Palladium-Catalyzed Conversion of Aryl and Vinyl Triflates to Bromides and Chlorides

*Xiaoqiang Shen, Alan M. Hyde, and Stephen L. Buchwald**

Department of Chemistry, Room 18-490
Massachusetts Institute of Technology
Cambridge, MA 02139 (USA)
FAX: (+1) 617-253-3297
E-mail: sbuchwal@mit.edu

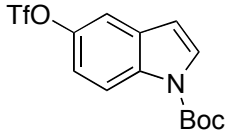
Supporting Information

GENERAL CONSIDERATIONS

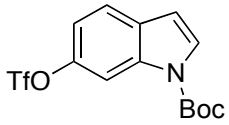
Reagents. Unless otherwise stated, all reactions were carried out in resealable screw-cap tubes under an argon atmosphere using standard Schlenk techniques or glovebox for the manipulation of solvents and reagents. Toluene was purchased from J.T. Baker in a CYCLE-TAINER solvent-deliver keg and vigorously purged with argon for 2 hours. The solvent was further purified by passing through successive alumina and Q5 reactant-packed columns on a solvent purification system. $Pd_2(dba)_3$ was purchased from Strem. PEG 3400 [poly(ethylene glycol), M_n = ~3400], Me_2PEG 2000 [poly(ethylene glycol) dimethyl ether, M_n = ~2000], and *i*-Bu_3Al solution (1.0 M in toluene, 25 wt.%, Sure/Seal™) were purchased from Aldrich, KBr (powdered, IR quality) was purchased from Harshaw, KCl was purchased from J.T. Baker Chemical Co., 2-butanone was purchased from Alfa Aesar, and all these chemicals were used as received. *i*-$Pr_3Al{\cdot}OEt_2$ was prepared by the method of Lehmkul[1] and *t*-BuBrettPhos was prepared as reported by Fors.[2] Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh) or using a Biotage SP4 instrument with prepacked silica cartridges (25 g).

Analytical Methods. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR (where applicable), IR spectroscopy and in most cases, elemental analysis. ^{1}H NMR and ^{13}C NMR spectra are included for all compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz or Bruker 400 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.27 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77 ppm) and were obtained with ^{1}H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase. The yields reported in tables 2 and 3 refer to isolated yields and represent an average of at least two independent runs. The pure compounds are estimated to be ≥ 95% pure as determined by ^{1}H NMR and GC analysis and/or combustion analysis.

Analytical Data for Trifluoromethanesulfonates:
4-methoxyphenyl trifluoromethanesulfonate and 6-quinolinyl trifluoromethanesulfonate were purchased from Aldrich. (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-chroman-6-yl trifluoromethanesulfonate,[3] (8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl trifluoromethanesulfonate,[4] (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl trifluoromethanesulfonate,[5] (8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate,[6] *tert*-butyl 2-(((trifluoromethyl)sulfonyl)oxy)-9*H*-carbazole-9-carboxylate,[7] *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate,[7] 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate,[8] 3-bromophenyl trifluoromethanesulfonate,[9] and ethyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate,[10] were prepared according to literature procedures.

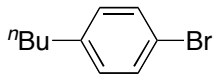


***tert*-butyl-5-((trifluoromethylsulfonyl)oxy)-1H-indole-1-carboxylate**: White solid, MP = 44.5-46.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 3.6 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 9.0, 2.4 Hz, 1H), 6.59 (dd, J = 3.9, 0.9 Hz, 1H), 1.68 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 145.2, 134.1, 131.2, 128.2, 118.8 (q, J = 319 Hz), 117.0, 116.3, 113.4, 107.0, 84.5, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –73.2. IR (thin film): 1742, 1464, 1423, 1208 cm^{-1}. Elemental analysis for $C_{14}H_{14}F_3NO_5S$: C, 46.03; H, 3.86. Found: C, 46.17; H, 3.78.



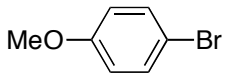
***tert*-butyl-6-((trifluoromethylsulfonyl)oxy)-1H-indole-1-carboxylate**: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.70 (d, J = 3.6 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.16 (dd, J = 8.7, 2.4 Hz, 1H), 6.61 (d, J = 3.9 Hz, 1H), 1.70 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 146.6, 134.7, 130.1, 128.0, 121.7, 118.8 (q, J = 319 Hz), 116.0, 108.8, 106.8, 84.7, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –73.2. IR (thin film): 1743, 1446, 1423, 1347, 1210 cm^{-1}; Elemental analysis for $C_{14}H_{14}F_3NO_5S$: C, 46.03; H, 3.86. Found: C, 46.28; H, 3.92.

General Procedure for the Bromination or Chlorination of Aryl Triflates: A screw-cap test tube (VWR catalog # 53283-810) or a Kontes Schlenk tube (with HI-VAC valve) equipped with a magnetic stir bar was charged with the $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), KBr or KCl (1.5 mmol), PEG3400 (120mg) and aryl triflate (1.0 mmol, 1.0 equiv). The tube was sealed off with a screw-cap, evacuated and backfilled with argon, this procedure was done two more times, 2-butanone (1.5 mmol) and toluene (6-8 mL; Note: the reaction concentration is about 0.1-0.13 M, at higher concentrations (0.2 M), PEG3400 sometime gives gelling and this can be prevented by using Me_2PEG 2000 as phase transfer catalyst) were injected into the tube sequentially, the mixture was stirred for 1 min, then 1.5 mL of *i*-Bu_3Al (1M solution in toluene, 1.5 mmol) was added dropwise. The resulting mixture was stirred vigorously at 100 °C for 20–24 h. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (~10 mL), and then filtered through a pad of silica gel (eluted with ether) and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel.

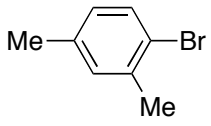


1-bromo-4-butylbenzene (CAS No. 41492-05-1): The title compound was prepared according to the general procedure with 4-*n*-butylphenyl trifluoromethanesulfonate (282 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a colorless oil (175 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J =

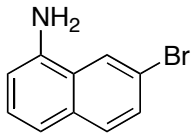
8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 2.58 (t, J = 7.8 Hz, 2H), 1.64-1.54 (m, 2H), 1.42-1.29 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 131.2, 130.1, 119.2, 35.0, 33.5, 22.2, 13.9.



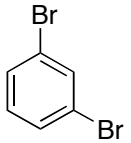
1-bromo-4-methoxybenzene (CAS No. 104-92-7): The title compound was prepared according to the general procedure with 4-methoxyphenyl trifluoromethanesulfonate (256 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (Biotage, eluted with 0-5% EtOAc in hexanes) to provide the desired product as a colorless oil (131 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 9.0 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 132.2, 115.7, 112.8, 55.4.



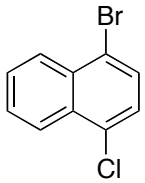
1-bromo-2,4-dimethylbenzene (CAS No. 583-70-0): The title compound was prepared according to the general procedure with 2,4-dimethylphenyl trifluoromethanesulfonate (254 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (18.3mg, 2.0 mol%), *t*-BuBrettPhos (24.2 mg, 5.0 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (8 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a colorless oil (122 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 1H), 7.08 (s, 1H), 6.88 (d, J = 8.1 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 137.0, 132.0, 131.6, 128.1, 121.5, 22.8, 20.8.



7-bromo-1-naphthylamine:[11] The title compound was prepared according to the general procedure with 8-amino-2-naphthyl trifluoromethanesulfonate (291 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (18.3mg, 2.0 mol%), *t*-BuBrettPhos (24.2 mg, 5.0 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-15% EtOAc in hexanes) to provide the desired product as a white solid (144 mg, 65%), turned darker upon standing. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.53 (dd, J = 8.7, 1.8 Hz, 1H), 7.34-7.27 (m, 2H), 6.79 (dd, J = 6.3, 2.1 Hz, 1H), 4.09 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 132.7, 130.2, 129.1, 126.8, 124.8, 123.5, 118.8, 118.7, 110.7.

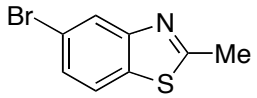


1,3-dibromobenzene (CAS No. 108-36-1): The title compound was prepared according to the general procedure with 3-bromophenyl trifluoromethanesulfonate (305 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a colorless oil (184 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (t, J = 1.8 Hz, 1H), 7.44 (dd, J = 7.8, 1.8 Hz, 2H), 7.12 (t, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 131.1, 130.2, 123.0.

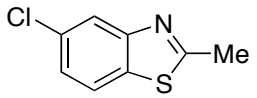


1-bromo-4-chloronaphthalene:[12] The title compound was prepared according to the general procedure with 4-chloro-1-naphthyl trifluoromethanesulfonate (311 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a white solid (217 mg, 90%), which contains inseperable 1,4-dichloronaphthalene and 1,4-dibromonaphthlene (4-10% total). ^{1}H NMR (300 MHz, $CDCl_3$) δ

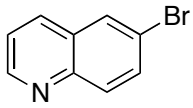
8.29-8.21 (m, 2H), 7.68-7.62 (m, 3H), 7.40 (d, J = 4.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.6, 131.7, 131.6, 129.5, 128.0, 127.7, 127.6, 126.3, 124.9, 121.5.



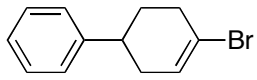
5-bromo-2-methylbenzo[d]thiazole (CAS No. 63837-11-6): The title compound was prepared according to the general procedure with 2-methylbenzo[*d*]thiazol-5-yl trifluoromethanesulfonate (297 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (18.3mg, 2.0 mol%), *t*-BuBrettPhos (24.2 mg, 5.0 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-15% EtOAc in hexanes) to provide the desired product as a white solid (171 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 1.9 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.44 (dd, J = 8.5, 1.9 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 154.4, 134.3, 127.6, 125.1, 122.3, 119.3, 20.1.



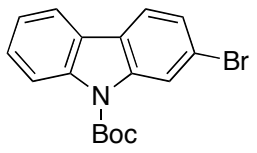
5-chloro-2-methylbenzo[d]thiazole (CAS No. 1006-99-1): The title compound was prepared according to the general procedure with 2-methylbenzo[*d*]thiazol-5-yl trifluoromethanesulfonate (297 mg, 1 mmol), potassium chloride (112 mg, 1.5 mmol), $Pd_2(dba)_3$ (18.3mg, 2.0 mol%), *t*-BuBrettPhos (24.2 mg, 5.0 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-20% EtOAc in hexanes) to provide the desired product as a white solid (154mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.26 (dd, J = 8.4, 1.9 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 154.1, 133.8, 131.8, 125.0, 122.1, 121.9, 20.1.



6-bromoquinoline (CAS No. 5332-25-2): The title compound was prepared according to the general procedure with 6-quinolinyl trifluoromethanesulfonate (227 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-30% EtOAc in hexanes) to provide the desired product as a colorless oil (131 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.2, 1.8 Hz, 1H), 8.05-8.01 (m, 1H), 7.96 (d, J = 6.0 Hz, 1H), 7.94 (s, 1H), 7.75 (dd, J = 9.0, 2.1 Hz, 1H), 7.39 (dd, J = 8.1, 4.2 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 146.7, 135.0, 132.8, 131.1, 129.7, 129.2, 121.8, 120.4.

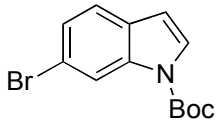


4-bromo-1,2,3,6-tetrahydro-1,1'-biphenyl: The title compound was prepared according to the general procedure with 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (306 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as an off-white solid (206 mg, 87%). MP = 44-45.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5H), 6.15 (br, 1H), 2.93-2.83 (m, 1H), 2.73-2.53 (m, 2H), 2.42-2.22 (m, 2H), 2.03-1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 128.5, 128.4, 126.7, 126.3, 121.9, 38.7, 35.5, 35.2, 31.4. IR (thin film): 2923, 1492, 1452, 1433, 961 cm^{-1}; Elemental analysis for $C_{12}H_{13}Br$: C, 60.78; H, 5.53. Found: C, 61.23; H, 5.59.

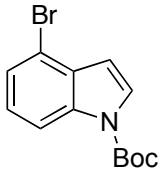


tert-butyl 2-bromo-9H-carbazole-9-carboxylate: The title compound was prepared according to the general procedure with *tert*-butyl 2-(((trifluoromethyl)sulfonyl)oxy)-9*H*-carbazole-9-carboxylate (415 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol),

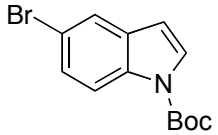
2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (8 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-10% EtOAc in hexanes) to provide the desired product as a white solid (251 mg, 73%). MP = 126-127.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.94-7.92 (m, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.52-7.46(m, 2H), 7.37 (t, J = 7.7 Hz, 1H), 1.79 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 139.1, 138.4, 127.4, 126.1, 124.9, 124.6, 123.2, 120.6, 120.5, 119.54, 119.52, 116.3, 84.5, 28.3. IR (thin film): 1729, 1418, 1331, 1155 cm^{-1}; Elemental analysis for $C_{17}H_{16}BrNO_2$: C, 58.97; H, 4.66. Found: C, 59.20; H, 4.84.



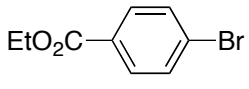
***tert*-butyl-6-bromo-1H-indole-1-carboxylate** (CAS No. 147621-26-9): The title compound was prepared according to the general procedure with *tert*-butyl 6-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (365 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-2% EtOAc in hexanes) to provide the desired product as a white solid (225 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.48 (d, J = 3.9 Hz, 1H), 7.33 (dd, J = 8.4, 0.3 Hz, 1H), 7.26 (dd, J = 8.1, 1.5 Hz, 1H), 6.45 (dd, J = 3.9, 0.9 Hz, 1H), 1.60 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 135.8, 129.3, 126.3, 125.8, 121.9, 118.3, 117.9, 107.0, 84.2, 28.1.



***tert*-butyl-4-bromo-1H-indole-1-carboxylate** (CAS No. 676448-17-2): The title compound was prepared according to the general procedure with *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (365 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-2% EtOAc in hexanes) to provide the desired product as a white solid (222 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 3.7 Hz, 1H), 7.40 (dd, J = 7.8, 0.7 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 6.65 (dd, J = 3.8, 0.7 Hz, 1H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 135.5, 131.1, 126.4, 125.5, 125.1, 114.6, 114.2, 107.0, 84.2, 28.1.

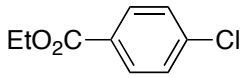


***tert*-butyl-5-bromo-1H-indole-1-carboxylate** (CAS No. 182344-70-3): The title compound was prepared according to the general procedure with *tert*-butyl 5-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (365 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-2% EtOAc in hexanes) to provide the desired product as a white solid (207 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 1.8 Hz, 1H), 7.60 (d, J = 3.6 Hz, 1H), 7.41 (dd, J = 8.7, 1.8 Hz, 1H), 6.51 (d, J = 3.9 Hz, 1H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 133.9, 132.2, 127.0, 123.5, 116.5, 115.9, 106.4, 84.1, 28.1.

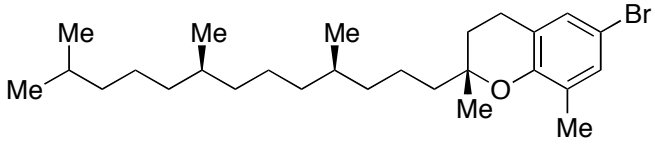


Ethyl-4-bromobenzoate (CAS No. 5798-75-4): The title compound was prepared according to the general procedure with ethyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (298 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.25 mL, 1.25 mmol), EtOH (58 mg, 1.25 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (Biotage, eluted with 0-8% EtOAc in hexanes) to provide the desired product as a colorless oil (183 mg, 80%) which contains about 5% of inseperable ethyl 4-*i*-butylbenzoate. ^{1}H NMR (300

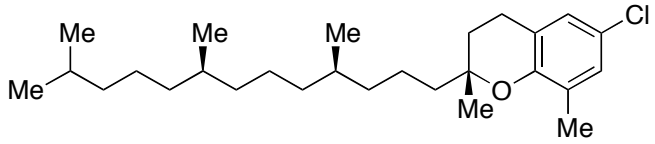
MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 131.6, 131.0, 129.3, 127.8, 61.2, 14.2.



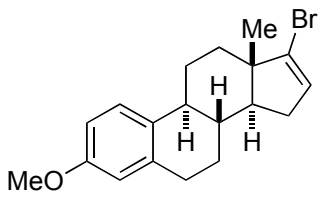
Ethyl-4-chlorobenzoate (CAS No. 7335-27-5): The title compound was prepared according to the general procedure with ethyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (298 mg, 1 mmol), potassium chloride (112 mg, 1.5 mmol), $Pd_2(dba)_3$ (13.7mg, 1.5 mol%), *t*-BuBrettPhos (18.2 mg, 3.75 mol%), *i*-Bu_3Al (1.25 mL, 1.25 mmol), EtOH (58 mg, 1.25 mmol) and PEG3400 (120 mg) in toluene (6 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (Biotage, eluted with 0-10% EtOAc in hexanes) to provide the desired product as a colorless oil (155 mg, 84%) which contains about 5% of inseperable ethyl 4-*i*-butylbenzoate. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 139.1, 130.8, 128.8, 128.5, 61.1, 14.2.



(*R*)-6-bromo-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman: The title compound was prepared according to the general procedure with (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl trifluoromethanesulfonate (535 mg, 1 mmol), potassium bromide (179 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (8 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a colorless oil (335 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.04 (s, 1H), 2.73 (t, J = 6.6 Hz, 2H), 2.15 (s, 3H), 1.85-1.72 (m, 3H), 1.63-1.07 (m, 20H), 1.27 (s, 3H), 0.91-0.86 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 130.8, 129.2, 128.6, 122.5, 110.7, 76.3, 39.9, 39.3, 37.42, 37.37, 37.36, 37.26, 32.8, 32.6, 30.9, 28.0, 24.8, 24.4, 24.1, 22.7, 22.6, 22.2, 20.9, 19.7, 19.6, 15.9. IR (thin film): 2927, 1468, 1219 cm^{-1}.

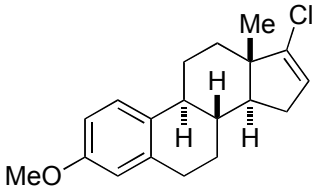


(*R*)-6-chloro-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman: The title compound was prepared according to the general procedure with (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl trifluoromethanesulfonate (535 mg, 1 mmol), potassium chloride (112 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (8 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (eluted with hexanes) to provide the desired product as a colorless oil (307 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.91 (s, 1H), 2.76-2.73 (m, 2H), 2.17 (s, 3H), 1.86-1.73 (m, 2H), 1.60-1.09 (m, 24H), 0.92-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 128.04, 127.97, 126.2, 123.3, 121.9, 76.2, 39.9, 39.4, 37.44, 37.38, 37.28, 32.8, 32.6, 31.0, 28.0, 24.8, 24.5, 24.1, 22.7, 22.6, 22.2, 20.9, 19.8, 19.7, 15.9. IR (thin film): 2927, 1469, 1220 cm^{-1}. Elemental analysis for $C_{27}H_{45}ClO$: C, 77.01; H, 10.77. Found: C, 77.04; H, 10.73.

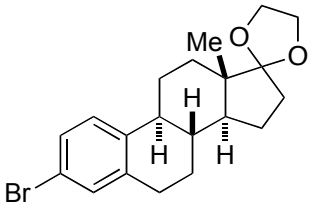


(8R,9S,13S,14S)-17-bromo-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[*a*]phenanthrene: The title compound was prepared according to the general procedure with (8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl

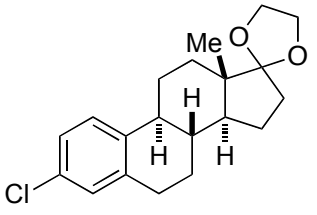
trifluoromethanesulfonate (208 mg, 0.5 mmol), potassium bromide (90 mg, 0.75 mmol), $Pd_2(dba)_3$ (11.5mg, 2.5 mol%), *t*-BuBrettPhos (15.2 mg, 6.25 mol%), *i*-Bu_3Al (0.75 mL, 0.75 mmol), 2-butanone (54 mg, 0.75 mmol) and PEG3400 (60 mg) in toluene (4 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-10% EtOAc in hexanes) to provide the desired product as a white solid (160 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.6 Hz, 1H), 6.74 (dd, J = 8.6, 2.8 Hz, 1H), 6.67 (d, J = 2.8 Hz, 1H), 5.90 (dd, J = 3.2, 1.6 Hz, 1H), 3.80 (s, 3H), 2.94-2.90 (m, 2H), 2.45-2.39 (m, 1H), 2.33-2.26 (m, 1H), 2.26 (ddd, J = 14.8, 6.3, 3.3 Hz, 1H), 2.03 (ddd, 14.7, 11.1, 1.7 Hz, 1H), 1.98-1.87 (m, 2H), 1.75 (td, 11.2, 6.3 Hz, 1H), 1.67-1.40 (m, 4H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 137.7, 135.7, 132.4, 128.9, 125.9, 113.8, 111.3, 55.1, 54.7, 48.8, 44.1, 37.4, 34.5, 31.5, 29.5, 27.2, 26.2, 15.2. IR (thin film): 2931, 1609, 1499, 1256 cm^{-1}. Elemental analysis for $C_{19}H_{23}BrO$: C, 65.71; H, 6.68. Found: C, 65.94; H, 6.73.



(8*R*,9*S*,13*S*,14*S*)-17-chloro-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[*a*]phenanthrene:[13] The title compound was prepared according to the general procedure with (8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl trifluoromethanesulfonate (208 mg, 0.5 mmol), potassium chloride (56 mg, 0.75 mmol), $Pd_2(dba)_3$ (11.5mg, 2.5 mol%), *t*-BuBrettPhos (15.2 mg, 6.25 mol%), *i*-Bu_3Al (0.75 mL, 0.75 mmol), 2-butanone (54 mg, 0.75 mmol) and PEG3400 (60 mg) in toluene (4 mL) at 100 ºC for 24h. The crude product was purified by flash chromatography (Biotage, eluted with 0-10% EtOAc in hexanes) to provide the desired product as a white solid (142 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.7 Hz, 1H), 6.77 (dd, J = 8.7, 2.7 Hz, 1H), 6.70 (d, J = 2.7 Hz, 1H), 5.70 (dd, J = 3.0, 1.6 Hz, 1H), 3.83 (s, 3H), 2.96-2.92 (m, 2H), 2.48-2.41 (m, 1H), 2.37-2.25 (m, 2H), 2.08 (ddd, J = 14.4, 10.8, 1.5 Hz, 1H), 2.01-1.93 (m, 2H), 1.81-1.68 (m, 1H), 1.68-1.41 (m, 4H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 144.7, 137.7, 132.5, 126.0, 124.5, 113.8, 111.4, 55.1, 54.9, 47.8, 44.2, 37.3, 33.7, 30.3, 29.6, 27.2, 26.2, 15.1.

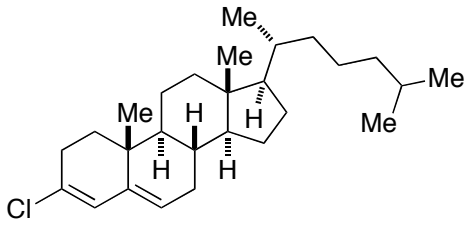


(8*R*,9*S*,13*S*,14*S*)-3-bromo-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane]: The title compound was prepared according to the general procedure with (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl trifluoromethanesulfonate (223 mg, 0.5 mmol), potassium bromide (90 mg, 0.75 mmol), $Pd_2(dba)_3$ (11.5mg, 2.5 mol%), *t*-BuBrettPhos (15.2 mg, 6.25 mol%), *i*-Bu_3Al (0.75 mL, 0.75 mmol), 2-butanone (54 mg, 0.75 mmol) and PEG3400 (60 mg) in toluene (4 mL) at 100 ºC for 24h. The crude product was purified by Preparative TLC (eluted with 9% EtOAc in hexanes) to provide the desired product as a white solid (128 mg, 68%). MP = 98.5-101.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.14 (m, 3H), 3.98-3.87 (m, 4H), 2.85-2.81 (m, 2H), 2.35-2.18 (m, 2H), 2.08-1.97 (m, 1H), 1.92-1.72 (m, 4H), 1.64-1.24 (m, 6H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.1, 131.5, 128.4, 127.1, 119.3, 119.2, 65.2, 64.5, 49.3, 46.0, 43.7, 38.5, 34.2, 30.6, 29.2, 26.7, 25.8, 22.3, 14.3. IR (thin film): 2937, 1481, 1106 cm^{-1}; Elemental analysis for $C_{20}H_{25}BrO_2$: C, 63.66; H, 6.68. Found: C, 63.89; H, 6.63.



(8*R*,9*S*,13*S*,14*S*)-3-chloro-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane]: The title compound was prepared according to the general procedure with (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl trifluoromethanesulfonate

(223 mg, 0.5 mmol), potassium chloride (56 mg, 0.75 mmol), $Pd_2(dba)_3$ (11.5mg, 2.5 mol%), *t*-BuBrettPhos (15.2 mg, 6.25 mol%), *i*-Bu_3Al (0.75 mL, 0.75 mmol), 2-butanone (54 mg, 0.75 mmol) and PEG3400 (60 mg) in toluene (4 mL) at 100 ºC for 24h. The crude product was purified by Preparative TLC (eluted with 10% EtOAc in hexanes) to provide the desired product as a white solid (108 mg, 65%). MP =104-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.4 Hz, 1H), 7.11-7.06 (m, 2H), 3.99-3.88 (m, 4H), 2.86-2.82 (m, 2H), 2.34-2.21 (m, 2H), 2.09-1.98 (m, 1H), 1.95-1.74 (m, 4H), 1.69-1.27 (m, 6H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 138.7, 131.0, 128.6, 126.7, 125.5, 119.3, 65.2, 64.5, 49.3, 46.0, 43.7, 38.6, 34.1, 30.6, 29.3, 26.6, 25.9, 22.3, 14.2. IR (thin film): 2938, 2873, 1483, 1108 cm^{-1}; Elemental analysis for $C_{20}H_{25}ClO_2$: C, 72.17; H, 7.57. Found: C, 72.05; H, 7.72.



(8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-chloro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthrene:[14] The title compound was prepared according to the general procedure with (8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*] phenanthren-3-yl trifluoromethanesulfonate (517 mg, 1 mmol), potassium chloride (112 mg, 1.5 mmol), $Pd_2(dba)_3$ (22.9mg, 2.5 mol%), *t*-BuBrettPhos (30.3 mg, 6.25 mol%), *i*-Bu_3Al (1.5 mL, 1.5 mmol), 2-butanone (108 mg, 1.5 mmol) and PEG3400 (120 mg) in toluene (8 mL) at 100 ºC for 20h. The crude product was purified by flash chromatography (Biotage, eluted with hexanes) to provide the desired product as a white solid (354 mg, 88%). MP = 64-66 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (d, J = 2.4 Hz, 1H), 5.41-5.39 (m, 1H), 2.57-2.46 (m, 1H), 2.32 (dd, J = 17.7, 4.5 Hz, 1H), 2.21-2.11 (m, 1H), 2.03 (dt, J = 12.3, 3.6 Hz, 1H), 1.91-1.79 (m, 2H), 1.70-1.00 (m, 20H), 0.97 (s, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 130.2, 127.0, 124.3, 56.8, 56.1, 47.9, 42.4, 39.7, 39.5, 36.2, 35.8, 34.8, 34.4, 31.8, 31.7, 30.7, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.1, 18.9, 18.7, 11.9;

References:

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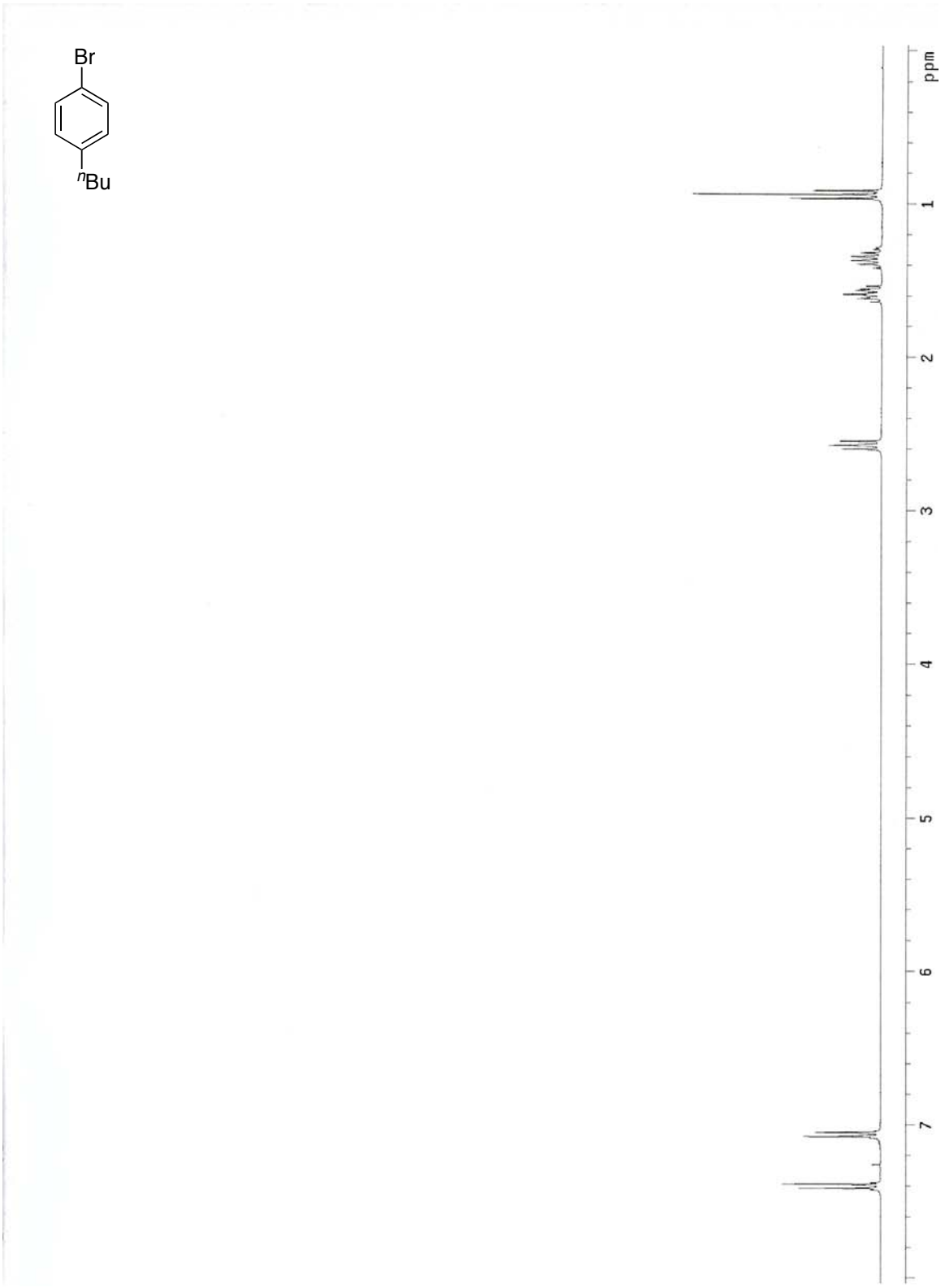
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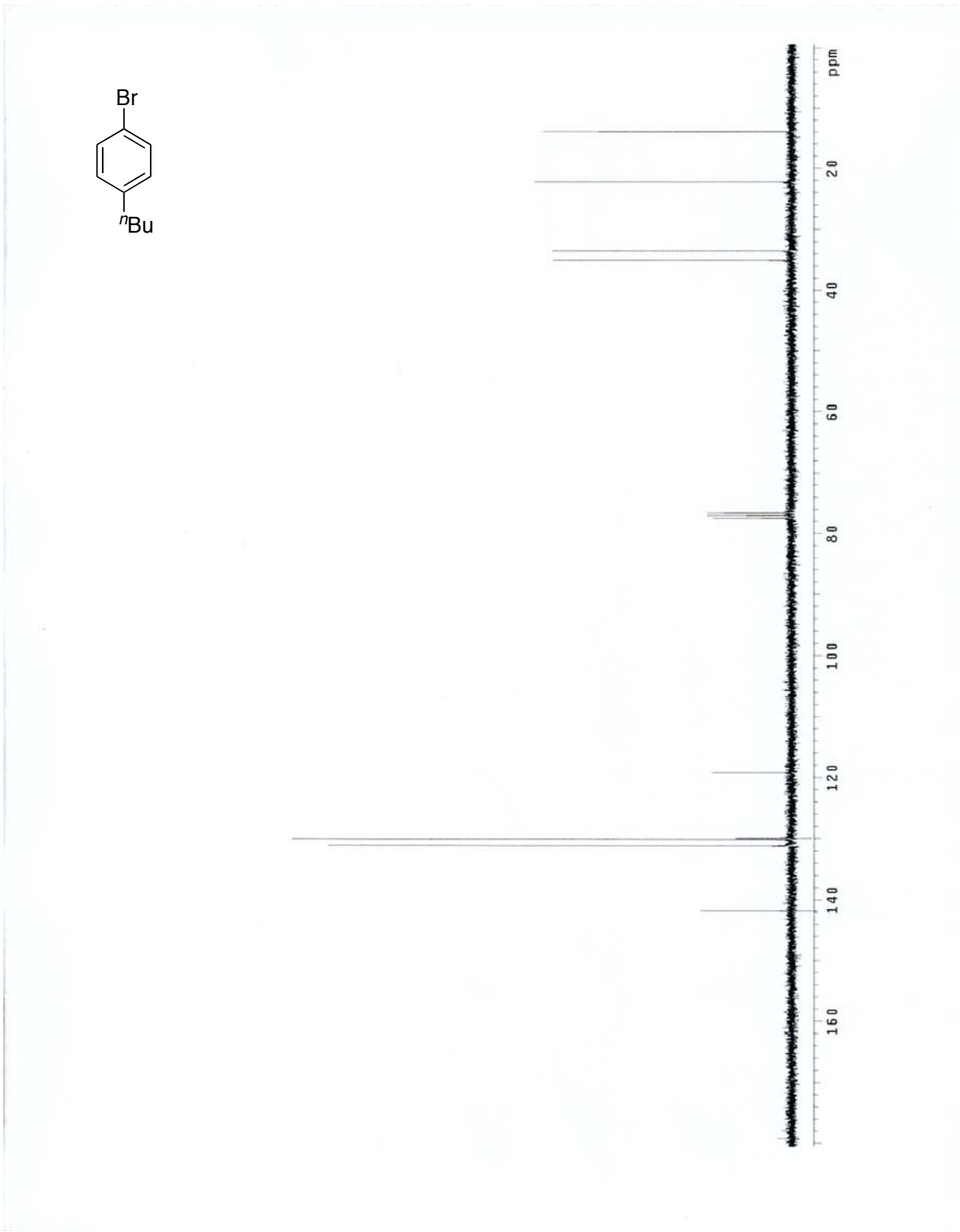
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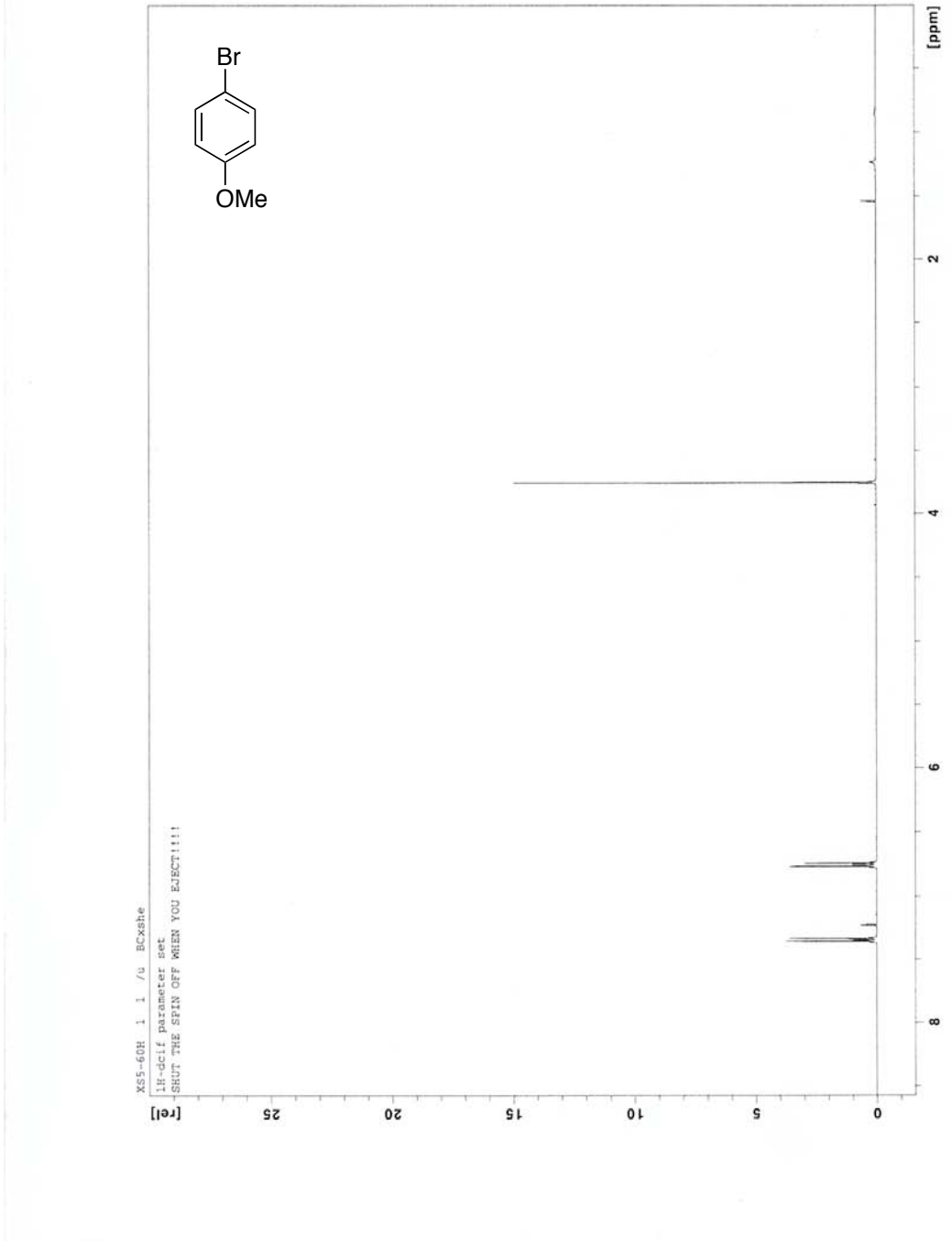
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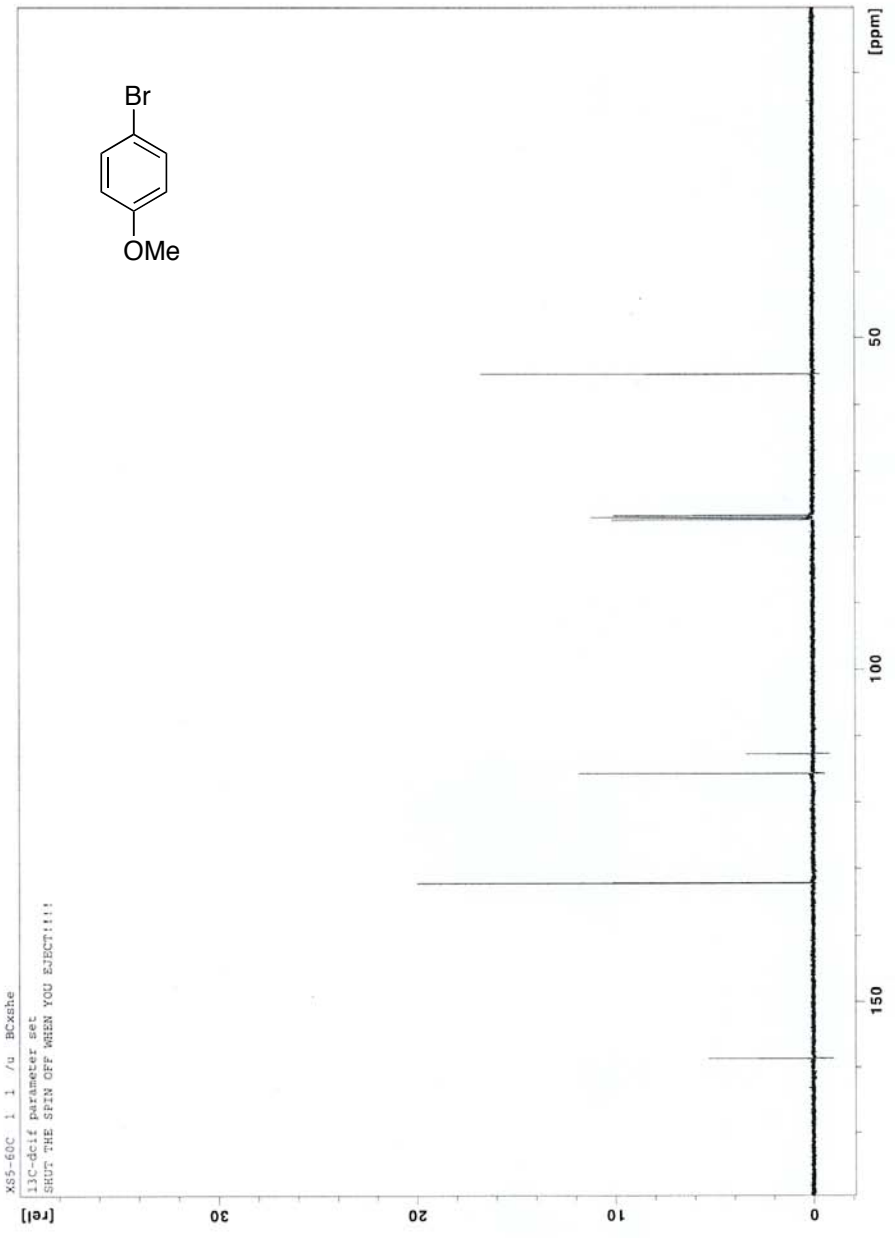
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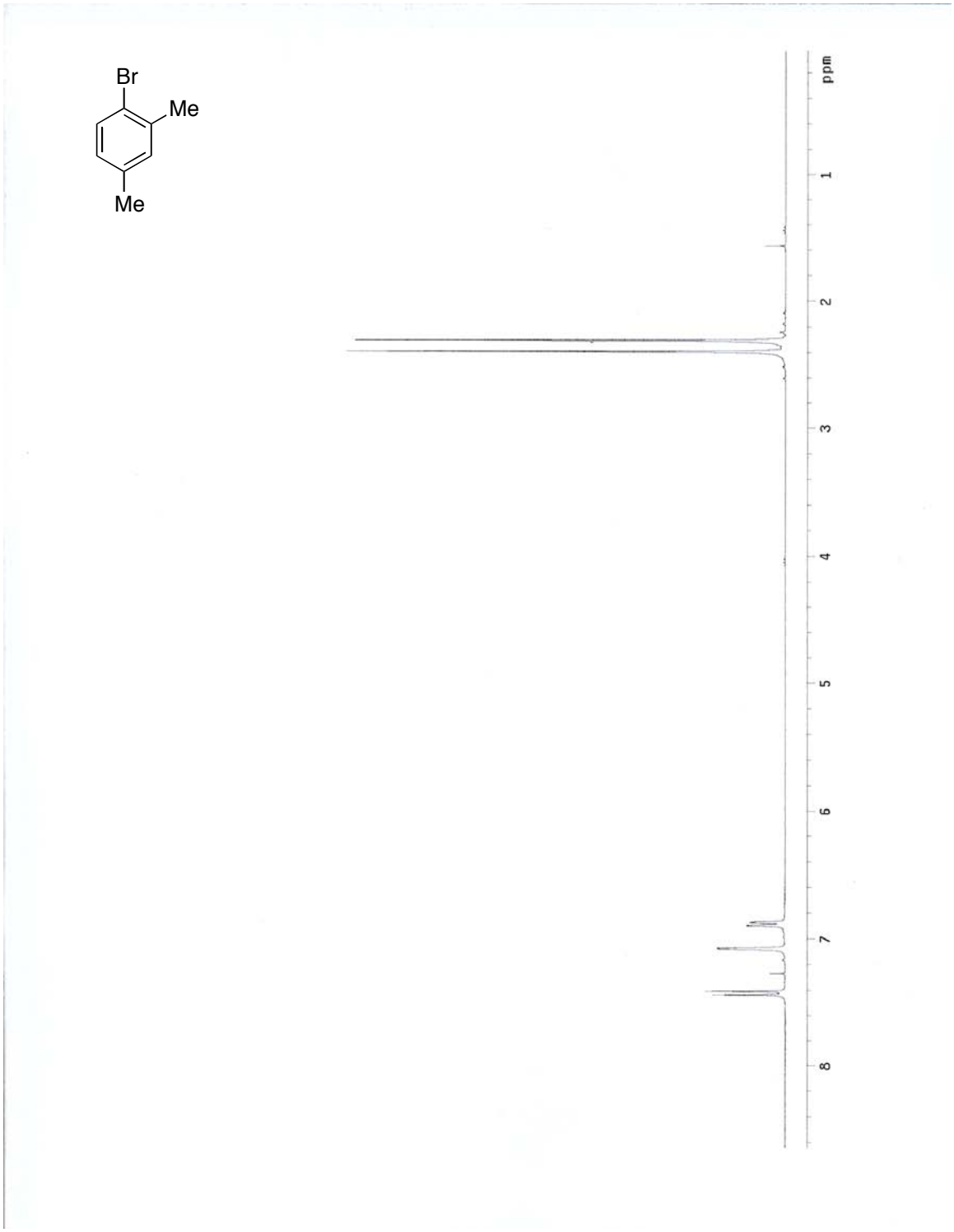
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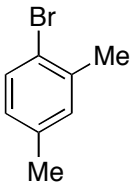
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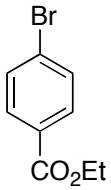
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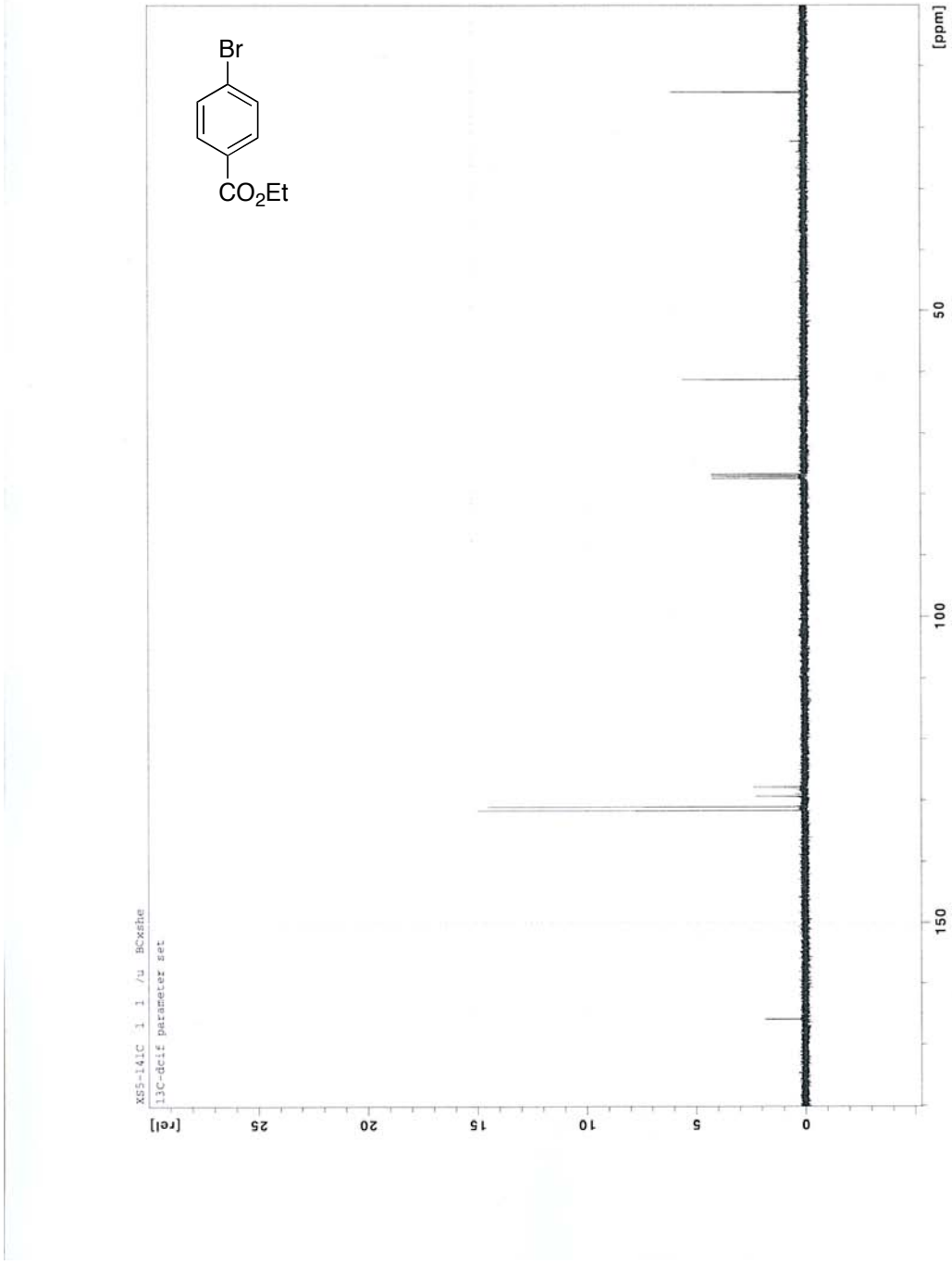
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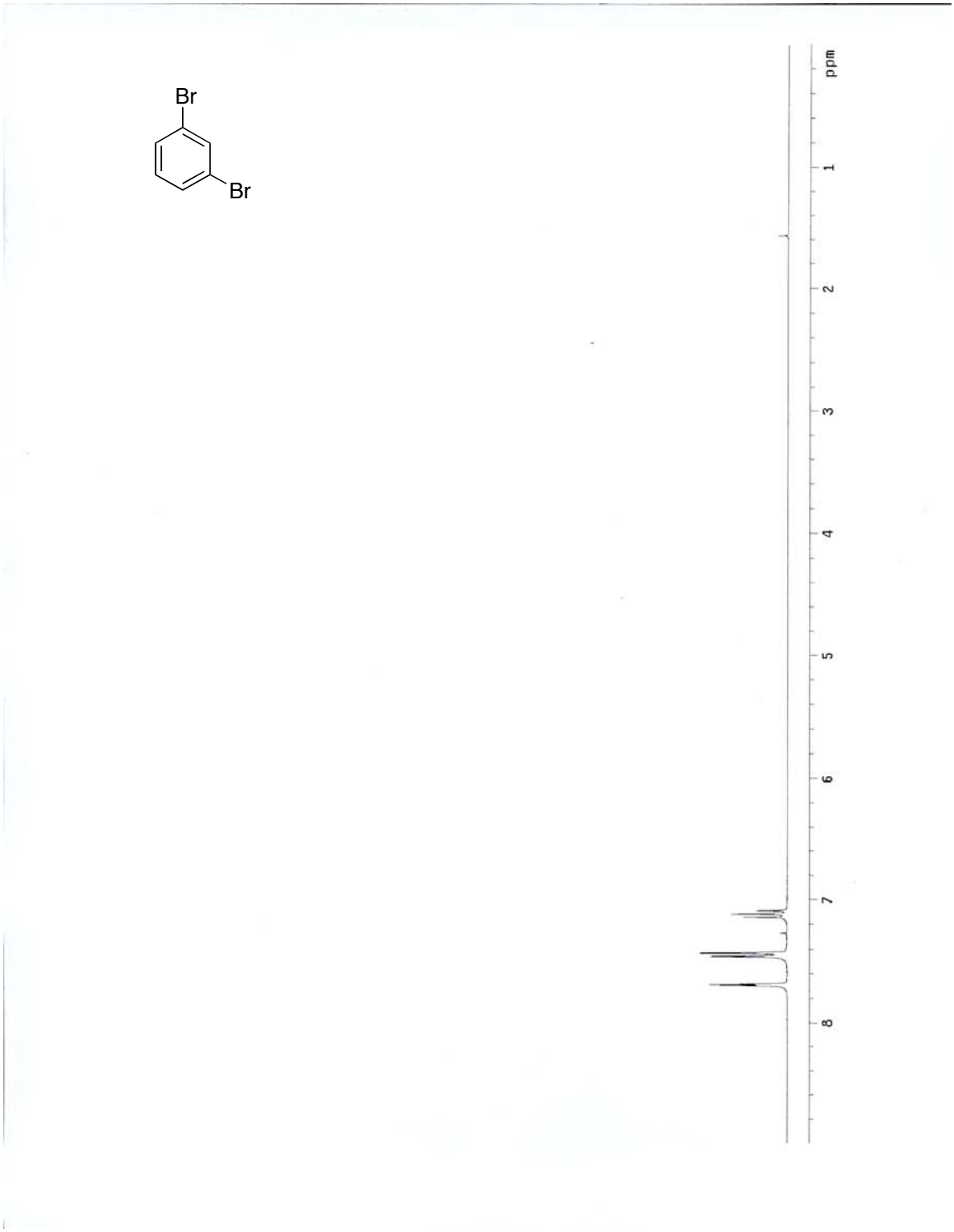
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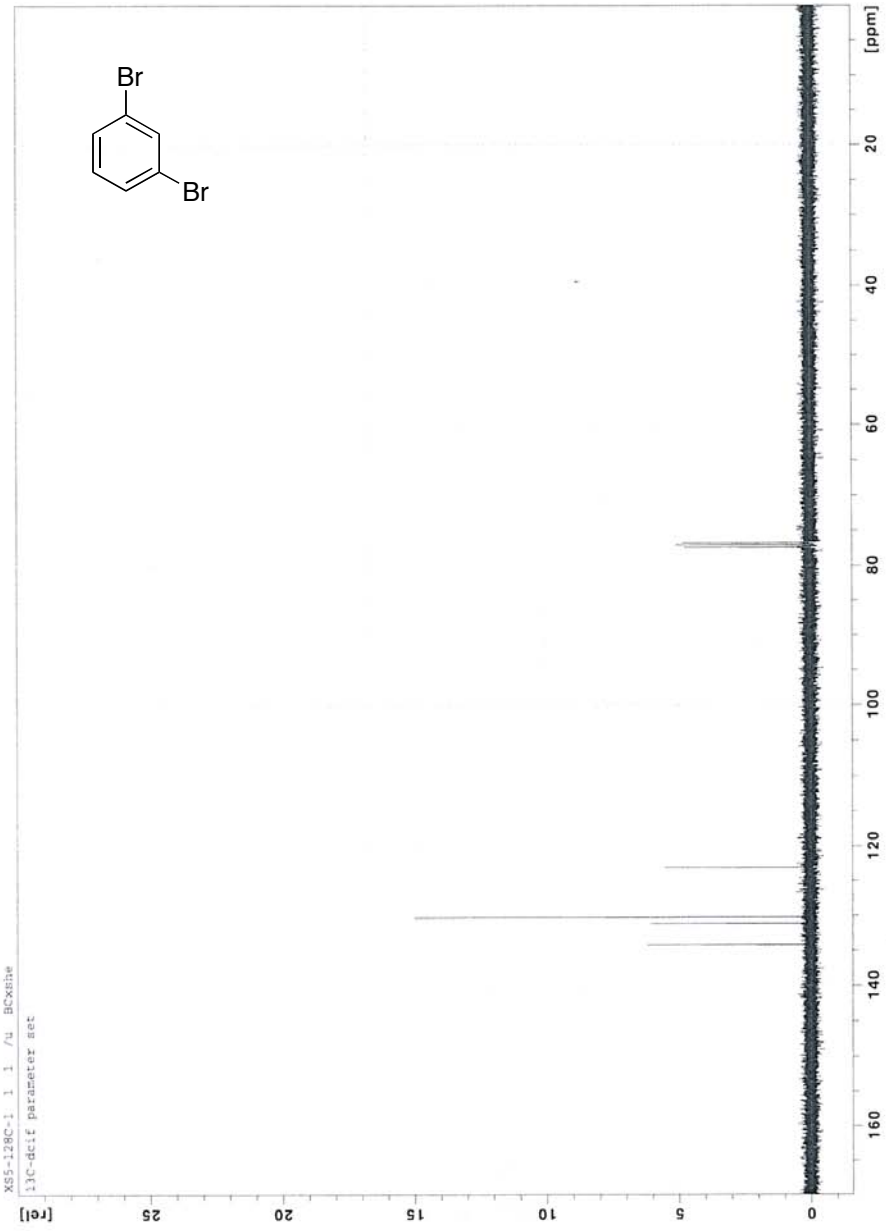
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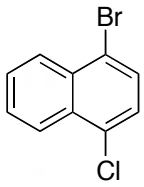
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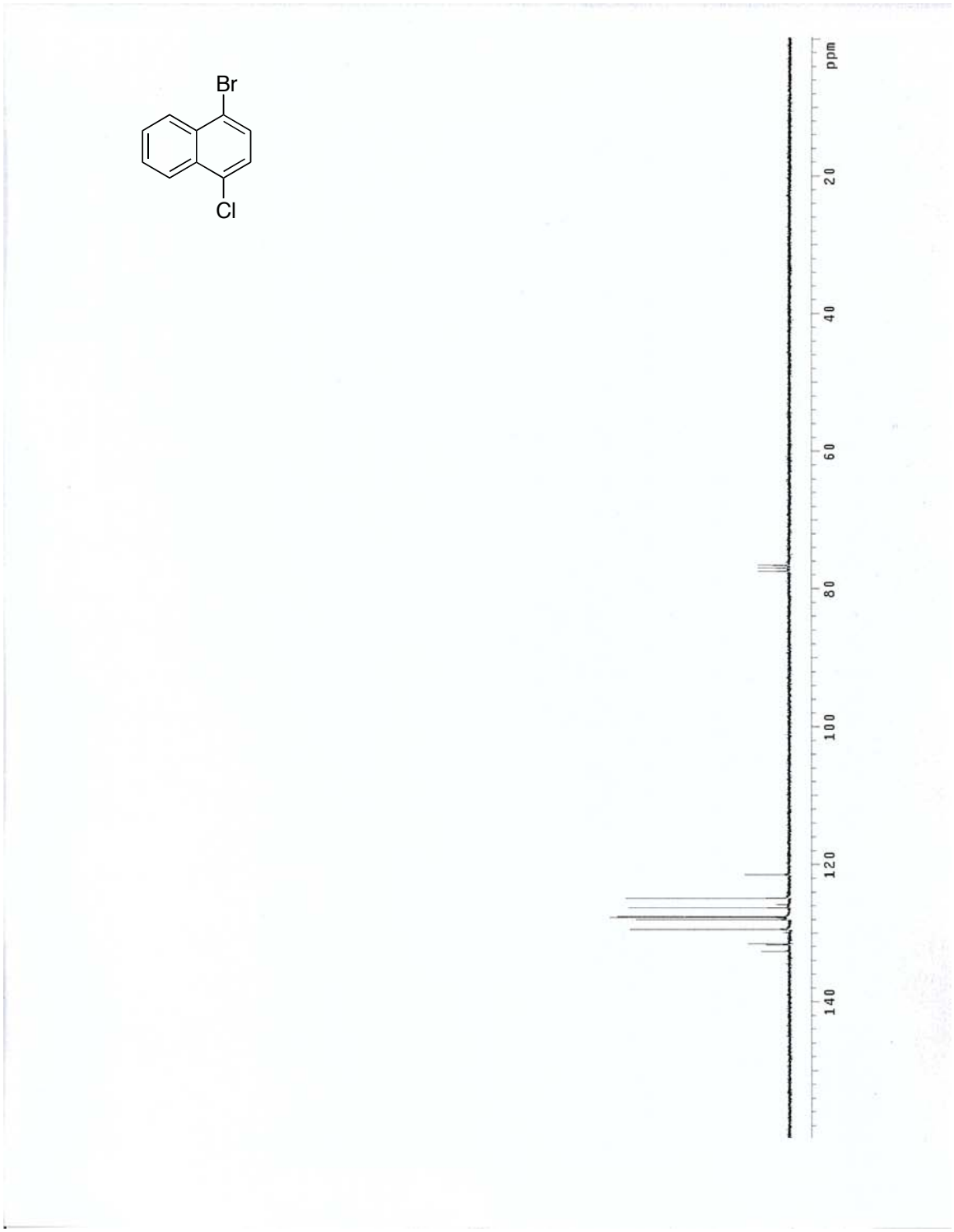
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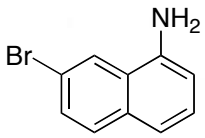
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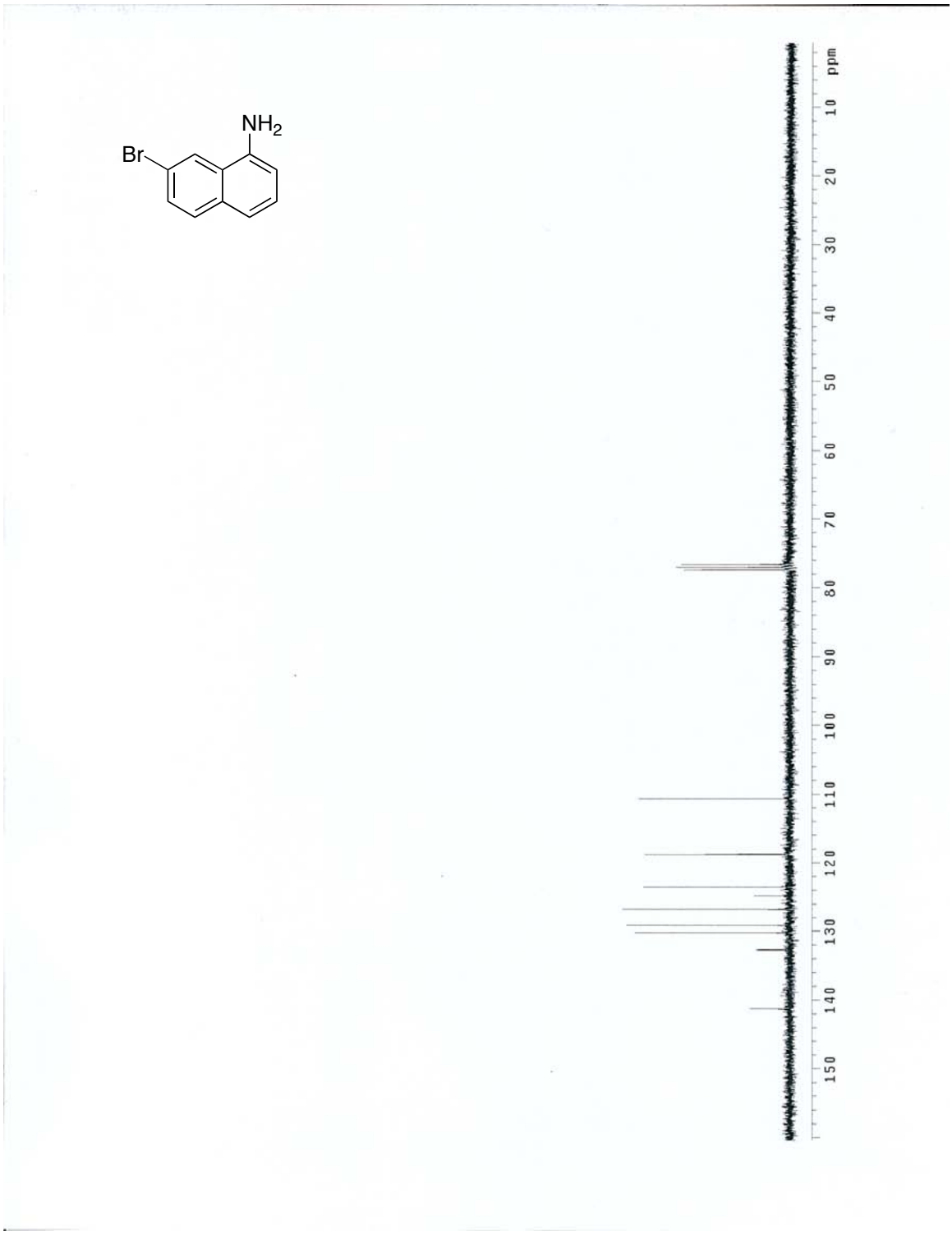
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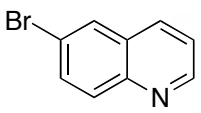
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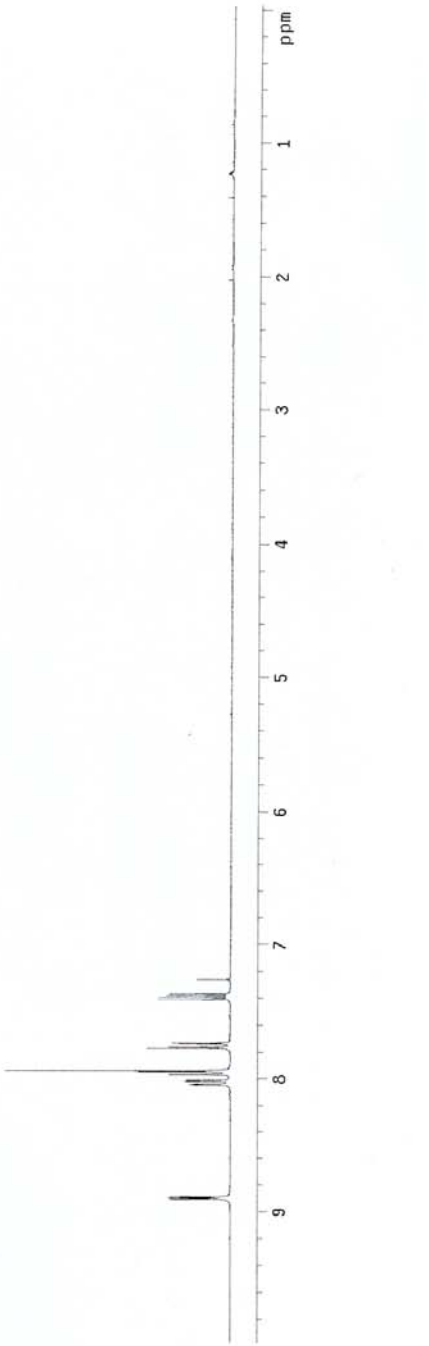
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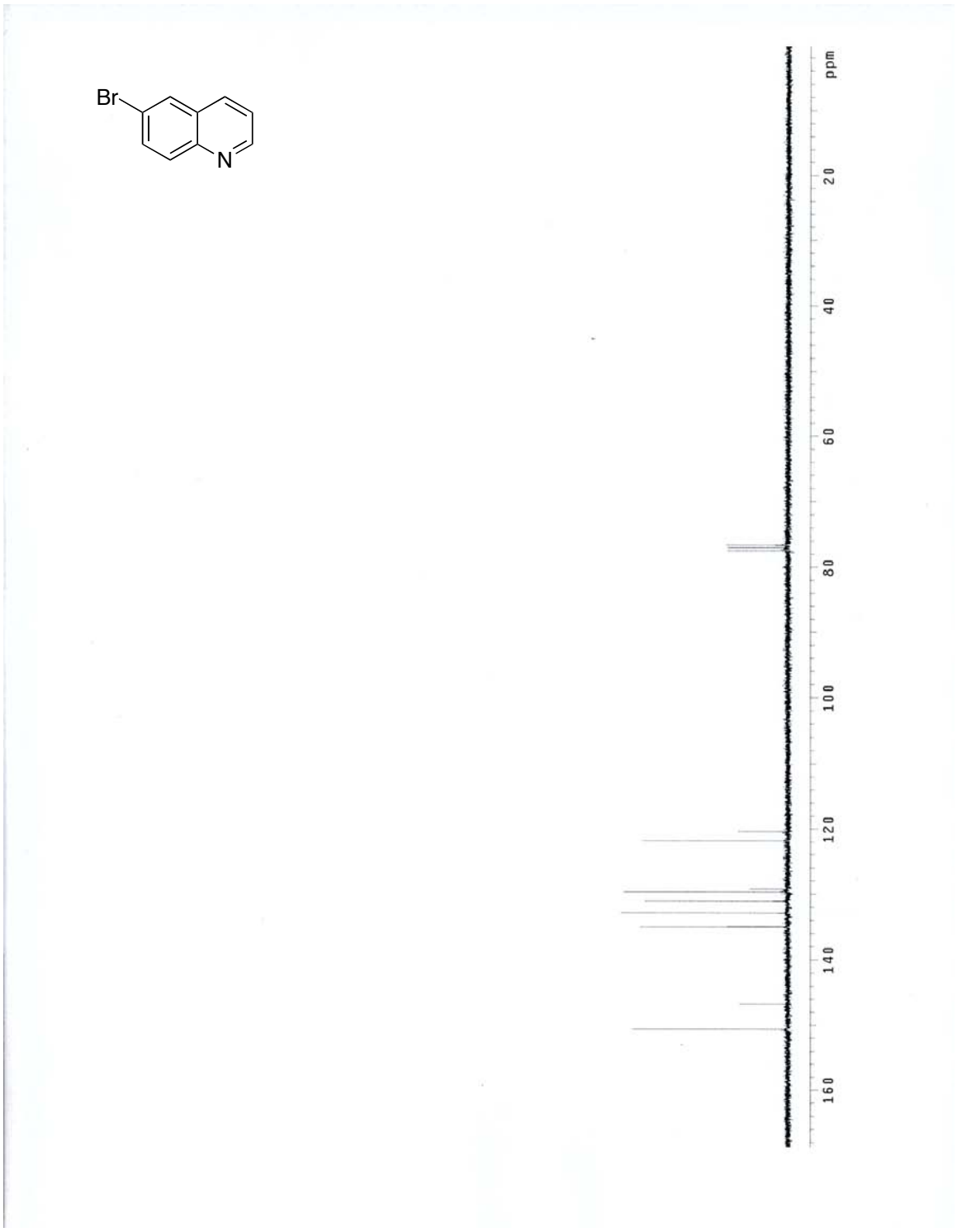
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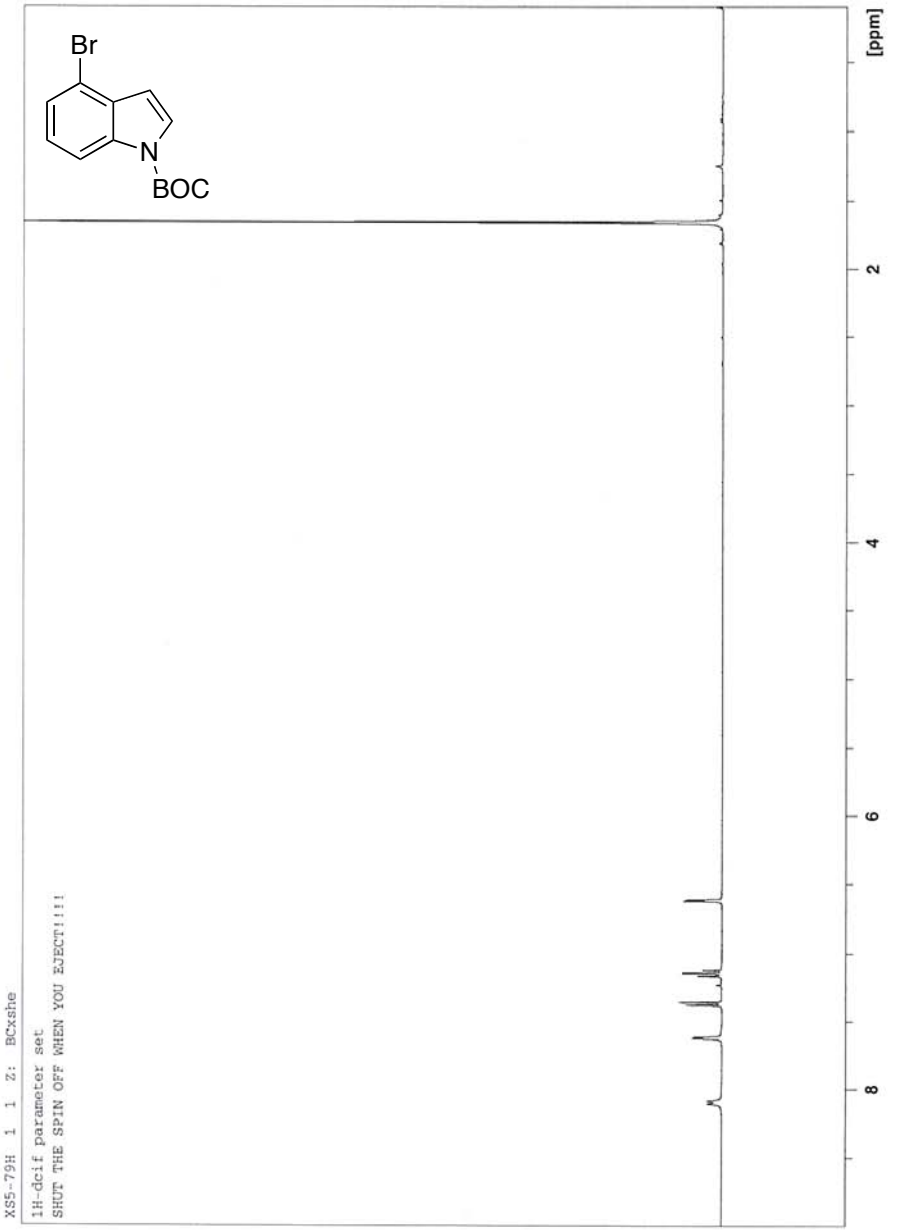
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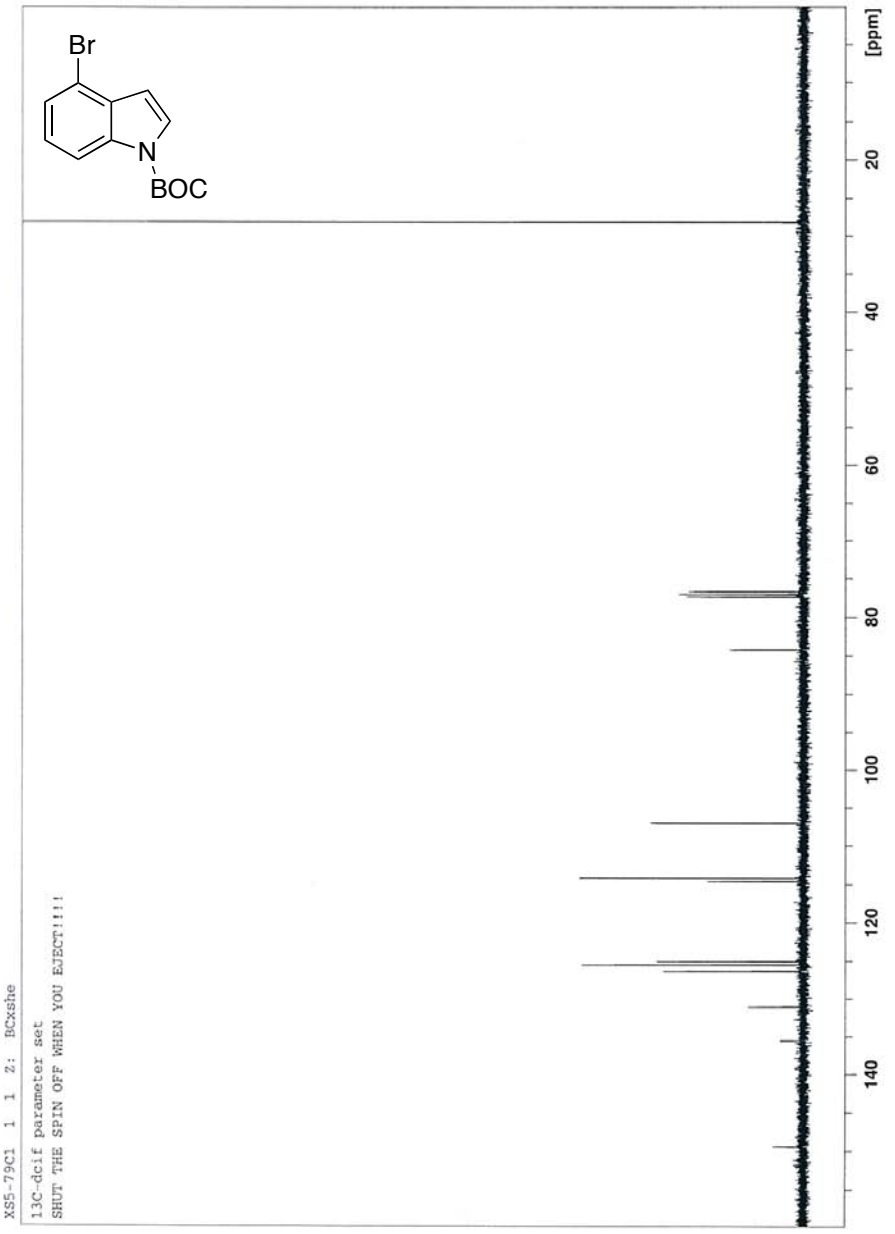
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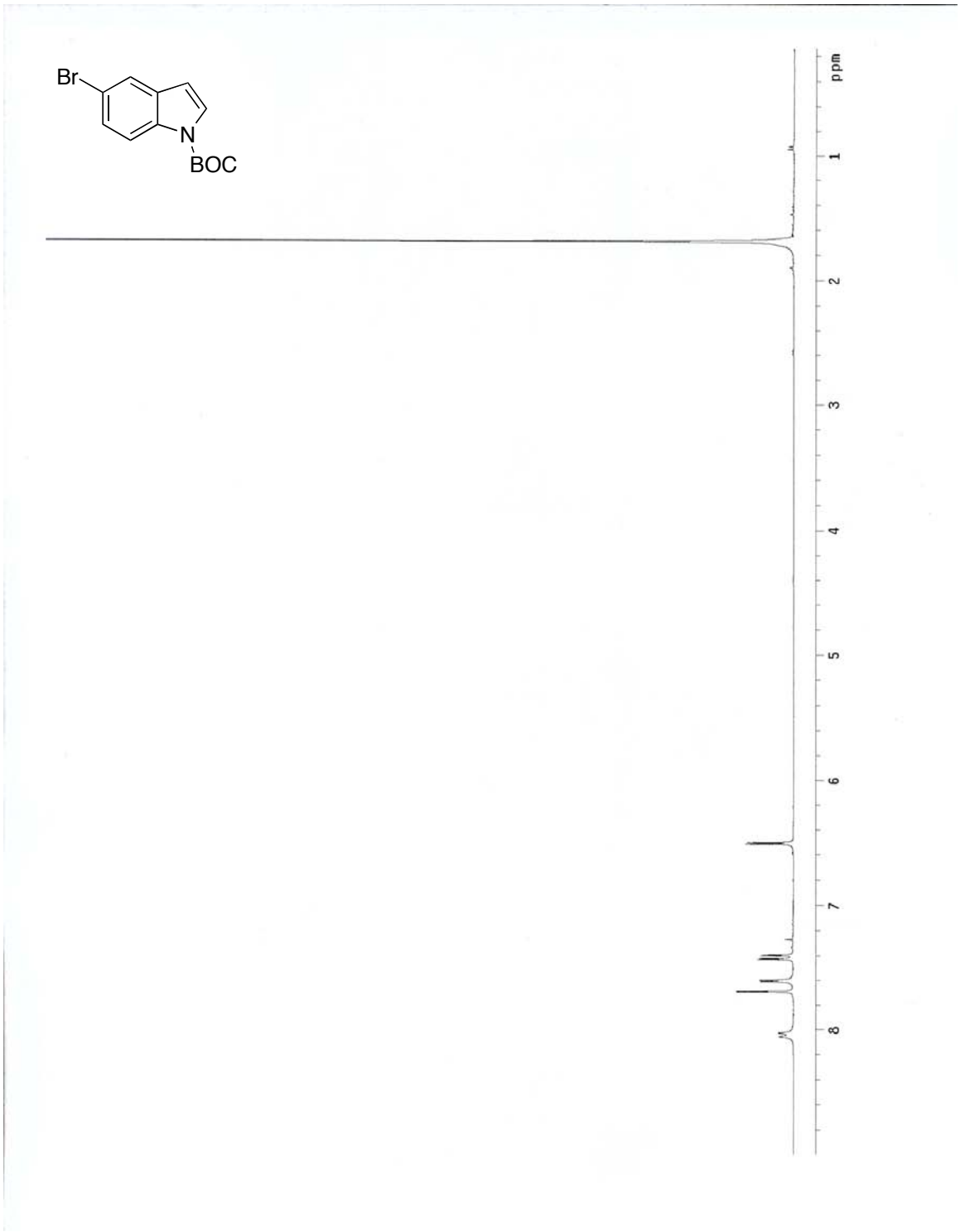
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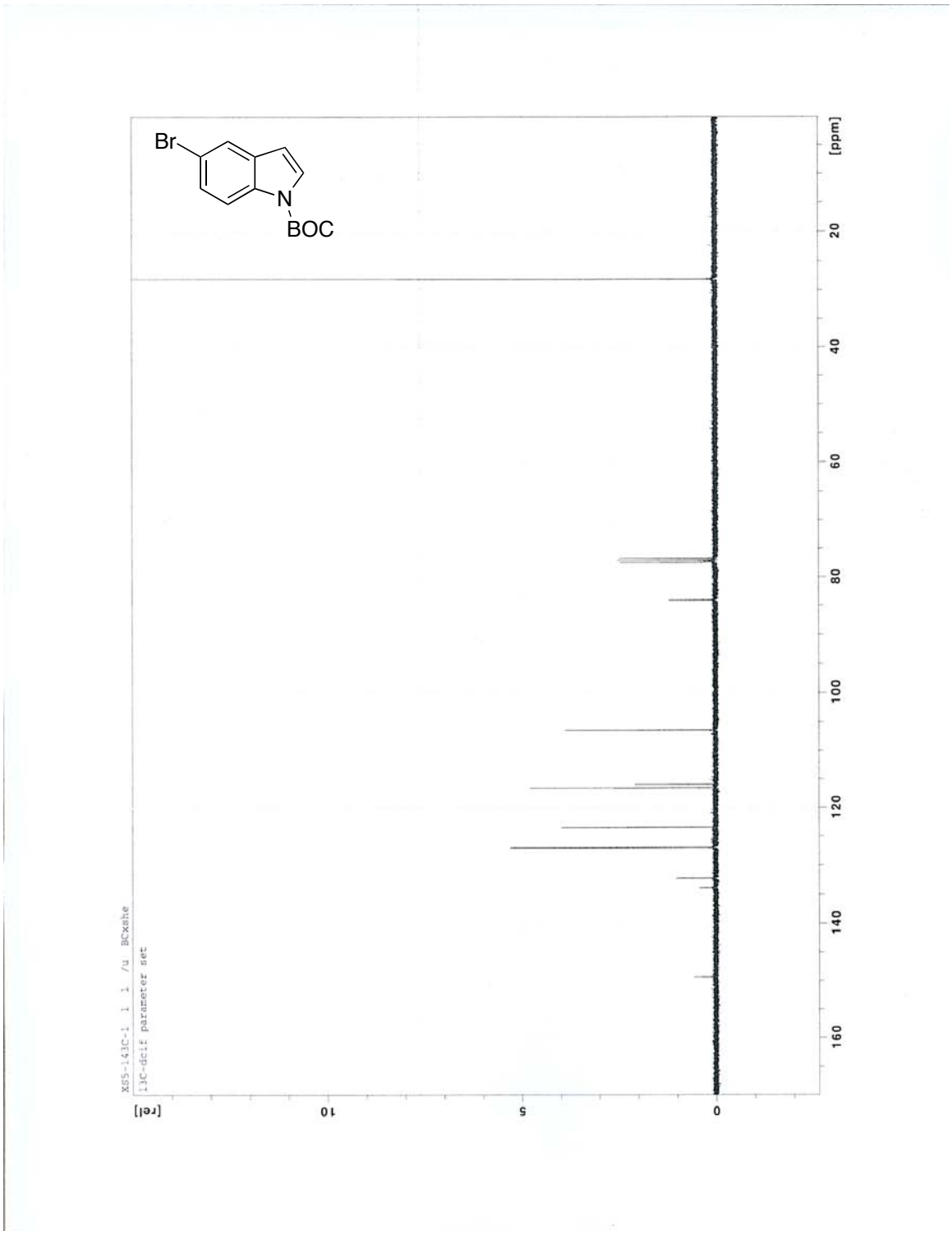
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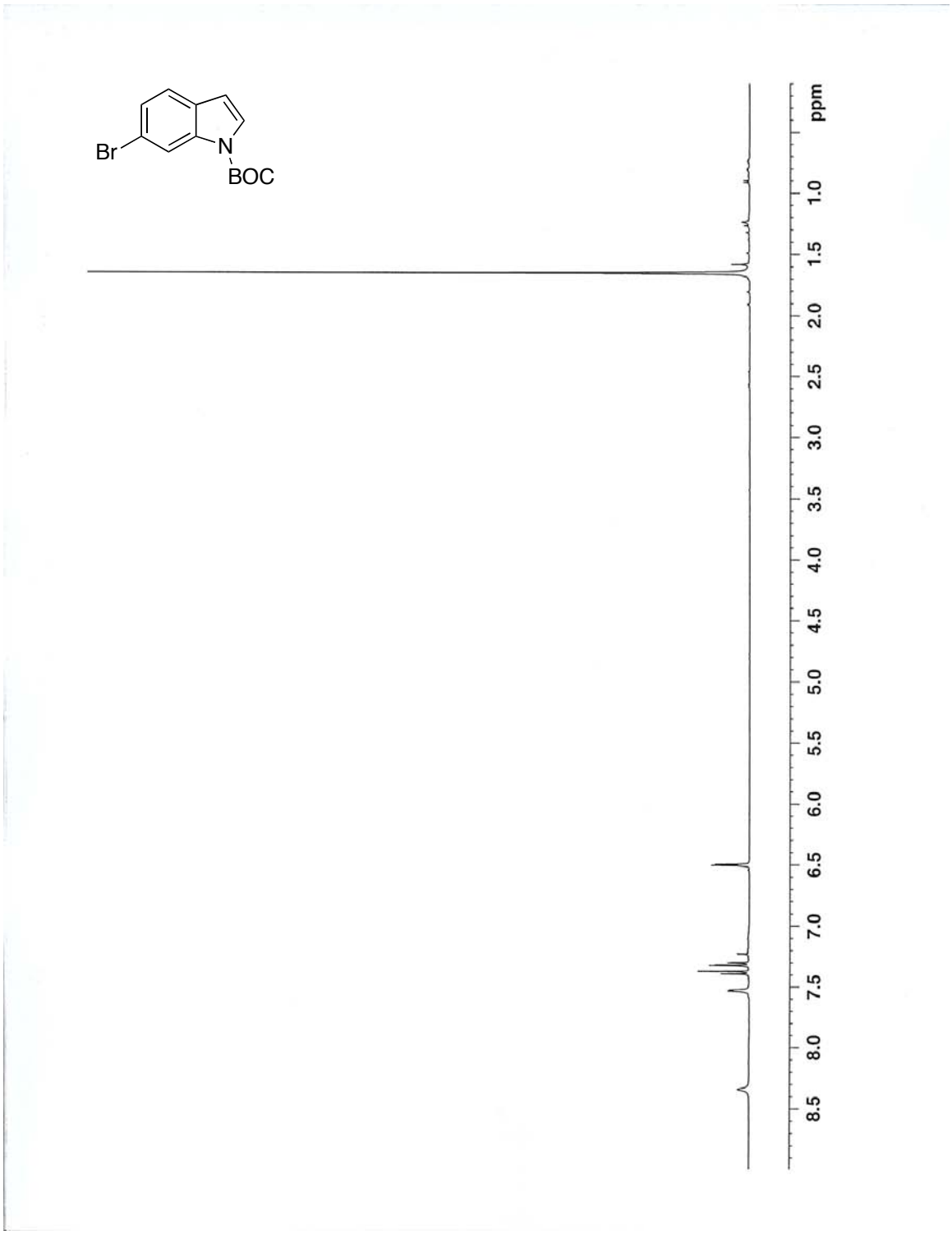
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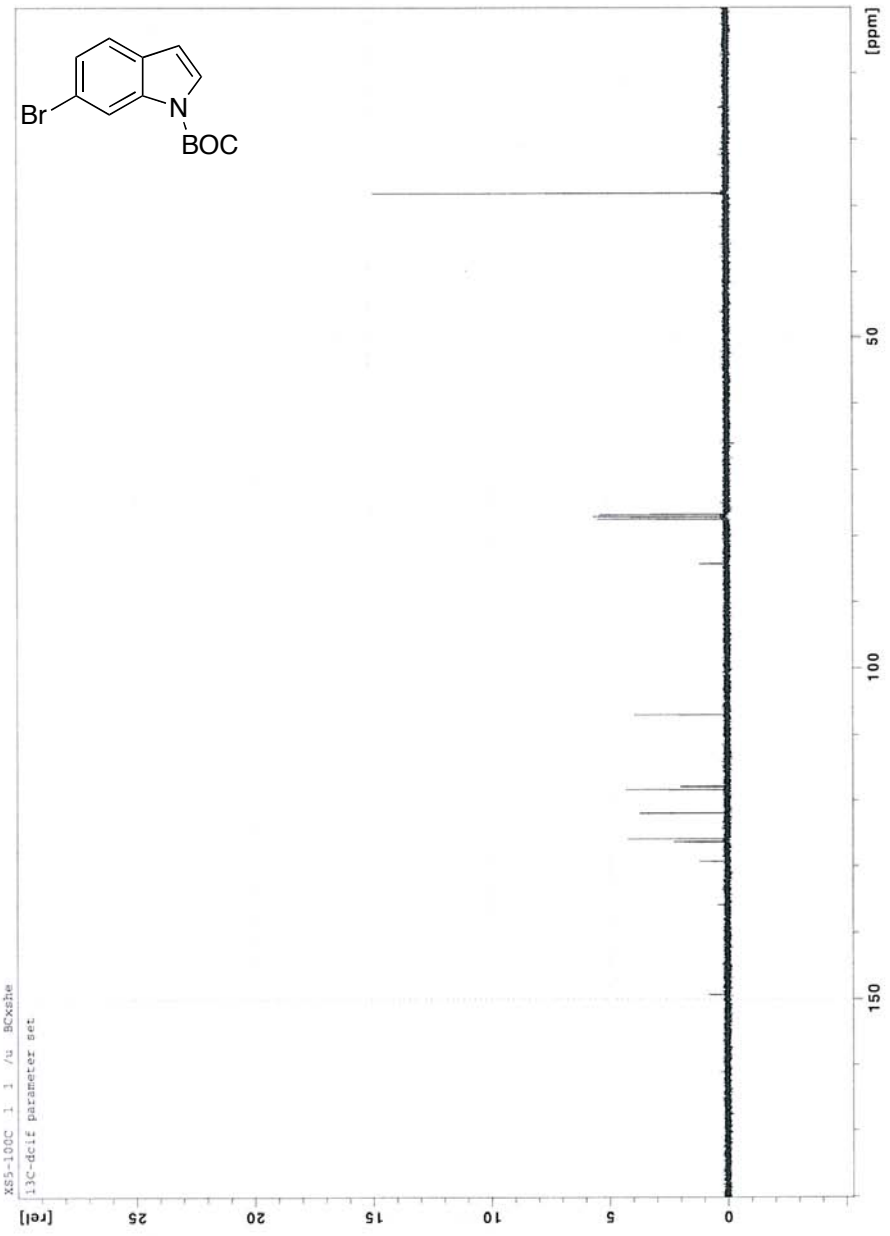
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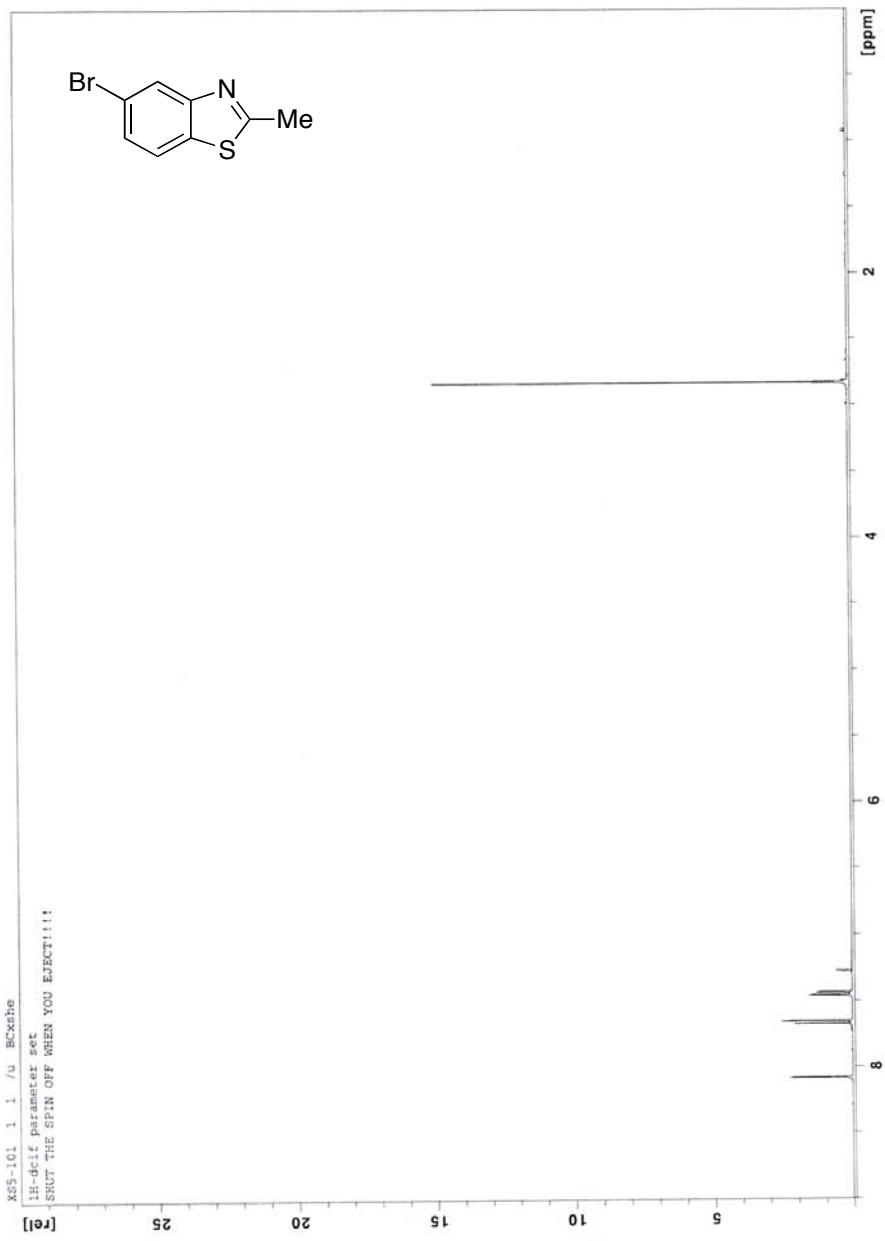
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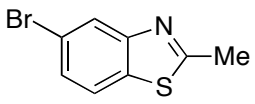
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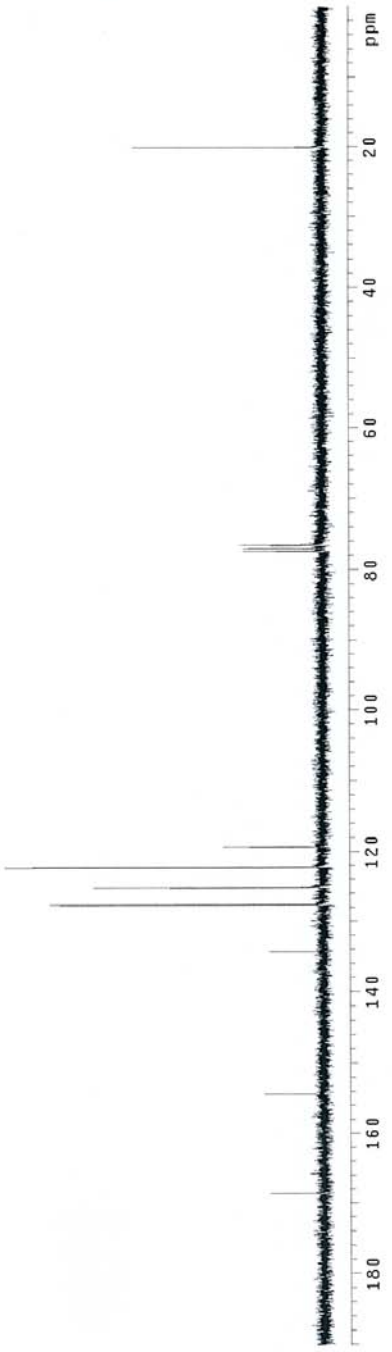
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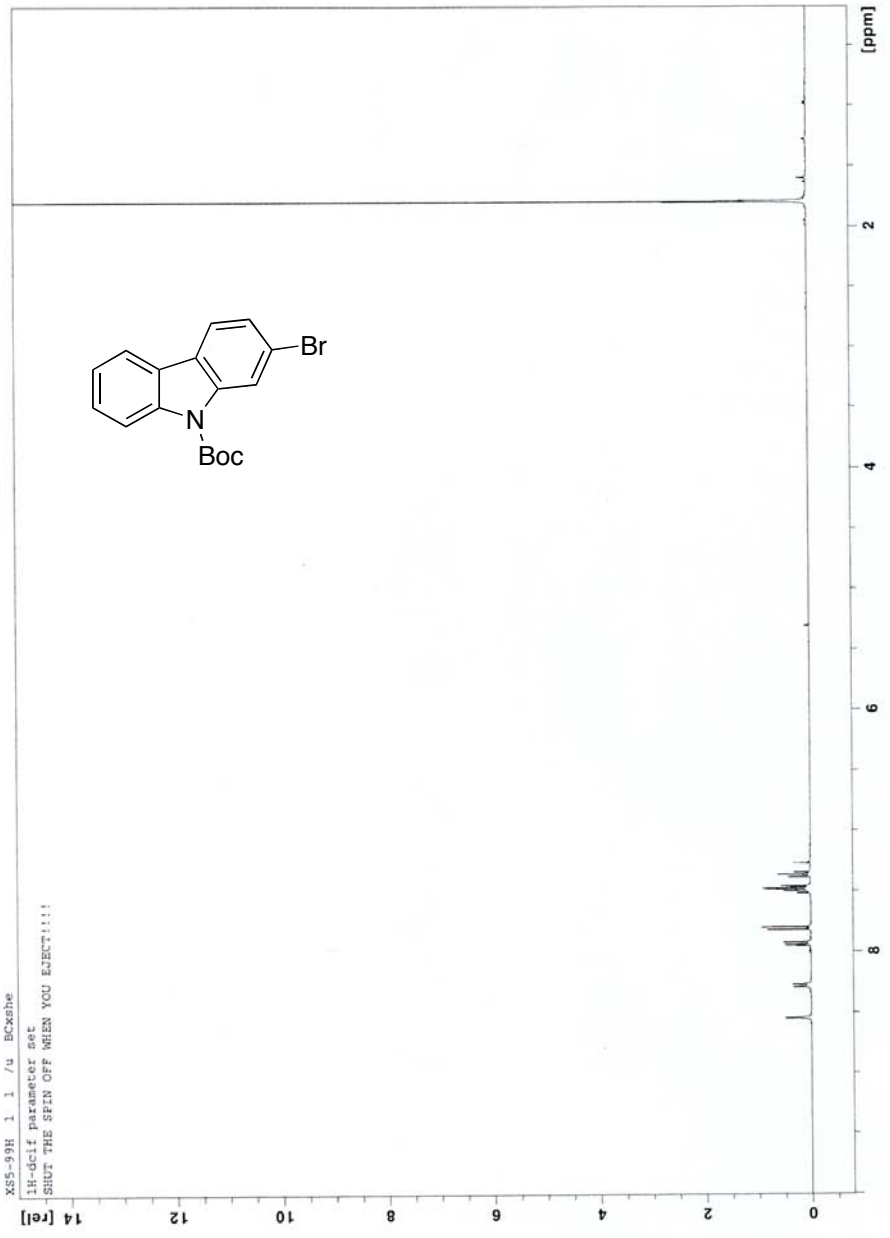
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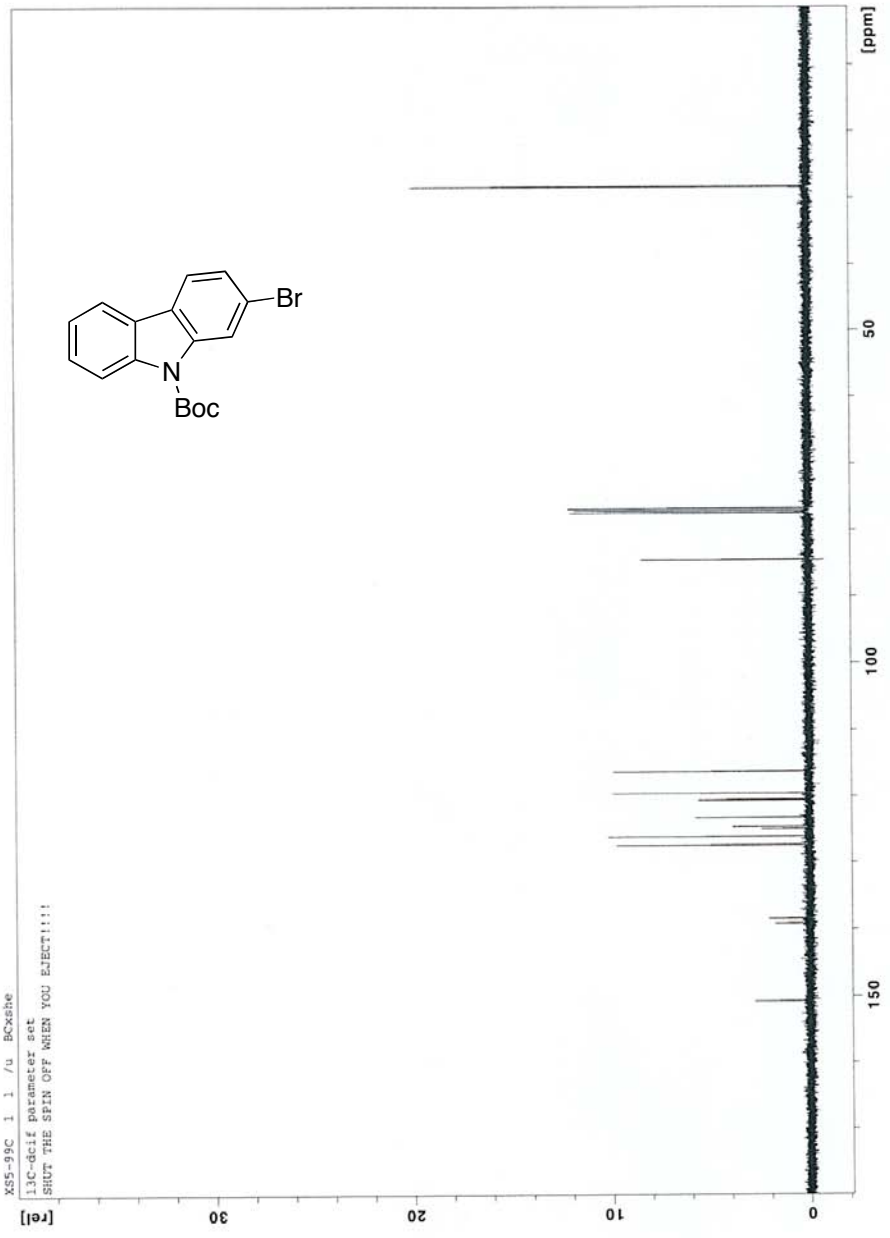
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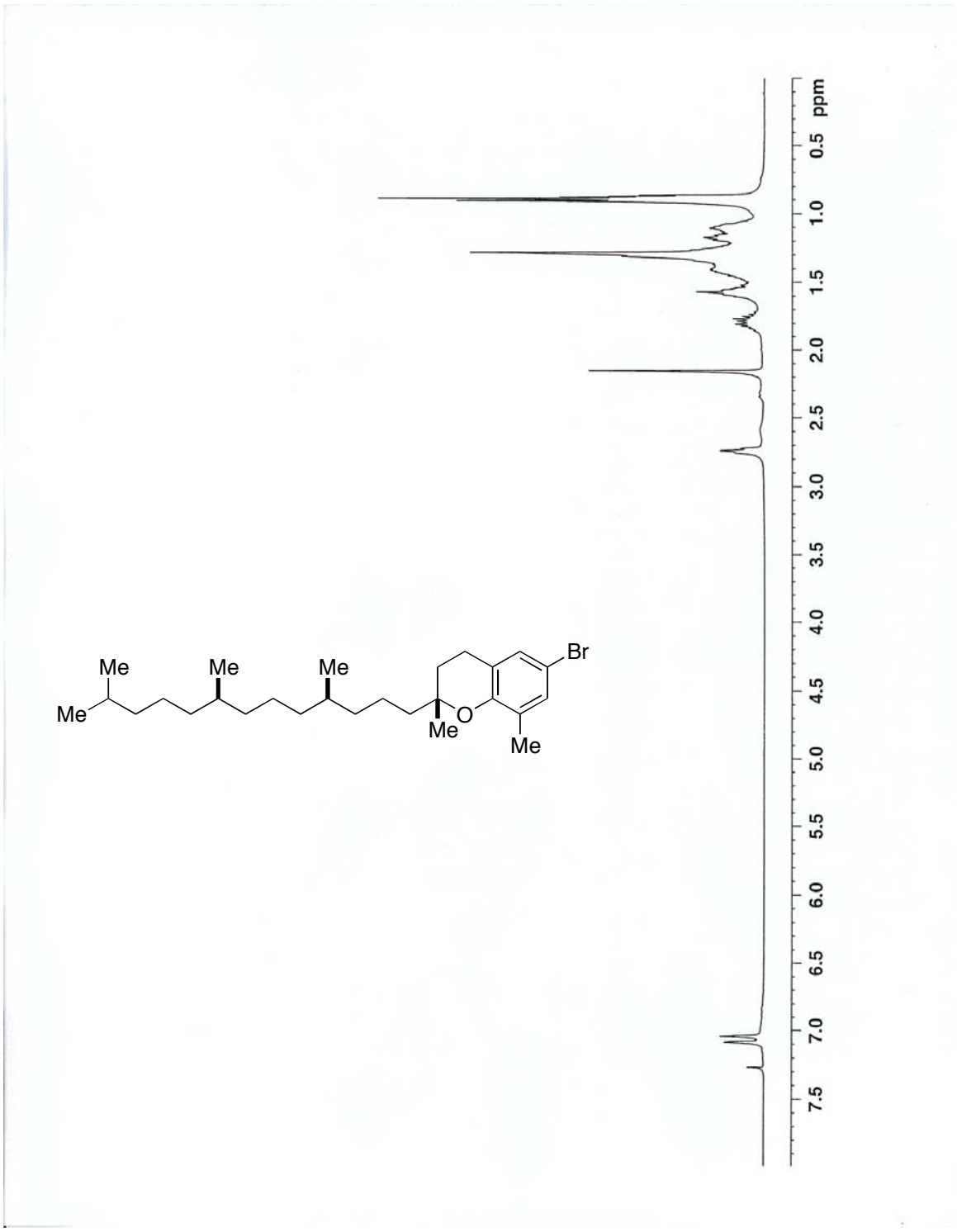
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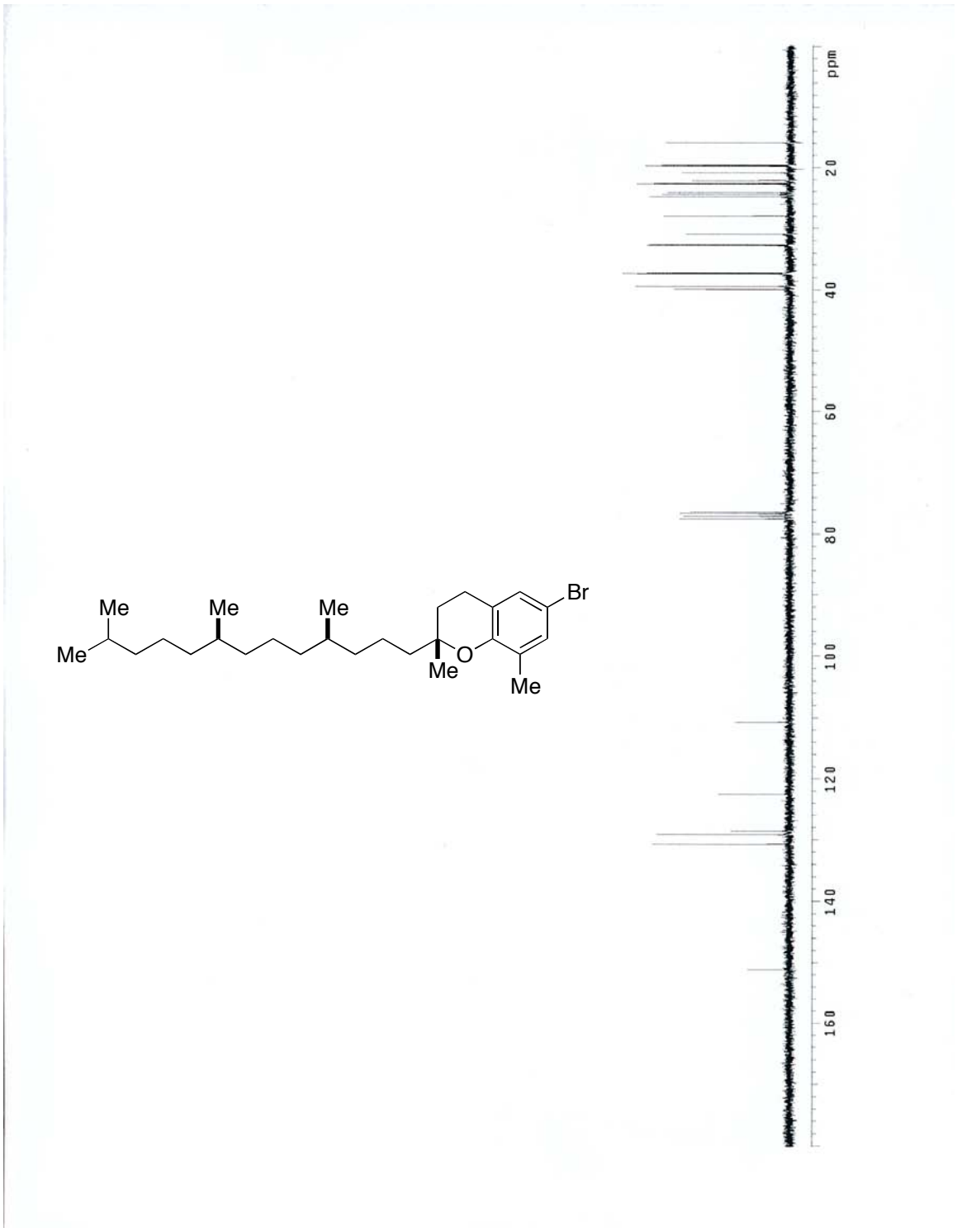
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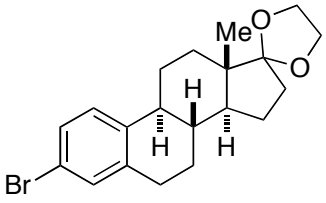
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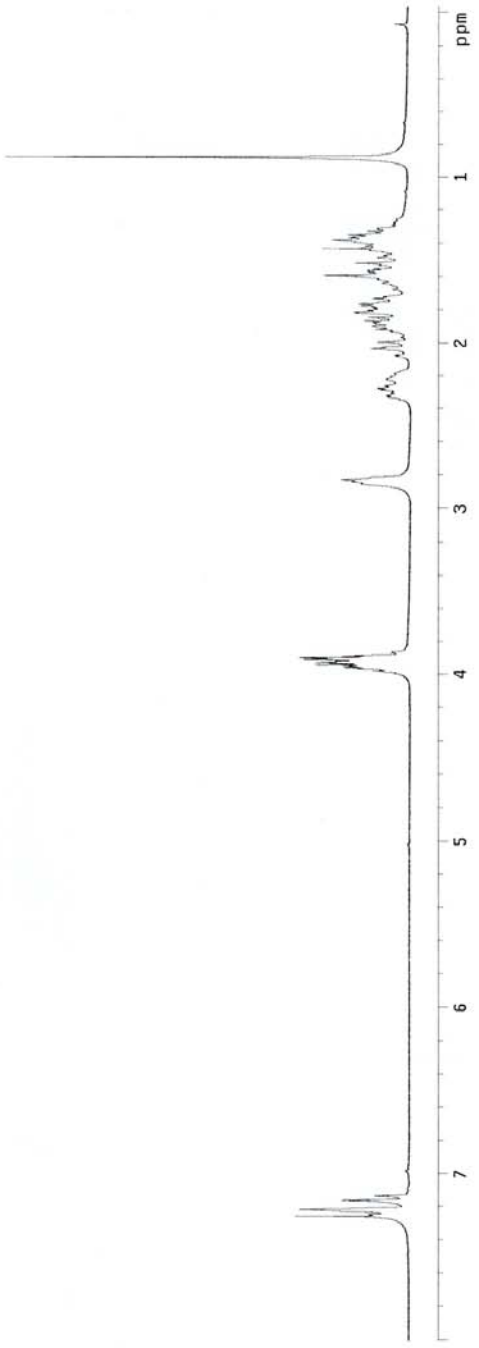
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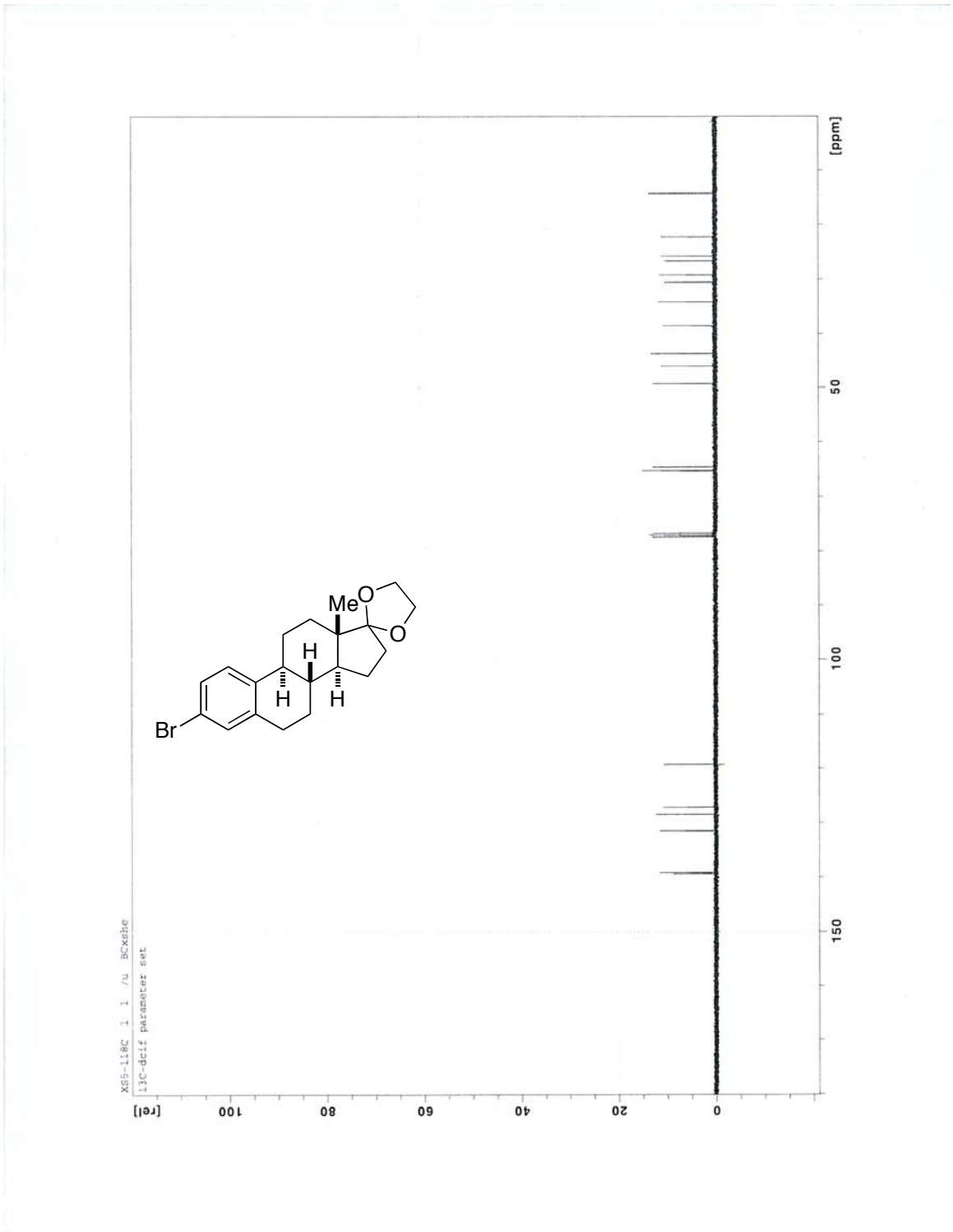
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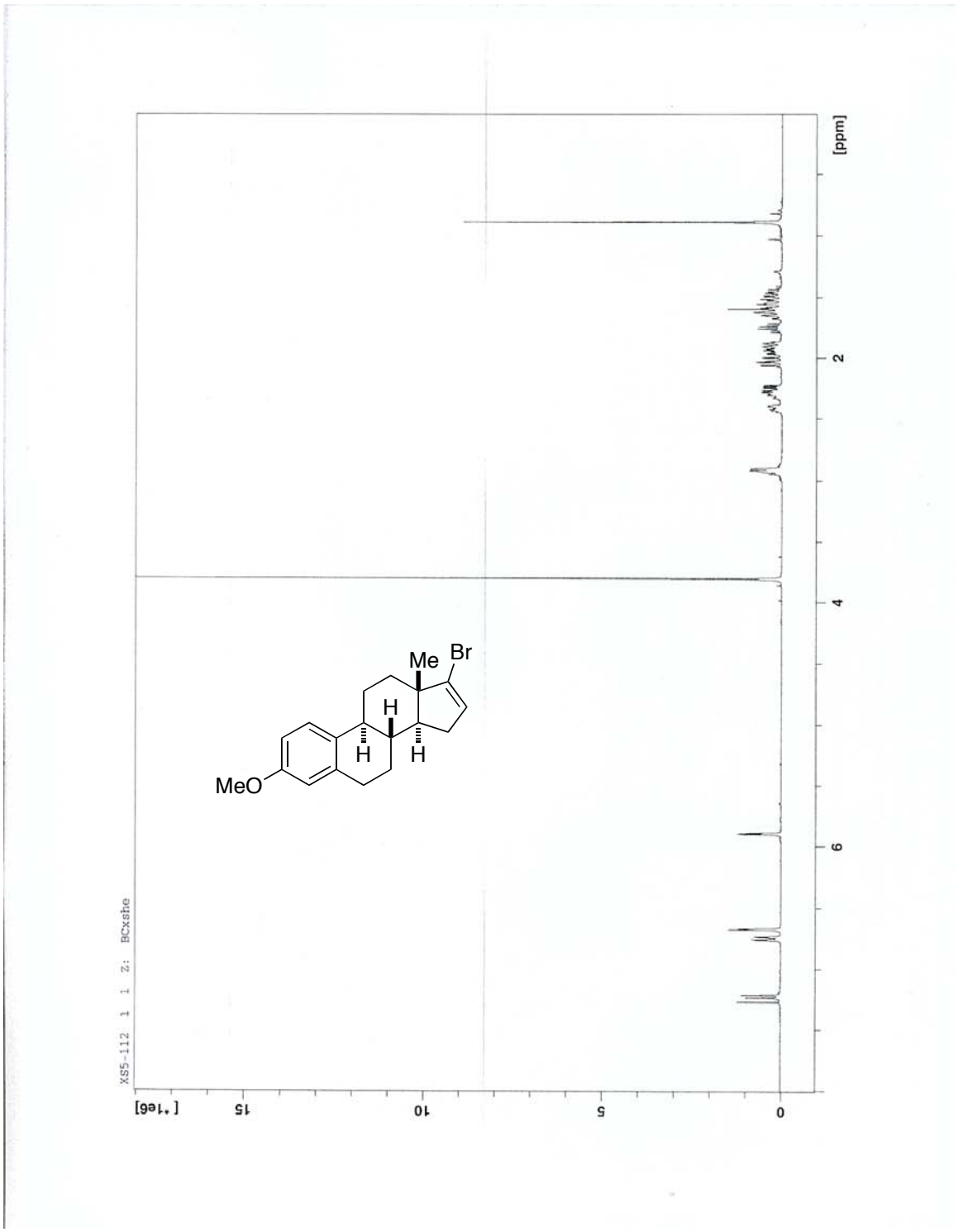
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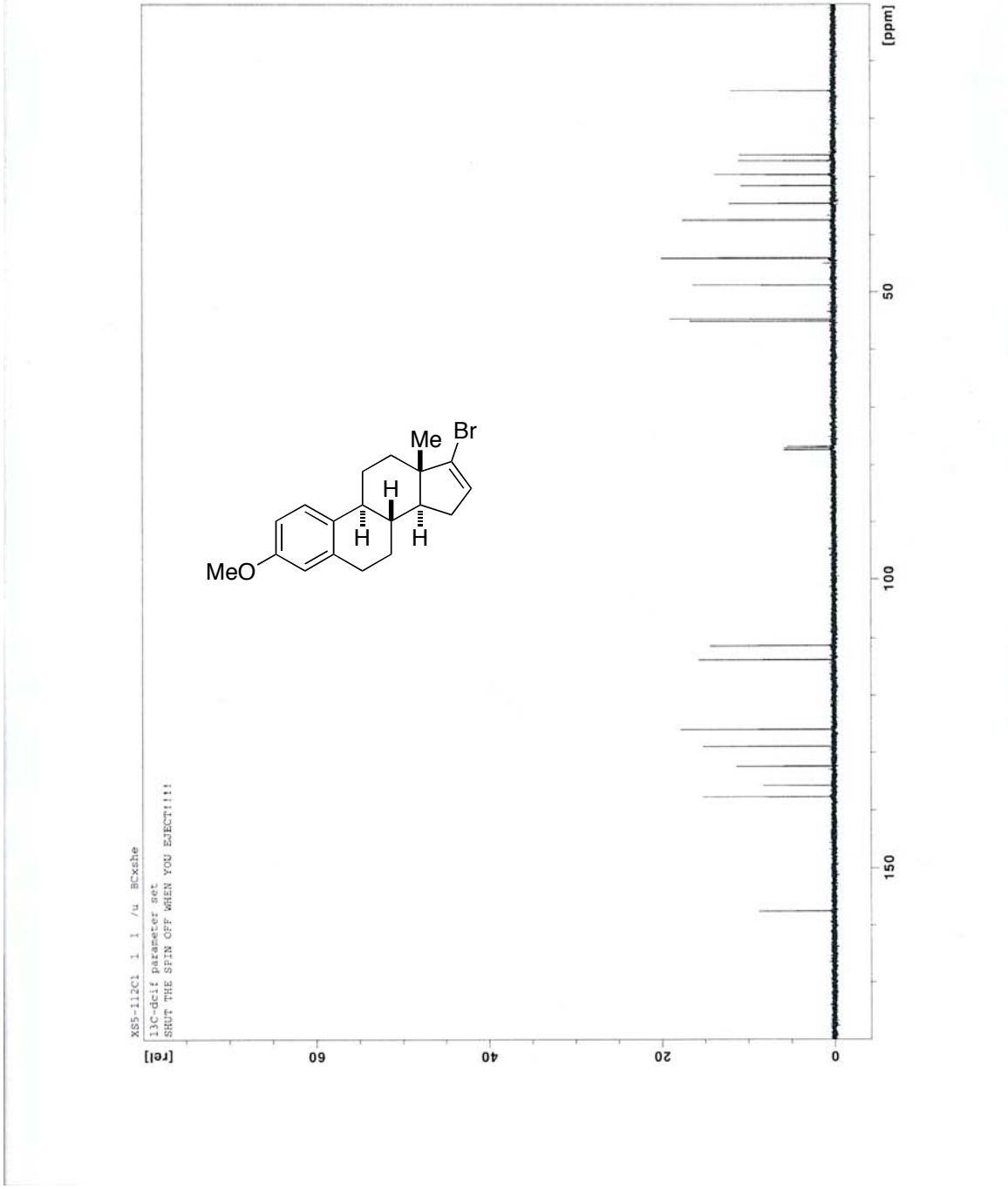
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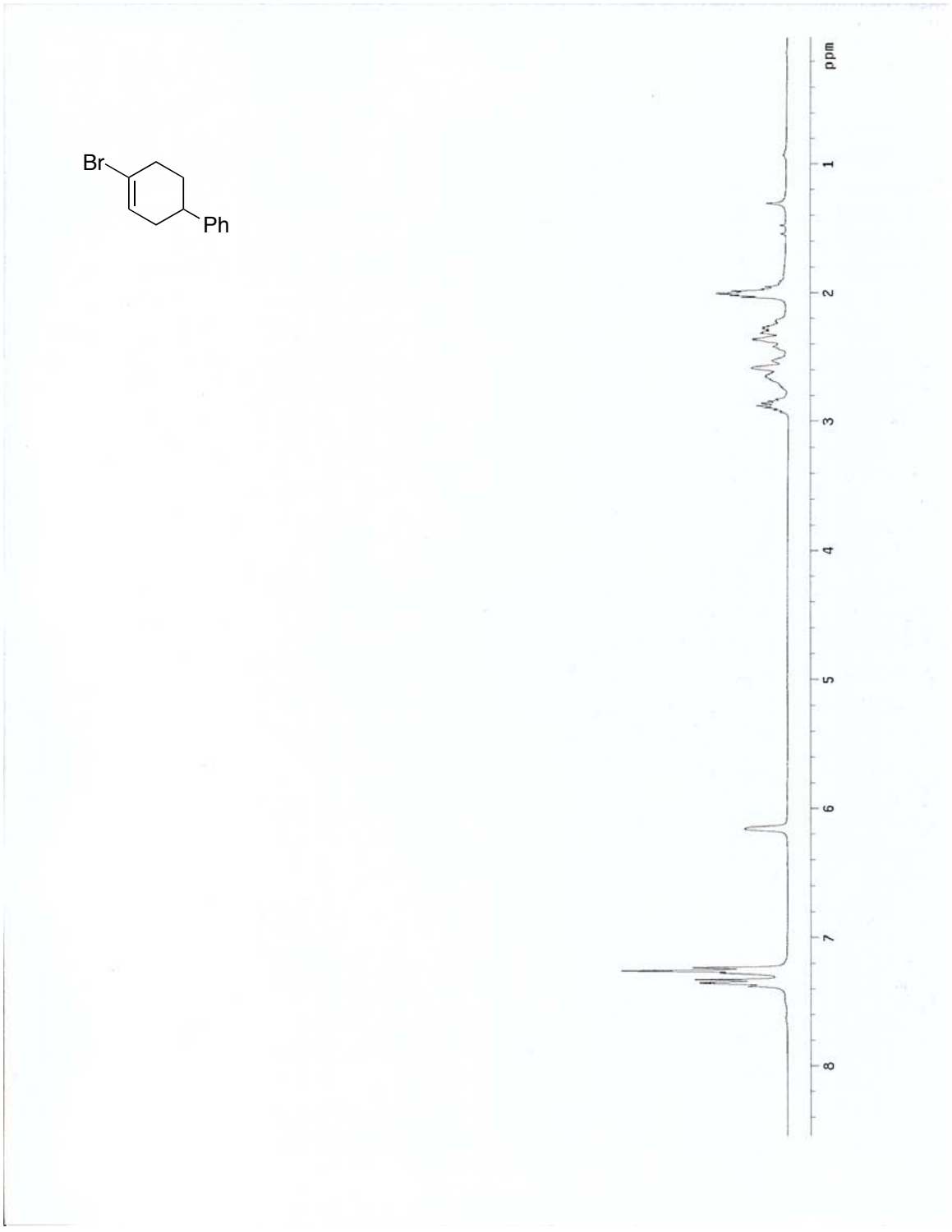
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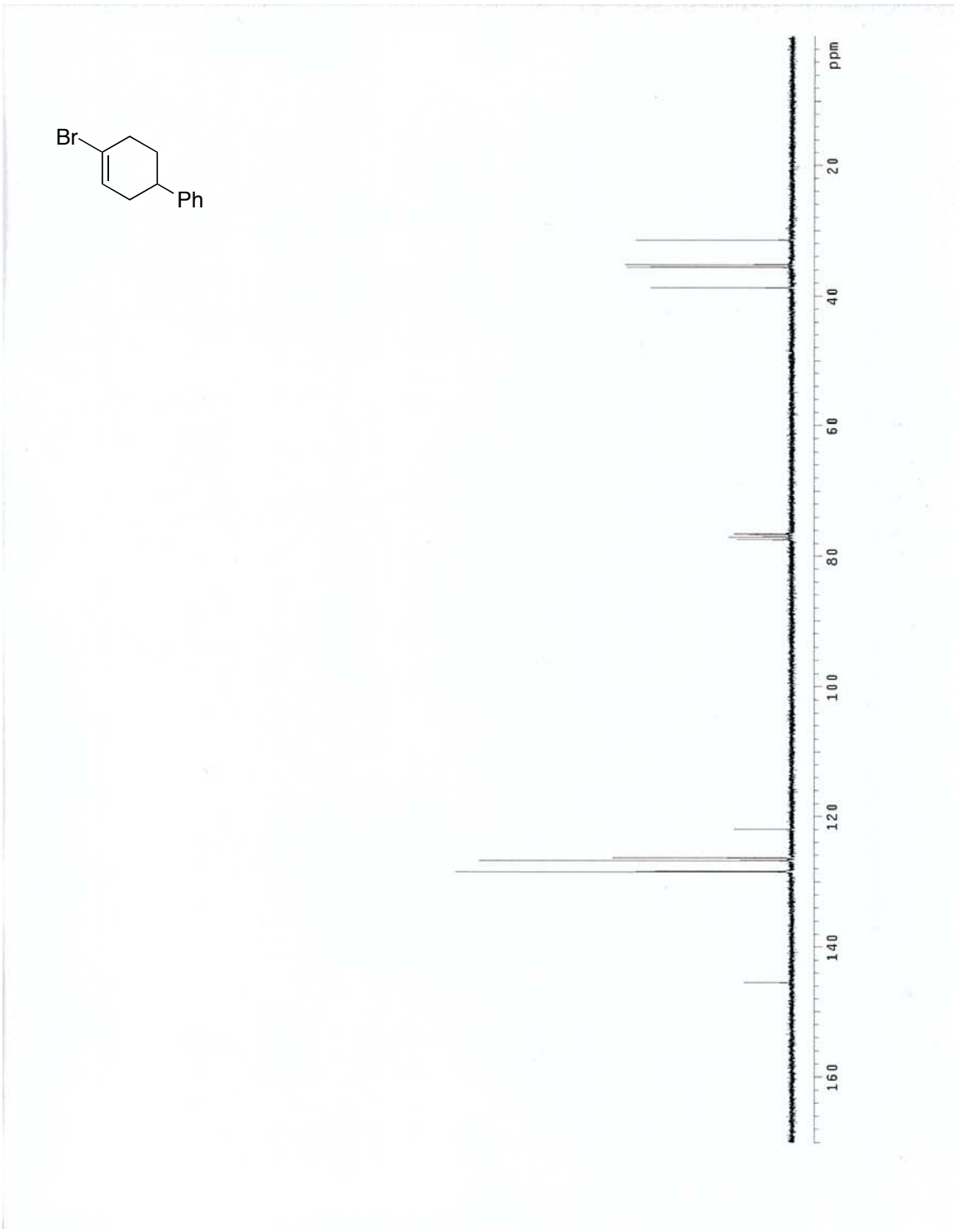
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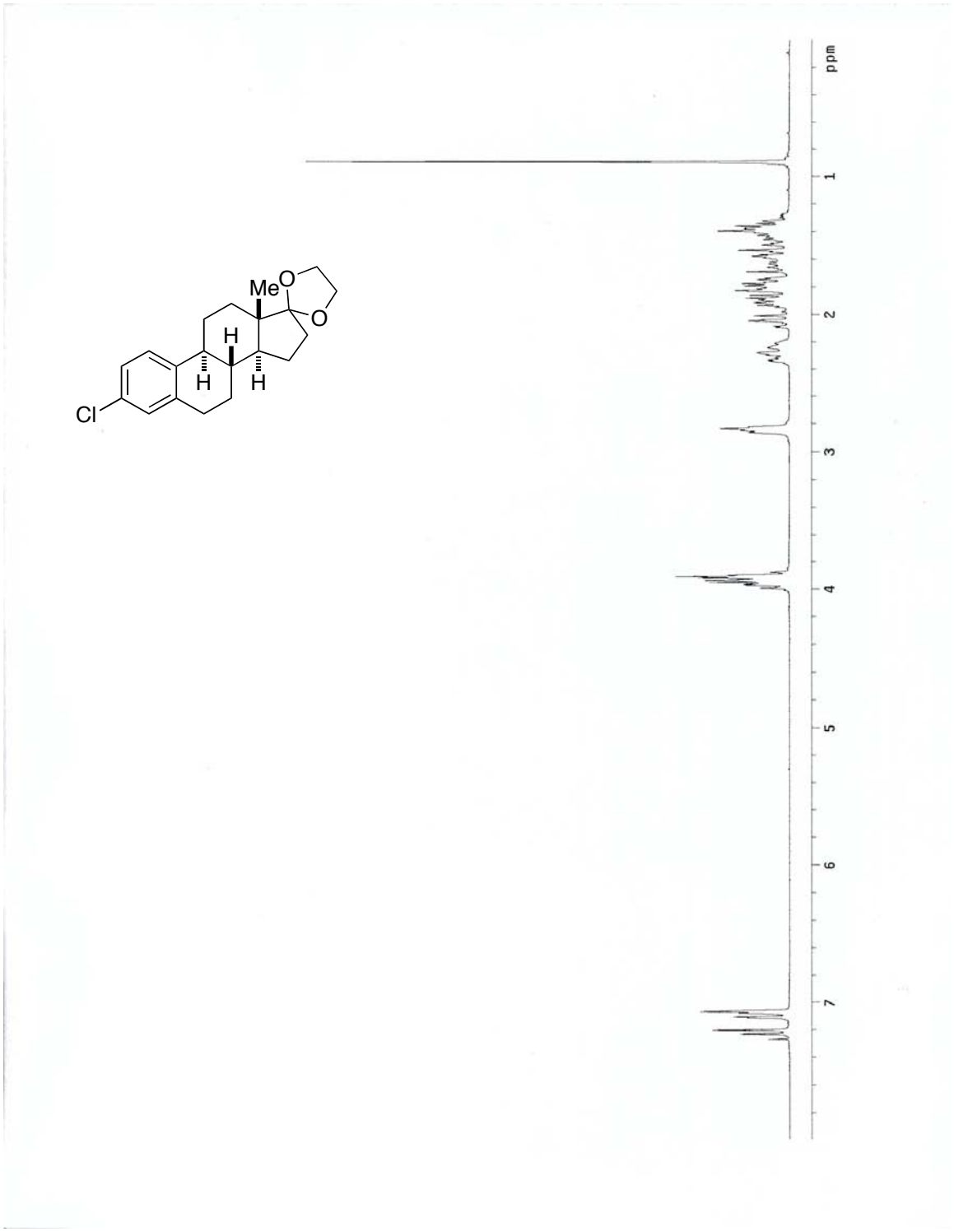
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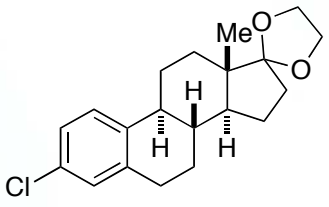
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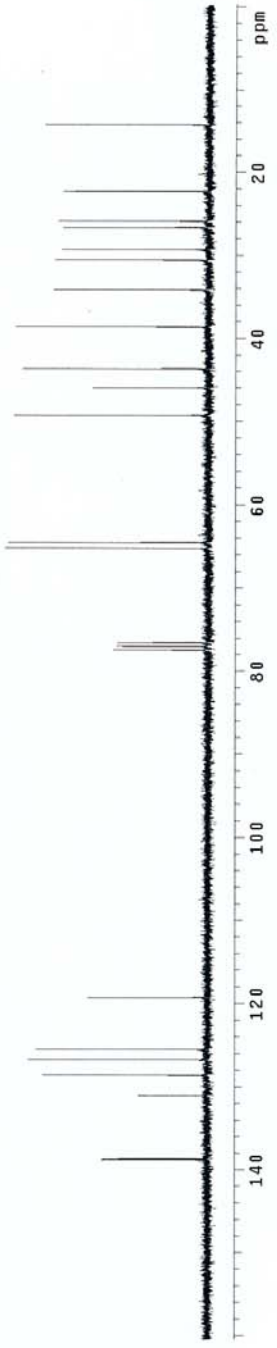
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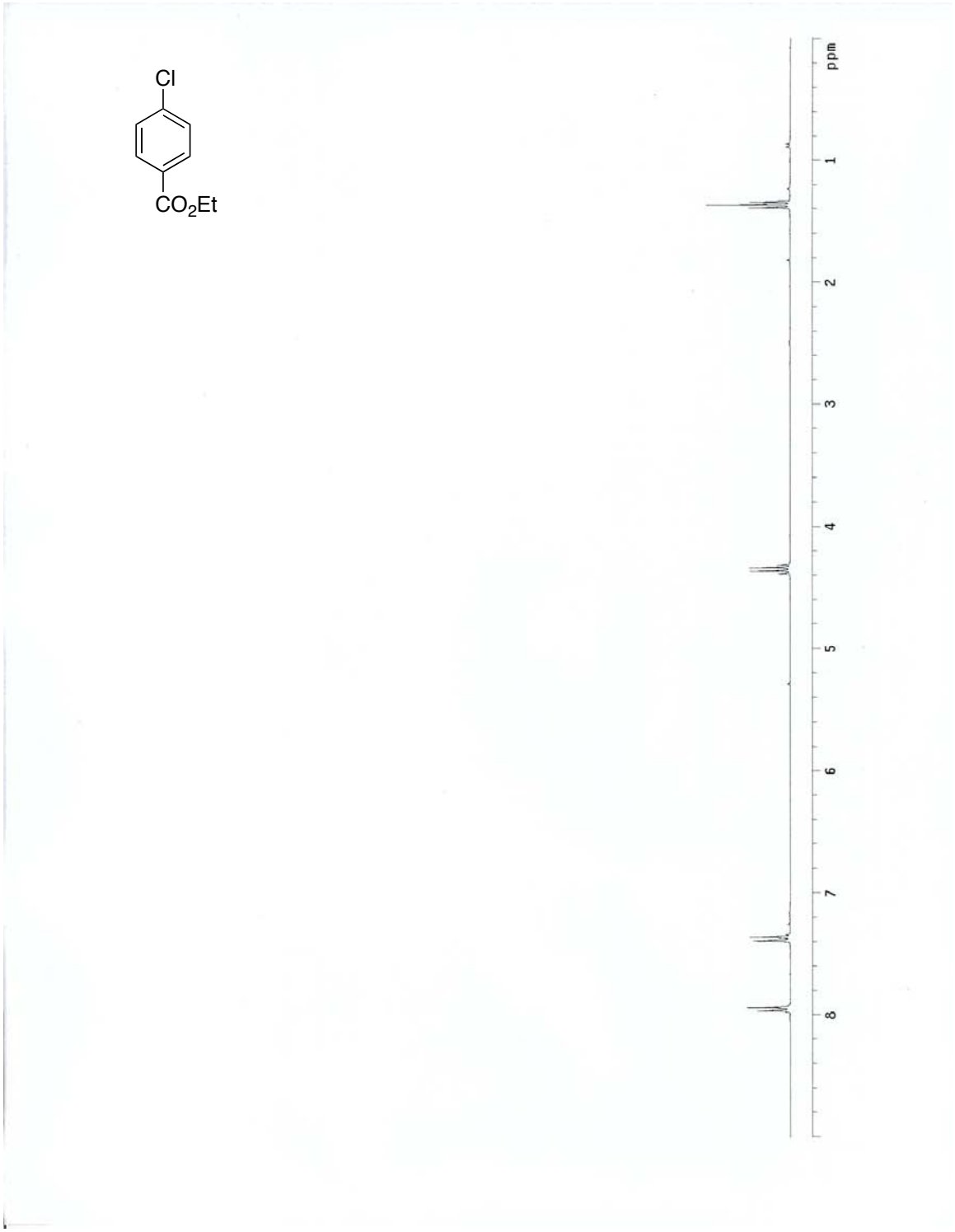
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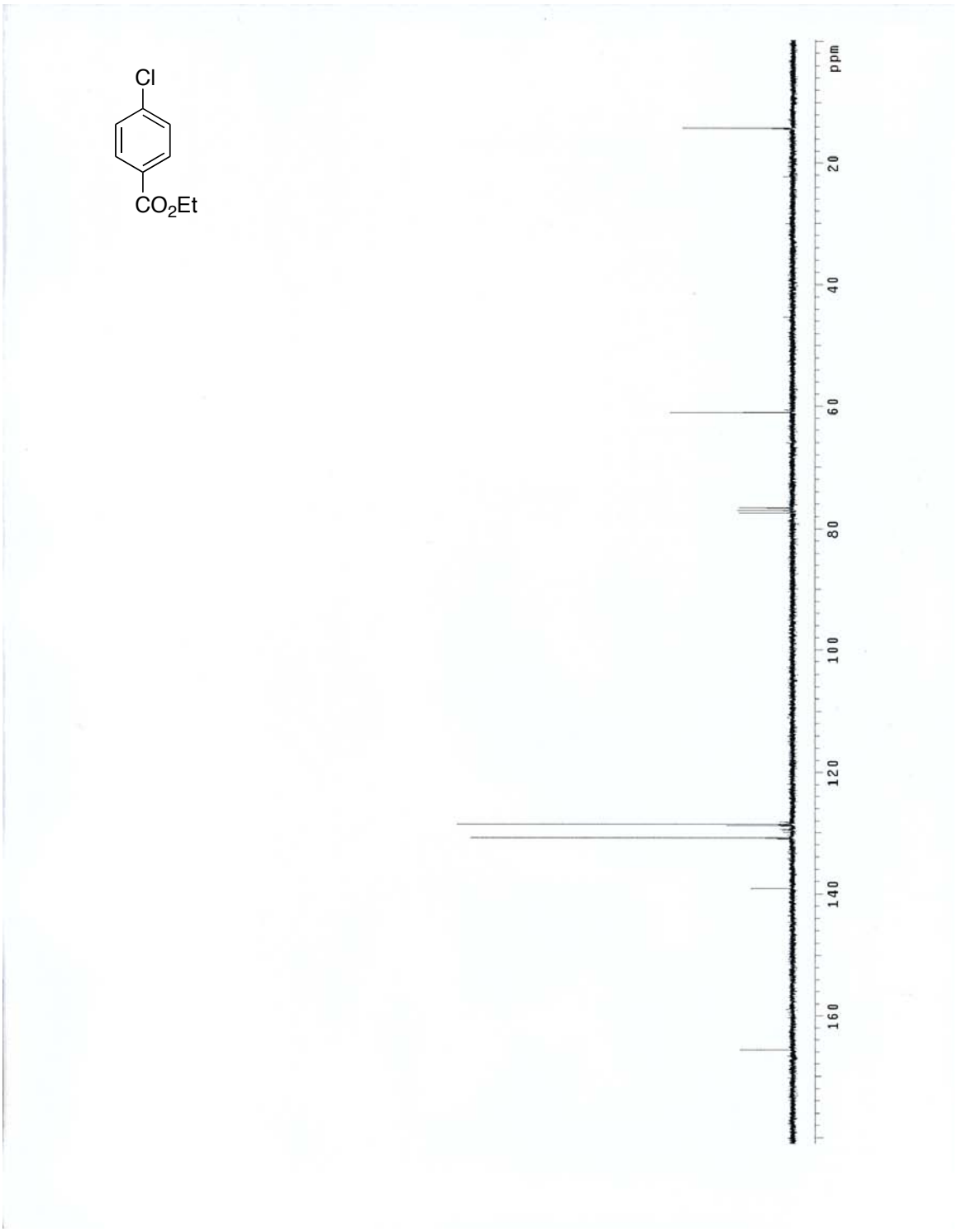
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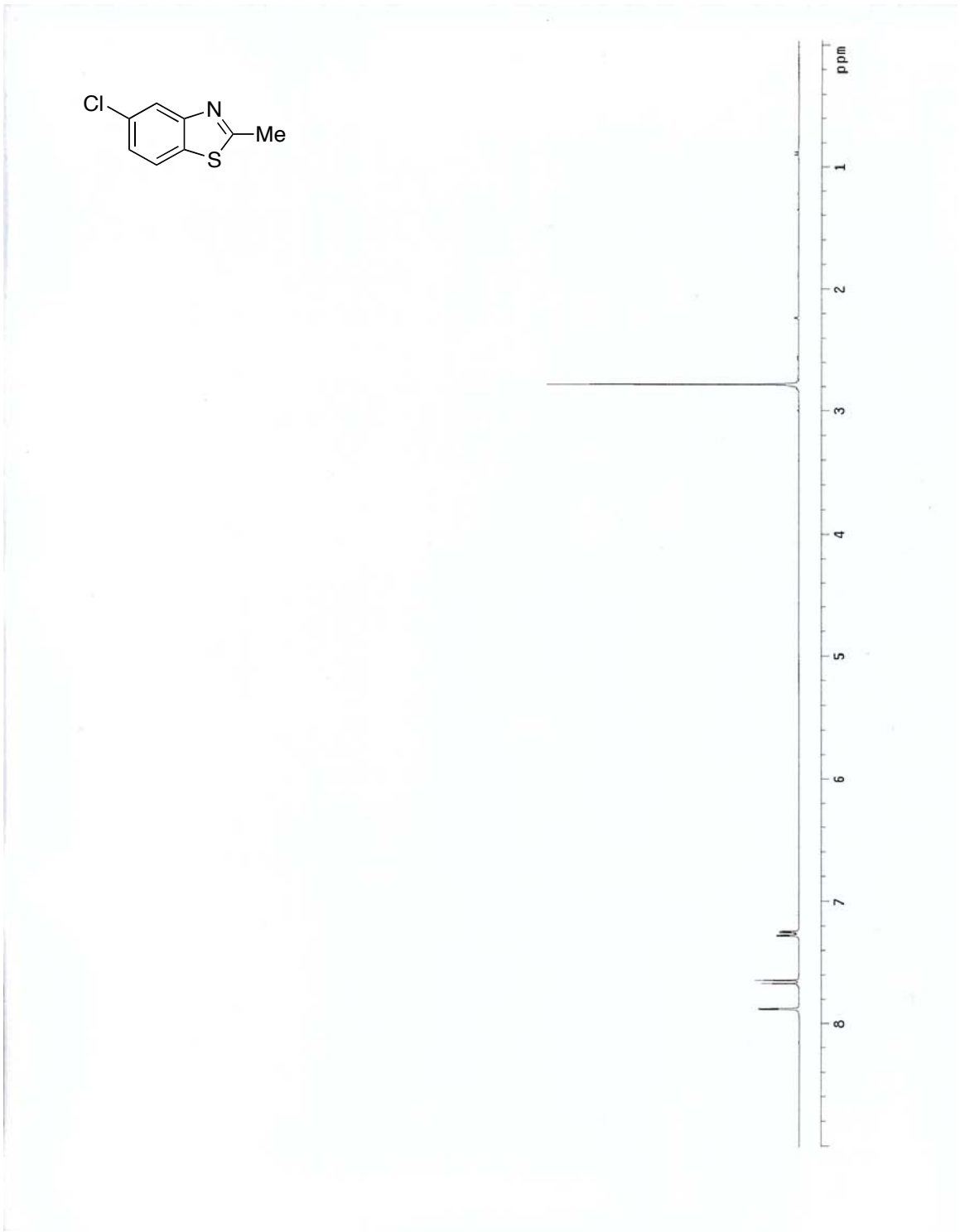
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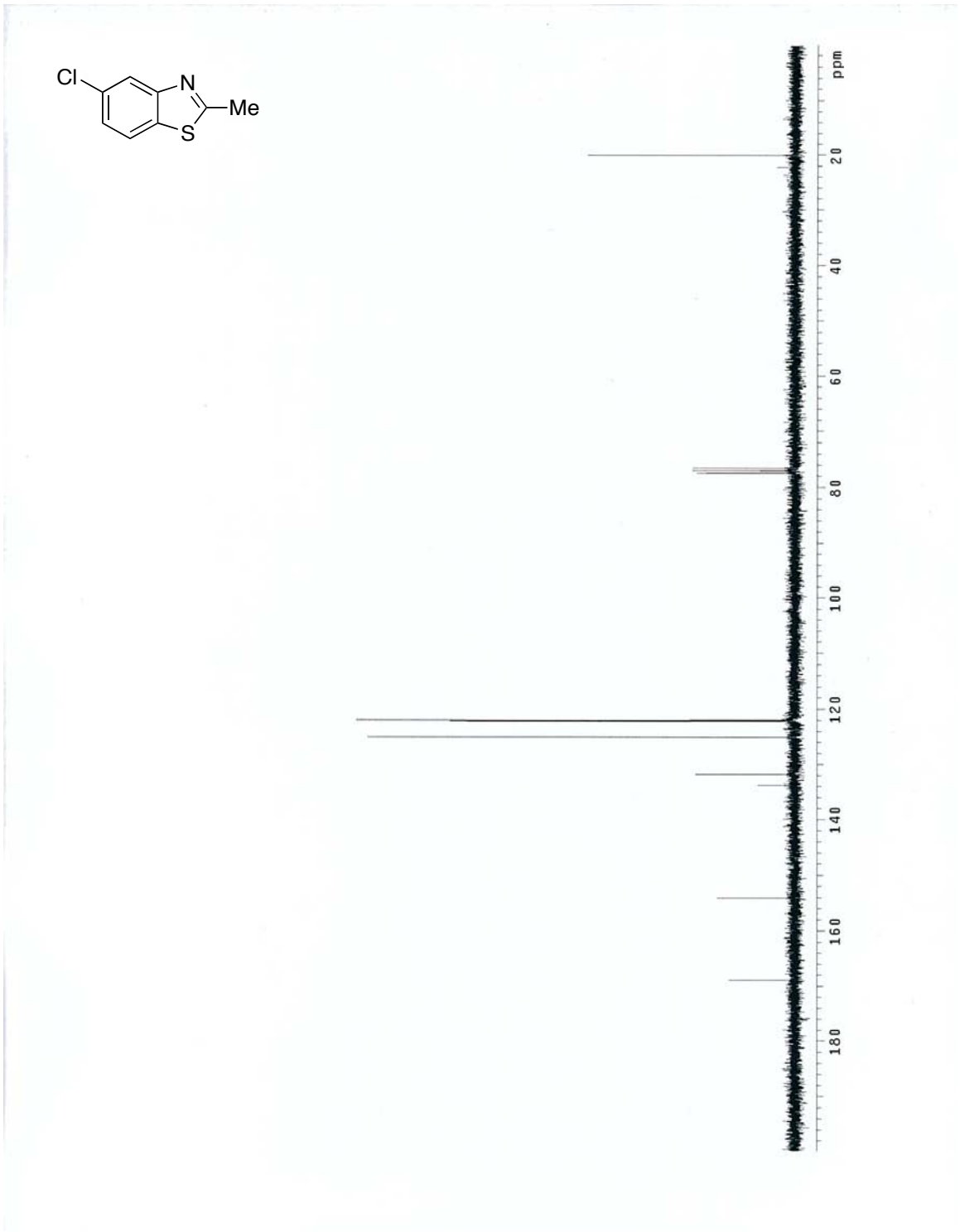
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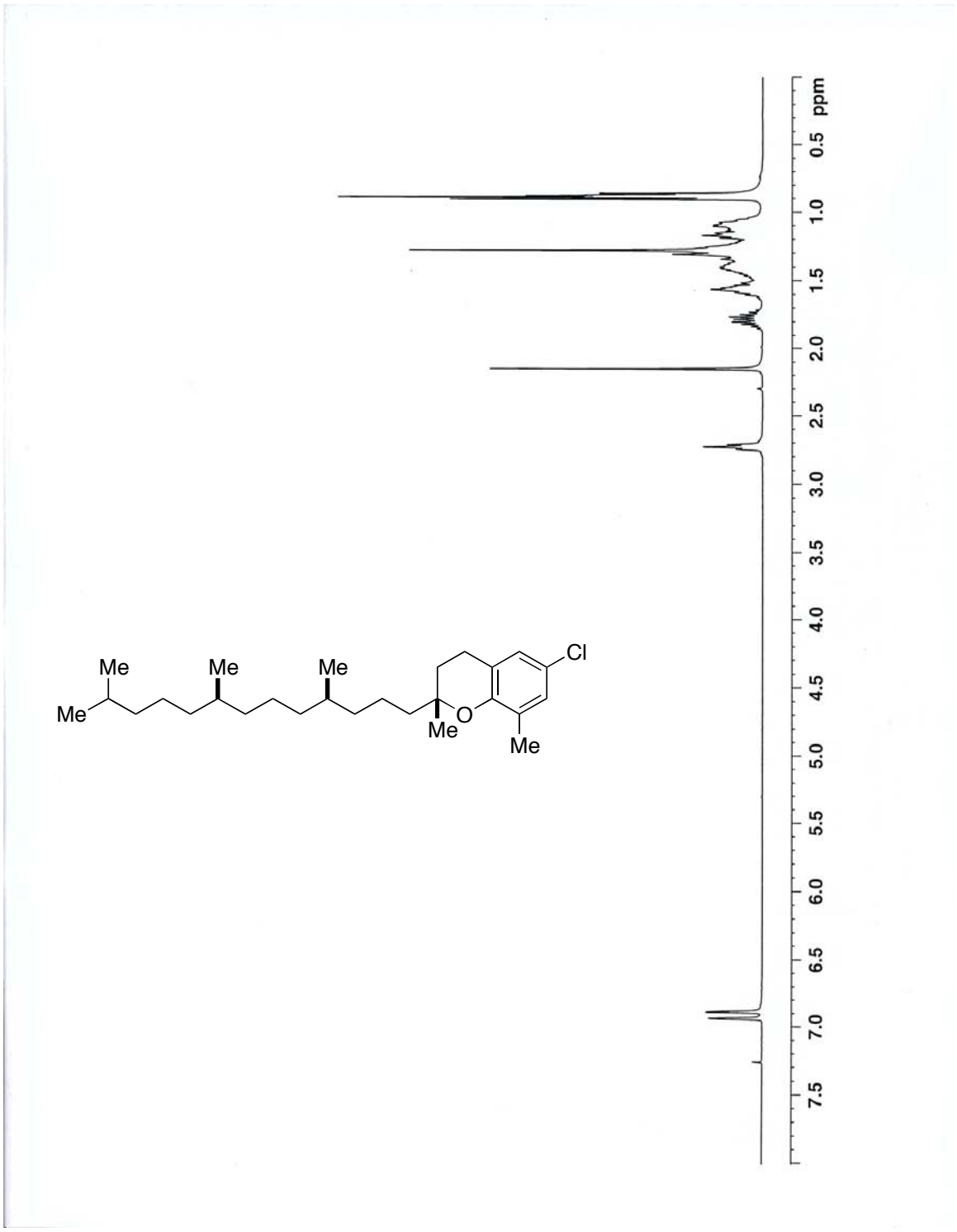
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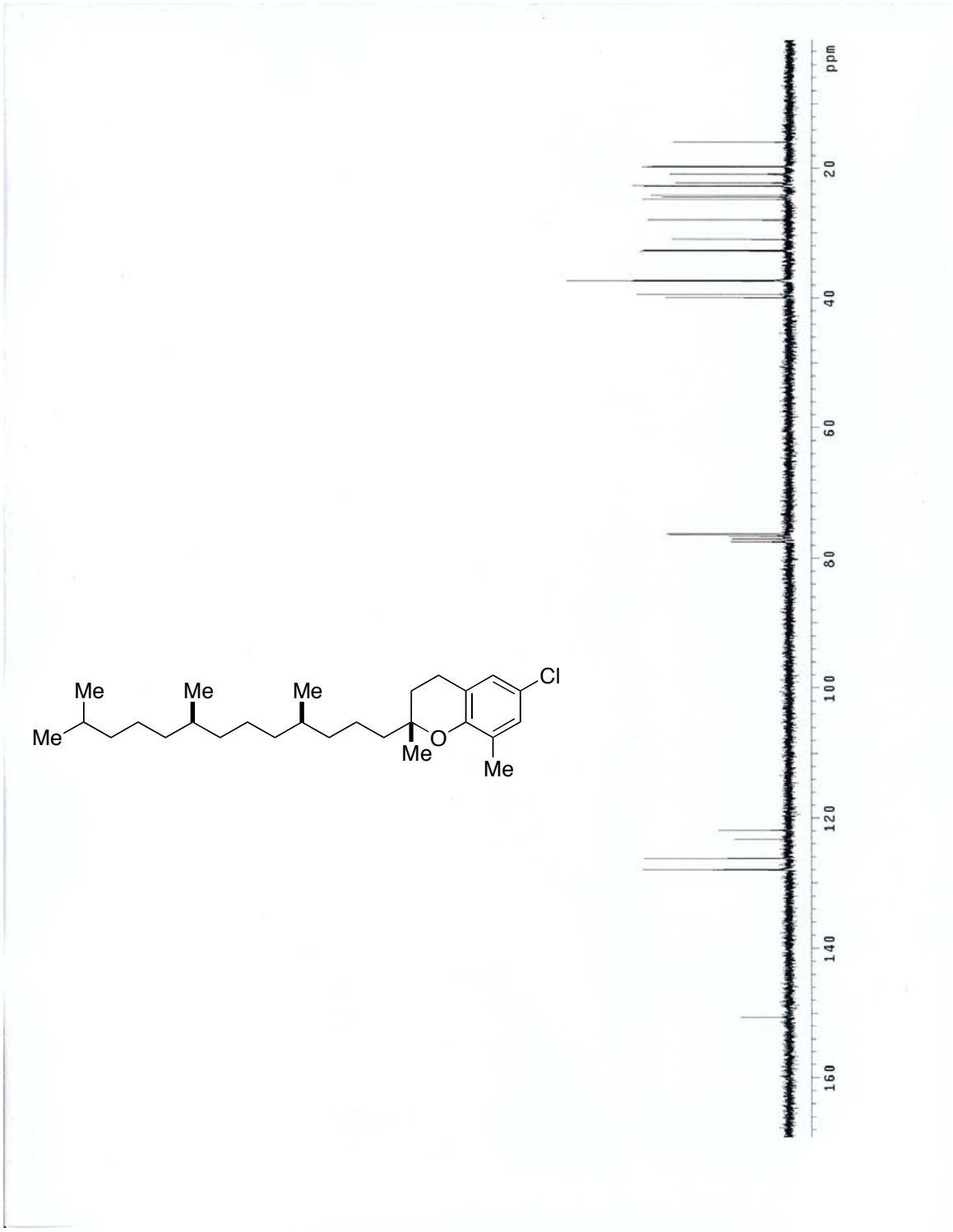
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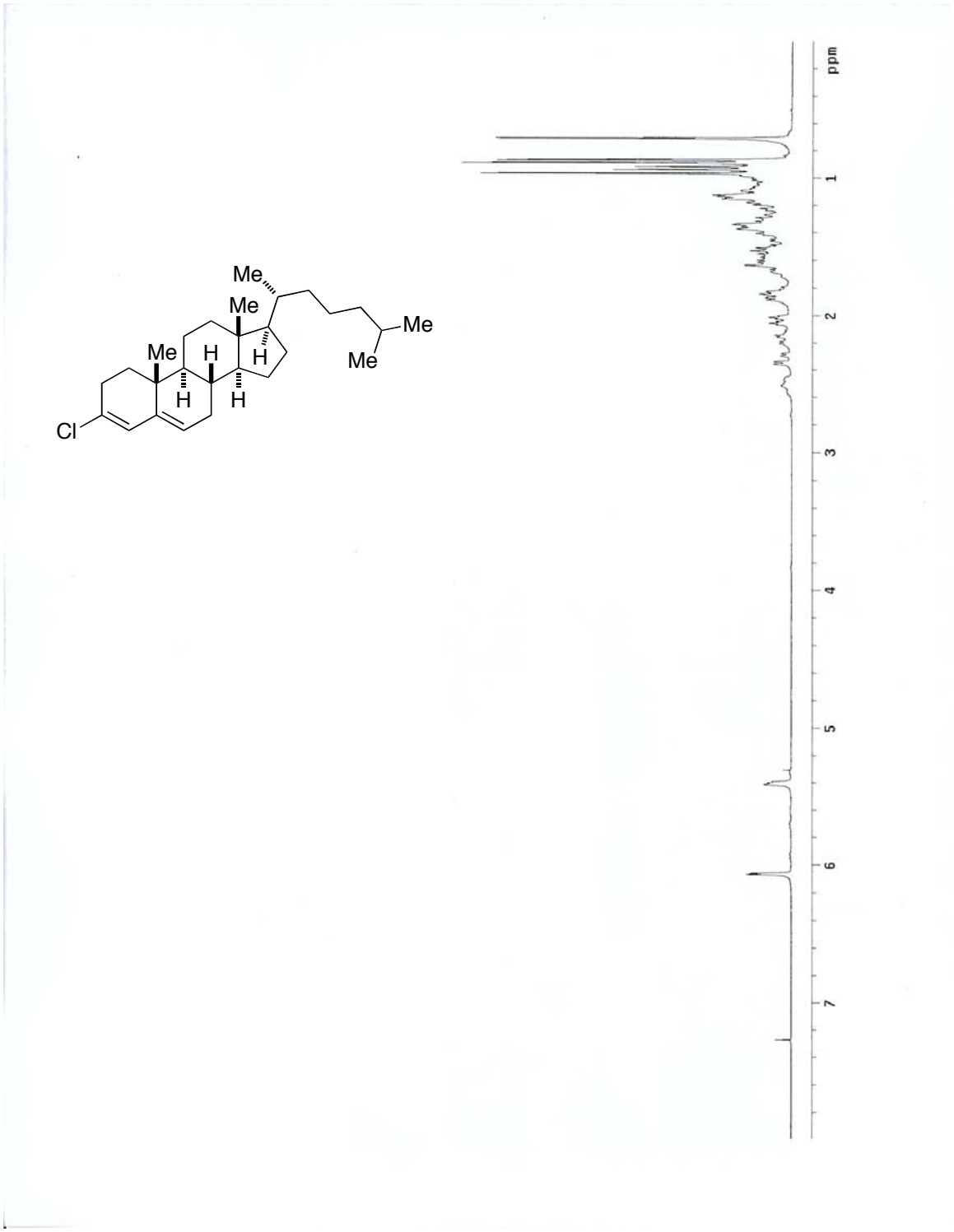
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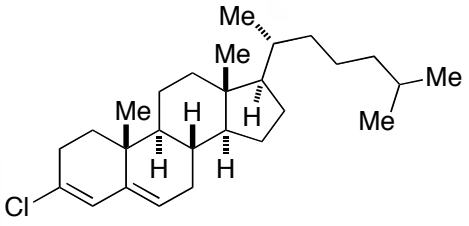
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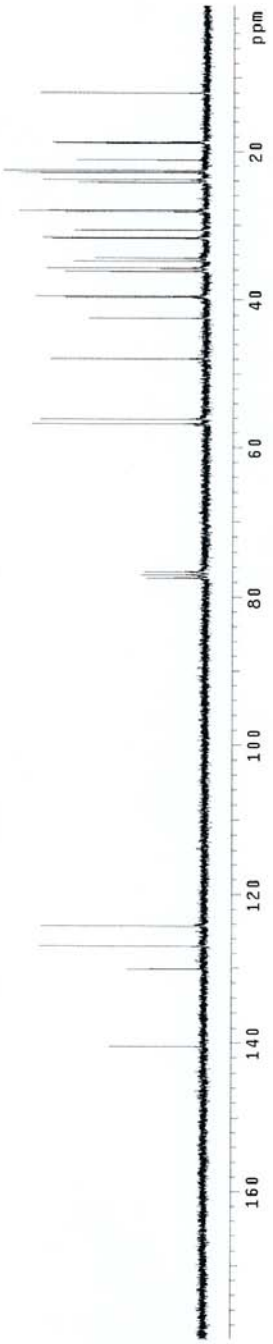
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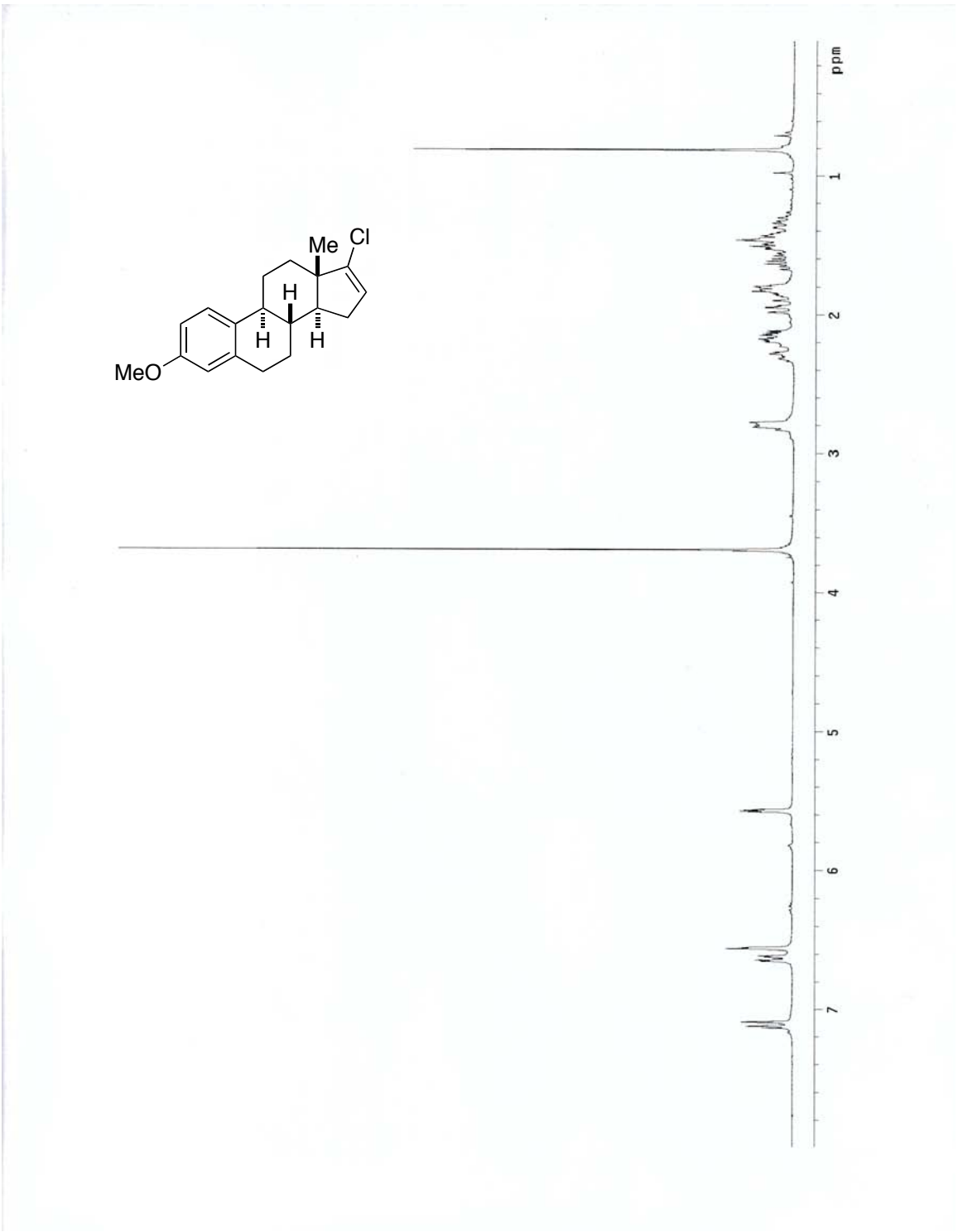
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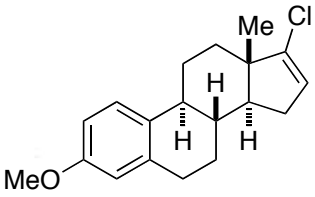
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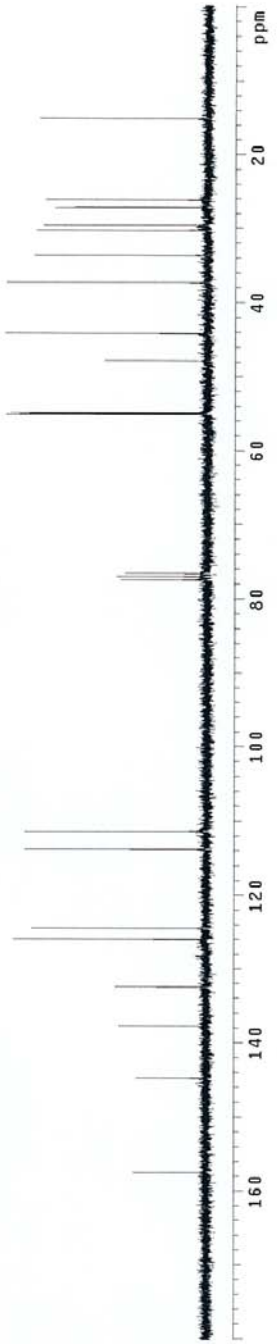
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