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# Hiyama Reactions of Activated and Unactivated Secondary Alkyl Halides Catalyzed by Nickel/Norephedrine

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## I. Preparation of Materials

**Trifluoroarylsilanes.** All trifluoroarylsilanes were prepared according to a literature procedure:[1] trifluorophenylsilane [368-47-8], trifluoro-(4-fluorophenyl)silane [24727-90-0], trifluoro-4-tolylsilane [13688-78-3], trifluoro-(4-methoxyphenyl)silane [50625-30-4], and trifluoro-2-tolylsilane [363-86-0].

**Alkyl electrophiles.** All compounds were either purchased or prepared according to the procedures described below.

These preparations have not been optimized.

**4-Bromotetrahydropyran** [25637-16-5]. $Ph_3PBr_2$ (4.55 g, 10.8 mmol) was added in two portions to a solution of tetrahydropyran-4-ol (0.93 mL, 9.8 mmol) and imidazole (0.80 g, 11.7 mmol) in $CH_2Cl_2$ (10 mL). After 28 h of stirring at room temperature, the reaction mixture was poured into a round-bottomed flask that contained silica gel, and the $CH_2Cl_2$ was removed by rotary evaporation. The silica gel was then loaded on top of a column of silica gel, which was eluted with $Et_2O$. Removal of the solvent on a rotary evaporator furnished 4-bromotetrahydropyran as a colorless oil (906 mg, 56%).

$^1H$ NMR (300 MHz, $CDCl_3$) δ 4.34 (tt, *J* = 8.4, 4.2 Hz, 1H), 3.93 (ddd, *J* = 11.7, 4.8, 4.2 Hz, 2H), 3.52 (ddd, *J* = 11.4, 5.1, 3.0 Hz, 2H), 2.22-2.11 (m, 2H), 2.01 (dtd, *J* = 13.5, 8.4, 3.6 Hz, 2H).

$^{13}C$ {$^1H$} NMR (75.5 MHz, $CDCl_3$) δ 66.7, 48.2, 37.2.

***t*-Butyl 2-bromoisovalerate** [42877-95-2]. $SOCl_2$ (30 mL) was added to 2-bromoisovaleric acid at room temperature, and then the stirred reaction mixture was heated at reflux for 2 h. Evaporation of the excess $SOCl_2$ in vacuo provided the crude acid chloride. This oil was dissolved in $CH_2Cl_2$ and added to a solution of *t*-BuOH (1.15 mL, 12.2 mmol) and $Et_3N$ (1.70 mL, 12.2 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature overnight, and then it was poured into saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 30 mL). The combined organic layers were washed ($H_2O$), dried ($MgSO_4$), and concentrated by rotary evaporation to give *t*-butyl-2-bromoisovalerate as a light-brown oil (1.53 g, 58%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 3.93 (d, *J* = 8.1 Hz, 1H), 2.19 (octet, *J* = 6.9 Hz, 1H), 1.48 (s, 9H), 1.08 (d, *J* = 6.6 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 168.8, 82.5, 56.7, 32.6, 28.0, 20.21, 20.17.

**2-Bromo-*N,N*-diisopropylbutyramide** [54367-89-4]. 2-Bromobutyryl bromide (2.92 mL, 25 mmol) was added over 5 min to a solution of diisopropylamine (3.85 mL, 27.5 mmol) and $Et_3N$ (3.83 mL, 27.5 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and then it was poured into $H_2O$ (200 mL). The mixture was extracted with $Et_2O$ (3 x 50 mL), and the combined organic layers were washed (brine), dried ($MgSO_4$), and concentrated by rotary evaporation. Flash chromatography (10:1 hexane/EtOAc) gave 2-bromo-*N,N*-diisopropylbutyramide ($R_f = 0.24$) as white crystals (1.58 g, 25%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 4.23 (t, *J* = 7.2 Hz, 1H), 4.04 (septet, *J* = 6.6 Hz, 1H), 3.46 (br s, 1H), 2.14 (septet, *J* = 7.2 Hz, 1H), 2.00 (septet, *J* = 7.2 Hz, 1H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 167.5, 49.1, 47.8, 46.5, 28.7, 21.4, 20.7, 20.6, 20.1, 12.6.

**Diethyl α-bromoethylphosphonate** [118512-84-8]. A solution of isopropylamine (3.35 mL, 24 mmol) in THF (20 mL) was added over 5 min to a solution of *n*-BuLi (1.6 M solution in hexane; 14.4 mL, 23 mmol) in THF (20 mL) at –78 °C. After 15 min, a solution of diethyl ethylphosphonate (1.62 mL, 10 mmol) in THF (20 mL) was added. This mixture was stirred for 10 min, and then a solution of trimethylsilyl chloride (1.40 mL, 11 mmol) in THF (20 mL) was added. The reaction mixture was allowed to warm to 0 °C over 15 min, and then it was cooled again to –78 °C. 1,2-Dibromoethane (1.03 mL, 12 mmol) in THF (20 mL) was added over 10 min, and the reaction mixture was allowed to warm to 0 °C over 15 min. A solution of LiOEt/EtOH (1.0 M; 20 mL) was added, and the reaction mixture was stirred for 30 min. Next, it was poured into a separatory funnel that contained $CH_2Cl_2$ (20 mL), aqueous HCl (2 M; 15 mL), and crushed ice. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated by rotary evaporation. Flash chromatography (1:1 hexane/EtOAc) provided diethyl α-bromoethylphosphonate ($R_f = 0.22$) as a pale-yellow oil (1.71 g, 70%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 4.24-4.11 (m, 4H), 3.87 (dq, $J$ = 9.0, 7.2 Hz, 1H), 1.80 (dd, $J$ = 16.8, 7.5 Hz, 3H), 1.315 (td, $J$ = 7.2, 0.6 Hz, 3H), 1.313 (td, $J$ = 7.2, 0.6 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 63.9 (d, $J$ = 6.9 Hz), 63.7 (d, $J$ = 6.9 Hz), 35.2 (d, $J$ = 159.9 Hz), 20.3 (d, $J$ = 2.9 Hz), 16.7 (d, $J$ = 1.1 Hz), 16.6 (d, $J$ = 1.1 Hz).

$^{31}$P {$^1$H} NMR (121.5 MHz, $CDCl_3$) δ 22.0.

**2-Chloro-1-morpholinopropan-1-one** [54022-76-3]. A solution of morpholine (2.40 mL, 27.5 mmol) and $Et_3N$ (3.83 mL, 27.5 mmol) in THF (50 mL) was stirred for 5 min at 0 °C. 2-Chloropropionyl chloride (2.43 mL, 25 mmol) was added over 5 min, and the reaction mixture was then stirred at 0 °C for 1 h. Next, the reaction mixture was poured into $H_2O$ (200 mL), and this mixture was extracted with $Et_2O$ (3 x 50 mL). The combined organic layers were washed (brine), dried ($MgSO_4$), and concentrated by rotary evaporation. Flash chromatography (1:1 hexane/EtOAc) furnished 2-chloro-1-morpholinopropan-1-one ($R_f = 0.19$) as a colorless oil (1.19 g, 27%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 4.51 (q, $J$ = 6.6 Hz, 1H), 3.84-3.57 (m, 6H), 3.51-3.40 (m 2H), 1.65 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 167.6, 66.9, 66.7, 49.4, 46.6, 42.9, 21.0.

**Diethyl α-chloropropylphosphonate** [56436-86-3]. Diethyl α-chloropropylphosphonate was prepared according to literature procedure.[2]

**6-Chloro-*trans*-4-nonene** [134296-23-4]. *trans*-2-Hexenal (4.64 mL, 40 mmol) was added dropwise to *n*-PrMgBr (2.0 M solution in $Et_2O$; 22 mL, 44 mmol) at 0 °C. After 2 h of stirring at 0 °C, a saturated aqueous solution of ammonium chloride was added. The aqueous layer was extracted with $Et_2O$, and the combined organic layers were dried ($MgSO_4$) and concentrated by rotary evaporation to give *trans*-non-4-en-6-ol. A portion of this unpurified allylic alcohol (2.43 g, 17.1 mmol) and pyridine (0.27 mL, 3.4 mmol) was added slowly to $PCl_3$ (0.55 mL, 6.3 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature over 3 h. The top layer of the biphasic mixture was distilled (31 °C/0.3 torr) to furnish 6-chloro-*trans*-4-nonene as a colorless oil (2.2 g, 80%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 5.67 (dt, $J$ = 15.3, 6.6 Hz, 1H), 5.51 (ddt, $J$ = 15.3, 8.7, 1.2 Hz, 1H), 4.35 (dt, $J$ = 8.7, 6.9 Hz, 1H), 2.13-1.93 (m, 2H), 1.88-1.67 (m, 2H), 1.55-1.30 (m, 4H), 0.92 (t, $J$ = 7.2 Hz, 3H), 0.90 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 133.6, 131.4, 63.8, 41.2, 34.2, 22.3, 20.1, 13.9, 13.7.

## II. Hiyama Cross-Coupling Reactions

**General procedure.** DMA (0.6 mL) was added to a mixture of LiHMDS (20.1 mg, 0.12 mmol), dry CsF (576 mg, 3.8 mmol; note: prior to use, this must be dried in a vacuum oven at 80 °C for 48 h), and $H_2O$ (1.4 μL, 0.080 mmol) in a 4-mL glass vial in a glove box. A solution of $NiCl_2$•glyme (22.0 mg, 0.10 mmol) and norephedrine (18.1 mg, 0.12 mmol) in DMA (1.0 mL) was added, and the reaction mixture was stirred at room temperature for 5 min. Next, the arylsilane (1.50 mmol) was added, and the reaction mixture was stirred for an additional 5 min. Last, the alkyl halide (1.00 mmol) was added. The reaction vial was capped, removed from the glove box, and stirred at 60 °C for 16 h. For certain aryltrifluorosilanes (e.g., the fluoro- and the methoxy-substituted compounds), the reaction mixture became highly viscous; in these cases, it was important that the vial be shaken periodically during the first 10 minutes of reaction, in order to assure proper mixing. After 16 h, the reaction mixture was allowed to cool to room temperature, and then EtOH (0.5 mL) and $Et_2O$ (1.5 mL) were added. This heterogeneous mixture was poured onto a pad of silica gel ($Et_2O$ as the eluent). The product was then purified by flash chromatography.

**Cyclohexylbenzene** [827-52-1] (Table 1, entry 1). After flash chromatography (hexanes; $R_f = 0.52$), the title compound was isolated as a colorless oil: run 1, 141 mg (88%); run 2, 139 mg (87%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 7.5, 0.9 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.20 (tt, *J* = 6.9 Hz, 1.5 Hz, 1H), 2.52 (tt, *J* = 11.7, 3.3 Hz, 1H), 1.96-1.82 (m, 4H), 1.83-1.73 (m, 1H), 1.53-1.20 (m, 5H)

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 148.4, 128.5, 127.1, 126.0, 44.9, 34.7, 27.2, 26.4.

**4-Fluorophenylcycloctane** [693258-54-7] (Table 1, entry 2). After flash chromatography (heptane; $R_f = 0.59$), the title compound was isolated as a colorless oil: run 1, 120 mg (58%); run 2, 124 mg (60%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.7, 5.7 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 2.76 (tt, *J* = 9.3, 3.6 Hz, 1H), 1.89-1.44 (m, 14H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 161.1 (d, *J* = 242.9 Hz), 146.2 (d, *J* = 2.9 Hz), 128.4 (d, *J* = 7.6 Hz), 115.1 (d, *J* = 20.9 Hz), 44.2, 34.9, 27.2, 26.5, 26.1.

$^{19}$F NMR (282 MHz, $CDCl_3$) δ –118.8.

**4-Phenyltetrahydropyran** [20638-52-2] (Table 1, entry 3). After flash chromatography (10:1 hexanes/$Et_2O$; $R_f = 0.20$), the title compound was isolated as a colorless oil: run 1, 136 mg (84%); run 2, 139 mg (86%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.33 (t, *J* = 6.9 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.23 (tt, *J* = 7.5, 1.4 Hz, 1H), 4.09 (ddd, *J* = 10.8, 3.6, 1.8 Hz, 2H), 3.54 (td, *J* = 11.4, 3.3 Hz, 2H), 2.76 (tt, *J* = 11.1, 1.8 Hz, 1H), 1.92-1.73 (m, 4H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 146.1, 128.8, 127.0, 126.6, 68.7, 41.8, 34.2.

**4-Phenyl-*N*-Cbz-piperidine** [733810-73-6] (Table 1, entry 4). After flash chromatography (5:1 pentane/$Et_2O$; $R_f$ = 0.23), the title compound was isolated as a colorless oil: run 1, 236 mg (80%); run 2, 245 mg (83%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 10H), 5.18 (s, 2H), 4.35 (br s, 2H), 2.90 (t, *J* = 12.3 Hz, 2H), 2.68 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.85 (d, *J* = 12.3 Hz, 2H), 1.68 (t, *J* = 12.0 Hz, 2H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 155.6, 145.8, 137.1, 128.81, 128.76, 128.24, 128.17, 127.0, 126.7, 67.3, 44.9, 42.8, 33.4.

**1-(4-Tolyl)benzocyclobutene** [661476-70-6] (Table 1, entry 5). After flash chromatography (heptane; $R_f$ = 0.25), the title compound was isolated as a colorless oil: run 1, 175 mg (90%); run 2, 171 mg (88%). This material contained 3 mol% of a homocoupling product.

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.20-7.08 (m, 6H), 4.67 (dd, *J* = 5.7, 2.7 Hz, 1H), 3.72 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.06 (dd, *J* = 13.8, 2.4 Hz, 1H), 2.34 (s, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 148.2, 144.4, 140.1, 136.2, 129.3, 127.8, 127.3, 127.1, 123.5, 122.9, 47.4, 40.3, 21.3.

**4-Methoxyisopropylbenzene** [4132-48-3] (Table 1, entry 6). After flash chromatography (5:1 hexanes/$CH_2Cl_2$; $R_f$ = 0.45), the title compound was isolated as a colorless oil: run 1, 117 mg (78%); run 2, 113 mg (75%). This material contained 3 mol% of anisole.

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.87 (septet, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 157.8, 141.3, 127.5, 113.4, 55.5, 33.5, 24.5.

**1-Phenyl-2-(2-tolyl)propane** (Table 1, entry 7). After flash chromatography (heptane; $R_f$ = 0.15), the title compound was isolated as a colorless oil: run 1, 139 mg (66%); run 2, 135 mg (64%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.39-7.20 (m, 5H), 7.19-7.11 (m, 4H), 3.29 (sextet, *J* = 7.0 Hz, 1H), 2.97 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.76 (dd, *J* = 13.2, 8.4 Hz, 1H), 2.28 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 3H).

$^{13}C$ {$^{1}H$} NMR (75.5 MHz, $CDCl_3$) δ 145.6, 141.3, 135.6, 130.5, 129.4, 128.4, 126.5, 126.1, 126.0, 125.7, 44.7, 37.0, 20.7, 19.7.

IR (film) 3062, 3026, 2962, 2927, 2871, 1603, 1494, 1453, 1376, 1089 $cm^{-1}$.

GC/MS calcd for $C_{16}H_{18}$ ($M^+$) 210, found 210.

**1,1,3-Trimethoxy-2-phenylpropane** [124791-76-0] (Table 1, entry 8). After flash chromatography (5:1 pentane/$Et_2O$; $R_f = 0.27$), the title compound was isolated as a colorless oil: run 1, 177 mg (84%); run 2, 183 mg (87%).

$^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.37-7.20 (m, 5H), 4.58 (d, $J = 6.3$ Hz, 1H), 3.72 (dd, $J = 9.3, 5.4$ Hz, 1H), 3.69 (dd, $J = 9.3, 6.9$ Hz, 1H), 3.41 (s, 3H), 3.301 (s, 3H), 3.299 (s, 3H), 3.17 (q, $J = 6.0$ Hz, 1H).

$^{13}C$ {$^{1}H$} NMR (75.5 MHz, $CDCl_3$) δ 139.5, 129.1, 128.5, 127.0, 106.3, 73.6, 59.3, 55.2, 55.1, 49.5.

**Cyclohexylbenzene** [827-52-1] (Table 1, entry 9). After flash chromatography (hexanes; $R_f = 0.52$), the title compound was isolated as a colorless oil: run 1, 151 mg (94%); run 2, 152 mg (95%).

**3-(4-Fluorophenyl)butan-2-one** [79341-86-9] (Table 2, entry 1). After flash chromatography (10:1 hexane/$Et_2O$; $R_f = 0.14$), the title compound was isolated as a colorless oil: run 1, 131 mg (79%); run 2, 127 mg (77%).

$^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, $J = 8.7, 5.2$ Hz, 2H), 7.02 (t, $J = 8.7$ Hz, 2H), 3.73 (q, $J = 7.2$ Hz, 1H), 2.04 (s, 3H), 1.37 (d, $J = 6.9$ Hz, 3H).

$^{13}C$ {$^{1}H$} NMR (75.5 MHz, $CDCl_3$) δ 208.9, 162.2 (d, $J = 246.0$ Hz), 136.5 (d, $J = 3.3$ Hz), 129.6 (d, $J = 7.9$ Hz), 116.0 (d, $J = 21.4$ Hz), 53.1. 28.6, 17.6.

***t*-Butyl 2-phenylisovalerate** (Table 2, entry 2). After flash chromatography (100:2 hexane/$Et_2O$; $R_f = 0.25$), the title compound was isolated as a colorless oil: run 1, 190 mg (81%); run 2, 198 mg (84%).

$^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 3.02 (d, $J = 10.8$ Hz, 1H), 2.29 (d septet, $J = 10.5, 6.6$ Hz, 1H), 1.40 (s, 9H), 1.06 (d, $J = 6.6$ Hz, 3H), 0.68 (d, $J = 6.6$ Hz, 3H).

$^{13}C$ {$^{1}H$} NMR (75.5 MHz, $CDCl_3$) δ 173.5, 139.2, 128.7, 128.5, 127.2, 80.7, 61.4, 32.2, 28.2, 21.6, 20.5.

IR (film) 3030, 3005, 2972, 2933, 2872, 1727, 1601, 1490, 1470, 1455, 1391, 1368, 1249, 1145, 1118 $cm^{-1}$.

GC/MS calcd for $C_{15}H_{22}O_2$ ($M^+$) 234, found 234.

***N,N*-Diisopropyl-2-phenylbutyramide** [94430-02-1] (Table 2, entry 3). After flash chromatography (10:1 hexane/EtOAc; $R_f = 0.30$), the title compound was isolated as white crystals: run 1, 210 mg (85%); run 2, 200 mg (81%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.33-7.16 (m, 5H), 4.05 (septet, *J* = 6.6 Hz, 1H), 3.48 (t, *J* = 7.2 Hz, 1H), 3.28 (br septet, *J* = 6.4 Hz, 1H), 2.09 (d pentet, *J* = 13.5, 7.5 Hz, 1H), 1.65 (d pentet, 13.5, 7.2 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.60 (d, *J* = 6.6 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 171.8, 141.4, 128.8, 128.0, 126.7, 52.4, 48.4, 46.0, 28.4, 21.2, 21.1, 20.3, 20.0, 12.7.

**Diethyl α-(4-tolyl)ethylphosphonate** [65797-28-6] (Table 2, entry 4). After flash chromatography (EtOAc; $R_f = 0.34$), the title compound was isolated as a colorless oil: run 1, 239 mg (93%); run 2, 230 mg (90%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.22 (dq, *J* = 8.4, 2.4 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.13-3.70 (m, 4H), 3.12 (dq, *J* = 22.5, 7.5 Hz, 1H), 2.31 (d, *J* = 2.1 Hz, 3H), 1.54 (dd, *J* = 18.6, 7.5 Hz, 3H), 1.26 (td, *J* = 7.2, 0.3 Hz, 3H), 1.14 (td, *J* = 7.2, 0.3 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 136.8 (d, *J* = 3.5 Hz), 135.1 (d, *J* = 7.1 Hz), 129.3 (d, *J* = 2.7 Hz), 128.7 (d, *J* = 6.3 Hz), 62.6 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.1 Hz), 38.2 (d, *J* = 138.0 Hz), 21.3, 16.7 (d, *J* = 6.0 Hz), 16.6 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.0 Hz).

$^{31}$P {$^1$H} NMR (121.5 MHz, $CDCl_3$) δ 31.1.

**2-(2-Tolyl)propionitrile** [58422-60-9] (Table 2, entry 5). After flash chromatography (5:1 hexane/$Et_2O$; $R_f = 0.39$), the title compound was isolated as a colorless oil: run 1, 110 mg (76%); run 2, 110 mg (76%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.0 Hz, 1H), 7.33-7.16 (m, 3H), 4.05 (q, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 135.5, 135.0, 131.2, 128.4, 127.2, 126.9, 122.1, 28.4, 20.3, 19.3.

***endo*-3-Phenyl-2-norbornanone** [7485-53-2] and ***exo*-3-phenyl-2-norbornanone** [10472-46-5] (Table 2, entry 6). A mixture of *endo*- and *exo*-3-phenyl-2-norbornanone was prepared from *exo*-3-chloro-2-norbornanone. GC analysis of the crude material showed 1.1:1 *endo*/*exo* (run 1) and 1.1:1 *endo*/*exo* (run 2). After flash chromatography (5:1 hexane/$Et_2O$; $R_f = 0.22$ (*endo*), $R_f = 0.31$ (*exo*)), the title compounds were isolated as a colorless oil: run 1, 148 mg (80%, 1.1:1 *endo*/*exo*); run 2, 150 mg (81%, 1.1:1 *endo*/*exo*).

***Endo*-3-phenyl-2-norbornanone.**

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.24 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 3.47 (d, *J* = 4.5 Hz, 1H), 2.88-2.82 (m, 1H), 2.78 (d, *J* = 4.8 Hz, 1H), 1.97-1.85 (m, 2H), 1.69 (d pentet, *J* = 10.2, 1.1 Hz, 1H), 1.63-1.39 (m, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 217.1, 136.7, 128.72, 128.71, 127.0, 59.0, 51.4, 42.2, 37.1, 24.6, 22.1.

***Exo*-3-phenyl-2-norbornanone.**

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.36-7.21 (m, 5H), 3.12 (d, *J* = 3.6 Hz, 1H), 2.91-2.86 (m, 1H), 2.69-2.64 (m, 1H), 2.05 (d pentet, *J* = 10.5, 1.8 Hz, 1H), 1.99-1.83 (m, 2H), 1.76-1.62 (m, 2H), 1.59 (dddd, *J* = 10.8, 3.6, 2.1, 1.2 Hz, 1H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 217.4, 137.4, 128.7, 128.0, 126.8, 58.7, 49.8, 41.7, 35.2, 28.3, 24.9.

**2-(4-Methoxylphenyl)ethylpropionate** [2901-41-9] (Table 2, entry 7). After flash chromatography (1:1 hexane/$CH_2Cl_2$; $R_f$ = 0.26), the title compound was isolated as a colorless oil: run 1, 176 mg (84%); run 2, 173 mg (83%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.13 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.09 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.79 (s, 3H), 3.66 (q, *J* = 7.2 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 175.1, 158.8, 133.0, 128.7, 114.2, 60.9, 55.5, 44.9, 18.9, 14.4.

**1-Morpholino-2-phenylpropan-1-one** [155222-99-4] (Table 2, entry 8). After flash chromatography (1:2 hexane/EtOAc; $R_f$ = 0.29), the title compound was isolated as a colorless oil: run 1, 191 mg (87%); run 2, 188 mg (86%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.25-7.18 (m, 3H), 3.83 (q, *J* = 6.8 Hz, 1H), 3.86-3.22 (m, 7H), 3.08 (ddd, *J* = 11.2, 7.1, 3.2 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, $CDCl_3$) δ 172.4, 142.1, 129.2, 127.4, 127.1, 67.0, 66.5, 46.2, 43.5, 42.6, 20.9.

**Diethyl α-phenylpropylphosphonate** [33973-50-1] (Table 2, entry 9). After flash chromatography (EtOAc; $R_f$ = 0.35), the title compound was isolated as a colorless oil: run 1, 150 mg (59%); run 2, 158 mg (62%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.34-7.20 (m, 5H), 4.11-3.96 (m, 2H), 3.87 (d pentet, *J* = 10.2, 7.2 Hz, 1H), 3.70 (ddq, *J* = 10.2, 8.1, 7.2 Hz, 1H), 2.87 (ddd, *J* = 22.2, 11.1, 3.9 Hz, 1H), 2.24-2.06 (m, 1H), 2.04-1.85 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.83 (td, *J* = 7.4, 0.6 Hz, 3H).

$^{13}C$ {$^1H$} NMR (75.5 MHz, $CDCl_3$) δ 136.3 (d, *J* = 7.1 Hz), 129.5 (d, *J* = 6.9 Hz), 128.6 (d, *J* =2.4 Hz), 127.2 (d, *J* = 3.2 Hz), 62.6 (d, *J* = 6.9 Hz), 61.9 (d, *J* = 6.9 Hz), 46.7 (d, *J* =136.8 Hz), 22.4 (d, *J* = 3.5 Hz), 16.7 (d, *J* = 5.8 Hz), 16.5 (d, *J* = 5.9 Hz), 12.8 (d, *J* = 16.1 Hz).

$^{31}P$ {$^1H$} NMR (121.5 MHz, $CDCl_3$) δ 30.1.

**2-Phenylpropionitrile** [1823-91-2] (Table 2, entry 10). After flash chromatography (10:1 pentane/$Et_2O$; $R_f$ = 0.27), the title compound was isolated as a colorless oil: run 1, 118 mg (90%); run 2, 113 mg (86%).

$^1H$ NMR (300 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 3.91 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

$^{13}C$ {$^1H$} NMR (75.5 MHz, $CDCl_3$) δ 137.3, 129.4, 128.3, 127.0, 121.9, 31.5, 21.8.

**6-Phenyl-*trans*-4-nonene** (Table 2, entry 11). After flash chromatography (EtOAc; $R_f$ = 0.34), the title compound was isolated as a colorless oil: run 1, 158 mg (78%); run 2, 152 mg (75%).

$^1H$ NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.24-7.16 (m, 3H), 5.56 (ddt, *J* = 15.3, 7.5, 0.9 Hz, 1H), 5.45 (dt, *J* = 15.6, 6.2 Hz, 1H), 3.22 (q, *J* = 7.5 Hz, 1H), 2.00 (q, *J* = 7.0 Hz, 2H), 1.67 (q, *J* = 7.5 Hz, 2H), 1.46-1.14 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H).

$^{13}C$ {$^1H$} NMR (75.5 MHz, $CDCl_3$) δ 146.0, 134.4, 130.2, 128.6, 127.8, 126.1, 48.9, 38.6, 34.9, 22.9, 21.0, 14.3, 13.9.

IR (film) 3027, 2958, 2929, 2872, 1602, 1493, 1465, 1453, 1378, 1030 $cm^{-1}$.

GC/MS calcd for $C_{15}H_{22}$ ($M^+$) 202, found 202.

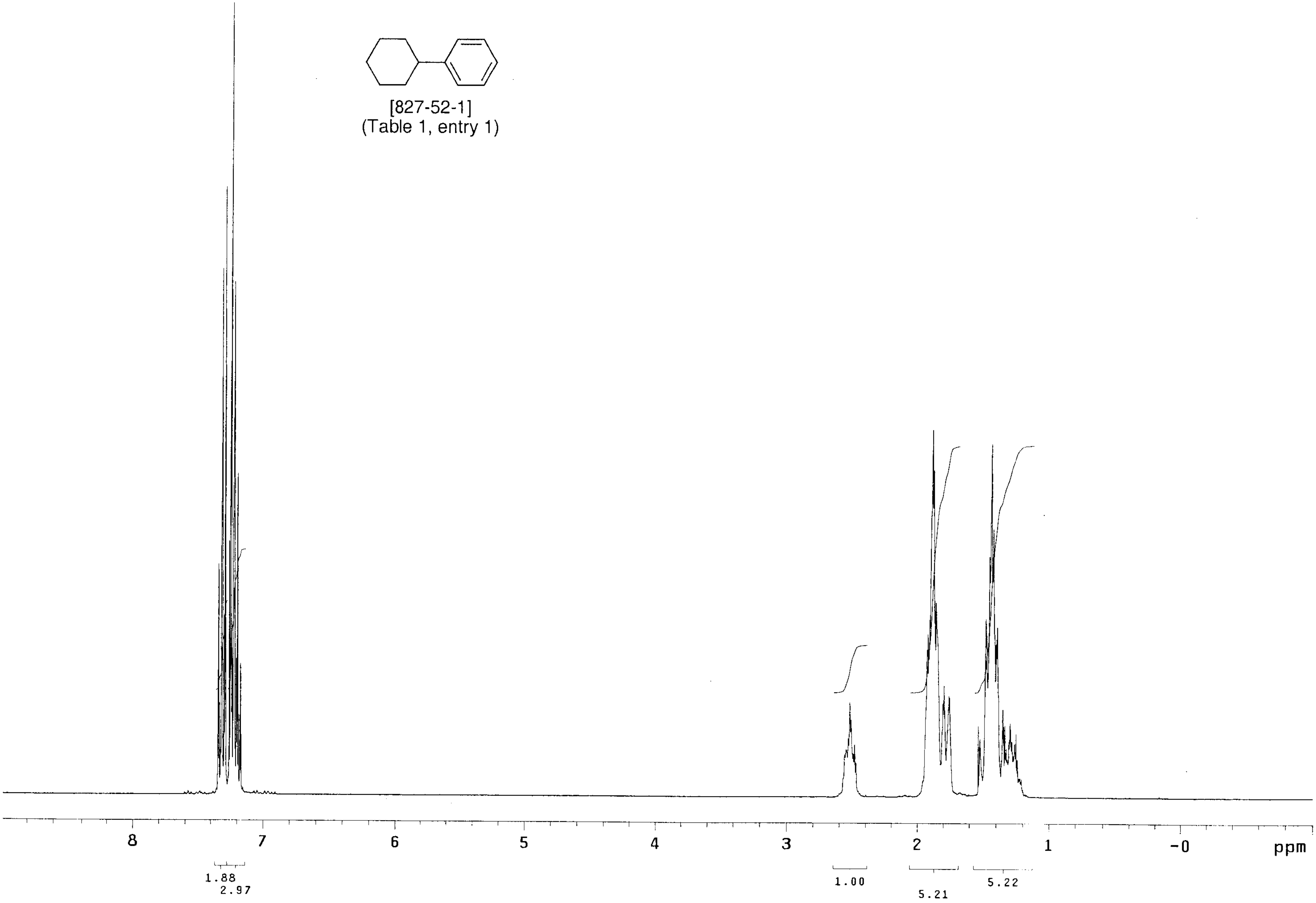
**Gram-scale reaction: Hiyama cross-coupling of ethyl 2-chloropropionate with $PhSiF_3$ to form ethyl 2-phenylpropionate** [2510-99-8]. DMA (6.0 mL) was added to a mixture of LiHMDS (201 mg, 1.2 mmol), dry CsF (5.76 g, 38 mmol), and $H_2O$ (14.0 μL, 0.80 mmol) in a 20-mL glass vial in a glove box. A solution of $NiCl_2$•glyme (220 mg, 1.0 mmol) and norephedrine (181 mg, 1.2 mmol) in DMA (10 mL) was added, and the reaction mixture was stirred at room temperature for 5 min. $PhSiF_3$ (2.00 mL, 15.0 mmol) was added, and the reaction mixture was stirred for an additional 5 min. Last, ethyl 2-chloropropionate (1.27 mL, 10.0 mmol) was added. The reaction vial was capped, removed from the glove box, and stirred at 60 °C for 16 hr. After 16 h, the reaction mixture was allowed to cool to room temperature, and then EtOH (2.0 mL) was added. This mixture was poured onto a pad of silica gel ($Et_2O$ as the eluent). The product was then purified by flash chromatography (10:1 hexane/$Et_2O$; $R_f$ = 0.37), which furnished the title compound, contaminated with a small amount of unreacted ethyl 2-chloropropionate. The ethyl 2-chloropropionate was removed under vacuum (bp = –15 °C/0.4 torr) to give ethyl 2-phenylpropionate as a colorless oil (1.44 g, 81%).

$^1$H NMR (300 MHz, CDCl$_3$) 7.37-7.22 (m, 5H), 4.14 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.10 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H).

$^{13}$C {$^1$H} NMR (75.5 MHz, CDCl$_3$) δ 174.8, 140.9, 128.8, 127.7, 127.3, 61.0, 45.8, 18.9, 14.4.

## References

(1) D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 7788–7789.
(2) Iorga, B.; Eymery, F.; Savignac, P. *Synthesis* **2000**, 576-580.



[827-52-1]
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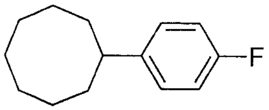

[693258-54-7]
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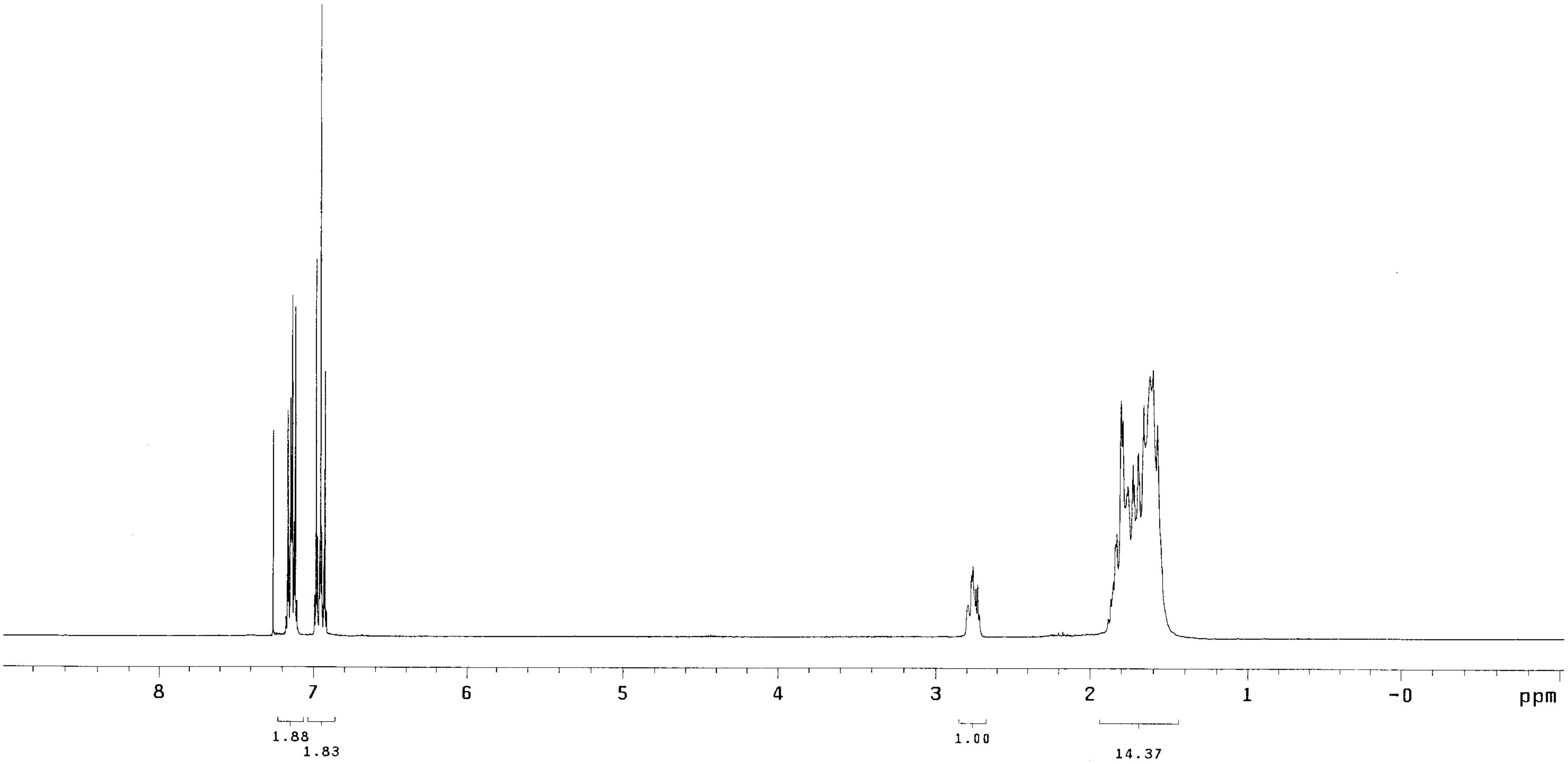

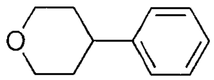
[20638-52-2]
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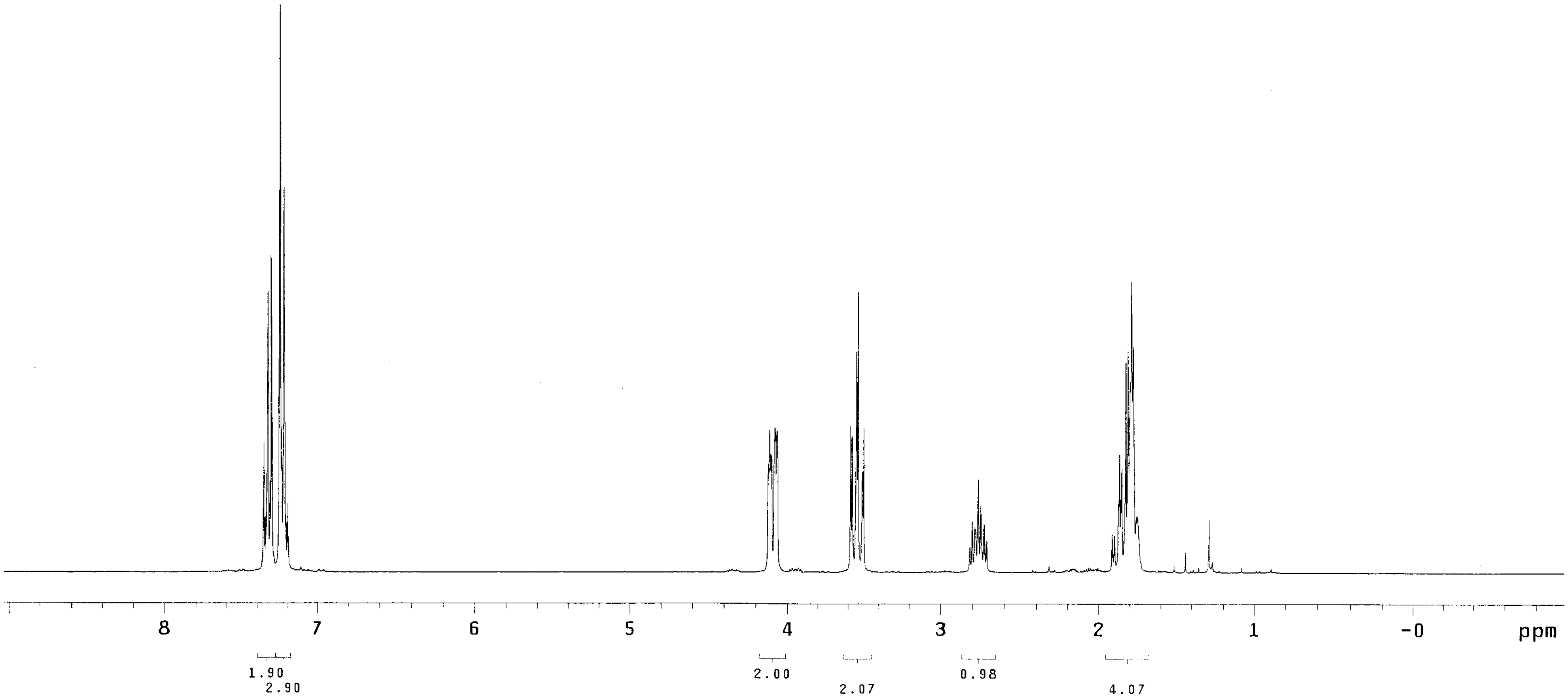
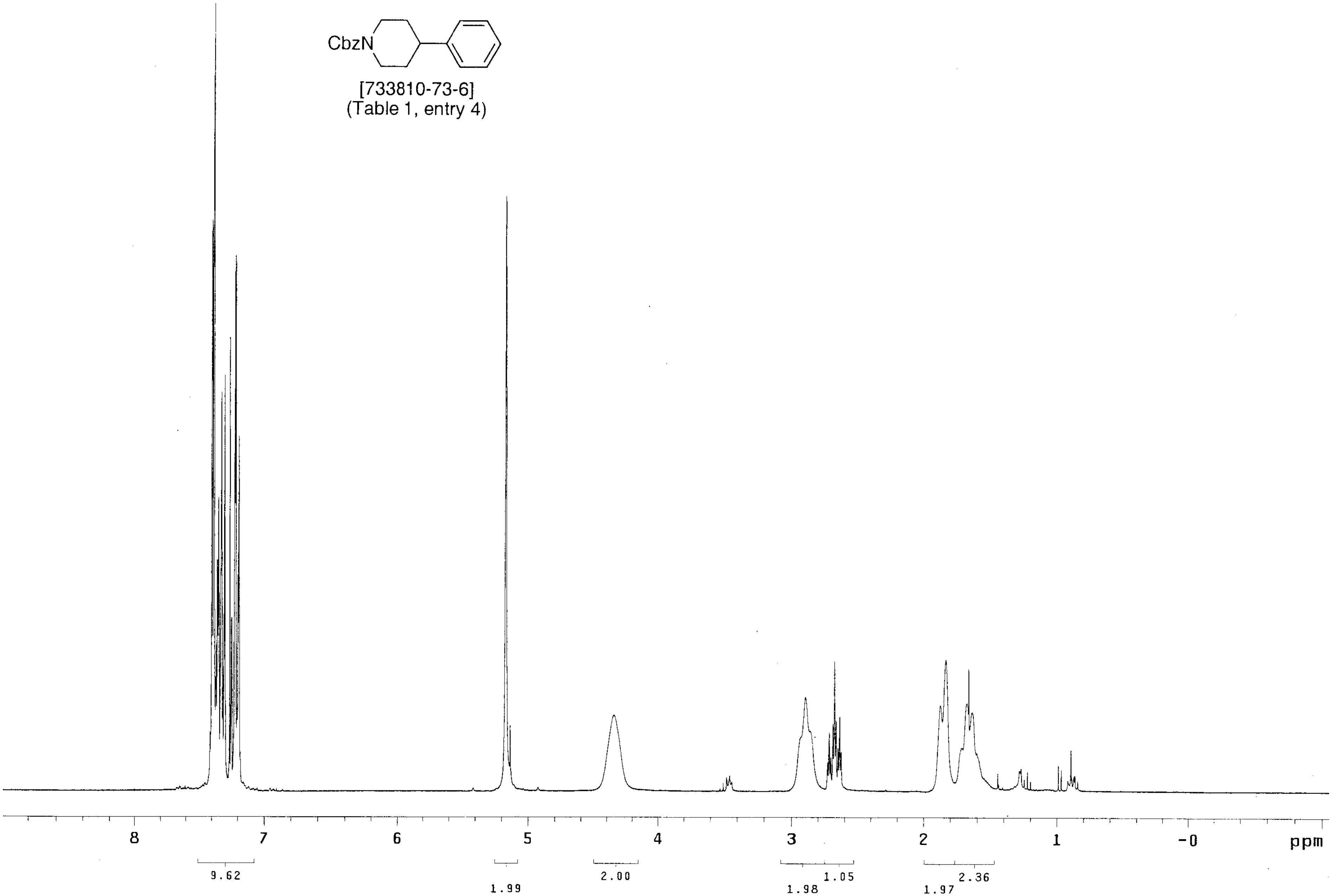
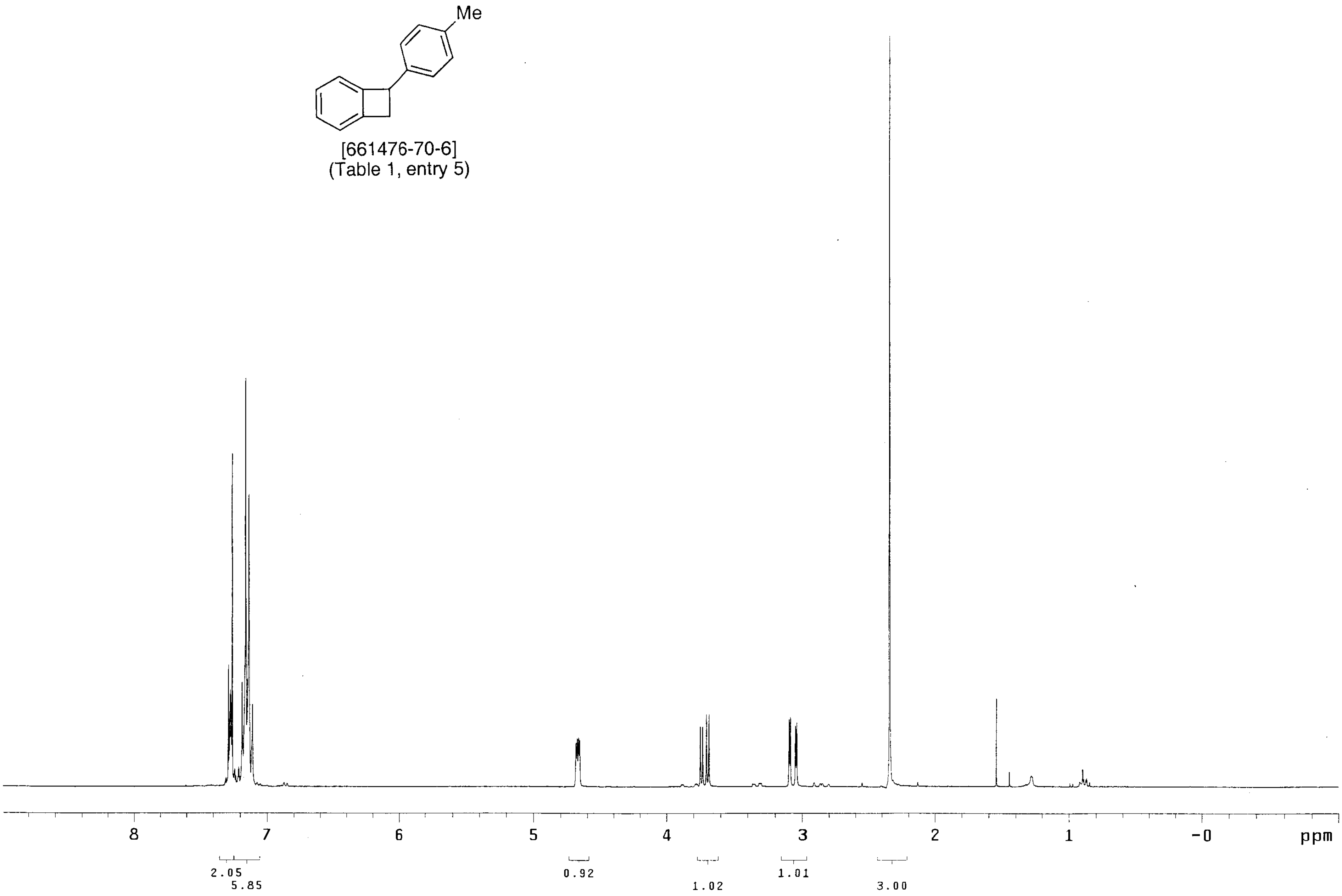




[733810-73-6]
(Table 1, entry 4)



[661476-70-6]
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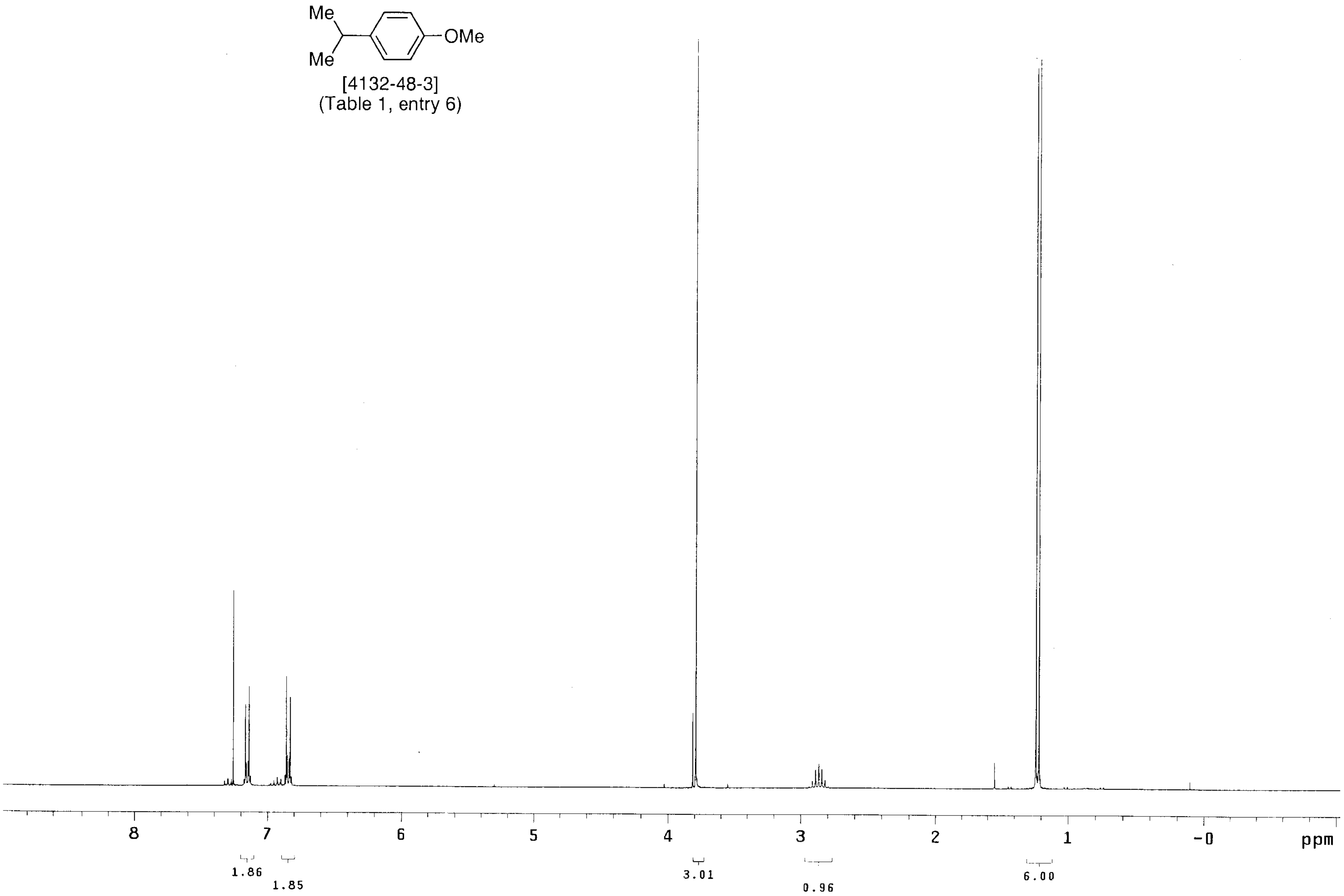
[4132-48-3]
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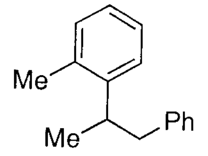

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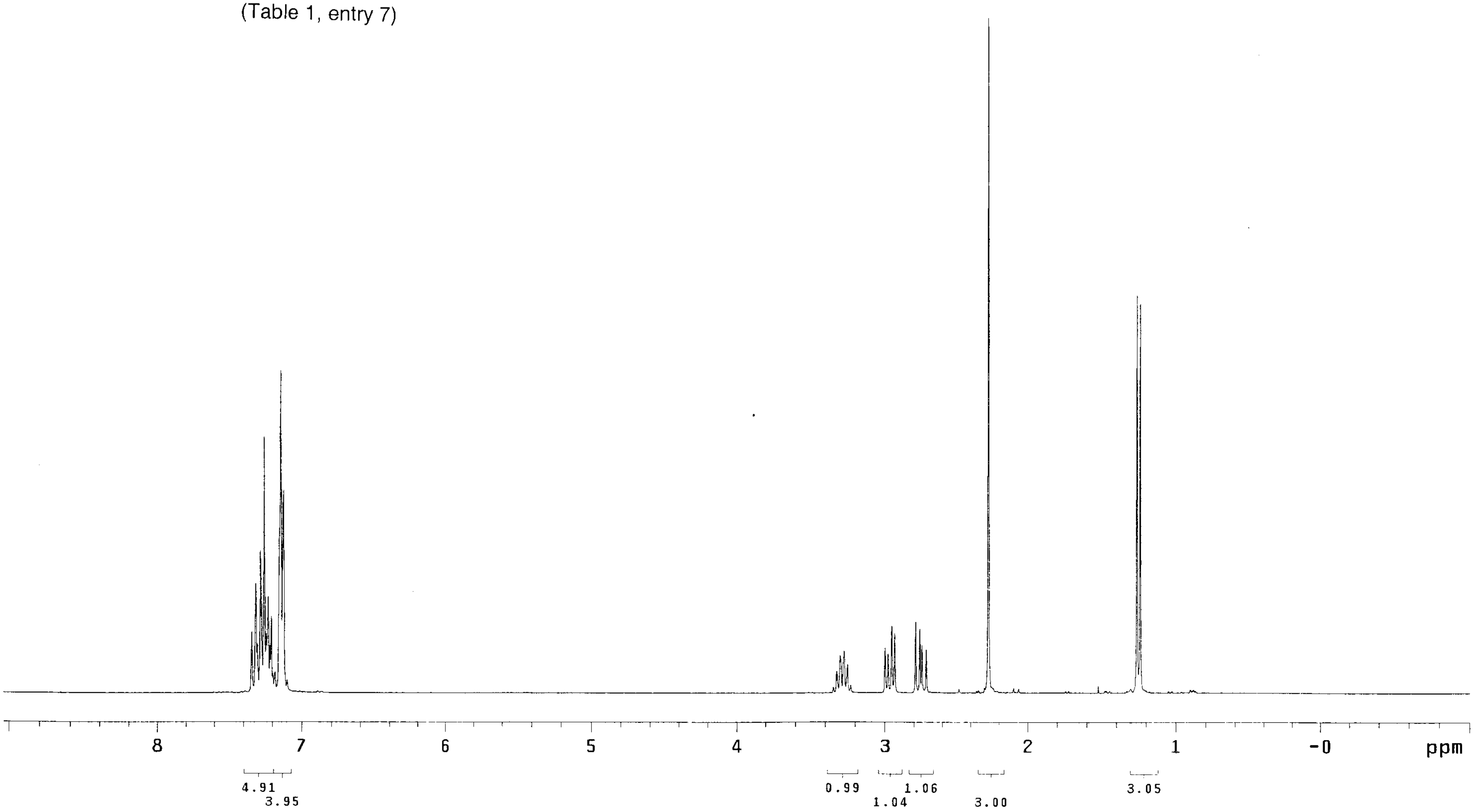

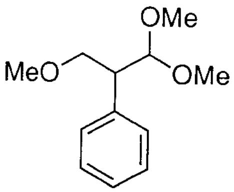

[124791-76-0]
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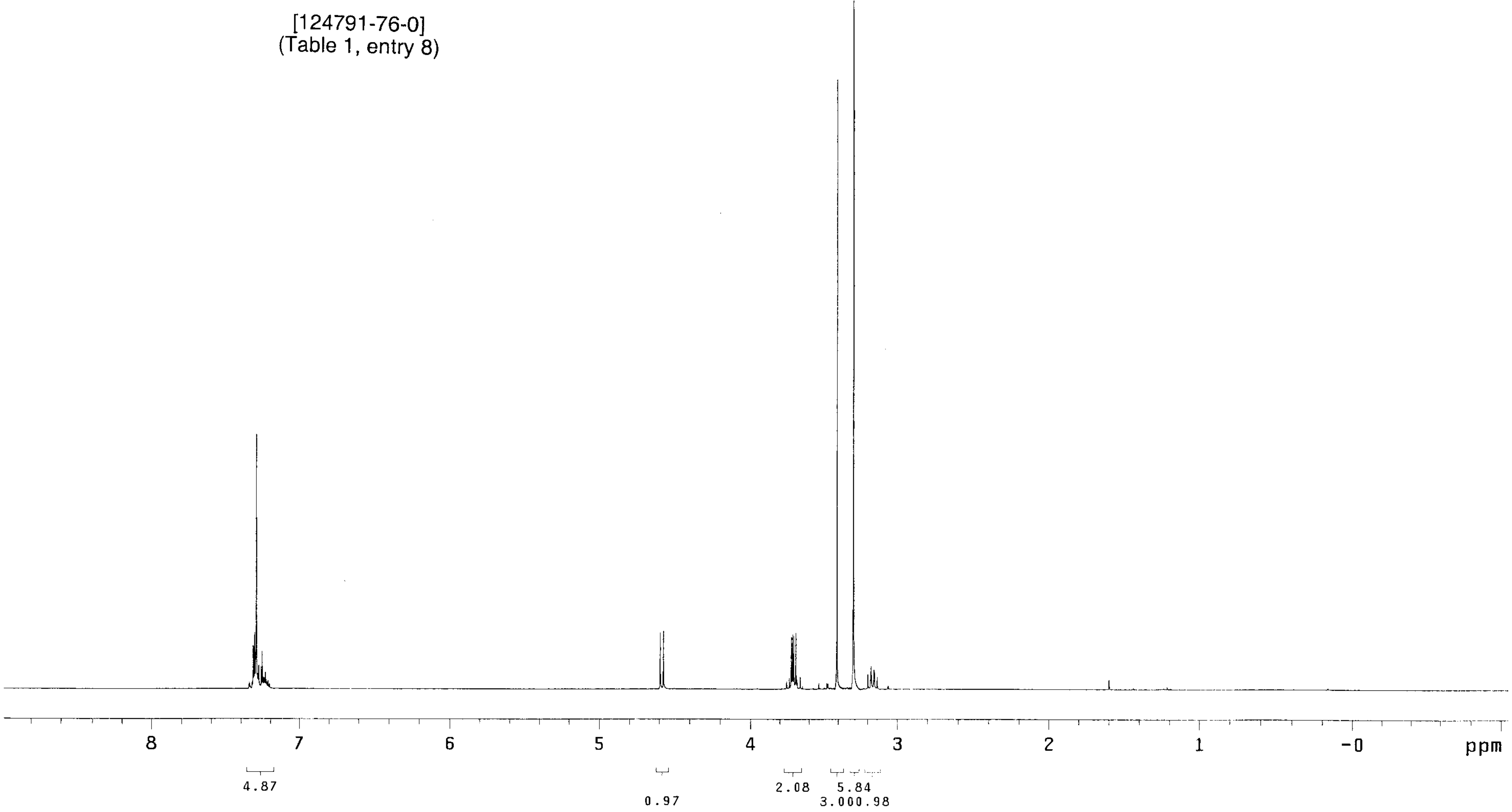
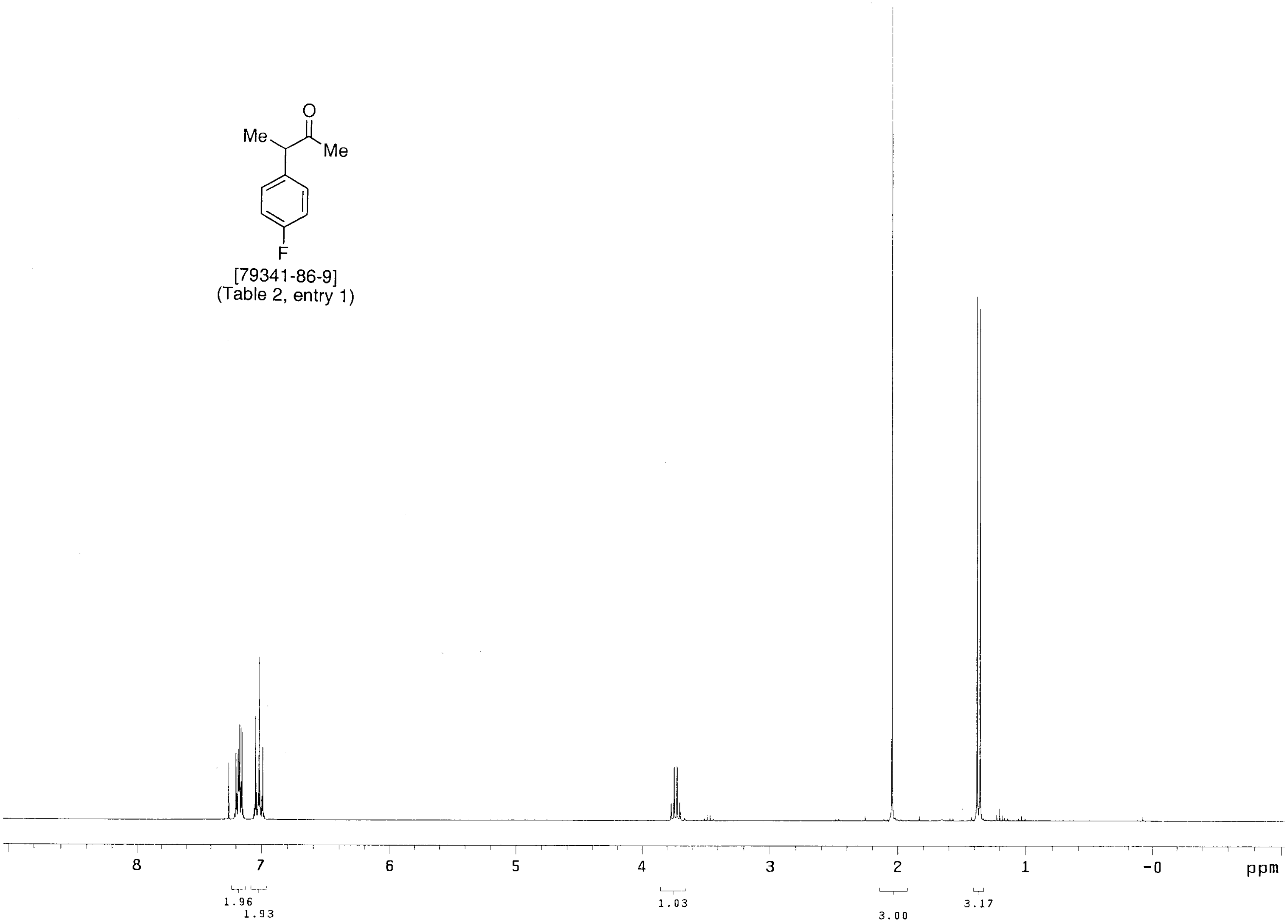
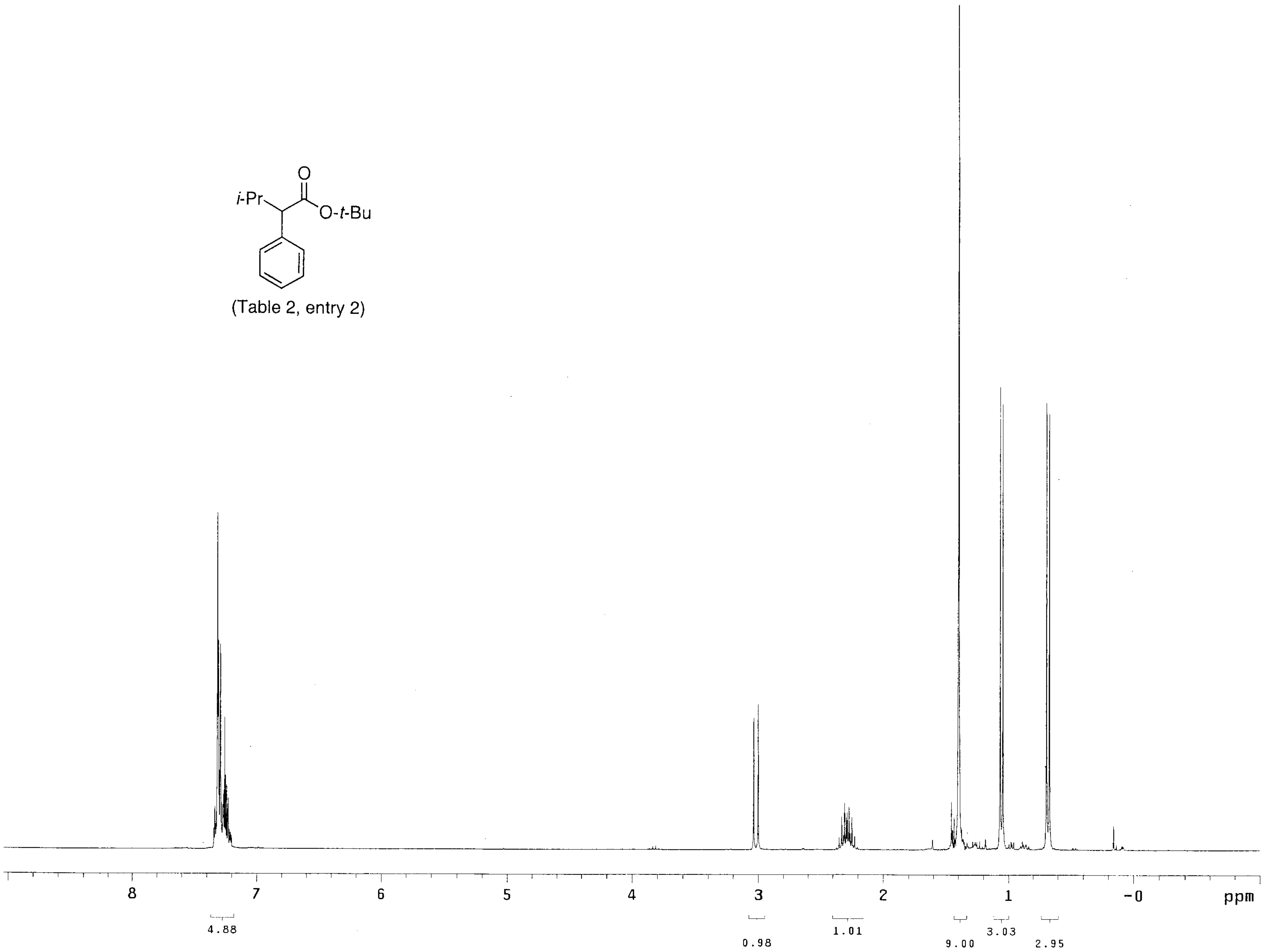
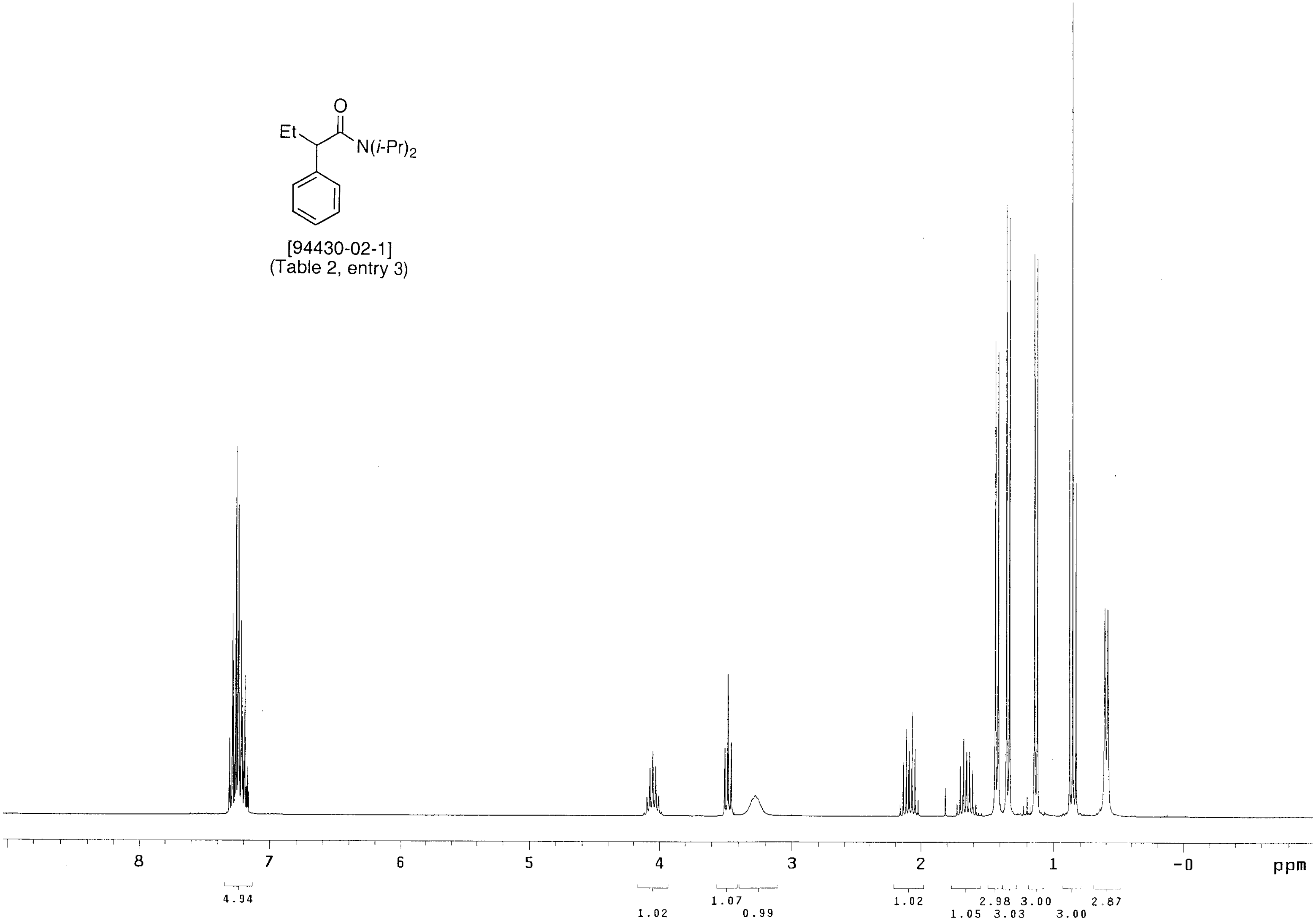




[79341-86-9]
(Table 2, entry 1)

(Table 2, entry 2)





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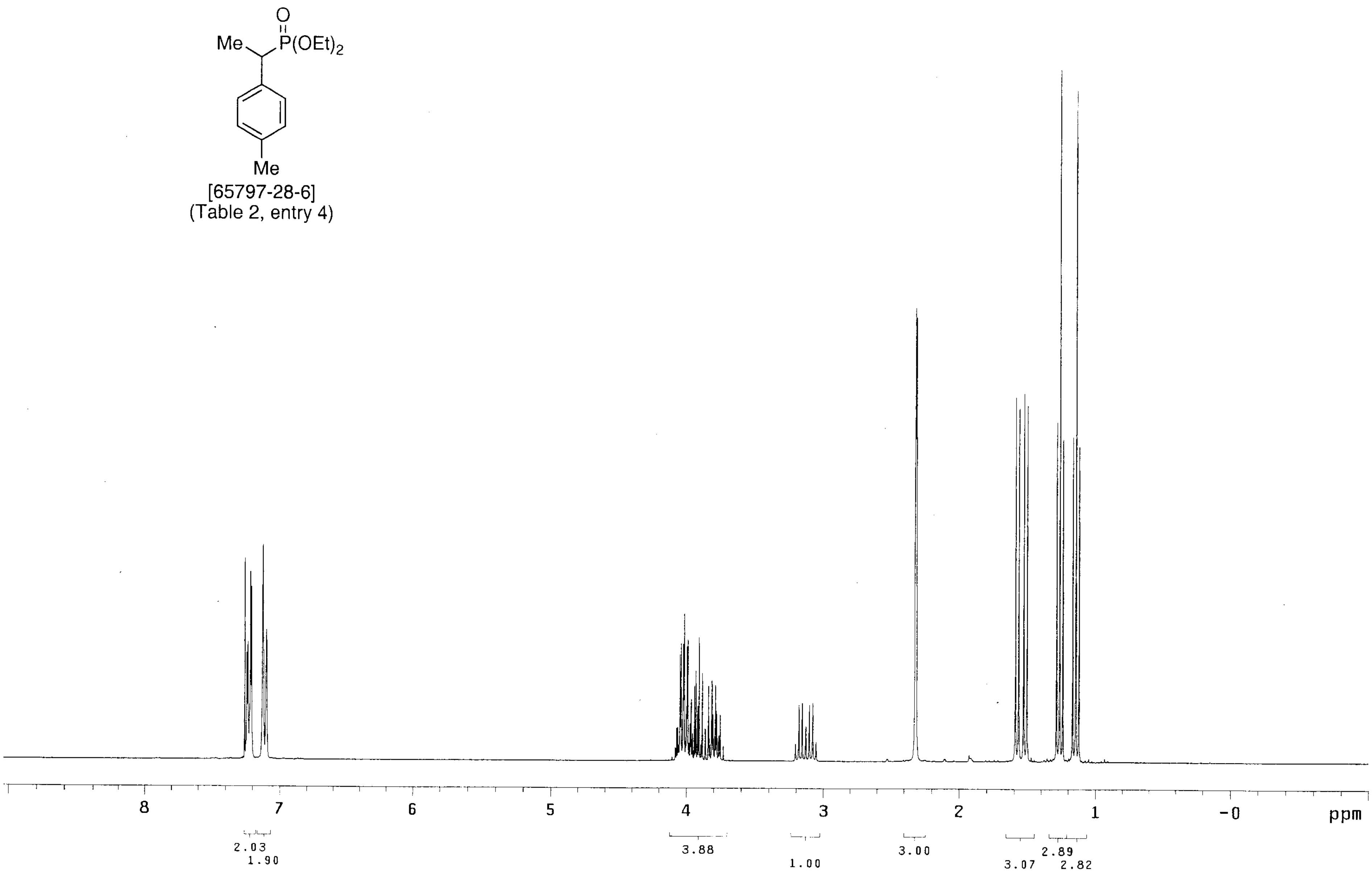

[65797-28-6]
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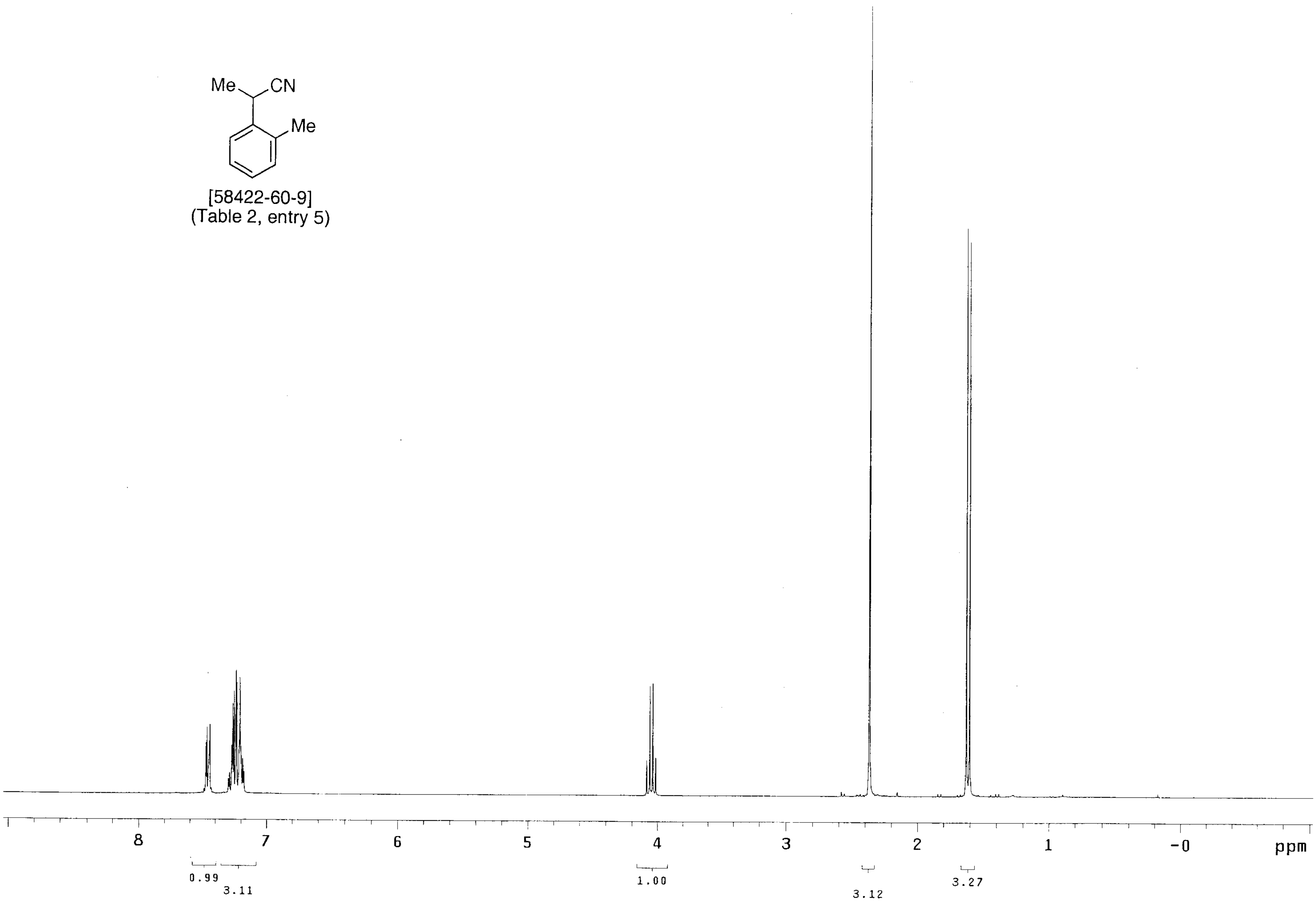

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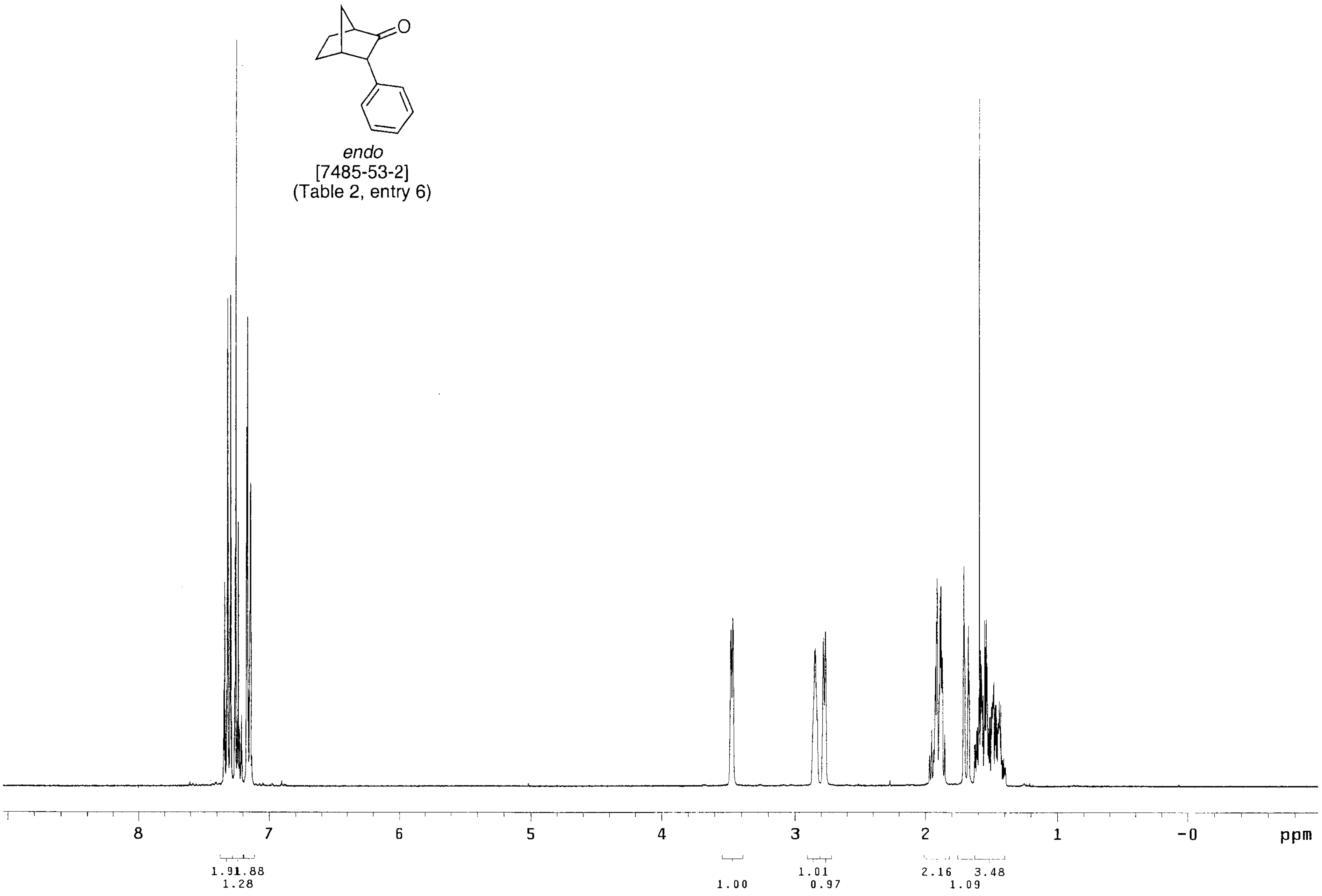

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[7485-53-2]
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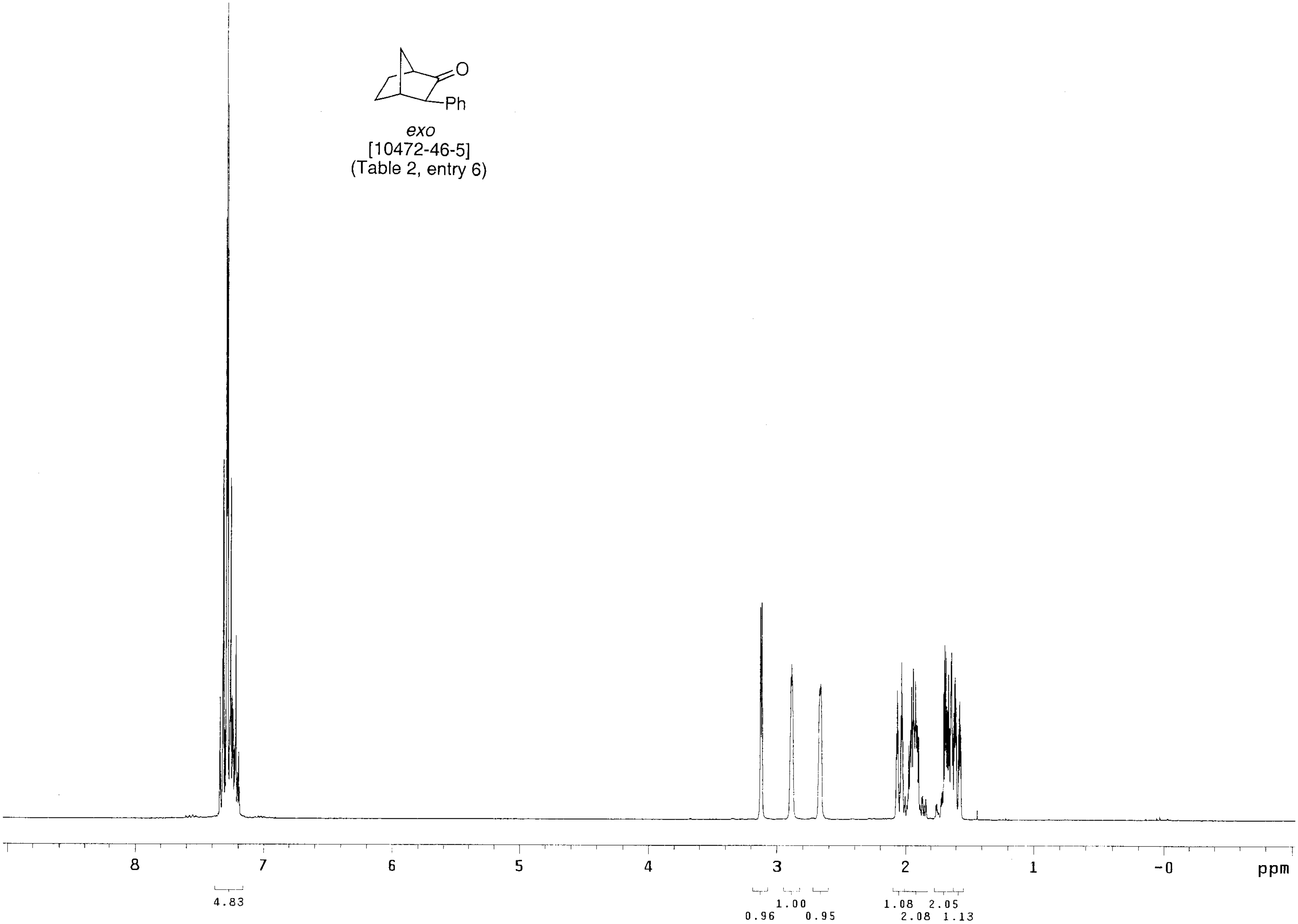

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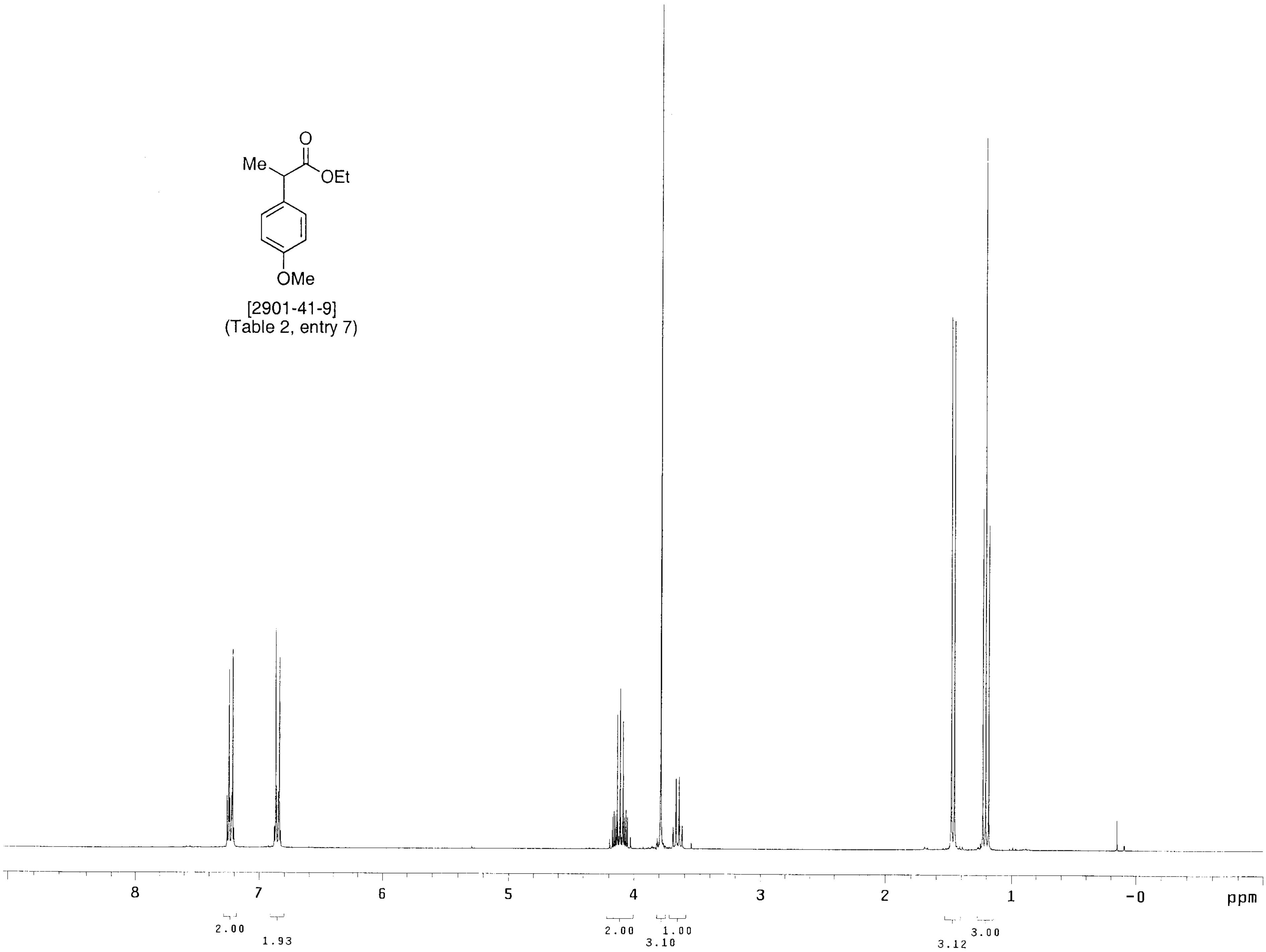
[10472-46-5]
(Table 2, entry 6)



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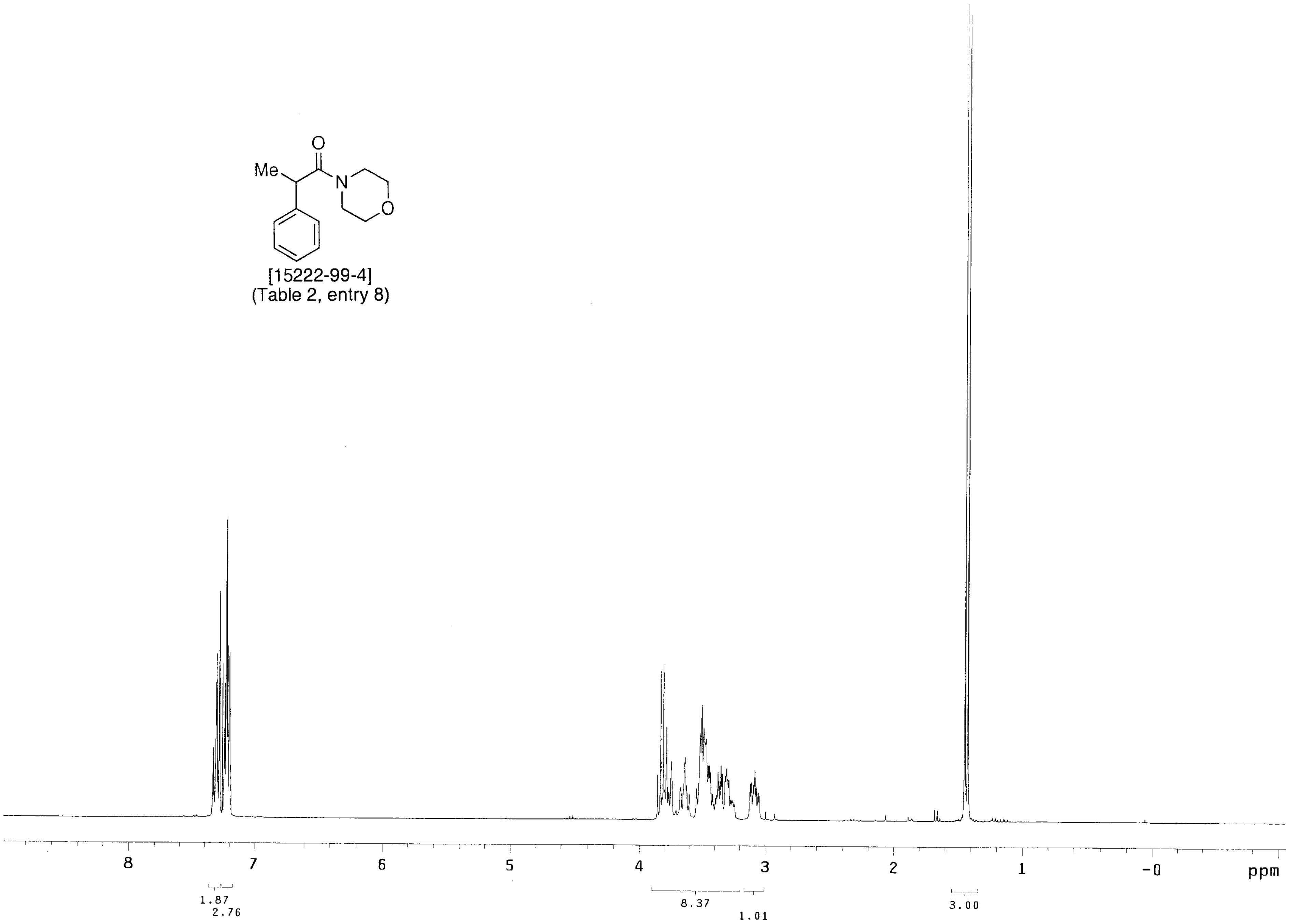

[15222-99-4]
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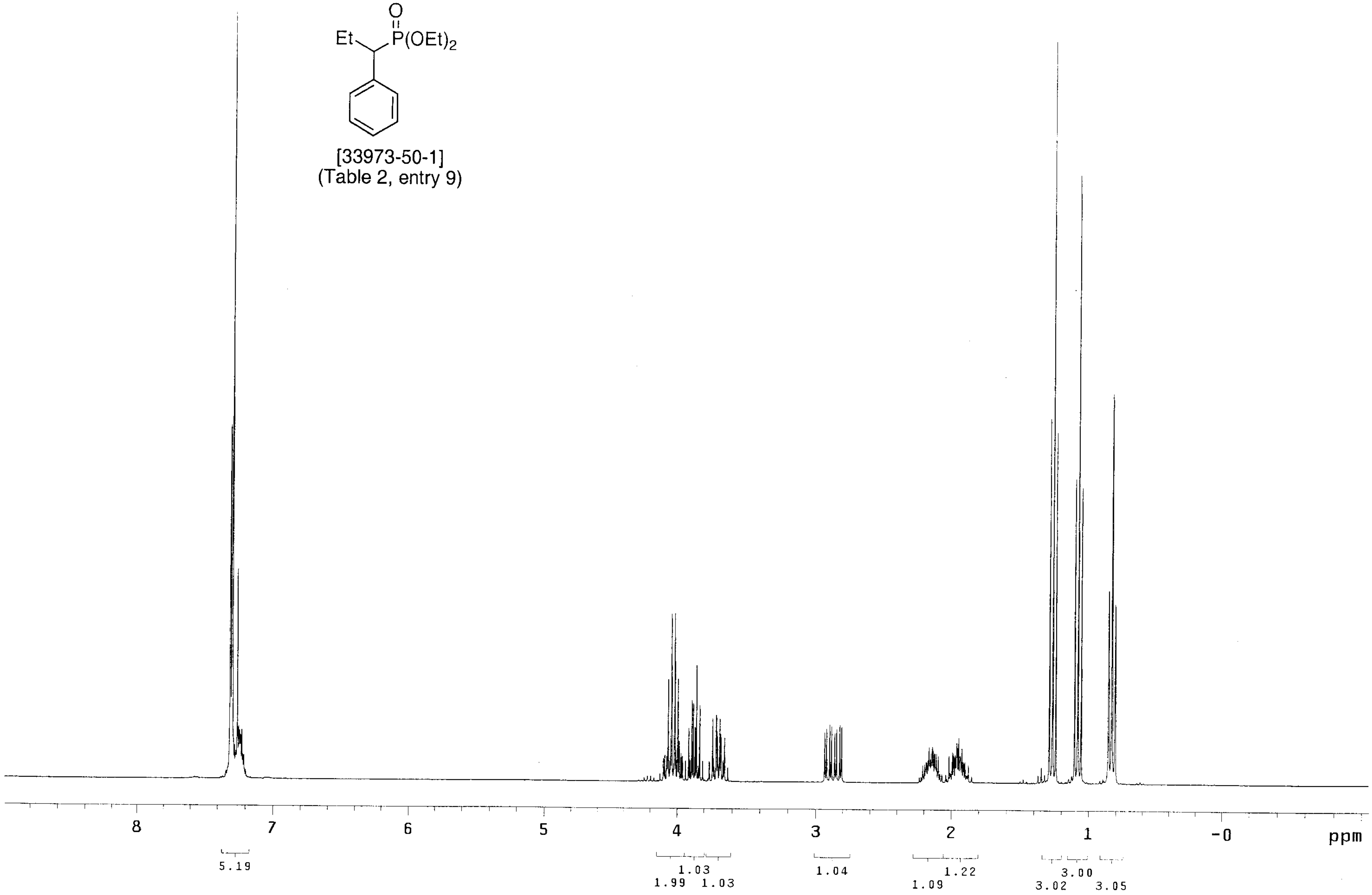

[33973-50-1]
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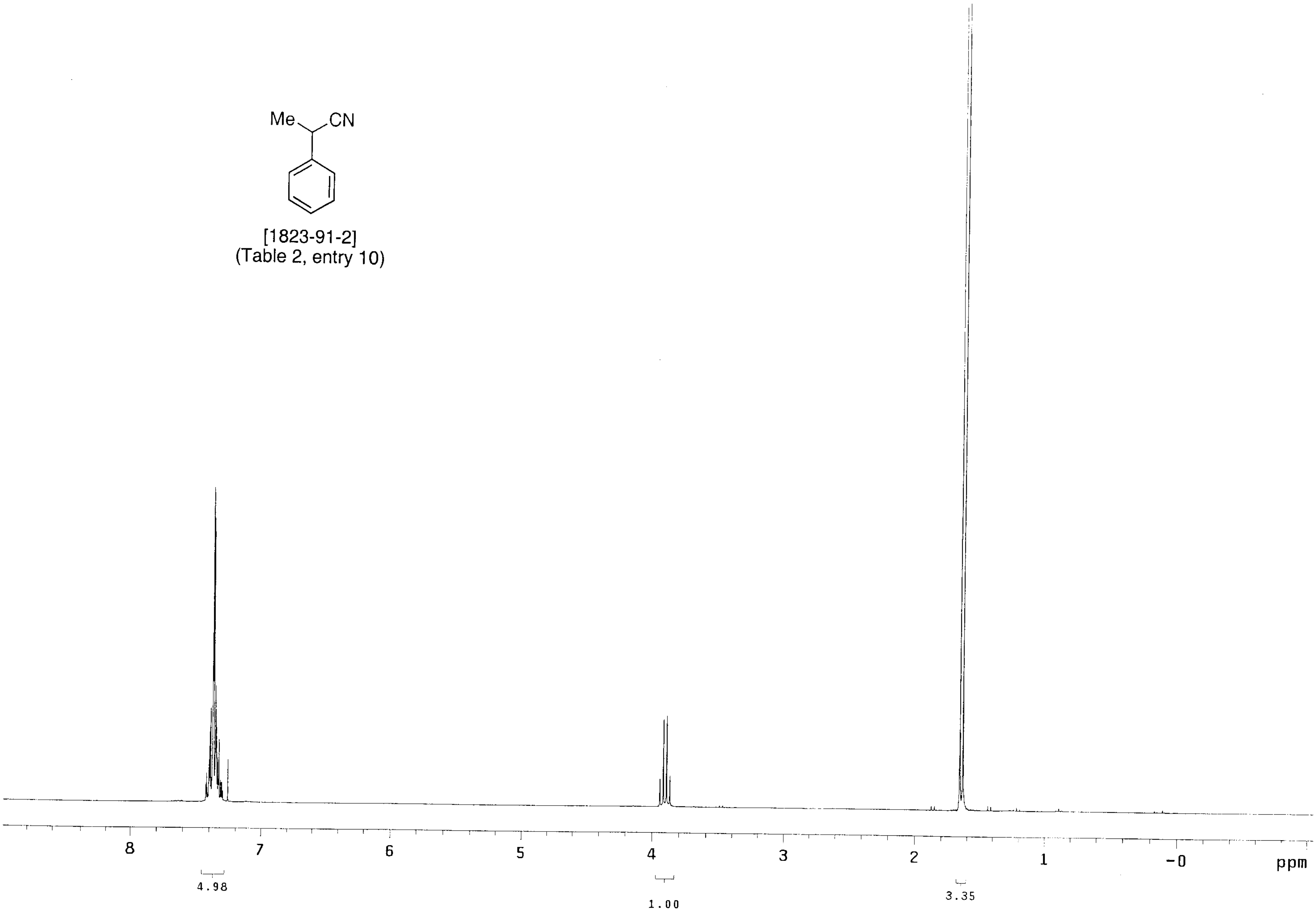

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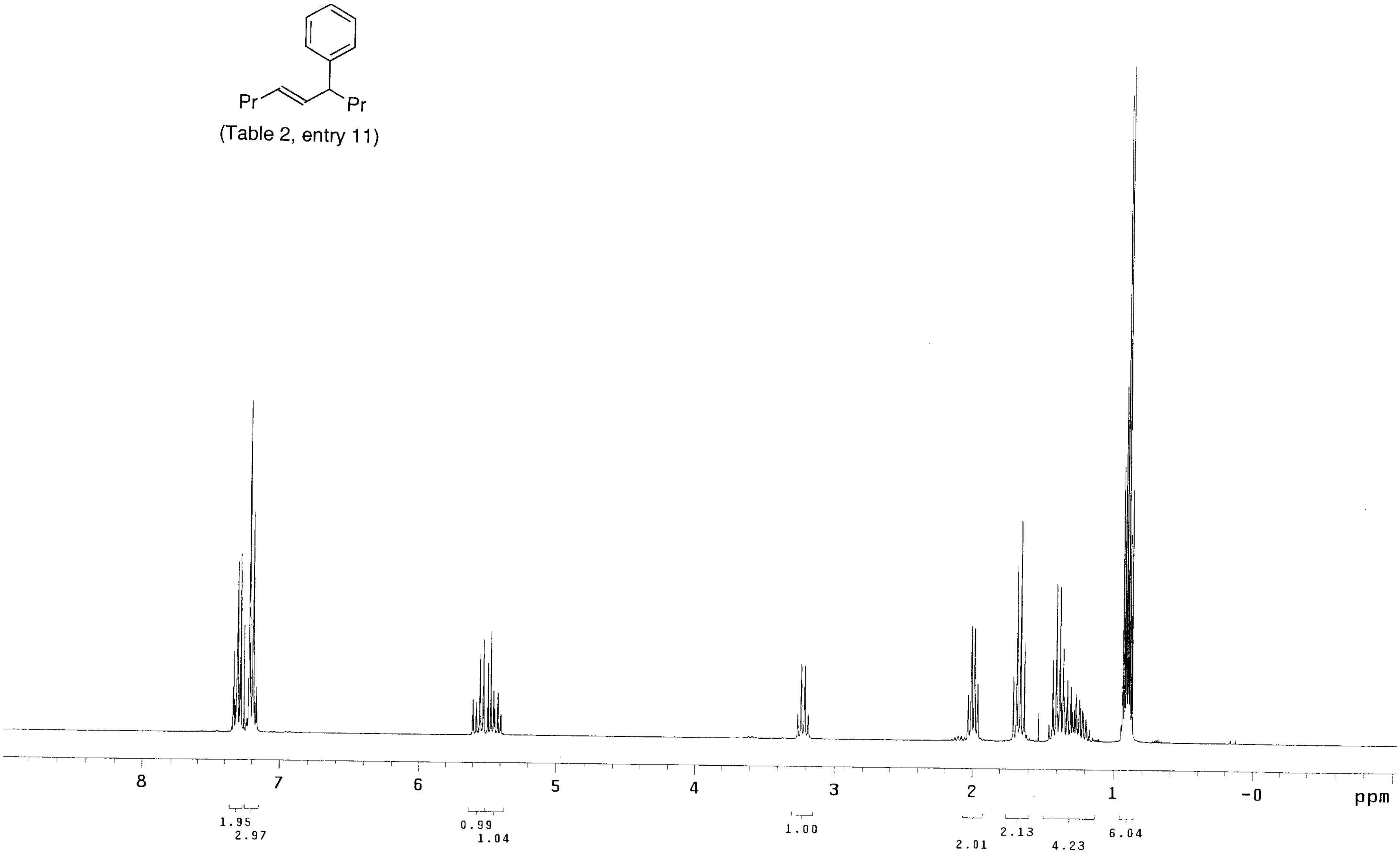

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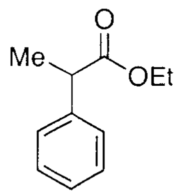

Ethyl 2-phenylpropionate
[79341-86-9]