Phosphine-Catalyzed Enantioselective Synthesis of Oxygen Heterocycles

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Supporting Information

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I. Phosphine-Catalyzed Asymmetric Synthesis of Oxygen Heterocycles

General Procedure: Table 2. In a glove box, a solution of catalyst (*S*)-**1**[1] (17.7 mg, 0.050 mmol) in THF (2.0 mL) was added to a mixture of the hydroxy-2-alkynoate (0.50 mmol) and benzoic acid (31 mg, 0.25 mmol) in a 4-mL vial. The vial was sealed with a cap and removed from the glove box. The reaction mixture was placed in an oil bath and stirred at 55 °C for 2 days. Next, the mixture was passed through a small column of silica gel (0.5 cm x 3 cm), which was washed with Et_2O. The solvents were removed, and the residue was purified by flash chromatography.

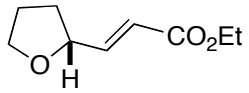
General Procedure: Table 3. In a glove box, a solution of catalyst (*S*)-**1** (17.7 mg, 0.050 mmol) in cyclopentyl methyl ether (2.0 mL) was added to a mixture of the hydroxy-2-ynoate (0.50 mmol) and 2-bromobenzoic acid (50 mg, 0.25 mmol) in a 4-mL vial. The vial was sealed with a cap and removed from the glove box. The reaction mixture was placed in an oil bath and stirred at 50 °C for 3 days. Next, the mixture was passed through a small column of silica gel (0.5 cm x 3 cm), which was washed with Et_2O. The solvents were removed, and the residue was purified by flash chromatography.

We have found the use of a glove box to be convenient, but not necessary. **Procedure without a Glove Box (Table 3, entry 1).** A solution of catalyst (*S*)-**1** (17.7 mg, 0.050 mmol) in cyclopentyl methyl ether (2.0 mL) under argon was added by syringe to a mixture of the hydroxy-2-alkynoate (116 mg, 0.50 mmol) and 2-bromobenzoic acid (50 mg, 0.25 mmol) in a 4-mL vial under argon. The vial was flushed with argon and sealed with a cap. The solution was stirred at 50 °C for 3 days,

(1) Zhu, S.-F.; Yang, Y.; Wang, L.-X.; Liu, B.; Zhou, Q.-L. *Org. Lett.* **2005**, *7*, 2333–2335.

and then it was passed through a small column of silica gel (0.5 cm x 3 cm), which was washed with Et_2O. The solvents were removed, and the residue was purified by flash chromatography, which furnished the desired product as a colorless oil (101 mg, 87%; 87% ee).

Notes on the stability of catalyst 1: After exposure of solid **1** to the air for three days at room temperature, no phosphine oxide is observed by ^{1}H NMR spectroscopy.



(*R*,*E*)-Ethyl 3-(tetrahydrofuran-2-yl)prop-2-enoate (Table 2, entry 1). The title compound was prepared according to the General Procedure with ethyl 7-hydroxy-2-heptynoate (85 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 69 mg (82%; 87% ee); run 2, 64 mg (75%; 87% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = –1.2 (*c* 1.0, $CHCl_3$);

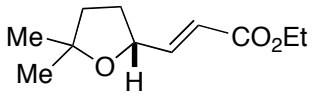
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.91 (dd, *J* = 4.8, 15.6 Hz, 1H), 6.01 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.54-4.49 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.96-3.91 (m, 1H), 3.86-3.81 (m, 1H), 2.17-2.09 (m, 1H), 1.96-1.89 (m, 2H), 1.74-1.65 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 148.6, 120.3, 77.6, 68.7, 60.5, 31.7, 25.7, 14.4;

IR (film) 2980, 2874, 1721, 1660, 1449, 1369, 1300, 1265, 1167, 1097, 1043 cm^{-1};

GCMS (EI) calcd for $C_9H_{14}O_3$ 170 $[M]^+$, found 170.

The enantiomeric excess was determined by chiral GC analysis: Chiraldex G-TA column (100 °C, hold 45 min, then 5 °C/min to 180 °C, hold 5 min; 1.0 mL/min), t_r (major) 38.5 min, t_r (minor) 40.3 min.



(*R*,*E*)-Ethyl 3-(5,5-dimethyltetrahydrofuran-2-yl)prop-2-enoate (Table 2, entry 2). The title compound was prepared according to the General Procedure with ethyl 7-hydroxy-7-methyl-2-octynoate (99 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 92 mg (93%; 94% ee); run 2, 87 mg (88%; 94% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +21 (*c* 2.0, $CHCl_3$);

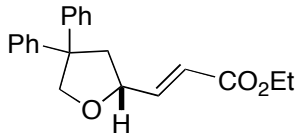
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.93 (dd, *J* = 5.2, 15.6 Hz, 1H), 6.03 (dd, *J* = 1.2, 15.2 Hz, 1H), 4.61-4.56 (m, 1H), 4.19 (q, *J* = 6.8 Hz, 2H), 2.25-2.16 (m, 1H), 1.83-1.75 (m, 3H), 1.30-1.27 (m, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 149.4, 120.1, 82.1, 77.4, 60.5, 38.3, 32.3, 29.0, 28.3, 14.4;

IR (film) 2972, 2872, 1722, 1660, 1463, 1368, 1298, 1267, 1163, 1099, 1044 cm^{-1};

GCMS (EI) calcd for $C_{11}H_{18}O_3$ 198 $[M]^+$, found 198.

The enantiomeric excess was determined by chiral GC analysis: Chiraldex G-TA column (110 °C, hold 50 min, then 10 °C/min to 180 °C, hold 2 min; 1.0 mL/min), t_r (minor) 27.4 min, t_r (major) 29.8 min.



(*R*,*E*)-Ethyl 3-(4,4-diphenyltetrahydrofuran-2-yl)prop-2-enoate (Table 2, entry 3). The title compound was prepared according to the General Procedure with ethyl 7-hydroxy-6,6-diphenyl-2-heptynoate (161 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 98 mg (61%; 87% ee); run 2, 104 mg (65%; 87% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +110 (*c* 1.0, $CHCl_3$);

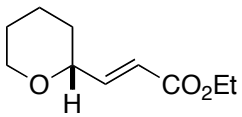
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.19 (m, 10H), 6.99 (dd, *J* = 5.2, 15.6 Hz, 1H), 6.08 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.75 (d, *J* = 8.8 Hz, 1H), 4.65-4.59 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.16 (d, *J* = 8.8 Hz, 1H), 2.73 (dd, *J* = 6.4, 11.6 Hz, 1H), 2.50 (dd, *J* = 10.0, 12.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 147.9, 145.6, 144.9, 128.7, 128.6, 127.22, 127.17, 126.8, 126.7, 120.6, 77.4, 77.3, 60.6, 56.2, 44.8, 14.4;

IR (film) 2980, 2871, 1717, 1660, 1494, 1447, 1368, 1299, 1273, 1175, 1042 cm^{-1};

GCMS (EI) calcd for $C_{21}H_{22}O_3$ 322 $[M]^+$, found 322.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AD-H column (2% *i*-PrOH:hexanes, 1.0 mL/min), t_r (major) 14.2 min, t_r (minor) 18.1 min.



(*R*,*E*)-Ethyl 3-(tetrahydro-2*H*-pyran-2-yl)prop-2-enoate (Table 2, entry 4). The title compound was prepared according to the General Procedure with ethyl 8-hydroxy-2-octynoate (92 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 82 mg (89%; 93% ee); run 2, 84 mg (91%; 92% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_{D}$ = +22 (*c* 1.0, $CHCl_3$);

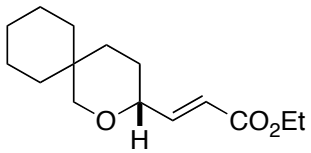
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (dd, *J* = 4.4, 16.0 Hz, 1H), 6.00 (dd, *J* = 2.0, 15.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.05-4.01 (m, 1H), 3.97-3.93 (m, 1H), 3.52-3.45 (m, 1H), 1.89-1.85 (m, 1H), 1.73-1.69 (m, 1H), 1.61-1.49 (m, 3H), 1.39-1.30 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 148.3, 119.9, 76.3, 68.4, 60.4, 31.5, 25.8, 23.5, 14.4;

IR (film) 2939, 2850, 1721, 1661, 1441, 1367, 1304, 1275, 1208, 1172, 1082, 1047 cm^{-1};

GCMS (EI) calcd for $C_{10}H_{16}O_3$ 184 $[M]^+$, found 184.

The enantiomeric excess was determined by chiral GC analysis: Chiraldex G-TA column (103 °C, hold 70 min, then 10 °C/min to 180 °C, hold 2 min; 1.0 mL/min), t_r (major) 56.8 min, t_r (minor) 58.5 min.



(*R*,*E*)-Ethyl 3-(2-oxaspiro[5.5]undecan-3-yl)prop-2-enoate (Table 2, entry 5). The title compound was prepared according to the General Procedure with ethyl 6-(1-(hydroxymethyl)cyclohexyl)hex-2-ynoate (126 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 104 mg (83%; 94% ee); run 2, 109 mg (87%; 94% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_{D}$ = +59 (*c* 1.0, $CHCl_3$);

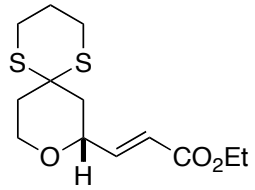
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.91 (dd, *J* = 4.4, 15.6 Hz, 1H), 6.02 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.92-3.87 (m, 1H), 3.81 (dd, *J* = 2.4, 11.2 Hz, 1H), 3.14 (d, *J* = 11.2 Hz, 1H), 1.82-1.78 (m, 1H), 1.57-1.42 (m, 11H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.16-1.14 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 148.2, 120.1, 76.9, 60.5, 36.5, 32.2, 31.2, 27.2, 26.9, 21.61, 21.58, 14.4;

IR (film) 2925, 2850, 1722, 1662, 1453, 1367, 1304, 1172, 1053 cm^{-1};

GCMS (EI) calcd for $C_{15}H_{24}O_3$ 252 $[M]^+$, found 252.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AS-H column (1% *i*-PrOH:hexanes, 1.0 mL/min), t_r (major) 5.1 min, t_r (minor) 7.4 min.



(*R*,*E*)-Ethyl 3-(9-oxa-1,5-dithiaspiro[5.5]undecan-8-yl)prop-2-enoate (Table 2, entry 6). The title compound was prepared according to the General Procedure with ethyl 5-(2-(2-hydroxyethyl)-1,3-dithian-2-yl)pent-2-ynoate (144 mg, 0.50 mmol). After purification by flash chromatography (10:20:70 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 108 mg (75%; 92% ee); run 2, 99 mg (69%; 92% ee).

R_f = 0.3 (10:20:70 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = –2.1 (*c* 1.0, $CHCl_3$);

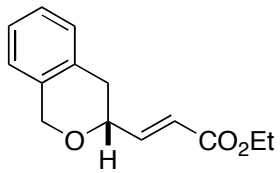
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (dd, *J* = 4.4, 15.6 Hz, 1H), 6.05 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.45-4.40 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.96-3.88 (m, 2H), 2.97-2.75 (m, 4H), 2.36 (td, *J* = 2.0, 14.0 Hz, 1H), 2.17-2.13 (m, 1H), 2.06-1.93 (m, 3H), 1.71 (dd, *J* = 11.6, 13.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 146.9, 120.9, 71.7, 63.4, 60.6, 47.5, 42.6, 37.6, 26.0, 25.9, 25.8, 14.4;

IR (film) 2952, 2864, 1715, 1660, 1424, 1367, 1305, 1178, 1077, 1034 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{20}O_3S_2$ 288 $[M]^+$, found 288.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AD-H column (3% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 15.0 min, t_r (major) 19.0 min.



(*R*,*E*)-Ethyl 3-(isochroman-3-yl)prop-2-enoate (Table 2, entry 7). The title compound was prepared according to the General Procedure with ethyl 5-(2-(hydroxymethyl)phenyl)pent-2-ynoate (116 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 96 mg (83%; 94% ee); run 2, 95 mg (82%; 94% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +150 (*c* 1.0, $CHCl_3$);

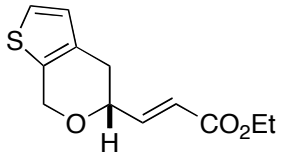
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21-7.02 (m, 5H), 6.17 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.94 (d, *J* = 15.2 Hz, 1H), 4.88 (d, *J* = 15.2 Hz, 1H), 4.41-4.36 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.85 (d, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 146.8, 134.3, 132.4, 129.0, 126.8, 126.5, 124.4, 121.1, 73.4, 68.2, 60.7, 33.5, 14.4;

IR (film) 2981, 2837, 1721, 1663, 1449, 1367, 1304, 1274, 1176, 1119, 1059, 1037 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{16}O_3$ 232 $[M]^+$, found 232.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (2% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 12.3 min, t_r (major) 14.5 min.



(*R*,*E*)-Ethyl 3-(5,7-dihydro-4*H*-thieno[2,3-*c*]pyran-5-yl)prop-2-enoate (Table 2, entry 8). The title compound was prepared according to the General Procedure with ethyl 5-(2-(hydroxymethyl)thiophen-3-yl)pent-2-ynoate (119 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 93 mg (78%; 91% ee); run 2, 97 mg (82%; 91% ee).

R_f = 0.2 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +160 (*c* 1.0, $CHCl_3$);

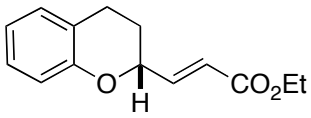
^1H NMR ($CDCl_3$, 400 MHz) δ 7.18 (d, *J* = 4.8 Hz, 1H), 7.04 (dd, *J* = 4.0, 15.6 Hz, 1H), 6.82 (d, *J* = 4.8 Hz, 1H), 6.17 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.99 (d, *J* = 14.4 Hz, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.38-4.33 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.84-2.79 (m, 1H), 2.72-2.65 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 146.5, 132.5, 132.4, 126.9, 123.3, 121.2, 73.3, 65.8, 60.7, 31.3, 14.4;

IR (film) 2980, 2924, 2848, 1720, 1663, 1559, 1445, 1394, 1367, 1304, 1287, 1176, 1100, 1034 cm^{-1};

GCMS (EI) calcd for $C_{12}H_{14}O_3S$ 238 $[M]^+$, found 238.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (2% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 13.9 min, t_r (major) 16.7 min.



(*R*,*E*)-Ethyl 3-(chroman-2-yl)prop-2-enoate (Table 3, entry 1). The title compound was prepared according to the General Procedure with ethyl 6-(2-hydroxyphenyl)hex-2-ynoate (116 mg, 0.50 mmol). After purification by flash chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 99 mg (85%; 89% ee); run 2, 100 mg (86%; 88% ee).

R_f = 0.3 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = –1.0 (*c* 3.0, $CHCl_3$);

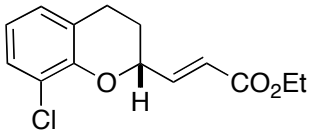
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15-7.11 (m, 1H), 7.07-7.00 (m, 2H), 6.89-6.86 (m, 2H), 6.18 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.78-4.74 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.92-2.74 (m, 2H), 2.19-2.12 (m, 1H), 1.92-1.83 (m, 1H), 1.31 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 154.0, 146.3, 129.7, 127.6, 121.6 (2), 120.7, 116.9, 74.1, 60.7, 27.1, 24.1, 14.4;

IR (film) 2921, 2850, 1717, 1663, 1583, 1489, 1457, 1367, 1257, 1177 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{16}O_3$ 232 $[M]^+$, found 232.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (1% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 7.2 min, t_r (major) 9.0 min.



(*R*,*E*)-Ethyl 3-(8-chlorochroman-2-yl)prop-2-enoate (Table 3, entry 2). The title compound was prepared according to the General Procedure with ethyl 6-(3-chloro-2-hydroxyphenyl)hex-2-ynoate (133 mg, 0.50 mmol). After purification by flash chromatography (3:20:77 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 110 mg (83%; 63% ee); run 2, 107 mg (80%; 63% ee).

R_f = 0.3 (3:20:77 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +34 (*c* 1.0, $CHCl_3$);

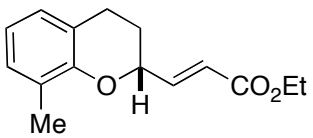
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22-7.20 (m, 1H), 7.02 (dd, *J* = 3.6, 15.6 Hz, 1H), 6.97-6.95 (m, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.21 (dd, *J* = 2.0, 15.6 Hz, 1H), 4.90-4.86 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.93-2.75 (m, 2H), 2.22-2.15 (m, 1H), 1.93-1.86 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 149.5, 145.4, 128.3, 128.0, 123.4, 121.9 (2), 120.8, 74.7, 60.8, 26.7, 24.2, 14.4;

IR (film) 2981, 2935, 2849, 1721, 1662, 1573, 1460, 1368, 1306, 1242, 1180, 1102, 1040 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{15}ClO_3$ 266 $[M]^+$, found 266.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (1% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 9.5 min, t_r (major) 12.6 min.



(*R*,*E*)-Ethyl 3-(8-methylchroman-2-yl)prop-2-enoate (Table 3, entry 3). The title compound was prepared according to the General Procedure with ethyl 6-(2-hydroxy-3-methylphenyl)hex-2-ynoate (123 mg, 0.50 mmol). After purification by flash

chromatography (5:20:75 Et_2O/CH_2Cl_2/hexanes), the desired product was isolated as a colorless oil: run 1, 108 mg (88%; 84% ee); run 2, 111 mg (90%; 84% ee).

R_f = 0.3 (5:20:75 Et_2O/CH_2Cl_2/hexanes);

$[\alpha]^{20}_D$ = +25 (*c* 2.0, $CHCl_3$);

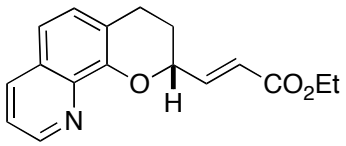
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05 (dd, *J* = 3.6, 15.6 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.18 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.79-4.75 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.93-2.74 (m, 2H), 2.25 (s, 3H), 2.19-2.13 (m, 1H), 1.90-1.80 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 152.1, 146.7, 128.8, 127.2, 126.2, 121.1, 121.0, 120.1, 74.0, 60.7, 27.2, 24.5, 16.2, 14.4;

IR (film) 2923, 1718, 1622, 1595, 1471, 1368, 1305, 1265, 1219, 1177, 1037 cm^{-1};

GCMS (EI) calcd for $C_{15}H_{18}O_3$ 246 $[M]^+$, found 246.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (1% *i*-PrOH:hexanes, 1.0 mL/min), t_r (minor) 6.6 min, t_r (major) 9.3 min.



(*R*,*E*)-Ethyl 3-(2,3-dihydro-1*H*-4-oxa-5-aza-phenanthren-3-yl)prop-2-enoate (Table 3, entry 4). The title compound was prepared according to the General Procedure with ethyl 6-(8-hydroxyquinolin-7-yl)hex-2-ynoate (142 mg, 0.50 mmol). The reaction mixture was filtered through a thin pad of neutral alumina (3 cm x 0.5 cm) and then washed through with EtOAc. The filtrate was concentrated to give the crude product. After purification by flash chromatography (30:70 EtOAc/hexanes) using neutral alumina, the desired product was isolated as a dark-green solid: run 1, 115 mg (81%; 84% ee); run 2, 110 mg (77%; 84% ee).

R_f = 0.3 (30:70 EtOAc/hexanes);

mp 69-71 °C;

$[\alpha]^{20}_D$ = +140 (*c* 1.0, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (dd, *J* = 2.0, 4.4 Hz, 1H), 8.09 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.39 (dd, *J* = 4.0, 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.12 (dd, *J* = 4.4, 15.6 Hz, 1H), 6.14 (dd, *J* = 1.6, 15.6 Hz, 1H), 5.21-5.16 (m, 1H), 4.22-4.14 (m, 2H), 3.00-2.87 (m, 2H), 2.32-2.25 (m, 1H), 2.15-2.07 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H);

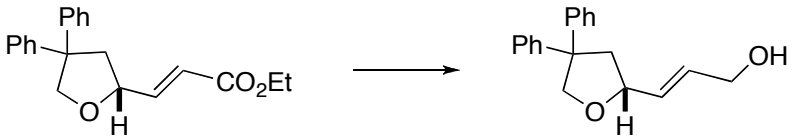
^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 149.6, 148.7, 145.8, 140.0, 135.9, 128.5, 128.3, 122.5, 121.2, 119.7, 119.2, 74.6, 60.6, 26.1, 23.5, 14.3;

IR (film) 2925, 1712, 1661, 1504, 1465, 1376, 1257, 1181, 1111 cm^{-1};

LCMS (ES + APCI) calcd for $C_{17}H_{18}NO_3$ 284.1 $[M+H]^+$, found 284.1.

The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AD-H column (5% *i*-PrOH:hexanes, 1.0 mL/min), t_r (major) 20.1 min, t_r (minor) 30.2 min.

II. Determination of Absolute Configuration



(*R*,*E*)-3-(4,4-diphenyltetrahydrofuran-2-yl)prop-2-en-1-ol. A solution of (*R*,*E*)-ethyl 3-(4,4-diphenyltetrahydrofuran-2-yl)prop-2-enoate (run 1 of Table 2, entry 3; 98 mg, 0.30 mmol; 87% ee) in THF (10 mL) at –78 °C was treated with diisobutylaluminium hydride (1.0 M in hexanes; 0.90 mL, 0.90 mmol). The reaction mixture was warmed to 0 °C and stirred at this temperature for 30 min. The resulting mixture was washed with aqueous HCl (1 M; 20 mL), and the aqueous layer was extracted with Et_2O (2 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give the crude product. Purification by column chromatography furnished the desired product (53 mg; 63%) as a colorless oil. The product was crystallized (1:5 TBME/hexanes), and an X-ray crystal structure was obtained.

mp 73-75 °C;

$[\alpha]^{20}_D$ = +54 (*c* 0.90, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.19 (m, 10H), 5.86 (dt, *J* = 5.0, 15.5 Hz, 1H), 5.78 (ddt, *J* = 1.5, 7.0, 15.5 Hz, 1H), 4.67 (dd, *J* = 1.0, 9.0 Hz, 1H), 4.50-4.46 (m, 1H), 4.16 (d, *J* = 8.5 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 1H), 2.66 (ddd, *J* = 1.0, 6.0, 12.0 Hz, 1H), 2.46 (dd, *J* = 9.5, 12.0 Hz, 1H), 1.35 (t, *J* = 6.0 Hz, 1H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.0, 145.6, 132.0, 131.3, 128.6, 128.5, 127.29, 127.25, 126.7, 126.5, 78.9, 77.1, 63.1, 56.3, 45.3.

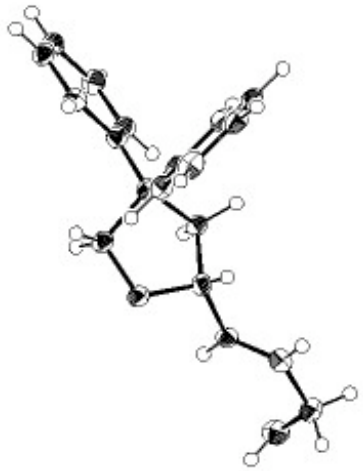


Table 1. Crystal data and structure refinement for d08013.

Identification code	d08013	
Empirical formula	C19 H20 O2	
Formula weight	280.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.0415(2) Å	α= 90°.
	b = 10.5219(2) Å	β= 91.9240(10)°.
	c = 17.8120(3) Å	γ = 90°.
Volume	1506.26(5) $Å^3$	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	0.619 mm^{-1}	
F(000)	600	
Crystal size	0.40 x 0.30 x 0.05 mm^3	
Theta range for data collection	2.48 to 67.73°.	
Index ranges	-9<=h<=9, -12<=k<=12, -21<=l<=21	
Reflections collected	33734	
Independent reflections	5436 [R(int) = 0.0256]	
Completeness to theta = 67.73°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9697 and 0.7900	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5436 / 3 / 385	
Goodness-of-fit on F^2	1.110	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.1012	
R indices (all data)	R1 = 0.0382, wR2 = 0.1016	
Absolute structure parameter	0.07(19)	
Largest diff. peak and hole	0.195 and -0.220 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d08013. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8060(2)	6245(1)	6985(1)	32(1)
O(2)	7557(2)	1497(1)	6697(1)	31(1)
C(1)	9070(2)	5430(2)	6521(1)	28(1)
C(2)	8761(2)	5932(2)	5725(1)	27(1)
C(3)	8476(2)	7360(2)	5850(1)	24(1)
C(4)	7361(3)	7256(2)	6531(1)	28(1)
C(5)	8591(3)	4067(2)	6628(1)	31(1)
C(6)	9674(3)	3131(2)	6668(1)	26(1)
C(7)	9286(3)	1741(2)	6715(1)	30(1)
C(11)	10152(2)	8002(2)	6046(1)	24(1)
C(12)	11335(2)	8083(2)	5489(1)	27(1)
C(13)	12887(3)	8622(2)	5641(1)	32(1)
C(14)	13284(3)	9109(2)	6346(1)	35(1)
C(15)	12124(3)	9041(2)	6901(1)	34(1)
C(16)	10573(3)	8484(2)	6754(1)	30(1)
C(21)	7566(2)	8053(2)	5202(1)	24(1)
C(22)	7356(2)	9366(2)	5247(1)	27(1)
C(23)	6512(2)	10028(2)	4679(1)	31(1)
C(24)	5859(2)	9391(2)	4055(1)	31(1)
C(25)	6024(3)	8086(2)	4011(1)	32(1)
C(26)	6880(2)	7424(2)	4578(1)	27(1)
O(3)	7236(2)	444(1)	8111(1)	26(1)
O(4)	7011(2)	-4359(1)	8403(1)	32(1)
C(101)	6052(2)	-300(2)	8538(1)	23(1)
C(102)	6312(2)	187(2)	9340(1)	23(1)
C(103)	6633(2)	1617(2)	9218(1)	23(1)
C(104)	7822(2)	1501(2)	8565(1)	24(1)
C(105)	6356(2)	-1695(2)	8455(1)	23(1)
C(106)	5158(2)	-2501(2)	8293(1)	28(1)
C(107)	5362(3)	-3927(2)	8272(1)	32(1)
C(31)	7508(2)	2310(2)	9875(1)	23(1)

C(32)	8178(2)	1696(2)	10505(1)	25(1)
C(33)	9015(2)	2366(2)	11076(1)	27(1)
C(34)	9192(2)	3675(2)	11021(1)	28(1)
C(35)	8543(2)	4304(2)	10390(1)	27(1)
C(36)	7705(2)	3629(2)	9822(1)	26(1)
C(41)	4967(2)	2258(2)	9001(1)	23(1)
C(42)	3746(2)	2325(2)	9535(1)	26(1)
C(43)	2189(3)	2834(2)	9360(1)	28(1)
C(44)	1828(3)	3297(2)	8645(1)	32(1)
C(45)	3035(3)	3243(2)	8110(1)	32(1)
C(46)	4588(3)	2722(2)	8284(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for d08013.

O(1)-C(4)	1.439(2)
O(1)-C(1)	1.457(2)
O(2)-C(7)	1.413(3)
C(1)-C(5)	1.499(3)
C(1)-C(2)	1.524(3)
C(2)-C(3)	1.538(3)
C(3)-C(21)	1.531(3)
C(3)-C(4)	1.536(3)
C(3)-C(11)	1.538(3)
C(5)-C(6)	1.315(3)
C(6)-C(7)	1.498(3)
C(11)-C(16)	1.390(3)
C(11)-C(12)	1.400(3)
C(12)-C(13)	1.389(3)
C(13)-C(14)	1.384(3)
C(14)-C(15)	1.383(3)
C(15)-C(16)	1.394(3)
C(21)-C(26)	1.392(3)
C(21)-C(22)	1.394(3)
C(22)-C(23)	1.387(3)
C(23)-C(24)	1.387(3)
C(24)-C(25)	1.381(3)
C(25)-C(26)	1.390(3)
O(3)-C(104)	1.445(2)
O(3)-C(101)	1.465(2)
O(4)-C(107)	1.414(3)
C(101)-C(105)	1.496(3)
C(101)-C(102)	1.525(3)
C(102)-C(103)	1.543(3)
C(103)-C(31)	1.530(3)
C(103)-C(104)	1.535(3)
C(103)-C(41)	1.538(3)
C(105)-C(106)	1.308(3)
C(106)-C(107)	1.510(3)
C(31)-C(32)	1.387(3)

C(31)-C(36)	1.401(3)
C(32)-C(33)	1.392(3)
C(33)-C(34)	1.388(3)
C(34)-C(35)	1.390(3)
C(35)-C(36)	1.392(3)
C(41)-C(46)	1.391(3)
C(41)-C(42)	1.391(3)
C(42)-C(43)	1.387(3)
C(43)-C(44)	1.386(3)
C(44)-C(45)	1.384(3)
C(45)-C(46)	1.389(3)

C(4)-O(1)-C(1)	109.36(14)
O(1)-C(1)-C(5)	109.89(16)
O(1)-C(1)-C(2)	104.26(16)
C(5)-C(1)-C(2)	114.52(18)
C(1)-C(2)-C(3)	103.01(16)
C(21)-C(3)-C(4)	110.67(16)
C(21)-C(3)-C(11)	110.81(15)
C(4)-C(3)-C(11)	112.45(16)
C(21)-C(3)-C(2)	115.28(16)
C(4)-C(3)-C(2)	97.92(16)
C(11)-C(3)-C(2)	109.17(16)
O(1)-C(4)-C(3)	105.59(15)
C(6)-C(5)-C(1)	123.45(19)
C(5)-C(6)-C(7)	126.6(2)
O(2)-C(7)-C(6)	112.47(17)
C(16)-C(11)-C(12)	118.02(19)
C(16)-C(11)-C(3)	123.47(18)
C(12)-C(11)-C(3)	118.50(17)
C(13)-C(12)-C(11)	120.96(19)
C(14)-C(13)-C(12)	120.41(19)
C(15)-C(14)-C(13)	119.2(2)
C(14)-C(15)-C(16)	120.5(2)
C(11)-C(16)-C(15)	120.8(2)
C(26)-C(21)-C(22)	118.20(19)
C(26)-C(21)-C(3)	122.83(18)

C(22)-C(21)-C(3)	118.93(18)
C(23)-C(22)-C(21)	120.8(2)
C(22)-C(23)-C(24)	120.3(2)
C(25)-C(24)-C(23)	119.4(2)
C(24)-C(25)-C(26)	120.2(2)
C(25)-C(26)-C(21)	121.0(2)
C(104)-O(3)-C(101)	109.02(14)
O(3)-C(101)-C(105)	111.16(15)
O(3)-C(101)-C(102)	103.61(15)
C(105)-C(101)-C(102)	113.91(16)
C(101)-C(102)-C(103)	102.40(15)
C(31)-C(103)-C(104)	109.59(15)
C(31)-C(103)-C(41)	110.97(15)
C(104)-C(103)-C(41)	113.83(16)
C(31)-C(103)-C(102)	115.59(16)
C(104)-C(103)-C(102)	98.06(15)
C(41)-C(103)-C(102)	108.34(15)
O(3)-C(104)-C(103)	106.59(15)
C(106)-C(105)-C(101)	122.42(18)
C(105)-C(106)-C(107)	124.72(19)
O(4)-C(107)-C(106)	114.70(17)
C(32)-C(31)-C(36)	118.27(18)
C(32)-C(31)-C(103)	123.57(18)
C(36)-C(31)-C(103)	118.10(17)
C(31)-C(32)-C(33)	121.34(19)
C(34)-C(33)-C(32)	119.96(19)
C(33)-C(34)-C(35)	119.48(19)
C(34)-C(35)-C(36)	120.29(19)
C(35)-C(36)-C(31)	120.65(19)
C(46)-C(41)-C(42)	118.13(18)
C(46)-C(41)-C(103)	123.17(18)
C(42)-C(41)-C(103)	118.62(17)
C(43)-C(42)-C(41)	121.24(19)
C(44)-C(43)-C(42)	120.1(2)
C(45)-C(44)-C(43)	119.19(19)
C(44)-C(45)-C(46)	120.6(2)
C(45)-C(46)-C(41)	120.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d08013. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(1)	25(1)	30(1)	6(1)	10(1)	7(1)
O(2)	36(1)	26(1)	32(1)	6(1)	-1(1)	-4(1)
C(1)	26(1)	29(1)	31(1)	2(1)	3(1)	4(1)
C(2)	27(1)	24(1)	31(1)	0(1)	2(1)	0(1)
C(3)	25(1)	22(1)	26(1)	1(1)	2(1)	1(1)
C(4)	27(1)	26(1)	30(1)	4(1)	6(1)	3(1)
C(5)	24(1)	35(1)	33(1)	4(1)	1(1)	1(1)
C(6)	30(1)	21(1)	29(1)	-3(1)	0(1)	-2(1)
C(7)	36(1)	25(1)	28(1)	1(1)	0(1)	1(1)
C(11)	27(1)	17(1)	28(1)	6(1)	-1(1)	4(1)
C(12)	28(1)	23(1)	30(1)	4(1)	1(1)	1(1)
C(13)	25(1)	30(1)	40(1)	9(1)	4(1)	4(1)
C(14)	24(1)	29(1)	51(1)	7(1)	-9(1)	-1(1)
C(15)	36(1)	31(1)	35(1)	0(1)	-11(1)	3(1)
C(16)	29(1)	30(1)	29(1)	4(1)	0(1)	3(1)
C(21)	20(1)	23(1)	28(1)	2(1)	5(1)	-2(1)
C(22)	24(1)	22(1)	35(1)	1(1)	-2(1)	-3(1)
C(23)	25(1)	24(1)	44(1)	8(1)	0(1)	-1(1)
C(24)	24(1)	35(1)	34(1)	11(1)	1(1)	0(1)
C(25)	28(1)	39(1)	27(1)	0(1)	1(1)	-3(1)
C(26)	28(1)	27(1)	27(1)	0(1)	3(1)	0(1)
O(3)	31(1)	21(1)	26(1)	-1(1)	5(1)	-3(1)
O(4)	44(1)	24(1)	31(1)	5(1)	7(1)	4(1)
C(101)	23(1)	18(1)	28(1)	3(1)	2(1)	1(1)
C(102)	25(1)	16(1)	27(1)	1(1)	2(1)	0(1)
C(103)	24(1)	18(1)	26(1)	1(1)	1(1)	1(1)
C(104)	25(1)	19(1)	29(1)	0(1)	2(1)	1(1)
C(105)	26(1)	18(1)	25(1)	0(1)	3(1)	3(1)
C(106)	26(1)	30(1)	27(1)	0(1)	3(1)	0(1)
C(107)	36(1)	25(1)	34(1)	-2(1)	6(1)	-6(1)
C(31)	19(1)	22(1)	27(1)	0(1)	4(1)	2(1)
C(32)	25(1)	22(1)	28(1)	1(1)	3(1)	0(1)

C(33)28(1)	26(1)	27(1)	3(1)	0(1)	-1(1)
C(34)22(1)	32(1)	28(1)	-6(1)	0(1)	-2(1)
C(35)24(1)	20(1)	38(1)	-2(1)	2(1)	0(1)
C(36)22(1)	24(1)	30(1)	1(1)	0(1)	3(1)
C(41)24(1)	15(1)	29(1)	-4(1)	0(1)	-3(1)
C(42)27(1)	24(1)	28(1)	-4(1)	-1(1)	-2(1)
C(43)25(1)	20(1)	39(1)	-9(1)	2(1)	-2(1)
C(44)22(1)	22(1)	50(1)	-6(1)	-8(1)	1(1)
C(45)34(1)	27(1)	36(1)	5(1)	-8(1)	-2(1)
C(46)29(1)	23(1)	29(1)	0(1)	1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for d08013.

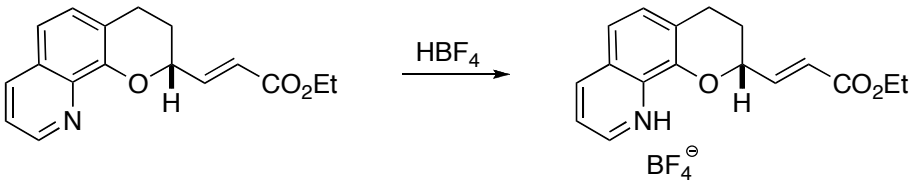
	x	y	z	U(eq)
H(2)	7320(30)	1100(20)	7086(11)	38
H(1A)	10271	5544	6669	34
H(2B)	7769	5527	5483	33
H(2C)	9735	5782	5412	33
H(4B)	7365	8064	6816	33
H(4C)	6202	7054	6368	33
H(5A)	7445	3869	6669	37
H(6A)	10817	3359	6668	32
H(7A)	9792	1296	6289	36
H(7B)	9792	1393	7185	36
H(12A)	11073	7764	5000	33
H(13A)	13680	8658	5258	38
H(14A)	14342	9485	6448	42
H(15A)	12385	9376	7385	41
H(16A)	9795	8434	7142	36
H(22A)	7796	9813	5673	32
H(23A)	6382	10923	4718	37
H(24A)	5302	9848	3661	37
H(25A)	5552	7641	3592	38
H(26A)	6997	6528	4539	33
H(4)	7570(30)	-4350(30)	8022(11)	39
H(10A)	4893	-97	8355	27
H(10B)	7280	-229	9595	27
H(10C)	5311	48	9638	27
H(10D)	7812	2293	8265	29
H(10E)	8972	1343	8758	29
H(10F)	7459	-2007	8521	27
H(10G)	4082	-2164	8181	33
H(10H)	4648	-4307	8655	38
H(10I)	4958	-4239	7775	38
H(32A)	8064	801	10547	30
H(33A)	9465	1928	11502	32

H(34A)	9753	4138	11411	33
H(35A)	8672	5198	10347	33
H(36A)	7262	4068	9394	31
H(42A)	3983	2016	10028	31
H(43A)	1370	2865	9732	34
H(44A)	764	3647	8523	38
H(45A)	2800	3565	7620	39
H(46A)	5400	2683	7909	33

Table 6. Hydrogen bonds for d08013 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(3)	0.835(17)	1.956(17)	2.771(2)	165(3)
O(4)-H(4)...O(1)#1	0.827(16)	2.002(19)	2.765(2)	153(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z



(*R*,*E*)-Ethyl 3-(2,3-dihydro-1*H*-4-oxa-5-aza-phenanthren-3-yl)prop-2-enoate hydrotetrafluoroborate. A solution of (*R*,*E*)-ethyl 3-(2,3-dihydro-1*H*-4-oxa-5-aza-phenanthren-3-yl)prop-2-enoate (run 2 of Table 3, entry 4; 110 mg, 0.388 mmol; 84% ee) in Et_2O (10 mL) was treated with HBF_4 (54% in Et_2O; 32 μL; 1.1 equiv), which produced a light-yellow precipitate. The mixture was filtered, and the solid was washed with Et_2O and then dried to give an off-white solid (131 mg; 90%). The salt was recrystallized (7:1 TBME/EtOH) to give off-white crystals, and an X-ray crystal structure was obtained.

mp = 155-157 °C;

$[\alpha]^{20}_D$ = +43 (*c* 1.5, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 500 MHz) δ 14.07 (br s, 1H), 9.15 (t, *J* = 6.0 Hz, 1H), 9.00 (d, *J* = 8.5 Hz, 1H), 8.03 (dd, *J* = 6.0, 7.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.05 (dd, *J* = 3.5, 16.0 Hz, 1H), 6.28 (d, *J* = 15.5 Hz, 1H), 5.19 (d, *J* = 2.5 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.16-3.09 (m, 1H), 3.02-2.97 (m, 1H), 2.39-2.36 (m, 1H), 2.09-2.01 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7, 147.5, 144.1, 143.8, 143.2, 132.3, 128.8, 128.5, 127.1, 122.5, 122.1, 120.0, 75.8, 61.1, 25.9, 23.9, 14.2.

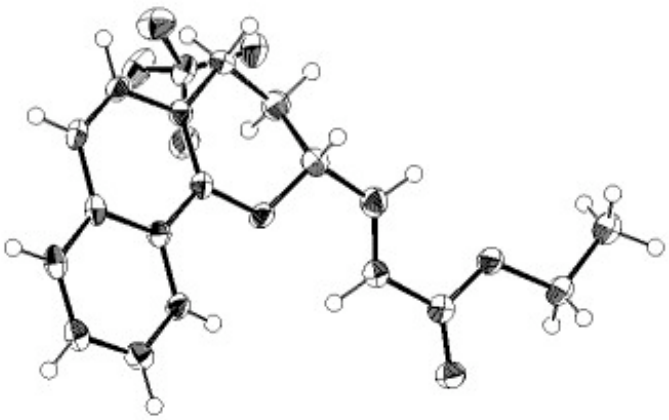


Table 1. Crystal data and structure refinement for d08029.

Identification code	d08029	
Empirical formula	C17 H18 B F4 N O3	
Formula weight	371.13	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.8043(2) Å	α= 90°.
	b = 19.9898(4) Å	β= 93.9780(10)°.
	c = 9.5230(2) Å	γ = 90°.
Volume	1671.97(6) $Å^3$	
Z	4	
Density (calculated)	1.474 Mg/m^3	
Absorption coefficient	1.115 mm^{-1}	
F(000)	768	
Crystal size	0.48 x 0.11 x 0.06 mm^3	
Theta range for data collection	4.42 to 67.90°.	
Index ranges	-10<=h<=10, -22<=k<=24, -11<=l<=11	
Reflections collected	27767	
Independent reflections	5624 [R(int) = 0.0229]	
Completeness to theta = 67.90°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9361 and 0.6168	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5624 / 71 / 477	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0897	
R indices (all data)	R1 = 0.0344, wR2 = 0.0903	
Absolute structure parameter	0.15(9)	
Largest diff. peak and hole	0.509 and -0.287 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d08029. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9822(2)	1756(1)	1764(1)	23(1)
O(2)	5188(2)	311(1)	1968(2)	26(1)
O(3)	4767(2)	1186(1)	3363(1)	24(1)
N(1)	11616(2)	1143(1)	7(2)	24(1)
C(1)	8738(2)	2190(1)	2376(2)	23(1)
C(2)	9460(2)	2497(1)	3721(2)	26(1)
C(3)	10803(2)	2936(1)	3381(2)	23(1)
C(4)	11755(2)	2603(1)	2330(2)	19(1)
C(5)	11208(2)	2042(1)	1617(2)	20(1)
C(6)	12131(2)	1712(1)	677(2)	20(1)
C(7)	13214(2)	2853(1)	2050(2)	22(1)
C(8)	14102(2)	2554(1)	1115(2)	22(1)
C(9)	13592(2)	1959(1)	410(2)	21(1)
C(10)	14454(2)	1593(1)	-518(2)	24(1)
C(11)	13883(2)	1013(1)	-1137(2)	26(1)
C(12)	12427(3)	800(1)	-867(2)	27(1)
C(13)	7340(2)	1801(1)	2617(2)	23(1)
C(14)	7021(2)	1185(1)	2193(2)	22(1)
C(15)	5588(2)	844(1)	2483(2)	21(1)
C(16)	3365(2)	882(1)	3784(2)	27(1)
C(17)	3691(3)	437(1)	5027(2)	37(1)
O(101)	5151(2)	3688(1)	7444(2)	25(1)
O(102)	9800(2)	5102(1)	7972(2)	29(1)
O(103)	10156(2)	4480(1)	6062(2)	28(1)
N(101)	3296(2)	4186(1)	9277(2)	24(1)
C(101)	5952(3)	3501(1)	6213(2)	28(1)
C(102)	6097(3)	2748(1)	6172(2)	31(1)
C(103)	4535(2)	2426(1)	5967(2)	24(1)
C(104)	3430(2)	2758(1)	6890(2)	22(1)
C(105)	3842(2)	3344(1)	7583(2)	21(1)
C(106)	2864(2)	3624(1)	8538(2)	21(1)

C(107)	1984(2)	2472(1)	7103(2)	23(1)
C(108)	1006(2)	2745(1)	7988(2)	24(1)
C(109)	1435(2)	3330(1)	8763(2)	22(1)
C(110)	539(2)	3635(1)	9753(2)	26(1)
C(111)	1050(2)	4195(1)	10480(2)	26(1)
C(112)	2456(2)	4467(1)	10223(2)	27(1)
C(113)	7427(3)	3864(1)	6266(2)	29(1)
C(114)	8002(2)	4253(1)	7306(2)	23(1)
C(115)	9395(2)	4651(1)	7175(2)	23(1)
C(116)	11440(3)	4902(1)	5759(2)	31(1)
C(117)	12094(3)	4642(2)	4462(3)	43(1)
B(1)	6809(3)	4009(1)	1954(3)	26(1)
F(1)	5629(2)	4442(1)	1748(3)	84(1)
F(2)	6488(2)	3531(1)	2954(2)	50(1)
F(3)	7037(2)	3657(1)	727(2)	58(1)
F(4)	8136(1)	4352(1)	2405(1)	34(1)
B(2)	8267(3)	1234(1)	7874(3)	27(1)
F(5)	9270(2)	1363(1)	6858(2)	42(1)
F(6)	6854(2)	1047(1)	7275(2)	40(1)
F(7)	8838(2)	723(1)	8757(2)	44(1)
F(8)	8102(2)	1807(1)	8701(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for d08029.

O(1)-C(5)	1.364(2)
O(1)-C(1)	1.443(2)
O(2)-C(15)	1.215(3)
O(3)-C(15)	1.333(2)
O(3)-C(16)	1.457(2)
N(1)-C(12)	1.325(3)
N(1)-C(6)	1.367(3)
C(1)-C(13)	1.487(3)
C(1)-C(2)	1.520(3)
C(2)-C(3)	1.525(3)
C(3)-C(4)	1.504(3)
C(4)-C(5)	1.381(3)
C(4)-C(7)	1.420(3)
C(5)-C(6)	1.413(3)
C(6)-C(9)	1.417(3)
C(7)-C(8)	1.363(3)
C(8)-C(9)	1.424(3)
C(9)-C(10)	1.408(3)
C(10)-C(11)	1.380(3)
C(11)-C(12)	1.392(3)
C(13)-C(14)	1.321(3)
C(14)-C(15)	1.477(3)
C(16)-C(17)	1.492(3)
O(101)-C(105)	1.355(2)
O(101)-C(101)	1.458(3)
O(102)-C(115)	1.216(3)
O(103)-C(115)	1.337(3)
O(103)-C(116)	1.455(3)
N(101)-C(112)	1.328(3)
N(101)-C(106)	1.366(3)
C(101)-C(113)	1.485(3)
C(101)-C(102)	1.513(3)
C(102)-C(103)	1.518(3)
C(103)-C(104)	1.510(3)
C(104)-C(105)	1.380(3)

C(104)-C(107)	1.423(3)
C(105)-C(106)	1.411(3)
C(106)-C(109)	1.419(3)
C(107)-C(108)	1.360(3)
C(108)-C(109)	1.420(3)
C(109)-C(110)	1.409(3)
C(110)-C(111)	1.376(3)
C(111)-C(112)	1.389(3)
C(113)-C(114)	1.331(3)
C(114)-C(115)	1.474(3)
C(116)-C(117)	1.493(3)
B(1)-F(1)	1.356(3)
B(1)-F(3)	1.390(3)
B(1)-F(2)	1.391(3)
B(1)-F(4)	1.396(3)
B(2)-F(5)	1.379(3)
B(2)-F(6)	1.384(3)
B(2)-F(7)	1.394(3)
B(2)-F(8)	1.402(3)

C(5)-O(1)-C(1)	114.25(15)
C(15)-O(3)-C(16)	117.73(16)
C(12)-N(1)-C(6)	123.29(18)
O(1)-C(1)-C(13)	108.99(16)
O(1)-C(1)-C(2)	109.51(16)
C(13)-C(1)-C(2)	112.54(17)
C(1)-C(2)-C(3)	109.79(16)
C(4)-C(3)-C(2)	111.30(17)
C(5)-C(4)-C(7)	118.82(18)
C(5)-C(4)-C(3)	119.68(17)
C(7)-C(4)-C(3)	121.50(17)
O(1)-C(5)-C(4)	125.04(18)
O(1)-C(5)-C(6)	115.35(17)
C(4)-C(5)-C(6)	119.59(18)
N(1)-C(6)-C(5)	119.80(18)
N(1)-C(6)-C(9)	118.80(18)
C(5)-C(6)-C(9)	121.41(18)

C(8)-C(7)-C(4) 122.46(19)
C(7)-C(8)-C(9) 119.81(18)
C(10)-C(9)-C(6) 117.87(18)
C(10)-C(9)-C(8) 124.30(18)
C(6)-C(9)-C(8) 117.82(18)
C(11)-C(10)-C(9) 120.52(19)
C(10)-C(11)-C(12) 119.43(19)
N(1)-C(12)-C(11) 120.1(2)
C(14)-C(13)-C(1) 126.97(19)
C(13)-C(14)-C(15) 122.66(19)
O(2)-C(15)-O(3) 123.33(18)
O(2)-C(15)-C(14) 123.81(18)
O(3)-C(15)-C(14) 112.85(17)
O(3)-C(16)-C(17) 110.33(17)
C(105)-O(101)-C(101)114.28(16)
C(115)-O(103)-C(116)116.59(17)
C(112)-N(101)-C(106)123.24(19)
O(101)-C(101)-C(113)108.57(17)
O(101)-C(101)-C(102)108.75(18)
C(113)-C(101)-C(102)114.34(19)
C(101)-C(102)-C(103)110.38(19)
C(104)-C(103)-C(102)110.67(17)
C(105)-C(104)-C(107)118.76(19)
C(105)-C(104)-C(103)119.54(18)
C(107)-C(104)-C(103)121.67(19)
O(101)-C(105)-C(104)125.46(18)
O(101)-C(105)-C(106)115.02(17)
C(104)-C(105)-C(106)119.51(18)
N(101)-C(106)-C(105)119.86(18)
N(101)-C(106)-C(109)118.77(18)
C(105)-C(106)-C(109)121.37(19)
C(108)-C(107)-C(104)122.54(19)
C(107)-C(108)-C(109)119.74(19)
C(110)-C(109)-C(106)117.72(19)
C(110)-C(109)-C(108)124.31(19)
C(106)-C(109)-C(108)117.98(18)
C(111)-C(110)-C(109)120.70(19)

C(110)-C(111)-C(112)119.6(2)
N(101)-C(112)-C(111)120.0(2)
C(114)-C(113)-C(101)126.69(19)
C(113)-C(114)-C(115)121.88(19)
O(102)-C(115)-O(103)122.90(19)
O(102)-C(115)-C(114)123.81(19)
O(103)-C(115)-C(114)113.26(18)
O(103)-C(116)-C(117)108.14(19)
F(1)-B(1)-F(3) 110.8(2)
F(1)-B(1)-F(2) 110.3(2)
F(3)-B(1)-F(2) 106.1(2)
F(1)-B(1)-F(4) 110.3(2)
F(3)-B(1)-F(4) 109.90(19)
F(2)-B(1)-F(4) 109.40(18)
F(5)-B(2)-F(6) 111.19(19)
F(5)-B(2)-F(7) 109.78(19)
F(6)-B(2)-F(7) 109.07(19)
F(5)-B(2)-F(8) 109.75(19)
F(6)-B(2)-F(8) 109.12(18)
F(7)-B(2)-F(8) 107.86(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d08029. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(1)	22(1)	27(1)	-3(1)	7(1)	-4(1)
O(2)	25(1)	22(1)	32(1)	-2(1)	5(1)	0(1)
O(3)	22(1)	25(1)	27(1)	-4(1)	6(1)	-4(1)
N(1)	22(1)	25(1)	26(1)	-1(1)	5(1)	-4(1)
C(1)	21(1)	21(1)	27(1)	2(1)	4(1)	2(1)
C(2)	24(1)	29(1)	25(1)	-4(1)	7(1)	-3(1)
C(3)	24(1)	22(1)	24(1)	0(1)	2(1)	-3(1)
C(4)	20(1)	18(1)	19(1)	3(1)	0(1)	1(1)
C(5)	18(1)	22(1)	20(1)	4(1)	2(1)	-1(1)
C(6)	21(1)	20(1)	19(1)	3(1)	2(1)	-1(1)
C(7)	22(1)	20(1)	23(1)	3(1)	0(1)	-3(1)
C(8)	17(1)	23(1)	26(1)	6(1)	2(1)	1(1)
C(9)	19(1)	22(1)	21(1)	6(1)	1(1)	3(1)
C(10)	21(1)	30(1)	20(1)	7(1)	3(1)	4(1)
C(11)	27(1)	31(1)	22(1)	1(1)	4(1)	6(1)
C(12)	31(1)	26(1)	24(1)	-4(1)	5(1)	1(1)
C(13)	20(1)	27(1)	23(1)	0(1)	4(1)	3(1)
C(14)	22(1)	24(1)	20(1)	3(1)	3(1)	2(1)
C(15)	22(1)	19(1)	22(1)	4(1)	0(1)	2(1)
C(16)	21(1)	30(1)	30(1)	-2(1)	6(1)	-2(1)
C(17)	43(1)	41(1)	27(1)	-2(1)	3(1)	-16(1)
O(101)	22(1)	23(1)	30(1)	-6(1)	8(1)	-6(1)
O(102)	28(1)	28(1)	30(1)	-4(1)	1(1)	-2(1)
O(103)	23(1)	30(1)	31(1)	-5(1)	6(1)	-6(1)
N(101)	20(1)	22(1)	30(1)	-2(1)	8(1)	-4(1)
C(101)	29(1)	29(1)	27(1)	-2(1)	6(1)	-1(1)
C(102)	28(1)	32(1)	36(1)	-6(1)	12(1)	-2(1)
C(103)	28(1)	24(1)	22(1)	-4(1)	4(1)	-2(1)
C(104)	25(1)	21(1)	19(1)	2(1)	1(1)	1(1)
C(105)	19(1)	23(1)	22(1)	3(1)	2(1)	-1(1)
C(106)	20(1)	21(1)	21(1)	2(1)	2(1)	1(1)
C(107)	26(1)	20(1)	22(1)	3(1)	-1(1)	-5(1)

C(108)21(1)	25(1)	26(1)	8(1)	0(1)	-4(1)
C(109)18(1)	26(1)	22(1)	9(1)	3(1)	2(1)
C(110)21(1)	30(1)	26(1)	11(1)	6(1)	6(1)
C(111)27(1)	27(1)	26(1)	6(1)	8(1)	8(1)
C(112)30(1)	23(1)	28(1)	-1(1)	4(1)	7(1)
C(113)28(1)	28(1)	32(1)	0(1)	9(1)	0(1)
C(114)22(1)	23(1)	24(1)	2(1)	3(1)	3(1)
C(115)21(1)	24(1)	24(1)	4(1)	-2(1)	4(1)
C(116)26(1)	33(1)	34(1)	-3(1)	3(1)	-10(1)
C(117)43(1)	46(2)	42(1)	-6(1)	12(1)	-21(1)
B(1) 22(1)	26(1)	29(1)	-1(1)	3(1)	-2(1)
F(1) 41(1)	42(1)	165(2)	-17(1)	-38(1)	11(1)
F(2) 53(1)	64(1)	33(1)	8(1)	1(1)	-25(1)
F(3) 58(1)	81(1)	37(1)	-18(1)	20(1)	-29(1)
F(4) 25(1)	35(1)	41(1)	4(1)	-1(1)	-7(1)
B(2) 21(1)	25(1)	34(1)	4(1)	3(1)	-3(1)
F(5) 41(1)	42(1)	46(1)	-3(1)	19(1)	-14(1)
F(6) 22(1)	48(1)	50(1)	-12(1)	-1(1)	-4(1)
F(7) 38(1)	29(1)	62(1)	16(1)	-10(1)	-7(1)
F(8) 32(1)	31(1)	41(1)	-1(1)	6(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for d08029.

	x	y	z	U(eq)
H(1N)	10690(20)	987(13)	140(30)	29
H(1)	8462	2558	1694	27
H(2A)	9814	2138	4382	31
H(2B)	8697	2770	4180	31
H(3A)	10420	3369	2997	28
H(3B)	11443	3028	4257	28
H(7)	13584	3242	2533	27
H(8)	15059	2743	933	27
H(10)	15436	1747	-720	28
H(11)	14479	761	-1742	32
H(12)	12014	408	-1309	32
H(13)	6597	2019	3132	28
H(14)	7742	951	1681	27
H(16A)	2888	618	2992	32
H(16B)	2642	1236	4024	32
H(17A)	4333	63	4763	55
H(17B)	2732	263	5345	55
H(17C)	4223	692	5790	55
H(01N)	4140(20)	4359(13)	9210(30)	28
H(101)	5326	3649	5352	34
H(10A)	6619	2587	7063	38
H(10B)	6720	2617	5390	38
H(10C)	4153	2465	4968	29
H(10D)	4615	1944	6204	29
H(107)	1690	2075	6607	28
H(108)	41	2545	8088	29
H(110)	-428	3452	9919	31
H(111)	445	4395	11153	31
H(112)	2817	4853	10723	32
H(113)	8020	3814	5477	35
H(114)	7500	4276	8156	28
H(11A)	12220	4892	6560	37

H(11B)	11098	5370	5612	37
H(11C)	12477	4187	4634	65
H(11D)	12932	4932	4214	65
H(11E)	11303	4636	3686	65

Table 6. Hydrogen bonds for d08029 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...F(7)#1	0.888(16)	2.09(2)	2.775(2)	133(2)
N(1)-H(1N)...O(102)#2	0.888(16)	2.58(2)	3.150(2)	123(2)
N(101)-H(01N)...O(2)#3	0.826(17)	2.31(2)	2.909(2)	130(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 -x+2,y-1/2,-z+1 #3 -x+1,y+1/2,-z+1

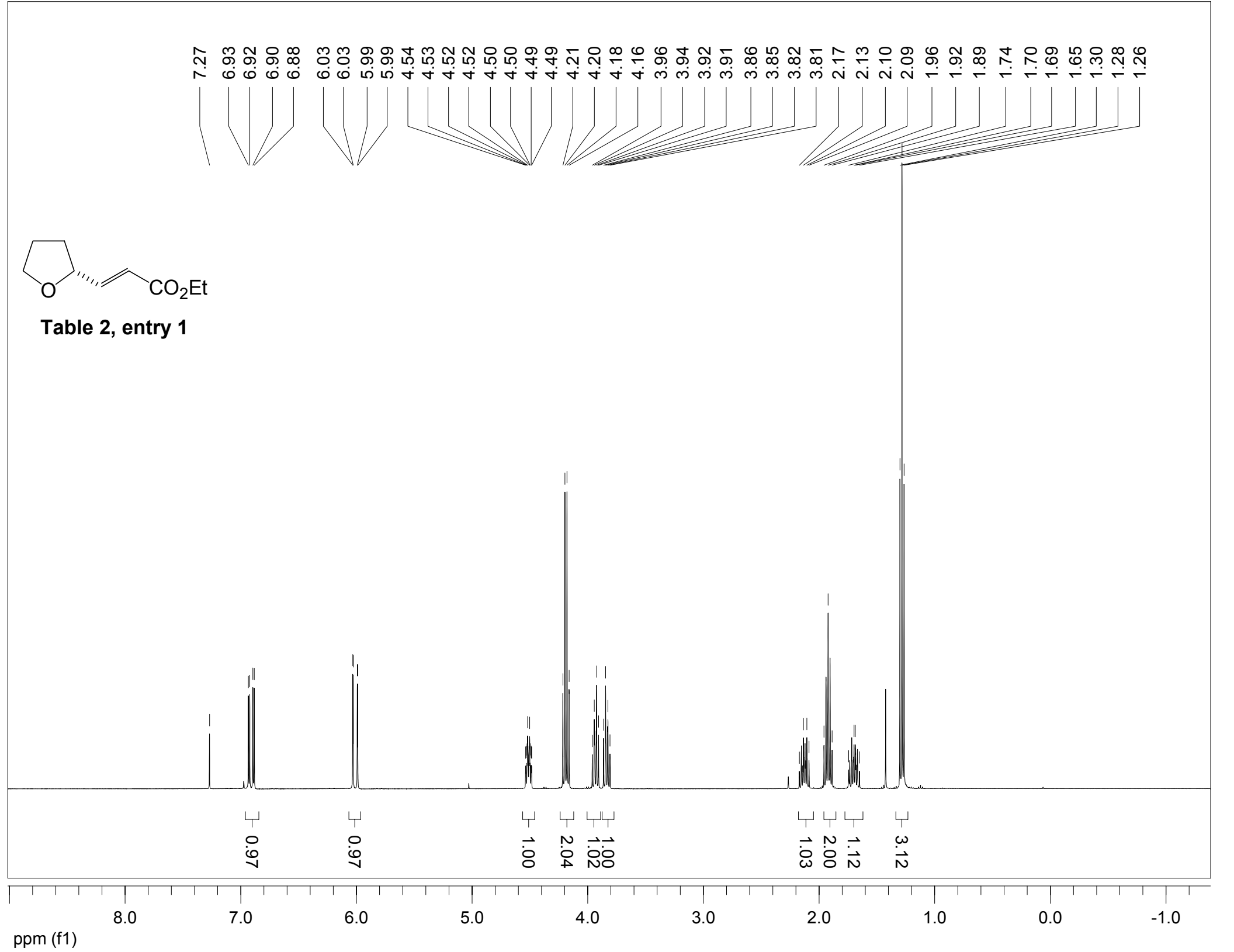
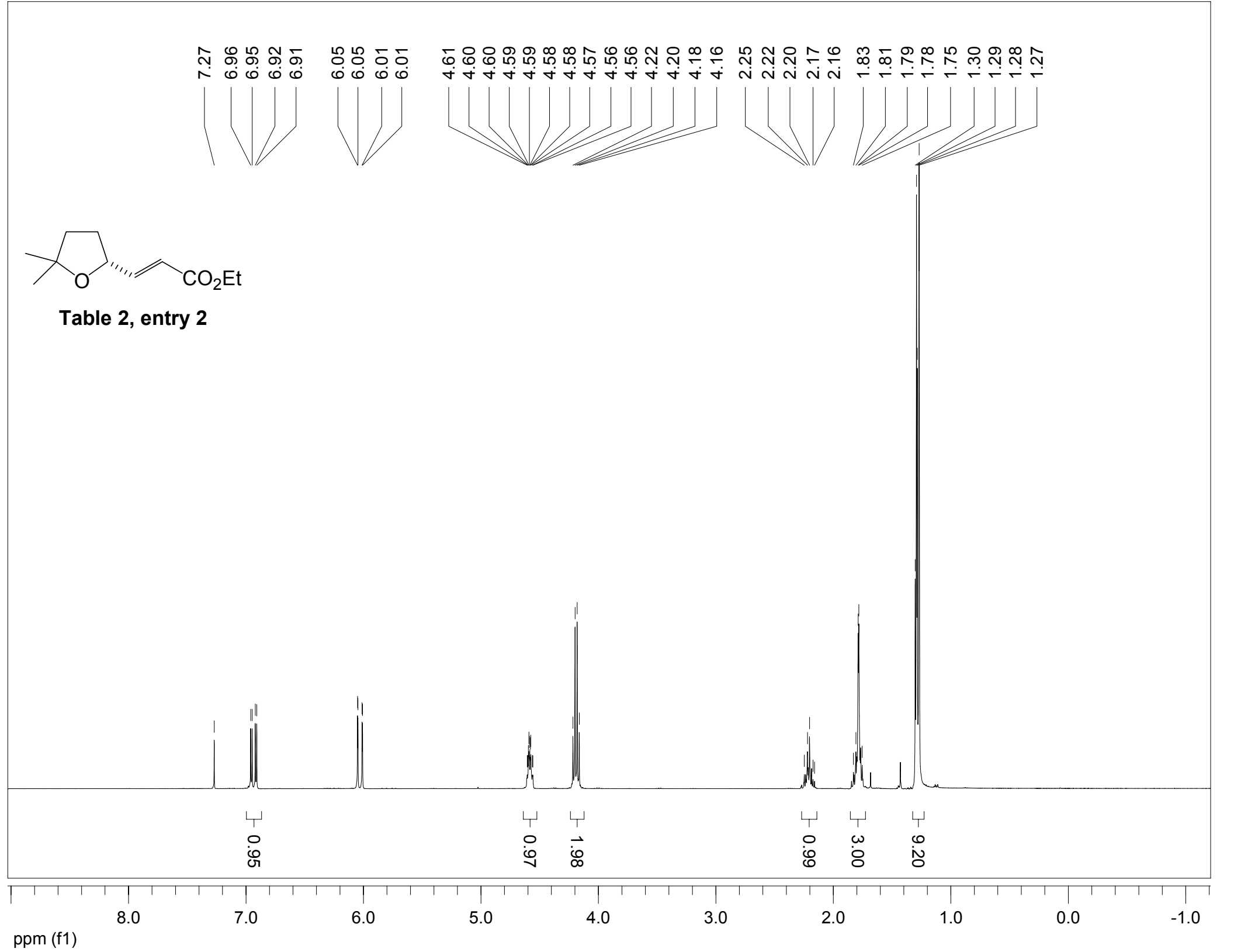


Table 2, entry 1



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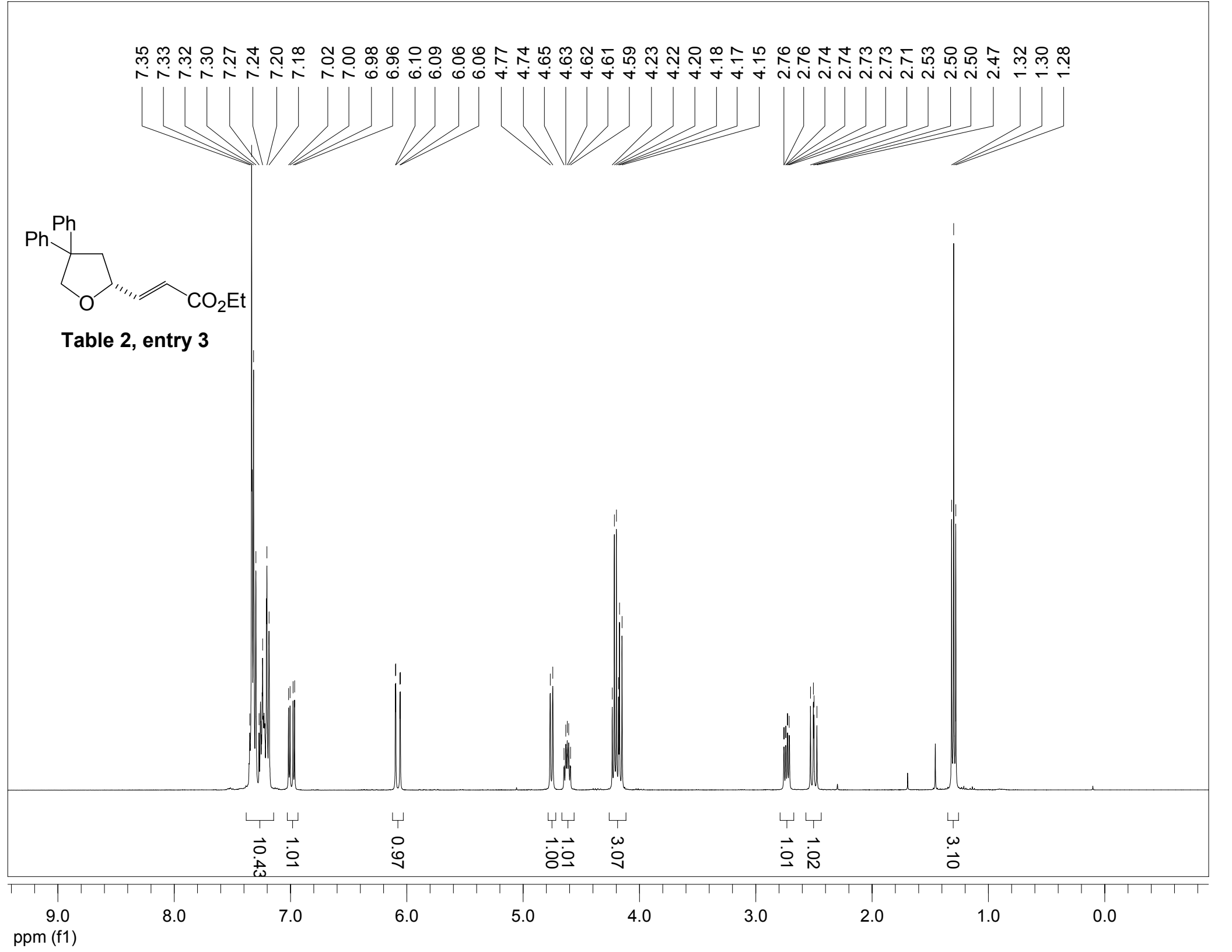
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7.33
7.32
7.30
7.27
7.24
7.20
7.18
7.02
7.00
6.98
6.96
6.10
6.09
6.06
6.06
4.77
4.74
4.65
4.63
4.62
4.61
4.59
4.23
4.22
4.20
4.18
4.17
4.15
2.76
2.76
2.74
2.74
2.73
2.73
2.71
2.53
2.50
2.50
2.47
1.32
1.30
1.28
Ph
Ph
O
CO2Et
Table 2, entry 3
10.43
1.01
0.97
1.00
1.01
3.07
1.01
1.02
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

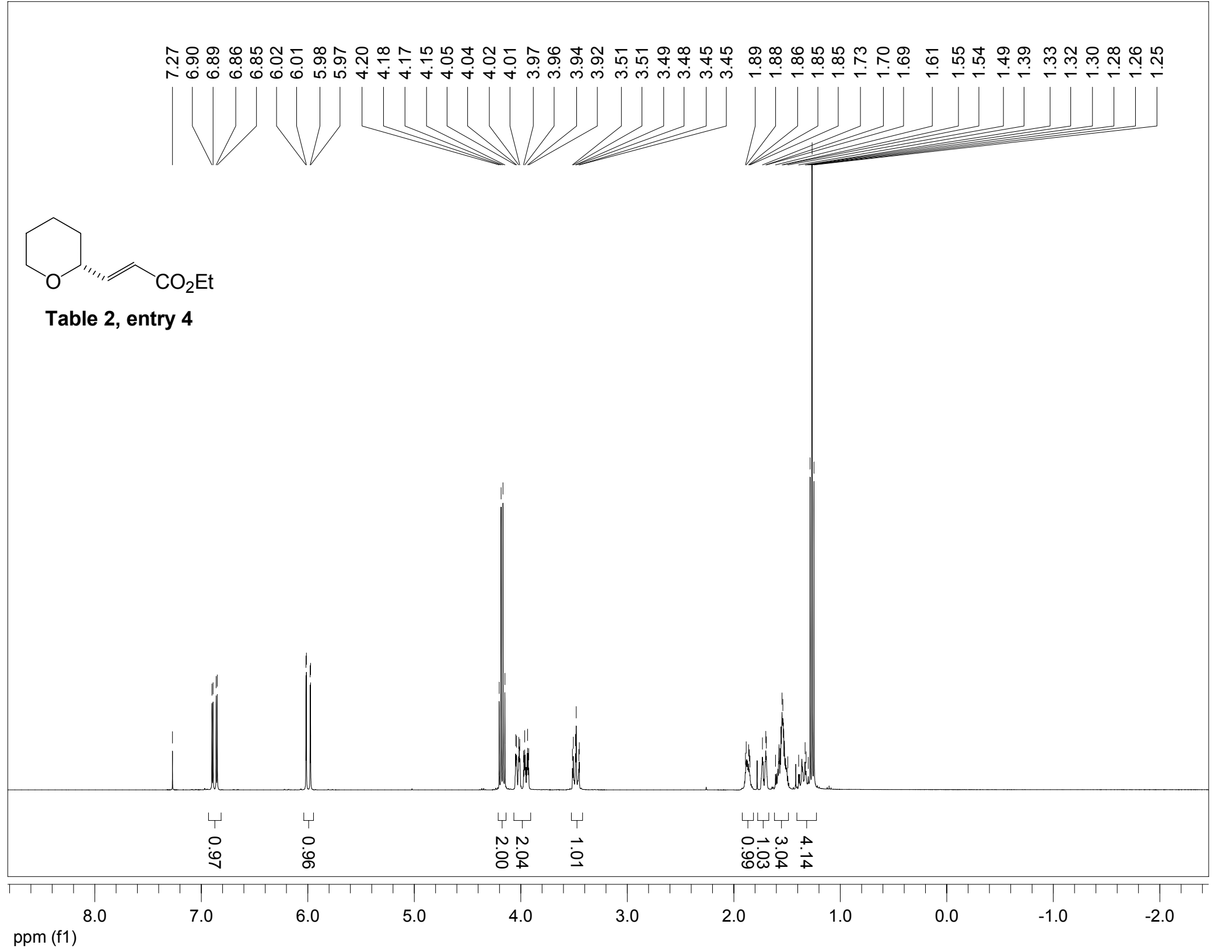
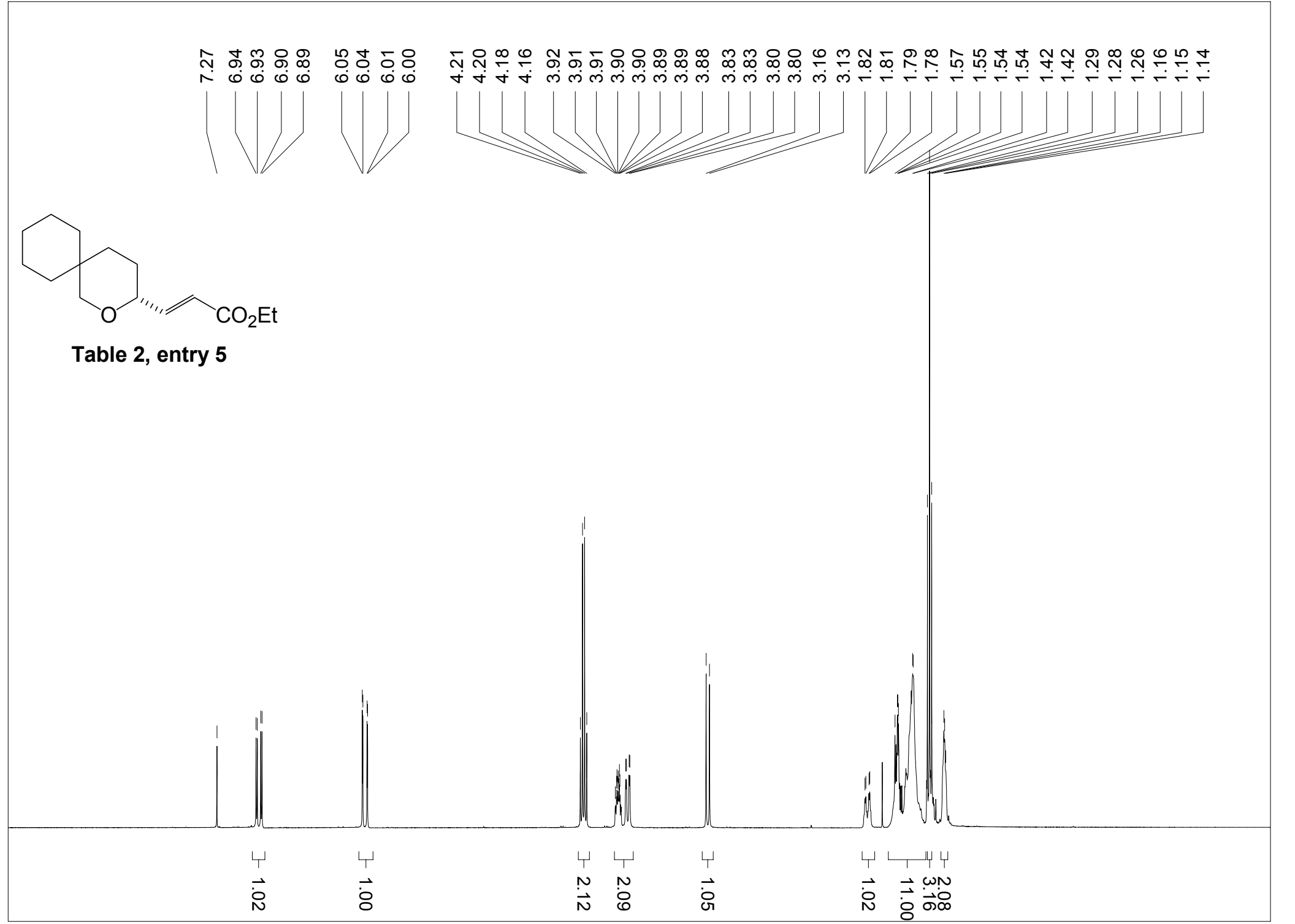


Table 2, entry 4



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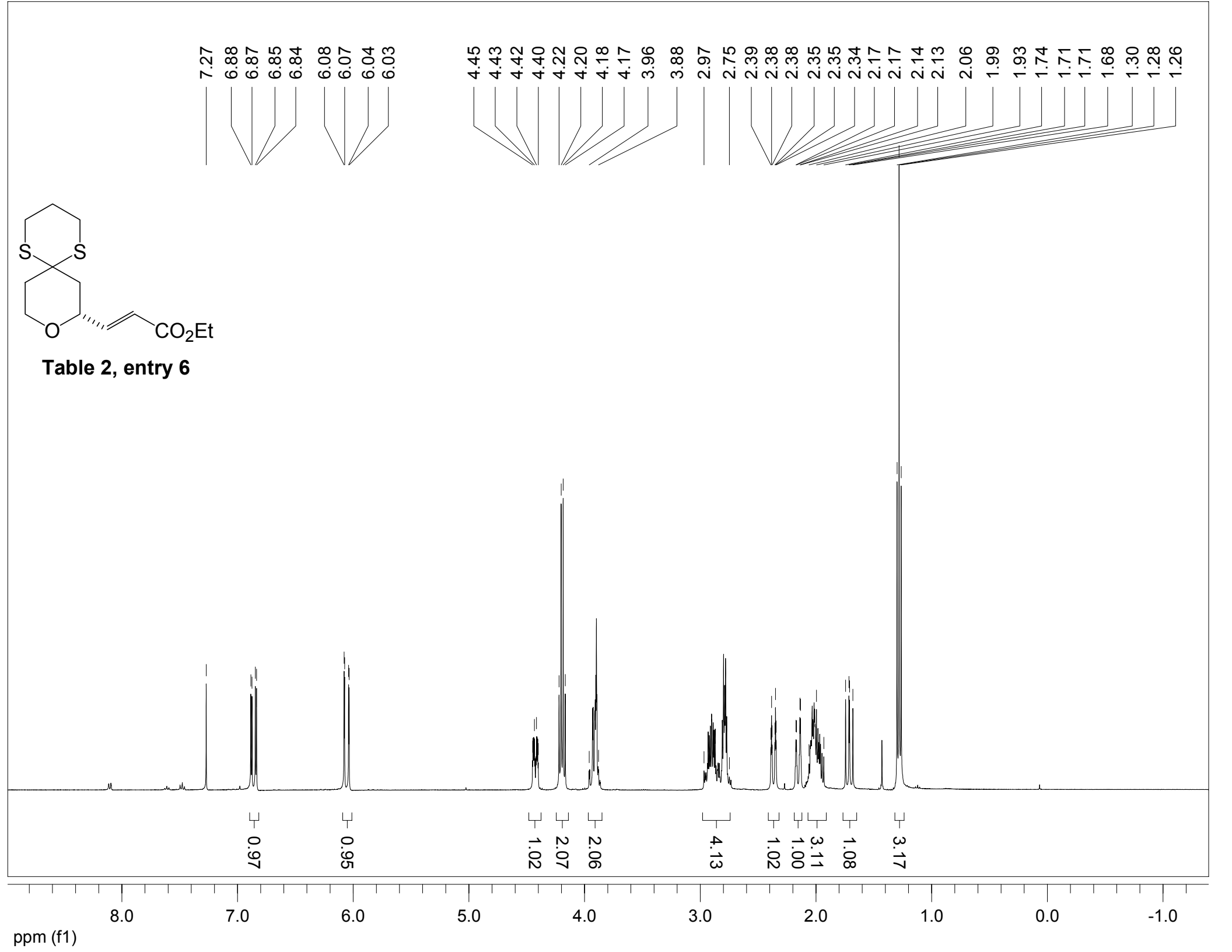

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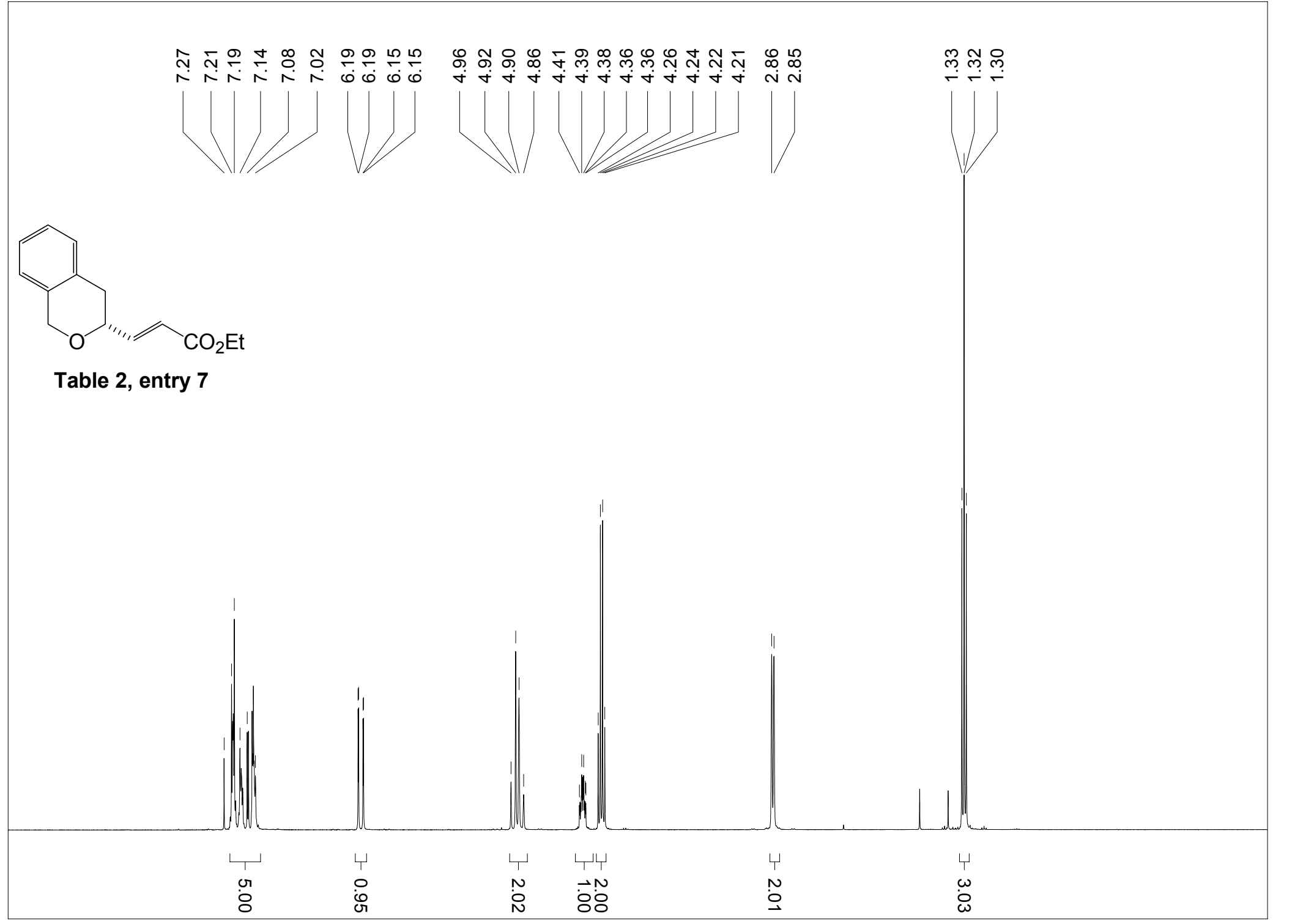

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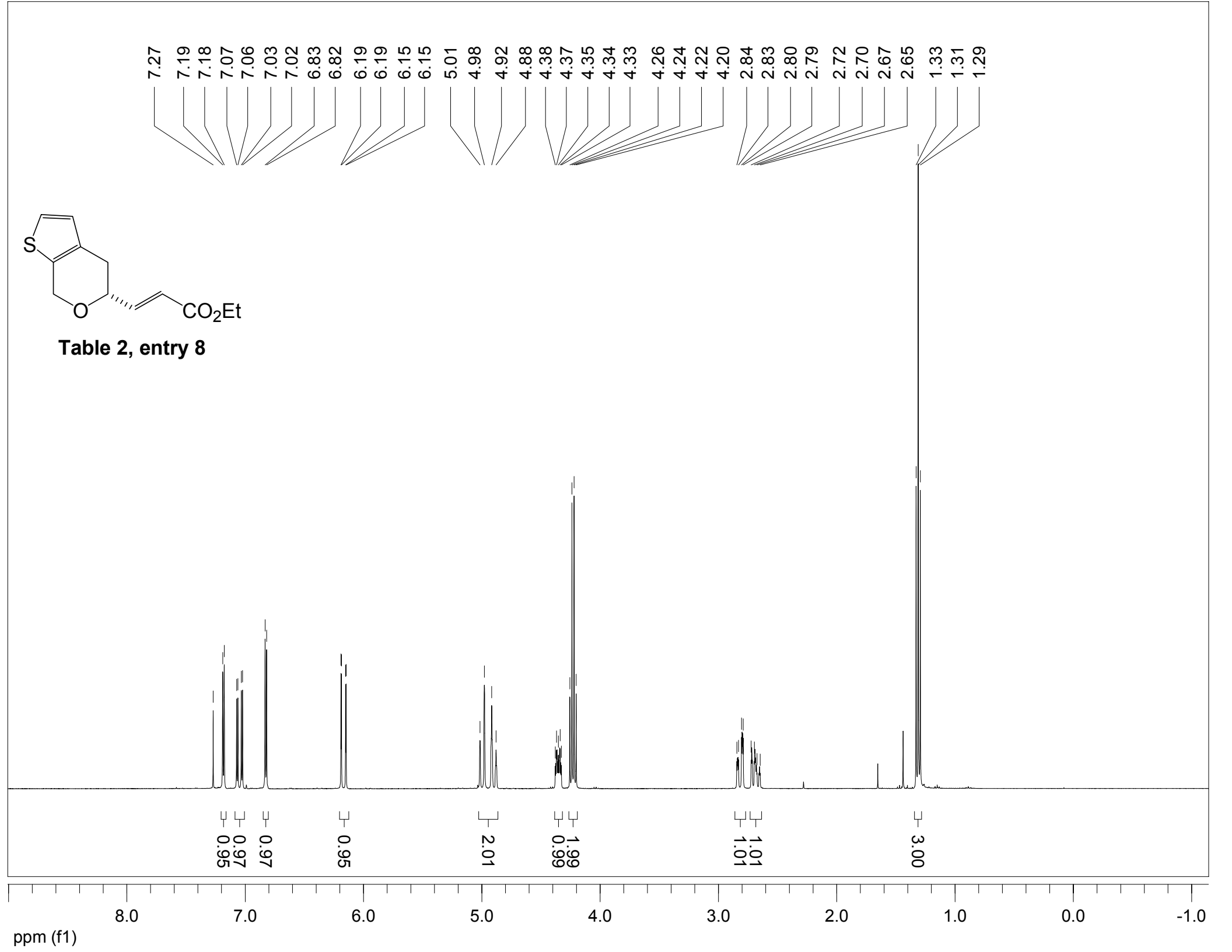

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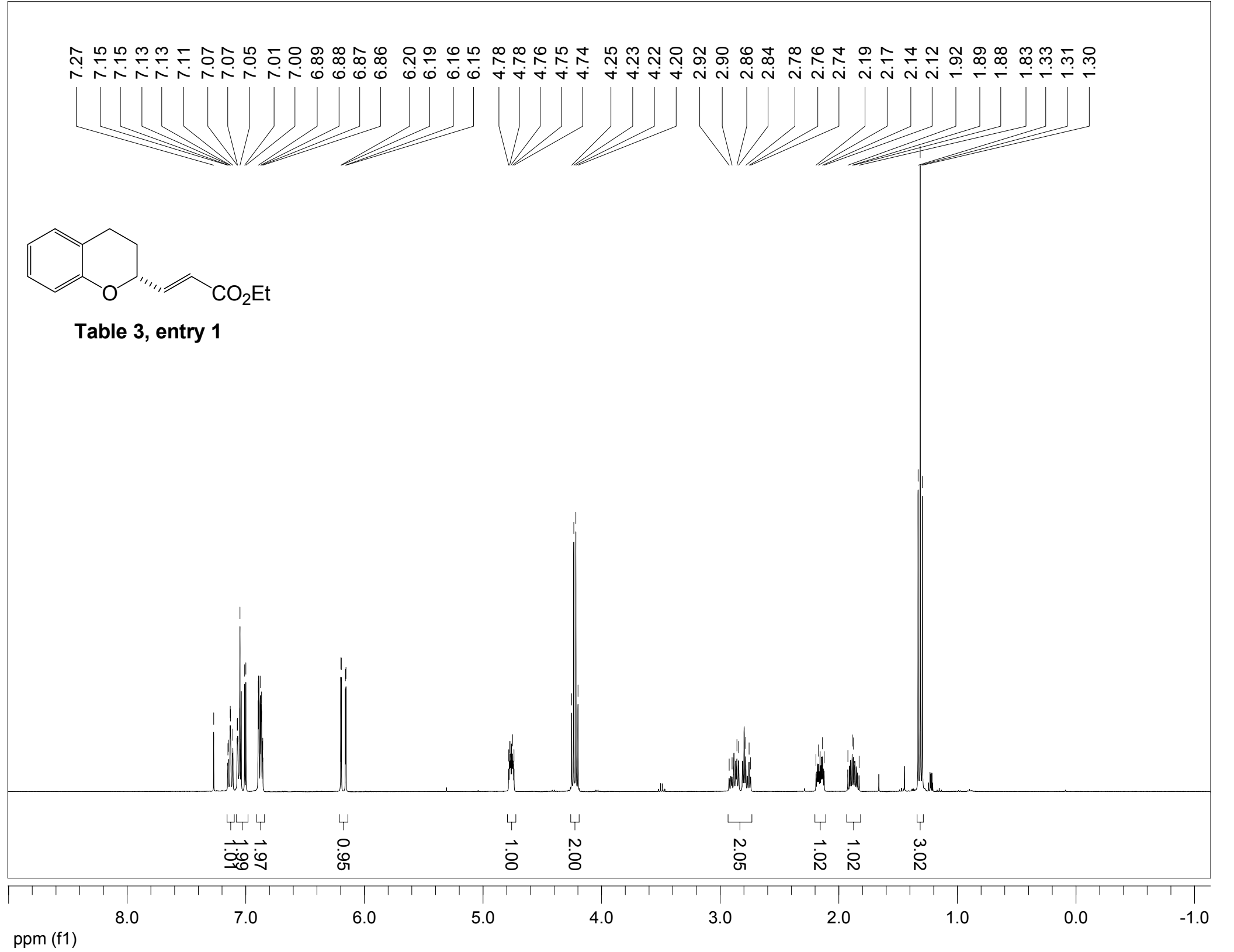

Table 3, entry 1

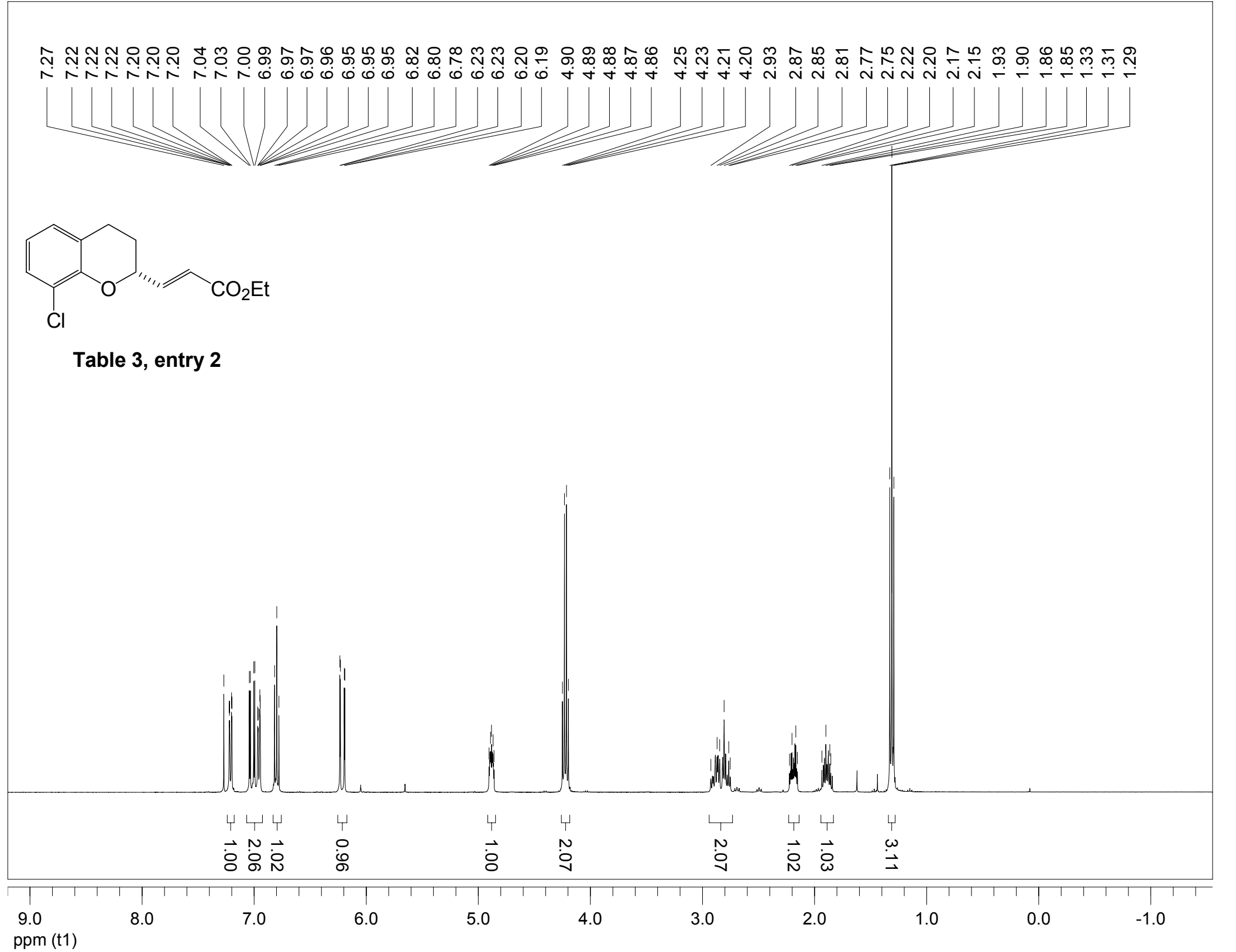

Table 3, entry 2

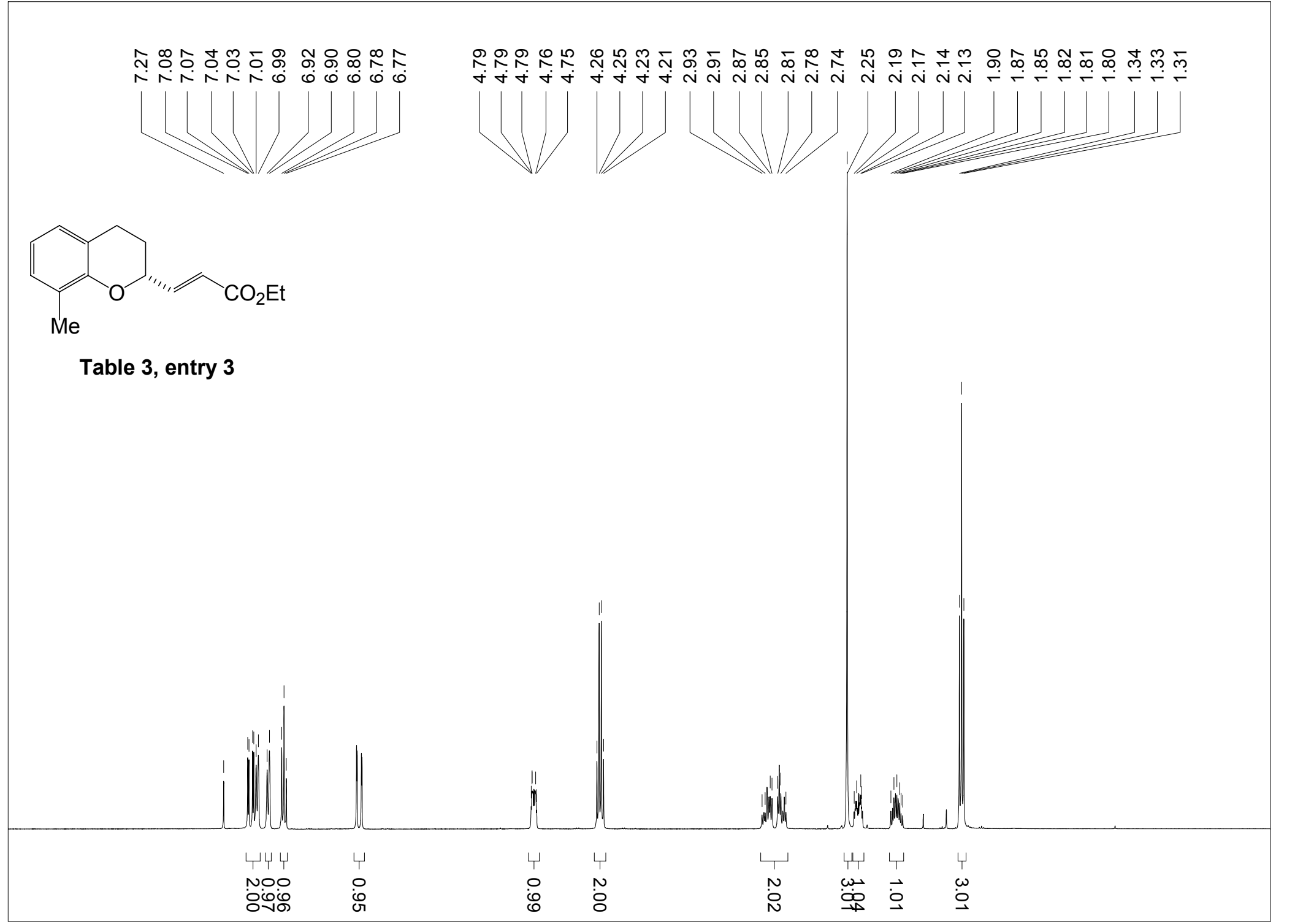

Table 3, entry 3

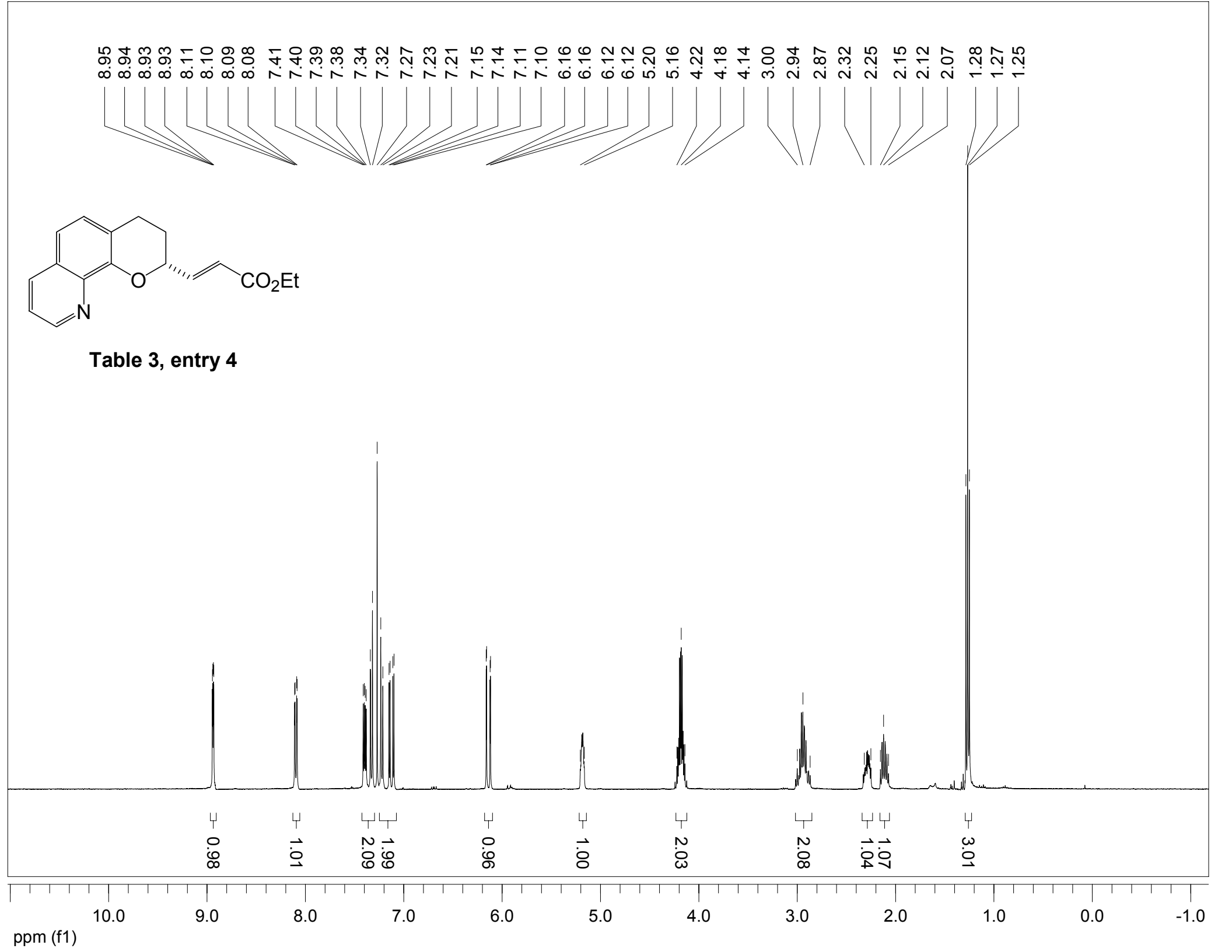

Table 3, entry 4