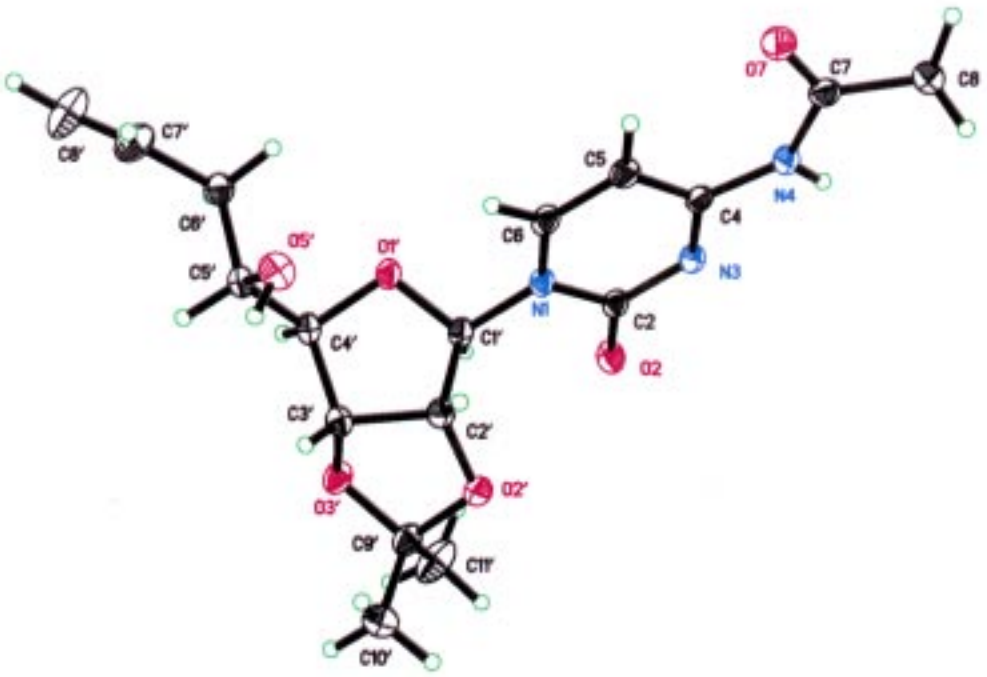
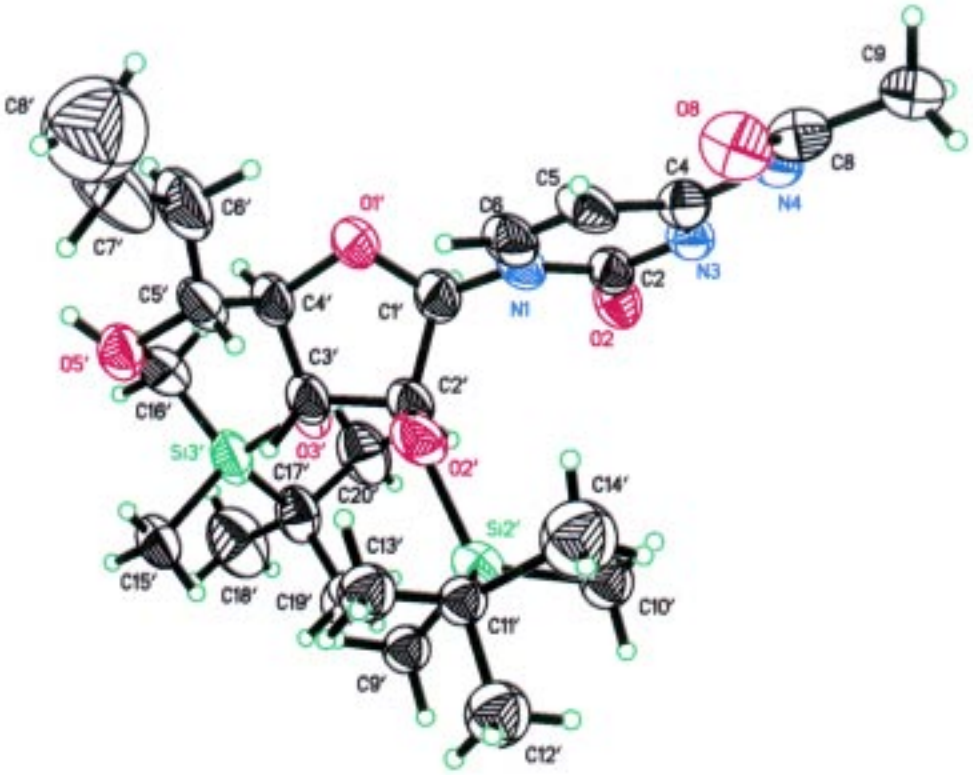


ORTEP Drawing of Compound **17**.



ORTEP Drawing of Compound **26**.

Table of Contents

General Experimental Procedures

Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Pyridine, CH_2Cl_2, and Et_3N were distilled from CaH_2 prior to use. All reagents were obtained from commercial sources and used without further purification, unless otherwise noted. All reactions were conducted in oven-dried glassware under an atmosphere of argon with magnetic stirring. Silica gel 60 (particle size 40-63 μm) was employed for flash chromatography. The HPLC purification was performed on a C_{18} reverse phase column. Standard ^1H (at 300 MHz), ^{13}C, and ^{31}P NMR spectra were recorded with $CDCl_3$ as solvent and $(CH_3)_4Si$ (^1H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.2 ppm) as internal standards, unless otherwise noted. The ^{31}P NMR chemical shifts are recorded in ppm relative to 85% H_3PO_4 (external standard).

5'(*S*)-Allyl-2',3'-di-*O*-*t*-butyldimethylsilyl-N^4-acetyl cytidine (20). Method A: Following Method A for the preparation of allyl alcohol **16,** aldehyde **19** (made from protected nucleoside **18**[2] (1.44 g, 2.8 mmol)) was treated with $BF_3 \cdot OEt_2$ (1.7 ml, 14.0 mmol) and allyltrimethylsilane (2.1 ml, 13.3 mmol). Standard workup and purification with flash chromatography (50% EtOAc in hexane) gave allyl alcohol **20** (1.04 g, 67% from nucleoside **18**) as a white solid.

Method C: Following Method C for the preparation of allyl alchohol **16,** aldehyde **19** (made from protected nucleoside **18** (436 mg, 0.8 mmol)) was treated with 5.0 M lithium perchlorate in diethyl ether (10 ml) and allyltributyltin (0.46 ml, 1.5 mmol). Standard workup and purification by flash chromatography (50% EtOAc in hexane) gave allyl alcohol **20** (371 mg, 79% from nucleoside **18**) as a white solid.

5'(*R*)-Allyl-2',3'-di-*O*-*t*-butyldimethylsilyl-N^4-acetyl cytosine arabinoside (26) and 5'(*S*)-allyl-2',3'-di-*O*-*t*-butyldimethylsilyl-N^4-acetyl cytosine arabinoside (27). Method A:

Following Method A for preparation of allyl alcohol **16**, aldehyde **25** (made from alcohol **24**[6a] (1.16 g, 2.3 mmol)) was treated with BF_3•OEt_2 (1.4 ml, 11.2 mmol) and allyltrimethylsilane (1.8 ml, 11.2 mmol). Standard workup and purification by flash chromatography (50% EtOAc in hexane) gave allyl alcohol **26** (896 mg), its epimer **27** (29 mg), and a mixture of compound **26** and **27** (129 mg) (*R*:*S* = 15:1, 85% yield from alcohol **24**). Alcohol **26**: ^{1}H NMR δ 9.19 (s, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 5.88 (m, 1H), 5.24 (br s, 1H), 5.20 (br d, *J* = 5.0 Hz, 1H), 4.36 (s, 1H), 4.26 (d, *J* = 2.4 Hz, 1H), 3.87 (m, 2H), 2.52 (m, 1H), 2.30 (m, 1H), 2.27 (s, 3H), 0.91 (s, 9H), 0.80 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), 0.05 (s, 3H), -0.20 (s, 3H); ^{13}C NMR δ 170.9, 162.7, 154.9, 146.6, 133.8, 119.3, 95.7, 90.1, 88.5, 78.2, 76.1, 70.5, 39.3, 25.9 (3C), 25.8 (3C), 25.2, 18.1, 18.0, -4.3, -4.5, -5.0, -5.2. Anal. Calcd for $C_{26}H_{47}N_3O_6Si_2$: C, 56.38; H, 8.55; N, 7.59. Found: C, 56.67; H, 8.61; N, 7.35.

Alcohol **27**: ^{1}H NMR δ 9.96 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 6.24 (d, *J* = 2.8 Hz, 1H), 5.87 (m, 1H), 5.18 (dd, *J* = 17.4, 1.7 Hz, 1H), 5.16 (br d, *J* = 10.1 Hz, 1H), 4.30 (d, *J* = 2.8 Hz, 1H), 4.15 (s, 1H), 4.0 (d, *J* = 3.0 Hz, 1H), 3.88 (m, 1H), 3.31 (d, *J* = 2.4 Hz, 1H), 2.40 (m, 2H), 2.29 (s, 3H), 0.91 (s, 9H), 0.80 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H), 0.05 (s, 3H), -0.17 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.0, 163.0, 155.0, 147.0, 134.2, 118.4, 96.1, 89.3, 88.3, 80.3, 76.3, 71.1, 38.8, 25.9 (3C),25.8 (3C), 25.1, 18.1, 18.0, -4.33, -4.35, -5.10, -5.16. Anal. Calcd for $C_{26}H_{47}N_3O_6Si_2$: C, 56.38; H, 8.55; N, 7.59. Found: C, 56.25; H, 8.82; N, 7.65.

Method B: Following Method B for preparation of allyl alcohol **20**, aldehyde **25** (made from alcohol **24** (196mg, 0.38 mmol)) was treated with 1M titanium (IV) chloride in methylene chloride (2.0 mL) and allyltrimethylsilane (0.32 mL, 2.0 mmol). Standard workup and purification by flash chromatography with 50% hexane in ethyl acetate afforded allyl alcohol **26** (130 mg) and its epimer **27** (46mg), (*R*:*S* = 3:1, 84% yield from alcohol **24**).

Method C: Following method C for preparation of allyl alcohol **16**, aldehyde **25** (made from alcohol **24** (666 mg, 1.3 mmol)) was treated with 5.0 M lithium perchlorate in diethyl ether (15 ml) and allyltributyltin (0.60 ml, 1.9 mmol). Standard workup and purification by flash chromatography (50% EtOAc in hexane) gave allyl alcohol **26** (447mg), a mixture of alcohol **26** and its epimer **27** (53 mg), alcohol **27** (63 mg) (*R*:*S* = 5:1, 78% yield from alcohol **24**).

5' (*S*)-Allyl-5'-*O*-diethylphosphonoacetyl-2', 3'-di-*O*-*t*-butylmethylsilyl-N^4-acetyl cytidine (31). According to the procedure described for compound **28**, homoallylic alcohol **20** (479 mg, 0.9 mmol) in CH_2Cl_2 (10 mL) was treated with EDC (199 mg, 1.0 mmol), DMAP (10 mg, 0.1 mmol), and phosphonoacetic acid (204 mg, 1.0 mmol). Standard workup and final purification by flash chromatography gave phosphonoacetate **31** as a white solid (515 mg, 80%): ^{1}H NMR δ 9.60 (br s, 1H), 8.45 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 5.83 (m, 1H), 5.47 (d, *J* = 0.8 Hz, 1H), 5.19 (m, 2H), 5.05 (ddd, *J* = 7.1, 7.0, 2.1 Hz, 1H), 4.29 – 4.16 (m, 6H), 3.82 (dd, *J* = 8.2, 4.0 Hz, 1H), 2.94 (d, *J* = 22.0 Hz, 2H), 2.62 (t, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 6H), 0.92 (s, 9H), 0.87 (s, 9H), 0.26 (s, 3H), 0.13 (s, 3H), 0.01 (s, 3H), -0.04 (s, 3H); ^{13}C NMR δ 170.8, 165.0 (d, J_{CP} = 5.5 Hz), 163.1, 155.3, 145.3, 132.5, 119.3, 96.5, 91.6, 81.9, 76.0, 72.7, 70.3, 63.2 (d, J_{CP} = 6.5 Hz), 63.1 (d, J_{CP} = 5.9 Hz), 35.8, 35.0 (d, J_{CP} = 133.3 Hz), 26.1 (3C), 26.0 (3C), 25.1, 18.3, 18.1, 16.6, 16.6, -3.8 (2C), -5.0, -5.2; ^{31}P NMR δ 18.5. Anal. Calcd for $C_{32}H_{58}N_3O_{10}PSi_2$: C, 52.51; H, 7.99; N, 5.74. Found: C, 52.31; H, 7.95; N, 5.67.

Phosphonoacetyl aldehyde of cytidine 32. According to the procedure described for compound **29**, allylic acetate **31** (520 mg, 0.7 mmol) was treated with $NaIO_4$ (380 mg, 1.8 mmol) and K_2OsO_4 (3 mg, 0.007 mmol) in a mixture solution of THF (5 mL) and water (5 mL). Standard workup and final purification by flash chromatography gave aldehyde **32** as an off-white solid (520 mg, 100%): ^{1}H NMR δ 9.81 (dd, *J* = 2.0, 1.2 Hz, 1H), 9.51 (br s, 1H), 8.40 (d, *J*

= 7.4 Hz, 1H), 7.52 (dd, J = 7.4 Hz, 1H), 5.73 (d, J = 0.9 Hz, 1H), 5.47 (ddd, J = 6.1, 4.8, 2.0 Hz, 1H), 4.31 (dd, J = 8.2, 2.0 Hz, 1H), 4.26 – 4.15 (m, 5H), 3.88 (dd, J = 8.0, 4.1 Hz, 1H), 2.95 (d, J = 22.1 Hz, 2H), 2.97 (m, 2H), 2.25 (s, 3H), 1.38 (td, J = 7.1, 3.1 Hz, 6H), 0.92 (s, 9H), 0.88 (s, 9H), 0.24 (s, 3H), 0.13 (s, 3H), 0.02 (s, 3H), -0.02 (s, 3H); ^{13}C NMR δ 198.2, 170.8, 165.0 (d, J_{CP} = 7.0 Hz), 163.2, 155.2, 145.1, 96.6, 91.7, 82.9, 76.0, 70.2, 68.5, 63.4 (d, J_{CP} = 2.6 Hz), 63.3 (d, J_{CP} = 2.9 Hz), 45.4, 35.0 (d, J_{CP} = 132.0 Hz), 26.1 (3C), 26.0 (3C), 25.1, 18.3, 18.1, 16.6, 16.6, -3.8 (2C), -5.0, -5.2; ^{31}P NMR δ18.1; HRMS (ESI) *m/z* calcd for $C_{31}H_{57}N_3O_{11}PSi_2$ $(M + H)^+$ 734.3269, found 734.3272.

5'(*R*)-Allyl-5'-*O*-acryloyl-2',3'-*O*-*t*-butyldimethylsilyl-N^4-acetyl cytosine arabinoside (38). According to the procedure described for compound **35**, allyl alcohol **26** (208.0 mg, 0.38 mmol) in THF (10 mL) was treated with acryloyl chloride (0.1 mL, 1.23 mmol), Et_3N (0.18 mL, 1.30mmol), and DMAP (4.6 mg, 0.04 mmol). Standard workup and final purification by flash chromatography gave acrylate ester **38** (145 mg, 63%) as a light yellow solid: ^{1}H NMR δ 10.11 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 6.44 (dd, J = 17.1, 1.2 Hz, 1H), 6.25 (d, J = 2.2 Hz, 1H), 6.12 (dd, J = 17.4, 10.4 Hz, 1H), 5.88 (dd, J = 10.4, 1.4 Hz, 1H), 5.80 (m, 1H), 5.23 (m, 1H), 5.16 (br d, J = 4.0 Hz, 1H), 5.12 (br, s, 1H), 4.22 (d, J = 2.5 Hz, 1H), 4.08 (s, 1H), 3.98 (d, J = 9.6 Hz, 1H), 2.70 (m, 1H), 2.45 (m, 1H), 2.30 (s, 3H), 0.90 (s, 9H), 0.79 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.00 (s, 3H), -0.18 (s, 3H); ^{13}C NMR δ 171.2, 164.9, 163.0, 154.9, 146.6, 132.5, 131.7, 128.2, 119.0, 95.9, 88.7, 86.7, 78.9, 76.1, 72.3, 36.0, 25.9 (3C), 25.8 (3C), 25.1, 18.0, 17.9, -4.5, -4.6, -4.8, -5.2; HRMS (ESI) *m/z* calcd for $C_{29}H_{50}N_3O_7Si_2$ $(M+H)^+$ 608.3187, found 608.3178. Anal. Calcd for $C_{29}H_{49}N_3O_7Si_2$: C, 57.30; H, 8.12; N, 6.91. Found: C, 57.32; H, 8.12; N, 6.81.

5'(S)-Allyl-5'-O-acryloyl-2',3'-O-t-butyldimethylsilyl-N^4-acetyl cytosine arabinoside (41). According to the procedure described for compound **35**, allyl alcohol **27** (141 mg, 0.25 mmol) was treated with acryloyl chloride (0.07 mL, 0.82 mmol), Et_3N (0.12 mL, 0.86 mmol), and DMAP (11 mg, 0.09 mmol) in THF (10 mL). Standard workup and final purification by flash chromatography gave acrylate ester **41** (123 mg, 81%) as a light yellow solid: ^{1}H NMR δ 9.17 (s, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 6.47 (dd, J = 17.3, 1.4 Hz, 1H), 6.27 (d, J = 2.6 Hz, 1H), 6.14 (dd, J = 17.3, 10.2 Hz, 1H), 5.87 (dd, J = 10.2, 1.4 Hz, 1H), 5.74 (m, 1H), 5.51 (ddd, J = 9.1, 8.8, 4.0 Hz, 1H), 5.13 (dd, J = 18.5, 1.3 Hz, 1H), 5.11 (br d, J = 9.4 Hz, 1H), 4.23 (d, J = 2.6 Hz, 1H), 4.10 (s, 1H), 4.02 (d, J = 9.1 Hz, 1H), 2.41 (m, 2H), 2.24 (s, 3H), 0.91 (s, 9H), 0.84 (d, 9H), 0.15 (d, 3H), 0.13 (s, 3H), 0.03 (s, 3H), -0.22 (s, 3H); ^{13}C NMR δ 170.4, 166.0, 162.4, 155.0, 148.0, 132.4, 131.7, 128.4, 118.9, 95.6, 88.8, 88.5, 78.8, 75.8, 72.4, 36.2, 25.8 (6C), 25.2, 18.03, 17.96, -4.2, -4.4, -5.0, -5.2; HRMS (ESI) *m/z* calcd for $C_{29}H_{50}N_3O_7Si_2$ $(M+H)^+$ 608.3187, found 608.3174. Anal. Calcd for $C_{29}H_{49}N_3O_7Si_2$: C, 57.30; H, 8.12; N, 6.91. Found: C, 56.85; H, 8.08; N, 6.64.

5'(*S*)-lactone 42. According to the procedure described for compound **40**, compound **41** (212 mg, 0.35 mmol) was treated with catalyst **39** (29.4 mg, 0.035 mmol) in CH_2Cl_2 (35 mL). Standard workup and final purification by flash chromatography gave unsaturated lactone **42** (156 mg, 77%) as a light brown solid: ^{1}H NMR δ 9.63 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 6.90 (m, 1H), 6.27 (d, J = 3.4 Hz, 1H), 6.10 (dd, J = 9.6, 1.7 Hz, 1H), 4.73 (ddd, J = 11.3, 6.9, 4.4 Hz, 1H), 4.36 (dd, J = 3.4, 1.3 Hz, 1H), 4.17 (s, 1H), 4.09 (dd, J = 6.9, 1.9 Hz, 1H), 2.54 (dddd, J = 18.4, 11.3, 2.5, 2.5 Hz, 1H), 2.37 (ddd, J= 18.4, 4.9, 4.4 Hz, 1H), 2.28 (s, 3H), 0.91 (s, 9H), 0.76 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.04 (s, 3H), -0.17 (s, 3H); ^{13}C NMR δ 170.6, 162.70, 162.67, 154.8, 146.6, 143.6, 121.8, 95.9, 88.2, 86.9, 78.3, 76.4, 76.1, 26.2, 25.65

(3C), 25.60 (3C), 25.0, 17.8, 17.7, -4.4, -4.6, -5.0, -5.3; HRMS (ESI) *m/z* calcd for $C_{27}H_{46}N_3O_7Si_2$ $(M+H)^+$ 580.2874, found 580.2870.

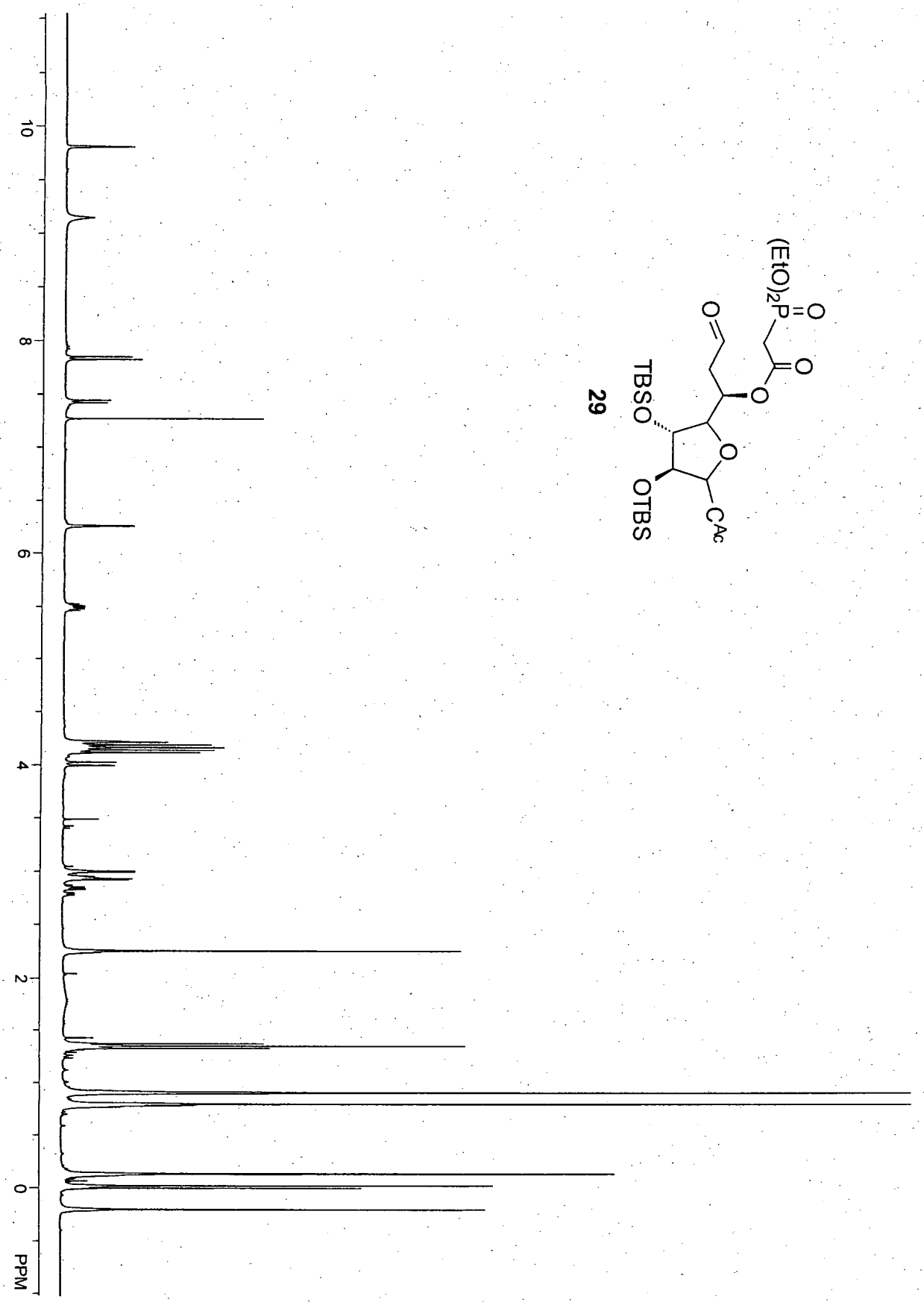
5'(*S*)-Allyl-5'-*O*-acryloyl-2', 3'-*O*-*t*-butyldimethylsilyl-N^4-acetyl cytidine (43). According to the procedure described for compound **35**, allyl alcohol **20** (369 mg, 0.66 mmol) was treated with acryloyl chloride (0.10 mL, 1.23 mmol), Et_3N (0.30 mL, 2.16 mmol) and DMAP (9.1 mg, 0.07 mmol) in THF (10 mL). Standard workup and final purification with flash chromatography gave compound **43** (295 mg, 73%) as a white solid: ^{1}H NMR δ 10.28 (s, 1H), 8.40 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* =7.5 Hz, 1H), 6.47 (dd, *J* = 17.0, 1.6 Hz, 1H), 6.12 (dd, *J* = 17.0, 10.4 Hz, 1H), 5.95 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.83 (m, 1H), 5.73 (d, *J* = 0.8 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.16 (br s, 1H), 5.13 (m, 1H), 4.31 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.18 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.78 (dd, *J* = 8.3, 3.8 Hz, 1H), 2.64 (dd, *J* = 7.2, 7.2 Hz, 2H), 2.32 (s, 3H), 0.92 (s, 9H), 0.86 (s, 9H), 0.25 (s, 3H), 0.12 (s, 3H), -0.02 (s, 3H), -0.08 (s, 3H); ^{13}C NMR δ 171.6, 165.2, 163.4, 155.1, 144.4, 132.7, 132.5, 127.9, 119.2, 96.4, 91.5, 82.4, 76.0, 71.3, 70.2, 36.3, 26.1 (3C), 26.0 (3C), 25.1, 18.3, 18.1, -3.8 (2C), -5.0, -5.3; HRMS (ESI) *m/z* calcd for $C_{29}H_{50}N_3O_7Si_2$ $(M+H)^+$ 608.318, found 608.3189. Anal. Calcd for $C_{29}H_{49}N_3O_7Si_2$: C, 57.30; H, 8.12; N, 6.91. Found: C, 56.84; H, 8.05; N, 6.79.

5'(*R*)-Lactone 46. According the procedure described for lactone **44**, unsaturated lactone **40** (97 mg, 0.17 mmol) in EtOAc (5 mL) was treat with palladium (10 wt. % on activated carbon, 19 mg) in presence of atmospheric H_2. Standard workup and purification by flash chromatography gave lactone **46** (89 mg, 90%) as a light brown solid: ^{1}H NMR δ 10.07 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 4.48 (ddd, *J* = 9.8, 9.8, 3.5 Hz, 1H), 4.41 (s, 1H), 4.26 (d, *J* = 2.4 Hz, 1H), 3.84 (d, *J* = 9.8 Hz, 1H), 2.58 (m, 2H), 2.30 (s, 3H), 2.23 (m, 1H), 2.03 (m, 1H), 1.91 (m, 1H), 1.65 (m, 1H), 0.91 (s, 9H), 0.78 (s, 9H),

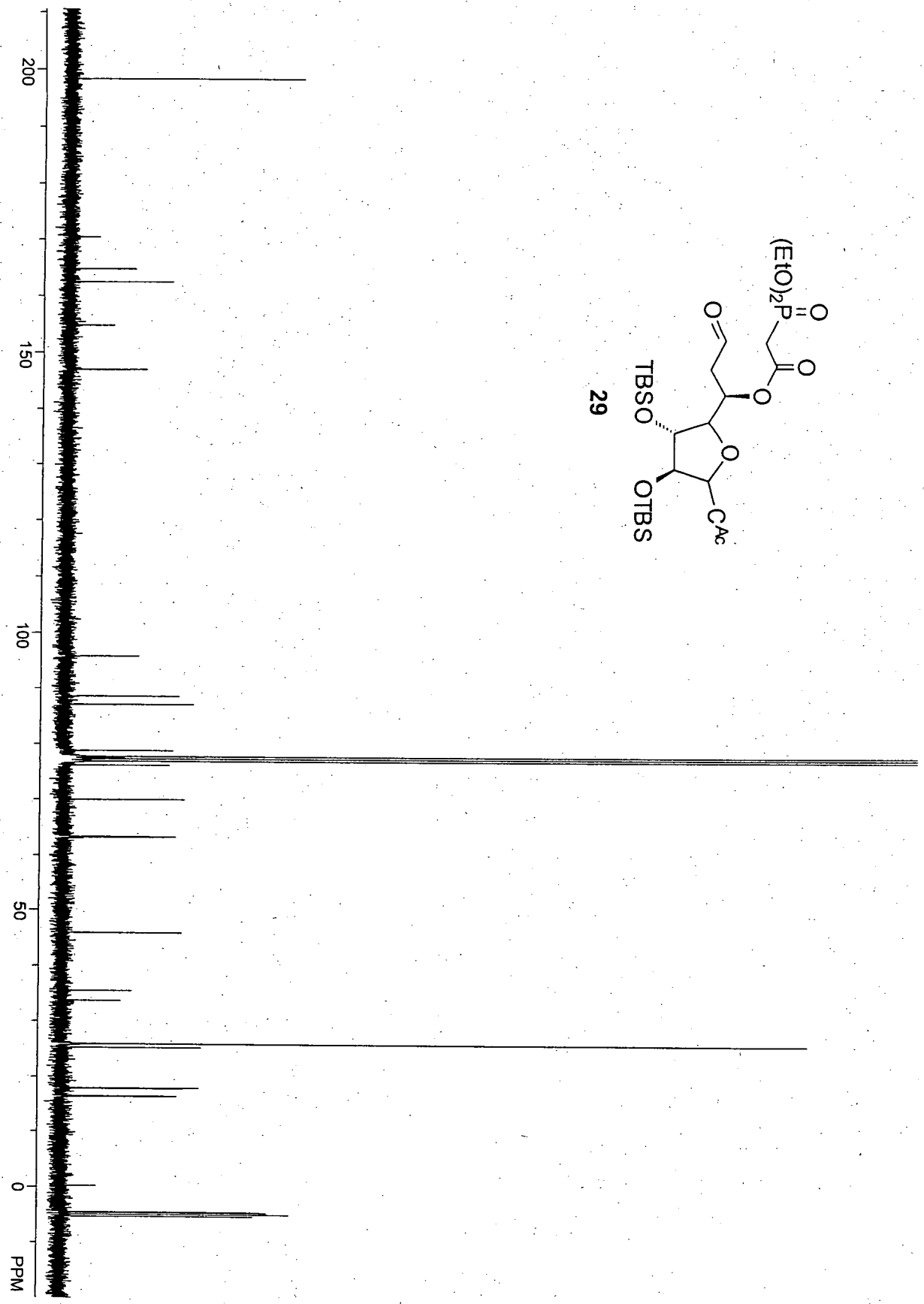
0.16 (s, 3H), 0.15 (s, 3H), 0.04 (s, 3H), -0.21 (s, 3H); ^{13}C NMR δ 171.2, 169.9, 163.0, 154.8, 146.0, 95.8, 88.9, 88.4, 78.8, 78.1, 75.9, 30.0, 25.9 (3C), 25.8 (3C), 25.1 (2C), 18.2, 18.0, 17.9, -4.51, -4.53, -5.0, -5.2; HRMS (ESI) *m/z* calcd for $C_{27}H_{48}N_3O_7Si_2$ $(M+H)^+$ 582.3031, found 582.3027.

5'(*R*)-[1'-(2',3'-*O*-Di-*t*-butyldimethylsilyl-β-D-arabino-5'-penta-1',4'-furanosyl)-N^4-acetylcytosyl]-α-diethylphosphonyl-δ-lactone (47). According to the procedure described for α-phosphono lactone **45**, lactone **46** (285 mg, 0.5 mmol) in ether (8 mL) was treated with LDA (1.22 mmol), following with addition of HMPA (0.1 mL, 0.5 mmol) and diethyl chlorophosphite (0.08 mL, 0.5 mmol). Standard workup and purification by flash chromatography (EtOAc gradient in Hexane) gave the α-phosphono lactone **47** (78 mg) as a mixture of two diastereomers (ratio = 1:1) in a yield of 31% based on recovered lactone **46** (84 mg, 29%). For α-phosphono lactone **47**: ^{1}H NMR δ 9.38 (s, 1H), 7.75 (d, J = 7.6 Hz, 0.5H), 7.74 (d, J = 7.7 Hz, 0.5H), 7.2 (d, J = 7.2 Hz, 1H), 6.26 (d, J = 2.3 Hz, 0.5H), 6.25 (d, J = 2.2 Hz, 0.5H), 4.57 (ddd, J = 9.6, 9.6, 3.0 Hz, 0.5H), 4.49 (ddd, J = 9.4, 9.4, 4.6 Hz, 0.5H), 4.40 (s, 1H), 4.28 –4.15 (m, 5H), 3.90 (d, J = 10.0 Hz, 0.5H), 3.80 (d, J = 9.6 Hz, 0.5H), 3.22 (m, 0.5H), 3.12 (m, 0.5H), 2.39 –2.33 (m, 2H), 2.27 (s, 3H), 2.20 –2.05 (m, 2H), 1.40 –1.33 (m, 6H), 0.91 (s, 4.5H), 0.91 (s, 4.5H), 0.78 (s, 4.5H), 0.77 (s, 4.5H), 0.16 (s, 3H), 0.15 (s, 3H), 0.04 (s, 3H), -0.19 (s, 1.5H), -0.21 (s, 1.5H); ^{13}C NMR δ 170.7, 165.2 (d, J_{CP} = 4.7 Hz, 0.5C), 164.8 (d, J_{CP} = 4.2 Hz, 0.5C), 162.6, 154.8, 146.2 (0.5C), 146.1 (0.5C), 95.6, 88.9 (0.5C), 88.7 (0.5C), 88.2, 79.6 (0.5C), 79.4 (0.5C), 78.3, 76.1 (0.5C), 76.0 (0.5C), 63.7 (d, J_{CP} = 6.5 Hz, 0.5C), 63.6 (d, J_{CP} = 6.6 Hz, 0.5C), 63.1 (d, J_{CP} = 6.4 Hz, 0.5C), 63.0 (d, J_{CP} = 6.8 Hz, 0.5C), 40.8 (d, J_{CP} = 138.8 Hz, 0.5C), 40.1 (d, J_{CP} = 136.6 Hz, 0.5C), 25.9 (6C), 25.4 (d, J_{CP} = 10.0 Hz, 0.5C), 25.2, 23.9 (d, J_{CP} = 5.0 Hz, 0.5C), 21.0 (d, J_{CP} = 3.5 Hz, 0.5C), 20.4 (d, J_{CP} = 4.4 Hz, 0.5C), 18.0, 18.0 (0.5C), 17.9 (0.5C), 16.6 (d, J_{CP} = 5.7 Hz),

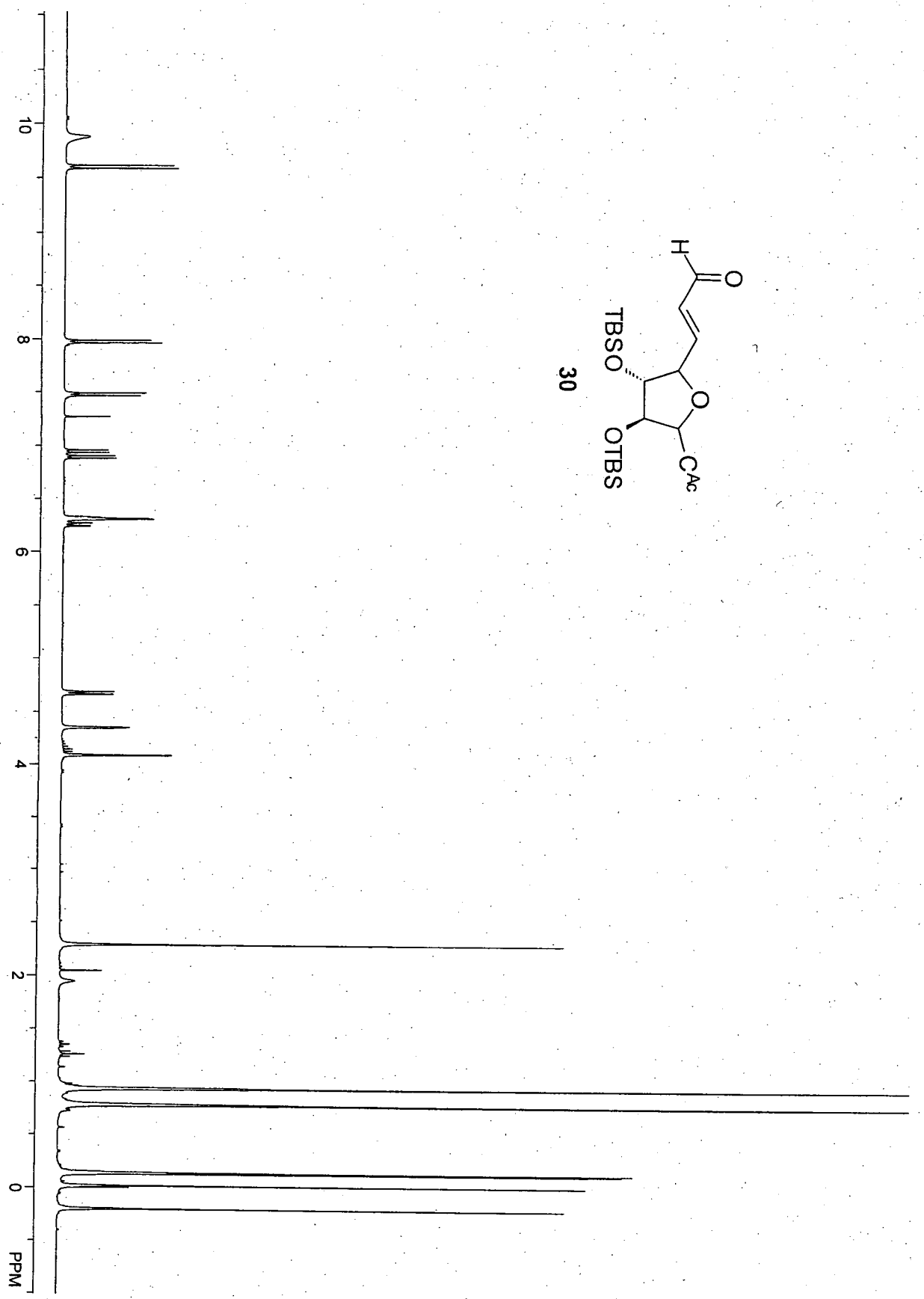
16.6 (d, J_{CP} = 6.0 Hz, 0.5C), 16.6 (d, J_{CP} = 5.6 Hz, 0.5C), -4.5 (0.5C), -4.5 (0.5C), -4.5 (0.5C), -4.6 (0.5C), -4.9 (0.5C), -5.0 (0.5C), -5.2 (0.5C), -5.2 (0.5C); ^{31}P NMR δ 22.0, 21.9; HRMS (ESI) *m/z* calcd for $C_{31}H_{57}N_3O_{10}PSi_2$ $(M+H)^+$ 718.3320, found 718.3317.

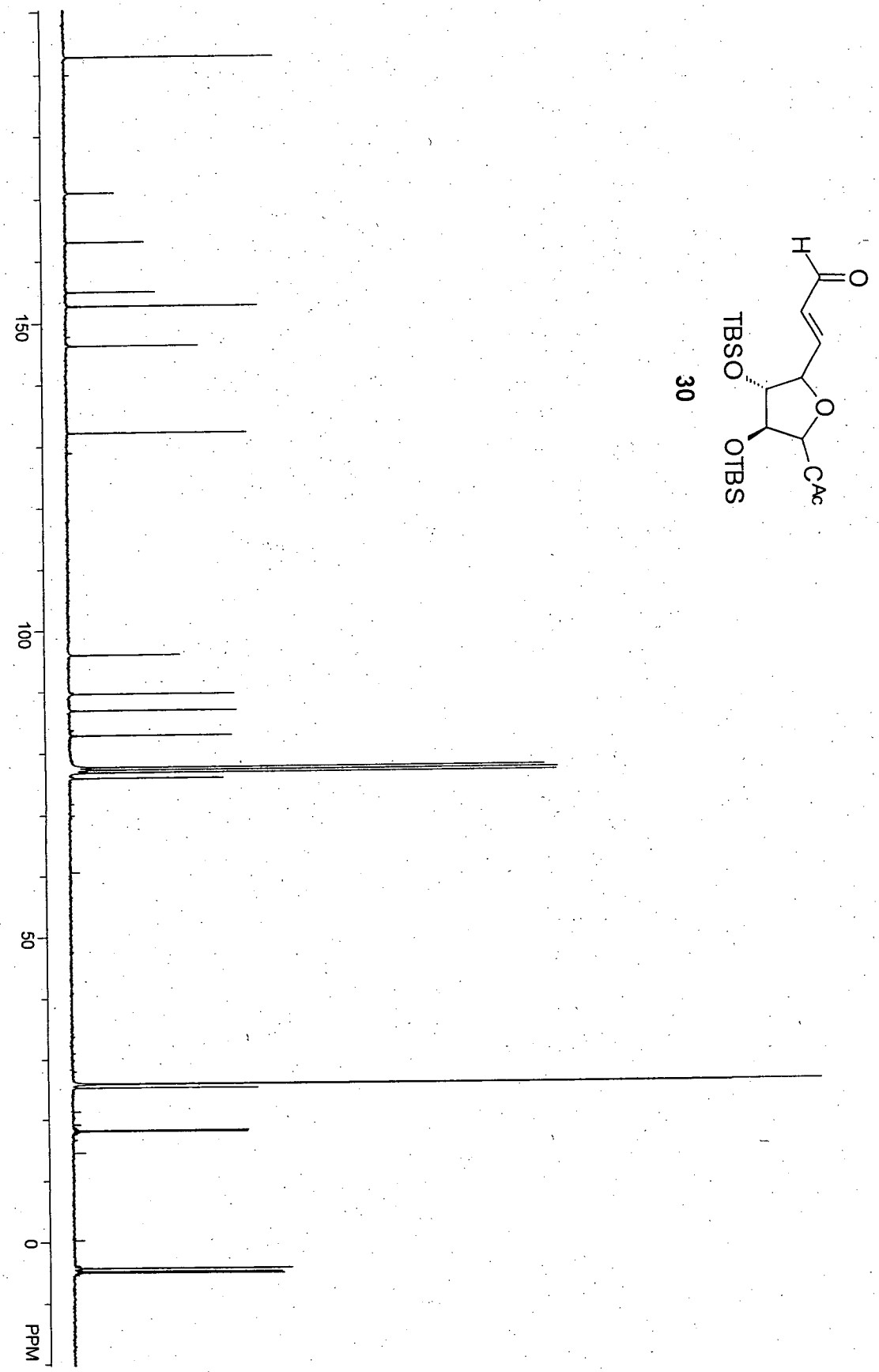


29

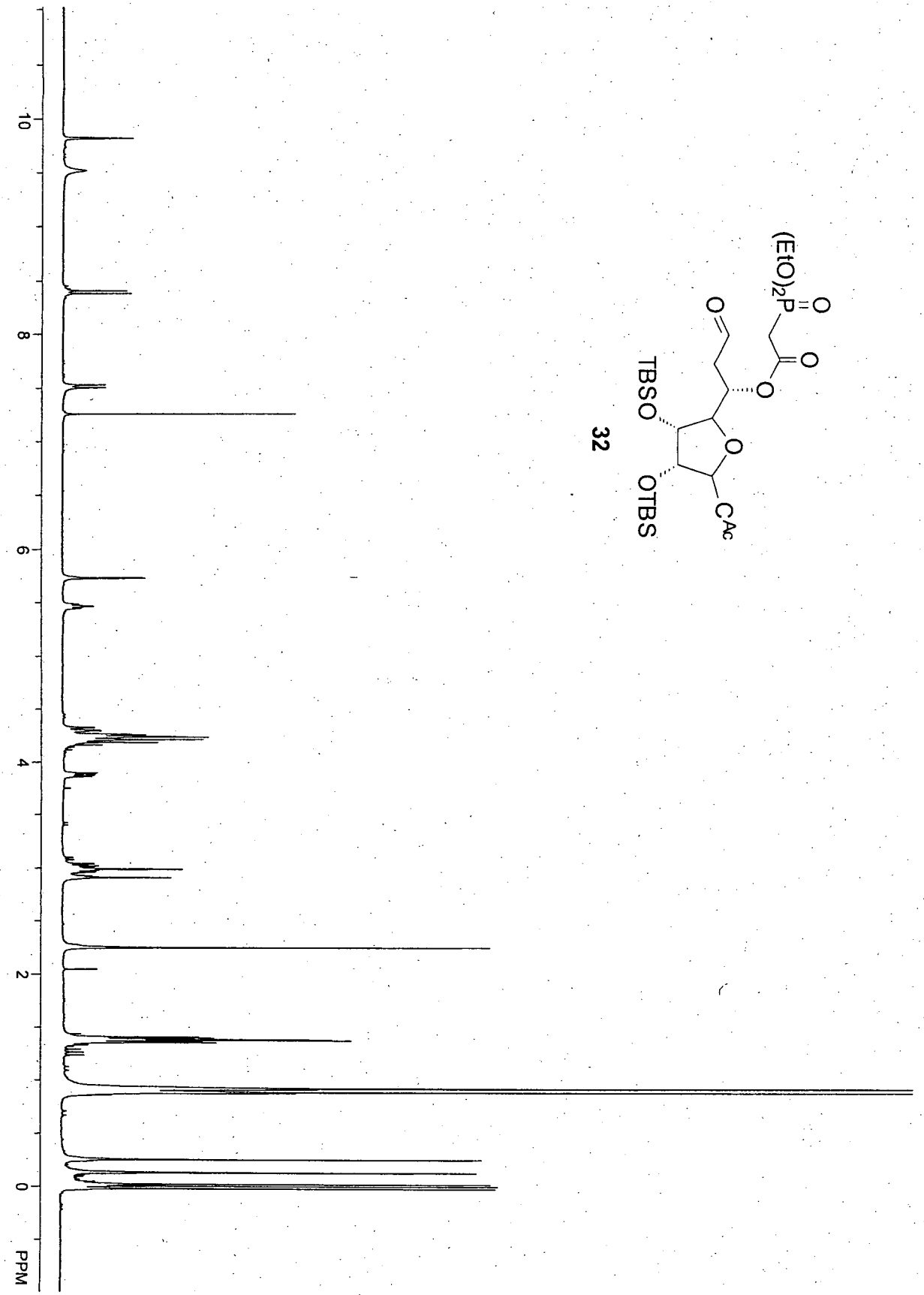


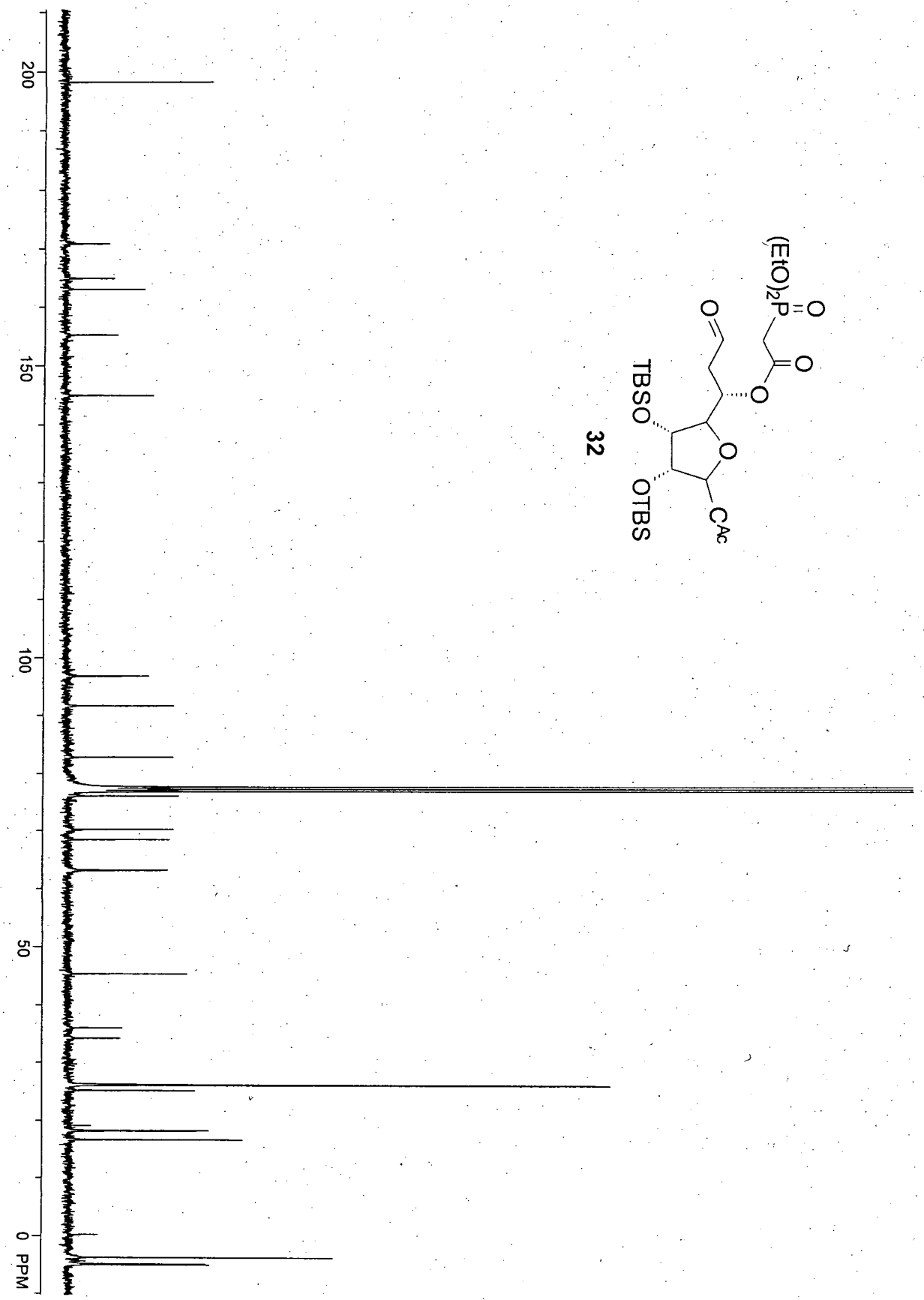
29

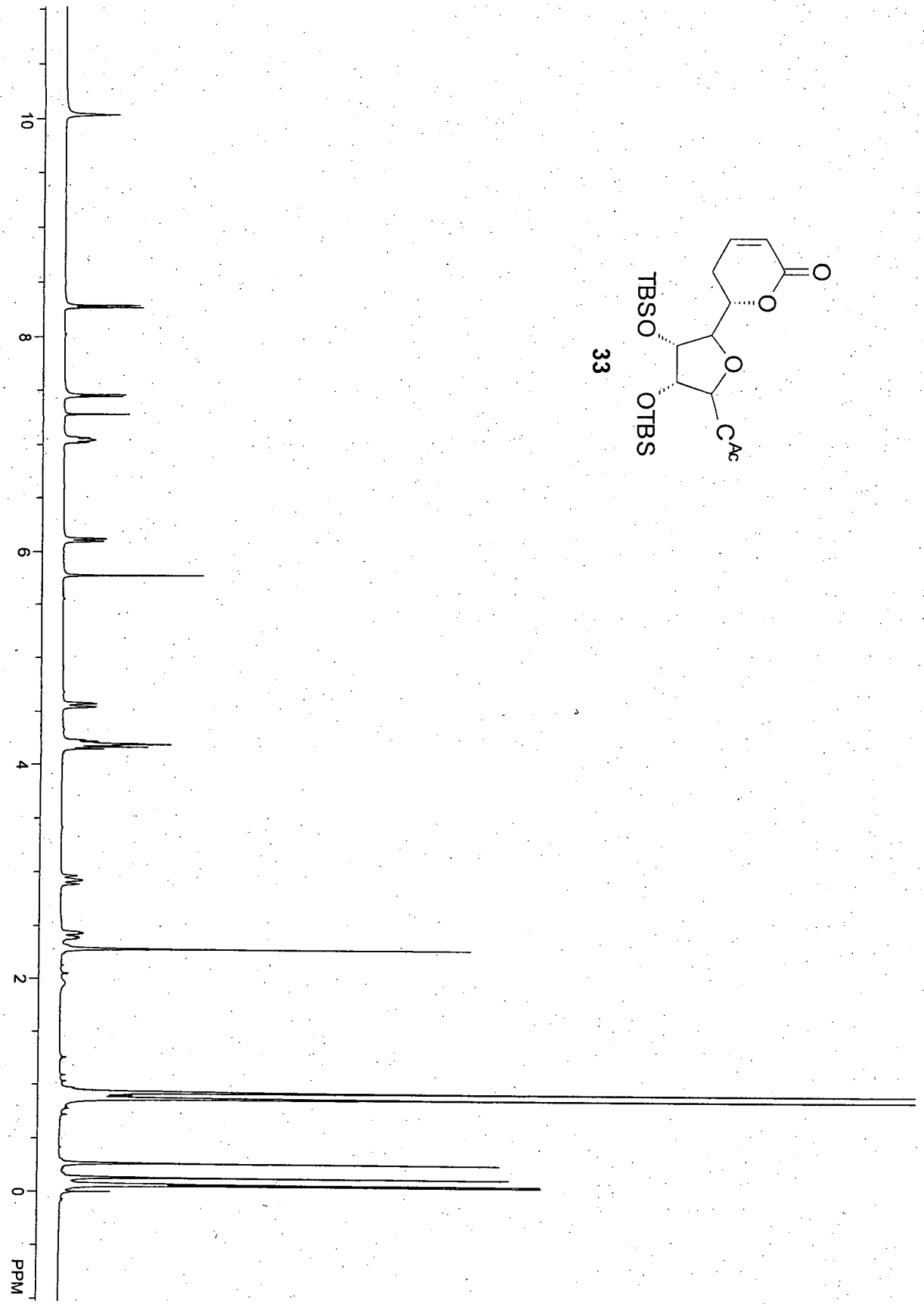

10
8
6
4
2
0
PPM
30
TBSO
OTBS
O
H
O
OAc



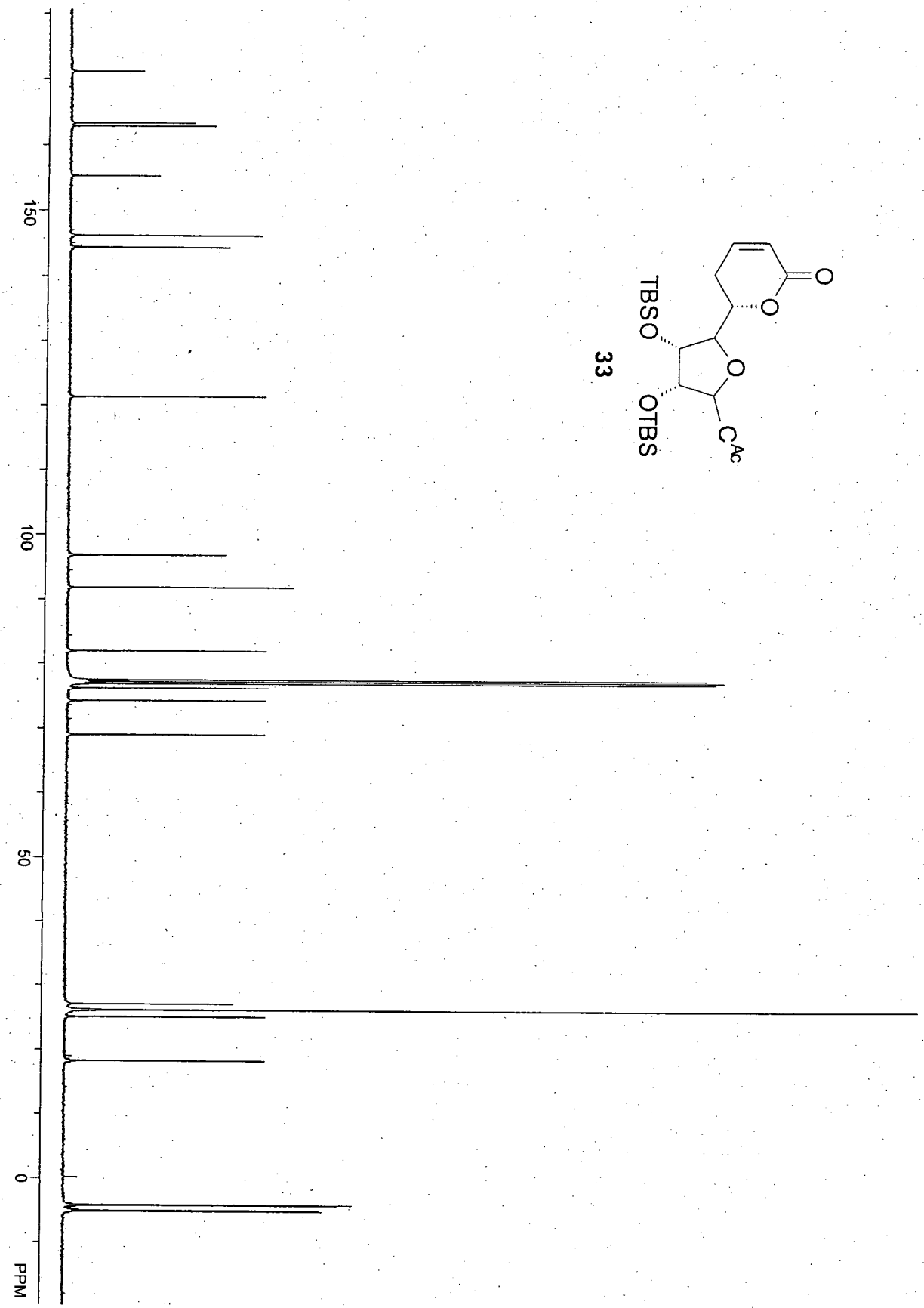
30


10
8
6
4
2
0
PPM
(EtO)2P
O
O
O
O
TBSO
OTBS
O
CAc
32

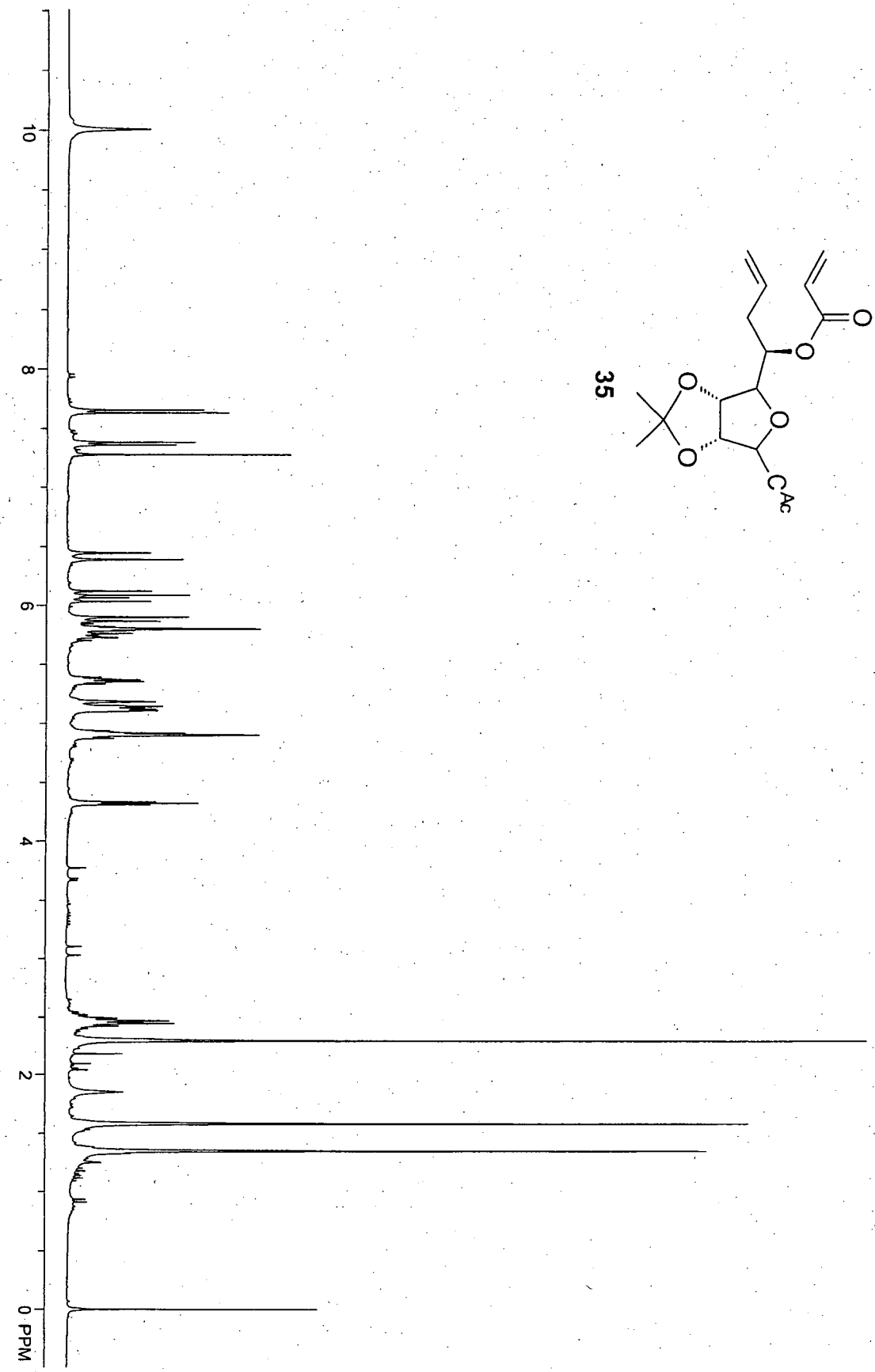

200
150
100
50
0 PPM
(EtO)2P
O
O
O
O
TBSO
OTBS
O
OAc
32



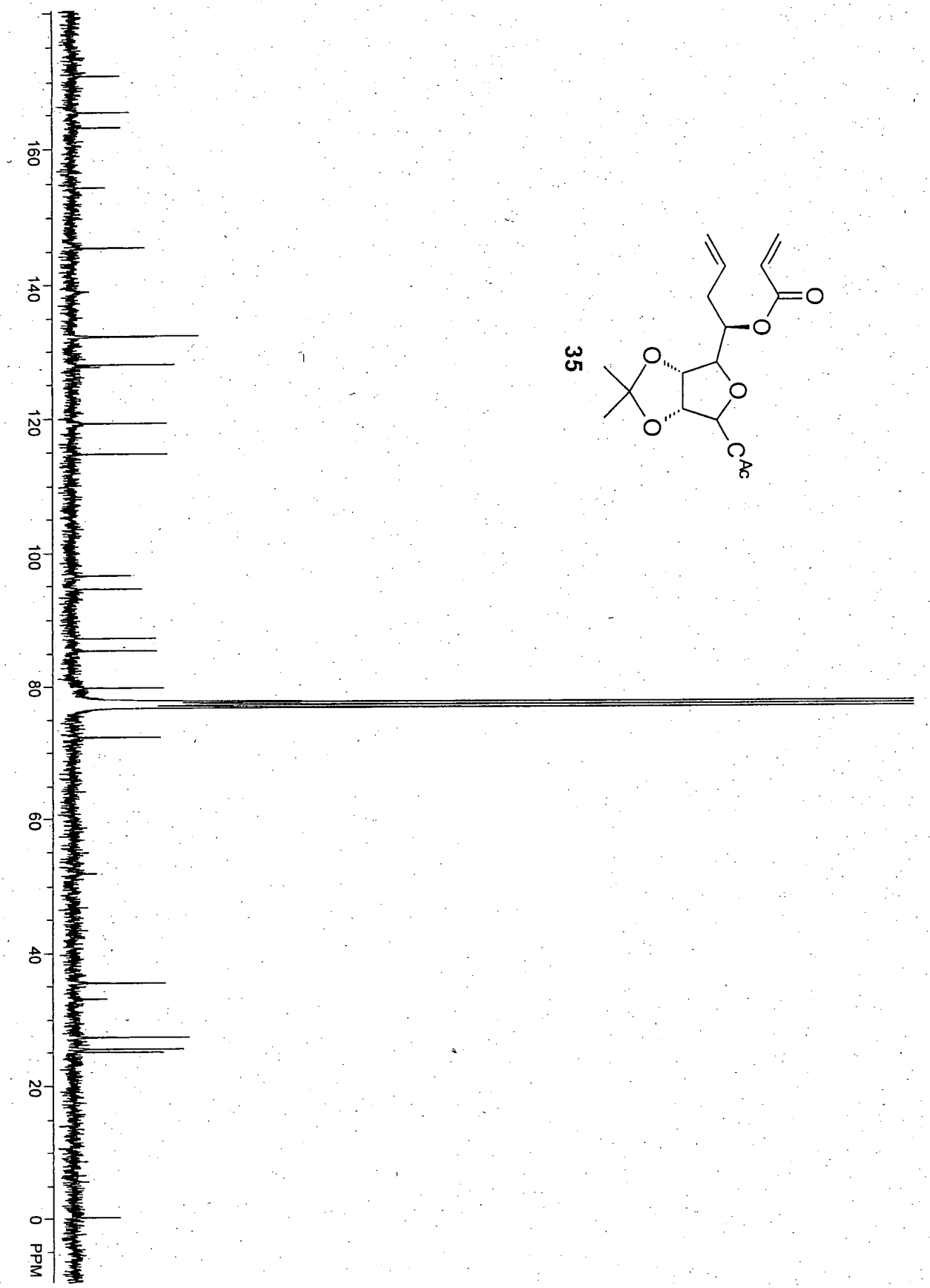
33

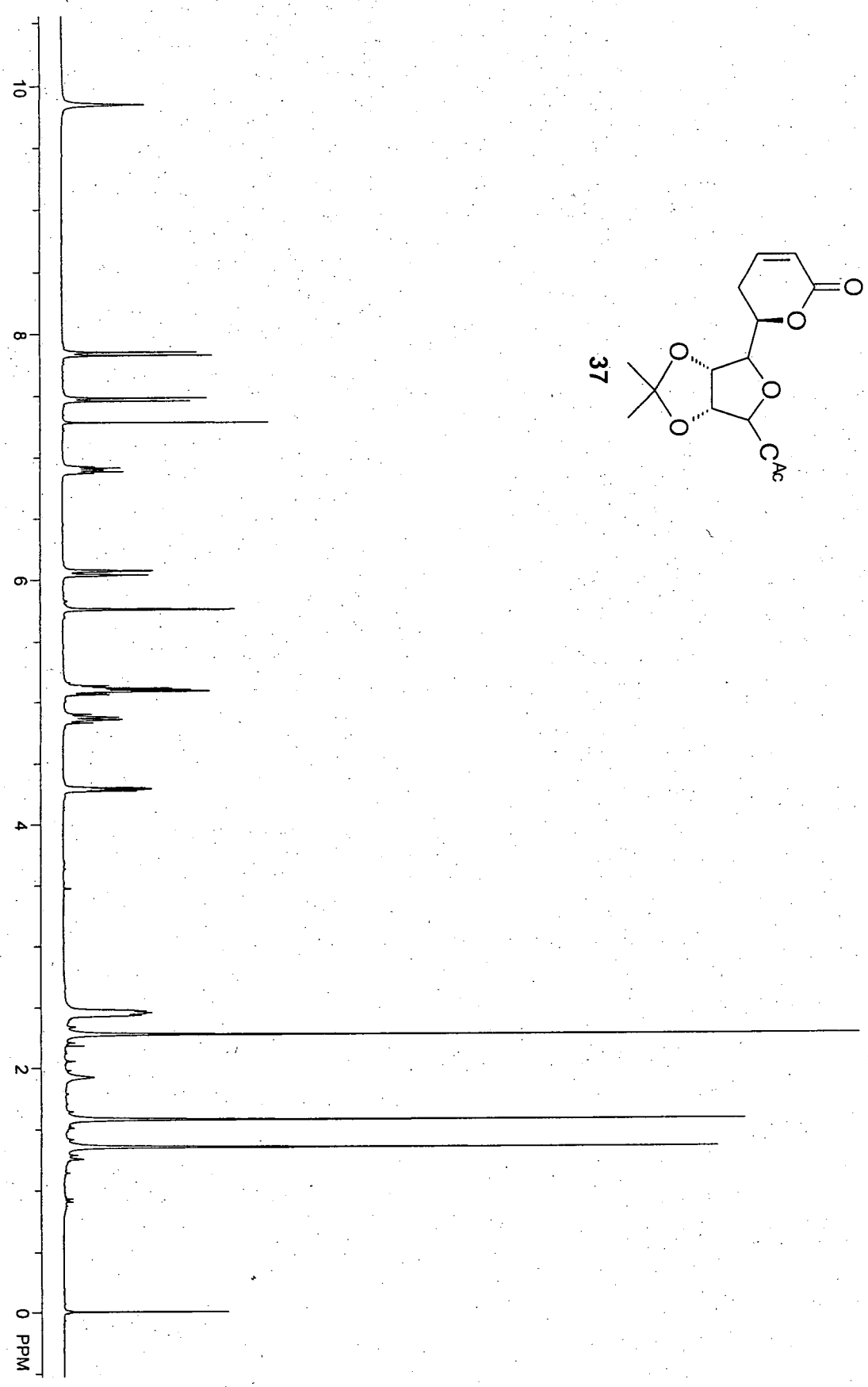


33

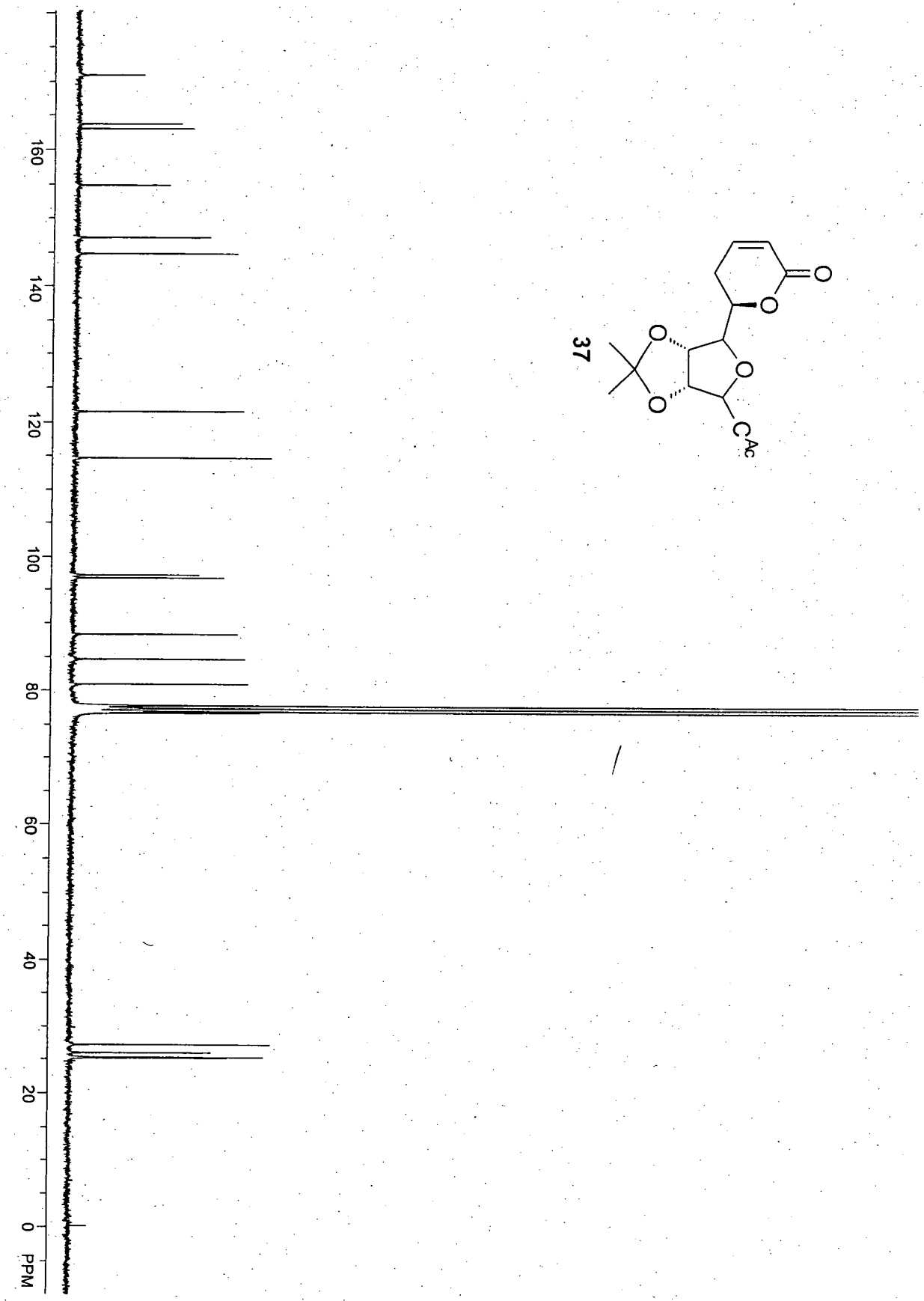


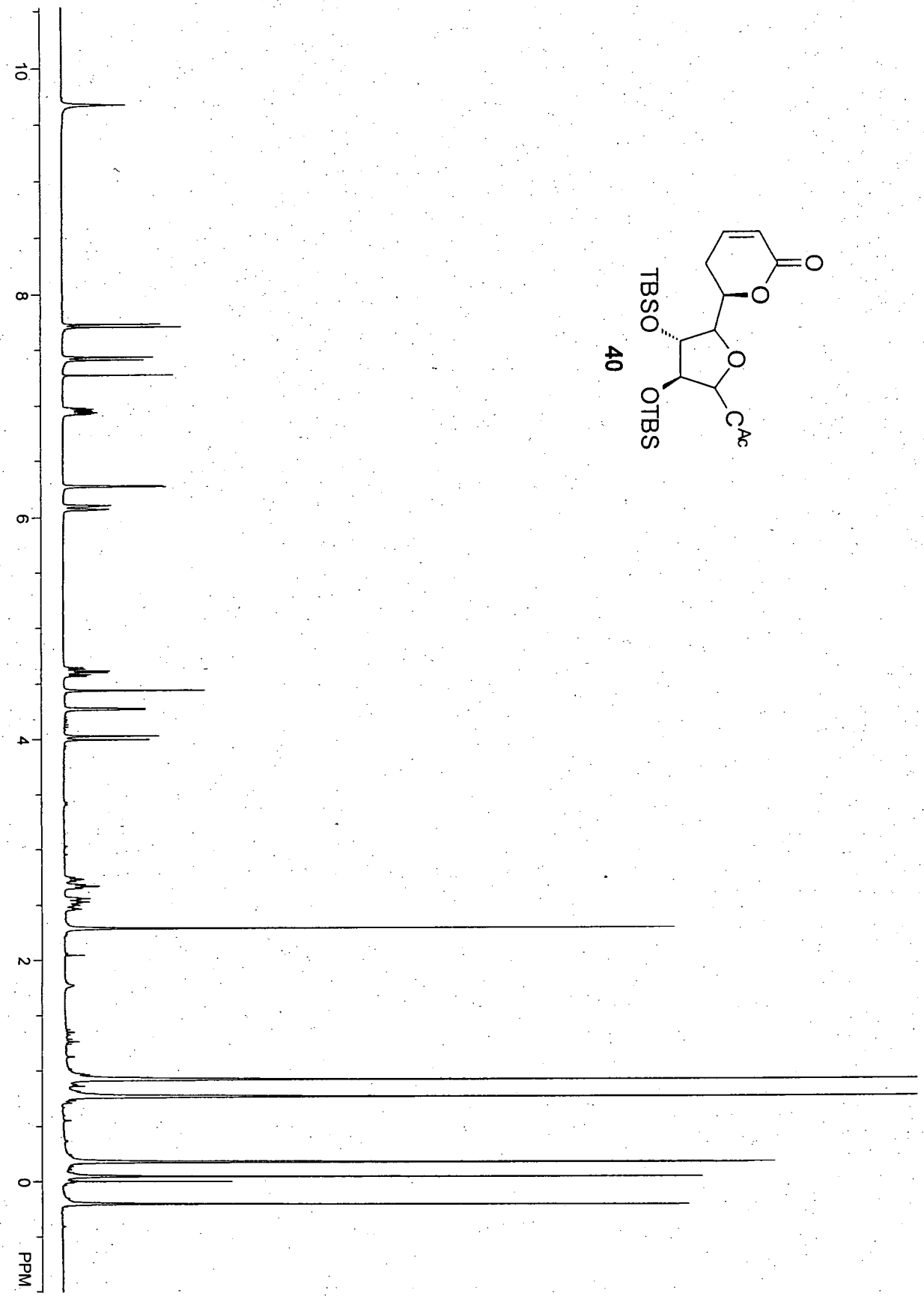
35

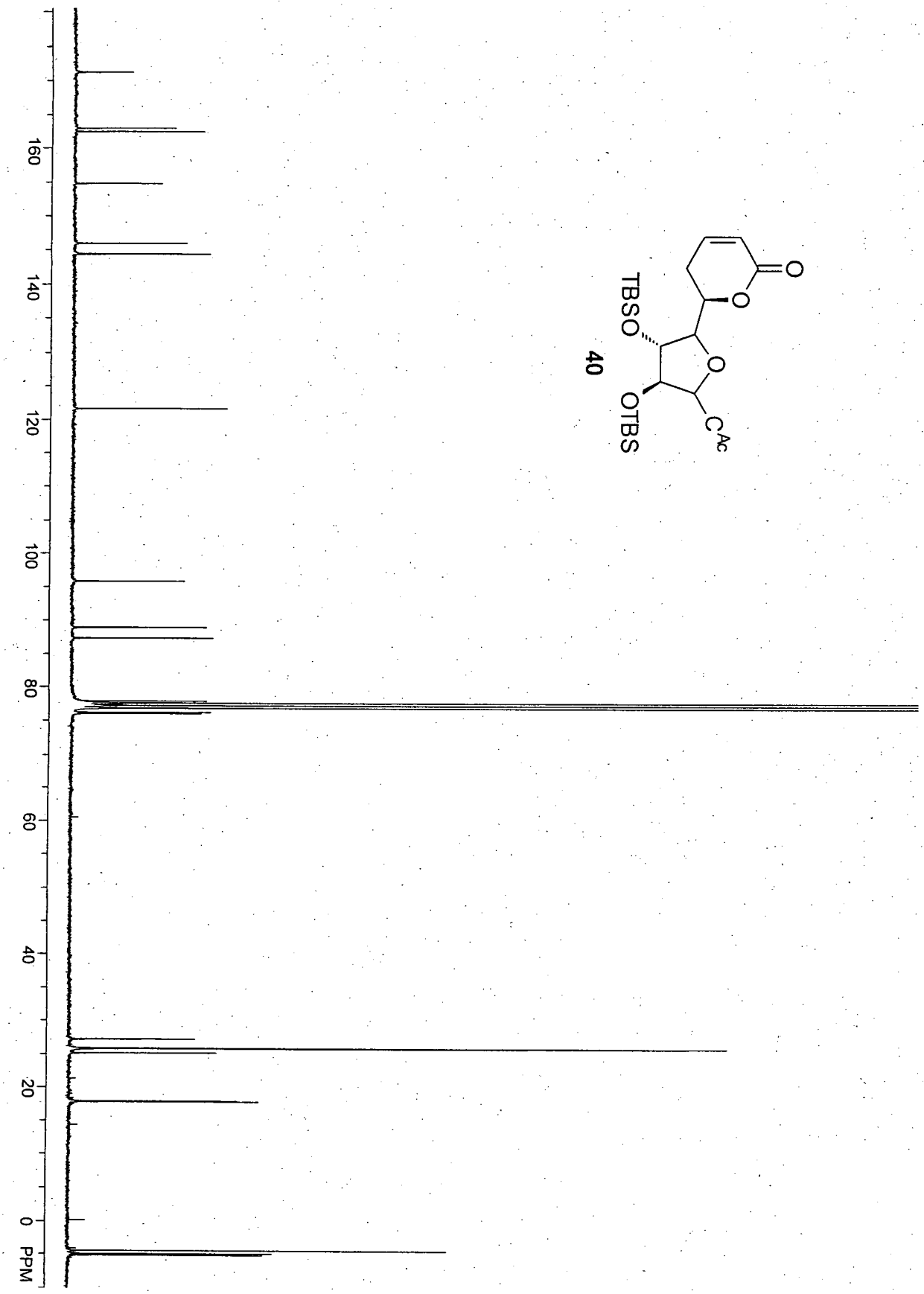

160
140
120
100
80
60
40
20
0 PPM
35
O
O
O
O
O
O
OAc

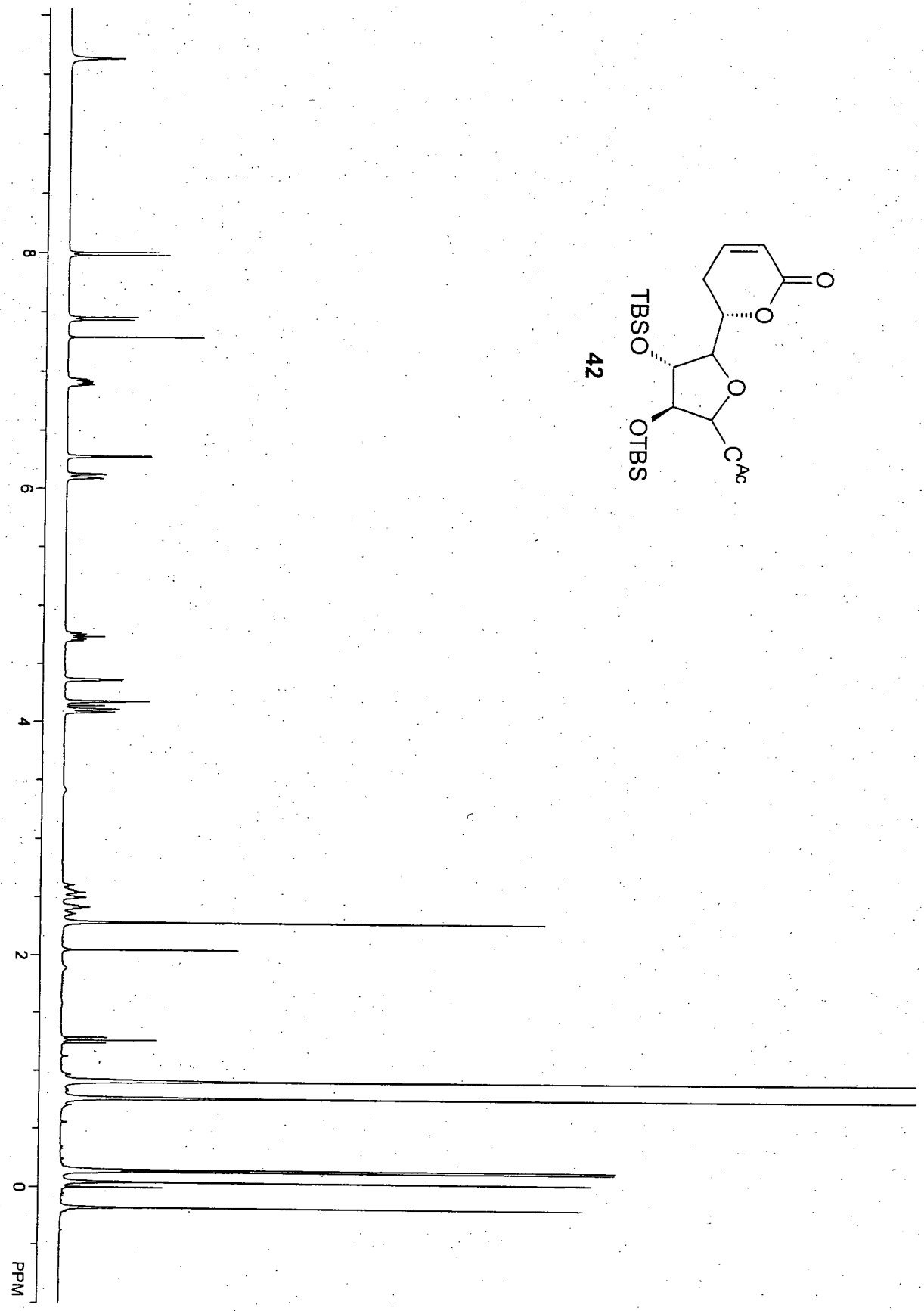

10
8
6
4
2
0 PPM

37
O
O
O
O
O
CAc

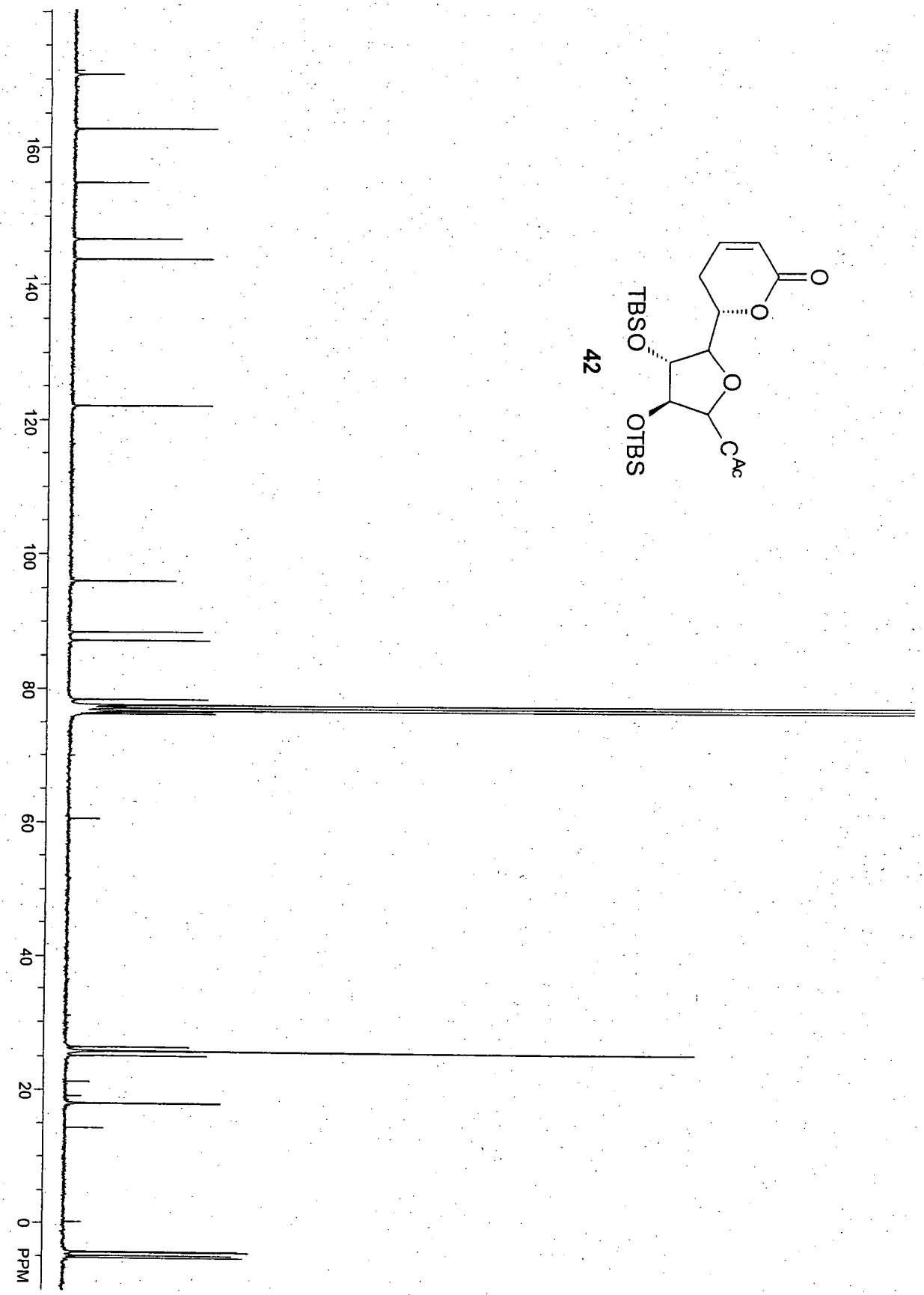

160
140
120
100
80
60
40
20
0
PPM
37
O
O
O
O
O
O
Ac


10
8
6
4
2
0
PPM
TBSO
OTBS
OAc
O
O
O
40

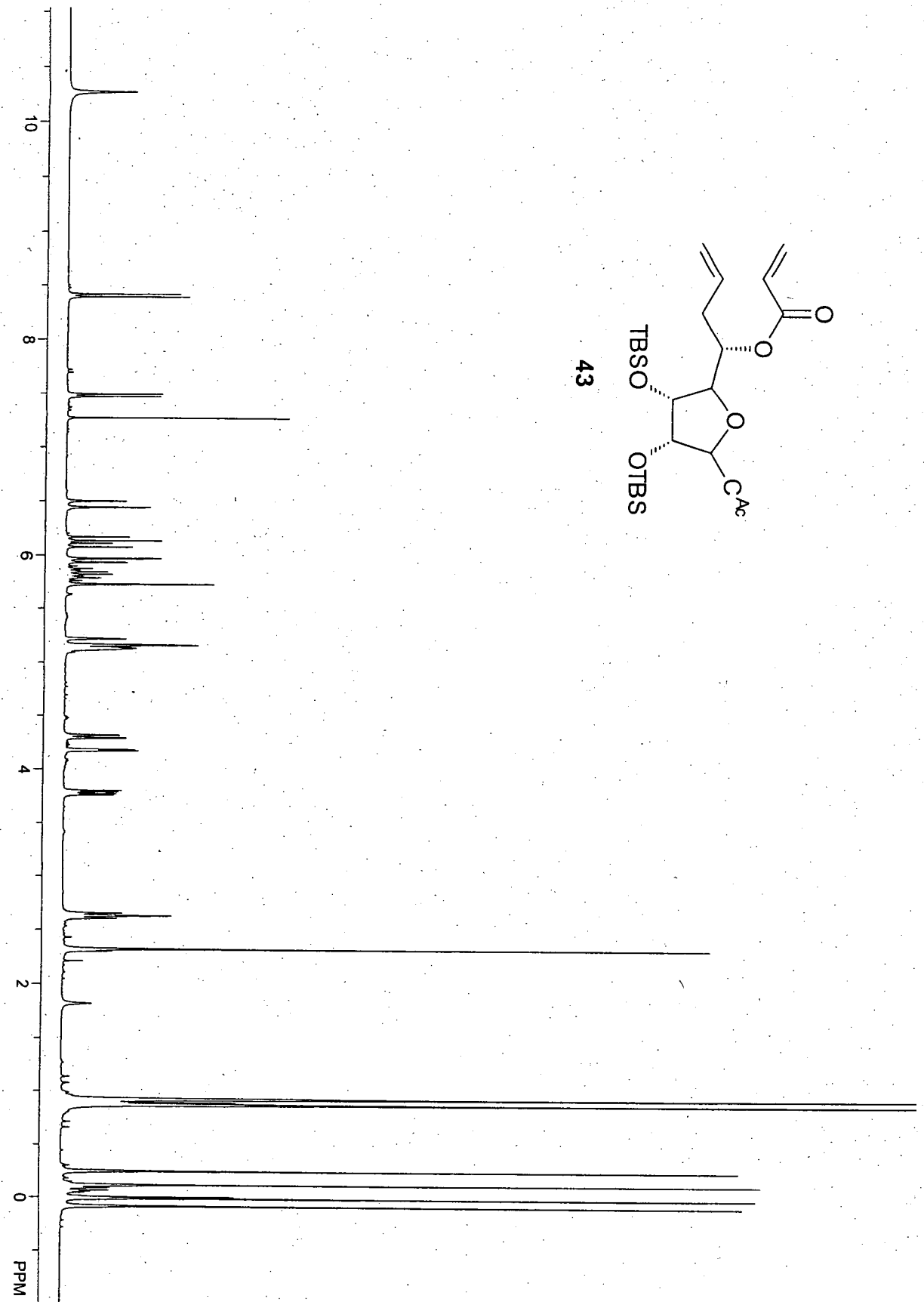

160
140
120
100
80
60
40
20
0
PPM
TBSO
OTBS
O
O
O
O
Ac
40



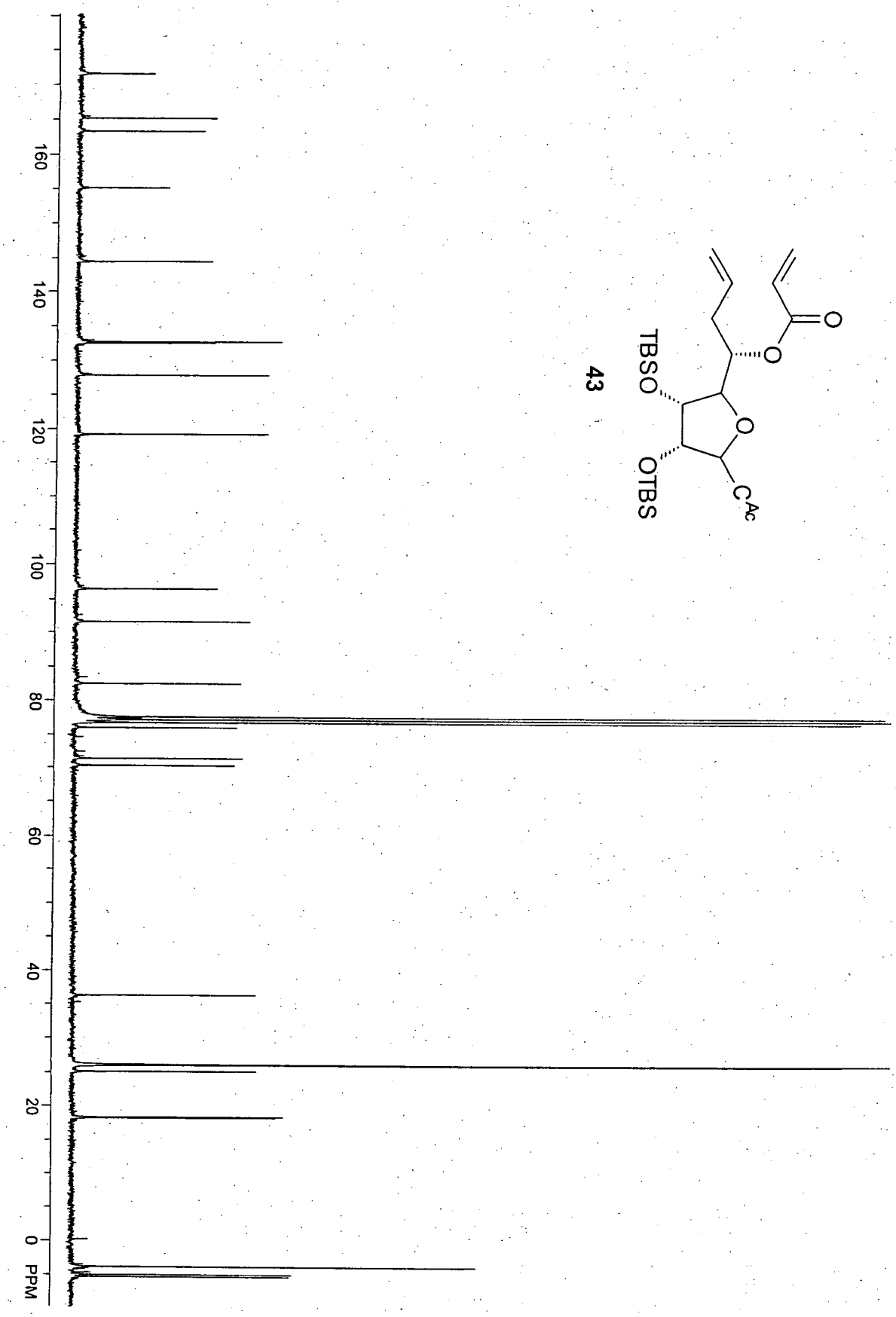
42



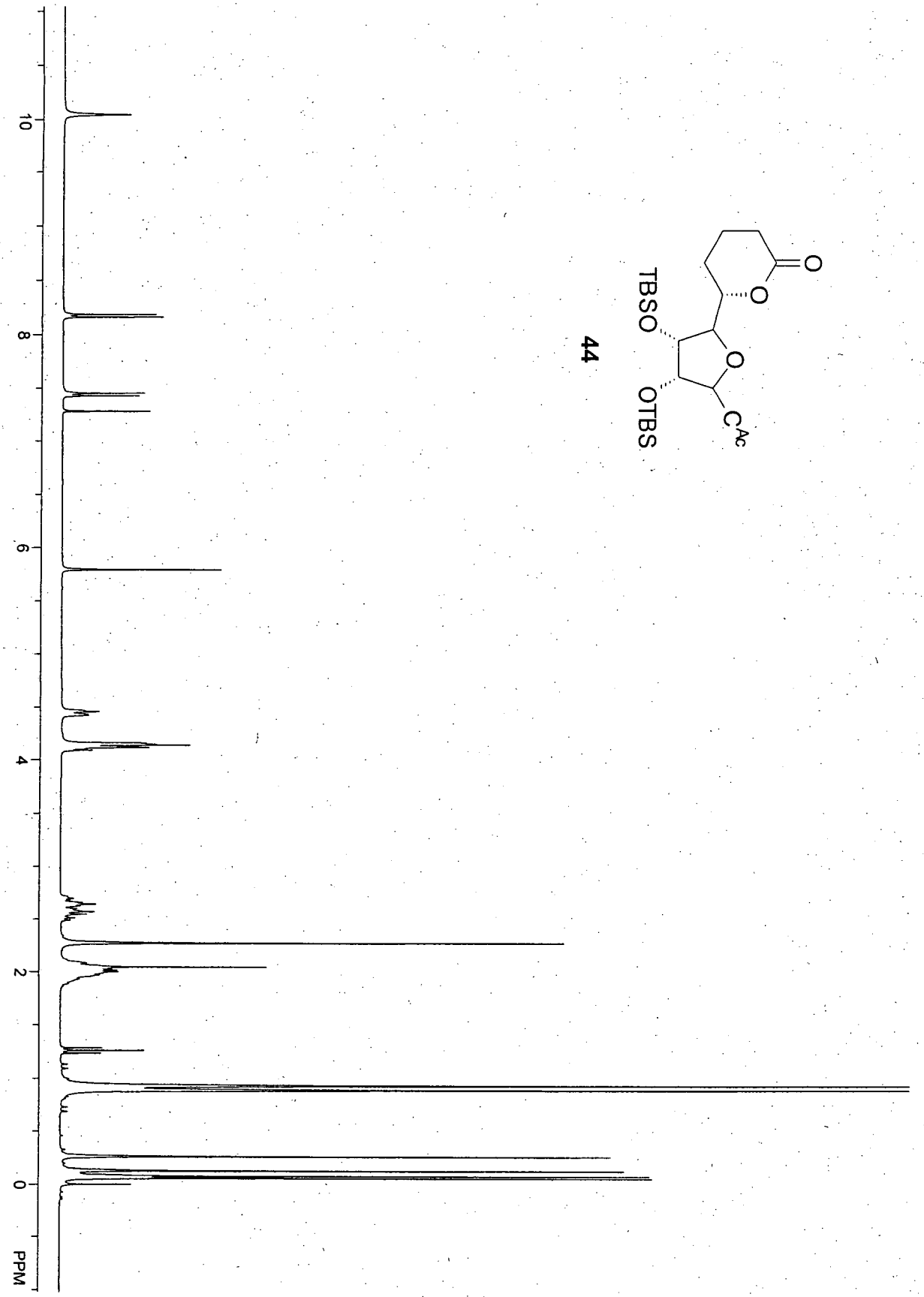
42



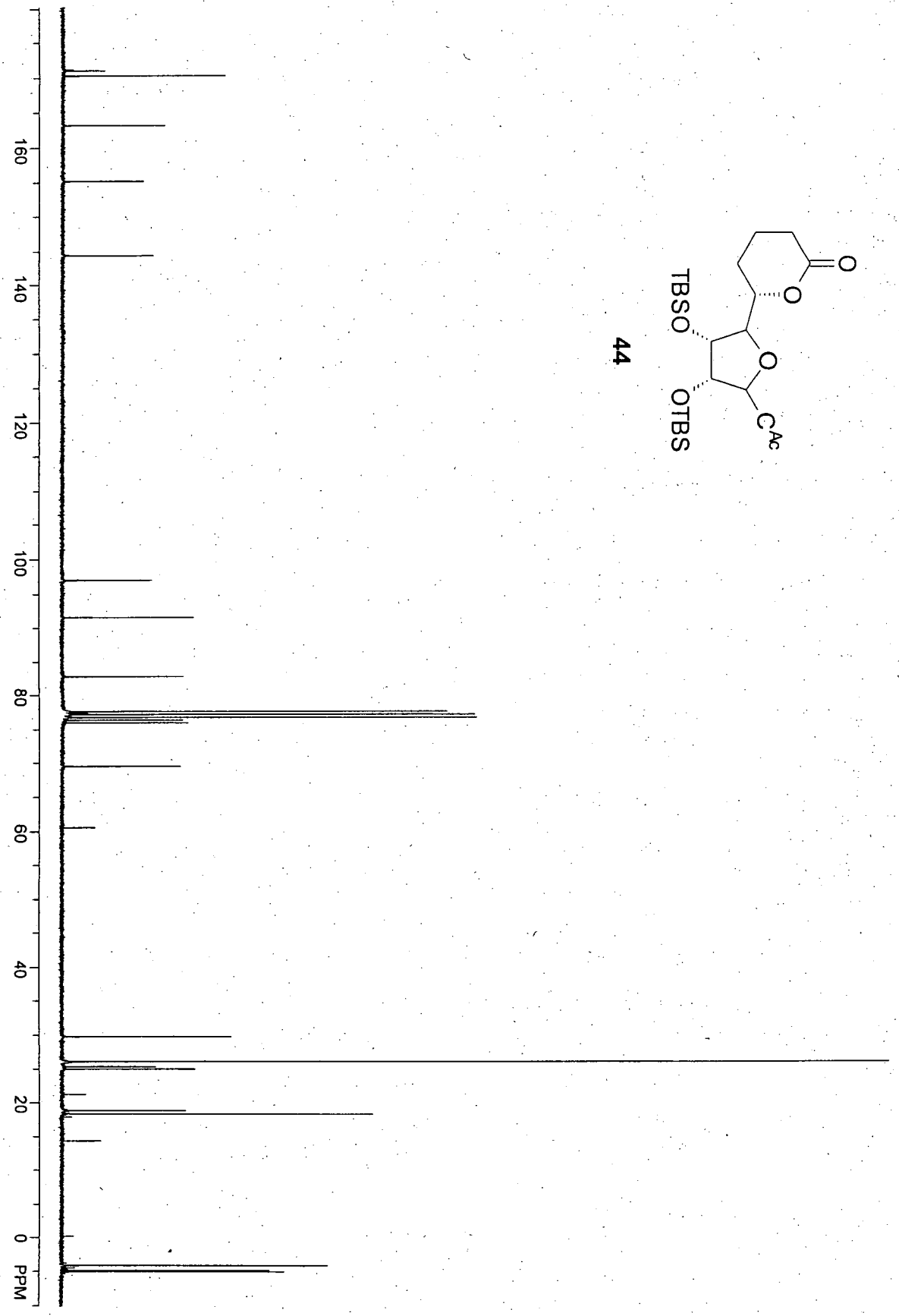
43



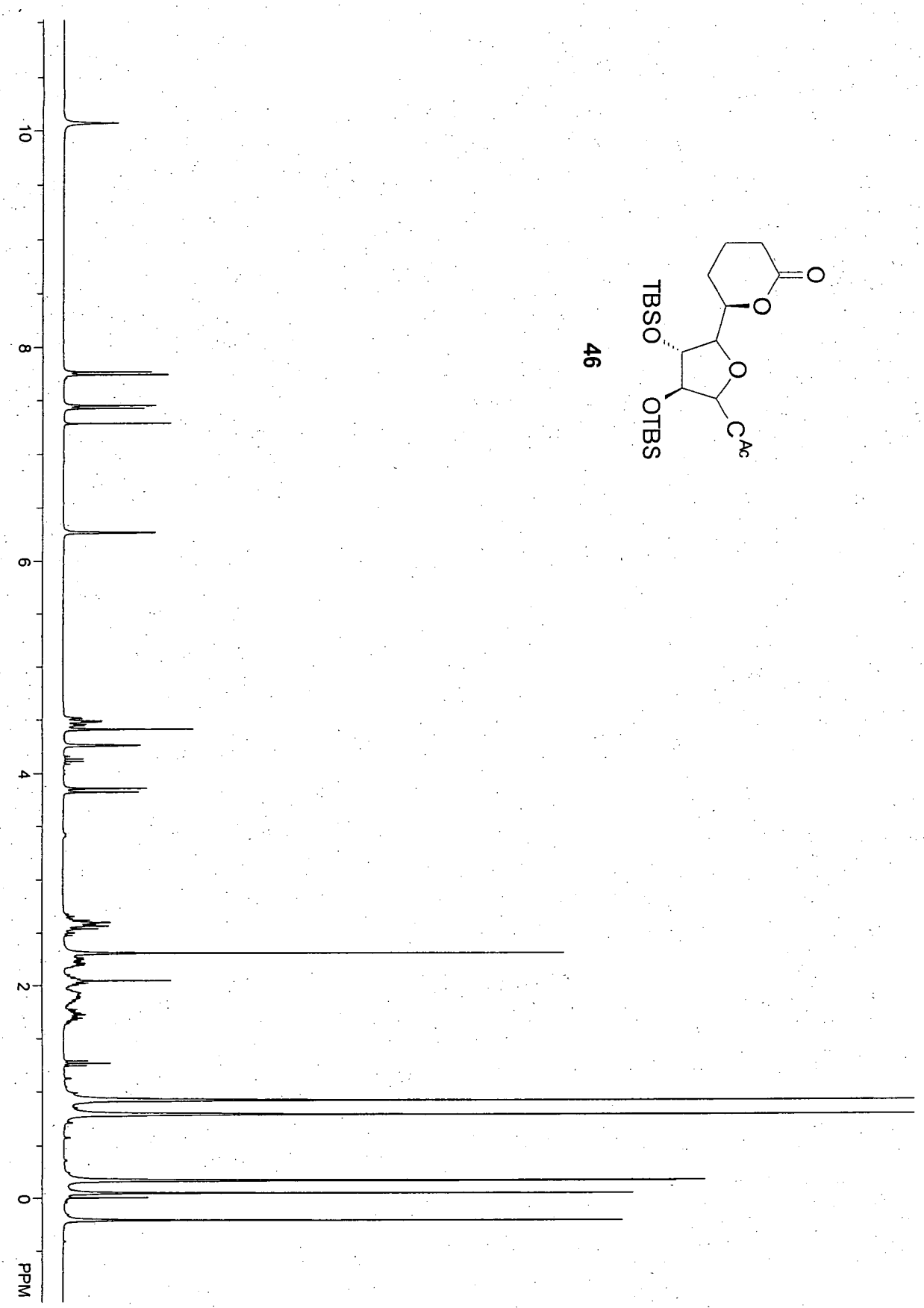
43



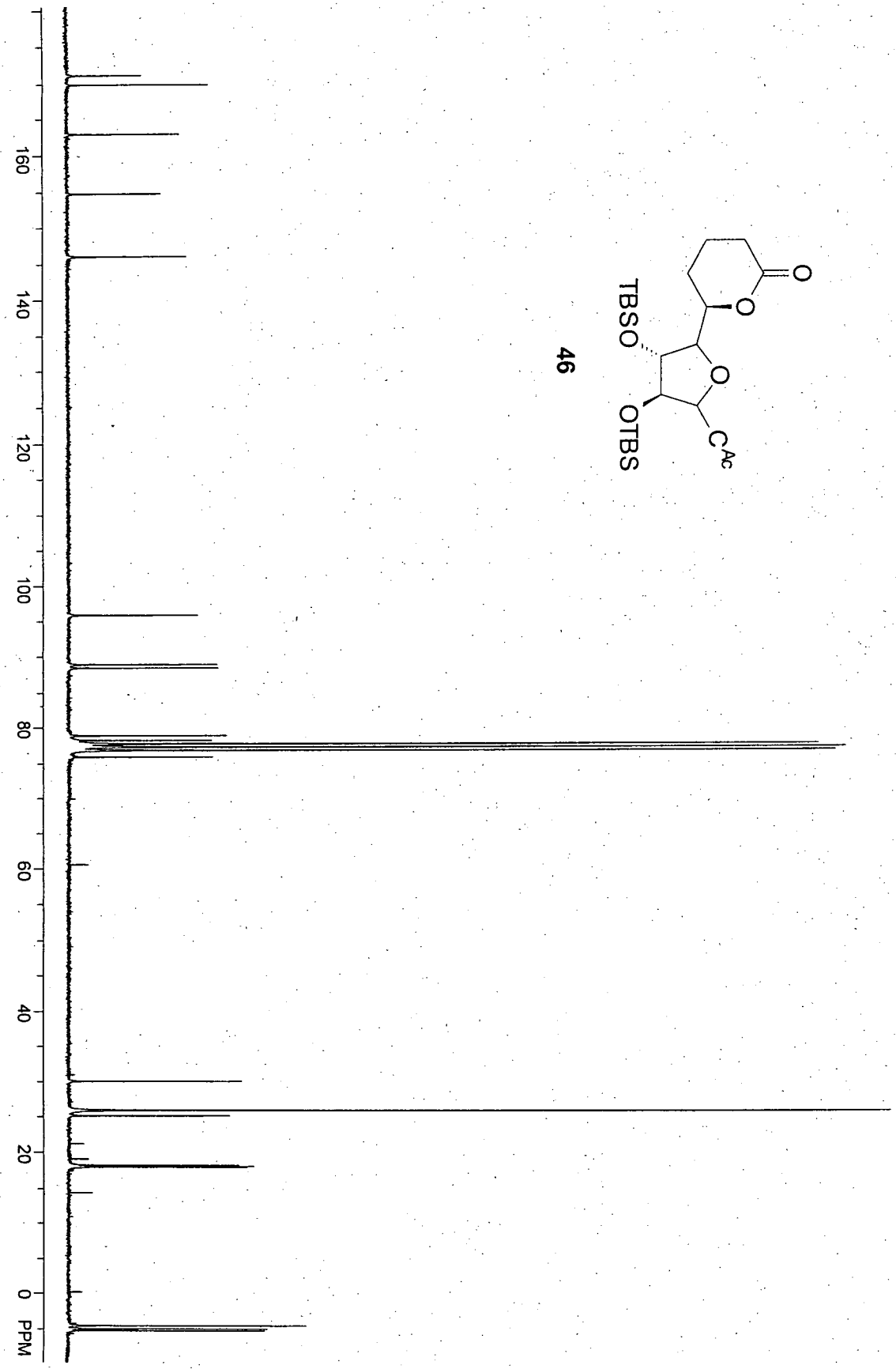
44



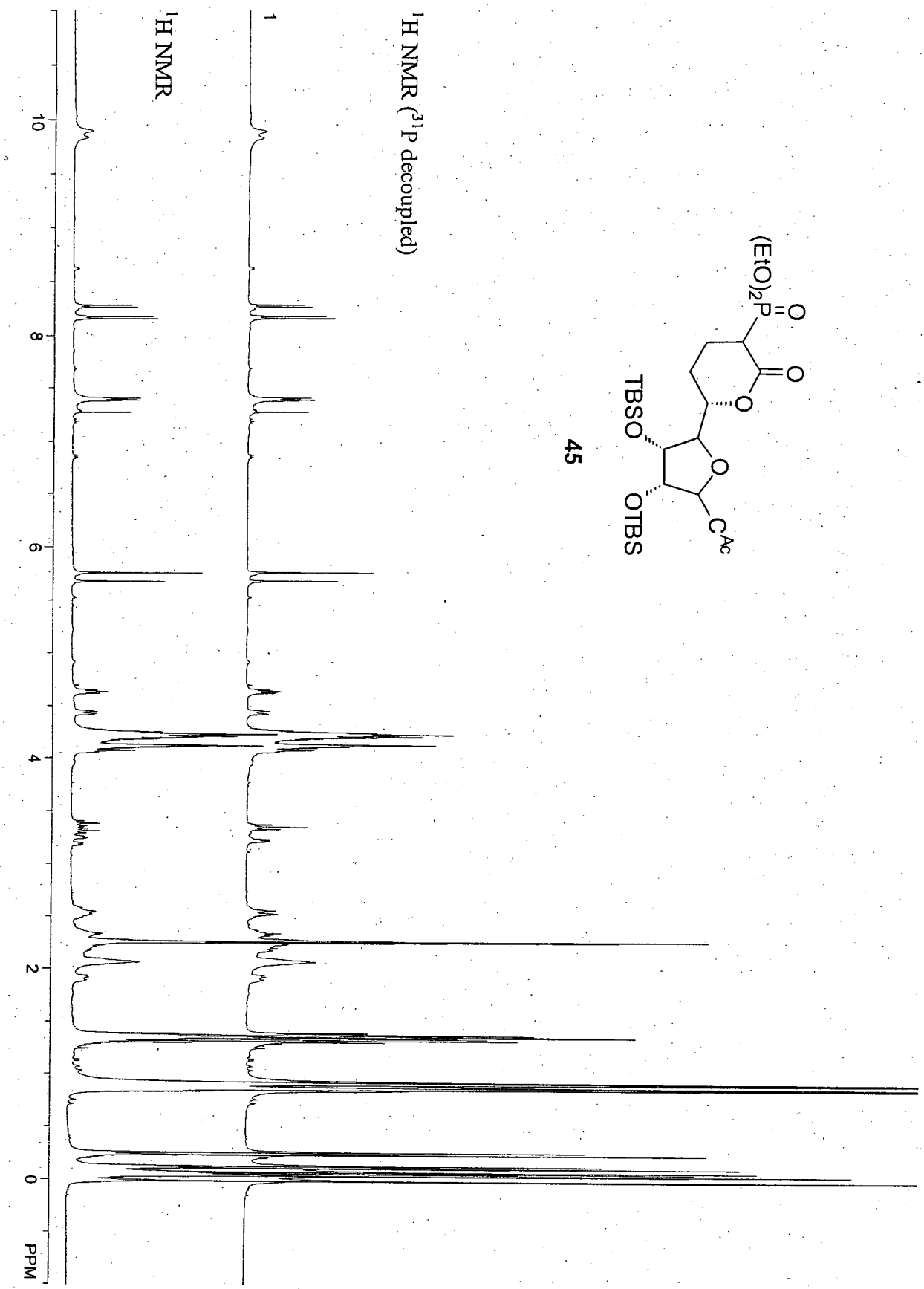
44

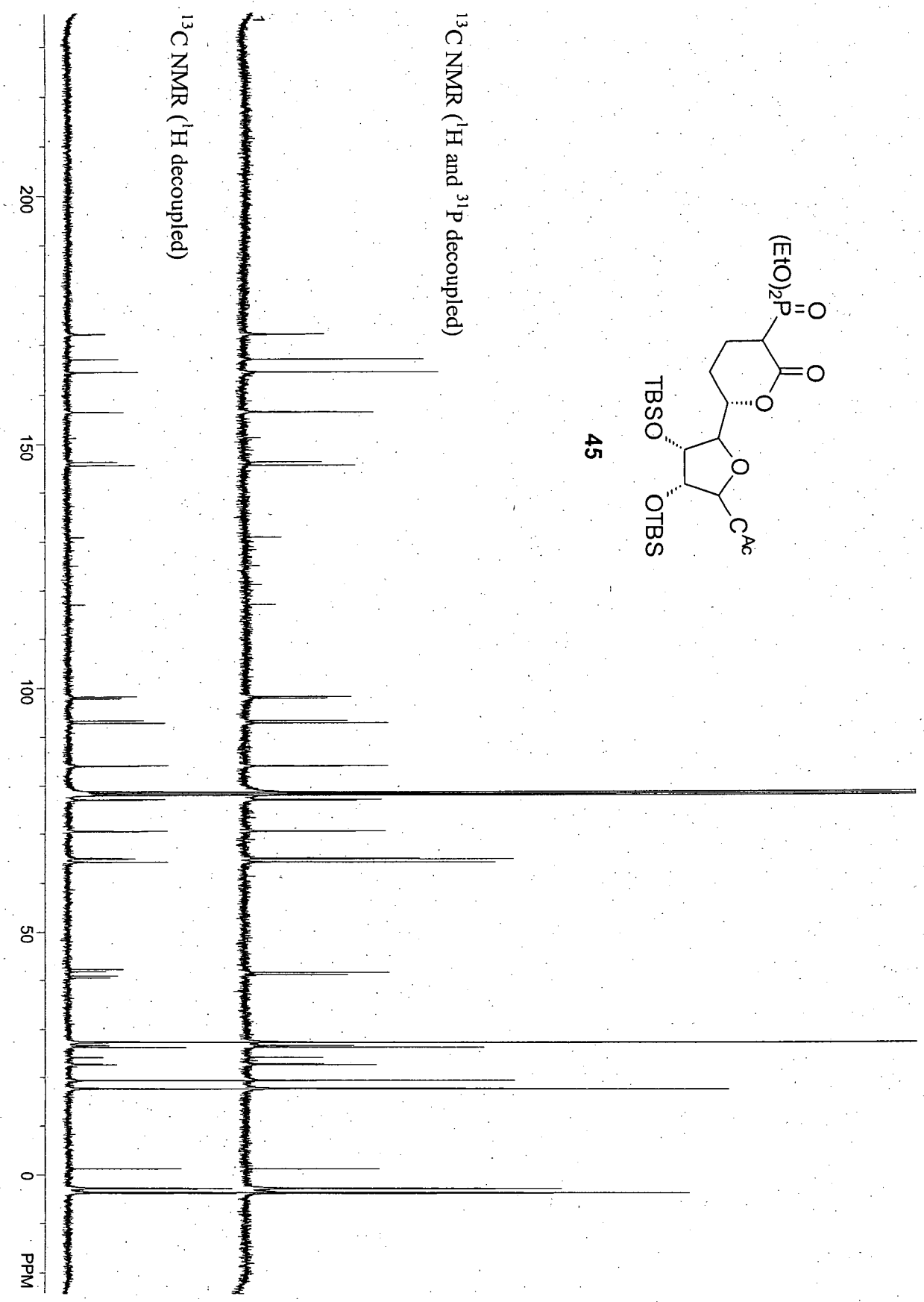


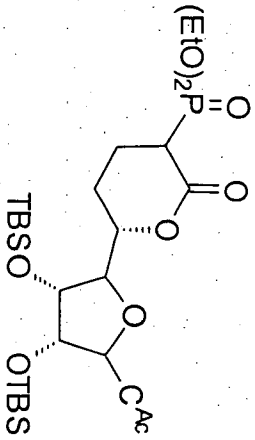
46



46

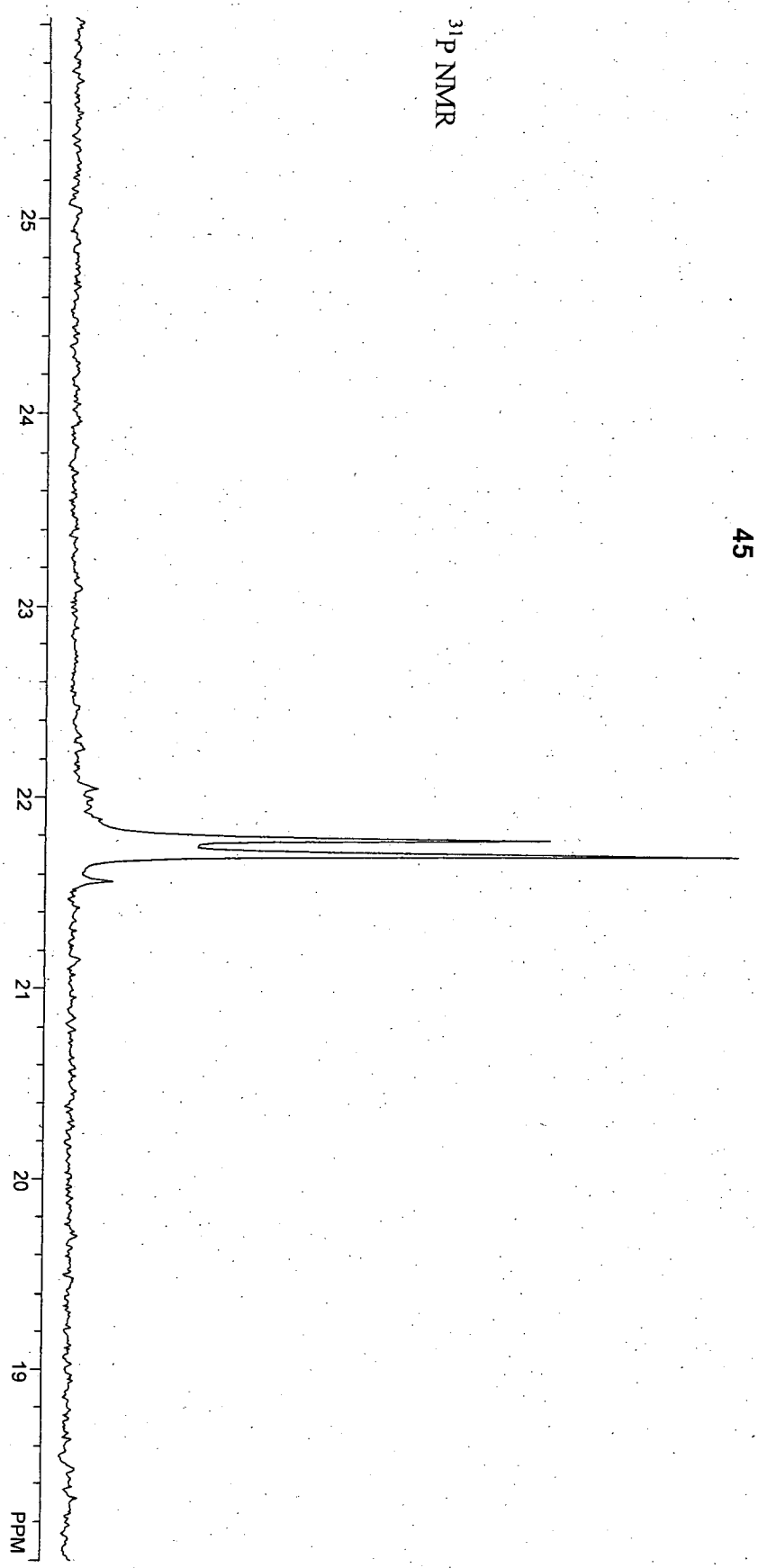


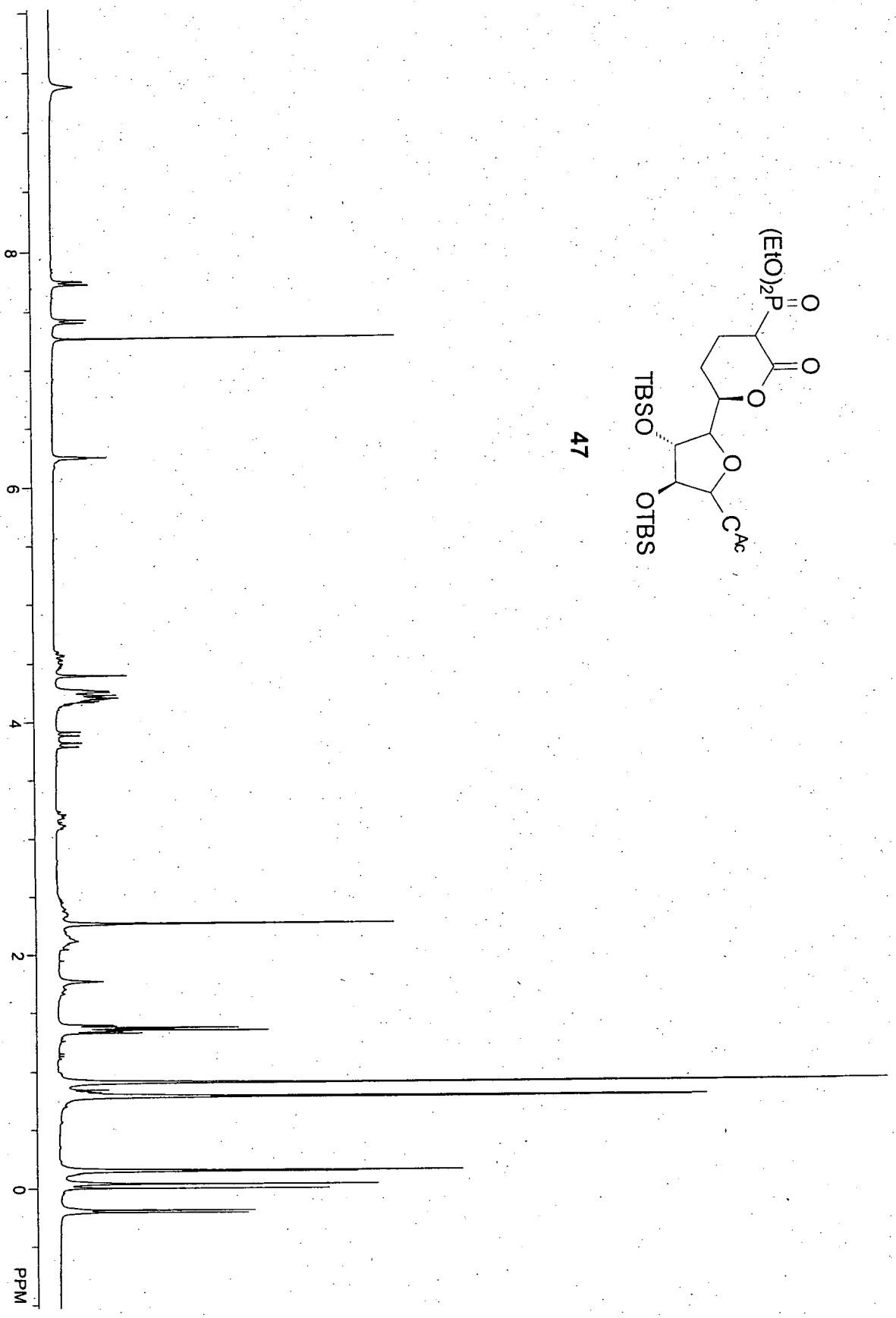

(EtO)2P
O
O
O
TBSO
OTBS
O
CAc
45
13C NMR (1H and 31P decoupled)
13C NMR (1H decoupled)
200
150
100
50
0
PPM



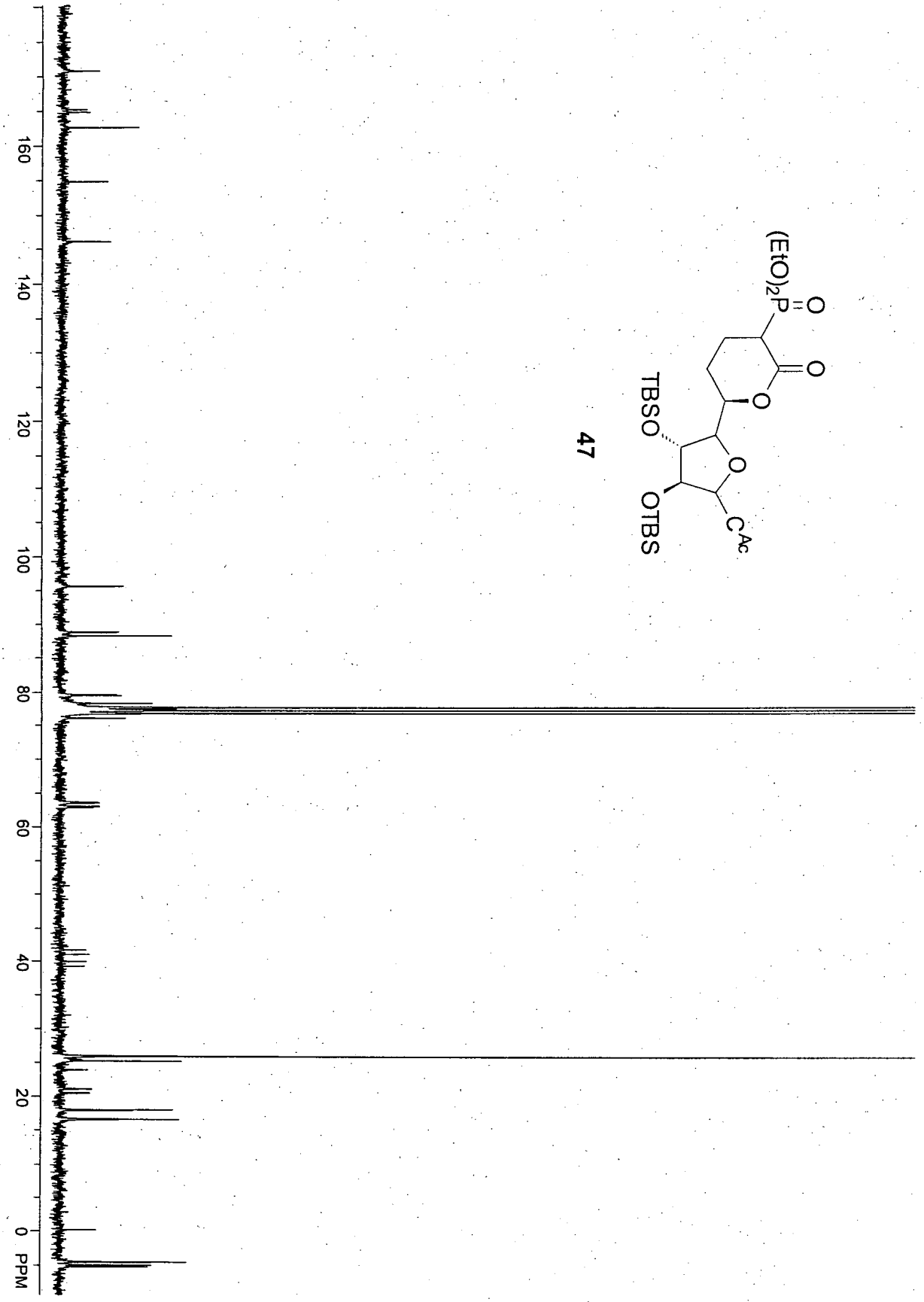
45

^{31}P NMR

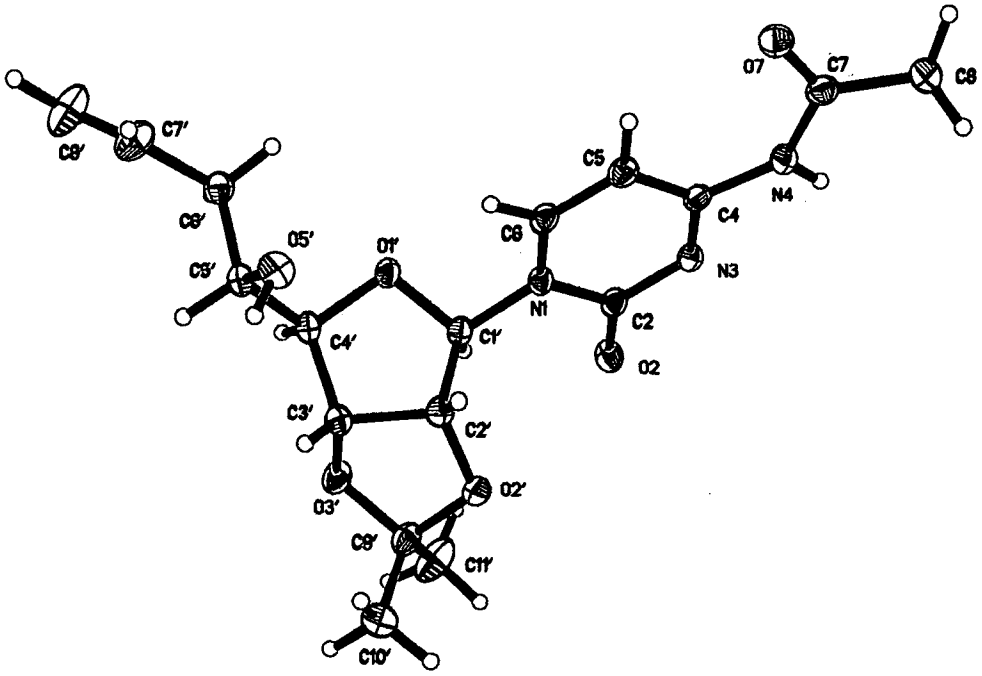




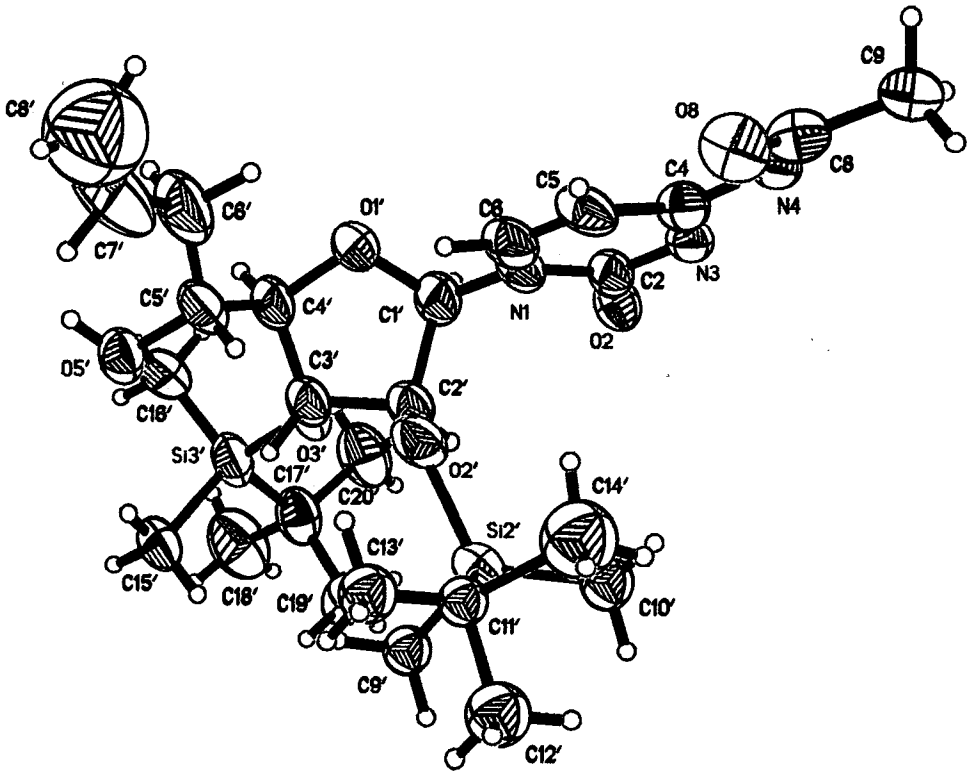
47



47



ORTEP Drawing of Compound 17.



ORTEP Drawing of Compound 26.