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Catalyzed Tandem Cyclization−Pinacol Reaction of 3-Silyloxy-1,5-enynes

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Representative experimental procedures for catalytic cyclopentene formation, and copies of ^{1}H and ^{13}C NMR.

(21 Pages)

General experimental details: All cyclization-pinacol precursors were synthesized by the reaction of the corresponding enones with propargyl bromide according to a procedure by Marshall and co-worker.[1] Subsequent Sonogashira coupling[2] of the terminal alkyne led to the formation of compounds **1**, **7**, **9**, **11**, **13**, **15**, **17**, **19**. Gold and silver salts were purchased from Aldrich. All commercially available chemicals were used without further purification.

^{1}H NMR spectra were obtained on Bruker 500 MHz FT-NMR, 360 MHz FT-NMR and 250 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 90.6 MHz. Chemical shifts are reported in ppm relative to solvent signal. High resolution mass spectra and EI were determined on a Finnigan MAT 95S and MAT 8200. Flash chromatography was performed with E. Merck silica gel SiO_2 (43-60 μm). Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F_{254}), and components were visualized by observation under UV light or by treating the plates with $KMnO_4/H_2SO_4$ followed by heating.

[1] J. A. Marshall, X.-j. Wang, *J. Org. Chem.* **1991**, *56*, 960-969.
[2] F. Diederich, P. J. Stang, *Metal-catalyzed Cross-coupling reactions*, Wiley-VCH, Weinheim, **1998**.

General Procedure for the Gold(I)-catalyzed Cyclization-Pinacol Reaction.

1-Phenyl-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (2a). A solution of $(Ph_3P)AuCl$ (22.4 mg, 10 mol %) in CH_2Cl_2 (0.3 mL) was added to a solution of $AgSbF_6$ (7.8 mg, 5 mol %) in CH_2Cl_2 (0.3 mL), and the mixture was stirred at room temperature for 10 min. The resulting suspension was filtered through Celite and concentrated under reduced pressure. To this residue, a solution of **1a** (156 mg, 0.45 mmol) and *i*PrOH (0.04 mL, 0.50 mmol) in CH_2Cl_2 (4.5 mL) was added. The pale purple solution was stirred at room temperature for 10 min. The mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (pentanes/EtOAc = 98/2) gave **2a** as a colorless oil (94.7 mg, 0.42 mmol, 93%). R_f = 0.42 (pentanes/EtOAc = 95/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-1.26 (m, 2 H), 1.43-1.45 (m, 1 H), 1.57-1.66 (m, 3 H), 1.68-1.72 (m, 1 H), 2.06-2.10 (m, 1 H), 2.53 (d, *J* = 16.7 Hz, 1 H), 2.70 (dd, *J* = 16.7, 2.7 Hz, 1 H), 3.16 (t, *J* = 5.8 Hz, 1 H), 6.02 (s, 1 H), 7.23 (t, *J* = 7.3 Hz, 1 H), 7.32 (t, *J* = 7.4 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 9.52 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 21.9, 22.9, 27.1, 28.5, 36.3, 44.1, 56.7, 123.5, 126.1, 127.4, 128.6, 135.4, 148.0, 205.6. LRMS (EI): 226 (58%) [M^+], 197 (100%), 156 (52%); HRMS calcd for $C_{16}H_{18}O$: 226.1358, found: 226.1356.

1-(2-Methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (2b). Following the general procedure, **2b** was obtained as a yellow oil (83%) after flash chromatography on silica. (P/EtOAc = 95/5). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.20–1.23 (m, 2 H), 1.37–1.47 (m, 1 H), 1.55–1.64 (m, 3 H), 1.67–1.73 (m, 1 H), 2.04–2.10 (m, 1 H), 2.52 (d, *J* = 16.6 Hz, 1 H), 2.67 (dd, *J* = 2.9, 16.6 Hz, 1 H), 3.08 (dd, *J* = 6.8, 8.4 Hz, 1 H), 3.80 (s, 3 H), 5.88 (t, *J* = 2.4 Hz, 1 H), 6.84–6.86 (m, 2 H), 7.33–7.36 (m, 2 H), 9.50 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 22.0, 23.0, 27.0, 28.7, 36.1, 44.2, 55.4, 56.6, 114.0, 121.3, 127.3, 128.2, 147.5, 159.1, 206.0. LRMS (EI): 256 (11%) [M^+], 120 (48%), 105 (100%), 84 (44%), 43 (57%); HRMS 256.1461 [256.1463 calcd for $C_{17}H_{20}O_2$ (M^+)].

1-(Thiophen-2-yl)-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (2c). Following the general procedure, **2c** was obtained as a yellow oil (81%) after flash chromatography on silica. (P/EtOAc = 97/3). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.20–1.23 (m, 2 H), 1.37–1.47 (m, 1 H), 1.55–1.64 (m, 3 H), 1.67–1.73 (m, 1 H), 2.04−2.10 (m, 1 H), 2.52 (d, *J* = 17.0 Hz, 1 H), 2.67 (dd, *J* = 3.0, 17.0 Hz, 1 H), 3.08 (dd, *J* = 6.2, 9.4 Hz, 1 H), 5.89 (t, *J* = 2.5 Hz, 1 H), 6.95–6.97 (m, 2 H), 7.15 (dd, *J* = 2.0, 4.1 Hz, 1 H), 9.47 (s, 1 H); ^{13}C NMR (62.9 MHz,

$CDCl_3$) δ = 21.9, 23.1, 26.8, 29.2, 35.8, 45.5, 56.8, 123.0, 124.0, 124.3, 127.4, 139.7, 142.2, 205.4. HRMS (EI): 232 (100%) [M^+], 203 (60%), 189 (51%), 161 (39%), 97 (31%); HRMS 232.0919 [232.0922 calcd for $C_{14}H_{16}OS$ (M^+)].

1-(Naphthalen-1-yl)-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (2d). Following the general procedure, **2d** was obtained as a pale yellow liquid (71 %) after flash chromatography on silica. (P/Et_2O = 80/20). R_f = 0.37 (P/Et_2O = 80/20); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.77−1.83 (m, 2 H), 1.85−1.94 (m, 4 H), 2.44 (d, *J* = 17.3 Hz, 1 H), 2.49 (dt, *J* = 1 H), 2.47 (dt, *J* = 16.3, 1.9 Hz , 1 H), 2.82 (dt, *J* = 16.3, 1.9 Hz , 1 H), 3.42−3.54 (m, 1 H), 5.76−5.85 (m, 1 H), 7.31 (dd, *J* = 7.0, 1.2 Hz, 1 H), 7.40−7.58 (m, 3 H), 7.78 (d, *J* = 8.2 Hz, 1 H), 7.81−7.92 (m, 1 H), 8.03−8.13 (m, 1 H), 9.78 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.4, 27.5, 39.7, 40.5, 42.1, 42.3, 56.0, 122.7, 125.6, 127.3, 128.5, 136.3, 139.7, 213.0; LRMS (EI): 276 (99%) [M^+], 247 (100%), 165 (43%), 84 (43%); HRMS 276.1518 [276.1514 calcd for $C_{20}H_{20}O$ (M^+)].

1-Methyl-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (2e). Following the general procedure, **2e** was obtained as a colorless liquid (54%) after flash chromatography on silica. (P/Et_2O = 98/2). R_f = 0.51 (P/EtOAc = 95/5); ^1H NMR (360 MHz, $CDCl_3$): δ = 1.28−1.37 (m, 2 H), 1.39−1.52 (m, 4 H), 1.63−1.80 (m, 5 H), 2.09 (dq, *J* = 15.7 Hz, *J* = 2.0 Hz, 1 H), 2.46 (dq, *J* = 15.7, 2.2 Hz, 1 H), 5.27 (t, *J* = 1.6 Hz, 1 H), 9.54 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.9, 22.3, 26.2, 27.8 (2 x C), 38.1, 46.6, 57.1, 121.8, 143.6, 205.6; LRMS (EI): 164 (6%) [M^+], 149 (31%), 135 (100%), 121 (42%).

3a,4,5,6,7,7a-Hexahydro-3*H*-indene-3a-carbaldehyde (2f). Following the general procedure, **2f** was obtained as a colorless liquid (68%) after flash chromatography on silica. (P/Et_2O = 98/2). R_f = 0.44 (P/EtOAc = 95/5); ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23−1.54 (m, 6 H), 1.60−1.83 (m, 2 H), 2.16 (d, *J* = 16.0 Hz, 1 H), 2.57 (d, *J* = 16.0 Hz, 1 H), 2.82−2.95 (m, 1 H), 5.67 (s, 1 H), 9.55 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.0, 22.1, 27.4, 27.9, 39.1, 44.3, 56.6, 128.4, 135.8, 205.6; LRMS (EI): 150 (26%) [M^+], 135 (19%), 121 (100%), 107 (38%).

6-Phenyl-1,2,3,3a,4,6a-hexahydropentalene-3a-carbaldehyde (8). Following the general procedure, **8** was obtained as a colorless liquid (73%) after flash chromatography on silica. (P/EtOAc = 95/5). R_f = 0.33 (P/EtOAc = 95/5); ^1H NMR (360 MHz, $CDCl_3$): δ = 1.59−1.79

(m, 4 H), 1.87−2.02 (m, 1 H), 2.09−2.22 (m, 1 H), 2.33 (dt, *J* = 18.2, 2.7 Hz, 1 H), 3.18 (dd, *J* = 18.2, 1.8 Hz, 1 H), 3.74 (d, *J* = 8.9 Hz, 1 H), 5.98−6.04 (m, 1 H), 7.20−7.25 (m, 1 H), 7.29−7.36 (m, 2 H), 7.39−7.45 (m, 2 H), 9.68 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 26.3, 32.5, 36.1, 40.4, 53.6, 64.2, 124.1, 126.4, 127.4, 128.6, 135.5, 143.7, 203.0; LRMS (EI): 212 (100%) [M^+], 183 (42%), 155 (52%), 141 (26%); HRMS 212.1201 [212.1201 calcd for $C_{15}H_{16}O$ (M^+)].

1,2-Dimethyl-3-phenylcyclopent-3-enecarbaldehyde (10). Following the general procedure, **10** was obtained as a yellow oil (72%) after flash chromatography on silica. (P/EtOAc =99/1). R_f =0.4 (P/EtOAc = 90/10); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 7.0 Hz, 3 H), 1.19 (s, 3 H), 2.41 (dt, *J* = 17.3, 2.0 Hz, 1 H), 2.81 (dd, *J* = 17.3, 3.2 Hz, 1 H), 3.33 (q, *J* = 6.9 Hz, 1 H), 5.97 (s, 1 H), 7.20−7.26 (m, 1 H), 7.29−7.36 (m, 2 H), 7.36−7.45 (m, 2 H), 9.56 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 14.2, 16.1, 39.7, 42.7, 56.1, 123.2, 126.3, 127.5, 128.6, 135.5, 147.8, 205.1; LRMS (EI): 200 (23%) [M^+], 185 (60%), 171 (100%), 157 (40%).

1-Methyl-3-phenylcyclopent-3-enecarbaldehyde (12). Following the general procedure, **12** was obtained as a colorless liquid (28%) after flash chromatography on silica. (P/Et_2O =98/2). R_f =0.64 (P/EtOAc = 90/10); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (s, 3 H), 2.38 (dq, *J* = 17.5, 2.2 Hz, 1 H), 2.56 (dq, *J* = 16.2, 2.1 Hz, 1 H), 2.97 (dq, *J* = 17.5, 2.3 Hz, 1 H), 3.18 (dq, *J* = 16.0, 2.2 Hz , 1 H), 6.04−6.09 (m, 1 H), 7.22−72.7 (m, 1 H), 7.29−7.36 (m, 2 H), 7.39−7.44 (m, 2 H), 9.64 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 21.9, 41.6, 41.7. 52.9, 123.2, 125.7, 127.6, 128.5, 135.8, 140.5, 203.9; LRMS (EI): 186 (92%) [M^+], 171 (100%), 157 (46%), 143 (94%).

1-(1,2-Dimethyl-3-phenylcyclopent-3-enyl)ethanone (14). Following the general procedure, **14** was obtained as a colorless oil (55%) after flash chromatography on silica (P/EtOAc = 80/20). ^{1}H NMR (360 MHz, $CDCl_3$) : δ = 1.06 (d, *J* = 7.0 Hz, 3 H), 1.26 (s, 3 H), 2.21 (s, 3 H), 2.34 (dt, *J* = 17.0, 2.1 Hz, 1 H), 1.82 (dt, *J* = 17.0, 2.1 Hz, 1 H), 3.50 (q, *J* = 7.1 Hz, 1 H), 5.91 (s, 1 H), 7.27 (dt, *J* = 31.2, 7.3 Hz, 3H), 7.38 (d, *J* = 7.3 Hz, 2 H); ^{13}C NMR (90.6 MHz $CDCl_3$) δ = 14.4, 19.5, 25.5, 42.1, 44.2, 58.1, 123.6, 126.4, 127.3, 128.5, 136.2, 147.5, 212.5; LRMS (EI) 214 (6%) [M^+], 199 (12%), 185 (14%), 171 (100%), 143 (15%), 91 (15%), 43 (22%); HRMS 214.1357 [214.1358 calcd for $C_{15}H_{18}O$ (M^+)].

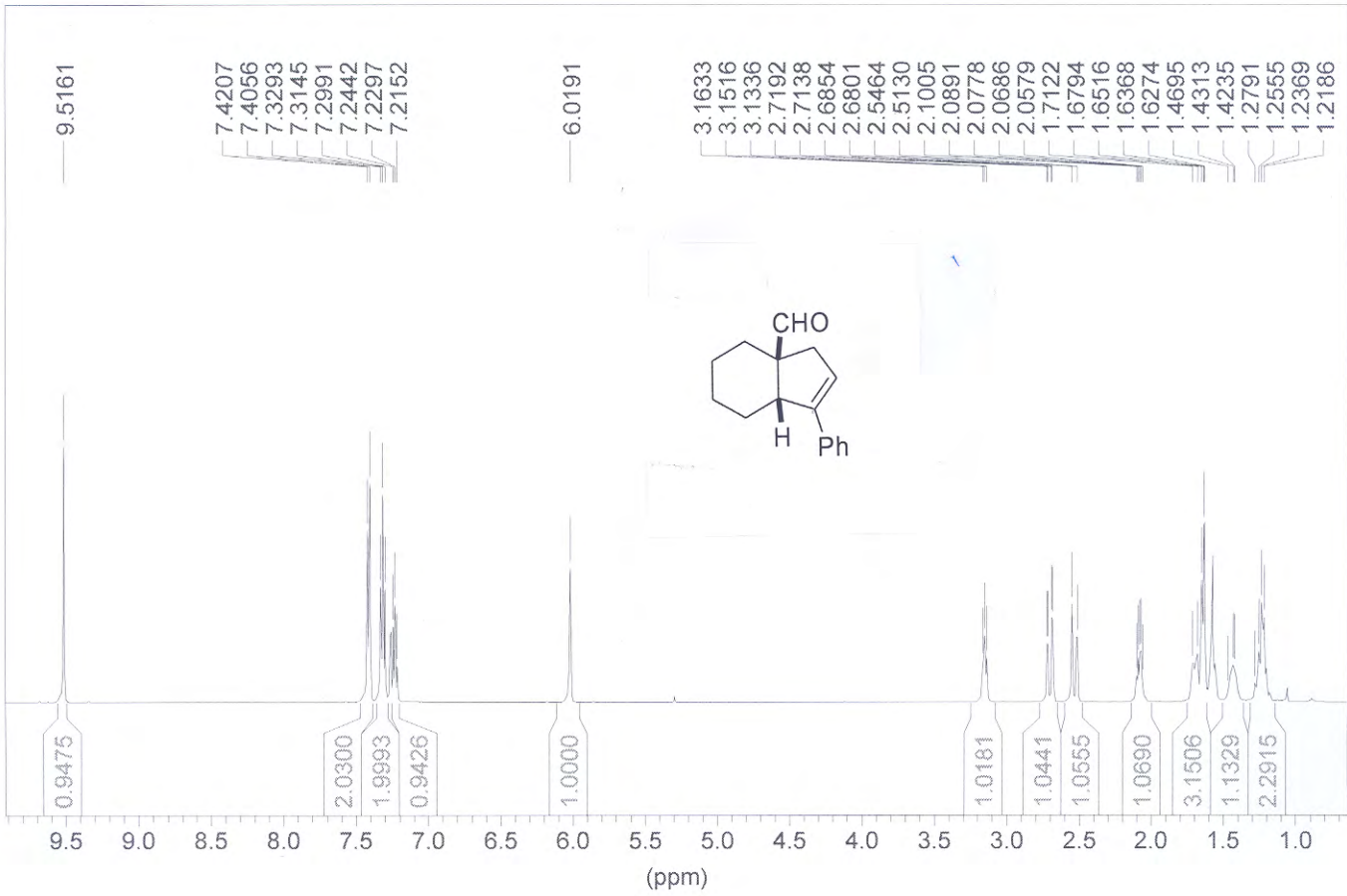
1-(1,2-Dimethylcyclopent-3-enyl)ethanone (16). Following the general procedure, **16** was obtained as a colorless oil (50%) after flash chromatography on silica (P/EtOAc = 80/20). ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 0.99 (d, *J* = 7.3 Hz, 3 H), 1.11 (s, 3 H), 2.14 (s, 3 H), 2.82 (dq, *J* = 16.6, 2.1 Hz, 1 H), 3.01−3.06 (m, 1 H), 5.47−5.48 (m, 1 H), 5.56−5.58 (m, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ = 14.9, 19.3, 25.8, 43.9, 44.6, 57.4, 127.0, 135.4, 212.6.

(3a*S*,6*S*,7a*R*)-3a-Methyl-1-phenyl-6-(prop-1-en-2-yl)-3,3a,5,6,7,7a-hexahydroinden-4-one (18). Following the general procedure, **18** was obtained as a pale yellow solid (67%) after flash chromatography on silica (pure P, then P/EtOAc = 95/5). ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 1.31 (s, 3 H), 1.64 (s, 3 H), 1.84−1.94 (m, 2 H), 2.28 (d, *J* = 17.0 Hz, 1 H), 2.40−2.46 (m, 2 H), 2.61 (q, *J* = 10.1 Hz, 1 H), 2.98 (d, *J* = 17.0 Hz, 1 H), 3.24 (bs, 1 H), 4.63 (s, 1 H), 4.76 (s, 1 H), 6.04 (s, 1 H), 7.26−7.29 (m, 1 H), 7.34−7.39 (m, 4 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ = 21.1, 24.1, 30.7, 38.9, 43.5, 43.6, 52.2, 54.0, 110.2, 125.5, 126.4, 127.4, 128.6, 135.9, 145.5, 147.3, 215.8; LRMS (EI) 266 (100%) [M^+], 223 (32%), 197 (36%), 185 (55%), 157 (88%), 155 (58%); HRMS 266.1671 [266.1671 calcd for $C_{19}H_{22}O$ (M^+)].

2-Phenyl-spiro[4.5]dec-2-en-6-one (20). Following the general procedure, **20** was obtained as a pale yellow liquid (65 %) after flash chromatography on silica. (P/Et_2O = 80/20). R_f = 0.37 (P/Et_2O = 80/20); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.77−1.83 (m, 2 H), 1.85−1.94 (m, 4 H), 2.44 (d, *J* = 17.3 Hz, 1 H), 2.49 (dt, *J* = 6.6, 1.7 Hz, 2 H), 2.55 (d, *J* = 16.1 Hz, 1 H), 3.03 (dd, *J* = 17.5, 2.2 Hz , 1 H), 3.33 (dd, *J* = 15.9, 2.2 Hz, 1 H), 5.98 (s, 1 H), 7.20−7.25 (m, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.41 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 22.4, 27.5, 39.7, 40.5, 42.1, 42.3, 56.0, 122.7, 125.6, 127.3, 128.5, 136.3, 139.7, 213.0; LRMS (EI): 226 (100%) [M^+], 211 (66%), 198 (37%), 169 (50%), 156 (80%), 142 (70%); HRMS 226.1358 [226.1358 calcd for $C_{16}H_{18}O$ (M^+)].

2-Iodo-1-phenyl-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (21). Following the general procedure, **19** was obtained as a yellow oil (48%) after flash chromatography on silica (P/EtOAc = 97/3). ^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.27−1.30 (m, 2 H), 1.45−1.50 (m, 3 H), 1.62–1.70 (m, 2 H), 1.79–1.86 (m, 1 H), 2.71 (dd, *J* =1.6, 16.1 Hz, 1 H), 3.02 (dd, *J* =1.8, 16.1 Hz, 1 H), 3.25 (t, *J* = 6.4 Hz, 1 H), 7.29–7.40 (m, 5 H), 9.63 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ = 21.8, 21.9, 26.6, 27.8, 47.3, 50.3, 57.2, 89.2, 128.0, 128.2, 128.4, 136.7, 151.4, 203.6. LRMS (EI): 352 (20%) [M^+], 225 (35%), 197 (100%), 115 (25%), 91 (31%); HRMS 352.0320 [352.0324 calcd for $C_{16}H_{17}IO$ (M^+)].

2-Iodo-3a,4,5,6,7,7a-hexahydro-3*H*-indene-3a-carbaldehyde (22). Following the general procedure, **20** was obtained as a yellow oil (30%) after flash chromatography on silica (P/EtOAc = 97/3).^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.34–1.58 (m, 6 H), 1.65–1.74 (m, 1 H), 1.77–1.84 (m, 1 H), 2.46 (dt, *J* =15.9, 1.6 Hz, 1 H), 2.85–2.94 (m, 2 H), 6.08–6.10 (m, 1 H), 9.52 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ = 21.6, 21.8, 27.3, 27.4, 46.1, 49.6, 57.7, 89.9, 144.3, 203.4. LRMS (EI): 376 (5%) (M^+), 149 (100%), 131 (30%), 121 (38%), 91 (41%); HRMS 276.0013 [276.0011 calcd for $C_{10}H_{13}IO$ (M^+)].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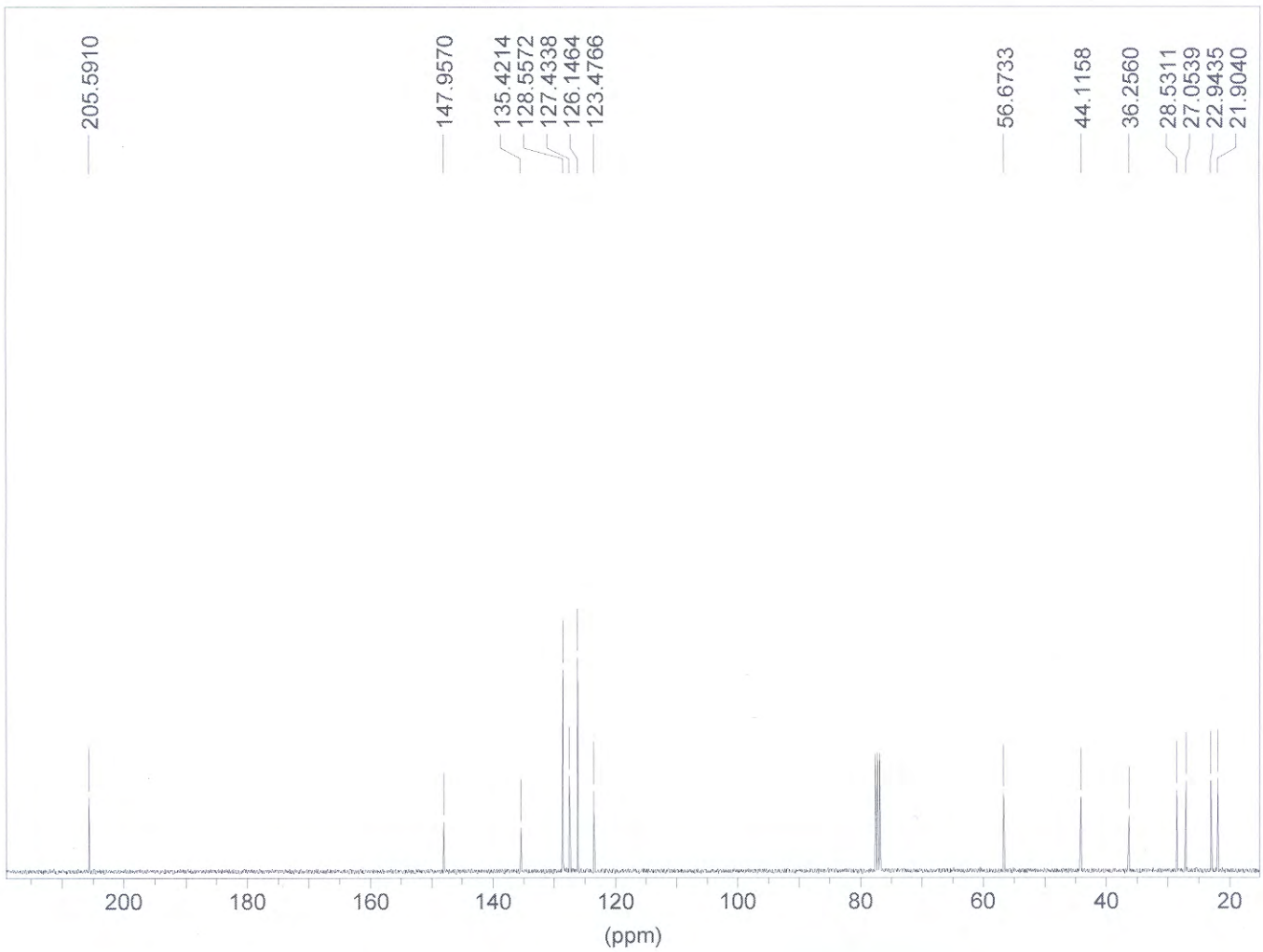
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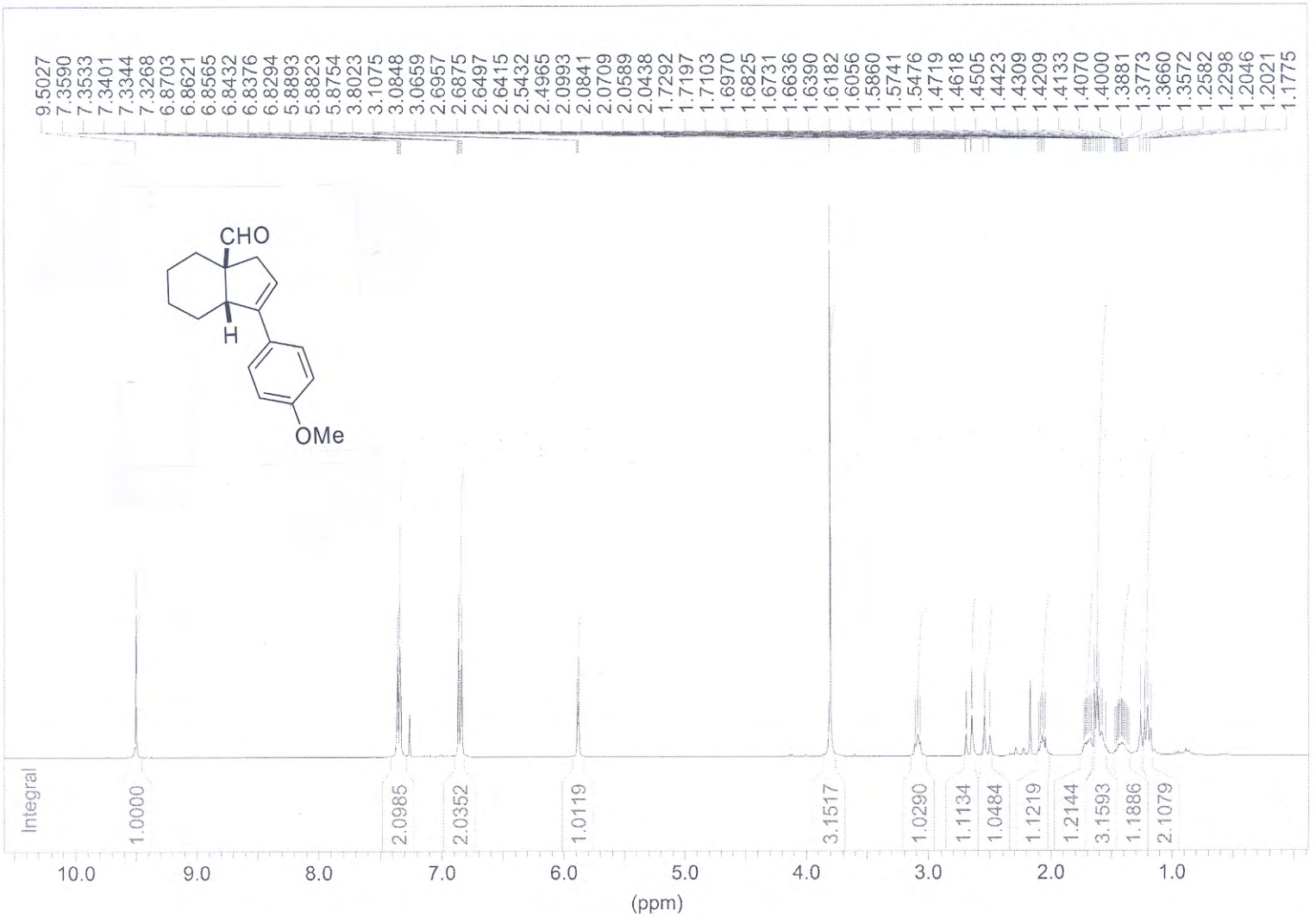
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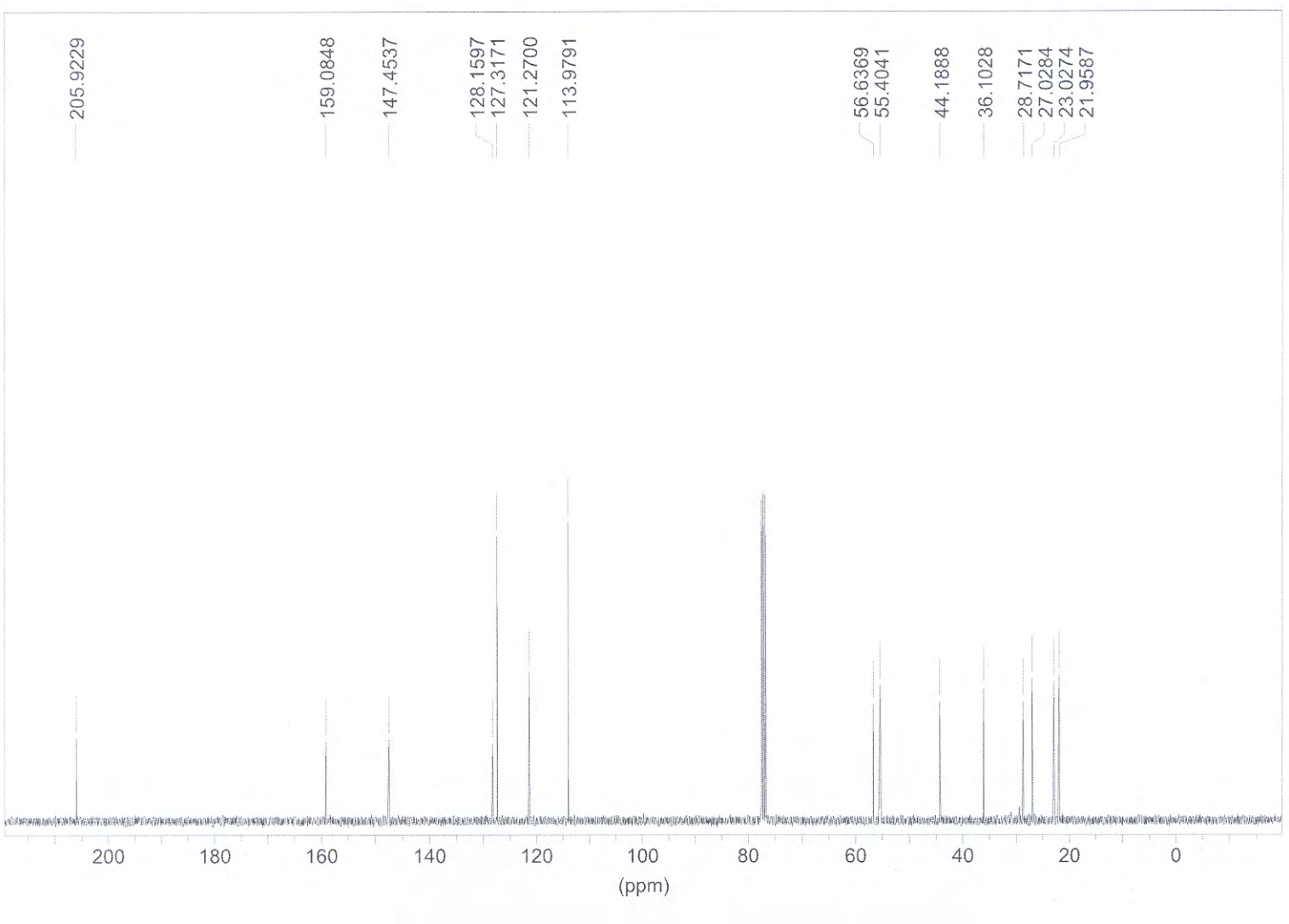
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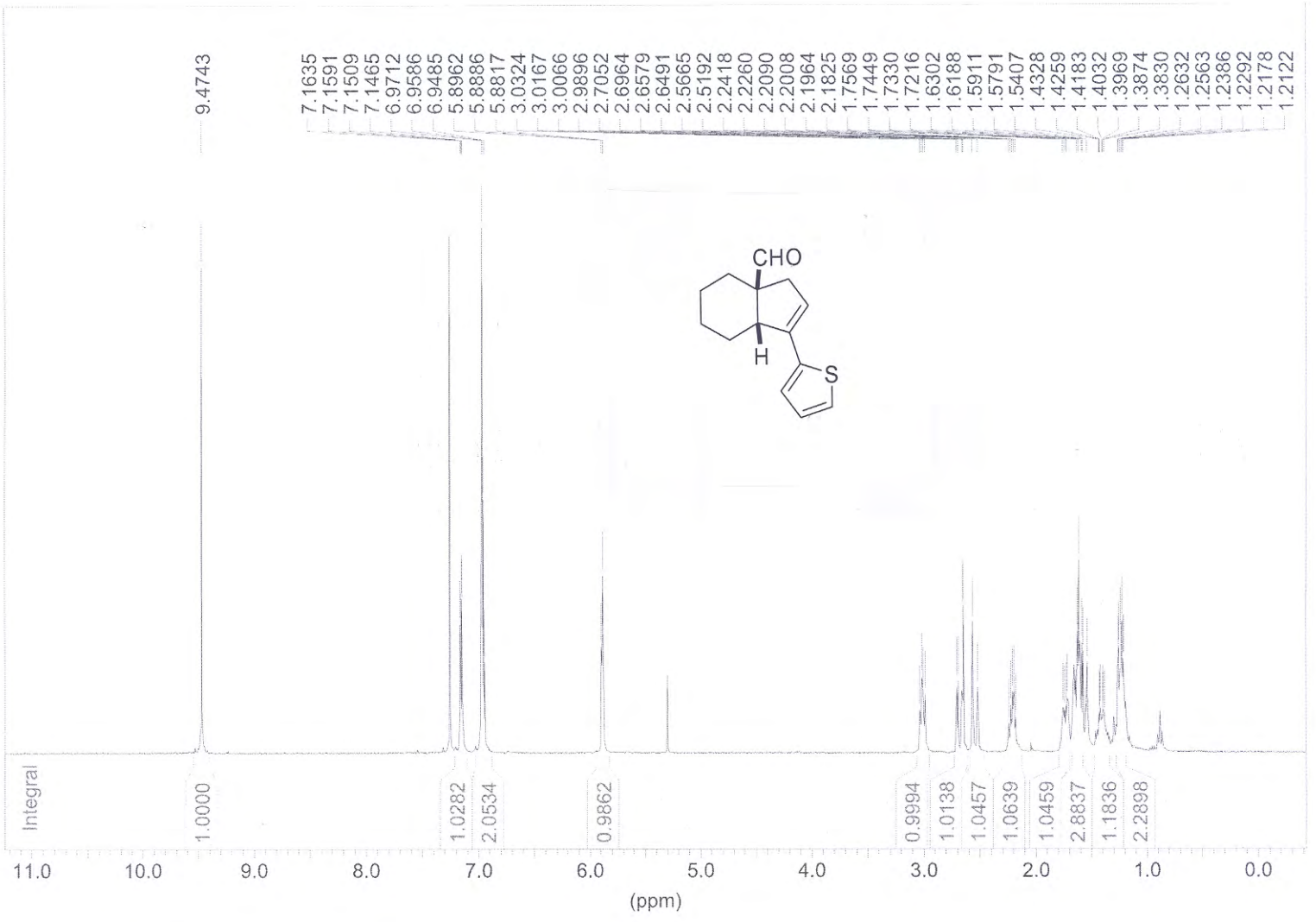
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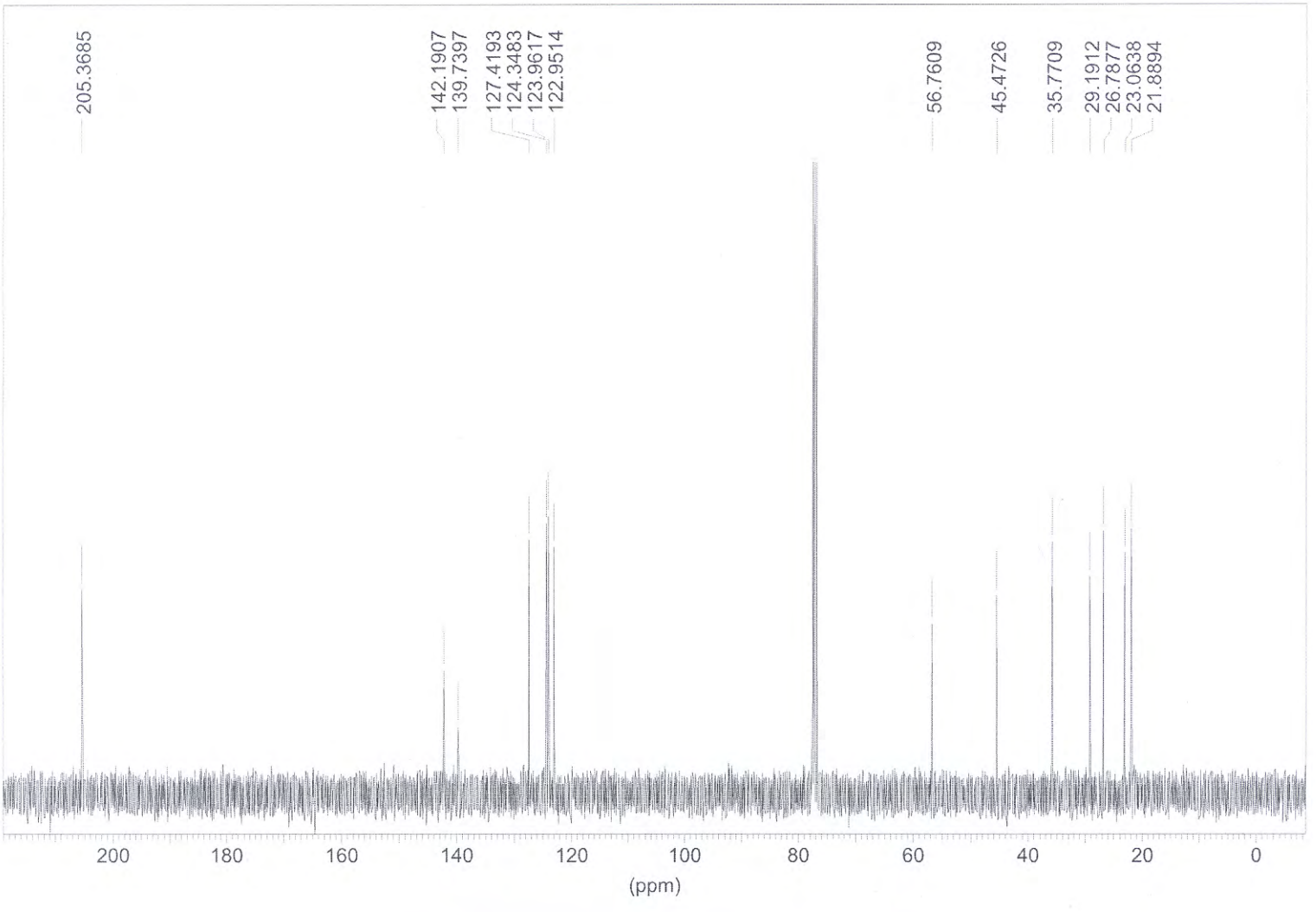
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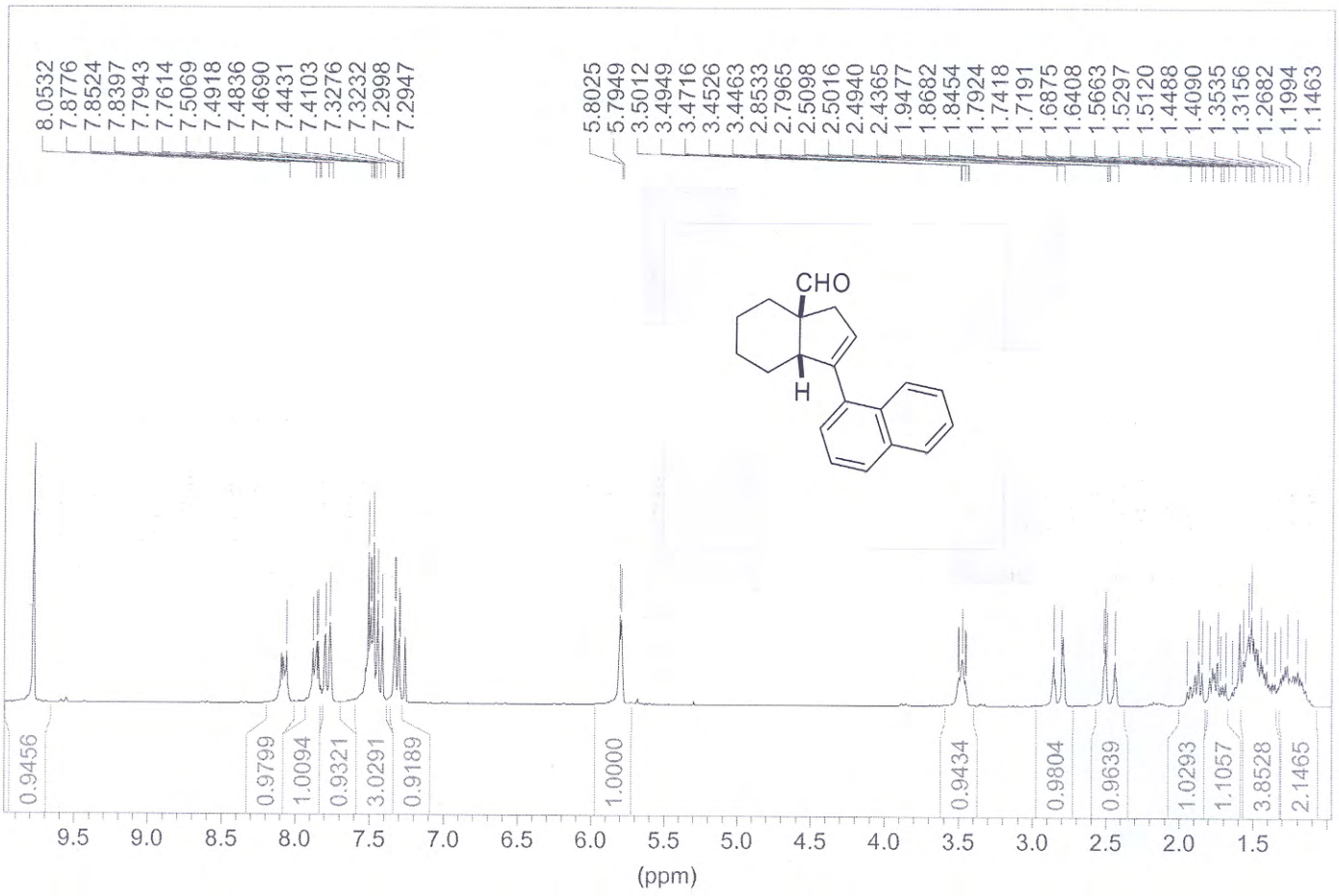
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7.0
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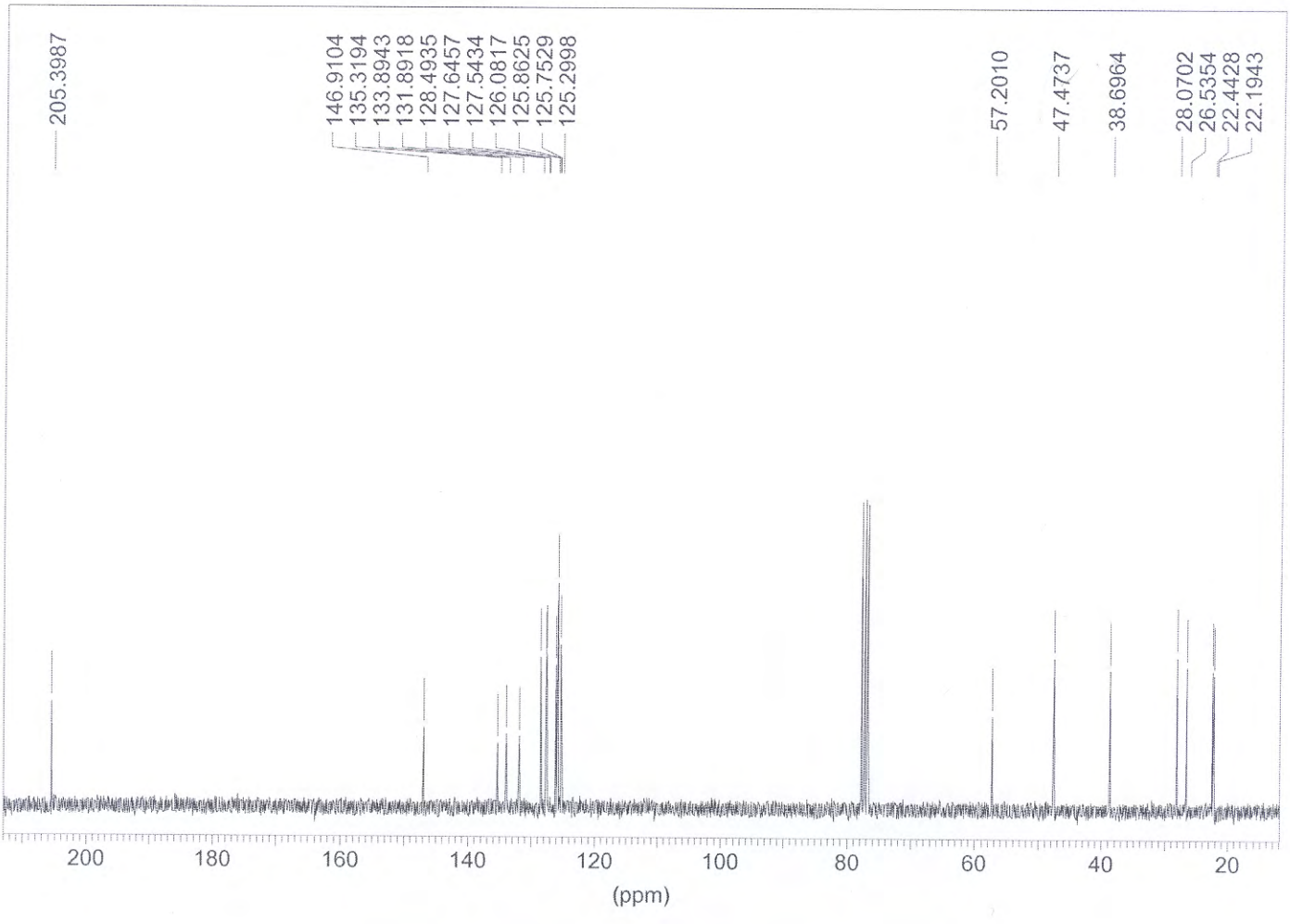
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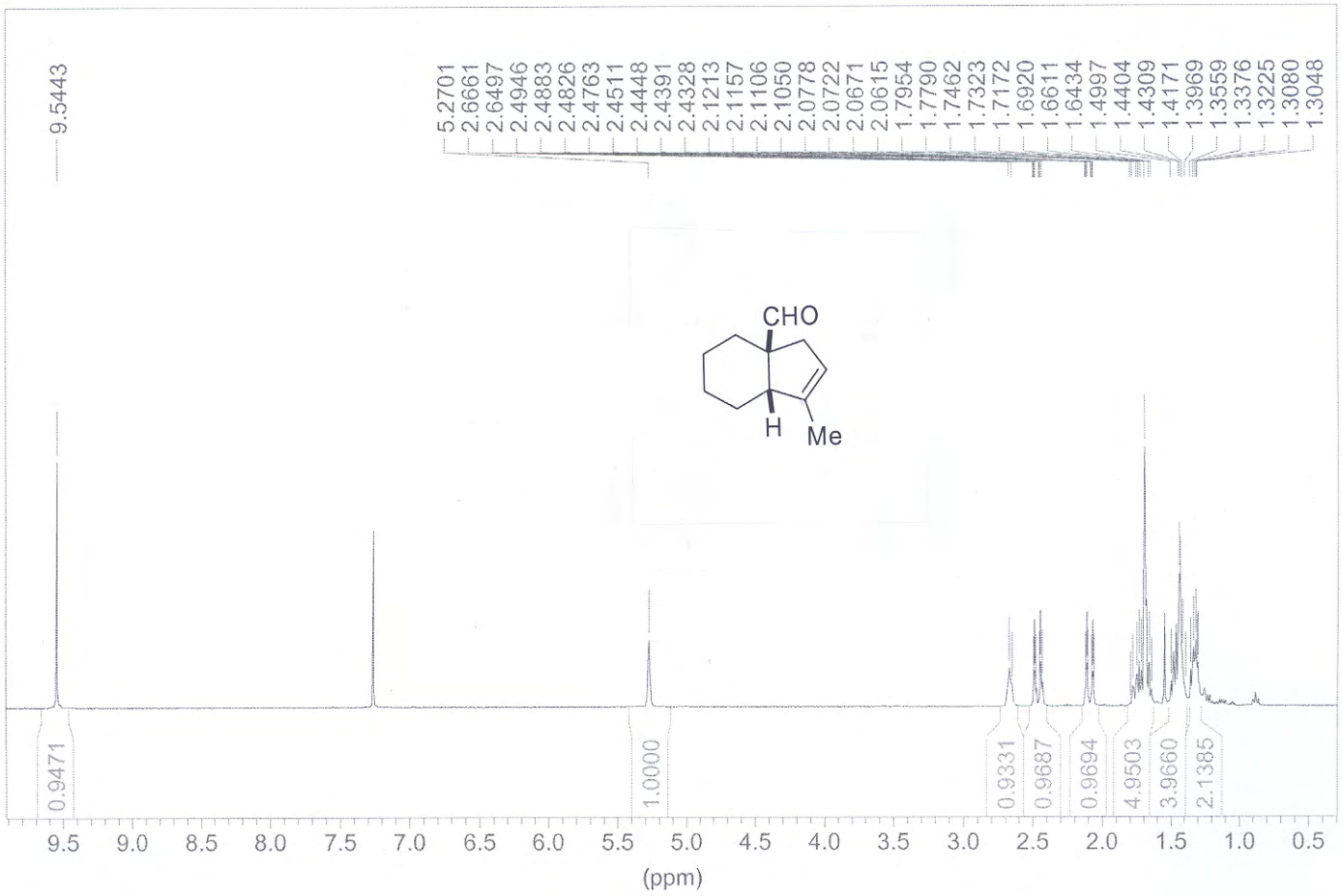
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0.9694
4.9503
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2.1385
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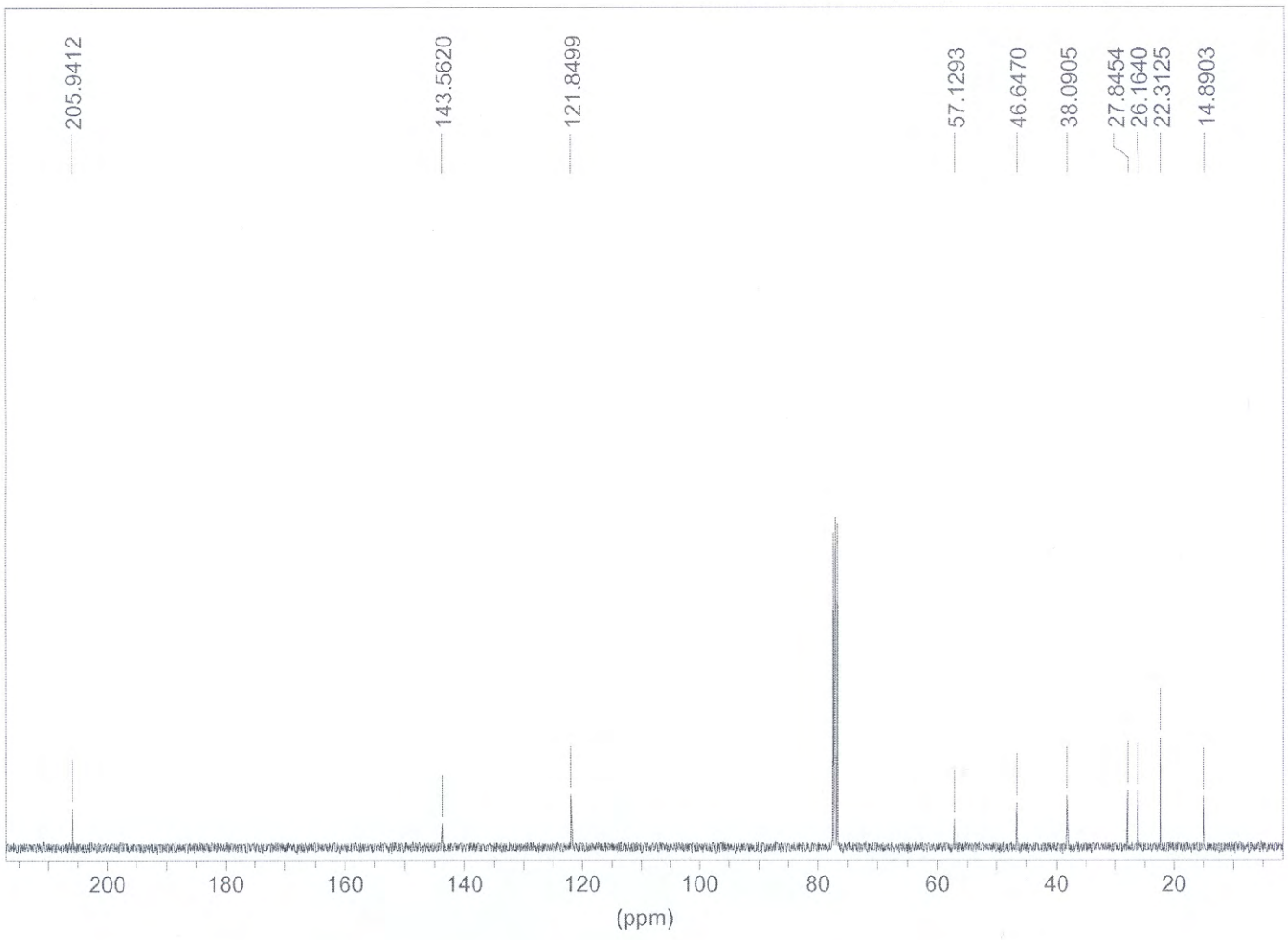
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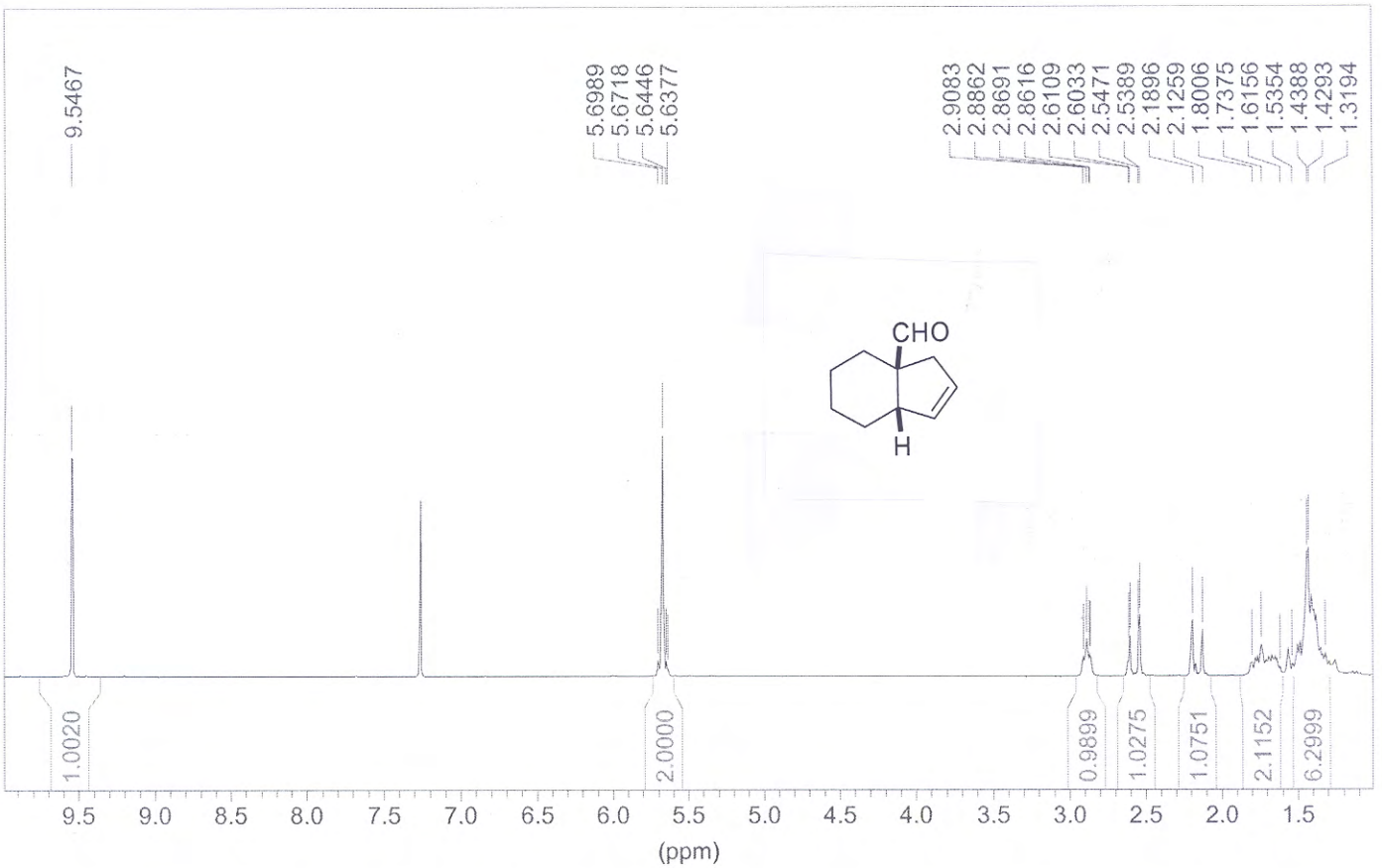
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1.8006
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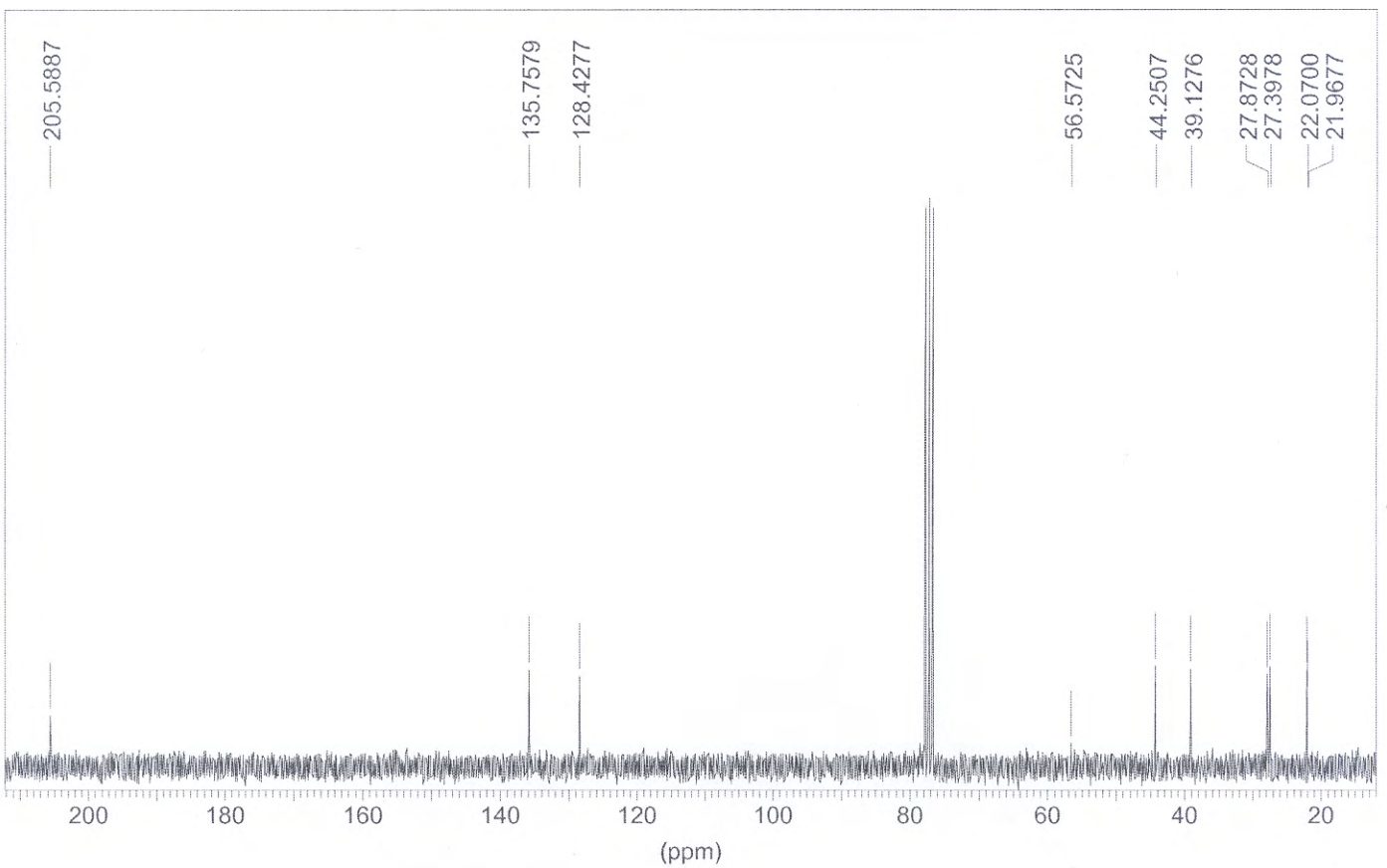
(ppm)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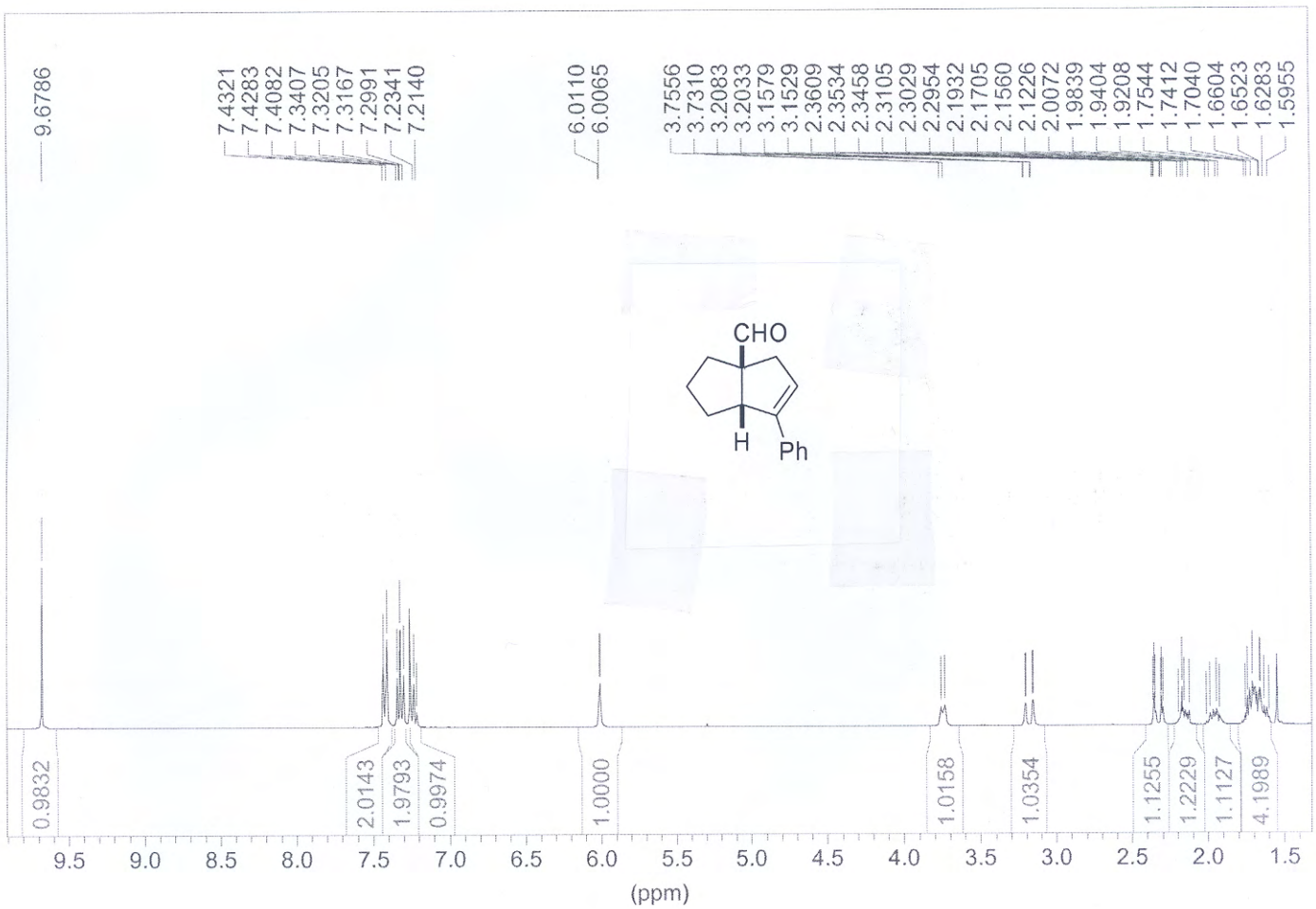
(ppm)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3.7556
3.7310
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3.2033
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3.1529
2.3609
2.3534
2.3458
2.3105
2.3029
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2.1932
2.1705
2.1560
2.1226
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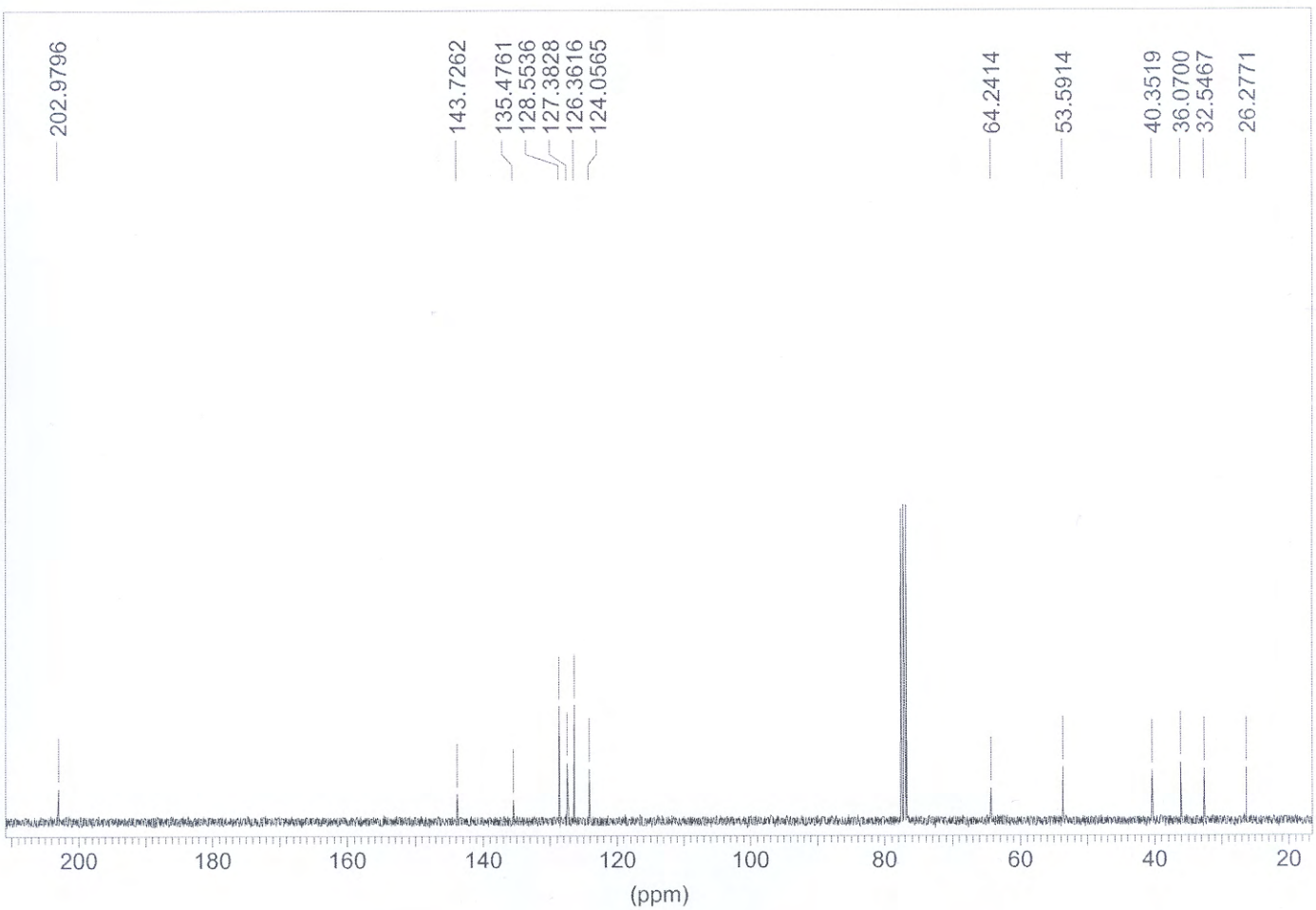
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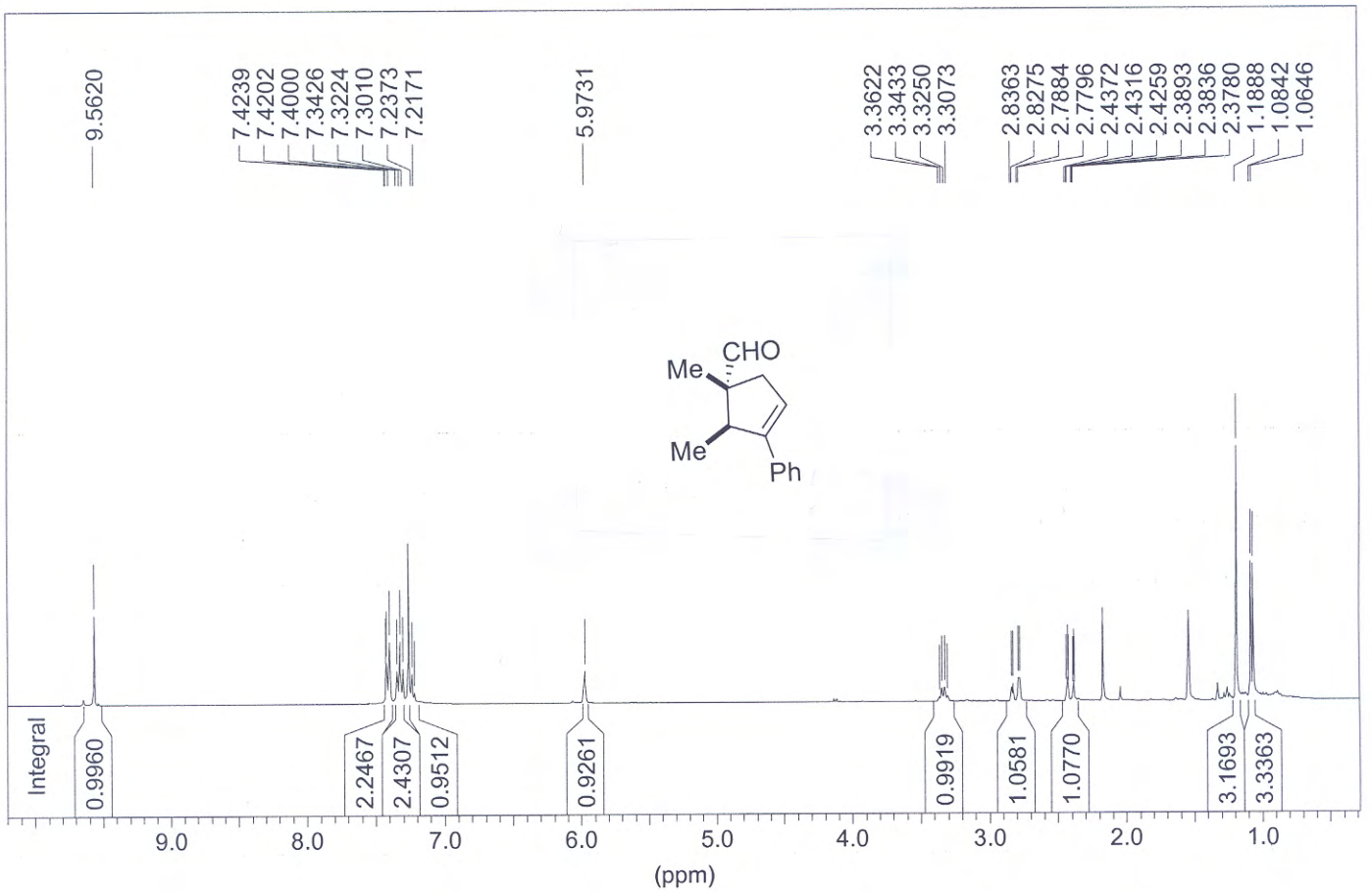
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2.3836
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Me
Ph
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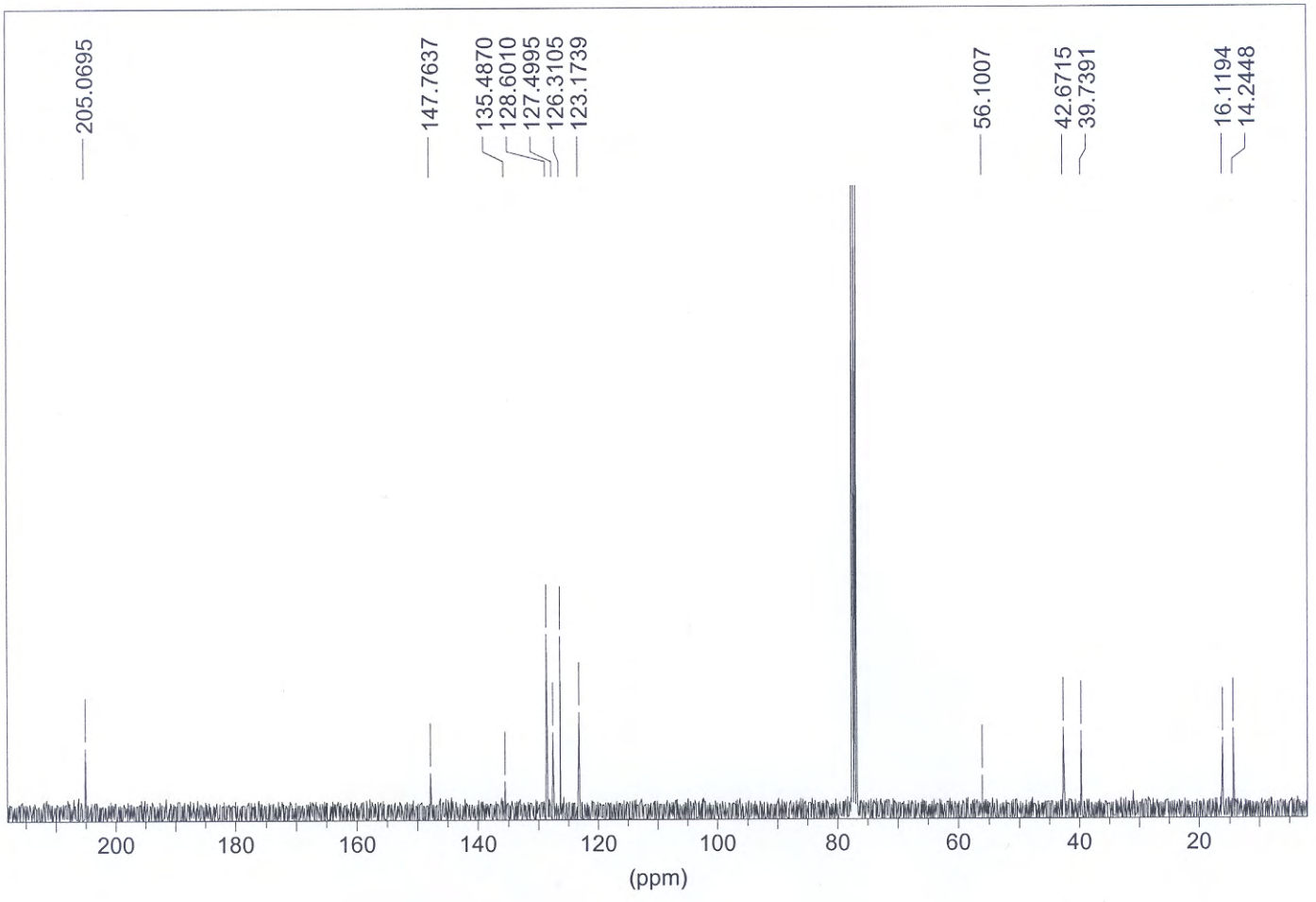
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120
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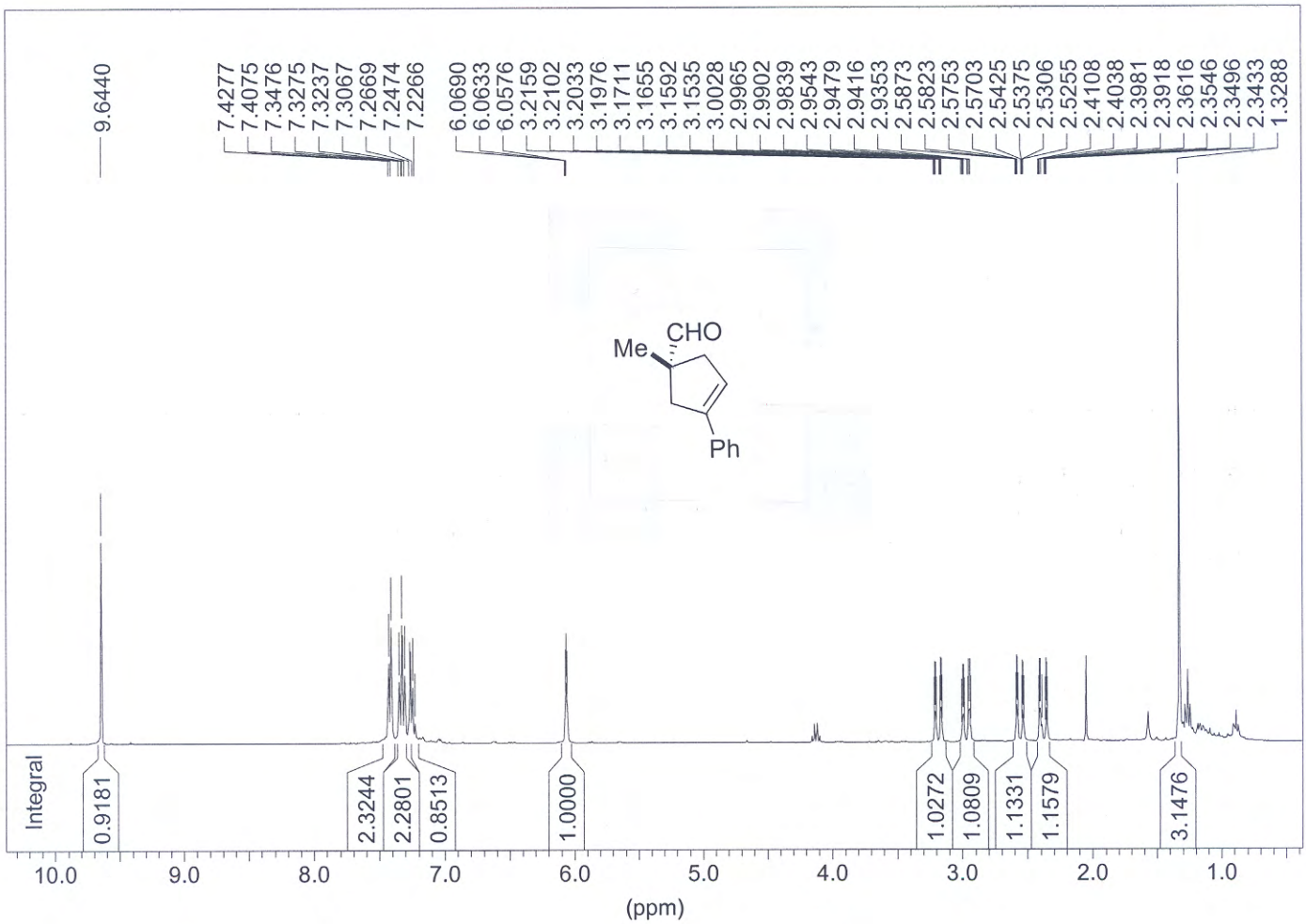
20
(ppm)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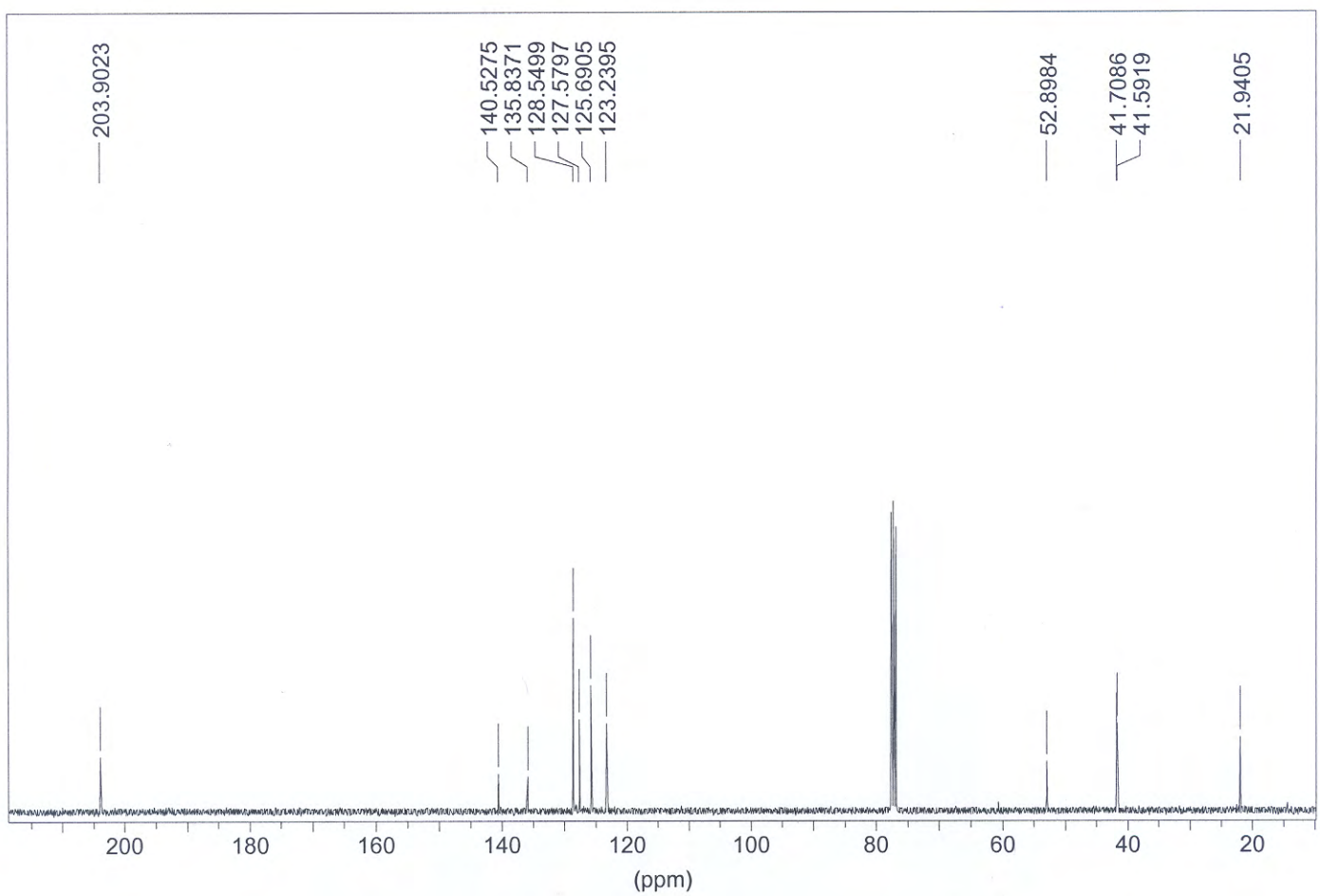
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120
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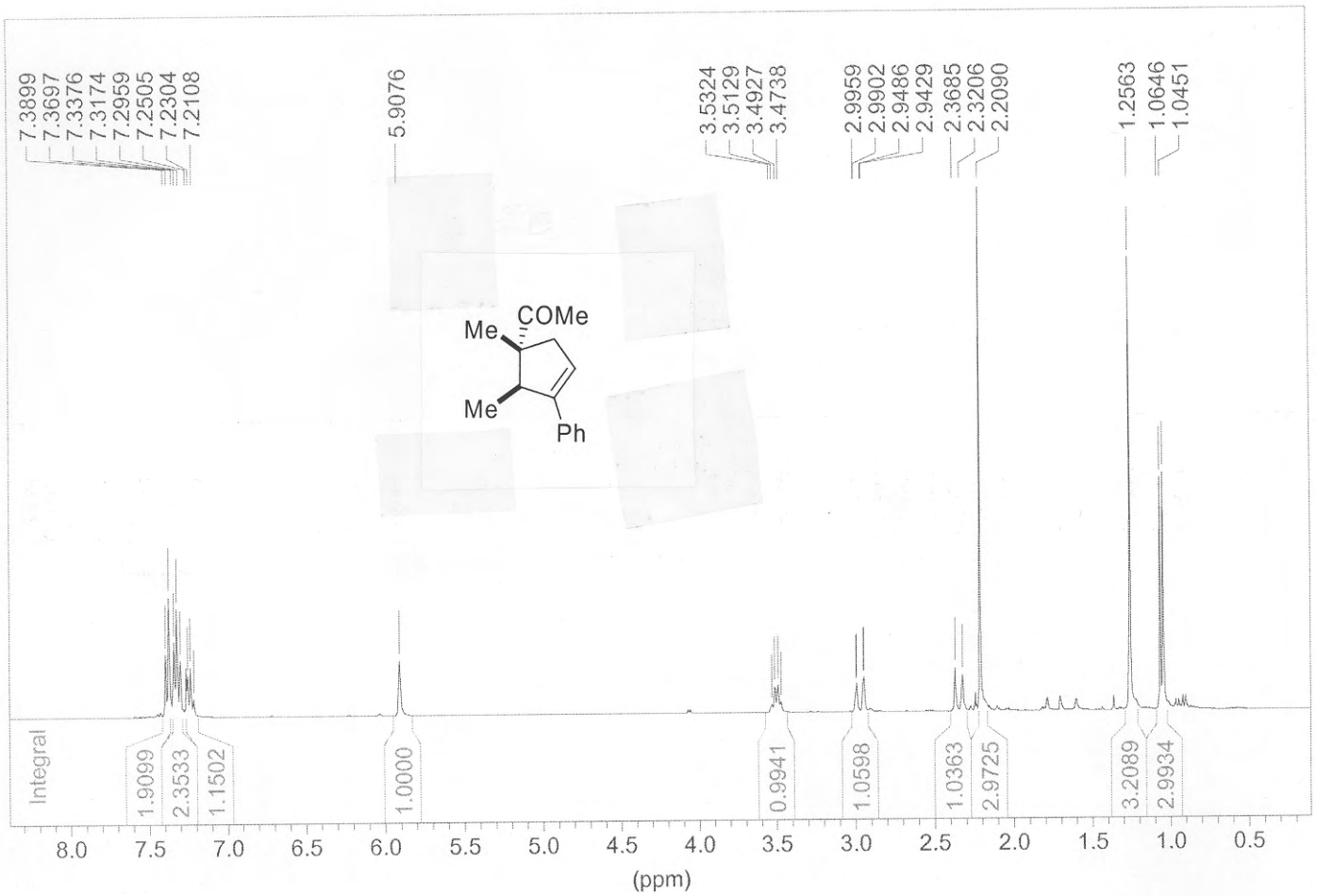
(ppm)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Me
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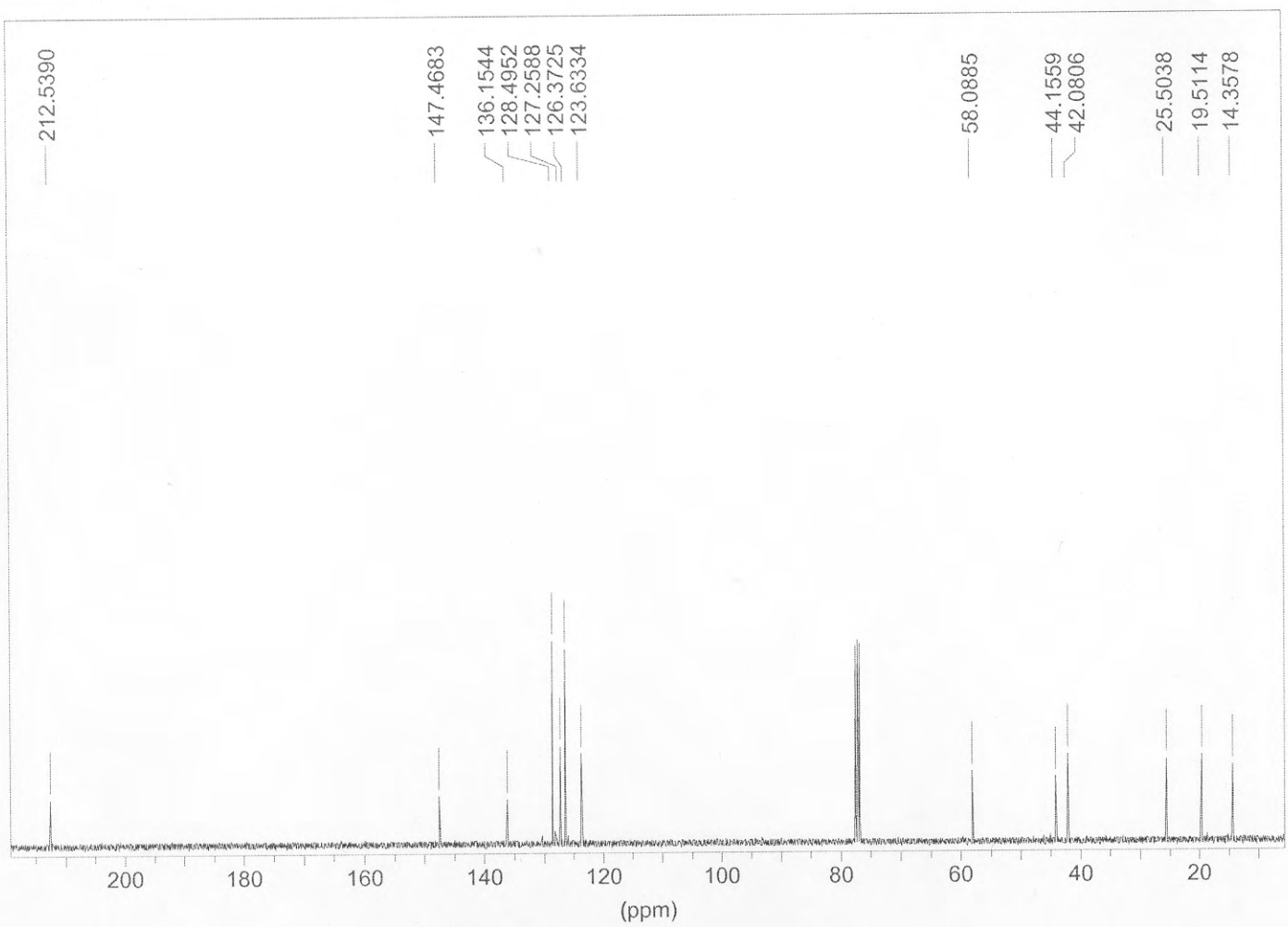
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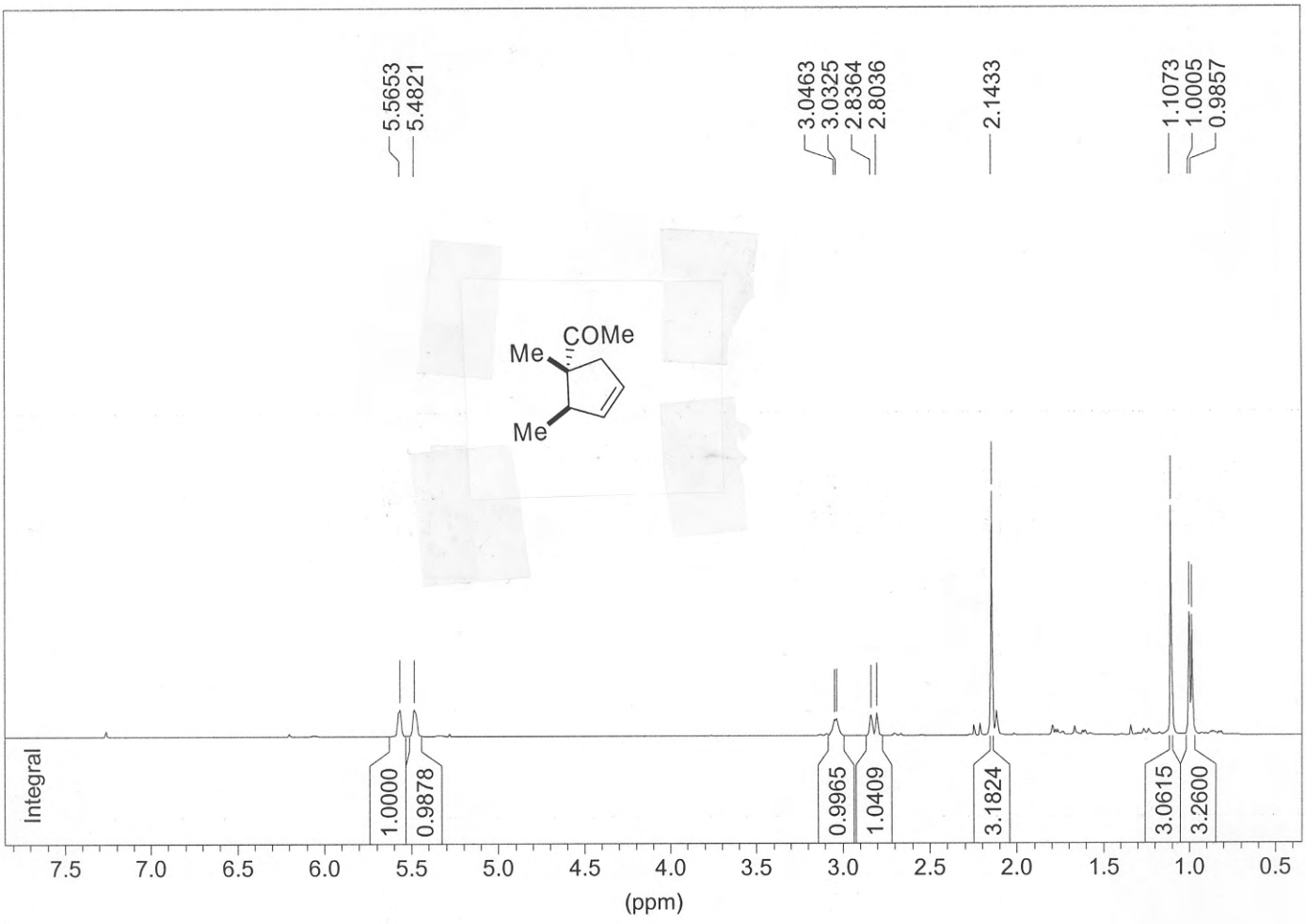
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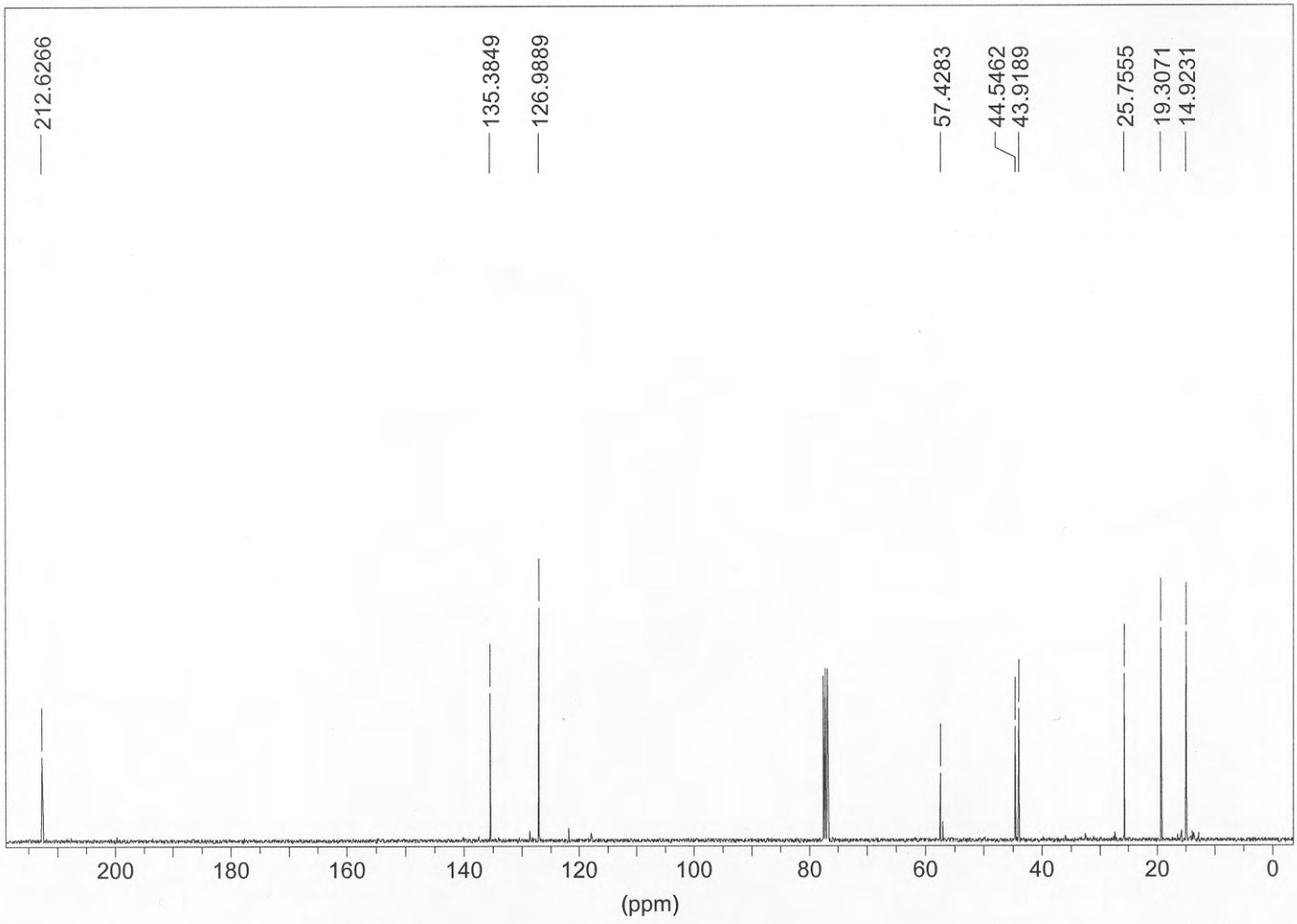
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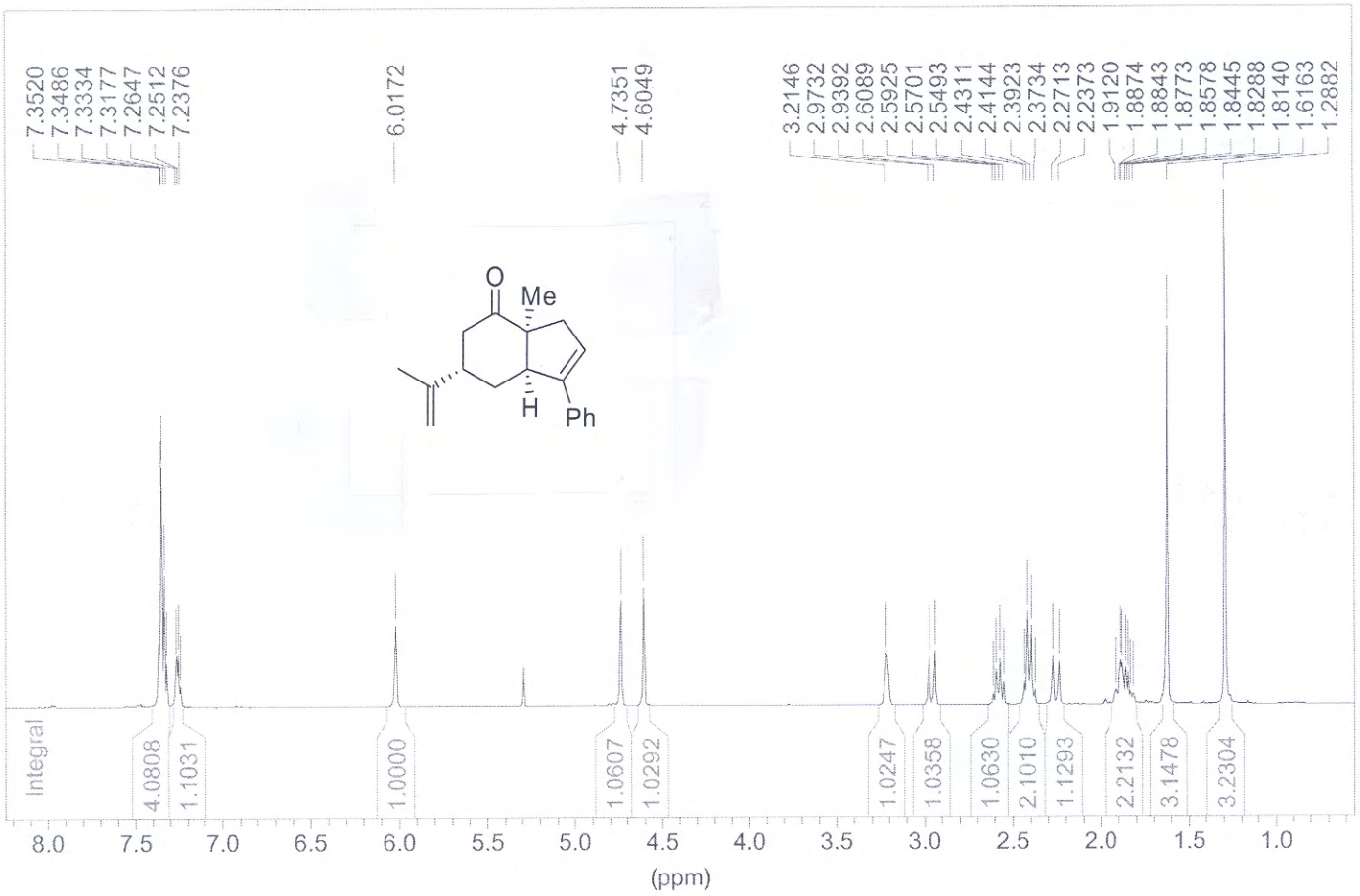
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H
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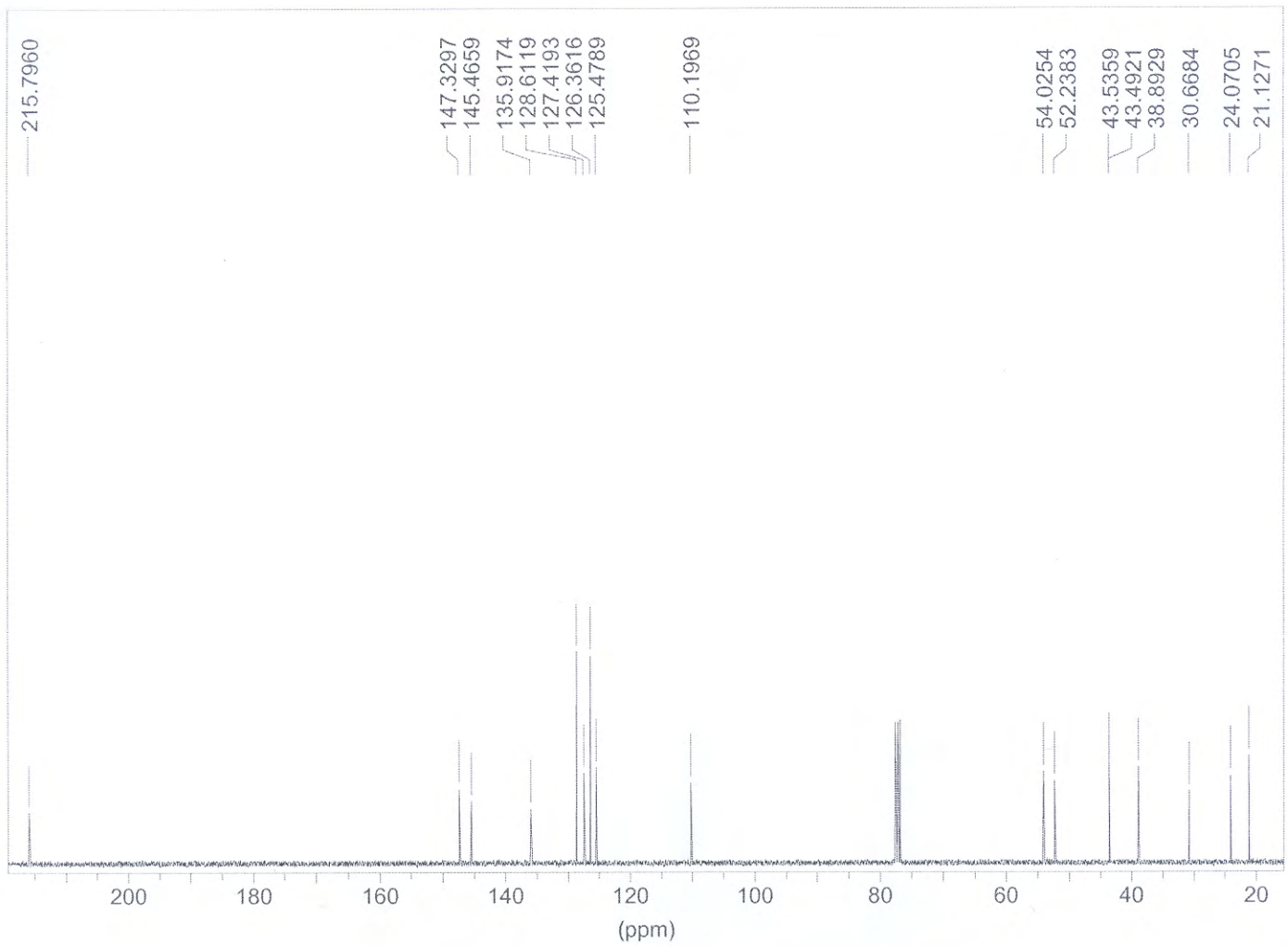
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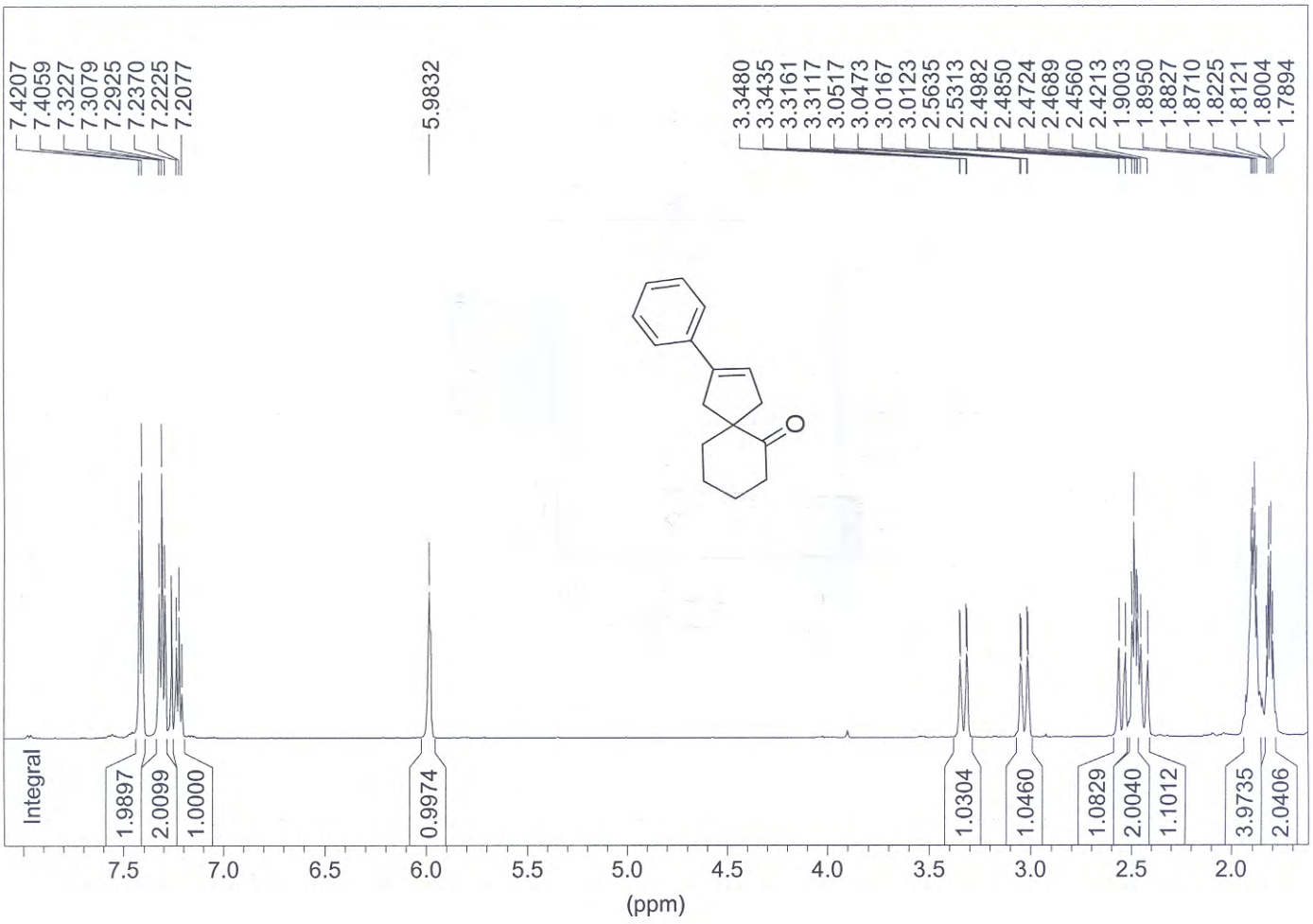
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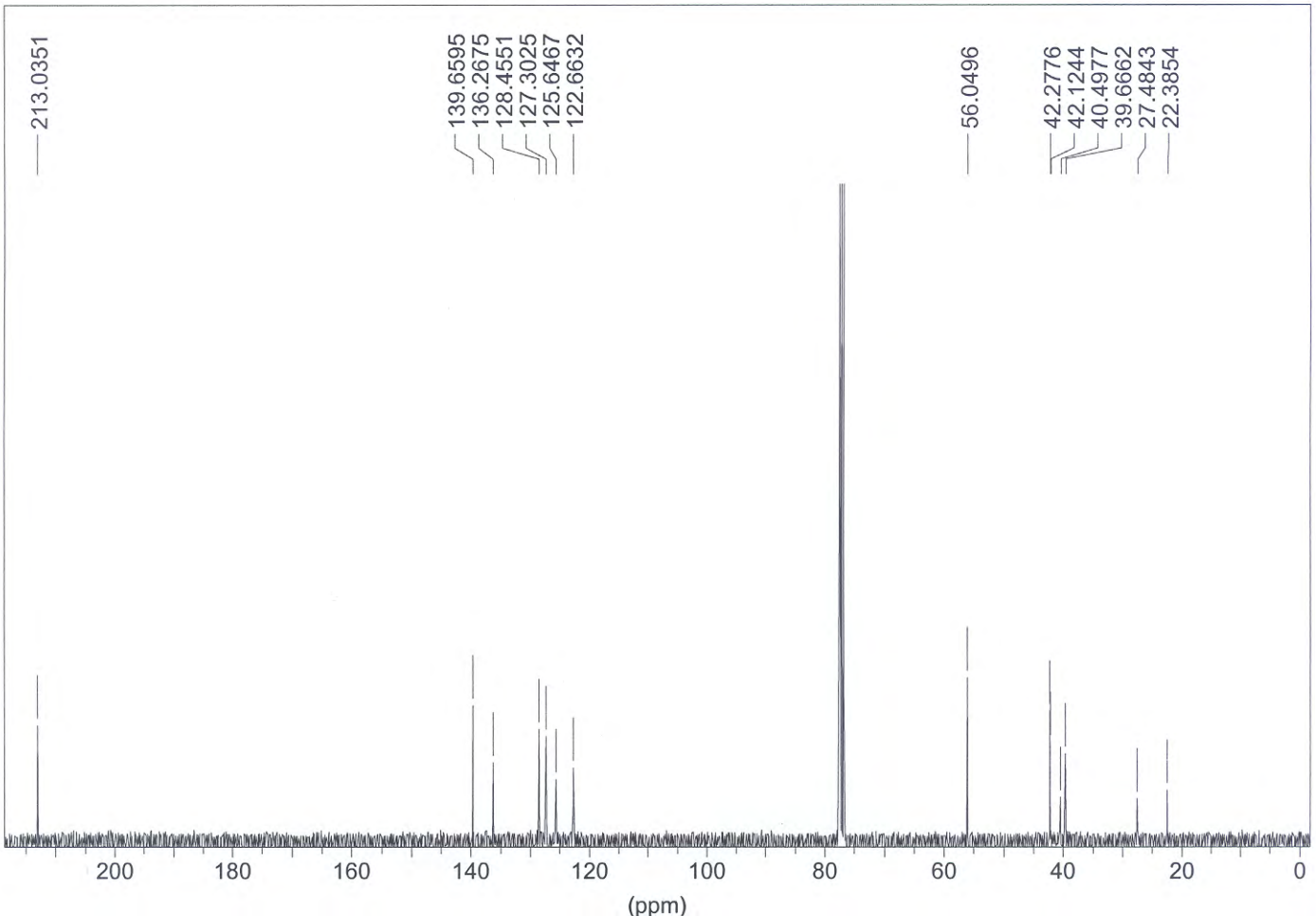
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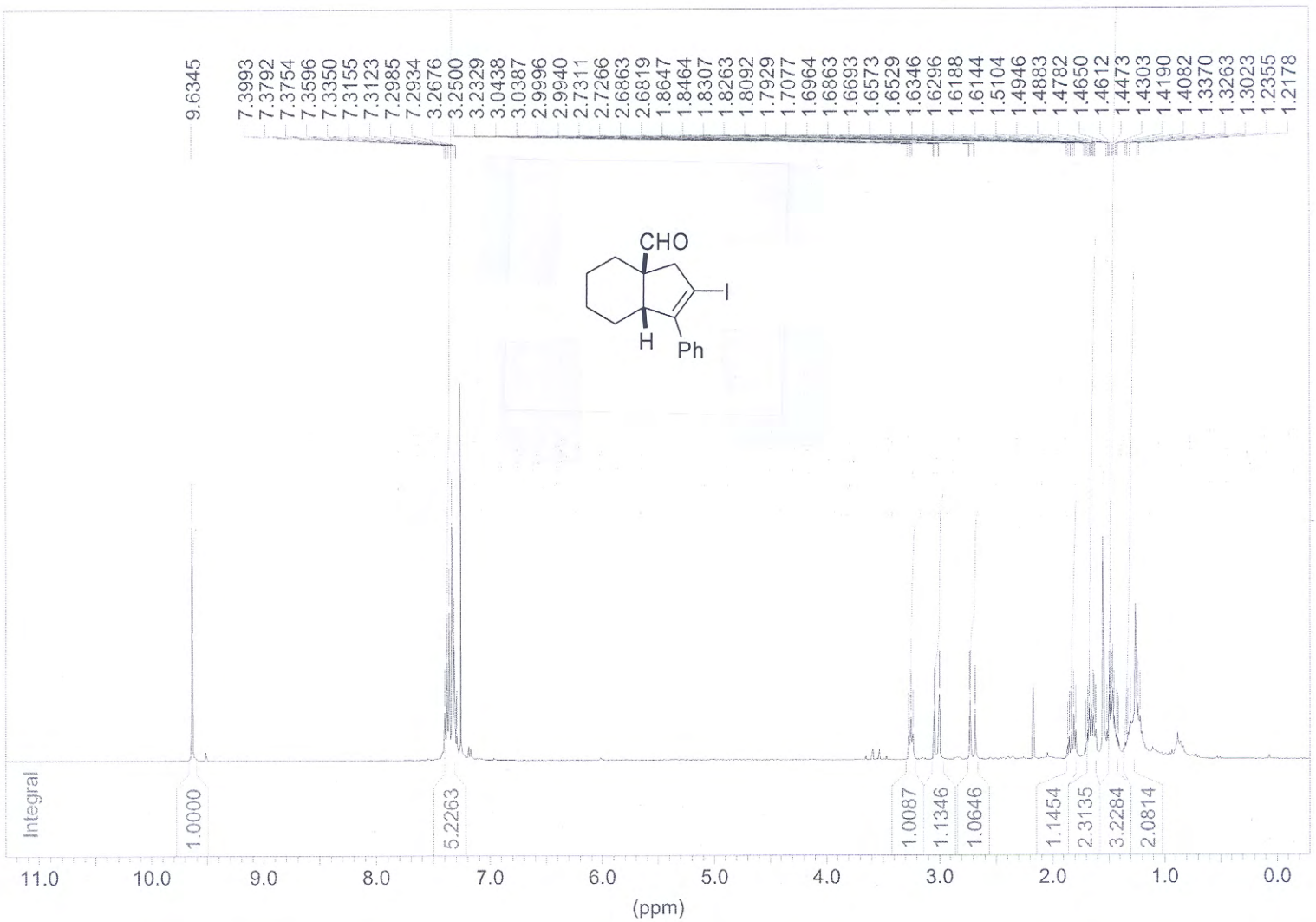
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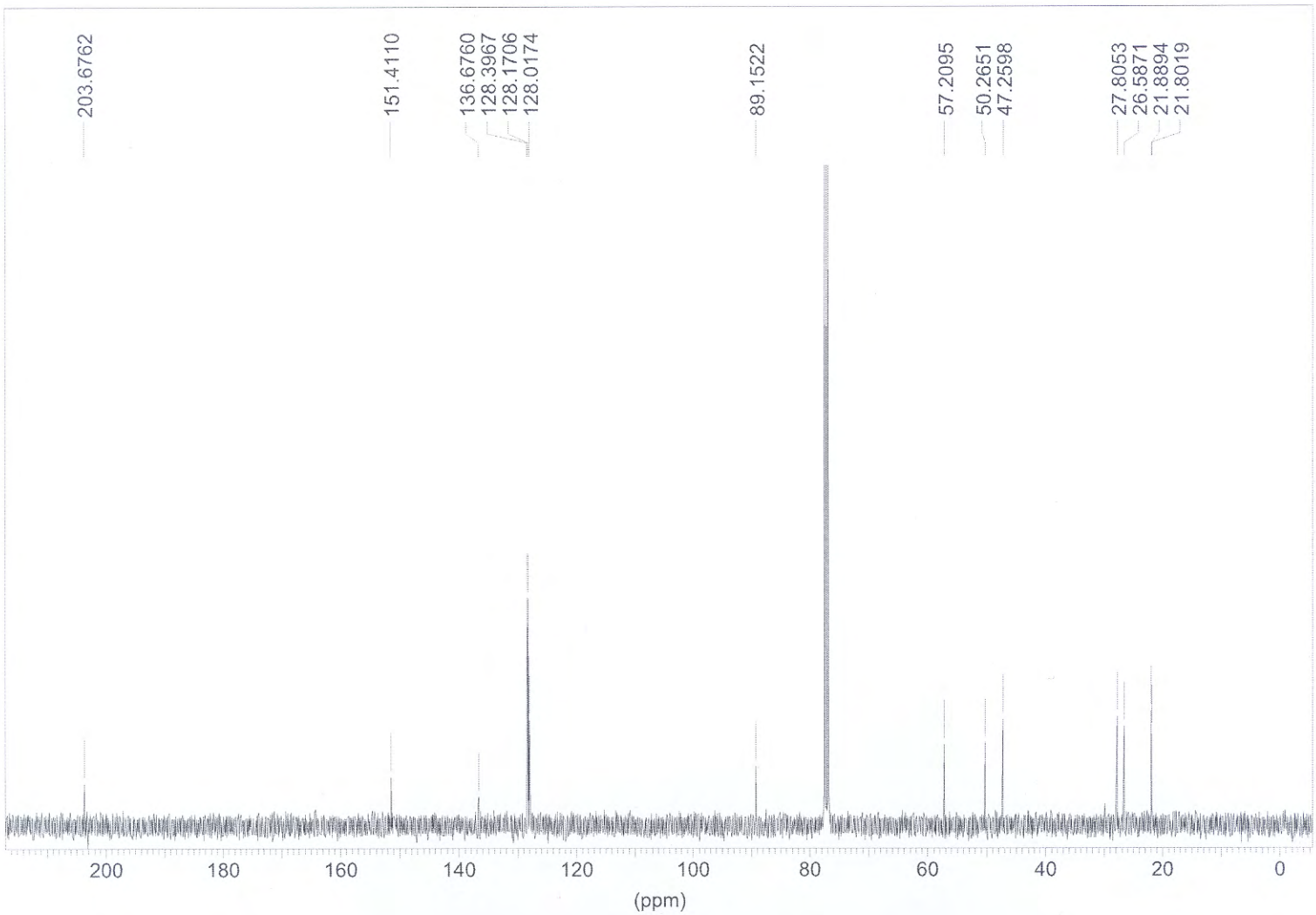
(ppm)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136.6760
128.3967
128.1706
128.0174
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50.2651
47.2598
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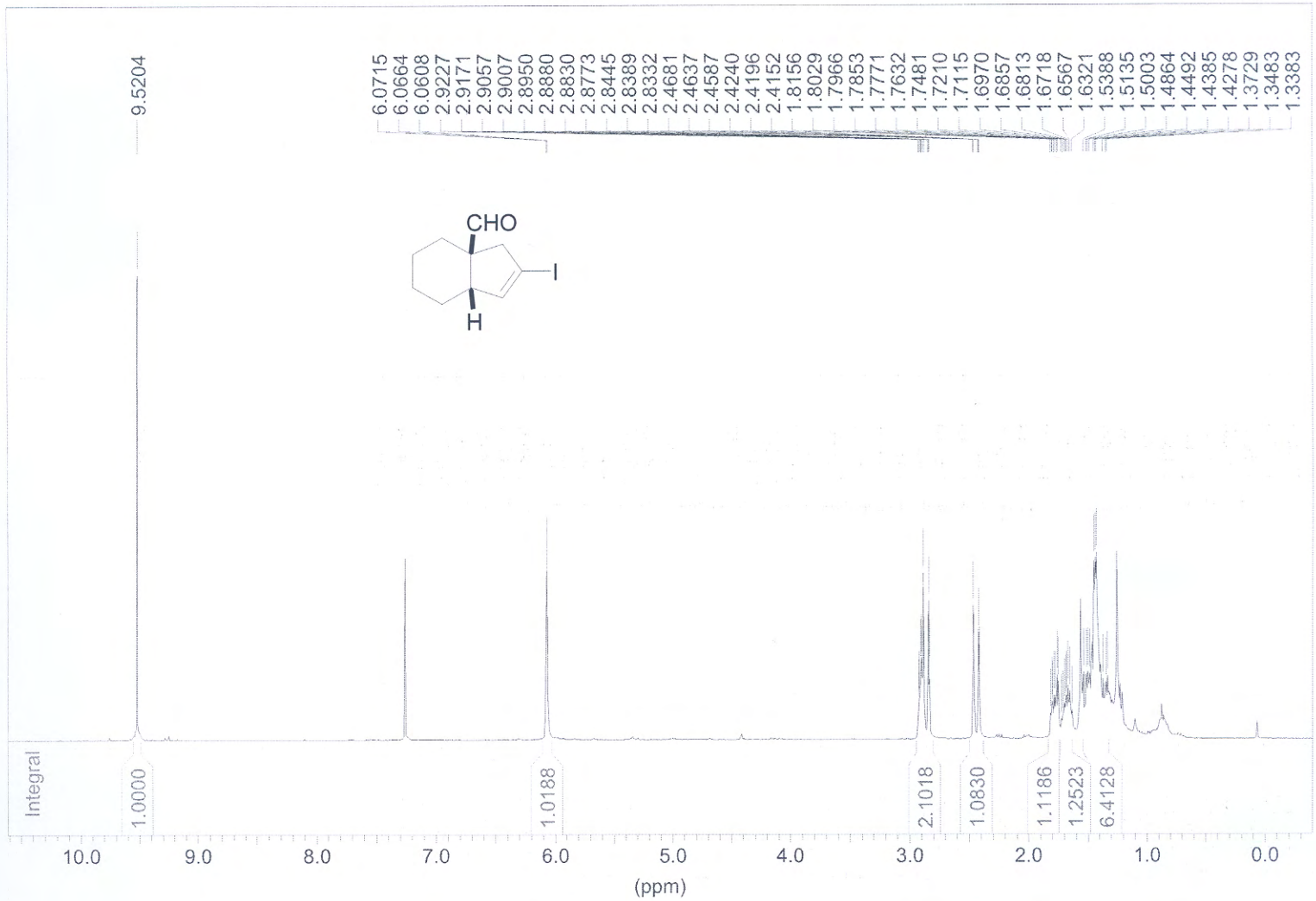
26.5871
21.8894
21.8019
200
180
160
140
120
100
80
60
40
20
0
(ppm)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6.0664
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2.9227
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2.8830
2.8773
2.8445
2.8389
2.8332
2.4681
2.4637
2.4587
2.4240
2.4196
2.4152
1.8156
1.8029
1.7966
1.7853
1.7771
1.7632
1.7481
1.7210
1.7115
1.6970
1.6857
1.6813
1.6718
1.6567
1.6321
1.5388
1.5135
1.5003
1.4864
1.4492
1.4385
1.4278
1.3729
1.3483
1.3383
CHO
I
H
Integral
1.0000
1.0188
2.1018
1.0830
1.1186
1.2523
6.4128
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4.0
3.0
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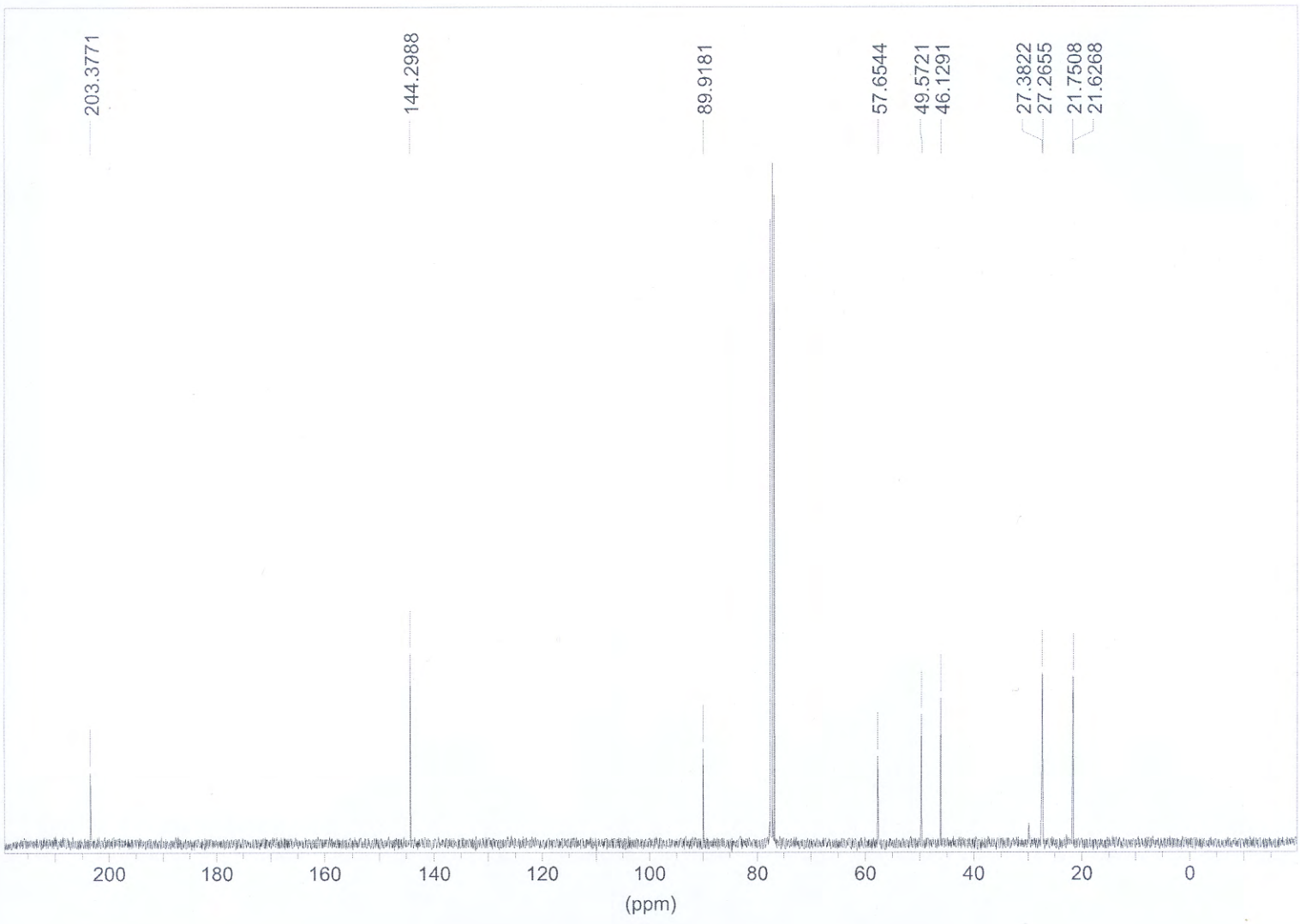
1.0
0.0
(ppm)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180
160
140
120
100
80
60
40
20
0
(ppm)