

# Iron-Catalyzed Cross-Coupling of Alkyl Sulfonates with Arylzinc Reagents

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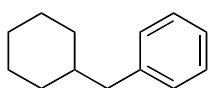
**General.** All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed using glass plates pre-coated with silica gel impregnated with a fluorescent indicator (Merck, #1.05715.0009) or glass plates pre-coated with silica gel RP-18 impregnated with a fluorescent indicator (Merck, #1.15685.0001). TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Flash column chromatography was performed on Merck Silica gel 60 (spherical, neutral, 70–230 mesh) as described by Still et al.<sup>1</sup>

**Instrumentation.** NMR spectra were recorded on JEOL EX-270 (<sup>1</sup>H: 270 MHz, <sup>13</sup>C: 68 MHz) and VARIAN MercuryVX (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz) NMR spectrometers. Chemical shift values for protons are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane as an internal standard. Chemical shift values for carbons are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl<sub>3</sub>:  $\delta$  77.0). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in Hertz (Hz), area integration in natural numbers, and assignments (*italic*). Gas chromatographic (GC) analyses were performed on Shimadzu GC-17A instruments equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness). Infrared (IR) spectra recorded on a PerkinElmer Spectrum One FT-IR Spectrometer are reported in cm<sup>-1</sup>. High resolution mass spectra (HRMS) are taken with EI (electron impact) method on a JEOL GC-mate II. Reversed-phase preparative liquid chromatography was performed on a Yamazen YFLC-Wprep with an ODS column.

**Materials.** Commercial reagents were purchased from Wako Chemical Co., Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used either distilled or recrystallized before use. Anhydrous tetrahydrofuran (THF) was purchased from Wako Chemical Co. and distilled from benzophenone ketyl at 760 Torr under an argon atmosphere immediately before use. The water content of the solvent was confirmed with a Karl-Fischer moisture titrator to be less than 20 ppm.  $\text{FeCl}_3$  purchased from Aldrich Inc. (>99.99%) was used without further purification and was handled under inert atmosphere. A 0.1-M THF solution of  $\text{FeCl}_3$  tends to form polyether compounds upon the storage at room temperature for days, and thus, was prepared immediately before use.

### Typical Procedure A for Cross-Coupling Reactions in Table 2:

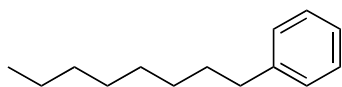
#### (Cyclohexylmethyl)benzene



In a dry reaction vessel, a mixture of  $\text{ZnI}_2(\text{tmeda})$  (521 mg, 1.2 mmol) and phenylmagnesium bromide (a 1.07-M THF solution, 2.24 mL, 2.4 mmol) was stirred for 0.5–1 h. To the resulting suspension was added cyclohexylmethyl *p*-toluenesulfonate (268 mg, 1.0 mmol), and then  $\text{FeCl}_3$  (a 0.10-M THF solution, 0.10 mL, 0.01 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 24 h. After quenching with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , the mixture was passed through a pad of Florisil<sup>®</sup> with  $\text{Et}_2\text{O}$ , and concentrated *in vacuo*. The title compound (165 mg, 95%) was obtained as a colorless liquid after silica gel column chromatography (pentane). Analytical data have been reported in literature.<sup>2</sup>

### Typical Procedure B for Cross-Coupling Reactions in Table 2:

#### Octylbenzene

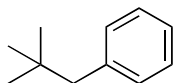


To a suspension of  $\text{ZnI}_2(\text{tmeda})$  (521 mg, 1.2 mmol) in THF (0.60 mL) was added phenyllithium (a 1.99-M  $\text{Bu}_2\text{O}$  solution, 0.60 mL, 2.4 mmol) at 0 °C, and the mixture was stirred for 10 min. To the resulting solution was added magnesium bromide (0.20 mmol), 1-octyl *p*-toluenesulfonate (270 mg, 1.0 mmol), and then  $\text{FeCl}_3$  (a 0.10-M THF solution, 0.10 mL, 0.01 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 3 h. After quenching with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , the mixture was passed through a pad of Florisil<sup>®</sup> with  $\text{Et}_2\text{O}$ , and concentrated *in vacuo*. The title compound (181 mg, 95%) was obtained as a colorless liquid after silica gel column chromatography (pentane).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J$  = 7.0 Hz, 3H,  $\text{CH}_3$ ), 1.24–1.40 (m, 10H,  $\text{CH}_3(\text{CH}_2)_5$ ), 1.56–1.64 (m, 2H,  $\text{CH}_2\text{CH}_2\text{C}$ ), 2.59 (t,  $J$  = 7.3 Hz, 2H,  $\text{CH}_2\text{C}$ ), 7.14–7.19 (m, 3H,  $\text{CH}(\text{CH}_3)\text{CH}$ ), 7.24–7.28 (m, 2H,  $\text{CHCCH}$ );  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 29.3, 29.4,

29.5, 31.5, 31.9, 36.0, 125.5, 128.2 (2C), 128.4 (2C), 142.9; All the analytical data were in good accordance with those of a commercially available sample.

## Compounds Data for Table 2

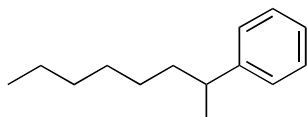
### Neopentylbenzene



The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using neopentyl *p*-toluenesulfonate (242 mg, 1.0 mmol). Conditions: 50 °C, 12 h. The title compound (28 mg, 19%) was obtained as a colorless liquid after silica gel column chromatography (pentane).

The reaction was carried out according to the typical procedure B on a 1.0-mmol scale by using neopentyl *p*-toluenesulfonate (242 mg, 1.0 mmol). Conditions: 50 °C, 12 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that the title compound was obtained in 5% yield. Analytical data have been reported in literature.<sup>3</sup>

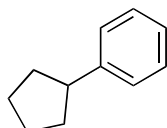
### 2-Octylbenzene



The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using 2-octyl *p*-toluenesulfonate (284 mg, 1.0 mmol). Conditions: 25 °C, 6 h. The title compound (171 mg, 90%) was obtained as a colorless liquid after silica gel column chromatography (pentane).

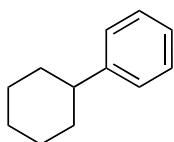
The reaction was carried out according to the typical procedure B on a 1.0-mmol scale by using octyl *p*-toluenesulfonate (284 mg, 1.0 mmol). Conditions: 25 °C, 1 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that the title compound was obtained in 86% yield. Analytical data have been reported in literature.<sup>4</sup>

### Cyclopentylbenzene



The reaction was carried out according to the typical procedure B on a 1.0-mmol scale by using cyclopentyl *p*-toluenesulfonate (240 mg, 1.0 mmol). Conditions: 25 °C, 1 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that the title compound was obtained in 91% yield. Analytical data have been reported in literature.<sup>5</sup>

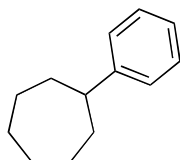
## Cyclohexylbenzene



The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using cyclohexyl *p*-toluenesulfonate (254 mg, 1.0 mmol). Conditions: 25 °C, 24 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that the title compound was obtained in 13% yield.

The reaction was carried out according to the typical procedure B on a 1.0-mmol scale by using cyclohexyl *p*-toluenesulfonate (254 mg, 1.0 mmol). Conditions: 25 °C, 12 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that the title compound was obtained in 15% yield. Analytical data have been reported in literature.<sup>6</sup>

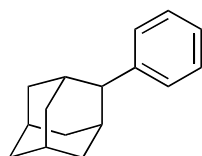
## Phenylcycloheptane



The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using cycloheptyl *p*-toluenesulfonate (268 mg, 1.0 mmol). Conditions: 25 °C, 1 h. The title compound (153 mg, 88%) was obtained as a colorless liquid after silica gel column chromatography (pentane).

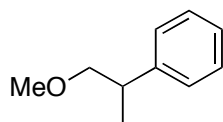
The reaction was carried out according to the typical procedure B on a 1.0-mmol scale by using cycloheptyl *p*-toluenesulfonate (268 mg, 1.0 mmol). Conditions: 25 °C, 1 h. The title compound (141 mg, 81%) was obtained as a colorless liquid after silica gel column chromatography (pentane). Analytical data have been reported in literature.<sup>7</sup>

## 2-Phenyladamantane



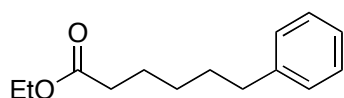
The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using 2-adamantyl *p*-toluenesulfonate (306 mg, 1.0 mmol). Conditions: 40 °C, 12 h, 60 °C, 6 h. The title compound (120 mg, 57%) was obtained as a colorless liquid after silica gel column chromatography (pentane). Analytical data have been reported in literature.<sup>8</sup>

### (1-Methoxypropan-2-yl)benzene



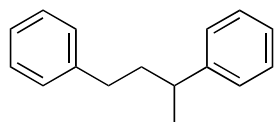
The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using 1-methoxypropan-2-yl *p*-toluenesulfonate (244 mg, 1.0 mmol). Conditions: 40 °C, 12 h. <sup>1</sup>H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed that a mixture of the title compound and (1-methoxypropan-1-yl)benzene was obtained in 87% and 9% yield, respectively. Analytical data have been reported in literature.<sup>9</sup>

### Ethyl 6-phenylhexanoate



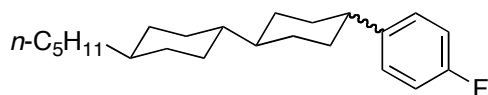
The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using ethyl 6-tosyloxyhexanoate (314 mg, 1.0 mmol). Conditions: 25 °C, 3 h. The title compound (298 mg, 95%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc). Analytical data have been reported in literature.<sup>10</sup>

### 1,3-Diphenylbutane



The reaction was carried out according to the typical procedure A on a 1.0-mmol scale by using 1,3-ditosyloxybutane (398 mg, 1.0 mmol), ZnI<sub>2</sub>(tmeda) (1.04 g, 2.4 mmol) and phenylmagnesium bromide (a 1.07-M THF solution, 4.5 mL, 4.8 mmol). Conditions: 25 °C, 6 h. The title compound (174 mg, 83%) was obtained as a colorless liquid after silica gel column chromatography (hexane). Analytical data have been reported in literature.<sup>11</sup>

### *trans*-4-(4-Fluorophenyl)-*trans*-4'-pentyl-1,1'-bi(cyclohexyl) and *cis*-4-(4-fluorophenyl)-*trans*-4'-pentyl-1,1'-bi(cyclohexyl)

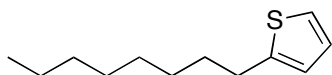


The reaction was carried out according to the typical procedure A on a 0.5-mmol scale by using *trans*-4-(*trans*-4'-pentylcyclohexan-1'-yl)cyclohexan-1-yl *p*-toluenesulfonate (203 mg, 0.5 mmol) and ZnI<sub>2</sub>(tmeda) (326 mg, 0.75 mmol) and 4-fluorophenylmagnesium bromide (a 1.03-M THF solution, 1.46 mL, 1.5 mmol). Conditions: 25 °C, 48 h, 40 °C, 12 h. The title compound (99 mg, 60%, *trans/cis* = 61:39 (determined by GC analysis)) was obtained as a colorless liquid after silica

gel column chromatography (hexane).  $R_f$  = 0.54 (hexane); IR (neat)  $\text{cm}^{-1}$  2918, 2847, 1603, 1509, 1447, 1220, 1159, 828, 532;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) For trans isomer:  $\delta$  0.70–2.00 (m, 27H,  $\text{ArCHC}_{15}\text{H}_{27}\text{CH}_3$ ), 0.88 (t,  $J$  = 6.6 Hz, 3H,  $\text{CH}_3$ ), 2.42 (tt,  $J$  = 12.1, 3.1 Hz, 1H, ArCH), 6.90–7.02 (m, 2H,  $\text{CHCFCH}$ ), 7.10–7.20 (m, 2H,  $\text{CHCCH}$ ), for cis isomer:  $\delta$  0.82–1.92 (m, 27H,  $\text{ArCHC}_{15}\text{H}_{27}\text{CH}_3$ ), 0.88 (t,  $J$  = 6.6 Hz, 3H,  $\text{CH}_3$ ), 2.64 (tt,  $J$  = 7.1, 7.1 Hz, 1H, ArCH), 6.91–7.04 (m, 2H,  $\text{CHCFCH}$ ), 7.15–7.24 (m, 2H,  $\text{CHCCH}$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) For trans isomer:  $\delta$  14.1, 22.7, 26.7, 30.2 (2C), 30.4 (2C), 32.3, 33.7 (2C), 34.9 (2C), 37.5, 38.0, 43.0, 43.5, 44.0, 114.9 (d,  $J$  = 21 Hz, 2C), 128.0 (d,  $J$  = 8 Hz, 2C), 143.5 (d,  $J$  = 3 Hz), 161.2 (d,  $J$  = 243 Hz), for cis isomer:  $\delta$  14.1, 22.7, 26.7, 27.5 (2C), 29.6 (2C), 31.0 (2C), 32.3, 33.6 (2C), 37.2, 37.5, 37.8, 39.5, 42.2, 114.8 (d,  $J$  = 21 Hz, 2C), 128.3 (d,  $J$  = 8 Hz, 2C), 143.0 (d,  $J$  = 3 Hz), 161.1 (d,  $J$  = 243 Hz). Anal. calcd for  $\text{C}_{23}\text{H}_{35}\text{F}$  C, 83.58; H, 10.67. found C, 83.42; H, 10.87.

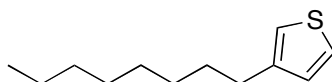
## Compounds Data for Table 3

### 2-Octylthiophene



To a suspension of 2-bromothiophene (244 mg, 1.5 mmol) in THF (2.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 1.42 mL, 1.6 mmol) at  $-40\text{ }^\circ\text{C}$ , and the mixture was stirred at  $-40\text{ }^\circ\text{C}$  for 20 min. To the resulting solution was slowly added  $\text{ZnI}_2$  (a 1.0-M THF solution, 1.5 mL, 1.5 mmol),  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (a 1.04-M THF solution, 1.44 mL, 1.5 mmol) at  $-40\text{ }^\circ\text{C}$ . After evaporation of the volatile matter, the mixture was dried under reduced pressure ( $<0.1$  Torr) for 1 h. To the residue was added THF (2.0 mL), TMEDA (0.45 mL, 3.0 mmol), 1-octyl *p*-toluenesulfonate (284 mg, 1.0 mmol) and then  $\text{FeCl}_3$  (a 0.10-M THF solution, 0.30 mL, 0.03 mmol) at  $0\text{ }^\circ\text{C}$ . The reaction mixture was stirred at  $40\text{ }^\circ\text{C}$  for 12 h. After quenching with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , the mixture was filtered through a pad of Florisil<sup>®</sup> with  $\text{Et}_2\text{O}$ , and concentrated *in vacuo*. The title compound (141 mg, 72%) was obtained as a colorless liquid after silica gel column chromatography (pentane). Analytical data have been reported in literature.<sup>12</sup>

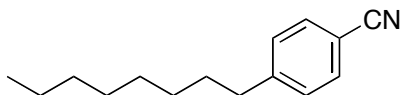
### 3-Octylthiophene



To a suspension of 3-bromothiophene (244 mg, 1.5 mmol) in THF (2.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 1.42 mL, 1.6 mmol) at room temperature, and the mixture was stirred for 24 h. To the resulting solution was slowly added  $\text{ZnI}_2$  (a 1.0-M THF solution, 1.5 mL, 1.5 mmol),  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (a 1.04-M THF solution, 1.44 mL, 1.5 mmol) at  $0\text{ }^\circ\text{C}$ . After evaporation of the volatile matter, the mixture was dried under reduced pressure ( $<0.1$  Torr) for 1 h. To the residue was added THF (2.0 mL), TMEDA (0.45 mL, 3.0 mmol), 1-octyl *p*-toluenesulfonate (213

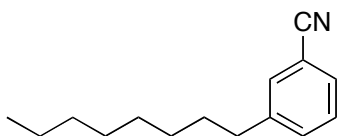
mg, 0.75 mmol) and then FeCl<sub>3</sub> (a 0.10-M THF solution, 0.25 mL, 0.025 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 12 h. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the mixture was filtered through a pad of Florisil<sup>®</sup> with Et<sub>2</sub>O, and concentrated *in vacuo*. The title compound (106 mg, 72%) was obtained as a colorless liquid after silica gel column chromatography (pentane). Analytical data have been reported in literature.<sup>13</sup>

#### 4-Octylbenzonitrile



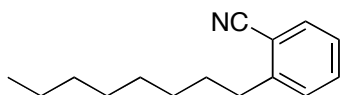
To a suspension of 4-iodobenzonitrile (343 mg, 1.5 mmol) in THF (2.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 1.42 mL, 1.6 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. To the resulting solution was slowly added ZnI<sub>2</sub> (a 1.0-M THF solution, 1.5 mL, 1.5 mmol), Me<sub>3</sub>SiCH<sub>2</sub>MgCl (a 1.04-M THF solution, 1.44 mL, 1.5 mmol) at 0 °C. After evaporation of the volatile matter, the mixture was dried under reduced pressure (< 0.1 Torr) for 1 h. To the residue was added THF (2.0 mL), TMEDA (0.225 mL, 1.5 mmol), 1-octyl *p*-toluenesulfonate (284 mg, 1.0 mmol), and then FeCl<sub>3</sub> (a 0.10-M THF solution, 0.10 mL, 0.01 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 10 h. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the mixture was passed through a pad of Florisil<sup>®</sup> with Et<sub>2</sub>O, and concentrated *in vacuo*. The title compound (200 mg, 93%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc). Analytical data have been reported in literature.<sup>14</sup>

#### 3-Octylbenzonitrile



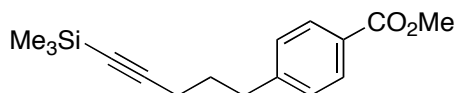
To a suspension of 3-bromobenzonitrile (136 mg, 0.75 mmol) in THF (1.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 0.71 mL, 0.8 mmol) at 0 °C, and the mixture was stirred at 0 °C for 24 h. To the resulting solution was slowly added ZnI<sub>2</sub> (a 1.0-M THF solution, 0.75 mL, 0.75 mmol), Me<sub>3</sub>SiCH<sub>2</sub>MgCl (a 1.04-M THF solution, 0.72 mL, 0.75 mmol) at 0 °C. After evaporation of the volatile matter, the mixture was dried under reduced pressure (< 0.1 Torr) for 1 h. To the residue was added THF (1.0 mL), TMEDA (0.225 mL, 1.5 mmol), 1-octyl *p*-toluenesulfonate (142 mg, 0.5 mmol), and then FeCl<sub>3</sub> (a 0.10-M THF solution, 0.15 mL, 0.015 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 6 h. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the mixture was filtered through a pad of Florisil<sup>®</sup> with Et<sub>2</sub>O, and concentrated *in vacuo*. The title compound (100 mg, 93%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc). Analytical data have been reported in literature.<sup>15</sup>

## 2-Octylbenzonitrile



To a suspension of 2-bromobenzonitrile (136 mg, 0.75 mmol) in THF (1.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 0.71 mL, 0.80 mmol) at 0 °C, and the mixture was stirred at 0 °C for 24 h. To the resulting solution was slowly added ZnI<sub>2</sub> (a 1.0-M THF solution, 0.75 mL, 0.75 mmol), Me<sub>3</sub>SiCH<sub>2</sub>MgCl (a 1.04-M THF solution, 0.72 mL, 0.75 mmol) at 0 °C. After evaporation of the volatile matter, the mixture was dried under reduced pressure (< 0.1 Torr) for 1 h. To the residue was added THF (1.0 mL), TMEDA (0.113 mL, 0.75 mmol), 1-octyl *p*-toluenesulfonate (71 mg, 0.25 mmol), and then FeCl<sub>3</sub> (a 0.10-M THF solution, 0.13 mL, 0.013 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 14 h. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the mixture was filtered through a pad of Florisil® with Et<sub>2</sub>O, and concentrated *in vacuo*. The title compound (32 mg, 60%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc). Analytical data have been reported in literature.<sup>16</sup>

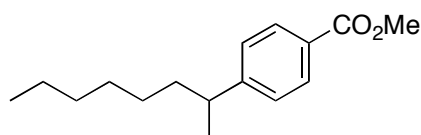
## Methyl 4-[5-(trimethylsilyl)-pent-4-ynyl]benzoate



To a suspension of methyl 4-iodobenzoate (393 mg, 1.5 mmol) in THF (2.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 1.42 mL, 1.6 mmol) at -20 °C, and the mixture was stirred at -20 °C for 10 min. To the resulting solution was slowly added ZnI<sub>2</sub> (a 1.0-M THF solution, 1.50 mL, 1.5 mmol), Me<sub>3</sub>SiCH<sub>2</sub>MgCl (a 1.04-M THF solution, 1.44 mL, 1.5 mmol) at 0 °C. After evaporation of the volatile matter, the mixture was dried under reduced pressure (< 0.1 Torr) for 1 h. To the residue was added THF (2.0 mL), TMEDA (0.225 mL, 1.5 mmol), 5-(trimethylsilyl)pent-4-ynyl *p*-toluenesulfonate (310 mg, 1.0 mmol), and then FeCl<sub>3</sub> (a 0.10-M THF solution, 0.10 mL, 0.01 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 12 h. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the mixture was filtered through a pad of Florisil® with Et<sub>2</sub>O, and concentrated *in vacuo*. The title compound (205 mg, 75%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc) and reversed phase column chromatography (MeOH/H<sub>2</sub>O). IR (neat) cm<sup>-1</sup> 2952, 2901, 2863, 1721 (C=O), 1611, 1436, 1276, 1248, 1178, 1102, 1034, 1020, 838, 758, 702, 637; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.76–1.91 (m, 2H, CCCH<sub>2</sub>CH<sub>2</sub>), 2.23 (t, *J* = 7.0 Hz, 2H, CCCH<sub>2</sub>), 2.77 (t, *J* = 7.6 Hz, 2H, CCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.90 (s, 3H, OCH<sub>3</sub>), 7.25 (d, *J* = 8.0 Hz, 2H, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 7.96 (d, *J* = 8.0 Hz, 2H, (CH)<sub>2</sub>CC(=O)); <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>) δ 0.1 (3C), 19.1, 29.7, 34.6, 51.9, 85.3, 106.5, 127.9, 128.5 (2C), 129.7 (2C), 147.1, 167.0.

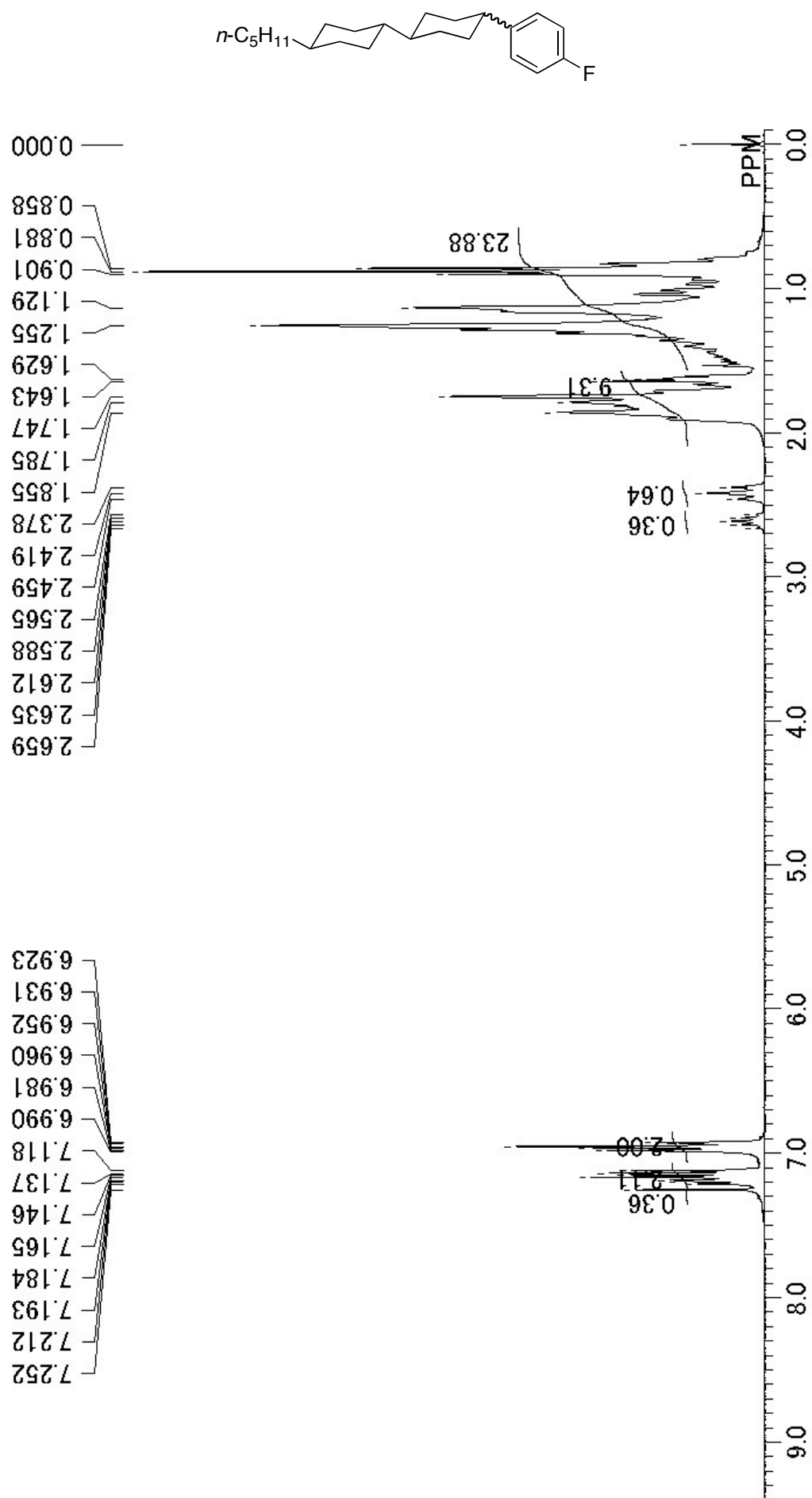


### Methyl 4-(octan-2-yl)benzoate

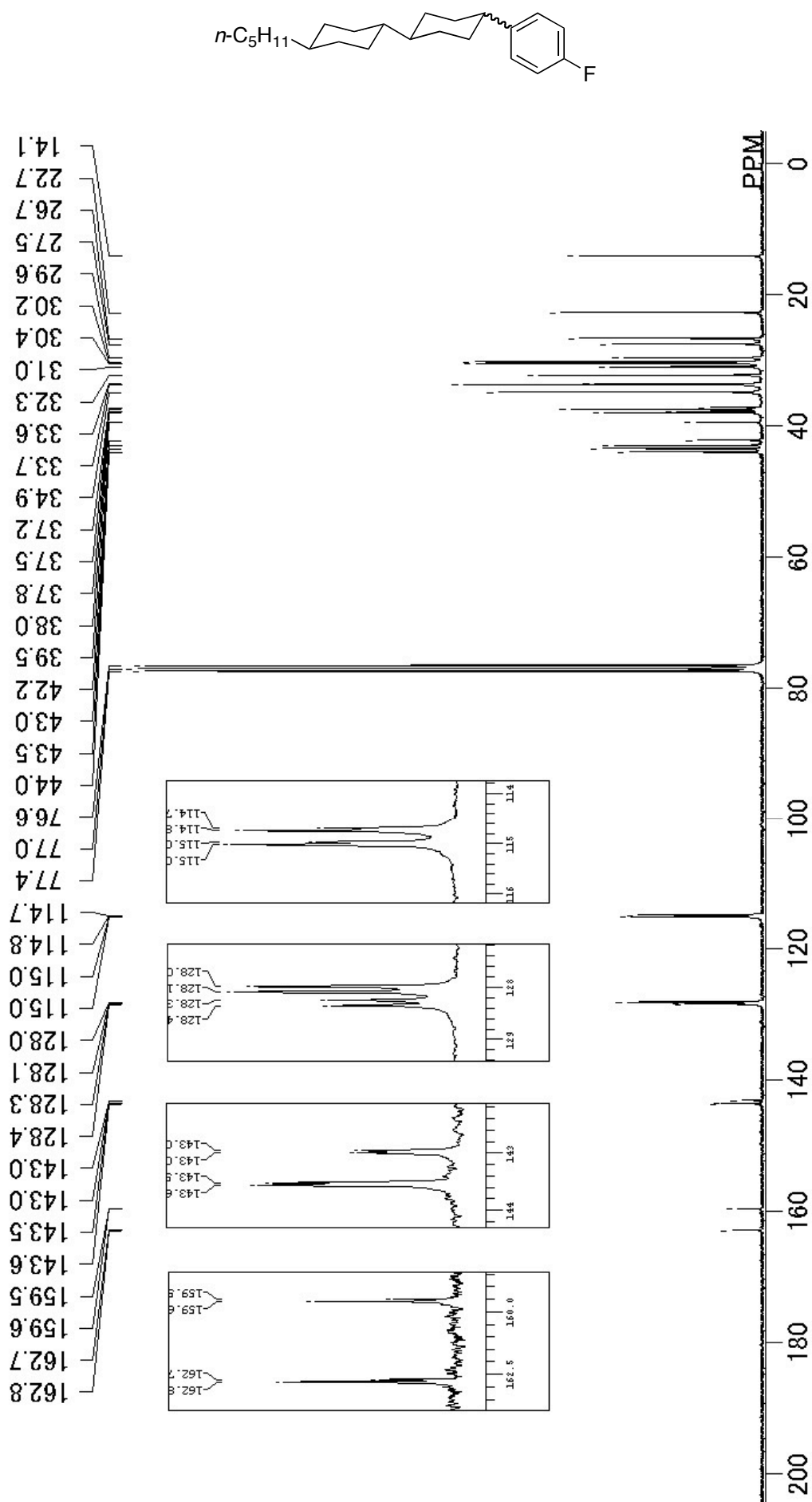


To a suspension of methyl 4-iodobenzoate (393 mg, 1.5 mmol) in THF (2.0 mL) was added *i*-PrMgCl·LiCl (a 1.13-M THF solution, 1.42 mL, 1.6 mmol) at  $-20\text{ }^{\circ}\text{C}$ , and the mixture was stirred at  $-20\text{ }^{\circ}\text{C}$  for 10 min. To the resulting solution was slowly added  $\text{ZnI}_2$  (a 1.0-M THF solution, 1.5 mL, 1.5 mmol),  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (a 1.04-M THF solution, 1.44 mL, 1.5 mmol) at  $0\text{ }^{\circ}\text{C}$ . After evaporation of the volatile matter, the mixture was dried under reduced pressure ( $< 0.1$  Torr) for 1 h. To the residue was added THF (2.0 mL), TMEDA (0.225 mL, 1.5 mmol), 2-octyl *p*-toluenesulfonate (284 mg, 1.0 mmol) and then  $\text{FeCl}_3$  (a 0.10-M THF solution, 0.10 mL, 0.01 mmol) at  $0\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred at  $25\text{ }^{\circ}\text{C}$  for 24 h. After quenching with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , the mixture was filtered through a pad of Florisil<sup>®</sup> with  $\text{Et}_2\text{O}$ , and concentrated *in vacuo*. The title compound (170 mg, 71%) was obtained as a colorless liquid after silica gel column chromatography (hexane/EtOAc) and reversed phase column chromatography (MeOH/ $\text{H}_2\text{O}$ ). IR (neat)  $\text{cm}^{-1}$  2955, 2926, 2856, 1720 (C=O), 1610, 1435, 1274, 1179, 1111, 1019, 969, 854, 774, 707;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (t,  $J = 6.7$  Hz, 3H,  $\text{CH}_3\text{CH}_2$ ), 1.24 (d,  $J = 7.1$  Hz, 3H,  $\text{CH}_3\text{CH}$ ), 1.03–1.35 (m, 8H,  $\text{CH}_3(\text{CH}_2)_5$ ), 1.49–1.65 (m, 2H,  $\text{CH}_2\text{CH}$ ), 2.73 (qt,  $J = 7.2, 6.9$  Hz, 1H,  $\text{CH}_3\text{CH}$ ), 3.90 (s, 3H,  $\text{OCH}_3$ ), 7.24 (d,  $J = 8.4$  Hz, 2H,  $(\text{CHCH})_2\text{CC}(=\text{O})$ ), 7.96 (d,  $J = 8.4$  Hz, 2H,  $(\text{CH})_2\text{CC}(=\text{O})$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.0, 22.6, 27.6, 29.3, 31.7, 38.2, 40.0, 51.9, 127.0 (2C), 127.7, 129.7 (2C), 153.5, 167.2.

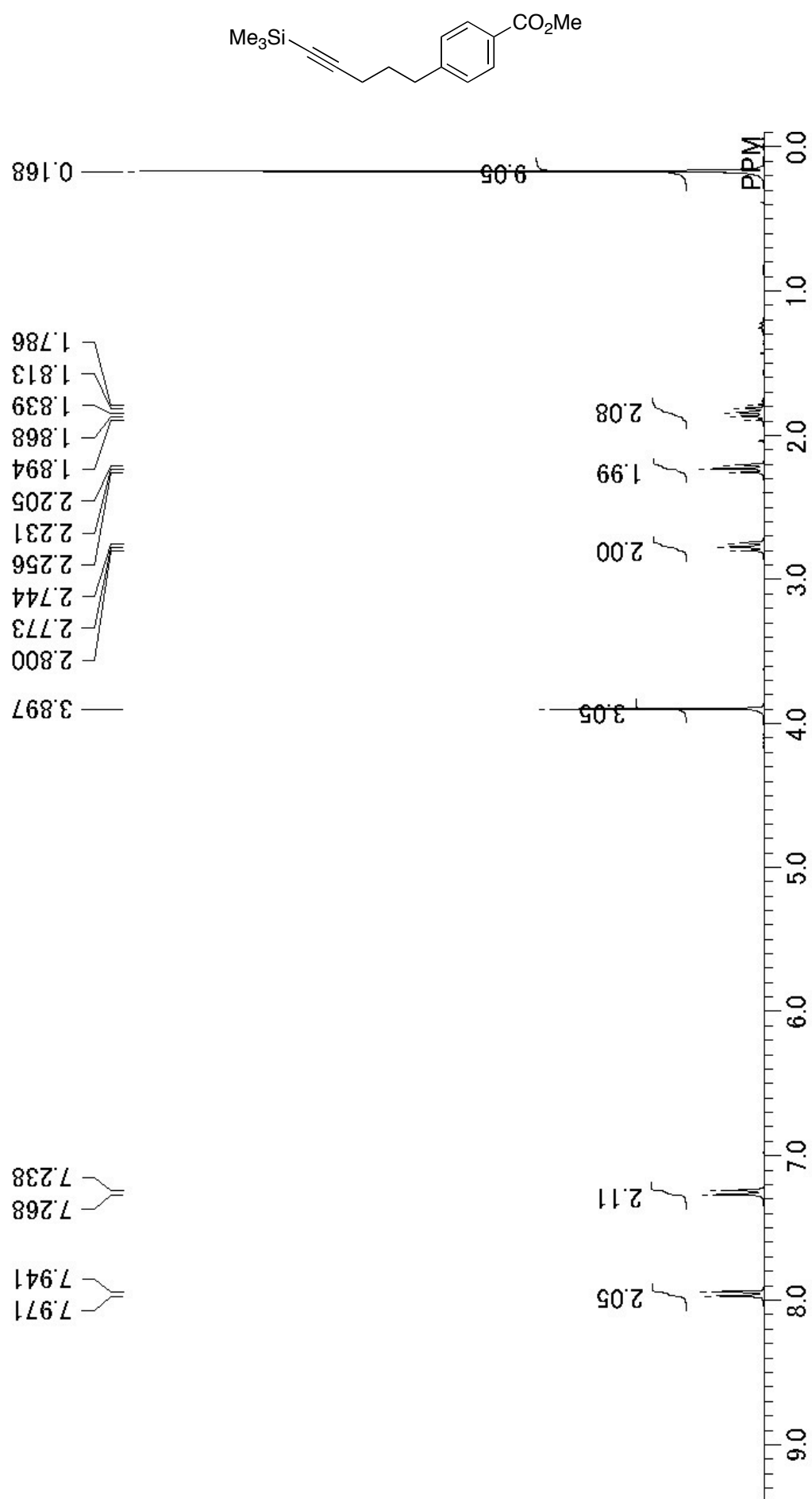
<sup>1</sup>H NMR spectrum of compound 8:



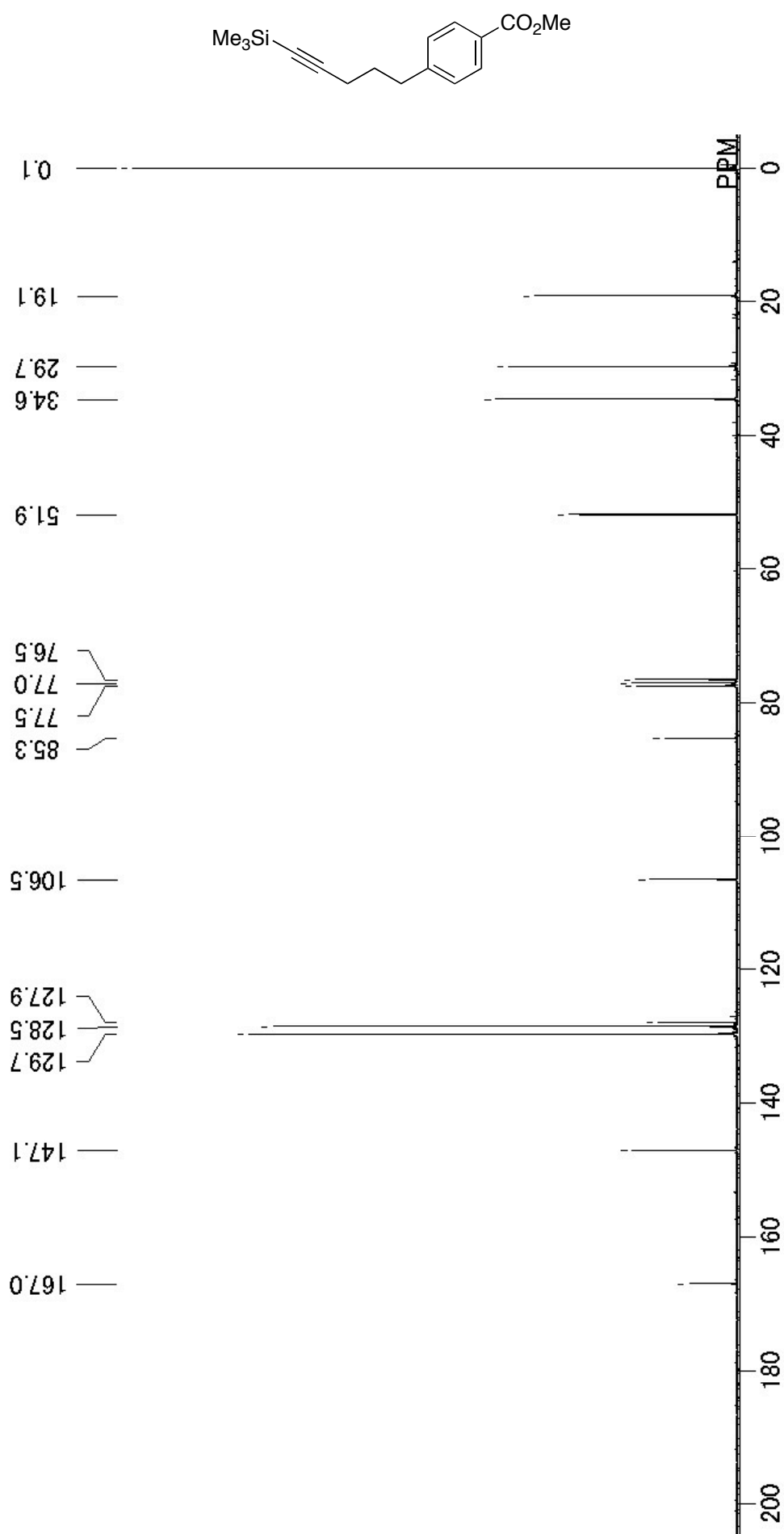
<sup>13</sup>C NMR spectrum of compound 8:



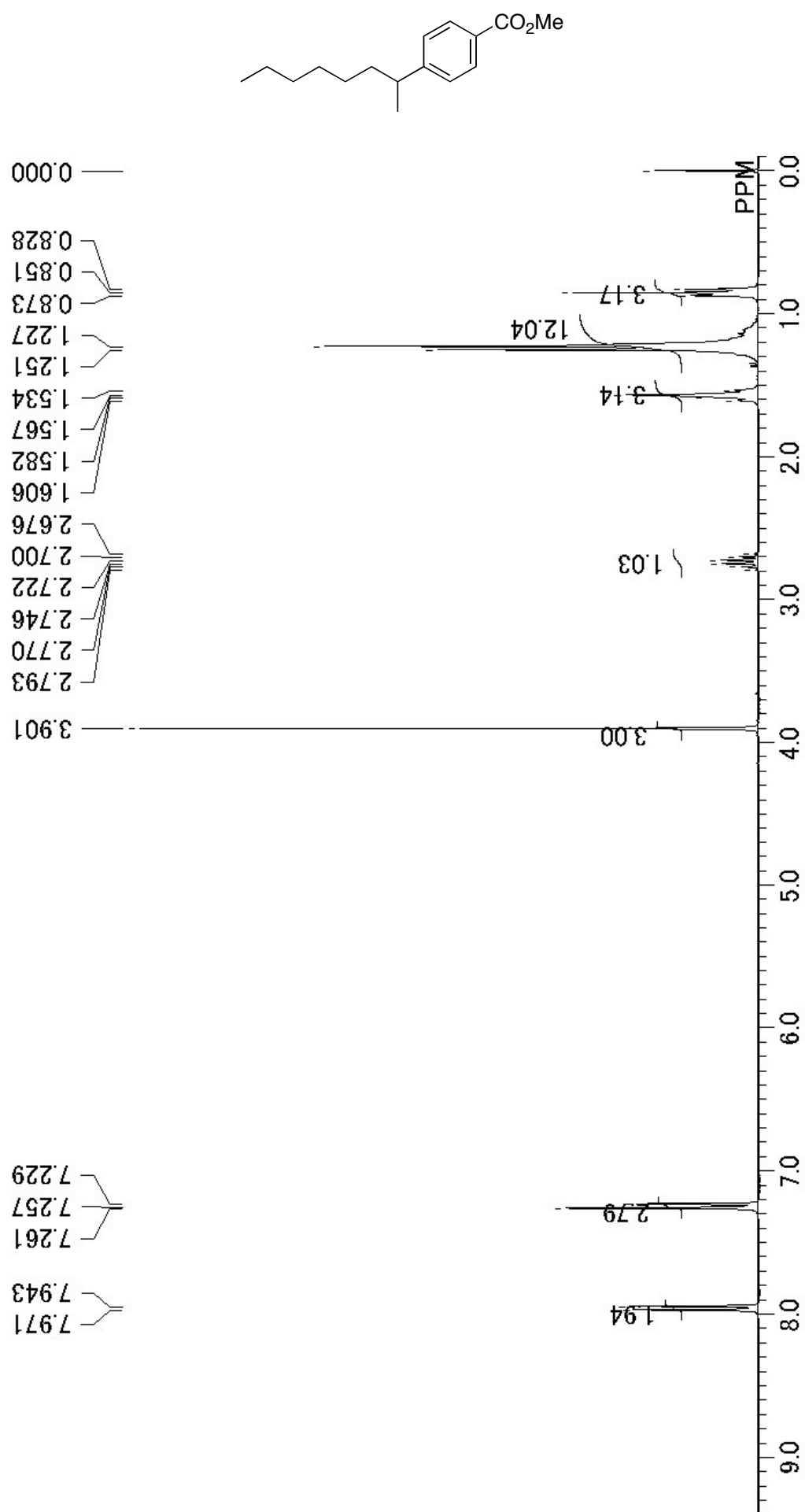
<sup>1</sup>H NMR spectrum of the product in entry 6 in Table 3:



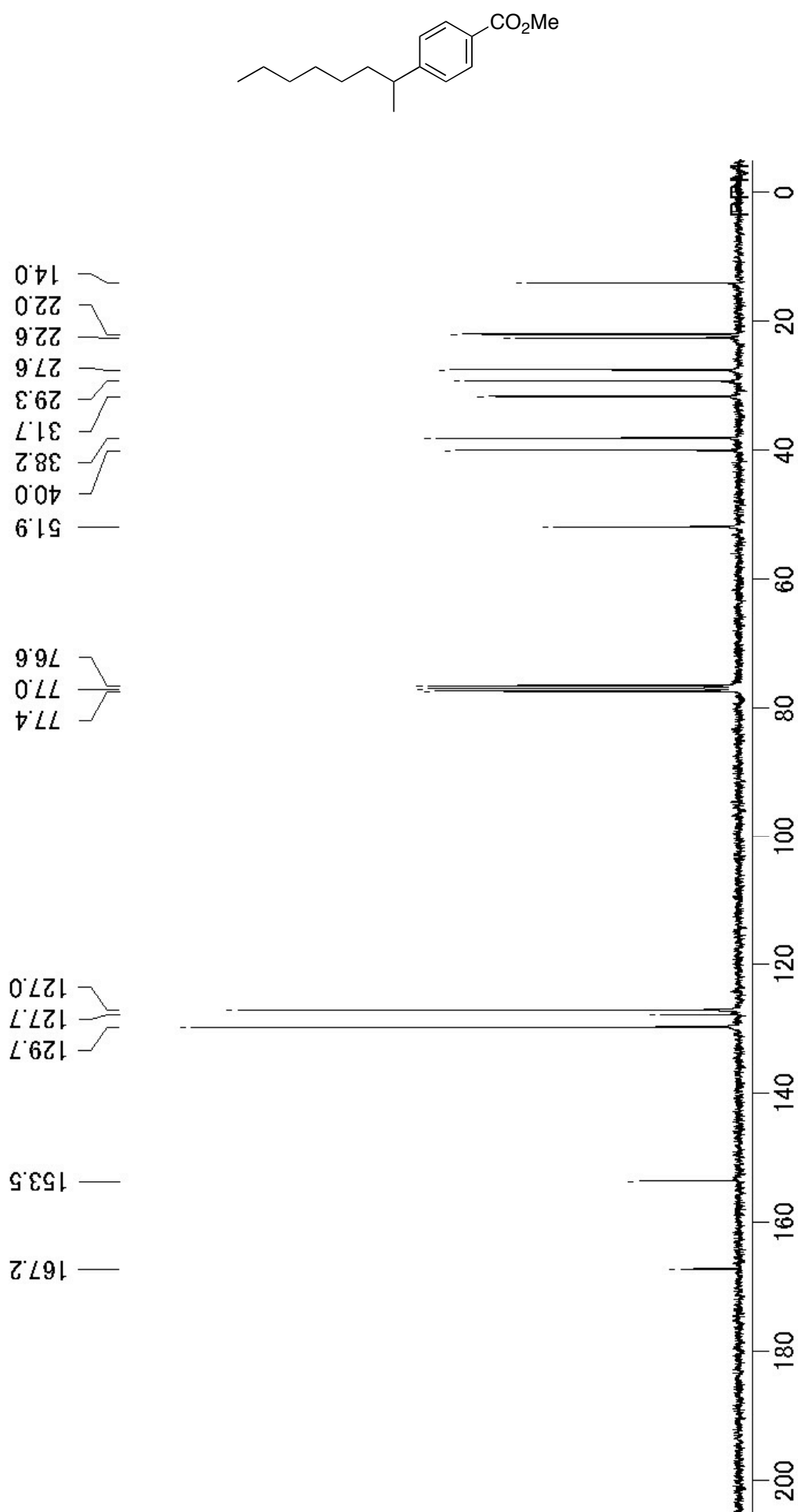
<sup>13</sup>C NMR spectrum of the product in entry 6 in Table 3:



<sup>1</sup>H NMR spectrum of the product in entry 7 in Table 3:



<sup>13</sup>C NMR spectrum of the product in entry 7 in Table 3:



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