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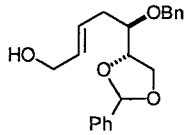
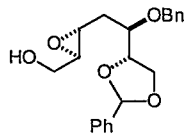
(5*R*)-5-Benzyloxy-5-[(2*S*,4*S*)- and (2*R*,4*S*)-2-phenyl-[1,3]dioxolan-4-yl]-pent-2(*E*)-en-1-ol (44).



To a stirred solution of (1*R*)-1-[(1*S*)-1,2-dihidroxy-ethyl]-5-(*tert*-butyl-diphenyl-silanyloxy)-pent-3(*E*)-enyl benzoate (5 g, 10 mmol) in dry CH_2Cl_2 (100 mL) were sequentially added benzaldehyde dimethyl acetal (2.25 mL, 15 mmol) and a catalytic amount of camphorsulfonic acid (232 mg) at rt. After 15 m TLC showed complete reaction. The reaction mixture was cooled at 0 °C, and NaH (390 mg, 13 mmol, 80% in mineral oil) was added. When evolution of hydrogen ceased, excess of MeOH (9 mL) was cautiously added. The reaction mixture was stirred until TLC showed complete reaction. Then the reaction mixture was poured into an ice-cooled 1:1 mixture of ether and 5% HCl aqueous solution. The organic layer was separated and the aqueous phase was extracted with ether (3 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. The resulting crude oil was dissolved in dry THF (100 mL) at 0 °C. Then, NaH (390 mg, 13 mmol, 80% in mineral oil), benzyl chloride (1.6 mL, 14 mmol), tetrabutylammonium iodide (369 mg, 1 mmol) were sequentially added. The reaction mixture was allowed to reach rt, and stirred overnight. After this period, TLC showed complete conversion. The reaction mixture was poured into an ice-cooled 1:1 mixture of ether and 5% HCl aqueous solution. The organic layer was separated and the aqueous phase was extracted with ether (2 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. The resulting crude oil was dissolved in dry THF (100 mL) and tetrabutylammonium fluoride (11 mL, 1.0 M solution in THF, 11 mmol)) was added. When TLC showed that the reaction was finished, the reaction mixture was diluted with ether (100 mL) and washed with saturated NaCl aqueous solution. The organic layer was dried over $MgSO_4$, filtered, concentrated and purified by silica gel column chromatography to afford **44** (2.48 g, 73% overall yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.43 (m, 2 H), 2.50 (m, 2 H), 3.65 (m, 1 H), 3.75 (m, 1 H), 4.00 (m, 1 H), 4.10 (br s, 6 H), 4.23 (m, 3 H), 4.59 (d, J = 11.4 Hz, 1 H), 4.65 (d, J = 11.5 Hz, 1 H), 4.67 (d, J = 11.4 Hz, 1 H), 4.71 (d, J = 11.5 Hz, 1 H), 5.75 (m, 2 H), 5.78(s, 1 H), 5.92 (s, 1 H), 7.32 (m, 4 H), 7.36 (m, 9 H), 7.47 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 33.7 (t), 34.0 (t), 63.3 (t), 63.4 (t), 67.5 (t), 67.7 (t), 72.3 (t), 72.5 (t), 77.4 (d), 77.6 (d), 78.8 (d), 79.0 (d), 103.8 (d), 104.2 (d), 126.5 (d), 126.7 (d), 127.3 (d), 127.4 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.3 (d), 129.4 (d), 132.4 (d), 137.4 (s), 138.0 (s), 138.2 (s); IR ($CHCl_3$) (cm^{-1}) 3450, 3030, 3013, 2927, 2877, 1211, 1092, 1071; MS *m/z* (relative intensity) 340 $(M)^+$ (1), 179 (12), 149 (29), 107 (19), 105 (31), 92 (36), 91 (100). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.08; H, 7.26.

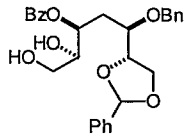
Preparation of (2*S*,3*R*)-{3-[(2*R*)-2-Benzyloxy-2-[(2*S*,4*S*)- and (2*R*,4*S*)-2-phenyl-[1,3]dioxolan-4-yl]-ethyl]-oxiranyl}-methanol (45).



The general asymmetric epoxidation procedure using (*S*,*S*)-(−)-DET as chiral auxiliary was used over **44** on a 2 g (5.88 mmol) scale for 4 h, yielding **45** (1.88 g, 90% yield) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 4 H), 2.98 (m, 2 H), 3.15 (m, 2 H), 3.60 (m, 2 H), 3.78 (m, 1 H), 3.85 (m, 2 H), 3.96 (m, 1 H), 4.09 (m, 3 H), 4.28 (m, 3 H), 4.65 (d, J = 11.4 Hz, 1 H), 4.69 (d, J = 11.4 Hz, 1 H), 4.73 (s, 2 H), 5.79 (s, 1 H), 5.93 (s, 1 H), 7.33 (m, 13 H), 7.37 (m, 9 H), 7.45 (m, 3 H), 8.05 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 33.5 (t), 33.8 (t), 52.6 (d), 58.8 (d), 58.9 (d), 61.4 (t), 61.5 (t), 67.5 (t), 67.6 (t), 72.8 (t), 73.1 (t), 77.2 (d), 77.3 (d), 77.7 (d), 77.9 (d), 103.9 (d), 104.2 (d), 126.3 (d), 126.6 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.2 (d), 129.4 (d), 137.0 (s), 137.9 (s); IR ($CHCl_3$) (cm^{-1}) 3500, 3014, 2943, 2923, 2878, 1732, 1248, 1092; MS *m/z* (relative intensity) 356 $(M)^+$ (1),

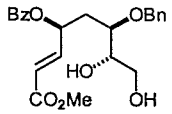
249 (17), 189 (22), 162 (41), 149 (100), 117 (33), 105 (100), 91 (100). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.55; H, 7.10.

Preparation of (1*S*,2*R*)-1-[(2*R*)-2-Benzyloxy-2-[(2*S*,4*S*)- and (2*R*,4*S*)-2-phenyl-[1,3]dioxolan-4-yl]-ethyl]-2,3-dihydroxy-propyl Benzoate (45a).



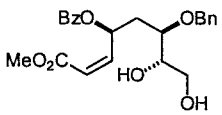
The general procedure for epoxide opening was applied to **45** on a 600 mg (1.68 mmol) scale for 12 h, yielding **45a** (676 mg, 84% yield) as an oil: ^{1}H NMR ($CDCl_3$) δ 2.24 (m, 2 H), 2.30 (m, 2 H), 3.4 (br s, 4 H), 3.57 (m, 2 H), 3.65 (m, 2 H), 3.75 (m, 2 H), 3.90 (m, 2 H), 4.06 (m, 4 H), 4.24 (m, 2 H), 4.65 (s, 2 H), 4.70 (s, 2 H), 5.29 (m, 2 H), 5.70 (s, 1 H), 5.89 (s, 1 H) , 7.25 (m, 10 H), 7.43 (m, 8 H), 7.57 (m, 2 H), 8.04 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 32.1 (t), 32.2 (t), 62.6 (t), 67.5 (t), 67.7 (t), 71.6 (d), 71.7 (d), 72.3 (t), 72.8 (d), 72.9 (d), 75.9 (d), 76.2 (d), 78.2 (d), 78.4 (d), 104.1 (d), 104.2 (d), 126.4 (d), 126.6 (d), 126.7 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 128.6 (d), 129.2 (d), 129.4 (d), 129.5 (d), 129.6 (d), 129.7 (d), 129.8 (d), 130.0 (s), 133.3 (d), 133.4 (d), 136.9 (s), 137.5 (s), 137.6 (s), 137.8 (s), 166.7 (s), 169.6 (s); IR ($CHCl_3$) (cm^{-1}) 3440, 3014, 2957, 2930, 1715, 1273, 1070; MS *m/z* (relative intensity) 478 $(M)^+$ (1), 221 (15), 148 (17), 105 (90), 91 (100), 81 (20), 77 (53). Anal. Calcd for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 69.86; H, 6.69.

Preparation of (1*S*)-1-[(2*R*,3*S*)-2-Benzyloxy-3,4-dihydroxy-butyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (45b).



The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*E*)-α,β-unsaturated esters was applied to diol **45a** on a 250 mg (0.52 mmol) scale, yielding the expected ester as an oil. The crude oil was dissolved in MeOH (5 mL) and a catalytic amount of CSA was added at rt. After 1 h TLC showed complete conversion. The solvent was evaporated and the crude was purified by silica gel column chromatography to yield the free diol **45b** (158 mg, 73% yield) as a solid: mp 90-92 °C; $[\alpha]^{25}_D$ = +31.7 (*c* 0.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.09 (m, 1 H), 2.23 (m, 1 H), 3.66 (ddd, *J* = 6.6, 5.0, 5.0 Hz, 1 H), 3.71 (s, 3 H), 3.72 (m, 2 H), 3.86 (m, 1 H), 4.58 (s, 2 H), 5.85 (m, 1 H), 6 (dd, *J* = 15.8, 1.2 Hz, 1 H), 6.98 (dd, *J* = 15.8, 5.3 Hz, 1 H), 7.31 (m, 5 H), 7.46 (m, 2 H), 7.59 (m, 1 H), 8.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.9 (t), 51.7 (q), 63.2 (t), 70.5 (d), 72.1 (t), 72.5 (d), 76.6 (d), 121.3 (d), 127.9 (d), 128.0 (d), 128.4 (d), 128.5 (d), 129.6 (d), 129.7 (d), 133.4 (d), 137.4 (s), 145.2 (d), 165.5 (s), 166.3 (s); IR ($CHCl_3$) (cm^{-1}) 3524, 3502, 3019, 2952, 2931, 1719, 1270; MS *m/z* (relative intensity) 293 $(M - 121)^+$ (2), 231 (19), 141 (12), 113 (17), 105 (95), 92 (40), 91 (100), 77 (73). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.63; H, 6.68.

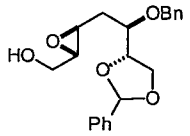
Preparation of (1*S*)-1-[(2*R*,3*S*)-2-Benzyloxy-3,4-dihydroxy-butyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (45c).



The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*Z*)-α,β-unsaturated esters was applied to diol **45a** on a 340 mg (0.71 mmol) scale, yielding the expected ester as an oil. The crude oil was dissolved in MeOH (7 mL) and a catalytic amount of CSA was added at rt. After 1 h TLC showed complete conversion. The solvent was evaporated and the crude was purified by silica gel column chromatography to yield the free diol **45c** (212 mg, 72% yield) as a solid: mp 82-84 °C; $[\alpha]^{25}_D$ = +16.27 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.13 (m, 1 H), 2.32 (m, 1 H), 3.75 (s, 3 H), 3.77 (m, 1 H), 3.77 (m, 2 H), 3.92 (m, 1 H), 4.56 (d, *J* = 11.4 Hz, 1 H), 4.69 (d, *J*

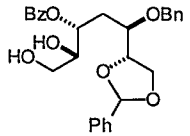
= 11.4 Hz, 1 H), 5.89 (dd, J = 11.6, 1.3 Hz, 1 H), 6.26 (dd, J = 11.6, 7.5 Hz, 1 H), 6.56 (m, 1 H), 7.27 (m, 5 H), 7.43 (m, 2 H), 7.57 (m, 1 H), 8.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.5 (t), 51.7 (q), 63.3 (t), 70.4 (d), 72.0 (t), 73.2 (d), 77.6 (d), 119.9 (d), 125.5 (s), 127.8 (d), 127.9 (d), 128.0 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.6 (d), 129.7 (d), 129.8 (d), 133.2 (d), 137.8 (s), 148.1 (d), 165.9 (d), 166.1 (s); IR ($CHCl_3$) (cm^{-1}) 3500, 3023, 3015, 1719, 1273, 1112, 1070; MS *m/z* (relative intensity) 307 (M – 107)$^+$ (4), 306 (11), 213 (27), 181 (17), 151 (15), 119 (17), 109 (20), 94 (23), 85 (71), 83 (100). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.47; H, 6.38.

Preparation of (2*R*,3*S*)-{3-[(2*R*)-2-Benzyloxy-2-[(2*S*,4*S*)- and (2*R*,4*S*)-2-phenyl-[1,3]dioxolan-4-yl-ethyl]-oxiranyl}-methanol (46).



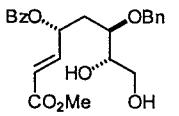
The general asymmetric epoxidation procedure using as chiral auxiliary (*R,R*)-(+)-DET was used over **44** on a 1 g (2.94 mmol) scale for 4 h, yielding **46** (837 mg, 80% yield) as an oil: ^{1}H NMR ($CDCl_3$) δ stereoisomers mixture; 2.00 (m, 2 H), 2.92 (m, 1 H), 3.13 (m, 1 H), 3.52 (m, 1 H), 3.75 (m, 2 H), 4.16 (m, 2 H), 4.27 (m, 1 H), 4.59 (d, J = 11.4 Hz, 1 H), 4.68 (d, J = 11.4 Hz, 1 H), 5.80 (s, 1 H), 7.35 (m, 8 H), 7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.5 (t), 52.8 (d), 58.4 (d), 61.6 (t), 68.0 (t), 72.2 (t), 77.5 (d), 78.1 (d), 104.3 (d), 126.3 (d), 127.9 (d), 128.0 (d), 128.2 (d), 129.4 (d), 137.2 (s), 137.8 (s); IR ($CHCl_3$) (cm^{-1}) 3500, 3014, 2942, 2925, 2878, 1732, 1248, 1092; MS m/z (relative intensity) 356 (M)$^+$ (1), 325 (1), 249 (8), 189 (9), 162 (14), 149 (81), 91 (100), 77 (56). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.60, H, 7.10.

Preparation of (1*R*,2*S*)-1-[(2*R*)-2-Benzyloxy-2-[(2*S*,4*S*)- and (2*R*,4*S*)-2-phenyl-[1,3] dioxolan-4-yl)-ethyl]-2,3-dihydroxy-propyl Benzoate (46a).



The general procedure for epoxide opening was applied to **46** on a 700 mg (1.97 mmol) scale, yielding **46a** (800 mg, 85% yield) as an oil: ^{1}H NMR ($CDCl_3$) δ 2.16 (m, 2 H), 2.80 (br s, 2 H), 3.56 (m, 1 H), 3.65 (m, 1 H), 3.73 (m, 1 H), 3.84 (m, 1 H), 4.12 (m, 2 H), 4.31 (m, 1 H), 4.50 (d, J = 10.8 Hz, 1 H), 4.64 (d, J = 10.8 Hz, 1 H), 5.38 (m, 1 H), 5.78 (s, 1 H), 7.27 (m, 4 H), 7.35 (m, 4 H), 7.47 (m, 4 H), 7.59 (m, 1 H), 8.03 (d, J = 7.44 Hz, 2 H); ^{13}C-NMR ($CDCl_3$) δ: 33.1 (t), 62.5 (t), 66.9 (t), 71.6 (d), 73.3 (d), 73.6 (t), 75.8 (d), 78.9 (d), 104.1 (d), 126.6 (d), 127.8 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.5 (d), 129.4 (d), 129.5 (d), 129.8 (d), 133.4 (d), 137.0 (s), 137.8 (s), 166.8 (s); IR ($CHCl_3$) (cm^{-1}) 3440, 3026, 3014, 2957, 2930, 1715, 1273, 1070; MS m/z (relative intensity) 478 (M)$^+$ (1), 221 (27), 149 (10), 105 (100), 91 (51), 81 (13), 77 (48). Anal. Calcd for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 69.90, H, 6.70.

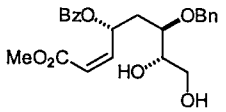
Preparation of (1*R*)-1-[(2*R*,3*S*)-2-Benzyloxy-3,4-dihydroxy-butyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (46b).



The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*E*)-α,β-unsaturated esters was applied to diol **46a** on a 300 mg (0.63 mmol) scale, yielding the expected ester as an oil. The crude was dissolved in MeOH (5 mL) and a catalytic amount of CSA was added at rt. After 1 h TLC showed complete conversion. The solvent was evaporated and the crude was purified by silica gel column chromatography to yield the free diol **46b** (196 mg, 75% yield) as a solid: mp 90-92°C; $[\alpha]^{25}_D$ = +1.6 (*c* 1.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.04 (m, 2 H), 3.69 (m, 2 H), 3.72 (s, 3 H), 3.88 (m, 1 H), 4.49 (d, J = 10.9 Hz, 1 H), 4.57 (d, J = 10.9 Hz, 1 H), 4.60 (m, 1 H),

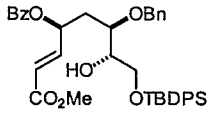
5.90 (m, 1 H), 6.03 (dd, J = 15.8, 1.52 Hz, 1 H), 6.99 (dd, J = 15.8, 5.1 Hz, 1 H), 7.29 (m, 5 H), 7.45 (m, 2 H), 7.59 (m, 1 H), 8.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.0 (t), 51.7 (q), 63.2 (t), 70.0 (d), 70.6 (d), 72.3 (d), 73.1 (t), 121.3 (d), 121.7 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.6 (d), 133.4 (d), 137.4 (s), 145.8 (d), 165.4 (s), 166.3 (s); IR ($CHCl_3$) (cm^{-1}) 3524, 3502, 3019, 2952, 2931, 1719, 1270; MS m/z (relative intensity) 415 $(M)^+$ (1), 307 (2), 292 (2), 267 (4), 231 (3), 193 (5), 186 (9), 168 (74), 105 (100), 91 (100). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.62, H, 6.68.

Preparation of (1*R*)-1-[(2*R*,3*S*)-2-Benzyloxy-3,4-dihydroxy-butyl)-3-methoxycarbonyl-(*Z*)-allyl Benzoate (46c).



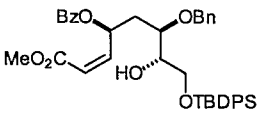
The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*Z*)-α,β-unsaturated esters was applied to diol **46a** on a 320 mg (0.7 mmol) scale, yielding the expected ester as an oil. The crude was dissolved in MeOH (7 mL) and a catalytic amount of CSA was added at rt. After 1 h TLC showed complete conversion. The solvent was evaporated and the crude was purified by silica gel column chromatography to yield the free diol **46c** (214 mg, 74% yield) as a solid: mp 80-82°C; $[\alpha]^{25}_D$ = –42.5 (*c* 1.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.11 (m, 1 H), 2.21 (m, 1 H), 2.32 (s, 1 H), 3.18 (s, 1 H), 3.71 (s, 3 H), 3.72 (m, 3 H), 3.94 (m, 1 H), 4.54 (d, J = 11.3 Hz, 1 H), 4.63 (d, J = 11.3 Hz, 1 H), 5.88 (dd, J = 11.6, 1.3 Hz, 1 H), 6.23 (dd, J = 11.6, 7.7 Hz, 1 H), 6.67 (m, 1 H), 7.25 (m, 5 H), 7.40 (m, 2 H), 7.55 (m, 1 H), 7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.2 (t), 51.7 (q), 63.5 (t), 69.4 (d), 72.3 (d), 72.4 (t), 76.9 (d), 120.0 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.5 (d), 129.7 (d), 129.9 (s), 133.1 (d), 137.7 (s), 148.0 (d), 165.7 (s), 166.1 (s); IR ($CHCl_3$) (cm^{-1}) 3500, 3023, 3015, 1719, 1273, 1112, 1070; MS m/z (relative intensity) 415 $(M)^+$ (1), 353 (3), 292 (4), 231 (45), 168 (10), 154 (14), 113 (28), 105 (100), 91 (100). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.50, H, 6.40.

Preparation of (1*S*)-1-[(2*R*,3*S*)-2-Benzyloxy-4-(*tert*-butyl-diphenyl-silanyloxy)-3-hydroxy-butyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (47).



The general silyl protection method was applied to **45b** on a 130 mg (0.31 mmol) scale to afford **47** (180 mg, 89% yield) as an oil: $[\alpha]^{25}_D$ = +31.3 (*c* 1.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 2.09 (m, 1 H), 2.19 (m, 1 H), 3.67 (m, 1 H), 3.70 (s, 3 H), 3.77 (m, 2 H), 3.83 (m, 1 H), 4.49 (s, 2 H), 5.87 (m, 1 H), 5.96 (dd, J = 15.7, 1.4 Hz, 1 H), 6.95 (dd, J = 15.7, 5.4 Hz, 1 H), 7.19 (m, 1 H), 7.26 (m, 2 H), 7.35 (m, 3 H), 7.44 (m, 7 H), 7.56 (m, 1 H), 7.62 (m, 4 H), 8.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.1 (s), 26.8 (q), 35.0 (t), 51.6 (q), 64.3 (t), 70.8 (d), 71.8 (t), 73 (d), 75.5 (d), 121.1 (d), 127.7 (d). 127.8 (d), 127.9 (d), 128.4 (d), 129.6 (d), 129.7 (d), 129.8 (d), 129.9 (d), 132.9 (s), 133.2 (d), 135.5 (d), 137.7 (s), 145.6 (d), 165.3 (s), 166.3 (s); IR ($CHCl_3$) (cm^{-1}) 3660, 3028, 3013, 2953, 2932, 2859, 1719, 1270, 1112; MS *m/z* (relative intensity) 474 $(M - 178)^+$ (1), 383 (1), 365 (2), 193 (16), 163 (9), 135 (5), 105 (29), 91 (100), 77 (11). Anal. Calcd for $C_{39}H_{44}O_7Si$: C, 71.75; H, 6.79. Found: C, 71.55; H, 6.91.

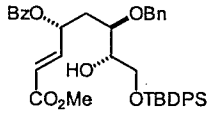
Preparation of (1*S*)-1-[(2*R*,3*S*)-2-Benzyloxy-4-(*tert*-butyl-diphenyl-silanyloxy)-3-hydroxy-butyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (48).



The general silyl protection method was applied to **45c** on a 300 mg (0.72 mmol) scale to afford **48** (415 mg, 88% yield) as an oil: $[\alpha]^{25}_D$ = +31.3 (*c* 2.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 9 H),

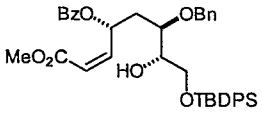
2.24 (m, 1 H), 2.29 (m, 1 H), 3.73 (s, 3 H), 3.87 (m, 3 H), 3.94 (m, 1 H), 4.54 (d, J = 11.2 Hz, 1 H), 4.69 (d, J = 11.2 Hz, 1 H), 5.89 (d, J = 11.6 Hz, 1 H), 6.26 (dd, J = 11.6, 7.9 Hz, 1 H), 6.71 (m, 1 H), 7.25 (m, 5 H), 7.37 (m, 3 H), 7.42 (m, 5 H), 7.57 (m, 1 H), 7.67 (m, 4 H), 8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.2 (s), 26.8 (q), 34.9 (t), 51.5 (q), 64.5 (t), 70.3 (d), 71.9 (t), 73.4 (d), 76.3 (d), 120 (d), 127.5 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.6 (d), 129.7 (d), 129.8 (d), 130.2 (s), 133.0 (d), 133.1 (d), 133.2 (d), 135.6 (d), 138.2 (s), 147.8 (d), 165.8 (s); IR ($CHCl_3$) (cm^{-1}) 3560, 3030, 3013, 2932, 2859, 1719, 1273, 1112; MS *m/z* (relative intensity) 474 (M – 178)$^+$ (2), 384 (2), 241 (3), 199 (9), 193 (11), 163 (11), 105 (36), 91 (100). Anal. Calcd for $C_{39}H_{44}O_7Si$: C, 71.75; H, 6.79. Found: C, 71.86; H, 6.86.

Preparation of (1*R*)-1-[(2*R*,3*S*)-2-Benzyloxy-4-(*tert*-butyl-diphenyl-silanyloxy)-3-hydroxy-butyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (49).



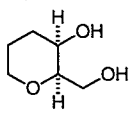
The general silyl protection method was applied to **46b** on a 150 mg (0.36 mmol) scale to afford **49** (214 mg, 89% yield) as an oil: $[\alpha]^{25}_D$ = +11.13 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.99 (m, 1 H), 2.05 (m, 1 H), 2.44 (br s, 1 H), 3.74 (s, 3 H), 3.81 (m, 3 H), 3.88 (m, 1 H), 4.40 (d, J = 10.8 Hz, 1 H), 4.46 (d, J = 10.8 Hz, 1 H), 5.91 (m, 1 H), 6.01 (d, J = 15.8 Hz, 1 H), 6.97 (dd, J = 15.8, 5.0 Hz, 1 H), 7.21 (m, 6 H), 7.38 (m, 7 H), 7.56 (m, 1 H), 7.64 (m, 4 H), 8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.2 (s), 26.8 (q), 34.8 (t), 51.6 (q), 64.2 (t), 70.0 (d), 72.6 (d), 72.9 (t), 75.3 (d), 120.9 (d), 127.6 (d), 127.8 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.4 (d), 129.7 (d), 129.9 (d), 132.9 (s), 133.2 (d), 135.4 (d), 135.5 (d), 137.5 (s), 146.1 (d), 165.4 (s), 166.3 (s); IR ($CHCl_3$) (cm^{-1}) 3660, 3013, 2953, 2930, 2860, 1719, 1270, 1112; MS m/z (relative intensity) 474 (M – 178)$^+$ (1), 381 (2), 365 (2), 241 (3), 199 (9), 193 (19), 163 (12), 105 (32), 91 (100). Anal. Calcd for $C_{39}H_{44}O_7Si$: C, 71.75; H, 6.79. Found: C, 71.65, H, 6.89.

Preparation of (1*R*)-1-[(2*R*,3*S*)-(2-Benzyloxy-4-(tert-butyl-diphenyl-silanyloxy)-3-hydroxy-butyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (50).



The general silyl protection method was applied to **46c** on a 100 mg (0.24 mmol) scale to afford **50** (144 mg, 90% yield) as an oil: $[\alpha]^{25}_D$ = –15.62 (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ: 1.06 (s, 9 H), 2.04 (m, 1 H), 2.15 (m, 1 H), 2.62 (s, 1 H), 3.70 (s, 3 H), 3.85 (m, 3 H), 3.89 (m, 1 H), 4.51 (m, 2 H), 5.85 (d, J = 11.7 Hz, 1 H), 6.19 (dd, J = 11.64, 7.84 Hz, 1 H), 6.67 (m, 1 H), 7.20 (m, 6 H), 7.36 (m, 7 H), 7.54 (m, 1 H), 7.65 (m, 4 H), 7.97 (d, J = 8.12 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ: 19.2 (s), 26.8 (q), 34.5 (t), 51.5 (q), 64.3 (t), 69.7 (d), 72.4 (t), 72.8 (d), 75.2 (d), 120.0 (d), 125.5 (d), 127.7 (d), 127.8(d), 128.1 (d), 128.2 (d), 128.3 (d), 129.6 (d), 129.8 (d), 130.0 (d), 132.9 (d), 133.0 (d), 134.8 (s), 135.5 (d), 137.9 (s), 147.5 (d), 165.8 (s). IR ($CHCl_3$) (cm^{-1}): 3560, 3030, 3013, 2932, 2859, 1719, 1273, 1112. MS *m/z* (relative intensity) 474 (M – 178)$^+$ (2), 384 (2), 241 (3), 199 (9), 193 (10), 163 (15), 105 (35), 91 (100). Anal. Calcd for $C_{39}H_{44}O_7Si$: C, 71.75; H, 6.79. Found: C, 71.85, H, 6.85.

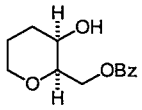
Preparation of (2*R*,3*R*)-2-(2-Hydroxy-ethyl)-tetrahydro-pyran-3-ol (55).



The general method for reduction of esters was applied to **12** on a 2.36 g (8.5 mmol) scale using $LiAlH_4$ (12.75 mL, 1.0 M in ether, 12.75 mmol) to afford **55** (1.0 g, 80% yield) as a solid: mp = 59-60 °C; $[\alpha]^{25}_D$ = +6.4 (*c* 2.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.40 (dd, J = 11.2, 4.4 Hz, 1 H), 1.68 (m, 2 H), 1.99 (m, 3 H), 2.63 (br s, 1 H), 2.75 (br s, 1 H), 3.54 (dd, J = 8.8, 4.4 Hz, 1 H), 3.66 (dd, J =

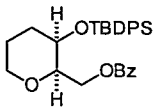
16, 6.4 Hz, 2 H), 3.75 (m, 2 H), 3.98 (dd, J = 11.2, 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.9 (t), 30.2 (t), 34.1 (t), 60.2 (t), 66.8 (d), 68.3 (t), 79.2 (d); IR ($CHCl_3$) (cm^{-1}) 3599, 3446, 2948, 2859, 1220; MS *m/z* (relative intensity) 147 $(M + 1)^+$ (14), 129 (100), 115 (31), 111 (40), 102 (35), 89 (34), 73 (90), 71 (70), 69 (46). Anal. Calcd for $C_7H_{14}O_3$ C, 57.50; H, 9.66. Found C, 57.51; H, 9.86.

Preparation of 2-[(2*R*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-yl]-ethyl Benzoate (56).



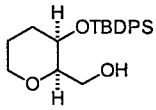
The general procedure for benzoylation was applied to **55** on a 1.0 g (6.8 mmol) scale to afford **56** (1.5 g, 89% yield) as an oil: $[\alpha]^{25}_D$ = +17.2 (*c* 2.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.40 (dd, J = 14.8, 2.4 Hz, 1 H), 1.69 (ddd, J = 16, 16, 3.2 Hz, 1 H), 1.92 (m, 3 H), 2.08 (m, 1 H), 3.43 (dd, J = 11.6, 2.4 Hz, 1 H), 3.50 (ddd, J = 8.8, 8.8, 4.8 Hz, 1 H), 3.66 (s, 2 H), 3.97 (dd, J = 11.6, 4.4 Hz, 1 H), 4.41 (m, 2 H), 7.42 (m, 2 H), 7.53 (m, 1 H), 8.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.0 (t), 30.5 (t), 31.2 (t), 61.7 (t), 66.7 (d), 68.4 (t), 76.6 (d), 128.2 (d), 129.4 (d), 130.2 (s), 132.8 (d), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3585, 3013, 2947, 2858, 1715, 1280, 1116; MS *m/z* (relative intensity) 250 $(M)^+$ (2), 233 (5), 217 (5), 199 (21), 122 (17), 105 (100), 91 (12), 77 (42). Anal. Calcd for $C_{14}H_{18}O_4$ C, 67.17; H, 7.25. Found C, 67.13; H, 7.29.

Preparation of 2-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl]-ethyl Benzoate (57).



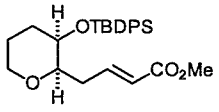
The general method for silyl protection was applied to **56** on a 1.3 g (5.2 mmol) scale to afford **57** (2.36 g, 93% yield) as an oil: $[\alpha]^{25}_D$ = +22.6 (*c* 2.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 9 H), 1.27 (m, 1 H), 1.44 (m, 1 H), 1.77 (m, 2 H), 2.05 (m, 1 H), 2.17 (m, 1 H), 3.46 (ddd, J = 11.2, 11.2, 2.6 Hz, 2 H), 3.77 (s, 1 H), 3.94 (d, J = 11.2 Hz, 1 H), 4.33 (dd, J = 5.8 Hz, 2H), 7.41 (m, 8 H), 7.55 (m, 1 H), 7.72 (m, 4 H), 8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (s), 21.4 (t), 27.1 (q), 30.3 (t), 30.4 (t), 62.0 (t), 66.7 (t), 68.9 (d), 76.3 (d), 127.6 (d), 128.3 (d), 129.5 (d), 130.5 (s), 132.8 (d), 133.8 (s), 134.3 (s), 135.3 (d), 136.0 (d), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3073, 3010, 2959, 2858, 1715, 1280; MS *m/z* (relative intensity) 431 $(M - 57)^+$ (19), 303 (100), 259 (19), 225 (11), 199 (79), 135 (17), 105 (89), 77 (18). Anal. Calcd for $C_{30}H_{36}O_4Si$ C, 73.73; H, 7.43. Found C, 73.75; H, 7.53.

Preparation of 2-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl]-ethanol (58).



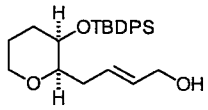
The general method for benzoate cleavage was applied to **57** on a 2.2 g (4.5 mmol) scale to afford **58** (1.64 g, 95% yield) as an oil: $[\alpha]^{25}_D$ = +11.7 (*c* 2.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.28 (d, J = 13.4 Hz, 1 H), 1.36 (m, 1 H), 1.45 (m, 1 H), 1.65 (m, 1 H), 1.72 (m, 1 H), 2.08 (m, 2 H), 2.37 (br s, 1 H), 3.46 (m, 2 H), 3.68 (m, 3 H), 3.97 (d, J = 11.2 Hz, 1 H), 7.41 (m, 6 H), 7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (s), 20.1 (t), 27.1 (q), 30.3 (t), 33.7 (t), 61.5 (t), 67.3 (t), 69.1 (d), 80.0 (d), 127.5 (d), 129.7 (d), 133.8 (s), 134.3 (s), 136.0 (d); IR ($CHCl_3$) (cm^{-1}) 3481, 3073, 3010, 2959, 2858, 1428, 1112; MS *m/z* (relative intensity) 327 $(M - 77)^+$ (2), 281 (6), 249 (97), 199 (100), 182 (27), 170 (19), 139 (27), 111 (54), 57 (28). Anal. Calcd for $C_{23}H_{32}O_3Si$ C, 71.84; H, 8.39. Found C, 71.95; H, 8.28.

Preparation of Methyl 4-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl]-but-2(*E*)-enoate (60).



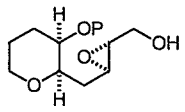
The general method for the preparation of (*E*)-α,β-unsaturated esters was applied to **58** on a 1.5 g (3.9 mmol) scale to afford **60** (1.49 g, 87% yield) as an oil: $[\alpha]^{25}_{D}$ = +42.2 (*c* 2.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.27 (m, 1 H), 1.46 (m, 1 H), 1.77 (m, 1 H), 2.03 (d, *J* = 12.9 Hz, 1 H), 2.16 (m, 1 H), 2.60 (m, 1 H), 3.35 (m, 1 H), 3.41 (ddd, *J* = 11.0, 11.0, 2.6 Hz, 1 H), 3.70 (s, 3 H), 3.72 (m, 1 H), 3.92 (d, *J* = 11.3 Hz, 1 H), 5.75 (d, *J* = 15.7 Hz, 1 H), 6.86 (ddd, *J* = 15.7, 7.1, 7.1 Hz, 1 H), 7.39 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (s), 21.1 (t), 27.1 (q), 30.3 (t), 34.1 (t), 51.3 (q), 67.0 (t), 68.7 (d), 78.7 (d), 122.4 (d), 127.6 (d), 129.7 (d), 133.7 (s), 134.1 (s), 136.0 (d), 166.9 (s); IR ($CHCl_3$) (cm^{-1}) 3072, 3009, 2953, 2858, 1716, 1655, 1475, 1112; MS *m/z* (relative intensity) 381 $(M - 57)^+$ (47), 348 (12), 303 (8), 270 (15), 213 (51), 199 (100), 153 (21), 135 (38), 105 (29), 84 (32). Anal. Calcd for $C_{26}H_{34}O_4Si$ C, 71.20; H, 7.82. Found C, 71.29; H, 8.04.

Preparation of 4-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl]-but-2(*E*)-en-1-ol (61).



The general method for reduction of esters was applied to **60** on a 3.9 g (8.9 mmol) scale using DIBAL® (19.5 mL, 1.0 M in hexane, 19.5 mmol) to afford **61** (3.3 g, 90% yield) as an oil: $[\alpha]^{25}_{D}$ = +25.6 (*c* 2.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.28 (m, 1 H), 1.44 (m, 1 H), 1.76 (m, 1 H), 2.05 (m, 1 H), 2.11 (m, 1 H), 2.44 (m, 1 H), 3.25 (m, 1 H), 3.41 (m, 1 H), 3.73 (s, 1 H), 3.93 (m, 1 H), 4.00 (d, *J* = 4.0 Hz, 2 H), 5.54 (m, 2 H), 7.40 (m, 6 H), 7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (s), 21.2 (t), 27.1 (q), 30.4 (t), 34.0 (t), 63.6 (t), 67.1 (d), 68.5 (d), 79.8 (d), 127.4 (d), 129.6 (d), 130.9 (d), 133.9 (s), 134.4 (s), 136.0 (d); IR ($CHCl_3$) (cm^{-1}) 3445, 3073, 3009, 2953, 2858, 1220, 1111; MS *m/z* (relative intensity) 353 $(M - 57)^+$ (5), 335 (9), 299 (33), 275 (13), 221 (14), 199 (100), 143 (56), 139 (60), 91 (68), 57 (94). Anal. Calcd for $C_{25}H_{34}O_3Si$ C, 73.13; H, 8.35. Found C, 73.20; H, 8.37.

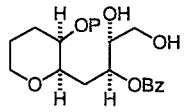
Preparation of (2*S*,3*R*)-{3-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-oxyranyl}-methanol (62).



P=TBDPS

The general asymmetric epoxidation procedure using as chiral auxiliary (*S,S*)-(−)-DET was used over **61** on a 2.9 g (7.05 mmol) scale for 2 h, yielding **62** (2.57 g, 86% yield) as an oil: $[\alpha]^{25}_{D}$ = +40.1 (*c* 2.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.27 (m, 1 H), 1.30 (m, 1 H), 1.47 (m, 1 H), 1.73 (m, 2 H), 2.08 (m, 1 H), 2.83 (dd, *J* = 2.1, 2.1 Hz, 1 H), 3.04 (m, 1 H), 3.45 (m, 2 H), 3.59 (m, 1 H), 3.70 (s, 1 H), 3.85 (d, *J* = 12.4 Hz, 1 H), 3.95 (d, *J* = 11.3 Hz, 1 H), 7.39 (m, 6 H), 7.67 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (s), 21.0 (t), 27.1 (q), 30.4 (t), 34.4 (t), 53.8 (d), 59.1(d), 61.8 (t), 67.3 (t), 69.1 (d), 77.3 (d), 127.6 (d), 129.7 (d), 133.7 (s), 134.2 (s), 136.0 (d); IR ($CHCl_3$) (cm^{-1}) 3426, 3073, 3008, 2955, 2858, 1428, 1110; MS *m/z* (relative intensity) 427 $(M + 1)^+$ (1), 369 (2), 269 (3), 225 (3), 199 (33), 181 (11), 135 (18), 71 (25), 57 (100). Anal. Calcd for $C_{25}H_{34}O_4Si$ C, 70.39; H, 8.04. Found C, 70.13; H, 8.15.

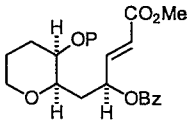
Preparation of (1*S*,2*S*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-2,3-dihydroxy-propyl Benzoate (63).



P=TBDPS

The general procedure for epoxide opening was applied to **62** on a 2.57 g (6.0 mmol) scale, yielding **63** (2.35 g, 71% yield) as an oil: $[\alpha]^{25}_D$ = +24.6 (*c* 2.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.28 (d, *J* = 13.6 Hz, 1 H), 1.45 (ddd, *J* = 13.3, 13.3, 2.6 Hz, 1 H), 1.73 (s, 1 H), 1.76 (s, 1 H), 2.08 (d, *J* = 12.4 Hz, 1 H), 2.32 (m, 2 H), 3.46 (ddd, *J* = 11.3, 11.3, 2.0 Hz, 1 H), 3.56 (m, 2 H), 3.67 (s, 2 H), 3.81 (s, 1 H), 4.00 (d, *J* = 11.6 Hz, 1 H), 5.13 (ddd, *J* = 7.8, 4.4, 4.4 Hz, 1 H), 7.38 (m, 8 H), 7.56 (m, 1 H), 7.69 (m, 4 H), 7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (s), 20.5 (t), 27.2 (q), 30.5 (t), 33.0 (t), 63.5 (t), 67.7 (t), 69.4 (d), 72.0 (d), 72.2 (d), 76.3 (d), 127.5 (d), 127.7 (d), 128.4 (d), 129.7 (d), 130.0 (s), 133.2 (d), 133.6 (s), 134.2 (s), 136.0 (d), 166.0 (s); IR ($CHCl_3$) (cm^{-1}) 3464, 3011, 2955, 2858, 1715, 1274, 1113; MS *m/z* (relative intensity) 491 $(M - 57)^+$ (1), 369 (6), 303 (23), 225 (10), 199 (64), 183 (23), 153 (22), 135 (30), 105 (100), 77 (21). Anal. Calcd for $C_{32}H_{40}O_6Si$ C, 70.04; H, 7.35. Found C, 69.91; H, 7.43.

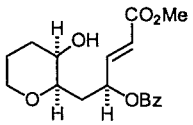
Preparation of (1*S*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (64).



P=TBDPS

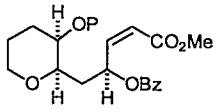
The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*E*)-α,β-unsaturated esters was applied to diol **63** on a 2.1 g (3.8 mmol) scale, yielding **64** (1.6 g, 73% yield) as an oil: $[\alpha]^{25}_D$ = +56.7 (*c* 2.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.29 (m, 1 H), 1.48 (m, 1 H), 1.70 (m, 1 H), 1.77 (dd, *J* = 13.9, 5.1 Hz, 1 H), 1.95 (m, 1 H), 2.27 (m, 1 H), 3.38 (dd, *J* = 9.3, 9.3 Hz, 2 H), 3.74 (s, 3 H), 3.76 (s, 1 H), 3.89 (d, *J* = 11.3 Hz, 1 H), 5.63 (m, 1 H), 5.97 (d, *J* = 15.7 Hz, 1 H), 6.84 (dd, *J* = 15.7, 5.6 Hz, 1 H), 7.41 (m, 8 H), 7.56 (m, 1 H), 7.69 (m, 4 H), 8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (s), 21.3 (t), 27.1 (q), 30.2 (t), 35.1 (t), 51.6 (q), 66.3 (t), 68.6 (d), 70.8 (d), 75.9 (d), 121.3 (d), 127.5 (d), 127.7 (d), 128.4 (d), 129.7 (d), 130.0 (s), 133.1 (d), 133.7 (s), 134.1 (s), 135.9 (d), 145.4 (d), 165.3 (s), 166.4 (s); IR ($CHCl_3$) (cm^{-1}) 3010, 2950, 2859, 1719, 1272, 1112; MS *m/z* (relative intensity) 515 $(M - 57)^+$ (8), 393 (13), 303 (100), 259 (11), 199 (21), 183 (14), 135 (18), 105 (95), 77 (34). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.68; H, 7.18.

Preparation of (1*S*)-1-[(2*R*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (65).



The general procedure to cleave silyl groups was applied to ester **64** on a 569 mg (0.99 mmol) scale, yielding **65** (299 mg, 90% yield) as a solid: mp = 91–92 °C; $[\alpha]^{25}_D$ = +38.9 (*c* 2.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.38 (m, 1 H), 1.68 (m, 1 H), 1.96 (m, 2 H), 2.20 (m, 2 H), 3.41 (dd, *J* = 11.7 Hz, 1 H), 3.45 (m, 1 H), 3.66 (s, 1 H), 3.75 (s, 3 H), 3.92 (s, 1 H), 5.85 (m, 1 H), 6.07 (d, *J* = 15.6 Hz, 1 H), 7.00 (dd, *J* = 15.6, 5.3 Hz, 1 H), 7.46 (m, 2 H), 7.58 (m, 1 H), 8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.0 (t), 30.6 (t), 36.3 (t), 51.7 (q), 66.6 (d), 68.3 (t), 70.5 (d), 76.4 (d), 121.5 (d), 128.4 (d), 129.7 (d), 129.9 (s), 133.2 (d), 145.3 (d), 165.4 (s), 166.4 (s); IR ($CHCl_3$) (cm^{-1}) 3574, 3013, 2952, 2852, 1719, 1658, 1271, 1110; MS *m/z* (relative intensity) 335 $(M + 1)^+$ (1), 213 (30), 194 (38), 181 (35), 135 (82), 124 (38), 113 (32), 105 (100), 77 (81). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.63; H, 6.77.

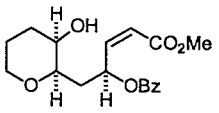
Preparation of (1*S*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (66).



P=TBDPS

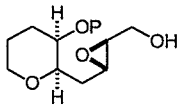
The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*Z*)-α,β-unsaturated esters was applied to diol **63** on a 960 mg (1.7 mmol) scale, yielding **66** (741 mg, 74% yield) as an oil: $[\alpha]^{25}_D$ = +43.0 (*c* 1.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 9 H), 1.28 (m, 1 H), 1.49 (m, 1 H), 1.74 (dd, *J* = 8.1, 3.6 Hz, 1 H), 1.82 (dd, *J* = 14.8, 6.2 Hz, 1 H), 1.94 (dd, *J* = 9.9, 3.6 Hz, 1 H), 2.42 (m, 2 H), 3.36 (ddd, *J* = 11.8, 11.8, 2.8 Hz, 1 H), 3.65 (d, *J* = 10.4 Hz, 1 H), 3.72 (s, 3 H), 3.75 (m, 1 H), 3.80 (m, 1 H), 5.83 (d, *J* = 11.7 Hz, 1 H), 6.27 (dd, *J* = 11.7, 8.1 Hz, 1 H), 6.59 (m, 1 H), 7.39 (m, 8 H), 7.54 (m, 1 H), 7.69 (m, 4 H), 8.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.4 (s), 21.7 (t), 27.1 (q), 30.0 (t), 34.9 (t), 51.4 (q), 65.5 (t), 69.5 (d), 70.5 (d), 76.1 (d), 119.5 (d), 127.5 (d), 127.7 (d), 128.3 (d), 129.7 (d), 130.5 (s), 132.8 (d), 133.8 (s), 134.3 (s), 135.9 (d), 147.5 (d), 165.8 (s), 165.7 (s); IR ($CHCl_3$) (cm^{-1}) 3065, 2955, 2865, 1718, 1652, 1277, 1112; MS *m/z* (relative intensity) 515 $(M - 57)^+$ (19), 393 (16), 303 (96), 199 (42), 195 (38), 135 (56), 105 (100), 77 (98). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.08; H, 7.09.

Preparation of (1*S*)-1-[(2*R*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (67).



The general procedure to cleave silyl groups was applied to ester **66** on a 415 mg (0.72 mmol) scale, yielding **67** (230 mg, 95% yield) as an oil: $[\alpha]^{25}_D$ = +30.0 (*c* 1.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.34 (d, *J* = 13.8 Hz, 1 H), 1.64 (m, 1 H), 1.95 (m, 2 H), 2.12 (m, 2 H), 3.11 (br s, 1 H), 3.43 (dd, *J* = 12.3, 12.3 Hz, 1 H), 3.47 (m, 1 H), 3.74 (s, 3 H), 3.91 (m, 2 H), 5.86, (d, *J* = 11.5 Hz, 1 H), 6.31 (dd, *J* = 11.5, 7.2 Hz, 1 H), 6.49 (m, 1 H), 7.44 (m, 2 H), 7.56 (m, 1 H), 8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (t), 30.1 (t), 36.2 (t), 51.7 (q), 64.9 (d), 68.3 (t), 69.6 (d), 76.3 (d), 119.4 (d), 128.3 (d), 129.6 (d), 129.9 (s), 133.1 (d), 148.9 (d), 165.9 (s), 166.4 (s); IR ($CHCl_3$) (cm^{-1}) 3535, 3010, 2953, 2852, 1716, 1645, 1271, 1110; MS *m/z* (relative intensity) 335 $(M + 1)^+$ (2), 213 (60), 194 (32), 181 (38), 135 (94), 124 (49), 105 (100), 77 (99). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.67; H, 6.89.

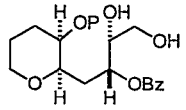
Preparation of (2*R*,3*S*)-{3-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-oxyranyl}-methanol (68).



P=TBDPS

The general asymmetric epoxidation procedure using as chiral auxiliary (*R*,*R*)-(+)-DET was used over **61** on a 2.0 g (4.86 mmol) scale for 2 h, yielding **68** (1.88 g, 90% yield) as an oil: $[\alpha]^{25}_D$ = +12.5 (*c* 2.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.32 (m, 1 H), 1.48 (m, 1 H), 1.67 (m, 2 H), 1.75 (m, 1 H), 1.98 (m, 1 H), 2.80 (s, 1 H), 2.85 (m, 1 H), 3.37 (m, 1 H), 3.40 (s, 1 H), 3.43 (m, 1 H), 3.76 (s, 2 H), 3.93 (d, *J* = 11.3 Hz, 1 H), 7.39 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (s), 21.2 (t), 27.1 (q), 30.2 (t), 32.7 (t), 53.4 (d), 57.9 (d), 61.8 (t), 66.8 (t), 68.6 (d), 76.9 (d), 127.6 (d), 129.7 (d), 133.7 (s), 134.2 (s), 136.0 (d); IR ($CHCl_3$) (cm^{-1}) 3449, 3020, 2954, 2932, 2859, 1220, 1108; MS *m/z* (relative intensity) 427 $(M + 1)^+$ (1), 369 (4), 339 (3), 271 (14), 199 (48), 163 (24), 135 (34), 91 (48), 57 (100). Anal. Calcd for $C_{25}H_{34}O_4Si$ C, 70.39; H, 8.04. Found C, 70.48; H, 8.37.

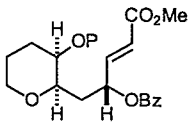
Preparation of (1*R*,2*R*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-2,3-dihydroxy-propyl Benzoate (69).



P=TBDPS

The general procedure for epoxide opening was applied to **68** on a 1.88 g (4.4 mmol) scale, yielding **69** (1.69 g, 70% yield) as an oil: $[\alpha]^{25}_D$ = +23.9 (*c* 2.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 9 H), 1.29 (m, 1 H), 1.47 (m, 1 H), 1.77 (m, 2 H), 2.05 (d, *J* = 11.6 Hz, 1 H), 2.33 (dd, *J* = 10.4, 10.4 Hz, 1 H), 2.52 (br s, 1 H), 3.39 (dd, *J* = 12.8, 12.8 Hz, 2 H), 3.45 (s, 1 H), 3.58 (m, 1 H), 3.66 (s, 1 H), 3.74 (s, 1 H), 3.95 (d, *J* = 10.7 Hz, 1 H), 5.14 (d, *J* = 5.1 Hz, 1 H), 7.35 (m, 6 H), 7.44 (m, 2 H), 7.58 (m, 1 H), 7.68 (m, 4 H), 7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (s), 20.9 (t), 27.1 (q), 30.4 (t), 34.2 (t), 62.8 (t), 67.0 (t), 69.2 (d), 72.9 (d), 73.5 (d), 76.6 (d), 127.6 (d), 128.4 (d), 129.7 (d), 129.8 (s), 133.3 (d), 133.8 (s), 134.1 (s), 136.0 (d), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3396, 3010, 2957, 2859, 1716, 1277, 1113; MS *m/z* (relative intensity) 491 $(M - 57)^+$ (2), 369 (15), 303 (22), 291 (20), 199 (54), 183 (24), 135 (28), 105 (100), 77 (33). Anal. Calcd for $C_{32}H_{40}O_6Si$ C, 70.04; H, 7.35. Found C, 70.25; H, 7.44.

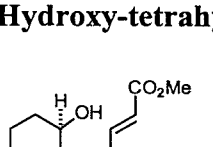
Preparation of (1*R*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (70).



P=TBDPS

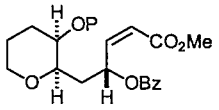
The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*E*)-α,β-unsaturated esters was applied to diol **69** on a 1.7 g (3.1 mmol) scale, yielding **70** (1.22 g, 69% yield) as an oil: $[\alpha]^{25}_D$ = +12.0 (*c* 2.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.27 (m, 1 H), 1.45 (dd, *J* = 12.6, 12.6 Hz, 1 H), 1.57 (dd, *J* = 14.4, 11.9 Hz, 1 H), 1.75 (m, 1 H), 2.02 (m, 1 H), 2.18 (ddd, *J* = 14.2, 14.2, 3.1 Hz, 1 H), 3.37 (m, 3 H), 3.74 (s, 3 H), 3.90 (d, *J* = 11.4 Hz, 1 H), 5.79 (dd, *J* = 5.0, 5.0 Hz, 1 H), 5.94 (d, *J* = 15.8 Hz, 1 H), 6.92 (dd, *J* = 15.8, 5.0 Hz, 1 H), 7.40 (m, 8 H), 7.57 (m, 1 H), 7.69 (m, 4 H), 8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (s), 21.2 (t), 27.2 (q), 30.3 (t), 35.9 (t), 51.6 (q), 66.7 (t), 69.1 (d), 70.1 (d), 75.4 (d), 120.6 (d), 127.4 (d), 127.6 (d), 128.4 (d), 129.7 (d), 129.8 (s), 133.1 (d), 133.7 (s), 134.2 (s), 135.9 (d), 146.4 (d), 165.4 (s), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3073, 3009, 2950, 2859, 1718, 1659, 1265, 1112; MS *m/z* (relative intensity) 515 $(M - 57)^+$ (1), 393 (10), 303 (40), 199 (13), 195 (18), 135 (18), 105 (100), 77 (37). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.14; H, 7.31.

Preparation of (1*R*)-1-[(2*R*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (71).



The general procedure to cleave silyl groups was applied to ester **70** on a 254 mg (0.44 mmol) scale, yielding **71** (138 mg, 93% yield) as an oil: $[\alpha]^{25}_D$ = −19.5 (*c* 2.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39 (m, 1 H), 1.67 (m, 1 H), 1.90 (m, 3 H), 2.15 (ddd, *J* = 14.8, 10.0, 3.6 Hz, 1 H), 3.35 (m, 1 H), 3.45 (dd, *J* = 10.8, 2.8 Hz, 1 H), 3.60 (s, 1 H), 3.70 (s, 3 H), 3.94 (dd, *J* = 12.0, 4.8 Hz, 1 H), 5.83 (m, 2 H), 6.01 (d, *J* = 15.6 Hz, 1 H), 6.99 (dd, *J* = 15.6 Hz, 1 H), 7.45 (m, 8.0 Hz, 2 H), 7.58 (m, 1 H), 8.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.0 (t), 30.6 (t), 36.9 (t), 51.6 (q), 67.1 (d), 68.4 (t), 70.1 (d), 75.9 (d), 120.7 (d), 128.5 (d), 129.6 (d), 130.1 (s), 133.2 (d), 146.0 (d), 165.4 (s), 166.3 (s); IR ($CHCl_3$) (cm^{-1}) 3574, 3025, 2952, 2858, 1720, 1665, 1270, 1103; MS *m/z* (relative intensity) 335 $(M + 1)^+$ (2), 317 (2), 213 (33), 194 (21), 181 (30), 135 (44), 105 (99), 77 (63), 71 (100). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.72; H, 6.84.

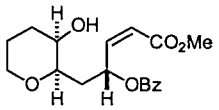
Preparation of (1*R*)-1-[(2*R*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (72).



P=TBDPS

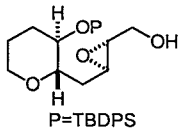
The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*Z*)-α,β-unsaturated esters was applied to diol **69** on a 857 mg (1.56 mmol) scale, yielding **72** (698 mg, 78% yield) as an oil: $[\alpha]^{25}_D$ = +14.2 (*c* 3.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 9 H), 1.29 (m, 1 H), 1.52 (m, 1 H), 1.74 (m, 1 H), 1.82 (dd, *J* = 11.7, 11.7 Hz, 1 H), 1.93 (m, 1 H), 2.31 (m, 1 H), 3.40 (dd, *J* = 8.6, 8.6 Hz, 1 H), 3.66 (d, *J* = 10.4 Hz,), 3.77 (s, 3 H), 3.83 (s, 1 H), 3.94 (m, 1 H), 5.86 (d, *J* = 11.6 Hz, 1 H), 6.17 (dd, *J* = 11.6, 7.9 Hz, 1 H), 6.53 (m, 1 H), 7.38 (m, 8 H), 7.54 (m, 1 H), 7.70 (m, 4 H), 8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.4 (s), 22.1 (t), 27.1 (q), 29.8 (t), 33.7 (t), 51.5 (q), 64.9 (t), 69.4 (d), 69.8 (d), 74.7 (d), 119.8 (d), 127.4 (d), 127.6 (d), 128.3 (d), 129.6 (d), 130.3 (s), 132.9 (d), 133.8 (s), 134.3 (s), 135.9 (d), 147.9 (d), 165.7 (s), 165.8 (s); IR ($CHCl_3$) (cm^{-1}) 3019, 2953, 2858, 1720, 1274, 1112; MS *m/z* (relative intensity) 516 $(M - 56)^+$ (19), 393 (23), 303 (97), 259 (17), 199 (47), 195 (46), 135 (57), 111 (53), 105 (100), 77 (80). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.58; H, 7.39.

Preparation of (1*R*)-1-[(2*R*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (73).



The general procedure to cleave silyl groups was applied to ester **72** on a 376 mg (0.66 mmol) scale, yielding **73** (202 mg, 92% yield) as an oil: $[\alpha]^{25}_D$ = –45.7 (*c* 1.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.36 (d, *J* = 13.4 Hz, 1 H), 1.67 (m, 1 H), 1.91 (m, 2 H), 2.00 (m, 1 H), 2.13 (m, 1 H), 3.36 (ddd, *J* =11.9, 11.9, 2.3 Hz, 1 H), 3.54 (m, 1 H), 3.66 (s, 1 H), 3.74 (s, 3 H), 3.96 (dd, *J* = 11.5, 4.5 Hz, 1 H), 5.86 (d, *J* = 11.6 Hz, 1 H), 6.19 (dd, *J* = 11.6, 8.0 Hz, 1 H), 6.56 (m, 1 H), 7.42 (m, 2 H), 7.54 (m, 1 H), 8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (t), 30.6 (t), 36.4 (t), 51.5 (q), 67.3 (d), 68.4 (t), 69.6 (d), 76.2 (d), 120.1 (d), 128.3 (d), 129.5 (d), 130.1 (s), 133.0 (d), 147.4 (d), 165.7 (s), 165.8 (s); IR ($CHCl_3$) (cm^{-1}) 3574, 3019, 2948, 2858, 1720, 1645, 1274, 1174; MS *m/z* (relative intensity) 335 $(M + 1)^+$ (7), 213 (92), 195 (25), 181 (39), 135 (64), 124 (38), 105 (100), 77 (100) 71 (100). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.65; H, 6.79.

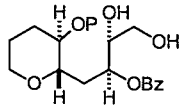
Preparation of (2*S*,3*R*)-{3-[(2*S*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-oxyranyl}-methanol (81).



P=TBDPS

The general asymmetric epoxidation procedure using as chiral auxiliary (*S*,*S*)-(–)-DET was used over **80** on a 2.58 g (6.3 mmol) scale for 2 h, yielding **81** (2.26 g, 84% yield) as an oil: $[\alpha]^{25}_D$ = –10.7 (*c* 2.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.45 (m, 3 H), 1.67 (m, 1 H), 1.82 (br s, 1 H), 2.09 (m, 1 H), 2.91 (m, 1 H), 3.05 (dd, *J* = 5.4, 5.4 Hz, 1 H), 3.28 (m, 2 H), 3.40 (m, 1 H), 3.59 (dd, *J* = 12.5, 4.6 Hz, 1 H), 3.79 (dd, *J* = 12.7, 1.4 Hz, 1 H), 3.88 (dd, *J* = 12.5, 2.6 Hz, 1 H), 7.39 (m, 6 H), 7.67 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.2 (s), 25.3 (t), 27.0 (q), 33.2 (t), 34.0 (t), 53.7 (d), 57.8 (d), 61.9 (t), 67.5 (t), 71.9 (d), 80.5 (d), 127.4 (d), 127.6 (d), 129.6 (d), 129.7 (d), 133.6 (s), 134.5 (s), 135.8 (d); IR ($CHCl_3$) (cm^{-1}) 3452, 3013, 2933, 2852, 1428, 1103; MS *m/z* (relative intensity) 369 $(M - 57)^+$ (1), 281 (8), 225 (11), 199 (100), 183 (19), 139 (13), 135 (15), 71 (18). Anal. Calcd for $C_{25}H_{34}O_4Si$ C, 70.39; H, 8.04. Found C, 70.50; H, 8.26.

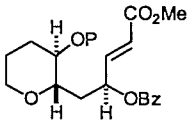
Preparation of (1*S*,2*S*)-1-[(2*S*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-2,3-dihydroxy-propyl Benzoate (82).



P=TBDPS

The general procedure for epoxide opening was applied to **81** on a 1.6 g (3.7 mmol) scale, yielding **82** (1.54 g, 75% yield) as an oil: $[\alpha]^{25}_D = -16.4$ (*c* 2.11, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.44 (m, 3 H), 1.65 (m, 1 H), 1.84 (m, 1 H), 2.48 (dd, *J* = 13.9, 8.2 Hz, 1 H), 3.23 (dd, *J* = 10.8, 10.8 Hz, 1 H), 3.29 (dd, *J* = 9.2, 9.2 Hz, 1 H), 3.38 (m, 1 H), 3.59 (dd, *J* = 11.8, 5.0 Hz, 1 H), 3.65 (d, *J* = 3.0 Hz, 1 H), 3.70 (m, 1 H), 3.78 (dd, *J* = 12.6, 2.9 Hz, 1 H), 5.24 (m, 1 H), 7.41 (m, 8 H), 7.61 (m, 1 H), 7.68 (m, 4 H), 8.08 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.3 (s), 25.3 (t), 26.9 (q), 33.2 (t), 34.7 (t), 62.7 (t), 67.6 (t), 72.1 (d), 72.6 (d), 73.5 (d), 79.5 (d), 127.5 (d), 127.7 (d), 128.5 (d), 129.7 (d), 129.8 (s), 133.1 (d), 133.5 (s), 134.3 (s), 135.9 (d), 166.8 (s); IR ($CHCl_3$) (cm^{-1}) 3020, 2933, 2860, 1714, 1277, 1111; MS *m/z* (relative intensity)) 492 $(M - 57)^+$ (2), 303 (10), 291 (7), 199 (54), 183 (22), 135 (34), 105 (100), 77 (37). Anal. Calcd for $C_{32}H_{40}O_6Si$ C, 70.04; H, 7.35. Found C, 70.05; H, 7.65.

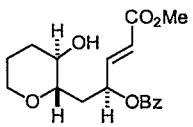
Preparation of (1*S*)-1-[(2*S*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (83).



P=TBDPS

The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*E*)-α,β-unsaturated esters was applied to diol **82** on a 1.45 g (2.6 mmol) scale, yielding **83** (1.16 g, 77% yield) as an oil: $[\alpha]^{25}_D = +5.6$ (*c* 1.76, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.26 (m, 1 H), 1.44 (m, 3 H), 1.85 (m, 1 H), 2.45 (dd, *J* = 14.5, 10.1 Hz, 1 H), 3.19 (dd, *J* = 11.1, 11.1 Hz, 1 H), 3.26 (dd, *J* = 8.9, 8.9 Hz, 1 H), 3.38 (m, 1 H), 3.74 (s, 3 H), 3.75 (m, 1 H), 5.82 (m, 1 H), 5.97 (d, *J* = 15.8 Hz, 1 H), 6.94 (dd, *J* = 15.8, 5.0 Hz, 1 H), 7.40 (m, 8 H), 7.63 (m, 1 H), 7.70 (m, 4 H), 8.11 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.3 (s), 25.4 (t), 27.0 (q), 33.3 (t), 37.0 (t), 51.6 (q), 67.5 (t), 70.0 (d), 72.1 (d), 78.7 (d), 120.5 (d), 127.5 (d), 127.7 (d), 128.3 (d), 129.7 (d), 130.0 (s), 133.1 (d), 133.5 (s), 134.3 (s), 135.8 (d), 146.5 (d), 165.5 (s), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3077, 2948, 2859, 1720, 1658, 1426, 1272, 1112; MS *m/z* (relative intensity) 515 $(M - 57)^+$ (4), 393 (11), 303 (52), 199 (31), 195 (41), 135 (46), 105 (100), 77 (86). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.52; H, 7.36.

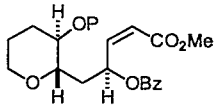
Preparation of (1*S*)-1-[(2*S*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*E*)-allyl Benzoate (84).



The general procedure to cleave silyl groups was applied to ester **83** on a 198 mg (0.35 mmol) scale, yielding **84** (112 mg, 97% yield) as an oil: $[\alpha]^{25}_D = +11.7$ (*c* 2.02, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.36 (m, 1 H), 1.63 (s, 2 H), 1.78 (ddd, *J* = 10.2, 10.2, 3.6 Hz, 1 H), 2.08 (d, *J* = 8.3 Hz, 1 H), 2.40 (m, 1 H), 3.13 (dd, *J* = 8.5, 8.5 Hz, 1 H), 3.22 (m, 1 H), 3.29 (m, 1 H), 3.71 (s, 3 H), 3.83 (dd, *J* = 11.6 Hz, 1 H), 5.86 (m, 1 H), 6.02 (d, *J* = 15.7 Hz, 1 H), 7.01 (dd, *J* = 15.7, 4.9 Hz, 1 H), 7.44 (m, 2 H), 7.57 (m, 1 H), 8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.4 (t), 33.1 (t), 37.0 (t), 51.6 (q), 67.5 (t), 69.9 (d), 70.5 (d), 78.4 (d), 120.7 (d), 128.4 (d), 129.7 (d), 129.8 (s), 133.1 (d), 146.4 (d), 165.6 (s), 166.5 (s); IR ($CHCl_3$) (cm^{-1}) 3019, 2949, 2856, 1720, 1272, 1113; MS *m/z* (relative intensity) 335

$(M + 1)^+$ (1), 212 (31), 194 (30), 180 (19), 135 (95), 124 (41), 105 (100), 77 (100), 71 (100). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.47; H, 6.73.

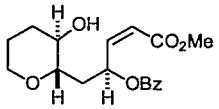
Preparation of (1*S*)-1-[(2*S*,3*R*)-3-(*tert*-Butyl-diphenyl-silanyloxy)-tetrahydro-pyran-2-yl-methyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (85).



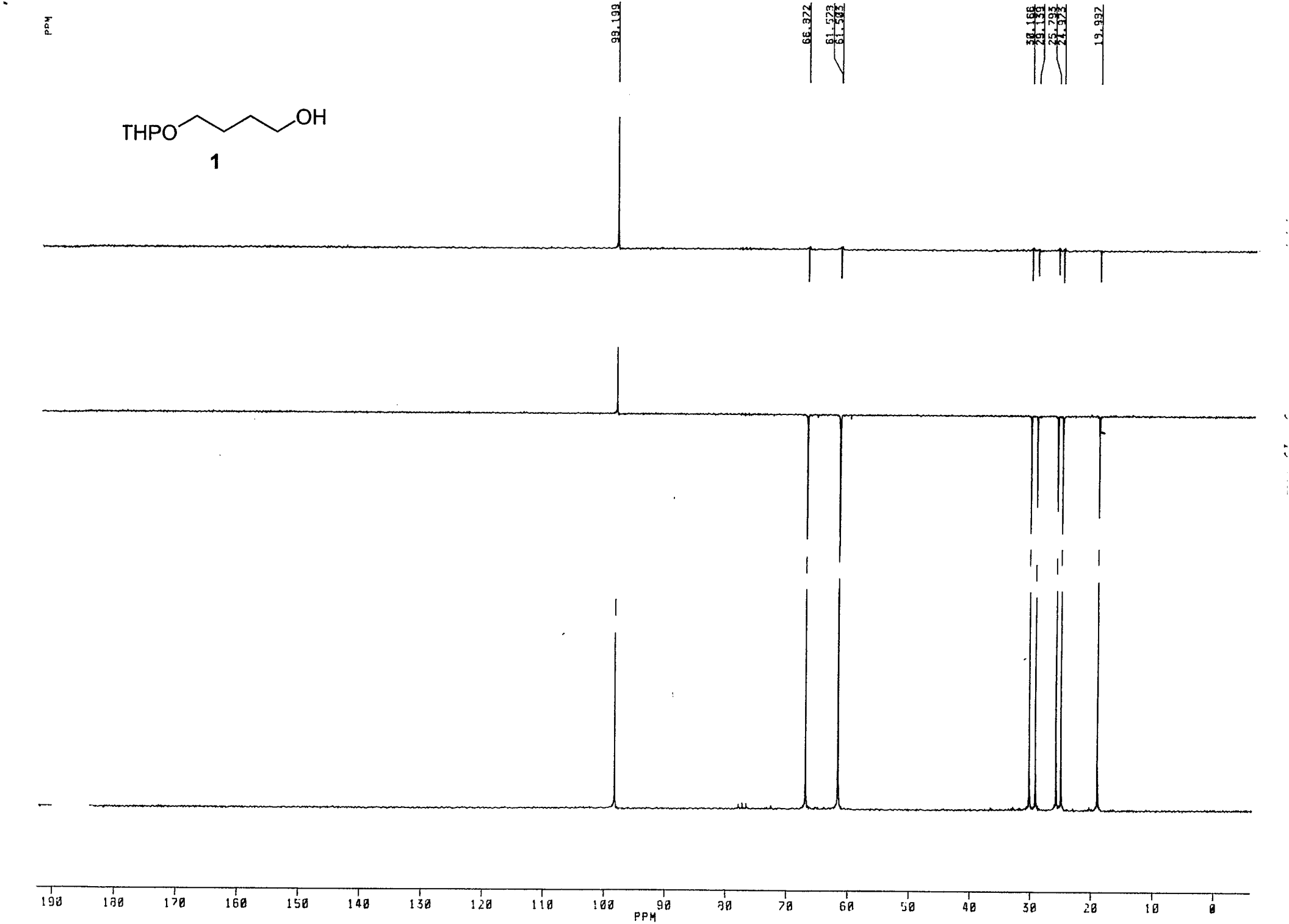
P=TBDPS

The general procedure to transform 3-benzoyloxy-1,2-diols into γ-benzoyloxy-(*Z*)-α,β-unsaturated esters was applied to diol **82** on a 1.34 g (2.4 mmol) scale, yielding **85** (1.1 g, 79% yield) as an oil: $[\alpha]^{25}_D = +7.2$ (*c* 1.81, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.27 (s, 1 H), 1.44 (m, 2 H), 1.56 (m, 1 H), 1.85 (s, 1 H), 2.49 (dd, *J* = 13.7, 10.2 Hz, 1 H), 3.19 (m, 1 H), 3.37 (m, 1 H), 3.42 (m, 1 H), 3.75 (s, 3 H), 3.80 (d, *J* = 10.2 Hz, 1 H), 5.83 (d, *J* = 11.7 Hz, 1 H), 6.15 (dd, *J* = 11.7, 7.9 Hz, 1 H), 6.58 (dd, *J* = 7.9, 7.9 Hz, 1 H), 7.40 (m, 8 H), 7.57 (m, 1 H), 7.68 (m, 4 H), 8.09 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.3 (s), 25.3 (t), 27.0 (q), 33.4 (t), 36.5 (t), 51.5 (q), 67.5 (t), 69.6 (d), 72.1 (d), 78.7 (d), 119.8 (d), 127.4 (d), 127.6 (d), 128.3 (d), 129.7 (d), 130.4 (s), 132.9 (d), 133.7 (s), 134.5 (s), 135.9 (d), 147.8 (d), 165.7 (s), 165.8 (s); IR ($CHCl_3$) (cm^{-1}) 2952, 2933, 2859, 1720, 1275, 1112; MS *m/z* (relative intensity) 515 $(M - 57)^+$ (10), 393 (7), 303 (40), 199 (21), 195 (19), 135 (28), 105 (100), 77 (52). Anal. Calcd for $C_{34}H_{40}O_6Si$ C, 71.30; H, 7.04. Found C, 71.27; H, 7.23.

Preparation of (1*S*)-1-[(2*S*,3*R*)-3-Hydroxy-tetrahydro-pyran-2-ylmethyl]-3-methoxycarbonyl-(*Z*)-allyl Benzoate (86).



The general procedure to cleave silyl group was applied to ester **85** on a 327 mg (0.57 mmol) scale, yielding **86** (174 mg, 91% yield) as an oil: $[\alpha]^{25}_D = +25.0$ (*c* 2.01, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.39 (m, 1 H), 1.64 (m, 2 H), 1.95 (m, 1 H), 2.10 (m, 1 H), 2.39 (m, 1 H), 2.61 (br s, 1 H), 3.21 (m, 2 H), 3.49 (ddd, *J* = 9.9, 9.9, 4.5 Hz, 1 H), 3.74 (s, 3 H), 3.81 (d, *J* = 9.2 Hz, 1 H), 5.86 (d, *J* = 11.6 Hz, 1 H), 6.26 (dd, *J* = 11.6, 7.7 Hz, 1 H), 6.66 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.42 (m, 2 H), 7.54 (m, 1 H), 8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.4 (t), 32.7 (t), 36.1 (t), 51.7 (q), 67.5 (t), 69.2 (d), 69.5 (d), 79.1 (d), 119.6 (d), 128.3 (d), 129.6 (d), 130.3 (s), 132.9 (d), 148.6 (d), 166.0 (s), 166.1 (s); IR ($CHCl_3$) (cm^{-1}) 3525, 3027, 2950, 1719, 1275, 1114; MS *m/z* (relative intensity) 335 $(M + 1)^+$ (1), 212 (12), 194 (9), 180 (9), 135 (36), 124 (21), 105 (100), 77 (82), 71 (98). Anal. Calcd for $C_{18}H_{22}O_6$ C, 64.64; H, 6.64. Found C, 64.53; H, 6.95.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66.322
61.523
61.503
30.166
29.139
25.793
21.973
19.932
THPO
OH
1
PPM
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150
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130
120
110
100
90
80
70
60
50
40
30
20
10
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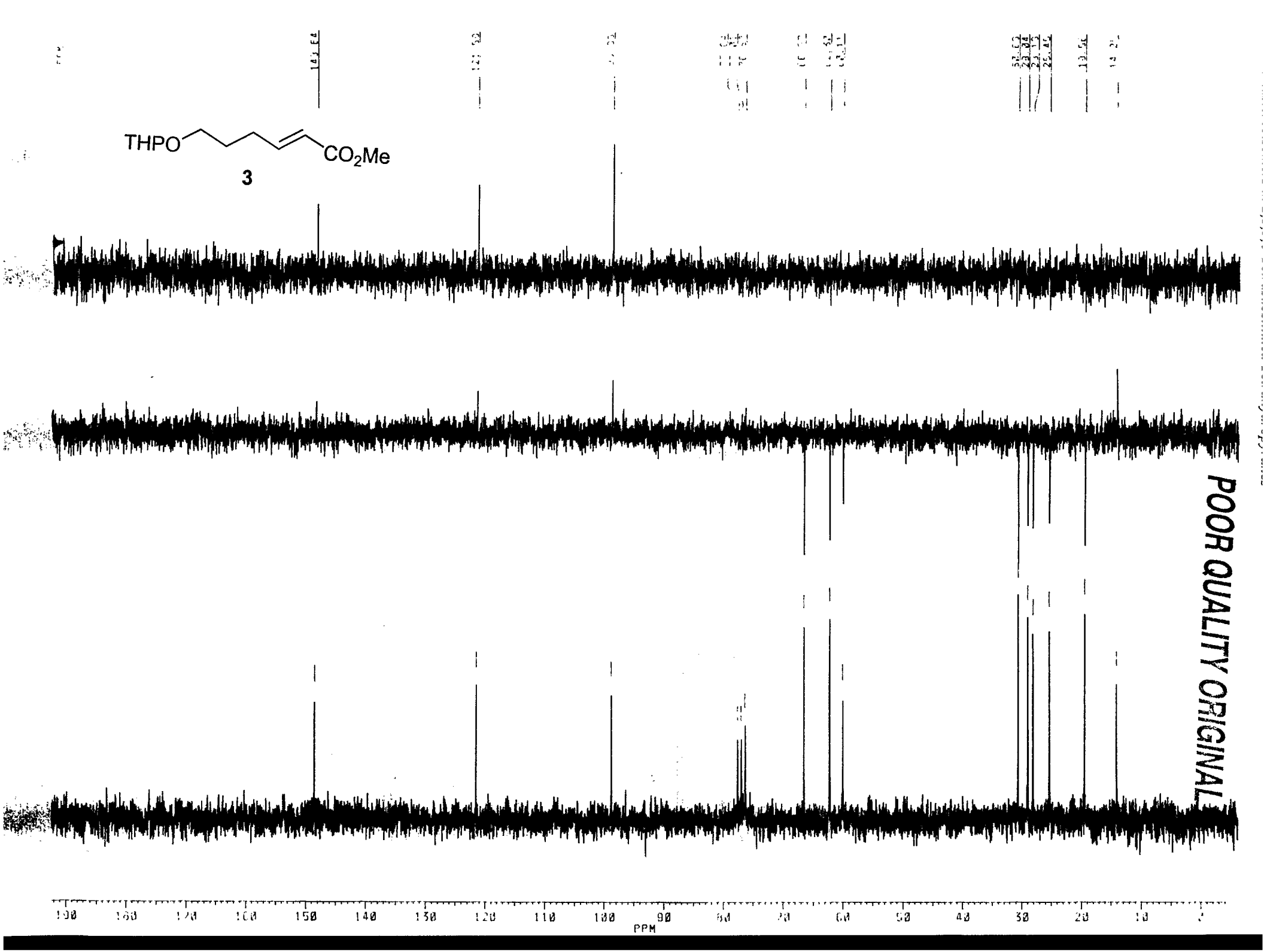
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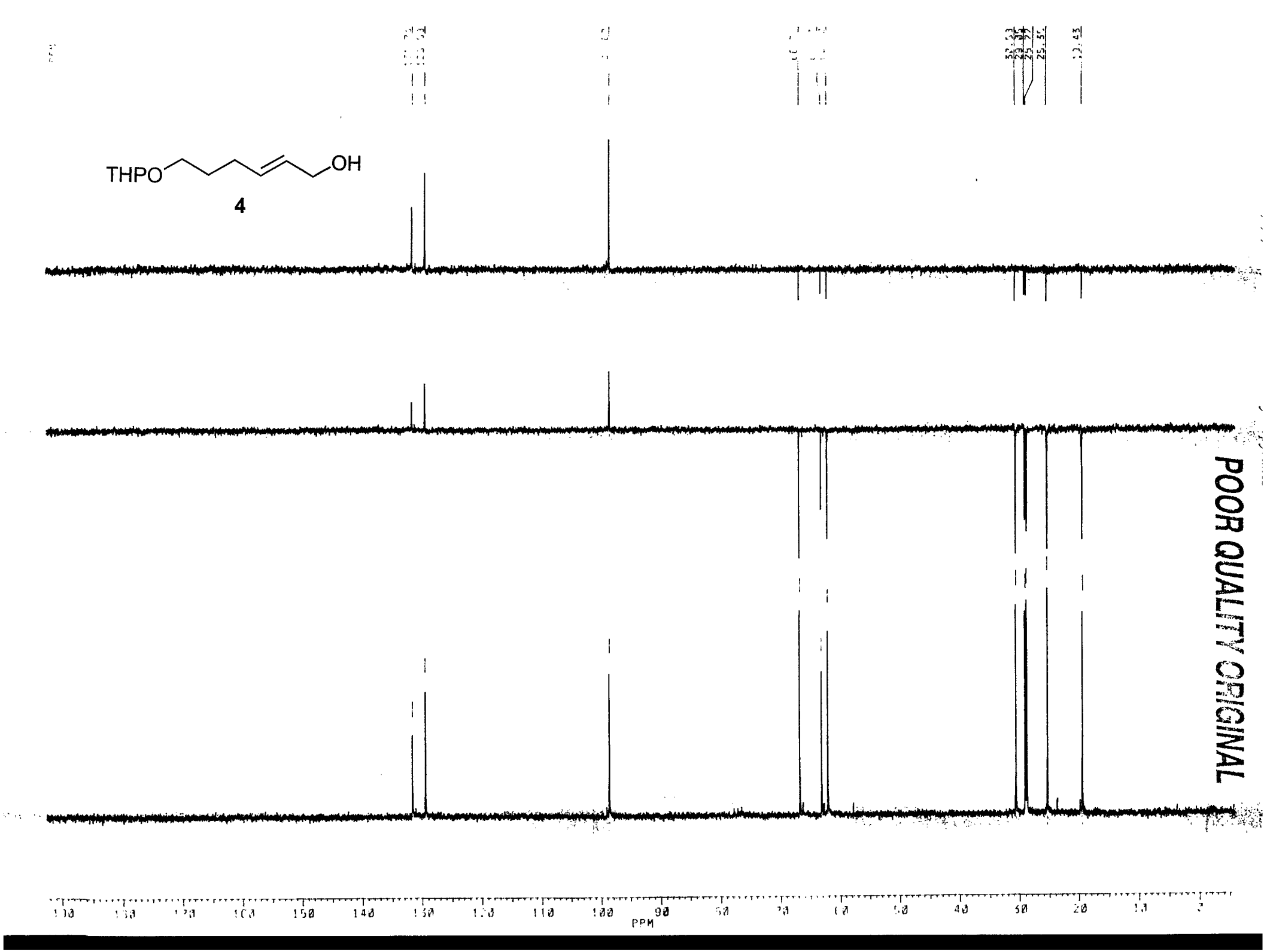
CO2Me
3
PPM
POOR QUALITY ORIGINAL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OH
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PPM
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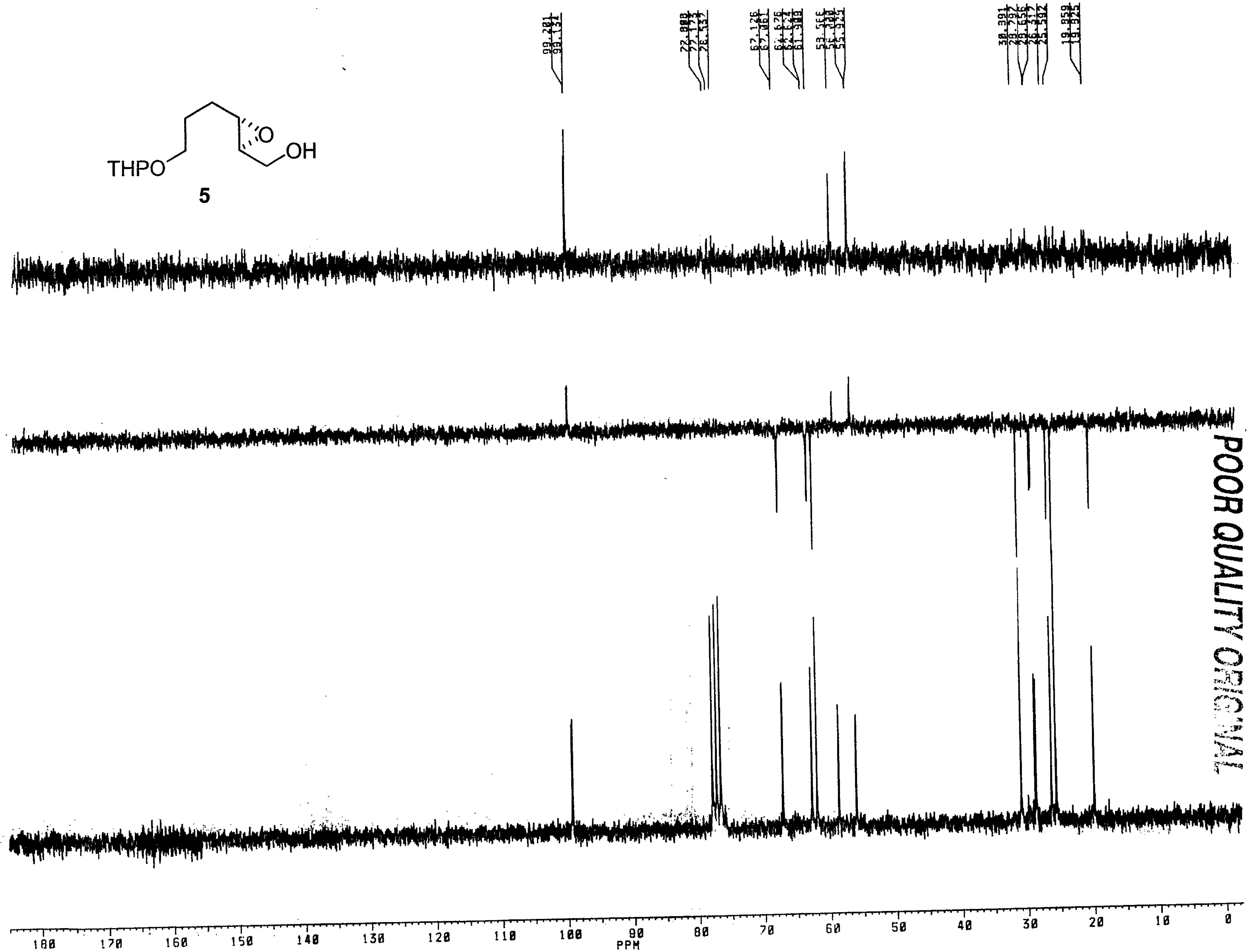
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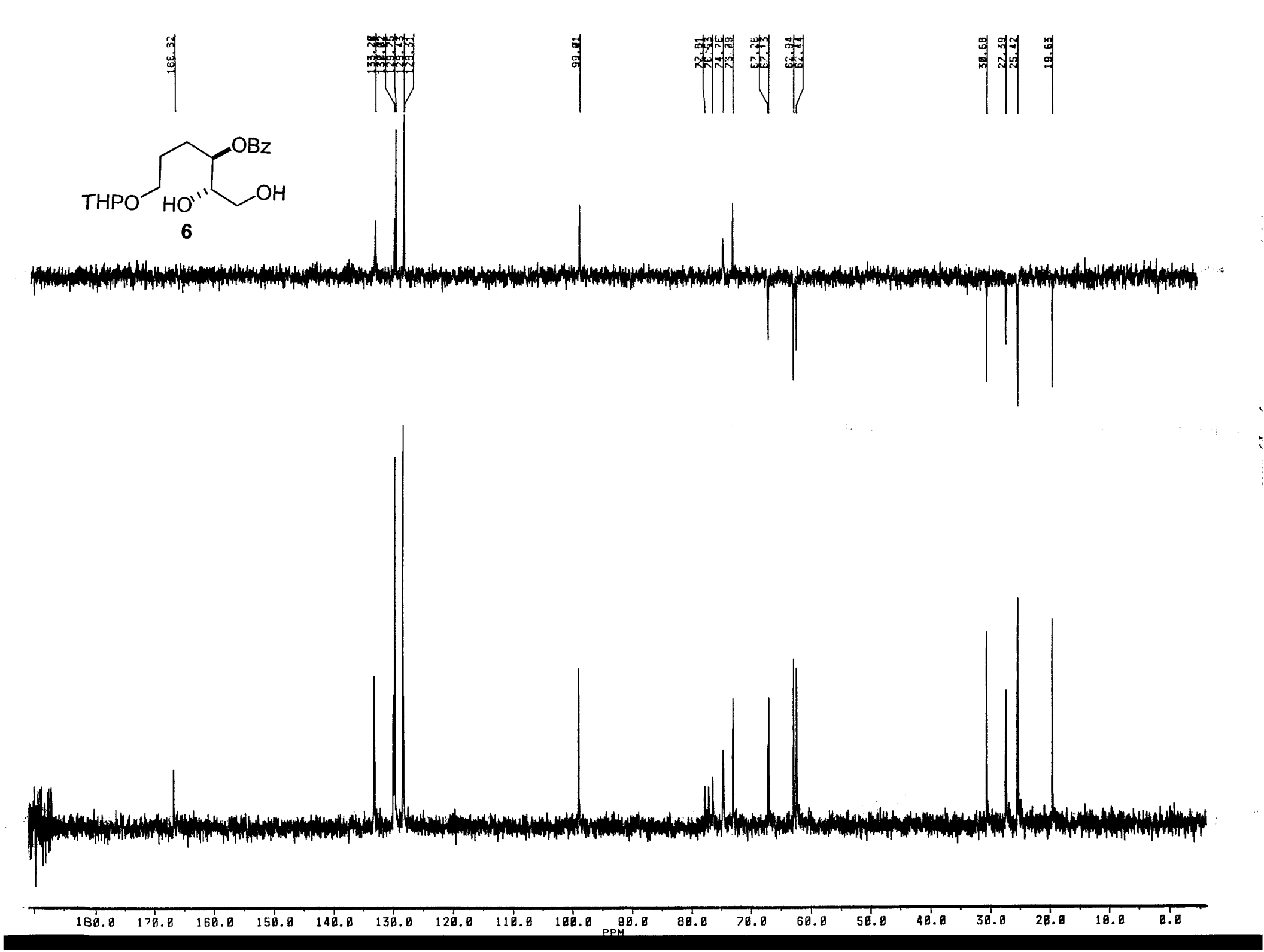
PPM
POOR QUALITY ORIGINAL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129.75
128.43
128.31
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72.81
70.53
64.75
63.09
62.24
62.13
60.34
60.11
38.68
27.39
25.42
19.63
OBz
THPO
HO
OH
6
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170.0
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150.0
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130.0
120.0
110.0
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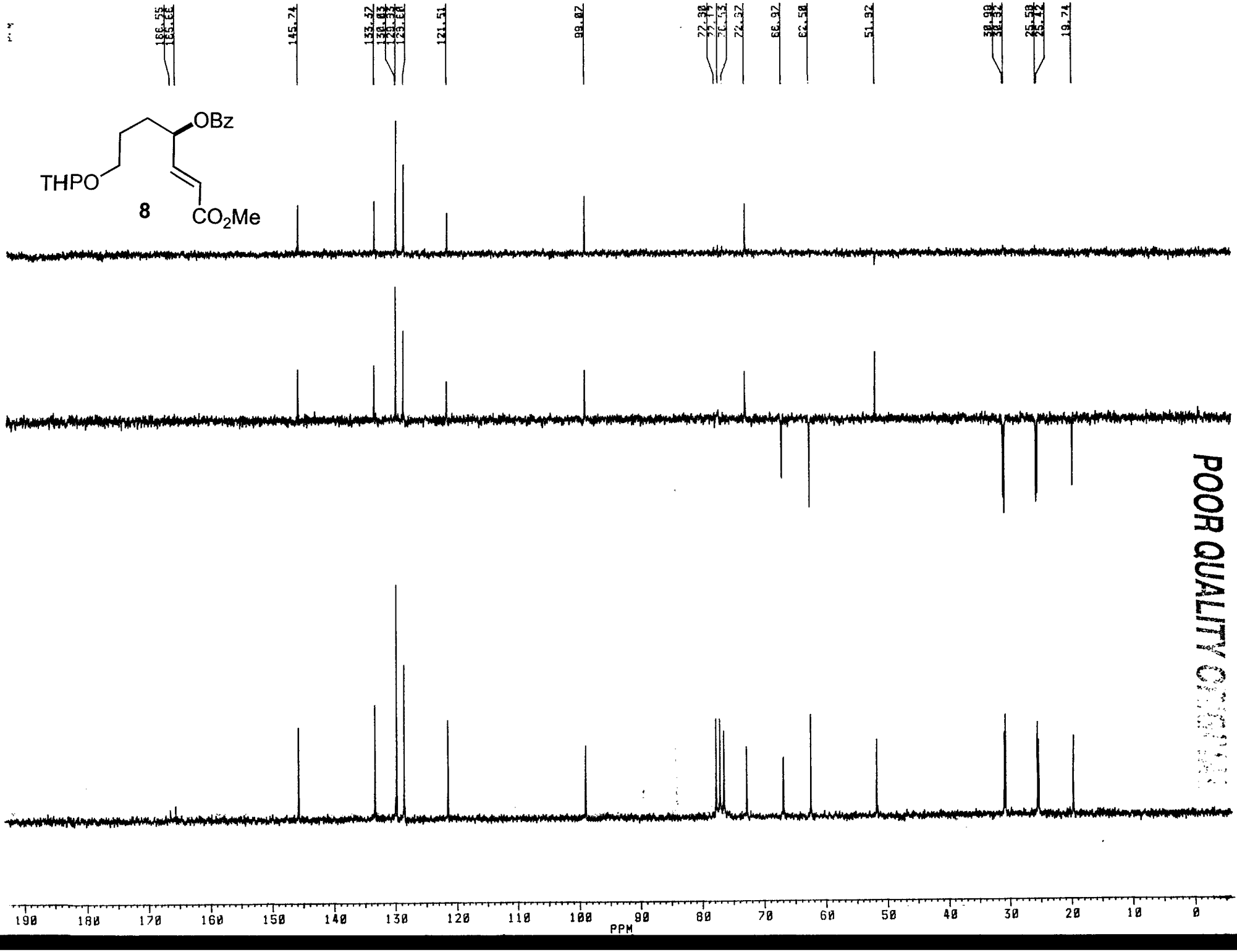
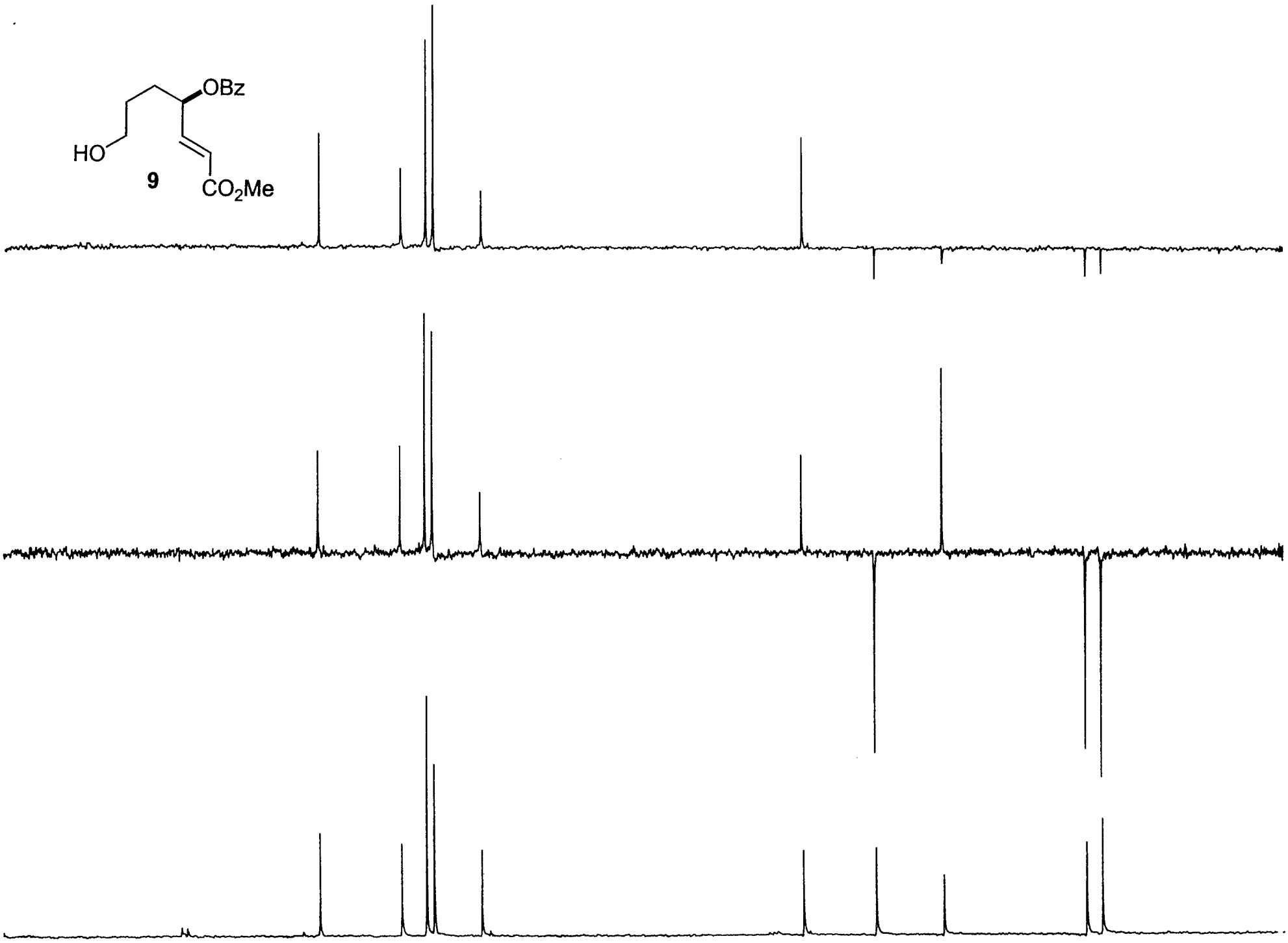
PPM

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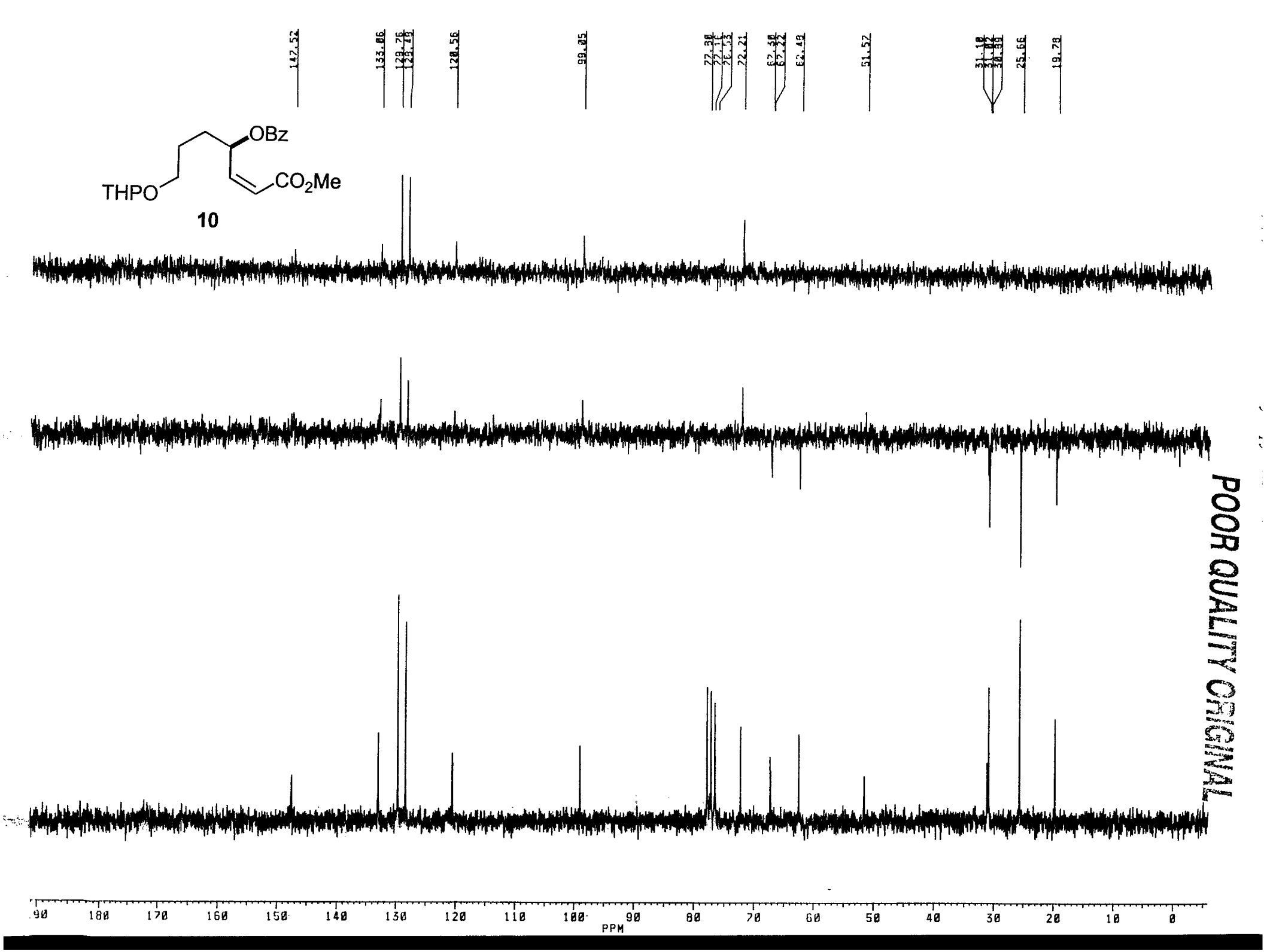
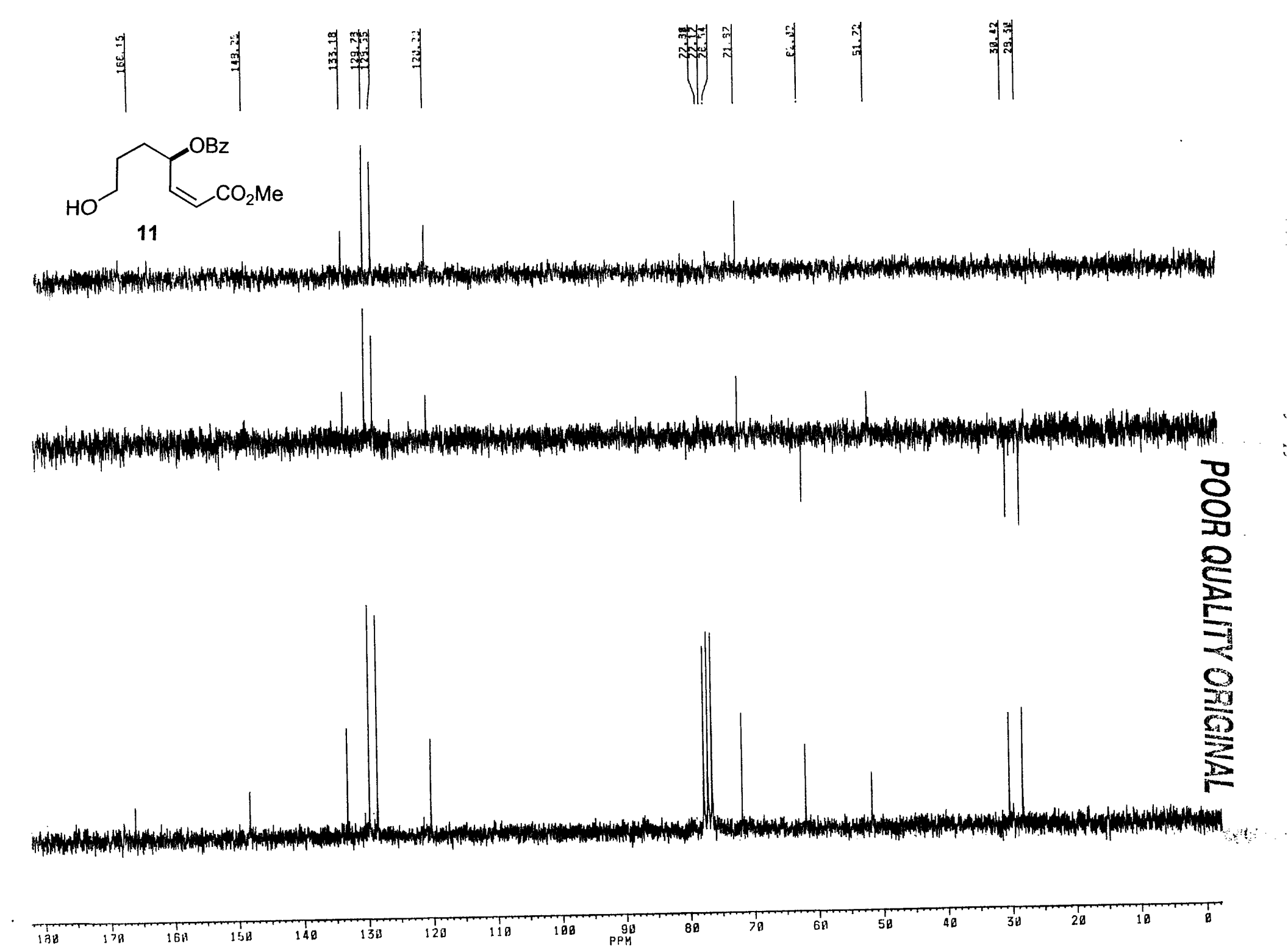
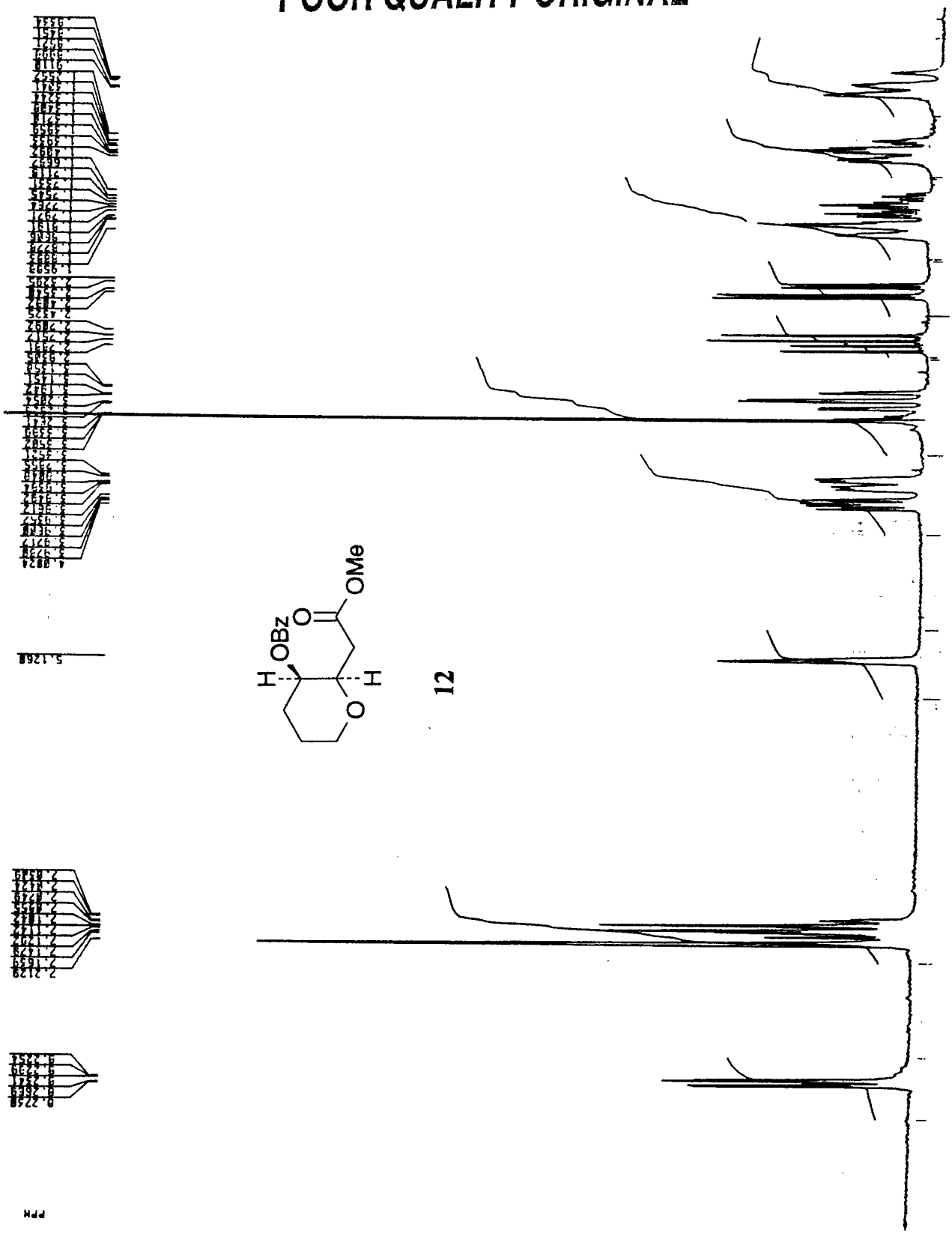
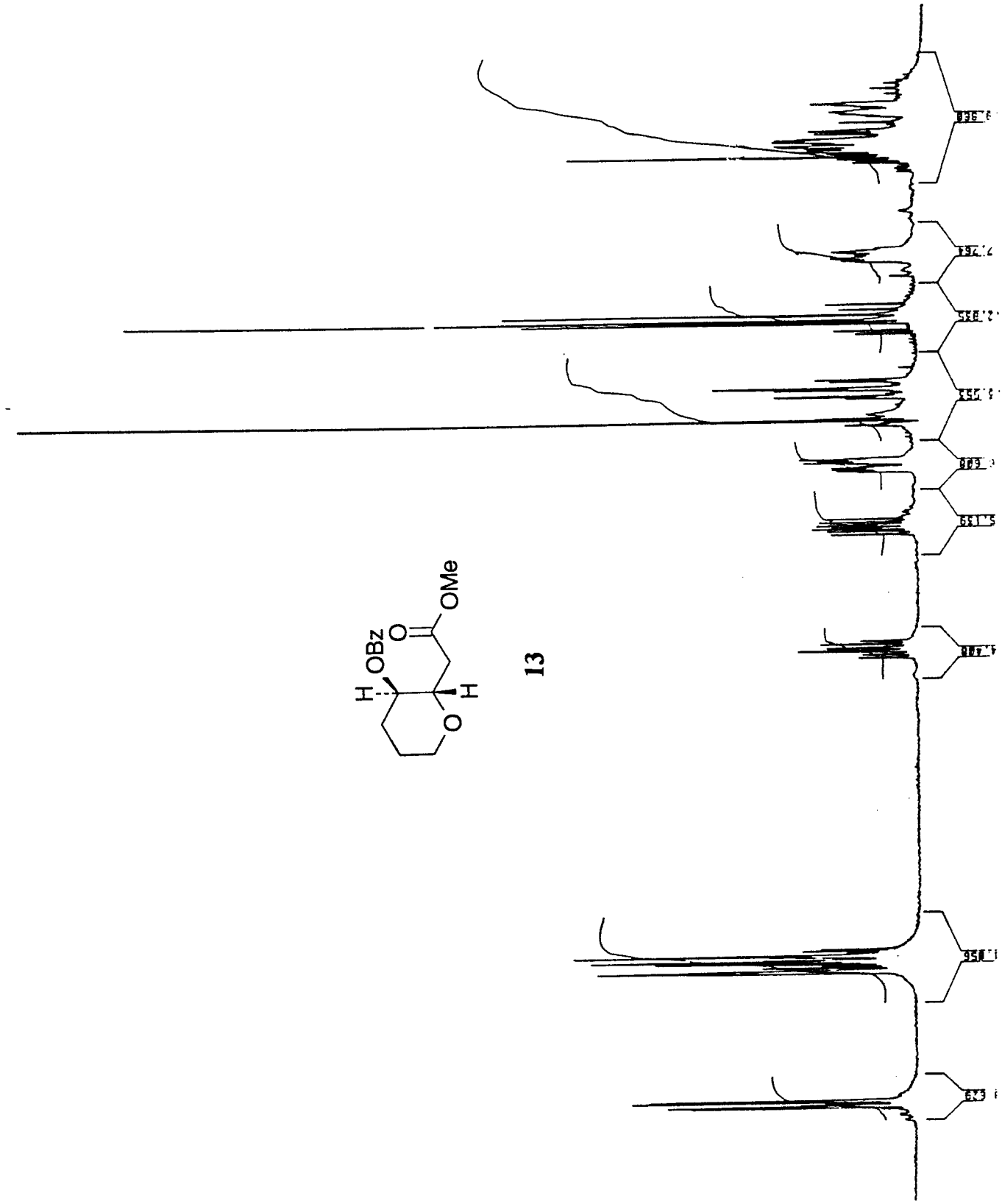
HO
9
CO2Me

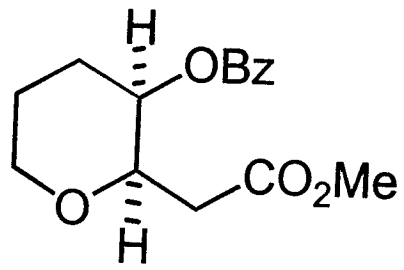




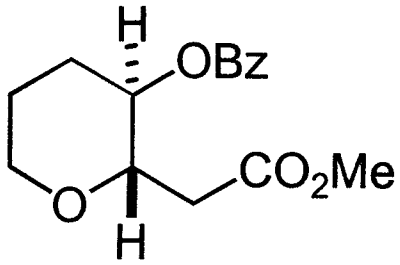




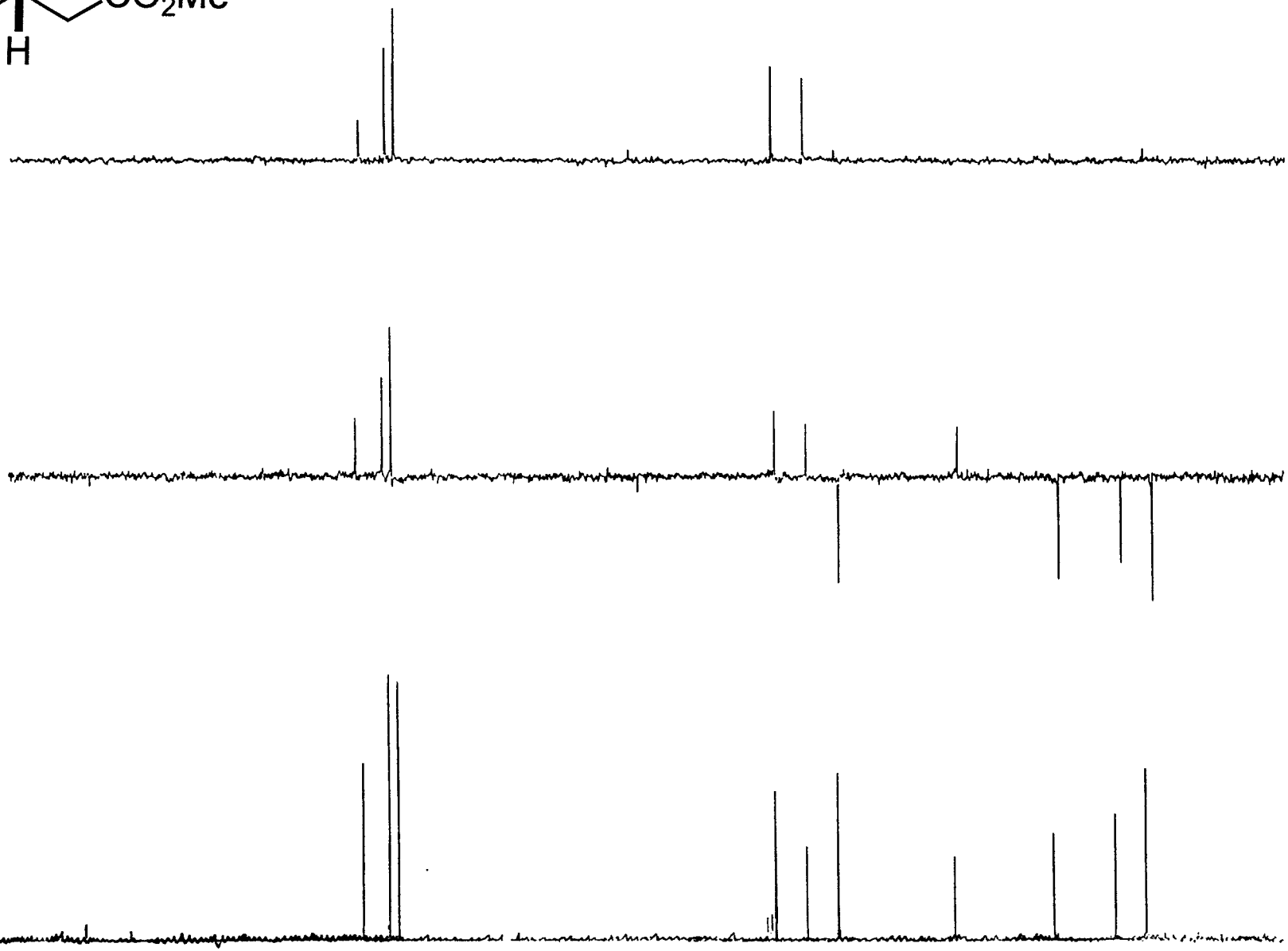
13



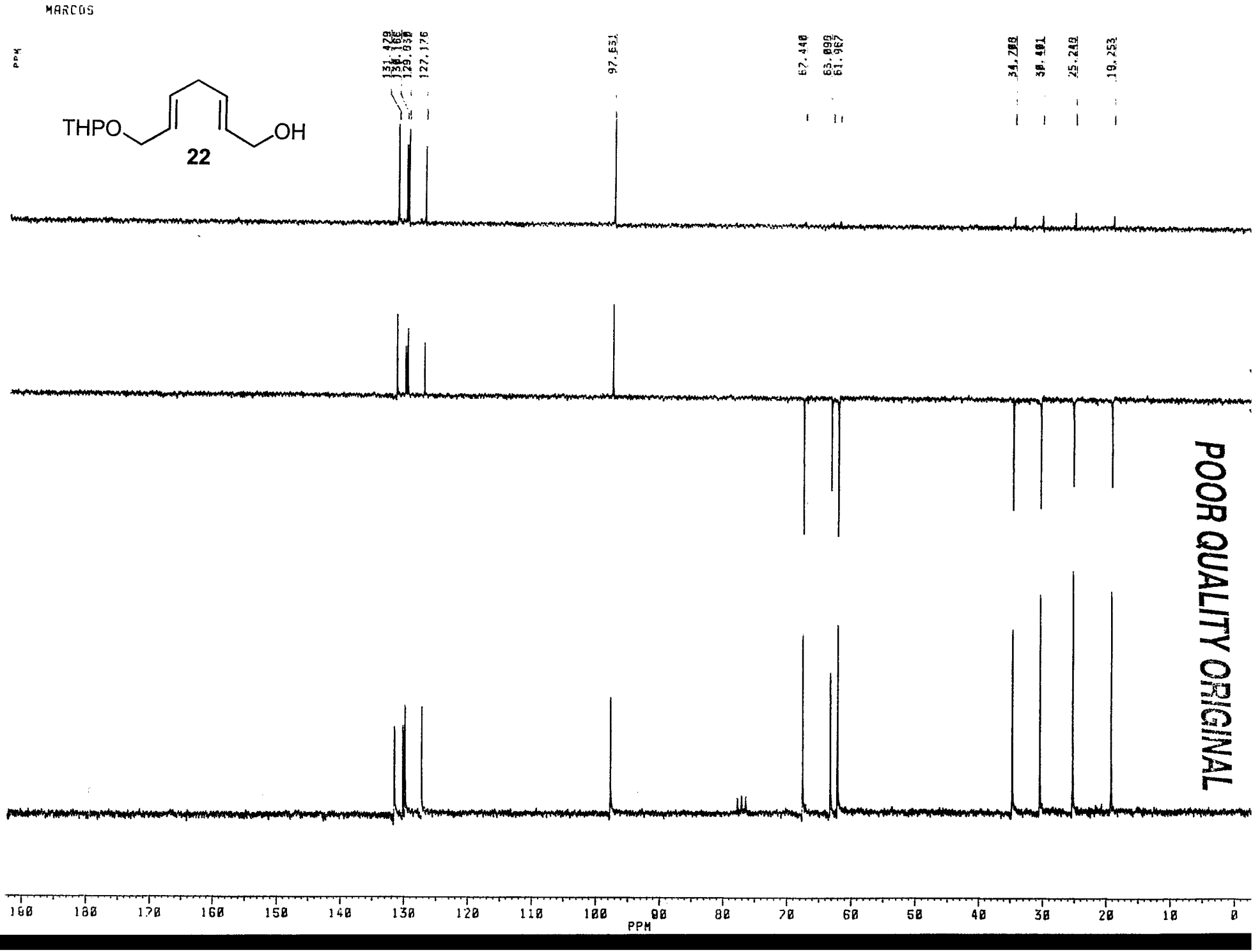
12



13



21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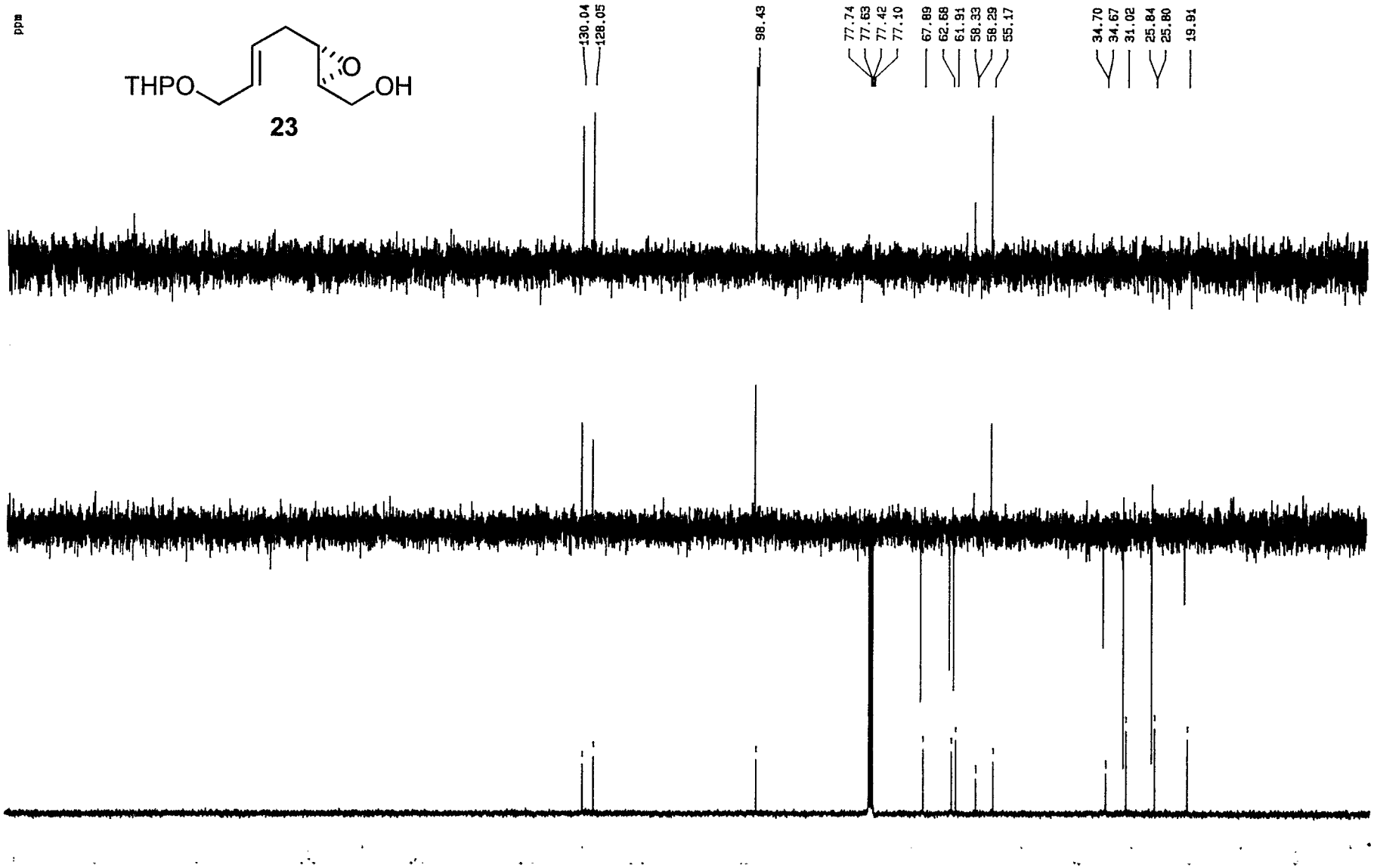
63.099
61.967
34.288
30.401
25.248
19.253
POOR QUALITY ORIGINAL
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM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OH
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128.05
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77.63
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77.10
67.89
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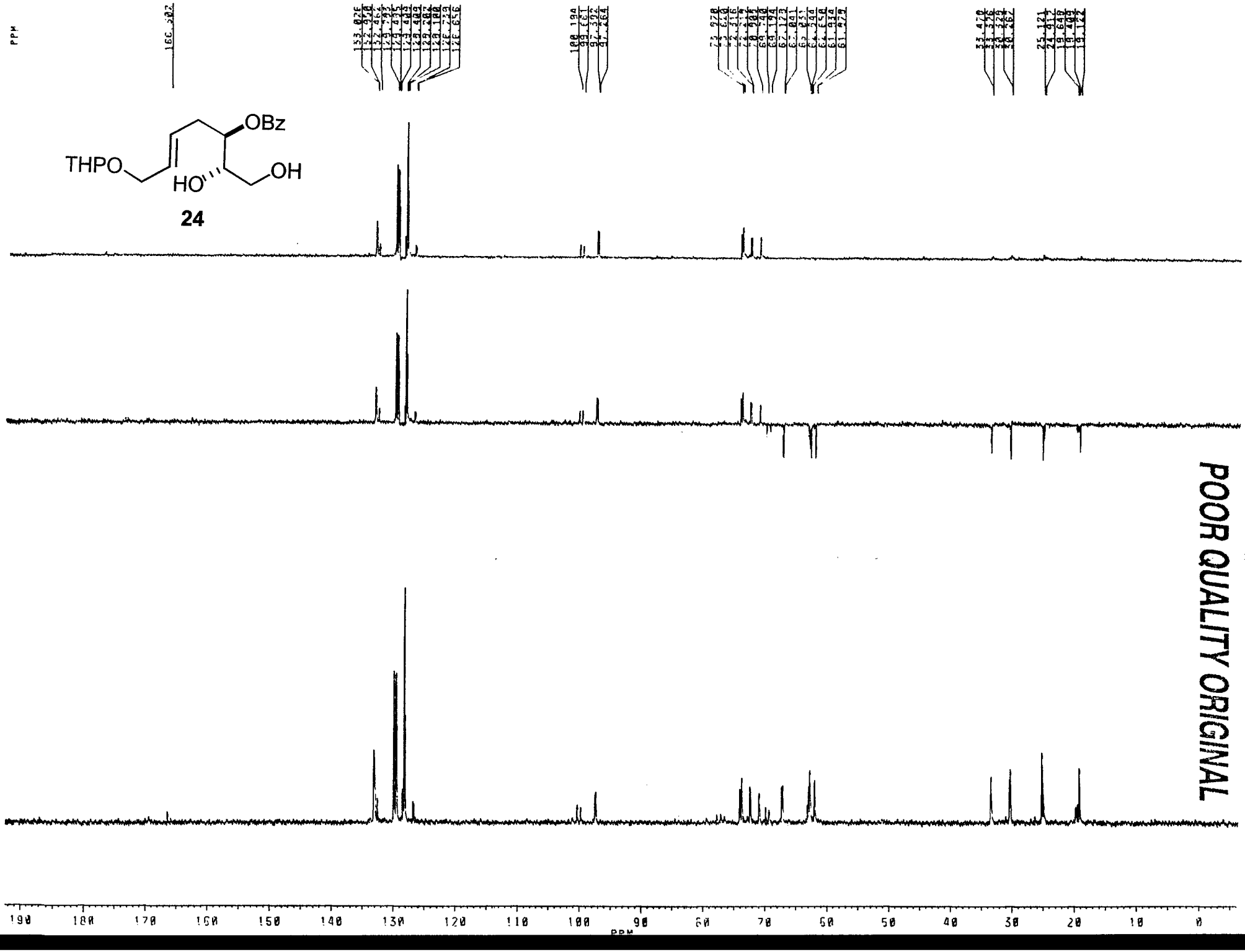
58.29
55.17
34.70
34.67
31.02
25.84
25.80
19.91


OBz
THPO
HO
OH
24
PPM
190
180
170
160
150
140
130
120
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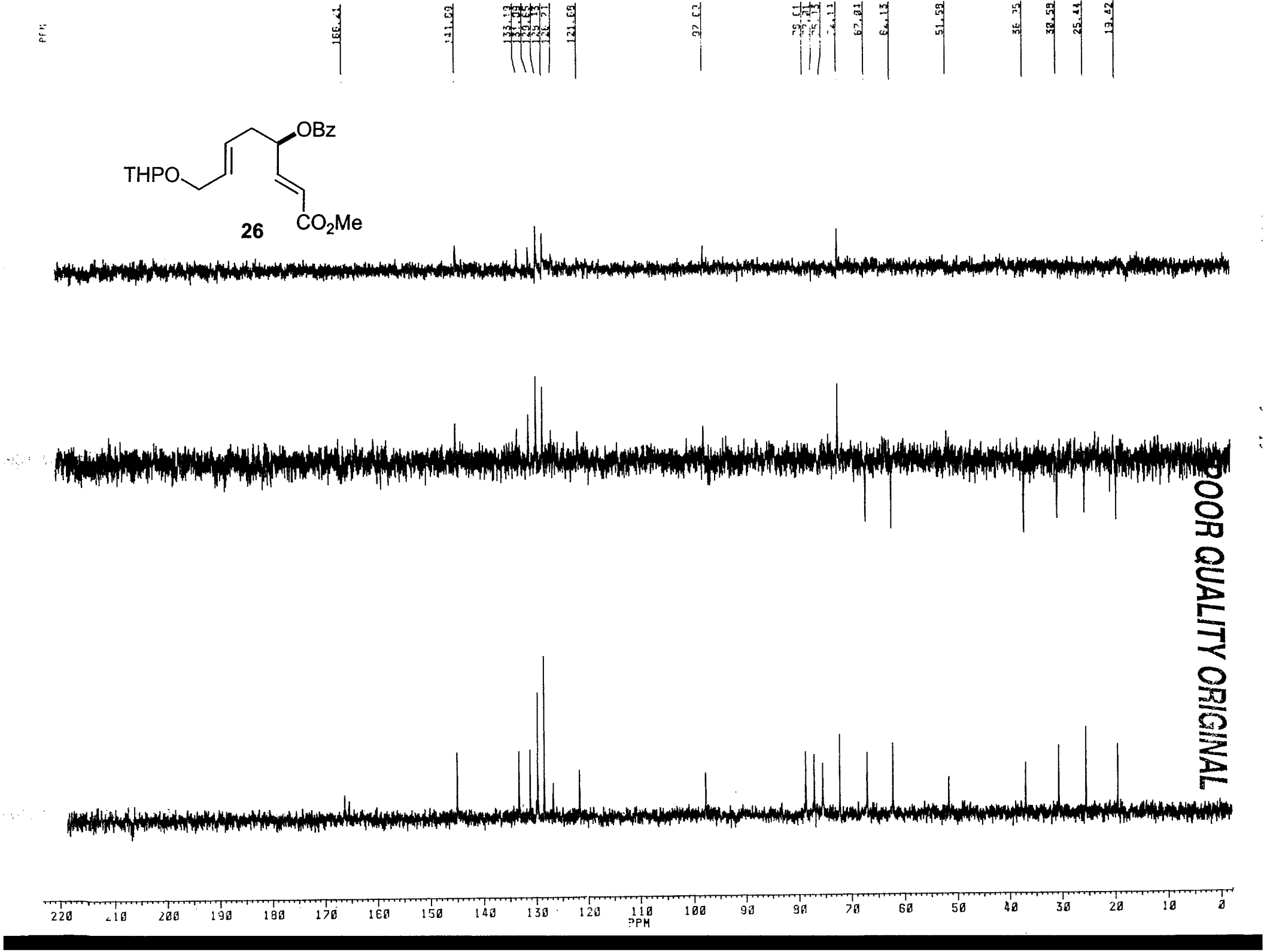
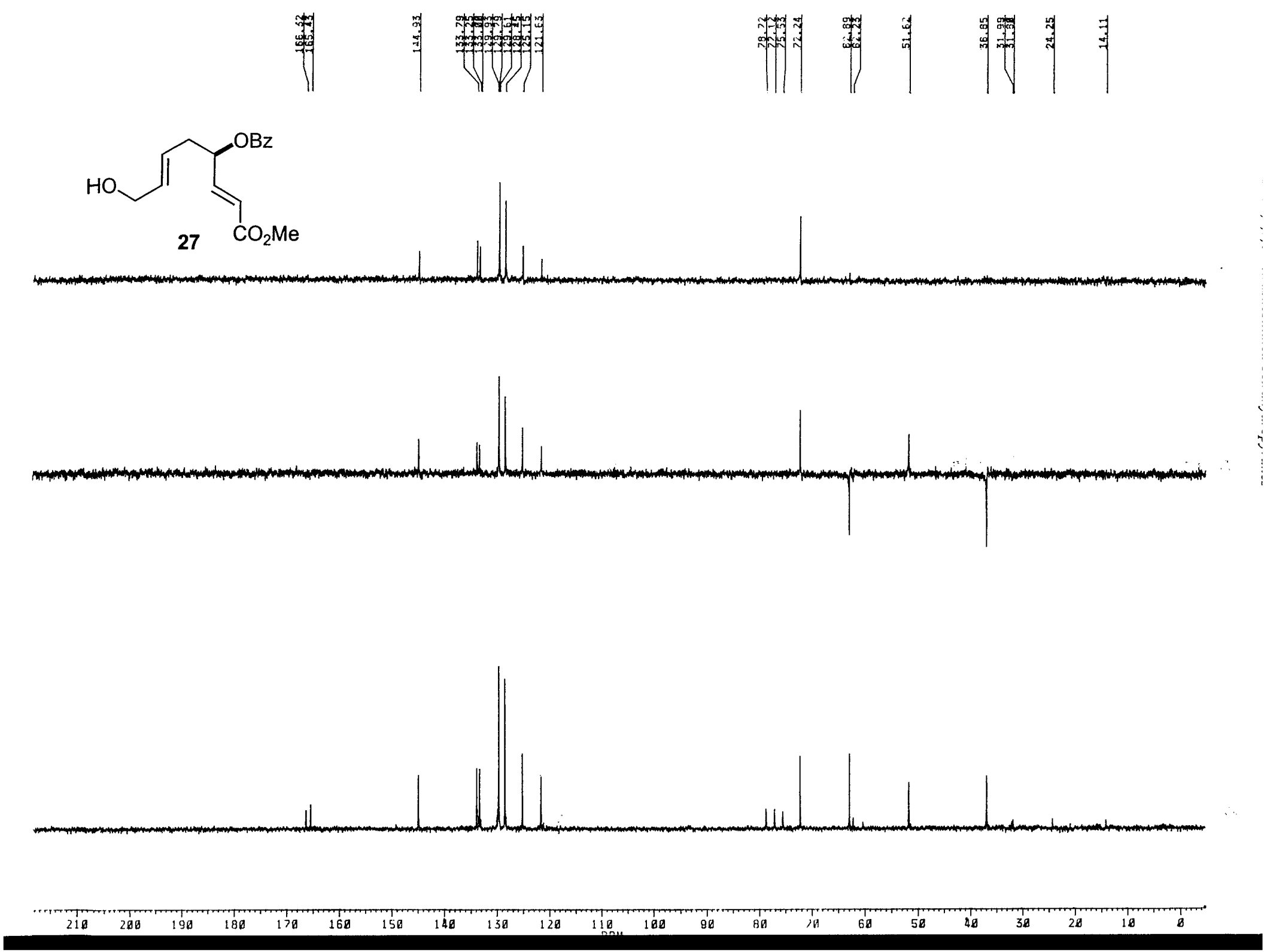
100
90
80
70
60
50
40
30
20
10
0
POOR QUALITY ORIGINAL

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165.41
144.33
133.79
133.27
133.00
132.88
129.78
129.61
128.45
128.15
121.63
78.22
77.14
75.32
72.24
64.89
62.23
51.62
36.85
31.99
31.58
24.25
14.11
OBz
HO
27
CO2Me
210
200
190
180
170
160
150
140
130
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100
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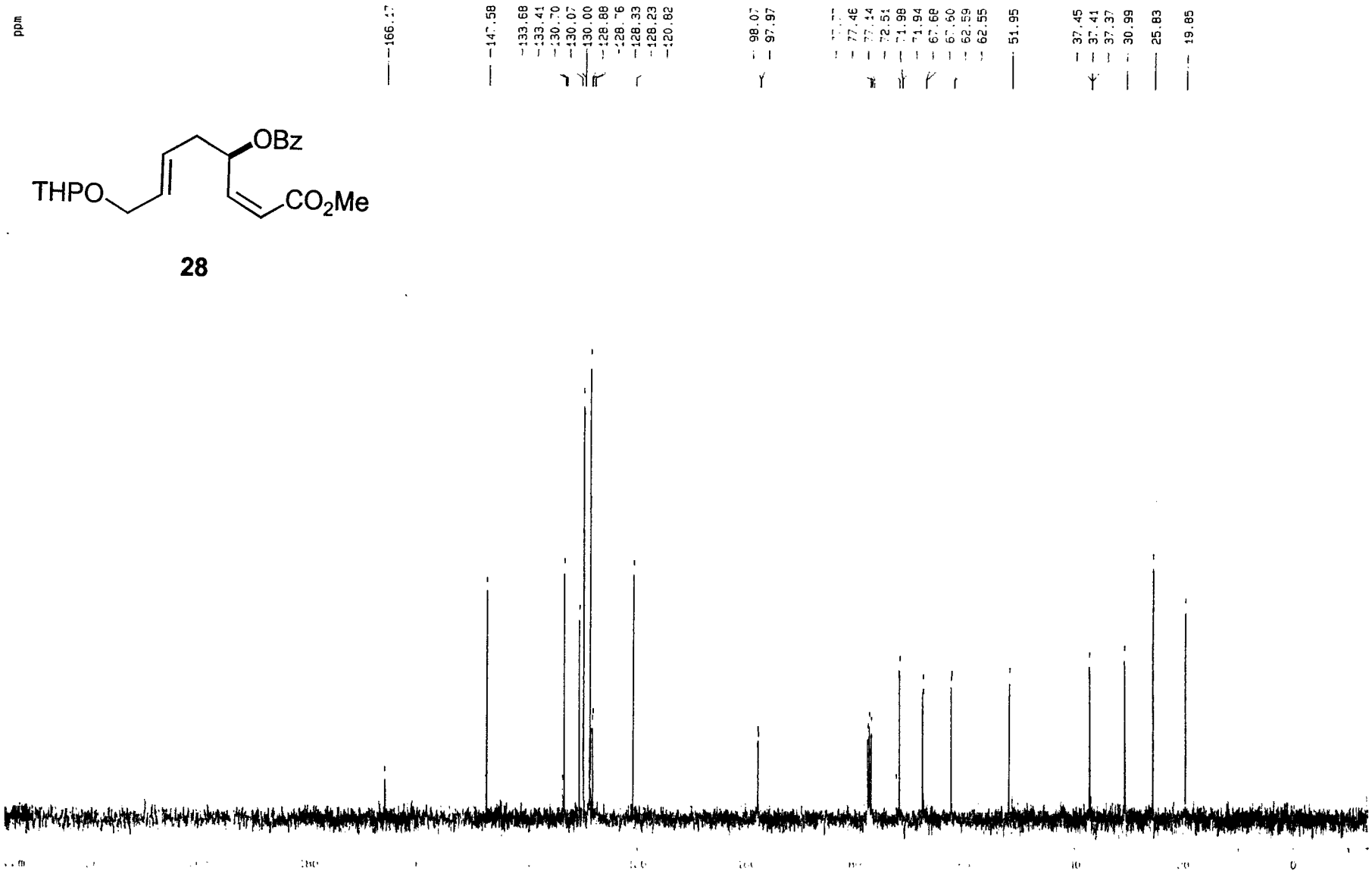
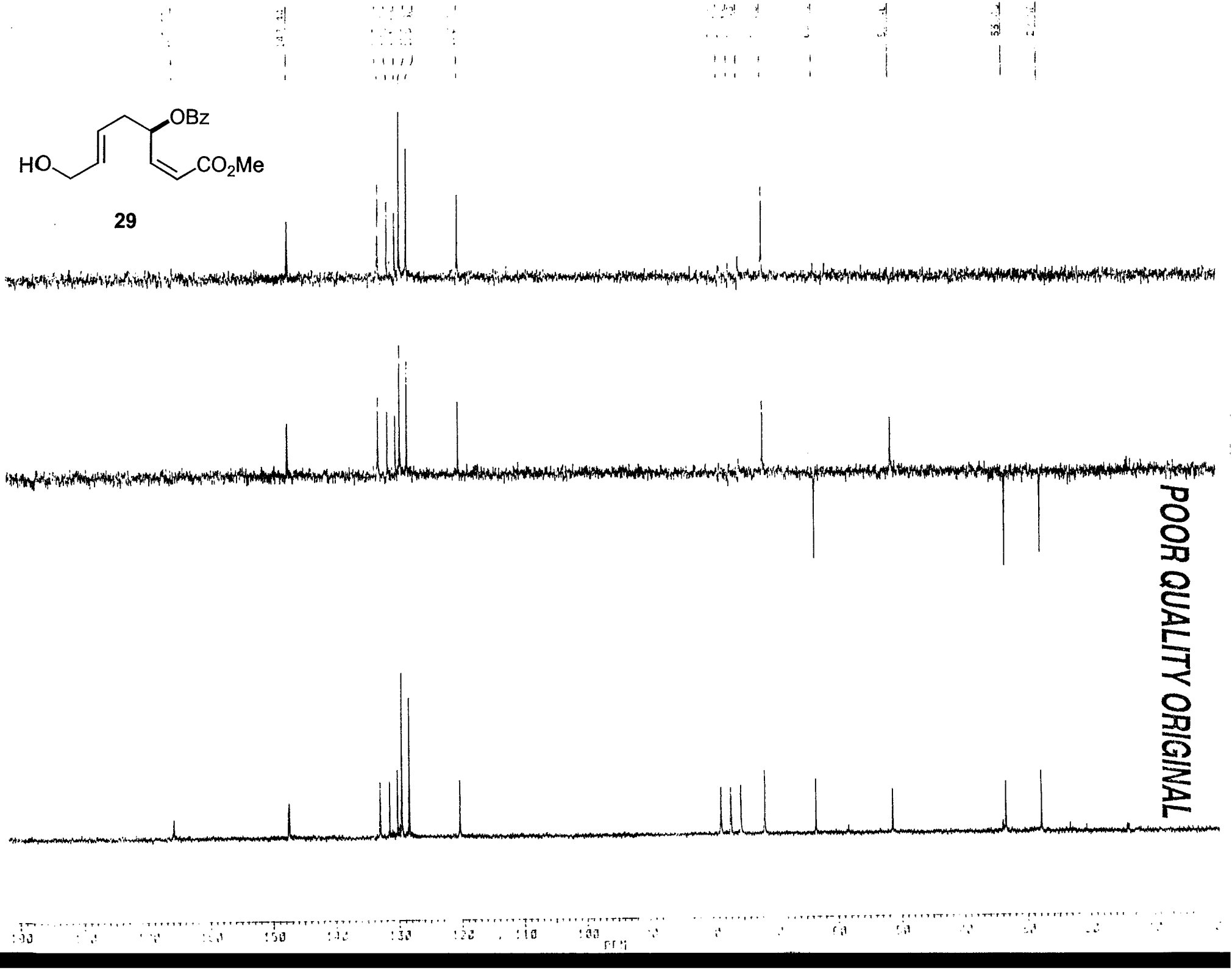
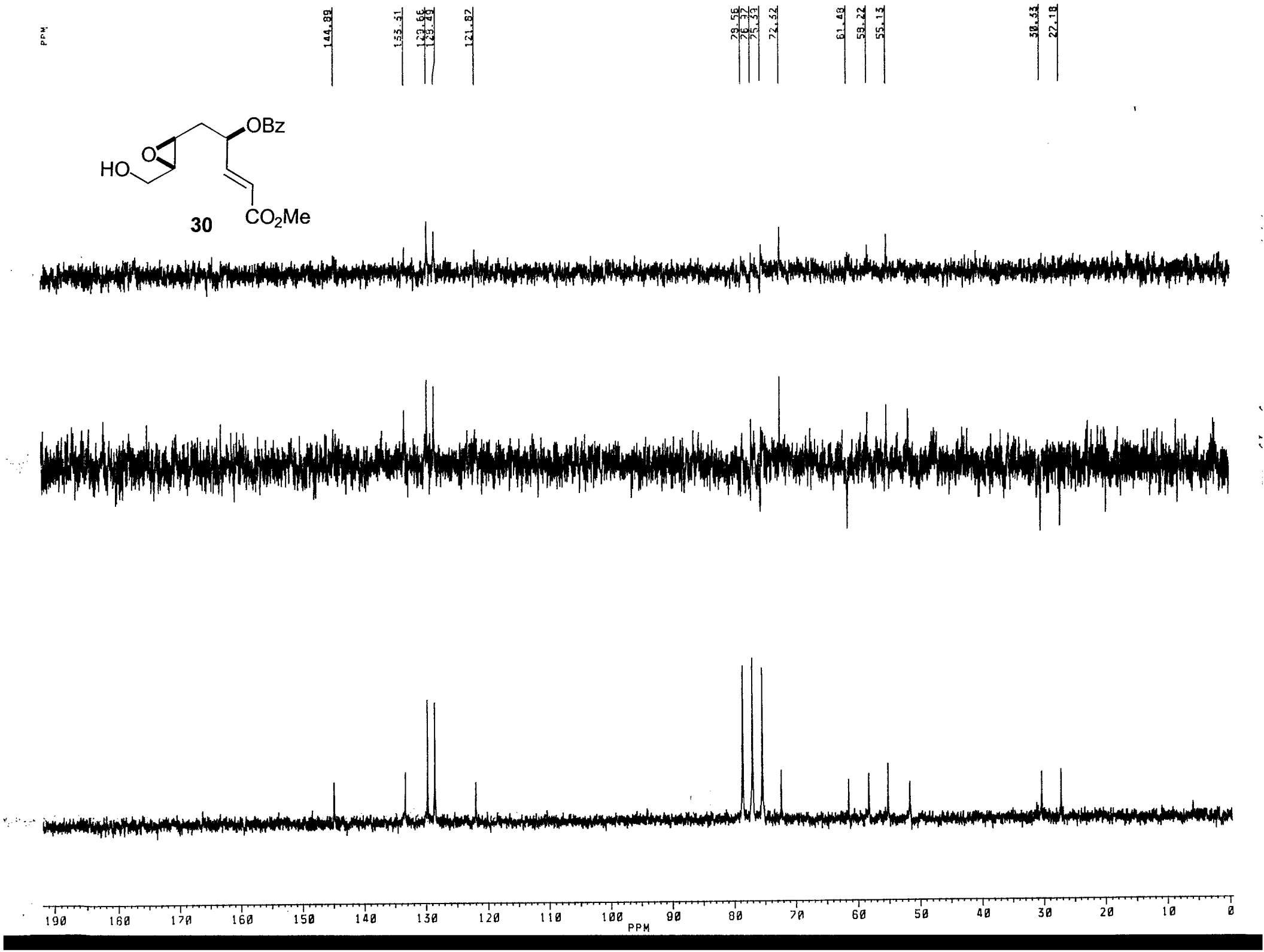
80
70
60
50
40
30
20
10
0
PPM




OBz
HO
CO2Me
29
POOR QUALITY ORIGINAL


PPM
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129.66
129.49
121.82
29.56
26.32
25.53
72.52
61.48
58.22
55.13
30.53
22.18
OBz
O
HO
CO2Me
30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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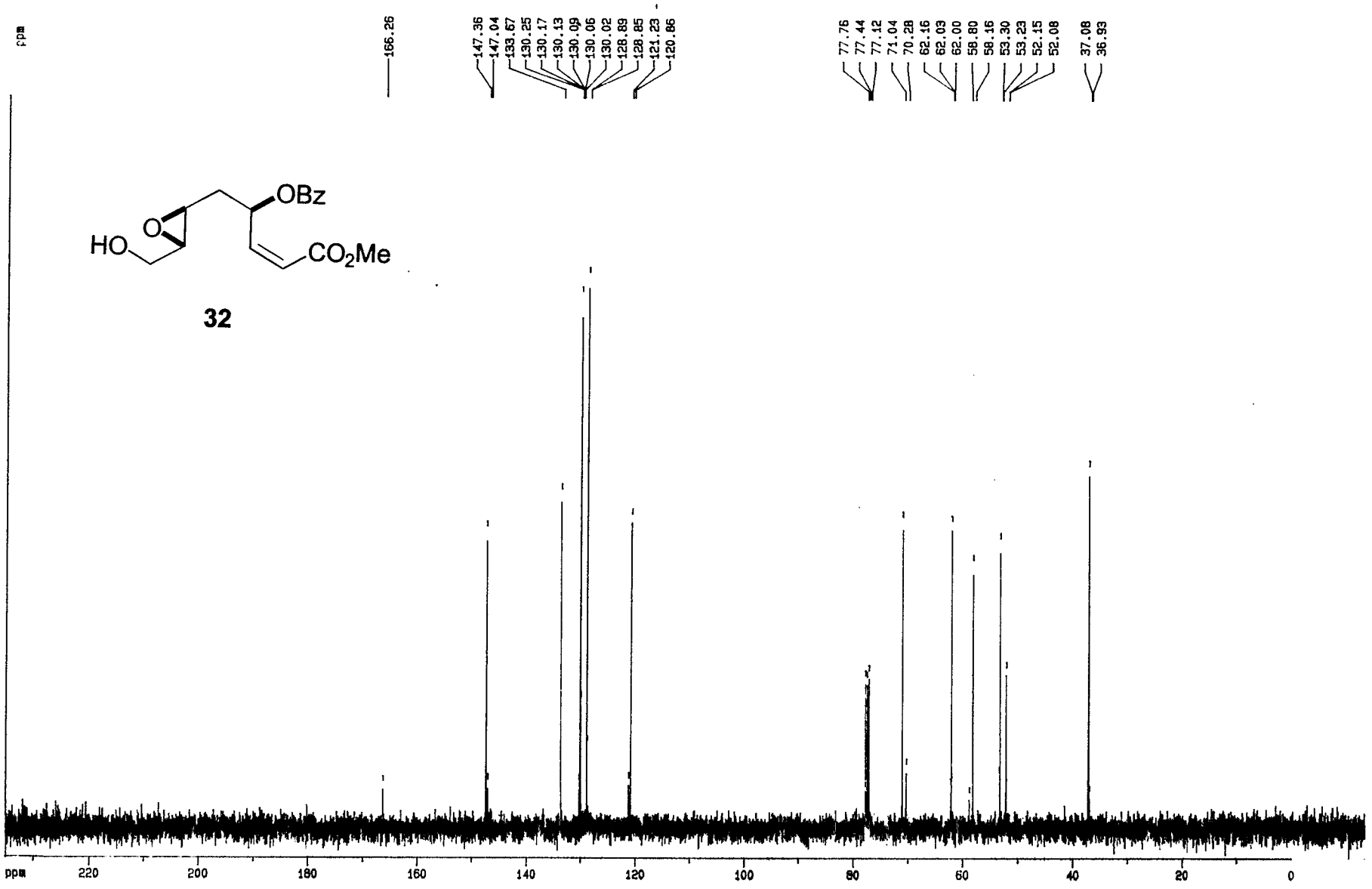
20
10
0
PPM


ppm
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133.67
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130.17
130.13
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130.06
130.02
128.89
128.85
121.23
120.86
77.76
77.44
77.12
71.04
70.28
62.16
62.03
62.00
58.80
58.16
53.30
53.23
52.15
52.08
37.08
36.93
OBz
O
HO
CO2Me
32
ppm
220
200
180
160
140
120
100
80
60
40
20
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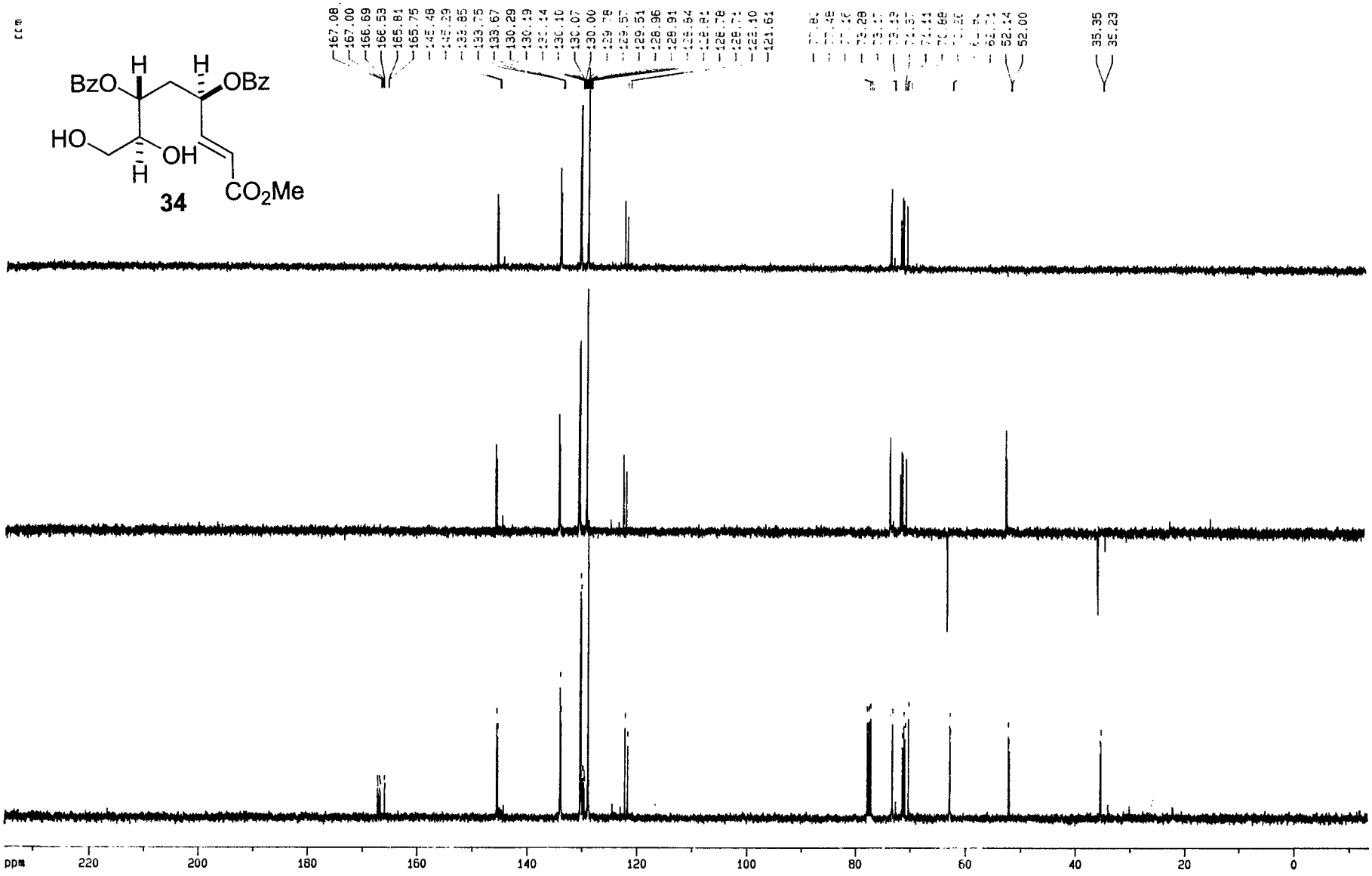

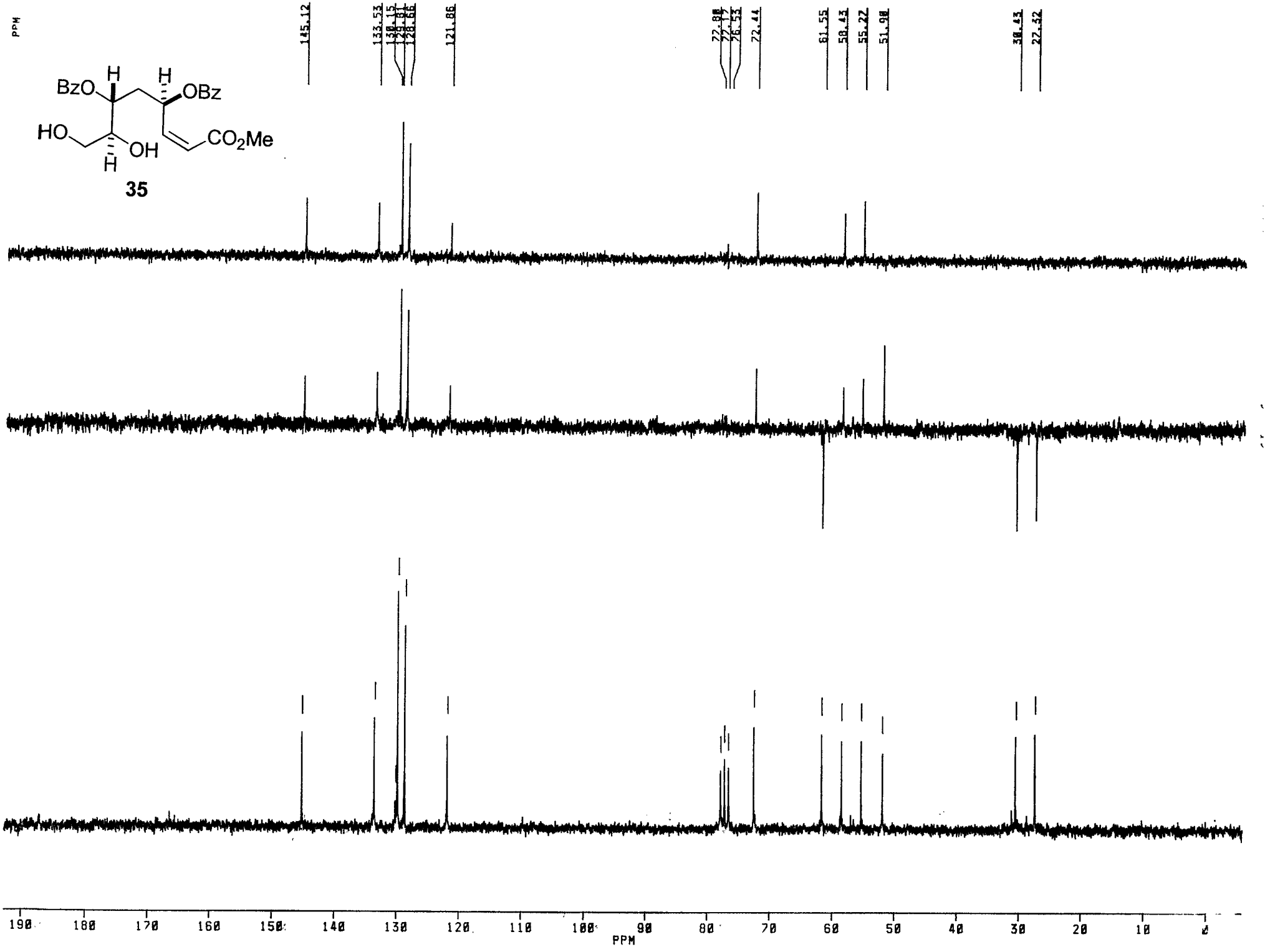
PPM
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130.15
129.81
128.66
121.86
77.27
76.53
72.44
61.55
58.43
55.22
51.98
30.43
22.32
BzO
H
H
OBz
HO
OH
H
CO2Me
35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM