

# Supporting Information

## **Manganese-Catalyzed Benzene Synthesis by [2+2+2] Coupling of 1,3-Dicarbonyl Compounds and Terminal Acetylene**

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**General.** All reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids or solutions were transferred via a syringe or teflon cannula. Analytical thin-layer chromatography was performed on a glass plate pre-coated with 0.25-mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV) and/or by immersion in an acidic solution of *p*-anisaldehyde or PMA followed by heating on a hot plate. Flash column chromatography was performed as described by Still *et al.*,<sup>1</sup> employing Kanto Silica gel 60 (spherical, neutral, 140–325 mesh).

**Materials.** Commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used either distilled or recrystallized before use. Toluene was distilled over CaH<sub>2</sub>. The water content of the solvent was determined on a Karl-Fischer moisture titrator to be less than 20 ppm. Anhydrous ethereal solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour).<sup>2</sup>

**Instrumentation.** Melting points are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a JEOL ECA-500 or an ECX 400 spectrometer and reported in parts per million from tetramethylsilane. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> were referenced internally to tetramethylsilane as a standard, and <sup>13</sup>C spectra to the solvent resonance (CDCl<sub>3</sub> 77.0 ppm. High resolution mass spectra (HRMS) were taken on a JEOL Accu TOF JMS-T100LC.

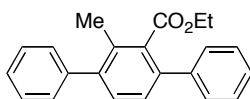
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(1) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

(2) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, *Organometallics* **1996**, *15*, 1518–1520.

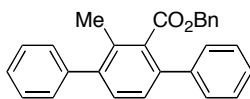
## General Procedure for Manganese-catalyzed Reaction

### Ethyl 2-methyl-3,6-diphenylbenzoate (Table 1, entry 1)



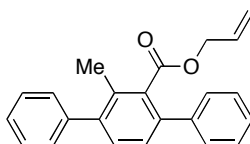
MgSO<sub>4</sub> (12.0 mg, 0.10 mmol) was dried in a Schlenk tube at 200 °C/0.37 Torr for 4 h. To the dried MgSO<sub>4</sub> was added ethyl acetoacetate (65 mg, 0.50 mmol), phenylacetylene (153 mg, 1.5 mmol), and 0.5 mL of toluene, followed by MnBr(CO)<sub>5</sub> (13.9 mg, 0.050 mmol) and NMO (6.2 mg, 0.053 mmol). After stirred at 65 °C for 48 h, anhydrous TsOH (17 mg, 0.10 mmol) was added into the mixture and the mixture was stirred for additional 1 h. After cooled to room temperature, the mixture was filtrated through a pad of silica gel using ethyl acetate as an eluent. Filtrate was concentrated *in vacuo* to obtain crude product. Flash column chromatography (silica gel: hexane/ethyl acetate = 95/5) gave the product (138 mg, 0.44 mmol, 87%) as a white solid; mp 107–108 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.98 (t, *J* = 7.0 Hz, 3H), 2.28 (s, 3H), 4.08 (q, *J* = 7.0 Hz, 2H), 7.20–7.30 (m, 2H), 7.32–7.45 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.7, 17.6, 61.0, 127.0, 127.1, 127.4, 128.20 (2C), 128.22 (2C), 128.4 (2C), 129.3 (2C), 130.8, 132.4, 134.4, 140.0, 140.7, 141.2, 141.7, 170.0; Anal. Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>: C, 83.51; H, 6.37. Found C, 83.32; H, 6.47.

### Benzyl 2-methyl-3,6-diphenylbenzoate (Table 1, entry 2)

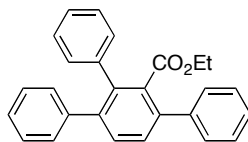


White solid; mp 106–107 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.26 (s, 3H), 5.04 (s, 2H), 7.00 (d, *J* = 5.8 Hz, 2H), 7.24–7.28 (m, 4H), 7.30–7.33 (m, 3H), 7.34–7.40 (m, 4H), 7.41–7.44 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 17.7, 61.2, 127.10, 127.14, 127.5, 128.19, 128.20 (2C), 128.38 (4C), 128.40 (2C), 128.5 (2C), 129.3 (2C), 130.9, 132.6, 134.0, 135.0, 139.0, 140.6, 141.1, 141.7, 169.9; Anal. Calcd for C<sub>27</sub>H<sub>22</sub>O<sub>2</sub>: C, 85.69; H, 5.86. Found C, 85.43; H, 6.12.

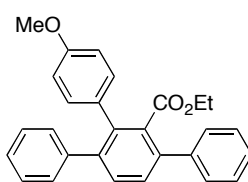
### 2-Propenyl 2-methyl-3,6-diphenylbenzoate (Table 1, entry 3)



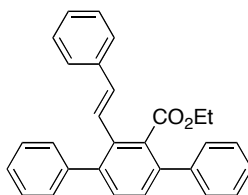
White solid; mp 95–96.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.28 (s, 3H), 4.51 (d, *J* = 5.7 Hz, 2H), 5.10 (d, *J* = 10.3 Hz, 2H), 5.12 (d, *J* = 17.2 Hz, 1H), 5.60 (tdd, *J* = 5.7 Hz, 10.3 Hz, 17.2 Hz, 1H), 7.25–7.45 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz) δ 18.0, 66.1, 119.2, 127.4, 127.5, 127.8, 128.6, 128.7, 128.8, 129.6, 131.3, 131.7, 131.8, 132.9, 134.5, 139.4, 141.0, 141.5, 142.1, 170.1; HRMS (APCI+) calcd for C<sub>23</sub>H<sub>21</sub>O<sub>2</sub>: 329.1542 ([M+H]<sup>+</sup>), found 329.1526.

**Ethyl 2,3,6-triphenylbenzoate (Table 1, entry 6)**

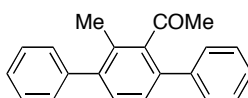
White solid; mp 121–122 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.76 (t,  $J$  = 6.9 Hz, 3H), 3.77 (q,  $J$  = 6.9 Hz, 2H), 7.08–7.24 (m, 10H), 7.35–7.54 (m, 7H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.4, 60.8, 126.5, 127.0, 127.5 (3C), 127.7 (2C), 128.3 (2C), 128.6 (2C), 129.0, 129.8 (2C), 130.2 (2C), 131.0, 134.7, 138.2, 138.7, 138.9, 140.3, 140.6, 140.6, 169.1; Anal. Calcd for  $\text{C}_{27}\text{H}_{22}\text{O}_2$ : C, 85.69; H, 5.86. Found C, 85.43; H, 6.12.

**Ethyl 2-(4-methoxyphenyl)-3,6-diphenylbenzoate (Table 1, entry 7)**

Pale-yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.80 (t,  $J$  = 7.5 Hz, 3H), 3.75 (s, 3H), 3.80 (q,  $J$  = 7.5 Hz, 2H), 6.72 (d,  $J$  = 8.6 Hz, 2H), 7.05 (d,  $J$  = 8.1 Hz, 2H), 7.09 (d,  $J$  = 6.3 Hz, 2H), 7.18–7.19 (m, 3H), 7.35–7.43 (m, 4H), 7.46–7.51 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  26.2, 59.4, 64.0, 105.8 (2C), 116.5, 117.4 (2C), 117.6 (2C), 118.0, 118.2 (2C), 118.4, 118.6, 119.2 (2C), 120.2, 120.4 (2C), 123.3, 125.7, 126.4, 127.6, 128.0 (2C), 142.2, 150.7; HRMS (APCI+) calcd for  $\text{C}_{28}\text{H}_{25}\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ): 409.1804, found 409.1806.

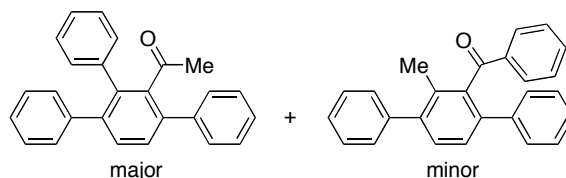
**Ethyl 2-[(E)-2-phenylethenyl]-3,6-diphenylbenzoate (Table 1, entry 8)**

White solid; mp 133–134 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.98 (t,  $J$  = 7.0 Hz, 3H), 4.08 (q,  $J$  = 7.0 Hz, 2H), 6.66 (d,  $J$  = 16.1 Hz, 1H), 7.00 (d,  $J$  = 16.1 Hz, 1H), 7.25–7.55 (br, 15H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.8, 61.1, 126.3, 126.4 (2C), 127.2, 127.5, 127.7, 128.1 (2C), 128.2 (2C), 128.55 (2C), 128.59 (2C), 128.8, 129.9 (2C), 130.9, 133.4, 133.7, 134.5, 137.2, 139.4, 140.3, 140.50, 140.51, 169.6; Anal. Calcd for  $\text{C}_{29}\text{H}_{24}\text{O}_2$ : C, 86.11; H, 5.98. Found C, 86.08; H, 6.17.

**2'-Ethanoyl-3'-methyl-1,1':4',1''-terphenyl (Table 1, entry 9)**

Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  2.00 (s, 3H), 2.18 (s, 3H), 7.25–7.44 (m, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  17.4, 32.4, 127.1 (2C), 127.7, 128.2 (2C), 128.6 (2C), 129.0 (2C), 129.3 (2C), 130.4, 130.7, 137.3, 140.2, 141.2, 142.0, 142.2, 208.3; HRMS (APCI+) calcd for  $\text{C}_{21}\text{H}_{20}\text{O}$ : 287.1436, found 287.1446.

**2'-Benzoyl-3'-methyl-1,1':4',1''-terphenyl and 2'-ethanoyl-3'-phenyl-1,1':4',1''-terphenyl (Table 1, entry 10)**

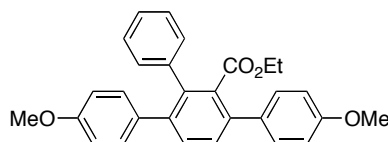


The reaction was carried out according to the general procedure. Regioisomers were separated by silica gel column chromatography (toluene/hexane = 5/95 to 30/70 to 50/50).

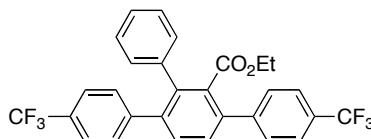
**2'-Ethanoyl-3'-phenyl-1,1':4',1''-terphenyl (major):**  $R_f$  = 0.17 (toluene/hexane = 50/50); yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.78 (s, 3H), 7.08–7.11 (m, 4H), 7.15–7.20 (m, 6H), 7.35–7.42 (m, 6H), 7.49 (d,  $J$  = 8.0 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  32.8, 126.5, 127.1, 127.6, 127.71 (2C), 127.74 (2C), 128.4 (2C), 129.2 (2C), 129.3, 129.8 (2C), 130.4, 130.8 (2C), 136.7, 137.6, 138.4, 140.1, 140.6, 140.8, 142.7, 206.3; HRMS (APCI+) calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ : 349.1592, found 349.1580.

**2'-Benzoyl-3'-methyl-1,1':4',1''-terphenyl (minor):**  $R_f$  = 0.39 (toluene/hexane = 50/50); yellow solid; mp 166–168 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  2.12 (s, 3H), 7.12–7.20 (m, 3H), 7.25–7.33 (m, 5H), 7.36–7.46 (m, 7H), 7.65 (d,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  17.8, 127.11, 127.16, 127.2, 128.0 (2C), 128.2 (2C), 128.3 (2C), 129.2 (2C), 129.38 (2C), 129.39 (2C), 130.5, 132.2, 133.2, 137.4, 138.9, 139.5, 140.1, 141.2, 141.8, 200.1; HRMS (APCI+) calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ : 349.1592, found 349.1601.

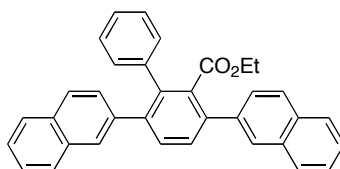
**Ethyl 2-phenyl-3,6-di(4-methoxyphenyl)benzoate (Table 2, entry 1)**



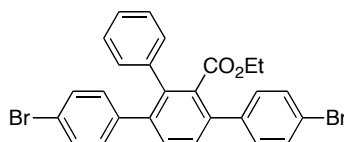
White solid; mp 143–144 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.79 (t,  $J$  = 7.2 Hz, 3H), 3.75 (s, 3H), 3.78 (q,  $J$  = 7.2 Hz, 2H), 3.84 (s, 3H), 6.70 (d,  $J$  = 8.6 Hz, 2H), 6.93 (d,  $J$  = 8.6 Hz, 2H), 6.99 (d,  $J$  = 8.6 Hz, 2H), 7.12–7.15 (m, 2H), 7.17–7.21 (m, 3H), 7.40 ( $J$  = 8.6 Hz, 3H), 7.47 (d,  $J$  = 8.0 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.5, 55.1, 55.3, 113.2, 113.7, 126.9, 127.6 (2C), 129.0, 129.7 (2C), 130.2 (2C), 130.9 (2C), 131.0, 132.7, 133.0, 134.6, 138.0, 138.1, 138.9, 139.8, 158.2, 159.1, 169.3; Anal. Calcd for  $\text{C}_{29}\text{H}_{26}\text{O}_4$ : C, 79.43; H, 5.98. Found C, 79.34; H, 6.00.

**Ethyl 2-phenyl-3,6-di(4-trifluoromethylphenyl)benzoate (Table 2, entry 2)**

White solid; mp 152–153 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.76 (t,  $J$  = 7.1 Hz, 3H), 3.77 (q,  $J$  = 7.1 Hz, 2H), 6.94 (d,  $J$  = 8.5 Hz, 2H), 7.08–7.12 (m, 2H), 7.18–7.24 (m, 5H), 7.44 (d,  $J$  = 7.4 Hz, 2H), 7.46 (d,  $J$  = 7.4 Hz, 1H), 7.53 (d,  $J$  = 8.1 Hz, 1H), 7.59 (d,  $J$  = 8.1 Hz, 2H), 7.58 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.3, 61.1, 124.10 (q,  $^1J_{\text{C-F}}$  = 271 Hz, 1C), 124.13 (q,  $^1J_{\text{C-F}}$  = 271 Hz, 1C), 124.8 (q,  $^3J_{\text{C-F}}$  = 3.6 Hz, 2C), 125.3 (q,  $^3J_{\text{C-F}}$  = 3.6 Hz, 2C), 127.5, 127.9 (2C), 128.91 (q,  $^2J_{\text{C-F}}$  = 32 Hz, 1C), 128.96 (2C), 128.99, 129.9 (q,  $^2J_{\text{C-F}}$  = 33 Hz, 1C), 130.0 (2C), 130.1 (2C), 131.0, 134.9, 137.8, 138.2, 138.6, 139.9, 143.6, 144.1, 168.5; Anal. Calcd for  $\text{C}_{29}\text{H}_{20}\text{F}_6\text{O}_2$ : C, 67.70; H, 3.92. Found C, 67.63; H, 3.91.

**Ethyl 2-phenyl-3,6-di(2-naphthyl)benzoate (Table 2, entry 4)**

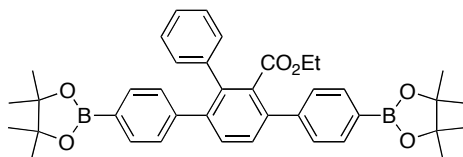
White solid; mp 198–199 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.73 (t,  $J$  = 7.2 Hz, 3H), 3.76 (q,  $J$  = 7.2 Hz, 2H), 7.13 (dd,  $J$  = 8.1, 1.8 Hz, 1H), 7.15–7.16 (m, 3H), 7.20–7.21 (m, 2H), 7.43–7.45 (m, 2H), 7.50–7.52 (m, 2H), 7.58–7.60 (m, 2H), 7.64 (dd,  $J$  = 10.3, 1.8 Hz, 1H), 7.67 (d,  $J$  = 8.0 Hz, 1H), 7.70 (s, 1H), 7.75 (dd,  $J$  = 8.6, 4.6 Hz, 2H), 7.85–7.88 (m, 2H), 7.90 (d,  $J$  = 8.6 Hz, 1H), 7.98 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.4, 60.9, 125.9, 126.0, 126.1, 126.3, 126.8, 127.0, 127.1, 127.5, 127.7, 127.95, 127.99, 127.10, 128.13, 128.7, 129.4, 130.3, 131.4, 132.0, 132.6, 133.1, 133.2, 138.0, 137.7, 138.3, 138.5, 138.6, 138.9, 140.5, 169.1 (three signals are overlapped); HRMS calcd for  $\text{C}_{35}\text{H}_{27}\text{O}_2$ : 479.2011 ( $[\text{M}+\text{H}]^+$ ), found: 479.2032.

**Ethyl 2-phenyl-3,6-di(4-bromophenyl)benzoate (Table 2, entry 5)**

White solid; mp 199–200 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  0.78 (t,  $J$  = 7.0 Hz, 3H), 3.77 (q,  $J$  = 7.0 Hz, 2H), 6.94 (d,  $J$  = 8.5 Hz, 2H), 7.11 (m, 2H), 7.21 (m, 3H), 7.30 (d,  $J$  = 8.5 Hz, 2H), 7.33 (d,  $J$  = 8.5 Hz, 2H), 7.40 (d,  $J$  = 8.0 Hz, 1H), 7.47 (d,  $J$  = 8.0 Hz, 1H), 7.53 (d,  $J$  = 8.6 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  13.4, 61.0, 121.1, 122.1, 127.3, 127.8 (2C), 128.9, 130.1 (2C), 130.2

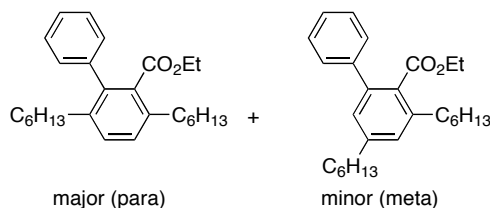
(2C), 130.90, 130.94 (2C), 131.3, 131.5, 134.7, 137.9, 138.1, 138.3, 139.0, 139.4, 139.7, 168.7 (two signals are overlapped); Anal. Calcd for  $C_{27}H_{20}O_2$ : C, 60.47; H, 3.76. Found C, 60.30; H, 3.84.

**Ethyl 2-phenyl-3,6-di[4-(2',3'-dimethylbutan-2',3'-dioxyboryl)phenyl]benzoate (Table 2, entry 6)**



White solid; mp 223.5–225 °C;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  0.77 (t,  $J$  = 6.9 Hz, 3H), 1.32 (s, 12H), 1.36 (s, 12H), 3.76 (q,  $J$  = 6.9 Hz, 2H), 7.10 (d,  $J$  = 8.0 Hz, 2H), 7.12–7.14 (m, 2H), 7.16–7.18 (m, 3H), 7.43 (d,  $J$  = 8.0 Hz, 2H), 7.47–7.51 (m, 3H), 7.61 (d,  $J$  = 8.0 Hz, 2H), 7.85 (d,  $J$  = 8.0 Hz, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  13.4, 24.86 (4C), 24.88 (4C), 60.8, 83.7 (2C), 83.8 (2C), 127.0, 127.6 (2C), 127.9 (2C), 129.0, 129.2 (2C), 130.2 (2C), 131.1, 134.1 (2C), 134.67, 134.75 (2C), 138.2, 138.5, 138.9, 140.6, 143.1, 143.5, 168.9 (Two carbon signals are missing, which are most probably attributed to the  $\alpha$ -carbons to the boron atoms); Anal. Calcd for  $C_{39}H_{44}B_2O_6$ : C, 74.31; H, 7.04. Found: C, 74.56; H, 7.16.

**Ethyl 3,6-dihexyl-2-phenylbenzoate and Ethyl 4,6-dihexyl-2-phenylbenzoate (Table 2, entry 7)**

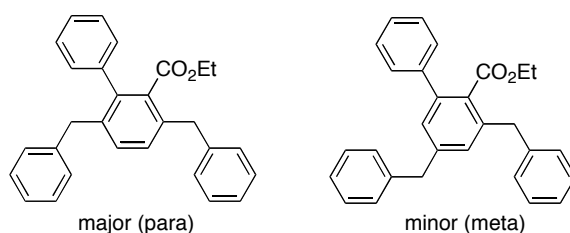


Colorless oil;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  0.80 (t,  $J$  = 6.9 Hz, 3H, major), 0.86–0.90 (m, methylene protons), 0.93 (t,  $J$  = 7.3 Hz, 3H), 1.11–1.12 (m, methylene protons), 1.29–1.36 (m, methylene protons), 1.61 (m, methylene protons), 2.37 (dd,  $J$  = 7.5, 6.3 Hz, 2H, major), 2.59 (dd,  $J$  = 8.1, 8.0 Hz, 2H, major), 2.62 (dd,  $J$  = 8.6, 7.5 Hz, 2H, minor), 2.67 (dd,  $J$  = 8.1, 8.0 Hz, 2H, minor), 3.89 (q,  $J$  = 6.9 Hz, 2H, major), 4.01 (q,  $J$  = 7.3 Hz, 2H, minor), 7.02 (s, 1H, minor), 7.03 (s, 1H, minor), 7.15 (d,  $J$  = 8.0 Hz, 1H, major), 7.21–7.23 (m, 3H), 7.30–7.36 (m, overlapped: major 3H, minor 5H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  13.6, 14.0, 14.1, 22.4, 22.6, 29.0, 29.3, 31.0, 31.3, 31.38, 31.42, 31.6, 31.7, 32.8, 33.4, 33.7, 35.8, 60.5, 60.7, 127.0, 127.1, 127.4, 127.6, 128.1, 128.2, 128.4, 128.5, 129.7, 129.9, 130.4, 134.4, 136.6, 138.4, 138.6, 139.2, 140.3, 140.5, 141.4, 144.2, 169.7, 170.0 (several signals are overlapped); HRMS (APCI+) calcd for  $C_{27}H_{39}O_2$ : 395.2950 ( $[M+H]^+$ ), found: 395.2946.

Details on structural determination are discussed below.

**Ethyl 3,6-dibenzyl-2-phenylbenzoate and Ethyl 4,6-dibenzyl-2-phenylbenzoate (Table 2, entry**

8)



Pale yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.78 (t, *J* = 7.1 Hz, 3H, major+minor, overlapped), 3.26 (s, 3H, major), 3.79 (q, *J* = 7.1 Hz, 2H, major), 3.86 (q, *J* = 7.1 Hz, 2H, minor), 3.96 (s, 2H, minor), 4.02 (s, 2H, major), 4.08 (s, 2H, minor), 6.89 (d, *J* = 6.9 Hz, 1H, major), 7.04–7.36 (m, aromatic, major 15H, minor 17H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.4, 13.5, 38.86, 38.93, 39.1, 41.7, 60.7, 60.8, 125.8, 126.07, 126.14, 126.2, 127.2, 127.8, 128.12, 128.17, 128.30, 128.35, 128.4, 128.5, 128.8, 129.0, 129.1, 129.2, 129.7, 129.8, 130.9, 131.3, 134.8, 135.7, 137.2, 138.76, 138.85, 139.3, 140.1, 140.2, 140.4, 140.77, 140.79, 141.0, 142.5, 169.4, 169.7 (several signals are overlapped); HRMS (APCI+) calcd for C<sub>29</sub>H<sub>27</sub>O<sub>2</sub>: 407.2011 ([M+H]<sup>+</sup>), found: 407.1997.

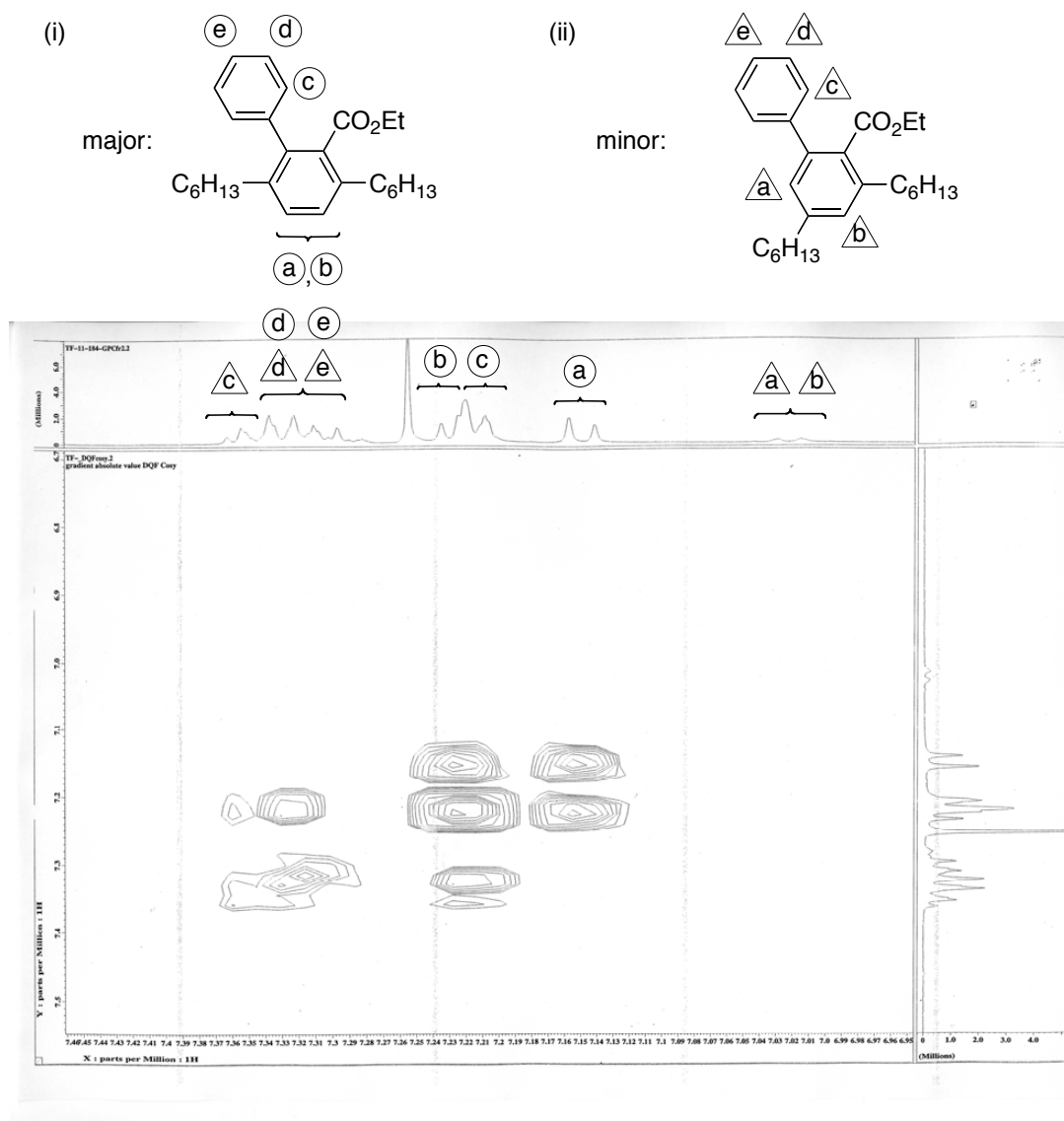
### Structural determination of ethyl dihexyl-2-phenylbenzoates (Table 2, entry 7)

<sup>1</sup>H NMR spectrum indicated that the crude product contains two isomers. The isomer ratio was determined by integration ratio of the methylene proton of the carboethoxy group (OCH<sub>2</sub>CH<sub>3</sub>) appearing about 4 ppm.

The structures of the isomers were investigated by the use of H-H DQF-COSY (Figure S1). The intense doublet signal at 7.15 ppm with a 1H intensity shows diagonal component and cross-peaks with those at 7.22–7.23 ppm, where another doublet partially overlaps with other signals. These signals due to the major isomer indicate that this compound is a 1,2,3,4-tetrasubstituted benzene and hence that the two hexyl groups are located para to each other (compound (i) in Figure S1).

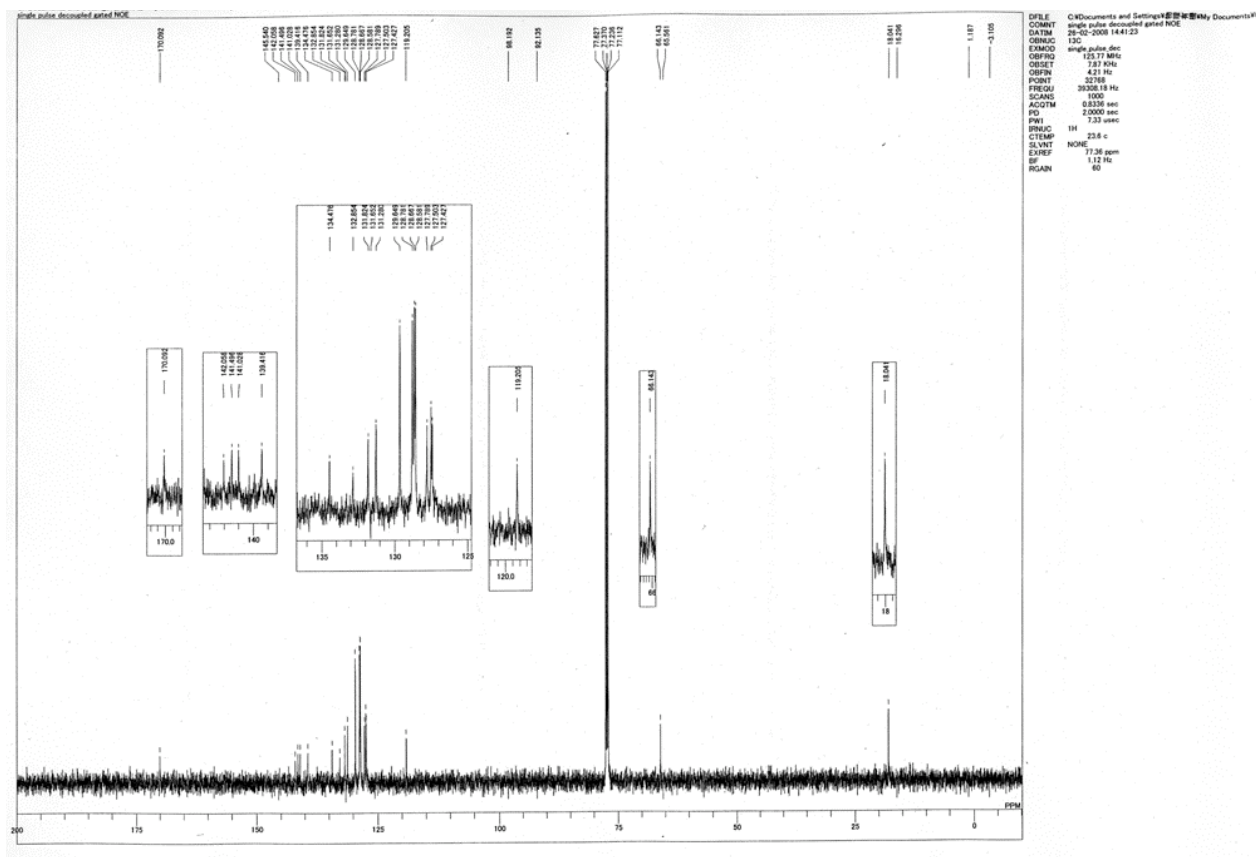
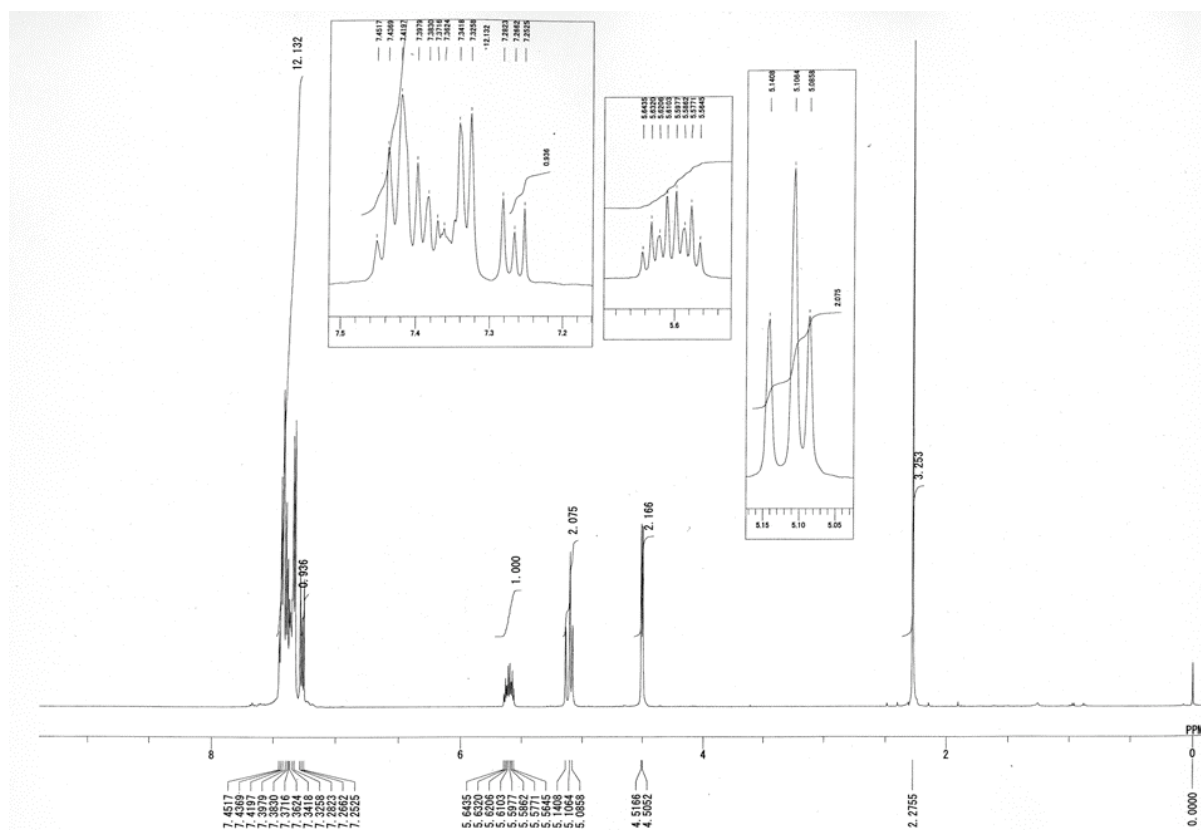
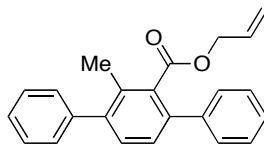
Minor signals at 7.02 and 7.03 ppm have no diagonal components and no correlation with other protons, indicating therefore that they are two singlets. These signals due to the minor isomer indicate that this compound is a meta isomer. We tentatively assigned this molecule to a meta-type, 1,2,4,6-tetrasubstituted compound (ii) as shown in Figure S1, though it is equally possible that the minor product is an alternative 1,2,3,5-isomer.



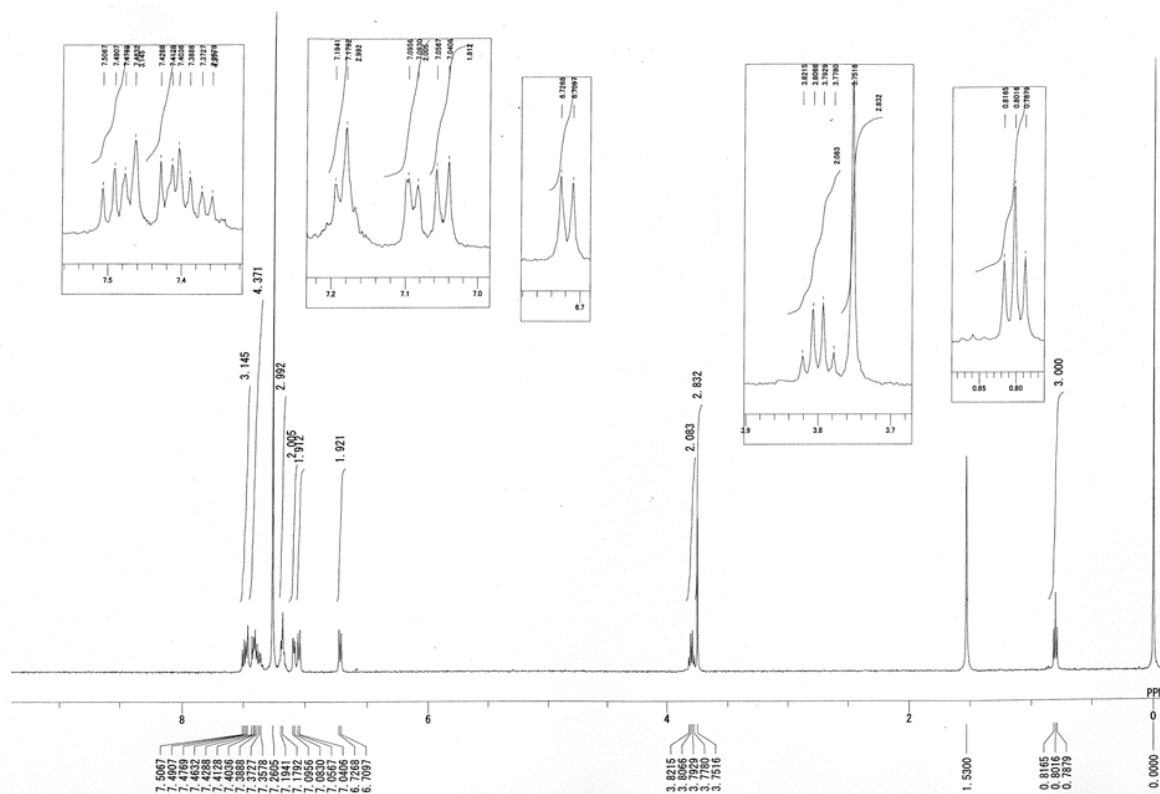
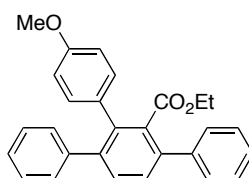


**Figure S1.** H-H DQF-COSY spectrum of a mixture of ethyl dihexyl-2-phenylbenzoates (aromatic region).

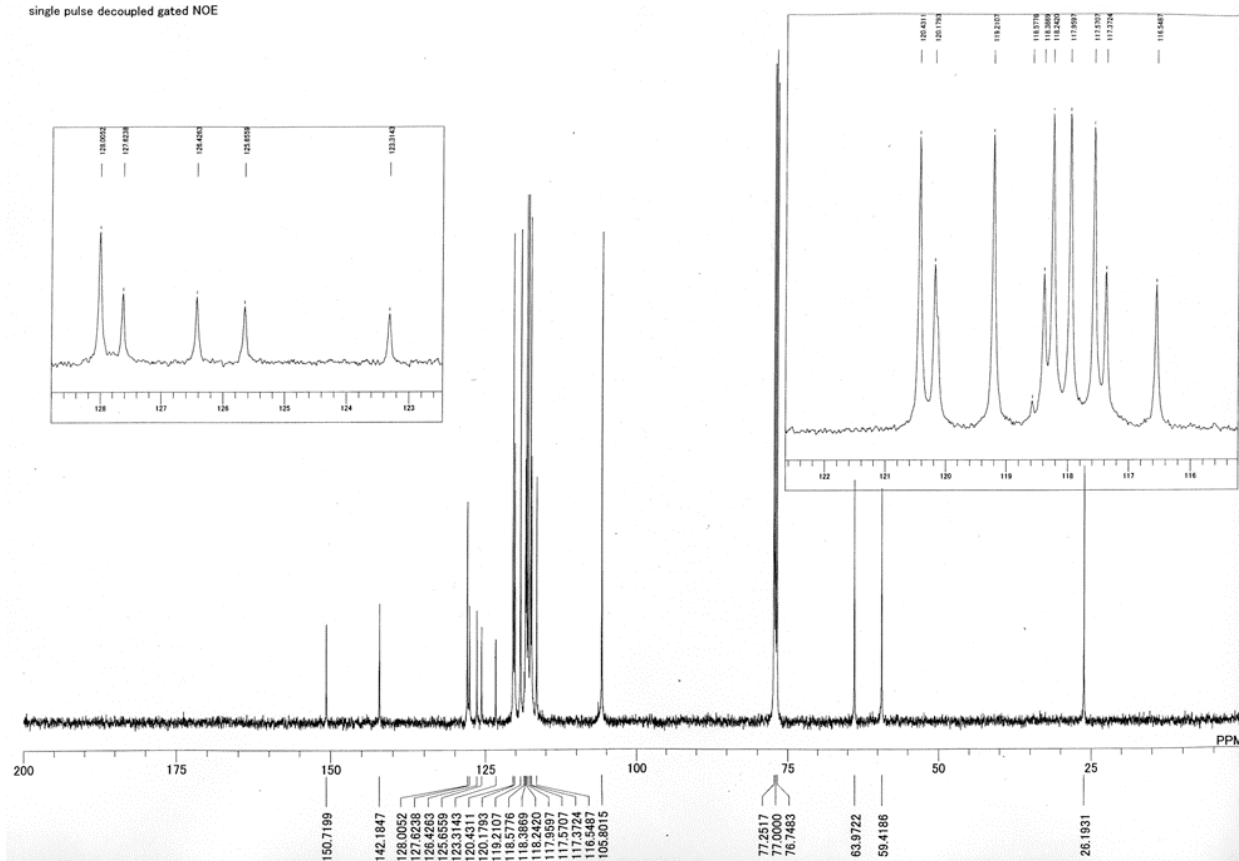
$^1\text{H}$  and  $^{13}\text{C}$  NMR Chart of 2-Propenyl 2-methyl-3,6-diphenylbenzoate (Table 1, entry 3)



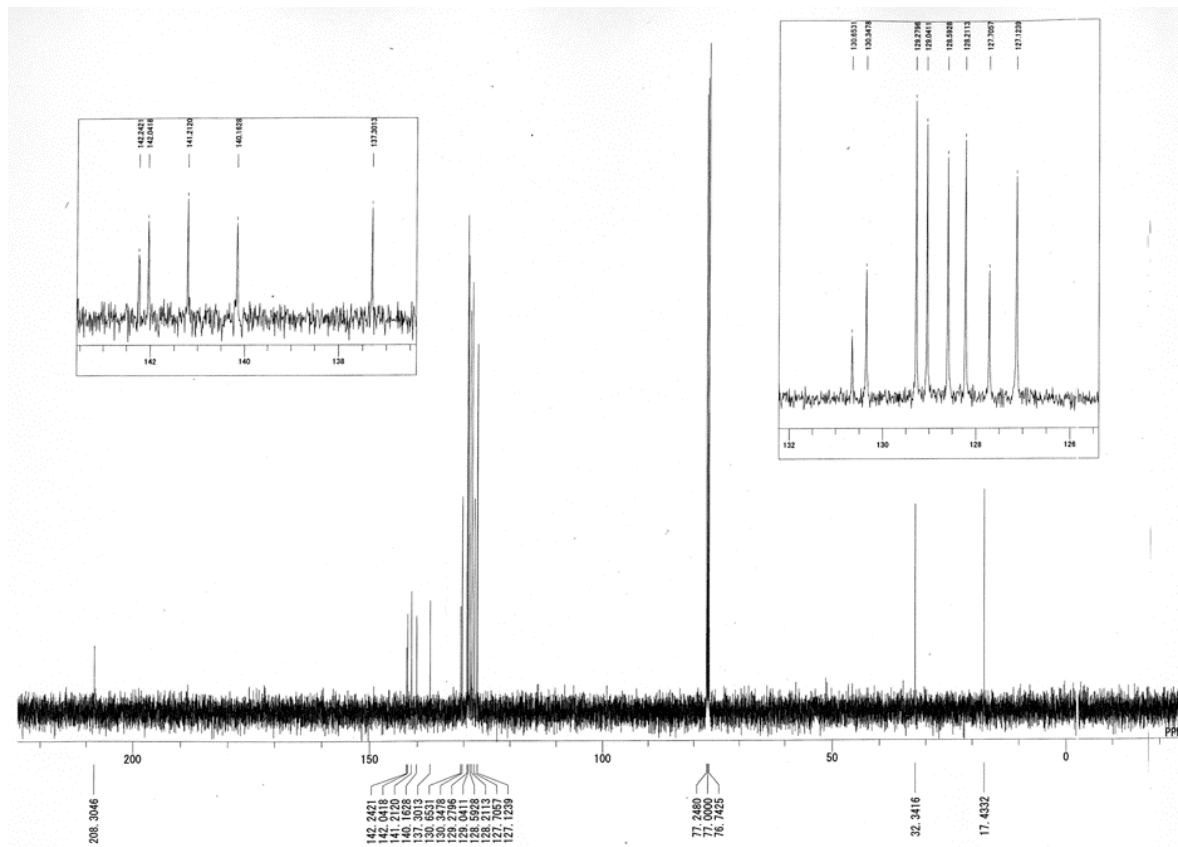
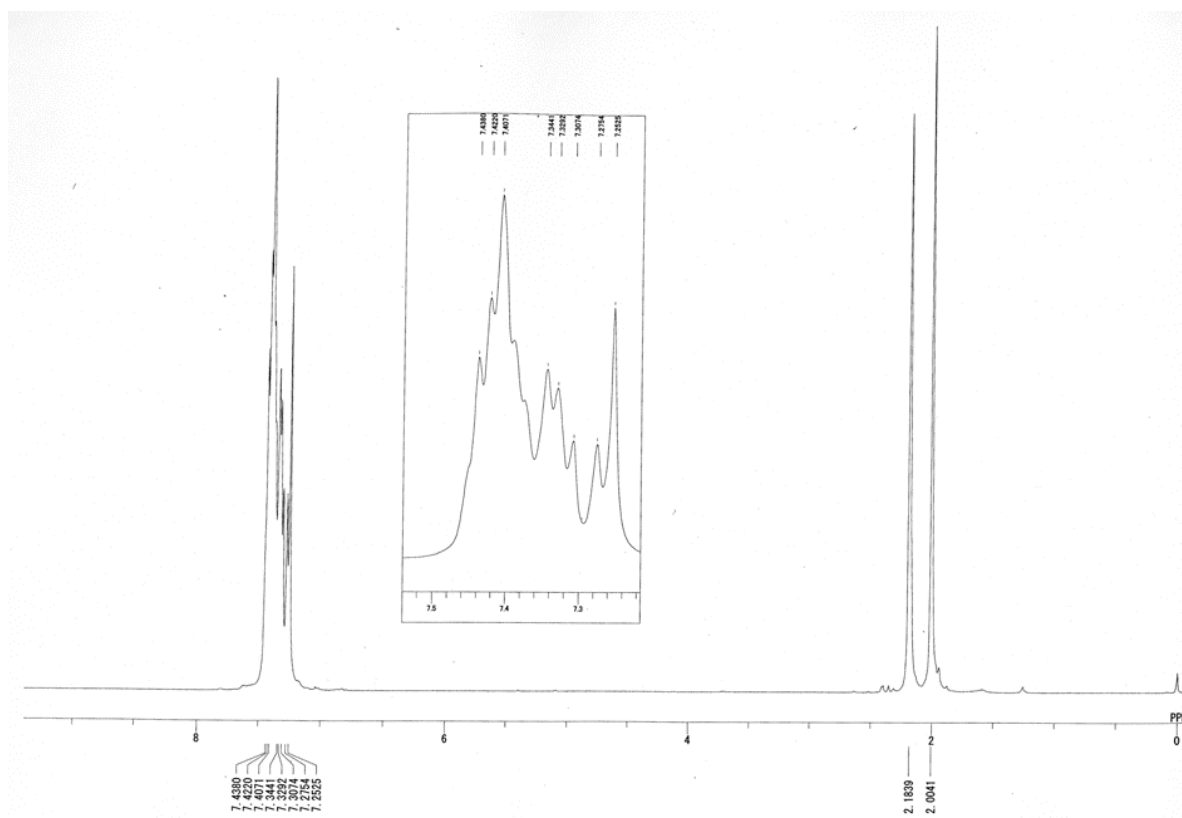
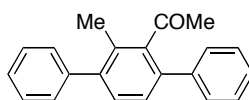
<sup>1</sup>H and <sup>13</sup>C NMR Chart of Ethyl 2-(4-methoxyphenyl)-3,6-diphenylbenzoate (Table 1, entry 7)

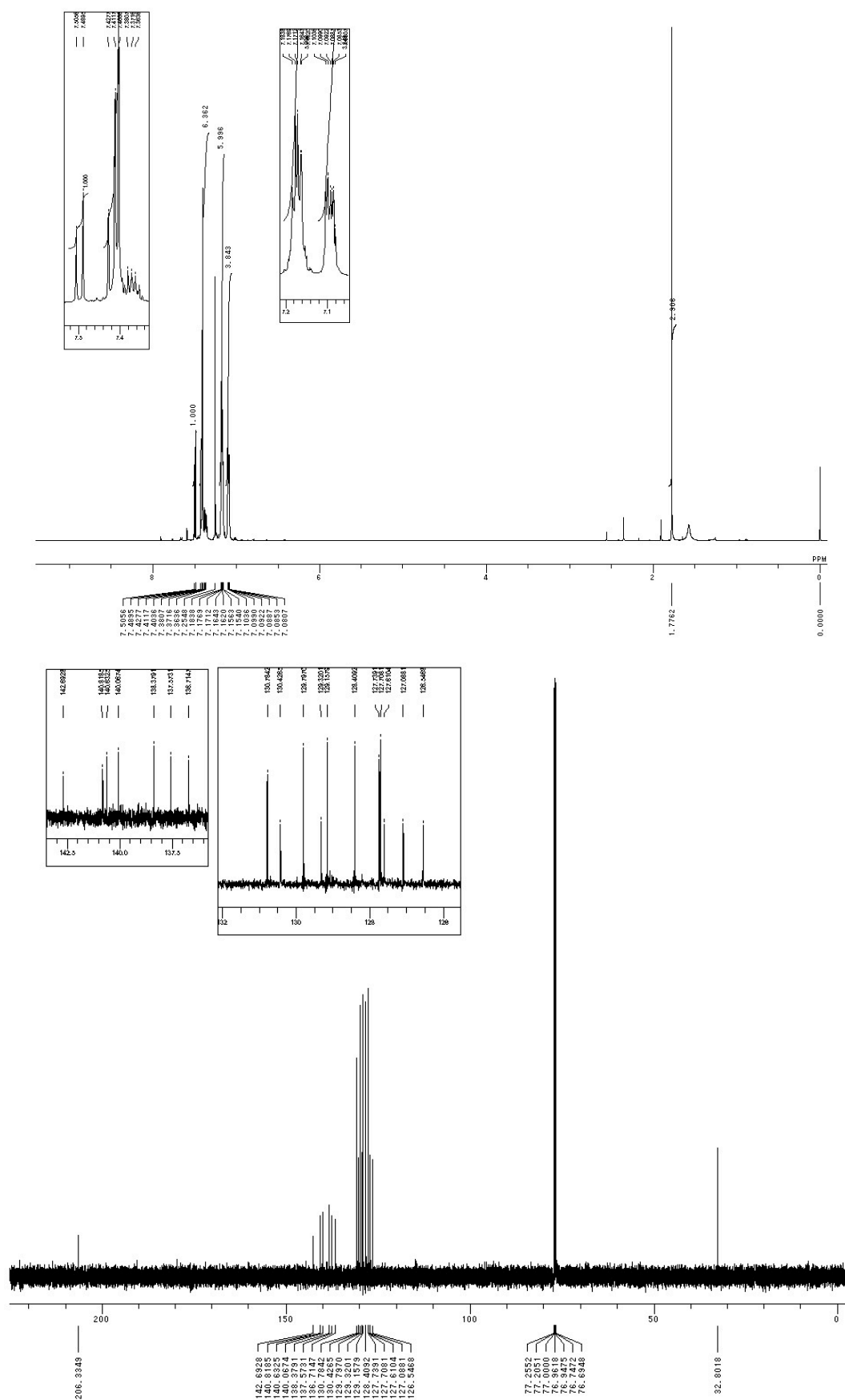


single pulse decoupled gated NOE

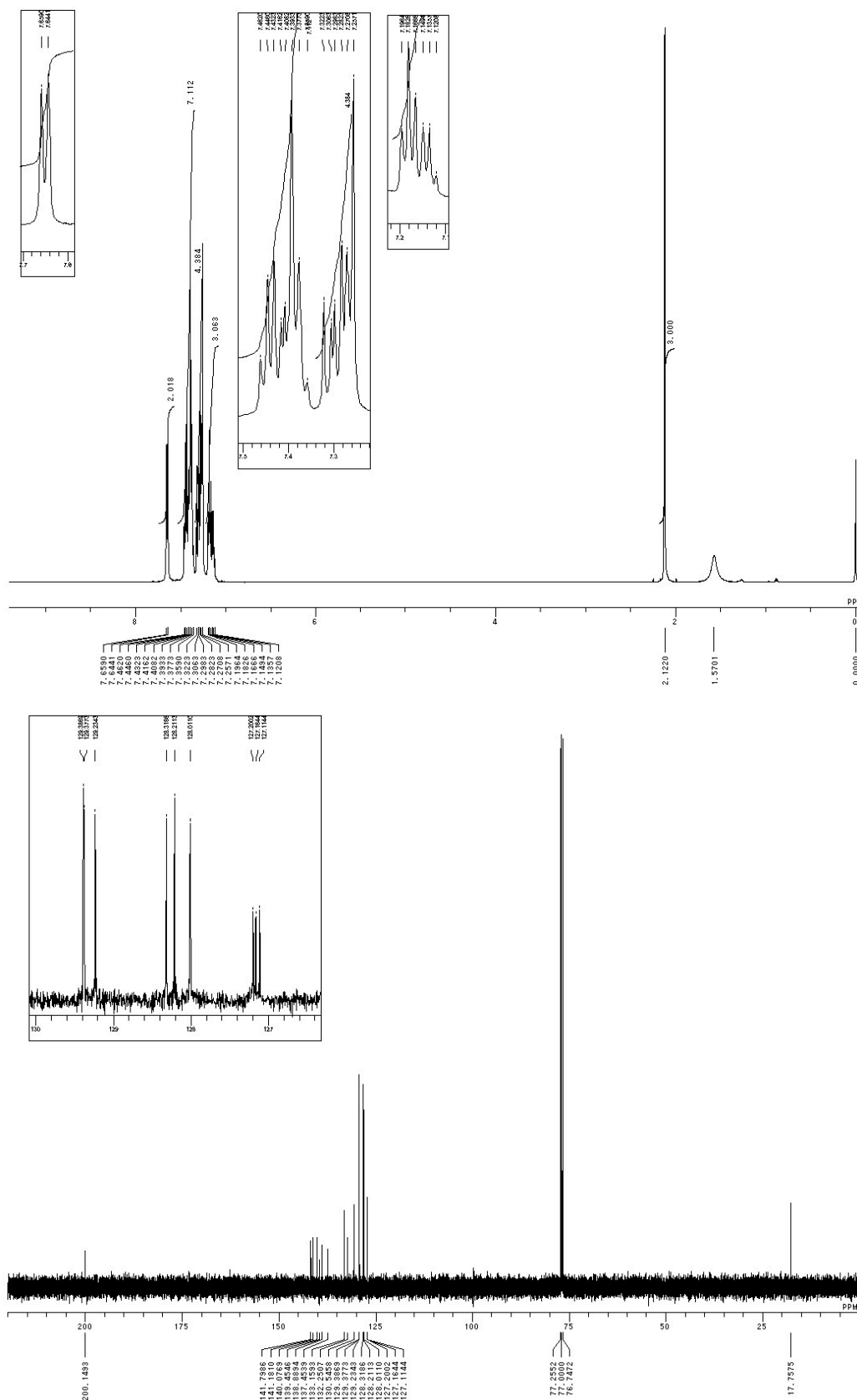
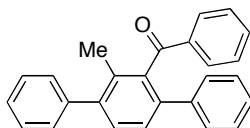


$^1\text{H}$  and  $^{13}\text{C}$  NMR Chart of 2'-Ethanoyl-3'-methyl-1,1':4',1''-terphenyl (Table 1, entry 9)

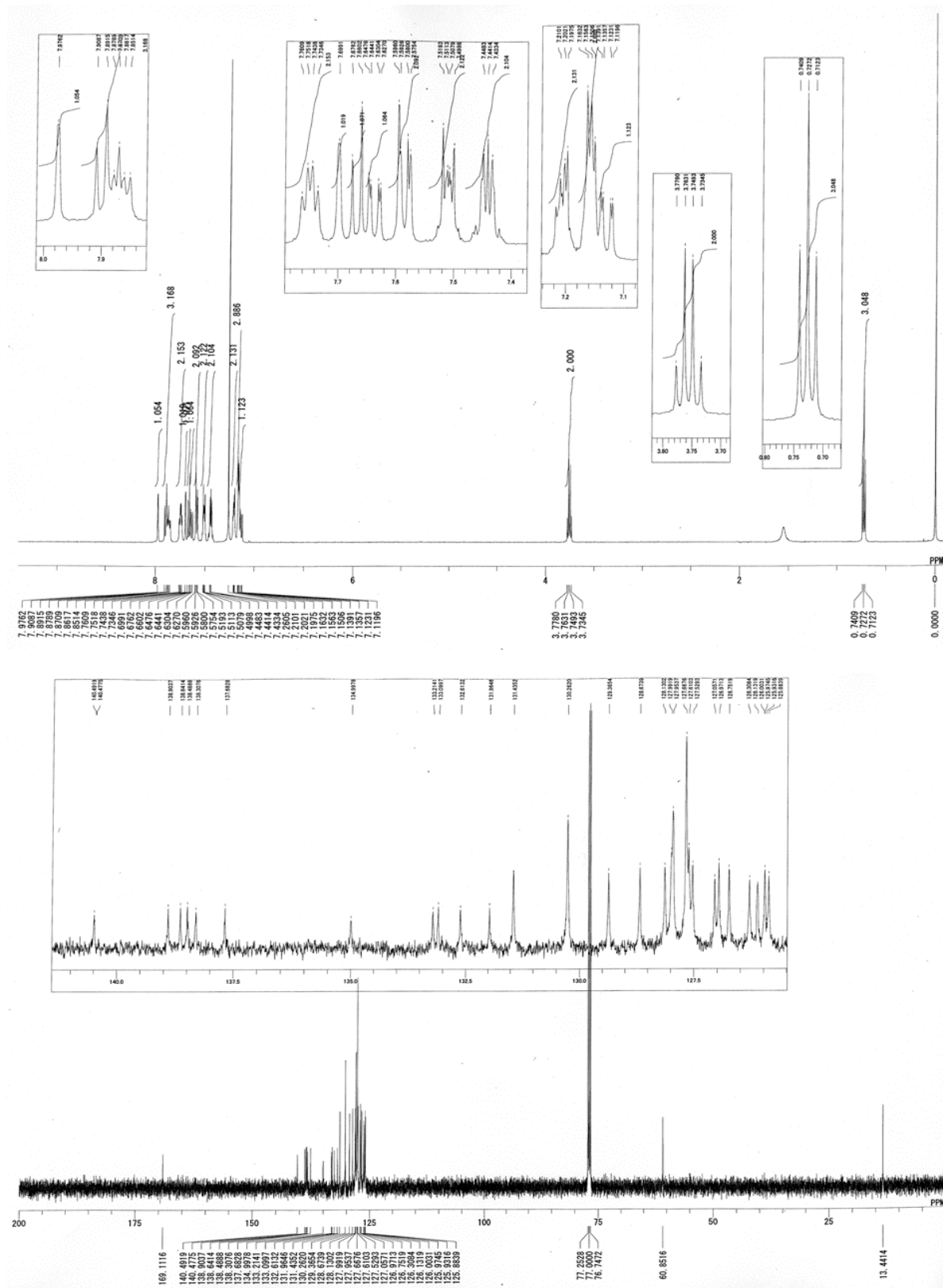
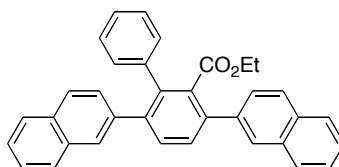




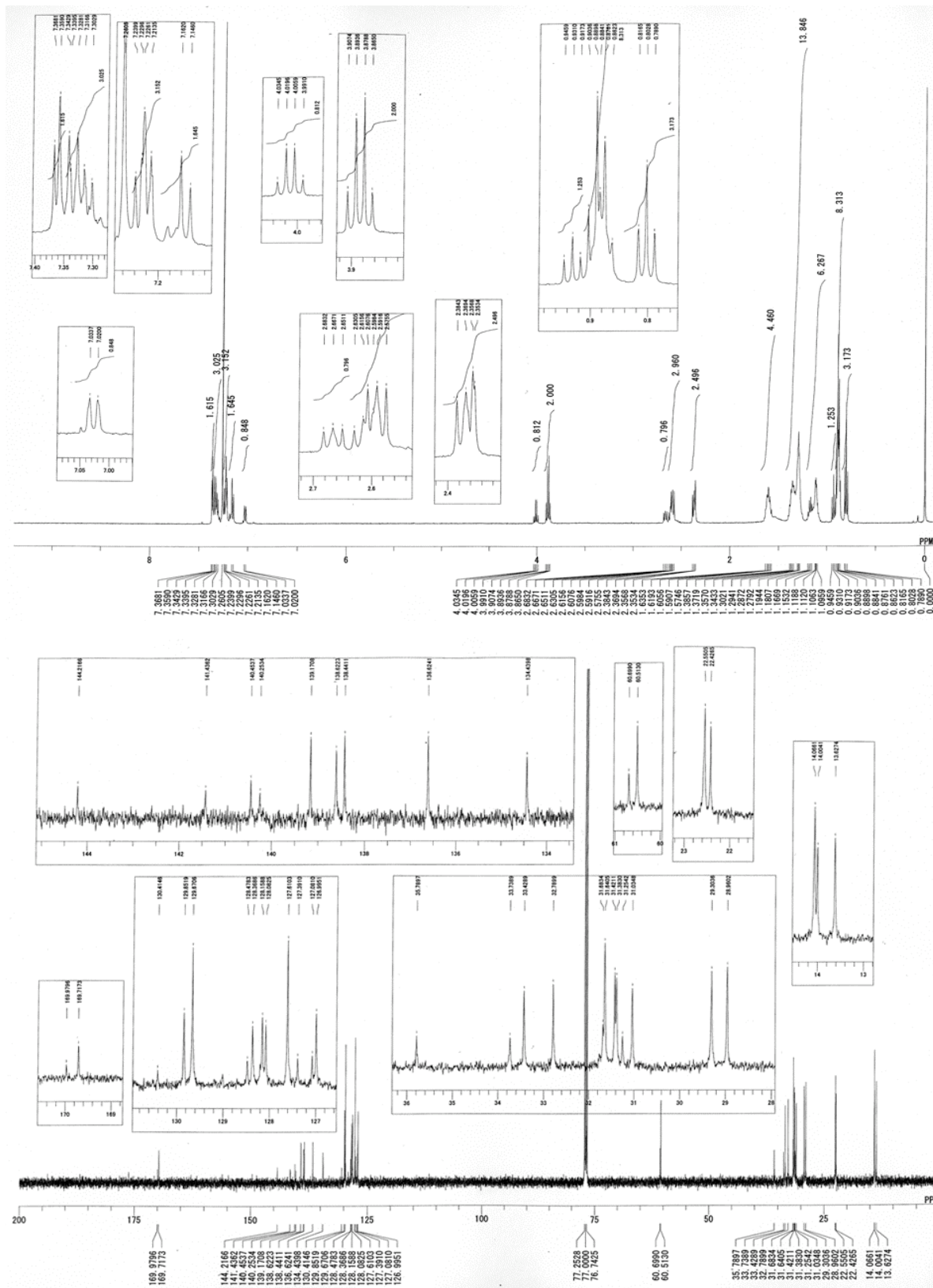
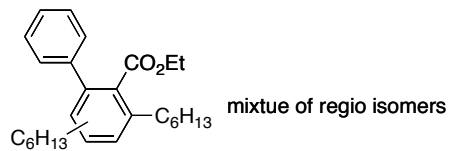
$^1\text{H}$  and  $^{13}\text{C}$  NMR Chart of 2'-Benzoyl-3'-methyl-1,1':4',1''-terphenyl (Table 1, entry 10)



<sup>1</sup>H and <sup>13</sup>C NMR Chart of Ethyl 2-phenyl-3,6-di(2-naphthyl)benzoate (Table 2, entry 4)



<sup>1</sup>H and <sup>13</sup>C NMR Chart of Ethyl 3,6-dihexyl-2-phenylbenzoate and Ethyl 3,5-dihexyl-2-phenylbenzoate (Table 2, entry 7)





<sup>1</sup>H and <sup>13</sup>C NMR Chart of Ethyl 3,6-dibenzyl-2-phenylbenzoate and Ethyl 4,6-dibenzyl-2-phenylbenzoate (Table 2, entry 8)

