A Facile Approach to Ketones via Pd-Catalyzed Sequential Carbonylation of Olefins with Formic Acid

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Supporting Information

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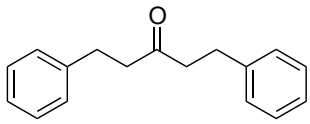
General Methods. All commercially available reagents were used without further purification. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. Olefins **1a**, **1b**, **1d-j**, **1l**, and **1n-p** were purchased from commercial suppliers. Olefins **1c**, **1k**, and **1m** were prepared from the corresponding aldehydes via Wittig reaction.[1]

1) Konishi, H.; Ueda, T.; Muto, T.; Manabe, K. *Org. Lett.* **2012**, *14*, 4722

Representative procedure for hydrocarbonylation (Table 2, 6a). To a mixture of $Pd(TFA)_2$ (0.0042 g, 0.0125 mmol), dppp (0.0103 g, 0.025 mmol), and CH_3CN (0.05 mL) in a vial (4.0 mL) were added styrene **1a** (0.1041 g, 1.00 mmol), HCOOH (0.069 g, 1.50 mmol), and Ac_2O (0.0766 g, 0.75 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 90 ^{o}C for 24 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: PE/EA = 50/1) to give ketone **6a** as a colorless oil (0.1072 g, 90% yield).

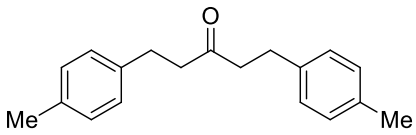
Table 2, 6a



Colorless oil; IR (film) 1713, 1492, 1452 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4H), 7.22-7.18 (m, 2H), 7.18-7.13 (m, 4H), 2.89 (t, J = 7.4 Hz, 4H), 2.71 (t, J = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 141.2, 128.7, 128.5, 126.3, 44.7, 29.9; HRMS (ESI) Calcd for $C_{17}H_{19}O$ (M+H): 239.1430; Found: 239.1427.

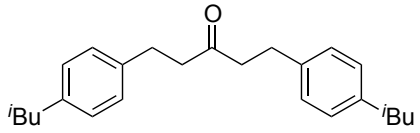
Margathe, J. F.; Shipman, M.; Smith, S. C. *Org. Lett.* **2005**, *7*, 4987

Table 2, 6b



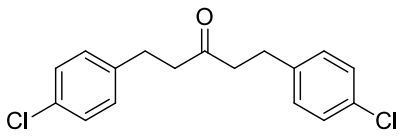
White solid; mp. 43-44 ^{o}C; IR (film) 1713, 1511 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.02 (m, 8H), 2.84 (t, J = 7.4 Hz, 4H), 2.68 (t, J = 7.4 Hz, 4H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 138.1, 135.7, 129.3, 128.4, 44.8, 29.5, 21.2; HRMS (ESI) Calcd for $C_{19}H_{23}O$ (M+H): 267.1743; Found: 267.1739.

Table 2, 6c



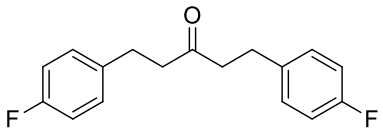
Colorless oil; IR (film) 1713, 1460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (br s, 8H), 2.88-2.82 (m, 4H), 2.72-2.65 (m, 4H), 2.43 (d, J = 7.2 Hz, 4H), 1.89-1.76 (m, 2H), 0.89 (d, J = 6.6 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 139.6, 138.4, 129.4, 128.2, 45.2, 44.9, 30.4, 29.6, 22.6; HRMS (ESI) Calcd for $C_{25}H_{34}NaO$ (M+Na): 373.2502; Found: 373.2508.

Table 2, 6d



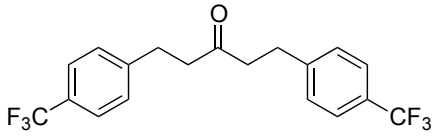
White solid; mp. 65-67 ^{o}C; IR (film) 1713, 1488 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 4H), 7.09-7.05 (m, 4H), 2.84 (t, J = 7.4 Hz, 4H), 2.67 (t, J = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 139.6, 132.1, 129.9, 128.8, 44.4, 29.1; HRMS (ESI) Calcd for $C_{17}H_{17}Cl_2O$ (M+H): 307.0651; Found: 307.0644.

Table 2, 6e



White solid; mp. 50-51 ^{o}C; IR (film) 1699, 1505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.06 (m, 4H), 6.98-6.90 (m, 4H), 2.85 (t, *J* = 7.5 Hz, 4H), 2.67 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 161.6 (d, *J* = 242.0 Hz), 136.8 (d, *J* = 4.0 Hz), 129.9 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.0 Hz), 44.7, 29.0; HRMS (ESI) Calcd for $C_{17}H_{17}F_2O$ (M+H): 275.1242; Found: 275.1239.

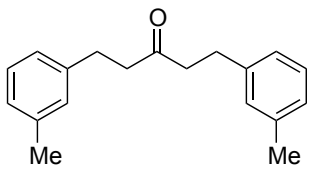
Table 2, 6f



White solid; mp. 54-56 ^{o}C; IR (film) 1702, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.94 (t, *J* = 7.4 Hz, 4H), 2.73 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 145.2, 128.9, 128.7 (q, *J* = 32.0 Hz), 125.6 (q, *J* = 4.0 Hz), 124.5 (q, *J* = 271.0 Hz), 44.1, 29.5; HRMS (ESI) Calcd for $C_{19}H_{17}F_6O$ (M+H): 375.1178; Found: 375.1171.

Levinger, S.; Sharabi-Ronen, Y.; Mainfeld, A.; Albeck, A. *J. Org. Chem.* **2008**, *73*, 7793

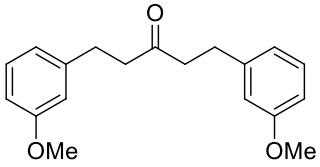
Table 2, 6g



Colorless oil; IR (film) 1716, 1609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 2H), 7.04-6.93 (m, 6H), 2.85 (t, *J* = 7.4 Hz, 4H), 2.70 (t, *J* = 7.5 Hz, 4H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 141.2, 138.3, 129.3, 128.6, 127.0, 125.5, 44.7, 29.9, 21.6; HRMS (ESI) Calcd for $C_{19}H_{23}O$ (M+H): 267.1743;

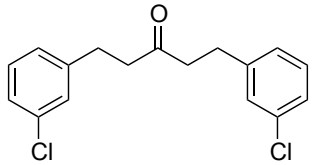
Found: 267.1738.

Table 2, 6h



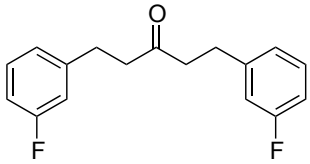
Colorless oil; IR (film) 1711, 1598 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 2H), 6.77-6.69 (m, 6H), 3.79 (s, 6H), 2.87 (t, *J* = 7.3 Hz, 4H), 2.71 (t, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 159.9, 142.8, 129.7, 120.8, 114.3, 111.6, 55.3, 44.6, 30.0; HRMS (ESI) Calcd for $C_{19}H_{23}O_3$ (M+H): 299.1642; Found: 299.1647.

Table 2, 6i



Colorless oil; IR (film) 1716, 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.13 (m, 6H), 7.03 (dt, *J* = 6.8 1,8 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 4H), 2.70 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 143.2, 134.4, 130.0, 128.7, 126.8, 126.6, 44.3, 29.4; HRMS (ESI) Calcd for $C_{17}H_{16}Cl_2NaO$ (M+Na): 329.0470; Found: 329.0471.

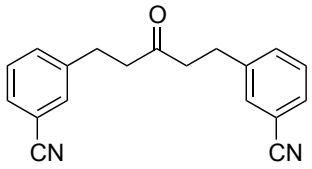
Table 2, 6j



Colorless oil; IR (film) 1713, 1584 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 2H), 6.96-6.82 (m, 6H), 2.89 (t, *J* = 7.4 Hz, 4H), 2.71 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 162.9 (d, *J* = 244.0 Hz), 143.5 (d, *J* = 7.0 Hz),

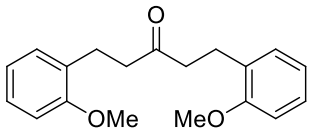
129.9 (d, J = 8.0 Hz), 124.0 (d, J = 3.0 Hz), 115.2 (d, J = 21.0 Hz), 113.1 (d, J = 20.0 Hz), 44.0, 29.3 (d, J = 1.0 Hz); HRMS (ESI) Calcd for $C_{17}H_{16}F_2NaO$ (M+Na): 297.1061; Found: 297.1069.

Table 2, 6k



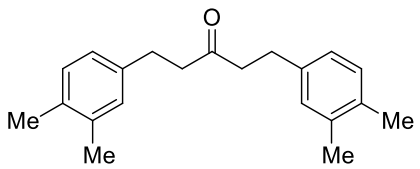
White solid; mp. 96-98 ^oC; IR (film) 2228, 1702, 1482 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, J = 7.0, 1.7 Hz, 2H), 7.46-7.43 (m, 2H), 7.42-7.34 (m, 4H), 2.92 (t, J = 7.4 Hz, 4H), 2.73 (t, J = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 142.5, 133.2, 132.0, 130.2, 129.5, 119.0, 112.7, 43.8, 29.1; HRMS (ESI) Calcd for $C_{19}H_{17}N_2O$ (M+H): 289.1335; Found: 289.1333.

Table 2, 6l



White solid; mp. 78-80 ^oC; IR (film) 1713, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, J = 8.0, 1.7 Hz, 2H), 7.11 (dd, J = 7.4, 1.6 Hz, 2H), 6.89-6.80 (m, 4H), 3.81 (s, 6H), 2.88 (t, J = 7.2 Hz, 4H), 2.68 (t, J = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 157.6, 130.2, 129.7, 127.6, 120.7, 110.4, 55.4, 43.0, 25.2; HRMS (ESI) Calcd for $C_{19}H_{23}O_3$ (M+H): 299.1642; Found: 299.1638.

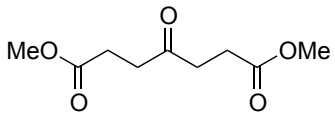
Table 2, 6m



Colorless oil; IR (film) 1713, 1504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 7.6 Hz, 2H), 6.93 (s, 2H), 6.89 (d, J = 7.6 Hz, 2H), 2.82 (t, J = 7.4 Hz, 4H), 2.68 (t,

J = 7.2 Hz, 4H), 2.23 (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 138.7, 136.8, 134.4, 129.93, 129.86, 125.8, 44.9, 29.5, 19.9, 19.5; HRMS (ESI) Calcd for $C_{21}H_{27}O$ (M+H): 295.2056; Found: 295.2055.

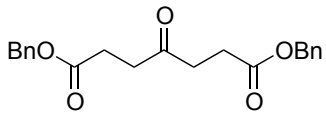
Table 2, 6n



White solid; mp. 42-44 °C; IR (film) 1739, 1702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H), 2.78 (t, *J* = 6.4 Hz, 4H), 2.61 (t, *J* = 6.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 173.3, 52.0, 37.2, 27.9; HRMS (ESI) Calcd for $C_9H_{15}O_5$ (M+H): 203.0914; Found: 203.0911.

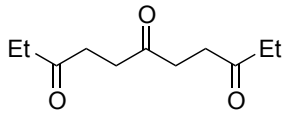
Zhang, Q.; Li, Y.; Wu, Y-K. *Chin. J. Chem.* **2007**, *25*, 1304

Table 2, 6o



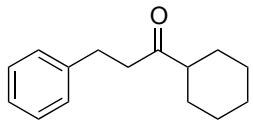
White solid; mp. 47-48 °C; IR (film) 1728, 1702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 10H), 5.11 (s, 4H), 2.78 (t, *J* = 6.2 Hz, 4H), 2.65 (t, *J* = 6.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 172.7, 136.0, 128.8, 128.44, 128.39, 66.7, 37.2, 28.2; HRMS (ESI) Calcd for $C_{21}H_{22}NaO_5$ (M+Na): 377.1359; Found: 377.1363.

Table 2, 6p



White solid; mp. 74-76 °C; IR (film) 1694, 1413 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78-2.72 (m, 4H), 2.71-2.66 (m, 4H), 2.47 (q, *J* = 7.4 Hz, 4H), 1.05 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 208.4, 36.3, 36.0, 35.9, 8.0; HRMS (ESI) Calcd for $C_{11}H_{18}NaO_3$ (M+Na): 221.1148; Found: 221.1148.

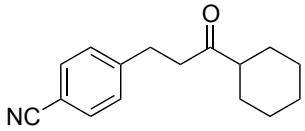
Table 2, 6q



Colorless oil; IR (film) 1706, 1447 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.78-2.72 (m, 2H), 2.35-2.26 (m, 1H), 1.85-1.71 (m, 4H), 1.68-1.60 (m, 1H), 1.40-1.10 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 141.6, 128.6, 128.5, 126.2, 51.2, 42.4, 29.9, 28.6, 26.0, 25.8; HRMS (ESI) Calcd for $C_{15}H_{20}NaO$ (M+Na): 239.1406; Found: 239.1409.

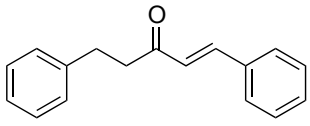
Kose, O.; Saito, S. *Org. Biomol. Chem.* **2010**, *8*, 896

Table 2, 6r



Colorless oil; IR (film) 2227, 1704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.31-7.26 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.39-2.25 (m, 1H), 1.83-1.71 (m, 4H), 1.69-1.61 (m, 1H), 1.36-1.10 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 147.4, 132.4, 129.4, 119.2, 110.1, 51.1, 41.5, 29.8, 28.6, 26.0, 25.8; HRMS (ESI) Calcd for $C_{16}H_{19}NNaO$ (M+Na): 264.1359; Found: 264.1363.

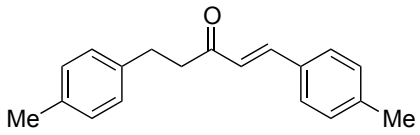
Table 3, 8a



White solid; mp. 49-50 ^oC; IR (film) 1679, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.50 (m, 3H), 7.42-7.37 (m, 3H), 7.33-7.27 (m, 2H), 7.27-7.18 (m, 3H), 6.74 (d, *J* = 16.2 Hz, 1H), 3.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 142.9, 141.4, 134.7, 130.7, 129.1, 128.7, 128.6, 128.5, 126.4, 126.3, 42.6, 30.3; HRMS (ESI) Calcd for $C_{17}H_{16}NaO$ (M+Na): 259.1093; Found: 259.1097.

Wu, X-F.; Neumann, H.; Beller, M. *Chem*. *Asian. J.* **2012**, *7*, 1199

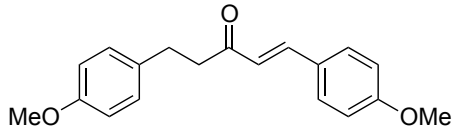
Table 3, 8b



White solid; mp. 82-84 ^{o}C; IR (film) 1676, 1642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 16.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15-7.09 (m, 4H), 6.69 (d, *J* = 16.2 Hz, 1H), 2.97 (s, 4H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 142.9, 141.1, 138.4, 135.8, 131.9, 129.9, 129.4, 128.5, 125.5, 42.7, 30.0, 21.7, 21.2; HRMS (ESI) Calcd for $C_{19}H_{20}NaO$ (M+Na): 287.1406; Found: 287.1411.

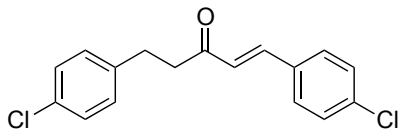
Wu, X-F.; Neumann, H.; Beller, M. *Chem*. *Asian. J.* **2012**, *7*, 1199

Table 3, 8c



White solid; mp. 94-95 ^{o}C; IR (film) 1638, 1601, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 16.2 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.94 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 161.8, 158.1, 142.7, 133.6, 130.2, 129.5, 127.3, 124.2, 114.6, 114.1, 55.6, 55.5, 42.8, 29.6; HRMS (ESI) Calcd for $C_{19}H_{20}NaO_3$ (M+Na): 319.1305; Found: 319.1310.

Table 3, 8d



White solid; mp. 84-86 ^{o}C; IR (film) 1679, 1605 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.43 (m, 3H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.16

(d, J = 8.4 Hz, 2H), 6.69 (d, J = 16.2 Hz, 1H), 2.97 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 141.5, 139.8, 136.7, 133.1, 132.1, 130.0, 129.6, 129.5, 128.8, 126.5, 42.6, 29.5; HRMS (ESI) Calcd for $C_{17}H_{14}Cl_2NaO$ (M+Na): 327.0314; Found: 327.0315.

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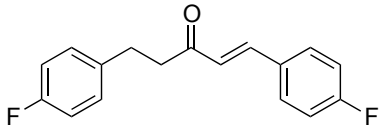
Table 3, 8e



White solid; mp. 57-58 ^{o}C; IR (film) 1679, 1611 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.47 (m, 3H), 7.22-7.15 (m, 2H), 7.12-7.05 (m, 2H), 7.01-6.94 (m, 2H), 6.65 (d, J = 16.2 Hz, 1H), 2.97 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 164.2 (d, J = 268.0 Hz), 161.7 (d, J = 260.0 Hz), 141.7, 136.98 (d, J = 3.0 Hz), 130.9 (d, J = 3.0 Hz), 130.4 (d, J = 9.0 Hz), 130.0 (d, J = 8.0 Hz), 126.0 (d, J = 3.0 Hz), 116.4 (d, J = 22.0 Hz), 115.5 (d, J = 22.0 Hz), 42.8, 29.4; HRMS (ESI) Calcd for $C_{17}H_{14}F_2NaO$ (M+Na): 295.0905; Found: 295.0907.

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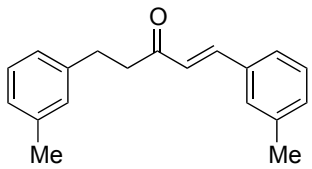
Table 3, 8f



Colorless oil; IR (film) 1686, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 16.2 Hz, 1H), 7.36-7.27 (m, 3H), 7.23-7.17 (m, 2H), 7.07-7.00 (m, 3H), 6.72 (d, J = 16.2 Hz, 1H), 2.99 (br s, 4H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 143.1, 141.4, 138.8, 138.3, 134.6, 131.5, 129.4, 129.1, 129.0, 128.6, 127.1, 126.2, 125.7, 125.6, 42.7, 30.3, 21.6, 21.5; HRMS (ESI) Calcd for $C_{19}H_{20}NaO$ (M+Na): 287.1406; Found: 287.1409.

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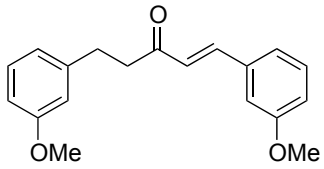
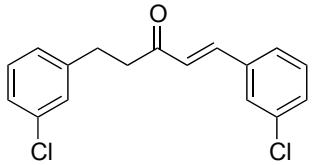
Table 3, 8g



Colorless oil; IR (film) 1689, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 16.2 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 2.3 Hz, 1H), 6.94 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 2.3 Hz, 1H), 6.75 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.00 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 160.1, 159.9, 143.0, 142.9, 136.0, 130.1, 129.7, 126.6, 121.2, 120.9, 116.6, 114.4, 113.3, 111.6, 55.5, 55.4, 42.5, 30.4; HRMS (ESI) Calcd for $C_{19}H_{20}NaO_3$ (M+Na): 319.1305; Found: 319.1309.

Table 3, 8h



Colorless oil; IR (film) 1691, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 16.2 Hz, 1H), 7.42-7.30 (m, 3H), 7.25-7.16 (m, 3H), 7.11 (dt, *J* = 7.2, 1.6 Hz, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 2.99 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 143.3, 141.3, 136.4, 135.2, 134.4, 130.6, 130.4, 130.0, 128.7, 128.1, 127.2, 126.8, 126.7, 126.6, 42.4, 29.7; HRMS (ESI) Calcd for $C_{17}H_{15}Cl_2O$ (M+H): 305.0494; Found: 305.0498.

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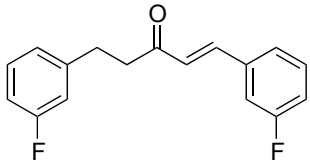
Table 3, 8i



Colorless oil; IR (film) 1691, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.2 Hz, 1H), 7.40-7.33 (m, 1H), 7.32-7.20 (m, 3H), 7.13-7.06 (m, 1H), 7.03-6.99 (m, 1H), 6.97-6.86 (m, 2H), 6.71 (d, *J* = 16.2 Hz, 1H), 3.00 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 163.2 (d, *J* = 245.0 Hz), 163.1 (d, *J* = 245.0 Hz), 143.8 (d, *J* = 8.0 Hz), 141.5 (d, *J* = 2.0 Hz), 136.9 (d, *J* = 7.0 Hz), 130.7 (d, *J* = 9.0 Hz), 130.1 (d, *J* = 8.0 Hz), 127.2, 124.5 (d, *J* = 3.0 Hz), 124.3 (d, *J* = 3.0 Hz), 117.6 (d, *J* = 21.0 Hz), 115.5 (d, *J* = 20.0 Hz), 114.6 (d, *J* = 22.0 Hz), 113.3 (d, *J* = 21.0 Hz), 42.4, 29.8 (d, *J* = 1.0 Hz); HRMS (ESI) Calcd for $C_{17}H_{14}F_2NaO$ (M+Na): 295.0905; Found: 295.0909.

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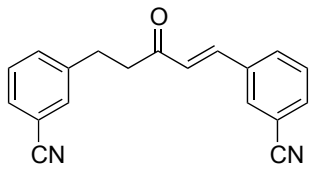
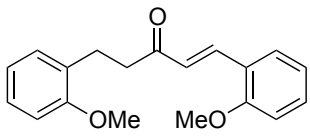
Table 3, 8j



White solid; mp. 97-98 °C; IR (film) 2221, 1663, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.6 Hz, 1H), 7.77-7.72 (m, 1H), 7.68 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.56-7.47 (m, 5H), 7.40 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 3.09-3.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 142.6, 140.3, 135.8, 133.7, 133.4, 132.4, 132.2, 131.7, 130.3, 130.1, 129.5, 127.9, 119.1, 118.2, 113.7, 112.8, 42.4, 29.4; HRMS (ESI) Calcd for $C_{19}H_{14}N_2NaO$ (M+Na): 309.0998; Found: 309.1004.

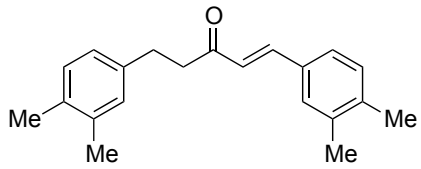
Table 3, 8k



White solid; mp. 85-87 °C; IR (film) 1692, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.5 Hz, 1H), 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38-7.32 (m, 1H), 7.23-7.17 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.93-6.84 (m, 3H), 6.77 (d, *J* = 16.5 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.99 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

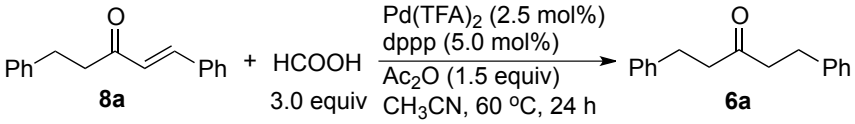
201.0, 158.5, 157.7, 138.0, 131.8, 130.3, 129.9, 128.5, 127.6, 127.3, 123.8, 121.0, 120.7, 111.3, 110.4, 55.7, 55.4, 40.5, 25.9; HRMS (ESI) Calcd for $C_{19}H_{20}NaO_3$ (M+Na): 319.1305; Found: 319.1308.

Table 3, 8l



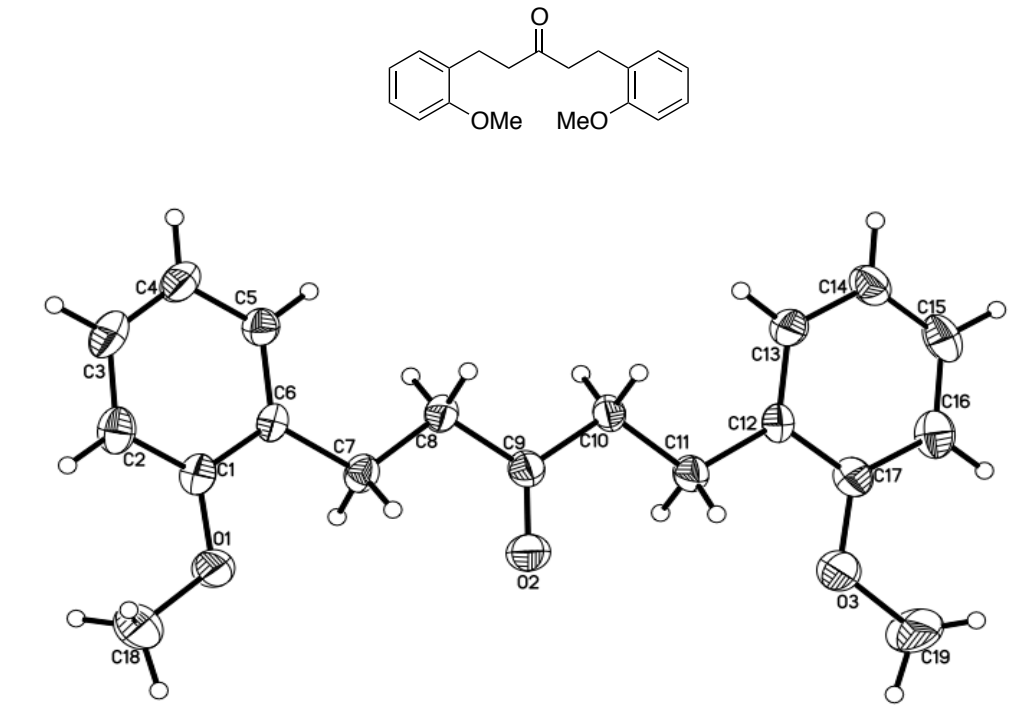
White solid; mp. 65-66 ^{o}C; IR (film) 1679, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 16.2 Hz, 1H), 7.31-7.25 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.98-6.95 (m, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 3.00-2.90 (m, 4H), 2.28 (s, 6H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 143.1, 139.9, 138.9, 137.4, 136.8, 134.4, 132.4, 130.4, 130.0, 129.7, 126.1, 125.9, 125.4, 42.8, 30.0, 20.0, 19.9, 19.5; HRMS (ESI) Calcd for $C_{21}H_{24}NaO$ (M+Na): 315.1719; Found: 315.1722.

Procedures for reduction of 1,5-diphenylpent-1-en-3-one (Scheme 6)



To a mixture of $Pd(TFA)_2$ (0.0017 g, 0.0050 mmol), dppp (0.0041 g, 0.010 mmol), and CH_3CN (0.05 mL) in a vial (4.0 mL) were added 1,5-diphenylpent-1-en-3-one (**8a**) (0.0473 g, 0.20 mmol), Ac_2O (0.0306 g, 0.30 mmol), and HCOOH (0.0276 g, 0.60 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 60 ^oC for 24 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether /diethyl ether = 50/1) to give compound **6a** as a colorless oil (0.0466 g, 98% yield).

The X-ray structure of compound **6l**



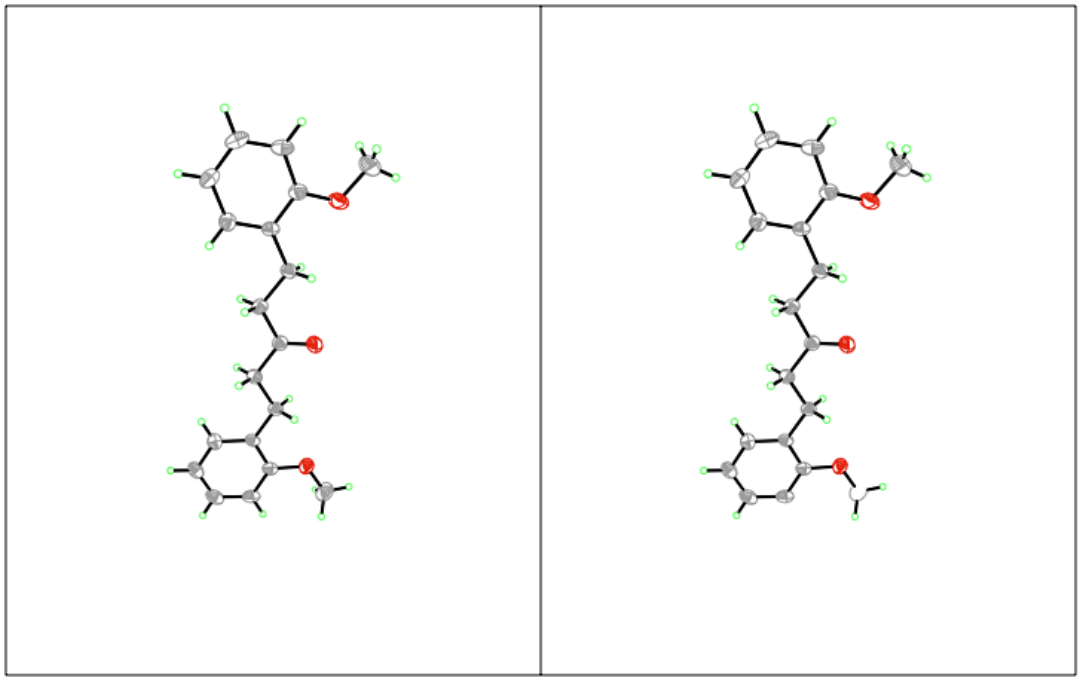


Table 1. Crystal data and structure refinement for **6l**.

Identification code	**6l**
Empirical formula	C_{19} H_{22} O_3
Formula weight	298.37
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/C
Unit cell dimensions	a = 28.543(6) A alpha = 90 deg.
	b = 7.3090(15) A beta = 105.04(3) deg.
	c = 16.361(3) A gamma = 90 deg.
Volume	3296.3(12) A^3
Z, Calculated density	8,1.202 Mg/m^3
Absorption coefficient	0.080 mm^-1
F(000)	1280
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	1.48 to 25.38 deg.
Limiting indices	0<=h<=34, 0<=k<=8, -18<=l<=19
Reflections collected /unique	3093 / 3030 [R(int) = 0.0929]
Completeness to theta = 25.38	100.0 %
Absorption correction	Psi-scan
Max. and min. transmission	0.9920 and 0.9764
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3030 / 0 / 199
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma (I)]	R1 = 0.0639, wR2 = 0.1064
R indices (all data)	R1 = 0.1583, wR2 = 0.1411
Largest diff. peak and hole	0.147 and -0.177 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **6l**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	1876(1)	1838(3)	7390(2)	63(1)
C(1)	1387(1)	1557(4)	7156(2)	46(1)
O(2)	1795(1)	7584(3)	5862(2)	75(1)
C(2)	1158(1)	75(5)	7415(2)	56(1)
O(3)	1889(1)	13246(3)	4395(2)	69(1)
C(3)	659(2)	-67(5)	7156(2)	61(1)
C(4)	385(1)	1234(5)	6644(2)	57(1)
C(5)	619(1)	2706(5)	6393(2)	48(1)
C(6)	1118(1)	2919(4)	6643(2)	39(1)
C(7)	1382(1)	4544(4)	6403(2)	46(1)
C(8)	1070(1)	5998(4)	5870(2)	45(1)
C(9)	1358(1)	7549(5)	5637(2)	45(1)
C(10)	1069(1)	9059(4)	5119(2)	44(1)
C(11)	1383(1)	10547(4)	4892(2)	48(1)
C(12)	1120(1)	12138(4)	4391(2)	42(1)
C(13)	623(1)	12340(5)	4153(2)	49(1)
C(14)	403(1)	13817(5)	3675(2)	57(1)
C(15)	679(2)	15133(5)	3434(2)	61(1)
C(16)	1179(2)	14995(5)	3670(2)	59(1)
C(17)	1401(1)	13506(5)	4142(2)	49(1)
C(18)	2179(1)	469(5)	7880(3)	86(1)
C(19)	2201(1)	14630(6)	4217(3)	98(2)

Table 3. Bond lengths [A] and angles [deg] for **6l**.

O(1)-C(1)	1.366(4)
O(1)-C(18)	1.425(4)
C(1)-C(2)	1.387(4)
C(1)-C(6)	1.396(4)
O(2)-C(9)	1.206(3)
C(2)-C(3)	1.382(4)
C(2)-H(2A)	0.93
O(3)-C(17)	1.360(4)
O(3)-C(19)	1.426(4)
C(3)-C(4)	1.369(5)
C(3)-H(3A)	0.93
C(4)-C(5)	1.384(4)
C(4)-H(4A)	0.93
C(5)-C(6)	1.383(4)
C(5)-H(5A)	0.93
C(6)-C(7)	1.513(4)
C(7)-C(8)	1.509(4)
C(7)-H(7A)	0.97
C(7)-H(7B)	0.97
C(8)-C(9)	1.505(4)
C(8)-H(8A)	0.97
C(8)-H(8B)	0.97
C(9)-C(10)	1.501(4)
C(10)-C(11)	1.516(4)
C(10)-H(10A)	0.97
C(10)-H(10B)	0.97
C(11)-C(12)	1.505(4)
C(11)-H(11A)	0.97
C(11)-H(11B)	0.97
C(12)-C(13)	1.378(4)
C(12)-C(17)	1.406(4)
C(13)-C(14)	1.385(4)
C(13)-H(13A)	0.93
C(14)-C(15)	1.364(4)
C(14)-H(14A)	0.93
C(15)-C(16)	1.384(5)
C(15)-H(15A)	0.93
C(16)-C(17)	1.388(4)
C(16)-H(16A)	0.93
C(18)-H(18A)	0.96
C(18)-H(18B)	0.96
C(18)-H(18C)	0.96

C(19)-H(19A)	0.96
C(19)-H(19B)	0.96
C(19)-H(19C)	0.96
C(1)-O(1)-C(18)	118.7(3)
O(1)-C(1)-C(2)	124.0(3)
O(1)-C(1)-C(6)	115.1(3)
C(2)-C(1)-C(6)	120.8(3)
C(3)-C(2)-C(1)	119.6(3)
C(3)-C(2)-H(2A)	120.2
C(1)-C(2)-H(2A)	120.2
C(17)-O(3)-C(19)	118.9(3)
C(4)-C(3)-C(2)	120.9(3)
C(4)-C(3)-H(3A)	119.5
C(2)-C(3)-H(3A)	119.5
C(3)-C(4)-C(5)	118.7(4)
C(3)-C(4)-H(4A)	120.7
C(5)-C(4)-H(4A)	120.7
C(6)-C(5)-C(4)	122.6(3)
C(6)-C(5)-H(5A)	118.7
C(4)-C(5)-H(5A)	118.7
C(5)-C(6)-C(1)	117.4(3)
C(5)-C(6)-C(7)	123.7(3)
C(1)-C(6)-C(7)	118.8(3)
C(8)-C(7)-C(6)	116.4(3)
C(8)-C(7)-H(7A)	108.2
C(6)-C(7)-H(7A)	108.2
C(8)-C(7)-H(7B)	108.2
C(6)-C(7)-H(7B)	108.2
H(7A)-C(7)-H(7B)	107.3
C(9)-C(8)-C(7)	113.5(3)
C(9)-C(8)-H(8A)	108.9
C(7)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8B)	108.9
C(7)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
O(2)-C(9)-C(10)	122.1(3)
O(2)-C(9)-C(8)	121.8(3)
C(10)-C(9)-C(8)	116.1(3)
C(9)-C(10)-C(11)	113.1(3)
C(9)-C(10)-H(10A)	109
C(11)-C(10)-H(10A)	109
C(9)-C(10)-H(10B)	109
C(11)-C(10)-H(10B)	109

H(10A)-C(10)-H(10B)	107.8
C(12)-C(11)-C(10)	116.5(3)
C(12)-C(11)-H(11A)	108.2
C(10)-C(11)-H(11A)	108.2
C(12)-C(11)-H(11B)	108.2
C(10)-C(11)-H(11B)	108.2
H(11A)-C(11)-H(11B)	107.3
C(13)-C(12)-C(17)	117.6(3)
C(13)-C(12)-C(11)	124.6(3)
C(17)-C(12)-C(11)	117.8(3)
C(12)-C(13)-C(14)	121.8(3)
C(12)-C(13)-H(13A)	119.1
C(14)-C(13)-H(13A)	119.1
C(15)-C(14)-C(13)	120.1(4)
C(15)-C(14)-H(14A)	120
C(13)-C(14)-H(14A)	120
C(14)-C(15)-C(16)	120.0(3)
C(14)-C(15)-H(15A)	120
C(16)-C(15)-H(15A)	120
C(15)-C(16)-C(17)	120.0(3)
C(15)-C(16)-H(16A)	120
C(17)-C(16)-H(16A)	120
O(3)-C(17)-C(16)	124.2(3)
O(3)-C(17)-C(12)	115.3(3)
C(16)-C(17)-C(12)	120.5(3)
O(1)-C(18)-H(18A)	109.5
O(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(3)-C(19)-H(19A)	109.5
O(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **6l**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	51(2)	58(2)	72(2)	19(1)	1(1)	-1(1)
C(1)	60(2)	41(2)	38(2)	0(2)	15(2)	-5(2)
O(2)	48(2)	61(2)	108(2)	36(2)	8(2)	-3(1)
C(2)	79(3)	45(2)	45(2)	9(2)	17(2)	-4(2)
O(3)	58(2)	60(2)	97(2)	29(2)	34(2)	2(1)
C(3)	79(3)	50(2)	60(2)	-6(2)	31(2)	-22(2)
C(4)	58(2)	51(2)	67(2)	-8(2)	25(2)	-16(2)
C(5)	49(2)	43(2)	53(2)	-7(2)	14(2)	-2(2)
C(6)	52(2)	31(2)	37(2)	-2(1)	16(2)	-6(2)
C(7)	53(2)	38(2)	44(2)	6(2)	7(2)	-6(2)
C(8)	50(2)	35(2)	50(2)	1(2)	14(2)	-4(2)
C(9)	48(2)	41(2)	46(2)	1(2)	10(2)	2(2)
C(10)	48(2)	32(2)	49(2)	-2(2)	7(2)	4(2)
C(11)	47(2)	40(2)	61(2)	9(2)	19(2)	3(2)
C(12)	54(2)	32(2)	39(2)	2(1)	12(2)	1(2)
C(13)	48(2)	46(2)	51(2)	-6(2)	10(2)	-3(2)
C(14)	57(2)	54(2)	54(2)	0(2)	0(2)	13(2)
C(15)	80(3)	50(2)	50(2)	11(2)	12(2)	20(2)
C(16)	82(3)	51(2)	49(2)	14(2)	24(2)	2(2)
C(17)	55(2)	50(2)	45(2)	6(2)	17(2)	5(2)
C(18)	74(3)	77(3)	94(3)	25(3)	0(2)	13(3)
C(19)	69(3)	103(4)	130(4)	46(3)	38(3)	-17(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6l**.

	x	y	z	U(eq)
H(2A)	1340	-819	7762	68
H(3A)	506	-1060	7332	73
H(4A)	49	1131	6469	68
H(5A)	434	3587	6043	58
H(7A)	1571	5113	6919	55
H(7B)	1608	4096	6098	55
H(8A)	876	5439	5355	54
H(8B)	850	6486	6178	54
H(10A)	858	9598	5434	53
H(10B)	864	8543	4603	53
H(11A)	1594	11019	5412	58
H(11B)	1588	9995	4571	58
H(13A)	431	11461	4318	59
H(14A)	67	13913	3518	69
H(15A)	530	16122	3112	73
H(16A)	1368	15901	3512	71
H(18A)	2512	847	7994	129
H(18B)	2137	-662	7571	129
H(18C)	2093	300	8404	129
H(19A)	2533	14258	4433	147
H(19B)	2147	15753	4483	147
H(19C)	2132	14808	3617	147

Table 6. Torsion angles [deg] for **6l**.

C(18)-O(1)-C(1)-C(2)	4.9(5)
C(18)-O(1)-C(1)-C(6)	-177.0(3)
O(1)-C(1)-C(2)-C(3)	178.7(3)
C(6)-C(1)-C(2)-C(3)	0.7(5)
C(1)-C(2)-C(3)-C(4)	0.2(5)
C(2)-C(3)-C(4)-C(5)	-0.4(5)
C(3)-C(4)-C(5)-C(6)	-0.4(5)
C(4)-C(5)-C(6)-C(1)	1.2(5)
C(4)-C(5)-C(6)-C(7)	-177.9(3)
O(1)-C(1)-C(6)-C(5)	-179.5(3)
C(2)-C(1)-C(6)-C(5)	-1.4(4)
O(1)-C(1)-C(6)-C(7)	-0.4(4)
C(2)-C(1)-C(6)-C(7)	177.8(3)
C(5)-C(6)-C(7)-C(8)	0.9(4)
C(1)-C(6)-C(7)-C(8)	-178.2(3)
C(6)-C(7)-C(8)-C(9)	-178.6(3)
C(7)-C(8)-C(9)-O(2)	0.3(5)
C(7)-C(8)-C(9)-C(10)	-179.0(3)
O(2)-C(9)-C(10)-C(11)	2.1(5)
C(8)-C(9)-C(10)-C(11)	-178.6(3)
C(9)-C(10)-C(11)-C(12)	-178.5(3)
C(10)-C(11)-C(12)-C(13)	1.8(4)
C(10)-C(11)-C(12)-C(17)	-177.5(3)
C(17)-C(12)-C(13)-C(14)	0.9(5)
C(11)-C(12)-C(13)-C(14)	-178.5(3)
C(12)-C(13)-C(14)-C(15)	-0.7(5)
C(13)-C(14)-C(15)-C(16)	-0.2(5)
C(14)-C(15)-C(16)-C(17)	0.9(5)
C(19)-O(3)-C(17)-C(16)	4.2(5)
C(19)-O(3)-C(17)-C(12)	-175.8(3)
C(15)-C(16)-C(17)-O(3)	179.4(3)
C(15)-C(16)-C(17)-C(12)	-0.6(5)
C(13)-C(12)-C(17)-O(3)	179.8(3)
C(11)-C(12)-C(17)-O(3)	-0.8(4)
C(13)-C(12)-C(17)-C(16)	-0.2(5)
C(11)-C(12)-C(17)-C(16)	179.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **6l** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

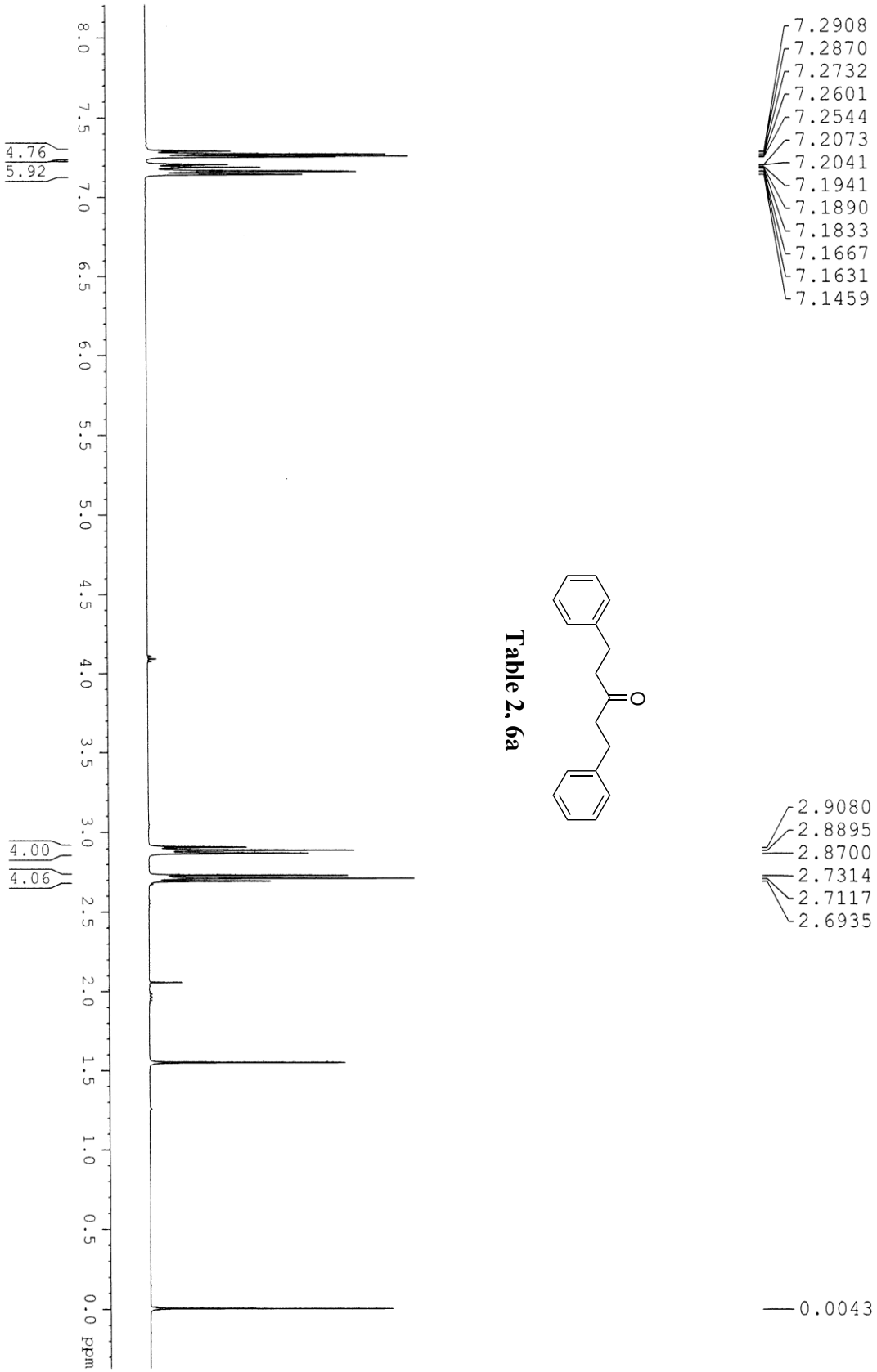

7.2908
7.2870
7.2732
7.2601
7.2544
7.2073
7.2041
7.1941
7.1890
7.1833
7.1667
7.1631
7.1459
4.76
5.92
4.00
4.06
2.9080
2.8895
2.8700
2.7314
2.7117
2.6935
0.0043
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2. 6a

209.30
141.20
128.69
128.50
126.30
77.55
77.23
76.91
44.69
29.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Table 2, 6a

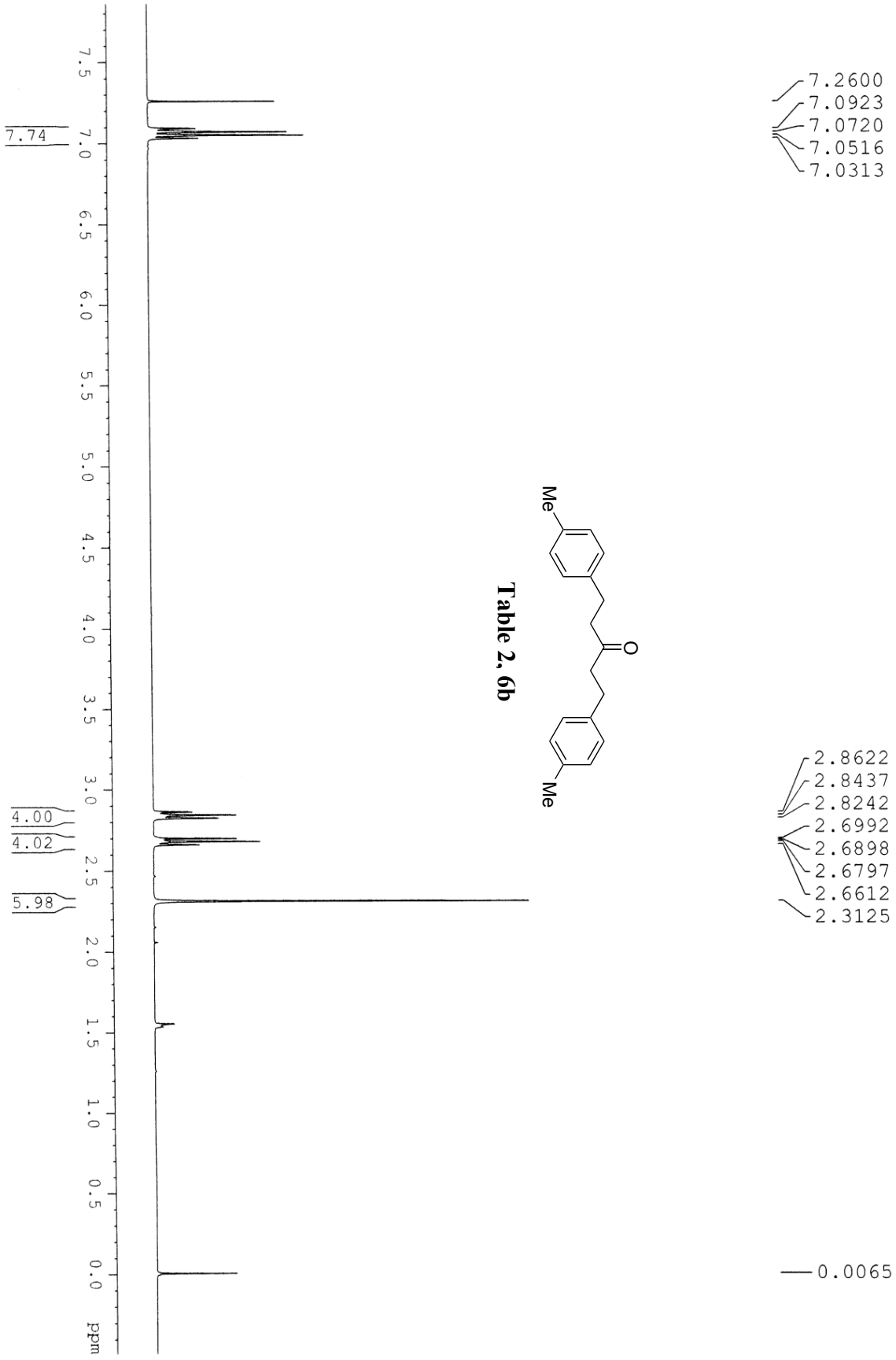

7.2600
7.0923
7.0720
7.0516
7.0313
Me
O
Me
2.8622
2.8437
2.8242
2.6992
2.6898
2.6797
2.6612
2.3125
0.0065
7.74
4.00
4.02
5.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6b

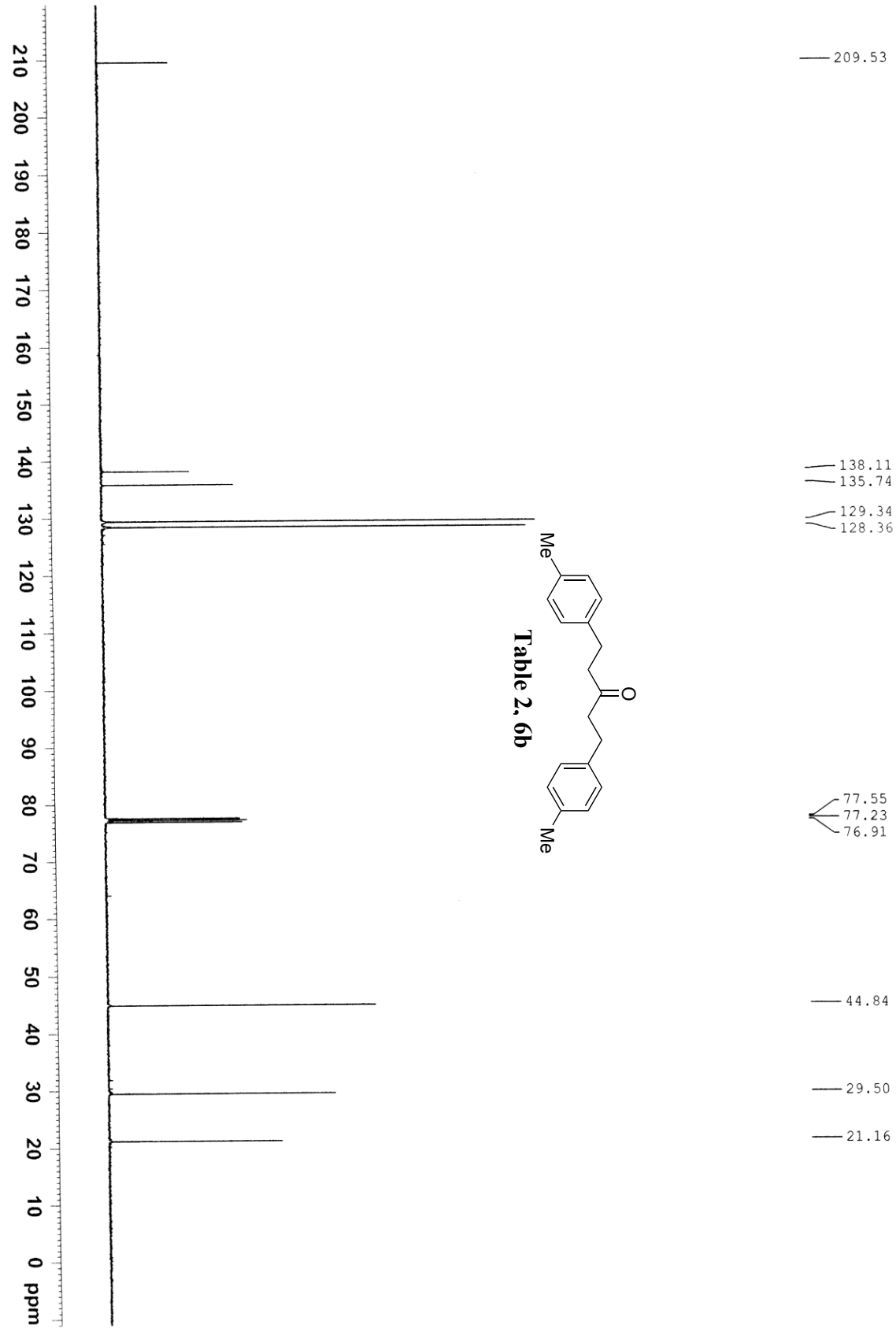

209.53
138.11
135.74
129.34
128.36
77.55
77.23
76.91
44.84
29.50
21.16
Me
Me
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6b

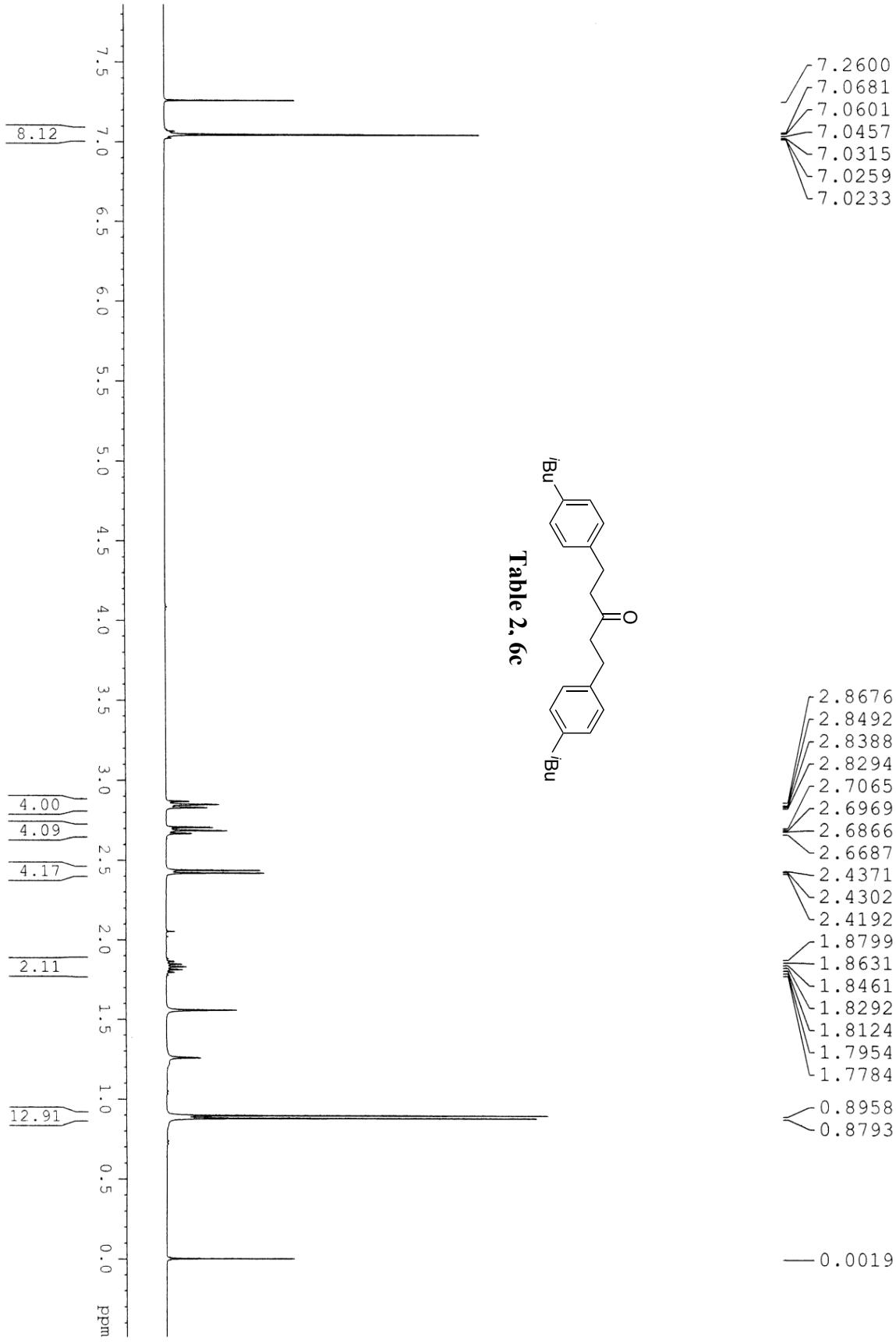

7.2600
7.0681
7.0601
7.0457
7.0315
7.0259
7.0233
2.8676
2.8492
2.8388
2.8294
2.7065
2.6969
2.6866
2.6687
2.4371
2.4302
2.4192
1.8799
1.8631
1.8461
1.8292
1.8124
1.7954
1.7784
0.8958
0.8793
0.0019
8.12
4.00
4.09
4.17
2.11
12.91
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
iBu
O
iBu

Table 2, 6c

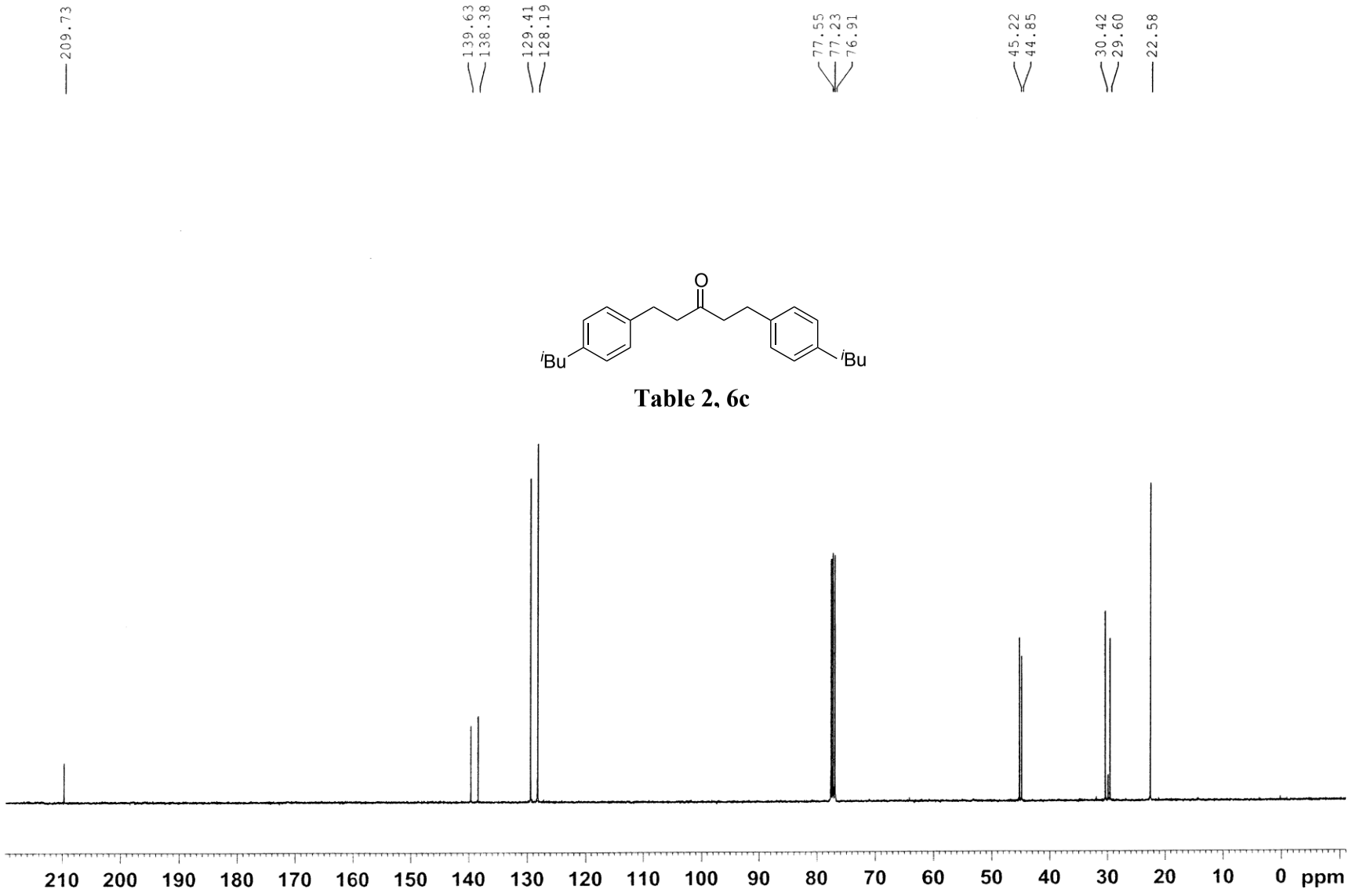

209.73
139.63
138.38
129.41
128.19
77.55
77.23
76.91
45.22
44.85
30.42
29.60
22.58
O
iBu
iBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6c

7.2599
7.2420
7.2356
7.2308
7.2195
7.2146
7.2083
7.0841
7.0781
7.0731
7.0616
7.0568
3.73
3.80
4.00
3.98
2.8625
2.8439
2.8256
2.6888
2.6702
2.6518
0.0001
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Cl
O
Cl

Table 2. 6d

208.50
139.56
132.08
129.89
128.77
77.55
77.23
76.92
44.43
29.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Cl
O
Cl

Table 2, 6d

7.2600
7.1205
7.1130
7.1076
7.0993
7.0912
7.0833
7.0777
7.0704
6.9720
6.9646
6.9592
6.9481
6.9427
6.9373
6.9262
6.9209
6.9134
2.8683
2.8496
2.8311
2.6921
2.6823
2.6734
2.6549
0.0015
3.85
3.83
4.00
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6e

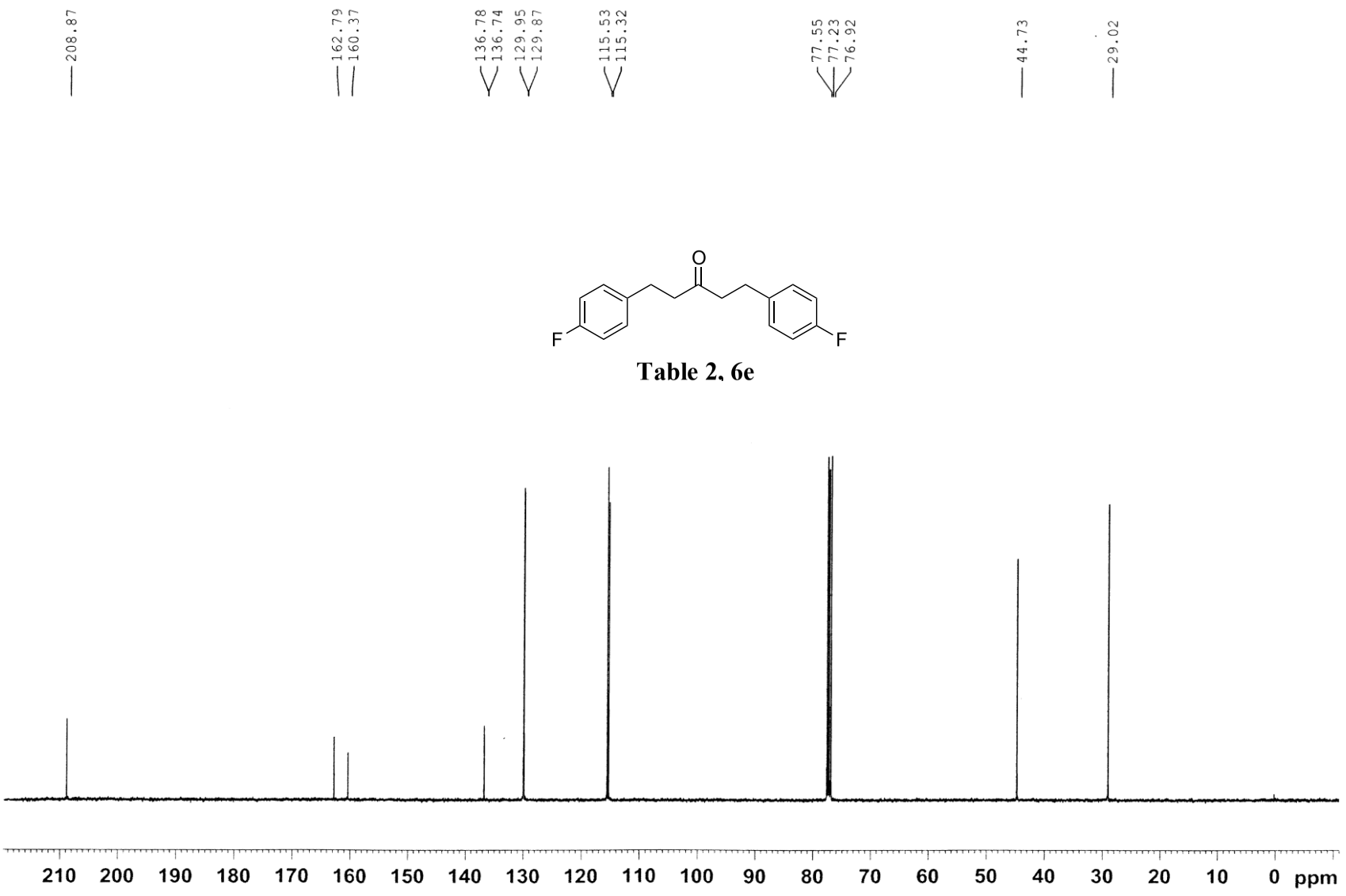

208.87
162.79
160.37
136.78
136.74
129.95
129.87
115.53
115.32
77.55
77.23
76.92
44.73
29.02
O
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6e

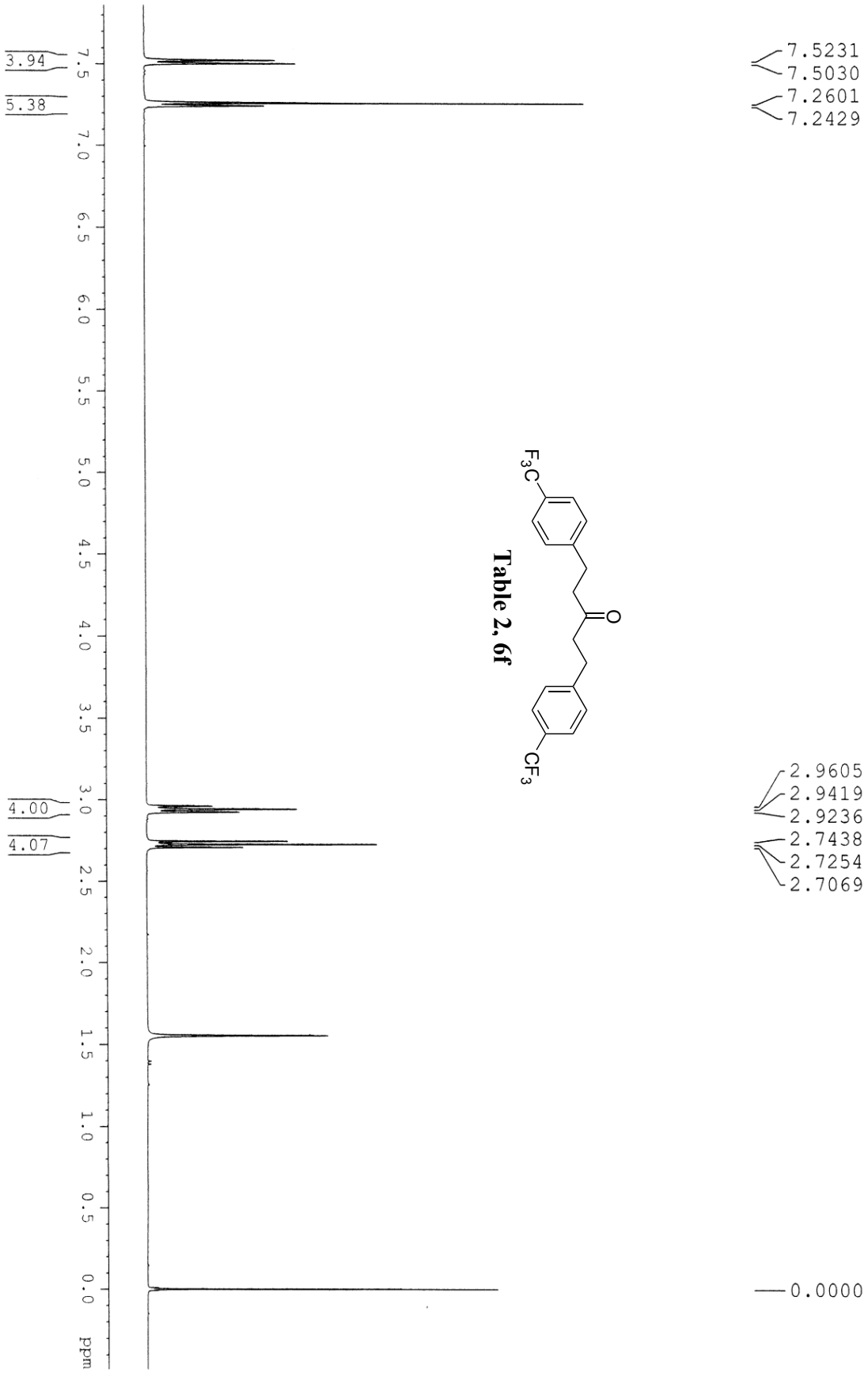
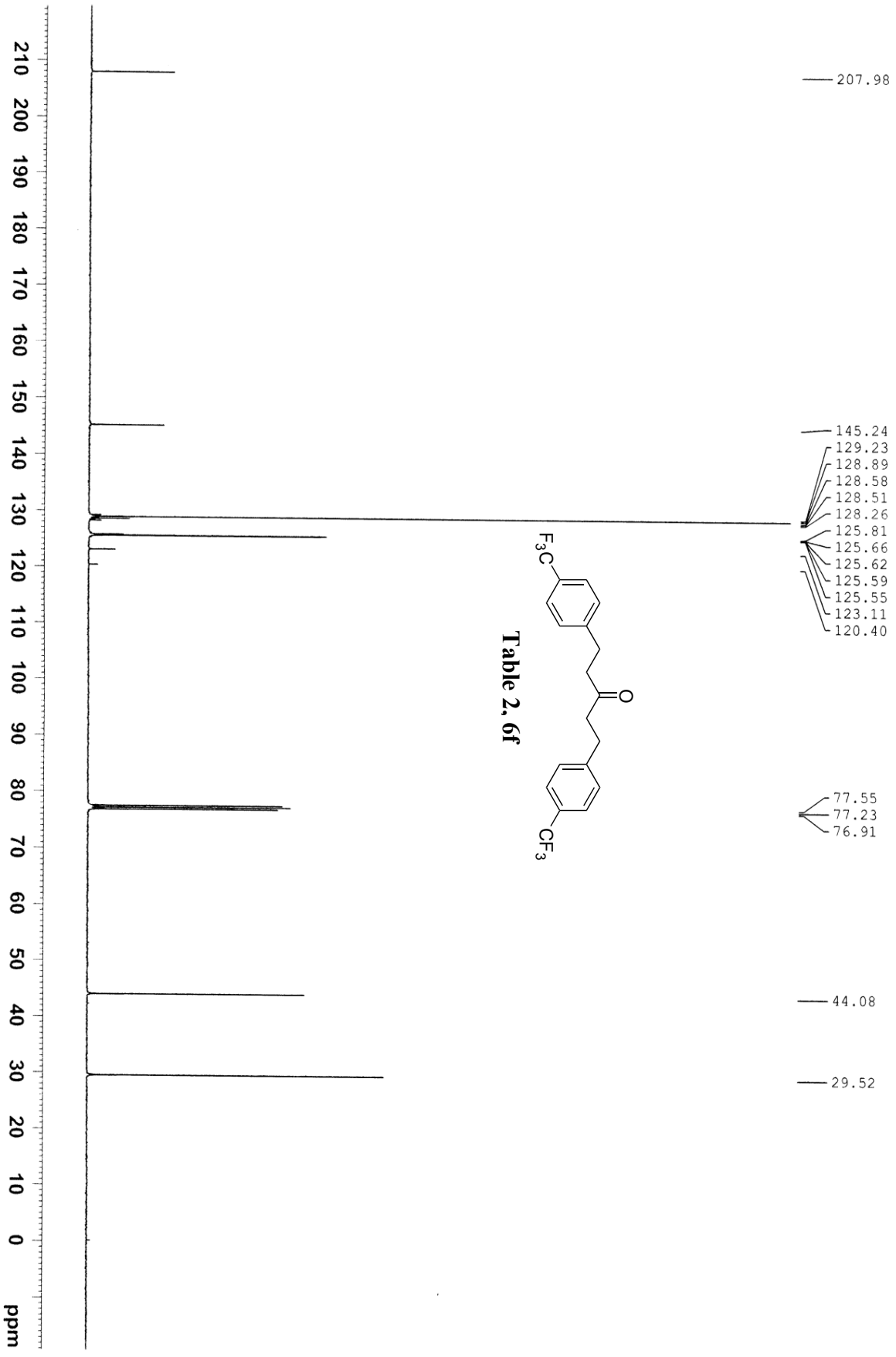

7.5231
7.5030
7.2601
7.2429
2.9605
2.9419
2.9236
2.7438
2.7254
2.7069
0.0000
3.94
5.38
4.00
4.07
ppm

Table 2. 6f


207.98
145.24
129.23
128.89
128.58
128.51
128.26
125.81
125.66
125.62
125.59
125.55
123.11
120.40
77.55
77.23
76.91
44.08
29.52
F3C
CF3
O
Table 2. 6f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

7.2599
7.1842
7.1656
7.1468
7.0171
6.9980
6.9790
6.9667
6.9477
2.8715
2.8531
2.8335
2.7207
2.7117
2.7009
2.6822
2.3211
0.0078
2.04
6.05
4.00
4.07
6.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Me
O
Me

Table 2, 6g

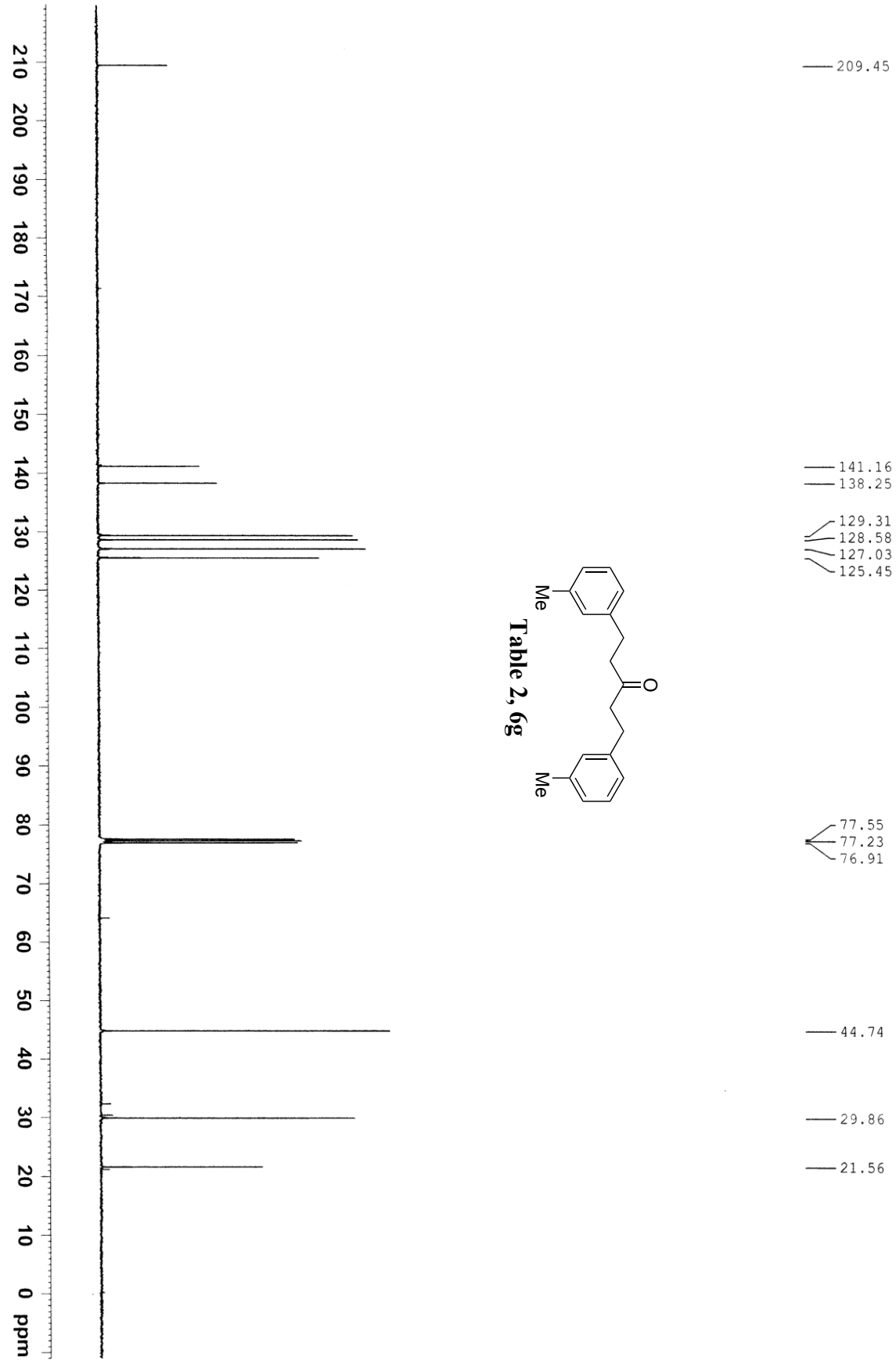
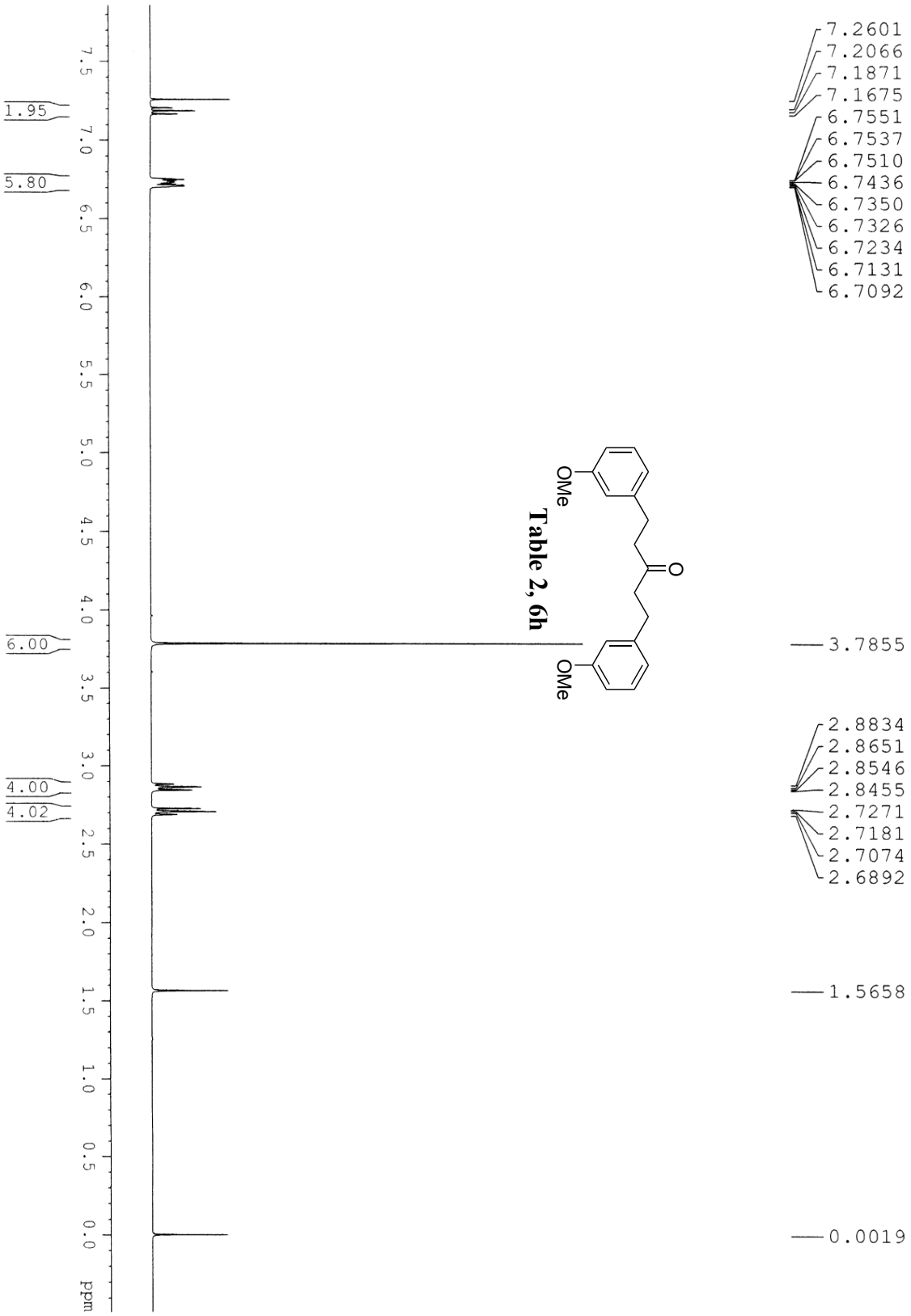

209.45
141.16
138.25
129.31
128.58
127.03
125.45
77.55
77.23
76.91
44.74
29.86
21.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Me
Me
O

Table 2, 6g


7.2601
7.2066
7.1871
7.1675
6.7551
6.7537
6.7510
6.7436
6.7350
6.7326
6.7234
6.7131
6.7092
OMe
OMe
O
Table 2, 6h
3.7855
2.8834
2.8651
2.8546
2.8455
2.7271
2.7181
2.7074
2.6892
1.5658
0.0019
1.95
5.80
6.00
4.00
4.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

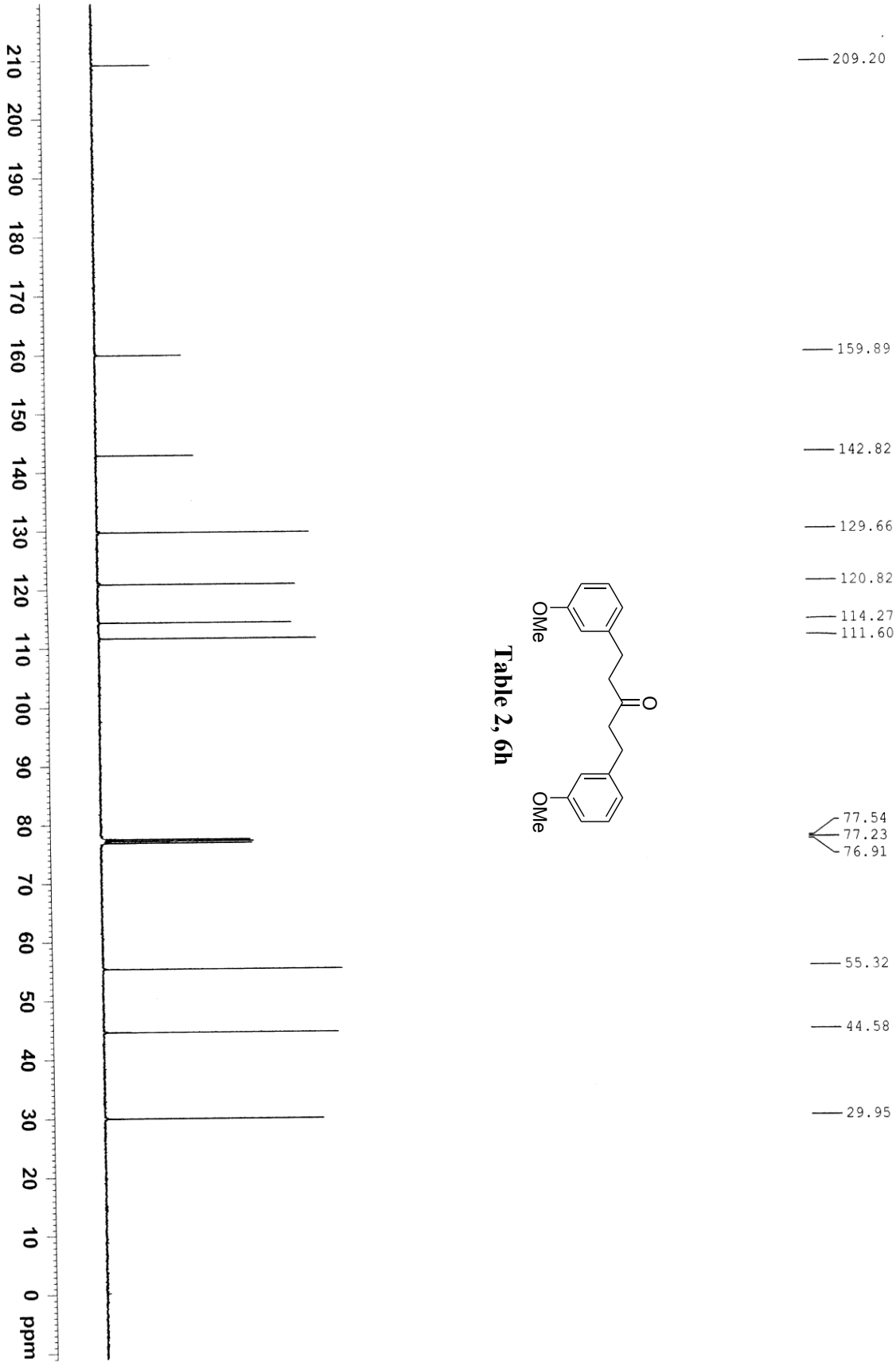

209.20
159.89
142.82
129.66
120.82
114.27
111.60
77.54
77.23
76.91
55.32
44.58
29.95
OMe
OMe
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6h

7.2601
7.2153
7.1961
7.1947
7.1887
7.1793
7.1770
7.1748
7.1702
7.1545
7.1504
7.0431
7.0387
7.0348
7.0263
7.0216
7.0174
5.90
1.91
4.00
4.10
2.8829
2.8642
2.8456
2.7194
2.7102
2.7005
2.6821
0.0010
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6i

Cl
O
Cl

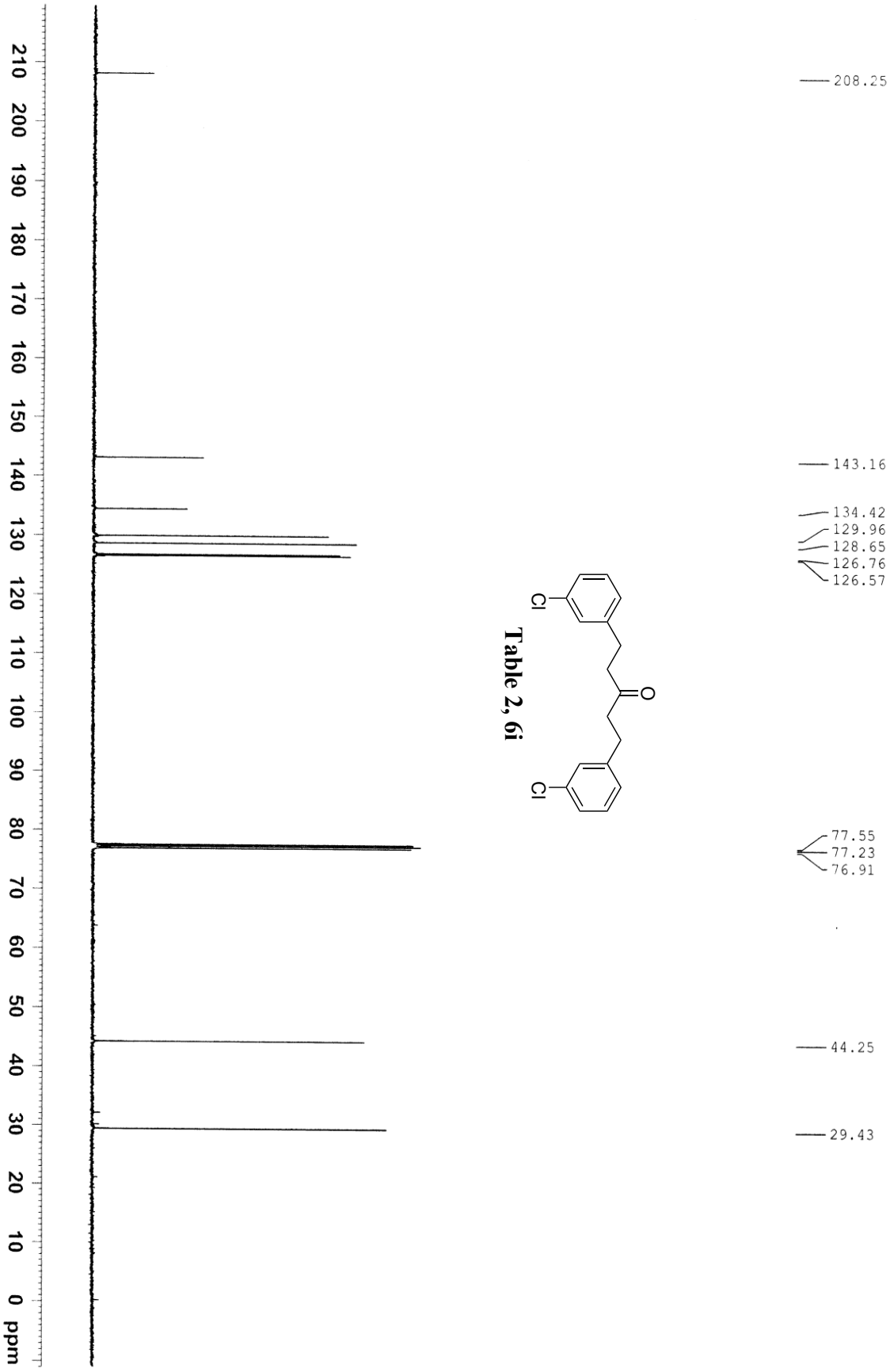

208.25
143.16
134.42
129.96
128.65
126.76
126.57
77.55
77.23
76.91
44.25
29.43
Cl
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6i


7.2599
7.2485
7.2328
7.2289
7.2136
7.2096
7.1940
6.9335
6.9136
6.9054
6.8988
6.8766
6.8683
6.8632
6.8568
6.8472
6.8434
2.9038
2.8852
2.8665
2.7267
2.7168
2.7077
2.6893
0.0008

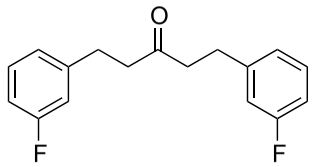
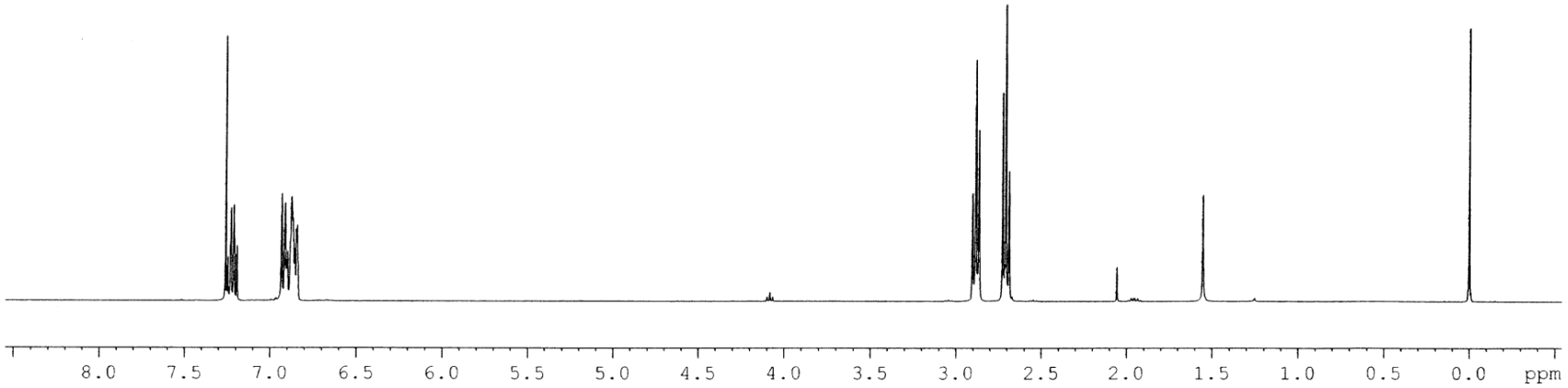

O
F
F

Table 2, 6j


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

208.20
164.13
161.69
143.54
143.47
129.98
129.90
124.01
123.98
115.30
115.09
113.15
112.95
77.38
77.06
76.75
44.04
29.32
29.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6j

F
O
F

7.5030
7.4988
7.4943
7.4854
7.4813
7.4769
7.4448
7.4436
7.4165
7.4121
7.4076
7.3970
7.3927
7.3874
7.3859
7.3682
7.3500
7.2600
2.9423
2.9238
2.9059
2.7502
2.7322
2.7138
-0.0025
1.87
1.94
3.90
4.00
4.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
CN
O
CN

Table 2, 6k

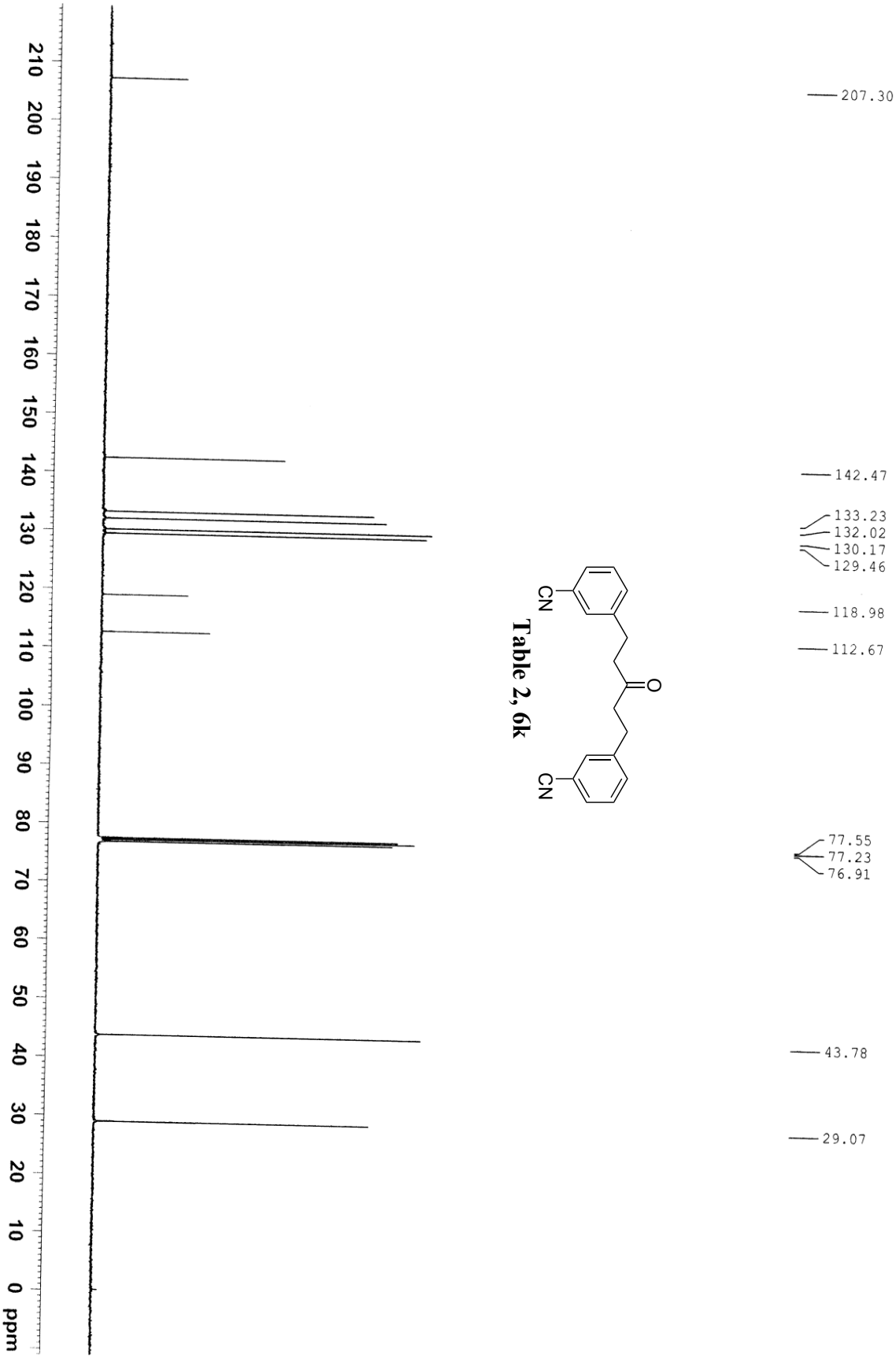

207.30
142.47
133.23
132.02
130.17
129.46
118.98
112.67
77.55
77.23
76.91
43.78
29.07
CN
CN
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6k

7.2600
7.2035
7.1992
7.1835
7.1798
7.1645
7.1602
7.1263
7.1223
7.1078
7.1039
6.8853
6.8827
6.8667
6.8642
6.8481
6.8422
6.8215
3.8073
2.8973
2.8792
2.8670
2.8589
2.7039
2.6959
2.6836
2.6761
2.6654
0.0028
1.94
1.93
3.89
5.95
4.00
3.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6l

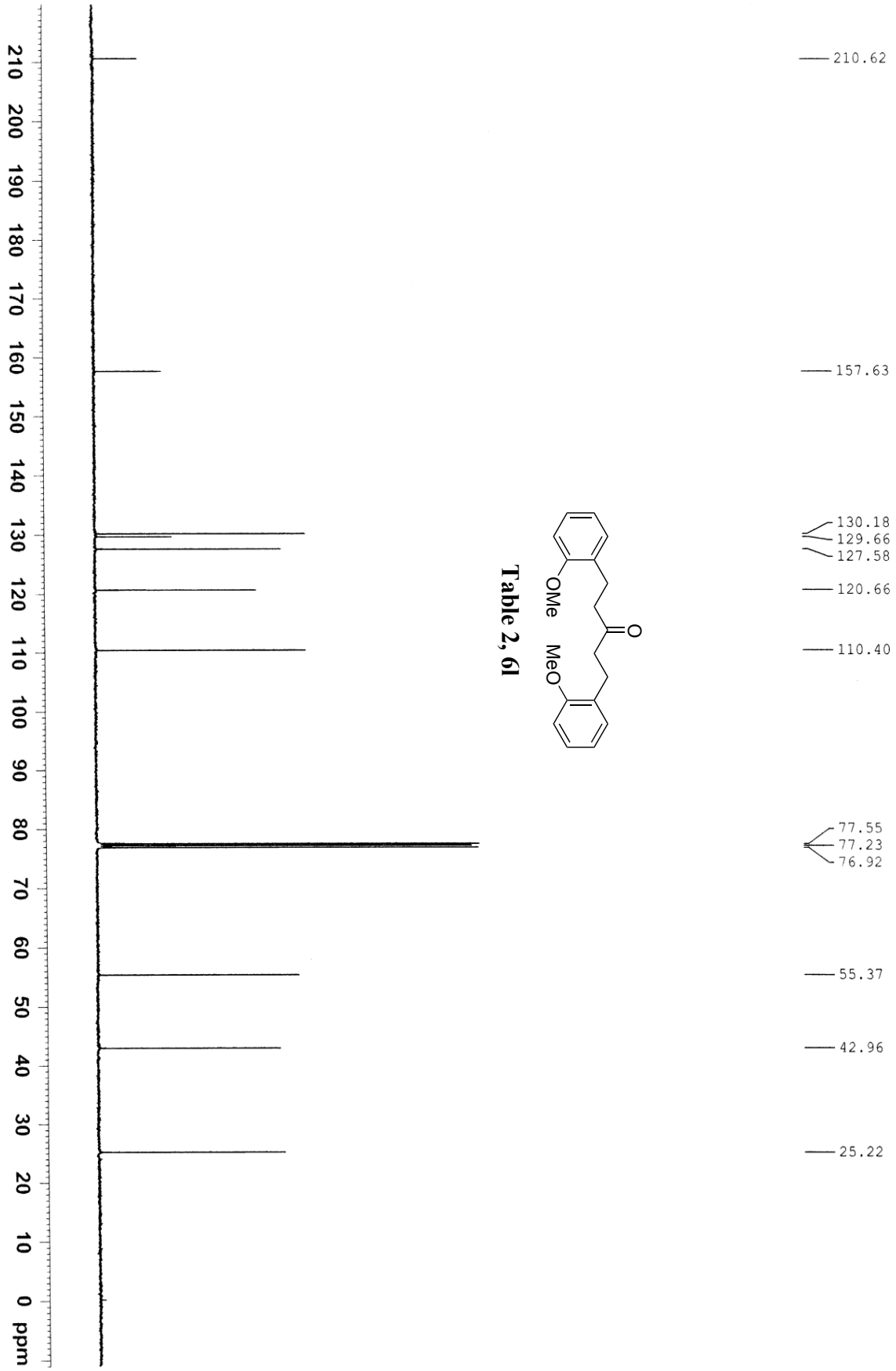

210.62
157.63
130.18
129.66
127.58
120.66
110.40
77.55
77.23
76.92
55.37
42.96
25.22
OMe
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6l

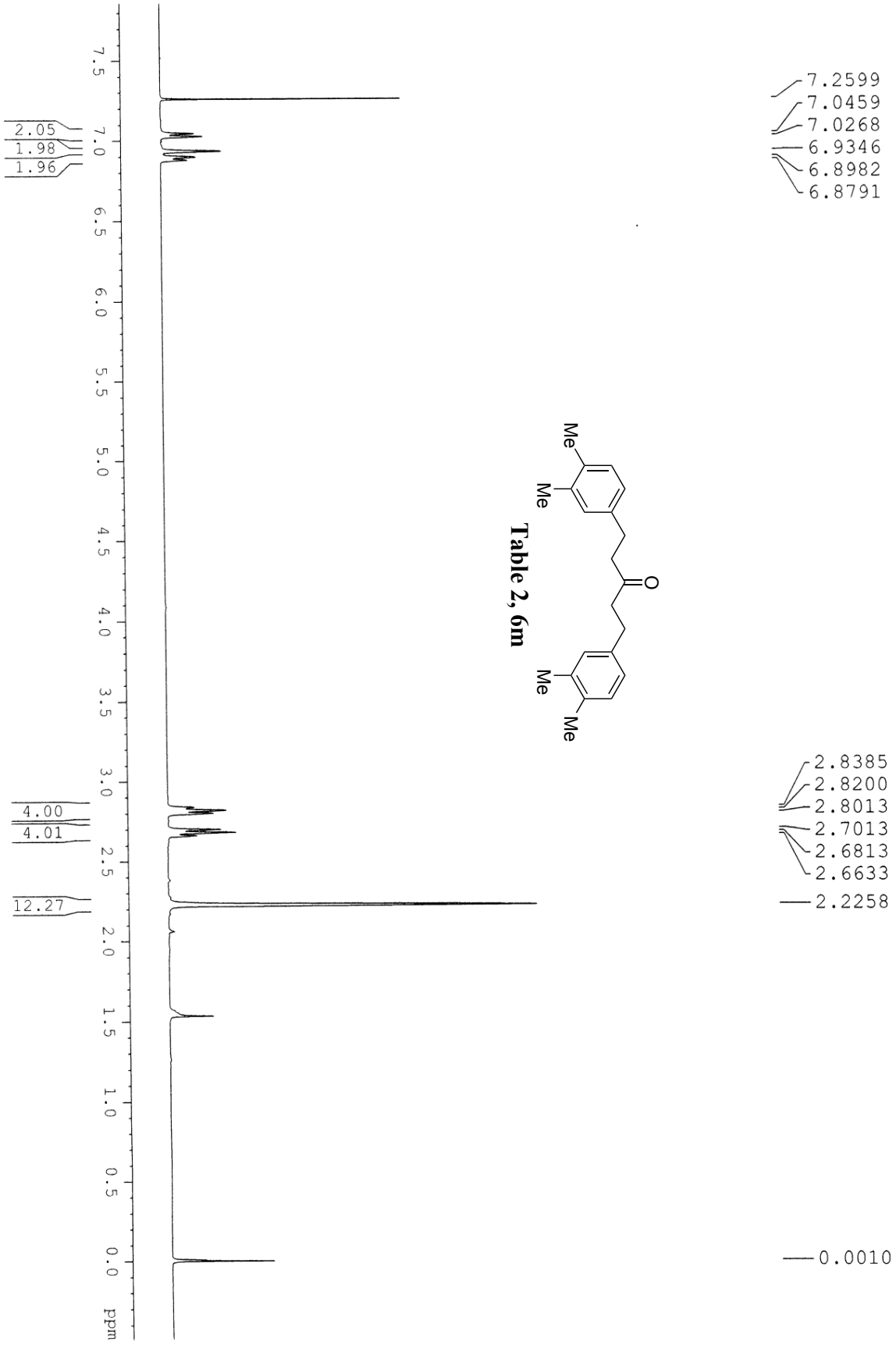

7.2599
7.0459
7.0268
6.9346
6.8982
6.8791
2.8385
2.8200
2.8013
2.7013
2.6813
2.6633
2.2258
0.0010
2.05
1.98
1.96
4.00
4.01
12.27
Me
Me
Me
Me
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6m

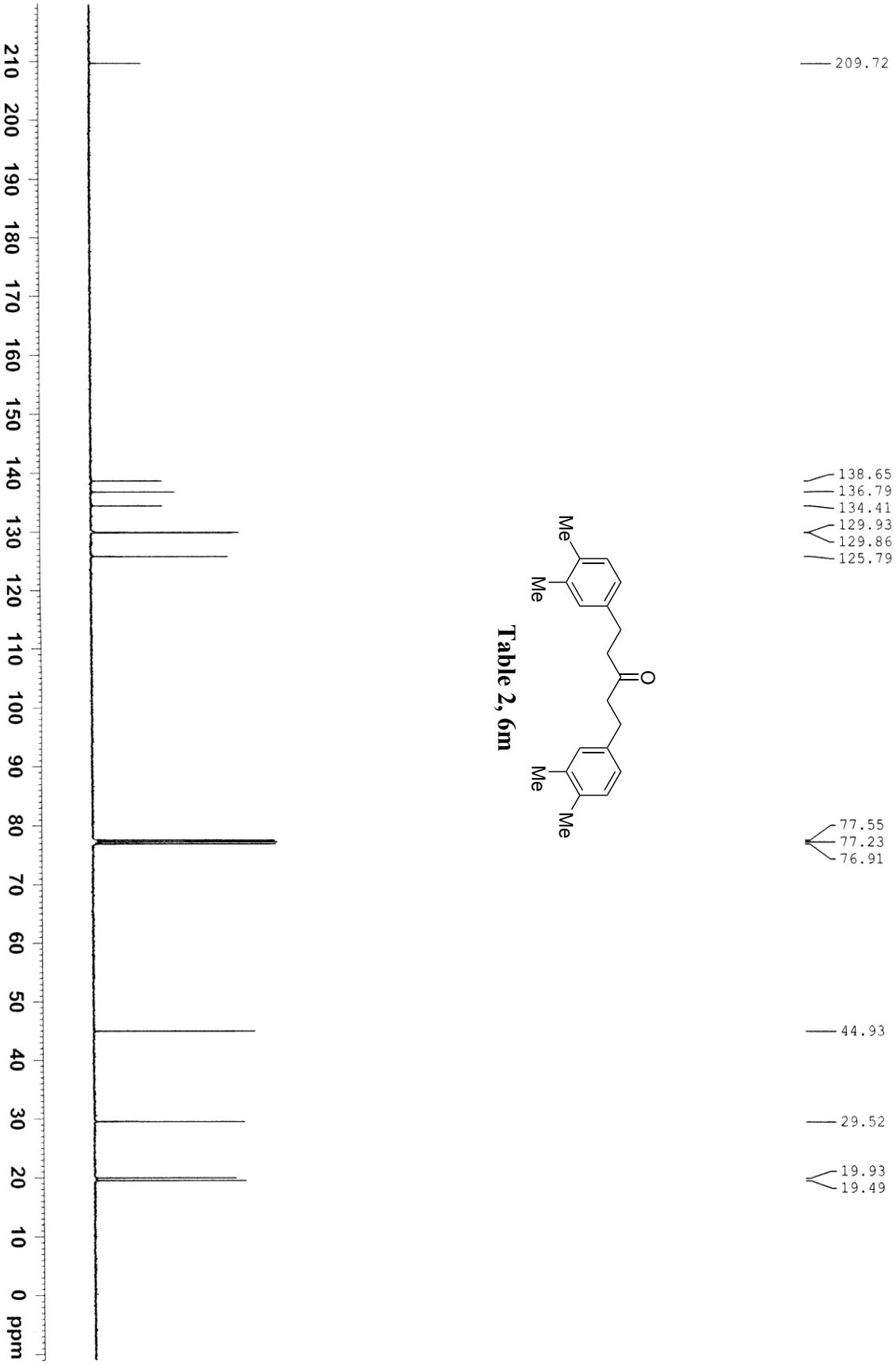

209.72
138.65
136.79
134.41
129.93
129.86
125.79
77.55
77.23
76.91
44.93
29.52
19.93
19.49
Me
Me
Me
Me
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6m

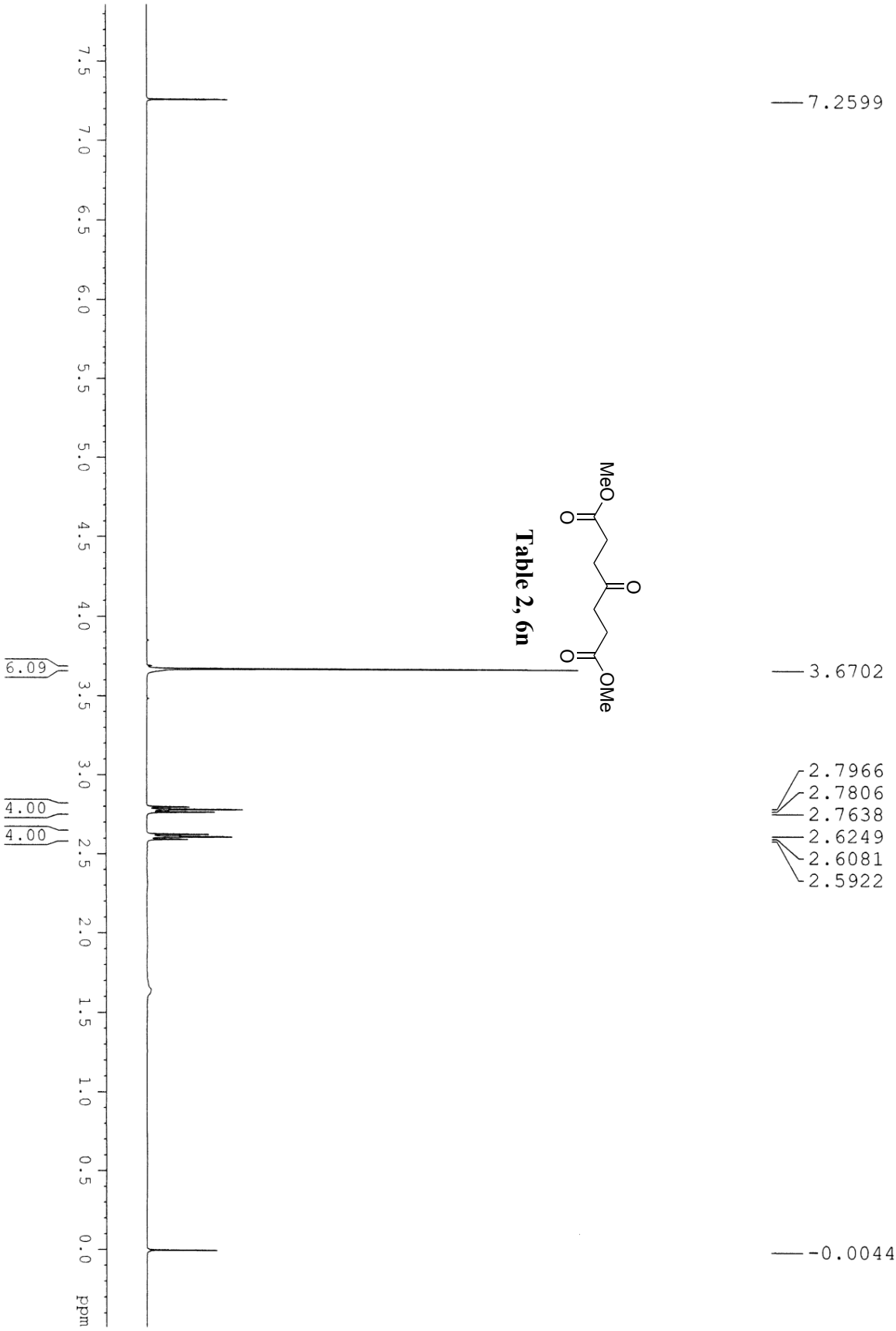


Table 2, 6n
MeO
O
O
O
O
OMe
7.2599
3.6702
2.7966
2.7806
2.7638
2.6249
2.6081
2.5922
-0.0044
6.09
4.00
4.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

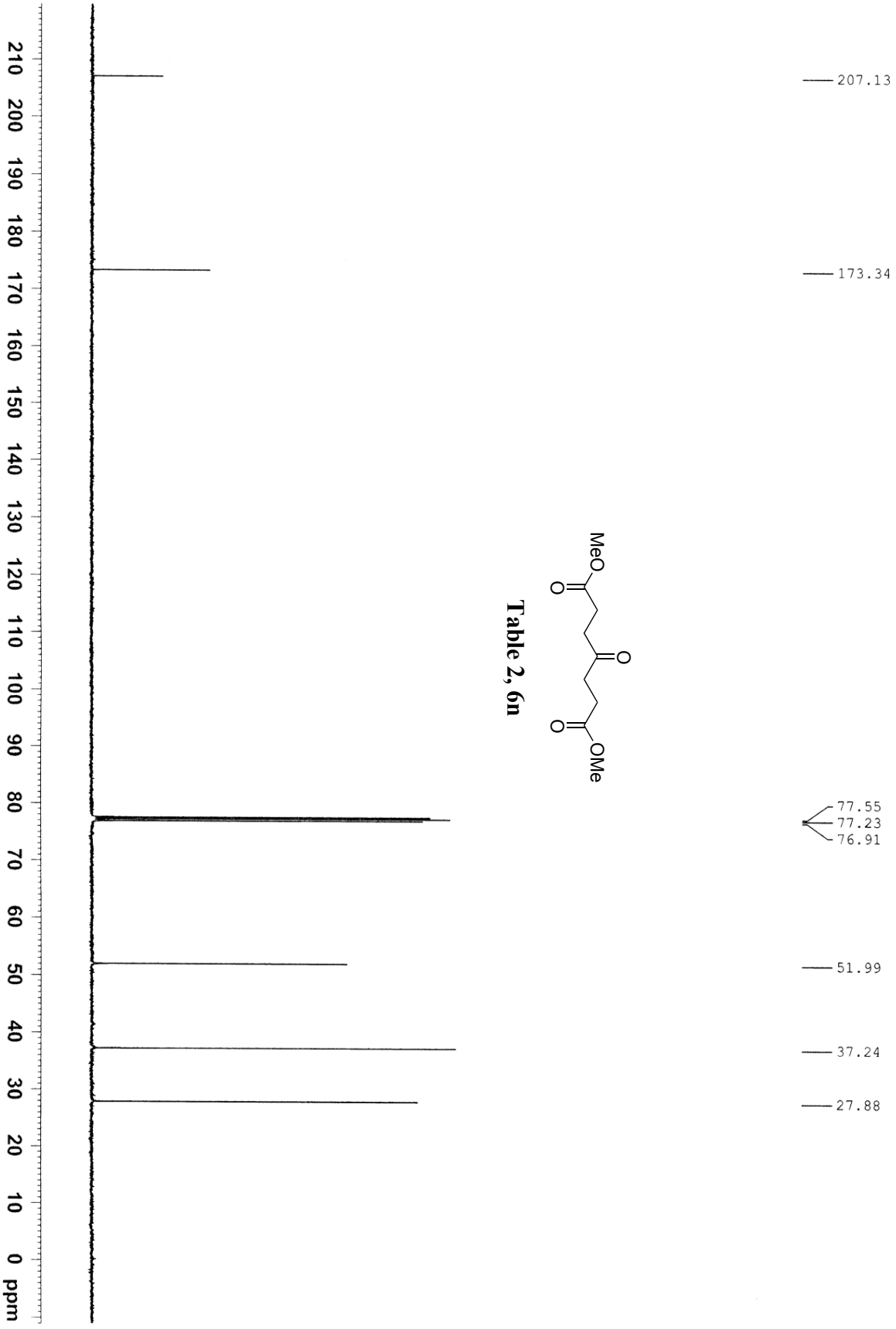

207.13
173.34
77.55
77.23
76.91
51.99
37.24
27.88
MeO
O
O
O
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6n

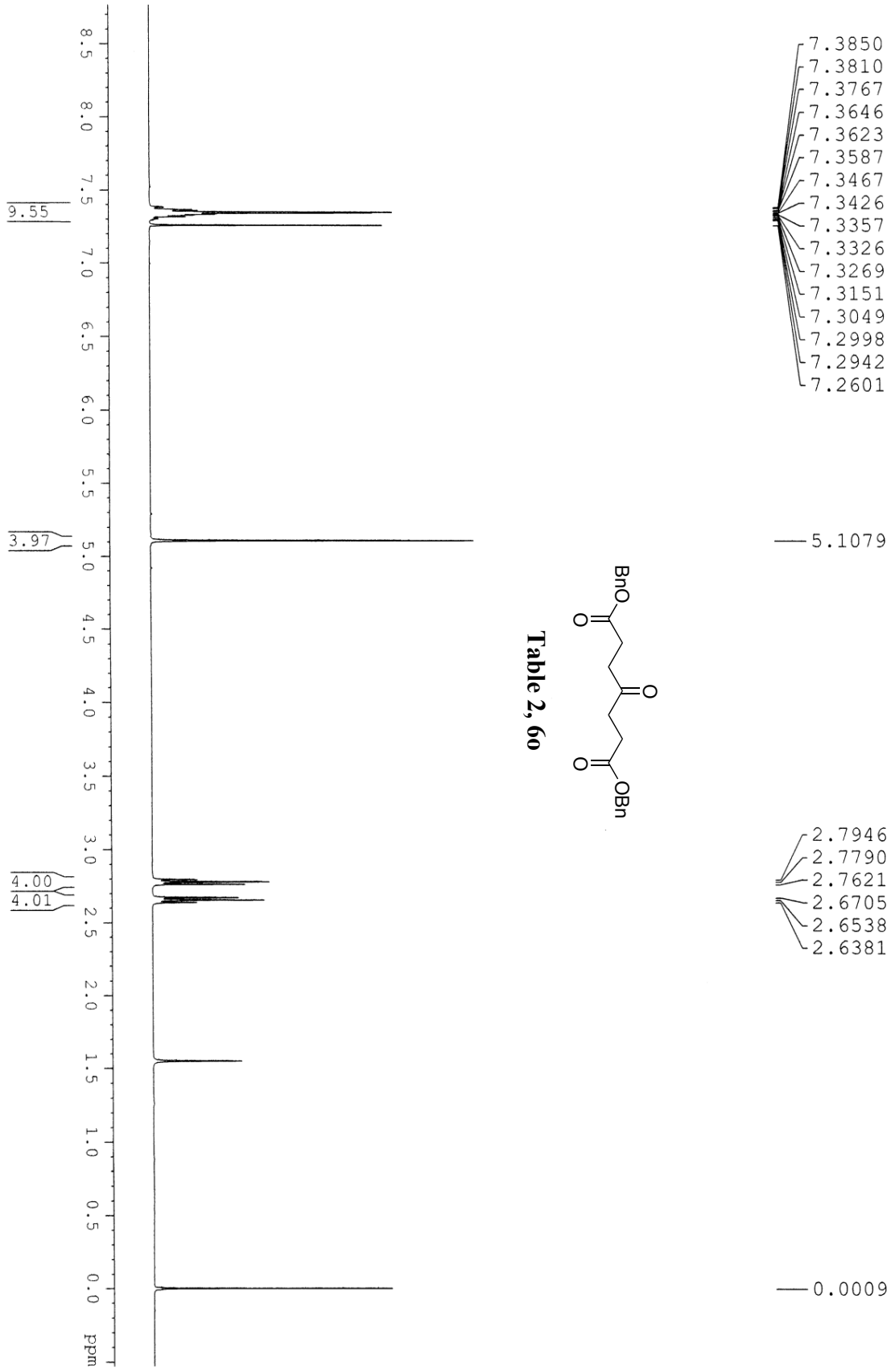

7.3850
7.3810
7.3767
7.3646
7.3623
7.3587
7.3467
7.3426
7.3357
7.3326
7.3269
7.3151
7.3049
7.2998
7.2942
7.2601
5.1079
2.7946
2.7790
2.7621
2.6705
2.6538
2.6381
0.0009
9.55
3.97
4.00
4.01
ppm

Table 2, 6o

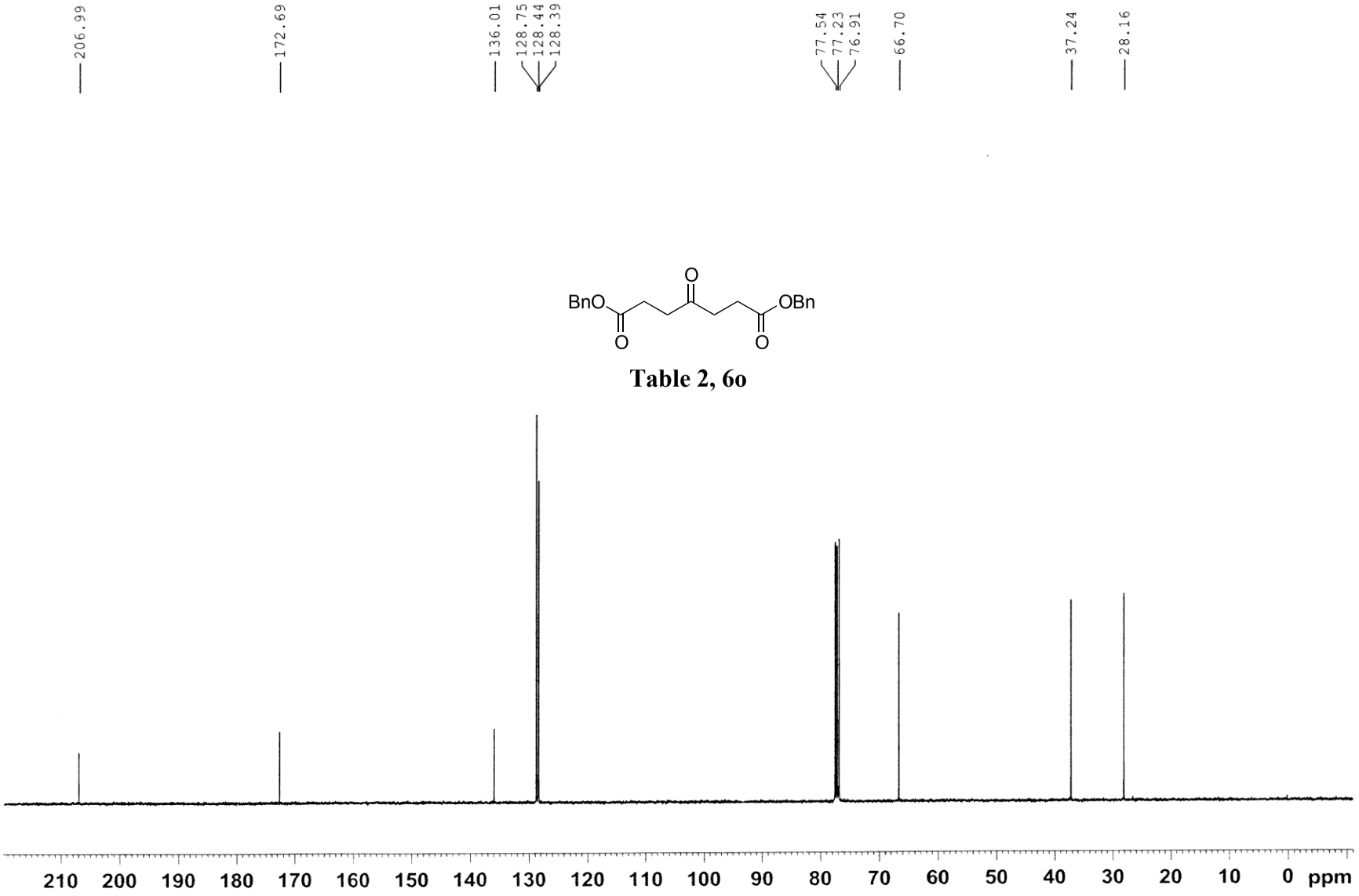

206.99
172.69
136.01
128.75
128.44
128.39
77.54
77.23
76.91
66.70
37.24
28.16
BnO
OBn
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6o

7.2601
2.7624
2.7576
2.7489
2.7450
2.7402
2.7290
2.7014
2.6907
2.6858
2.6733
2.6685
2.4928
2.4744
2.4561
2.4377
1.0679
1.0496
1.0312
-0.0041
4.00
3.96
3.91
5.86
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 2, 6p

Et
O
O
O
Et

210.24
208.42
77.55
77.23
76.91
36.31
36.04
35.88
7.96
Et
O
O
O
O
Et
Table 2, 6p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

7.2873
7.2743
7.2719
7.2542
7.1980
7.1853
7.1808
7.1662
2.8977
2.8796
2.8601
2.7727
2.7645
2.7565
2.7531
2.7360
2.7330
2.3355
2.3275
2.3163
2.3077
2.2994
2.2798
2.2711
1.8204
1.8171
1.8059
1.7862
1.7834
1.7755
1.7616
1.7532
1.7475
1.6684
1.6651
1.6576
1.6539
1.6429
1.6360
1.6285
1.3663
1.3558
1.3314
1.3259
1.3009
1.2819
1.2710
1.2641
1.2580
1.2392
1.2334
1.2200
1.2097
1.1923
1.1839
1.1672
1.1621
0.0012

Table 2, 6q

O

2.62
2.91
2.00
2.03
0.98
5.79
5.72
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

213.37
141.62
128.63
128.52
126.20
77.55
77.23
76.91
51.17
42.43
29.93
28.60
26.03
25.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6q

7.5669
7.5625
7.5506
7.5461
7.2934
7.2726
7.2600
2.9536
2.9352
2.9170
2.7852
2.7673
2.7492
2.3774
2.3681
2.3585
2.3493
2.3367
2.3286
2.3208
2.3088
2.3006
2.2926
2.2810
2.2725
2.2643
1.7976
1.7843
1.7693
1.7527
1.7470
1.6720
1.6612
1.6571
1.6490
1.6449
1.6368
1.3424
1.3076
1.2833
1.2610
1.2554
1.2365
1.2311
1.2163
1.2077
1.1963
1.1883
1.1806
1.1640
1.1569
1.1497
-0.0025
1.87
1.97
2.00
2.01
1.07
4.35
1.22
5.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

Table 2, 6r

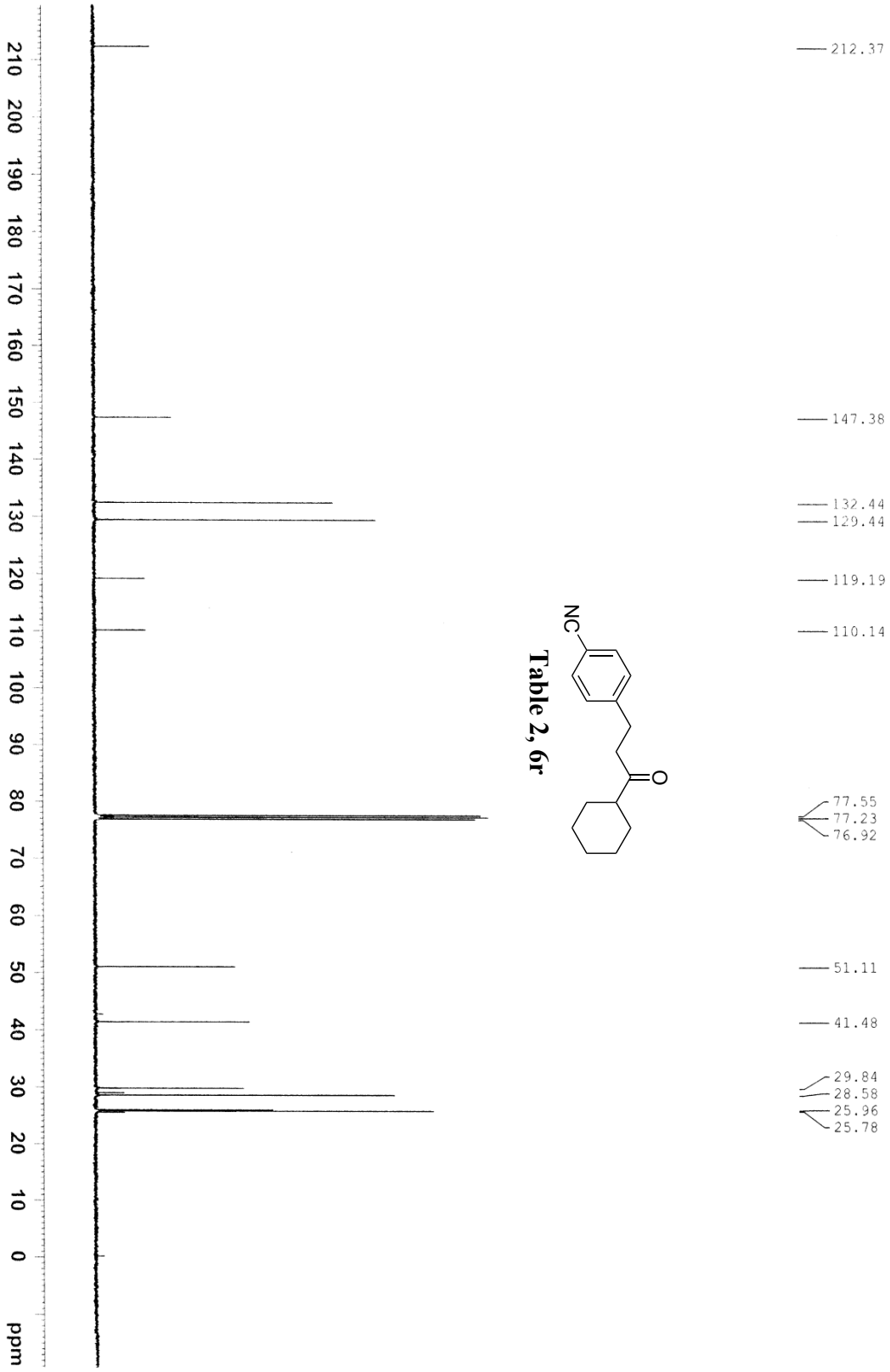

212.37
147.38
132.44
129.44
119.19
110.14
77.55
77.23
76.92
51.11
41.48
29.84
28.58
25.96
25.78
NC
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 2, 6r

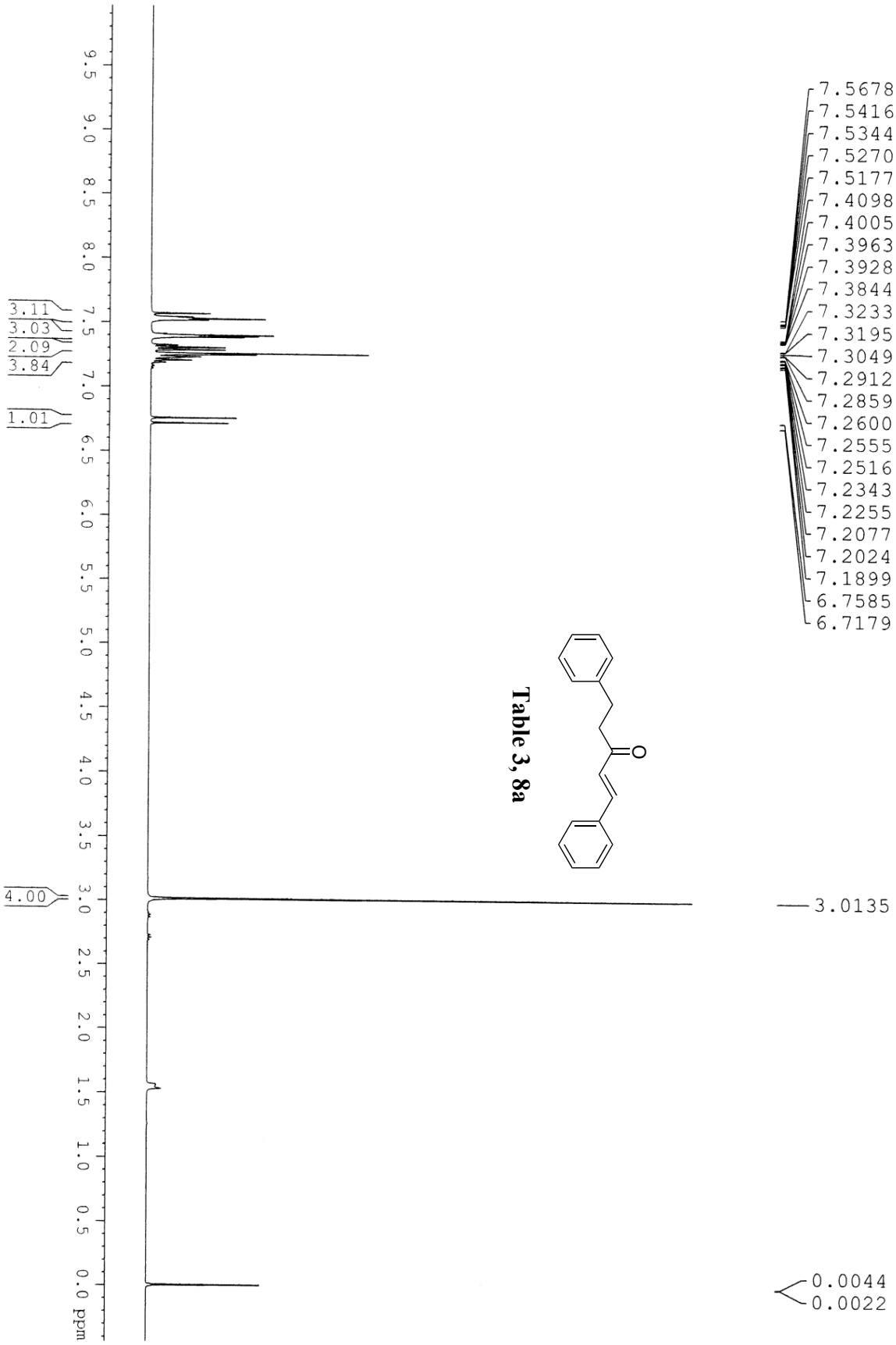

7.5678
7.5416
7.5344
7.5270
7.5177
7.4098
7.4005
7.3963
7.3928
7.3844
7.3233
7.3195
7.3049
7.2912
7.2859
7.2600
7.2555
7.2516
7.2343
7.2255
7.2077
7.2024
7.1899
6.7585
6.7179
3.11
3.03
2.09
3.84
1.01
4.00
3.0135
0.0044
0.0022
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
O

Table 3, 8a

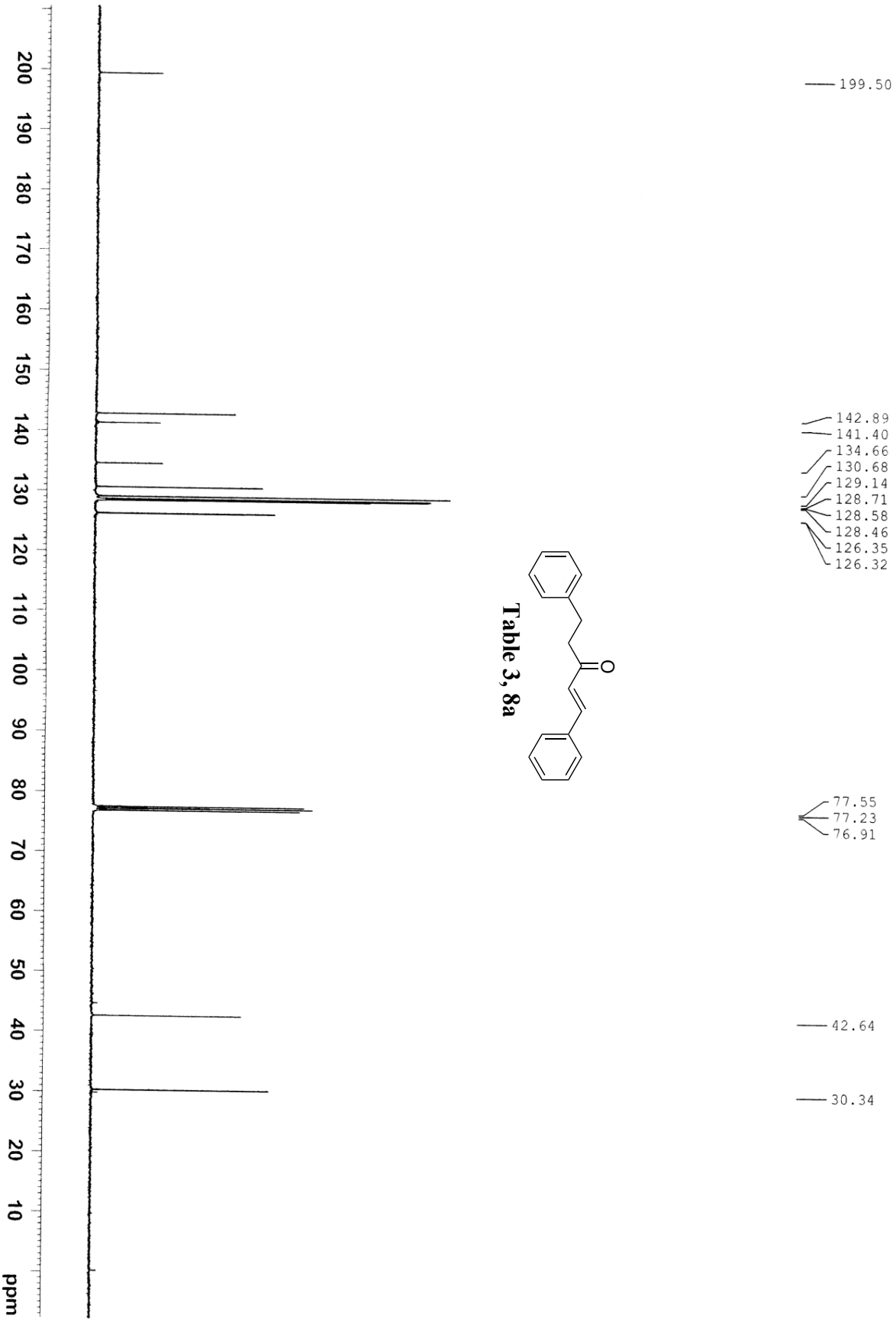
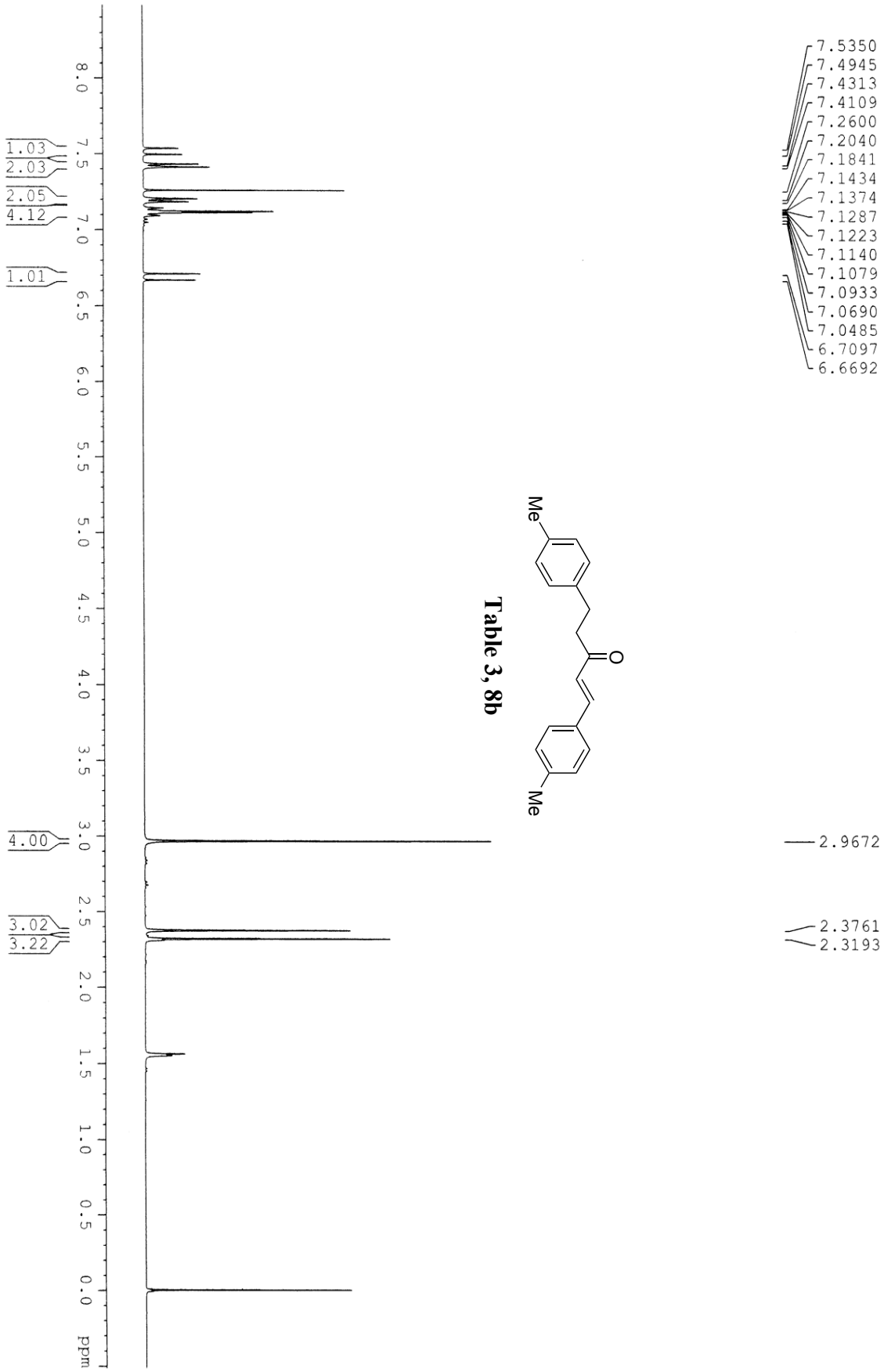
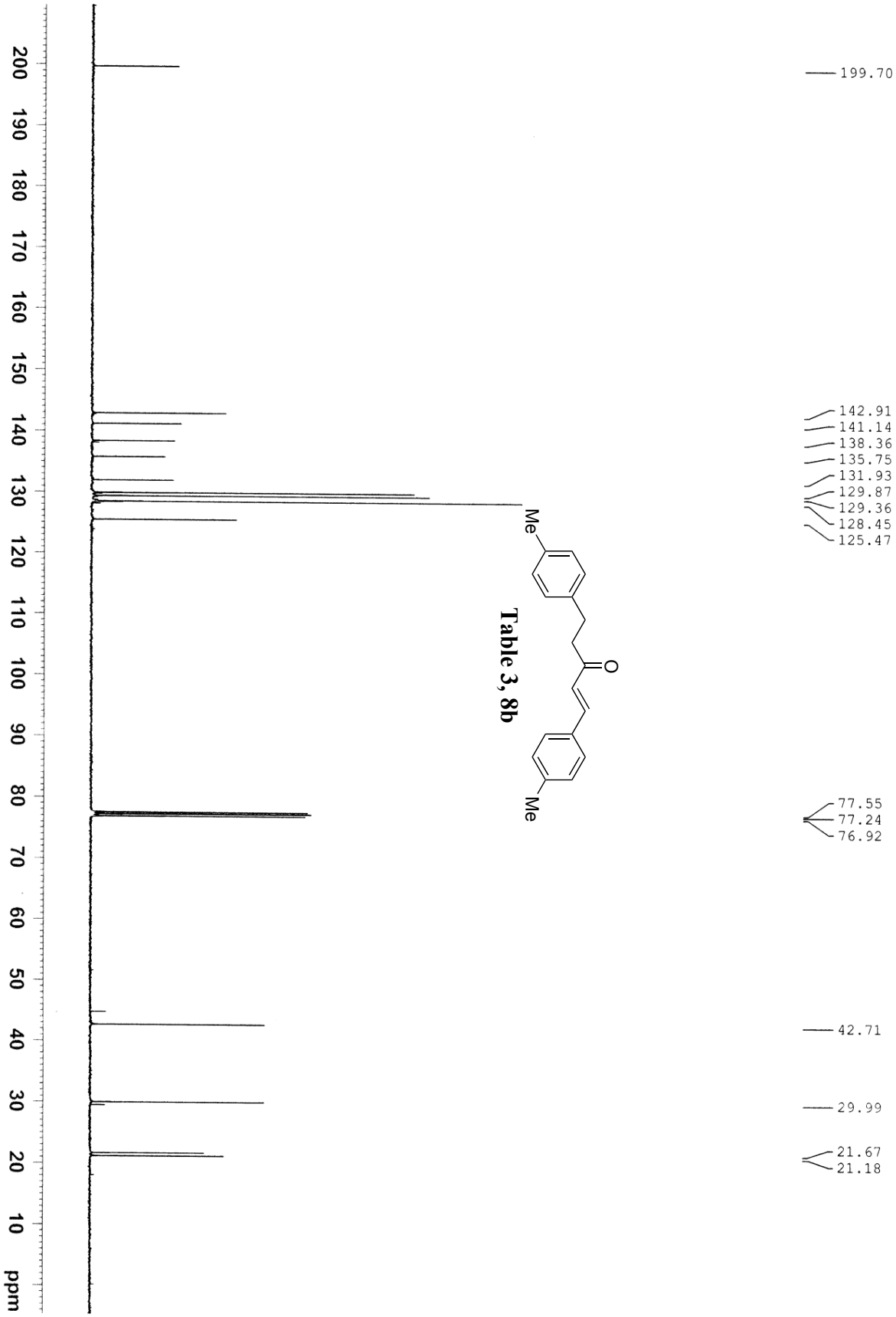

199.50
142.89
141.40
134.66
130.68
129.14
128.71
128.58
128.46
126.35
126.32
77.55
77.23
76.91
42.64
30.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm
O

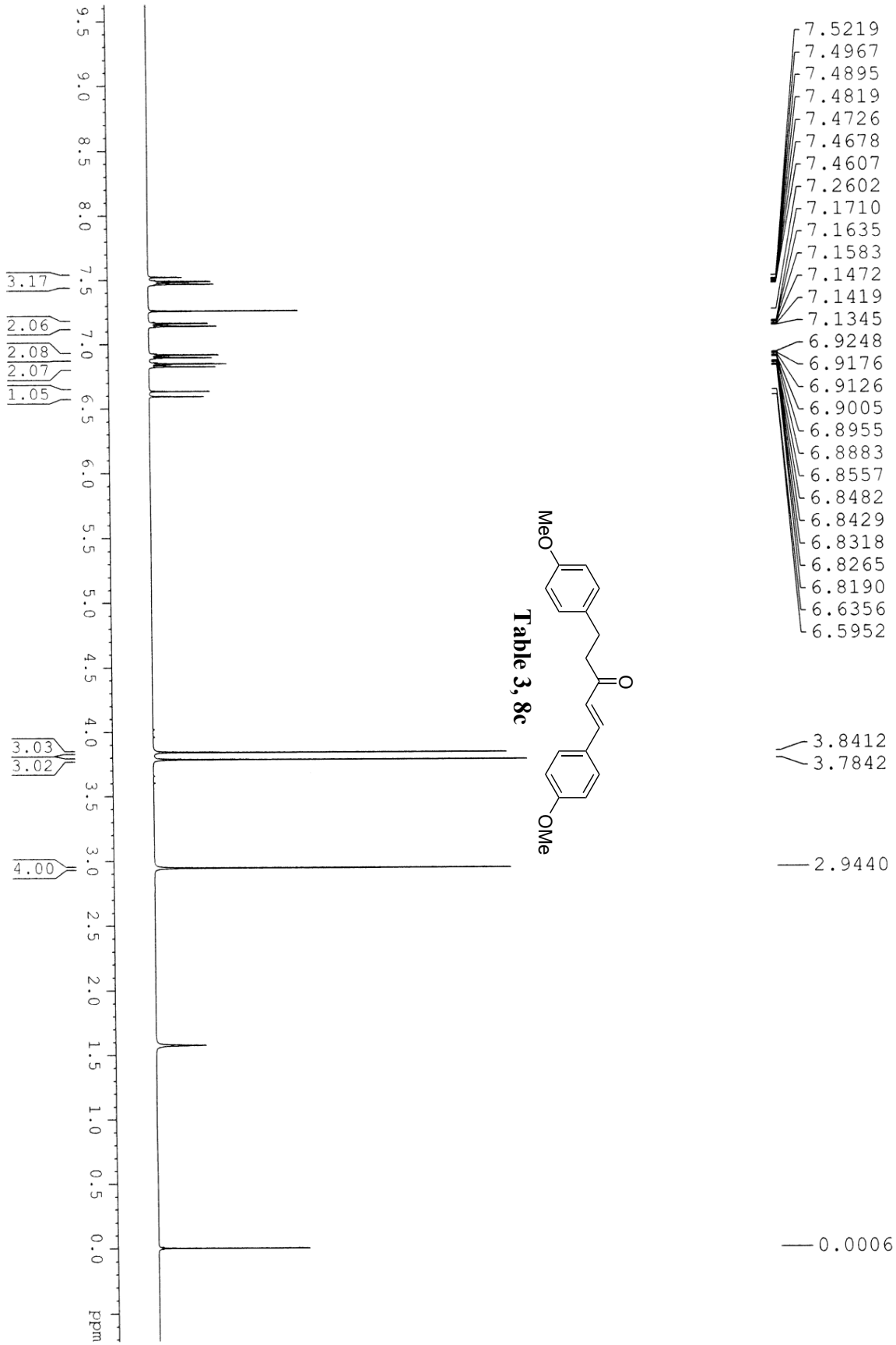
Table 3, 8a

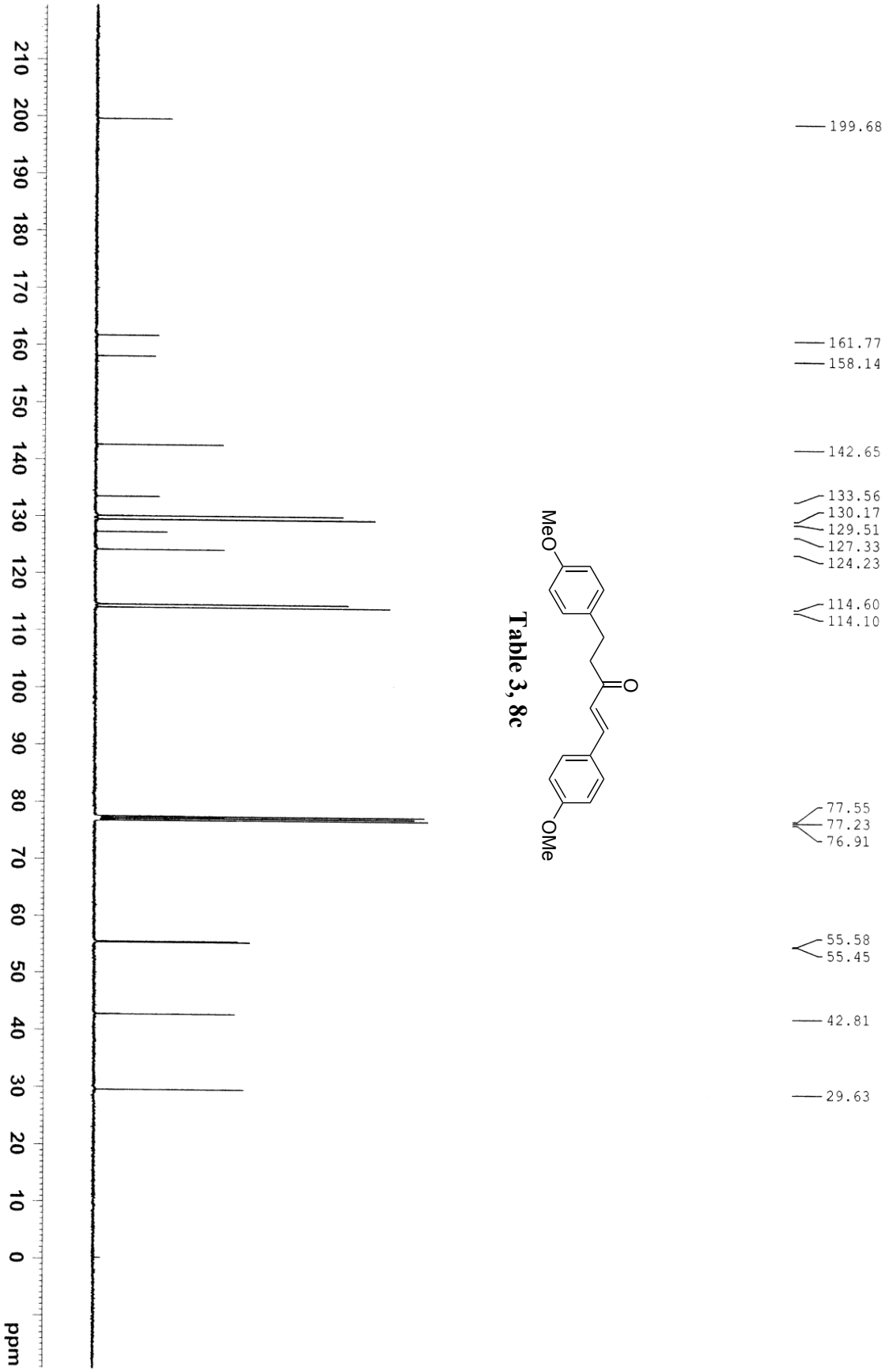

7.5350
7.4945
7.4313
7.4109
7.2600
7.2040
7.1841
7.1434
7.1374
7.1287
7.1223
7.1140
7.1079
7.0933
7.0690
7.0485
6.7097
6.6692
1.03
2.03
2.05
4.12
1.01
4.00
3.02
3.22
2.9672
2.3761
2.3193
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Me
O
Me

Table 3, 8b


199.70
142.91
141.14
138.36
135.75
131.93
129.87
129.36
128.45
125.47
77.55
77.24
76.92
42.71
29.99
21.67
21.18
Me
Me
O
Table 3, 8b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.5219
7.4967
7.4895
7.4819
7.4726
7.4678
7.4607
7.2602
7.1710
7.1635
7.1583
7.1472
7.1419
7.1345
6.9248
6.9176
6.9126
6.9005
6.8955
6.8883
6.8557
6.8482
6.8429
6.8318
6.8265
6.8190
6.6356
6.5952
3.8412
3.7842
2.9440
0.0006
3.17
2.06
2.08
2.07
1.05
3.03
3.02
4.00
MeO
OMe
O
Table 3, 8c
ppm


199.68
161.77
158.14
142.65
133.56
130.17
129.51
127.33
124.23
114.60
114.10
77.55
77.23
76.91
55.58
55.45
42.81
29.63
MeO
OMe
O
Table 3, 8c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

7.5028
7.4704
7.4644
7.4483
7.4437
7.4382
7.3802
7.3744
7.3694
7.3577
7.3529
7.3470
7.2667
7.2599
7.2507
7.2455
7.2394
7.1763
7.1702
7.1651
7.1539
7.1491
6.7058
6.6653
2.9709
-0.0003
3.14
2.05
3.94
2.01
1.02
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Cl
O
Cl

Table 3, 8d

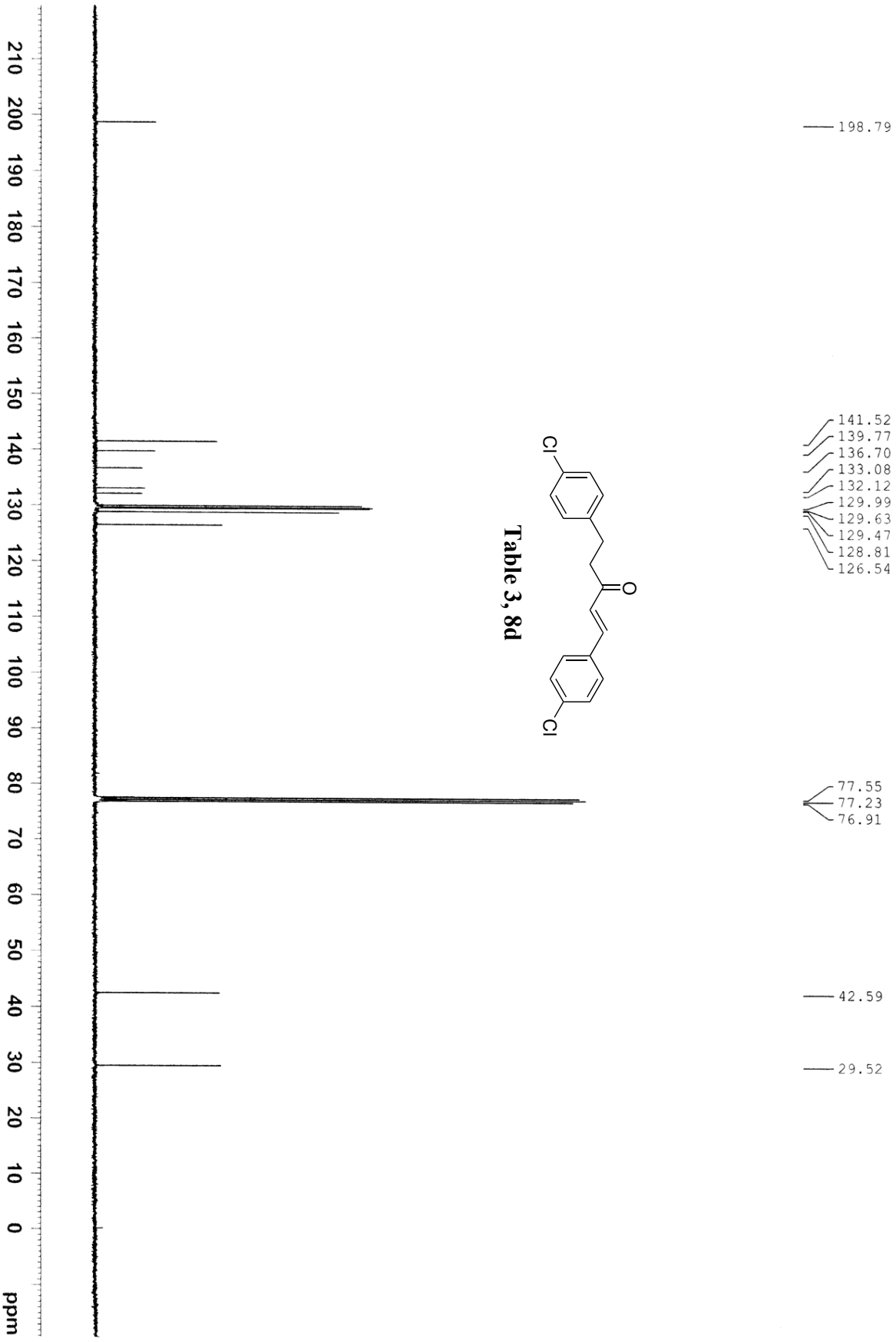

198.79
141.52
139.77
136.70
133.08
132.12
129.99
129.63
129.47
128.81
126.54
77.55
77.23
76.91
42.59
29.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
Cl
O
Cl

Table 3, 8d

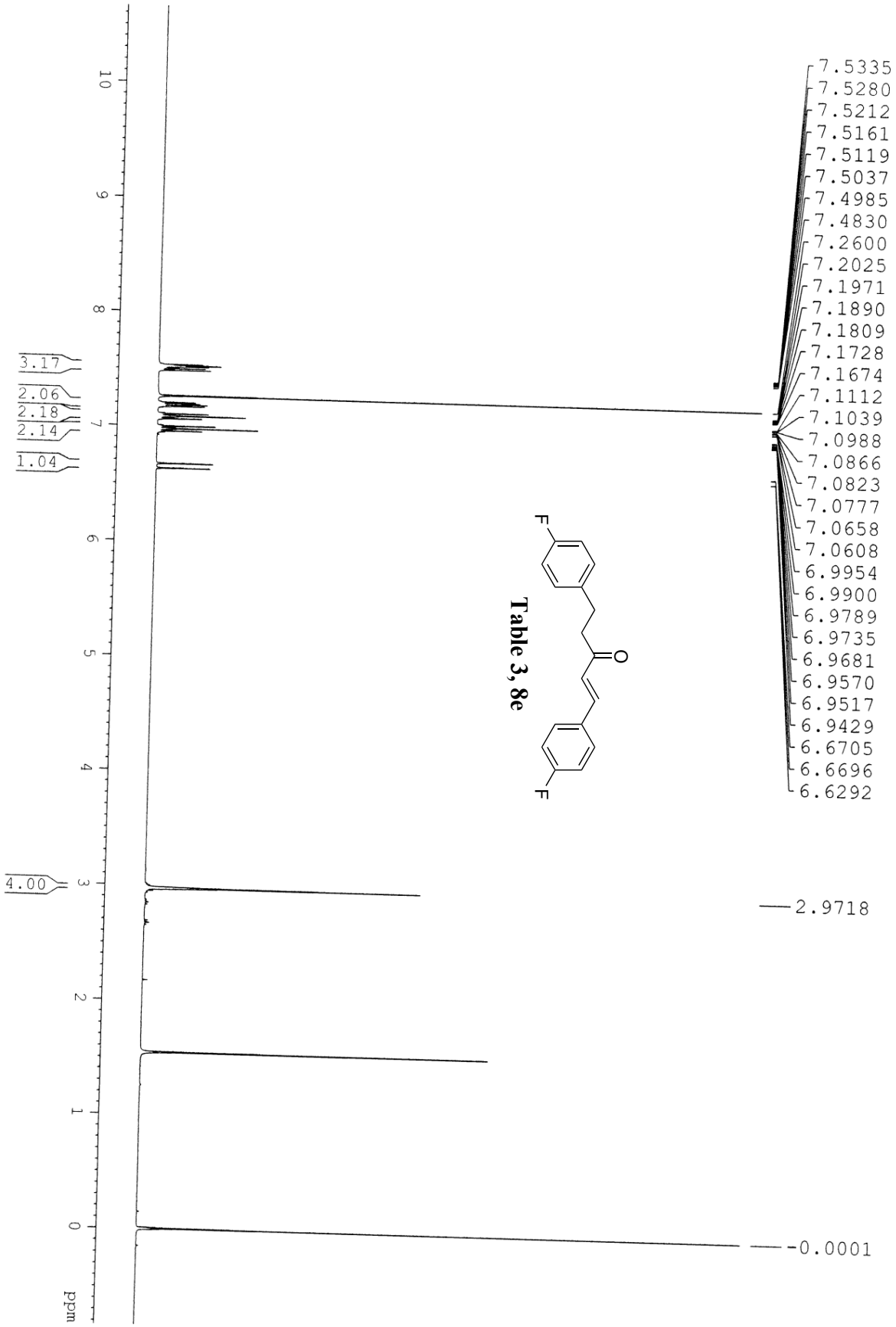
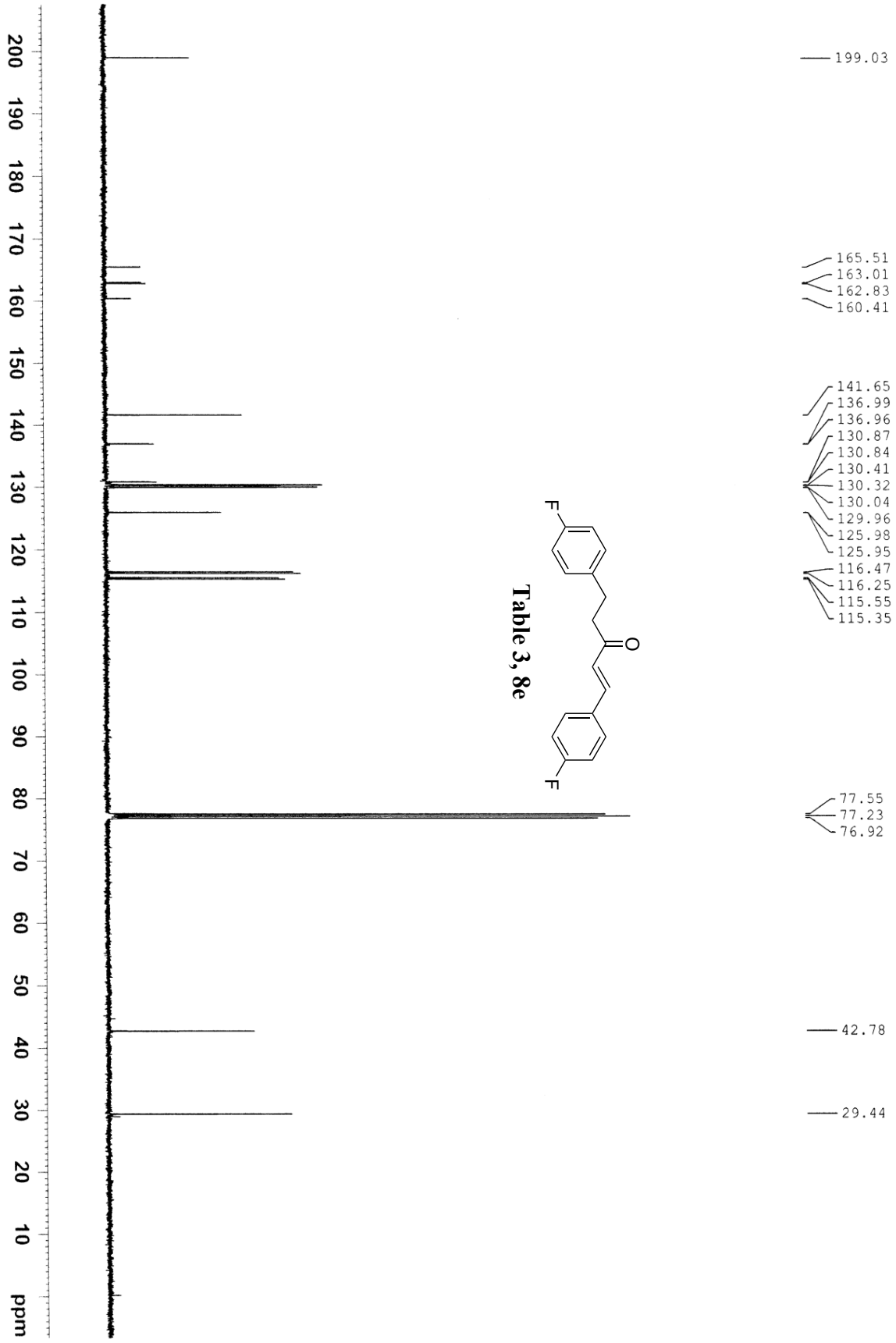
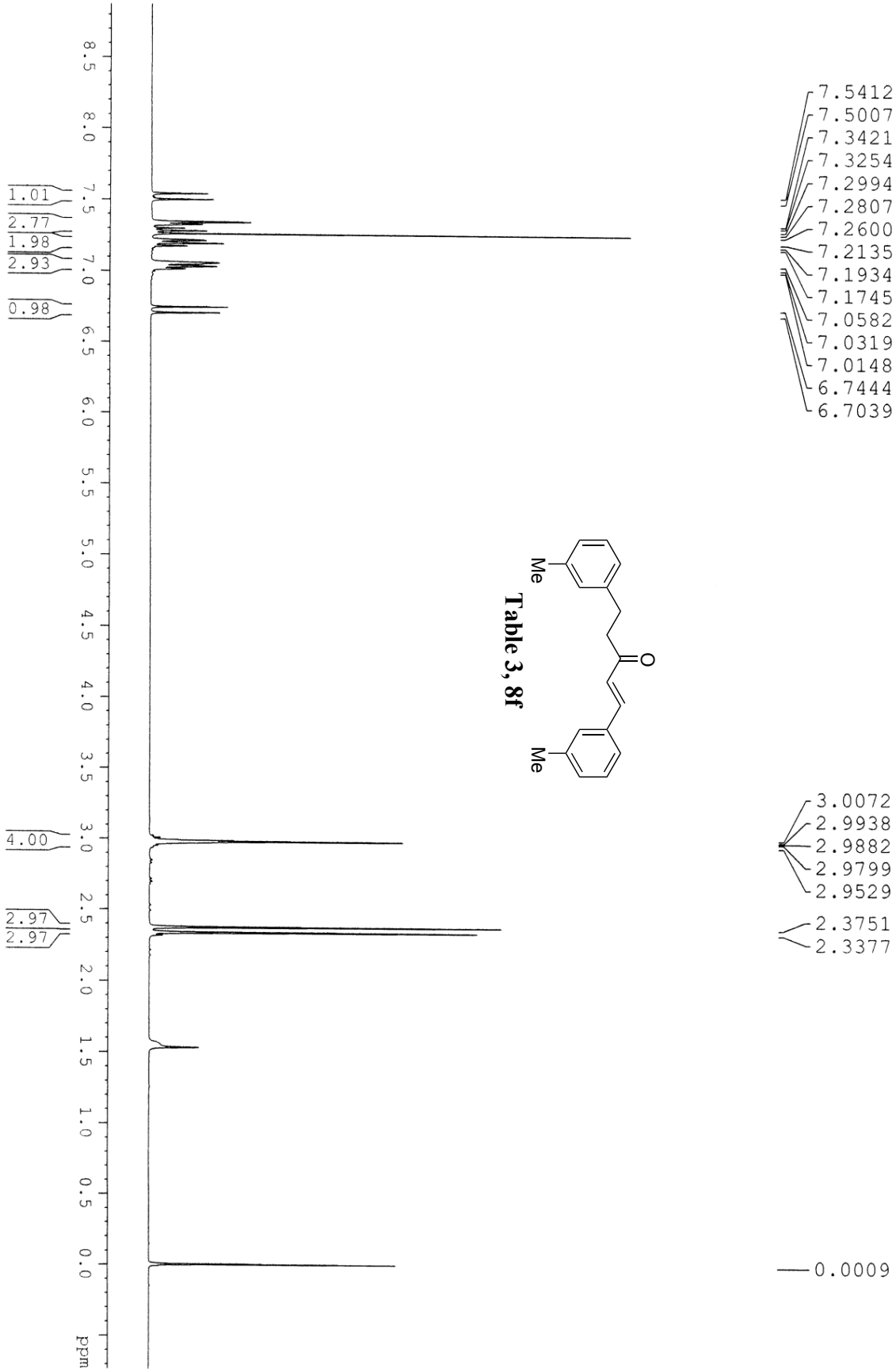
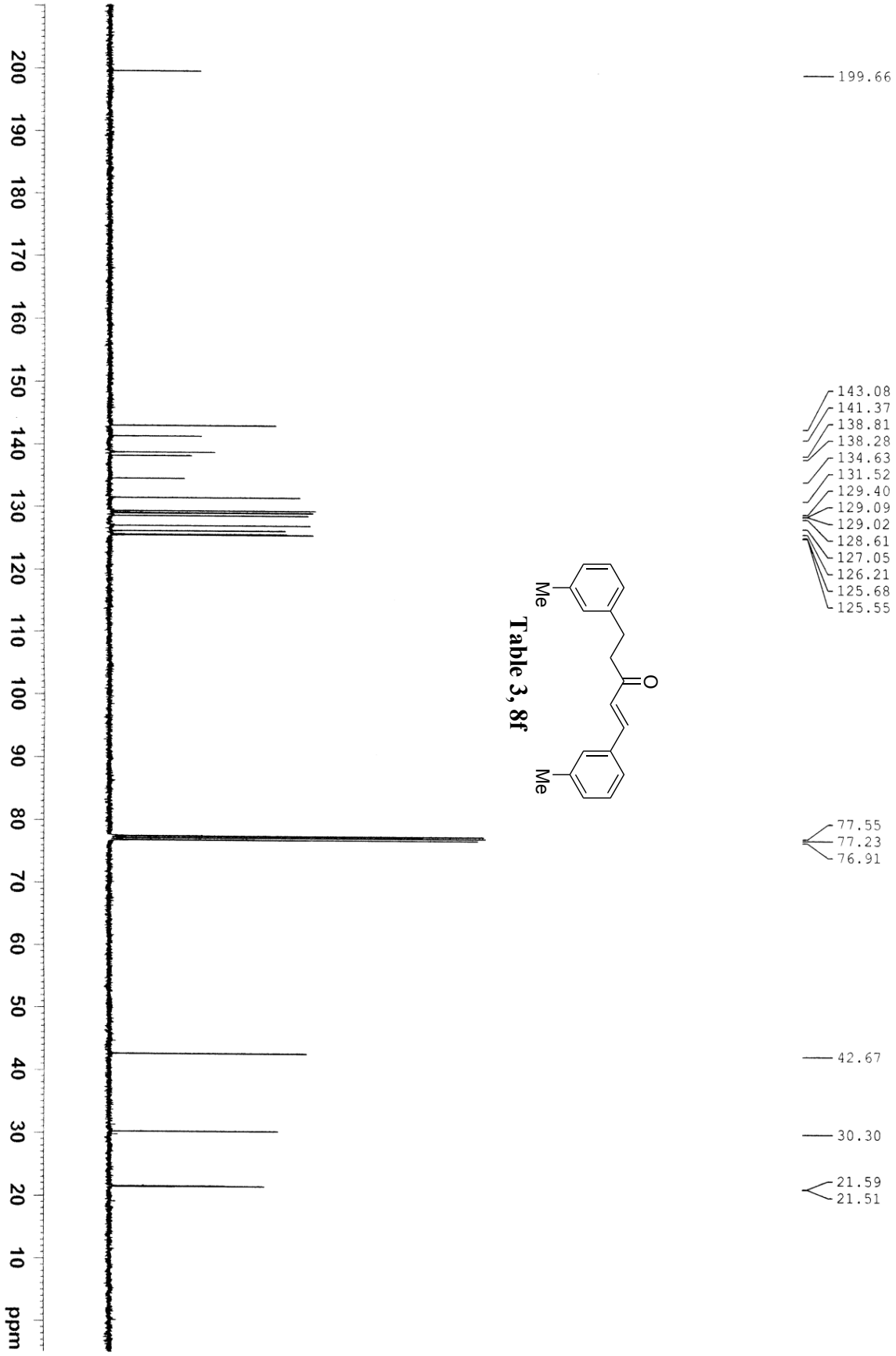

7.5335
7.5280
7.5212
7.5161
7.5119
7.5037
7.4985
7.4830
7.2600
7.2025
7.1971
7.1890
7.1809
7.1728
7.1674
7.1112
7.1039
7.0988
7.0866
7.0823
7.0777
7.0658
7.0608
6.9954
6.9900
6.9789
6.9735
6.9681
6.9570
6.9517
6.9429
6.6705
6.6696
6.6292
3.17
2.06
2.18
2.14
1.04
4.00
2.9718
-0.0001
ppm
F
O
F

Table 3, 8e


199.03
165.51
163.01
162.83
160.41
141.65
136.99
136.96
130.87
130.84
130.41
130.32
130.04
129.96
125.98
125.95
116.47
116.25
115.55
115.35
77.55
77.23
76.92
42.78
29.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
F
O
F
Table 3, 8e


7.5412
7.5007
7.3421
7.3254
7.2994
7.2807
7.2600
7.2135
7.1934
7.1745
7.0582
7.0319
7.0148
6.7444
6.7039
Me
O
Me
Table 3, 8f
3.0072
2.9938
2.9882
2.9799
2.9529
2.3751
2.3377
0.0009
1.01
2.77
1.98
2.93
0.98
4.00
2.97
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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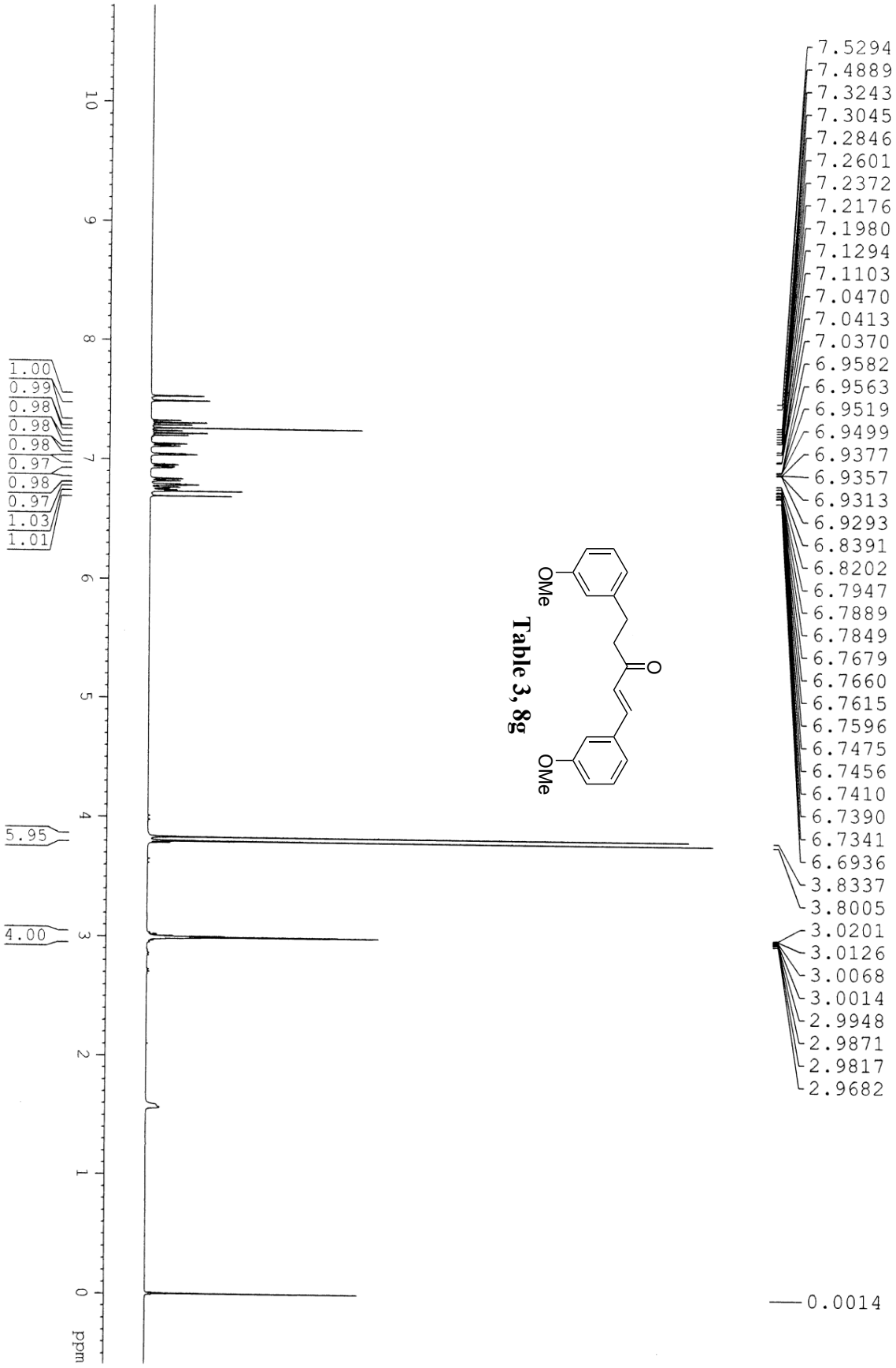
143.08
141.37
138.81
138.28
134.63
131.52
129.40
129.09
129.02
128.61
127.05
126.21
125.68
125.55
77.55
77.23
76.91
42.67
30.30
21.59
21.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Me
O
Me

Table 3, 8f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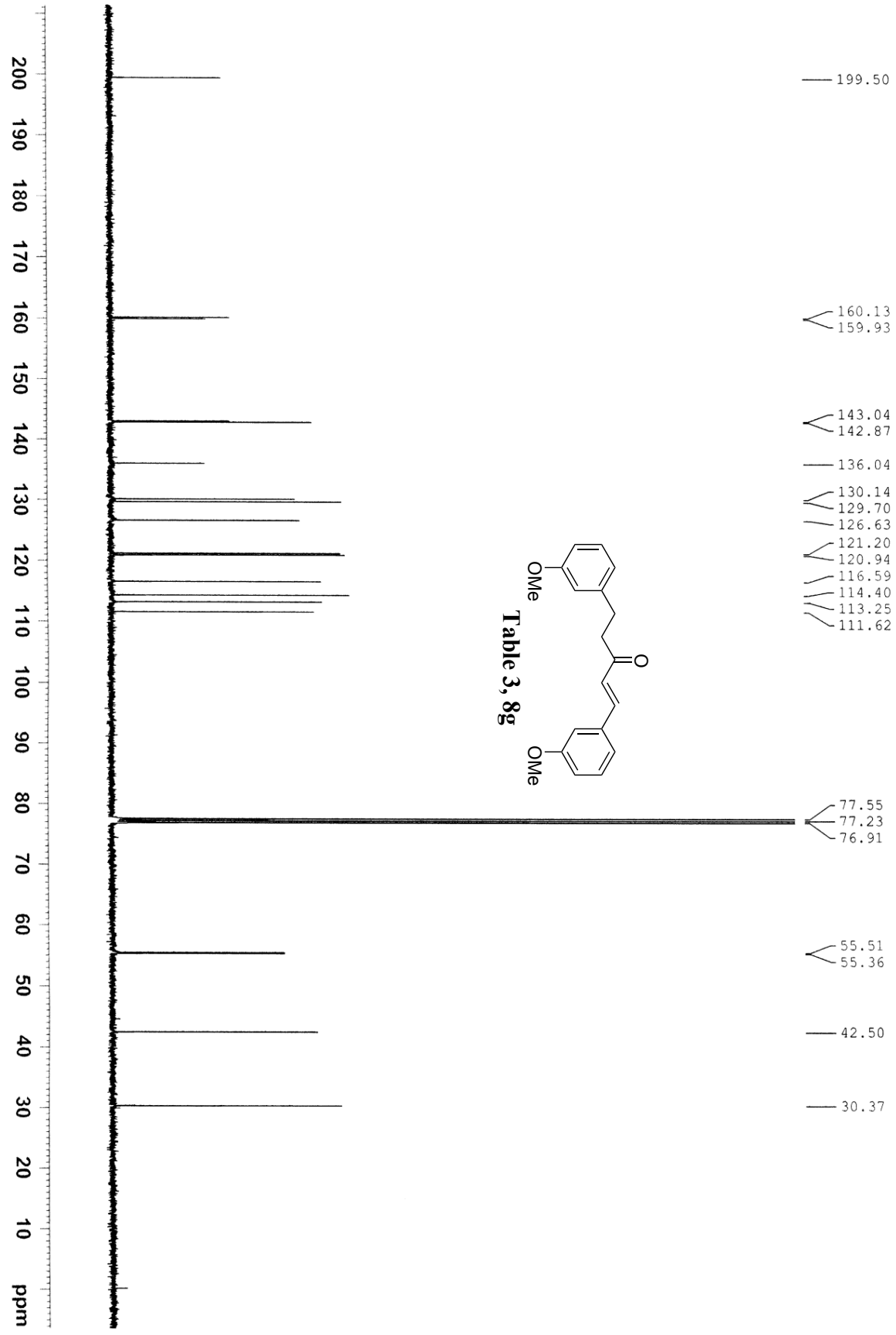
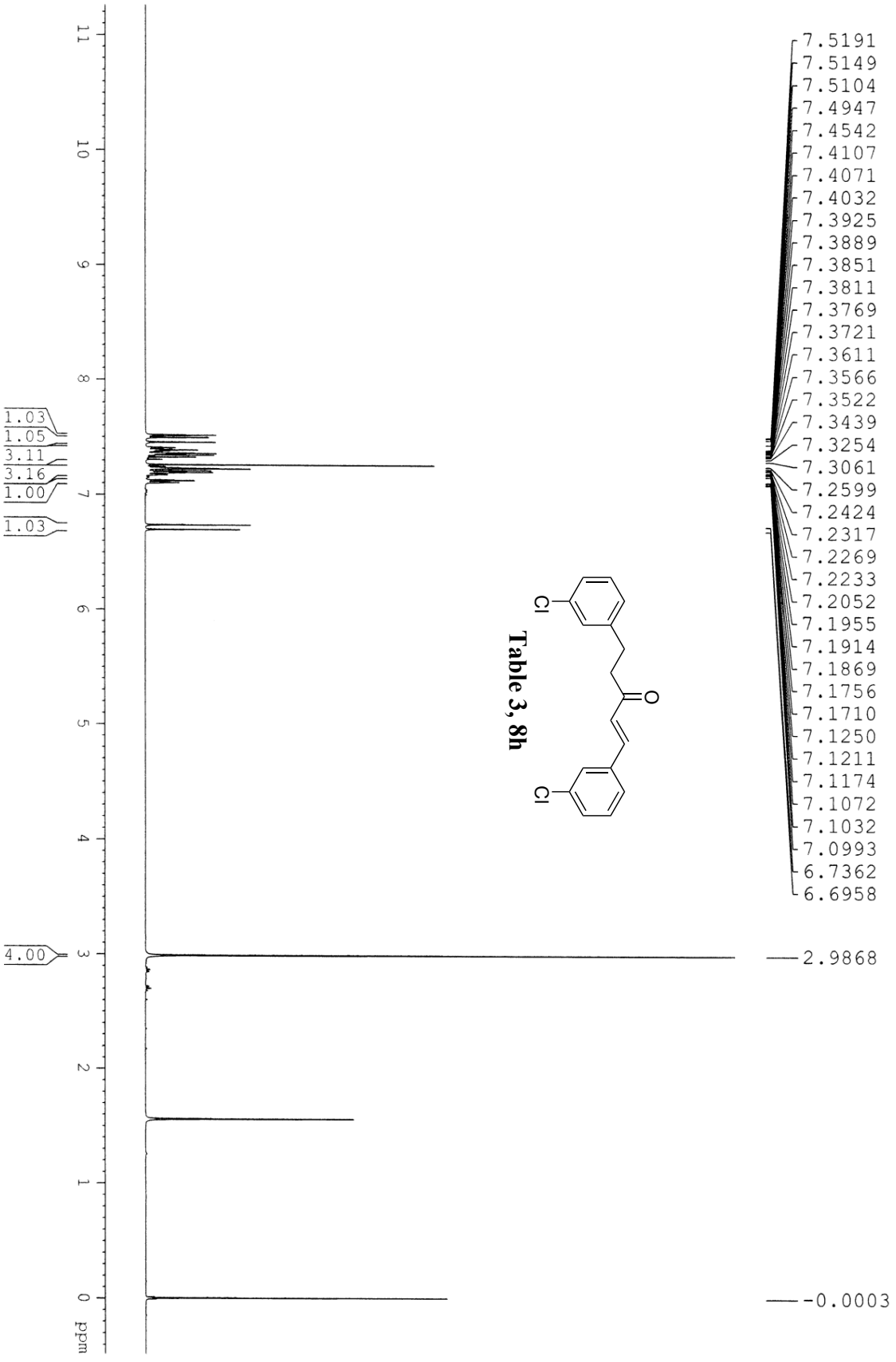
7.4889
7.3243
7.3045
7.2846
7.2601
7.2372
7.2176
7.1980
7.1294
7.1103
7.0470
7.0413
7.0370
6.9582
6.9563
6.9519
6.9499
6.9377
6.9357
6.9313
6.9293
6.8391
6.8202
6.7947
6.7889
6.7849
6.7679
6.7660
6.7615
6.7596
6.7475
6.7456
6.7410
6.7390
6.7341
6.6936
3.8337
3.8005
3.0201
3.0126
3.0068
3.0014
2.9948
2.9871
2.9817
2.9682
0.0014
1.00
0.99
0.98
0.98
0.98
0.97
0.98
0.97
1.03
1.01
5.95
4.00
OMe
OMe
O
Table 3, 8g
10
9
8
7
6
5
4
3
2
1
0
ppm


199.50
160.13
159.93
143.04
142.87
136.04
130.14
129.70
126.63
121.20
120.94
116.59
114.40
113.25
111.62
77.55
77.23
76.91
55.51
55.36
42.50
30.37
OMe
OMe
O
Table 3, 8g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.5191
7.5149
7.5104
7.4947
7.4542
7.4107
7.4071
7.4032
7.3925
7.3889
7.3851
7.3811
7.3769
7.3721
7.3611
7.3566
7.3522
7.3439
7.3254
7.3061
7.2599
7.2424
7.2317
7.2269
7.2233
7.2052
7.1955
7.1914
7.1869
7.1756
7.1710
7.1250
7.1211
7.1174
7.1072
7.1032
7.0993
6.7362
6.6958
2.9868
-0.0003
1.03
1.05
3.11
3.16
1.00
1.03
4.00
Cl
O
Cl
Table 3, 8h
ppm

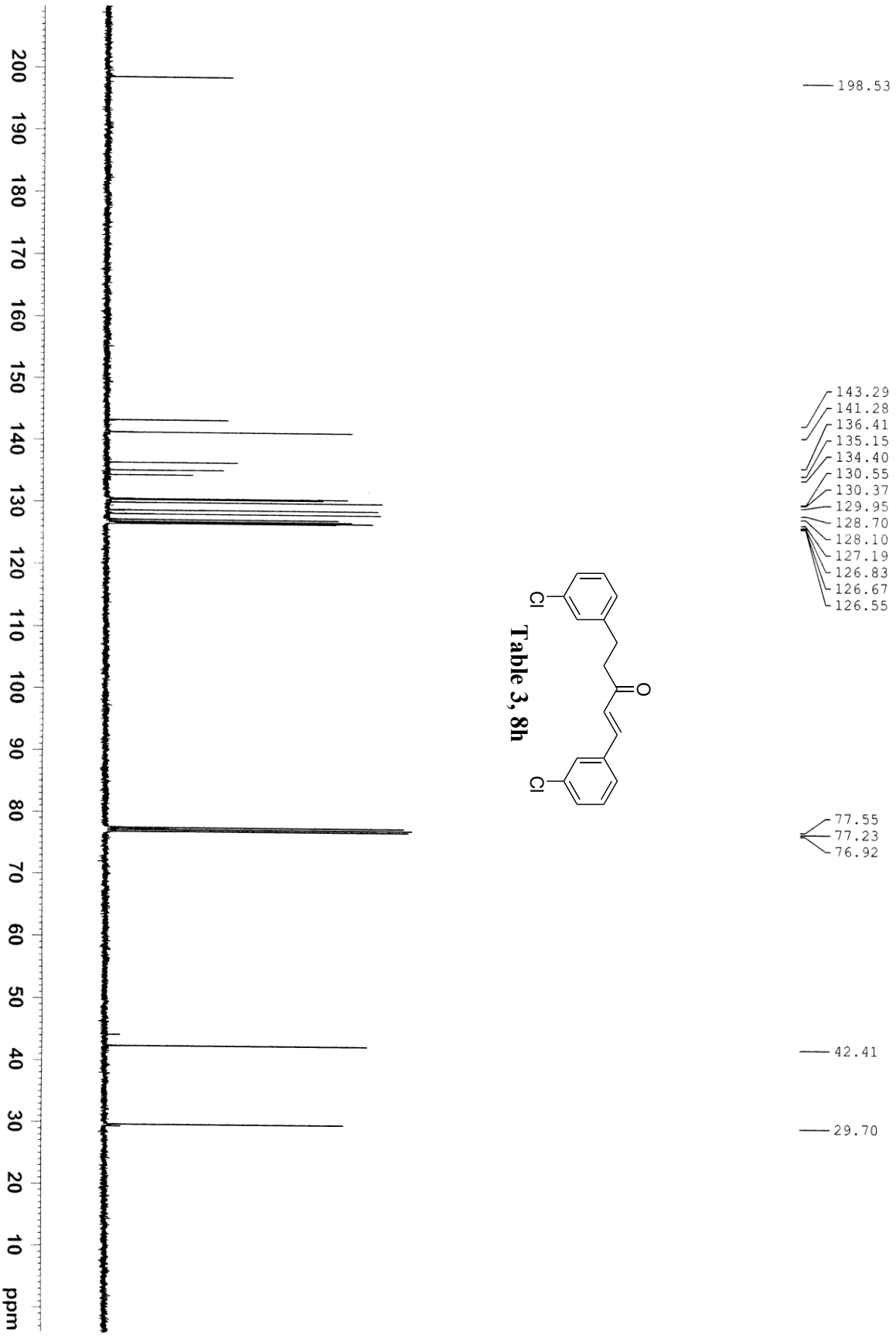
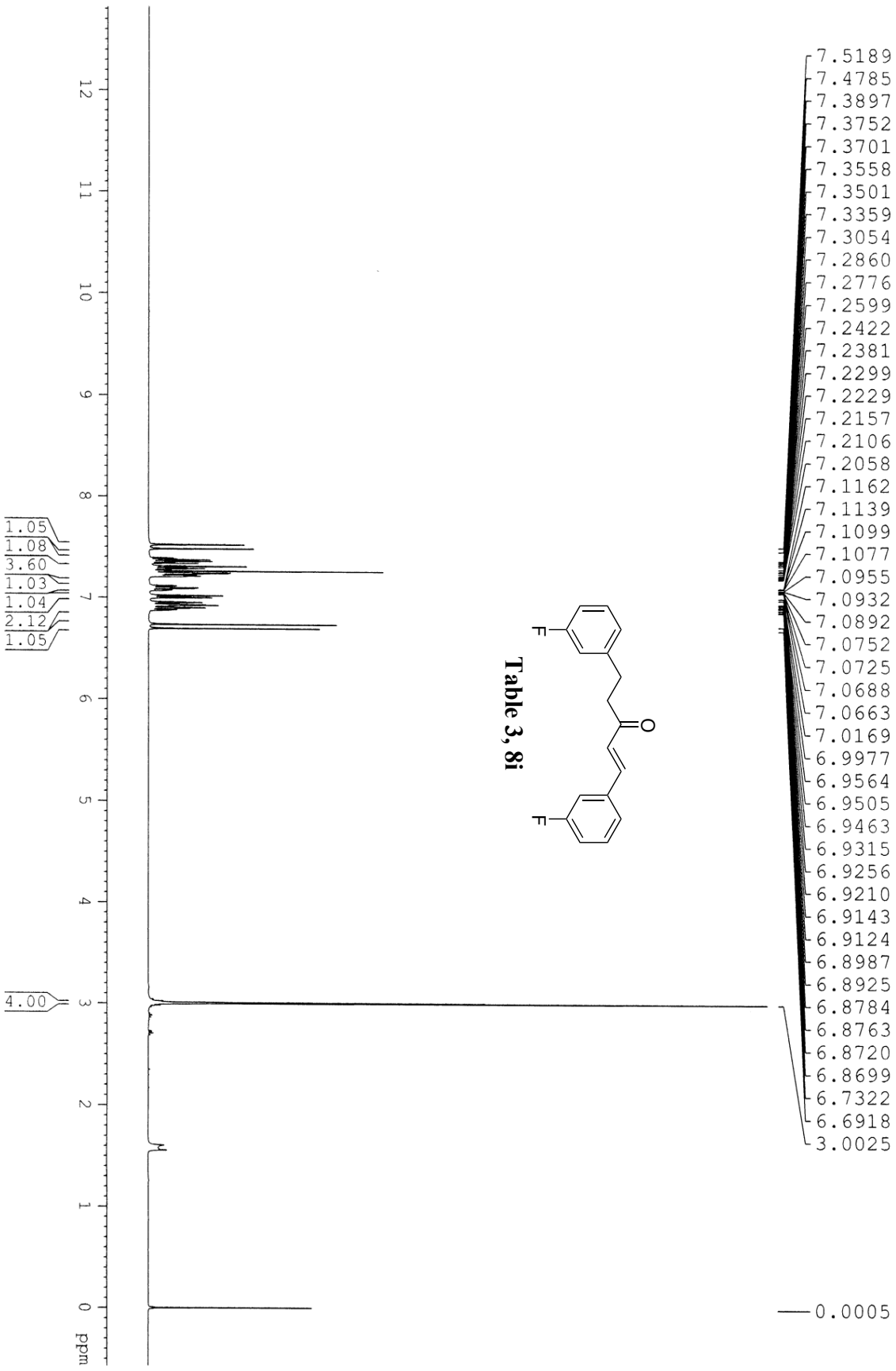

198.53
143.29
141.28
136.41
135.15
134.40
130.55
130.37
129.95
128.70
128.10
127.19
126.83
126.67
126.55
77.55
77.23
76.92
42.41
29.70
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Cl
O
Cl

Table 3, 8h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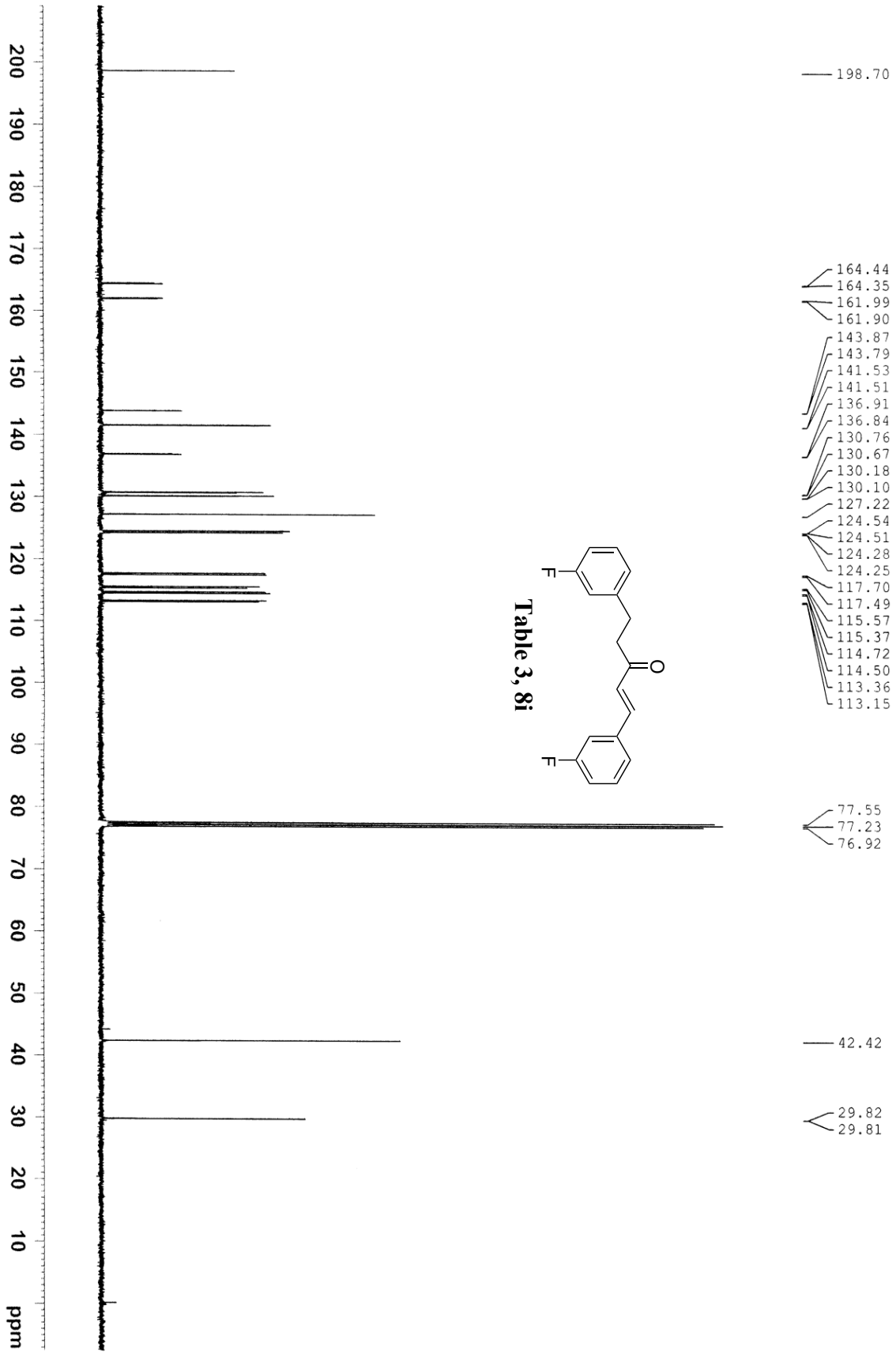
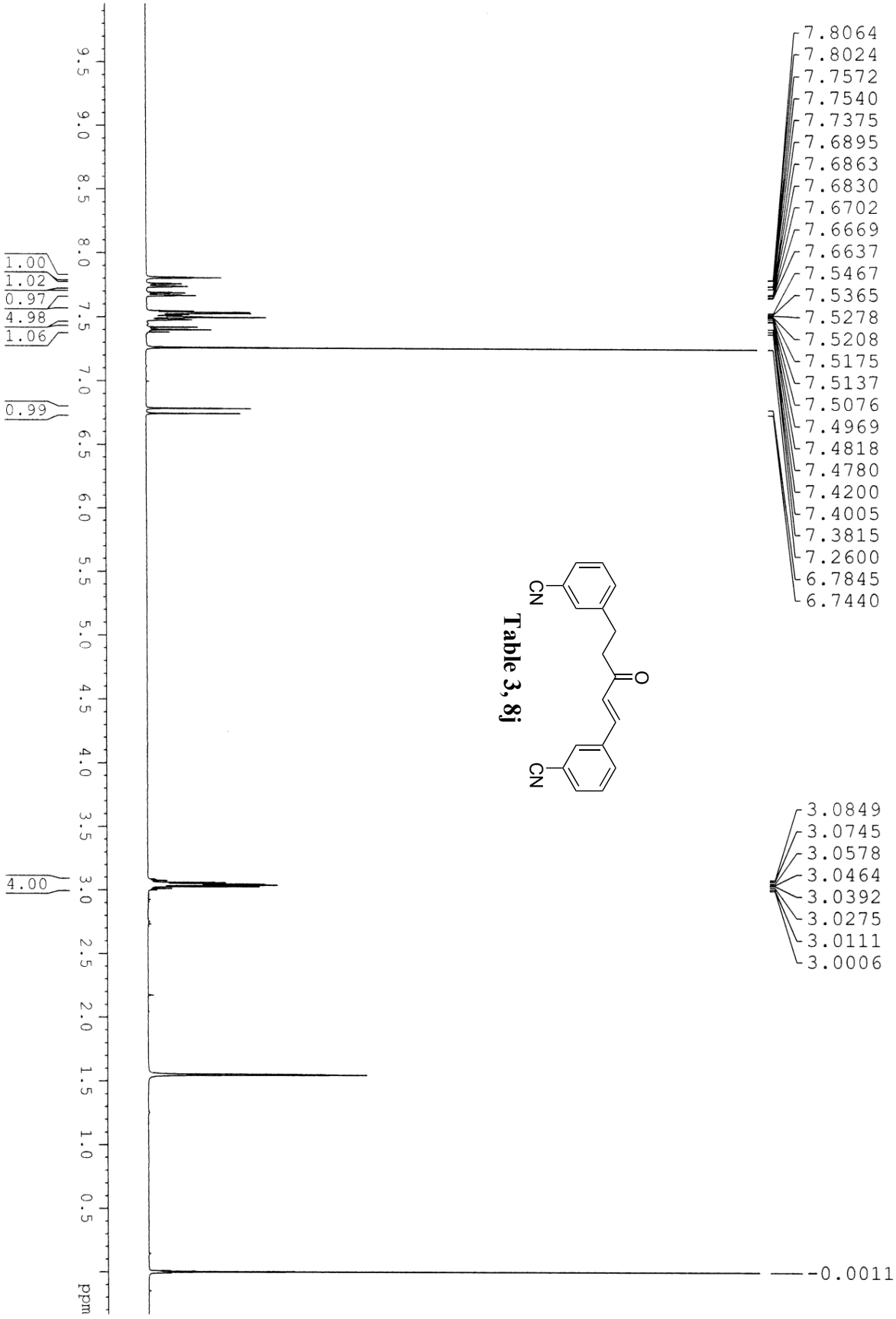
7.4785
7.3897
7.3752
7.3701
7.3558
7.3501
7.3359
7.3054
7.2860
7.2776
7.2599
7.2422
7.2381
7.2299
7.2229
7.2157
7.2106
7.2058
7.1162
7.1139
7.1099
7.1077
7.0955
7.0932
7.0892
7.0752
7.0725
7.0688
7.0663
7.0169
6.9977
6.9564
6.9505
6.9463
6.9315
6.9256
6.9210
6.9143
6.9124
6.8987
6.8925
6.8784
6.8763
6.8720
6.8699
6.7322
6.6918
3.0025
0.0005
1.05
1.08
3.60
1.03
1.04
2.12
1.05
4.00
F
O
F
Table 3, 8i
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


198.70
164.44
164.35
161.99
161.90
143.87
143.79
141.53
141.51
136.91
136.84
130.76
130.67
130.18
130.10
127.22
124.54
124.51
124.28
124.25
117.70
117.49
115.57
115.37
114.72
114.50
113.36
113.15
77.55
77.23
76.92
42.42
29.82
29.81
Table 3, 8i
F
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.8064
7.8024
7.7572
7.7540
7.7375
7.6895
7.6863
7.6830
7.6702
7.6669
7.6637
7.5467
7.5365
7.5278
7.5208
7.5175
7.5137
7.5076
7.4969
7.4818
7.4780
7.4200
7.4005
7.3815
7.2600
6.7845
6.7440
3.0849
3.0745
3.0578
3.0464
3.0392
3.0275
3.0111
3.0006
-0.0011
1.00
1.02
0.97
4.98
1.06
0.99
4.00
CN
O
CN
Table 3, 8j
ppm

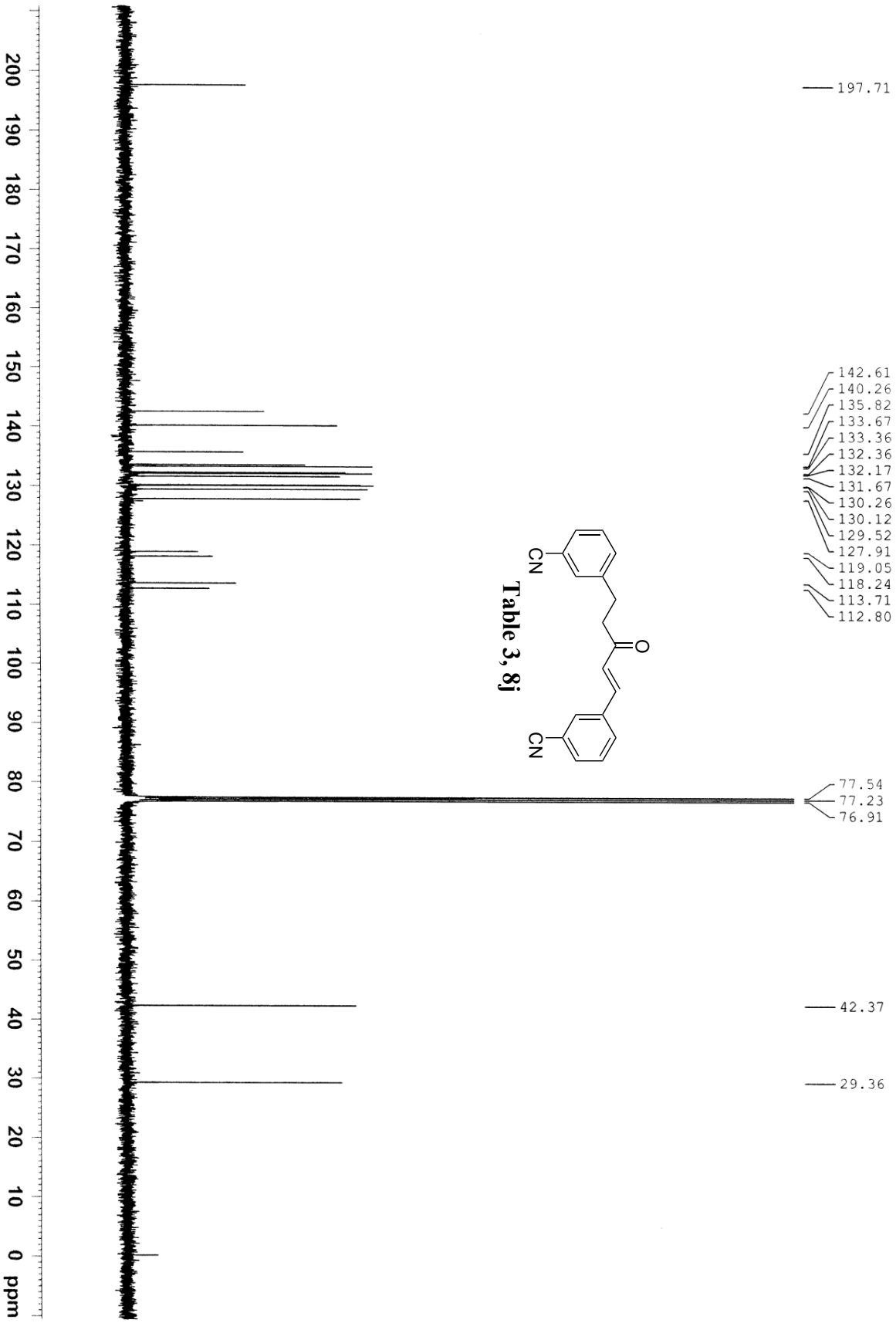
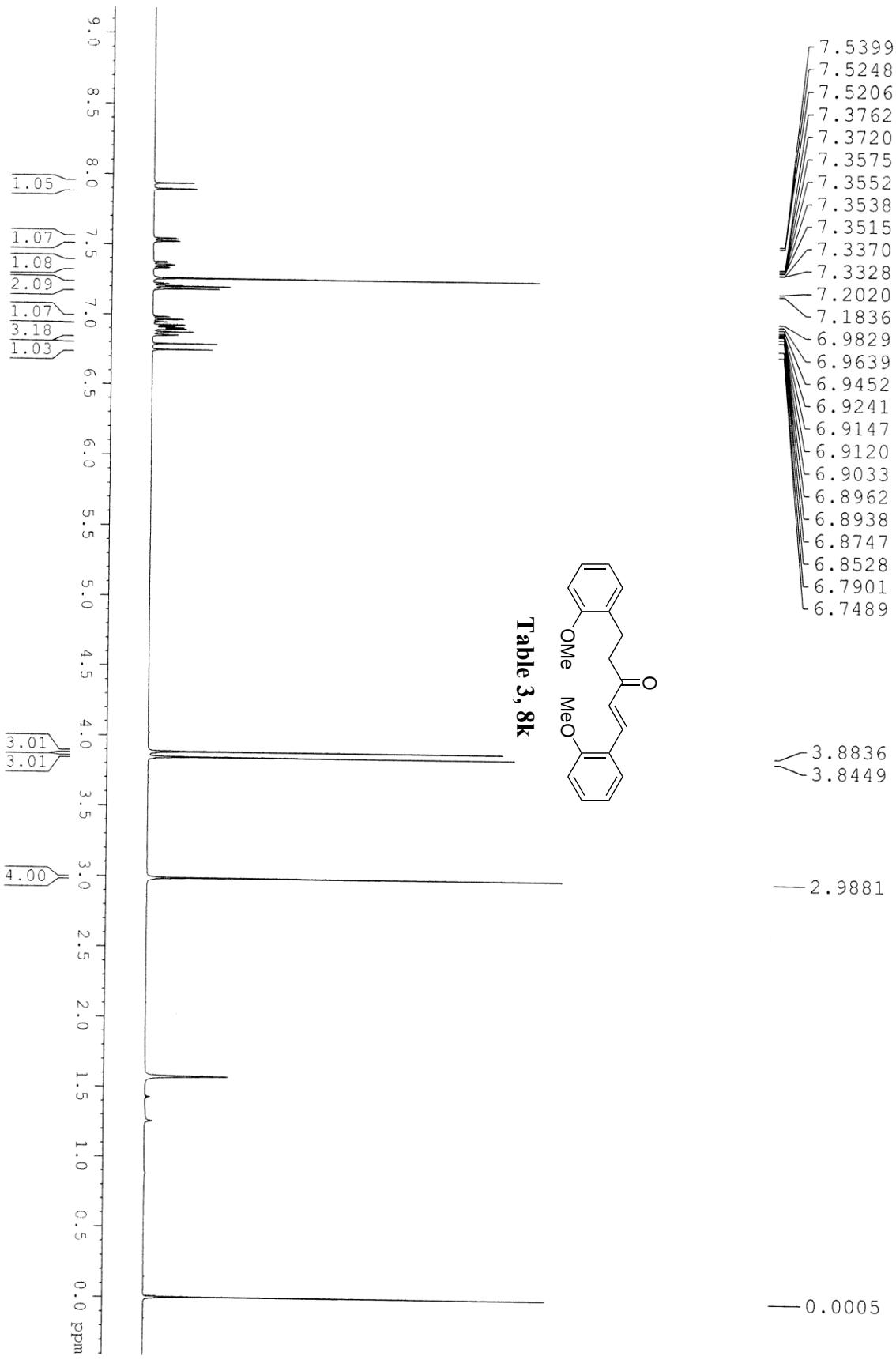

197.71
142.61
140.26
135.82
133.67
133.36
132.36
132.17
131.67
130.26
130.12
129.52
127.91
119.05
118.24
113.71
112.80
77.54
77.23
76.91
42.37
29.36
CN
CN
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Table 3, 8j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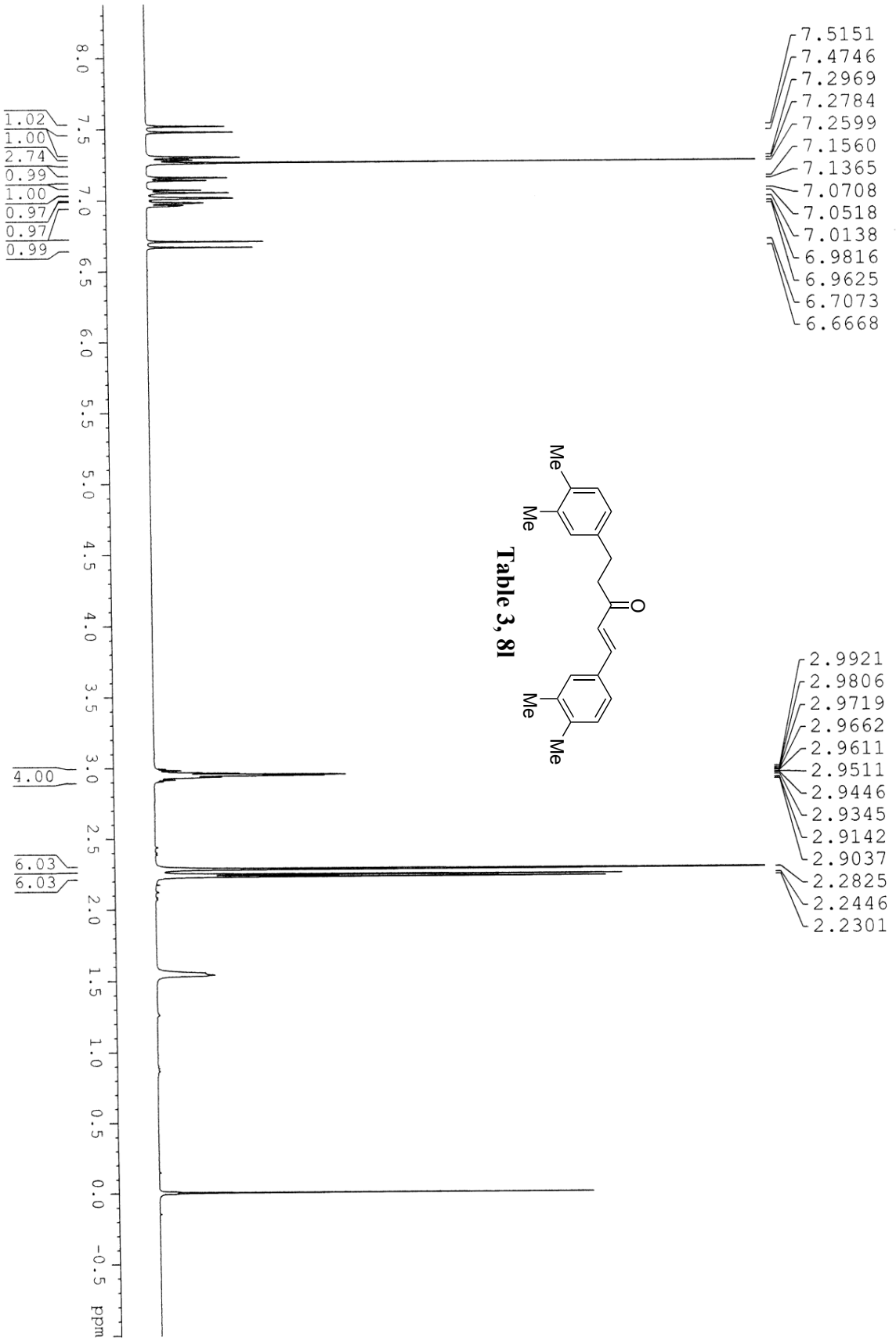
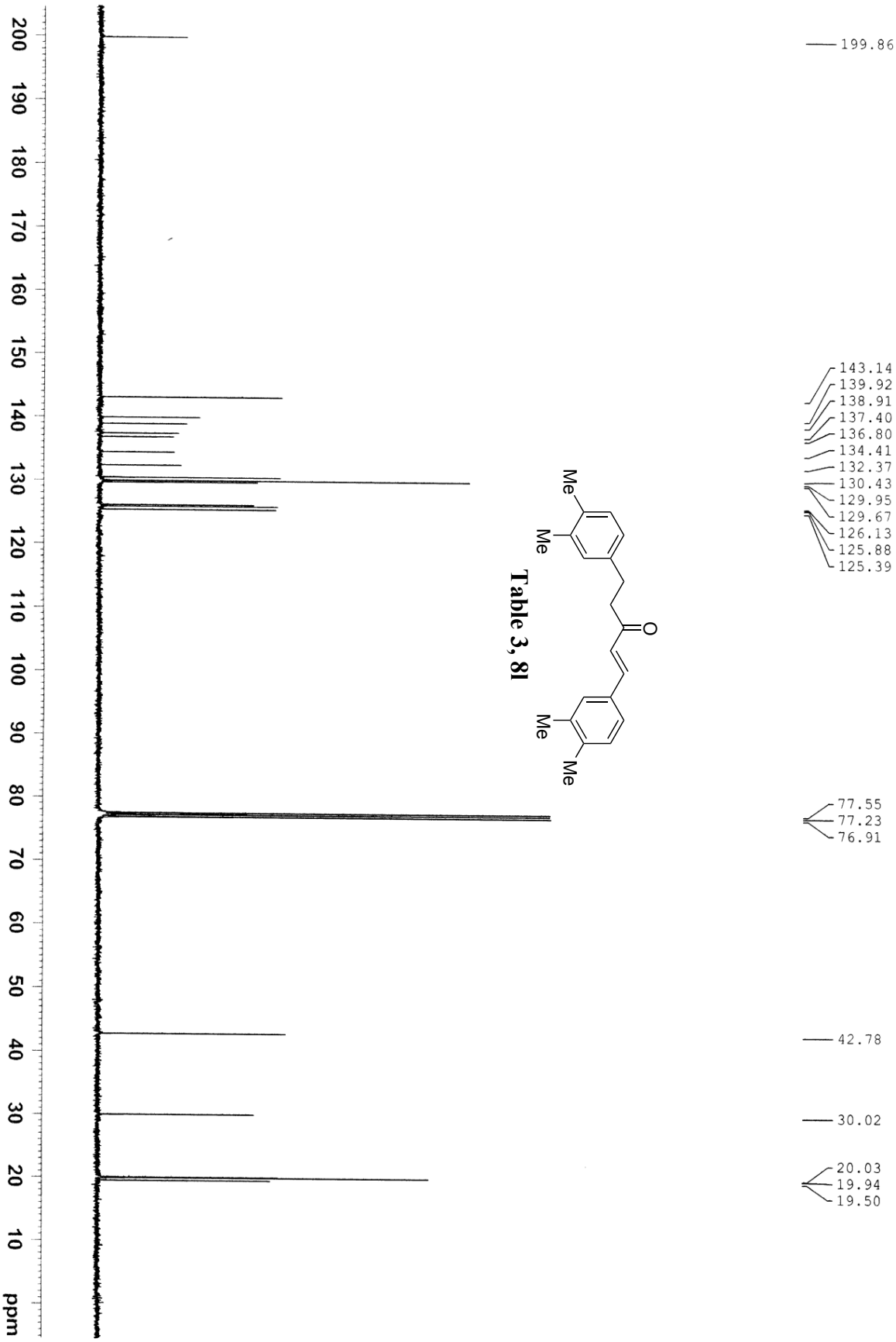
7.5206
7.3762
7.3720
7.3575
7.3552
7.3538
7.3515
7.3370
7.3328
7.2020
7.1836
6.9829
6.9639
6.9452
6.9241
6.9147
6.9120
6.9033
6.8962
6.8938
6.8747
6.8528
6.7901
6.7489
3.8836
3.8449
2.9881
0.0005
1.05
1.07
1.08
2.09
1.07
3.18
1.03
3.01
3.01
4.00
OMe
MeO
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Table 3, 8k

200.97
158.49
157.69
137.95
131.79
130.25
129.85
128.54
127.58
127.26
123.76
120.96
120.67
111.31
110.41
77.54
77.23
76.91
55.65
55.37
40.54
25.86
OMe
MeO
O
Table 3, 8k
ppm


7.5151
7.4746
7.2969
7.2784
7.2599
7.1560
7.1365
7.0708
7.0518
7.0138
6.9816
6.9625
6.7073
6.6668
1.02
1.00
2.74
0.99
1.00
0.97
0.97
0.99
4.00
6.03
6.03
2.9921
2.9806
2.9719
2.9662
2.9611
2.9511
2.9446
2.9345
2.9142
2.9037
2.2825
2.2446
2.2301
Me
Me
Me
Me
O
Table 3, 8l
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


199.86
143.14
139.92
138.91
137.40
136.80
134.41
132.37
130.43
129.95
129.67
126.13
125.88
125.39
77.55
77.23
76.91
42.78
30.02
20.03
19.94
19.50
Me
Me
Me
Me
O
Table 3, 8l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm