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Supporting Information

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Enantioselective Nucleophilic Catalysis:
The Synthesis of Aza-β-Lactams via [2+2] Reactions of Ketenes with Azo Compounds

Supporting Information

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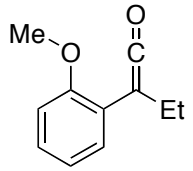
I. General

Phenyl methyl ketene,[1] phenyl ethyl ketene,[2] *m*-tolyl ethyl ketene,[3] *o*-tolyl ethyl ketene,[4] phenyl benzyl ketene,[5] phenyl isobutyl ketene,[6] phenyl cyclopentyl ketene,[7] phenyl cyclohexyl ketene,[6] phenyl isopropyl ketene,[6] *p*-anisyl isopropyl ketene,[8] *p*-chlorophenyl isopropyl ketene,[6] 3-thiophenyl isopropyl ketene,[9] catalysts (–)-**1** and (+)-**1**,[10] and SmI_2 (0.1 M in THF)[11] were prepared according to literature procedures. All of the azodicarboxylates were purchased and used as received (dimethyl azodicarboxylate was also prepared according to a literature procedure[12]). CH_2Cl_2 was purified by passage through activated alumina. Other chemicals were purchased from commercial suppliers and used as received.

All reactions were carried out in oven-dried glassware with magnetic stirring.

II. Preparation of Materials



***o*-Anisyl ethyl ketene.** Step 1: Synthesis of the α,α,-disubstituted acid. A solution of 2-(2-methoxyphenyl)acetic acid (5.0 g, 31 mmol) in THF (31 mL) was cooled to –78 °C, and then *n*-BuLi (1.6 M in THF; 47 mL, 75 mmol) was added. The reaction was stirred for 30 minutes, and then bromoethane (9.2 mL, 125 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 16 hours. Next, the reaction was quenched by the addition of aqueous HCl (1 N; 100 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with aqueous $Na_2S_2O_3$ (5%), dried over $MgSO_4$, concentrated, and passed through a glass frit. The resulting clear yellow oil (5.65 g) was used in the next step without further purification.

Step 2: Synthesis of the acid chloride. $SOCl_2$ (6.4 mL) was added to the yellow oil obtained in Step 1, and the resulting mixture was stirred at reflux for 2.5 hours. Next, the excess $SOCl_2$ was removed, and the residue (4.43 g) was used in the next step without further purification.

Step 3: Synthesis of the ketene. A solution of the acid chloride in THF (20 mL) was cooled to 0 °C, and then Et_3N (14.6 mL) was added. The reaction mixture was stirred for 2 hours at 0 °C, warmed to room temperature, and then stirred for 16 hours. The resulting suspension was filtered through a glass frit, concentrated, and purified by distillation under vacuum to give *o*-anisyl ethyl ketene as a yellow oil (500 mg, 9% over 3 steps; not optimized).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (1H, app dt, J = 8.0, 2.0 Hz), 7.00 (1H, app dt, J = 7.5, 1.0 Hz), 6.93 (1H, dd, J = 8.0, 2.0 Hz), 6.81 (1H, dd, J = 8.0 Hz, 1.0 Hz), 3.89 (3H, s), 2.46 (2H, q, J = 7.5 Hz), 1.26 (3H, t, J = 7.5 Hz);

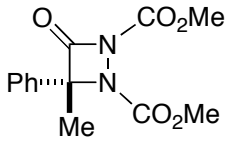
^{13}C (125 MHz, $CDCl_3$) δ 200.8, 152.7, 124.3, 123.7, 122.5, 121.8, 109.6, 55.6, 37.7, 18.2, 13;

IR (neat) 2969, 2974, 2089 (C=O), 1748, 1597, 1496, 1463, 1438, 1310, 1274, 1240, 1125, 1027, 747.

III. Enantioselective Synthesis of Aza-β-Lactams (Table 2)

General procedure for Table 2: In a glove box, a solution was prepared of the ketene (0.68 mmol) and dimethyl azodicarboxylate (100 mg, 0.68 mmol) in CH_2Cl_2 (49 mL). A solution was also prepared of catalyst (–)-**1** (13 mg, 0.035 mmol) in CH_2Cl_2 (0.8 mL). Both vessels were removed from the glove box and placed in a –20 °C bath. After 10 minutes, the solution of the catalyst was added by syringe to the solution of ketene and dimethyl azodicarboxylate. The reaction mixture was stirred for 2 hours at –20 °C (the reaction is temperature-sensitive), and then the solvent was removed and the residue was purified by column chromatography.

For a reaction conducted without the use of a glove box, see the procedure for Table 2, entry 2 (below).



(*R*)-Dimethyl 3-methyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 1). A variation of the General Procedure was employed (the reaction was conducted at lower concentration, which led to higher ee and yield).

First run: Phenyl methyl ketene (45 mg, 0.35 mmol), (–)-**1** (6.5 mg, 0.017 mmol), dimethyl azodicarboxylate (50 mg, 0.35 mmol), and CH_2Cl_2 (300 mL; 0.0012 M) were used. The product was purified by column chromatography (30% EtOAc/hexanes), which furnished a viscous colorless oil (51 mg, 54%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 5% isopropanol/hexanes, 1.0 mL/min): 85% ee (retention times: 12.4 [minor], 14.4 [major]).

$[\alpha]_D^{23}$ = +6.5 (c = 1.0, $CHCl_3$).

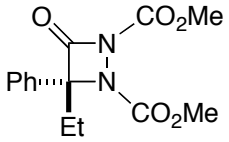
Second run: Identical to the first run, except that (+)-**1** was used: 49 mg, 52%; 84% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (2H, d, J = 7.0 Hz), 7.43-7.37 (3H, m), 3.92 (3H, s), 3.83 (3H, s), 1.94 (3H, s);

^{13}C (125 MHz, $CDCl_3$) δ 165.1, 158.6, 148.9, 135.6, 129.3, 129.1, 125.8, 86.4, 54.8, 54.3, 22.0;

IR (neat) 2959, 1836 (C=O), 1775 (C=O), 1750 (C=O), 1495, 1440, 1377, 1311, 1243, 1193, 1071, 1052, 751, 711;

HRMS (EI+) calc for Na + $C_{13}H_{14}N_2O_5$, 301.0795, found 301.0801.



(*R*)-Dimethyl 3-ethyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 2).

First run: Phenyl ethyl ketene (100 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (174 mg, 87%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 84% ee (retention times: 8.5 [major], 9.0 [minor]).

$[\alpha]_D^{23} = -20$ (c = 1.4, $CHCl_3$).

Slow evaporation of a solution of the oil in isopropanol produced colorless crystals of the racemate and a colorless mother liquor. The crystals were washed with hexanes (three times) and cold isopropanol (once). The mother liquor and the washes were concentrated to yield a viscous colorless oil (142 mg, 71%; >99% ee).

Second run: Identical to the first run, except that (+)-**1** was used: 180 mg, 90%; 87% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (2H, d, J = 7.5 Hz), 7.39-7.34 (3H, m), 3.88 (3H, s), 3.77 (3H, s), 2.37 (1H, app hex, J = 7.0 Hz), 2.25 (1H, app hex, J = 7.0 Hz), 1.04 (3H, t, J = 7.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.8, 158.3, 148.7, 135.2, 129.2, 129.0, 126.2, 91.1, 54.7, 54.2, 29.0, 8.8;

IR (neat) 2959, 1837 (C=O), 1775 (C=O), 1747 (C=O), 1494, 1440, 1315, 1273, 1171, 1062, 914, 734;

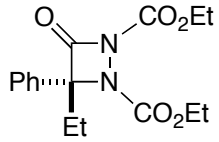
HRMS (EI+) calc for Na + $C_{14}H_{16}N_2O_5$, 315.0951, found 315.0949.

Gram-scale reaction. In a glove box, a solution was prepared of phenyl ethyl ketene (1.00 g, 6.8 mmol) and dimethyl azodicarboxylate (1.00 g, 6.8 mmol) in CH_2Cl_2 (490 mL). A solution was also prepared of catalyst (–)-**1** (130 mg, 0.35 mmol) in CH_2Cl_2 (8 mL). The vessels were removed from the glove box, and both were placed in a –20 °C bath. After 1 hour, the solution of the catalyst was added by syringe to the solution of the substrates. The reaction mixture stirred for 2 hours, and then the solvent was removed

and the residue was purified by column chromatography (20% EtOAc), which furnished a viscous colorless oil (1.53 g, 77%; 84% ee).

Without-a-glove-box reaction. First run: The General Procedure was followed, except that the reaction was set up, open to the air, in a fume hood and unpurified, reagent-grade CH_2Cl_2 was used: 158 mg, 79%; 82% ee.

Second run: Identical to the first run, except that (+)-**1** was used: 148 mg, 74%; 84% ee.



(*R*)-Diethyl 3-ethyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate. dicarboxylate (diethyl azodicarboxylate analogue of Table 2, entry 2; footnote 14).

First run: Phenyl ethyl ketene (100 mg) and diethyl azodicarboxylate (119 mg) were used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (182 mg, 83%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 10% isopropanol/hexanes, 1.0 mL/min): 80% ee (retention times: 8.2 [major], 10.4 [minor]).

$[\alpha]_D^{23} = -14$ (c = 2.0, $CHCl_3$).

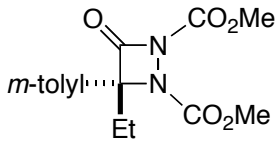
Second run: Identical to the first run, except that (+)-**1** was used: 192 mg, 88%; 80% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (2H, d, J = 7.5 Hz), 7.41-7.35 (3H, m), 4.35 (2H, q, J = 7.0 Hz), 4.25-4.18 (2H, m), 2.41 (1H, app hex, J = 7.5 Hz), 2.27 (1H, app hex, J = 7.5 Hz), 1.36 (3H, t, J = 7.0 Hz), 1.21 (3H, br s), 1.08 (3H, t, J = 7.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.9, 157.8, 148.2, 135.3, 129.2, 129.0, 126.4, 90.7, 64.4, 63.6, 28.9, 14.5, 14.4, 8.8;

IR (neat) 2982, 1837 (C=O), 1771 (C=O), 1744 (C=O), 1465, 1450, 1371, 1305, 1177, 1057, 915, 749;

HRMS (EI+) calc for Na + $C_{16}H_{20}N_2O_5$, 343.1264, found 343.1253.



(*R*)-Dimethyl 3-ethyl-4-oxo-3-*meta*-methyl-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 3).

First run: *meta*-Tolyl ethyl ketene (110 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (163 mg, 78%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 5% isopropanol/hexanes, 1.0 mL/min): 86% ee (retention times: 11.3 [major], 14.0 [minor]).

$[\alpha]_D^{23} = -19$ (c = 2.1, $CHCl_3$).

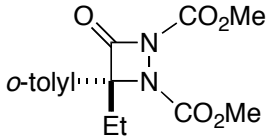
Second run: Identical to the first run, except that (+)-**1** was used: 166 mg, 79%; 84% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (2H, m), 7.28 (1H, app t, J = 8.0 Hz), 7.16 (1H, d, J = 7.5 Hz), 3.90 (3H, s), 3.80 (3H, s), 2.40-2.34 (4H, m), 2.25 (1H, app hex, J = 7.5 Hz), 1.05 (3H, t, J = 7.5 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.9, 158.4, 148.8, 138.8, 135.1, 130.0, 128.8, 126.7, 123.3, 91.2, 54.7, 54.2, 29.0, 21.7, 8.8;

IR (neat) 2958, 1836 (C=O), 1774 (C=O), 1747 (C=O), 1490, 1440, 1315, 1251, 1192, 1062, 913, 733;

HRMS (EI+) calc for Na + $C_{15}H_{18}N_2O_5$, 329.1108, found 329.1105.



(*R*)-Dimethyl 3-ethyl-4-oxo-3-*ortho*-methylphenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 4).

First run: *ortho*-Tolyl ethyl ketene (110 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (98 mg, 47%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 5% isopropanol/hexanes, 1.0 mL/min): 67% ee (retention times: 12.7 [minor], 14.4 [major]).

$[\alpha]_D^{23} = -1.9$ (c = 1.5, $CHCl_3$).

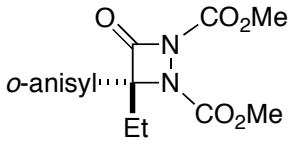
Second run: Identical to the first run, except that (+)-**1** was used: 95 mg, 45%; 67% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (1H, d, J = 7.0 Hz), 7.27-7.19 (3H, m), 3.91 (3H, s), 3.89 (3H, s), 2.58 (3H, s), 2.47-2.35 (2H, m), 1.06 (3H, t, J = 7.5 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.3, 158.2, 148.8, 135.6, 133.9, 132.4, 128.9, 128.4, 126.4, 94.0, 54.7, 54.3, 27.5, 20.8, 8.9;

IR (neat) 2959, 1834 (C=O), 1773 (C=O), 1745 (C=O), 1440, 1317, 1269, 1229, 1161, 1064, 914, 730;

HRMS (EI+) calc for Na + $C_{15}H_{18}N_2O_5$, 329.1108, found 329.1116.



(*R*)-Dimethyl 3-ethyl-4-oxo-3-*ortho*-methoxyphenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 5).

First run: *ortho*-Anisyl ethyl ketene (110 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a white solid (202 mg, 91%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 20% isopropanol/hexanes, 1.0 mL/min): 93% ee (retention times: 11.6 [minor], 6.5 [major]).

$[\alpha]_D^{23} = -65$ (c = 1.3, $CHCl_3$).

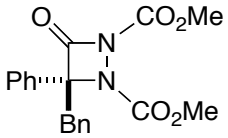
Second run: Identical to the first run, except that (+)-**1** was used: 190 mg, 86%; 92% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.34 (2H, m), 7.00 (1H, app t, J = 6.5 Hz), 6.90 (1H, d, J = 6.5 Hz), 3.95 (3H, s), 3.76 (3H, s), 3.58 (3H, s), 2.49-2.46 (2H, m), 1.13-1.11 (3H, m);

^{13}C (125 MHz, $CDCl_3$) δ 166.7, 158.3, 158.0, 149.9, 131.6, 128.8, 121.4, 121.2, 111.7, 87.2, 55.9, 54.5, 53.6, 25.8, 8.3;

IR (neat) 2957, 1842 (C=O), 1771 (C=O), 1740 (C=O), 1495, 1465, 1439, 1305, 1256, 1056, 753;

LCMS (EI+) calc for H + $C_{15}H_{18}N_2O_6$, 323.1, found 323.1.



(*R*)-Dimethyl 3-benzyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 6). A variation of the General Procedure was employed (the reaction was conducted at lower concentration, which led to higher yield).

First run: Phenyl benzyl ketene (71 mg, 0.35 mmol), dimethyl azodicarboxylate (50 mg, 0.35 mmol), (–)-**1** (6.5 mg, 0.0175 mmol), and CH_2Cl_2 (150 mL; 0.0023 M) were used. The vessels were cooled for 1 hour at –20 °C before the catalyst solution was added to the flask that contained the substrates. Reaction time: 16 hours. The product was purified by column chromatography (30% EtOAc/hexanes), which furnished a viscous colorless oil (91 mg, 75%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 80% ee (retention times: 16.2 [minor], 17.7 [major]).

$[\alpha]_D^{23}$ = +14 (c = 0.80, $CHCl_3$).

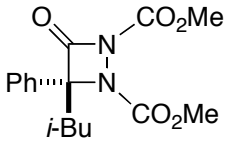
Second run: Identical to the first run, except that (+)-**1** was used: 86 mg, 71%; 82% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.57 (2H, m), 7.44-7.40 (3H, m), 7.32-7.26 (5H, m), 3.76 (3H, s), 3.68 (1H, d, J = 14.5 Hz), 3.65 (3H, s), 3.55 (1H, d, J = 14.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 165.0, 157.9, 148.5, 132.9, 131.1, 129.6, 129.0, 128.6, 128.1, 126.6, 90.7, 54.6, 53.9, 41.3, 25.6;

IR (neat) 2957, 1839 (C=O), 1774 (C=O), 1749 (C=O), 1440, 1267, 1226, 1137, 1075, 913, 731;

HRMS (EI+) calc for Na + $C_{19}H_{18}N_2O_5$, 377.1108, found 377.1120.



(*R*)-Dimethyl 3-*iso*-butyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 7).

First run: The General Procedure was followed, except that the reaction was run on half of the usual scale (phenyl *iso*-butyl ketene: 58 mg, 0.35 mmol) and that the reaction time was 3 hours. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (87 mg, 82%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 3% isopropanol/hexanes, 1.0 mL/min): 82% ee (retention times: 12.1 [major], 13.0 [minor]).

$[\alpha]_D^{23}$ = +26 (c = 2.5, $CHCl_3$).

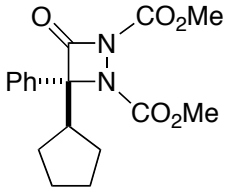
Second run: The General Procedure was followed (phenyl *iso*-butyl ketene: 119 mg, 0.68 mmol), except that (+)-**1** was used and the reaction was stirred for 3 hours. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (199 mg, 91%; 83% ee).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (2H, d, J = 7.5 Hz), 7.40-7.34 (3H, m), 3.89 (3H, s), 3.81 (3H, s), 2.28-2.09 (2H, m), 1.74 (1H, br s), 0.96 (3H, d, J = 6.5 Hz), 0.93 (3H, d, J = 6.5 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 165.0, 158.1, 148.8, 135.9, 129.2, 128.9, 126.2, 90.4, 54.7, 54.2, 44.8, 24.5, 24.2, 23.8;

IR (neat) 2960, 1838 (C=O), 1775 (C=O), 1745 (C=O), 1440, 1314, 1267, 1230, 1158, 1064, 914, 734;

HRMS (EI+) calc for Na + $C_{16}H_{20}N_2O_5$, 343.1264, found 343.1250.



(*R*)-Dimethyl 3-cyclopentyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 8).

First run: Phenyl cyclopentyl ketene (127 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (188 mg, 83%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 86% ee (retention times: 10.9 [minor], 16.0 [major]).

$[\alpha]_D^{23}$ = +65 (c = 0.90, $CHCl_3$).

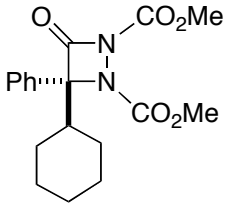
Second run: Identical to the first run, except that (+)-**1** was used: 191 mg, 84%; 86% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (2H, d, J = 7.5 Hz), 7.38-7.33 (3H, m), 3.89 (3H, s), 3.77 (3H, s), 2.91-2.89 (1H, m), 1.77 (1H, br s), 1.66 (4H, br s), 1.56 (1H, br s), 1.43 (2H, br s);

^{13}C (125 MHz, $CDCl_3$) δ 164.6, 158.3, 148.6, 135.4, 129.1, 128.8, 126.6, 93.3, 54.7, 54.2, 44.8, 29.1, 27.7, 25.9, 25.7;

IR (neat) 2959, 1833 (C=O), 1774 (C=O), 1747 (C=O), 1439, 1314, 1273, 1232, 1065, 914, 734;

HRMS (EI+) calc for Na + $C_{17}H_{20}N_2O_5$, 355.1264, found 355.1258.



(*R*)-Dimethyl 3-cyclohexyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 9).

First run: Phenyl cyclohexyl ketene (135 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a white foam (209 mg, 89%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 94% ee (retention times: 8.6 [minor], 11.4 [major]).

$[\alpha]_D^{23}$ = +56 (c = 0.90, $CHCl_3$).

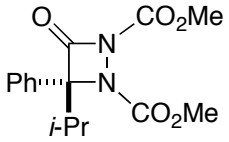
Second run: Identical to the first run, except that (+)-**1** was used: 214 mg, 91%; 94% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 6.5 Hz), 7.39-7.34 (3H, m), 3.90 (3H, s), 3.64 (3H, s), 2.43-2.38 (1H, m), 1.97 (1H, br s), 1.82 (1H, d, J = 7.0 Hz), 1.70-1.65 (2H, m), 1.37-1.11 (6H, m);

^{13}C (125 MHz, $CDCl_3$) δ 164.6, 158.2, 148.6, 133.3, 129.4, 128.8, 127.3, 94.3, 64.5, 54.7, 53.9, 41.8, 28.0, 27.8, 26.3, 26.1, 26.0, 25.5;

IR (neat) 2935, 2856, 1832 (C=O), 1774 (C=O), 1746 (C=O), 1439, 1315, 1276, 1232, 1064, 914, 733;

HRMS (EI+) calc for Na + $C_{18}H_{22}N_2O_5$, 369.14, found 369.1415.



(*R*)-Dimethyl 3-isopropyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 10).

First run: Phenyl isopropyl ketene (110 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (190 mg, 90%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 7% isopropanol/hexanes, 1.0 mL/min): 95% ee (retention times: 10.3 [minor], 11.0 [major]).

$[\alpha]_D^{23}$ = +48 (c = 2.5, $CHCl_3$).

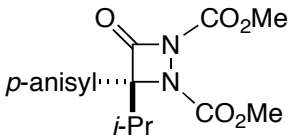
Second run: Identical to the first run, except that (+)-**1** was used: 193 mg, 92%; 95% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 7.0 Hz), 7.36-7.35 (3H, m), 3.88 (3H, s), 3.64 (3H, s), 2.77 (1H, sept, J = 6.0 Hz), 1.15 (3H, d, J = 5.5 Hz), 0.93 (3H, d, J = 6.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.4, 158.2, 148.6, 133.7, 129.4, 128.8, 127.2, 94.6, 54.7, 53.9, 32.6, 18.0, 17.5;

IR (neat) 2960, 1833 (C=O), 1772 (C=O), 1748 (C=O), 1440, 1197, 1064, 997, 734;

HRMS (EI+) calc for Na + $C_{15}H_{18}N_2O_5$, 329.1108, found 329.1111.



(*R*)-Dimethyl 3-isopropyl-4-oxo-3-*para*-methoxyphenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 11).

First run: *para*-Anisyl isopropyl ketene (130 mg) was used. The product was purified by column chromatography (30% EtOAc/hexanes), which furnished a white solid (210 mg, 91%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD, 3% isopropanol/hexanes, 1.0 mL/min): 96% ee (retention times: 29.2 [minor], 31.3 [major]).

$[\alpha]_D^{23}$ = +46 (c = 1.0, $CHCl_3$).

A crystal structure was obtained of this product, in order to assign the absolute stereochemistry of the aza-β-lactam (for additional information, see Section V).

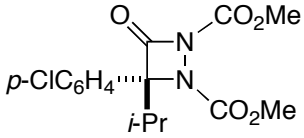
Second run: Identical to the first run, except that (+)-**1** was used: 210 mg, 91%; 96% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.5 Hz), 6.89 (2H, d, J = 9.0 Hz), 3.91 (3H, s), 3.79 (3H, s), 3.60 (3H, s), 2.78 (1H, sept, J = 7.0 Hz), 1.18 (3H, d, J = 7.0 Hz), 0.95 (3H, d, J = 7.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.7, 160.4, 158.3, 148.6, 128.8, 125.2, 114.1, 94.6, 55.5, 54.7, 53.8, 32.5, 17.9, 17.6;

IR (neat) 2960, 1832 (C=O), 1773 (C=O), 1746 (C=O), 1611, 1516, 1440, 1302, 1277, 1258, 1235, 1188, 1063, 738;

HRMS (EI+) calc for Na + $C_{16}H_{20}N_2O_6$, 359.1214, found 359.1219.



(*R*)-Dimethyl 3-isopropyl-4-oxo-3-*para*-chlorophenyl-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 12).

First run: *para*-Chlorophenyl isopropyl ketene (133 mg) was used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (210 mg, 90%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 92% ee (retention times: 9.1 [major], 9.9 [minor]).

$[\alpha]_D^{23}$ = +48 (c = 1.4, $CHCl_3$).

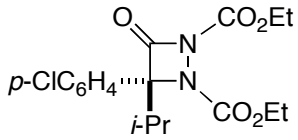
Second run: Identical to the first run, except that (+)-**1** was used: 209 mg, 90%; 92% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (2H, d, J = 6.5 Hz), 7.34 (2H, d, J = 6.0 Hz), 3.89 (3H, s), 3.72 (3H, s), 2.71 (1H, sept, J = 7.0 Hz), 1.12 (3H, d, J = 6.0 Hz), 0.91 (3H, d, J = 6.5 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.0, 157.9, 148.5, 135.4, 132.6, 129.0, 128.5, 93.7, 54.8, 54.2, 32.8, 18.1, 17.5;

IR (neat) 2960, 1833 (C=O), 1775 (C=O), 1747 (C=O), 1495, 1440, 1319, 1282, 1234, 1065, 733;

HRMS (EI+) calc for Na + $C_{15}H_{17}ClN_2O_5$, 363.0718, found 363.0727.



(*R*)-Diethyl 3-isopropyl-4-oxo-3-*para*-chlorophenyl-1,2-diazetidine-1,2-dicarboxylate (diethyl azodicarboxylate analogue of Table 2, entry 12; footnote 14).

First run: *para*-Chlorophenyl isopropyl ketene (133 mg) and diethyl azodicarboxylate (119 mg) were used. The product was purified by column chromatography (20% EtOAc/hexanes), which furnished a viscous colorless oil (250 mg, 99%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 10% isopropanol/hexanes, 1.0 mL/min): 86% ee (retention times: 7.7 [major], 8.9 [minor]).

$[\alpha]_D^{23}$ = +38 (c = 0.85, $CHCl_3$).

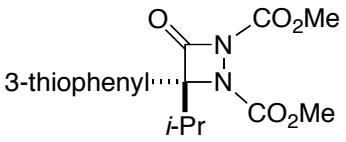
Second run: Identical to the first run: 237 mg, 94%; 86% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (2H, d, J = 7.5 Hz), 7.34 (2H, d, J = 7.0 Hz), 4.33 (2H, q, J = 6.5 Hz), 4.21-4.11 (2H, m), 2.73 (1H, sept, J = 6.5 Hz), 1.34 (3H, t, J = 7.0 Hz), 1.20 (3H, t, J = 7.0 Hz), 1.15 (3H, d, J = 7.0 Hz), 0.93 (3H, d, J = 7.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.2, 157.4, 148.0, 135.3, 132.7, 129.0, 128.7, 93.3, 64.4, 63.6, 32.7, 18.1, 17.6, 14.5, 14.4;

IR (neat) 2983, 1834 (C=O), 1771 (C=O), 1743 (C=O), 1495, 1372, 1313, 1228, 1095, 1058, 1016, 732;

HRMS (EI+) calc for Na + $C_{17}H_{21}ClN_2O_5$, 391.10, found 391.1028.



(*R*)-Dimethyl 3-isopropyl-4-oxo-3-(thiophen-3-yl)-1,2-diazetidine-1,2-dicarboxylate (Table 2, entry 13).

First run: 3-Thiophenyl isopropyl ketene (133 mg) was used. The product was purified by column chromatography (40% EtOAc/hexanes), which furnished a viscous colorless oil (184 mg, 86%).

The enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD, 5% isopropanol/hexanes, 1.0 mL/min): 96% ee (retention times: 13.7 [major], 14.7 [minor]).

$[\alpha]_D^{23} = +4.7$ (c = 1.0, $CHCl_3$).

Second run: Identical to the first run, except that (+)-**1** was used: 199 mg, 93%; 96% ee.

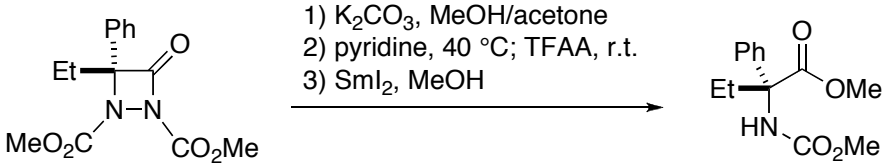
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (1H, dd, J = 3.0, 1.5 Hz), 7.35 (1H, dd, J = 5.5, 3.0 Hz), 7.12 (1H, d, J = 4.5 Hz), 3.93 (3H, s), 3.55 (3H, s), 2.74 (1H, sept, J = 7.0 Hz), 1.20 (3H, d, J = 6.5 Hz), 1.01 (3H, d, J = 7.0 Hz);

^{13}C (125 MHz, $CDCl_3$) δ 164.3, 158.3, 148.6, 133.3, 126.8, 126.4, 125.4, 91.5, 54.8, 53.8, 33.0, 17.8, 17.6;

IR (neat) 2960, 1833 (C=O), 1773 (C=O), 1747 (C=O), 1439, 1307, 1277, 1156, 1063, 988, 914, 736;

HRMS (EI+) calc for Na + $C_{13}H_{16}N_2O_5S$, 335.0672, found 335.0663.

IV. Derivatization of the Aza-β-Lactams



Ring opening of the aza-β-lactam: (*R*)-methyl 2-(methoxycarbonylamino)-2-phenylbutanoate.[13] K_2CO_3 (126 mg, 0.91 mmol) was added to a solution of (*R*)-dimethyl 3-ethyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (252 mg, 0.86 mmol; 84% ee; synthesized with catalyst (–)-**1**) in MeOH (28 mL) and acetone (10 mL). The reaction mixture was stirred for 20 hours, and then the solvent was removed. The residue was suspended in CH_2Cl_2 and filtered through a glass frit. A white solid was collected (280 mg, 100%), which was used without further purification.

Pyridine (8 mL) was added to the white solid, and the reaction mixture was stirred at 40 °C for 24 hours. Then, it was cooled to room temperature, and trifluoroacetic

anhydride (600 μL; 4.3 mmol) was added. The reaction mixture was stirred for 48 hours, and then it was concentrated. Water and EtOAc were added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (three times), and the combined organic layers were dried, concentrated, and then passed through a pad of silica gel (washing with EtOAc). The filtrate was concentrated, yielding a yellow residue.

This residue was dissolved in MeOH (16 mL). Argon was bubbled through the solution for 5 minutes, and then a solution of SmI_2 (0.1 M in THF; 40 mL, 4 mmol) was added. The reaction mixture was stirred for 30 minutes, and then it was concentrated. Water and EtOAc were added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (three times), and the combined organic layers were dried and concentrated. The residue was purified by column chromatography (10% EtOAc/hexanes), which furnished (*R*)-methyl 2-(methoxycarbonylamino)-2-phenylbutanoate as a viscous colorless oil (146 mg, 68%).

$[\alpha]_D^{23}$ = +50 (c = 1.4, $CHCl_3$).

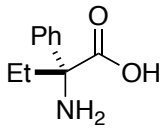
Second run: By an analogous procedure, a second batch of the aza-β-lactam (160 mg; 92% ee) was converted into the desired product (90 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (2H, d, J = 7.5 Hz), 7.35 (2H, app t, J = 7.5 Hz), 7.29 (1H, app t, J = 7.5 Hz), 6.38 (1H, s), 3.68 (3H, s), 3.60 (3H, s), 2.78 (1H, br s), 2.51 (1H, app hex, J = 6.5 Hz), 0.90 (3H, t, J = 7.0 Hz).

^{13}C (125 MHz, $CDCl_3$) δ 173.5, 154.6, 140.4, 128.7, 128.0, 126.2, 66.0, 53.5, 52.1, 8.8, 1.3;

IR (neat) 2959, 1725 (C=O), 1497, 1449, 1310, 1256, 1088, 1005, 789, 698;

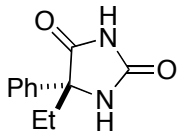
HRMS (EI+) calc for Na + $C_{13}H_{17}NO_4$, 274.1050, found 274.1055.



(*R*)-2-Amino-2-phenylbutanoic acid. Water (380 μL) and concentrated HCl (736 μL) were added to a solution of (*R*)-methyl 2-(methoxycarbonylamino)-2-phenylbutanoate (146 mg, 0.58 mmol) in dioxane (8 mL). The reaction mixture was stirred for 48 hours at 80 °C, and then it was poured into a mixture of water:Et_2O (1:2; 0 °C). The organic layer was separated, and the aqueous layer was washed with Et_2O and then concentrated. The residue was dissolved in HCl (1 N; 20 mL) and purified by ion exchange chromatography (AG 50w-X8 resin; elution with water until pH=7 and then with 10% NH_4OH), which furnished (*R*)-2-amino-2-phenylbutanoic acid (104 mg, 99%).

Second run: By an analogous procedure, a second batch of (*R*)-methyl 2-(methoxycarbonylamino)-2-phenylbutanoate (88 mg, 0.35 mmol) furnished (*R*)-2-amino-2-phenylbutanoic acid (62 mg, 100%).

$[\alpha]_D^{23}$ = +22 (c = 0.9, 1 N HCl). The absolute stereochemistry was determined by comparison to literature data ($[\alpha]_D^{23}$ = –57 for the S enantiomer (c = 0.5, 2 N HCl)).[14]



(*R*)-5-Ethyl-5-phenylimidazolidine-2,4-dione ((*R*)-(–)-nirvanol; 50-12-4). To (*R*)-dimethyl 3-ethyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (183 mg, 0.63 mmol) was added THF (25 mL), HMPA (0.92 mL), and then SmI_2 (0.1 M in THF; 25 mL, 2.5 mmol). The reaction mixture was stirred for 1 hour, and then the reaction was quenched by exposure to air. Water and EtOAc were added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (three times). The organic layers were combined, and saturated aqueous $NaHCO_3$ (100 mL) was added. The reaction mixture was stirred for 48 hours, and then it was concentrated. The residue was purified by column chromatography (40% EtOAc/40% hexanes/20% CH_2Cl_2), which furnished a mixture of the desired compound and an acyclic precursor. Saturated aqueous $NaHCO_3$ (20 mL) and THF (2 mL) were added to the mixture, and the solution was stirred for 48 hours. The solvent was removed, and the residue was purified by column chromatography (5% MeOH/45% CH_2Cl_2/50% hexanes), which furnished the hydantoin as a white solid (44 mg, 34%).

Second run: By an analogous procedure, a second batch of (*R*)-dimethyl 3-ethyl-4-oxo-3-phenyl-1,2-diazetidine-1,2-dicarboxylate (48 mg, 0.16 mmol) furnished the hydantoin (16 mg, 48%).

This process has not been optimized.

V. Assignment of Absolute Configuration

Entry 2 of Table 2 (correlation): The aza-β-lactam (synthesized with catalyst (–)-**1**) was converted into the α-amino acid and determined to have the (*R*) configuration (see Section IV).

Entry 2 of Table 11 (X-ray crystallography with Cu radiation): The crystal structure of the aza-β-lactam produced by catalyst (–)-**1** was obtained.

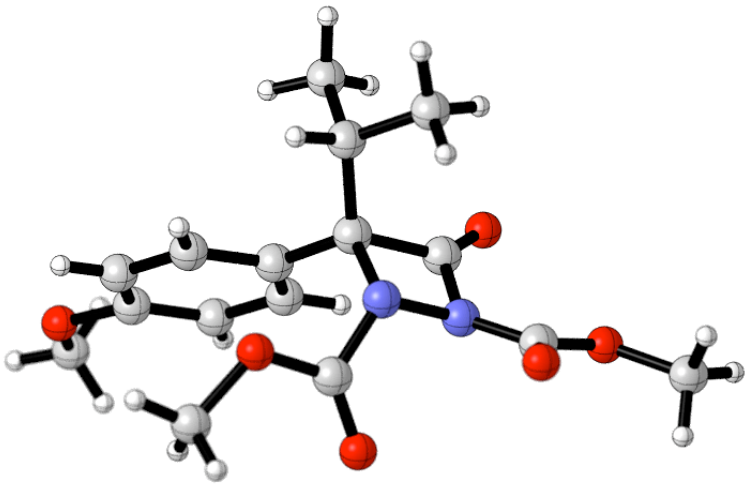


Table 1. Crystal data and structure refinement.

Empirical formula	C16 H20 N2 O6	
Formula weight	336.34	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.71550(10) Å	a= 90°.
	b = 16.5325(2) Å	b= 118.4850(10)°.
	c = 10.83790(10) Å	g = 90°.
Volume	1687.55(3) $Å^3$	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.858 mm^{-1}	
F(000)	712	
Crystal size	0.35 x 0.07 x 0.03 mm^3	
Theta range for data collection	4.64 to 67.55°.	
Index ranges	-12<=h<=12, -19<=k<=19, -12<=l<=12	
Reflections collected	28887	
Independent reflections	5917 [R(int) = 0.0254]	
Completeness to theta = 67.55°	98.6%	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.9747 and 0.7532
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5917 / 1 / 443
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0722
R indices (all data)	R1 = 0.0282, wR2 = 0.0756
Absolute structure parameter	0.08(10)
Largest diff. peak and hole	0.164 and -0.218 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for D08001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(6)	5645(1)	3828(1)	1644(1)	20(1)
O(1)	2852(1)	6462(1)	-917(1)	22(1)
O(10)	7091(1)	4005(1)	6756(1)	22(1)
O(5)	4851(1)	3855(1)	-701(1)	23(1)
O(3)	6517(1)	5389(1)	-1000(1)	23(1)
O(7)	8733(1)	3157(1)	4014(1)	22(1)
O(2)	101(1)	3434(1)	1518(1)	26(1)
O(11)	7408(1)	5591(1)	5535(1)	23(1)
O(9)	6337(1)	3117(1)	4950(1)	26(1)
O(12)	9752(1)	5869(1)	6870(1)	20(1)
N(1)	4548(1)	5466(1)	-698(1)	19(1)
N(4)	9149(1)	4597(1)	6259(1)	17(1)
N(3)	8082(1)	4026(1)	5357(1)	19(1)
N(2)	5197(1)	5024(1)	606(1)	18(1)
O(8)	10491(1)	6777(1)	2031(1)	28(1)
O(4)	4625(1)	6156(1)	-2429(1)	22(1)
C(2)	3635(2)	5911(1)	-349(2)	17(1)
C(56)	9203(2)	5011(1)	3168(2)	21(1)
C(4)	5169(2)	4184(1)	400(2)	18(1)
C(60)	11279(2)	3302(1)	7451(2)	24(1)
C(54)	10319(2)	6183(1)	2816(2)	22(1)
C(55)	9284(2)	5583(1)	2269(2)	23(1)
C(11)	3059(2)	4881(1)	1100(2)	18(1)
C(41)	5531(2)	2952(1)	1600(2)	23(1)
C(7)	7084(2)	3658(1)	5648(2)	18(1)
C(71)	5915(2)	3766(1)	6983(2)	29(1)
C(8)	8637(2)	5395(1)	6130(2)	18(1)
C(19)	6004(2)	6545(1)	2201(2)	27(1)
C(52)	11185(2)	5621(1)	5130(2)	23(1)
C(1)	4152(2)	5434(1)	1030(2)	18(1)
C(3)	5354(2)	5658(1)	-1365(2)	18(1)

C(6)	8898(2)	3722(1)	4762(2)	18(1)
C(15)	623(2)	4405(1)	127(2)	21(1)
C(5)	10057(2)	4363(1)	5539(2)	18(1)
C(51)	10156(2)	5009(1)	4599(2)	18(1)
C(53)	11264(2)	6201(1)	4255(2)	25(1)
C(58)	11479(2)	3986(1)	6607(2)	19(1)
C(16)	1653(2)	4878(1)	37(2)	20(1)
C(18)	4972(2)	5961(1)	2348(2)	22(1)
C(17)	-1377(2)	3461(1)	487(2)	31(1)
C(20)	3934(2)	6421(1)	2684(2)	29(1)
C(12)	3423(2)	4387(1)	2276(2)	21(1)
C(31)	5349(2)	6365(1)	-3235(2)	30(1)
C(59)	12258(2)	3669(1)	5833(2)	26(1)
C(13)	2419(2)	3911(1)	2373(2)	23(1)
C(81)	9461(2)	6728(1)	6750(2)	31(1)
C(14)	1007(2)	3920(1)	1303(2)	21(1)
C(57)	9523(2)	6778(1)	566(2)	36(1)

Table 3. Bond lengths [Å] and angles [°] for D08001.

O(6)-C(4)	1.3301(19)
O(6)-C(41)	1.4526(18)
O(1)-C(2)	1.1905(19)
O(10)-C(7)	1.3275(19)
O(10)-C(71)	1.449(2)
O(5)-C(4)	1.2033(19)
O(3)-C(3)	1.1984(19)
O(7)-C(6)	1.1939(19)
O(2)-C(14)	1.364(2)
O(2)-C(17)	1.439(2)
O(11)-C(8)	1.2018(19)
O(9)-C(7)	1.198(2)
O(12)-C(8)	1.330(2)
O(12)-C(81)	1.446(2)
N(1)-C(3)	1.403(2)
N(1)-C(2)	1.412(2)
N(1)-N(2)	1.4412(17)
N(4)-C(8)	1.410(2)
N(4)-N(3)	1.4448(18)
N(4)-C(5)	1.558(2)
N(3)-C(7)	1.391(2)
N(3)-C(6)	1.404(2)
N(2)-C(4)	1.405(2)
N(2)-C(1)	1.5537(19)
O(8)-C(54)	1.370(2)
O(8)-C(57)	1.423(2)
O(4)-C(3)	1.3260(19)
O(4)-C(31)	1.460(2)
C(2)-C(1)	1.541(2)
C(56)-C(55)	1.391(2)
C(56)-C(51)	1.392(2)
C(60)-C(58)	1.533(2)
C(54)-C(55)	1.392(2)
C(54)-C(53)	1.397(2)

C(11)-C(16)	1.393(2)
C(11)-C(12)	1.404(2)
C(11)-C(1)	1.517(2)
C(19)-C(18)	1.532(2)
C(52)-C(53)	1.380(2)
C(52)-C(51)	1.401(2)
C(1)-C(18)	1.541(2)
C(6)-C(5)	1.542(2)
C(15)-C(14)	1.391(2)
C(15)-C(16)	1.393(2)
C(5)-C(51)	1.514(2)
C(5)-C(58)	1.539(2)
C(58)-C(59)	1.530(2)
C(18)-C(20)	1.527(2)
C(12)-C(13)	1.376(2)
C(13)-C(14)	1.400(2)

C(4)-O(6)-C(41)	115.04(12)
C(7)-O(10)-C(71)	113.89(12)
C(14)-O(2)-C(17)	117.32(13)
C(8)-O(12)-C(81)	115.48(13)
C(3)-N(1)-C(2)	134.08(13)
C(3)-N(1)-N(2)	119.48(12)
C(2)-N(1)-N(2)	94.26(11)
C(8)-N(4)-N(3)	113.55(12)
C(8)-N(4)-C(5)	119.29(12)
N(3)-N(4)-C(5)	88.91(10)
C(7)-N(3)-C(6)	131.41(13)
C(7)-N(3)-N(4)	125.38(12)
C(6)-N(3)-N(4)	94.54(11)
C(4)-N(2)-N(1)	112.41(12)
C(4)-N(2)-C(1)	120.92(12)
N(1)-N(2)-C(1)	89.42(10)
C(54)-O(8)-C(57)	116.80(14)
C(3)-O(4)-C(31)	113.92(12)
O(1)-C(2)-N(1)	131.92(14)

O(1)-C(2)-C(1)	136.96(15)
N(1)-C(2)-C(1)	91.02(11)
C(55)-C(56)-C(51)	121.66(15)
O(5)-C(4)-O(6)	126.52(14)
O(5)-C(4)-N(2)	125.38(14)
O(6)-C(4)-N(2)	107.95(12)
O(8)-C(54)-C(55)	124.22(15)
O(8)-C(54)-C(53)	115.96(15)
C(55)-C(54)-C(53)	119.82(15)
C(56)-C(55)-C(54)	119.27(15)
C(16)-C(11)-C(12)	118.12(15)
C(16)-C(11)-C(1)	121.14(14)
C(12)-C(11)-C(1)	120.66(14)
O(9)-C(7)-O(10)	127.42(15)
O(9)-C(7)-N(3)	122.57(14)
O(10)-C(7)-N(3)	109.99(13)
O(11)-C(8)-O(12)	127.20(15)
O(11)-C(8)-N(4)	125.41(14)
O(12)-C(8)-N(4)	107.22(13)
C(53)-C(52)-C(51)	120.89(15)
C(11)-C(1)-C(18)	114.04(12)
C(11)-C(1)-C(2)	115.38(13)
C(18)-C(1)-C(2)	113.05(13)
C(11)-C(1)-N(2)	115.78(12)
C(18)-C(1)-N(2)	110.36(12)
C(2)-C(1)-N(2)	85.00(11)
O(3)-C(3)-O(4)	127.38(15)
O(3)-C(3)-N(1)	122.98(14)
O(4)-C(3)-N(1)	109.63(13)
O(7)-C(6)-N(3)	132.03(15)
O(7)-C(6)-C(5)	136.80(15)
N(3)-C(6)-C(5)	91.07(11)
C(14)-C(15)-C(16)	119.26(15)
C(51)-C(5)-C(58)	115.48(13)
C(51)-C(5)-C(6)	114.48(12)
C(58)-C(5)-C(6)	112.48(13)

C(51)-C(5)-N(4)	114.95(12)
C(58)-C(5)-N(4)	110.80(12)
C(6)-C(5)-N(4)	84.93(11)
C(56)-C(51)-C(52)	118.12(15)
C(56)-C(51)-C(5)	120.10(14)
C(52)-C(51)-C(5)	121.78(14)
C(52)-C(53)-C(54)	120.21(15)
C(59)-C(58)-C(60)	110.05(13)
C(59)-C(58)-C(5)	109.28(13)
C(60)-C(58)-C(5)	112.20(13)
C(11)-C(16)-C(15)	121.62(14)
C(20)-C(18)-C(19)	110.81(14)
C(20)-C(18)-C(1)	110.13(13)
C(19)-C(18)-C(1)	112.41(13)
C(13)-C(12)-C(11)	120.89(15)
C(12)-C(13)-C(14)	120.34(15)
O(2)-C(14)-C(15)	124.92(15)
O(2)-C(14)-C(13)	115.32(14)
C(15)-C(14)-C(13)	119.76(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for D08001. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(6)	25(1)	16(1)	18(1)	1(1)	9(1)	2(1)
O(1)	21(1)	20(1)	24(1)	5(1)	11(1)	1(1)
O(10)	22(1)	24(1)	25(1)	-4(1)	16(1)	-5(1)
O(5)	27(1)	24(1)	19(1)	-2(1)	12(1)	-2(1)
O(3)	21(1)	25(1)	23(1)	2(1)	12(1)	1(1)
O(7)	24(1)	22(1)	24(1)	-5(1)	13(1)	-3(1)
O(2)	26(1)	26(1)	31(1)	5(1)	17(1)	-3(1)
O(11)	18(1)	27(1)	23(1)	1(1)	9(1)	3(1)
O(9)	25(1)	28(1)	27(1)	-7(1)	16(1)	-9(1)
O(12)	20(1)	16(1)	22(1)	-1(1)	8(1)	-1(1)
N(1)	20(1)	18(1)	18(1)	4(1)	10(1)	2(1)
N(4)	15(1)	19(1)	19(1)	-4(1)	9(1)	-4(1)
N(3)	17(1)	20(1)	20(1)	-7(1)	9(1)	-5(1)
N(2)	19(1)	19(1)	16(1)	5(1)	9(1)	3(1)
O(8)	32(1)	27(1)	30(1)	8(1)	19(1)	1(1)
O(4)	26(1)	24(1)	22(1)	7(1)	16(1)	5(1)
C(2)	15(1)	18(1)	18(1)	-1(1)	7(1)	-3(1)
C(56)	18(1)	22(1)	23(1)	-3(1)	10(1)	-2(1)
C(4)	14(1)	22(1)	18(1)	1(1)	9(1)	-1(1)
C(60)	23(1)	23(1)	25(1)	3(1)	11(1)	1(1)
C(54)	24(1)	21(1)	29(1)	4(1)	18(1)	5(1)
C(55)	24(1)	26(1)	19(1)	2(1)	10(1)	4(1)
C(11)	20(1)	17(1)	18(1)	-1(1)	11(1)	1(1)
C(41)	28(1)	15(1)	26(1)	0(1)	13(1)	-1(1)
C(7)	18(1)	19(1)	19(1)	-1(1)	9(1)	0(1)
C(71)	31(1)	32(1)	37(1)	-5(1)	26(1)	-6(1)
C(8)	20(1)	22(1)	14(1)	1(1)	9(1)	0(1)
C(19)	25(1)	24(1)	27(1)	-5(1)	9(1)	-5(1)
C(52)	20(1)	27(1)	21(1)	-1(1)	8(1)	-2(1)
C(1)	19(1)	19(1)	17(1)	2(1)	10(1)	2(1)
C(3)	20(1)	17(1)	17(1)	-2(1)	9(1)	-2(1)

C(6)	19(1)	19(1)	18(1)	0(1)	9(1)	-1(1)
C(15)	20(1)	22(1)	21(1)	-1(1)	9(1)	-1(1)
C(5)	17(1)	20(1)	19(1)	-4(1)	11(1)	-1(1)
C(51)	17(1)	21(1)	20(1)	-2(1)	12(1)	0(1)
C(53)	22(1)	23(1)	31(1)	-1(1)	14(1)	-5(1)
C(58)	17(1)	20(1)	21(1)	-1(1)	9(1)	-1(1)
C(16)	23(1)	19(1)	18(1)	2(1)	11(1)	1(1)
C(18)	25(1)	18(1)	19(1)	-1(1)	9(1)	0(1)
C(17)	24(1)	29(1)	43(1)	3(1)	19(1)	-4(1)
C(20)	37(1)	27(1)	28(1)	-7(1)	18(1)	0(1)
C(12)	20(1)	24(1)	18(1)	2(1)	9(1)	2(1)
C(31)	36(1)	35(1)	28(1)	10(1)	23(1)	8(1)
C(59)	20(1)	27(1)	33(1)	1(1)	16(1)	3(1)
C(13)	28(1)	24(1)	21(1)	5(1)	14(1)	2(1)
C(81)	32(1)	17(1)	38(1)	0(1)	11(1)	1(1)
C(14)	26(1)	18(1)	25(1)	-1(1)	17(1)	0(1)
C(57)	49(1)	33(1)	29(1)	7(1)	20(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for D08001.

	x	y	z	U(eq)
H(56)	8480	4611	2797	25
H(60A)	10778	2850	6823	35
H(60B)	10721	3500	7889	35
H(60C)	12209	3117	8181	35
H(55)	8639	5565	1291	28
H(41A)	4533	2795	1040	35
H(41B)	5901	2742	2557	35
H(41C)	6083	2727	1174	35
H(71A)	5018	3914	6161	43
H(71B)	5989	4043	7814	43
H(71C)	5943	3179	7126	43
H(19A)	5466	6953	1487	40
H(19B)	6615	6243	1921	40
H(19C)	6591	6813	3103	40
H(52)	11837	5636	6106	28
H(15)	-332	4414	-606	25
H(53)	11963	6614	4631	30
H(58)	12074	4417	7275	23
H(16)	1390	5207	-769	24
H(18)	5542	5592	3154	26
H(17A)	-1738	4012	430	47
H(17B)	-1913	3088	760	47
H(17C)	-1486	3301	-430	47
H(20A)	3270	6728	1857	44
H(20B)	4462	6793	3466	44
H(20C)	3405	6035	2945	44
H(12)	4374	4380	3015	25
H(31A)	6267	6615	-2612	44
H(31B)	4765	6746	-3981	44
H(31C)	5503	5874	-3651	44

H(59A)	13124	3387	6498	38
H(59B)	12508	4123	5413	38
H(59C)	11640	3293	5093	38
H(13)	2685	3574	3171	28
H(81A)	9024	6888	5760	47
H(81B)	10350	7026	7284	47
H(81C)	8810	6851	7123	47
H(57A)	9626	6273	147	54
H(57B)	9727	7238	122	54
H(57C)	8550	6821	420	54

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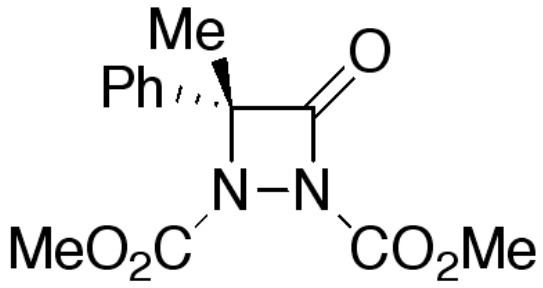
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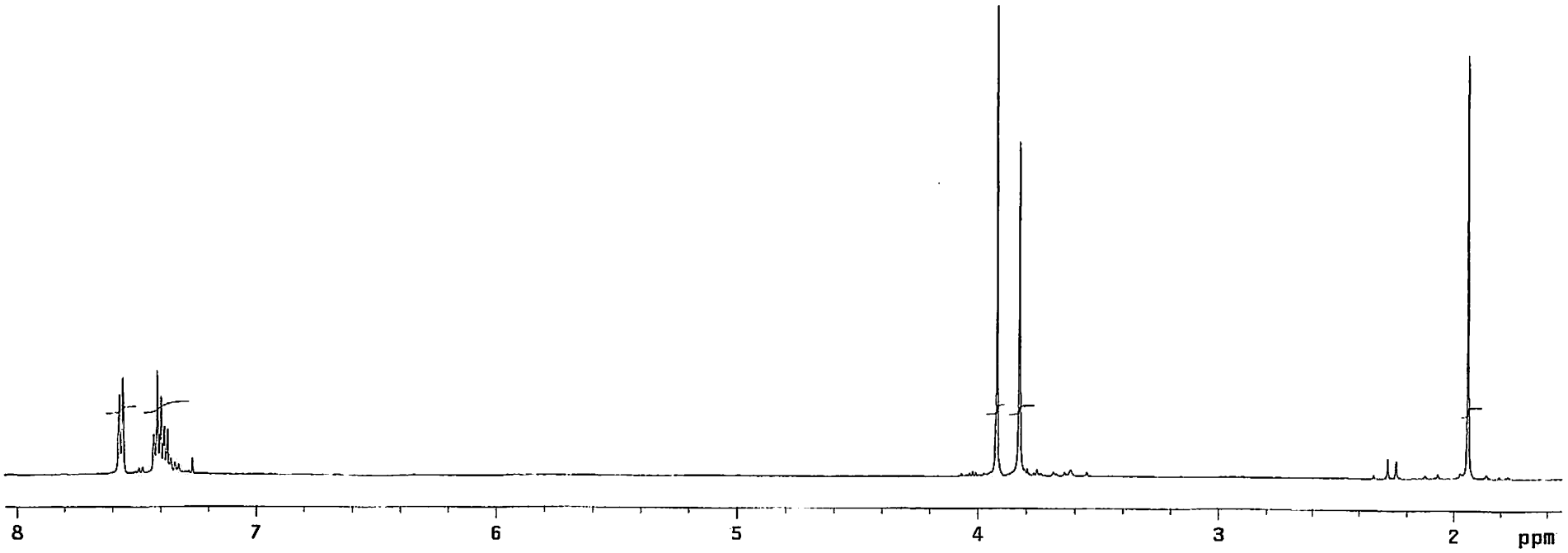
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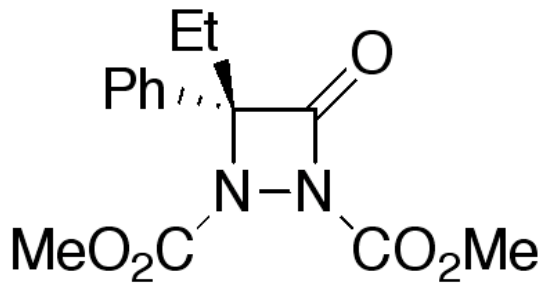
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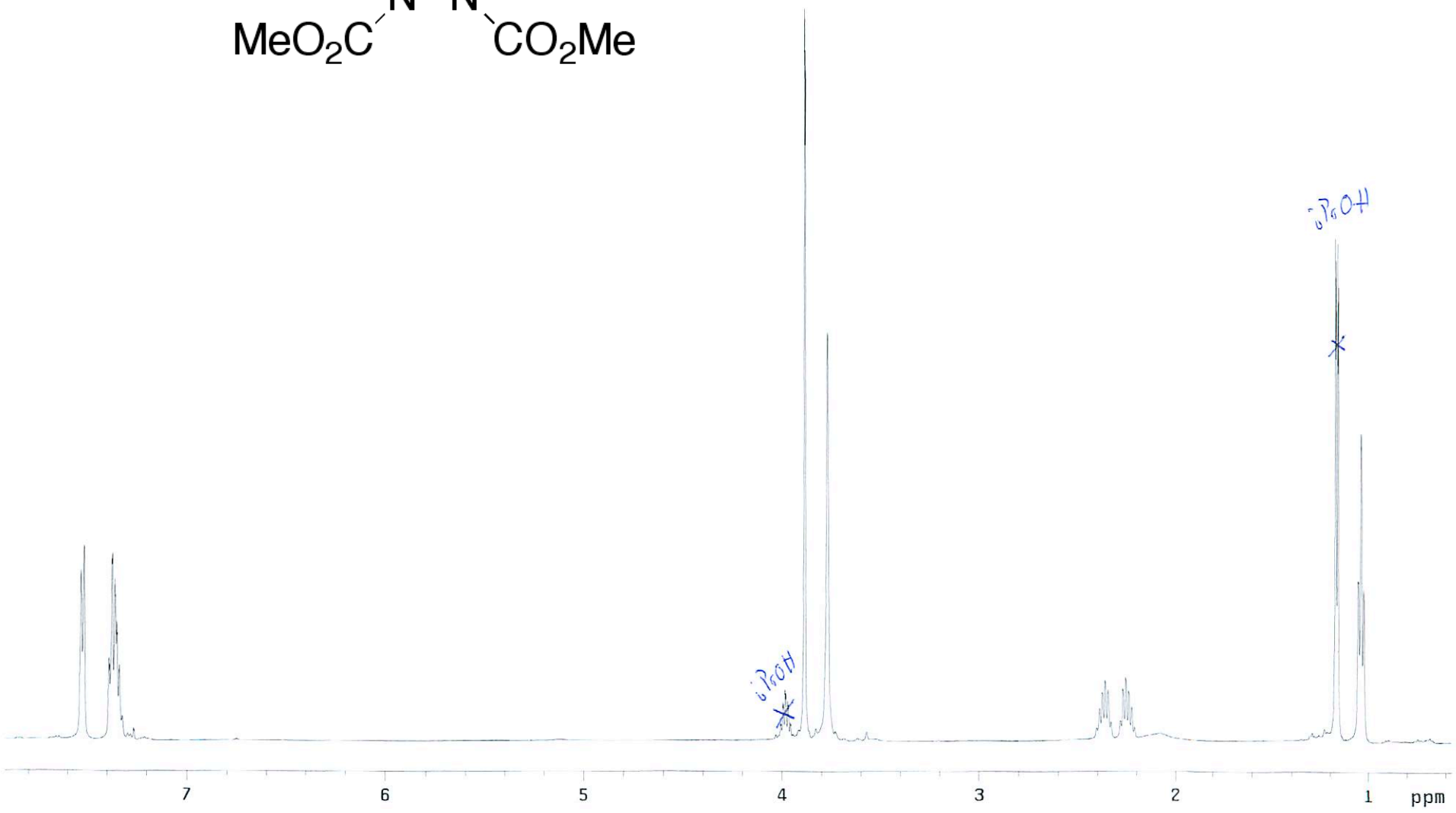
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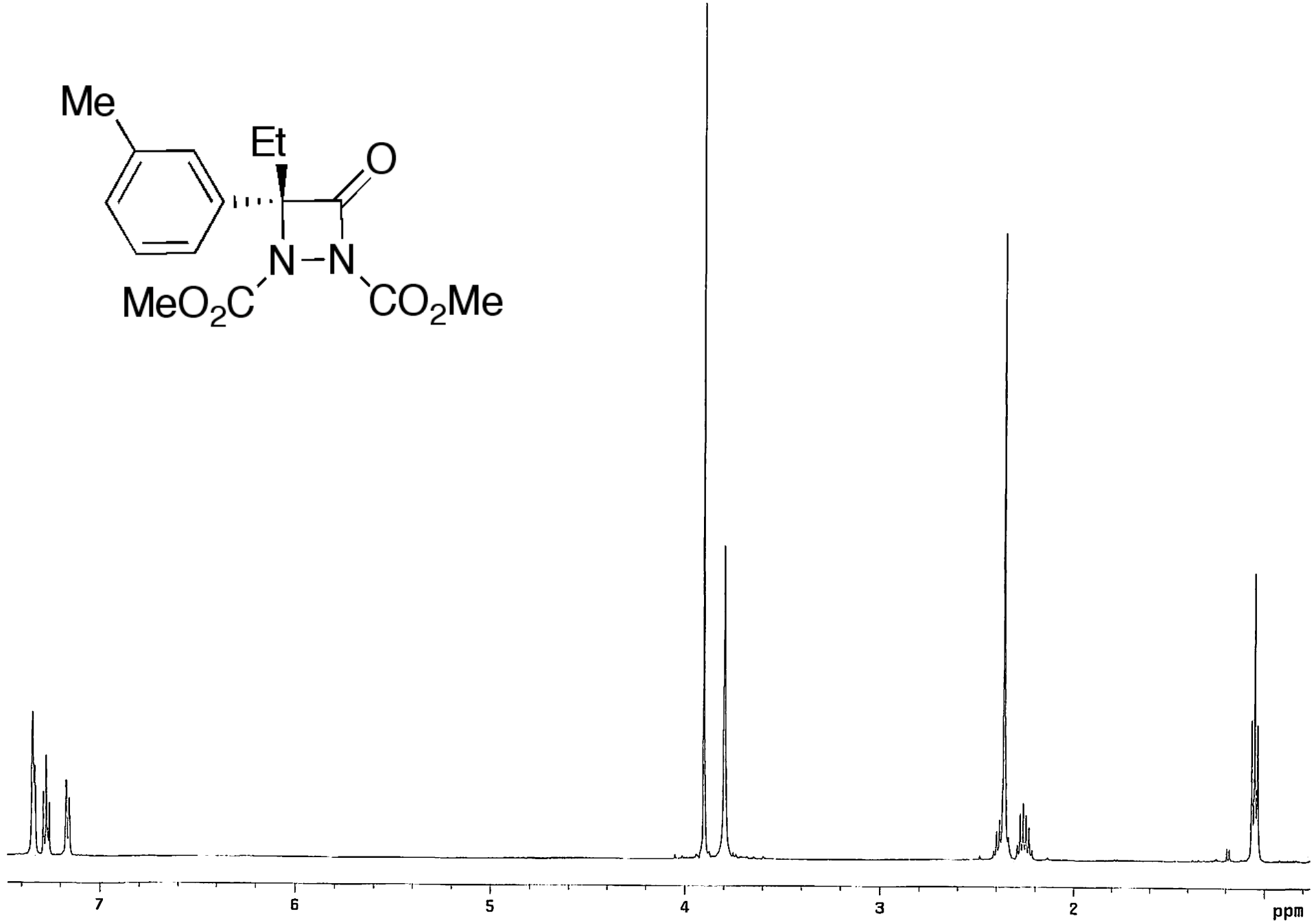
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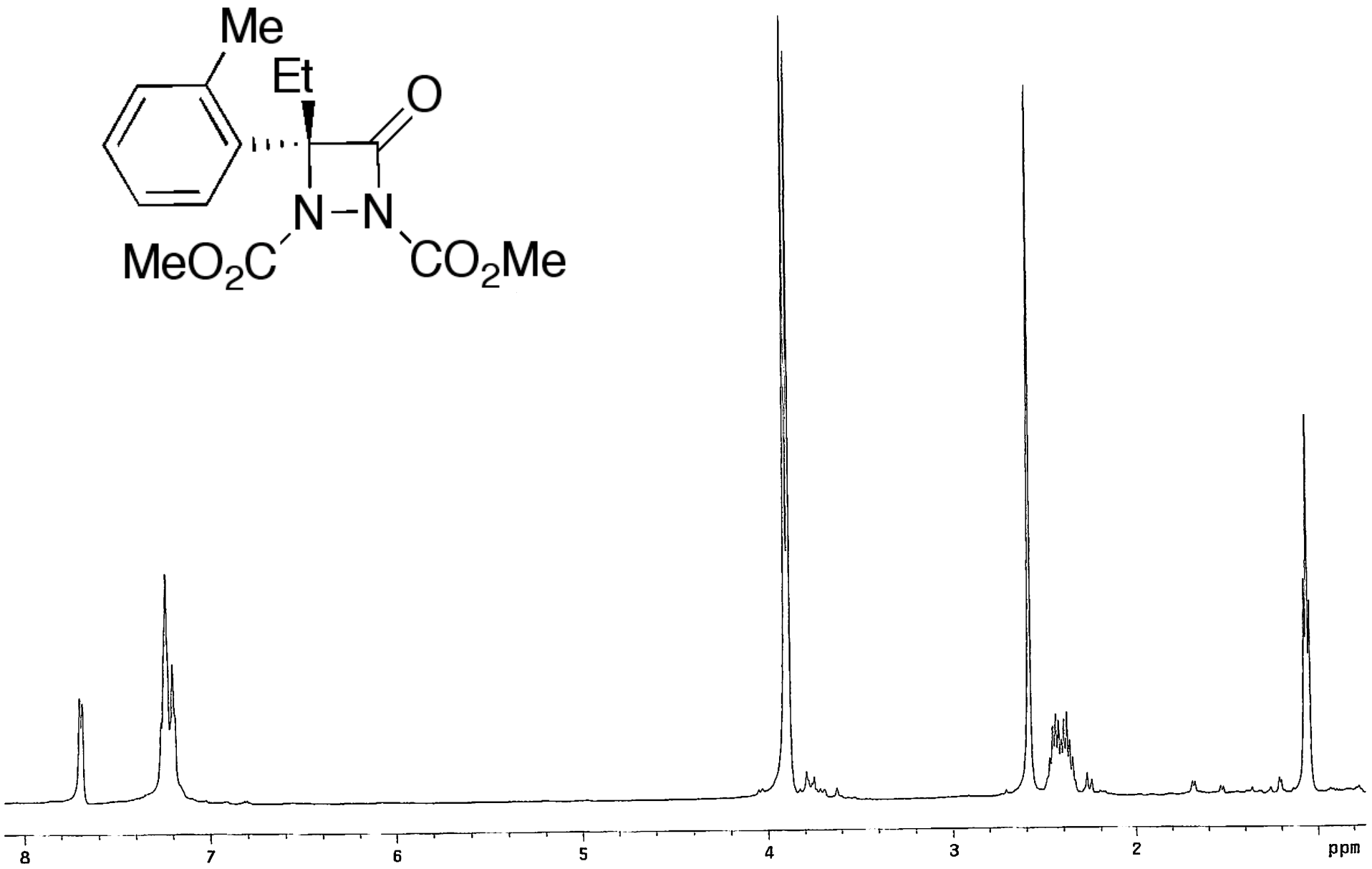
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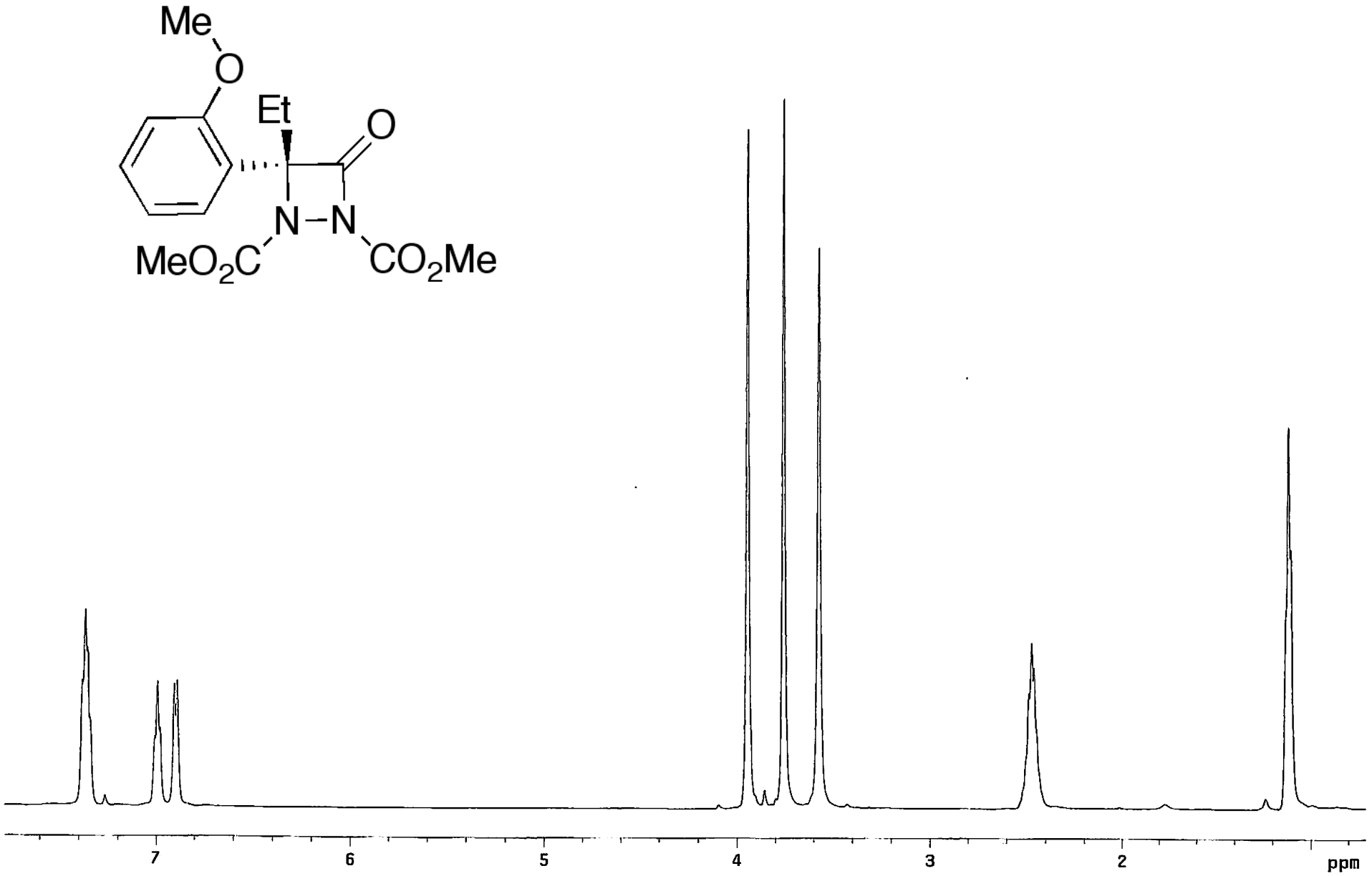
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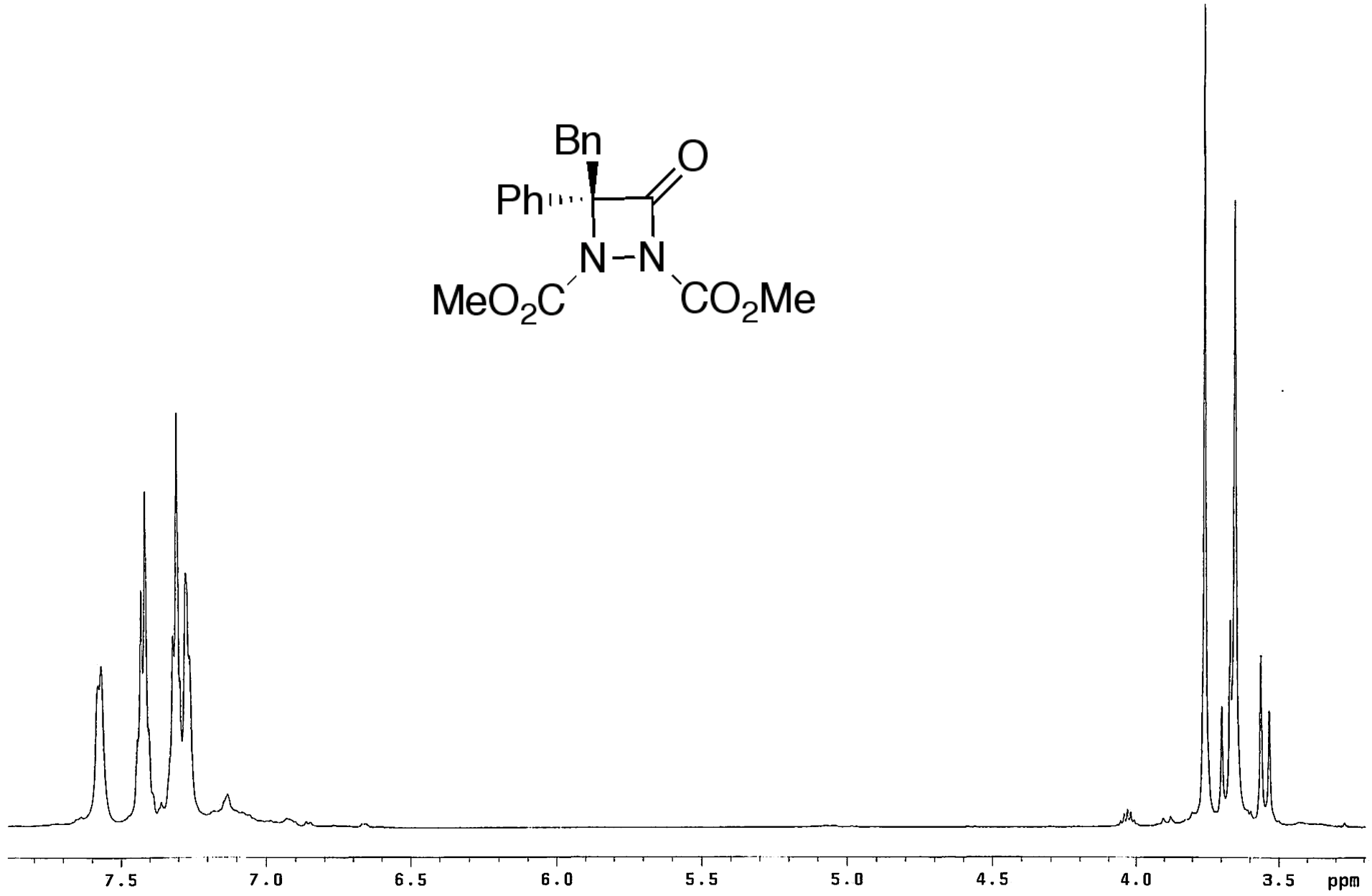
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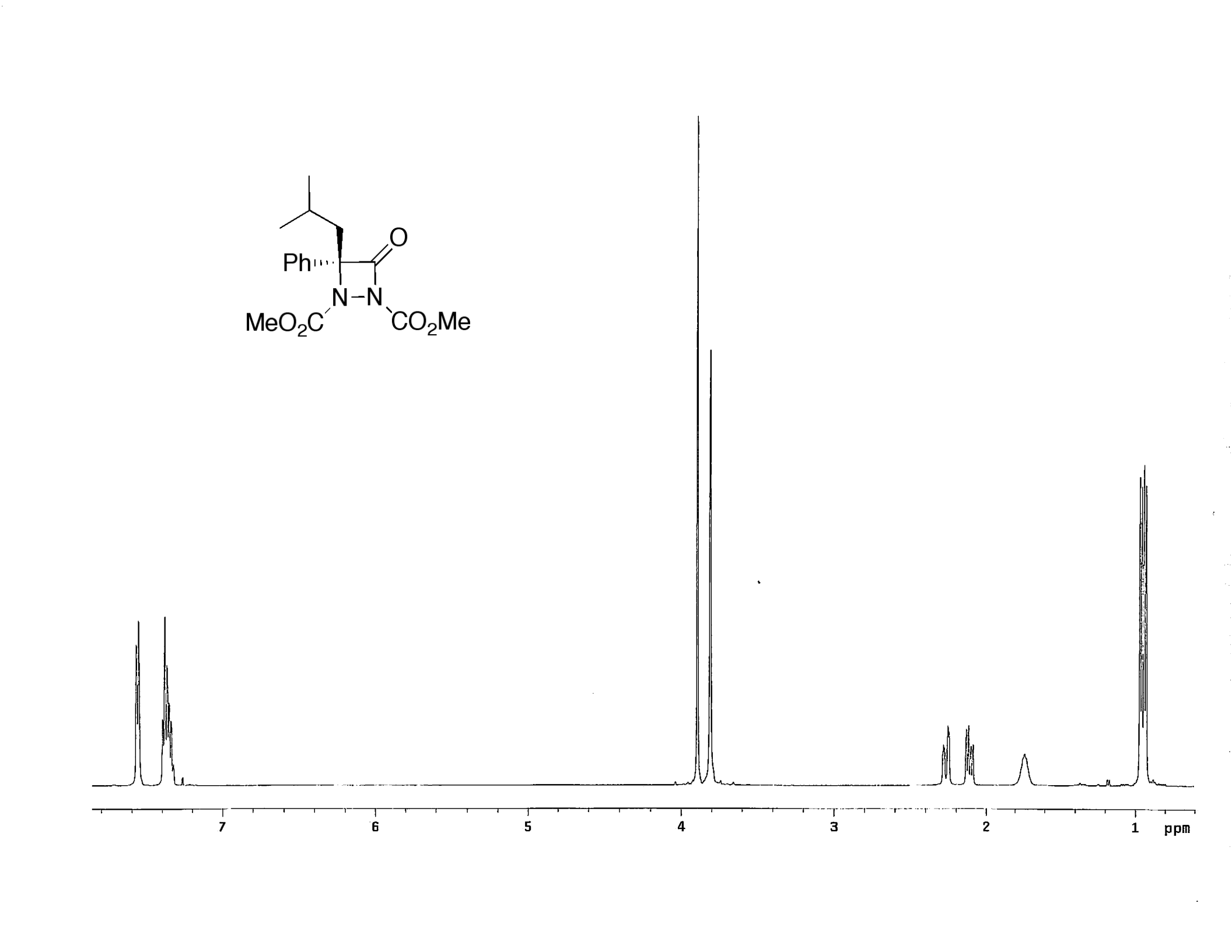
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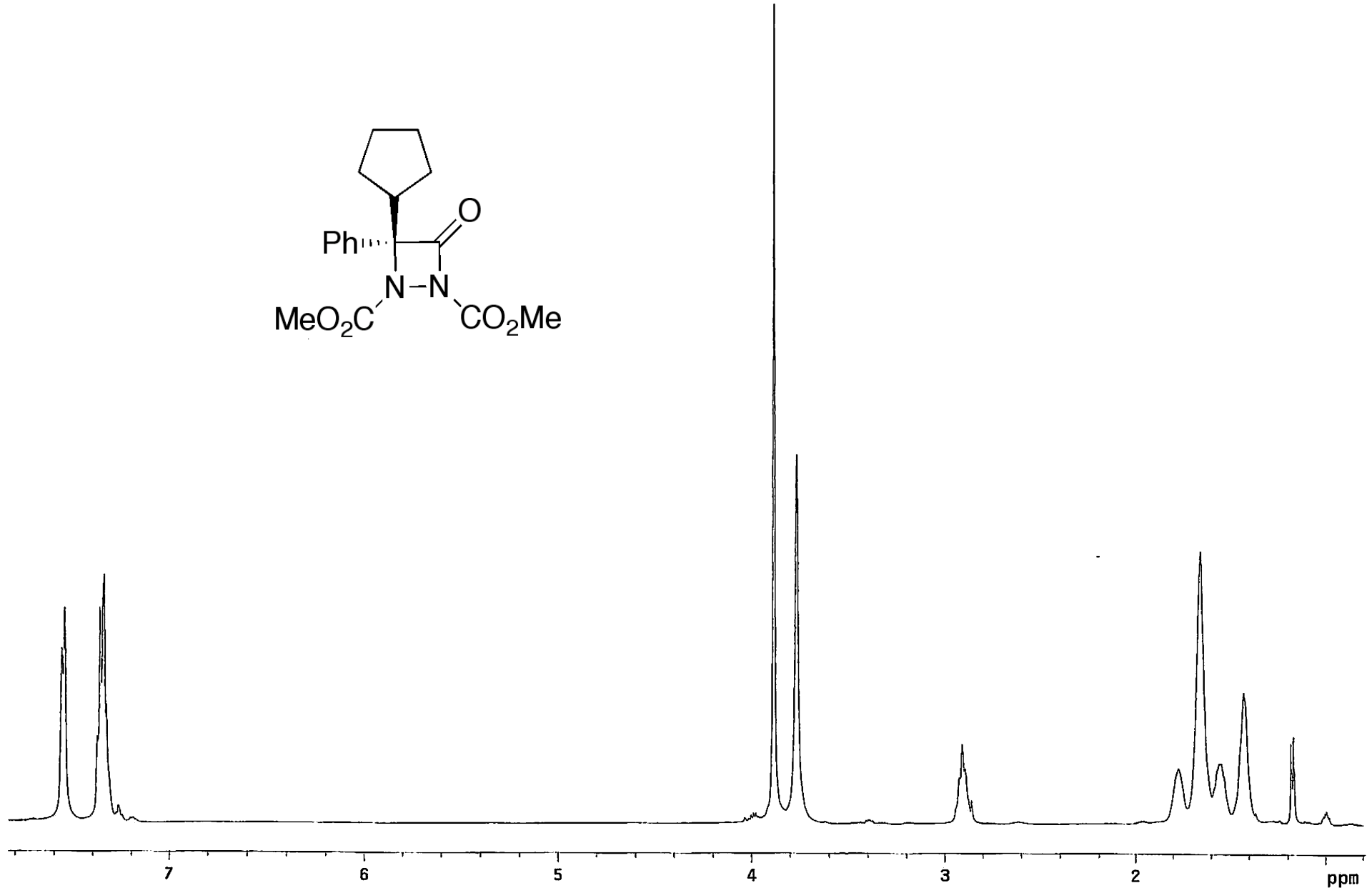
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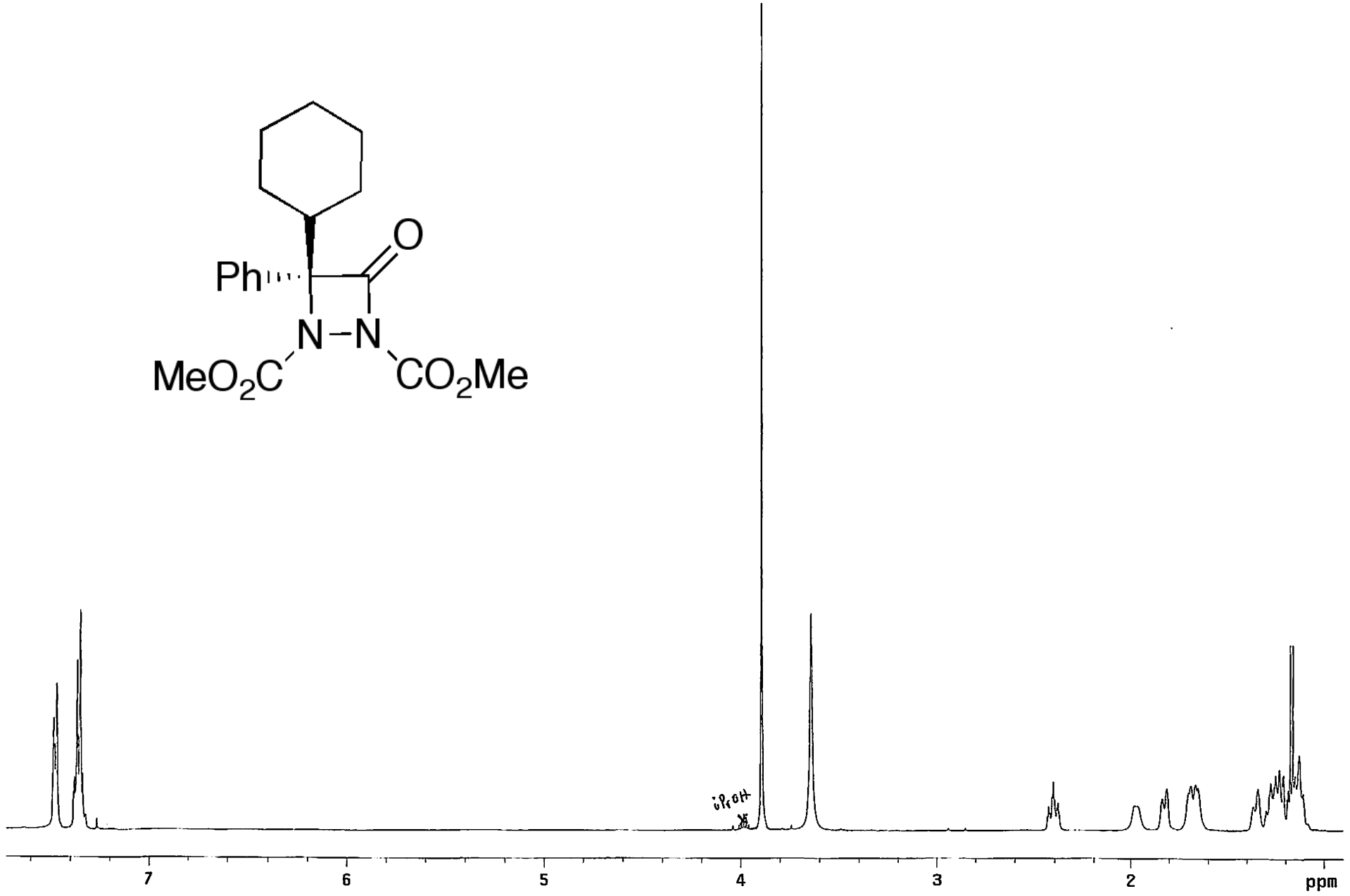
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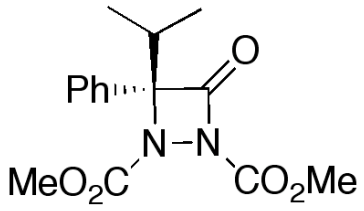
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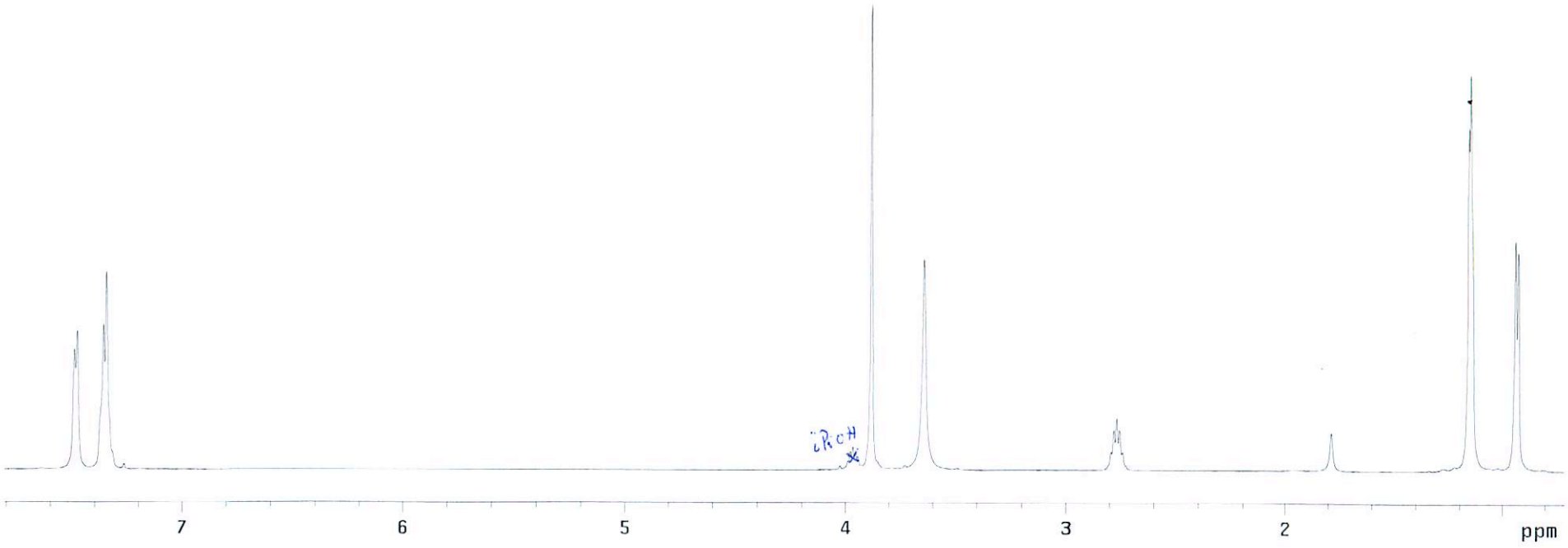
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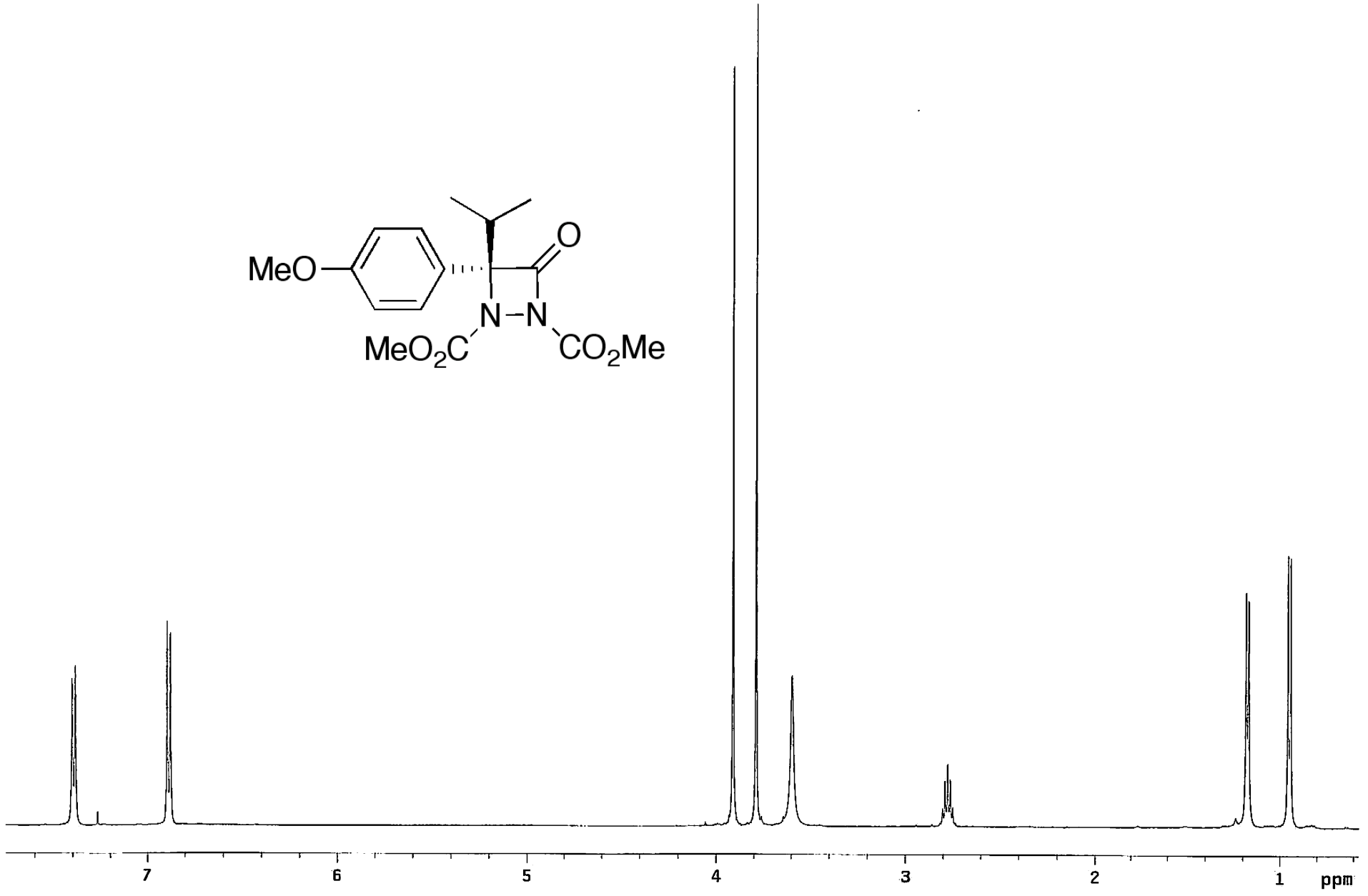
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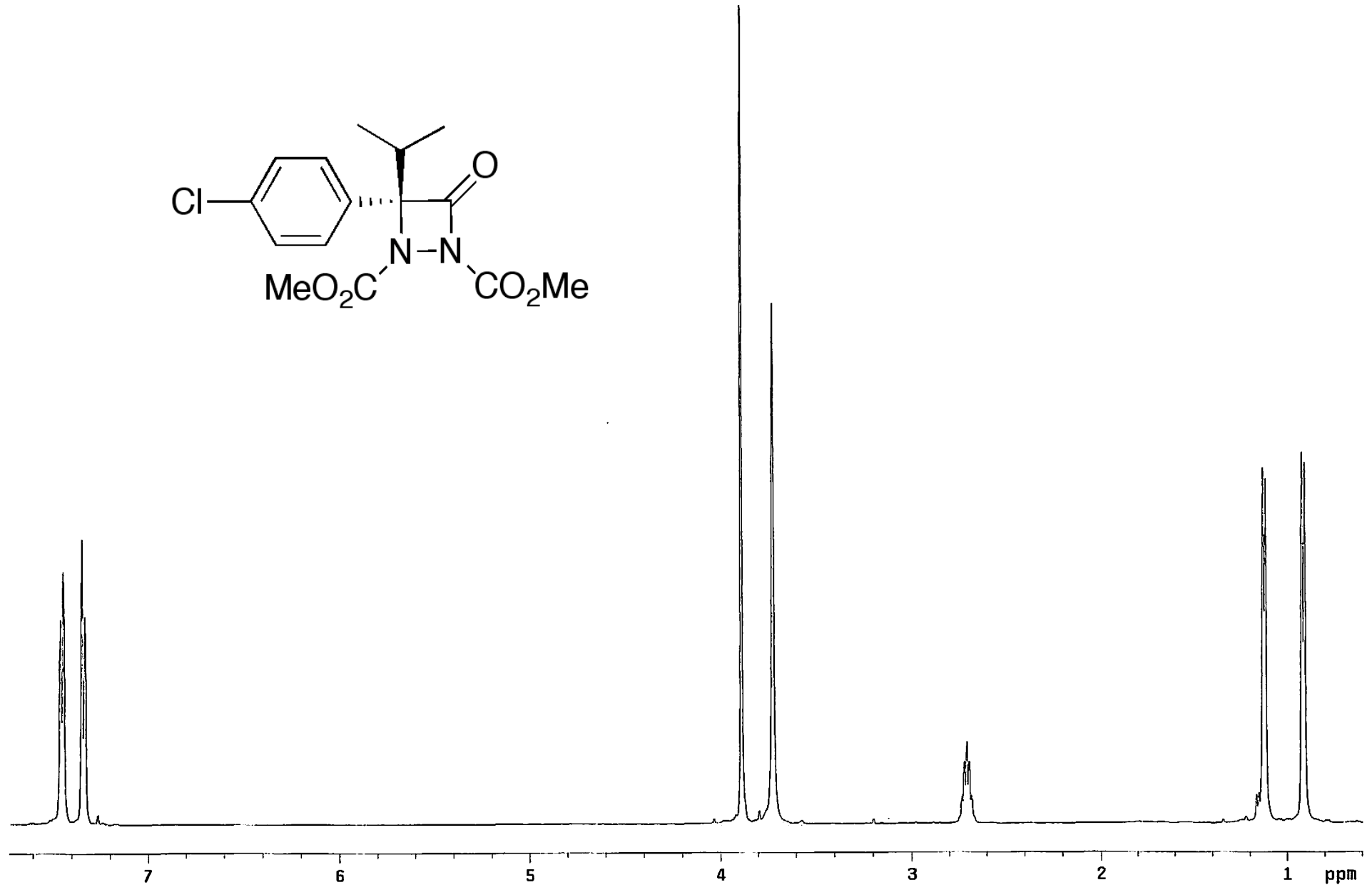
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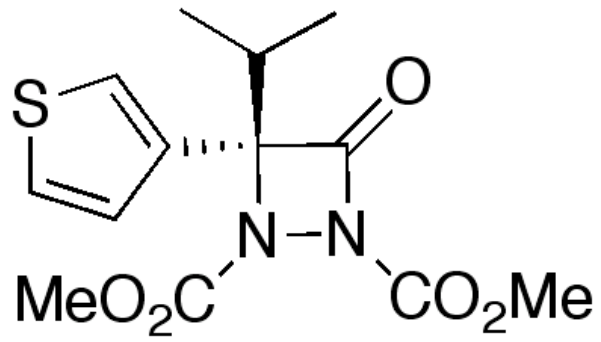
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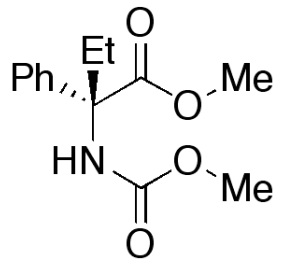
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O
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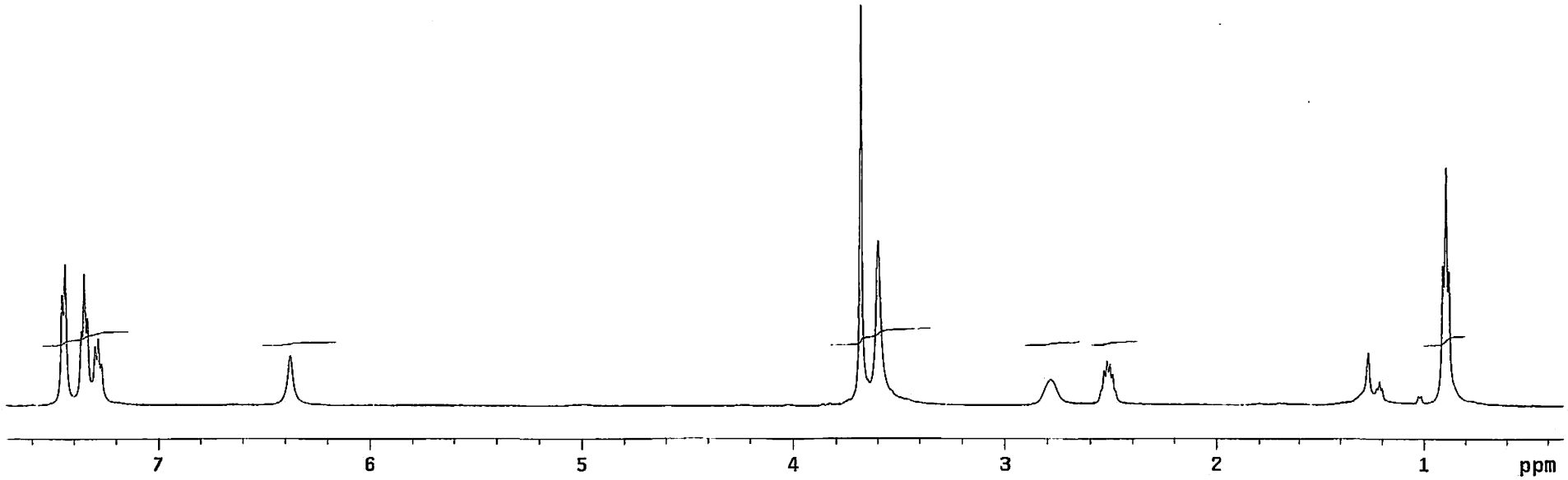
O
Me
O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5
4
3
2
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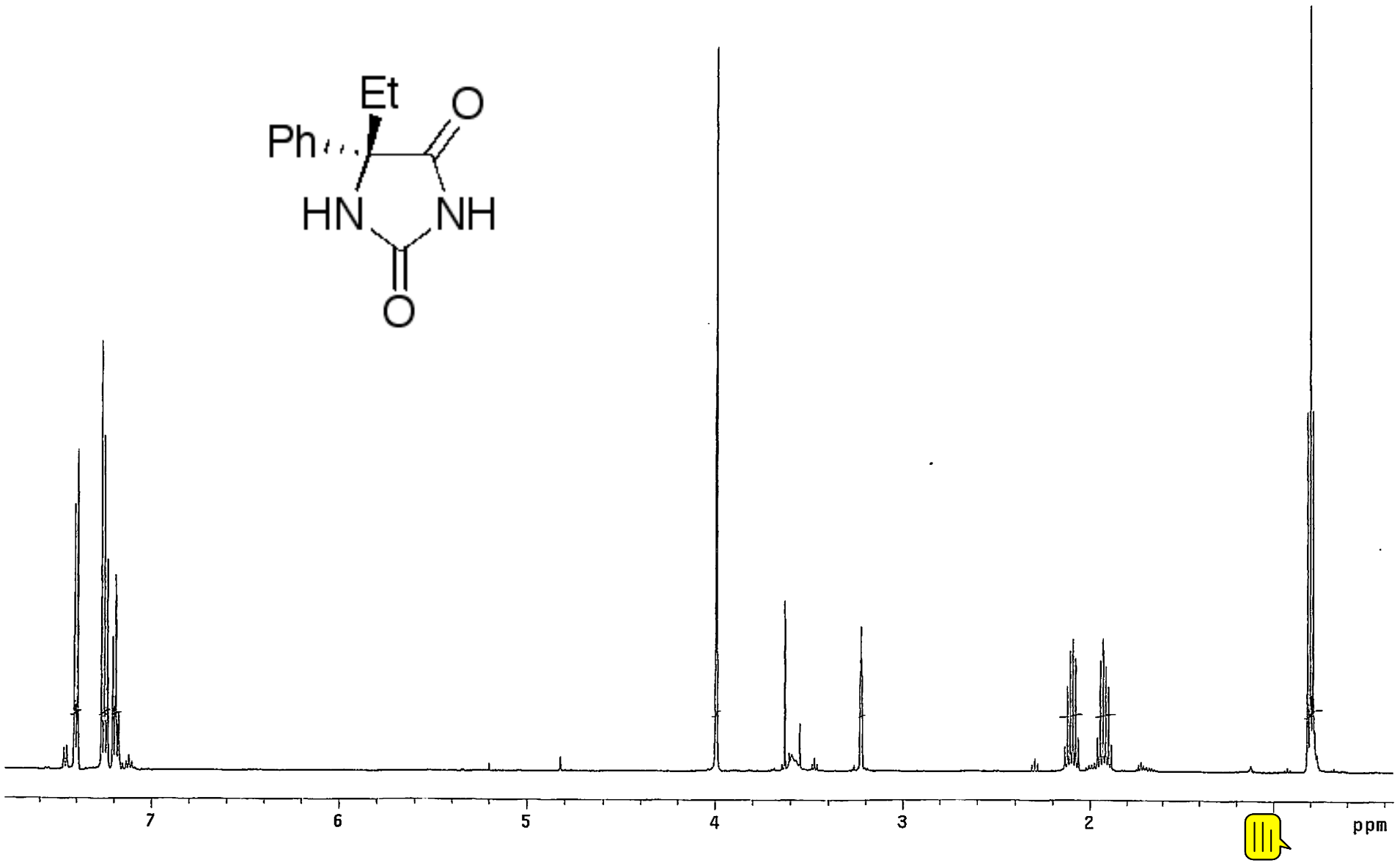
ppm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NH
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7
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4
3
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ppm