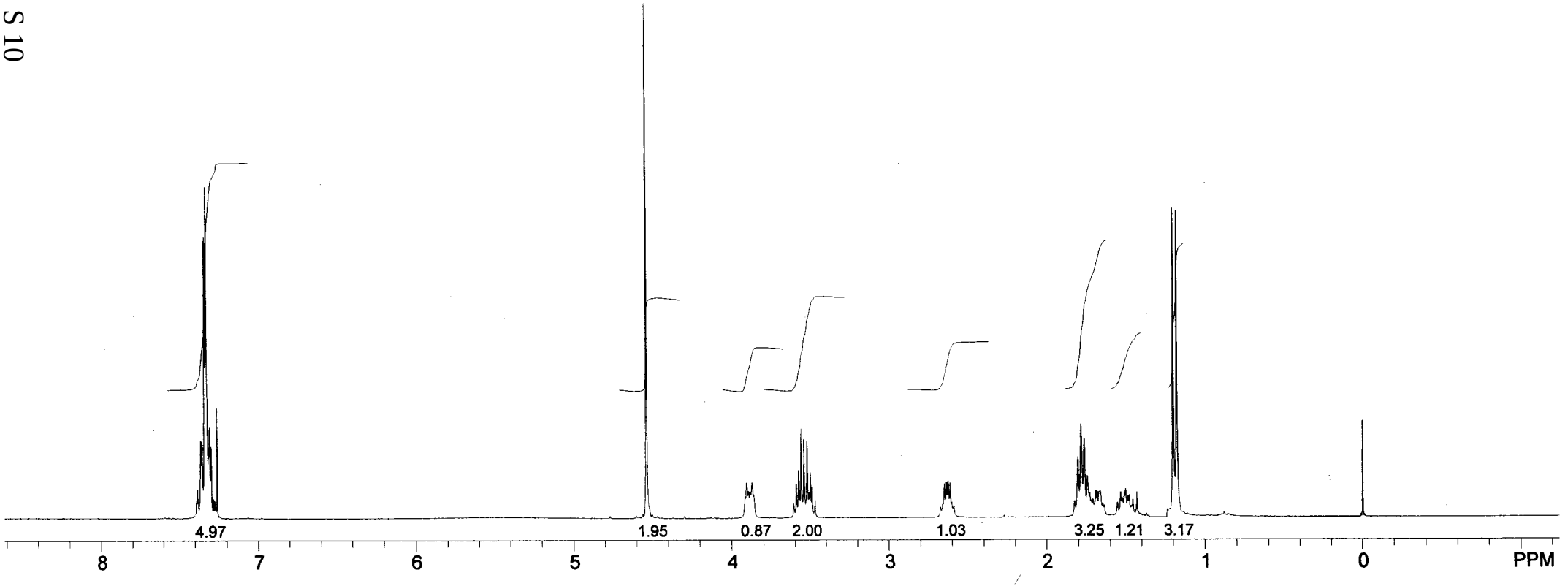


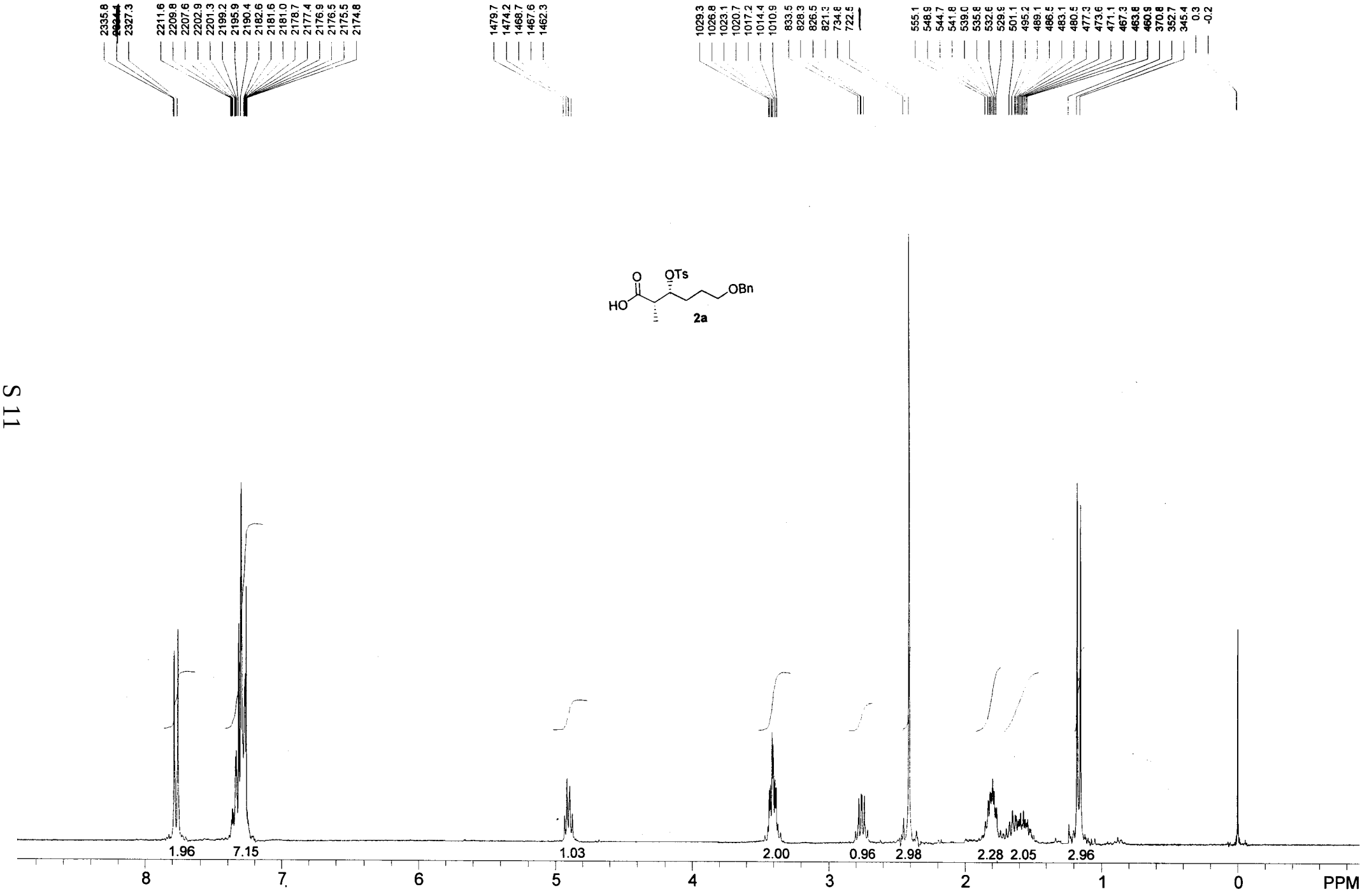
Compound **5**: A colorless oil. $[\alpha]^{27}_{D}$ +7.3 (*c* 0.2, $CHCl_3$). ^{1}H NMR δ 4.50 (s, 2H), 4.42 (dt, *J* = 4.3, 6.3 Hz, 1H), 3.66-3.53 (m, 2H), 3.36-3.25 (m, 1H), 2.13-2.06 (m, 2H), 1.76-1.56 (m, 3H), 0.92 (d, *J* = 6.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); FT-IR (film) 1822, 1600, 1454, 1119, 893 cm^{-1}; ESI-MS m/z 280.1 ($[M+NH_4]^+$). ESI-HRMS: Calcd for $C_{16}H_{22}O_3Na$ ($[M+Na]^+$): 285.1461. Found: 285.1465.

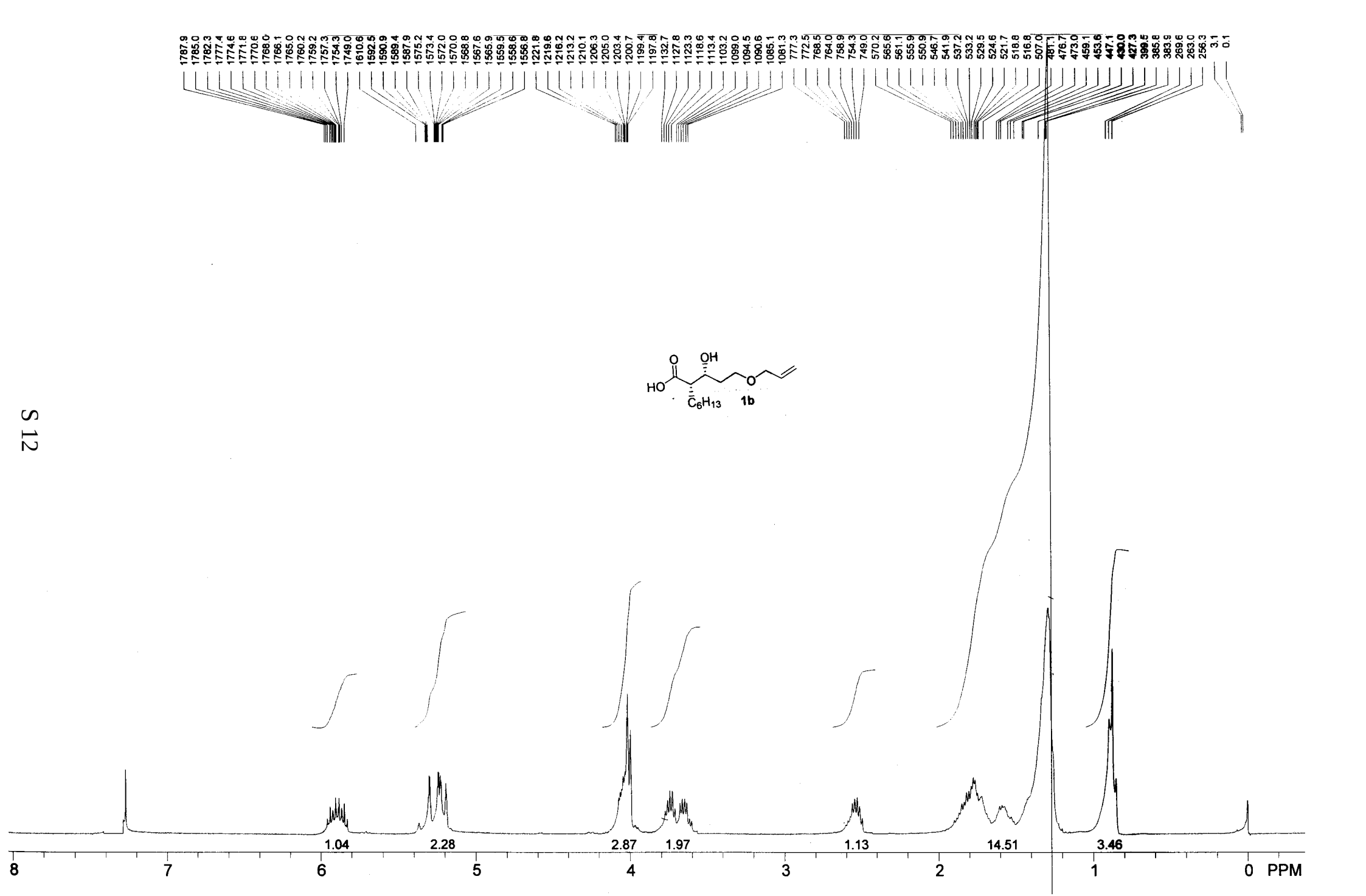


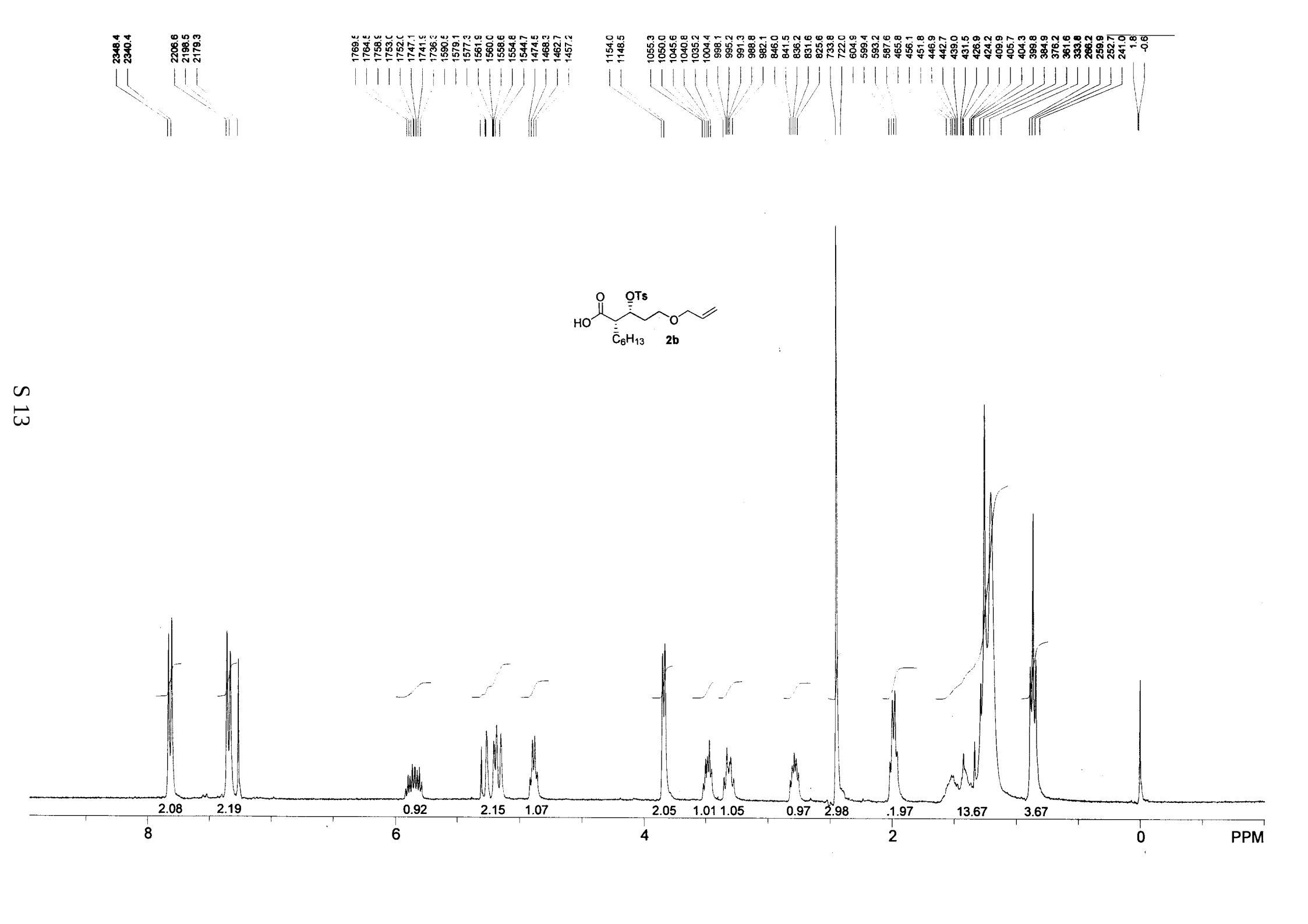


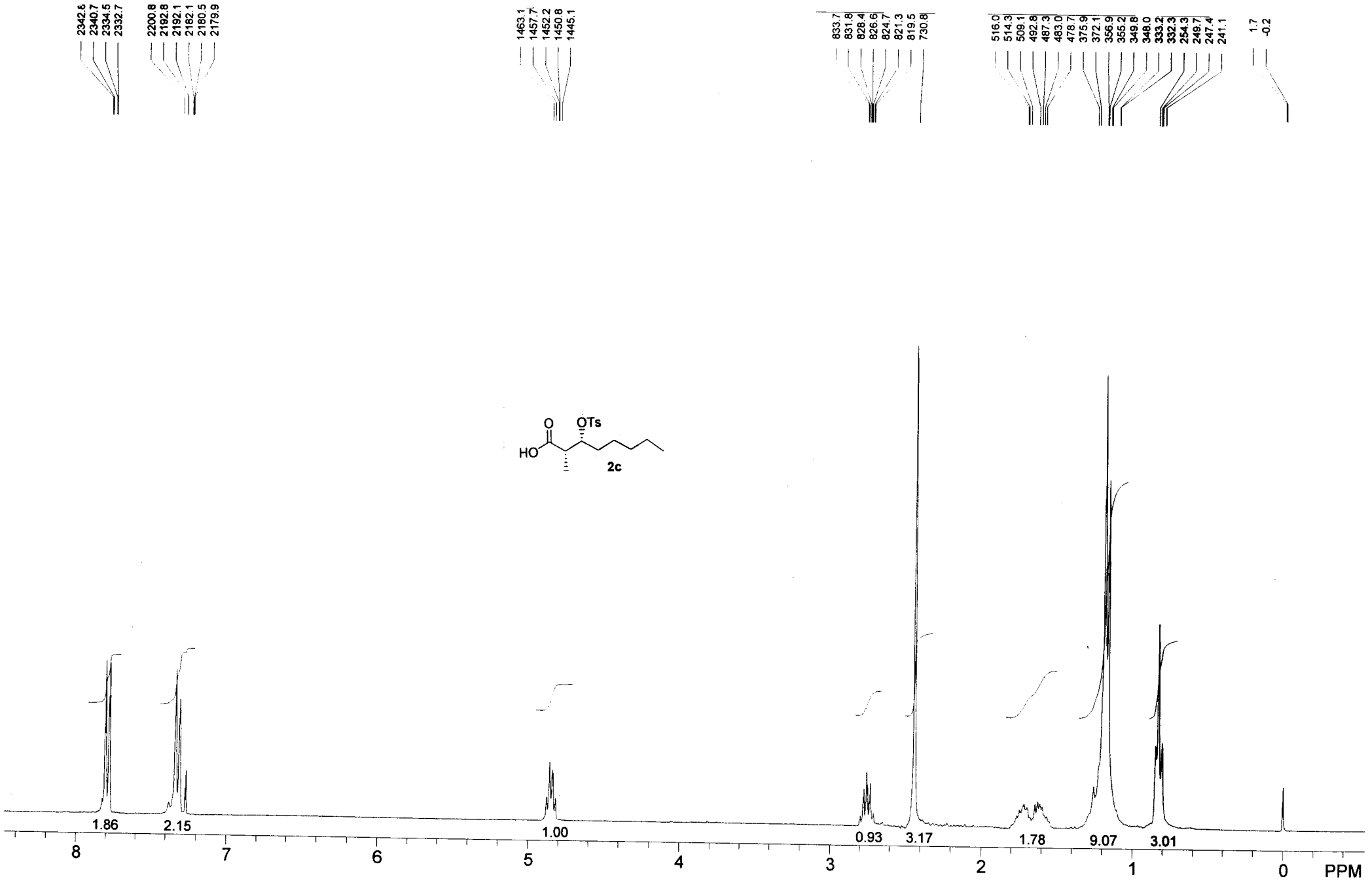
1a

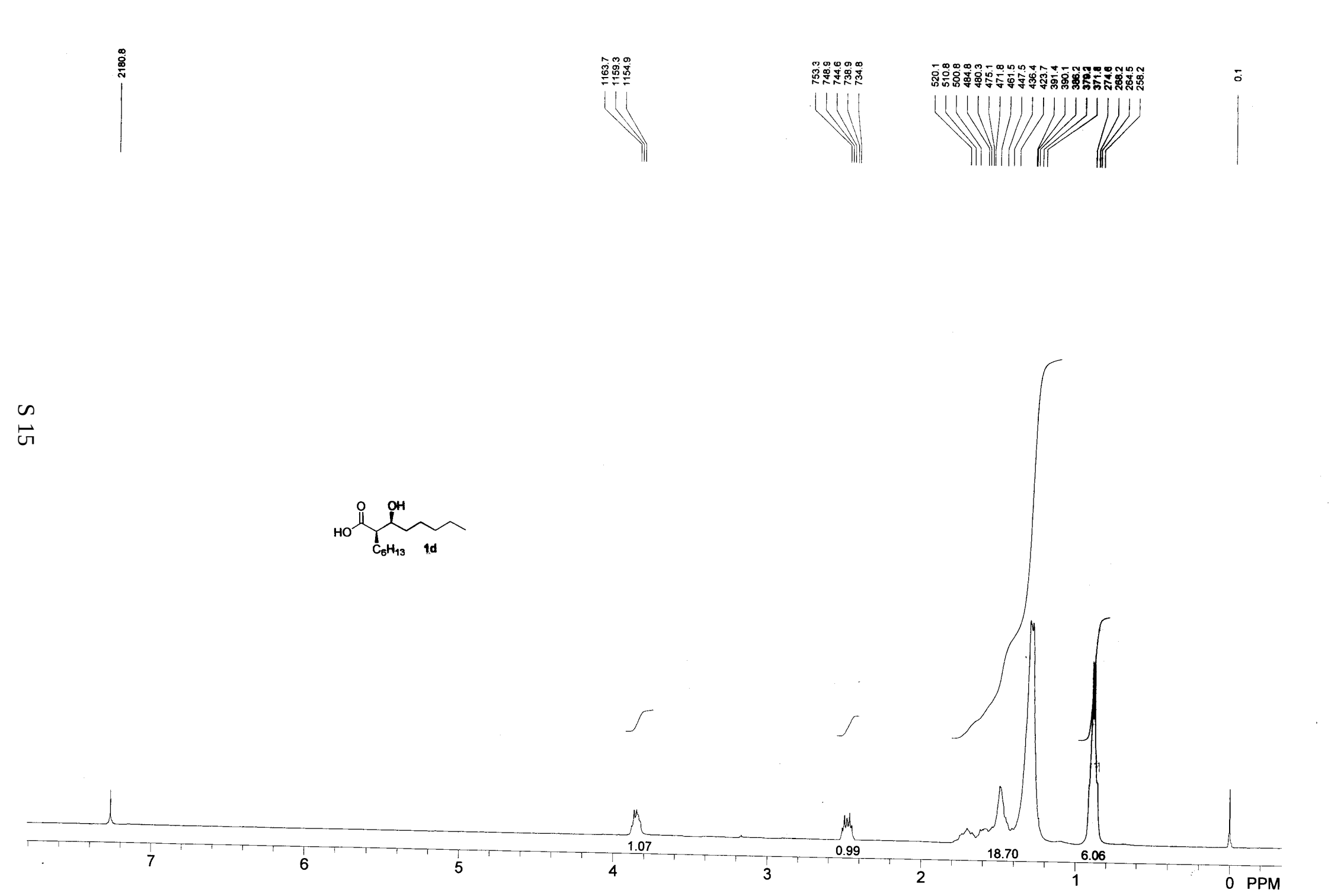


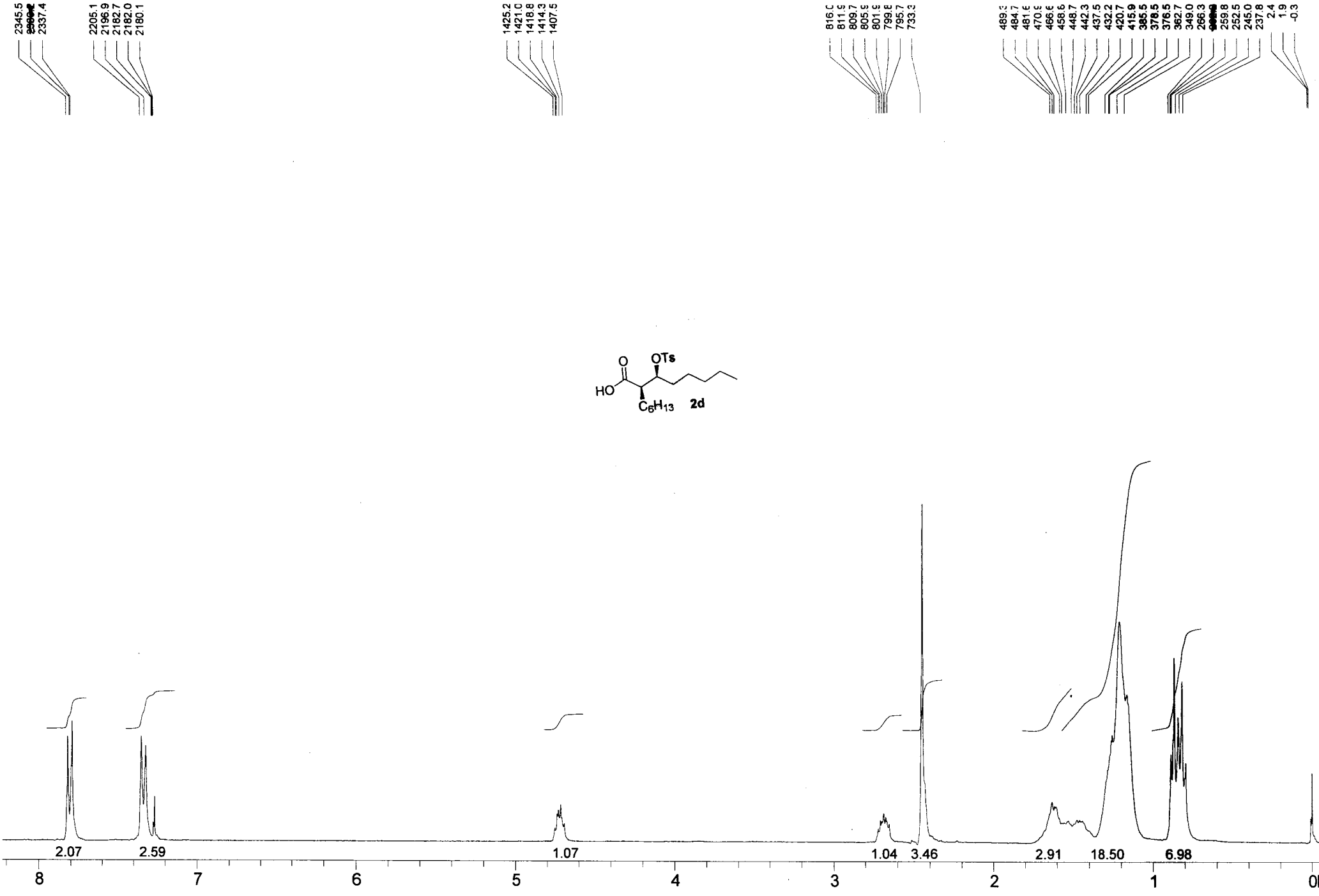

2335.8
2327.3
2211.6
2209.8
2207.6
2202.9
2201.3
2199.2
2195.9
2190.4
2182.6
2181.6
2181.0
2178.7
2177.4
2176.9
2176.5
2175.5
2174.8
1479.7
1474.2
1468.7
1467.6
1462.3
1029.3
1026.8
1023.1
1020.7
1017.2
1014.4
1010.9
833.5
828.3
826.5
722.5
555.1
548.9
544.7
541.8
539.0
535.8
532.6
501.1
495.2
489.1
483.1
477.3
473.6
471.1
467.3
460.9
370.8
352.7
345.4
0.3
-0.2
HO
O
OTs
OBn
2a
1.96
7.15
1.03
2.00
0.96
2.98
2.28
2.05
2.96
8
7
6
5
4
3
2
1
0
PPM

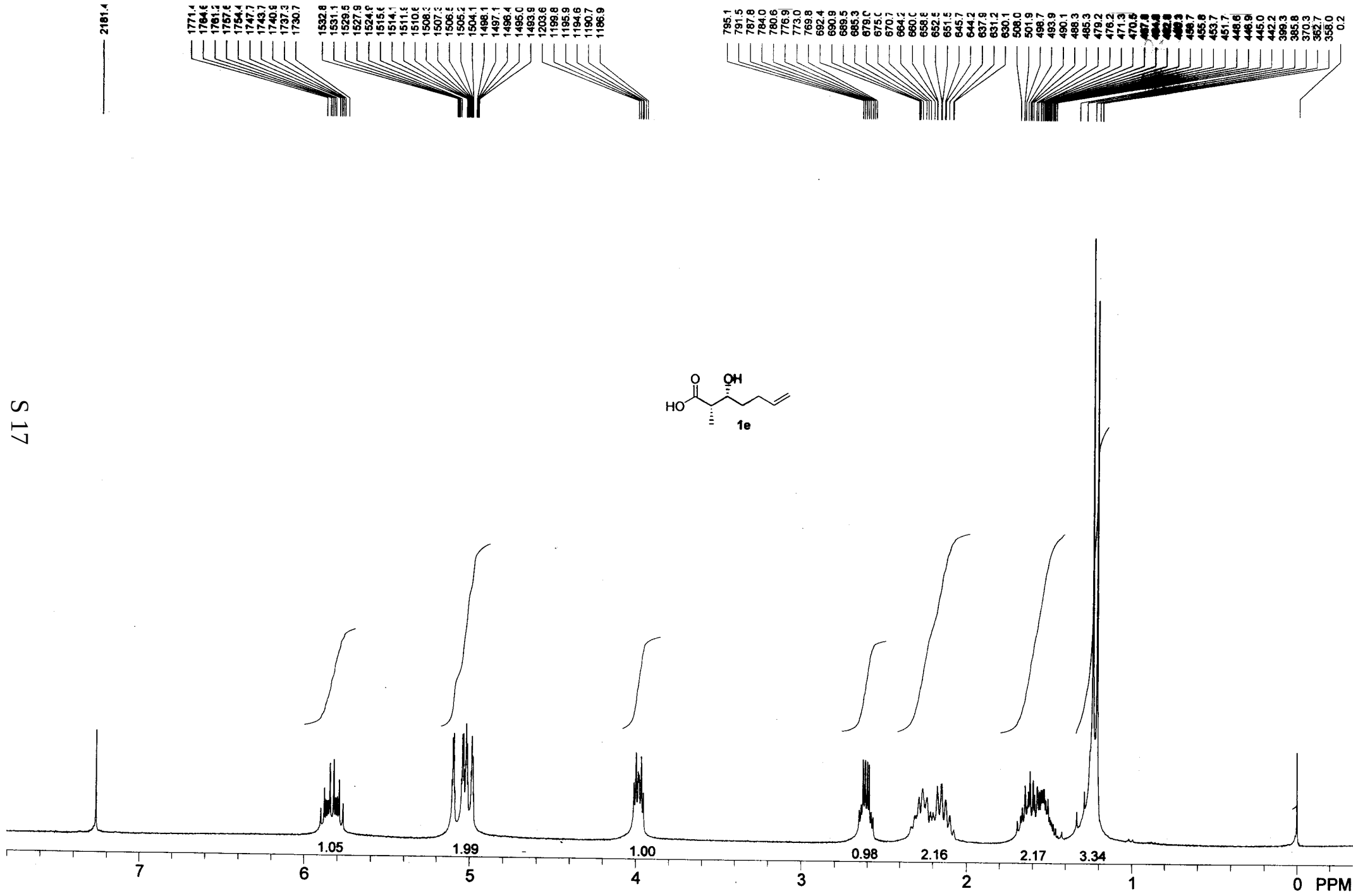

1787.9
1785.0
1782.3
1777.4
1774.6
1771.8
1770.6
1768.0
1766.1
1765.0
1760.2
1759.2
1757.3
1754.3
1749.0
1610.6
1592.5
1590.9
1589.4
1587.9
1575.2
1573.4
1572.0
1570.0
1568.8
1567.6
1565.9
1559.5
1558.6
1556.8
1221.8
1219.6
1216.2
1213.2
1210.1
1206.3
1205.0
1203.4
1200.7
1199.4
1197.8
1132.7
1127.8
1123.3
1118.6
1113.4
1103.2
1099.0
1094.5
1090.6
1085.1
1081.3
777.3
772.5
768.5
764.0
758.9
754.3
749.0
570.2
565.6
561.1
555.9
550.9
546.7
541.9
537.2
533.2
529.5
524.6
521.7
518.8
516.8
507.0
481.1
476.7
473.0
459.1
453.6
447.1
430.0
427.3
399.5
385.8
383.9
269.6
263.0
256.3
3.1
0.1
HO
O
OH
O
C6H13
1b
1.04
2.28
2.87
1.97
1.13
14.51
3.46
8
7
6
5
4
3
2
1
0
PPM

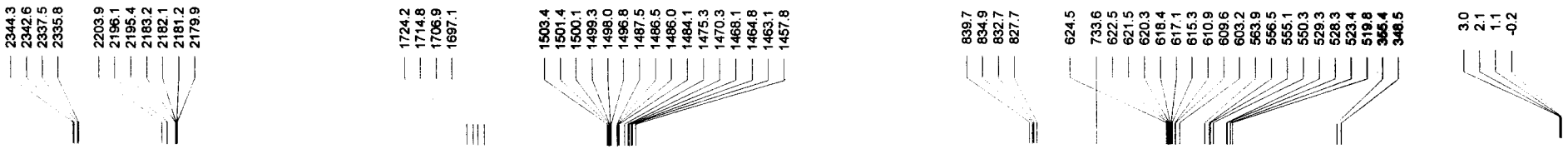

2348.4
2340.4
2206.6
2198.5
2179.3
1769.5
1764.5
1758.9
1753.0
1752.0
1747.1
1741.9
1736.3
1590.5
1579.1
1577.3
1561.9
1560.0
1558.6
1554.8
1544.7
1474.5
1468.3
1462.7
1457.2
1154.0
1148.5
1055.3
1050.0
1045.6
1040.8
1035.2
1004.4
998.1
995.2
991.3
988.8
982.1
846.0
841.5
836.2
831.6
825.6
733.8
722.0
604.9
599.4
593.2
587.6
465.8
456.1
451.8
446.9
442.7
439.0
431.5
426.9
424.2
409.9
405.7
404.3
399.8
384.9
376.2
361.6
333.8
266.2
259.9
252.7
241.0
1.8
-0.6
HO
O
OTs
C6H13
2b
2.08
2.19
0.92
2.15
1.07
2.05
1.01
1.05
0.97
2.98
1.97
13.67
3.67
8
6
4
2
0
PPM

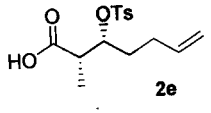

2342.6
2340.7
2334.5
2332.7
2200.8
2192.8
2192.1
2182.1
2180.5
2179.9
1463.1
1457.7
1452.2
1450.8
1445.1
833.7
831.8
828.4
826.6
824.7
821.3
819.5
730.8
516.0
514.3
509.1
492.8
487.3
483.0
478.7
375.9
372.1
356.9
355.2
349.8
348.0
333.2
332.3
254.3
249.7
247.4
241.1
1.7
-0.2
O
OTs
HO
2c
1.86
2.15
1.00
0.93
3.17
1.78
9.07
3.01
8
7
6
5
4
3
2
1
0
PPM


2180.8
1163.7
1159.3
1154.9
753.3
748.9
744.6
738.9
734.8
520.1
510.8
500.8
484.8
480.3
475.1
471.8
461.5
447.5
436.4
423.7
391.4
390.1
0.1
HO
O
OH
C6H13
1d
1.07
0.99
18.70
6.06
7
6
5
4
3
2
1
0
PPM

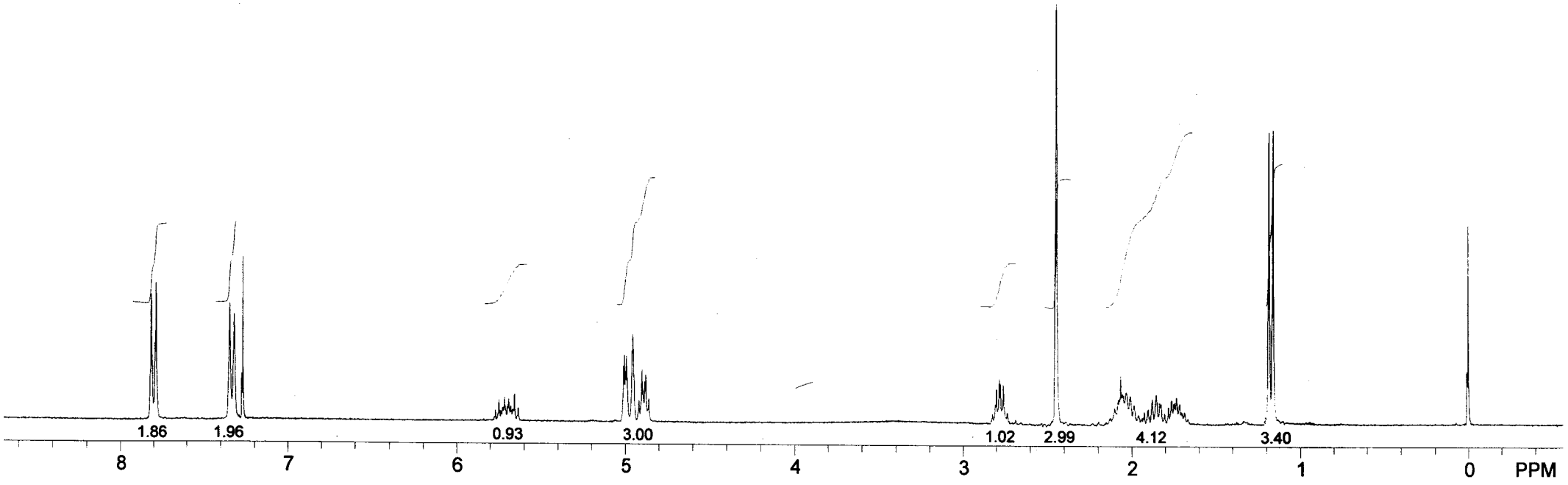

2345.5
2337.4
2205.1
2196.9
2182.7
2182.0
2180.1
1425.2
1421.0
1418.8
1414.3
1407.5
816.0
811.9
809.7
805.9
801.9
799.8
795.7
733.3
489.3
484.7
481.6
470.9
466.6
458.6
448.7
442.3
437.5
432.2
420.7
415.9
385.5
378.5
376.5
362.7
349.0
266.3
259.8
252.5
245.0
237.8
2.4
1.9
-0.3
HO
O
OTs
C6H13
2d
2.07
2.59
1.07
1.04
3.46
2.91
18.50
6.98
8
7
6
5
4
3
2
1
0PPM

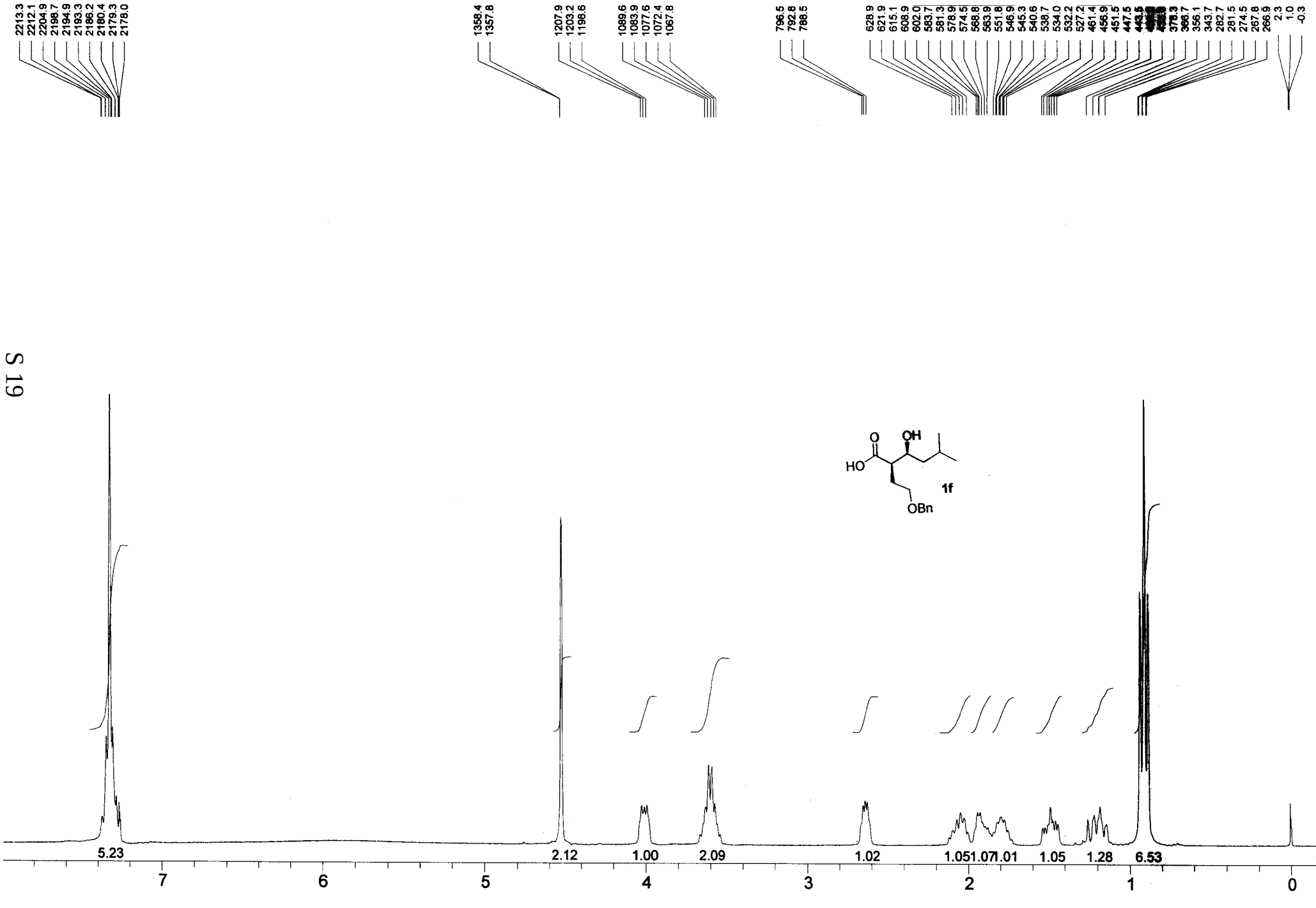

HO
O
OH
1e
1.05
1.99
1.00
0.98
2.16
2.17
3.34
7
6
5
4
3
2
1
0
PPM

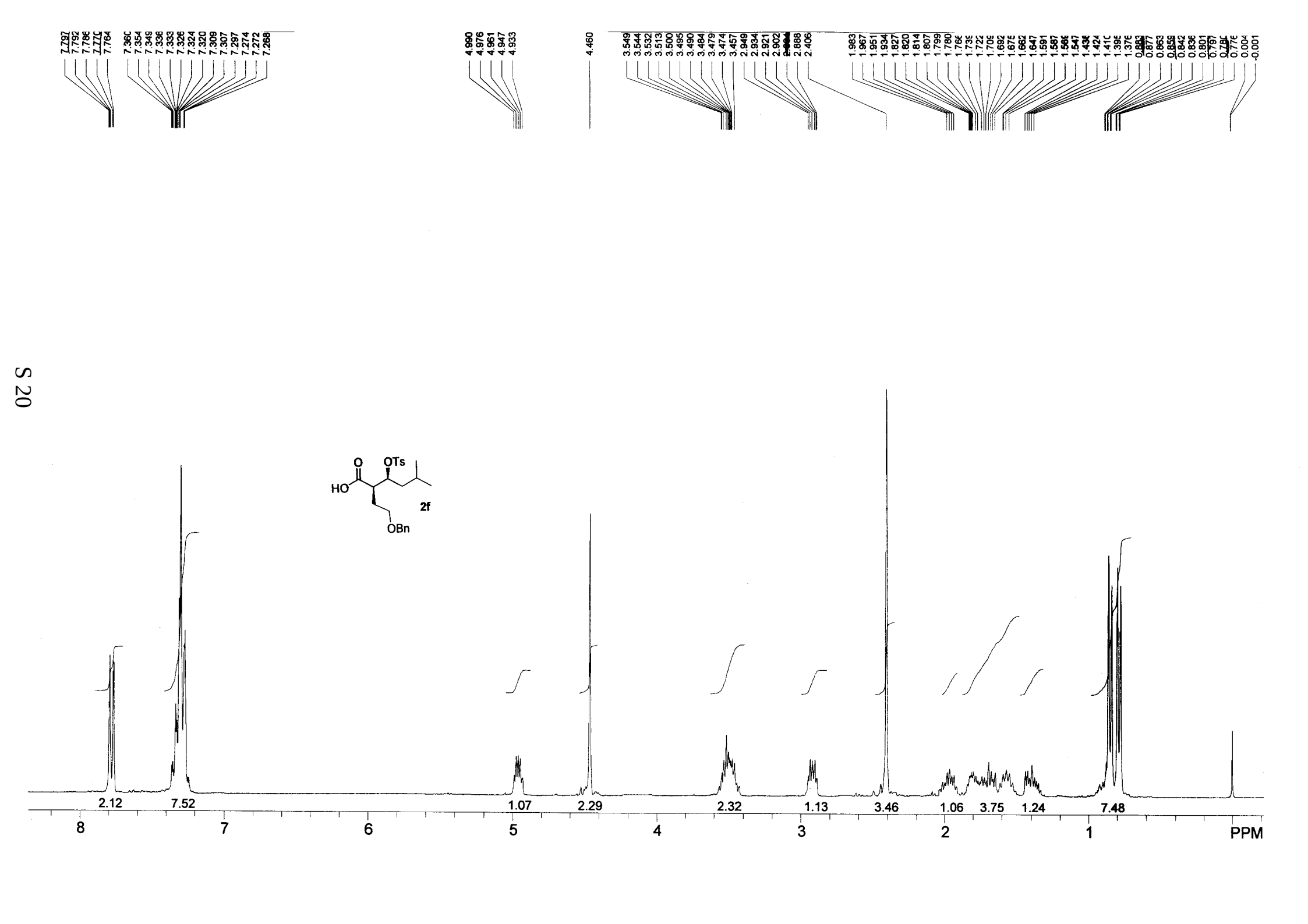

2344.3
2342.6
2337.5
2335.8
2203.9
2196.1
2195.4
2183.2
2182.1
2181.2
2179.9
1724.2
1714.8
1706.9
1697.1
1503.4
1501.4
1500.1
1499.3
1498.0
1496.8
1487.5
1486.5
1486.0
1484.1
1475.3
1470.3
1468.1
1464.8
1463.1
1457.8
839.7
834.9
832.7
827.7
624.5
733.6
622.5
621.5
620.3
618.4
617.1
615.3
610.9
609.6
603.2
563.9
556.5
555.1
550.3
529.3
528.3
523.4
519.8
3.0
2.1
1.1
-0.2

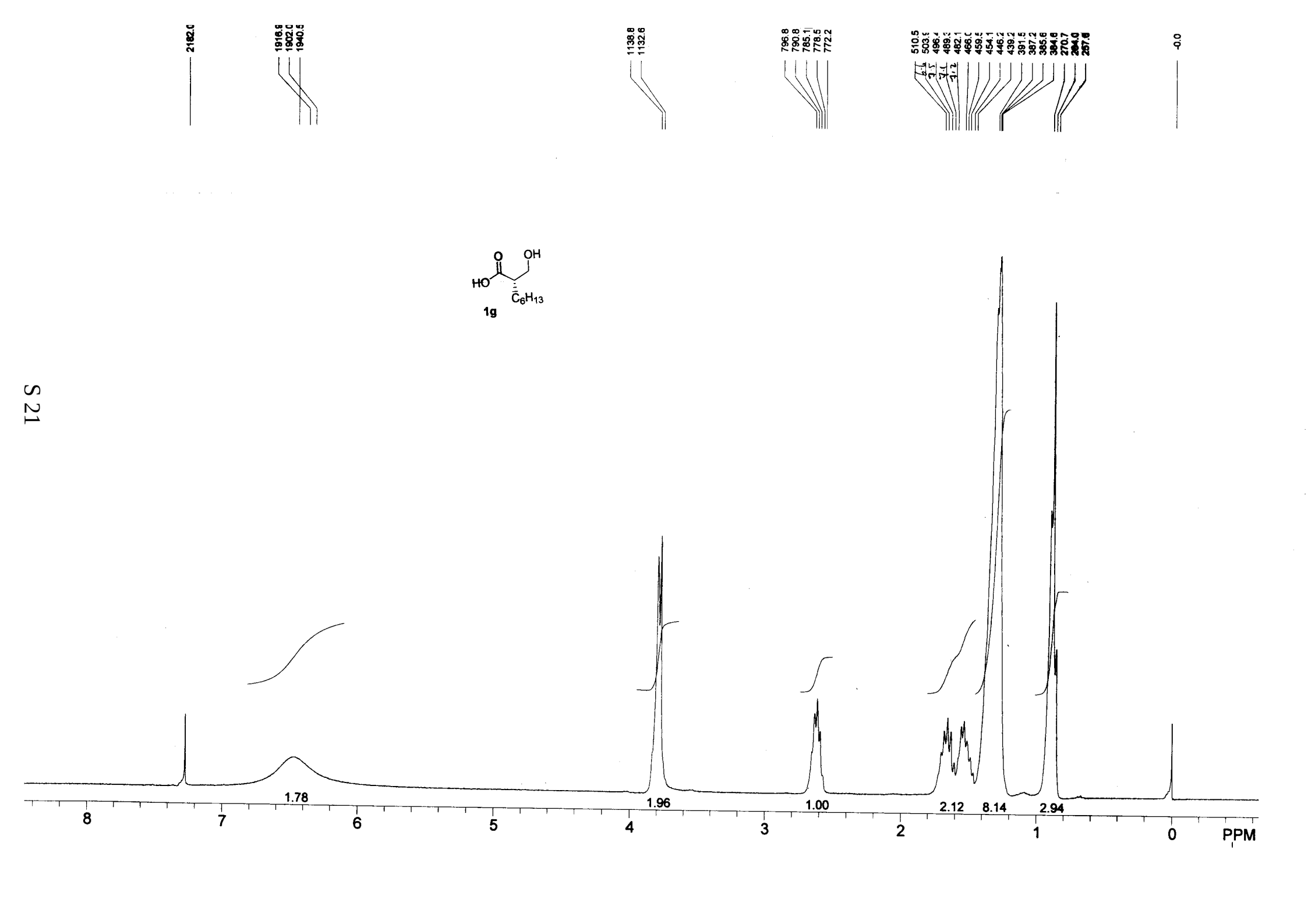

O
OTs
HO

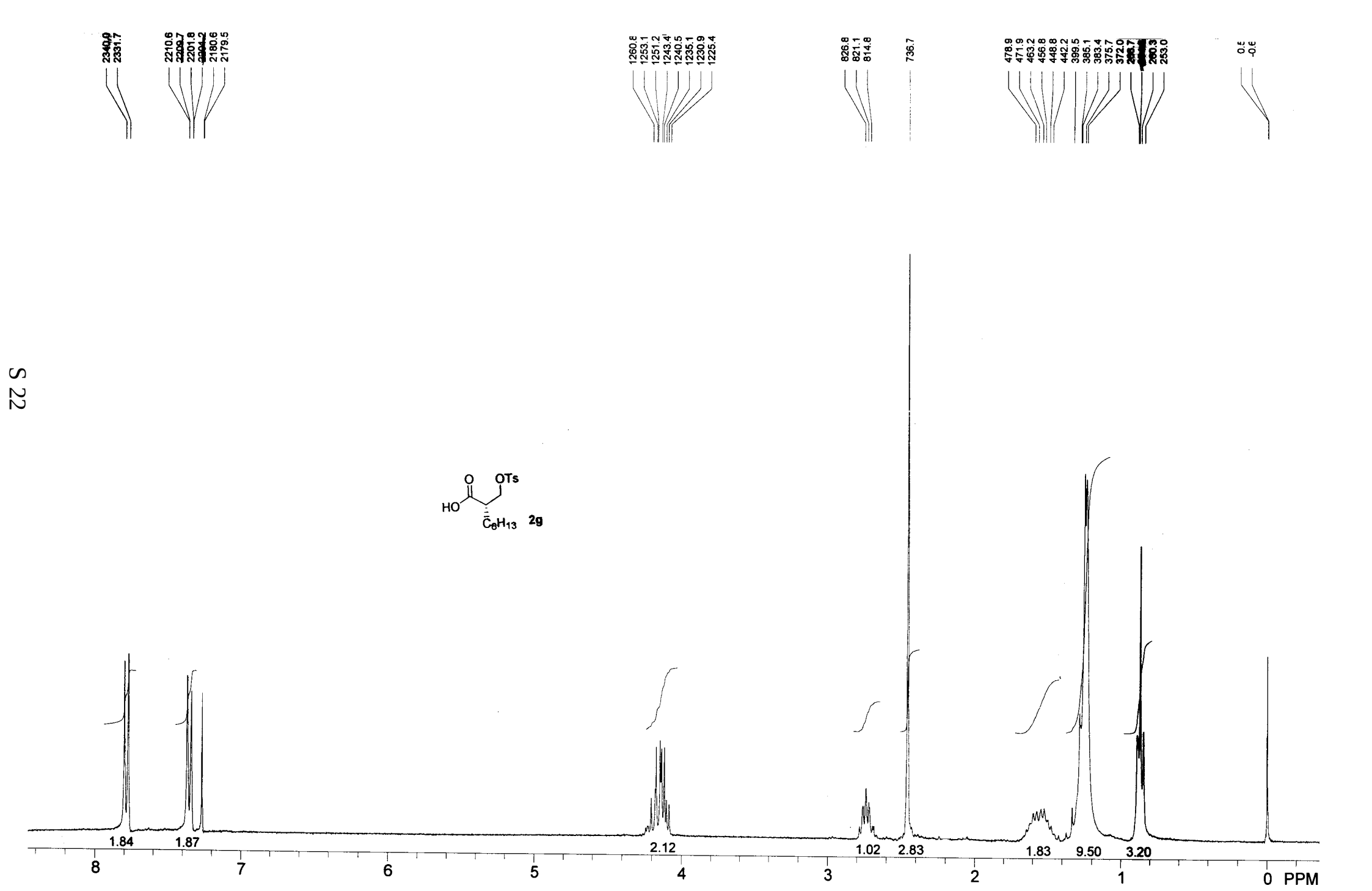
2e

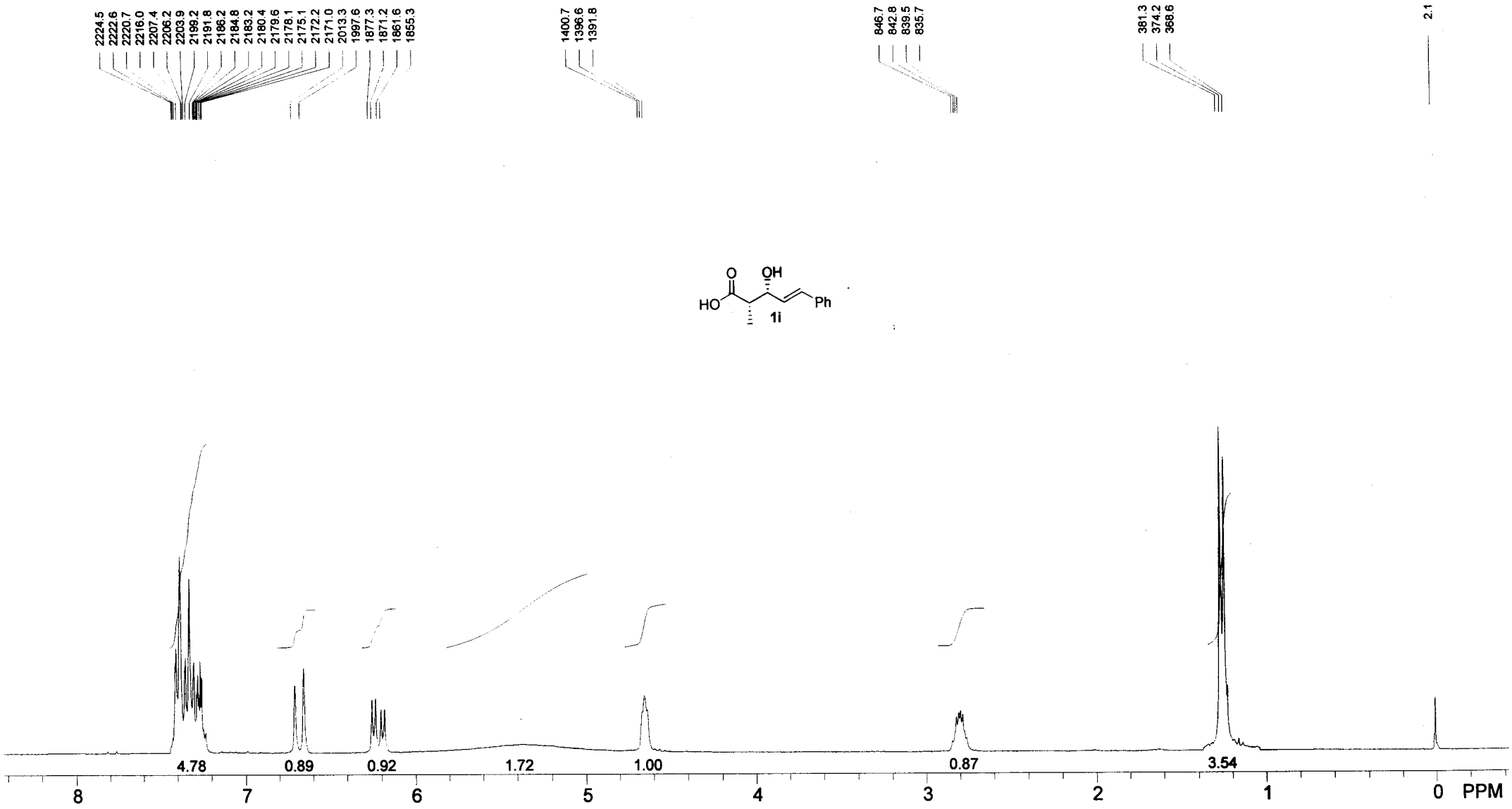

1.86
1.96
0.93
3.00
1.02
2.99
4.12
3.40
8
7
6
5
4
3
2
1
0
PPM

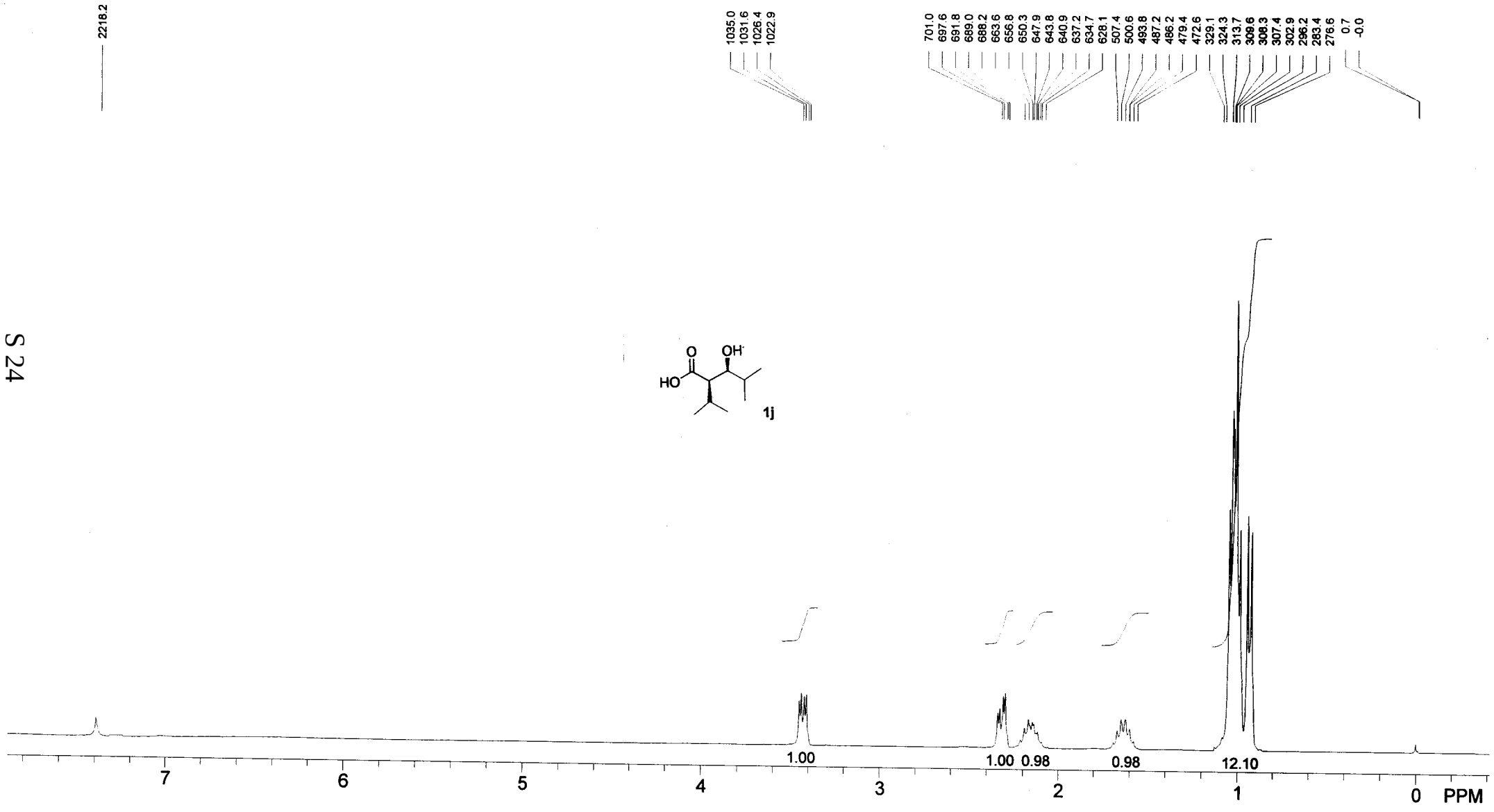

2213.3
2212.1
2204.9
2198.7
2194.9
2193.3
2186.2
2180.4
2179.3
2178.0
1358.4
1357.8
1207.9
1203.2
1198.6
1089.6
1083.9
1077.6
1072.4
1067.8
796.5
792.8
788.5
628.9
621.9
615.1
608.9
602.0
583.7
581.3
578.9
574.5
568.8
563.9
551.8
546.9
545.3
540.6
538.7
534.0
532.2
527.2
461.4
456.9
451.5
447.5
376.3
366.7
356.1
343.7
282.7
281.5
274.5
267.8
266.9
2.3
1.0
-0.3
HO
O
OH
OBn
1f
5.23
2.12
1.00
2.09
1.02
1.05
1.07
1.01
1.05
1.28
6.53
7
6
5
4
3
2
1
0
PPM

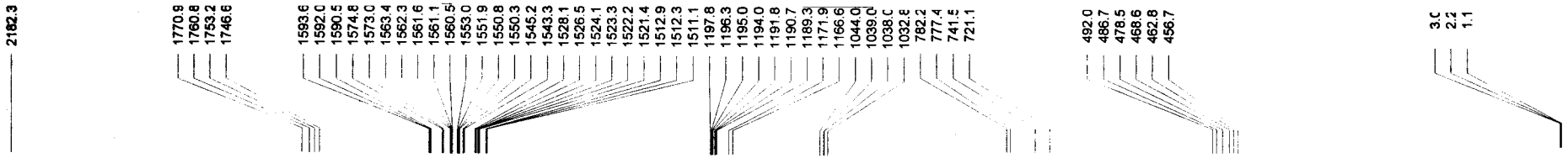

HO
O
OTs
OBn
2f
2.12
7.52
1.07
2.29
2.32
1.13
3.46
1.06
3.75
1.24
7.48
8
7
6
5
4
3
2
1
PPM

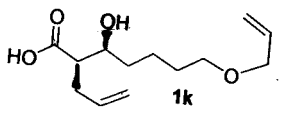

1916.9
1902.0
1940.5
1138.8
1132.6
796.8
790.8
785.1
778.5
772.2
510.5
-0.0
HO
OH
O
C_6H_{13}
1g
1.78
1.96
1.00
2.12
8.14
2.94
8
7
6
5
4
3
2
1
0
PPM

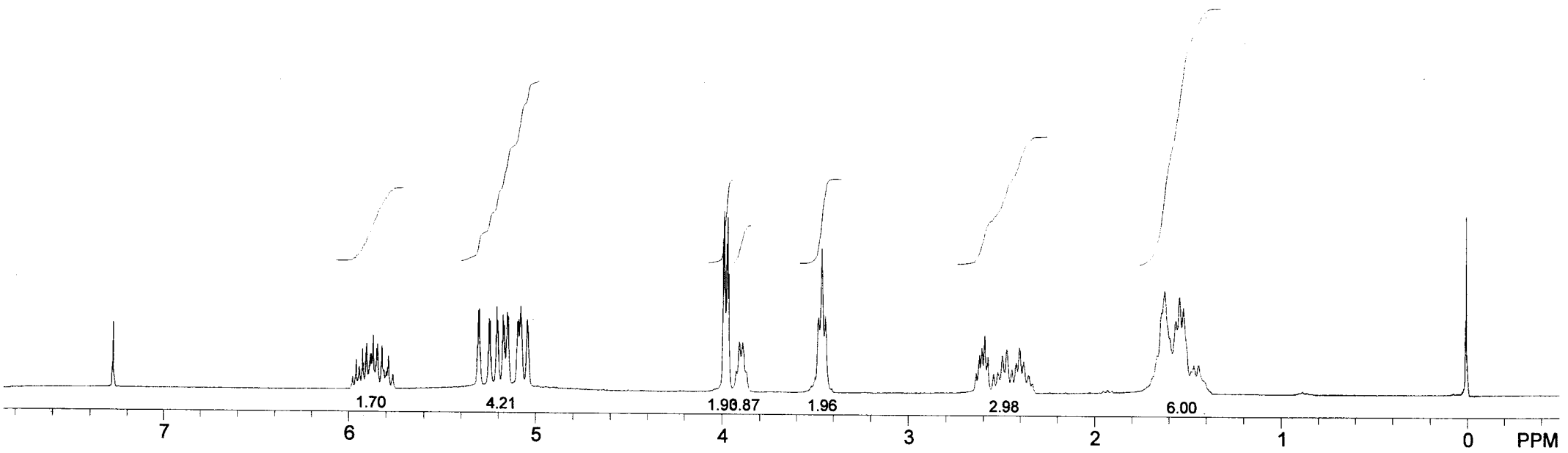

2340.0
2331.7
2210.6
2201.8
2180.6
2179.5
1260.8
1253.1
1251.2
1243.4
1240.5
1235.1
1230.9
1225.4
826.8
821.1
814.8
736.7
478.9
471.9
463.2
456.8
448.8
442.2
399.5
386.1
383.4
375.7
372.0
0.8
-0.6
HO
O
OTs
C6H13
2g
1.84
1.87
2.12
1.02
2.83
1.83
9.50
3.20
8
7
6
5
4
3
2
1
0 PPM

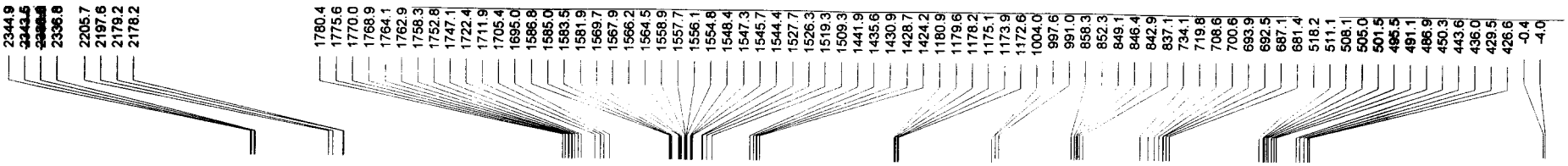

2224.5
2222.6
2220.7
2216.0
2207.4
2206.2
2203.9
2199.2
2191.8
2186.2
2184.8
2183.2
2180.4
2179.6
2178.1
2175.1
2172.2
2171.0
2013.3
1997.6
1877.3
1871.2
1861.6
1855.3
1400.7
1396.6
1391.8
846.7
842.8
839.5
835.7
381.3
374.2
368.6
2.1
O
OH
HO
Ph
1i
4.78
0.89
0.92
1.72
1.00
0.87
3.54
8
7
6
5
4
3
2
1
0
PPM

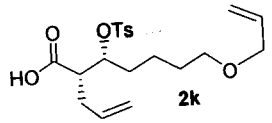

2218.2
1035.0
1031.6
1026.4
1022.9
701.0
697.6
691.8
689.0
688.2
663.6
656.8
650.3
647.9
643.8
640.9
637.2
634.7
628.1
507.4
500.6
493.8
487.2
486.2
479.4
472.6
329.1
324.3
313.7
309.6
308.3
307.4
302.9
296.2
283.4
276.6
0.7
-0.0
HO
O
OH
1j
1.00
1.00
0.98
0.98
12.10
7
6
5
4
3
2
1
0
PPM

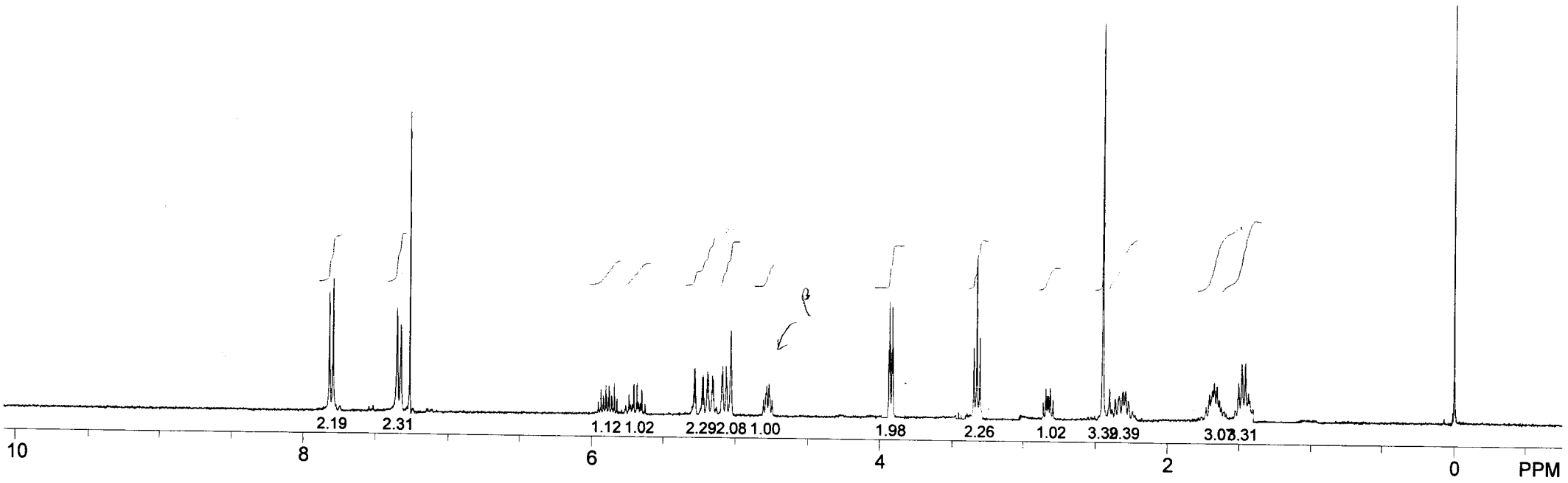

2182.3
1770.9
1760.8
1753.2
1746.6
1593.6
1592.0
1590.5
1574.8
1573.0
1563.4
1562.3
1561.6
1561.1
1560.5
1553.0
1551.9
1550.8
1550.3
1545.2
1543.3
1528.1
1526.5
1524.1
1523.3
1522.2
1521.4
1512.9
1512.3
1511.1
1197.8
1196.3
1195.0
1194.0
1191.8
1190.7
1189.3
1171.9
1166.6
1044.0
1039.0
1038.0
1032.8
782.2
777.4
741.5
721.1
492.0
486.7
478.5
468.6
462.8
456.7
3.0
2.2
1.1

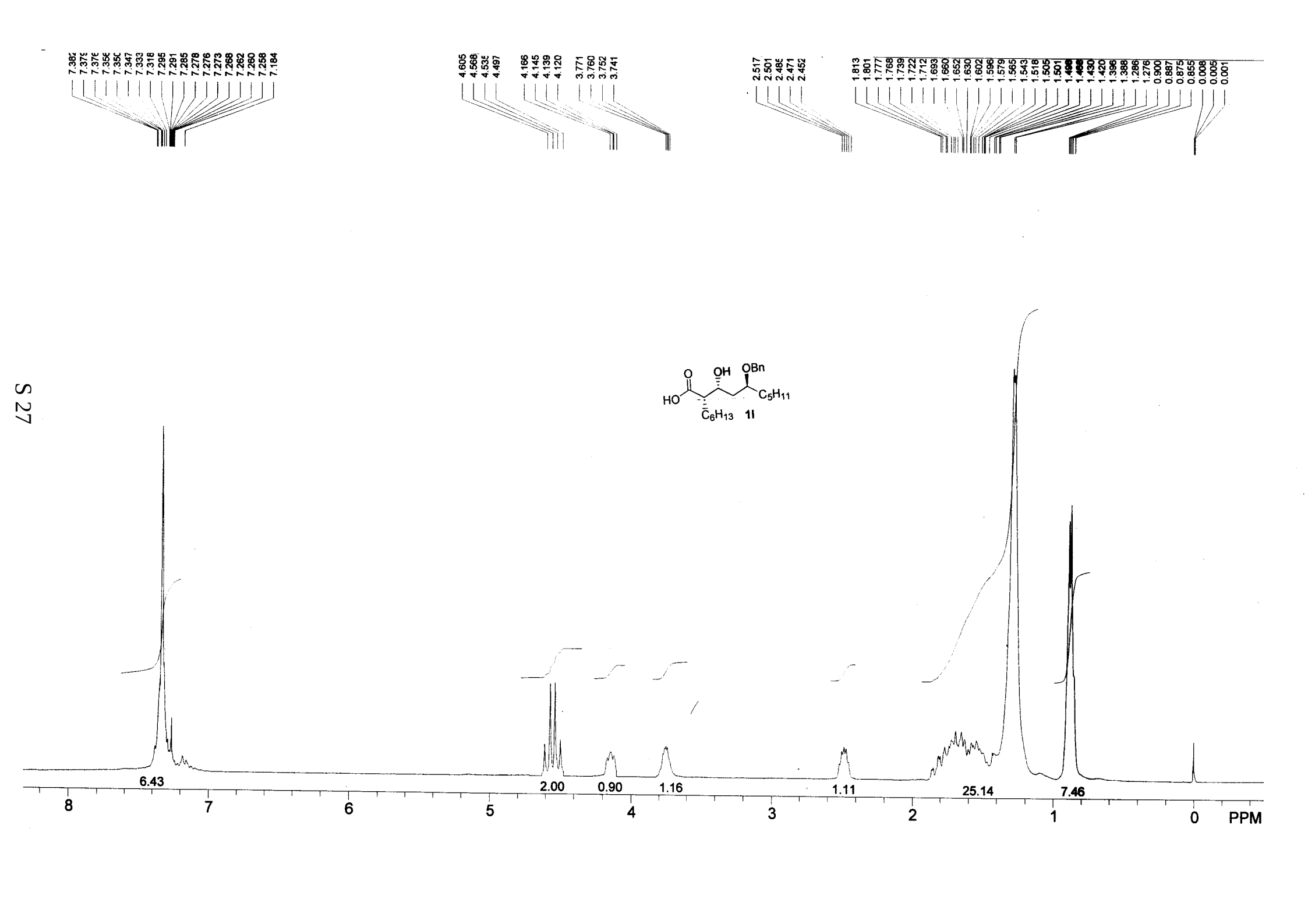

HO
O
OH
O
1k

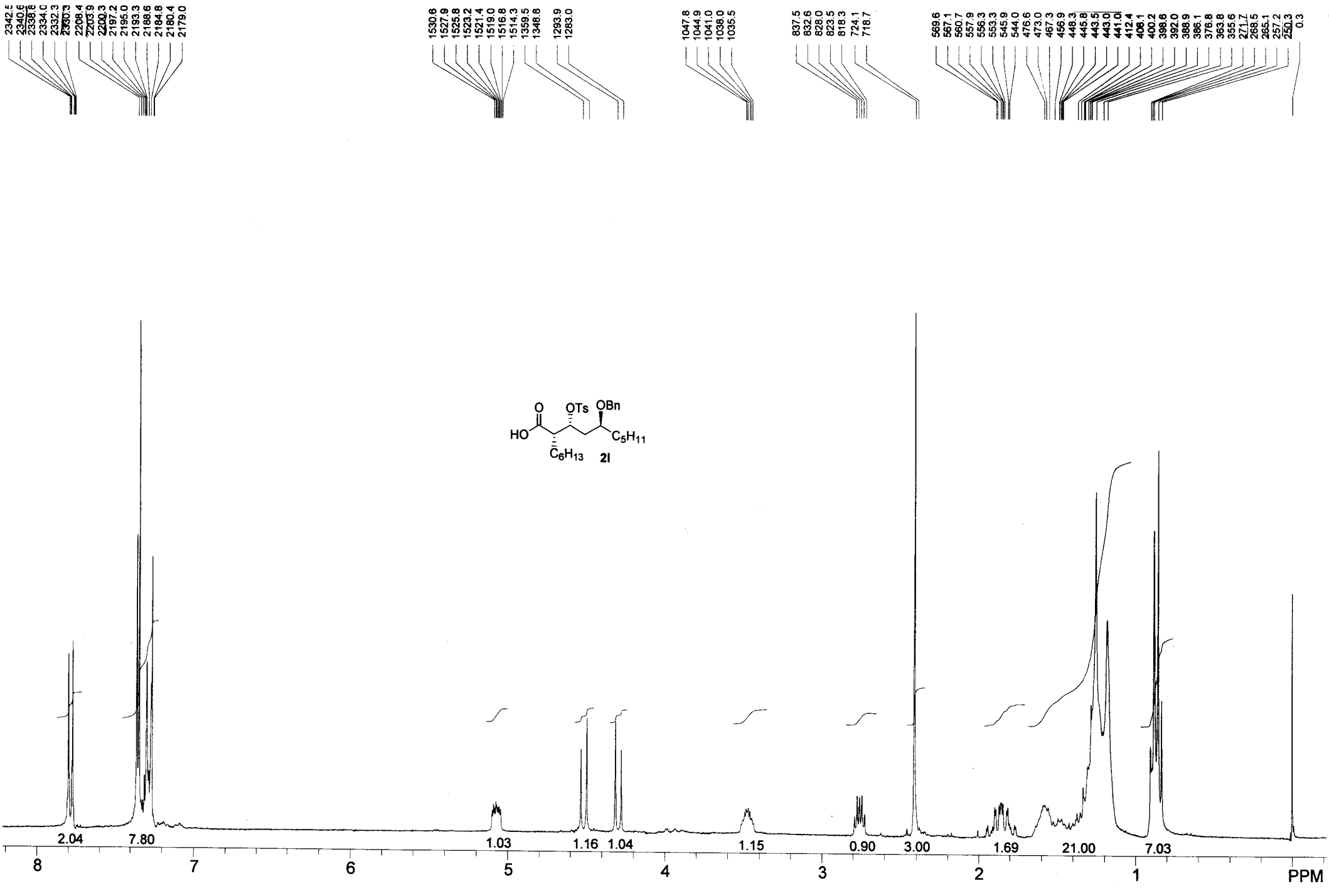

1.70
4.21
1.90
0.87
1.96
2.98
6.00
7
6
5
4
3
2
1
0
PPM

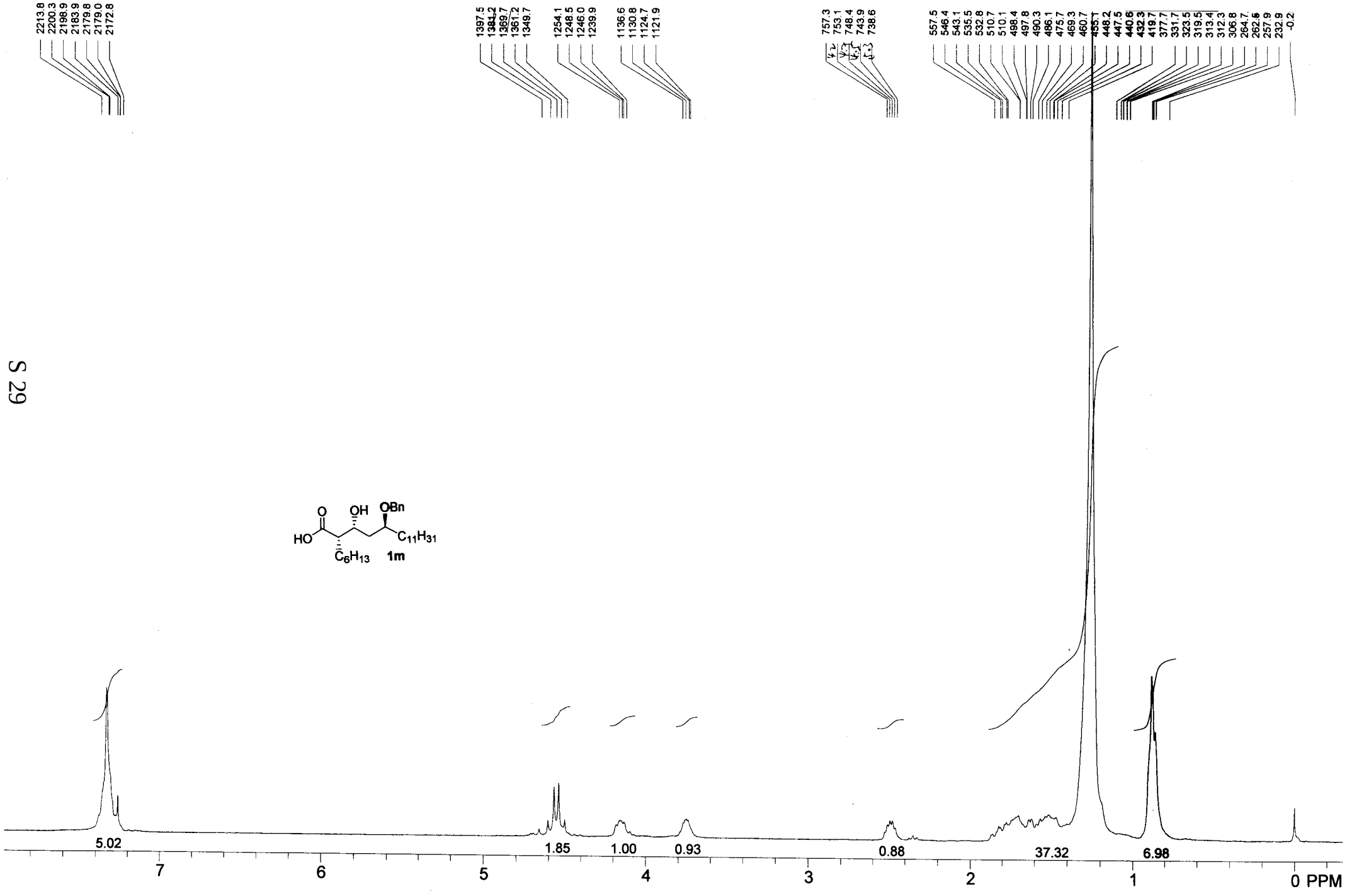


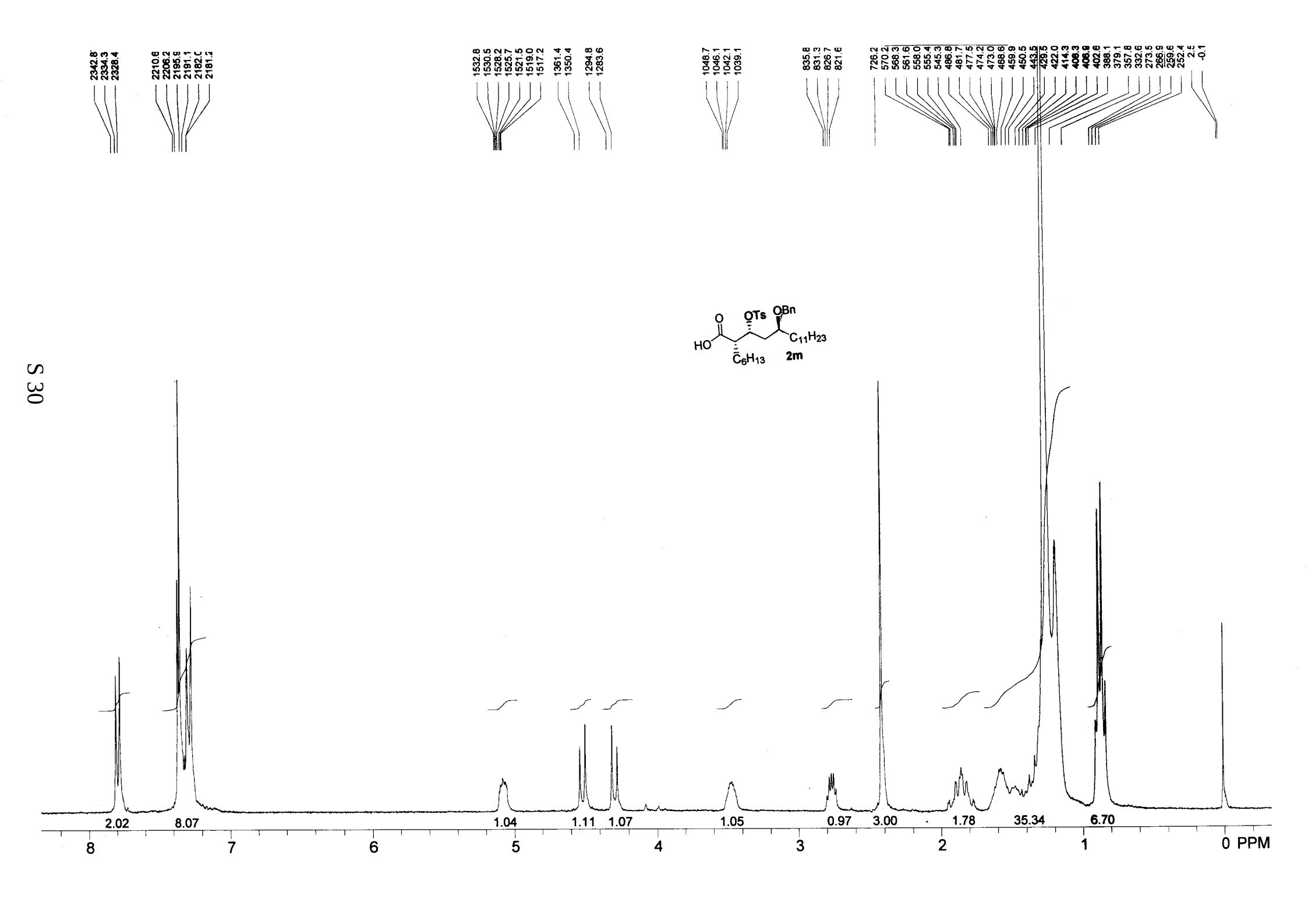

O
OTs
HO
O
2k

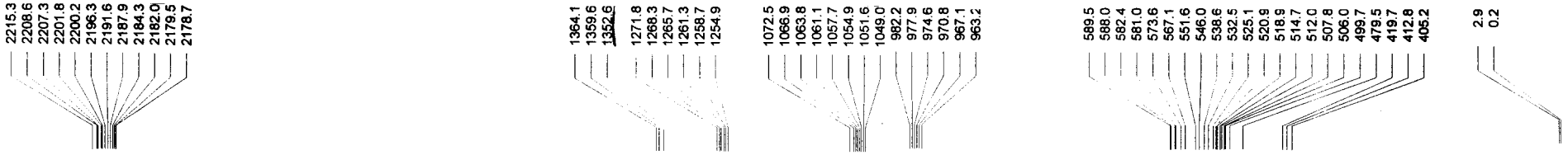

2.19
2.31
1.12
1.02
2.29
2.08
1.00
1.98
2.26
1.02
3.39
3.39
3.07
3.31
10
8
6
4
2
0
PPM

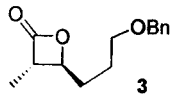

7.385
7.378
7.376
7.356
7.350
7.347
7.333
7.318
7.295
7.291
7.285
7.278
7.276
7.273
7.268
7.262
7.260
7.258
7.184
4.605
4.568
4.535
4.497
4.166
4.145
4.139
4.120
3.771
3.760
3.752
3.741
2.517
2.501
2.485
2.471
2.452
1.813
1.801
1.777
1.768
1.739
1.722
1.712
1.693
1.660
1.652
1.630
1.602
1.596
1.579
1.565
1.543
1.518
1.505
1.501
1.430
1.420
1.396
1.388
1.286
1.276
0.900
0.887
0.875
0.855
0.008
0.005
0.001
HO
O
OH
OBn
C5H11
C6H13
1l
6.43
2.00
0.90
1.16
1.11
25.14
7.46
8
7
6
5
4
3
2
1
0
PPM


2342.5
2340.6
2338.6
2334.0
2332.3
2208.4
2203.9
2200.3
2197.2
2195.0
2193.3
2188.6
2184.8
2180.4
2179.0
1530.6
1527.9
1525.8
1523.2
1521.4
1519.0
1516.8
1514.3
1359.5
1348.8
1293.9
1283.0
1047.8
1044.9
1041.0
1038.0
1035.5
837.5
832.6
828.0
823.5
818.3
724.1
718.7
569.6
567.1
560.7
557.9
556.3
553.3
545.9
544.0
476.6
473.0
467.3
456.9
448.3
445.8
443.5
443.0
441.0
412.4
408.1
400.2
398.6
392.0
388.9
386.1
376.8
363.8
355.6
271.7
268.5
265.1
257.2
250.3
0.3
O
OTs
OBn
HO
C_5H_{11}
C_6H_{13}
2l
2.04
7.80
1.03
1.16
1.04
1.15
0.90
3.00
1.69
21.00
7.03
8
7
6
5
4
3
2
1
PPM

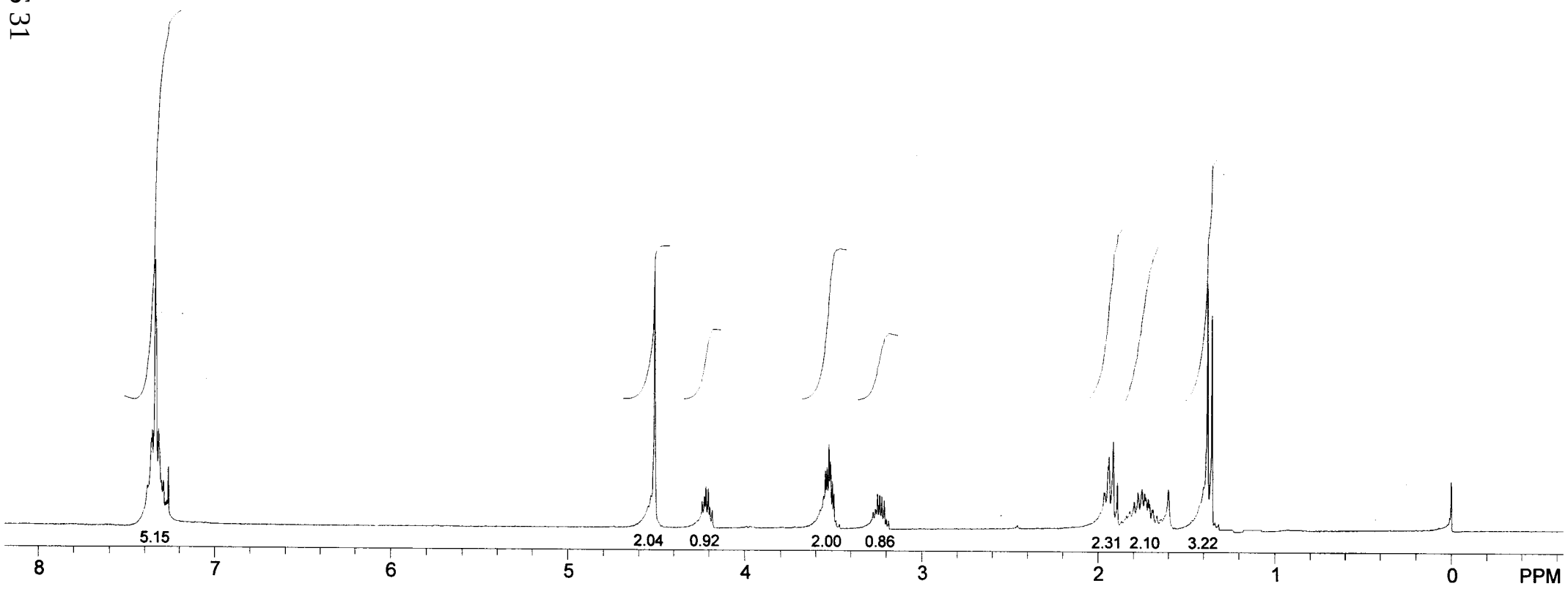

2213.8
2200.3
2198.9
2183.9
2179.8
2179.0
2172.8
1397.5
1254.1
1248.5
1246.0
1239.9
1136.6
1130.8
1124.7
1121.9
757.3
753.1
748.4
743.9
738.6
557.5
546.4
543.1
535.5
532.8
510.7
510.1
498.4
497.8
490.3
486.1
475.7
469.3
460.7
448.2
447.5
440.6
432.3
419.7
377.7
331.7
323.5
319.5
313.4
312.3
306.8
264.7
257.9
232.9
O
OH
OBn
HO
C11H31
C6H13
1m
5.02
1.85
1.00
0.93
0.88
37.32
6.98
7
6
5
4
3
2
1
0 PPM

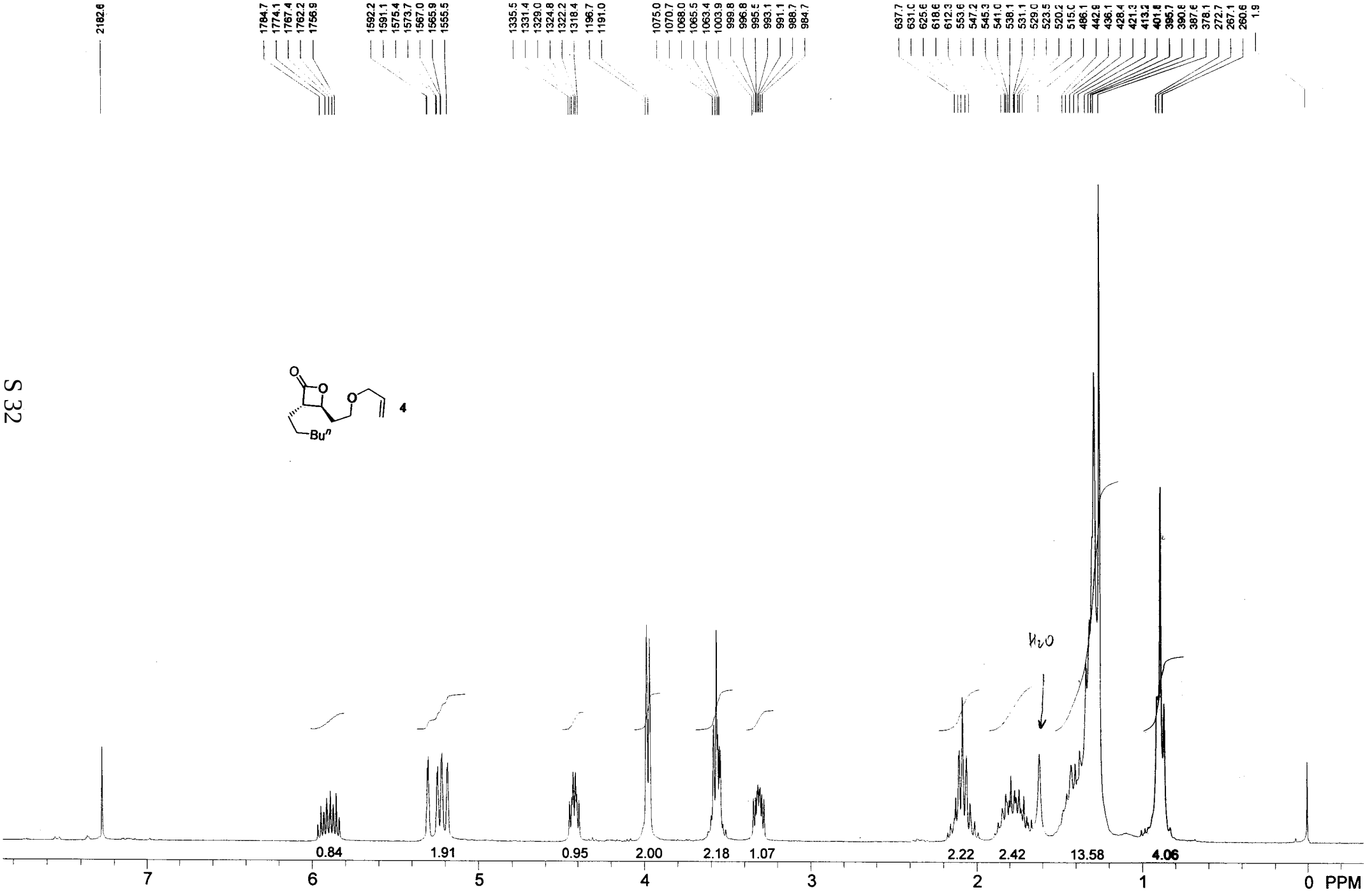

2342.8
2334.3
2328.4
2210.6
2206.2
2195.9
2191.1
2182.0
2181.2
1532.8
1530.5
1528.2
1525.7
1521.5
1519.0
1517.2
1361.4
1350.4
1294.8
1283.6
1048.7
1046.1
1042.1
1039.1
835.8
831.3
826.7
821.6
726.2
570.2
568.3
561.6
558.0
555.4
545.3
486.8
481.7
477.5
474.2
473.0
468.6
459.9
450.5
443.5
429.5
422.0
414.3
408.3
406.9
402.6
388.1
379.1
357.8
332.6
273.5
266.9
259.6
252.4
2.5
-0.1
HO
O
OTs
OBn
C11H23
C6H13
2m
2.02
8.07
1.04
1.11
1.07
1.05
0.97
3.00
1.78
35.34
6.70
8
7
6
5
4
3
2
1
0 PPM

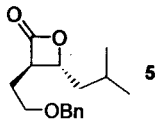

2215.3
2208.6
2207.3
2201.8
2200.2
2196.3
2191.6
2187.9
2184.3
2182.0
2179.5
2178.7
1364.1
1359.6
1352.6
1271.8
1268.3
1265.7
1261.3
1258.7
1254.9
1072.5
1066.9
1063.8
1061.1
1057.7
1054.9
1051.6
1049.0
982.2
977.9
974.6
970.8
967.1
963.2
589.5
588.0
582.4
581.0
573.6
567.1
551.6
546.0
538.6
532.5
525.1
520.9
518.9
514.7
512.0
507.8
506.0
499.7
479.5
419.7
412.8
405.2
2.9
0.2

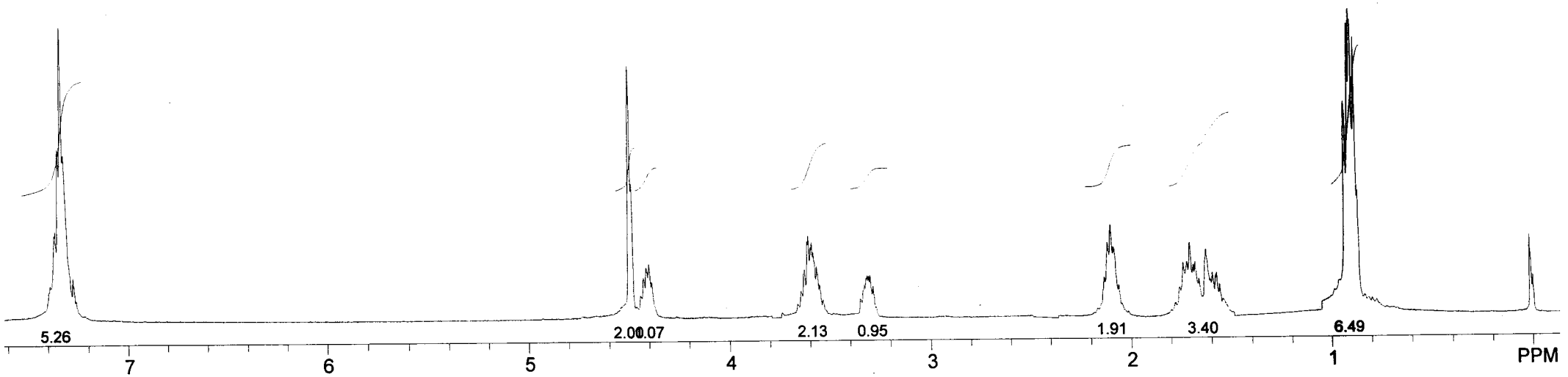

O
O
OBn

3


5.15
2.04
0.92
2.00
0.86
2.31
2.10
3.22
8
7
6
5
4
3
2
1
0
PPM


2182.6
1784.7
1774.1
1767.4
1762.2
1756.9
1592.2
1591.1
1575.4
1573.7
1567.0
1565.9
1555.5
1335.5
1331.4
1329.0
1324.8
1322.2
1318.4
1196.7
1191.0
1075.0
1070.7
1068.0
1065.5
1063.4
1003.9
999.8
996.8
995.5
993.1
991.1
988.7
984.7
637.7
631.0
625.6
618.6
612.3
553.6
547.2
545.3
541.0
538.1
531.1
529.0
523.5
520.2
515.0
486.1
442.9
436.1
428.4
421.3
413.2
401.8
395.7
390.8
387.6
378.1
272.7
267.1
260.6
1.9
O
O
O
Bu^n
4
H2O
0.84
1.91
0.95
2.00
2.18
1.07
2.22
2.42
13.58
4.06
7
6
5
4
3
2
1
0 PPM


O
O
OBn
5


5.26
2.00
0.07
2.13
0.95
1.91
3.40
6.49
7
6
5
4
3
2
1
PPM