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Supporting Information

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Palladium-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Heterocyclic Acceptors

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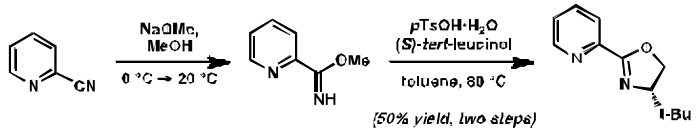
Materials and Methods

Unless otherwise stated, reactions were performed with no extra precautions taken to exclude air or moisture. Commercially available reagents were used as received from Sigma Aldrich unless otherwise stated. Enone substrates were purchased from Sigma Aldrich (3-methylcyclohexenone, 2-cyclohexene-1-one, chromone) or prepared according to literature procedure.[1] Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (250 nm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silicycle Silia*Flash* P60 Academic silica gel (particle size 40-63 nm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralcel OJ column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm and flow rate of 1 mL/min, unless otherwise stated. Analytical chiral SFC was performed with a JASCO 2000 series instrument utilizing Chiralpak (AD-H or AS-H) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm), or a Chiralpak IC column (4.6 mm x 10 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 210 or 254 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (500 MHz and 125 MHz, respectively) and a Varian Mercury 300 spectrometer (300 MHz and 75 MHz, respectively). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Data for ^{1}H NMR spectra are referenced to the centerline of $CHCl_3$ (δ 7.26) or $(CH_3)_2CO$ (δ 2.05) as the internal standard and are reported in terms of chemical shift relative to Me_4Si (δ 0.00). Data for ^{13}C NMR spectra are referenced to the

centerline of $CDCl_3$ (δ 77.0) or $(CD_3)_2CO$ (δ 29.8, 206.3)and are reported in terms of chemical shift relative to Me_4Si (δ 0.00). Infrared spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MultiMode ESI/APCI) ionization mode. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

Experimental Procedures

(*S*)-4-(*tert*-butyl)-2-(pyridin-2-yl)-4,5-dihydrooxazole (XX).



Adapted from: Brunner, H.; Obermann., U. *Chem. Ber.* **1989**, *122*, 499–507.

A flame-dried round bottom flask was charged with a stir bar and MeOH (110 mL). Sodium metal ingot (295 mg, 12.8 mmol, 0.1 equiv) was cut with a razor into small portions, washed in a beaker of hexanes, and added in five portions over 5 min to the stirring flask of MeOH. The reaction mixture was stirred vigorously at ambient temperature until no sodium metal remained, at which time it was cooled to 0 °C in an ice/water bath. At this time, 2-cyanopyridine (13.0 g, 125 mmol, 1.0 equiv) was added dropwise, and the clear, colorless reaction mixture was allowed to warm to ambient temperature with stirring. When all the starting material was consumed as indicated by TLC analysis (50% EtOAc/Hexanes, *p*-anisaldehyde stain), the reaction was cooled to 0

°C in an ice/water bath and quenched by dropwise addition of glacial AcOH (1 mL). The crude reaction mixture was evaporated *in vacuo*, redissolved in CH_2Cl_2 (100 mL) and washed with brine (2 x 50 mL). The organic phase was dried ($MgSO_4$), concentrated *in vacuo*, and dried under high vacuum for 1 h. The resulting crude methoxyimidate (light yellow oil) was suitable for use in the next step without further purification.

To a flame-dried round bottom flask charged with a stir bar was added crude methoxyimidate (2.55 g, 18.7 mmol, 1.0 equiv), (*S*)–*tert*-leucinol (2.10 g, 17.9 mmol, 0.96 equiv), and toluene (100 mL), and *p*-TsOH•H_2O (167 mg, 0.88 mmol, 5 mol%). The mixture was stirred at 80 °C in an oil bath for 3 h, at which time the starting material was consumed as indicated by TLC analysis (20% acetone/hexanes, *p*-anisaldehyde stain). The reaction was cooled to ambient temperature and quenched with sat. $NaHCO_3$ (60 mL). The reaction was partitioned with EtOAc and water, and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with water (2 x 50 mL), brine (1 x 25 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude mixture was purified by flash column chromatography (eluent: 20% acetone/hexanes) to afford 1.85 g (9.06 mmol, 51%) (*S*)-*t*-BuPyOX as an off-white solid. R_f = 0.44 with 3:2 hexanes/acetone; mp 70.2 - 71.0 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.08 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.77 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.37 (ddd, *J* = 7.0, 4.5, 1.0 Hz, 1H), 4.45 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.31 (t, *J* = 8.5 Hz, 1H), 4.12 (dd, *J* = 10.2, 8.5 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 149.6, 147.0, 136.5, 125.4, 124.0, 76.5, 69.3, 34.0, 26.0; IR (Neat film, NaCl): 2981, 2960, 2863, 1641, 1587, 1466, 1442, 1358, 1273, 1097, 1038, 968 cm^{-1}; HRMS

(MultiMode ESI/APCI) *m*/*z* calc'd for $C_{12}H_{17}ON_2$ $[M+H]^+$: 205.1335, found 205.1327; $[\alpha]^{25}_D$ –90.5º (c 1.15, $CHCl_3$).

Representative General Procedure for the Enantioselective 1,4-Addition of Arylboronic Acids to Heteroaromatic Conjugate Acceptors

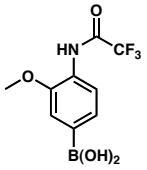
A screw-top 1 dram vial was charged with a stir bar, $Pd(OCOCF_3)_2$ (4.2 mg, 0.0125 mmol, 5 mol%), (*S*)-*t*-BuPyOX (3.1 mg, 0.015 mmol, 6 mol%), NH_4PF_6 (12.5 mg, 0.075 mmol, 30 mol%) and $PhB(OH)_2$ (61 mg, 0.50 mmol, 2.0 equiv). The solids were suspended in dichloroethane (0.5 mL) and stirred for 2 min at ambient temperature, at which time a yellow color was observed. Not all solids were dissolved at this time. Conjugate acceptor substrate (0.25 mmol) and water (0.025 mL, 1.25 mmol, 5.0 equiv) were added. The walls of the vial were rinsed with an additional portion of dichloroethane (0.5 mL), and the vial was capped with a Teflon/silicone septum and stirred at 60 °C in an oil bath for 12 h. Upon complete consumption of the starting material (monitored by TLC, 4:1 hexanes/EtOAc, *p*-anisaldehyde or iodine/silica gel stain) the reaction mixture was filtered through a pipet plug of silica gel using CH_2Cl_2 as the eluent and concentrated *in vacuo*. The crude residue was purified by column chromatography (gradient: 9:1 hexanes/EtOAc to 7:3 hexanes/EtOAc) to afford the title compound.

General Procedure for the Synthesis of Racemic Products

Racemic products were synthesized in a manner analogous to the general procedure using PyOX synthesized from racemic *tert*-leucinol (3.1 mg, 0.015 mmol, 6 mol%) as an achiral ligand.

General Procedure for the synthesis of *N*-trifluoroacetamide Boronic Acids from Bromo-trifluoroacetanilides

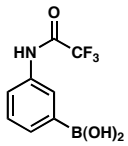
A flame round bottom flask was charged with bromo-trifluoroacetanilide (3.7 mmol, 1 equiv). The flask was sealed, evacuated and backfilled with argon. THF (20 ml) was added via syringe and the obtained mixture was cooled to -78 °C. *n*-BuLi (2.3 M solution in hexane, 3.6 mL, 8.2 mmol, 2.2 equiv) was added dropwise and the reaction was stirred for 2 h. Triisopropylborate (2.7 mL, 11.7 mmol, 3 equiv) was then added via syringe and the mixture was stirred for 10 minutes, at which time the cooling bath was removed and the reaction was allowed to stir and warm to room temperature for 1 h. A solution of HCl (2 M in water, 10 mL) was added and the biphasic mixture was vigorously stirred for 1 and then extracted with EtOAc (3 x 30 mL). The combined organic extracts where washed with brine (2 x 20 ml) and dried over $MgSO_4$. Upon concentration *in vacuo* an off-white solid was obtained. The solid was suspended in hexane and stirred until a fine powder was formed, filtered, and dried in high vacuum for 30 minutes to obtain the title boronic acid.



3-(2,2,2-trifluroacetamide)-4-methylphenylboronic acid

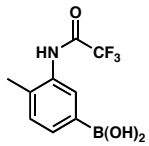
Obtained as an off-white solid in 35% yield following the general procedure. ^{1}H NMR (300 MHz, acetone) δ 9.34 (s, 1H), 8.05 (dd, J = 3.0, 6.9 Hz, 1H), 7.58 (s 1H), 7.54 (dd, J = 7.9, 1.0 Hz, 1H) 7.29 (s, 1H), 3.93 (s, 3H); 13C NMR (125 MHz, acetone) δ 154.3 (q, $J_{C\text{-}F}$ = 150 Hz), 149.3, 126.8, 126.6, 120.5, 116.1, 115.8 (q, $J_{C\text{-}F}$ = 288 Hz), 112.5, 55.4;

IR (Neat Film, NaCl): 3298, 1708, 1591, 1537, 1503, 1465, 1404, 1342, 1294, 1273, 1224, 1161, 1123, 1015; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_9H_8BO_4NF_3$ $[M-H]^-$: 261.0590, found: 261.0497.



3-(2,2,2-trifluroacetamide)-phenylboronic acid

Obtained as an off-white solid in 66 % yield following the general procedure. ^{1}H NMR (300 MHz, Aceton-d6) δ 8.11 (bs, 1H), 7.81 (m, 1H), 7.74 (dt, *J* = 7.4, 1.0 Hz 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.28 (s, 1H); (The obtained ^{13}C NMR is complex due to the presence of two rotamers in solution) ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8 (q, *J* = 36.9 Hz), 135.8, 135.7, 131.5, 128.2, 126.7, 126.6, 123.0, 122.9, 116.2 (q, *J* = 288.1 Hz); IR (Neat Film, NaCl): 3305, 1701, 1585, 1554, 1437, 1334, 1264, 1182, 1031, 780 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_8H_7BrF_3NO$ $[M-H]^-$: 231.0435, found: 231.0433.



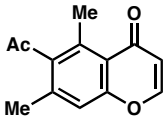
3-(2,2,2-trifluroacetamide)-4-methylphenylboronic acid.

Obtained as an off-white solid in 66% yield following the general procedure. ^{1}H NMR (300 MHz, acetone) δ 9.91 (bs, 1H), 7.82 (s, 1H), 7.75 (dd, *J* = 6.5, 10 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H) 7.24 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, Acetone d_6) δ 155.4 (q, *J* = 37.5 Hz), 136.2, 133.5, 132.9, 132.1, 130.1, 116.4 (q, *J* = 288.0 Hz), 16.8; FTIR (Neat Film, NaCl) 3270, 1708, 1617, 1533, 1406, 1351, 1259, 1180, 1162, 1092, 1036, 898,

825 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_9H_8BF_3NO_3$ $[M-H]^-$: 245.0477, found 245.0591.

General Procedure for the Synthesis of Substituted Chromones

A known literature procedure was used.[2] An Erlenmeyer flask charged with the corresponding hydroxy acetophenone (26.2 mmol, 1 equiv) was suspended in triethylorthoformate (12 mL). A 70 % aqueous solution of $HClO_4$ was added rapidly via syringe (1.3 mL) and the obtained mixture was stirred for 30 minutes at room temperature. A moderate increase in temperature is observed. Et_2O was added to precipitate a red-brown solid that was filtered and transferred into a flask. Water (10 mL) was added and the flask was warmed to 100 °C for 10 minutes. The solid rapidly dissolve and re-precipitate. The mixture is cooled to room temperature and filtered. The obtained solid can be purified via crystallization from ethanol (17 mL EtOH/ 4 mL H_2O, 80 °C) and the obtained powder is pure by NMR analysis, but often contains colored impurities. This compound is typically further purified by flash chromatography to obtain off-white powders. All characterization data for the following chromones matches previously reported data: 7-hydroxychromone,[2] 7-methoxychromone,[3] 7-acetoxy-chromone,[4] 5,7-dimethylchromone,[5]

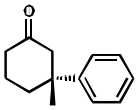


7-acetoxy-chromen-4-one

Synthesized from 1,1'-(4-hydroxy-2,6-dimethyl-1,3-phenylene)diethanone in 82% yield by the general procedure, obtained as an off-white powder solid. ^1H NMR (500 MHz,

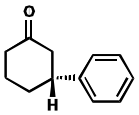
$CDCl_3$) δ 7.68–7.62 (m, 1H), 7.06 (d, *J* = 3.5 Hz, 1H), 6.18–6.13 (m, 1H), 2.71–2.65 (m, 3H), 2.44 (q, *J* = 1.4 Hz, 3H), 2.28–2.23 (m, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 179.3, 157.4, 153.4, 140.8, 138.5, 135.4, 121.1, 117.5, 114.4, 32.5, 19.5, 18.8; IR (Neat Film, NaCl): 3086, 2987, 2918, 1701, 1649, 1604, 1443, 1354, 1339, 1245, 1221, 1182, 1060 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{13}H_{13}O_3$ $[M+H]^+$: 217.0859, found: 217.0858.

Spectroscopic Data for Enantioenriched Products



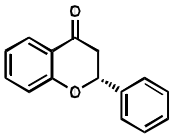
(*R*)-3-phenyl-3-methylcyclohexanone (Table 1, Entry 1)

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford a pale yellow oil (99% yield). $[\alpha]^{25}_D$ –56.1° (*c* 1.36, $CHCl_3$, 93% ee). All characterization data matches previously reported data.[6, 7, 8, 9, 10, 11, 12]



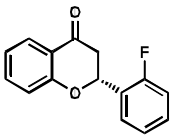
(*R*)-3-phenylcyclohexanone (Table 1, Entry 2).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford a pale yellow oil (89% yield). $[\alpha]^{25}_D$ –2.93° (*c* 1.01, $CHCl_3$, 18% ee). All characterization data matches previously reported data.[13]



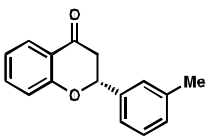
(*R*)-2-phenylchroman-4-one (Table 1, Entry 3).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (91% yield). $[\alpha]^{25}_{D}$ 67.3° (*c* 0.95, $CHCl_3$, 92% ee). All characterization data matches previously reported data.[14]



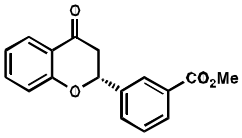
(*R*)-2-(2-fluorophenyl)chroman-4-one (Table 2, Entry 1).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.67 (dt, *J* = 1.7, 7.6 Hz, 1H), 7.54 (ddd, *J* = 1.8, 7.1, 8.2 Hz, 1H), 7.39 (ddt. *J* = 1.7, 5.4, 7.8 Hz, 1H), 7.25–7.28 (m, 1H), 7.07–7.16 (m, 3H), 5.81 (dd, *J* = 2.9, 13.4 Hz, 1H), 3.08 (dd, *J* = 13.4, 16.9 Hz, 1H), 2.93 (dd, *J* = 2.9, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 161.5, 160.6, 158.6, 136.2, 130.6, 130.2, 127.5, 127.4, 126.2, 126.1, 124.5, 124.5, 121.8, 120.9, 118.9, 118.0, 115.8, 115.6, 73.8, 73.8, 43.7; IR (Neat Film, NaCl): 1698, 1609, 1577, 1493, 1463, 1370, 1305, 1224, 1149, 1116, 1068 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{15}H_{12}FO_2$ $[M+H]^+$: 243.0816, found 243.0814; $[\alpha]^{25}_{D}$ 63.6° (*c* 3.0, $CHCl_3$, 76% ee).



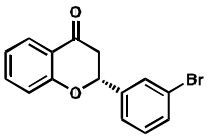
(*R*)-2-(m-tolyl)chroman-4-one (Table 2, Entry 2).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (66% yield). $[\alpha]^{25}_{D}$ 45.5° (*c* 6.9, $CHCl_3$, 90% ee). All characterization data matches previously reported data.[14,15]



(*R*)-methyl 3-(4-oxochroman-2-yl)benzoate (Table 2, Entry 3).

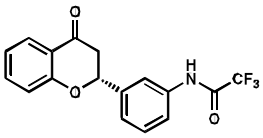
Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (t, *J* = 1.8 Hz, 1H), 8.06 (dt, *J* = 1.4, 7.8 Hz, 1H), 7.93 (dd, *J* = 1.7, 8.1 Hz, 1H), 7.68 (dq, *J* = 1.2, 7.8 Hz, 1H), 7.57–7.44 (m, 2H), 7.10–6.93 (m, 2H), 5.53 (dd, *J* = 2.8, 13.4 Hz, 1H), 3.93 (s, 3H), 3.07 (dd, *J* = 13.4, 16.8, Hz, 1H), 2.91 (dd, *J* = 2.9, 16.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 166.7, 161.4, 139.4, 136.4, 130.9, 130.6, 130.0, 129.1, 127.4, 127.2, 121.9, 121.0, 118.2, 79.00, 52.4, 44.8; IR (Neat Film, NaCl): 2951, 1720, 1691, 1606, 1577, 1463, 1431, 1359, 1304, 1225, 1214, 1149, 1114, 1068 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{17}H_{15}O_4$ $[M+H]^+$: 283.0965, found 285.0967; $[\alpha]^{25}_{D}$ 66.5° (*c* 1.00, $CHCl_3$, 93% ee).



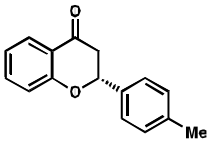
(*R*)-2-(3-bromophenyl)chroman-4-one (Table 2, Entry 4).

Synthesized according to the general procedure and purified by flash chromatography

(9:1 hexanes/EtOAc) to afford an off-white solid (40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.68 (bs, 1H), 7.53 (dt, *J* = 1.7, 7.8 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 5.46 (dd, *J* = 2.9, 13.2 Hz, 1H), 3.04 (dd, *J* = 13.2, 16.9 Hz, 1H), 2.89 (dd, *J* = 2.9, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.3, 161.2, 140.9, 136.3, 131.7, 130.3, 129.2, 127.0, 124.6, 122.9, 121.8, 121.6, 118.1, 78.6, 44.6; IR (Neat Film, NaCl): 1691, 1605, 1575, 1463, 1362, 1304, 1226, 1152, 1115, 1067 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{15}H_{12}BrO_2$ $[M+H]^+$: 300.9871, found 300.9870; $[\alpha]^{25}_D$ 53.5° (*c* 3.0, $CHCl_3$, 89% ee).

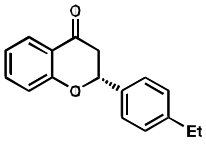


(*R*)-2,2,2-trifluoro-N-(3-(4-oxochroman-2-yl)phenyl)acetamide (Table 2, Entry 5). Synthesized according to the general procedure and purified by flash chromatography (gradient: 8:2 hexanes/EtOAc to 7:3 hexanes/EtOAc) to afford an off-white solid (40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (bs, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.79 (s, 1H), 7.67–7.58 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 8.9 Hz, 2H), 5.51 (dd, *J* = 3.1, 13.3 Hz, 1H), 3.06 (dd, *J* = 13.1, 16.9 Hz, 1H), 2.92 (dd, *J* = 3.1, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 161.2, 154.6–154.9 (m), 140.4, 136.4, 135.7, 129.9, 127.1, 123.9, 121.9, 120.9, 120.6, 118.1, 118.1, 114.4–116.7 (m), 78.9, 44.7; IR (Neat Film, NaCl): 3304, 1718, 1684, 1607, 1565, 1465, 1307, 1208, 1148, 1116 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{17}H_{13}O_3F_3N$ $[M+H]^+$: 336.0847, found 336.0854; $[\alpha]^{25}_D$ 74.4° (*c* 1.02, $CHCl_3$, 98% ee).



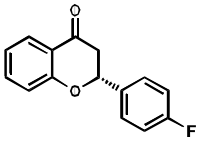
(*R*)-2-(*p*-tolyl)chroman-4-one (Table 2, Entry 6).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (64% yield). $[\alpha]^{25}_{D}$ 30.0° (*c* 1.85, $CHCl_3$, 94% ee). All characterization data matches previously reported data.[14]



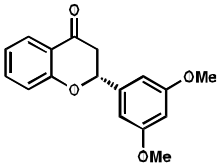
(*R*)-2-(4-ethylphenyl)chroman-4-one (Table 2, Entry 7)

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (36% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 1.8, 8.2 Hz, 1H), 7.51 (ddd, *J* = 1.7, 7.1, 8.3 Hz, 1H), 7.45–7.34 (m, 2H), 7.32–7.21 (m, 2H), 7.12 –6.92 (m, 2H), 5.46 (dd, *J* = 2.8, 13.4 Hz, 1H), 3.11 (dd, *J* = 13.5, 16.9 Hz, 1H), 2.88 (dd, *J* = 2.8, 16.9 Hz, 1H), 2.69 (q, *J* = 7.7 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 161.6, 145.0, 136.1, 135.8, 128.3, 126.9, 126.2, 121.5, 120.8, 118.1, 79.5, 44.5, 28.6, 15.5; IR (Neat Film, NaCl): 2964, 2930, 2896, 2872, 1691, 1605, 1576, 1516, 1472, 1463, 1420, 1367, 1319, 1304, 1225, 1148, 1114, 1068 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found 253.1225; $[\alpha]^{25}_{D}$ 20.7° (*c* 0.4, $CHCl_3$, 95% ee).



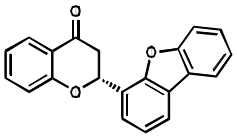
(*R*)-2-(4-fluorophenyl)chroman-4-one (Table 2, Entry 8).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford an off-white solid (51% yield). $[\alpha]^{25}_{D}$ 29.6° (*c* 3.4, $CHCl_3$, 90% ee). All characterization data matches previously reported data.[15]



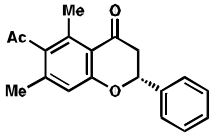
(*R*)-2-(3,5-dimethoxyphenyl)chroman-4-one (Table 2, Entry 9).

Synthesized according to the general procedure and purified by flash chromatography (gradient: 8:2 hexanes/EtOAc to 7:3 hexanes/EtOAc) to afford an off-white solid (69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (ddd, *J* = 0.7, 1.8, 7.5 Hz, 1H), 7.52 (ddd, *J* = 1.8, 7.3, 8.3Hz, 1H), 7.15–6.93 (m, 2H), 6.63 (dd, *J* = 0.6, 2.2 Hz, 2H), 6.47 (t, *J* = 2.3 Hz, 1H), 5.51–5.30 (m, 1H), 3.82 (s, 6H), 3.07 (dd, *J* = 13.3, 16.9 Hz, 1H), 2.89 (dd, *J* = 2.9, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 161.4, 161.1, 141.0, 136.2, 127.0, 121.6, 120.9, 118.1, 104.1, 100.4, 79.6, 55.4, 44.8; IR (Neat Film, NaCl): 3852, 3744, 3674, 3648, 2933, 1695, 1606, 1464, 1362, 1303, 1205, 1157, 1115, 1063 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{17}H_{17}O_4$ $[M+H]^+$: 285.1127, found 285.1127; $[\alpha]^{25}_{D}$ 46.7° (*c* 0.98, $CHCl_3$, 95% ee).



(*R*)-2-(dibenzo[*b*,*d*]furan-4-yl)chroman-4-one (Table 2, Entry 10).

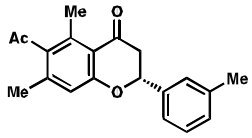
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford an off-white solid (64% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–7.92 (m, 3H), 7.70 (dd, *J* = 1.2, 7.7 Hz, 1H), 7.62–7.52 (m, 2H), 7.49 (ddt, *J* = 1.1, 7.2, 8.4 Hz, 1H), 7.44 (td, *J* = 0.9, 7.6 Hz, 1H), 7.40–7.34 (m, 1H), 7.16–7.07 (m, 2H), 6.11 (dd, *J* = 2.9, 13.5 Hz, 1H), 3.35 (ddd, *J* = 1.0, 13.4, 17.0 Hz, 1H), 3.17 (ddd, *J* = 1.0, 3.0, 17.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 161.7, 156.1, 152.8, 136.2, 127.5, 127.6, 124.8, 124.4, 123.9, 123.1, 123.1, 122.9, 121.7, 121.1, 120.9, 120.8, 118.2, 111.9, 75.3, 43.4; IR (Neat Film, NaCl): 3060, 1690, 1604, 1576, 1471, 1463, 1450, 1428, 1303, 1223, 1187, 1118 1066 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{21}H_{15}O_3$ $[M+H]^+$: 315.1016, found 315.1017; $[\alpha]^{25}_D$ 74.1° (*c* 0.77, $CHCl_3$, 77% ee).



(*R*)-6-acetyl-5,7-dimethyl-2-phenylchroman-4-one (Table 3, Entry 1).

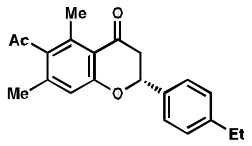
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford a colorless solid (98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.37 (m, 5H), 6.79 (s, 1H), 5.43 (dd, *J* = 2.9, 13.1 Hz, 1H), 3.07 (dd, *J* = 13.2, 16.5 Hz, 1H), 2.87 (dd, *J* = 3.0, 16.5 Hz, 1H), 2.56 (s, 3H), 2.47 (s, 3H), 2.23 (s, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 207.7, 192.9, 162.3, 140.8, 138.6, 138.0, 136.5, 128.8, 128.7, 126.0, 117.7, 117.3, 78.8, 46.2, 32.8, 19.8, 18.9; IR (Neat Film, NaCl): 3034, 2974, 2916, 1700, 1696, 1684, 1559, 1425, 1354, 1314, 1278, 1258, 1211, 1182, 1074, 1029, 895, 856, 766 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found 295.1320; $[\alpha]^{25}_D$ 22.2° (*c* 1.14, $CHCl_3$, 90% ee).



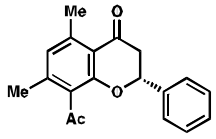
(*R*)-6-acetyl-5,7-dimethyl-2-(*m*-tolyl)chroman-4-one (Table 3, Entry 2).

Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc to 8:2 hexanes/EtOAc) to afford a colorless solid (76% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.18 (m, 4H), 6.79 (m, 1H), 5.38 (dd, *J* = 2.8, 13.3 Hz, 1H), 3.07 (dd, *J* = 13.3, 16.5 Hz, 1H), 2.85 (dd, *J* = 2.9, 16.5 Hz, 1H), 2.56 (s, 3H), 2.48 (s, 3H), 2.40 (s, 3H), 2.22 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 193.0, 162.3, 140.8, 138.6, 138.5, 138.0, 136.5, 129.5, 128.7, 126.7, 123.1, 117.7, 117.3, 78.9, 46.2, 32.8, 21.5, 19.8, 18.9; IR (Neat Film, NaCl): 2918, 1701, 1683, 1600, 1558, 1464, 1427, 1354, 1313, 1278, 1258, 1216, 1182, 1072, 969, 876, 786, 705 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485, found 309.1483; $[\alpha]^{25}_D$ 22.2° (*c* 1.14, $CHCl_3$, 88% ee).



(*R*)-6-acetyl-2-(3-ethylphenyl)-5,7-dimethylchroman-4-one (Table 3, Entry 3).

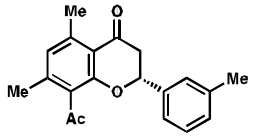
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc to 6:1 hexanes/EtOAc) to afford a colorless solid (45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.27–7.25 (m, 2H), 6.77 (s, 1H), 5.40 (dd, *J* = 2.8, 13.2 Hz, 1H), 3.09 (dd, *J* = 13.2, 16.5 Hz, 1H), 2.86 (dd, *J* = 2.9, 16.5 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.47 (s, 3H), 2.22 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7,193.1, 162.4, 145.0, 140.7, 138.0, 136.5, 135.8, 128.3, 126.2, 117.7, 117.3, 78.8, 46.1, 32.8, 28.6, 19.8, 19.0, 15.6; IR (Neat Film, NaCl): 3379, 2965, 2930, 2873, 1910, 1685, 1601, 1559, 1517, 1465, 1427, 1379, 1354, 1313, 1278, 1258, 1212, 1182, 1117, 1073, 1021, 988, 969, 895, 858, 831, 777, 736 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found 323.1627; $[\alpha]^{25}_D$ 8.8° (*c* 1.00, $CHCl_3$, 86% ee).



(*R*)-8-acetyl-5,7-dimethyl-2-phenylchroman-4-one (Table 3, Entry 4).

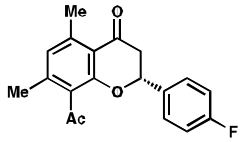
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford a colorless solid (79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.36 (m, 5H), 6.72 (s, 1H), 5.48 (dd, *J* = 2.9, 13.2 Hz, 1H), 3.06 (dd, *J* = 13.2, 16.6 Hz, 1H), 2.89 (dd, *J* = 2.9, 16.6 Hz, 1H), 2.64 (s, 3H), 2.48 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 192.4, 159.4, 143.1, 142.2, 138.5, 128.9, 128.7, 127.5, 125.8, 117.6, 110.0, 79.4, 46.1, 32.3, 22.7, 19.7; IR (Neat Film, NaCl): 2946, 2924, 1684, 1599, 1559, 1473, 1444, 1352, 1317, 1281, 1163, 1079, 763 cm^{-1}; HRMS (MultiMode

ESI/APCI) *m*/*z* calc'd for $C_{19}H_{17}O_3$ $[M-H]^-$: 293.1183, found 293.1178; $[\alpha]^{25}_D$ 65.5° (*c* 1.02, $CHCl_3$, 95% ee).



(*R*)-8-acetyl-5,7-dimethyl-2-(*m*-tolyl)chroman-4-one (Table 3, Entry 5).

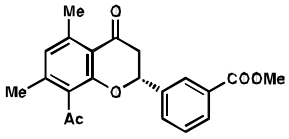
Synthesized according to the general procedure and purified by flash chromatography (5:1 hexanes/EtOAc) to afford a colorless solid (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.17 (m, 4H), 6.71 (s, 1H), 5.44 (dd, *J* = 2.9, 13.1 Hz, 1H), 3.05 (dd, *J* = 13.2, 16.6 Hz, 1H), 2.86 (dd, *J* = 3.0, 16.6 Hz, 1H), 2.64 (s, 3H), 2.48 (s, 3H), 2.39 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7,192.5, 159.4, 143.1, 142.2, 138.6, 138.4, 129.4, 129.3, 128.7, 127.4, 126.5, 122.9, 117.6, 79.5, 46.2, 32.3, 22.7, 21.5, 19.7; IR (Neat Film, NaCl): 2945, 2923,1684, 1599, 1558, 1472, 1447, 1353, 1316, 1281, 1173, 1085, 960, 892, 811, 789, 757 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485, found 309.1494; $[\alpha]^{25}_D$ 60.6° (*c* 1.03, $CHCl_3$, 86% ee).



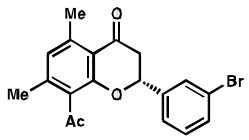
(*R*)-8-acetyl-2-(4-fluorophenyl)-5,7-dimethylchroman-4-one (Table 3, Entry 6).

Synthesized according to the general procedure and purified by flash chromatography (1:1 hexanes/EtOAc) to afford a colorless solid (68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.38 (m, 2H), 7.26 (s, 1H), 7.12–7.09 (m, 2H), 5.45 (dd, *J* = 2.9, 13.1 Hz, 1H),

3.03 (dd, J = 13.1, 16.6 Hz, 1H), 2.87 (dd, J = 2.9, 16.6 Hz, 1H), 2.63 (s, 3H), 2.46 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 192.1, 162.8 (d, $^1J_{(C,F)}$ = 247.8 Hz), 159.1, 143.1, 142.2, 134.3 (d, $^4J_{(C,F)}$ = 3.3 Hz), 129.3, 127.7 (d, $^3J_{(C,F)}$ = 8.4 Hz) , 127.5, 117.5, 115.8 (d, $^2J_{(C,F)}$ = 21.7 Hz), 78.7, 46.0, 32.3, 22.7, 19.7; IR (Neat Film, NaCl): 3354, 3073, 2967, 2925, 1895, 1685, 1603, 1560, 1513, 1474, 1445, 1353, 1316, 1283, 1265, 1254, 1227, 1187, 1161, 1087, 1041, 1014, 992, 961, 897, 880, 837, 811, 731, 727 cm^{-1}; HRMS (MultiMode ESI/APCI) m/z calc'd for $C_{19}H_{18}FO_3$ $[M+H]^+$: 313.1234, found 313.1240; $[\alpha]^{25}_D$ 53.4° (*c* 1.05, $CHCl_3$, 91% ee).

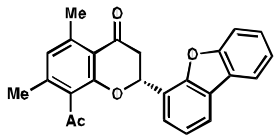


(*R*)-methyl 3-(8-acetyl-5,7-dimethyl-4-oxochroman-2-yl) benzoate (Table 3, Entry 7). Synthesized according to the general procedure and purified by flash chromatography (5:1 hexanes/EtOAc) to afford a colorless solid (60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (t, J = 1.7 Hz, 1H), 8.06–8.04 (m, 1H), 7.64–7.62 (m, 1H), d 7.51 (t, J = 7.7 Hz, 1H), 6.73 (s, 1H), 5.52 (dd, J = 2.9, 13.1 Hz, 1H), 3.94 (s, 3H), 3.07 (dd, J = 13.3, 16.6 Hz, 1H), 2.90 (dd, J = 2.9, 16.6 Hz, 1H), 2.64 (s, 3H), 2.48 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 191.9, 166.5, 159.1, 143.1, 142.3, 138.9, 130.8, 130.2, 129.9, 129.3, 129.1, 127.7, 127.0, 117.5, 78.9, 52.3, 46.0, 32.3, 22.7, 19.7; IR (Neat Film, NaCl): 2953, 2924, 2360, 1722, 1684, 1600, 1559, 1473, 1436, 1354, 1316, 1283, 1210. 1163, 1084, 961, 892, 860, 822, 755 cm^{-1}; HRMS (MultiMode ESI/APCI) m/z calc'd for $C_{21}H_{21}O_5$ $[M+H]^+$: 353.1384, found 353.1385; $[\alpha]^{25}_D$ 83.5° (*c* 1.53, $CHCl_3$, 86% ee).



(*R*)-8-acetyl-2-(3-bromophenyl)-5,7-dimethylchroman-4-one (Table 3, Entry 8).

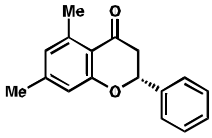
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford a colorless solid (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.6 Hz, 1H), 7.53–7.48 (m, 1H), 7.35–7.28 (m, 2H), 6.73 (s, 1H), 5.44 (dd, *J* = 2.9, 13.2 Hz, 1H), 3.02 (dd, *J* = 13.2, 16.6 Hz, 1H), 2.87 (dd, *J* = 3.0, 16.6 Hz, 1H), 2.64 (s, 3H), 2.48 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 191.7, 158.9, 143.1, 142.3, 140.7, 131.8, 130.5, 129.3, 128.9, 127.7, 124.4, 122.9, 117.5, 78.6, 46.0, 32.3, 22.7, 19.7; IR (Neat Film, NaCl): 3583, 2919, 1685, 1597, 1559, 1473, 1444, 1355, 1316, 1282, 1263, 1163, 1084, 959, 891, 789 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{19}H_{18}BrO_3$ $[M+H]^+$: 373.0434, found 373.0435; $[\alpha]^{25}_D$ 97.6° (*c* 0.81, $CHCl_3$, 95% ee).



(*R*)-8-acetyl-2-(dibenzo[b,d]furan-4-yl)-5,7-dimethylchroman-4-one (Table 3, Entry 9).

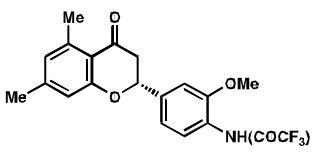
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford a colorless solid (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.60–7.55 (m, 2H), 7.48 (dt, *J* = 0.9, 7.8 Hz, 1H), 7.46–7.35 (m, 2H), 6.75 (s, 1H), 6.09 (dd, *J* = 3.1, 12.9 Hz, 1H), 3.30 (dd, *J* = 13.0, 16.6 Hz, 1H), 3.16 (dd, *J* = 3.3, 16.7 Hz, 1H), 2.69 (s, 3H), 2.48 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 203.7, 192.4, 159.4, 156.1, 152.8, 143.2, 142.2, 129.3, 127.6, 127.5, 124.8, 124.0, 123.8, 123.1, 123.0, 122.6, 121.0, 120.8, 117.7, 111.8, 75.2, 45.0, 32.3, 22.8, 19.7; IR (Neat Film, NaCl): 3583, 3017, 2963, 2923, 1683, 1600, 1557, 1474, 1450, 1428, 1378, 1352, 1317, 1282, 1188, 1171, 1078, 961, 893, 843, 800, 754 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{25}H_{21}O_4$ $[M+H]^+$: 385.1438, found 385.1440, found; $[\alpha]^{25}_D$ 52.4° (*c* 0.75, $CHCl_3$, 83% ee).



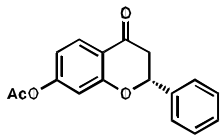
(*R*)-5,7-dimethyl-2-phenylchroman-4-one (Table 3, Entry 10).

Synthesized according to the general procedure and purified by flash chromatography (6:1 hexanes/EtOAc) to afford a colorless solid (84% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.38 (m, 5H), 6.75 (s, 1H), 6.66 (s, 1H), 5.42 (dd, *J* = 2.8, 13.3 Hz, 1H), 3.05 (dd, *J* = 13.3, 16.5 Hz, 1H), 2.84 (dd, *J* = 2.9, 16.5 Hz, 1H), 2.64 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 162.7, 146.1, 141.9, 139.1, 128.8, 128.6, 126.1, 126.0, 117.2, 116.2, 78.8, 46.1, 22.8, 21.7; IR (Neat Film, NaCl): 3650, 3586, 2916, 2360, 1675, 1616, 1559, 1320, 1279, 1159, 1072, 843, 763 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found 253.1217; $[\alpha]^{25}_D$ 46.8° (*c* 1.00, $CHCl_3$, 92% ee).



(*R*)-*N*-(4-(5,7-dimethyl-4-oxochroman-2-yl)-2-methoxyphenyl)-2,2,2-trifluoroacetamide (Table 3, Entry 11).

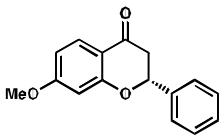
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford a colorless solid (80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) d 8.57 (s, 1H), 8.35 (d,*J* = 8.7 Hz, 1H), 7.11-7.07 (m, 2H), 6.75 (s, 1H), 6.67 (s, 1H), 5.40 (dd, *J* = 2.8, 13.1 Hz, 1H), 3.97 (s, 3H), 3.02 (dd, *J* = 13.2, 16.5 Hz, 1H), 2.83 (dd, *J* = 2.9, 16.5 Hz, 1H), 2.63 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 162.4, 152.42 (q, $^{2}J_{(C,F)}$ = 37.3 Hz), 148.5, 146.2, 142.0, 137.1, 126.3, 125.1, 120.3, 118.8, 117.2, 116.1, 112.6 (m, $^{1}J_{(C,F)}$ = 211.0 Hz), 107.9, 78.4, 56.1, 46.1, 22.7, 21.7; IR (Neat Film, NaCl): 3401, 2917, 2848, 1721, 1682, 1613, 1545, 1499, 1464, 1425, 1362, 1322, 1302, 1291, 1266, 1226, 1156, 1119, 1078, 1033, 901, 864, 846, 826, 790, 733 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{20}H_{19}F_3NO_4$ $[M]^+$: 393.1261, found 393.1269; $[\alpha]^{25}_D$ 46.8° (*c* 0.93, $CHCl_3$, 95% ee).



(*R*)-4-oxo-2-phenylchroman-7-yl acetate (Table 3, Entry 12).

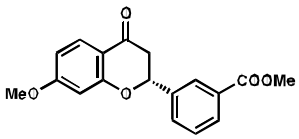
Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc to 8:2 hexanes/EtOAc) to afford a colorless solid (77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 1H), 7.49–7.38 (m, 5H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 2.2, 8.6 Hz, 1H), 5.51 (dd, *J* = 2.9, 13.4 Hz, 1H), 3.08 (dd, *J* = 13.4, 16.9 Hz, 1H), 2.89 (dd, *J* = 2.9, 16.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 168.5, 162.3, 156.5, 138.3, 128.8, 128.7, 128.4, 126.0, 118.7, 115.6,

111.1, 79.9, 44.3, 21.1; IR (Neat Film, NaCl): 3034, 1768, 1691, 1611, 1580, 1481, 1437, 1369, 1340, 1286, 1243, 1192, 1140, 1117, 1062, 1012, 965, 905, 884, 843, 819, 758 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{17}H_{15}O_4$ $[M+H]^+$: 283.0965, found 283.0969; $[\alpha]^{25}_D$ 41.7° (*c* 1.00, $CHCl_3$, 93% ee).



(*R*)-7-methoxy-2-phenylchroman-4-one (Table 3, Entry 13).

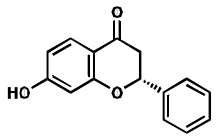
Synthesized according to the general procedure and purified by flash chromatography (9:1 hexanes/EtOAc) to afford a colorless solid (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.49–7.39 (m, 5H), 6.62 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 5.47 (dd, *J* = 2.9, 13.3 Hz, 1H), 3.83 (s, 3H), 3.04 (dd, *J* = 13.3, 16.9 Hz, 1H), 2.83 (dd, *J* = 2.9, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 166.2, 163.5, 138.8, 128.9, 128.8, 128.7, 126.2, 114.8, 110.3, 100.9, 80.0, 55.7, 44.3; IR (Neat Film, NaCl): 3583, 2915, 1677, 1602, 1496, 1437, 1355, 1255, 1198, 1156, 1113, 1058, 1022, 996, 953, 835, 764 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1016, found 255.1017; $[\alpha]^{25}_D$ 63.5° (*c* 0.97, $CHCl_3$, 94% ee).



(*R*)-methyl 3-(7-methoxy-4-oxochroman-2-yl)benzoate (Table 3, Entry 14).

Synthesized according to the general procedure and purified by flash chromatography

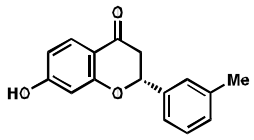
(2:1 hexanes/EtOAc) to afford a colorless solid (81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.06 (dt, *J* = 1.3, 7.7 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 6.64 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 3.0, 13.2 Hz, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 3.03 (dd, *J* = 13.2, 16.8 Hz, 1H), 2.85 (dd, *J* = 3.1, 16.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 166.6, 166.3, 163.3, 139.3, 130.8, 130.5, 129.9, 129.0, 128.8, 127.3, 114.8, 110.5, 100.9, 79.4, 55.7, 52.3, 44.3; IR (Neat Film, NaCl): 3431, 2951, 2841, 1721, 1683, 1608, 1575, 1496, 1443, 1353, 1335, 1289, 1258, 1210, 1159, 1132, 1114, 1060, 1023, 1000, 953, 838, 824, 752 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{18}H_{17}O_5$ $[M+H]^+$: 313.1071, found 313.1067; $[\alpha]^{25}_D$ 86.8° (*c* 0.89, $CHCl_3$, 96% ee).



(*R*)-7-hydroxy-2-phenylchroman-4-one (Table 3, Entry 15).

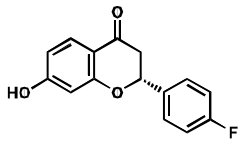
Synthesized according to the general procedure and purified by flash chromatography (6:4 hexanes/EtOAc) to afford a colorless solid (77% yield). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 9.46 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.62–7.54 (m, 2H), 7.48–7.42 (m, 2H), 7.41–7.36 (m, 1H), 6.60 (dd, *J* = 2.3, 8.7 Hz, 1H), 6.46 (d, *J* = 2.3 Hz, 1H), 5.57 (dd, *J* = 2.9, 12.9 Hz, 1H), 3.04 (dd, *J* = 12.9, 16.7 Hz, 1H), 2.75 (dd, *J* = 3.0, 16.7 Hz, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 190.1, 165.2, 164.3, 140.5, 129.5, 129.4, 129.3, 127.3, 115.2, 111.3, 103.7, 80.6, 44.8; IR (Neat Film, NaCl): 3376, 1657, 1601, 1464, 1332, 1279, 1255, 1219, 1156, 1121, 1062, 1002, 963, 850, 752 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{15}H_{13}O_3$ $[M+H]^+$: 241.0859, found 241.0858; $[\alpha]^{25}_D$ 76.9° (*c*

0.98, $CHCl_3$, 93% ee).



(*R*)-7-hydroxy-2-(m-tolyl)chroman-4-one (Table 3, Entry 16).

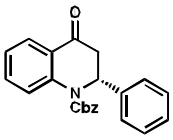
Synthesized according to the general procedure and purified by flash chromatography (6:4 hexanes/EtOAc) to afford a colorless solid (66% yield). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 9.47 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.43–7.28 (m, 3H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.59 (dd, *J* = 0.9, 8.7 Hz, 1H), 6.46 (d, *J* = 1.4 Hz, 1H), 5.51 (dd, *J* = 2.4, 13.0 Hz, 1H), 3.03 (dd, *J* = 13.0, 16.7 Hz, 1H), 2.72 (dd, *J* = 2.6, 16.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 189.4, 164.4, 163.5, 139.6, 138.1, 129.1, 128.6, 128.5, 127.0, 123.5, 114.4, 110.4, 102.8, 79.8, 44.0, 20.6; IR (Neat Film, NaCl): 3207, 2918, 2360, 1657, 1601, 1575, 1464, 1332, 1279, 1244, 1221, 1189, 1155, 1121, 1065, 1000, 964, 851, 819, 785, 731 cm^{-1}; HRMS (MultiMode ESI/APCI) *m*/*z* calc'd for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1016, found 255.1012; $[\alpha]^{25}_D$ 58.5° (*c* 1.15, $CHCl_3$, 90% ee).



(*R*)-2-(4-fluorophenyl)-7-hydroxychroman-4-one (Table 3, Entry 17).

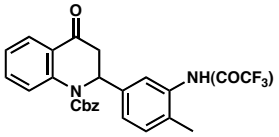
Synthesized according to the general procedure and purified by flash chromatography (1:1 hexanes/EtOAc) to afford a colorless solid (50% yield). ^{1}H NMR (500 MHz,

$(CD_3)_2CO$) δ 9.47 (s, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.69–7.55 (m, 2H), 7.28-7.09 (m, 2H), 6.60 (dd, J = 2.9, 8.7 Hz, 1H), 6.46 (d, J = 2.3 Hz, 1H), 5.59 (dd, J = 2.9, 13.0 Hz, 1H), 3.04 (dd, J = 13.0, 16.7 Hz, 1H), 2.75 (dd, J = 2.9, 16.7 Hz, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 189.1, 164.3, 163.3, 162.6 (d, $^1J_{(C,F)}$ = 245.0 Hz), 135.8 (d, $^4J_{(C,F)}$ = 3.0 Hz), 128.7, 128.6 (d, $^3J_{(C,F)}$ = 8.3 Hz), 115.3 (d, $^2J_{(C,F)}$ = 21.7 Hz), 114.3, 110.5, 102.8, 79.0, 43.8; IR (Neat Film, NaCl): 3256, 2922, 2852, 1661, 1602, 1511, 1464, 1331, 1280, 1225, 1156, 1125, 1003, 853 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{15}H_{10}FO_3$ $[M-H]^-$: 257.0619, found 257.0623; $[\alpha]^{25}_D$ 54.1° (*c* 1.54, $CHCl_3$, 93% ee).



(*R*)-benzyl 4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 1)

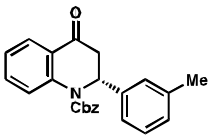
Synthesized according to the general procedure and purified by flash chromatography (8:2 hexanes/EtOAc) to afford an off-white solid (50% yield). $[\alpha]^{25}_D$ 110.9° (*c* 0.98, $CHCl_3$, 80% ee). All characterization data matches previously reported data.[16,17]



(*R*)–benzyl 2-(4-methyl-3-(2,2,2-trifluoroacetamido)phenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 2)

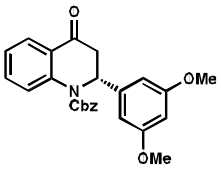
Synthesized according to the general procedure and purified by flash chromatography

(7:3 hexanes/EtOAc) to afford an off-white solid (45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.75 (bs, 1H), 7.64 (s, 1H), 7.45–7.47 (m, 1H), 7.35–7.42 (m, 5H), 7.07 (dd, *J* = 5.6, 7.6 Hz, 2H), 6.98 (dd, *J* = 1.1, 7.9 Hz, 1H), 6.20 (t, *J* = 3.5 Hz, 1H), 5.39 (d, *J* = 12.0 Hz, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 3.27 (d, *J* = 3.9 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 155.0, 154.9 (q, *J* = 37.2 Hz), 154.2, 141.3, 137.4, 135.4, 134.6, 133.2, 131.1, 129.6, 128.7, 128.5, 128.4, 128.1, 126.8, 124.9, 124.8, 124.5, 124.3, 121.7, 115.8 (m), 68.6, 55.7, 42.1, 16.9; IR (Neat Film, NaCl): 3281, 1719, 1711, 1683, 1600, 1480, 1460, 1390, 1320, 1303, 1268, 1222, 1162, 1041 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{26}H_{22}O_4N_2F_3$ $[M+H]^+$: 483.1532, found 481.1545; $[\alpha]^{25}_D$ 65.3° (*c* 1.0, $CHCl_3$, 79% ee).



(*R*)-benzyl 4-oxo-2-(*m*-tolyl)-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 3)

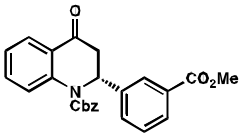
Synthesized according to the general procedure and purified by flash chromatography (2:1 hexanes/EtOAc) to afford an off-white solid (51% yield). $[\alpha]^{25}_D$ 116.5° (*c* 1.05, $CHCl_3$, 87% ee). All characterization data matches previously reported data.[17]



(*R*)-benzyl 2-(3,5-dimethoxyphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate

(Table 4, Entry 4).

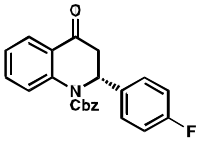
Synthesized according to the general procedure and purified by flash chromatography (gradient: 9:1 hexanes/EtOAc to 7:3 hexanes/EtOAc) to afford a pale yellow solid (50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.47 (ddd, *J* = 1.7, 7.2, 8.4 Hz, 1H) 7.35–7.42 (m, 5H), 7.1–7.2 (m, 1H), 6.31 (dd, *J* = 0.7, 2.2 Hz, 2H), 6.24 (t, *J* = 2.1 Hz, 1H), 6.16 (t, *J* = 3.8 Hz, 1H), 5.38 (d, *J* = 12.2, 1H), 5.33 (d, *J* = 12.2, 1H), 3.64 (s, 6H), 3.26–3.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 160.9, 154.2, 141.5, 140.5, 135.6, 134.5, 128.7, 128.6, 128.5, 128.4, 128.1, 126.9, 125.3, 125.0, 124.2, 105.0, 99.1, 68.4, 56.2, 55.2, 42.4; IR (Neat Film, NaCl): 2958, 1708, 1686, 1598, 1479, 1460, 1427, 1389, 1315, 1286, 1221, 1159, 1041 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{25}H_{23}NO_5$ $[M-H]^-$: 416.1500, found 416.1520; $[\alpha]^{25}_D$ 116.8° (*c* 1.4, $CHCl_3$, 85% ee).



(*R*)-benzyl 2-(3-(methoxycarbonyl)phenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 5).

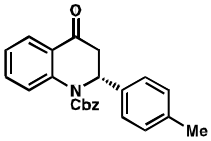
Synthesized according to the general procedure and purified by flash chromatography (gradient 9:1 hexanes/EtOAc to 7:3 hexanes/EtOAc) to afford a pale yellow solid (34% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (q, *J* = 1.2 Hz, 1H), 7.89 (ddd, *J* = 0.5, 1.7, 7.8 Hz, 1H), 7.81–7.86 (m, 2H), 7.47 (ddd, *J* = 1.8, 7.3, 8.4 Hz, 1H), 7.35–7.40 (m, 6H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.09 (ddd, *J* = 1.1, 7.6, 7.6 Hz, 1H), 6.27 (t, *J* = 3.8 Hz, 1H), 5.41 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 3.87 (s, 3H), 3.34–3.35 (m, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 192.1, 166.5, 154.2, 141.2, 138.5, 134.6, 130.7, 130.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 126.9, 124.9, 124.4, 124.3, 68.6, 55.9, 52.4, 42.2; IR (Neat Film, NaCl): 2950, 1720, 1688, 1600, 1479, 1460, 1389, 1298, 1281, 1221, 1130, 1041 cm^{-1}; HRMS (MultiMode ESI/APCI) *m/z* calc'd for $C_{25}H_{21}NO_5$ $[M-H]^-$: 415.1420, found 415.1419; $[\alpha]^{25}_D$ 109.7° (*c* 0.9, $CHCl_3$, 69% ee).



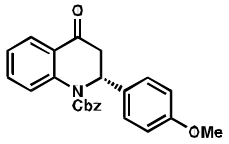
(*R*)-benzyl 2-(4-fluorophenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 6).

Synthesized according to the general procedure and purified by flash chromatography (gradient: 2:1 hexanes/EtOAc) to afford a colorless solid (65% yield). $[\alpha]^{25}_D$ 96.4° (*c* 1.19, $CHCl_3$, 89% ee). All characterization data matches previously reported data.[17]



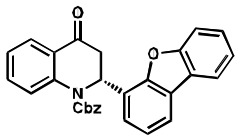
(*R*)-benzyl 4-oxo-2-(*p*-tolyl)-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 7).

Synthesized according to the general procedure and purified by flash chromatography (gradient 9:1 hexanes/EtOAc to 8:2 hexanes/EtOAc) to afford a colorless solid (65% yield). $[\alpha]^{25}_D$ 71.2° (*c* 0.5, $CHCl_3$, 67% ee). All characterization data matches previously reported data.[17]



(*R*)-benzyl 2-(4-methoxyphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (Table 4, Entry 8).

Synthesized according to the general procedure and purified by flash chromatography (gradient: 9:1 hexanes/EtOAc to 8:2 hexanes/EtOAc) to afford a colorless solid (36% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.37–7.46 (m, 6H), 7.07–7.12 (m, 3H), 6.72–6.74 (m, 2H), 6.20 (t, *J* = 3.9 Hz, 1H), 5.41 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 3.71 (s, 3H), 3.28 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ192.9, 158.8, 154.2, 141.3, 135.6, 134.5, 130.0, 128.7, 128.4, 128.1, 127.8, 126.8, 125.0, 124.4, 124.1, 113.9, 68.4, 55.7, 55.1, 42.4; IR (Neat Film, NaCl): 2957, 1705, 1683, 1601, 1513, 1479, 1460, 1380, 1320, 1302, 1252, 1224, 1181, 1128, 1035 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{22}O_4N$ $[M+H]^+$: 388.1549, found 388.1548; $[\alpha]^{25}_D$ 54.8° (*c* 2.5, $CHCl_3$, 53% ee).



(*R*)-benzyl 2-(dibenzo[b,d]furan-4-yl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (Talbe 4, Entry 9).

Synthesized according to the general procedure and purified by flash chromatography (gradient: 9:1 hexanes/EtOAc to 8:2 hexanes/EtOAc) to afford a colorless solid (31%

yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.89–7.90 (m, 1H), 7.77–7.79 (m, 1H), 7.44–7.50 (m, 3H), 7.32–7.41 (m, 6H), 7.09–7.13 (m, 2H), 7.05 (td, *J* = 1.1, 7.8 Hz, 1H), 6.76 (dd, *J* = 0.9, 5.3 Hz, 1H), 5.44 (d, *J* = 12.5 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 3.63 (dd, *J* = 2.0, 17.9 Hz, 1H), 3.44 (dd, *J* = 6.4, 17.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 155.9, 153.9, 153.3, 142.1, 135.7, 134.6, 128.6, 128.3, 128.1, 127.3, 126.9, 124.9, 124.8, 124.7, 124.1, 123.9, 123.7, 122.9, 122.7, 122.6, 120.6, 120.3, 111.7, 68.4, 53.4, 42.3; IR (Neat Film, NaCl): 3032, 1710, 1683, 1600, 1459, 1479, 1420, 1388, 1344, 1319, 1298, 1269, 1223, 1186, 1133, 1041, 1027 cm^{-1}; HRMS (MultiMode ESI/APCI**)** *m*/*z* calc'd for $C_{29}H_{20}NO_4$ $[M-H]^-$: , found 446.1393; $[\alpha]^{25}_D$ 27.4° (*c* 2.2, $CHCl_3$, 40% ee).

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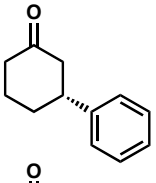
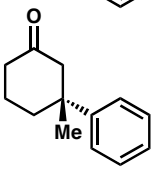
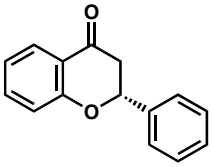
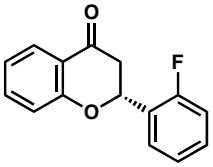
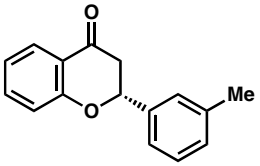
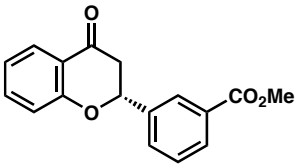
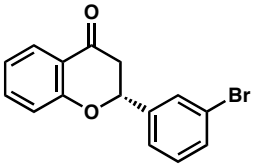
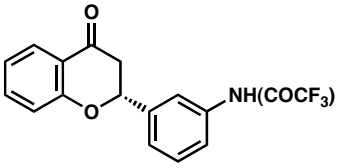
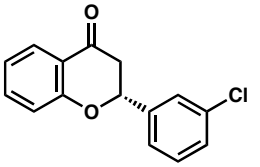
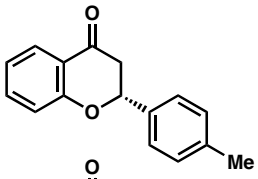
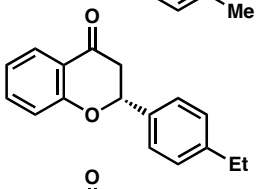
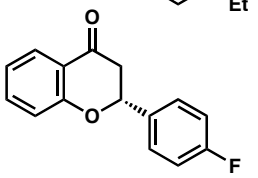
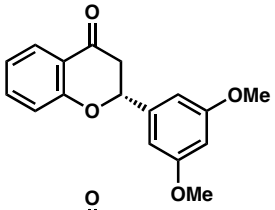
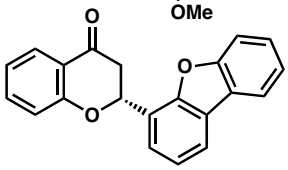
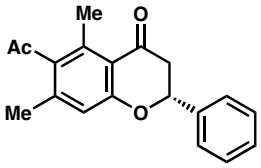
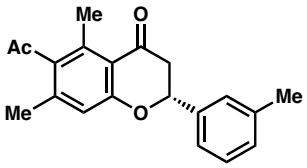
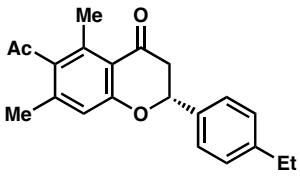
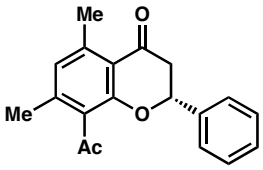
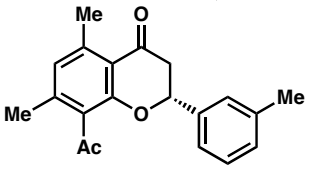
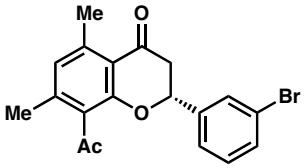
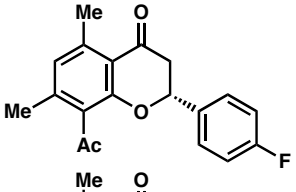
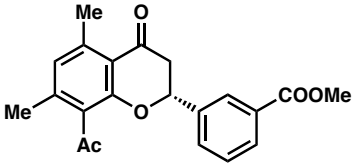
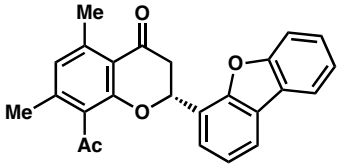
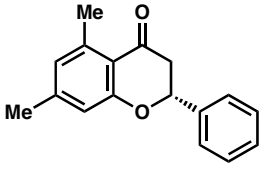
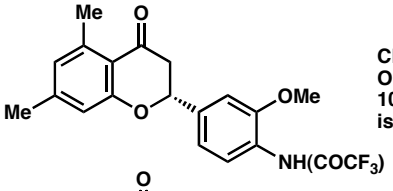
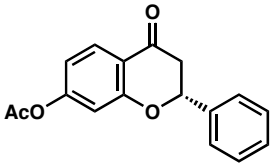
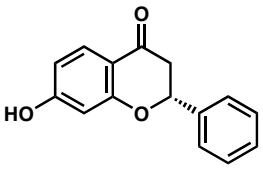
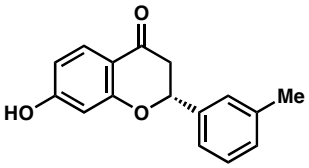
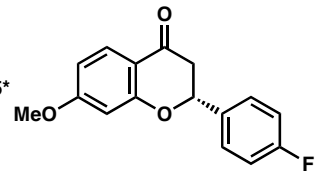
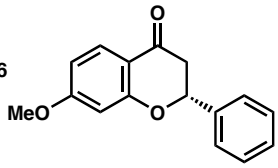
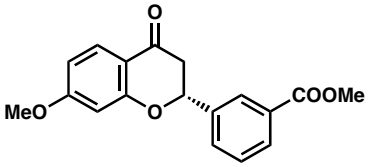
Chiral Assays (Table S1)

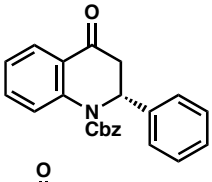
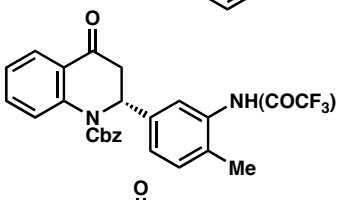
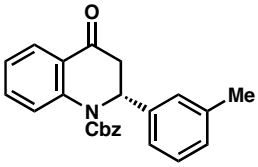
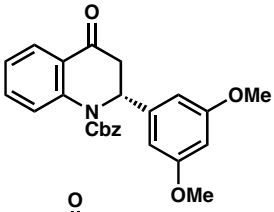
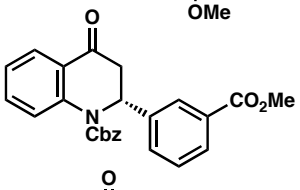
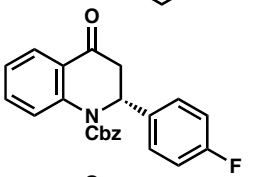
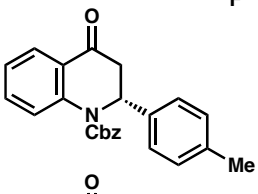
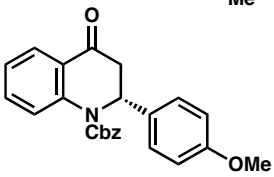
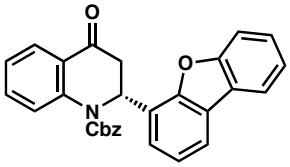
Compound	product	SFC or HPLC conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
Table 1 Entry 1		Chiralcel HPLC OJ-H 1% IPA/Hexanes isocratic 1 mL/min	17.0	19.1	18
Table 1 Entry 2		Chiralcel HPLC OJ-H 1% IPA/Hexanes isocratic 1 mL/min	15.3	19.6	93
Table 1 Entry 3		Chiralcel SFC OB-H 4% MeOH/CO_2 isocratic 5 mL/min	2.71	2.51	94
Table 2 Entry 2		Chiralcel SFC OJ-H 1% MeOH/CO_2 isocratic 5 mL/min	4.57	4.21	76
Table 2 Entry 3		Chiralcel SFC OJ-H 3% MeOH/CO_2 isocratic 5 mL/min	2.53	2.29	90
Table 2 Entry 4		Chiralcel SFC OD-H 20% MeOH/CO_2 isocratic 5 mL/min	2.09	1.85	93
Table 2 Entry 5		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 5 mL/min	4.59	3.55	89
Table 2 Entry 6		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 5 mL/min	3.21	2.68	98
Table 2 Entry 7		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	4.02	4.96	94

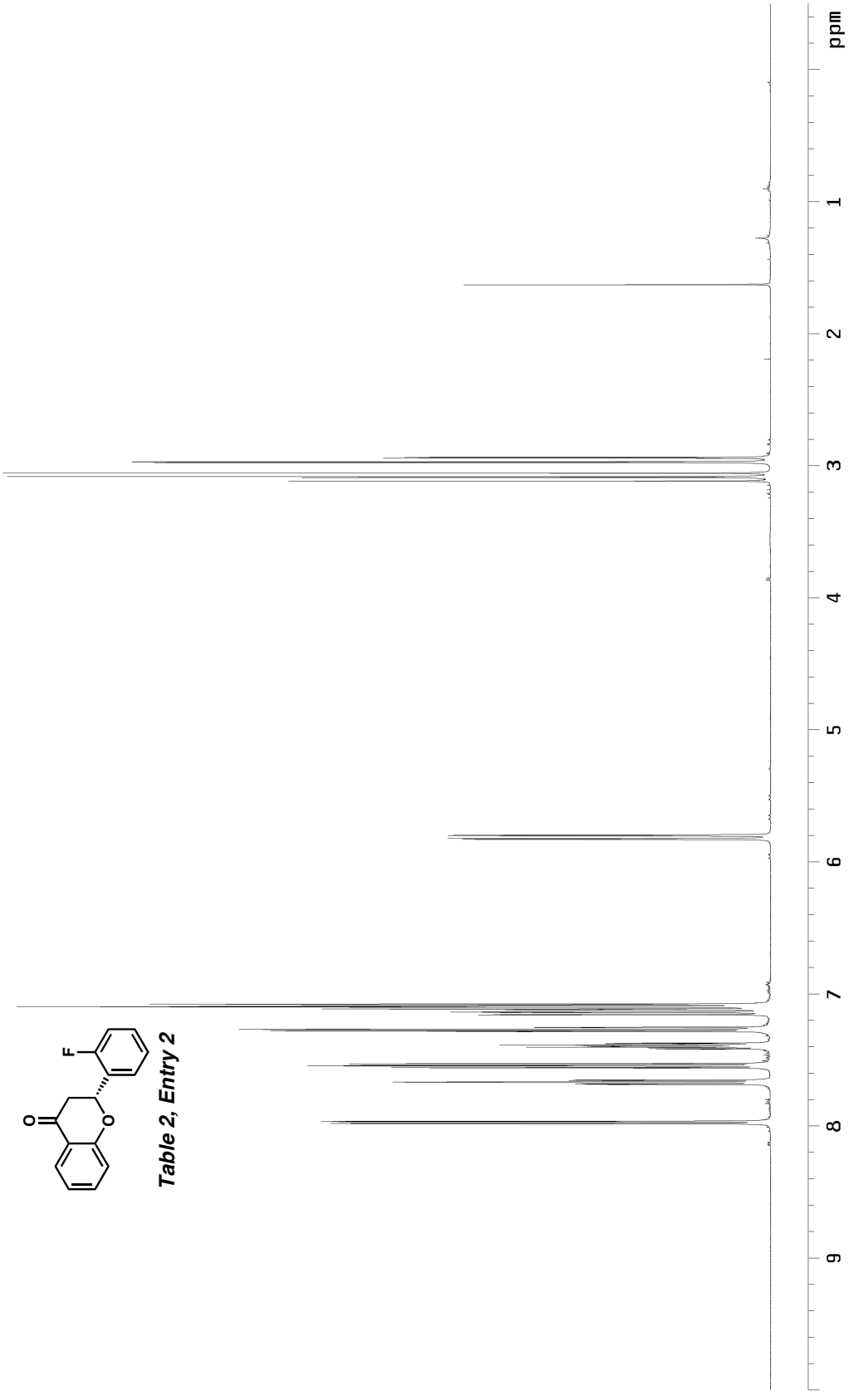
Compound	product	SFC or HPLC conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
Table 2 Entry 8		Chiralcel SFC OB-H 3% MeOH/CO_2 isocratic 5 mL/min	3.70	3.44	94
Table 2 Entry 9		Chiralcel HPLC OJ-H 1% IPA/Hexanes isocratic 1 mL/min	15.3	19.6	85
Table 2 Entry 10		Chiralpak HPLC AD-H 10% IPA/Hexanes isocratic 1 mL/min	22.7	27.2	90
Table 2 Entry 11		Chiralcel SFC OD-H 20% MeOH/CO_2 isocratic 5 mL/min	2.33	1.98	95
Table 2 Entry 12		Chiralcel SFC OD-H 25% MeOH/CO_2 isocratic 4 mL/min	9.92	5.69	77
Table 3 Entry 1		Chiralcel SFC OD-H 15% MeOH/CO_2 isocratic 4 mL/min	4.93	3.87	90
Table 3 Entry 2		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 5 mL/min	4.64	3.37	88
Table 3 Entry 3		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 5 mL/min	3.67	3.17	86

Compound	product	SFC or HPLC conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
Table 3 Entry 4		Chiralcel SFC AS-H 4% IPA/CO_2 isocratic 5 mL/min	3.49	4.19	95
Table 3 Entry 5		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	4.07	3.76	86
Table 3 Entry 6		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	6.87	5.83	95
Table 3 Entry 7		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	5.89	5.42	91
Table 3 Entry 8		Chiralcel SFC OD-H 15% MeOH/CO_2 isocratic 4 mL/min	3.68	4.13	86
Table 3 Entry 9		Chiralcel SFC OD-H 25% MeOH/CO_2 isocratic 4 mL/min	9.19	6.31	83
Table 3 Entry 10		Chiralcel SFC OJ-H 5% MeOH/CO_2 isocratic 5 mL/min	4.13	3.67	92
Table 3 Entry 11		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	4.30	5.38	95
Table 3 Entry 12		Chiralcel SFC OJ-H 5% MeOH/CO_2 isocratic 5 mL/min	5.45	5.00	93

Compound	product	SFC or HPLC conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
Table 3 Entry 13		Chiralcel HPLC OD-H 10% IPA/Hexanes isocratic 1 mL/min	18.30	16.63	93
Table 3 Entry 14		Chiralcel SFC OD-H 10% MeOH/CO_2 isocratic 4 mL/min	9.01	8.44	90
Table 3 Entry 15*		Chiralcel SFC OD-H 5% MeOH/CO_2 isocratic 4 mL/min	6.71	6.23	93
Table 3 Entry 16		Chiralcel SFC OJ-H 5% MeOH/CO_2 isocratic 5 mL/min	5.88	5.07	94
Table 3 Entry 17		Chiralcel SFC OD-H 15% MeOH/CO_2 isocratic 4 mL/min	5.81	4.70	96

*** The free-OH compound from Table 3 Entry 15 was unsuccessfully separated by analytical SFC or HPLC. The compound was methylated under standard conditions, and the methyl ether was used to determine the ee.**

Compound	product	SFC or HPLC conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
Table 4 Entry 1		Chiralpak AS-H 5% MeOH/CO_2 isocratic 5 mL/min	4.65	4.19	80
Table 4 Entry 2		Chiralcel SFC OB-H 10% MeOH/CO_2 isocratic 5 mL/min	3.28	3.67	85
Table 4 Entry 3		Chiralcel SFC AS-H 5% MeOH/CO_2 isocratic 5 mL/min	4.93	4.43	85
Table 4 Entry 4		Chiralpak SFC IC 10% MeOH/CO_2 isocratic 5 mL/min	4.87	3.71	85
Table 4 Entry 5		Chiralpak SFC AD-H 10% MeOH/CO_2 isocratic 5 mL/min	5.47	6.07	60
Table 4 Entry 6		Chiralcel SFC AS-H 5% MeOH/CO_2 isocratic 5 mL/min	4.44	3.91	89
Table 4 Entry 7		Chiralpak SFC IC 10% MeOH/CO_2 isocratic 5 mL/min	2.91	2.53	67
Table 4 Entry 8		Chiralpak SFC IC 10% MeOH/CO_2 isocratic 5 mL/min	3.87	3.36	54
Table 4 Entry 9		Chiralpak AS-H 10% MeOH/CO_2 isocratic 5 mL/min	6.24	5.24	40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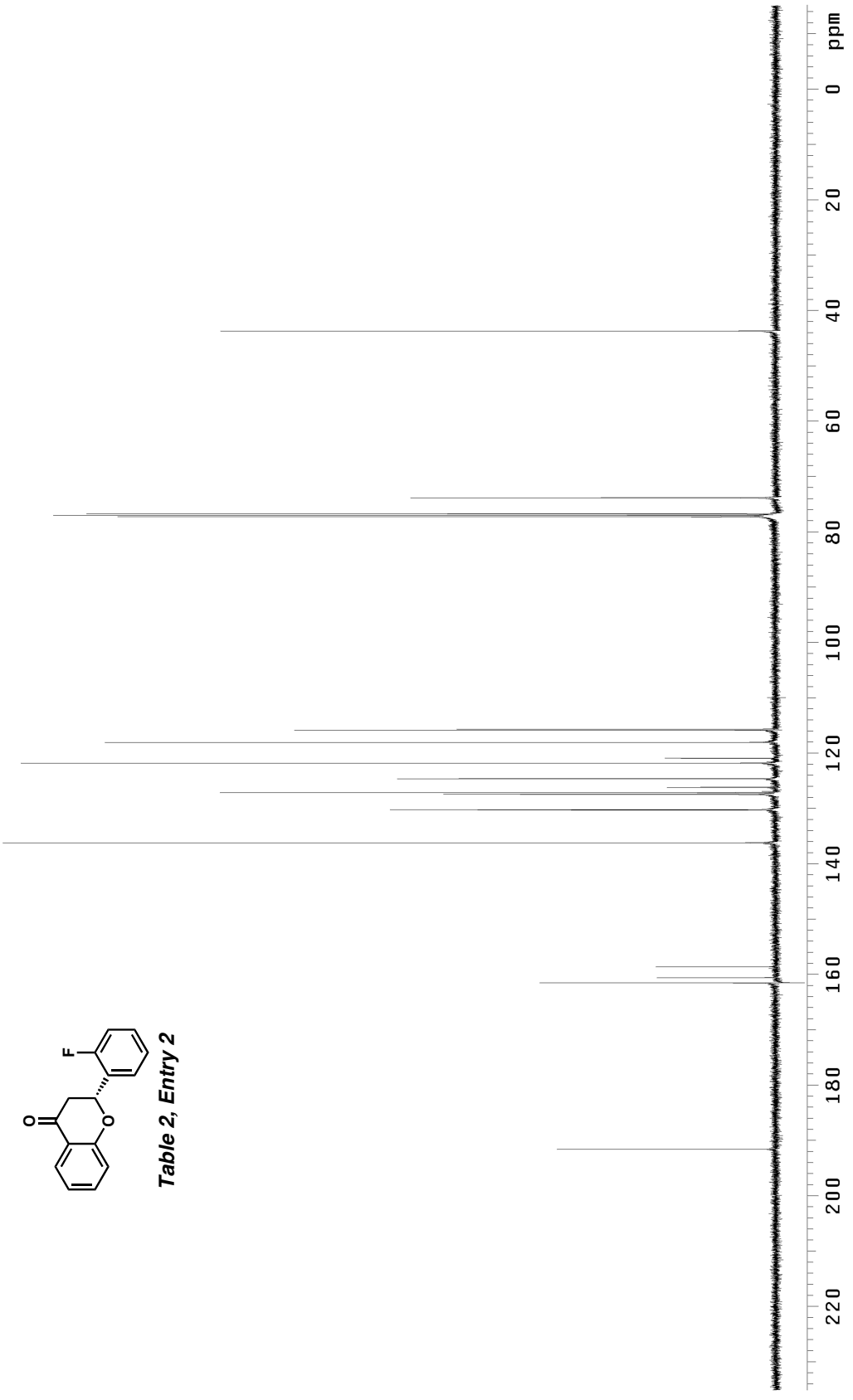
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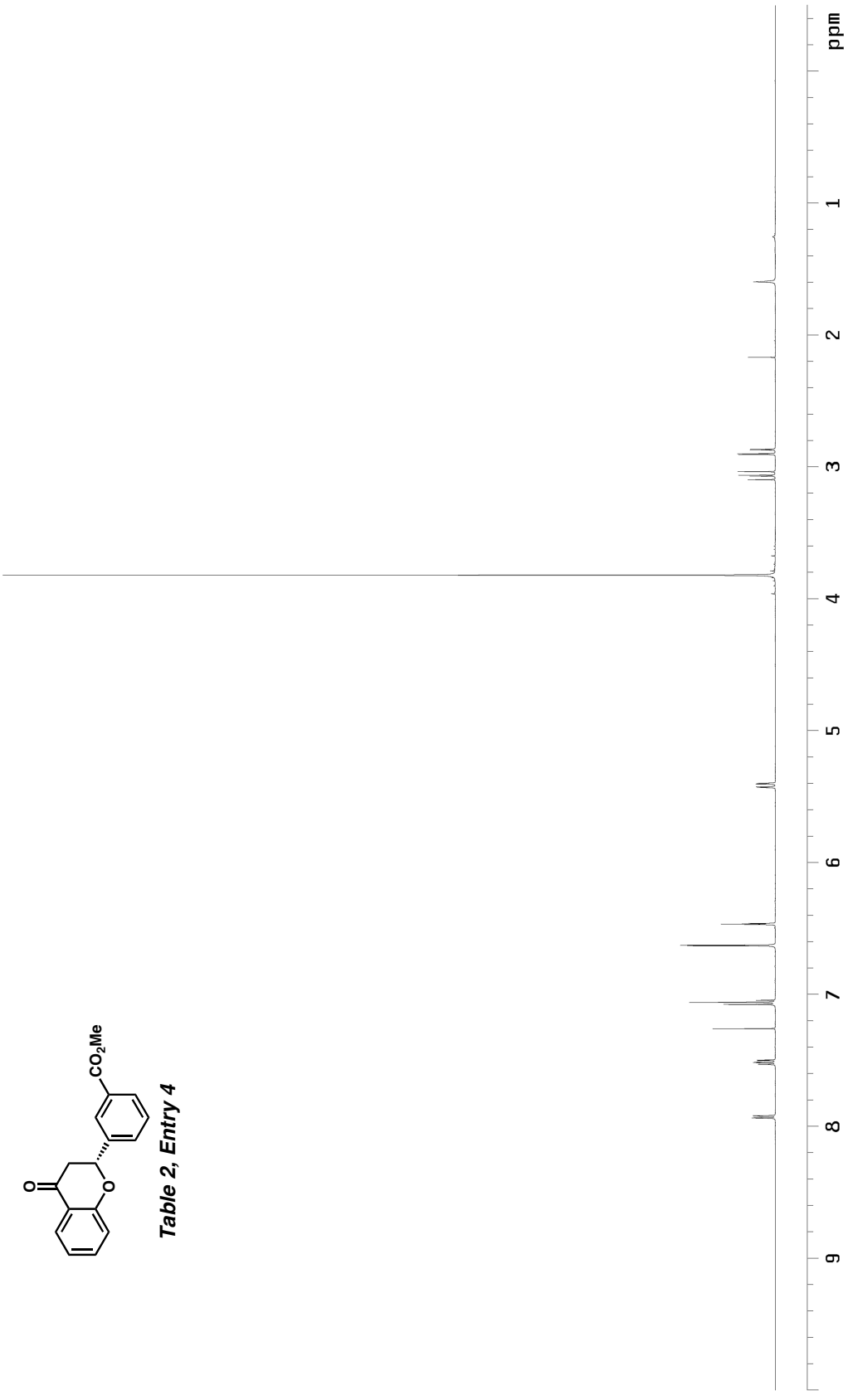

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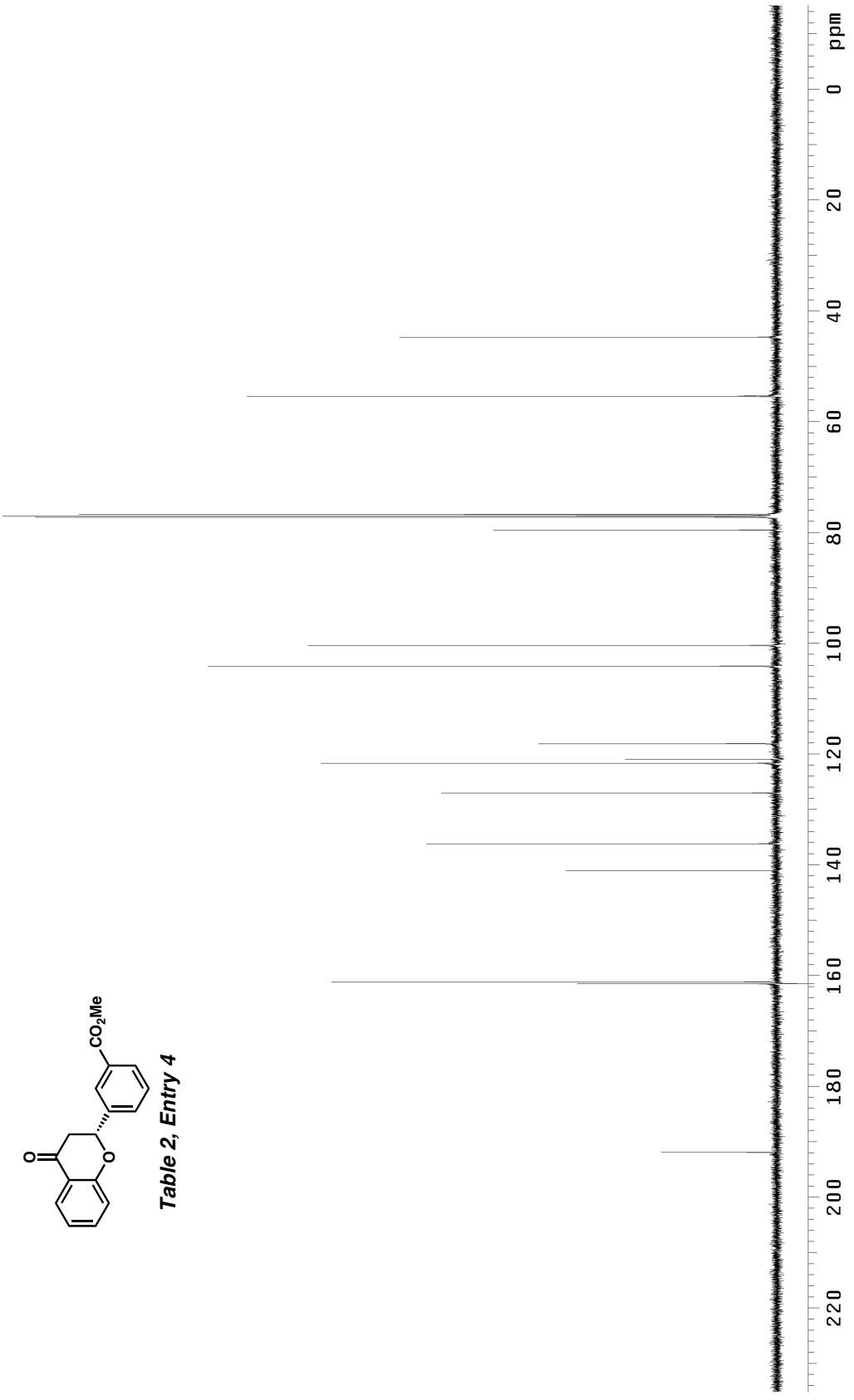

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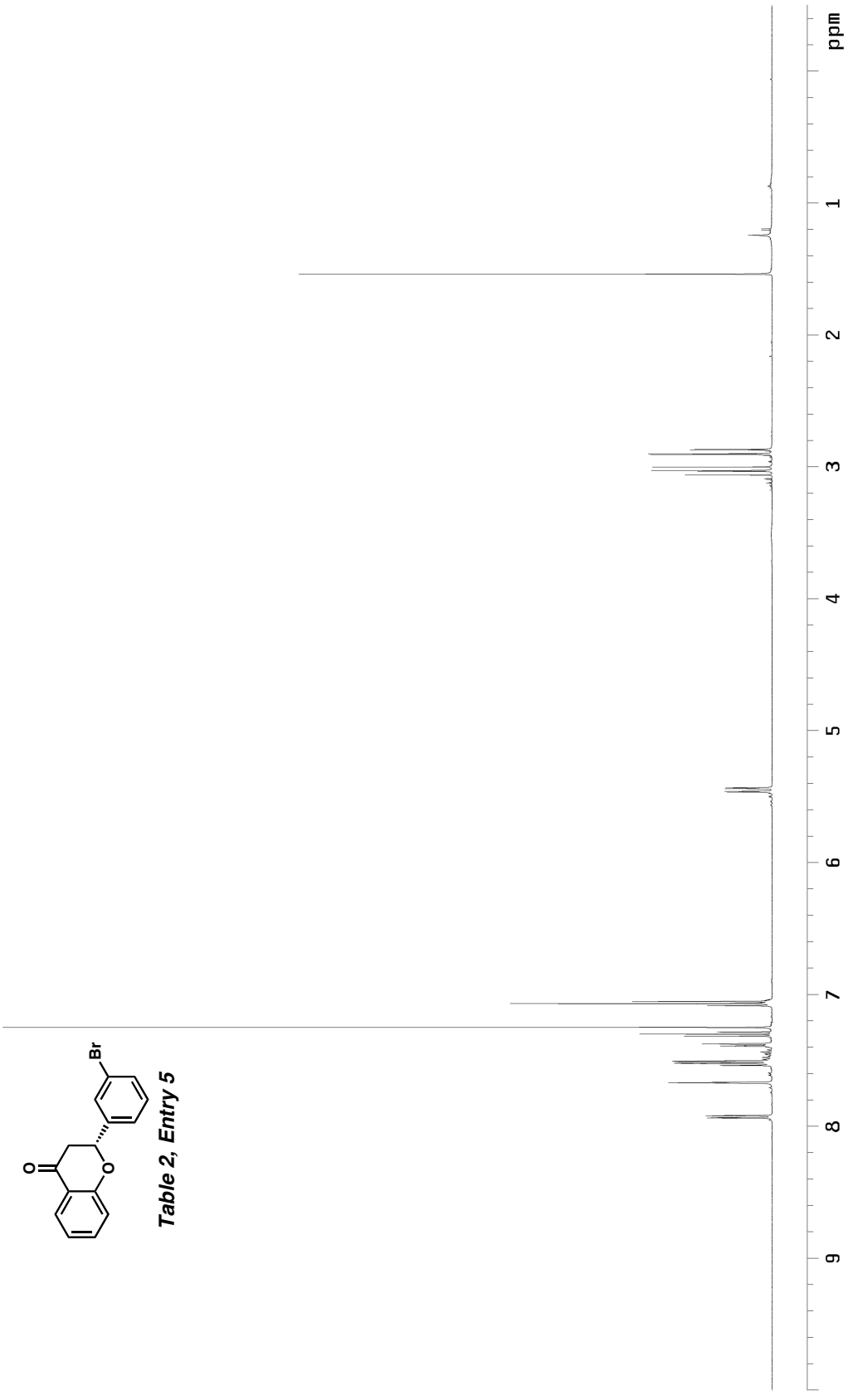
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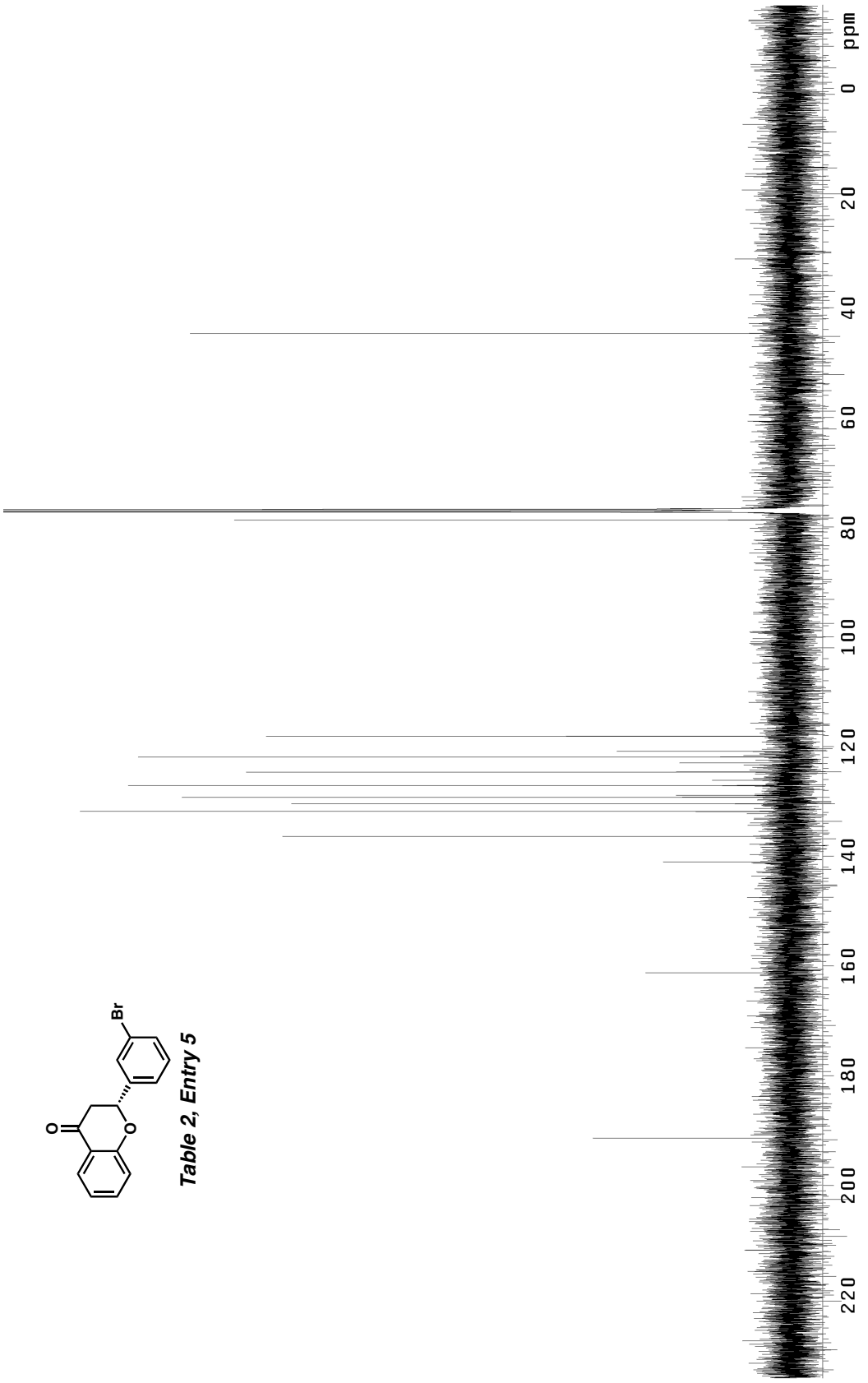

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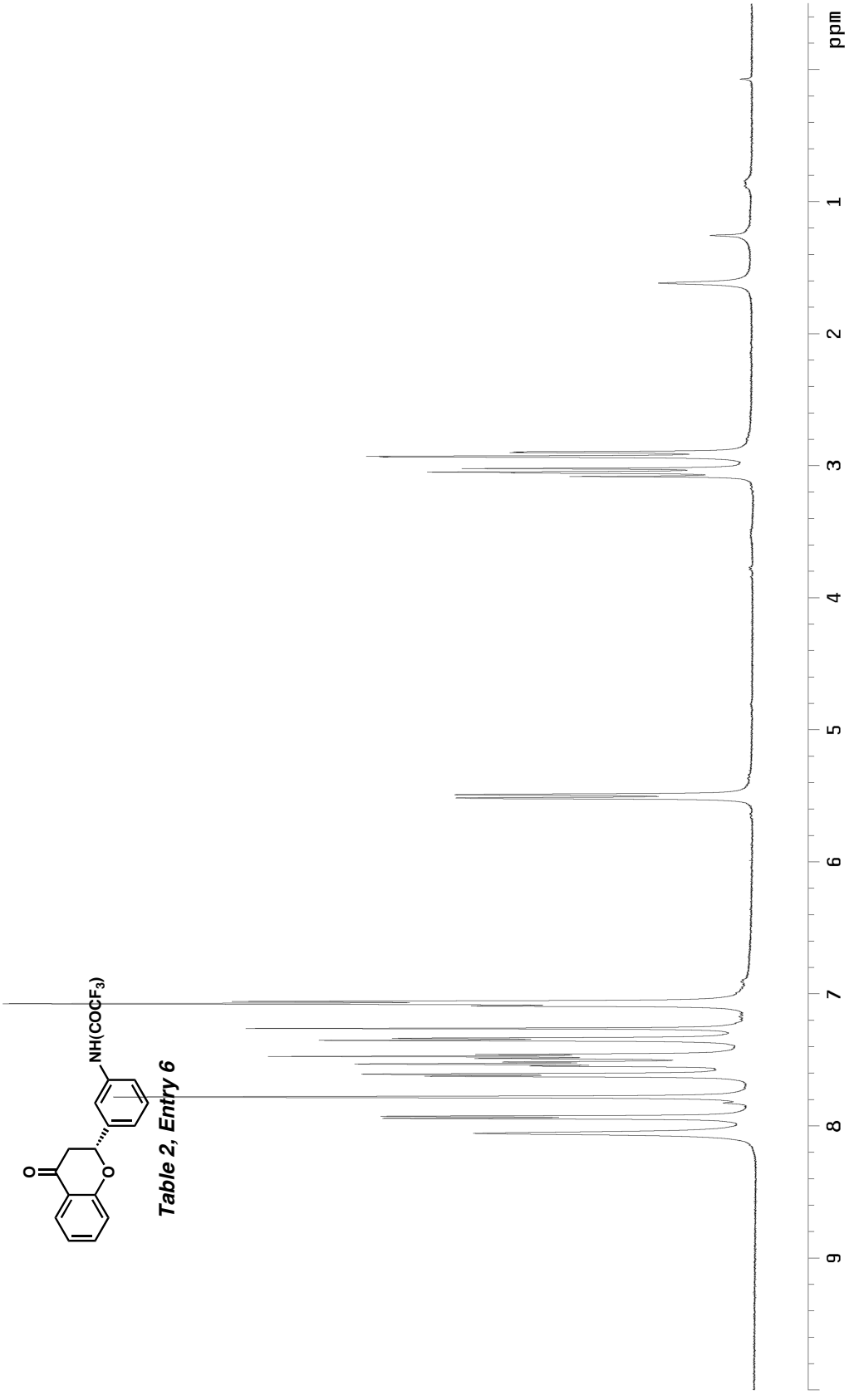
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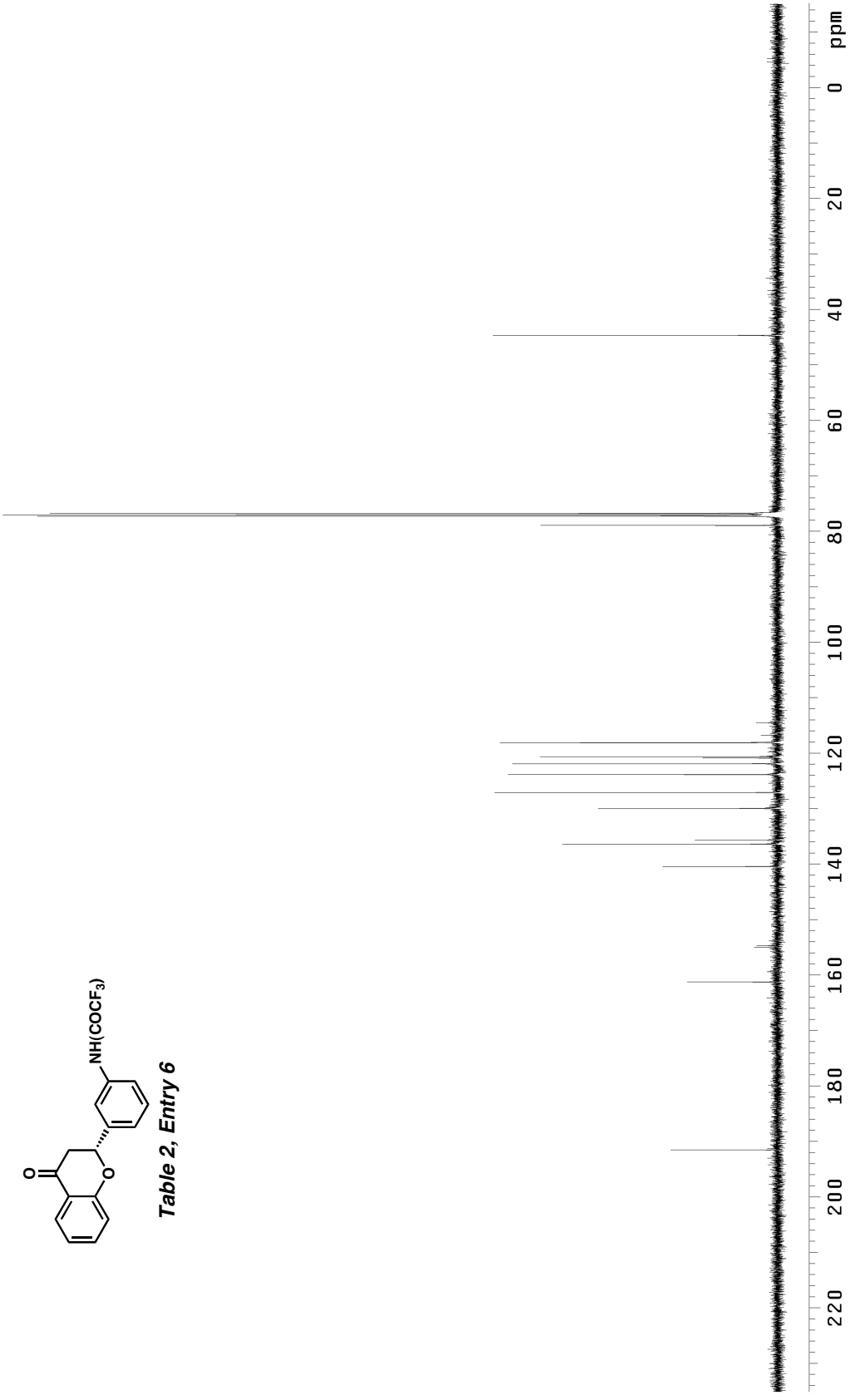

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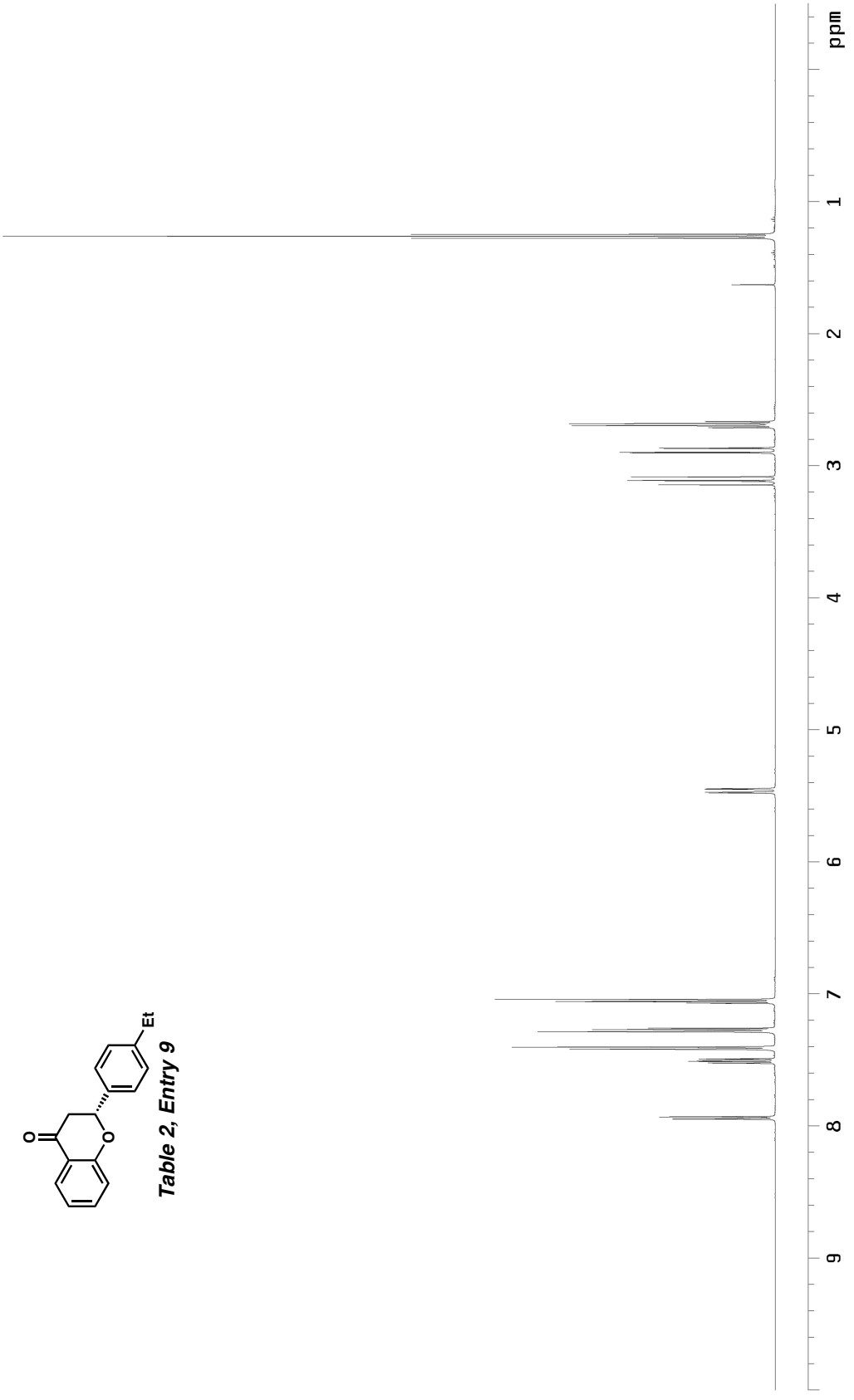

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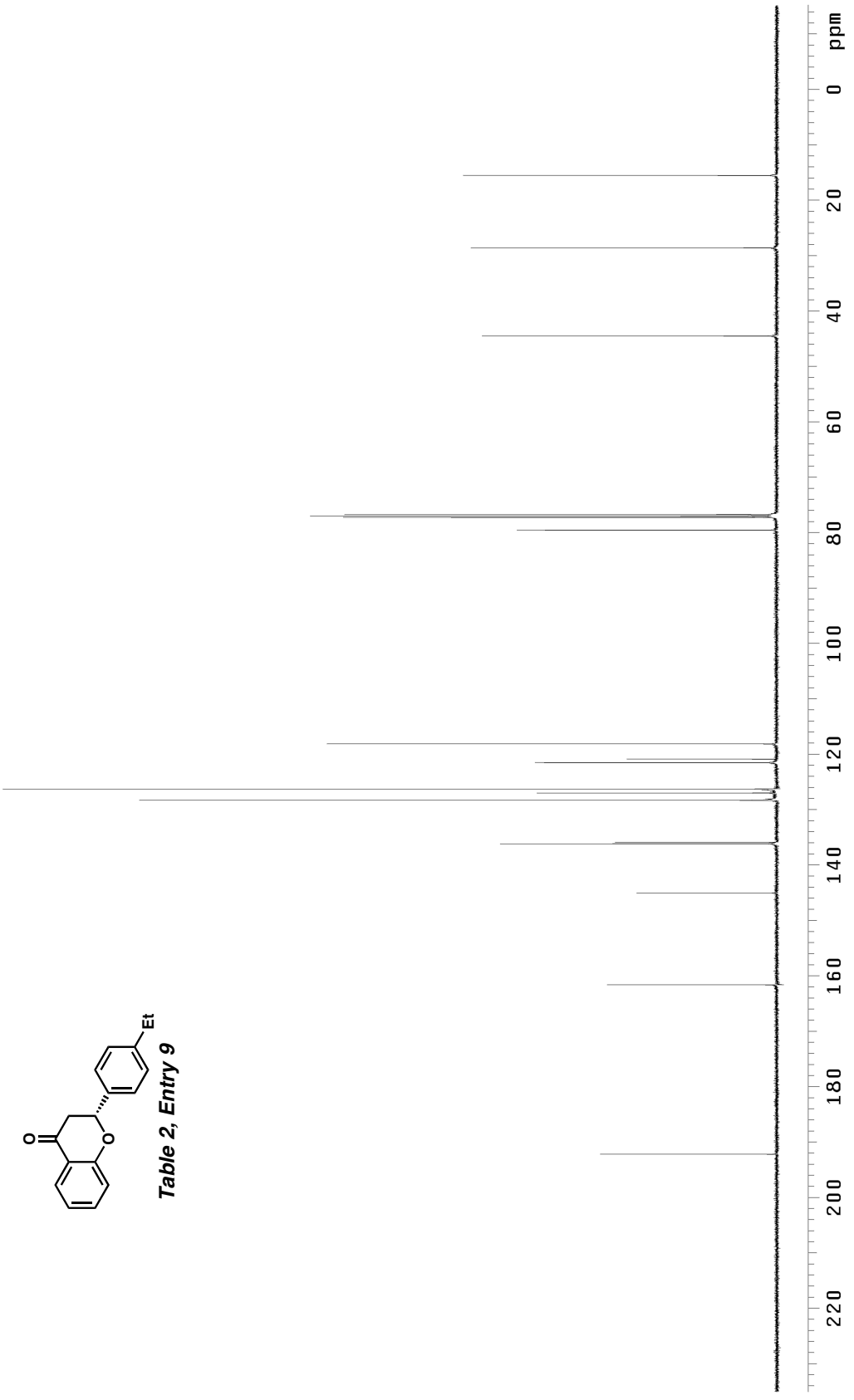
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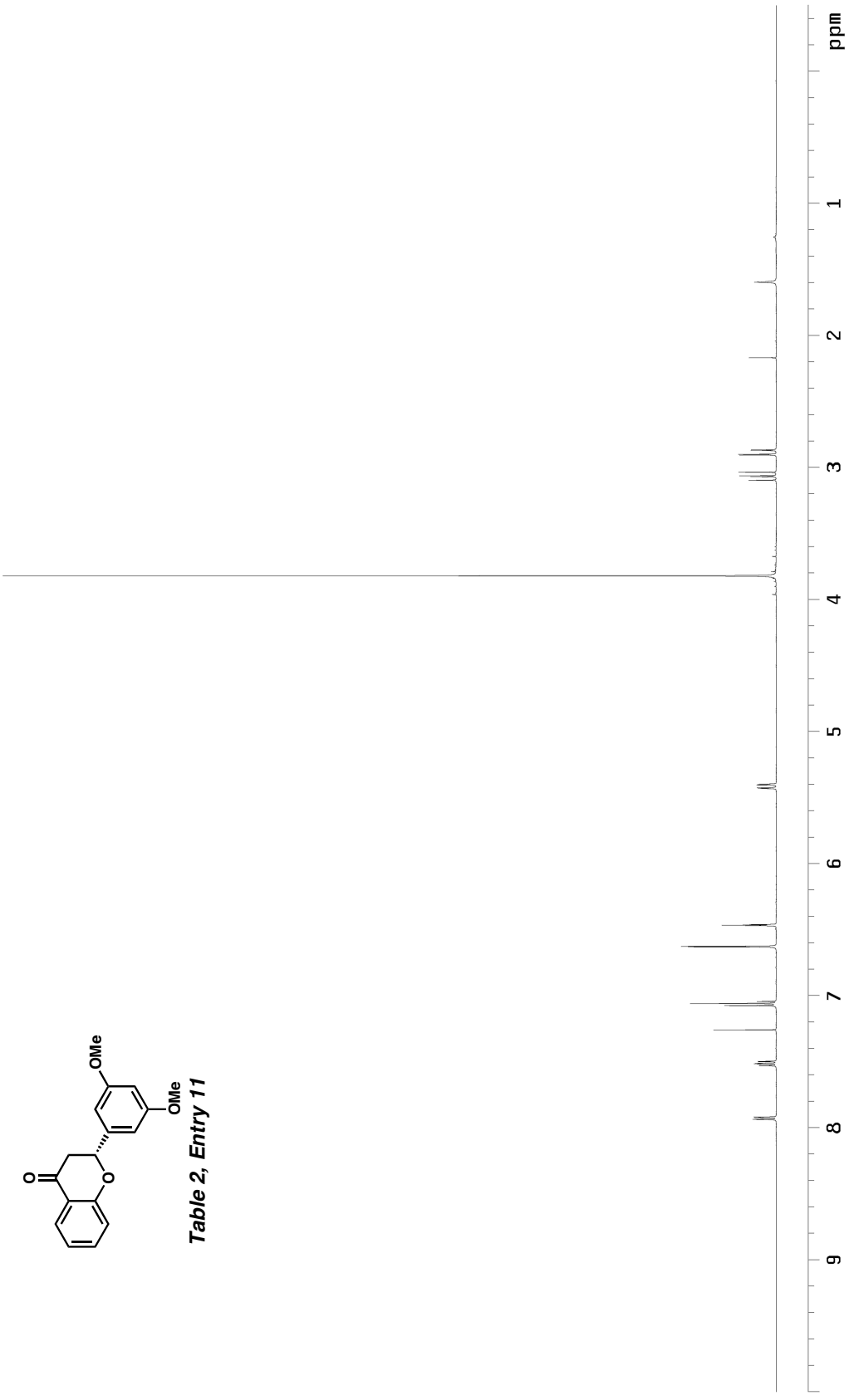

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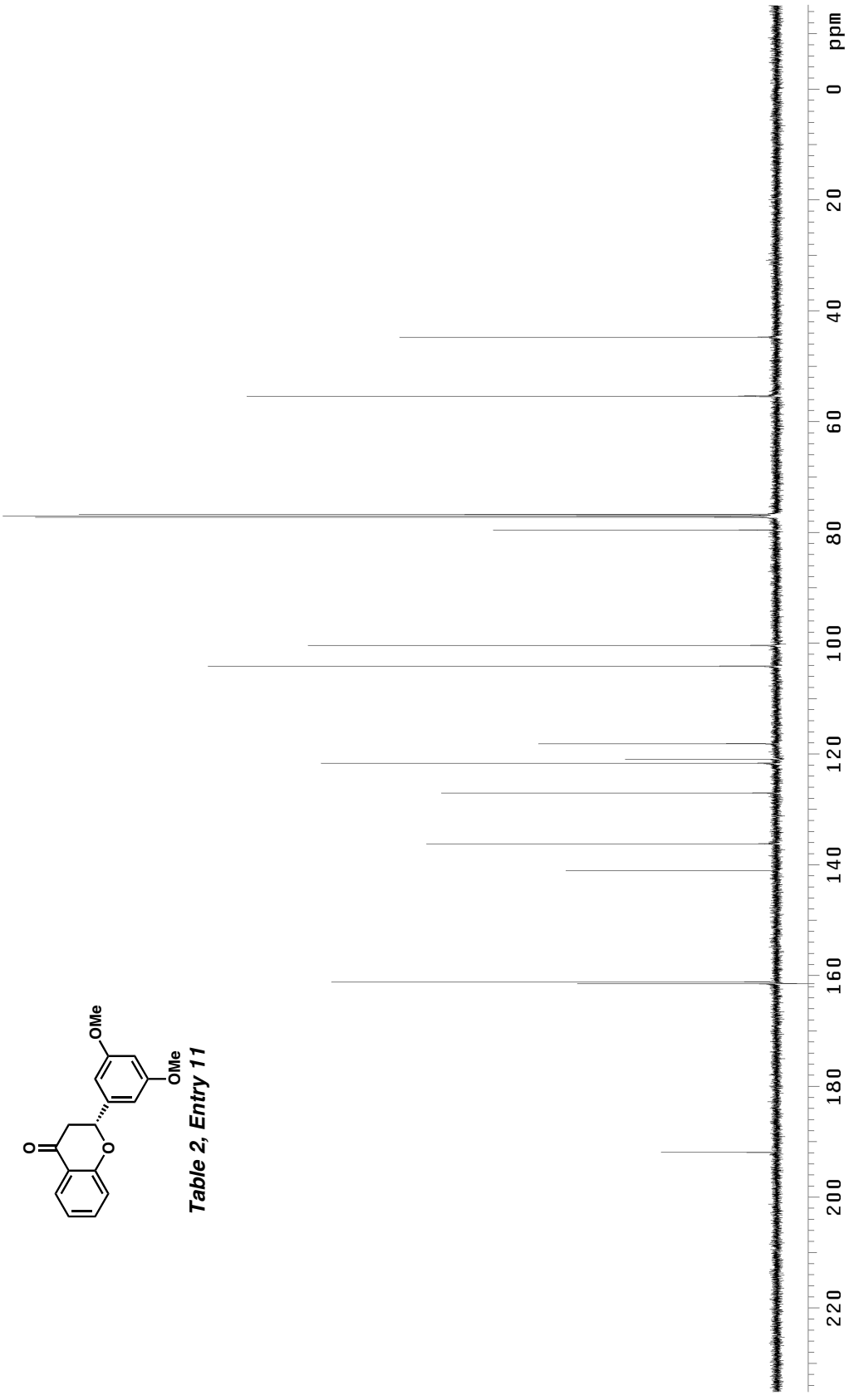

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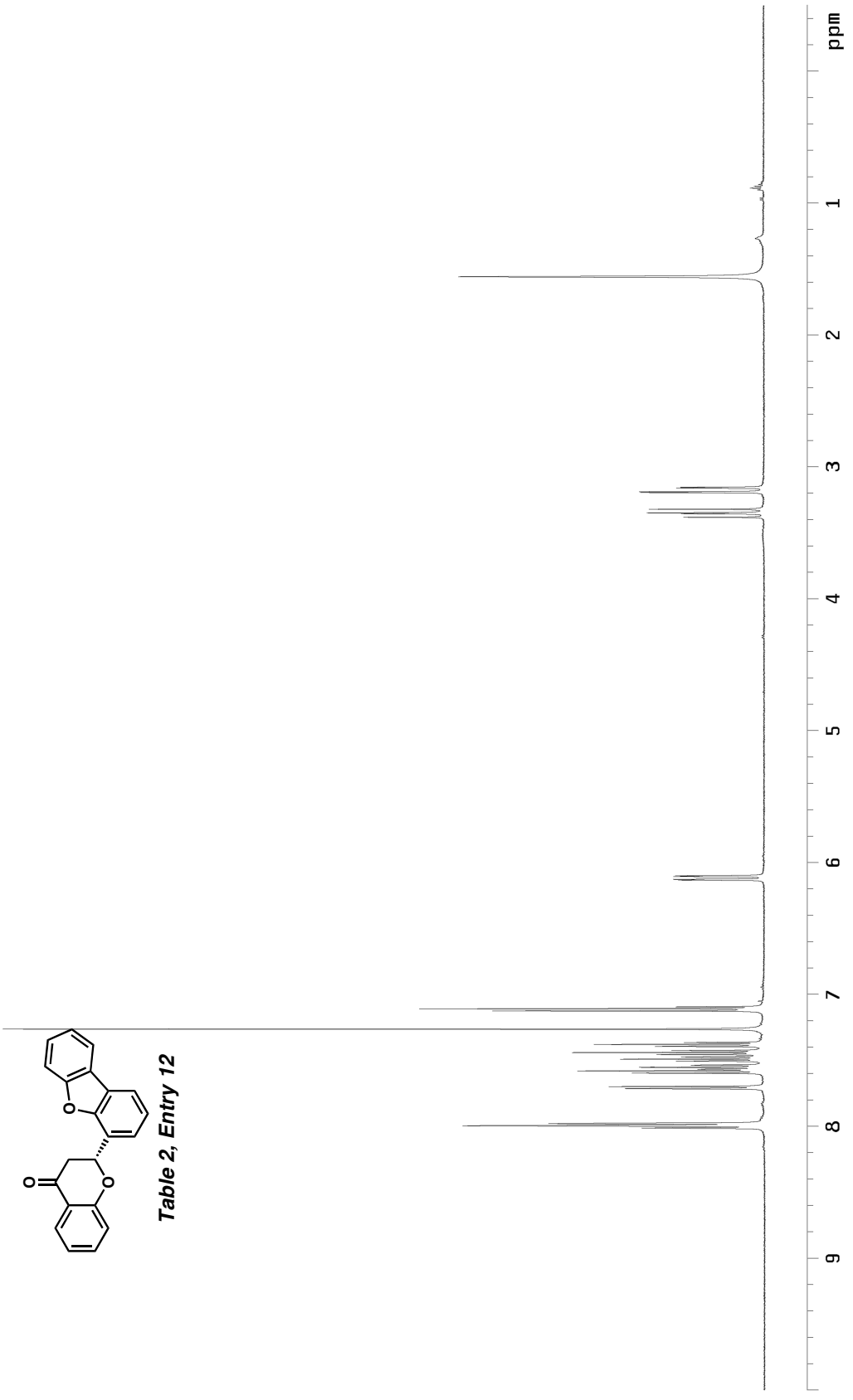
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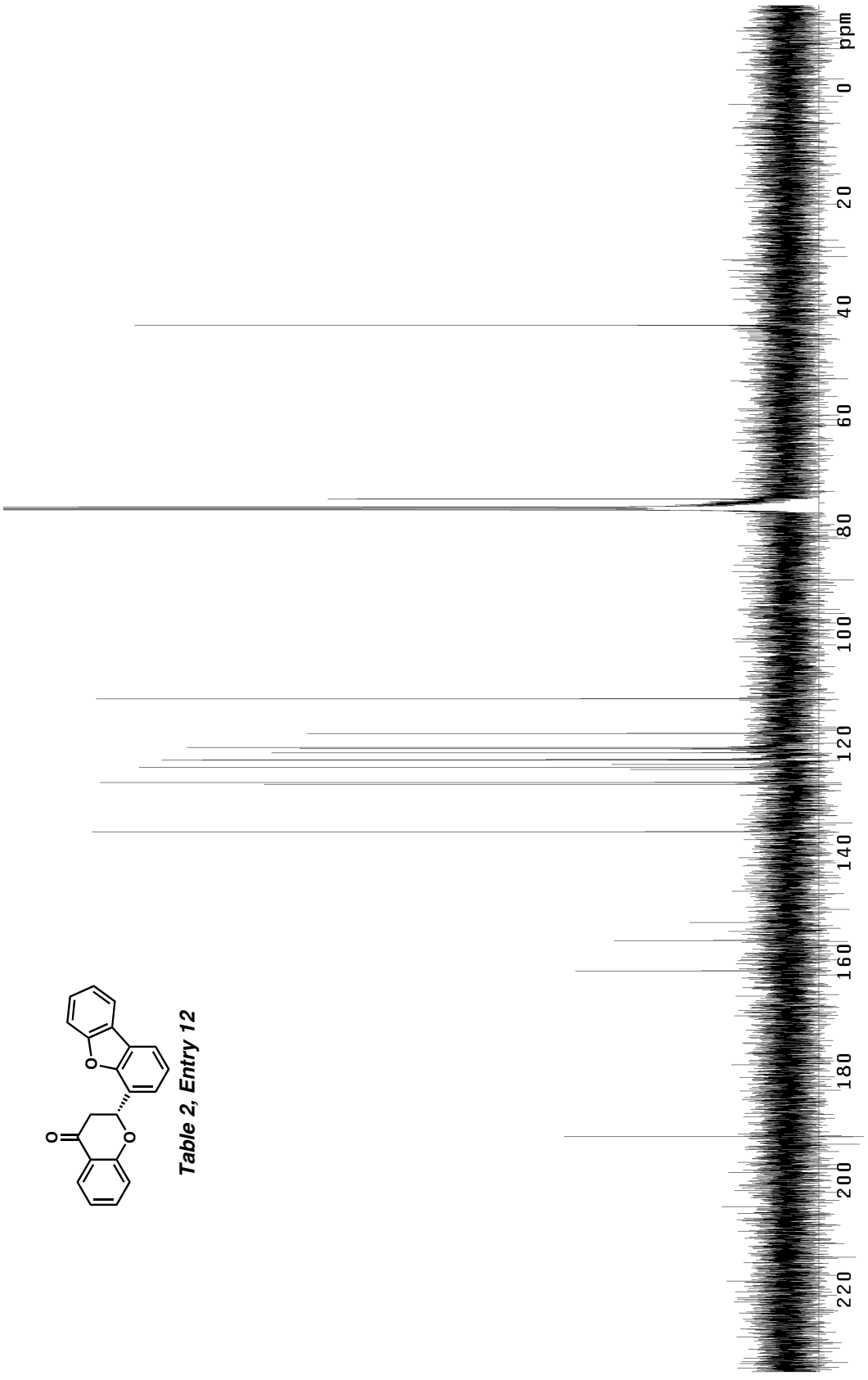

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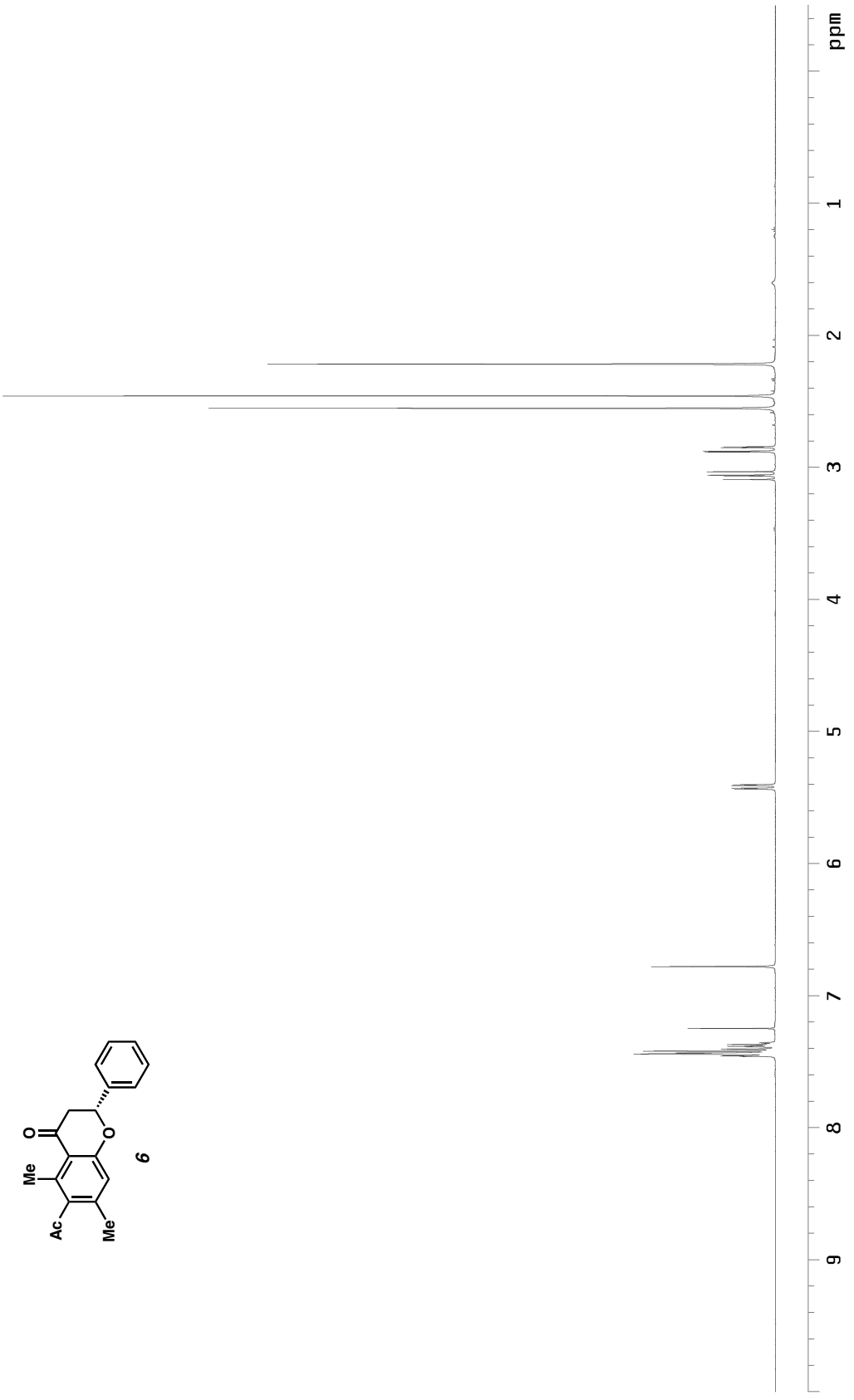
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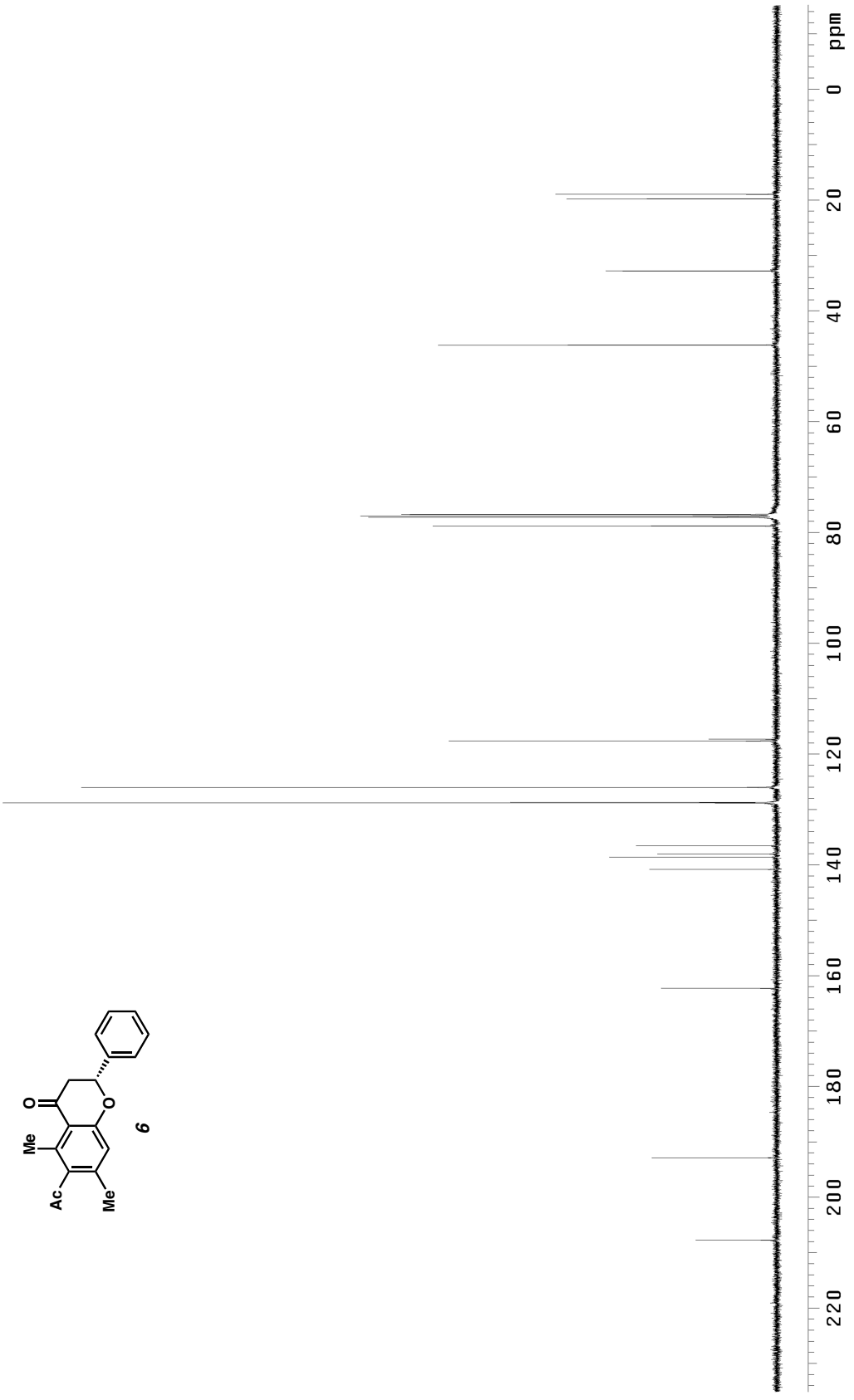
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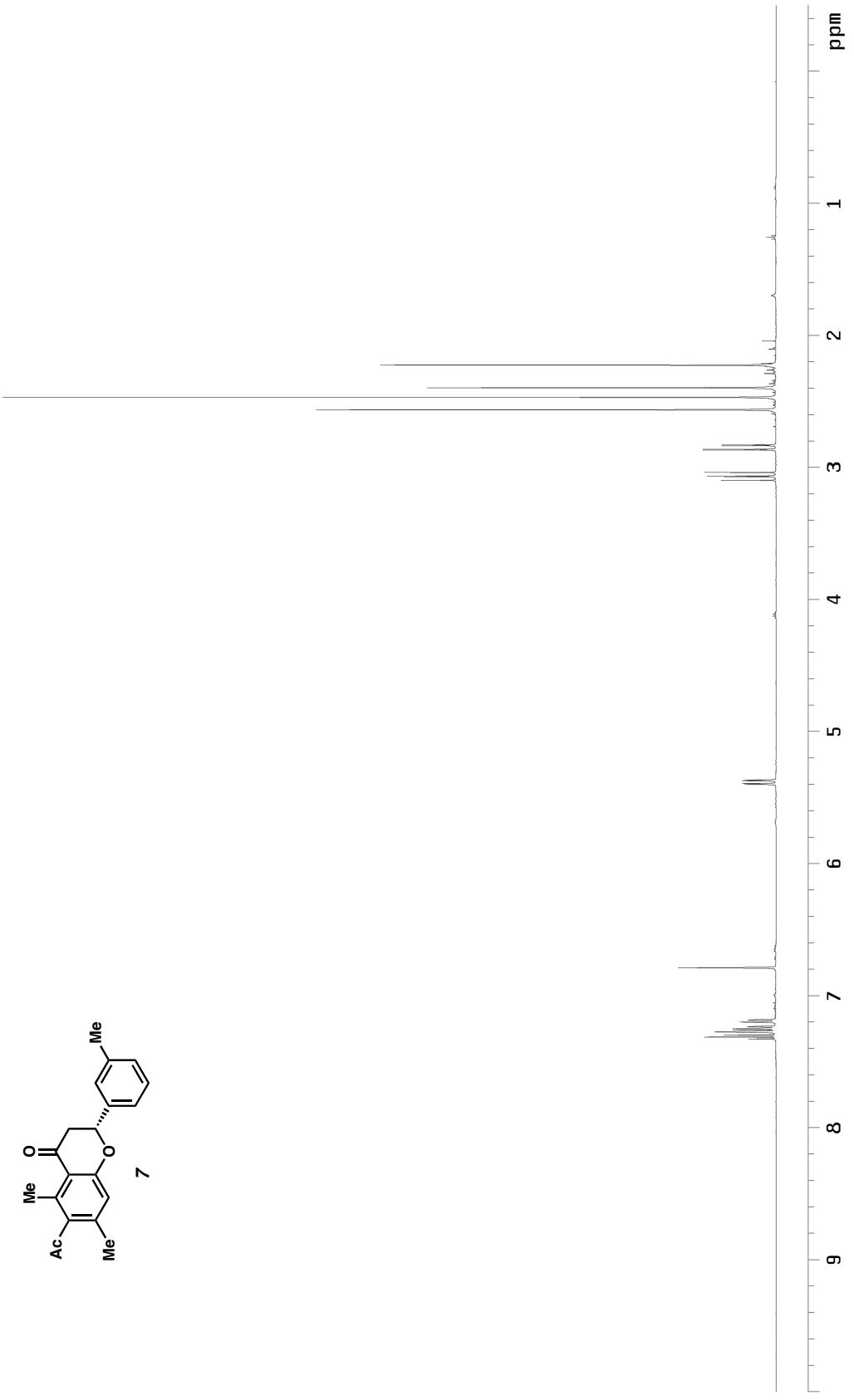
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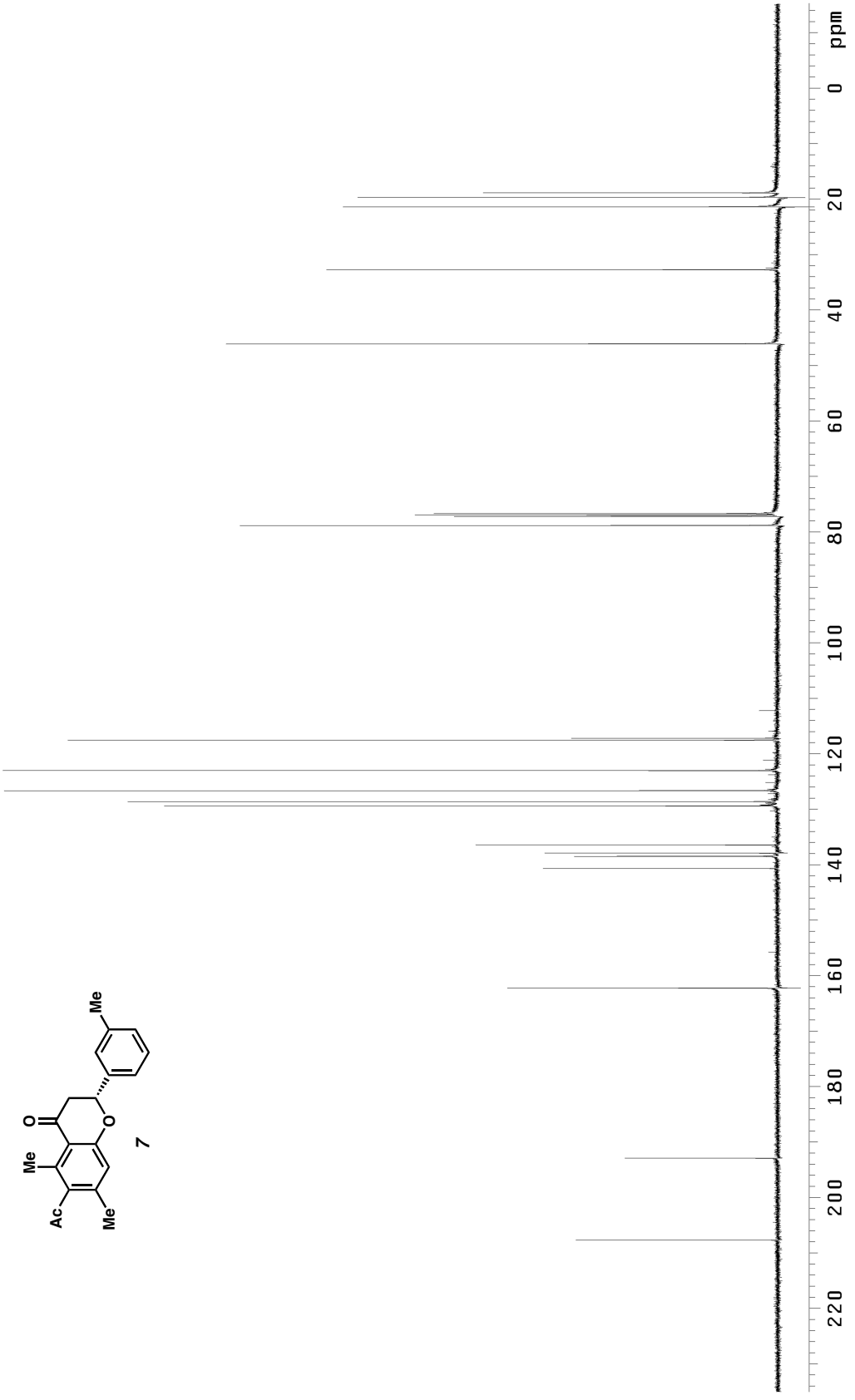
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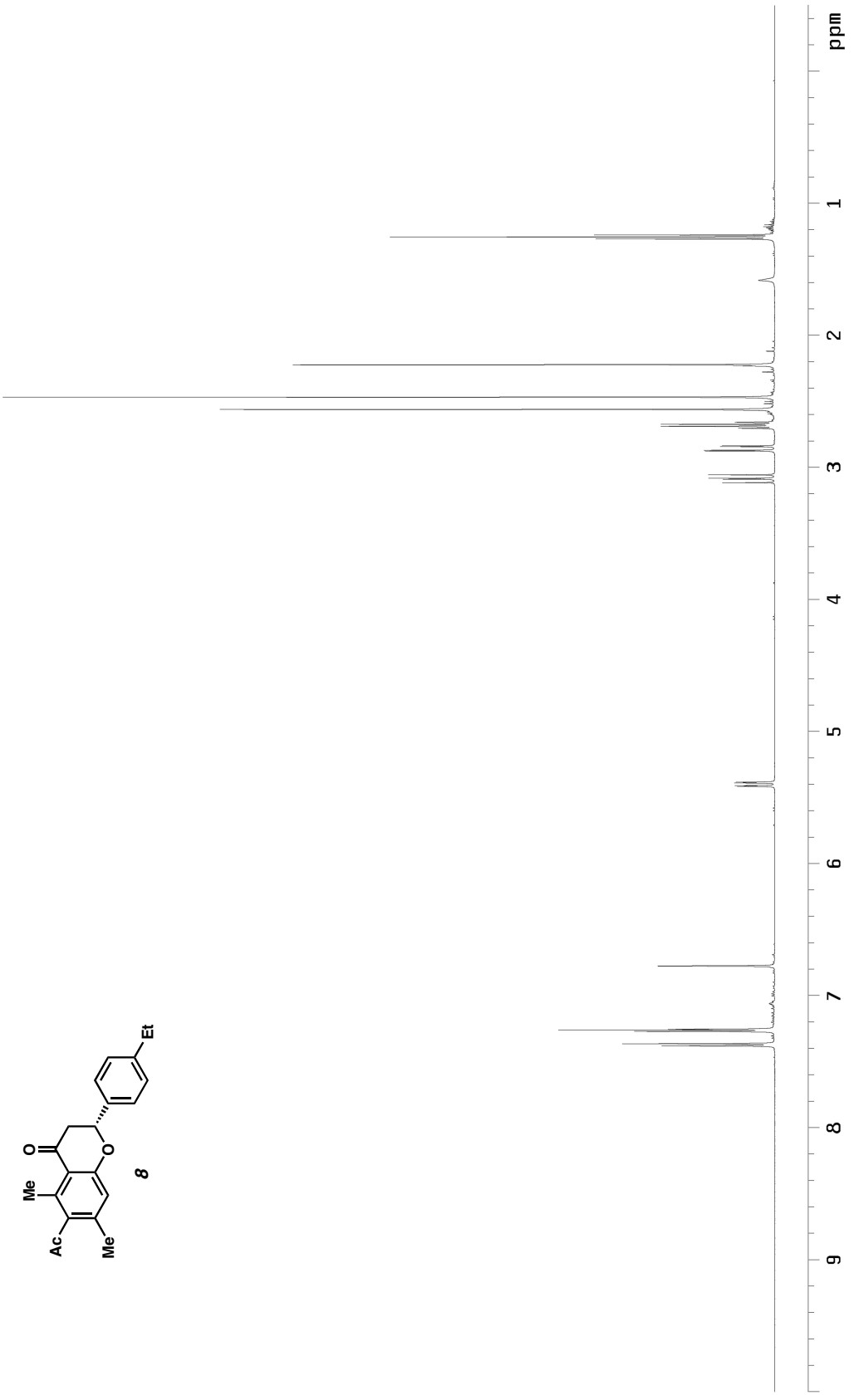
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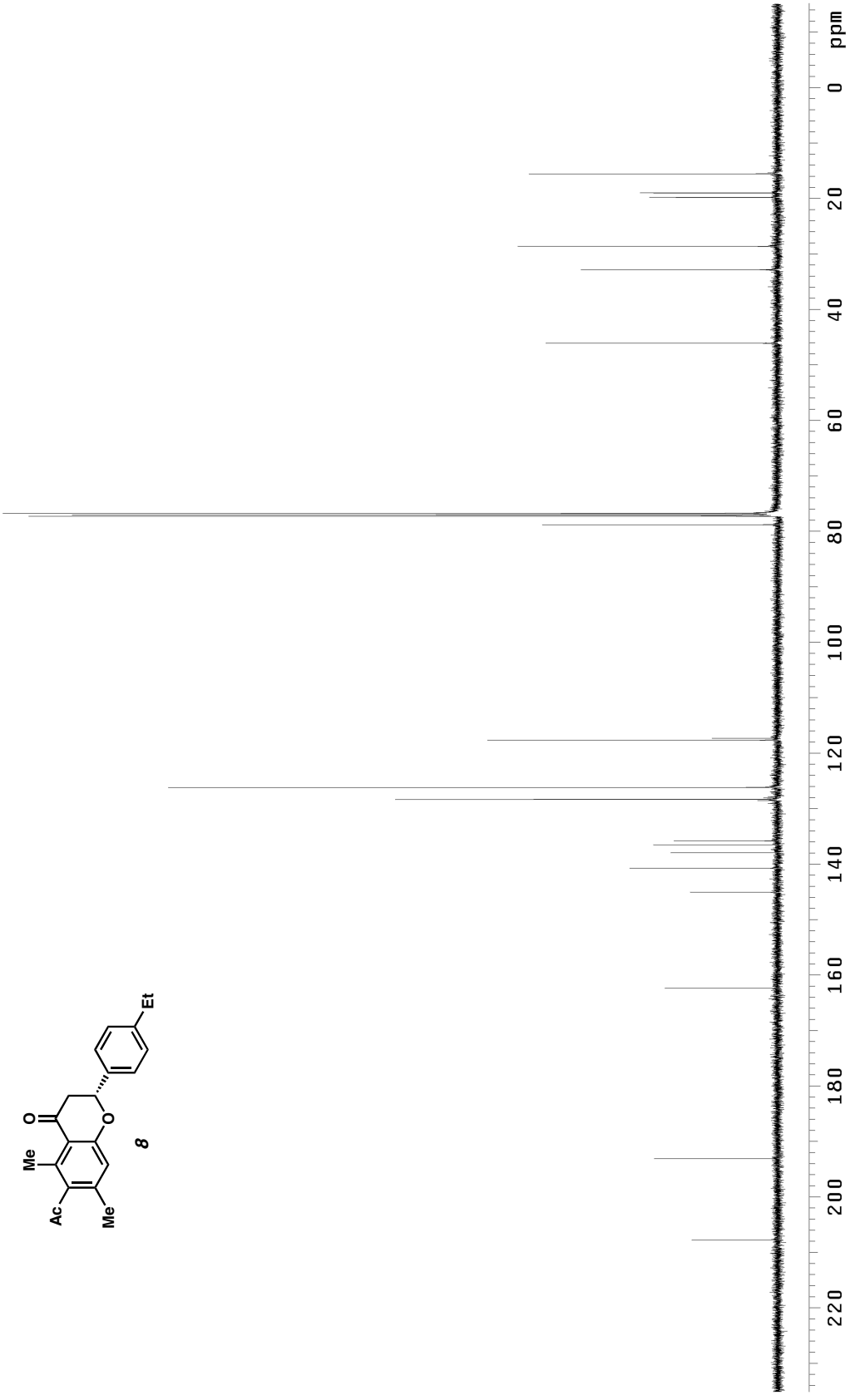
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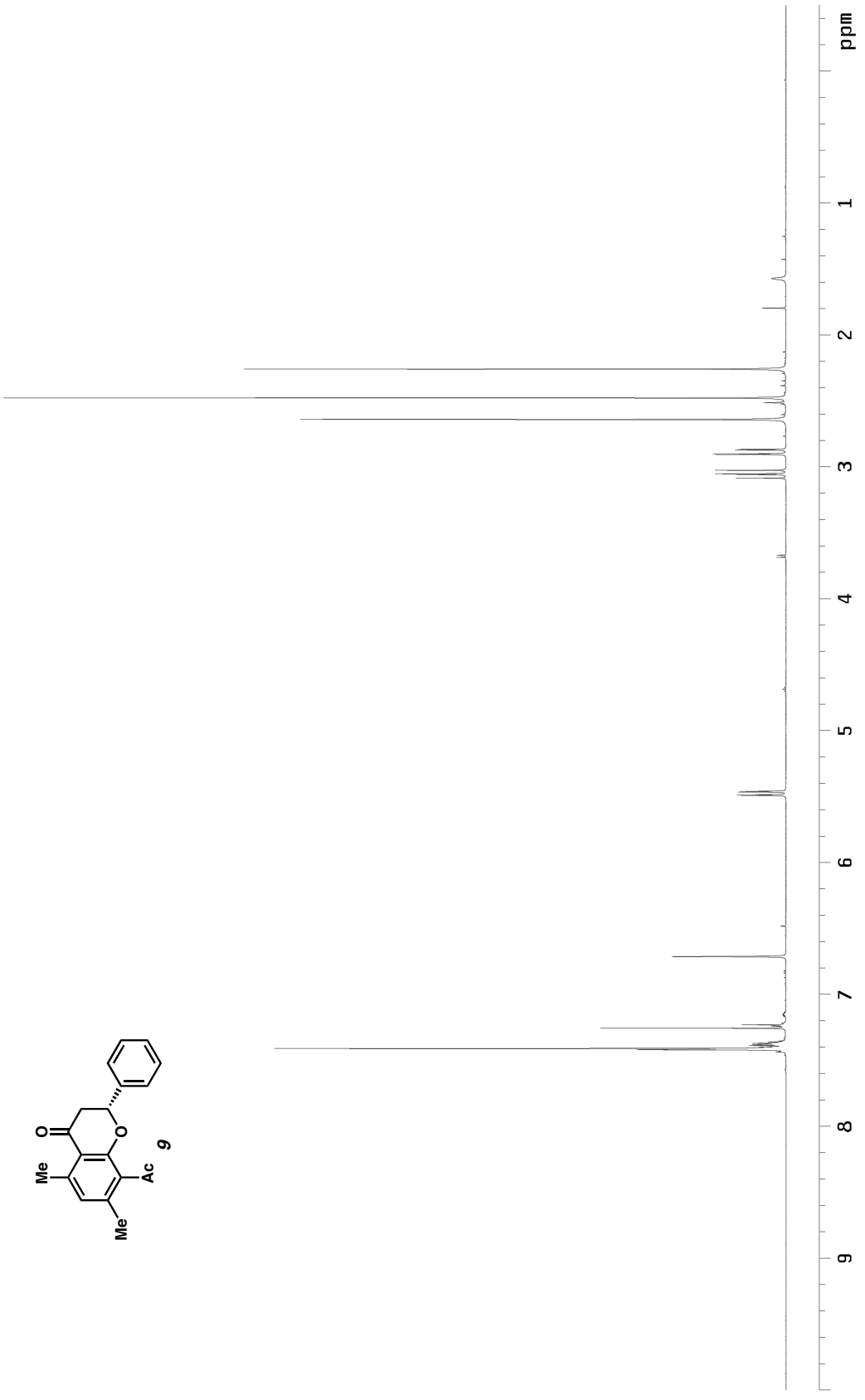
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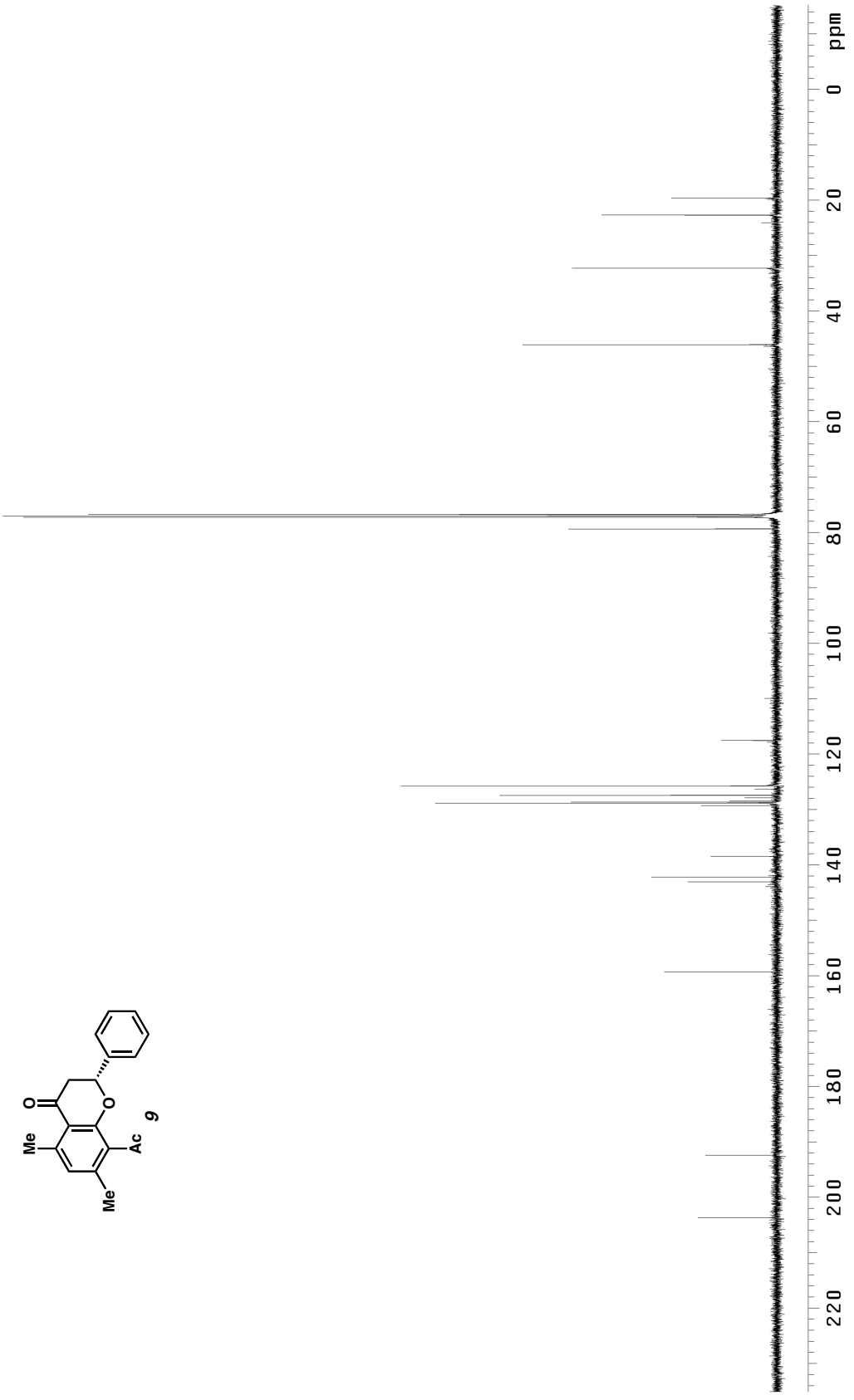
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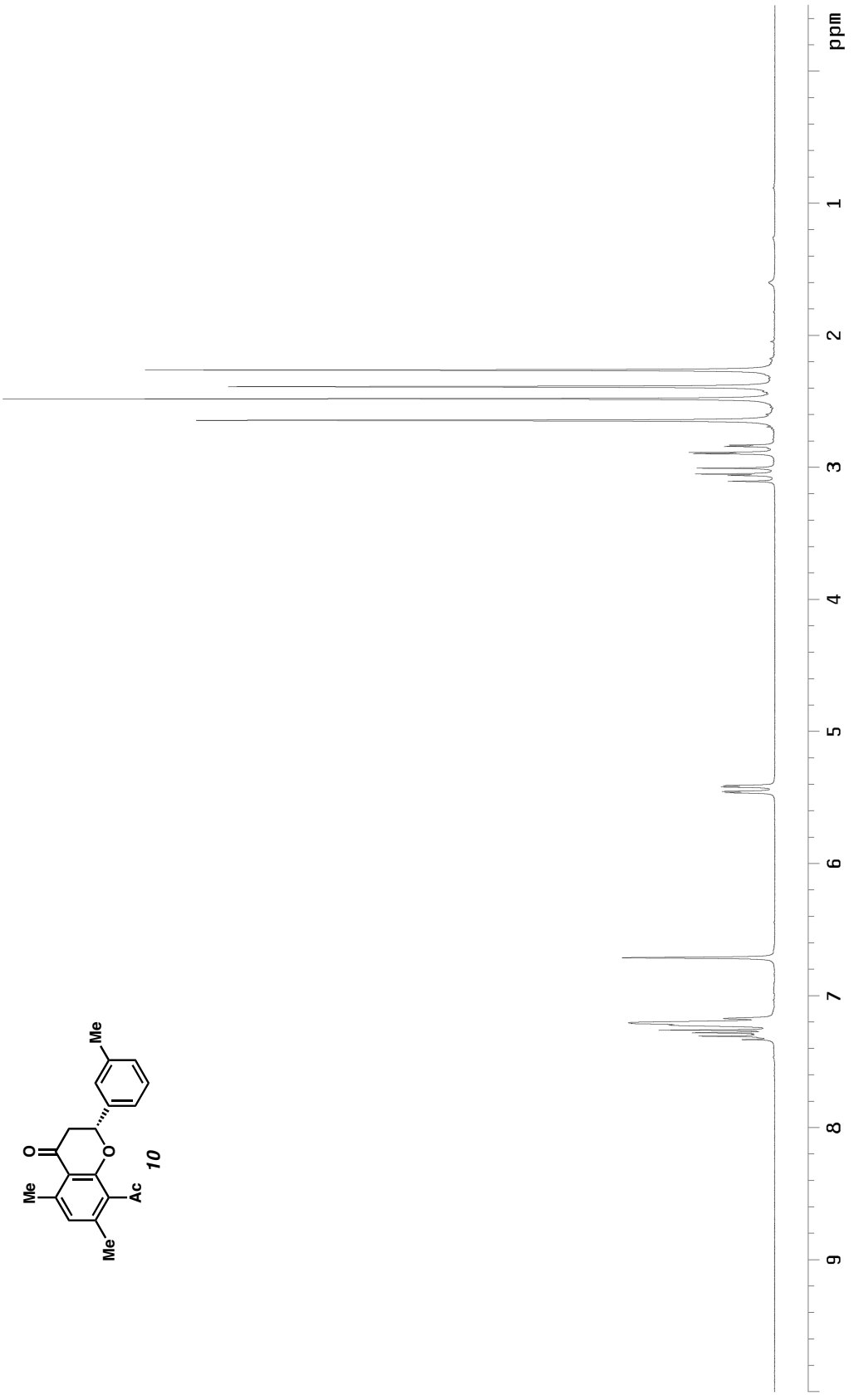
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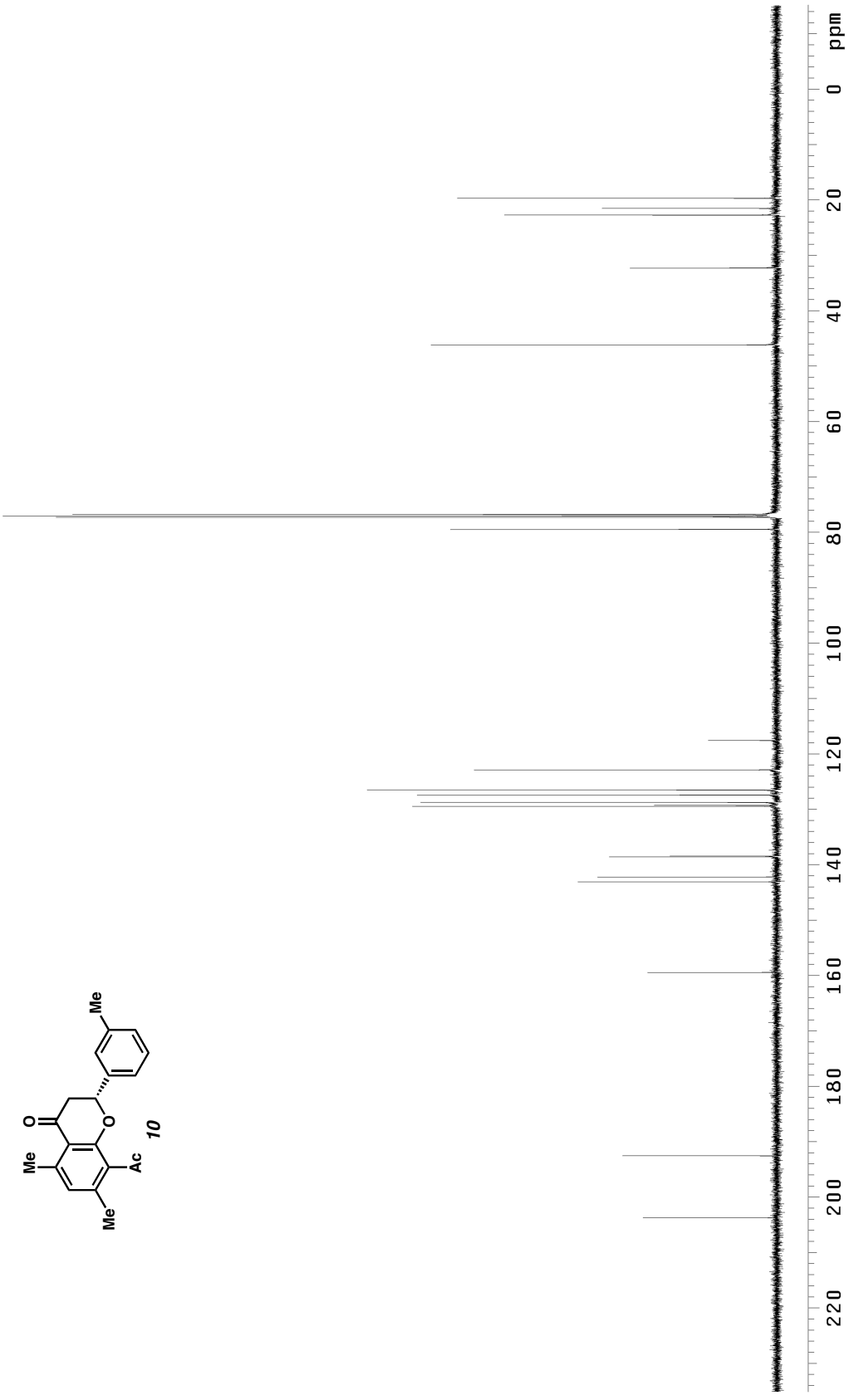
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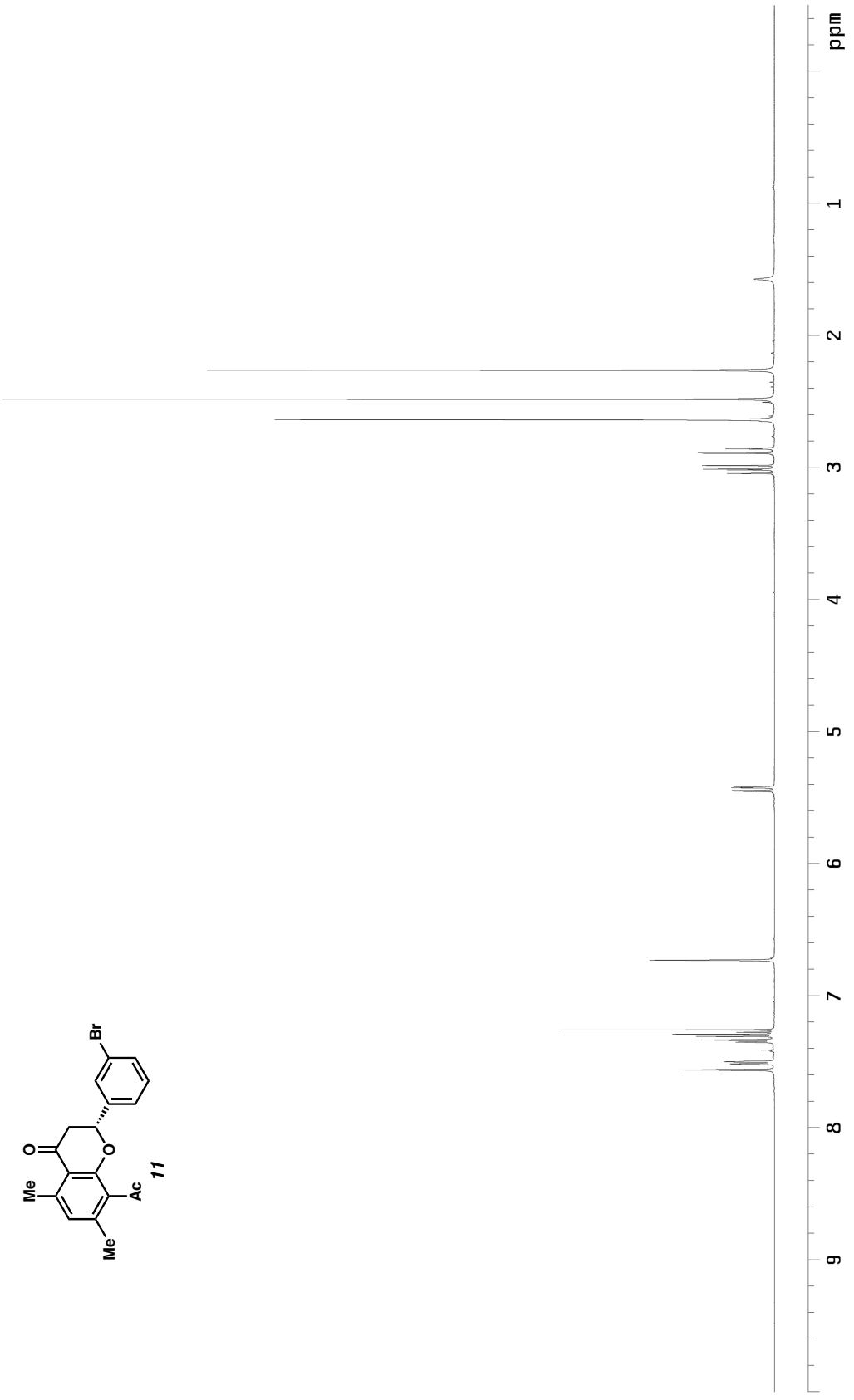
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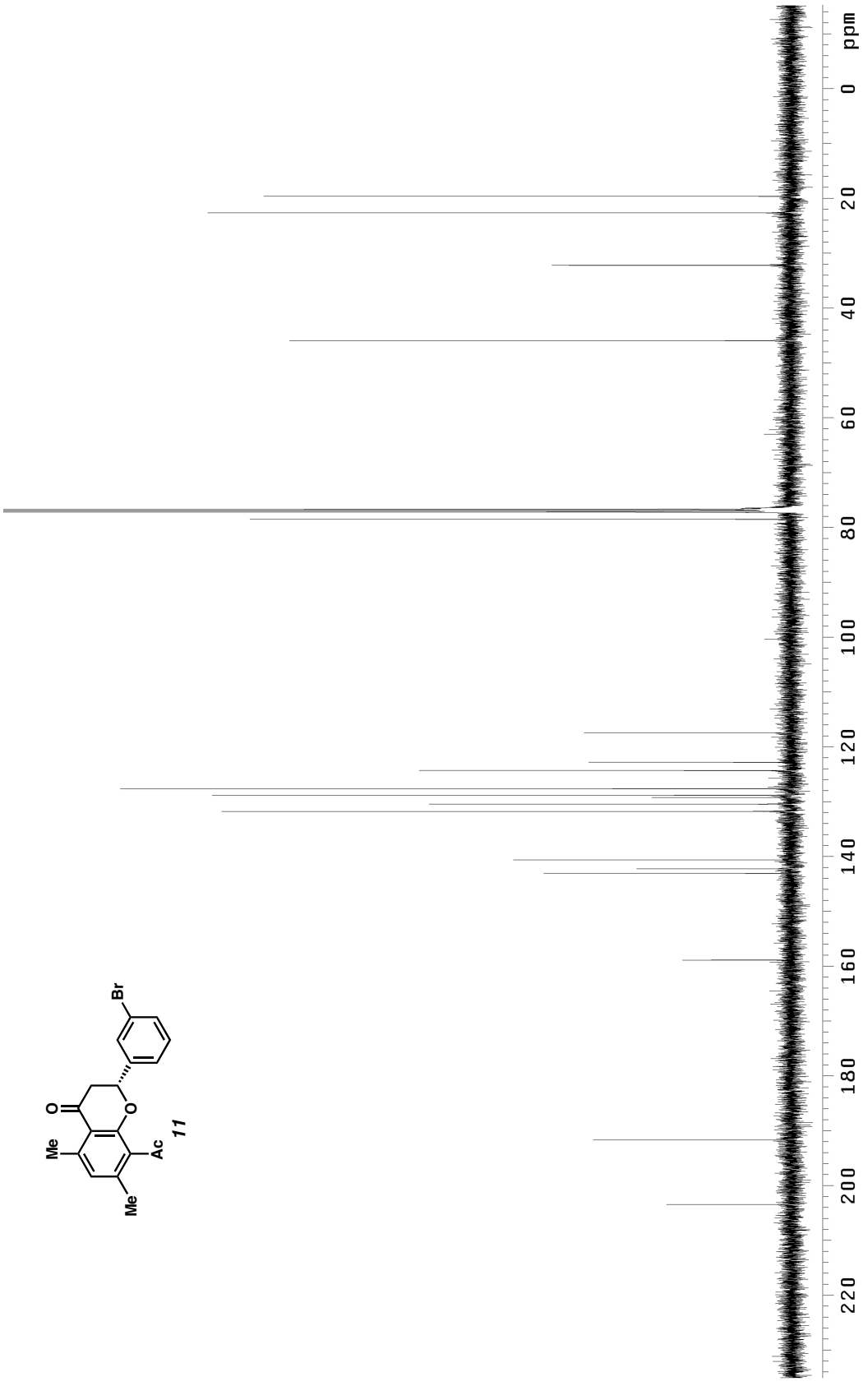
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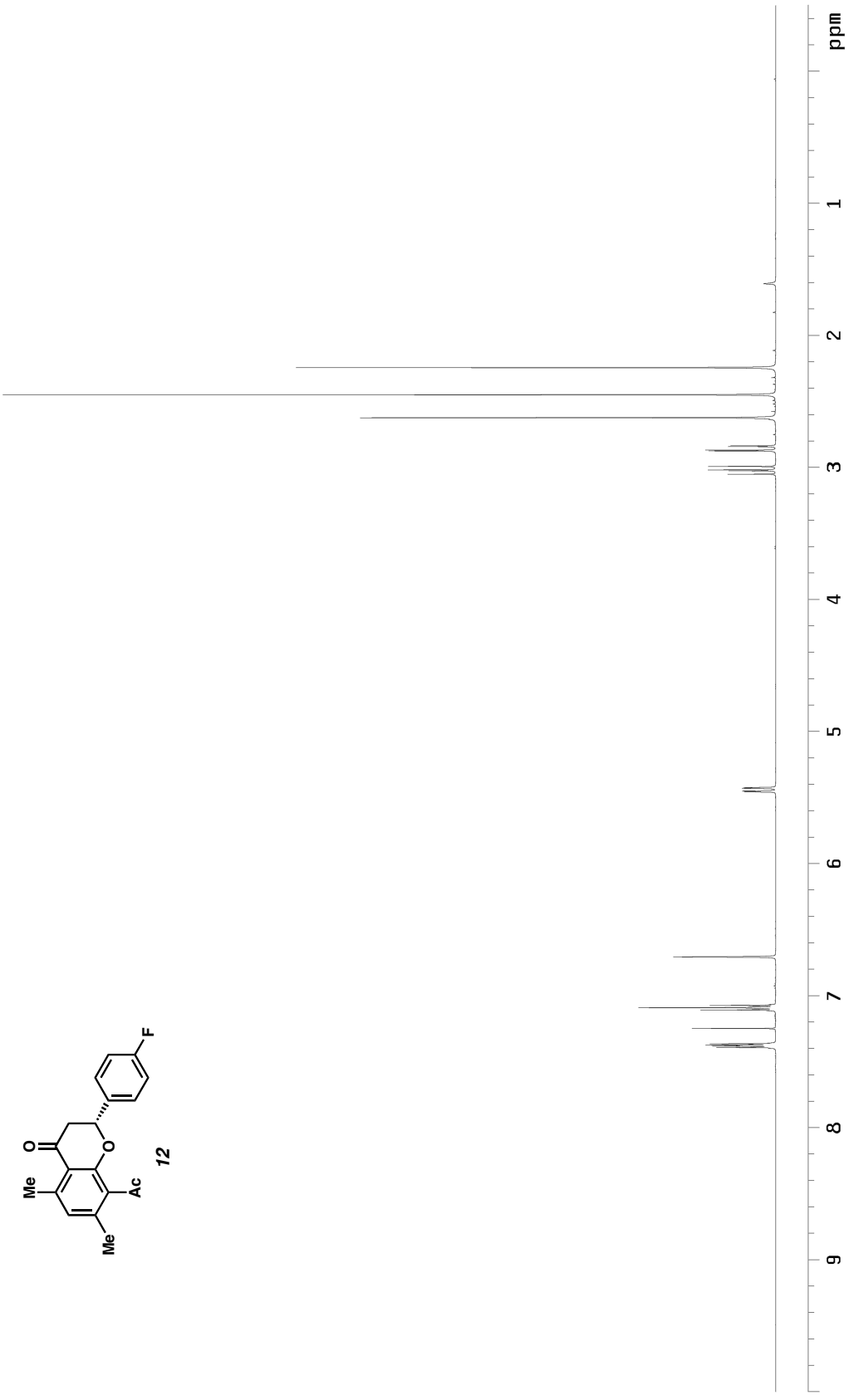
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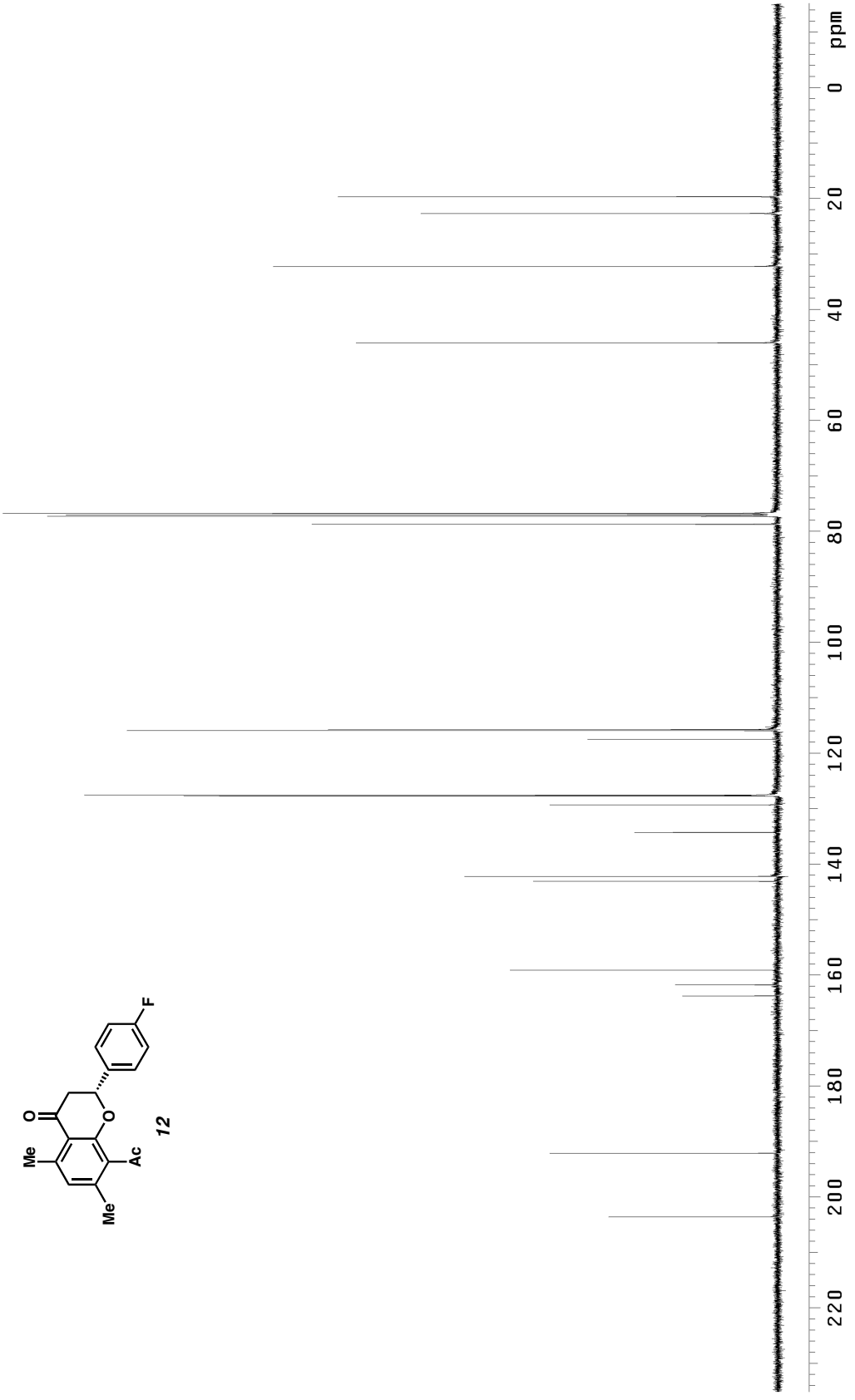
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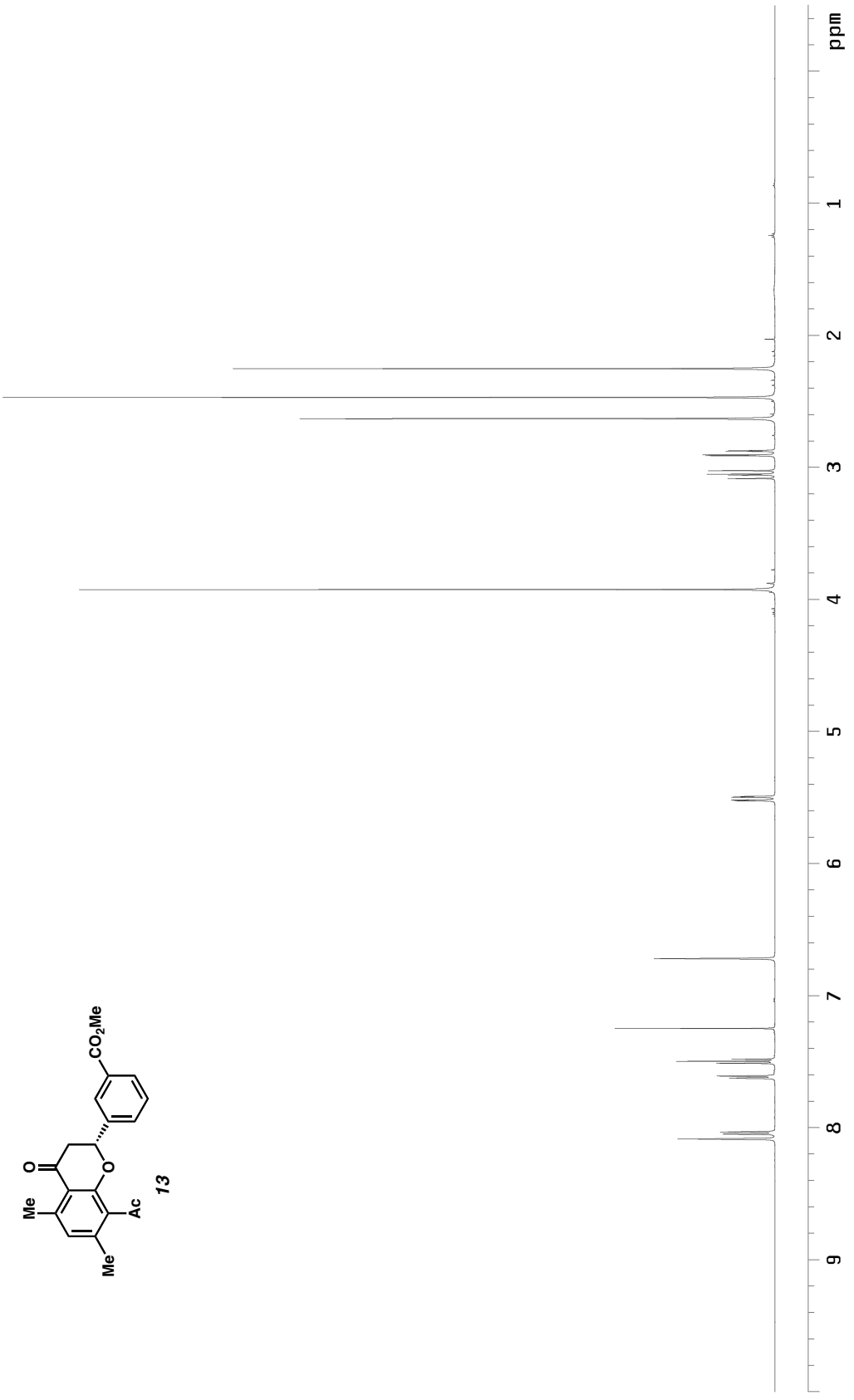
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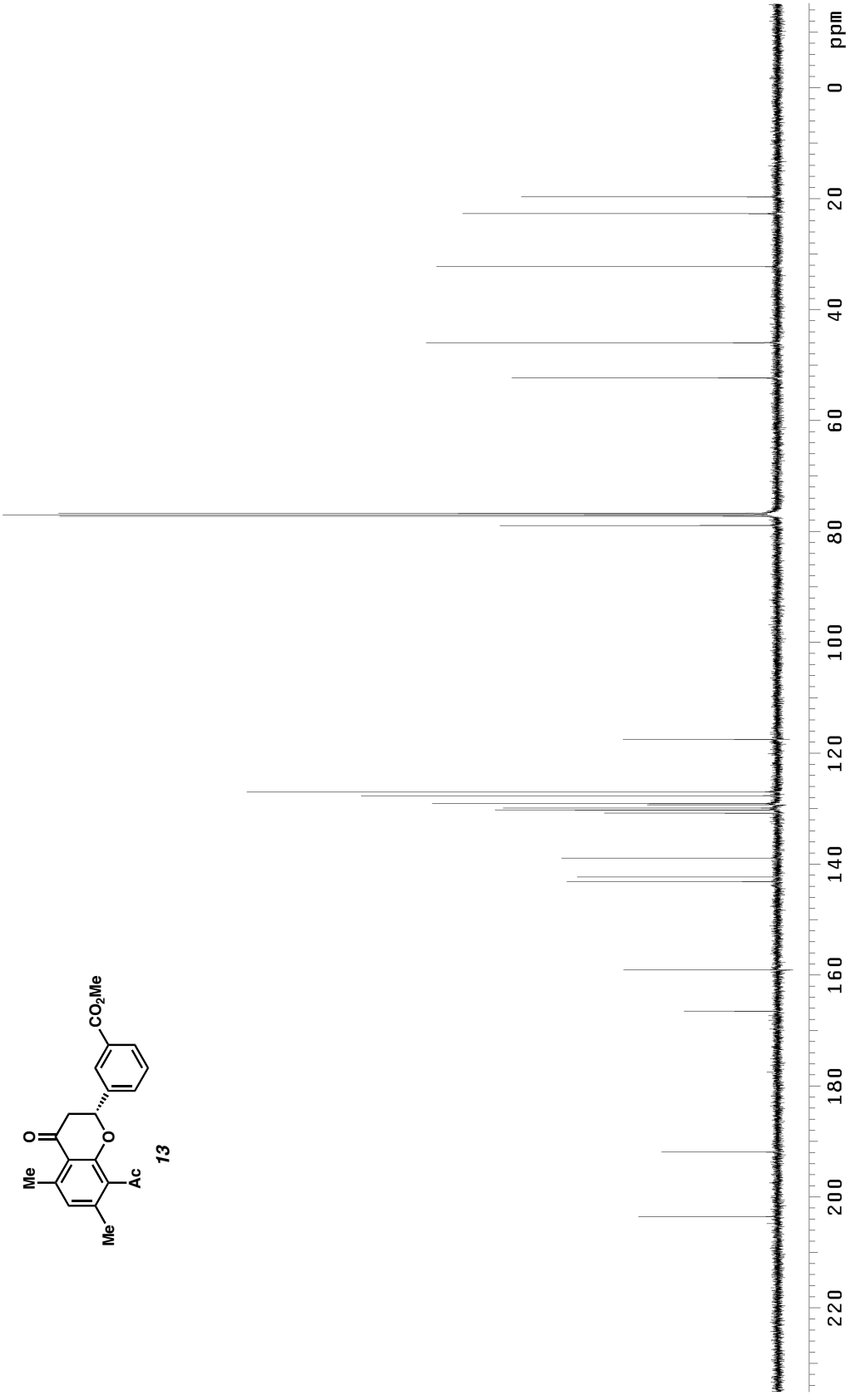
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CO2Me
O
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Me
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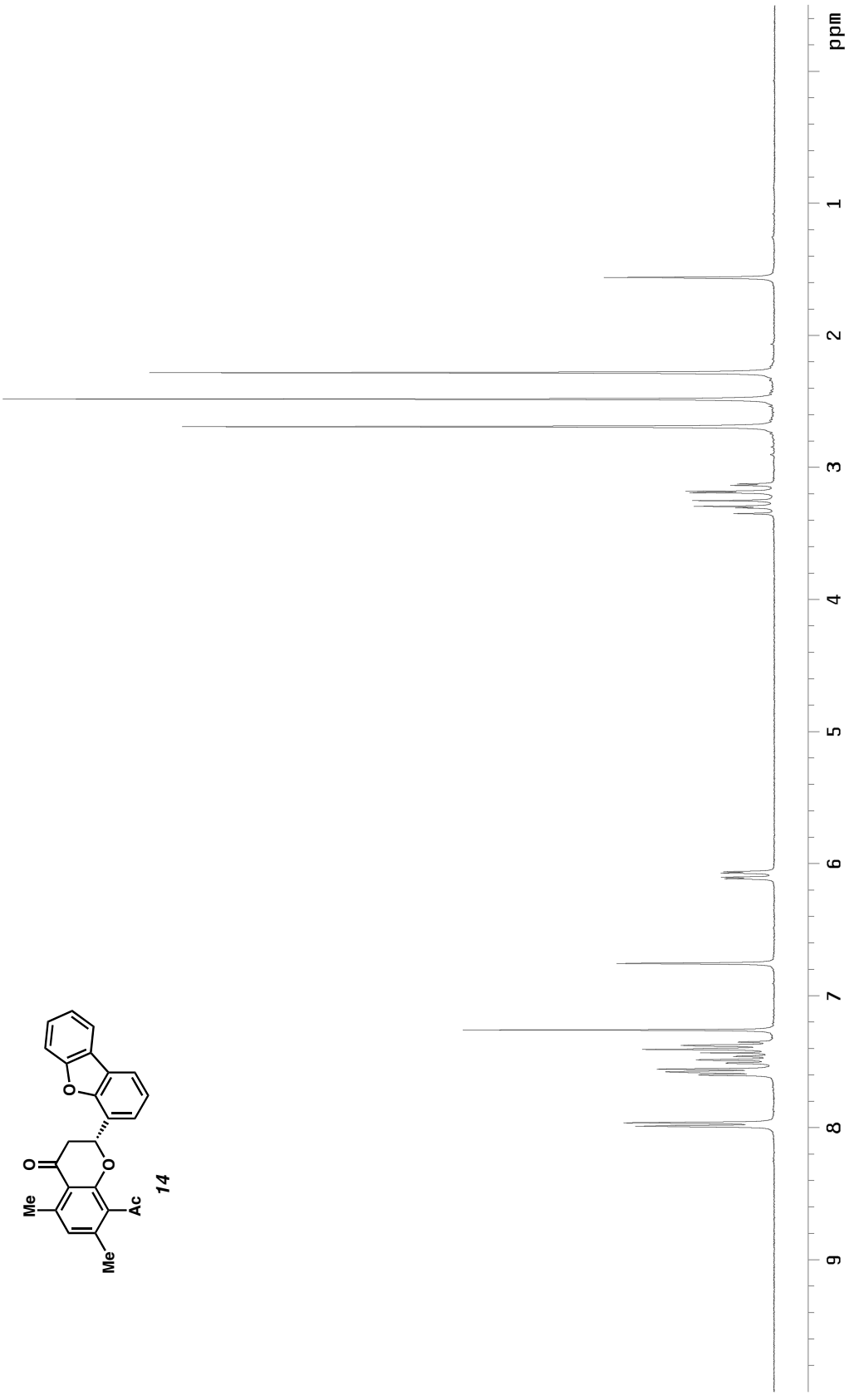

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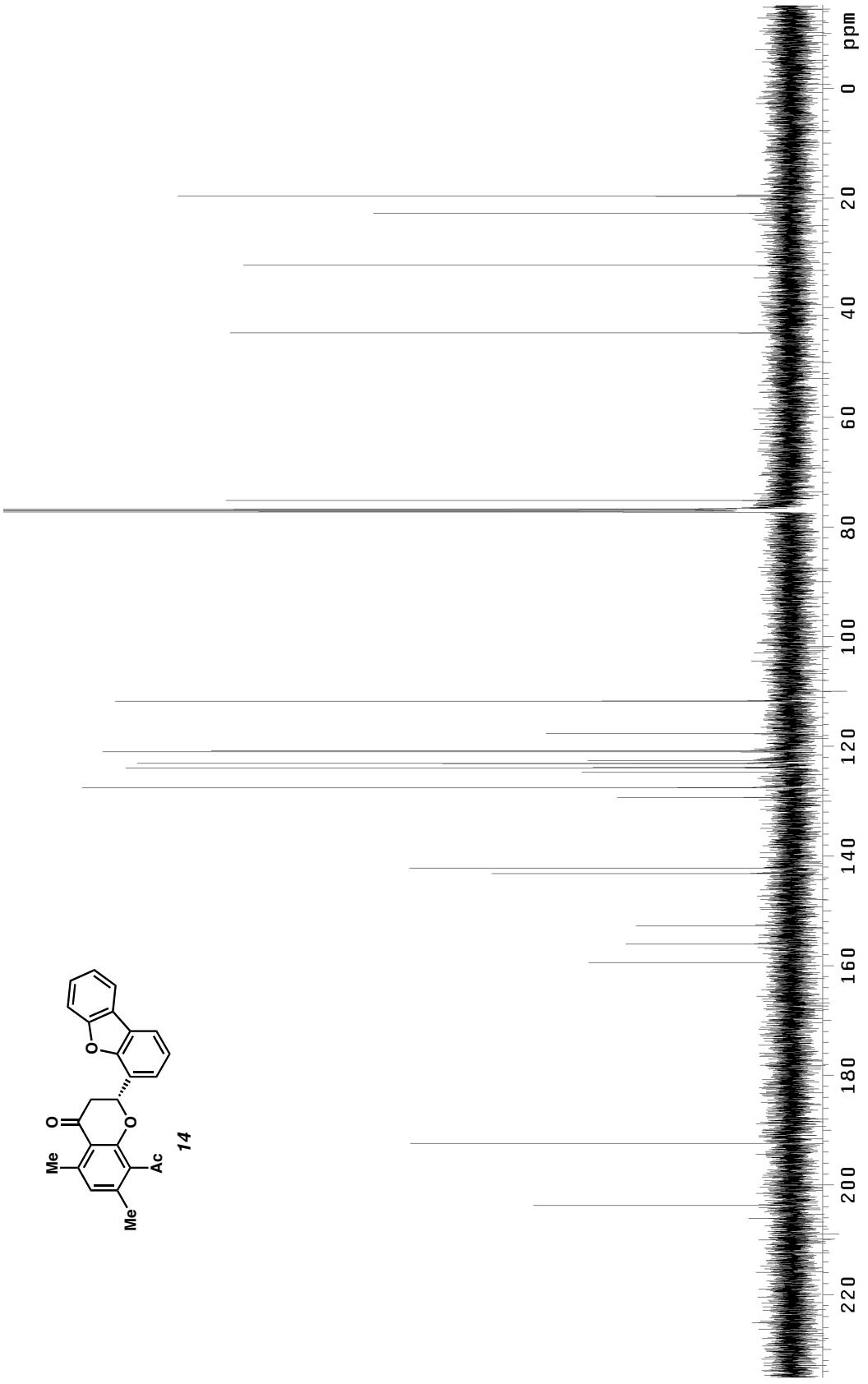
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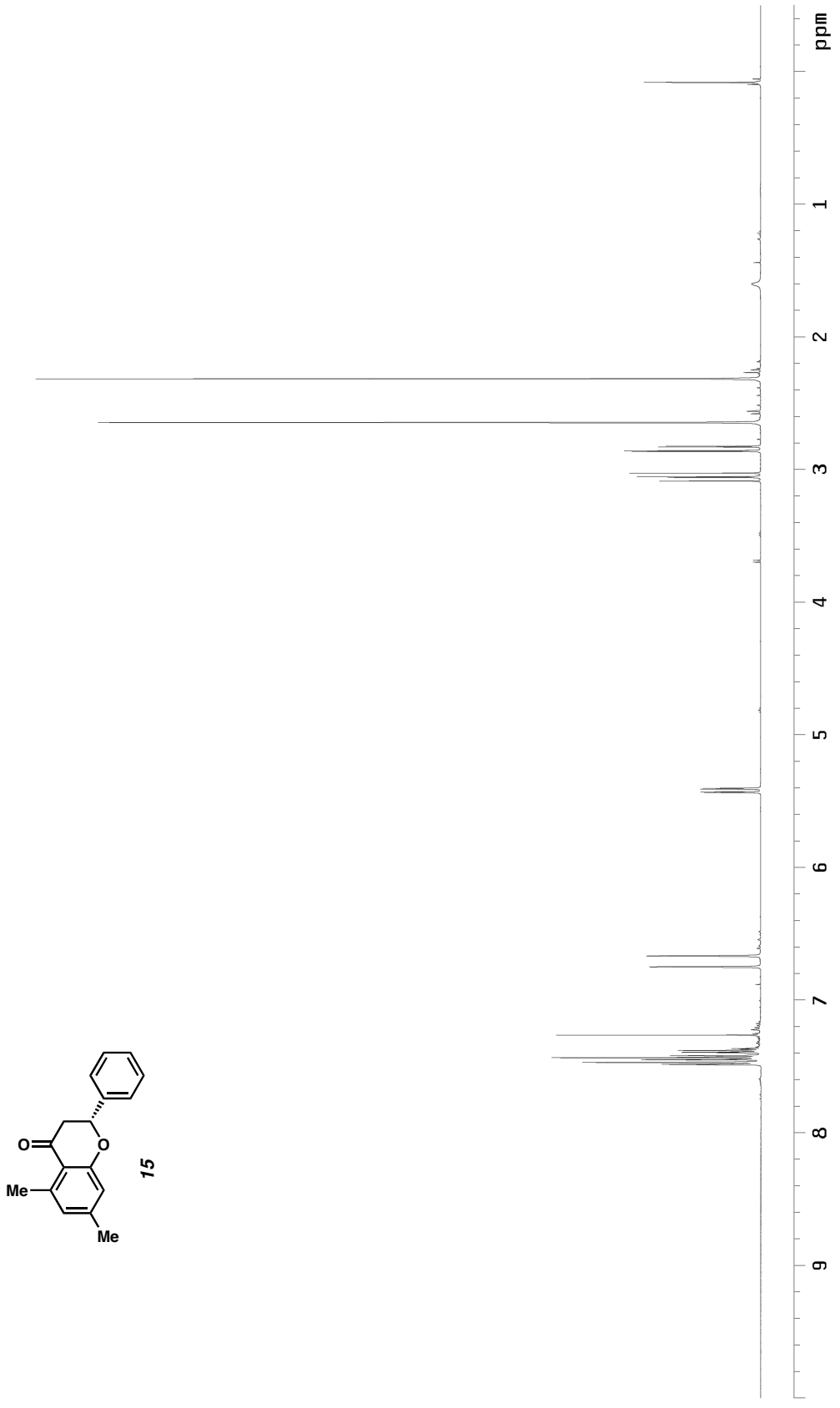

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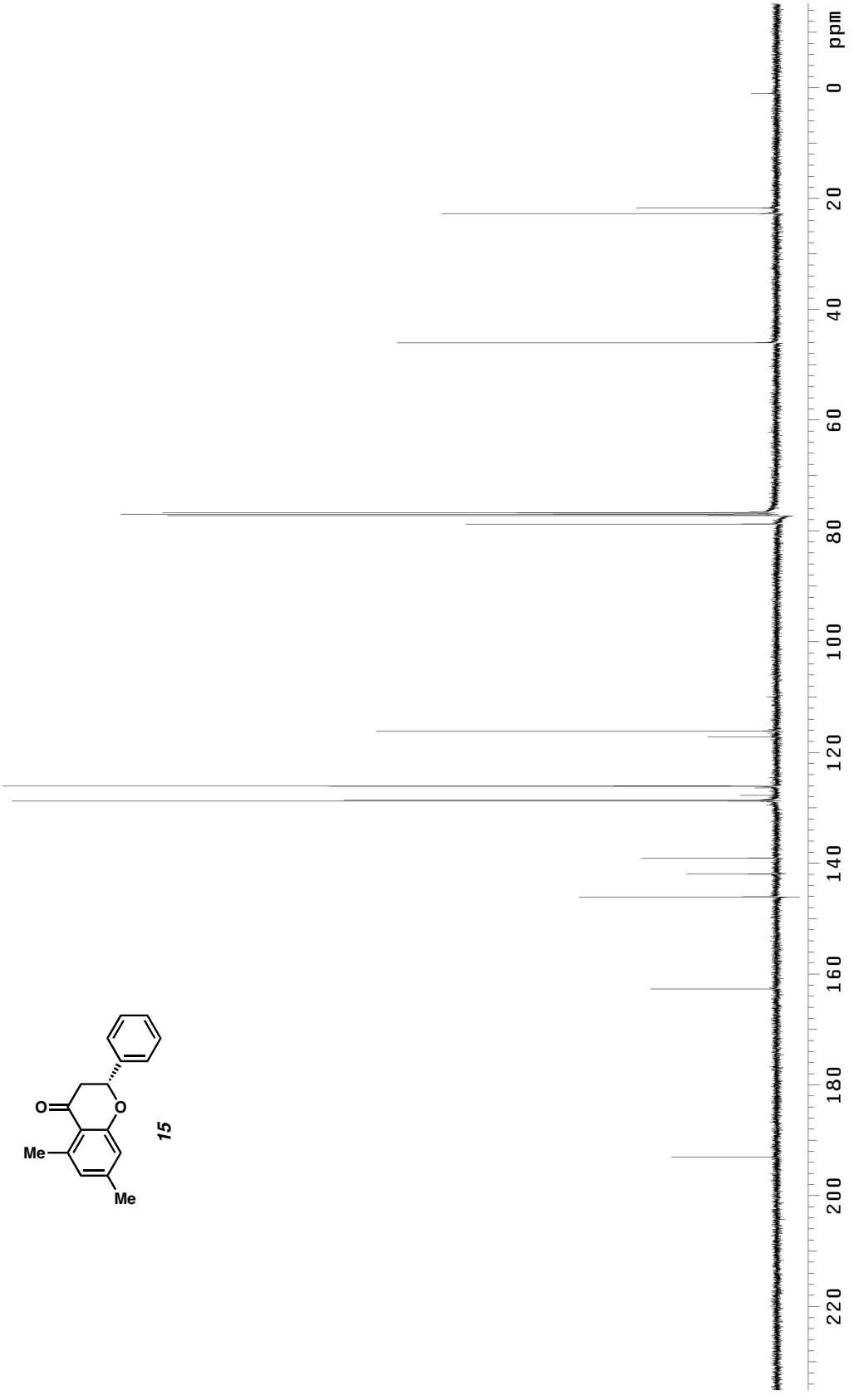
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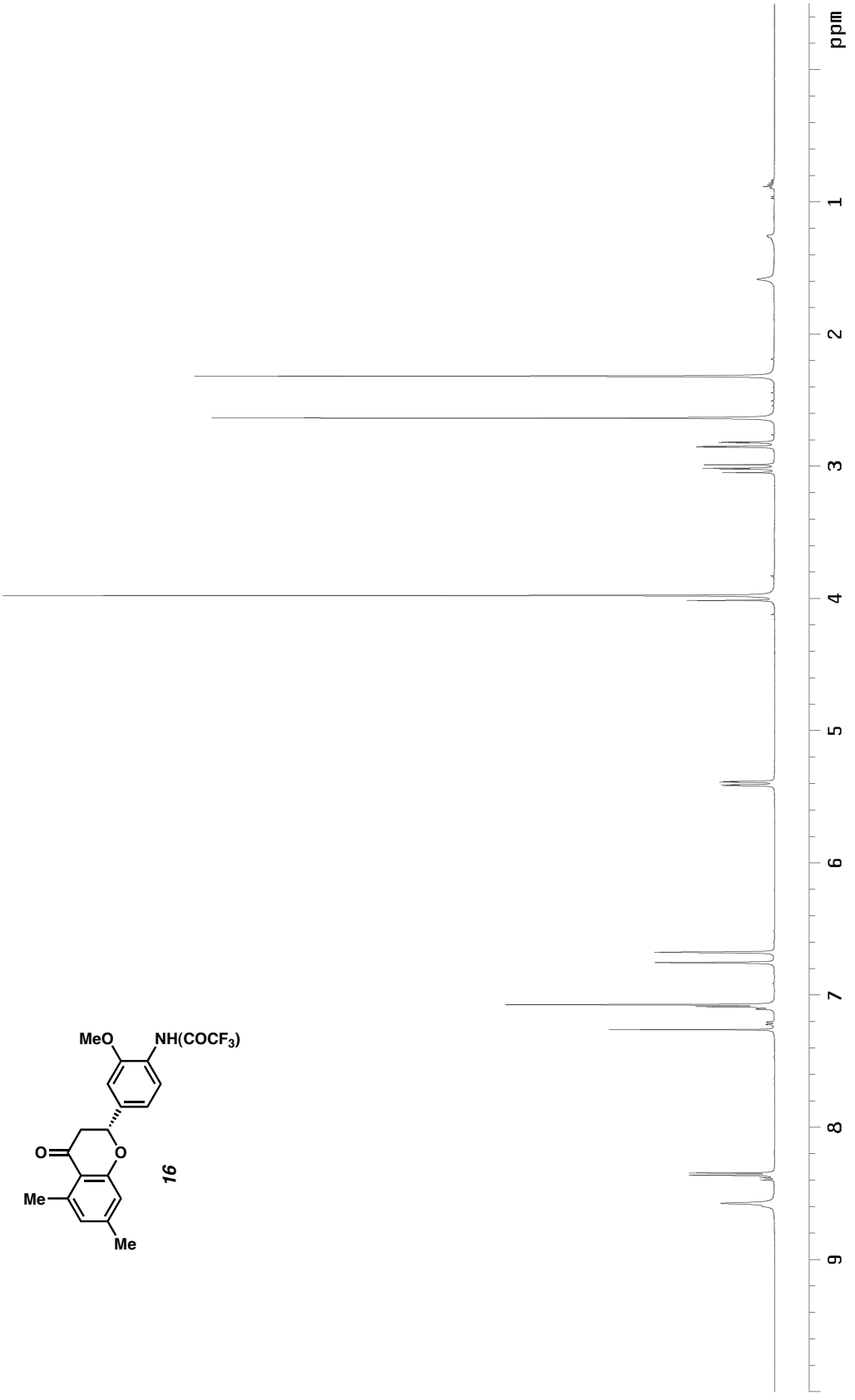

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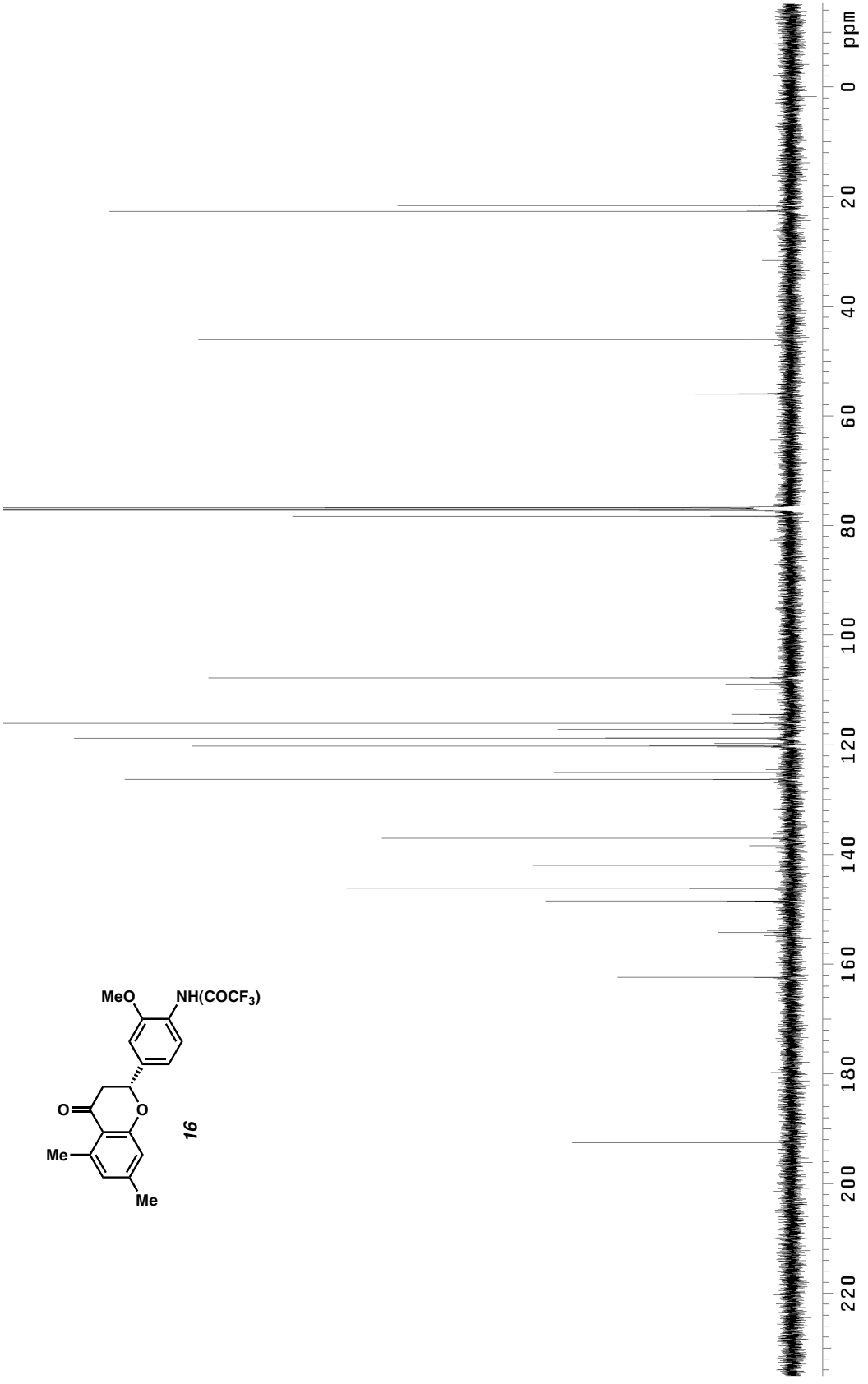
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Me
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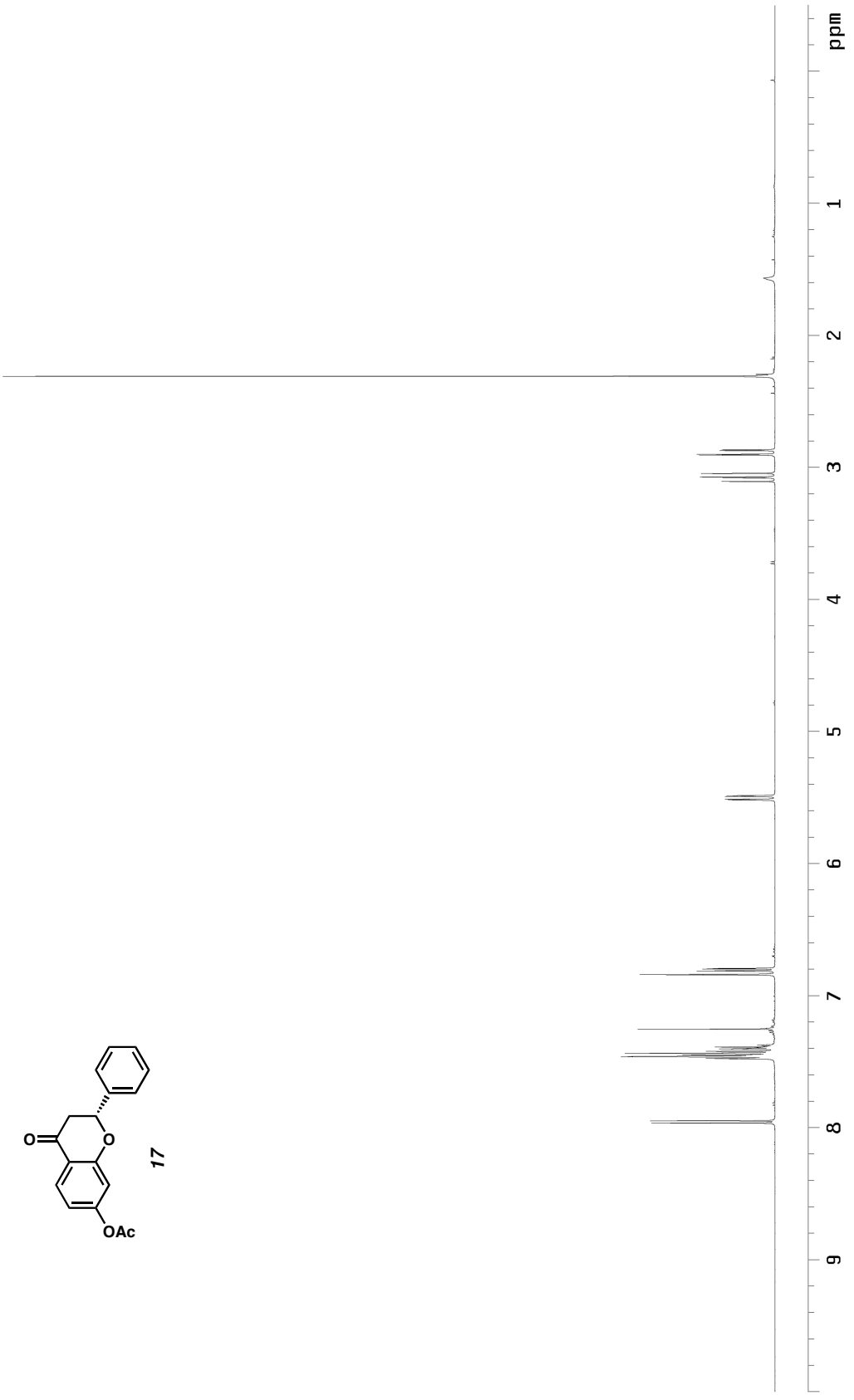
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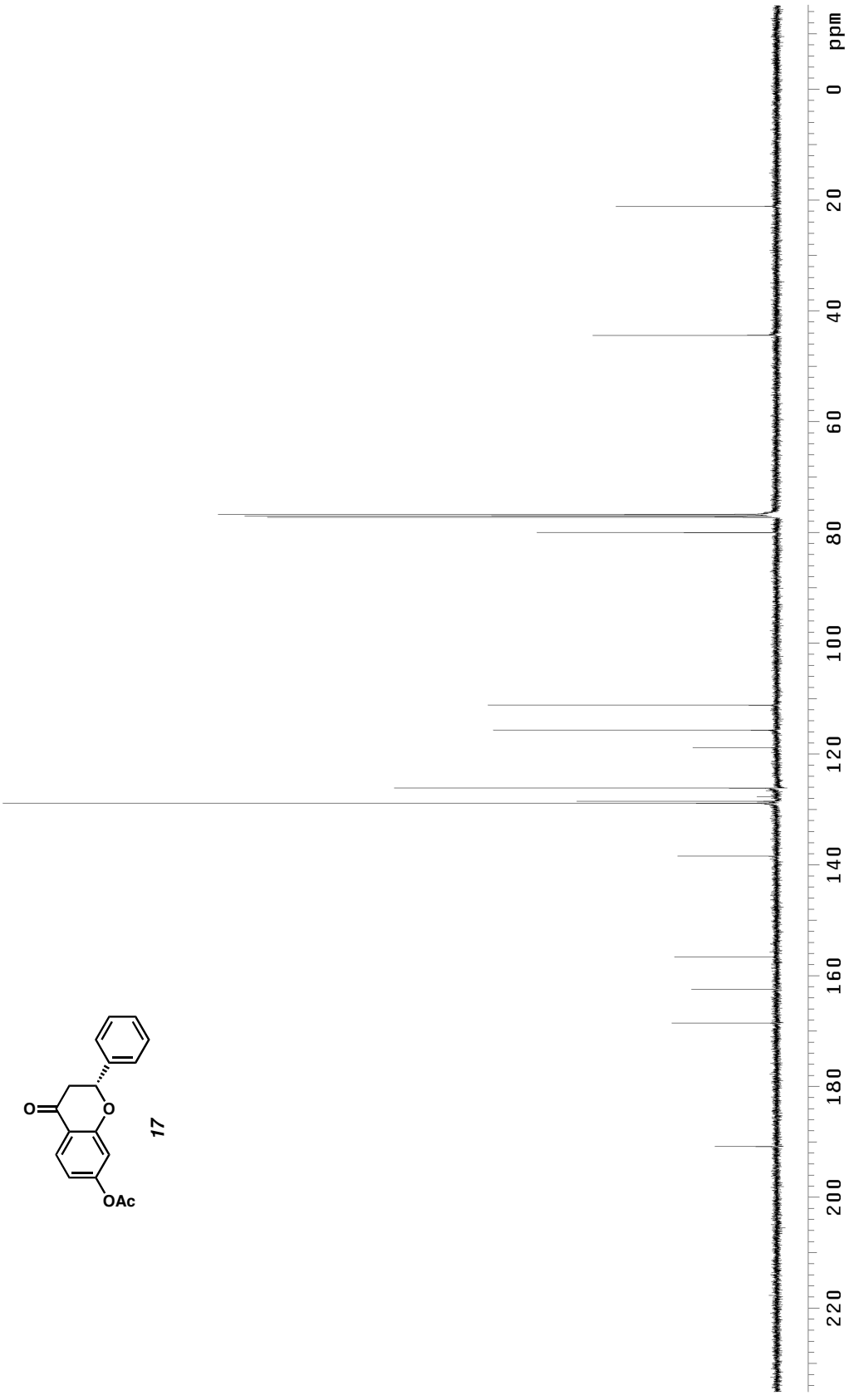
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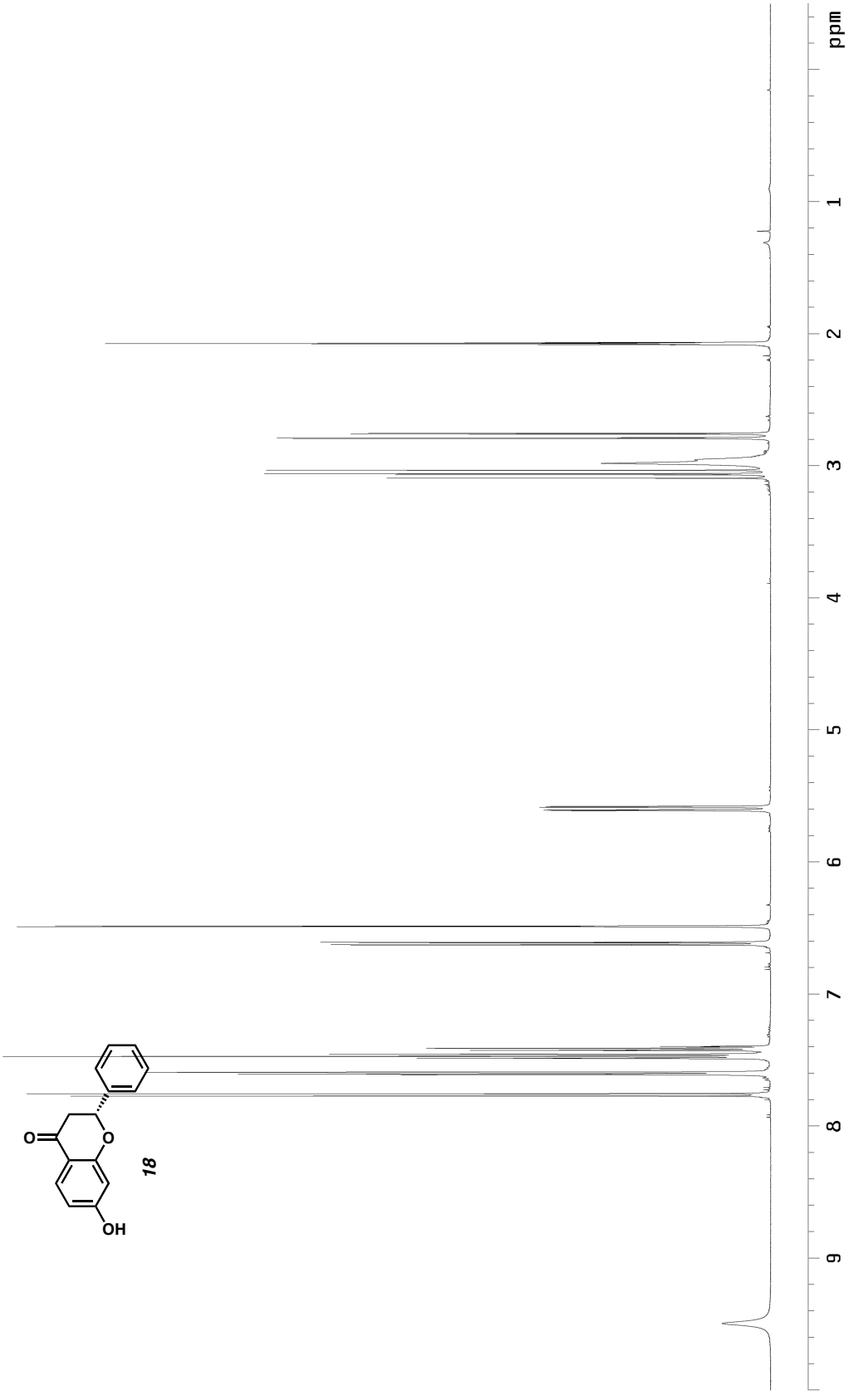
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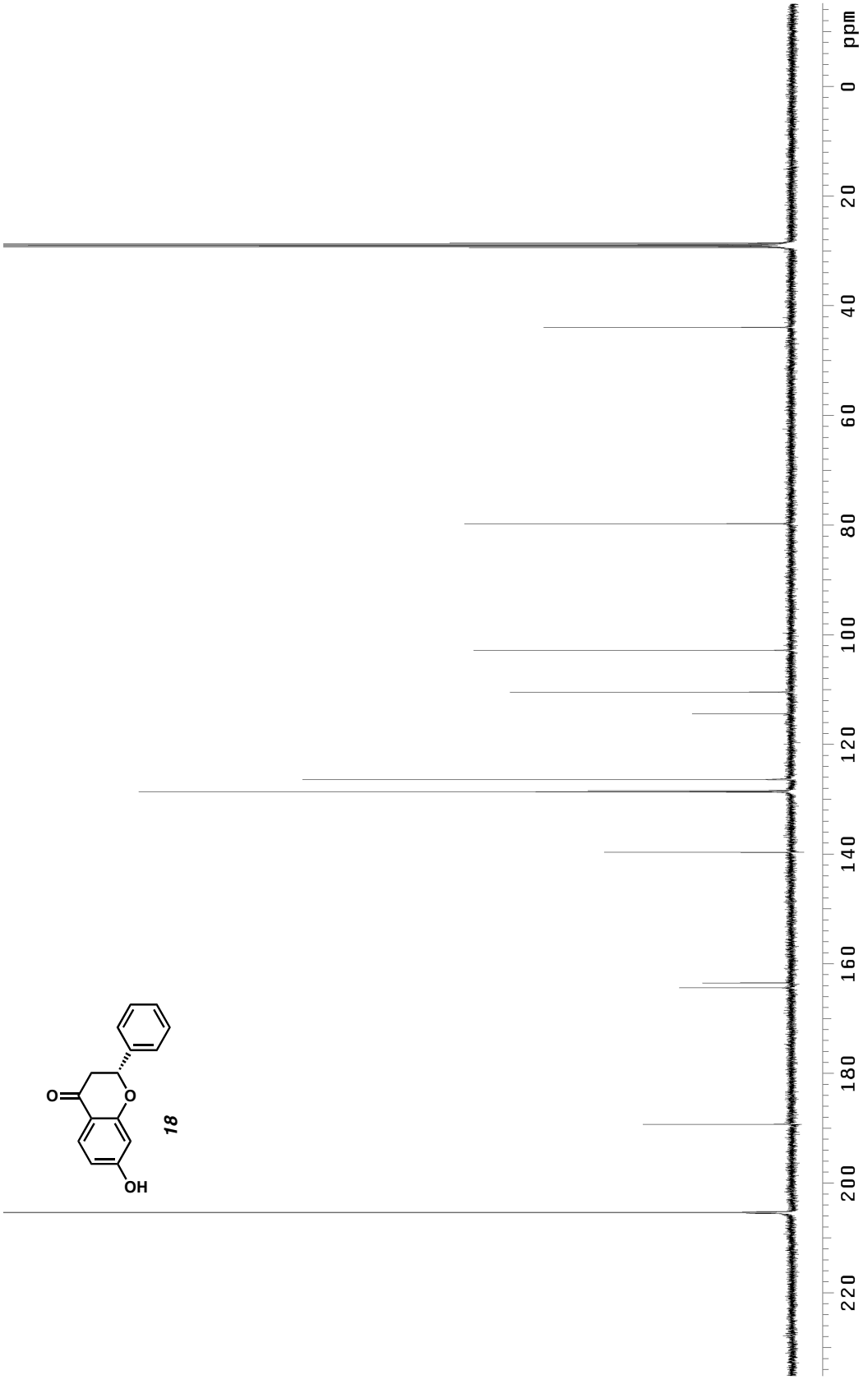
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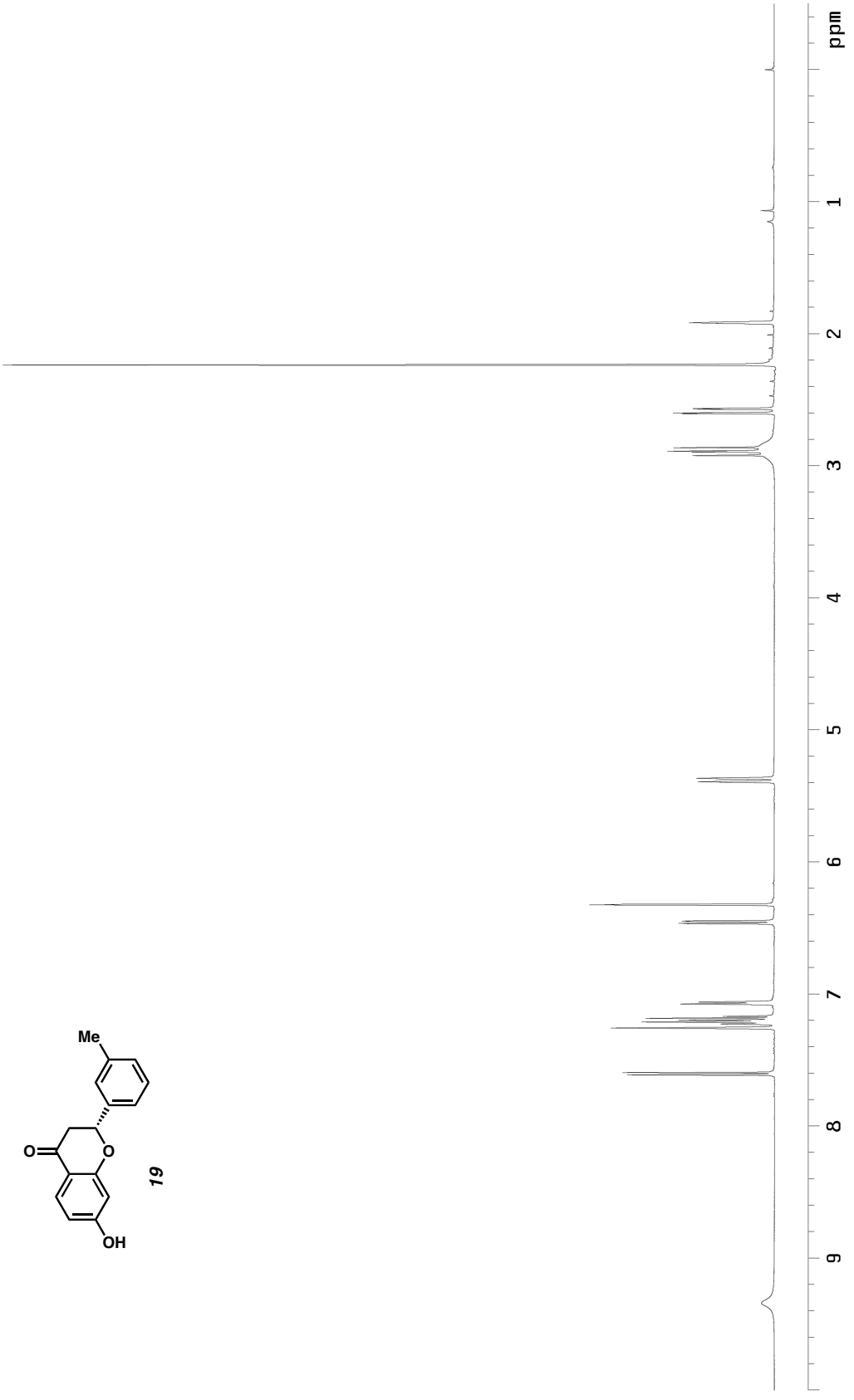

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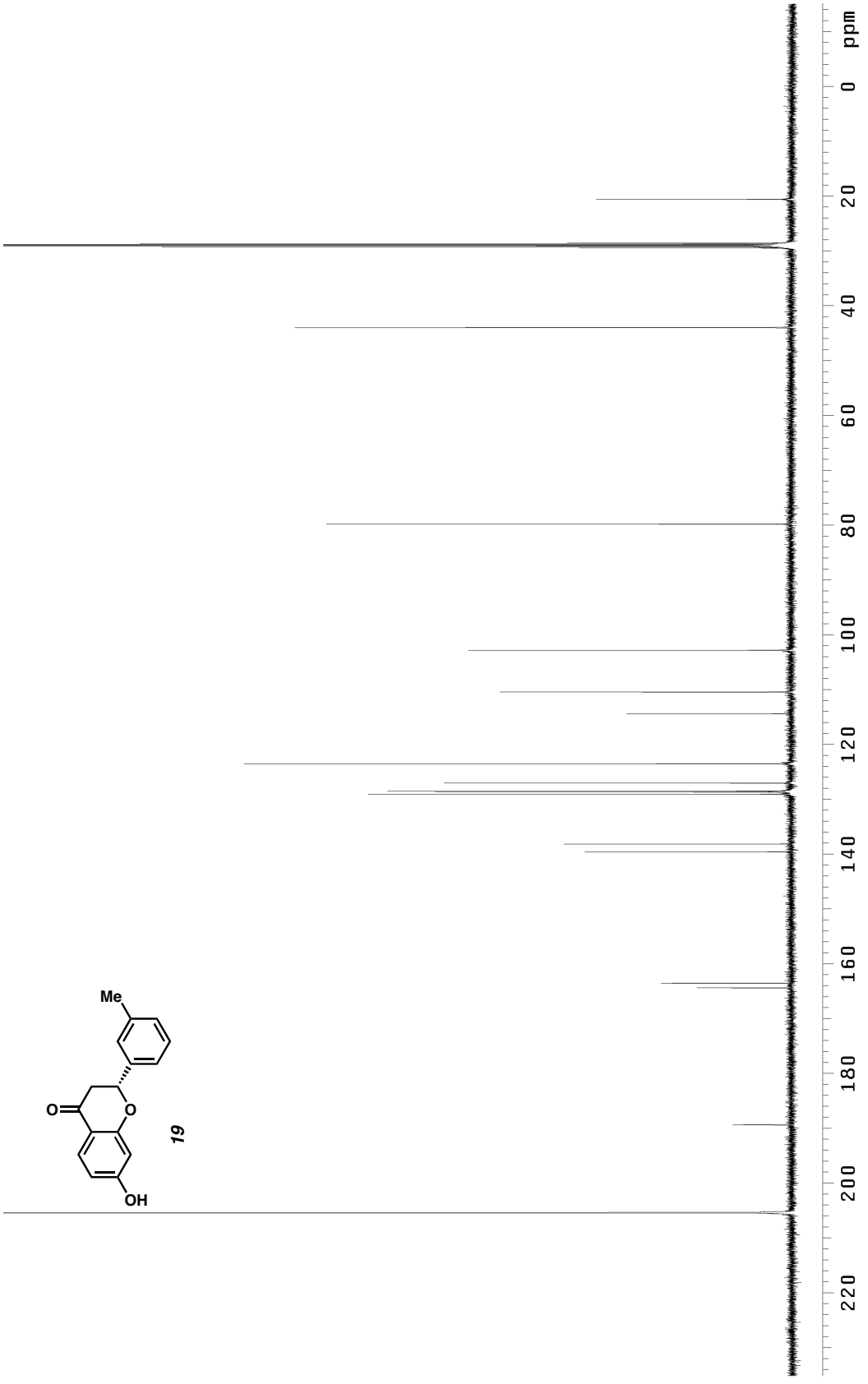
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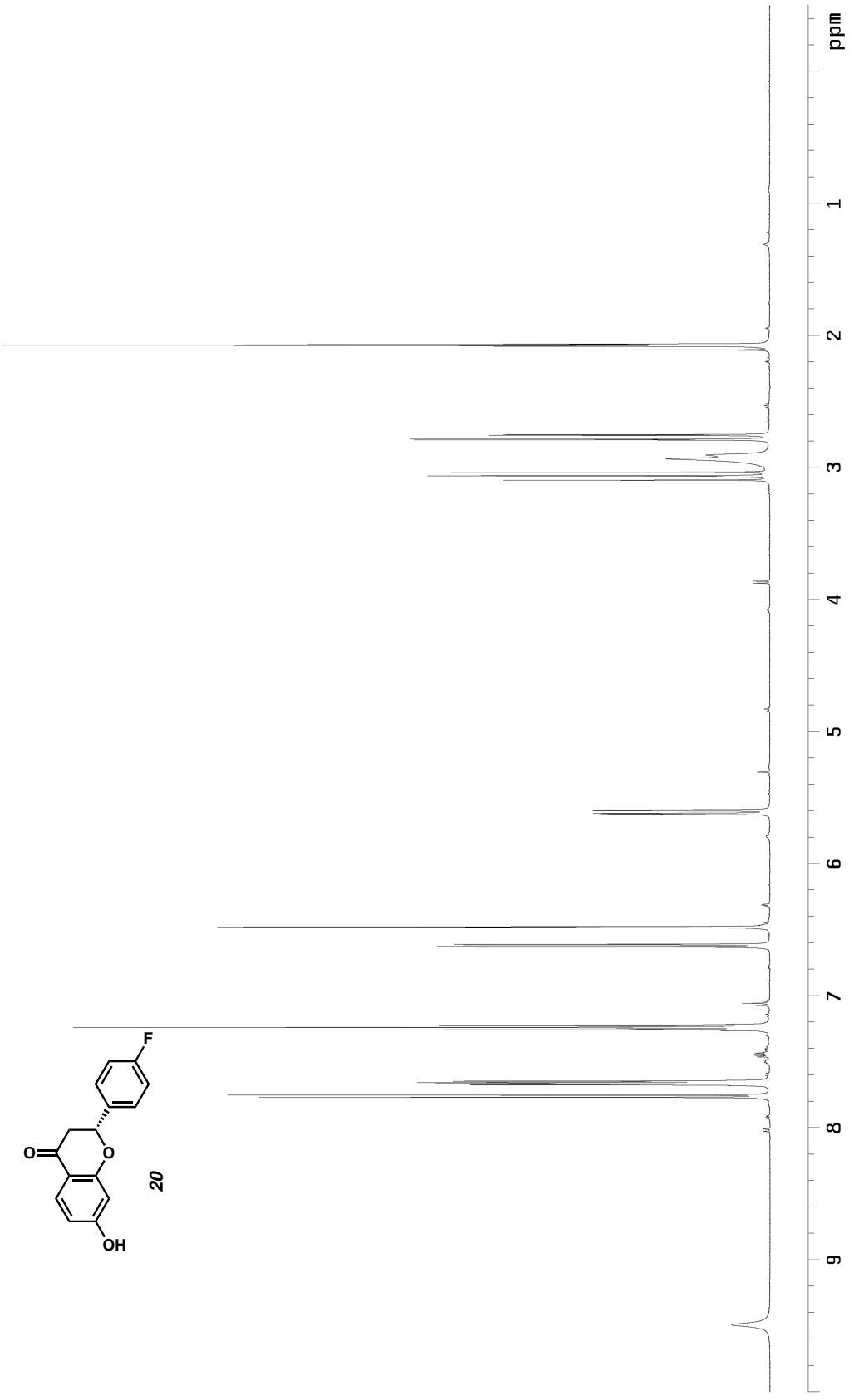
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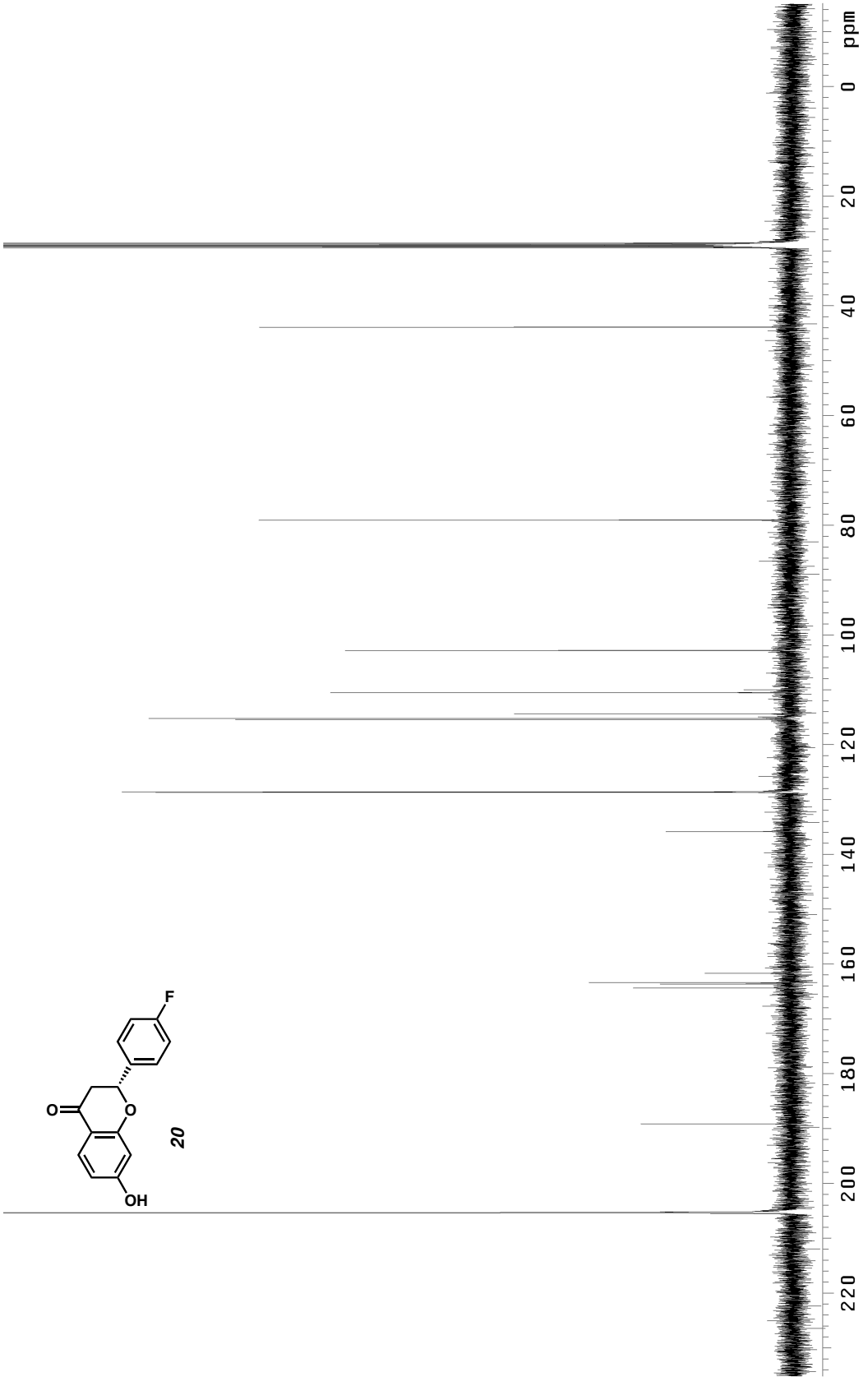
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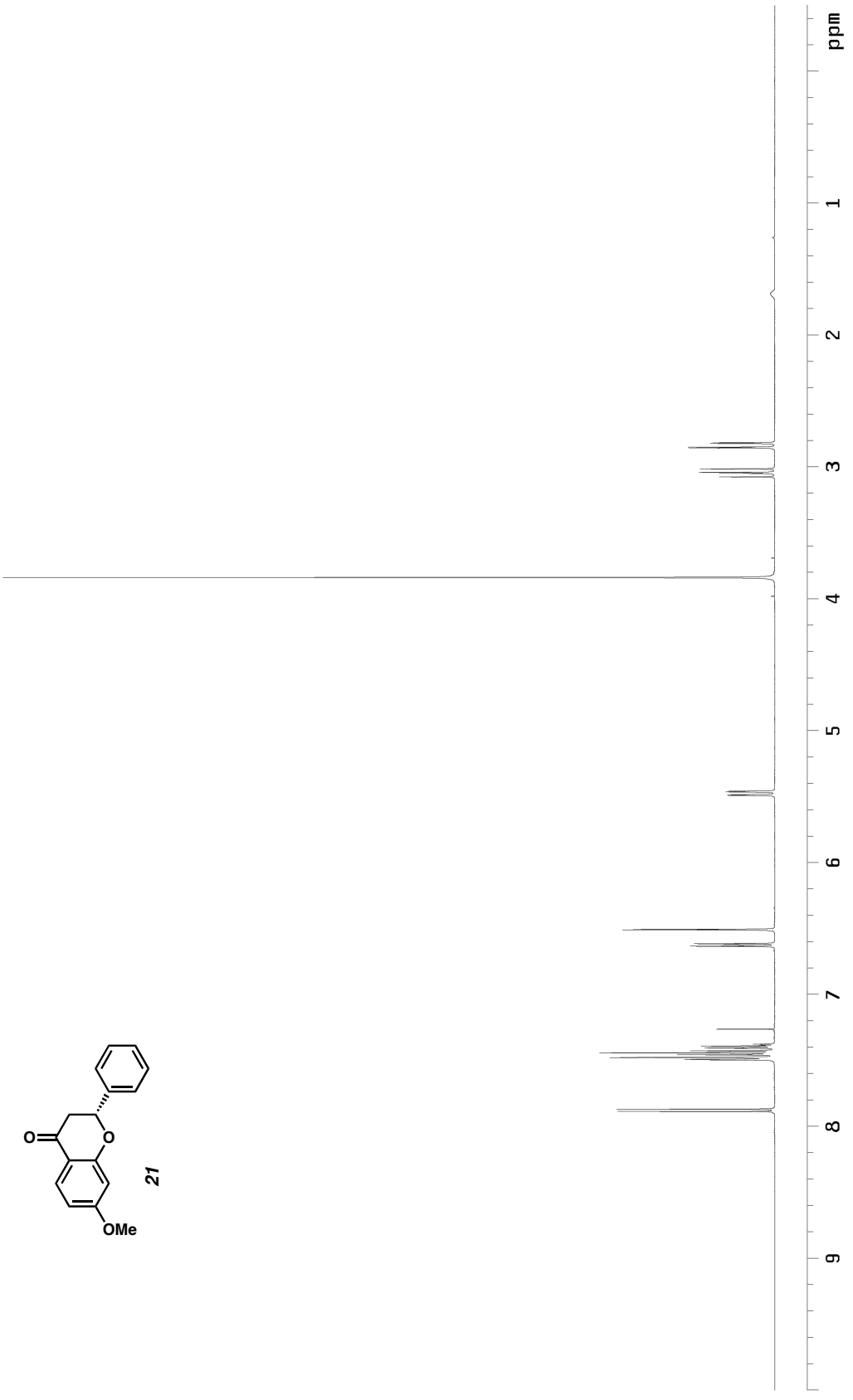
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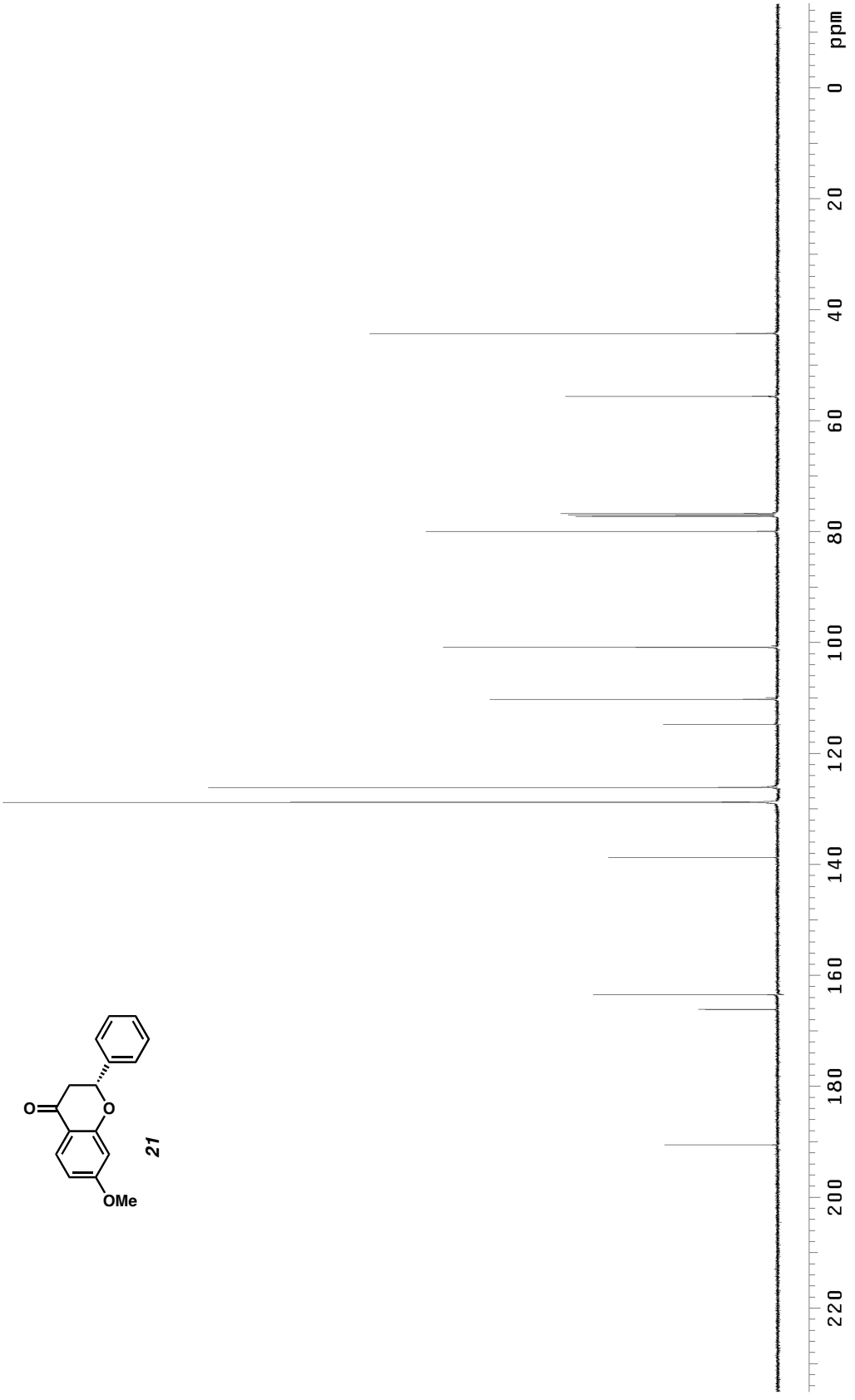
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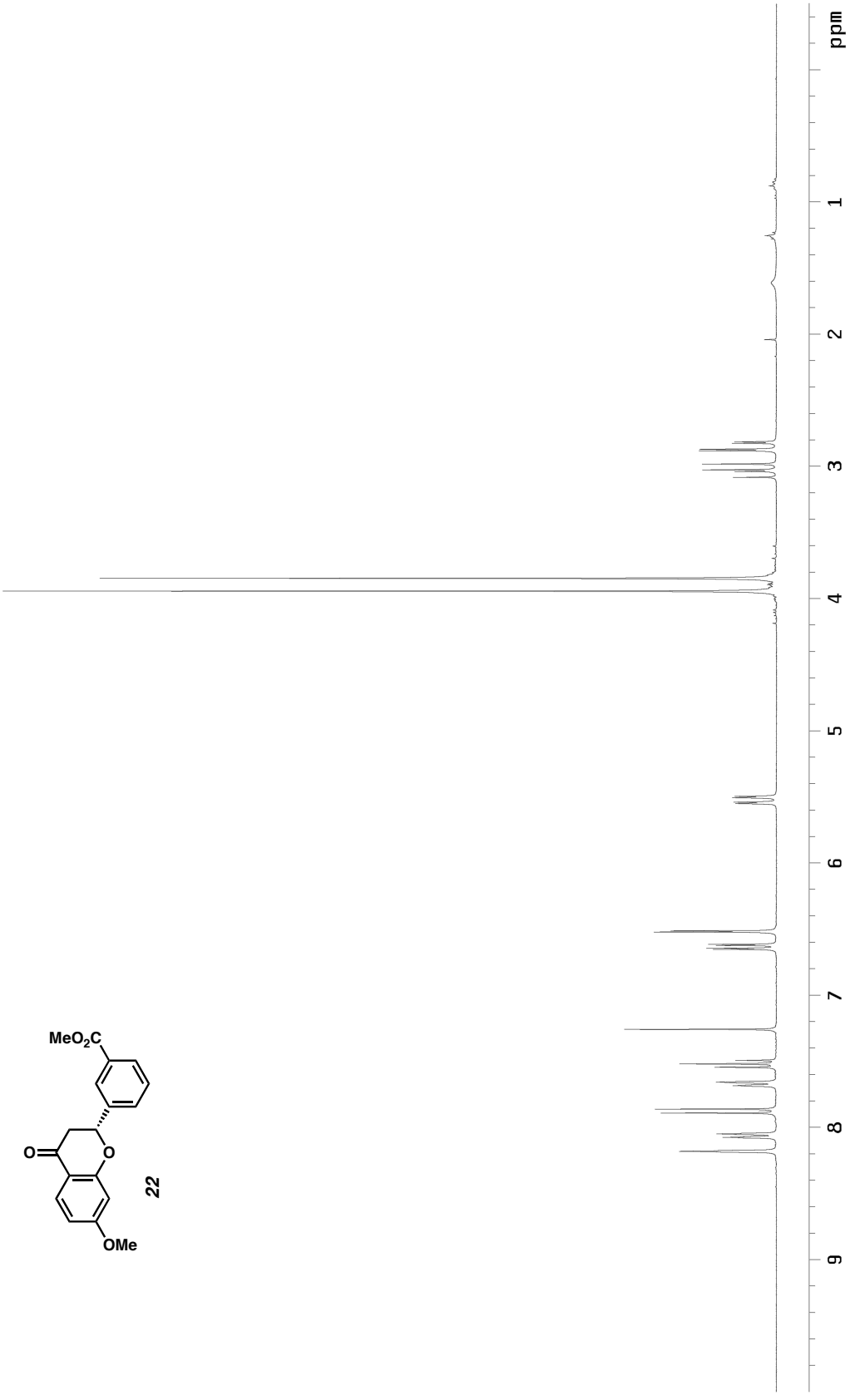
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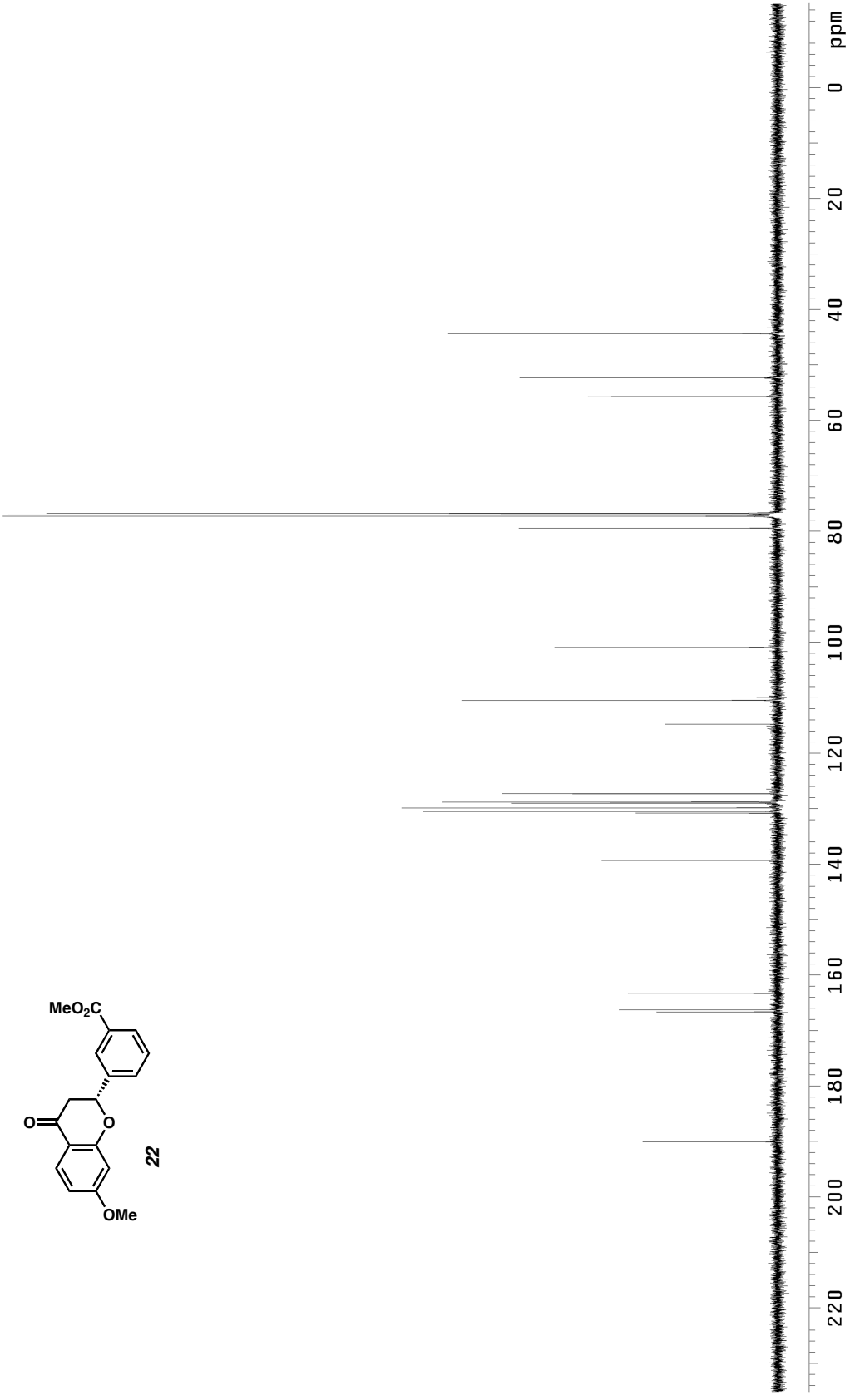
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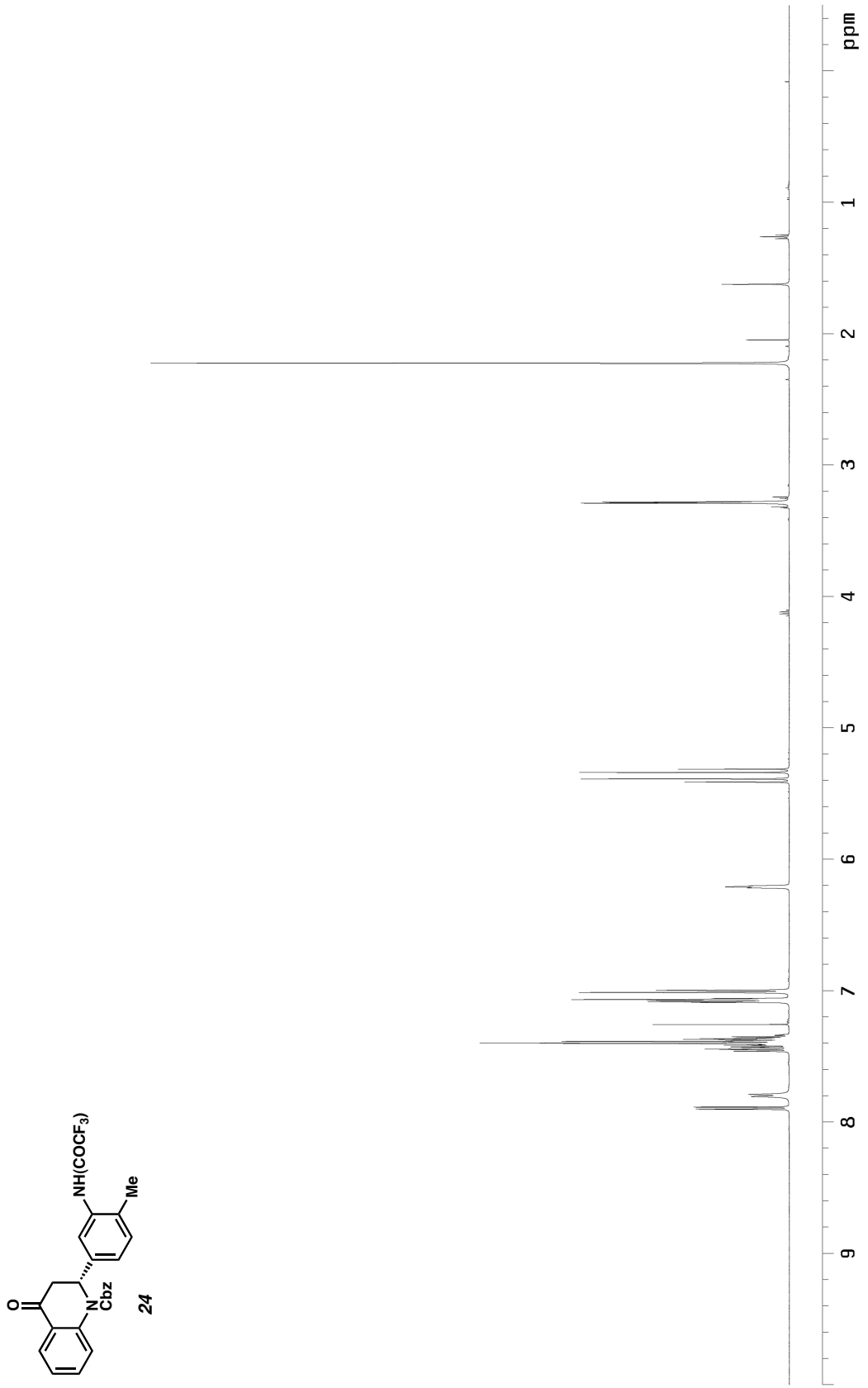
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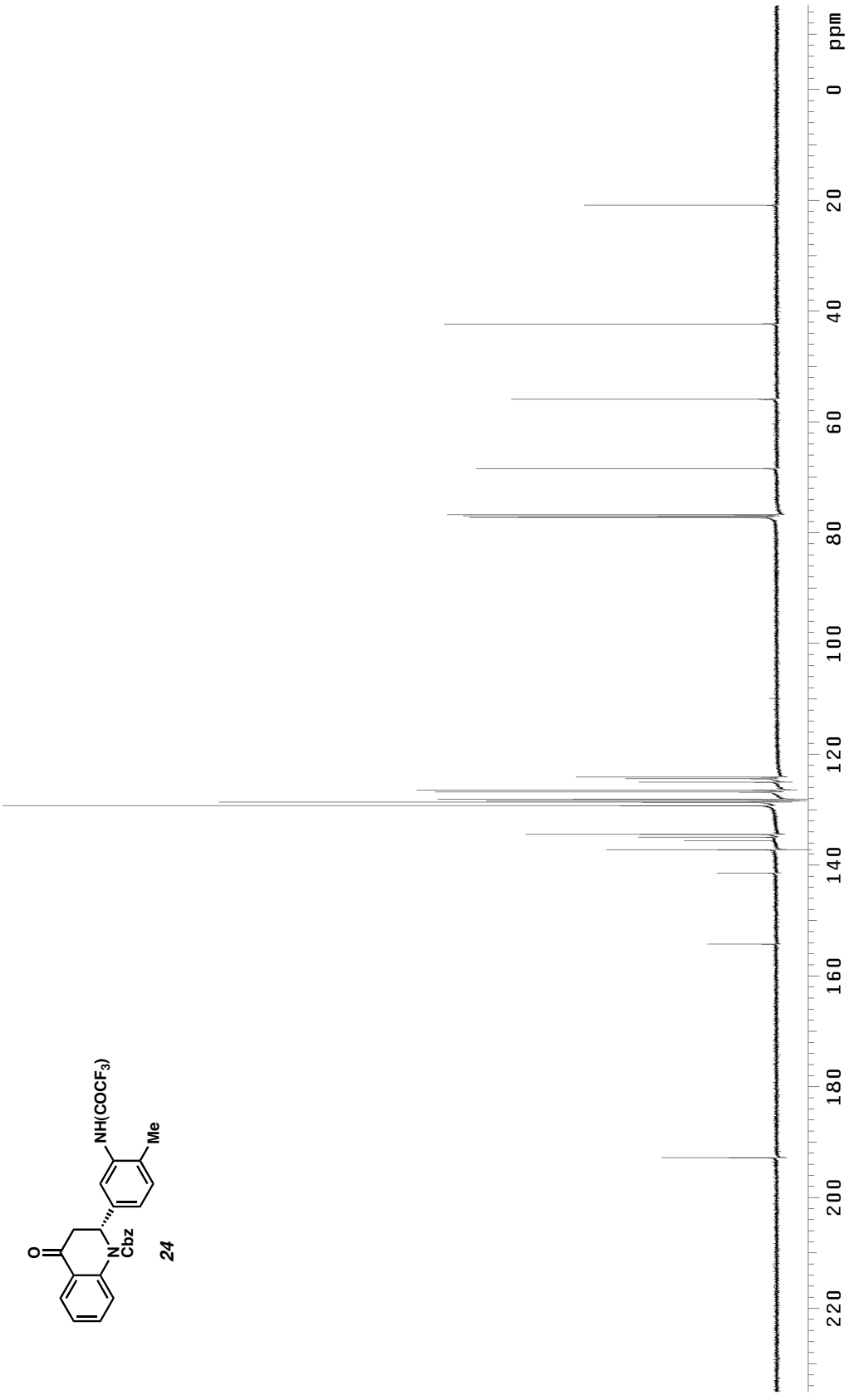
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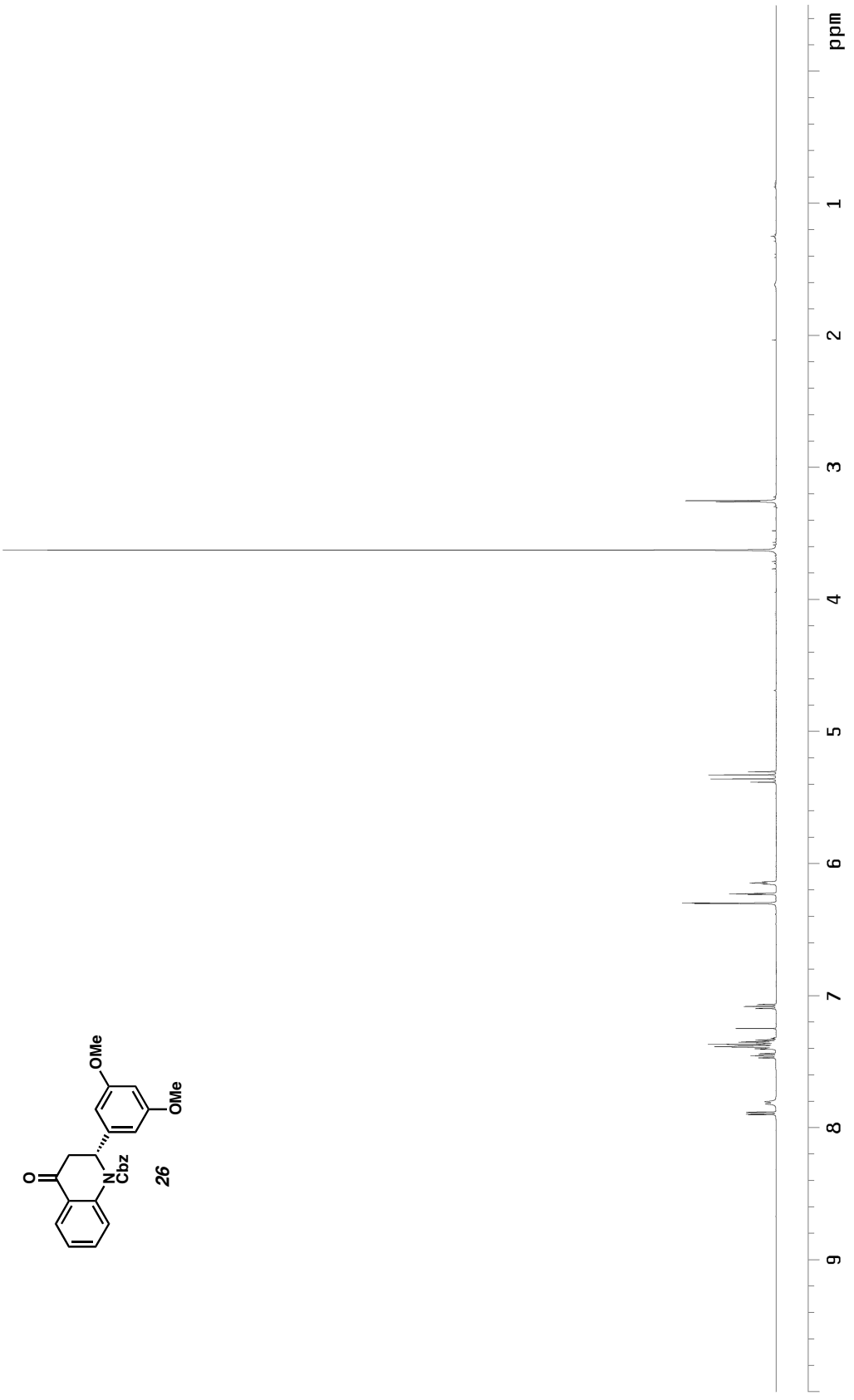
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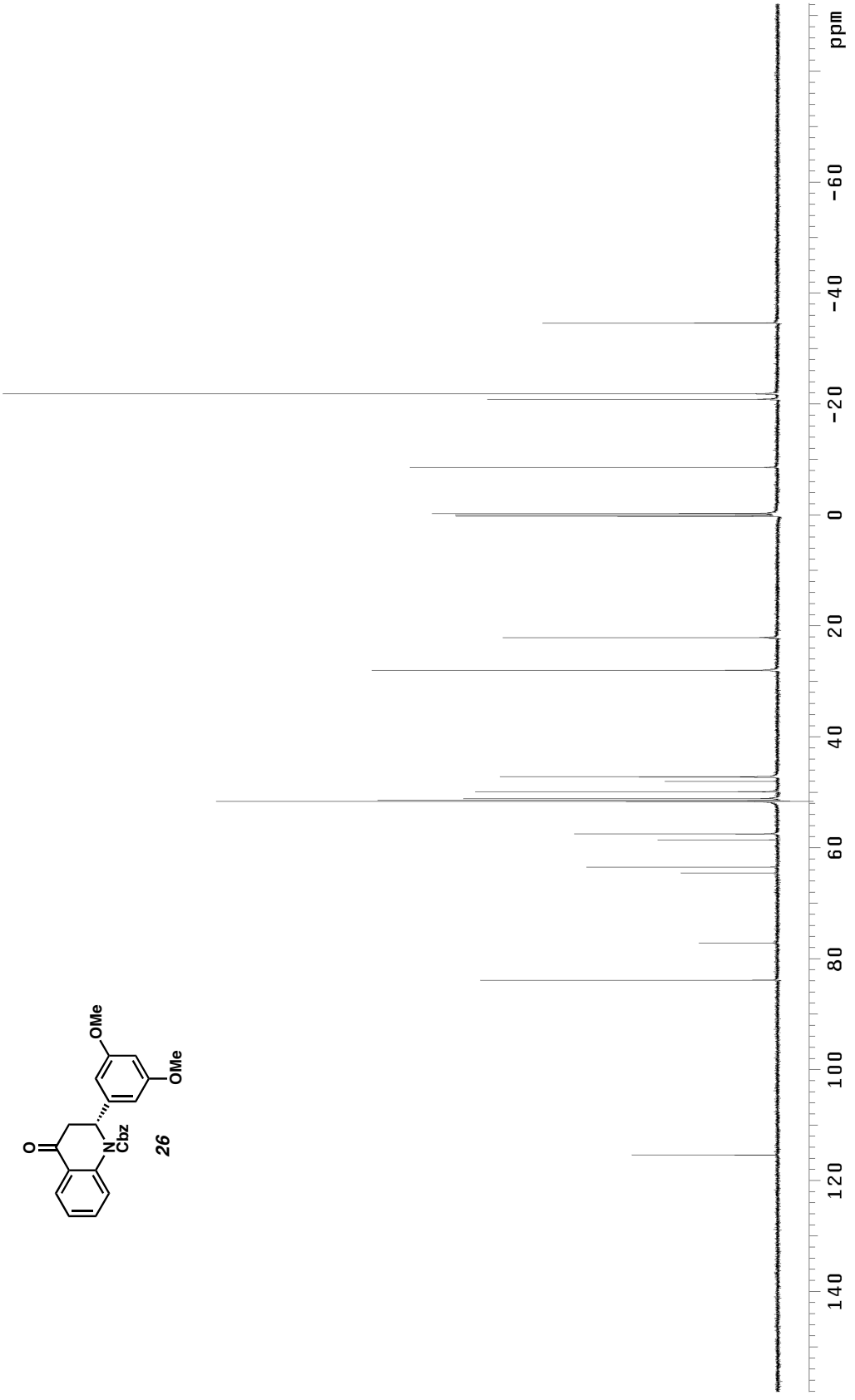
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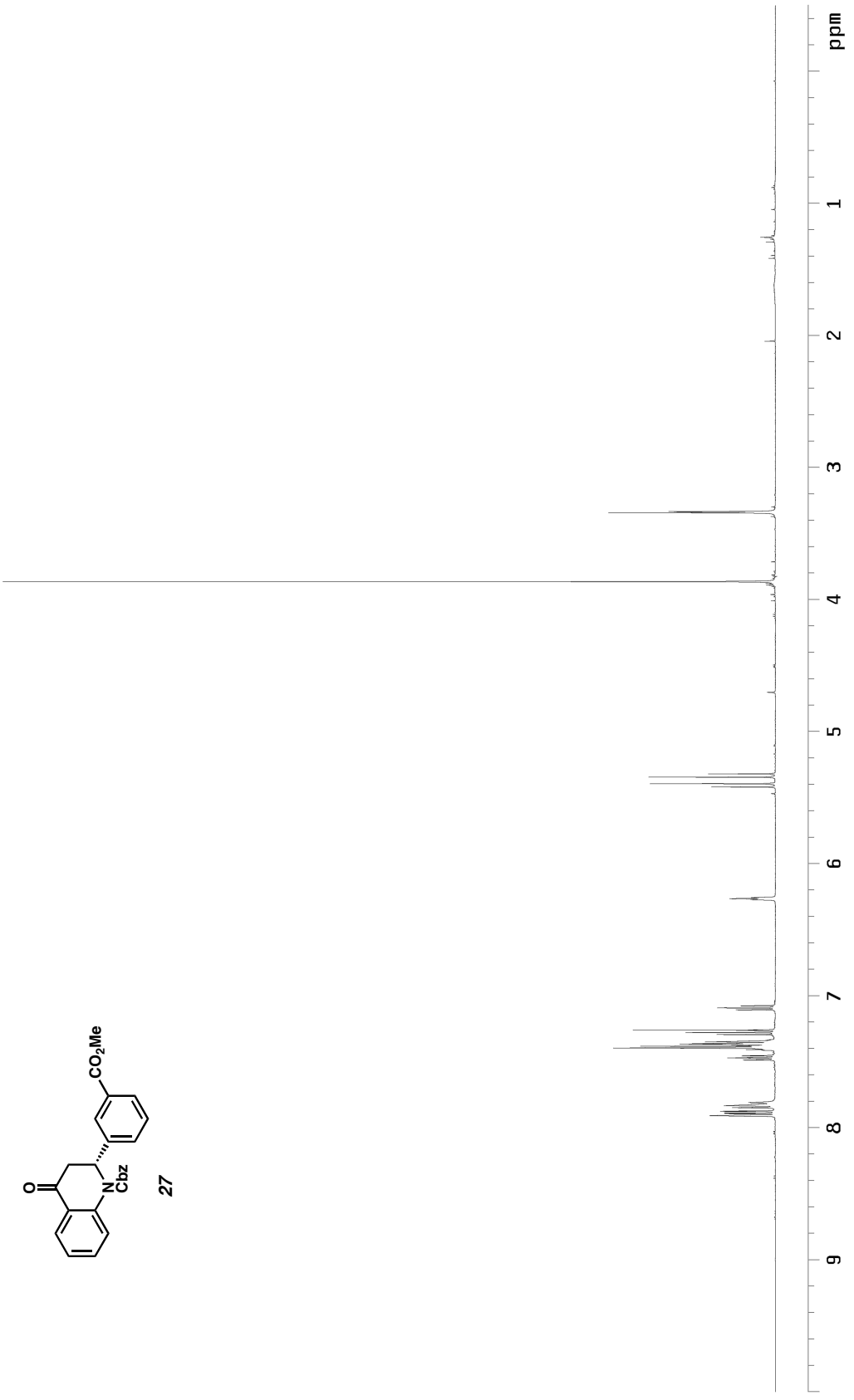
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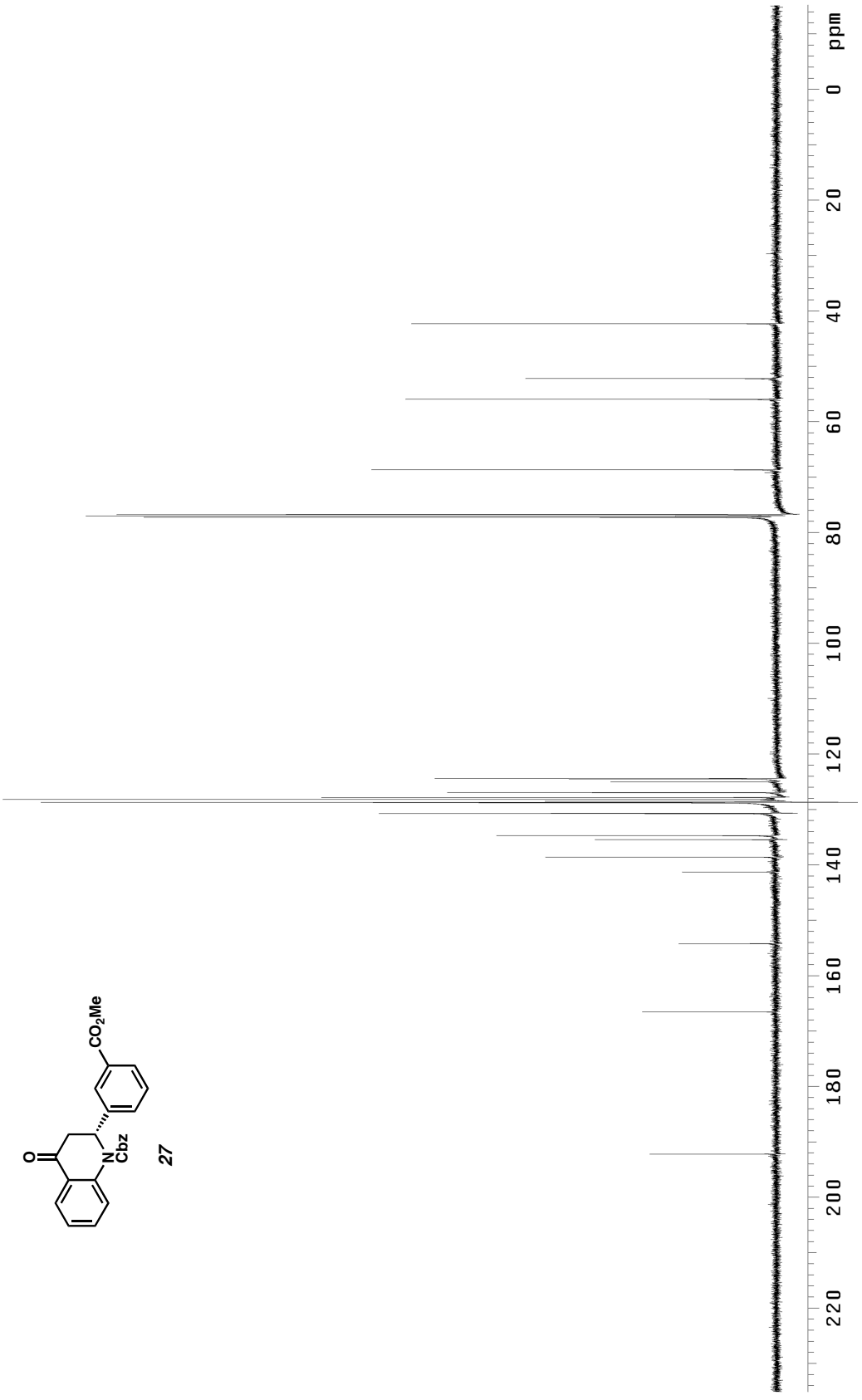
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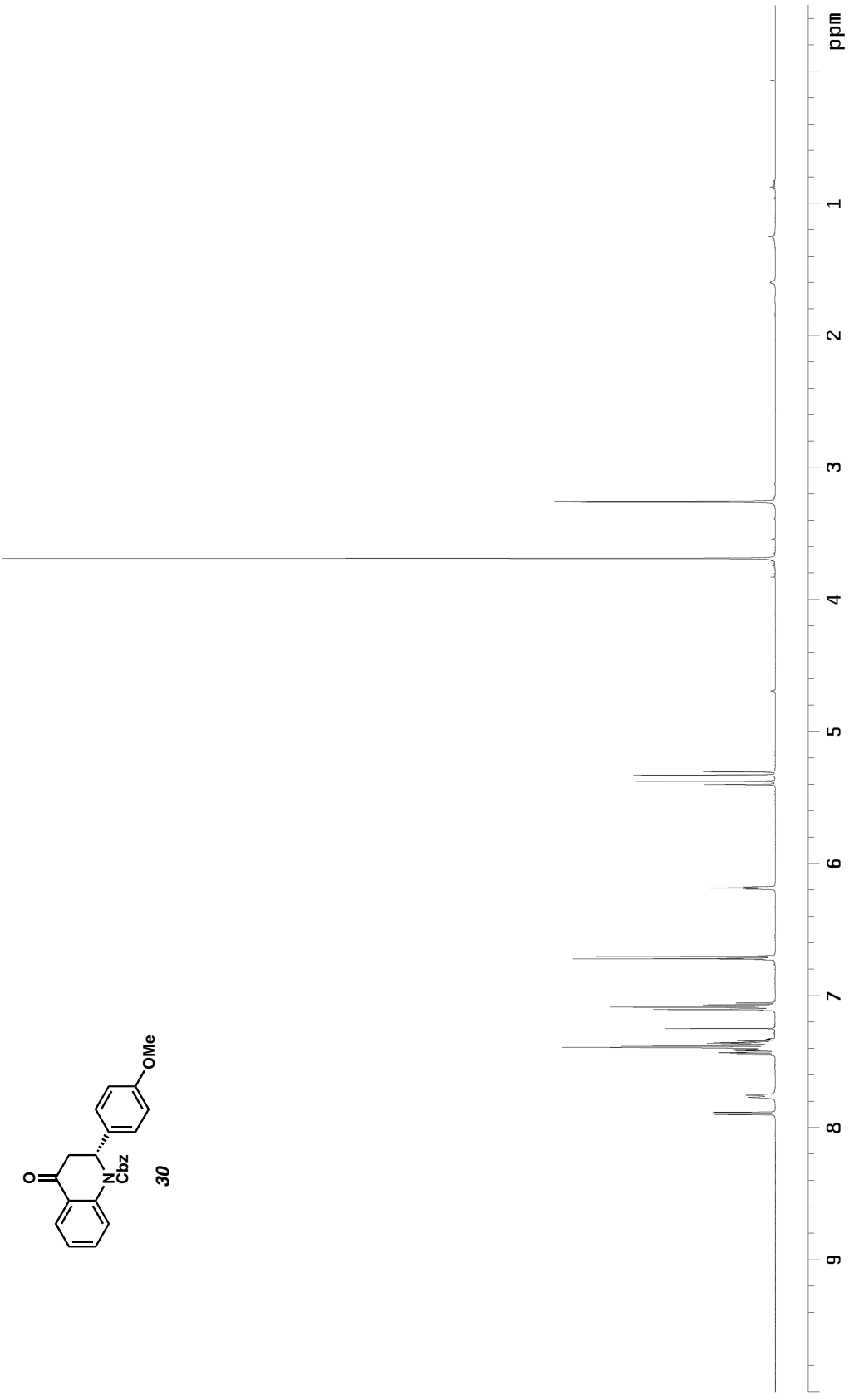

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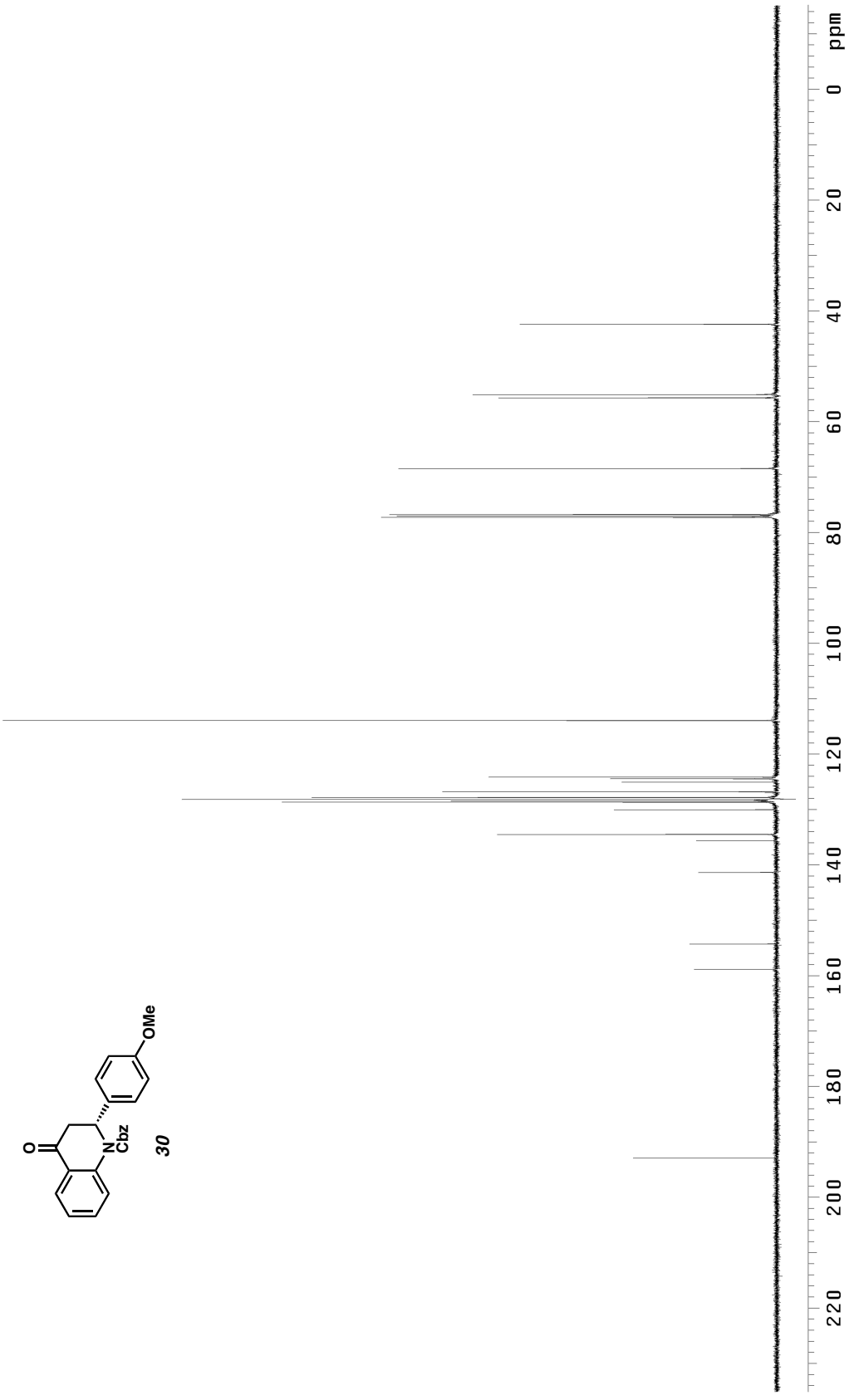

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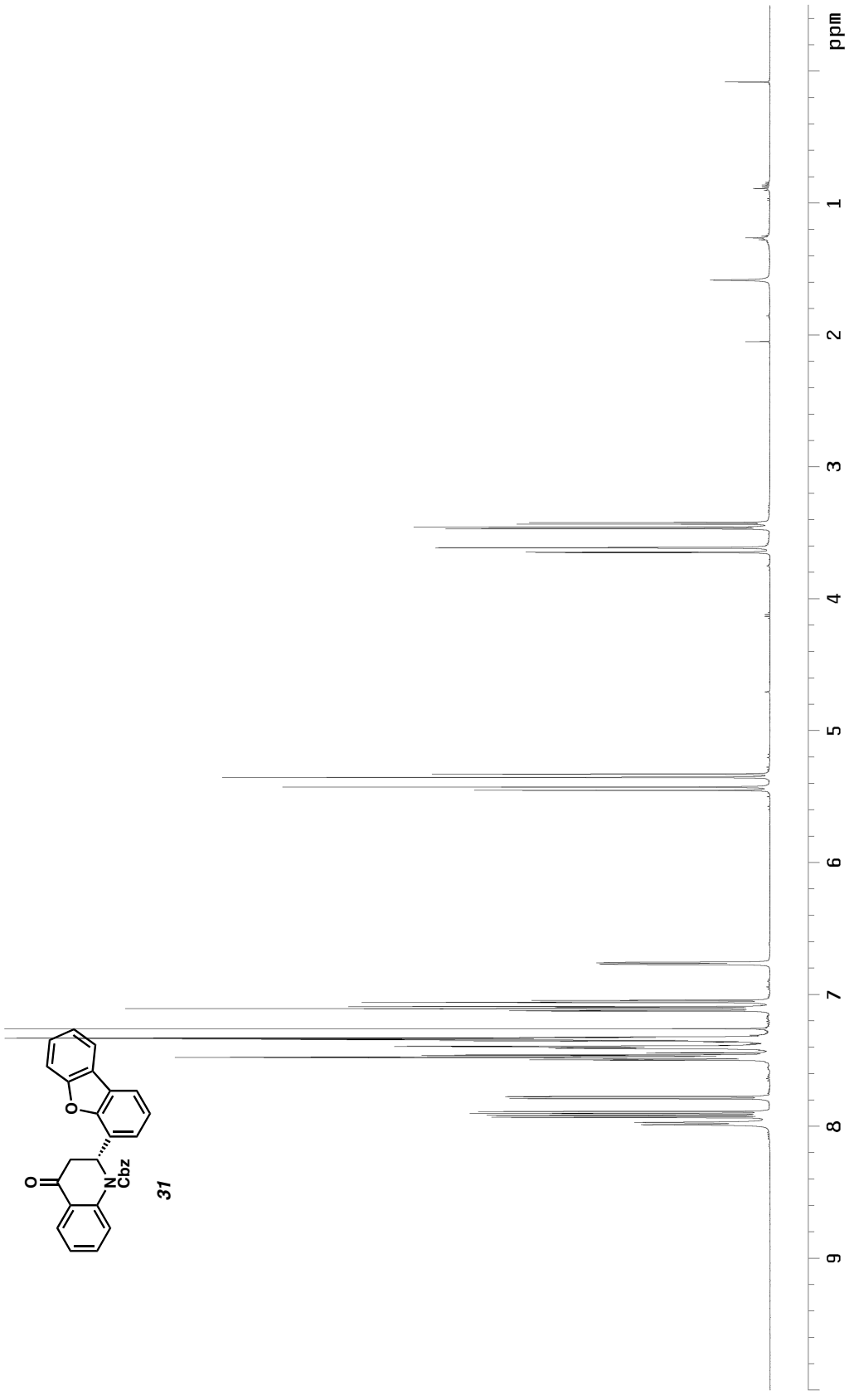
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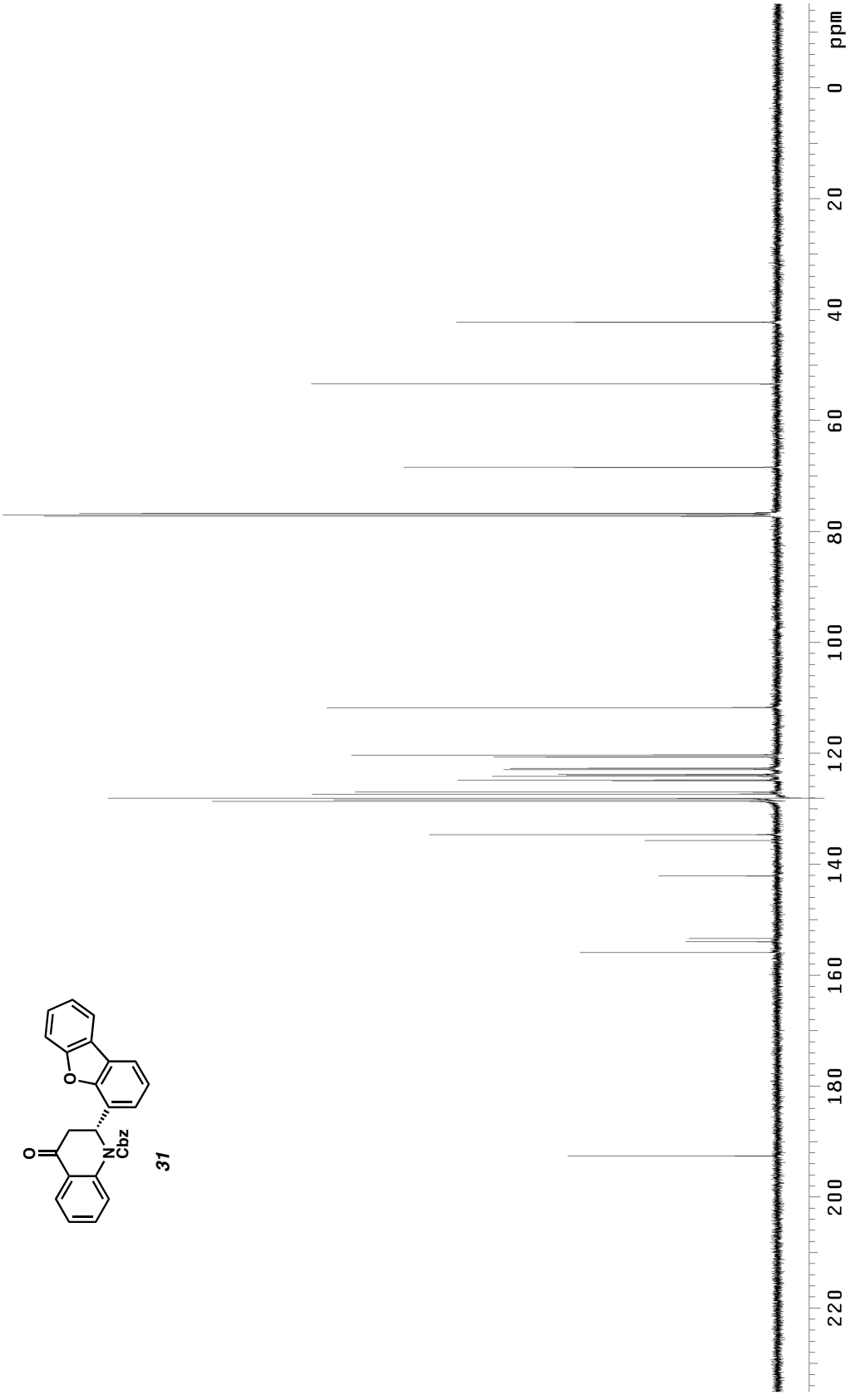

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