Supporting Information

Catalytic Intramolecular Formal [3 + 2] Cycloaddition for the Synthesis of Benzobicyclo[4.3.0] Compounds.

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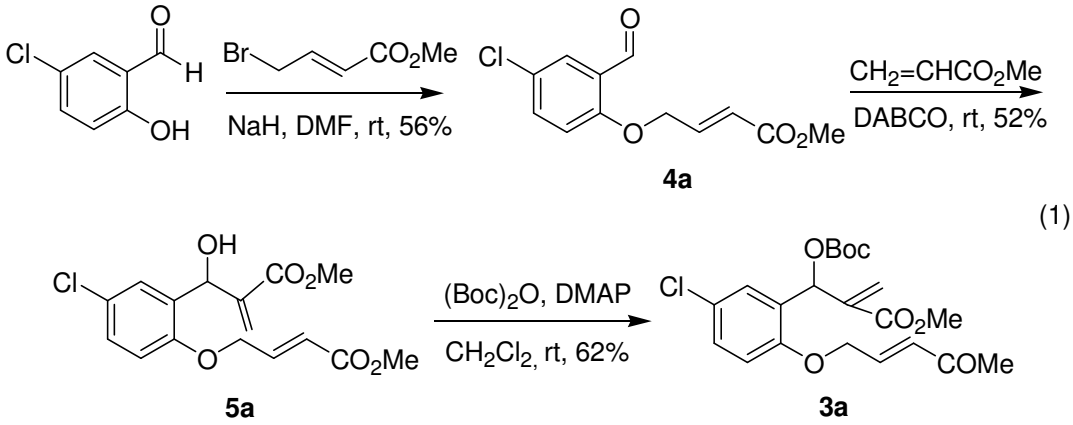
General Information. All reaction flasks were dried by flame. And all reactions were carried out under N_2 unless otherwise noted. All solvents were purified according to standard methods unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded in chloroform-d_3. ^{1}H NMR Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). ^{13}C NMR Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

General procedure for synthesis of the substrates 3a-3h (substrate 3a as example):

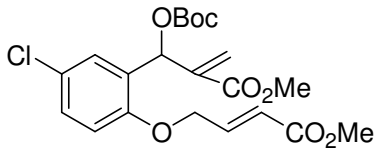


To an ice-cooled suspension of NaH (1.20 g, 30.0 mmol) in DMF (10 mL) was added a solution of 5-chloro-2-hydroxy-benzaldehyde (3.91 g, 25.0 mmol) in dry DMF (10 mL). The resulting mixture was stired at room temperature for 3 h, and treated with 4-bromo-but-2-enoic acid methyl ester (8.95 g, 50.0 mmol) in DMF (10 mL) at 0 ^{o}C. After being stirred for another 3 h at room temperature, the resulting mixture was poured into brine (15 mL) and extracted with ether (3 x 100 mL). The combined organic extracts were washed with 1 M NaOH (10 mL), brine (2 x 10 mL), and dried (Na_2SO_4). The solution was concentrated under reduced pressure and the residue was subjected to column chromatography (EtOAc: Hexane = 1:12) to provide **4a** (3.57 g, 56 %) as white solid.[1] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 10.5 (s, 1H), 7.81 (d, *J* = 2.7 Hz, 1H), 7.49 (dd, *J* = 2.7 and 9.0 Hz, 1H), 7.10 (dt, *J* = 4.2 and 15.6 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.20 (dt, *J* = 1.8 and 15.9 Hz, 1H), 4.84 (dd, *J* = 2.1 and 3.9 Hz, 2H), 3.78 (s, 3H).

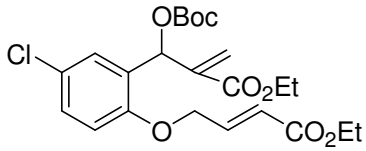
In a flame-dried 25 mL round bottom flask, **4a** (2.55 g, 10.0 mmol) was dissolved in methyl acrylate (2.58 g, 30.0 mmol), 1,4-diazabicyclo [2.2.2] octane (DABCO) (1.12 g, 10.0 mmol) was added to the solution directly and the solution was then allowed to stir at ambient temperature for 15 h. The solution was concentrated in vacuo and the residue was subjected to column chromatography (EtOAc : Hexane = 1:8) to provide **5a** (1.77 g, 52 %) as colourless oil.[2] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.42 (d, *J* = 2.4 Hz, 1H), 7.18 (dd, *J* = 2.7 and 9.0 Hz, 1H), 7.03 (dt, *J* = 4.5 and 15.9 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 6.31 (s, 1H), 6.09 (dt, *J* = 1.8 and 15.6 Hz, 1H), 5.94 (d, *J* = 5.4 Hz, 1H), 5.70 (s, 1H), 4.67 (dd, *J* = 2.1

and 3.9 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.70 (d, J = 5.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 166.2, 153.1, 142.0, 141.0, 131.6, 128.3, 127.5, 126.2, 126.1, 121.3, 112.6, 66.6, 66.3, 51.9, 51.5.

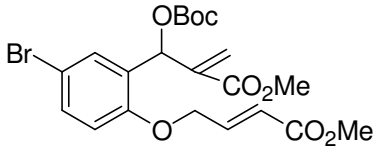
In a strirred solution of DMAP (0.015 g) and **5a** (1.33 g, 3.9 mmol) in dry CH_2Cl_2 (10 mL), $(Boc)_2O$ (1.13 g, 5.2 mmol) in CH_2Cl_2 (8 mL) was added dropwise. After stirring for 3 h at RT, the mixture was diluted with CH_2Cl_2 (15 mL). The combined organic extracts were washed with brine (10 mL) and water (10 mL), dried (Na_2SO_4). The solution was concentrated in vacuo and the residue was subjected to column chromatography (EtOAc : Hexane = 1:10) to give **3a** (0.91 g, 62%) as white solid.[3]



3a: white solid, m.p. 70-71 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.30-7.21 (m, 2H), 7.04 (dt, J = 15.6 and 3.6 Hz, 1H), 6.92 (s, 1H), 6.77 (d, J = 9.0 Hz, 1H), 6.49 (s, 1H), 6.19 (d, J = 15.9 Hz, 1H), 5.78 (s, 1H), 4.71 (t, J = 2.4 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 164.8, 153.3, 151.9, 141.5, 137.9, 129.0, 127.6, 127.3, 127.2, 125.7, 120.9, 112.8, 82.3, 69.3, 66.4, 51.7, 51.1, 27.2. IR ν/cm^{-1} 2954 (m), 1751 (s), 1729 (s), 1666 (s), 1489 (m), 1277 (m), 855 (m); MS (ESI, positive mode, m/z) 399 (M-HOtBu+MeOH+H$^+$). Anal. calcd for $C_{21}H_{25}O_8Cl$: C, 57.21; H, 5.72. Found: C, 57.14; H, 5.73.

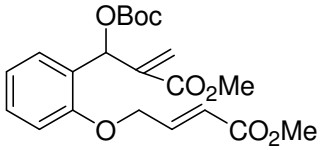


3b: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.29-7.21 (m, 2H), 7.04 (dt, J = 15.6 and 3.6 Hz, 1H), 6.93 (s, 1H), 6.77 (d, J = 8.7 Hz, 1H), 6.48 (s, 1H), 6.18 (d, J = 15.6 Hz, 1H), 5.75 (s, 1H), 4.71 (d, J = 1.5 Hz, 2H), 4.25-4.17 (m, 4H), 1.49 (s, 9H), 1.31-1.23 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 164.7, 153.6, 152.2, 141.4, 138.3, 129.2, 128.0, 127.8, 127.3, 126.1, 121.8, 112.9, 82.7, 69.7, 66.8, 61.0, 60.4, 27.6, 14.1, 14.0. IR ν/cm^{-1} 2981 (m), 1748 (s), 1723 (s), 1665 (s), 1488 (m), 1277 (m), 851 (m); MS (EI, m/z, rel. intensity) 468 (M$^+$, 5.17), 57 (100). HRMS (EI) calcd for $C_{23}H_{29}O_8Cl$ (M$^+$): 468.1551; Found: 468.1542.

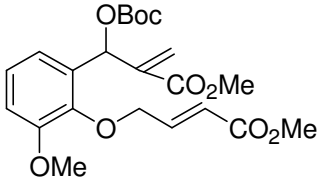


3c: white solid, m.p. 89-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.41-7.31 (m, 2H), 7.04 (dt, J = 15.6 and 3.6 Hz, 1H), 6.91 (s, 1H), 6.72 (d, J = 8.7 Hz, 1H), 6.48 (s, 1H), 6.18 (dt, J = 15.6 and 2.1 Hz, 1H), 5.78 (s, 1H), 4.71 (dd, J = 2.4 Hz and 3.6 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 165.1, 154.1, 152.1, 141.6, 138.1, 132.2, 130.5, 128.3, 127.6, 121.4, 113.4 (1), 113.3 (9), 82.7, 69.5, 66.6, 52.0, 51.5, 27.5. IR ν/cm^{-1} 2953 (m), 1749 (s), 1728 (s), 1667 (s), 1488 (m),

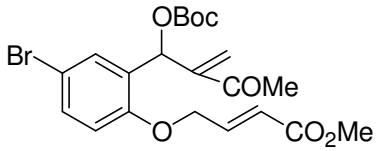
1278 (m), 851 (m); MS (EI, *m/*z, rel. intensity) 484 (M^+), 486 (M^+). HRMS (EI) calcd for $C_{21}H_{25}O_8BrNa$ ($M+Na^+$): 507.0625; Found: 507.0606.



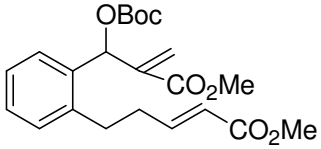
3d: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.32-7.25 (m, 2H), 7.07 (dt, *J* = 15.6 and 3.6 Hz, 1H), 7.00-6.95 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.46 (s, 1H), 6.22 (dt, *J* = 15.6 and 1.8 Hz, 1H), 5.74 (s, 1H), 4.74 (dd, *J* = 2.1 Hz and 3.3 Hz, 2H), 3.75 (s, 6H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 165.4, 155.0, 152.3, 142.3, 138.6, 129.6, 127.6, 127.3, 125.9, 121.1, 121.0, 111.5, 82.3, 70.2, 66.3, 51.9, 51.4, 27.5. IR *v*/cm^{-1} 2953 (m), 1749 (s), 1728 (s), 1666 (s), 1493 (m), 1279 (m), 885 (m), 756 (m); MS (EI, *m/*z, rel. intensity) 406 (M^+, 3.63), 57 (100). HRMS (EI) calcd for $C_{21}H_{26}O_8$ (M^+): 406.1628; Found: 406.1626.



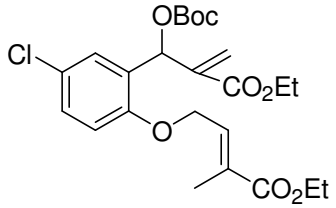
3e: white solid, m.p. 73-74 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.15-7.04 (m, 2H), 6.92-6.85 (m, 3H), 6.44 (s, 1H), 6.26 (dt, *J* = 15.6 and 1.8 Hz, 1H), 5.72 (s, 1H), 4.76 (dd, *J* = 1.8 Hz and 3.9 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 165.2, 152.3, 152.1, 144.9, 143.6, 138.7, 131.1, 127.0, 124.2, 120.5, 119.3, 112.4, 82.2, 70.8, 70.3, 55.5, 51.8, 51.3, 27.5. IR *v*/cm^{-1} 2953 (m), 1747 (s), 1728 (s), 1667 (s), 1588 (s), 1481 (m), 1283 (m), 1159 (m), 964 (m), 855 (m); MS (EI, *m/*z, rel. intensity) 436 (M^+, 13.2), 57 (100). HRMS (EI) calcd for $C_{22}H_{28}O_9$ (M^+): 436.1733; Found: 436.1747.



3f: white solid, 119-120 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.37-7.30 (m, 2H), 7.03 (dt, *J* = 15.6 and 3.6 Hz, 1H), 6.95 (s, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 6.32 (s, 1H), 6.19 (dt, *J* = 15.6 and 2.1 Hz, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 4.71 (dd, *J* = 3.6 and 2.1 Hz, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 166.3, 154.1, 152.1, 146.1, 141.7, 132.1, 130.4, 128.6, 127.0, 121.4, 113.5, 113.4, 82.7, 69.0, 66.7, 51.5, 27.5, 26.0. IR *v*/cm^{-1} 2979 (m), 1746 (s), 1727 (s), 1682 (s), 1487 (m), 1278 (m), 1160 (m), 1083 (m), 970 (m); MS (ESI, positive mode, m/z) 491 ($M+Na^+$), 493 ($M+Na^+$). HRMS (EI) calcd for $C_{21}H_{25}O_7Br$ (M^+): 468.0784; Found: 468.0782.



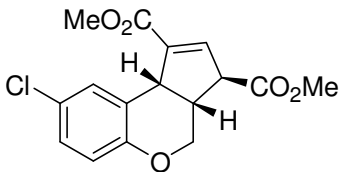
3g: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.35-7.17 (m, 4H), 7.04 (dt, *J* = 15.6 and 6.6 Hz, 1H), 6.75 (s, 1H), 6.45 (s, 1H), 5.88 (d, *J* = 15.6 Hz, 1H), 5.73 (s, 1H), 3.73 (s, 6H), 2.97-2.79 (m, 2H), 2.59-2.51 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 165.3, 152.3, 148.2, 139.2, 139.0, 134.8, 129.5, 128.6, 127.6, 127.0, 126.5, 121.4, 82.5, 72.1, 51.9, 51.2, 33.1, 30.9, 27.6. IR *v*/cm^{-1} 2953 (m), 1748 (s), 1727 (s), 1657 (s), 1438 (m), 1278 (m), 1156 (m), 1082 (m), 981 (m), 760 (m); MS (ESI, positive mode, *m/*z) 427 (M+Na$^+$). HRMS (MALDI/DHB) calcd for $C_{22}H_{28}O_7Na$ (M+Na$^+$): 427.1733; Found: 427.1727.



3h: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.29 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 9.0 and 2.7 Hz, 1H), 6.88-6.84 (m, 2H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.46 (s, 1H), 5.73 (s, 1H), 4.72 (d, *J* = 5.4 Hz, 2H), 4.25-4.17 (m, 4H), 1.91 (d, *J* = 0.6 Hz, 3H), 1.48 (s, 9H), 1.33-1.23 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 164.8, 154.0, 152.2, 138.5, 135.7, 130.0, 129.2, 128.2, 127.8, 127.4, 126.0, 112.9, 82.6, 69.9, 65.5, 60.9, 60.8, 27.6, 14.1, 14.0, 13.0. IR *v*/cm^{-1} 2982 (m), 1749 (s), 1717 (s), 1655 (s), 1489 (m), 1277 (m), 852 (m); MS (EI, *m/*z, rel. intensity) 482 (M$^+$, 1.1), 59 (100). HRMS (EI) calcd for $C_{24}H_{31}O_8Cl$ (M$^+$): 482.1707; Found: 482.1724.

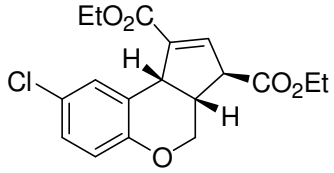
Representative Procedure for the Tributylphosphine-Catalyzed Synthesis of Benzobicyclo[4.3.0] Compounds 2. Preparation of 8-chloro-3,3a,4,9b-tetrahydro-cyclopenta[*c*]chromene-1,3-dicarboxylic acid dimethyl ester 2a.

To a solution of substrate **3a** (110 mg, 0.25 mmol) in CH_3Ph (2.5 mL) was added Ti(O^{i}Pr)$_4$ (14.2 mg, 0.050 mmol) and tributylphosphine (5.1 mg, 0.025 mmol) at room temperature. The resulting mixture was further stirred for 1 h. After the reaction was complete, the mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate (50 mL). 20% Aqueous H_2O_2 (0.3 mL) solution was added and the resultant mixture was stirred for another 2 h at room temperature, then saturated Na_2SO_3 (0.5 mL) was added. After the resulting mixture was stirred for 1 h, the residue was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel to afford the desired products **2a**.

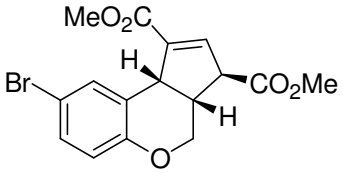


2a: 99% yield (white solid, m.p. 82-83 ^{o}C, 1 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.56 (d, *J* = 2.1 Hz, 1H), 7.05 (dd, *J* = 8.7 and 2.4 Hz, 1H), 6.80-6.77 (m, 2H), 4.40-4.31 (m, 2H), 4.05-3.97 (m, 2H), 3.81

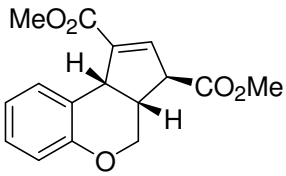
(s, 3H), 3.78 (s, 3H), 3.23-3.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 164.8, 153.6, 141.2, 139.8, 129.7, 127.7, 126.4, 125.3, 119.1, 66.2, 52.4, 52.0, 50.6, 43.4, 42.2. IR v/cm^{-1} 2982 (m), 2935 (m), 1734 (s), 1714 (s), 1628 (m), 1485 (m), 1242 (m), 821 (m), 735 (m), 639 (m); MS (ESI, positive mode, *m/*z) 377 (M+MeOH+Na$^+$), 345 (M+Na$^+$). HRMS (EI) calcd for $C_{16}H_{15}O_5Cl$ (M$^+$): 322.0608; Found: 322.0607.



8-Chloro-3,3a,4,9b-tetrahydro-cyclopenta[*c*]chromene-1,3-dicarboxylic acid diethyl ester (2b): 99% yield (oil, 1.5 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.4 and 2.1 Hz, 1H), 6.80-6.77 (m, 2H), 4.40-4.19 (m, 6H), 4.05-3.95 (m, 2H), 3.23-3.15 (m, 1H), 1.38-1.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 164.4, 153.5, 141.1, 140.0, 129.7, 127.6, 126.3, 125.4, 119.0, 66.2, 61.3, 61.0, 50.7, 43.3, 42.1, 14.2. IR v/cm^{-1} 2982 (m), 1734 (s), 1713 (s), 1628 (m), 1484 (m), 1242 (m), 1028 (m), 821 (m), 639 (m); MS (ESI, positive mode, *m/*z) 405 (M+MeOH+Na$^+$), 373 (M+Na$^+$). HRMS (EI) calcd for $C_{18}H_{19}O_5Cl$ (M$^+$): 350.0921; Found: 350.0922.

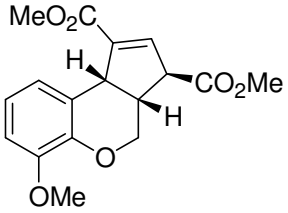


8-Bromo-3,3a,4,9b-tetrahydro-cyclopenta[*c*]chromene-1,3-dicarboxylic acid dimethyl ester (2c): 99% yield (white solid, m.p. 79-80 ^{o}C, 1 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.70 (d, *J* = 1.5 Hz, 1H), 7.19 (dd, *J* = 8.7 and 2.4 Hz, 1H), 6.79-6.72 (m, 2H), 4.40-4.31 (m, 2H), 4.04-3.97 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 3.23-3.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 164.7, 154.1, 141.2, 139.8, 132.6, 130.6, 125.8, 119.5, 113.8, 66.1, 52.4, 52.0, 50.6, 43.3, 42.1. IR *v*/cm^{-1} 2952 (m), 2925 (m), 1739 (s), 1717 (s), 1628 (m), 1482 (m), 819 (m), 614 (m); MS (EI, *m/*z, rel. intensity) 368 (M$^+$, 51.5), 366 (M$^+$, 50.1), 168 (100). Anal. calcd for $C_{16}H_{15}O_5Br$: C, 52.34; H, 4.12. Found: C, 52.26; H, 4.37.

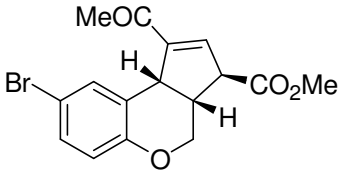


3,3a,4,9b-Tetrahydro-cyclopenta[*c*]chromene-1,3-dicarboxylic acid dimethyl ester (2d): 94% yield (white solid, m.p. 109-110 ^{o}C, 2 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.12-7.08 (m, 1H), 6.91-6.84 (m, 2H), 6.76 (d, *J* = 0.9 Hz, 1H), 4.44 (d, *J* = 8.1 Hz, 1H), 4.34 (dd, *J* = 12.0 and 2.1 Hz, 1H), 4.09-4.02 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.24-3.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 165.0, 154.9, 140.8, 140.3, 130.0, 127.6, 123.8, 121.8, 117.8, 66.0, 52.3, 51.8, 50.7, 43.8, 42.2. IR *v*/cm^{-1} 2955 (m), 2925 (m), 1738 (s), 1716 (s), 1628 (m), 1488 (m), 1246 (m), 759

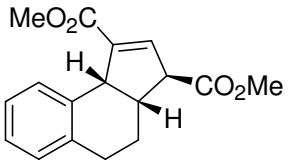
(m); MS (EI, *m/*z, rel. intensity) 288 (M^+, 7.58), 44 (100). HRMS (EI) calcd for $C_{16}H_{16}O_5$ (M^+): 288.0998; Found: 288.1003.



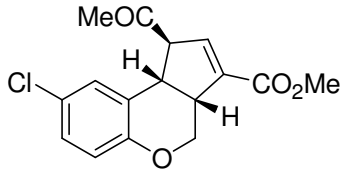
6-Methoxy-3,3a,4,9b-tetrahydro-cyclopenta[*c*]chromene-1,3-dicarboxylic acid dimethyl ester (2e): 75% yield (white solid, m.p. 123-124 °C, 2.5 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.15 (d, *J* = 7.8 Hz, 1H), 6.87-6.71 (m, 3H), 4.51-4.44 (m, 2H), 4.11-4.05 (m, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.76 (s, 3H), 3.25-3.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 165.0, 148.7, 144.2, 140.9, 140.2, 124.6, 121.5, 121.3, 109.4, 66.4, 55.8, 52.3, 51.8, 50.5, 43.8, 42.1. IR *v*/cm^{-1} 2919 (m), 1737 (s), 1720 (s), 1630 (m), 1584 (m), 1485 (m), 1263 (m), 1096 (m), 753 (m), 736 (m); MS (EI, *m/*z, rel. intensity) 318 (M^+, 5.09), 57 (100). Anal. calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.27; H, 6.09.



1-Acetyl-8-bromo-3,3a,4,9b-tetrahydro-cyclopenta[*c*]chromene-3-carboxylic acid methyl ester (2f): 95% yield (pale yellow solid, m.p. 95-96 °C, 2 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.59 (s, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 6.76-6.71 (m, 2H), 4.47-4.35 (m, 2H), 4.11-4.00 (m, 2H), 3.80 (s, 3H), 3.12 (t, *J* = 9.3 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 172.1, 153.9, 148.4, 141.9, 133.1, 130.5, 126.0, 119.4, 113.9, 65.9, 52.5, 50.7, 43.5, 41.2, 27.0. IR *v*/cm^{-1} 2925 (m), 2853 (m), 1734 (s), 1671 (m), 1481 (m), 1223 (m), 810 (m); MS (EI, *m/*z, rel. intensity) 349 (M^+, 12.6), 351 (M^+, 17.8), 168 (100). HRMS (EI) calcd for $C_{16}H_{15}O_4Br$ (M^+): 350.0154; Found: 350.0164.



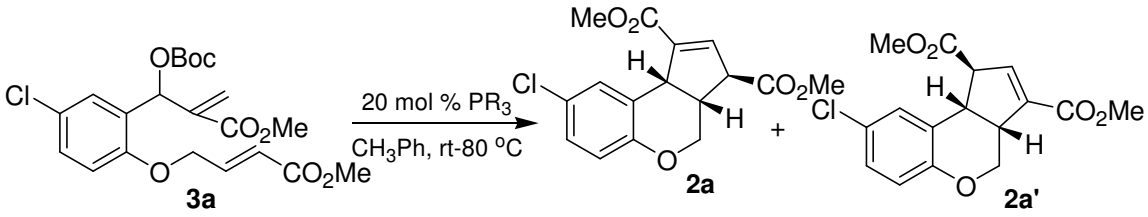
3a,4,5,9b-Tetrahydro-3H-cyclopenta[*a*]naphthalene-1,3-dicarboxylic acid dimethyl ester (2g): 93% yield (oil, 1.5 h). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.51-7.48 (m, 1H), 7.16-7.08 (m, 3H), 6.72 (t, *J* = 1.2 Hz, 1H), 4.39 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.63 (dt, *J* = 8.4 and 2.1 Hz, 1H), 3.26-3.19 (m, 1H), 2.78-2.62 (m, 2H), 2.00-1.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 165.4, 141.4, 140.2, 137.5, 136.0, 129.5, 128.6, 126.2, 126.1, 53.8, 52.2, 51.7, 46.3, 41.7, 26.2, 26.1. IR *v*/cm^{-1} 2951 (m), 1735 (s), 1719 (s), 1630 (m), 1492 (m), 1435 (m), 1251 (m), 1101 (m), 756 (m); MS (EI, *m/*z, rel. intensity) 286 (M^+, 1.42), 167 (100). HRMS (EI) calcd for $C_{17}H_{18}O_4$ (M^+): 286.1205; Found: 286.1211.

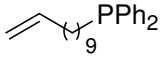


2a': white solid, m.p. 83-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.29 (d, *J* = 2.7 Hz, 1H), 7.09 (dd, *J* = 8.4 and 2.4 Hz, 1H), 6.84-6.81 (m, 2H), 4.41 (dd, *J* = 10.8 and 4.5 Hz, 1H), 3.92 (t, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.74-3.64 (m, 2H), 3.49-3.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 164.0, 153.5, 141.7, 137.3, 129.4, 127.8, 126.2, 125.9, 118.6, 66.7, 58.5, 52.7, 51.9, 42.6, 39.3. IR *v*/cm^{-1} 2953 (m), 2926 (m), 1736 (s), 1720 (s), 1632 (m), 1485 (m), 1436 (m), 1248 (m), 819 (m), 748 (m), 640 (m); MS (ESI, positive mode, *m/*z) 377 (M+MeOH+Na^+), 345 (M+Na^+). HRMS (EI) calcd for $C_{16}H_{15}O_5Cl$ (M^+): 322.0608; Found: 322.0606.

Appendix:

Table 1. Effects of phosphines on the formal [3 + 2] Cycloaddition[a]



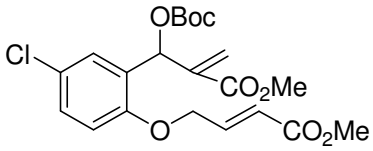
entry	*T* (°C)	PR_3	**2a**:**2a'**[b]	Yield(%)[c]
1	rt	PPh_3	>95:5	95
2	rt		33:67	94
3	rt	$(Cy)_3P$	22:78	93
4	rt	Bu_3P	19:81	99
5[d]	rt	Bu_3P	19:81	98
6	80	Bu_3P	19:81	99
7[e]	rt	Bu_3P	19:81	96

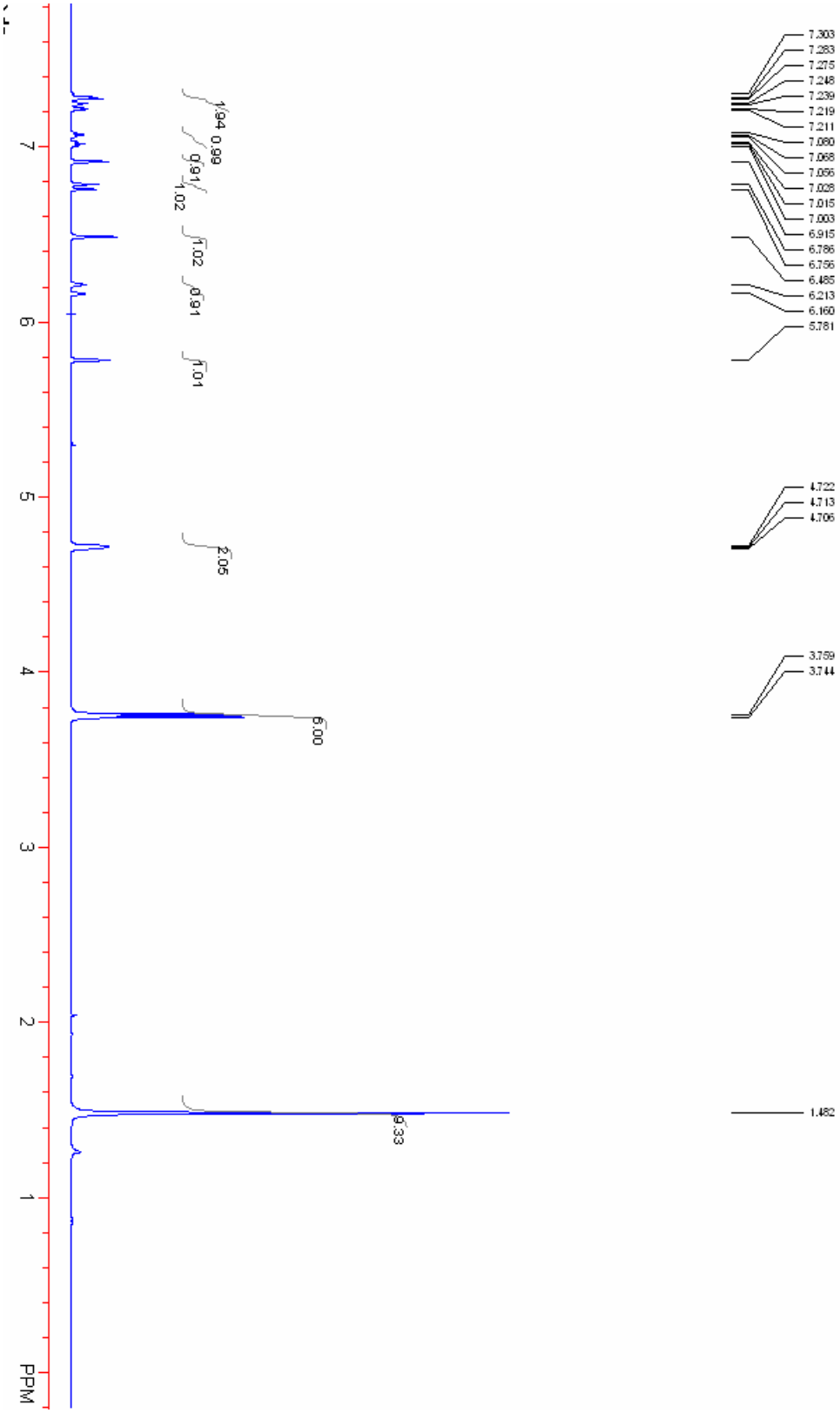
[a] Reagents and conditions: PR_3 (20 mol %), **3a** (110 mg, 0.25 mmol) in CH_3Ph (0.10 M), rt-80 °C, 2-32 h. [b] Determined by 300 MHz ^1H NMR. [c] Isolated yield. [d] Prolonging the reaction time. [e] 10 mol % of PBu_3.

Reference:

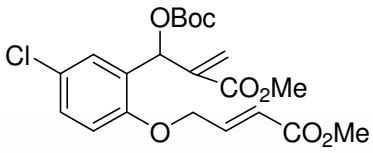
1. (a) Aurrecoechea, J. M.; López, B.; Fernández, A.; Arrieta, A.; Cossío, F. P. *J. Org. Chem.* **1997**, *62,* 1125. (b) Mori, K.; Tanaka, T. I.; Honda, H.; Yamamoto, I. *Tetrahedron* **1983**, *39*, 2303.
2. Roush, W. R.; Brown1, B. B. *J. Org. Chem.* **1993**, *58,* 2151.
3. Erent, D.; Keinan, E. *J. Am. Chem. Soc.* **1988**, *110*, 4356.
4. **2h** is the known compound, details please see: Ye, L.-W.; Han, X.; Sun, X.-L.; Tang, Y. *Tetrahedron* **2008**, *64*, 1487.

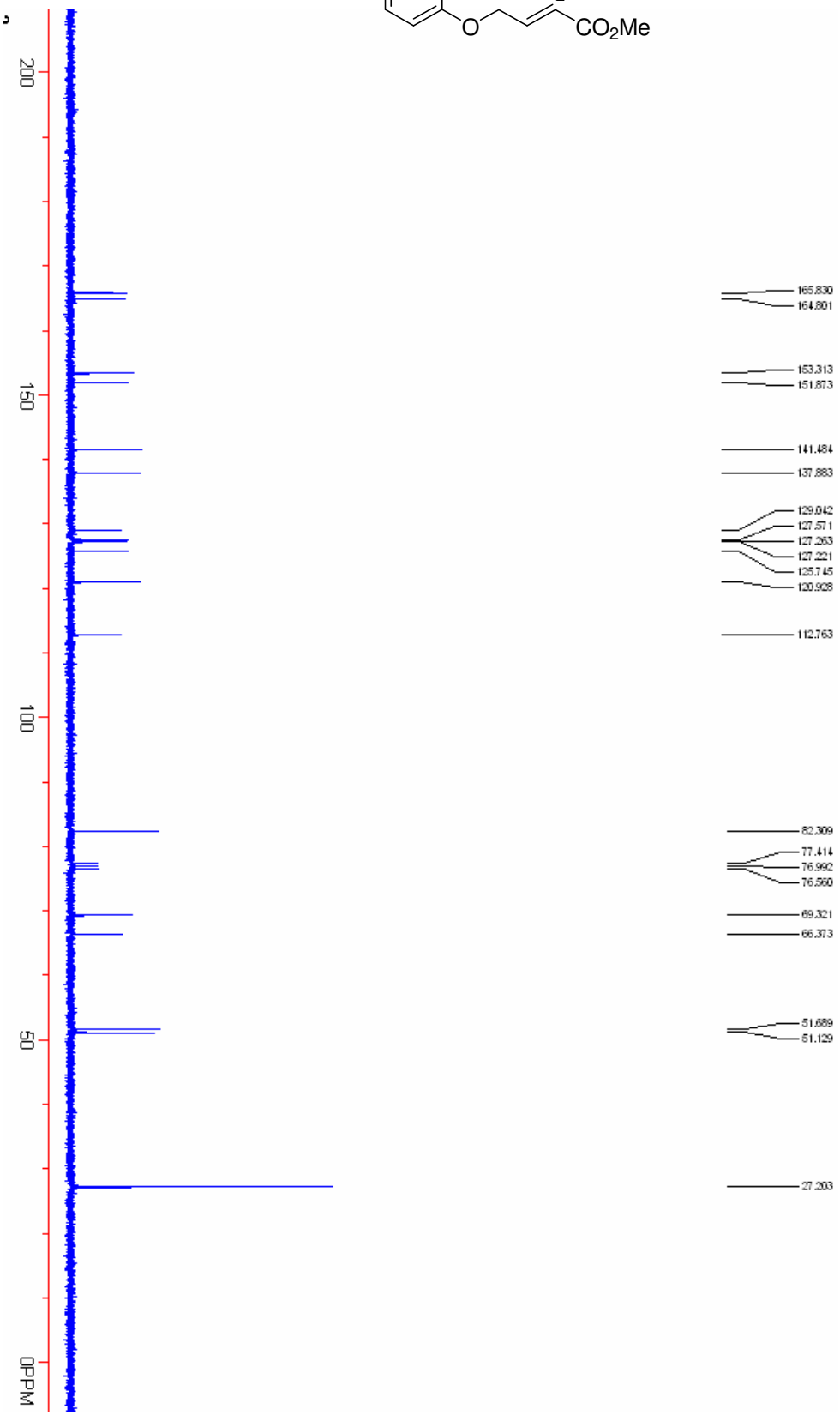
Compound **3a**
300 MHz in $CDCl_3$



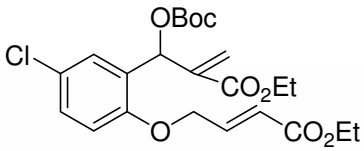


Compound **3a**
75 MHz in $CDCl_3$

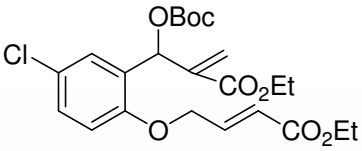


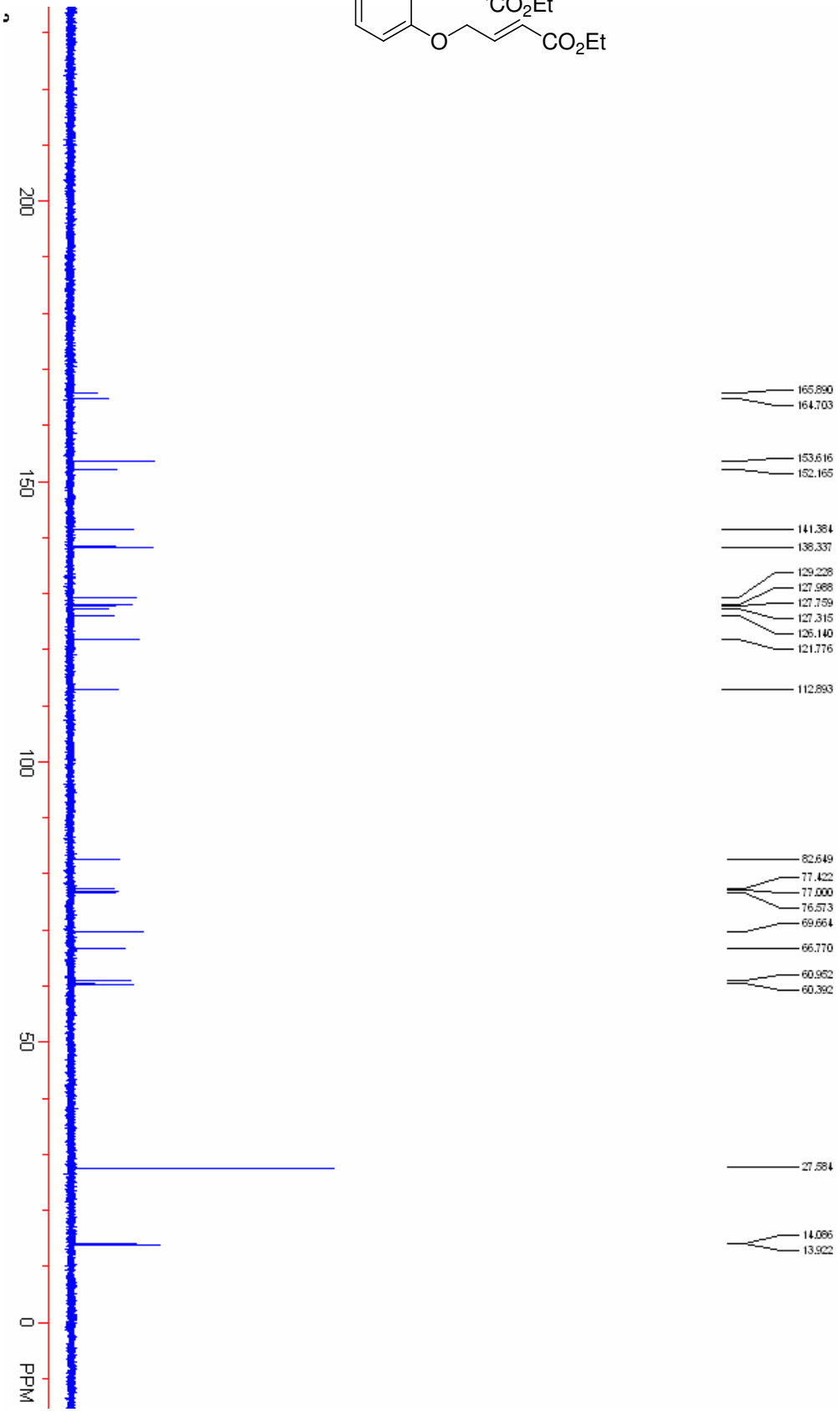


Compound **3b**
300 MHz in $CDCl_3$



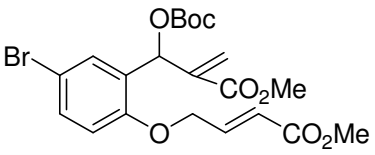
Compound **3b**
75 MHz in $CDCl_3$

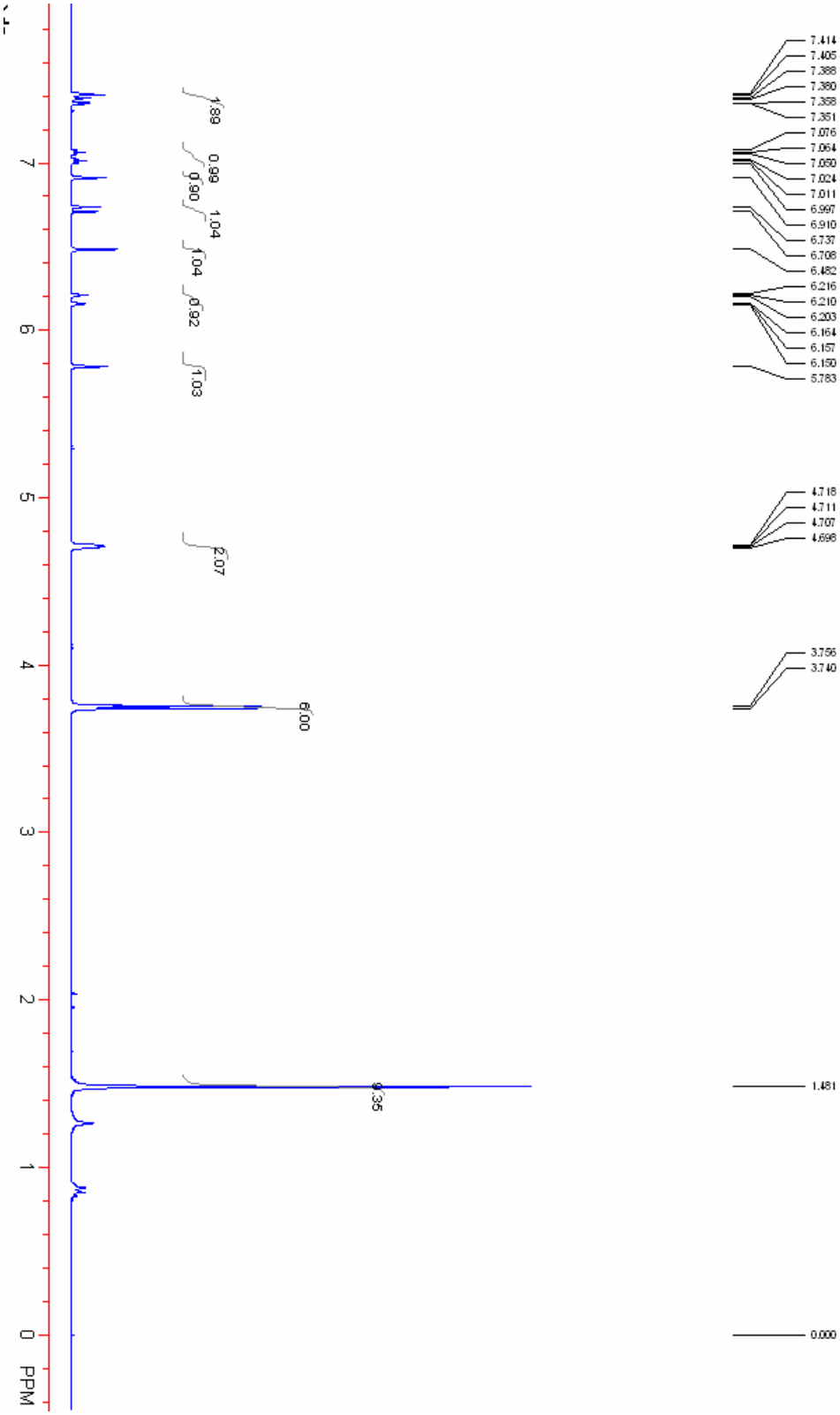




Compound **3c**

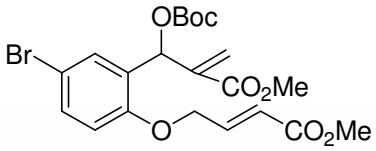
300 MHz in $CDCl_3$

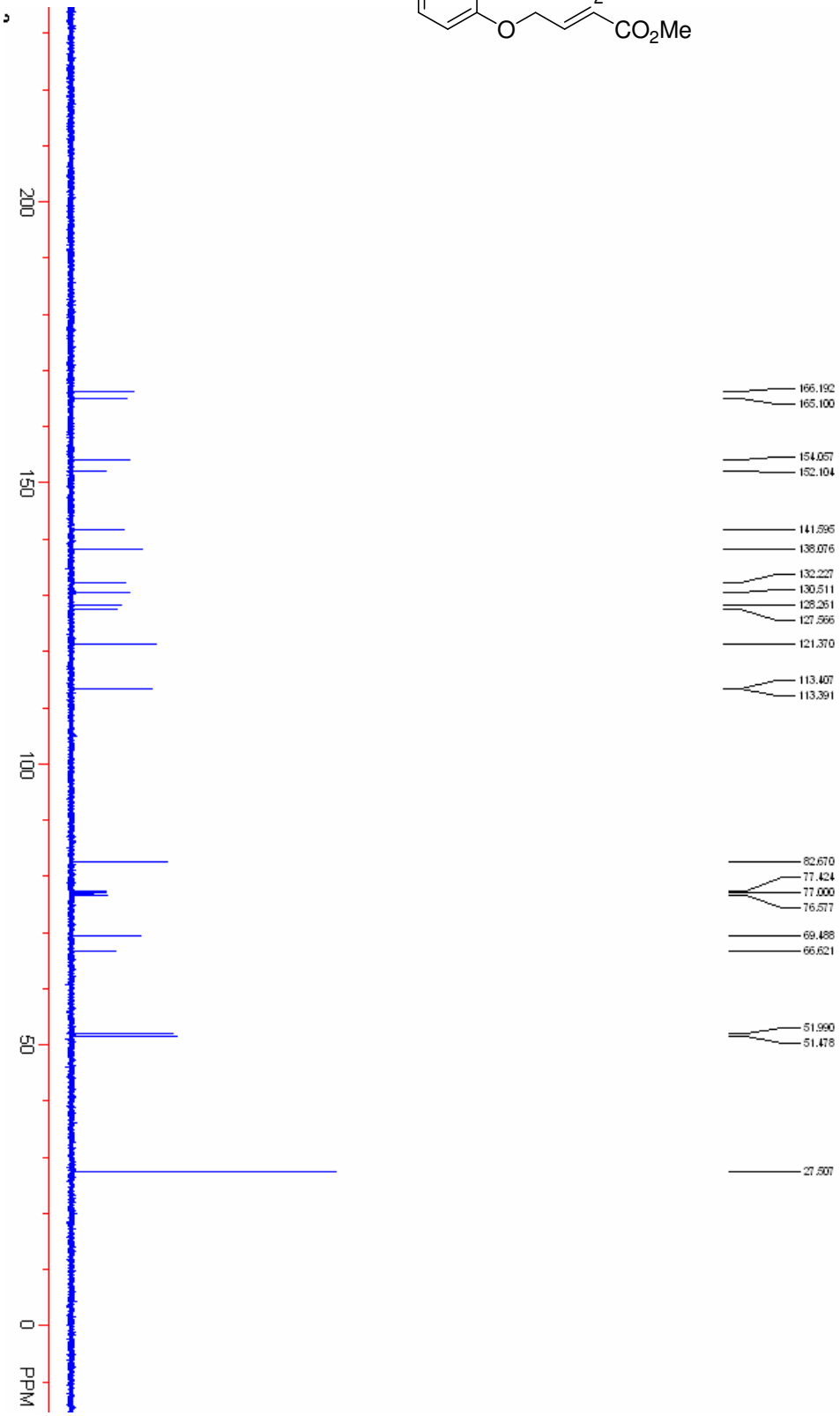




Compound **3c**

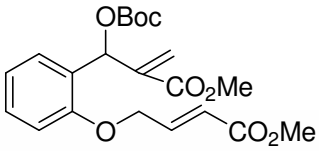
75 MHz in $CDCl_3$

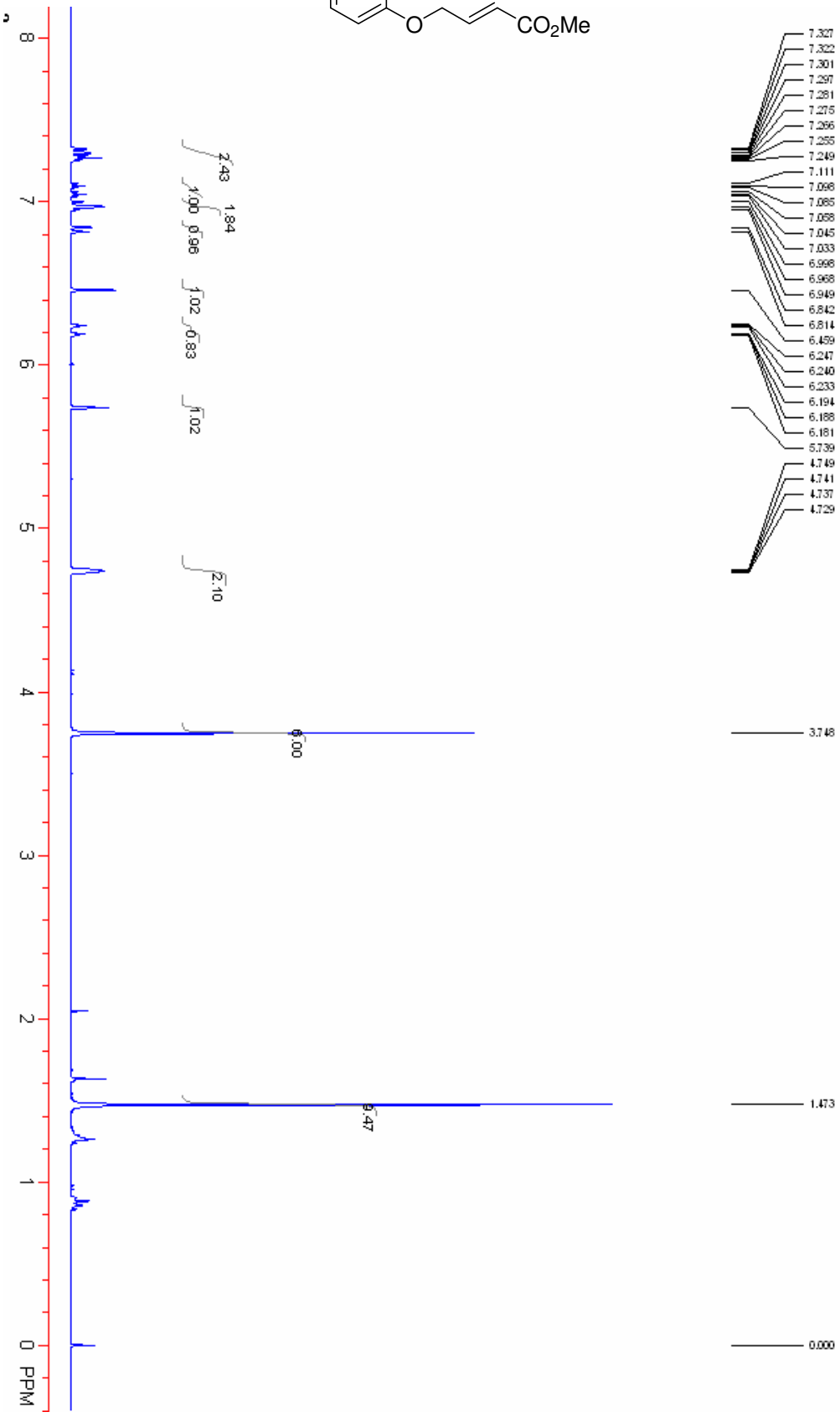




Compound **3d**

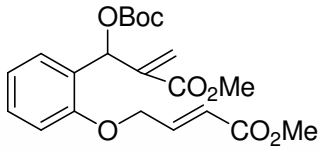
300 MHz in $CDCl_3$

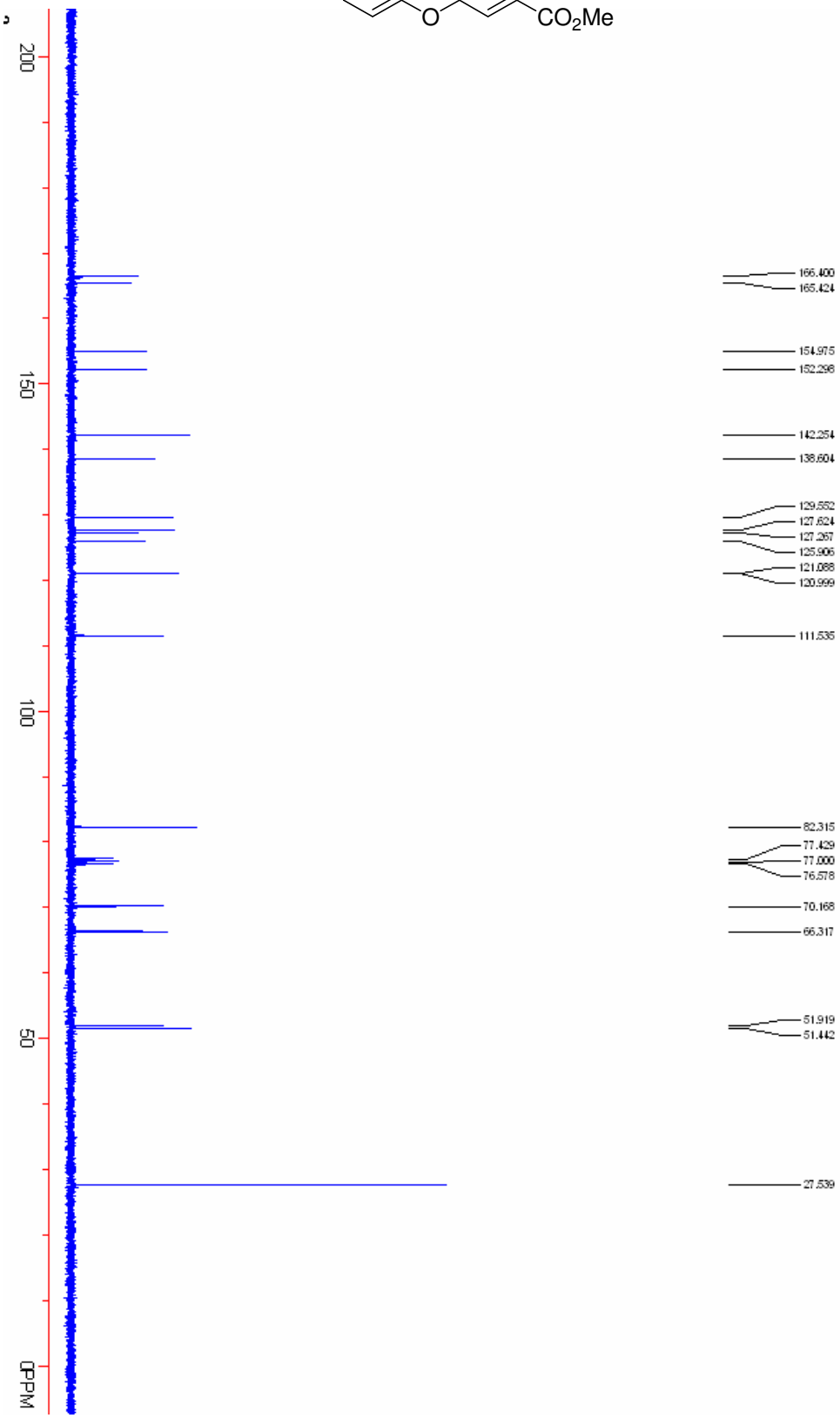




Compound **3d**

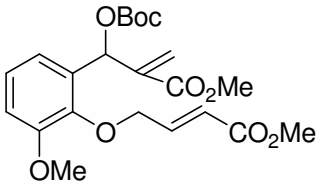
75 MHz in $CDCl_3$

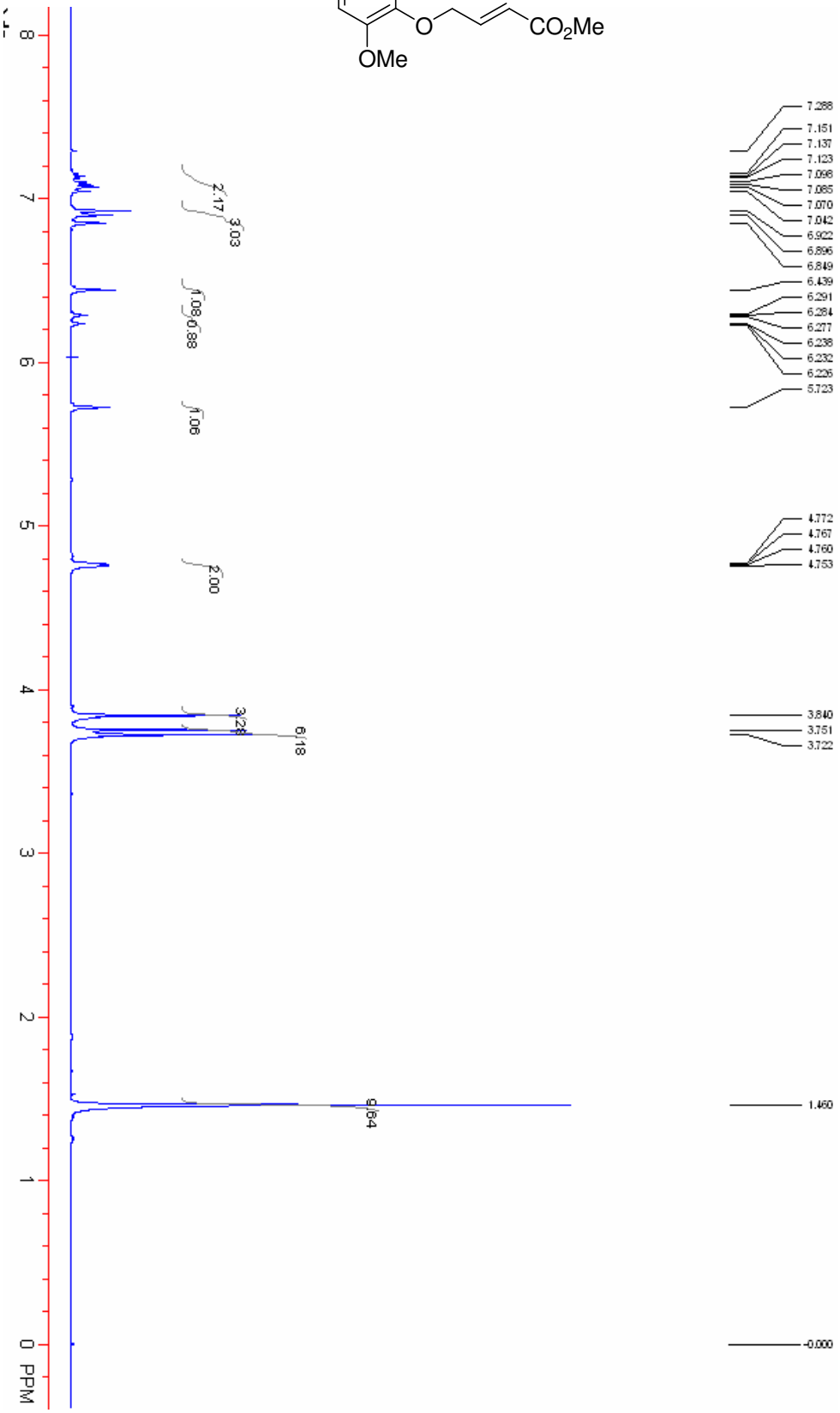




Compound **3e**

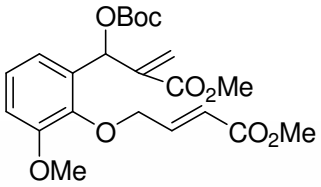
300 MHz in $CDCl_3$

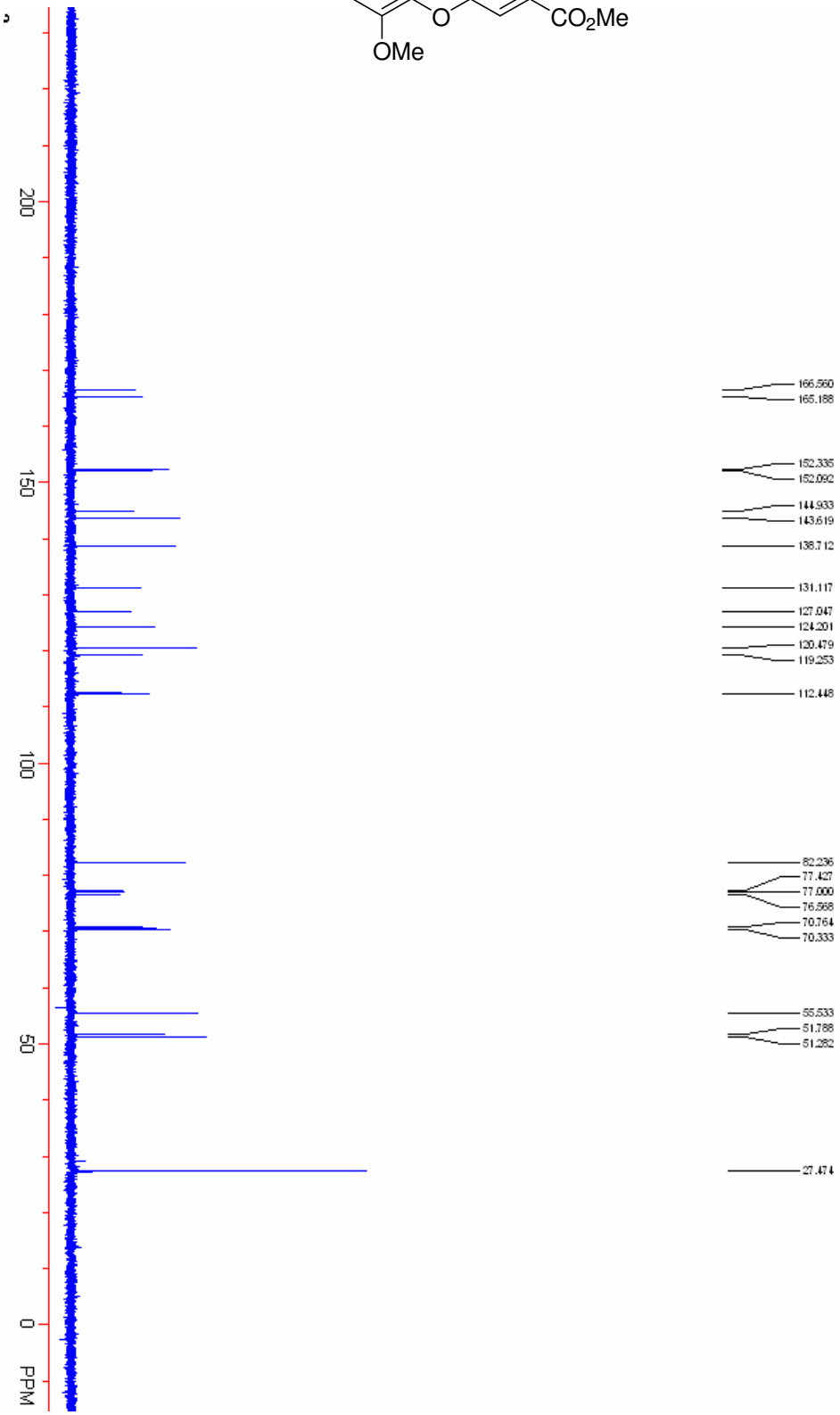




Compound **3e**

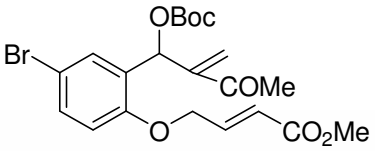
75 MHz in $CDCl_3$

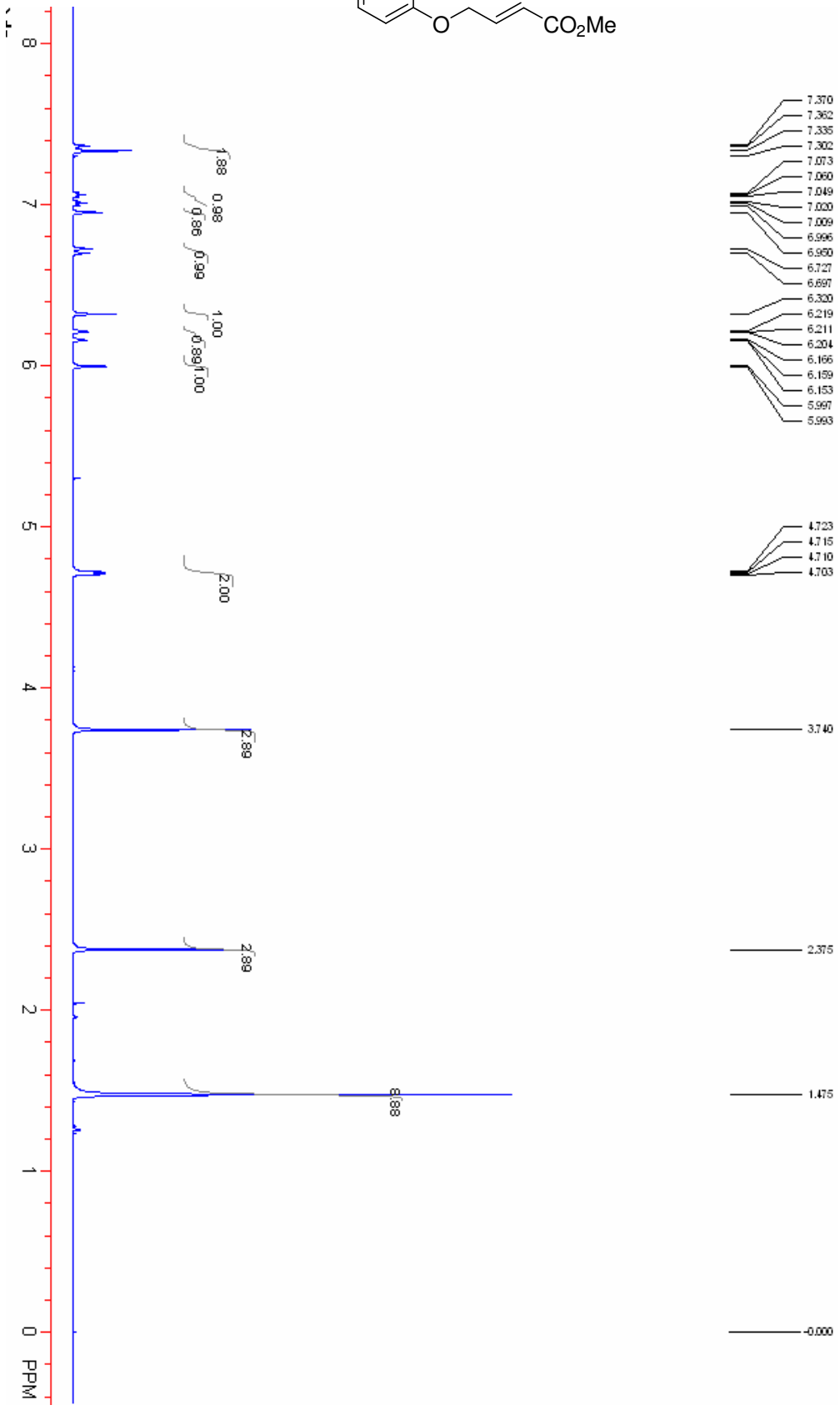




Compound **3f**

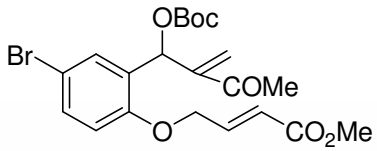
300 MHz in $CDCl_3$

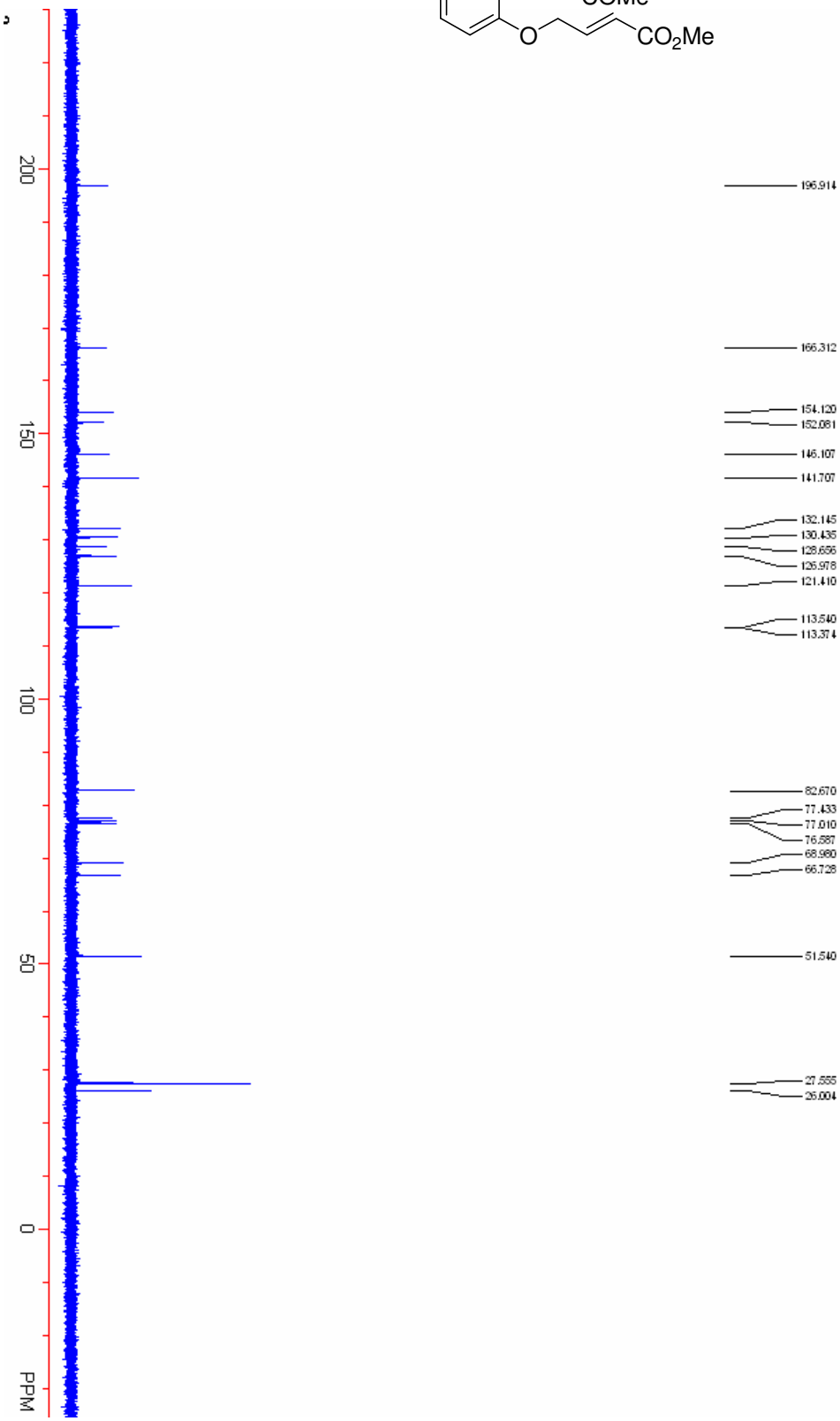




Compound **3f**

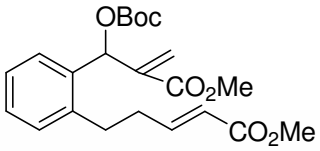
75 MHz in $CDCl_3$

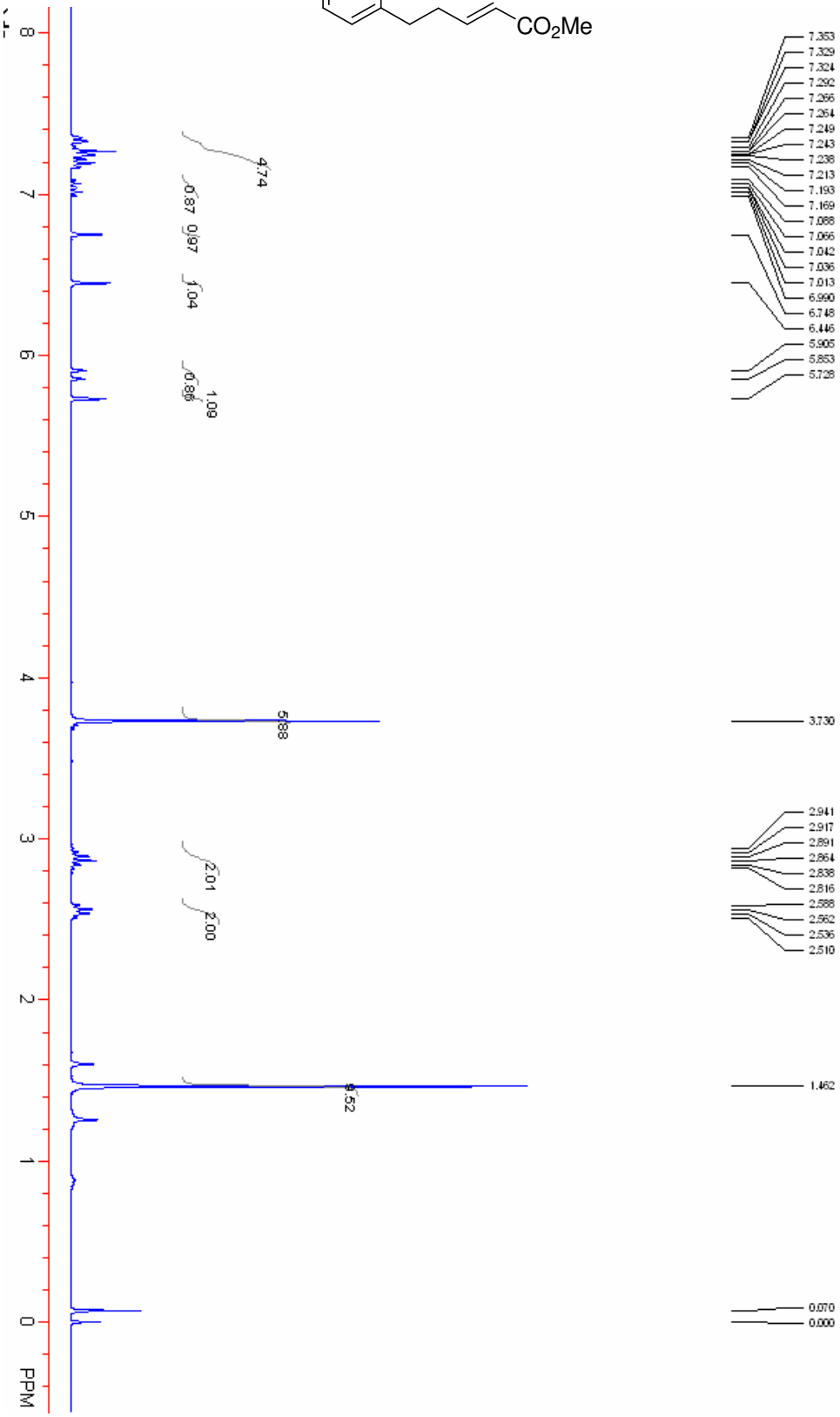




Compound **3g**

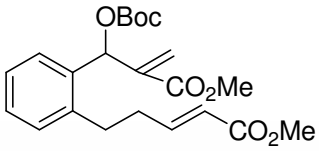
300 MHz in $CDCl_3$

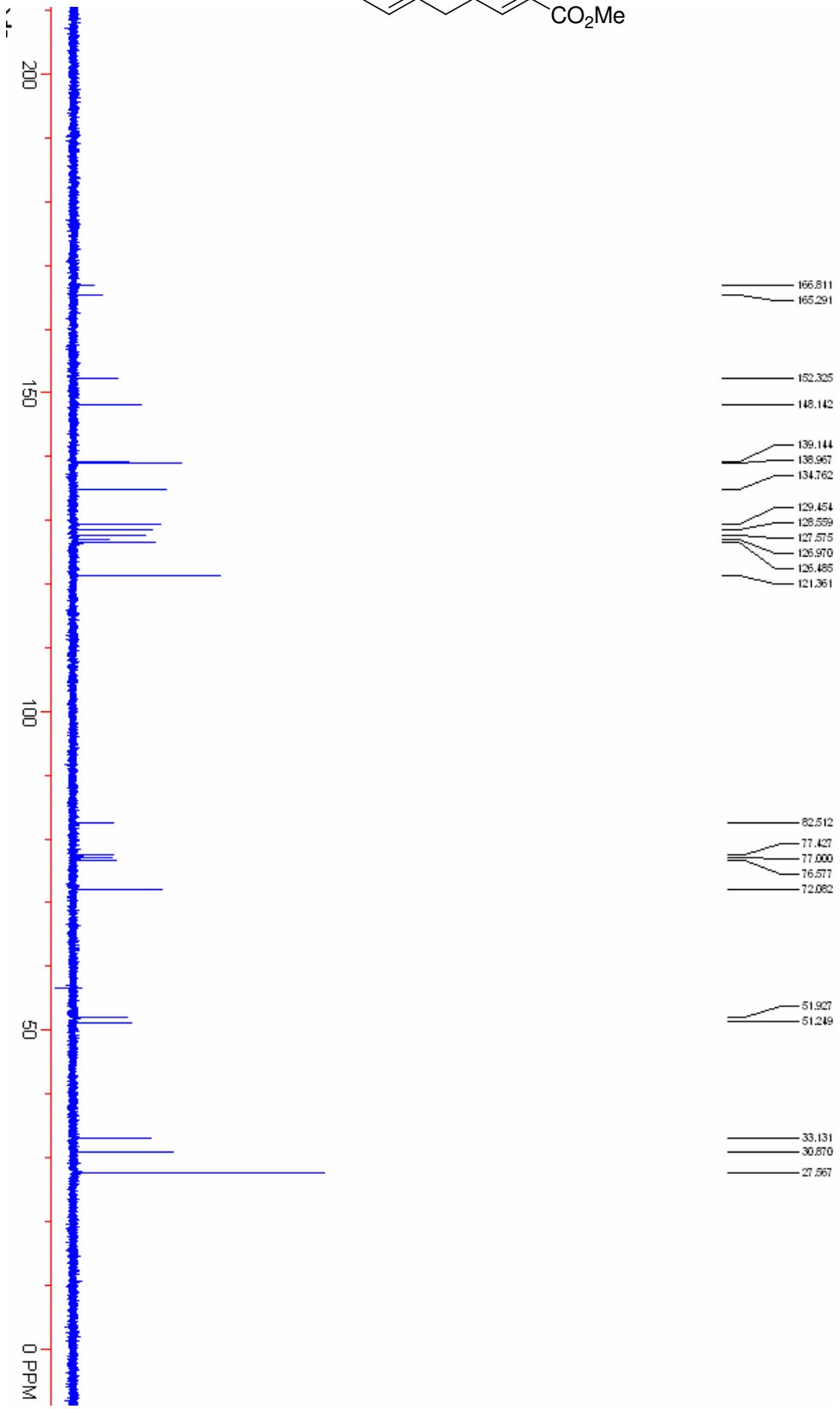




Compound **3g**

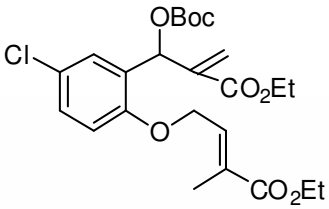
75 MHz in $CDCl_3$





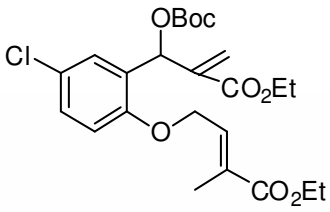
Compound **3h**

300 MHz in $CDCl_3$



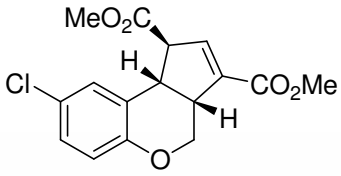
Compound **3h**

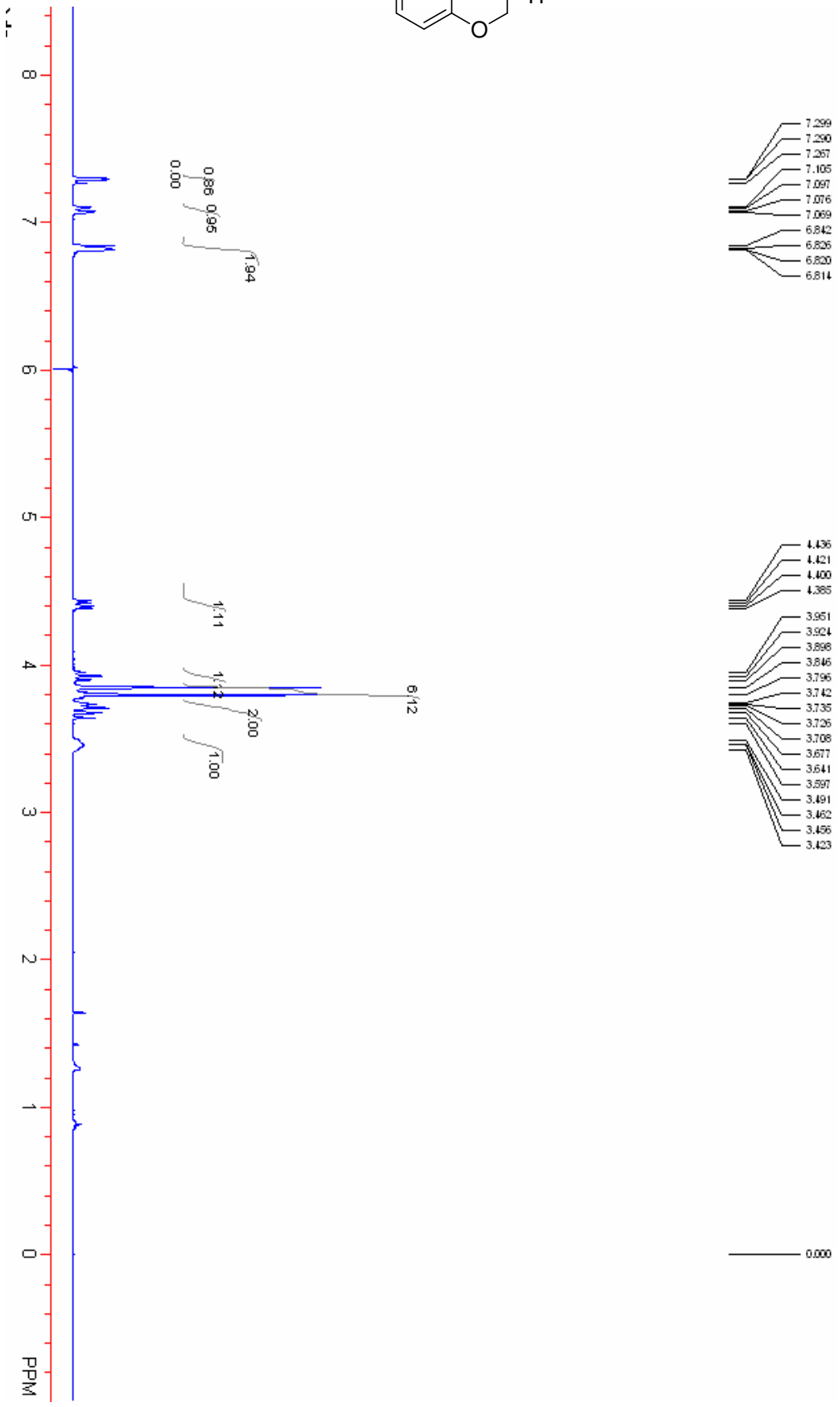
75 MHz in $CDCl_3$



Compound **2a'**

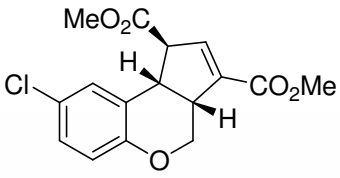
300 MHz in $CDCl_3$

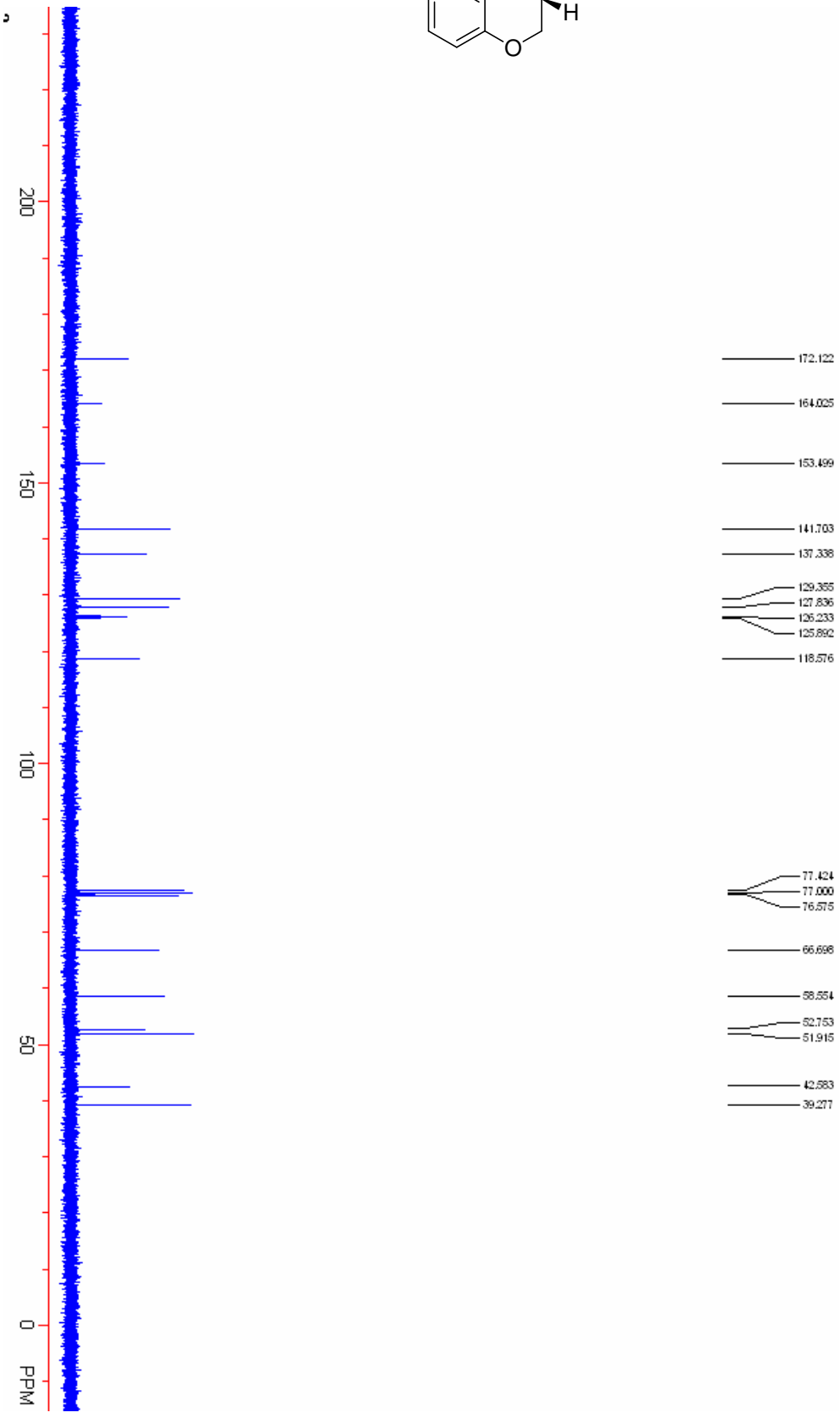




Compound **2a'**

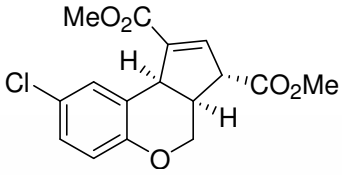
75 MHz in $CDCl_3$

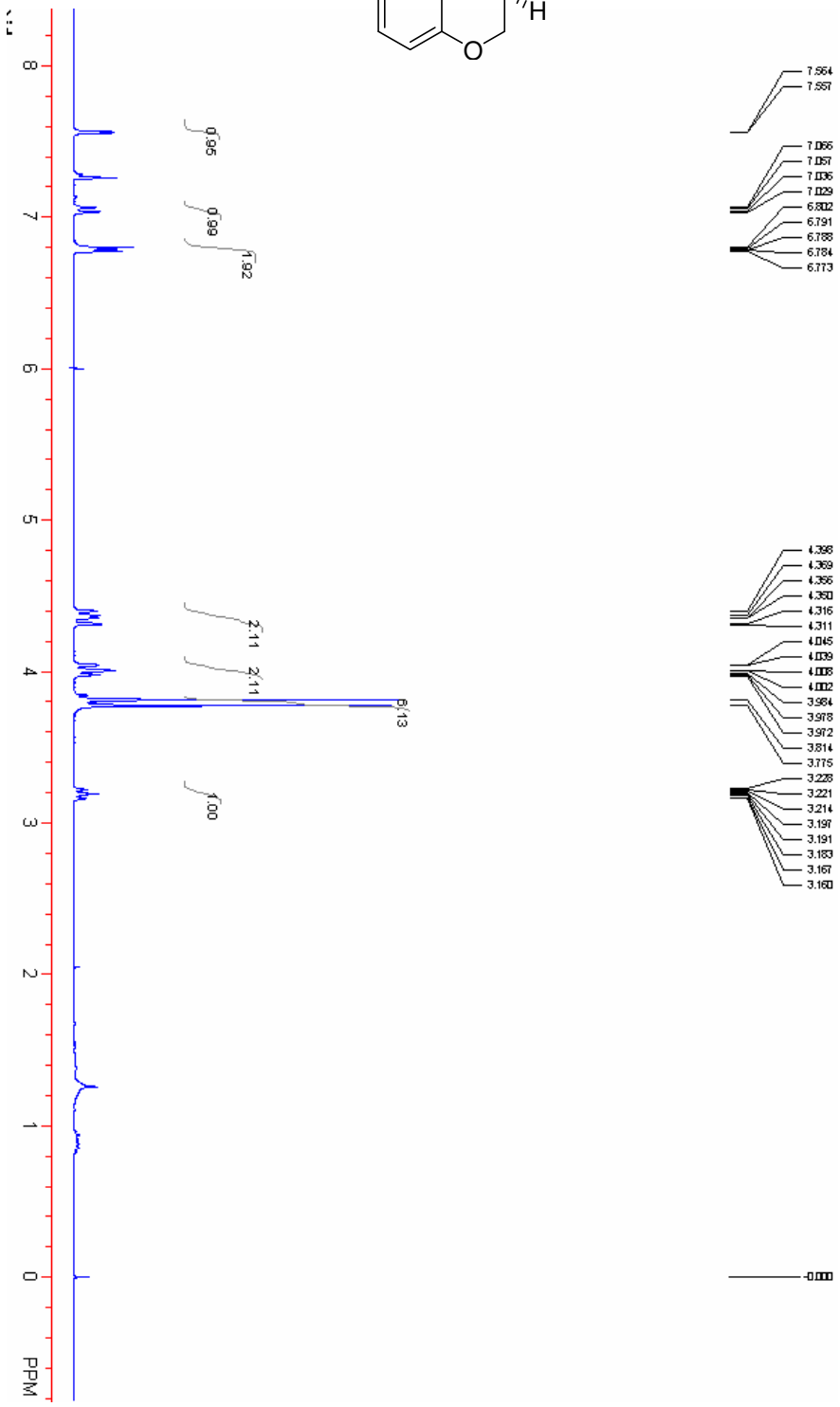




Compound **2a**

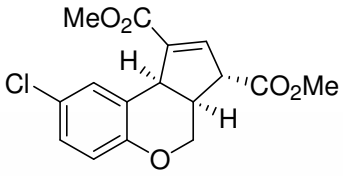
300 MHz in $CDCl_3$

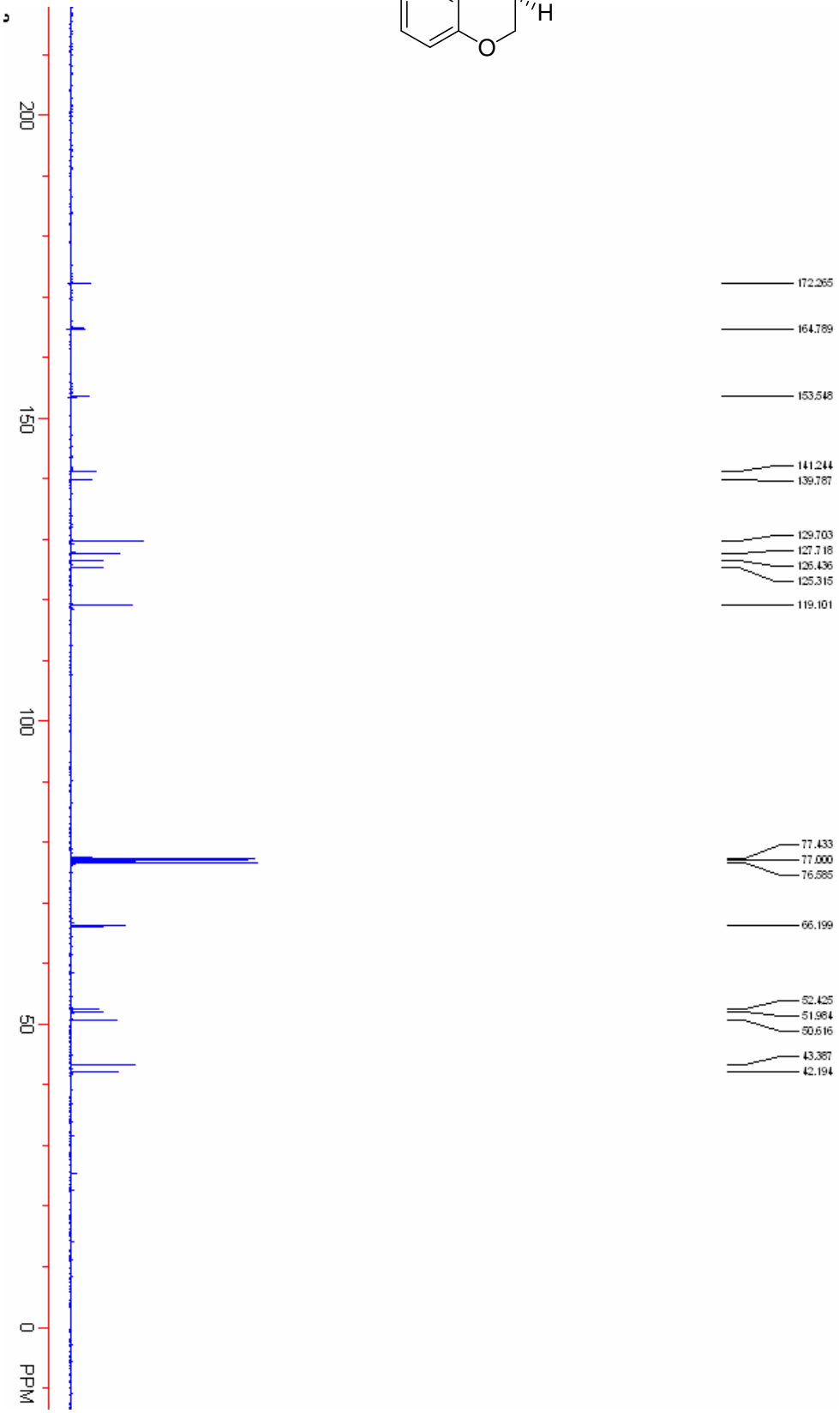




Compound **2a**

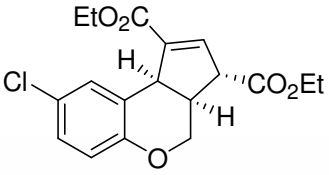
75 MHz in $CDCl_3$

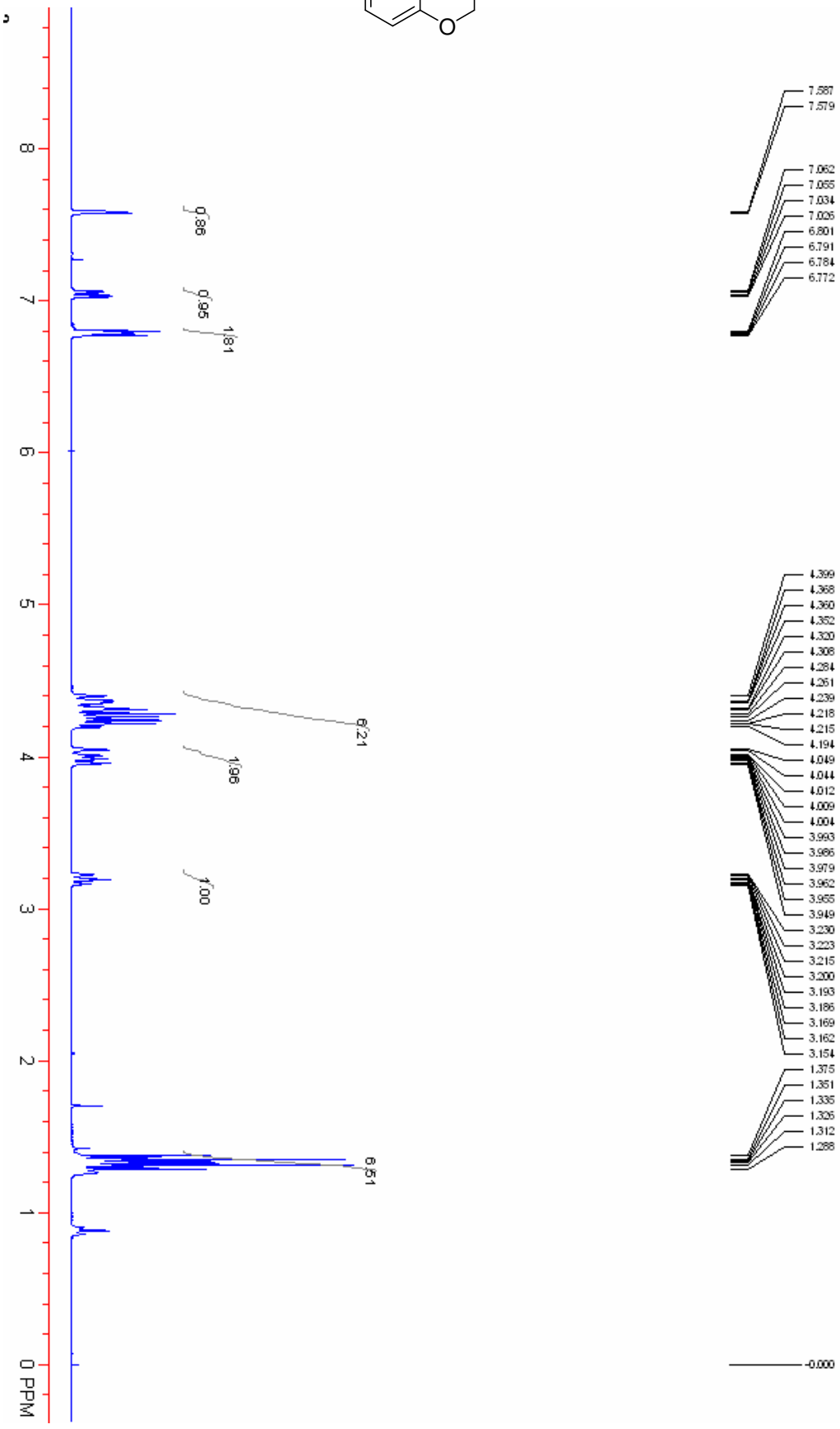




Compound **2b**

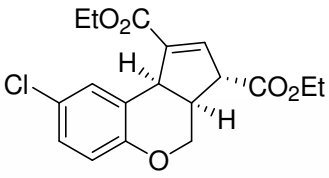
300 MHz in $CDCl_3$

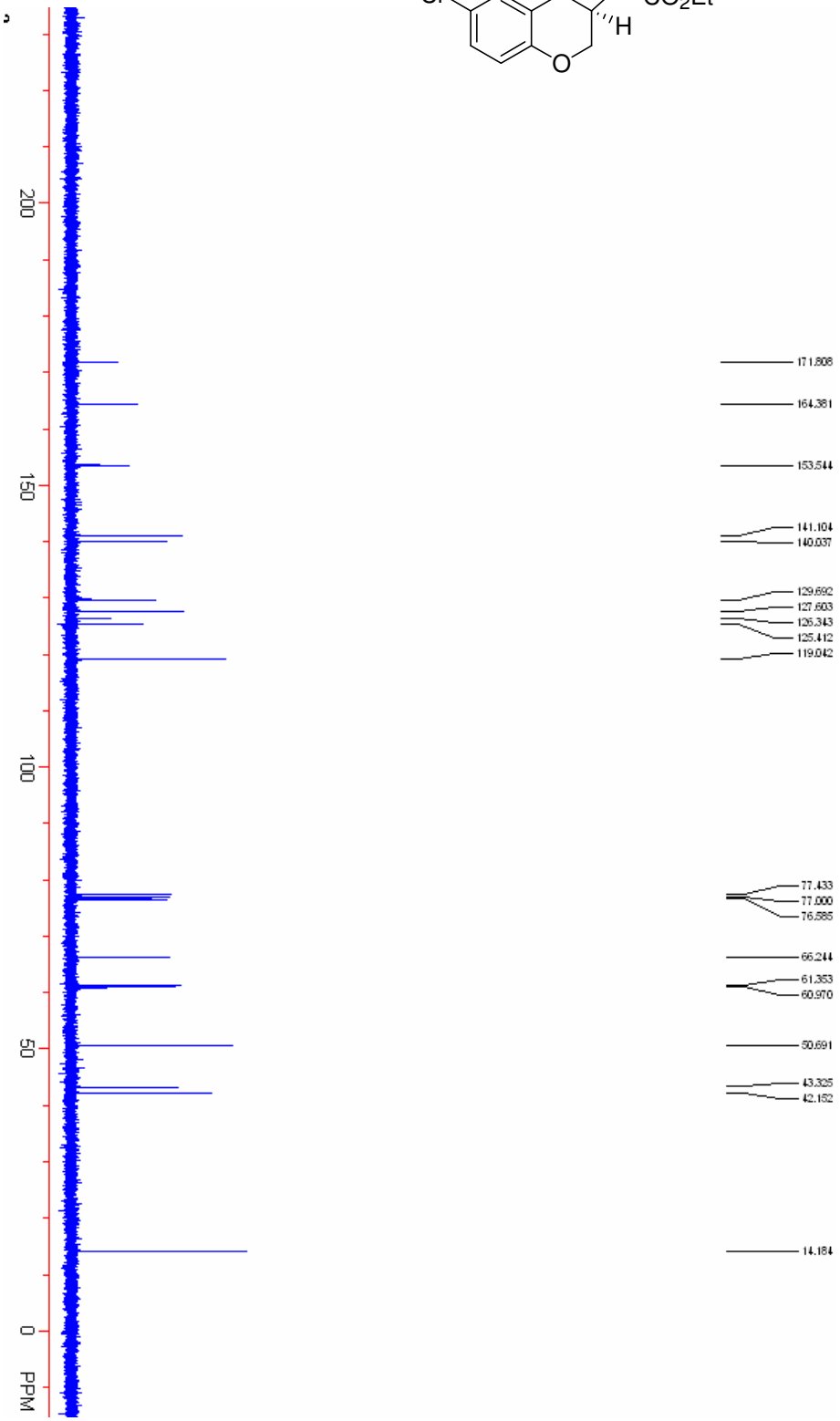




Compound **2b**

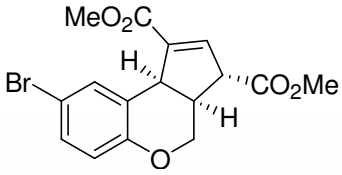
75 MHz in $CDCl_3$

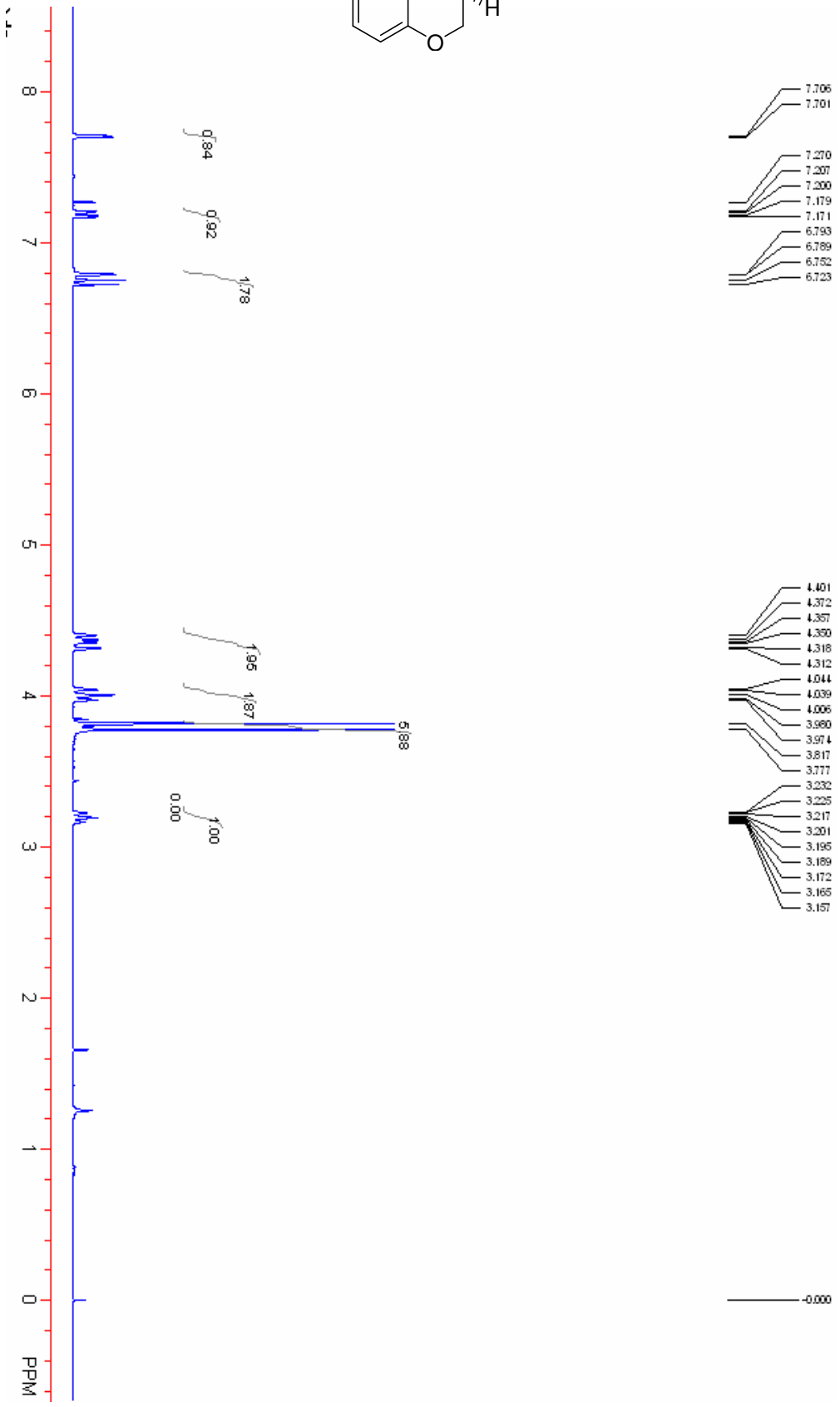




Compound **2c**

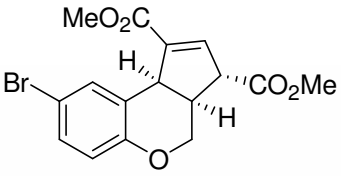
300 MHz in $CDCl_3$





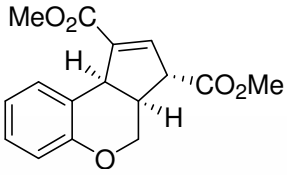
Compound **2c**

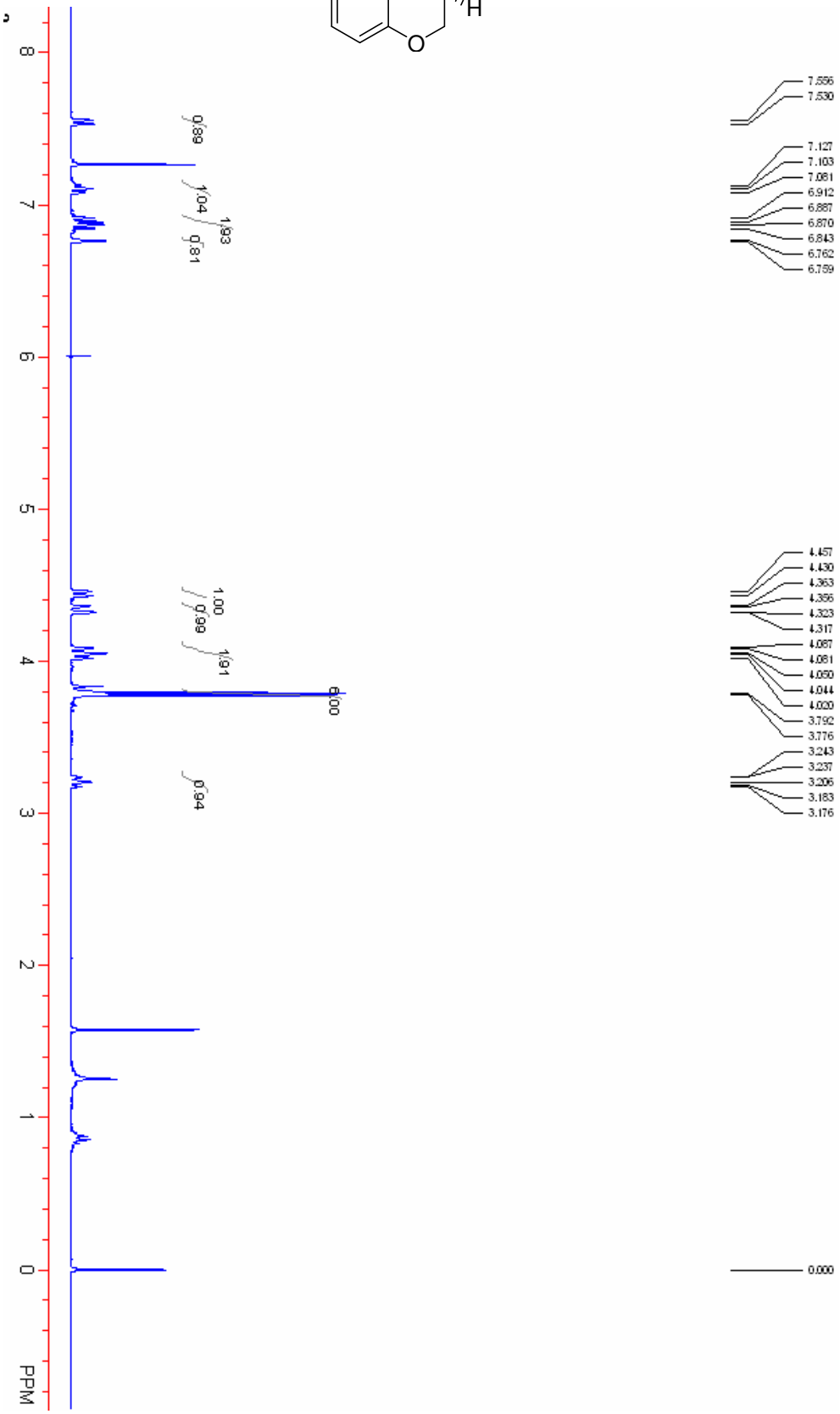
75 MHz in $CDCl_3$



Compound **2d**

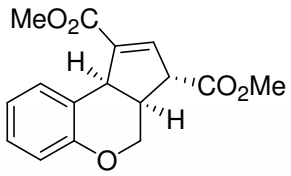
300 MHz in $CDCl_3$

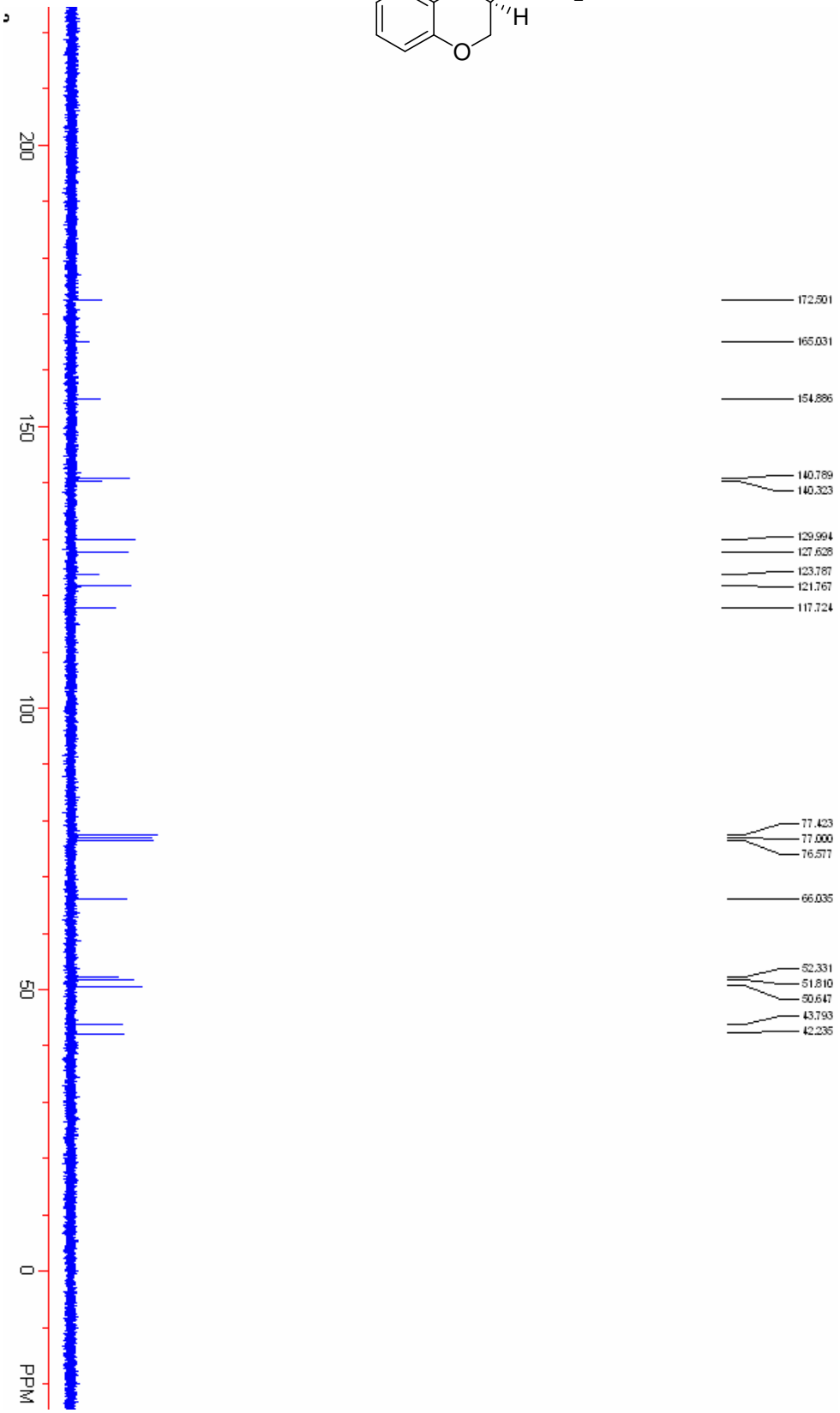




Compound **2d**

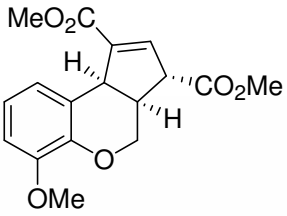
75 MHz in $CDCl_3$





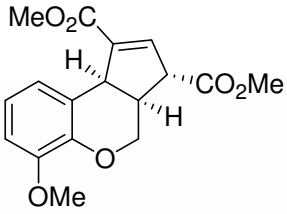
Compound **2e**

300 MHz in $CDCl_3$



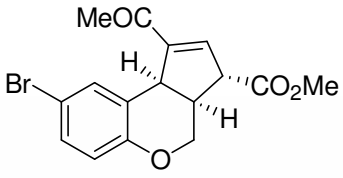
Compound **2e**

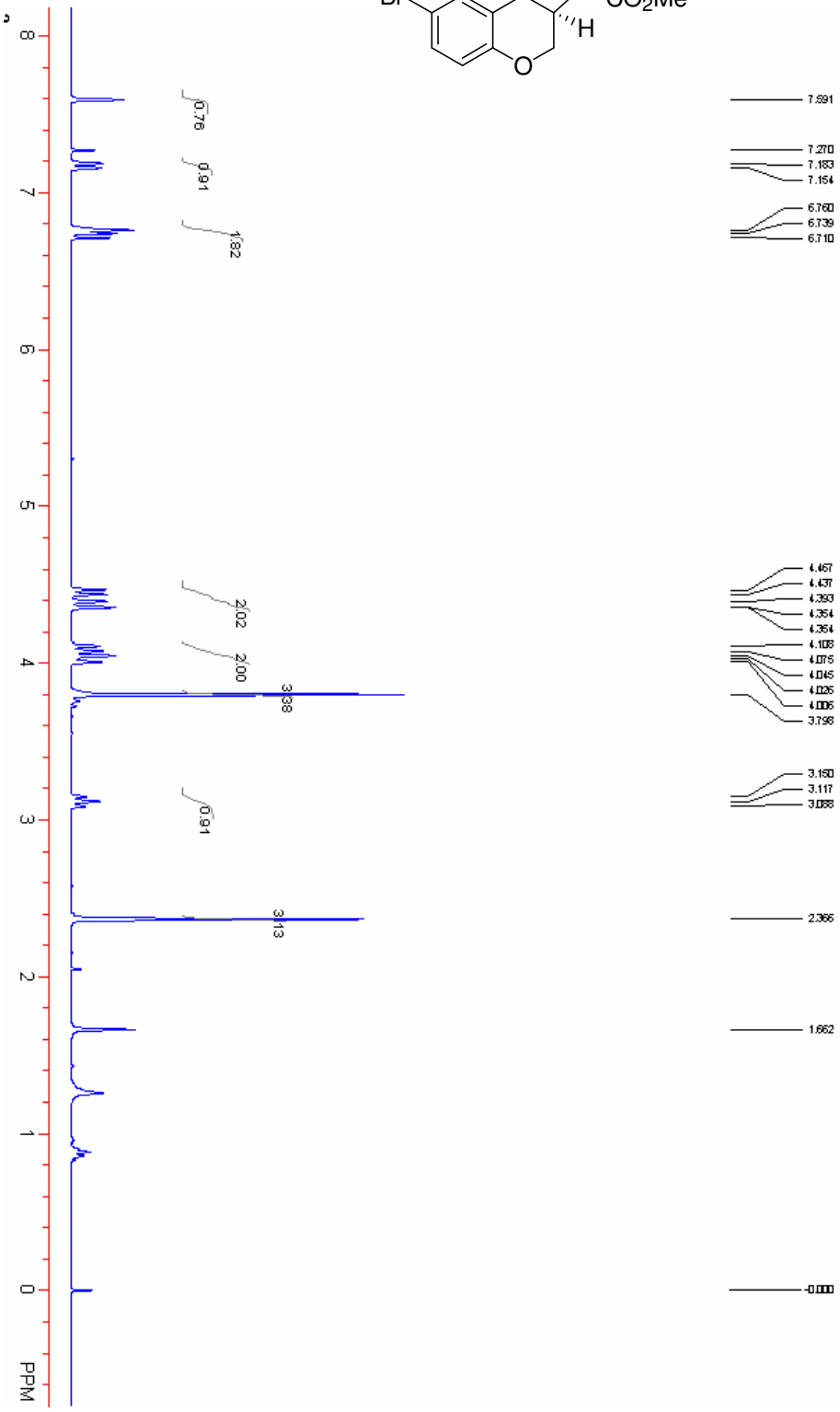
75 MHz in $CDCl_3$



Compound **2f**

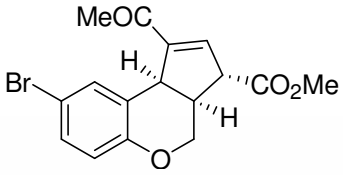
300 MHz in $CDCl_3$

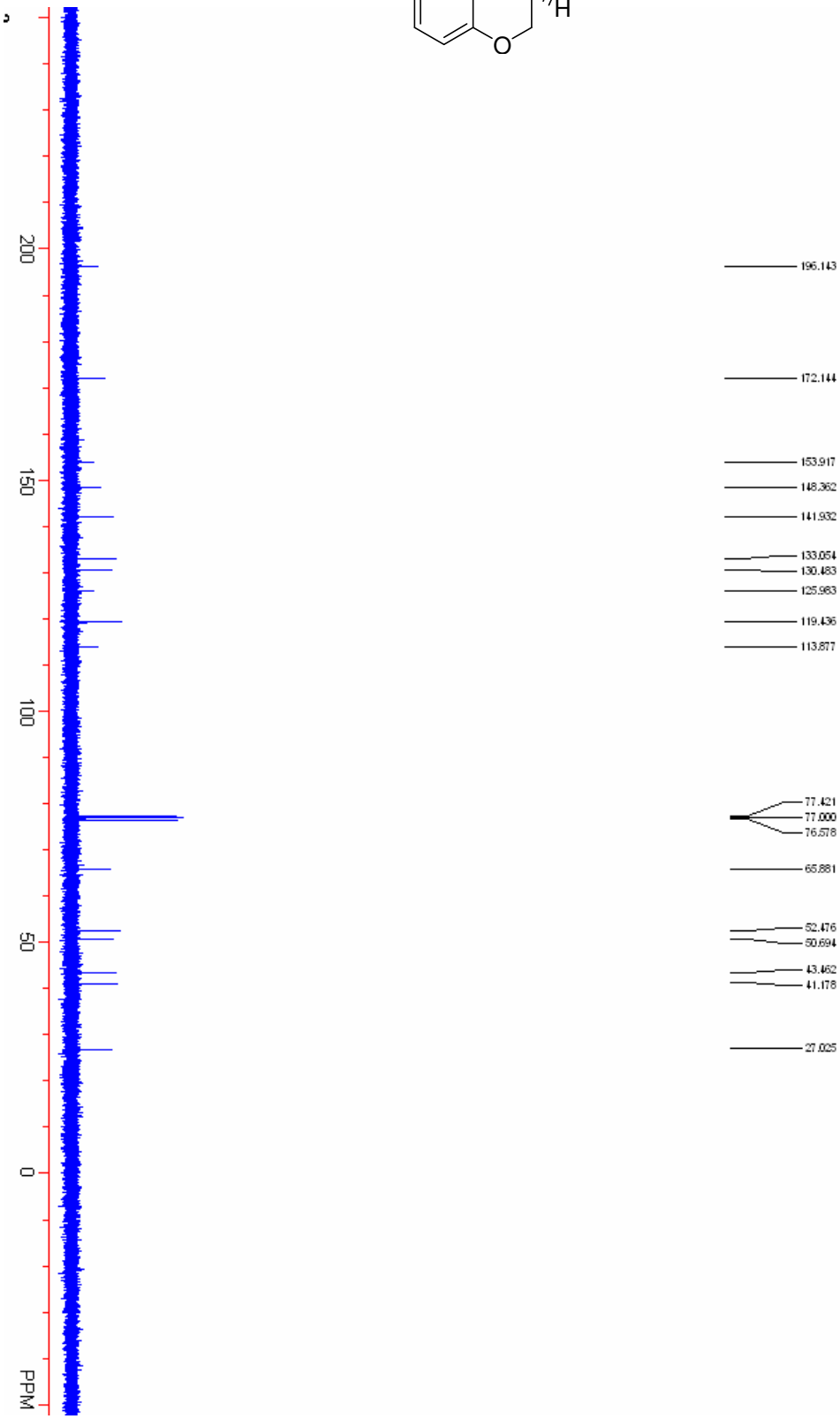




Compound **2f**

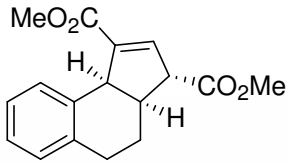
75 MHz in $CDCl_3$

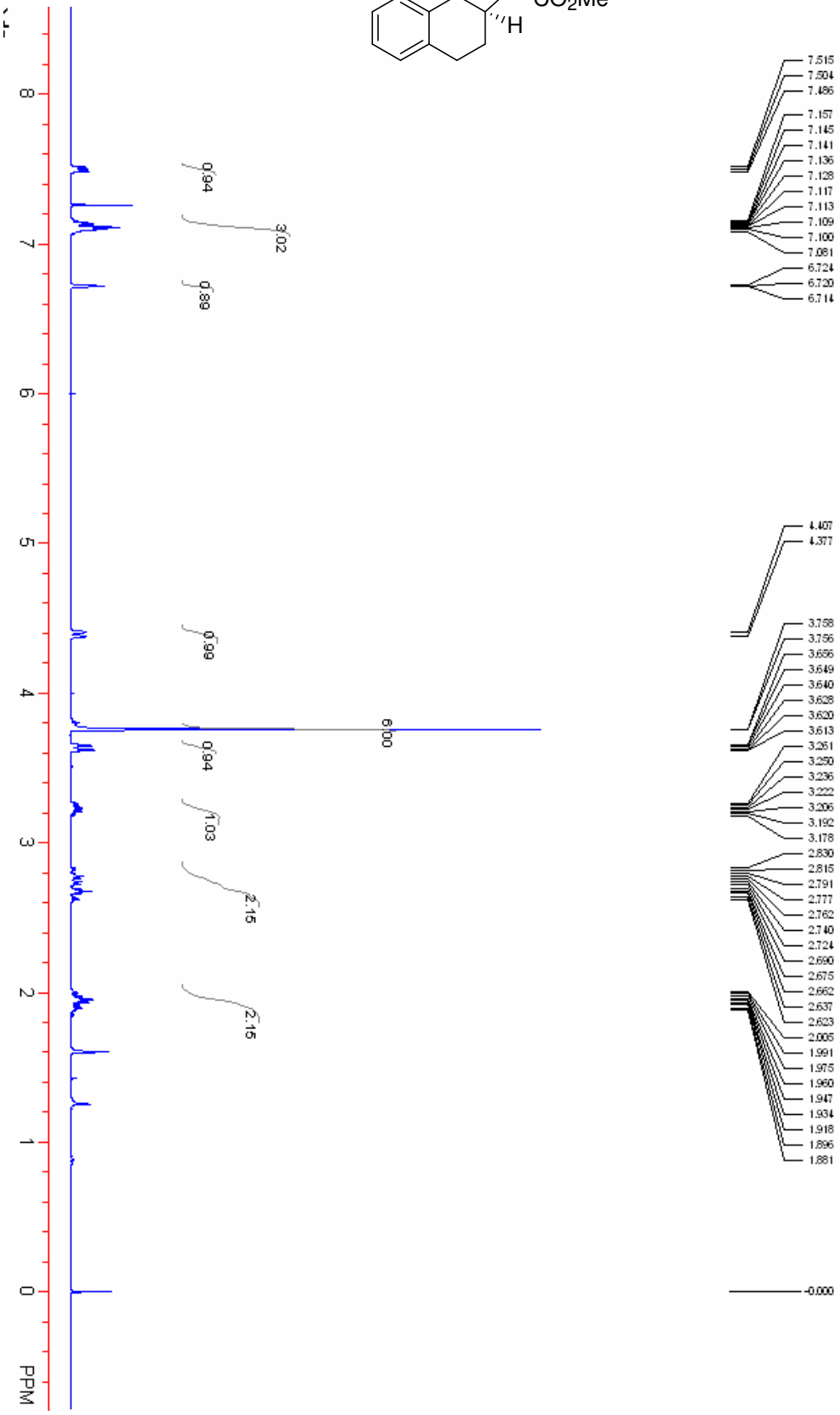




Compound **2g**

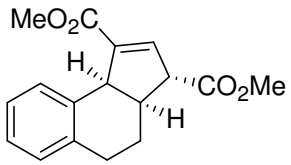
300 MHz in $CDCl_3$

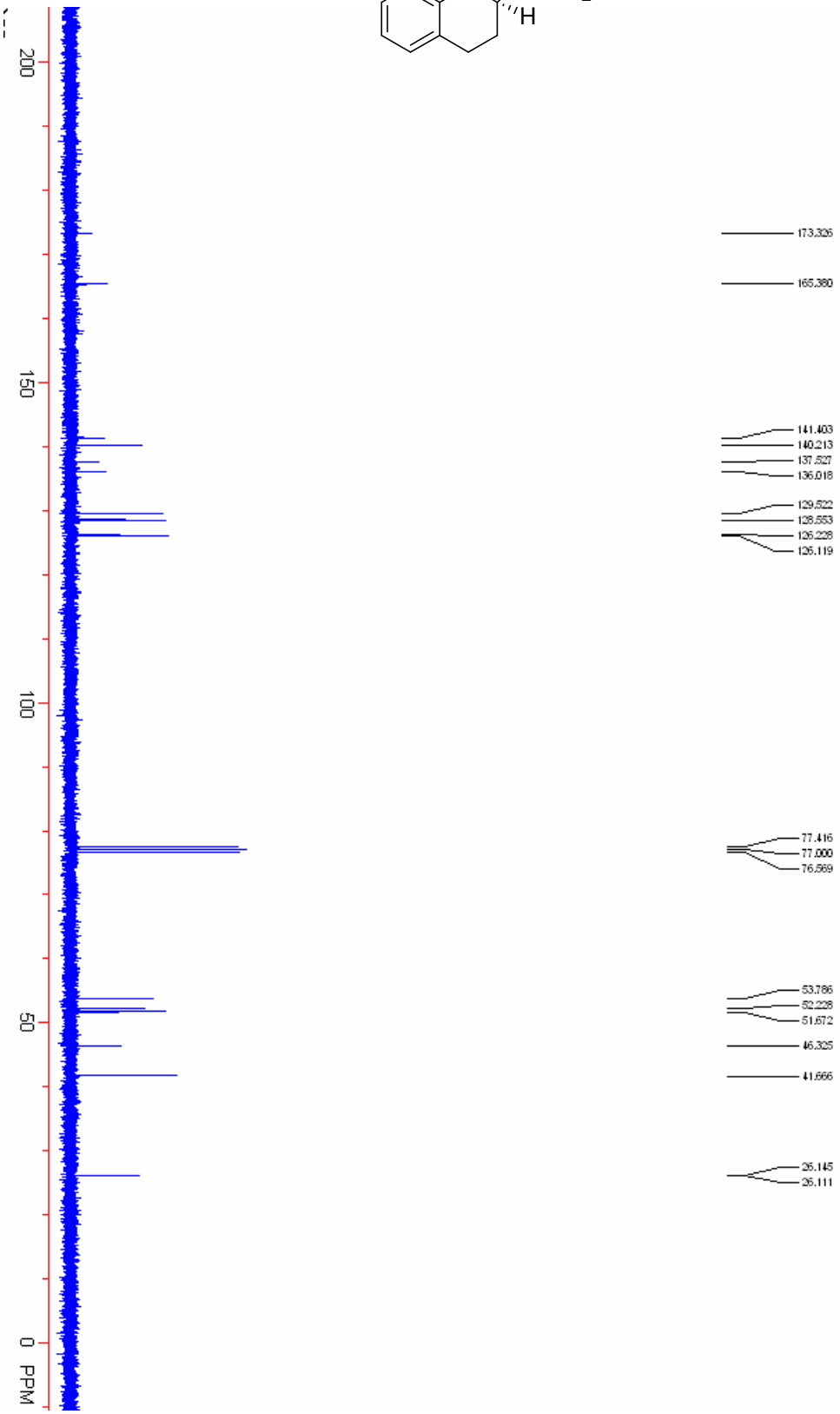




Compound **2g**

75 MHz in $CDCl_3$





Compound **2h**

300 MHz in $CDCl_3$