Electronic Supplementary Information

An Enantioselective Total Synthesis of Natural Antibiotic Marasin

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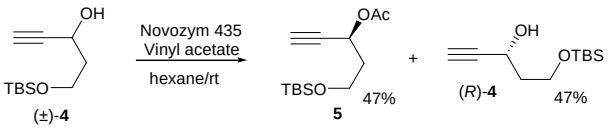
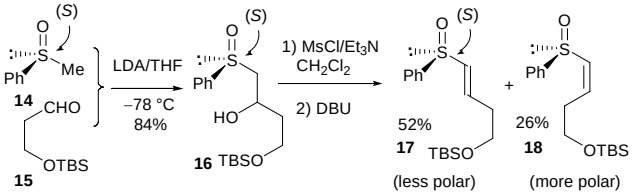


(*R*)-5-*tert*-Butyldimethylsilyl-pent-1-yn-3-ol (4) and (*S*)-5-*tert*-Butyldimethylsilyl-pent-1-yn-3-yl acetate (5). A mixture of racemic **4** (800 mg, 3.73 mmol), Novozyme 435 (200 mg), vinyl acetate (2.6 cm^3) in *n*-hexane (26 cm^3) was stirred at ambient temperature (22 to 24 °C) until ^{1}H NMR showed that the amount of **4** and **5** was about the same (ca. 16 h). Solids were filtered off. The filtrate was chromatographed (gradient elution with 30:1 to 10:1 PE/EtOAc) on silica gel to give the known[10] acetate **5** (449 mg, 1.75 mmol, 47%) and the known[9] (*R*)-**4** (376 mg, 1.75 mmol, 47%) as colorless oils. Data for (*R*)-**4**: $[\alpha]_D^{25}$ +21.8 (*c* 0.9, $CHCl_3$); ESI-MS *m/z* 215.2 ($[M+H]^+$). Data for **5**: $[\alpha]_D^{27}$ –54.8 (*c* 1.1, $CHCl_3$); FT-IR (film): 3300, 1740, 1470, 1370 cm^{-1}; ESI-MS *m/z* 279.2 ($[M+Na]^+$).



(*E*)-4-*tert*-Butyldimethylsilyloxy-1-((*S*)-phenylsulphinyl)-butene (17) and (*Z*)-4-*tert*-Butyldimethylsilyloxy-1-((*S*)-phenylsulphinyl)-butene (18). *n*-BuLi (2.5 M, in hexanes, 0.604 cm^3, 1.51 mmol) was added to a solution of *i*-Pr_2NH (0.21 cm^3, 1.51 mmol) in dry THF (2.0 cm^3) stirred at 0 ºC under argon. Stirring was continued at the same temperature for 15 min. The bath was cooled to –78 ºC. A solution of sulfoxide **14** (176 mg, 1.257 mmol) in dry THF (5.0 cm^3) was added slowly. After completion of the addition, the mixture was stirred at the same temperature for 1 h before a solution of aldehyde **15** (283 mg, 1.51 mmol) in THF (2.0 cm^3) was introduced. Stirring was continued at –78 ºC for another 2 h. The bath was then allowed to warm naturally to ambient temperature. Aq. sat. NH_4Cl was added. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (1:1 PE/EtOAc) on silica gel afforded the less polar isomer of the intermediate alcohol (157 mg, 0.478 mmol, 38%) and the more polar one (189 mg, 0.578 mmol, 46%) as colorless oils.

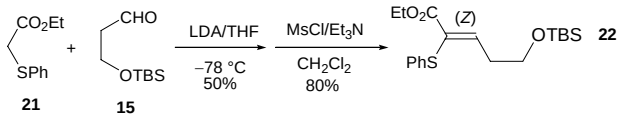
The data for the less polar isomer of **16**: $[\alpha]_D^{27}$ –153.75 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68-7.62 (m, 2H), 7.58-7.48 (m, 3H), 4.45 (br dt, *J* = 2.3, 10.4 Hz, 1H), 4.29 (br s, 1H), 3.82 (br t, *J* = 5.4 Hz, 2H), 3.00 (dd, *J* = 13.2, 9.9 Hz, 1H), 2.77 (dd, *J* = 13.2, 2.5 Hz, 1H), 1.85-1.55 (m, 2H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 130.8, 129.2, 123.8, 65.7, 63.8, 61.1, 38.5, 25.7, 18.0, –5.7; FT-IR (film) 3364, 3053, 2928, 2857, 1472, 1444, 1255, 1089, 1020, 836, 691 cm^{-1}; ESI-MS *m/z* 329.0 ($[M+H]^+$), 351.1 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{16}H_{29}SiO_3S$ 329.1601 ($[M+H]^+$), found 329.1615.

The data for the more polar isomer of **16**: $[\alpha]_D^{27}$ –92.33 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63-7.60 (m, 2H), 7.48-7.46 (m, 3H), 4.29-4.23 (m, 1H), 4.08 (d, *J* = 1.7 Hz, 1H), 3.85-3.69 (m, 2H), 3.09 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.89 (dd, *J* = 13.0, 3.8 Hz, 1H), 1.87-1.68 (m, 2H), 0.81 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.8, 131.2, 129.3, 124.0, 67.6, 63.5, 61.0, 38.4, 25.8, 18.1, –5.56, –5.61; FT-IR (film) 3373, 3059, 2954, 2856, 1468, 1255, 1089, 1020, 836, 777, 748 cm^{-1}; ESI-MS *m/z* 329.1 ($[M+H]^+$), 351.0 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{16}H_{29}SiO_3S$ 329.1601 ($[M+H]^+$), found 329.1610.

To a solution of the above obtained intermediate alcohol (either of the isomers or a mixture of both, 37 mg, 0.113 mmol) stirred in an ice-water bath was added Et_3N (0.063 cm^3, 0.452 mmol), followed by MsCl (0.017 cm^3, 0.226 mmol). The mixture was stirred at ambient temperature for 2 h. DBU (0.17 cm^3, 1.13 mmol) was introduced. The mixture was stirred at ambient temperature overnight before being diluted with Et_2O, washed in turn with aq. sat. NH_4Cl, water, and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (5:1 PE/EtOAc) on silica gel afforded **17** (18 mg, 0.0588 mmol, 52%) and **18** (9 mg, 0.0294 mmol, 26%).

Data for **17** (the (*E*)-isomer, less polar than **18**): $[\alpha]_D^{25}$ +59.39 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64-7.58 (m, 2H), 7.54-7.45 (m, 3H), 6.62 (dt, *J* = 15.2, 6.8 Hz, 1H), 6.31 (d, *J* = 15.2 Hz, 1H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.43 (q, *J* = 6.3 Hz, 2H), 0.85 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 137.9, 136.4, 130.8, 129.2, 124.4, 61.2, 35.3, 25.8, 18.1, –5.5; FT-IR (film) 3396, 2933, 2874, 1623, 1472, 1444, 1039, 959, 748, 690 cm^{-1}; ESI-MS *m/z* 311.1 ($[M+H]^+$), 333.1 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{16}H_{27}SiO_2S$ 311.1496 ($[M+H]^+$), found 311.1505.

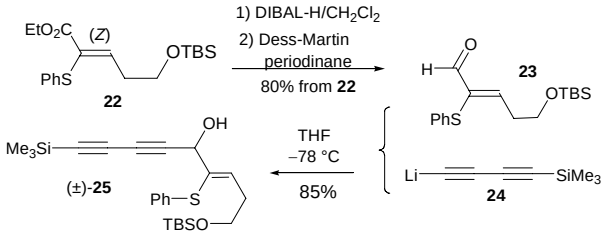
Data for **18** (the (*Z*)-isomer, more polar than **17**): $[\alpha]_D^{25}$ –123.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66-7.60 (m, 2H), 7.55-7.46 (m, 3H), 6.34-6.27 (m, 2H), 3.83-3.74 (m, 2H), 2.83 (br q, *J* = 6.0 Hz, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 139.3, 137.9, 130.6, 129.2, 124.1, 61.8, 32.7, 25.8, 18.3, –5.4; FT-IR (film) 3396, 2933, 2874, 1623, 1472, 1444, 1039, 959, 748, 690 cm^{-1}; ESI-MS *m/z* 311.2 ($[M+H]^+$), 333.1 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{16}H_{27}SiO_2S$ 311.1496 ($[M+H]^+$), found 311.1501.



Ethyl (*Z*)-2-phenylthio-5-*tert*-bytuldimethylsilyloxy pent-2-enoate (22). *n*-BuLi (2.5 M, in hexanes, 0.48 cm^3, 1.2 mmol) was added to a solution of *i*-Pr_2NH (0.17 cm^3, 1.2 mmol) in dry THF (2.0 cm^3) stirred at 0 ºC under argon. The mixture was stirred at the same temperature for 15 min. The bath was cooled to –78 ºC. A solution of **21** (196 mg, 1.0 mmol) in dry THF (4.0 cm^3) was added slowly. After completion of the addition, the mixture was stirred at –78 ºC for 1 h before a solution of aldehyde **15** (226 mg, 1.2 mmol) in THF (2.0 cm^3) was introduced. Stirring was then continued at the same temperature for another 2 h. The bath was allowed to warm naturally to ambient temperature. Aq. sat. NH_4Cl was added. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (30:1 PE/EtOAc) on silica gel delivered the intermediate alcohol (a mixture of the diastereomers, 192 mg, 0.5 mmol, 50%) as a colorless oil, along with recovered **21** (78 mg, 0.4 mmol, 40%).

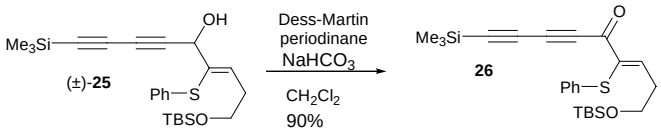
To a solution of the above obtained intermediate alcohol (192 mg, 0.5 mmol) in CH_2Cl_2 (4.0 cm^3) stirred in an ice-water bath were added Et_3N (0.35 cm^3, 2.5 mmol) and MsCl (0.064 cm^3, 0.75 mmol). The mixture was then stirred at ambient temperature for 2 h before being diluted with Et_2O, washed with aq. sat. NH_4Cl, water, and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (60:1 PE/EtOAc) on silica gel gave **22** (146 mg, 0.4 mmol, 80% from the intermediate alcohol, 40% from **21**) as a colorless oil, along with a small amount of the corresponding (*E*)-isomer (less polar than **22**, 8 mg, 0.022 mmol).

Data for **22**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (t, *J* = 7.4 Hz, 1H), 7.25-7.21 (m, 4H), 7.18-7.11(m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.76 (t, *J* = 6.2 Hz, 2H), 2.75 (q, *J* = 6.5 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.1, 149.9, 135.8, 128.8, 128.2, 128.1, 126.0, 61.43, 61.38, 34.4, 25.8, 18.2, 13.8, –5.4; FT-IR (film) 3076, 2955, 2928, 2857, 1716, 1611, 1581, 1473, 1253, 1097, 1045, 837, 777, 739, 690 cm^{-1}; ESI-MS *m/z* 367.1 ($[M+H]^+$), 389.1 ($[M+Na]^+$); ESI-HRMS calcd. for $C_{19}H_{31}SiO_3S$ 367.1758 ($[M+H]^+$), found 367.1761.

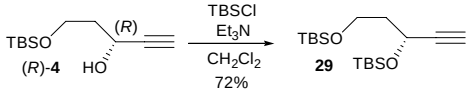


(6*Z*)-9-(*tert*-Butyldimethylsilyloxy)-6-phenylthio-1-trimethylsilyl-non-6-ene-1,3-diyn-5-ol ((±)-25). DIBAL-H (1.0 M, in cyclohexane, 1.83 cm^3, 1.83 mmol) was added to a solution of **22** (222 mg, 0.61 mmol) in dry CH_2Cl_2 (5.0 cm^3) stirred at –78 ºC under argon. After completion of the addition, the mixture was stirred at the same temperature for 1 h. 1 N HCl (0.6 cm^3) was carefully added to quench the excess hydride, followed by EtOAc (10 cm^3). The phases were separated. The aqueous layer was back-extracted with EtOAc (4 × 5 cm^3). The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent on a rotary evaporator left an oil, which was dissolved in CH_2Cl_2 (5.0 cm^3) and treated with Dess-Martin periodinane (259 mg, 0.61 mmol) and $NaHCO_3$ (93 mg, 1.1 mmol) at ambient temperature for 0.5 h. Aq. sat. Na_2SO_3 (2 cm^3) was added. The mixture was stirred until all the solids dissolved before being extracted with Et_2O (2 × 20 cm^3), washed with aq. sat. NH_4Cl, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography on silica gel afforded the intermediate aldehyde **23** (eluting with 20:1 PE/Et_2O, 157 mg, 0.486 mmol, 80% from **22**) as a colorless oil.

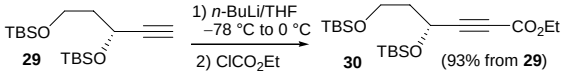
To a solution of *bis*-trimethylsilylbutadiene (125 mg, 0.644 mmol) in dry THF (3 cm^3) stirred at –10 ºC under argon was added MeLi (1.5 M, in Et_2O, 0.38 cm^3, 0.57 mmol). The flask was wrapped up with aluminum foil to exclude light. Stirring was then continued at ambient temperature for 50 min to yield a solution of the lithiated diyne **24**. The bath was cooled down to –78 ºC and the cooled solution of **24** was added dropwise to (via a cannula) another flask containing a solution of the above obtained aldehyde **23** (122 mg, 0.38 mmol) in dry THF (2 cm^3) stirred at –78 ºC under argon. The resulting mixture was stirred at –78 ºC for another 2 h before being diluted with Et_2O, washed with aq. sat. NH_4Cl (twice), and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (30:1 PE/EtOAc) on silica gel gave racemic **25** (143 mg, 0.322 mmol, 85% from aldehyde **23**, 68% from ester **22**) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.23 (m, 4H), 7.19-7.15 (m, 1H), 6.67 (dt, *J* = 0.8, 7.2 Hz, 1H), 4.87 (dd, *J* = 6.8, 0.7 Hz, 1H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.61 (br q, *J* = 7.0 Hz, 2H), 2.54 (d, *J* = 7.0 Hz, 1H), 0.91 (s, 9H), 0.20 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.6, 134.5, 133.2, 129.1, 128.7, 126.4, 88.3, 87.1, 75.7, 71.5, 65.9, 61.7, 33.5, 25.9, 18.3, –0.5, –5.3; FT-IR (film) 3403, 3068, 2956, 2928, 2857, 2222, 2106, 1577, 1472, 1252, 1098, 844, 777, 739, 690 cm^{-1}; ESI-MS *m/z* 445.2 ($[M+H]^+$), 467.1 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{24}H_{37}Si_2O_2S$ 445.20473 ($[M+H]^+$), found 445.2054.



(6*Z*)-9-(*tert*-Butyldimethylsilyloxy)-6-phenylthio-1-trimethylsilyl-non-6-ene-1,3-diyn-5-one (26). To a solution of racemic **25** (350 mg, 0.788 mmol) in dry CH_2Cl_2 (6 cm^3) stirred at ambient temperature was added Dess-Martin periodinane (402 mg, 0.946 mmol), followed by $NaHCO_3$ (119 mg, 1.42 mmol). The mixture was stirred for another 30 min. Aq. sat. Na_2SO_3 (2 cm^3) was added. Stirring was continued until all solids dissolved. The mixture was extracted with Et_2O (2 × 25 cm^3), washed with aq. sat. NH_4Cl, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (100:1 PE/EtOAc) on silica gel afforded ketone **26** (313 mg, 0.707 mmol, 90%) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (t, *J* = 6.9 Hz, 1H), 7.27-7.13 (m, 5H), 3.80 (t, *J* = 5.9 Hz, 2H), 2.85 (q, *J* = 6.3 Hz, 2H), 0.92 (s, 9H), 0.24 (s, 9H), 0.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.6, 157.4, 137.4, 134.6, 129.0, 128.5, 126.3, 97.2, 85.8, 77.5, 71.9, 61.0, 35.0, 25.9, 18.2, –0.79, –5.4; FT-IR (film) 3068, 2956, 2928, 2851, 2195, 2098, 1648, 1593, 1468, 1253, 1097, 848, 777 cm^{-1}; ESI-MS *m/z* 465.1 ([M+Na]$^+$); ESI-HRMS calcd. for $C_{24}H_{34}Si_2O_2SNa$ 465.1710 ([M+Na]$^+$), found 465.1712.

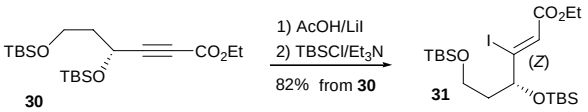


(3*R*)-3,5-di-*tert*-Butyldimethylsilyloxy-pent-1-yne (29). To a solution of (*R*)-**4** (321 mg, 1.5 mmol) in dry CH_2Cl_2 (6 cm^3) stirred at ambient temperature were added TBSCl (271 mg, 1.8 mmol), Et_3N (0.31 cm^3, 2.25 mmol) and DMAP (18 mg, 0.15 mmol). Stirring was continued at ambient temperature overnight. The mixture was diluted with Et_2O (50 cm^3), washed with aq. sat. NH_4Cl twice, and dried over anhydrous Na_2SO_4. Removal of the solvent on a rotary evaporator and column chromatography (200:1 PE/EtOAc) on silica gel delivered alkyne **29** (356 mg, 1.08 mmol, 72%) as a colorless oil. $[\alpha]_D^{24}$ +31.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.57 (dt, *J* = 1.8, 6.5 Hz, 1H) 3.78-3.70 (m, 2H), 2.39 (d, *J* = 1.8 Hz, 1H), 1.97-1.80 (m, 2H), 0.92 (s, 9H), 0.90 (m, 9H), 0.17 (s, 3H), 0.11 (s, 3H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 85.5, 72.1, 59.5, 58.8, 41.6, 25.9, 25.8, 18.2, –4.6, –5.2, –5.36, –5.40; FT-IR (film) 3300, 2955, 2930, 2858, 1227, 1103 cm^{-1}; ESI-MS *m/z* 351.1([M+Na]$^+$); MALDI-HRMS calcd. for $C_{17}H_{36}Si_2O_2Na$ 351.2146 ([M+Na]$^+$), found 351.2156.



Ethyl (4*R*)-4,6-Di-*tert*-butyldimethylsilyloxy-hex-2-ynoate (30). *n*-BuLi (2.5 M, in hexanes, 0.81 cm^3, 2.03 mmol) was added to a solution of alkyne **29** (604 mg, 1.84 mmol) in dry THF (13 cm^3) stirred at –78 ºC under argon. The mixture was then stirred at –10 ºC for 10 min. The bath was re-cooled to –78 ºC. $ClCO_2Et$ (0.211 cm^3, 2.21 mmol) was added. Stirring was continued while the bath was allowed to warm naturally to ambient temperature. Aq. sat. NH_4Cl (10 cm^3) was added, followed by Et_2O (50 cm^3). The phases were separated. The organic layer was dried over anhydrous Na_2SO_4. Removal of the solvent on a rotary evaporator and column chromatography (200:1 PE/EtOAc) gave **30** (684 mg, 1.71 mmol, 93%) as a colorless oil. $[\alpha]_D^{23}$ +26.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.70 (dd, *J* = 7.1, 6.1 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.79-3.65 (m, 2H), 1.99-1.82 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.89 (s, 9H), 0.18 (s, 3H), 0.10 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.4, 88.6, 76.1, 61.8, 59.2, 58.3, 40.8, 25.8, 25.7, 18.13, 18.10, 14.0, –4.7, –5.3, –5.45, –5.48; FT-IR (film) 2956, 2931, 2858, 2237, 1720, 1472, 1247, 1096, 1027, 837, 778 cm^{-1}; ESI-MS *m/z* 423.1 ([M+Na]$^+$); MALDI-HRMS calcd. for $C_{20}H_{40}Si_2O_4Na$ 423.2357 ([M+Na]$^+$), found 423.2357.

Ethyl (4*S*)-4,6-Di-*tert*-butyldimethylsilyloxy-hex-2-ynoate (*ent*-30). Prepared using the same procedure for convertion of **29** into **30** except using *ent*-**29** to replace **29** as the starting material; $[\alpha]_D^{24}$ –20.3 (*c* 1.1, $CHCl_3$).



Ethyl (2*Z*,4*R*)-4,6-Di-*tert*-butyldimethylsilyloxy-3-iodo-hex-2-enoate (31). LiI (111 mg, 0.825 mmol) was added in three portions at 30 min intervals to a solution of **30** (300 mg, 0.75 mmol) in glacial acetic acid (0.7 cm^3) stirred in a 75 ºC oil bath. Stirring was continued at the same temperature until the overall heating time reached 5 h. The bath was removed. The mixture was diluted with EtOAc (50 cm^3), washed with aq. sat. $Na_2S_2O_3$ and aq. sat. $Na_2S_2O_3$. The aqueous layers were extracted with EtOAc (3 × 10 cm^3). The combined organic layers were washed with aq. sat. $NaHCO_3$ and brine before being dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. The residue was dissolved in dry CH_2Cl_2 (6 cm^3) and cooled in an ice-water bath. TBSCl (226 mg, 1.5 mmol) was added, followed by Et_3N (0.23 cm^3, 1.65 mmol) and

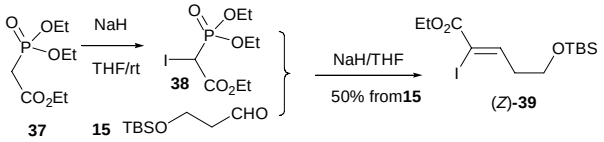
DMAP (18 mg, 0.15 mmol). The mixture was stirred at ambient temperature overnight before being diluted with Et_2O (40 cm^3), washed with aq. sat. NH_4Cl twice, and dried over anhydrous Na_2SO_4. Removal of the solvent on a rotary evaporator and column chromatography (200:1 PE/EtOAc) gave **31** (329 mg, 0.622 mmol, 83%) as a colorless oil. $[\alpha]_D^{24}$ +18.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.69 (s, 1H), 4.29 (dd, *J* = 7.5, 3.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.72-3.55 (m, 2H), 1.96-1.86 (m, 1H), 1.75-1.62 (m, 1H) 1.29 (t, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.06-0.03 (several singlets, 12 H altogether); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.6, 127.5, 123.7, 77.2, 60.6, 58.3, 40.0, 25.8, 25.7, 18.1, 18.0, 14.1, 0.96, –4.5, –5.1, –5.37, –5.42; FT-IR (film) 2956, 2930, 2885, 2858, 1731, 1618, 1464, 1258, 1173, 1096 cm^{-1}; ESI-MS *m/z* 551.0 ($[M+Na]^+$); MALDI-HRMS calcd. for $C_{20}H_{41}Si_2O_4INa$ 551.14803 ($[M+Na]^+$), found 551.1480.

Ethyl (2*Z*,4*S*)-4,6-Di-*tert*-butyldimethylsilyloxy-3-iodo-hex-2-enoate (*ent*-31). Prepared using the same procedure for convertion of **30** into **31** except using *ent*-**30** to replace **30** as the starting material; $[\alpha]_D^{27}$ –17.7 (*c* 1.2, $CHCl_3$).

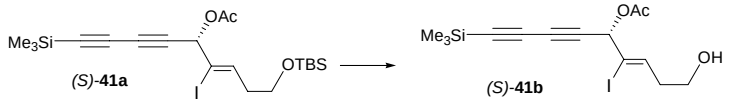
(2*Z*,5*S*)-5,7-Di-*tert*-butyldimethylsilyloxy-4-iodo-hept-2-en-1-yne (*ent*-33). Prepared using the same procedure for converting **31** into **33** except using *ent*-**31** to replace **31** as the starting material; $[\alpha]_D^{25}$ –16.6 (*c* 1.1, $CHCl_3$).

(2*Z*,5*S*)-5,7-Diacetoxy-4-iodo-hept-2-en-1-yne (*ent*-34). Prepared using the same procedure for converting **33** into **34** except using *ent*-**33** to replace **33** as the starting material; $[\alpha]_D^{27}$ –15.4 (*c* 1.1, $CHCl_3$).

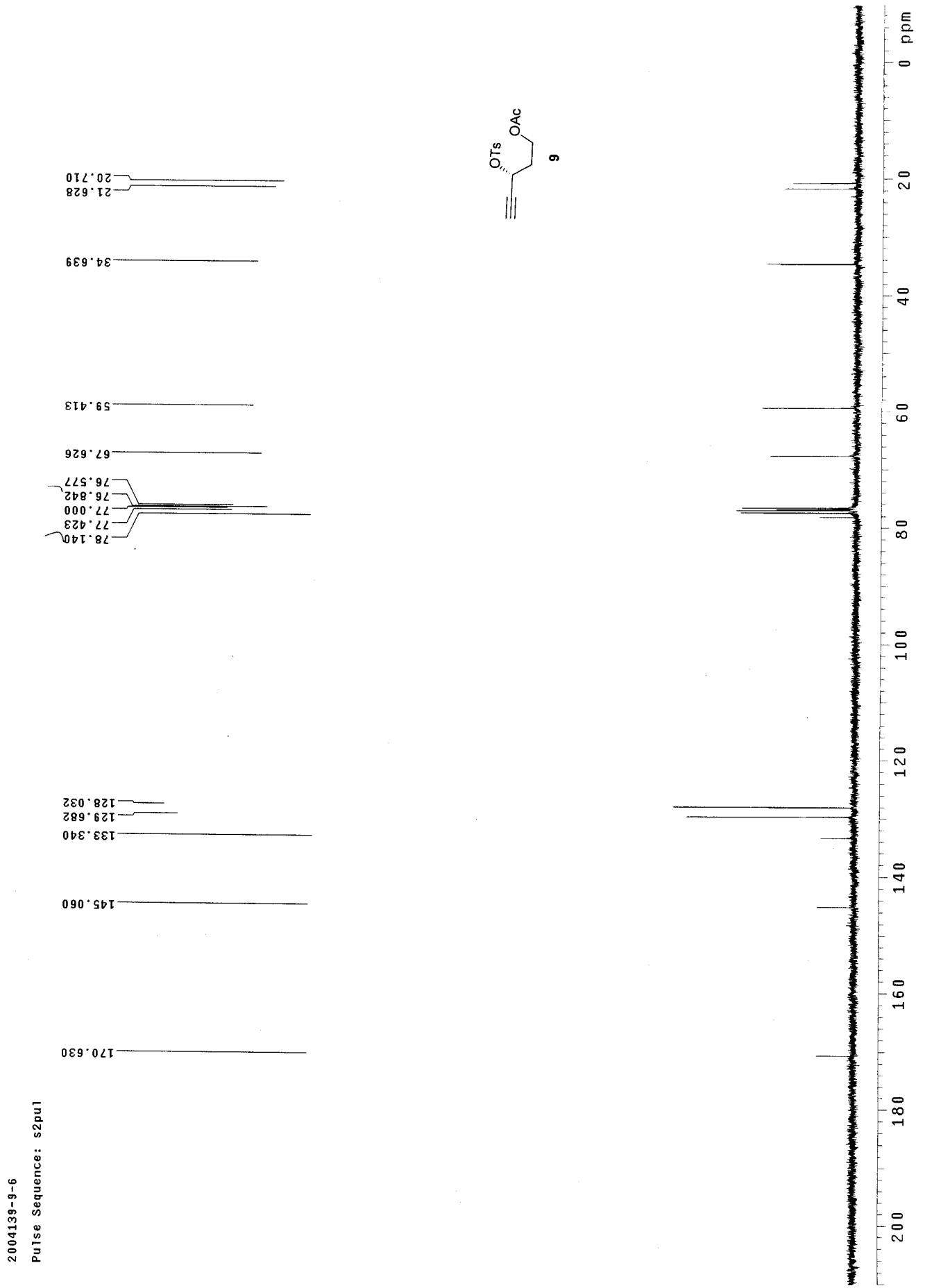
(a*R*)-Hepta-3,4-diene-6-yn-1-yl acetate (*ent*-35). Prepared using the same procedure for converting **34** into **35** except using *ent*-**34** to replace **34** as the starting material; $[\alpha]_D^{27}$ –147 (*c* 1.0, $CHCl_3$), 81.4% e. e..



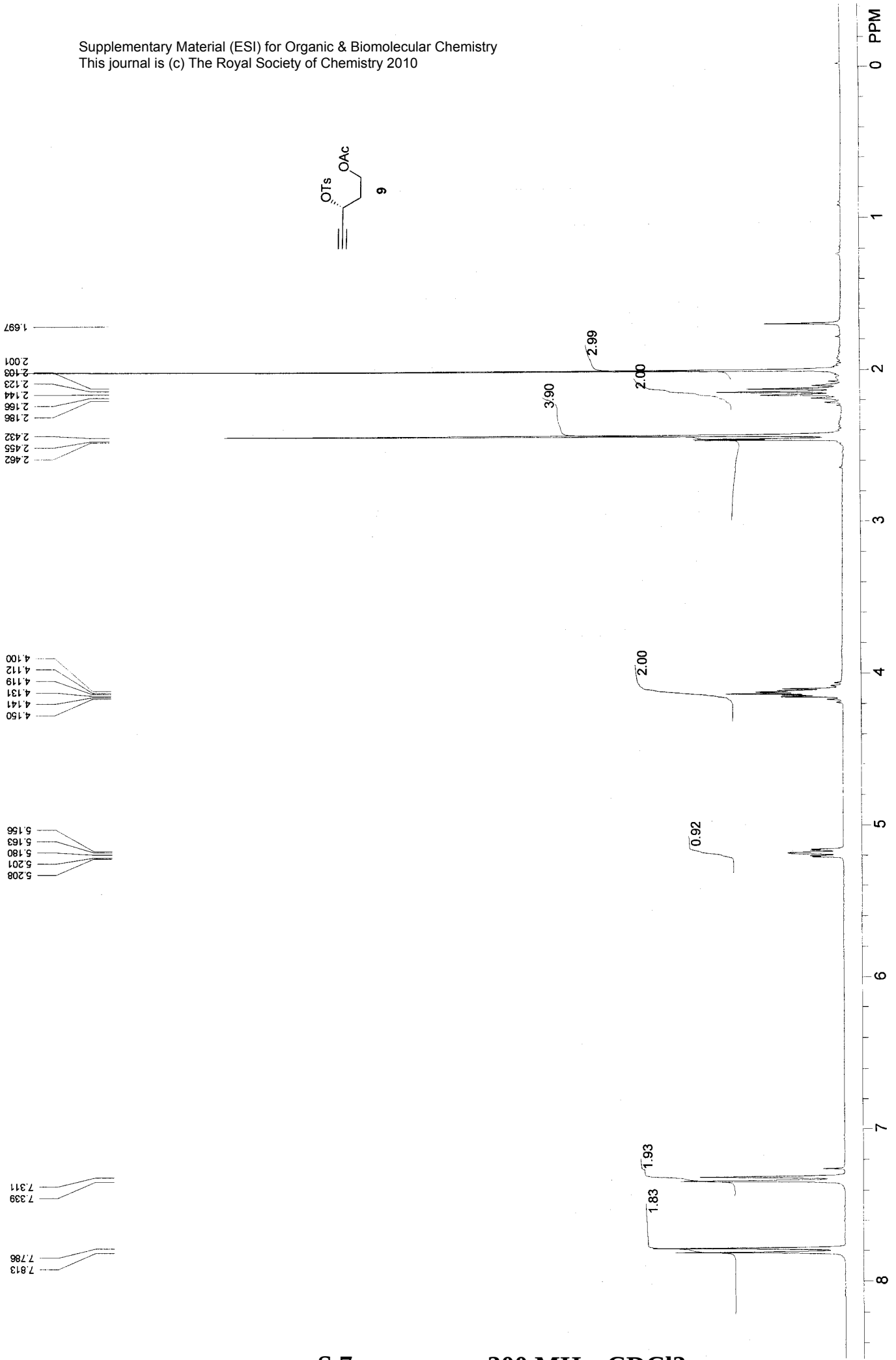
Ethyl (*Z*)-5-*tert*-Butyldimethylsilyloxy-2-iodo-pent-2-enoate ((*Z*)-39). NaH (264 mg, 6.6 mmol) was added in portions to a solution of $EtO_2CCH_2P(O)(OEt)_2$ (1.2 cm^3, 6.0 mmol) in THF (25 cm^3) stirred in an ice-water bath. After completion of the addition, the stirring was continued at ambient temperature for 1 h before being re-cooled in an ice-water bath. A solution of solid iodine (I_2, 1.676 g, 6.6 mmol) in THF (5 cm^3) was added. Stirring was continued at ambient temperature for another 2 h. NaH (264 mg, 6.6 mmol) was added in portions. The mixture was stirred at the same temperature for 30 min. A solution of aldehyde **15** (1.128 g, 6.0 mmol) in THF (5 cm^3) was introduced dropwise. The mixture was stirred at ambient temperature overnight before being diluted with Et_2O (100 cm^3), washed in turn with aq. $Na_2S_2O_3$, water, and aq. sat. NH_4Cl, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (100:1:1 PE/CH_2Cl_2/Et_2O) on silica gel gave **39** (1.153 g altogether, with most of them being pure (*Z*)-**39** and over all (*Z*)/(*E*) = 6:1, 3.0 mmol, 50% from **15**) as colorless oil(s). Data for pure (*Z*)-**39**: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (t, *J* = 6.7 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 6.4 Hz, 2H), 2.52 (q, *J* = 6.4 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.7, 150.3, 96.5, 62.6, 60.5, 40.5, 25.8, 18.2, 14.1, –5.4; FT-IR (film) 3533, 2955, 2929, 2857, 1721, 1608, 1252, 1096, 1044, 837, 777 cm^{-1}; ESI-MS *m/z* 407.0 ($[M+Na]^+$); ESI-HRMS calcd. for $C_{13}H_{25}O_3SiINa$ 407.0510 ($[M+Na]^+$), found 407.0515.



(6*Z*,5*S*)-6-Iodo-1-trimethylsilyl-non-6-ene-1,3-diyn-5,9-diol ((*S*)-41b). Conc. HCl (0.1 cm^3) was added to a solution of (*S*)-**41a** (15 mg, 0.032 mmol) in THF (0.3 cm^3) and MeOH (0.1 cm^3) stirred in an ice-water bath. The mixture was stirred at the same temperature for 1 h before being diluted with Et_2O (15 cm^3), washed with aq. sat. $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent by rotary evaporation and column chromatography (2:3 PE/Et_2O) on silica gel afforded diol (*S*)-**41b** (10 mg, 0.029 mmol, 90%) as a colorless oil. $[\alpha]_D^{24}$ –21.9 (*c* 0 .94, $CHCl_3$); 89% e.e. (t_R (major) = 6.89 min, t_R(minor) = 7.69 min) as determined by chiral HPLC analysis on a CHIRALPAK OJ-H column (0.46 × 25 cm) eluting with 80:20 *n*-hexane/*i*-PrOH at a flow rate of 0.7 cm^3/min with the UV detector set to 214 nm. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.24 (t, *J* = 6.9 Hz, 1H), 4.87 (d, *J* = 7.8 Hz, 1H), 3.78 (br t, *J* = 6.2 Hz, 2H), 2.76 (d, *J* = 7.6 Hz, 1H), 2.48 (q, *J* = 6.5 Hz, 2H), 1.66 (br s, 2H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.5, 109.9, 89.1, 86.9, 75.1, 71.7, 70.2, 60.9, 38.9, –0.53; FT-IR (film) 3347, 2958, 2925, 2222, 2107, 1634, 1405, 1251, 1044, 847, 761 cm^{-1}; ESI-MS *m/z* 370.9 ($[M+Na]^+$); ESI-HRMS calcd. for $C_{12}H_{17}O_2SiINa$ 370.9935 ($[M+Na]^+$), found 370.9951.



S 6 **75 MHz, CDCl3**



S 7 **300 MHz, CDCl3**

色谱分析报告

样品名称:

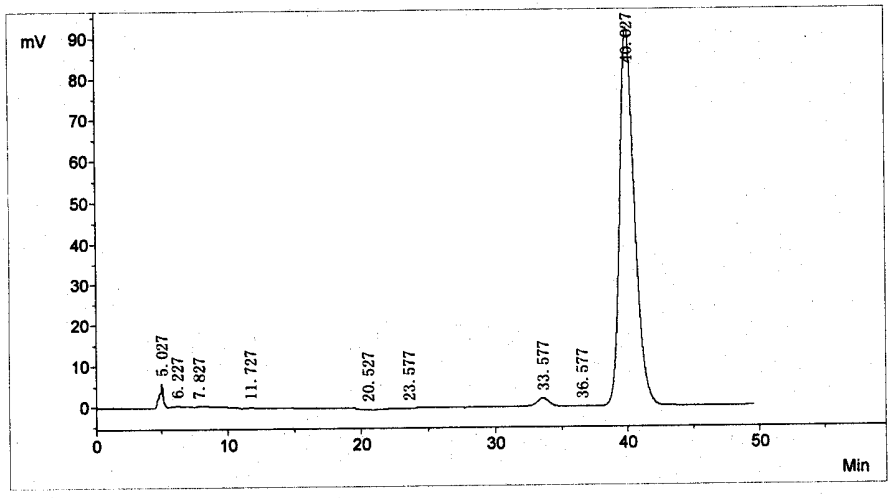
样品批号:

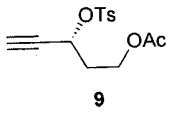
分析日期:2007-06-28

样品文件名:9-50-2.che

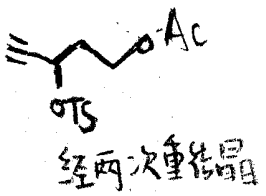
分析者:

分析时间:08:57





9



经两次重结晶

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2	2		6.227	426.2	27439.5	0.3666
3	3		7.827	183.4	8692.3	0.1161
4	4		11.727	105.6	5189.2	0.0693
5	5		20.527	79.3	995.5	0.0133
6	6		23.577	41.6	7766.3	0.1038
7	7		33.577	2012.5	129014.8	1.7238
8	8		36.577	99.9	4691.2	0.0627
9	9		40.027	92201.0	7185055.0	96.0015
合计:				101035.1	7484315.9	100.0000

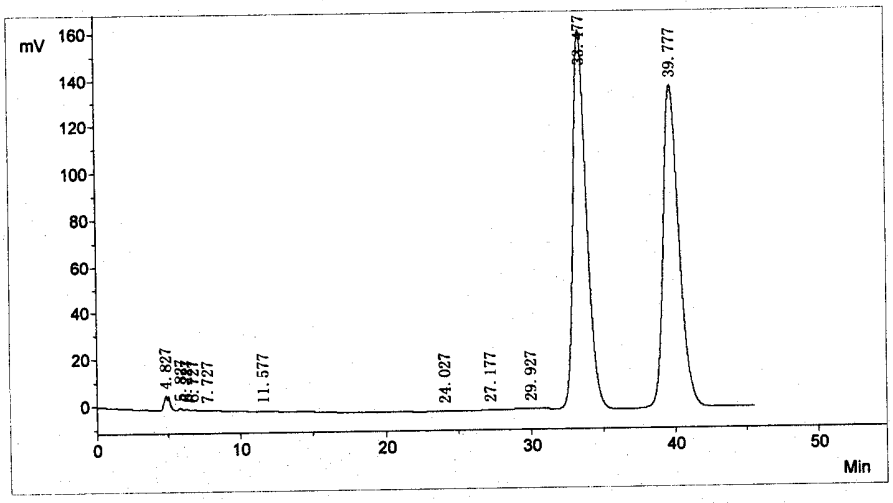
96.5% ee

(After 2 re-crystallizations)

色谱分析报告

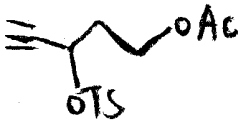
样品名称:
样品批号:
分析日期:2007-06-28

样品文件名:9-50+-.che
分析者:
分析时间:08:09



racemic tosylate 9

(+/-)-9



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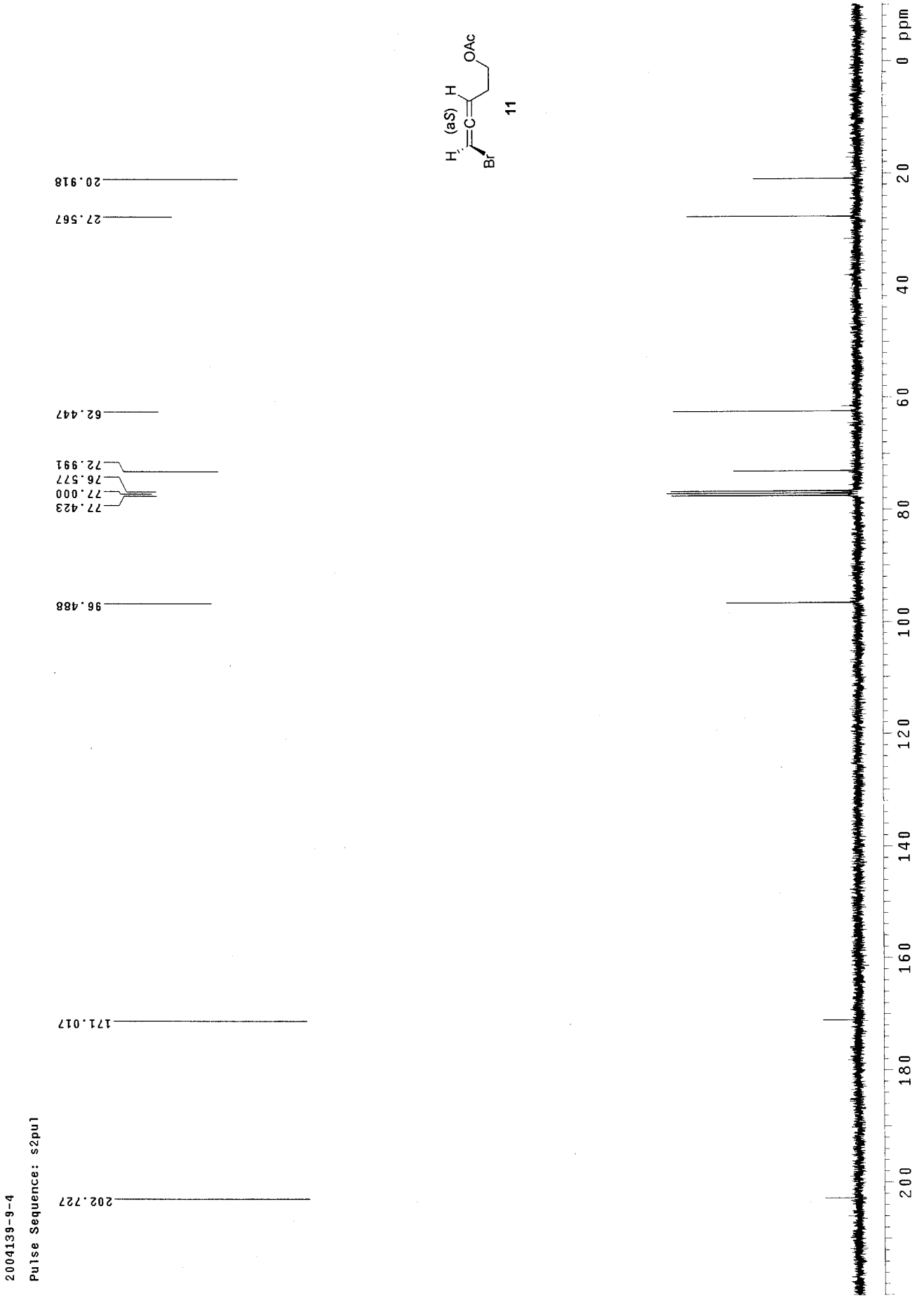
3	3		6.227	372.1	9468.4	0.0447
4	4		6.727	357.7	9774.6	0.0461
5	5		7.727	160.1	6168.0	0.0291
6	6		11.577	152.6	11051.9	0.0521
7	7		24.027	119.4	3864.3	0.0182
8	8		27.177	220.9	9808.8	0.0463
9	9		29.927	34.8	3492.3	0.0165
10	10		33.477	162401.9	10430535.5	49.1947
11	11		39.777	138836.4	10546931.1	49.7437
合计:				309231.7	21202560.9	100.0000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H
H (aS)
C
Br
11
20.918
27.567
62.447
72.991
76.577
77.000
77.423
96.488
171.017
202.727
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60
80
100
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140
160
180
200
2004139-9-4
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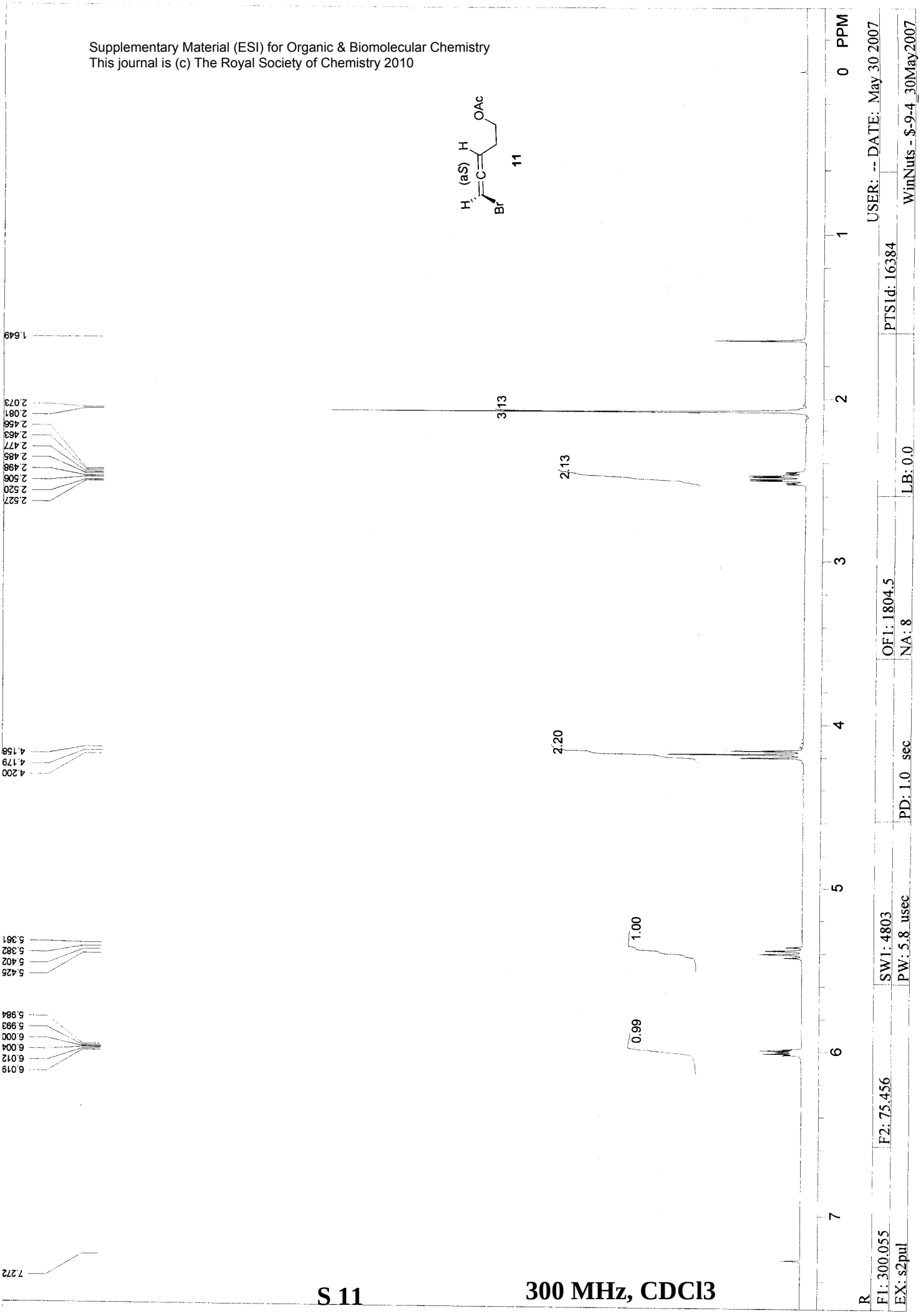
75 MHz, CDCl3



300 MHz, CDCl3

色谱分析报告

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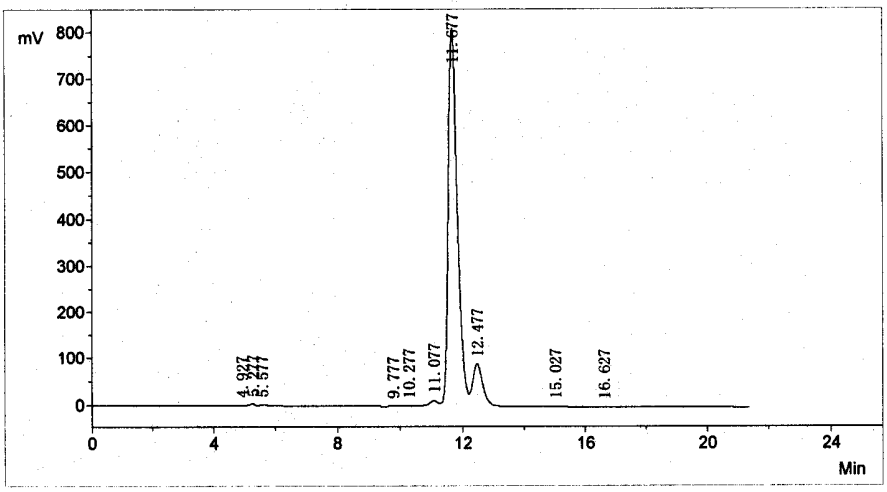
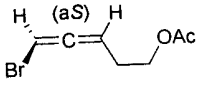
样品批号:
分析日期:2007-07-06

样品文件名:9-56.che
分析者:
分析时间:08:54





11

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3	3		5.577	2765.0	80687.7	0.4244
4	4		9.777	308.0	4744.8	0.0250
5	5		10.277	873.0	16367.6	0.0861
6	6		11.077	11477.2	228367.0	1.2012
7	7		11.677	810172.7	16535122.8	86.9741
8	8		12.477	89812.6	2055088.1	10.8097
9	9		15.027	625.3	13886.0	0.0730
10	10		16.627	193.9	4930.2	0.0259
合计:				921785.3	19011547.3	100.0000

78% ee

色谱分析报告

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样品批号:
分析日期:2007-07-12

样品文件名:9-56+-...che
分析者:
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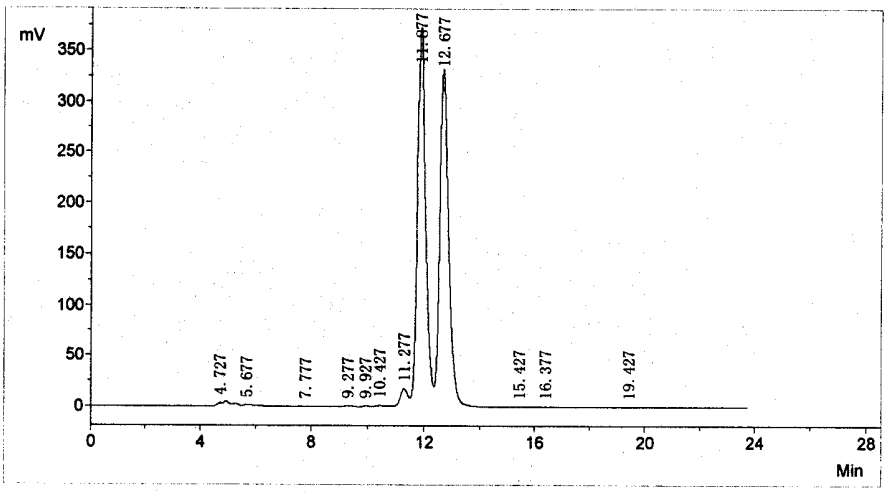

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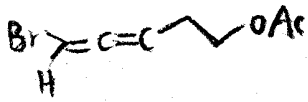
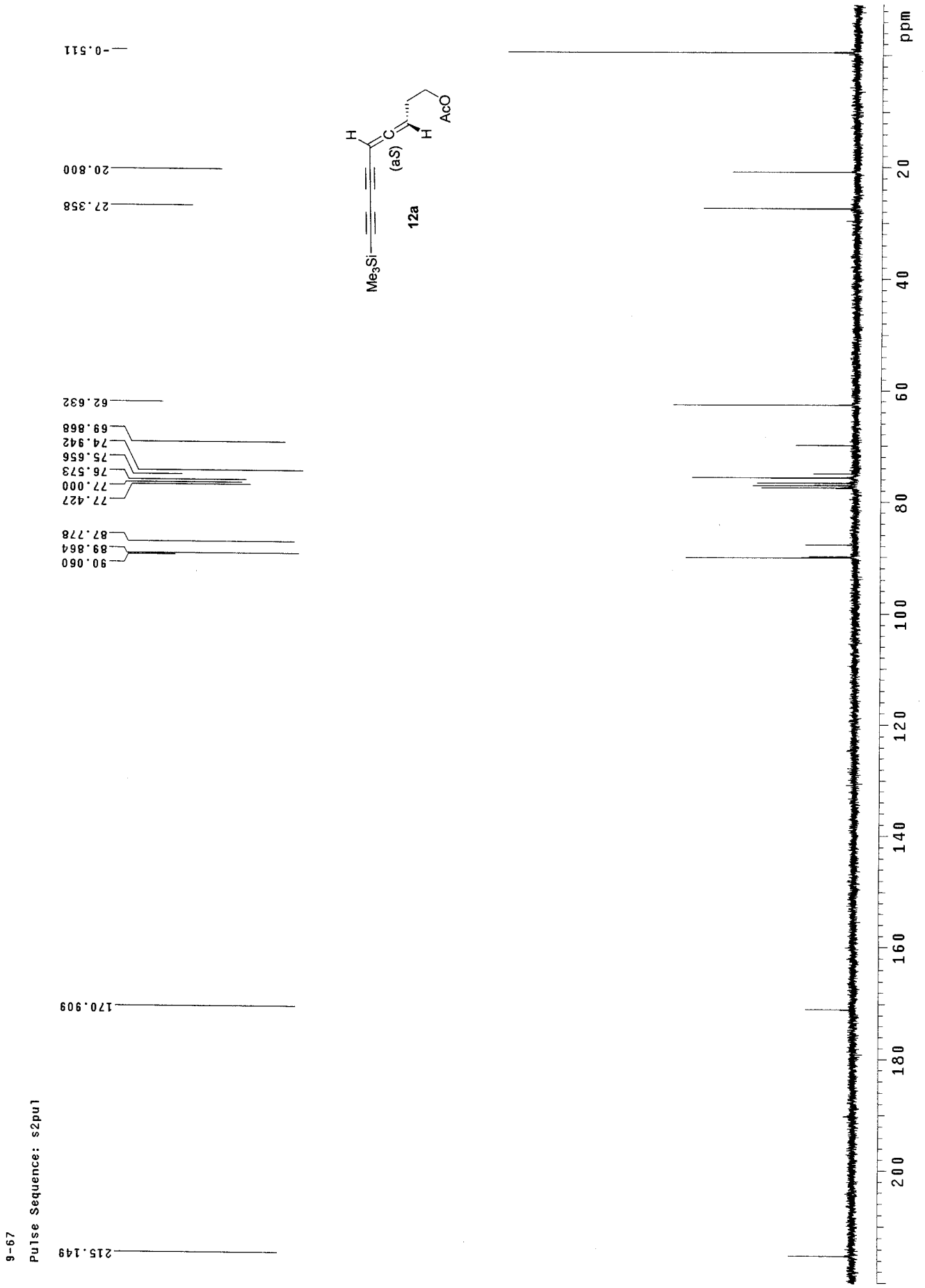
3	3		7.777	81.7	1681.8	0.0107
4	4		9.277	1054.8	33098.3	0.2104
5	5		9.927	879.3	18195.3	0.1157
6	6		10.427	1504.4	34862.5	0.2216
7	7		11.277	17611.7	354290.5	2.2522
8	8		11.877	372450.4	7627036.2	48.4855
9	9		12.677	328086.5	7436767.4	47.2760
10	10		15.427	138.0	3740.8	0.0238
11	11		16.377	39.0	2721.9	0.0173
12	12		19.427	38.8	2407.2	0.0153
合计:				726992.5	15730538.7	100.0000

(+/-)-11

racemic bromoallene 11

for comparison

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62.632
69.868
74.942
75.656
76.573
77.000
77.427
87.778
89.864
90.060
170.909
215.149
H
C
(aS)
H
AcO
Me3Si
12a
ppm
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40
60
80
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160
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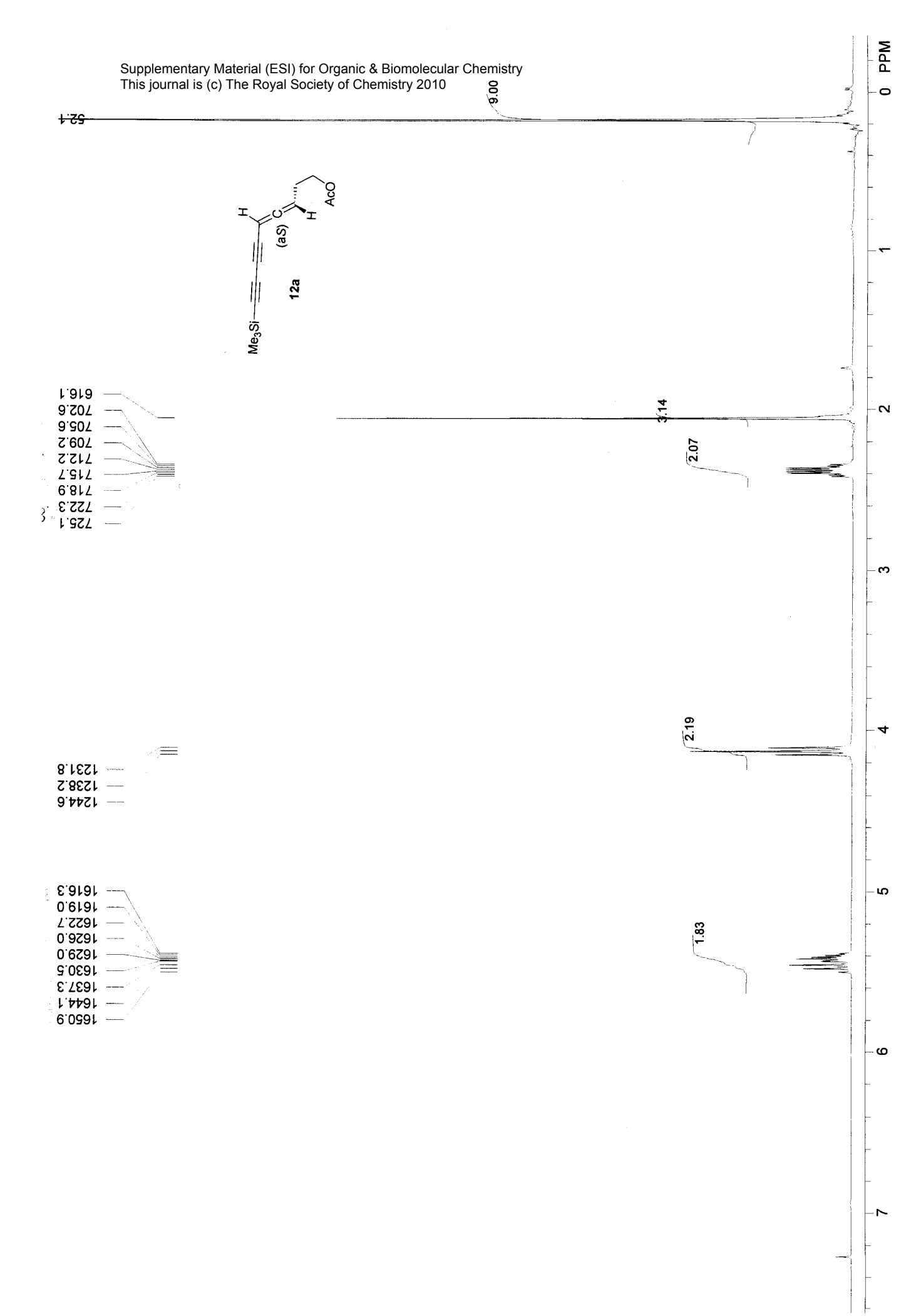
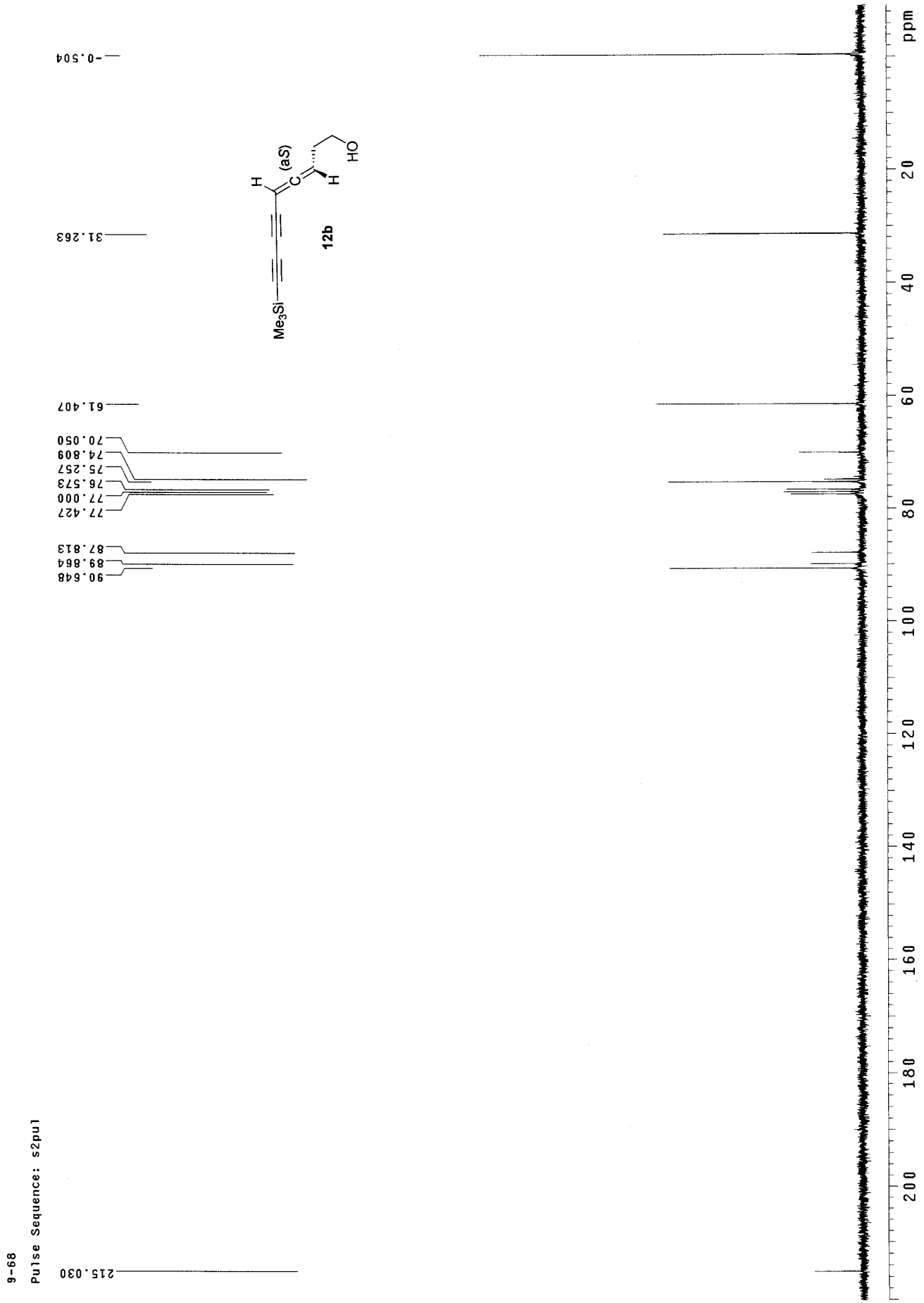
200
9-67
Pulse Sequence: s2pul

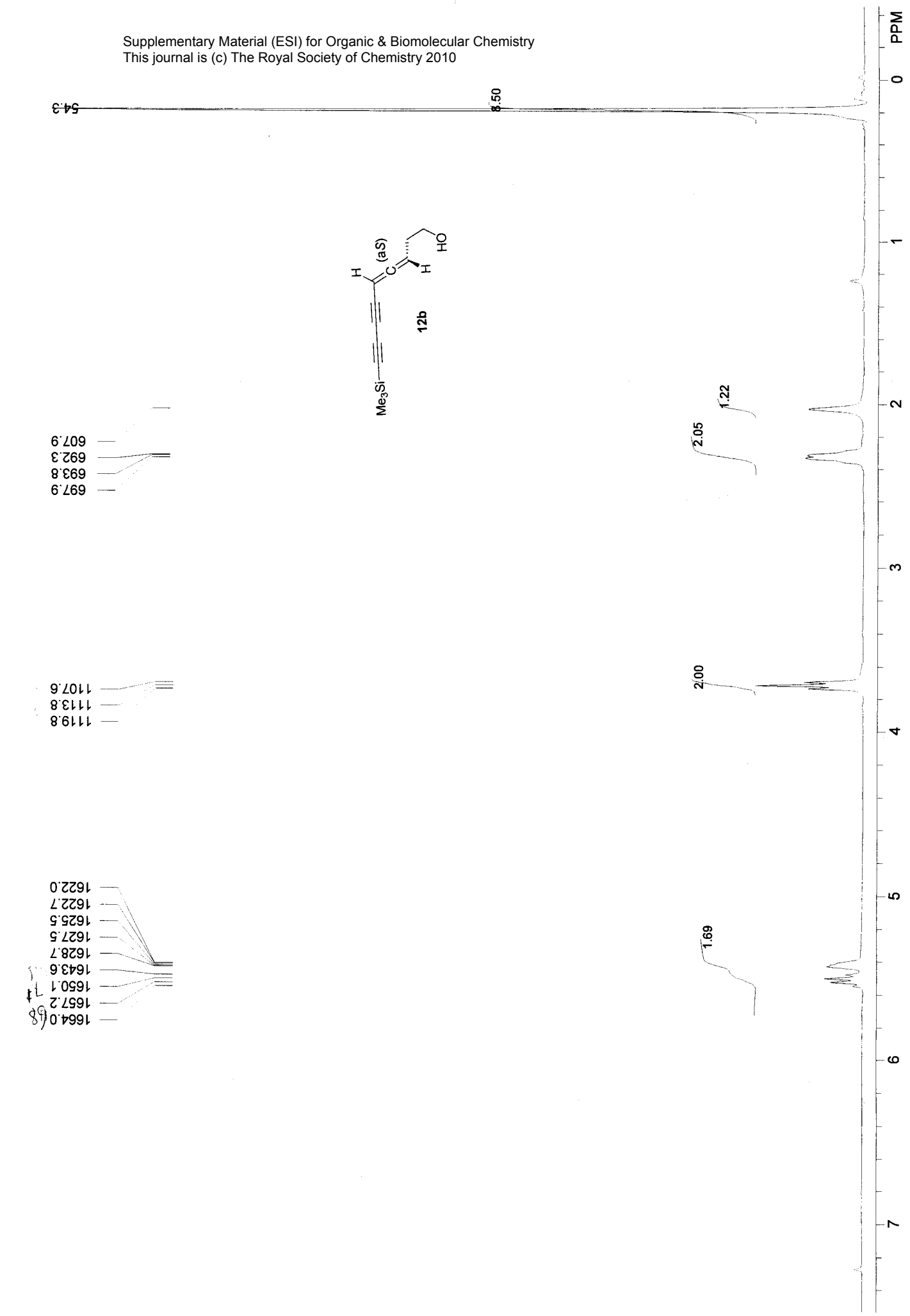
75 MHz, CDCl3



S 15 **300 MHz, CDCl3**



S 16 **75 MHz, CDCl3**



 300 MHz, CDCl3

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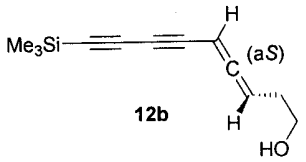
Sample Name : ZY13-39
Data File : D:\CS\D___643.RAW Date: 08-7-9 10:23
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: d-1
Sample Amount : 1.0000 Dilution Factor : 1.00

DEFAULT REPORT



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3	14.856	8634075.80	432726.15	93.57	VB
		9227535.50	464828.24	100.00	

88.67% ee

Derived from tosylate 9

Software Version: 4.1<2F12>
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Sample Name : 9-68-/+
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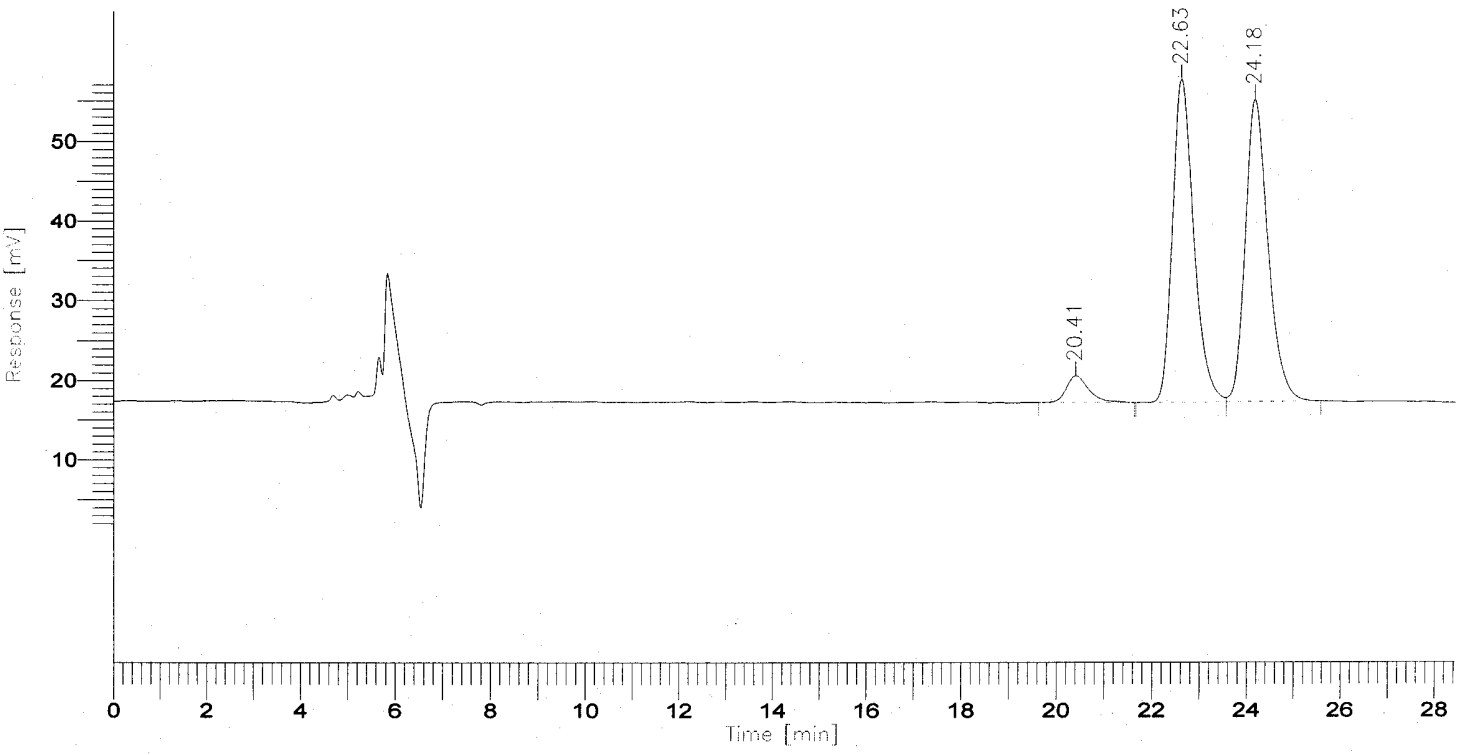
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: d-1
Sample Amount : 1.0000 Dilution Factor : 1.00



(±) – 12b

DEFAULT REPORT

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2	22.628	1270096.92	40403.04	47.78	BV
3	24.184	1276713.08	37795.70	48.03	VB
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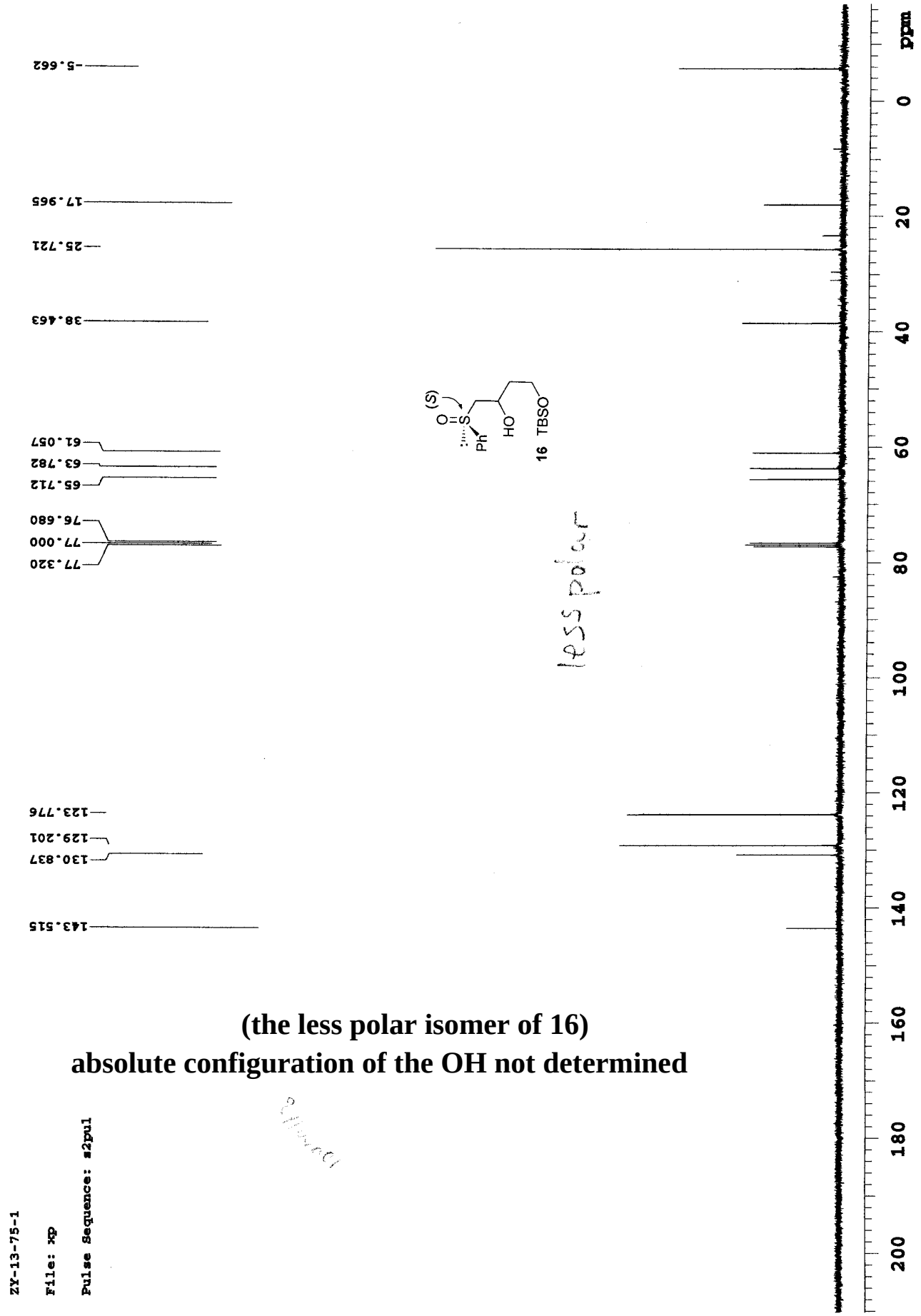
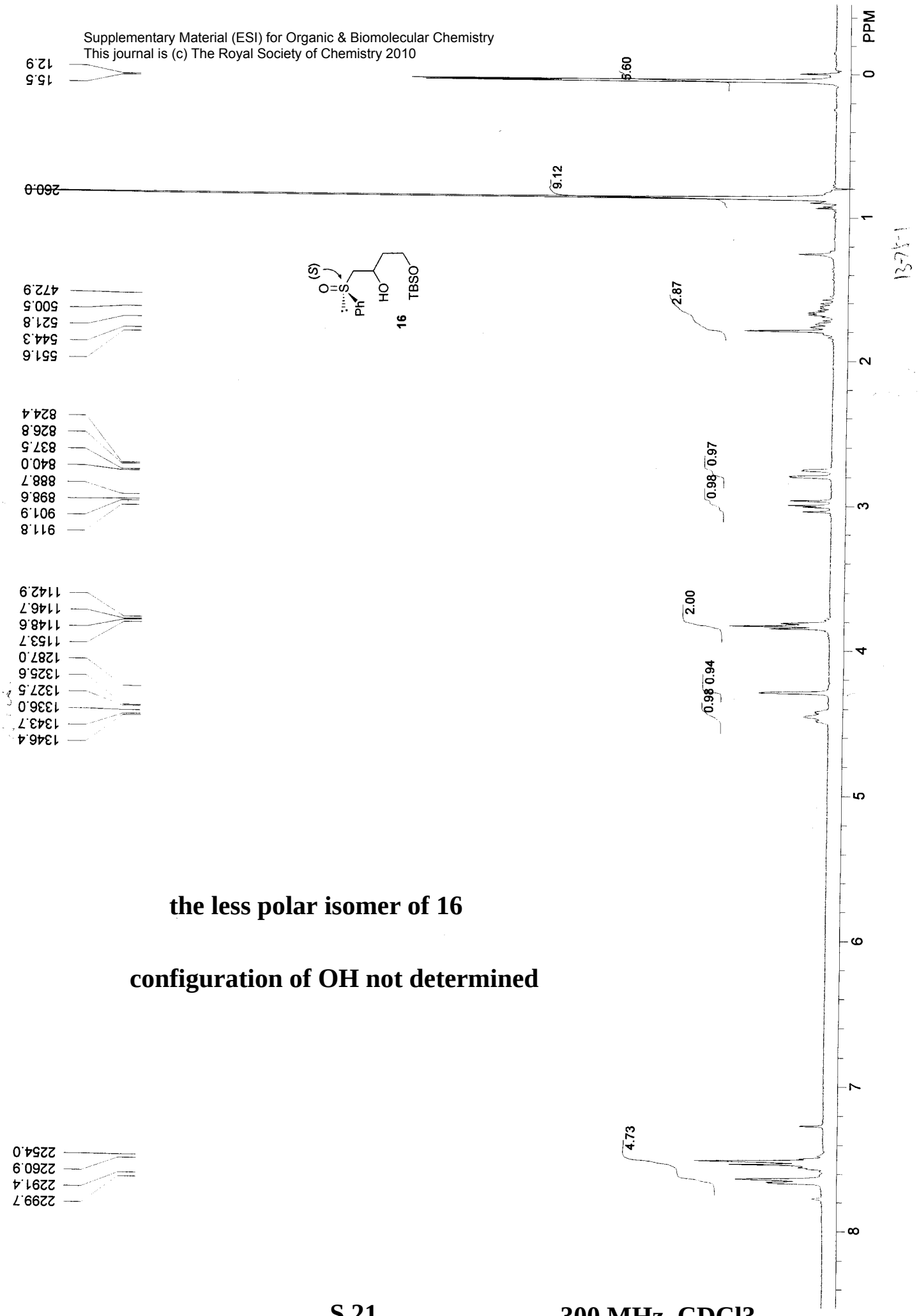
racemic 12b, for comparison

SJ-1 98/2
PE/iPrOH



(the less polar isomer of 16)
absolute configuration of the OH not determined

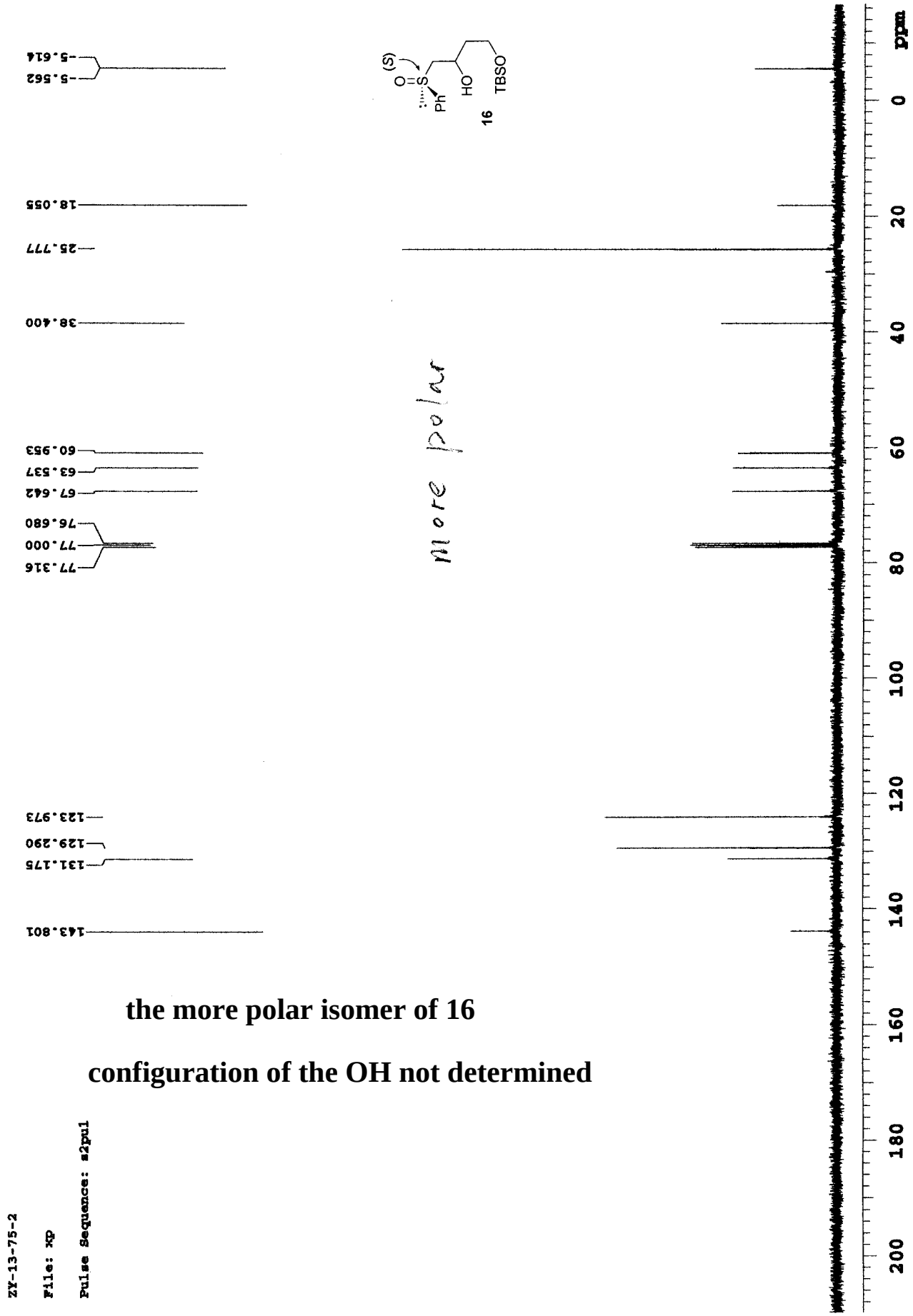
100 MHz, CDCl3



the less polar isomer of 16

configuration of OH not determined

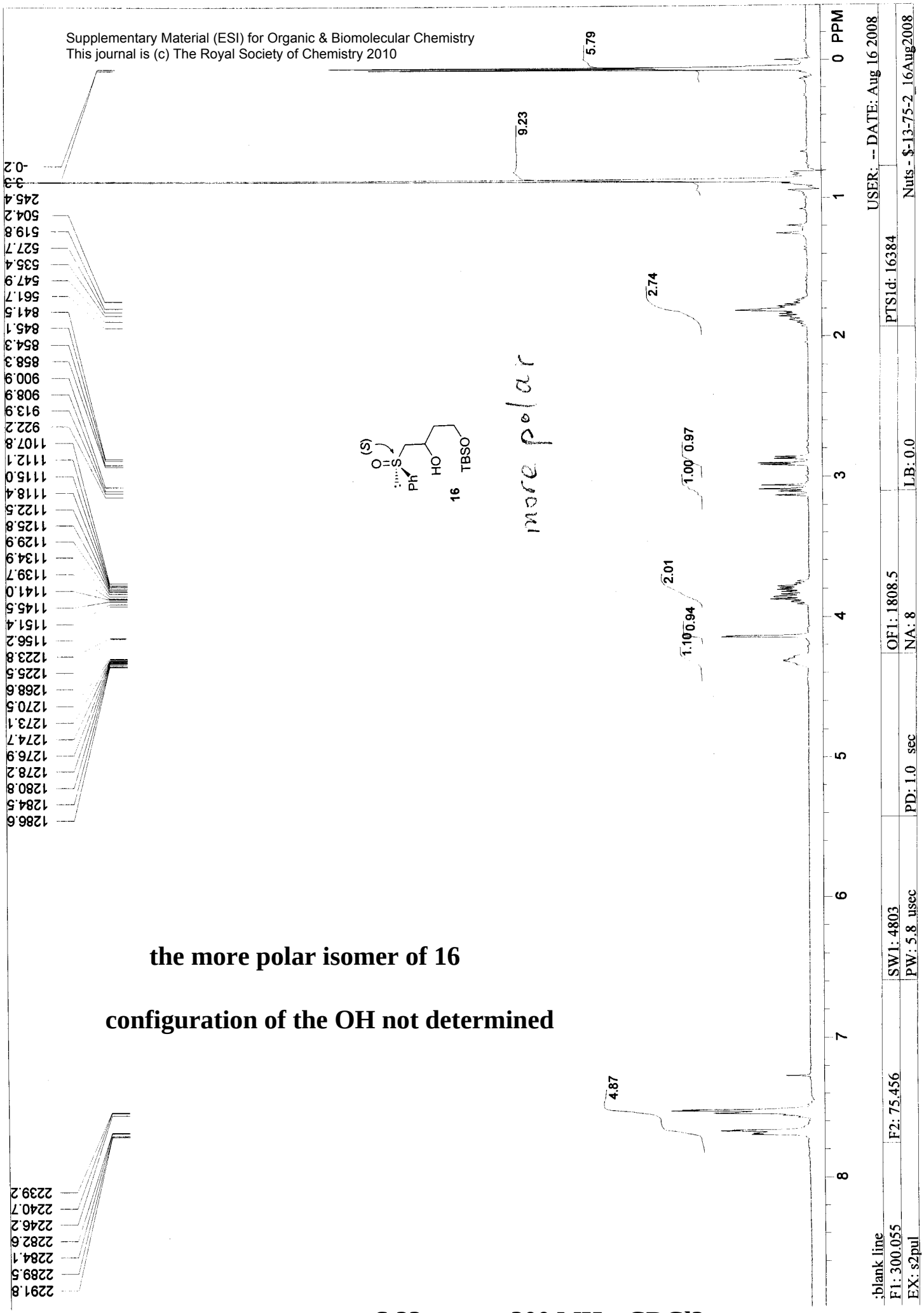
300 MHz, CDCl3



the more polar isomer of 16

configuration of the OH not determined

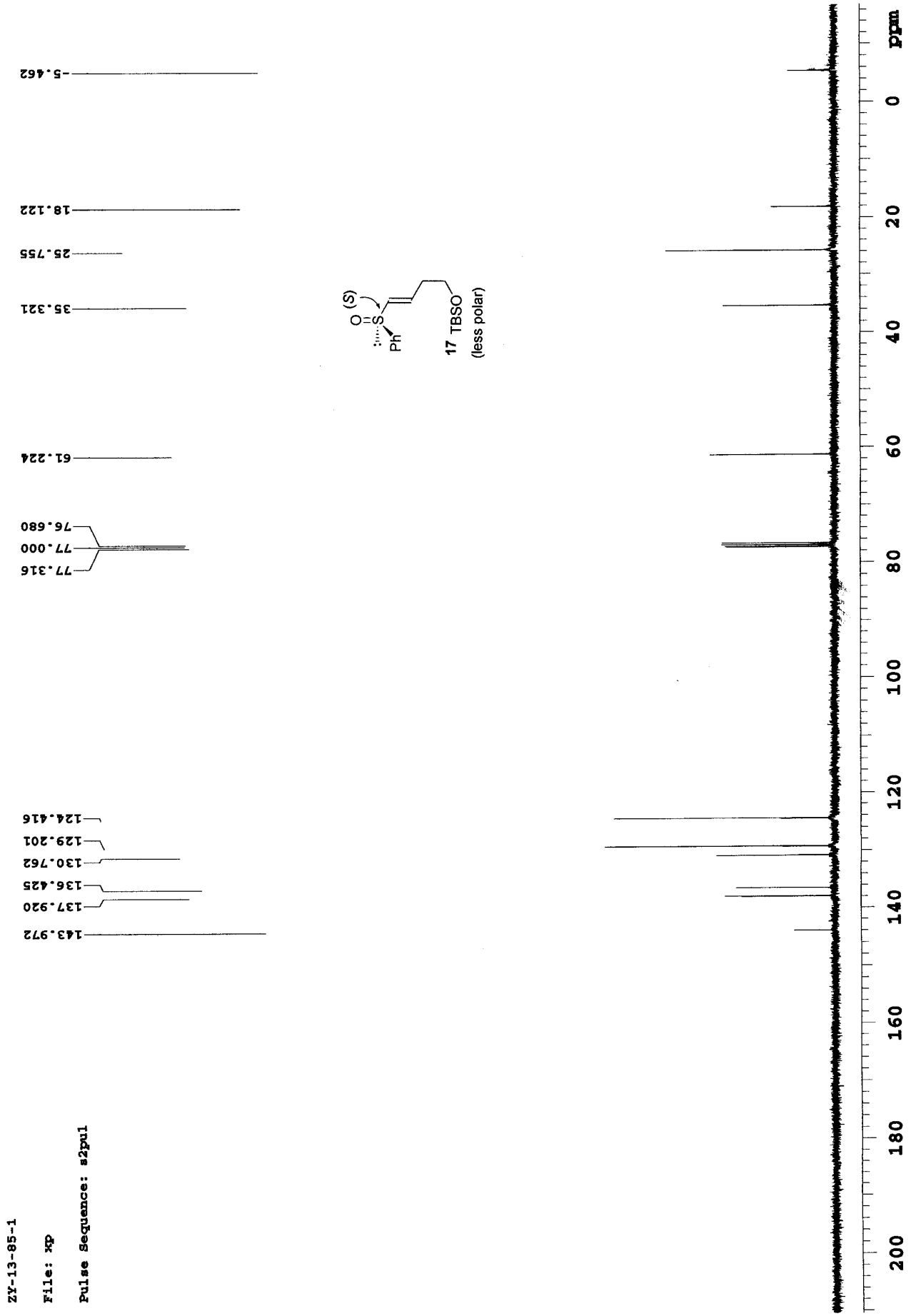
100 MHz, CDCl3



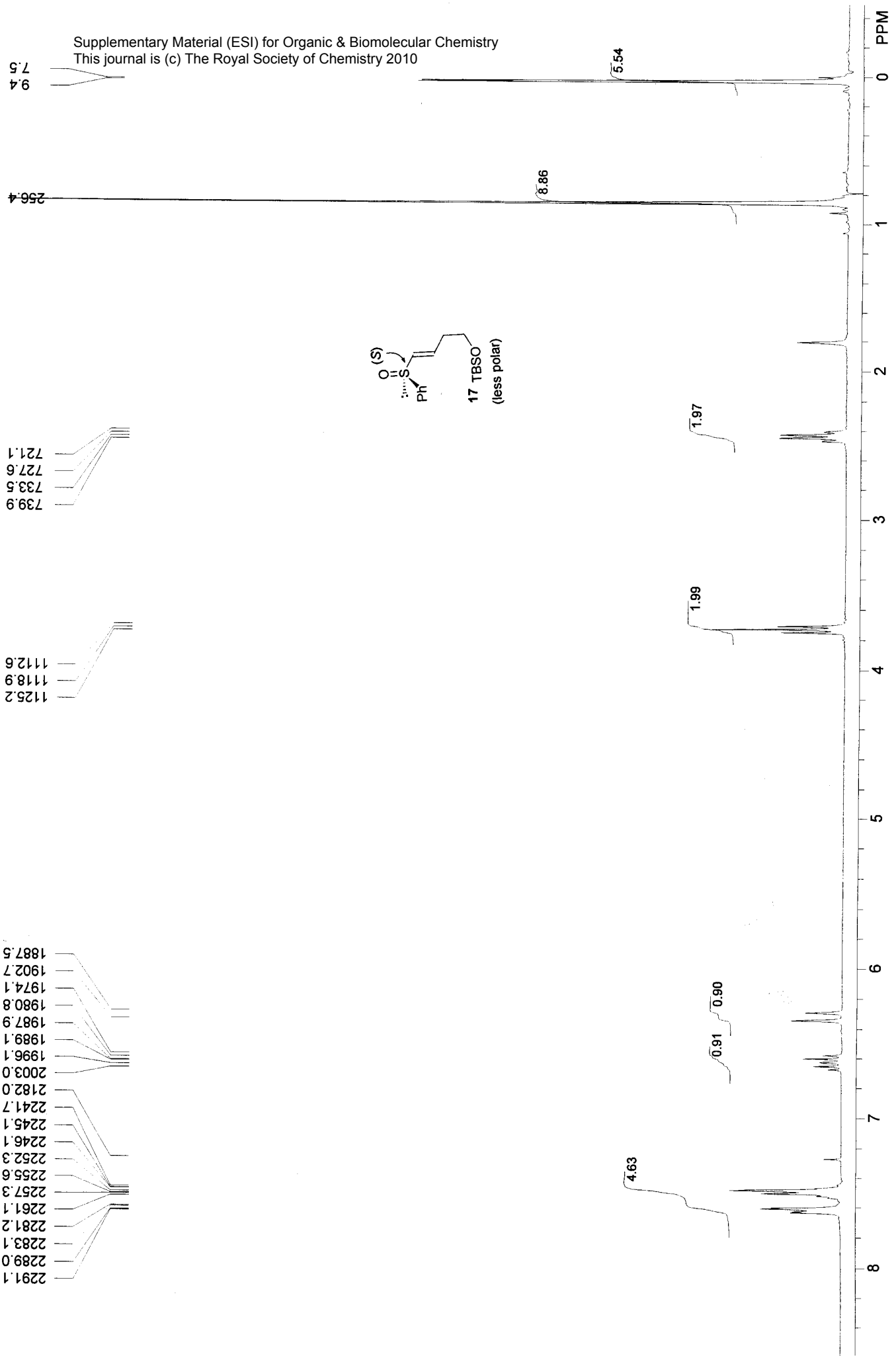
the more polar isomer of 16

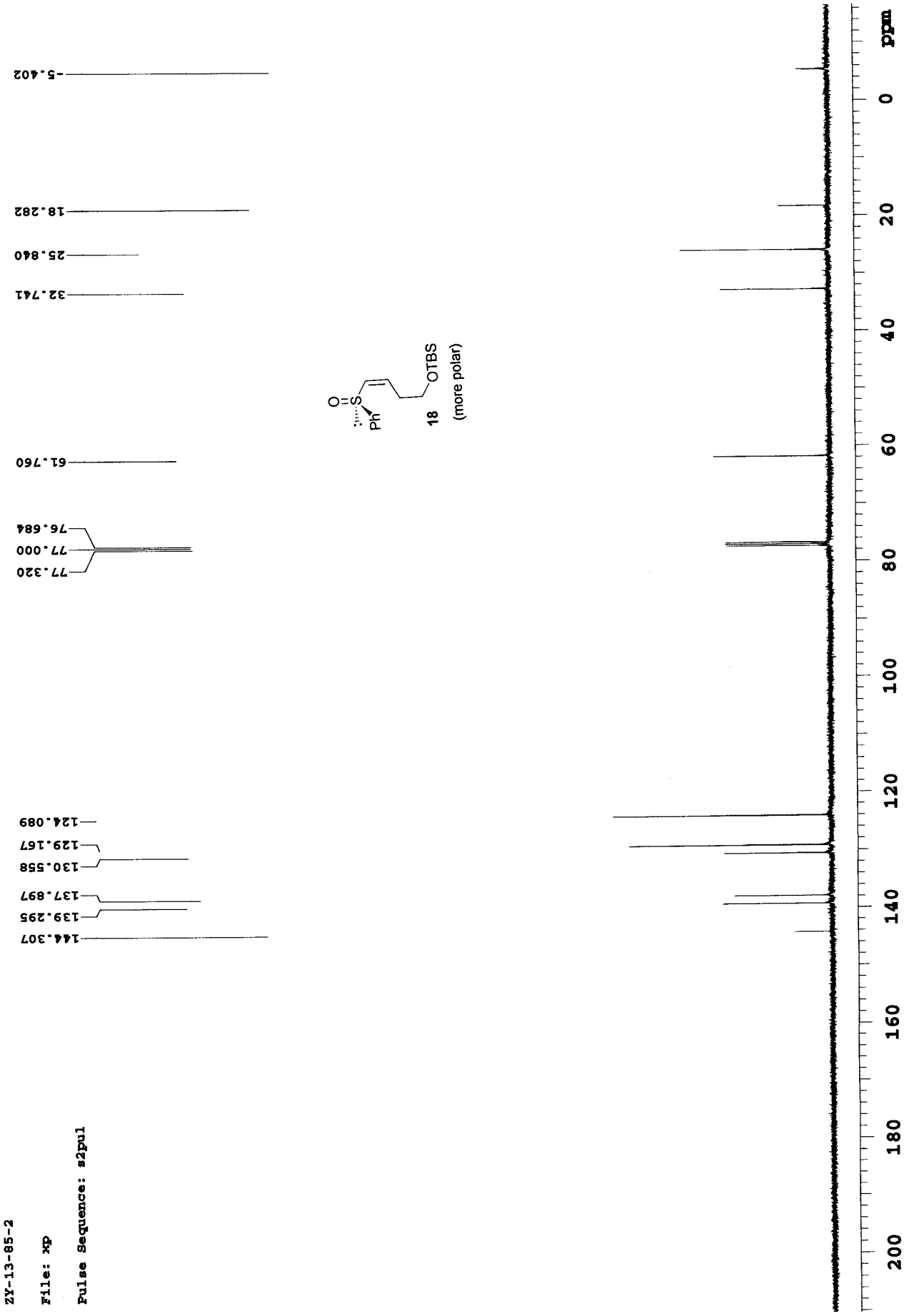
configuration of the OH not determined

S 23 300 MHz, CDCl3

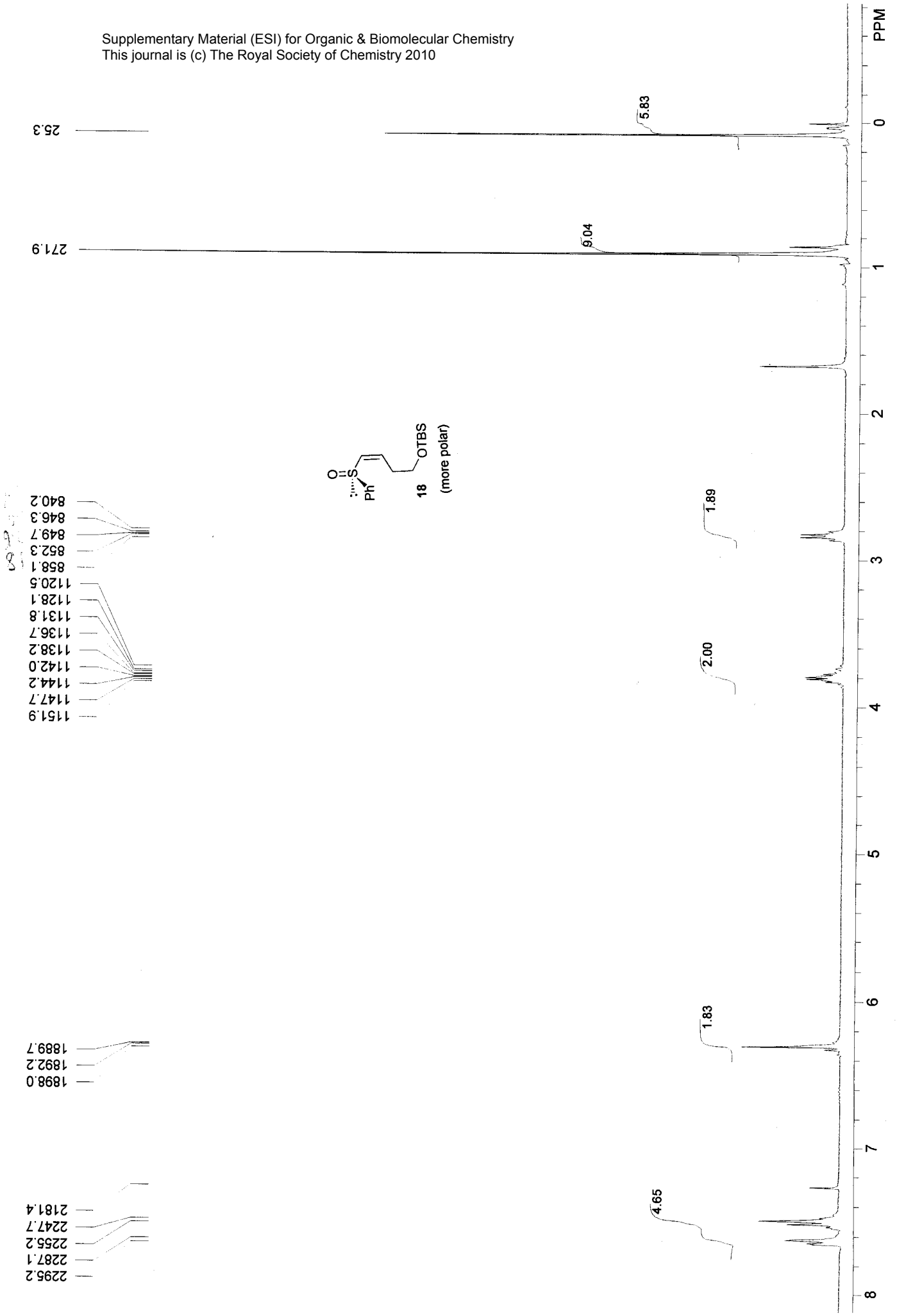


 100 MHz, CDCl3

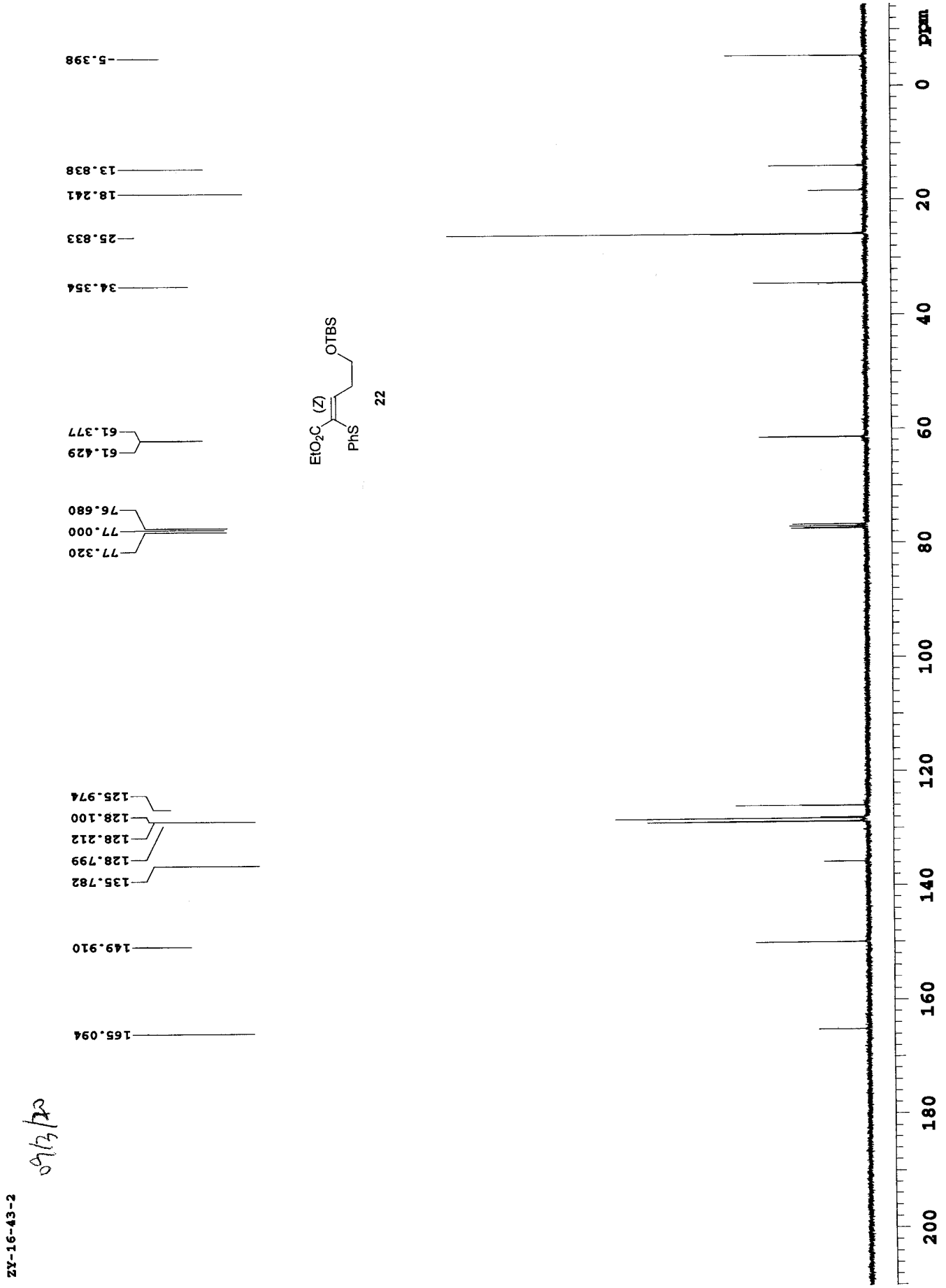

PPM
0
1
2
3
4
5
6
7
8
5.54
8.86
1.97
1.99
0.90
0.91
4.63
(S)
O=S
Ph
17 TBSO
(less polar)
7.5
9.4
256.4
721.1
727.6
733.5
739.9
1112.6
1118.9
1125.2
1887.5
1902.7
1974.1
1980.8
1987.9
1989.1
1996.1
2003.0
2182.0
2241.7
2245.1
2246.1
2252.3
2255.6
2257.3
2261.1
2281.2
2283.1
2289.0
2291.1



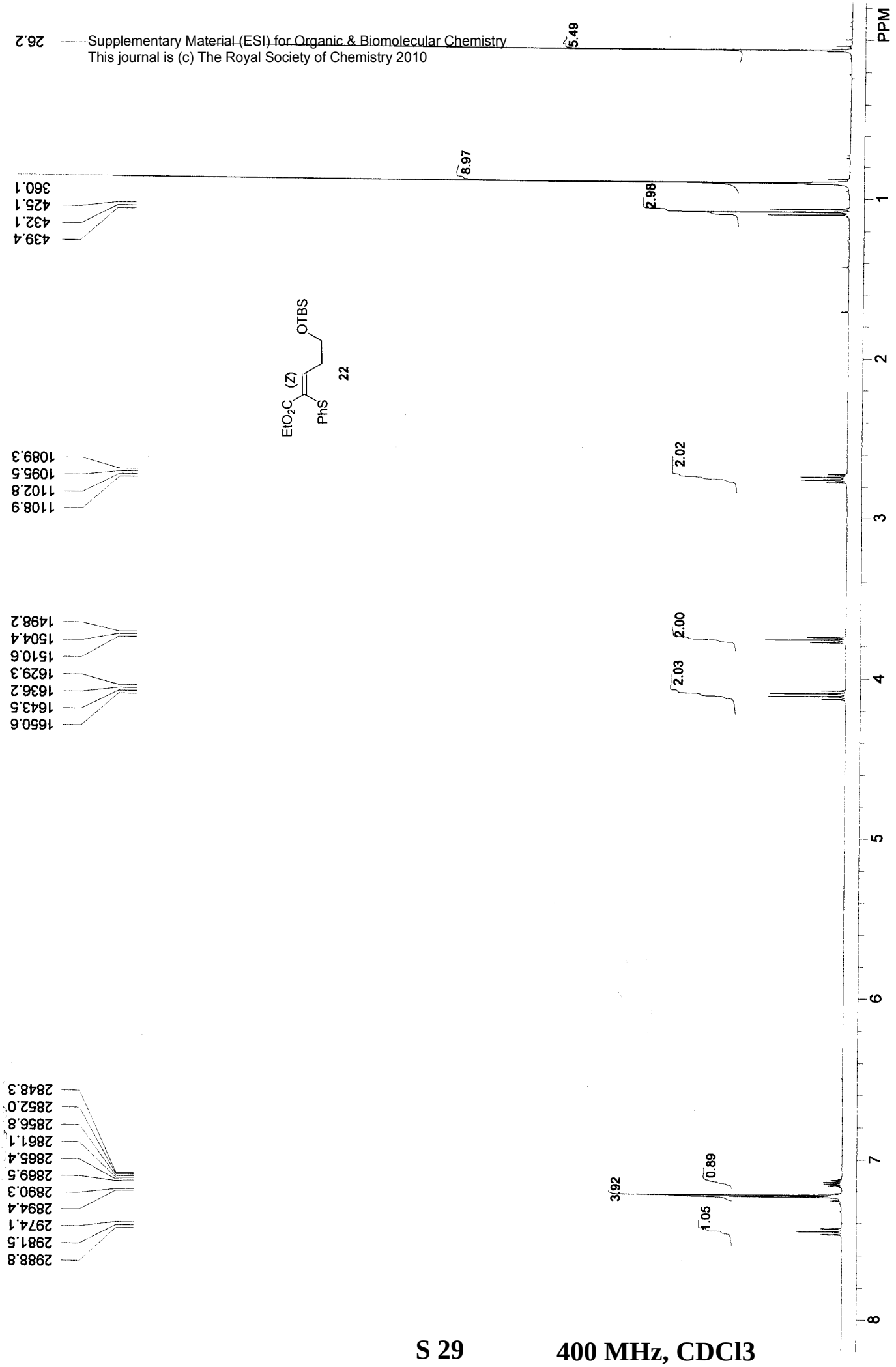
100 MHz, CDCl3



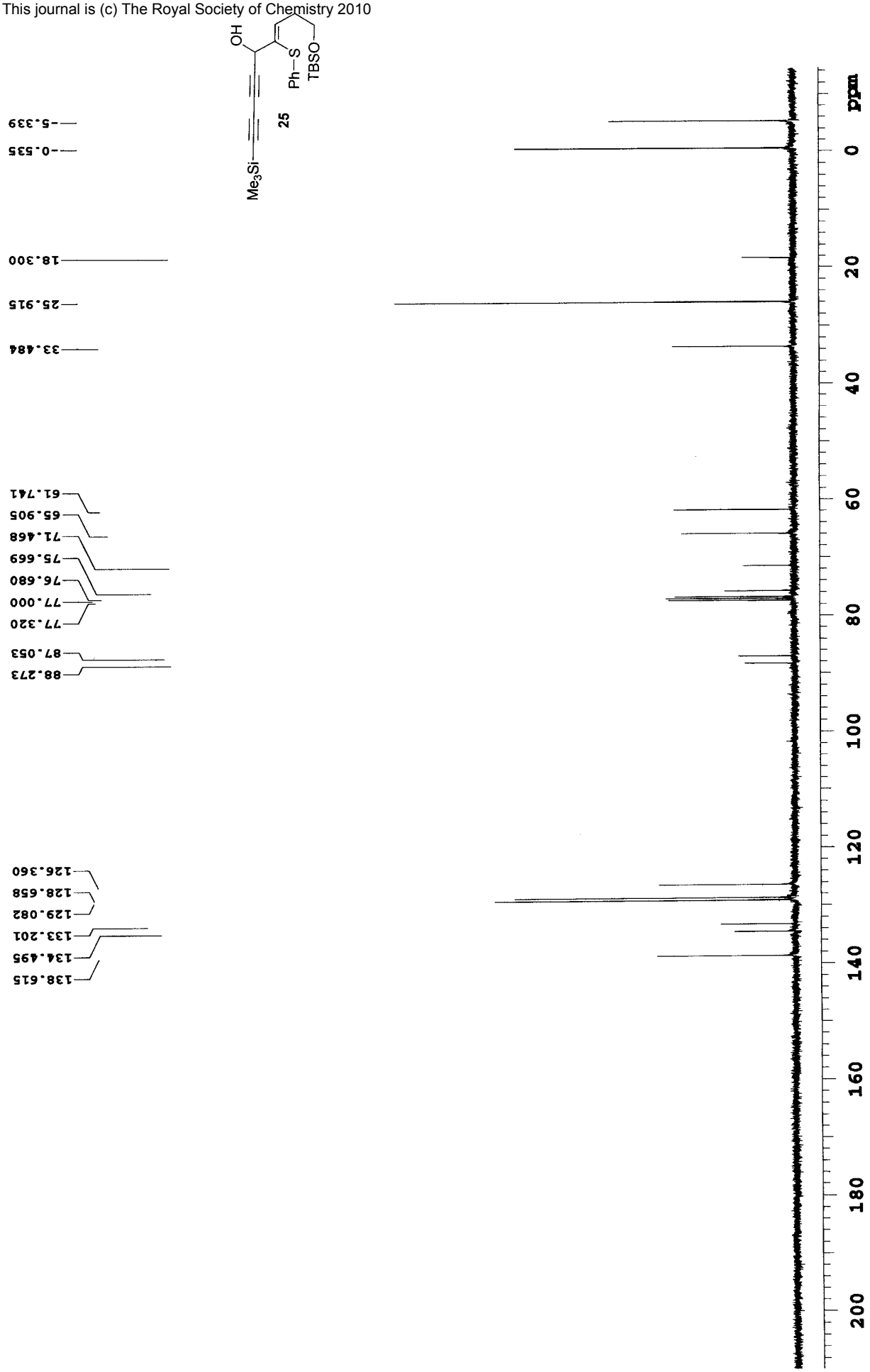
300 MHz, CDCl3



100 MHz, CDCl3

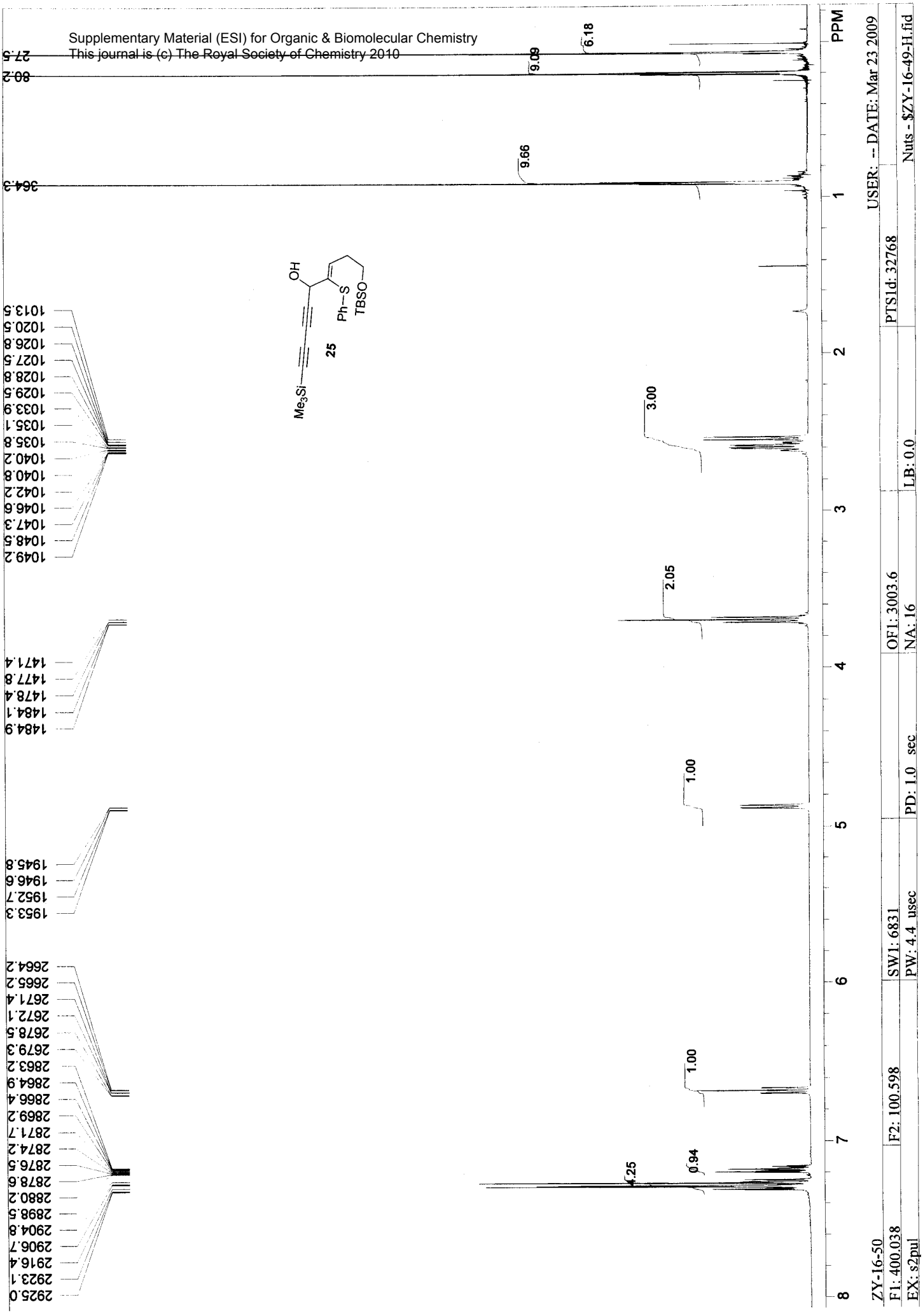


400 MHz, CDCl3

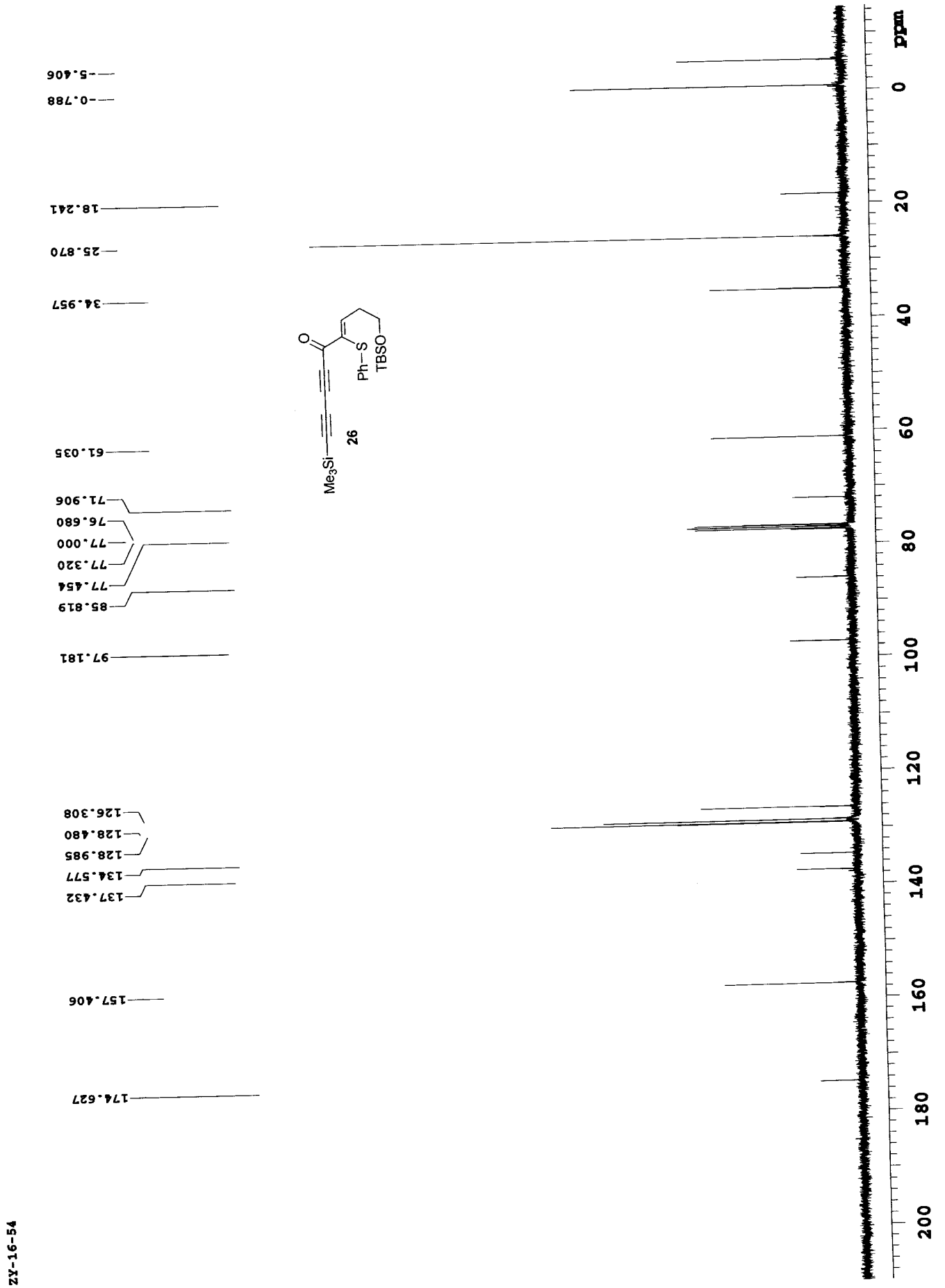


ZY-16-49

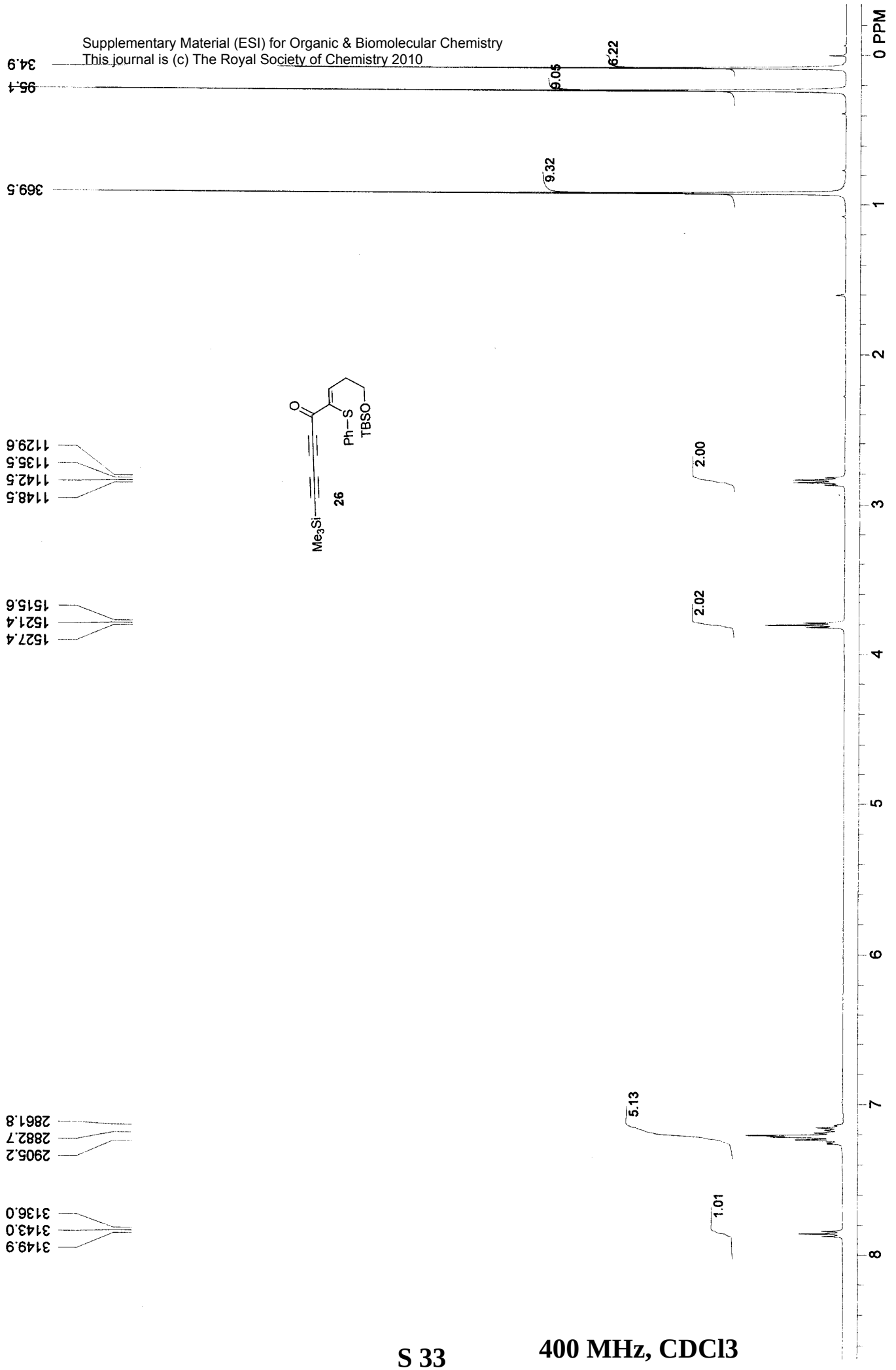
S 30 **100 MHz, CDCl3**



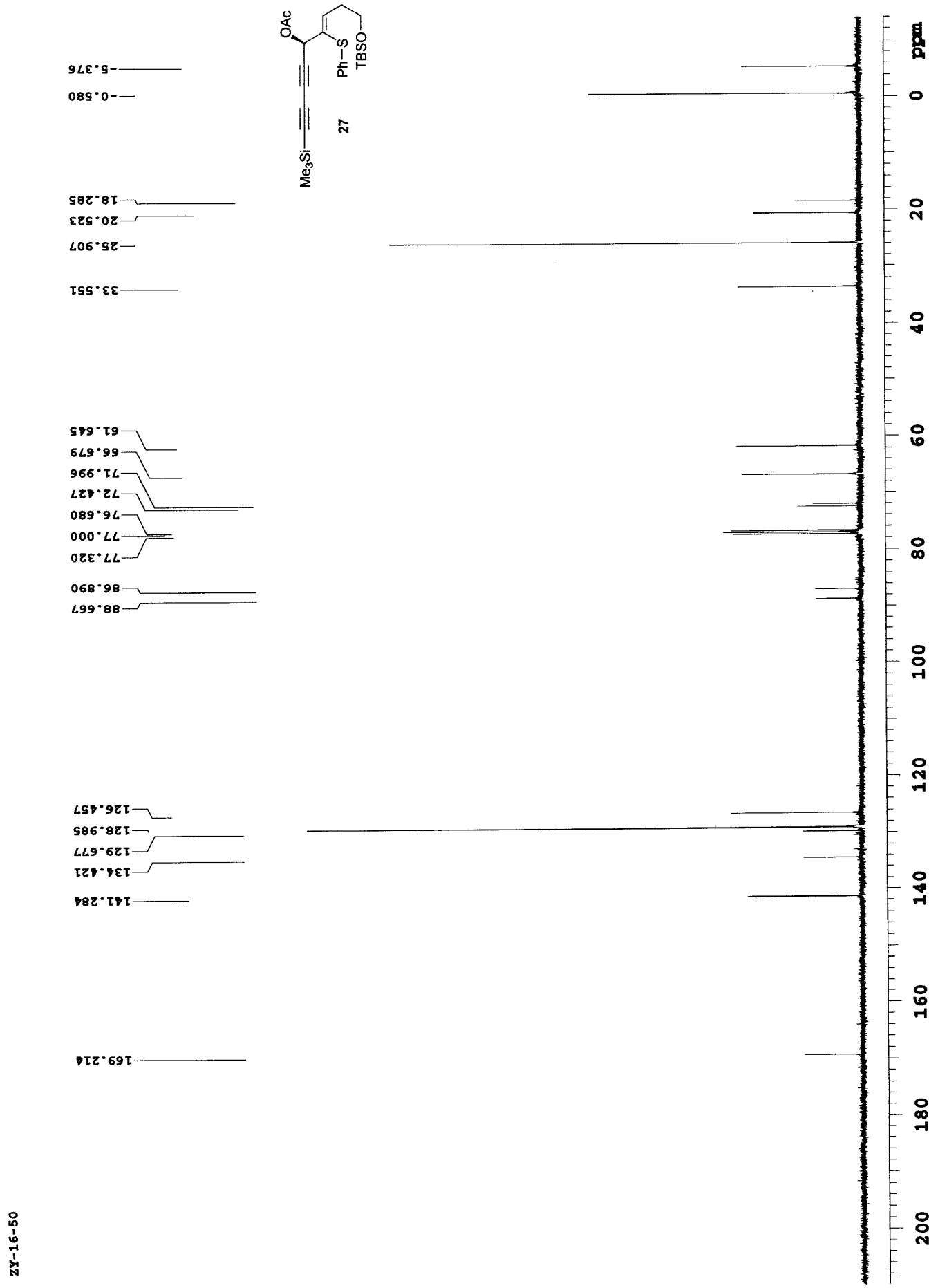
400 MHz, CDCl2



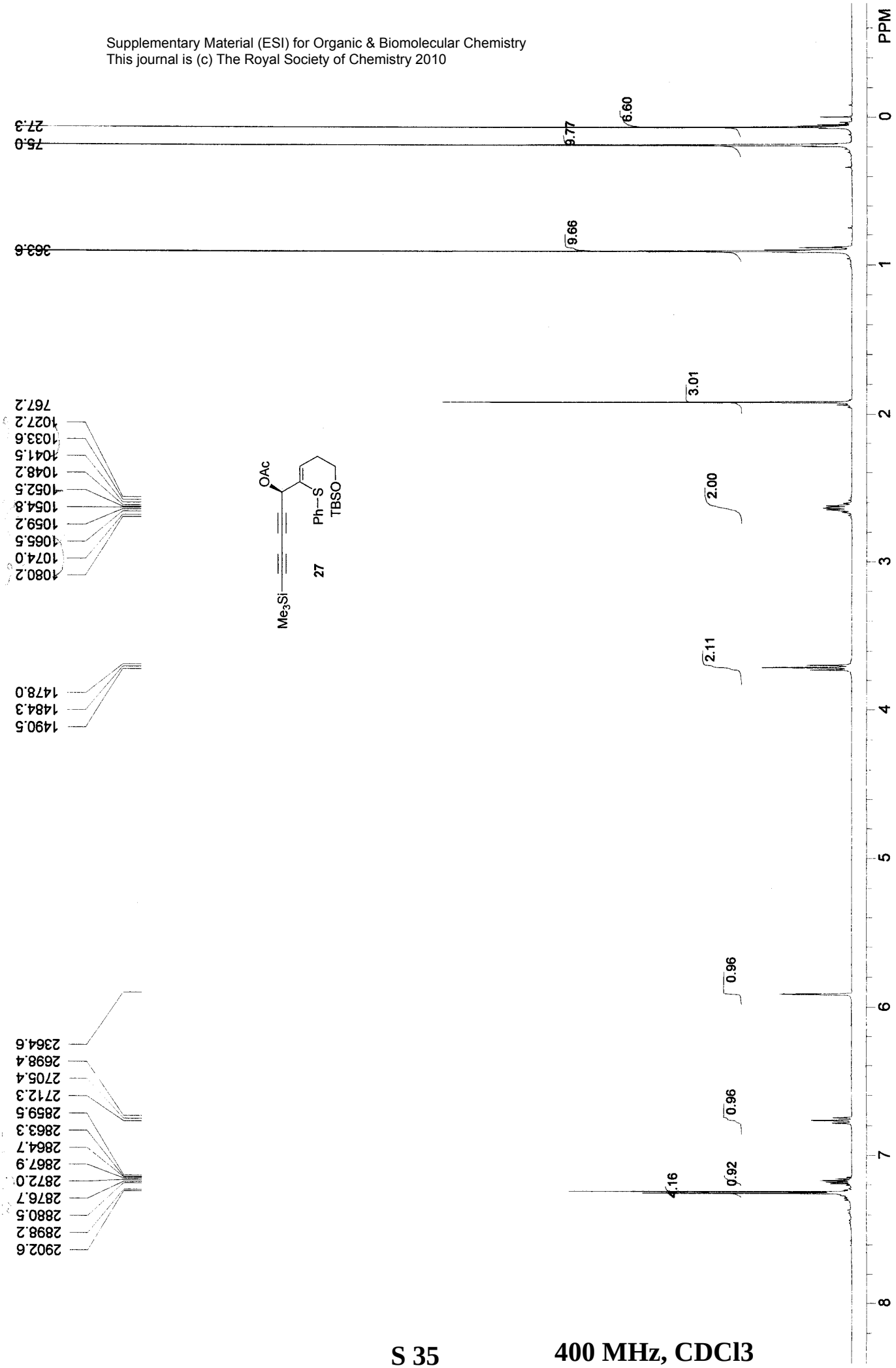
 100 MHz, CDCl3



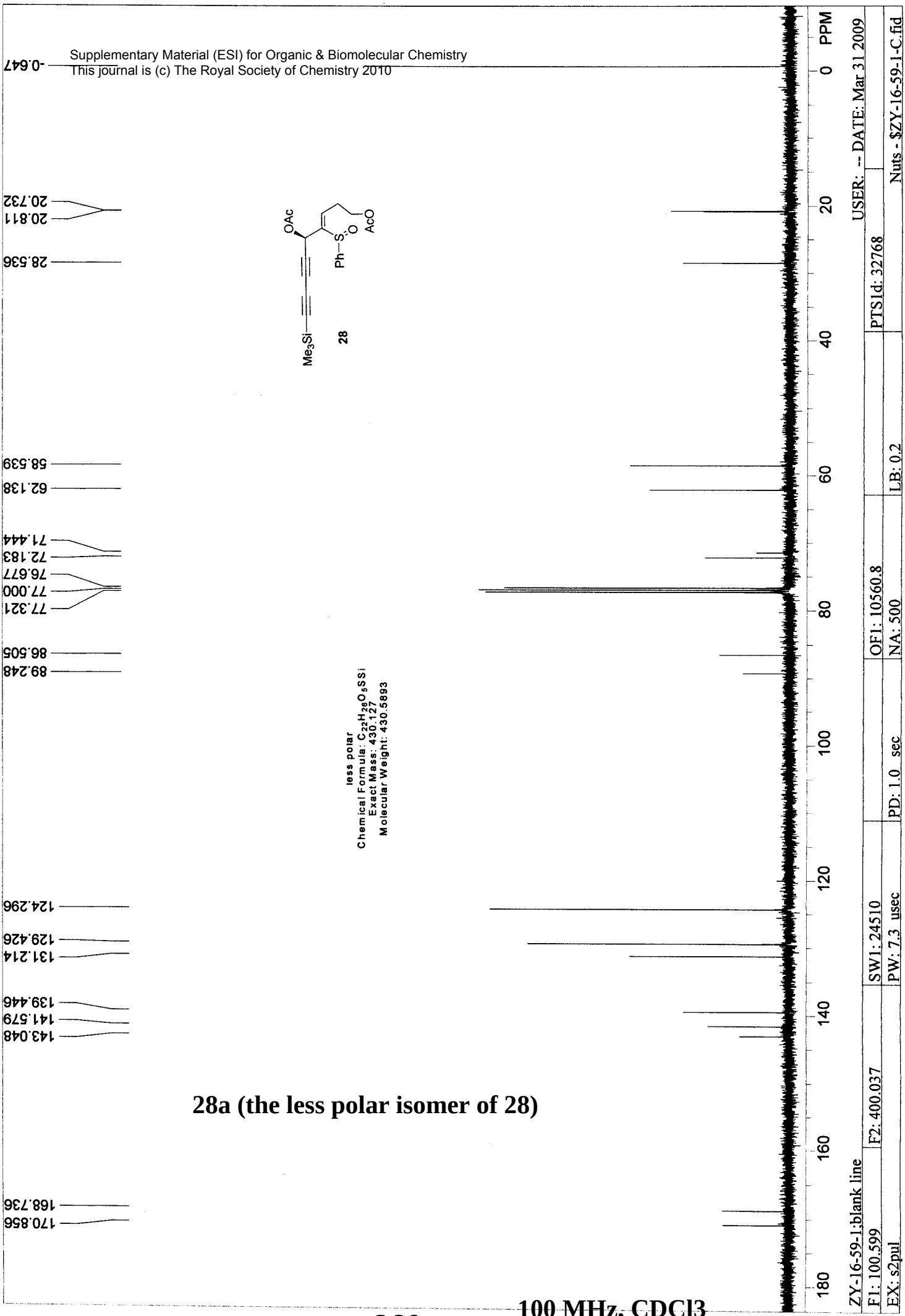
400 MHz, CDCl3



100 MHz, CDCl3

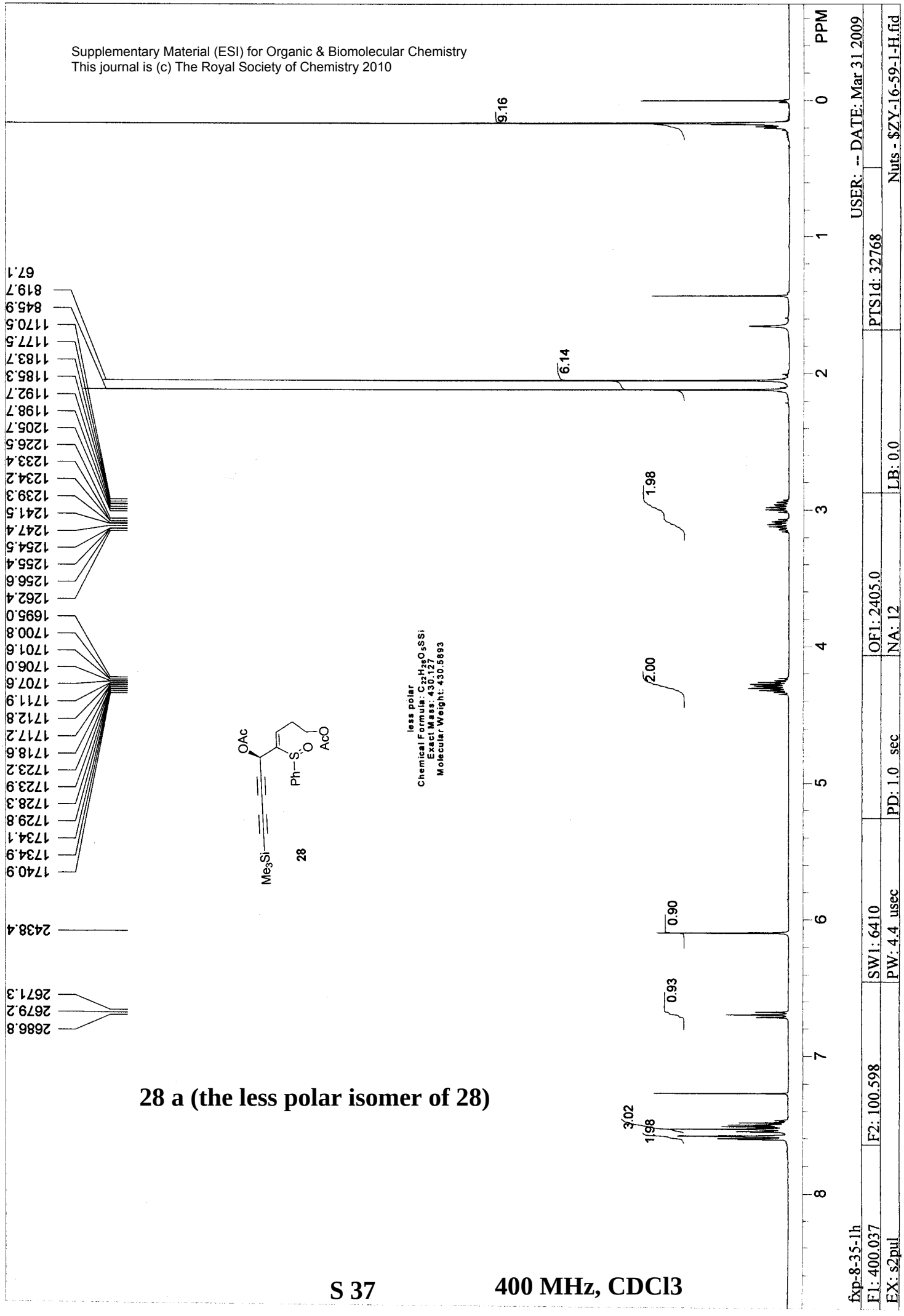


400 MHz, CDCl3



28a (the less polar isomer of 28)

100 MHz, CDCl3



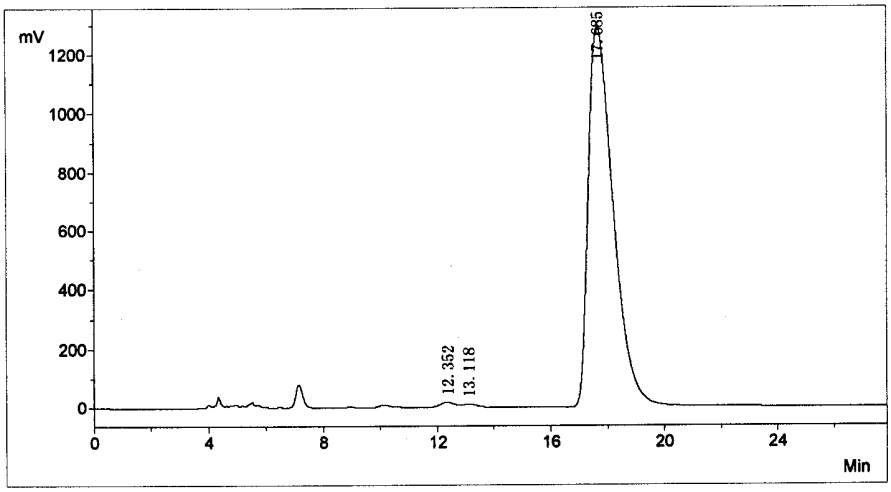
28 a (the less polar isomer of 28)

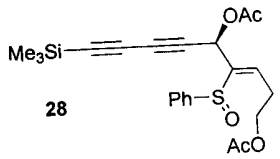
400 MHz, CDCl3

色谱分析报告

样品名称:
样品批号:
分析日期:2009-04-09

样品文件名:ZY-16-59-1.che
分析者:
分析时间:17:51





28

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		12.352	18218.3	650907.6	0.8051
2	2		13.118	11444.6	434995.3	0.5381
3	3		17.685	1294247.9	79758755.3	98.6568
合计:				1323910.7	80844658.2	100.0000

97.85% ee

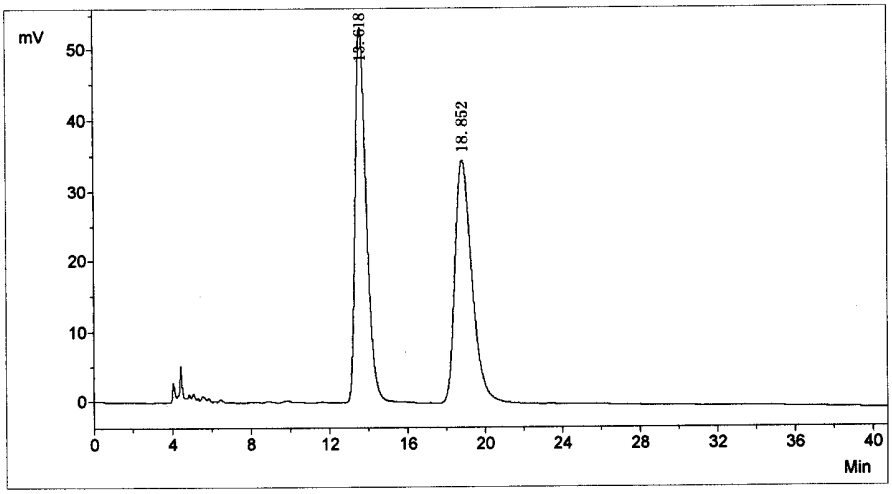
less polar

28 a (the less polar isomer of 28)

色谱分析报告

样品名称:
样品批号:
分析日期:2009-04-09

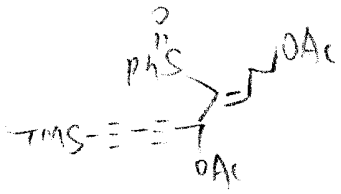
样品文件名:ZY-16-57b2.che
分析者:
分析时间:10:14

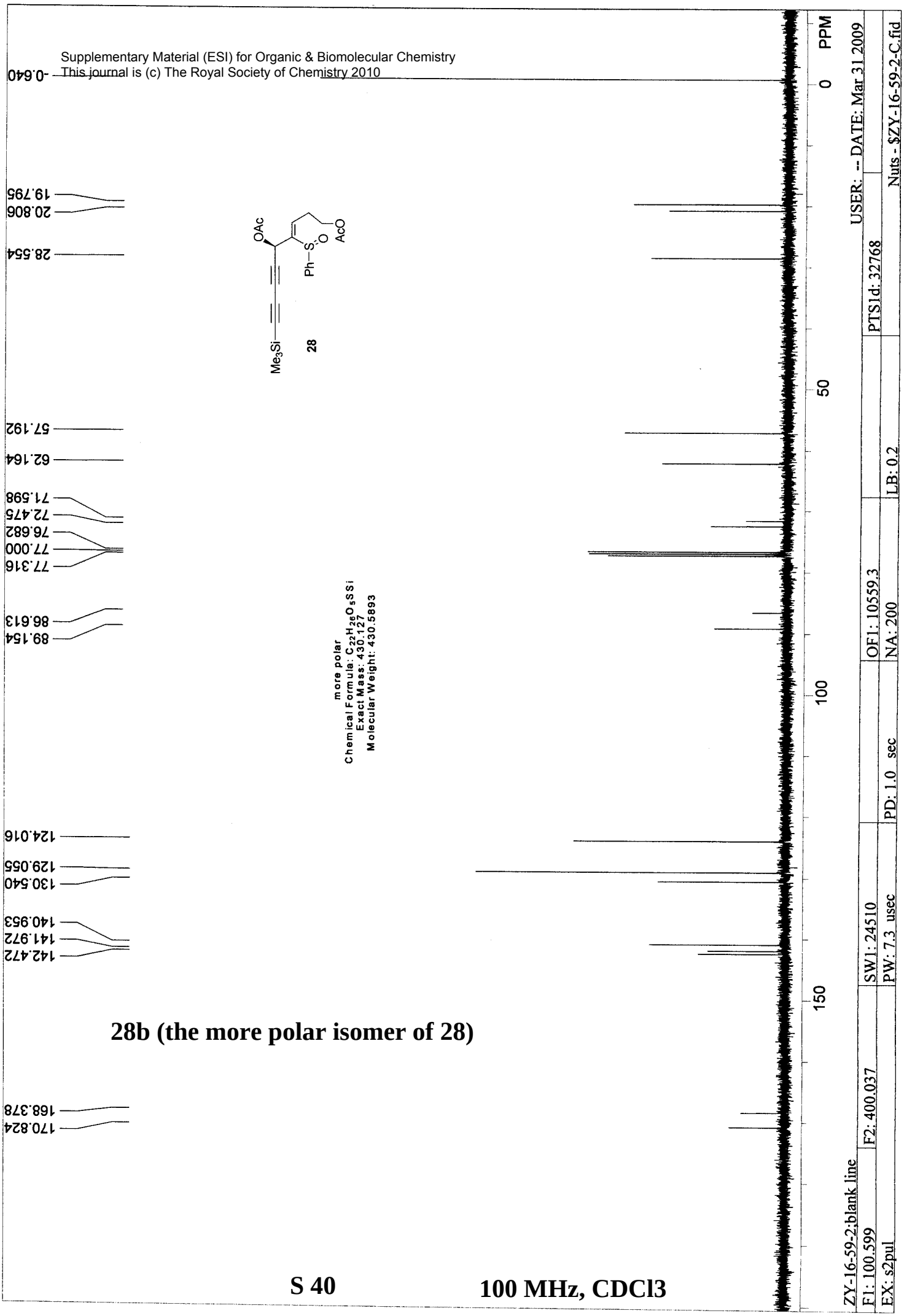


28

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		13.618	53282.8	2114853.2	49.9779
2	2		18.852	34687.1	2116722.0	50.0221
合计:				87969.8	4231575.1	100.0000

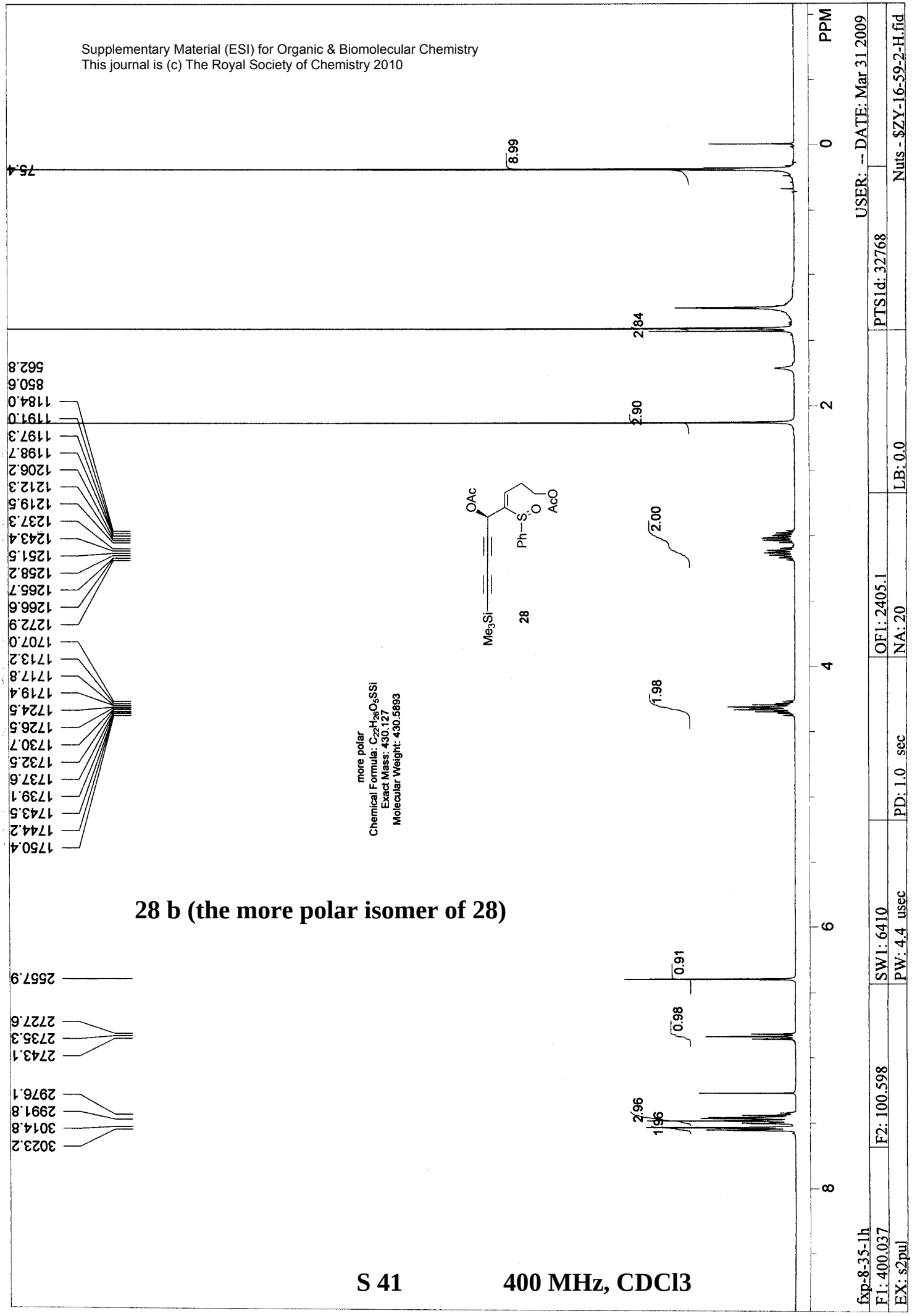
Racemic 28a (the less polar isomer of 28), for comparison





28b (the more polar isomer of 28)

100 MHz, CDCl3



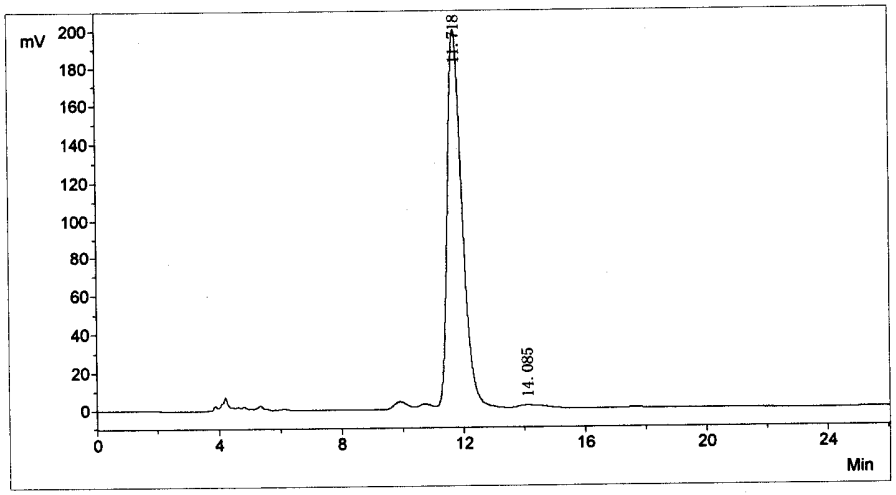
28 b (the more polar isomer of 28)

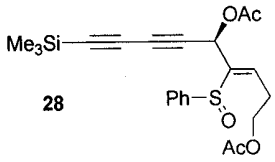
 400 MHz, CDCl3

色谱分析报告

样品名称:
样品批号:
分析日期:2009-04-09

样品文件名:ZY-16-59-2.che
分析者:
分析时间:18:20



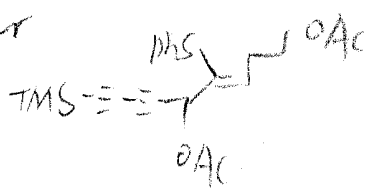


28

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		11.718	198686.2	6585078.6	98.9164
2	2		14.085	1355.5	72139.3	1.0836
合计:				200041.7	6657217.9	100.0000

97.83% ee

more polar

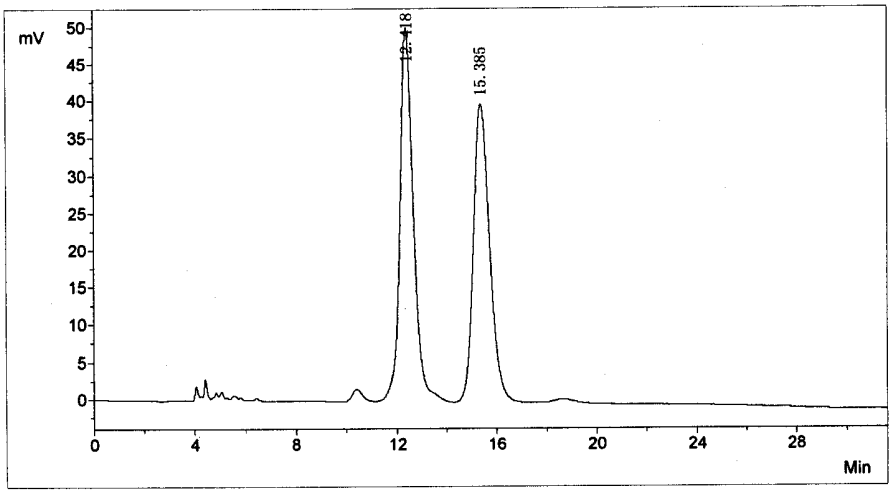


28b (the more polar isomer of 28)

色谱分析报告

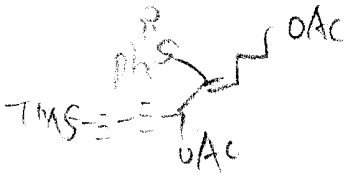
样品名称:
样品批号:
分析日期:2009-04-09

样品文件名:ZY-16-57b3.che
分析者:
分析时间:10:58

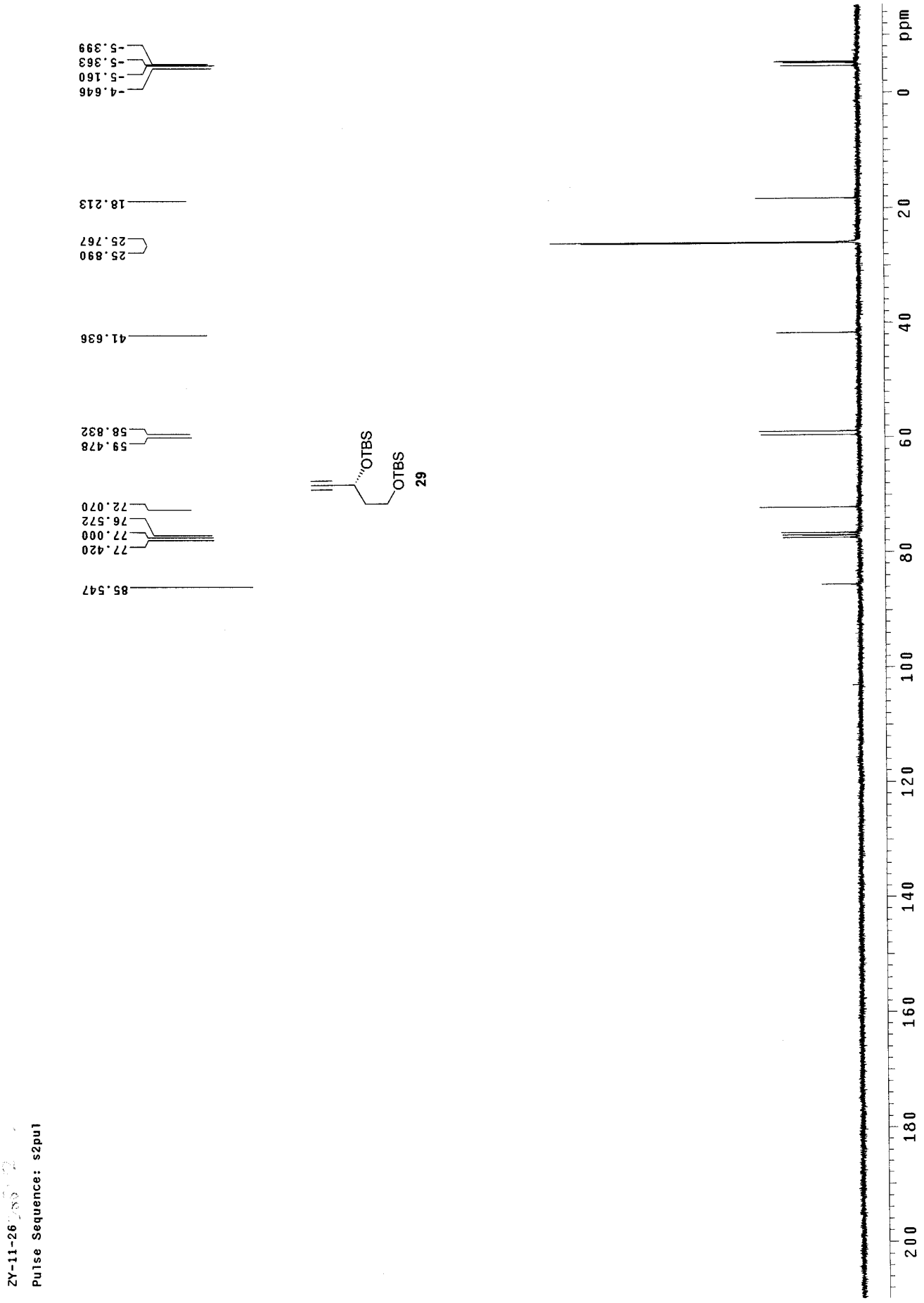


序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		12.418	50189.0	1870671.2	51.0252
2	2		15.385	39944.3	1795499.5	48.9748
合计:				90133.3	3666170.7	100.0000

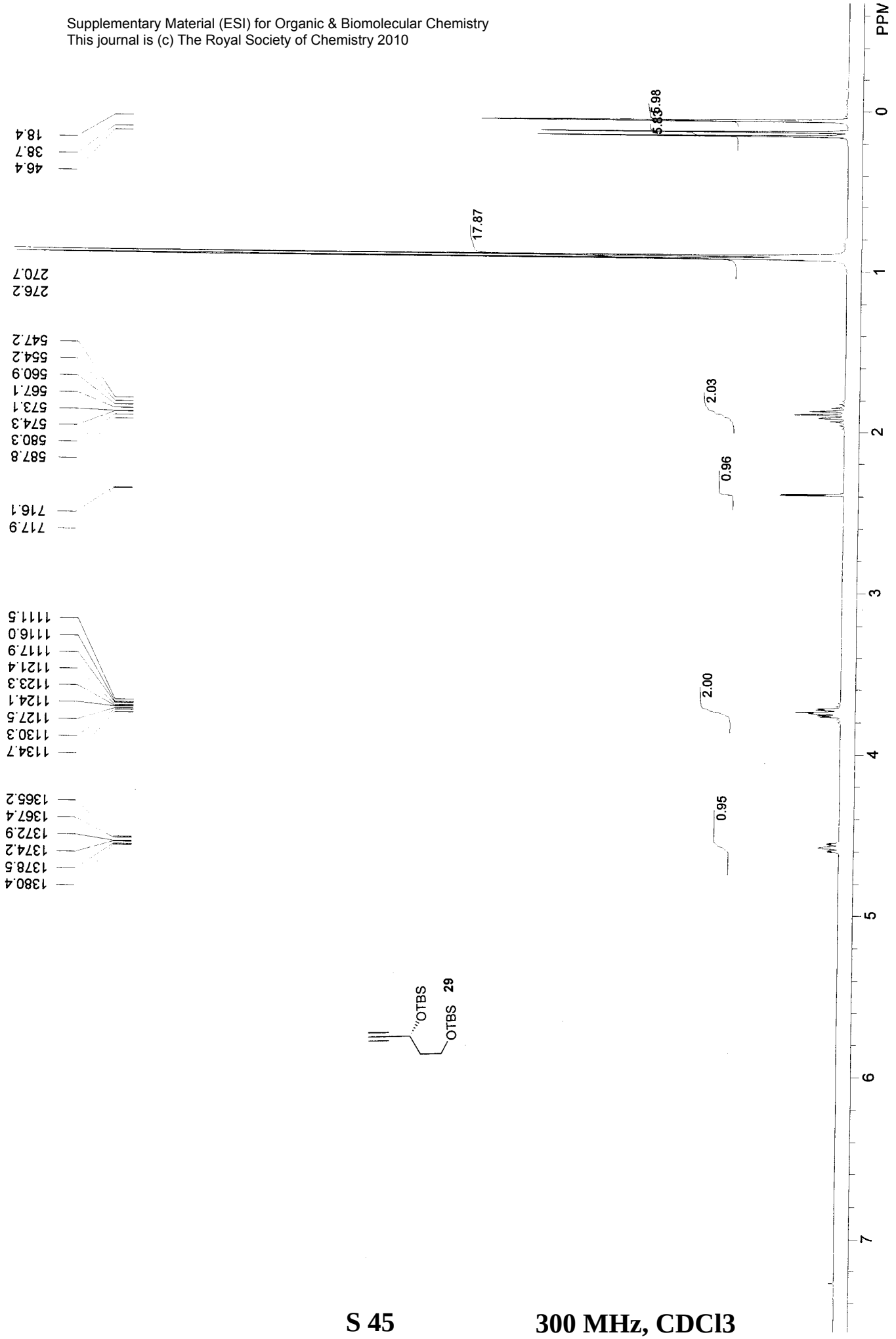
mixture of the less and more polar isomers of sulfoxide 28



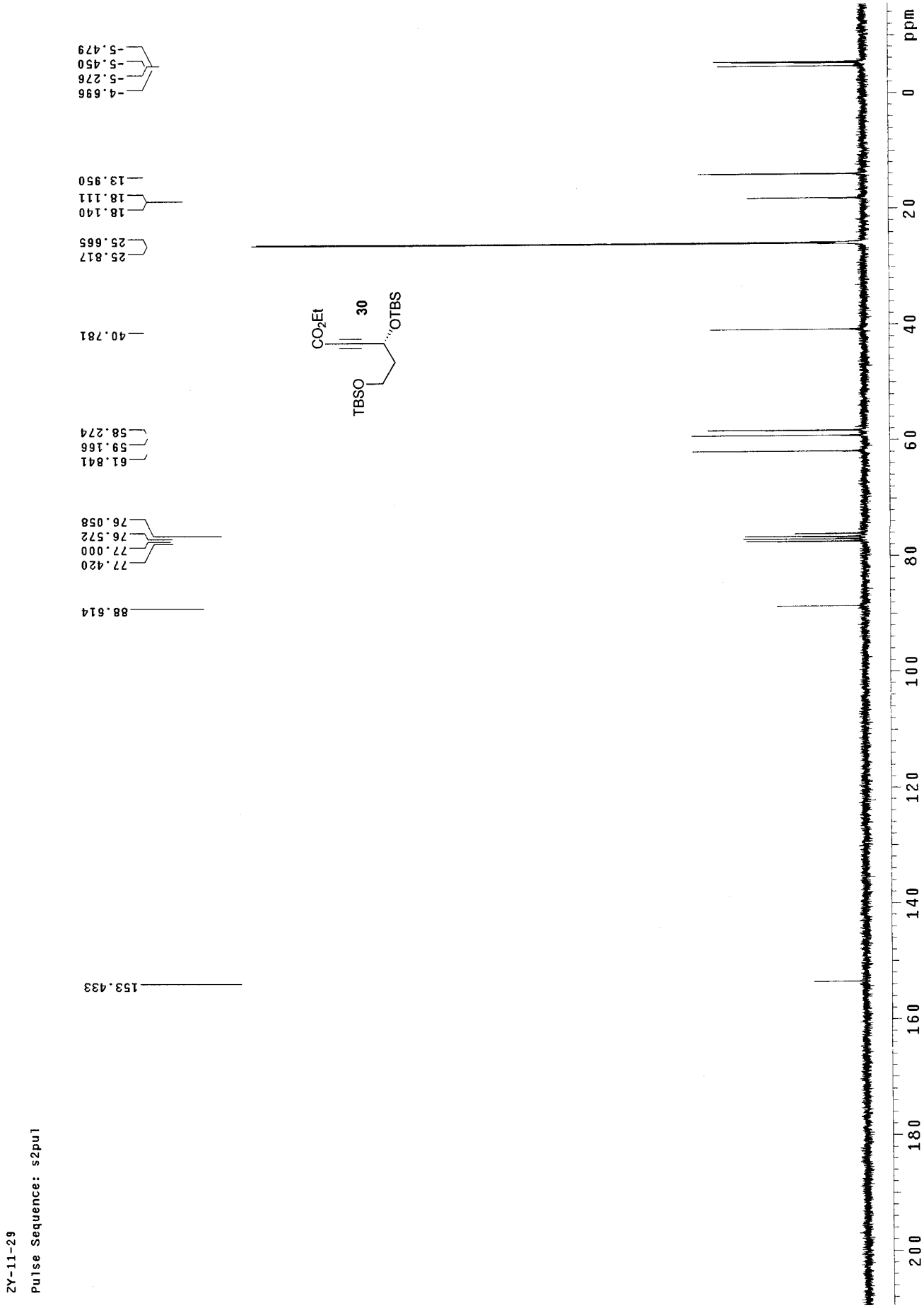
(Racemic 28b (the more polar isomer of 28)



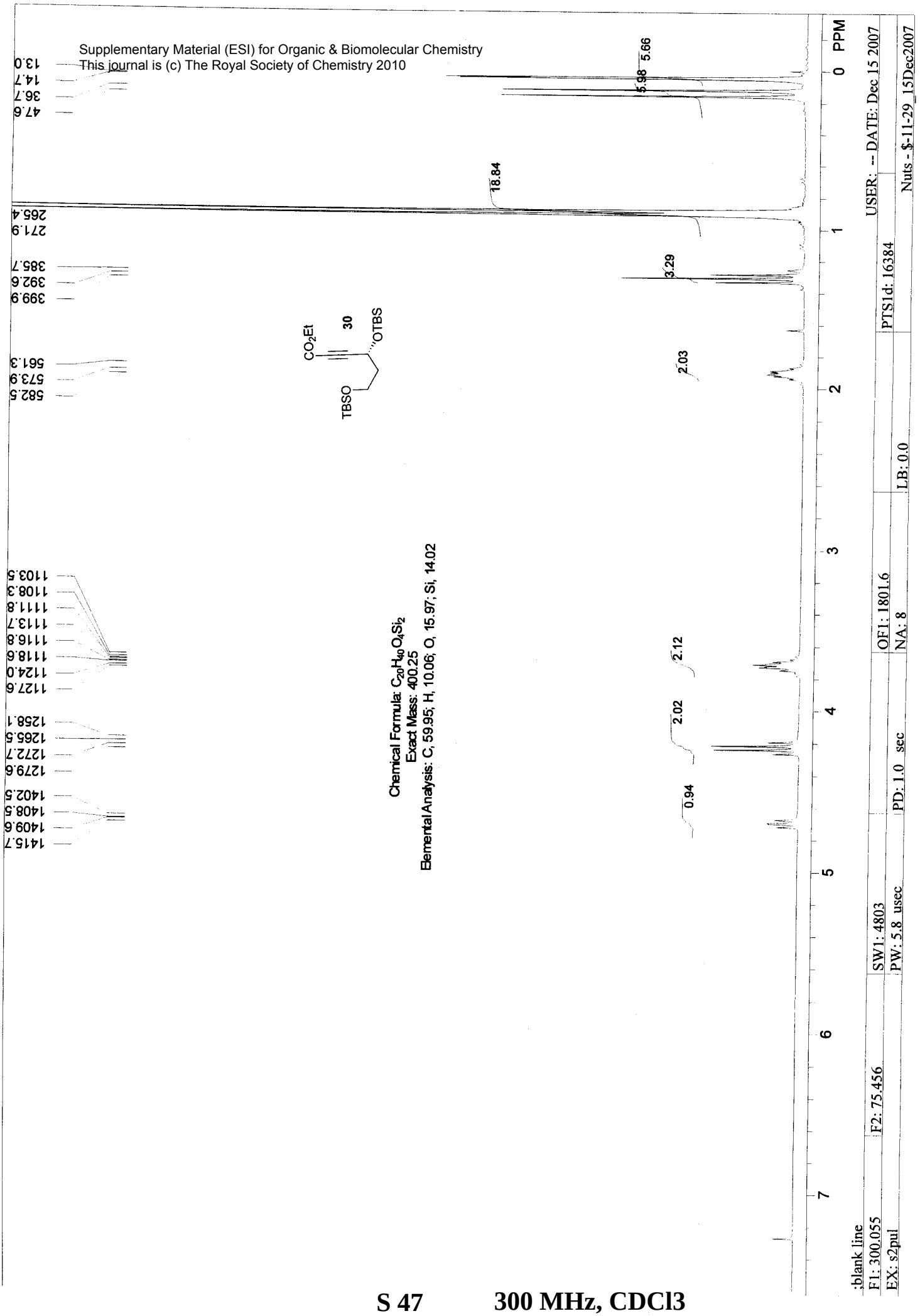
S 44 **75 MHz, CDCl3**



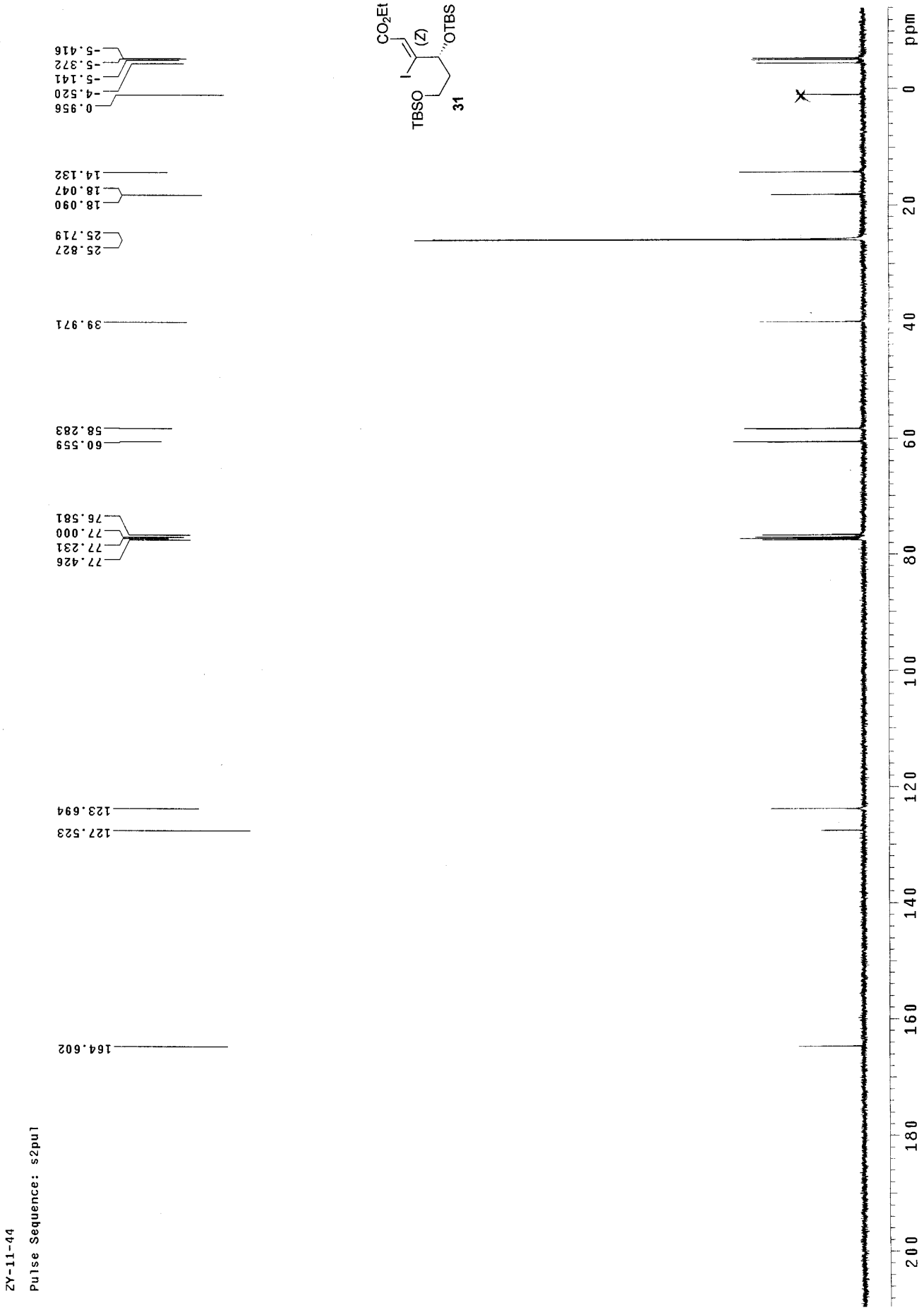
300 MHz, CDCl3



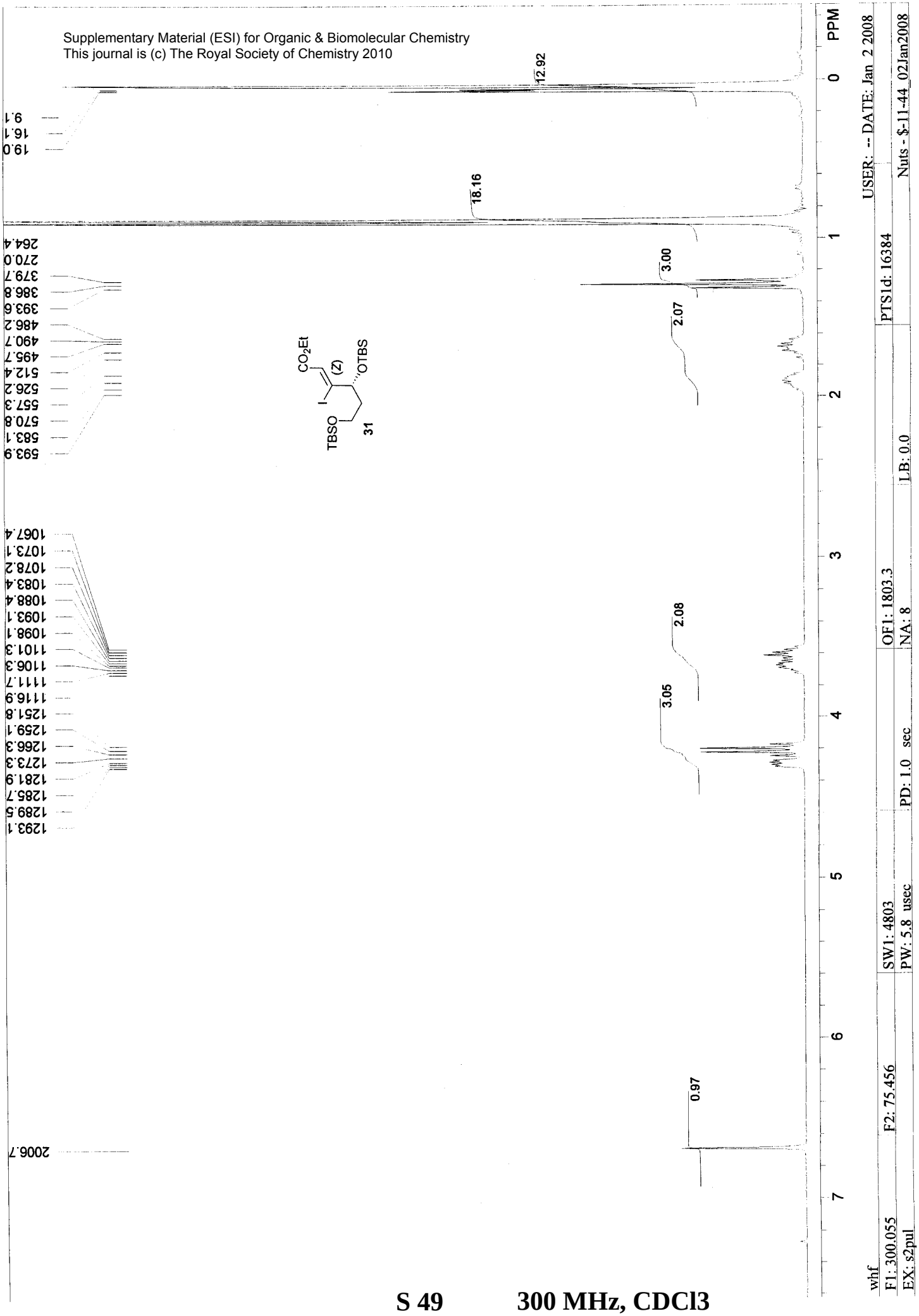
S 46 **75 MHz, CDCl3**



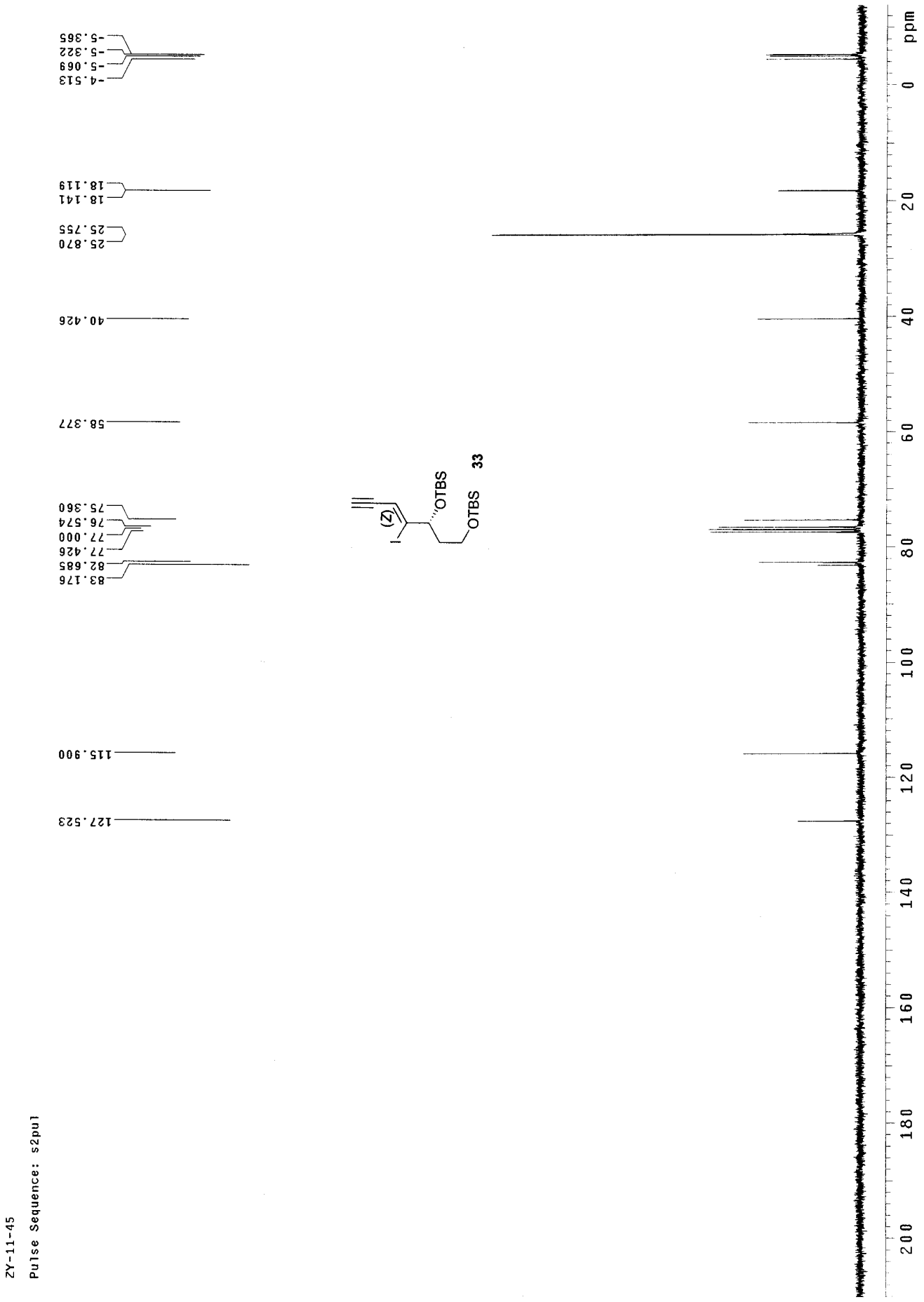
S 47 300 MHz, CDCl3



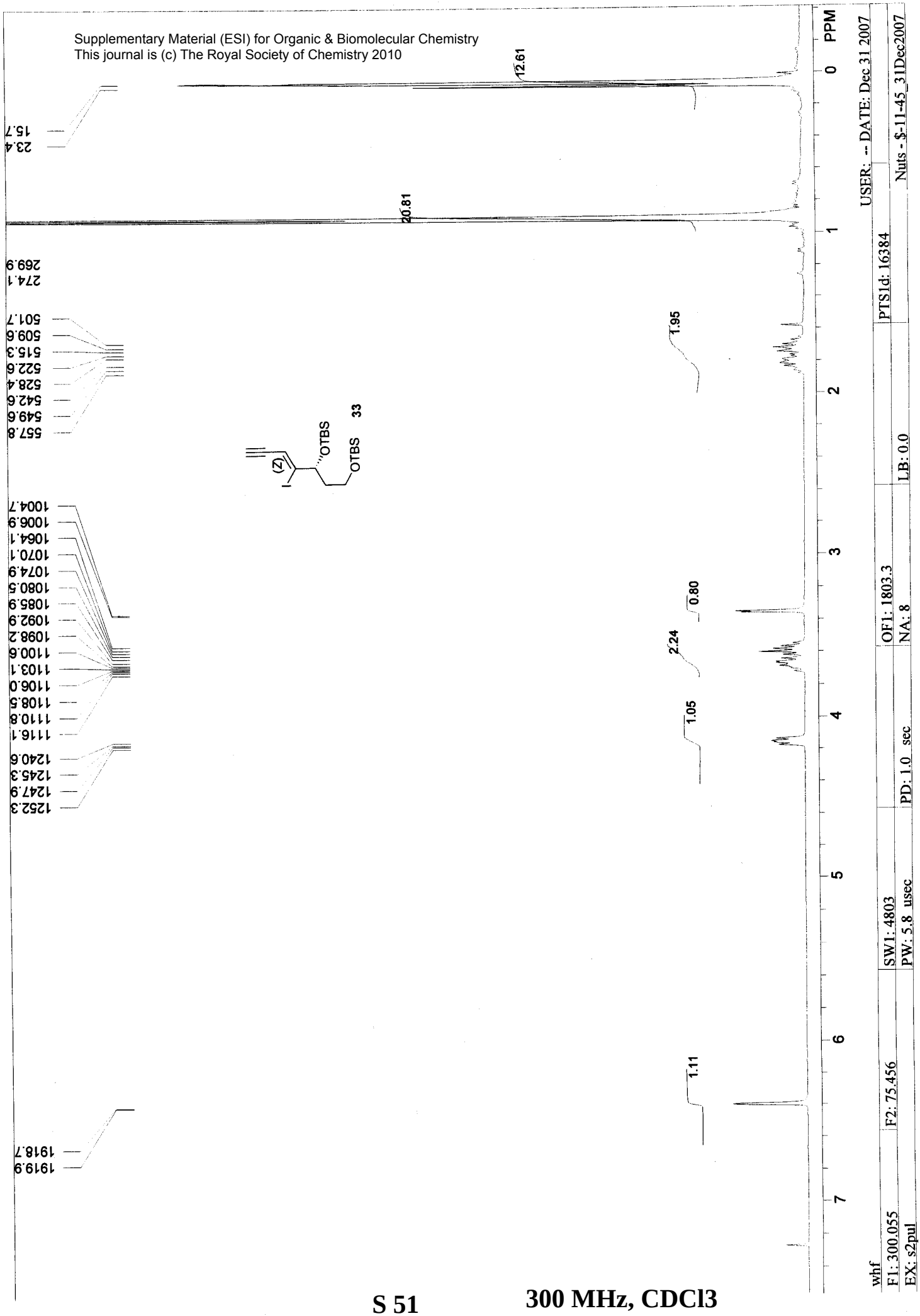
S 48 **75 MHz, CDCl3**



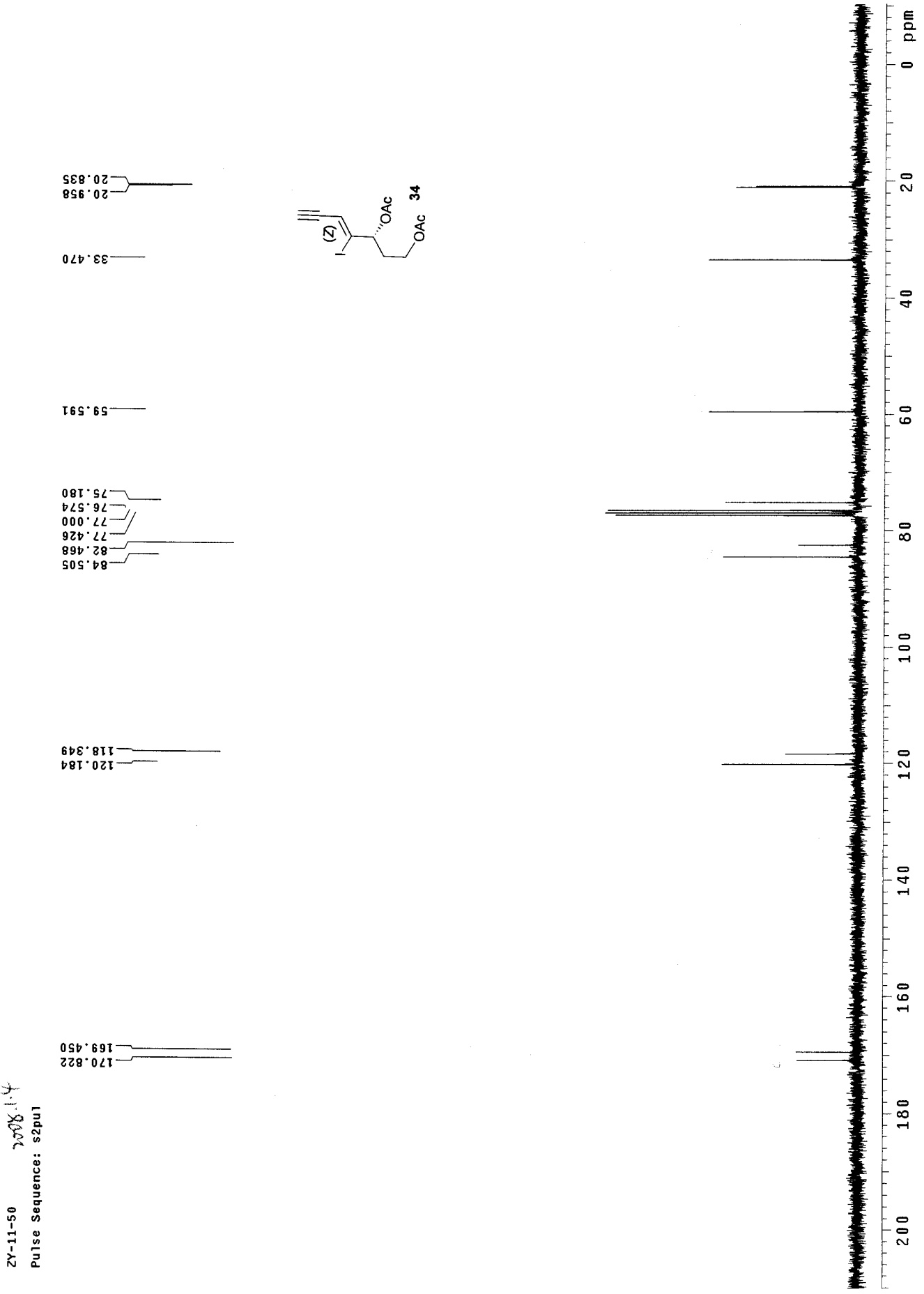
S 49 300 MHz, CDCl3


-5.365
-5.322
-5.069
-4.513
18.119
18.141
25.755
25.870
40.426
58.377
75.360
76.574
77.000
77.426
82.685
83.176
115.900
127.523
(Z)
I
OTBS
OTBS
33
ppm
0
20
40
60
80
100
120
140
160
180
200
ZY-11-45
Pulse Sequence: s2pul

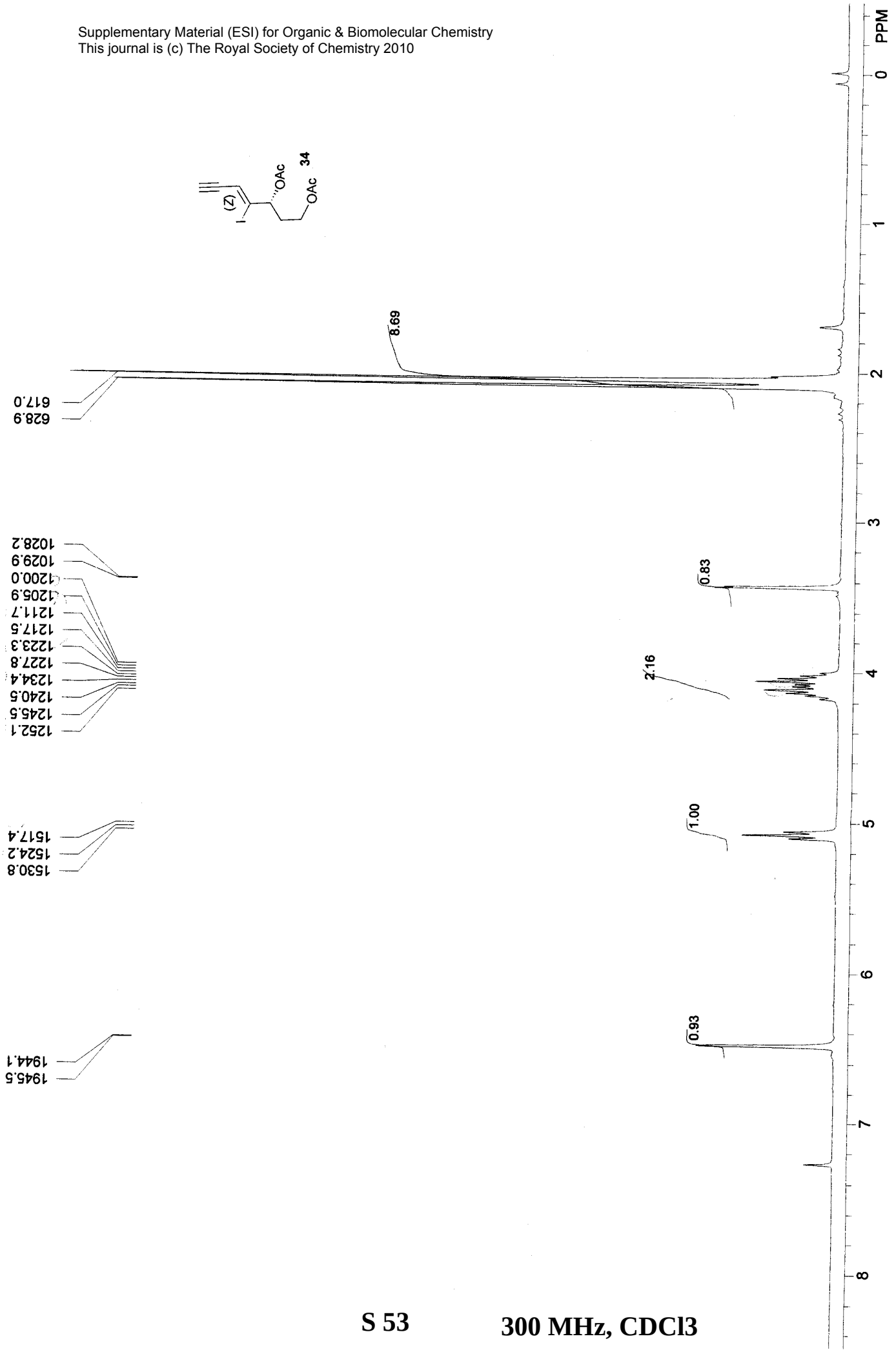
75 MHz, CDCl3



300 MHz, CDCl3

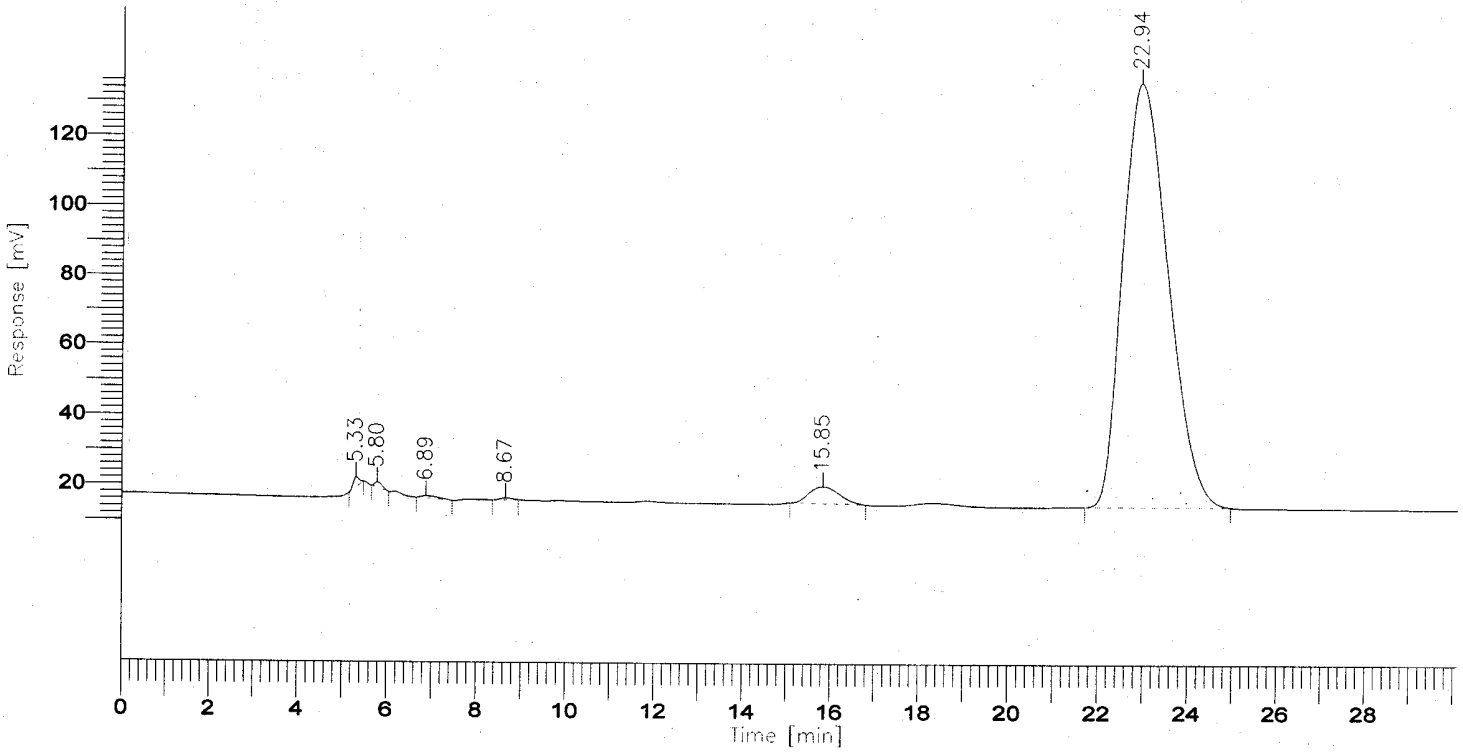


S 52 75 MHz, CDCl3

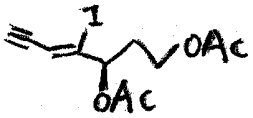


300 MHz, CDCl3

Software Version: 4.1<2F12>
Date: 08-2-28 14:22
Sample Name : 11-70-3
Data File : D:\CS\D___063.RAW Date: 08-2-28 13:53
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: d-1
Sample Amount : 1.0000 Dilution Factor : 1.00



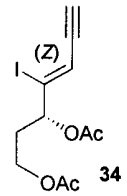
DEFAULT REPORT



AS 正己烷/异丙醇=90/10

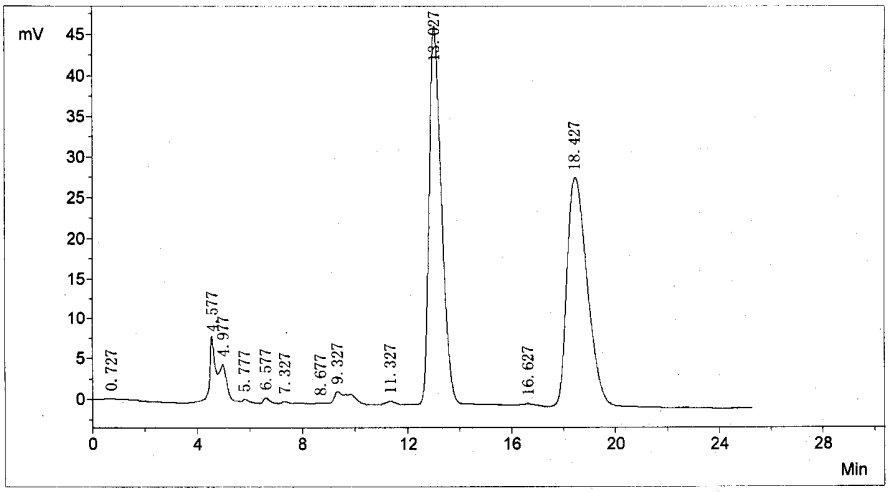
Peak #	Time [min]	Area [uv*sec]	Height [uv]	Area [%]	BL
1	5.327	26845.50	2760.21	0.30	BB
2	5.796	17525.00	1503.01	0.20	BB
3	6.887	18442.00	639.87	0.21	BB
4	8.665	8917.50	499.39	0.10	BB
5	15.847	229685.00	4765.12	2.60	BB
6	22.937	8515731.50	121626.89	96.58	BB
		8817146.50	131794.49	100.00	

95%



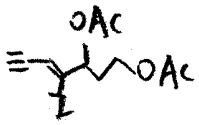
色谱分析报告

样品名称:
样品文件名:ZY11-50+-.che
样品批号:
分析者:
分析日期:2008-01-08
分析时间:10:36



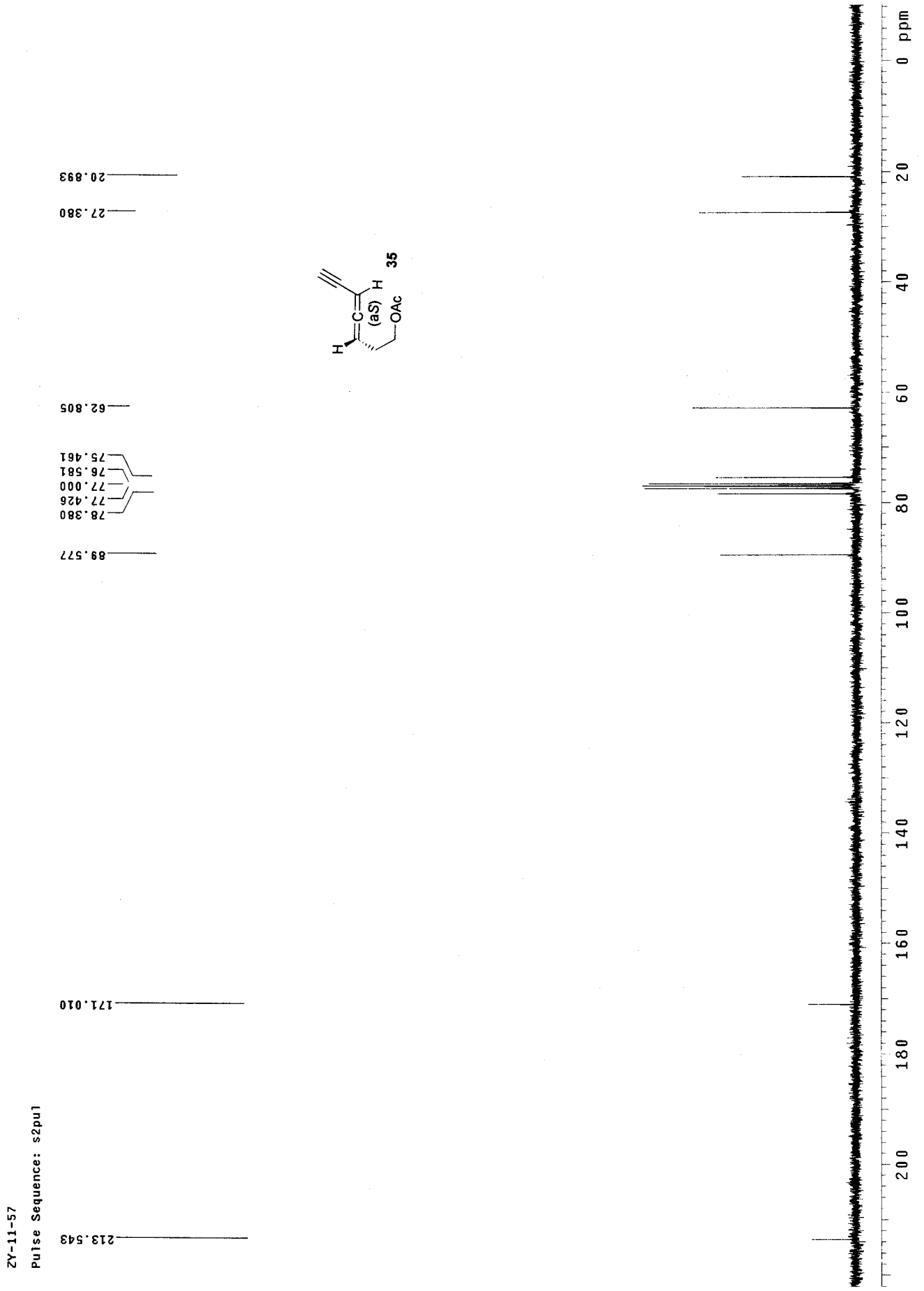
序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		0.727	167.4	15597.9	0.4562
2	2		4.577	7843.0	120647.5	3.5290
3	3		4.977	4691.1	101396.9	2.9659
4	4		5.777	470.1	9322.8	0.2727
5	5		6.577	675.9	11299.6	0.3305
6	6		7.327	257.7	4858.0	0.1421
7	7		8.677	80.5	1702.6	0.0498
8	8		9.327	1518.0	69442.6	2.0312
9	9		11.327	412.6	11224.5	0.3283
10	10		13.027	46621.6	1528457.9	44.7085
11	11		16.627	217.0	7619.6	0.2229
12	12		18.427	28249.7	1537148.3	44.9627
合计:				91204.4	3418718.2	100.0000

34

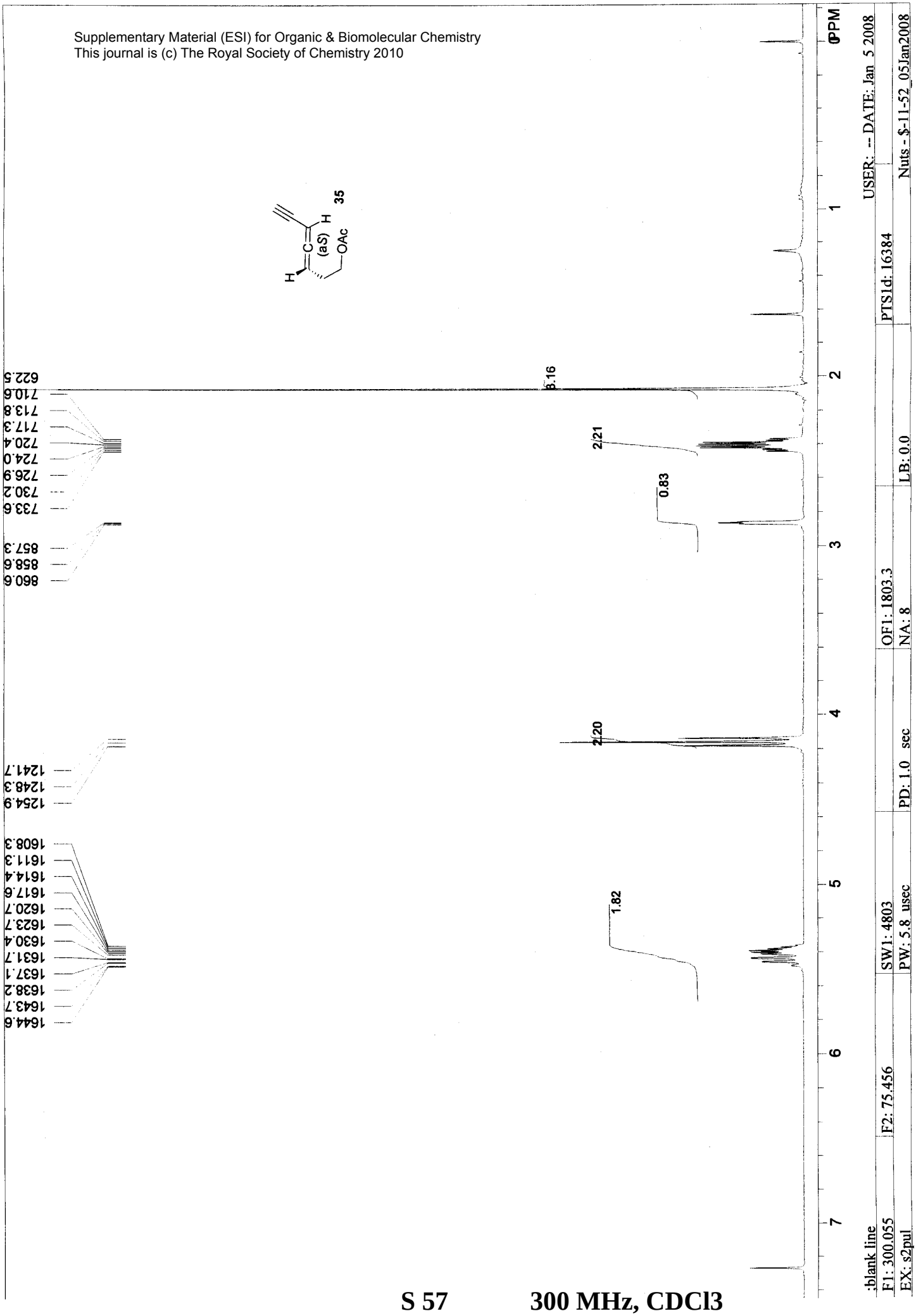


("racemic")

"Racemic" 34, for comparison

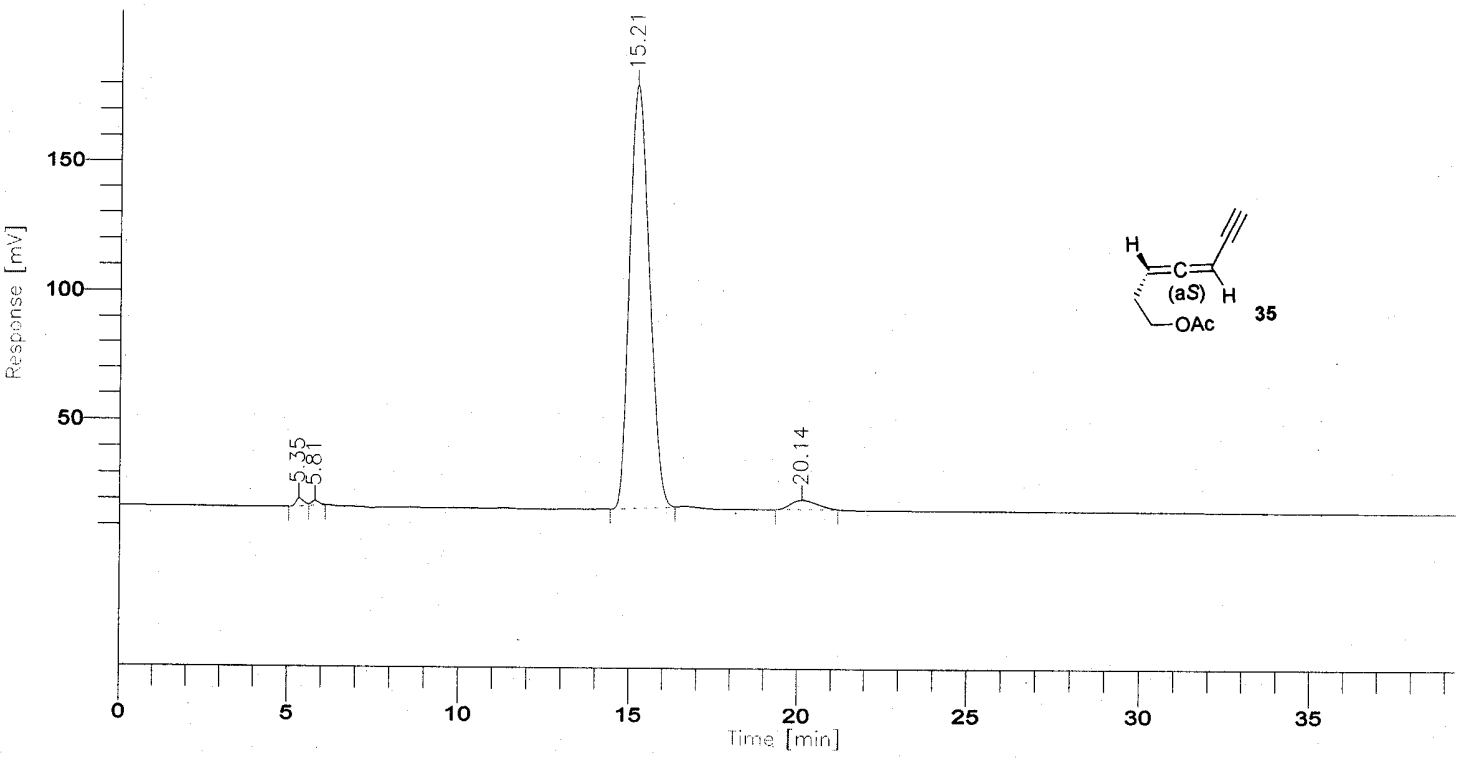


S 56 **75 MHz, CDCl3**



S 57 300 MHz, CDCl3

Software Version: 4.1<2F12>
Date: 08-2-28 15:52
Sample Name : 11-80
Data File : D:\CS\D___065.RAW Date: 08-2-28 15:12
Sequence File: D:\CS\D.SEQ Cycle: 1 Channel : A
Instrument : 970A_-_0 Rack/Vial: 0/0 Operator: d-1
Sample Amount : 1.0000 Dilution Factor : 1.00



DEFAULT REPORT

OAc
AS柱 正辛烷/异丙醇=90/10

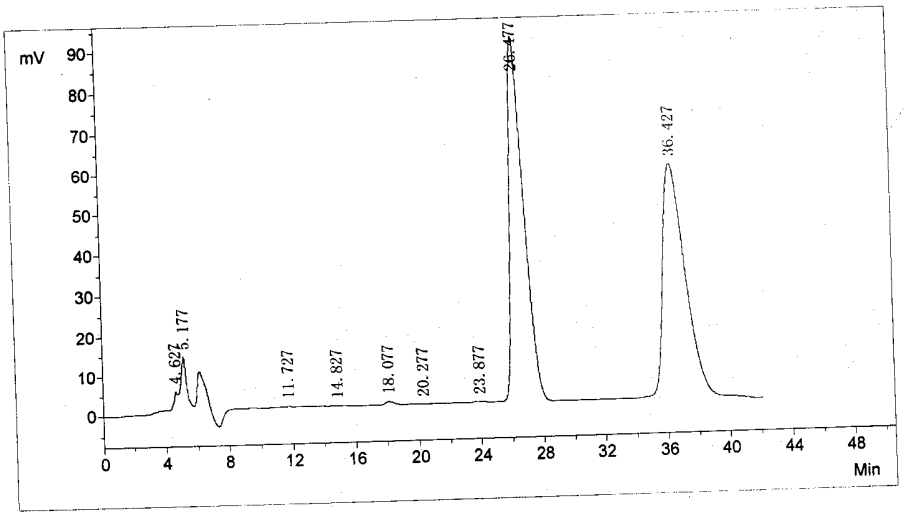
Peak #	Time [min]	Area [uv*sec]	Height [uv]	Area [%]	BL
1	5.345	48031.80	2989.61	0.70	BV
2	5.813	27753.20	1779.32	0.40	VB
3	15.205	6586117.00	163004.50	96.02	BB
4	20.136	197080.00	3636.59	2.87	BB
		6858982.00	171410.02	100.00	

94%

色谱分析报告

样品名称:
样品批号:
分析日期:2008-01-08

样品文件名:ZY11-52+-.che
分析者:
分析时间:14:17



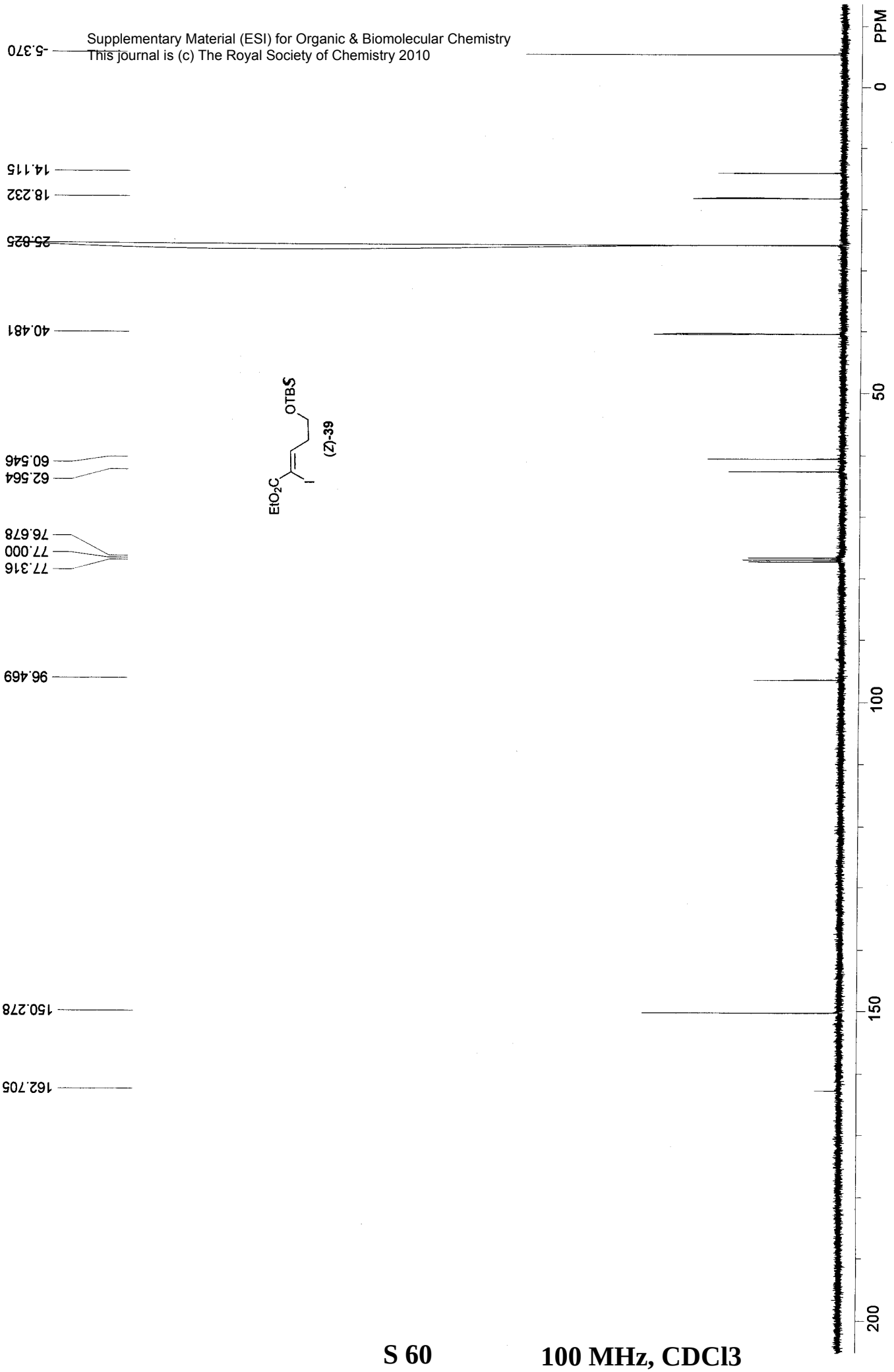
序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		4.627	4309.9	10568.6	0.0892
2	2		5.177	12789.4	315106.4	2.6581
3	3		11.727	181.5	9398.2	0.0793
4	4		14.827	142.4	7466.5	0.0630
5	5		18.077	812.1	29078.6	0.2453
6	6		20.277	53.0	1551.3	0.0131
7	7		23.877	274.0	17288.0	0.1458
8	8		26.477	90224.7	5688730.6	47.9868
9	9		36.427	58225.0	5775589.7	48.7195
合计:				167012.0	11854777.9	100.0000

35

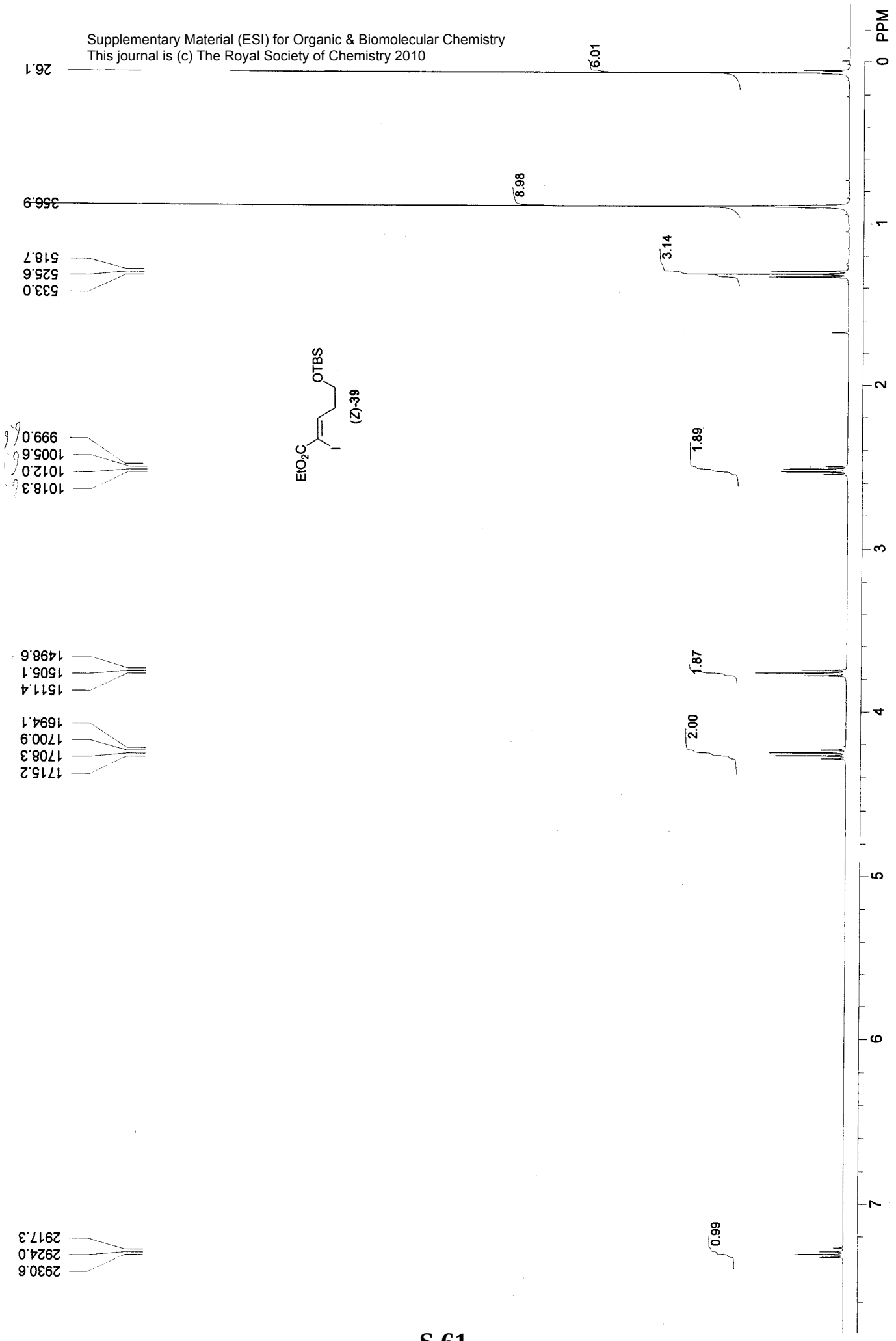
11-52

racemic

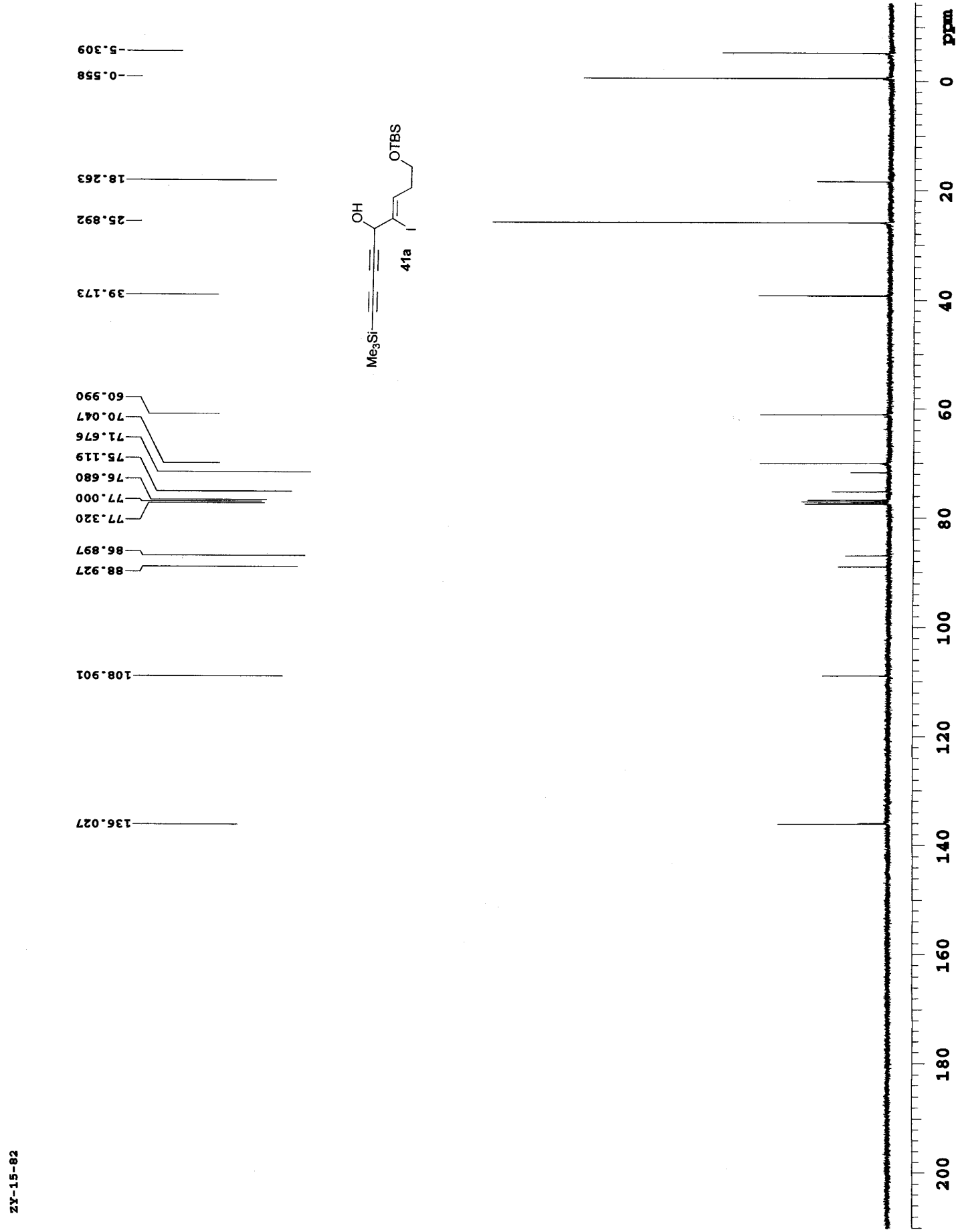
"Racemic" 35, for comparison



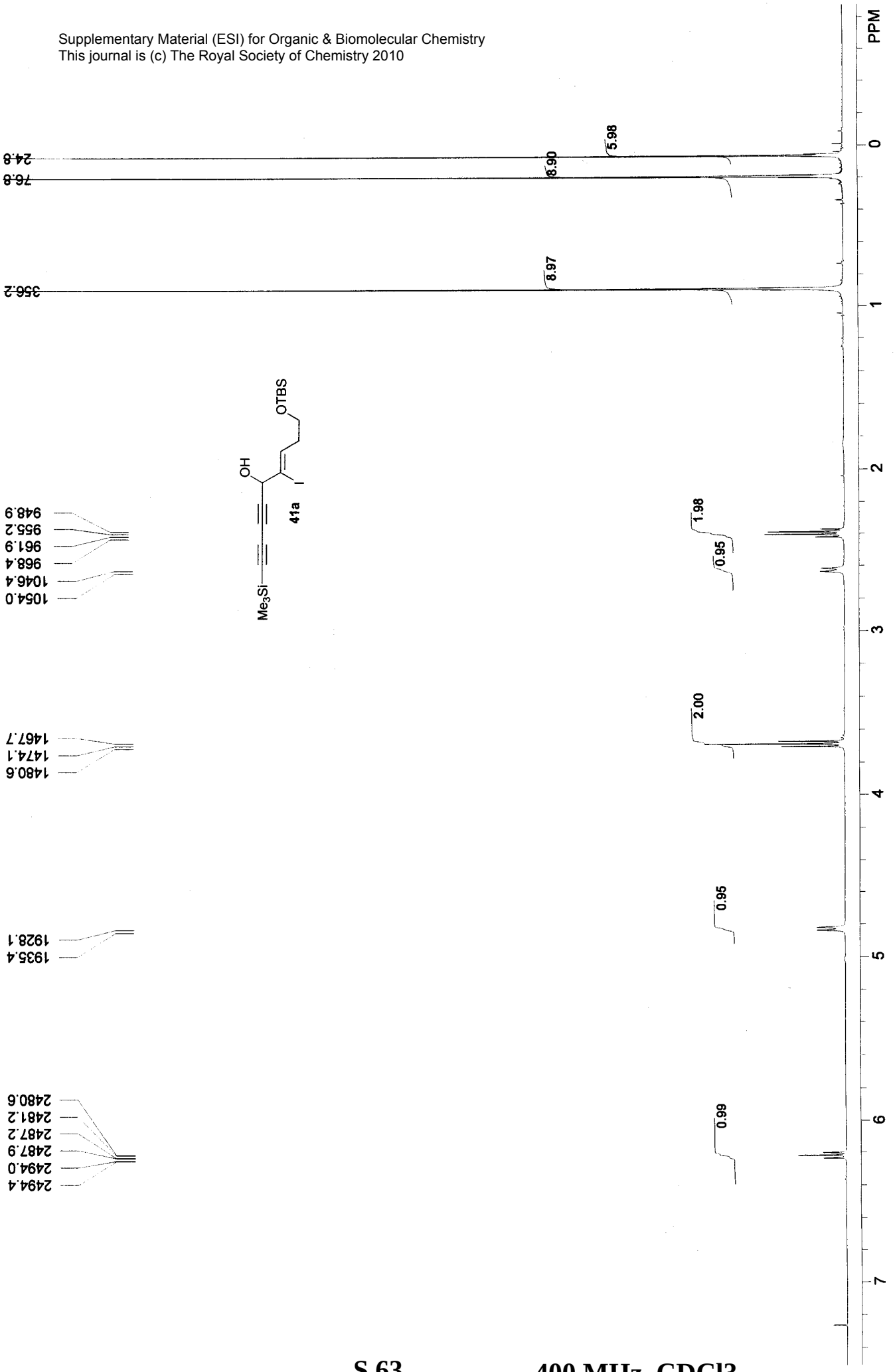
100 MHz, CDCl3



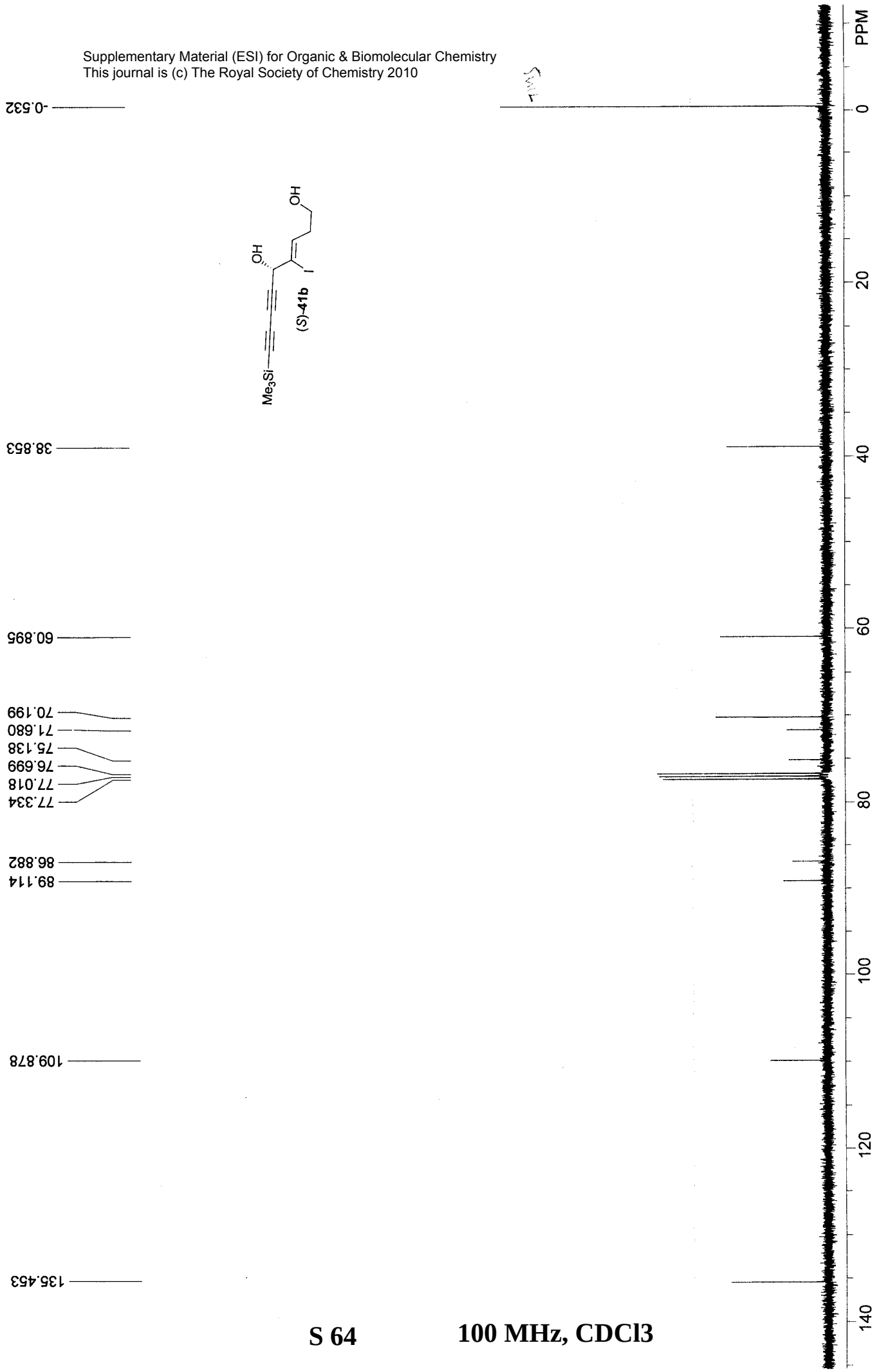
400 MHz, CDCl3



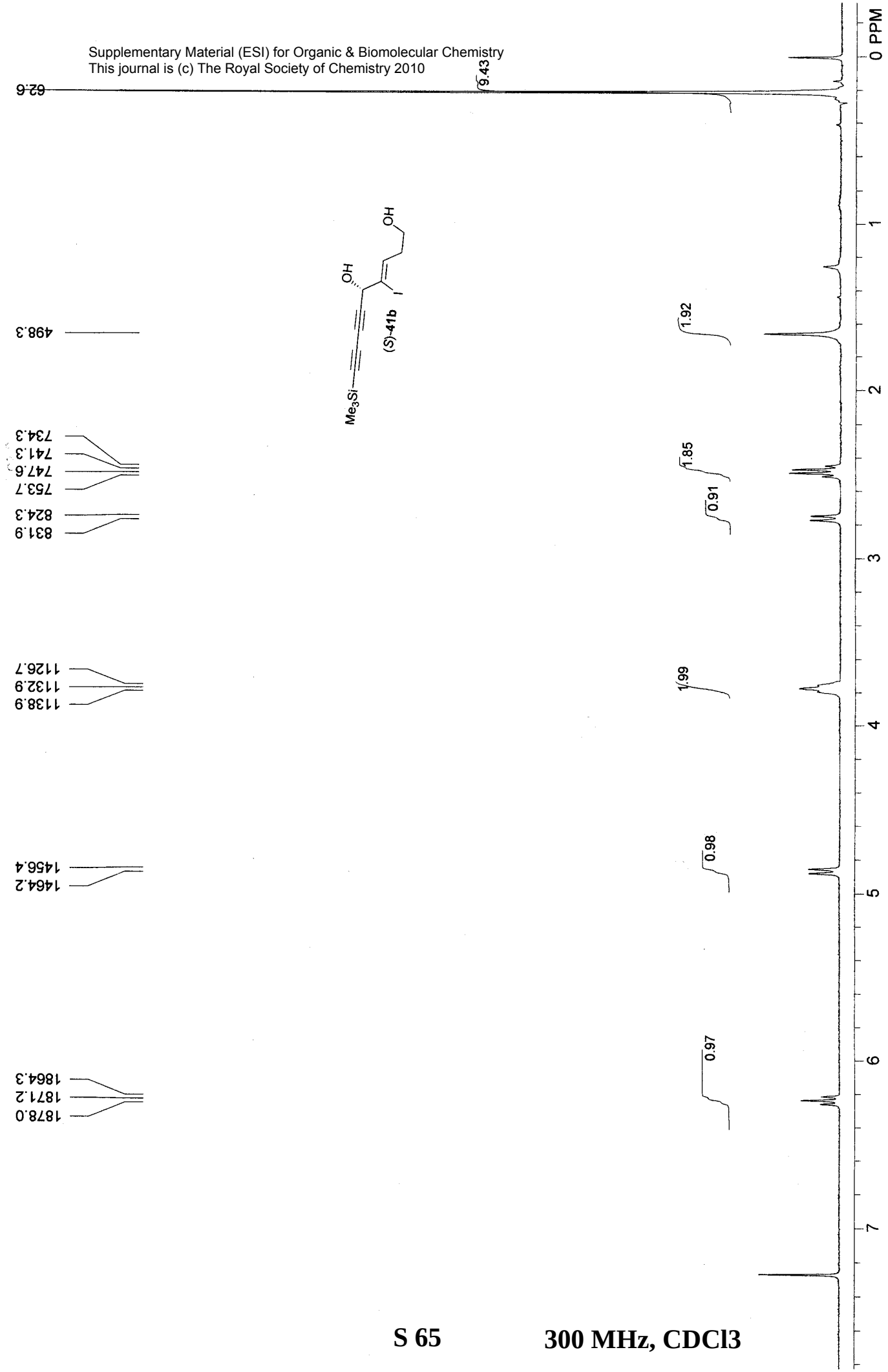
100 MHz, CDCl3



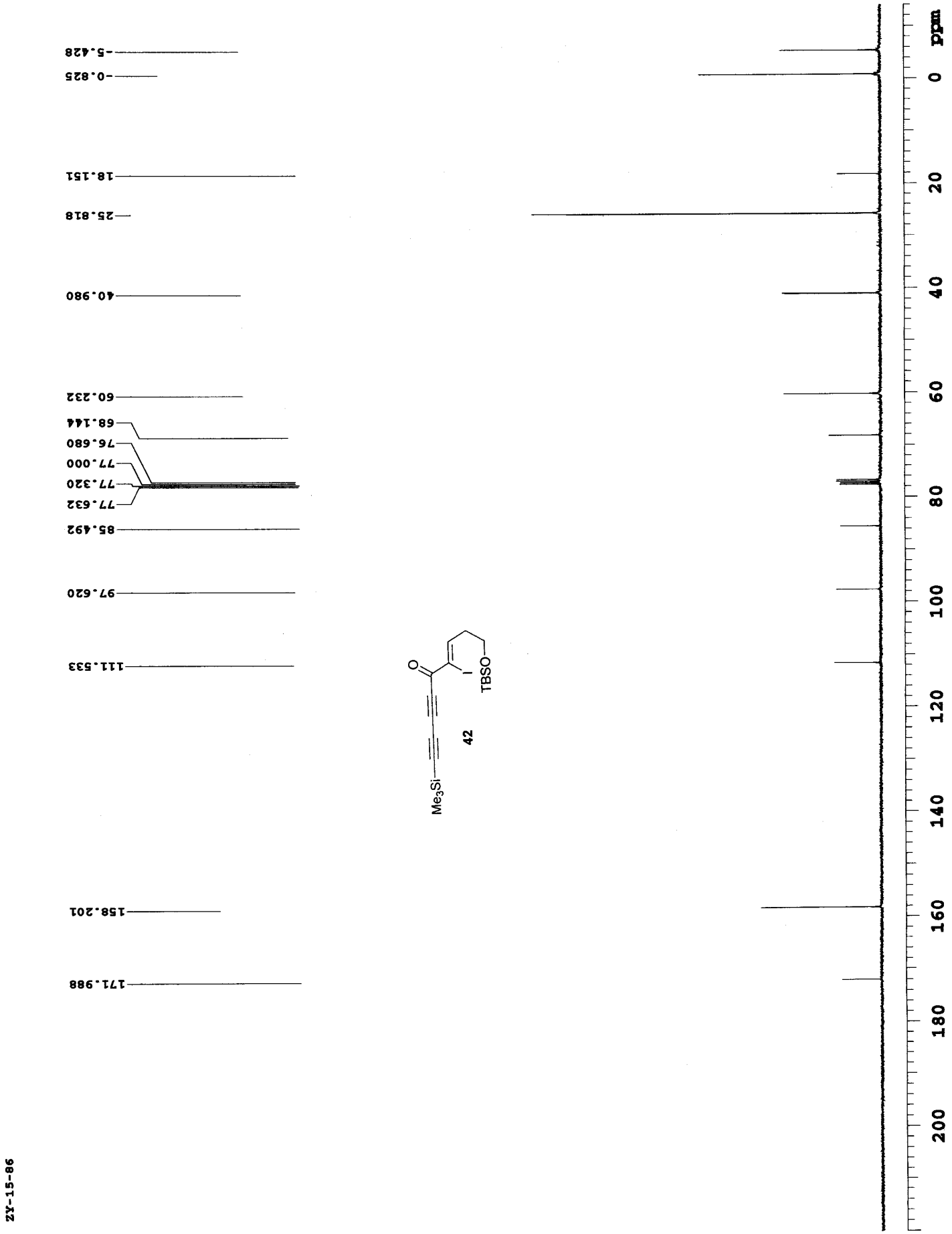
S 63 **400 MHz, CDCl3**



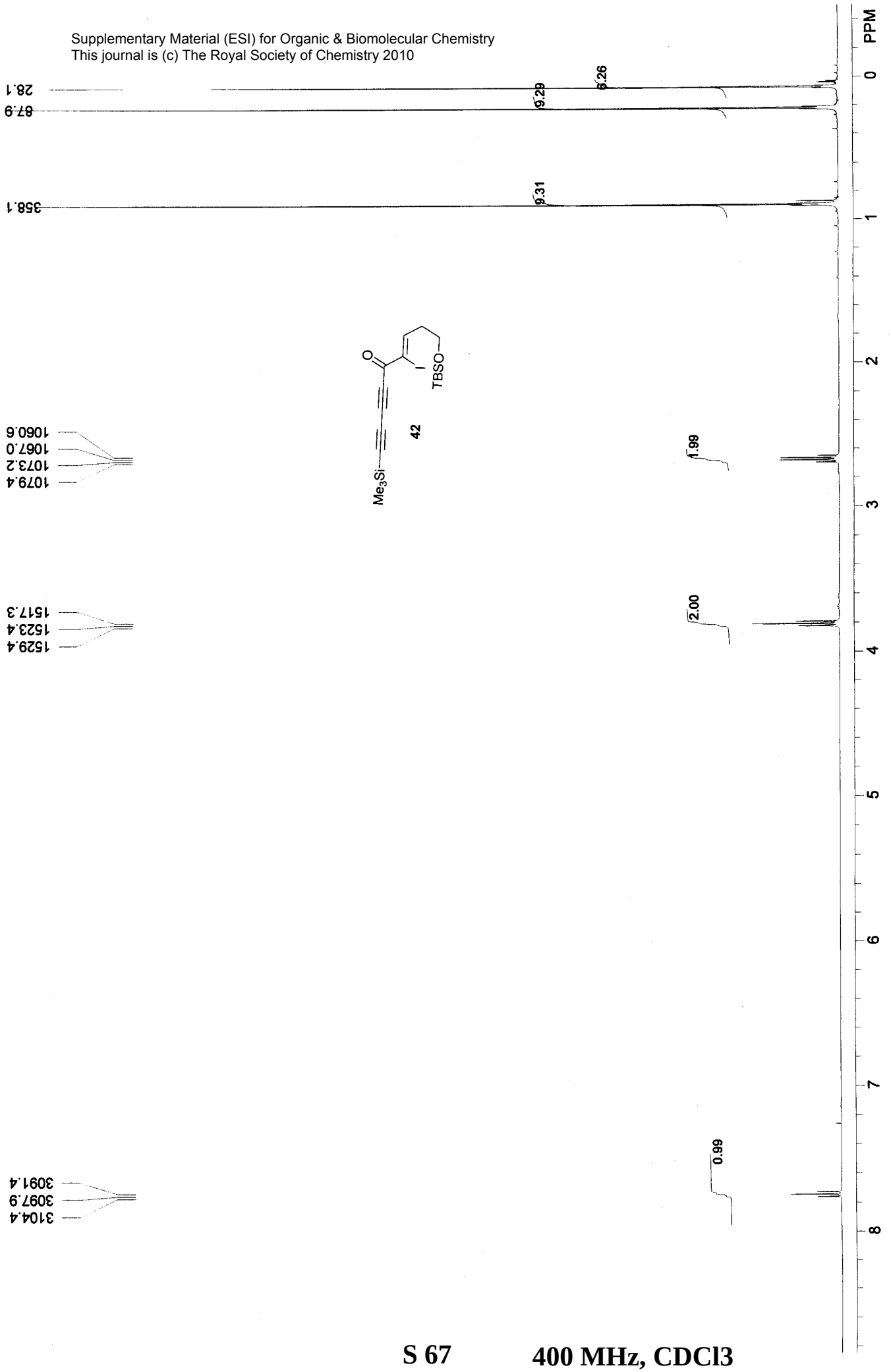
100 MHz, CDCl3



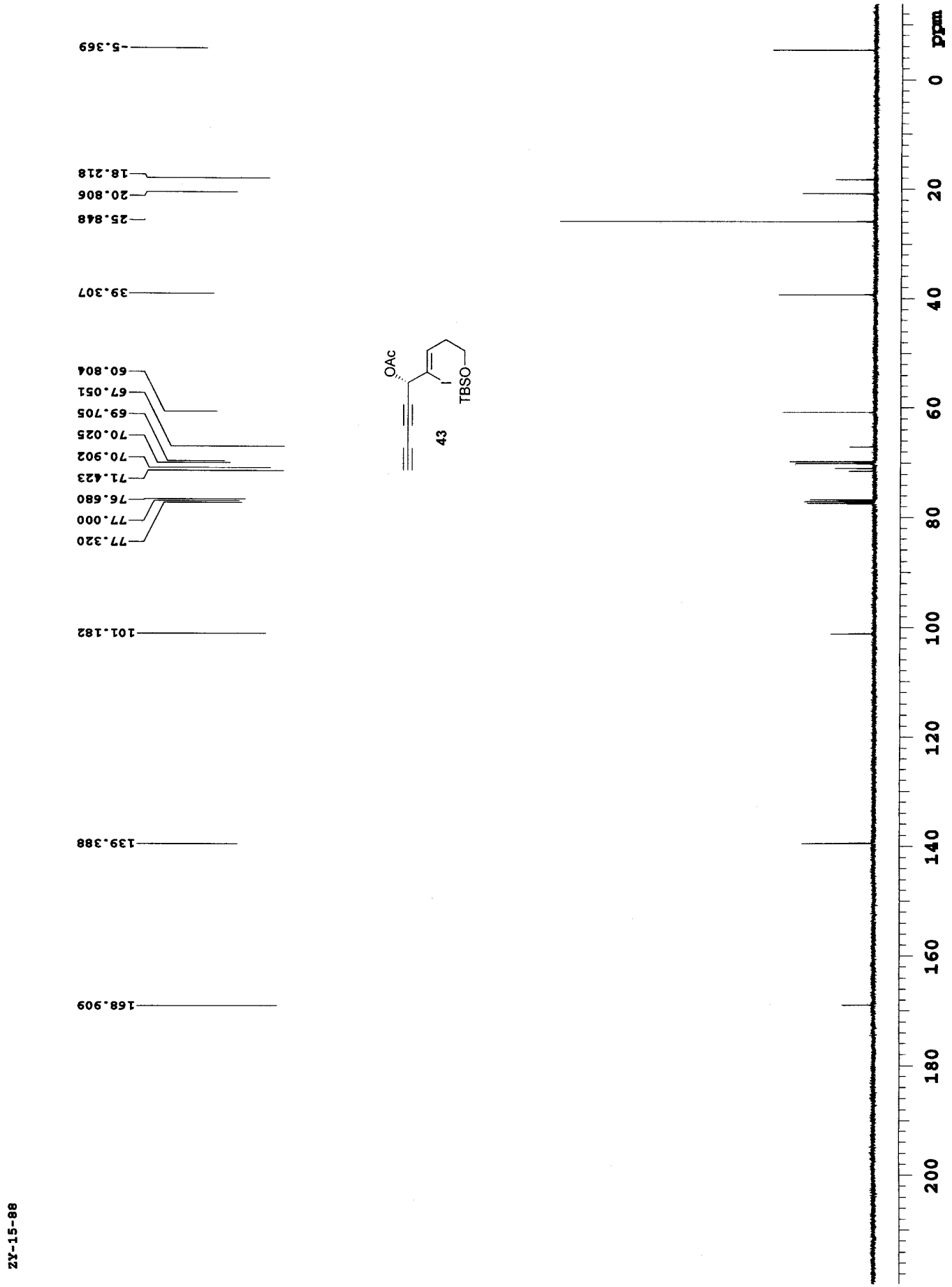
300 MHz, CDCl3



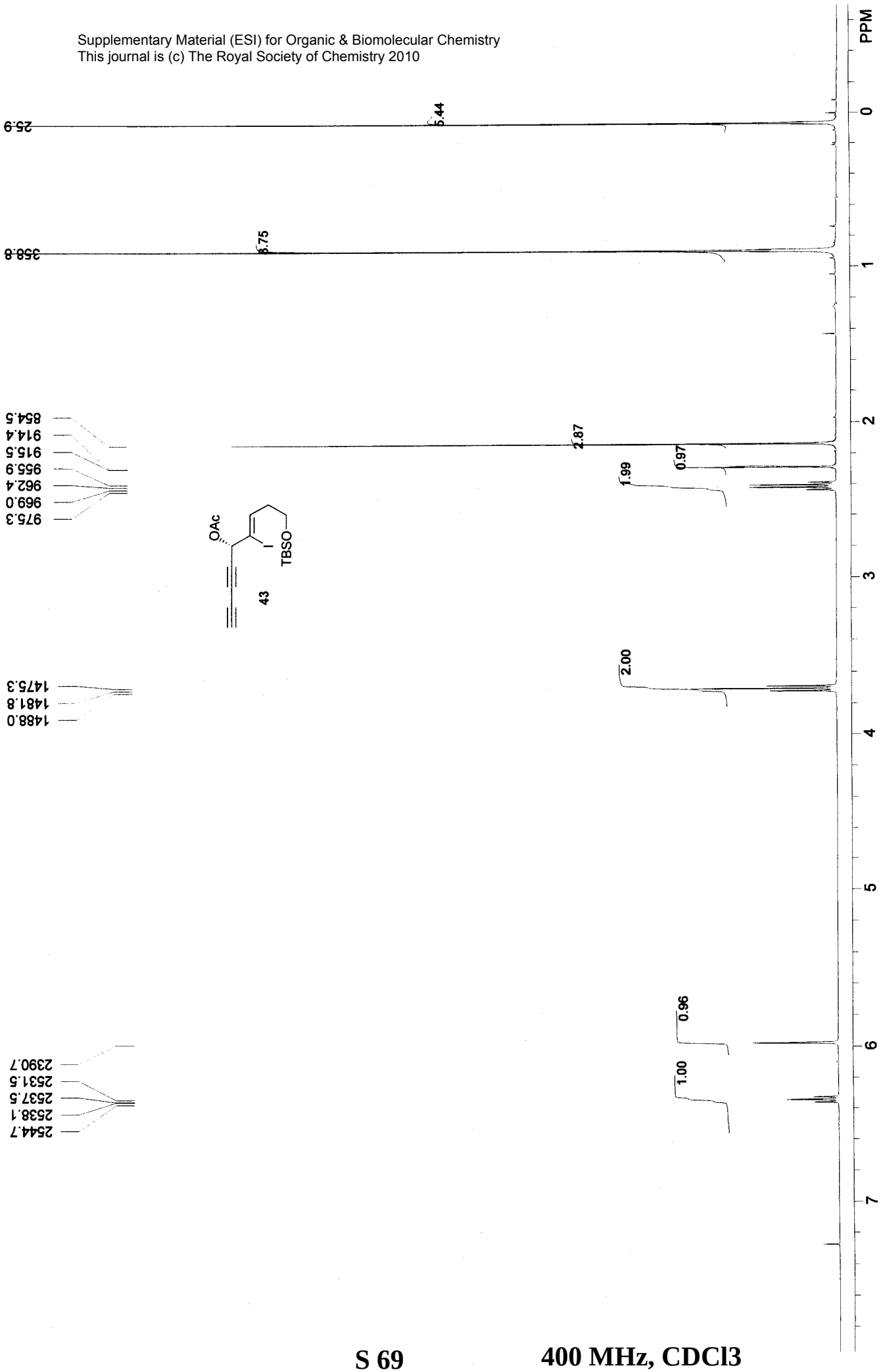
S 66 **100 MHz, CDCl3**



S 67 **400 MHz, CDCl3**



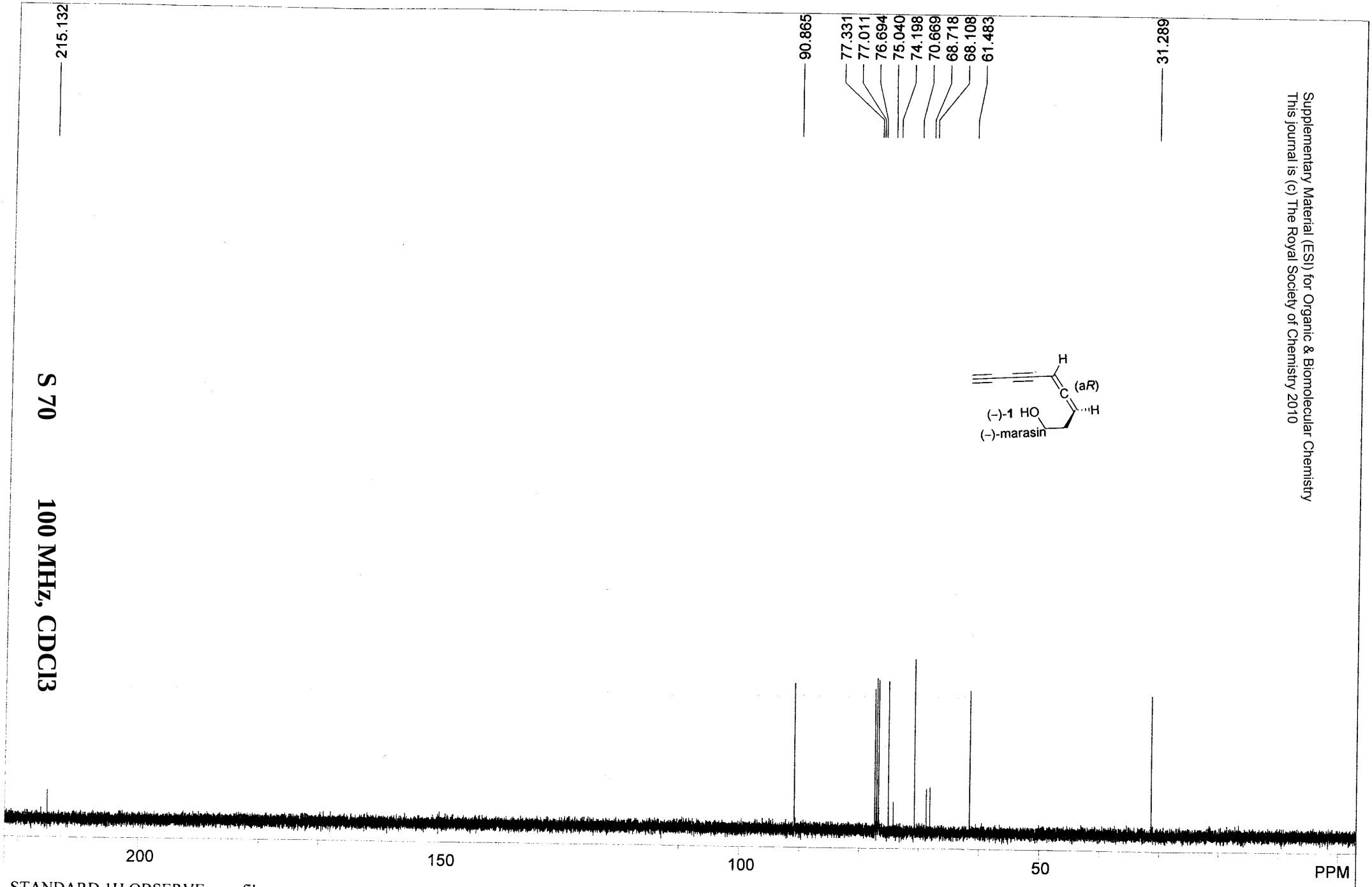
S 68 **100 MHz, CDCl3**



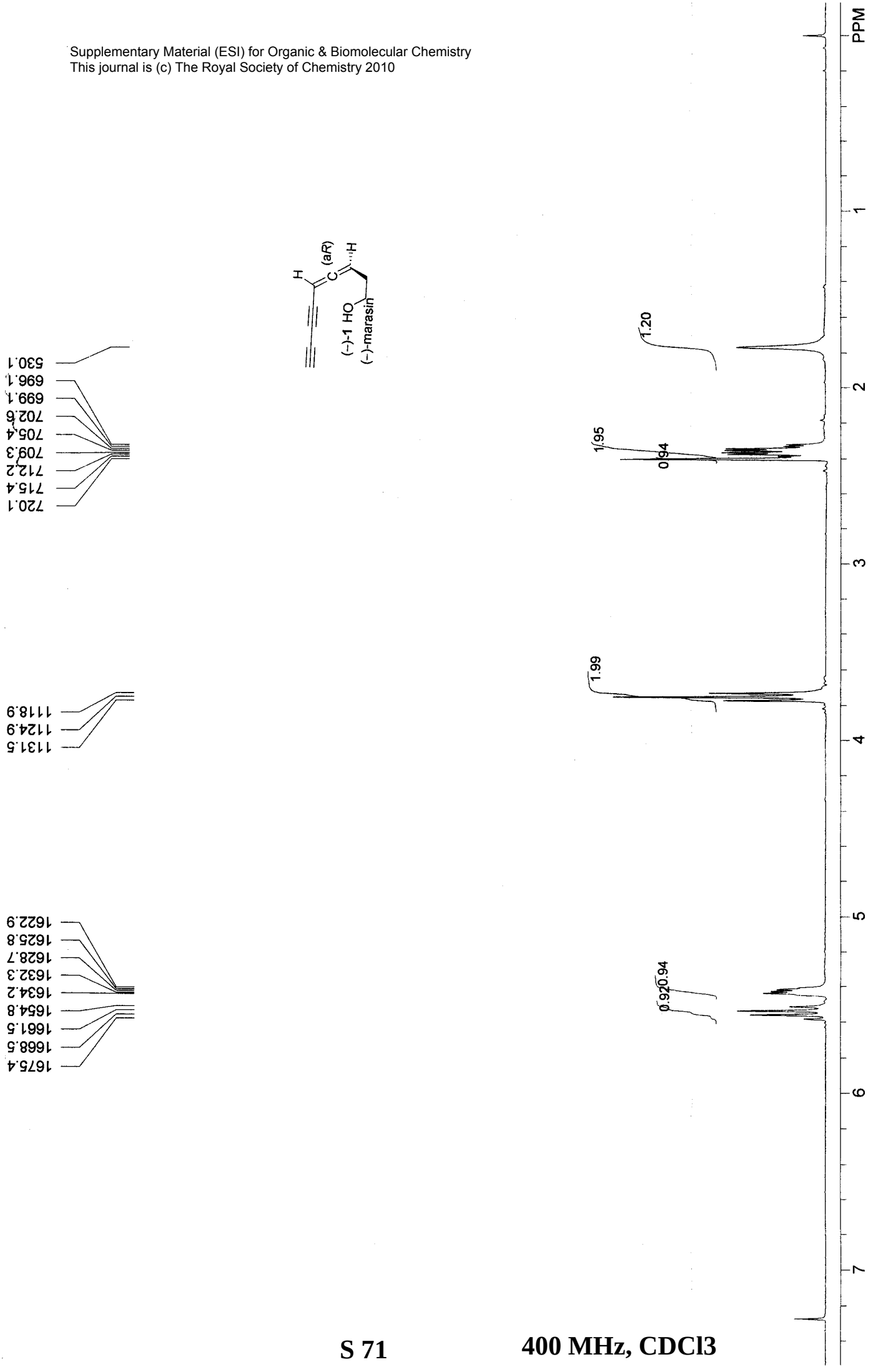
400 MHz, CDCl3

S 70

100 MHz, CDCl3



STANDARD 1H OBSERVE - profile							USER: -- DATE: Jan 8 2009
F1: 100.492	F2: 399.609	SW1: 28409		OF1: 11114.2		PTS1d: 65536	
EX: s2pul		PW: 4.5 usec	PD: 1.0 sec	NA: 64	LB: 0.2		Nuts - $c-1592.fid



400 MHz, CDCl3

色谱分析报告

样品名称:

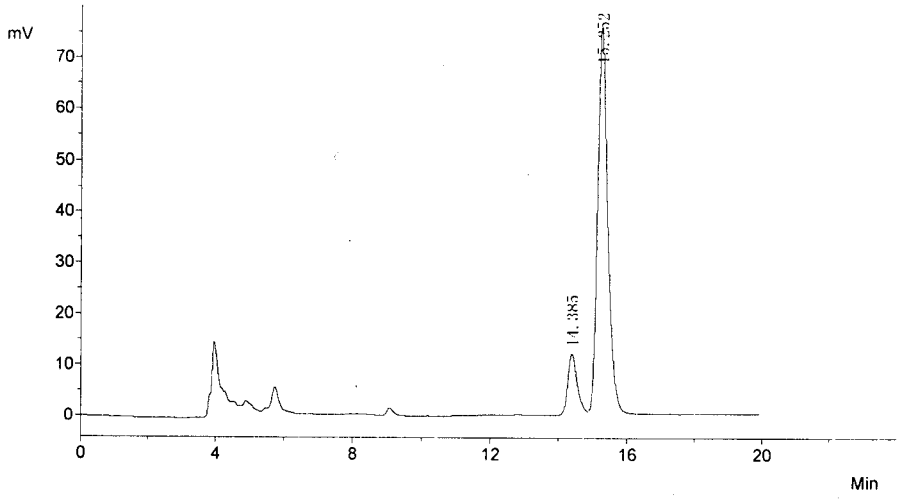
样品文件名:ZY-16-2.che

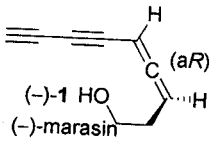
样品批号:

分析者:

分析日期:2009-01-15

分析时间:14:58



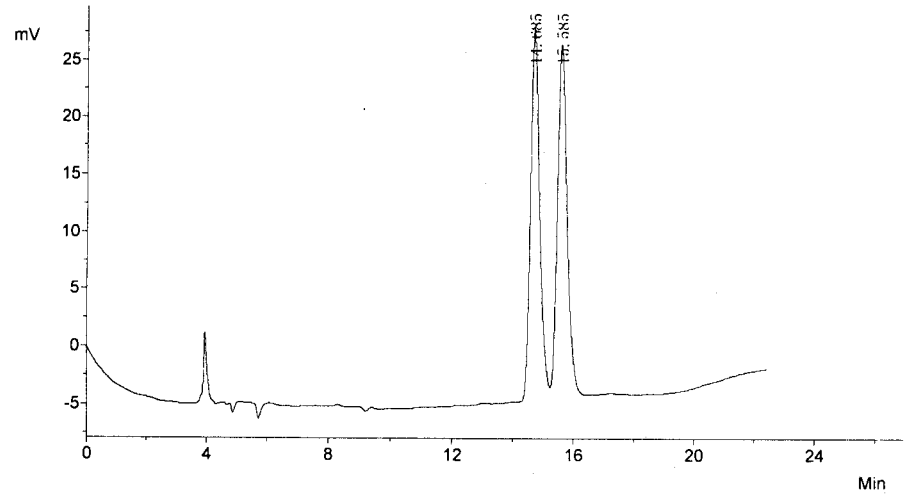


序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		14.385	12062.7	234234.0	12.8118
2	2		15.252	75436.4	1594031.8	87.1882
合计:				87499.1	1828265.8	100.0000

色谱分析报告

样品名称:
样品批号:
分析日期:2009-01-15

样品文件名:15-92+-.che
分析者:
分析时间:14:25

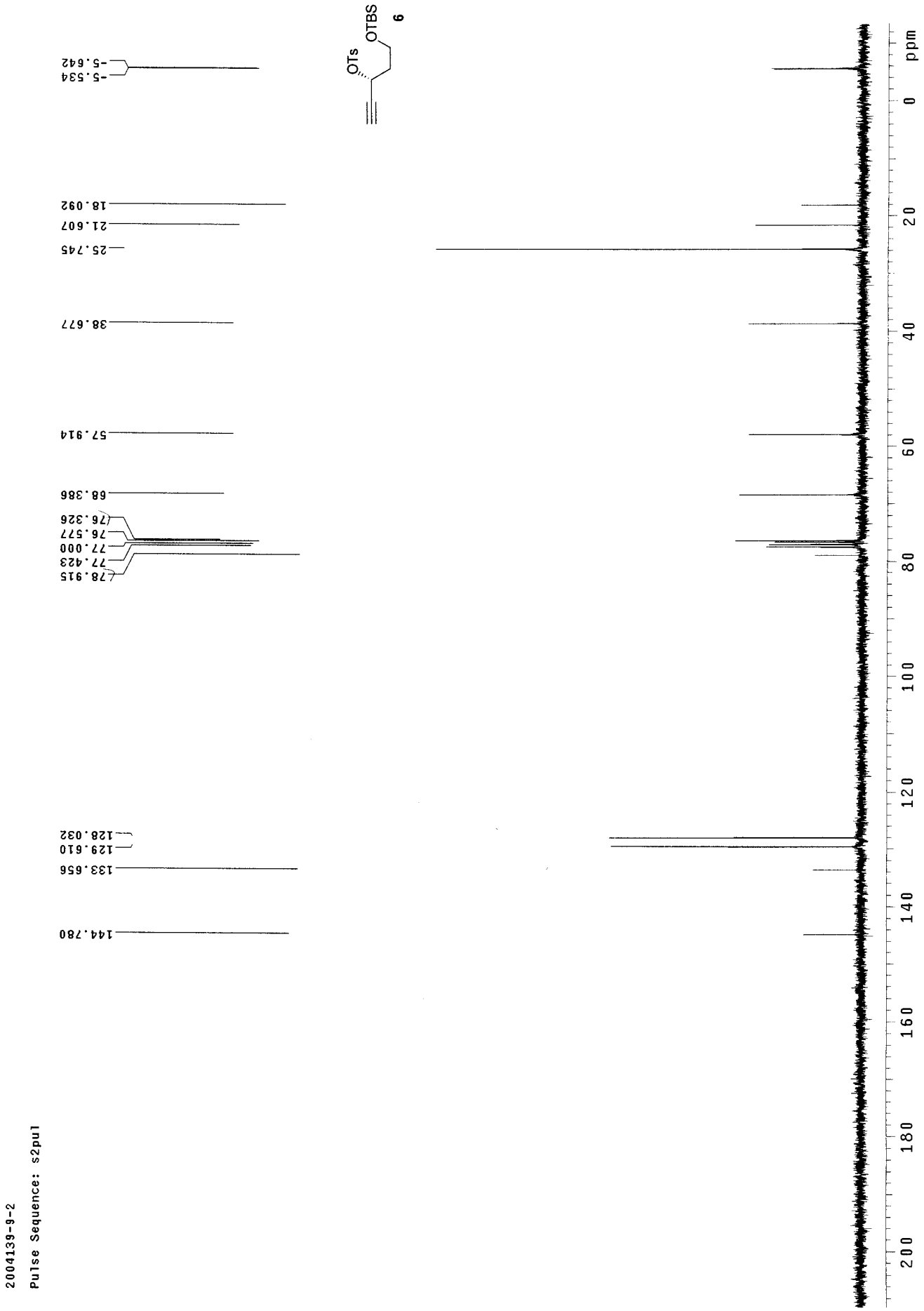


序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		14.685	32336.2	682330.9	49.3913
2	2		15.585	30829.2	699148.4	50.6087
合计:				63165.4	1381479.3	100.0000

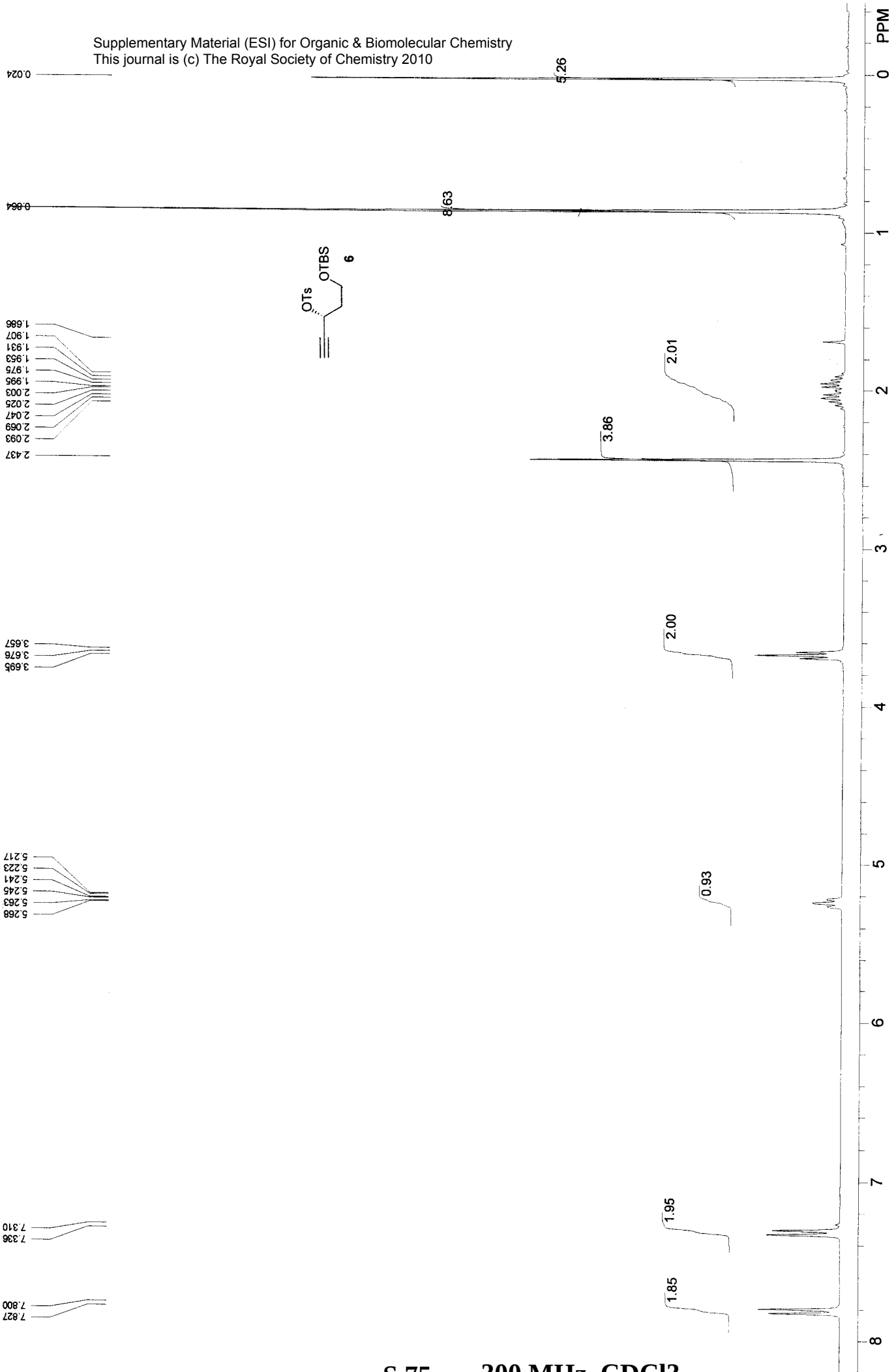
(±) -1

(±)marasin

Racemic Marasin, for comparison


OTs
OTBS
6
-5.642
-5.534
18.092
21.607
25.745
38.677
57.914
68.386
76.326
76.577
77.000
77.423
78.915
128.032
129.610
133.656
144.780
ppm
0
20
40
60
80
100
120
140
160
180
200
2004139-9-2
Pulse Sequence: s2pul

75 MHz, CDCl3

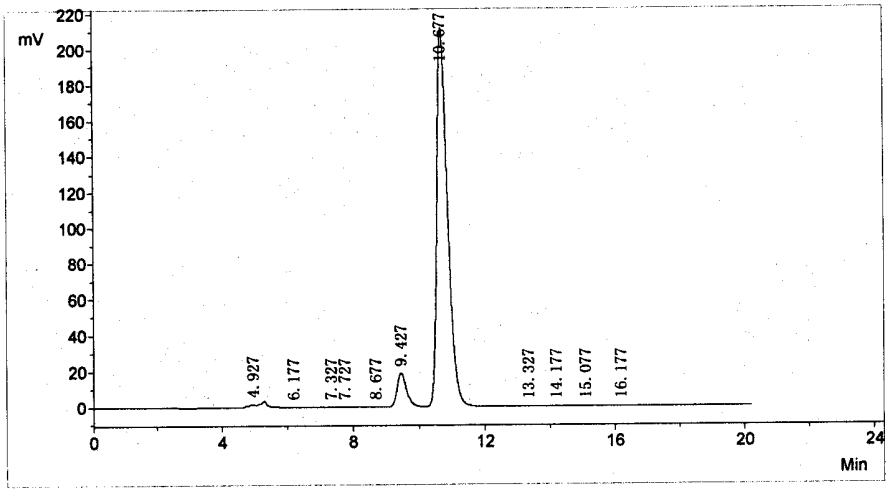


S 75 300 MHz, CDCl3

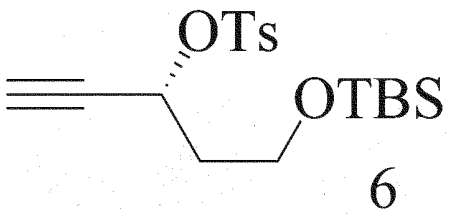
色谱分析报告

样品名称:
样品批号:
分析日期:2007-06-20

样品文件名:9-37-2...che
分析者:
分析时间:08:45



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		4.927	1875.6	27957.8	0.5295
2	2		6.177	241.9	70700.3	1.3391
3	3		7.327	39.1	1106.8	0.0210
4	4		7.727	138.2	2577.8	0.0488
5	5		8.677	92.6	1628.0	0.0308
6	6		9.427	18685.2	379097.7	7.1802
7	7		10.677	209194.0	4788691.7	90.6992
8	8		13.327	27.7	1057.6	0.0200
9	9		14.177	30.1	635.5	0.0120
10	10		15.077	143.0	4166.8	0.0789
11	11		16.177	64.5	2133.6	0.0404
合计:				230531.8	5279753.5	100.0000

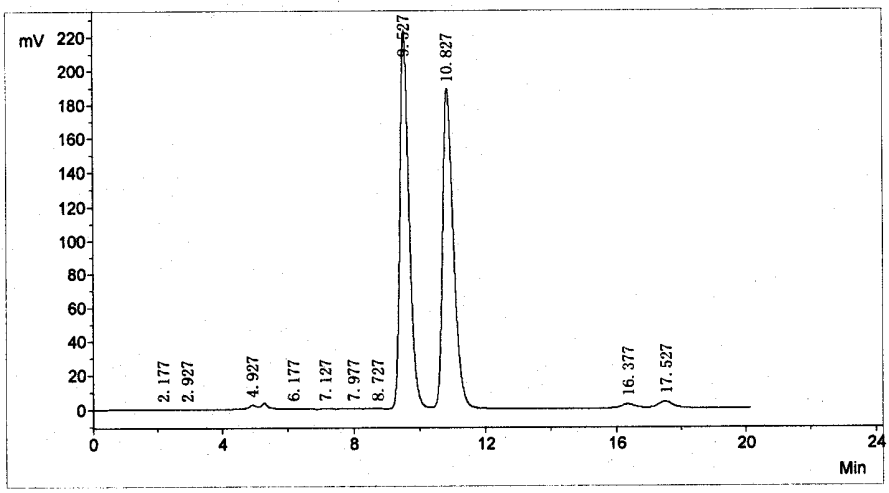


6

色谱分析报告

样品名称:
样品批号:
分析日期:2007-06-20

样品文件名:9-37-2+-.che
分析者:
分析时间:08:20



"(+/-)-6"

"racemic" tosylate 6 for comparison

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		2.177	102.8	3283.4	0.0364
2	2		2.927	154.0	3950.9	0.0438
3	3		4.927	2626.0	62462.5	0.6929
4	4		6.177	633.9	94038.0	1.0432
5	5		7.127	373.7	9686.2	0.1075
6	6		7.977	444.9	13535.9	0.1502
7	7		8.727	242.5	8970.8	0.0995
8	8		9.527	222886.8	4306862.7	47.7765
9	9		10.827	188175.8	4297861.7	47.6767
10	10		16.377	2441.9	83364.1	0.9248
11	11		17.527	3935.2	130586.9	1.4486
合计:				422017.6	9014603.0	100.0000