Phosphine-Catalyzed Formation of Carbon–Sulfur Bonds: Catalytic Asymmetric Synthesis of γ-Thioesters

Jianwei Sun and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Supporting Information

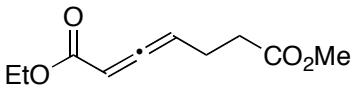
Table of Contents

I. General Information

The following reagents were purchased and used as received: toluene (Sigma-Aldrich; anhydrous in a Sure-Seal bottle), (+)-**1** (Strem Chemicals), (–)-**1** (Chiral Quest), and 2-phenylisobutyric acid (**2**; TCI). HPLC analyses were carried out on an Agilent 1100 Series system with Daicel Chiralpak® columns in hexane/isopropanol mixtures.

II. Preparation of Allenes

General Procedure A: Preparation of Allenes. A 250-mL flask was charged with (carbethoxymethylene)triphenylphosphorane (6.97 g, 20.0 mmol), evacuated, and back-filled with argon. CH_2Cl_2 (100 mL) and Et_3N (2.50 mL, 18.0 mmol) were added via syringe, and the solution was cooled to –78 °C. The acid chloride (20.0 mmol) was then added dropwise via syringe over 10 min. The solution was allowed to warm to room temperature over 3-4 h. Then, the reaction mixture was concentrated to one-third of the original volume, and pentane (100 mL) was added. The mixture was stirred for 1 h, and then it was passed through a pad of celite. The filtrate was concentrated on a rotary evaporator, and the residue was purified by flash chromatography (hexanes/Et_2O), which furnished the allene as an oil.



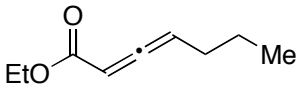
(±)-1-Ethyl 7-methyl hepta-2,3-dienedioate. Prepared from methyl 5-chloro-5-oxopentanoate according to General Procedure A (purification by flash chromatography: 10% Et_2O in hexanes; 70% yield).

^1H NMR ($CDCl_3$, 400 MHz) δ 5.72-5.67 (m, 1H), 5.64-5.61 (m, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.68 (s, 3H), 2.51-2.41 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.9, 172.7, 165.7, 94.1, 89.3, 60.8, 51.6, 32.6, 22.5, 14.1.

IR (film) 2984, 2955, 1963, 1716, 1436, 1037 cm^{-1}.

LRMS (ES^+) calcd for $C_{10}H_{15}O_4$ $(M+H)^+$ 199.1, found 199.0.



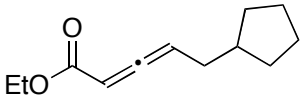
(±)-Ethyl hepta-2,3-dienoate. Prepared from valeroyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 65% yield).

^1H NMR ($CDCl_3$, 400 MHz) δ 5.62-5.54 (m, 2H), 4.21-4.14 (m, 2H), 2.10 (dq, J = 3.2 Hz, J = 7.2 Hz, 2H), 1.52-1.43 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.3, 166.3, 95.1, 88.1, 60.7, 29.5, 21.9, 14.2, 13.4.

IR (film) 2962, 2935, 2875, 1961, 1718, 1465, 1418, 1253, 1160 cm^{-1}.

LRMS (ES^+) calcd for $C_9H_{15}O_2$ $(M+H)^+$ 155.1, found 155.1.



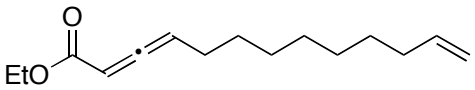
(±)-Ethyl 5-cyclopentylpenta-2,3-dienoate. Prepared from 3-cyclopentylpropanoyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 72% yield).

^1H NMR ($CDCl_3$, 400 MHz) δ 5.61-5.53 (m, 2H), 4.22-4.13 (m, 2H), 2.15-2.11 (m, 2H), 2.00-1.89 (m, 1H), 1.83-1.73 (m, 2H), 1.65-1.46 (m, 4H), 1.27 (q, J = 7.2 Hz, 3H), 1.21-1.15 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.6, 166.3, 94.6, 87.8, 60.7, 39.4, 33.9, 32.21, 32.17, 25.22, 25.19, 14.2.

IR (film) 2952, 2869, 1961, 1717, 1450, 1419, 1255, 1158, 1041 cm^{-1}.

LRMS (ES^+) calcd for $C_{12}H_{19}O_2$ $(M+H)^+$ 195.1, found 195.0.



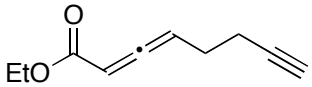
(±)-Ethyl trideca-2,3,12-trienoate. Prepared from 10-undecenoyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 75% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.84-5.72 (m, 1H), 5.64-5.53 (m, 2H), 5.01-4.91 (m, 2H), 4.21-4.15 (m, 2H), 2.15-2.09 (m, 2H), 2.06-2.00 (m, 2H), 1.48-1.41 (m, 2H), 1.38-1.30 (m, 8H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.3, 166.3, 139.1, 114.1, 95.4, 88.2, 60.7, 33.8, 29.2, 29.0, 28.8, 28.7, 27.5, 14.2.

IR (film) 3077, 2979, 2928, 2856, 1961, 1717, 1641, 1465, 1419, 1160, 1041 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{15}H_{25}O_2$ (M+H)$^+$ 237.2, found 237.1.



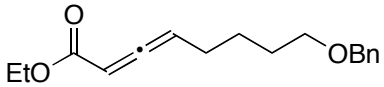
(±)-Ethyl octa-2,3-dien-7-ynoate. Prepared from hex-5-ynoyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 68% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.71-5.66 (m, 1H), 5.62-5.60 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.37-2.30 (m, 4H), 1.98 (s, 1H), 1.25 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.0, 165.9, 93.8, 89.1, 82.8, 69.3, 60.8, 26.6, 18.0, 14.2.

IR (film) 3295, 2983, 2936, 1963, 1717, 1420, 1255, 1162, 1037 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{10}H_{13}O_2$ (M+H)$^+$ 165.1, found 165.1.



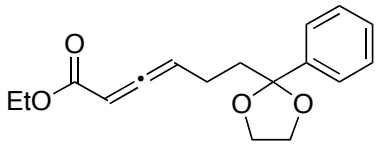
(±)-Ethyl 8-(benzyloxy)octa-2,3-dienoate. Prepared from 6-(benzyloxy)hexanoyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 60% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.30 (m, 4H), 7.29-7.26 (m, 1H), 5.63-5.57 (m, 2H), 4.50 (s, 2H), 4.21-4.16 (m, 2H), 3.48 (t, J = 6.4 Hz, 2H), 2.16 (ddd, J = 3.2 Hz, J = 11.2 Hz, J = 14.0 Hz, 2H), 1.72-1.65 (m, 2H), 1.60-1.53 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.2, 166.1, 138.5, 128.3, 127.5, 127.4, 95.0, 88.3, 72.8, 69.8, 60.7, 28.9, 27.2, 25.3, 14.2.

IR (film) 3088, 3064, 3030, 2981, 2938, 2860, 1961, 1714, 1454, 1255, 1160 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{17}H_{23}O_3$ (M+H)$^+$ 275.2, found 275.1.



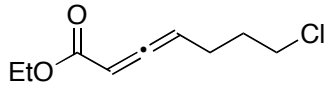
(±)-Ethyl 6-(2-phenyl-1,3-dioxolan-2-yl)hexa-2,3-dienoate. Prepared from 4-(2-phenyl-1,3-dioxolan-2-yl)butanoyl chloride according to General Procedure A (purification by flash chromatography: 10% EtOAc in hexanes; 50% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.43 (m, 2H), 7.37-7.28 (m, 3H), 6.66-6.14 (m, 1H), 5.57-5.54 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 4.04-3.98 (m, 2H), 3.82-3.77 (m, 2H), 2.24-2.18 (m, 2H), 2.06-2.02 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.0, 166.2, 142.1, 128.2, 128.0, 125.7, 109.8, 95.2, 88.8, 64.6, 64.5, 60.8, 39.1, 21.8, 14.2.

IR (film) 3060, 3028, 2981, 2890, 1961, 1743, 1717, 1448, 1259, 1039 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{17}H_{21}O_4$ (M+H)$^+$ 289.2, found 289.1.



(±)-Ethyl 7-chlorohepta-2,3-dienoate. Prepared from 5-chlorovaleroyl chloride according to General Procedure A (purification by flash chromatography: 5% Et_2O in hexanes; 70% yield).

^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.63-5.61 (m, 2H), 4.23-4.17 (m, 2H), 3.62 (t, J = 6.6 Hz, 2H), 2.33-2.29 (m, 2H), 1.97-1.92 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.2, 165.9, 93.8, 88.9, 60.8, 43.7, 31.1, 24.4, 14.1.

IR (film) 2983, 2961, 1962, 1717, 1445, 1418, 1257, 1177 cm^{-1}.

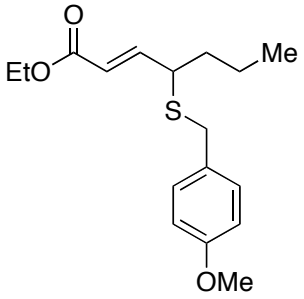
LRMS (ES$^+$) calcd for $C_9H_{14}ClO_2$ (M+H)$^+$ 189.1, found 189.0.

III. Phosphine-Catalyzed Enantioselective γ Additions of Thiols (Tables 2 and 3)

General Procedure B. In a glovebox, an oven-dried 4-mL vial was charged with (+)-**1** (14 mg, 0.050 mmol), 2-phenylisobutyric acid (41 mg, 0.25 mmol), and anhydrous toluene (2.0 mL). Next, the thiol (1.5 mmol) and the allene (0.50 mmol) were added. The vial was capped and removed from the glovebox, and the reaction mixture was stirred at room temperature for 48 h. Next, it was passed through a small plug of silica gel (0.5 cm × 2 cm), which was washed with Et_2O (3 mL × 2). The solvent was evaporated in vacuo, and the product was purified by flash chromatography.

Procedure without a glovebox (Table 2, entry 7): An oven-dried 4-mL vial was charged with (+)-**1** (14 mg, 0.050 mmol), 2-phenylisobutyric acid (41 mg, 0.25 mmol), and anhydrous toluene (2.0 mL). Next, 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol) and (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) were added. The vial was capped and then purged with nitrogen (three cycles of evacuate/refill).

The reaction mixture was stirred at room temperature for 48 h. Next, it was passed through a small plug of silica gel (0.5 cm × 2 cm), which was washed with Et_2O (3 mL × 2). The solvent was evaporated in vacuo, and the product was purified by flash chromatography (69% yield, 92% ee).



(*E*)-Ethyl 4-(4-methoxybenzylthio)hept-2-enoate (Table 2, entry 1). The compound was prepared according to General Procedure B from (±)-ethyl hepta-2,3-dienoate (77 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (5→12% Et_2O in hexanes), the title compound was isolated as a colorless oil (125 mg, 81% yield) with 91% ee.

$[\alpha]_D^{22}$ = +234 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC-H column; 2.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 10.8 min (minor), 11.6 min (major).

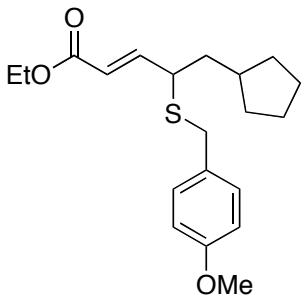
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (123 mg, 80% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (dd, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 15.6 Hz, *J* = 10.0 Hz, 1H), 5.70 (d, *J* = 15.6 Hz, 1H), 4.22 (qd, *J* = 7.2 Hz, *J* = 0.8 Hz, 2H), 3.79 (s, 3H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.16-3.10 (m, 1H), 1.60-1.53 (m, 2H), 1.37-1.24 (m, 5H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 158.6, 148.2, 130.0, 129.8, 120.9, 113.9, 60.5, 55.2, 45.6, 35.5, 34.5, 20.4, 14.3, 13.7.

IR (film) 3032, 2959, 2933, 2873, 1717, 1647, 1611, 1512, 1174 cm^{-1}.

LRMS (ES^+) calcd for $C_{17}H_{24}NaO_3S$ $(M+Na)^+$ 331.1, found 331.1.



(*E*)-Ethyl 5-cyclopentyl-4-(4-methoxybenzylthio)pent-2-enoate (Table 2, entry 2). The compound was prepared according to General Procedure B from (±)-ethyl 5-cyclopentylpenta-2,3-dienoate (97 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (5→20% Et_2O in hexanes), the title compound was isolated as a colorless oil (139 mg, 80% yield) with 92% ee.

$[\alpha]_D^{22}$ = +167 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 8.0 min (minor), 9.2 min (major).

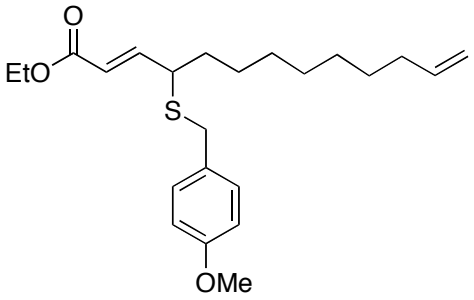
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (132 mg, 76% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 9.6 Hz, *J* = 15.2 Hz, 1H), 5.69 (d, *J* = 15.2 Hz, 1H), 4.20 (q, *J* = 7.6 Hz, 2H), 3.77 (s, 3H), 3.60 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H), 3.18-3.12 (m, 1H), 1.87-1.79 (m, 1H), 1.70-1.42 (m, 8H), 1.30 (t, *J* = 7.2 Hz, 3H) , 1.03-0.95 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 158.5, 148.3, 129.9, 129.6, 120.6, 113.8, 60.3, 55.1, 45.2, 39.7, 37.6, 34.4, 32.6, 32.0, 24.91, 24.89, 14.2.

IR (film) 2950, 2868, 1718, 1646, 1610, 1512, 1368, 1174 cm^{-1}.

LRMS (ES^+) calcd for $C_{20}H_{28}KO_3S$ $(M+K)^+$ 387.1, found 387.1.



(*E*)-Ethyl 4-(4-methoxybenzylthio)trideca-2,12-dienoate (Table 2, entry 3). The compound was prepared according to General Procedure B from (±)-ethyl trideca-2,3,12-trienoate (118 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (3→10% Et_2O in hexanes), the title compound was isolated as a colorless oil (160 mg, 82% yield) with 91% ee.

$[\alpha]_D^{22}$ = +168 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 7.1 min (major), 7.7 min (minor).

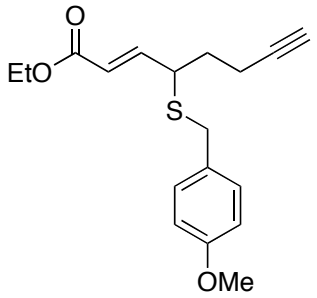
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (156 mg, 80% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 10.0 Hz, *J* = 15.6 Hz, 1H), 5.84-5.74 (m, 1H), 5.70 (d, *J* = 15.6 Hz, 1H), 5.00-4.91 (m, 2H), 4.25-4.18 (m, 2H), 3.78 (s, 3H), 3.60 (d, *J* = 13.6 Hz, 1H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.13-3.07 (m, 1H), 2.04-1.98 (m, 2H), 1.62-1.50 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.35-1.22 (m, 10H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 158.5, 148.2, 139.0, 129.9, 129.7, 120.8, 114.1, 113.8, 60.4, 55.1, 45.8, 34.4, 33.7, 33.3, 29.10, 29.07, 28.9, 28.7, 27.0, 14.2.

IR (film) 3032, 2959, 2933, 2873, 2836, 1717, 1647, 1610, 1512, 1465, 1368, 1174, 1037 cm^{-1}.

LRMS (ES^+) calcd for $C_{23}H_{34}NaO_3S$ $(M+Na)^+$ 413.2, found 413.1.



(*E*)-Ethyl 4-(4-methoxybenzylthio)oct-2-en-7-ynoate (Table 2, entry 4). The compound was prepared according to General Procedure B from (±)-ethyl octa-2,3-dien-7-ynoate (82 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (5→20% Et_2O in hexanes), the title compound was isolated as a colorless oil (145 mg, 91% yield) with 85% ee.

$[\alpha]_D^{22}$ = +177 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC column; 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 20.1 min (minor), 22.8 min (major).

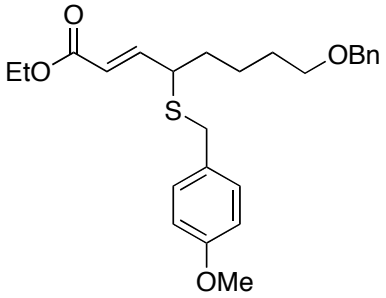
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (130 mg, 82% yield) with 85% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.17 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.68 (dd, *J* = 9.6 Hz, *J* = 15.2 Hz, 1H), 5.72 (d, *J* = 15.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 3.60 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.32-3.26 (m, 1H), 2.28-2.15 (m, 2H), 1.89 (t, *J* = 2.8 Hz, 1H), 1.80-1.73 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.0, 158.6, 146.9, 129.9, 129.3, 121.4, 113.8, 82.6, 69.3, 60.4, 55.1, 44.5, 34.4, 31.8, 16.2, 14.1.

IR (film) 3293, 3032, 2980, 2935, 2836, 1713, 1647, 1610, 1512, 1034 cm^{-1}.

LRMS (ES^+) calcd for $C_{18}H_{22}NaO_3S$ $(M+Na)^+$ 341.1, found 341.1.



(*E*)-Ethyl 8-(benzyloxy)-4-(4-methoxybenzylthio)oct-2-enoate (Table 2, entry 5). The compound was prepared according to General Procedure B from (±)-ethyl 8-(benzyloxy)octa-2,3-dienoate (137 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (5→20% Et_2O in hexanes), the title compound was isolated as a colorless oil (175 mg, 82% yield) with 92% ee.

$[\alpha]_D^{22}$ = +143 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 3.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 13.8 min (minor), 15.1 min (major).

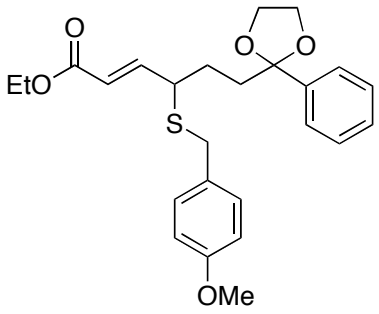
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (171 mg, 80% yield) with 93% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.26 (m, 5H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.73 (dd, *J* = 10.0 Hz, *J* = 15.6 Hz, 1H), 5.71 (d, *J* = 15.6 Hz, 1H), 4.47 (s, 2H), 4.23 (dq, *J* = 1.2 Hz, *J* = 7.2 Hz, 2H), 3.79 (m, 3H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.42 (d, *J* = 6.4 Hz, 2H), 3.15-3.09 (m, 1H), 1.65-1.52 (m, 4H), 1.45-1.39 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 158.5, 148.0, 138.4, 129.9, 129.6, 128.3, 127.5, 127.4, 121.0, 113.8, 72.8, 69.8, 60.4, 55.1, 45.7, 34.4, 33.2, 29.2, 23.8, 14.2.

IR (film) 3063, 3031, 2980, 2937, 2859, 1713, 1647, 1610, 1512, 1367, 1103 cm^{-1}.

LRMS (ES^+) calcd for $C_{25}H_{33}O_4S$ $(M+H)^+$ 429.2, found 429.1.



(*E*)-Ethyl 4-(4-methoxybenzylthio)-6-(2-phenyl-1,3-dioxolan-2-yl)hex-2-enoate (Table 2, entry 6). The compound was prepared according to General Procedure B from (±)-ethyl 6-(2-phenyl-1,3-dioxolan-2-yl)hexa-2,3-dienoate (144 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (10→30% Et_2O in hexanes), the title compound was isolated as a colorless oil (199 mg, 90% yield) with 90% ee.

$[\alpha]_D^{22}$ = +151 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 13.8 min (major), 19.0 min (minor).

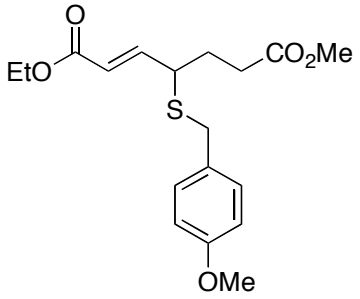
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (192 mg, 87% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.38 (m, 2H), 7.34-7.28 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.67 (dd, *J* = 15.6 Hz, *J* = 9.6 Hz, 1H), 5.65 (d, *J* = 15.6 Hz, 1H), 4.20 (dq, *J* = 1.6 Hz, *J* = 7.2 Hz, 2H), 3.99-3.93 (m, 2H), 3.79 (s, 3H), 3.76-3.70 (m, 2H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.11-3.05 (m, 1H), 1.96-1.83 (m, 2H), 1.74-1.65 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 158.6, 147.8, 142.2, 130.0, 129.7, 128.1, 127.9, 125.6, 121.1, 113.9, 109.8, 64.51, 64.46, 60.5, 55.2, 45.6, 37.8, 34.3, 27.4, 14.2.

IR (film) 3060, 3030, 2957, 2892, 2836, 1767, 1716, 1646, 1610, 1512, 1447, 1036 cm^{-1}.

LRMS (ES^+) calcd for $C_{25}H_{30}NaO_5S$ $(M+Na)^+$ 465.2, found 465.1.



(*E*)-1-Ethyl 7-methyl 4-(4-methoxybenzylthio)hept-2-enedioate (Table 2, entry 7). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (first column with 15→30%

Et_2O in hexanes; second column with 3→4% Et_2O in CH_2Cl_2), the title compound was isolated as a white solid (130 mg, 74% yield) with 91% ee.

$[\alpha]_D^{22}$ = +188 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC column; 10.0% *i*-PrOH in hexanes; 0.5 mL/min; retention times: 44.5 min (minor), 46.3 min (major).

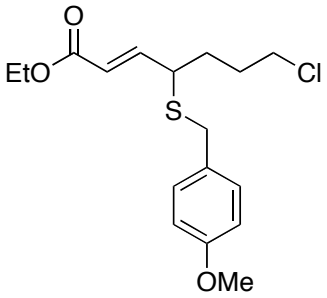
The second run was also performed with (+)-**1**. The product was isolated as a white solid (123 mg, 70% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.68 (dd, *J* = 9.6 Hz, *J* = 15.2 Hz, 1H), 5.69 (d, *J* = 15.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 3.59 (s, 3H), 3.59 (d, *J* = 13.2 Hz, 1H), 3.49 (d, *J* = 13.6 Hz, 1H), 3.15-3.08 (m, 1H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.91-1.86 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 166.0, 158.6, 147.0, 130.0, 129.4, 121.5, 113.9, 60.5, 55.2, 51.6, 45.0, 34.4, 31.3, 28.2, 14.2.

IR (film) 2982, 2953, 2837, 1736, 1717, 1647, 1610, 1512, 1250 cm^{-1}.

LRMS (ES^+) calcd for $C_{18}H_{24}NaO_5S$ $(M+Na)^+$ 375.1, found 375.1.



(*E*)-Ethyl 7-chloro-4-(4-methoxybenzylthio)hept-2-enoate (Table 2, entry 8). The compound was prepared according to General Procedure B from (±)-ethyl 7-chlorohepta-2,3-dienoate (94 mg, 0.50 mmol) and 4-methoxybenzyl mercaptan (210 μL, 1.50 mmol). After purification by flash chromatography (5→15% Et_2O in hexanes), the title compound was isolated as a colorless oil (142 mg, 83% yield) with 93% ee.

$[\alpha]_D^{22}$ = +167 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 2.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 17.1 min (minor), 18.4 min (major).

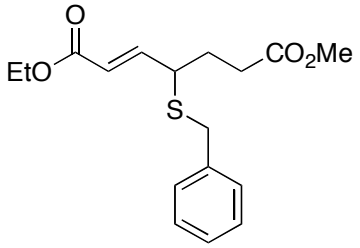
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (137 mg, 80% yield) with 93% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 15.6 Hz, *J* = 9.6 Hz, 1H), 5.73 (d, *J* = 15.6 Hz, 1H), 4.25-4.19 (m, 2H), 3.80 (s, 3H), 3.64 (d, *J* = 13.6 Hz, 1H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.46 (t, *J* = 6.0 Hz, 2H), 3.15-3.10 (m, 1H), 1.85-1.73 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 158.6, 147.3, 129.9, 129.4, 121.2, 113.9, 60.5, 55.2, 44.9, 44.2, 34.4, 30.5, 29.9, 14.2.

IR (film) 2978, 2959, 2935, 1717, 1648, 1611, 1512, 1251 cm^{-1}.

LRMS (ES^+) calcd for $C_{17}H_{23}ClNaO_3S$ $(M+Na)^+$ 365.1, found 365.0.



(*E*)-1-Ethyl 7-methyl 4-(benzylthio)hept-2-enedioate (Table 3, entry 1). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and benzyl mercaptan (180 μL, 1.50 mmol). After purification by flash chromatography (first column with 10→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (126 mg, 78% yield) with 92% ee.

$[\alpha]_D^{22}$ = +161 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AS-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 15.9 min (major), 20.5 min (minor).

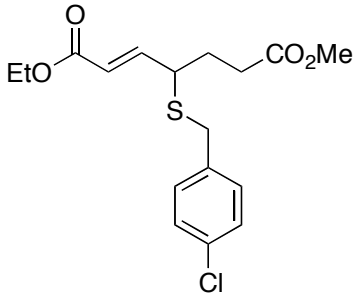
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (122 mg, 76% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.21 (m, 4H), 7.20-7.16 (m, 1H), 6.67 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz, 1H), 5.69 (d, *J* = 15.2 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.56 (s, 3H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.14-3.08 (m, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.90-1.84 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 166.0, 147.0, 137.6, 128.9, 128.6, 127.2, 121.6, 60.6, 51.7, 45.1, 35.0, 31.3, 28.3, 14.3.

IR (film) 3029, 2981, 2952, 1717, 1648, 1495, 1453, 1438, 1368, 1161 cm^{-1}.

LRMS (ES^+) calcd for $C_{17}H_{23}O_4S$ $(M+H)^+$ 323.1, found 323.1.



(*E*)-1-Ethyl 7-methyl 4-(4-chlorobenzylthio)hept-2-enedioate (Table 3, entry 2). The compound was prepared according to General Procedure B (except that the

reaction concentration was 0.05 M) from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 4-chlorobenzyl mercaptan (200 μL, 1.50 mmol). After purification by flash chromatography (first column with 5→20% Et_2O in hexanes; second column with 2→3% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (134 mg, 75% yield) with 90% ee.

$[\alpha]_D^{22}$ = +177 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 2.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 18.5 min (minor), 20.0 min (major).

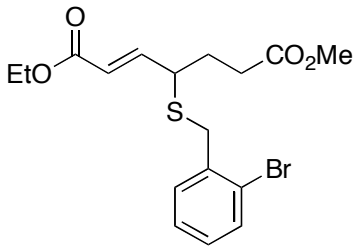
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (139 mg, 78% yield) with 90% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.40 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz, 1H), 5.66 (d, *J* = 15.6 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.57 (s, 3H), 3.48 (d, *J* = 13.6 Hz, 1H), 3.13-3.07 (m, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.89-1.84 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 165.9, 146.8, 136.2, 132.9, 130.3, 128.7, 121.8, 60.6, 51.7, 45.2, 34.4, 31.3, 28.2, 14.3.

IR (film) 2982, 2952, 1717, 1648, 1491, 1438, 1368, 1160 cm^{-1}.

LRMS (ES^+) calcd for $C_{17}H_{22}ClO_4S$ $(M+H)^+$ 357.1, found 357.0.



(*E*)-1-Ethyl 7-methyl 4-(2-bromobenzylthio)hept-2-enedioate (Table 3, entry 3). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 2-bromobenzyl mercaptan (200 μL, 1.50 mmol). After purification by flash chromatography (first column with 10→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (154 mg, 77% yield) with 92% ee.

$[\alpha]_D^{22}$ = +108 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AS-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 18.4 min (major), 22.7 min (minor).

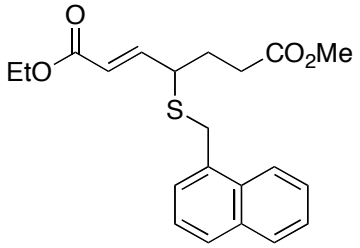
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (150 mg, 75% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 4.8 Hz, 1H), 7.31-7.26 (m, 1H), 7.23-7.18 (m, 1H), 7.07-7.03 (m, 1H), 6.71 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.66 (d, *J* = 13.2 Hz, 1H), 3.58 (s, 3H), 3.28-3.23 (m, 1H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.93-1.87 (m, 2H), 1.53 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0, 166.0, 146.9, 137.0, 133.2, 130.8, 128.8, 127.5, 124.6, 121.8, 60.6, 51.7, 45.9, 35.4, 31.3, 28.3, 14.3.

IR (film) 3057, 2981, 2952, 1736, 1648, 1469, 1439, 1368, 1161 cm^{-1}.

LRMS (ES^+) calcd for $C_{17}H_{22}BrO_4S$ $(M+H)^+$ 401.0, found 401.0.



(*E*)-1-Ethyl 7-methyl 4-(naphthalen-1-ylmethylthio)hept-2-enedioate (Table 3, entry 4). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and naphthalen-1-ylmethanethiol (261 mg, 1.50 mmol). After purification by flash chromatography (first column with 5→30% Et_2O in hexanes; second column with 2→3% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (145 mg, 78% yield) with 94% ee.

$[\alpha]_D^{22}$ = +175 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 28.8 min (minor), 38.9 min (major).

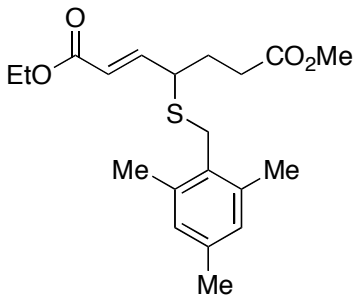
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (140 mg, 75% yield) with 93% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.55-7.50 (m, 2H), 7.40-7.37 (m, 2H), 6.82 (dd, *J* = 15.6 Hz, *J* = 9.6 Hz, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 13.2 Hz, 1H), 4.00 (d, *J* = 13.2 Hz, 1H), 3.60 (s, 3H), 3.34-3.30 (m, 1H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.98-1.92 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 166.0, 147.0, 134.0, 132.9, 131.4, 128.7, 128.3, 127.2, 126.1, 125.9, 125.1, 123.9, 121.7, 60.6, 51.6, 46.0, 32.9, 31.3, 28.3, 14.2.

IR (film) 3047, 2981, 2952, 1736, 1647, 1437, 1368, 1264, 1161 cm^{-1}.

LRMS (ES^+) calcd for $C_{21}H_{25}O_4S$ $(M+H)^+$ 373.2, found 373.1.



(*E*)-1-Ethyl 7-methyl 4-(2,4,6-trimethylbenzylthio)hept-2-enedioate (Table 3, entry 5). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 2,4,6-trimethylbenzyl mercaptan (250 mg, 1.50 mmol). After purification by flash chromatography (first column with 10→20% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (151 mg, 83% yield) with 94% ee.

$[\alpha]_D^{22}$ = +13 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IC column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 15.6 min (minor), 17.3 min (major).

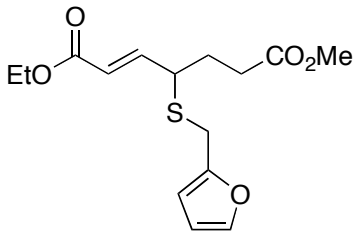
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (149 mg, 82% yield) with 95% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.82 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz, 1H), 6.78 (s, 2H), 5.83 (d, *J* = 15.6 Hz, 1H), 4.21 (qd, *J* = 7.2 Hz, *J* = 1.2 Hz, 2H), 3.66 (s, 3H), 3.59 (d, *J* = 10.0 Hz, 1H), 3.57 (d, *J* = 10.8 Hz, 1H), 3.40-3.31 (m, 1H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 6H), 2.20 (s, 3H), 2.01-1.95 (m, 2H), 1.29 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0, 166.0, 146.8, 136.9, 136.6, 129.7, 128.9, 121.1, 60.4, 51.6, 46.8, 31.3, 29.6, 28.1, 20.8, 19.4, 14.2.

IR (film) 2952, 2867, 1736, 1647, 1613, 1440, 1368, 1160 cm^{-1}.

LRMS (ES^+) calcd for $C_{20}H_{28}NaO_4S$ $(M+Na)^+$ 387.2, found 387.1.



(*E*)-1-Ethyl 7-methyl 4-(furan-2-ylmethylthio)hept-2-enedioate (Table 3, entry 6). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 2-furylmethanethiol (154 μL, 1.50 mmol). After purification by flash chromatography (first column with 10→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (108 mg, 69% yield) with 92% ee.

$[\alpha]_D^{22}$ = +179 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 5.0% *i*-PrOH in hexanes; 0.8 mL/min; retention times: 18.8 min (minor), 19.7 min (major).

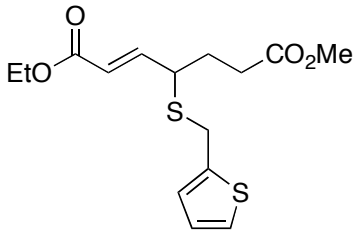
The second run was performed with (–)-**1**. The product was isolated as a colorless oil (115 mg, 74% yield) with 91% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.34 (m, 1H), 6.69 (dd, *J* = 9.5 Hz, *J* = 15.5 Hz, 1H), 6.30-6.29 (m, 1H), 6.16-6.15 (m, 1H), 5.80 (d, *J* = 15.0 Hz, 1H), 4.24-4.17 (m, 2H), 3.65 (s, 3H), 3.64 (d, *J* = 15.0 Hz, 1H), 3.60 (d, *J* = 15.0 Hz, 1H), 3.34-3.26 (m, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.97-1.93 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.9, 166.0, 151.2, 146.4, 142.2, 122.0, 110.4, 107.7, 60.6, 51.7, 45.4, 31.4, 28.2, 27.1, 14.2.

IR (film) 2982, 2953, 1736, 1648, 1438, 1369, 1161 cm^{-1}.

LRMS (ES^+) calcd for $C_{15}H_{21}O_5S$ $(M+H)^+$ 313.1, found 313.1.



(*E*)-1-Ethyl 7-methyl 4-(thiophen-2-ylmethylthio)hept-2-enedioate (Table 3, entry 7). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and thiophen-2-ylmethanethiol (163 μL, 1.50 mmol). After purification by flash chromatography (first column with 5→30% Et_2O in hexanes; second column with 2→3% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (105 mg, 64% yield) with 89% ee.

$[\alpha]_D^{22}$ = +162 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 27.3 min (major), 32.9 min (minor).

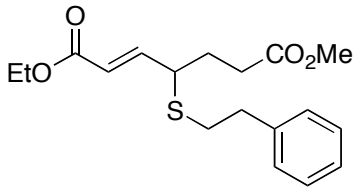
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (113 mg, 69% yield) with 88% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21-7.17 (m, 1H), 6.92-6.90 (m, 2H), 6.70 (dd, *J* = 15.6 Hz, *J* = 9.6 Hz, 1H), 5.74 (d, *J* = 15.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.85 (d, *J* = 14.8 Hz, 1H), 3.79 (d, *J* = 14.8 Hz, 1H), 3.63 (s, 3H), 3.29-3.22 (m, 1H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.97-1.92 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 166.0, 146.4, 141.4, 126.7, 126.2, 125.1, 121.8, 60.6, 51.7, 45.2, 31.3, 29.4, 28.2, 14.2.

IR (film) 2981, 2952, 1736, 1648, 1437, 1368, 1261, 1163 cm^{-1}.

LRMS (ES^+) calcd for $C_{15}H_{21}O_4S_2$ $(M+H)^+$ 329.1, found 329.0.



(*E*)-1-Ethyl 7-methyl 4-(phenethylthio)hept-2-enedioate (Table 3, entry 8). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and phenylethylmercaptan (201 μL, 1.50 mmol). After purification by flash chromatography (first column with 10→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (136 mg, 81% yield) with 87% ee.

$[\alpha]_D^{22}$ = +54 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 2.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 28.7 min (major), 33.8 min (minor).

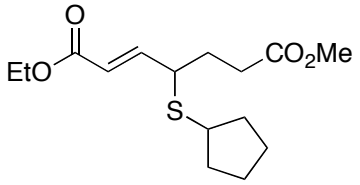
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (128 mg, 76% yield) with 87% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.20 (m, 2H), 7.20-7.13 (m, 3H), 6.65 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz, 1H), 5.71 (d, *J* = 15.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.63 (s, 3H), 3.25-3.19 (m, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.64-2.60 (m, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.93-1.87 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1, 166.0, 147.1, 140.2, 128.6, 128.5, 126.5, 121.4, 60.6, 51.8, 45.9, 36.1, 32.1, 31.4, 28.5, 14.3.

IR (film) 3028, 2981, 2952, 1717, 1647, 1438, 1368, 1160 cm^{-1}.

LRMS (ES^+) calcd for $C_{18}H_{25}O_4S$ $(M+H)^+$ 337.2, found 337.1.



(*E*)-1-Ethyl 7-methyl 4-(cyclopentylthio)hept-2-enedioate (Table 3, entry 9). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and cyclopentanethiol (161 μL, 1.50 mmol). After purification by flash chromatography (2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (123 mg, 82% yield) with 93% ee.

$[\alpha]_D^{22}$ = +106 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 10.2 min (major), 11.4 min (minor).

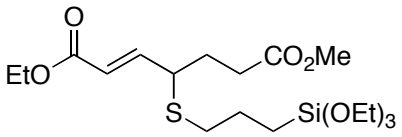
The second run was performed with (–)-**1**. The product was isolated as a colorless oil (117 mg, 78% yield) with 92% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.69 (dd, J = 10.0 Hz, J = 15.6 Hz, 1H), 5.74 (d, J = 15.2 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.63 (s, 3H), 3.35-3.28 (m, 1H), 2.93-2.88 (m, 1H), 2.42 (t, J = 7.6 Hz, 2H), 1.94-1.67 (m, 4H), 1.75-1.62 (m, 2H), 1.52-1.35 (m, 4H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0, 166.1, 147.7, 120.8, 60.4, 51.6, 45.8, 42.4, 34.4, 31.3, 28.6, 24.9, 24.6, 14.1, 9.8.

IR (film) 2955, 2870, 1716, 1647, 1439, 1368, 1157 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{15}H_{25}O_4S$ $(M+H)^+$ 301.2, found 301.1.



(*E*)-1-Ethyl 7-methyl 4-(3-(triethoxysilyl)propylthio)hept-2-enedioate (Table 3, entry 10). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and (3-mercaptopropyl)triethoxysilane (380 μL, 1.50 mmol). After purification by flash chromatography (first column with 5→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (153 mg, 70% yield) with 84% ee.

$[\alpha]_D^{22}$ = +44 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK IA-H column; 1.0% *i*-PrOH in hexanes; 0.5 mL/min; retention times: 18.8 min (major), 20.0 min (minor).

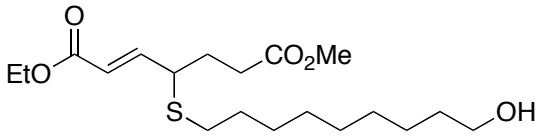
The second run was also performed with (+)-**1**. The product was isolated as a colorless oil (164 mg, 75% yield) with 85% ee.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.61 (dd, J = 9.6 Hz, J = 15.6 Hz, 1H), 5.67 (d, J = 15.6 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.72 (q, J = 6.8 Hz, 6H), 3.58 (s, 3H), 3.25-3.19 (m, 1H), 2.39-2.31 (m, 4H), 1.86 (q, J = 7.6 Hz, 2H), 1.61-1.51 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 6.8 Hz, 9H), 0.70-0.57 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0, 165.9, 147.2, 121.0, 60.4, 58.3, 51.6, 45.4, 33.4, 31.3, 28.4, 26.9, 22.8, 18.2, 14.1, 9.8.

IR (film) 2976, 2928, 1740, 1721, 1648, 1368, 1263, 1165 cm^{-1}.

LRMS (ES$^+$) calcd for $C_{19}H_{36}NaO_7SSi$ $(M+Na)^+$ 459.2, found 459.1.



(*E*)-1-Ethyl 7-methyl 4-(9-hydroxynonylthio)hept-2-enedioate (Table 3, entry 11). The compound was prepared according to General Procedure B from (±)-1-ethyl 7-

methyl hepta-2,3-dienedioate (99 mg, 0.50 mmol) and 9-mercapto-1-nonanol (282 μL, 1.50 mmol). After purification by flash chromatography (first column with 10→30% Et_2O in hexanes; second column with 2% Et_2O in CH_2Cl_2), the title compound was isolated as a colorless oil (155 mg, 83% yield) with 87% ee.

$[\alpha]_D^{22}$ = +42 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 49.7 min (minor), 53.7 min (major).

The second run was performed with (–)-**1**. The product was isolated as a colorless oil (140 mg, 75% yield) with 88% ee.

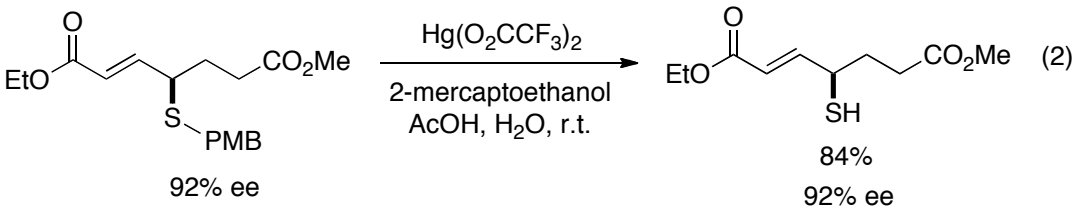
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.62 (dd, *J* = 9.6 Hz, *J* = 15.6 Hz 1H), 5.68 (d, *J* = 15.6 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 3.54 (t, *J* = 6.8 Hz, 2H), 3.25-3.21 (m, 1H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.34-2.28 (m, 2H), 1.90-1.84 (m, 2H), 1.81 (br s, 1H), 1.51-1.40 (m, 4H), 1.30-1.16 (m, 10H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1, 166.1, 147.3, 121.1, 62.9, 60.6, 51.7, 45.7, 32.7, 31.4, 30.5, 29.4, 29.29, 29.26, 29.1, 28.8, 28.5, 25.7, 14.2.

IR (film) 3431, 2978, 2929, 2856, 1721, 1647, 1438, 1368, 1160 cm^{-1}.

LRMS (ES^+) calcd for $C_{19}H_{35}O_5S$ $(M+H)^+$ 375.2, found 375.1.

IV. Functionalization of the γ-Addition Products (eq 2 and eq 3)



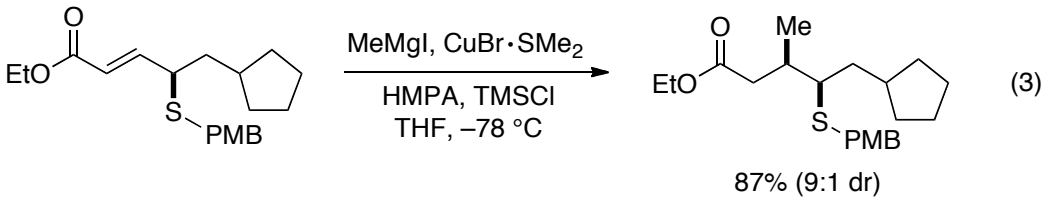
(2)

(*R*,*E*)-1-Ethyl 7-methyl 4-mercaptohept-2-enedioate (Eq 2). (*E*)-1-Ethyl 7-methyl 4-(4-methoxybenzylthio)hept-2-enedioate (92% ee; 59 mg, 0.17 mmol), $Hg(O_2CCF_3)_2$ (93 mg, 22 mmol), and aqueous AcOH (80% by weight; 3.5 mL) were added to a 10-mL flask. The reaction mixture was stirred for 10 h, and then 2-mercaptoethanol (24 μL, 0.34 mmol) was added. The resulting mixture was stirred for 2 h, and then it was filtered through a pad of silica gel. The silica gel was washed with Et_2O (2 × 15 mL). Water (30 mL) was added to the filtrate, and then the organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. After purification by flash chromatography (10→20% EtOAc in hexanes), the title compound was obtained as a colorless oil (33 mg, 84% yield; 92% ee).

$[\alpha]_D^{22}$ = +100 (c = 1.0, $CHCl_3$). HPLC analysis of the product: Daicel CHIRALPAK AS-H column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 13.5 min (minor), 14.8 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (dd, *J* = 15.6 Hz, *J* = 8.8 Hz, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 3.57-3.50 (m, 1H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.09-1.94 (m, 2H), 1.63 (d, *J* = 6.8 Hz, 1H), 1.29 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 166.1, 148.9, 120.6, 60.6, 51.8, 40.0, 32.0, 31.4, 14.2.
IR (film) 2982, 2954, 1722, 1651, 1438, 1369, 1036 cm^{-1}.
LRMS (ES$^+$) calcd for $C_{10}H_{17}O_4S$ $(M+H)^+$ 233.1, found 233.0.



(3)

87% (9:1 dr)

(*R*,*R*)-Ethyl 5-cyclopentyl-4-(4-methoxybenzylthio)-3-methylpentanoate (Eq 3). MeMgI (3.0 M solution in Et_2O; 0.43 mL, 1.3 mmol) was added to a –78 °C solution of HMPA (0.15 mL, 0.86 mmol) and CuBr•SMe_2 (8.8 mg, 0.043 mmol) in THF (6.0 mL). A solution of the enoate (150 mg, 0.43 mmol) and TMSCl (0.11 mL, 0.86 mmol) in THF (6.0 mL) was added dropwise over 15 min. This solution was stirred at –78 °C for 5 h. Next, the solution was diluted with Et_2O (15 mL), and the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (5 mL). The mixture was allowed to warm to room temperature, the aqueous and organic layers were separated, and the aqueous layer was extracted with Et_2O (10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography furnished 136 mg of a colorless oil (87% yield). HPLC analysis showed a 9:1 mixture of diastereomers.

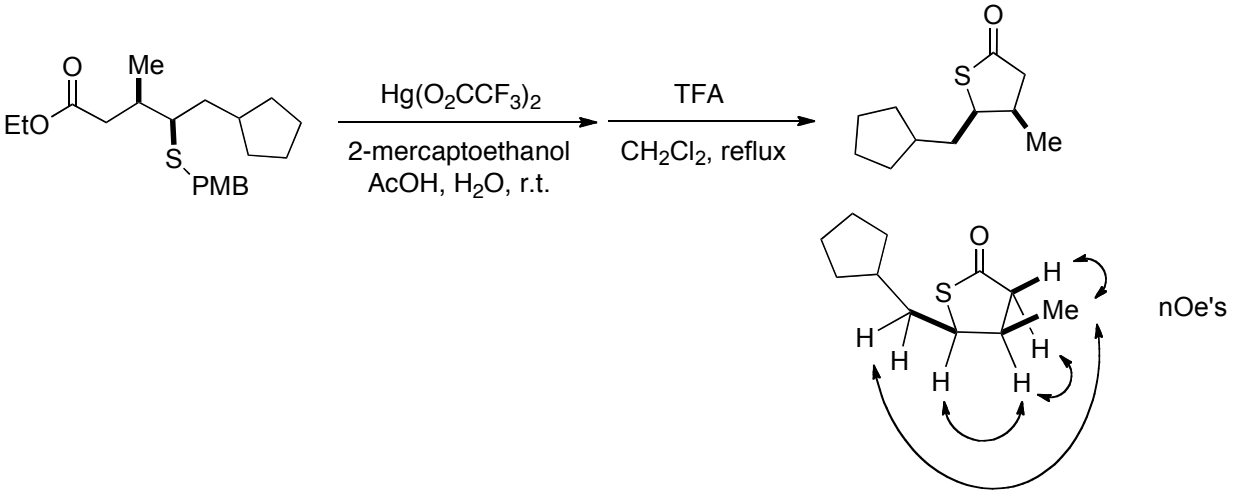
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.13-4.08 (m, 2H), 3.78 (s, 3H), 3.66 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 2.57-2.32 (m, 2H), 2.36-2.26 (m, 1H), 2.19-1.93 (m, 1H), 1.97-1.88 (m, 1H), 1.76-1.67 (m, 1H), 1.55-1.41 (m, 7H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.02-0.94 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 158.5, 130.7, 130.0, 113.7, 60.2, 55.3, 49.2, 39.2, 38.6, 37.4, 35.7, 33.3, 32.7, 32.4, 25.1, 25.0, 15.7, 14.2.

IR (film) 2950, 1732, 1611, 1512, 1464, 1250, 1035, 830 cm^{-1}.

LRMS (ES+) calcd for $C_{20}H_{30}O_3S$ $(M–Me+H)^+$ 350.2, found 350.7.

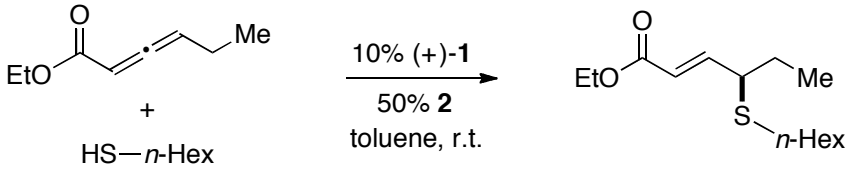
Proof of stereochemistry:



V. Determination of Absolute Configuration

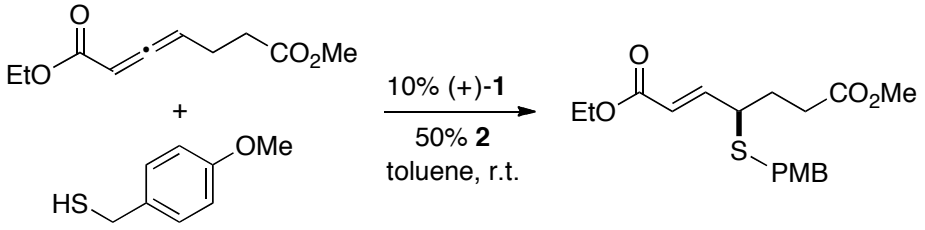
The absolute configurations of two γ-addition products were determined. The stereochemistry of the other products was assigned by analogy.

(***R,E*)-Ethyl 4-(hexylthio)hex-2-enoate**.[1] The product has $[\alpha]_D^{22} = +87$ (c = 2.0, CH_2Cl_2; 85% ee).



(1) Armstrong, A.; Challinor, L.; Moir, J. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5369–5372.

(*R,E*)-1-Ethyl 7-methyl 4-(4-methoxybenzylthio)hept-2-enedioate.



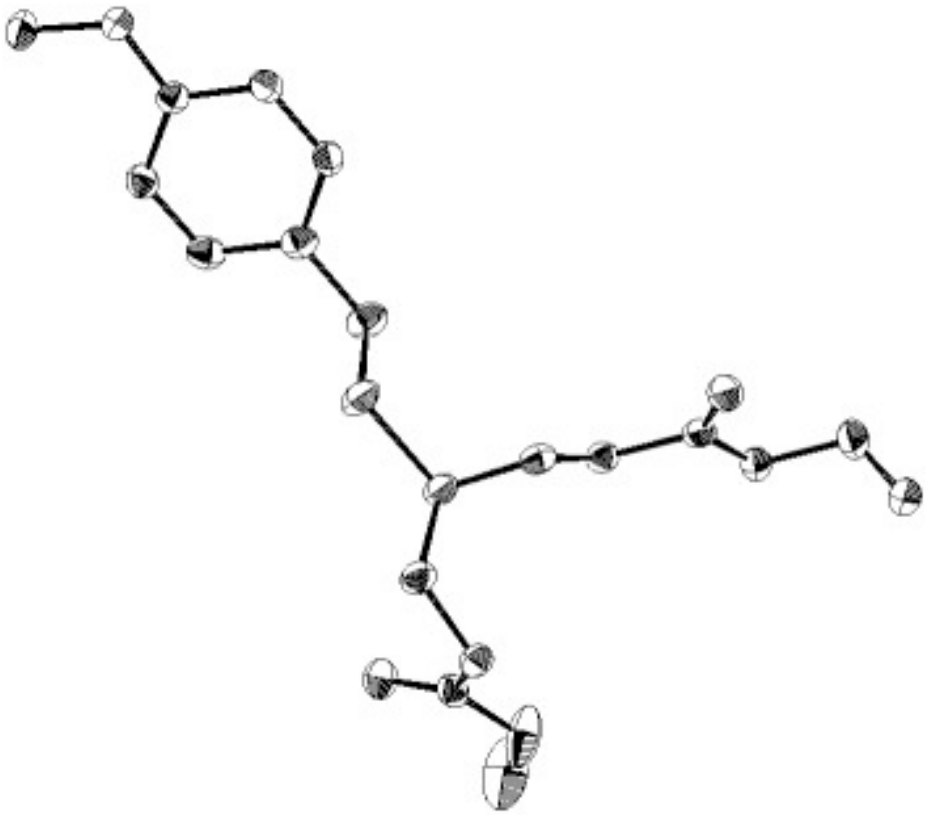


Table 1. Crystal data and structure refinement for d09063.

Identification code	d09063	
Empirical formula	C18 H24 O5 S	
Formula weight	352.43	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.6979(2) Å	a= 90°.
	b = 5.66190(10) Å	b= 95.9520(10)°.
	c = 16.9349(3) Å	g = 90°.
Volume	924.86(3) $Å^3$	
Z	2	
Density (calculated)	1.266 Mg/m^3	
Absorption coefficient	1.757 mm^{-1}	
F(000)	376	
Crystal size	0.45 x 0.40 x 0.04 mm^3	
Theta range for data collection	2.62 to 67.73°.	
Index ranges	-10<=h<=8, -6<=k<=6, -20<=l<=20	
Reflections collected	17826	
Independent reflections	3228 [R(int) = 0.0234]	
Completeness to theta = 67.73°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9330 and 0.5053	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3228 / 47 / 229	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0658	
R indices (all data)	R1 = 0.0259, wR2 = 0.0659	
Absolute structure parameter	0.046(12)	
Largest diff. peak and hole	0.155 and -0.265 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d09063. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5920(1)	5039(1)	2780(1)	33(1)
C(1)	4441(1)	5166(3)	2015(1)	25(1)
C(2)	3535(2)	7208(2)	2161(1)	24(1)
C(3)	2189(2)	7035(2)	2239(1)	23(1)
C(4)	1337(2)	9168(2)	2323(1)	25(1)
O(1)	-12(1)	8670(2)	2136(1)	30(1)
C(5)	-979(2)	10580(3)	2245(1)	42(1)
C(6)	-2280(3)	9988(6)	1829(2)	35(1)
C(6A)	-1220(4)	12106(6)	1627(2)	34(1)
O(2)	1771(1)	11116(2)	2511(1)	30(1)
C(7)	5001(2)	5369(3)	1199(1)	28(1)
C(8)	3836(2)	5249(3)	519(1)	25(1)
C(9)	3138(2)	2875(2)	457(1)	24(1)
O(3)	1858(1)	3047(2)	88(1)	48(1)
C(10)	1129(2)	830(4)	-40(2)	66(1)
O(4)	3643(1)	1036(2)	684(1)	33(1)
O(5)	9314(1)	2526(2)	6149(1)	27(1)
C(11)	5103(2)	3696(3)	3596(1)	30(1)
C(12)	6217(2)	3317(3)	4273(1)	25(1)
C(13)	6436(1)	4970(3)	4882(1)	24(1)
C(14)	7467(2)	4646(3)	5505(1)	24(1)
C(15)	8310(2)	2647(2)	5522(1)	22(1)
C(16)	8105(2)	963(2)	4920(1)	26(1)
C(17)	7057(2)	1320(3)	4302(1)	27(1)
C(18)	10162(2)	455(3)	6219(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for d09063.

S(1)-C(11)	1.8285(15)
S(1)-C(1)	1.8318(13)
C(1)-C(2)	1.489(2)
C(1)-C(7)	1.5405(17)
C(1)-H(1)	1.0000
C(2)-C(3)	1.329(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.4781(19)
C(3)-H(3)	0.9500
C(4)-O(2)	1.2116(18)
C(4)-O(1)	1.3444(19)
O(1)-C(5)	1.4554(18)
C(5)-C(6A)	1.359(4)
C(5)-C(6)	1.419(3)
C(5)-C(5A)	0.9900
C(5)-C(5B)	0.9900
C(5)-C(5C)	0.9900
C(5)-C(5D)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(6A)-H(6D)	0.9800
C(6A)-H(6E)	0.9800
C(6A)-H(6F)	0.9800
C(7)-C(8)	1.5285(18)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.504(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(4)	1.1974(18)
C(9)-O(3)	1.3348(19)
O(3)-C(10)	1.446(2)
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
O(5)-C(15)	1.3658(17)
O(5)-C(18)	1.4304(17)
C(11)-C(12)	1.508(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(17)	1.391(2)
C(12)-C(13)	1.392(2)
C(13)-C(14)	1.389(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.395(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.395(2)
C(16)-C(17)	1.397(2)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

C(11)-S(1)-C(1)	100.46(7)
C(2)-C(1)-C(7)	111.15(12)
C(2)-C(1)-S(1)	110.21(10)
C(7)-C(1)-S(1)	108.31(9)
C(2)-C(1)-H(1)	109.0
C(7)-C(1)-H(1)	109.0
S(1)-C(1)-H(1)	109.0
C(3)-C(2)-C(1)	124.23(13)
C(3)-C(2)-H(2)	117.9
C(1)-C(2)-H(2)	117.9
C(2)-C(3)-C(4)	120.90(13)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
O(2)-C(4)-O(1)	123.79(13)
O(2)-C(4)-C(3)	125.93(14)

O(1)-C(4)-C(3)	110.25(12)
C(4)-O(1)-C(5)	116.02(12)
C(6A)-C(5)-C(6)	72.3(2)
C(6A)-C(5)-O(1)	115.87(19)
C(6)-C(5)-O(1)	108.23(18)
C(6A)-C(5)-C(5A)	130.5
C(6)-C(5)-C(5A)	110.1
O(1)-C(5)-C(5A)	110.1
C(6A)-C(5)-C(5B)	38.6
C(6)-C(5)-C(5B)	110.1
O(1)-C(5)-C(5B)	110.1
C(5A)-C(5)-C(5B)	108.4
C(6A)-C(5)-C(5C)	108.3
C(6)-C(5)-C(5C)	41.0
O(1)-C(5)-C(5C)	108.3
C(5A)-C(5)-C(5C)	72.1
C(5B)-C(5)-C(5C)	138.4
C(6A)-C(5)-C(5D)	108.3
C(6)-C(5)-C(5D)	138.3
O(1)-C(5)-C(5D)	108.3
C(5A)-C(5)-C(5D)	36.9
C(5B)-C(5)-C(5D)	75.0
C(5C)-C(5)-C(5D)	107.4
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(6A)-H(6D)	109.5
C(5)-C(6A)-H(6E)	109.5
H(6D)-C(6A)-H(6E)	109.5
C(5)-C(6A)-H(6F)	109.5
H(6D)-C(6A)-H(6F)	109.5
H(6E)-C(6A)-H(6F)	109.5
C(8)-C(7)-C(1)	111.74(11)

C(8)-C(7)-H(7A)	109.3
C(1)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7B)	109.3
C(1)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
C(9)-C(8)-C(7)	112.62(12)
C(9)-C(8)-H(8A)	109.1
C(7)-C(8)-H(8A)	109.1
C(9)-C(8)-H(8B)	109.1
C(7)-C(8)-H(8B)	109.1
H(8A)-C(8)-H(8B)	107.8
O(4)-C(9)-O(3)	122.96(14)
O(4)-C(9)-C(8)	126.07(14)
O(3)-C(9)-C(8)	110.95(12)
C(9)-O(3)-C(10)	115.06(13)
O(3)-C(10)-H(10A)	109.5
O(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(15)-O(5)-C(18)	117.57(11)
C(12)-C(11)-S(1)	107.56(10)
C(12)-C(11)-H(11A)	110.2
S(1)-C(11)-H(11A)	110.2
C(12)-C(11)-H(11B)	110.2
S(1)-C(11)-H(11B)	110.2
H(11A)-C(11)-H(11B)	108.5
C(17)-C(12)-C(13)	118.52(13)
C(17)-C(12)-C(11)	120.85(14)
C(13)-C(12)-C(11)	120.63(14)
C(14)-C(13)-C(12)	121.07(13)
C(14)-C(13)-H(13)	119.5
C(12)-C(13)-H(13)	119.5
C(13)-C(14)-C(15)	119.82(13)
C(13)-C(14)-H(14)	120.1

C(15)-C(14)-H(14)	120.1
O(5)-C(15)-C(14)	115.20(12)
O(5)-C(15)-C(16)	124.74(12)
C(14)-C(15)-C(16)	120.06(13)
C(15)-C(16)-C(17)	119.10(13)
C(15)-C(16)-H(16)	120.4
C(17)-C(16)-H(16)	120.4
C(12)-C(17)-C(16)	121.43(13)
C(12)-C(17)-H(17)	119.3
C(16)-C(17)-H(17)	119.3
O(5)-C(18)-H(18A)	109.5
O(5)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(5)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

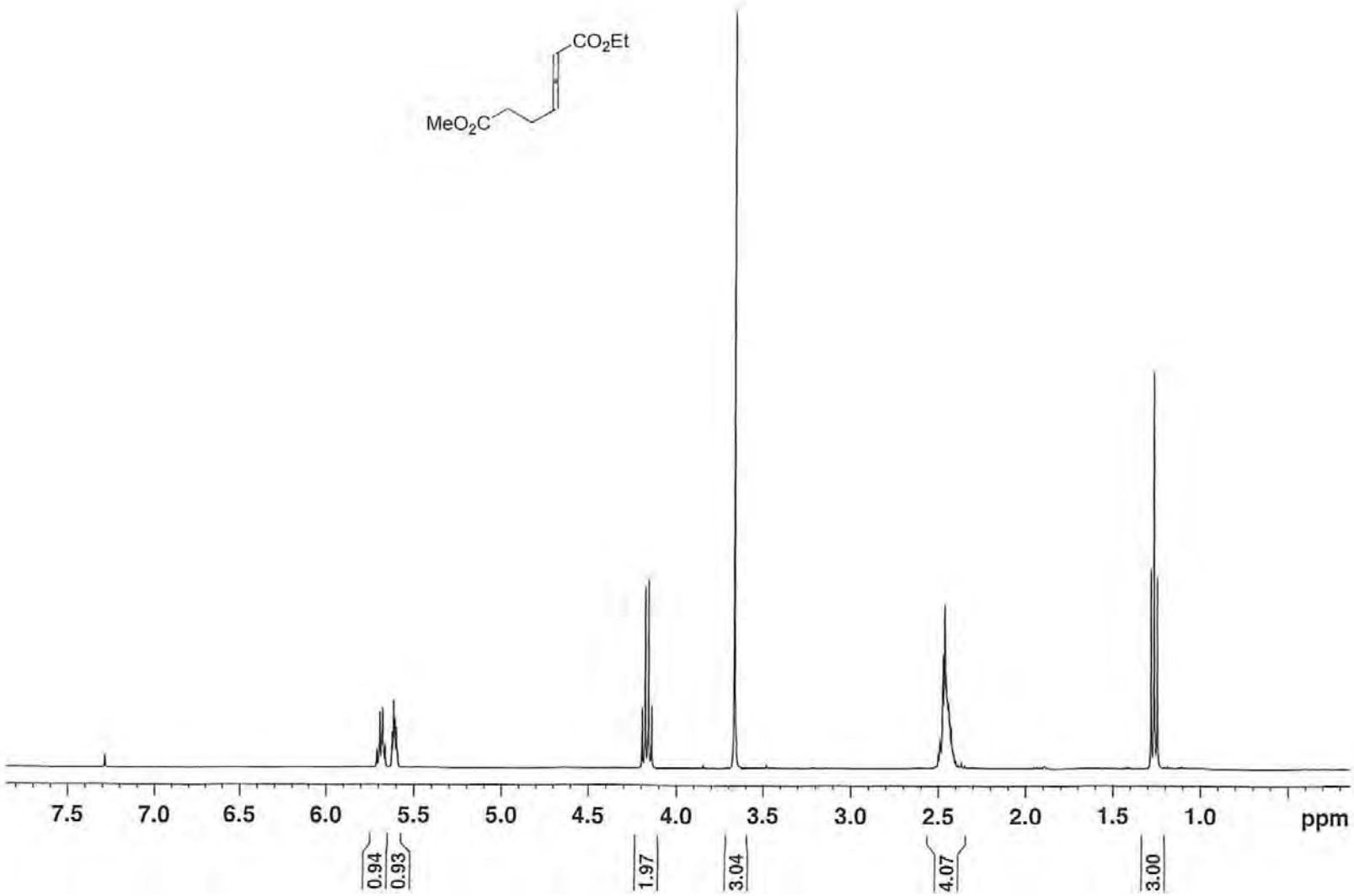
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d09063. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	22(1)	54(1)	22(1)	9(1)	1(1)	2(1)
C(1)	22(1)	31(1)	20(1)	3(1)	0(1)	1(1)
C(2)	29(1)	24(1)	19(1)	2(1)	0(1)	-3(1)
C(3)	27(1)	21(1)	20(1)	1(1)	1(1)	0(1)
C(4)	32(1)	25(1)	17(1)	0(1)	-1(1)	3(1)
O(1)	29(1)	31(1)	29(1)	-8(1)	-5(1)	10(1)
C(5)	39(1)	41(1)	44(1)	-18(1)	-9(1)	18(1)
C(6)	32(2)	35(2)	38(2)	-1(2)	-3(1)	6(1)
C(6A)	33(2)	35(2)	31(2)	-2(1)	-3(1)	11(1)
O(2)	37(1)	23(1)	30(1)	-1(1)	1(1)	3(1)
C(7)	26(1)	35(1)	22(1)	4(1)	3(1)	2(1)
C(8)	28(1)	24(1)	22(1)	4(1)	2(1)	2(1)
C(9)	26(1)	25(1)	23(1)	2(1)	8(1)	4(1)
O(3)	28(1)	24(1)	88(1)	6(1)	-12(1)	-1(1)
C(10)	37(1)	33(1)	122(2)	4(1)	-14(1)	-10(1)
O(4)	43(1)	22(1)	33(1)	4(1)	2(1)	8(1)
O(5)	28(1)	29(1)	23(1)	0(1)	-1(1)	7(1)
C(11)	27(1)	41(1)	24(1)	7(1)	3(1)	-5(1)
C(12)	24(1)	31(1)	21(1)	4(1)	5(1)	-4(1)
C(13)	24(1)	24(1)	25(1)	3(1)	6(1)	5(1)
C(14)	28(1)	24(1)	22(1)	-2(1)	5(1)	0(1)
C(15)	22(1)	26(1)	19(1)	4(1)	4(1)	0(1)
C(16)	31(1)	21(1)	25(1)	2(1)	5(1)	4(1)
C(17)	35(1)	24(1)	23(1)	-1(1)	4(1)	-4(1)
C(18)	29(1)	32(1)	32(1)	5(1)	0(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d09063.

	x	y	z	U(eq)
H(1)	3893	3674	2032	30
H(2)	3945	8733	2202	29
H(3)	1768	5520	2242	27
C(5A)	-1078	10793	2817	51
C(5B)	-632	12075	2036	51
C(5C)	-1875	9877	2353	51
C(5D)	-621	11491	2722	51
H(6A)	-2945	11259	1893	53
H(6B)	-2620	8515	2043	53
H(6C)	-2172	9781	1264	53
H(6D)	-1875	13324	1760	50
H(6E)	-1611	11244	1154	50
H(6F)	-346	12852	1520	50
H(7A)	5503	6884	1170	33
H(7B)	5667	4072	1140	33
H(8A)	3137	6475	601	30
H(8B)	4222	5600	13	30
H(10A)	1678	-247	-335	99
H(10B)	229	1111	-346	99
H(10C)	985	125	473	99
H(11A)	4372	4750	3763	36
H(11B)	4672	2169	3425	36
H(13)	5870	6342	4870	29
H(14)	7598	5783	5919	29
H(16)	8671	-408	4931	31
H(17)	6915	175	3891	33
H(18A)	9573	-946	6234	47
H(18B)	10794	541	6709	47
H(18C)	10702	353	5762	47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6.5
6.0
5.5
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4.0
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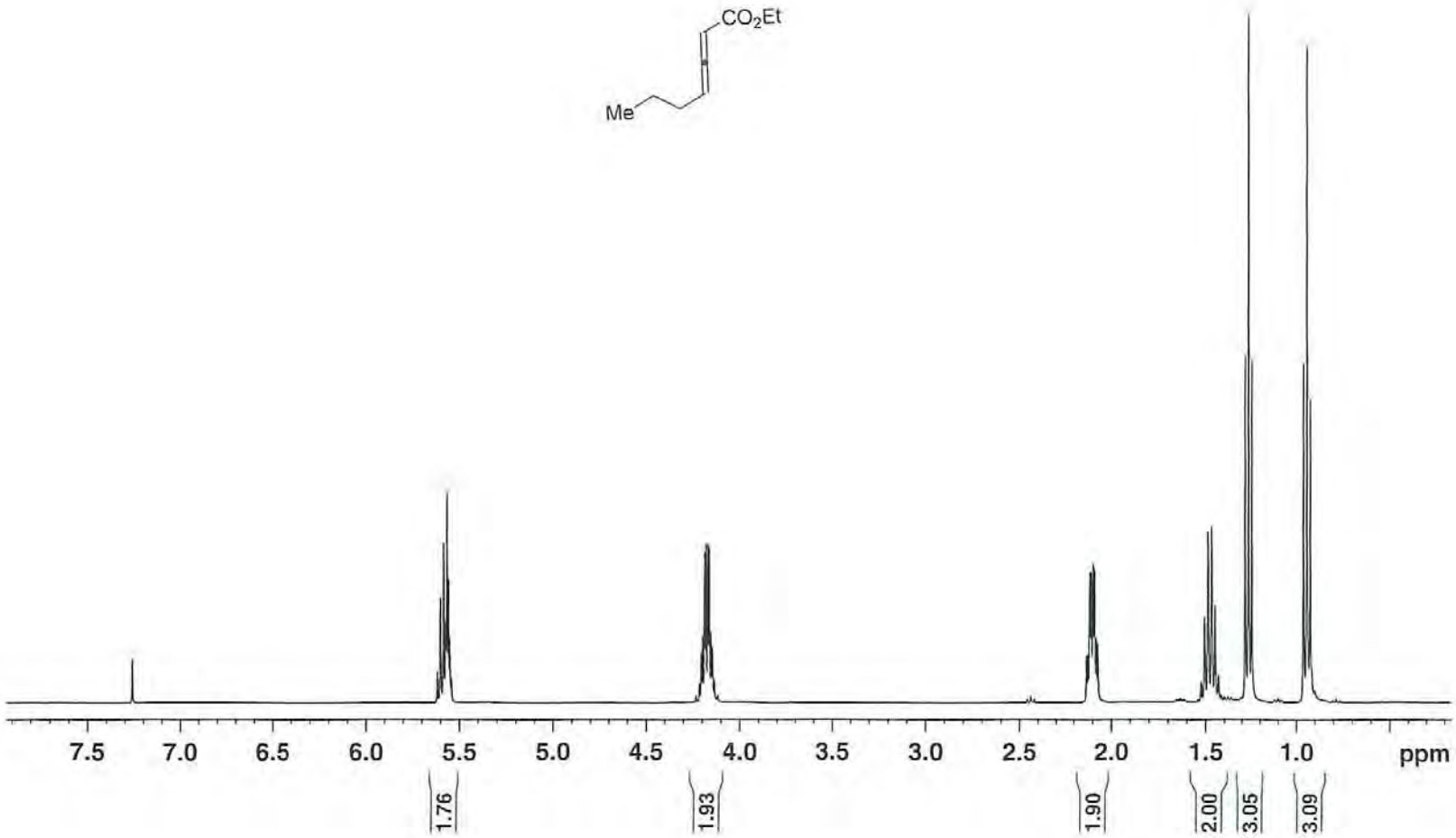
3.00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Me
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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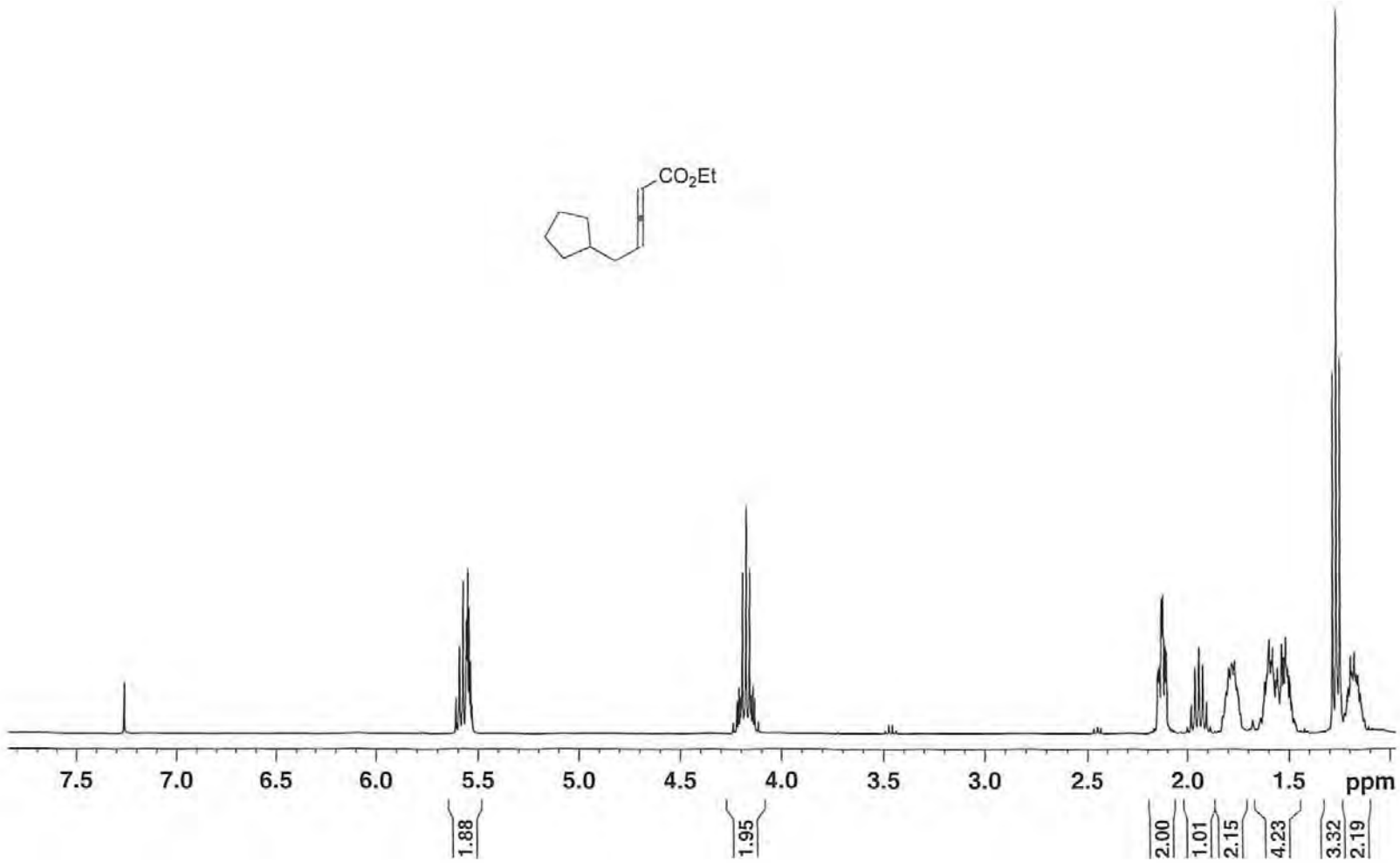
2.0
1.5
1.0
ppm
1.76
1.93
1.90
2.00
3.05
3.09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5.5
5.0
4.5
4.0
3.5
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2.0
1.5
ppm
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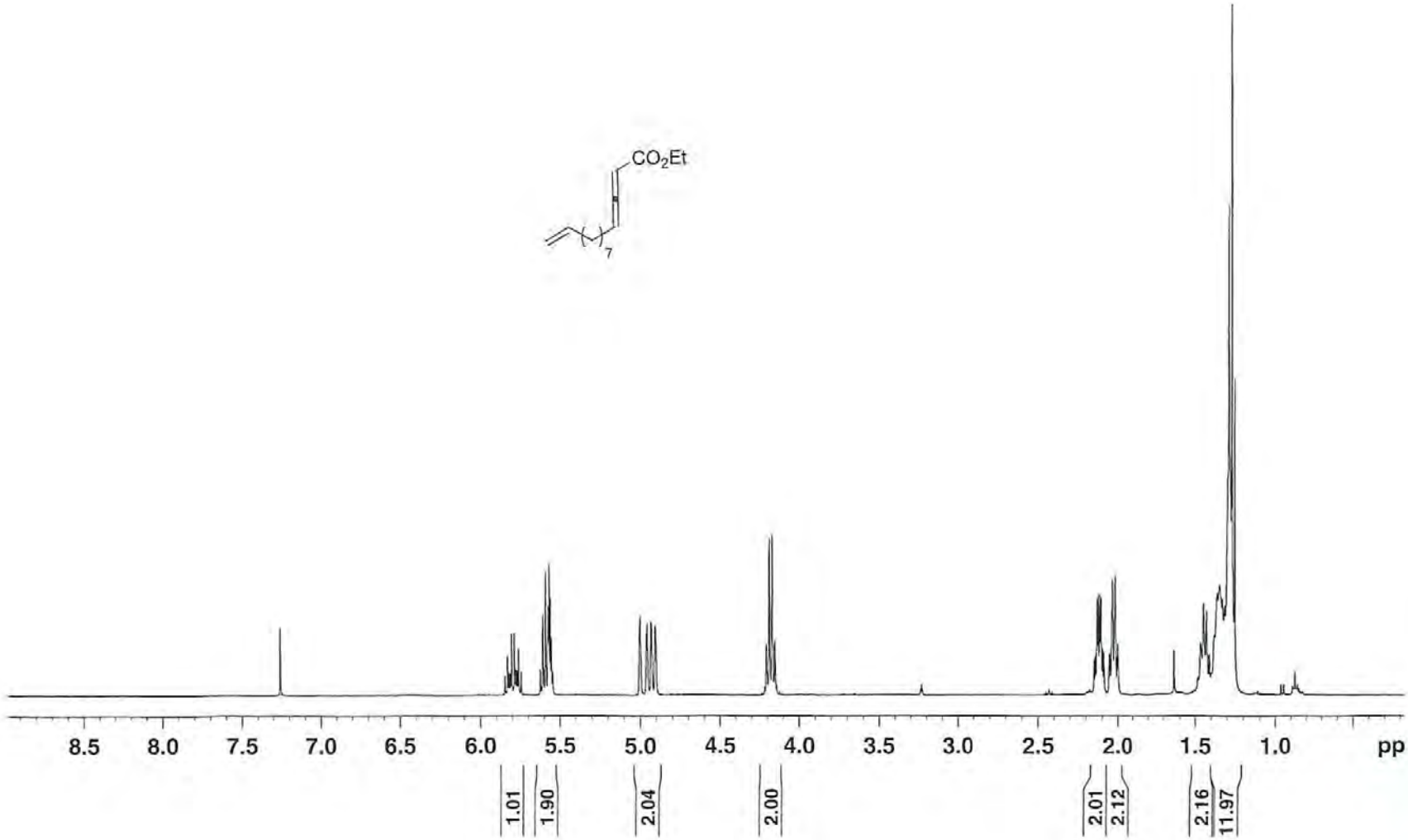
2.00
1.01
2.15
4.23
3.32
2.19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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
pp
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2.00
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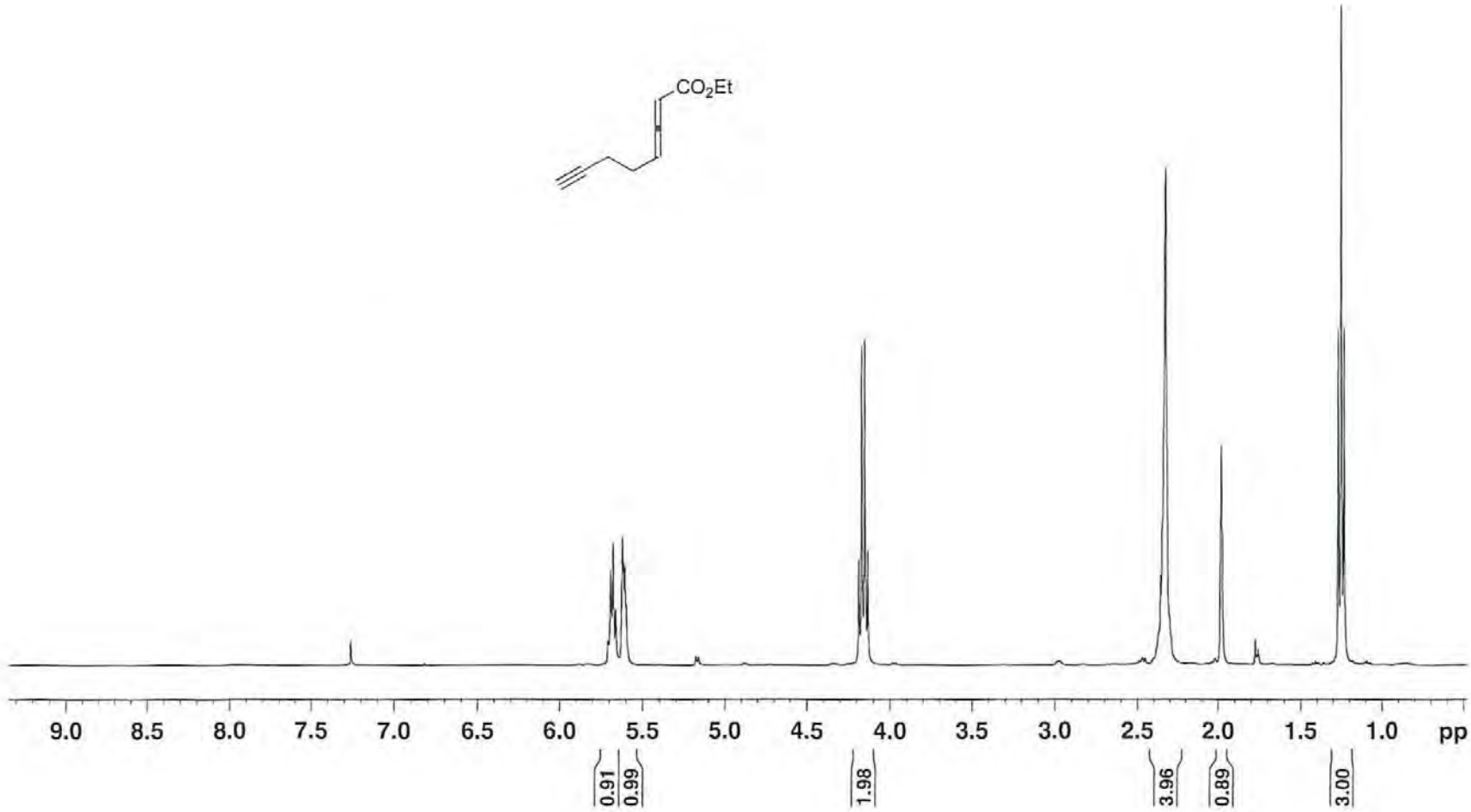
2.12
2.16
11.97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5.0
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4.0
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3.0
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2.0
1.5
1.0
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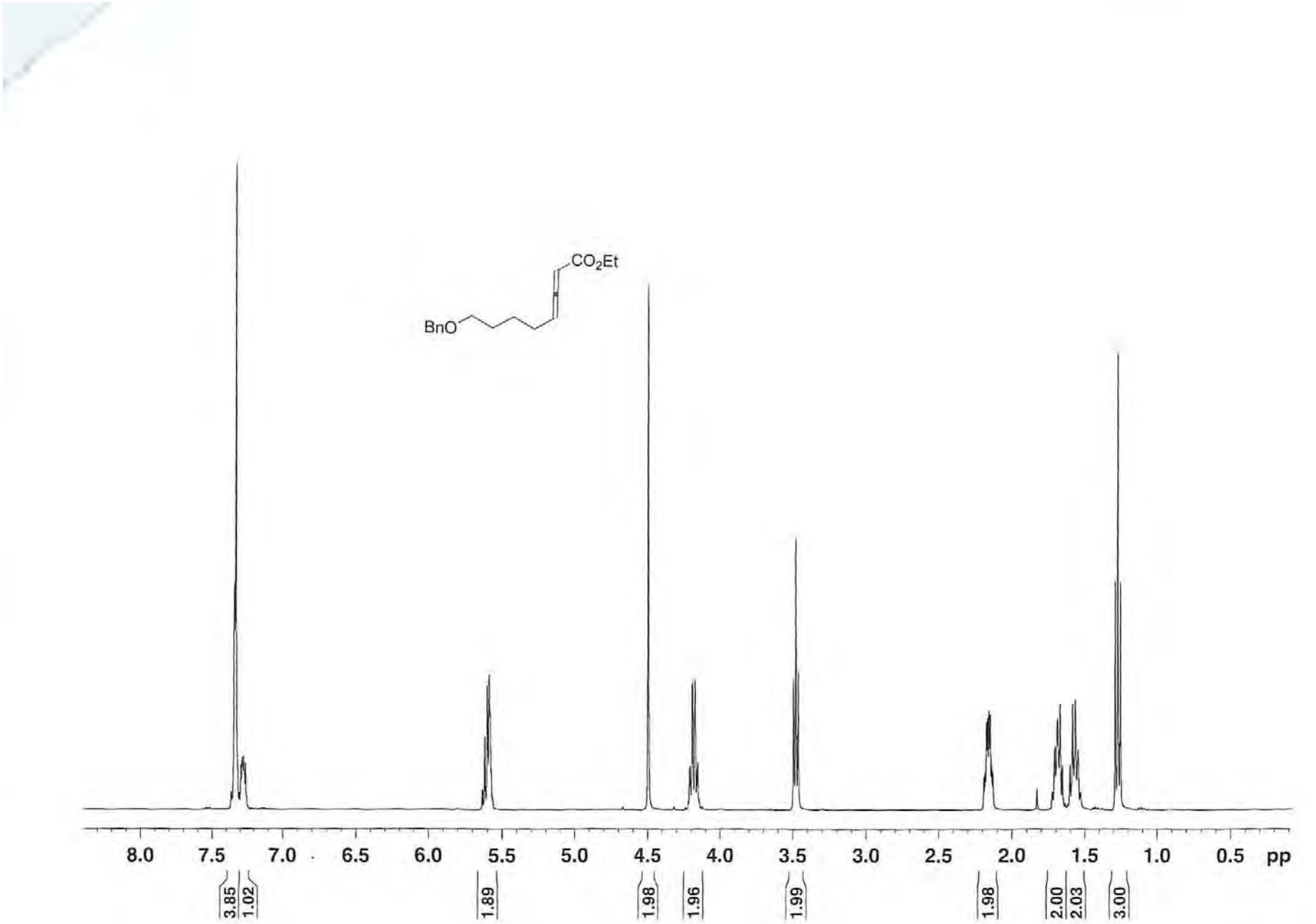
3.00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5.5
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3.0
2.5
2.0
1.5
1.0
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1.99
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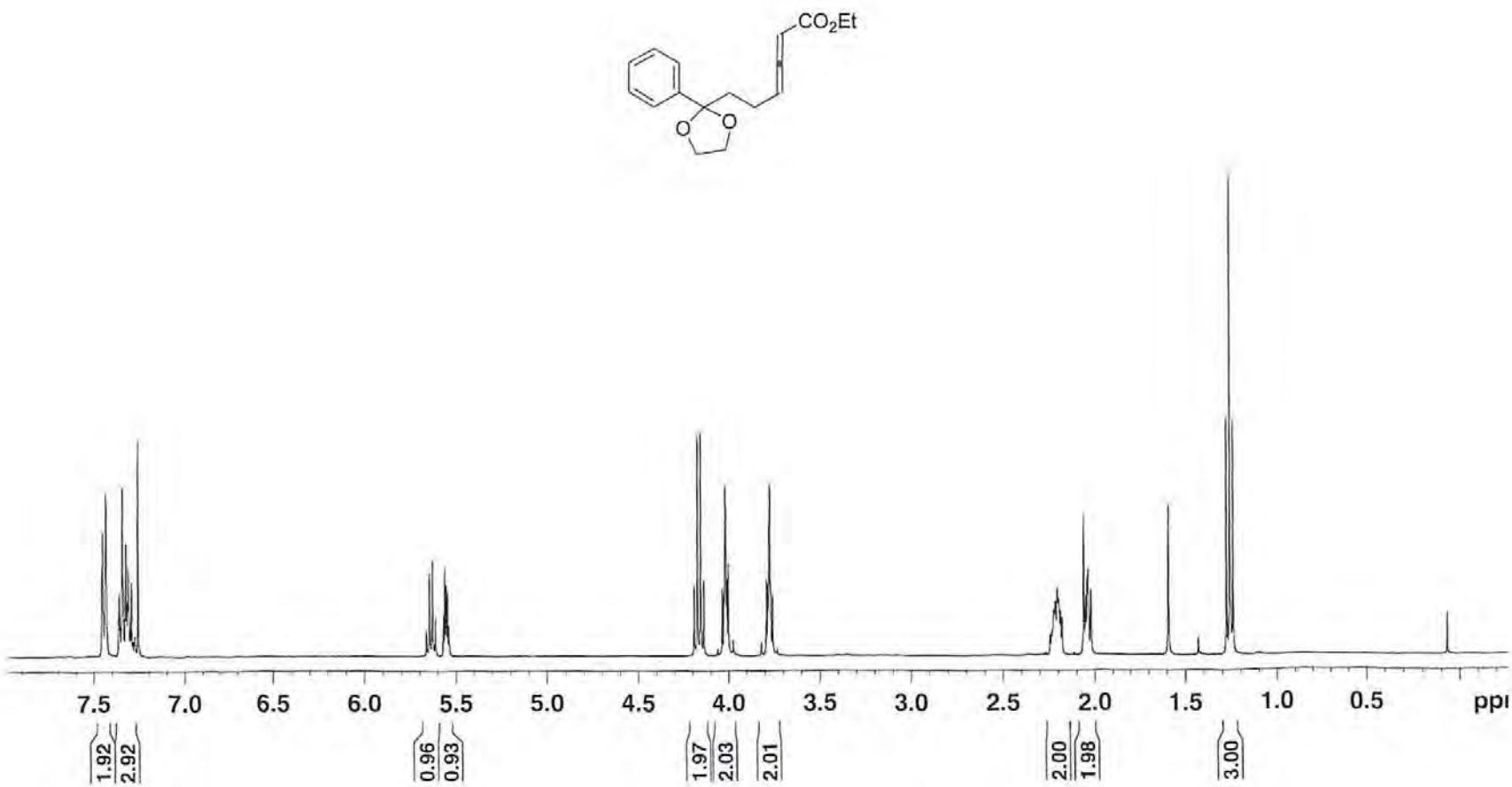
2.03
3.00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O
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3.0
2.5
2.0
1.5
1.0
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ppı
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2.03
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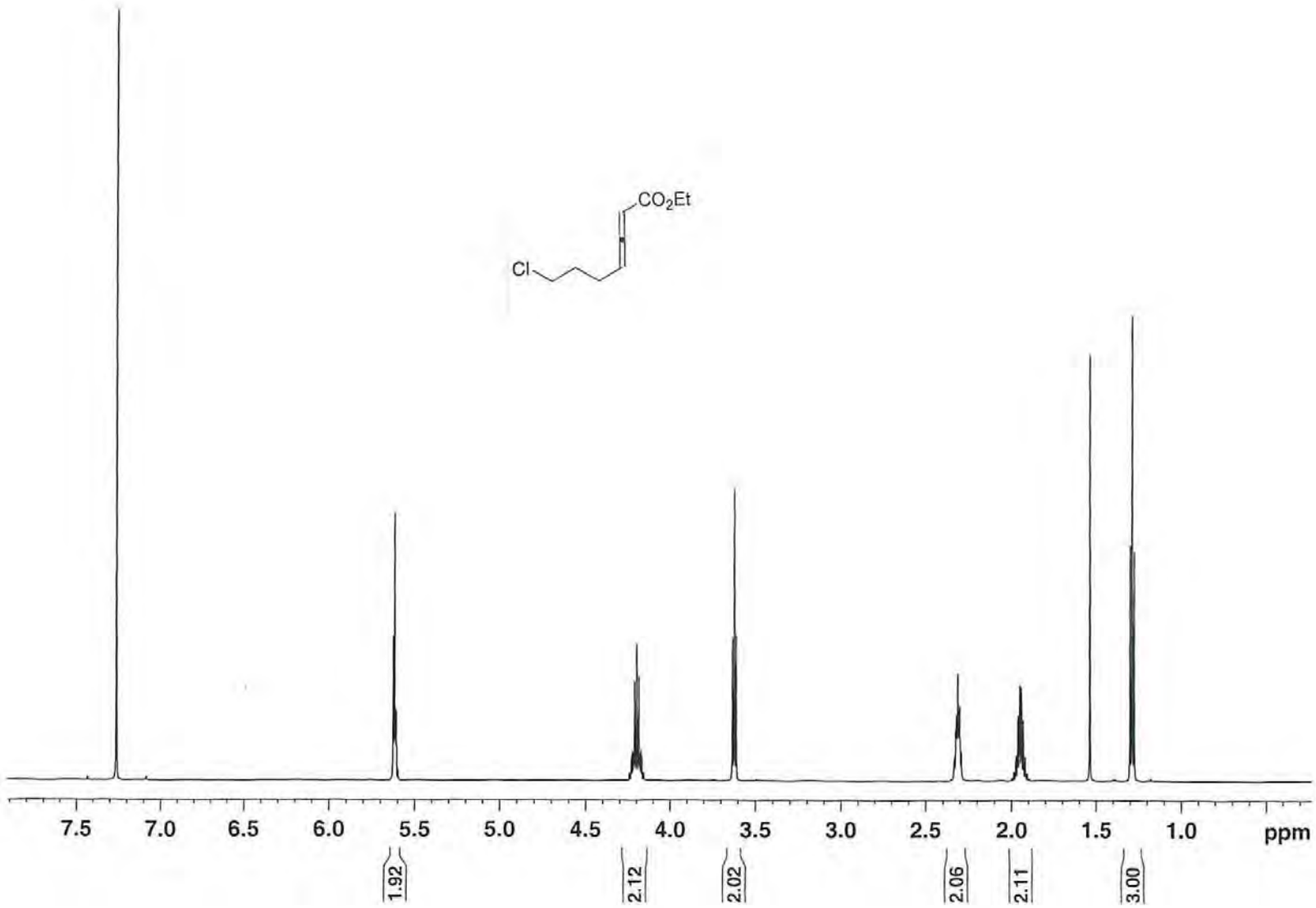
2.00
1.98
3.00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5.5
5.0
4.5
4.0
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3.0
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2.0
1.5
1.0
ppm
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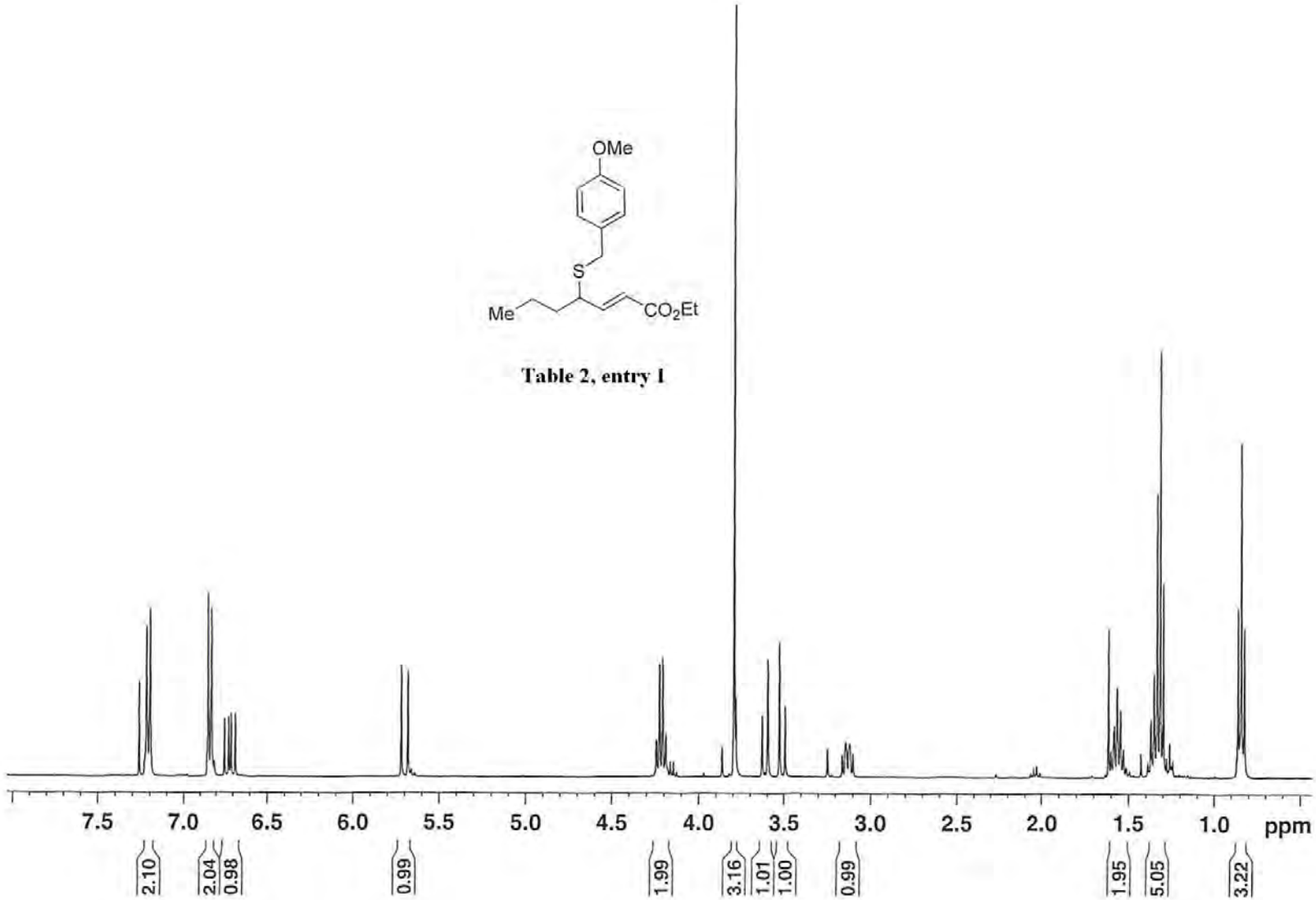
2.02
2.06
2.11
3.00



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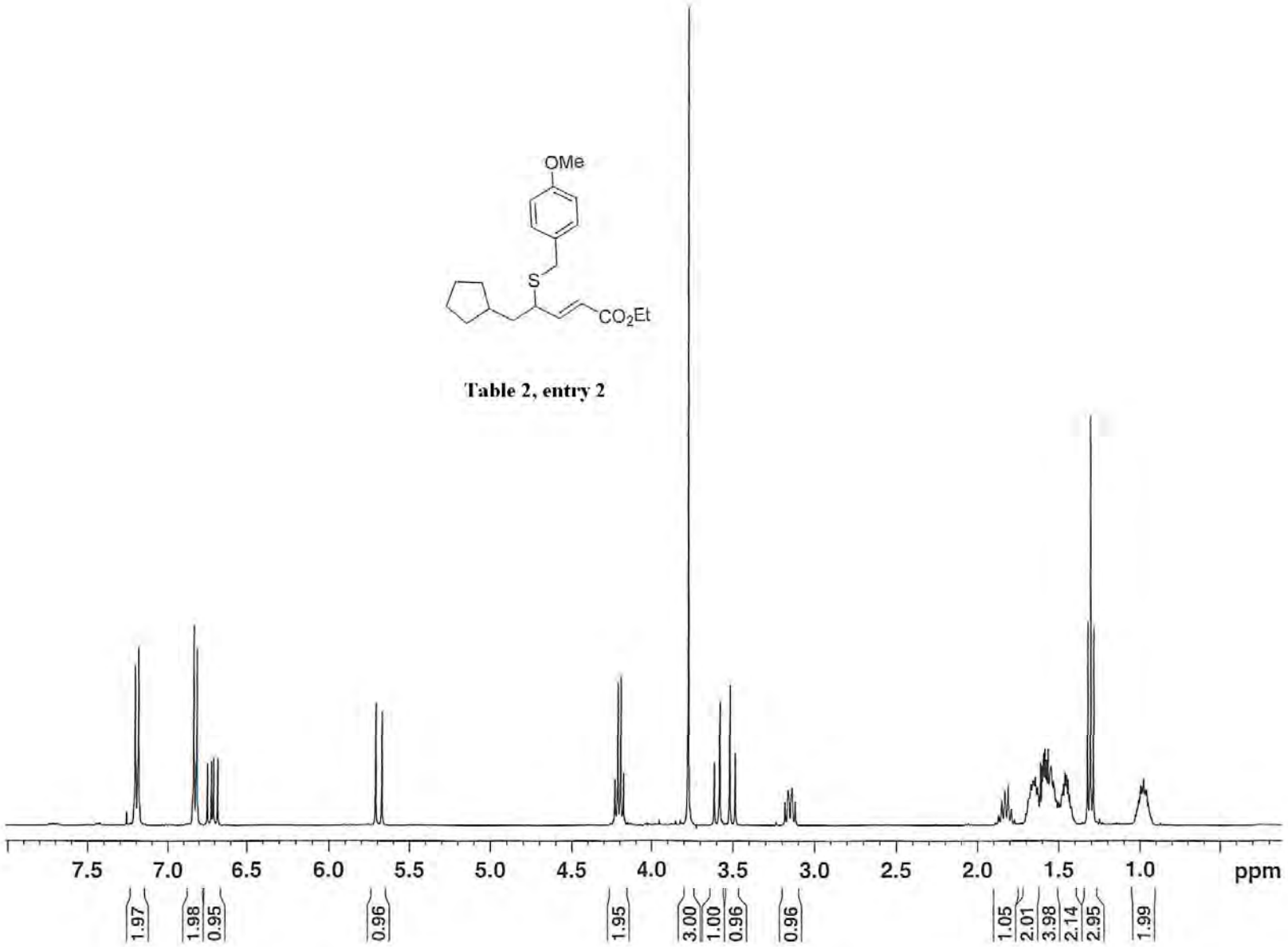

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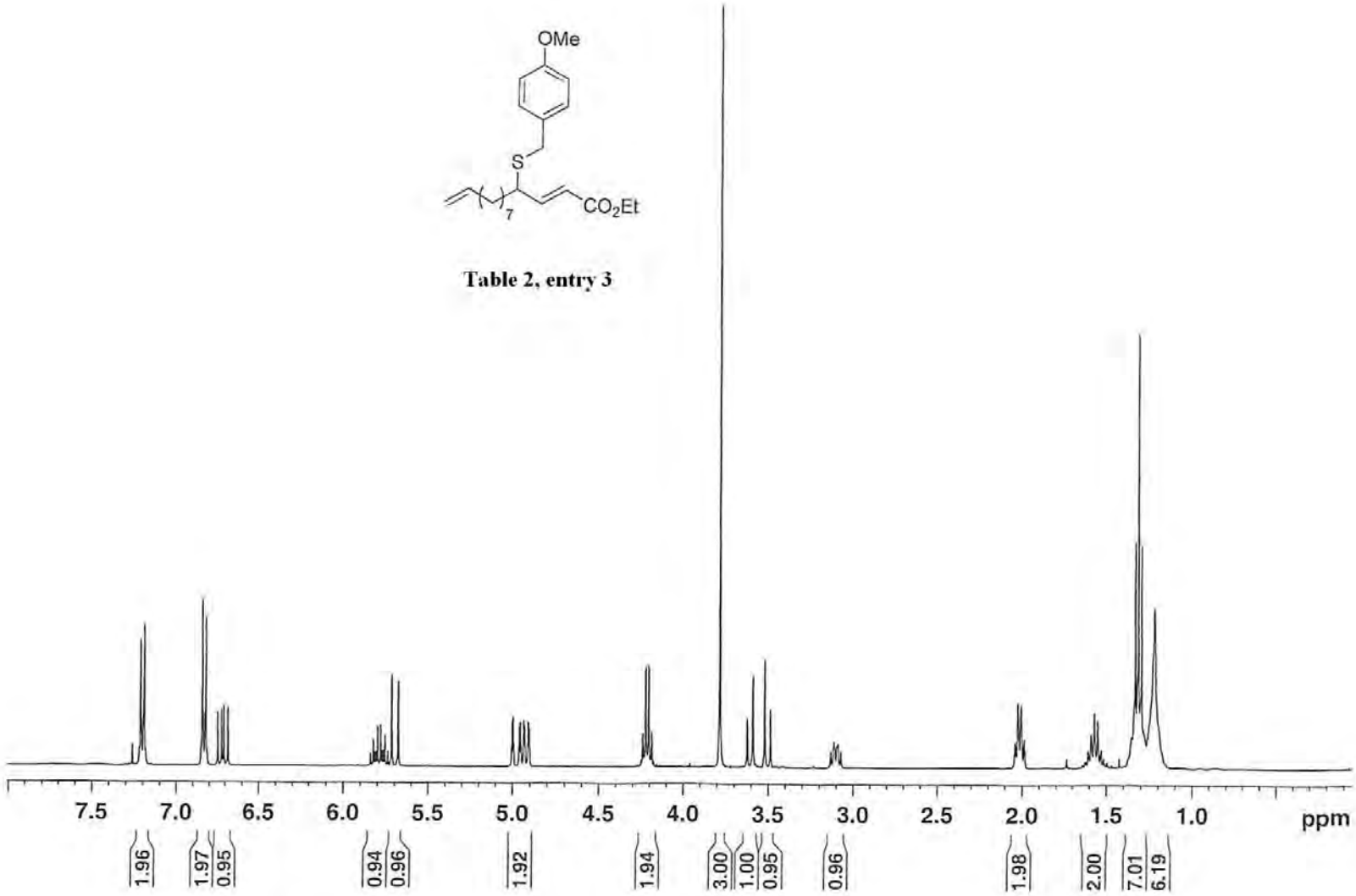

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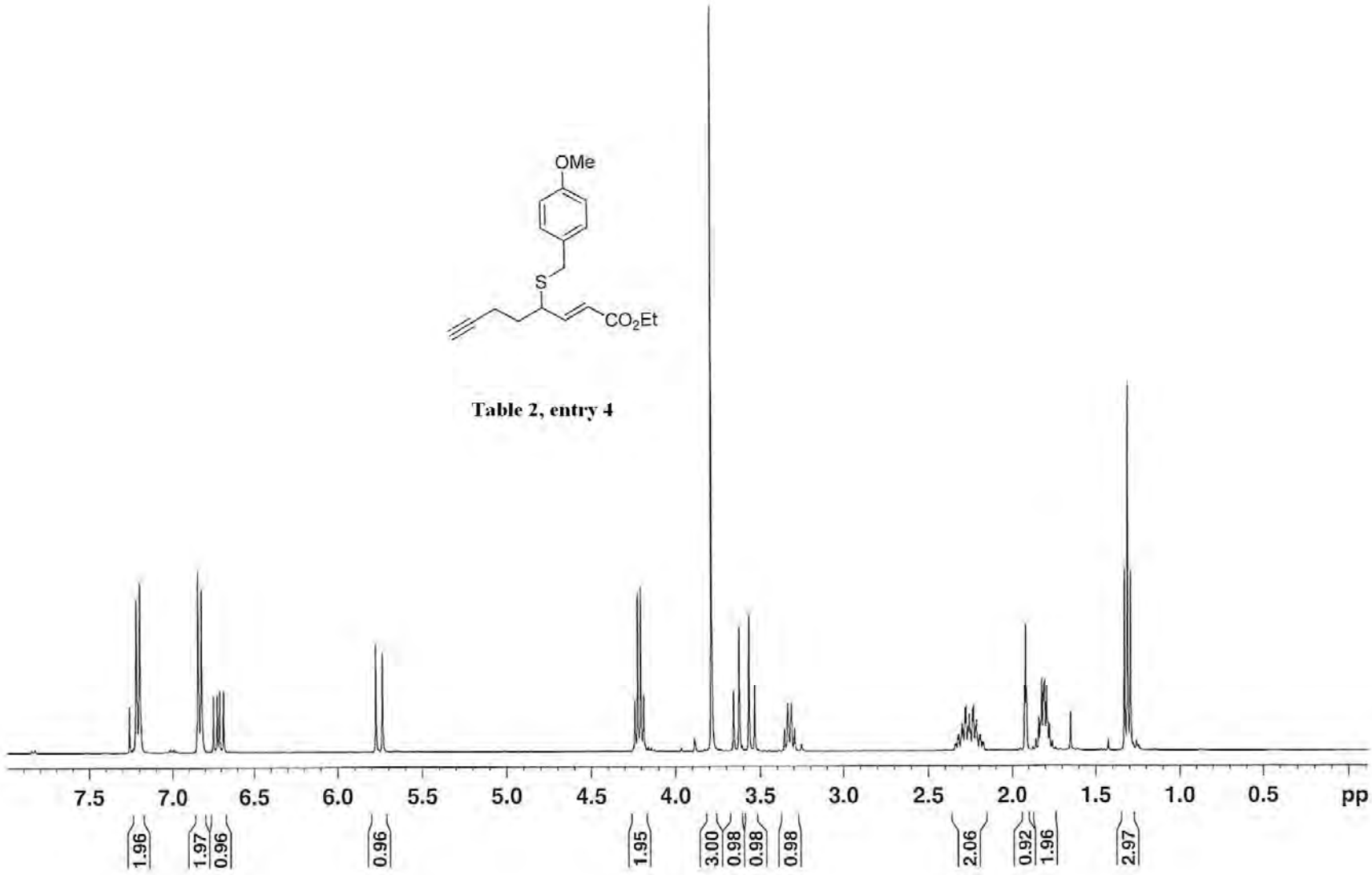

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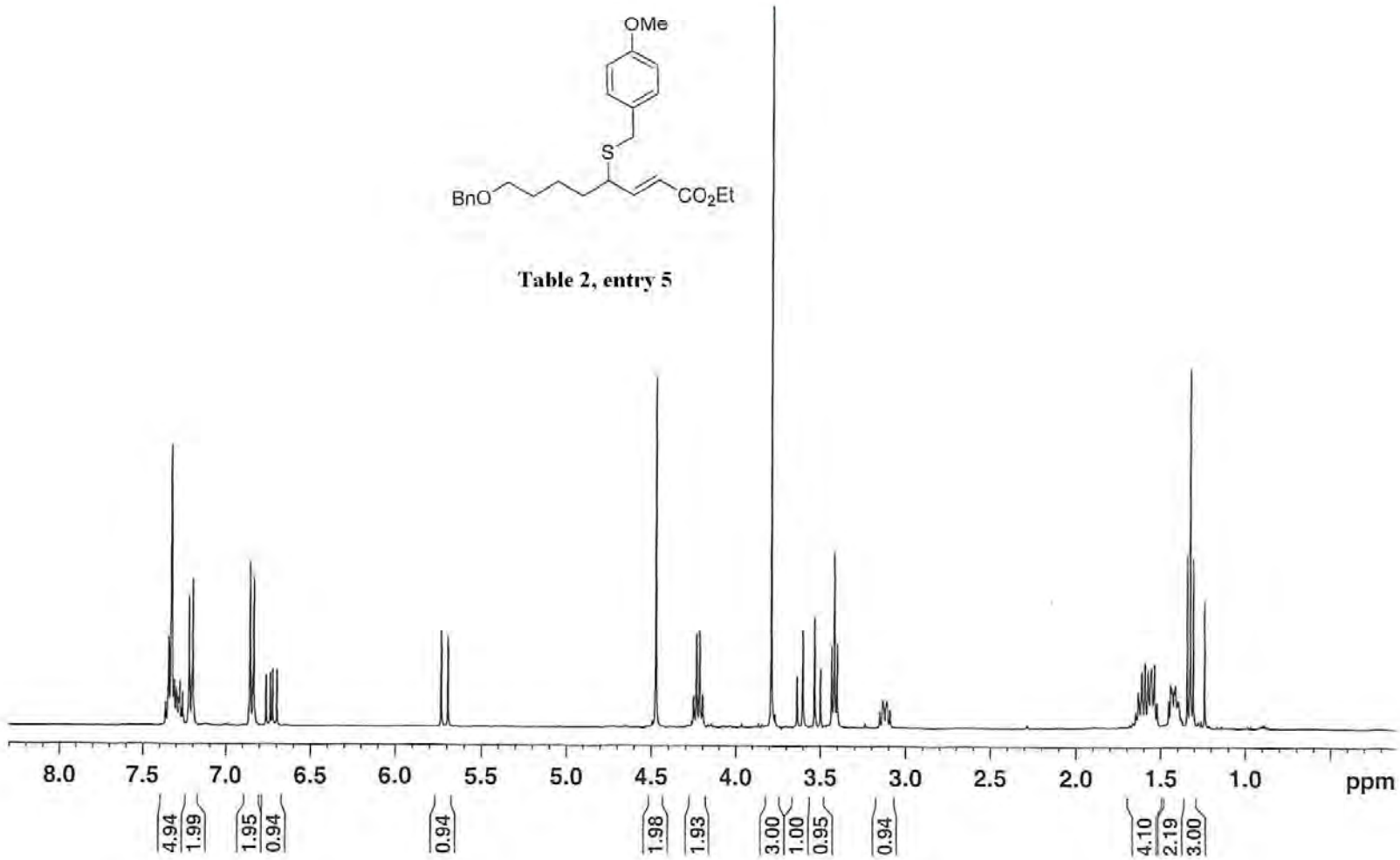

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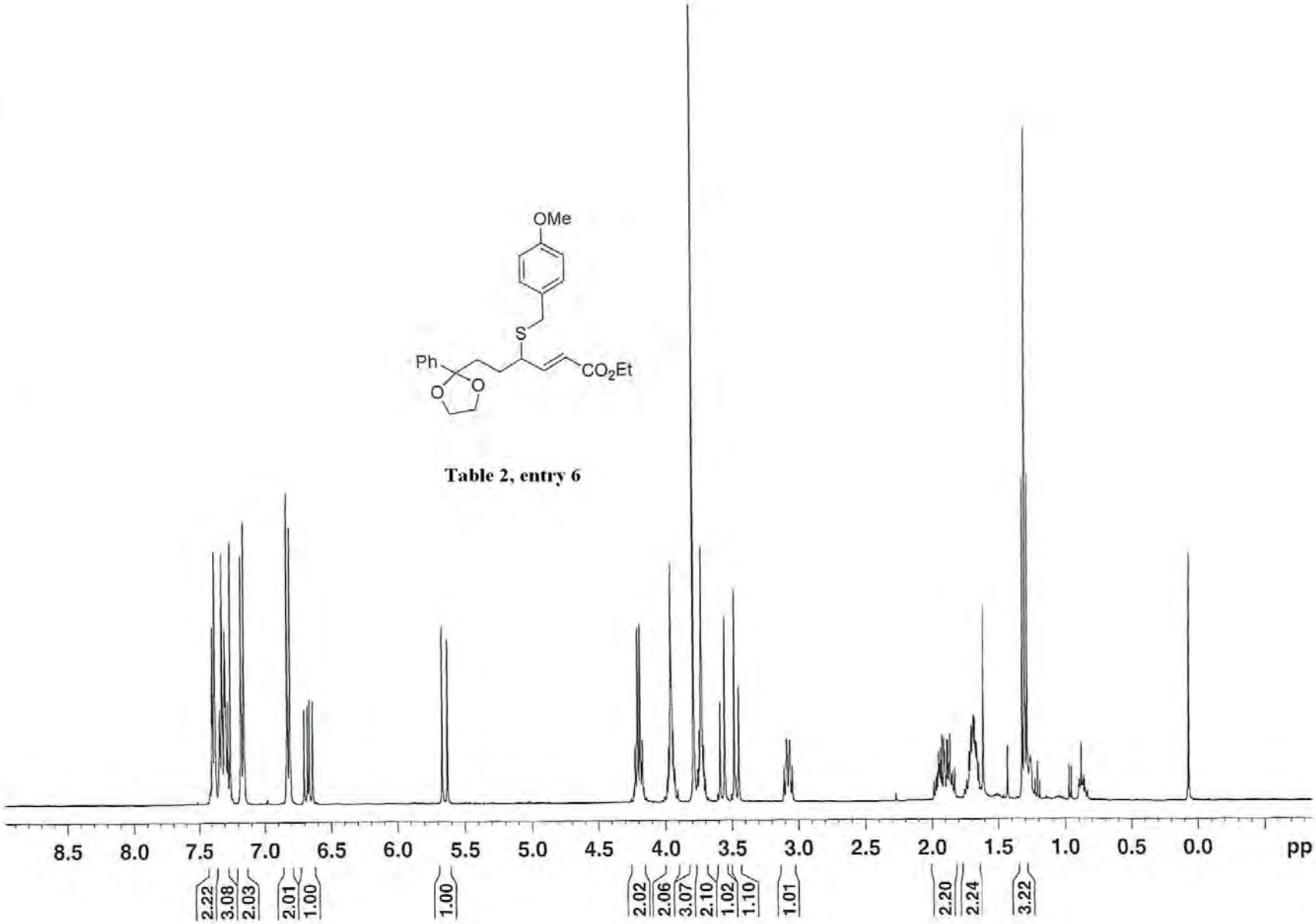

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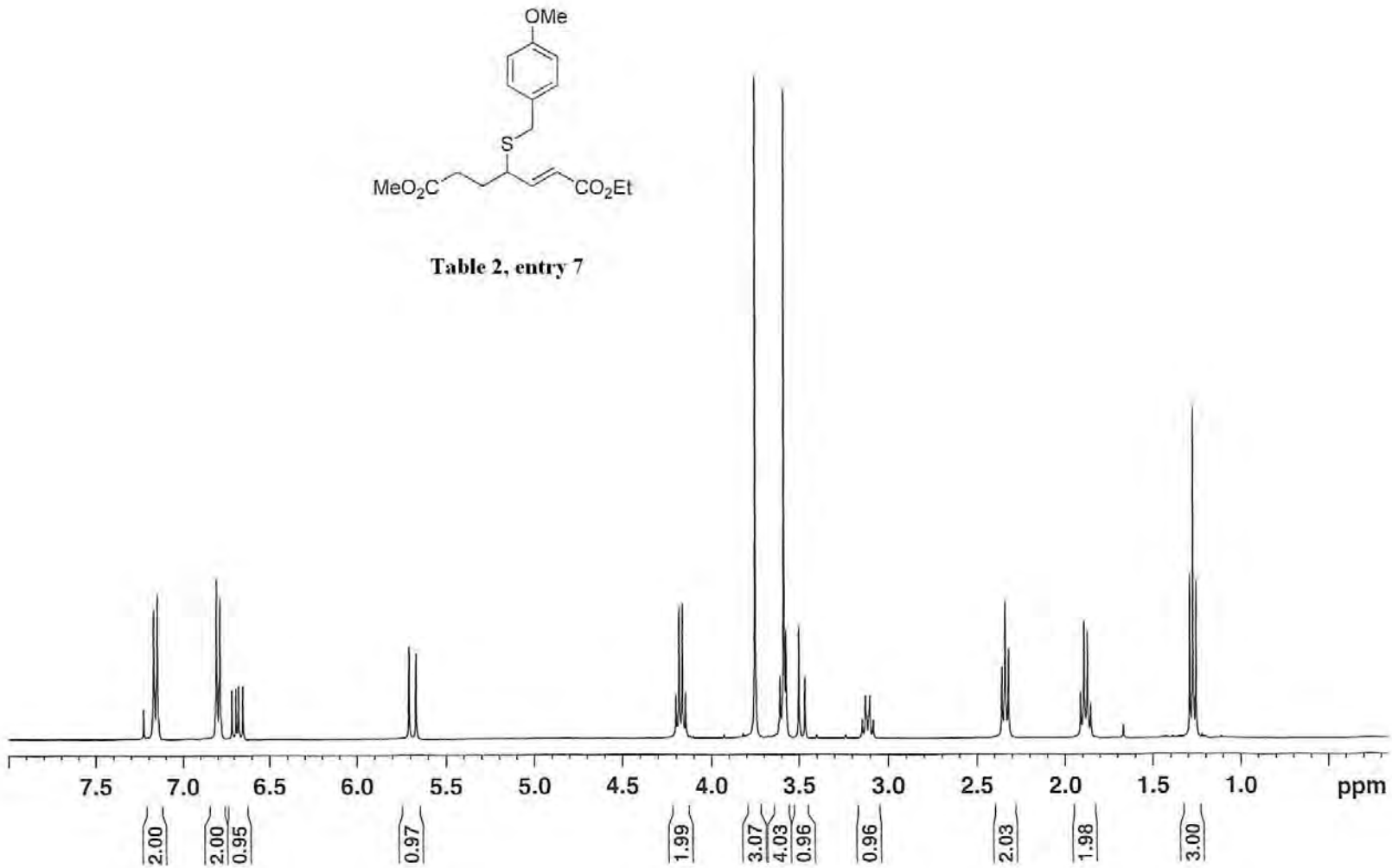

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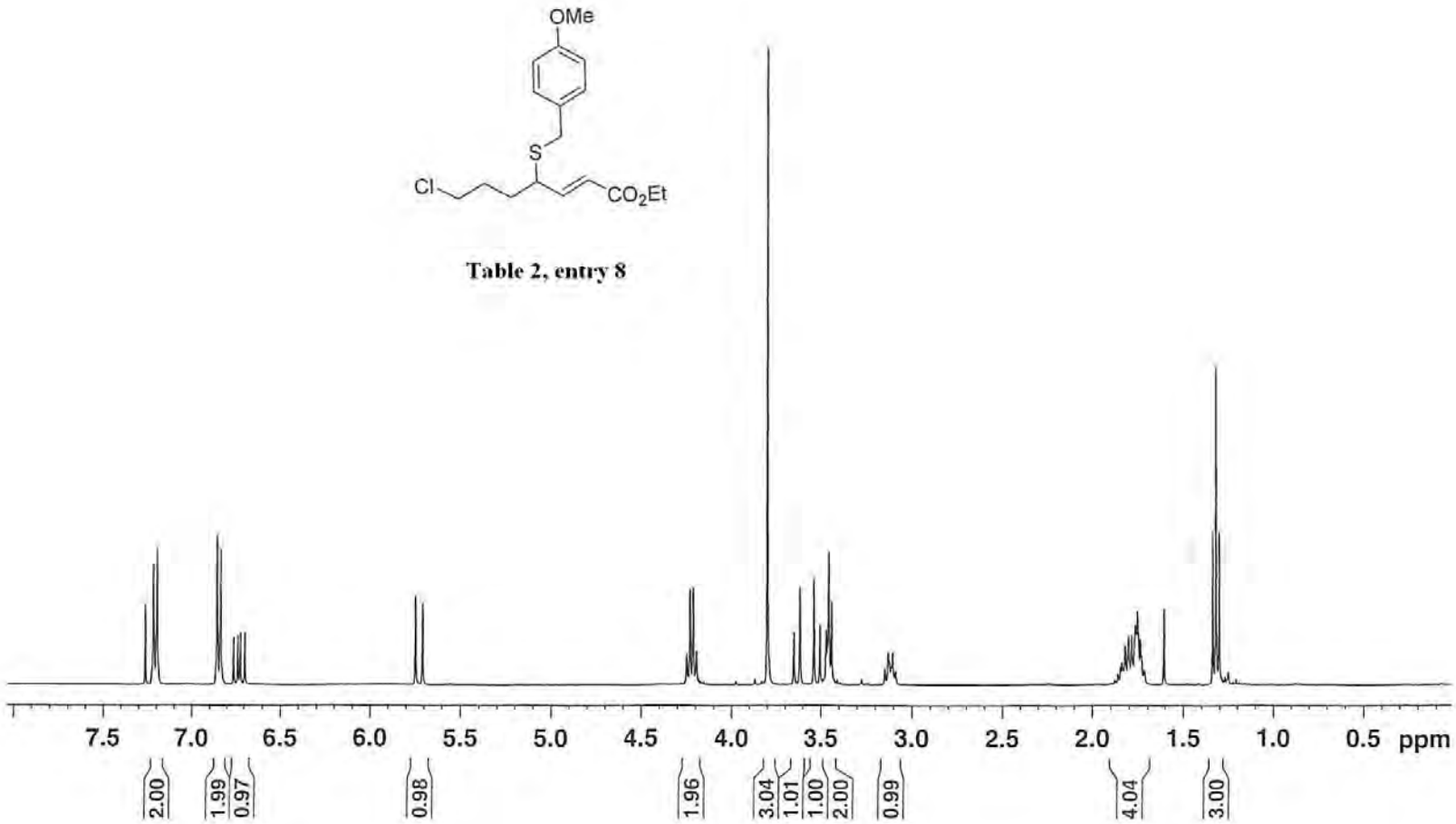

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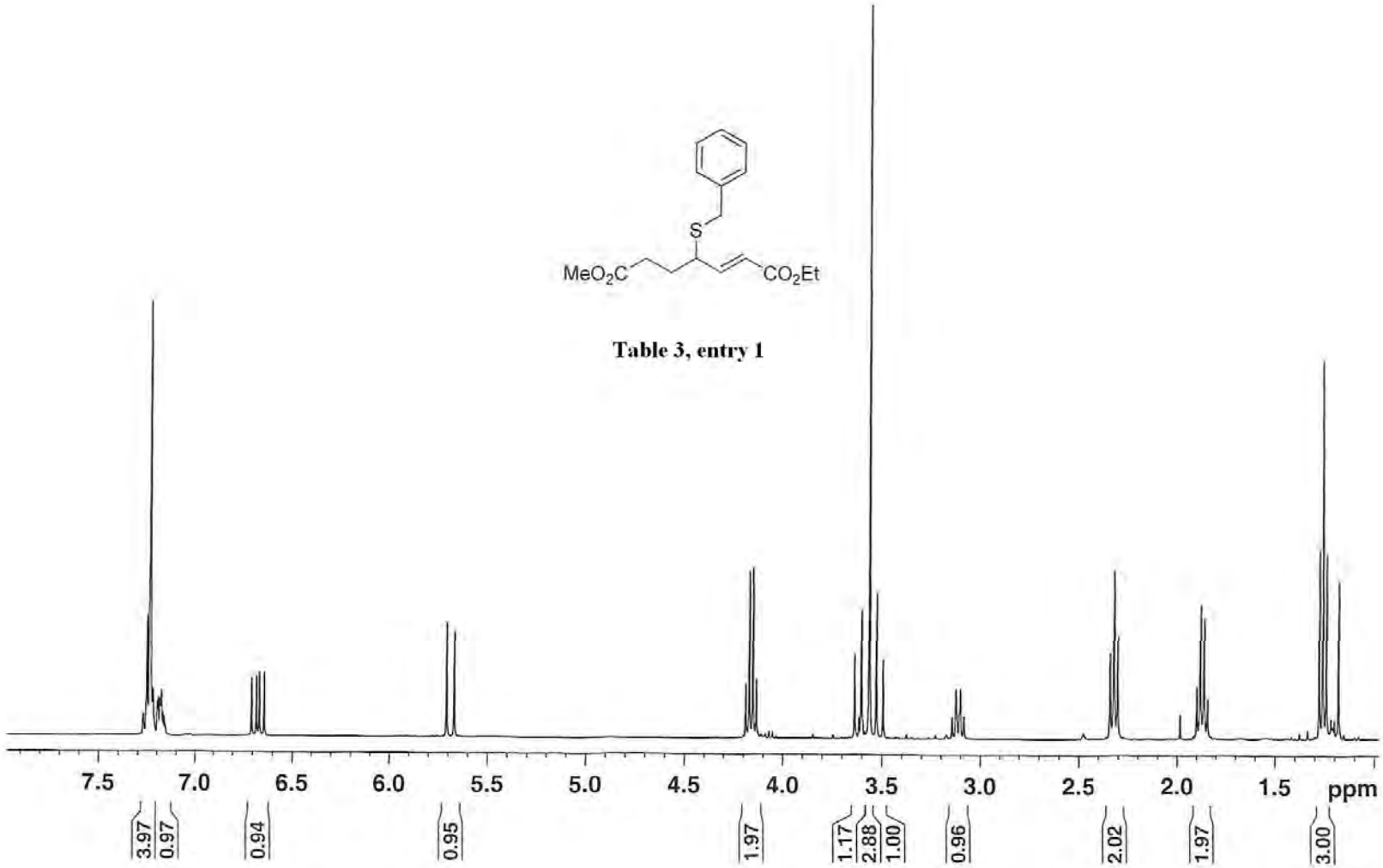

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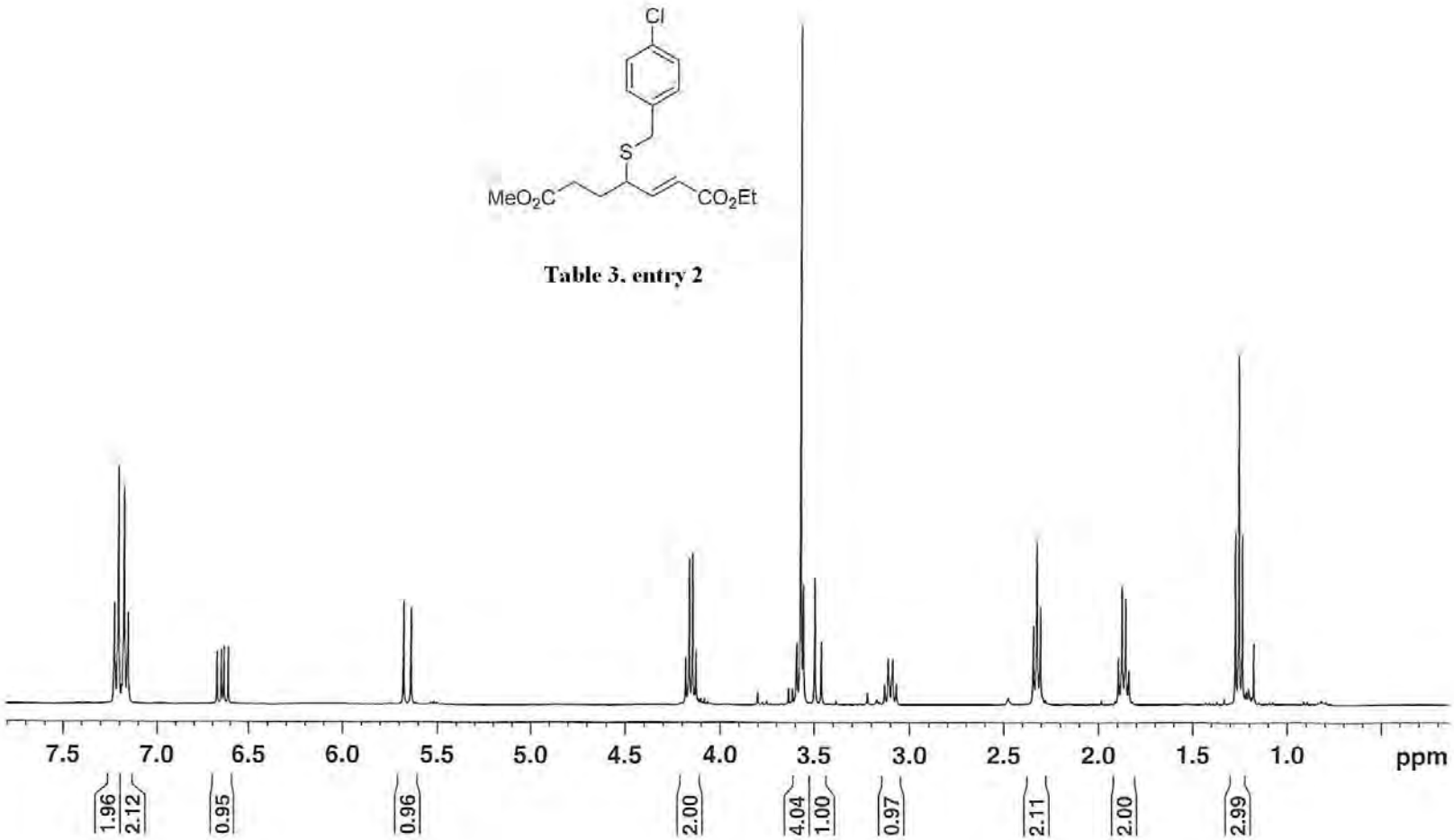

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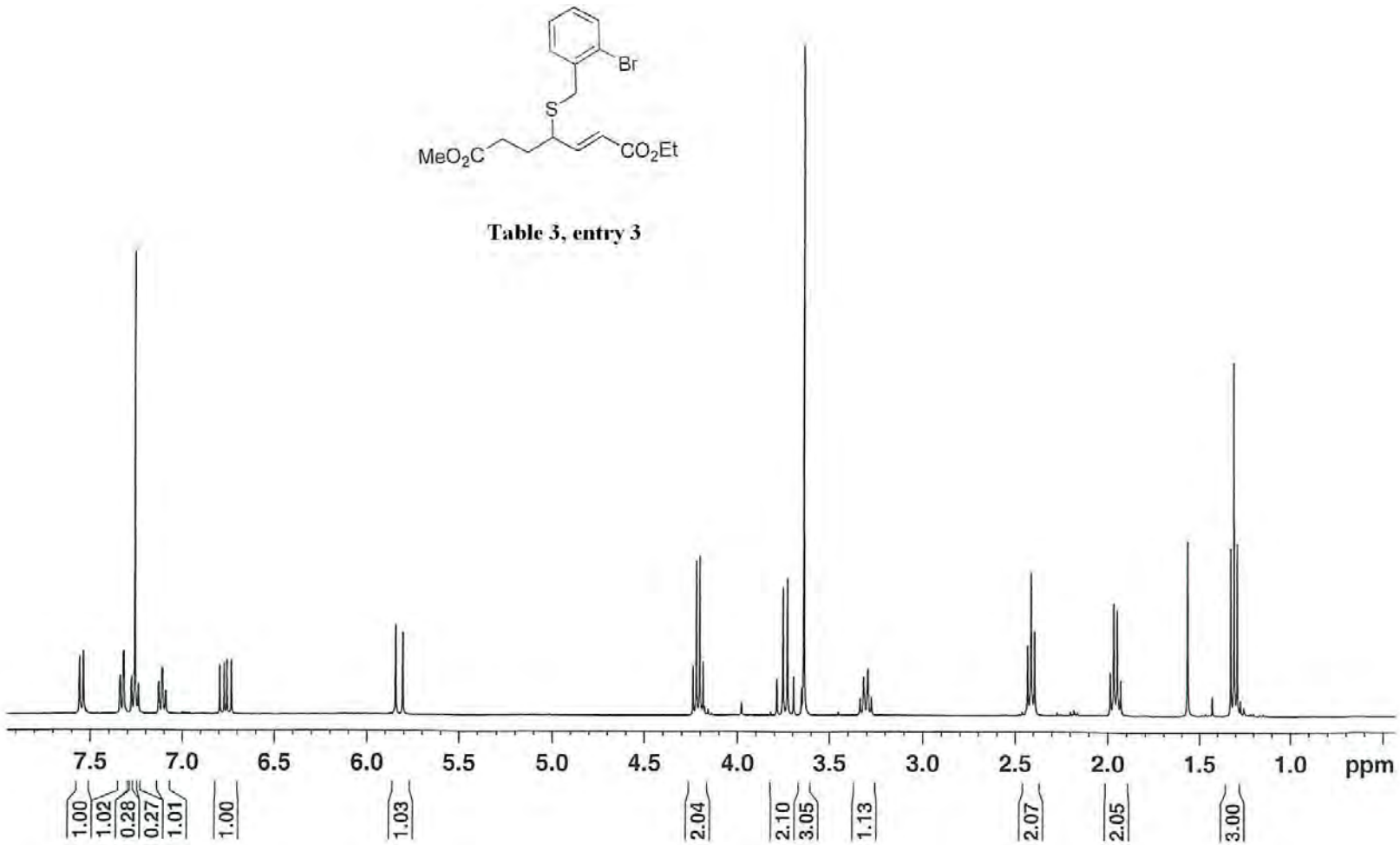

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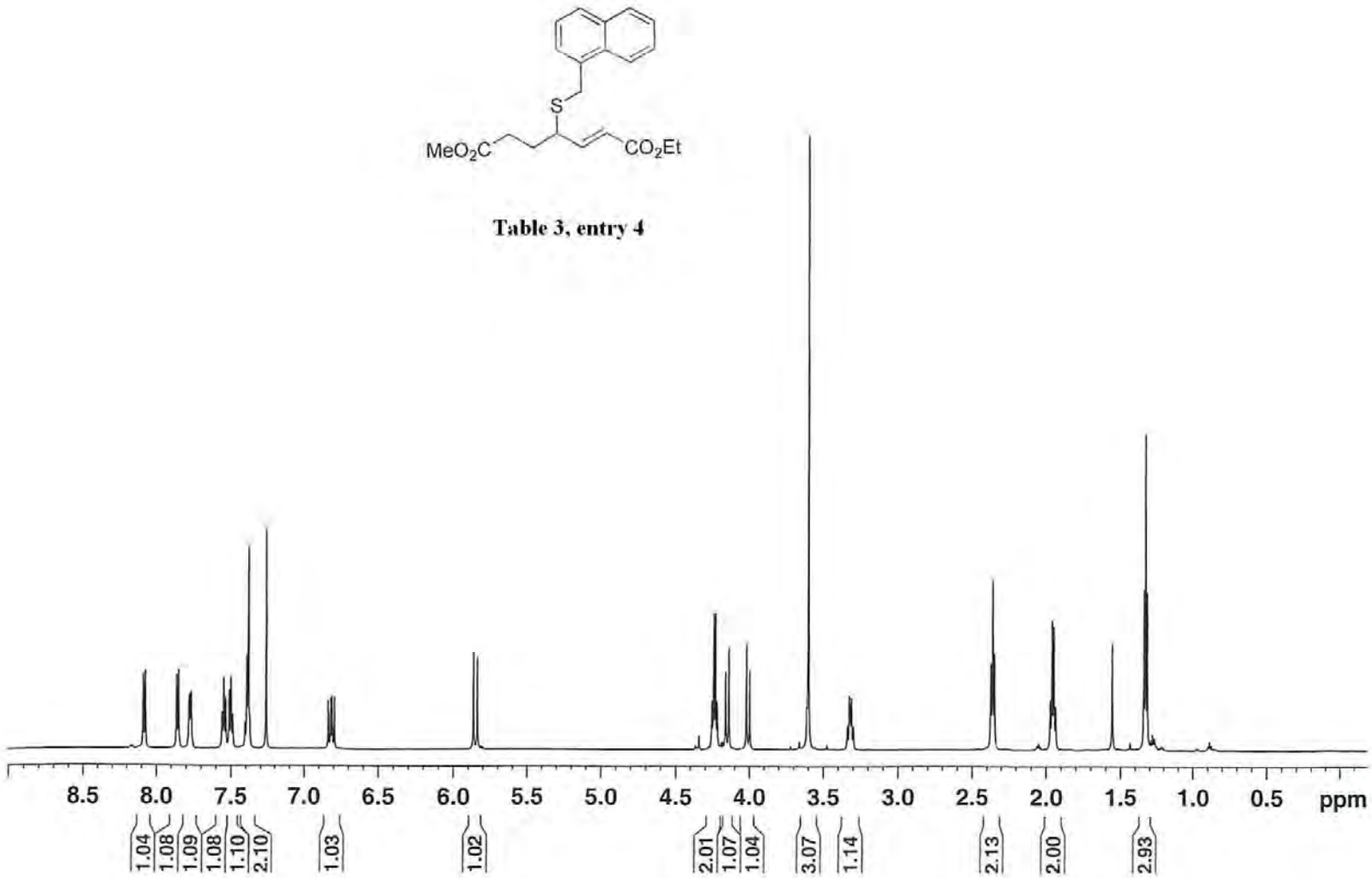

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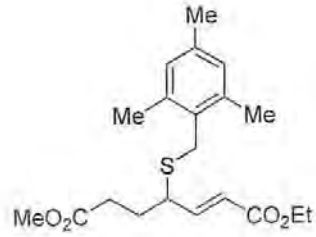

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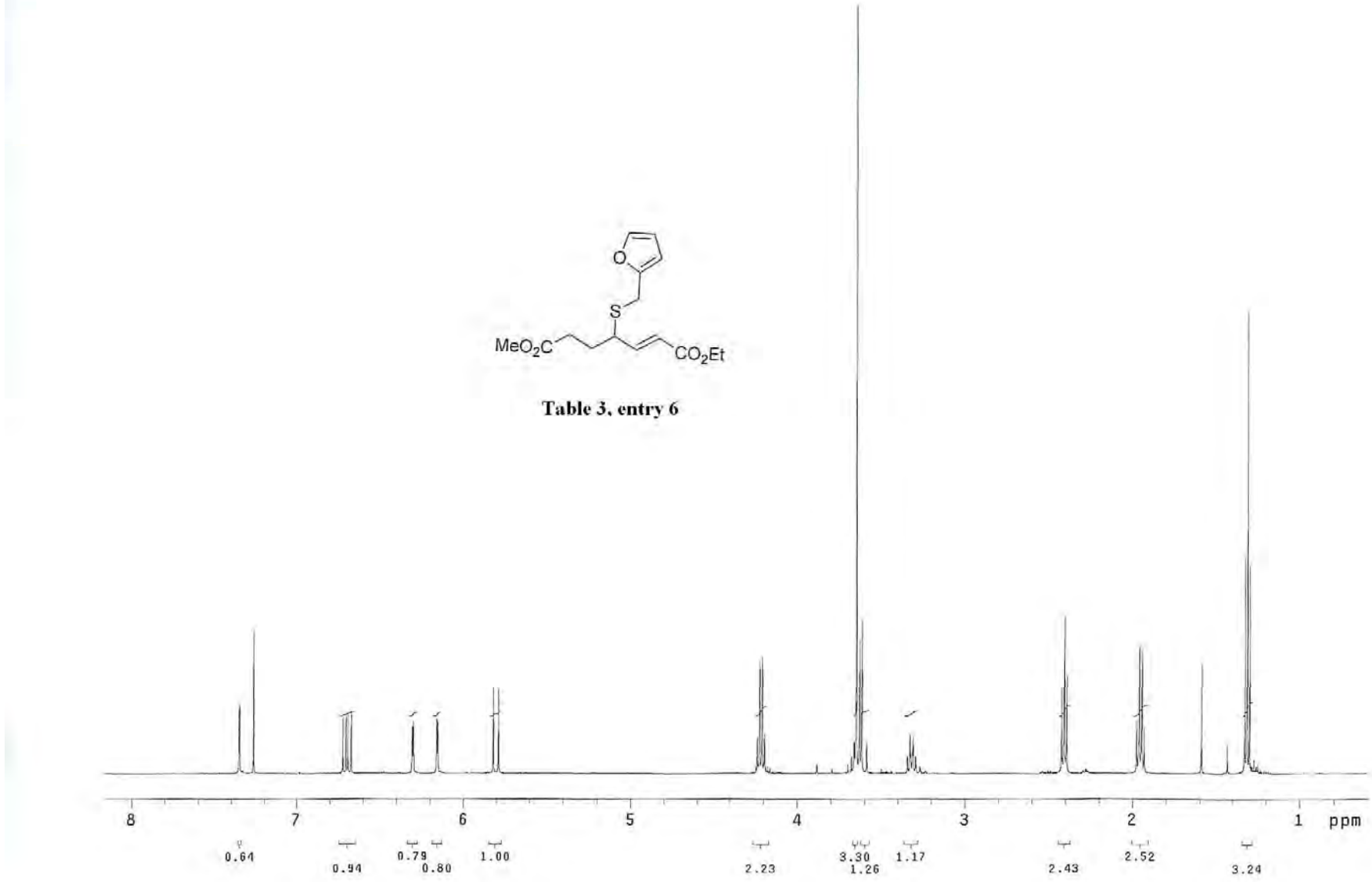

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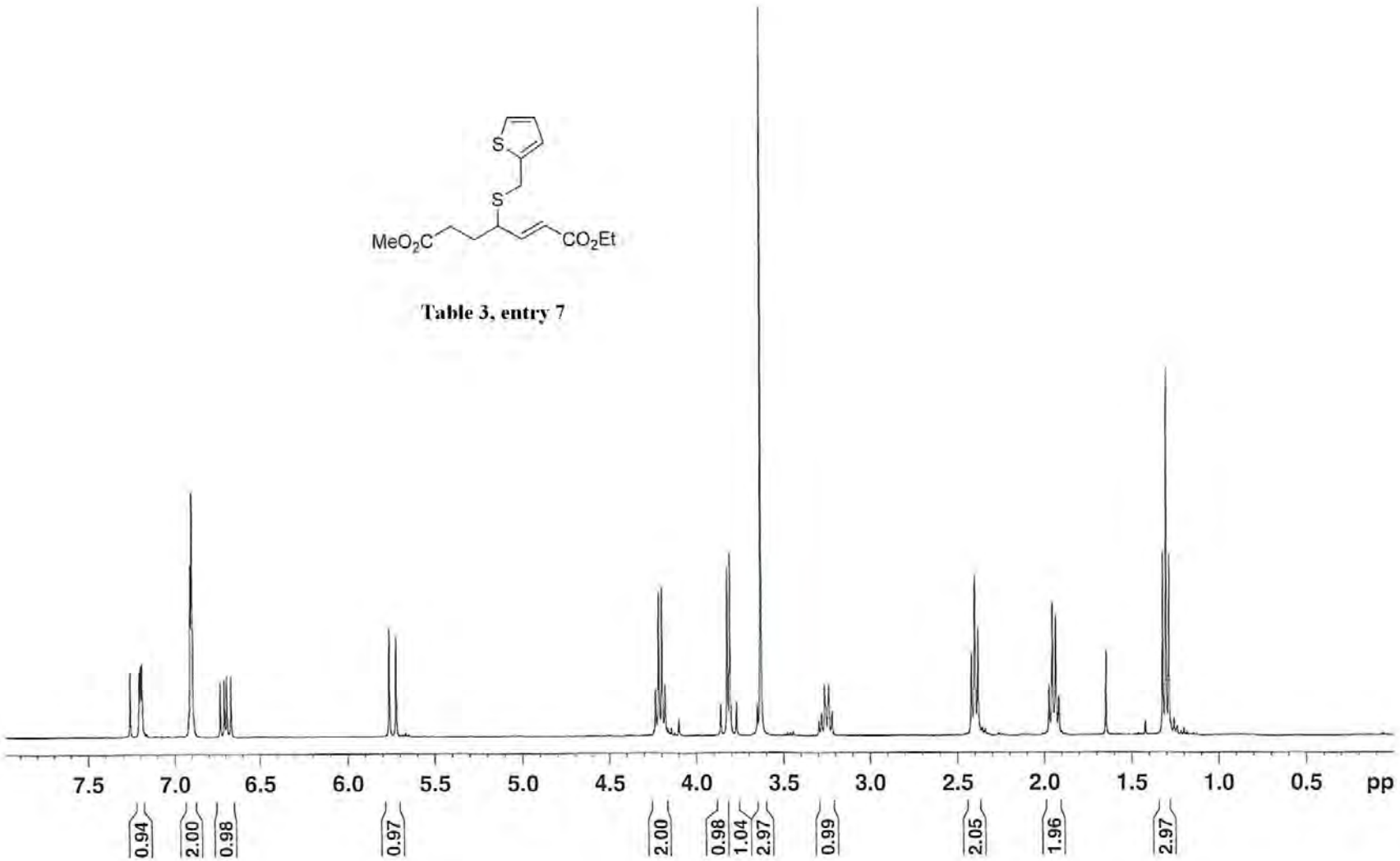

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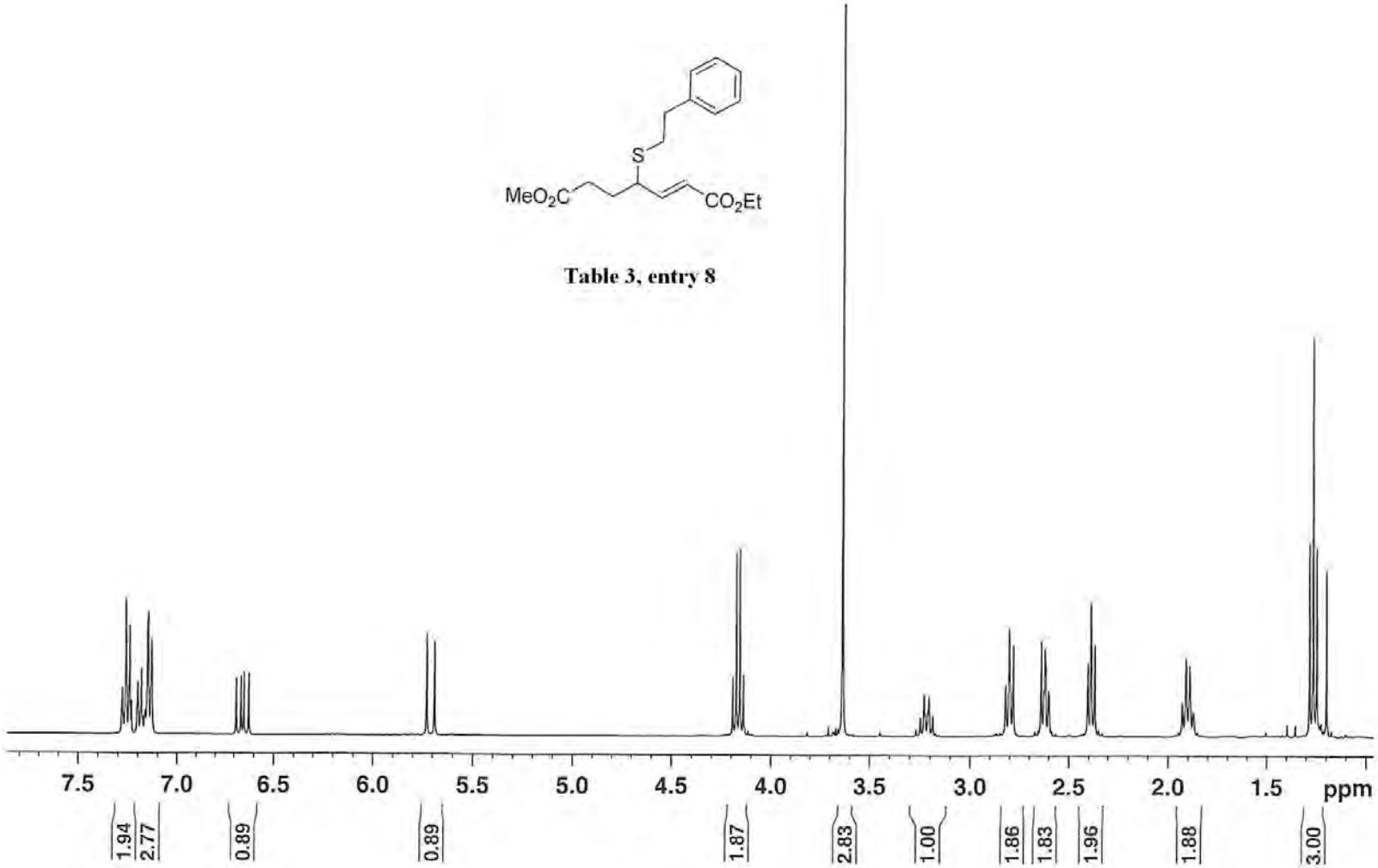


Table 3, entry 8

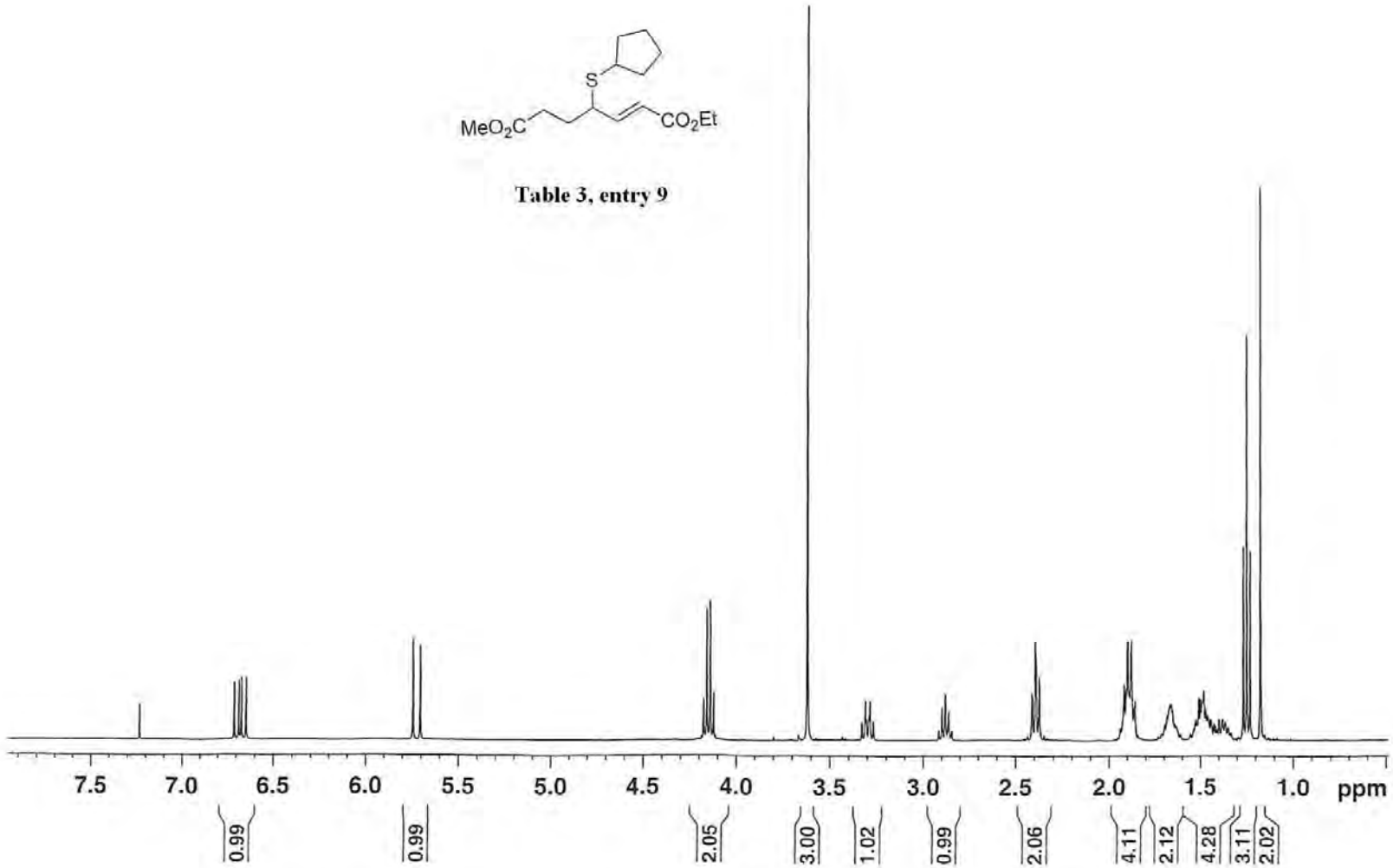


Table 3, entry 9

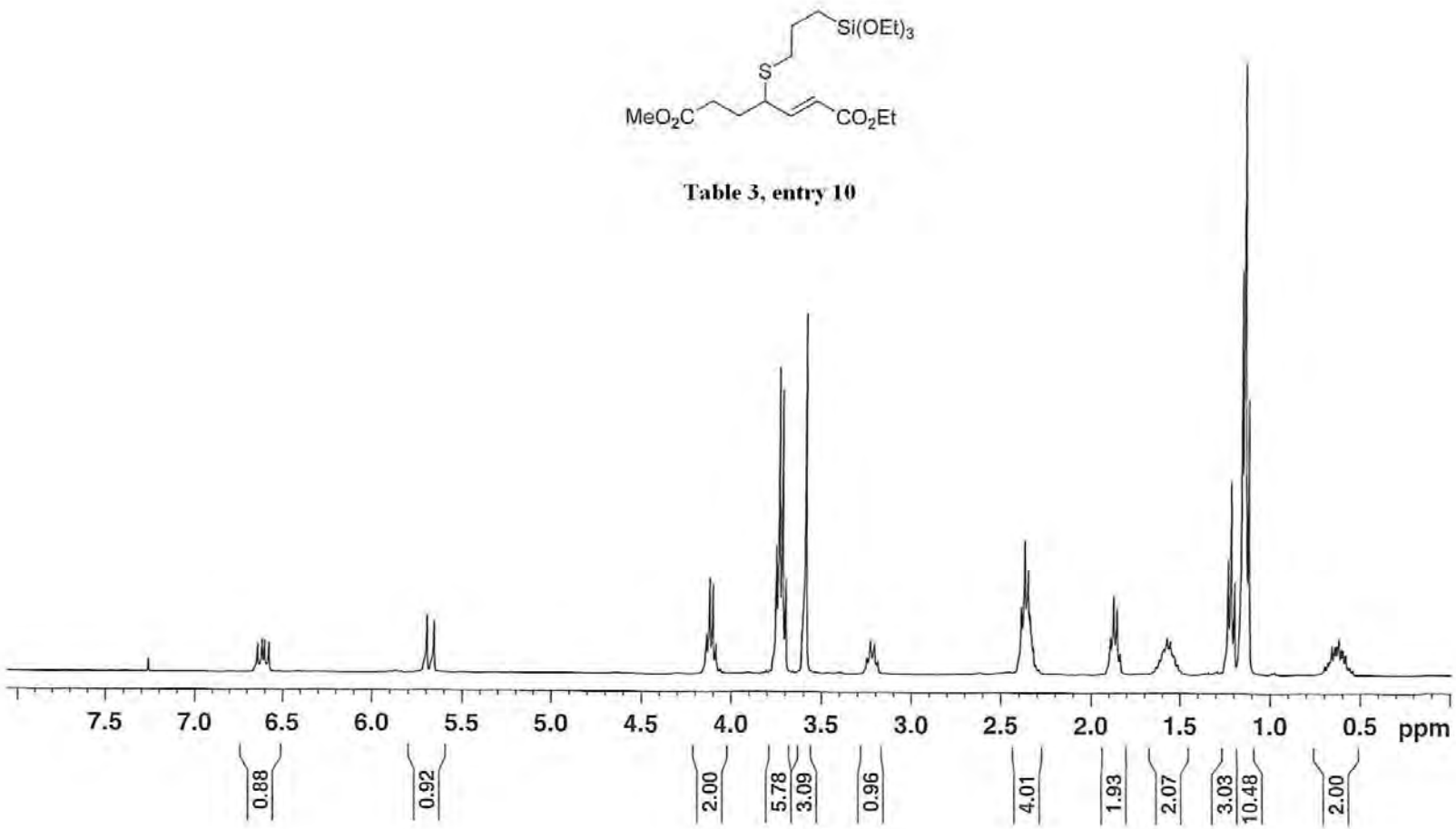


Table 3, entry 10

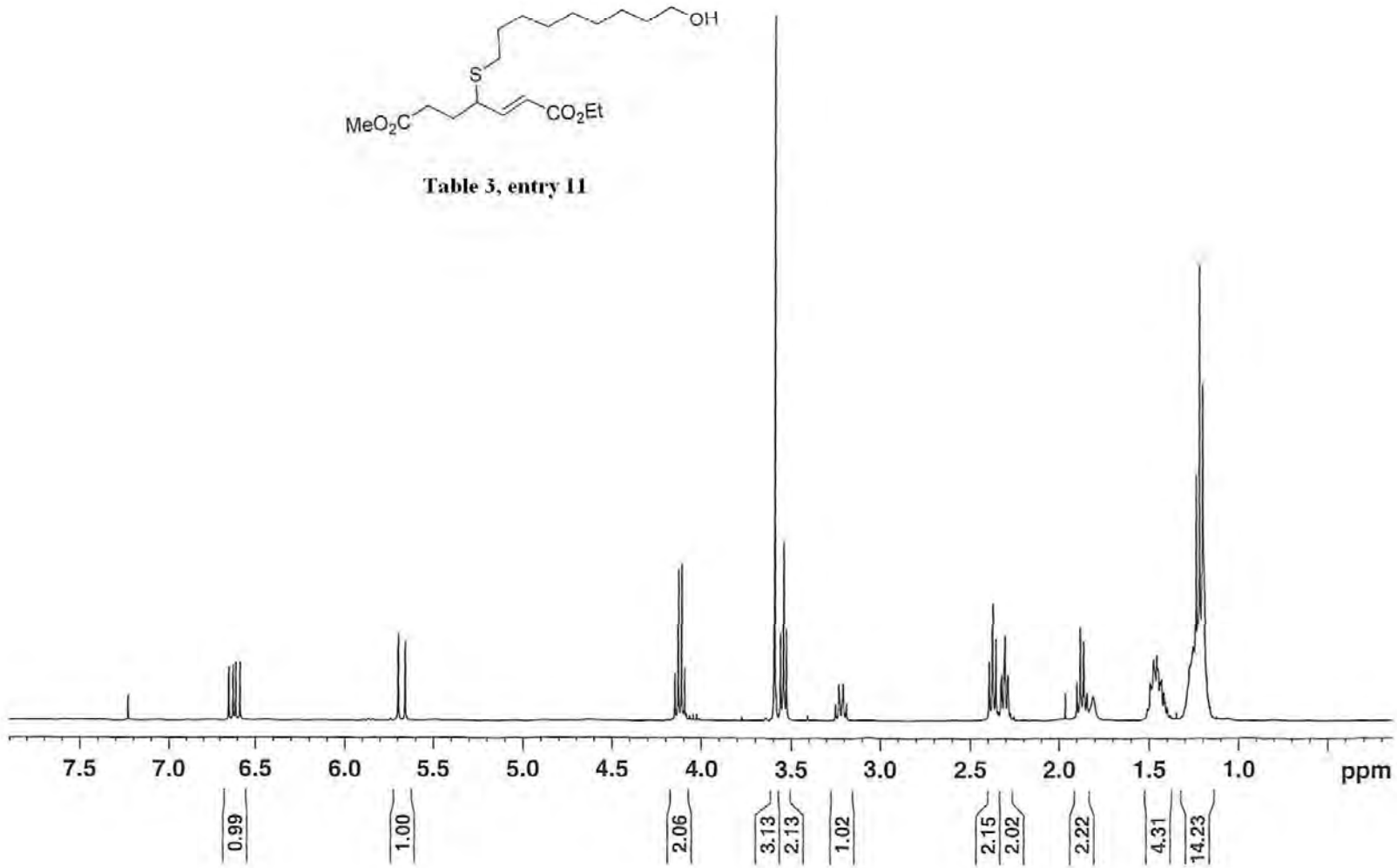
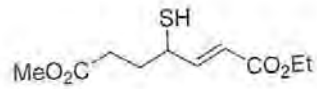
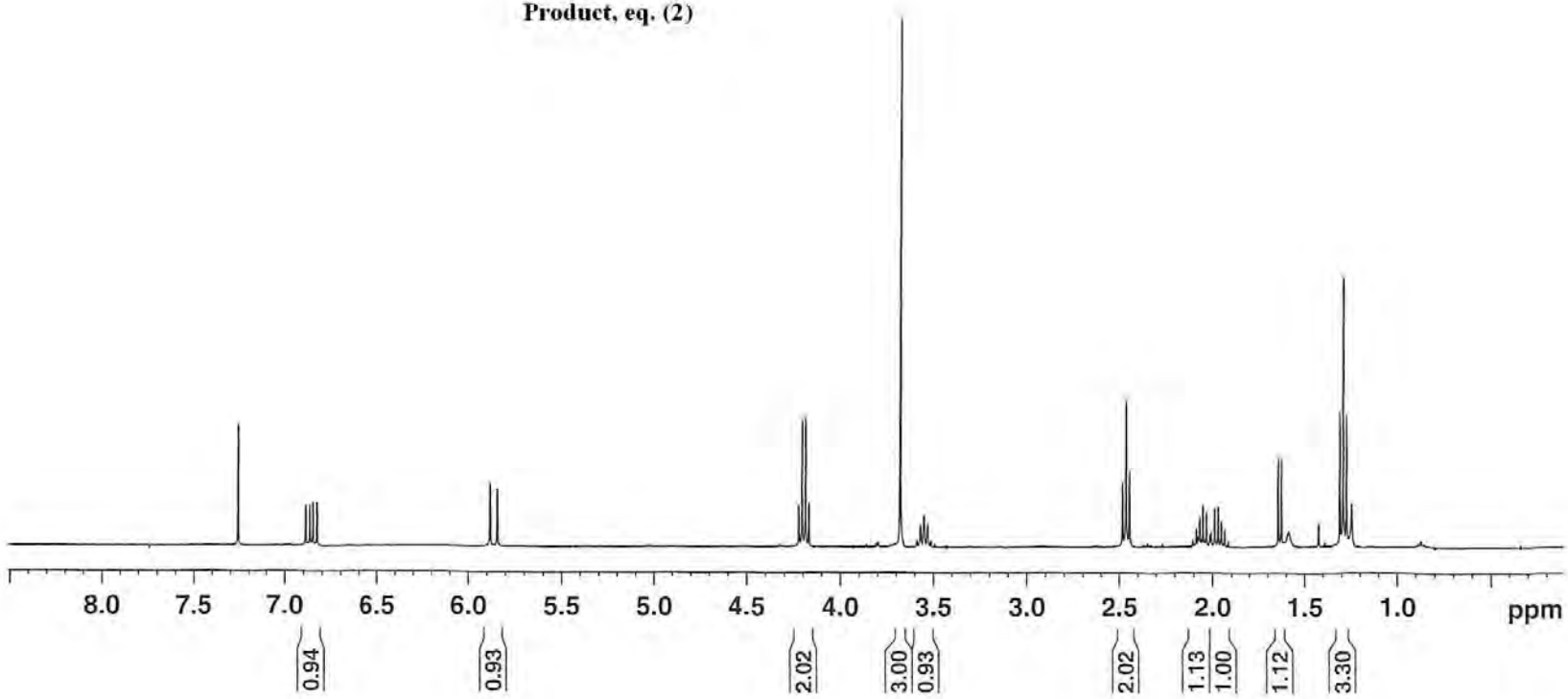
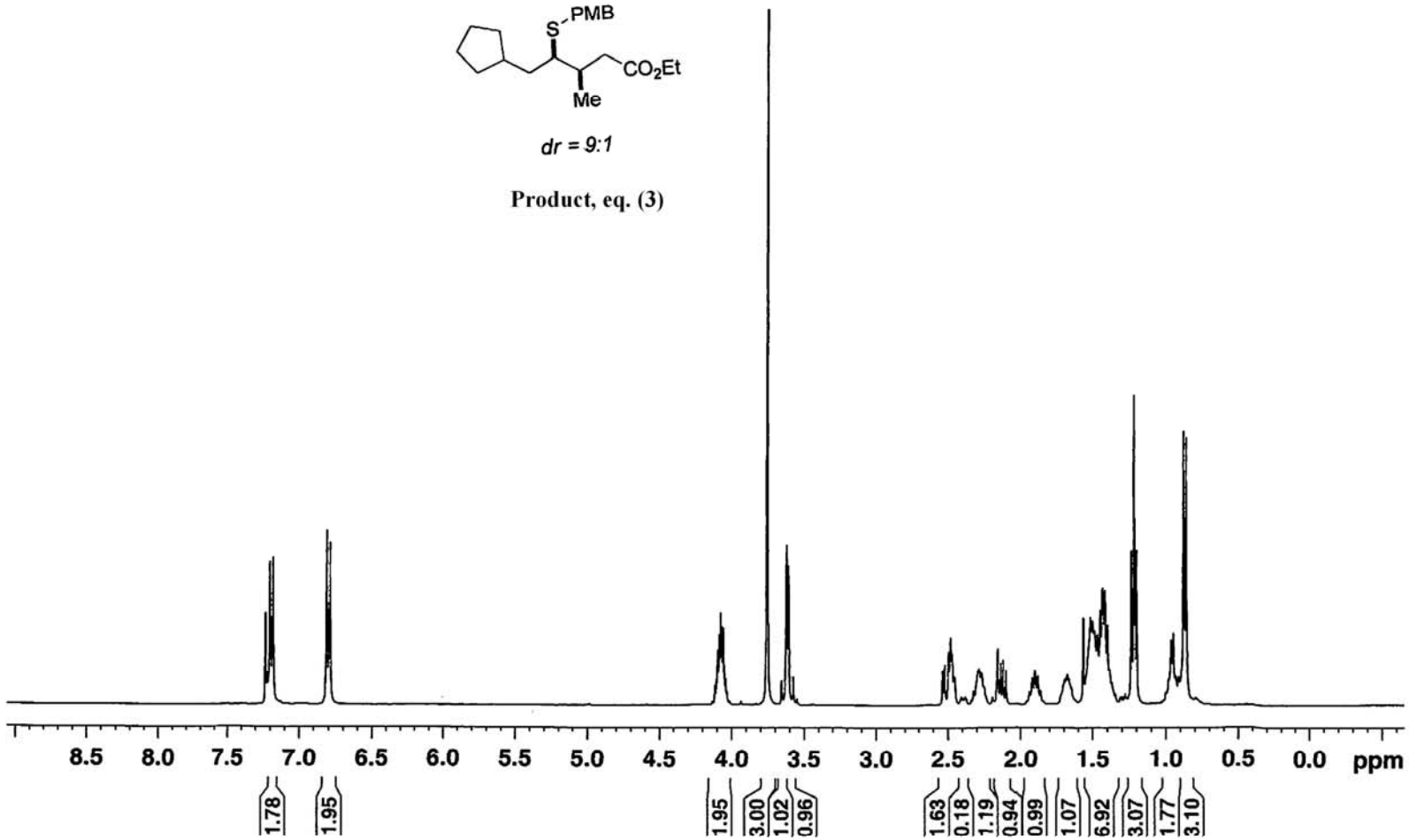


Table 3, entry 11


SH
MeO2C
CO2Et

Product, eq. (2)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.94
0.93
2.02
3.00
0.93
2.02
1.13
1.00
1.12
3.30


PMB
S
CO2Et
Me
dr = 9:1
Product, eq. (3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.78 1.95 1.95 3.00 1.02 0.96 1.63 0.18 1.19 0.94 0.99 1.07 6.92 3.07 1.77 3.10