Supporting Information

Cp*Rh(III)/Boron Hybrid Catalysis for Directed C–H Addition to β-Substituted α,β-Unsaturated Carboxylic Acids.

Ryo Tanaka,[†] Yuki Hirata,[†] Masahiro Kojima,[†] Tatsuhiko Yoshino,[†,‡,*] Shigeki Matsunaga[†,‡,*]

[†] Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan.

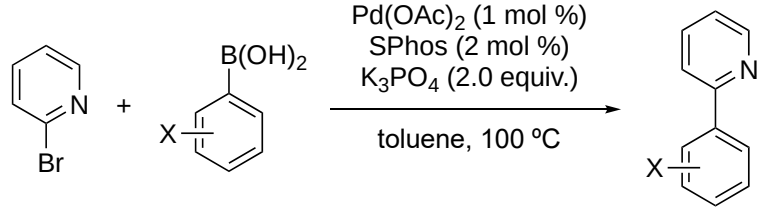
[‡] Global Station for Biosurfaces and Drug Discovery, Hokkaido University, Sapporo 060-0812, Japan.

Table of Contents

General

Reported melting points were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wave numbers (cm^{-1}). NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^{1}H NMR and 98.52 MHz for ^{13}C NMR, JOEL JNM-ECX400 spectrometers, operating at 395.88 MHz for ^{1}H NMR and 99.55 MHz for ^{13}C NMR, JEOL JNM-ECZ400 spectrometers, operating at 399.78 MHz for ^{1}H NMR and 100.53 MHz for ^{13}C NMR and 368.62 MHz for ^{19}F NMR, and JNM-ECA500 spectrometers, operating at 500.16 MHz for ^{1}H NMR and 125.77 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^{1}H NMR), $CHCl_3$ (7.26 ppm for ^{1}H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR), and benzotrifluoride (-62.75 ppm for ^{19}F NMR) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Silica gel column chromatography was performed with Kanto Silica gel 60 N (40-50 mesh) or Wakogel® C-200. Dichloromethane (CH_2Cl_2) and toluene were purified by Glass Contour solvent purification system. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) were distilled from CaH_2, purged with argon for over 30 min, and stored over activated molecular sieves 4A under argon atmosphere before use. Commercially available 1,2-dichloroethane (DCE, KANTO CHEMICAL Co.,INC., dehydrated -Super-), 1,4-dioxane (FUJIFILM Wako Pure Chemical Corporation, super dehydrated grade), and dimethylformamide (DMF, FUJIFILM Wako Pure Chemical Corporation, super dehydrated grade) were used without further manipulation unless otherwise stated. Caboxylic acids **2a**, **2c**, **2d**, and **2e** were synthesized according to the literature.[1,2] Carboxylic acid **2b** was commercially available and distilled under reduced pressure before use. All other reagents were commercially available and used as received.

General procedure for the synthesis of 2-arylpyridine derivatives

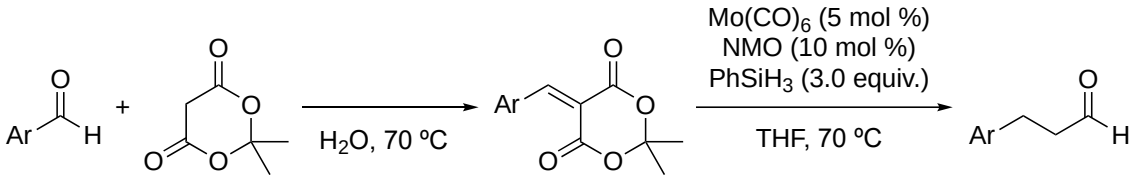


S1 **S2** **1**

To a flamed dried test tube were added 2-bromopyridine **S1**, arylboronic acid **S2** (2.0 equiv.), $Pd(OAc)_2$ (1 mol %), SPhos (2 mol %), K_3PO_4 (2.0 equiv.), and toluene (0.4 M). The resulting mixture was heated at 100 ºC. After 2-bromopyridine was disappeared (confirmed by TLC

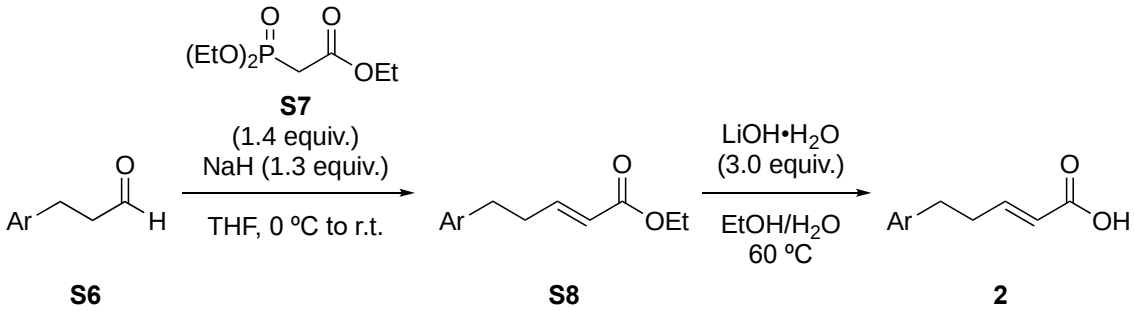
analysis), the reaction mixture was cooled to room temperature and H_2O was added. The mixture was extracted with AcOEt, and the organic layer was washed with H_2O and brine. After drying with Na_2SO_4, filtration, and evaporation, the crude mixture was purified by SiO_2 column chromatography (hexane/AcOEt) to afford the corresponding product **1**. The spectroscopic data of **1** were matched with those in previously reports.[3–8]

General procedure for the synthesis of α,β-unsaturated carboxylic acids



S6 was prepared from corresponding aldehyde **S3** according to the literature.[9] To a recovery flask were added aldehyde **S3** (1.0 equiv.), Meldrum's acid **S4** (1.1 equiv.), and H_2O (0.5 M). The mixture was heated at 70 ºC for 4 h. After cooling to room temperature, the precipitates were collected by filtration and washed by MeOH to give the corresponding product **S5**.

To a flame dried recovery flask were added **S5** (1.0 equiv.), $Mo(CO)_6$ (5 mol %), NMO (10 mol %), and THF (0.2 M). To the resulting solution was added $PhSiH_3$ (3.0 equiv.) and the reaction mixture was heated at 70 ºC overnight. After cooling to room temperature, H_2O was added. The mixture was extracted with AcOEt, and the organic layer was washed with sat. $NaHCO_3$ *aq*, H_2O, and brine. After drying with Na_2SO_4, filtration, and evaporation, the crude mixture was purified by SiO_2 column chromatography (hexane/AcOEt) to afford the corresponding aldehyde **S6**.



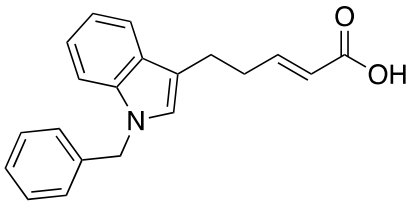
To a solution of NaH (1.3 equiv.) and THF (0.2 M) was added diethylphosphonoacetic acid ethyl ester **S7** (1.4 equiv.) at 0 ºC. After 30 min., aldehyde **S6** (1.0 equiv.) in THF was slowly adde. After stirring at room temperature for 1 h, the reaction mixture was quenched by sat.

NH_4Cl *aq* and extracted with AcOEt. The organic layer was washed with H_2O and brine, dried with Na_2SO_4. After filtration and evaporation, the crude mixture was purified by SiO_2 column chromatography (hexane/AcOEt) to afford **S8**.

To a recovery flask were added **S8** (1.0 equiv.), $LiOH•H_2O$ (3.0 equiv.), and $EtOH/H_2O$ (1:1, 0.2 M). The resulting mixture was heated at 60 ºC until **S8** disappeared (confirmed by TLC). After cooling to room temperature, the reaction mixture was quenched by 10% HCl *aq*, and extracted with AcOEt. The organic layer was washed with brine, dried with Na_2SO_4. After filtration and evaporation, the crude mixture was purified by SiO_2 column chromatography (hexane/AcOEt) or recrystallization (CH_2Cl_2/hexane) to afford **2**.

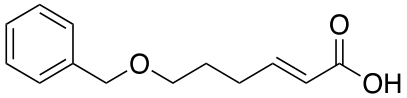
Characterization data of new α,β-unsaturated caboxylic acids

(*E*)-5-(1-benzyl-1*H*-indol-3-yl)pent-2-enoic acid (**2f**)



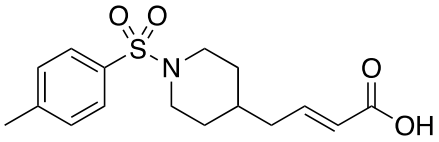
673.4 mg; a yellow solid; mp 88-90 ºC; IR (KBr) ν 3028, 1687, 1646, 1468, 1285, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.61-2.70 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 5.28 (s, 2H), 5.86 (dt, *J* = 15.6, 1.5 Hz, 1H), 6.92 (s, 1H), 7.07-7.21 (m, 5H), 7.24-7.32 (m, 4H), 7.59 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.7, 32.8, 49.8, 109.7, 114.1, 118.9, 119.0, 121.0, 121.8, 125.6, 126.7, 127.5, 127.8, 128.7, 136.7, 137.6, 151.8, 171.9; HRMS (ESI): *m/z* calculated for $C_{20}H_{18}O_2N$ [M-H]: 304.1343, found: 304.1347.

(*E*)-6-(benzyloxy)hex-2-enoic acid (**2g**)



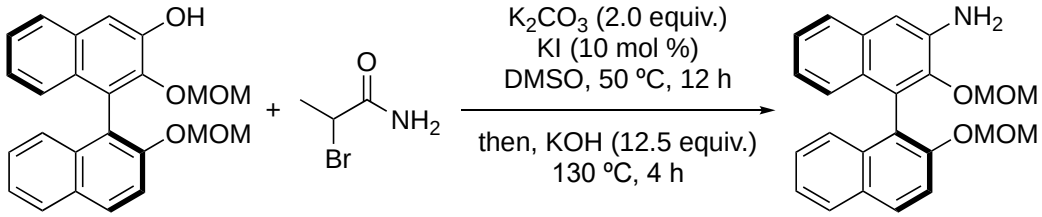
650.5 mg; a colorless oil; IR (KBr) ν 2861, 1696, 1651, 1421, 1288, 1104, 983, 739, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.79 (tt, *J* = 7.1, 6.3 Hz, 2H), 2.32-2.40 (m, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 4.50 (s, 2H), 5.82-5.87 (m, 1H), 7.09 (dt, *J* = 15.6, 7.2 Hz, 1H), 7.25-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 29.0, 69.1, 73.0, 121.0, 127.62, 127.65, 128.4, 138.3, 151.5, 171.9; HRMS (ESI): *m/z* calculated for $C_{13}H_{15}O_3$ [M-H]: 219.1027, found: 219.1028.

(*E*)-4-(1-tosylpiperidin-4-yl)but-2-enoic acid (**2h**)



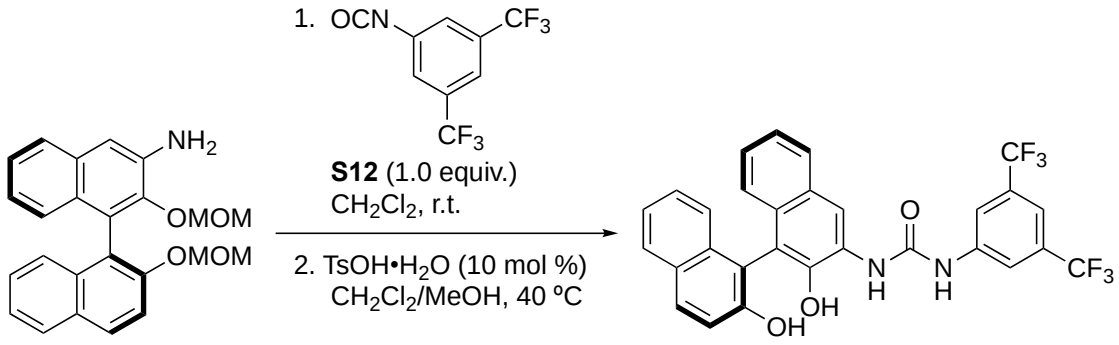
809.2 mg; a colorless solid; mp 136-138 ºC; IR (KBr) ν 2924, 1693, 1649, 1424, 1338, 1162, 1095, 931, 734 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30-1.42 (m, 3H), 1.73 (d, *J* = 9.9 Hz, 2H), 2.13-2.27 (m, 4H), 2.44 (s, 3H), 3.78 (d, *J* = 11.9 Hz, 2H), 5.81 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.94 (dt, *J* = 15.5, 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 31.3, 34.7, 38.7, 46.2, 122.3, 127.7, 129.6, 133.2, 143.4, 149.1, 170.9; HRMS (ESI): *m/z* calculated for $C_{16}H_{20}O_4NS$ [M-H]: 322.1119, found: 322.1122.

Synthesis of BINOL-urea ligand 5



S9 **S10** **S11**

S11 was prepared from **S9**[10] according to the literature.[11] To a 100 mL recovery flask were added **S9** (3.9 g, 10.1 mmol), 2-bromopropionamide **S10** (3.1 g, 20.2 mmol, 2.0 equiv.), K_2CO_3 (2.8 g, 0.2 mmol, 2.0 equiv.), KI (166 mg, 1.0 mmol, 0.1 equiv.), and DMSO (40 mL, 0.25 M). The reaction mixture was stirred at 50 ºC for 2 h. To the resulting mixture was added KOH (7.1 g, 126 mmol, 12.5 equiv.), and the mixture was heated at 150 ºC for 4 h. After the mixture was cooled to room temperature, H_2O and AcOEt were added. The organic layer was separated, and the aqueous layer was extracted with AcOEt three times. The combined organic layers were washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation, the obtained crude mixture was purified by silica gel column chromatography (hexane/AcOEt) to give corresponding product **S11** (*ca.* 6.7 mmol, *ca.* 66%) with inseparable byproducts. **S11** was used for the next step without further purification.



To a 100 mL recovery flask were added **S11**, 3,5-(bis)trifluoromethylphenyl isocyanate (1.1 mL, 6.7 mmol, 1.0 equiv.), and CH_2Cl_2 (33 mL, 0.2 M). The resulting mixture was stirred at room temperature for 1 h. After evaporation, TsOH•H_2O (ca. 10 mol %) and CH_2Cl_2/MeOH (1/1, 67 mL, 0.1 M) were added to the crude mixture. After stirring at 40 ºC for overnight, the reaction mixture was quenched by the addition of *sat.* $NaHCO_3$ *aq*. The aqueous layer was extracted with AcOEt three times. The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, and evaporated in *vacuo*. Product **5** was obtained as a yellow solid (2.1 g, 3.73 mmol, 37% from **S9**) after purification by silica gel column chromatography (hexane/AcOEt). mp 138-140 ºC; IR (KBr) ν 3374, 1545, 1474, 1385, 1349, 1279, 1179, 1133, 884 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1H), 6.20-6.50 (brs, 1H), 6.71 (s, 1H), 6.94-7.04 (m, 3H), 7.08 (d, J = 8.2 Hz, 1H), 7.22-7.37 (m, 4H), 7.47-7.64 (m, 4H), 7.87 (dd, J = 8.5, 2.6 Hz, 2H), 8.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.2, 114.2, 115.9, 116.7, 118.3, 118.5, 118.9, 121.7, 123.4, 123.7, 124.1, 124.4, 126.0, 126.4, 127.3, 127.6, 128.8, 129.1, 129.3, 131.3, 131.5 (q, J_{CF} = 33.7 Hz), 133.5, 139.1, 141.9, 152.1, 152.8; ^{19}F NMR (400 MHz, $CDCl_3$) δ -63.0; HRMS (ESI): *m/z* calculated for $C_{29}H_{18}O_3N_2F_6Na$ [M+Na^+]: 579.1114, found: 579.1105.

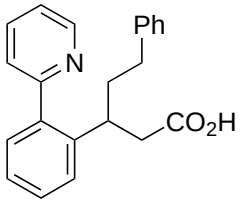
General procedure for Cp*Rh(III)/BH_3•SMe_2-catalyzed C–H addition to α,β-unsaturated carboxylic acids

To a flame dried test tube were added carboxylic acid **2** (0.30 mmol) and toluene (1.5 mL). BH_3•SMe_2 (1.0 M in CH_2Cl_2, 60 μL, 20 mol %) was added to the reaction mixture at 0 ºC. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under vacuum. To the resulting residue were added $[Cp^*RhCl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), **5** (33.4 mg, 20 mol %), DMF (0.6 mL), and **1** (1.0 equiv.) in a glove box. The test tube was capped and heated at 50 ºC for 15 h with stirring. After the mixture was cooled to

room temperature, acetic acid was added and an insoluble solids were removed by filtration through a short pad of SiO_2. After evaporation, obtained crude mixture was purified by SiO_2 column chromatography (CH_2Cl_2/MeOH) to give **3**.

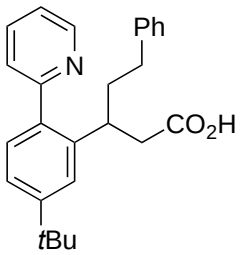
Characterization data of 3

5-phenyl-3-(2-(pyridin-2-yl)phenyl)pentanoic acid (**3aa**)



81.4 mg (82%) in 0.30 mmol scale; 253.8 mg (77%) in 1.0 mmol scale; a colorless solid; mp 130–132 ºC; IR (KBr) ν 2915, 2475, 1946, 1710, 1593, 1427, 1220, 1185, 768 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.78-1.92 (m, 2H), 2.11 (ddd, *J* = 14.9, 8.9, 6.7 Hz, 1H), 2.24 (ddd, *J* = 14.9, 8.7, 6.0 Hz, 1H), 2.96-3.04 (m, 2H), 3.63 (tt, *J* = 9.7, 6.3 Hz, 1H), 6.78-6.84 (m, 2H), 7.02-7.10 (m, 3H), 7.32-7.40 (m, 3H), 7.46-7.50 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.93 (ddd, *J* = 7.8, 7.6, 1.6 Hz, 1H), 8.52 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 33.0, 34.3, 39.4, 43.4, 122.5, 125.0, 125.7, 126.9, 127.0, 127.9, 128.2, 130.0, 130.1, 137.8, 138.9, 141.1, 141.5, 146.3, 158.1, 173.7; HRMS (ESI): *m/z* calculated for $C_{22}H_{22}O_2N$ $[M+H^+]$: 332.1645, found: 332.1642.

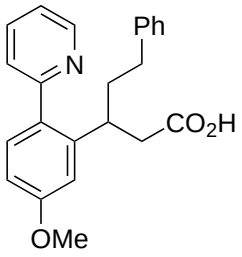
3-(5-(*tert*-butyl)-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ba**)



92.9 mg (80%); a yellow solid; mp 51–53 ºC; IR (KBr) ν 3481, 2961, 1722, 1608, 1468, 792, 659 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 9H), 1.74-1.95 (m, 2H), 2.08-2.27 (m, 2H), 2.98 (d, *J* = 8.4 Hz, 2H), 3.55 (tt, *J* = 16.4, 8.4 Hz, 1H), 6.80-6.85 (m, 2H), 7.02-7.12 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.33-7.42 (m, 2H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.94 (ddd, *J* = 7.9, 7.8, 1.6 Hz, 1H), 8.48 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.2, 33.0, 34.4, 34.8, 39.6, 43.4, 122.6, 123.6, 124.1, 125.3, 125.6, 127.9, 128.2, 129.8, 134.2,

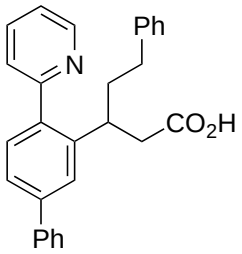
139.6, 141.1, 141.2, 145.5, 153.4, 157.4, 174.4; HRMS (ESI): *m/z* calculated for $C_{26}H_{30}O_2N$ [M+H$^+$]: 388.2271, found: 388.2272.

3-(5-methoxy-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ca**)



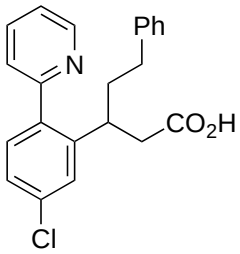
65.4 mg (60%); a yellow solid; mp 144–146 ºC; IR (KBr) ν 2932, 1712, 1607, 1467, 1289, 1235, 753, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.74-1.93 (m, 2H), 2.12 (ddd, *J* = 14.9, 8.7, 6.9 Hz, 1H), 2.26 (ddd, *J* = 14.9, 8.7, 6.2 Hz, 1H), 2.89-3.02 (m, 2H), 3.54 (tt, *J* = 9.9, 5.9 Hz, 1H), 3.84 (s, 3H), 6.80-6.89 (m, 3H), 6.96 (d, *J* = 2.5 Hz, 1H), 7.03-7.11 (m, 3H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.37 (dd, *J* = 7.0, 5.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.93 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 8.46 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 34.3, 39.4, 43.5, 55.3, 112.4, 112.6, 122.4, 125.3, 125.7, 127.9, 128.1, 129.5, 131.6, 139.8, 141.0, 143.4, 145.2, 157.1, 161.1, 174.3; HRMS (ESI): *m/z* calculated for $C_{23}H_{24}O_3N$ [M+H$^+$]: 362.1751, found: 362.1751.

5-phenyl-3-(4-(pyridin-2-yl)-[1,1'-biphenyl]-3-yl)pentanoic acid (**3da**)



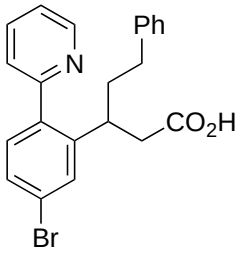
80.4 mg (66%); a yellow solid; mp 59–61 ºC; IR (KBr) ν 3436, 2922, 1712, 1598, 1468, 1287, 764, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.82-1.98 (m, 2H), 2.17 (ddd, *J* = 14.8, 8.2, 8.2 Hz, 1H), 2.29 (ddd, *J* = 14.8, 6.6, 6.6 Hz, 1H), 2.98-3.10 (m, 2H), 3.65 (tt, *J* = 9.0, 7.1 Hz, 1H), 6.83 (d, *J* = 6.6 Hz, 2H), 7.01-7.11 (m, 3H), 7.34-7.49 (m, 5H), 7.51-7.67 (m, 5H), 7.92 (dd, *J* = 7.8, 7.7 Hz, 1H), 8.52 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.0, 34.3, 39.4, 43.4, 122.6, 125.1, 125.68, 125.74, 127.2, 127.8, 127.9, 128.2, 128.8, 130.6, 136.4, 139.2, 140.2, 141.0, 142.0, 143.0, 146.1, 157.5, 173.9; One of the aromatic signals was missing probably due to overlapping; HRMS (ESI): *m/z* calculated for $C_{28}H_{26}O_2N$ [M+H$^+$]: 408.1958, found: 408.1957.

3-(5-chloro-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ea**)



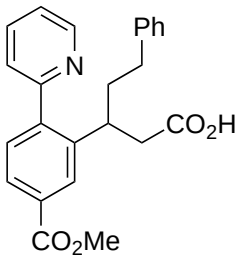
53.6 mg (49%); a yellow solid; mp 46–48 ºC; IR (KBr) ν 2926, 2469, 1709, 1600, 1467, 1274, 756, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.76-1.97 (m, 2H), 2.11-2.22 (m, 1H), 2.25-2.34 (m, 1H), 2.87-3.03 (m, 2H), 3.53-3.65 (m, 1H), 6.84 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.03-7.13 (m, 3H), 7.29-7.35 (m, 2H), 7.37-7.42 (m, 1H), 7.44 (s, 1H), 7.51 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.87-7.96 (m, 1H), 8.51-8.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 34.4, 39.1, 43.0, 122.8, 125.0, 125.8, 127.2, 127.9, 128.2, 131.4, 136.1, 136.3, 138.9, 140.8, 143.6, 146.7, 157.0, 173.4; One of the aromatic signals was missing probably due to overlapping; HRMS (ESI): *m/z* calculated for $C_{22}H_{21}O_2NCl$ [$M+H^+$]: 366.1255, found: 366.1257.

3-(5-bromo-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3fa**)



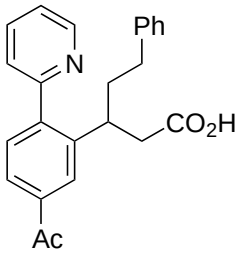
52.5 mg (43%); an orange solid; mp 98–100 ºC; IR (KBr) ν 2926, 2484, 1712, 1598, 1466, 1245, 1026, 788 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.75-1.96 (m, 2H), 2.15 (ddd, *J* = 14.9, 8.6, 6.8 Hz, 1H), 2.29 (ddd, *J* = 14.9, 8.5, 6.4 Hz, 1H), 2.88-3.04 (m, 2H), 3.52-3.63 (m, 1H), 6.83 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.03-7.12 (m, 3H), 7.22-7.27 (m, 1H), 7.40 (dd, *J* = 5.7, 5.4 Hz, 1H), 7.46-7.54 (m, 2H), 7.59 (d, *J* = 1.3 Hz, 1H), 7.88-7.96 (m, 1H), 8.53 (ddd, *J* = 5.0, 1.7, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 34.4, 39.1, 42.9, 122.8, 124.4, 124.9, 125.8, 127.9, 128.2, 130.2, 131.6, 136.9, 138.8, 140.8, 143.9, 146.8, 157.1, 173.4; One of the aromatic signals was missing probably due to overlapping; HRMS (ESI): *m/z* calculated for $C_{22}H_{21}O_2NBr$ [$M+H^+$]: 410.0750, found: 410.0751.

3-(5-(methoxycarbonyl)-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ga**)



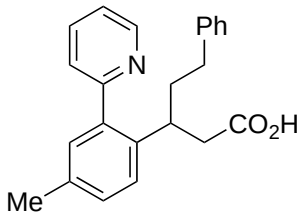
73.0 mg (62%); an orange solid; mp 152–153 ºC; IR (KBr) ν 2921, 1718, 1596, 1431, 1292, 1251, 1173, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.81-1.99 (m, 2H), 2.08-2.20 (m, 1H), 2.21-2.31 (m, 1H), 3.02 (d, *J* = 7.9 Hz, 2H), 3.64 (tt, *J* = 7.4, 7.3 Hz, 1H), 3.96 (s, 3H), 6.83 (d, *J* = 7.3 Hz, 2H), 7.03-7.12 (m, 3H), 7.39-7.48 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.94 (dd, *J* = 7.9, 7.9 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.15 (d, *J* = 1.6 Hz, 1H), 8.56 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.0, 34.6, 38.9, 42.7, 52.3, 123.0, 125.1, 125.7, 127.87, 127.91, 128.2, 130.2, 131.39, 131.45, 138.7, 140.9, 142.2, 142.3, 146.9, 157.2, 166.4, 173.9; HRMS (ESI): *m/z* calculated for $C_{24}H_{24}O_4N$ [M+H^+]: 390.1700, found: 390.1699.

3-(5-acetyl-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ha**)



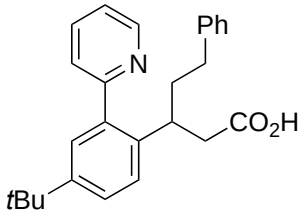
88.3 mg (79%); a yellow solid; mp 152–154 ºC; IR (KBr) ν 2929, 2513, 1715, 1675, 1594, 1284, 1227, 1175, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.81-2.01 (m, 2H), 2.17 (ddd, *J* = 14.8, 8.5, 6.9 Hz, 1H), 2.27 (ddd, 14.8, 8.8, 6.3 Hz, 1H), 2.65 (s, 3H), 2.92-3.03 (m, 2H), 3.57-3.70 (m, 1H), 6.84 (d, *J* = 7.3 Hz, 2H), 7.03-7.13 (m, 3H), 7.36-7.43 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 8.05 (s, 1H), 8.57 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.7, 33.0, 34.5, 39.0, 42.8, 123.0, 125.0, 125.8, 126.77, 126.84, 127.9, 128.2, 130.5, 138.0, 138.6, 140.9, 142.3, 142.5, 147.1, 157.2, 173.6, 197.5; HRMS (ESI): *m/z* calculated for $C_{24}H_{24}O_3N$ [M+H^+]: 374.1751, found: 374.1751.

3-(4-methyl-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ia**)



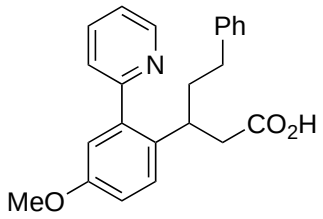
54.3 mg (52%); a yellow solid; mp 123–125 ºC; IR (KBr) ν 2929, 2449, 1736, 1704, 1597, 1234, 1008 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72-1.93 (m, 2H), 2.10 (ddd, *J* = 14.4, 9.0, 7.2 Hz, 1H), 2.23 (ddd, *J* = 14.4, 8.5, 5.8 Hz, 1H), 2.38 (s, 3H), 2.90-2.99 (m, 2H), 3.50 (tt, *J* = 15.3, 6.3 Hz, 1H), 6.83 (d, *J* = 6.7 Hz, 2H), 7.02-7.11 (m, 3H), 7.17 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.0, 5.6 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.95 (td, *J* = 7.7, 1.6 Hz, 1H), 8.50 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 32.9, 33.9, 39.4, 43.5, 122.7, 125.3, 125.7, 126.9, 127.9, 128.1, 130.6, 131.2, 136.6, 136.9, 138.4, 139.6, 141.1, 145.6, 157.6, 174.3; HRMS (ESI): *m/z* calculated for $C_{23}H_{24}O_2N$ $[M+H^+]$: 346.1802, found: 346.1802.

3-(4-(*tert*-butyl)-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ja**)



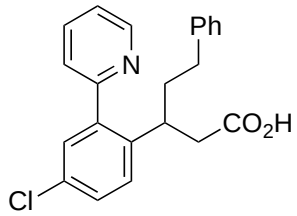
62.0 mg (53%); a yellow solid; mp 156–158 ºC; IR (KBr) ν 2962, 1711, 1595, 1469, 1363, 1254, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (s, 9H), 1.76-1.93 (m, 2H), 2.14 (ddd, *J* = 15.0, 8.5, 6.5 Hz, 1H), 2.26 (ddd, *J* = 15.0, 8.4, 6.6 Hz, 1H), 2.93-2.99 (m, 2H), 3.49 (tt, *J* = 15.4, 6.1 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.02-7.11 (m, 3H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.43 (ddd, *J* = 7.6, 5.2, 1.1 Hz, 1H), 7.51 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.98 (td, *J* = 7.8, 1.7 Hz, 1H), 8.50 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.2, 33.0, 33.9, 34.5, 39.3, 43.4, 122.7, 125.4, 125.7, 126.7, 126.9, 127.7, 127.9, 128.2, 136.3, 138.4, 139.8, 141.2, 145.4, 149.7, 157.9, 174.4; HRMS (ESI): *m/z* calculated for $C_{26}H_{30}O_2N$ $[M+H^+]$: 388.2271, found: 388.2271.

3-(4-methoxy-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ka**)



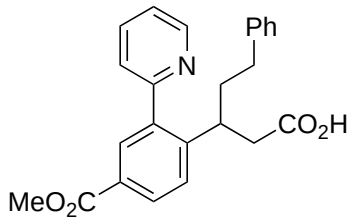
89.0 mg (82%); a yellow solid; mp 48–50 ºC; IR (KBr) ν 2940, 1712, 1608, 1469, 1299, 1226, 1034, 660 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.71-1.92 (m, 2H), 2.11 (ddd, *J* = 15.0, 9.1, 6.7 Hz, 1H), 2.25 (ddd, *J* = 15.0, 9.1, 6.0 Hz, 1H), 2.84-2.97 (m, 2H), 3.46 (tt, *J* = 9.9, 6.0 Hz, 1H), 3.82 (s, 3H), 6.84 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.87 (d, *J* = 2.7 Hz, 1H), 7.00-7.11 (m, 4H), 7.33-7.41 (m, 2H), 7.54 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.91 (td, *J* = 7.9, 1.6 Hz, 1H), 8.51 (dd, *J* = 5.1, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.0, 33.8, 39.4, 43.4, 55.4, 115.2, 115.9, 122.7, 125.1, 125.6, 127.9, 128.1, 133.3, 138.5, 139.2, 141.2, 146.0, 157.6, 158.0, 174.1; One of the aromatic signals was missing probably due to overlapping; HRMS (ESI): *m/z* calculated for $C_{23}H_{24}O_3N$ [M+H^+]: 362.1751, found: 362.1750.

3-(4-chloro-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3la**)



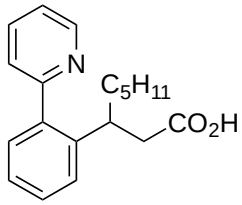
87.6 mg (80%); a yellow solid; mp 145.5–146 ºC; IR (KBr) ν 2914, 2469, 1721, 1598, 1472, 1210, 1180, 1007, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.72-1.84 (m, 1H), 1.84-1.96 (m, 1H), 2.16 (ddd, *J* = 14.9, 8.6, 8.6 Hz, 1H), 2.26 (ddd, *J* = 14.9, 9.3, 6.1 Hz, 1H), 2.88 (d, *J* = 7.3 Hz, 2H), 3.45-3.57 (m, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 7.03-7.13 (m, 3H), 7.31-7.51 (m, 5H), 7.86 (t, *J* = 7.7 Hz, 1H), 8.55 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 34.2, 39.0, 42.8, 123.0, 125.0, 125.7, 127.9, 128.2, 128.4, 129.8, 130.0, 132.4, 138.8, 139.6, 140.1, 140.9, 146.9, 156.7, 173.8; HRMS (ESI): *m/z* calculated for $C_{22}H_{21}O_2NCl$ [M+H^+]: 366.1255, found: 366.1258.

3-(4-(methoxycarbonyl)-2-(pyridin-2-yl)phenyl)-5-phenylpentanoic acid (**3ma**)



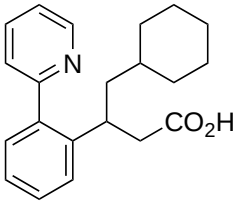
81.9 mg (70%); a yellow solid; mp 120.5–121.5 ºC; IR (KBr) ν 2923, 2483, 1721, 1597, 1436, 1314, 1252, 1113, 1010, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.77-1.99 (m, 2H), 2.15 (ddd, *J* = 14.2, 9.1, 6.6 Hz, 1H), 2.24 (ddd, *J* = 14.2, 9.1, 6.1 Hz, 1H), 2.96 (d, *J* = 8.0 Hz, 2H), 3.58-3.71 (m, 1H), 3.92 (s, 3H), 6.84 (d, *J* = 6.2 Hz, 2H), 7.03-7.12 (m, 3H), 7.39 (dd, *J* = 7.4, 5.0 Hz, 1H), 7.56 (dd, *J* = 9.2, 9.2 Hz, 2H), 7.91 (t, *J* = 7.7 Hz, 1H), 8.06 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.56 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 34.8, 39.0, 42.7, 52.2, 122.9, 125.1, 125.7, 127.2, 127.9, 128.2, 128.7, 130.7, 131.3, 138.3, 138.8, 140.8, 146.8, 147.0, 157.1, 166.3, 173.6; HRMS (ESI): *m/z* calculated for $C_{24}H_{24}O_4N$ $[M+H^+]$: 390.1700, found: 390.1702.

3-(2-(pyridin-2-yl)phenyl)octanoic acid (**3ab**)



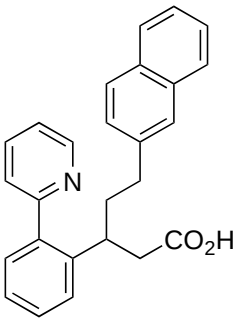
52.9 mg (59%); an orange solid; mp 115–115.5 ºC; IR (KBr) ν 2955, 2922, 2856, 2488, 1709, 1594, 1428, 1219, 1004, 768 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.68 (t, *J* = 7.2 Hz, 3H), 0.73-1.12 (m, 6H), 1.48 (dt, *J* = 7.4, 7.2 Hz, 2H), 2.96 (d, *J* = 7.9 Hz, 2H), 3.48-3.67 (m, 1H), 7.28-7.37 (m, 2H), 7.40-7.48 (m, 3H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.97 (dd, *J* = 7.9, 7.5 Hz, 1H), 8.62 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 22.2, 26.5, 31.2, 34.5, 37.9, 43.6, 122.5, 125.0, 126.7, 126.9, 129.8, 130.0, 137.7, 139.0, 141.8, 146.3, 158.4, 173.8; HRMS (ESI): *m/z* calculated for $C_{19}H_{24}O_2N$ $[M+H^+]$: 298.1802, found: 298.1799.

4-cyclohexyl-3-(2-(pyridin-2-yl)phenyl)butanoic acid (**3ac**)



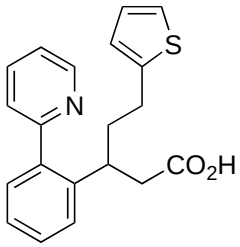
77.4 mg (80%); a yellow solid; mp 164–166 ºC; IR (KBr) ν 2920, 2849, 2522, 1704, 1604, 1449, 1248, 1002, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.43-0.57 (m, 1H), 0.62-0.74 (m, 2H), 0.76-1.09 (m, 5H), 1.22-1.57 (m, 7H), 2.87 (dd, *J* = 17.0, 5.4 Hz, 1H), 2.96 (dd, *J* = 17.0, 11.0 Hz, 1H), 3.60 (tt, *J* = 10.8, 5.4 Hz, 1H), 7.31-7.39 (m, 2H), 7.42-7.52 (m, 2H), 7.53-7.60 (m, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 8.08 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 8.71 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.8, 26.0, 26.3, 31.9, 32.5, 33.7, 34.7, 43.6, 46.0, 123.0, 125.5, 126.7, 126.8, 127.1, 129.8, 130.5, 139.9, 142.1, 145.6, 157.8, 173.8; HRMS (ESI): *m/z* calculated for $C_{21}H_{16}O_2N$ [$M+H^+$]: 324.1958, found: 324.1957.

5-(naphthalen-2-yl)-3-(2-(pyridin-2-yl)phenyl)pentanoic acid (**3ad**)



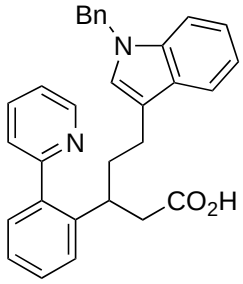
86.1 mg (75%); a yellow solid; mp 145-146 ºC; IR (KBr) ν 2925, 2491, 1712, 1598, 1427, 1223, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.92 (ddt, *J* = 14.4, 7.9, 7.3 Hz, 1H), 2.05 (ddt, *J* = 14.4, 7.2, 6.9 Hz, 1H), 2.37 (dt, *J* = 14.4, 7.3 Hz, 1H), 2.51 (dt, *J* = 14.4, 7.2 Hz, 1H), 2.93-3.08 (m, 2H), 3.49-3.61 (m, 1H), 7.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.06-7.12 (m, 1H), 7.23 (s, 1H), 7.29-7.36 (m, 3H), 7.38-7.45 (m, 2H), 7.51 (d, *J* = 3.1 Hz, 2H), 7.53-7.59 (m, 2H), 7.59-7.64 (m, 1H), 7.69-7.76 (m, 1H), 8.32-8.38 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.8, 33.7, 38.6, 43.2, 122.2, 125.0, 125.1, 125.8, 126.0, 126.6, 126.8, 126.9, 127.3, 127.4, 127.7, 130.0, 130.2, 131.8, 133.3, 137.2, 138.4, 138.8, 141.4, 145.5, 157.2, 173.8; HRMS (ESI): *m/z* calculated for $C_{26}H_{24}O_2N$ [$M+H^+$]: 382.1802, found: 382.1799.

3-(2-(pyridin-2-yl)phenyl)-5-(thiophen-2-yl)pentanoic acid (**3ae**)



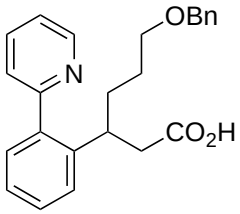
52.0 mg (51%); a colorless solid; mp 150-151 ºC; IR (KBr) ν 2916, 2467, 1708, 1593, 1428, 1286, 1223, 1188, 769, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.82-2.01 (m, 2H), 2.36 (dt, *J* = 14.7, 7.0 Hz, 1H), 2.48 (dt, *J* = 14.7, 6.6 Hz, 1H), 2.97 (d, *J* = 8.3 Hz, 2H), 3.59-3.71 (m, 1H), 6.41-6.45 (m, 1H), 6.71 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.95 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.31-7.42 (m, 3H), 7.44-7.51 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.88-7.96 (m, 1H), 8.54 (ddd, *J* = 5.2, 1.7, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.5, 34.4, 39.7, 43.6, 123.0, 123.2, 124.3, 125.6, 126.8, 127.3, 130.4, 130.6, 137.7, 139.6, 141.4, 144.3, 146.3, 158.0, 173.8; HRMS (ESI): *m/z* calculated for $C_{20}H_{19}O_2NSNa$ [M+Na^+]: 360.1029, found: 360.1025.

5-(1-benzyl-1*H*-indol-3-yl)-3-(2-(pyridin-2-yl)phenyl)pentanoic acid (**3af**)



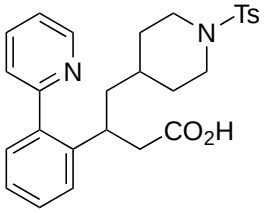
89.9 mg (65%); a yellow solid; mp 80-82 ºC; IR (KBr) ν 2925, 1728, 1596, 1468, 1332, 1243, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.84-2.04 (m, 2H), 2.27 (dt, *J* = 14.9, 7.6 Hz, 1H), 2.40 (dt, *J* = 14.9, 6.7 Hz, 1H), 2.92-3.03 (m, 2H), 3.56-3.68 (m, 1H), 5.09 (s, 2H), 6.53 (s, 1H), 6.96-7.03 (m, 3H), 7.07-7.34 (m, 10H), 7.45-7.51 (m, 2H), 7.58-7.66 (m, 1H), 8.36 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.2, 34.1, 37.8, 43.1, 49.6, 109.5, 114.3, 118.69, 118.73, 121.6, 122.4, 125.0, 125.1, 126.7, 126.8, 127.0, 127.5, 127.7, 128.6, 129.9, 130.3, 136.4, 137.0, 137.5, 139.3, 141.8, 145.3, 157.2, 174.2; HRMS (ESI): *m/z* calculated for $C_{31}H_{29}O_2N_2$ [M+H^+]: 461.2224, found: 461.2220.

6-(benzyloxy)-3-(2-(pyridin-2-yl)phenyl)hexanoic acid (**3ag**)



77.1 mg (68%); a yellow solid; mp 110-112 ºC; IR (KBr) ν 2938, 2860, 2488, 1704, 1428, 1362, 1222, 1094, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.05-1.23 (m, 2H), 1.50-1.59 (m, 1H), 1.60-1.68 (m, 1H), 2.94 (d, *J* = 8.0 Hz, 2H), 3.11-3.17 (m, 2H), 3.50-3.58 (m, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 7.18-7.22 (m, 2H), 7.23-7.27 (m, 1H), 7.27-7.34 (m, 4H), 7.38-7.47 (m, 3H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.90-7.96 (m, 1H), 8.58 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.3, 34.5, 34.9, 43.5, 69.7, 72.8, 122.7, 125.2, 126.8, 126.9, 127.50, 127.52, 128.3, 130.0, 130.2, 137.4, 138.2, 139.4, 141.5, 146.1, 158.0, 173.8; HRMS (ESI): *m/z* calculated for $C_{24}H_{26}O_3N$ [M+H^+]: 376.1907, found: 376.1902.

3-(2-(pyridin-2-yl)phenyl)-4-(1-tosylpiperidin-4-yl)butanoic acid (**3ah**)



98.0 mg (68%); a yellow solid; mp 86-88 ºC; IR (KBr) ν 2914, 1731, 1597, 1468, 1336, 1248, 1163, 934, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.63-0.76 (m, 1H), 0.81-0.93 (m, 2H), 1.05 (dddd, *J* = 12.0, 12.0, 12.0, 4.4 Hz, 1H), 1.24-1.40 (m, 2H), 1.43-1.54 (m, 1H), 1.86 (dt, *J* = 11.6, 7.6 Hz, 1H), 2.01 (ddd, *J* = 11.7, 11.4, 2.2 Hz, 1H), 2.41 (s, 3H), 2.75-2.94 (m, 2H), 3.40-3.67 (m, 3H), 7.25-7.46 (m, 7H), 7.48-7.58 (m, 3H), 7.88-7.98 (m, 1H), 8.62 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 30.7, 31.7, 32.2, 43.3, 44.3, 45.7, 45.9, 122.8, 124.9, 126.8, 126.9, 127.5, 129.5, 130.0, 130.1, 133.3, 137.6, 138.9, 141.3, 143.3, 146.7, 158.1, 173.7; One of the aliphatic signals was missing probably due to overlapping; HRMS (ESI): *m/z* calculated for $C_{27}H_{31}O_4N_2S$ [M+H^+]: 479.1999, found: 479.1996.

A preparative scale synthesis of 3aa

To a flame dried 20mL flask equipped with a stirring bar were added **2a** (176 mg, 1.0 mmol, azeotroped with toluene before use) and toluene (5 mL). BH_3•SMe_2 (1.0 M in CH_2Cl_2, 200 μL,

20 mol %) was added to the reaction mixture at 0 ºC. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under vacuum, and the mixture was brough into a glove box. To another screw-capped test tube were added **1a** (142 μL, 1.0 mmol, azeotroped with toluene before use), $[Cp^*RhCl_2]_2$ (15.5. mg, 2.5 mol %), $AgSbF_6$ (34.3 mg, 10 mol %), **5** (111 mg, 20 mol %), and the above-prepared mixture dissolved in DMF (2 mL). The test tube was capped and heated at 50 ºC for 15 h with stirring. After the mixture was cooled to room temperature, acetic acid was added and an insoluble solids were removed by filtration through a short pad of SiO_2. After evaporation, obtained crude mixture was purified by SiO_2 column chromatography (CH_2Cl_2/MeOH = 100/1; 40/1; 30/1) to give **3aa** (253.8 mg, 77%).

Computational study on acyloxyborane intermediate

We prepared a initial structure of acyloxyborane intermediate **IV** (Fig. 4) without hydrogen bonding between the urea and carbonyl moiety. A conformation search was run using Grimme's crest 2.11.1 and xtb 6.4.1 programs[12] (GFN2-xTB, iMTD-GC, 10 kcal/mol energy window, and default settings for others), and 432 conformers were generated. There were 42 conformations within a 3.0 kcal/mol window, all of which showed similar hydrogen bonding between the urea, carbonyl, and phenolic oxygen. As a representative structure, we selected the most stable conformation and its geometry was further optimized at the M06-2X/def2-SVP+SMD(DMF) level of theory[13] using Gaussian 16 Rev.C.01.[14] The optimized structure has no imaginary frequencies in the vibrational calculation at the same level. The cartesian coordinates of the initial structure for the conformation search and the optimized structure are shown below.

Initial structure

C	-4.16881604	1.38218675	-2.61372820
C	-4.41593686	0.04392744	-2.21023399
C	-3.31467786	-0.79073080	-1.84148728
C	-2.07795270	-0.21117060	-1.67757485
C	-1.83537466	1.14319839	-2.03985144
C	-2.85469293	1.89312901	-2.57113621
C	-5.24695024	2.18825284	-3.03666493
C	-6.52827972	1.71288538	-3.00820680
C	-6.78319554	0.41781142	-2.53533195
C	-5.75451978	-0.39808730	-2.14934512
C	-3.52470869	-2.23820663	-1.62797823
C	-4.23151496	-3.01002848	-2.60177952
C	-4.58688109	-4.35327881	-2.30598281
C	-4.19200985	-4.91763556	-1.07487600
C	-3.40050143	-4.21360702	-0.21591864
C	-3.04671963	-2.88412017	-0.50734508
C	-4.53711638	-2.50960093	-3.88673423
C	-5.21099519	-3.27389769	-4.79935048
C	-5.62040290	-4.57630020	-4.47870262

C	-5.30468872	-5.10625417	-3.25939680
O	-0.97919385	-0.86671656	-1.14120569
O	-2.16715833	-2.30184215	0.39538483
B	-1.08133882	-1.59951435	0.01168827
N	-0.51706780	1.59678786	-1.89786915
C	-0.01695662	2.79416462	-1.47169266
O	1.18127066	2.97718343	-1.40183755
N	-0.97318317	3.73423322	-1.13097473
C	-0.77730534	5.04391879	-0.73769482
C	-1.89069314	5.77994267	-0.32138818
C	-1.74511540	7.10071829	0.06939580
C	-0.50746734	7.72956892	0.05342924
C	0.58908100	6.98881608	-0.36399635
C	0.47233023	5.66523076	-0.75930407
O	0.07637402	-1.57450800	0.76003800
C	0.33553965	-2.24100468	1.91962476
C	1.75104535	-2.15307665	2.27174510
O	-0.51531277	-2.81736932	2.55511999
C	2.23404936	-2.75304937	3.36309724
C	3.65493338	-2.74537086	3.78567395
C	4.19898702	-4.18432080	3.89664737
C	1.95844456	7.61065444	-0.40510004
F	1.98510987	8.87702604	0.03393420
F	2.46943358	7.63727339	-1.65109263
F	2.84961276	6.93622191	0.34422982
C	-2.97261976	7.86399473	0.48594877
F	-3.80723837	7.12752837	1.23942970
F	-3.70239650	8.26626005	-0.57550558
F	-2.70102577	8.96943103	1.19015662
C	5.63312605	-4.16868837	4.34503669
C	5.95139508	-4.17766932	5.69762984
C	7.27084790	-4.13650103	6.11268745
C	8.29146446	-4.08171098	5.17818680
C	7.98471213	-4.06917033	3.82795483
C	6.66420308	-4.11078927	3.41573954
H	-2.66912335	2.87962274	-2.96885683
H	-5.03999492	3.19570910	-3.36629444
H	-7.34932926	2.33670502	-3.32754774
H	-7.80138214	0.06461557	-2.47352328
H	-5.96531102	-1.38673860	-1.77423843
H	-4.48992270	-5.92817311	-0.83948079
H	-3.02968328	-4.63782717	0.70408158
H	-4.21204630	-1.51757646	-4.15793381
H	-5.42582571	-2.87535148	-5.77972284
H	-6.16524808	-5.15964158	-5.20586022
H	-5.58350546	-6.11927791	-3.00883935
H	0.16901881	0.85056310	-1.89539171
H	-1.92923019	3.39979581	-1.07384537
H	-2.86800265	5.32052766	-0.29640872
H	-0.40204888	8.75744644	0.36082724
H	1.34094603	5.10943274	-1.07480531
H	2.37135306	-1.58169002	1.59813529
H	1.54429006	-3.31186952	3.98444065
H	4.26250223	-2.17255815	3.08440756
H	3.72750809	-2.27586294	4.77042155
H	3.59031420	-4.74247251	4.60989374
H	4.11774106	-4.66806034	2.92168114
H	5.15968589	-4.22343299	6.43226851
H	7.50440612	-4.14764138	7.16785159
H	9.32210384	-4.05038514	5.50100650
H	8.77690551	-4.02793353	3.09397785
H	6.43076184	-4.10405073	2.36026348

Optimized structure

C	-3.45669800	2.63879300	0.95503200
C	-4.50253500	1.67376300	0.86494900
C	-4.25901700	0.45662000	0.13342500
C	-2.98506900	0.22251400	-0.32512500
C	-1.91871800	1.17428200	-0.21542100
C	-2.17744400	2.38410000	0.38714900
C	-3.69535800	3.85652300	1.65193000
C	-4.90138500	4.09488500	2.26548600
C	-5.92273300	3.11581900	2.21916500
C	-5.72841900	1.93733500	1.53601800
C	-5.31591500	-0.56495600	-0.10506800
C	-6.58735600	-0.21221100	-0.68499700
C	-7.61663900	-1.19536600	-0.77781000
C	-7.35675000	-2.52411400	-0.34270300
C	-6.11428400	-2.87371000	0.11055600
C	-5.09314600	-1.89643500	0.19957300
C	-6.85077000	1.08212200	-1.21879200
C	-8.07471300	1.38703600	-1.76661200
C	-9.10938300	0.42097800	-1.81142000
C	-8.87869700	-0.84503100	-1.33244100
O	-2.63332600	-0.98171600	-0.89648800
O	-3.86752900	-2.36849700	0.60808100
B	-2.73442900	-2.08795200	-0.08944200
N	-0.70068500	0.74955700	-0.73715500
C	0.53035800	1.33340400	-0.55977300
O	0.70591600	2.43244900	-0.07149400
N	1.54691800	0.50859300	-1.00523000
C	2.91126300	0.77755700	-1.01353100
C	3.46771100	2.03880400	-0.75558600
C	4.85324400	2.19042300	-0.78155500
C	5.71438800	1.13077600	-1.04523900
C	5.14551800	-0.11667700	-1.29871500
C	3.77025600	-0.29769000	-1.29724700
O	-1.69308800	-2.97961800	0.08667500
C	-0.41079000	-2.83320200	-0.32197000
C	0.50038700	-3.76521300	0.36045400
O	-0.07524100	-2.01604900	-1.14635000
C	1.81784900	-3.51802900	0.34819900
C	2.84721800	-4.32046600	1.07224400
C	3.23096600	-3.67689900	2.42147200
C	6.04141200	-1.29198300	-1.58315500
F	5.45143700	-2.45476200	-1.29090300
F	7.17335400	-1.23218600	-0.87658900
F	6.39549700	-1.35054700	-2.87176900
C	5.43894400	3.52755500	-0.41833900
F	6.59275200	3.75651000	-1.04902100
F	5.69766700	3.60836600	0.89560100
F	4.61687400	4.53707100	-0.70886000
C	3.76111600	-2.26716300	2.30825600
C	5.12227700	-2.03025800	2.07265600
C	5.61840600	-0.72824100	1.99681200
C	4.75697100	0.36058000	2.14327900
C	3.39545400	0.13801600	2.35243600
C	2.90340600	-1.16609200	2.43538900
H	-1.39421100	3.13344500	0.47079400
H	-2.88949200	4.59204700	1.69938500
H	-5.06922900	5.03041700	2.80176400
H	-6.86850300	3.29385700	2.73356600
H	-6.51996000	1.18792300	1.51960100
H	-8.15370300	-3.26748900	-0.40650600
H	-5.87676800	-3.89539300	0.40884500
H	-6.06488500	1.83718000	-1.20879800
H	-8.24753900	2.38312800	-2.17779000
H	-10.07811200	0.68094300	-2.24105200
H	-9.65456000	-1.61221200	-1.37982800

H	-0.72354100	-0.17192600	-1.17230100
H	1.29061400	-0.44292900	-1.26620300
H	2.82431200	2.88458600	-0.52904800
H	6.79651400	1.26765400	-1.03859700
H	3.34800700	-1.28127100	-1.51177500
H	0.06238400	-4.60208200	0.90839900
H	2.16388200	-2.62603600	-0.18578300
H	2.47062700	-5.33582800	1.26131100
H	3.74864800	-4.39639200	0.44391800
H	2.34283400	-3.67946100	3.07111100
H	3.98925700	-4.31622300	2.89633700
H	5.80325700	-2.87885000	1.96420800
H	6.68351600	-0.56231500	1.82259800
H	5.14347800	1.37951100	2.08092600
H	2.71305400	0.98443900	2.45801900
	1.83858700	-1.33554000	2.61740300

References

(1) N. Hayama, T. Azuma, Y. Kobayashi and Y. Takemoto, *Chem. Pharm. Bull.*, 2016, **64**, 704.

(2) J. Fried and R. C. Elderfield, *J. Org. Chem.*, 1941, **6**, 566.

(3) L.-Y. Xi, R.-Y. Zhang, S. Liang, S.-Y. Chen and X.-Q. Yu, *Org. Lett.* 2014, **16**, 5269.

(4) W. Miao, C. Ni, P. Xiao, R. Jia, W. Zhang and J. Hu, *Org. Lett.*, 2021, **23**, 711.

(5) V. P. Reddy, R. Qiu, T. Iwasaki and N. Kambe, *Org. Lett.*, 2013, **15**, 1290.

(6) N. Yoshikai, S. Asako, T. Yamakawa, L. Ilies and E. Nakamura, *Chem. Asian J.*, 2011, **6**, 3059.

(7) A. Sagadevan and M. F. Greaney, *Angew. Chem., Int. Ed.*, 2019, **58**, 9826.

(8) H. L. Barlow, C. J. Teskey, M. F. Greaney, M. F. *Org. Lett.*, 2017, **19**, 6662.

(9) B. E. Maki and K. A. Scheidt, *Org. Lett.*, 2008, **10**, 4331.

(10) T. Kano, Q. Lan, X. Wang and K. Maruoka, *Adv. Synth. Catal.*, 2007, **349**, 556.

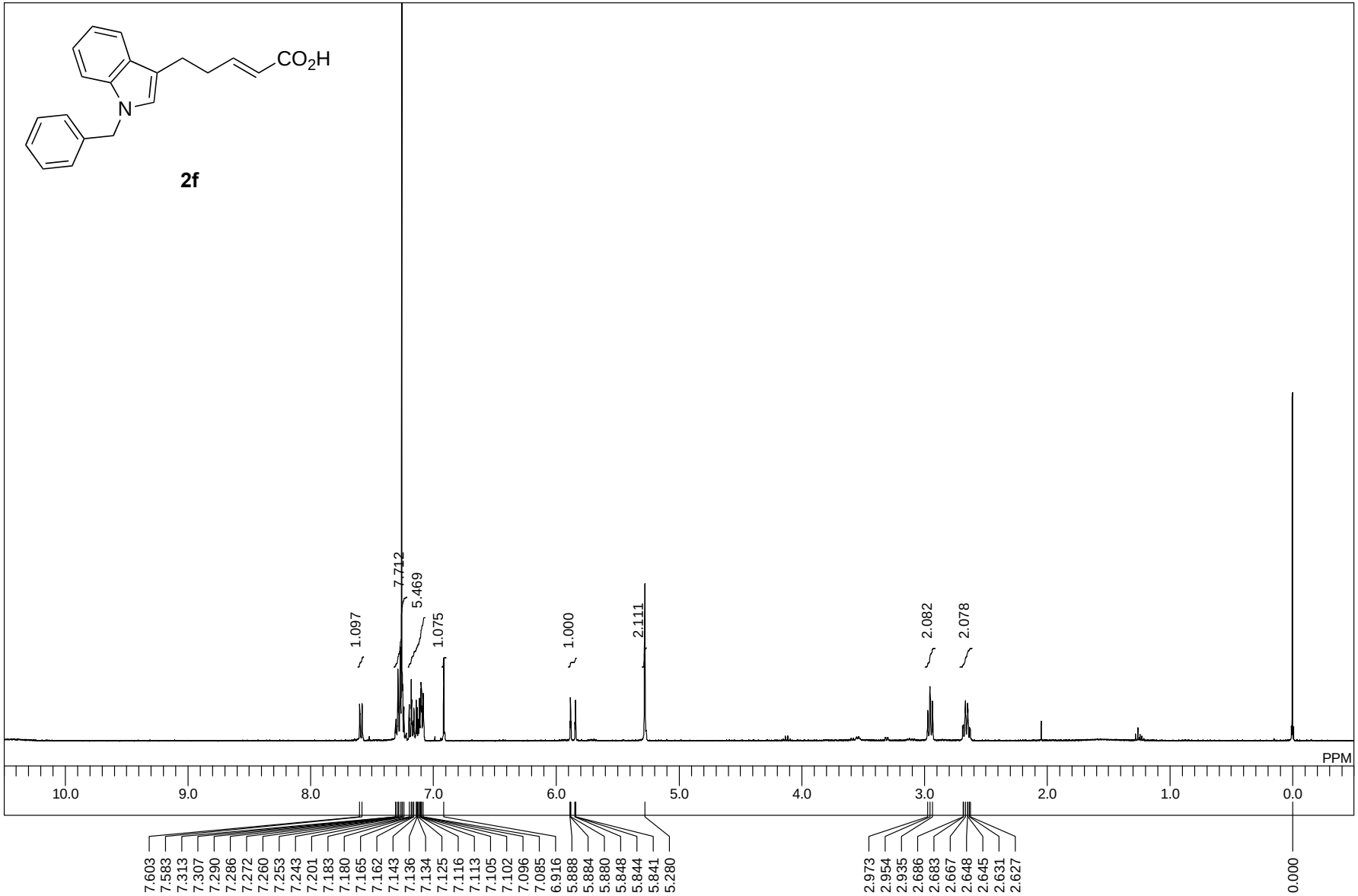
(11) X. Chang, Q. Zhang and C. Guo, *Org. Lett.*, 2019, **21**, 4915.

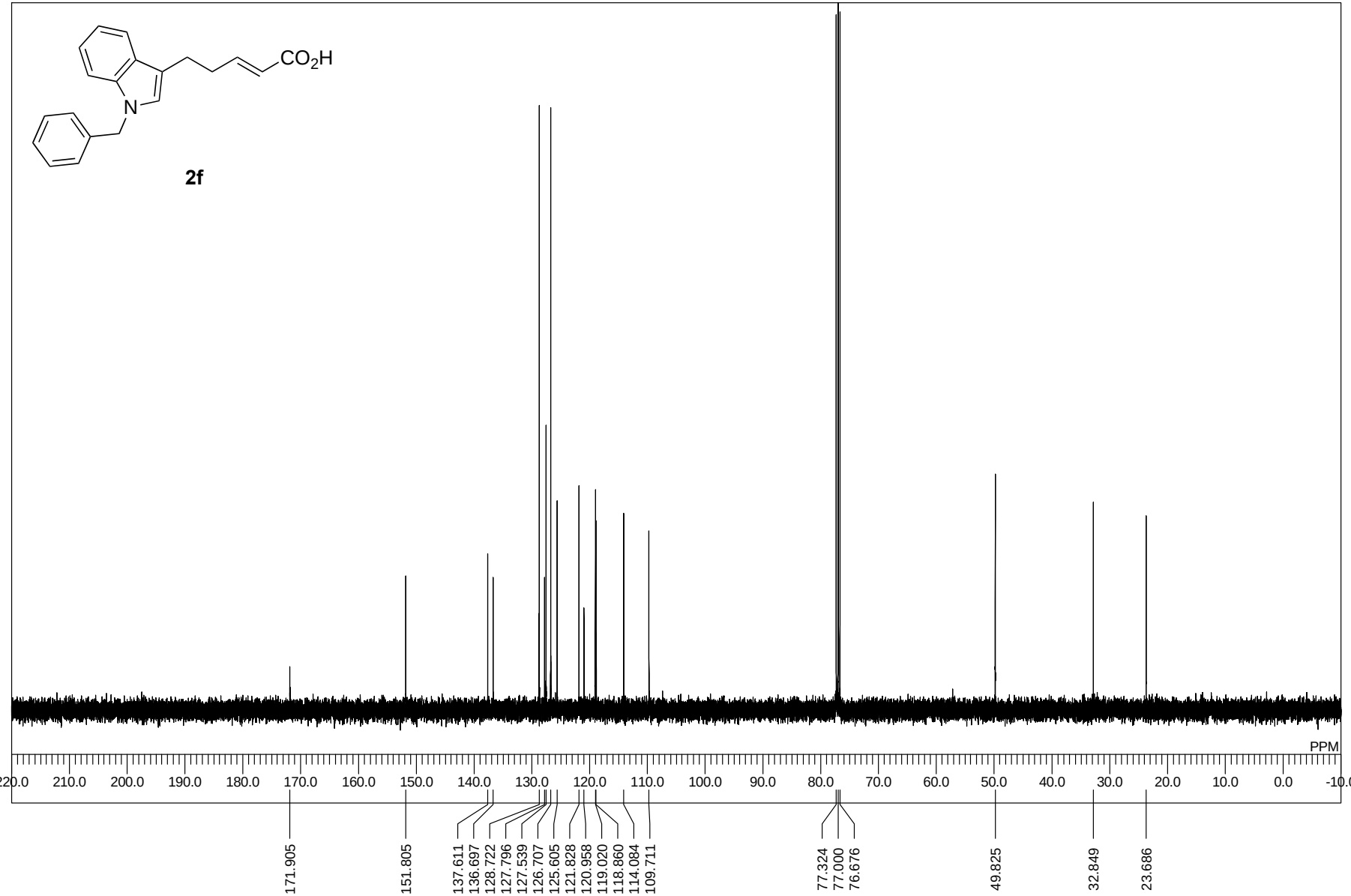
(12) (a) C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher and S. Grimme, *WIREs Comput. Mol. Sci.*, 2020, e01493; (b) P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169; (c) S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 2847.

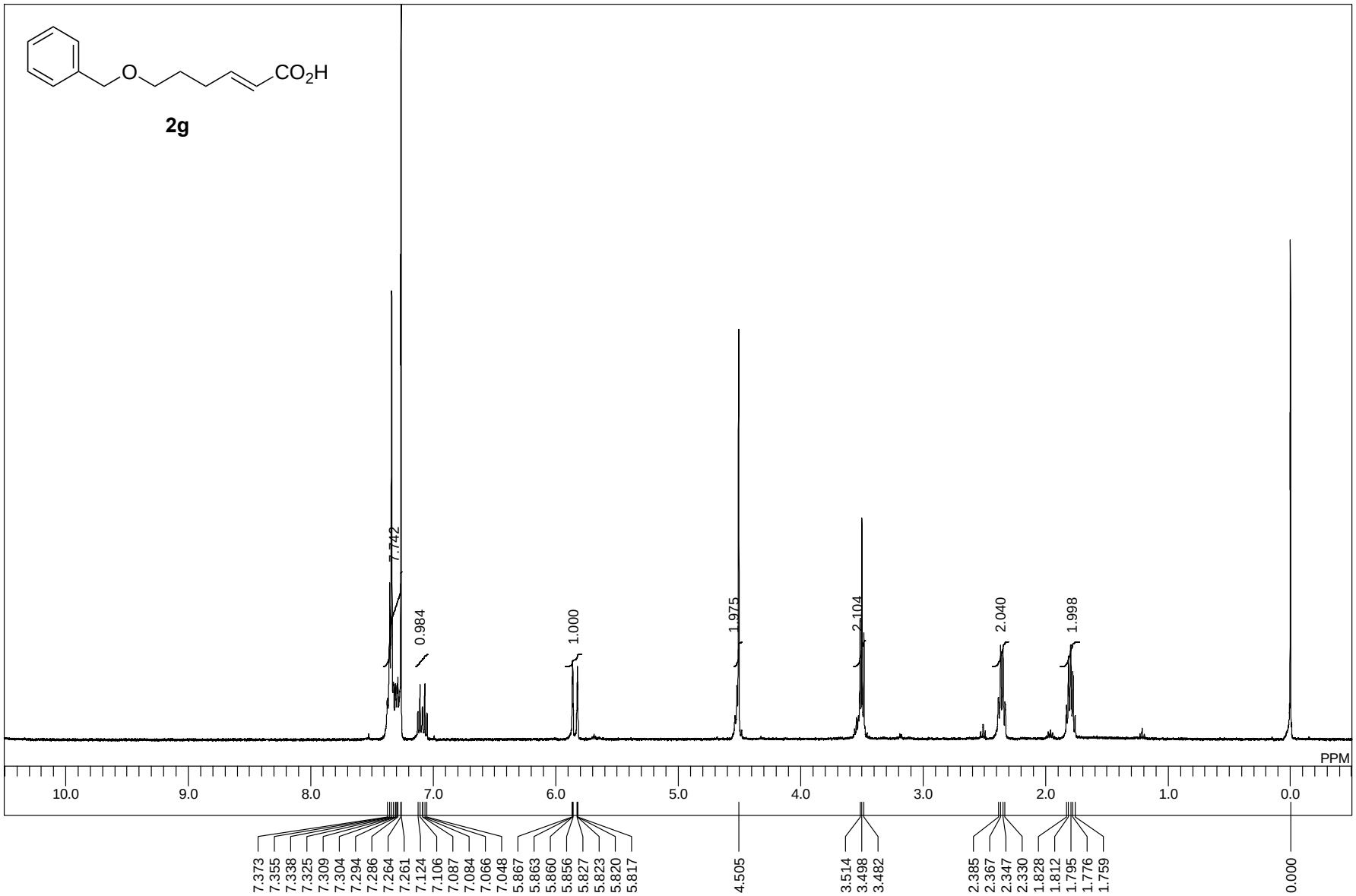
(13) (a) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215; (b) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297; (c) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

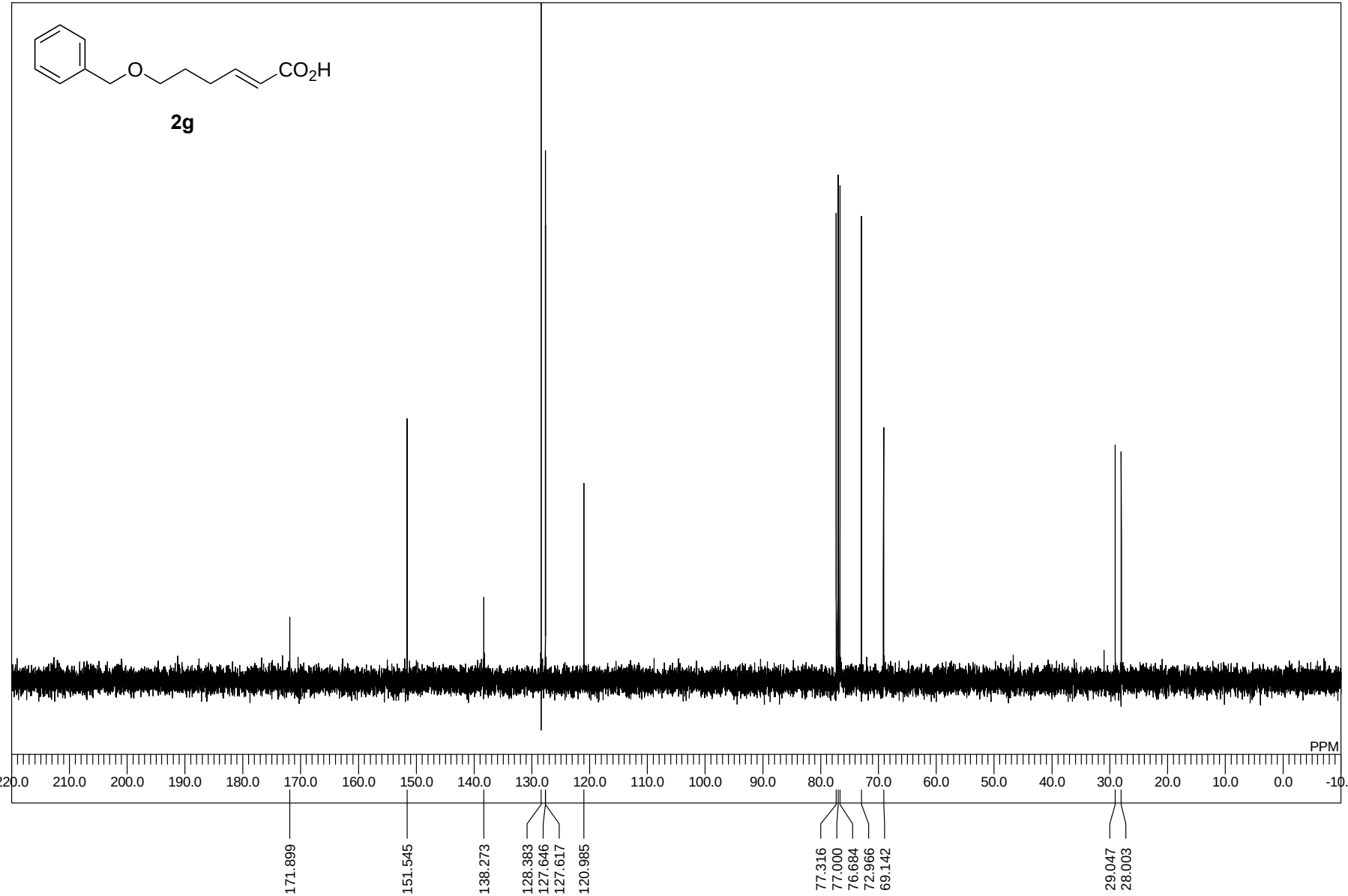
(14) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi,

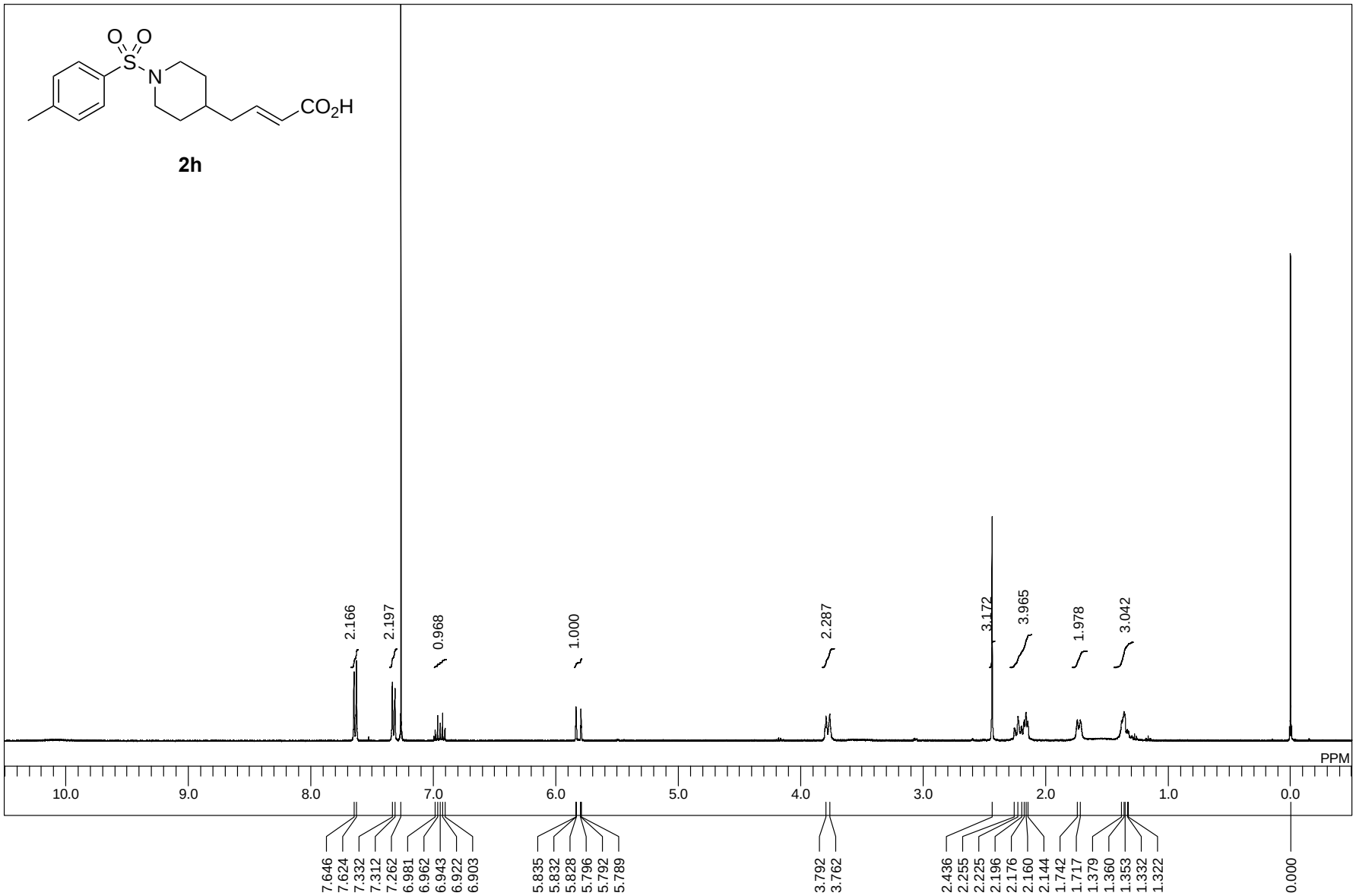
J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

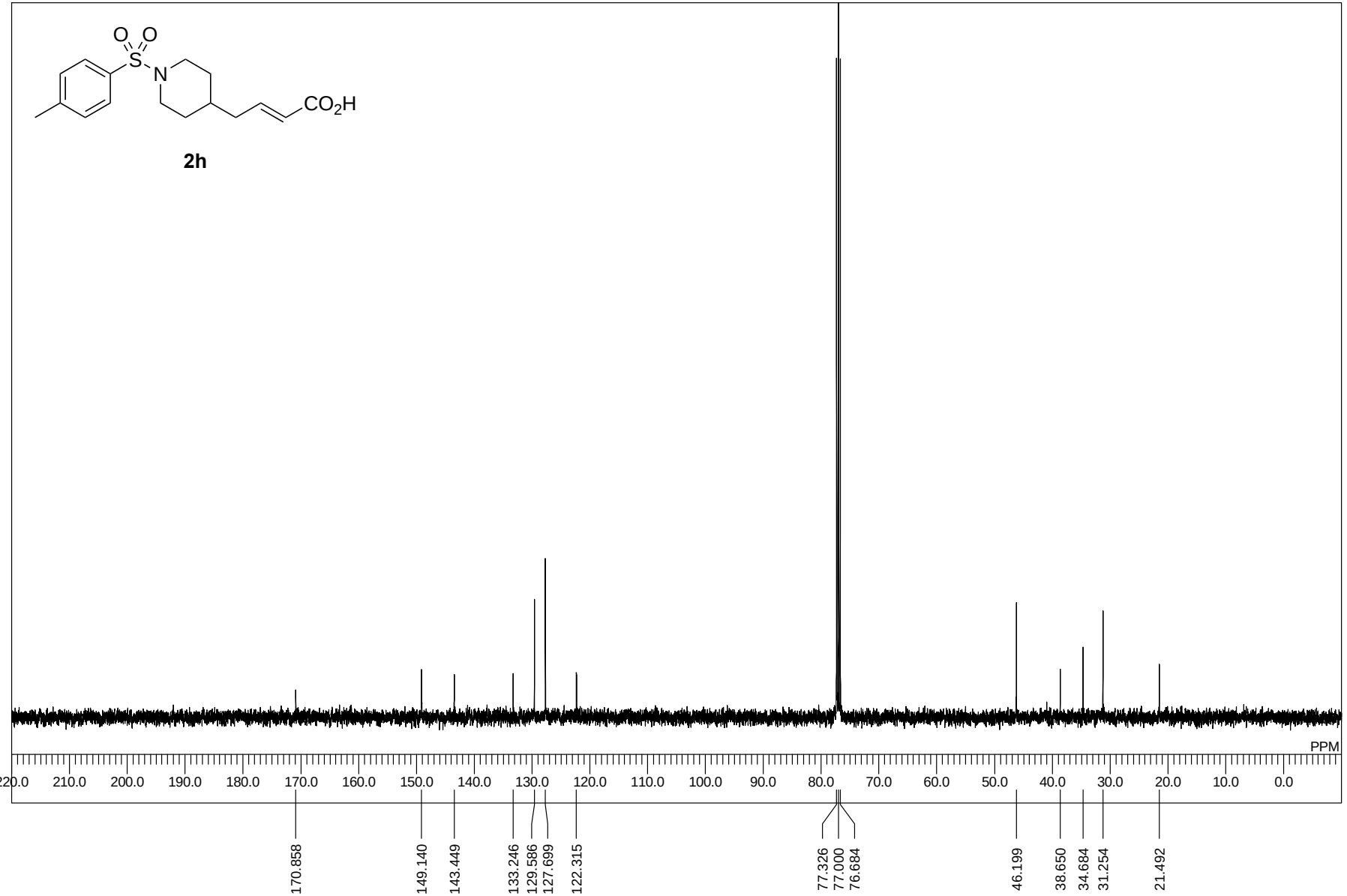

CO2H
N
2f
1.097
7.712
5.469
1.075
1.000
2.111
2.082
2.078
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.603
7.583
7.313
7.307
7.290
7.286
7.272
7.260
7.253
7.243
7.201
7.183
7.180
7.165
7.162
7.143
7.136
7.134
7.125
7.116
7.113
7.105
7.102
7.096
7.085
6.916
5.888
5.884
5.880
5.848
5.844
5.841
5.280
2.973
2.954
2.935
2.686
2.683
2.667
2.648
2.645
2.631
2.627
0.000

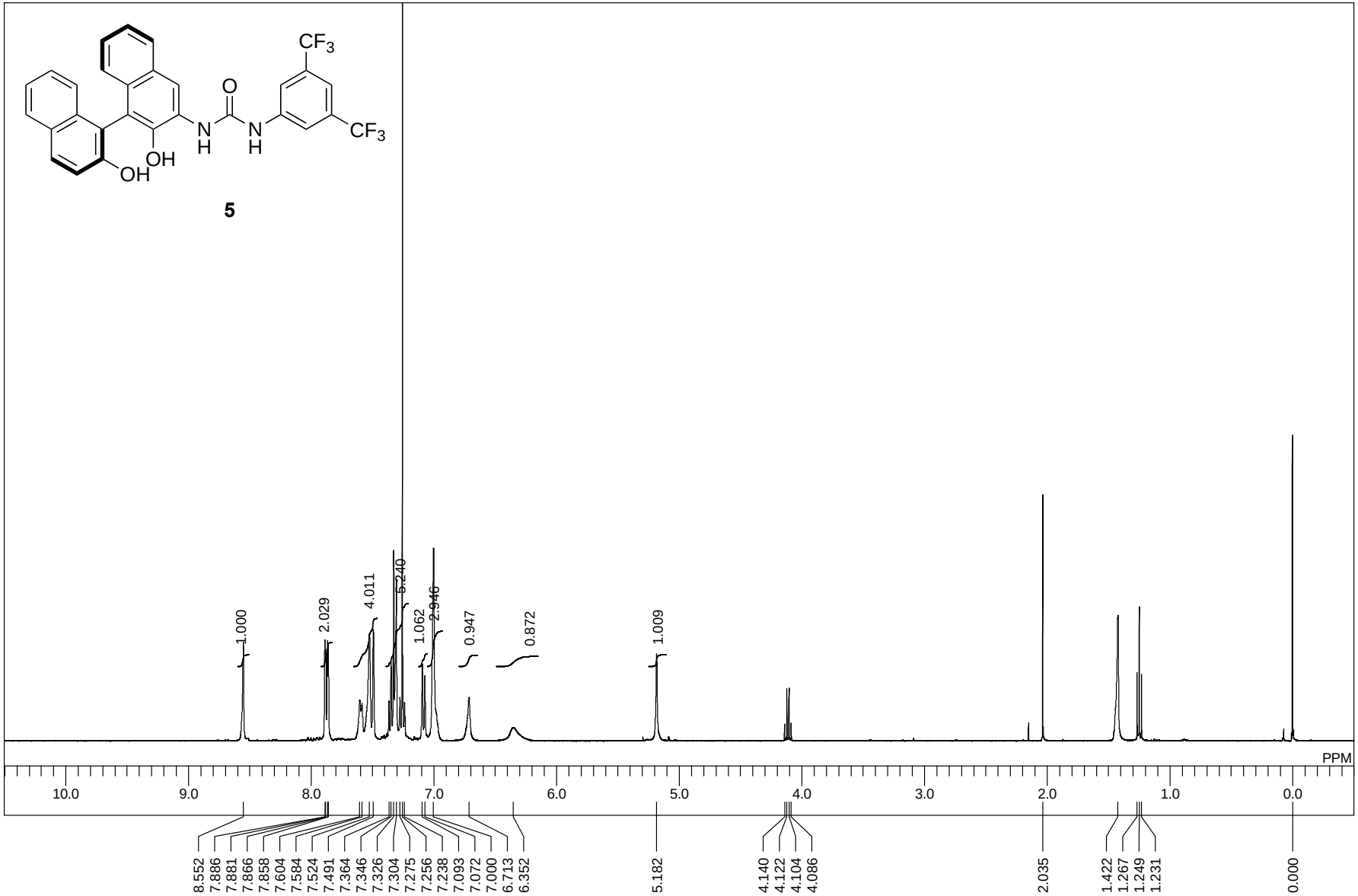

CO2H
N
2f
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
171.905
151.805
137.611
136.697
128.722
127.796
127.539
126.707
125.605
121.828
120.958
119.020
118.860
114.084
109.711
77.324
77.000
76.676
49.825
32.849
23.686

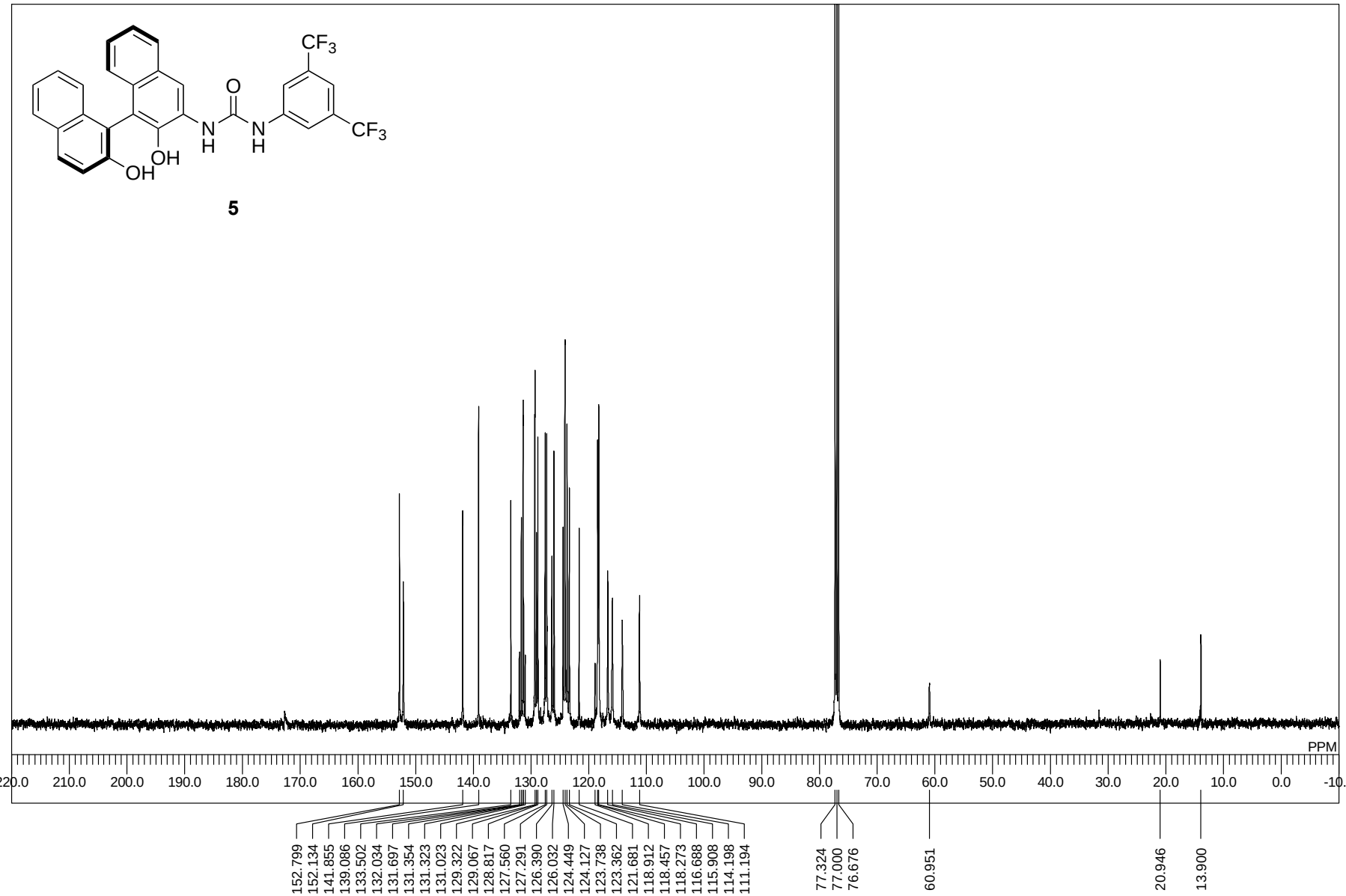

O
CO2H
2g
7.742
0.984
1.000
1.975
2.104
2.040
1.998
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.373
7.355
7.338
7.325
7.309
7.304
7.294
7.286
7.264
7.261
7.124
7.106
7.087
7.084
7.066
7.048
5.867
5.863
5.860
5.856
5.827
5.823
5.820
5.817
4.505
3.514
3.498
3.482
2.385
2.367
2.347
2.330
1.828
1.812
1.795
1.776
1.759
0.000

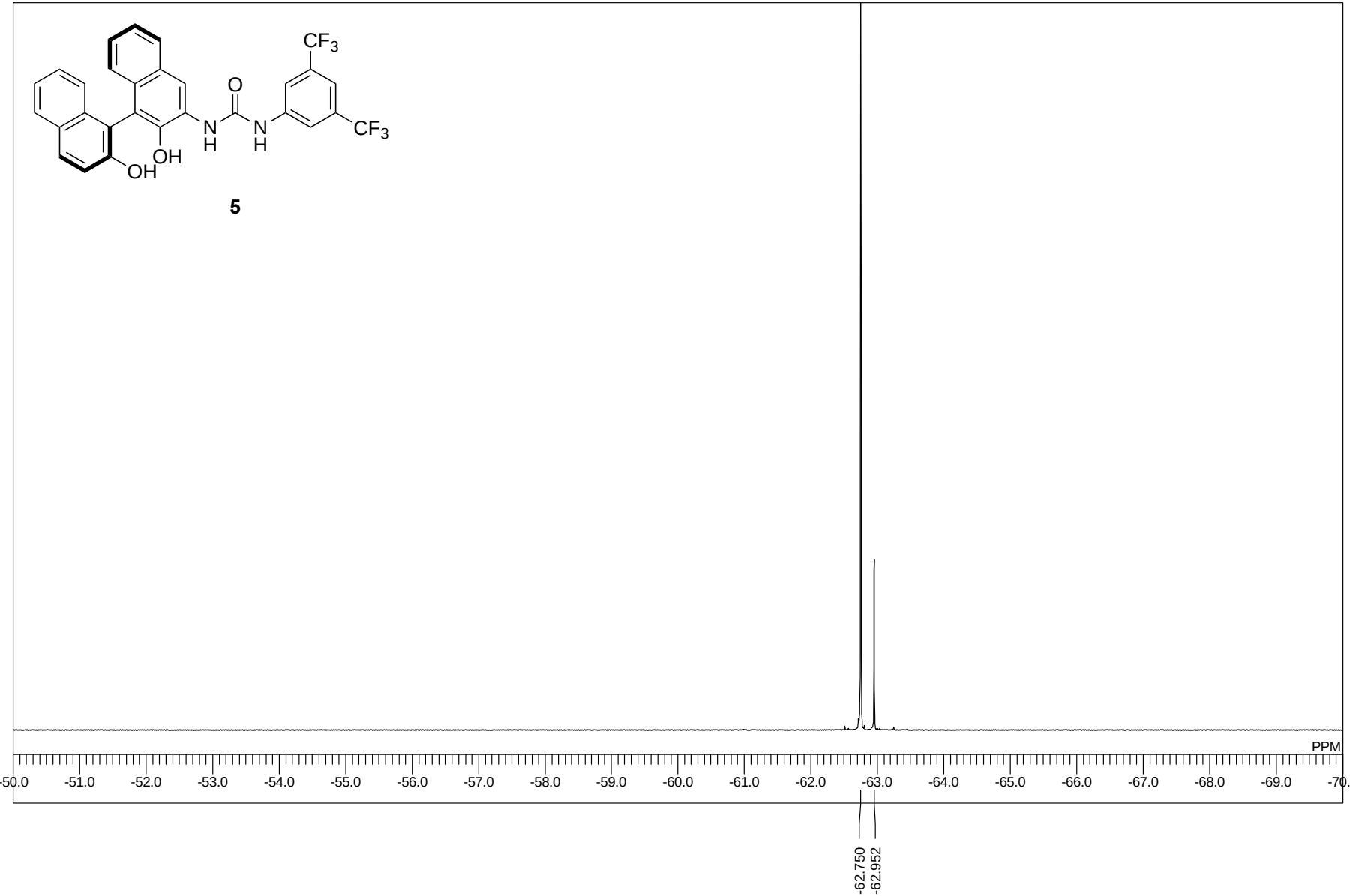

O
CO2H
2g
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
171.899
151.545
138.273
128.383
127.646
127.617
120.985
77.316
77.000
76.684
72.966
69.142
29.047
28.003

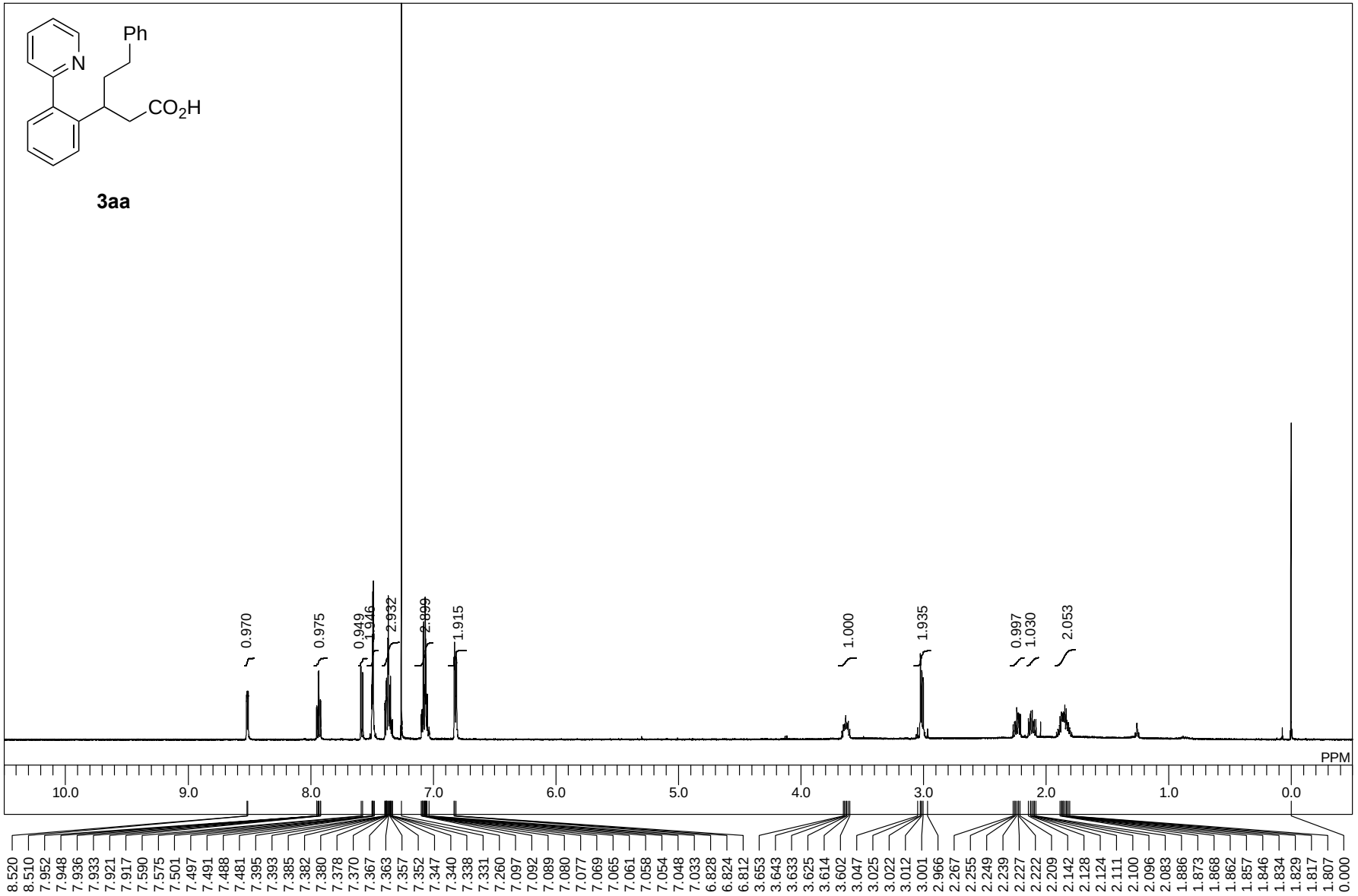

O
O
S
N
CO2H
2h
2.166
2.197
0.968
1.000
2.287
3.172
3.965
1.978
3.042
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.646
7.624
7.332
7.312
7.262
6.981
6.962
6.943
6.922
6.903
5.835
5.832
5.828
5.796
5.792
5.789
3.792
3.762
2.436
2.255
2.225
2.196
2.176
2.160
2.144
1.742
1.717
1.379
1.360
1.353
1.332
1.322
0.000

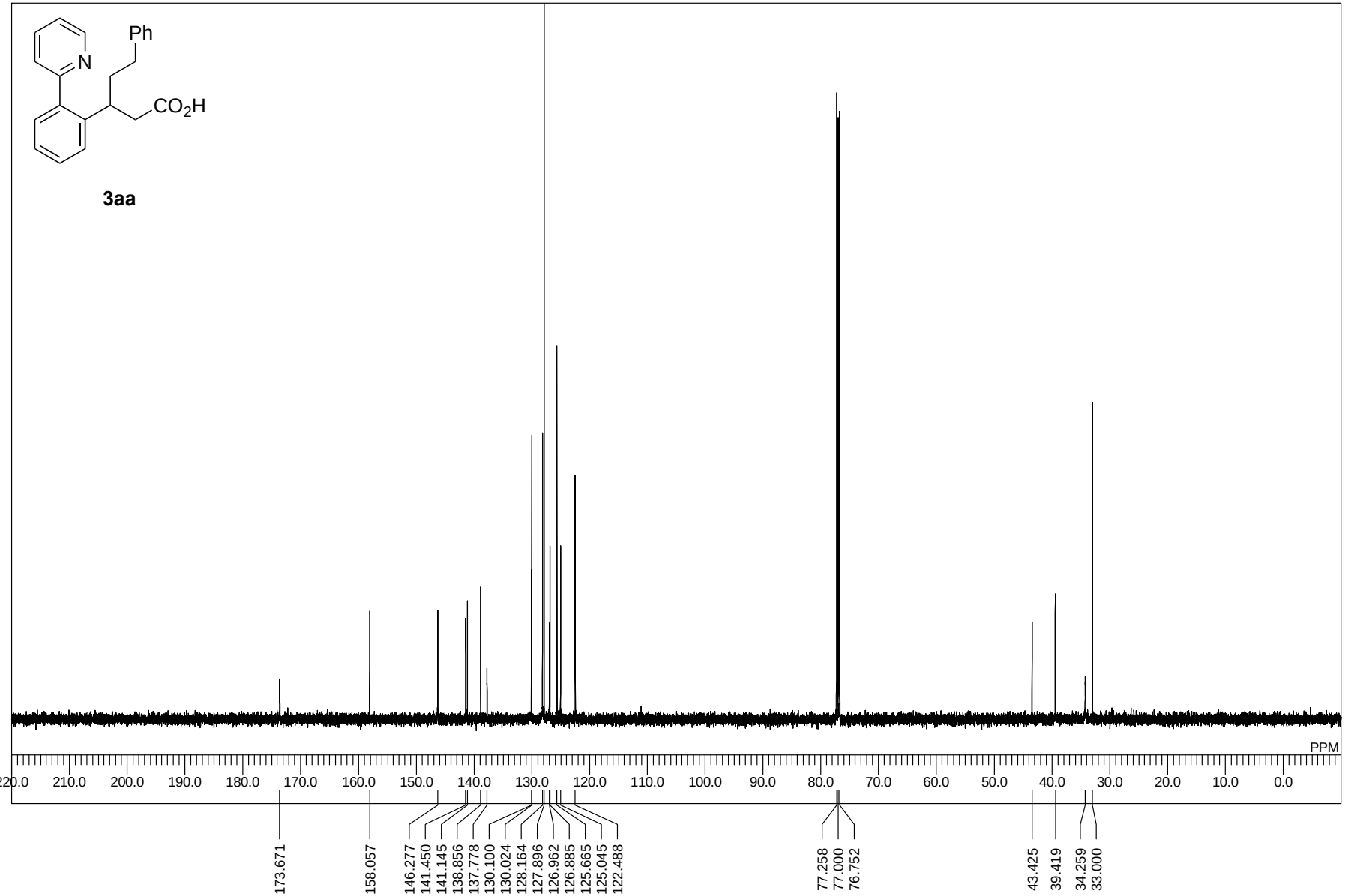

O
O
S
N
CO2H
2h
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
170.858
149.140
143.449
133.246
129.586
127.699
122.315
77.326
77.000
76.684
46.199
38.650
34.684
31.254
21.492

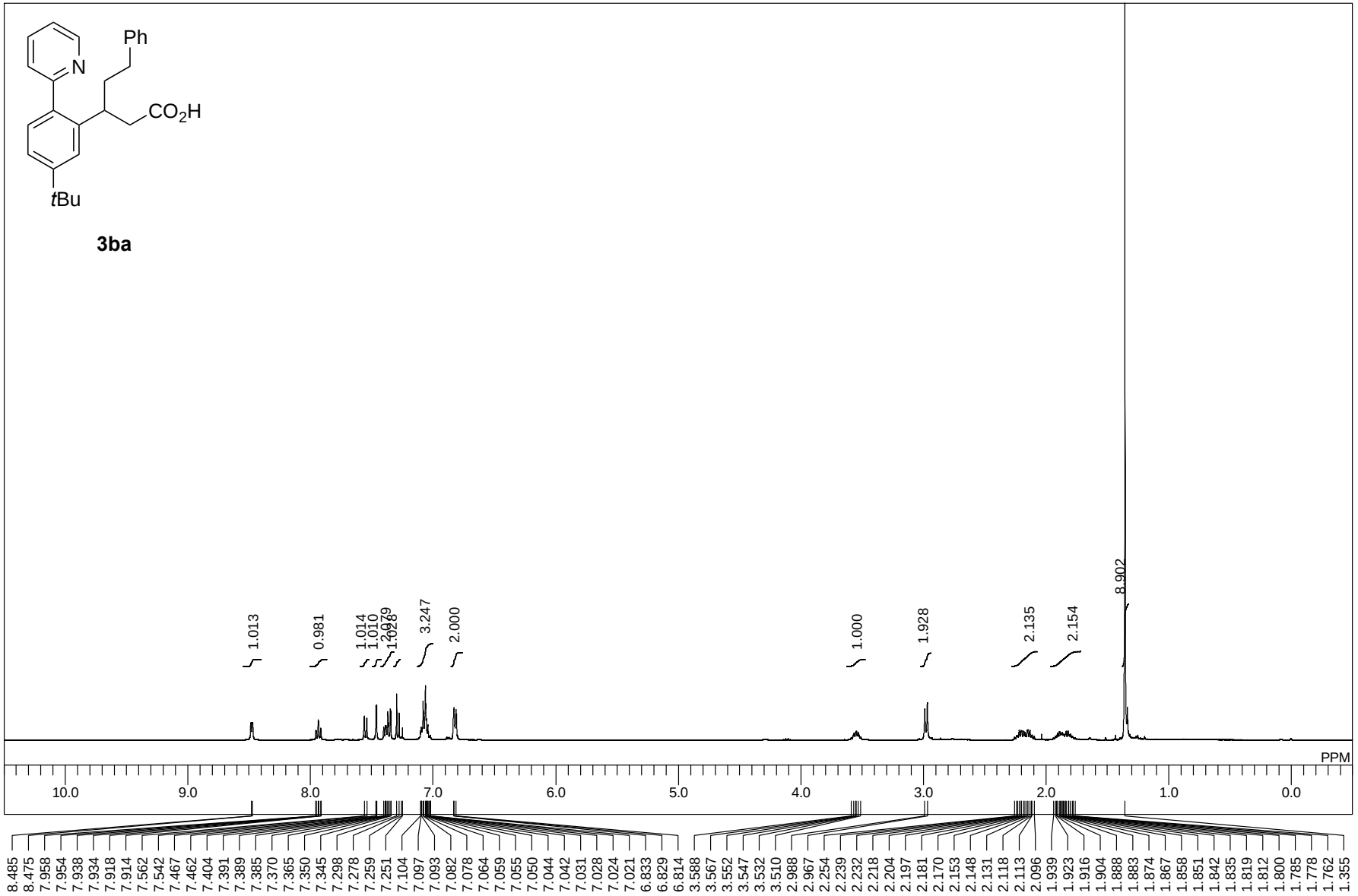

CF3
O
N
H
N
H
CF3
OH
OH
5
1.000
2.029
4.011
5.240
1.062
2.946
0.947
0.872
1.009
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.552
7.886
7.881
7.866
7.858
7.604
7.584
7.524
7.491
7.364
7.346
7.326
7.304
7.275
7.256
7.238
7.093
7.072
7.000
6.713
6.352
5.182
4.140
4.122
4.104
4.086
2.035
1.422
1.267
1.249
1.231
0.000

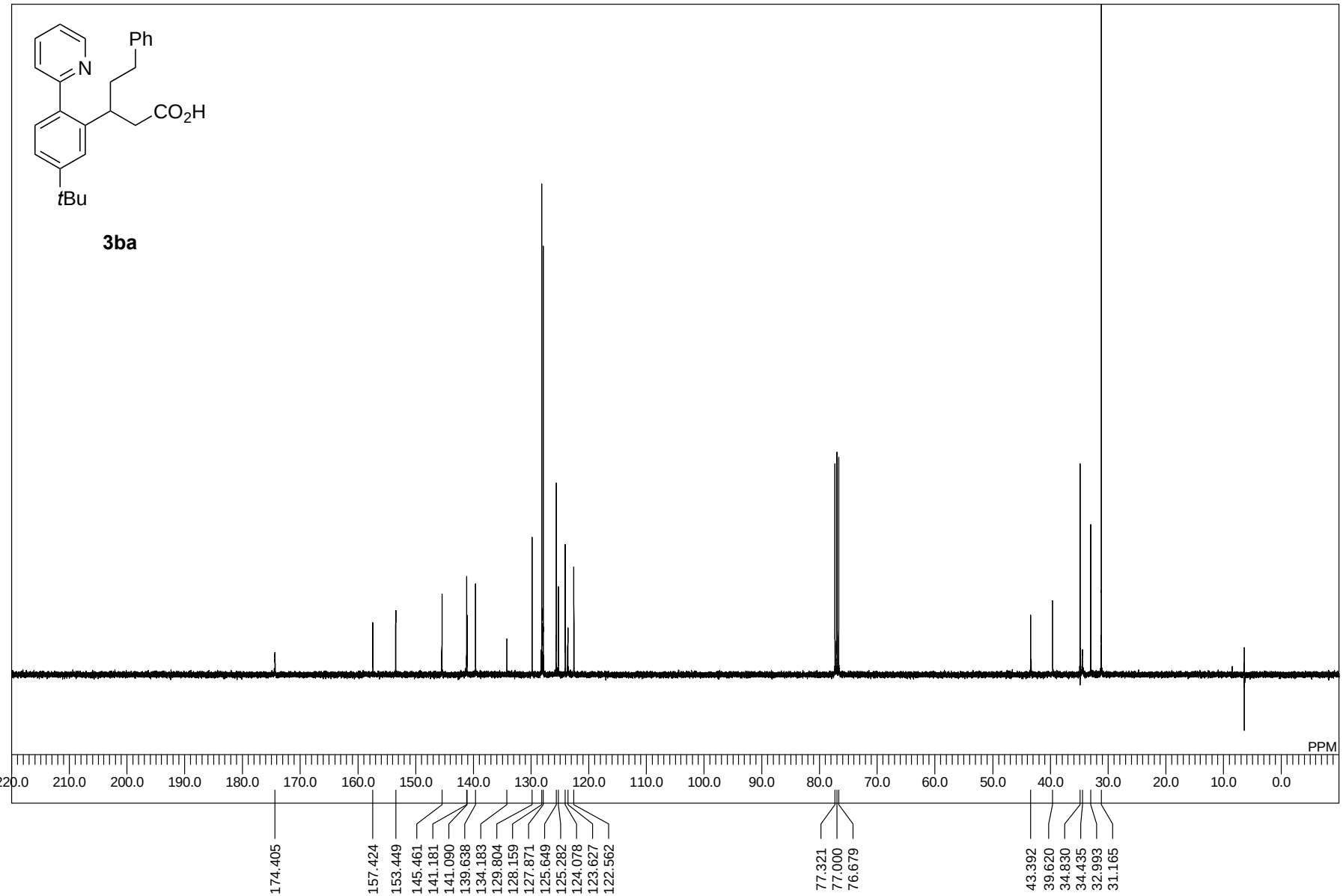

CF3
O
N
H
N
H
CF3
OH
OH
5
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
152.799
152.134
141.855
139.086
133.502
132.034
131.697
131.354
131.323
131.023
129.322
129.067
128.817
127.560
127.291
126.390
126.032
124.449
124.127
123.738
123.362
121.681
118.912
118.457
118.273
116.688
115.908
114.198
111.194
77.324
77.000
76.676
60.951
20.946
13.900

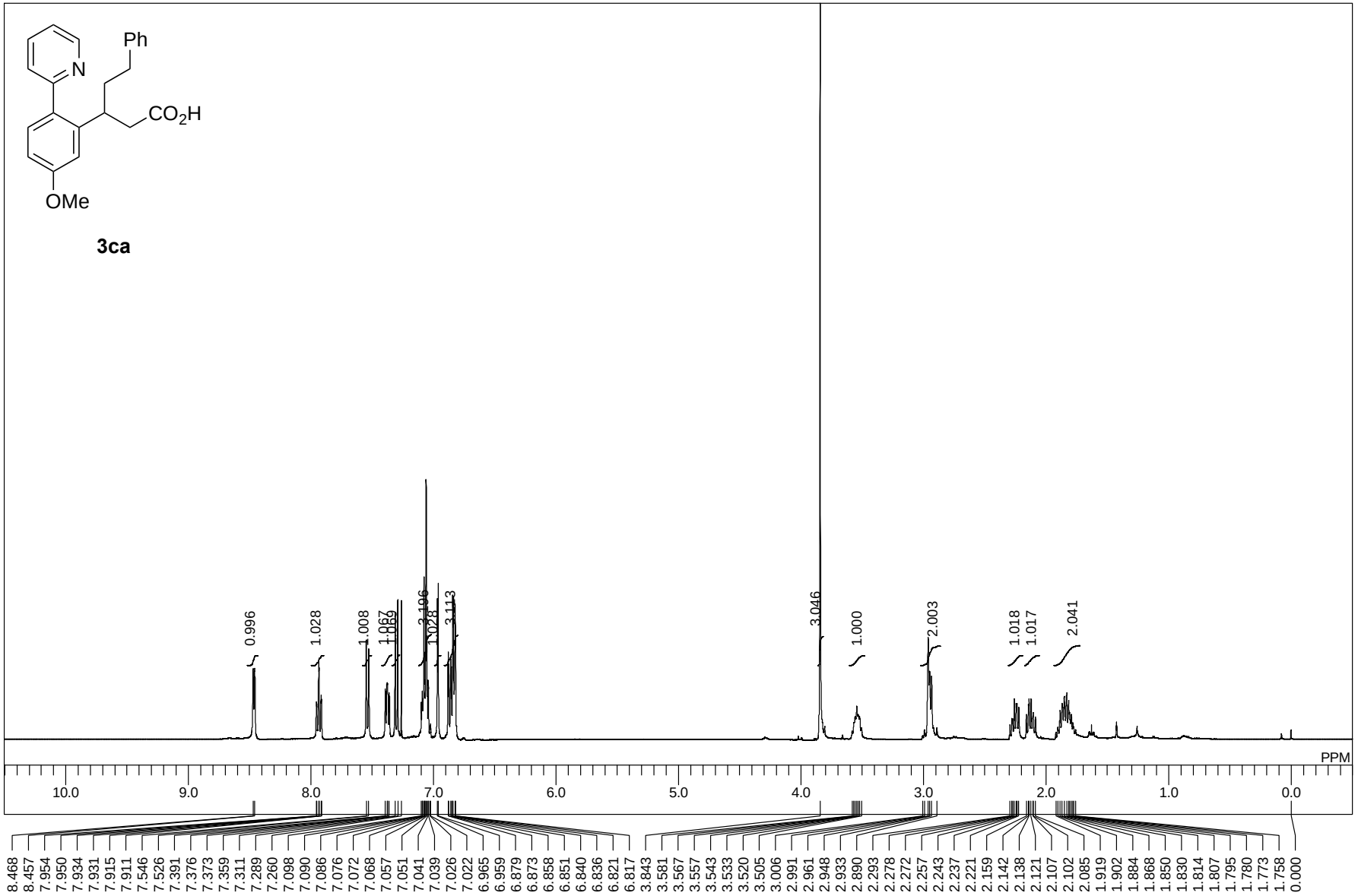

CF3
O
N
H
N
H
CF3
OH
OH
5
PPM
-50.0
-51.0
-52.0
-53.0
-54.0
-55.0
-56.0
-57.0
-58.0
-59.0
-60.0
-61.0
-62.0
-63.0
-64.0
-65.0
-66.0
-67.0
-68.0
-69.0
-70.0
-62.750
-62.952

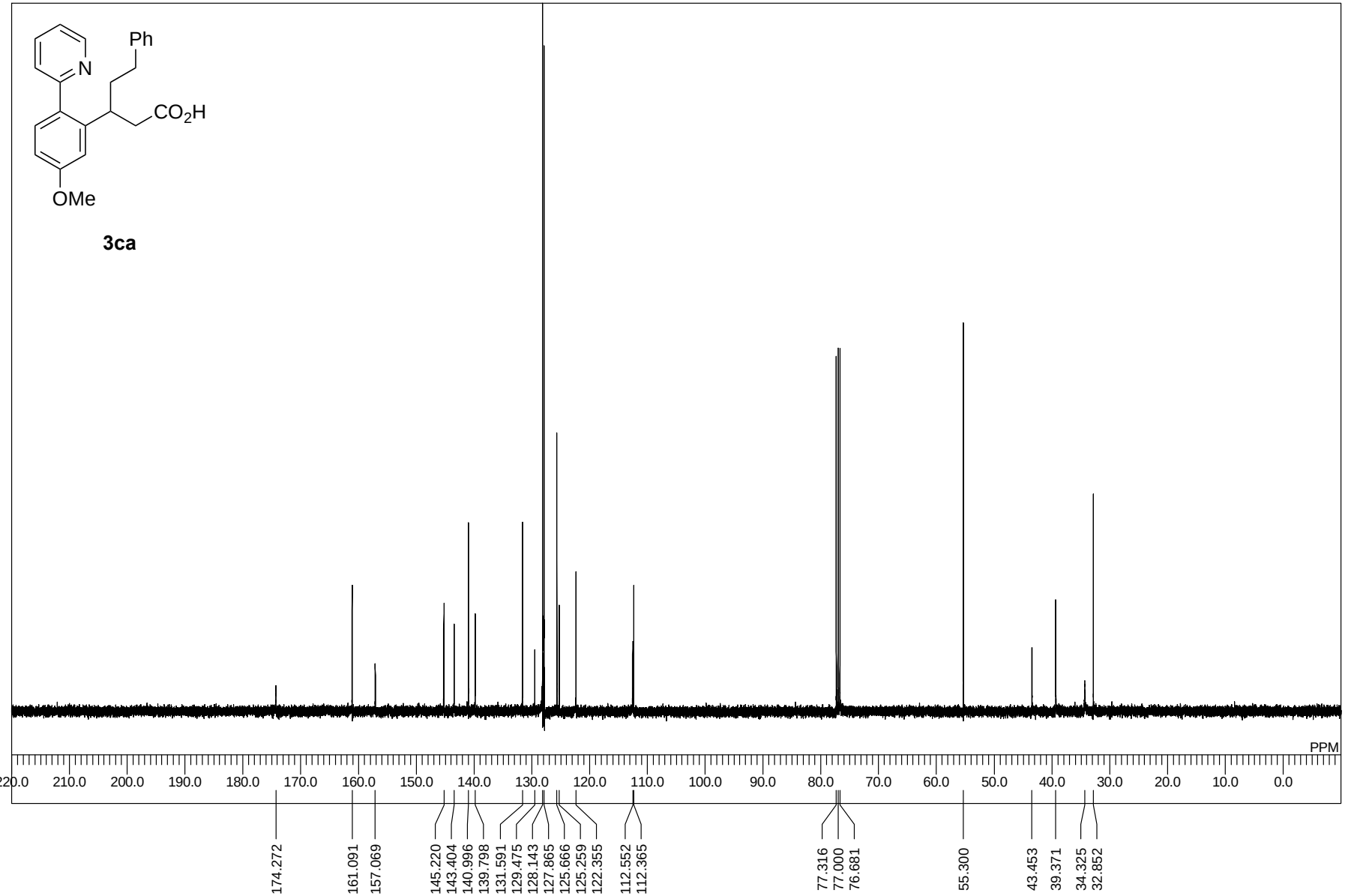

Ph
N
CO2H
3aa
0.970
0.975
0.949
1.946
2.932
2.899
1.915
1.000
1.935
0.997
1.030
2.053
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.520
8.510
7.952
7.948
7.936
7.933
7.921
7.917
7.590
7.575
7.501
7.497
7.491
7.488
7.481
7.395
7.393
7.385
7.382
7.380
7.378
7.370
7.367
7.363
7.357
7.352
7.347
7.340
7.338
7.331
7.260
7.097
7.092
7.089
7.080
7.077
7.069
7.065
7.061
7.058
7.054
7.048
7.033
6.828
6.824
6.812
3.653
3.643
3.633
3.625
3.614
3.602
3.047
3.025
3.022
3.012
3.001
2.966
2.267
2.255
2.249
2.239
2.227
2.222
2.209
2.142
2.128
2.124
2.111
2.100
2.096
2.083
1.886
1.873
1.868
1.862
1.857
1.846
1.834
1.829
1.817
1.807
0.000

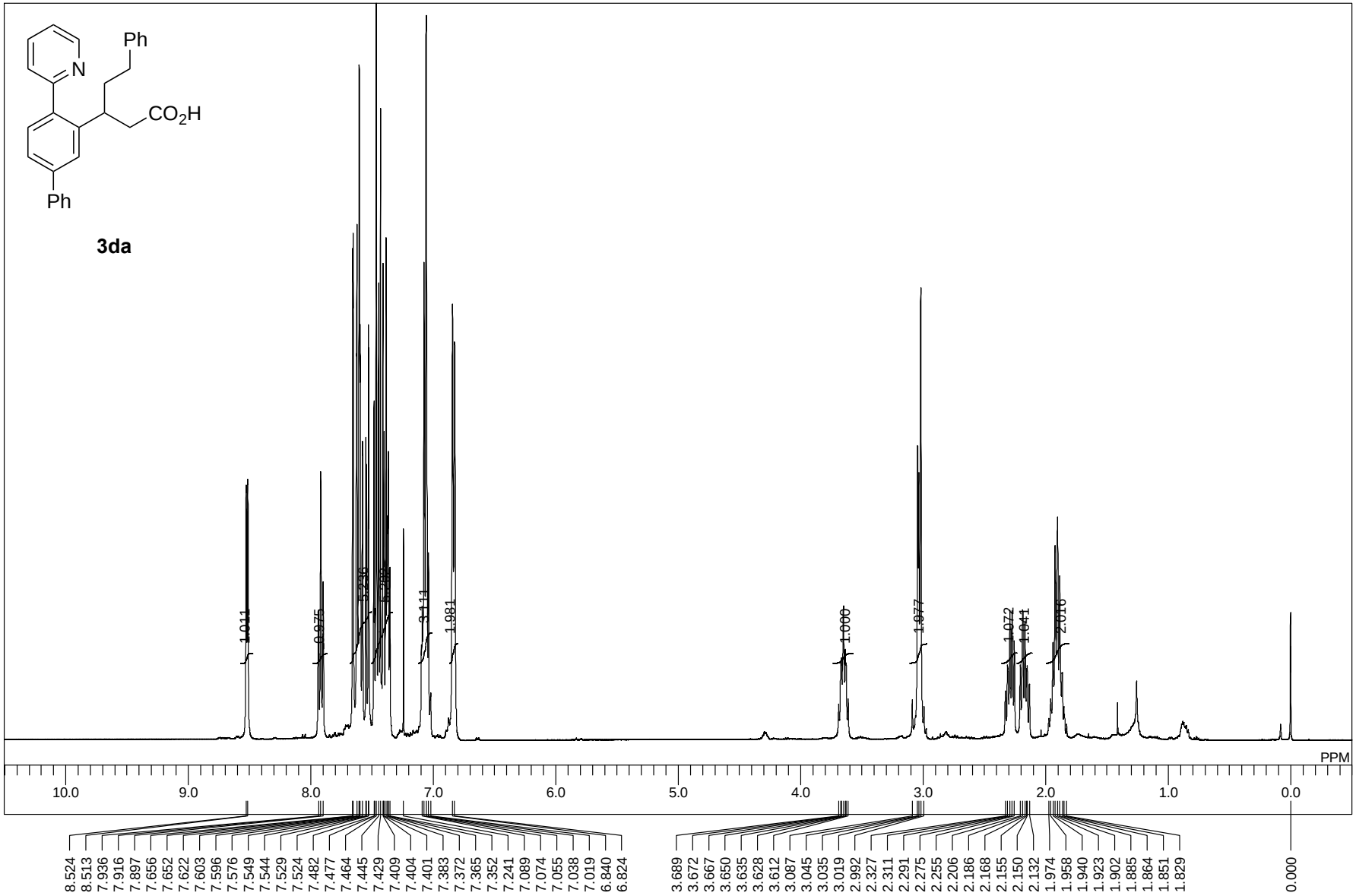

Ph
N
CO2H
3aa
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
173.671
158.057
146.277
141.450
141.145
138.856
137.778
130.100
130.024
128.164
127.896
126.962
126.885
125.665
125.045
122.488
77.258
77.000
76.752
43.425
39.419
34.259
33.000

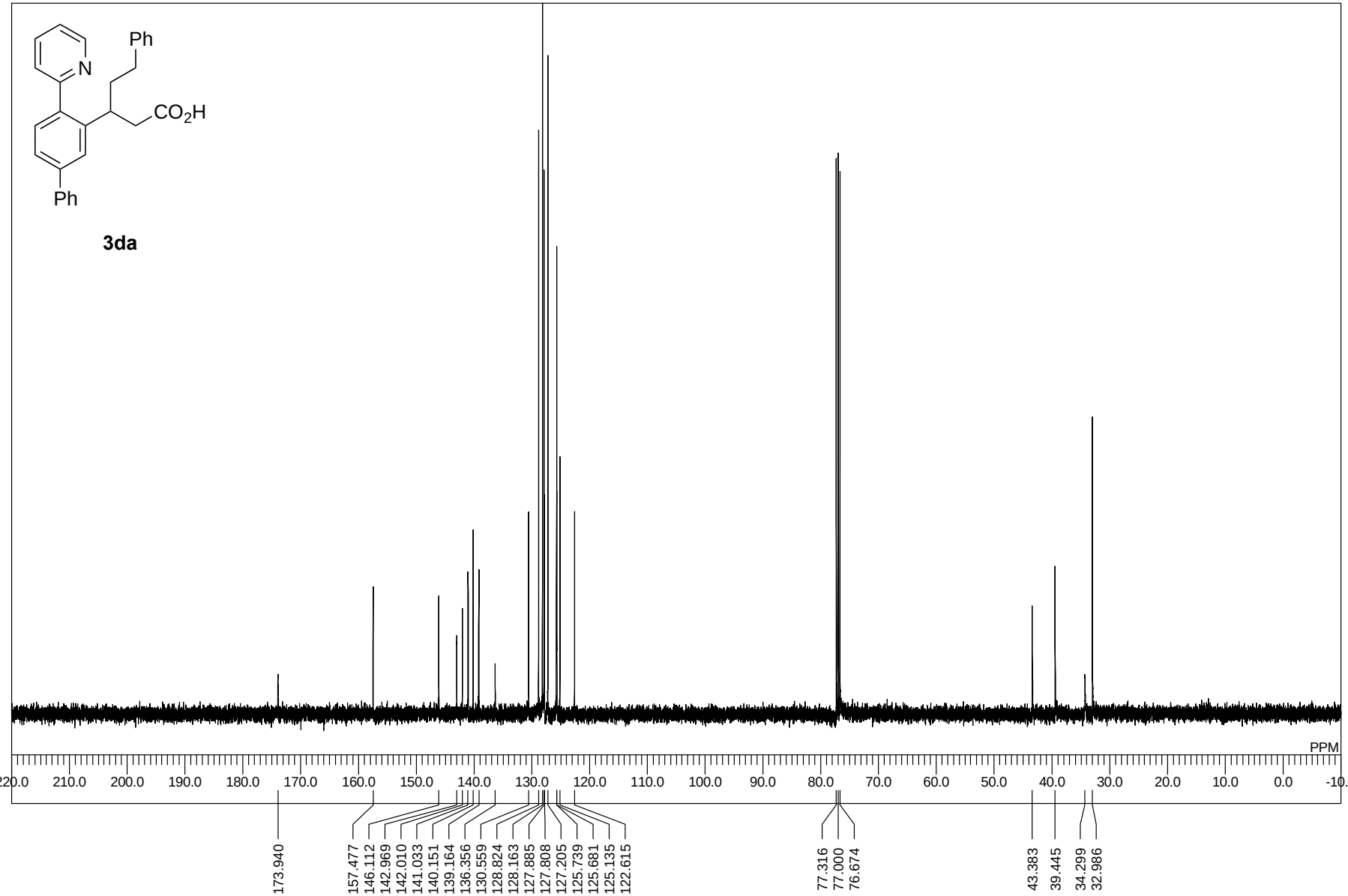

Ph
N
CO2H
tBu
3ba
1.013
0.981
1.014
1.010
1.029
1.028
3.247
2.000
1.000
1.928
2.135
2.154
8.902
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.485
8.475
7.958
7.954
7.938
7.934
7.918
7.914
7.562
7.542
7.467
7.462
7.404
7.391
7.389
7.385
7.370
7.365
7.350
7.345
7.298
7.278
7.259
7.251
7.104
7.097
7.093
7.082
7.078
7.064
7.059
7.055
7.050
7.044
7.042
7.031
7.028
7.024
7.021
6.833
6.829
6.814
3.588
3.567
3.552
3.547
3.532
3.510
2.988
2.967
2.254
2.239
2.232
2.218
2.204
2.197
2.181
2.170
2.153
2.148
2.131
2.118
2.113
2.096
1.939
1.923
1.916
1.904
1.888
1.883
1.874
1.867
1.858
1.851
1.842
1.835
1.819
1.812
1.800
1.785
1.778
1.762
1.355

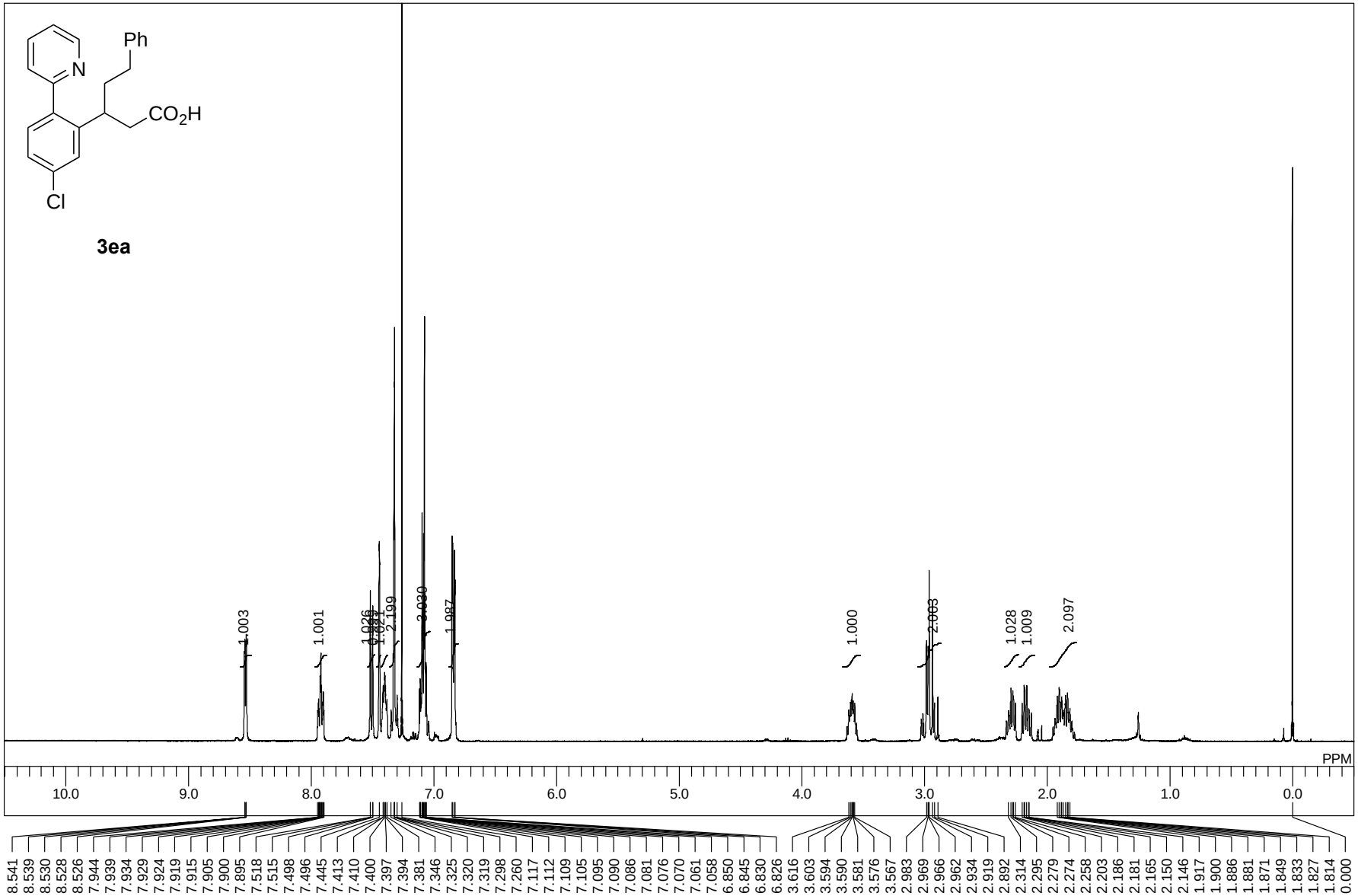

Ph
N
CO2H
tBu
3ba
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
174.405
157.424
153.449
145.461
141.181
141.090
139.638
134.183
129.804
128.159
127.871
125.649
125.282
124.078
123.627
122.562
77.321
77.000
76.679
43.392
39.620
34.830
34.435
32.993
31.165

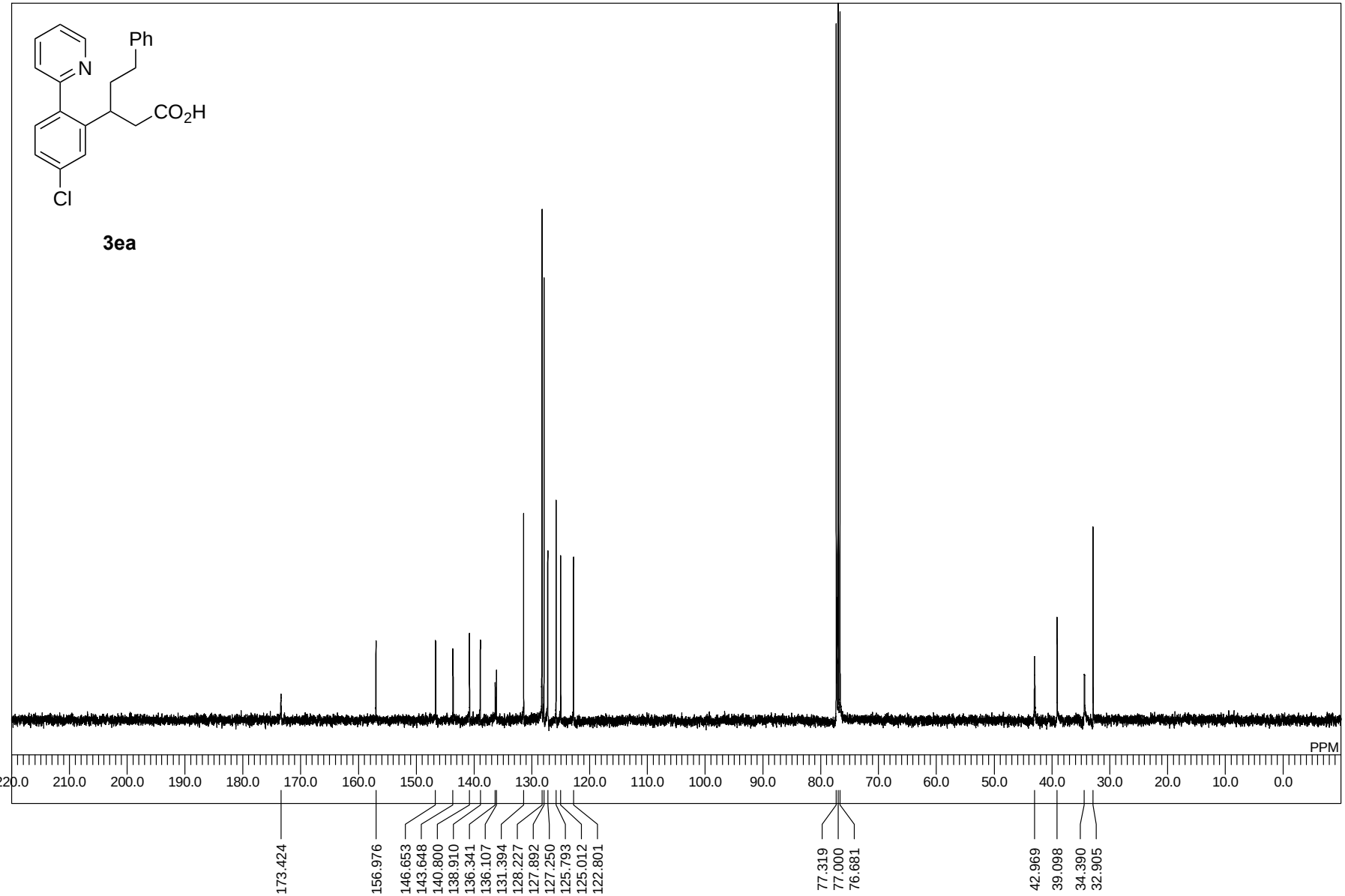

Ph
N
CO2H
OMe
3ca
0.996
1.028
1.008
1.087
1.069
3.196
3.028
3.113
3.046
1.000
2.003
1.018
1.017
2.041
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

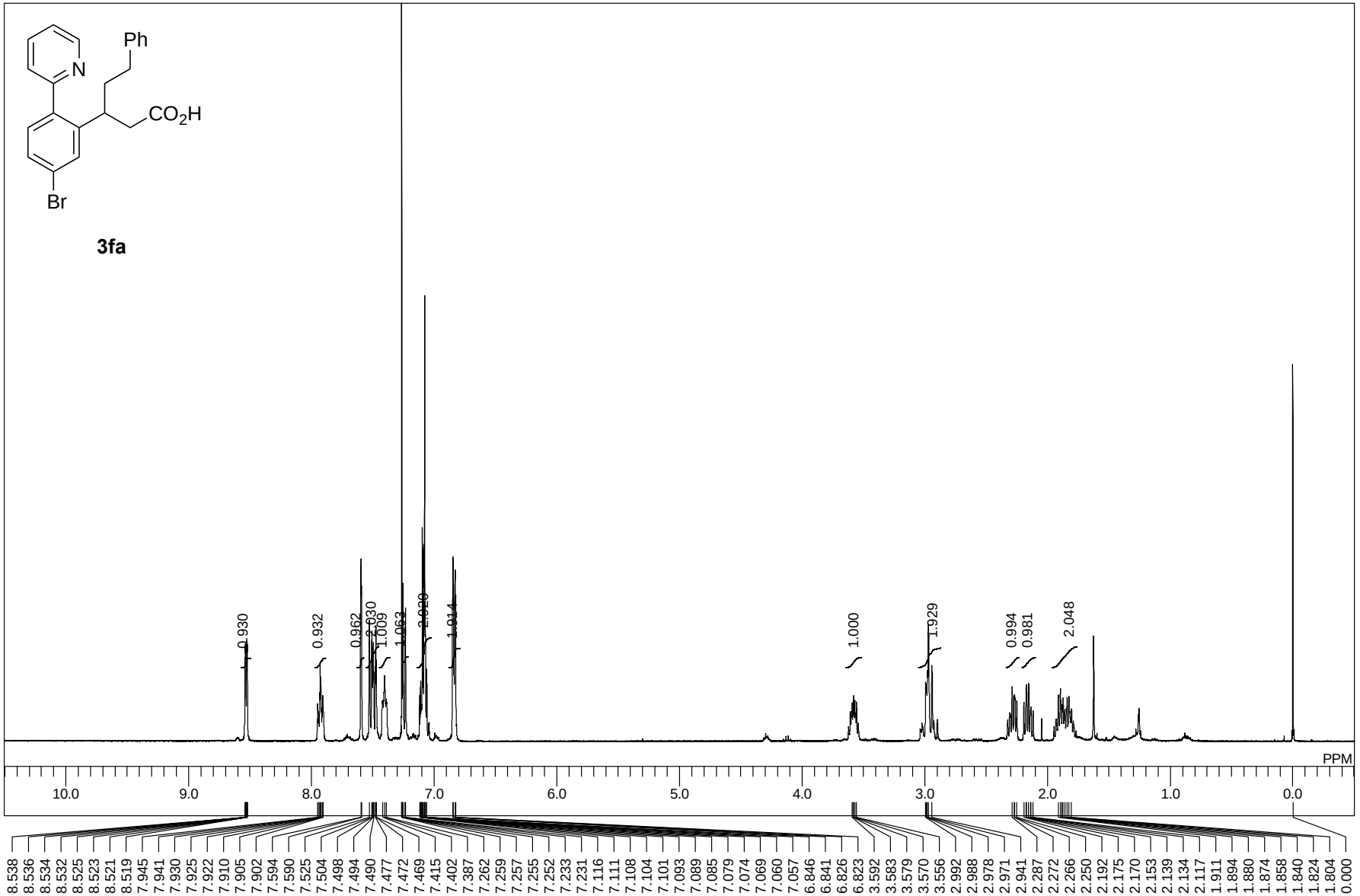

Ph
N
CO2H
OMe
3ca
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
174.272
161.091
157.069
145.220
143.404
140.996
139.798
131.591
129.475
128.143
127.865
125.666
125.259
122.355
112.552
112.365
77.316
77.000
76.681
55.300
43.453
39.371
34.325
32.852

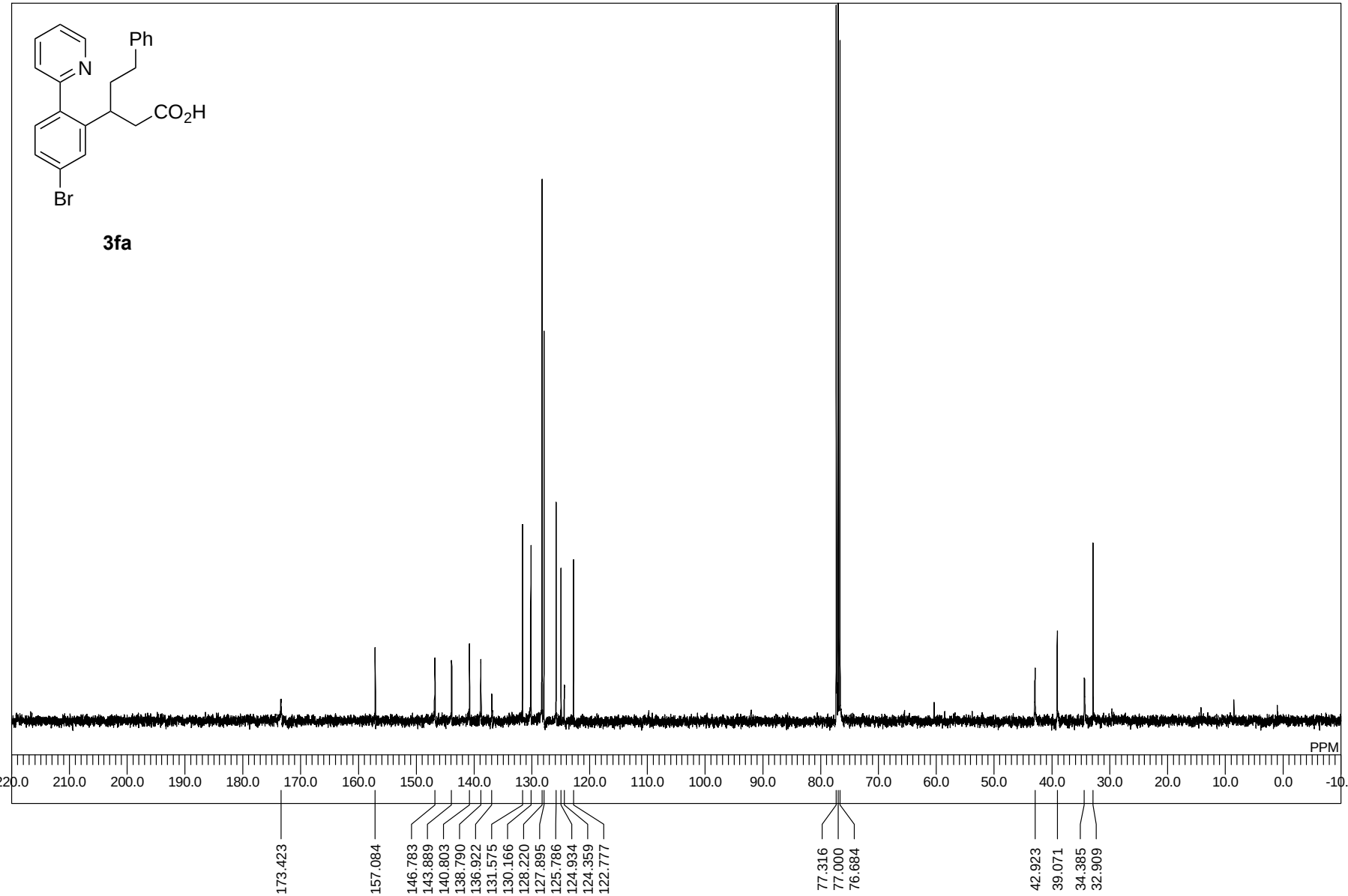

Ph
N
CO2H
Ph
3da
1.011
0.975
3.111
1.081
1.000
1.977
1.072
1.041
2.016
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.524
8.513
7.936
7.916
7.897
7.656
7.652
7.622
7.603
7.596
7.576
7.549
7.544
7.529
7.524
7.482
7.477
7.464
7.445
7.429
7.409
7.404
7.401
7.383
7.372
7.365
7.352
7.241
7.089
7.074
7.055
7.038
7.019
6.840
6.824
3.689
3.672
3.667
3.650
3.635
3.628
3.612
3.087
3.045
3.035
3.019
2.992
2.327
2.311
2.291
2.275
2.255
2.206
2.186
2.168
2.155
2.150
2.132
1.974
1.958
1.940
1.923
1.902
1.885
1.864
1.851
1.829
0.000

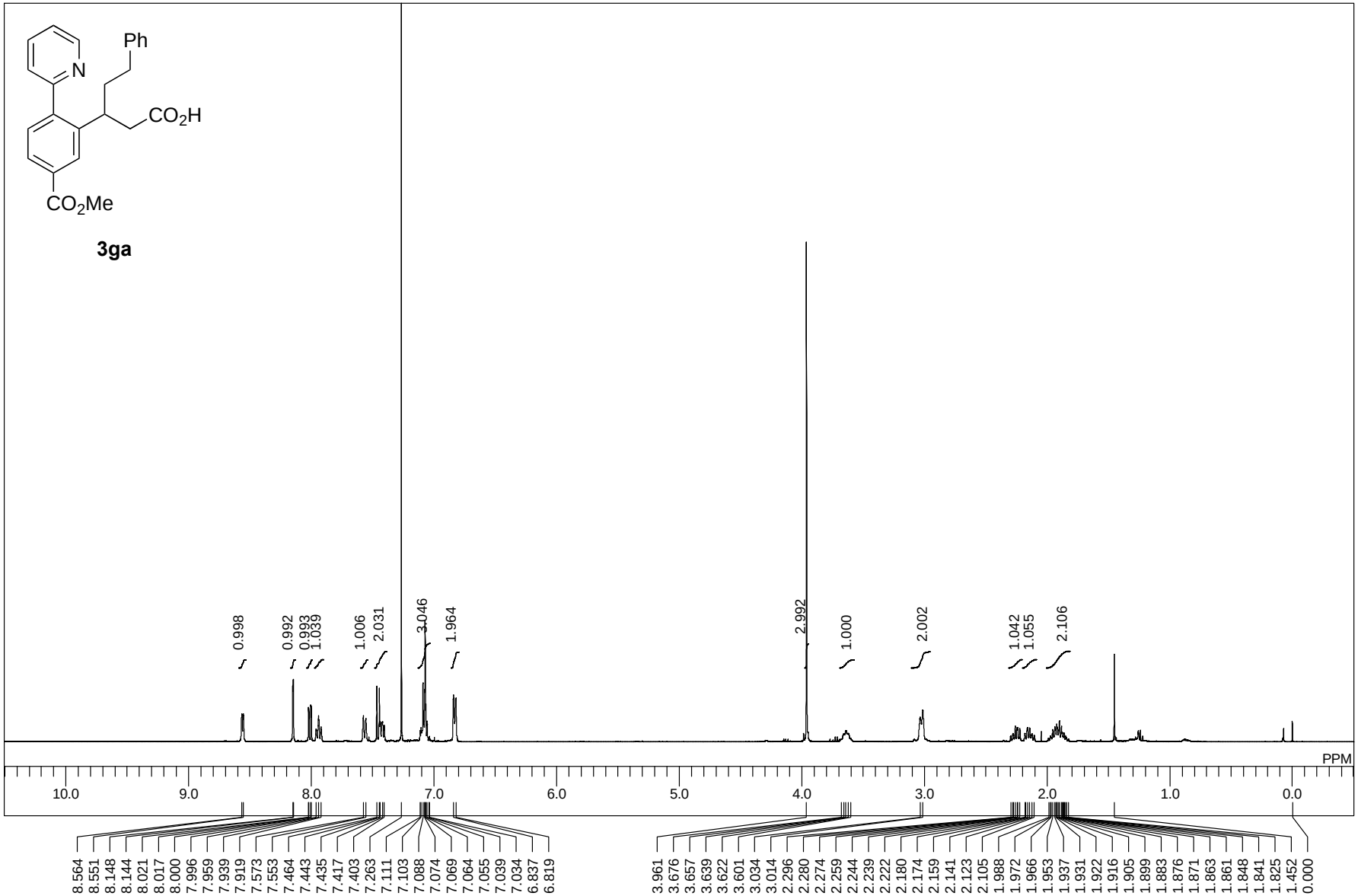

Ph
N
CO2H
Ph
3da
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
173.940
157.477
146.112
142.969
142.010
141.033
140.151
139.164
136.356
130.559
128.824
128.163
127.885
127.808
127.205
125.739
125.681
125.135
122.615
77.316
77.000
76.674
43.383
39.445
34.299
32.986

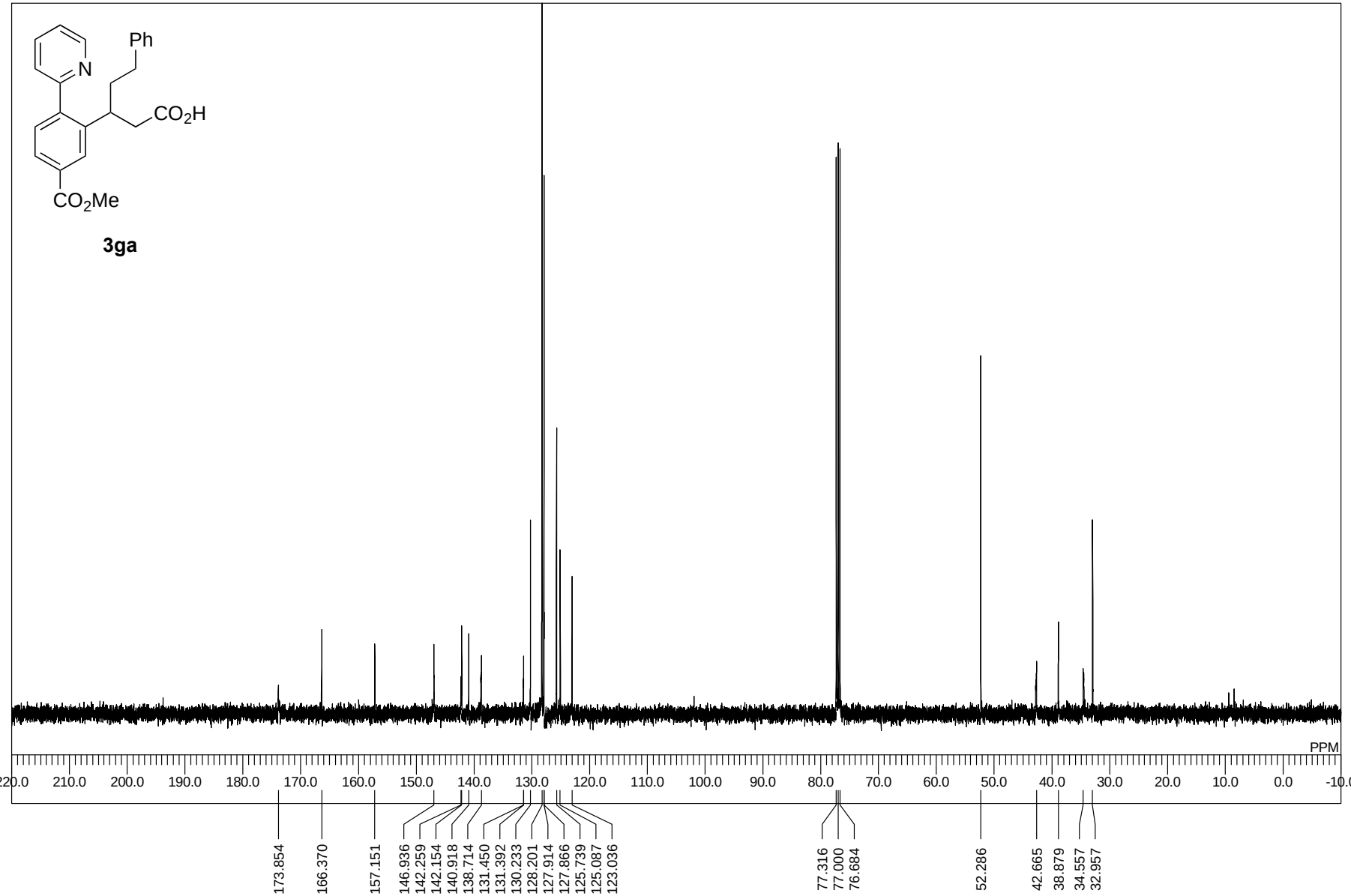

Ph
N
CO2H
Cl
3ea
1.003
1.001
1.026
0.837
1.027
2.199
2.030
1.987
1.000
2.003
1.028
1.009
2.097
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.541
8.539
8.530
8.528
8.526
7.944
7.939
7.934
7.929
7.924
7.919
7.915
7.905
7.900
7.895
7.518
7.515
7.498
7.496
7.445
7.413
7.410
7.400
7.397
7.394
7.381
7.346
7.325
7.320
7.319
7.298
7.260
7.117
7.112
7.109
7.105
7.095
7.090
7.086
7.081
7.076
7.070
7.061
7.058
6.850
6.845
6.830
6.826
3.616
3.603
3.594
3.590
3.581
3.576
3.567
2.983
2.969
2.966
2.962
2.934
2.919
2.892
2.314
2.295
2.279
2.274
2.258
2.203
2.186
2.181
2.165
2.150
2.146
1.917
1.900
1.886
1.881
1.871
1.849
1.833
1.827
1.814
0.000

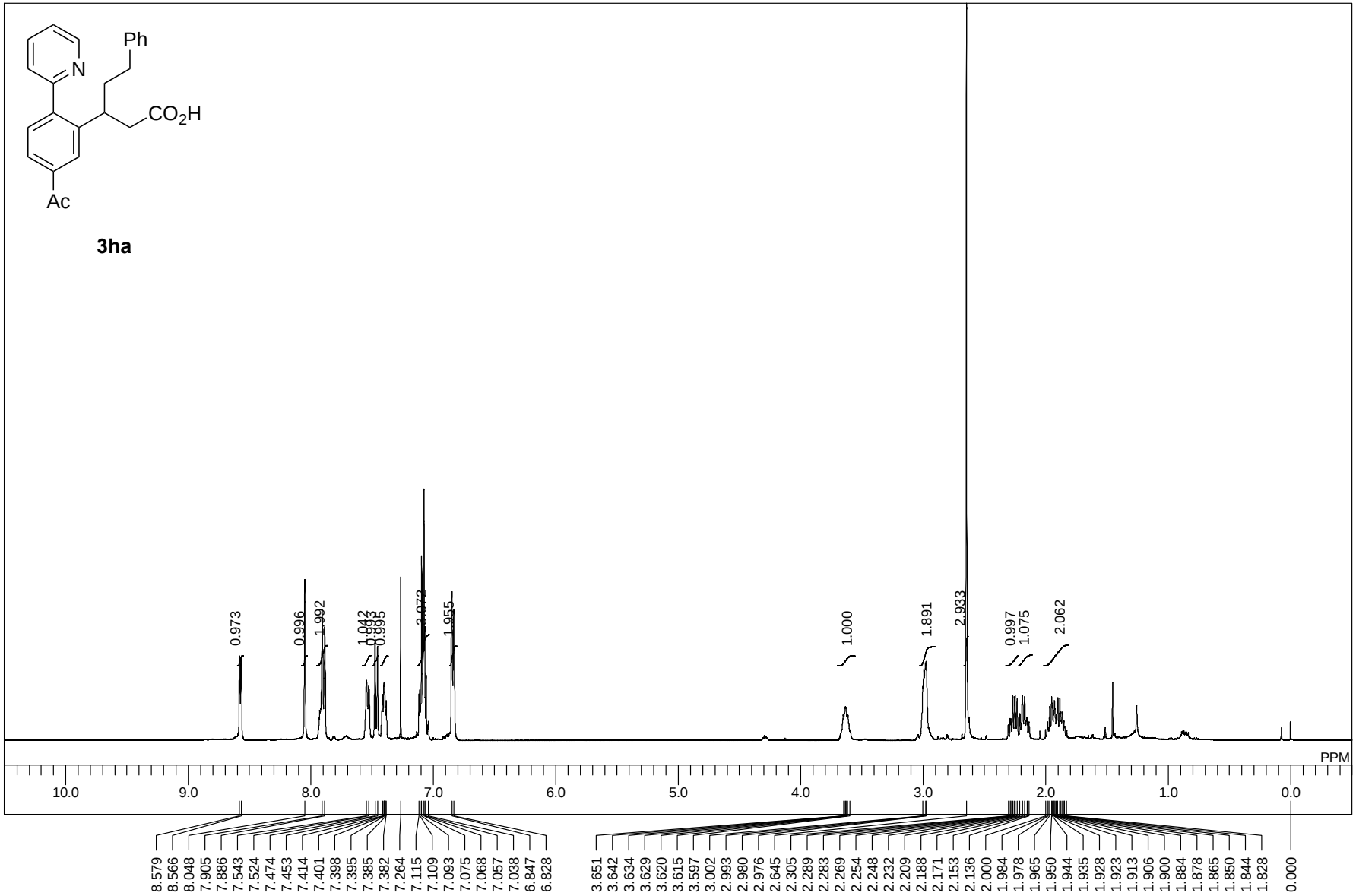

Ph
N
CO2H
Cl
3ea
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
173.424
156.976
146.653
143.648
140.800
138.910
136.341
136.107
131.394
128.227
127.892
127.250
125.793
125.012
122.801
77.319
77.000
76.681
42.969
39.098
34.390
32.905

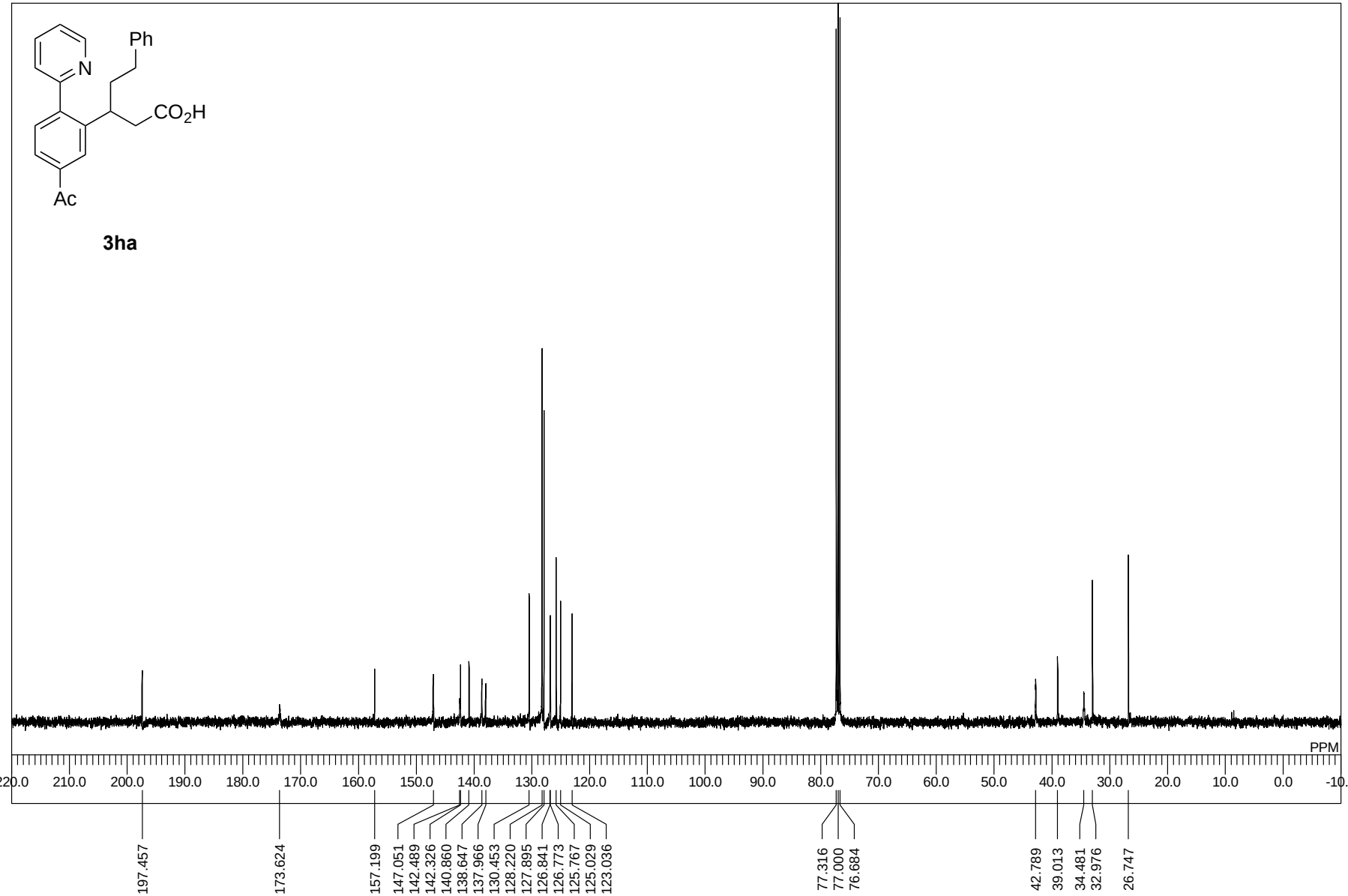

Ph
N
CO2H
Br
3fa
0.930
0.932
0.962
0.630
1.009
1.063
2.020
1.014
1.000
1.929
0.994
0.981
2.048
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

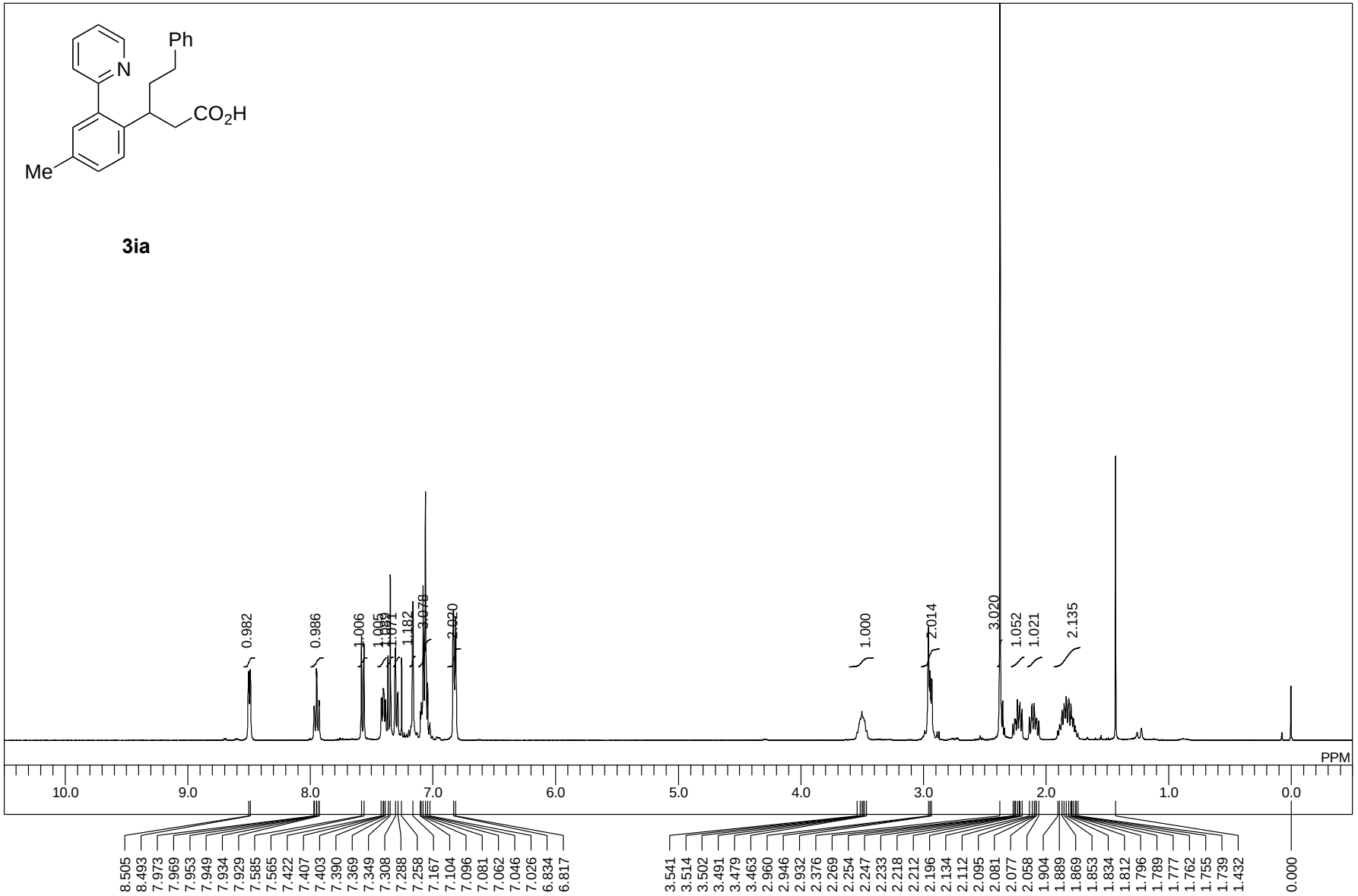

Ph
N
CO2H
Br
3fa
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
173.423
157.084
146.783
143.889
140.803
138.790
136.922
131.575
130.166
128.220
127.895
125.786
124.934
124.359
122.777
77.316
77.000
76.684
42.923
39.071
34.385
32.909

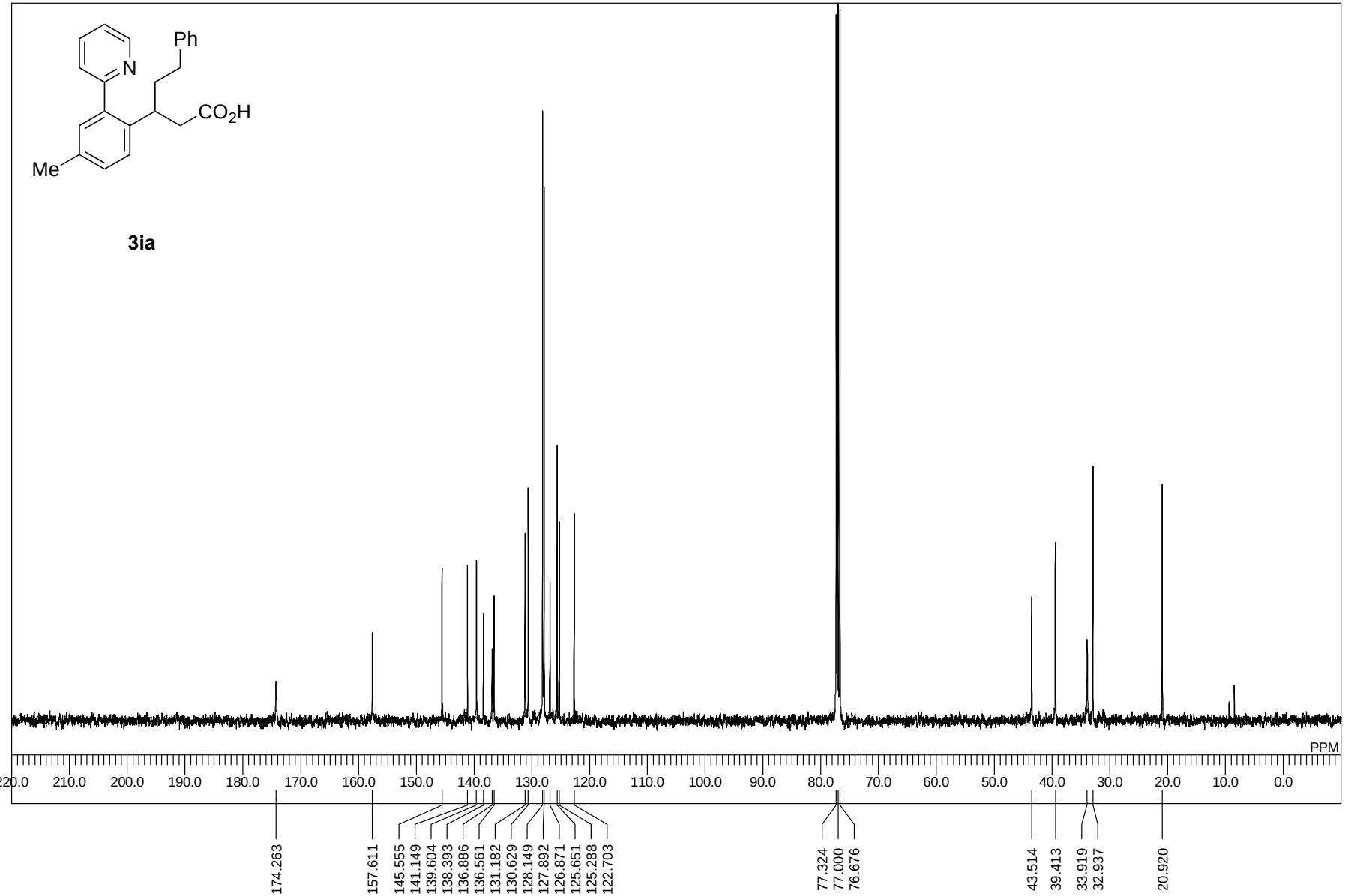

Ph
N
CO2H
CO2Me
3ga
0.998
0.992
0.993
1.039
1.006
2.031
3.046
1.964
2.992
1.000
2.002
1.042
1.055
2.106
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.564
8.551
8.148
8.144
8.021
8.017
8.000
7.996
7.959
7.939
7.919
7.573
7.553
7.464
7.443
7.435
7.417
7.403
7.263
7.111
7.103
7.088
7.074
7.069
7.064
7.055
7.039
7.034
6.837
6.819
3.961
3.676
3.657
3.639
3.622
3.601
3.034
3.014
2.296
2.280
2.274
2.259
2.244
2.239
2.222
2.180
2.174
2.159
2.141
2.123
2.105
1.988
1.972
1.966
1.953
1.937
1.931
1.922
1.916
1.905
1.899
1.883
1.876
1.871
1.863
1.861
1.848
1.841
1.825
1.452
0.000

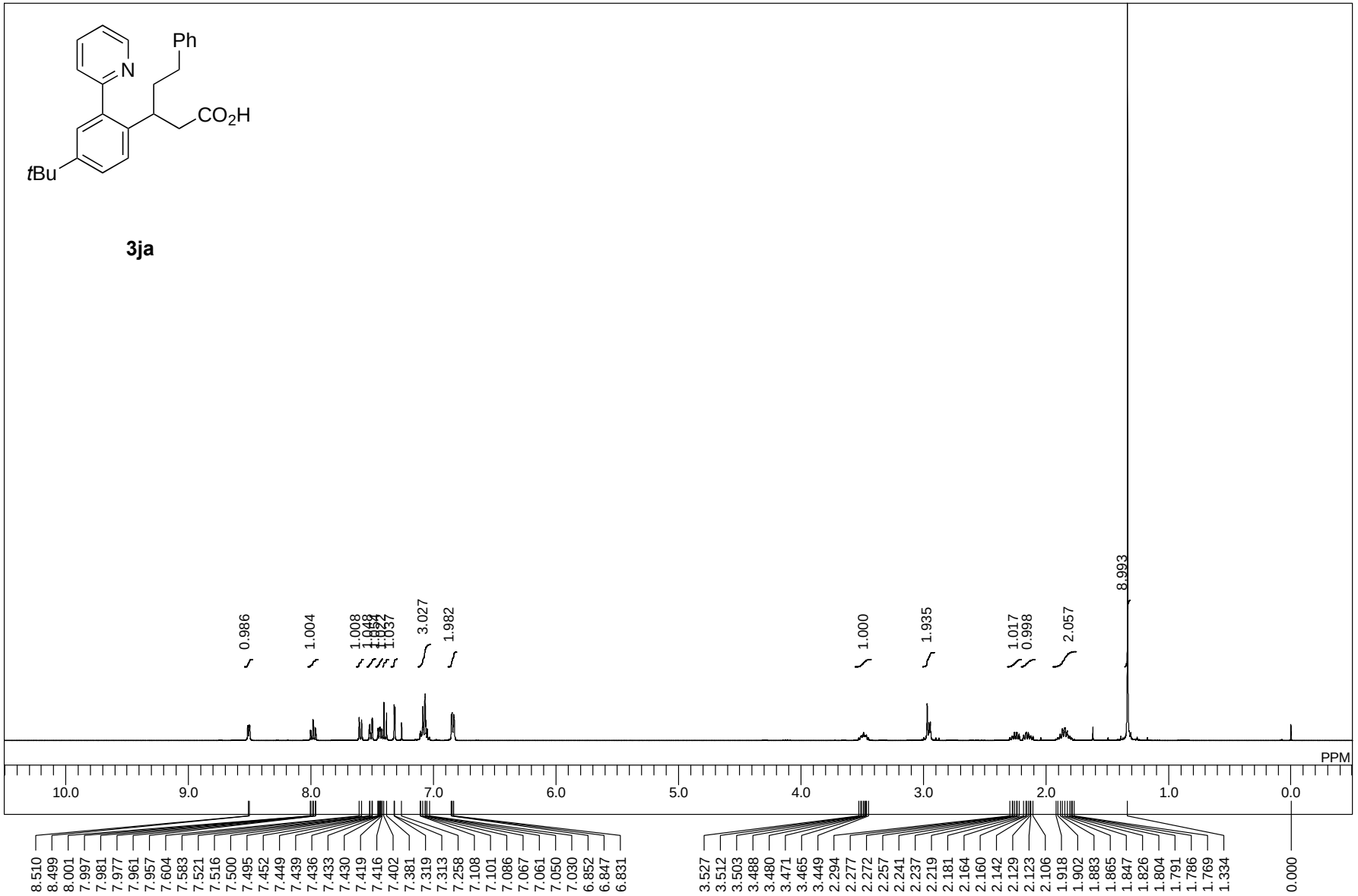

Ph
N
CO2H
CO2Me
3ga
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
173.854
166.370
157.151
146.936
142.259
142.154
140.918
138.714
131.450
131.392
130.233
128.201
127.914
127.866
125.739
125.087
123.036
77.316
77.000
76.684
52.286
42.665
38.879
34.557
32.957

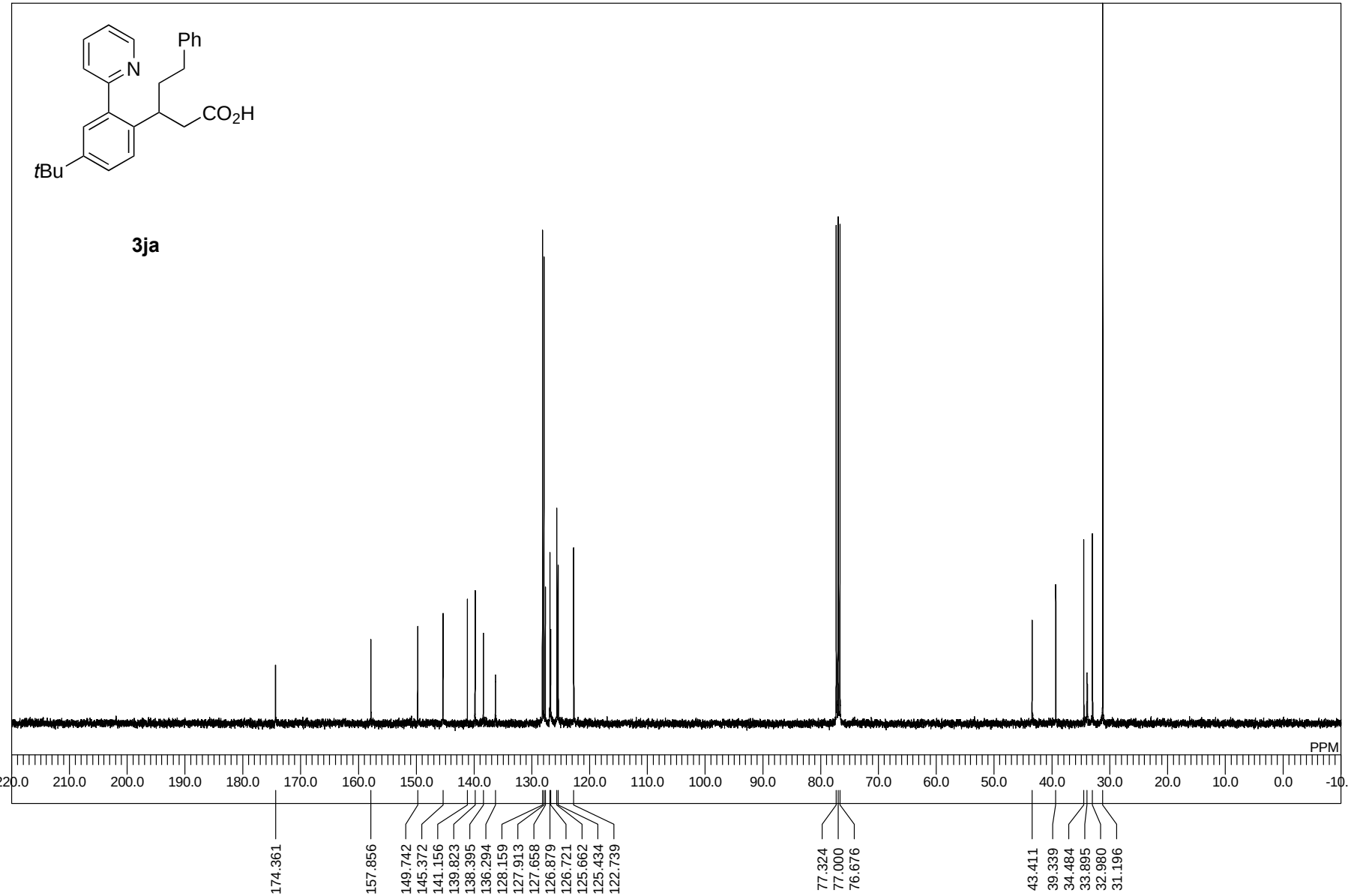

Ph
N
CO2H
Ac
3ha
0.973
0.996
1.992
1.042
1.023
0.995
2.072
1.955
1.000
1.891
2.933
0.997
1.075
2.062
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.579
8.566
8.048
7.905
7.886
7.543
7.524
7.474
7.453
7.414
7.401
7.398
7.395
7.385
7.382
7.264
7.115
7.109
7.093
7.075
7.068
7.057
7.038
6.847
6.828
3.651
3.642
3.634
3.629
3.620
3.615
3.597
3.002
2.993
2.980
2.976
2.645
2.305
2.289
2.283
2.269
2.254
2.248
2.232
2.209
2.188
2.171
2.153
2.136
2.000
1.984
1.978
1.965
1.950
1.944
1.935
1.928
1.923
1.913
1.906
1.900
1.884
1.878
1.865
1.850
1.844
1.828
0.000

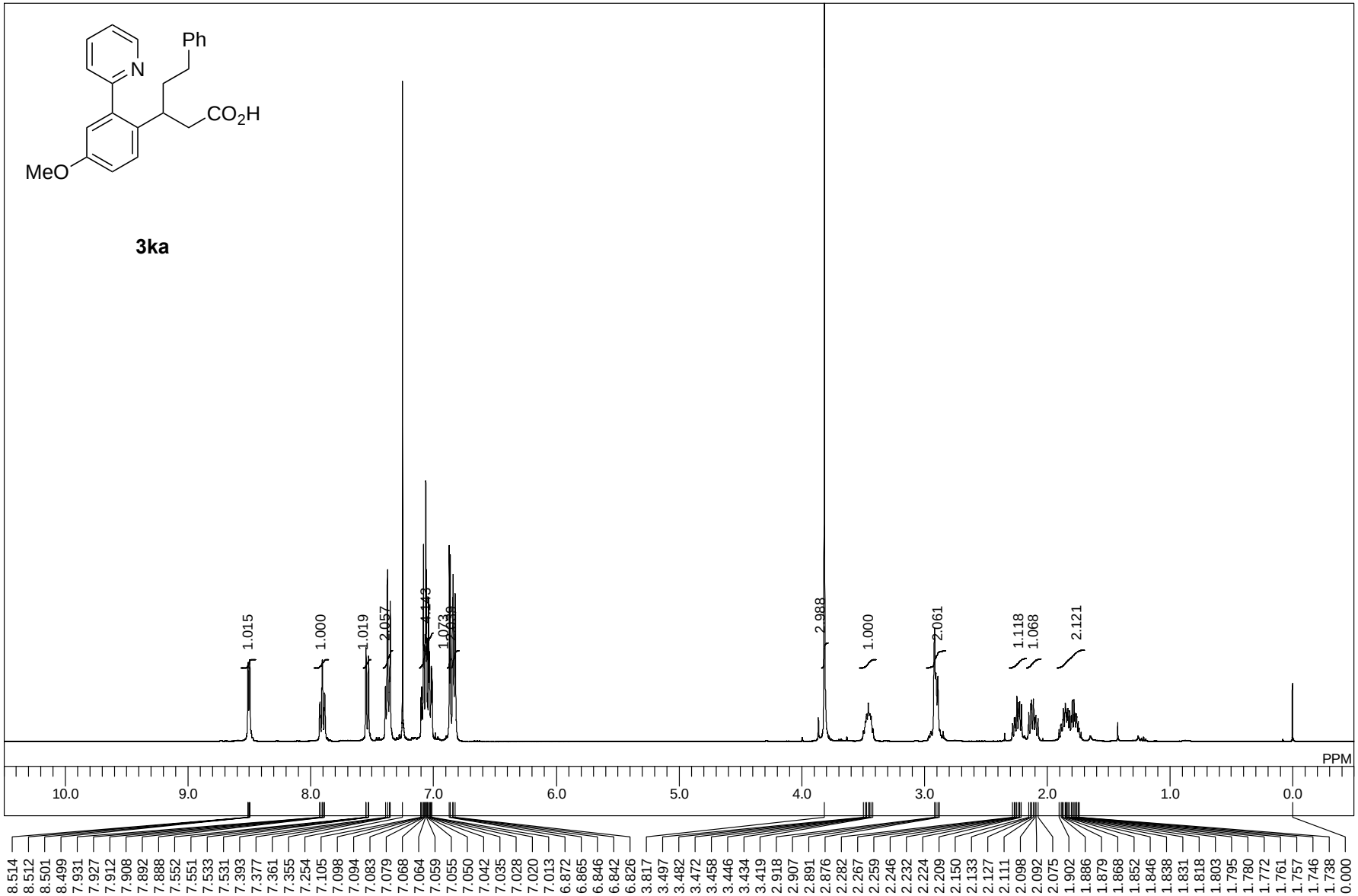

Ph
N
CO2H
Ac
3ha
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
197.457
173.624
157.199
147.051
142.489
142.326
140.860
138.647
137.966
130.453
128.220
127.895
126.841
126.773
125.767
125.029
123.036
77.316
77.000
76.684
42.789
39.013
34.481
32.976
26.747

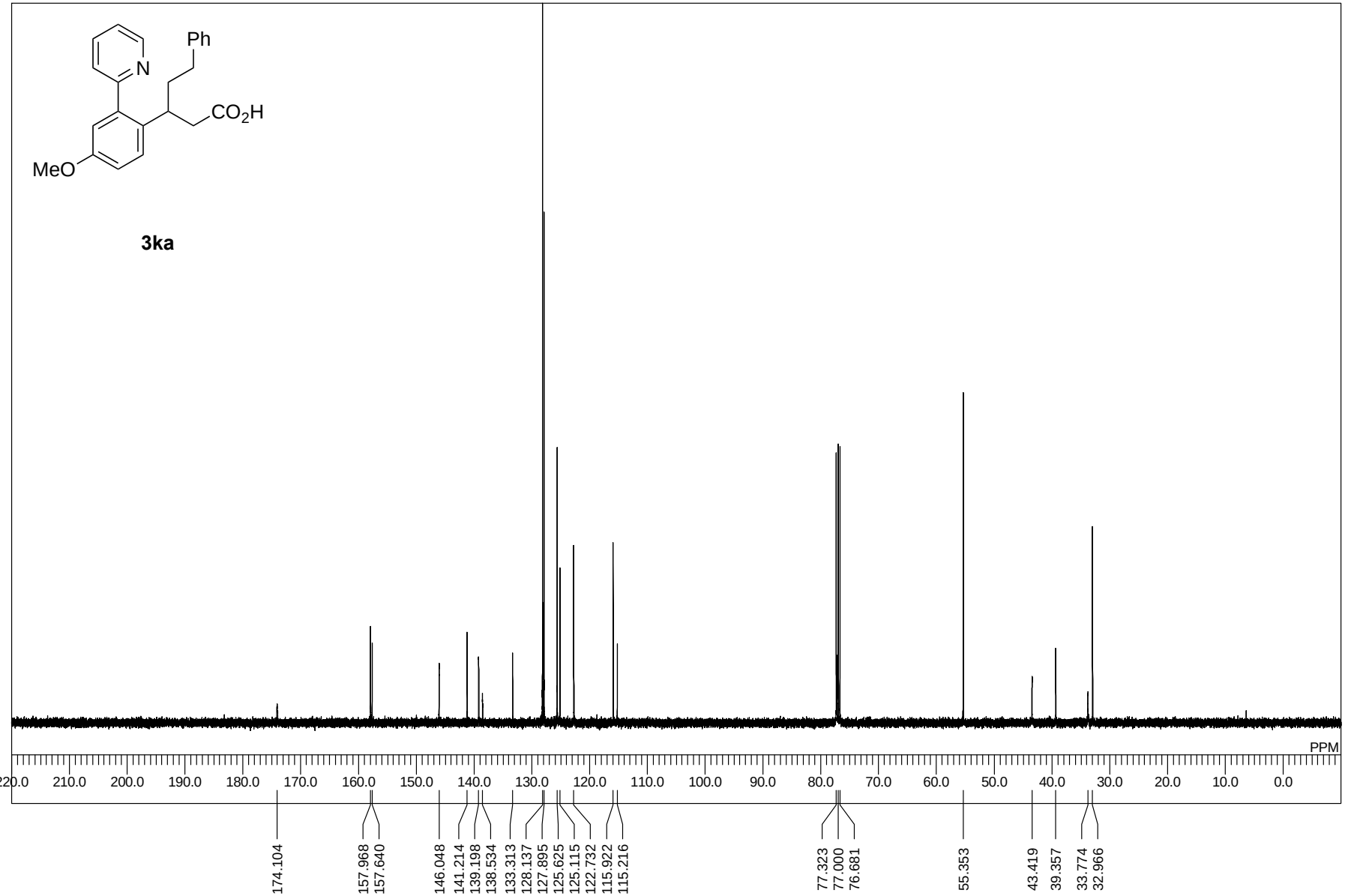

Ph
N
CO2H
Me
3ia
0.982
0.986
1.006
1.005
1.089
1.071
1.182
3.078
2.020
1.000
2.014
3.020
1.052
1.021
2.135
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.505
8.493
7.973
7.969
7.953
7.949
7.934
7.929
7.585
7.565
7.422
7.407
7.403
7.390
7.369
7.349
7.308
7.288
7.258
7.167
7.104
7.096
7.081
7.062
7.046
7.026
6.834
6.817
3.541
3.514
3.502
3.491
3.479
3.463
2.960
2.946
2.932
2.376
2.269
2.254
2.247
2.233
2.218
2.212
2.196
2.134
2.112
2.095
2.081
2.077
2.058
1.904
1.889
1.869
1.853
1.834
1.812
1.796
1.789
1.777
1.762
1.755
1.739
1.432
0.000

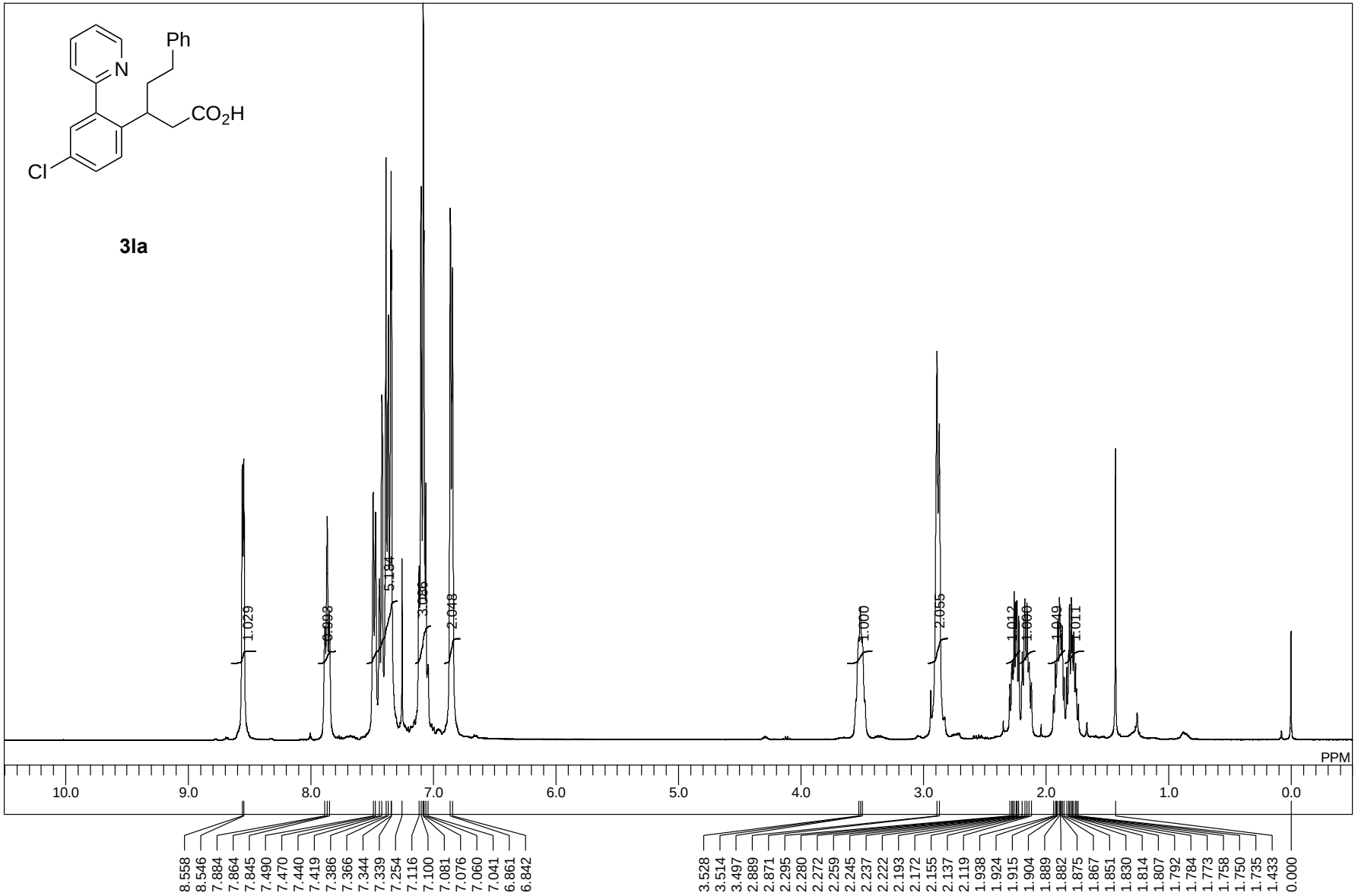

Ph
N
CO2H
Me
3ia
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
174.263
157.611
145.555
141.149
139.604
138.393
136.886
136.561
131.182
130.629
128.149
127.892
126.871
125.651
125.288
122.703
77.324
77.000
76.676
43.514
39.413
33.919
32.937
20.920

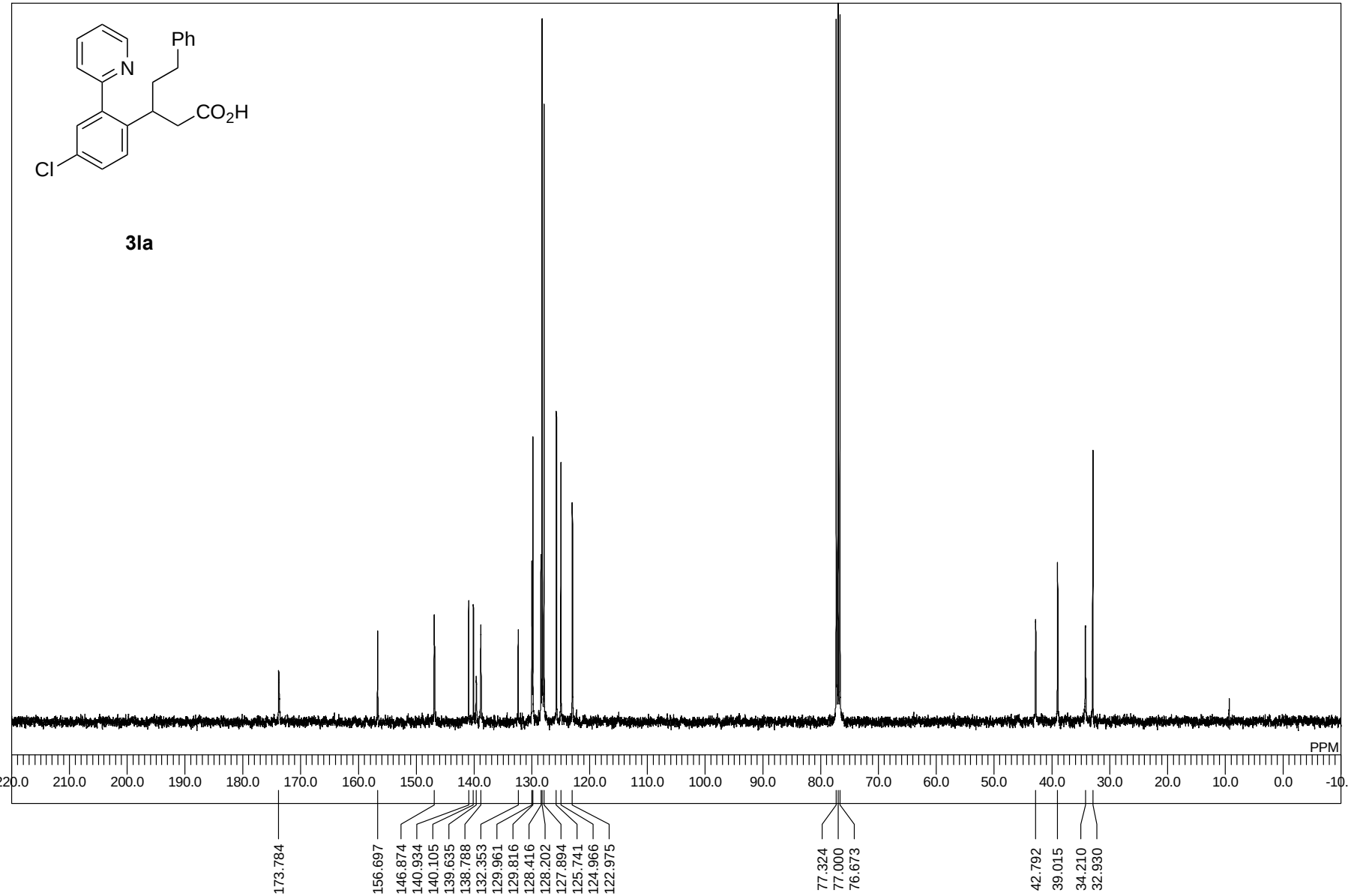

Ph
N
CO2H
tBu
3ja
0.986
1.004
1.008
1.048
1.037
3.027
1.982
1.000
1.935
1.017
0.998
2.057
8.993
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.510
8.499
8.001
7.997
7.981
7.977
7.961
7.957
7.604
7.583
7.521
7.516
7.500
7.495
7.452
7.449
7.439
7.436
7.433
7.430
7.419
7.416
7.402
7.381
7.319
7.313
7.258
7.108
7.101
7.086
7.067
7.061
7.050
7.030
6.852
6.847
6.831
3.527
3.512
3.503
3.488
3.480
3.471
3.465
3.449
2.294
2.277
2.272
2.257
2.241
2.237
2.219
2.181
2.164
2.160
2.142
2.129
2.123
2.106
1.918
1.902
1.883
1.865
1.847
1.826
1.804
1.791
1.786
1.769
1.334
0.000

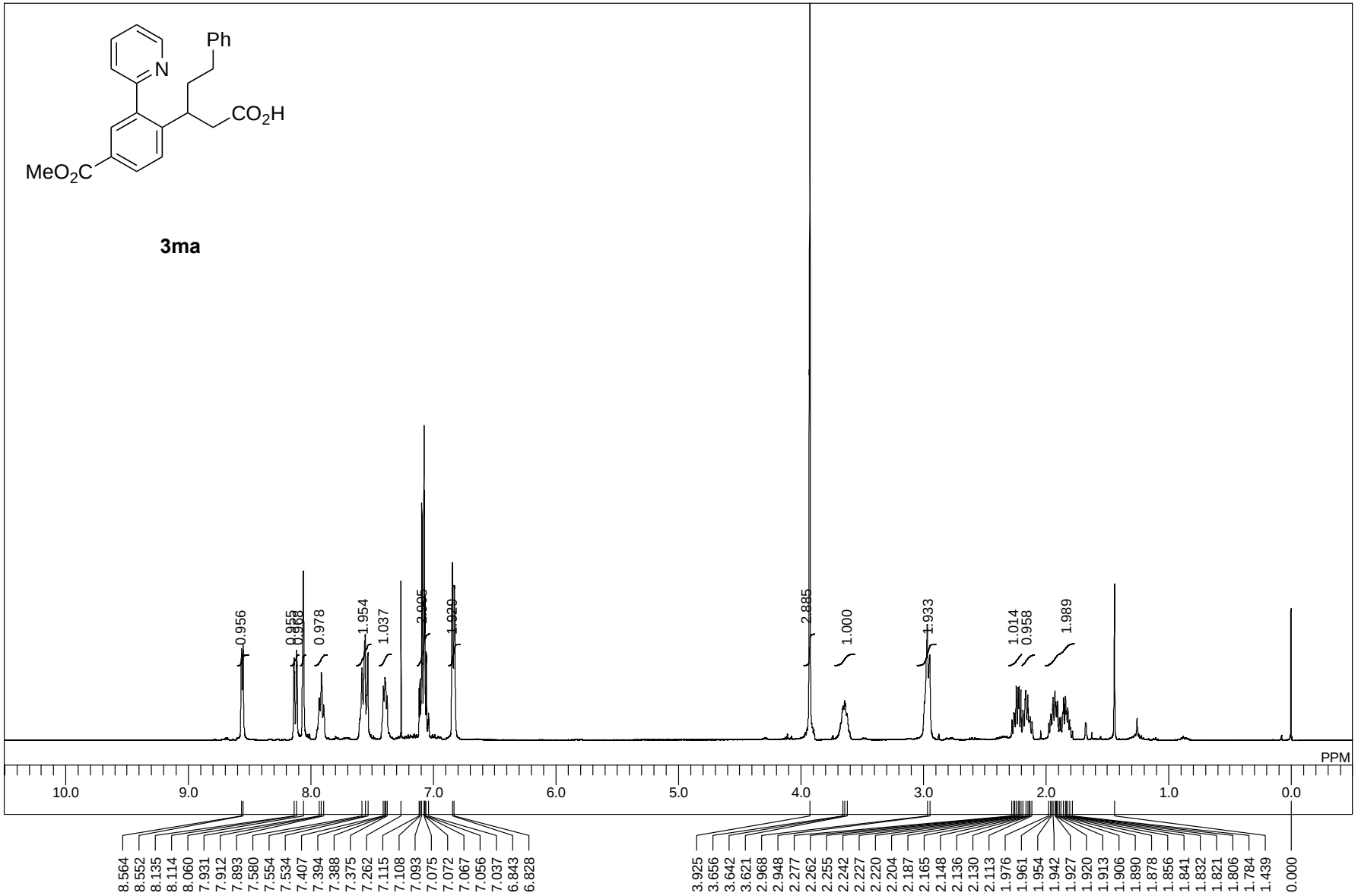

Ph
N
CO2H
tBu
3ja
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
174.361
157.856
149.742
145.372
141.156
139.823
138.395
136.294
128.159
127.913
127.658
126.879
126.721
125.662
125.434
122.739
77.324
77.000
76.676
43.411
39.339
34.484
33.895
32.980
31.196

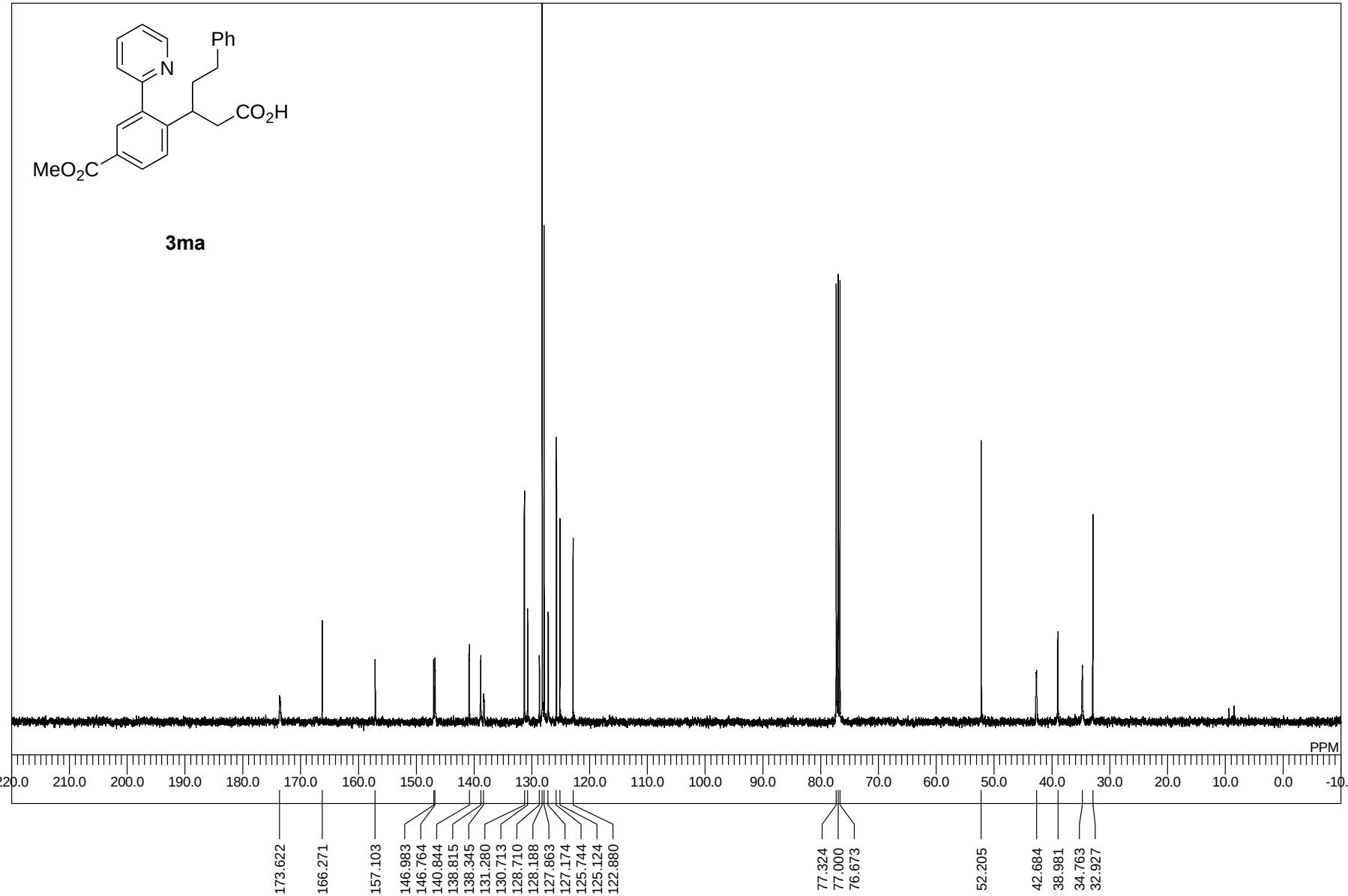

Ph
N
CO2H
MeO
3ka
1.015
1.000
1.019
2.057
4.143
1.073
1.038
2.988
1.000
2.061
1.118
1.068
2.121
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

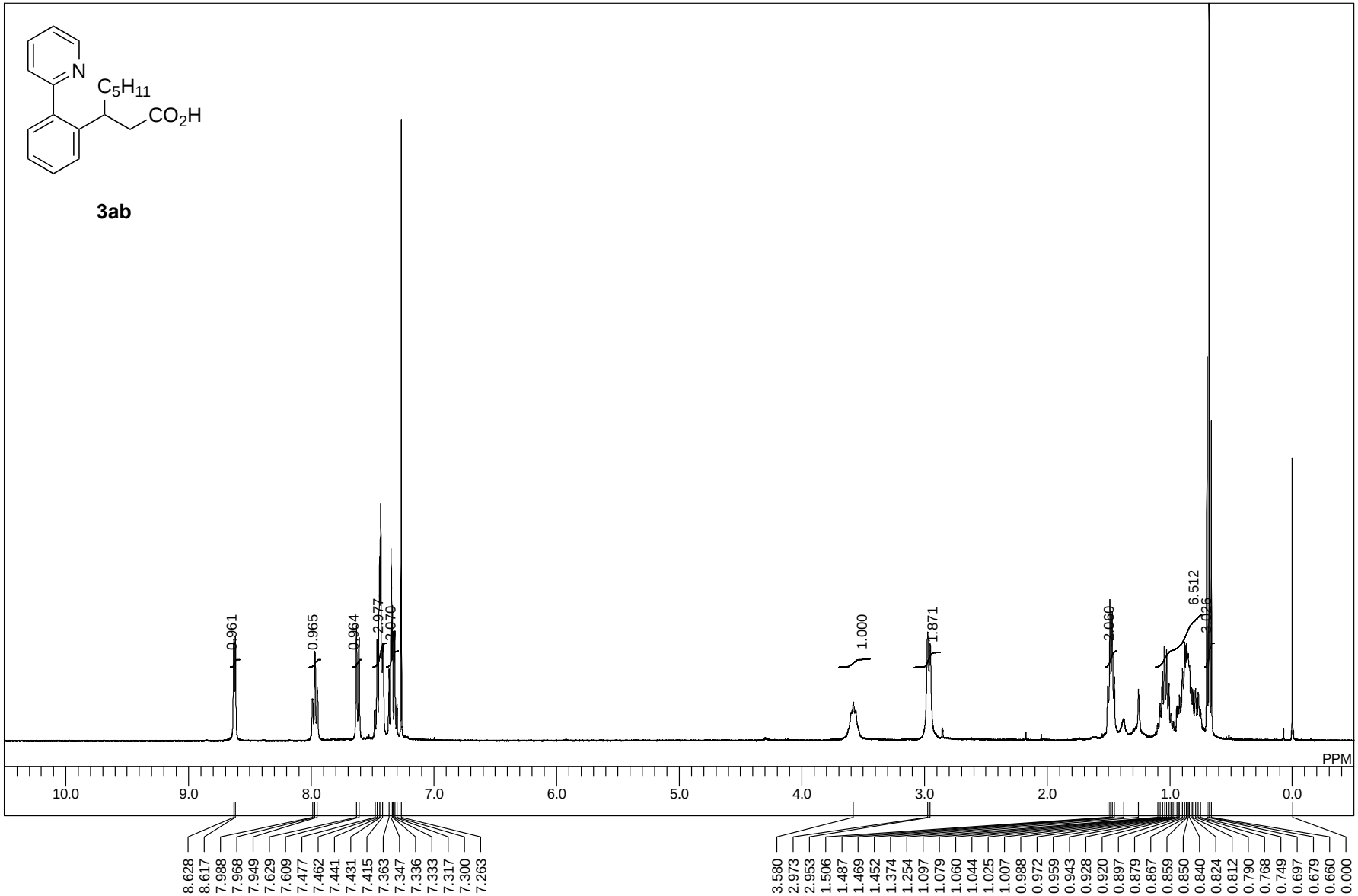

Ph
N
CO2H
MeO
3ka
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
174.104
157.968
157.640
146.048
141.214
139.198
138.534
133.313
128.137
127.895
125.625
125.115
122.732
115.922
115.216
77.323
77.000
76.681
55.353
43.419
39.357
33.774
32.966

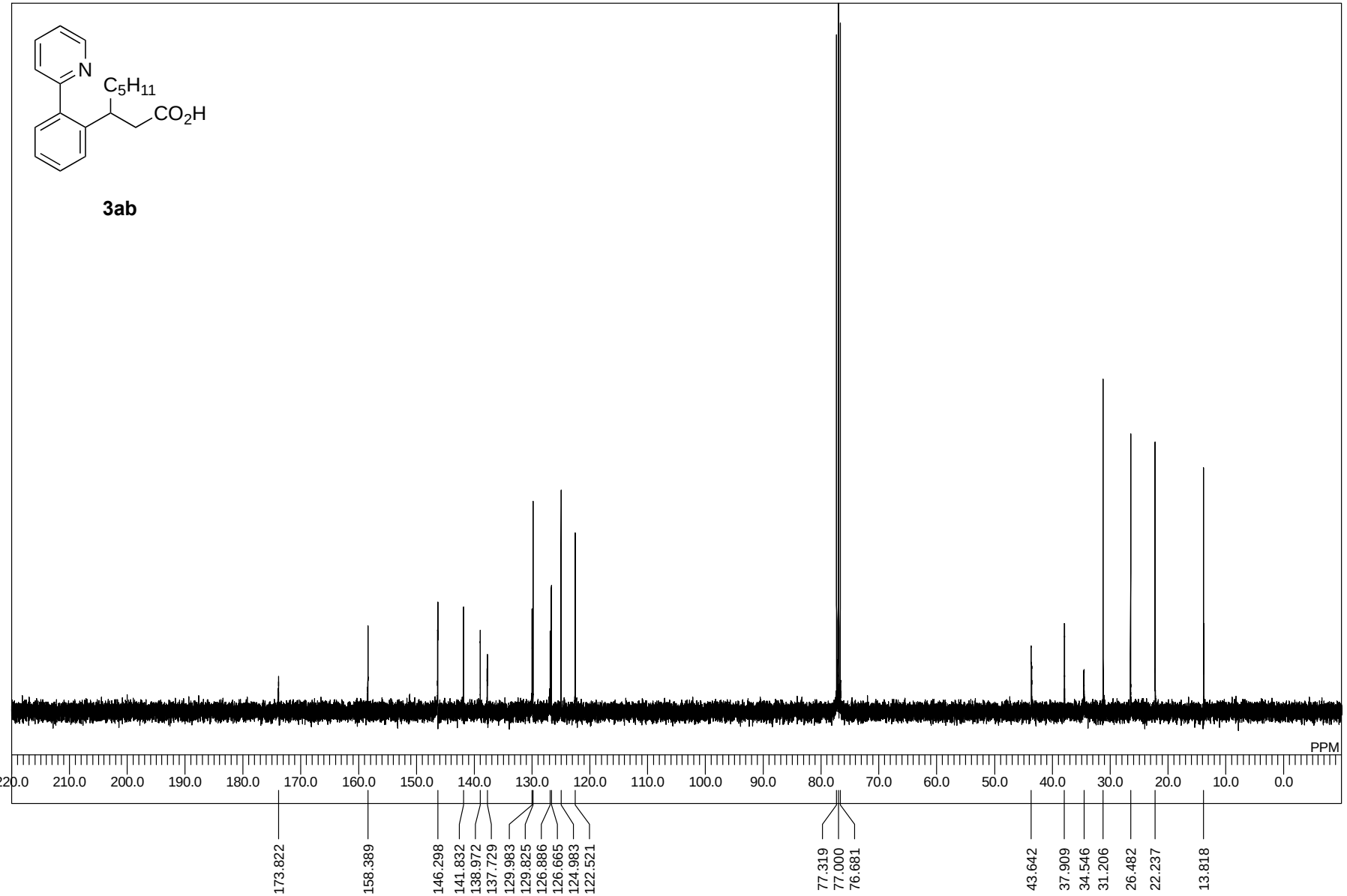

Ph
N
CO2H
Cl
3la
1.029
5.184
3.086
2.048
1.000
2.055
1.012
1.086
1.049
1.011
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.558
8.546
7.884
7.864
7.845
7.490
7.470
7.440
7.419
7.386
7.366
7.344
7.339
7.254
7.116
7.100
7.081
7.076
7.060
7.041
6.861
6.842
3.528
3.514
3.497
2.889
2.871
2.295
2.280
2.272
2.259
2.245
2.237
2.222
2.193
2.172
2.155
2.137
2.119
1.938
1.924
1.915
1.904
1.889
1.882
1.875
1.867
1.851
1.830
1.814
1.807
1.792
1.784
1.773
1.758
1.750
1.735
1.433
0.000

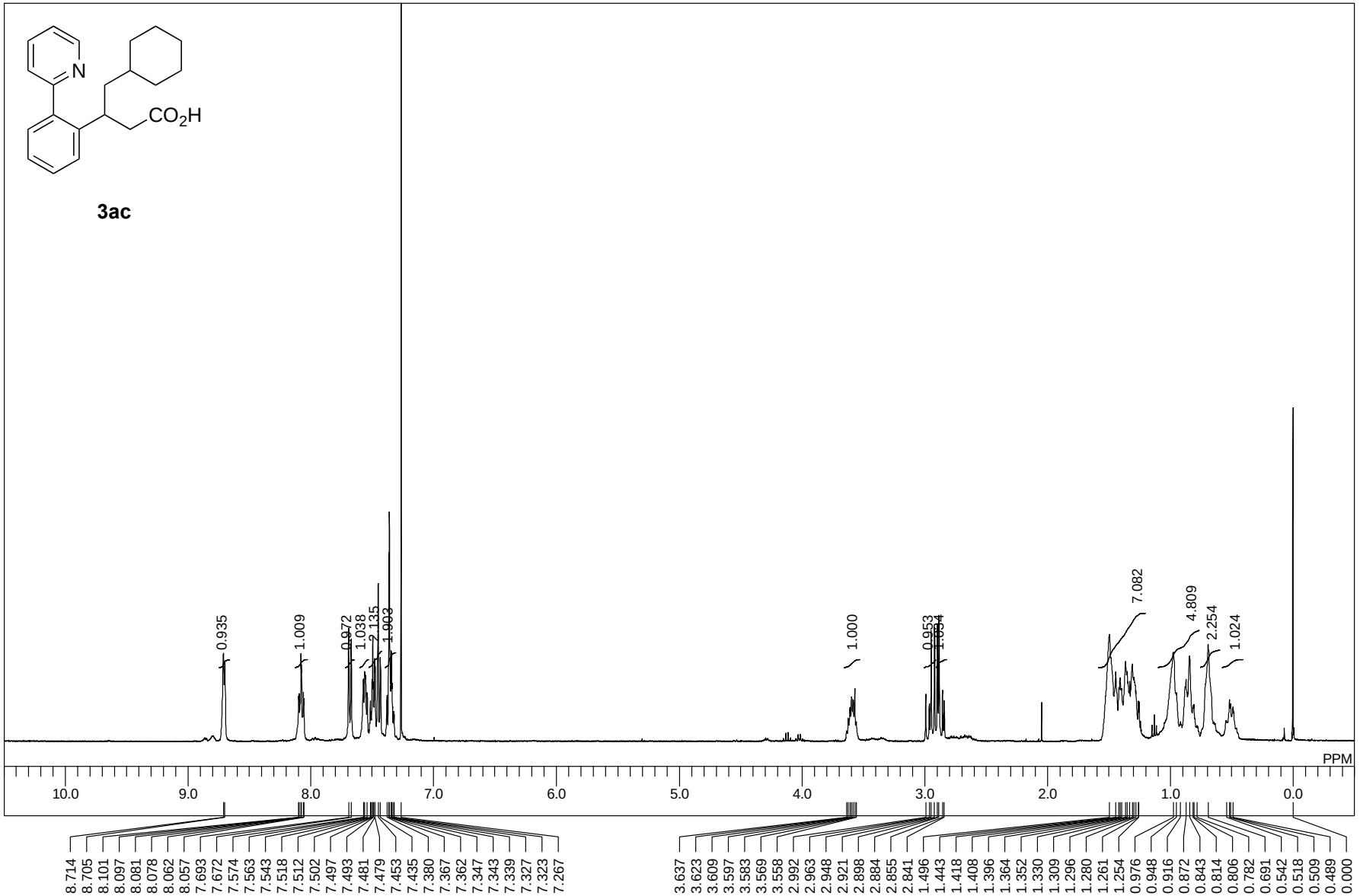

Ph
N
CO2H
Cl
3la
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
173.784
156.697
146.874
140.934
140.105
139.635
138.788
132.353
129.961
129.816
128.416
128.202
127.894
125.741
124.966
122.975
77.324
77.000
76.673
42.792
39.015
34.210
32.930

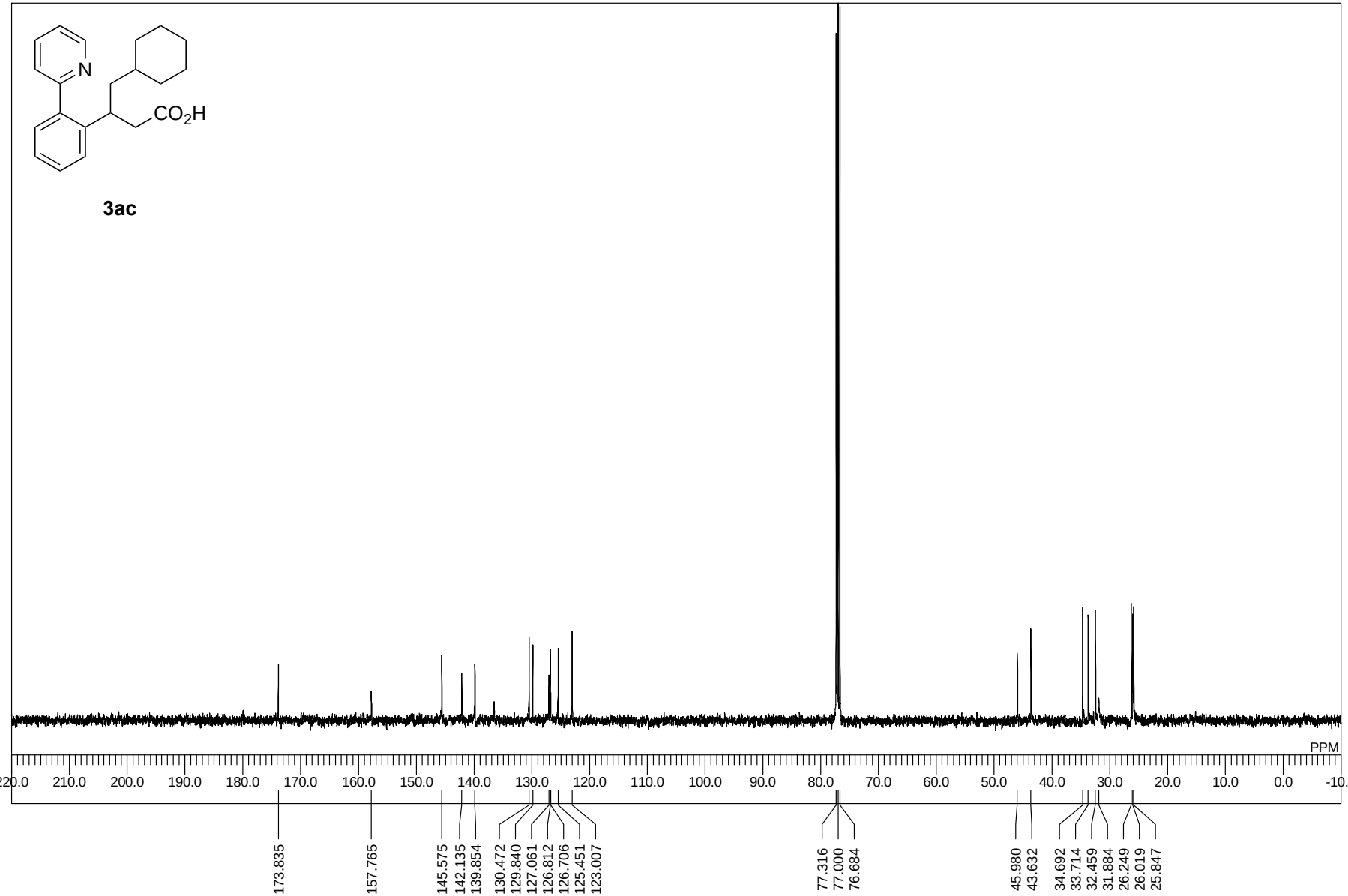

Ph
N
CO2H
MeO2C
3ma
0.956
0.955
0.968
0.978
1.954
1.037
2.005
1.920
2.885
1.000
1.933
1.014
0.958
1.989
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.564
8.552
8.135
8.114
8.060
7.931
7.912
7.893
7.580
7.554
7.534
7.407
7.394
7.388
7.375
7.262
7.115
7.108
7.093
7.075
7.072
7.067
7.056
7.037
6.843
6.828
3.925
3.656
3.642
3.621
2.968
2.948
2.277
2.262
2.255
2.242
2.227
2.220
2.204
2.187
2.165
2.148
2.136
2.130
2.113
1.976
1.961
1.954
1.942
1.927
1.920
1.913
1.906
1.890
1.878
1.856
1.841
1.832
1.821
1.806
1.784
1.439
0.000

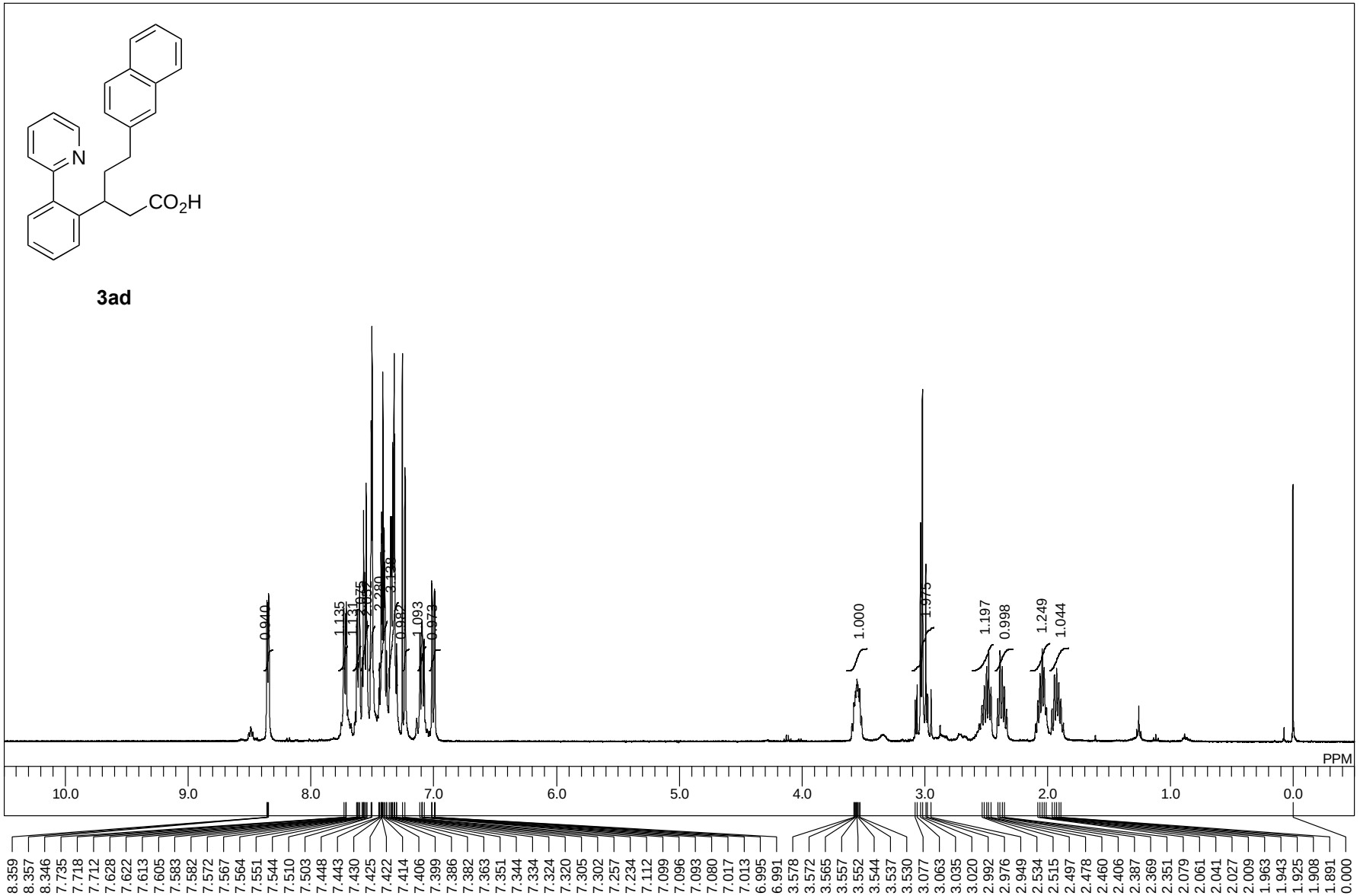

Ph
N
CO2H
MeO2C
3ma
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
173.622
166.271
157.103
146.983
146.764
140.844
138.815
138.345
131.280
130.713
128.710
128.188
127.863
127.174
125.744
125.124
122.880
77.324
77.000
76.673
52.205
42.684
38.981
34.763
32.927

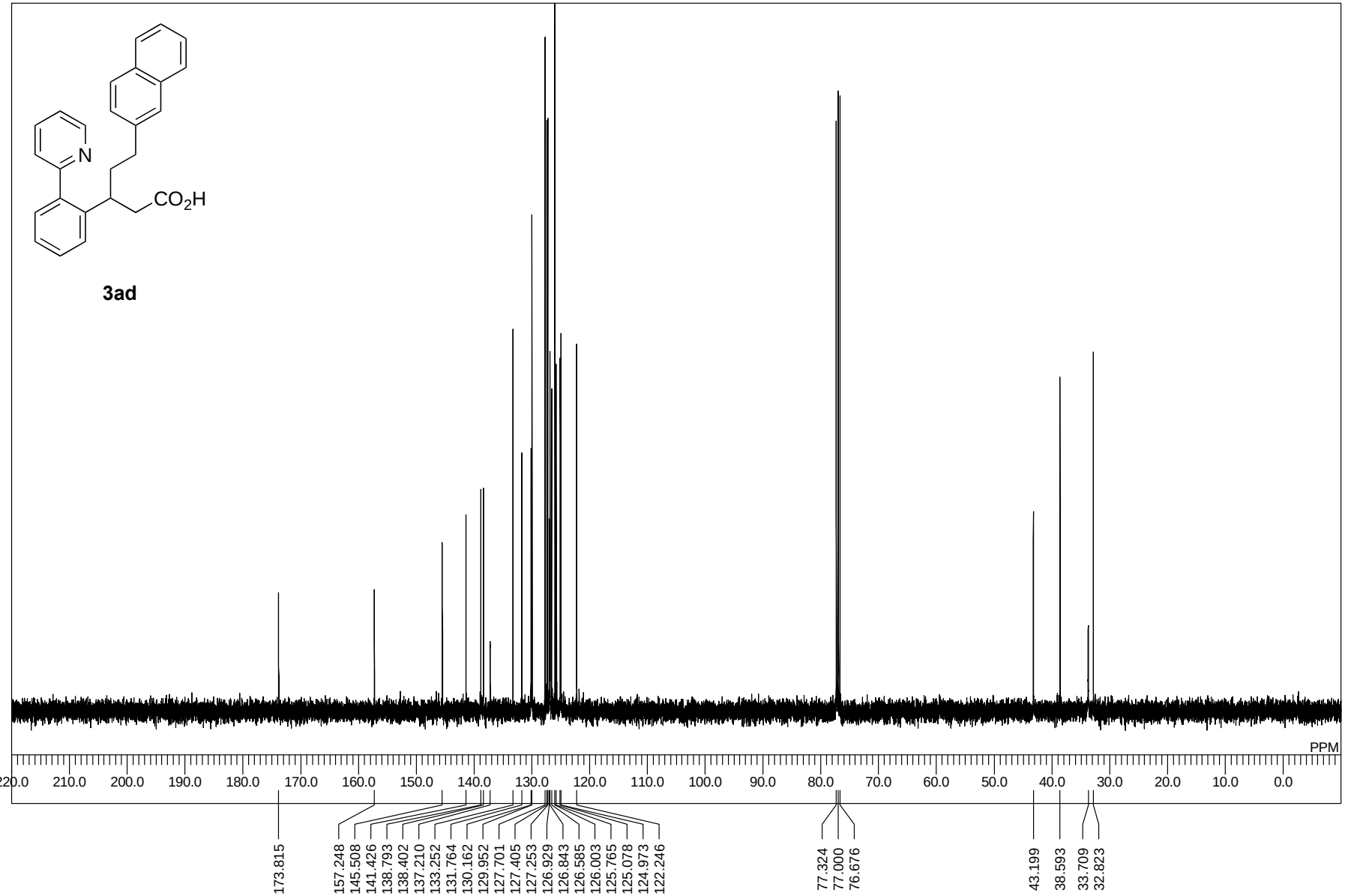

N
C5H11
CO2H
3ab
0.961
0.965
0.964
2.977
2.070
1.000
1.871
2.060
6.512
3.026
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.628
8.617
7.988
7.968
7.949
7.629
7.609
7.477
7.462
7.441
7.431
7.415
7.363
7.347
7.336
7.333
7.317
7.300
7.263
3.580
2.973
2.953
1.506
1.487
1.469
1.452
1.374
1.254
1.097
1.079
1.060
1.044
1.025
1.007
0.988
0.972
0.959
0.943
0.928
0.920
0.897
0.879
0.867
0.859
0.850
0.840
0.824
0.812
0.790
0.768
0.749
0.697
0.679
0.660
0.000

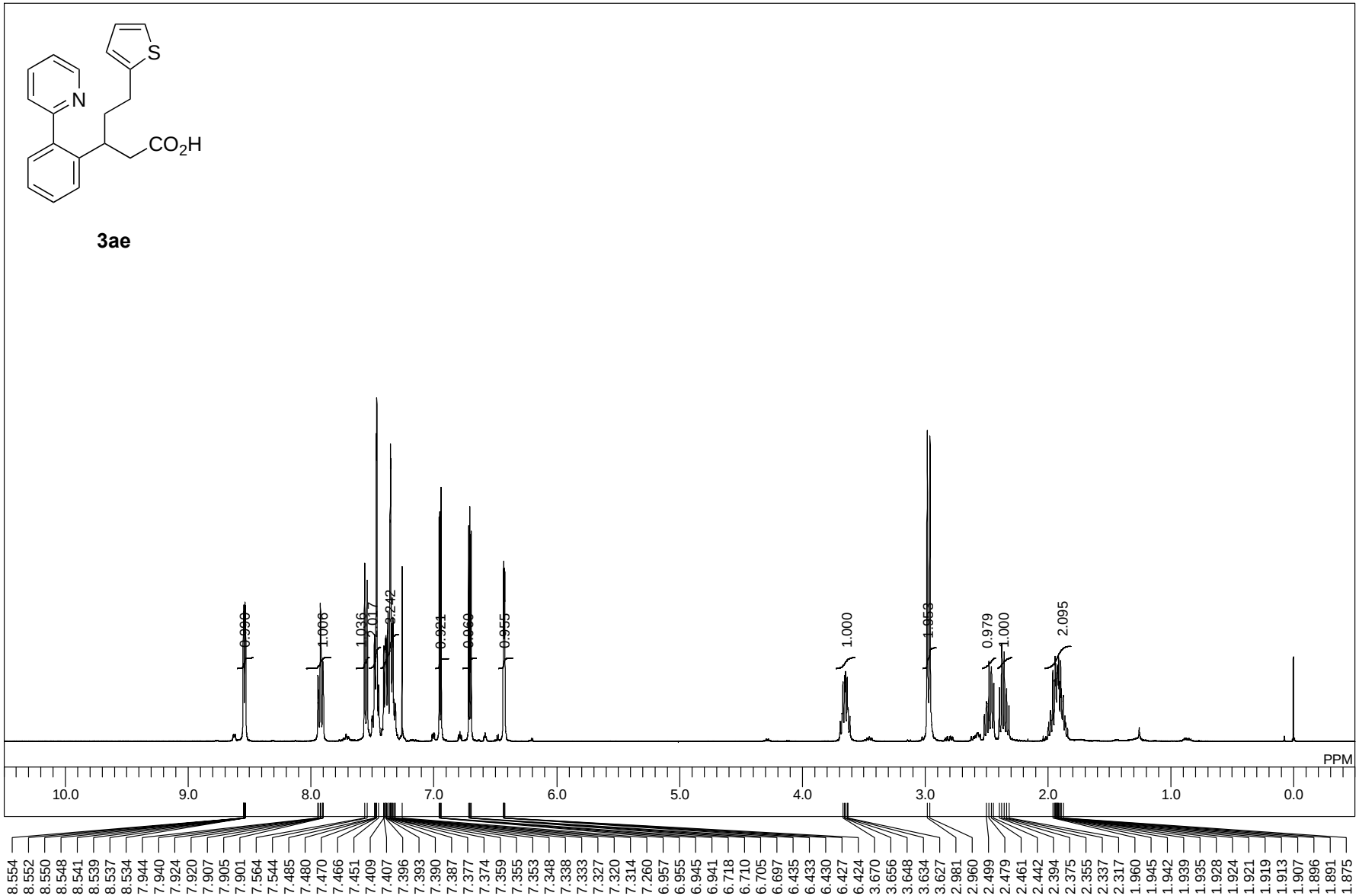

N
C5H11
CO2H
3ab
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
173.822
158.389
146.298
141.832
138.972
137.729
129.983
129.825
126.886
126.665
124.983
122.521
77.319
77.000
76.681
43.642
37.909
34.546
31.206
26.482
22.237
13.818

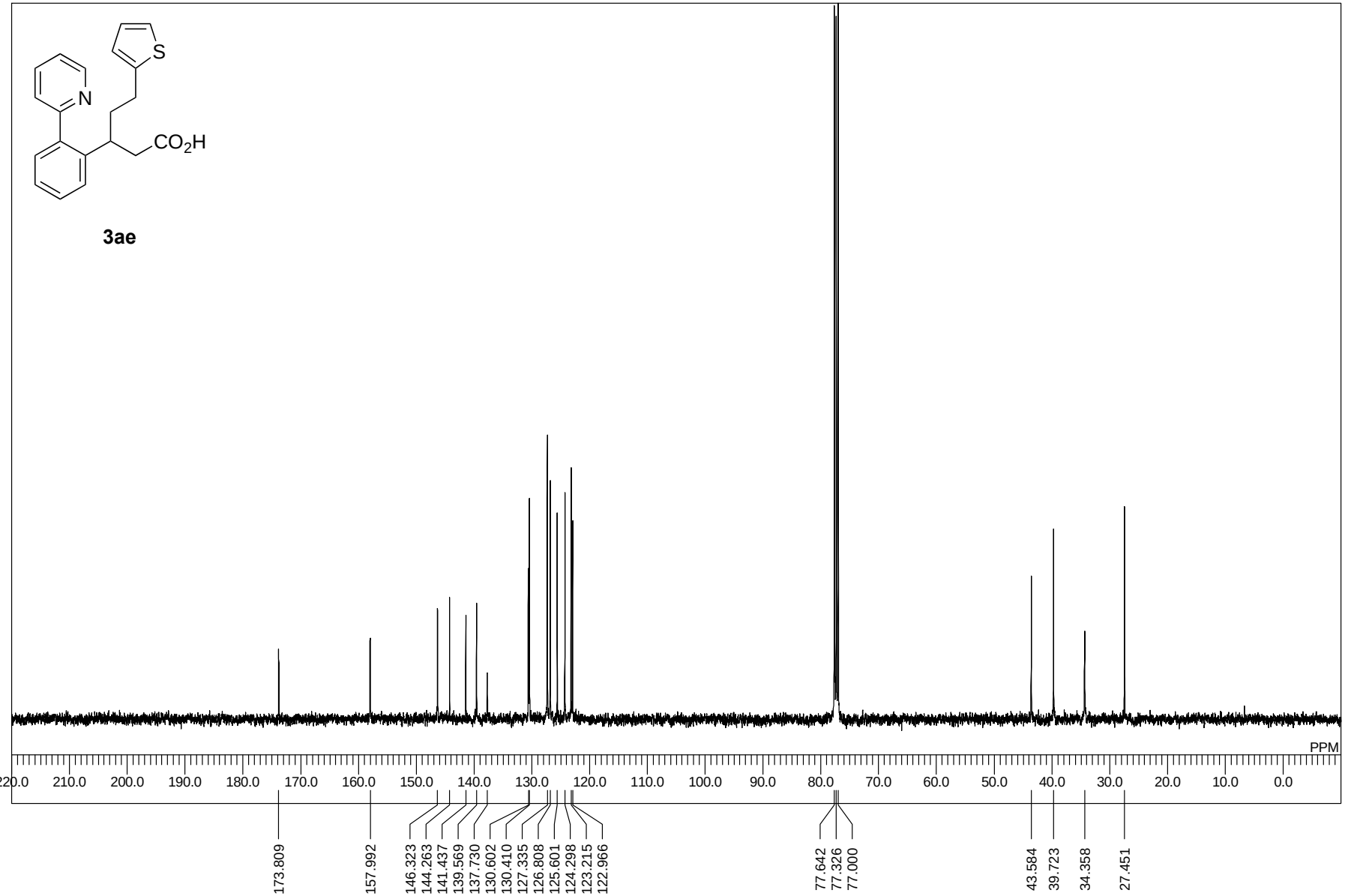

N
CO2H
3ac
0.935
1.009
0.972
1.038
2.135
1.903
1.000
0.953
1.034
7.082
4.809
2.254
1.024
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.714
8.705
8.101
8.097
8.081
8.078
8.062
8.057
7.693
7.672
7.574
7.563
7.543
7.518
7.512
7.502
7.497
7.493
7.481
7.479
7.453
7.435
7.380
7.367
7.362
7.347
7.343
7.339
7.327
7.323
7.267
3.637
3.623
3.609
3.597
3.583
3.569
3.558
2.992
2.963
2.948
2.921
2.898
2.884
2.855
2.841
1.496
1.443
1.418
1.408
1.396
1.364
1.352
1.330
1.309
1.296
1.280
1.261
1.254
0.976
0.948
0.916
0.872
0.843
0.814
0.806
0.782
0.691
0.542
0.518
0.509
0.489
0.000

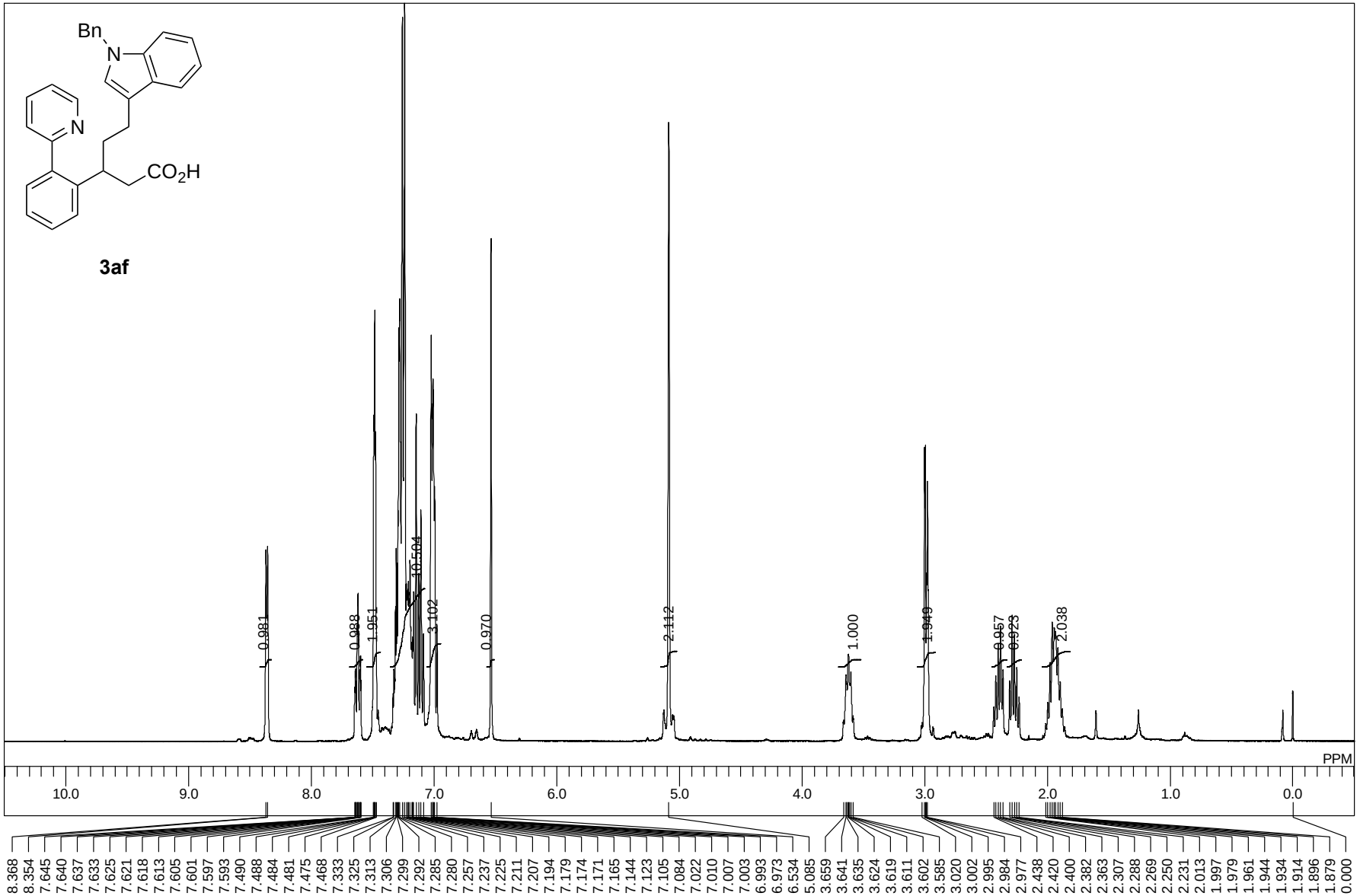

N
CO2H
3ac
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
173.835
157.765
145.575
142.135
139.854
130.472
129.840
127.061
126.812
126.706
125.451
123.007
77.316
77.000
76.684
45.980
43.632
34.692
33.714
32.459
31.884
26.249
26.019
25.847

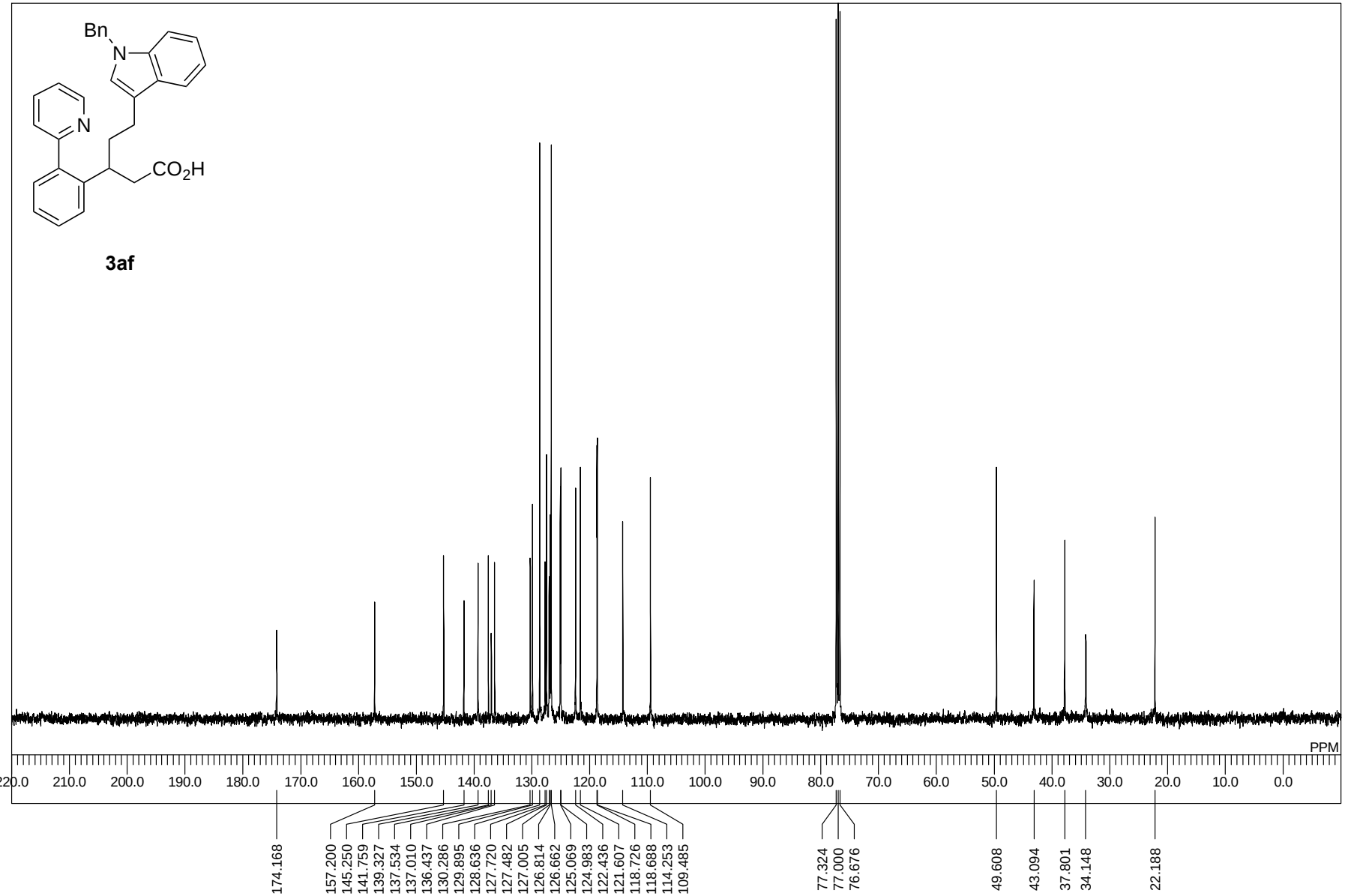

N
CO2H
3ad
0.940
1.135
1.131
1.000
1.975
1.197
0.998
1.249
1.044
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

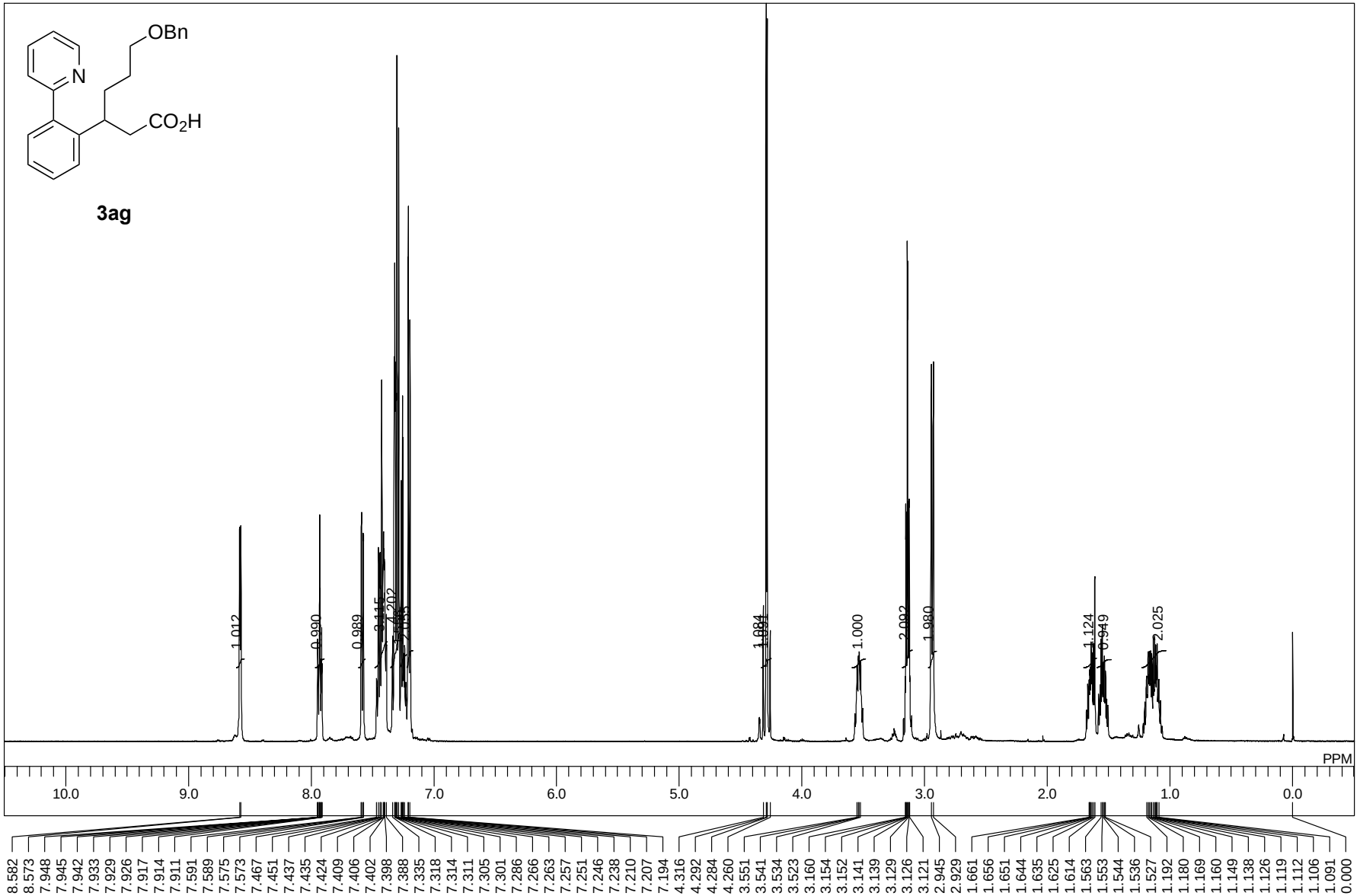

N
CO2H
3ad
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
173.815
157.248
145.508
141.426
138.793
138.402
137.210
133.252
131.764
130.162
129.952
127.701
127.405
127.253
126.929
126.843
126.585
126.003
125.765
125.078
124.973
122.246
77.324
77.000
76.676
43.199
38.593
33.709
32.823

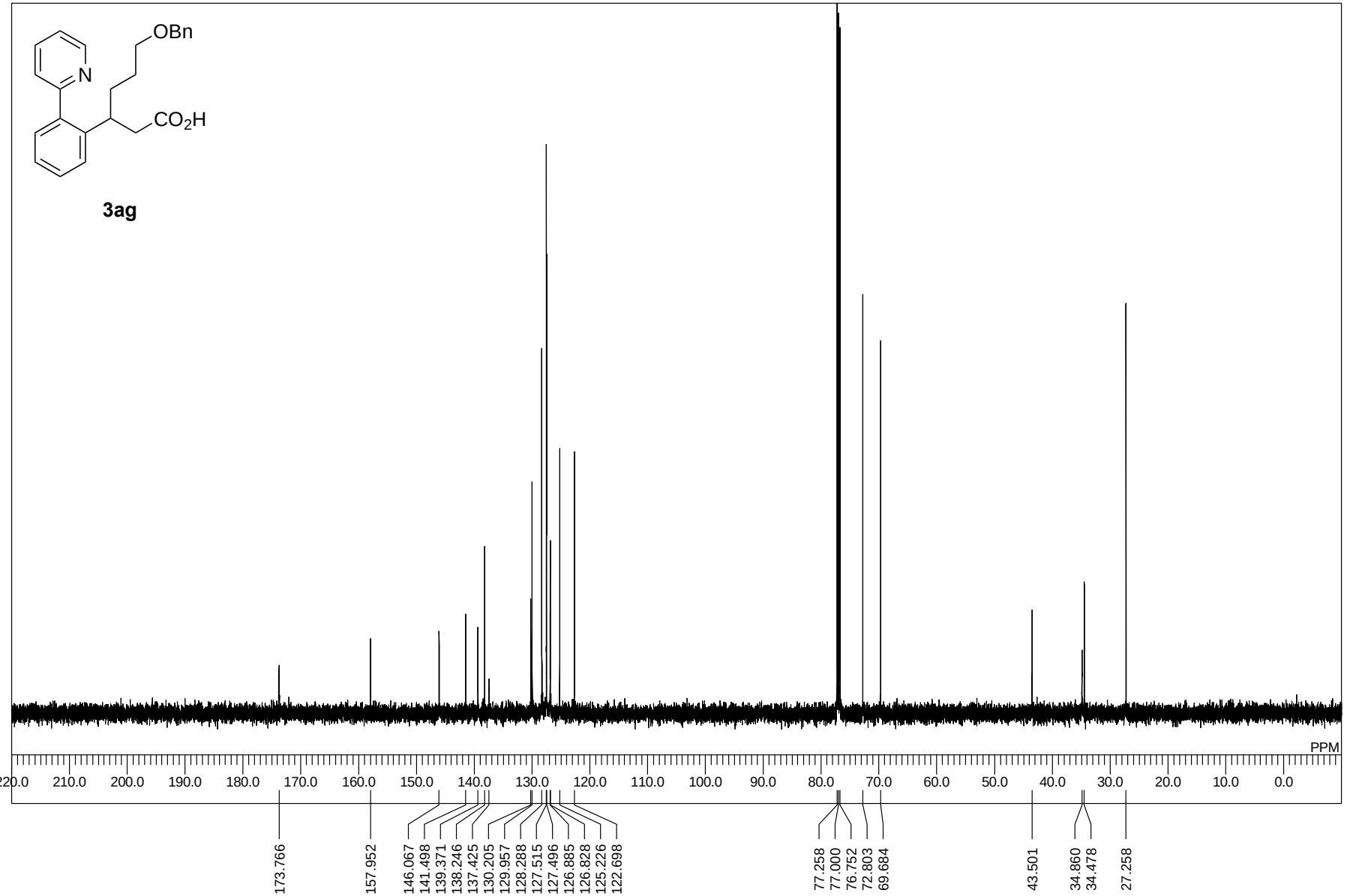

S
N
CO2H
3ae
0.990
1.006
1.036
2.017
3.242
0.921
0.969
0.955
1.000
1.953
0.979
1.000
2.095
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.554
8.552
8.550
8.548
8.541
8.539
8.537
8.534
7.944
7.940
7.924
7.920
7.907
7.905
7.901
7.564
7.544
7.485
7.480
7.470
7.466
7.451
7.409
7.407
7.396
7.393
7.390
7.387
7.377
7.374
7.359
7.355
7.353
7.348
7.338
7.333
7.327
7.320
7.314
7.260
6.957
6.955
6.945
6.941
6.718
6.710
6.705
6.697
6.435
6.433
6.430
6.427
6.424
3.670
3.656
3.648
3.634
3.627
2.981
2.960
2.499
2.479
2.461
2.442
2.394
2.375
2.355
2.337
2.317
1.960
1.945
1.942
1.939
1.935
1.928
1.924
1.921
1.919
1.913
1.907
1.896
1.891
1.875

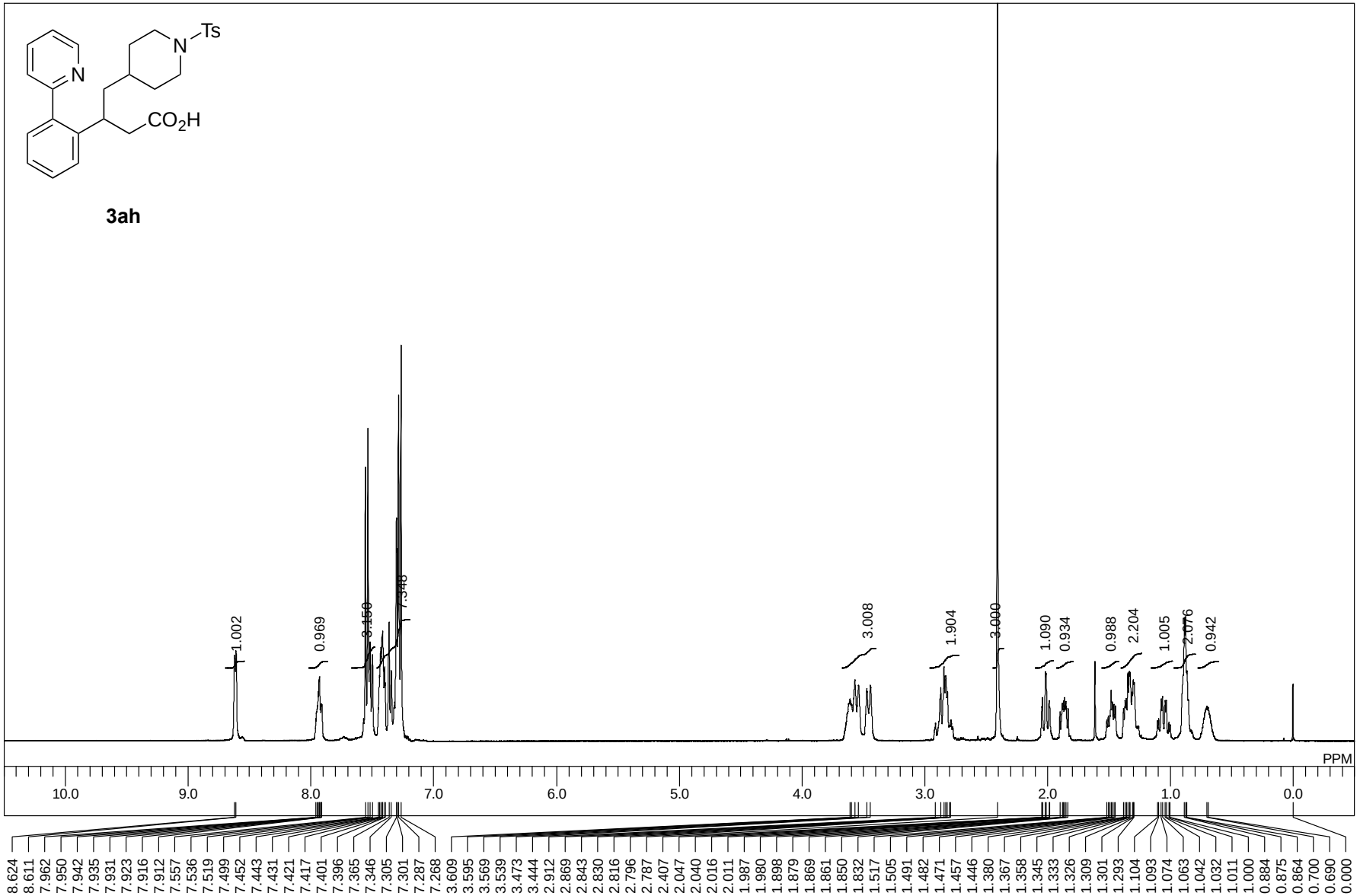

S
N
CO2H
3ae
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
173.809
157.992
146.323
144.263
141.437
139.569
137.730
130.602
130.410
127.335
126.808
125.601
124.298
123.215
122.966
77.642
77.326
77.000
43.584
39.723
34.358
27.451

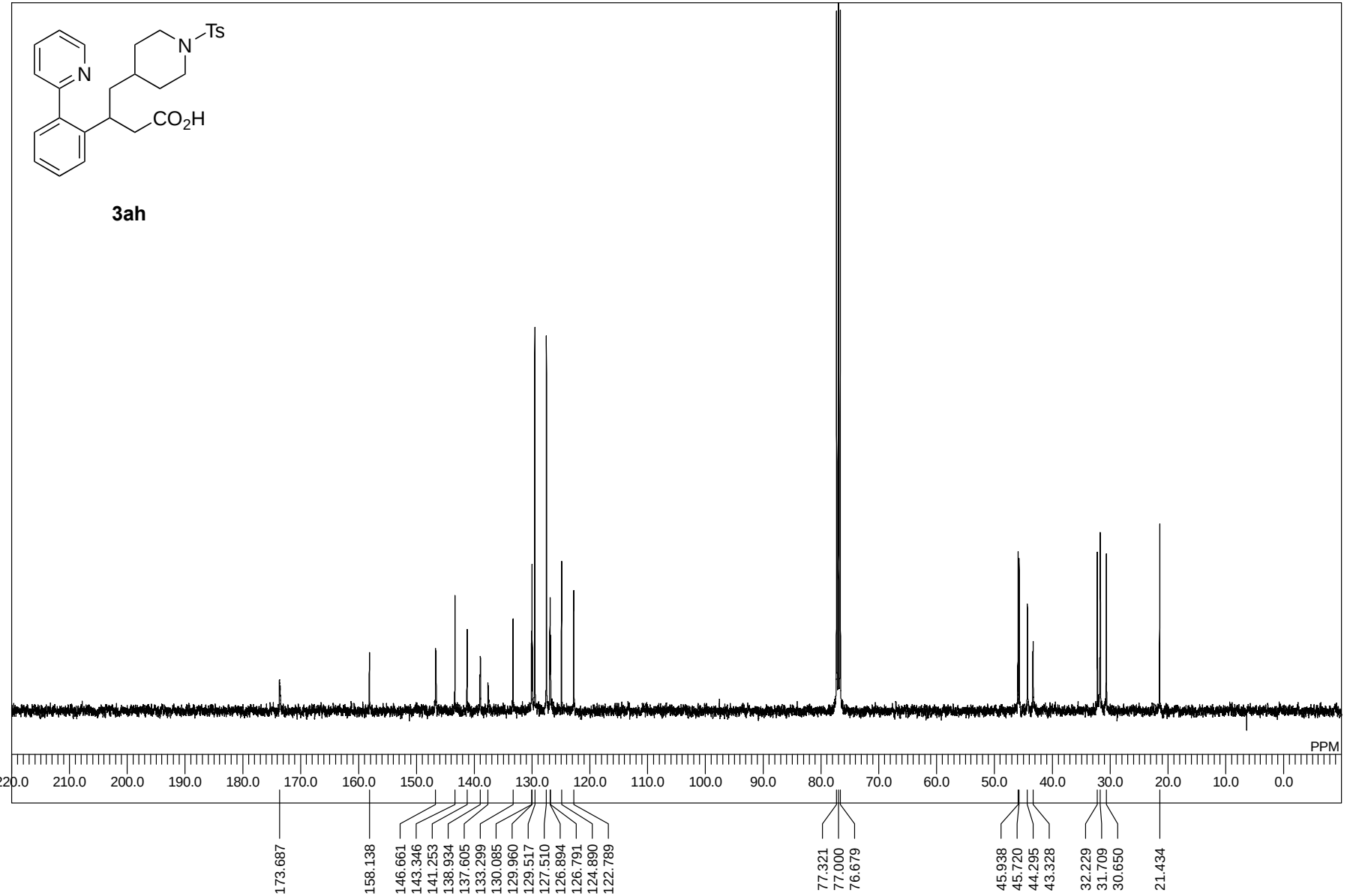

Bn
N
N
CO2H
3af
0.981
0.988
1.951
10.504
3.102
0.970
2.112
1.000
1.949
0.957
0.923
2.038
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

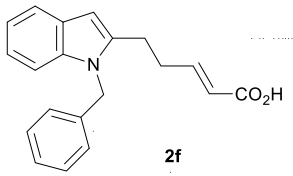

Bn
N
N
CO2H
3af
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
174.168
157.200
145.250
141.759
139.327
137.534
137.010
136.437
130.286
129.895
128.636
127.720
127.482
127.005
126.814
126.662
125.069
124.983
122.436
121.607
118.726
118.688
114.253
109.485
77.324
77.000
76.676
49.608
43.094
37.801
34.148
22.188


OBn
N
CO2H
3ag
1.012
0.990
0.989
3.115
4.202
1.084
1.000
2.092
1.980
1.124
0.949
2.025
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.582
8.573
7.948
7.945
7.942
7.933
7.929
7.926
7.917
7.914
7.911
7.591
7.589
7.575
7.573
7.467
7.451
7.437
7.435
7.424
7.409
7.406
7.402
7.398
7.388
7.335
7.318
7.314
7.311
7.305
7.301
7.286
7.266
7.263
7.257
7.251
7.246
7.238
7.210
7.207
7.194
4.316
4.292
4.284
4.260
3.551
3.541
3.534
3.523
3.160
3.154
3.152
3.141
3.139
3.129
3.126
3.121
2.945
2.929
1.661
1.656
1.651
1.644
1.635
1.625
1.614
1.563
1.553
1.544
1.536
1.527
1.192
1.180
1.169
1.160
1.149
1.138
1.126
1.119
1.112
1.106
1.091
0.000


OBn
N
CO2H
3ag
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
173.766
157.952
146.067
141.498
139.371
138.246
137.425
130.205
129.957
128.288
127.515
127.496
126.885
126.828
125.226
122.698
77.258
77.000
76.752
72.803
69.684
43.501
34.860
34.478
27.258


N
N
Ts
CO2H
3ah
1.002
0.969
3.150
7.340
3.008
1.904
3.000
1.090
0.934
0.988
2.204
1.005
2.076
0.942
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


N
Ts
N
CO2H
3ah
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
173.687
158.138
146.661
143.346
141.253
138.934
137.605
133.299
130.085
129.960
129.517
127.510
126.894
126.791
124.890
122.789
77.321
77.000
76.679
45.938
45.720
44.295
43.328
32.229
31.709
30.650
21.434



2f

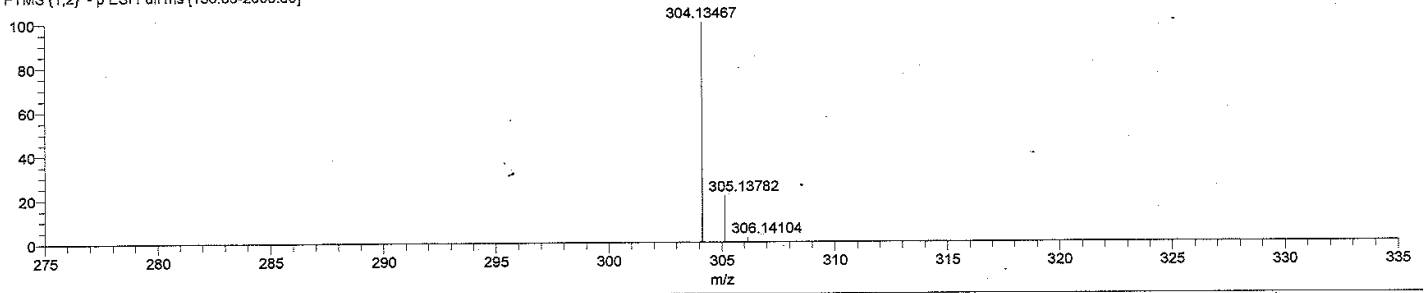
202060

Sample No. : C:\Xcalibur\...\0222\202060_13147_pn
Operator name :
Date : 2/22/2021 5:56:06 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

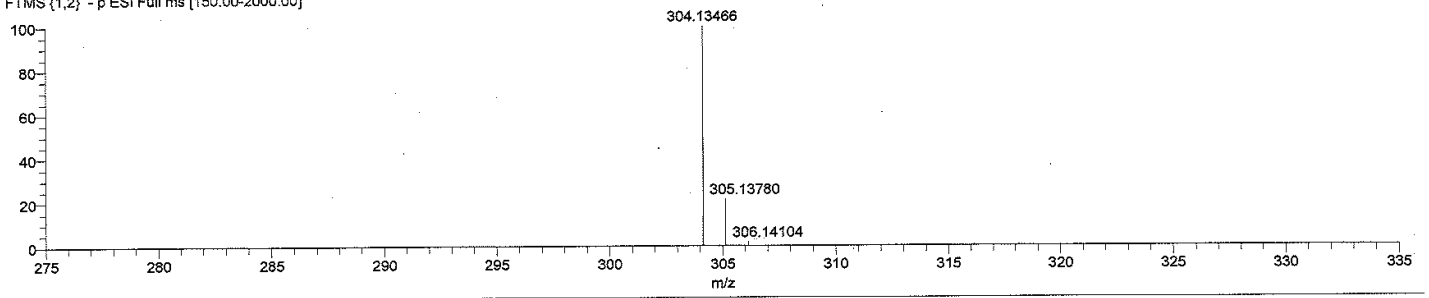
Instrument : Exactive

Neg
Mobile phase solvent : MeOH
Sample solvent : submitting solution

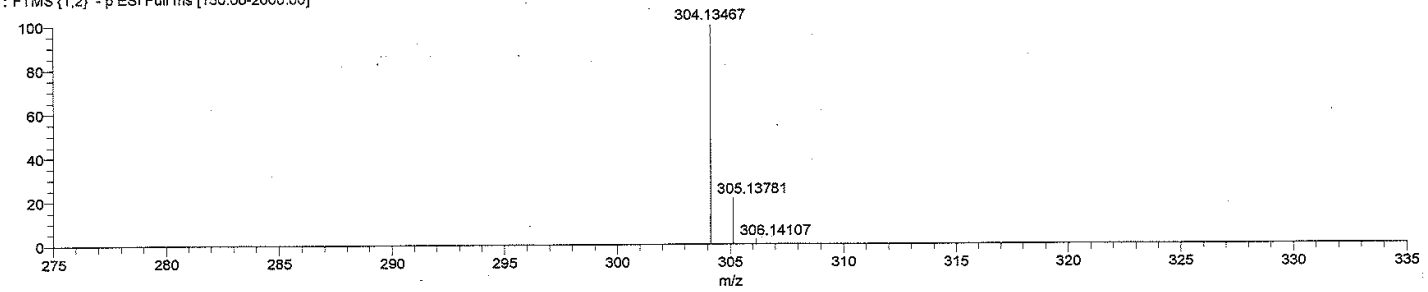
202060_13147_pn #20-23 RT: 0.31-0.33 AV: 2 NL: 7.92E6
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]

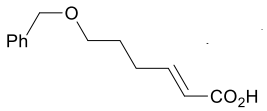


202060_13147_pn #23-27 RT: 0.35-0.38 AV: 2 NL: 3.44E7
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]



202060_13147_pn #27-31 RT: 0.40-0.42 AV: 2 NL: 4.95E7
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]





202059

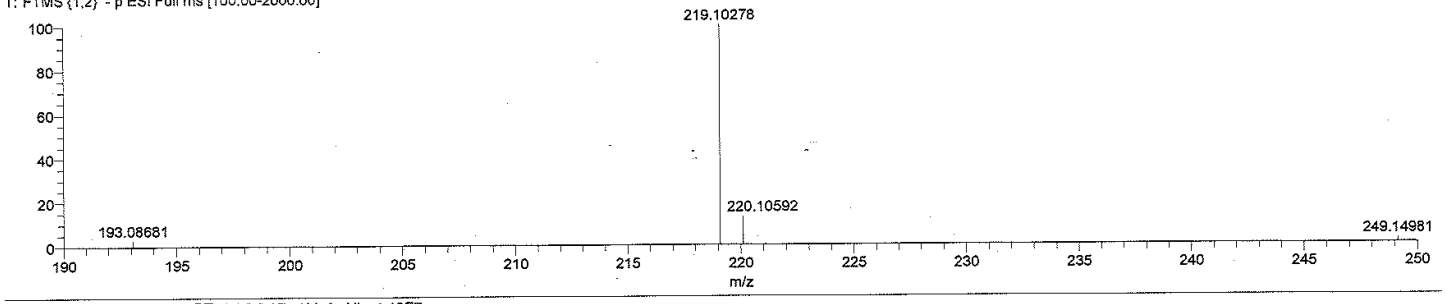
2g

Sample No. : C:\Xcalibur\...\0222\202059_13118_pn
Operator name :
Date : 2/22/2021 5:51:03 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30_100.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

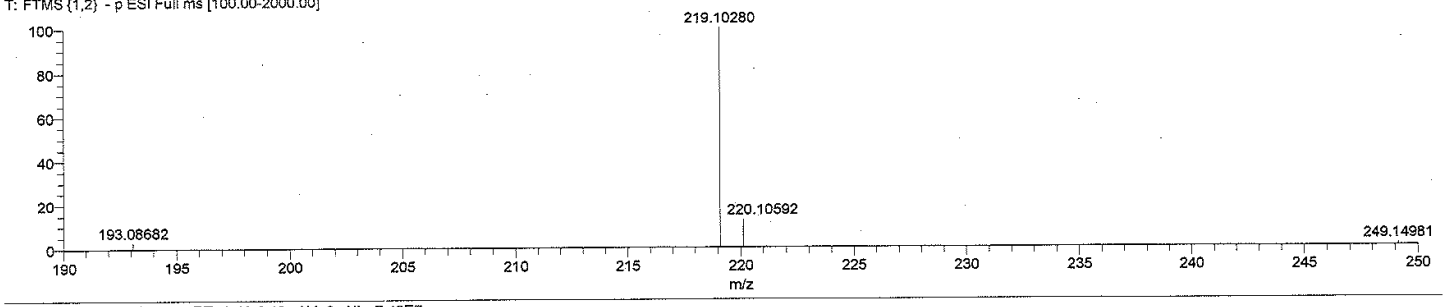
Instrument : Exactive

Neg
Mobile phase solvent : MeOH
Sample solvent : submitting solution

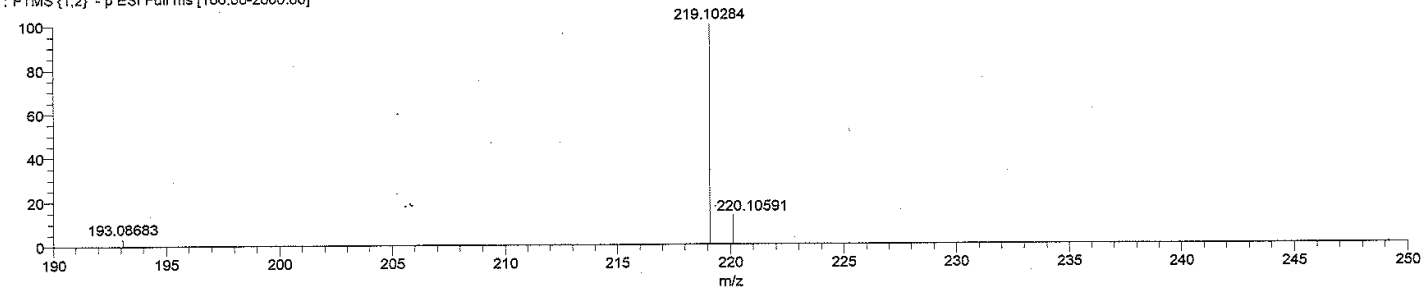
202059_13118_pn #21-24 RT: 0.33-0.35 AV: 2 NL: 2.47E7
T: FTMS {1,2} - p ESI Full ms [100.00-2000.00]

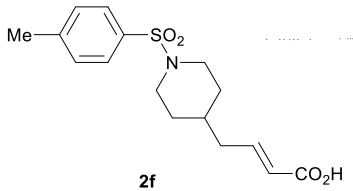


202059_13118_pn #24-27 RT: 0.35-0.37 AV: 2 NL: 4.40E7
T: FTMS {1,2} - p ESI Full ms [100.00-2000.00]



202059_13118_pn #27-31 RT: 0.40-0.42 AV: 2 NL: 7.46E7
T: FTMS {1,2} - p ESI Full ms [100.00-2000.00]





2f

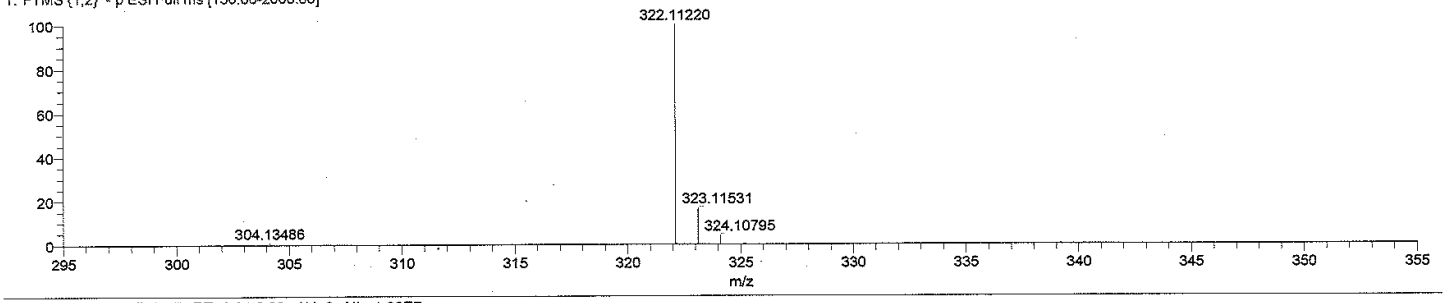
202061

Sample No. : C:\Xcalibur\...\0222\202061_13168_pn
Operator name :
Date : 2/22/2021 6:01:08 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

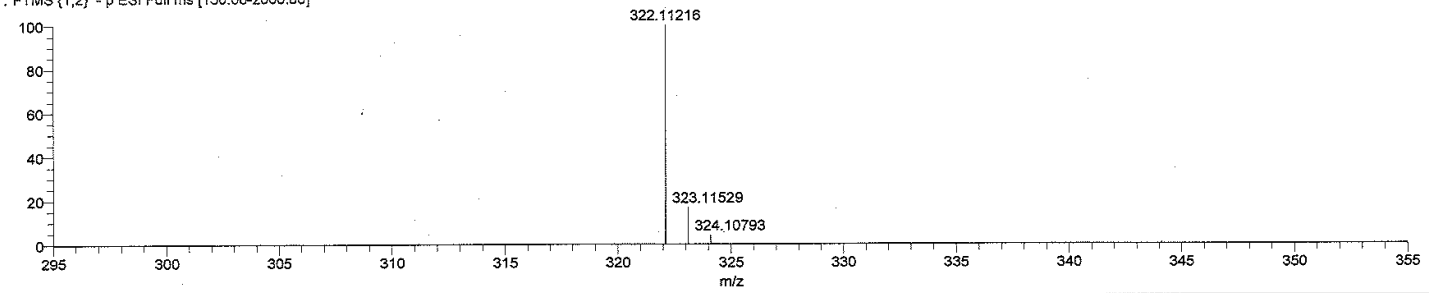
Instrument : Exactive

Neg
Mobile phase solvent : MeOH
Sample solvent : submitting solution

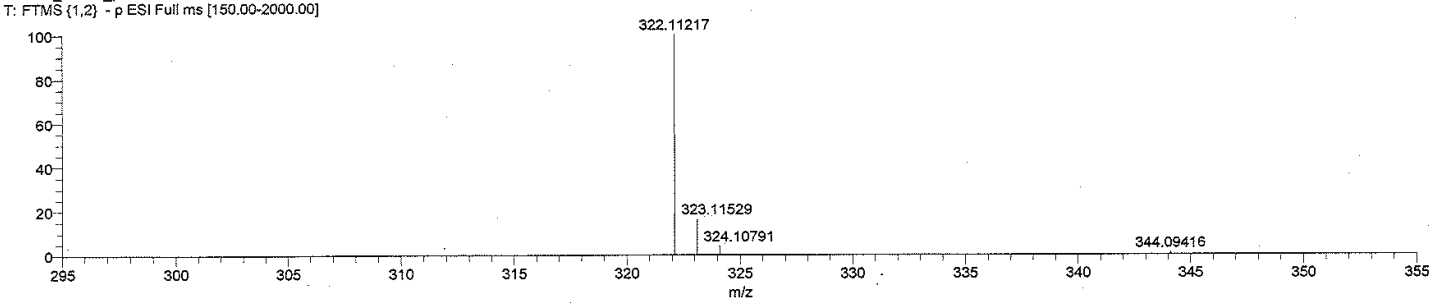
202061_13168_pn #19-22 RT: 0.31-0.34 AV: 2 NL: 3.49E6
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]

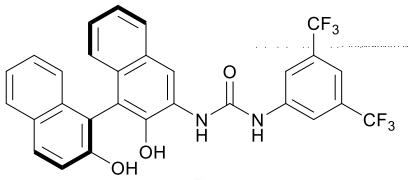


202061_13168_pn #22-27 RT: 0.34-0.38 AV: 3 NL: 1.22E7
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]



202061_13168_pn #27-30 RT: 0.41-0.43 AV: 2 NL: 2.21E7
T: FTMS {1,2} - p ESI Full ms [150.00-2000.00]





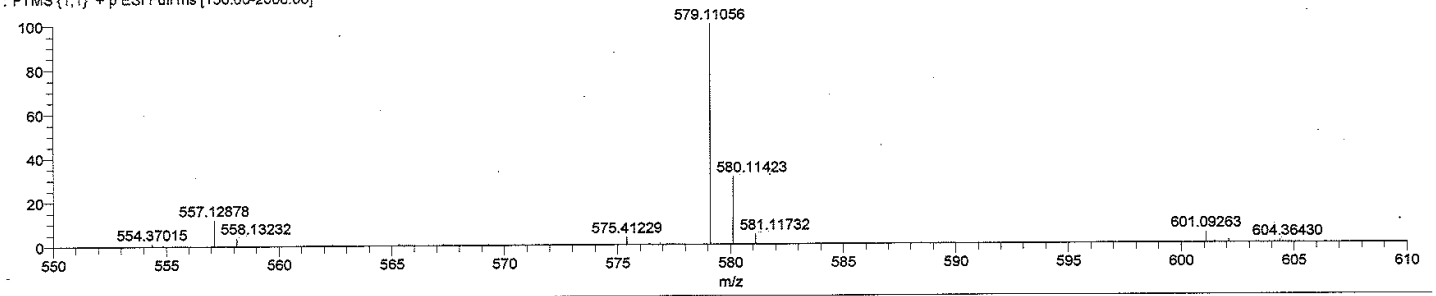
5

Sample No. : C:\Xcalibur\...\201419_BINOL_urea_pn
Operator name : hayashi harumi
Date : 12/2/2020 12:20:13 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

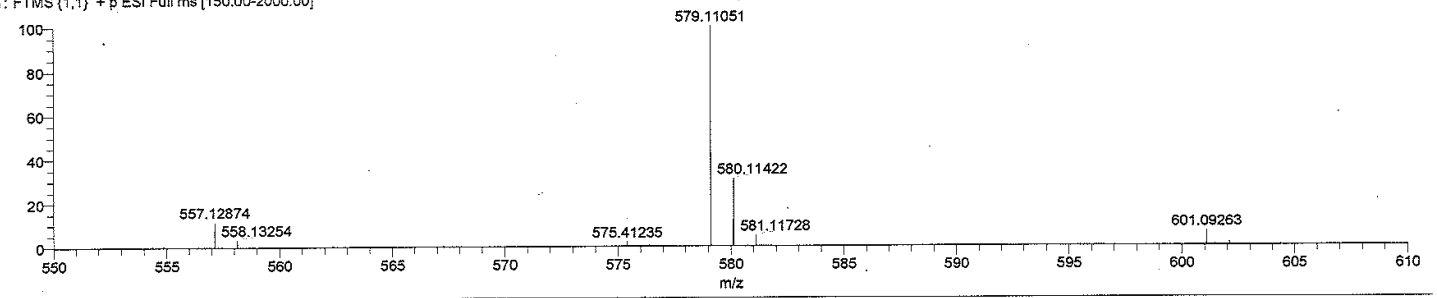
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

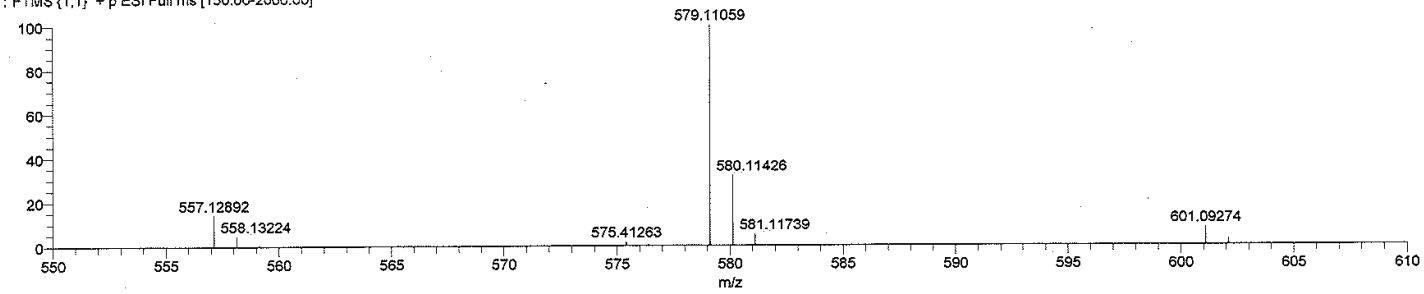
201419_BINOL_urea_pn #16-21 RT: 0.26-0.31 AV: 3 NL: 6.77E5
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

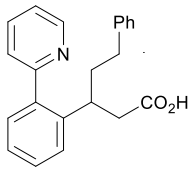


201419_BINOL_urea_pn #21-25 RT: 0.31-0.35 AV: 3 NL: 5.20E5
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201419_BINOL_urea_pn #26-29 RT: 0.35-0.41 AV: 3 NL: 2.91E5
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

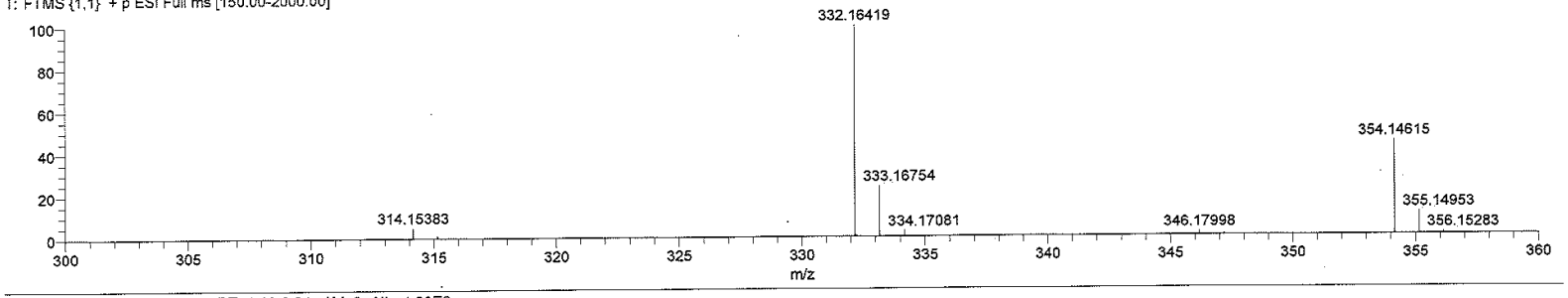




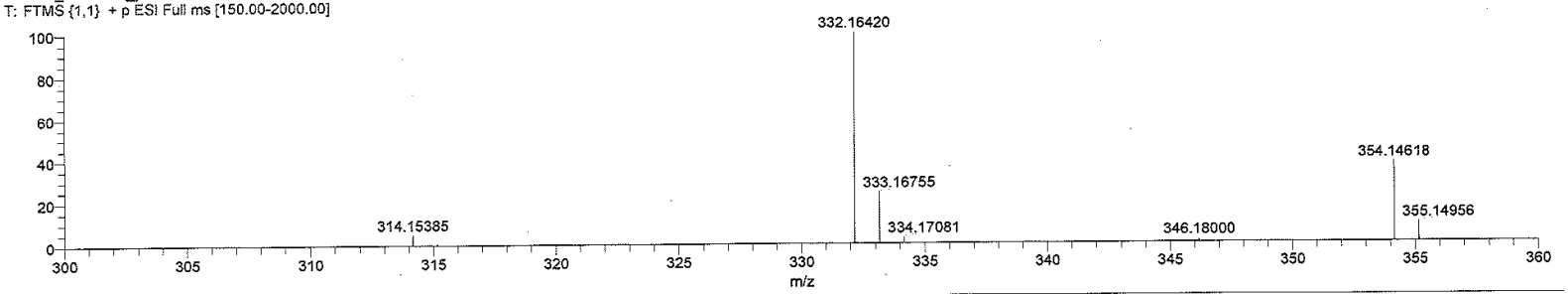
3aa

Sample No. : C:\Xcalibur\...\0820\2xxxx0_RT12170_pn
Operator name : hirose tomohiro
Date : 8/20/2020 9:36:49 AM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrument : Exactive
Mobile phase solvent : MeOH
Sample solvent : submitting solution
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

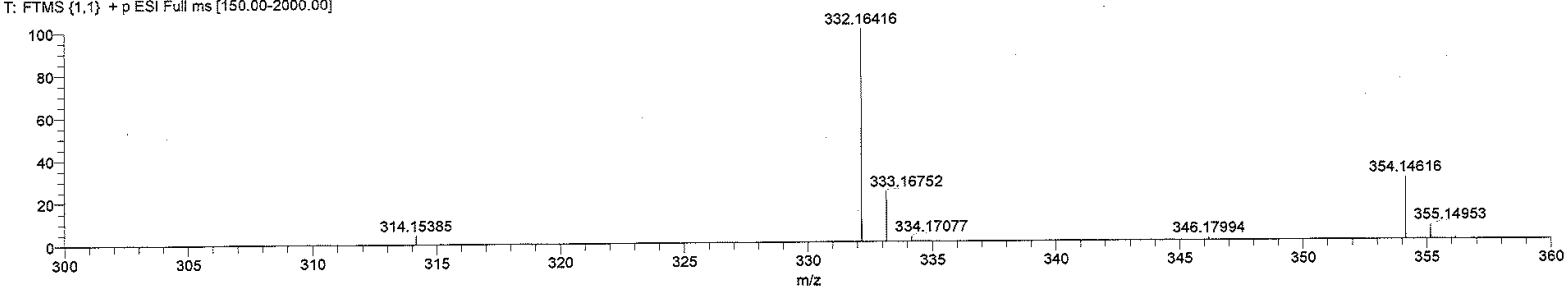
200600_RT12170_pn #21-25 RT: 0.25-0.29 AV: 3 NL: 1.20E8
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

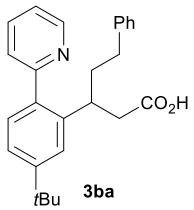


200600_RT12170_pn #25-30 RT: 0.29-0.34 AV: 3 NL: 1.30E8
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



200600_RT12170_pn #30-34 RT: 0.36-0.38 AV: 2 NL: 1.46E8
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ba

3ba

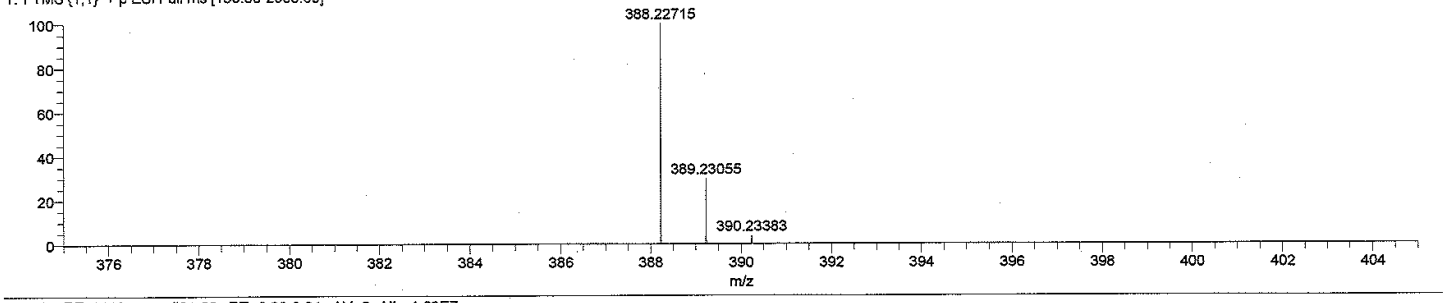
201251

Sample No. : C:\Xcalibur\...\1119\201251_RT13110_a_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:35:01 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

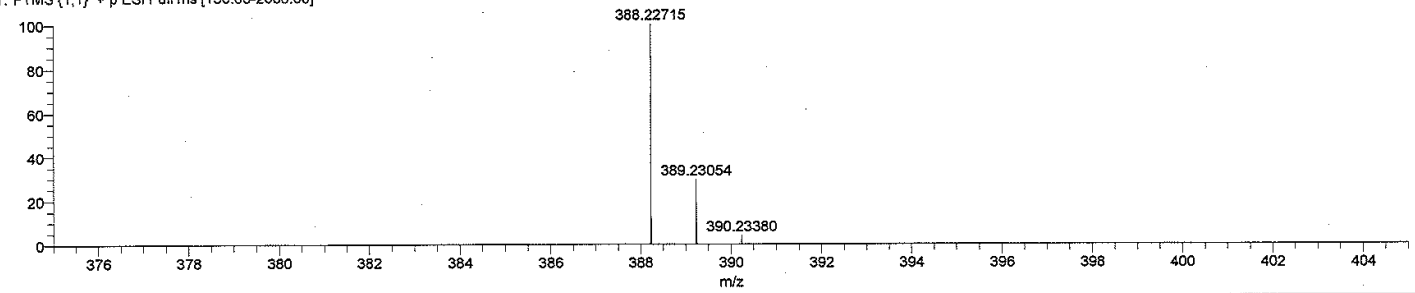
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

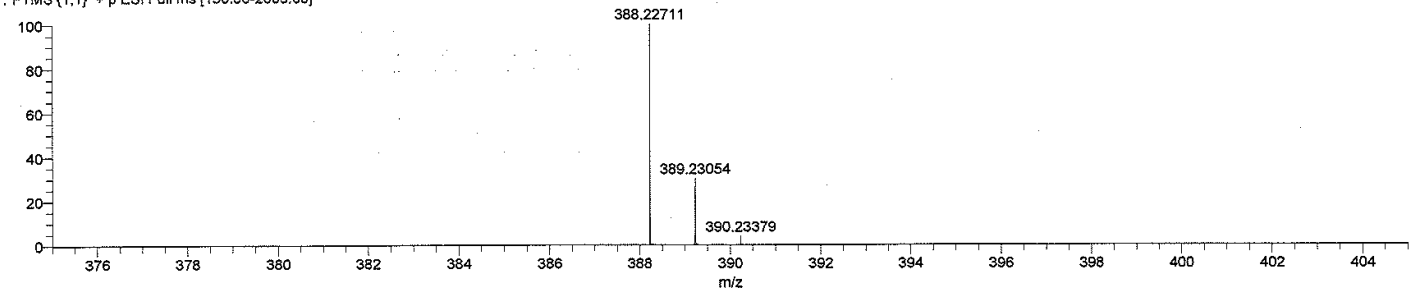
201251_RT13110_a_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 2.10E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

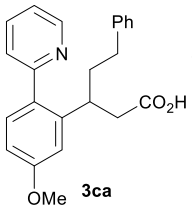


201251_RT13110_a_pn #21-26 RT: 0.30-0.34 AV: 3 NL: 1.63E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201251_RT13110_a_pn #26-30 RT: 0.37-0.39 AV: 2 NL: 1.07E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ca

3ca

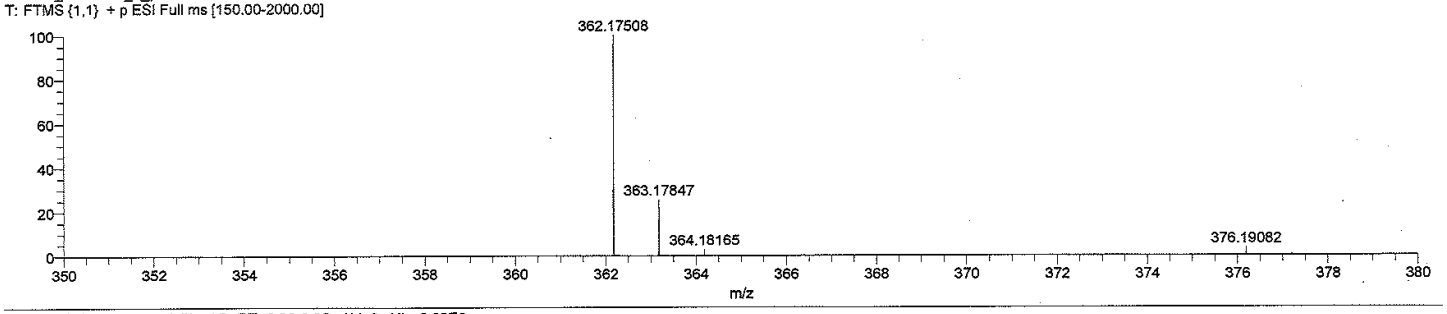
201247

Sample No. : C:\Xcalibur\...\201247_RT13107_a_pn2
Operator name : hayashi harumi
Date : 11/19/2020 2:24:55 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

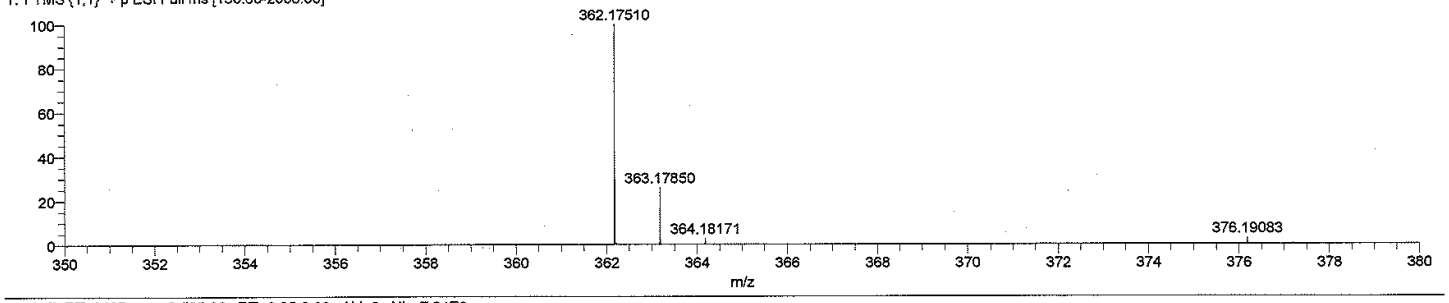
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

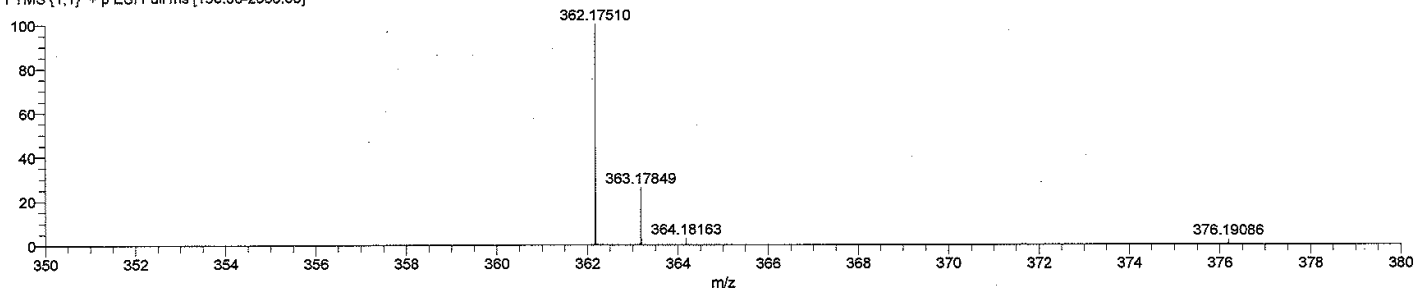
201247_RT13107_a_pn2 #17-21 RT: 0.25-0.30 AV: 3 NL: 1.24E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

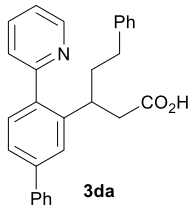


201247_RT13107_a_pn2 #21-25 RT: 0.30-0.35 AV: 3 NL: 9.83E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201247_RT13107_a_pn2 #25-30 RT: 0.35-0.39 AV: 3 NL: 7.94E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3da

201252

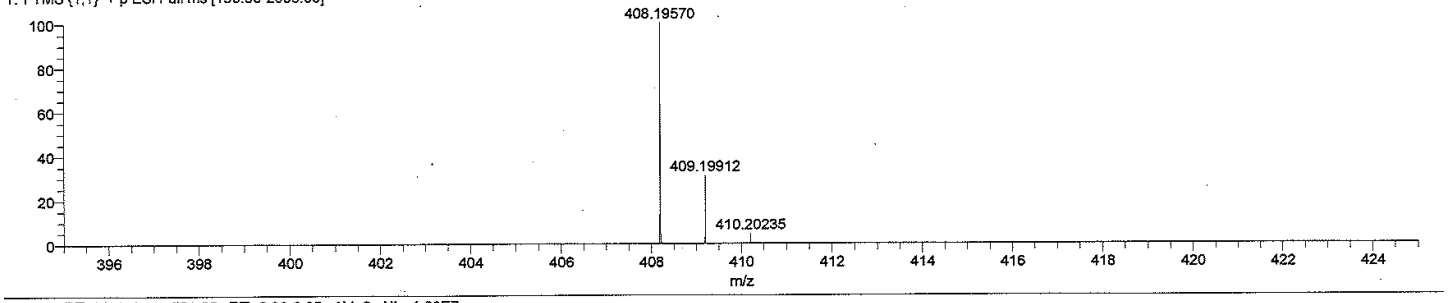
3da

Sample No. : C:\Xcalibur\...\1119\201252_RT13110_b_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:40:03 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

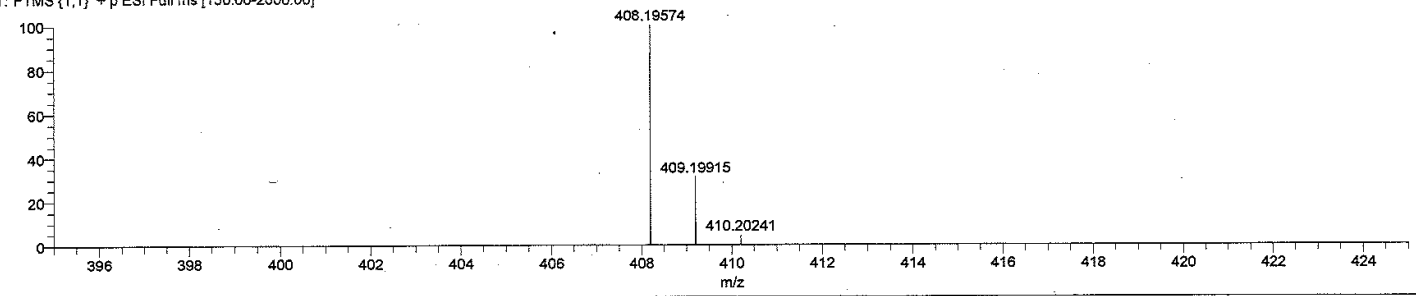
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

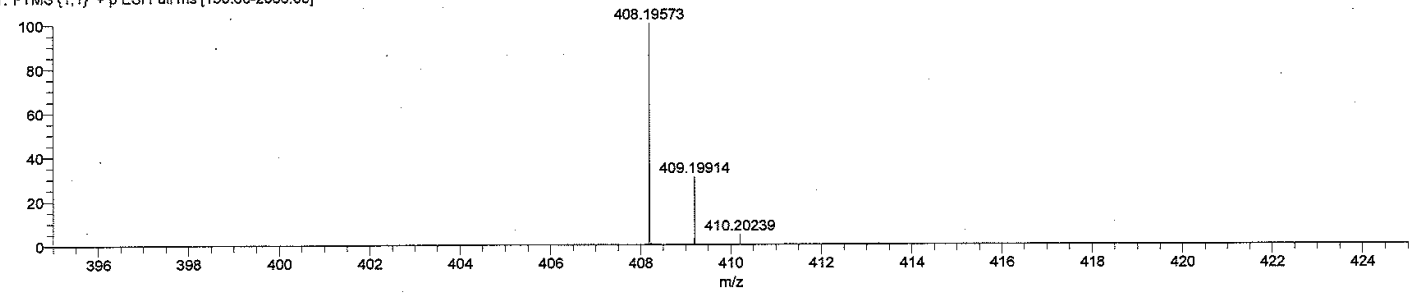
201252_RT13110_b_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 1.62E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

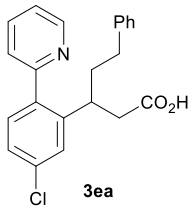


201252_RT13110_b_pn #21-25 RT: 0.30-0.35 AV: 3 NL: 1.20E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201252_RT13110_b_pn #25-30 RT: 0.35-0.39 AV: 3 NL: 9.66E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ea

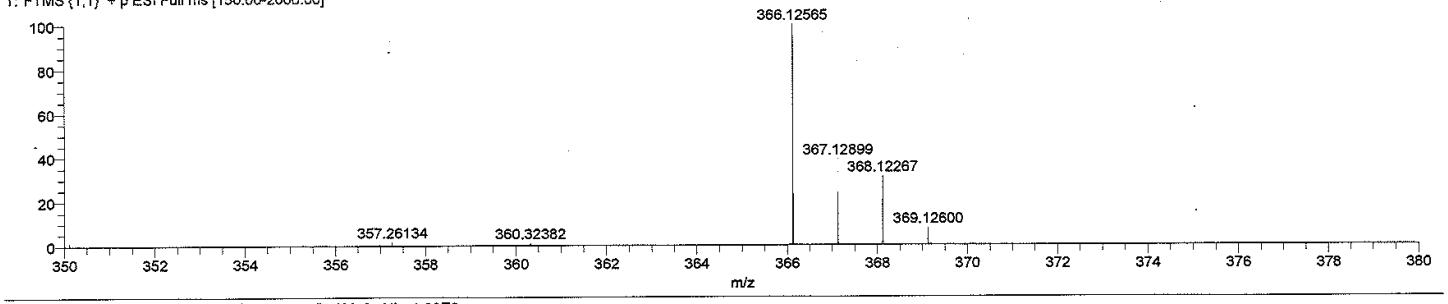
201246

Sample No. : C:\Xcalibur\...\1119\201246_RT13102_a_pn
Operator name : hayashi harumi
Date : 11/19/2020 1:30:55 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

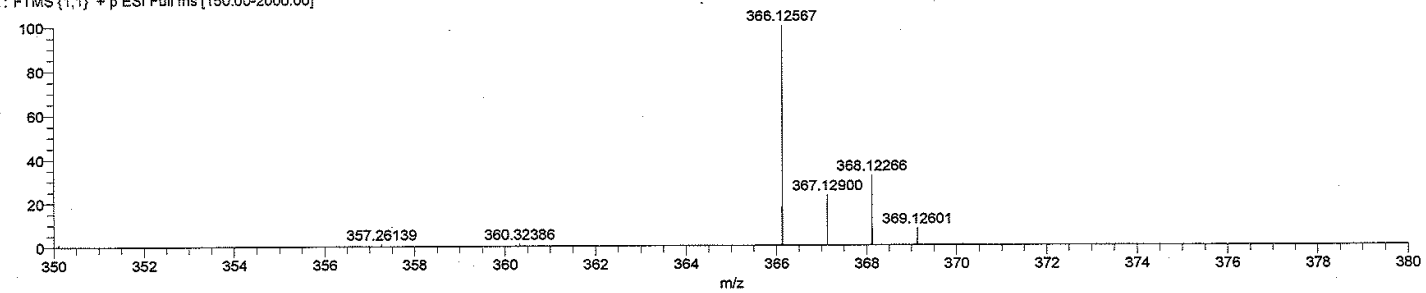
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

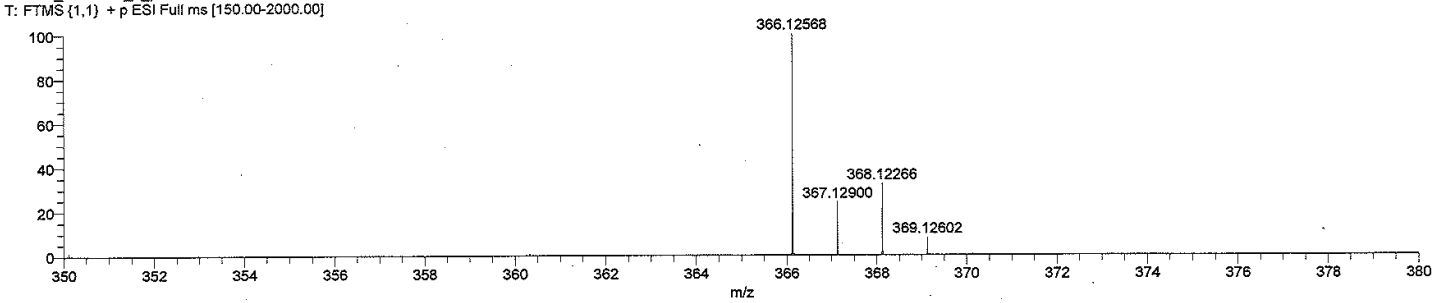
201246_RT13102_a_pn #16-19 RT: 0.27-0.30 AV: 2 NL: 1.63E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

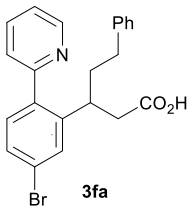


201246_RT13102_a_pn #19-23 RT: 0.30-0.35 AV: 3 NL: 1.22E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201246_RT13102_a_pn #23-26 RT: 0.35-0.38 AV: 2 NL: 7.85E5
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3fa

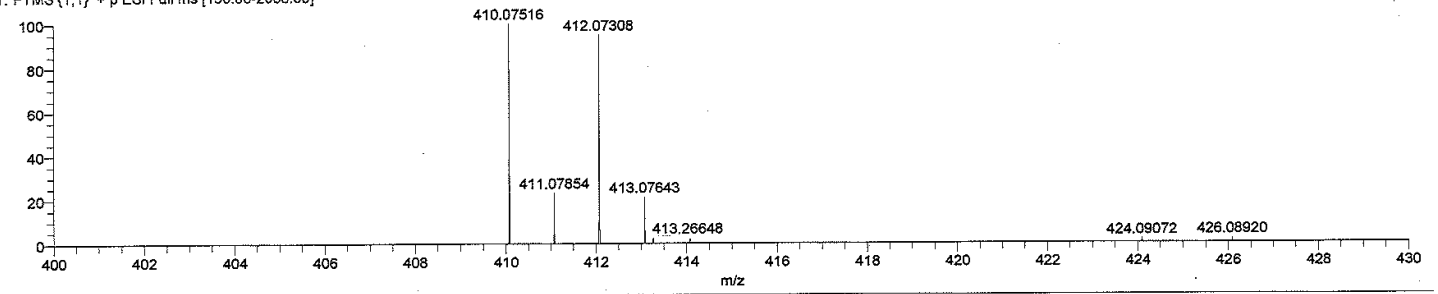
201250

Sample No. : C:\Xcalibur\...\1119\201250_RT13104_a_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:29:59 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

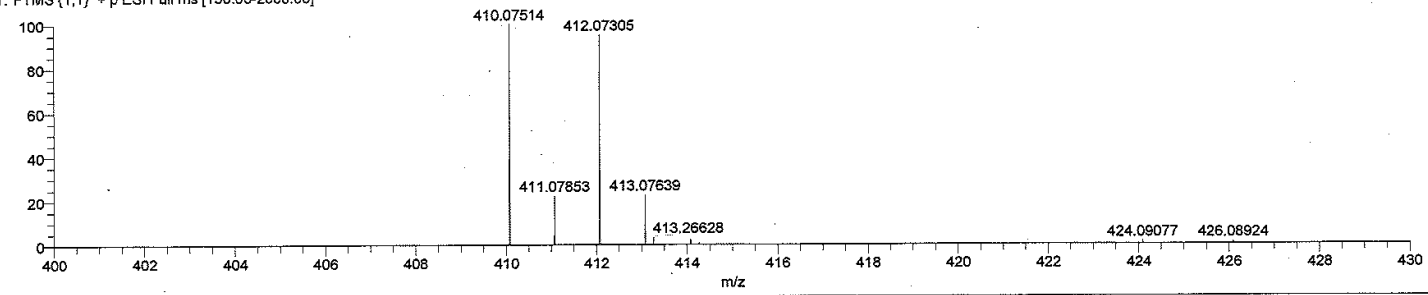
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

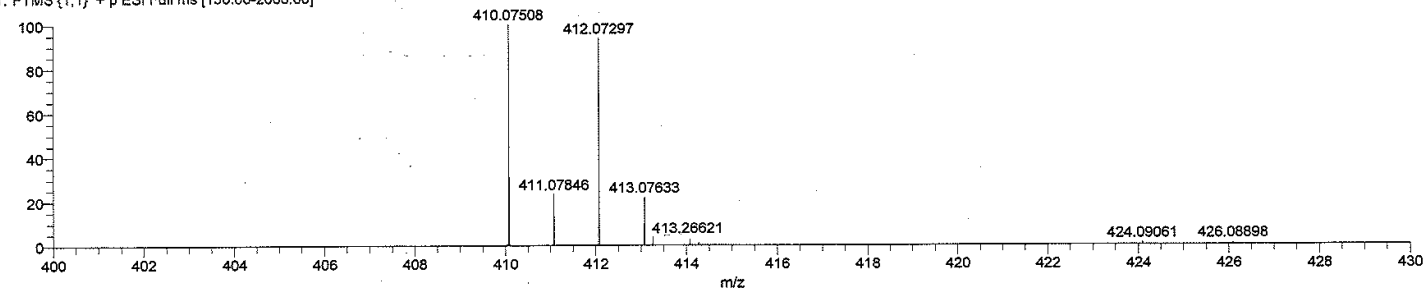
201250_RT13104_a_pn #17-22 RT: 0.25-0.29 AV: 3 NL: 4.69E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

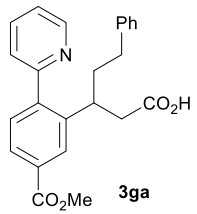


201250_RT13104_a_pn #22-26 RT: 0.32-0.34 AV: 2 NL: 3.53E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201250_RT13104_a_pn #26-30 RT: 0.36-0.39 AV: 2 NL: 3.32E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ga

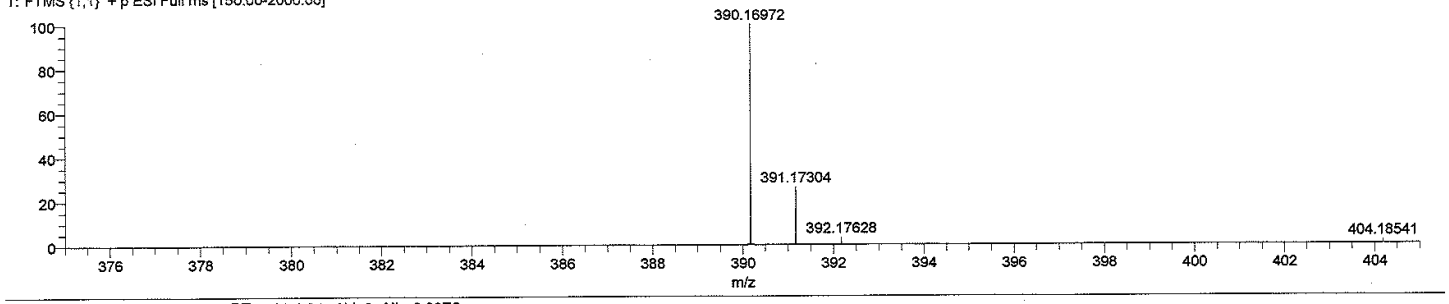
201248

Sample No. : C:\Xcalibur\...\1119\201248_RT13104_b_pn
Operator name : hayashi harumi
Date : 11/19/2020 1:56:47 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

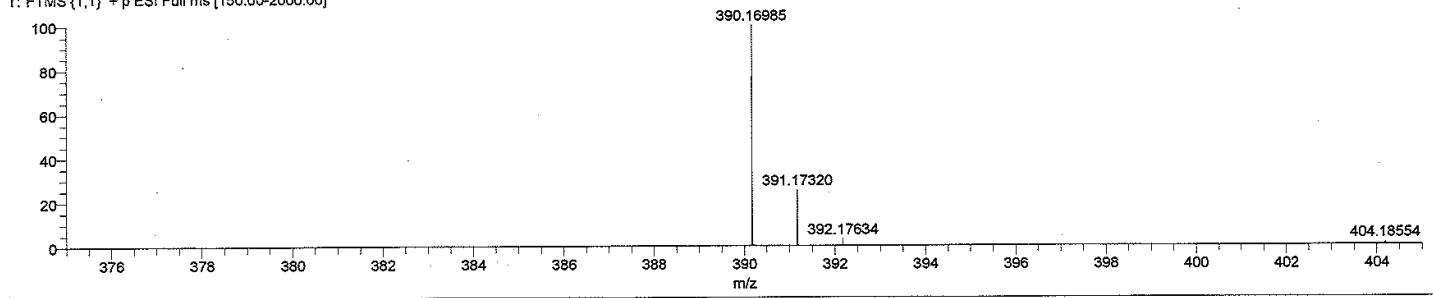
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

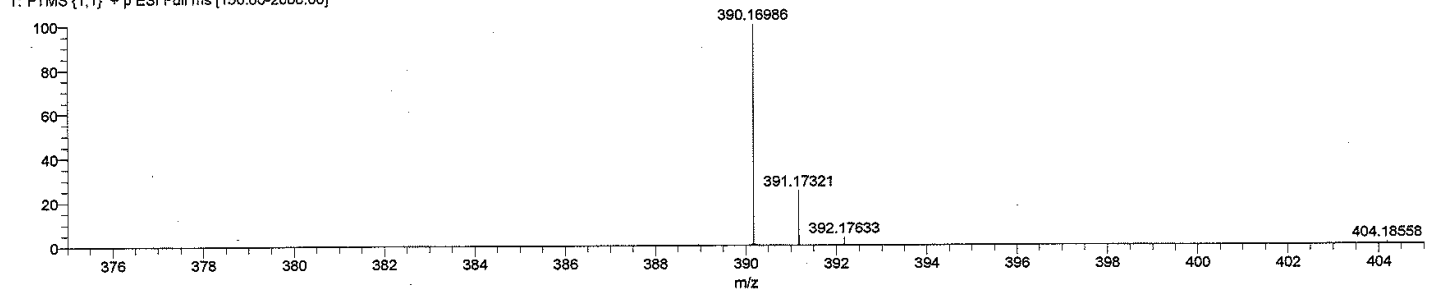
201248_RT13104_b_pn #17-22 RT: 0.25-0.29 AV: 3 NL: 9.95E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

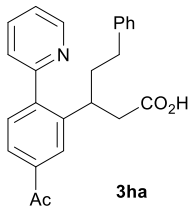


201248_RT13104_b_pn #22-26 RT: 0.32-0.34 AV: 2 NL: 9.82E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201248_RT13104_b_pn #26-30 RT: 0.36-0.38 AV: 2 NL: 7.98E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ha

3ha

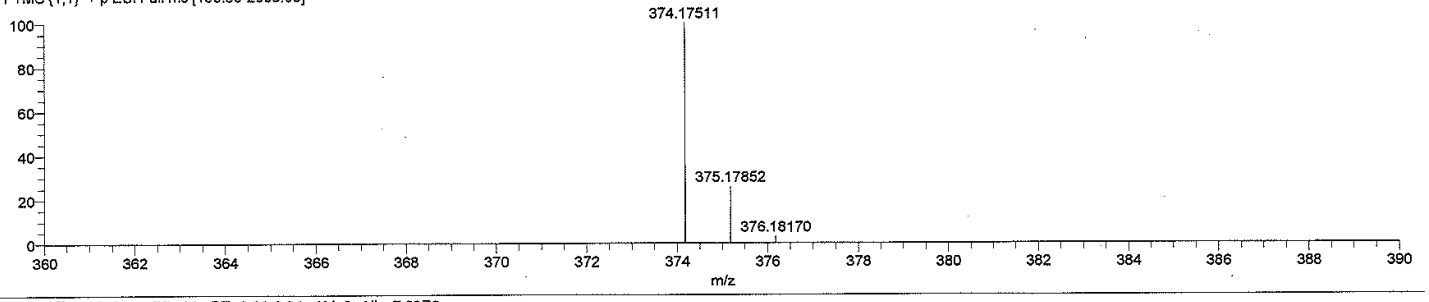
201249

Sample No. : C:\Xcalibur\...\1119\201249_RT13107_b_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:01:49 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

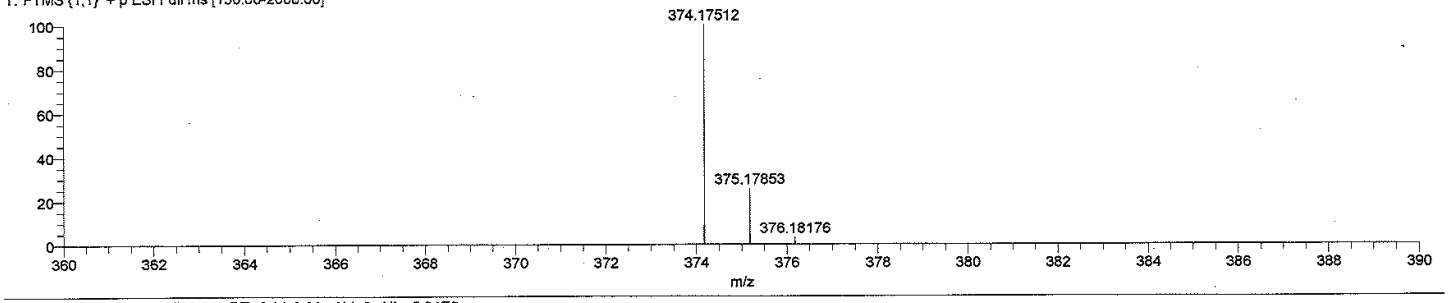
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

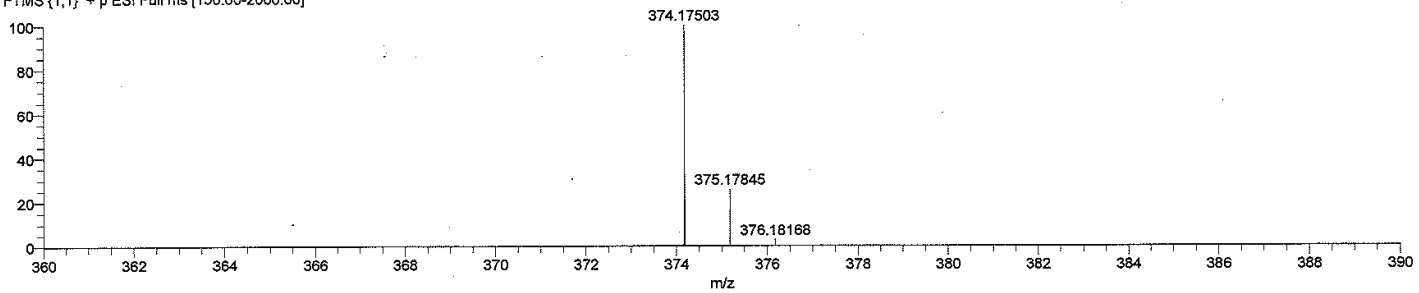
201249_RT13107_b_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 8.40E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

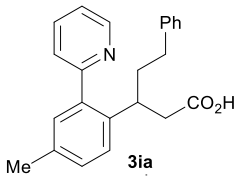


201249_RT13107_b_pn #21-26 RT: 0.30-0.34 AV: 3 NL: 7.23E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201249_RT13107_b_pn #26-30 RT: 0.36-0.39 AV: 2 NL: 5.94E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ia

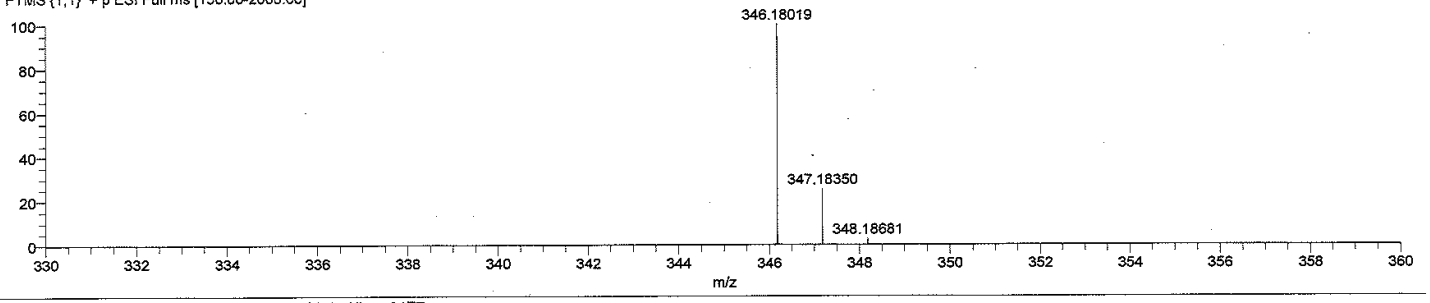
201253

Sample No. : C:\Xcalibur\...\1119\201253_RT13137_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:45:05 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

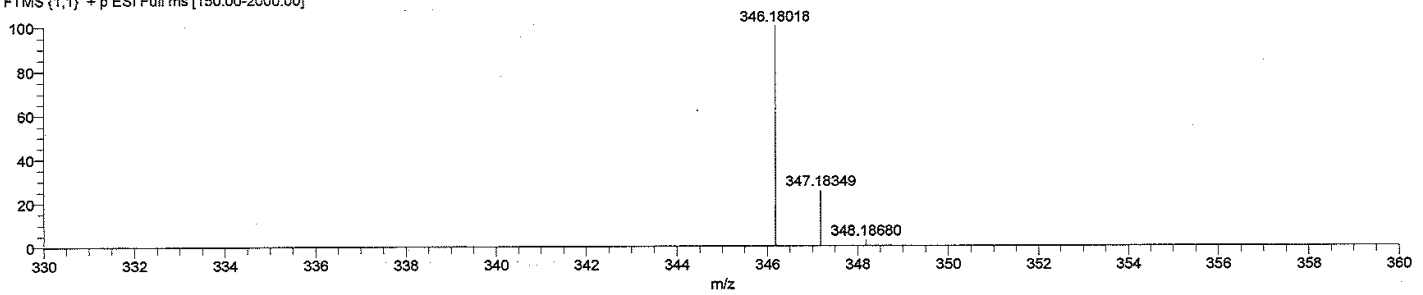
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

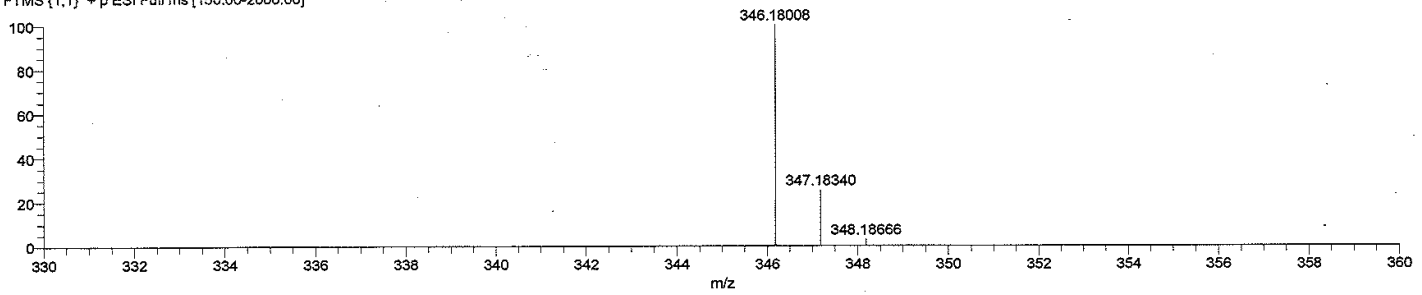
201253_RT13137_pn #17-21 RT: 0.25-0.29 AV: 3 NL: 2.54E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

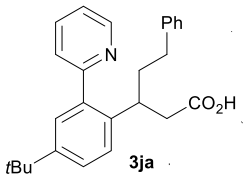


201253_RT13137_pn #21-26 RT: 0.29-0.34 AV: 3 NL: 1.94E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201253_RT13137_pn #26-30 RT: 0.36-0.39 AV: 2 NL: 1.50E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ja

201256

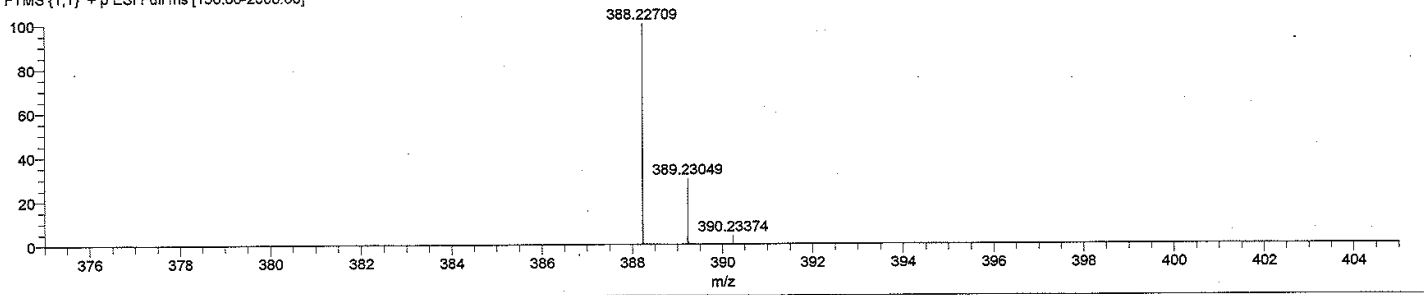
3ja

Sample No. : C:\Xcalibur\...\1119\201256_RT13130_pn
Operator name : hayashi harumi
Date : 11/19/2020 3:00:12 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

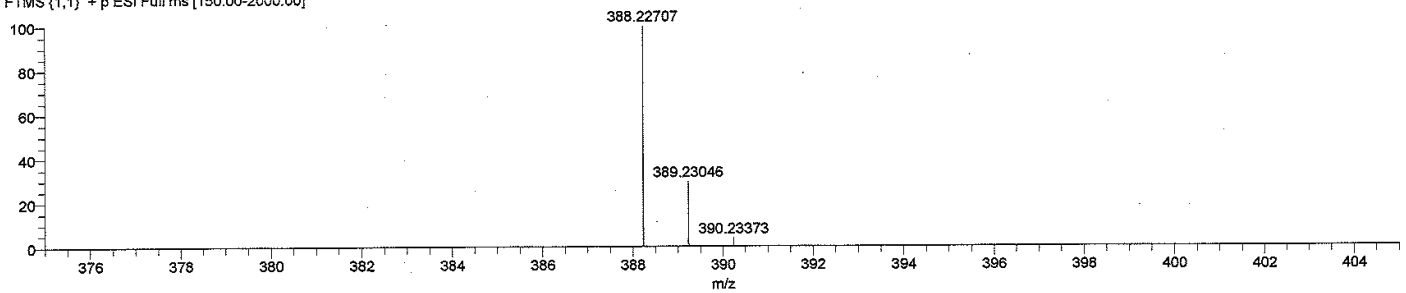
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

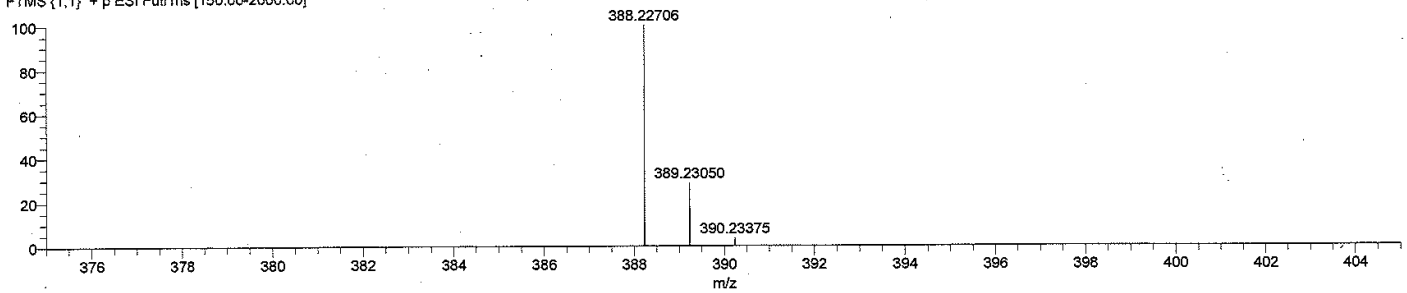
201256_RT13130_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 2.46E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

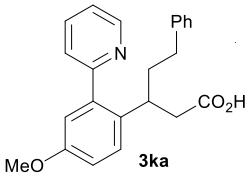


201256_RT13130_pn #21-26 RT: 0.30-0.34 AV: 3 NL: 1.88E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201256_RT13130_pn #26-30 RT: 0.36-0.39 AV: 2 NL: 1.45E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ka

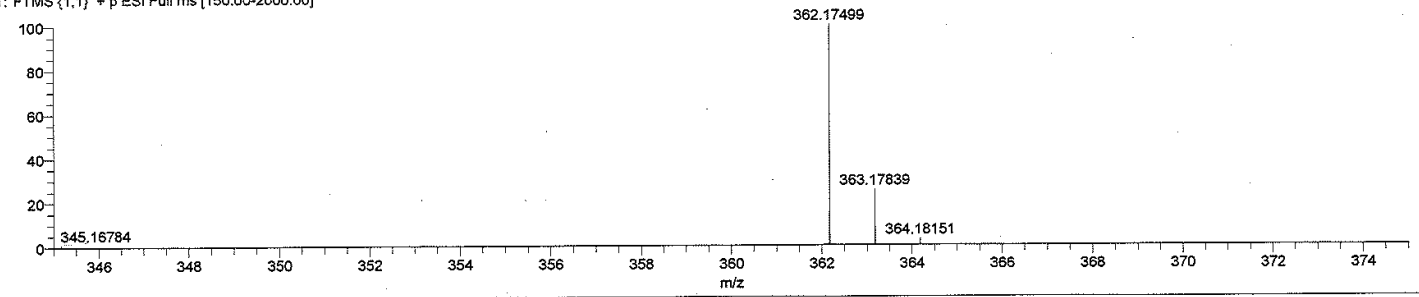
201255

Sample No. : C:\Xcalibur\...\1119\20[illegible]_RT13114_b_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:55:10 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

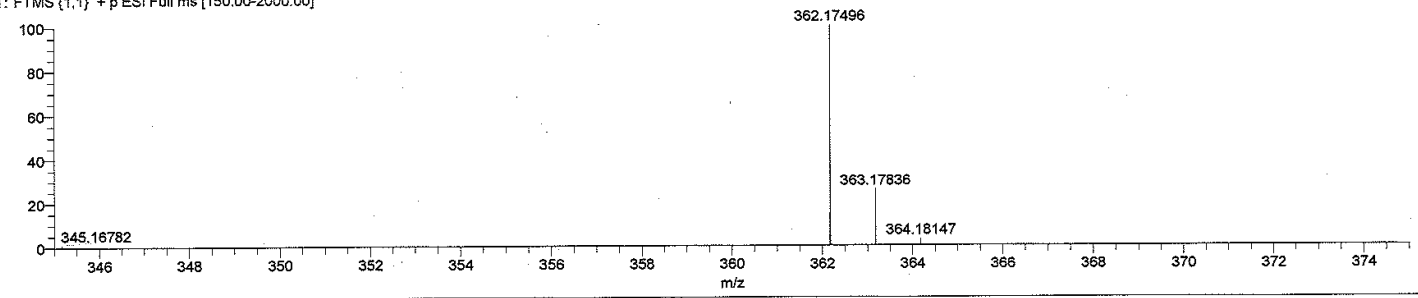
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

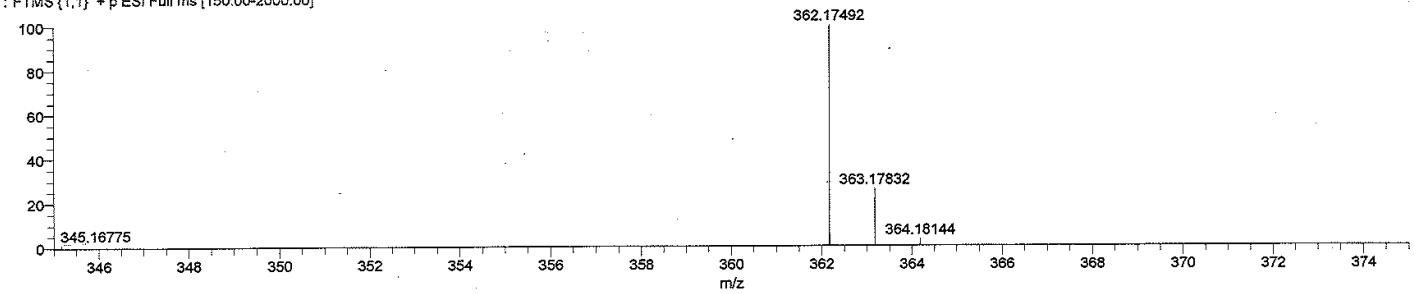
201255_RT13114_b_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 2.25E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

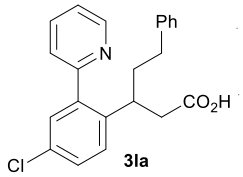


201255_RT13114_b_pn #21-26 RT: 0.30-0.34 AV: 3 NL: 1.77E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201255_RT13114_b_pn #26-30 RT: 0.37-0.39 AV: 2 NL: 1.31E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3la

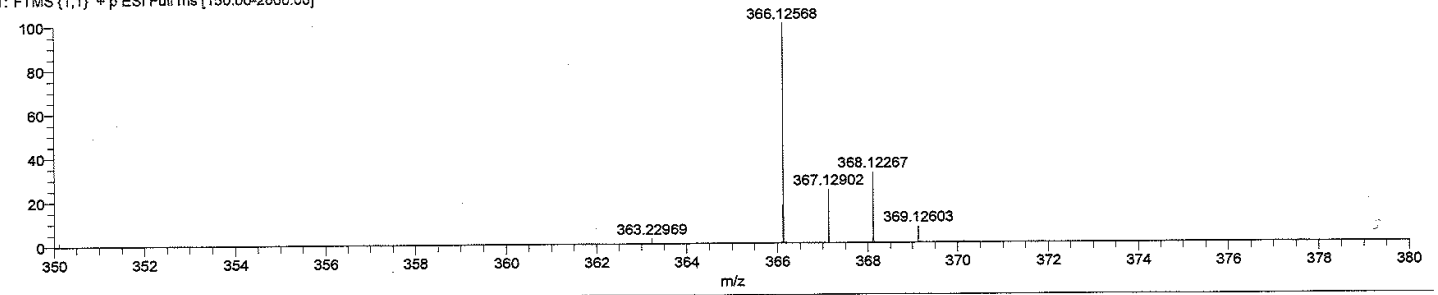
201254

Sample No. : C:\Xcalibur\...\1119\201254_RT13114_a_pn
Operator name : hayashi harumi
Date : 11/19/2020 2:50:07 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

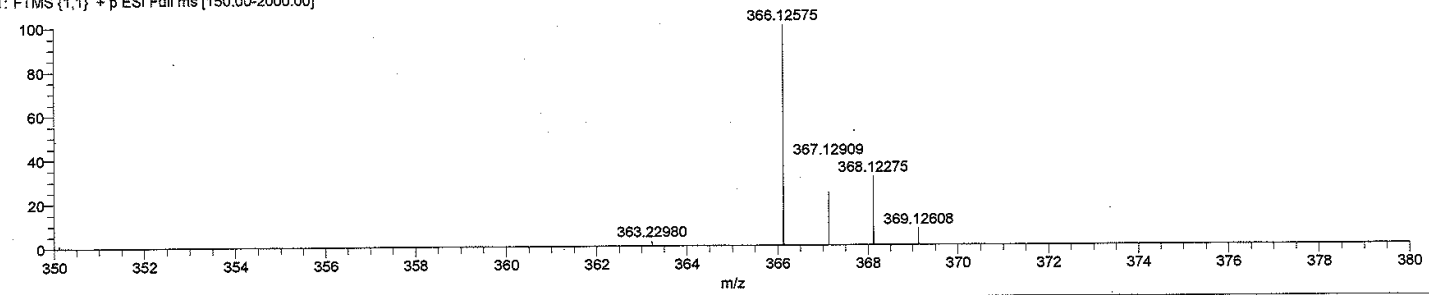
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

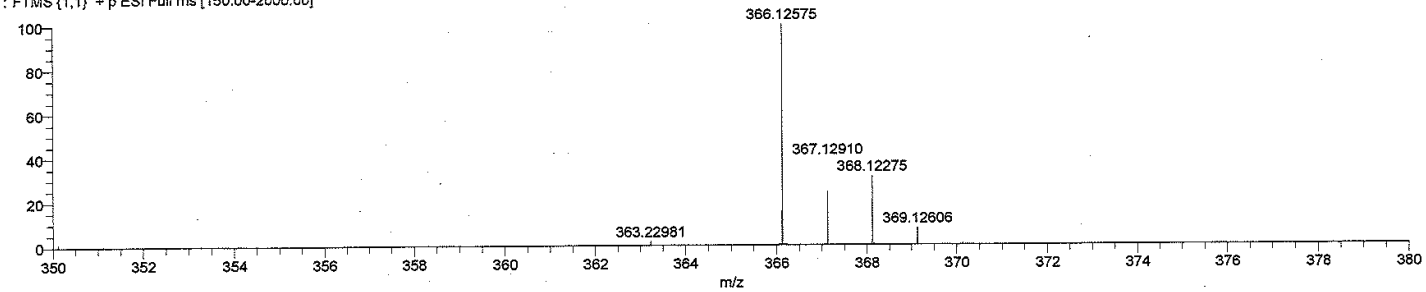
201254_RT13114_a_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 6.06E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

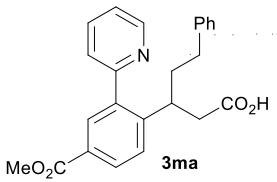


201254_RT13114_a_pn #21-25 RT: 0.30-0.34 AV: 3 NL: 5.22E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201254_RT13114_a_pn #25-30 RT: 0.34-0.39 AV: 3 NL: 3.83E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ma

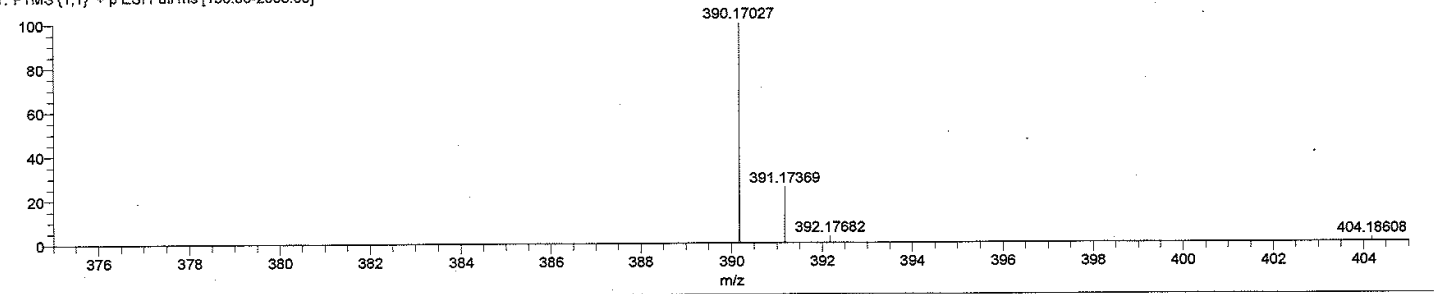
201257

Sample No. : C:\Xcalibur\...\1119\201257_RT13131_a_pn
Operator name : hayashi harumi
Date : 11/19/2020 3:05:14 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

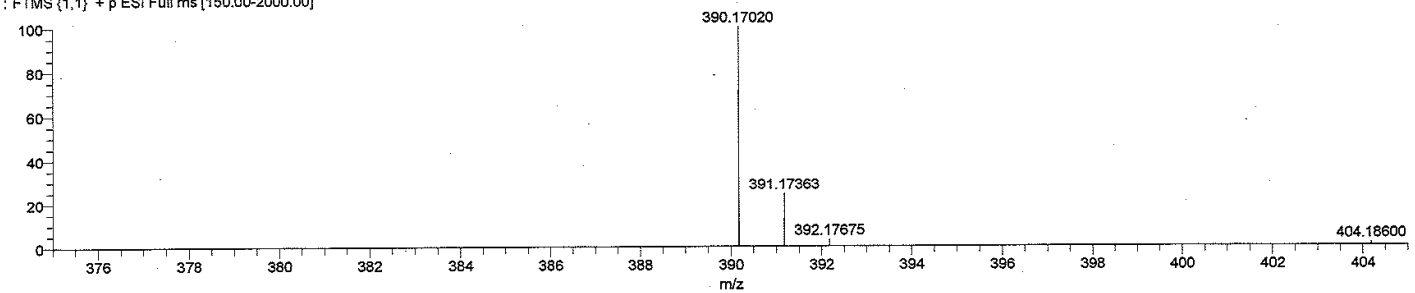
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

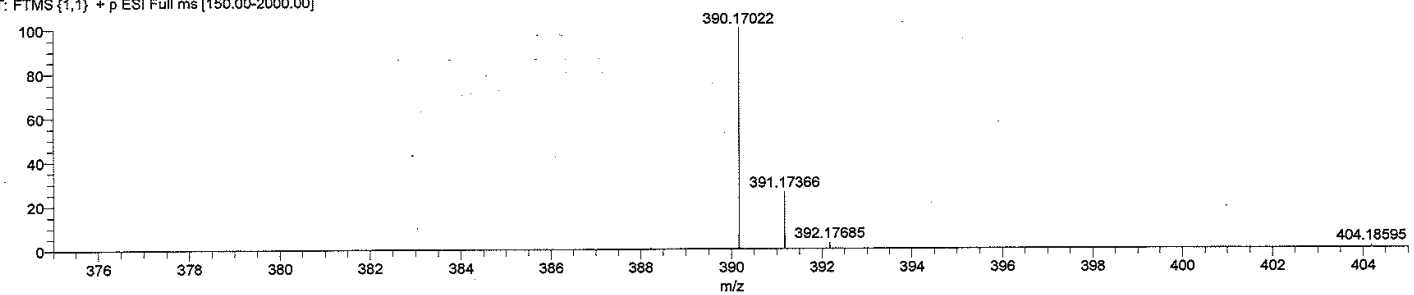
201257_RT13131_a_pn #17-21 RT: 0.25-0.30 AV: 3 NL: 5.90E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

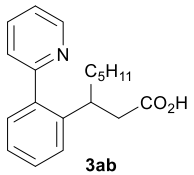


201257_RT13131_a_pn #21-26 RT: 0.30-0.34 AV: 3 NL: 4.96E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201257_RT13131_a_pn #26-30 RT: 0.37-0.39 AV: 2 NL: 4.23E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ab

201526

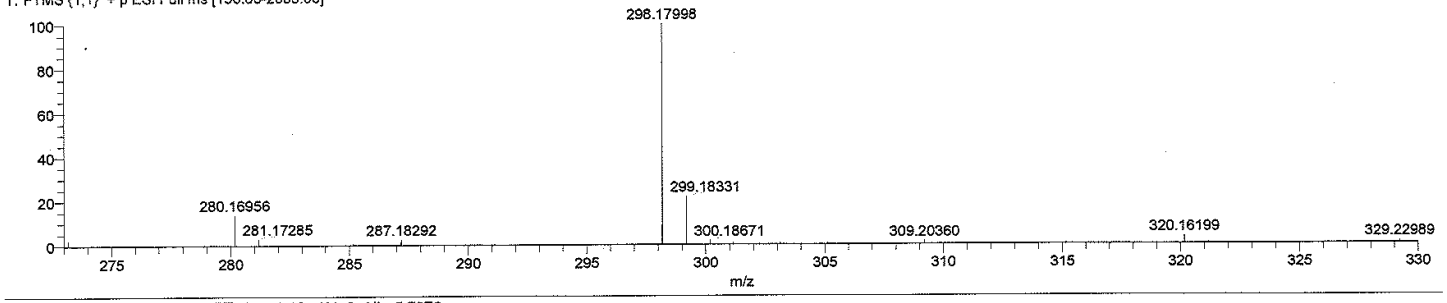
3ab

Sample No. : C:\Xcalibur\...\1214\201526_RT13080_pn
Operator name : hayashi harumi
Date : 12/14/2020 11:35:22 AM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

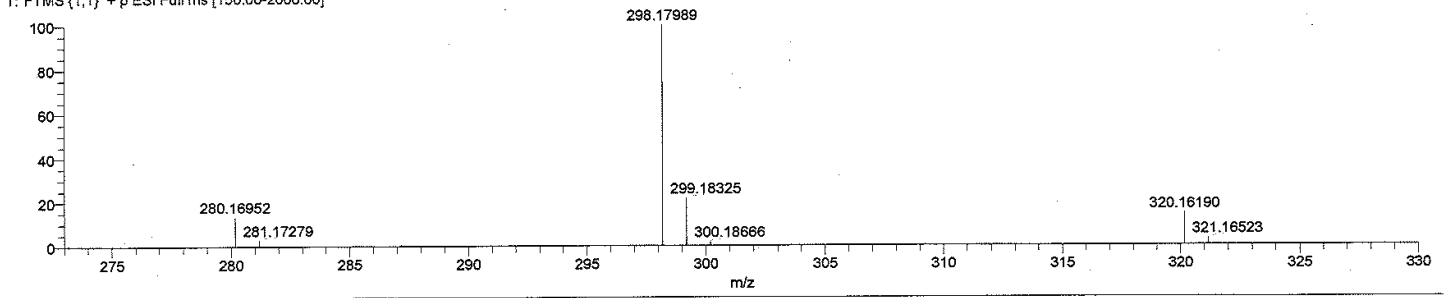
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

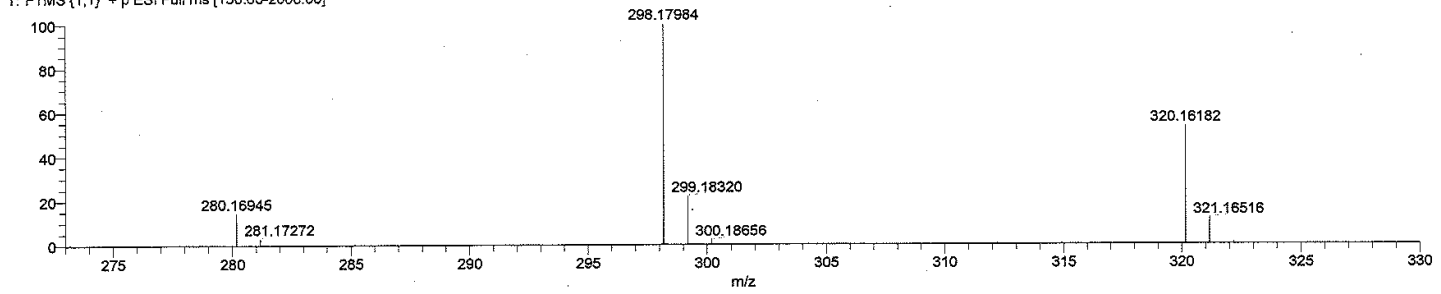
201526_RT13080_pn #16-19 RT: 0.27-0.31 AV: 2 NL: 1.84E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

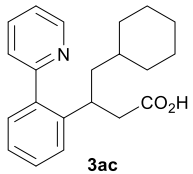


201526_RT13080_pn #19-22 RT: 0.31-0.33 AV: 2 NL: 5.76E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201526_RT13080_pn #22-26 RT: 0.36-0.38 AV: 2 NL: 1.43E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ac

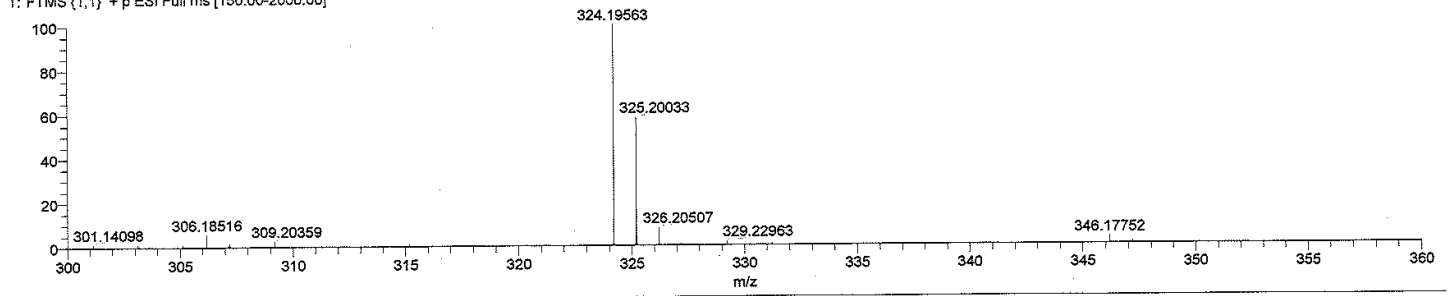
201527

Sample No. : C:\Xcalibur\...\1214\201527_RT13142_b_pn
Operator name : hayashi harumi
Date : 12/14/2020 11:40:24 AM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

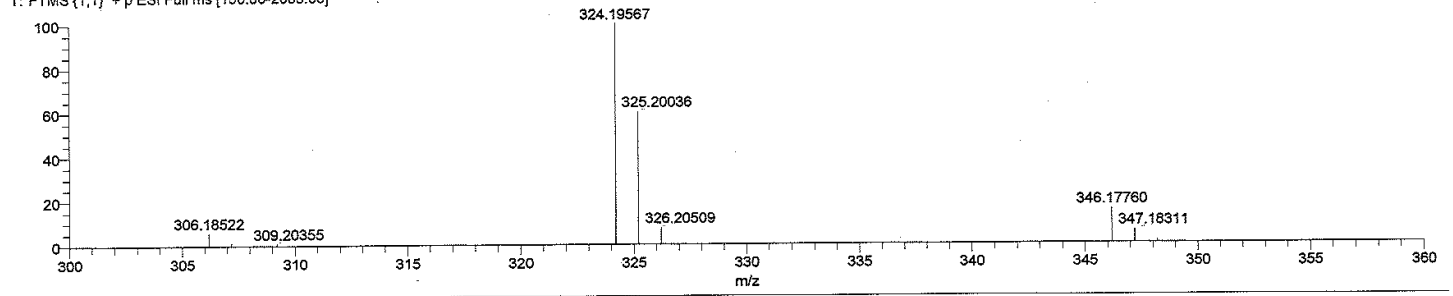
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

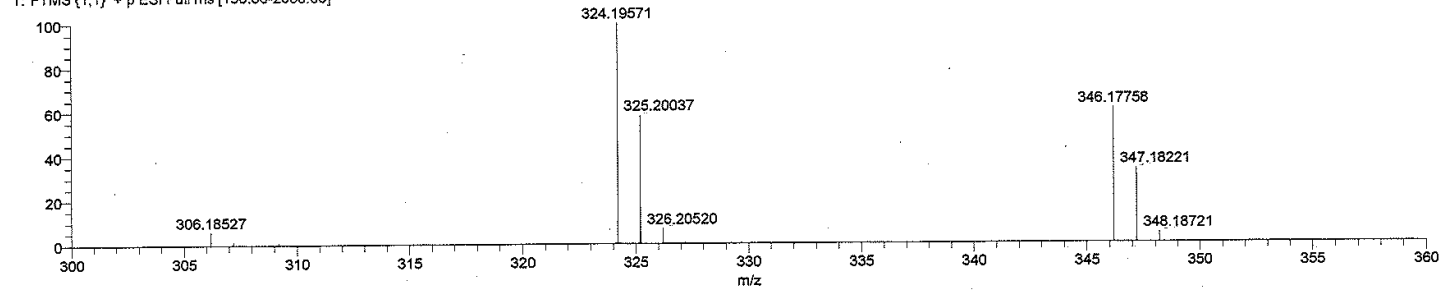
201527_RT13142_b_pn #16-19 RT: 0.28-0.31 AV: 2 NL: 1.09E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

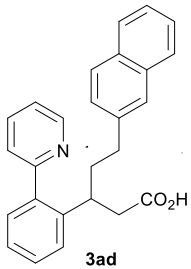


201527_RT13142_b_pn #19-22 RT: 0.31-0.34 AV: 2 NL: 3.91E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201527_RT13142_b_pn #22-26 RT: 0.36-0.38 AV: 2 NL: 1.26E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ad

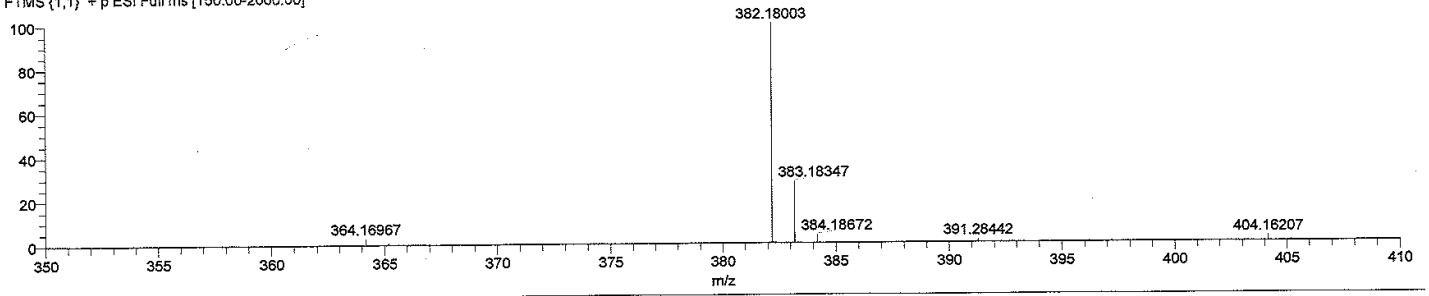
201528

Sample No. : C:\Xcalibur\...\1214\201528_RT13145_a_pn
Operator name : hayashi harumi
Date : 12/14/2020 11:45:26 AM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

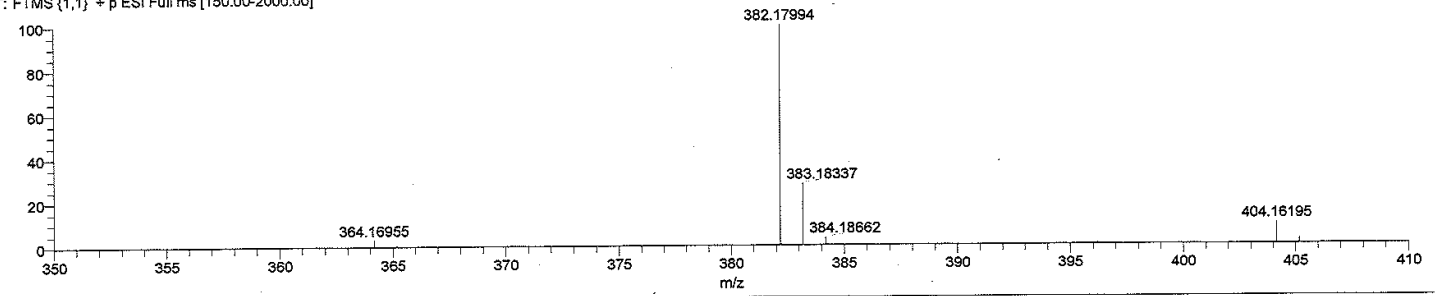
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

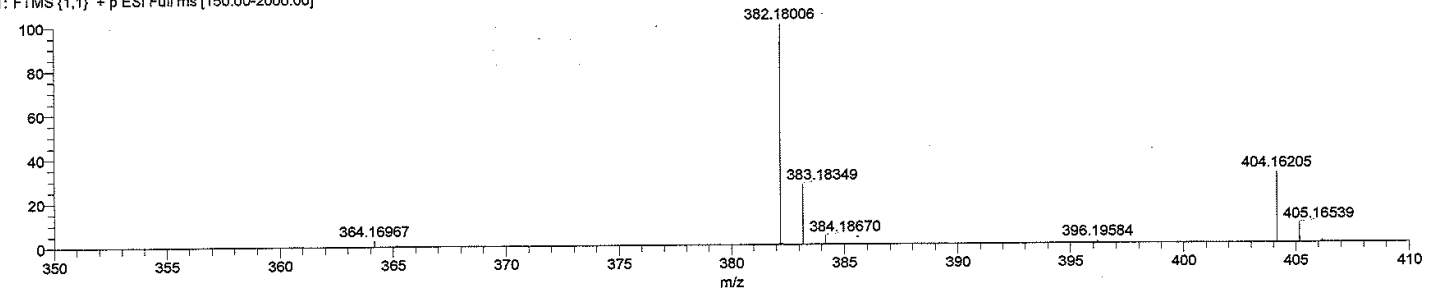
201528_RT13145_a_pn #16-19 RT: 0.27-0.30 AV: 2 NL: 8.85E5
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

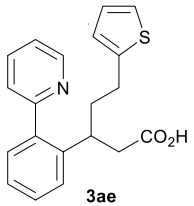


201528_RT13145_a_pn #19-22 RT: 0.30-0.33 AV: 2 NL: 3.43E6
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201528_RT13145_a_pn #22-26 RT: 0.36-0.39 AV: 2 NL: 1.21E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ae

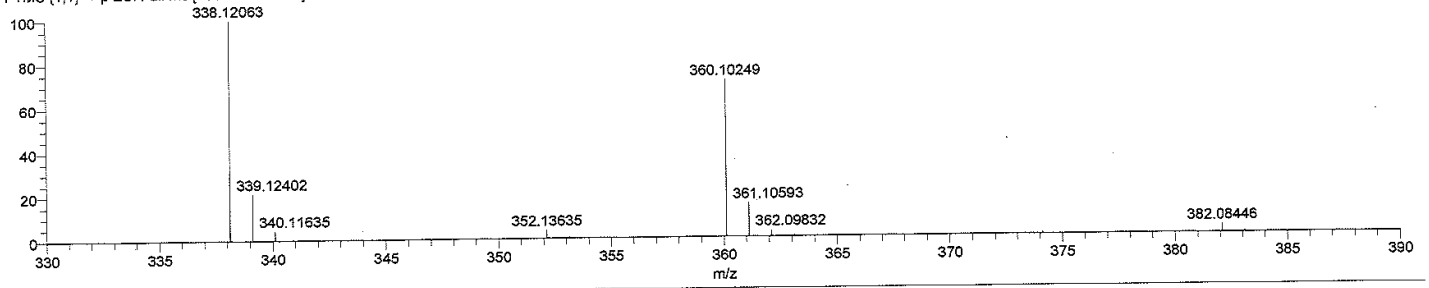
201813

Sample No. : C:\Xcalibur\...\0121\201813_RT13146_a_pn
Operator name : hirose tomohiro
Date : 1/21/2021 1:39:00 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

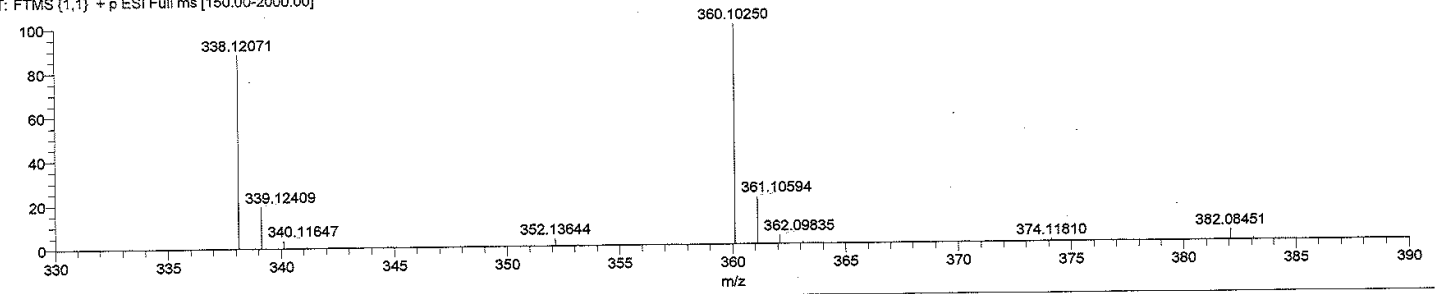
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

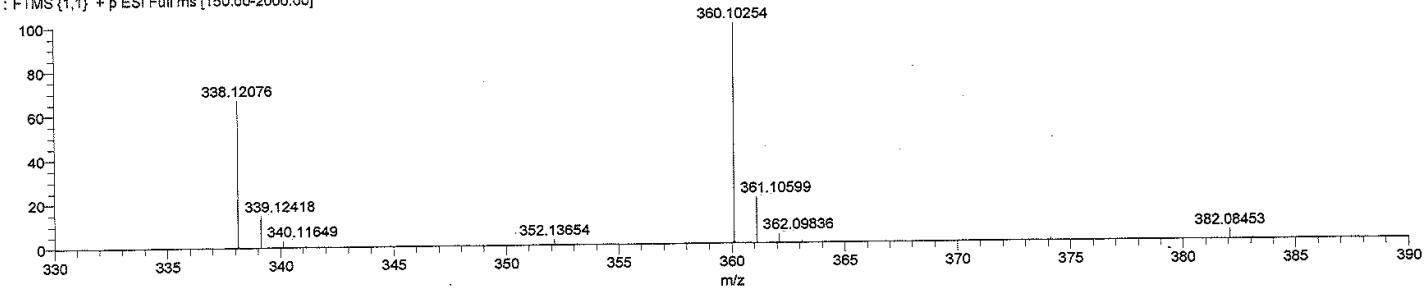
201813_RT13146_a_pn #22-25 RT: 0.34-0.37 AV: 2 NL: 1.97E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

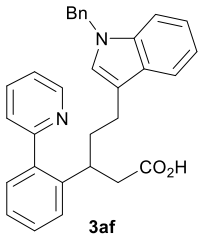


201813_RT13146_a_pn #25-30 RT: 0.37-0.41 AV: 3 NL: 2.43E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201813_RT13146_a_pn #30 RT: 0.44 AV: 1 NL: 2.90E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3af

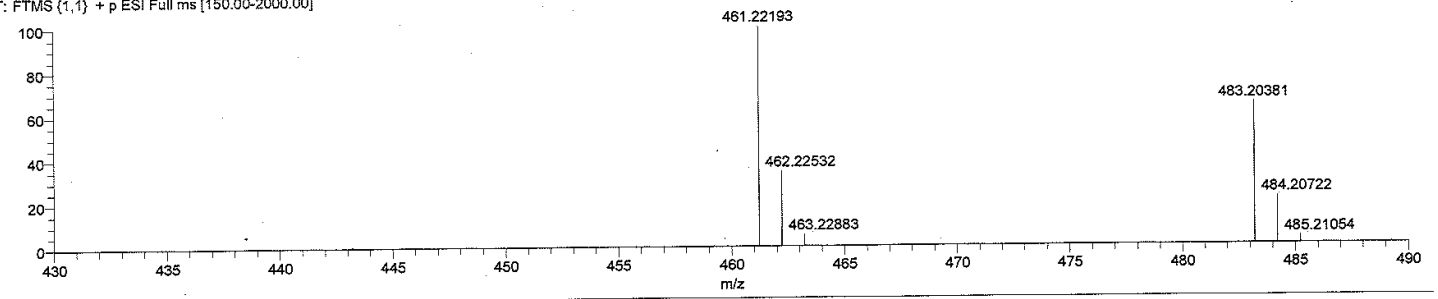
201815

Sample No. : C:\Xcalibur\...\0121\201815_RT13151_b_pn
Operator name : hirose tomohiro
Date : 1/21/2021 1:49:07 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

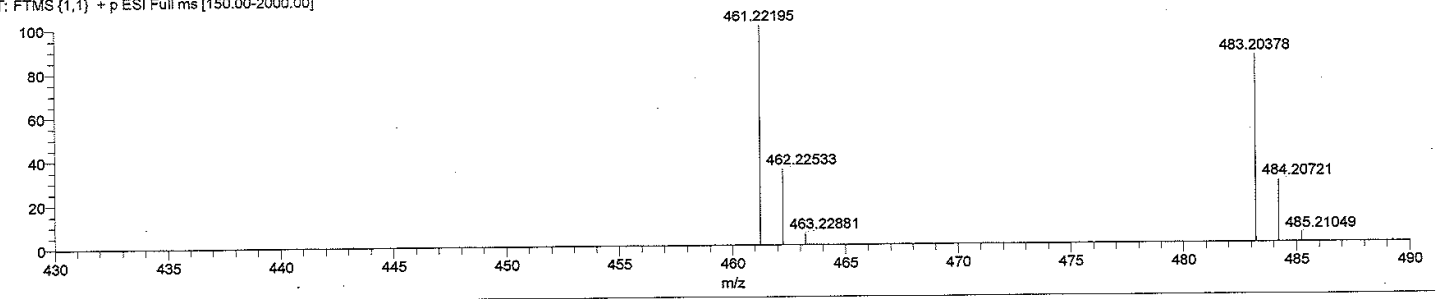
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

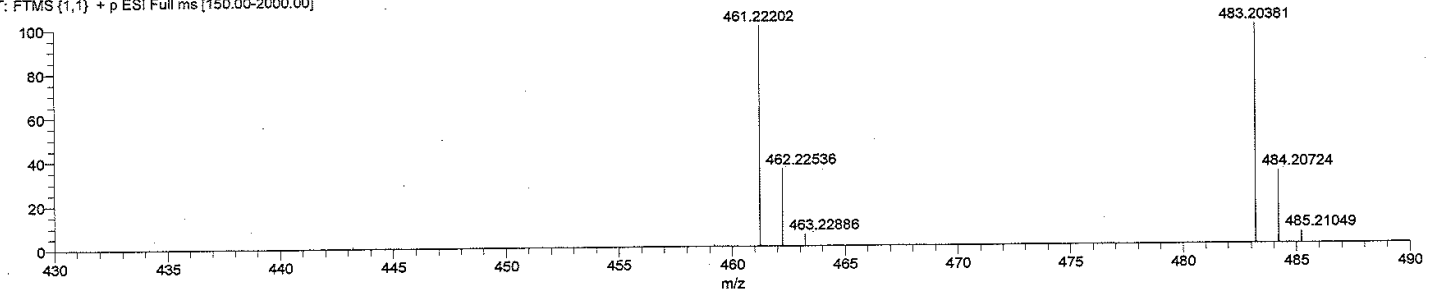
201815_RT13151_b_pn #22-25 RT: 0.35-0.37 AV: 2 NL: 2.27E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

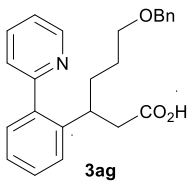


201815_RT13151_b_pn #25-29 RT: 0.37-0.42 AV: 3 NL: 2.42E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201815_RT13151_b_pn #29-32 RT: 0.42-0.44 AV: 2 NL: 2.05E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ag

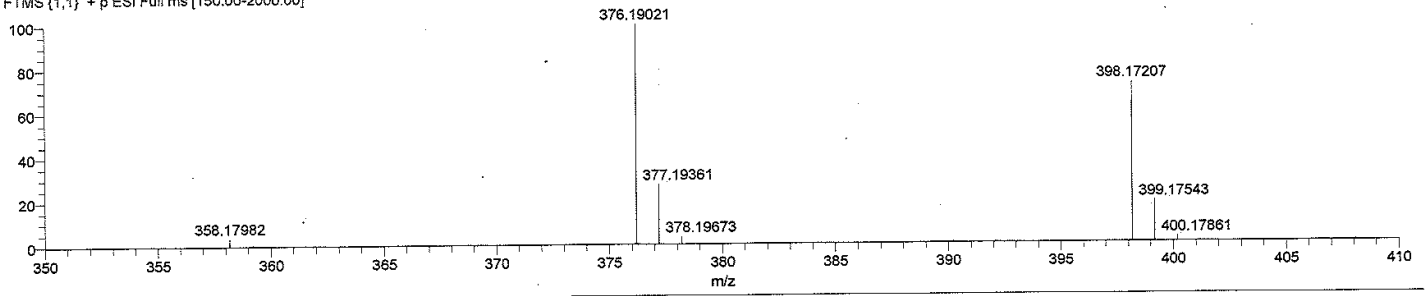
201814

Sample No. : C:\Xcalibur\...\0121\201814_RT13151_a_pn
Operator name : hirose tomohiro
Date : 1/21/2021 1:44:03 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

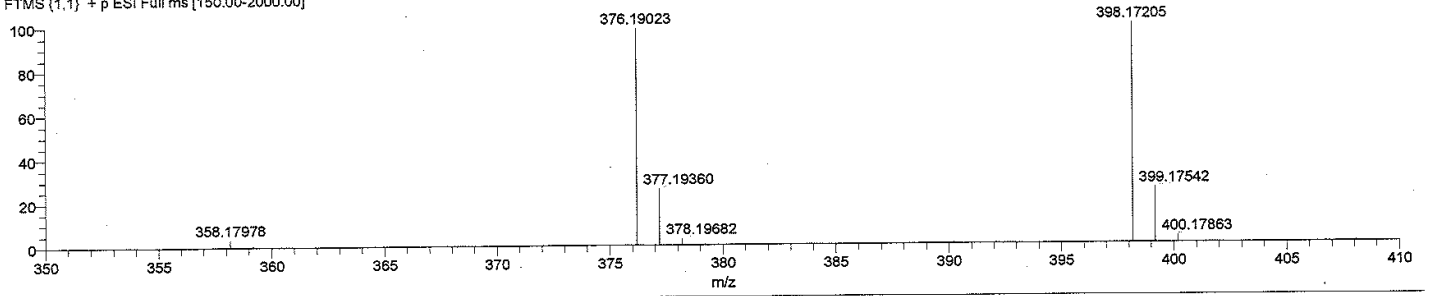
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

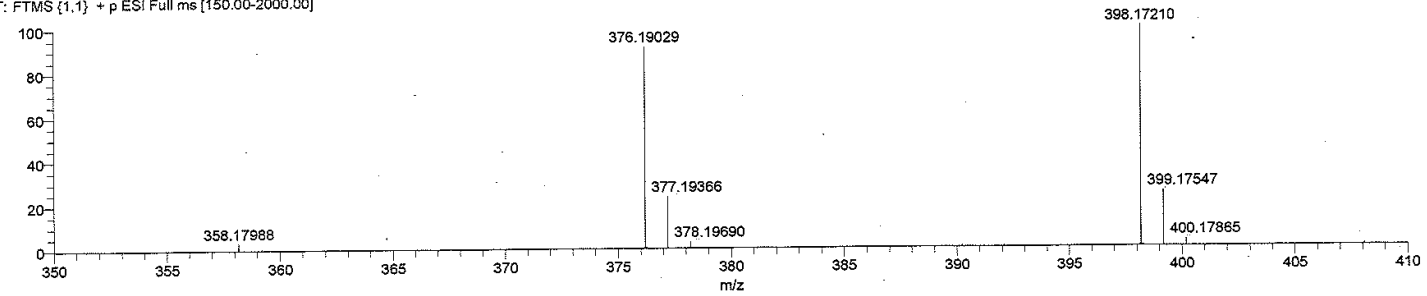
201814_RT13151_a_pn #22-26 RT: 0.34-0.36 AV: 2 NL: 4.06E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]

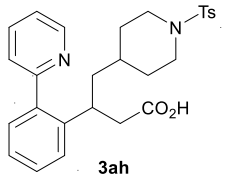


201814_RT13151_a_pn #26-30 RT: 0.38-0.41 AV: 2 NL: 4.69E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



201814_RT13151_a_pn #30-33 RT: 0.43-0.45 AV: 2 NL: 4.60E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]





3ah

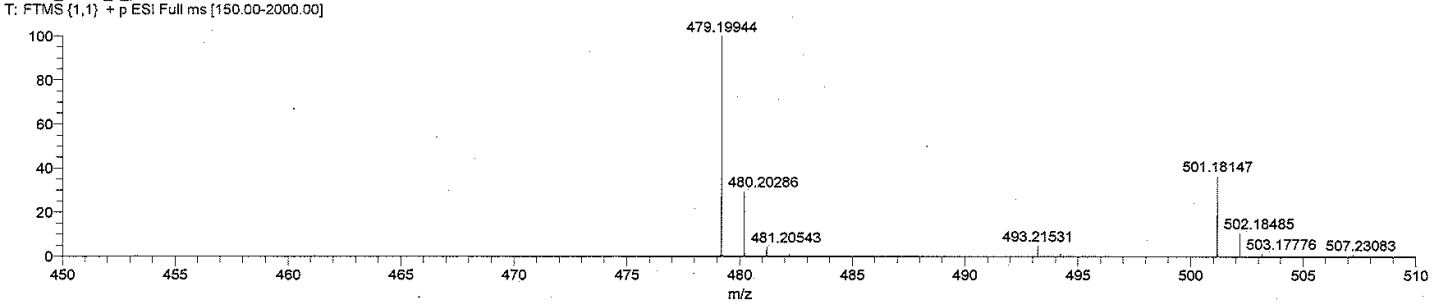
202062

Sample No. : C:\Xcalibur\...\0222\202062_13176_b_pn
Operator name :
Date : 2/22/2021 6:06:10 PM
Instrumental method : C:\Xcalibur\methods\HESI_100ul\pn_H80_S30.meth
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

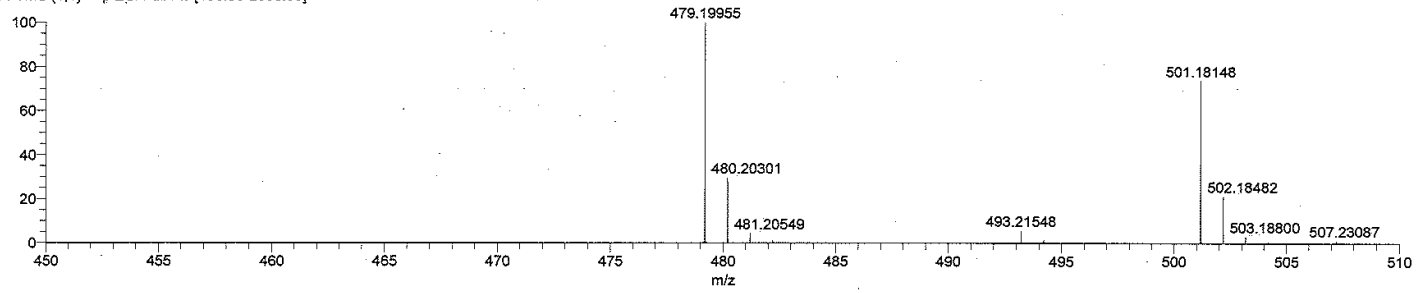
Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : submitting solution

202062_13176_b_pn #22-25 RT: 0.34-0.37 AV: 2 NL: 3.72E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



202062_13176_b_pn #25-30 RT: 0.37-0.41 AV: 3 NL: 3.56E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]



202062_13176_b_pn #30 RT: 0.43 AV: 1 NL: 3.12E7
T: FTMS {1,1} + p ESI Full ms [150.00-2000.00]