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A. CHARACTERIZATION DATA FOR COMPOUNDS 19-24, 26-30, 32-36, 41, 43, 45 AND 46.

Compound **19a:** colorless oil; R_f 0.3 (hexane-EtOAc, 5:1); IR (neat) υ_{max} 1740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 3H), 3.35 (s, 3H), 3.45 (s, 3H), 3.56 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.76 (s, 3H), 3.88 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.95 (dd, *J* = 7.0, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 53.0, 59.0, 59.1, 60.1, 73.3, 83.2, 170.6. Anal. calcd for $C_8H_{15}BrO_4$: C 37.67%, H 5.93%; found: C 37.43%, H 6.09%.

Compound **19b:** colorless oil; R_f 0.25 (hexane-EtOAc, 5:1); IR (neat) υ_{max} 1740 cm^{-1}; MS (CI, isobutane) m/e 257 (58%, MH^+, ^{81}Br), 255 (58%, MH+, ^{79}Br) 225 (99%, MH^+-CH_3OH, ^{81}Br), 223 (100%, MH^+-MeOH, ^{79}Br); ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3H), 3.12 (s, 3H), 3.27 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.34 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.39 (s, 3H), 3.58 (s, 3H), 3.67 (dd, *J* = 5.7, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 52.9, 59.1, 60.6, 62.7, 72.8, 83.7, 170.4. Anal. calcd for $C_8H_{15}BrO_4$: C 37.67%, H 5.93%; found: C 37.59%, H 6.06%.

Methyl (±)-3,4-dimethoxy-2-methylbutyrates (20 and 21). Compounds **20** and **21** were isolated prior to purification as a 2:1 mixture (ratio determined by ^1H NMR): colorless oil; R_f 0.6, 0.55 (hexane-EtOAc, 5:1); IR (neat), υ_{max} 1730 cm^{-1}; MS (CI, isobutane) m/e 177 (56%, MH^+), 145 (100%, MH^+-MeOH); ^1H NMR (200 MHz, $CDCl_3$, 2:1 mixture of diastereomers, major *anti* product underlined) δ <u>1.11</u> (d, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 3H), 2.70 (qd, *J* = 7.1, 5.6 Hz, 1H), <u>2.80</u> (quint, *J* = 7.1 Hz, 1H), 3.33 (s, 3H), <u>3.34</u> (s, 3H), 3.4-3.6 (m, 3H), <u>3.38</u> (s, 3H), 3.40 (s, 3H), 3.68 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.81, 12.6, 41.25, <u>41.32</u>, <u>51.59</u>, 51.62, <u>58.03</u>, 58.55, 59.11, <u>59.23</u>, <u>71.31</u>, 72.53, 80.53, <u>81.46</u>, 175.09, <u>175.12</u>.

***t*-Butyl (±)-2(2*R**,4*R**)-2-[2-phenyl-1,3-dioxan-4-yl]-2-(phenylselenenyl)propionate (22).** Compound **22b**, prepared from **40b**, was isolated as a colorless oil (80%); R_f 0.3 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 1720, 1575 cm^{-1}; MS (EI) m/e 448 (31%, M^+), 163 (100%, M^+-$CH_3(PhSe)CHCO_2tBu$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.40 (s, 3H), 1.8-2.1 (m, 2H), 3.92 (qd, *J* = 11, 4.4 Hz, 1H), 4.2-4.35 (m, 2H), 5.40 (s, 1H), 7.2-7.6 (m, 10H); ^{13}C NMR

(50 MHz, $CDCl_3$) δ 17.5, 25.9, 27.8, 52.7, 67.2, 80.2, 81.0, 101.0, 125.8, 126.5, 128.0, 128.5, 128.8, 129.3, 138.1, 138.4, 171.5; HRMS (EI) calcd for $C_{23}H_{28}O_4Se$: 448.1153, found: 448.1169 (+3.6 ppm). Anal. calcd: C 61.74%, H 6.31%; found: C 61.63%, H 6.36%.

***t*-Butyl (±)-[2*R**,2(2*R**,4*R**)]-2-(2-phenyl-1,3-dioxan-4-yl)propionate (23):** colorless oil; R_f 0.3 (hexane-EtOAc, 5:1); IR (neat), υ_{max} 1730 cm^{-1}; MS (EI) m/e 292 (6%, M^+), 235 (31%, M^+-C_4H_9), 163 (14%, M^+-CH_2CHCO_2tBu); ^1H NMR (200 MHz, $CDCl_3$) δ 1.14 (d, J = 7 Hz, 3H), 1.44 (s, 9H), 1.82 (qd, J = 13, 5 Hz, 1H), 2.60 (quint, J = 7 Hz, 1H), 3.91-4.12 (m, 2H), 4.30 (ddd, J = 11, 5, 1 Hz, 1H), 5.53 (s, 1H), 7.3-7.5 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.2, 27.8, 27.9, 45.9, 66.7, 78.4, 80.2, 100.6, 125.8, 127.8, 128.4, 138.5, 173.6; HRMS calcd for $C_{17}H_{24}O_4$: 292.1675, found: 292.1666 (-3.0 ppm). Anal. calcd for $C_{17}H_{24}O_4$: C 69.84%, H 8.27%; found: C 69.86%, H 8.34%. GC t_R 15.4 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 220 °C/5min, 1 °C/min, 240 °C, 10 °C/min, 280 °C).

***t*-Butyl (±)-[2*S**,2(2*R**,4*R**)]-2-(2-phenyl-1,3-dioxan-4-yl)propionate (24):** colorless oil; R_f 0.4 (hexane-EtOAc, 5:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (EI) m/e 292 (4%, M^+), 235 (18%, M^+-C_4H_9), 163 (9%, M^+-CH_3CHCO_2tBu); ^1H NMR (200 MHz, $CDCl_3$) δ 1.26 (d, J = 7 Hz, 3H), 1.45 (s, 9H), 1.55 (qd, J = 2, 13 Hz, 1H), 1.85 (qd, J = 12.4, 5 Hz, 1H), 2.53 (quint, J = 7 Hz, 1H), 3.88-4.02 (m, 2H), 4.26 (ddd, J = 11, 5, 1 Hz, 1H), 5.51 (s, 1H), 7.3-7.5 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.9, 27.8, 28.9, 45.9, 66.5, 77.9, 80.2, 100.8, 125.7, 127.8, 128.3, 138.5, 173.1; HRMS calcd for $C_{17}H_{24}O_4$: 292.1675, found: 292.1664 (-3.5 ppm). Anal. calcd: C 69.84%, H 8.27%; found: C 69.86%, H 8.34%. GC t_R 14.7 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 220 °C/5 min, 1 °C/min, 240 °C, 10 °C/min, 280 °C).

***t*-Butyl (±)-[2*R**,2(4*R**)]-2-(2,2-dimethyl-1,3-dioxan-4-yl)propionate (26):** colorless oil; R_f 0.3 (hexane-EtOAc, 5:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (EI) m/e 229 (8%, M^+-CH_3), 121 (100%, M^+-123), 57 (40%, C_4H_9); ^1H NMR (200 MHz, $CDCl_3$) δ 1.07 (d, J = 7 Hz, 3H), 1.35 (s, 3H), 1.43 (s, 3H), 1.44 (s, 9H), 1.45-1.65 (m, 2H), 2.36 (qd, J = 7.1, 8.4 Hz, 1H), 3.8-4.08 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.3, 19.1, 28.0, 29.7, 46.5, 59.8, 71.0, 80.1, 98.3, 174.0; HRMS calcd for $C_{12}H_{21}O_4$ (M^+-CH_3): 229.1440, found: 229.1431 (-4.0 ppm). Anal. calcd for

$C_{13}H_{24}O_4$: C 63.91%, H 9.90%; found: C 63.74%, H 10.13%. GC t_R 15.0 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/2 min, 2 °C/min, 150 °C, 10 °C/min, 280 °C).

***t*-Butyl (±)-[2*S**,2(4*R**)]-2-(2,2-dimethyl-1,3-dioxan-4-yl)propionate (27):** colorless oil; R_f 0.4 (hexane-EtOAc, 5:1); IR (neat), υ_{max} 1720 cm^{-1}; MS (EI) m/e 229 (70%, M^+-CH_3), 173 (100%, M^+-71), 131 (70%, M^+-113), 113 (90%, M^+-$CH_3CHCOtBu$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.15 (d, J = 7 Hz, 3H), 1.37 (s, 3H), 1.44 (s, 12H), 1.68 (qd, J = 13, 6 Hz, 1H), 2.35 (quint, J = 7 Hz, 1H), 3.83 (ddd, J = 12, 6, 2 Hz, 1H), 3.95 (ddd, J = 12, 4, 3 Hz, 1H), 3.96 (td, J = 13, 3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.6, 19.1, 28.0, 28.9, 29.7, 46.1, 59.7, 70.2, 80.2, 98.4, 173.7; HRMS calcd for $C_{12}H_{21}O_4$ (M^+-CH_3): 229.1440, found: 229.1443 (+1.2 ppm). Anal. calcd for $C_{13}H_{24}O_4$: C 63.91%, H 9.90%; found: C 63.54%, H 9.89%. GC t_R 13.7 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/2 min, 2 °C/min, 150 °C, 10 °C/min, 280 °C).

***t*-Butyl (±)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(phenylselenenyl)propionate (28).** Compound **28a**, prepared from **41a**, was isolated as a colorless oil (81%); R_f 0.4 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 1720, 1575 cm^{-1}; MS (EI) m/e 386 (41%, M^+), 230 (66%, M^+-PhSe), 101 (100%, M^+-CH_3(PhSe)$CHCO_2tBu$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.39 (s, 3H), 1.43 (s, 3H), 1.49 (s, 3H), 3.72 (dd, J = 8.6, 6.2 Hz, 1H), 4.04 (dd, J = 8.6, 7.0 Hz, 1H), 4.43 (dd, J = 7.0, 6.2 Hz, 1H), 7.26-7.45 (m, 3H), 7.56-7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 24.4, 26.1, 27.8, 51.3, 66.1, 77.4, 81.6, 109.7, 126.7, 128.7, 129.3, 138.3, 171.4; HRMS calcd for $C_{18}H_{26}O_4Se$: 386.0996, found: 386.1012 (-3.9 ppm). Anal. calcd: C 56.10%, H 6.80%; found: C 56.47%, H 6.93%.

Compound **28b**, prepared from **41b**, was isolated as a colorless oil (92%); R_f 0.4 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 1710, 1580 cm^{-1}; MS (EI) m/e 386 (16%, M^+), 101 (100%, M^+-CH_3(PhSe)$CHCO_2tBu$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.39 (s, 9H), 1.41 (s, 3H), 1.43 (s, 3H), 4.09 (dd, J = 9.0, 6.2 Hz, 1H), 4.16 (dd, J = 9.0, 6.8 Hz, 1H), 4.53 (t, J = 6.5 Hz, 1H), 7.25-7.45 (m, 3H), 7.56-7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 24.7, 26.1,

27.8, 51.3, 66.3, 78.5, 81.3, 109.7, 126.1, 128.8, 129.3, 138.1, 171.4; HRMS calcd for $C_{18}H_{26}O_4Se$: 386.0996, found: 386.1003 (-1.7 ppm). Anal. calcd: C 56.10%, H 6.80%; found: C 56.23%, H 6.85%.

***t*-Butyl (±)-[2*R**,2(4*S**)]-2-(2,2-dimethyl-1,3-dioxolan-4-yl)propionate (29):** R_f 0.5 (hexane-EtOAc, 9:1); IR (neat), υ_{max} 1720, 1470, 1450 cm^{-1}; MS (EI) m/e 215 (5%, M^+-CH_3), 159 (100%, M^+-71), 101 (80%, M^+-CH_3CHCO_2tBu), 99 (90%, M^+-131); ^1H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, J = 7.1 Hz, 3H), 1.34 (s, 3H), 1.42 (s, 3H), 1.46 (s, 9H), 2.59 (quint, J = 7.1 Hz, 1H), 3.72 (dd, J = 8.4, 6.2 Hz, 1H), 4.01 (dd, J = 8.4, 6.4 Hz, 1H), 4.27 (td, J = 6.0, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 25.3, 26.6, 28.0, 43.9, 66.5, 76.8, 80.5, 109.0, 173.4; HRMS calcd for $C_{11}H_{19}O_4$ (M^+-CH_3): 215.1289, found: 215.1283 (-2.6 ppm). Anal. calcd for $C_{12}H_{22}O_4$: C 62.58%, H 9.63%; found: C 62.35%, H 9.87%. GC t_R 8.4 min ($t_{inj.}$ 300 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/2 min, 2 °C/min, 150 °C, 10 °C/min, 280 °C).

***t*-Butyl (±)-[2*S**,2(4*S**)]-2-(2,2-dimethyl-1,3-dioxolan-4-yl)propionate (30):** R_f 0.6 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 1720, 1480, 1460 cm^{-1}; MS (EI) m/e 207 (10%, M^+-23), 159 (20%, M^+-71), 101 (100%, M^+-CH_3CHCO_2tBu); ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, J = 7.1 Hz, 3H), 1.36 (s, 3H), 1.40 (s, 3H), 1.44 (s, 9H), 2.47 (qd, J = 7.1, 8.4 Hz, 1H), 3.68-3.77 (m, 2H), 4.06-4.18 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 25.4, 26.7, 28.0, 68.4, 77.2, 80.8, 109.0, 173.3. Anal. calcd for $C_{12}H_{22}O_4$: C 62.58%, H 9.63%; found: C 62.33%, H 9.77%. GC t_R 7.4 min ($t_{inj.}$ 300 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/2 min, 2°/min, 150 °C, 10 C °/min, 280 °C).

***t*-Butyl (±)-[2*R**,2(4*S**,5*S**)]-2-(2,2-dimethyl-5-methyl-1,3-dioxolan-4-yl)propionate (32):** colorless oil; R_f0.5 (hexane-EtOAc, 5:1); IR (neat), υ_{max} 1720 cm^{-1}; MS (CI, isobutane) m/e 245 (30%, MH^+), 189 (100%, MH^+-isobutylene), 131 (92%, M^+-113); ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 7.3 Hz, 3H), 1.29 (d, J = 6.0 Hz, 3H), 1.37 (s, 3H), 1.40 (s, 3H), 1.46 (s, 9H), 2.60 (quint, J = 7.0 Hz, 1H), 3.75 (dd, J = 7.6, 6.7 Hz, 1H), 3.97 (qd, J = 6.0, 7.6 Hz; 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 19.1, 27.0, 27.4, 28.1, 43.3, 74.4, 80.6, 83.4, 107.9, 173.0.

GC t_R 11.4 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/10 min, 1 °C/min, 130 °C, 20 °C/min, 280 °C).

***t*-Butyl (±)-[2*S**,2(4*S**,5*S**)]-2-(2,2-dimethyl-5-methyl-1,3-dioxolan-4-yl)propionate (33):** colorless oil; R_f 0.7 (hexane-EtOAc, 3:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (CI, NH_3) m/e 262 (50%, MH^+NH_3), 245 (15%, MH^+), 206 (100%, M^+-38), 189 (5%, MH^+-isobutylene), 148 (10%, M^+-96); ^1H NMR (200 MHz, $CDCl_3$) δ 1.23 (d, J = 6.9 Hz, 3H), 1.28 (d, J = 6.0 Hz, 3H), 1.37 (s, 3H), 1.41 (s, 3H), 1.46 (s, 9H), 2.48 (quint, J = 7.1 Hz, 1H), 3.72 (t, J = 7.7 Hz, 1H), 3.97 (qd, J = 7.7, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 18.7, 27.1, 27.4, 28.1, 43.6, 75.4, 80.8, 83.1, 108.0, 173.3. GC t_R 10.2 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/10 min, 1 °C/min, 130 °C, 20 °C/min, 280 °C).

***t*-Butyl (±)-[2(4*S**,5*S**)]-2-(2,2-dimethyl-5-methyl-1,3-dioxolan-4-yl)-2-(phenylselenenyl)propionate (34).** Compound **34a**, prepared from **43a**, was isolated as a colorless oil (27%), with lactone as side-product; R_f 0.6 (hexane-EtOAc, 5:1); IR (neat) ν_{max} 1720, 1705, 1575 cm^{-1}; MS (CI, isobutane) m/e 400 (17%, MH^+), 343 (67%), 341 (34%), 287 (100%), 285 (100%, $CH_3(PhSe)CHCO_2tBu$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (d, J = 6.4 Hz, 3H), 1.36 (s, 3H), 1.42 (s, 9H), 1.54 (s, 3H), 1.55 (s, 3H), 4.30-4.39 (m, 2H), 7.3-7.7 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 18.2, 24.8, 27.2, 27.8, 51.6, 74.0, 78.2, 81.4, 107.1, 127.7, 128.6, 129.5, 138.5, 171.4. Anal. calcd for $C_{19}H_{28}O_4Se$: C 57.14%, H 7.07%; found: C 57.48%, H 7.13%.

***t*-Butyl (±)-[2*S**,2(4*R**,5*S**)]-2-(2,2-dimethyl-5-methyl-1,3-dioxolan-4-yl)propionate (35):** colorless oil; R_f 0.4 (hexane-EtOAc, 5:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (CI, isobutane) m/e 245 (32%, MH^+), 189 (100%, MH^+-isobutylene), 173 (31%, M^+-71), 131 (44%, M^+-113); ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, J = 7.0 Hz, 3H), 1.17 (d, J = 6.4 Hz, 3H), 1.31 (s, 3H), 1.43 (s, 3H), 1.46 (s, 9H), 2.52 (qd, J = 7.0, 10.2 Hz, 1H), 4.10 (dd, J = 10.2, 5.1 Hz, 1H), 4.25 (quint, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 15.6, 25.8, 28.0, 28.0, 41.4, 73.1, 79.6, 80.4, 107.7, 173.7. Anal. calcd for $C_{13}H_{24}O_4$: C 63.91%, H 9.90%; found: C 63.97%, H

10.16%. GC t_R 14.0 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/10 min, 1 °C/min, 130 °C, 20 °C/min, 280 °C).

***t*-Butyl (±)-[2*R**,2(4*R**,5*S**)]-2-(2,2-dimethyl-5-methyl-1,3-dioxolan-4-yl)propionate (36):** colorless oil: R_f 0.75 (hexane-EtOAc,3:1); IR (neat) υ_{max} 1720 cm^{-1}; MS (CI, NH_3) m/e 262 (70%, MH^+NH_3), 245 (25%, MH^+), 206 (98%, M^+-38), 178 (100%, MH^+-isobutylene), 148 (45%, M^+-96%); ^1H NMR (200 MHz, $CDCl_3$) δ 1.15 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 7.0 Hz, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.44 (s, 9H), 2.50 (qd, J = 7.1, 10.2 Hz, 1H), 4.16 (dd, J = 10.2, 5.7 Hz, 1H), 4.34 (qd, J = 5.7, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 15.8, 25.7, 27.9, 28.1, 28.3, 41.0, 73.8, 79.0, 80.6, 107.3, 174.0. GC t_R 10.2 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/10 min, 1 °C/min, 130 °C, 20 °C/min, 280 °C).

***t*-Butyl (±)-4-*t*-butyldimethylsiloxy-3-hydroxy-2-methyl-2-(phenylselenenyl)butyrate (41).** Compound **41a** was isolated as a colorless oil (30%): R_f 0.35 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 3500, 1720, 1575 cm^{-1}; MS (CI, isobutane) m/e 461 (5%, MH^+), 387 (30%, M^+-74), 233 (100%, MH^+-228), 175 (30%, M^+-CH_3(PhSe)$CHCO_2t$Bu); ^1H NMR (200 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.93 (s, 9H), 1.40 (s, 3H), 1.46 (s, 9H), 3.22 (d, J = 6.2 Hz, 1H, OH), 3.75-3.87 (m, 2H), 4.02 (td, J = 3.5, 3.3 Hz, 1H), 7.29-7.42 (m, 3H), 7.68-7.73 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -5.5, 18.2, 25.8, 27.8, 54.2, 63.7, 73.5, 81.5, 127.0, 128.7, 129.2, 138.2, 171.7. Anal. calcd for $C_{21}H_{36}O_4SeSi$: C 54.88%, H 7.90%; found: C 54.85%, H 8.12%.

Compound **41b** was isolated as a colorless oil (20%): R_f 0.30 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 3500, 1720, 1680 cm^{-1}; MS (CI, isobutane) m/e 461 (1%, MH^+), 443 (10%, MH^+-H_2O), 387 (100%, M^+-74), 249 (30%, MH^+-212), 175 (25%, M^+-CH_3(PhSe)$CHCO_2t$Bu); ^1H NMR (200 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.90 (s, 9H), 1.36 (s, 3H), 1.42 (s, 9H), 3.19 (d, J = 6.2 Hz, 1H, OH), 3.75-3.84 (m, 1H), 4.00 (t, J = 3.7 Hz, 1H), 4.03-4.08 (m, 1H), 7.28-7.44 (m, 3H), 7.58-7.65 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -5.35, -5.42, 18.3, 18.6, 25.8, 27.8, 53.1, 63.8, 75.2, 81.6, 98.9, 126.7, 128.7, 129.2, 138.1, 172.3. Anal. calcd for $C_{21}H_{36}O_4SeSi$: C 54.88%, H 7.90%; found: C 55.18%, H 8.08%.

***t*-Butyl (±)-(3*S**,4*S**)-4-*t*-butyldimethylsiloxy-3-hydroxy-2-methyl-2-(phenylselenenyl)pentanoate (43).** Compound **43a** was isolated as a colorless oil (32%): R_f 0.3 (hexane-EtOAc, 9:1); IR (neat), υ_{max} 3500, 1730, 1585 cm^{-1}; MS (CI, isobutane) m/e 474 (0.5%, M^+), 286 (100%, M^+-TBDMSO-isobutylene); ^1H NMR (200 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.04 (s, 3H), 0.86 (s, 9H), 1.17 (d, J = 6.2 Hz, 3H), 1.39 (s, 9H), 1.43 (s, 3H), 3.00 (d, J = 3.7 Hz, 1H, OH), 3.89 (dd, J = 4.6, 3.7 Hz, 1H), 4.00 (qd, J = 6.2, 4.6 Hz, 1H), 7.30-7.39 (m, 3H), 7.65-7.70 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -4.7, -4.6, 17.5, 17.9, 20.1, 25.8, 27.7, 55.8, 69.9, 75.3, 81.0, 127.6, 128.5, 129.1, 138.0, 171.4. Anal. calcd for $C_{22}H_{38}O_4SeSi$: C 55.80%, H 8.09%; found: C 55.42%, H 8.06%.

Compound **43b** was isolated as a colorless oil (20%): R_f 0.2 (hexane-EtOAc, 9:1); IR (neat) υ_{max} 3450, 1725, 1690, 1580 cm^{-1}; MS (EI) m/e 474 (1%, M^+), 361 (48%, M^+-113), 159 (100%, M^+-315); ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.86 (s, 9H), 1.26 (d, J = 6.2 Hz, 3H), 1.40 (s, 3H), 1.44 (s, 9H), 3.46 (d, J = 8.8 Hz, 1H, OH), 3.82 (dd, J = 8.8, 5.5 Hz, 1H), 4.07 (qd, J = 6.2, 5.5 Hz, 1H), 7.25-7.43 (m, 3H), 7.60-7.64 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -4.7, -4.2, 15.1, 17.9, 20.2, 21.0, 25.6, 27.6, 54.2, 70.4, 80.7, 81.9, 127.2, 128.3, 128.9, 138.1, 173.0; HRMS calcd for $C_{22}H_{38}O_4SeSi$: 474.1705, found: 474.1703 (-0.4 ppm). Anal. calcd for $C_{22}H_{38}O_4SeSi$: C 55.80%, H 8.09%; found: C 56.17%, H 8.40%.

(±)-*endo*-2-carbomethoxy-7-oxabicyclo[2.2.1]heptane (45).[1] Colorless oil: R_f 0.75 (CH_2Cl_2-acetone, 10:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (CI, isobutane) m/e 157 (100%, MH^+); ^1H NMR (400 MHz, $CDCl_3$) δ 1.52-1.61 (m, 2H), 1.62-1.78 (m, 2H), 1.87-1.97 (m, 2H), 3.04 (tdd, J = 5.7, 10.5, 1.9 Hz, 1H), 3.70 (s, 3H), 4.61 (t, J = 4.8 Hz, 1H), 4.72 (d, J = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 29.9, 33.2, 47.8, 51.8, 77.5, 77.8, 173.0. GC t_R 4.3 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/5 min, 10 °C/min, 220 °C/5 min).

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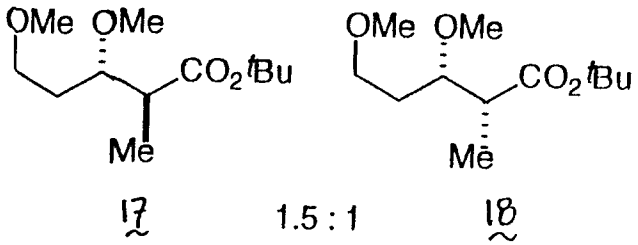
(1) (a) Senda, Y.; Ohno, A.; Ishiyama, J.; Imaizumi, S.; Kamiyama, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 613. (b) Lambert, J.B.; Larson, E.G. *J. Am. Chem. Soc.* **1985**, *107*, 7546. (c) Kotsuki, H.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 496.

(±)-*exo*-2-carbomethoxy-7-oxabicyclo[2.2.1]heptane (46).[1] Colorless oil: R_f 0.75 (CH_2Cl_2-acetone, 10:1); IR (neat) υ_{max} 1730 cm^{-1}; MS (CI, isobutane) m/e 157 (100%, MH^+); ^1H NMR (400 MHz, $CDCl_3$) δ 1.40-1.60 (m, 2H), 1.65-1.80 (m, 2H), 2.06-2.20 (m, 2H), 2.62 (dd, J = 9.1, 4.8 Hz, 1H), 3.67 (s, 3H), 4.66 (t, J = 4.6 Hz, 1H), 4.82 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 29.3, 34.1, 47.7, 51.7, 76.1, 78.6, 173.8. GC t_R 5.3 min ($t_{inj.}$ 280 °C, t_{FID} 320 °C, split method, 83:1, 0.6 mL/min, program 120 °C/5 min, 10 °C/min, 220 ° C/5 min).



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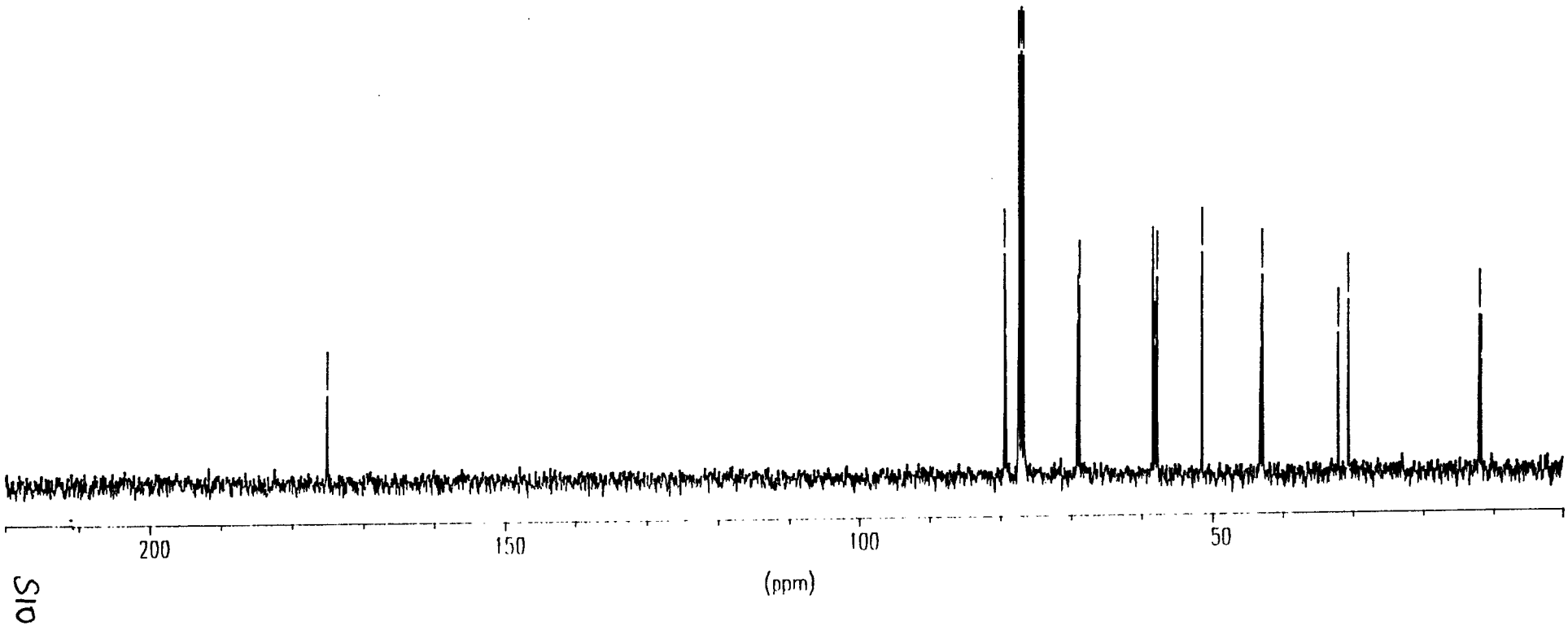

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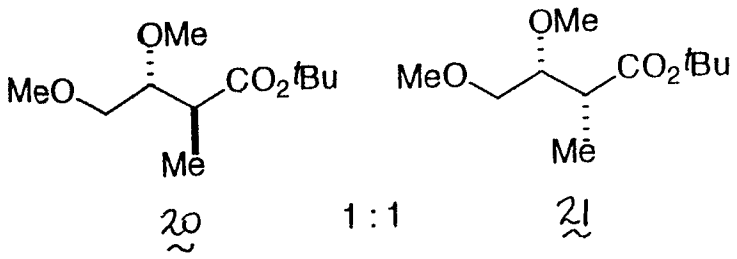

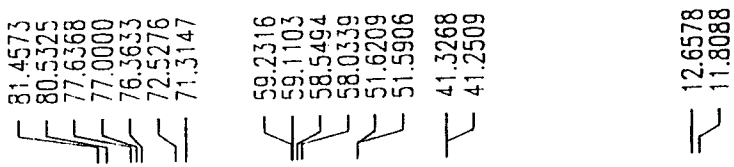

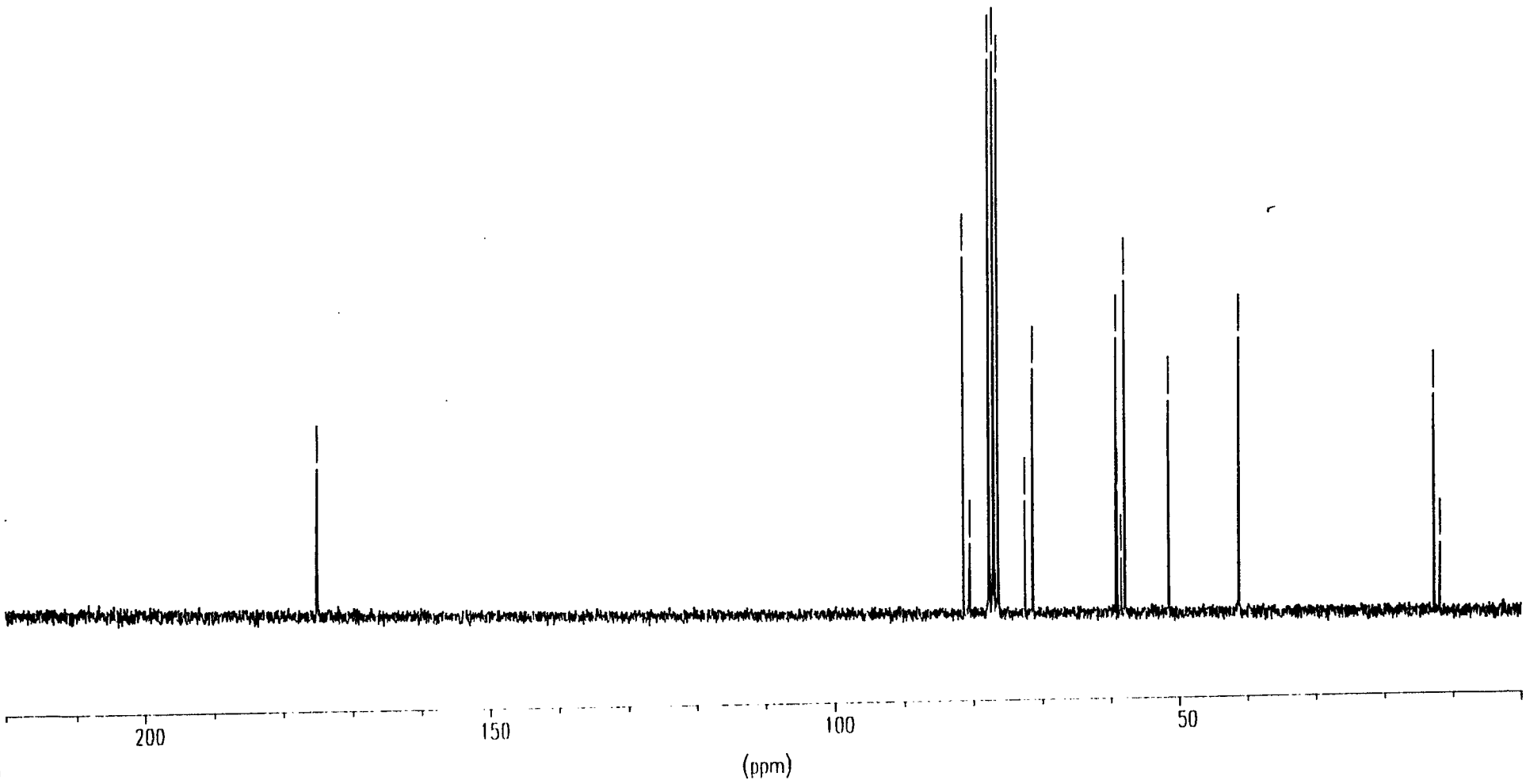

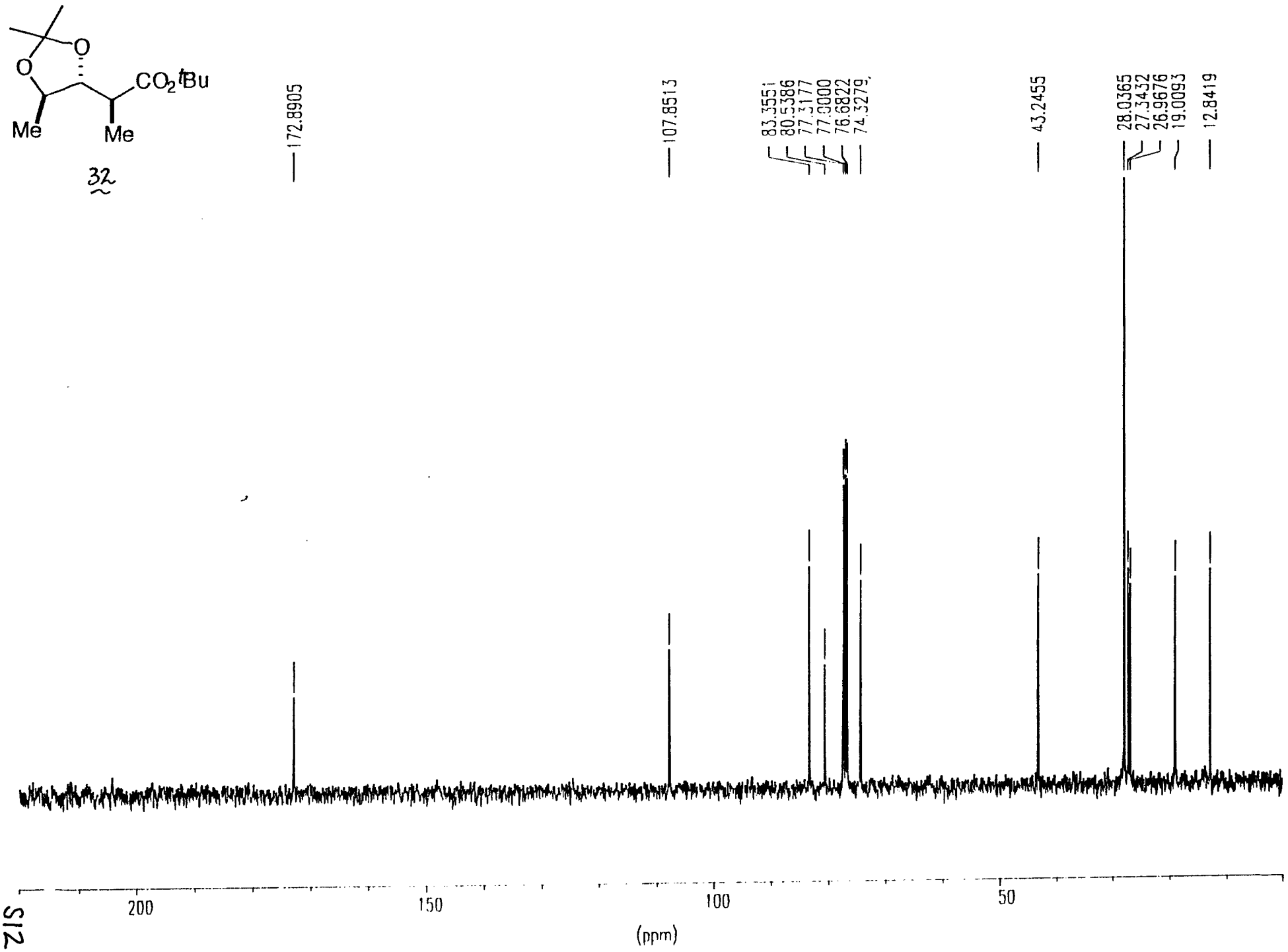

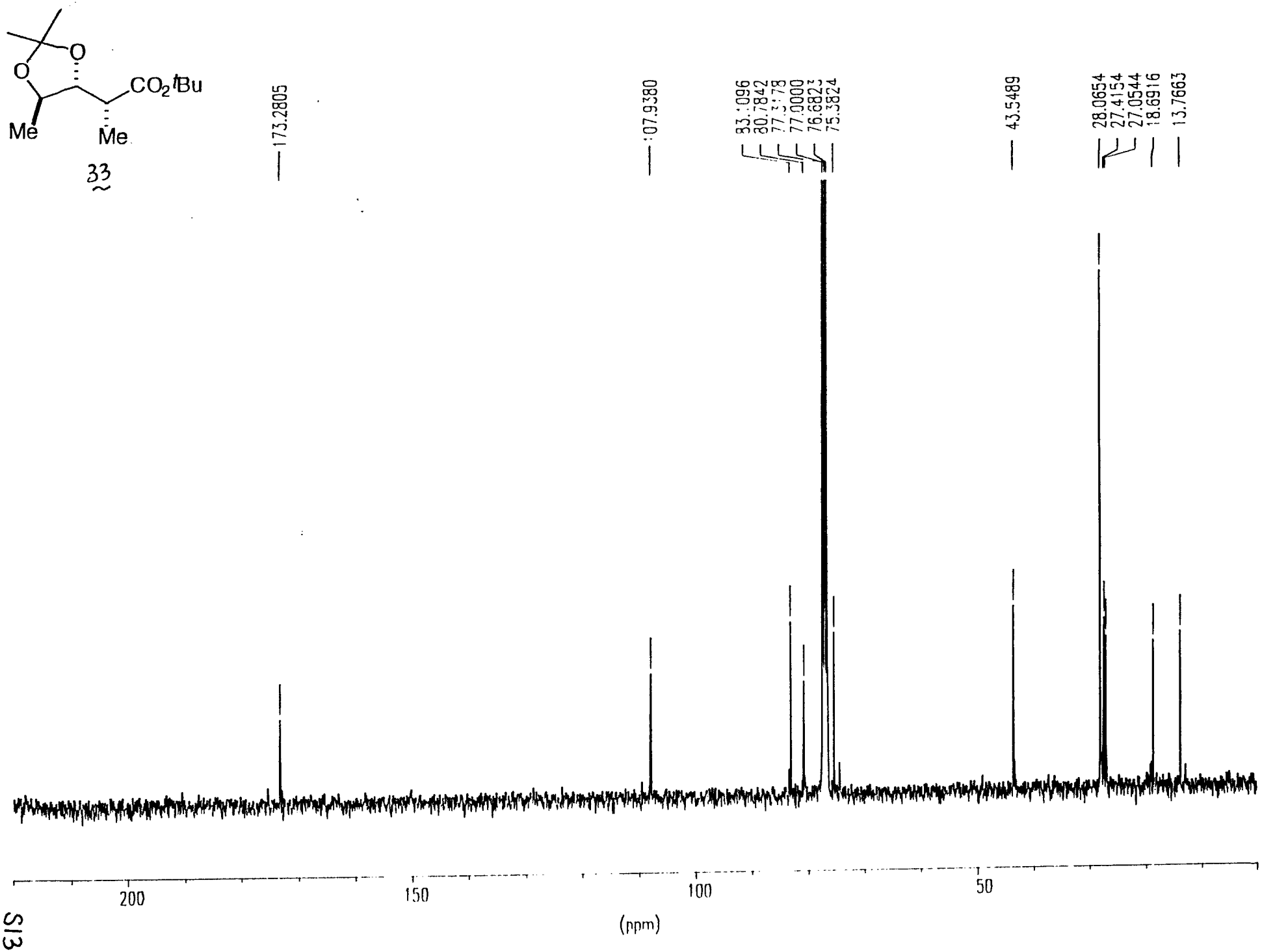

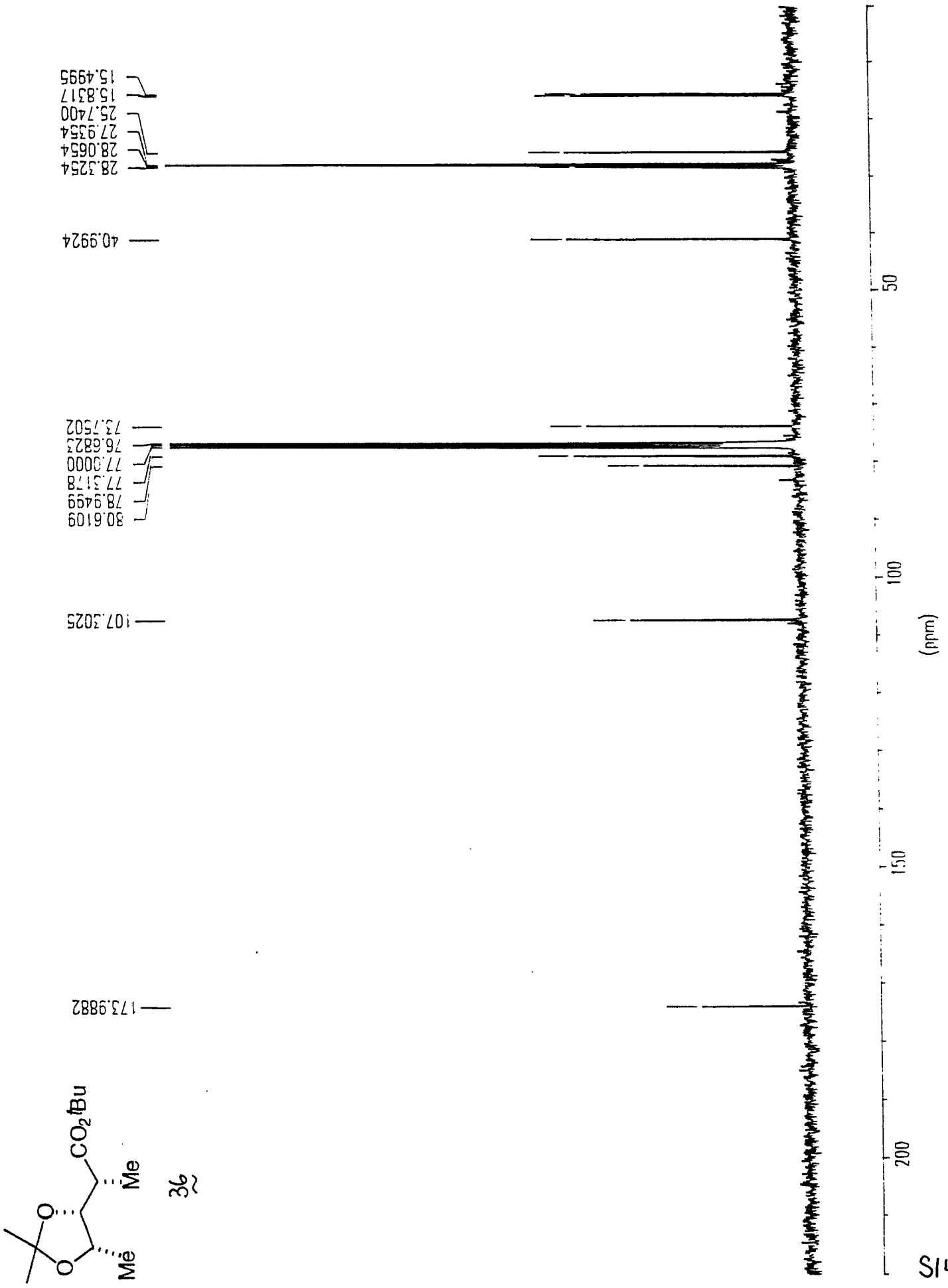
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