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Alcohol 7b: from column chromatography (EtOAc/hexane 1:9), a colorless oil that solidified in the freezer (79%): ^1H NMR (300 MHz) δ 1.23-1.73 (m, 11H), 4.87 (d, $J = 6.7$ Hz, 2H), 5.30 (t, $J = 6.7$ Hz, 1H); ^{13}C NMR (100.6 MHz) δ 22.4, 25.4, 38.1, 70.4, 77.9, 99.3, 206.2; IR 3360, 1955, 1445 cm^{-1} ; HRMS (CI) calcd for $\text{C}_9\text{H}_{15}\text{O}$ ($\text{M} + \text{H}$) $^+$ 139.1123, found 139.1123.

Alcohol 7c: from distillation at atmospheric pressure (bp 100-120 $^\circ\text{C}$), a volatile colorless liquid (50%) that was invariably contaminated with EtOAc: ^1H NMR (300 MHz) δ 1.36 (s, 6H), 1.66 (s, 1H), 4.88 (d, $J = 6.6$ Hz, 2H), 5.35 (t, $J = 6.6$ Hz, 1H); ^{13}C NMR (100.6 MHz) δ 29.6, 69.1, 77.4, 100.1, 205.3; IR 3360, 1955, 1460, 1375, 1360 cm^{-1} ; HRMS (CI) calcd for $\text{C}_6\text{H}_{11}\text{O}$ ($\text{M} + \text{H}$) $^+$ 99.0810, found 99.0810.

Alcohol 7d: from column chromatography (EtOAc/hexane 7:93), a colorless oil (45%): ^1H NMR (400 MHz) δ 0.97 (s, 9H), 1.29 (s, 3H), 1.65 (br s, 1H), 4.90 (d, $J = 6.7$ Hz, 2H), 5.41 (t, $J = 6.7$ Hz, 1H); ^{13}C NMR (100.6 MHz) δ 23.4, 25.2, 38.2, 75.2, 78.2, 97.6, 205.7; IR 3470, 1960, 1370 cm^{-1} .

Alcohol 7e: from column chromatography (Et₂O/hexane 1:2), a colorless liquid (89%): ^1H NMR (300 MHz) δ 0.87 (br t, 3H), 1.17-1.41 (m, 17H), 1.50-1.60 (m, 2H), 1.72 (s, 1H), 4.86 (d, $J = 6.7$ Hz, 2H), 5.26 (t, $J = 6.7$ Hz, 1H); ^{13}C NMR (100.6 MHz) δ 14.0, 22.6, 24.1, 27.7, 29.2, 29.49, 29.54, 29.9, 31.8, 42.8, 71.3, 78.0, 99.3, 205.6; IR 3360, 1960, 1465, 1375 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{O}$: C, 79.94; H, 12.46. Found: C, 79.66; H, 12.58.

Alcohol 7f: from column chromatography (EtOAc/hexane 1:9), a colorless oil (58%): ^1H NMR (300 MHz) δ 1.65 (s, 3H), 2.05 (s, 1H), 2.34 (s, 3H), 4.95 (m, 2H), 5.55 (t, $J = 6.6$ Hz, 1H), 7.15 (m, 2H), 7.39 (m, 2H); ^{13}C NMR (100.6 MHz) δ 20.9, 30.2, 72.8, 78.8, 100.2, 124.8, 128.8, 136.5, 144.2, 205.8; IR 3390, 3090, 3050, 3020, 1960, 1510, 1370 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.72; H, 8.10. Found: C, 82.57; H, 7.93.

Alcohol 7g: from column chromatography (Et₂O/hexane 2:3), a colorless liquid (87%): ¹H NMR (300 MHz) δ 1.56-1.81 (m, 4H), 1.86 (s, 1H), 1.88-2.09 (m, 2H), 4.86 (d, *J* = 6.7 Hz, 2H), 5.31 (t, *J* = 6.7 Hz, 1H), 5.61 (dt, *J* = 10.0, 2.1 Hz, 1H), 5.80 (dt, *J* = 10.0, 3.6 Hz, 1H); ¹³C NMR (75.5 MHz) δ 19.2, 24.9, 36.6, 68.7, 78.4, 98.8, 129.7, 131.4, 206.2; IR 3350, 3050, 3020, 1955, 1645, 1430 cm⁻¹; HRMS (CI) calcd for C₉H₁₃O (M + H)⁺ 137.0966, found 137.0966.

Alcohol 7h: from column chromatography (Et₂O/hexane 1:2), a colorless oil that solidified in the freezer (79%): ¹H NMR (300 MHz) δ 1.51 (s, 1H), 1.55-1.66 (m, 2H), 1.69-1.93 (m, 6H), 3.92 (m, 4H), 4.87 (d, *J* = 6.7 Hz, 2H), 5.28 (t, *J* = 6.7 Hz, 1H); ¹³C NMR (100.6 MHz) δ 30.6, 35.2, 63.90, 63.94, 69.0, 78.0, 98.7, 108.3, 205.9; IR 3440, 1955, 1430, 1365 cm⁻¹. Anal. Calcd for C₁₁H₁₆O₃: C, 67.32; H, 8.22. Found: C, 67.41; H, 8.14.

Alcohol 7i: from column chromatography (Et₂O/hexane 1:2), a colorless oil that solidified in the freezer (50%): ¹H NMR (300 MHz) δ 1.06 (br s, 21H), 1.48-1.60 (m, 3H), 1.63-1.89 (m, 6H), 3.78 (m, 1H), 4.87 (d, *J* = 6.7 Hz, 2H), 5.28 (t, *J* = 6.7 Hz, 1H); ¹³C NMR (100.6 MHz) δ 12.3, 18.1, 31.4, 35.1, 68.9, 69.7, 78.2, 98.8, 206.2; IR 3350, 1955, 1460, 1440, 1380, 1365 cm⁻¹; HRMS (CI) calcd for C₁₈H₃₂OSi (M - H₂O)⁺ 292.2222, found 292.2224.

α'-Iodoenone 6b: from column chromatography (CHCl₃/hexane 1:1→3:2), a pale yellow oil (58%): ¹H NMR (300 MHz) δ 1.56-1.64 (m, 6H), 2.24 (m, 2H), 2.84 (m, 2H), 3.79 (s, 2H), 6.13 (s, 1H); ¹³C NMR (100.6 MHz) δ 8.6, 26.0, 27.8, 28.6, 29.9, 38.0, 117.2, 166.3, 192.7; IR 3020, 1675, 1610, 1445, 1440 cm⁻¹. Anal. Calcd for C₉H₁₃IO: C, 40.93; H, 4.96. Found: C, 40.90; H, 5.03.

α'-Iodoenone 6c: from column chromatography (CHCl₃/hexane 1:1), a yellow oil (54%): ¹H NMR (400 MHz) δ 1.97 (s, 3H), 2.20 (s, 3H), 3.78 (s, 2H), 6.23 (s, 1H); ¹³C NMR (100.6 MHz) δ 8.4, 20.9, 27.8, 120.2, 159.8, 192.2; IR 3030, 1680, 1615, 1440, 1380 cm⁻¹.

α' -Iodoenone 6d: from column chromatography (CHCl₃/hexane 1:1), a pale yellow oil that solidified in the freezer (66%): ¹H NMR (300 MHz) δ 1.13 (s, 9H), 2.18 (s, 3H), 3.83 (s, 2H), 6.29 (s, 1H); ¹³C NMR (100.6 MHz) δ 9.0, 16.0, 28.4, 38.2, 116.6, 170.2, 193.1; IR 3030, 1680, 1600, 1465, 1380, 1370 cm⁻¹; HRMS (FAB) calcd for C₉H₁₆IO (M + H)⁺ 267.0246, found 267.0246.

α' -Iodoenones (*E*)/(*Z*)-6e: from column chromatography (CHCl₃/hexane 2:3), in the order, (*Z*)-6e (20%), (*E*)-6e (39%), both as a pale yellow oil and mixed fractions (8%) for a total yield of 67%. (*Z*)-6e: ¹H NMR (300 MHz) δ 0.88 (br t, 3H), 1.20-1.50 (m, 14H), 1.95 (s, 3H), 2.61 (m, 2H), 3.77 (s, 2H), 6.18 (s, 1H); ¹³C NMR (100.6 MHz) δ 8.6, 14.0, 22.6, 25.6, 28.1, 29.2, 29.4, 29.5, 29.7, 31.8, 33.9, 120.0, 164.4, 191.7; IR 3020, 1680, 1615, 1455, 1440, 1375 cm⁻¹. Anal. Calcd for C₁₄H₂₅IO: C, 50.01; H, 7.49. Found: C, 49.67; H, 7.28. (*E*)-6e: ¹H NMR (300 MHz) δ 0.88 (br t, 3H), 1.27 (br s, 12H), 1.49 (m, 2H), 2.18 (m, 5H), 3.79 (s, 2H), 6.20 (s, 1H); ¹³C NMR (100.6 MHz) δ 8.5, 14.0, 19.5, 22.6, 27.4, 29.1, 29.2, 29.3, 29.4, 31.8, 41.3, 119.5, 163.5, 192.2; IR 3020, 1680, 1610, 1465 cm⁻¹. Anal. Calcd for C₁₄H₂₅IO: C, 50.01; H, 7.49. Found: C, 49.98; H, 7.36.

α' -Iodoenone 6f: from column chromatography (EtOAc/hexane 3:100), a pale yellow solid (36%): ¹H NMR (300 MHz) δ 2.39 (s, 3H), 2.59 (s, 3H), 3.90 (s, 2H), 6.66 (s, 1H), 7.21 (m, 2H), 7.42 (m, 2H); ¹³C NMR (100.6 MHz) δ 8.9, 18.3, 21.2, 119.7, 126.4, 129.2, 138.8, 139.8, 157.7, 192.4; IR 3030, 1670, 1590, 1560, 1510, 1430, 1410, 1375, 1355 cm⁻¹. Anal. Calcd for C₁₂H₁₃IO: C, 48.02; H, 4.37. Found: C, 48.12; H, 4.44.

α' -Iodoenone 6g: from column chromatography (CHCl₃/hexane 3:2), an inseparable mixture of *E*- and *Z*-isomers as a pale yellow oil (29%): IR 3020, 1665, 1610, 1575 cm⁻¹; HRMS (FAB) calcd for C₉H₁₂IO (M + H)⁺ 262.9933, found 262.9932.

α' -Iodoenone 6h. The rearrangement being slower than in previous examples, the optimal yield was obtained when the reaction mixture was stirred for 7 days at rt

before NIS was added. Column chromatography (EtOAc/hexane 1:4) afforded a pale yellow oil that solidified in the freezer (48%): ^1H NMR (400 MHz) δ 1.75 (t, $J = 6.6$ Hz, 2H), 1.82 (t, $J = 6.6$ Hz, 2H), 2.43 (t, $J = 6.6$ Hz, 2H), 3.01 (t, $J = 6.6$ Hz, 2H), 3.80 (s, 2H), 3.98 (s, 4H), 6.19 (s, 1H); ^{13}C NMR (100.6 MHz) δ 8.4, 26.2, 34.7, 34.8, 35.7, 64.4, 107.6, 118.3, 162.9, 192.7; IR 3020, 1675, 1620, 1450, 1440 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{16}\text{IO}_3$ ($\text{M} + \text{H}$) $^+$ 323.0144, found 323.0145.

α' -Iodoenone 6i. The rearrangement being slower than in previous examples, the optimal yield was obtained when the reaction was carried out in refluxing CHCl_3 for 20 h before the addition of NIS at rt. Column chromatography (CHCl_3 /hexane 1:1) afforded a pale yellow oil (48%): ^1H NMR (300 MHz) δ 1.07 (br s, 21H), 1.71-1.82 (m, 4H), 2.13 (m, 1H), 2.60 (m, 1H), 2.89-3.05 (m, 2H), 3.79 (s, 2H), 4.09 (m, 1H), 6.15 (s, 1H); ^{13}C NMR (100.6 MHz) δ 8.5, 12.3, 18.1, 25.2, 33.5, 35.4, 36.2, 67.5, 117.5, 165.7, 192.9; IR 1680, 1625, 1460 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{33}\text{IO}_2\text{Si}$: C, 49.54; H, 7.62. Found: C, 49.54; H, 7.44.

Ketophosphonate 10b: colorless oil (89%): ^1H NMR (300 MHz) δ 1.33 (t, $J = 7.1$ Hz, 6H), 1.57-1.74 (m, 6H), 2.19 (m, 2H), 2.80 (m, 2H), 3.08 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 4.14 (m, 4H), 6.15 (s, 1H); ^{13}C NMR (100.6 MHz) δ 16.0 (d, $J_{\text{CP}} = 6.2$), 25.9, 27.6, 28.5, 29.8, 37.8, 43.6 (d, $J_{\text{CP}} = 126.8$), 62.1 (d, $J_{\text{CP}} = 6.3$), 120.9, 164.3, 191.2 (d, $J_{\text{CP}} = 5.8$); IR 1685, 1615, 1445, 1390, 1255, 1040, 1020 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_4\text{P}$: C, 56.92; H, 8.45. Found: C, 56.62; H, 8.36.

Ketophosphonate 10c: colorless oil (87%): ^1H NMR (400 MHz) δ 1.33 (t, $J = 7.1$ Hz, 6H), 1.92 (s, 3H), 2.16 (s, 3H), 3.07 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 4.14 (m, 4H), 6.25 (s, 1H); ^{13}C NMR (100.6 MHz) δ 16.0 (d, $J_{\text{CP}} = 6.3$), 20.7, 27.5, 43.4 (d, $J_{\text{CP}} = 126.9$), 62.1 (d, $J_{\text{CP}} = 6.4$), 123.6, 157.6, 190.5 (d, $J_{\text{CP}} = 5.8$); IR 1685, 1620, 1445, 1390, 1255, 1050, 1025 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{O}_4\text{P}$: C, 51.28; H, 8.18. Found: C, 51.12; H, 8.06.

Ketophosphonate 10d: colorless oil (93%): ^1H NMR (300 MHz) δ 1.12 (s, 9H), 1.33 (t, $J = 7.1$ Hz, 6H), 2.14 (s, 3H), 3.11 (d, $J_{\text{HP}} = 22.4$ Hz, 2H), 4.14 (m, 4H), 6.31 (s, 1H); ^{13}C NMR (100.6 MHz) δ 15.7, 16.0 (d, $J_{\text{CP}} = 6.4$), 28.1, 37.8, 43.8 (d, $J_{\text{CP}} = 126.8$), 61.9 (d, $J_{\text{CP}} = 6.4$), 120.1, 167.9, 191.4 (d, $J_{\text{CP}} = 6.0$); IR 1685, 1605, 1390, 1370, 1260, 1050, 1025 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{O}_4\text{P}$: C, 56.51; H, 9.12. Found: C, 56.24; H, 8.89.

Ketophosphonate (E)-10e: with acetone/toluene 15:85 as an eluent, a colorless oil (91%): ^1H NMR (300 MHz) δ 0.88 (br t, 3H), 1.19-1.37 (m, 18H), 1.40 (m, 2H), 2.14 (m, 5H), 3.08 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 4.14 (m, 4H), 6.22 (s, 1H); ^{13}C NMR (100.6 MHz) δ 13.8, 16.0 (d, $J_{\text{CP}} = 6.3$), 19.3, 22.3, 27.2, 29.0, 29.1, 29.2, 31.6, 41.0, 43.5 (d, $J_{\text{CP}} = 126.8$), 62.0 (d, $J_{\text{CP}} = 6.5$), 122.8, 161.5, 190.6 (d, $J_{\text{CP}} = 5.9$); IR 1685, 1610, 1465, 1450, 1440, 1390, 1255, 1040, 1025 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{35}\text{O}_4\text{P}$: C, 62.40; H, 10.18. Found: C, 62.76; H, 9.95.

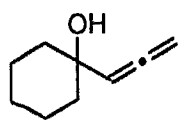
Ketophosphonate (Z)-10e: with acetone/toluene 15:85 as an eluent, a colorless oil (88%): ^1H NMR (300 MHz) δ 0.88 (br t, 3H), 1.18-1.49 (m, 20H), 1.90 (s, 3H), 2.58 (m, 2H), 3.06 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 4.13 (m, 4H), 6.21 (s, 1H); ^{13}C NMR (100.6 MHz) δ 13.9, 16.1 (d, $J_{\text{CP}} = 6.2$), 22.5, 25.5, 27.9, 29.1, 29.3, 29.4, 29.6, 31.7, 33.8, 43.7 (d, $J_{\text{CP}} = 126.6$), 62.2 (d, $J_{\text{CP}} = 6.4$), 123.5, 162.5, 190.2 (d, $J_{\text{CP}} = 5.9$); IR 1685, 1615, 1465, 1455, 1440, 1390, 1255, 1040, 1025 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{36}\text{O}_4\text{P}$ ($\text{M} + \text{H}$) $^+$ 347.2351, found 347.2353.

Ketophosphonate 10f: colorless oil (94%): ^1H NMR (300 MHz) δ 1.33 (t, $J = 7.1$ Hz, 6H), 2.37 (s, 3H), 2.54 (s, 3H), 3.19 (d, $J_{\text{HP}} = 22.4$ Hz, 2H), 4.16 (m, 4H), 6.70 (s, 1H), 7.19 (m, 2H), 7.43 (m, 2H); ^{13}C NMR (100.6 MHz) δ 16.1 (d, $J_{\text{CP}} = 6.2$), 18.1, 21.0, 44.1 (d, $J_{\text{CP}} = 126.7$), 62.1 (d, $J_{\text{CP}} = 6.4$), 123.0, 126.3, 129.0, 138.8, 139.5, 155.6, 190.8 (d, $J_{\text{CP}} = 5.9$); IR 3030, 1680, 1595, 1565, 1510, 1440, 1390, 1255, 1045, 1020 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_4\text{P}$: C, 61.93; H, 7.47. Found: C, 61.58; H, 7.65.

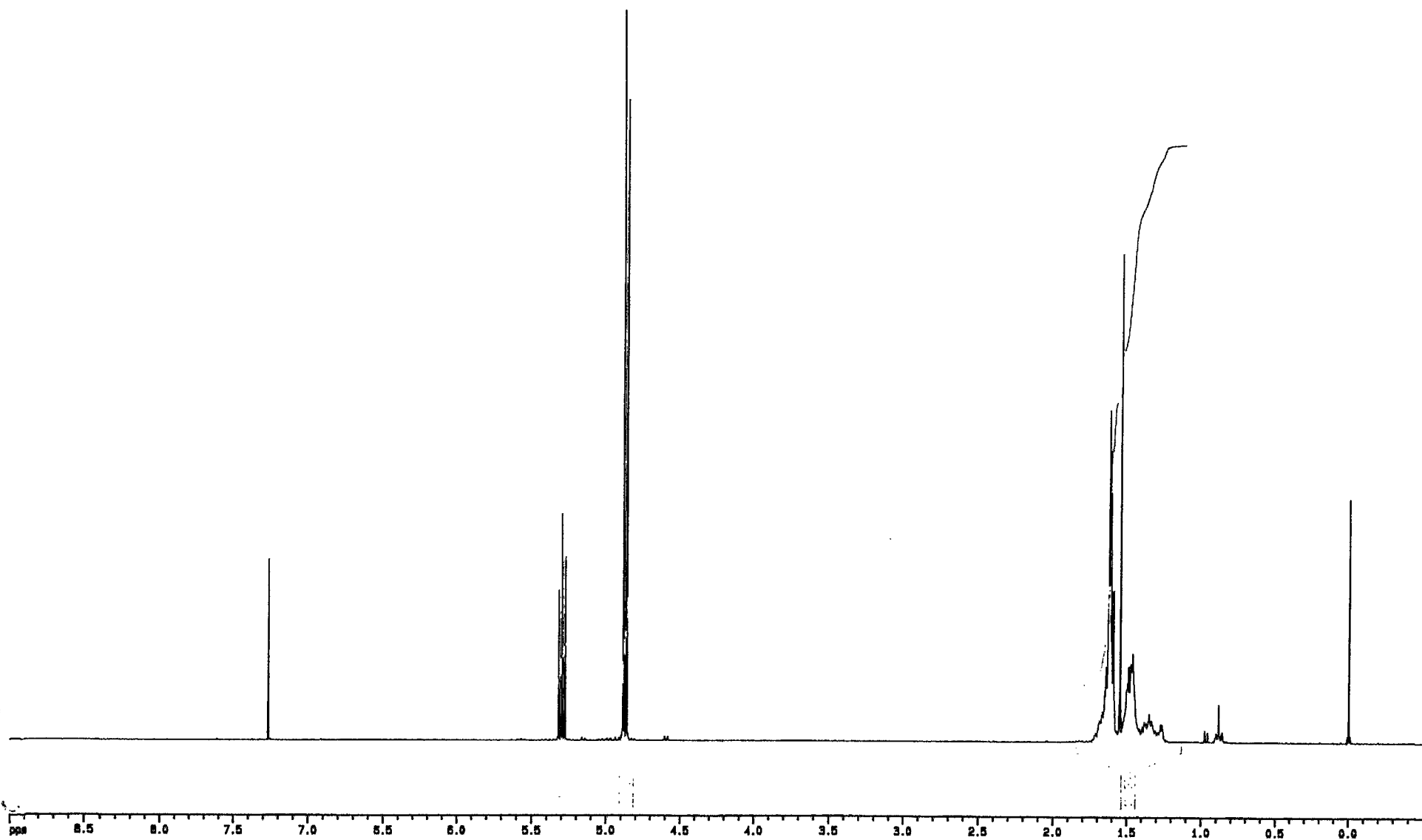
Ketophosphonate 10g: pale yellow oil (84%): IR 3020, 1670, 1610, 1575, 1385, 1250, 1040, 1020 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_4\text{P}$ ($\text{M} + \text{H}$)⁺ 273.1256, found 273.1256.

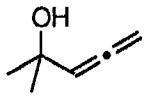
Ketophosphonate 10h: with acetone/toluene 1:3→3:7 as an eluent, a colorless oil (86%): ^1H NMR (300 MHz) δ 1.33 (t, $J = 7.1$ Hz, 6H), 1.73 (m, 2H), 1.80 (m, 2H), 2.39 (m, 2H), 2.97 (m, 2H), 3.09 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 3.97 (s, 4H), 4.14 (m, 4H), 6.22 (s, 1H); ^{13}C NMR (100.6 MHz) δ 15.9 (d, $J_{\text{CP}} = 6.2$), 25.8, 34.3, 34.5, 35.3, 43.4 (d, $J_{\text{CP}} = 126.8$), 62.0 (d, $J_{\text{CP}} = 6.4$), 64.0, 107.4, 121.7, 160.6, 191.0 (d, $J_{\text{CP}} = 5.9$); IR 1685, 1620, 1445, 1390, 1250, 1035 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4\text{P}$ ($\text{M} + \text{H}$)⁺ 333.1457, found 333.1467.

Ketophosphonate 10i: with acetone/toluene 15:85 as an eluent, a colorless oil (88%): ^1H NMR (300 MHz) δ 1.06 (br s, 21H), 1.33 (t, $J = 7.1$ Hz, 6H), 1.69-1.82 (m, 4H), 2.09 (m, 1H), 2.55 (m, 1H), 2.92 (m, 2H), 3.08 (d, $J_{\text{HP}} = 22.5$ Hz, 2H), 4.05-4.22 (m, 5H), 6.18 (s, 1H); ^{13}C NMR (100.6 MHz) δ 12.2, 16.2 (d, $J_{\text{CP}} = 6.2$), 18.0, 25.1, 33.3, 35.3, 36.1, 43.8 (d, $J_{\text{CP}} = 126.8$), 62.3 (d, $J_{\text{CP}} = 6.4$), 67.5, 121.2, 163.6, 191.3 (d, $J_{\text{CP}} = 5.8$); IR 1685, 1620, 1460, 1445, 1390, 1365, 1260, 1030 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{44}\text{O}_5\text{PSi}$ ($\text{M} + \text{H}$)⁺ 447.2696, found 447.2696.

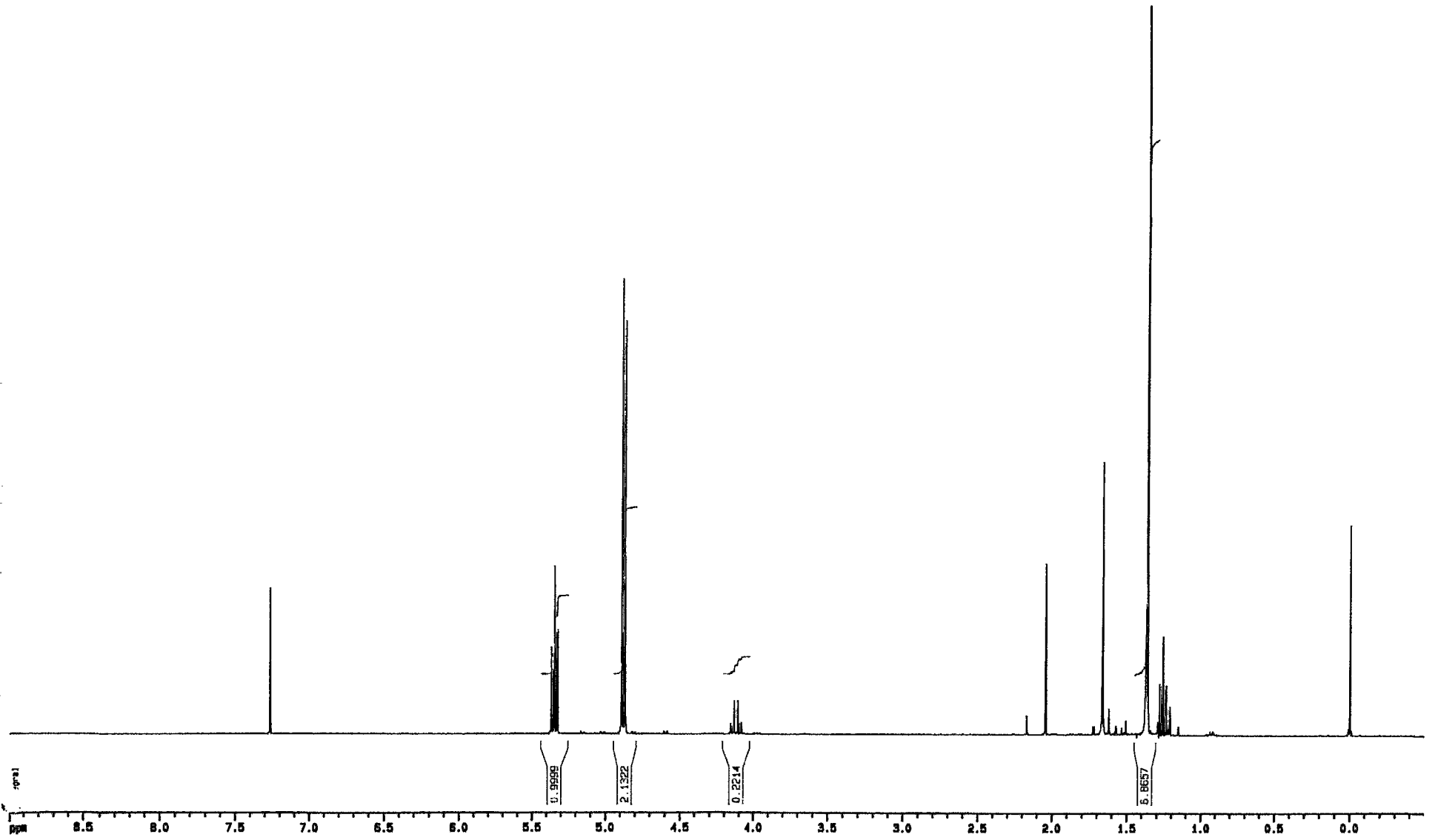


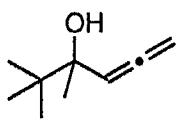
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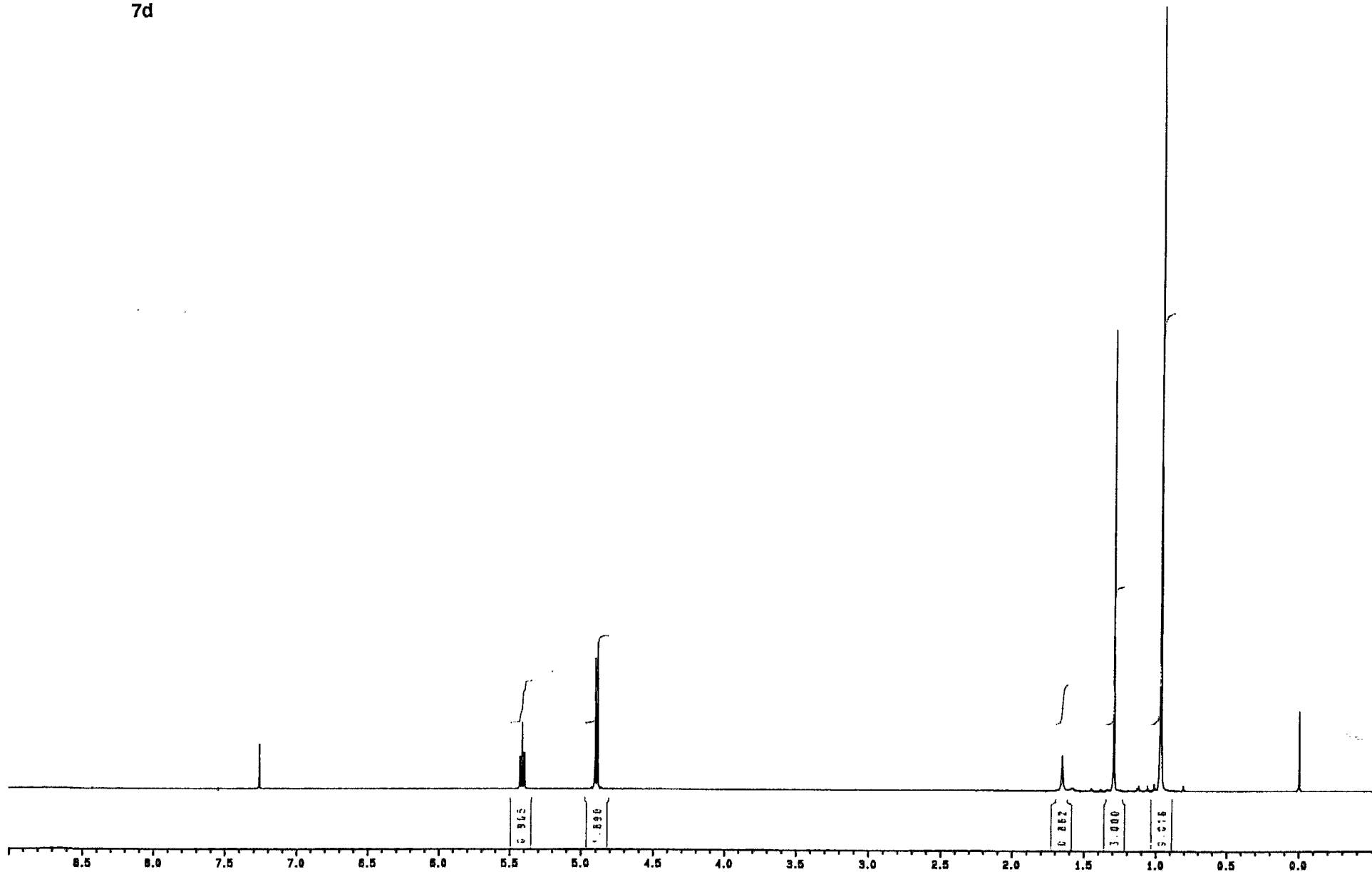


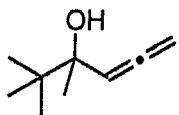
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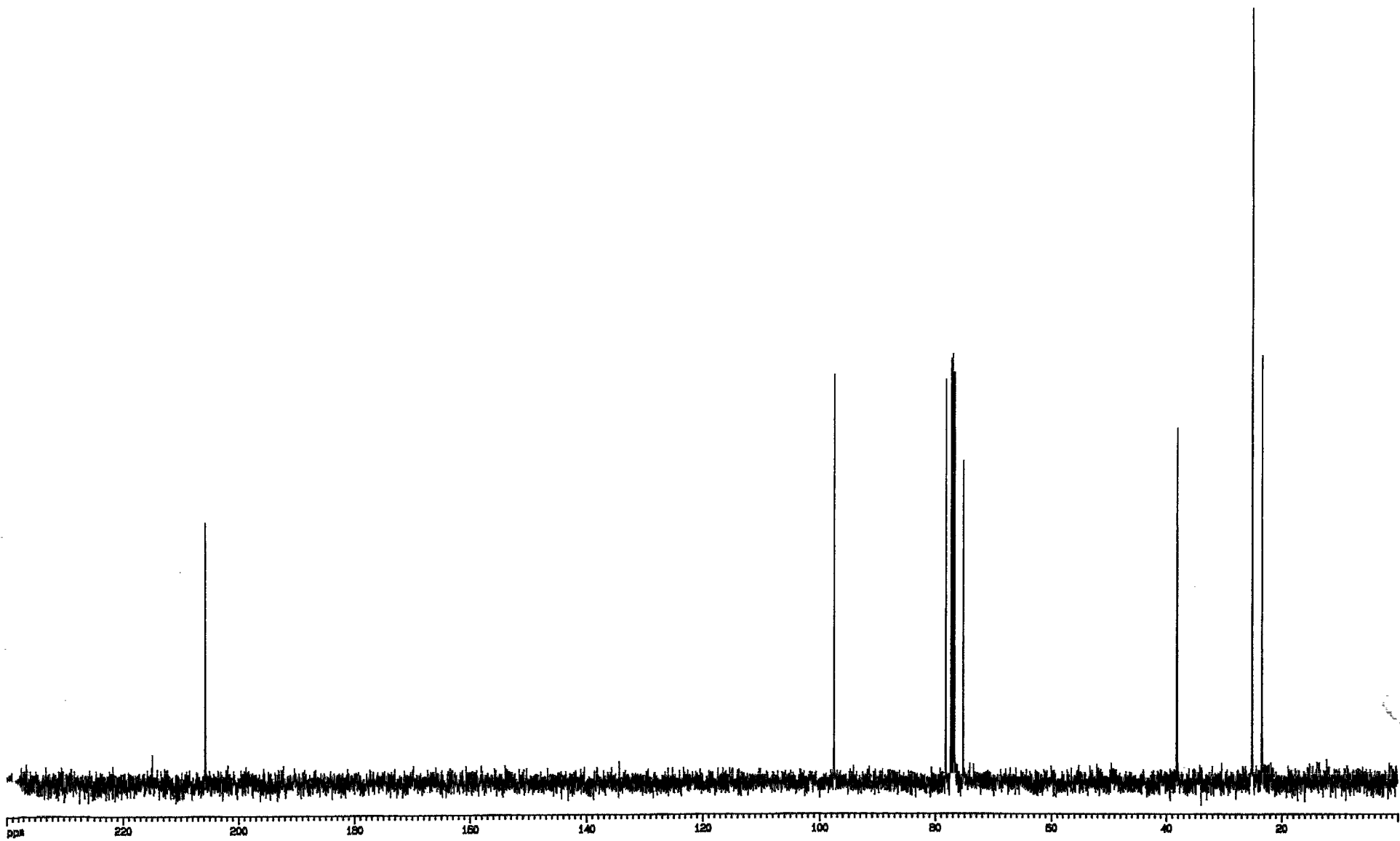


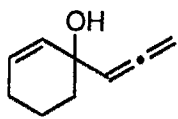
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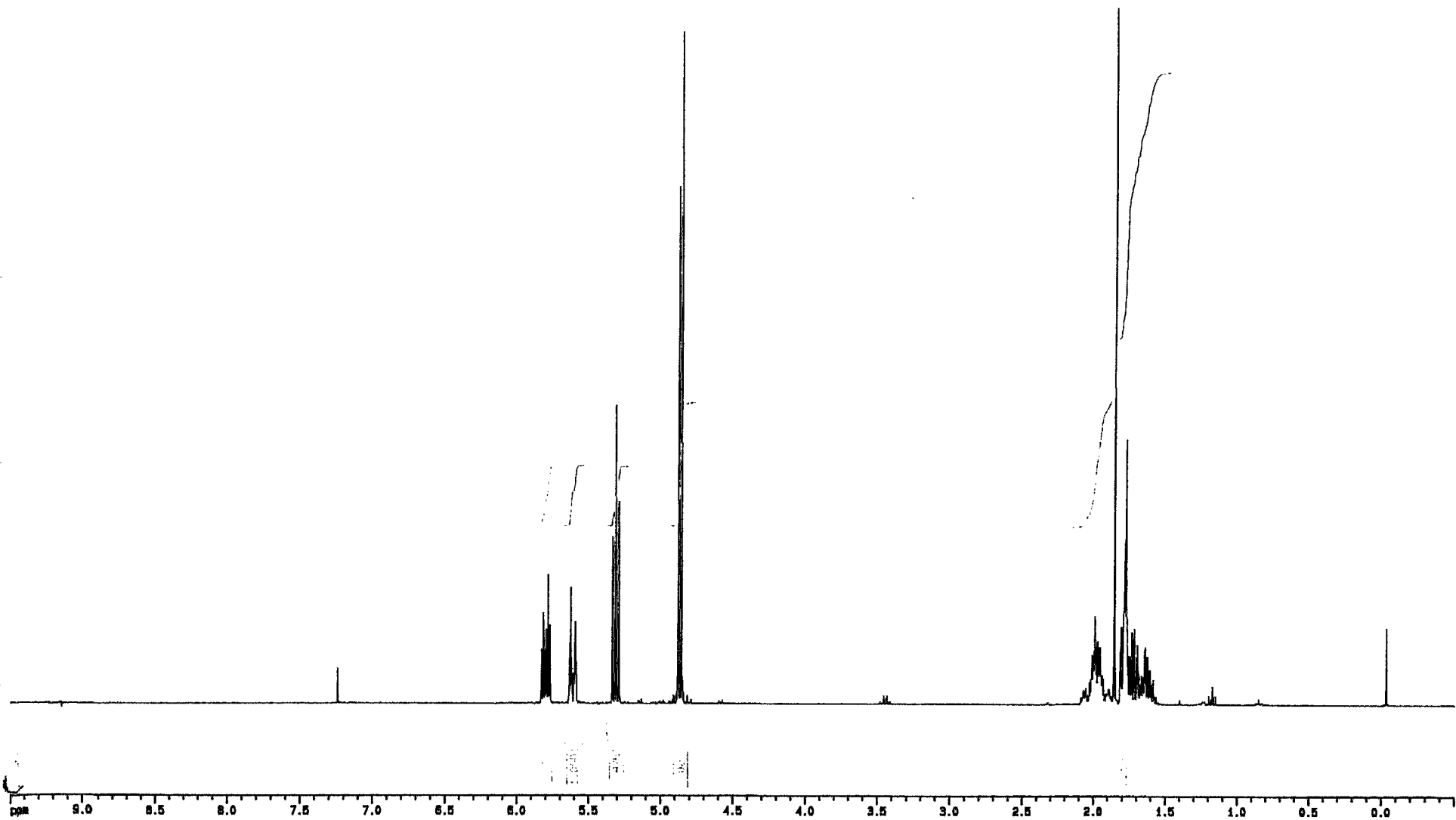


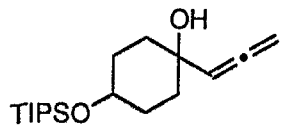
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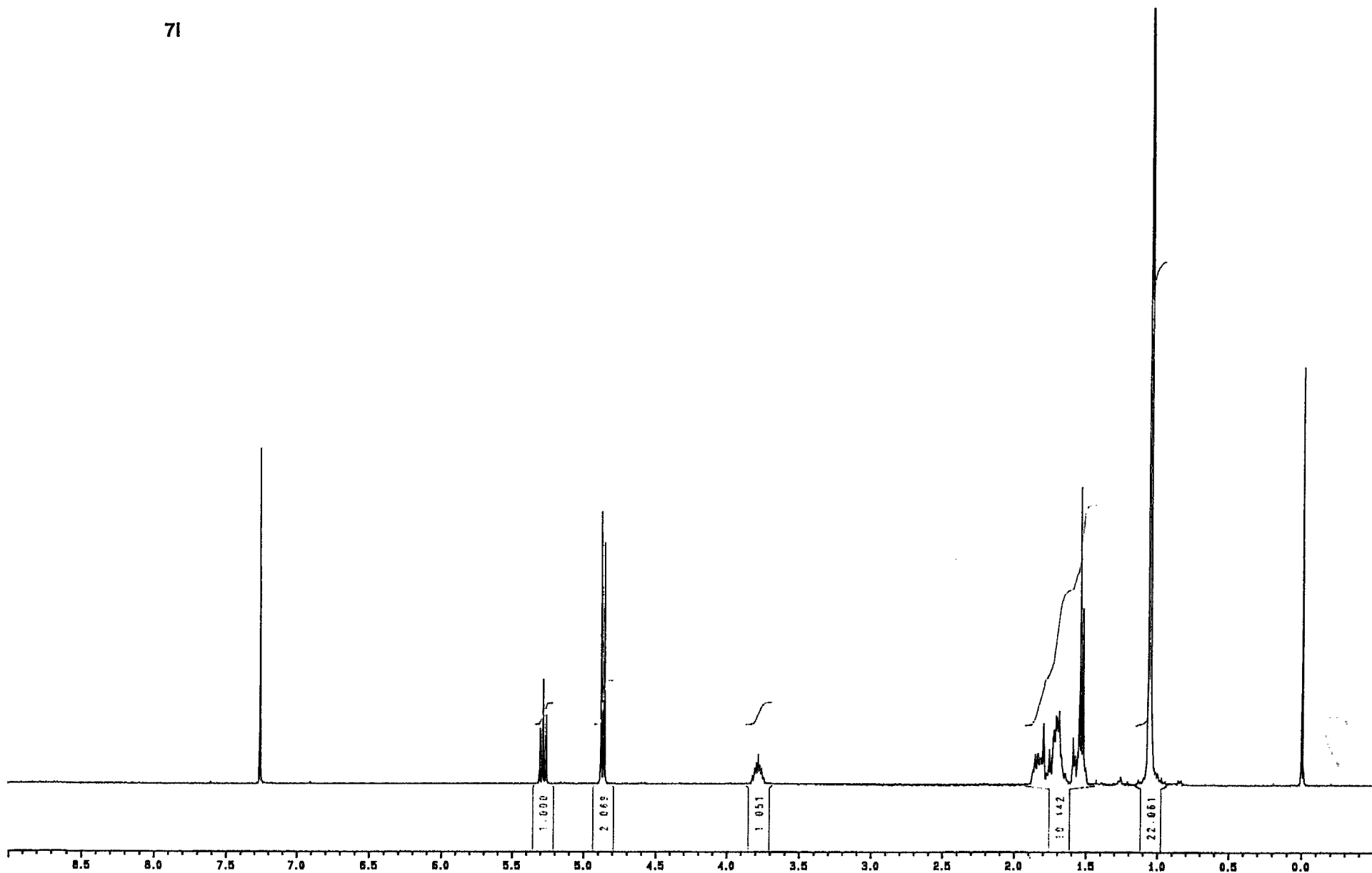


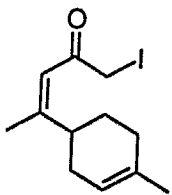
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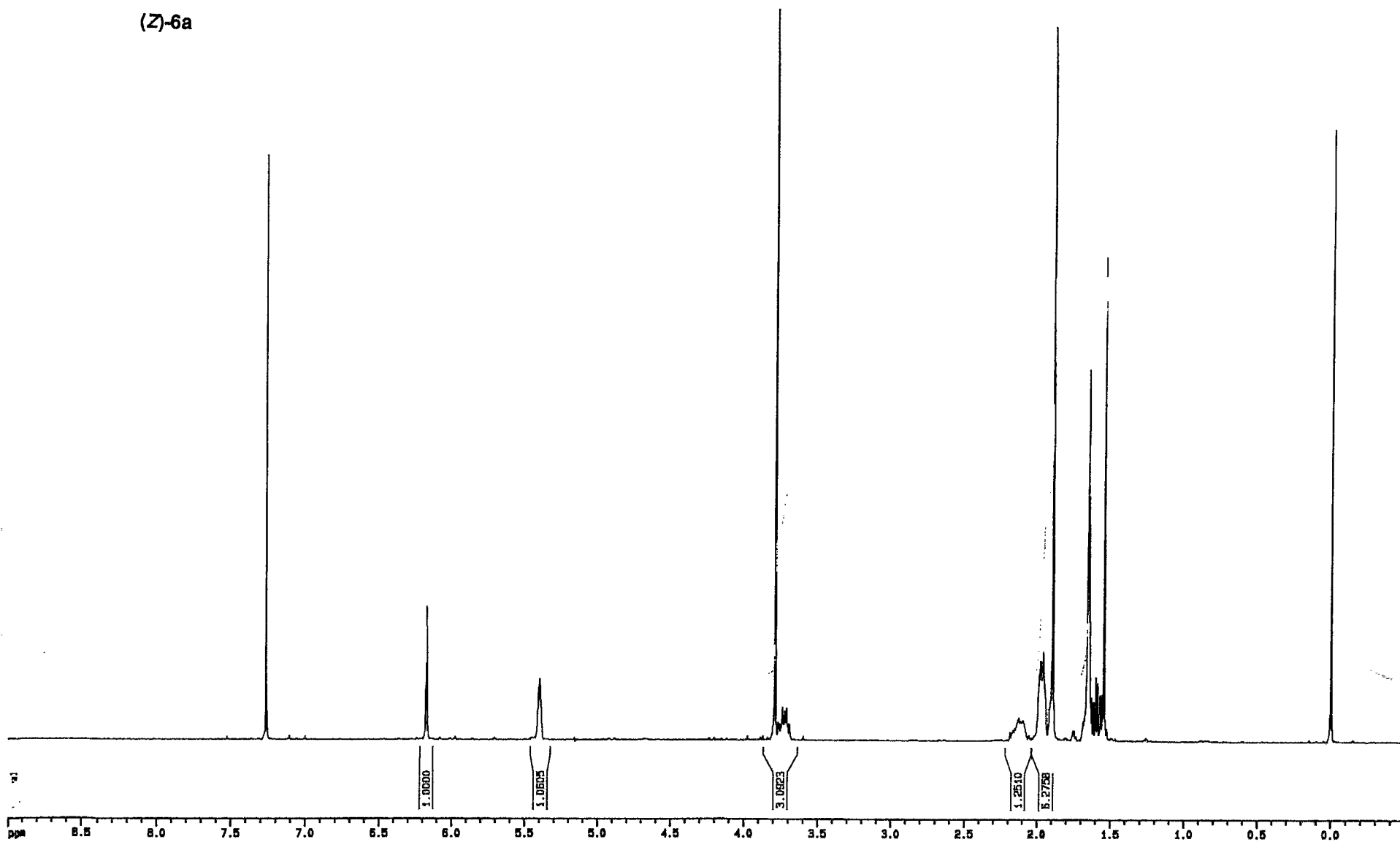


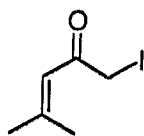
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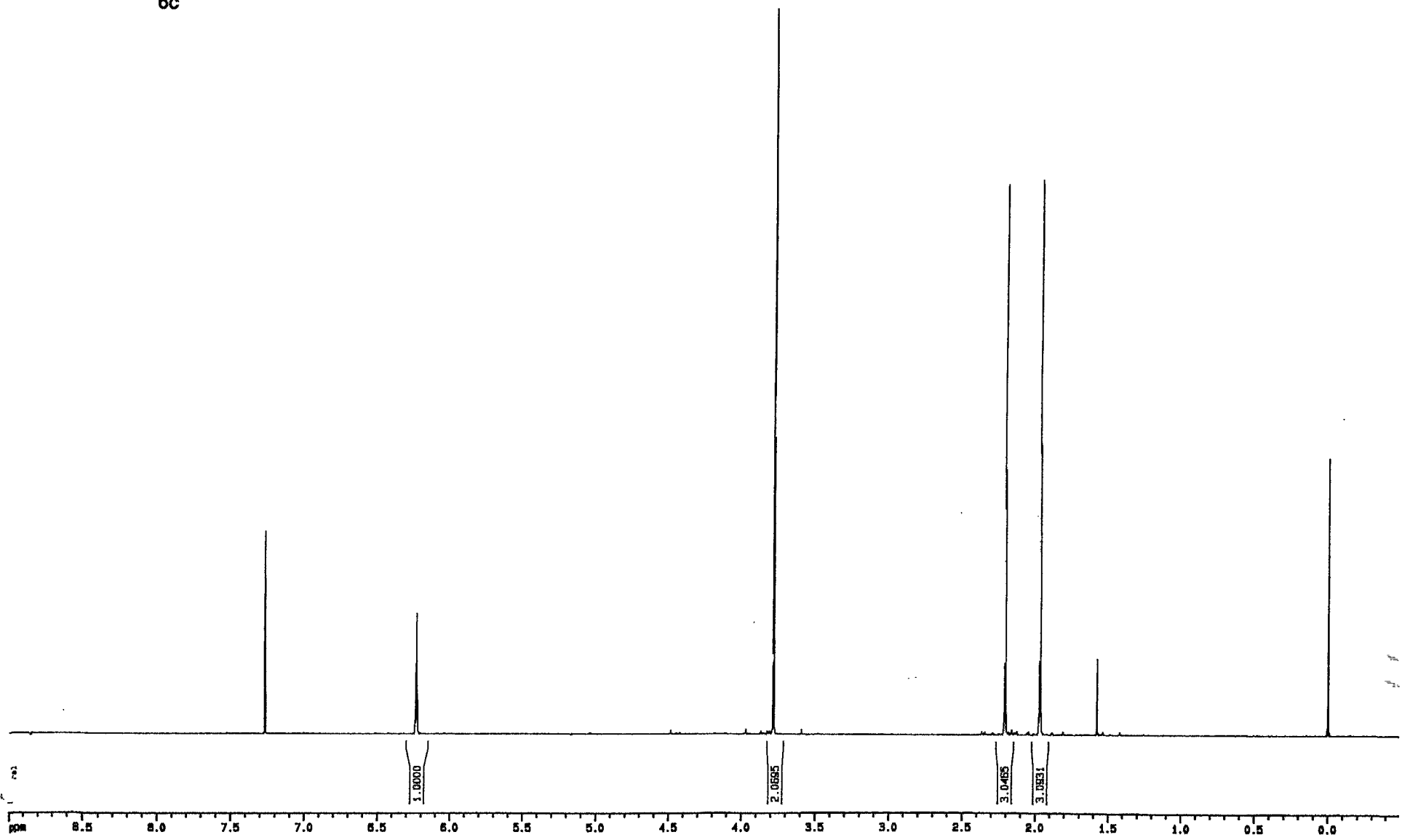


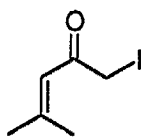
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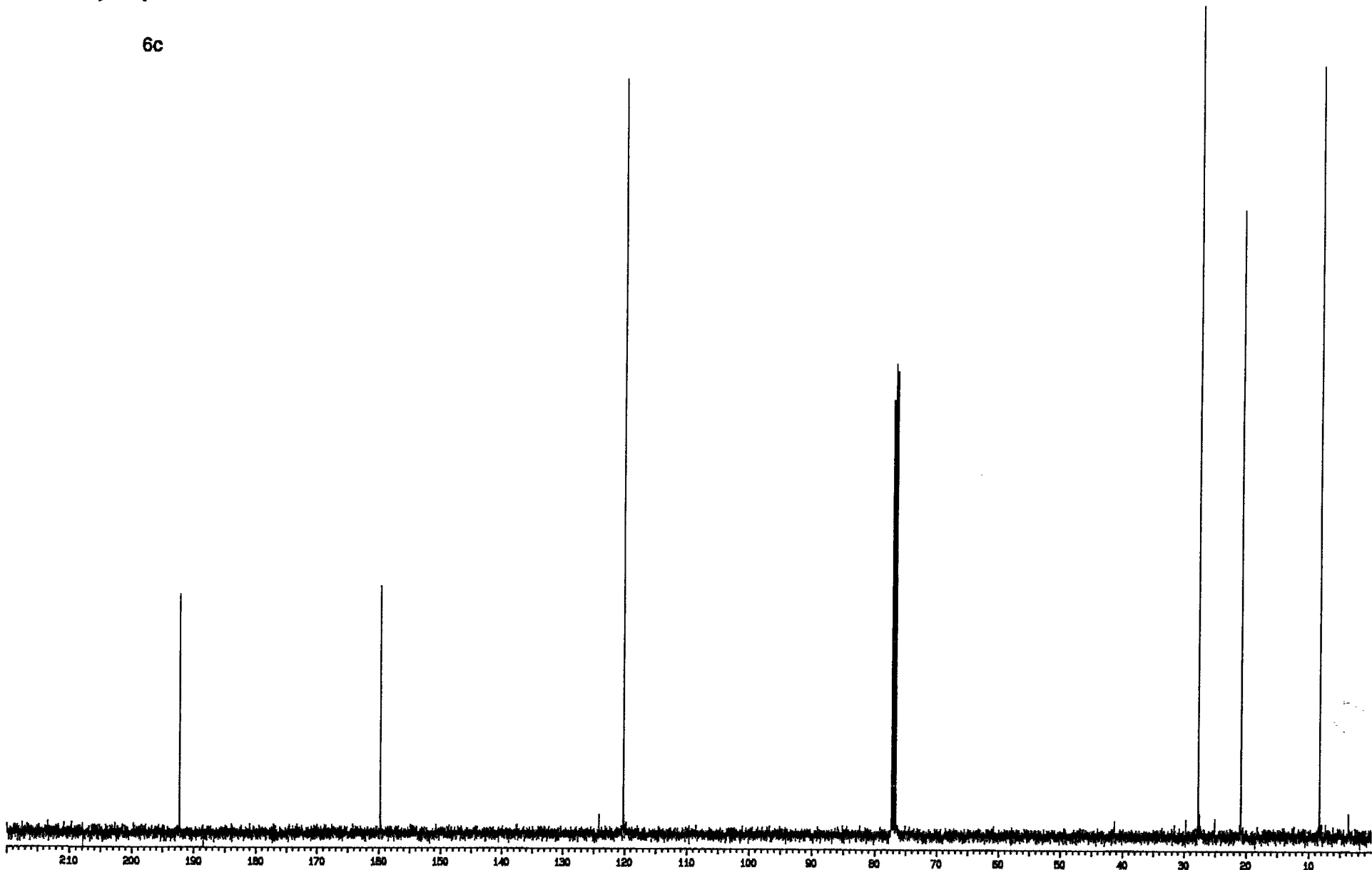


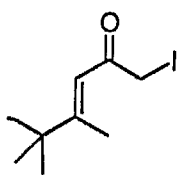
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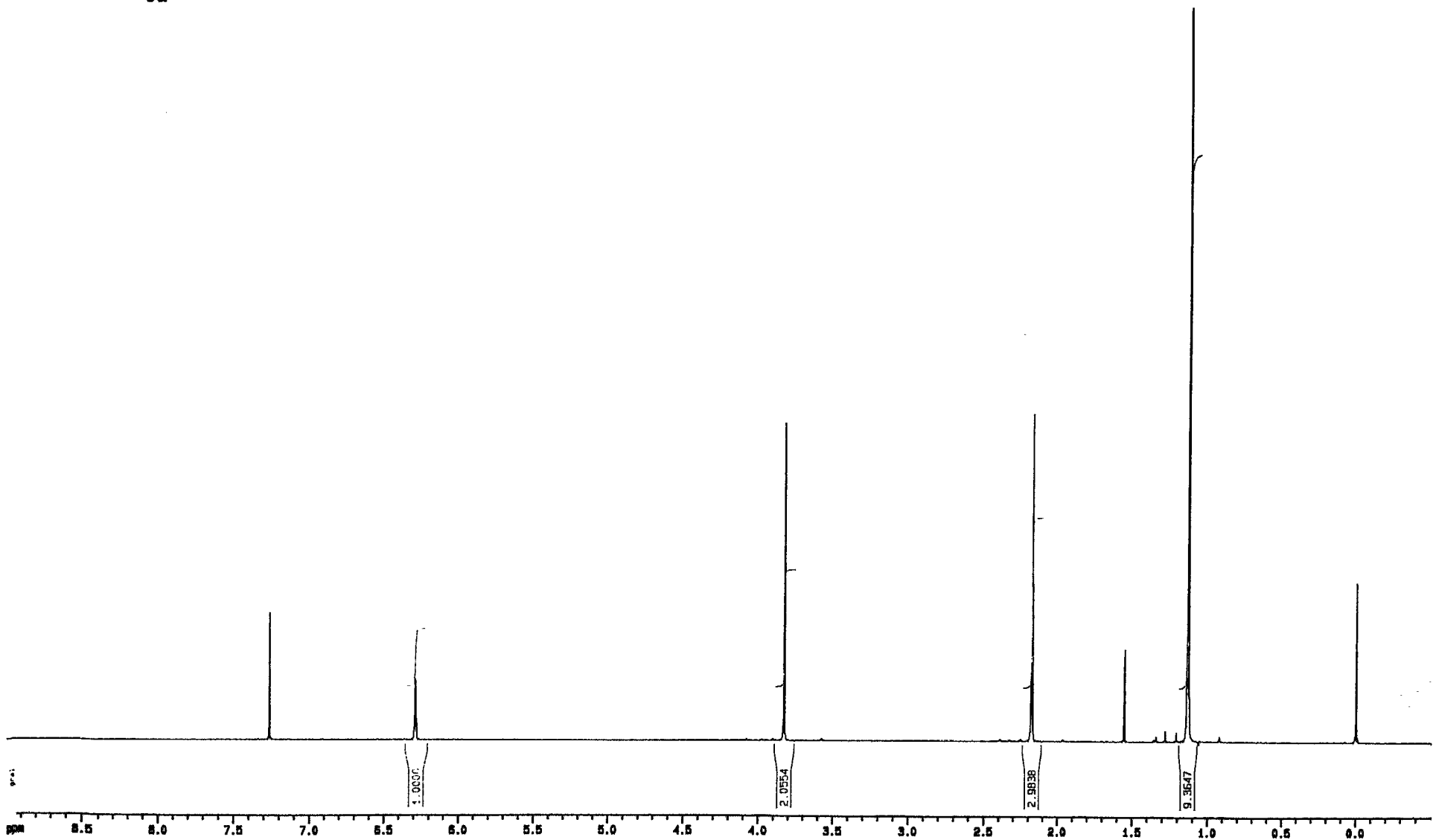


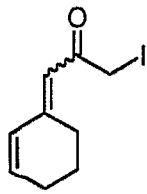
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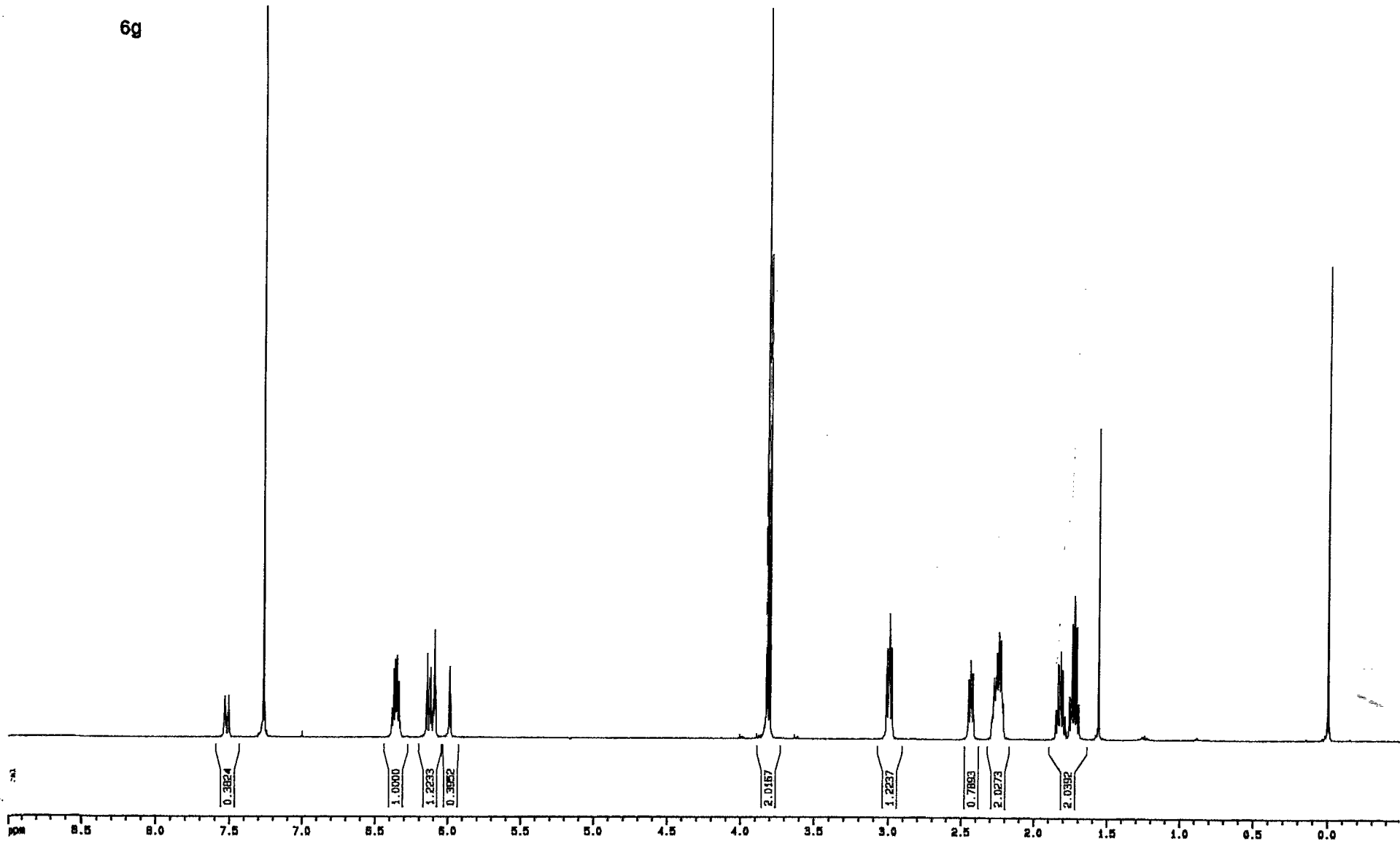


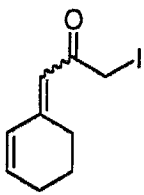
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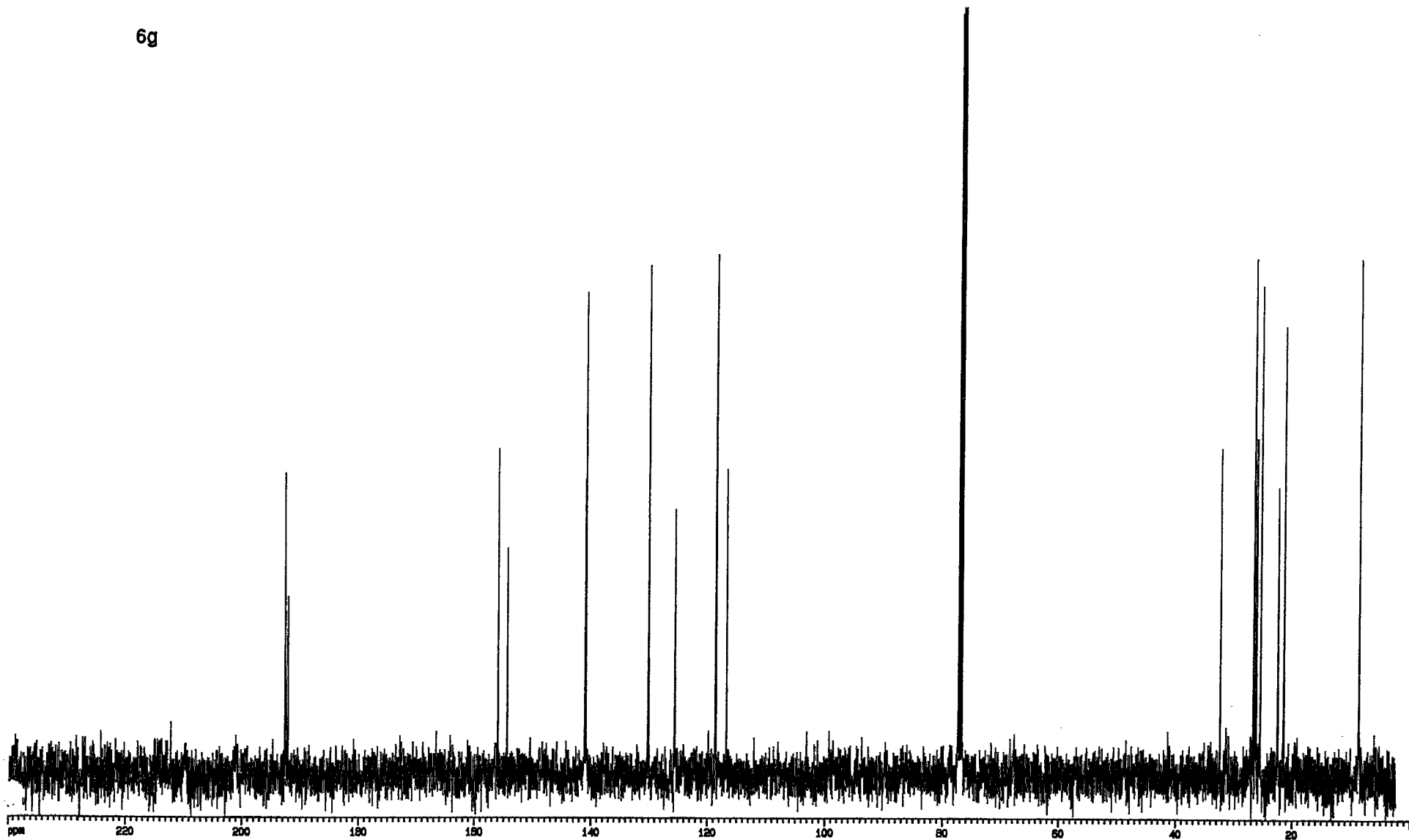


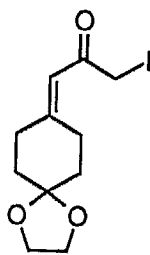
6g



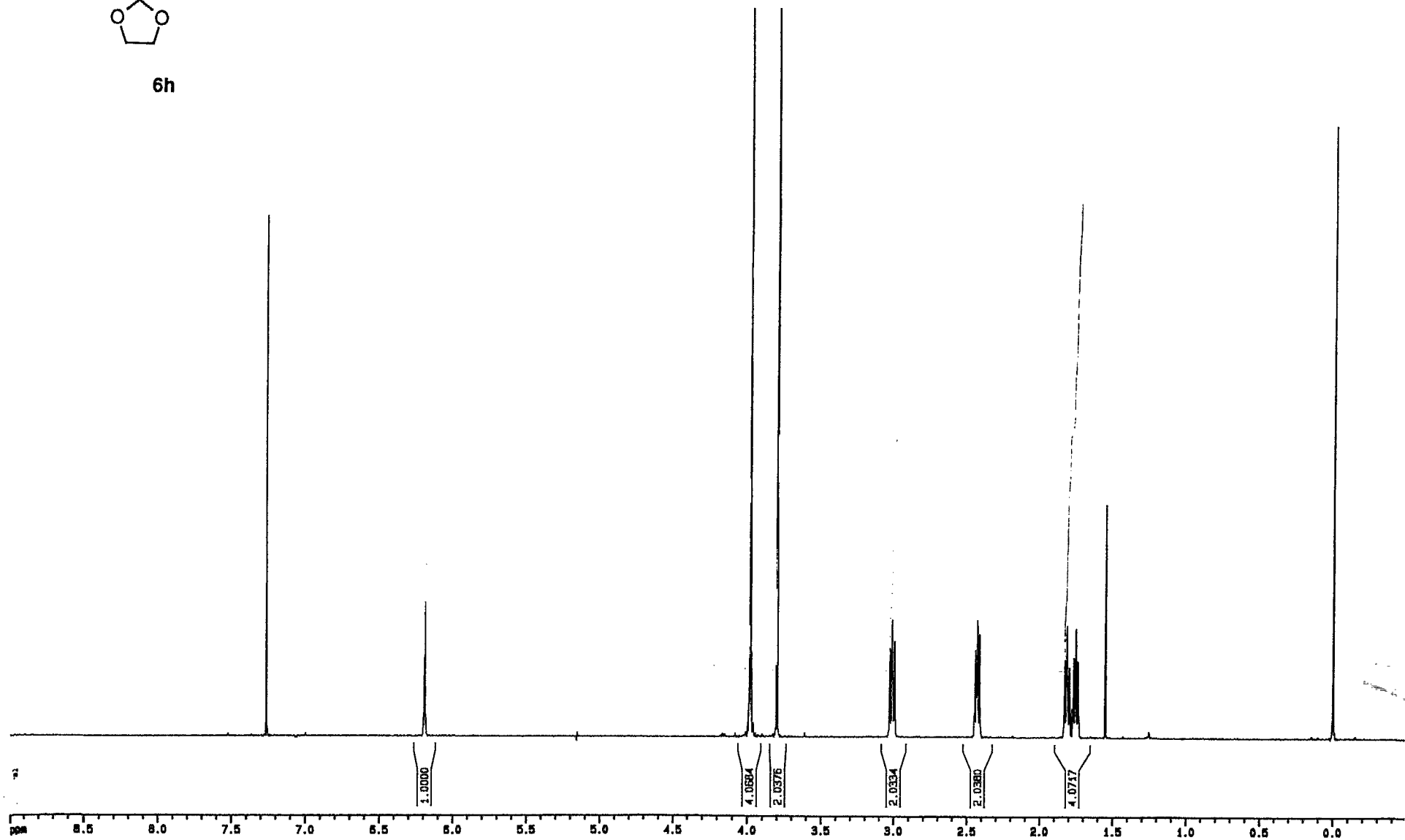


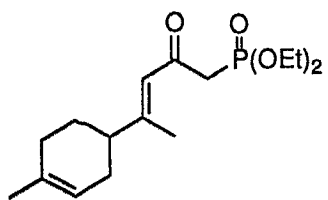
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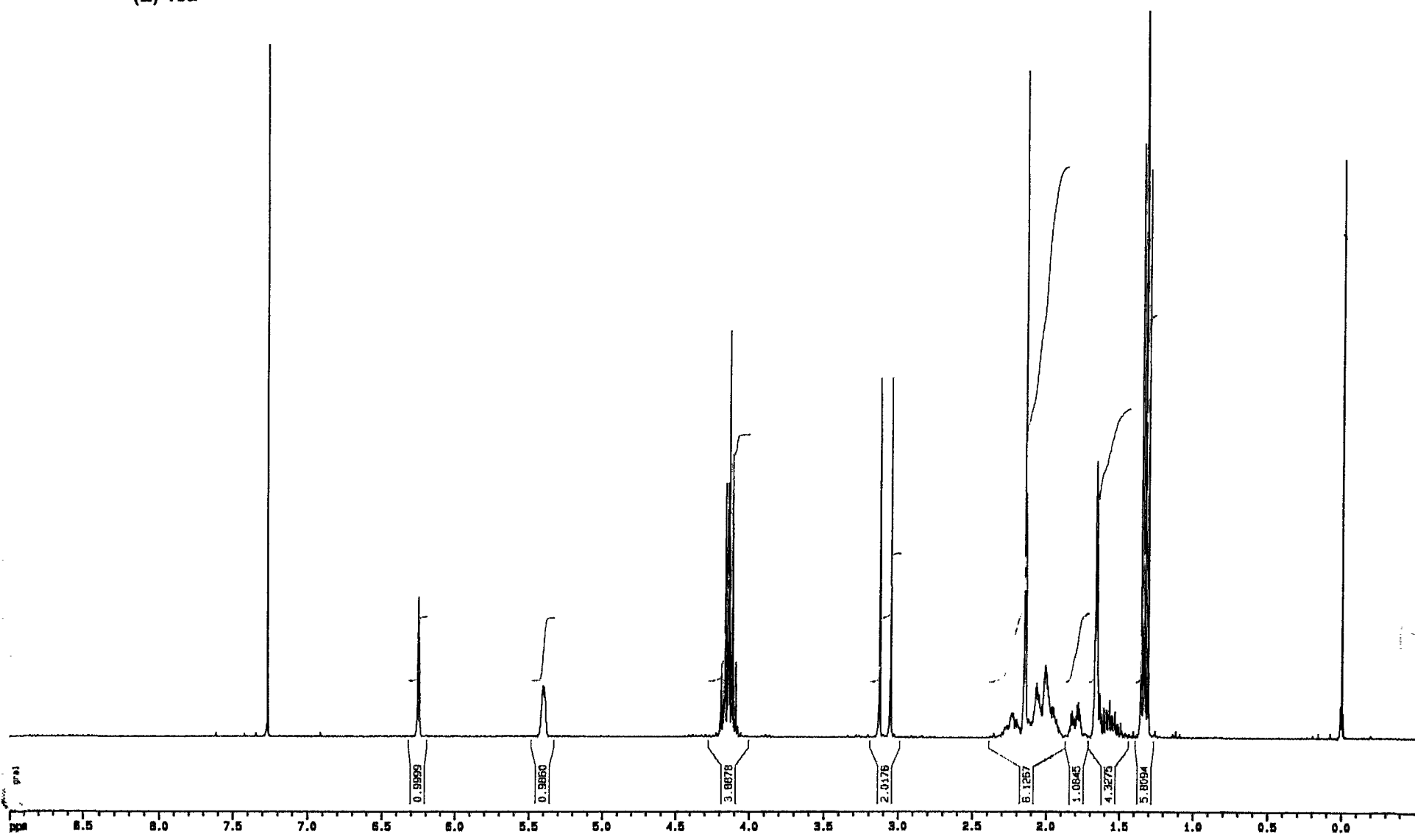


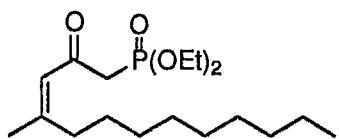
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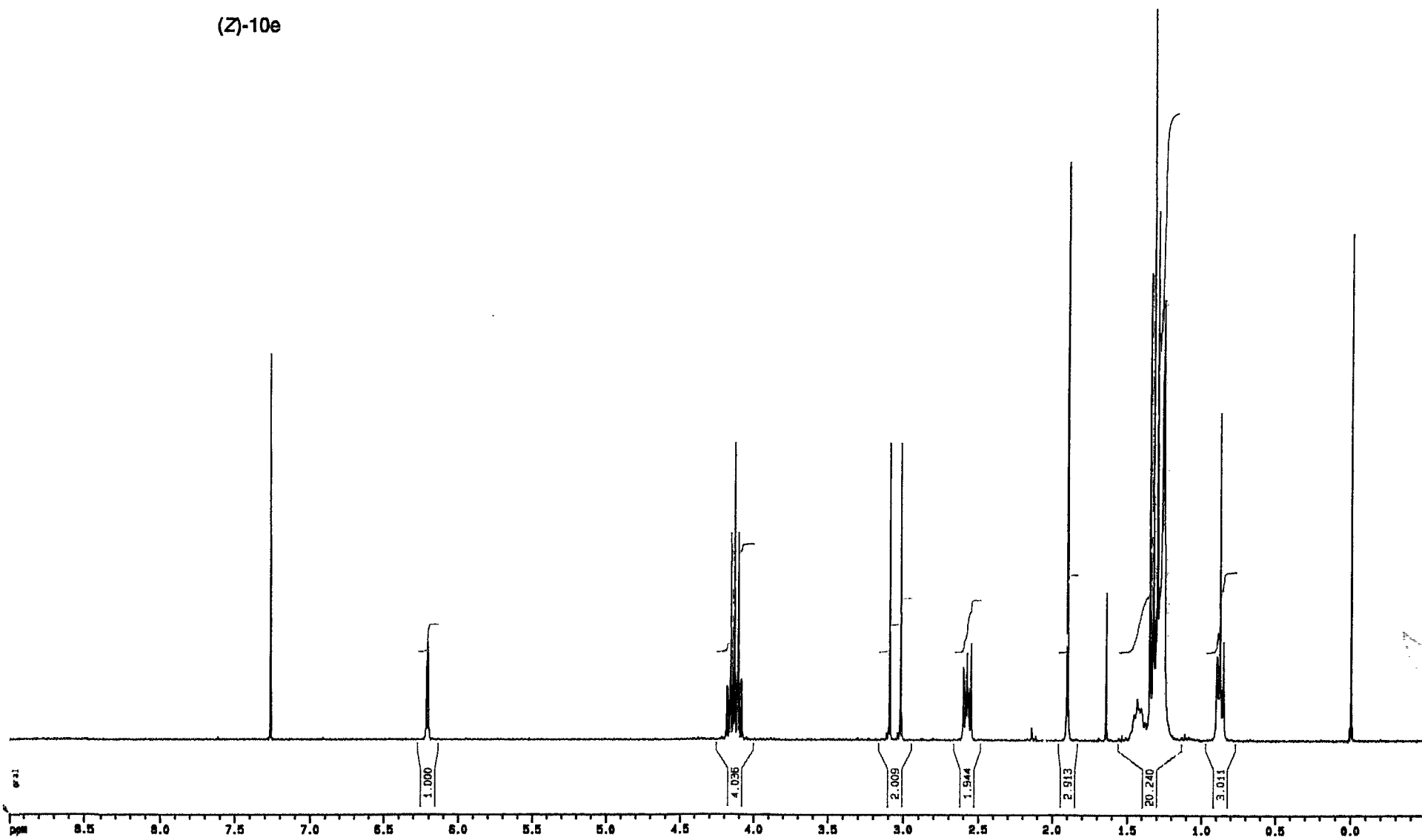


(E)-10a

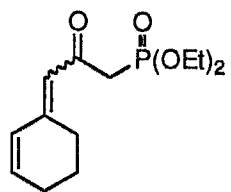




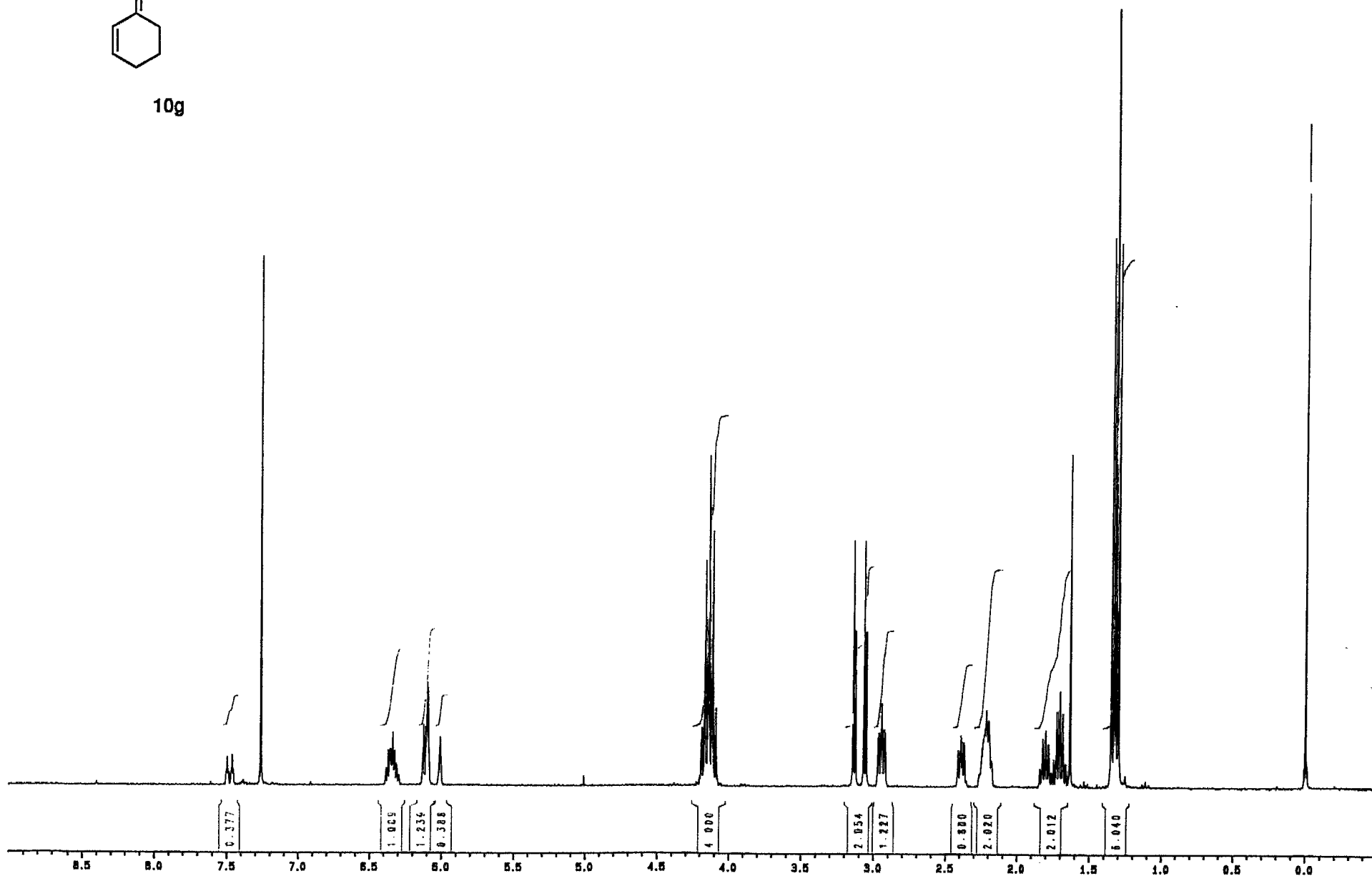
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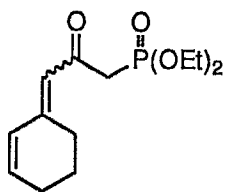


21

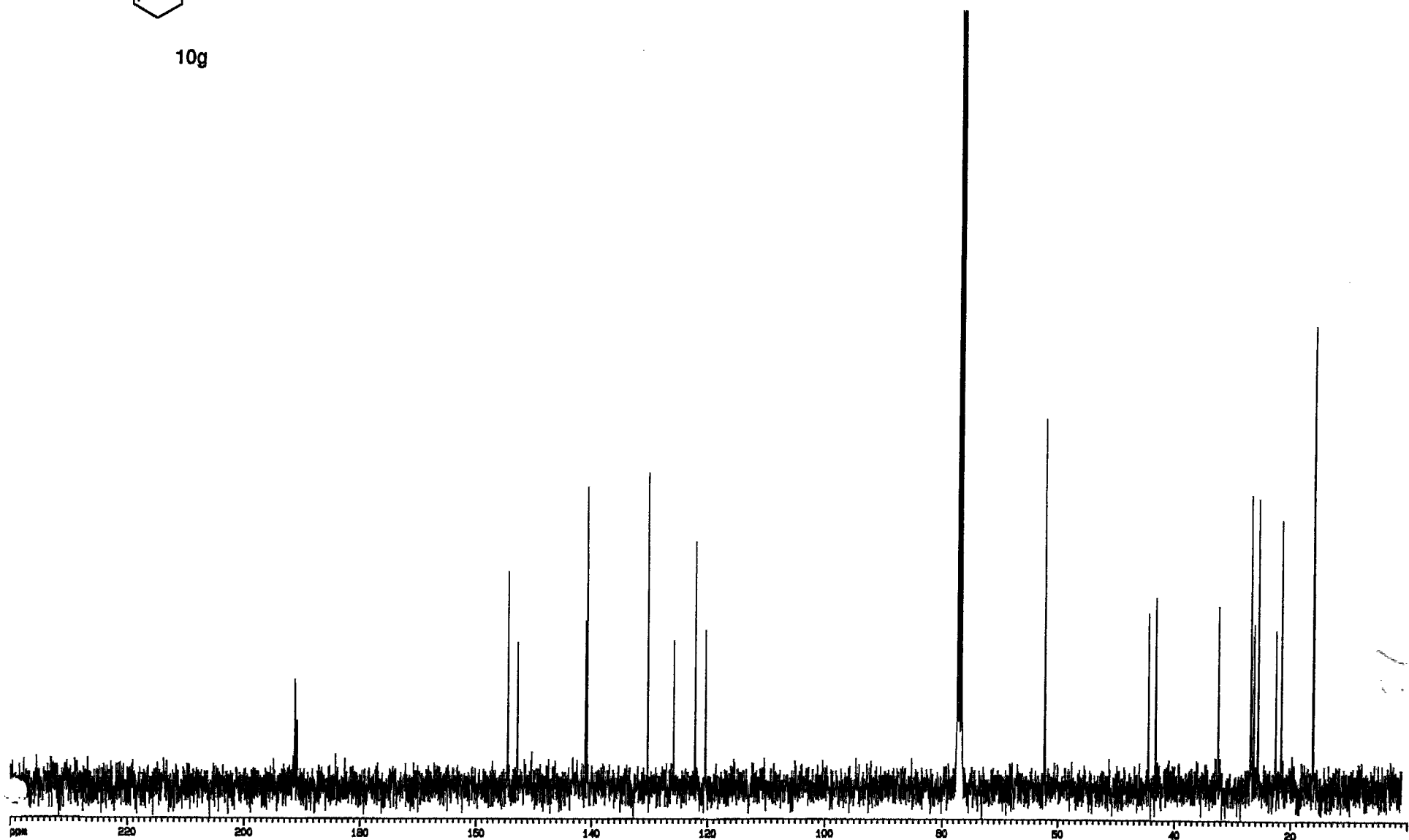


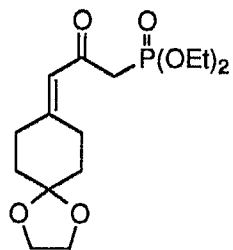
10g





10g





10h

