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Radical Carboxylation: Ester Synthesis from Alkyl Iodides, Carbon Monoxide, and Alcohols under Irradiation Conditions

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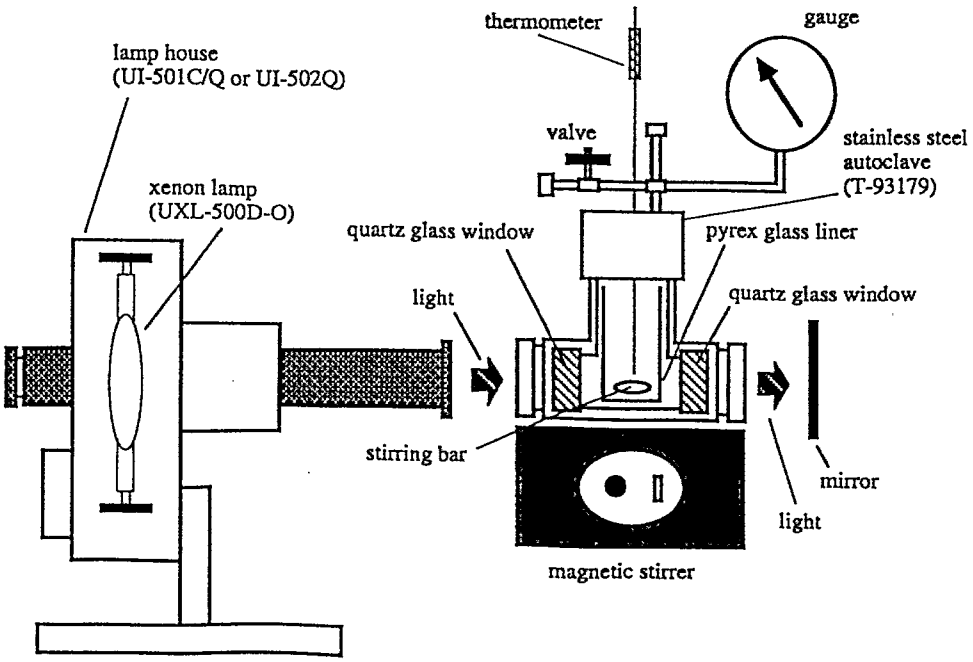
Supporting Information

Typical Experimental Procedure and Characterization Data for Products 3.

^{1}H NMR spectra were recorded with a JEOL JNM-GX67S (270 MHz) spectrometer and a JEOL JNM-Alice 400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal TMS. ^{13}C NMR spectra were recorded with a JEOL JNM-GX67S (68MHz) spectrometer and a JEOL JNM-Alice 400 (100MHz) spectrometer. Infrared spectra were recorded with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC yields were assayed with a Shimadzu GC-14A gas chromatograph equipped with Supelco fused silica capillary Column SPB-5. Photolyses were carried out using a stainless autoclave with quartz glass windows lined with a 10 mmϕ Pyrex glass liner (Taiatsu Techno Corp., T-93179) and using a 500-W xenon short arc lamp (Ushio Co., LTD., lamp house, UI-501C/Q or UI-502Q; xenon short arc lamp, UXL-500D-O; power supply, XB-50101AA-A; starter, XS-50102AA-A). The products were purified by flash chromatography on silica gel (Fuji Silysia BW-820MH, 70-200 mesh) and, if necessary, were further purified by recycling preparative HPLC (JAI LC-908) equipped with GPC columns using $CHCl_3$ as an eluant.



Phenylmethyl 2-Methyloctanoate (3b). General Procedure. Magnetic stirring bar, anhydrous K_2CO_3 (265 mg), hexane (0.5 mL), 2-iodooctane (**1a**) (243 mg, 1 mmol), and benzyl alcohol (**2a**) (152 mg, 1.4 mmol) were placed in a stainless steel autoclave for photo-reaction equipped with an inserted pyrex glass liner. The autoclave was then pressurized with 30 atm of CO and was irradiated by a xenon arc lamp (500 W), with stirring, for 12 h. Excess CO was discharged. Salts were filtered, and the filtrate was chromatographed on silica gel (0%, 3%, 10% ether/hexane eluent). The 3% ether/hexane eluent contained **3b** (219 mg, 87%). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.87 (t, 3 H, J = 7.08 Hz), 1.16 (d, 3 H, J = 7.08 Hz), 1.25 (br. s, 8 H), 1.38-1.45 (m, 1 H), 1.64-1.69 (m, 1 H), 2.48 (sextet, 1 H, J = 7.08 Hz), 5.12 (s, 2 H), 7.31-7.36 (m, 5 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 14.03, 17.01, 22.54, 27.11, 29.13, 31.65, 33.79, 39.52, 65.91, 128.02, 128.05, 128.48, 136.26, 176.72; IR(neat) 2857, 1736, 1498, 1456, 1381, 1352, 1166, 1142, 750, 697 cm^{-1}; EIMS (relative intensity) m/z 248 (M^+, 10), 175 (3), 164 (20), 157 (14), 141 (15), 113 (11), 108 (19), 91 (100), 83 (6), 71 (32), 65 (6), 57 (33), 43 (17), 29 (4); HRMS (EI) calcd for $C_{16}H_{24}O_2$: m/z 248.1776, found: 248.1767.

Ethyl 2-Methyloctanoate (3a). By the method described for **3b**. (**1a**: 238 mg (1.0 mmol), EtOH: 140 mg (3.0 mmol), K_2CO_3: 286 mg (2.1 mmol), hexane: 0.5 mL, CO: 20 atm, 15 h); yield 72%: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3 H, J = 6.84 Hz), 1.13 (d, 3 H, J = 6.84 Hz), 1.25 (t, 3 H, J = 7.08 Hz), 1.24-1.35 (m, 8 H), 1.37-1.43 (m, 1 H), 1.62-1.69 (m, 1 H), 2.41 (sextet, 1 H, J = 6.84 Hz), 4.13 (q, 2 H, J = 7.08 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.22, 14.45, 17.24, 22.74, 27.31, 29.31, 31.83, 33.95, 39.68, 60.09, 176.69; IR(neat) 2958, 2931, 2858, 1736, 1464, 1378, 1255, 1177, 1148, 1096 cm^{-1}. This compound is already known and the properties (^{1}H-NMR, ^{13}C-NMR, IR) were consistent with those previously reported, see: Vörde, C.; Högberg, H.-E.; Hedenström, E *Tetrahedron Asymmetry*, **1996**, *7*, 1507.

Ethyl 2-Butylhexanoate (3c). By the similar method described for **3b** except for using EtOH both as a solvent and an alcohol. (**1b**: 279 mg (1.1 mmol), K_2CO_3: 293 mg (2.1 mmol), EtOH: 0.5

mL, CO: 40 atm, 16 h); yield 73%: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 6 H, J = 6.84 Hz), 1.26 (t, 3 H, J = 7.08 Hz), 1.20-1.37 (m, 8 H), 1.41-1.48 (m, 2 H), 1.55-1.64 (m, 2 H), 2.30 (tt, 1 H, J = 8.91, 5.37 Hz), 4.14 (q, 2 H, J = 7.08 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11, 14.52, 22.78, 29.76, 32.33, 45.81, 59.96, 176.34; IR(neat) 2958, 2934, 2860, 1736, 1467, 1378, 1176, 1034, 734 cm^{-1}; EIMS (relative intensity) m/z 200 (M^+, 1), 171 (2), 157 (11), 144 (76), 127 (9), 115 (30), 101 (100), 98 (2), 85 (9), 73 (25), 57 (15), 43 (19), 29 (11); HRMS (EI) calcd for $C_{12}H_{24}O_2$: m/z 200.1776, found: 200.1789.

3-Methylbutyl 2-Butylhexanoate (3d). By the method described for **3b** except for using KOH as a base. (**1b**: 245mg (1.0 mmol), **2b**: 181 mg (2.1 mmol), KOH: 133 mg (2.4 mmol), hexane: 0.5 mL, CO: 20 atm, 18 h); NMR yield 79%: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, 6 H, J = 7.00 Hz), 0.93 (d, 6 H, J = 6.59 Hz), 1.20-1.37 (m, 8 H), 1.39-1.68 (m, 4 H), 1.52 (q, 2 H, J = 6.84 Hz), 1.62-1.75 (m, 1 H), 2.31 (tt, 1 H, J = 8.91, 5.37 Hz), 4.11 (t, 2 H, J = 6.84 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 13.89 (q), 22.39 (q), 22.60 (t), 25.05 (d), 29.63 (t), 32.22 (t), 37.44 (t), 45.78 (d), 62.59 (t), 176.66 (s); IR(neat) 2958, 2872, 1736, 1467, 1369, 1167, 1143 cm^{-1}; EIMS (relative intensity) m/z 242 (M^+, 1), 227 (1), 199 (3), 186 (16), 173 (37), 155 (19), 143 (11), 127 (13), 116 (23), 98 (2), 85 (13), 70 (100), 55 (16), 43 (32), 28 (6); HRMS (EI) calcd for $C_{15}H_{30}O_2$: m/z 242.2246, found: 242.2240.

Cyclohexyl 2-Butylhexanoate (3e). By the method described for **3b**. (**1b**: 254 mg (1.0 mmol), **2c**: 200 mg (2.0 mmol), K_2CO_3: 300 mg (2.2 mmol), hexane: 0.5 mL, CO: 30 atm, 12 h); yield 73%: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, 6 H, J = 6.90 Hz), 1.14-1.43 (m, 15 H), 1.48-1.60 (m, 3 H), 1.62-1.74 (m, 2 H), 1.75-1.84 (m, 2 H), 2.21-2.28 (m, 1 H), 4.73-4.77 (m, 1 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 13.90, 22.58, 23.66, 25.40, 29.55, 31.64, 32.26, 45.86, 71.83, 175.98; IR(neat) 2936, 2860, 1731, 1467, 1454, 1380, 1363, 12858, 1218, 1174, 1145, 1123, 1104, 1040, 1019 cm^{-1}; EIMS (relative intensity) m/z 255 (M^++1, 0.2), 198 (10), 173 (100), 155 (9), 127 (13), 116 (51), 99 (3), 83 (35), 71 (21), 67 (10), 55 (23), 43 (14), 29 (4);

HRMS (EI) calcd for $C_{16}H_{30}O_2$: m/z 254.2245, found: 254.2239. Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.88. Found: C, 75.61; H, 11.92.

3-Methylbutyl 2-Methyl-3-phenylpropanoate (3f). By the method described for **3b**. (**1c**: 251 mg (1.0 mmol), **2b**: 175 mg (2.0 mmol), K_2CO_3: 276 mg (2.0 mmol), hexane: 0.5 mL, CO: 55 atm, 33 h); yield 60%: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, 3 H, J = 6.59 Hz), 0.89 (d, 3 H, J = 6.59 Hz), 1.15 (d, 3 H, J = 6.59 Hz), 1.44 (q, 2 H, J = 6.84 Hz), 1.55-1.63 (m, 1 H), 2.63-2.76 (m, 2 H), 3.01 (dd, 1 H, J = 12.70, 6.35 Hz), 4.06 (t, 2 H, J = 6.84 Hz), 7.15-7.21 (m, 3 H), 7.25-7.29 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 16.82, 22.40, 24.95, 37.27, 39.74, 41.53, 62.95, 126.24, 128.29, 128.94, 139.41, 176.17; IR(neat) 2958, 2872, 1735, 1496, 1454, 1368, 1281, 1250, 1201, 1166, 1118, 744, 700 cm^{-1}; EIMS (relative intensity) m/z 234 (M^+, 19), 164 (17), 147 (9), 118 (53), 107 (8), 91 (100), 78 (3), 71 (33), 65 (5), 55 (5), 43 (29), 29 (2); HRMS (EI) calcd for $C_{15}H_{22}O_2$: m/z 234.1620, found: 234.1612. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.88; H, 9.54.

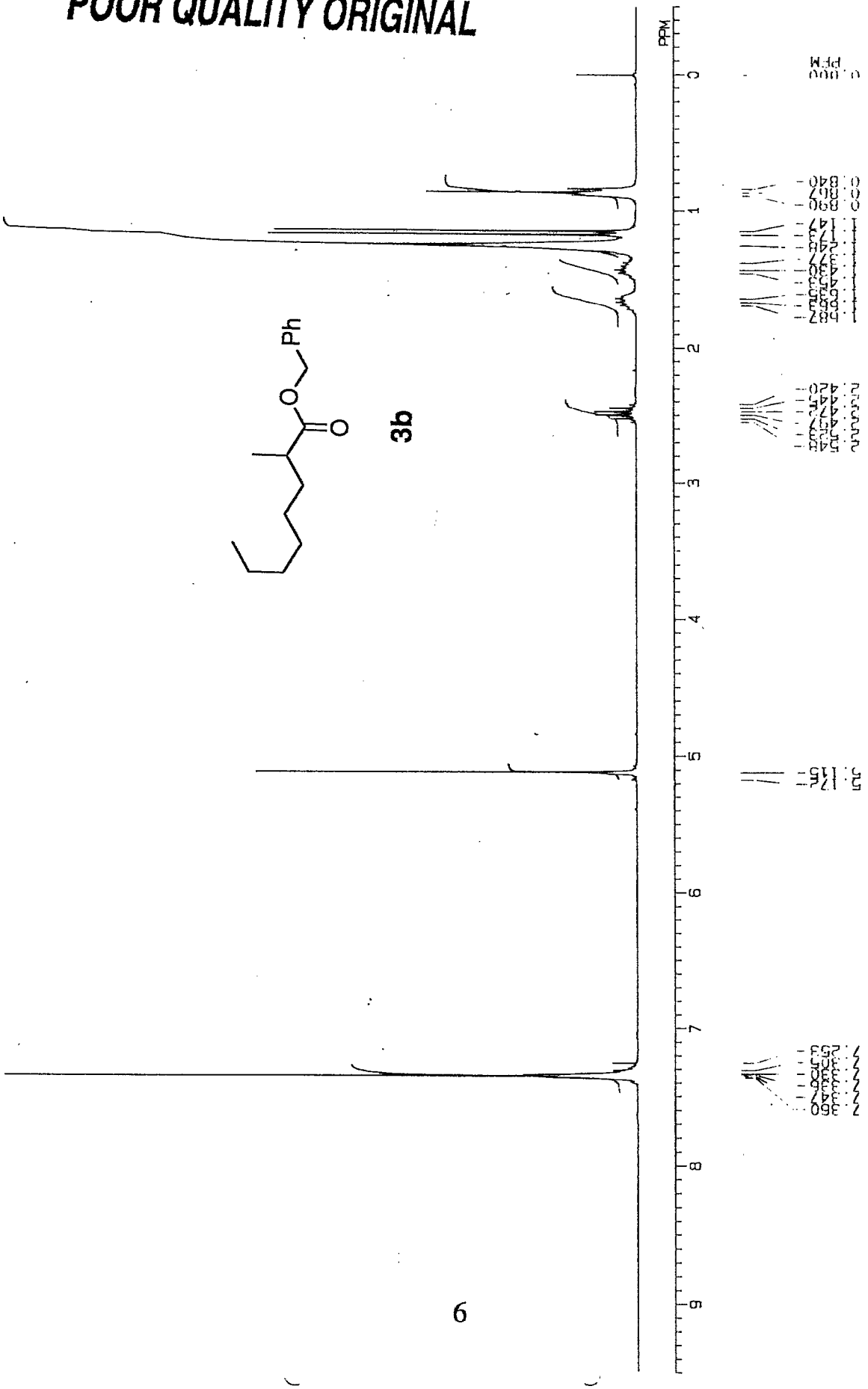
6-Chlorohexyl Cyclohexanecarboxylate (3g). By the method described for **3b**. (**1d**: 206 mg (1.0 mmol), **2d**: 190 mg (1.4 mmol), K_2CO_3: 279 mg (2.0 mmol), hexane: 0.5 mL, CO: 20 atm, 24 h); yield 67% (91% conversion): ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.23-1.53 (m, 9H), 1.64 (quint, 2 H, J = 6.90 Hz), 1.72-1.84 (m, 5 H), 1.86-1.92 (m, 2 H), 2.29 (tt, 1 H, J = 11.11, 3.66 Hz), 3.53 (t, 2 H, J = 6.60 Hz), 4.06 (t, 2 H, J = 6.47 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 25.56, 25.73, 26.06, 26.79, 28.81, 29.32, 32.73, 43.53, 45.18, 64.21, 176.45; IR(neat) 2934, 2857, 1732, 1452, 1312, 1247, 1170, 1133, 1039, 730, 651 cm^{-1}; EIMS (relative intensity) m/z 246 (M^+, 1), 191 (3), 129 (100), 118 (14), 111 (28), 83 (56), 67 (10), 55 (34), 41 (16), 29 (4); HRMS (EI) calcd for $C_{13}H_{23}O_2Cl$: m/z 246.1386, found: 246.1401.

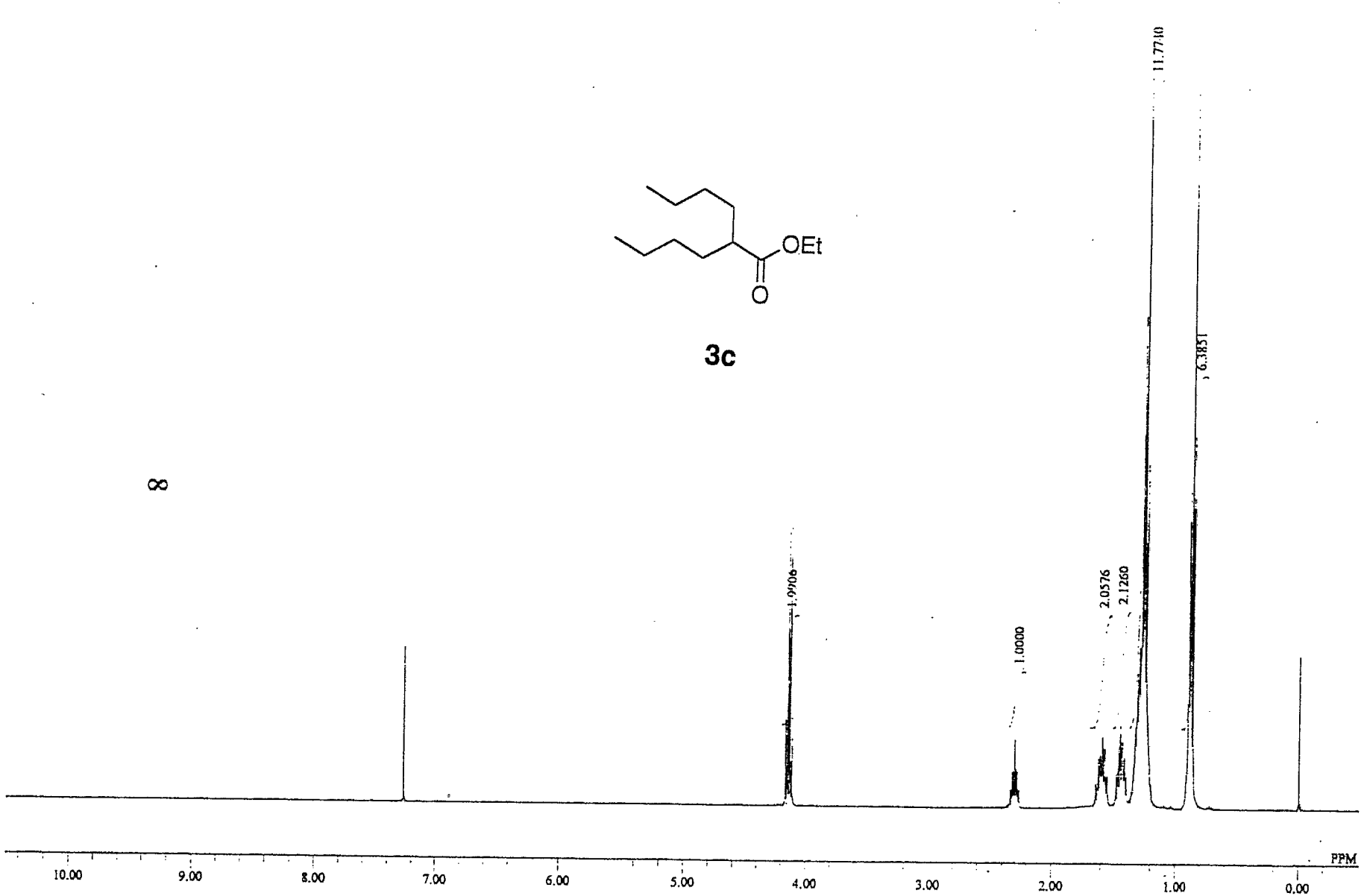
Ethyl 2-Methyl-4-(phenylthio)butanoate (3h). By the method described for **3b**. (**1e**: 292 mg (1.0 mmol), **2b**: 139 mg (3.0 mmol), K_2CO_3: 417 mg (3.0 mmol), hexane: 0.5 mL, CO: 50 atm,

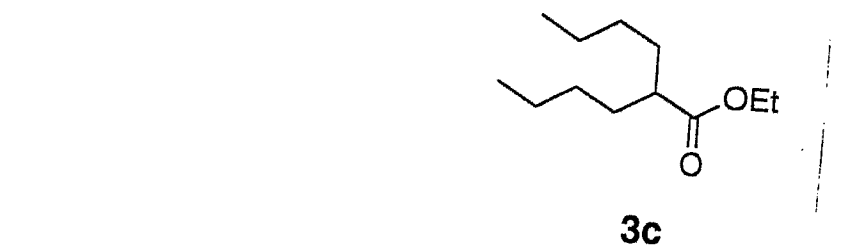
17 h); yield 59%: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, 3 H, J = 7.08 Hz), 1.24 (t, 3 H, J = 7.08 Hz), 1.68-1.77 (m, 1 H), 1.98-2.07 (m, 1 H), 2.60-2.65 (m, 1 H), 2.80-2.95 (m, 2 H), 4.13 (q, 2 H, J = 7.08 Hz), 7.15-7.40 (m, 5 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.37, 17.16, 31.39, 33.11, 38.63, 60.40, 125.78, 128.70, 129.00, 136.01, 175.60; IR(neat) 2977, 2935, 1731, 1584, 1481, 1439, 1377, 1259, 1196, 1156, 1093, 1026, 739, 691 cm^{-1}; EIMS (relative intensity) m/z 238 (M^+, 80), 193 (47), 136 (21), 129 (100), 123 (58)., 115 (7), 109 (24), 101 (79), 91 (6), 87 (11), 74 (36), 65 (10), 55 (18), 51 (7), 45 (22), 39 (5), 29 (13); HRMS (EI) calcd for $C_{13}H_{18}O_2S$: m/z 238.1028, found: 238.1023. Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.79; H, 7.55.

Ethyl Nonanoate (3i). By the method described for **3b**. (**1f**: 479 mg (2.0 mmol), K_2CO_3: 559 mg (4.0 mmol), EtOH: 1 mL, CO: 40 atm, 50 h); NMR yield 73% (74% conversion). This compound is commercially available and the ^{1}H- and ^{13}C-NMR spectra are consistent with those of the authentic sample.

3-Methylbutyl 1-Adamantanecarboxylate (3j). By the method described for **3b**. (**1g**: 257 mg (1.0 mmol), **2b**: 132 mg (1.5 mmol), K_2CO_3: 269 mg (1.9 mmol), hexane: 0.5 mL, CO: 40 atm, 18 h): For the complete separation from 1-adamantyl 3-methylbutyl ether, a byproduct of this reaction, recycling preparative HPLC was used (5 cycles in the recycle mode for separation, GPC columns using $CHCl_3$ as an eluant). Yield 68%: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.92 (d, 6 H, J = 6.60 Hz), 1.51 (q, 2 H, J = 6.83 Hz), 1.62-1.80 (m, 1 H), 1.71 (br. s, 6 H), 1.88 (d, 6 H, J = 2.93 Hz), 2.01 (br. s, 3 H), 4.07 (t, 2 H, J = 6.83 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 22.45, 25.07, 27.93, 36.50, 37.32, 38.81, 40.62, 62.66, 177.79; IR(neat) 2907, 2852, 1728, 1454, 1268, 1234, 1184, 1104, 1079 cm^{-1}; CIMS (relative intensity) m/z 251 (M^++1, 48), 235 (4), 221 (4), 209 (17), 181 (100), 163 (5), 135 (37), 93 (3), 79 (3), 70 (9); HRMS (CI) calcd for $C_{16}H_{27}O_2$ (M+H): m/z 251.2011, found: 251.2004.



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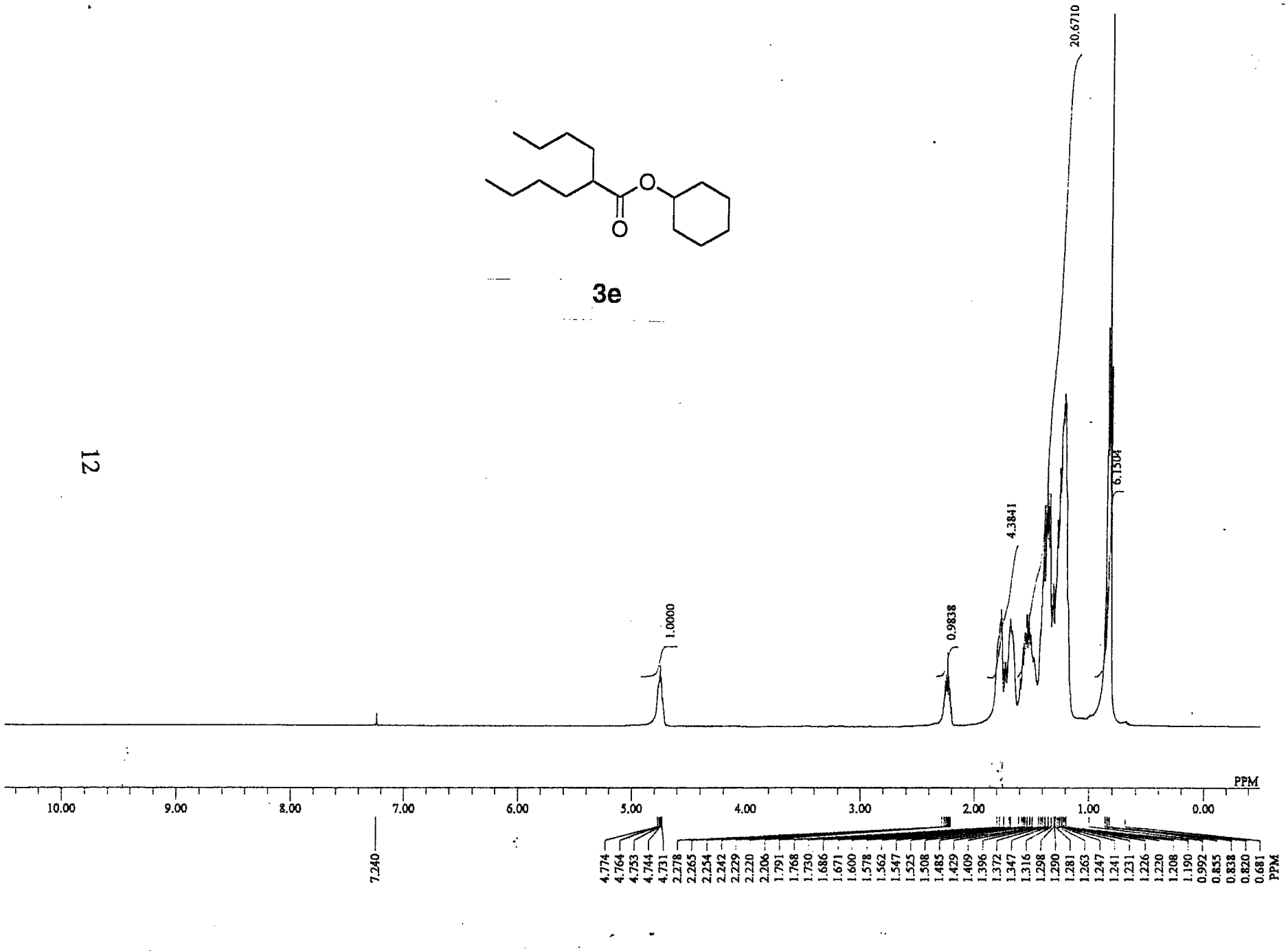
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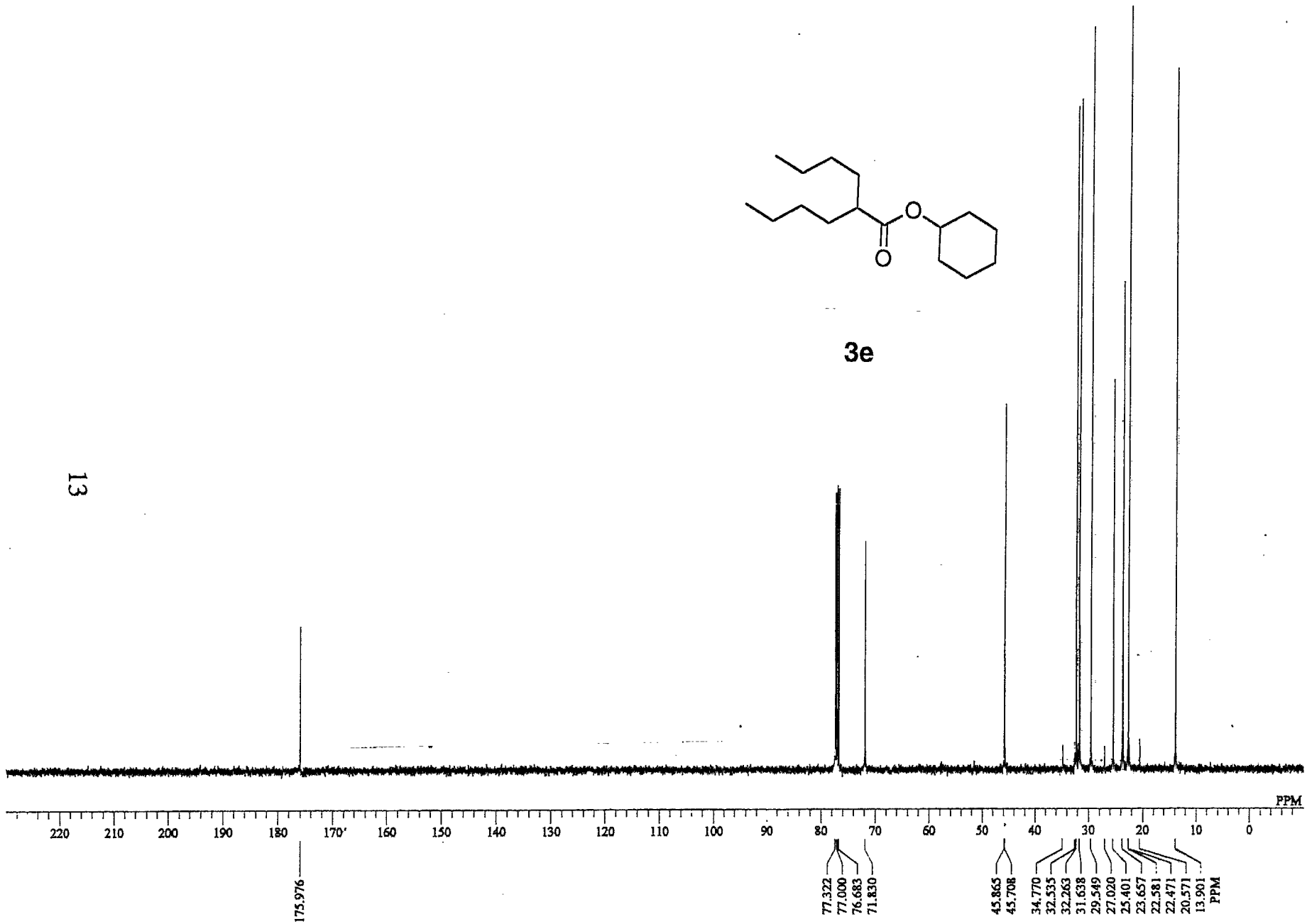
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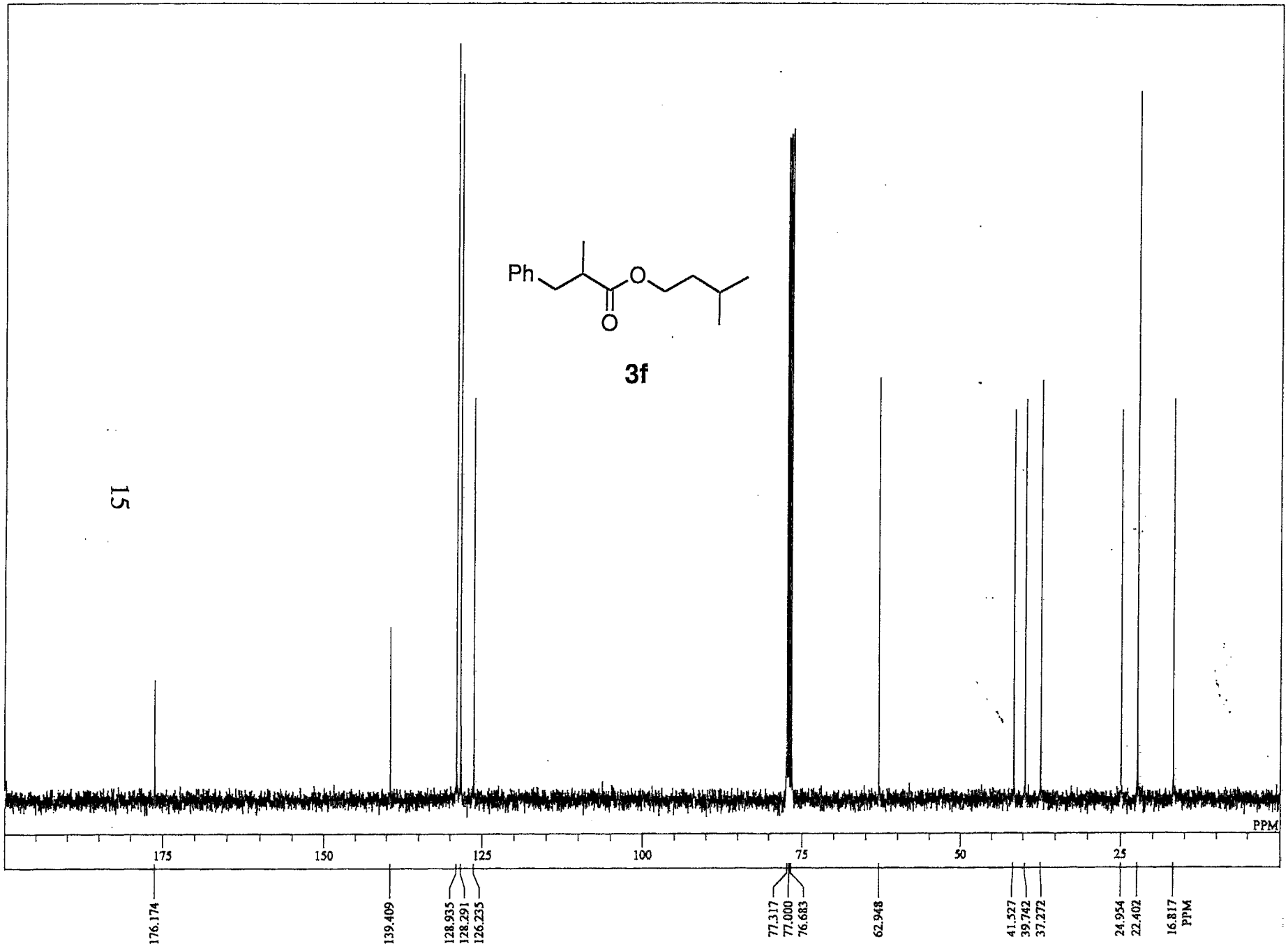
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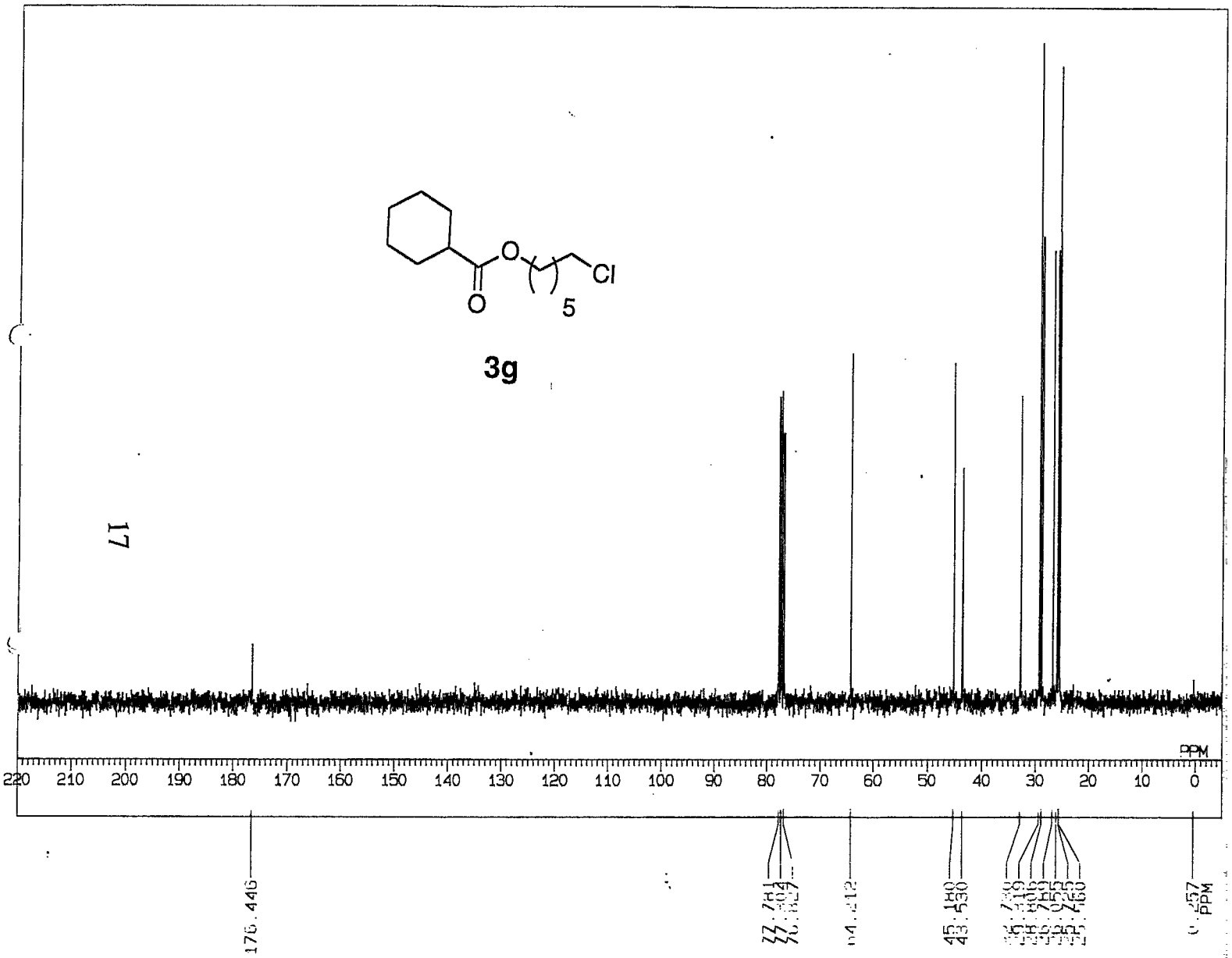

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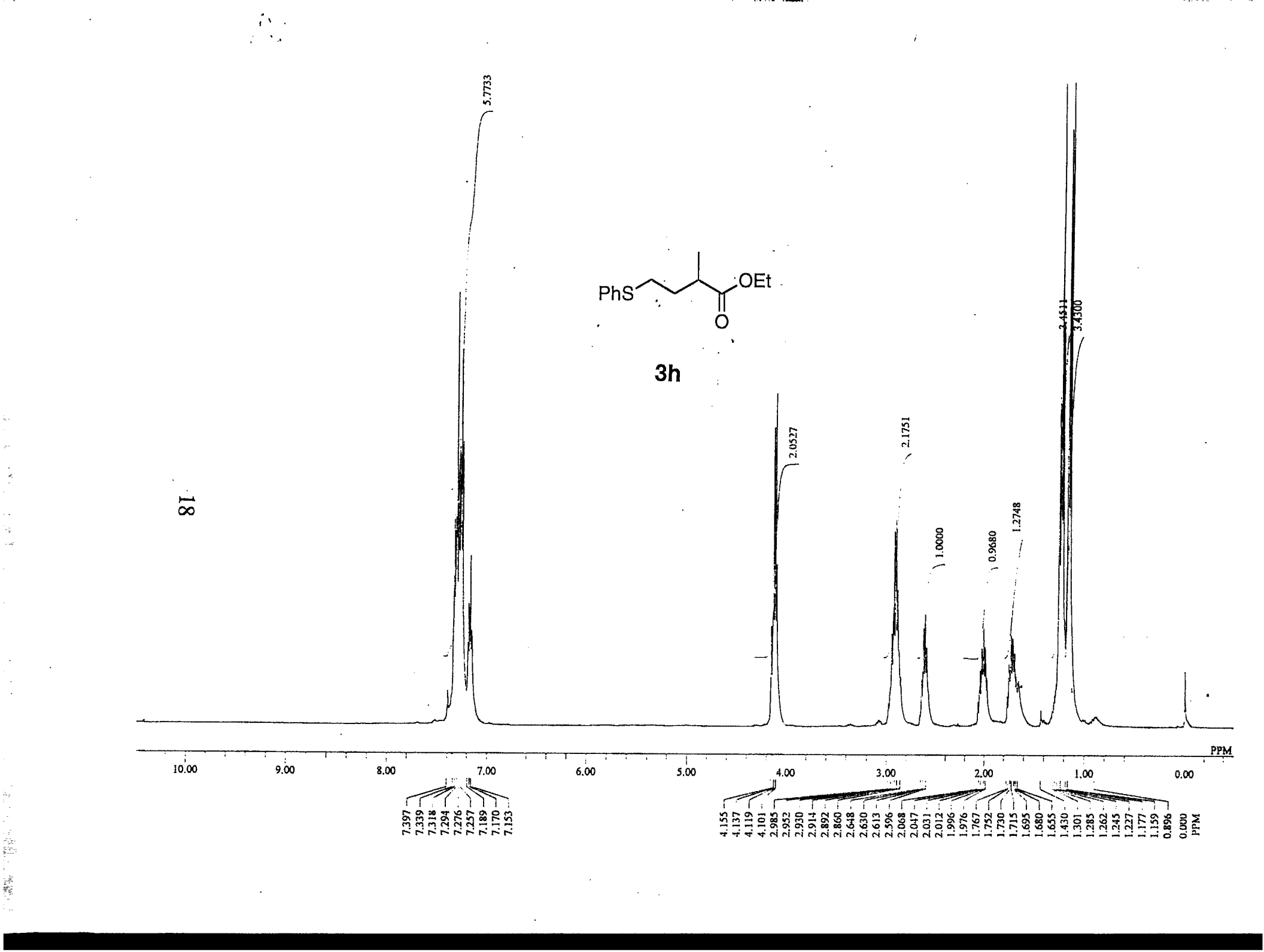
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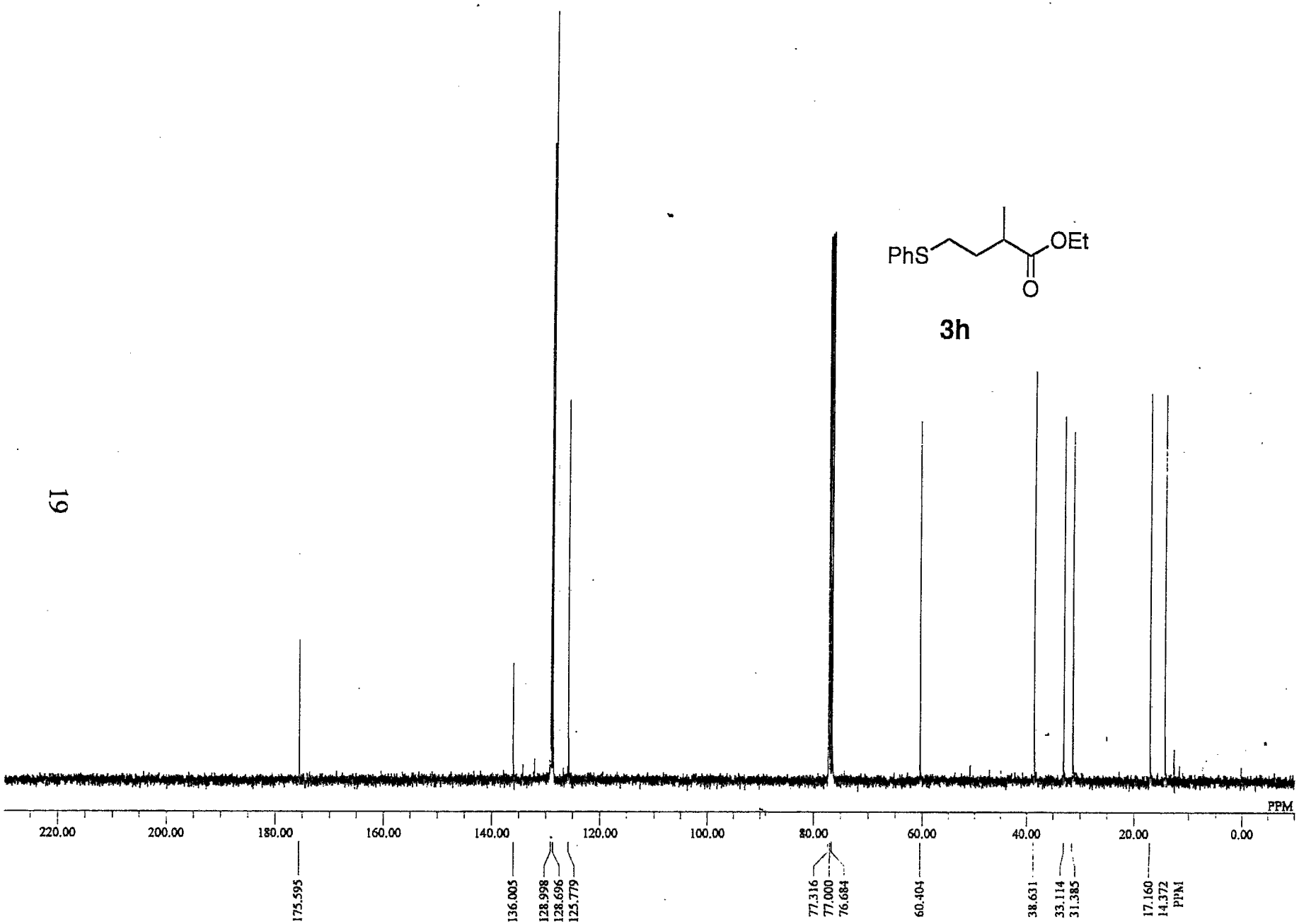
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