Pd-Catalyzed Regioselective Hydroesterification of 2-Allylphenols to Seven-Membered Lactones without External CO

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Supporting Information

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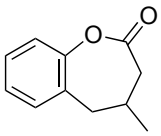
General Methods. All commercially available reagents were used without further purification. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. All ligands were purchased from commercial suppliers. Olefins **1a**, **1c,** and **1f** were prepared by reacting the corresponding phenols with 3-bromo-2-methyl-1-propene and NaH in toluene at 0 ^{o}C.[1] Olefins **1d**, **1e** and **1g-1n** were prepared via allylation of the corresponding phenols with 3-bromo-2-methyl-1-propene and K_2CO_3 in acetone at reflux, followed by the Claisen rearrangement of the resulting allyl ethers in 1,3-dichlorobenzene at 190 ^{o}C.[2] Olefin **1b** was prepared by following the reported procedures.[3] Olefin **1o** was purchased from commercial supplier. Phenyl formate was prepared from the corresponding phenols according to the reported procedure.[4]

1) R. M. Trend, Y. K. Ramtohul and B. M. Stoltz, *J. Am. Chem. Soc*., 2005, **127**, 17778.
2) M. Amézquita-Valencia and H. Alper, *Org. Lett*., 2014, **16**, 5827.
3) G. T. Hoang, V. J. Reddy, H. H. K. Nguyen and C. J. Douglas, *Angew. Chem. Int. Ed.,* 2011, **50**, 1882.
4) Y. Katafuchi, T. Fujihara, T. Iwai, J. Terao and Y. Tsuji, *Adv. Synth. Catal*., 2011, **353**, 475.

Representative procedure for hydroesterification (Table 2, 1a)

To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), (±)-DTBM-SEGPHOS (0.015 g, 0.0125 mmol), and THF (0.20 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added HCOOPh (0.073 g, 0.60 mmol), 2-(2-methylallyl)phenol (**1a**) (0.074 g, 0.50 mmol), and HCOOH (0.023 g, 0.50 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 50 ^{o}C for 24 h and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 30/1) to give lactone **2a** as a colorless oil (0.079 g, 90% yield).

Table 2, 2a

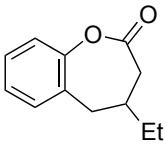


Colorless oil (0.079 g, 0.45 mmol, 90% yield); IR (film) 1756, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 1H), 7.21-7.13 (m, 2H), 7.10-7.06 (m, 1H), 2.97 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.63-2.51 (m, 2H), 2.47 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.17-2.07 (m, 1H), 1.09 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 152.0, 130.5, 129.2, 128.6, 125.8, 119.5, 38.8, 36.4, 33.9, 20.6; HRMS (ESI) Calcd for $C_{11}H_{13}O_2$ (M+H): 177.0910; Found: 177.0907.

1) B. E. Ali, K. Okuro, G. Vasapollo and H. Alper, *J. Am. Chem. Soc.*, 1996, **118**, 4264.

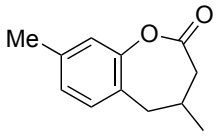
2) T. Matsuda, M. Shigeno and M. Murakami, *J. Am. Chem. Soc*., 2007, **129**, 12086.

Table 2, 2b



Colorless oil (0.067 g, 0.35 mmol, 70% yield); IR (film) 1759, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 7.20-7.11 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 2.95 (dd, *J* = 13.9, 6.7 Hz, 1H), 2.54 (dd, *J* = 11.8, 6.9 Hz, 1H), 2.53 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.36-2.23 (m, 1H), 2.16 (dd, *J* = 12.0, 6.8 Hz, 1H), 1.52-1.33 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 151.9, 130.4, 129.3, 128.5, 125.8, 119.3, 40.6, 36.7, 34.2, 27.6, 11.8; HRMS (ESI) Calcd for $C_{12}H_{15}O_2$ (M+H): 191.1067; Found: 191.1068.

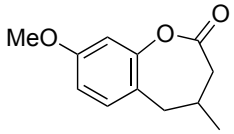
Table 2, 2c



Colorless oil (0.084 g, 0.44 mmol, 88% yield); IR (film) 1761, 1233 cm^{-1}; ^1H NMR (400

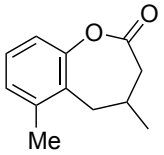
MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 2.92 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.60-2.49 (m, 2H), 2.41 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.34 (s, 3H), 2.16-2.06 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 151.7, 138.6, 130.1, 126.3, 125.9, 119.9, 38.7, 35.9, 33.9, 21.1, 20.5; HRMS (ESI) Calcd for $C_{12}H_{15}O_2$ (M+H): 191.1067; Found: 191.1065.

Table 2, 2d



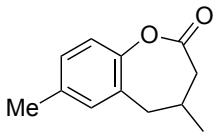
Colorless oil (0.090 g, 0.44 mmol, 88% yield); IR (film) 1759, 1618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 2.90 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.62-2.47 (m, 2H), 2.39 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.16-2.05 (m, 1H), 1.06 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.8, 152.5, 130.7, 121.0, 111.1, 105.4, 55.6, 38.8, 35.5, 34.1, 20.4; HRMS (ESI) Calcd for $C_{12}H_{15}O_3$ (M+H): 207.1016; Found: 207.1014.

Table 2, 2e



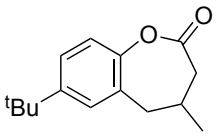
Colorless oil (0.090 g, 0.47 mmol, 93% yield); IR (film) 1761, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 2.97-2.86 (m, 1H), 2.62-2.47 (m, 3H), 2.36 (s, 3H), 2.18-2.08 (m, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 152.1, 137.4, 127.8, 127.5, 127.4, 117.0, 38.6, 33.5, 31.4, 20.6, 19.7; HRMS (ESI) Calcd for $C_{12}H_{15}O_2$ (M+H): 191.1067; Found: 191.1066.

Table 2, 2f



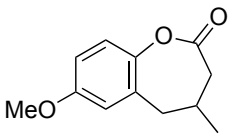
Colorless oil (0.080 g, 0.42 mmol, 84% yield); IR (film) 1758, 1491 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 2.91 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.60-2.48 (m, 2H), 2.41 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.33 (s, 3H), 2.16-2.07 (m, 1H), 1.08 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 149.7, 135.3, 130.9, 128.8, 128.7, 119.0, 38.6, 36.2, 33.7, 20.8, 20.6; HRMS (ESI) Calcd for $C_{12}H_{15}O_2$ (M+H): 191.1067; Found: 191.1064.

Table 2, 2g



Colorless oil (0.087 g, 0.37 mmol, 75% yield); IR (film) 1764, 1494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 2.94 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.62-2.51 (m, 2H), 2.45 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.17-2.08 (m, 1H), 1.32 (s, 9H), 1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 149.6, 148.8, 128.4, 127.3, 125.2, 118.7, 38.8, 36.7, 34.6, 33.9, 31.6, 20.7; HRMS (ESI) Calcd for $C_{15}H_{21}O_2$ (M+H): 233.1536; Found: 233.1534.

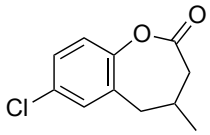
Table 2, 2h



Light yellow oil (0.089 g, 0.43 mmol, 86% yield); IR (film) 1756, 1488 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 3.80 (s, 3H), 2.92 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.61-2.49 (m, 2H), 2.42 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.16-2.07 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3,

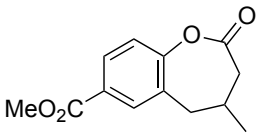
157.1, 145.6, 130.2, 120.0, 115.9, 112.6, 55.7, 38.6, 36.5, 33.6, 20.7; HRMS (ESI) Calcd for $C_{12}H_{15}O_3$ (M+H): 207.1016; Found: 207.1014.

Table 2, 2i



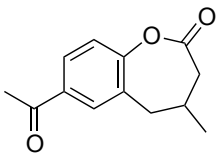
Colorless oil (0.095 g, 0.45 mmol, 90% yield); IR (film) 1761, 1471 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 2.93 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.64-2.52 (m, 2H), 2.44 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.18-2.08 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 150.4, 131.0, 130.7, 130.2, 128.4, 120.7, 38.5, 36.1, 33.6, 20.5; HRMS (ESI) Calcd for $C_{11}H_{12}ClO_2$ (M+H): 211.0520; Found: 211.0519.

Table 2, 2j



White solid (0.073 g, 0.31 mmol, 62% yield); mp. 112-113 ^oC; IR (film) 1767, 1716, 1286 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz 1H), 3.92 (s, 3H), 3.01 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.67-2.48 (m, 3H), 2.17-2.09 (m, 1H), 1.11 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.4, 155.4, 132.1, 130.4, 129.4, 127.7, 119.6, 52.5, 38.8, 36.3, 33.8, 20.6; HRMS (ESI) Calcd for $C_{13}H_{14}NaO_4$ (M+Na): 257.0784; Found: 257.0784.

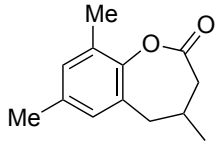
Table 2, 2k



White solid (0.070 g, 0.32 mmol, 64% yield); mp. 97-98 ^oC; IR (film) 1764, 1680, 1105 cm^{-1};

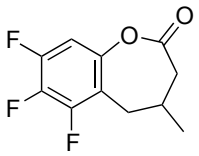
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.83 (d, *J* = 2.1 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 3.02 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.67-2.50 (m, 3H), 2.61 (s, 3H), 2.18-2.10 (m, 1H), 1.11 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 169.6, 155.5, 134.7, 130.6, 129.6, 129.4, 119.7, 38.8, 36.4, 33.8, 26.8, 20.5; HRMS (ESI) Calcd for $C_{13}H_{15}O_3$ (M+H): 219.1016; Found: 219.1015.

Table 2, 2l



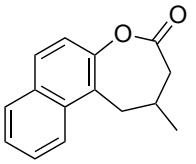
Colorless oil (0.084 g, 0.41 mmol, 82% yield); IR (film) 1761, 1477 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.80 (s, 1H), 2.88 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.60-2.46 (m, 2H), 2.39 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.15-2.05 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 148.0, 134.8, 130.5, 128.5, 128.4, 128.0, 38.7, 36.3, 33.7, 20.8, 20.5, 16.2; HRMS (ESI) Calcd for $C_{13}H_{17}O_2$ (M+H): 205.1223; Found: 205.1222.

Table 2, 2m



White solid (0.073 g, 0.32 mmol, 63% yield); mp. 110-111 ^{o}C; IR (film) 1756, 1505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (ddd, *J* = 10.0, 6.2, 2.4 Hz, 1H), 3.00-2.89 (m, 1H), 2.69-2.53 (m, 3H), 2.21-2.09 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.7 (ddd, *J* = 248.3, 10.9, 5.2 Hz), 149.3 (ddd, *J* = 246.8, 10.9, 5.0 Hz), 146.9 (ddd, *J* = 11.5, 7.2, 4.2 Hz), 138.0 (ddd, *J* = 248.8, 16.0, 14.7 Hz), 114.7 (ddd, *J* = 17.5, 4.4, 1.0 Hz), 104.5 (dd, *J* = 20.6, 3.7 Hz), 38.6, 33.3, 27.9, 20.5; HRMS (ESI) Calcd for $C_{11}H_{10}F_3O_2$ (M+H): 231.0627; Found: 231.0626.

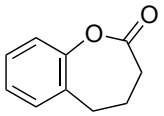
Table 2, 2n



White soild (0.105 g, 0.47 mmol, 93% yield); mp. 81-82 ^{o}C; IR (film) 1761, 1216 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.61-7.54 (m, 1H), 7.52-7.46 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 3.33 (dd, *J* = 14.3, 6.2 Hz, 1H), 3.02 (dd, *J* = 14.3, 6.6 Hz, 1H), 2.83-2.69 (m, 1H), 2.59 (dd, *J* = 12.2, 7.0 Hz, 1H), 2.18 (dd, *J* = 12.2, 6.8 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 149.6, 132.6, 131.8, 128.9, 128.8, 127.2, 125.5, 123.7, 123.5, 119.1, 39.1, 34.7, 30.3, 21.1; HRMS (ESI) Calcd for $C_{15}H_{15}O_2$ (M+H): 227.1067; Found: 227.1066.

G. Vasapollo and G. Mele, *Can. J. Chem*., 2005, **83**, 674.

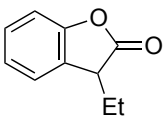
Table 2, 2o



Colorless oil (0.031 g, 0.19 mmol, 38% yield); IR (film) 1764, 1486 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 7.22-7.13 (m, 2H), 7.09 (dd, *J* = 8.0, 0.8 Hz, 1H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.25-2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 152.0, 130.3, 129.8, 128.5, 126.1, 119.5, 31.3, 28.4, 26.7; HRMS (ESI) Calcd for $C_{10}H_{11}O_2$ (M+H): 163.0754; Found: 163.0752.

M. Amezquita-Valencia and H. Alper, *Org. Lett*., 2014, **16**, 5827.

Table 2, 3o

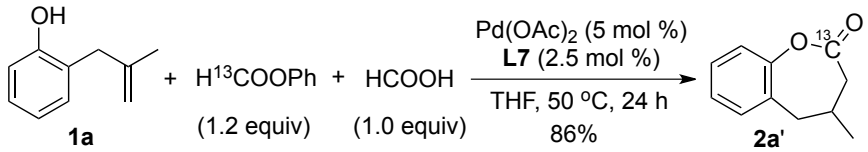


Colorless oil (0.033 g, 0.20 mmol, 40% yield); IR (film) 1802, 1460 cm^{-1}; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.15 (td, *J* = 7.5, 0.9 Hz, 1H), 7.10 (dd, *J* = 8.1, 0.3 Hz, 1H), 3.70 (t, *J* = 5.9 Hz, 1H), 2.10-2.01 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 154.1, 128.9, 127.4, 124.3, 124.2, 110.8, 44.8, 24.5, 10.4; HRMS (ESI) Calcd for $C_{10}H_{11}O_2$ (M+H): 163.0754; Found: 163.0756.

H. Wang, B. Dong, Y. Wang, J. Li and Y. Shi, *Org. Lett.*, 2014, **16**, 186.

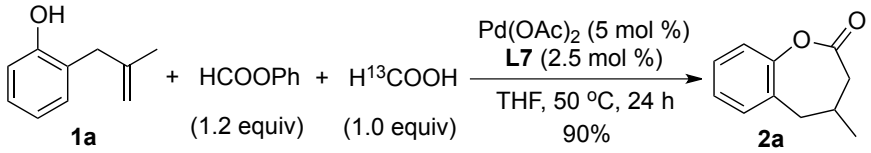
Procedure for Scheme 2



Scheme 2

To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), (±)-DTBM-SEGPHOS (0.015 g, 0.0125 mmol), and THF (0.20 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added $H^{13}COOPh$ (0.074 g, 0.60 mmol), 2-(2-methylallyl)phenol (**1a**) (0.074 g, 0.50 mmol), and HCOOH (0.023 g, 0.50 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 50 ^oC for 24 h. The product was purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 30/1) to give lactone **2a'** as a colorless oil (0.076 g, 86% yield). IR (film) 1718, 1480, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 7.21-7.12 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 2.97 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.64-2.50 (m, 2H), 2.46 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.18-2.06 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 151.9 (d, *J* = 1.2 Hz), 130.4, 129.1, 128.4, 125.7, 119.3 (d, *J* = 2.2 Hz), 38.6 (d, *J* = 53.3 Hz), 36.2 (d, *J* = 1.2 Hz), 33.8 (d, *J* = 2.6 Hz), 20.5 (d, *J* = 3.3 Hz); HRMS (ESI) Calcd for $C_{10}{}^{13}CH_{13}O_2$ (M+H): 178.0944; Found: 178.0942.

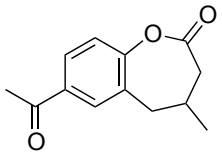
Procedure for Scheme 3



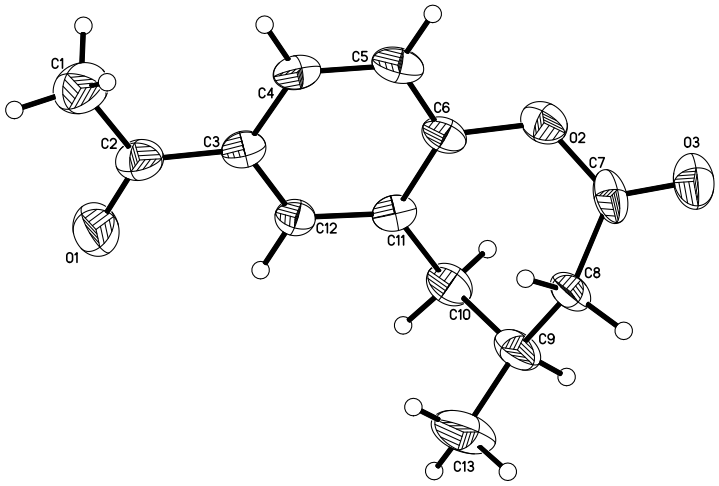
Scheme 3

To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), (±)-DTBM-SEGPHOS (0.015 g, 0.0125 mmol), and THF (0.20 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added HCOOPh (0.073 g, 0.60 mmol), 2-(2-methylallyl)phenol (**1a**) (0.074 g, 0.50 mmol), and $H^{13}COOH$ (0.024 g, 0.50 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 50 °C for 24 h. The product was purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 30/1) to give lactone **2a** as a colorless oil (0.079 g, 90% yield).

The X-ray structure of compound **2k**



2k



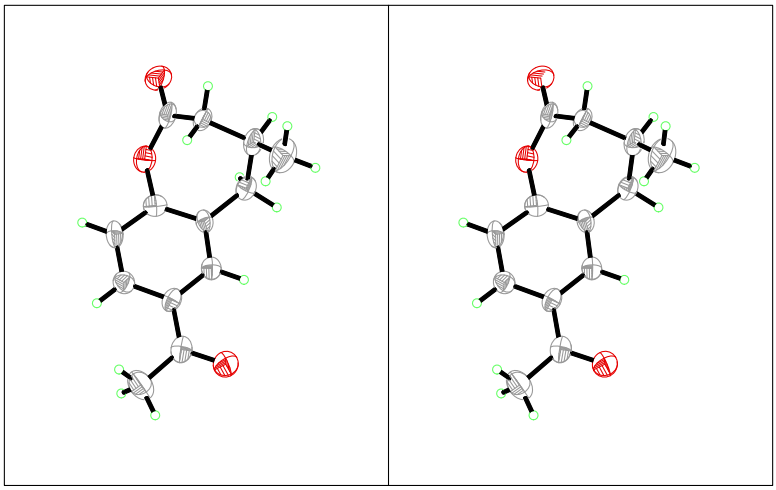


Table S1. Crystal data and structure refinement for: **2k**.

Identification code	2k
Empirical formula	C_{13} H_{14} O_3
Formula weight	218.24
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 7.3630(15) A alpha = 90 deg.
	b = 17.941(4) A beta = 91.50(3) deg.
	c = 8.5680(17) A gamma = 90 deg.
Volume	1131.4(4) A^3
Z, Calculated density	4, 1.281 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	464
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collectio	n 2.27 to 25.37 deg.
Limiting indices	0<=h<=8, 0<=k<=21, -10<=l<=10
Reflections collected / unique	2245 / 1622 [R(int) = 0.0990]
Completeness to theta = 25.37	98.00%
Absorption correction	Psi-scan
Max. and min. transmission	0.9910 and 0.9821
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1622 / 1 / 145
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0771, wR2 = 0.1257
R indices (all data)	R1 = 0.1981, wR2 = 0.1561
Largest diff. peak and hole	0.194 and -0.183 $e.A^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for: **2k**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	13623(6)	1785(3)	9870(5)	109(2)
C(1)	12805(9)	1574(4)	12454(7)	102(2)
O(2)	6065(5)	320(2)	8067(5)	70(1)
C(2)	12432(9)	1546(4)	10741(7)	73(2)
O(3)	3727(5)	321(2)	6383(4)	88(2)
C(3)	10790(7)	1220(3)	10046(7)	54(2)
C(4)	9451(8)	931(3)	10953(6)	62(2)
C(5)	7836(8)	648(3)	10295(7)	63(2)
C(6)	7651(8)	653(3)	8700(7)	54(2)
C(7)	4998(8)	660(4)	6909(7)	65(2)
C(8)	5577(6)	1417(3)	6434(6)	60(2)
C(9)	7213(8)	1412(4)	5354(7)	72(2)
C(10)	8687(7)	874(3)	5980(6)	62(2)
C(11)	8972(8)	910(3)	7708(6)	49(1)
C(12)	10511(7)	1205(3)	8432(6)	55(2)
C(13)	7971(8)	2161(3)	5190(8)	111(3)

Table S3. Bond lengths [A] and angles [deg] for: **2k**.

O(1)-C(2)	1.243(6)
C(1)-C(2)	1.487(7)
C(1)-H(1A)	0.96
C(1)-H(1B)	0.96
C(1)-H(1C)	0.96
O(2)-C(7)	1.390(6)
O(2)-C(6)	1.407(6)
C(2)-C(3)	1.455(7)
O(3)-C(7)	1.194(6)
C(3)-C(4)	1.374(6)
C(3)-C(12)	1.392(6)
C(4)-C(5)	1.397(6)
C(4)-H(4A)	0.93
C(5)-C(6)	1.370(7)
C(5)-H(5A)	0.93
C(6)-C(11)	1.387(7)
C(7)-C(8)	1.484(7)
C(8)-C(9)	1.538(6)
C(8)-H(8A)	0.97
C(8)-H(8B)	0.97
C(9)-C(13)	1.464(7)
C(9)-C(10)	1.539(7)
C(9)-H(9A)	0.98
C(10)-C(11)	1.491(6)
C(10)-H(10A)	0.97
C(10)-H(10B)	0.97
C(11)-C(12)	1.383(6)
C(12)-H(12A)	0.93
C(13)-H(13A)	0.96
C(13)-H(13B)	0.96
C(13)-H(13C)	0.96
C(2)-C(1)-H(1A)	10950.00%
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(7)-O(2)-C(6)	122.5(5)
O(1)-C(2)-C(3)	119.0(6)
O(1)-C(2)-C(1)	117.8(6)

C(3)-C(2)-C(1)	123.2(6)
C(4)-C(3)-C(12)	117.7(6)
C(4)-C(3)-C(2)	121.4(6)
C(12)-C(3)-C(2)	120.9(5)
C(3)-C(4)-C(5)	121.6(5)
C(3)-C(4)-H(4A)	119.2
C(5)-C(4)-H(4A)	119.2
C(6)-C(5)-C(4)	117.5(5)
C(6)-C(5)-H(5A)	121.2
C(4)-C(5)-H(5A)	121.2
C(5)-C(6)-C(11)	124.1(5)
C(5)-C(6)-O(2)	116.2(5)
C(11)-C(6)-O(2)	119.5(5)
O(3)-C(7)-O(2)	118.0(6)
O(3)-C(7)-C(8)	126.2(6)
O(2)-C(7)-C(8)	115.8(5)
C(7)-C(8)-C(9)	113.2(5)
C(7)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8A)	108.9
C(7)-C(8)-H(8B)	108.9
C(9)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
C(13)-C(9)-C(8)	111.0(5)
C(13)-C(9)-C(10)	110.0(5)
C(8)-C(9)-C(10)	110.5(5)
C(13)-C(9)-H(9A)	108.4
C(8)-C(9)-H(9A)	108.4
C(10)-C(9)-H(9A)	108.4
C(11)-C(10)-C(9)	113.5(5)
C(11)-C(10)-H(10A)	108.9
C(9)-C(10)-H(10A)	108.9
C(11)-C(10)-H(10B)	108.9
C(9)-C(10)-H(10B)	108.9
H(10A)-C(10)-H(10B)	107.7
C(12)-C(11)-C(6)	115.6(5)
C(12)-C(11)-C(10)	123.7(5)
C(6)-C(11)-C(10)	120.8(5)
C(11)-C(12)-C(3)	123.4(5)
C(11)-C(12)-H(12A)	118.3
C(3)-C(12)-H(12A)	118.3
C(9)-C(13)-H(13A)	109.5
C(9)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5

C(9)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for: **2k**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
O(1)	87(3)	160(5)	80(3)	7(3)	-2(3)	-40(3)
C(1)	129(7)	111(6)	66(5)	10(5)	-7(4)	-12(5)
O(2)	79(3)	58(3)	74(3)	5(2)	12(2)	-9(2)
C(2)	76(5)	72(5)	71(5)	7(4)	18(4)	-2(4)
O(3)	72(3)	107(4)	84(3)	-19(3)	-3(2)	-23(3)
C(3)	52(4)	44(3)	66(4)	1(3)	15(3)	-5(3)
C(4)	63(4)	60(4)	61(4)	8(3)	3(3)	5(3)
C(5)	80(5)	55(4)	54(4)	17(3)	24(3)	7(4)
C(6)	61(4)	34(3)	69(4)	-5(3)	-3(3)	-1(3)
C(7)	65(5)	79(5)	53(4)	-16(4)	27(3)	-21(4)
C(8)	47(4)	69(4)	64(4)	8(3)	16(3)	-6(3)
C(9)	78(5)	70(5)	68(4)	-4(4)	19(3)	-31(4)
C(10)	59(4)	64(4)	64(4)	-5(3)	16(3)	-3(3)
C(11)	61(4)	49(4)	38(3)	-2(3)	12(3)	9(3)
C(12)	60(4)	50(4)	54(4)	3(3)	9(3)	5(3)
C(13)	115(6)	74(5)	147(7)	29(5)	36(5)	-3(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for: **2k**.

	x	y	z	U(eq)
H(1A)	13938	1824	12659	153
H(1B)	12871	1075	12861	153
H(1C)	11845	1839	12948	153
H(4A)	9622	922	12032	74
H(5A)	6922	464	10916	75
H(8A)	5889	1704	7362	72
H(8B)	4565	1665	5903	72
H(9A)	6799	1238	4321	86
H(10A)	8351	369	5690	75
H(10B)	9824	989	5486	75
H(12A)	11407	1404	7809	66
H(13A)	7041	2494	4807	167
H(13B)	8945	2148	4467	167
H(13C)	8425	2333	6187	167

Table S6. Torsion angles [deg] for: **2k**.

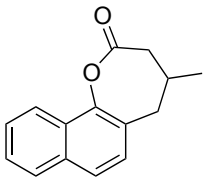
O(1)-C(2)-C(3)-C(4)	178.4(6)
C(1)-C(2)-C(3)-C(4)	1.5(9)
O(1)-C(2)-C(3)-C(12)	-2.8(9)
C(1)-C(2)-C(3)-C(12)	-179.7(6)
C(12)-C(3)-C(4)-C(5)	-1.8(8)
C(2)-C(3)-C(4)-C(5)	177.1(6)
C(3)-C(4)-C(5)-C(6)	1.6(8)
C(4)-C(5)-C(6)-C(11)	1.0(8)
C(4)-C(5)-C(6)-O(2)	175.9(5)
C(7)-O(2)-C(6)-C(5)	133.1(5)
C(7)-O(2)-C(6)-C(11)	-51.7(7)
C(6)-O(2)-C(7)-O(3)	176.3(5)
C(6)-O(2)-C(7)-C(8)	-3.1(7)
O(3)-C(7)-C(8)-C(9)	-102.1(7)
O(2)-C(7)-C(8)-C(9)	77.3(6)
C(7)-C(8)-C(9)-C(13)	-167.9(5)
C(7)-C(8)-C(9)-C(10)	-45.5(6)
C(13)-C(9)-C(10)-C(11)	81.7(6)
C(8)-C(9)-C(10)-C(11)	-41.3(6)
C(5)-C(6)-C(11)-C(12)	-3.1(8)
O(2)-C(6)-C(11)-C(12)	-177.9(5)
C(5)-C(6)-C(11)-C(10)	178.0(5)
O(2)-C(6)-C(11)-C(10)	3.3(8)
C(9)-C(10)-C(11)-C(12)	-109.7(6)
C(9)-C(10)-C(11)-C(6)	69.0(7)
C(6)-C(11)-C(12)-C(3)	2.9(8)
C(10)-C(11)-C(12)-C(3)	-178.3(5)
C(4)-C(3)-C(12)-C(11)	-0.5(8)
C(2)-C(3)-C(12)-C(11)	-179.4(5)

Symmetry transformations used to generate equivalent atoms:

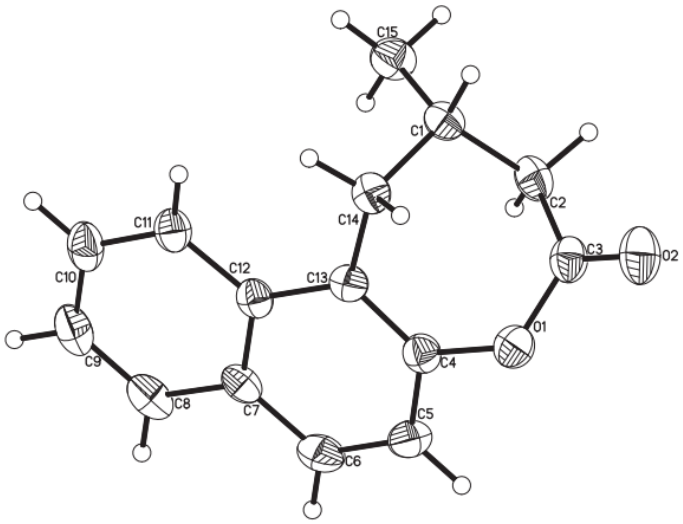
Table S7. Hydrogen bonds for: **2k** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

The X-ray structure of compound **2n**



2n



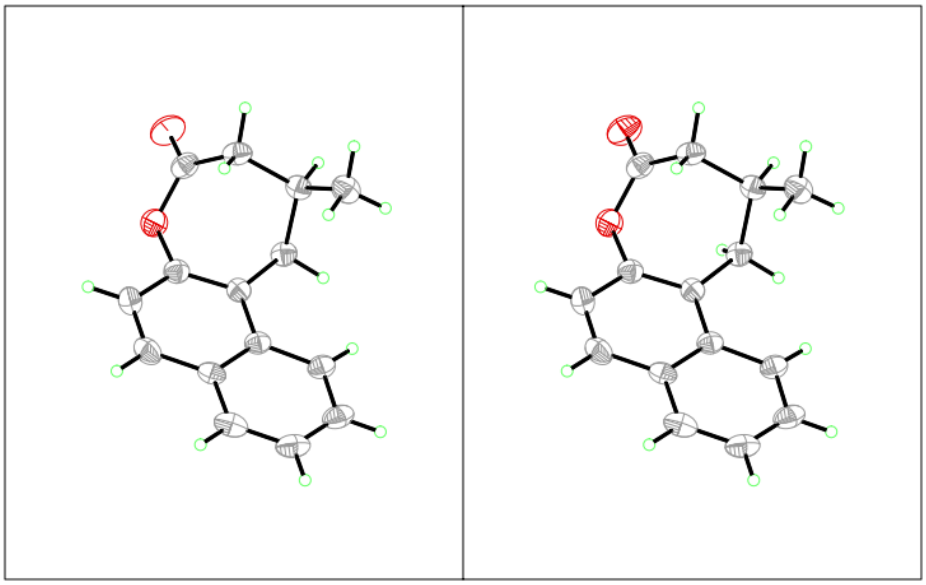


Table S1. Crystal data and structure refinement for: **2n**.

Identification code	**2n**
Empirical formula	$C_{15}H_{14}O_2$
Formula weight	226.26
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/N
Unit cell dimensions	a = 5.3480(11) A alpha = 90 deg. b = 12.242(2) A beta = 93.89(3) deg. c = 17.786(4) A gamma = 90 deg.
Volume	1161.8(4) A^3
Z, Calculated density	4, 1.294 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F(000)	480
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	2.02 to 25.39 deg.
Limiting indices	0<=h<=6, 0<=k<=14, -21<=l<=21
Reflections collected / unique	2386 / 2147 [R(int) = 0.0643]
Completeness to theta = 25.39	100.00%
Absorption correction	Psi-scan
Max. and min. transmission	0.9916 and 0.9750
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2147 / 0 / 154
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1693
R indices (all data)	R1 = 0.1251, wR2 = 0.2067
Largest diff. peak and hole	0.215 and -0.257 $e.A^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for: **2n**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-869(4)	8585(2)	5503(1)	59(1)
C(2)	546(6)	6756(3)	5191(2)	52(1)
O(2)	-3282(5)	7607(3)	4720(2)	76(1)
C(3)	-1361(6)	7643(3)	5103(2)	53(1)
C(4)	1172(6)	8648(3)	6044(2)	47(1)
C(5)	2671(7)	9578(3)	6001(2)	58(1)
C(6)	4610(7)	9723(3)	6527(2)	57(1)
C(7)	5108(6)	8958(3)	7110(2)	47(1)
C(8)	7157(6)	9090(3)	7647(2)	59(1)
C(9)	7648(7)	8352(3)	8206(2)	62(1)
C(10)	6091(7)	7445(3)	8259(2)	59(1)
C(12)	3556(6)	8029(3)	7150(2)	42(1)
C(11)	4098(6)	7280(3)	7752(2)	50(1)
C(13)	1515(6)	7876(3)	6594(2)	42(1)
C(14)	-197(6)	6898(3)	6573(2)	47(1)
C(1)	343(6)	6119(3)	5925(2)	45(1)
C(15)	2693(7)	5437(3)	6101(2)	59(1)

Table S3. Bond lengths [A] and angles [deg] for: **2n**.

O(1)-C(3)	1.371(4)
O(1)-C(4)	1.407(4)
C(2)-C(3)	1.491(5)
C(2)-C(1)	1.530(4)
C(2)-H(2A)	0.97
C(2)-H(2B)	0.97
O(2)-C(3)	1.195(4)
C(4)-C(13)	1.363(4)
C(4)-C(5)	1.397(5)
C(5)-C(6)	1.360(5)
C(5)-H(5A)	0.93
C(6)-C(7)	1.409(5)
C(6)-H(6A)	0.93
C(7)-C(12)	1.413(4)
C(7)-C(8)	1.413(5)
C(8)-C(9)	1.356(5)
C(8)-H(8A)	0.93
C(9)-C(10)	1.395(5)
C(9)-H(9A)	0.93
C(10)-C(11)	1.364(4)
C(10)-H(10A)	0.93
C(12)-C(11)	1.424(4)
C(12)-C(13)	1.435(4)
C(11)-H(11A)	0.93
C(13)-C(14)	1.506(4)
C(14)-C(1)	1.538(4)
C(14)-H(14A)	0.97
C(14)-H(14B)	0.97
C(1)-C(15)	1.524(4)
C(1)-H(1A)	0.98
C(15)-H(15A)	0.96
C(15)-H(15B)	0.96
C(15)-H(15C)	0.96
C(3)-O(1)-C(4)	120.9(3)
C(3)-C(2)-C(1)	111.9(3)
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
O(2)-C(3)-O(1)	117.0(4)

O(2)-C(3)-C(2)	126.0(4)
O(1)-C(3)-C(2)	116.9(3)
C(13)-C(4)-C(5)	123.7(3)
C(13)-C(4)-O(1)	120.8(3)
C(5)-C(4)-O(1)	115.4(3)
C(6)-C(5)-C(4)	118.9(3)
C(6)-C(5)-H(5A)	120.6
C(4)-C(5)-H(5A)	120.6
C(5)-C(6)-C(7)	121.1(3)
C(5)-C(6)-H(6A)	119.5
C(7)-C(6)-H(6A)	119.5
C(6)-C(7)-C(12)	119.3(3)
C(6)-C(7)-C(8)	121.4(3)
C(12)-C(7)-C(8)	119.3(3)
C(9)-C(8)-C(7)	121.5(4)
C(9)-C(8)-H(8A)	119.3
C(7)-C(8)-H(8A)	119.3
C(8)-C(9)-C(10)	119.6(3)
C(8)-C(9)-H(9A)	120.2
C(10)-C(9)-H(9A)	120.2
C(11)-C(10)-C(9)	121.1(4)
C(11)-C(10)-H(10A)	119.5
C(9)-C(10)-H(10A)	119.5
C(7)-C(12)-C(11)	117.8(3)
C(7)-C(12)-C(13)	119.5(3)
C(11)-C(12)-C(13)	122.7(3)
C(10)-C(11)-C(12)	120.7(3)
C(10)-C(11)-H(11A)	119.6
C(12)-C(11)-H(11A)	119.6
C(4)-C(13)-C(12)	117.5(3)
C(4)-C(13)-C(14)	118.8(3)
C(12)-C(13)-C(14)	123.6(3)
C(13)-C(14)-C(1)	111.5(3)
C(13)-C(14)-H(14A)	109.3
C(1)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14B)	109.3
C(1)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108
C(15)-C(1)-C(2)	110.4(3)
C(15)-C(1)-C(14)	112.3(3)
C(2)-C(1)-C(14)	110.5(3)
C(15)-C(1)-H(1A)	107.8
C(2)-C(1)-H(1A)	107.8

C(14)-C(1)-H(1A)	107.8
C(1)-C(15)-H(15A)	109.5
C(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for: **2n**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
O(1)	57(2)	57(2)	60(2)	1(1)	-8(1)	8(1)
C(2)	50(2)	64(2)	43(2)	-10(2)	7(2)	-9(2)
O(2)	54(2)	105(2)	65(2)	1(2)	-16(1)	-4(2)
C(3)	47(2)	67(3)	44(2)	5(2)	3(2)	-8(2)
C(4)	44(2)	49(2)	46(2)	-4(2)	2(2)	3(2)
C(5)	72(2)	43(2)	59(2)	5(2)	5(2)	1(2)
C(6)	59(2)	44(2)	68(2)	-6(2)	10(2)	-13(2)
C(7)	49(2)	47(2)	48(2)	-15(2)	8(2)	0(2)
C(8)	48(2)	63(2)	67(3)	-24(2)	5(2)	-5(2)
C(9)	52(2)	82(3)	52(2)	-22(2)	-7(2)	7(2)
C(10)	59(2)	77(3)	39(2)	-11(2)	2(2)	16(2)
C(12)	40(2)	49(2)	38(2)	-7(2)	9(1)	5(2)
C(11)	54(2)	59(2)	39(2)	-5(2)	9(2)	1(2)
C(13)	40(2)	42(2)	43(2)	-2(2)	11(1)	-1(1)
C(14)	44(2)	53(2)	44(2)	-2(2)	7(2)	-3(2)
C(1)	37(2)	46(2)	51(2)	-4(2)	7(2)	-8(2)
C(15)	52(2)	55(2)	70(2)	-7(2)	1(2)	2(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for: **2n**.

	x	y	z	U(eq)
H(2A)	2208	7071	5186	62
H(2B)	322	6257	4768	62
H(5A)	2348	10088	5620	70
H(6A)	5623	10337	6501	69
H(8A)	8192	9697	7616	71
H(9A)	9013	8450	8551	75
H(10A)	6417	6945	8647	70
H(11A)	3081	6671	7799	60
H(14A)	-1924	7142	6511	56
H(14B)	23	6509	7048	56
H(1A)	-1080	5617	5851	53
H(15A)	2957	4964	5682	89
H(15B)	2492	5004	6543	89
H(15C)	4113	5911	6187	89

Table S6. Torsion angles [deg] for: **2n**.

C(4)-O(1)-C(3)-O(2)	171.4(3)
C(4)-O(1)-C(3)-C(2)	-8.2(5)
C(1)-C(2)-C(3)-O(2)	-100.7(4)
C(1)-C(2)-C(3)-O(1)	78.8(4)
C(3)-O(1)-C(4)-C(13)	-51.1(4)
C(3)-O(1)-C(4)-C(5)	132.9(3)
C(13)-C(4)-C(5)-C(6)	1.0(5)
O(1)-C(4)-C(5)-C(6)	176.9(3)
C(4)-C(5)-C(6)-C(7)	-0.4(5)
C(5)-C(6)-C(7)-C(12)	-0.4(5)
C(5)-C(6)-C(7)-C(8)	178.4(3)
C(6)-C(7)-C(8)-C(9)	-179.6(3)
C(12)-C(7)-C(8)-C(9)	-0.9(5)
C(7)-C(8)-C(9)-C(10)	-0.5(5)
C(8)-C(9)-C(10)-C(11)	0.9(5)
C(6)-C(7)-C(12)-C(11)	-179.3(3)
C(8)-C(7)-C(12)-C(11)	1.9(4)
C(6)-C(7)-C(12)-C(13)	0.5(4)
C(8)-C(7)-C(12)-C(13)	-178.3(3)
C(9)-C(10)-C(11)-C(12)	0.2(5)
C(7)-C(12)-C(11)-C(10)	-1.6(5)
C(13)-C(12)-C(11)-C(10)	178.6(3)
C(5)-C(4)-C(13)-C(12)	-0.8(5)
O(1)-C(4)-C(13)-C(12)	-176.5(3)
C(5)-C(4)-C(13)-C(14)	-179.0(3)
O(1)-C(4)-C(13)-C(14)	5.3(4)
C(7)-C(12)-C(13)-C(4)	0.0(4)
C(11)-C(12)-C(13)-C(4)	179.9(3)
C(7)-C(12)-C(13)-C(14)	178.1(3)
C(11)-C(12)-C(13)-C(14)	-2.1(5)
C(4)-C(13)-C(14)-C(1)	71.3(4)
C(12)-C(13)-C(14)-C(1)	-106.7(3)
C(3)-C(2)-C(1)-C(15)	-164.9(3)
C(3)-C(2)-C(1)-C(14)	-40.0(4)
C(13)-C(14)-C(1)-C(15)	76.5(3)
C(13)-C(14)-C(1)-C(2)	-47.3(3)

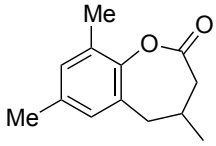
Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for: **2n** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

The chromatograms for determination of enantioselectivity

Table 2

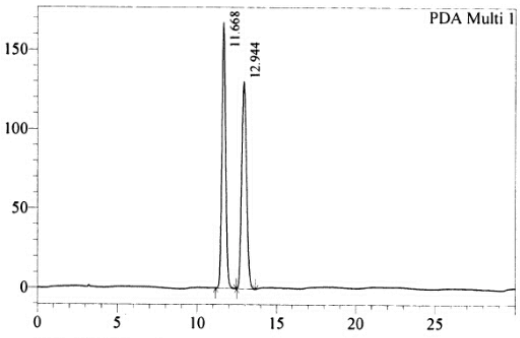


2l

HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99.5/0.5); **Flow rate:** 1.0 mL/min; **Detection:** UV213 nm.

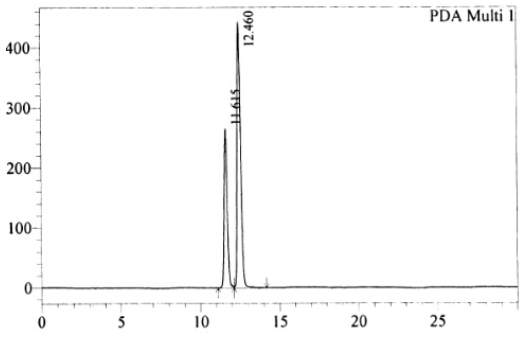
Racemic



PDA Ch1 213nm 4nm

Peak#	Ret. Time	Area %	Peak Start	Peak End
1	11.668	50.875	11.157	12.448
2	12.944	49.125	12.480	13.685
Total		100.000		

Chiral



PDA Ch1 213nm 4nm

Peak#	Ret. Time	Area %	Peak Start	Peak End
1	11.615	35.152	11.104	12.117
2	12.460	64.848	12.117	14.165
Total		100.000		

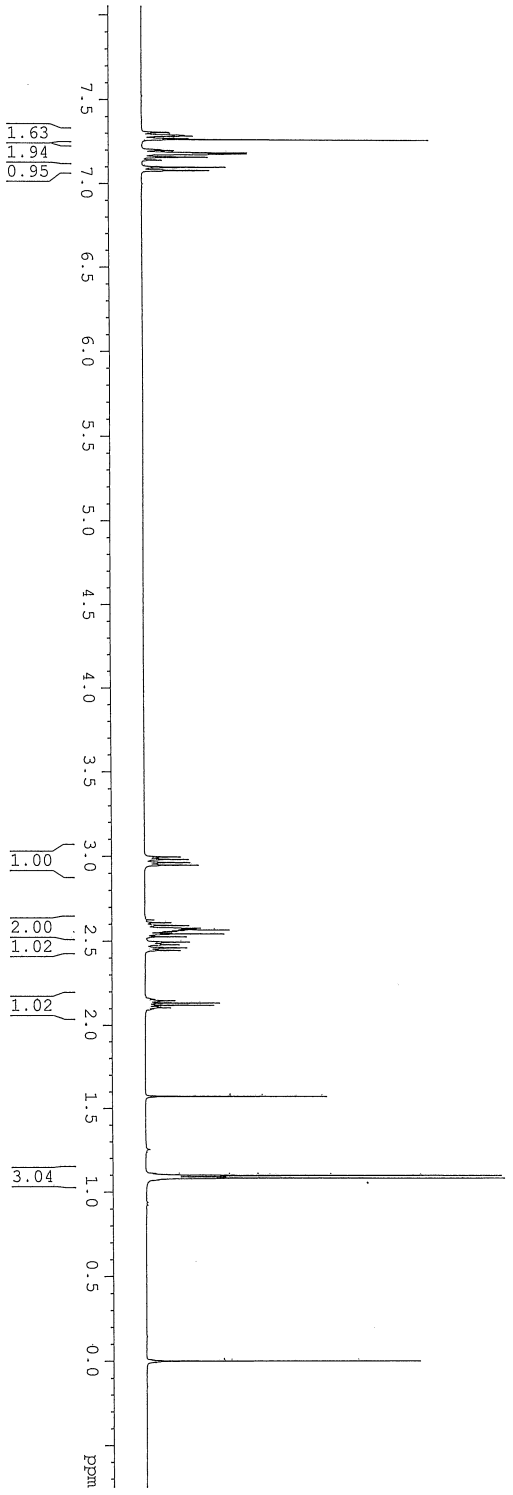
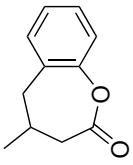

1.63
1.94
0.95
1.00
2.00
1.02
1.02
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, **2a**



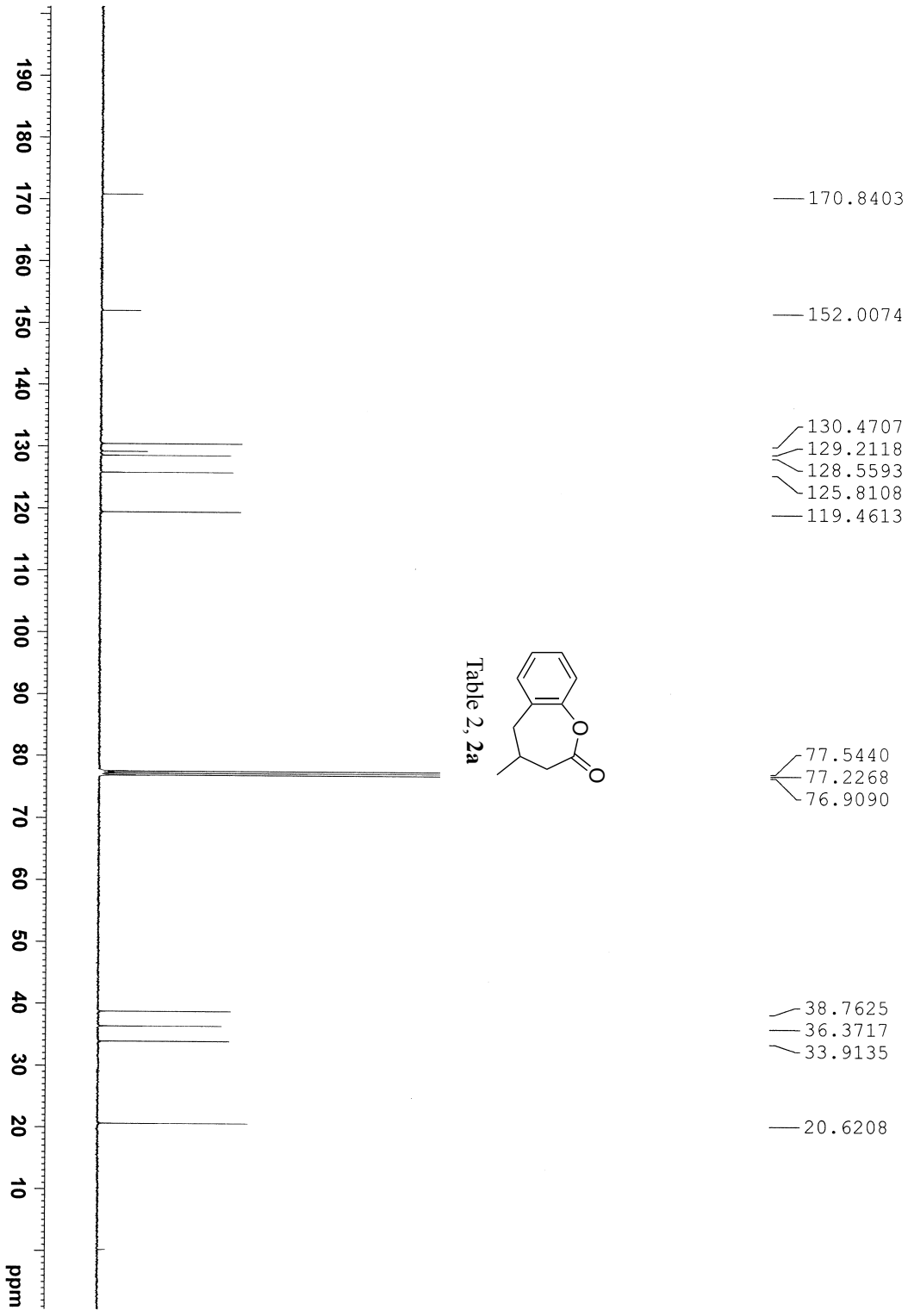

170.8403
152.0074
130.4707
129.2118
128.5593
125.8108
119.4613
77.5440
77.2268
76.9090
38.7625
36.3717
33.9135
20.6208
ppm

Table 2, **2a**

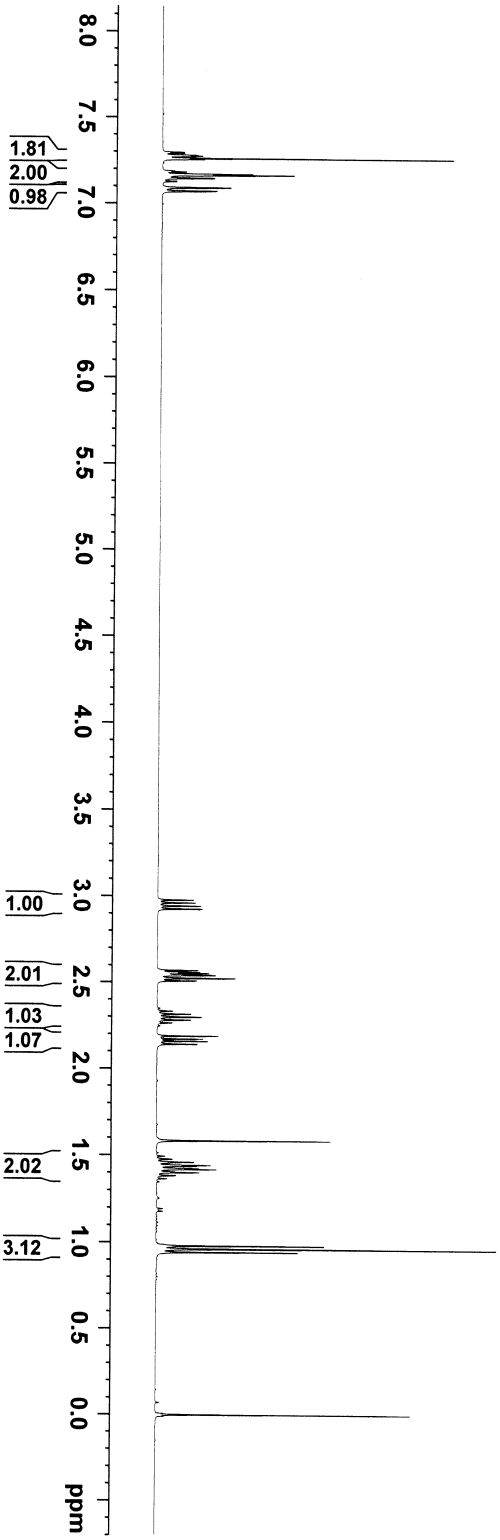
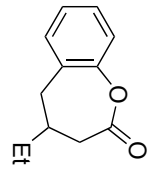

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.81
2.00
0.98
1.00
2.01
1.03
1.07
2.02
3.12

Table 2, **2b**


O
O
Et

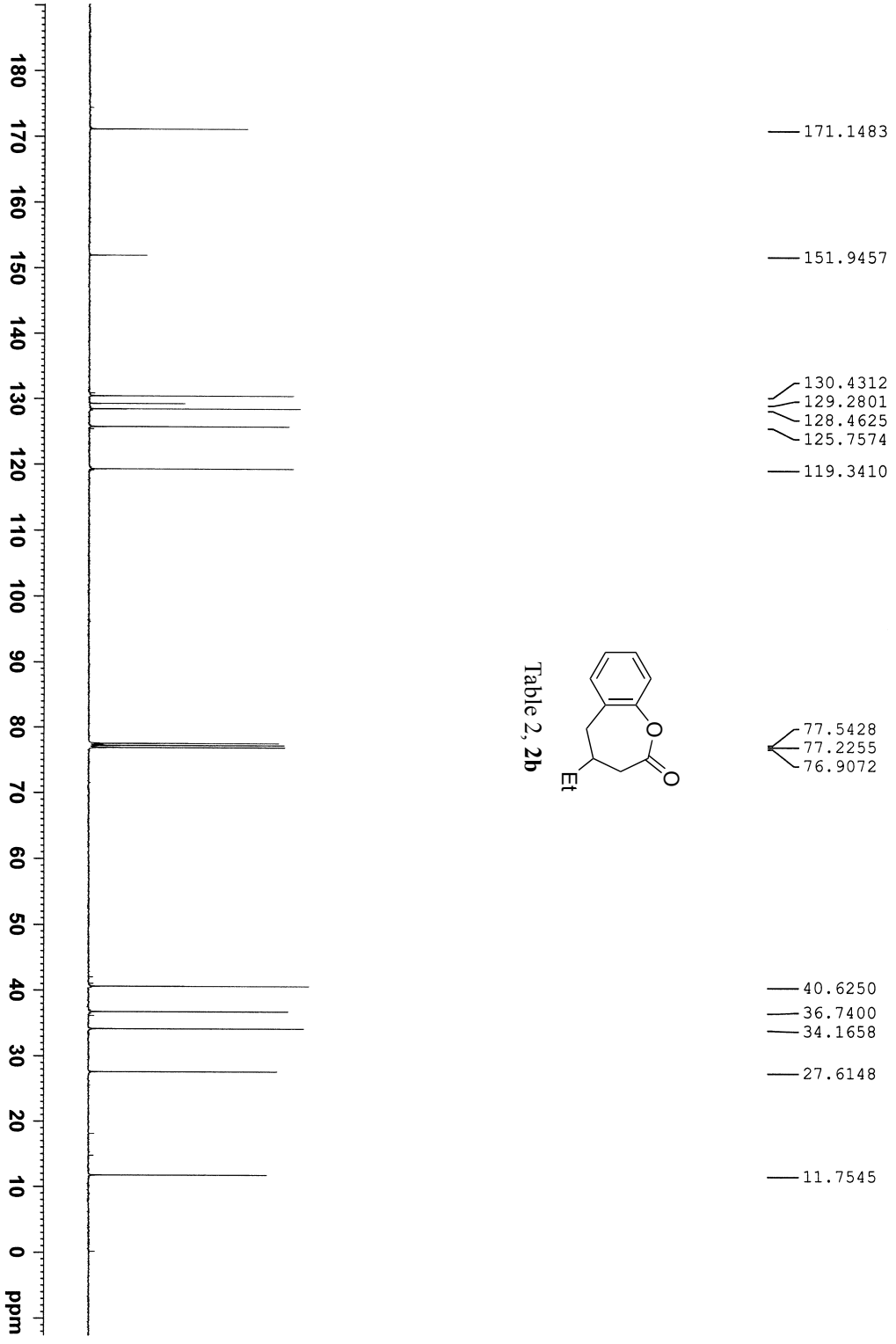

171.1483
151.9457
130.4312
129.2801
128.4625
125.7574
119.3410
77.5428
77.2255
76.9072
40.6250
36.7400
34.1658
27.6148
11.7545
Et
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Table 2, **2b**

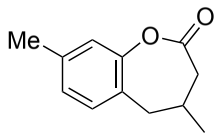
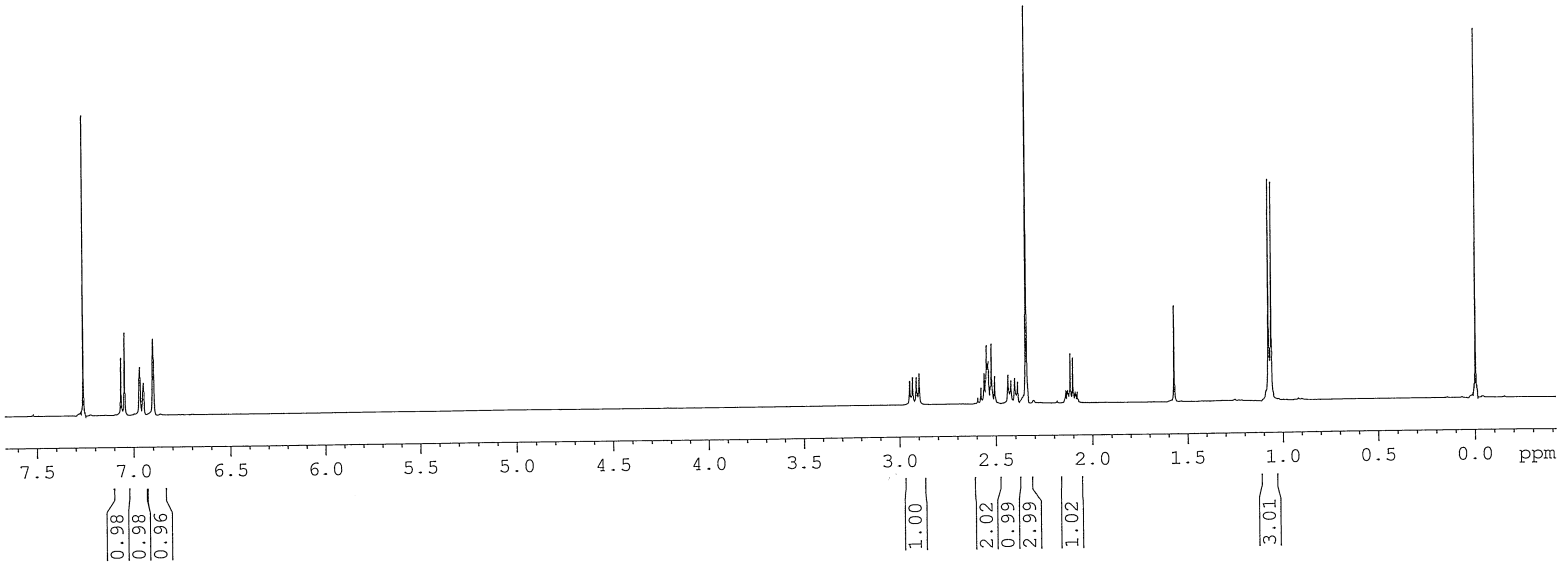

Me
O
O

Table 2, **2c**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.98
0.98
0.96
1.00
2.02
0.99
2.99
1.02
3.01

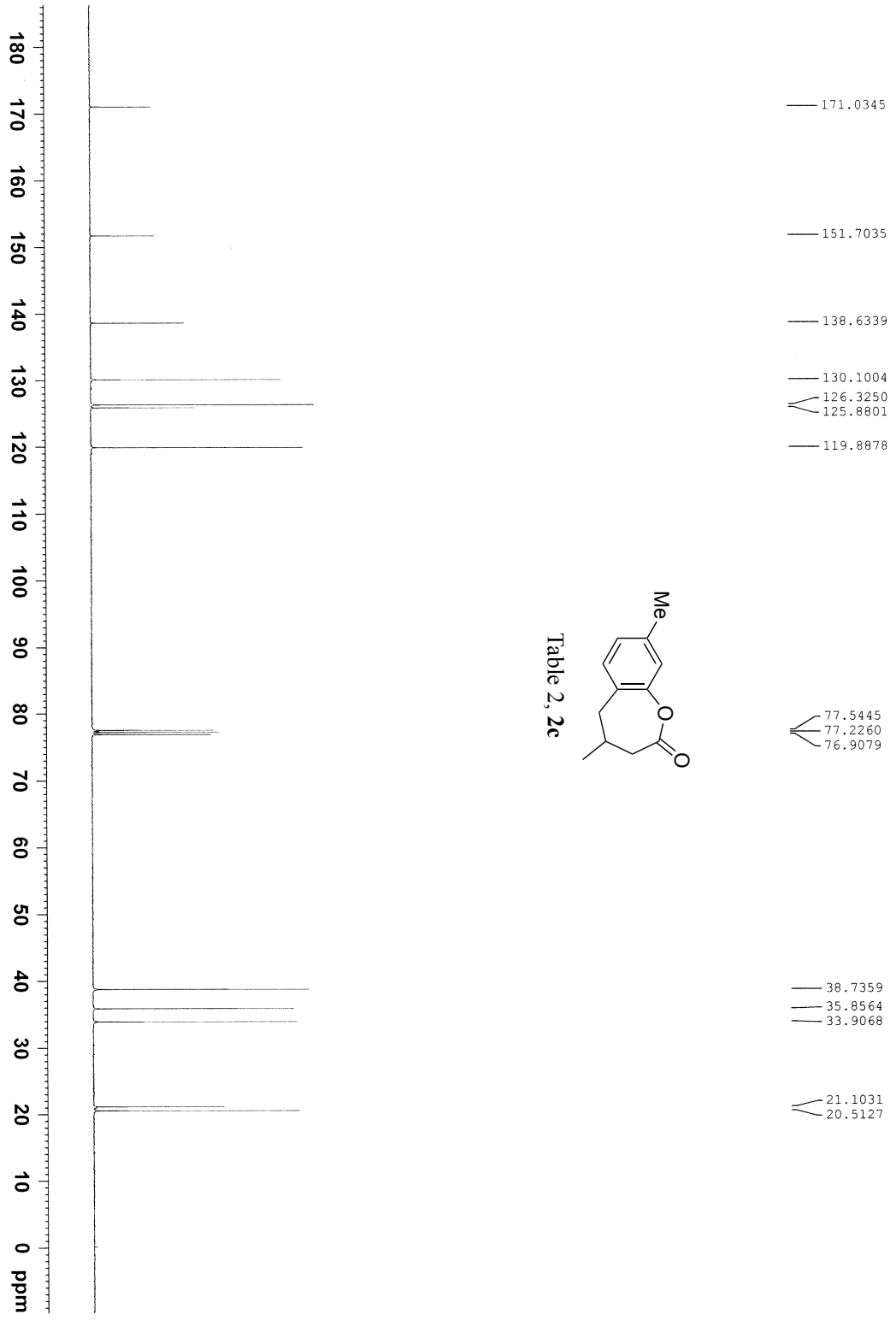

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
171.0345
151.7035
138.6339
130.1004
126.3250
125.8801
119.8878
77.5445
77.2260
76.9079
38.7359
35.8564
33.9068
21.1031
20.5127
Me
O
O

Table 2, **2c**

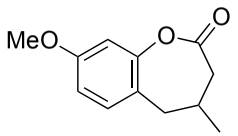
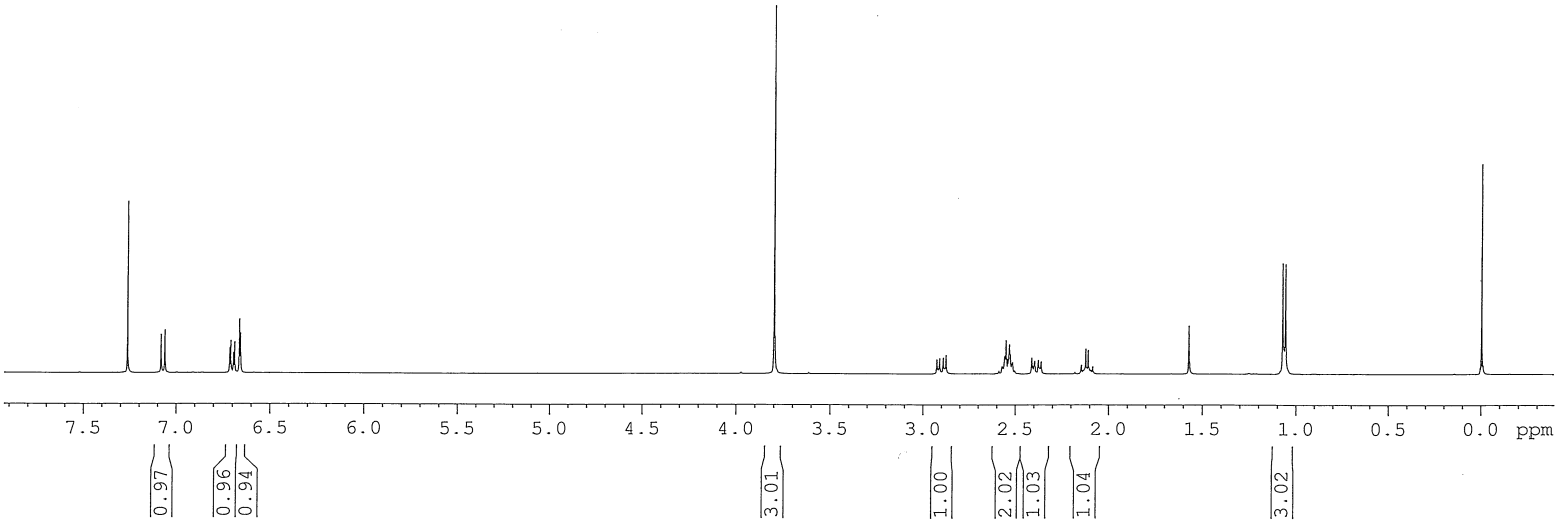
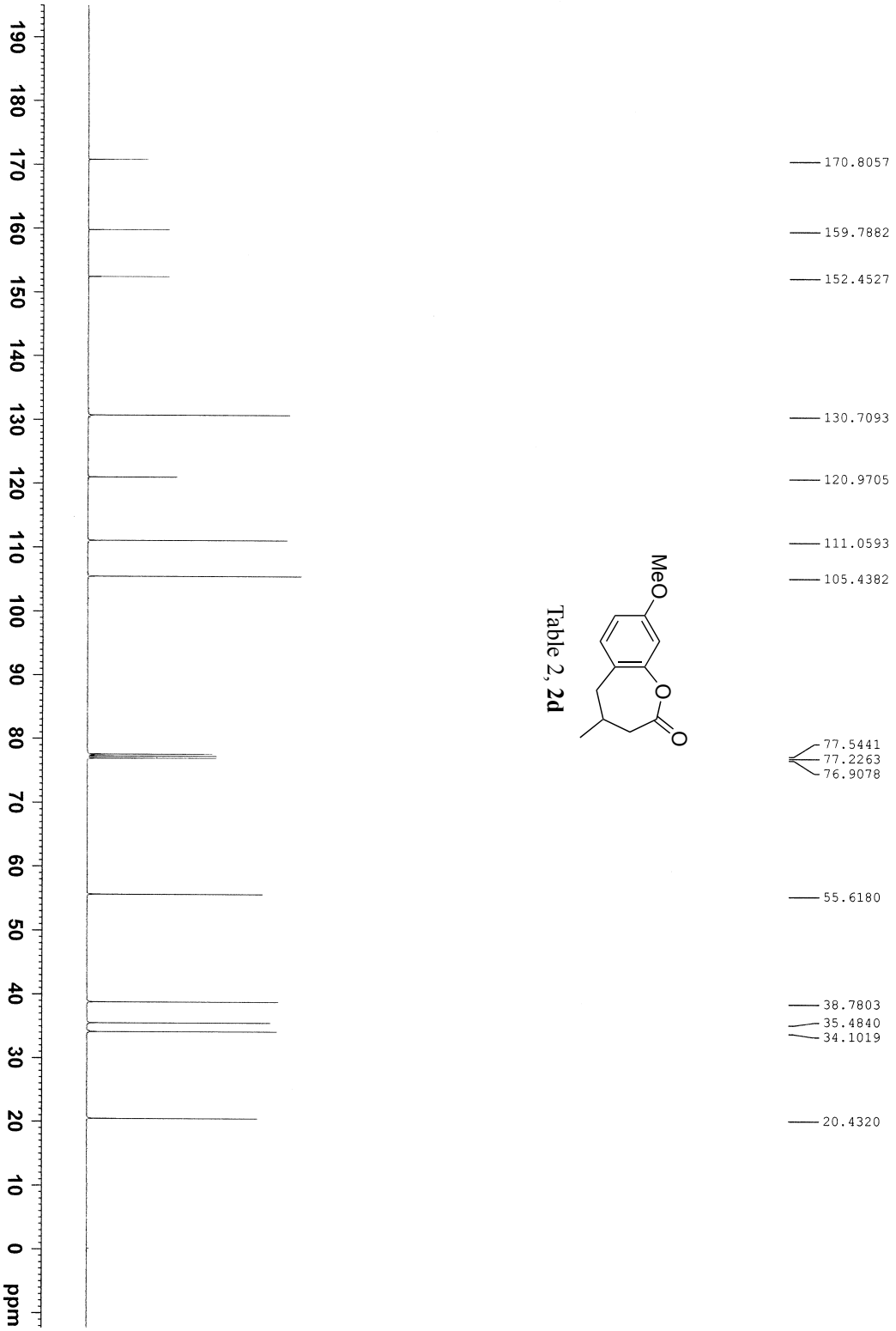

MeO
O
O

Table 2, **2d**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
0.96
0.94
3.01
1.00
2.02
1.03
1.04
3.02


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
170.8057
159.7882
152.4527
130.7093
120.9705
111.0593
105.4382
77.5441
77.2263
76.9078
55.6180
38.7803
35.4840
34.1019
20.4320
MeO
O
O
Table 2, **2d**

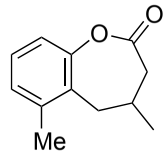
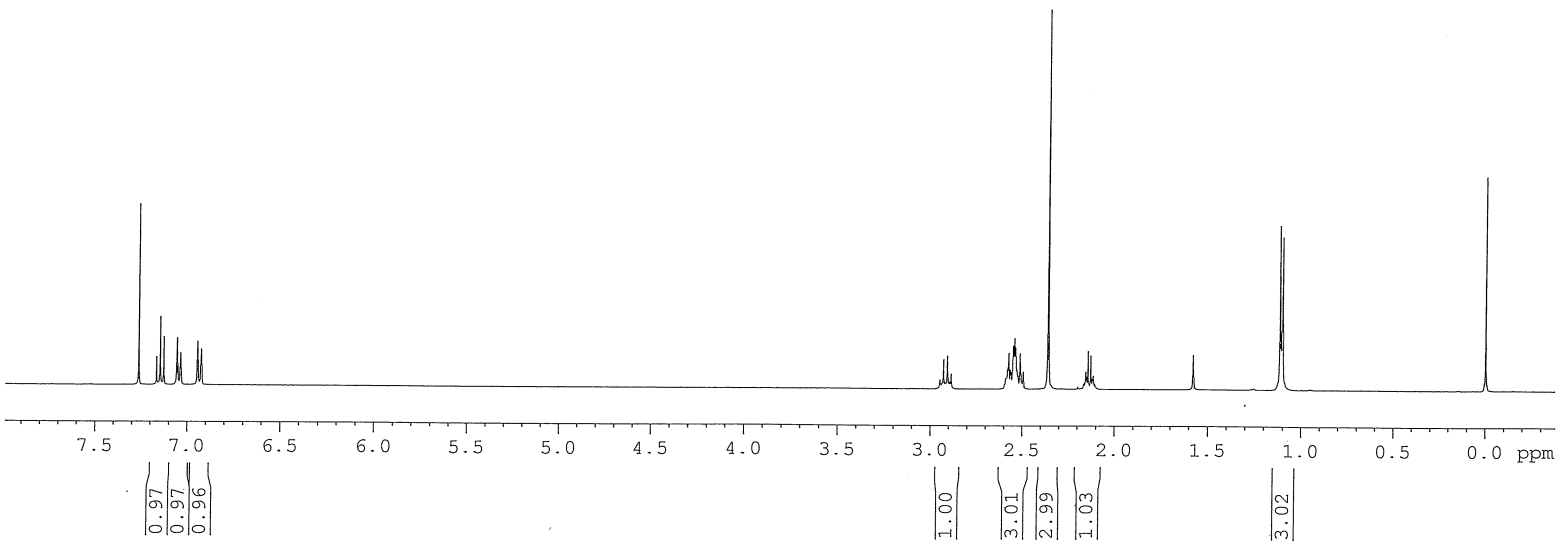

O
O
Me

Table 2, **2e**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.97
0.97
0.96
1.00
3.01
2.99
1.03
3.02

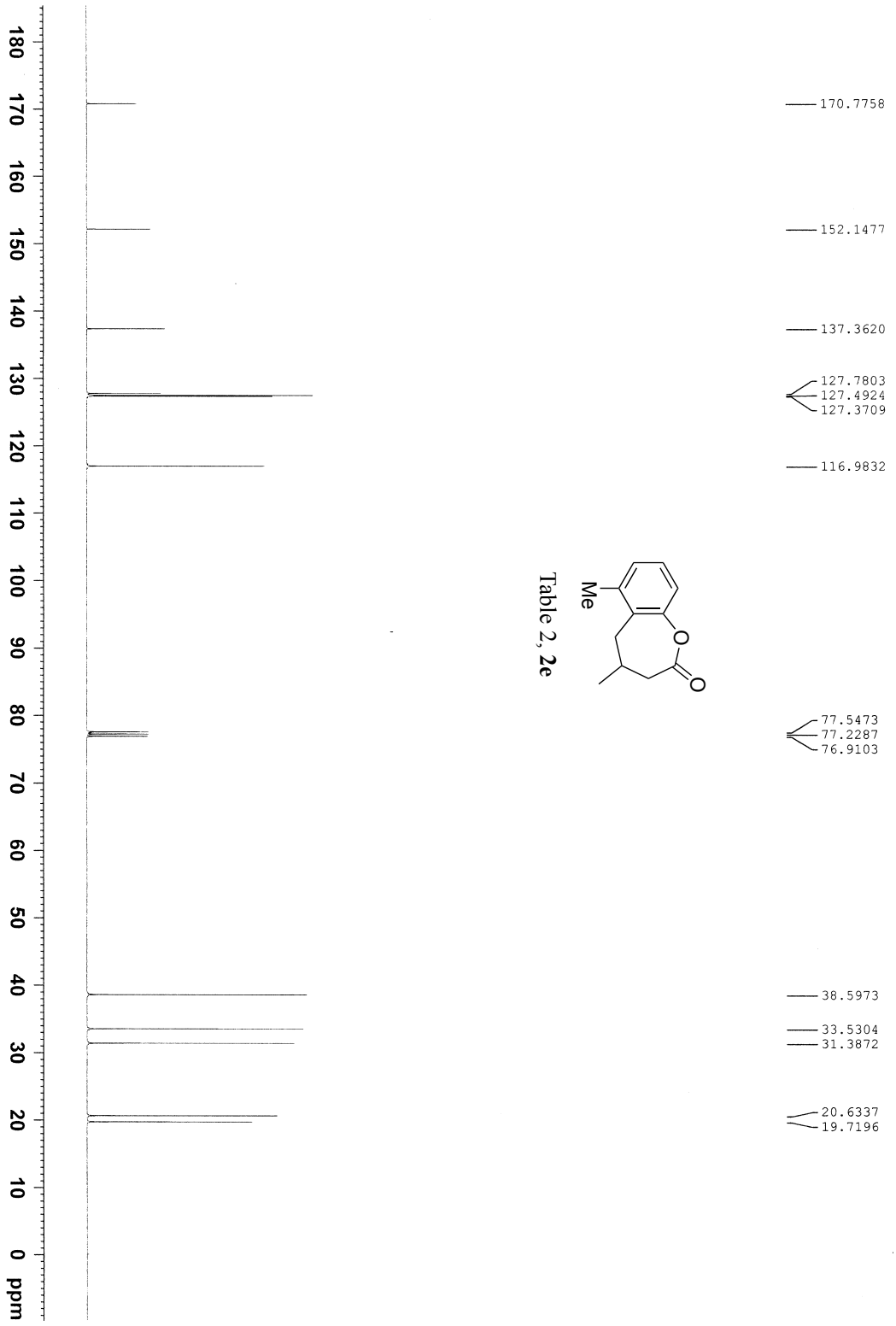

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
170.7758
152.1477
137.3620
127.7803
127.4924
127.3709
116.9832
77.5473
77.2287
76.9103
38.5973
33.5304
31.3872
20.6337
19.7196
Me
O
O

Table 2, **2e**

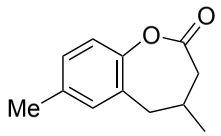
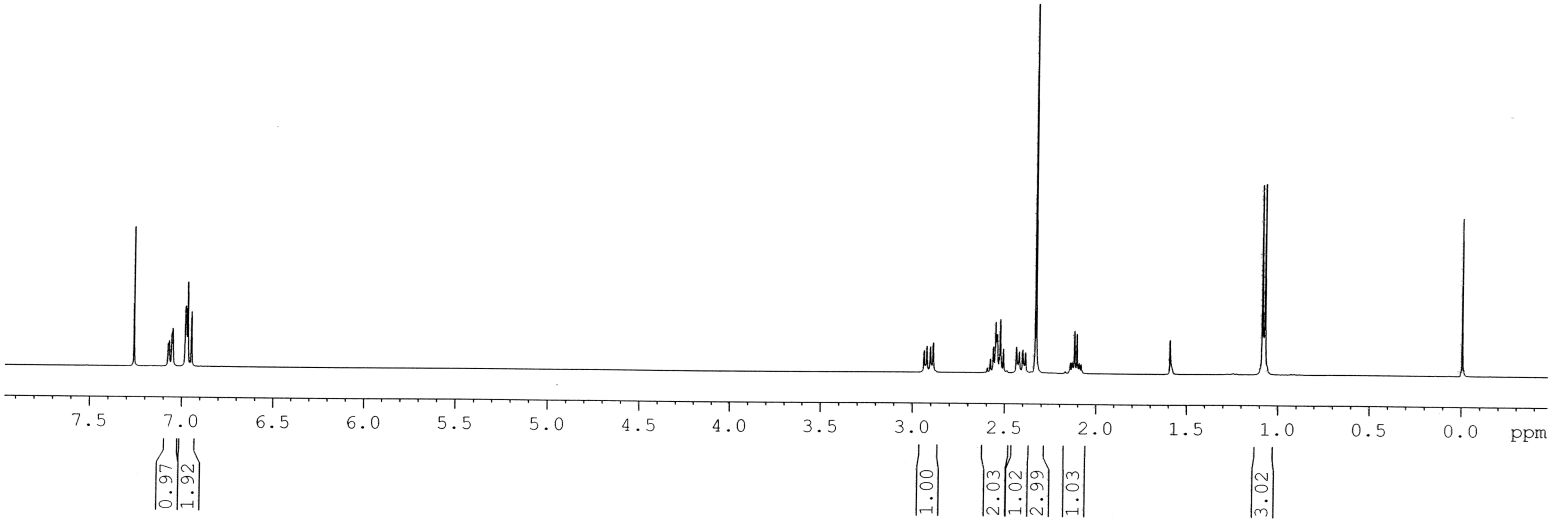

O
O
Me

Table 2, **2f**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
1.92
1.00
2.03
1.02
2.99
1.03
3.02

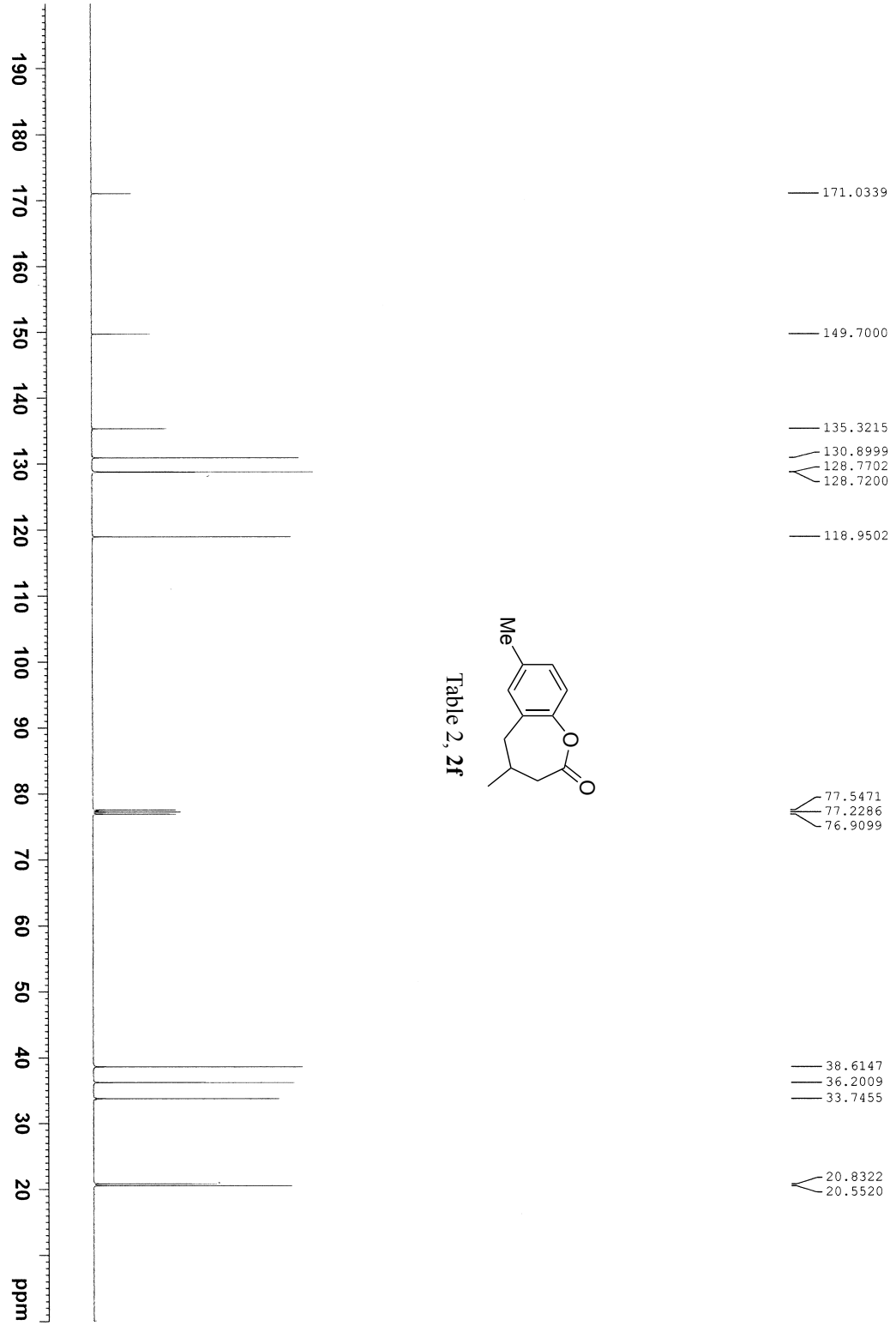

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
171.0339
149.7000
135.3215
130.8999
128.7702
128.7200
118.9502
77.5471
77.2286
76.9099
38.6147
36.2009
33.7455
20.8322
20.5520
Me
O
O

Table 2, **2f**

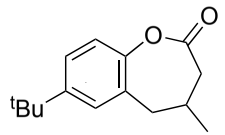

O
O
tBu

Table 2, **2g**

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.12
0.98
0.96
1.00
2.01
1.03
1.00
9.02
3.03

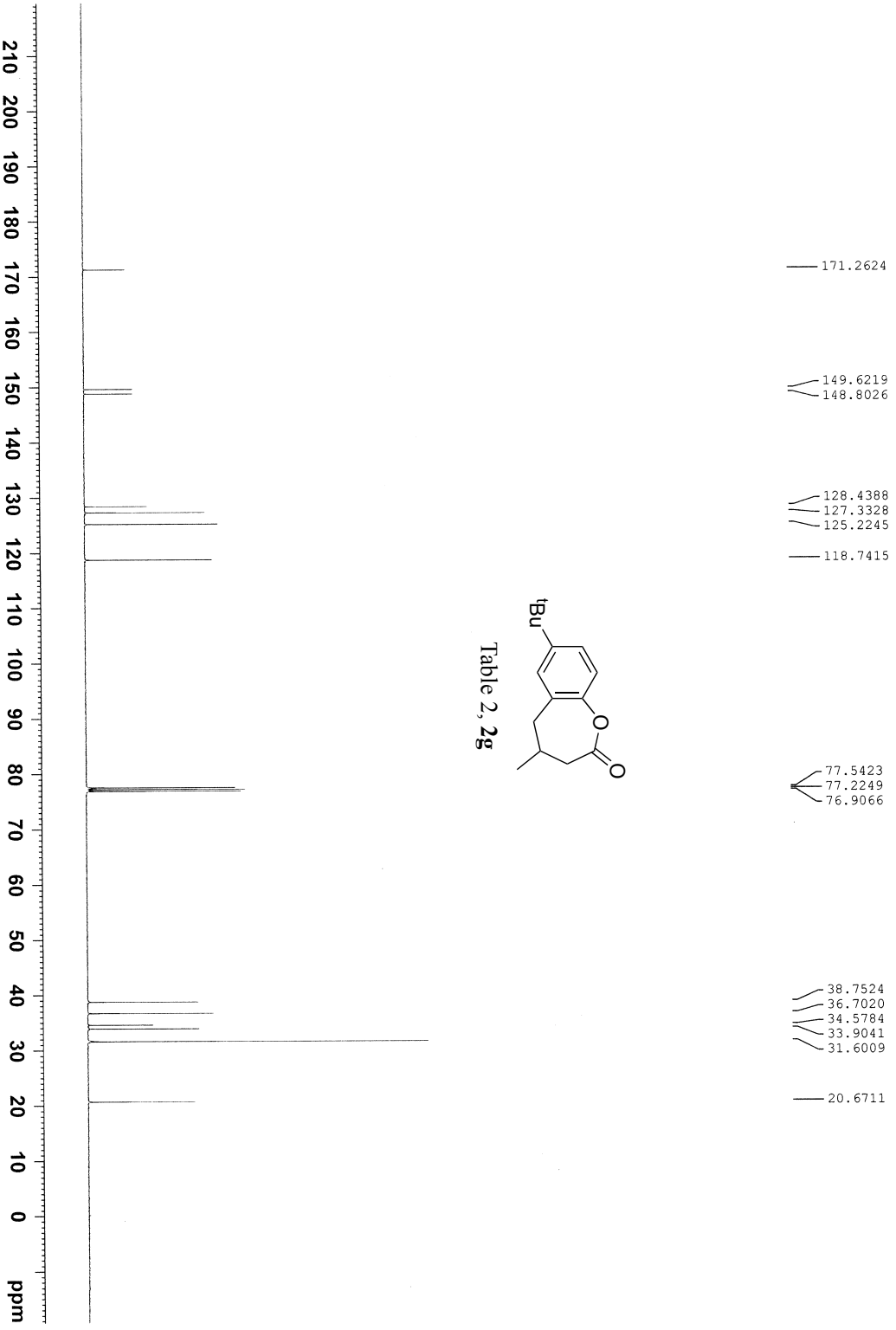

171.2624
149.6219
148.8026
128.4388
127.3328
125.2245
118.7415
77.5423
77.2249
76.9066
38.7524
36.7020
34.5784
33.9041
31.6009
20.6711
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, **2g**

0.96
0.99
0.97
3.00
1.00
2.01
1.03
1.02
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

MeO
O
O

Table 2, **2h**

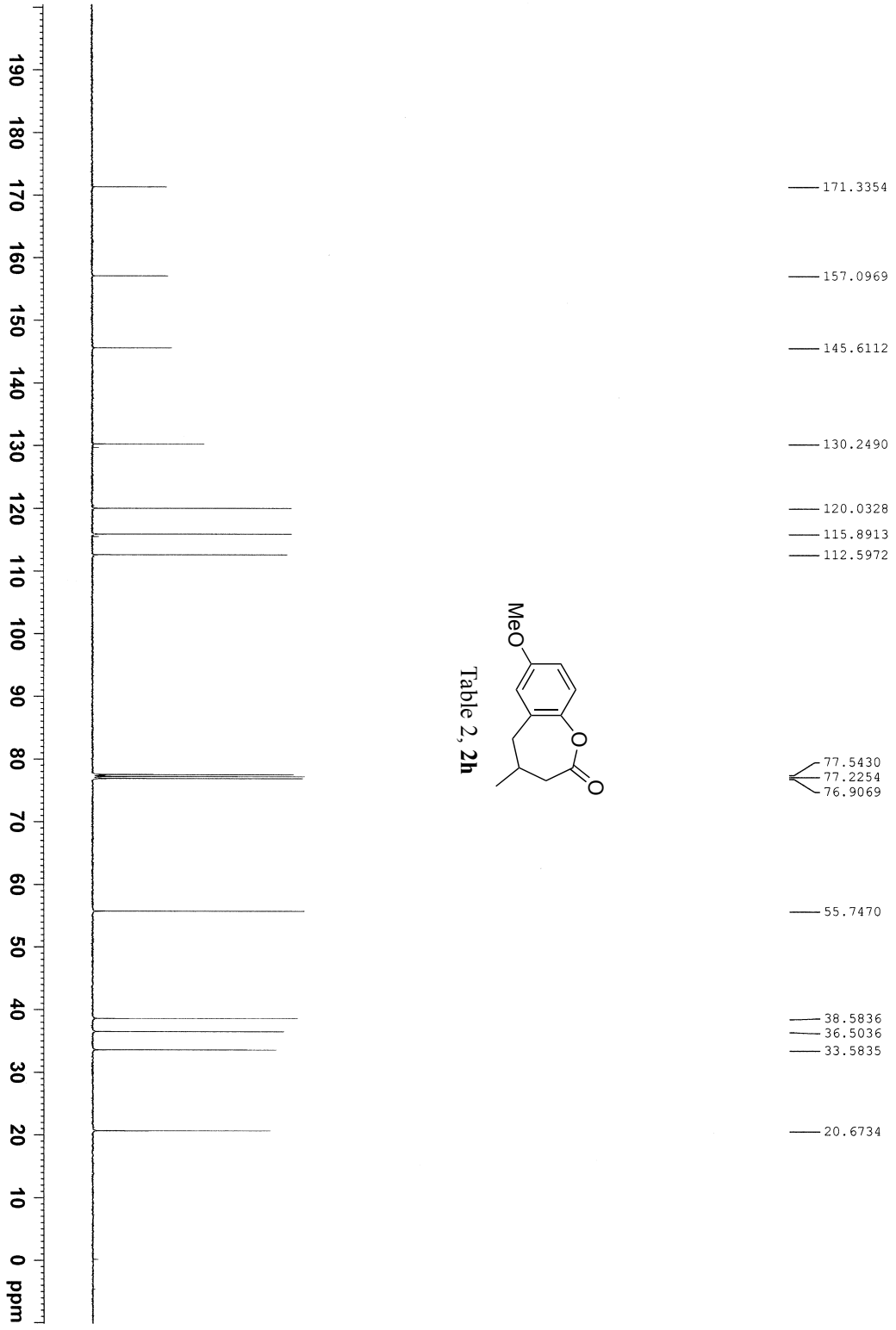

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
171.3354
157.0969
145.6112
130.2490
120.0328
115.8913
112.5972
77.5430
77.2254
76.9069
55.7470
38.5836
36.5036
33.5835
20.6734
MeO
O
O

Table 2, **2h**

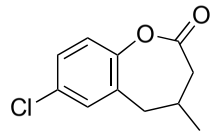
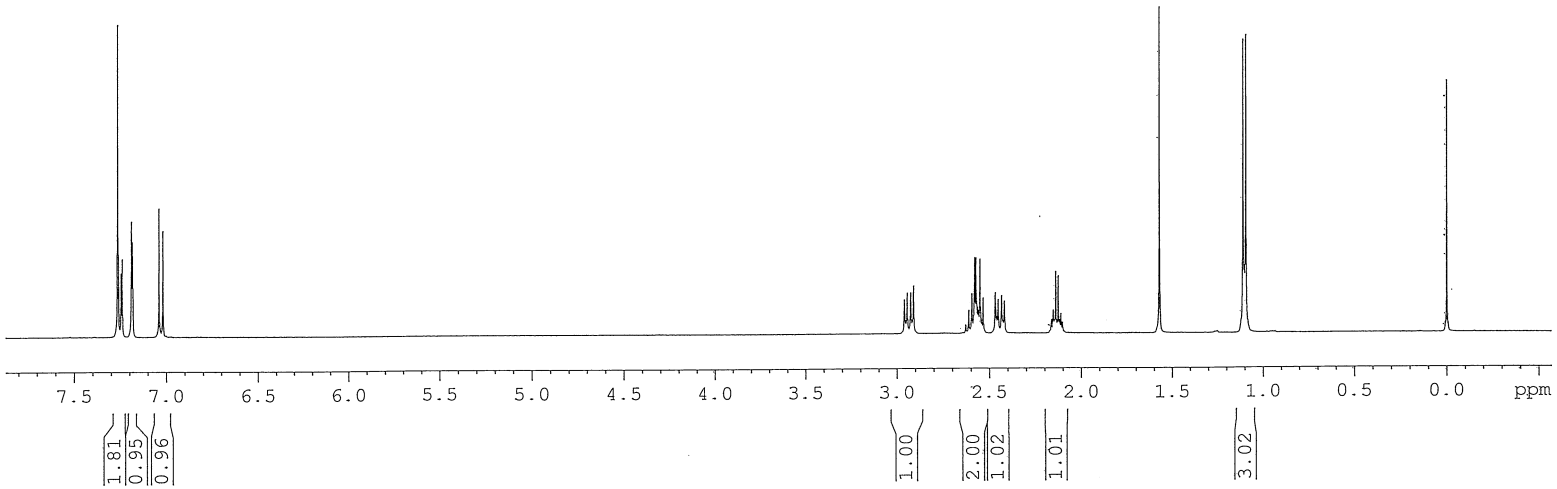

O
O
Cl

Table 2, **2i**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.81
0.95
0.96
1.00
2.00
1.02
1.01
3.02

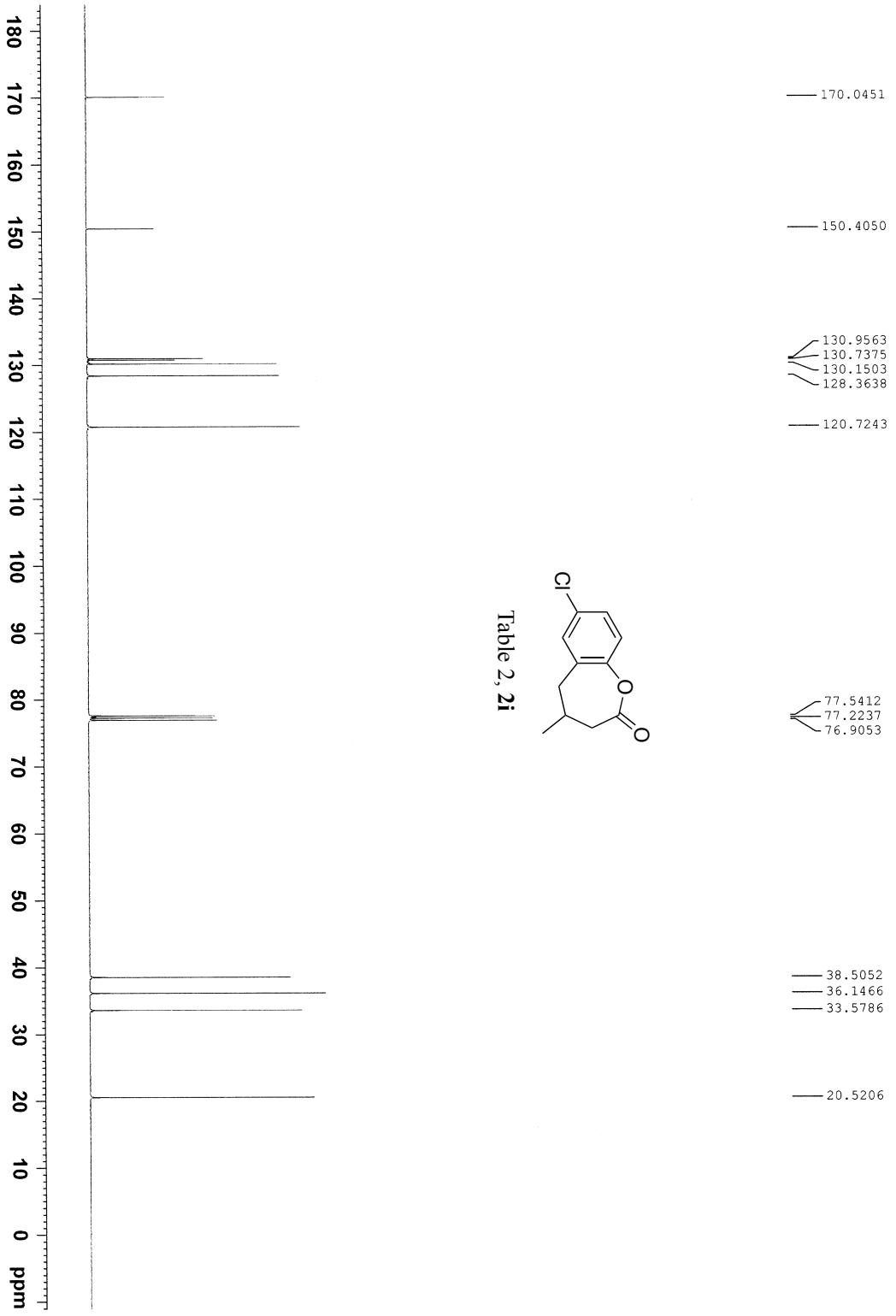

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
170.0451
150.4050
130.9563
130.7375
130.1503
128.3638
120.7243
77.5412
77.2237
76.9053
38.5052
36.1466
33.5786
20.5206
Cl
O
O

Table 2, **2i**

MeO2C
O
O

Table 2, **2j**

0.97
0.97
0.97
2.96
1.00
3.04
1.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

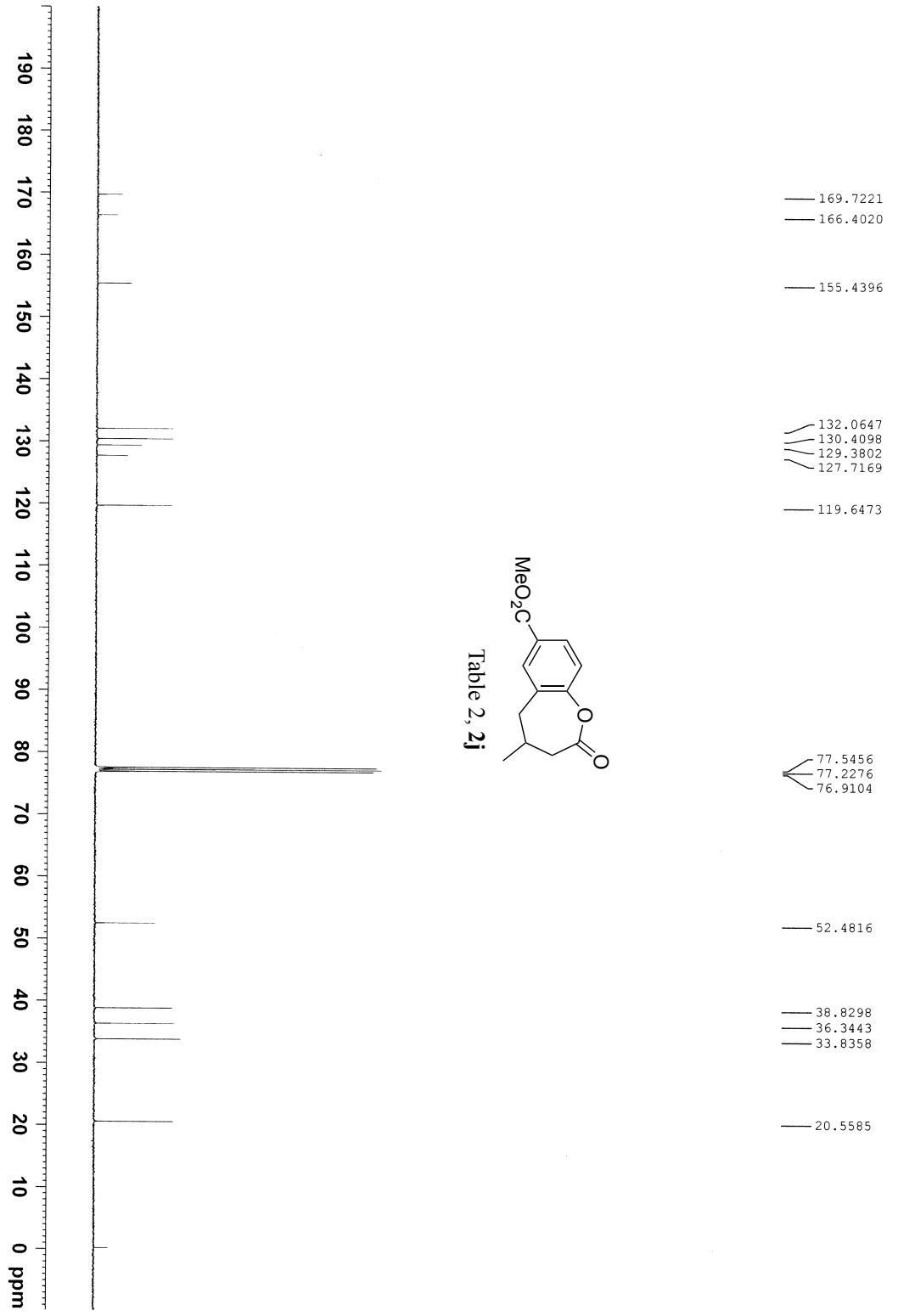

169.7221
166.4020
155.4396
132.0647
130.4098
129.3802
127.7169
119.6473
77.5456
77.2276
76.9104
52.4816
38.8298
36.3443
33.8358
20.5585
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
MeO2C
O
O

Table 2, **2j**

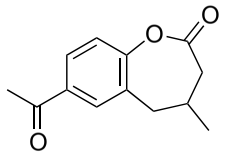
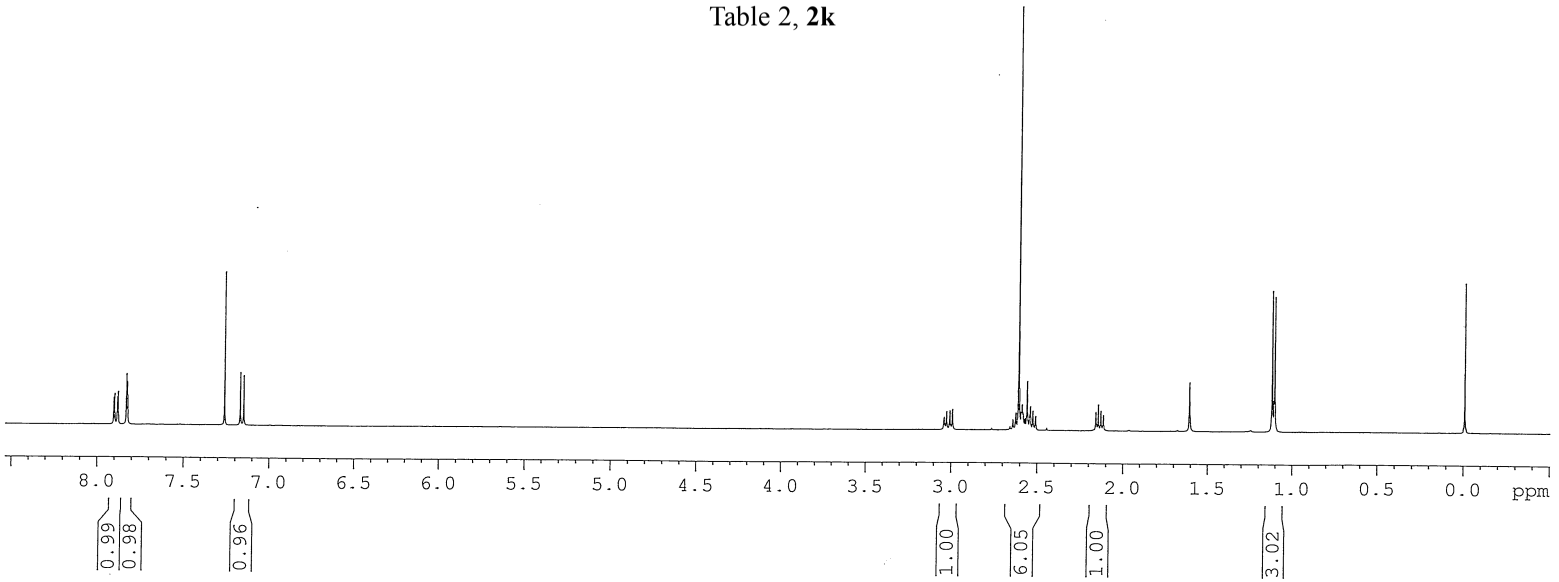


Table 2, **2k**


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.99
0.98
0.96
1.00
6.05
1.00
3.02

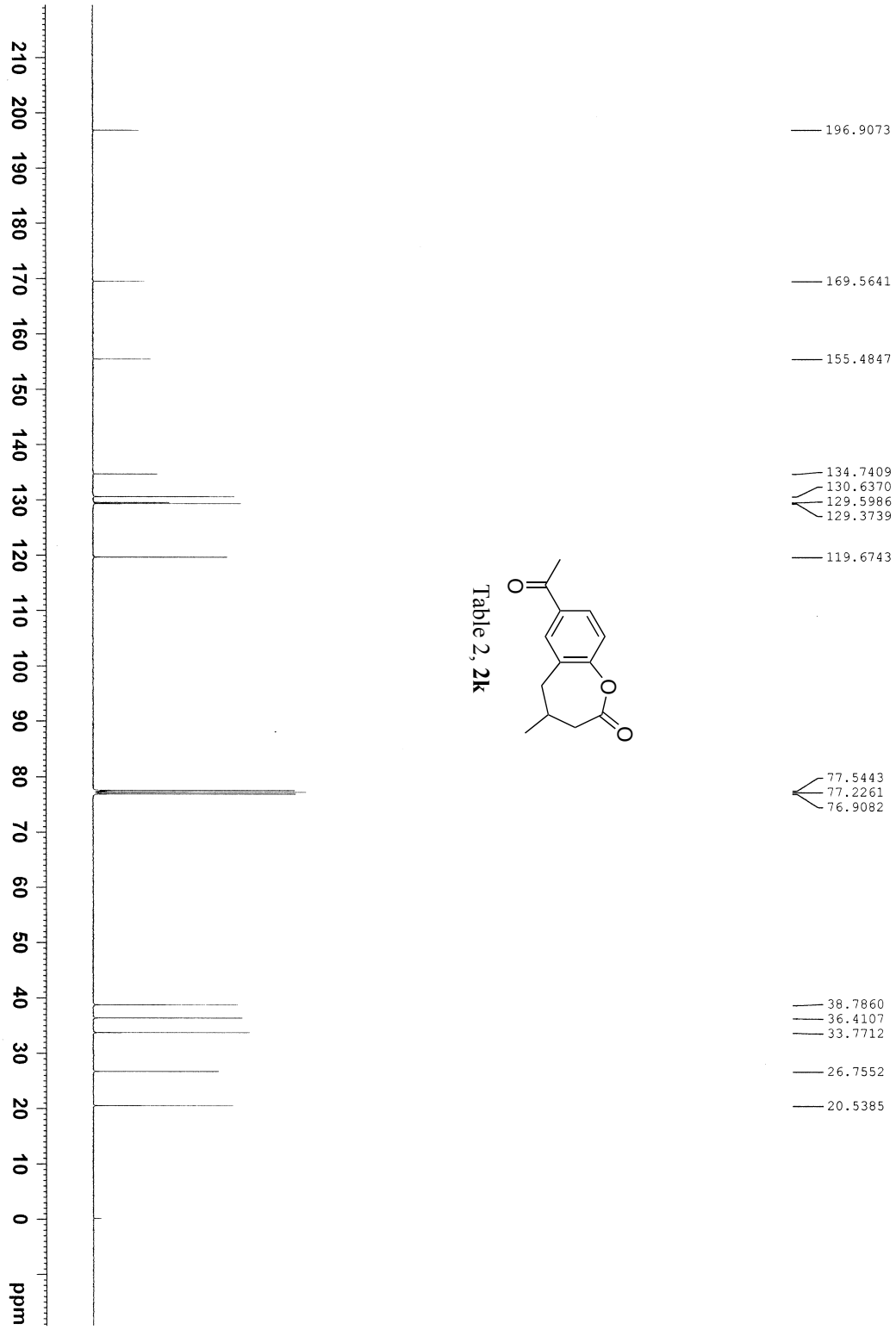

196.9073
169.5641
155.4847
134.7409
130.6370
129.5986
129.3739
119.6743
77.5443
77.2261
76.9082
38.7860
36.4107
33.7712
26.7552
20.5385
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, **2k**

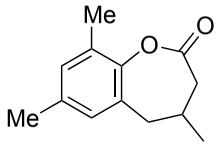
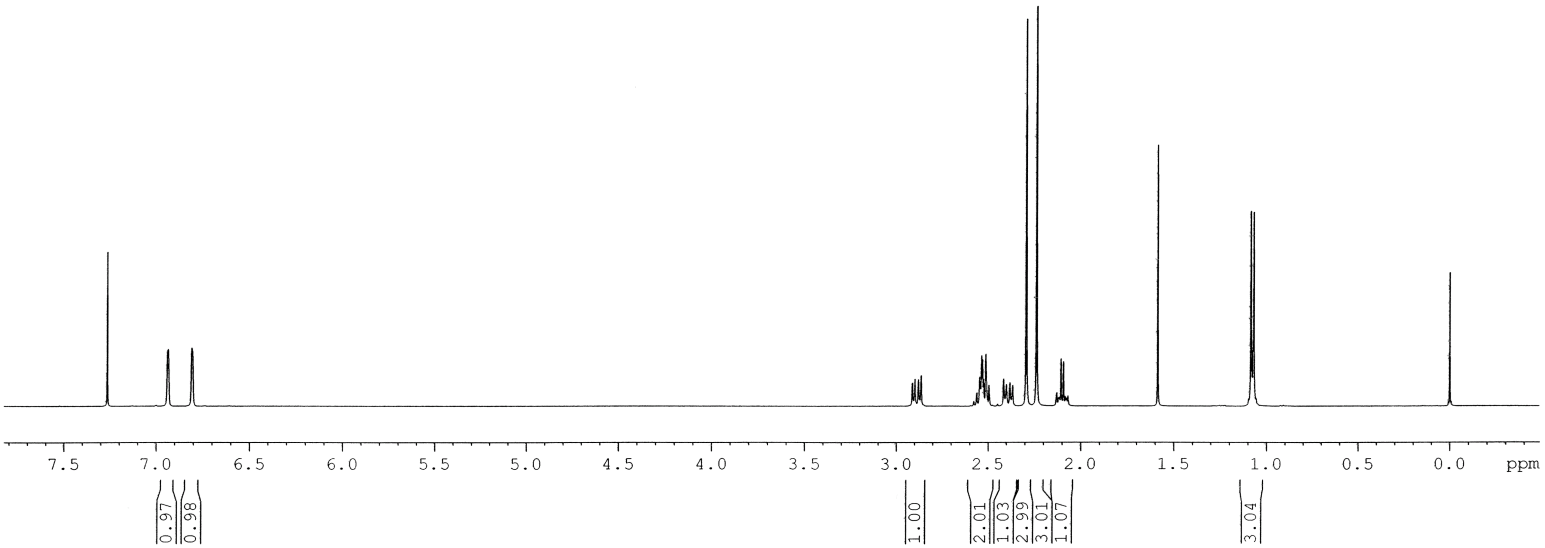

Me
O
O
Me

Table 2, **2l**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
0.98
1.00
2.01
1.03
2.99
3.01
1.07
3.04

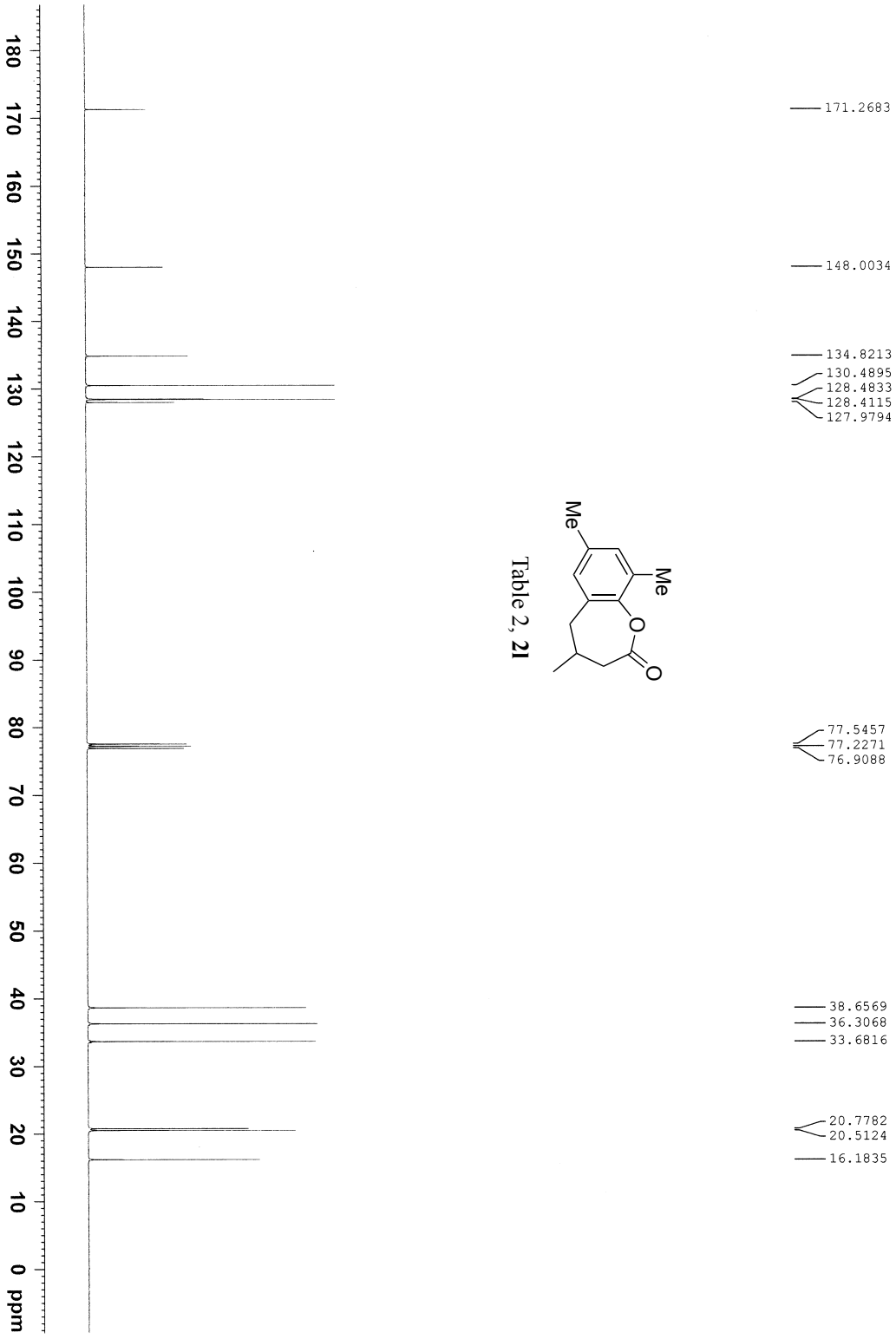
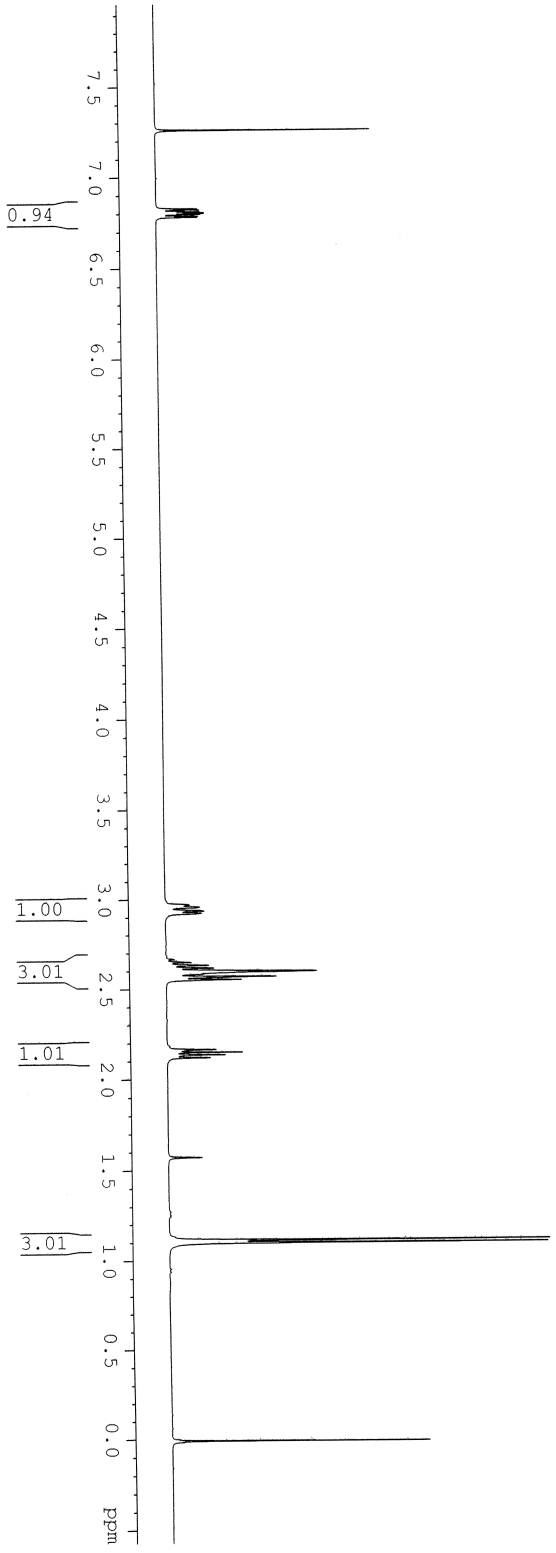

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
171.2683
148.0034
134.8213
130.4895
128.4833
128.4115
127.9794
77.5457
77.2271
76.9088
38.6569
36.3068
33.6816
20.7782
20.5124
16.1835
Me
Me
O
O

Table 2, **2l**


0.94
1.00
3.01
1.01
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

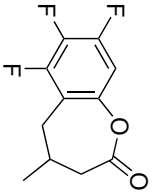

F
F
F
O
O

Table 2, **2m**

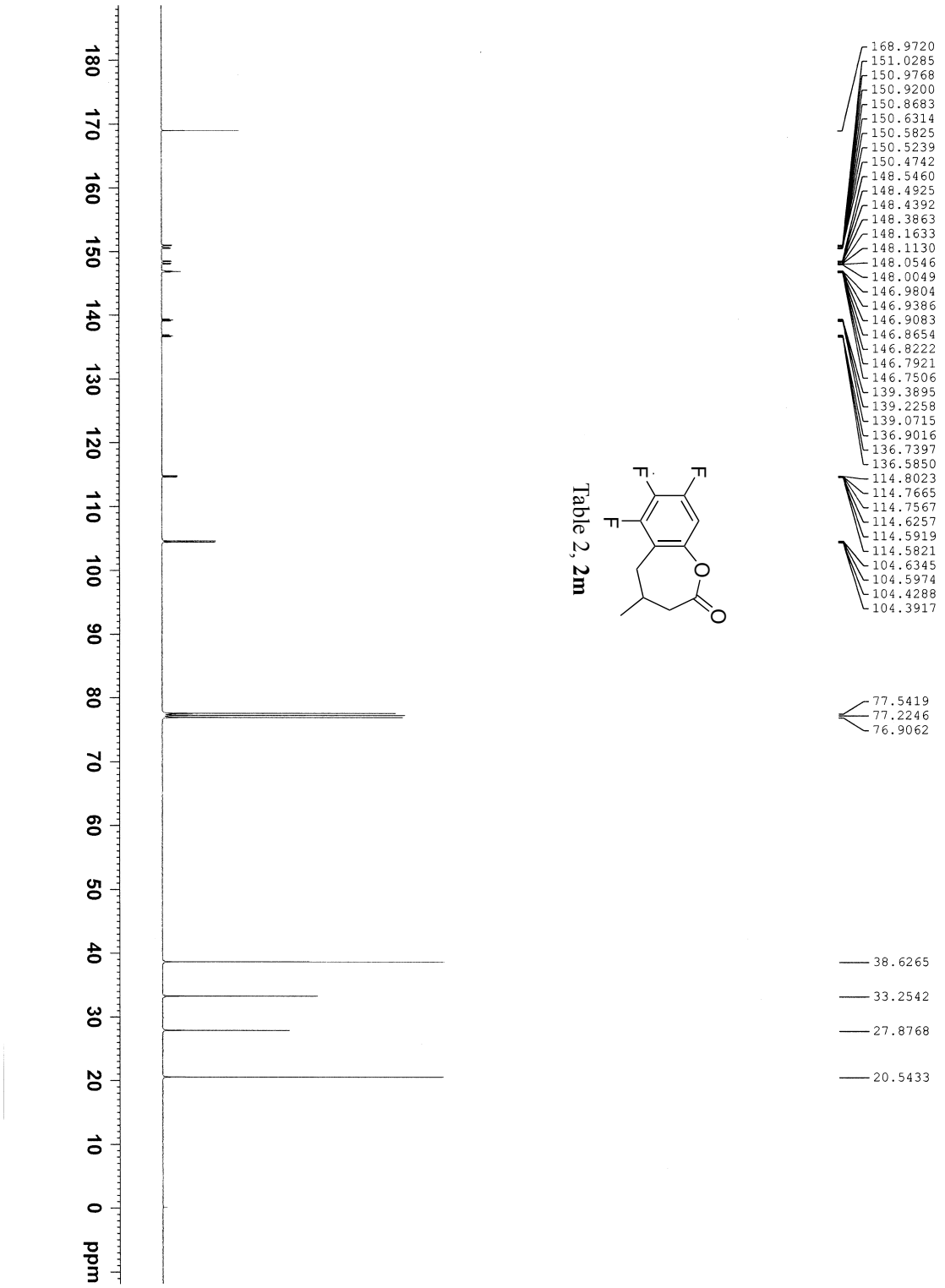

168.9720
151.0285
150.9768
150.9200
150.8683
150.6314
150.5825
150.5239
150.4742
148.5460
148.4925
148.4392
148.3863
148.1633
148.1130
148.0546
148.0049
146.9804
146.9386
146.9083
146.8654
146.8222
146.7921
146.7506
139.3895
139.2258
139.0715
136.9016
136.7397
136.5850
114.8023
114.7665
114.7567
114.6257
114.5919
114.5821
104.6345
104.5974
104.4288
104.3917
77.5419
77.2246
76.9062
38.6265
33.2542
27.8768
20.5433
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Table 2, **2m**

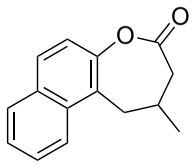
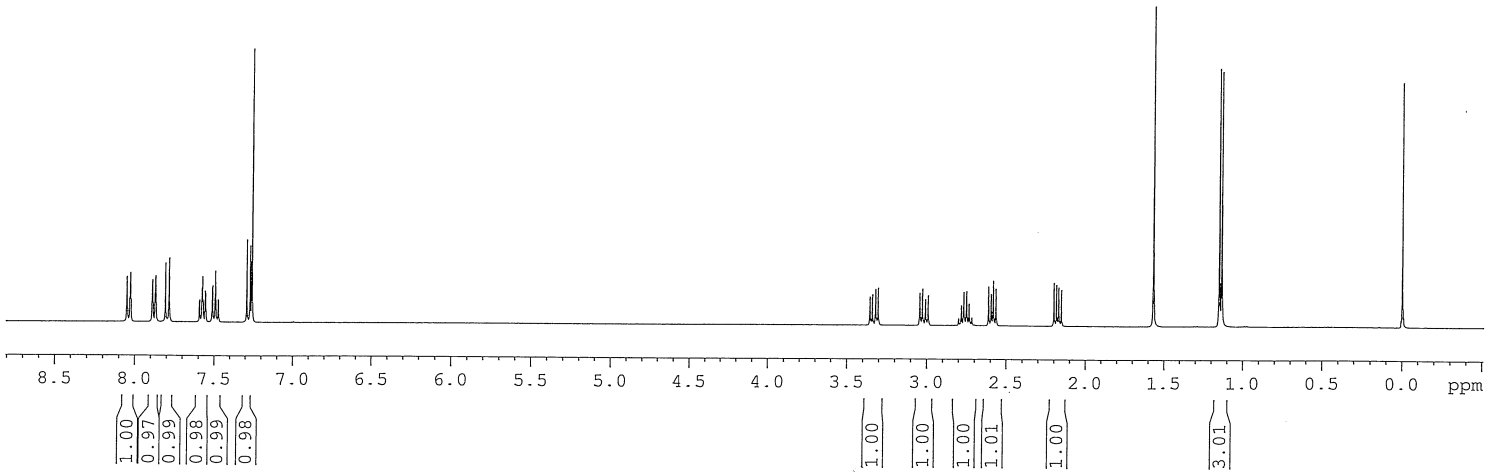


Table 2, **2n**


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.97
0.99
0.98
0.99
0.98
1.00
1.00
1.00
1.01
1.00
3.01

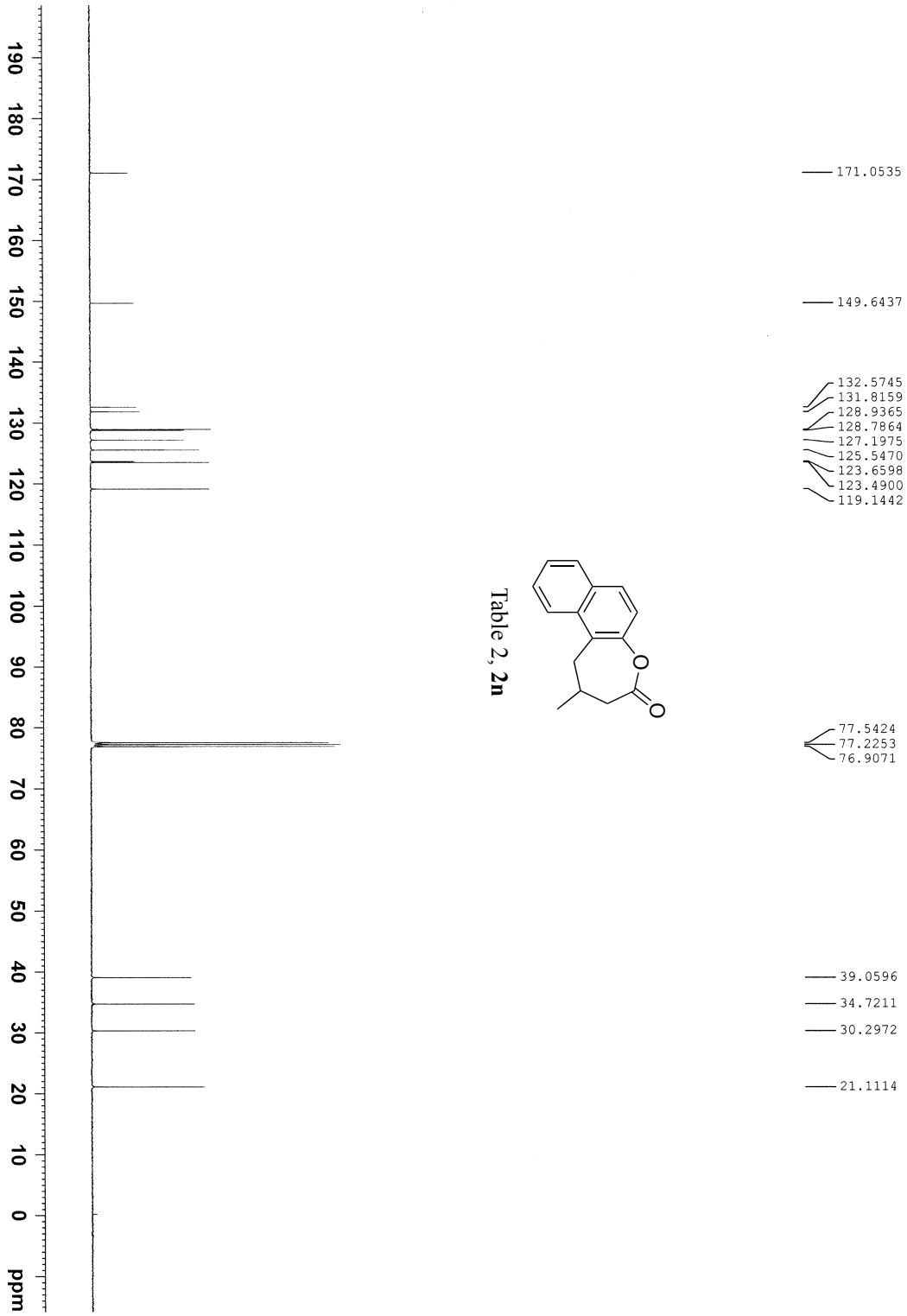

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
171.0535
149.6437
132.5745
131.8159
128.9365
128.7864
127.1975
125.5470
123.6598
123.4900
119.1442
77.5424
77.2253
76.9071
39.0596
34.7211
30.2972
21.1114
O
O

Table 2, **2n**

2.00
1.92
0.96
2.00
1.94
1.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

Table 2, **2o**

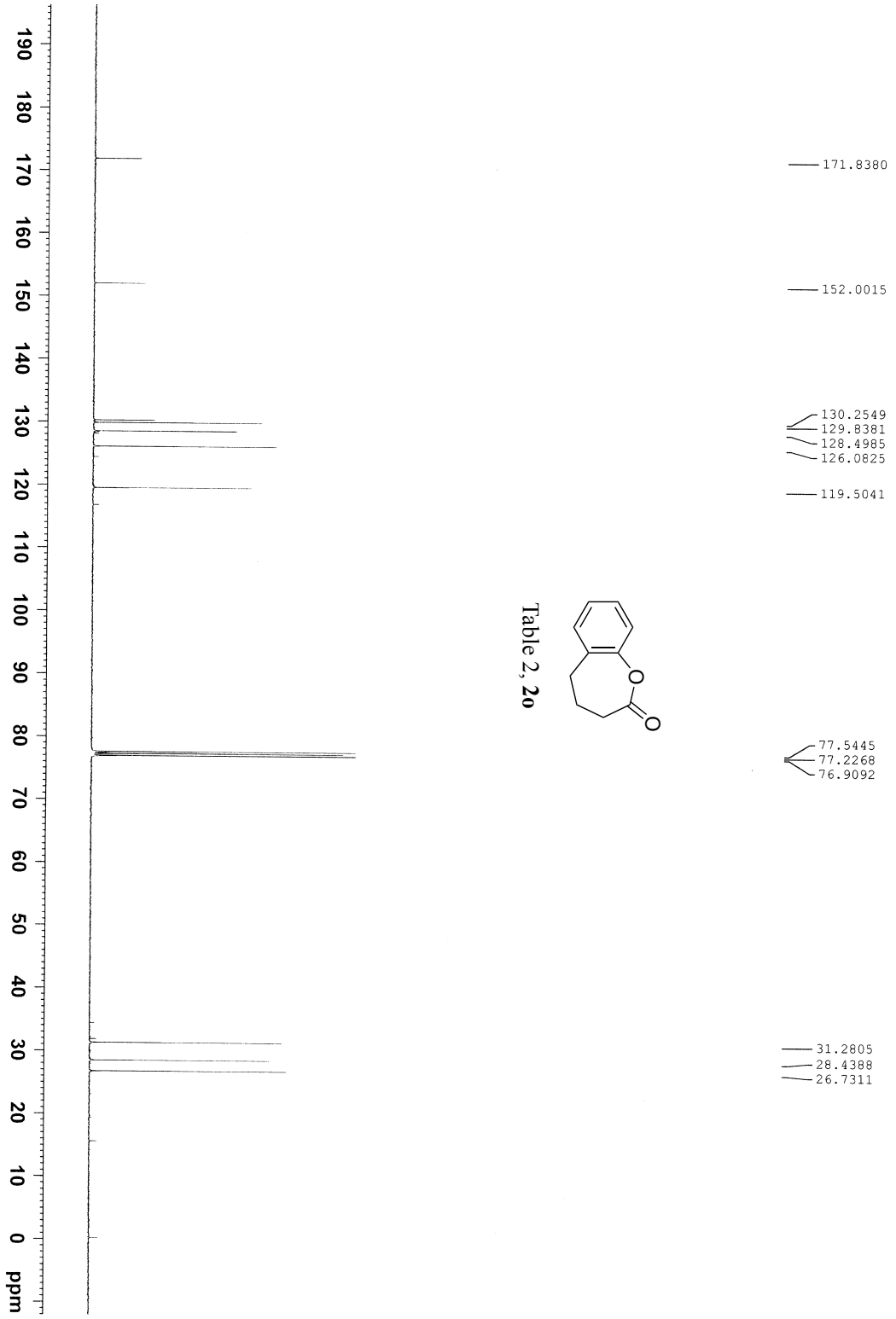

171.8380
152.0015
130.2549
129.8381
128.4985
126.0825
119.5041
77.5445
77.2268
76.9092
31.2805
28.4388
26.7311
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, **2o**

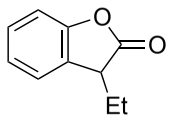
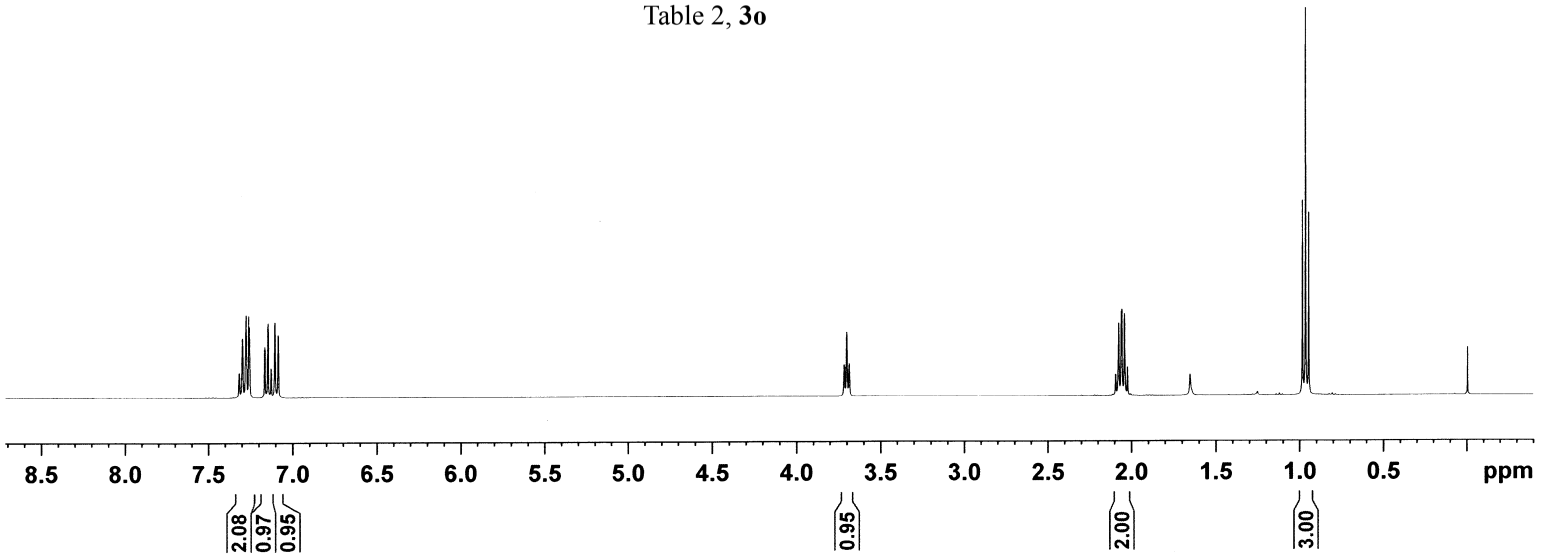

O
O
Et

Table 2, **3o**


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
0.97
0.95
0.95
2.00
3.00

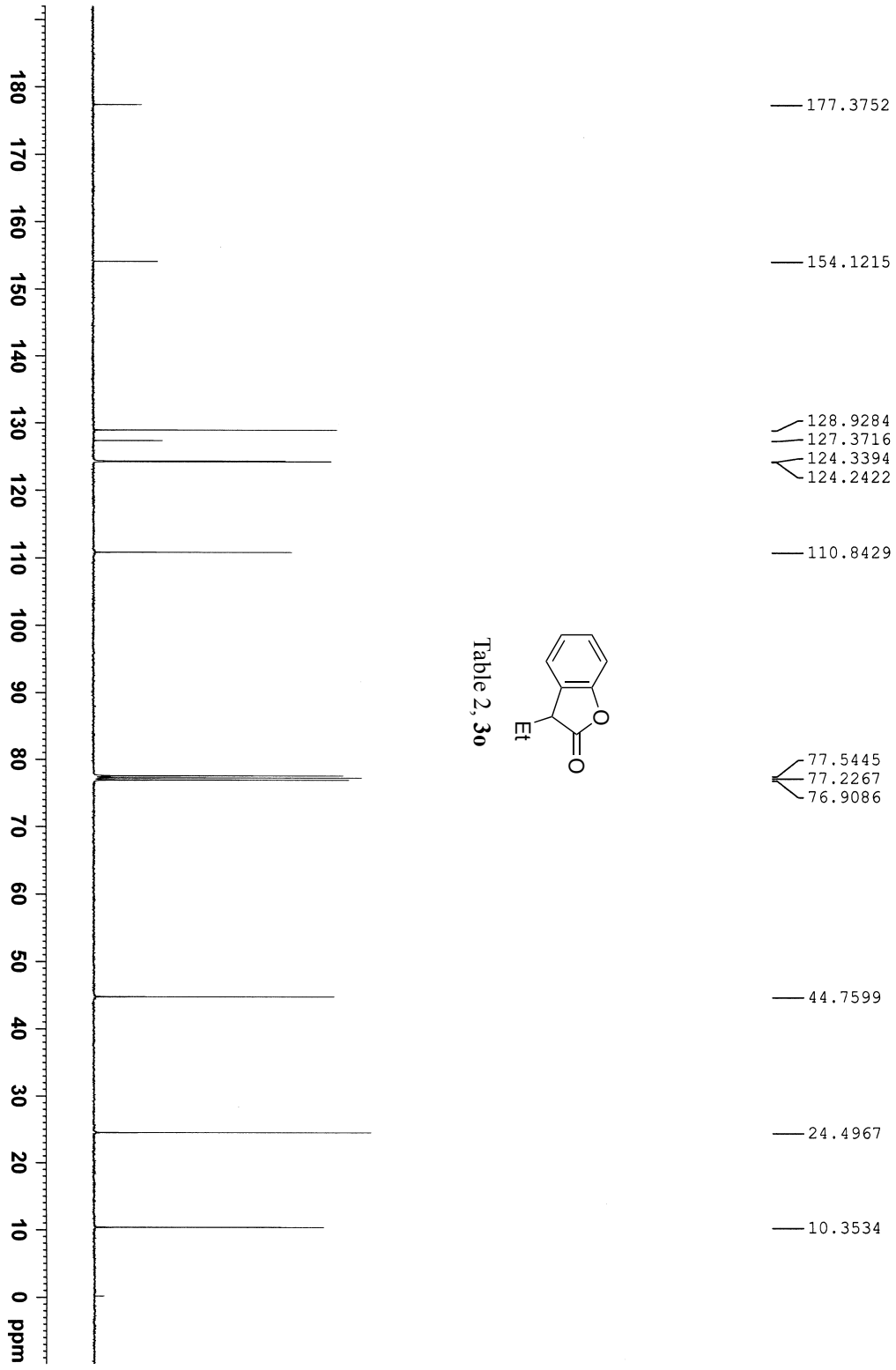
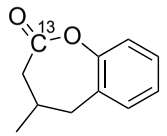
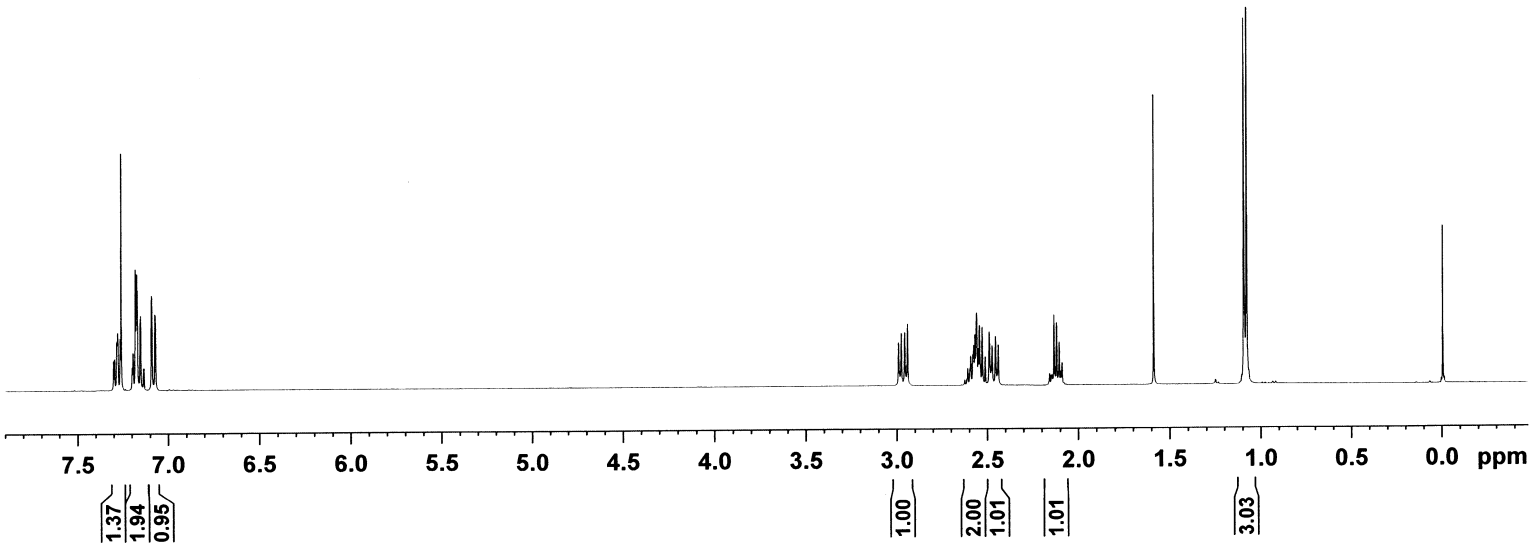

177.3752
154.1215
128.9284
127.3716
124.3394
124.2422
110.8429
77.5445
77.2267
76.9086
44.7599
24.4967
10.3534
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

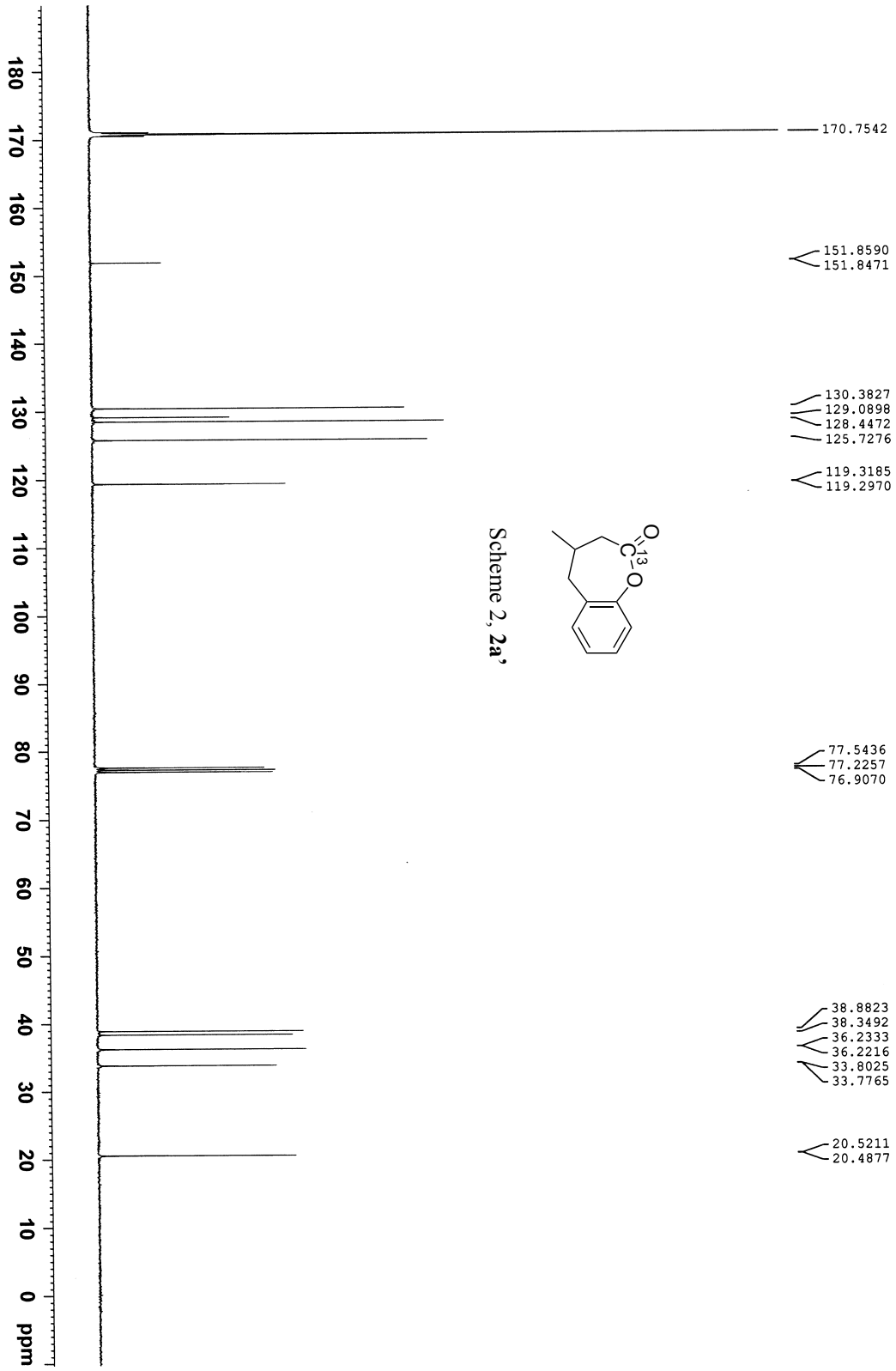
Table 2, **3o**

Et
O
O


O
13
C
O

Scheme 2, **2a'**


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.37
1.94
0.95
1.00
2.00
1.01
1.01
3.03


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
170.7542
151.8590
151.8471
130.3827
129.0898
128.4472
125.7276
119.3185
119.2970
77.5436
77.2257
76.9070
38.8823
38.3492
36.2333
36.2216
33.8025
33.7765
20.5211
20.4877
O
13
C
O

Scheme 2, **2a'**