Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Expedient Cobalt(II)-Catalyzed Site-Selective C7 Arylation of Indolines with Arylboronic Acids

Table of Contents

1	General Information	S2
2	Preparation of Directing Groups **1, 1a-A, 1a-B and 1a-C**	S2-S3
3	General Procedure for Cobalt(II)-Catalyzed C7 Arylation of Indolines	S3
4	Procedure for Isotope Effect Study and Directing Group Removal	S4-S5
5	Characterization Data of the Products **3a-z, 4** and **5**	S5-S16
6	NMR (^{1}H and ^{13}C) Spectra	S17-S62
7	Mass Spectra	S63-S73

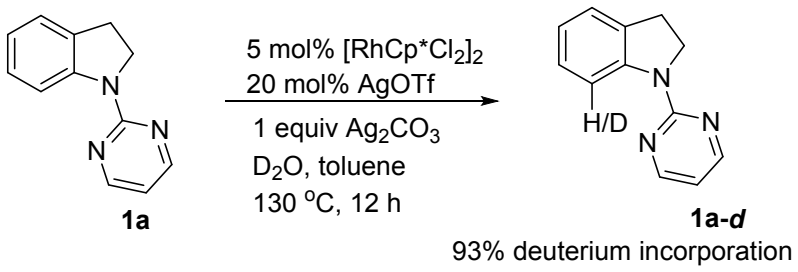
General Information. Indoles, 2-chloropyrimidine (95%), boronic acids, $Co(acac)_2$ (97%), $Co(OAc)_2$ (99.995%), PCy_3, 1,1,1,3,3,3-hexafluoro-2-propanol (99%), 2,2,2-trifluoroethanol, DDQ (98%) and 2,2,6,6-tetramethylpiperdine-1-oxyl (99%) purchased of Aldrich, $NaCNBH_3$ procured of Spectrochem, $Mn(OAc)_2{\cdot}4H_2O$ and butylated hydroxytoluene (BHT) of Merck were used as received. Tricyclohexylphosphine oxide ($O{=}PCy_3$) was synthesized according to the literature.[1] Merck silica gel G/GF 254 plates for analytical TLC and Rankem silica gel (100-200 mesh) for column chromatography were used. DRX-400 Varian spectrometer and Bruker Avance III 600 and 400 spectrometers were used for recording NMR (^1H and ^{13}C) spectra using $CDCl_3$ and as solvent and TMS as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (J) are reported in ppm and in Hz respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. FT-IR were collected on PerkinElmer IR spectrometer. Q-Tof ESI-MS instrument (model HAB 273) was used for recording mass spectra.

General Procedure for the Preparation of N-Pyrimidyl Indolines 1.[2a] To a stirred solution of indoles (1.0 equiv, 5.0 mmol) in AcOH (25 mL) at 0 ^oC was added $NaBH_3CN$ (5.0 equiv, 25.0 mmol) in portions. Then, the reaction mixture was stirred at room temperature until completion. The resultant mixture was diluted with water and basified with aq. NaOH solution, and extracted with ethyl acetate (3 x 30 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford analytically pure indolines. Next, indolines (1.0 equiv) and 2-chloropyrimidine (1.2 equiv) were dissolved in DMSO. The resultant mixture was stirred at 100 ^oC and the progress of the reaction was monitored by TLC using ethyl acetate and hexane as an eluent. The reaction mixture was then cooled to room temperature and diluted with ethyl acetate (3 x 30 mL) and washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and ethyl acetate as an eluent to afford substituted 1-(pyrimidin-2-yl)indolines **1**.

General Procedure for the Synthesis of *N*-Acetyl, *N*-Pivaloyl and *N*-Carbamoyl Indolines (1a-A-C).[2b] To a stirred solution of indoline (0.7 mmol, 1.0 equiv) and triethylamine (2.1 mmol, 3.0 equiv) in CH_2Cl_2 (5 mL) was added dropwise a solution of corresponding acid chloride or *N*-carbamoyl chloride (0.84 mmol, 1.2 equiv) in CH_2Cl_2 (3 mL) at 0 ° C. The reaction mixture was stirred at this temperature for 15 min and further stirred at room temperature for 3 h. The resulting mixture was with water (1 ML) and extracted with CH_2Cl_2 (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford analytically pure corresponding directing groups.

General Procedure for Cobalt(II)-Catalyzed C7 Arylation of Indolines. To a stirred solution of 1-(pyrimidin-2-yl)indoline (0.1 mmol), $Co(acac)_2$ (20 mol %, 0.02 mmol, 5.1 mg), $Mn(OAc)_2.4H_2O$ (0.2 mmol, 49 mg) and PCy_3 (40 mol %, 0.04 mmol, 11.2 mg) in HFIP (0.5 mL) under O_2 atmosphere, boronic acid (0.2 mmol) was added. The resultant mixture was stirred at 60 ^oC and the progress of the reaction was monitored by TLC using ethyl acetate and hexane as an eluent. The reaction mixture was then cooled to room temperature and diluted with ethyl acetate (3 x 10 mL) and then washed with brine (2 x 5 mL) and water (1 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford analytically pure substituted C7 arylated indolines.

Preparation of 1-(pyrimidin-2-yl)indoline-7-*d* (1a-*d*).[3] The titled compound was prepared according to the reported procedure as a pale yellow liquid. The deuterium incorporation was determined using 400 MHz ^1H NMR as 93%.



Scheme S1

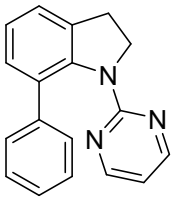
Intermolecular Kinetic Isotope Effect Study.[4a] Phenylboronic acid **2a** (0.2 mmol, 24 mg) was reacted with 1-(pyrimidin-2-yl)indoline **1a** (0.1 mmol, 19.7 mg) and 1-(pyrimidin-2-yl)indoline-7-*d* **1a-*d*** (0.1 mmol, 19.8 mg) for 3 h under standard reaction condition. The resulting solution was then diluted with ethyl acetate (3 x 10 mL) and washed with brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford **3a** and a mixture of unreacted **1a** and **1a-*d*** as a yellowish liquid. The intermolecular k_H/k_D was found to be 1.04 after 3 h at 14% conversion, based on 400 MHz ^{1}H NMR of the recovered substrates **1a** and **1a-*d***.

Independent Kinetic Isotope Effect Study.[4b] In a set of two experiments: in first set, phenylboronic acid **2a** (0.2 mmol, 24 mg) was reacted with 1-(pyrimidin-2-yl)indoline **1a** (0.1 mmol, 19.7 mg) under standard reaction conditions. Whereas in another set, 1-(pyrimidin-2-yl)indoline-7-*d* **1a-*d*** (0.1 mmol, 19.8 mg, 93% D) was used instead of **1a** in the reaction with phenyl boronic acid **2a** under the standard reaction conditions. The two reactions were allowed to stir at 60 ^oC for 5 h. For the both cases, the resulting solution was then diluted with ethyl acetate (3 x 10 mL) and washed with brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford **3a**. The yield of **3a** was obtained as 16 and 11% yields, respectively. The KIE value of 1.56 was determined by the ratio of obtained yield of **3a** (KIE = 16%/11%/93% = 1.56).

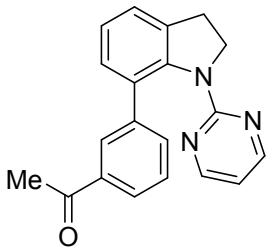
Procedure for the Late-stage Removal of Pyrimidyl Directing Group.[5] To a stirred solution of 7-phenyl-1-(pyrimidin-2-yl)indoline **3a** (0.1 mmol, 27.3 mg) in 1,4-dioxane, DDQ (0.2 mmol, 45.4 mg) was added at room temperature. The resultant solution was further stirred at 90 °C for 14 h. After completion, as indicated by TLC, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (1 x 15 mL). The mixture was successively washed with brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford 7-phenyl-1-(pyrimidin-2-yl)-1H-

indole **4** as a colorless liquid. Next, indole **4** (0.1 mmol, 27.1 mg) was dissolved in DMSO (1 mL) and NaOEt (5 equiv.) in EtOH (0.2 mL) was added to the mixture. The mixture was stirred at 100 ^{o}C for 3 h. After completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (1 x 15 mL). The mixture was then washed with 2 N HCl (1 x 5 mL), brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford 7-phenyl-1H-indole **5** as a brown liquid.

Characterization Data

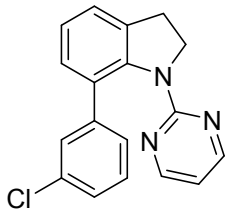


7-Phenyl-1-(pyrimidin-2-yl)indoline 3a. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; yellowish liquid; yield 61% (16.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.28-7.23 (m, 2H), 7.17-7.07 (m, 4H), 6.37 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 156.6, 142.4, 141.2, 135.1, 130.5, 129.1, 128.0, 126.8, 126.2, 123.9, 123.8, 111.9, 52.3, 29.7.; FT-IR (neat) 2917, 2851, 1696, 1577, 1550, 1458, 1443, 1439, 1105 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}N_3$: 274.1339, found: 274.1349.

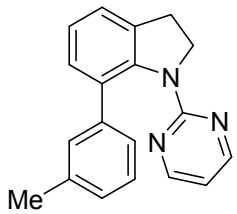


1-(3-(1-(Pyrimidin-2-yl)indolin-7-yl)phenyl)ethan-1-one 3c. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.39; colorless sticky oil; yield 60% (18.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 4.8 Hz, 3H), 7.73-7.70 (m, 1H), 7.56-7.53 (m, 1H), 7.30 – 7.23 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.37

(t, J = 4.8 Hz, 1H), 4.48 (t, J = 8.0 Hz, 2H), 3.20 (t, J = 8.0 Hz, 2H), 2.49 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 159.2, 156.7, 142.9, 141.2, 137.1, 135.4, 131.5, 129.3, 129.0, 128.4, 127.2, 125.9, 124.3, 124.1, 112.2, 52.4, 29.6, 26.8.; FT-IR (neat) 2958, 2924, 2853, 1682, 1575, 1550, 1455, 1433, 1110 cm^{-1}; HRMS (ESI) m/z [M+H]+ calcd for $C_{20}H_{18}N_3O$: 316.1444, found: 316.1443.

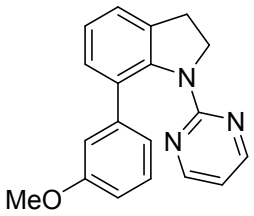


7-(3-Chlorophenyl)-1-(pyrimidin-2-yl)indoline 3d. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; yellow liquid; yield 58% (17.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 4.8 Hz, 2H), 7.366-7.361 (m, 1H), 7.26-7.22 (m, 2H), 7.21–7.18 (m, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.43 (t, J = 4.8 Hz, 1H), 4.45 (t, J = 8.0 Hz, 2H), 3.18 (t, J = 8.0 Hz, 2H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 156.8, 144.3, 141.2, 135.3, 134.0, 129.2, 129.1, 128.9, 127.0, 126.2, 125.1, 124.3, 124.0, 112.2, 52.3, 29.6.; FT-IR (neat) 2960, 2923, 2852, 1637, 1576, 1550, 1455, 1432 ,1110 cm^{-1}; HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{18}H_{15}ClN_3$: 308.0949, found: 308.0946.

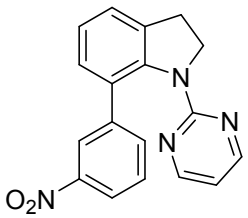


1-(Pyrimidin-2-yl)-7-(*m*-tolyl)indoline 3e. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.42; yellowish gummy liquid; yield 54% (15.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 4.8 Hz, 2H), 7.28-7.26 (m, 1H), 7.23-7.21 (m, 1H), 7.15-7.07 (m, 3H), 7.03 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.38 (t, J = 4.8 Hz, 1H), 4.44 (t, J = 8.0 Hz, 2H), 3.18 (t, J = 8.0 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (150 MHz) δ 159.3, 156.6, 142.2, 141.2, 137.6, 135.0, 130.3, 129.1, 127.9, 127.5, 126.9, 124.0, 123.8,

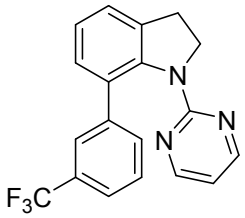
123.7, 111.9, 52.4, 29.7, 21.4; FT-IR (neat) 2958, 2924, 2953, 1637, 1597, 1576, 1550, 1441, 1261, 1222, 1198, 1108 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3$: 288.1495, found: 288.1496.



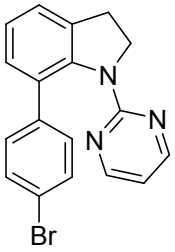
7-(3-Methoxyphenyl)-1-(pyrimidin-2-yl)indoline 3f. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; brown sticky liquid; yield 60% (18.1 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 4.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.918-6.915 (m, 1H), 6.66-6.64 (m, 1H), 6.40 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.68 (s, 3H), 3.18 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 159.4, 157.3, 156.7, 143.7, 141.1, 135.1, 130.1, 129.0, 123.95, 123.90, 119.5, 112.6, 112.0, 111.7, 55.4, 52.4, 29.7; FT-IR (neat) 2960, 2923, 2851, 1602, 1575, 1550, 1457, 1435, 1380, 1224, 1176, 1042 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3O$: 304.1444, found: 304.1455.



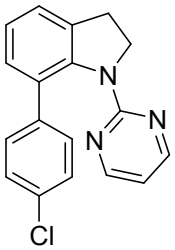
7-(3-Nitrophenyl)-1-(pyrimidin-2-yl)indoline 3g. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.41; brown liquid; yield 65% (20.6 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (t, *J*= 1.6 Hz, 1H), 7.98-7.95 (m, 3H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.41 (t, *J* = 4.8 Hz, 1H), 4.49 (t, *J* = 8.0 Hz, 2H), 3.20 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 156.9, 148.3, 144.4, 141.3, 135.6, 133.0, 128.86, 128.84, 128.3, 124.9, 124.3, 121.8, 121.0, 112.4, 52.3, 29.5.; FT-IR (neat) 2958, 2923, 2852, 1575, 1551, 1527, 1455, 1434, 1350, 1261, 1003 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}N_4O_2$: 319.1189, found: 319.1187.



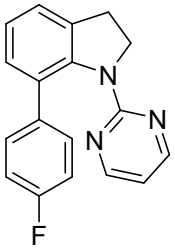
1-(Pyrimidin-2-yl)-7-(3-(trifluoromethyl)phenyl)indoline 3h. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; yellow liquid; yield 65% (22.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.60 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.39 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 7.6 Hz, 2H), 3.19 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 156.7, 143.3, 141.3, 135.4, 130.9 (q, $J_{C\text{-}F}$ = 31.65 Hz), 130.126, 130.120, 128.94, 128.91, 128.4, 124.5, 124.07, 124.00 (q, $J_{C\text{-}F}$ = 3.6 Hz), 122.83 (q, $J_{C\text{-}F}$ = 3.75 Hz), 112.27, 52.3, 29.6; FT-IR (neat) 2956, 2923, 2852, 1638, 1575, 1552, 1456, 1440, 1339, 1260, 1163, 1122, 1071 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{15}F_3N_3$: 342.1212, found: 342.1219.



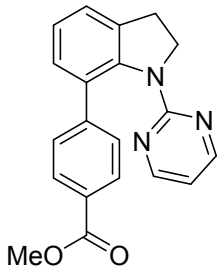
7-(4-Bromophenyl)-1-(pyrimidin-2-yl)indoline 3i. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; colorless gummy liquid; yield 60% (21 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 4.8 Hz, 2H), 7.31-7.29 (m, 2H), 7.28-7.24 (m, 4H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.47 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 7.8 Hz, 2H), 3.20 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 156.8, 141.4, 141.1, 135.3, 131.1, 129.3, 128.8, 128.5, 124.1, 124.0, 120.0, 112.3, 52.3, 29.6; FT-IR (KBr) 2957, 2924, 2852, 1574, 1548, 1451, 1427, 1261, 1065 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}BrN_3$: 352.0443, found: 352.0441.



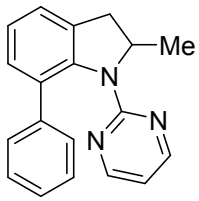
7-(4-Chlorophenyl)-1-(pyrimidin-2-yl)indoline 3j. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.45; yellowish sticky liquid; yield 67% (20.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 4.8 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.14-7.08 (m, 3H), 6.44 (t, *J* = 4.4 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 156.8, 141.2, 141.0, 135.3, 132.0, 129.4, 128.9, 128.2, 128.1, 124.1, 124.0, 112.3, 52.4, 29.7; FT-IR (neat) 2954, 2922, 2852, 1638, 1576, 1551, 1453, 1429, 1112, 1068 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}ClN_3$: 308.0949, found: 308.0954.



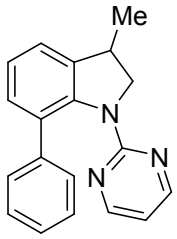
7-(4-Fluorophenyl)-1-(pyrimidin-2-yl)indoline 3k. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.41; colorless sticky liquid; yield 62% (18 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 4.8 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.24-7.22 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.86–6.83 (m, 2H), 6.42 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.17 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2(J_{C-F} = 243.3), 159.1, 156.6, 141.0, 138.3(J_{C-F} = 3.3), 135.1, 129.4, 128.7, 128.2 (J_{C-F} = 7.8), 123.8, 123.7, 114.7(J_{C-F} = 21.3), 112.0, 52.2, 29.5; FT-IR (KBr) 2955, 2924, 2853, 1636, 1575, 1549, 1508, 1455, 1426, 1377, 1283, 1153, 1093 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}FN_3$: 292.1244, found: 292.1251.



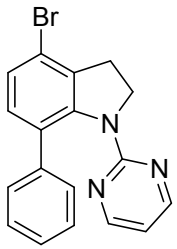
Methyl 4-(1-(pyrimidin-2-yl)indolin-7-yl)benzoate 3l. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; sticky liquid; yield 57% (18.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 4.8 Hz, 2H), 7.85-7.82 (m, 2H), 7.44-7.41(m, 2H), 7.28-7.26(m, 2H), 7.14 – 7.10 (m, 1H), 6.38 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 3.19 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 159.3, 156.8, 147.4, 141.2, 135.3, 129.5, 129.4, 128.9, 127.7, 126.7, 124.5, 124.0, 112.4, 52.2, 52.1, 29.6; FT-IR (neat) 2952, 2924, 2853, 1721, 1609, 1575, 1551, 1454, 1434, 1275, 1103 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{18}N_3O_2$: 332.1393, found: 332.1397.



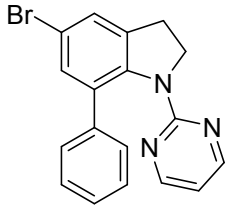
2-Methyl-7-phenyl-1-(pyrimidin-2-yl)indoline 3r. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.42; Purification (hexane/ethyl acetate 88/12); yellow liquid; yield 62% (17.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 4.8 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24-7.22 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.36 (t, *J* = 4.8 Hz, 1H), 4.94 – 4.89 (m, 1H), 3.52 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.65 (d, *J* = 15.6 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 156.7, 142.5, 139.7, 133.9, 130.9, 129.0, 128.1, 126.7, 126.1, 124.3, 124.0, 111.9, 59.7, 37.0, 21.3; FT-IR (neat) 3054, 3031, 2972, 2923, 2851, 1638, 1598, 1577, 1549, 1461, 1436, 1384, 1209 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3$: 288.1495, found: 288.1512.



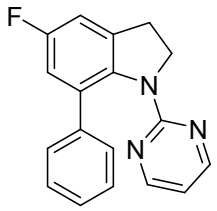
3-Methyl-7-phenyl-1-(pyrimidin-2-yl)indoline 3s. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; yellow liquid; yield 64% (18.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.16-7.13 (m, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.37 (t, *J* = 4.8 Hz, 1H), 4.61 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.99 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.52 – 3.46 (m, 1H), 1.37 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 156.7, 142.3, 140.8, 140.3, 130.4, 129.2, 128.0, 126.9, 126.2, 124.1, 122.6, 111.9, 60.2, 36.4, 19.2; FT-IR (neat) 2958, 2924, 2854, 1597, 1576, 1550, 1459, 1441, 1380, 1261, 1222, 1108 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3$: 288.1495, found: 288.1509.



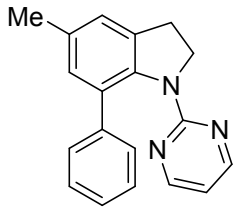
4-Bromo-7-phenyl-1-(pyrimidin-2-yl)indoline 3t. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; colorless sticky liquid; yield 56% (19.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.29 – 7.28 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 3H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.41 (t, *J* = 4.8 Hz, 1H), 4.46 (t, *J* = 7.8 Hz, 2H), 3.19 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 156.7, 142.2, 141.5, 135.5, 130.8, 129.3, 128.2, 126.7, 126.6, 126.5, 118.4, 112.5, 51.6, 31.1; FT-IR (neat) 2954, 2923, 2852, 1638, 1576, 1552, 1467, 1434, 1407, 1286, 1078 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}BrN_3$: 352.0443, found: 352.0441.



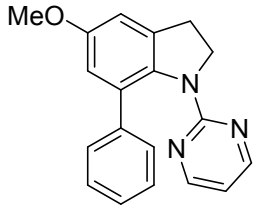
5-Bromo-7-phenyl-1-(pyrimidin-2-yl)indoline 3u. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.41; colorless solid; mp 122-123 °C; yield 52% (18.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.407-7.404 (m, 1H), 7.344 – 7.340 (m, 1H), 7.30-7.28 (m, 2H), 7.16 – 7.13 (m, 2H), 7.11 – 7.08 (m, 1H), 6.40 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 8.4 Hz, 2H), 3.17 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 156.7, 141.1, 140.5, 137.4, 132.0, 131.7, 128.2, 126.77, 126.71, 126.6, 116.2, 112.3, 52.4, 29.5; FT-IR (KBr) 2924, 2852, 1644, 1637, 1576, 1459, 1439, 1112 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}BrN_3$: 352.0443, found: 352.0459.



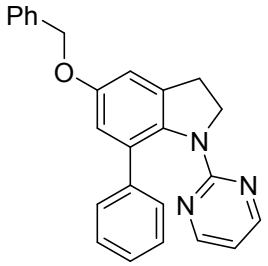
5-Fluoro-7-phenyl-1-(pyrimidin-2-yl)indoline 3v. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.42; yellow liquid; yield 58% (16.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.2 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.00-6.98 (m, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.38 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 7.8 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7($J_{C\text{-}F}$ = 240), 159.4, 156.7, 141.3, 137.3($J_{C\text{-}F}$ = 1.95), 137.2($J_{C\text{-}F}$ = 8.85), 131.7($J_{C\text{-}F}$ = 7.95), 128.2, 126.78, 126.70, 115.2 ($J_{C\text{-}F}$ = 23.55), 112.0, 111.1($J_{C\text{-}F}$ = 23.7), 52.6, 30.03($J_{C\text{-}F}$ = 1.95); FT-IR (neat) 2962, 2924, 2853, 1636, 1578, 1551, 1462, 1443, 1433, 1149 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}FN_3$: 292.1244, found: 292.1254.



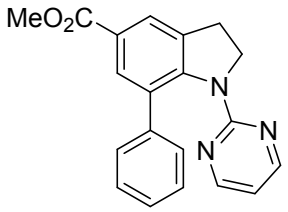
5-Methyl-7-phenyl-1-(pyrimidin-2-yl)indoline 3w. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.42; yellow liquid; yield 61% (17.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.06 (m, 3H), 6.34 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 7.8 Hz, 2H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 156.7, 142.4, 138.9, 135.3, 133.6, 130.3, 129.5, 128.0, 126.8, 126.1, 124.6, 111.7, 52.4, 29.8, 21.2; FT-IR (neat) 2952, 2922, 2852, 1577, 1549, 1465, 1441, 1222, 1104 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3$: 288.1501, found: 288.1507.



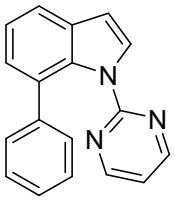
5-Methoxy-7-phenyl-1-(pyrimidin-2-yl)indoline 3x. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.39; colorless stick liquid; yield 64% (19.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.84-6.83 (m, 2H), 6.34 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.83 (s, 3H), 3.13 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 156.7, 156.5, 142.0, 136.6, 134.6, 131.2, 127.9, 126.6, 126.2, 113.39, 111.38, 110.2, 55.8, 52.3, 30.0; FT-IR (neat) 2961, 2921, 2850, 1637, 1578, 1548, 1463, 1443, 1261, 1160, 1104 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}N_3O$: 304.1444, found: 304.1455.



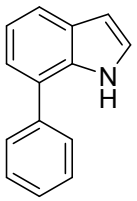
5-(Benzyloxy)-7-phenyl-1-(pyrimidin-2-yl)indoline 3y. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; yellowish sticky liquid; yield 57% (21.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.37–7.31 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.93-6.90 (m, 2H), 6.34 (t, *J* = 4.2 Hz, 1H), 5.08 (s, 2H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.13 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 156.7, 156.1, 142.2, 137.4, 136.8, 135.0, 131.4, 128.7, 128.1, 127.6, 126.8, 126.4, 114.8, 111.6, 111.2, 70.8, 52.5, 30.2; FT-IR (neat) 2956, 2921, 2849, 1635, 1578, 1462, 1443, 1431, 1166, 1110 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}N_3O$: 380.1757, found: 380.1769.



Methyl 7-phenyl-1-(pyrimidin-2-yl)indoline-5-carboxylate 3z. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.3; yellowish sticky liquid; yield 51% (16.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 3H), 7.89 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.16-7.09 (m, 3H), 6.45 (t, *J* = 4.4 Hz, 1H), 4.47 (t, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.23 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 158.8, 156.7, 145.5, 141.6, 135.2, 132.0, 129.3, 128.1, 126.8, 126.5, 125.1, 125.0, 112.9, 52.6, 52.1, 29.0; FT-IR (neat) 2958, 2922, 2854, 1652, 1638, 1464, 1386, 1179, 1113, 990 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{18}N_3O_2$: 332.1393, found: 332.1398.



7-Phenyl-1-(pyrimidin-2-yl)-1H-indole 4.[5] Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; Colourless liquid; yield 90% (24.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.2 Hz, 2H), 7.79 (d, *J* = 3.6 Hz, 1H), 7.66-7.65 (m, 1H), 7.33–7.29 (m, 2H), 7.22-7.20 (m, 2H), 7.10-7.09 (m, 3H), 6.80-6.78 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 157.1, 142.3, 132.9, 132.2, 129.4, 128.7, 127.9, 127.7, 126.1, 125.8, 122.3, 120.4, 116.9, 106.6; FT-IR (neat) 2958, 2921, 1639, 1652, 1435, 1386, 1183, 1114 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}N_3$: 272.1182, found: 272.1180.



7-Phenyl-1H-indole 5.[6] Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.53; brown liquid; yield 84% (16.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (br s, 1H), 7.66 (d, *J* = 7.2 Hz, 3H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.22-7.19 (m, 3H), 6.63 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 133.9, 129.3, 128.47, 128.45, 127.6, 125.8, 124.5, 122.1, 120.5, 120.2, 103.2; FT-IR (neat) 2952, 2924, 2853, 1637, 1476, 1461, 1420, 1338, 1113, 1027 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{12}N$: 194.0964, found: 194.0956.

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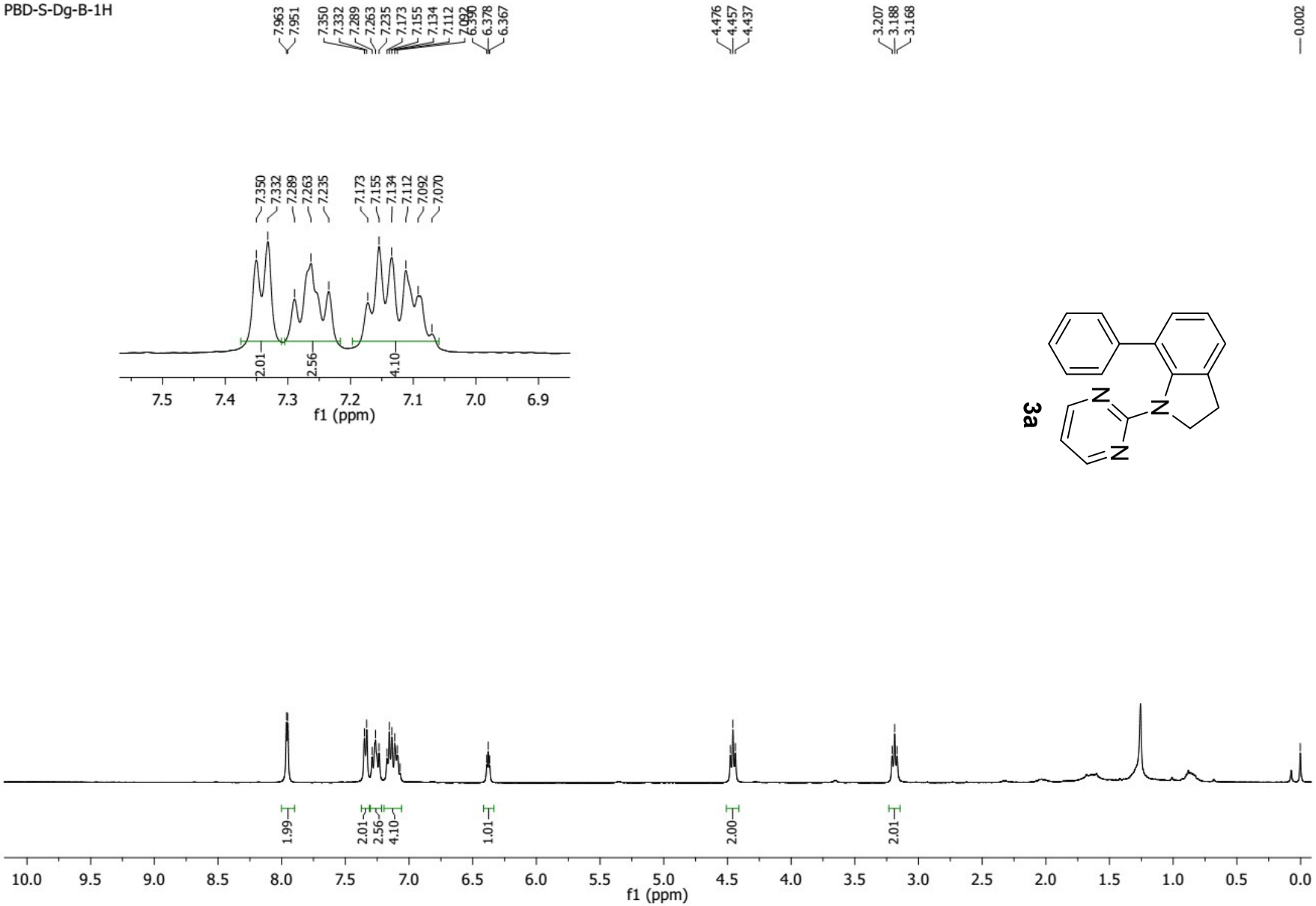
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6.378
6.367
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4.437
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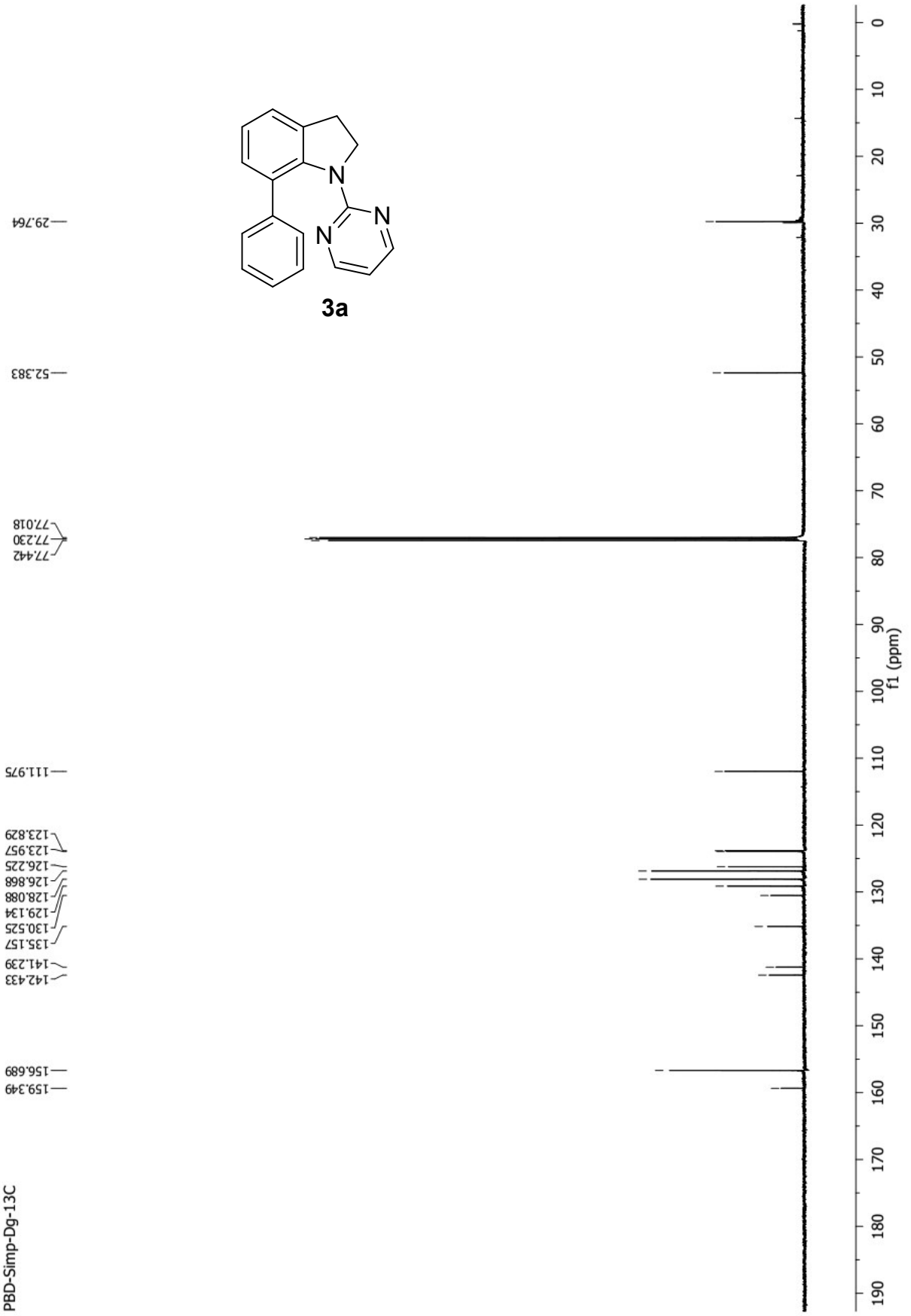
2.00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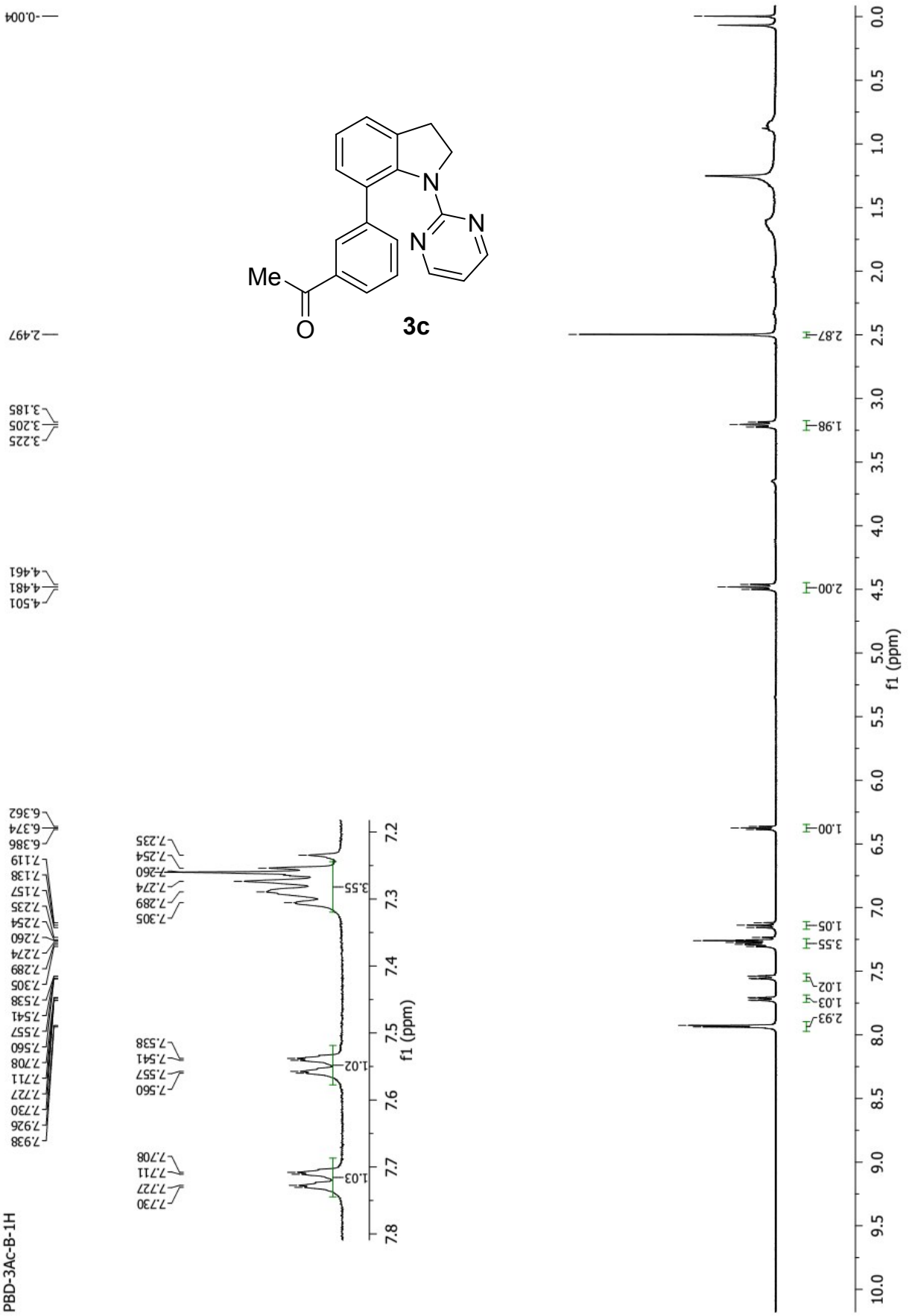
Me
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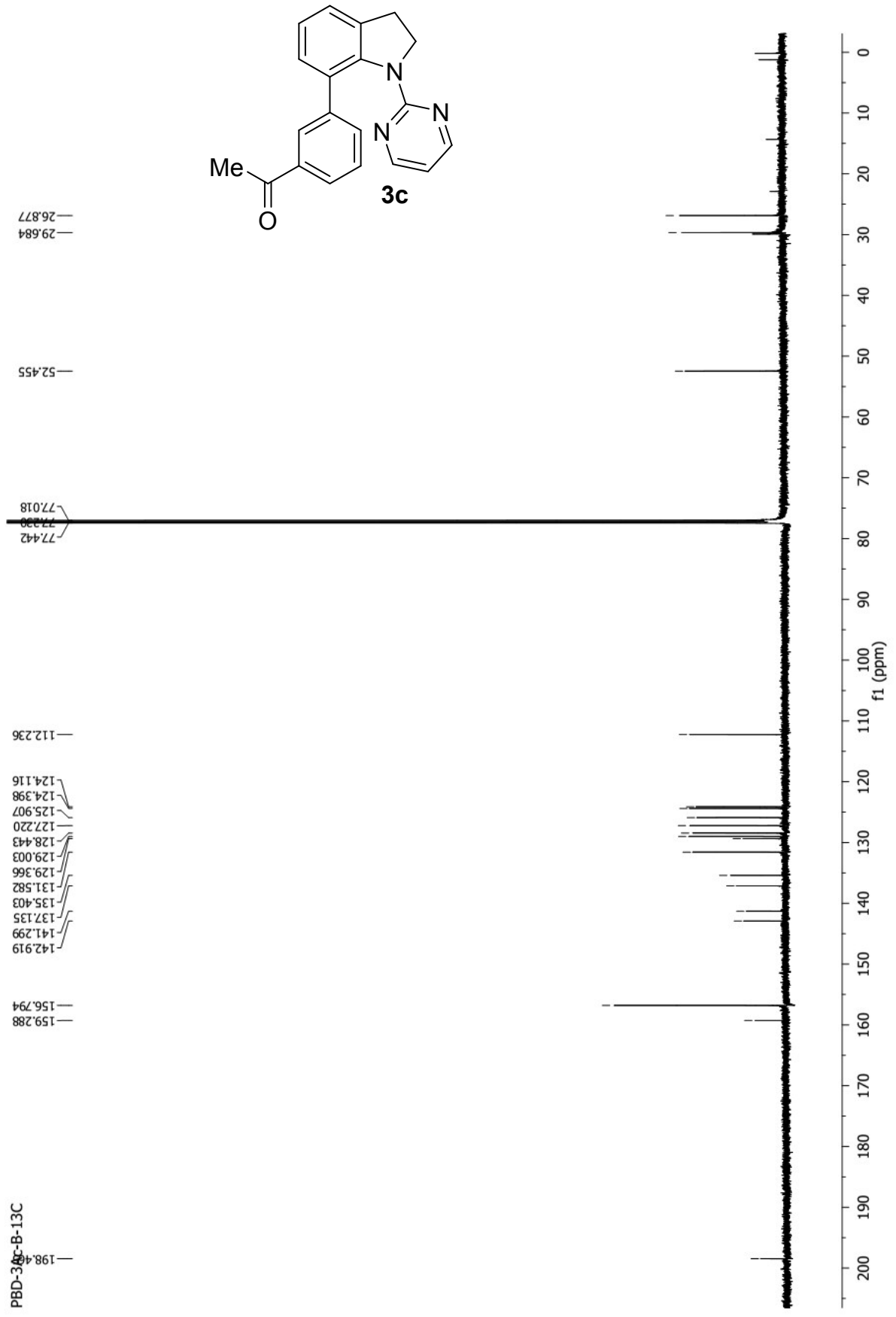
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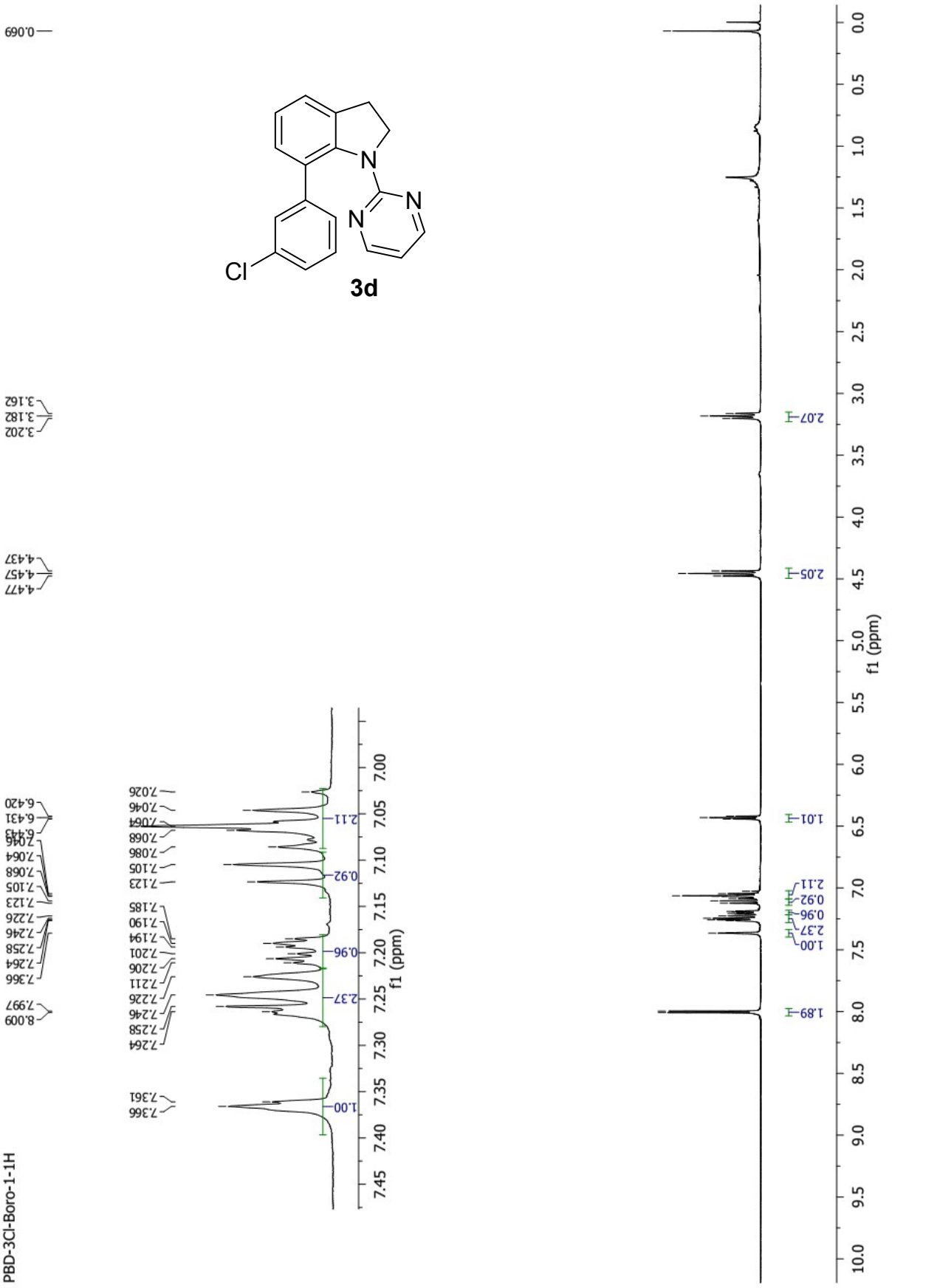
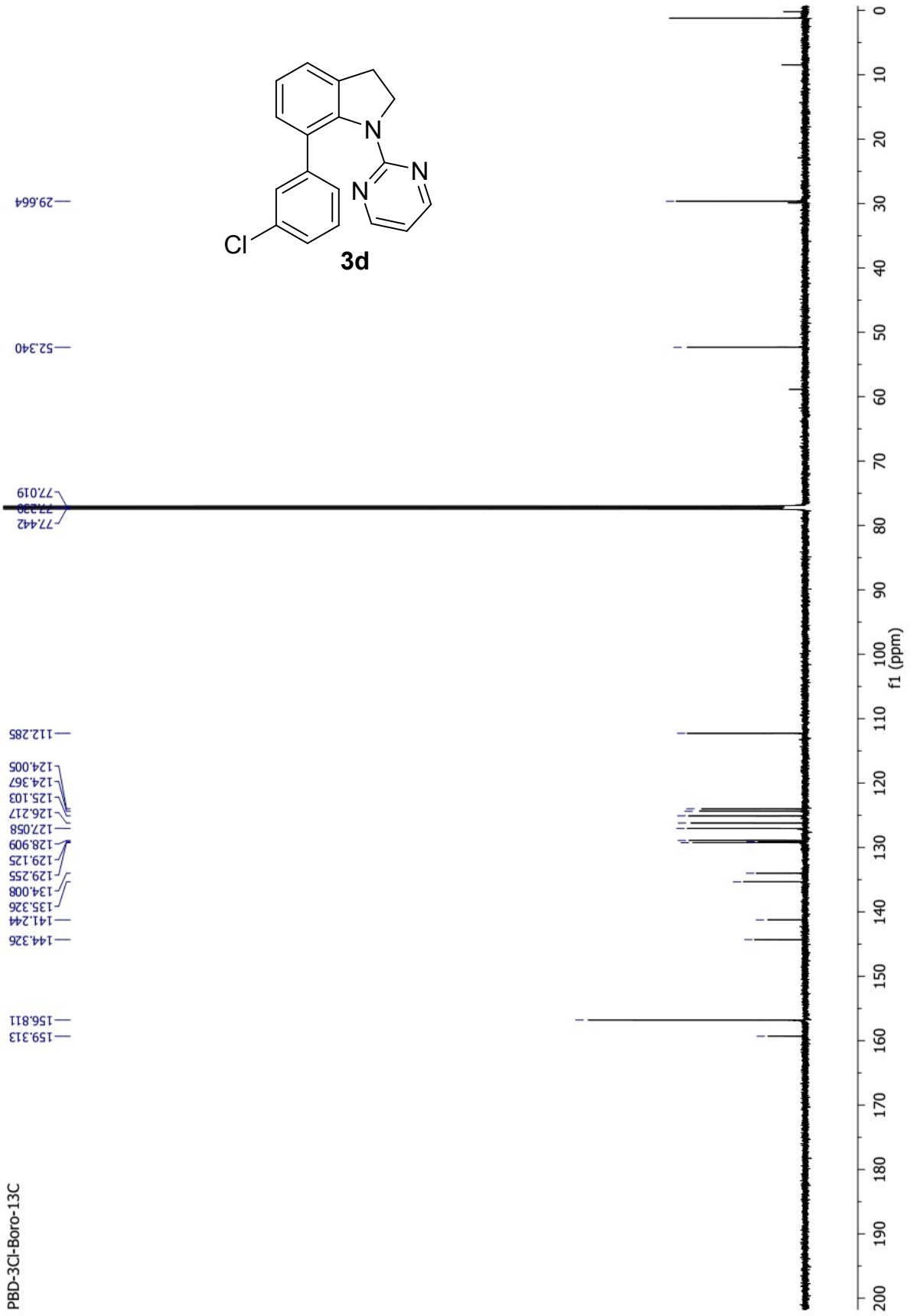
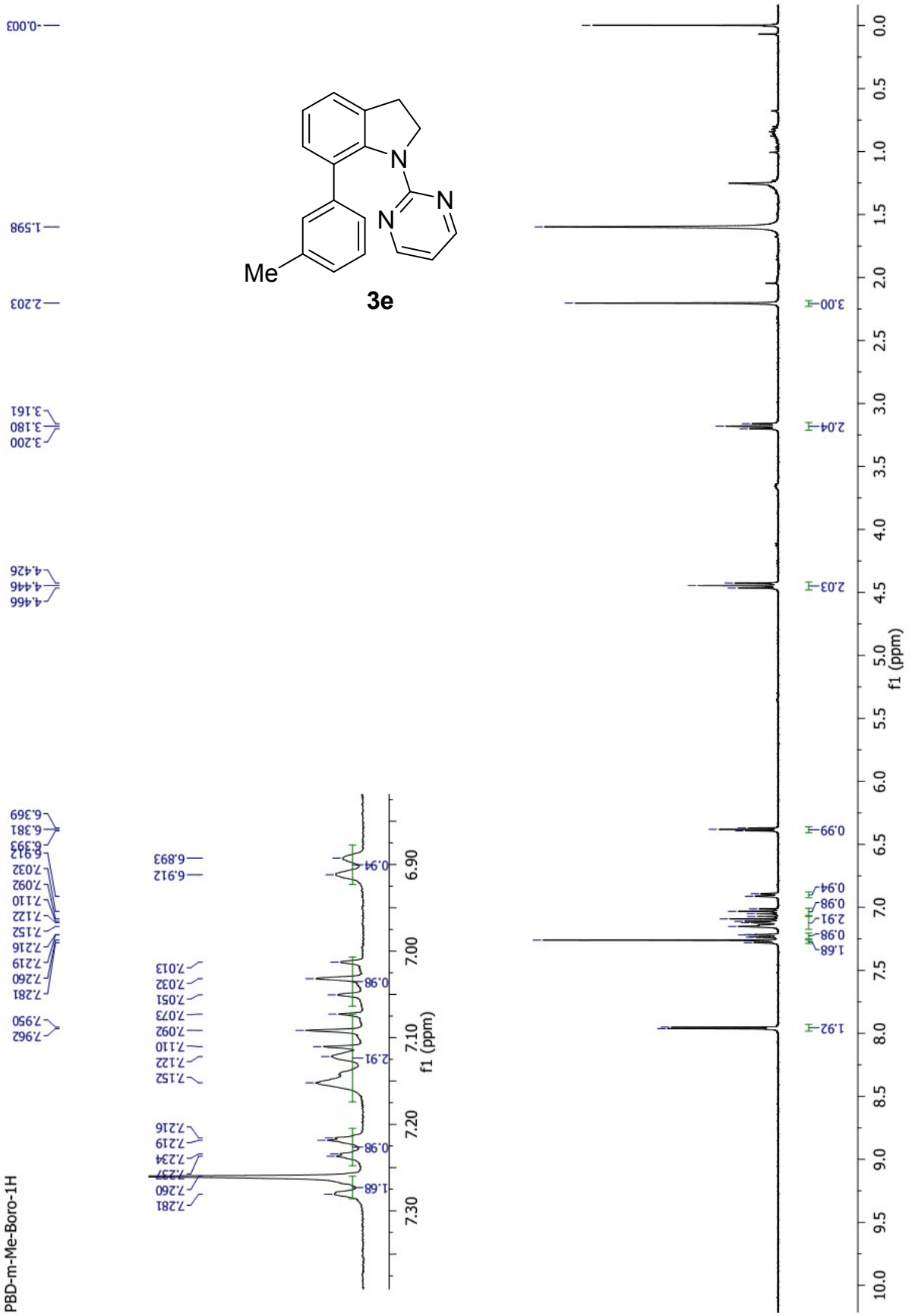
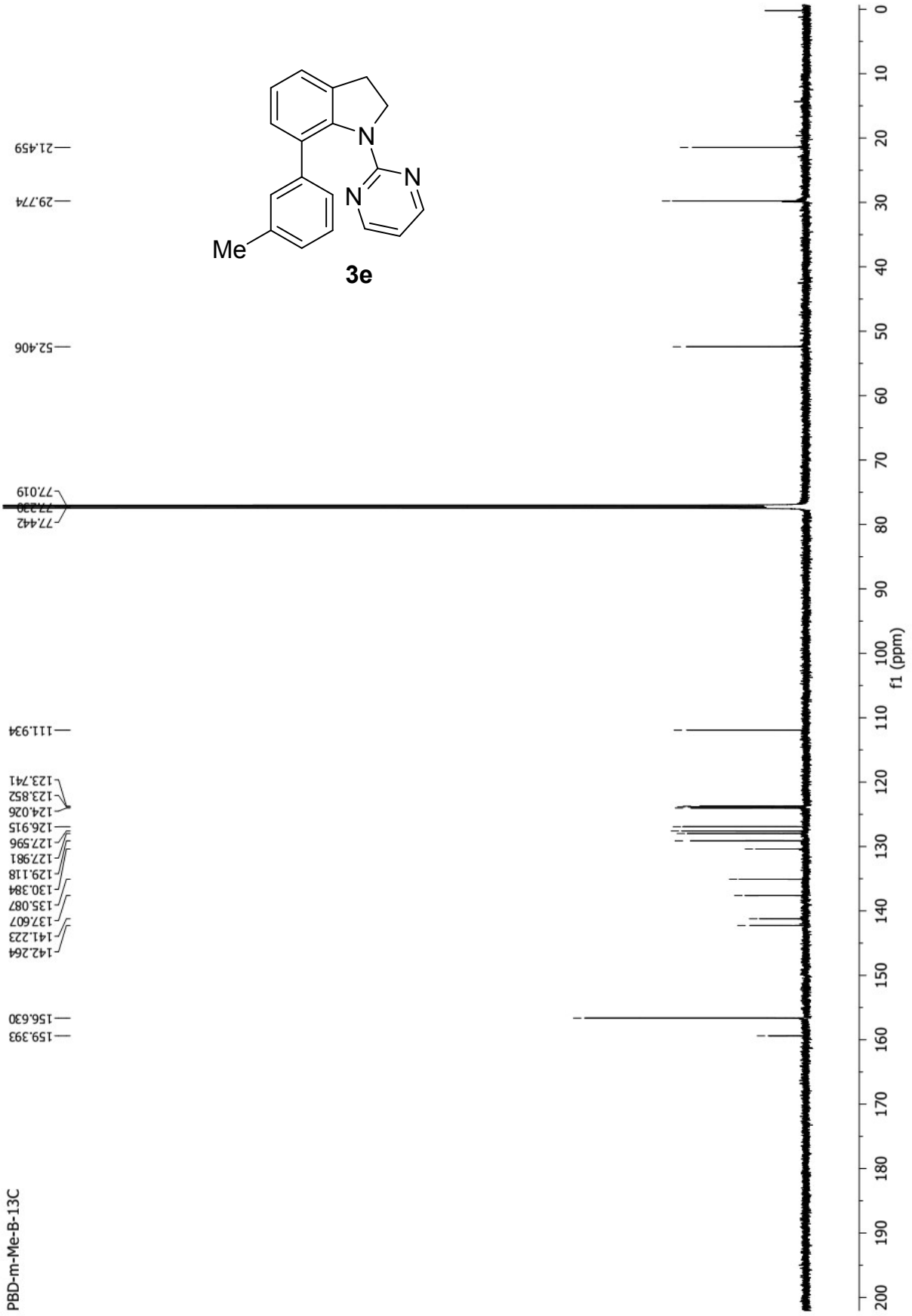
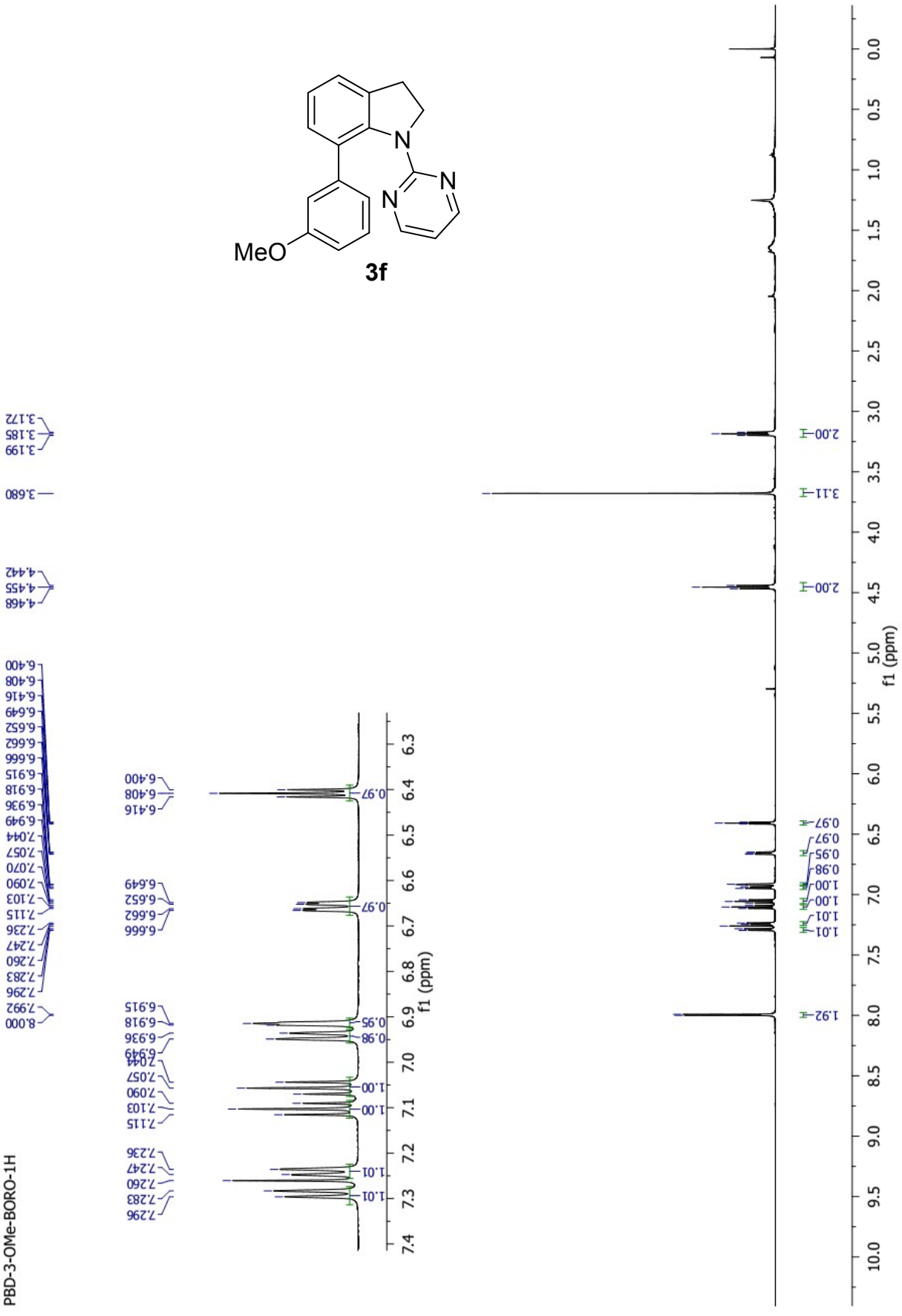
PBD-3
f1 (ppm)

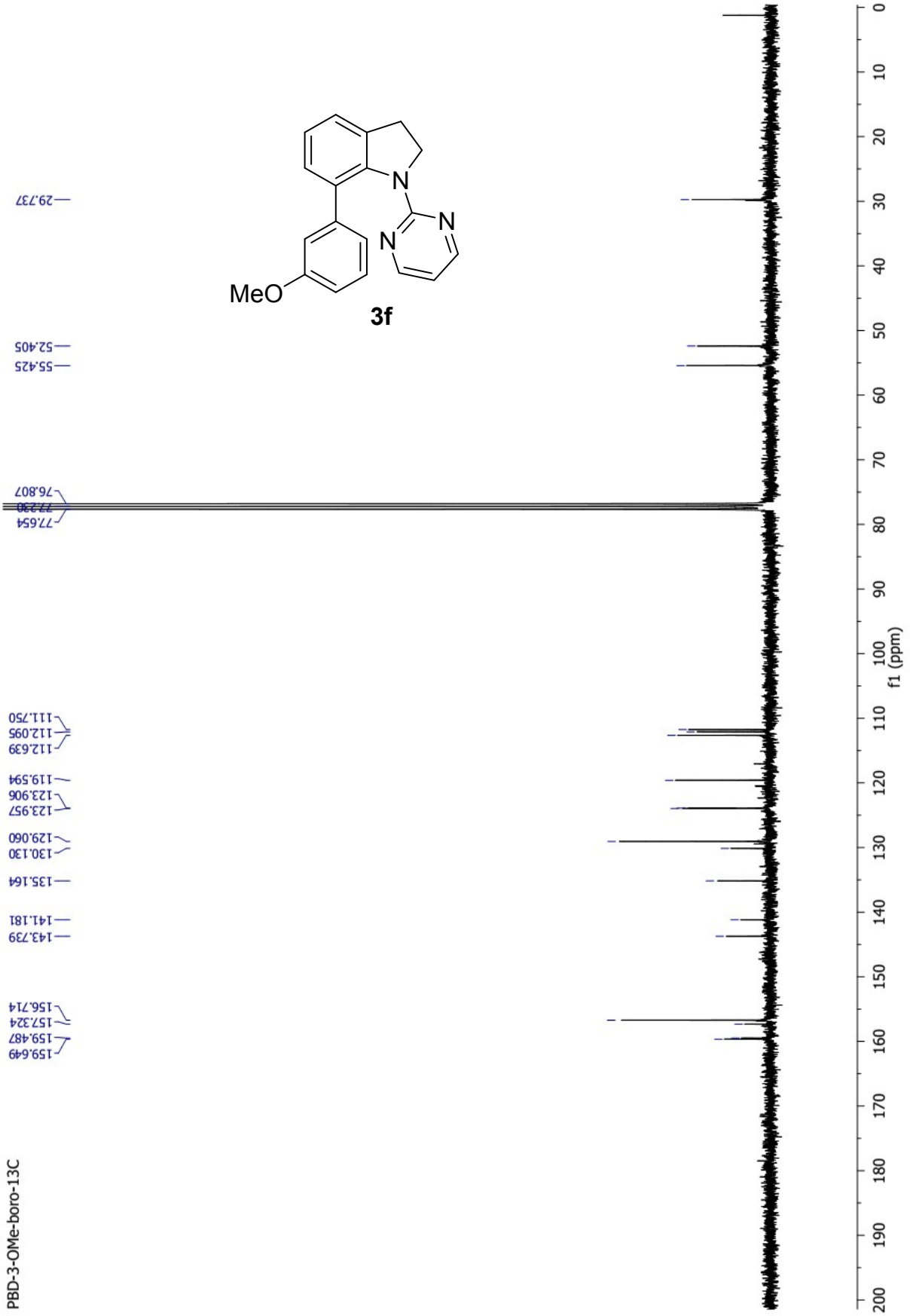

PBD-3Cl-Boro-1-1H
f1 (ppm)
3d
Cl
N
N
N

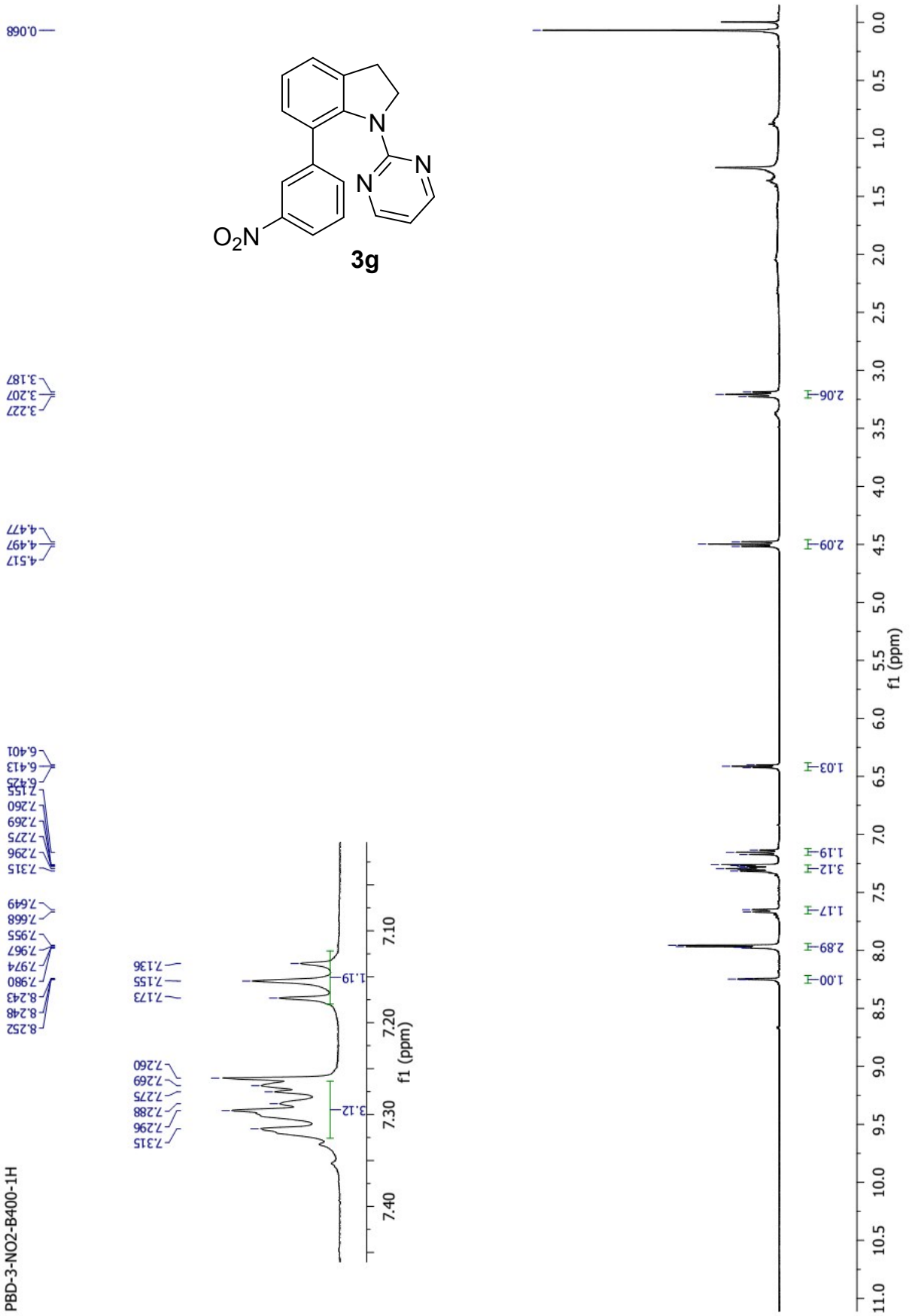

Cl
N
N
N
3d
29.664
52.340
77.019
77.330
77.442
112.285
124.005
124.367
125.103
126.217
127.058
128.909
129.125
129.255
134.008
135.326
141.244
144.326
156.811
159.313
PBD-3Cl-Boro-13C
f1 (ppm)

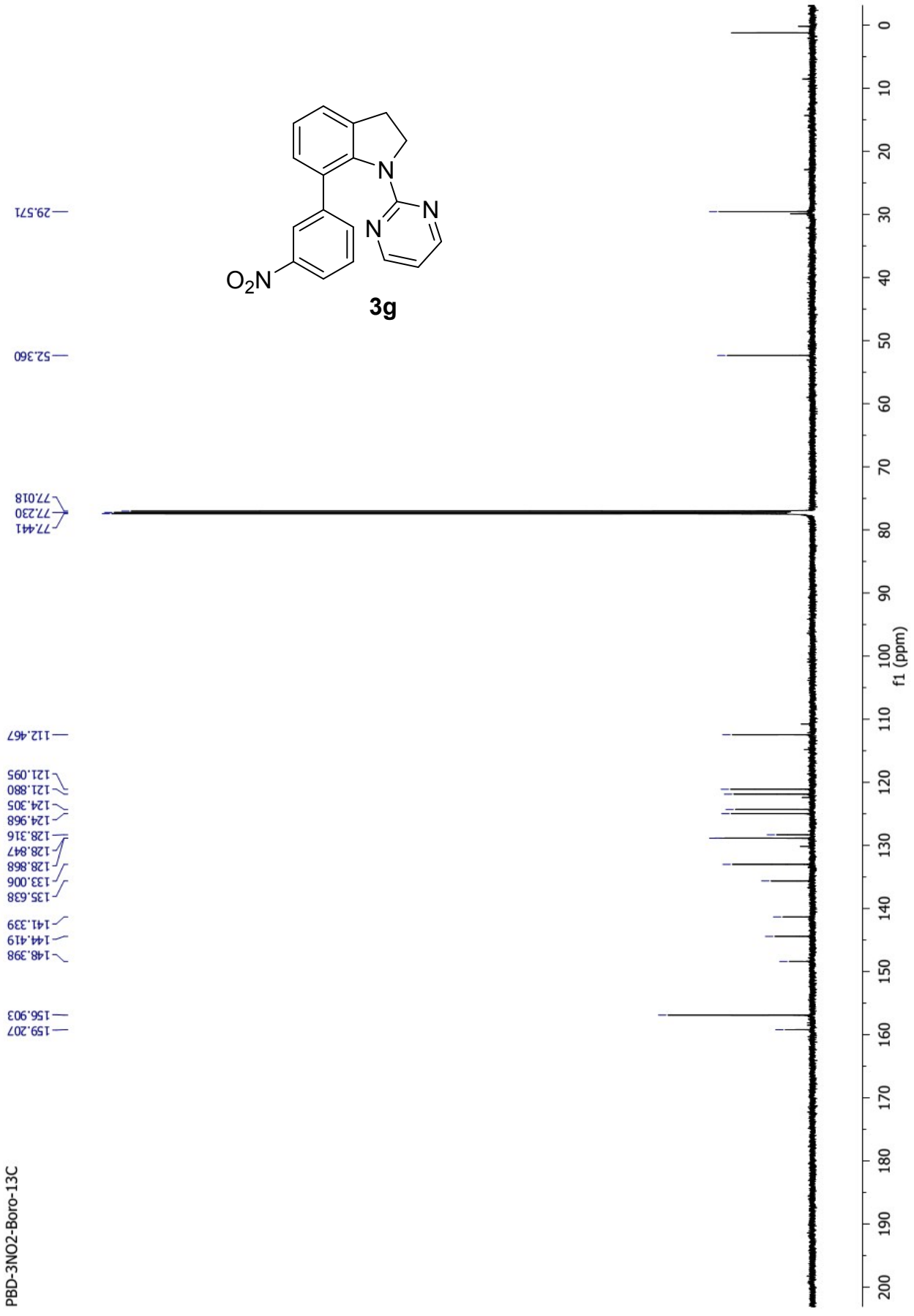

Me
N
N
N
3e
PBD-m-Me-Boro-1H
f1 (ppm)


N
N
N
Me
3e
21.459
29.774
52.406
77.019
77.330
77.442
111.934
123.741
123.852
124.026
126.915
127.596
127.981
129.118
130.384
135.087
137.607
141.223
142.264
156.630
159.393
PBD-m-Me-B-13C
f1 (ppm)

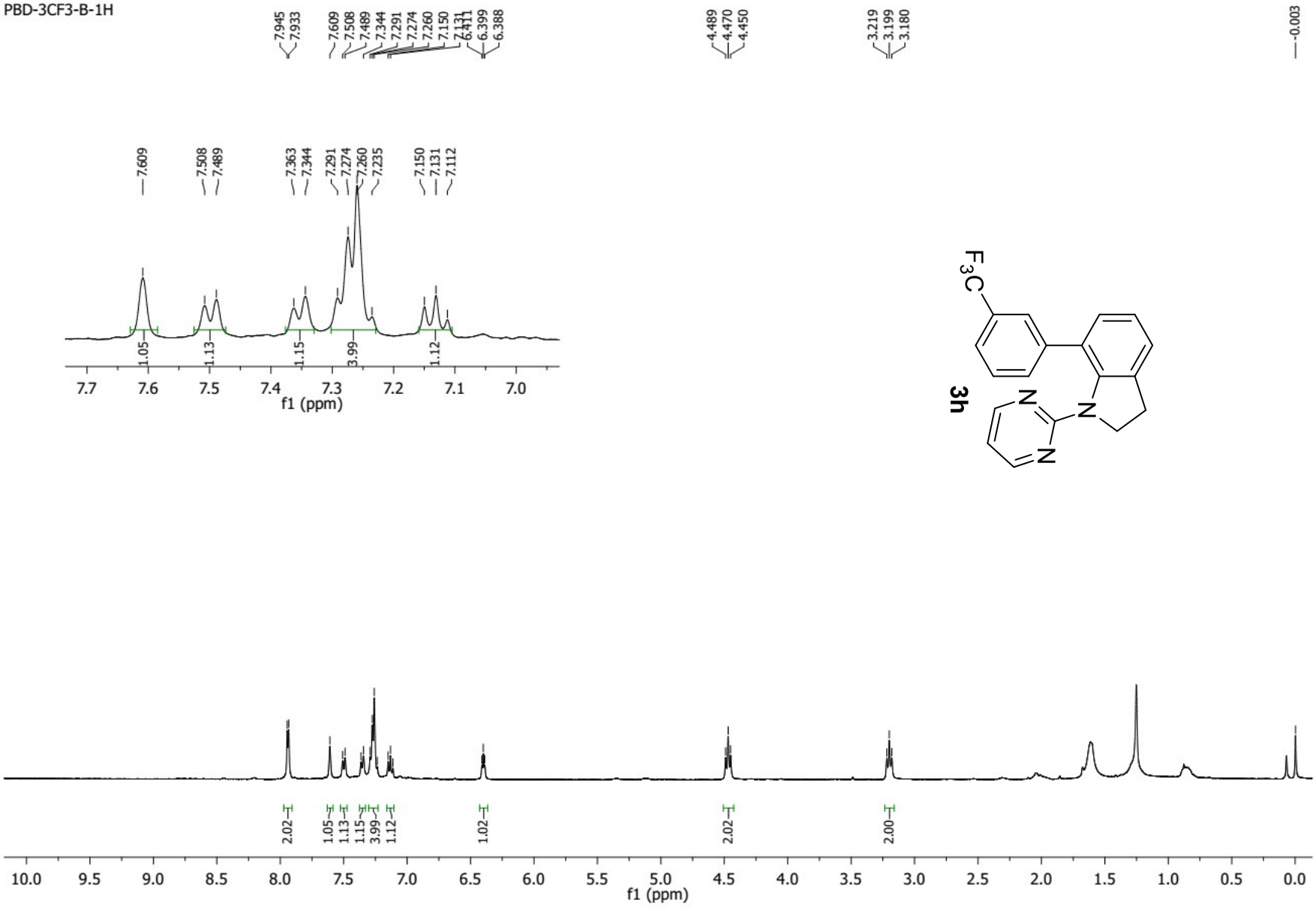

MeO
N
N
N
3f
PBD-3-OMe-BORO-1H
f1 (ppm)

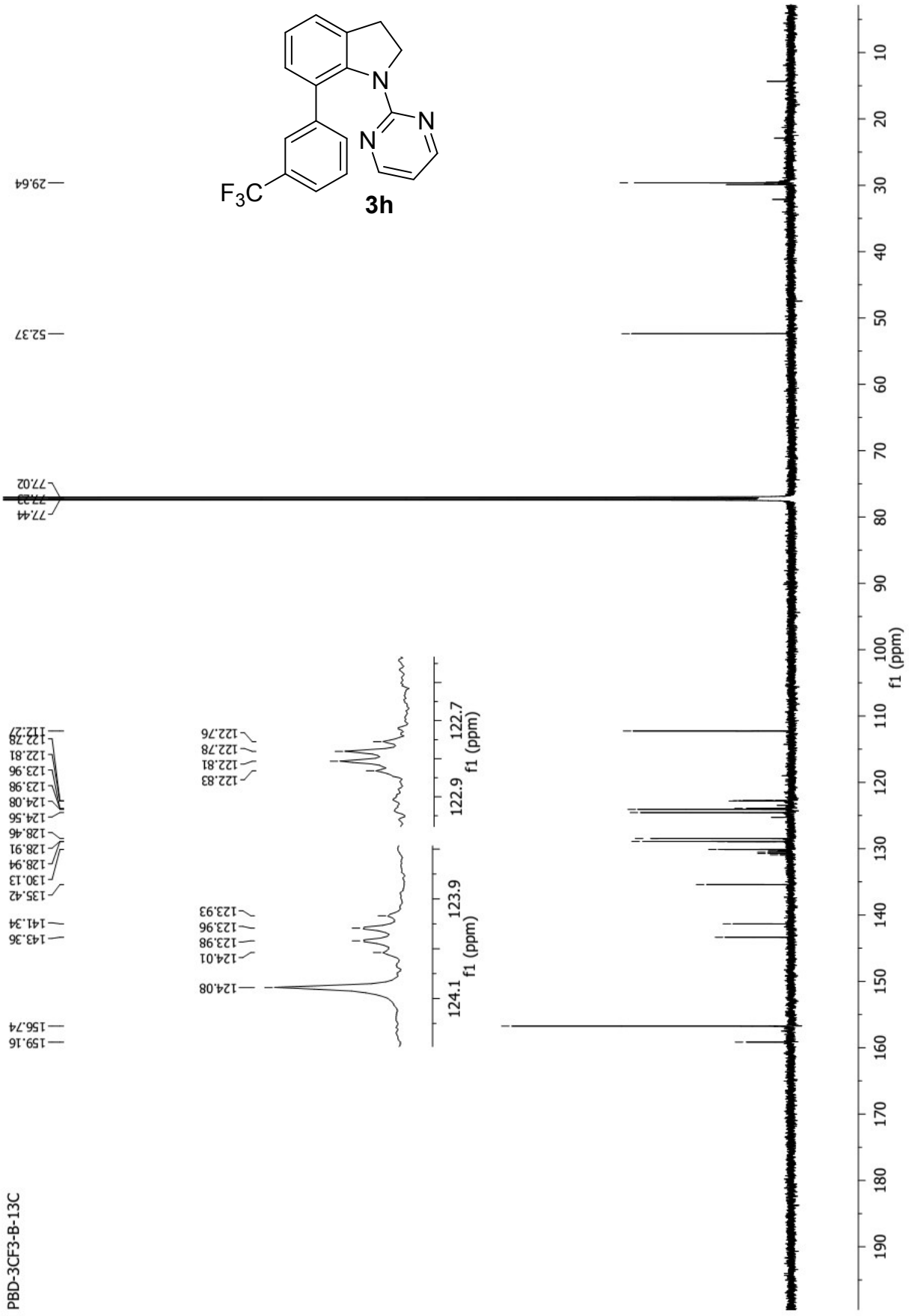

MeO
3f
29.737
52.405
55.425
76.807
77.654
111.750
112.095
112.639
119.594
123.906
123.957
129.060
130.130
135.164
141.181
143.739
156.714
157.324
159.487
159.649
PBD-3-OMe-boro-13C
f1 (ppm)

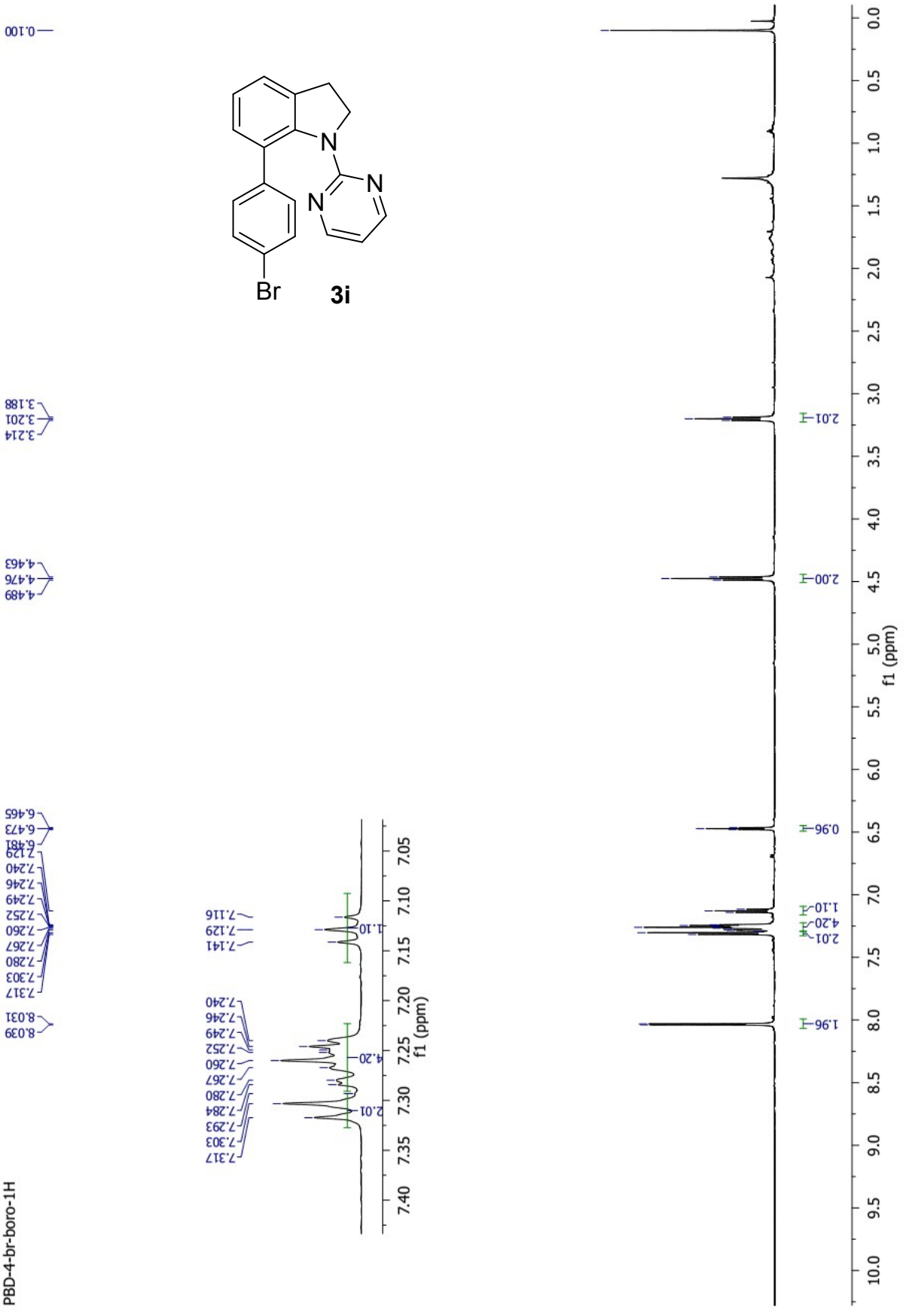

PBD-3-NO2-B400-1H
f1 (ppm)
3g

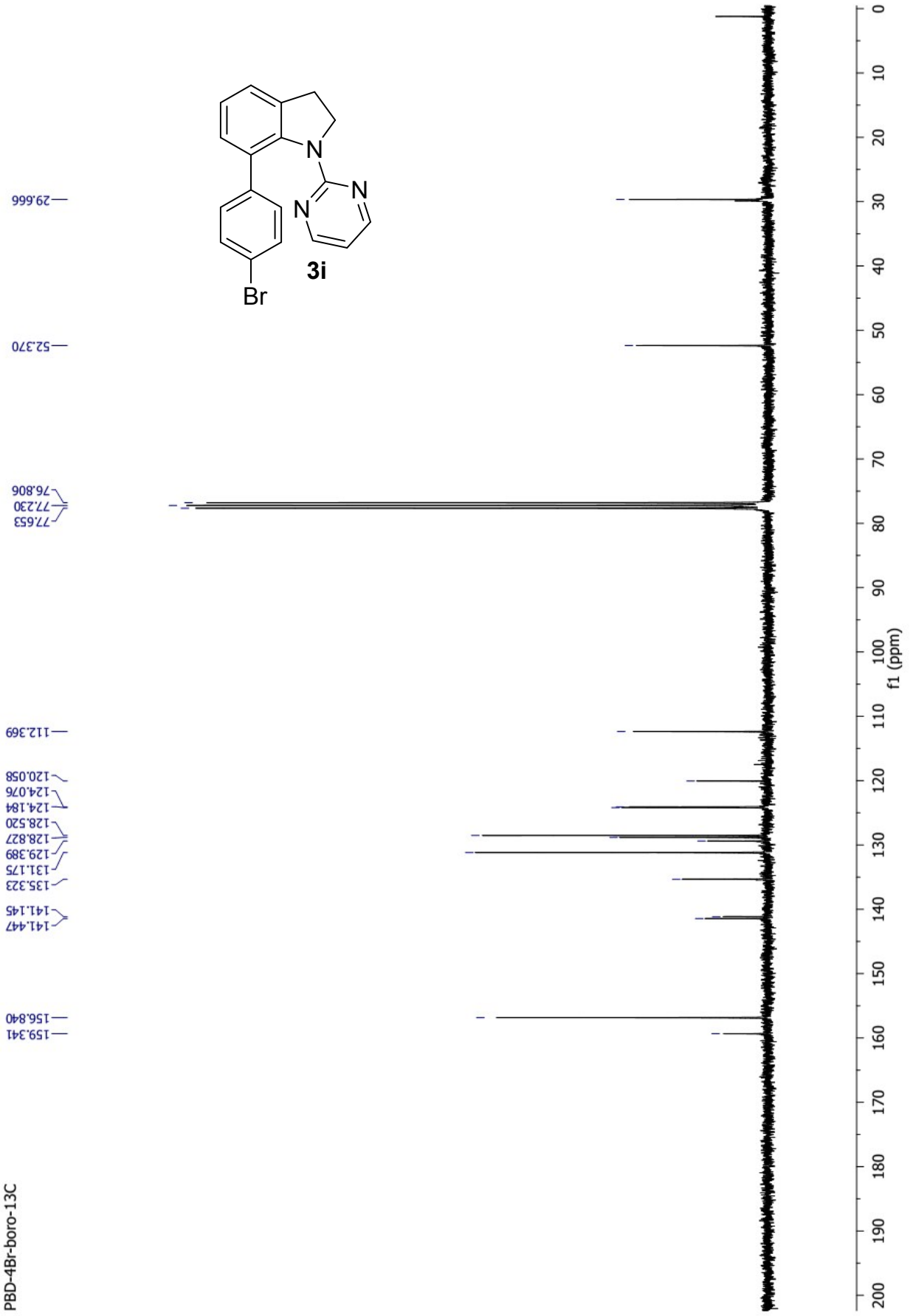

29.571
52.360
77.018
77.230
77.441
112.467
121.095
121.880
124.305
124.968
128.316
128.847
128.868
133.006
135.638
141.339
144.419
148.398
156.903
159.207
PBD-3NO2-Boro-13C
f1 (ppm)

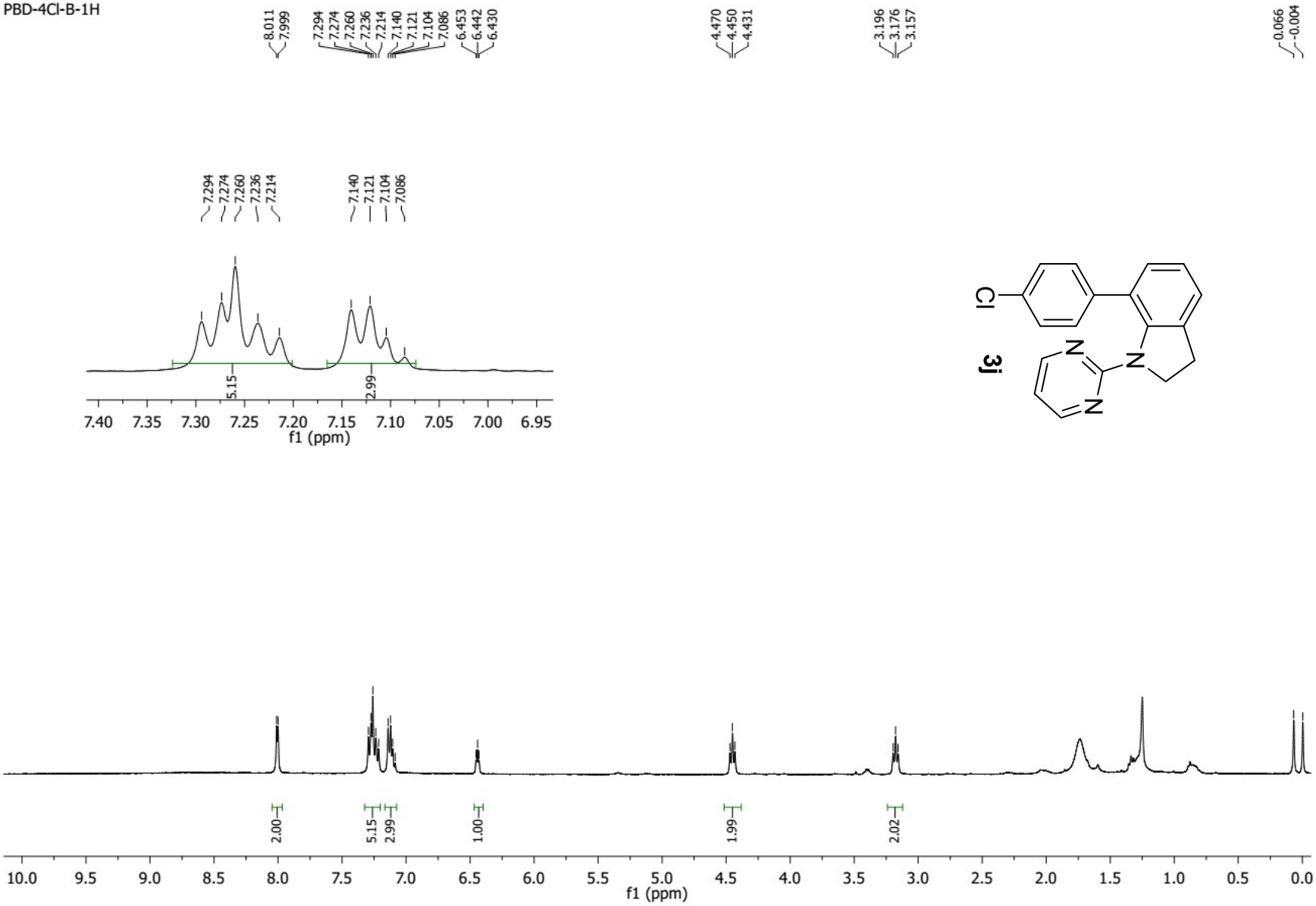
3g

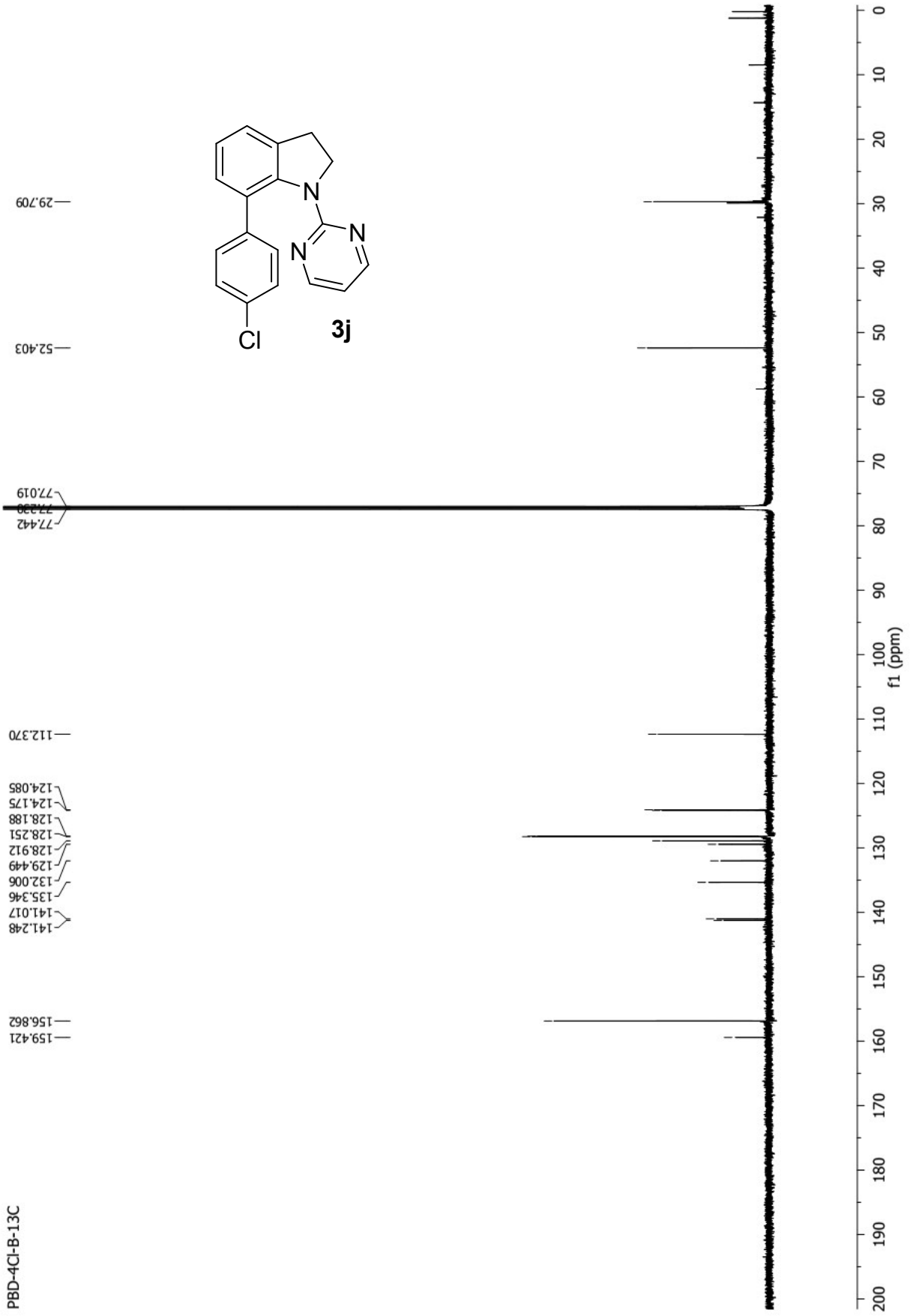

PBD-3CF3-B-1H
7.945
7.933
7.609
7.508
7.489
7.344
7.291
7.274
7.260
7.150
7.131
6.411
6.399
6.388
4.489
4.470
4.450
3.219
3.199
3.180
-0.003
7.609
7.508
7.489
7.363
7.344
7.291
7.274
7.260
7.235
7.150
7.131
7.112
1.05
1.13
1.15
3.99
1.12
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
F3C
N
N
N
3h
2.02
1.05
1.13
1.15
3.99
1.12
1.02
2.02
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

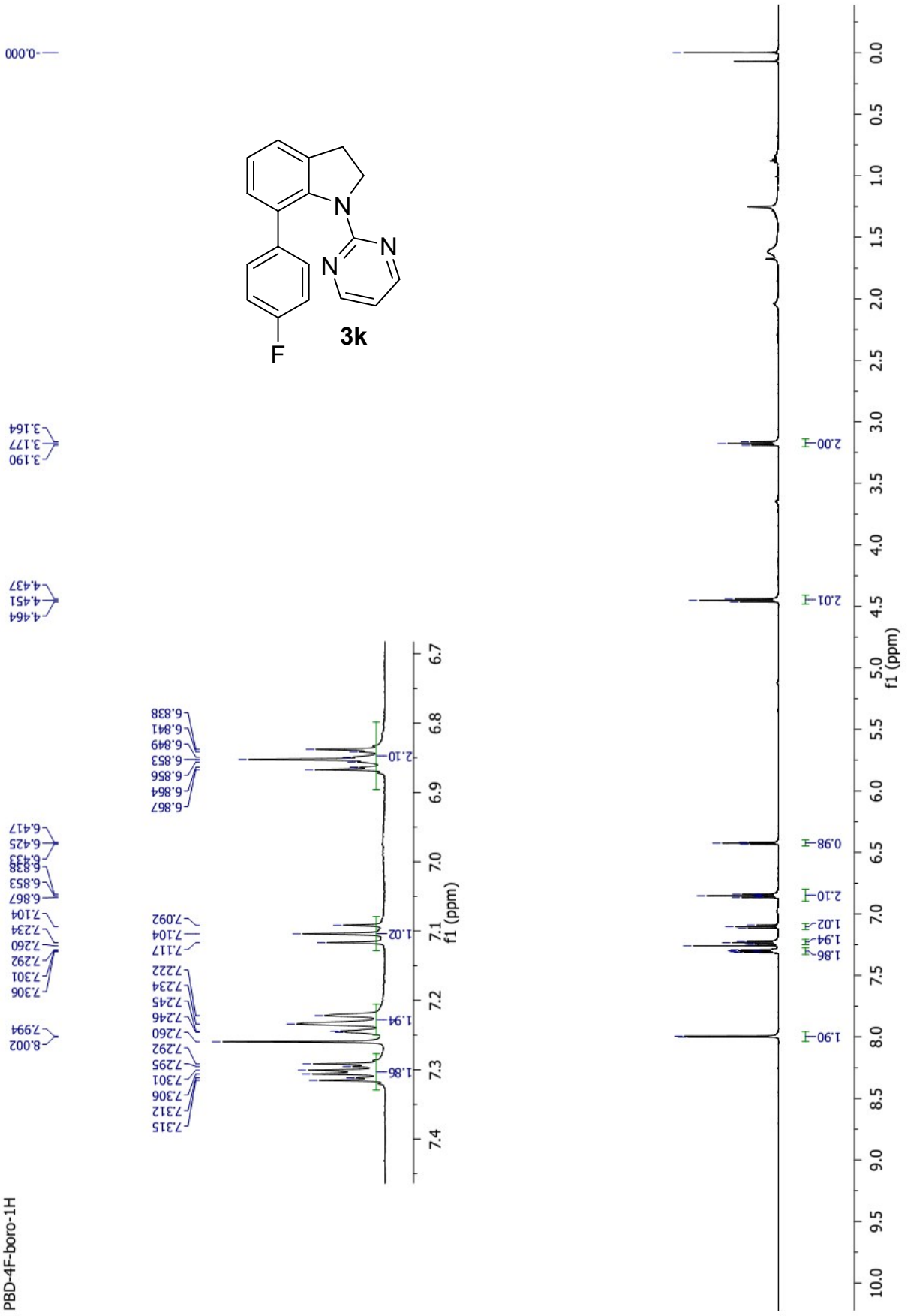

PBD-3CF3-B-13C
3h
F3C
N
N
N
29.64
52.37
77.02
77.23
77.44
112.27
112.79
122.81
123.96
123.98
124.08
124.56
128.46
128.91
128.94
130.13
135.42
141.34
143.36
156.74
159.16
122.83
122.81
122.78
122.76
124.08
124.01
123.98
123.96
123.93
122.9
122.7
124.1
123.9
f1 (ppm)
f1 (ppm)
f1 (ppm)

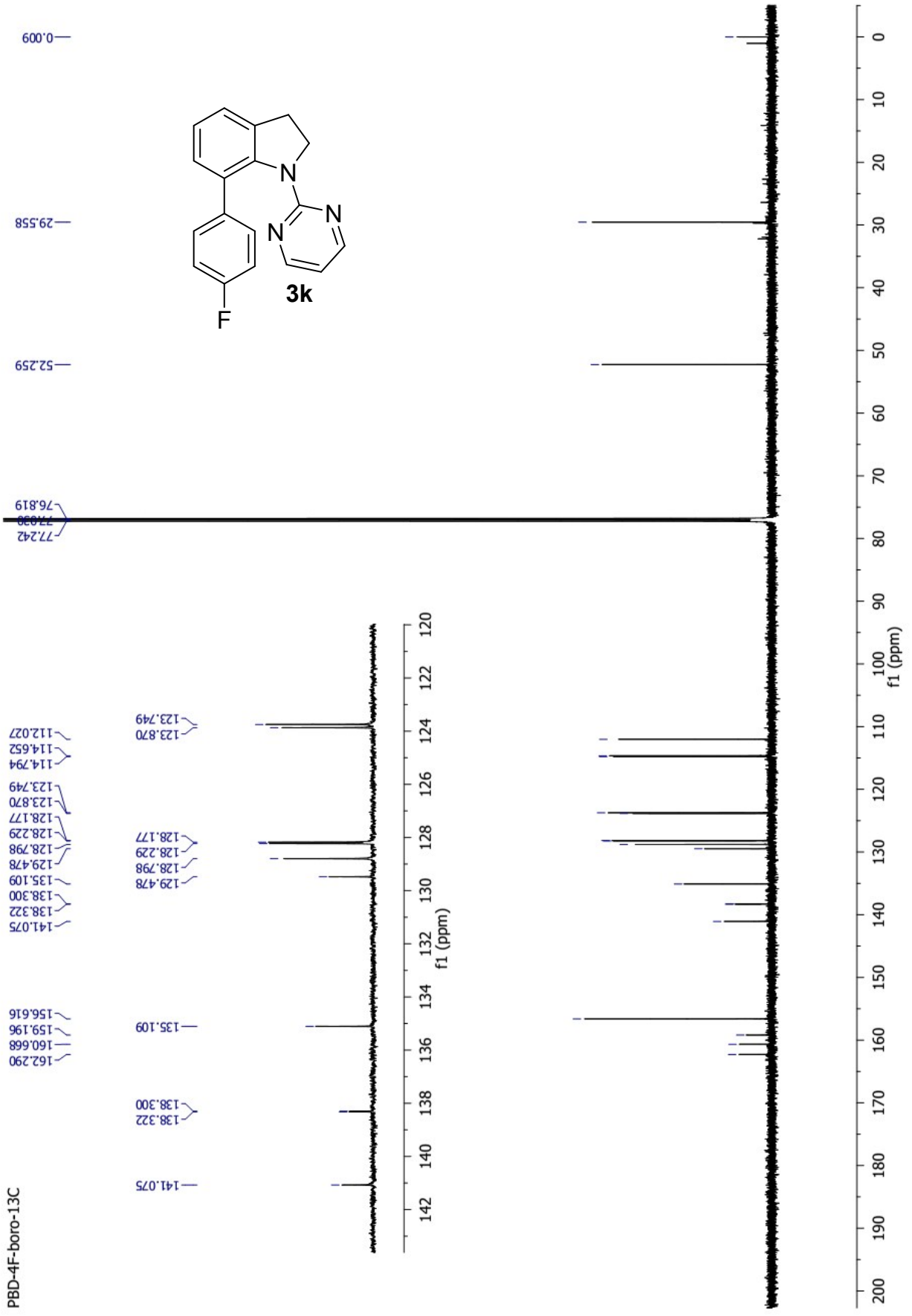

Br
3i
PBD-4-br-boro-1H
f1 (ppm)

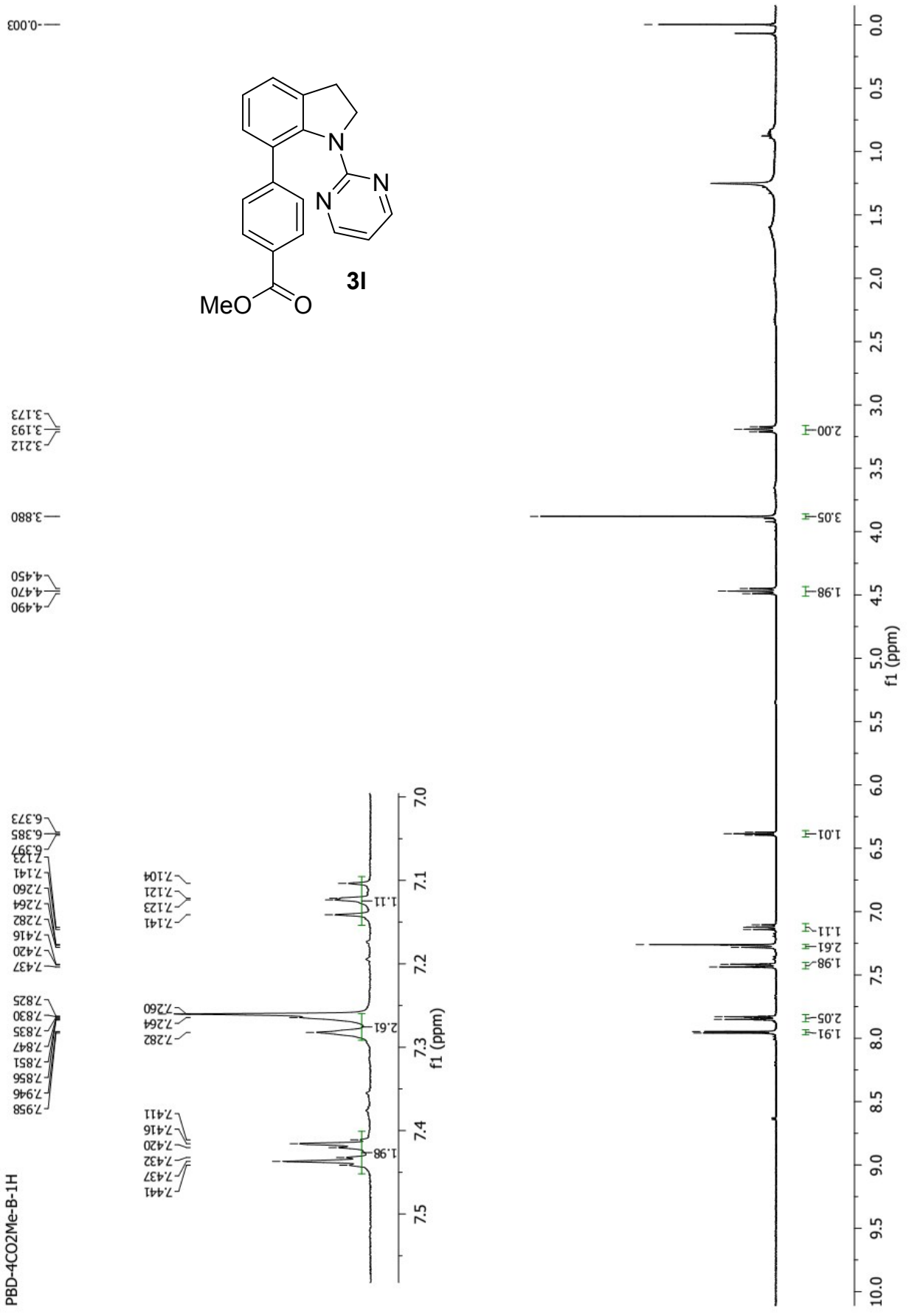

N
N
N
Br
3i
29.666
52.370
76.806
77.230
77.653
112.369
120.058
124.076
124.184
128.520
128.827
129.389
131.175
135.323
141.145
141.447
156.840
159.341
PBD-4Br-boro-13C
f1 (ppm)

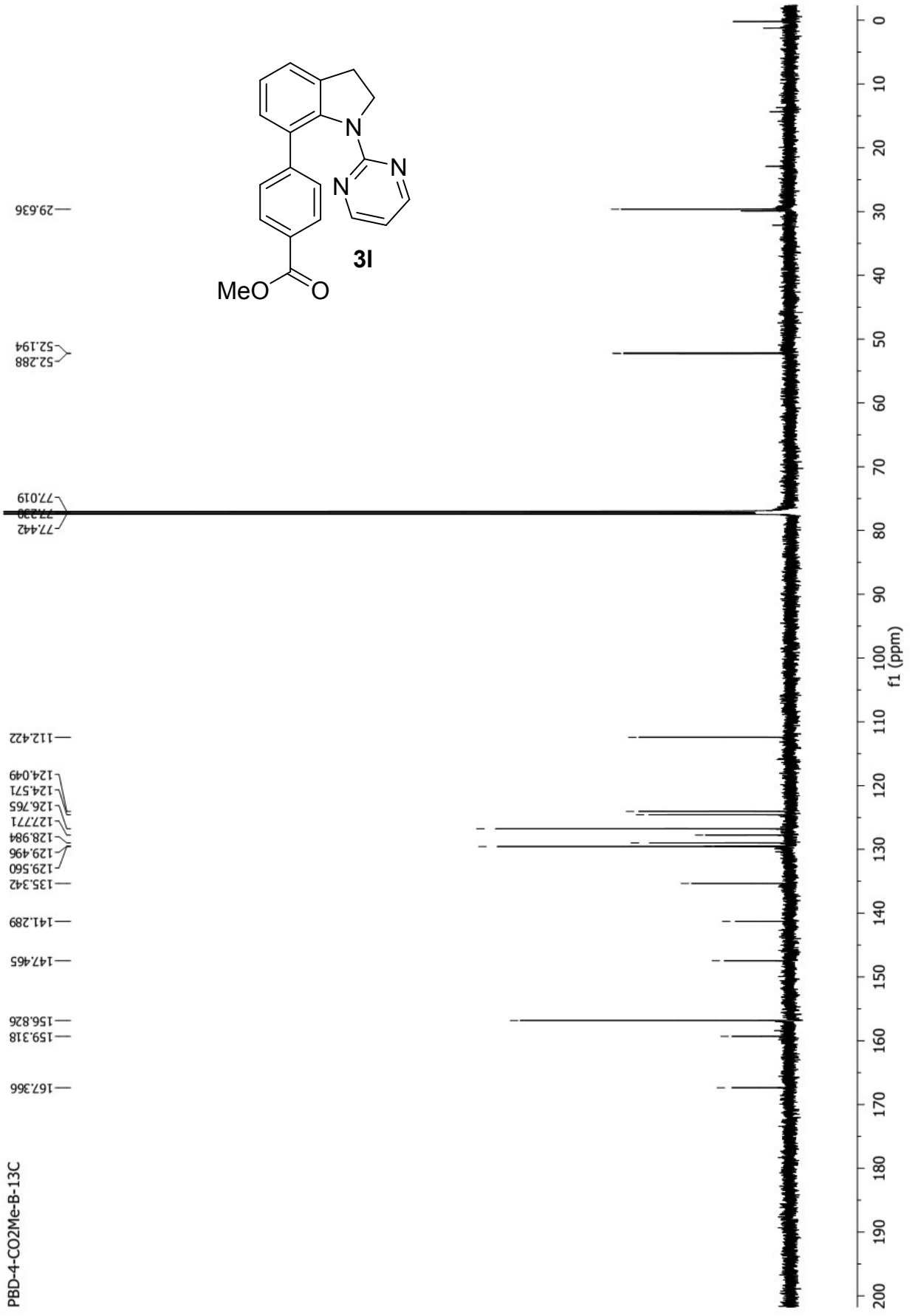

PBD-4Cl-B-1H
8.011
7.999
7.294
7.274
7.260
7.236
7.214
7.140
7.121
7.104
7.086
6.453
6.442
6.430
4.470
4.450
4.431
3.196
3.176
3.157
0.066
-0.004
5.15
2.99
f1 (ppm)
Cl
3j
2.00
5.15
2.99
1.00
1.99
2.02
f1 (ppm)

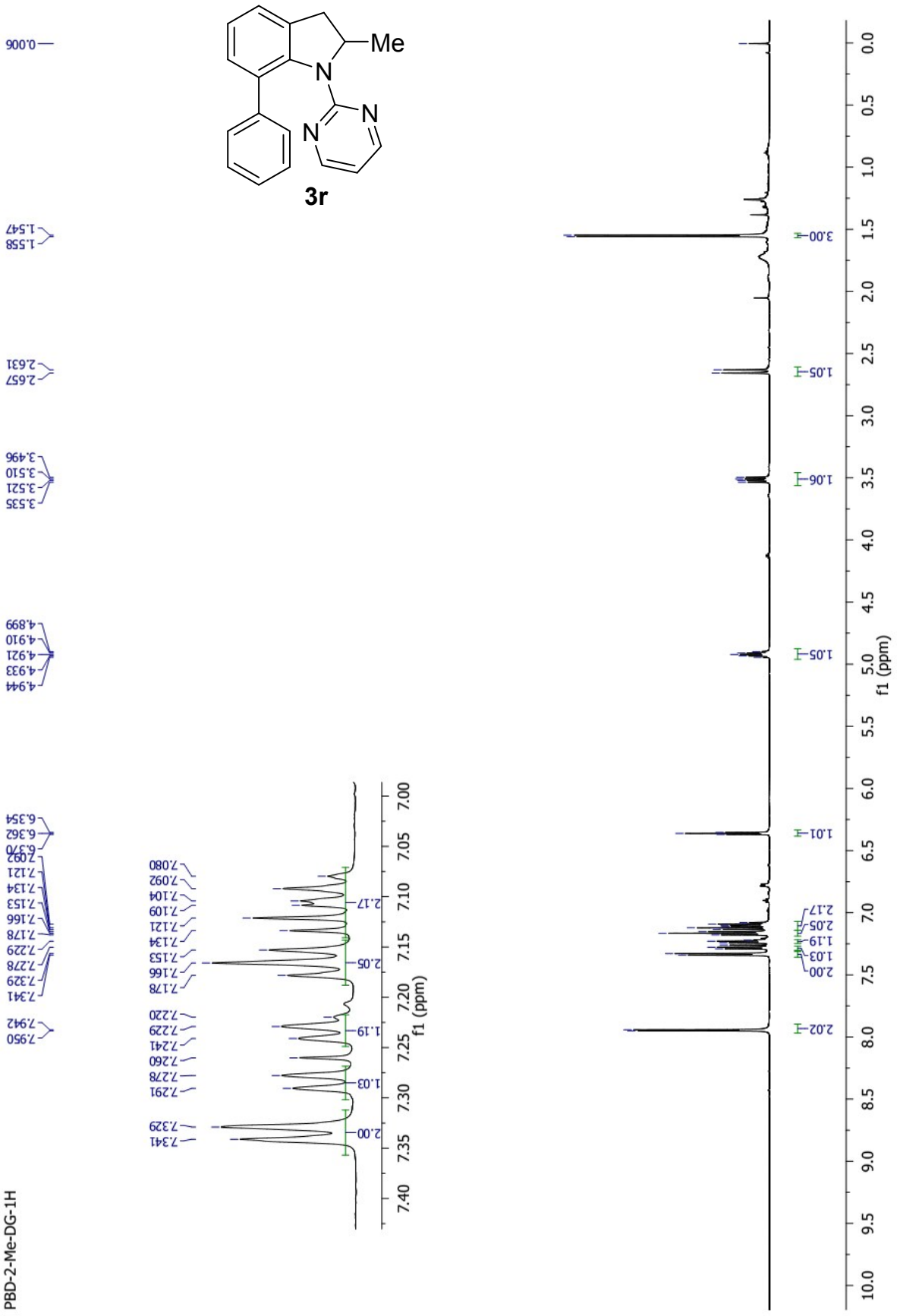

PBD-4Cl-B-13C
159.421
156.862
141.248
141.017
135.346
132.006
129.449
128.912
128.251
128.188
124.175
124.085
112.370
77.442
77.230
77.019
52.403
29.709
Cl
N
N
N
3j
f1 (ppm)

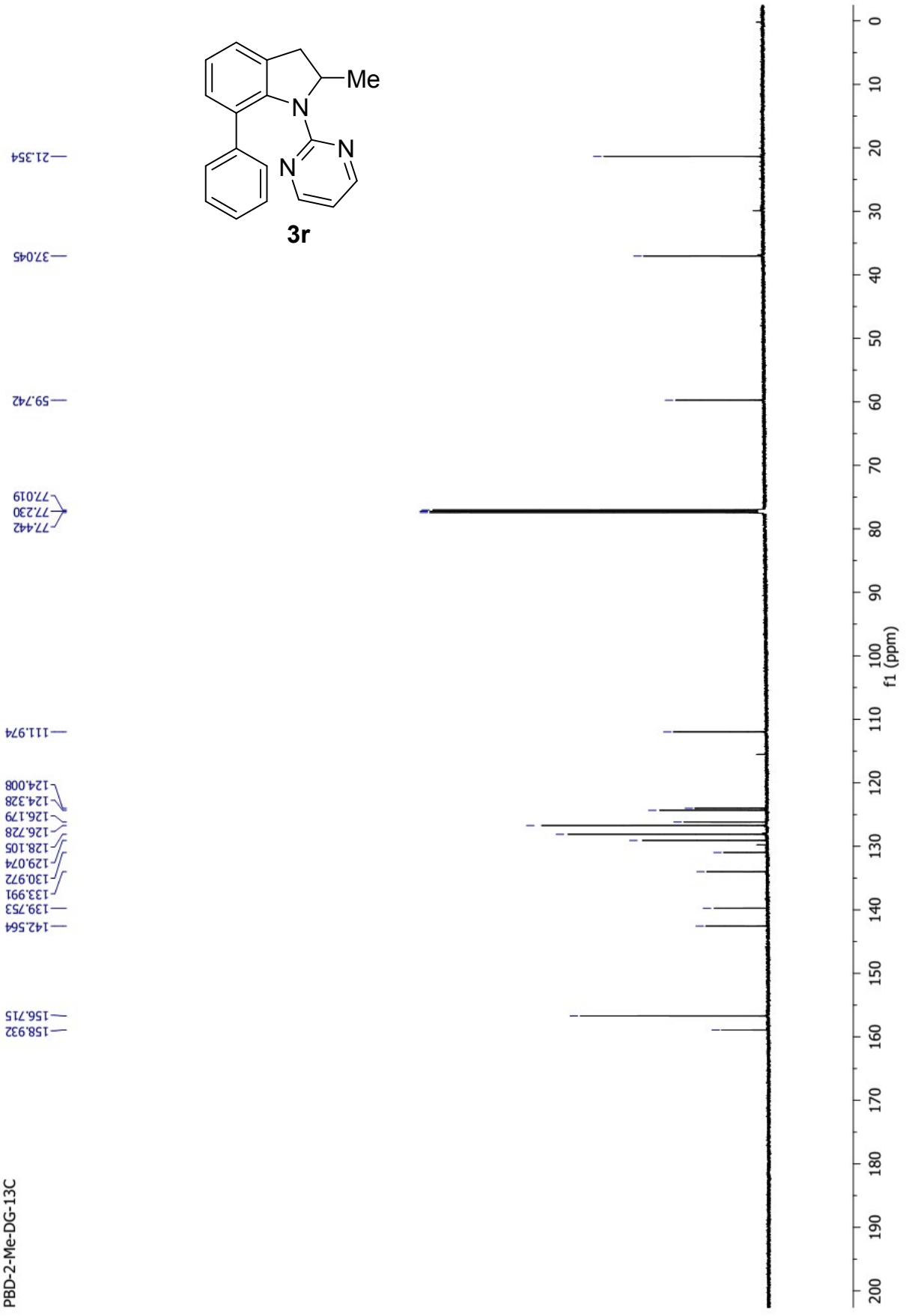

PBD-4F-boro-1H
3k
F
N
N
N
f1 (ppm)

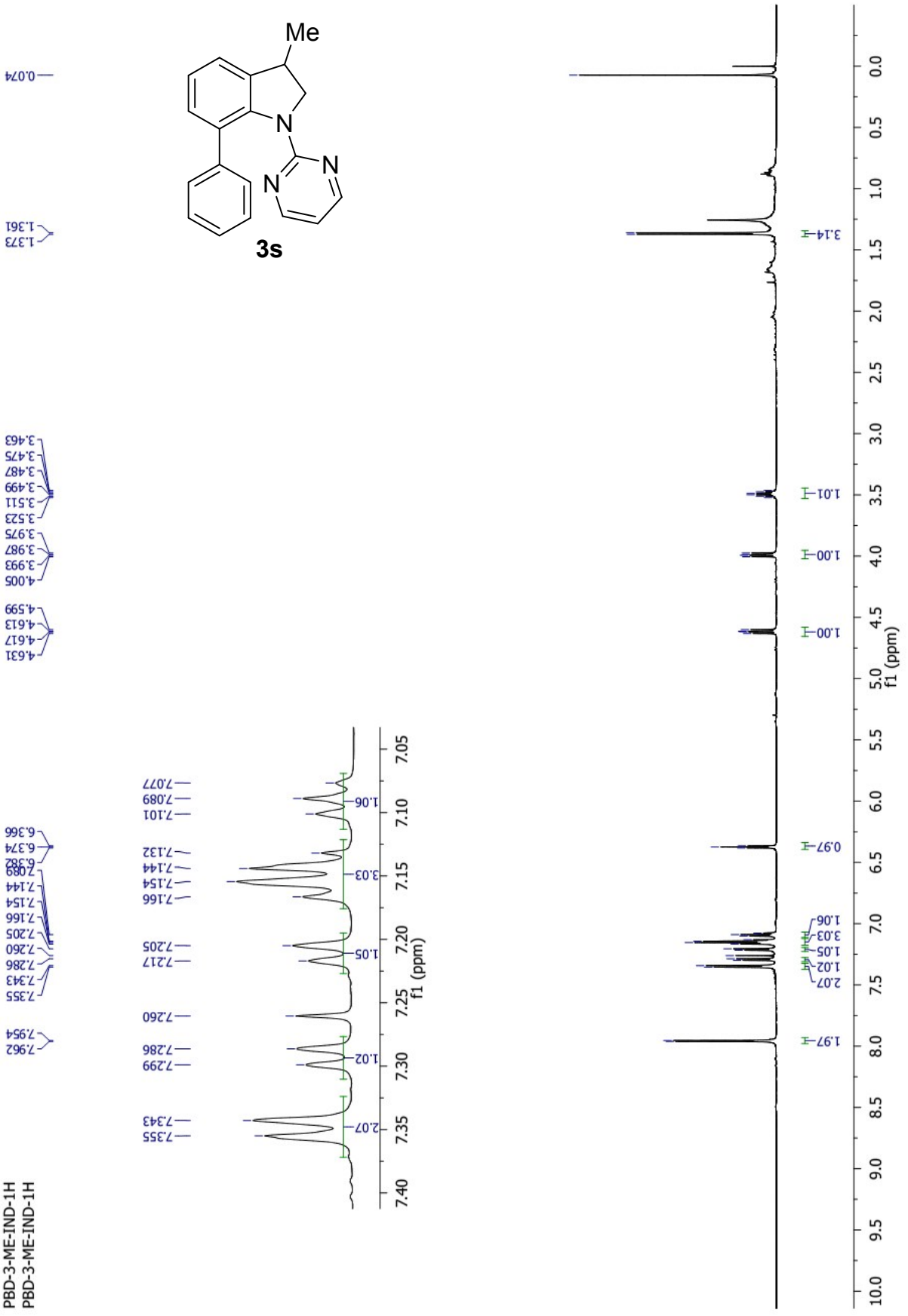

3k
F
N
N
N
PBD-4F-boro-13C
f1 (ppm)
f1 (ppm)

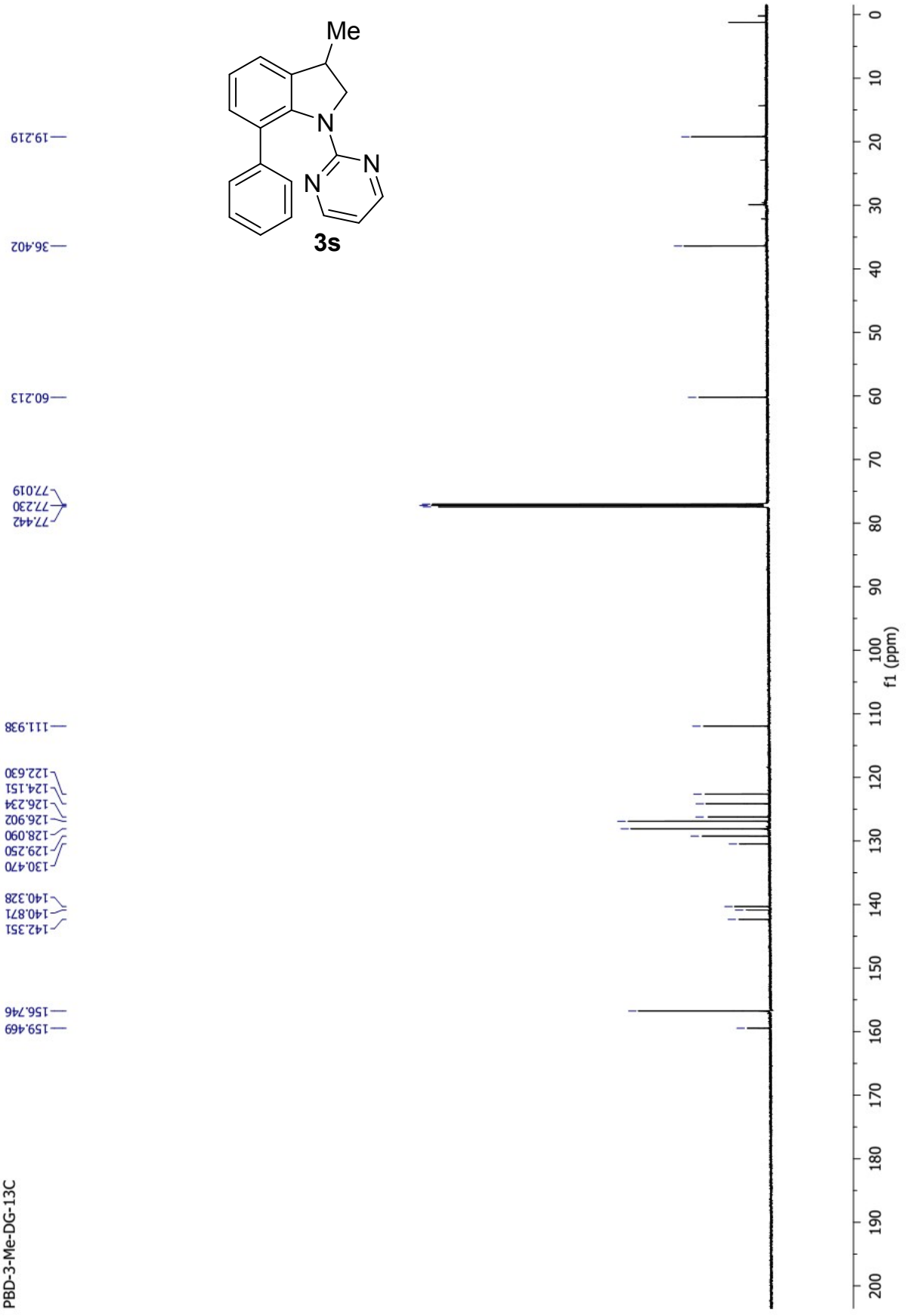

3I
MeO
O
N
N
N
PBD-4CO2Me-B-1H
f1 (ppm)

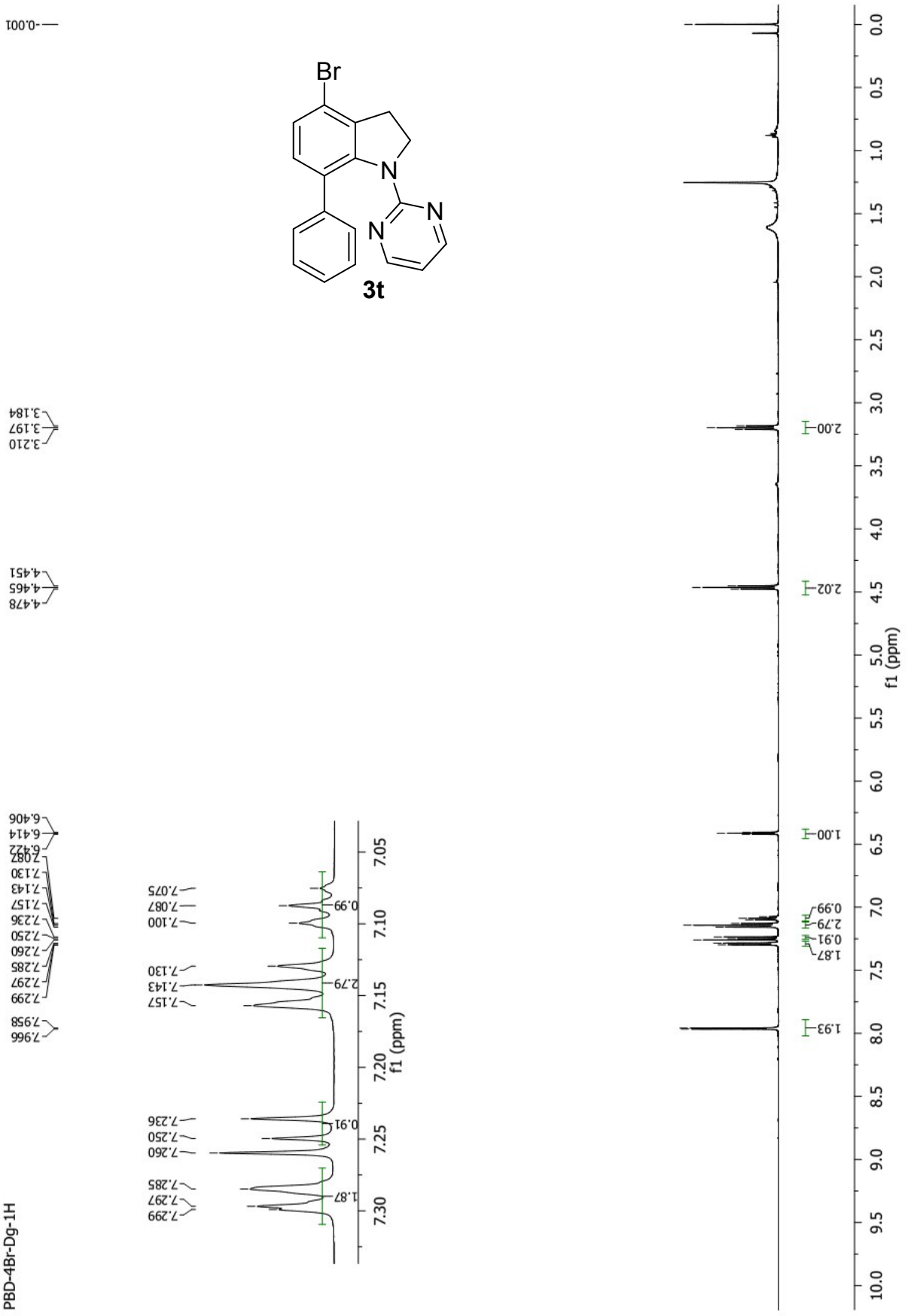

3l
MeO
O
N
N
N
29.636
52.288
52.194
77.019
77.238
77.442
112.422
124.049
124.571
126.765
127.771
128.984
129.496
129.560
135.342
141.289
147.465
156.826
159.318
167.366
PBD-4-CO2Me-B-13C
f1 (ppm)

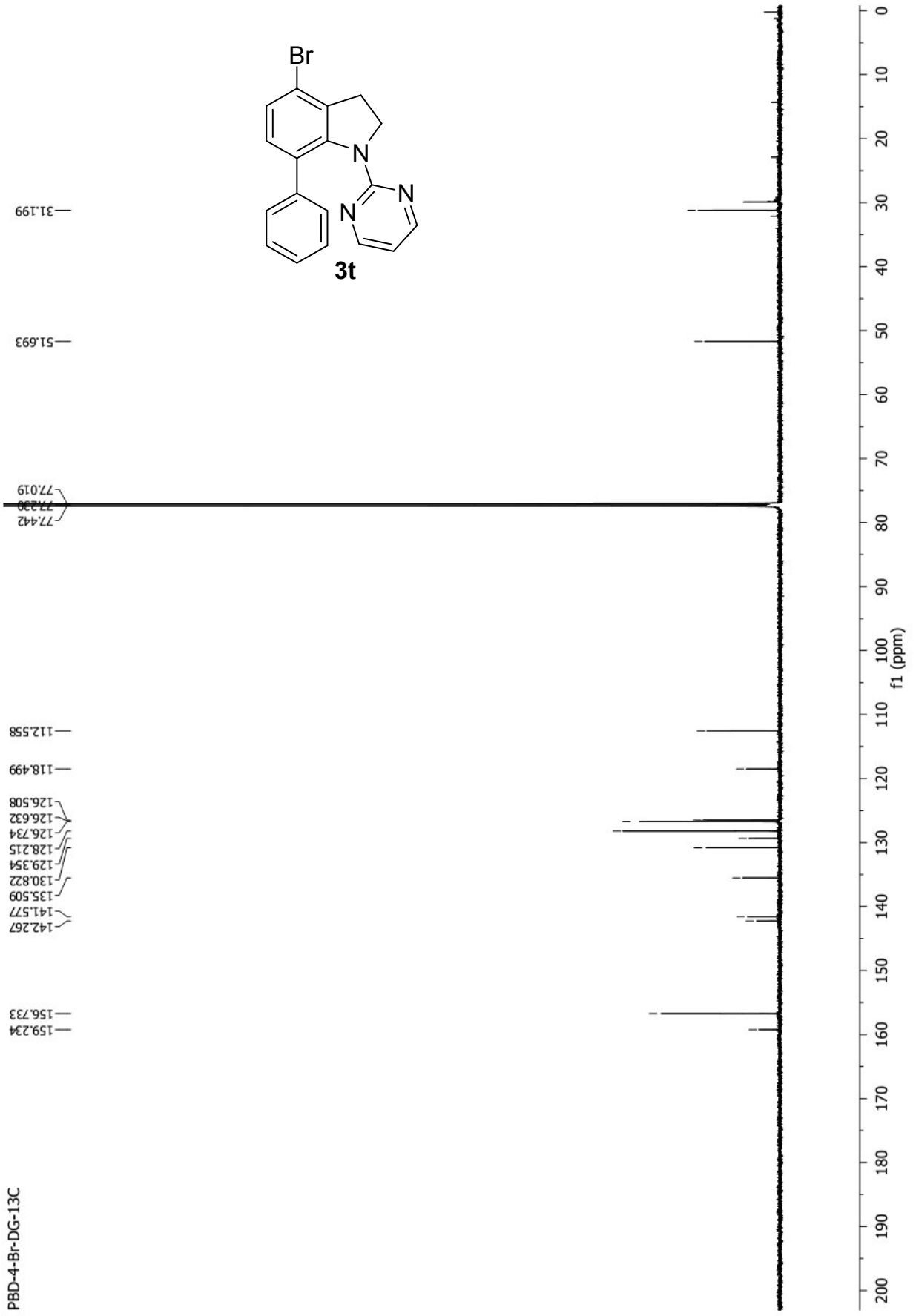

Me
N
N
N
3r
PBD-2-Me-DG-1H
f1 (ppm)

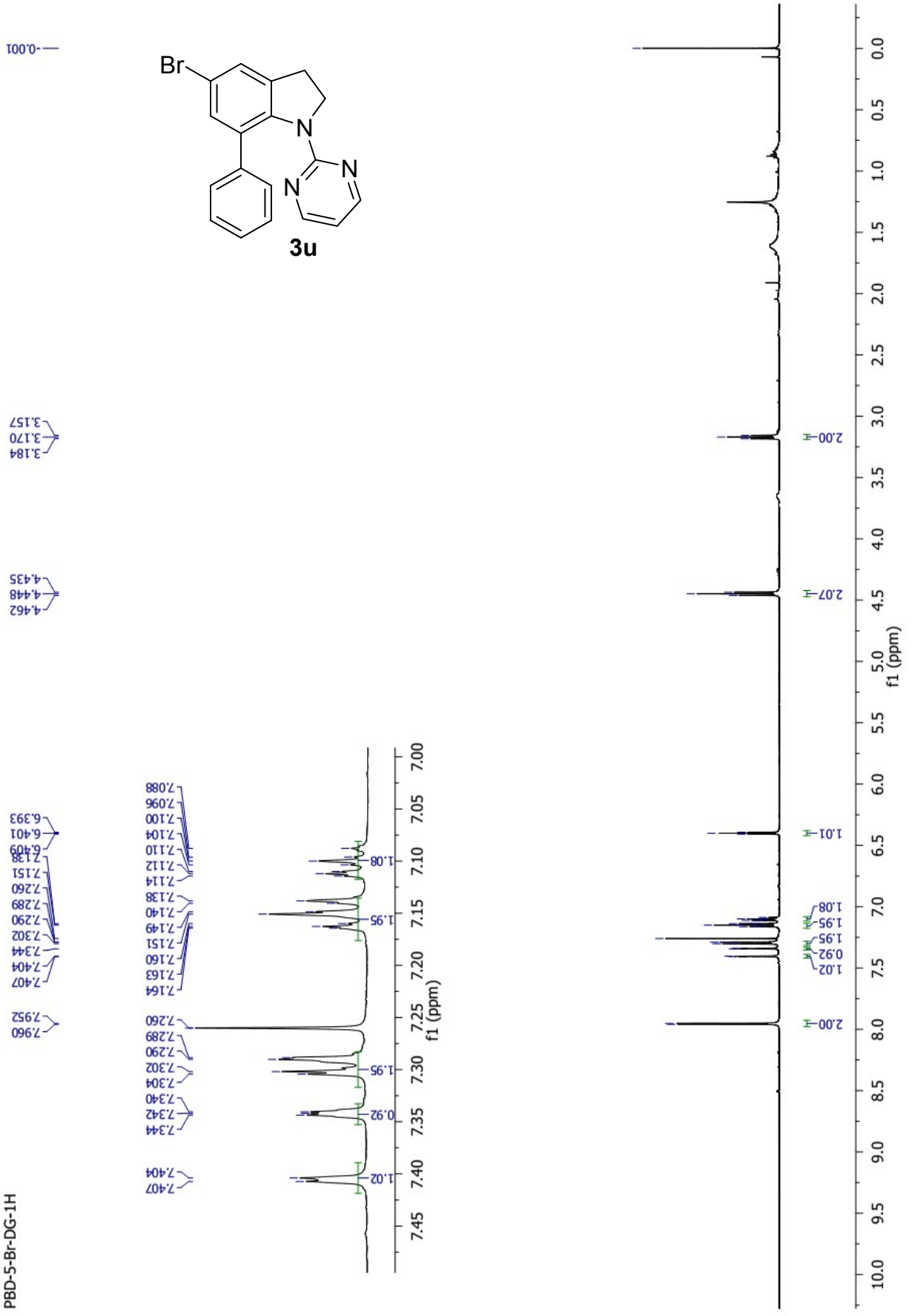

Me
N
N
N
3r
21.354
37.045
59.742
77.019
77.230
77.442
111.974
124.008
124.328
126.179
126.728
128.105
129.074
130.972
133.991
139.753
142.564
156.715
158.932
f1 (ppm)
PBD-2-Me-DG-13C

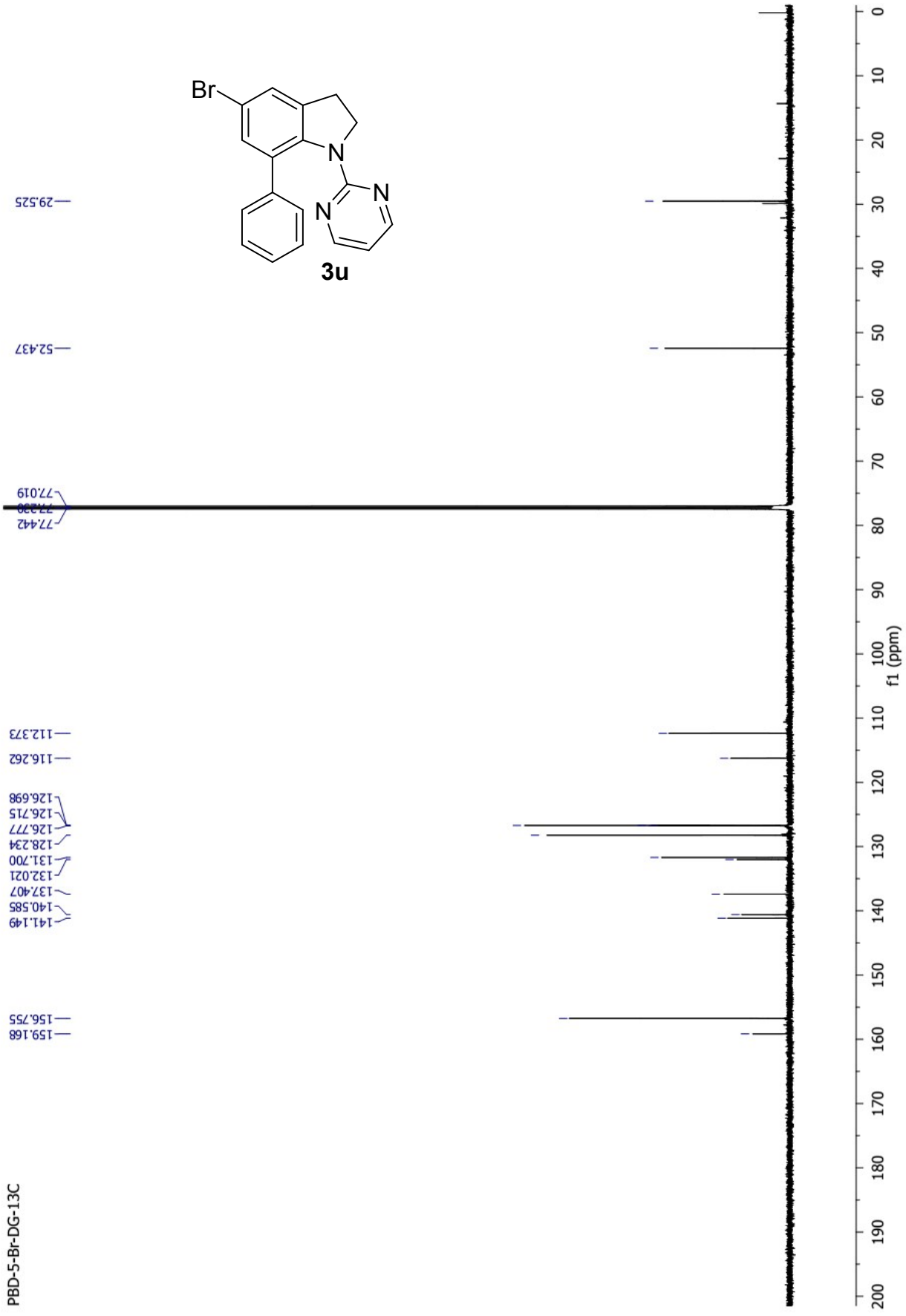

Me
N
N
N
3s
PBD-3-ME-IND-1H
PBD-3-ME-IND-1H
f1 (ppm)
f1 (ppm)

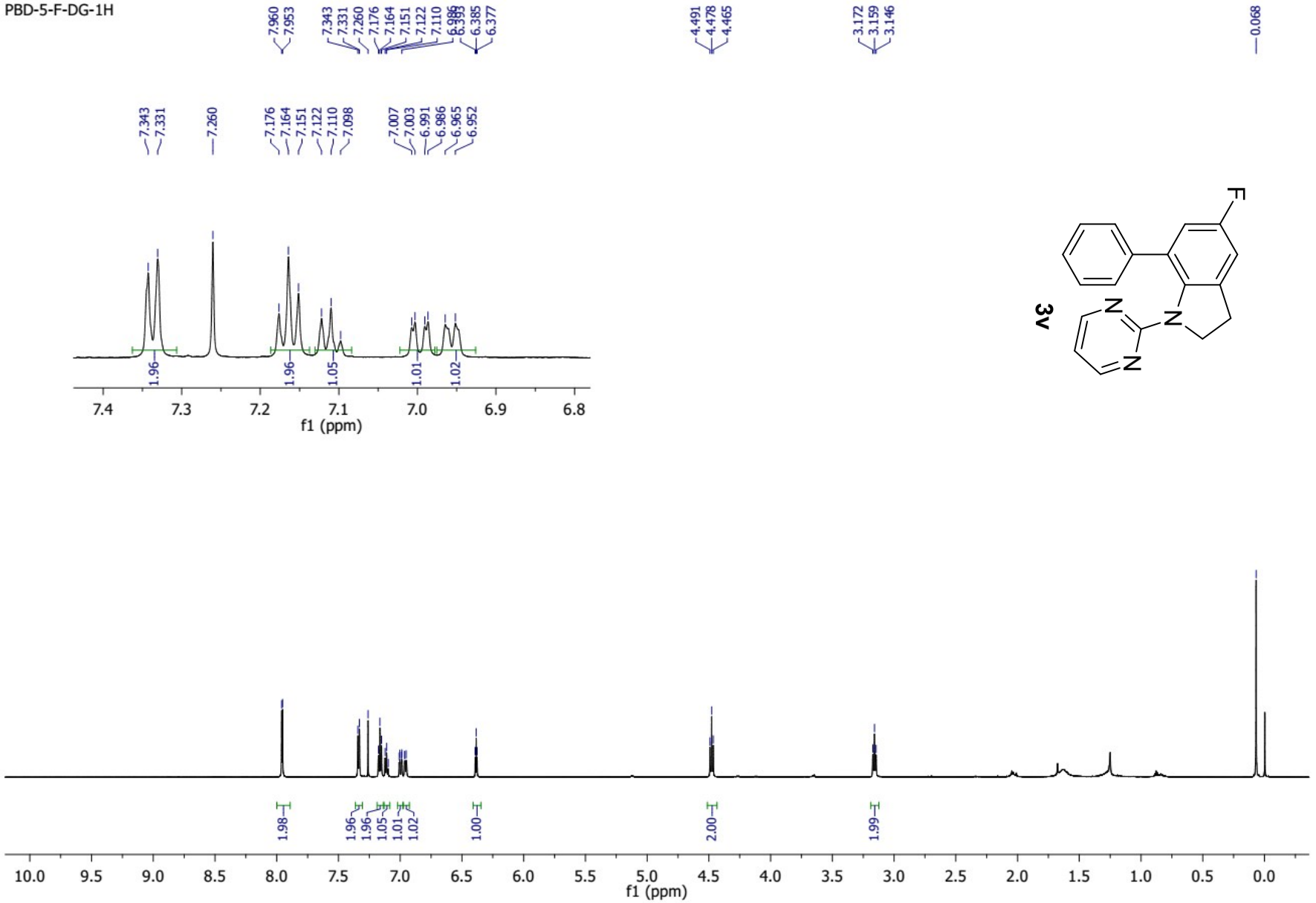

Me
N
N
N
3s
19.219
36.402
60.213
77.019
77.230
77.442
111.938
122.630
124.151
126.234
126.902
128.090
129.250
130.470
140.328
140.871
142.351
156.746
159.469
PBD-3-Me-DG-13C
f1 (ppm)

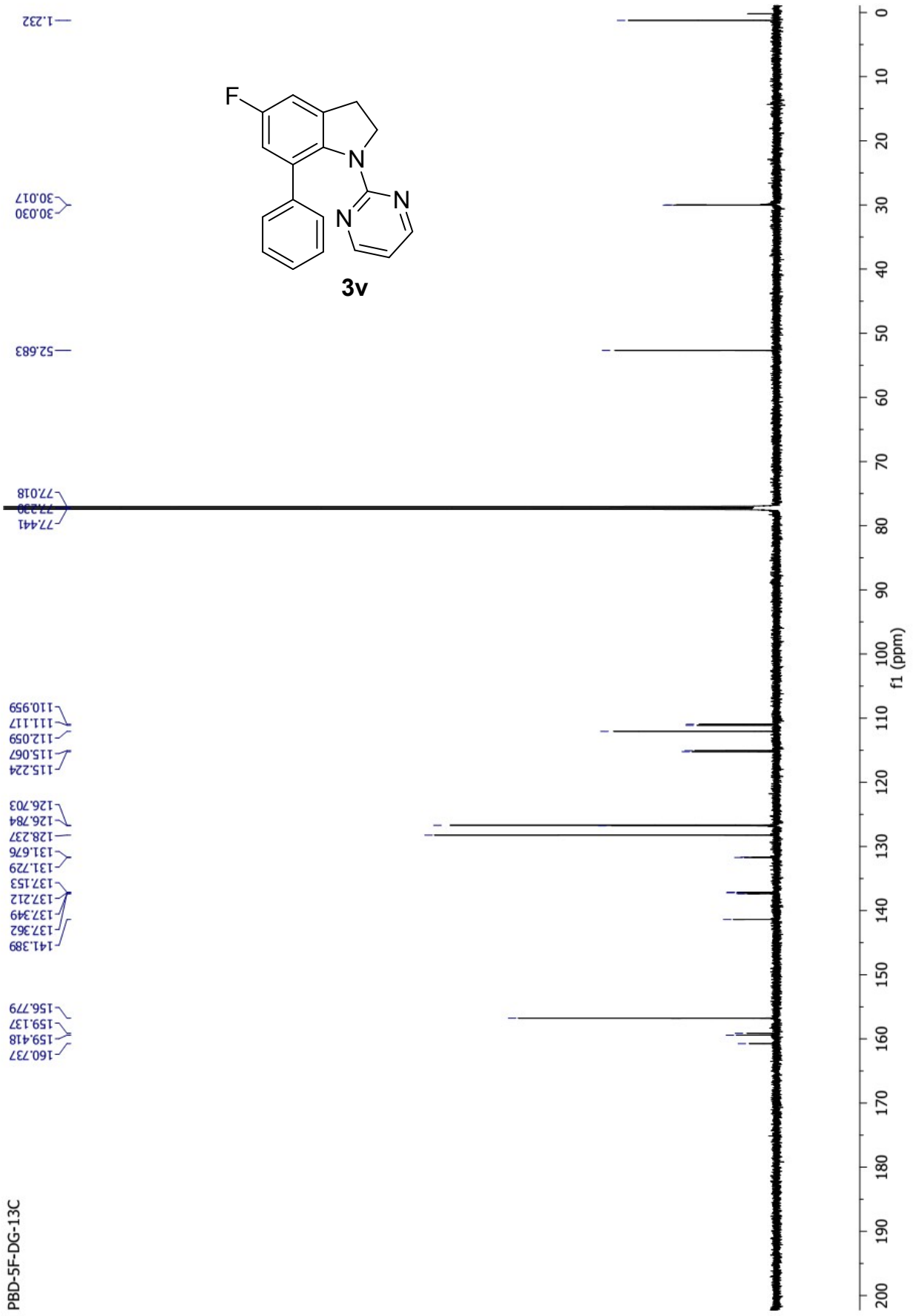

Br
N
N
N
3t
PBD-4Br-Dg-1H
f1 (ppm)

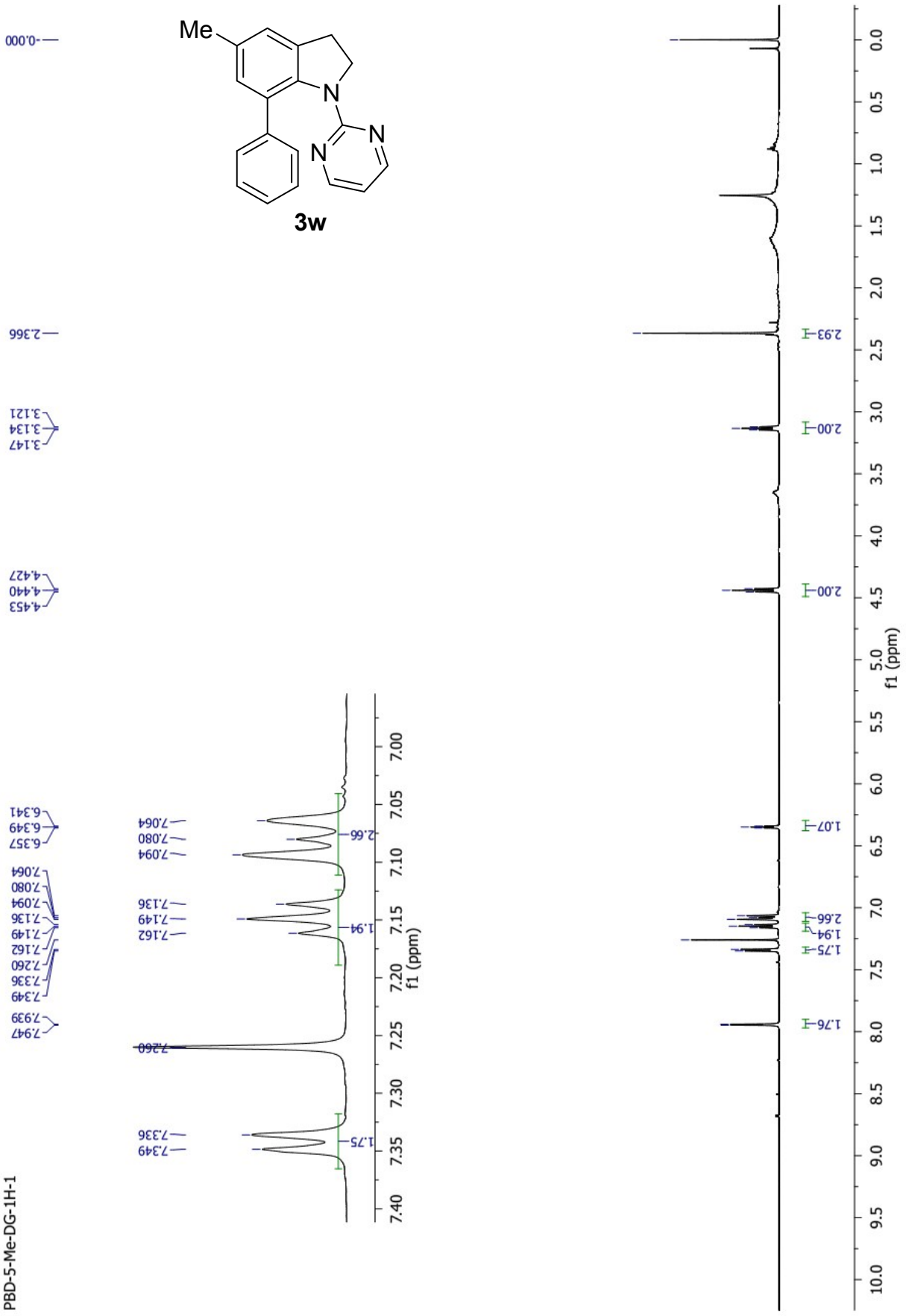

Br
N
N
N
3t
31.199
51.693
77.019
77.230
77.442
112.558
118.499
126.508
126.632
126.734
128.215
129.354
130.822
135.509
141.577
142.267
156.733
159.234
PBD-4-Br-DG-13C
f1 (ppm)

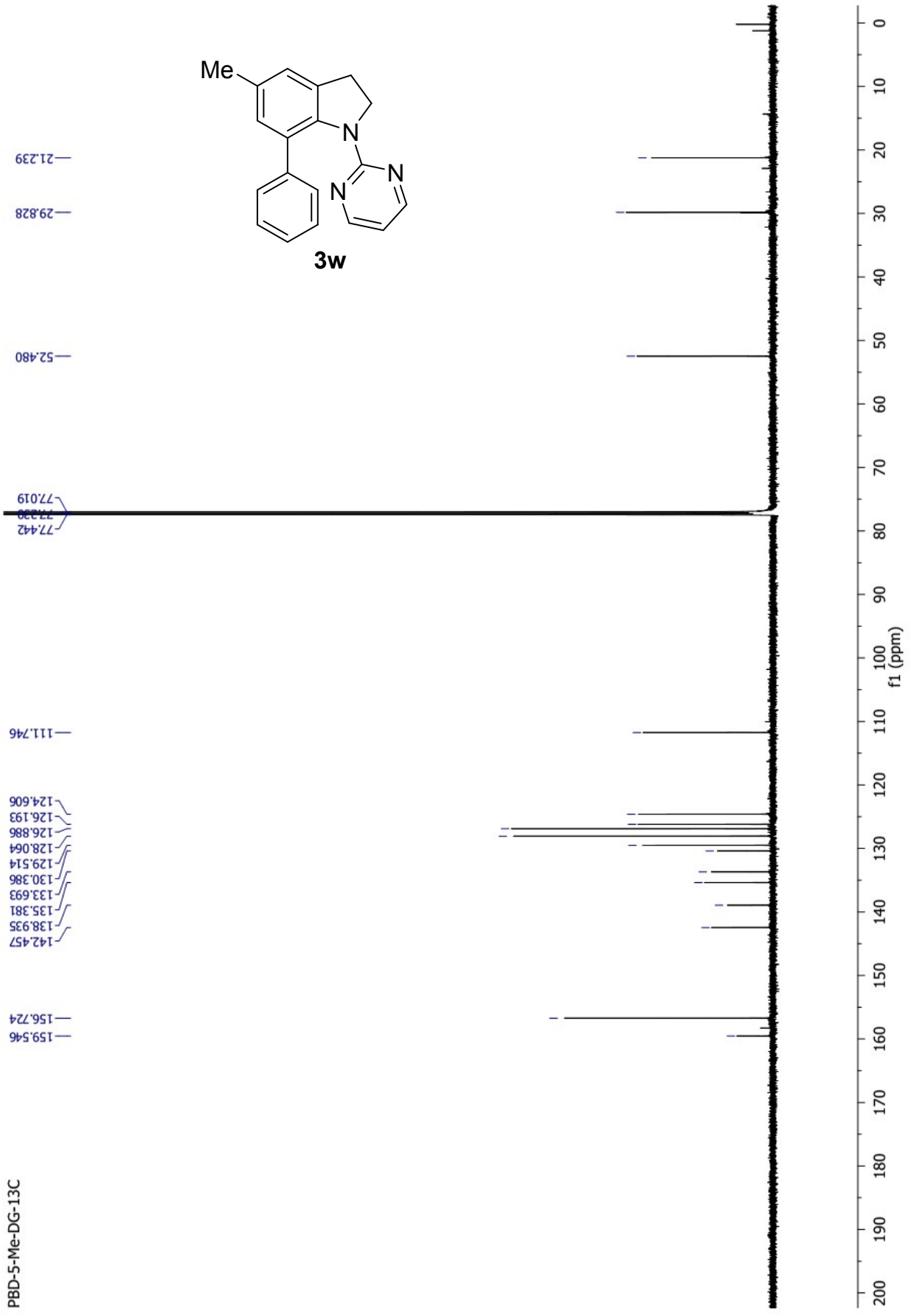

Br
N
N
N
3u
PBD-5-Br-DG-1H
f1 (ppm)

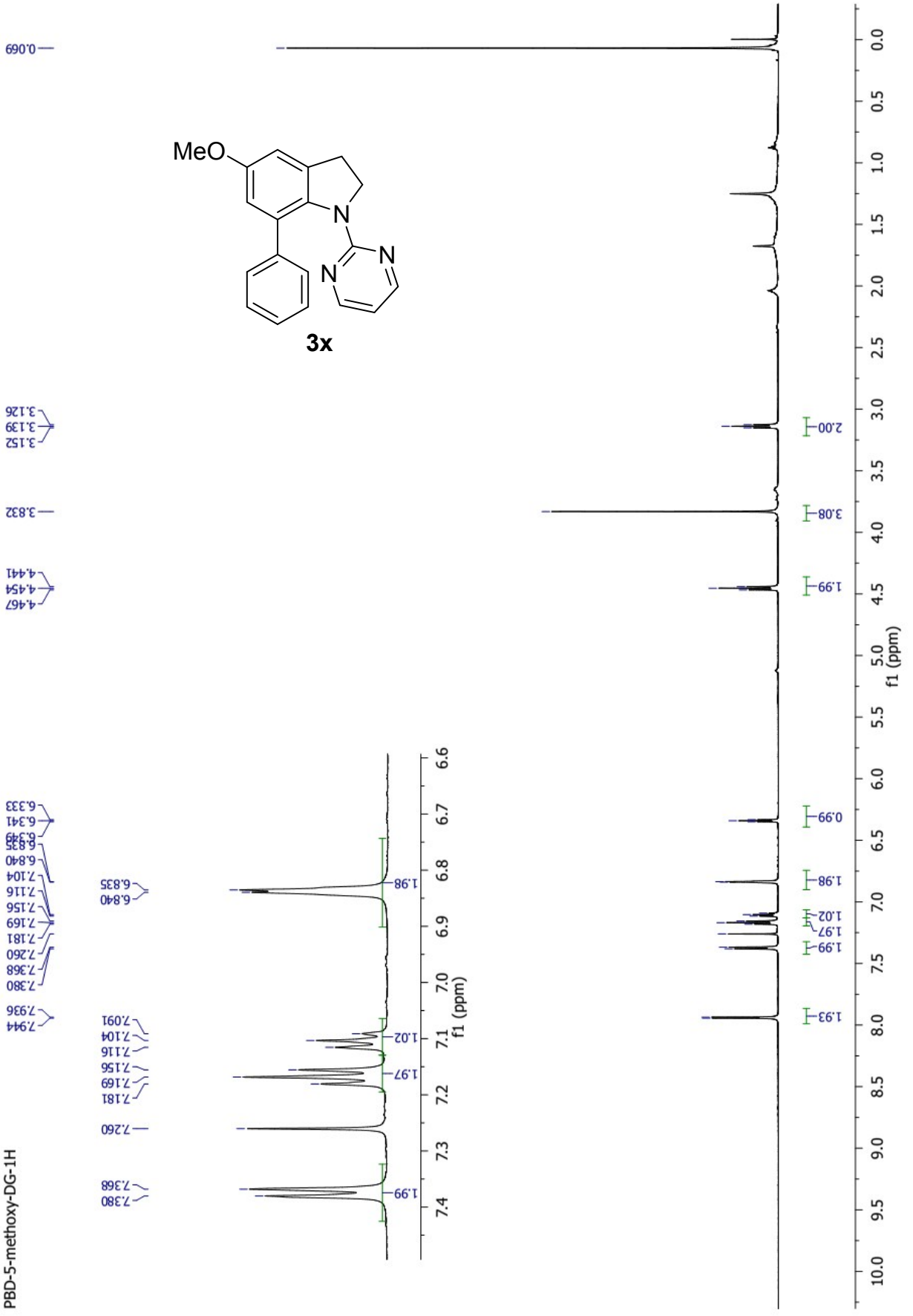

Br
N
N
N
3u
29.525
52.437
77.019
77.330
77.442
112.373
116.262
126.698
126.715
126.777
128.234
131.700
132.021
137.407
140.585
141.149
156.755
159.168
PBD-5-Br-DG-13C
f1 (ppm)

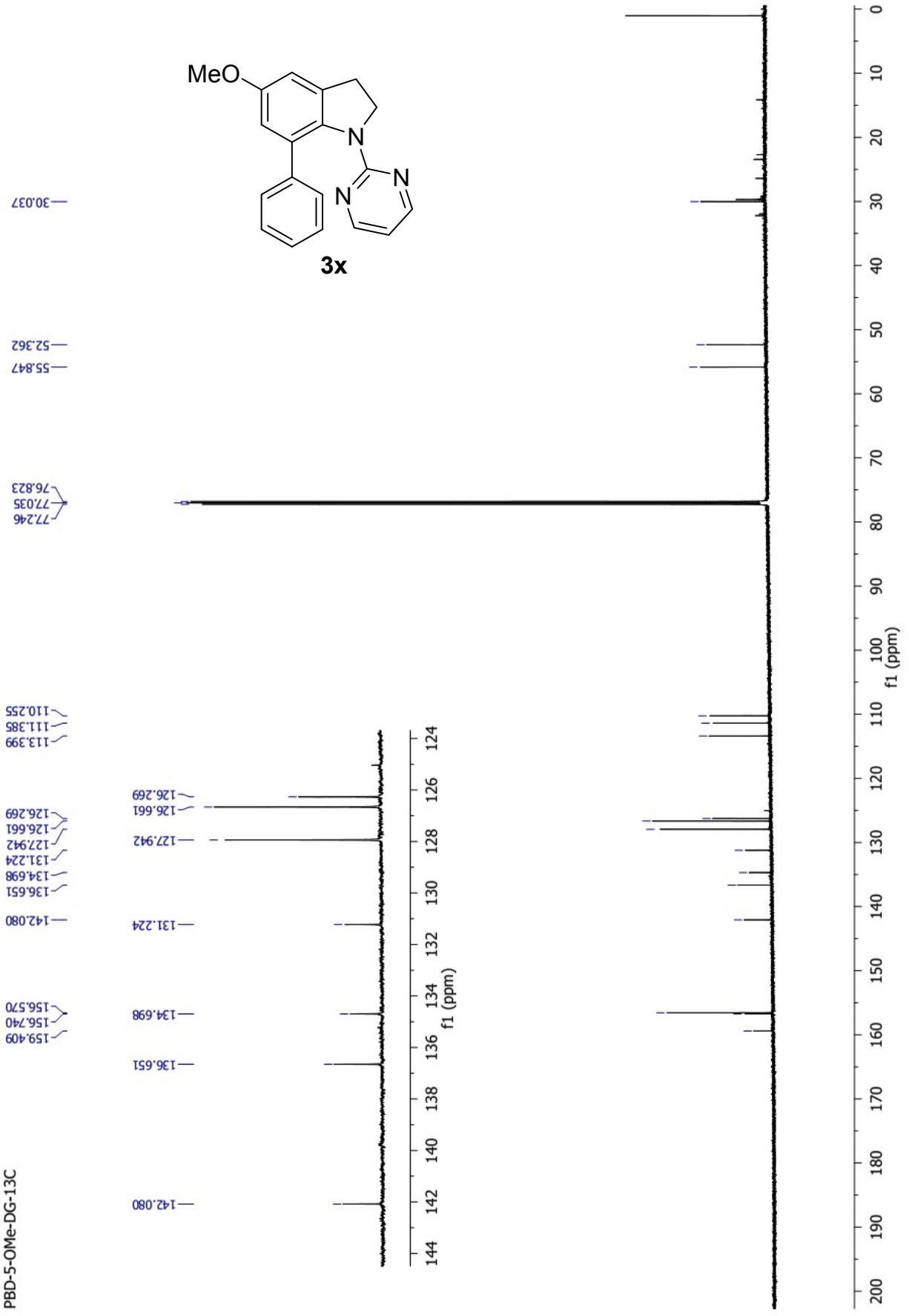

PBD-5-F-DG-1H
7.960
7.953
7.343
7.331
7.260
7.176
7.164
7.151
7.122
7.110
6.385
6.377
4.491
4.478
4.465
3.172
3.159
3.146
0.068
7.343
7.331
7.260
7.176
7.164
7.151
7.122
7.110
7.098
7.007
7.003
6.991
6.986
6.965
6.952
1.96
1.96
1.05
1.01
1.02
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
F
N
N
N
3v
1.98
1.96
1.96
1.05
1.01
1.02
1.00
2.00
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

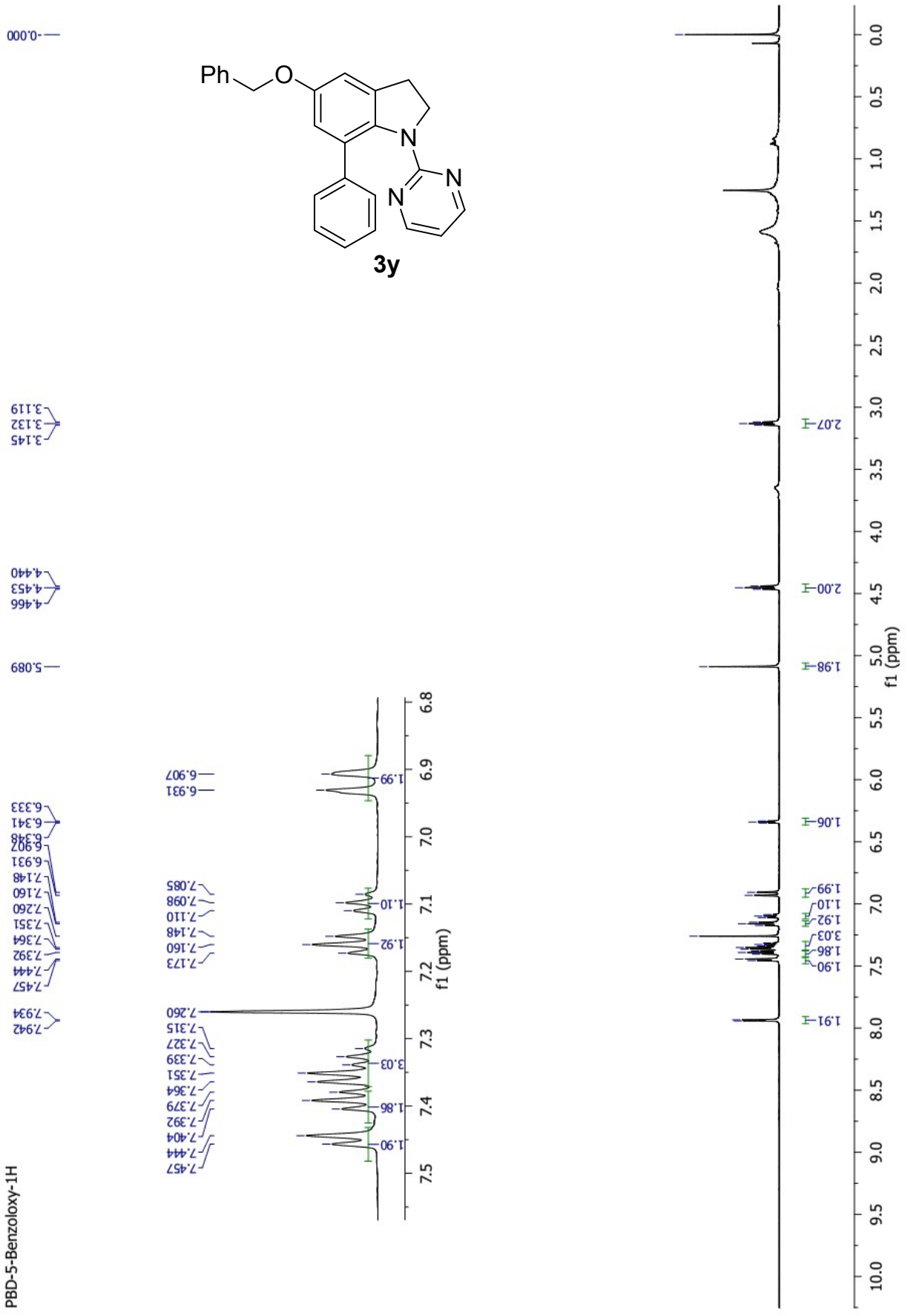

F
N
N
N
3v
1.232
30.017
30.030
52.683
77.018
77.330
77.441
110.959
111.117
112.059
115.067
115.224
126.703
126.784
128.237
131.676
131.729
137.153
137.212
137.349
137.362
141.389
156.779
159.137
159.418
160.737
PBD-5F-DG-13C
f1 (ppm)

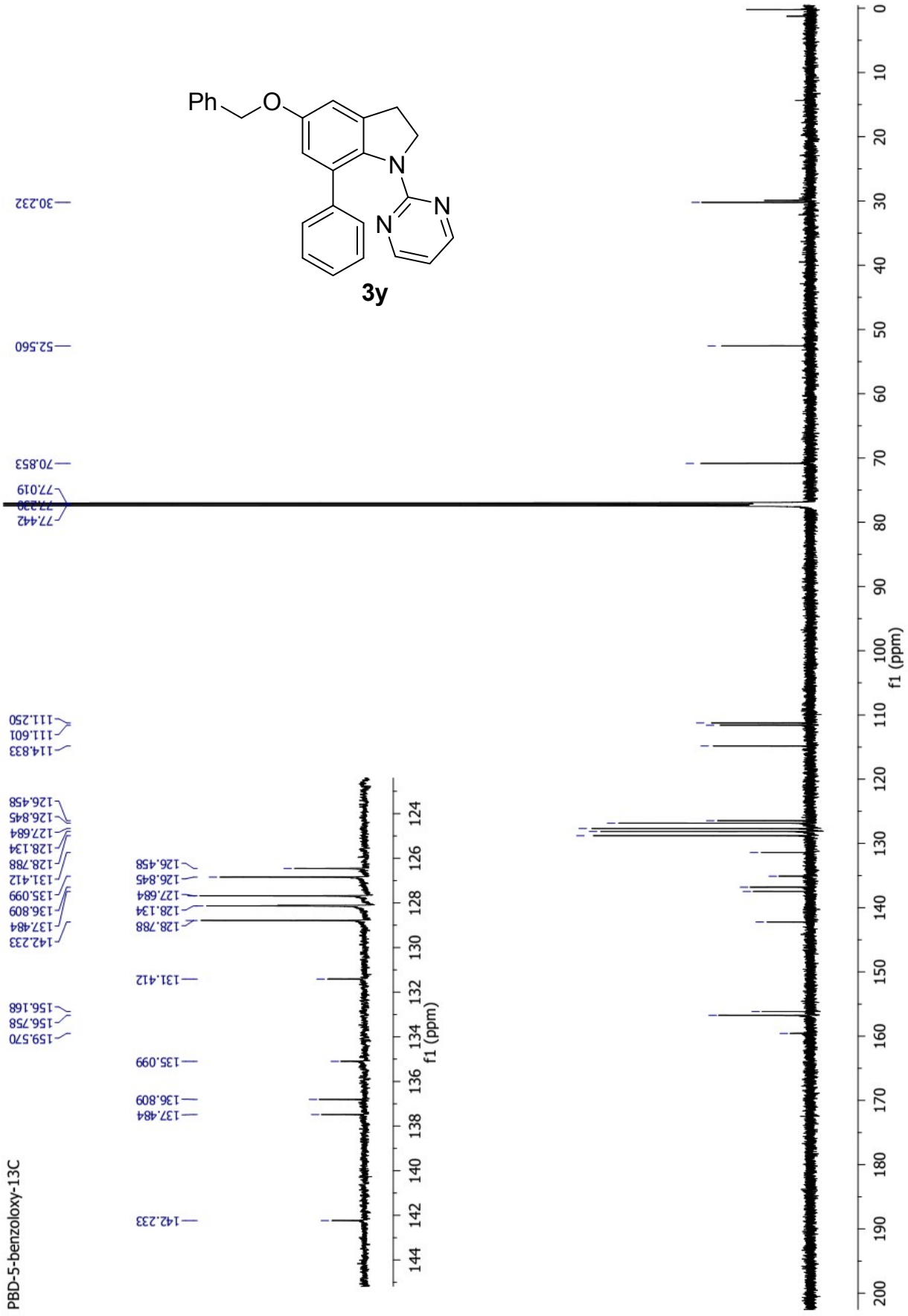

Me
N
N
N
3w
PBD-5-Me-DG-1H-1
f1 (ppm)


Me
N
N
N
3w
21.239
29.828
52.480
77.019
77.238
77.442
111.746
124.606
126.193
126.886
128.064
129.514
130.386
133.693
135.381
138.935
142.457
156.724
159.546
PBD-5-Me-DG-13C
f1 (ppm)

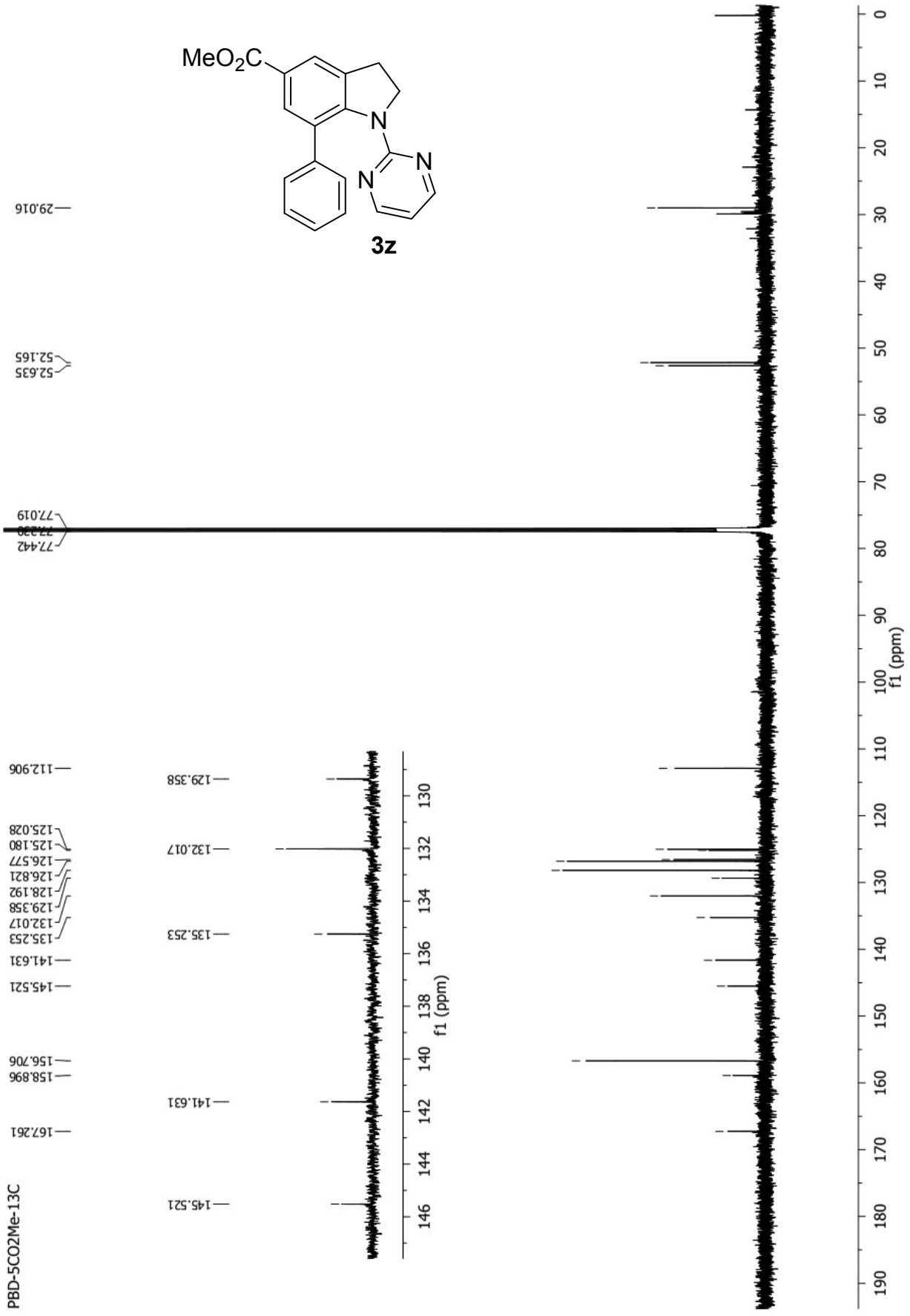

MeO
N
N
N
3x
PBD-5-methoxy-DG-1H
f1 (ppm)

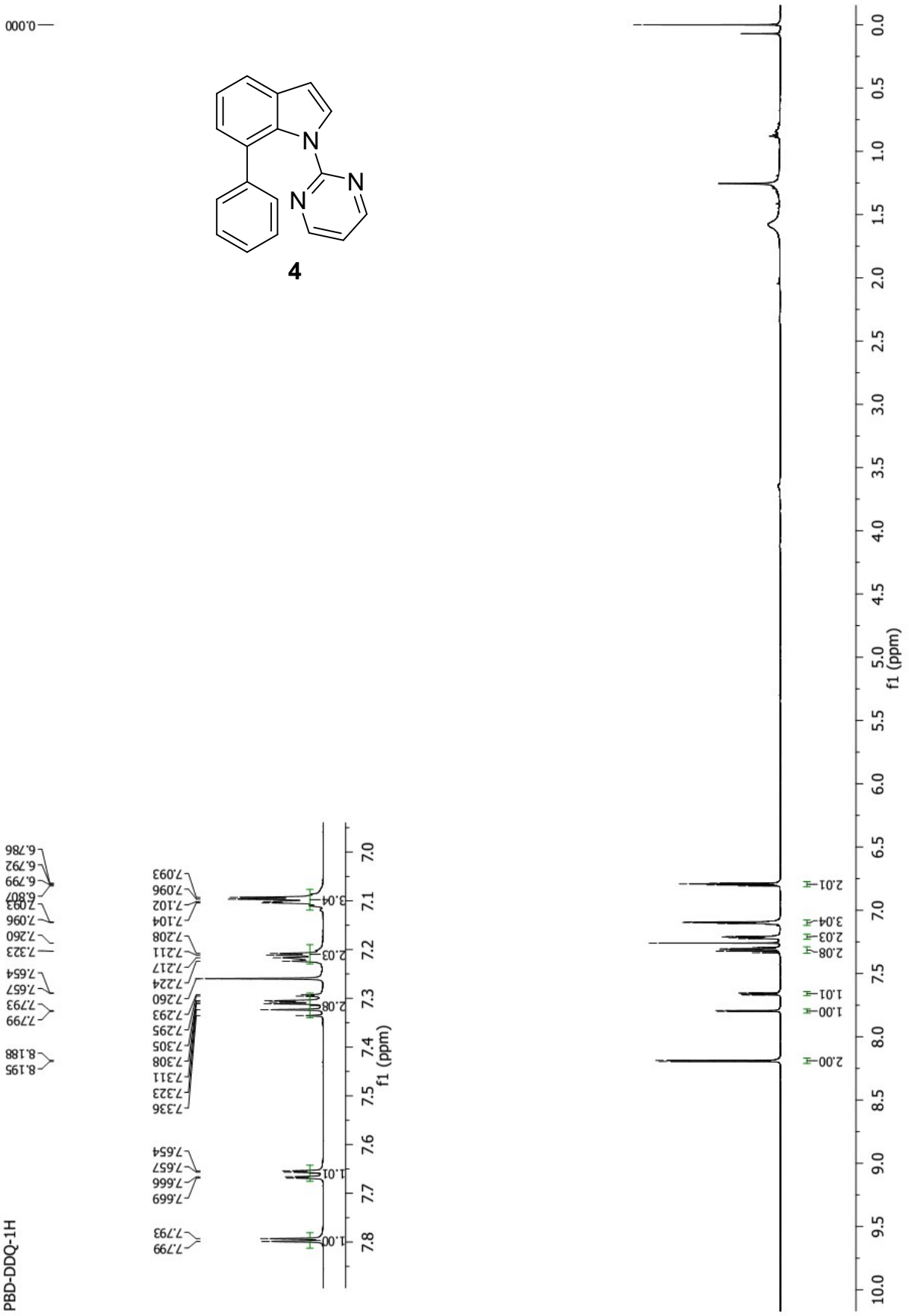

MeO
N
N
N
3x
PBD-5-OMe-DG-13C
f1 (ppm)
f1 (ppm)

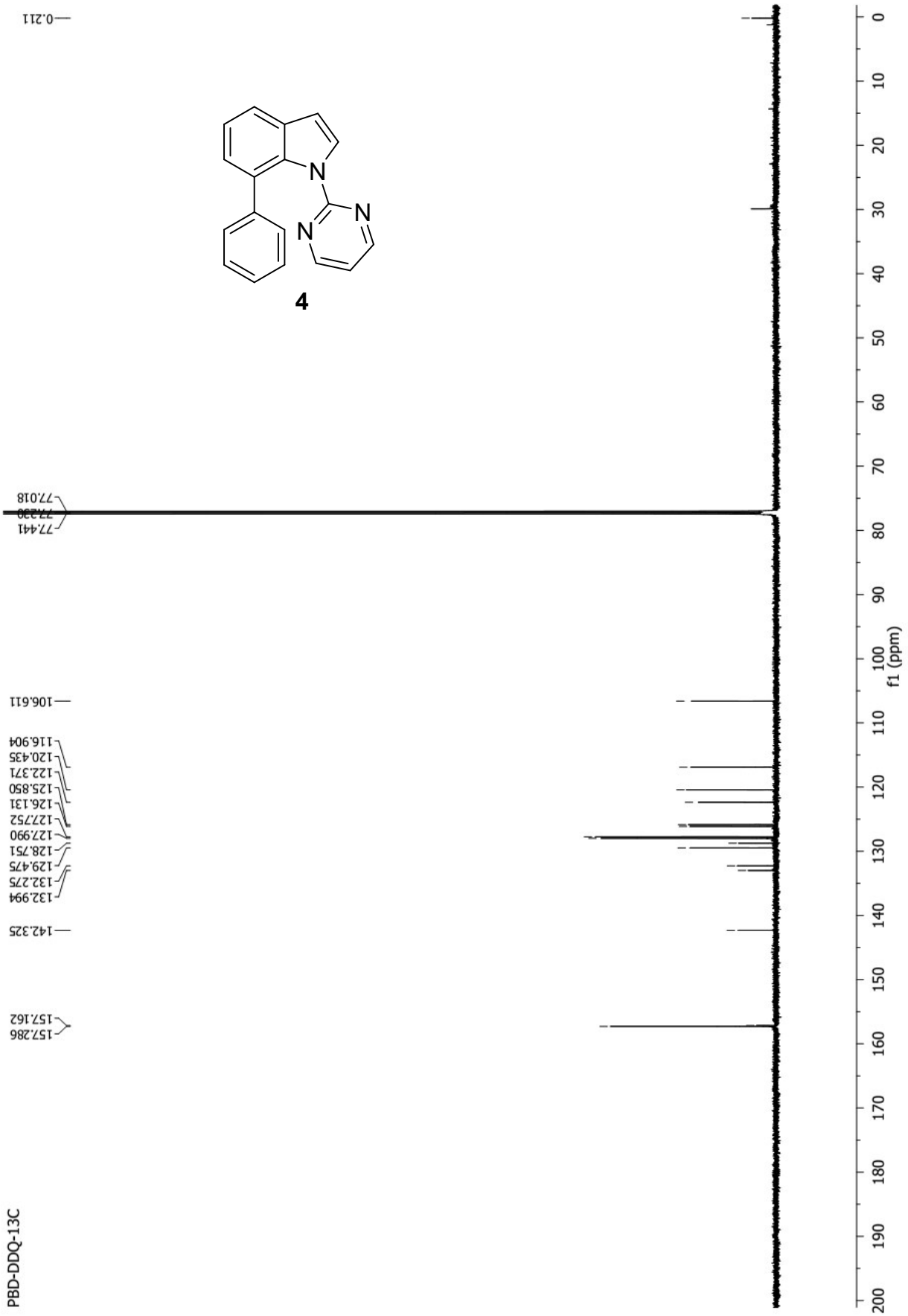

Ph
O
N
N
N
3y
PBD-5-Benzoloxy-1H
f1 (ppm)


Ph
O
N
N
N
3y
PBD-5-benzoloxy-13C
f1 (ppm)

MeO2C
N
N
N
3z
PBD- 5CO2Me-1H
f1 (ppm)

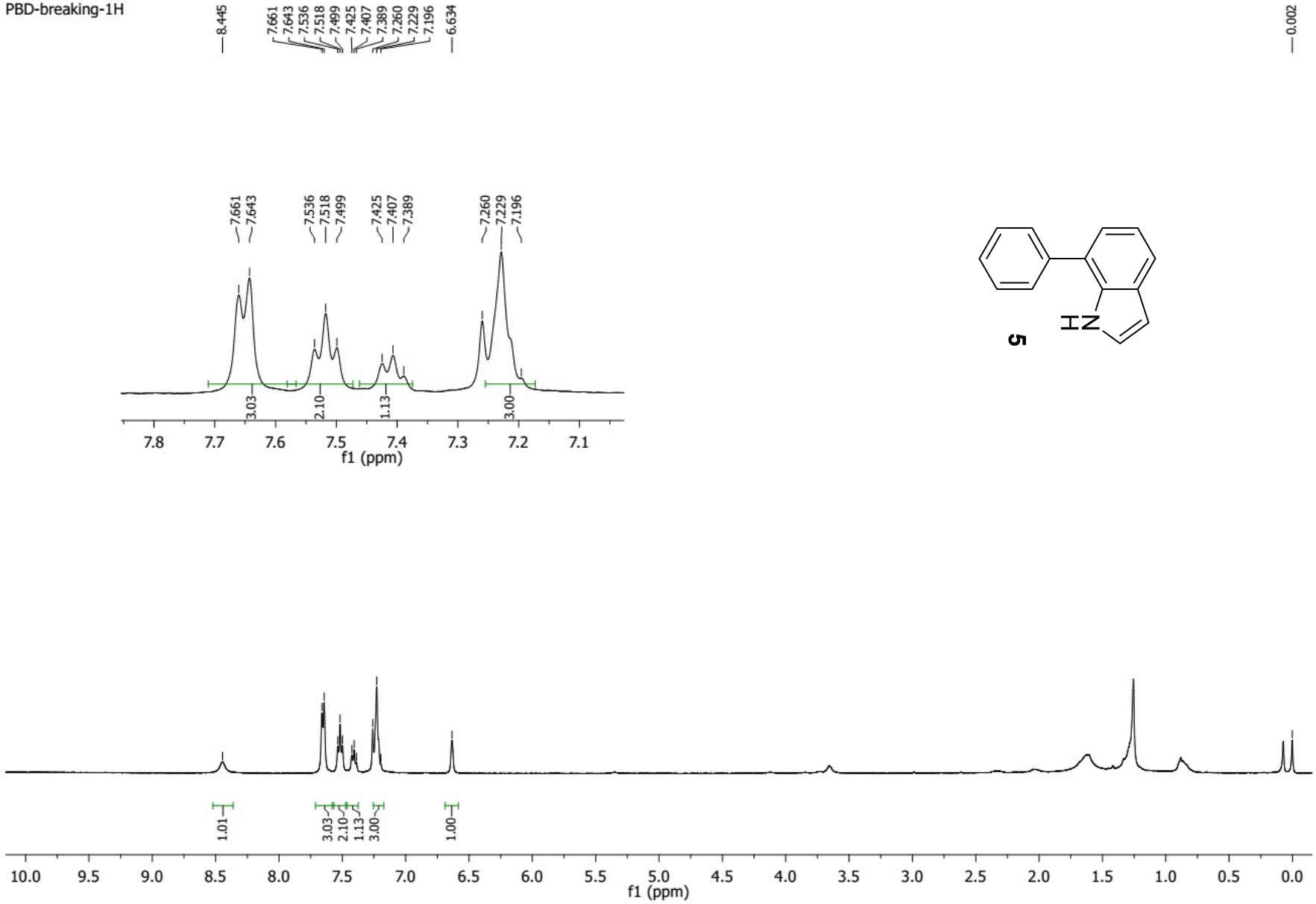

MeO2C
N
N
N
3z
29.016
52.635
52.165
77.442
77.330
77.019
112.906
129.358
132.017
135.253
141.631
145.521
156.706
158.896
167.261
PBD-5CO2Me-13C
f1 (ppm)


0.000
N
N
N
4
PBD-DDQ-1H
8.195
8.188
7.799
7.793
7.657
7.654
7.323
7.260
7.096
7.093
6.807
6.799
6.792
6.786
7.799
7.793
7.669
7.666
7.657
7.654
7.336
7.323
7.311
7.308
7.305
7.295
7.293
7.260
7.224
7.217
7.211
7.208
7.104
7.102
7.096
7.093
1.00
1.01
2.08
2.03
3.04
f1 (ppm)
2.00
1.00
1.01
2.08
2.03
3.04
2.01
f1 (ppm)

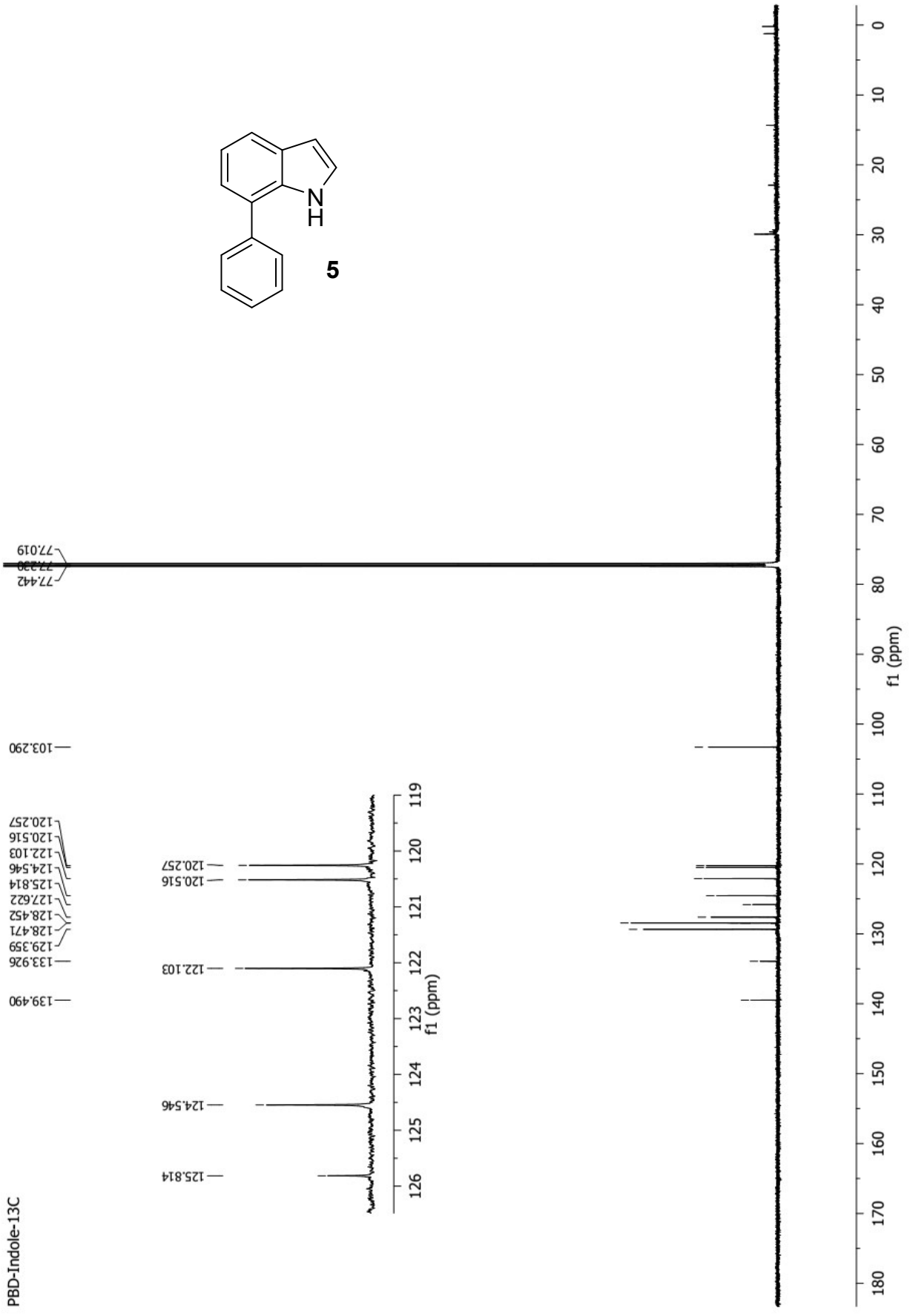

0.211
77.441
77.330
77.018
106.611
116.904
120.435
122.371
125.850
126.131
127.752
127.990
128.751
129.475
132.275
132.994
142.325
157.162
157.286
PBD-DDQ-13C
f1 (ppm)

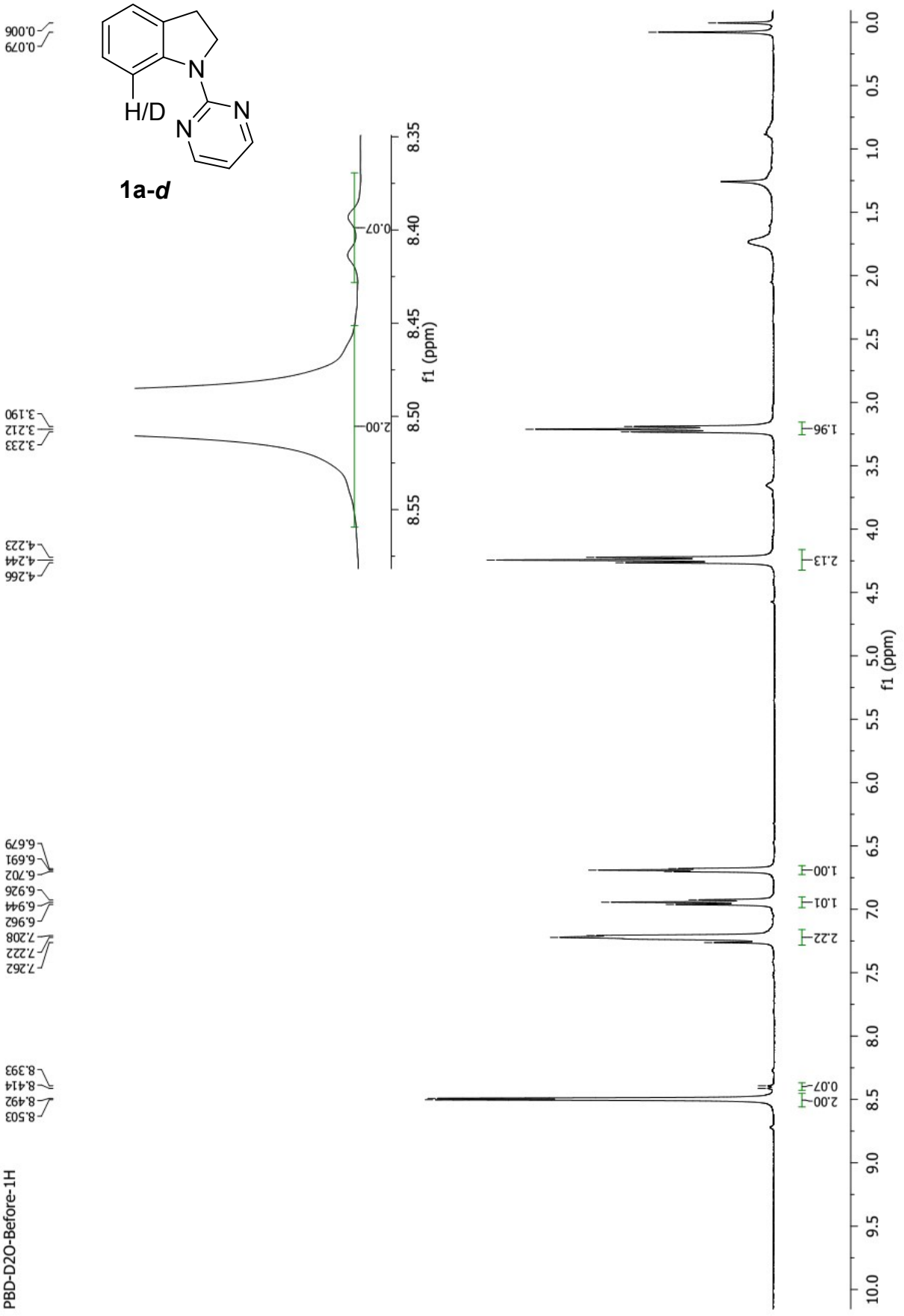
4

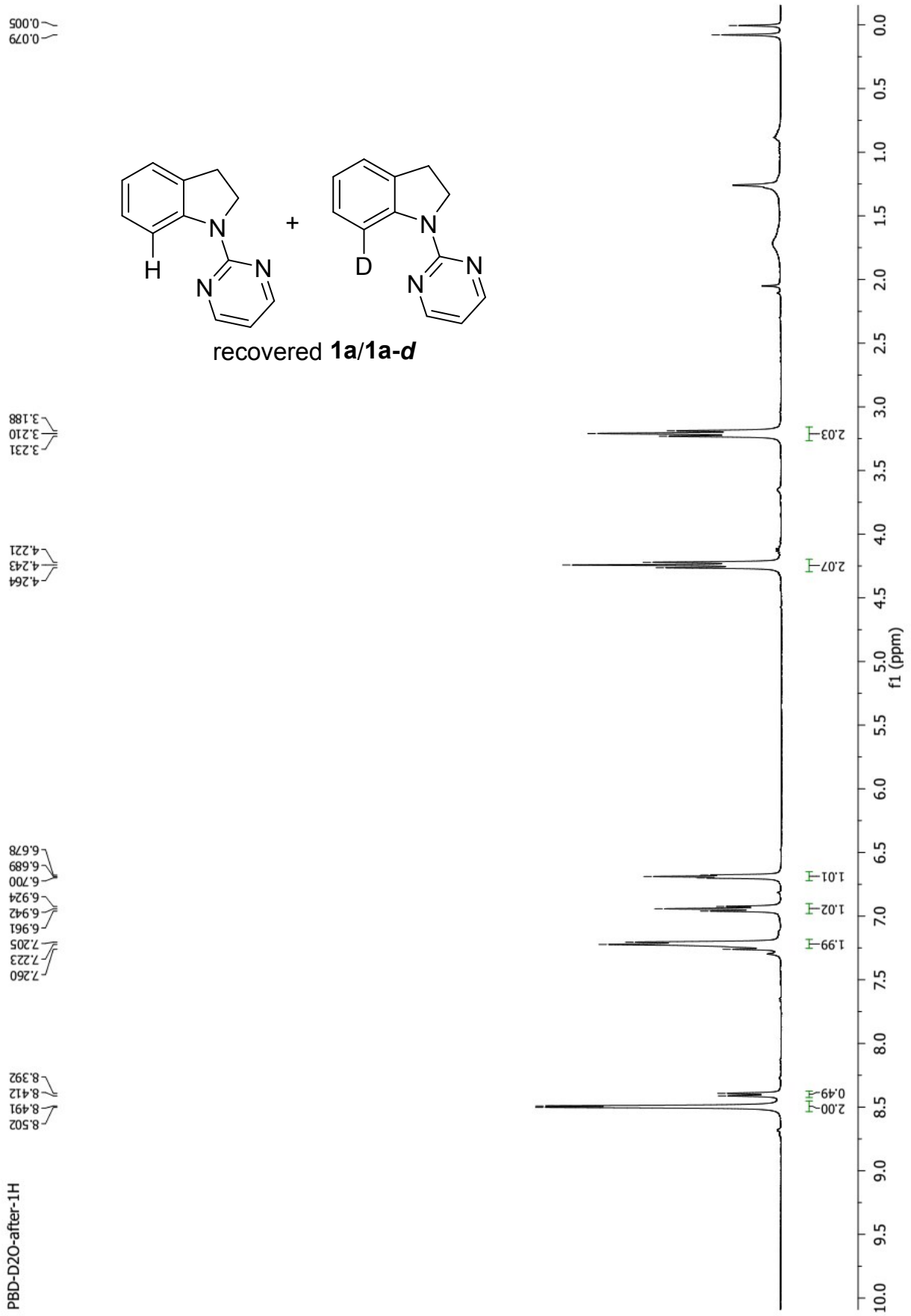
PBD-breaking-1H



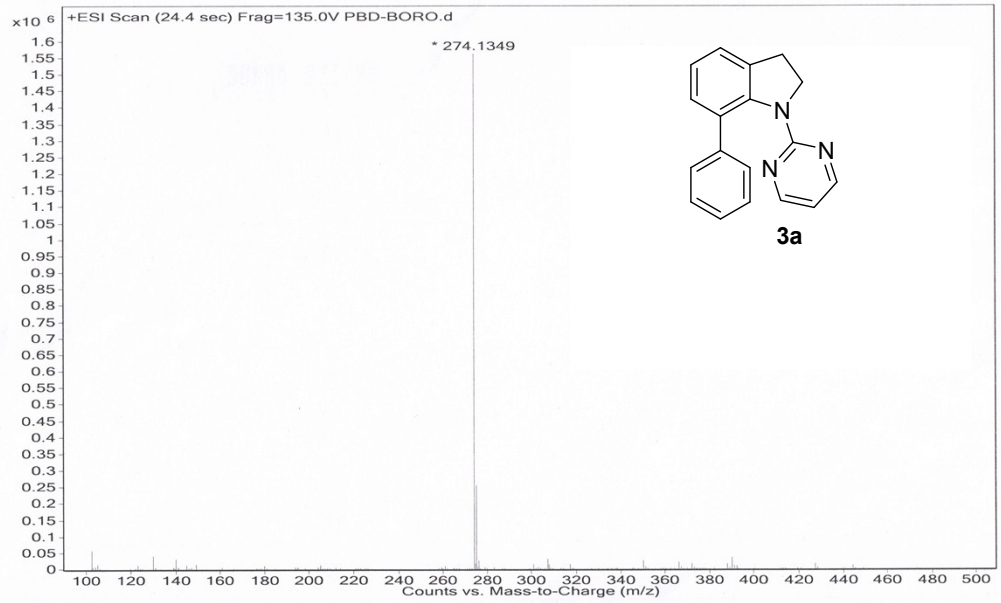
5


N
H
5
PBD-Indole-13C
f1 (ppm)


PBD-D2O-Before-1H
8.503
8.492
8.414
8.393
7.262
7.222
7.208
6.962
6.944
6.926
6.702
6.691
6.679
4.266
4.244
4.223
3.233
3.212
3.190
0.079
0.006
H/D
N
N
N
1a-d
f1 (ppm)
f1 (ppm)
2.00
0.07
1.96
2.13
1.00
1.01
2.22
2.00
0.07

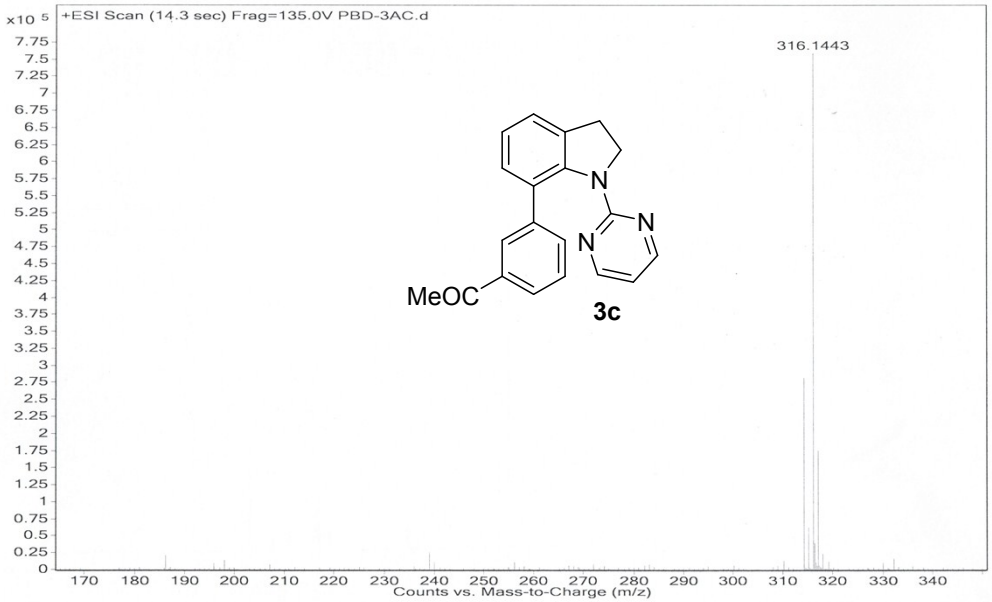

PBD-D2O-after-1H
8.502
8.491
8.412
8.392
7.260
7.223
7.205
6.961
6.942
6.924
6.700
6.689
6.678
4.264
4.243
4.221
3.231
3.210
3.188
0.079
0.005
2.00
0.49
1.99
1.02
1.01
2.07
2.03
f1 (ppm)
recovered 1a/1a-d

Sample Name	PBD-BORO	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-BORO.d	**ACQ Method**		**Comment**		**Acquired Time**	7/19/2017 4:06:02 PM



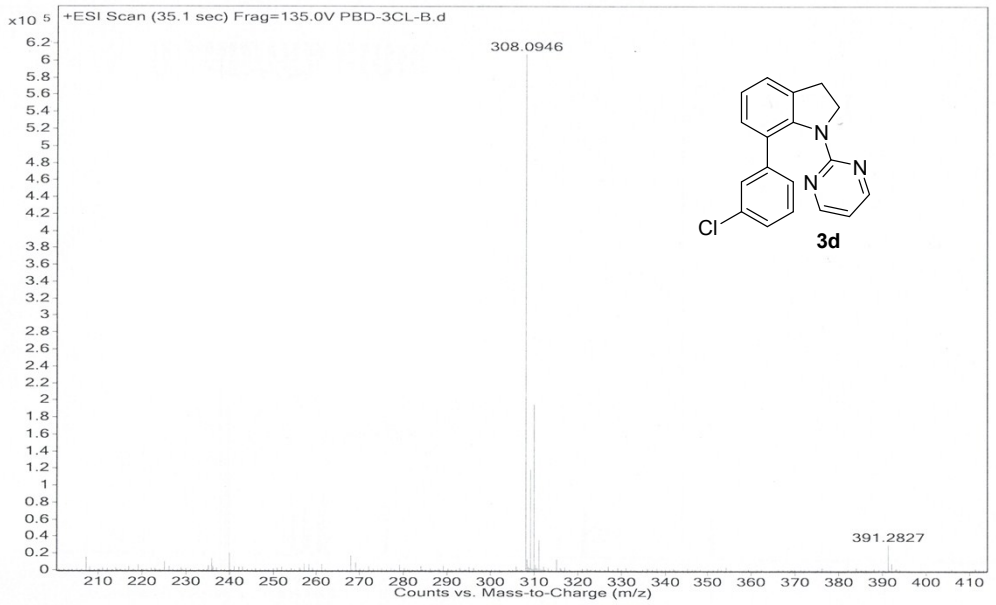
3a

Sample Name	PBD-3AC	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-3AC.d	**ACQ Method**		**Comment**		**Acquired Time**	9/20/2017 4:54:32 PM



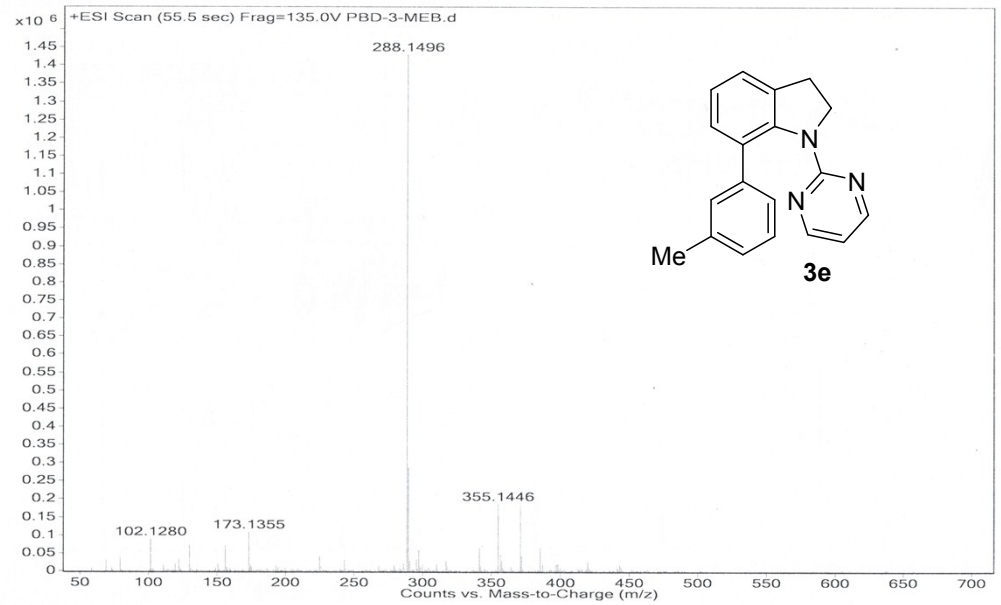
3c

Sample Name	PBD-3CL-B	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-3CL-B.d	**ACQ Method**		**Comment**		**Acquired Time**	9/20/2017 4:49:52 PM



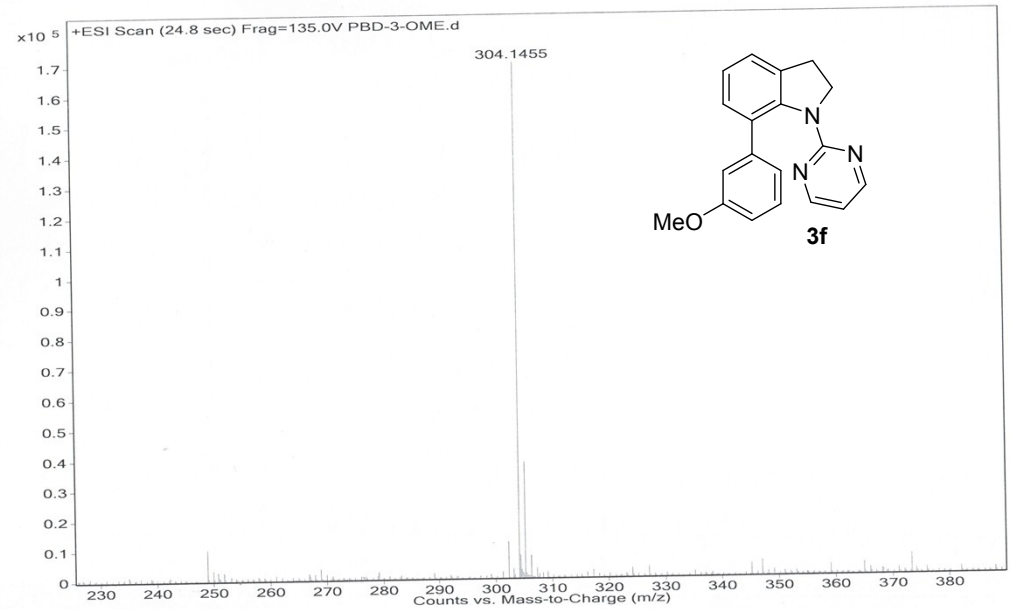
3d

Sample Name	PBD-3-MEB	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-3-MEB.d	**ACQ Method**		**Comment**		**Acquired Time**	9/22/2017 3:31:00 PM



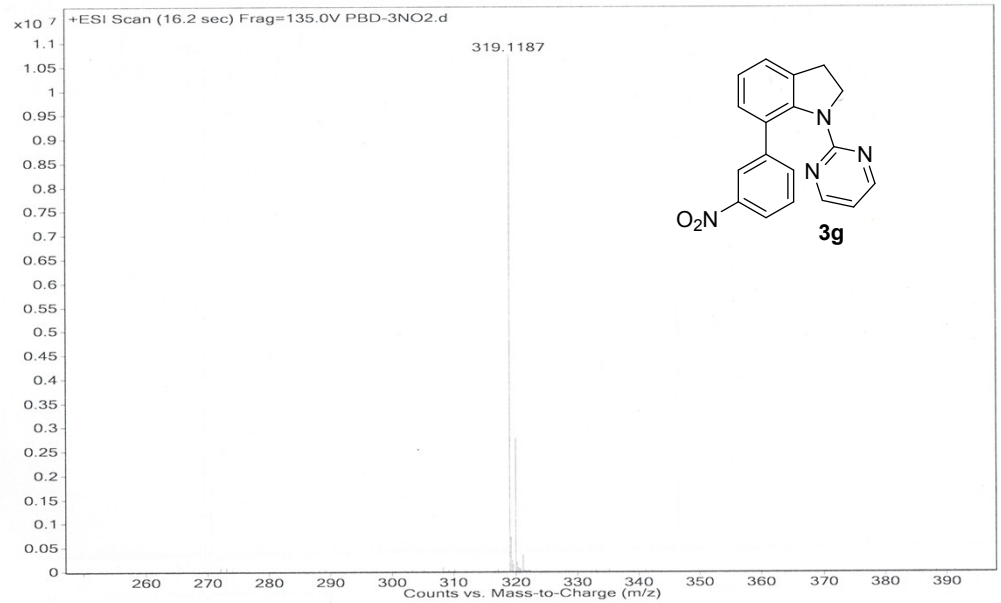
3e

Sample Name	PBD-3-OME	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-3-OME.d	**ACQ Method**		**Comment**		**Acquired Time**	7/21/2017 10:34:45 AM



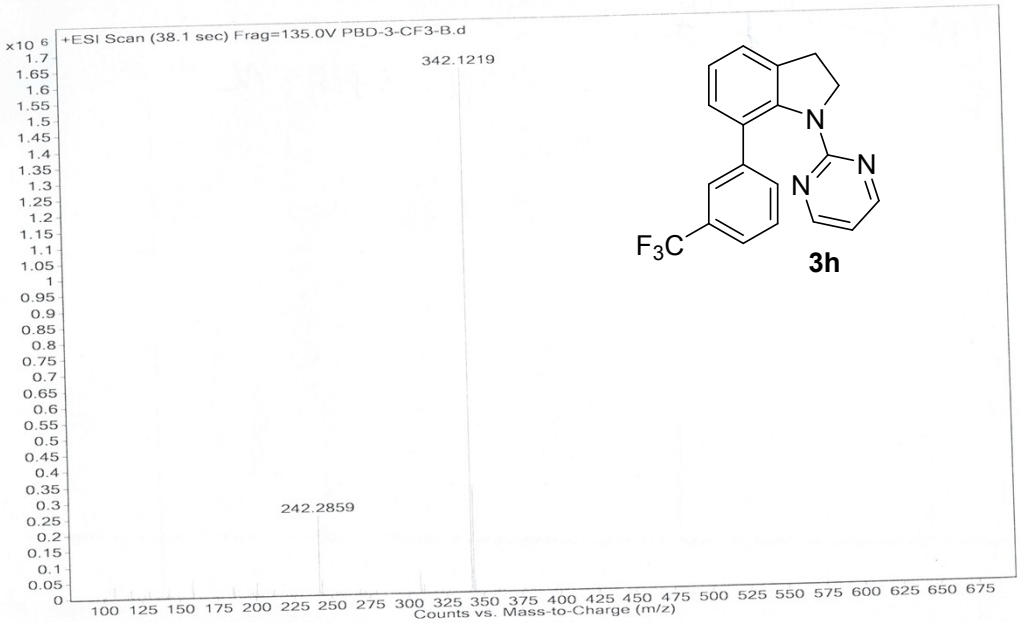
3f

Sample Name	PBD-3NO2	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-3NO2.d	**ACQ Method**		**Comment**		**Acquired Time**	9/20/2017 4:51:34 PM



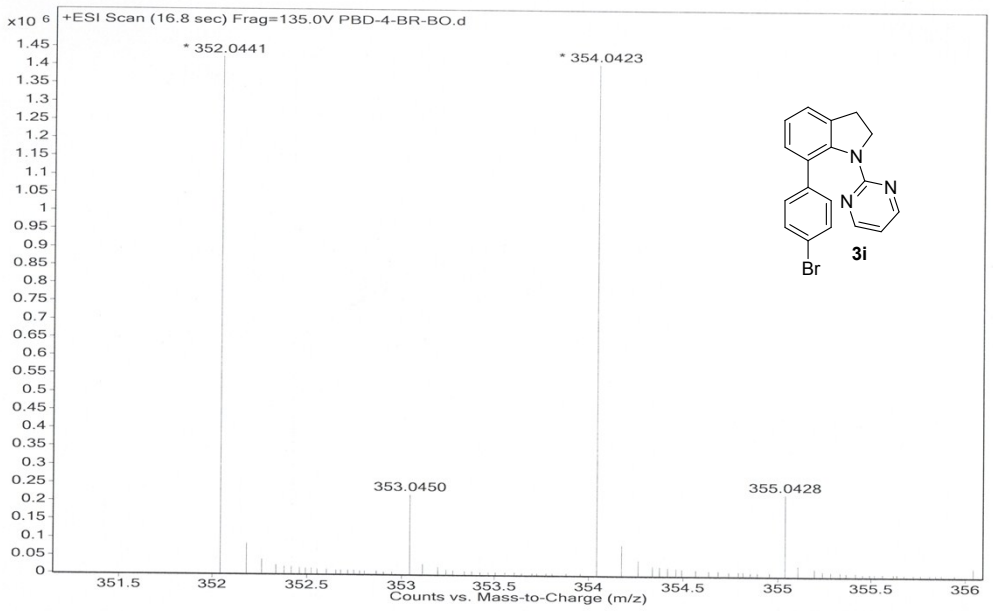
3g

Sample Name	PBD-3-CF3-B	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PBD-3-CF3-B.d	**ACQ Method**		**Comment**		**Acquired Time**	10/20/2017 2:40:15 PM



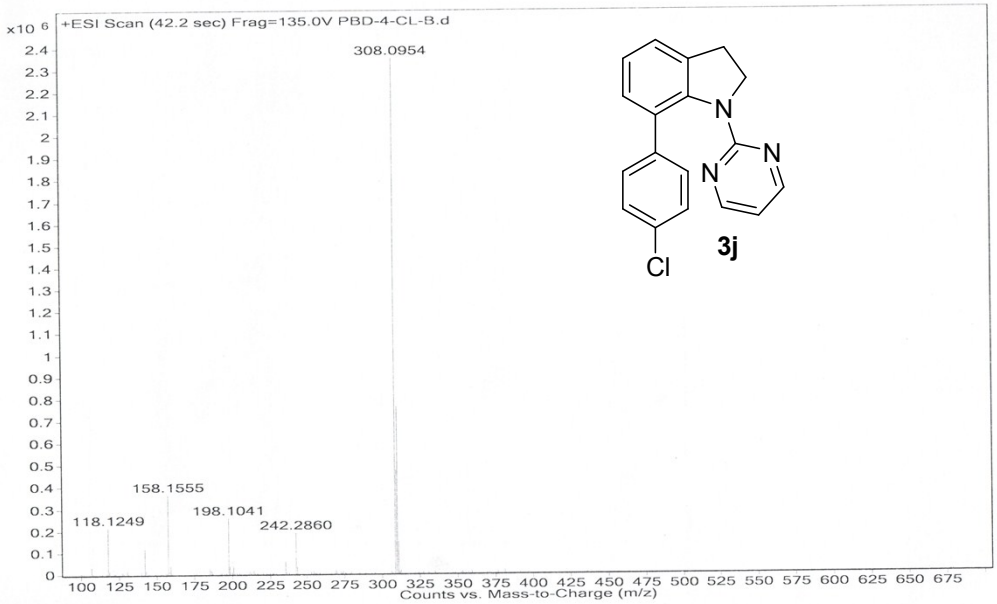
3h

Sample Name	PBD-4-BR-BO	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-4-BR-BO.d	**ACQ Method**		**Comment**		**Acquired Time**	8/18/2017 3:42:19 PM



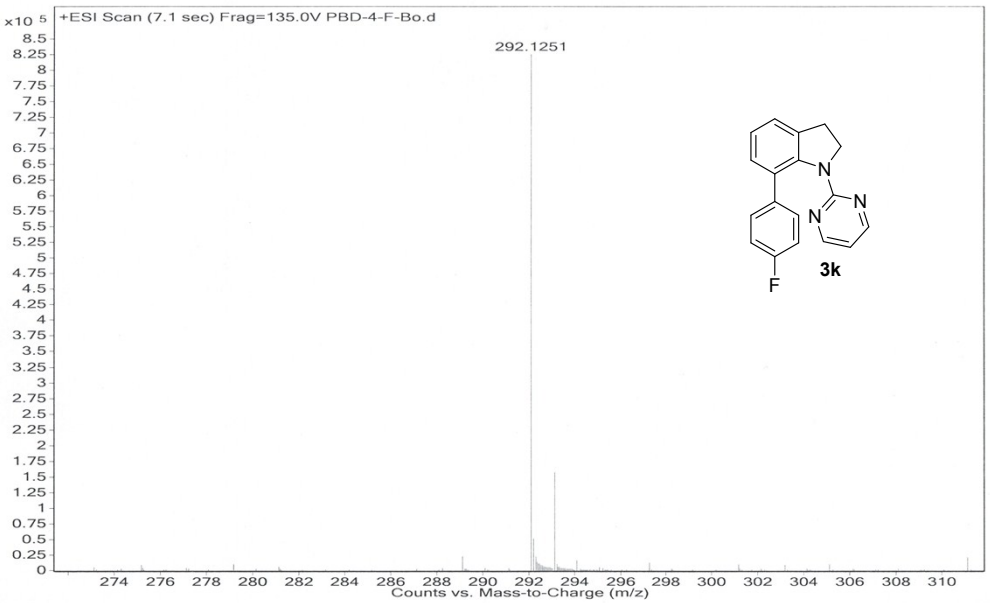
3i

Sample Name	PBD-4-CL-B	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PBD-4-CL-B.d	**ACQ Method**		**Comment**		**Acquired Time**	10/20/2017 2:38:27 PM



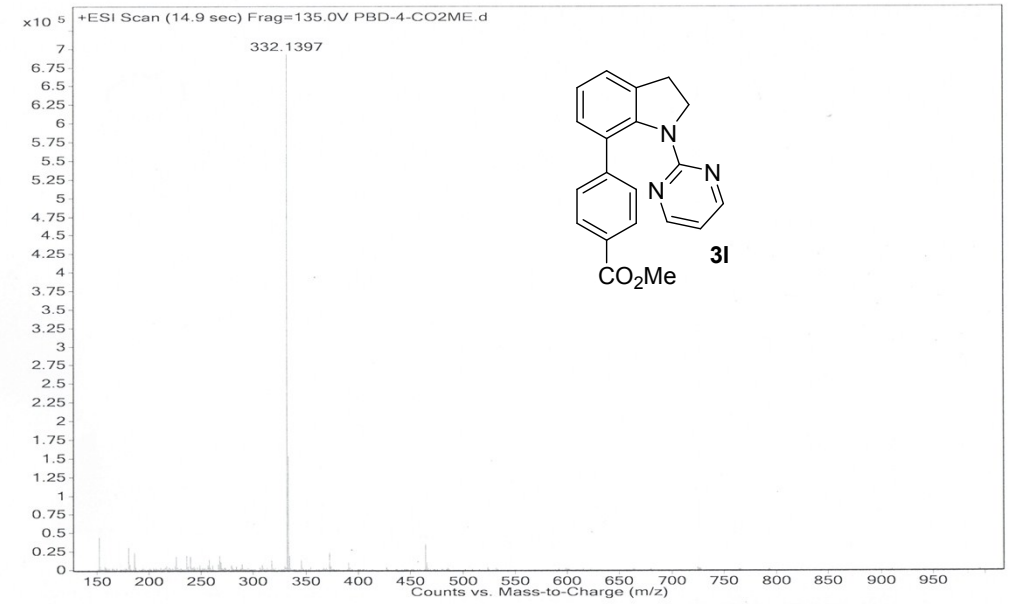
3j

Sample Name	PBD-4-F-Bo	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-4-F-Bo.d	**ACQ Method**		**Comment**		**Acquired Time**	8/22/2017 3:28:32 PM

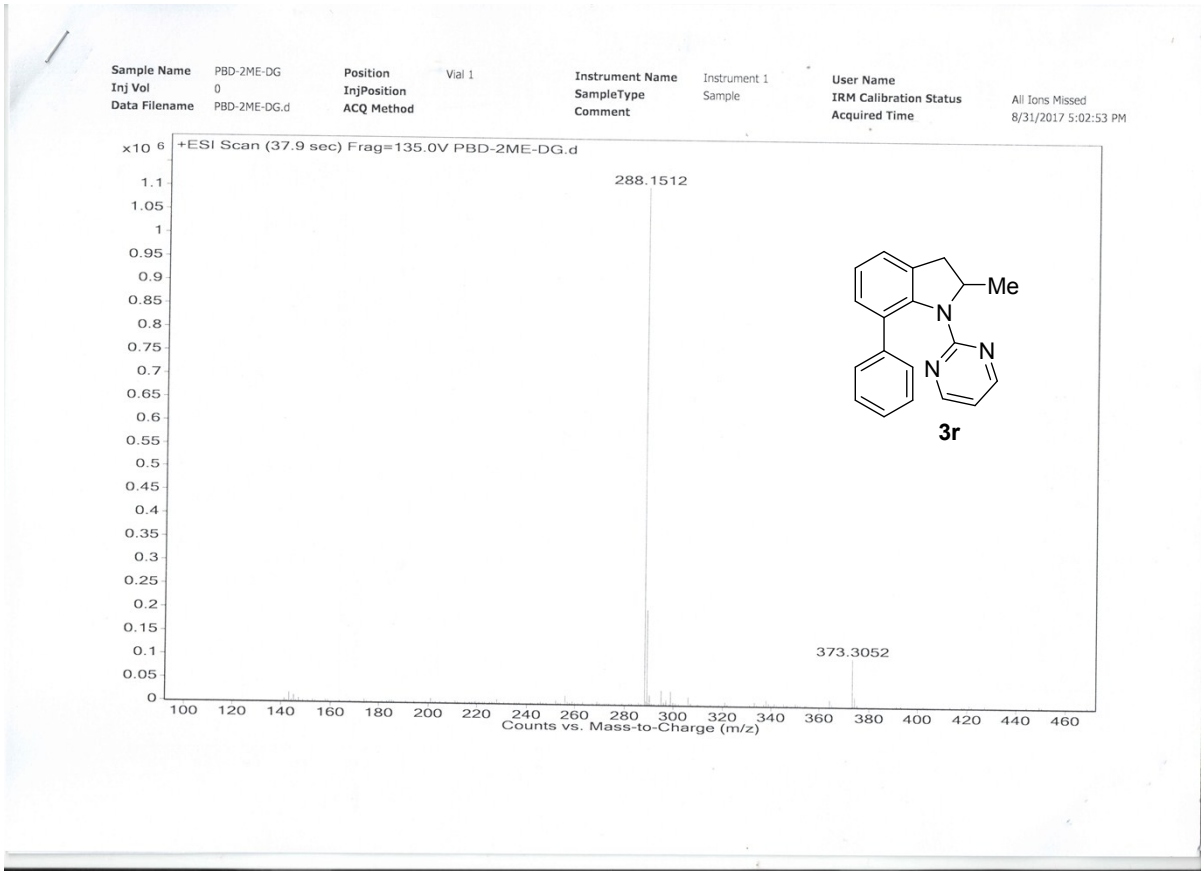


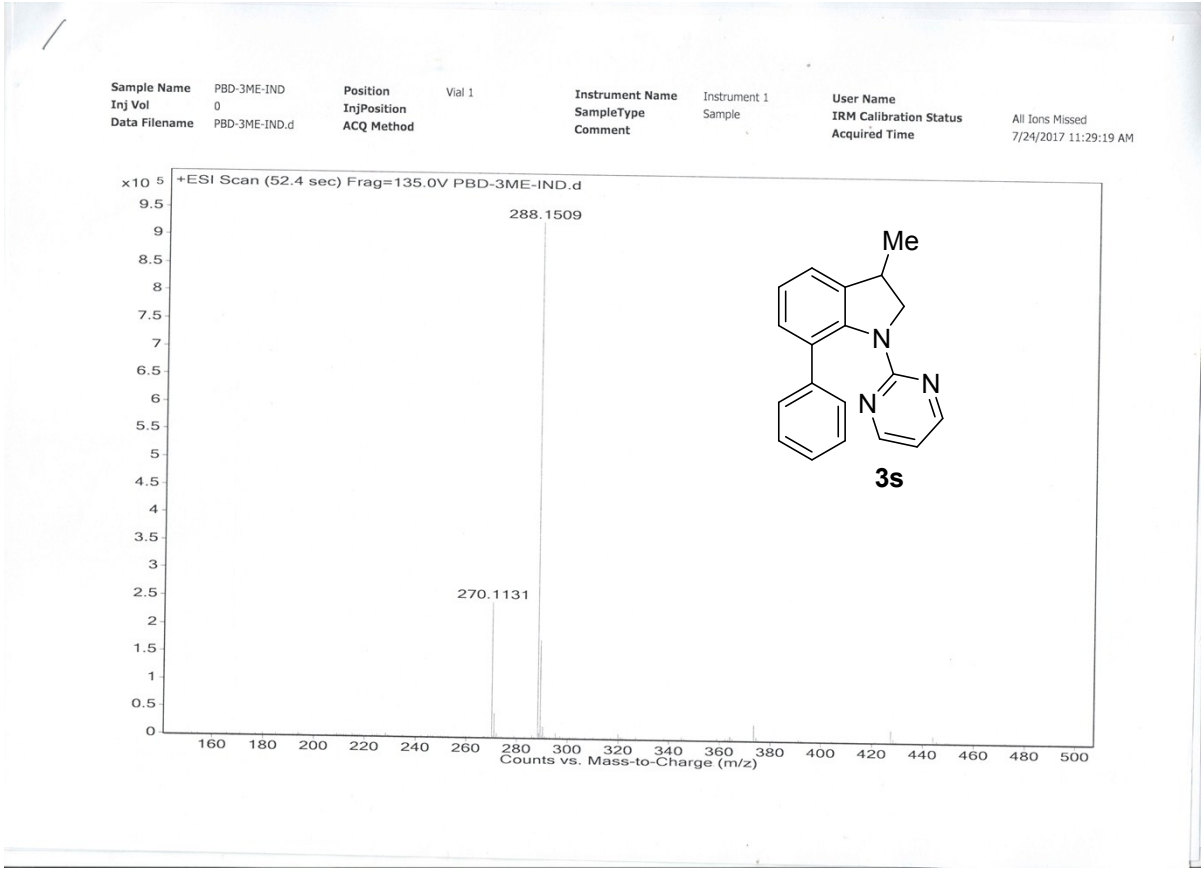
3k

Sample Name	PBD-4-CO2ME	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-4-CO2ME.d	**ACQ Method**		**Comment**		**Acquired Time**	9/21/2017 4:48:41 PM

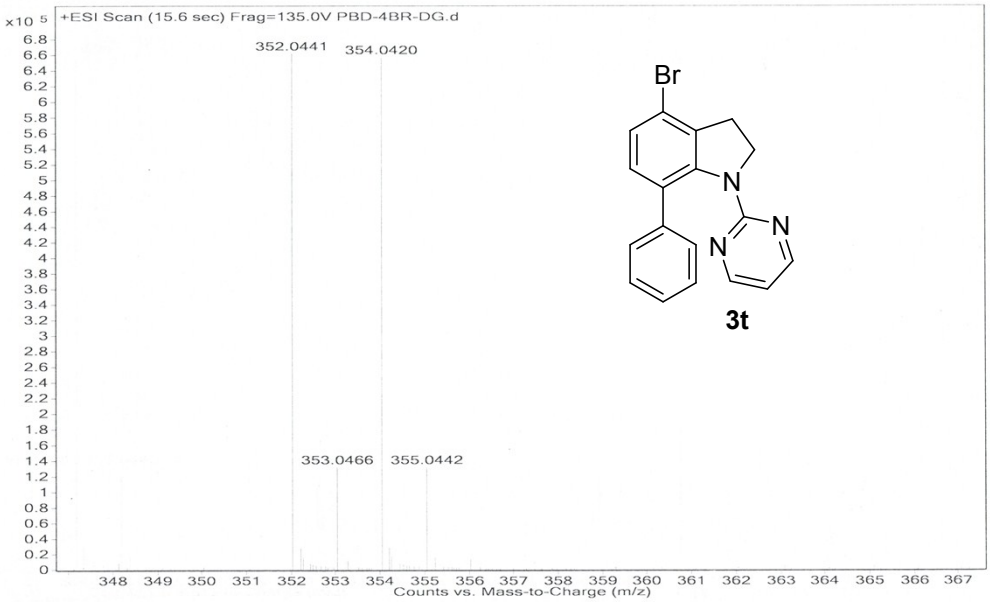


3l


Sample Name PBD-2ME-DG
Inj Vol 0
Data Filename PBD-2ME-DG.d
Position Vial 1
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status All Ions Missed
Acquired Time 8/31/2017 5:02:53 PM
x10 6
+ESI Scan (37.9 sec) Frag=135.0V PBD-2ME-DG.d
288.1512
373.3052
Counts vs. Mass-to-Charge (m/z)
Me
N
N
N
3r

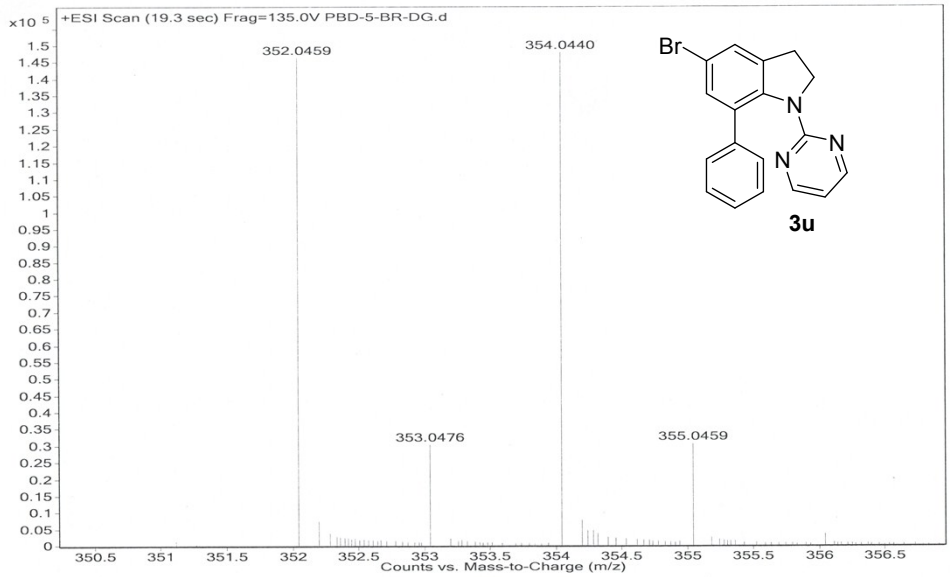

Sample Name PBD-3ME-IND
Inj Vol 0
Data Filename PBD-3ME-IND.d
Position Vial 1
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status All Ions Missed
Acquired Time 7/24/2017 11:29:19 AM
x10 5
+ESI Scan (52.4 sec) Frag=135.0V PBD-3ME-IND.d
288.1509
270.1131
Counts vs. Mass-to-Charge (m/z)
Me
N
N
N
3s

Sample Name	PBD-4BR-DG	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PBD-4BR-DG.d	**ACQ Method**		**Comment**		**Acquired Time**	10/17/2017 11:56:37 AM



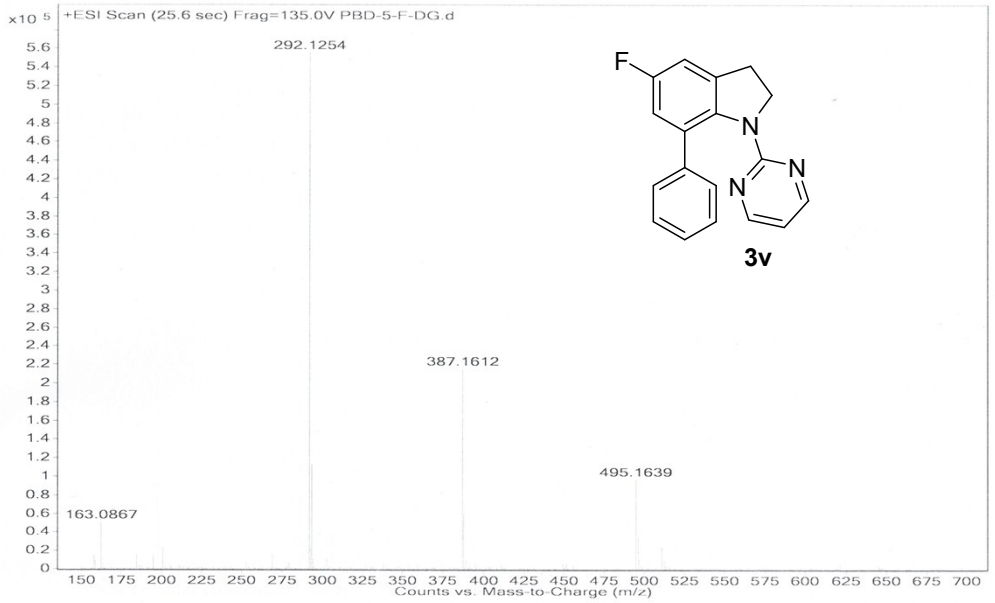
3t

Sample Name	PBD-5-BR-DG	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-5-BR-DG.d	**ACQ Method**		**Comment**		**Acquired Time**	8/18/2017 3:35:01 PM



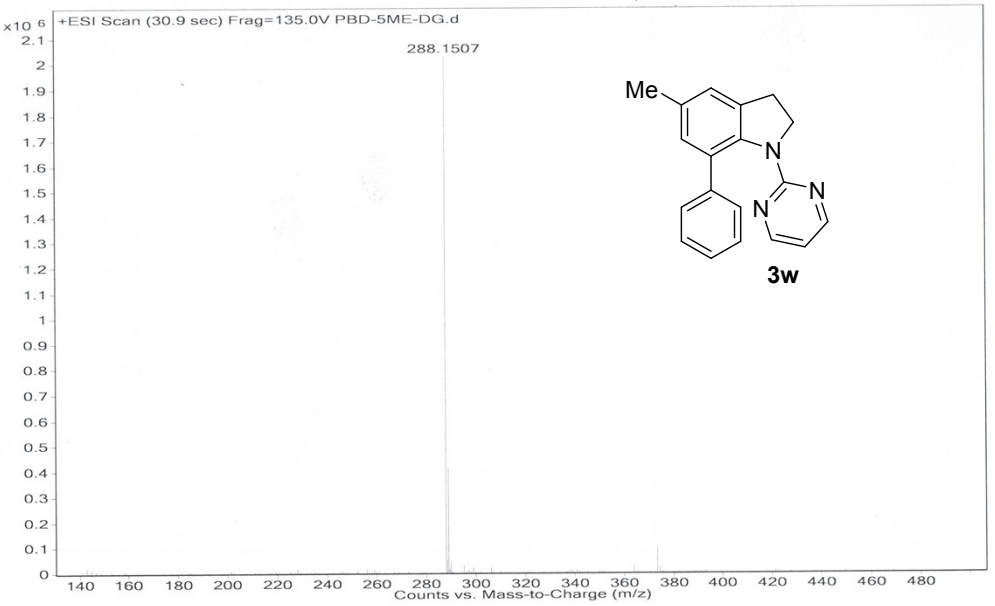
3u

Sample Name	PBD-5-F-DG	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	0	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	PBD-5-F-DG.d	ACQ Method		Comment		Acquired Time	10/27/2017 3:17:07 PM



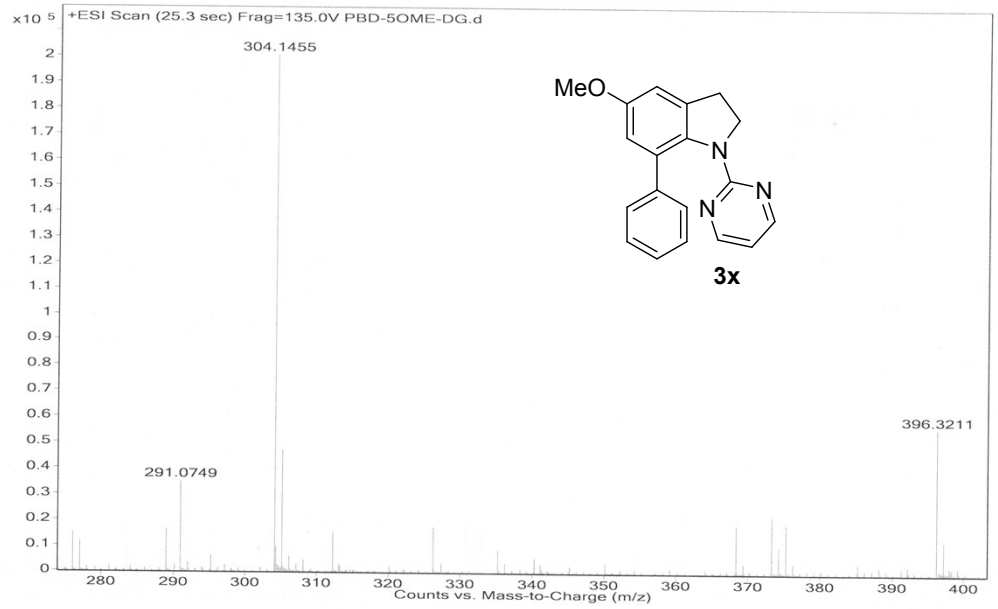
3v

Sample Name	PBD-5ME-DG	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	0	InjPosition		SampleType	Sample	IRM Calibration Status	All Ions Missed
Data Filename	PBD-5ME-DG.d	ACQ Method		Comment		Acquired Time	8/31/2017 5:04:51 PM



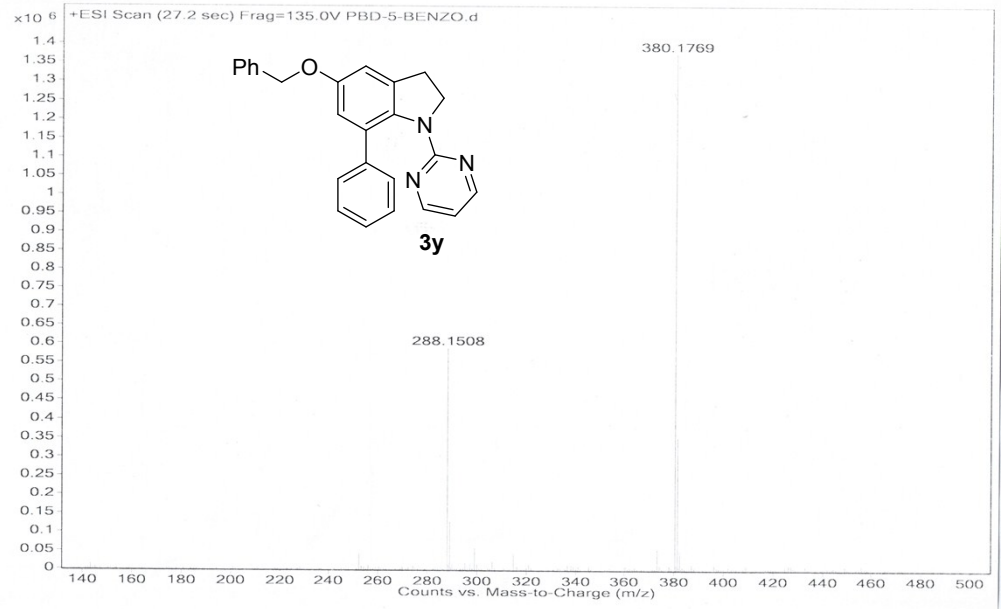
3w

Sample Name	PBD-5OME-DG	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-5OME-DG.d	**ACQ Method**		**Comment**		**Acquired Time**	8/21/2017 3:46:17 PM



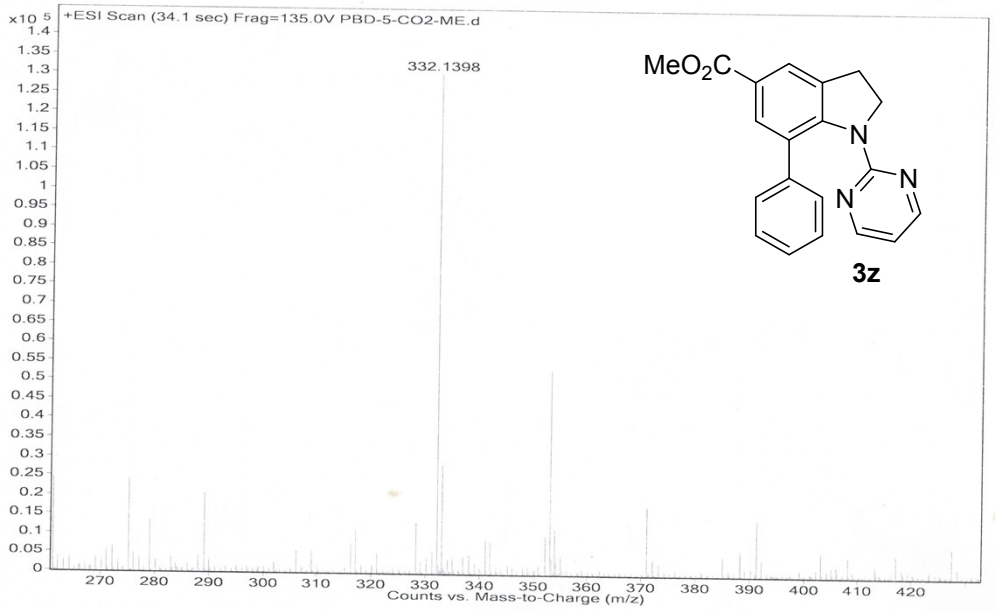
3x

Sample Name	PBD-5-BENZO	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	All Ions Missed
Data Filename	PBD-5-BENZO.d	**ACQ Method**		**Comment**		**Acquired Time**	8/31/2017 5:09:21



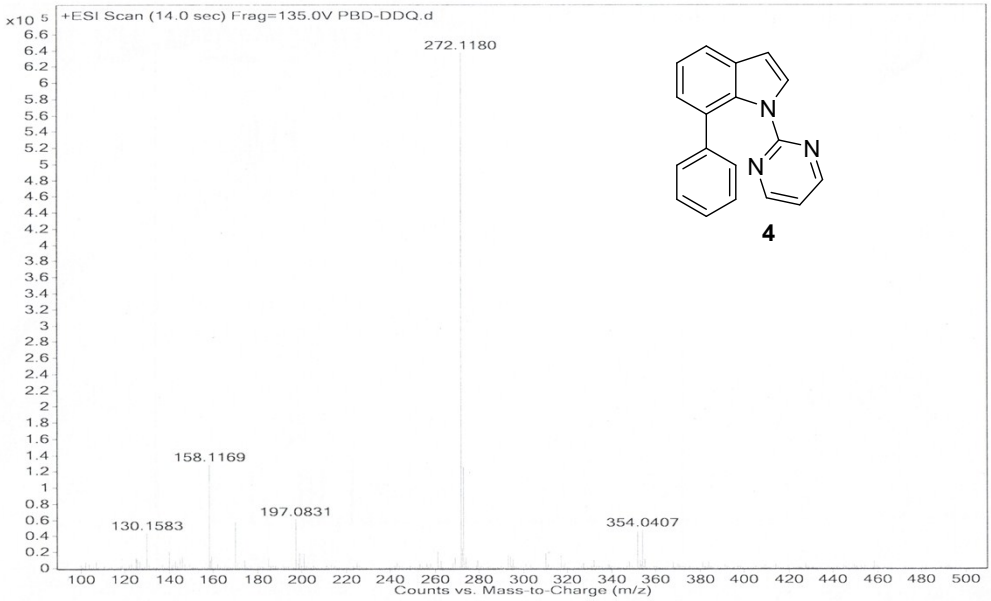
3y

Sample Name	PBD-5-CO2-ME	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	PBD-5-CO2-ME.d	**ACQ Method**		**Comment**		**Acquired Time**	9/18/2017 12:01:04



3z

Sample Name	PBD-DDQ	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PBD-DDQ.d	**ACQ Method**		**Comment**		**Acquired Time**	10/17/2017 11:58:47 AM



4

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	PBD-NAOET.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable