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Supporting Information
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# Copper-Catalyzed Aromatic C–H Bond Halogenation Using Lithium Halides as Halogenating Reagents

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## Supporting Information

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## I. General procedures

Cu-catalyzed C-H halogenation of 2-arylpyridines was performed in sealed vials. Substrates **1**, **2**, **9**, **11**, **12**, and **13** were purchased from Alfa Aesar or Acros and used without purification, substrates **3**,[1a] **4**,[1b] **5**,[1a] **6**,[1a] **7**,[1b] **8**,[1b] and **10**[1b] were synthesized according to the literature reported methods.[1] The HOAc and $Ac_2O$ were purified prior to use following the guidelines of Perrin and Armarego.[2] The Reactions were monitored by thin-layer chromatography (TLC). $^1H$ and $^{13}C$ NMR spectra were obtained on a MERCURYplus 400 at 400 MHz and 100 MHz, respectively. Data for $^1H$ NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling

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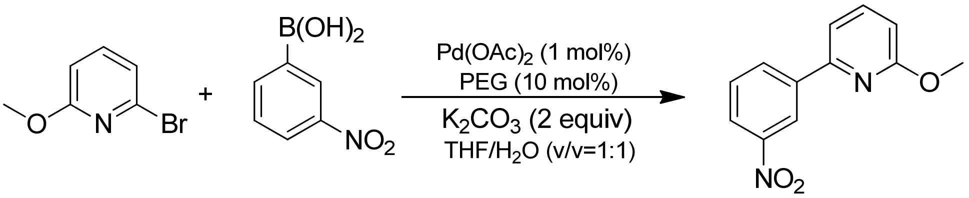
[1] (a) Liu, C.; Yang, W.-B. *Chem. Comm.* **2009**, 6267; (b) Razler, T.; Hsiao, Y.; Qian, F.; Fu, R.; Khan, R.; Doubleday, W. *J. Org. Chem*. **2009**, *74*, 1381.

[2] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals;* 5th ed., Pergamon Press, Oxford, 1988.

constant (Hz), and assignment. Data for $^{13}C$ NMR are reported in terms of chemical shift (δ ppm). Mass spectra were recorded on an AMD 402/3 or a HP 5989A mass selective detector. Infrared spectra were recorded on a AVATAR 370 machine.

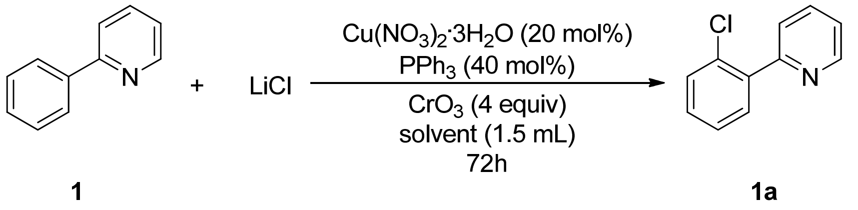
## II. The synthesis of 2-Methoxy-6-(3-nitrophenyl)pyridine[1b]



Under air, a mixture of 2-bromo-6-methoxypyridine (945 mg, 5 mmol), (3-nitrophenyl)boronic acid (1098.5 mg, 6.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), PEG (1 g, 0.5 mmol), $K_2CO_3$ (1.38 g, 10 mmol), THF (8 mL) and $H_2O$ (8 mL) was stirred for 3 days at 80 °C. Then the mixture was diluted with $H_2O$ and extracted with EtOAc (3 x 50 mL). The extract was washed with brine (2 x 50 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via chromatography on silica gel with petroleum ether/$Et_2O$ (20/1 (v/v)) as the eluent to afford the white solid in 35% yield; m.p.: 102-104 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H), 6.79 (d, $J$ = 8.4 Hz, 1H), 7.42 (d, $J$ = 7.2 Hz, 1H), 7.63 (t, $J$ = 8.0 Hz, 1H), 7.70 (t, $J$ = 8.0 Hz, 1H), 8.23-8.25 (m, 1H), 8.39 (d, $J$ = 7.6 Hz, 1H), 8.90 (t, $J$ = 2.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 53.4, 110.8, 113.1, 121.5, 123.3, 129.5, 132.4, 139.4, 140.7, 148.7, 151.9, 164.0; IR (KBr): ν 1575, 1523, 1469, 1429, 1248, 794, 739 $cm^{-1}$; MS (EI) m/z: 230.1 ($M^+$), 229.1 $(M-1)^+$, 200.1, 184.1, 155.1, 154.1, 153.1, 141.1, 140.1, 127.1, 114.0, 77.0; HRMS (EI) Calcd for $C_{12}H_{10}N_2O_3$: 230.0691, Found: 230.0685.

## III. The optimization for the C-H halogenation

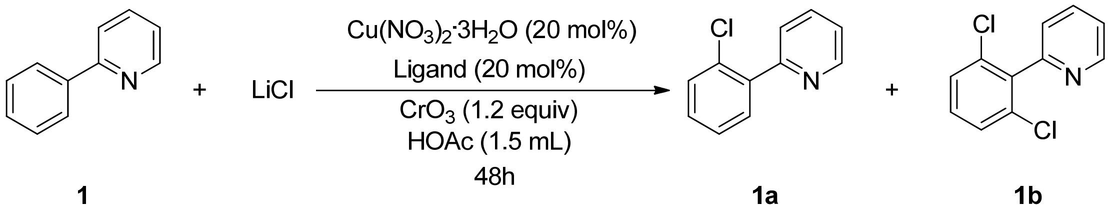
**STable 1.** Screening of Solvents for the Cu-Catalyzed C-H Halogenation[a]



| Entry | Solvent | Yield (%) (**1a**)[b] |
|---|---|---|
| 1 | NMP | N.R. |
| 2 | DMSO | N.R. |
| 3 | DMF | N.R. |
| 4 | $CH_3CN$ | 30 |
| 5 | THF | N.R. |
| 6 | $CH_3NO_2$ | N.R. |
| 7 | 1,4-dioxane | 30 |
| 8 | $^i$PrOH | N.R. |
| 9 | acetone | N.R. |
| 10 | toluene | 31 |

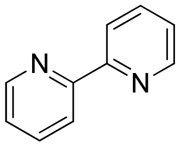
[a] Conditions: **1** (31 mg, 0.2 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (9.7 mg, 20 mol%), $PPh_3$ (21 mg, 40 mol%), LiCl (34 mg, 0.8 mmol), $CrO_3$ (80 mg, 0.8 mmol), solvent (1.5 mL), 150 °C. [b] GC yield with *n*-dodecane as an internal standard.

**STable 2.** Screening of Ligands for the Cu-Catalyzed C-H Halogenation[a]

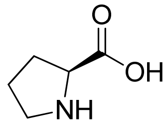


| Entry | Ligand | Yield (%) (**1a**)[b] | Yield (%) (**1b**)[b] |
|---|---|---|---|
| 1 | 2,2-bipyridine | 8 | 3 |
| 2 | L-proline | 33 | 34 |
| 3 | 1,2-Diaminocyclohexane | 24 | - |
| 4 | dppp | 26 | 29 |
| 5 | dppe | 11 | 62 |
| 6 | dppf | <5 | - |
| 7 | TEMDA | 52 | 13 |
| 8 | 1,10-phenanthroline | 23 | 42 |

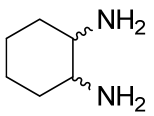
[a] Conditions: **1** (31 mg, 0.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (9.7 mg, 20 mol%), LiCl (34 mg, 0.8 mmol), $CrO_3$ (24 mg, 0.24 mmol), HOAc (1.5 mL), ligand (20 mol%), 150□. [b] GC yield with *n*-dodecane as internal standard.



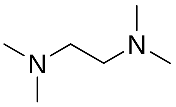
2,2-bipyridine



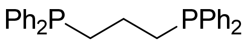
L-proline



1,2-Diaminocyclohexane



TMEDA



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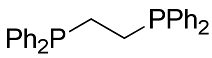

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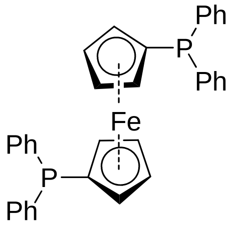
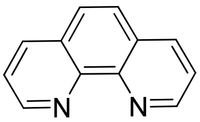
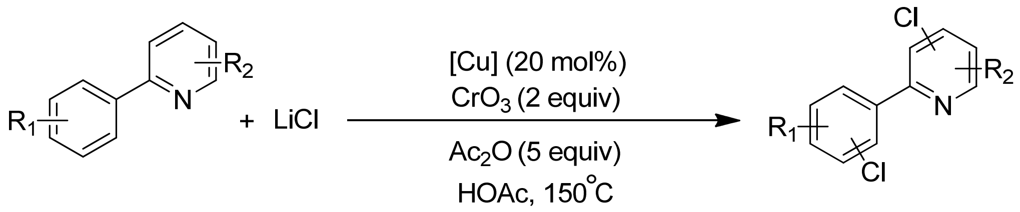


dppf

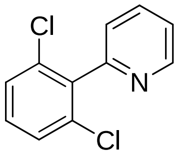


1,10-phenanthroline

## IV. Representative procedure for Cu-catalyzed C-H bond chlorination



### Synthesis of 2-(2,6-dichlorophenyl)pyridine (1b)[3] as a typical example:



**1b**

In a sealed tube, a solution of subtrate **1** (31 mg, 0.2 mmol), LiCl (34 mg, 0.8 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (9.7 mg, 0.04 mmol), $CrO_3$ (40 mg, 0.4 mmol), $Ac_2O$ (102 mg, 1.0 mmol) in HOAc (1.5 mL) was stirred at 150 °C for 2 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The extract was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via chromatography on silica gel with petroleum

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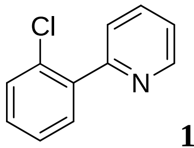
[3] Chen, X.; Hao, X. S.; Goodhue, C. E.; Yu, J. Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790.

ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford oil **1b** in 71% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.34-7.37 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.82 (td, *J* = 2.0, 7.6 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 2929, 1593, 1566, 1422, 1191, 1116, 773, 747 $cm^{-1}$; MS (EI) m/z: 227.0 [$M^+$ ($^{37}Cl^{37}Cl$)] (3.43), 225.0 [$(M-1)^+$ ($^{37}Cl^{35}Cl$)] (20.26), 223.0 [$M^+$ ($^{35}Cl^{35}Cl$)] (32.07), 190.0, 188.0, 161.0, 153.1, 152.1.

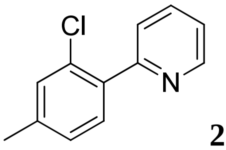
**2-(2-Chlorophenyl)pyridine (1a)**[3]



**1a**

The separative method of product (**1a)** is the same as that of **1b**. Oil, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.29-7.32 (m, 1H), 7.32-7.39 (m, 2H), 7.48 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.60 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.77 (td, *J* = 1.6, 7.6 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 2919, 1573, 1421, 1128, 751 $cm^{-1}$; MS (EI) m/z: 191.0 [$M^+$ ($^{37}Cl$)] (19.72), 189.0 [$M^+$ ($^{35}Cl$)] (51.25), 188.0, 155.1, 154.1, 153.0, 128.0, 127.0, 126.0.

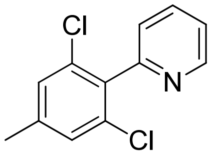
**2-(2-Chloro-4-methylphenyl)pyridine (2a)**



**2a**

In a sealed tube, a solution of substrate **2** (67.6 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 $^oC$ for 6 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford oil **2a** in 32% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.30 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 8.71 (d, *J* = 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.9, 122.1, 124.8, 127.8, 130.5, 131.3, 131.7, 135.7, 136.2, 139.9, 149.4, 156.8; IR (KBr): ν 2924, 1609, 1585, 1463, 1430, 874, 783 cm$^{-1}$; MS (EI) m/z: 205.1 [M$^+$ ($^{37}$Cl)] (19.72), 203.1 [M$^+$ ($^{35}$Cl)] (66.28), 169.1, 168.1, 167.1, 153.1. HRMS (EI) Calcd for $C_{12}H_{10}ClN$: 203.0502, Found: 203.0505.

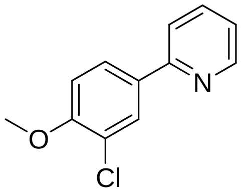
**2-(2,6-Dichloro-4-methylphenyl)pyridine (2b)**[3]



**2b**

The separative method of product (**2b)** is the same as that of **2a**. Oil, 30% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.16 (s, 2H), 7.31-7.35 (m, 2H), 7.73 (td, *J* = 1.6, 7.6 Hz, 1H), 8.68 (d, *J* = 4.8 Hz, 1H ); IR (KBr): ν 2923, 1731, 1600, 1494, 1452, 736, 696 cm$^{-1}$; MS (EI) m/z: 241.0 [M$^+$ ($^{37}$Cl$^{37}$Cl)] (3.10), 239.0 [M$^+$ ($^{37}$Cl$^{35}$Cl)] (19.70), 237.0 [M$^+$ ($^{35}$Cl$^{35}$Cl)] (30.51), 205.0, 204.0, 202.0, 167.1, 166.1, 139.1, 138.0.

**2-(3-Chloro-4-methoxyphenyl)pyridine (3a)**

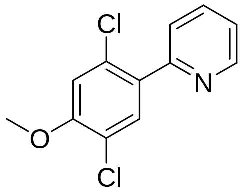


**3a**

In a sealed tube, a solution of subtrate **3** (74 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 °C for 19 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/1,4-dioxane (15/1 (v/v)) as the eluent to afford yellow oil **3a** in 24% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.02 (d, *J* = 8.8 Hz, 1H), 7.20-7.22 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 2.0, 7.6 Hz, 1H), 7.88 (dd, *J* = 2.2, 8.8 Hz, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 8.66 (d, *J* = 4.8 Hz, 1H); $^{13}$C NMR (100

MHz, $CDCl_3$) δ 56.2, 112.0, 119.8, 121.9, 122.9, 126.2, 128.7, 132.5, 136.8, 149.6, 155.6, 155.7; IR (KBr): ν 2922, 1595, 1507, 1463, 1274, 1058, 774 $cm^{-1}$; MS (EI) m/z: 221.0 [$M^+$ ($^{37}Cl$)] (23.53), 219.0 [$M^+$ ($^{35}Cl$)] (100.00), 206.0, 204.0, 176.0, 169.1, 141.1, 78.0; HRMS (EI) Calcd for $C_{12}H_{10}ClNO$: 219.0451, Found: 219.0456.

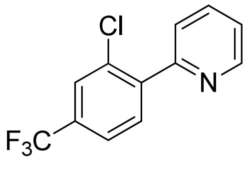
### 2-(2,5-Dichloro-4-methoxyphenyl)pyridine (3b)



**3b**

The separative method of product (**3b**) is the same as that of **3a**. Yellow solid, 35% yield; m.p.: 118-120 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.02 (s, 1H), 7.26-7.29 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.75 (td, *J* = 2.0, 8.0 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 56.5, 113.5, 121.5, 122.4, 124.8, 130.9, 132.2, 132.5, 135.9, 149.6, 155.2, 155.4; IR (KBr): ν 2916, 1591, 1489, 1461, 1282, 1068, 746 $cm^{-1}$. MS (EI) m/z: 257.0 [$M^+$ ($^{37}Cl^{37}Cl$)] (9.92), 256.0 [$(M-1)^+$ ($^{37}Cl^{37}Cl$)] (8.21), 255.0 [$M^+$ ($^{37}Cl^{35}Cl$)] (62.80), 254.0 [$(M-1)^+$ ($^{37}Cl^{35}Cl$)] (13.21), 253.0 [$M^+$ ($^{35}Cl^{35}Cl$)] (100.00), 240.0, 238.0, 220.0, 218.0, 203.0, 177.0, 175.0, 140.1, 99.0; HRMS (EI) Calcd for $C_{12}H_9Cl_2NO$: 253.0061, Found: 253.0054.

### 2-(2-Chloro-4-(trifluoromethyl)phenyl)pyridine (4a)[3]

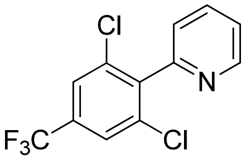


**4a**

In a sealed tube, a solution of subtrate **4** (44.6 mg, 0.2 mmol), LiCl (34 mg, 0.8 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (9.7 mg, 0.04 mmol), $CrO_3$ (40 mg, 0.4 mmol), $Ac_2O$ (102 mg, 1 mmol) in HOAc (1.5 ml) was stirred at 150 °C for 2 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via chromatography on silica gel with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford yellow oil **4a** in 23%

yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34-7.37 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 10.8 Hz, 2H), 7.81 (td, *J* = 2.0, 8.0 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 2924, 1654, 1560, 1508, 1458, 1395, 1324, 1134 cm$^{-1}$; MS (EI) m/z: 259.0 [M$^+$ ($^{37}$Cl)] (13.65), 257.0 [M$^+$ ($^{35}$Cl)] (43.92), 223.0, 222.0, 191.1, 91.1, 71.1.

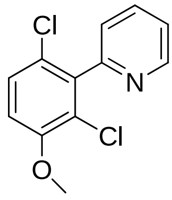
**2-(2,6-Dichloro-4-(trifluoromethyl)phenyl)pyridine (4b)**[3]



**4b**

The separative method of product (**4b**) is the same as that of **4a**. Oil, 58% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.38-7.41 (m, 1H), 7.68 (s, 2H), 7.85 (td, *J* = 1.6, 7.6 Hz, 1H), 8.77-8.78 (m, 1H); IR (KBr): ν 2925, 1587, 1558, 1486, 1384, 1316, 1137, 1101 cm$^{-1}$; MS (EI) m/z: 295.0 [M$^+$ ($^{37}$Cl$^{37}$Cl)] (2.73), 293.0 [M$^+$ ($^{37}$Cl$^{35}$Cl)] (17.57), 291.0 [M$^+$ ($^{35}$Cl$^{35}$Cl)] (27.46), 258.0, 257.0, 256.0, 236.0, 191.1, 78.0.

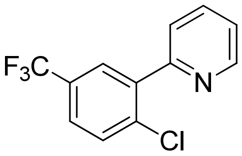
**2-(2,6-Dichloro-3-methoxyphenyl)pyridine (5a)**



**5a**

In a sealed tube, a solution of subtrate **5** (55.5 mg, 0.3 mmol), LiCl (50.4 mg, 1.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (14.5 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.25 ml) was stirred at 150 °C for 19 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/1,4-dioxane (5/1 (v/v)) as the eluent to afford oil **5a** in 38% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.94 (d, *J* = 9.2 Hz, 1H), 7.30-7.36 (m, 3H), 7.81 (td, *J* = 2.0, 8.0 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 56.6, 112.3, 122.9, 123.2, 124.9, 125.4, 128.1, 136.4, 139.3, 149.6, 154.2, 155.6; IR (KBr): ν 2938, 1565, 1457, 1427, 1297, 1027, 771 $cm^{-1}$. MS (EI) m/z: 257.0 [$M^+$ ($^{37}Cl^{37}Cl$)] (5.37), 256.0 [$(M-1)^+$ ($^{37}Cl^{37}Cl$)] (4.79), 255.0 [$M^+$ ($^{37}Cl^{35}Cl$)] (36.58), 254.0 [$(M-1)^+$ ($^{37}Cl^{35}Cl$)] (7.63), 253.0 [$M^+$ ($^{35}Cl^{35}Cl$)] (58.88), 220.0, 218.0, 203.0, 175.0, 140.1; HRMS (EI) Calcd for $C_{12}H_9ClNO$: 253.0061, Found: 253.0061.

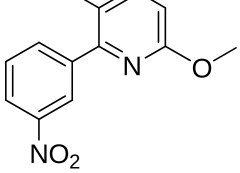
### 2-(2-Chloro-5-(trifluoromethyl)phenyl)pyridine (6a)[4]



**6a**

In a sealed tube, a solution of subtrate **6** (89.2 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 °C for 4.5 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (5/1 (v/v)) as the eluent to afford bright yellow oil **6a** in 44% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.33-7.36 (m, 1H), 7.58-7.63 (m, 2H), 7.68 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.81 (td, *J* = 2.0, 7.6 Hz, 1H), 7.90 (s, 1H), 8.76 (ddd, *J* = 0.8, 1.6, 4.8 Hz, 1H); IR (KBr): ν 2962, 1612, 1587, 1462, 1403, 1337, 1129, 826, 788 $cm^{-1}$; MS (EI) m/z: 259.0 [$M^+$ ($^{37}Cl$)](15.19), 257.0 [$M^+$ ($^{35}Cl$)] (48.25), 223.1, 222.1, 202.1, 188.0, 99.0, 71.1, 43.1.

### 3-Chloro-6-methoxy-2-(3-nitrophenyl)pyridine (7a)



**7a**

In a sealed tube, a solution of subtrate **7** (69 mg, 0.3 mmol), LiCl (50.4 mg, 1.2 mmol),

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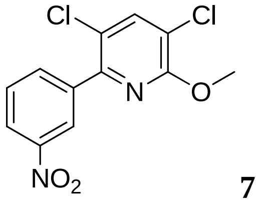
[4] Kakiuchi, F.; Kochi, T.; Mutsutani, H.; Kobayashi, N.; Urano, S.; Sato, M.; Nishiyama, S.; Tanabe, T. *J. Am. Chem. Soc.* **2009**, *131*, 11310.

$Cu(NO_3)_2{\cdot}3H_2O$ (14.5 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.25 ml) was stirred at 150 °C for 22 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (15/1 (v/v)) as the eluent to afford white solid **7a** in 28% yield; m.p.: 138-140 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 6.76 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.26-8.29 (m, 1H), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 53.9, 112.0, 121.7, 123.4, 124.6, 128.8, 135.4, 139.6, 141.0, 148.0, 149.8, 162.2; IR (KBr): ν 2977, 1586, 1526, 1463, 1410, 1351, 1251, 1027, 734 cm$^{-1}$; MS (EI) m/z: 266.0 [$M^+$ ($^{37}$Cl)] (26.84), 265.0 [$(M-1)^+$ ($^{37}$Cl)] (37.36), 264.0 [$M^+$ ($^{35}$Cl)] (100.00), 263.0 [$(M-1)^+$ ($^{35}$Cl)] (84.25), 235.0, 218.0, 217.0, 203.0, 140.1; HRMS (EI) Calcd for $C_{12}H_9ClN_2O_3$: 264.0302, Found: 264.0295.

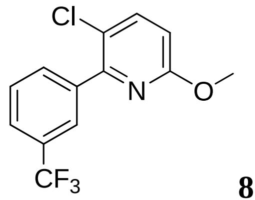
**3,5-Dichloro-2-methoxy-6-(3-nitrophenyl)pyridine (7b)**



**7b**

The separative method of product (**7b**) is the same as that of **7a**. White solid, 17% yield; m.p.: 131-132 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 4.07 (s, 3H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.69 (t, *J* = 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.0, 118.8, 121.7, 123.9, 124.8, 129.2, 135.6, 135.7, 138.9, 140.3, 148.3, 157.8; IR (KBr): ν 2954, 1530, 1463, 1404, 1350, 1249, 731 cm$^{-1}$; MS (EI) m/z: 302.0 [$M^+$ ($^{37}$Cl$^{37}$Cl)] (10.16), 301.0 [$(M-1)^+$ ($^{37}$Cl$^{37}$Cl)] (13.74), 300.0 [$M^+$ ($^{37}$Cl$^{35}$Cl)] (61.04), 299.0 [$(M-1)^+$ ($^{37}$Cl$^{35}$Cl)] (50.71), 298.0 [$M^+$ ($^{35}$Cl$^{35}$Cl)] (100.00), 297.0 [$(M-1)^+$ ($^{35}$Cl$^{35}$Cl)] (65.29), 271.0, 269.0, 239.0, 237.0, 174.0; HRMS (EI) Calcd for $C_{12}H_8Cl_2N_2O_3$: 297.9912, Found: 297.9906.

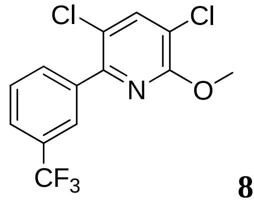
### 3-Chloro-6-methoxy-2-(3-(trifluoromethyl)phenyl)pyridine (8a)[5]



**8a**

In a sealed tube, a solution of subtrate **8** (101.2 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 °C for 14 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether as the eluent to afford oil **8a** in 30% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 6.72 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.64-7.69 (m, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 1H); IR (KBr): ν 2922, 1581, 1463, 1408, 1330, 1125, 701 cm$^{-1}$; MS (EI) m/z: 289.0 [M$^+$ ($^{37}$Cl)] (19.53), 288.0 [(M-1)$^+$ ($^{37}$Cl)] (29.75), 287.0 [M$^+$ ($^{35}$Cl)] (72.09), 286.0 [(M-1)$^+$ ($^{35}$Cl)] (100.00), 258.0, 222.0, 202.0.

### 3,5-Dichloro-2-methoxy-6-(3-(trifluoromethyl)phenyl)pyridine (8b)



**8b**

The separative method of product (**8b**) is the same as that of **8a**. Yellow solid, 33% yield; m.p.: 50-52 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 54.7, 117.9, 121.3, 125.57, 125.61, 126.32, 126.36, 128.5, 132.7, 137.9, 139.9, 149.1, 157.5; IR (KBr): ν 2953, 1570, 1467, 1405, 1326, 1248, 1128, 751 cm$^{-1}$; MS (EI) m/z: 325.0 [M$^+$ ($^{37}$Cl$^{37}$Cl)] (9.56), 324.0 [(M-1)$^+$ ($^{37}$Cl$^{37}$Cl)] (15.91), 323.0 [M$^+$ ($^{37}$Cl$^{35}$Cl)] (59.97), 322.0 [(M-1)$^+$ ($^{37}$Cl$^{35}$Cl)] (66.37), 321.0 [M$^+$ ($^{35}$Cl$^{35}$Cl)] (100.00), 320.0 [(M-1)$^+$ ($^{35}$Cl$^{35}$Cl)] (86.36), 294.0, 292.0, 256.0, 236.0;

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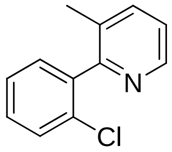
[5] Kalyani, D.; Dick, A. R.; Anani, W. Q.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 11483.

HRMS (EI) Calcd for $C_{13}H_8Cl_2F_3NO$: 320.9935, Found: 320.9923.

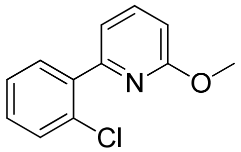
**2-(2-Chlorophenyl)-3-methylpyridine (9a)**[3]



**9a**

In a sealed tube, a solution of subtrate **9** (67.6 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 °C for 6 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford oil **9a** in 32% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 7.25 (dd, *J* = 4.8, 7.6 Hz, 1H), 7.30-7.36 (m, 3H), 7.46-7.48 (m, 1H), 7.60 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.53 (dd, *J* = 0.8, 4.8 Hz, 1H); IR (KBr): ν 2923, 1569, 1430, 1080, 1021, 792, 755 $cm^{-1}$; MS (EI) m/z: 205.0 [$M^+$ ($^{37}Cl$)] (17.68), 204.0 [$(M-1)^+$ ($^{37}Cl$)] (37.19), 203.0 [$M^+$ ($^{35}Cl$)] (53.60), 202.0 [$(M-1)^+$ ($^{35}Cl$)] (100.00), 168.1, 167.1.

**2-(2-Chlorophenyl)-6-methoxypyridine (10a)**

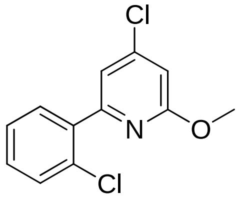


**10a**

In a sealed tube, a solution of subtrate **10** (74 mg, 0.4 mmol), LiCl (67.2 mg, 1.6 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (19.4 mg, 0.08 mmol), $CrO_3$ (80 mg, 0.8 mmol), $Ac_2O$ (204 mg, 2 mmol) in HOAc (3 ml) was stirred at 150 °C for 14 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/1,4-dioxane (5/1 (v/v)) as the eluent to afford oil **10a** in 21% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 7.28-7.31 (m, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.0

Hz, 1H), 7.77 (td, *J* = 1.6, 7.6 Hz, 1H), 8.72 (d, *J* = 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.6, 116.0, 116.1, 122.5, 123.4, 124.9, 130.8, 135.8, 139.8, 149.4, 156.8, 158.4; IR (KBr): ν 2928, 1734, 1585, 1460, 1224, 1034, 787 cm$^{-1}$; MS (EI) m/z: 221.0 [M$^+$ ($^{37}$Cl)] (16.59), 220.0 [(M-1)$^+$ ($^{37}$Cl)] (34.80), 219.0 [M$^+$ ($^{35}$Cl)] (58.71), 218.0 [(M-1)$^+$ ($^{35}$Cl)] (100.00), 190.0, 189.0, 154.1, 78.0; HRMS (EI) Calcd for $C_{12}H_{10}ClNO$: 219.0451, Found: 219.0446.

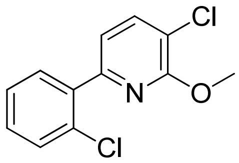
**4-Chloro-2-(2-chlorophenyl)-6-methoxypyridine (10b)**



**10b**

The separative method of product (**10b**) is the same as that of **10a**. Yellow solid, 18% yield; m.p.: 94-95 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.22 (s, 1H), 7.30-7.33 (m, 1H), 7.50 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 56.4, 114.5, 122.7, 123.3, 123.4, 124.9, 131.1, 136.0, 138.3, 149.6, 154.0, 155.8; IR (KBr): ν 2921, 1735, 1560, 1458, 1370, 1245 cm$^{-1}$; MS (EI) m/z: 257.0 [M$^+$ ($^{37}$Cl$^{37}$Cl)] (5.10), 256.0 [(M-1)$^+$ ($^{37}$Cl$^{37}$Cl)] (13.32), 255.0 [M$^+$ ($^{37}$Cl$^{35}$Cl)] (31.47), 254.0 [(M-1)$^+$ ($^{37}$Cl$^{35}$Cl)] (66.55), 253.0 [M$^+$ ($^{35}$Cl$^{35}$Cl)] (49.75), 252.0 [(M-1)$^+$ ($^{35}$Cl$^{35}$Cl)] (100.00), 223.0, 188.0, 78.0; HRMS (EI) Calcd for $C_{12}H_9Cl_2NO$: 253.0061, Found: 253.0059.

**3-Chloro-6-(2-chlorophenyl)-2-methoxypyridine (10c)**

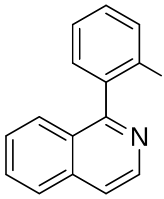


**10c**

The separative method of product (**10c**) is the same as that of **10a**. Oil, 36% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 7.31-7.37 (m, 3H), 7.80 (td, *J* = 2.0, 8.0 Hz, 1H), 8.74 (d, *J* = 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 56.6, 112.3, 122.9, 123.2, 124.9, 125.4, 128.1, 136.4, 139.3, 149.6, 154.2, 155.6; IR (KBr): ν 2935, 1565, 1457, 1427, 1297, 1241, 1080, 1027, 772 cm$^{-1}$; MS (EI) m/z:

257.0 [M$^+$ ($^{37}$Cl$^{37}$Cl)] (5.76), 256.0 [(M-1)$^+$ ($^{37}$Cl$^{37}$Cl)] (4.63), 255.0 [M$^+$ ($^{37}$Cl$^{35}$Cl)] (35.30), 254.0 [(M-1)$^+$ ($^{37}$Cl$^{35}$Cl)] (7.51), 253.0 [M$^+$ ($^{35}$Cl$^{35}$Cl)] (56.45), 220.0, 218.0, 203.0, 175.0, 78.0; HRMS (EI) Calcd for $C_{12}H_9Cl_2NO$: 253.0061, Found: 253.0068.

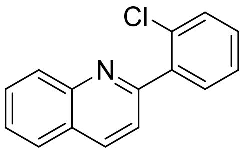
### 1-(2-Chlorophenyl)isoquinoline (11a)[6]



**11a**

In a sealed tube, a solution of subtrate **11** (41 mg, 0.2 mmol), LiCl (34 mg, 0.8 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (9.7 mg, 0.04 mmol), $MnO_2$ (69.6 mg, 0.8 mmol) in HOAc (1.5 mL) was stirred at 150 $^oC$ for 4 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The extract was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/ethyl acetate (10/1 (v/v)) as the eluent to afford oil **11a** in 33% yield; $^1$H NMR (400 MHz, Acetone-D6) δ 7.36-7.51 (m, 6H), 7.64-7.67 (m, 1H), 7.74 (d, *J* = 5.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.47 (dd, *J* = 0.8, 5.6 Hz, 1H); IR (KBr): ν 1582, 1430, 1388, 1357, 1051, 826, 754 cm$^{-1}$; MS (EI) m/z: 241.0 [M$^+$ ($^{37}$Cl)] (15.29), 240.0 [(M-1)$^+$ ($^{37}$Cl)] (30.52), 239.0 [M$^+$ ($^{35}$Cl)] (53.66), 238.0 [(M-1)$^+$ ($^{35}$Cl)] (100.0), 204.1, 202.1, 201.1, 177.1, 176.1, 175.1, 71.1, 43.0.

### 2-(2-Chlorophenyl)quinoline (12a)[7]



**12a**

In a sealed tube, a solution of subtrate **12** (61.5 mg, 0.3 mmol), LiCl (50.4 mg, 1.2 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (14.5 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.25 ml) was stirred at 150 $^oC$ for 5.5 days. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc

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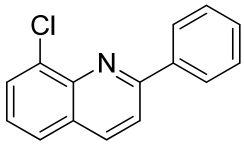
[6] Kalyani, D.; Dick, A. R.; Anani, W. Q.; Sanford, M. S. *Org. Lett.* **2006**, *8*, 2523.

[7] Han, R. B.; Chen, S.; Lee, S. J.; Qi, F.; Wu, X.; Kim, B. H. *Heterocycles*, **2006**, *68*, 1675.

(3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (20/1 (v/v)) as the eluent to afford oil **12a** in 21% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.36-7.43 (m, 2H), 7.50-7.52 (m, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 2.0, 7.2 Hz, 1H), 7.73-7.77 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H); IR (KBr): ν 1597, 1506, 1486, 1455, 760 $cm^{-1}$; MS (EI) m/z: 241.0 [$M^+$ ($^{37}Cl$)] (14.39), 239.0 [$M^+$ ($^{35}Cl$)] (44.87), 238.0 [$(M-1)^+$ ($^{35}Cl$)] (7.48), 205.1, 204.1, 203.1, 176.1.

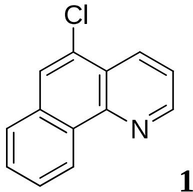
### 8-Chloro-2-phenylquinoline (12b)[8]



**12b**

The separative method of product (**12b**) is the same as that of **12a**. **O**il, 28% yield; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8.0 Hz, 1H), 7.46-7.56 (m, 3H), 7.74-7.75 (m, 1H), 7.83-7.85 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.28-8.30 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 119.3, 126.3, 126.5, 127.5, 127.7, 128.4, 128.9, 129.7, 133.9, 137.2, 139.0, 144.3, 157.4; IR (KBr): ν 1744, 1567, 1416, 1123, 762 $cm^{-1}$; MS (EI) m/z: 241.0 [$M^+$ ($^{37}Cl$)] (30.23), 240.0 [$(M-1)^+$ ($^{37}Cl$)] (26.90), 239.0 [$M^+$ ($^{35}Cl$)] (100.00), 238.0 [$(M-1)^+$ ($^{35}Cl$)] (40.66), 204.1, 203.1; HRMS (EI) Calcd for $C_{15}H_{10}ClN$: 239.0502, Found: 239.0495.

### 5-Chlorobenzo[h]quinoline (13a)[5]



**13a**

In a sealed tube, a solution of subtrate **13** (53.7 mg, 0.3 mmol), LiCl (50.4 mg, 1.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (14.5 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.25 ml) was stirred at 150 °C for 5.5 days. Then the

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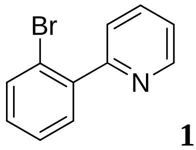
[8] Demaude, T.; Knerr, L.; Pasau, P. *J. Comb. Chem.* **2004**, *6*, 768.

mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford yellow solid **13a** in 36% yield; m.p.: 110-112 $^{o}$C (lit.[5] m.p.: 113.6-115.0 $^{o}$C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 4.4, 8.0 Hz, 1H), 7.67-7.74 (m, 2H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.90 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 9.03 (d, *J* = 4.4 Hz, 1H), 9.24 (d, *J* = 7.2 Hz, 1H); IR (KBr): ν 2922, 1586, 1565, 1444, 1398, 935, 757 cm$^{-1}$; MS (EI) m/z: 215.0 [M$^+$ ($^{37}$Cl)] (26.83), 214.0 [(M-1)$^+$ ($^{37}$Cl)] (14.88), 213.0 [M$^+$ ($^{35}$Cl)] (100.00), 212.0 [(M-1)$^+$ ($^{35}$Cl)] (11.71), 178.1, 151.1.

## Representative procedure for the Cu-catalyzed C-H bond bromination

### Synthesis of 2-(2-bromophenyl)pyridine (1c)[3] as a typical example:

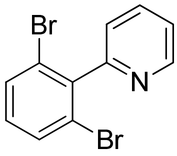
### 2-(2-Bromophenyl)pyridine (1c)[3]



**1c**

In a sealed tube, a solution of subtrate **1** (31 mg, 0.2 mmol), LiBr (69 mg, 0.8 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (9.7 mg, 0.04 mmol), $CrO_3$ (40 mg, 0.4 mmol), $Ac_2O$ (102 mg, 1 mmol) in HOAc (1.5 mL) was stirred at 150 $^{o}$C for 19 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The extract was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford oil **1c** in 22% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24-7.31 (m, 2H), 7.41 (td, *J* = 1.2, 7.2 Hz, 1H), 7.54 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.77 (td, *J* = 1.6, 7.6 Hz, 1H), 8.72 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 2926, 1636, 1566, 1415, 1114 cm$^{-1}$; MS (EI) m/z: 235.0 [M$^+$ ($^{81}$Br)] (23.53), 234.0 [(M-1)$^+$ ($^{81}$Br)] (12.80), 233.0 [M$^+$ ($^{79}$Br)] (24.63), 232.0 [(M-1)$^+$ ($^{79}$Br)] (10.77), 154.1, 127.1, 43.0.

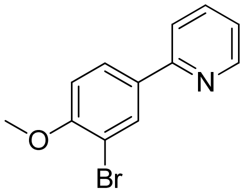
### 2-(2,6-Dibromophenyl)pyridine (1d)[3]



**1d**

The separative method of product (**1d**) is the same as that of **1c**. Yellow solid, 48% yield; m.p.: 63-65 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.34-7.37 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.82 (td, *J* = 1.6, 7.6 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 2927, 1635, 1567, 1415, 1106 cm$^{-1}$; MS (EI) m/z: 314.9 [M$^+$ ($^{81}$Br$^{81}$Br)] (11.08), 312.9 [M$^+$ ($^{81}$Br$^{79}$Br)] (21.96), 310.9 [M$^+$ ($^{79}$Br$^{79}$Br)] (11.55), 234.0, 232.0, 153.1, 126.0.

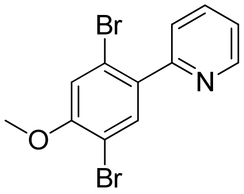
### 2-(3-Bromo-4-methoxyphenyl)pyridine (3c)



**3c**

In a sealed tube, a solution of subtrate **3** (55.5 mg, 0.3 mmol), LiBr (104 mg, 1.2 mmol), CuO(nano) (4.8 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.3 mL) was stirred at 150 °C for 17 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The extract was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/$Et_2O$ (2/1 (v/v)) as the eluent to afford white solid **3c** in 51% yield; m.p.: 77-78 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.97 (d, *J* = 8.8 Hz, 1H), 7.17-7.21 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.71 (td, *J* = 1.6, 7.6 Hz, 1H), 7.92 (dd, *J* = 2.4, 8.8 Hz, 1H), 8.23 (d, *J* = 2.4 Hz, 1H), 8.65 (d, *J* = 4.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 56.2, 111.7, 112.0, 119.8, 121.9, 126.9, 131.7, 133.2, 136.7, 149.5, 155.5, 156.4; IR (KBr): ν 1598, 1506, 1464, 1279, 1054, 773 cm$^{-1}$; MS (EI) m/z: 265.0 [M$^+$ ($^{81}$Br)] (96.78), 263.0 [M$^+$ ($^{79}$Br)] (100.00), 250.0, 169.1, 154.1, 141.1; HRMS (EI) Calcd for $C_{12}H_{10}BrNO$: 262.9946, Found: 262.9940.

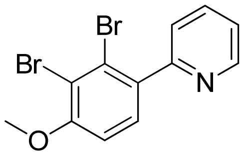
### 2-(2,5-Dibromo-4-methoxyphenyl)pyridine (3d)



**3d**

The separative method of product (**3d**) is the same as that of **3c**. Yellow solid, 13% yield; m.p.: 127-128 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.95 (s, 3H), 7.17 (s, 1H), 7.27-7.30 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 56.6, 111.0, 116.4, 120.8, 122.4, 124.8, 134.8, 135.4, 135.9, 149.5, 156.2, 156.8; IR (KBr): ν 2926, 1596, 1458, 1430, 1056 cm$^{-1}$; MS (EI) m/z: 344.9 [M$^+$ ($^{81}$Br$^{81}$Br)] (28.31), 342.9 [M$^+$ ($^{81}$Br$^{79}$Br)] (72.17), 340.9 [M$^+$ ($^{79}$Br$^{79}$Br)] (33.77), 264.0, 262.0, 247.0, 221.0, 140.1; HRMS (EI) Calcd for $C_{12}H_9Br_2NO$: 340.9051, Found: 340.9092.

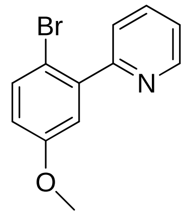
### 2-(2,3-Dibromo-4-methoxyphenyl)pyridine (3e)



**3e**

The separative method of product (**3e**) is the same as that of **3c**. Yellow solid, 10% yield; m.p.: 139-141 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.96 (s, 3H), 6.98 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.85 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.91 (dd, *J* = 2.0, 8.4 Hz, 1H), 8.20 (d, *J* = 2.0 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 56.6, 112.1, 112.5, 119.2, 121.1, 127.1, 131.9, 132.3, 139.6, 150.9, 154.27, 154.34; IR (KBr): ν 2924, 1557, 1422, 1290, 1056, 801 cm$^{-1}$; MS (EI) m/z: 344.9 [M$^+$ ($^{81}$Br$^{81}$Br)] (45.26), 342.9 [M$^+$ ($^{81}$Br$^{79}$Br)] (100.00), 340.9 [M$^+$ ($^{79}$Br$^{79}$Br)] (50.05), 327.9, 247.0, 221.0, 140.1; HRMS (EI) Calcd for $C_{12}H_9Br_2NO$: 340.9051, Found: 340.9042.

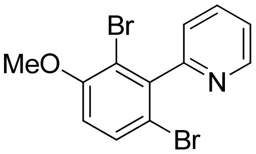
### 2-(2-Bromo-5-methoxyphenyl)pyridine (5b)



**5b**

In a sealed tube, a solution of subtrate **5** (55.5 mg, 0.3 mmol), LiBr (104 mg, 1.2 mmol), CuO(nano) (4.8 mg, 0.06 mmol), $CrO_3$ (60 mg, 0.6 mmol), $Ac_2O$ (153 mg, 1.5 mmol) in HOAc (2.3 ml) was stirred at 150 °C for 17 hours. Then the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The combined organic layers was washed with brine (2 x 15 mL) and dried over $Na_2SO_4$. After evaporation, the residue was purified via thin-layer chromatography (TLC) with petroleum ether/ethyl acetate (5/1 (v/v)) as the eluent to afford yellow oil **5b** in 40% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.83 (dd, *J* = 3.2, 8.8 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.28-7.31 (m, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.76 (td, *J* = 2.0, 7.6 Hz, 1H), 8.71-8.72 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.5, 112.1, 116.2, 116.3, 122.4, 124.7, 133.9, 135.8, 141.8, 149.3, 158.1, 158.9; IR (KBr): ν 2926, 1636, 1567, 1415, 1112 cm$^{-1}$; MS (EI) m/z: 265.0 [M$^+$ ($^{81}$Br)] (62.51), 264.0 [(M-1)$^+$ ($^{81}$Br)] (96.51), 263.0 [M$^+$ ($^{79}$Br)] (65.06), 262.0 [(M-1)$^+$ ($^{79}$Br)] (100.00), 184.1, 154.1, 141.1; HRMS (EI) Calcd for $C_{12}H_{10}BrNO$: 262.9946, Found: 262.9940.

**2-(2,6-Dibromo-3-methoxyphenyl)pyridine (5c)**

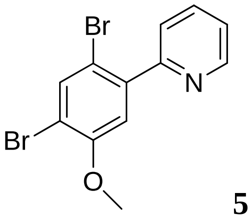


**5c**

The separative method of product (**5c**) is the same as that of **5b**. Yellow oil, 17% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.33-7.36 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.82 (td, *J* = 2.0, 7.6 Hz, 1H), 8.75 (d, *J* = 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 56.7, 109.7, 112.7, 113.9, 122.9, 124.6, 131.9, 136.5, 142.8, 149.4, 155.7, 158.9; IR (KBr): ν 2924, 1559, 1423, 1293, 1024, 799 cm$^{-1}$. MS (EI) m/z: 344.9 [M$^+$ ($^{81}$Br$^{81}$Br)] (14.91), 342.9 [M$^+$ ($^{81}$Br$^{79}$Br)] (32.02), 340.9 [M$^+$ ($^{79}$Br$^{79}$Br)] (16.57), 264.0, 262.0, 247.0, 140.1; HRMS

(EI) Calcd for $C_{12}H_9Br_2NO$: 340.9051, Found: 340.9054.

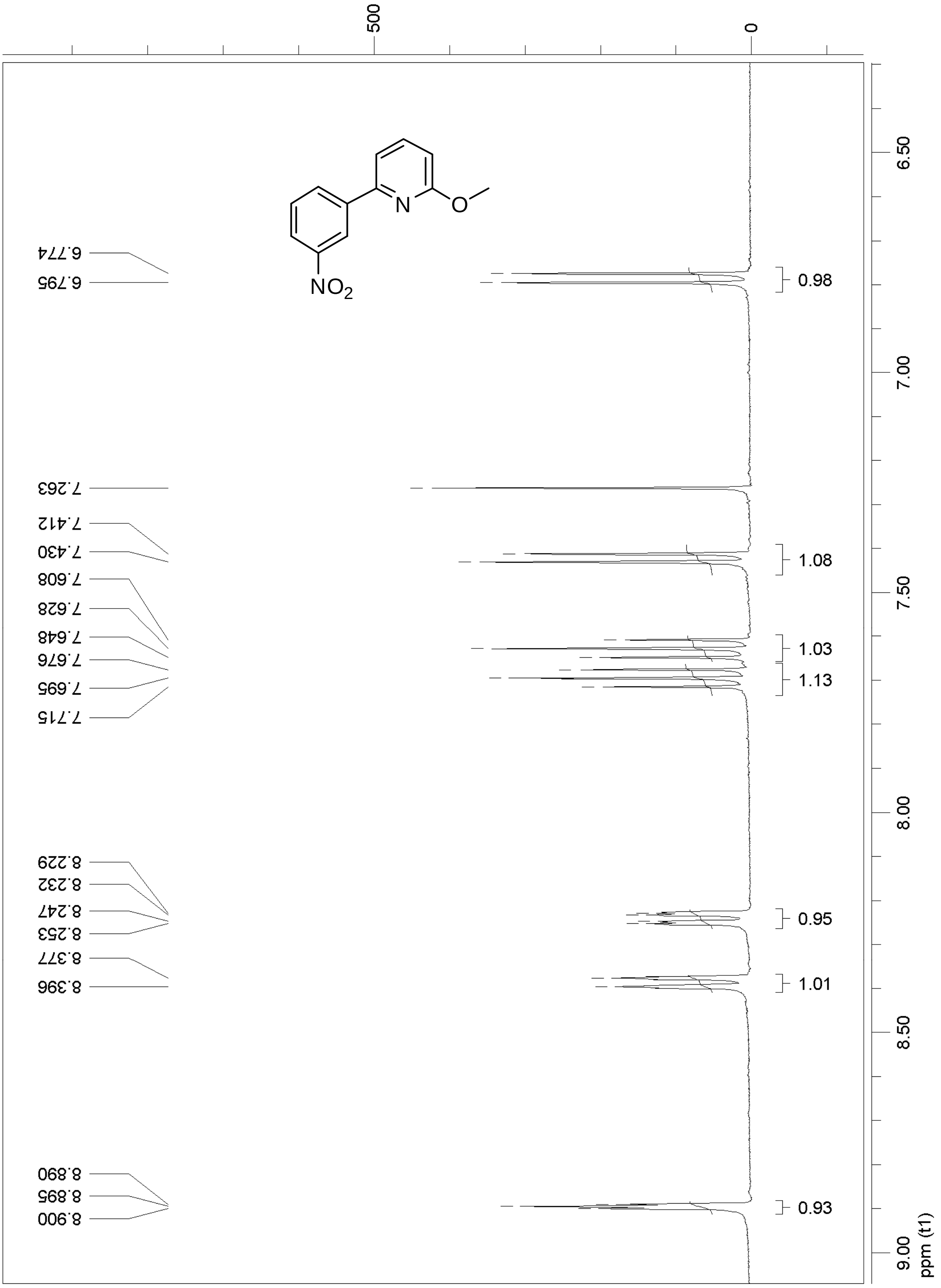
### 2-(2,4-Dibromo-5-methoxyphenyl)pyridine (5d)

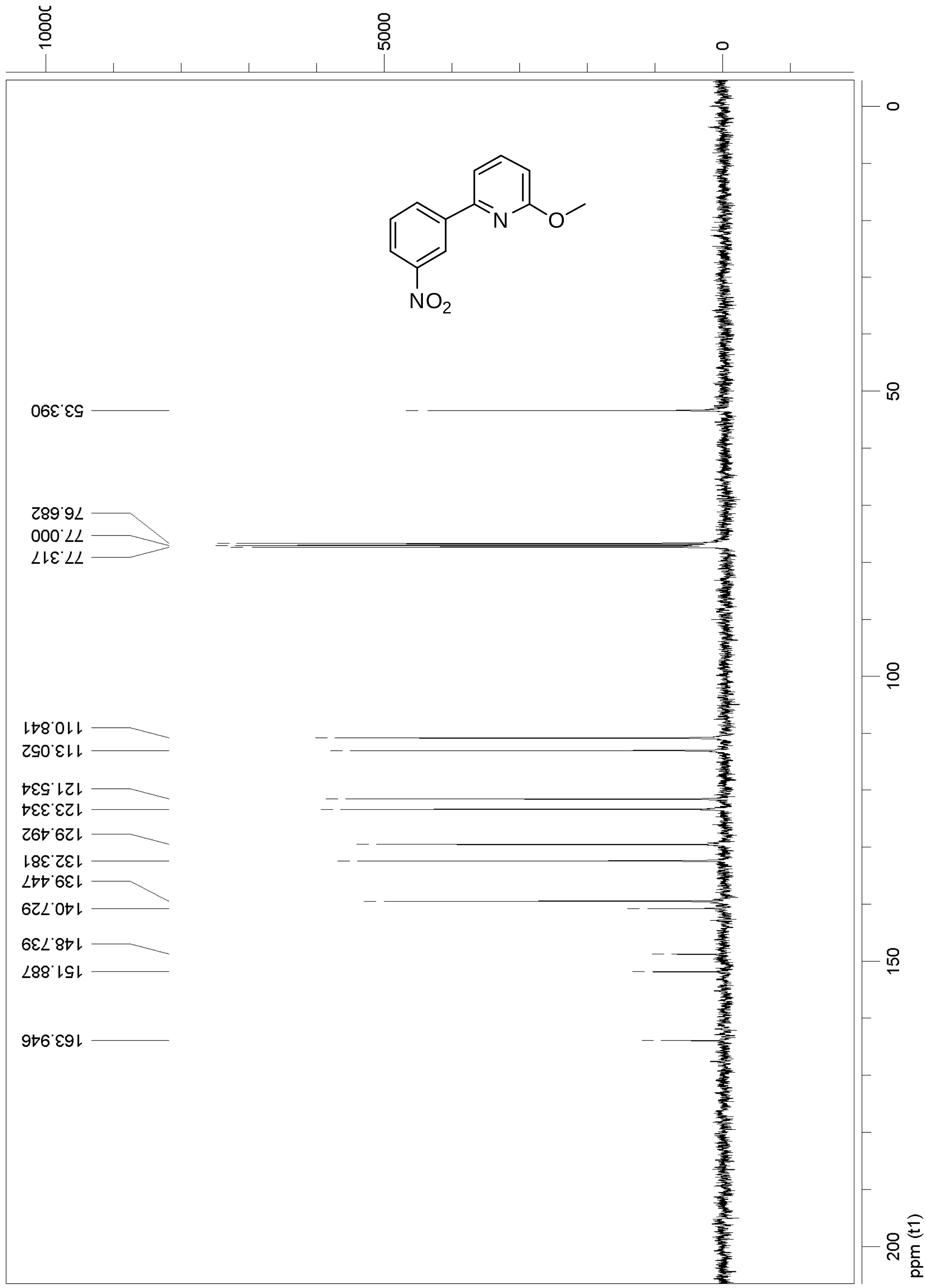


**5d**

The separative method of product (**5d**) is the same as that of **5b**. White solid, 26% yield; m.p.: 109-111 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.12 (s, 1H), 7.31-7.34 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.78 (td, *J* = 1.6, 7.6 Hz, 1H), 7.84 (s, 1H), 8.72 (d, *J* = 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 56.5, 112.1, 114.4, 122.7, 124.8, 135.9, 136.8, 141.1, 149.5, 155.4, 157.3, 168.8; IR (KBr): ν 2924, 1457, 1363, 1226, 1055, 786 cm$^{-1}$; MS (EI) m/z: 344.9 [M$^+$ ($^{81}$Br$^{81}$Br)] (19.94), 343.9 [(M-1)$^+$ ($^{81}$Br$^{81}$Br)] (38.62), 342.9 [M$^+$ ($^{81}$Br$^{79}$Br)] (46.07), 341.9 [(M-1)$^+$ ($^{81}$Br$^{79}$Br)] (100.00), 340.9 [M$^+$ ($^{79}$Br$^{79}$Br)] (24.49), 339.9 [(M-1)$^+$ ($^{79}$Br$^{79}$Br)] (42.96), 232.0, 140.1; HRMS (EI) Calcd for $C_{12}H_9Br_2NO$: 340.9051, Found: 340.9058.

# IV. Spectral data of NMR



N
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123.334
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140.729
148.739
151.887
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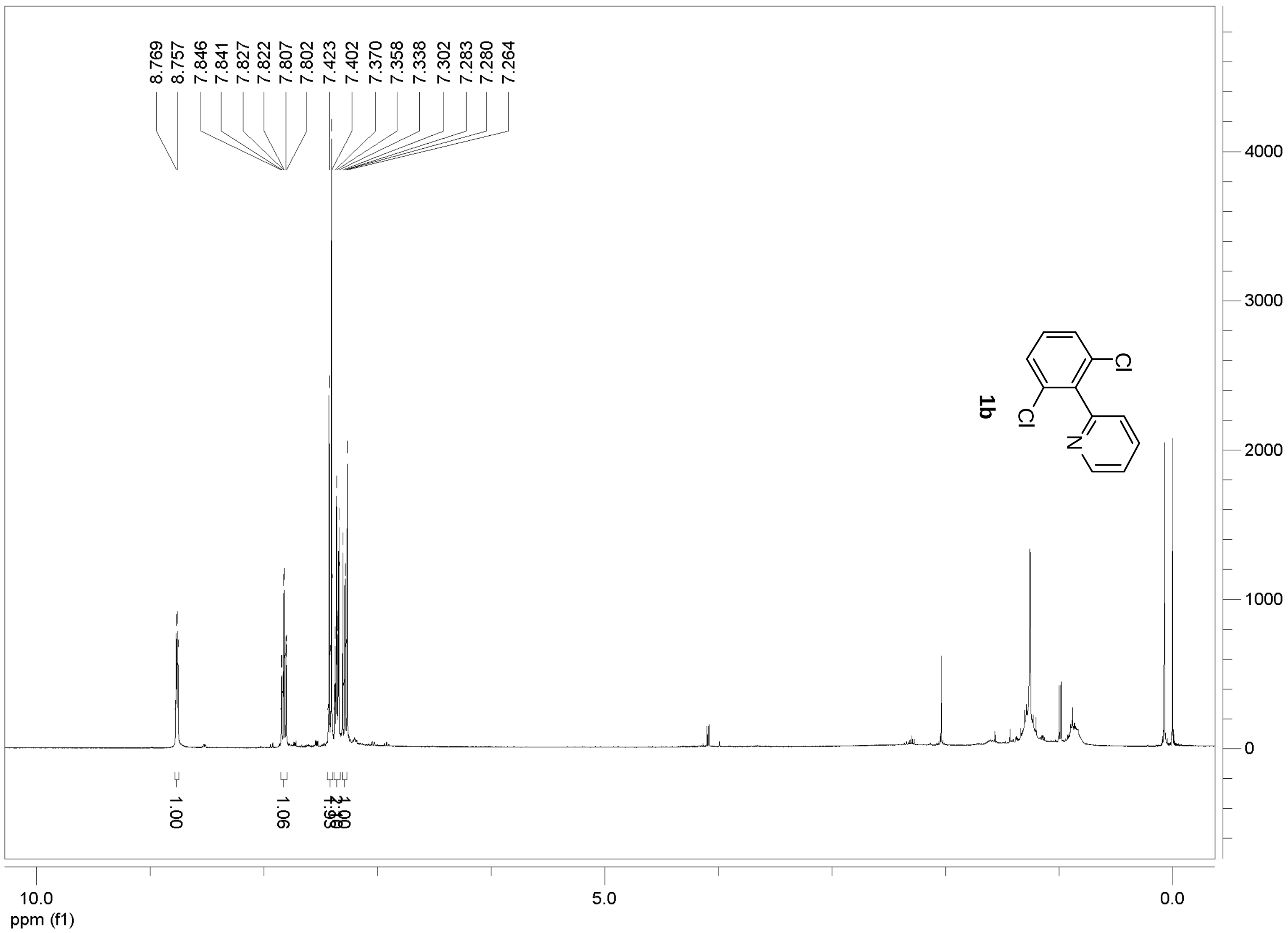
0
50
100
150
200
ppm (t1)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7.827
7.822
7.807
7.802
7.423
7.402
7.370
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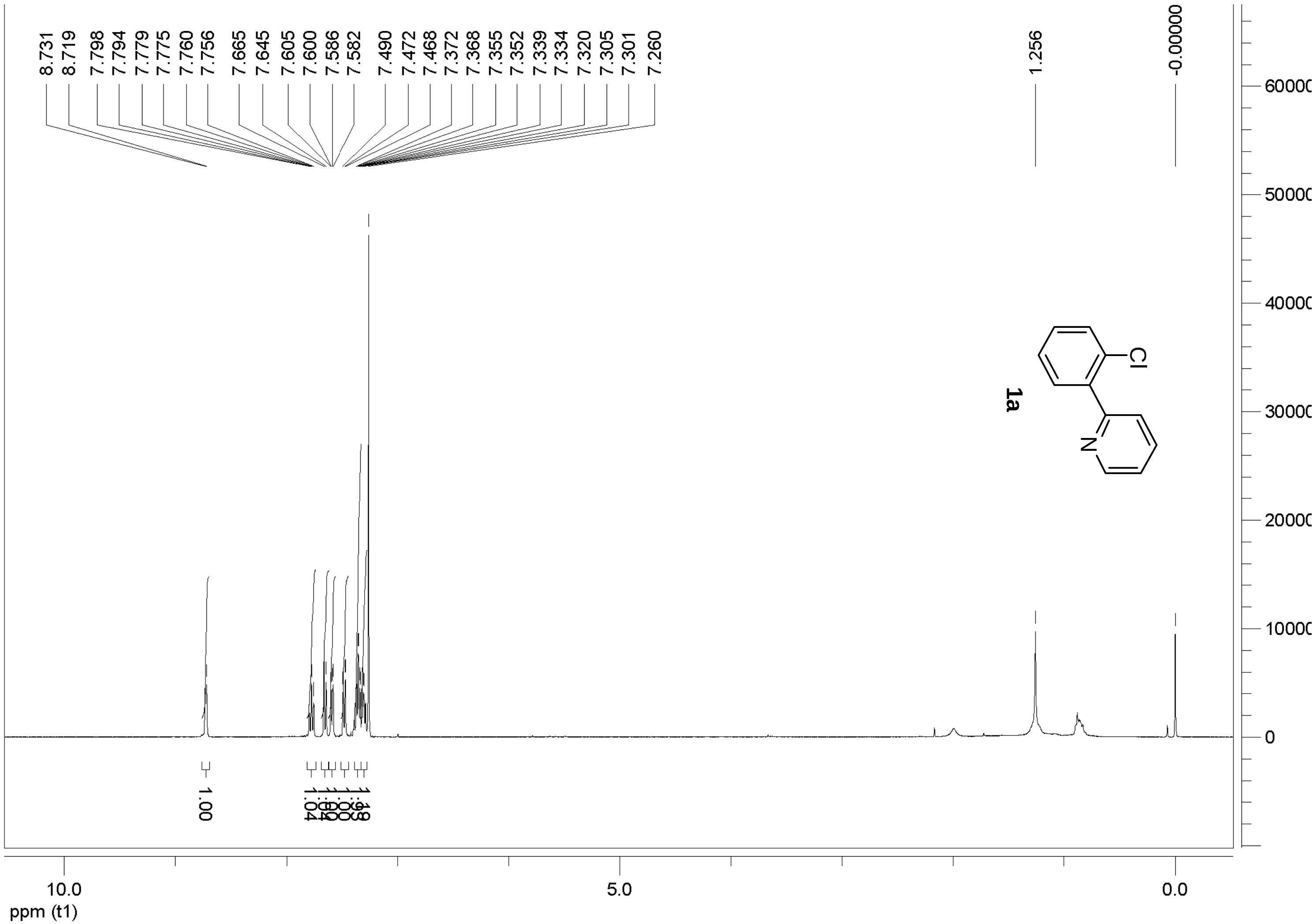
7.302
7.283
7.280
7.264
Cl
Cl
N
4000
3000
2000
1000
0
1.00
1.06
1.93
2.10
1.00
10.0
5.0
0.0
ppm (f1)

**1b**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7.779
7.775
7.760
7.756
7.665
7.645
7.605
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7.582
7.490
7.472
7.468
7.372
7.368
7.355
7.352
7.339
7.334
7.320
7.305
7.301
7.260
1.256
-0.00000
Cl
N
1a
60000
50000
40000
30000
20000
10000
0
1.00
1.04
1.04
1.00
1.00
1.95
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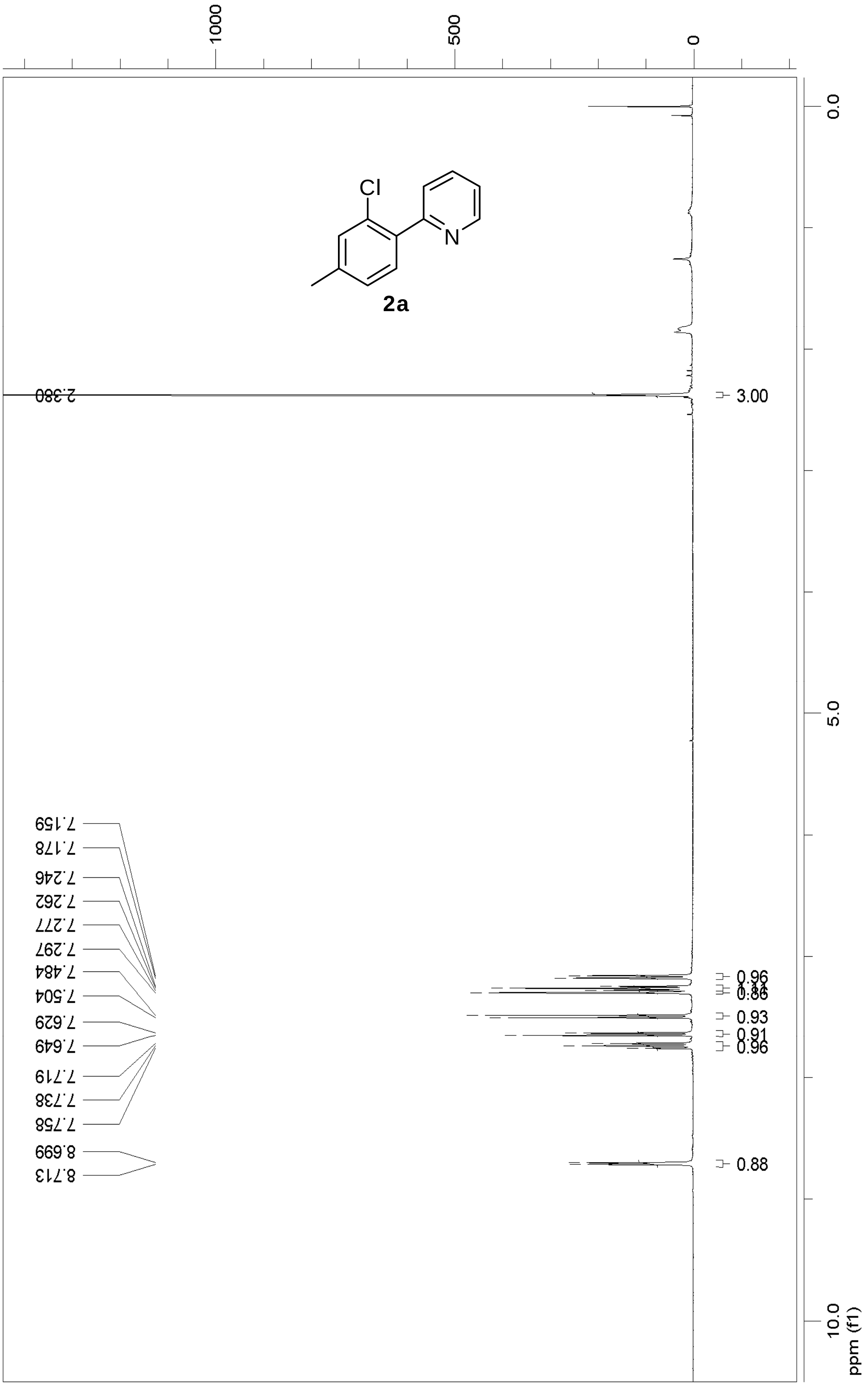
10.0
5.0
0.0
ppm (t1)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8.699
8.713
3.00
0.96
1.11
0.86
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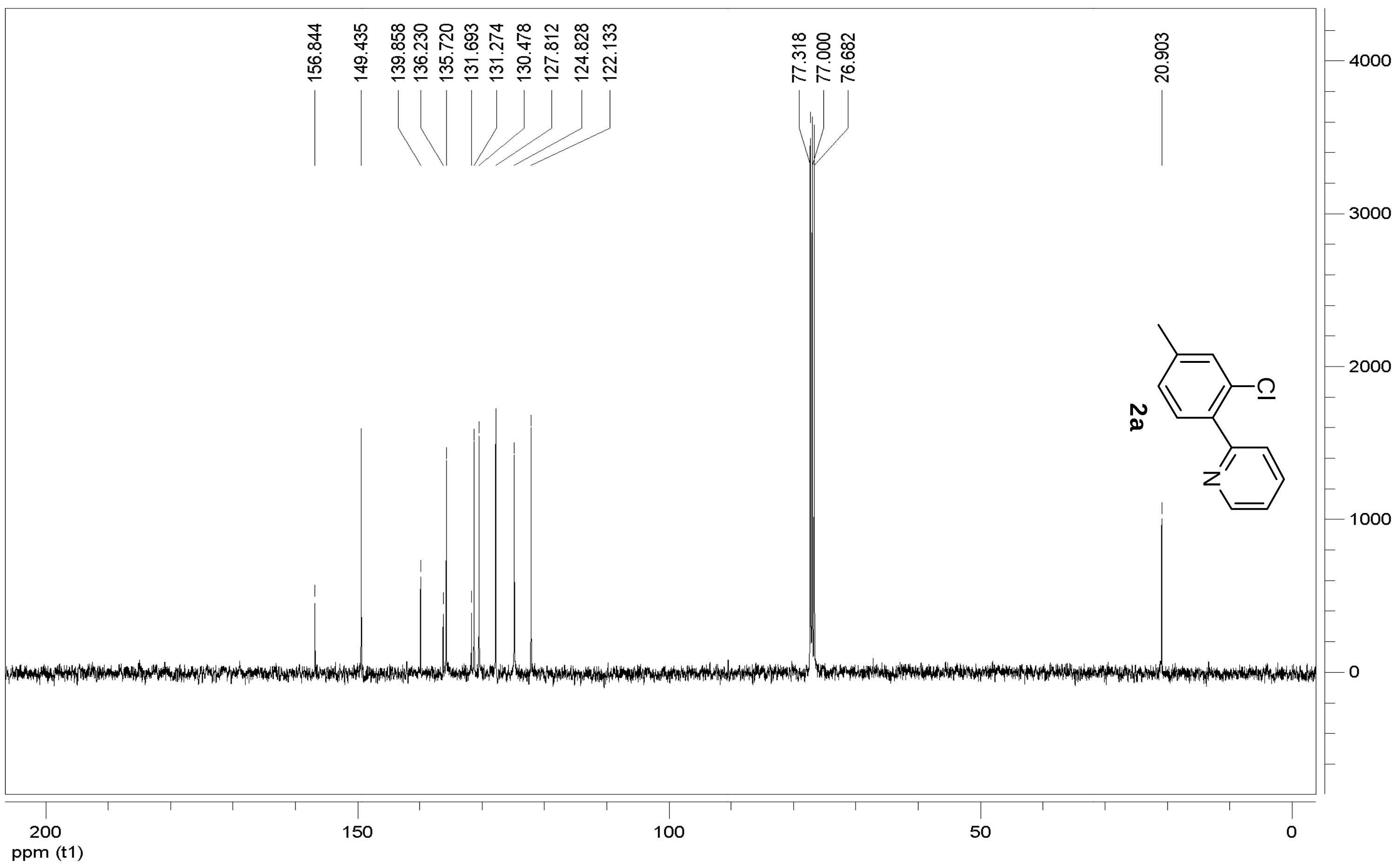
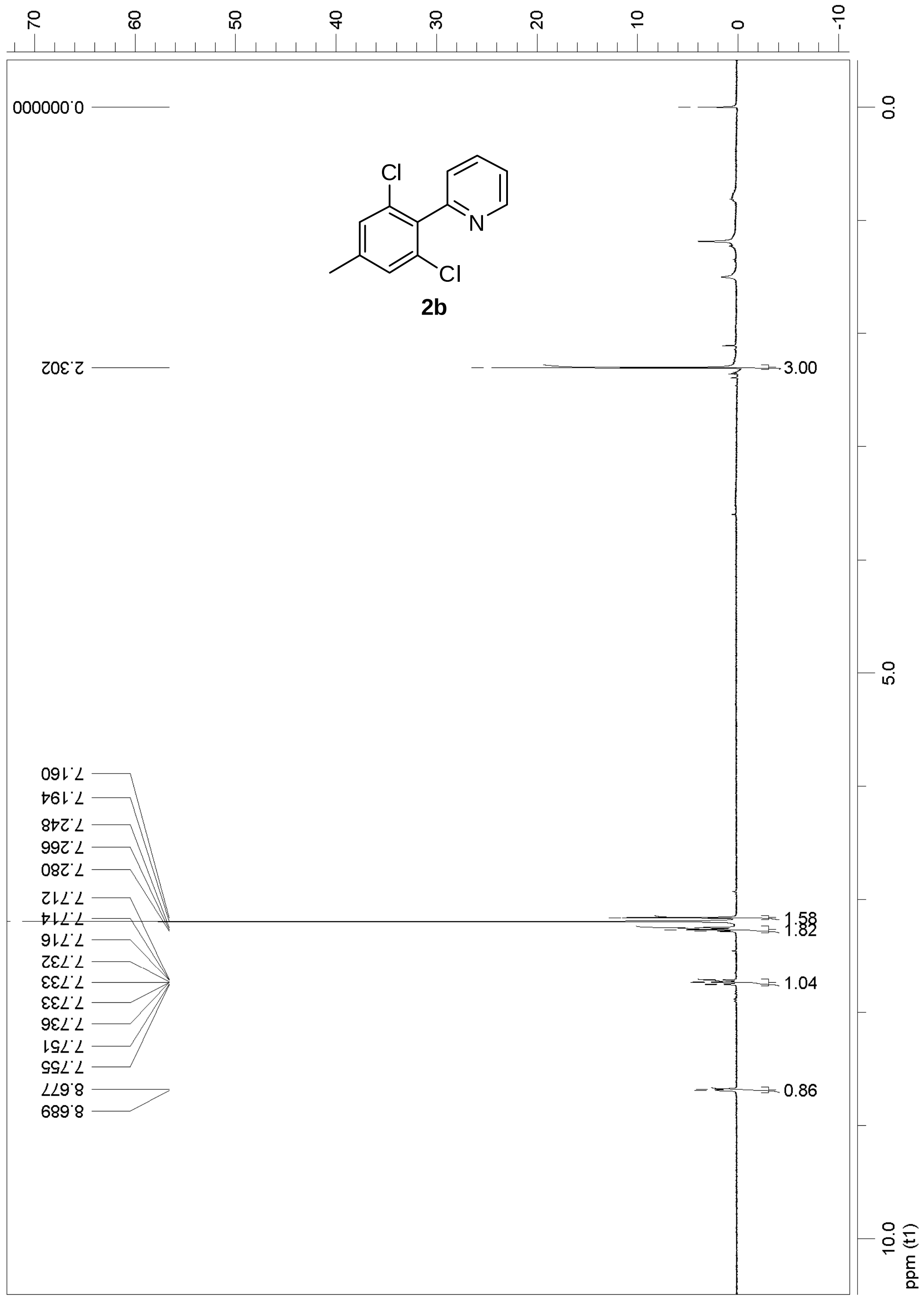
0.96
0.88
1000
500
0
0.0
5.0
10.0
ppm (f1)


156.844
149.435
139.858
136.230
135.720
131.693
131.274
130.478
127.812
124.828
122.133
77.318
77.000
76.682
20.903
Cl
N
2a
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)



**2b**

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7.266
7.280
7.712
7.714
7.716
7.732
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7.733
7.736
7.751
7.755
8.677
8.689
3.00
1.58
1.82
1.04
0.86
0.0
5.0
10.0
ppm (t1)
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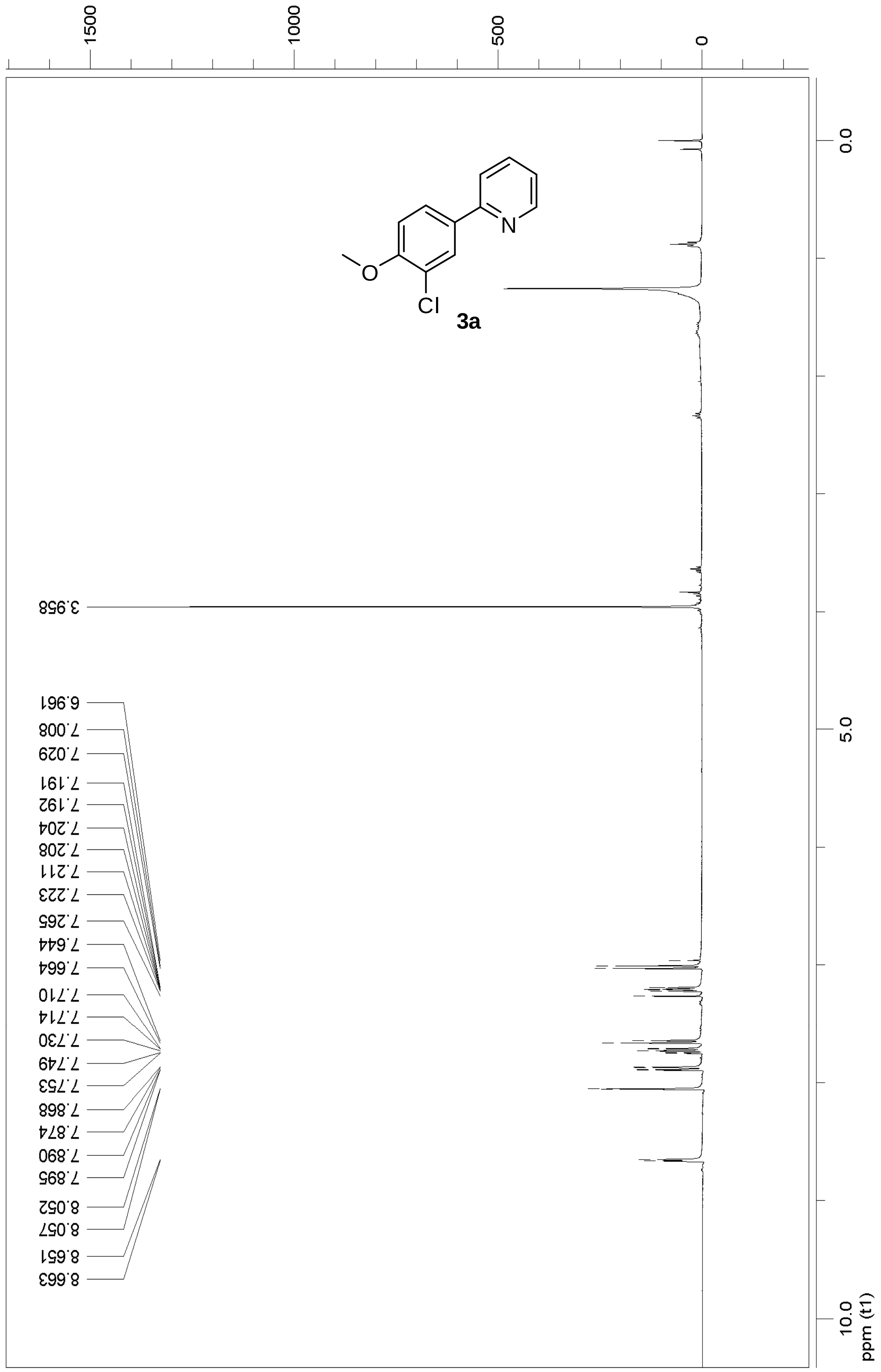
60
50
40
30
20
10
0
-10


3a
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N
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7.192
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7.208
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7.714
7.730
7.749
7.753
7.868
7.874
7.890
7.895
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8.057
8.651
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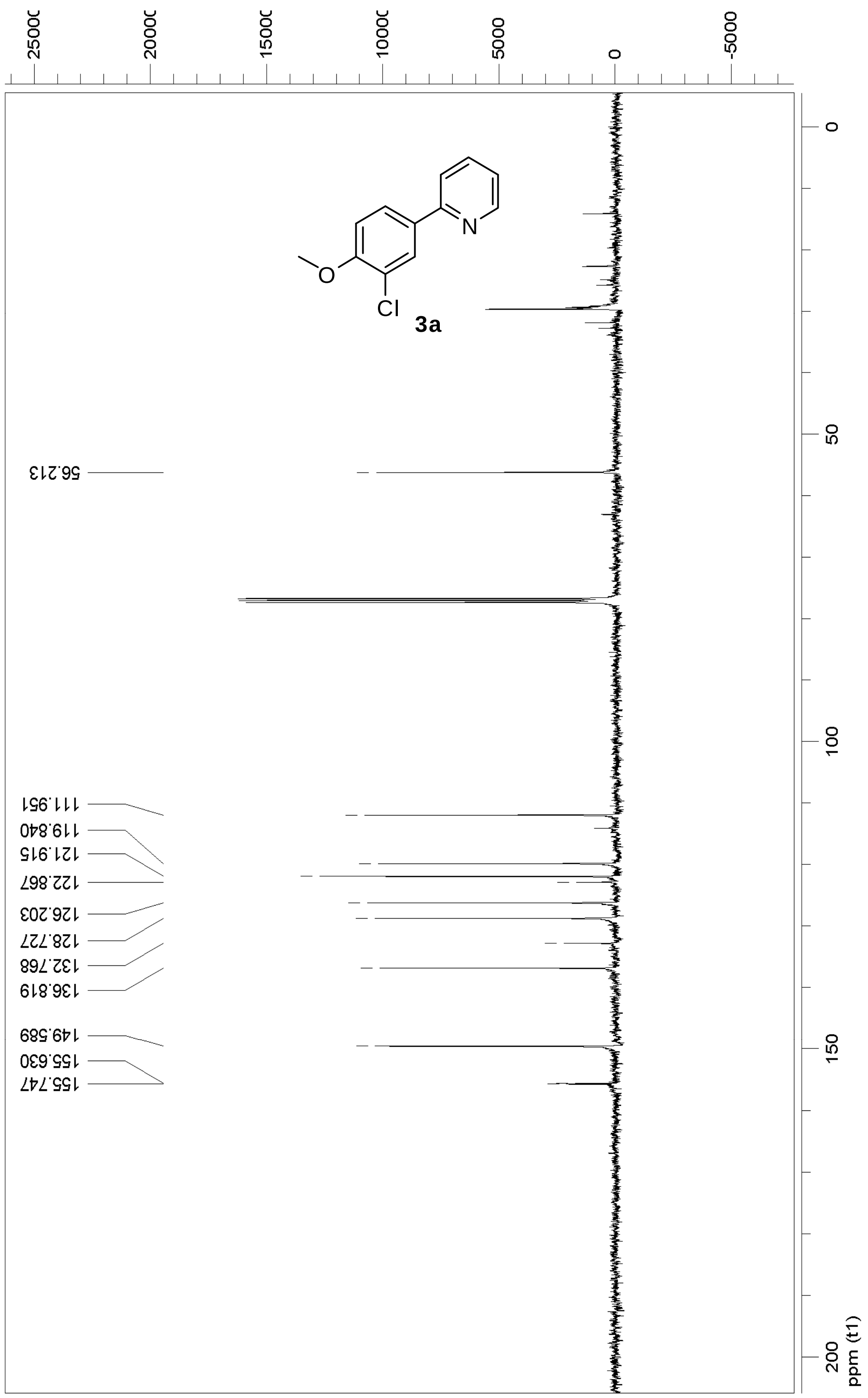
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)


O
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N
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15000
10000
5000
0
-5000
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128.727
132.768
136.819
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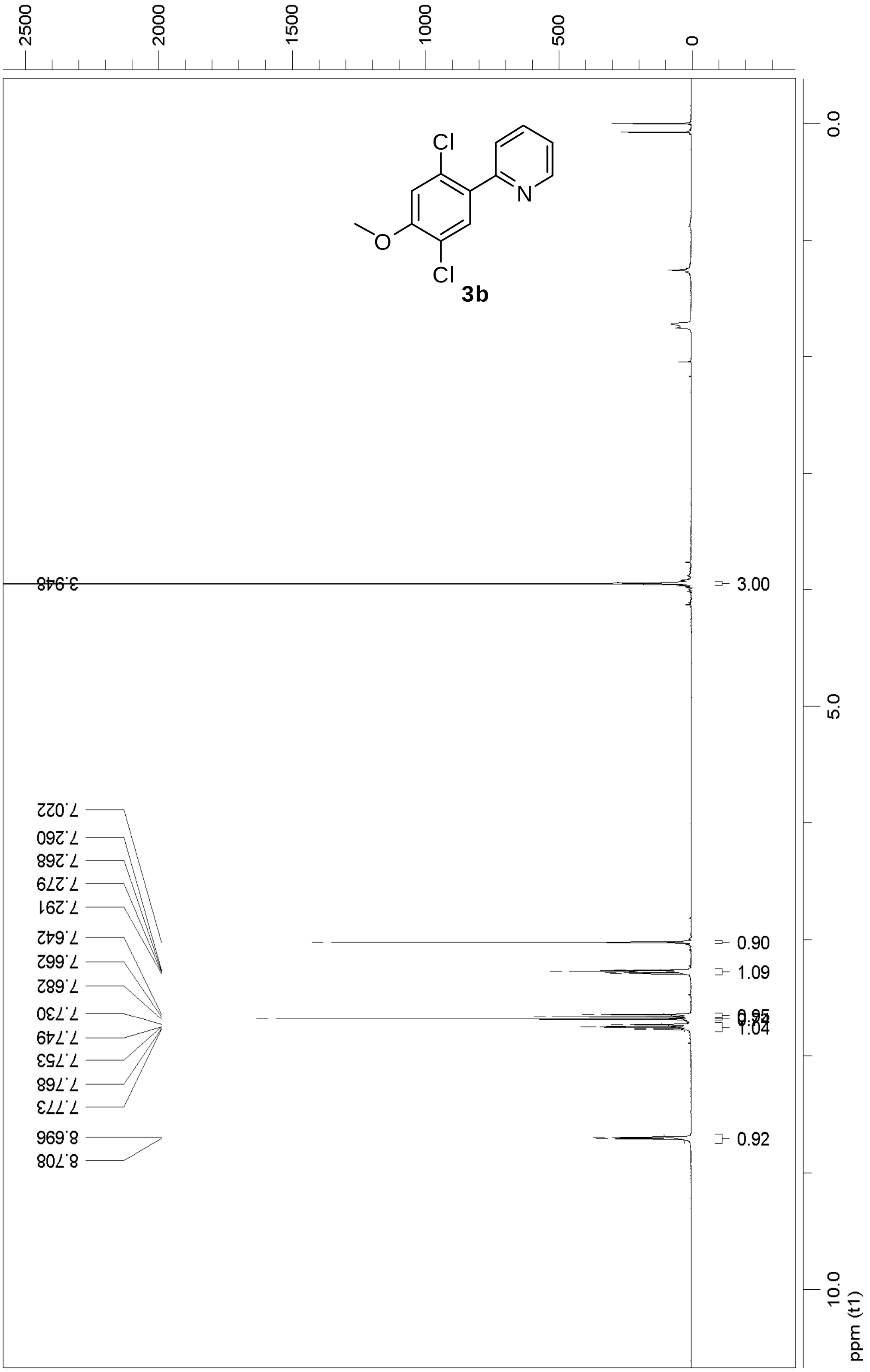
155.630
155.747
0
50
100
150
200
ppm (t1)

3a



**3b**

Cl
Cl
O
N
2500
2000
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)
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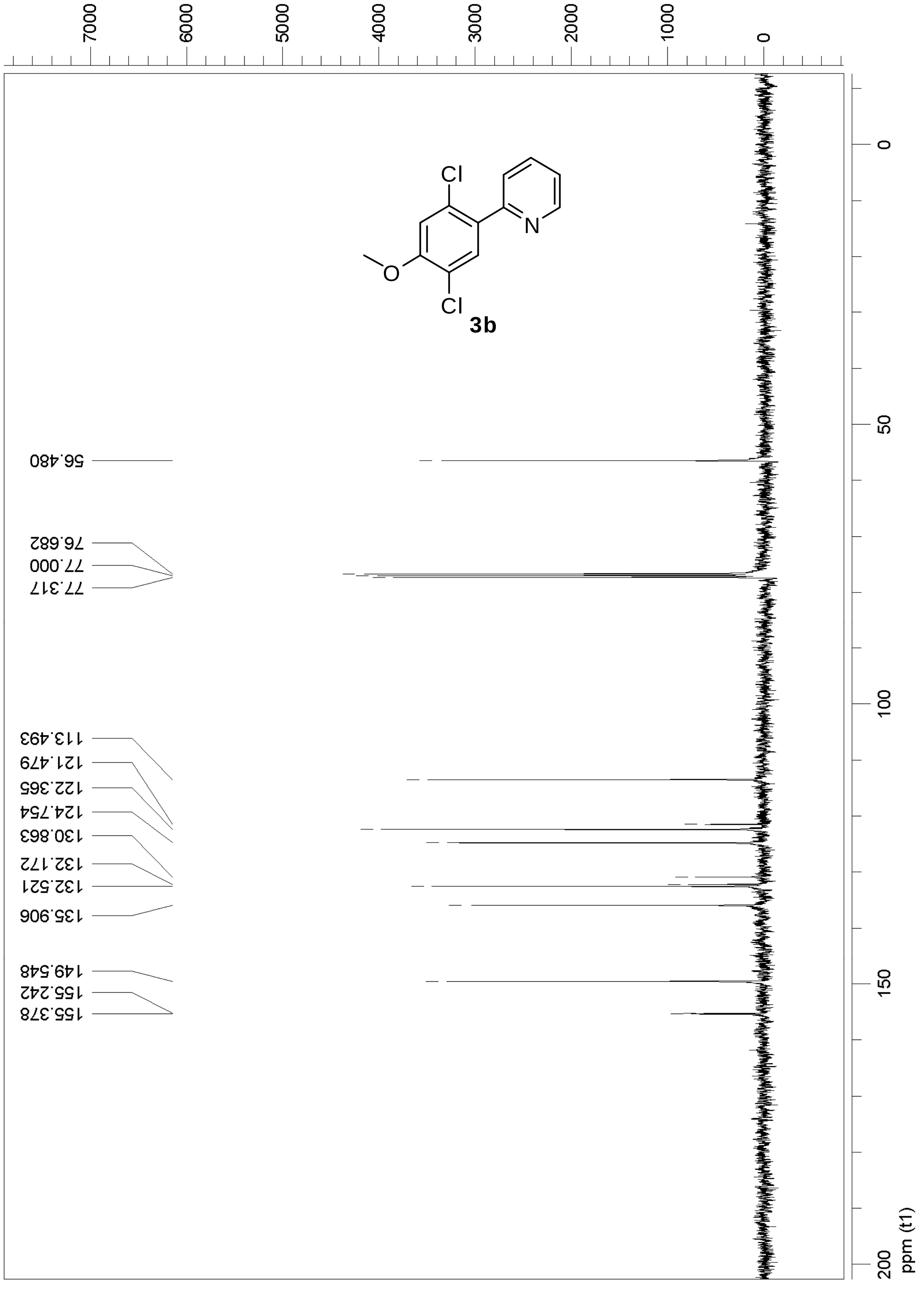
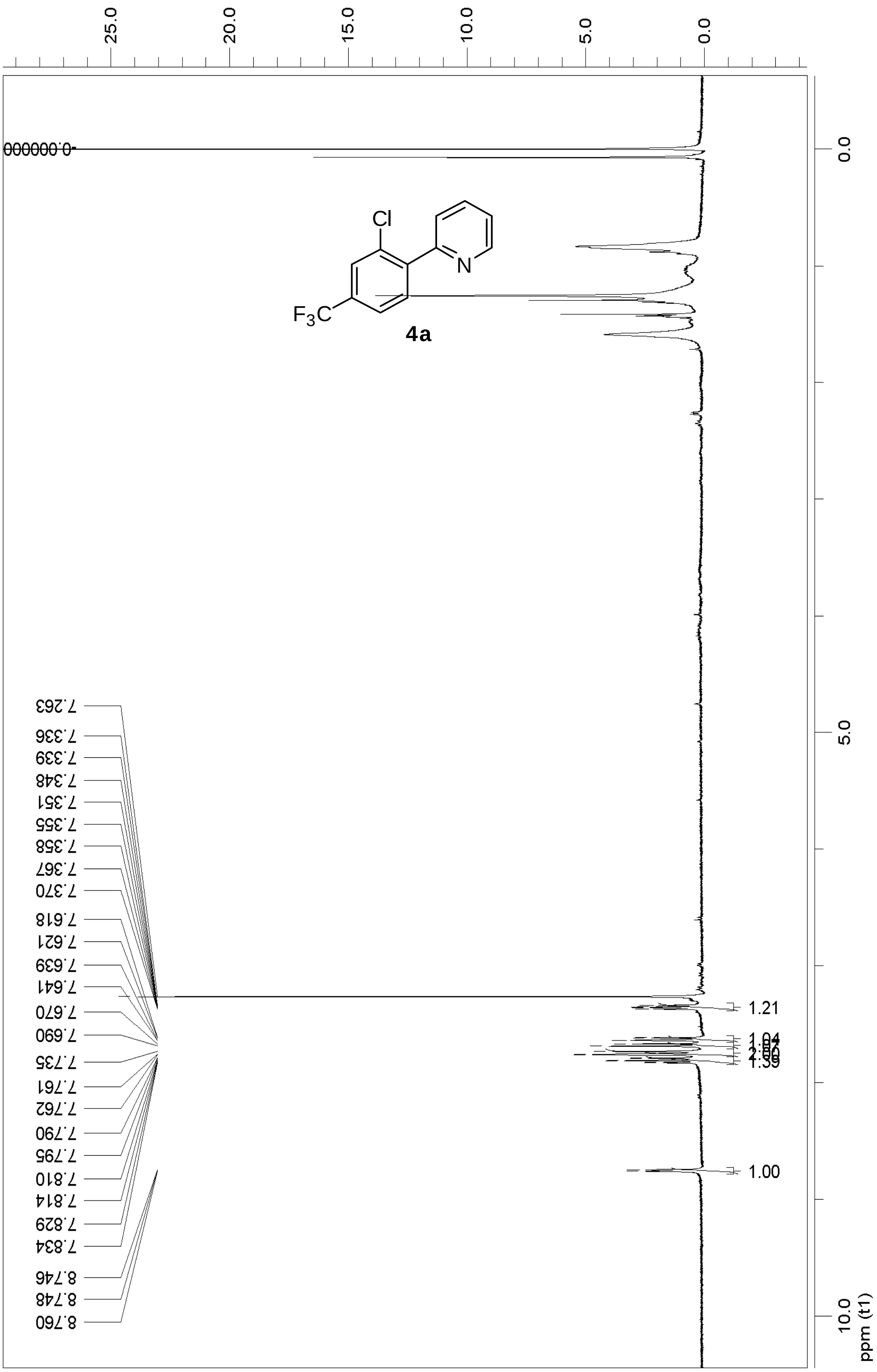
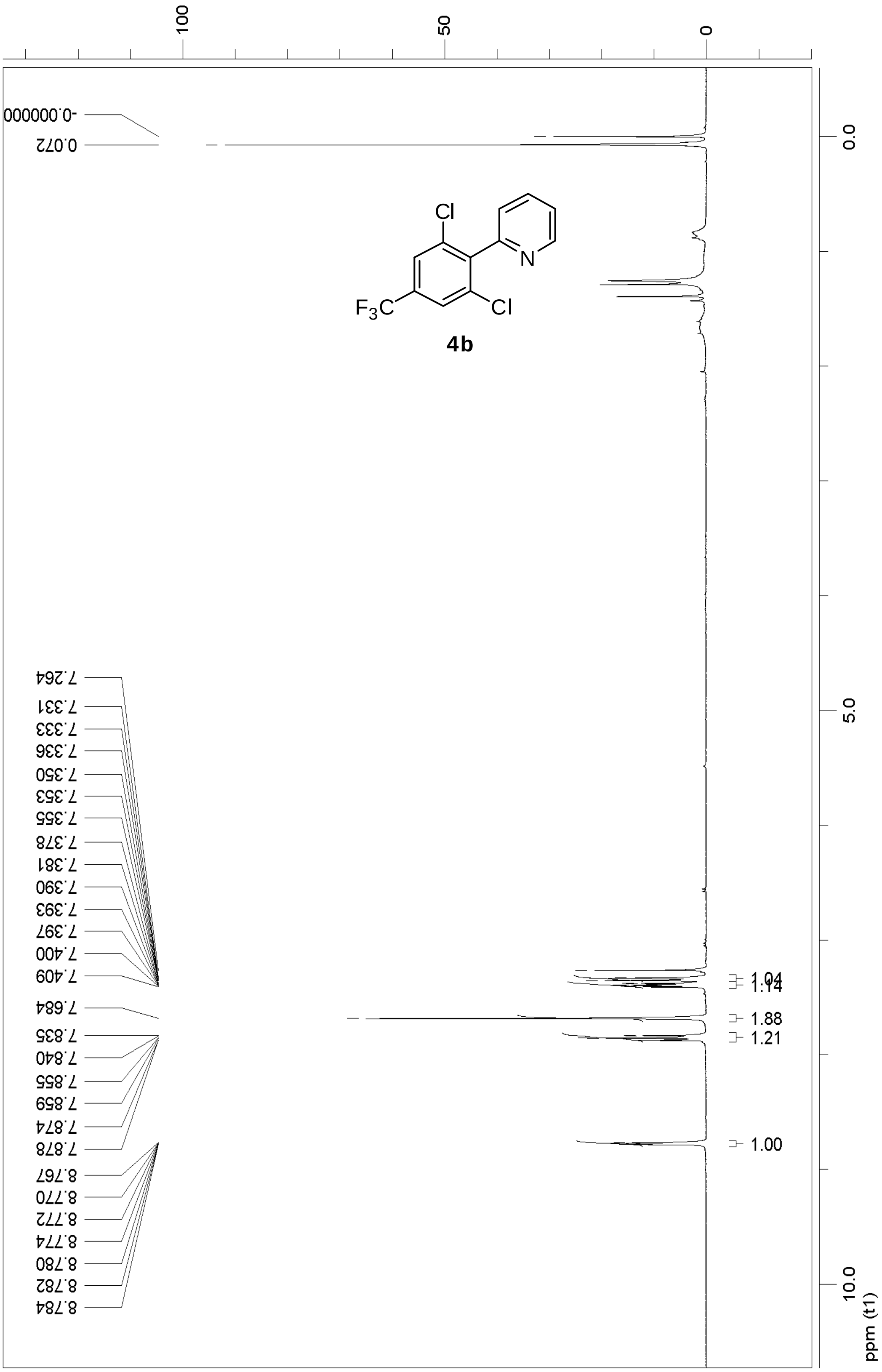
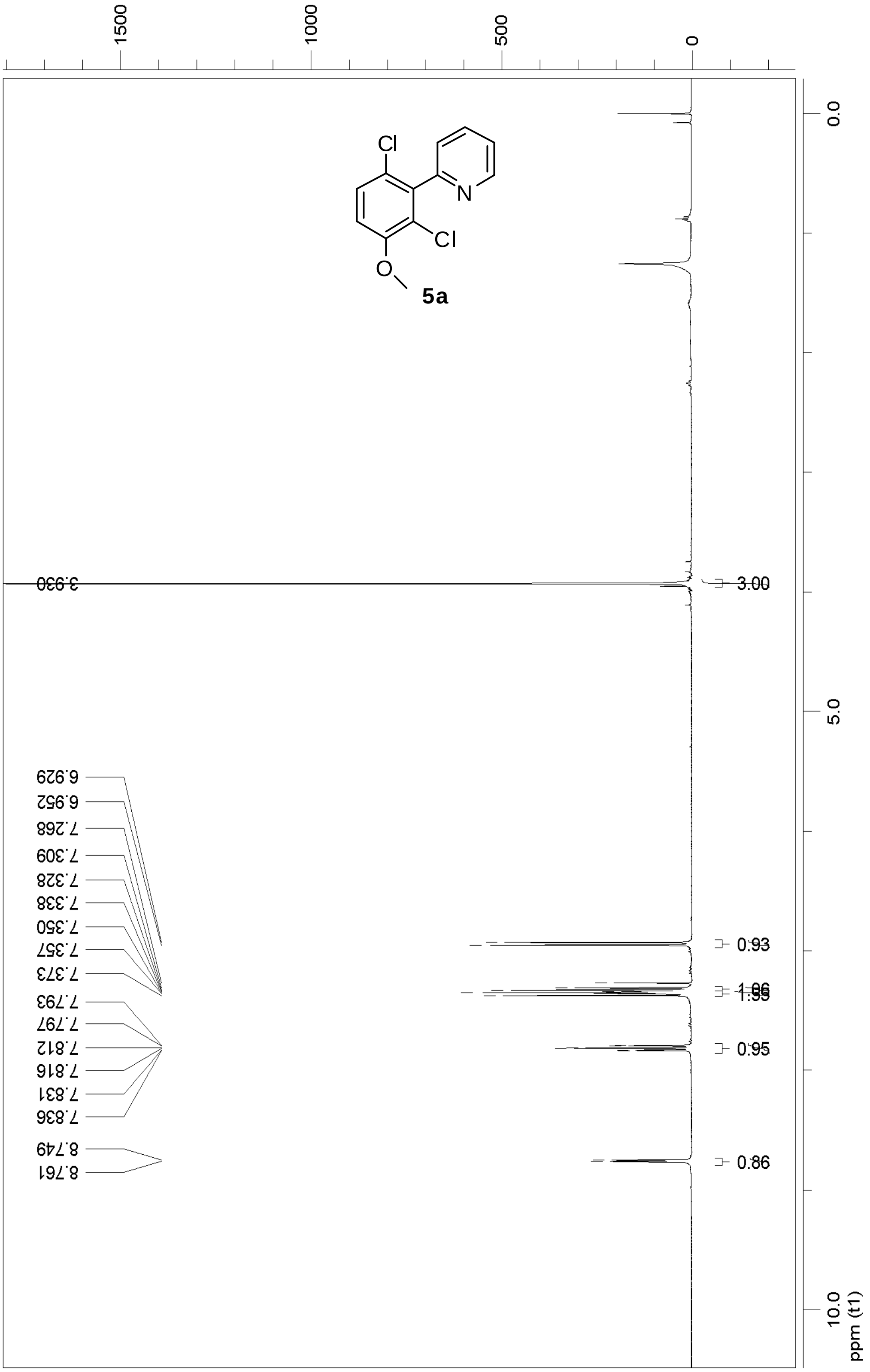
7.260
7.268
7.279
7.291
7.642
7.662
7.682
7.730
7.749
7.753
7.768
7.773
8.696
8.708
3.00
0.90
1.09
0.95
1.04
0.92

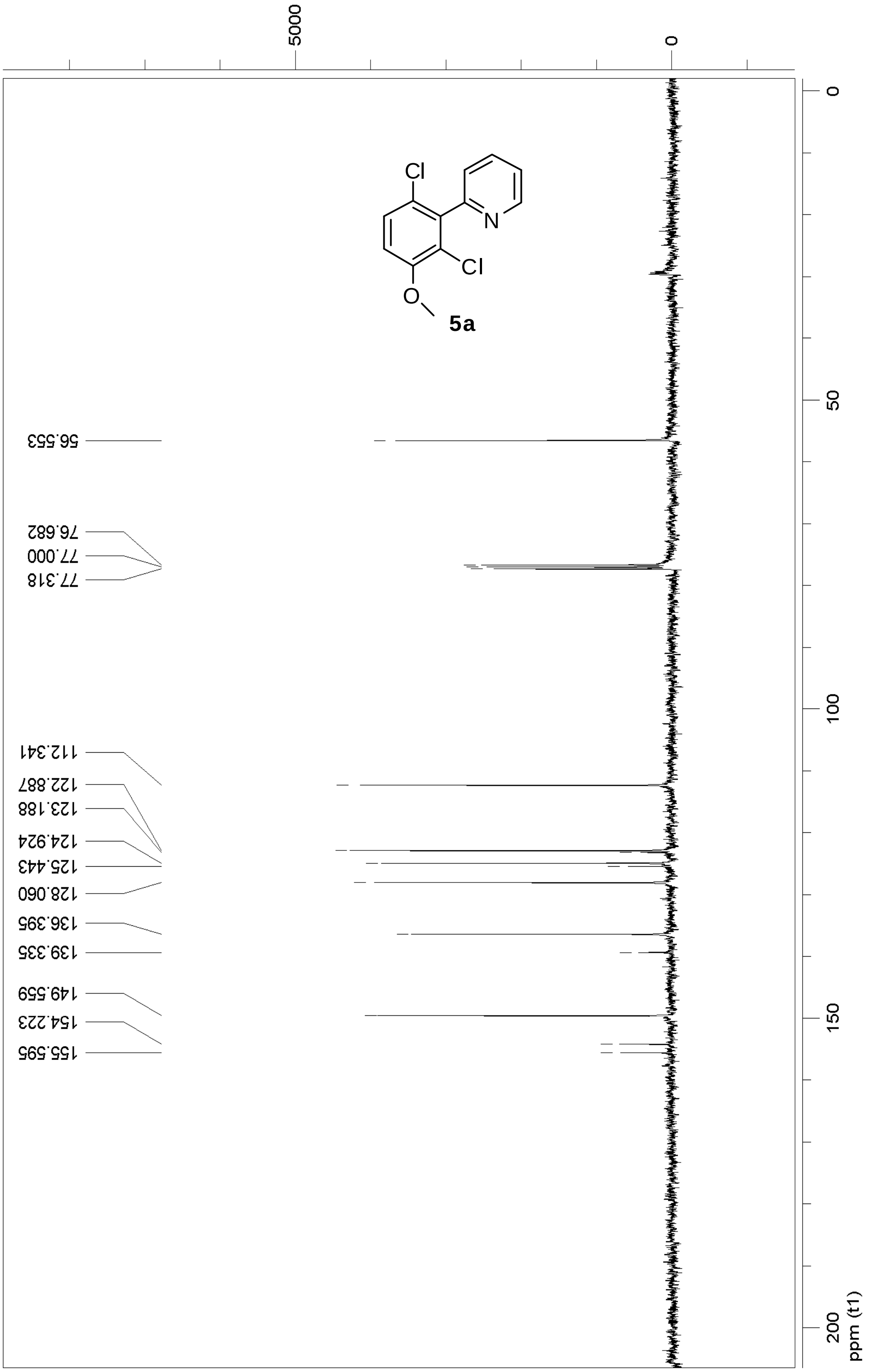

3b
Cl
Cl
O
N
56.480
76.682
77.000
77.317
113.493
121.479
122.365
124.754
130.863
132.172
132.521
135.906
149.548
155.242
155.378
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
ppm (t1)

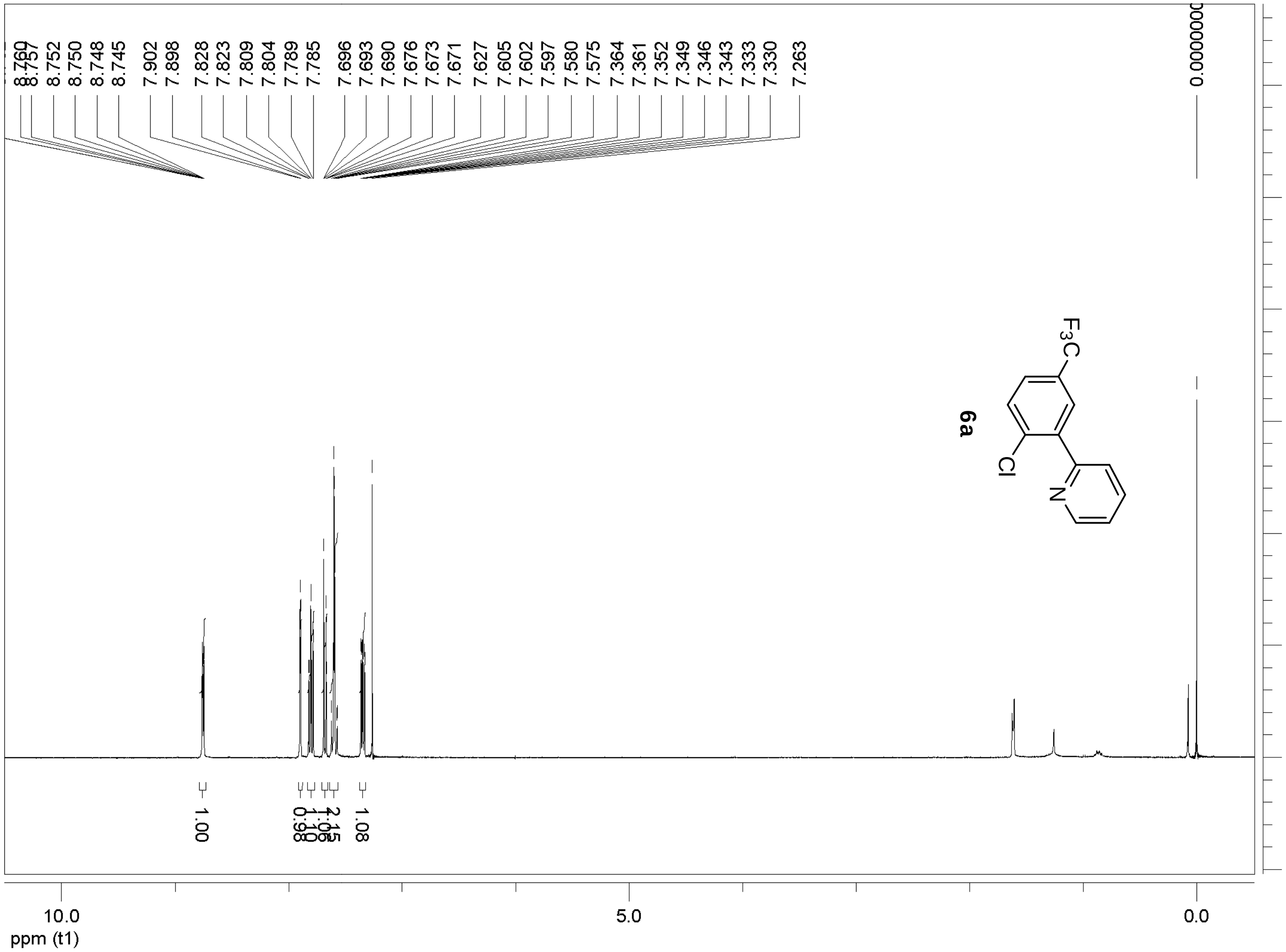

Cl
N
F3C
4a
0.000000
7.263
7.336
7.339
7.348
7.351
7.355
7.358
7.367
7.370
7.618
7.621
7.639
7.641
7.670
7.690
7.735
7.761
7.762
7.790
7.795
7.810
7.814
7.829
7.834
8.746
8.748
8.760
1.21
1.04
1.07
2.00
1.39
1.00
25.0
20.0
15.0
10.0
5.0
0.0
0.0
5.0
10.0
ppm (t1)

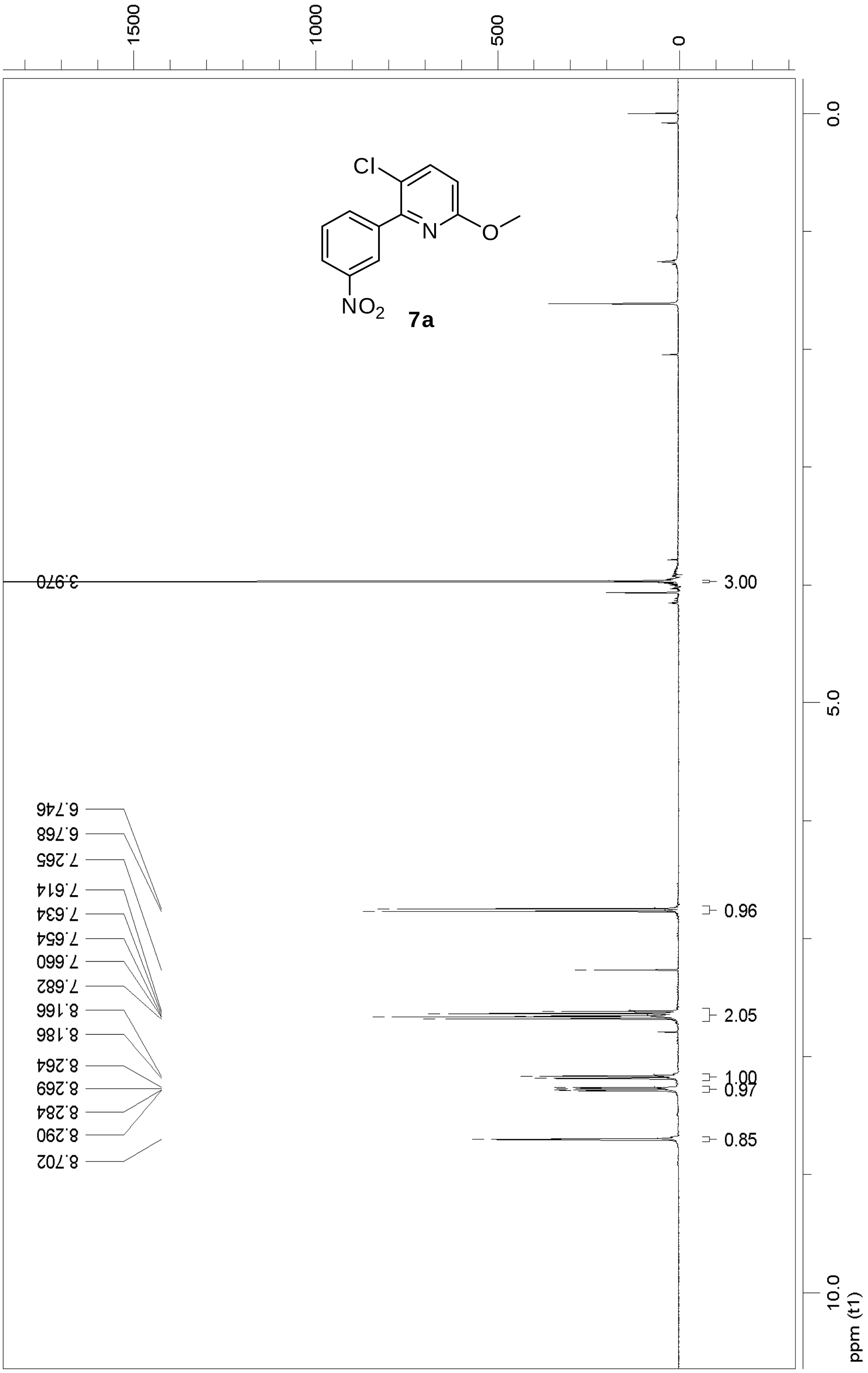


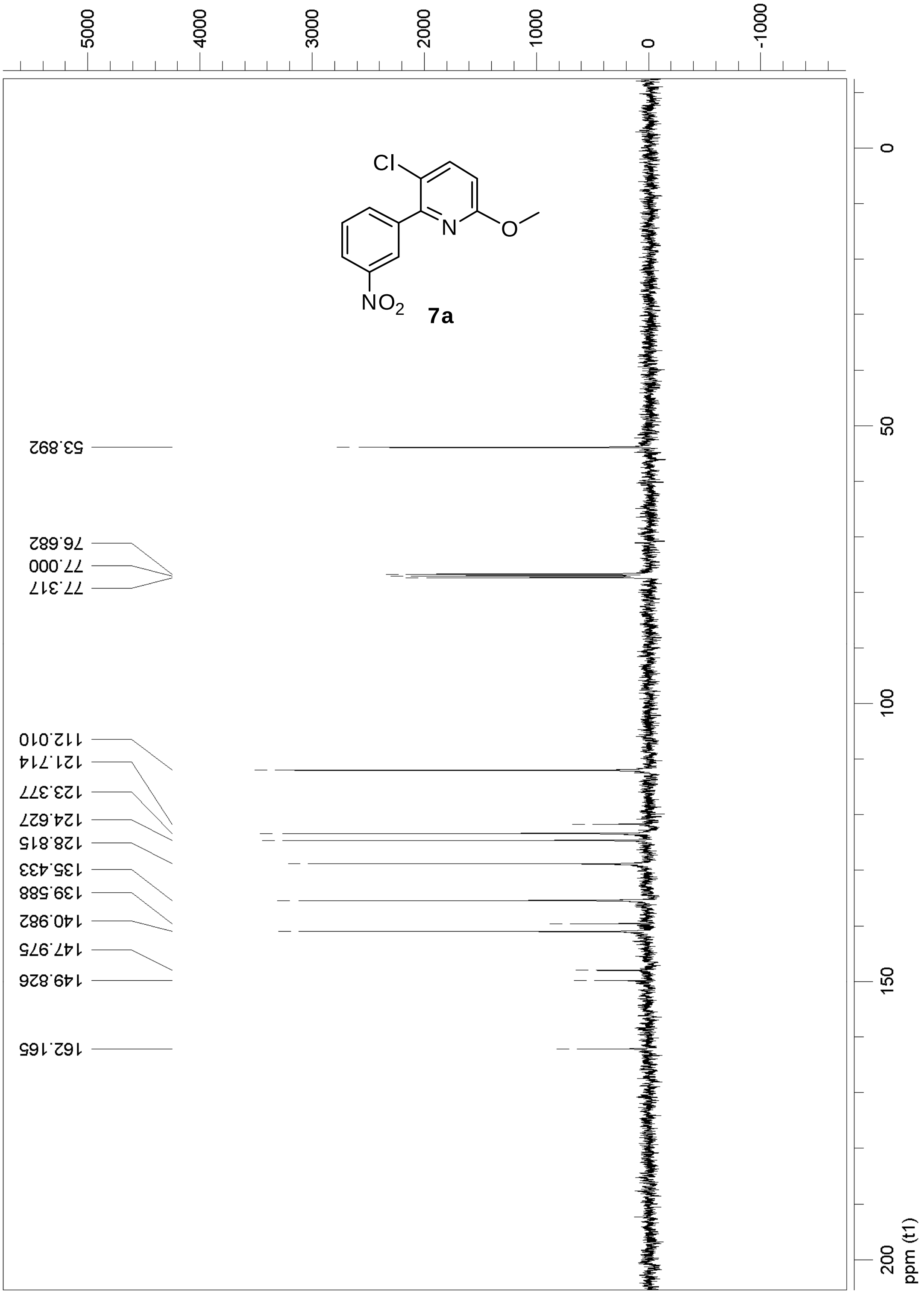
-0.000000
0.072
7.264
7.331
7.333
7.336
7.350
7.353
7.355
7.378
7.381
7.390
7.393
7.397
7.400
7.409
7.684
7.835
7.840
7.855
7.859
7.874
7.878
8.767
8.770
8.772
8.774
8.780
8.782
8.784
1.04
1.14
1.88
1.21
1.00
0.0
5.0
10.0
ppm (t1)
100
50
0
Cl
N
Cl
$F_3C$
4b

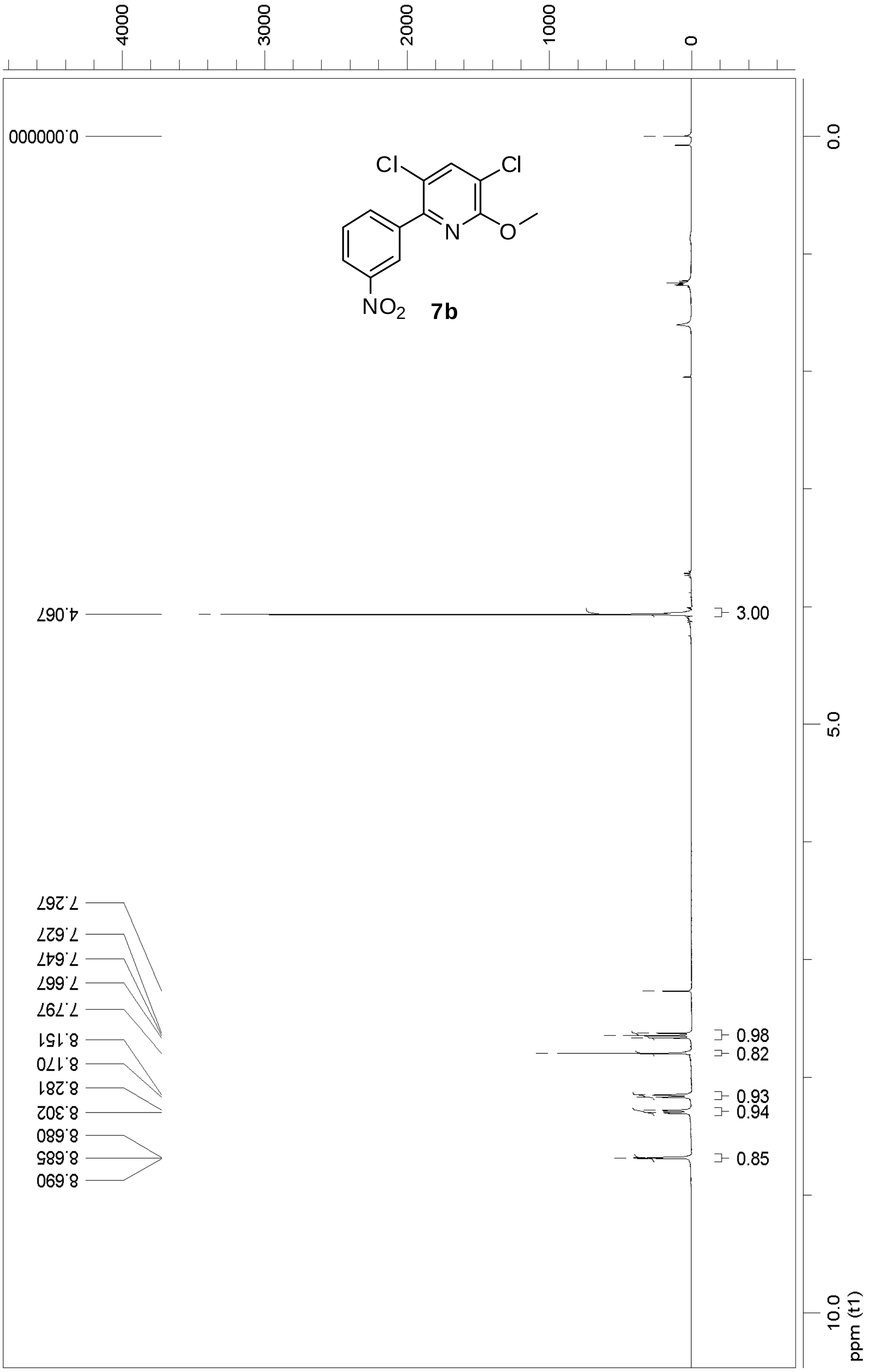

Cl
Cl
N
O
5a
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)
3.930
6.929
6.952
7.268
7.309
7.328
7.338
7.350
7.357
7.373
7.793
7.797
7.812
7.816
7.831
7.836
8.749
8.761
3.00
0.93
1.96
1.95
0.95
0.86

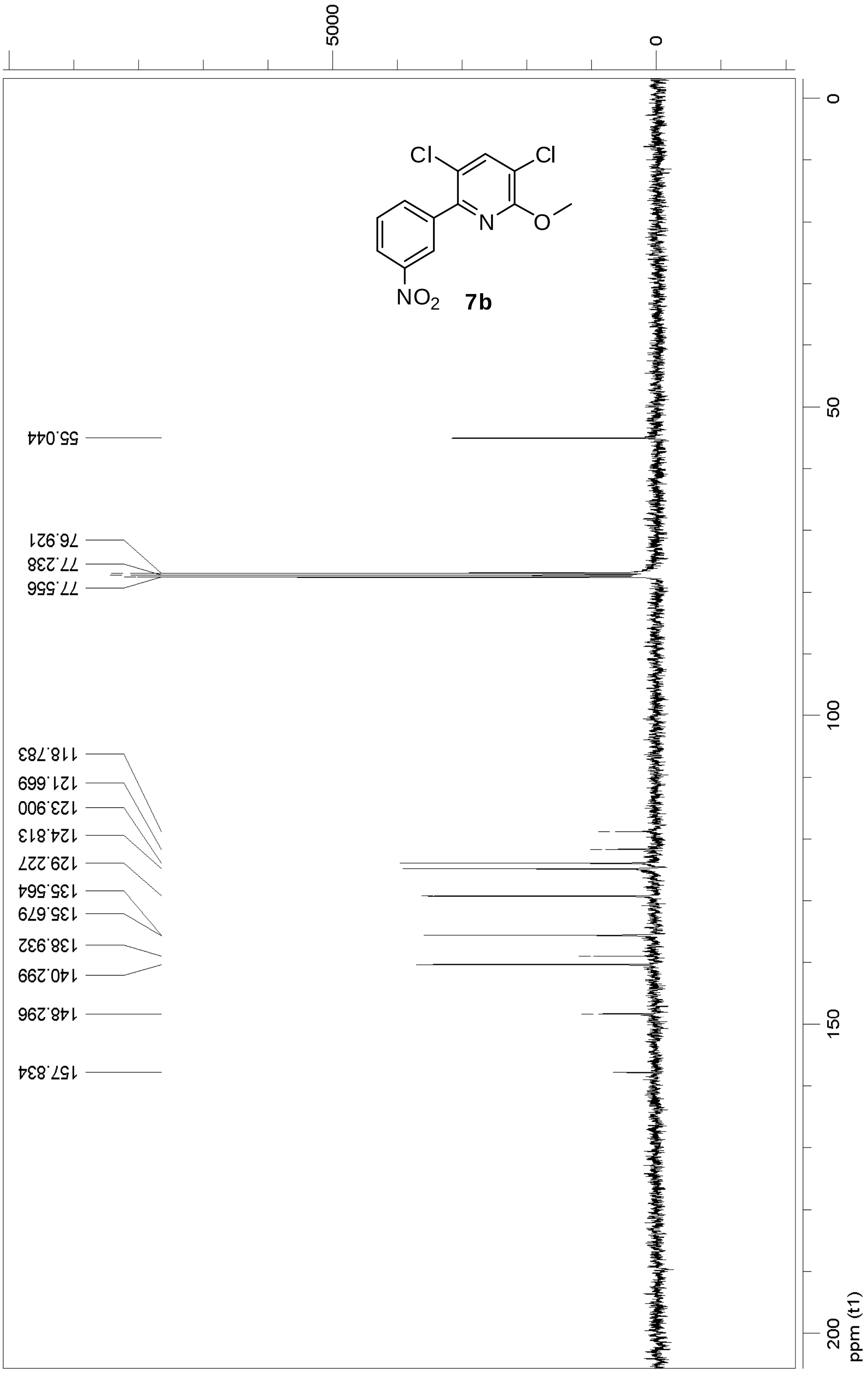

5a
Cl
Cl
N
O
56.553
76.682
77.000
77.318
112.341
122.887
123.188
124.924
125.443
128.060
136.395
139.335
149.559
154.223
155.595
5000
0
0
50
100
150
200
ppm (t1)

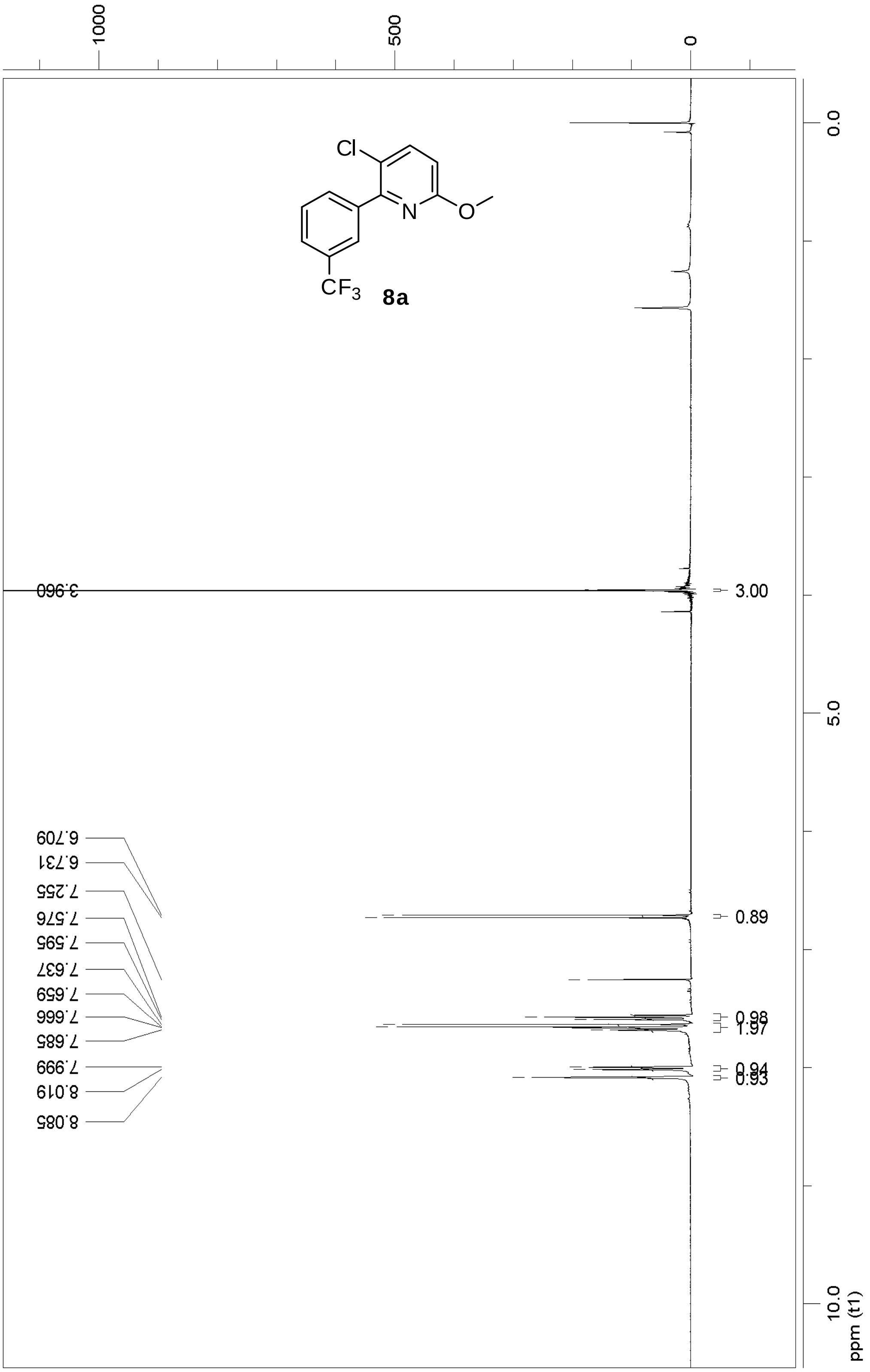

8.760
8.757
8.752
8.750
8.748
8.745
7.902
7.898
7.828
7.823
7.809
7.804
7.789
7.785
7.696
7.693
7.690
7.676
7.673
7.671
7.627
7.605
7.602
7.597
7.580
7.575
7.364
7.361
7.352
7.349
7.346
7.343
7.333
7.330
7.263
0.000000
F3C
Cl
N
6a
1.00
0.98
1.10
1.06
2.15
1.08
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

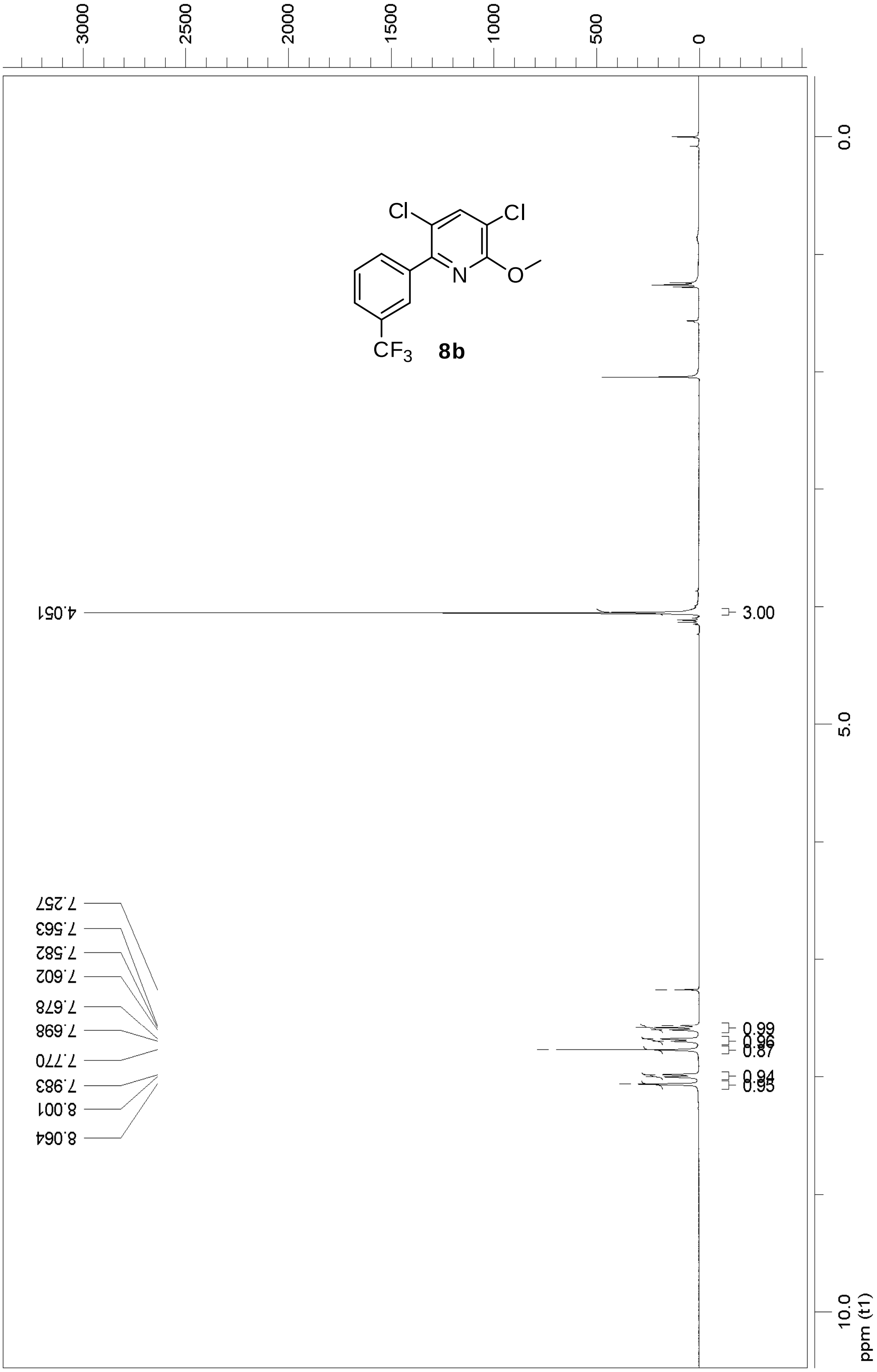

7a
Cl
N
O
NO2
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)
3.970
6.746
6.768
7.265
7.614
7.634
7.654
7.660
7.682
8.166
8.186
8.264
8.269
8.284
8.290
8.702
3.00
0.96
2.05
1.00
0.97
0.85


Cl
N
O
NO2
7a
53.892
76.682
77.000
77.317
112.010
121.714
123.377
124.627
128.815
135.433
139.588
140.982
147.975
149.826
162.165
5000
4000
3000
2000
1000
0
-1000
0
50
100
150
200
ppm (t1)

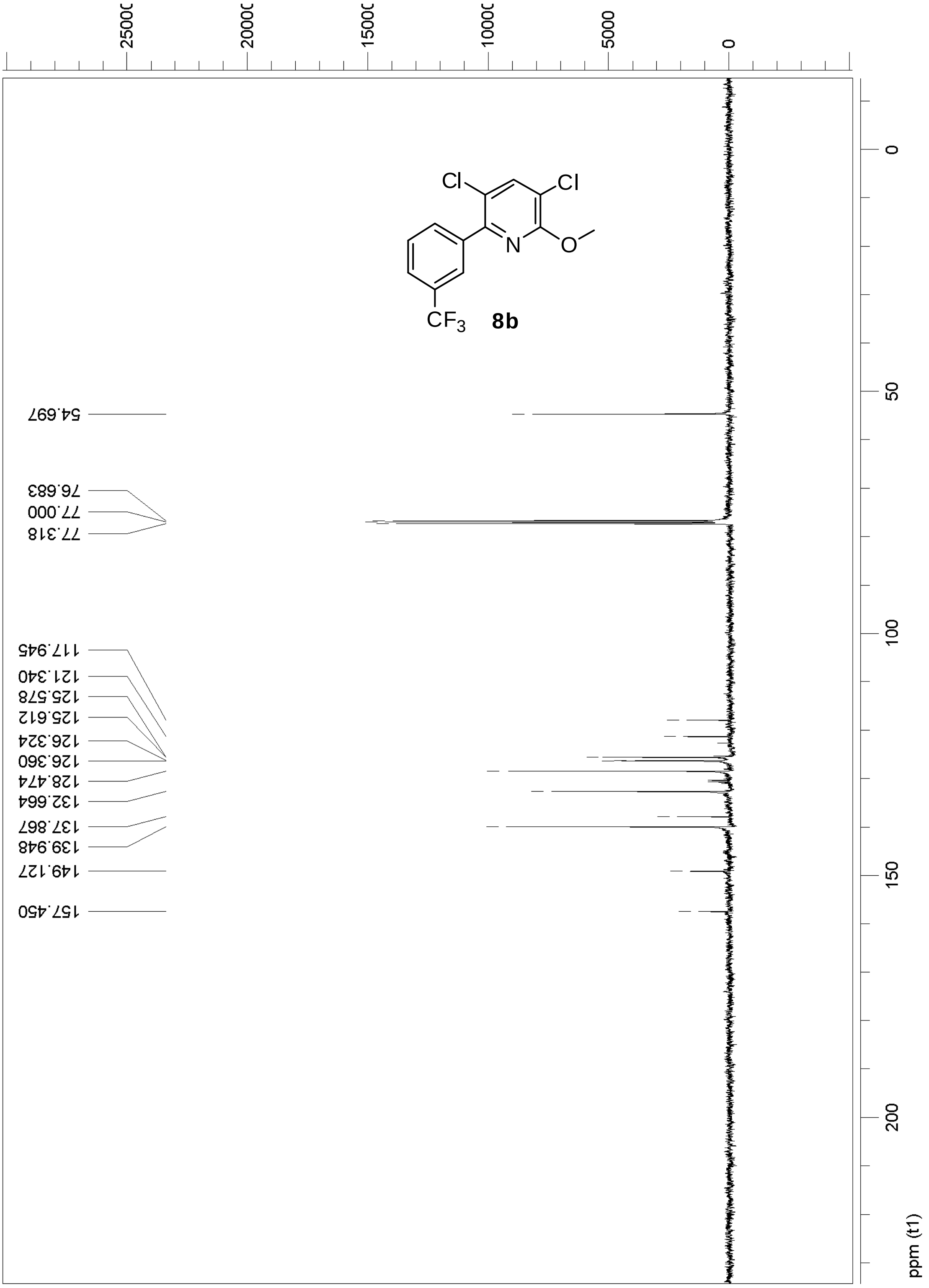
4000
3000
2000
1000
0
0.000000
4.067
7.267
7.627
7.647
7.667
7.797
8.151
8.170
8.281
8.302
8.680
8.685
8.690
3.00
0.98
0.82
0.93
0.94
0.85
0.0
5.0
10.0
ppm (t1)
Cl
Cl
N
O
NO2
7b


5000
0
Cl
Cl
N
O
$NO_2$
7b
55.044
76.921
77.238
77.556
118.783
121.669
123.900
124.813
129.227
135.564
135.679
138.932
140.299
148.296
157.834
0
50
100
150
200
ppm (t1)

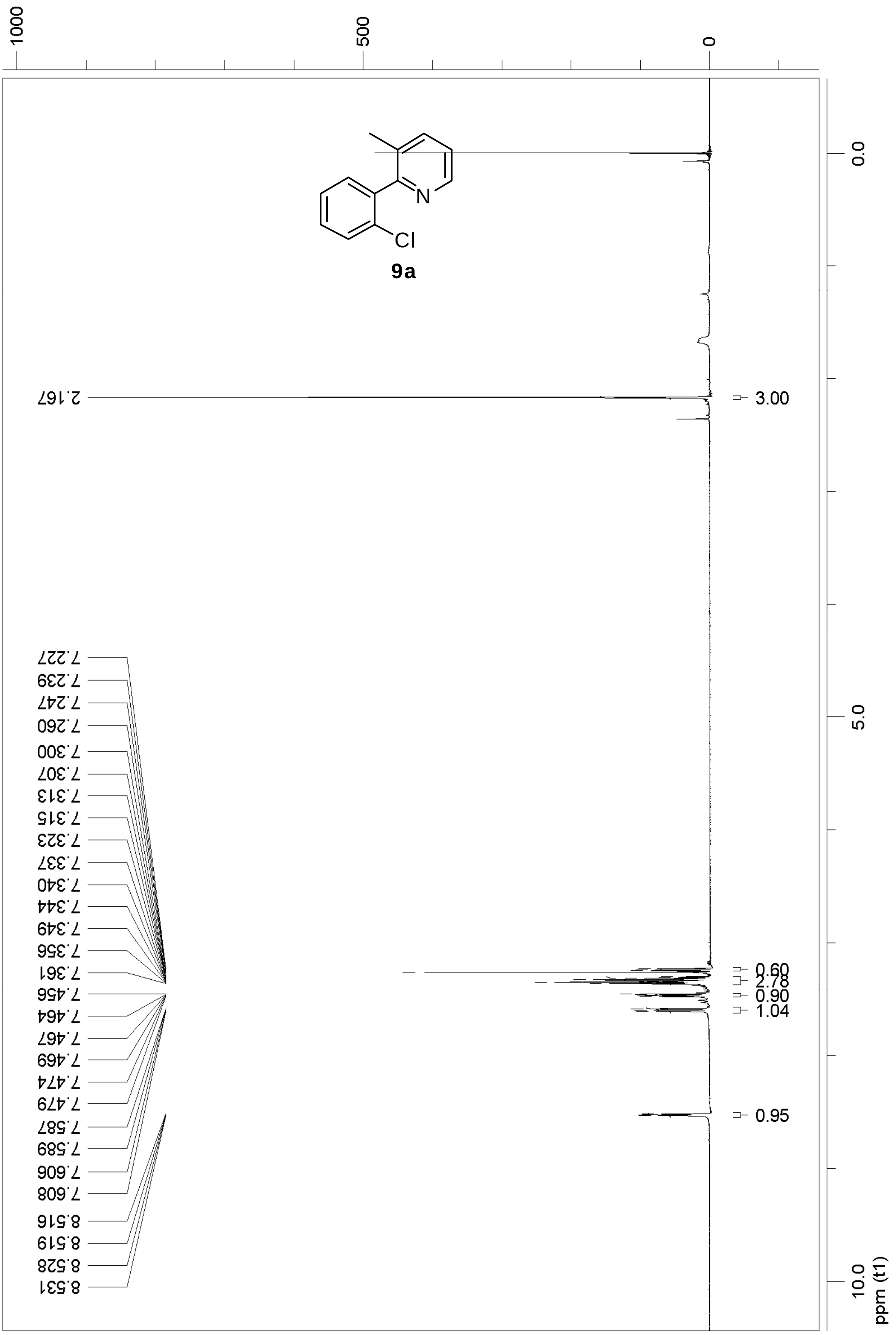

Cl
N
O
CF3
8a
1000
500
0
0.0
5.0
10.0
ppm (t1)
3.960
6.709
6.731
7.255
7.576
7.595
7.637
7.659
7.666
7.685
7.999
8.019
8.085
3.00
0.89
0.98
1.97
0.94
0.93



Cl
Cl
N
O
CF3
8b
3000
2500
2000
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)
4.051
7.257
7.563
7.582
7.602
7.678
7.698
7.770
7.983
8.001
8.064
3.00
0.99
0.96
0.87
0.94
0.95

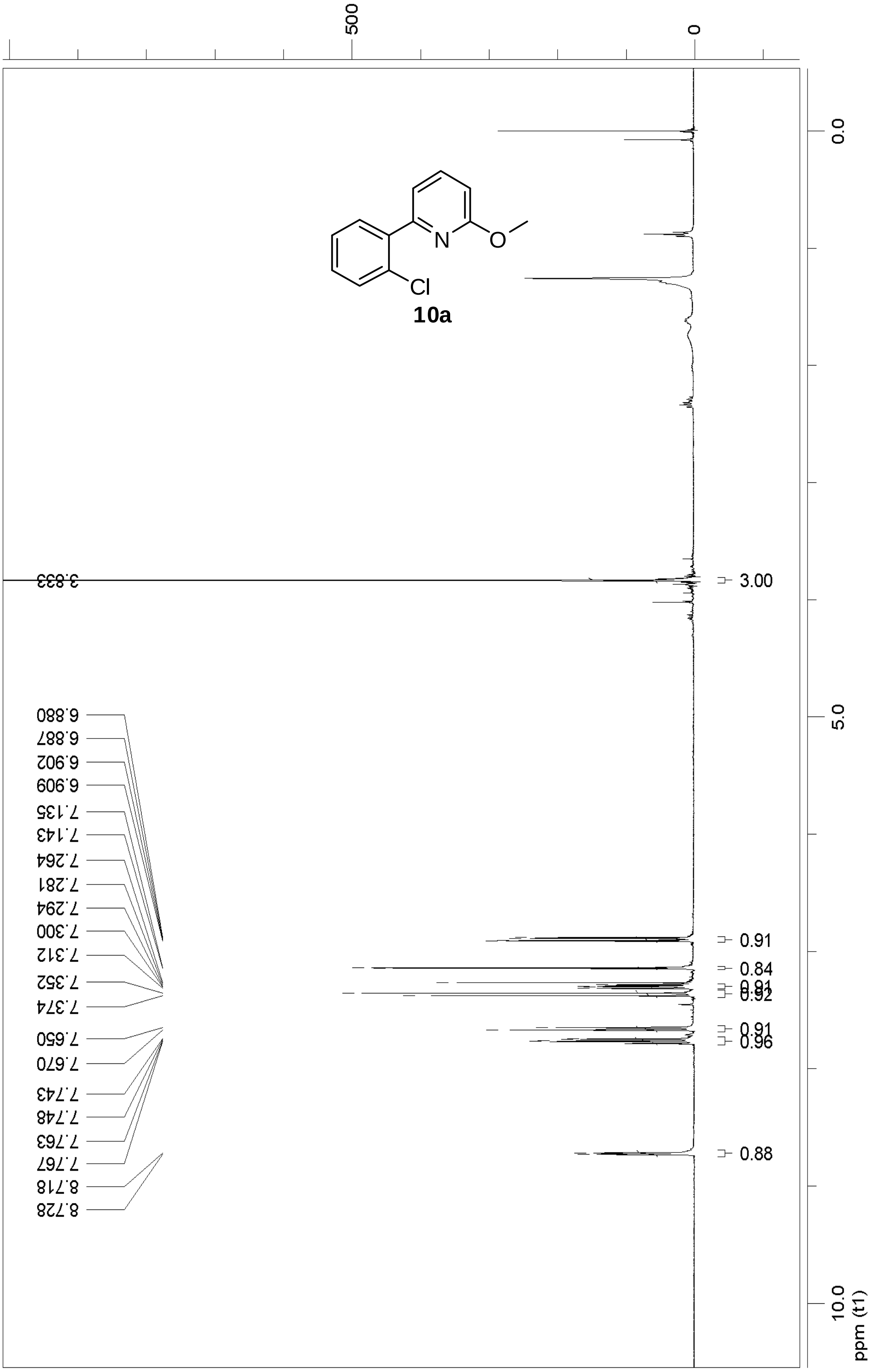


8b
Cl
Cl
N
O
CF3
54.697
76.683
77.000
77.318
117.945
121.340
125.578
125.612
126.324
126.360
128.474
132.664
137.867
139.948
149.127
157.450
25000
20000
15000
10000
5000
0
0
50
100
150
200
ppm (t1)



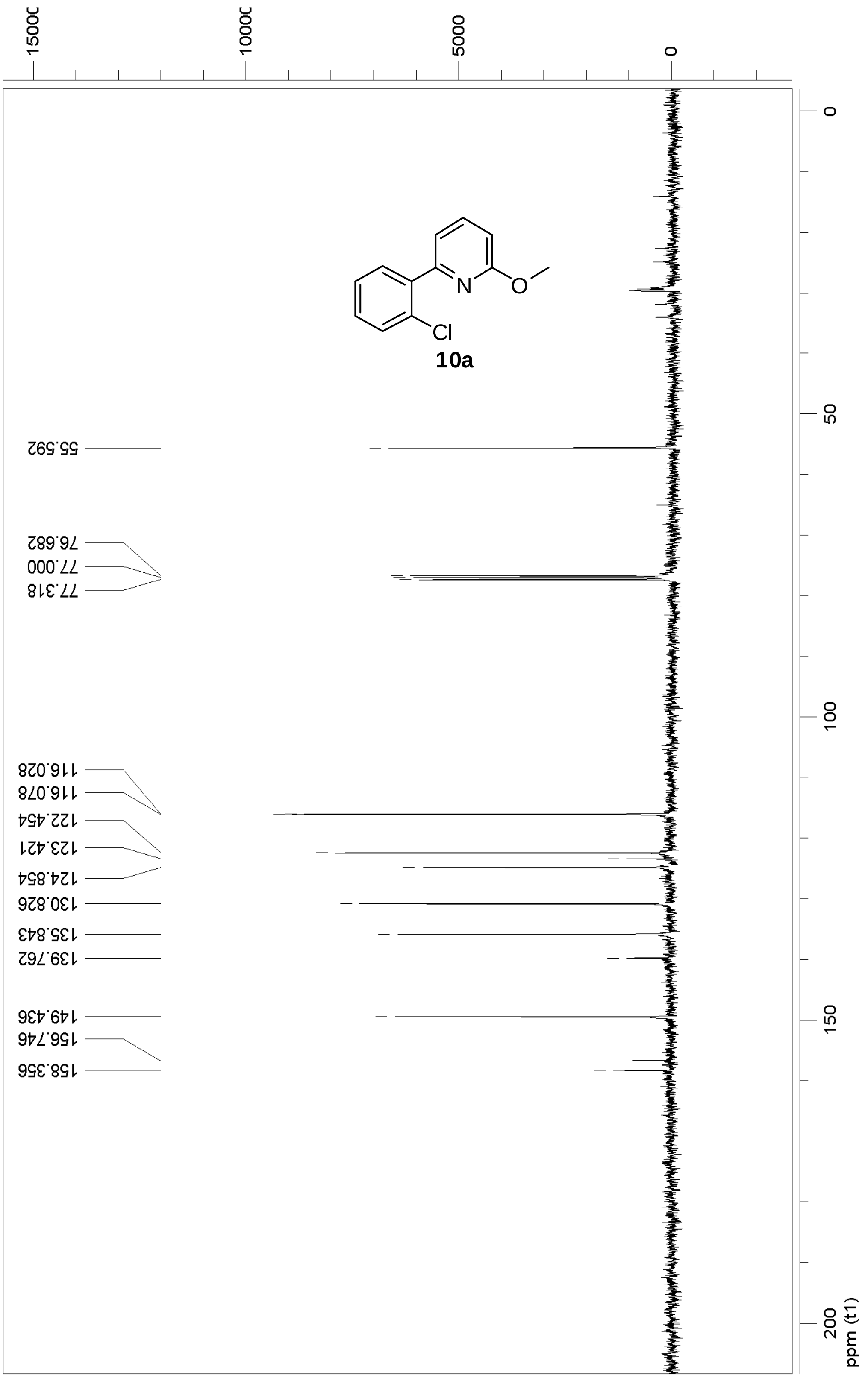
1000
500
0
0.0
5.0
10.0
ppm (t1)
2.167
7.227
7.239
7.247
7.260
7.300
7.307
7.313
7.315
7.323
7.337
7.340
7.344
7.349
7.356
7.361
7.456
7.464
7.467
7.469
7.474
7.479
7.587
7.589
7.606
7.608
8.516
8.519
8.528
8.531
3.00
0.60
2.78
0.90
1.04
0.95
N
Cl

**9a**

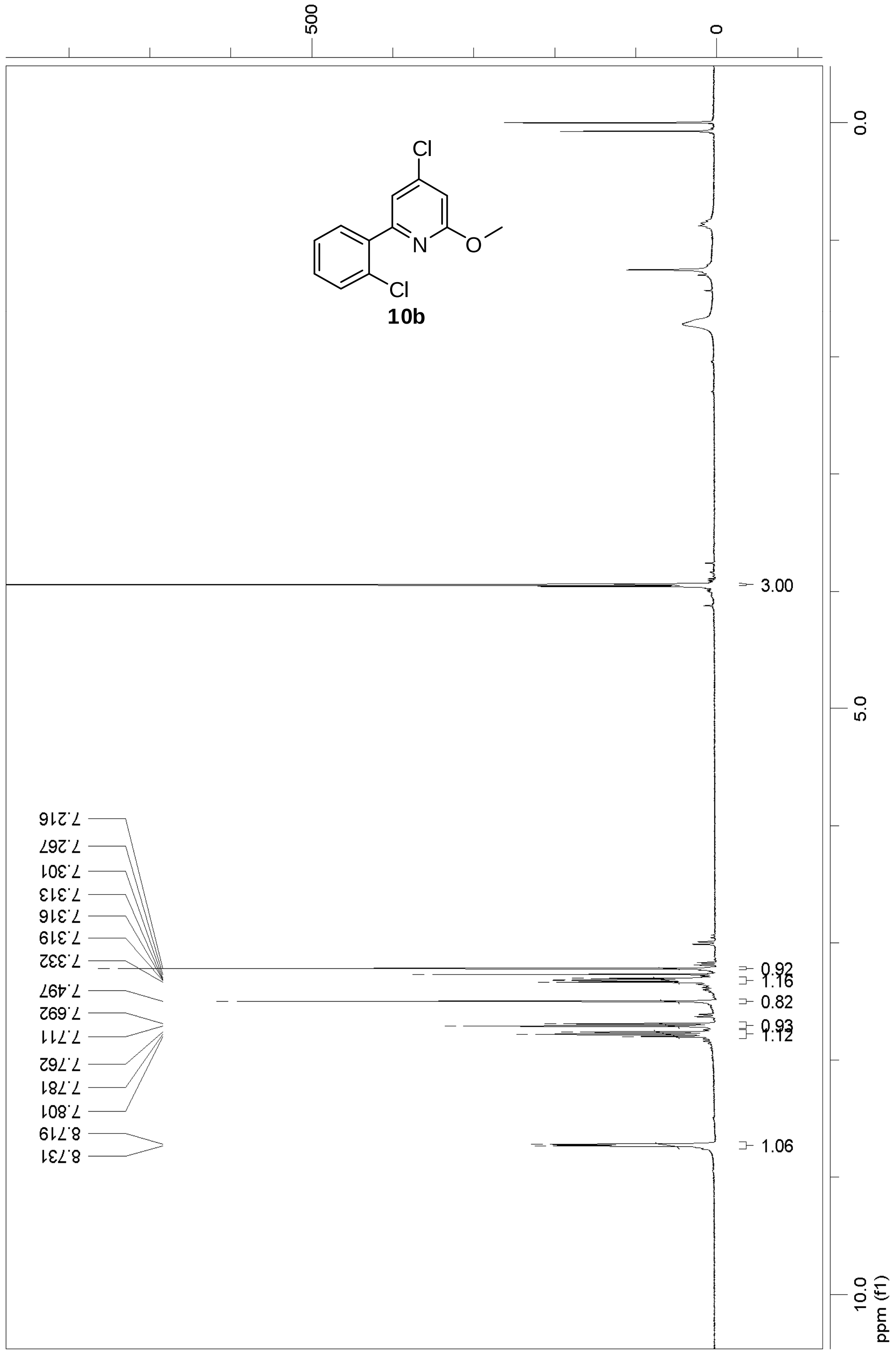


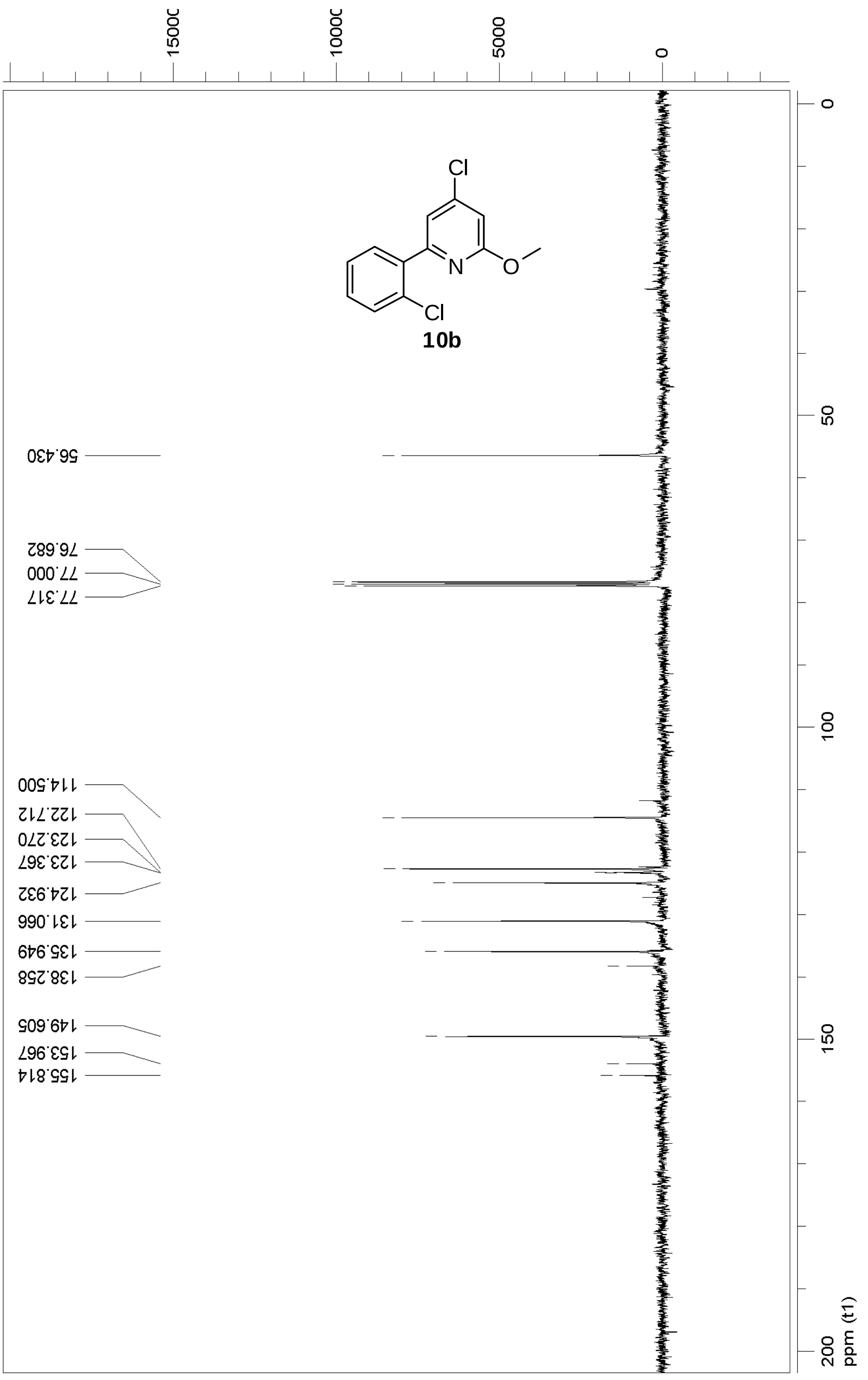
**10a**

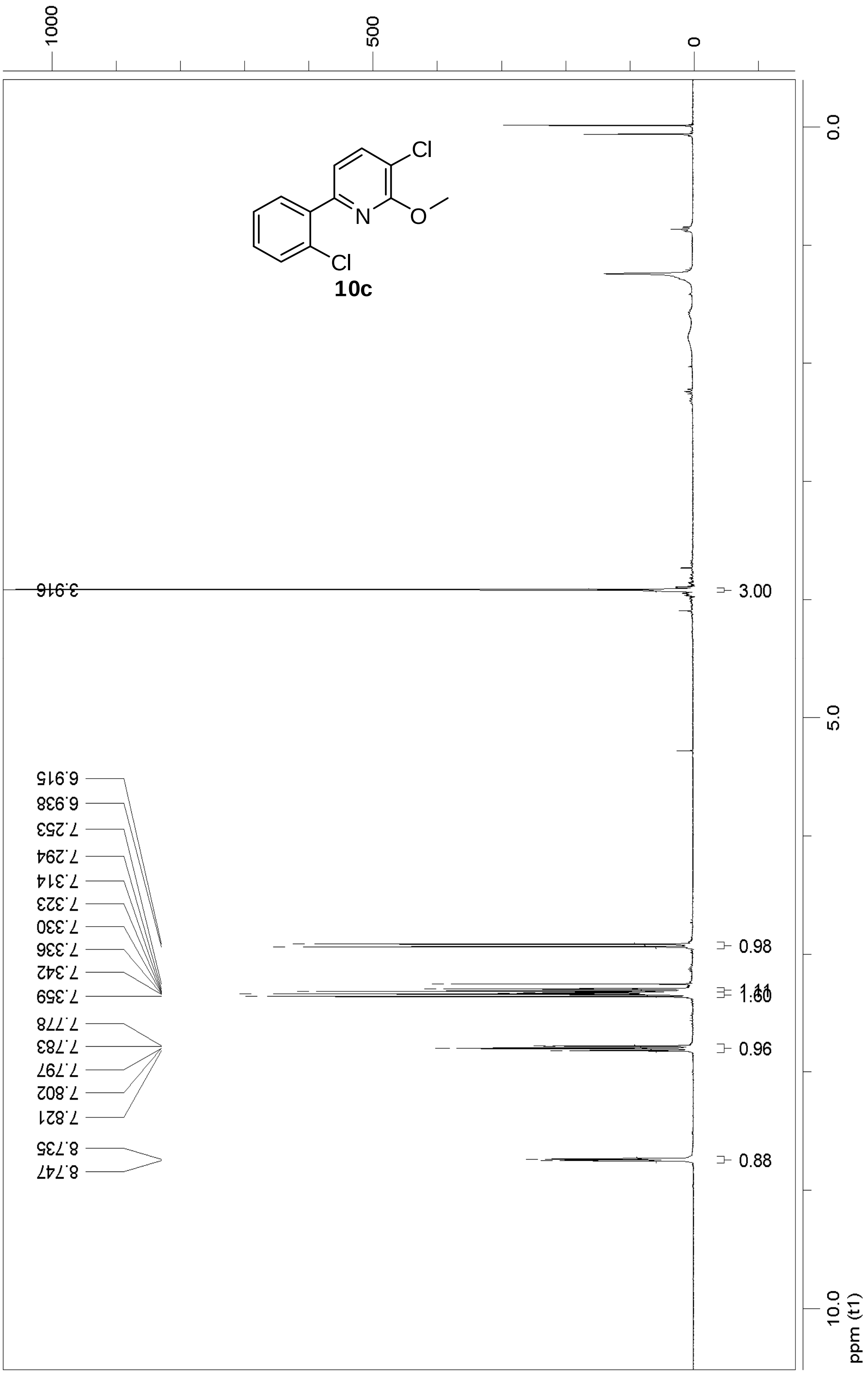
500
0
0.0
5.0
10.0
ppm (t1)
3.833
6.880
6.887
6.902
6.909
7.135
7.143
7.264
7.281
7.294
7.300
7.312
7.352
7.374
7.650
7.670
7.743
7.748
7.763
7.767
8.718
8.728
3.00
0.91
0.84
0.91
0.92
0.91
0.96
0.88
N
O
Cl


15000
10000
5000
0
55.592
76.682
77.000
77.318
116.028
116.078
122.454
123.421
124.854
130.826
135.843
139.762
149.436
156.746
158.356
N
O
Cl
0
50
100
150
200
ppm (t1)

**10a**

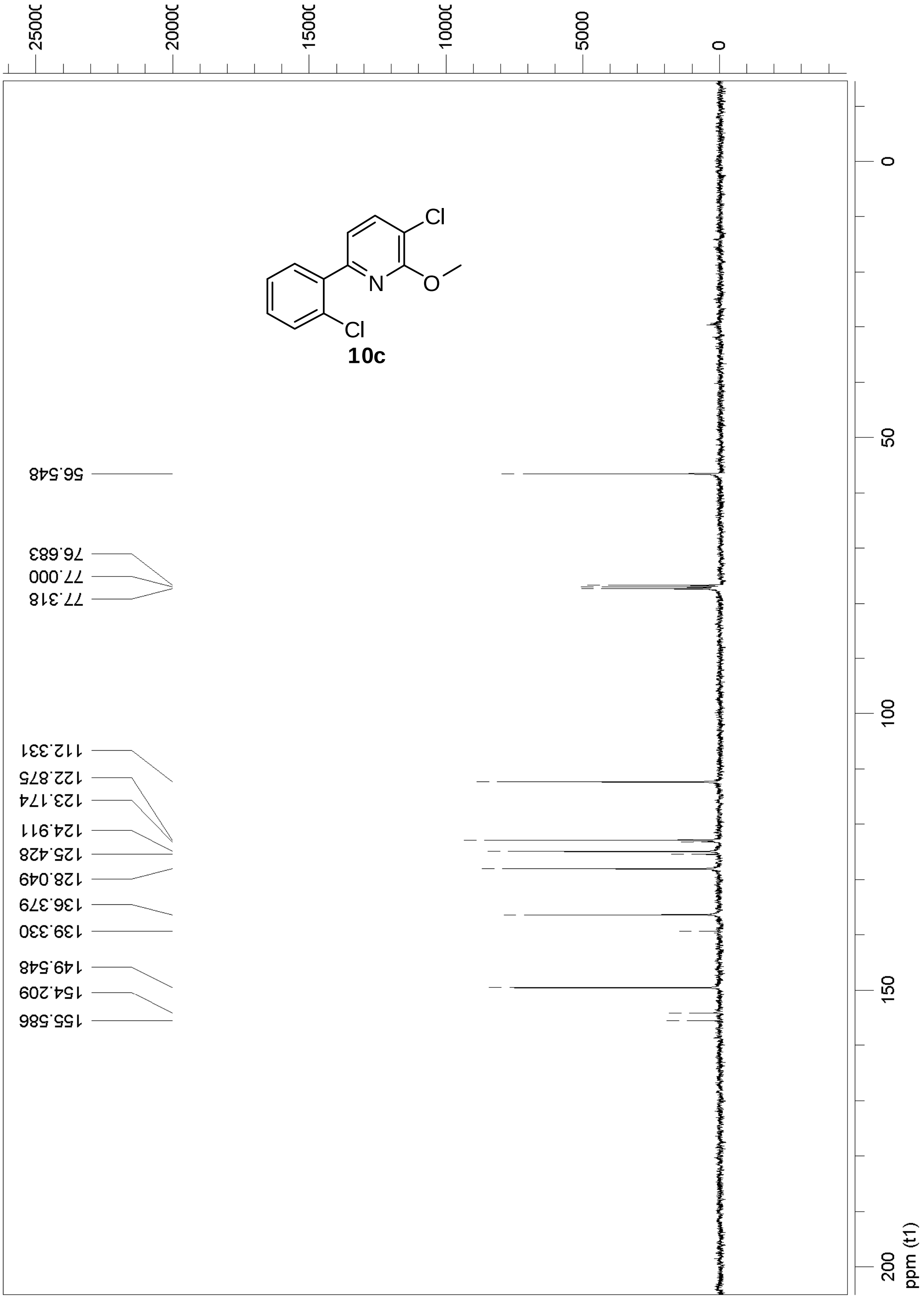

Cl
N
O
Cl
10b
500
0
0.0
5.0
10.0
ppm (f1)
3.00
0.92
1.16
0.82
0.93
1.12
1.06
7.216
7.267
7.301
7.313
7.316
7.319
7.332
7.497
7.692
7.711
7.762
7.781
7.801
8.719
8.731

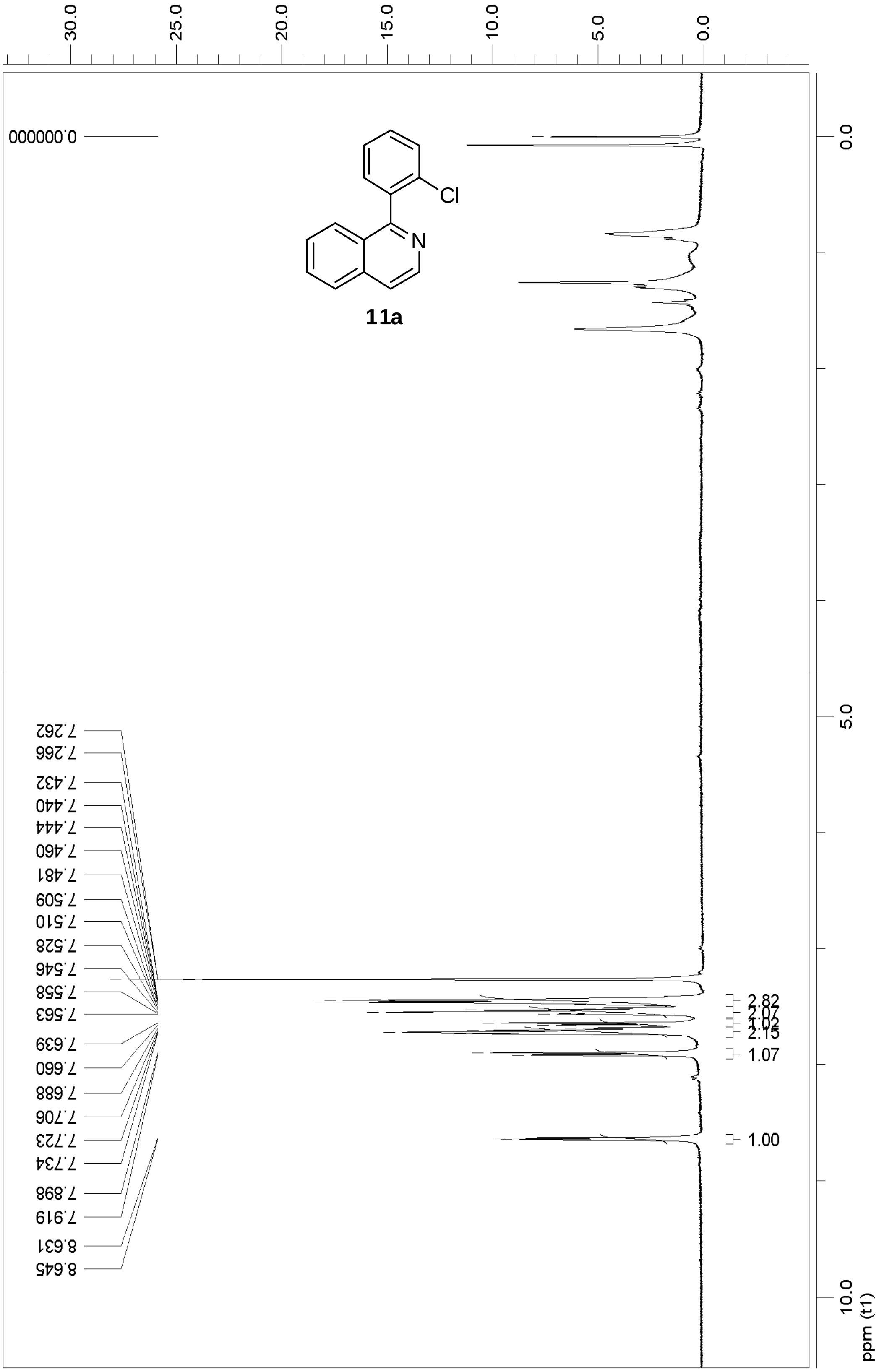

10b
Cl
Cl
N
O
15000
10000
5000
0
56.430
76.682
77.000
77.317
114.500
122.712
123.270
123.367
124.932
131.066
135.949
138.258
149.605
153.967
155.814
0
50
100
150
200
ppm (t1)

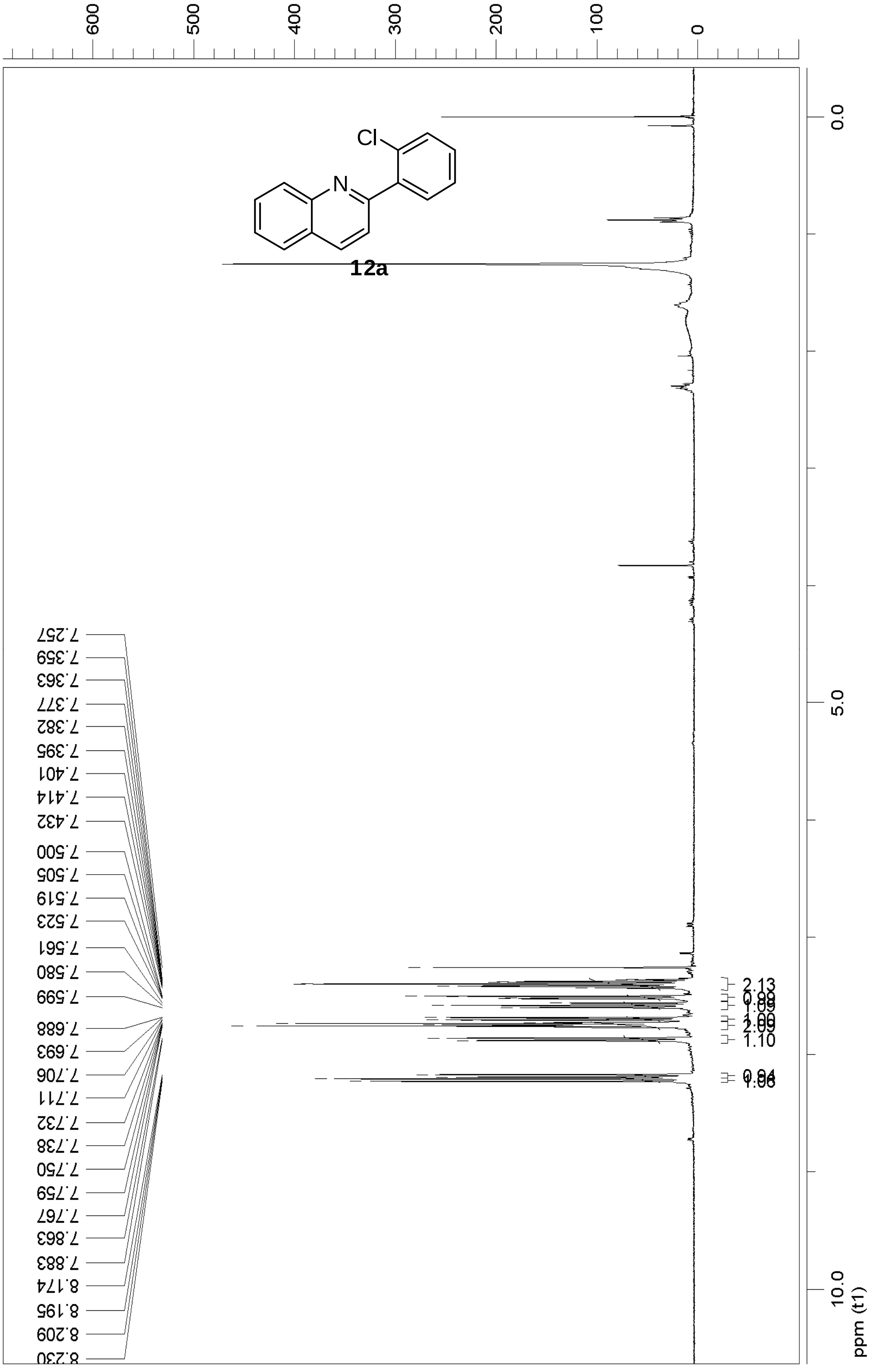


Cl
N
O
Cl
1000
500
0
3.916
6.915
6.938
7.253
7.294
7.314
7.323
7.330
7.336
7.342
7.359
7.778
7.783
7.797
7.802
7.821
8.735
8.747
3.00
0.98
1.11
1.60
0.96
0.88
0.0
5.0
10.0
ppm (t1)

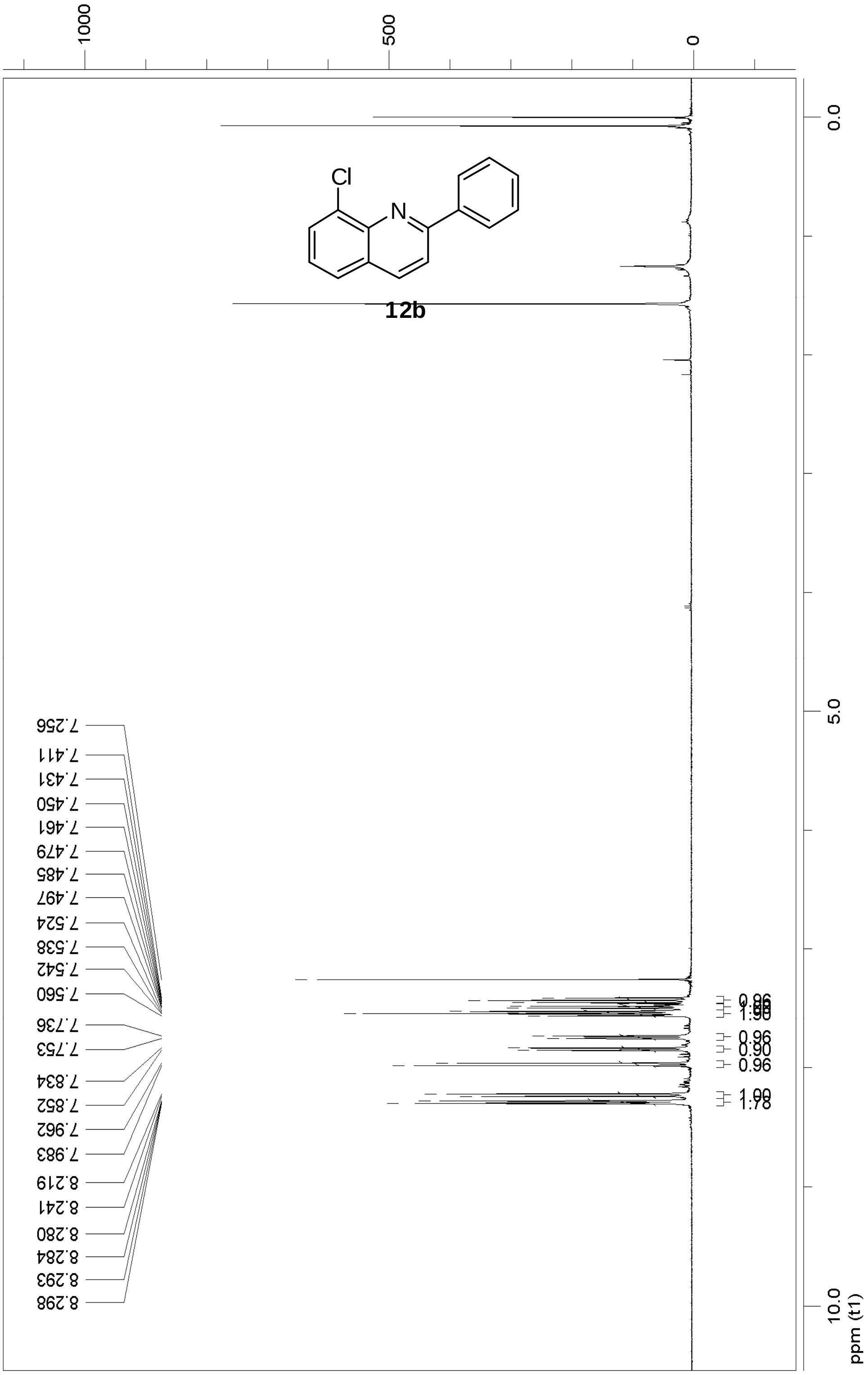
**10c**


10c
56.548
76.683
77.000
77.318
112.331
122.875
123.174
124.911
125.428
128.049
136.379
139.330
149.548
154.209
155.586
ppm (t1)
0
50
100
150
200
25000
20000
15000
10000
5000
0
Cl
N
O
Cl

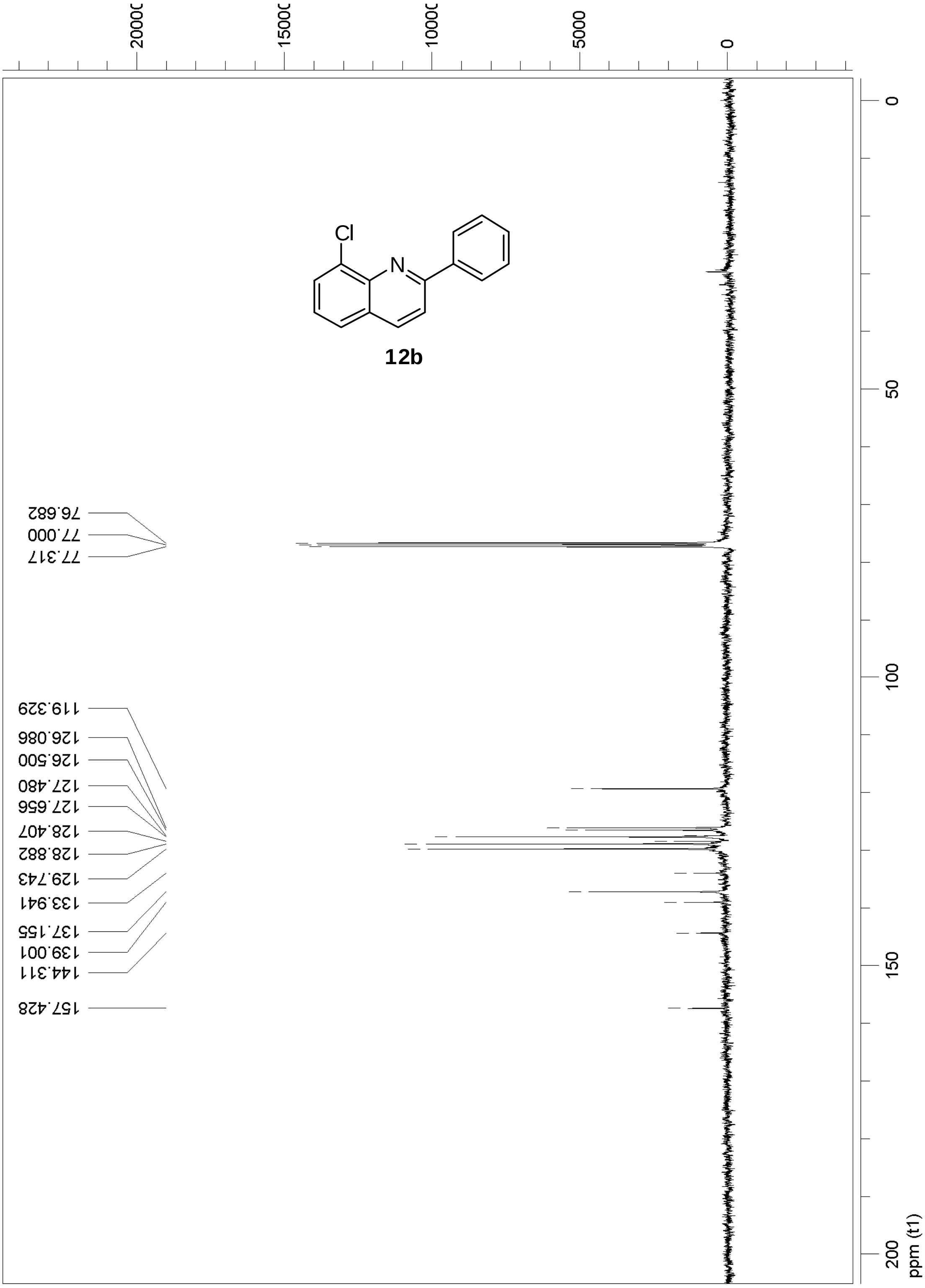

11a
Cl
N
ppm (t1)
10.0
5.0
0.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0.000000
7.262
7.266
7.432
7.440
7.444
7.460
7.481
7.509
7.510
7.528
7.546
7.558
7.563
7.639
7.660
7.688
7.706
7.723
7.734
7.898
7.919
8.631
8.645
2.82
2.07
1.02
2.15
1.07
1.00

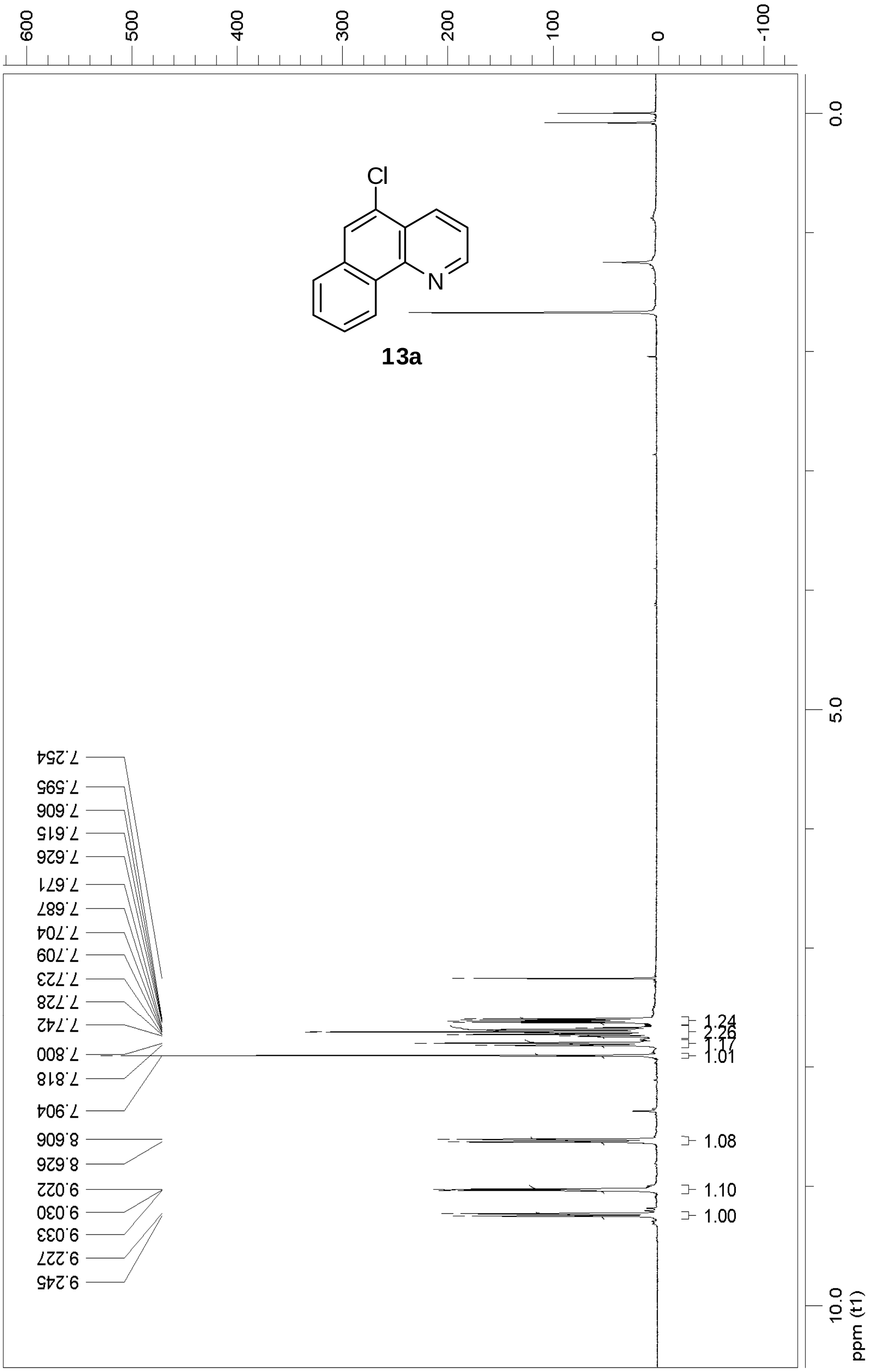


Cl
N
12a
600
500
400
300
200
100
0
0.0
5.0
10.0
ppm (t1)
7.257
7.359
7.363
7.377
7.382
7.395
7.401
7.414
7.432
7.500
7.505
7.519
7.523
7.561
7.580
7.599
7.688
7.693
7.706
7.711
7.732
7.738
7.750
7.759
7.767
7.863
7.883
8.174
8.195
8.209
8.230
2.13
0.99
1.09
1.00
2.09
1.10
0.94
1.06



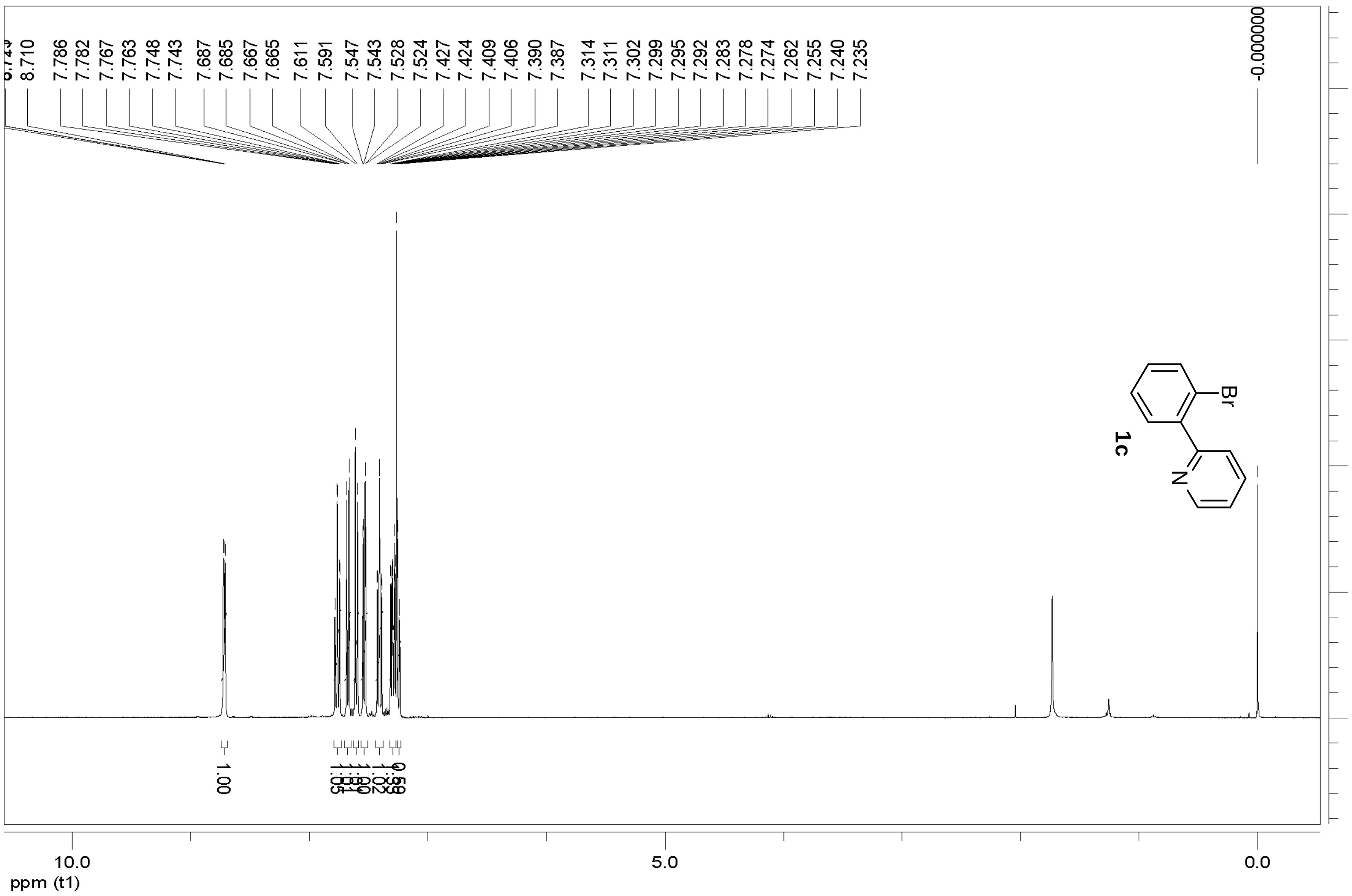
12b
Cl
N
1000
500
0
0.0
5.0
10.0
ppm (t1)
7.256
7.411
7.431
7.450
7.461
7.479
7.485
7.497
7.524
7.538
7.542
7.560
7.736
7.753
7.834
7.852
7.962
7.983
8.219
8.241
8.280
8.284
8.293
8.298
0.96
1.00
1.90
0.96
0.90
0.96
1.00
1.78

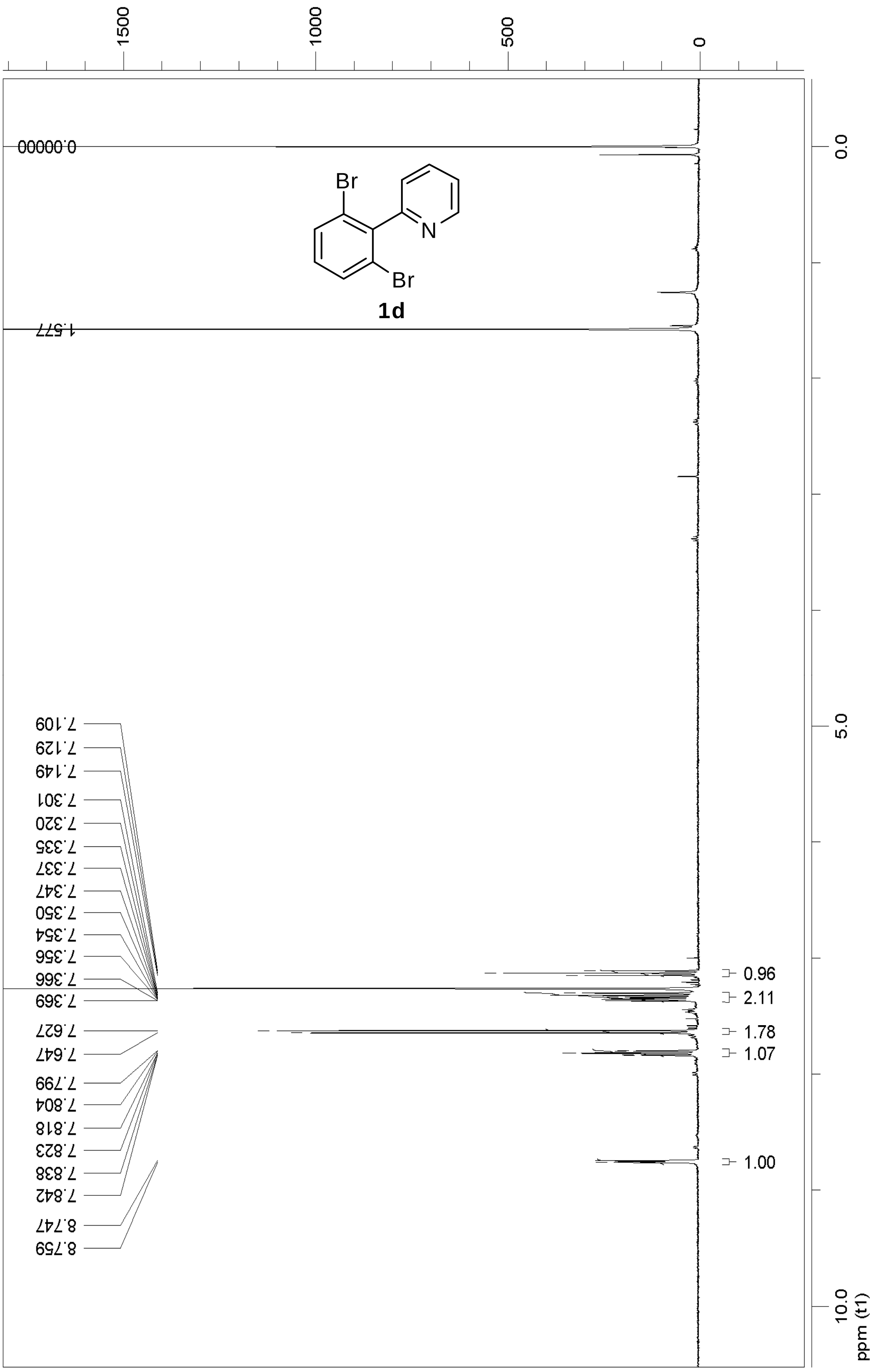

Cl
N
12b
76.682
77.000
77.317
119.329
126.086
126.500
127.480
127.656
128.407
128.882
129.743
133.941
137.155
139.001
144.311
157.428
20000
15000
10000
5000
0
0
50
100
150
200
ppm (t1)

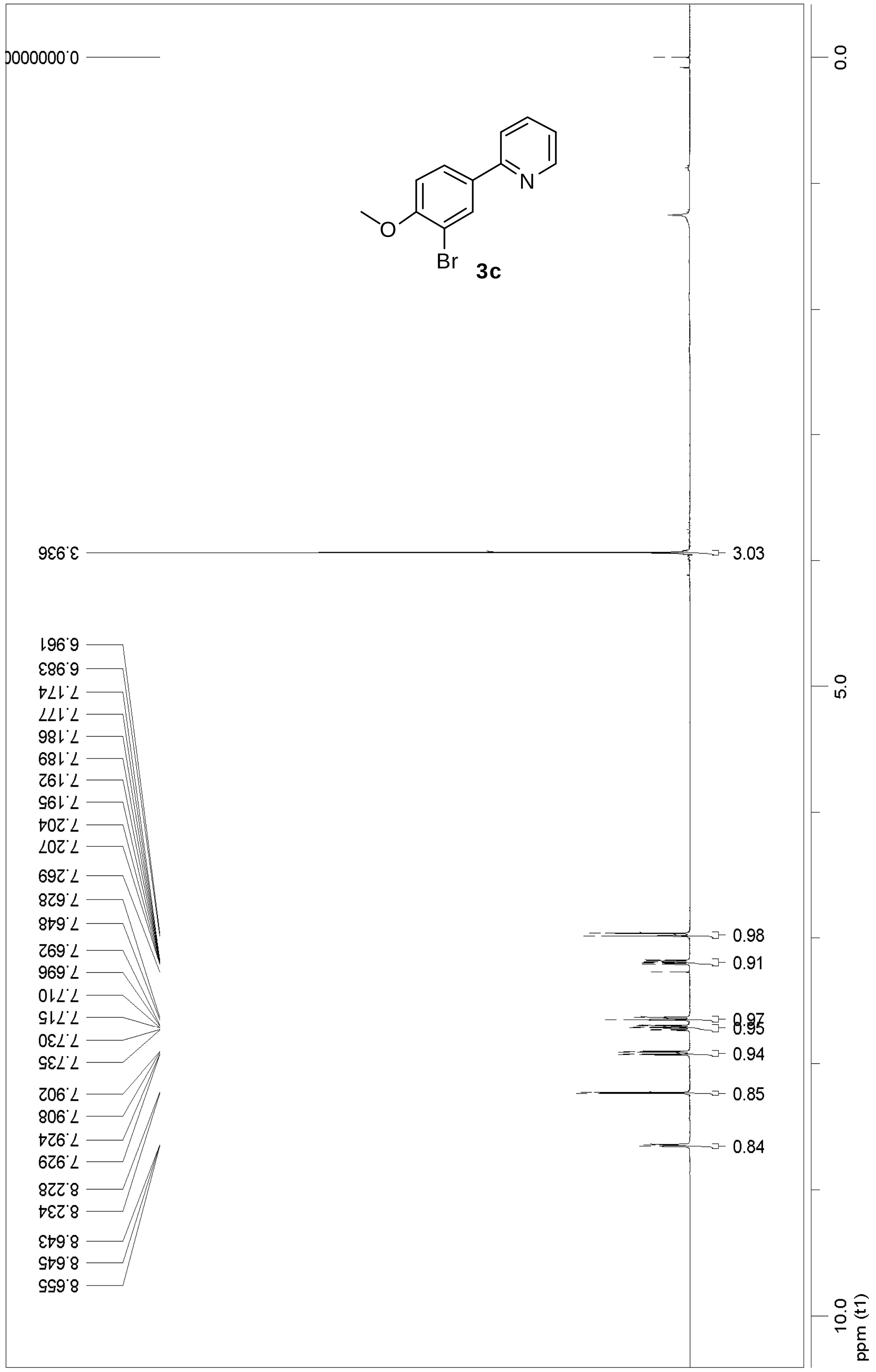


Cl
N
600
500
400
300
200
100
0
-100
0.0
5.0
10.0
ppm (t1)
7.254
7.595
7.606
7.615
7.626
7.671
7.687
7.704
7.709
7.723
7.728
7.742
7.800
7.818
7.904
8.606
8.626
9.022
9.030
9.033
9.227
9.245
1.24
2.26
1.17
1.01
1.08
1.10
1.00

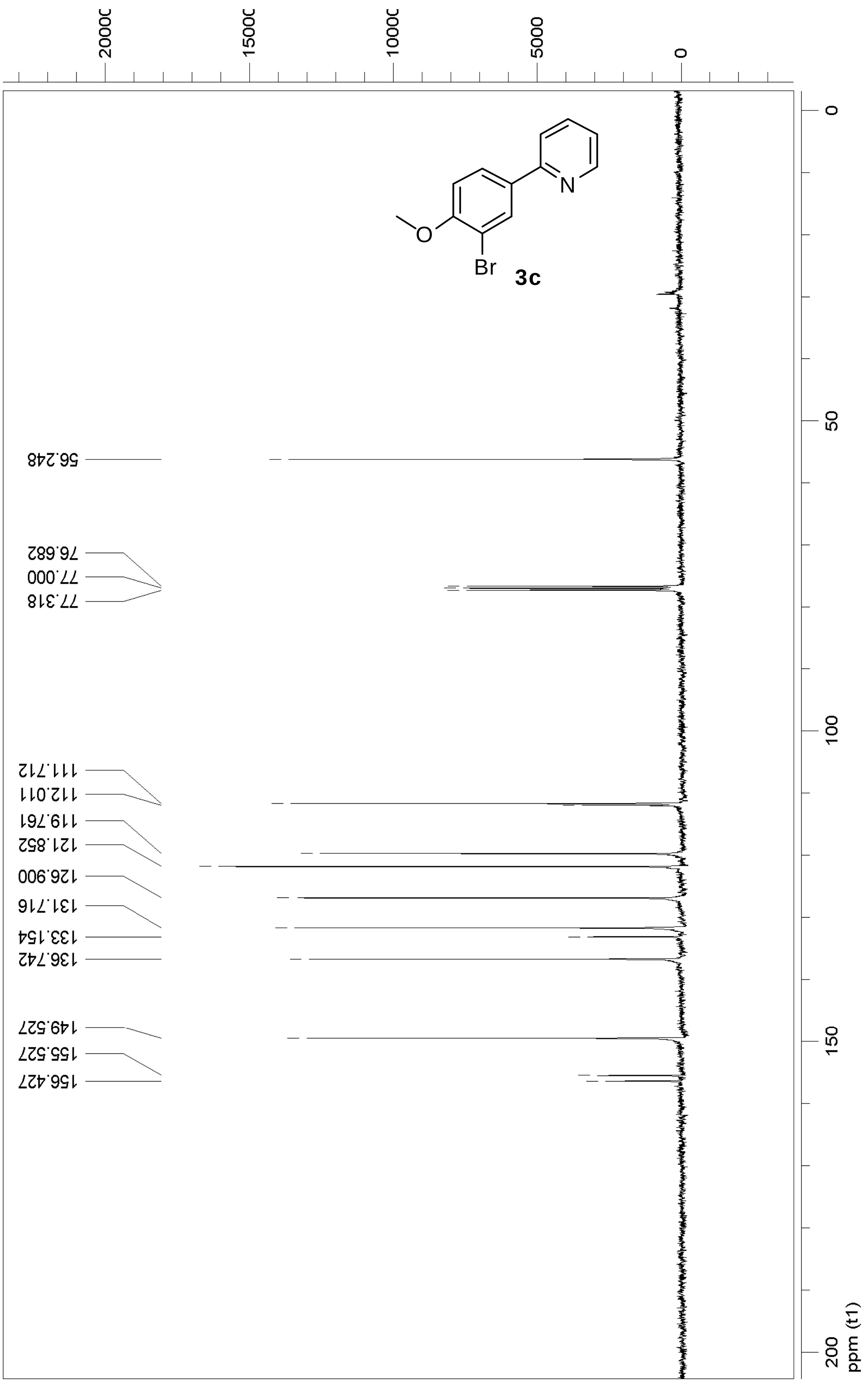
**13a**

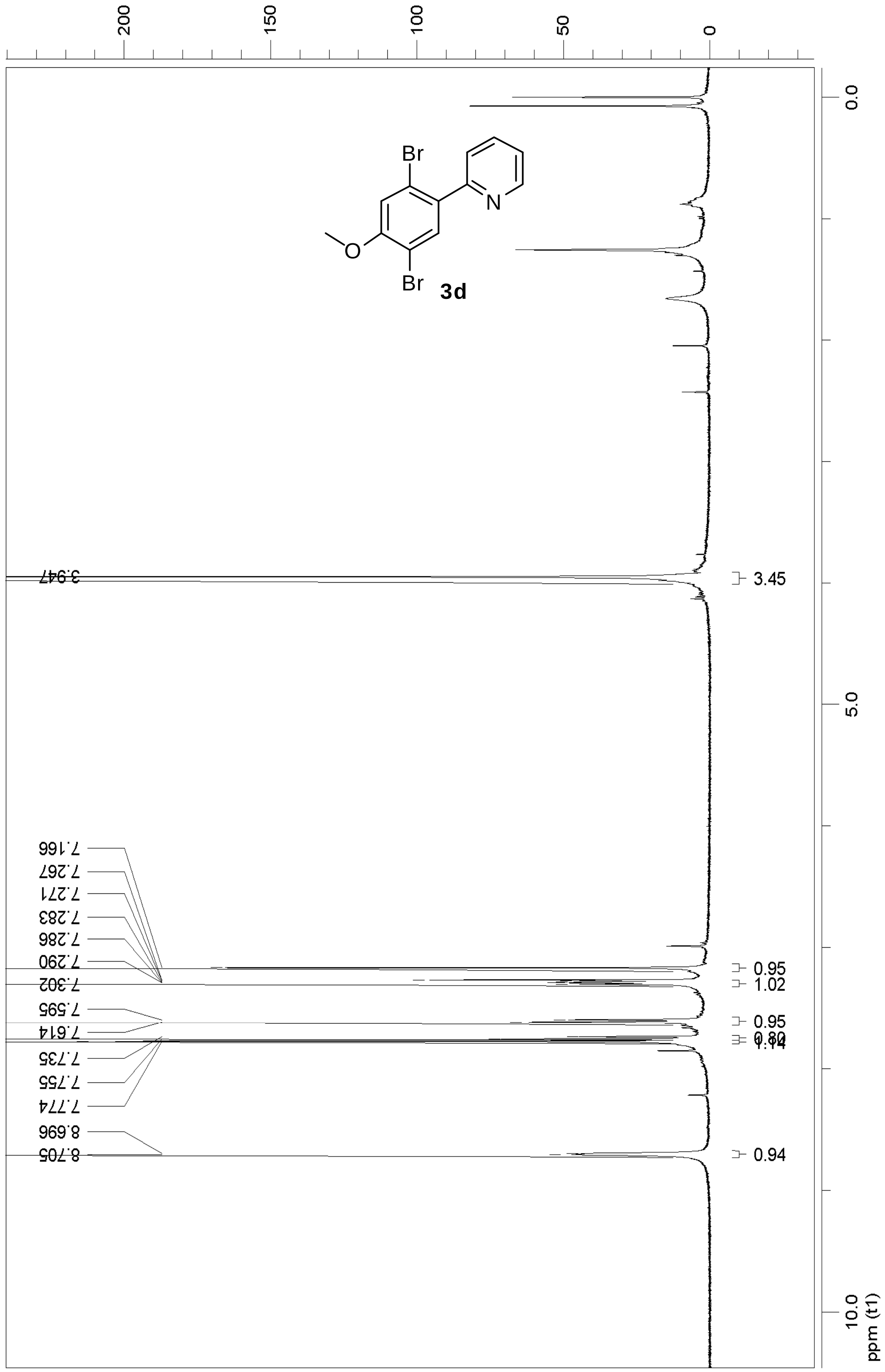

8.710
7.786
7.782
7.767
7.763
7.748
7.743
7.687
7.685
7.667
7.665
7.611
7.591
7.547
7.543
7.528
7.524
7.427
7.424
7.409
7.406
7.390
7.387
7.314
7.311
7.302
7.299
7.295
7.292
7.283
7.278
7.274
7.262
7.255
7.240
7.235
-0.000000
Br
N
1c
1.00
1.05
1.02
0.59
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)


1500
1000
500
0
0.0
5.0
10.0
ppm (t1)
0.00000
1.577
7.109
7.129
7.149
7.301
7.320
7.335
7.337
7.347
7.350
7.354
7.356
7.366
7.369
7.627
7.647
7.799
7.804
7.818
7.823
7.838
7.842
8.747
8.759
0.96
2.11
1.78
1.07
1.00
Br
Br
N
1d

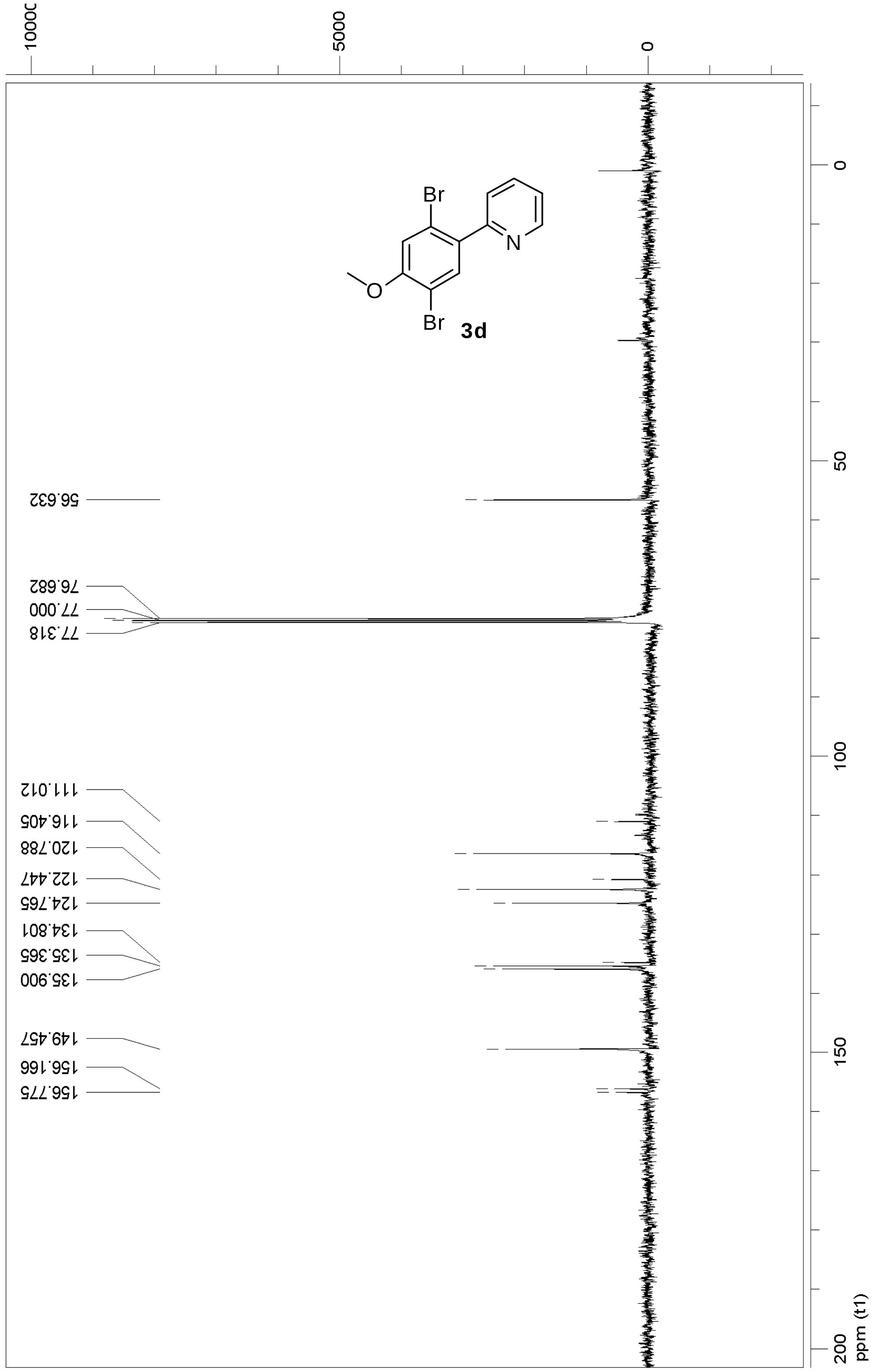


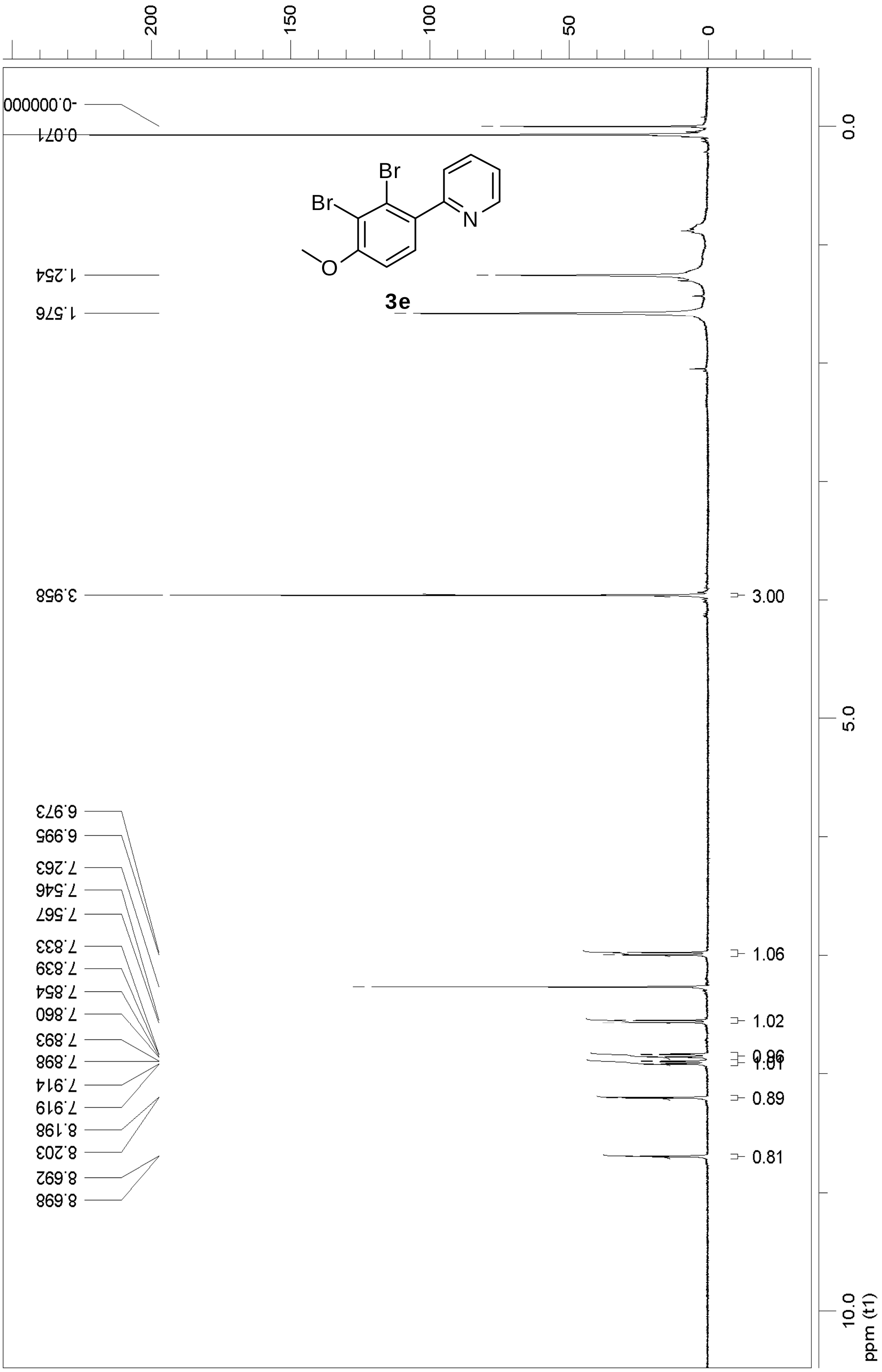
0.0000000
3.936
6.961
6.983
7.174
7.177
7.186
7.189
7.192
7.195
7.204
7.207
7.269
7.628
7.648
7.692
7.696
7.710
7.715
7.730
7.735
7.902
7.908
7.924
7.929
8.228
8.234
8.643
8.645
8.655
3.03
0.98
0.91
0.97
0.95
0.94
0.85
0.84
0.0
5.0
10.0
ppm (t1)
N
O
Br
3c

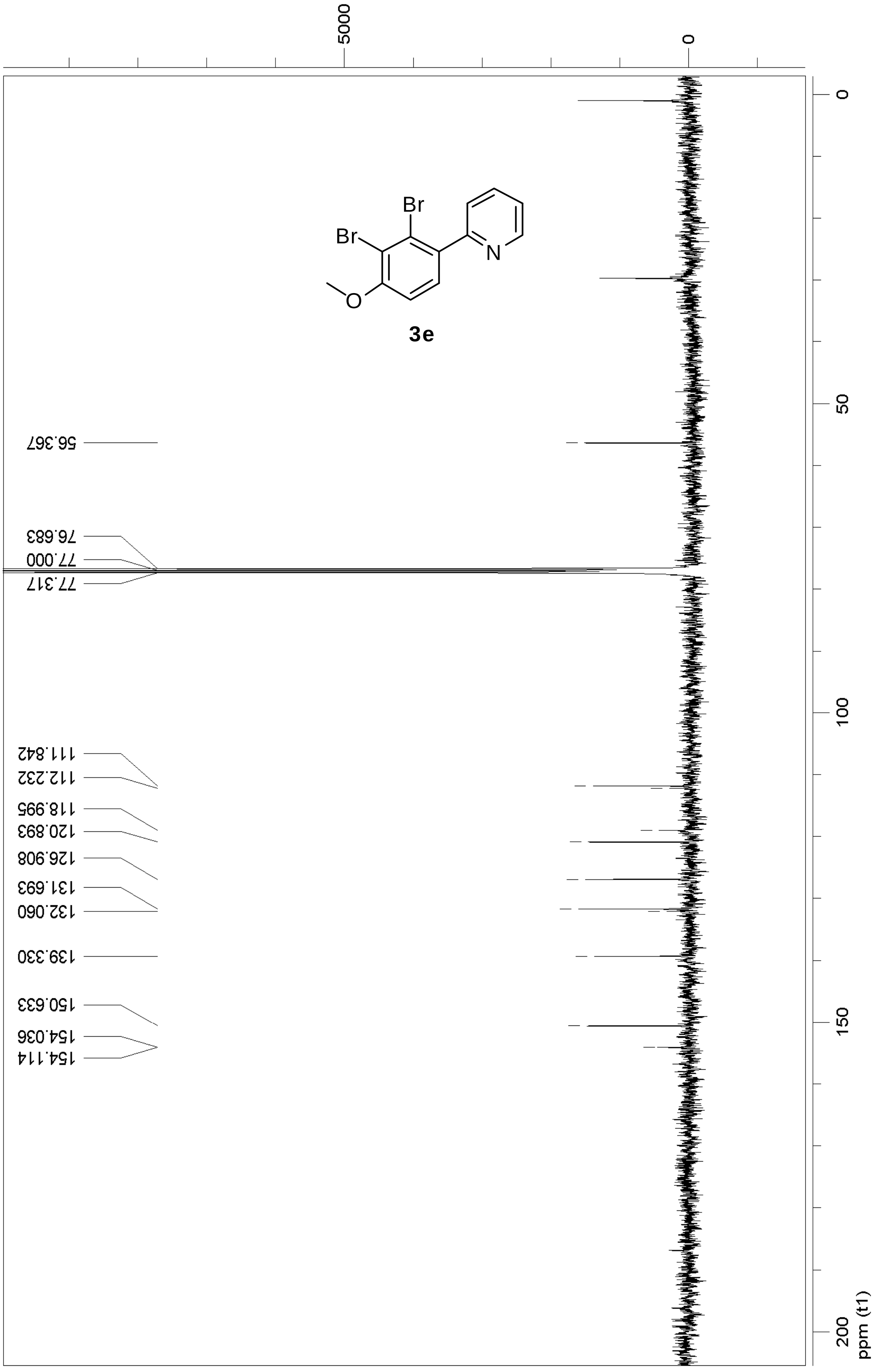

3c
Br
O
N
156.427
155.527
149.527
136.742
133.154
131.716
126.900
121.852
119.761
112.011
111.712
77.318
77.000
76.682
56.248
ppm (t1)
0
50
100
150
200
20000
15000
10000
5000
0

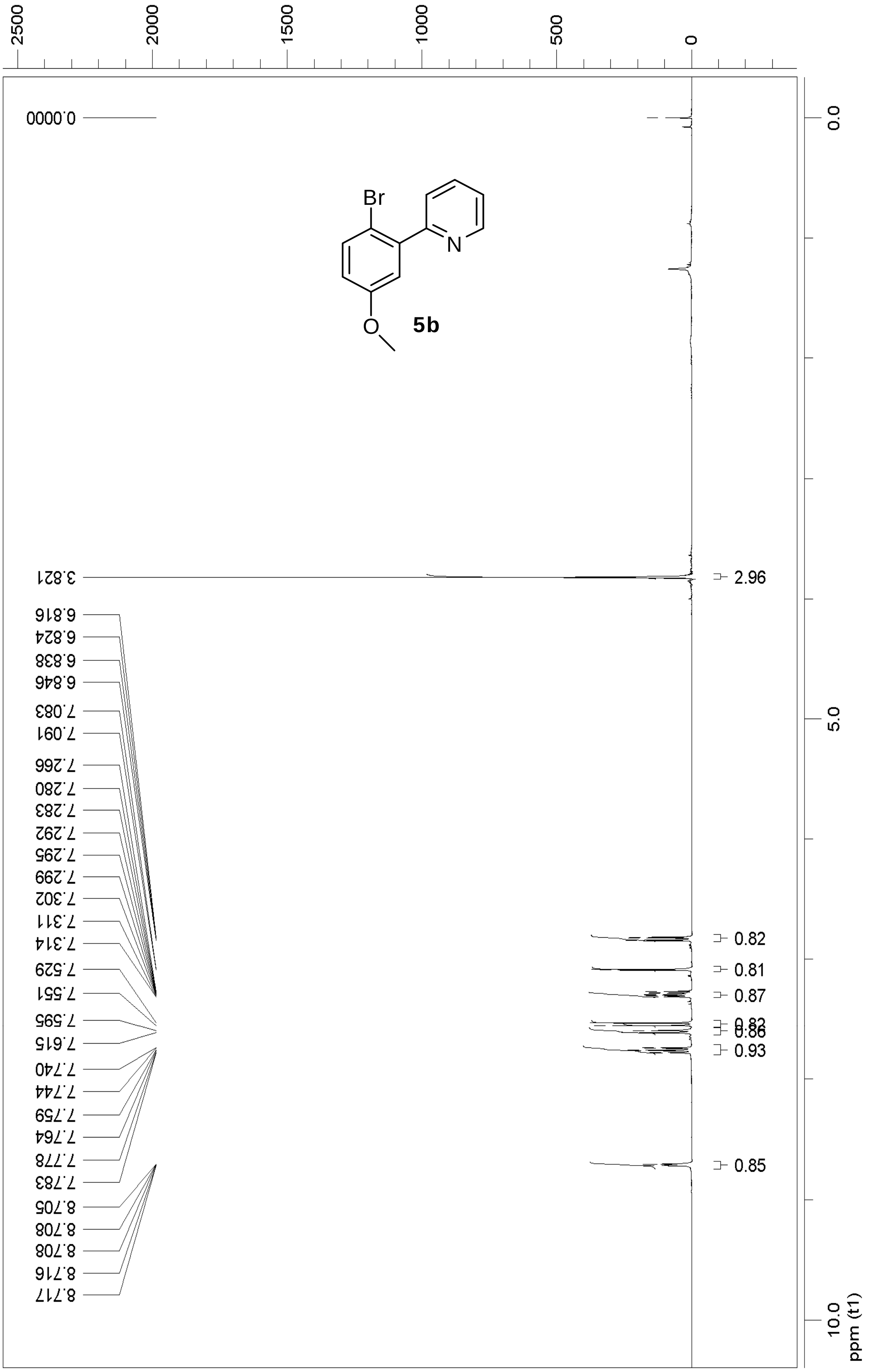


Br
N
O
Br
3d
200
150
100
50
0
0.0
5.0
10.0
ppm (t1)
3.947
7.166
7.267
7.271
7.283
7.286
7.290
7.302
7.595
7.614
7.735
7.755
7.774
8.696
8.705
3.45
0.95
1.02
0.95
0.80
1.14
0.94

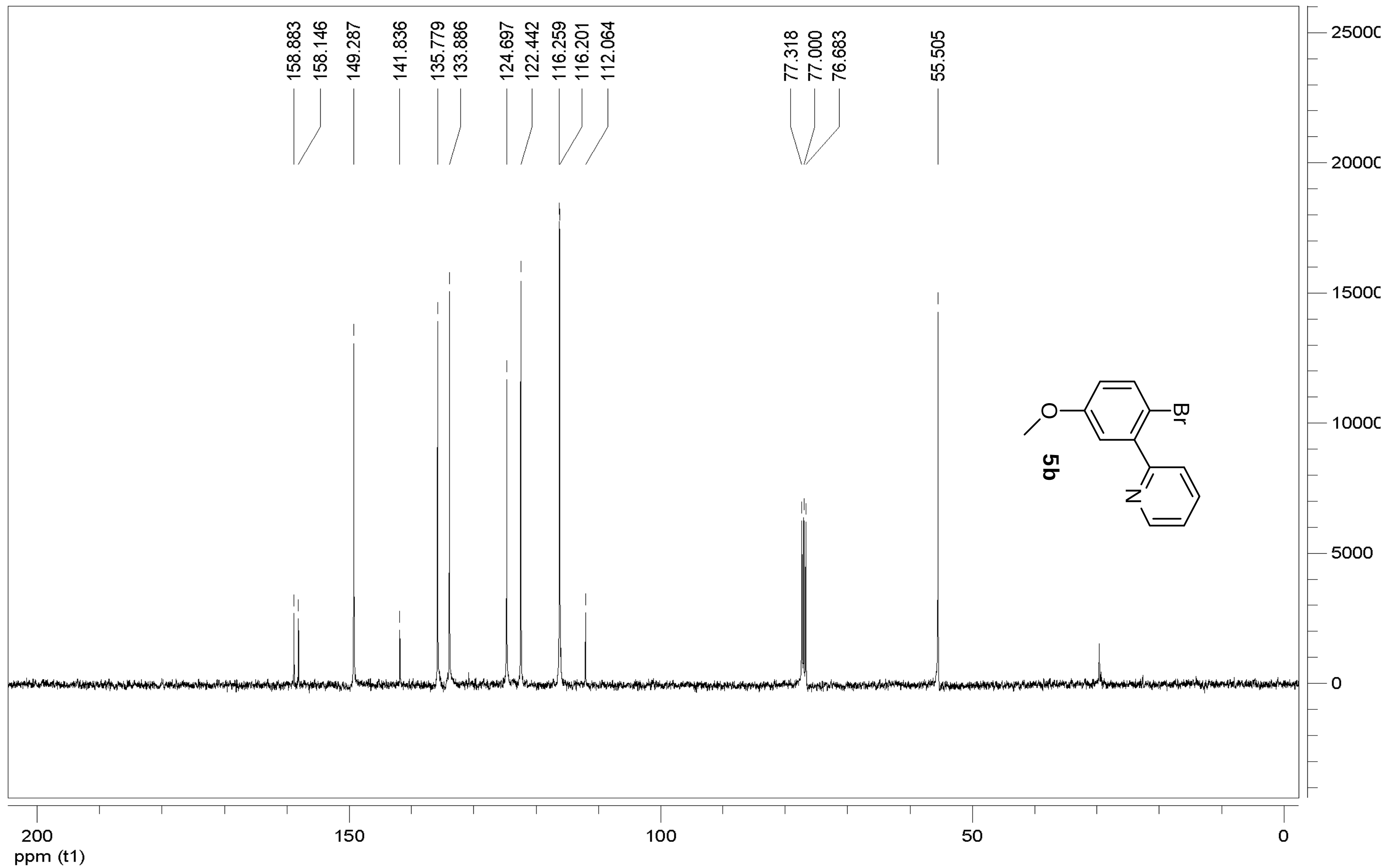

10000
5000
0
56.632
76.682
77.000
77.318
111.012
116.405
120.788
122.447
124.765
134.801
135.365
135.900
149.457
156.166
156.775
Br
N
O
Br
3d
0
50
100
150
200
ppm (t1)

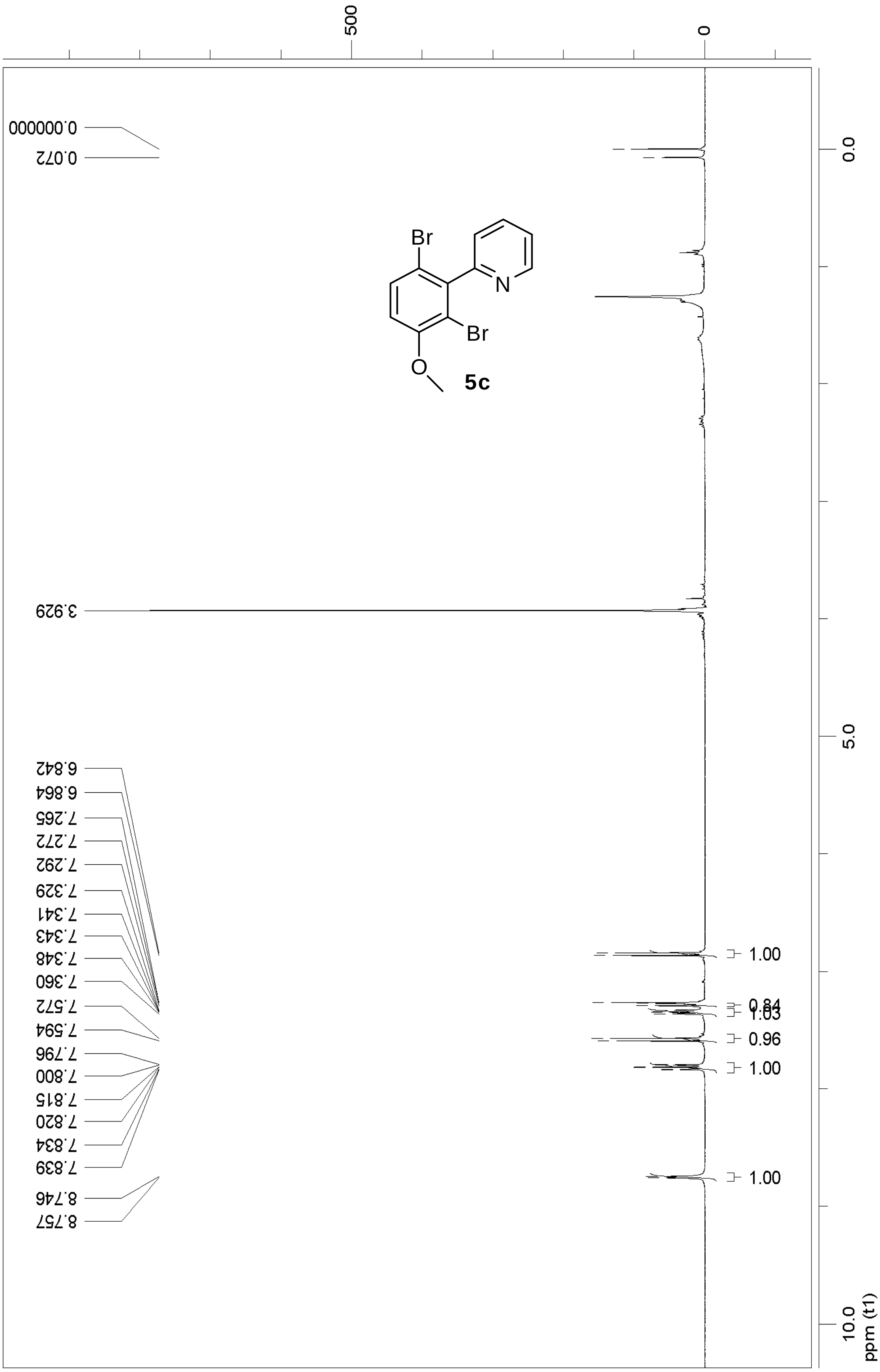

-0.000000
0.071
1.254
1.576
3.958
6.973
6.995
7.263
7.546
7.567
7.833
7.839
7.854
7.860
7.893
7.898
7.914
7.919
8.198
8.203
8.692
8.698
Br
Br
N
O
3e
3.00
1.06
1.02
0.96
1.01
0.89
0.81
200
150
100
50
0
0.0
5.0
10.0
ppm (t1)

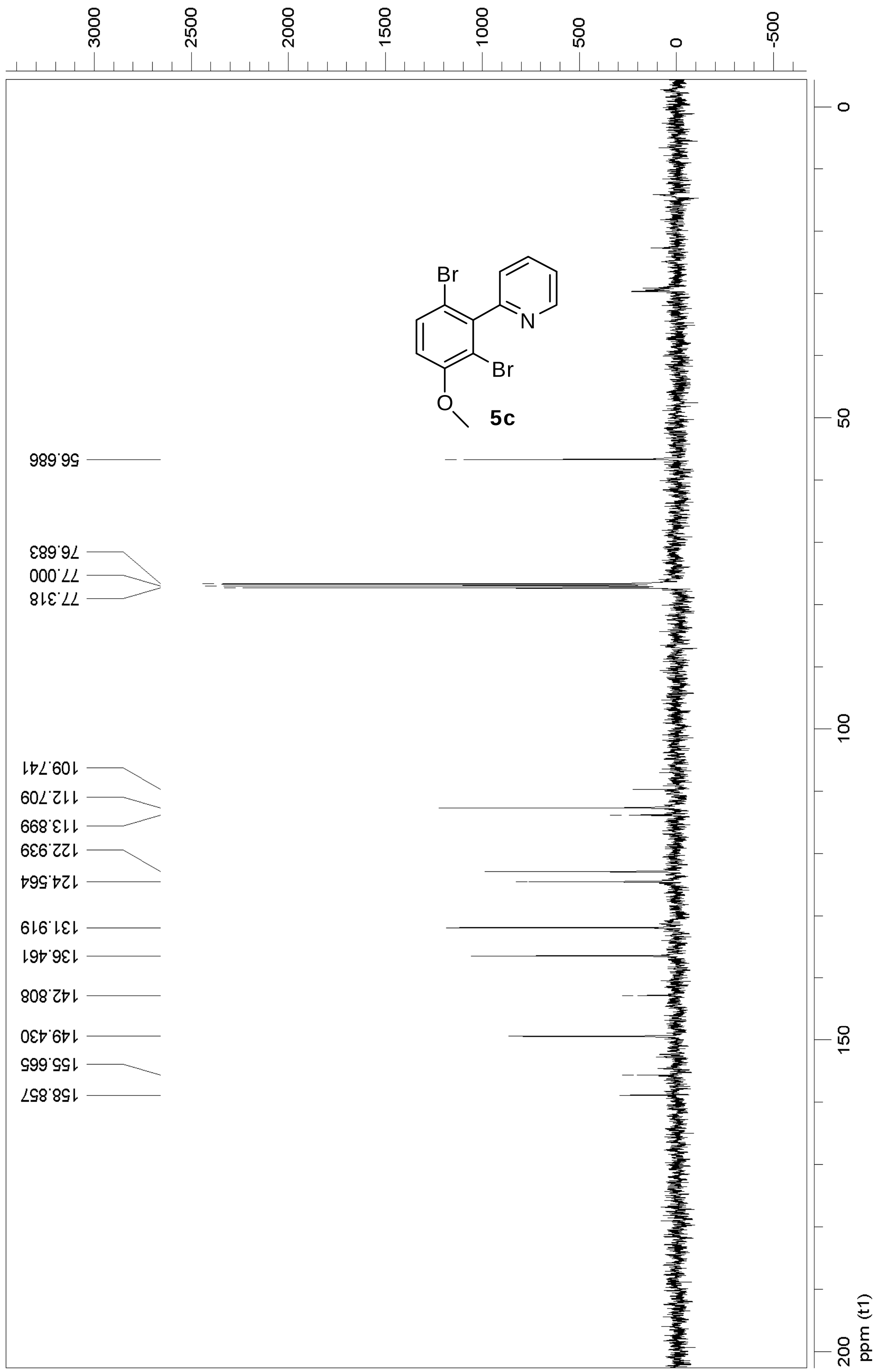

3e
Br
Br
N
O
56.367
76.683
77.000
77.317
111.842
112.232
118.995
120.893
126.908
131.693
132.060
139.330
150.633
154.036
154.114
5000
0
0
50
100
150
200
ppm (t1)



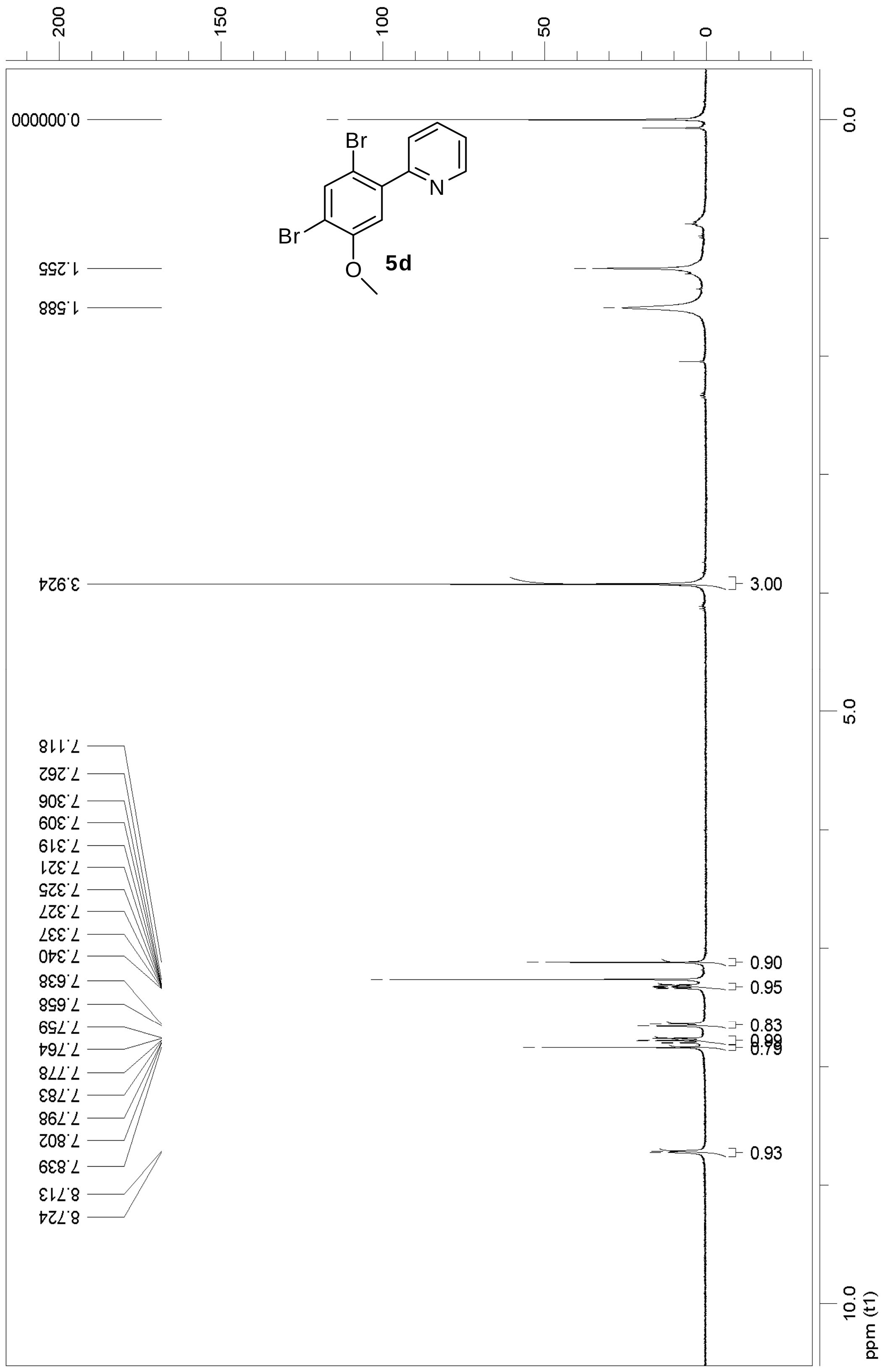
0.0000
3.821
6.816
6.824
6.838
6.846
7.083
7.091
7.266
7.280
7.283
7.292
7.295
7.299
7.302
7.311
7.314
7.529
7.551
7.595
7.615
7.740
7.744
7.759
7.764
7.778
7.783
8.705
8.708
8.708
8.716
8.717
Br
N
O
5b
2.96
0.82
0.81
0.87
0.82
0.86
0.93
0.85
2500
2000
1500
1000
500
0
0.0
5.0
10.0
ppm (t1)


158.883
158.146
149.287
141.836
135.779
133.886
124.697
122.442
116.259
116.201
112.064
77.318
77.000
76.683
55.505
Br
N
O
5b
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)


500
0
0.000000
0.072
3.929
6.842
6.864
7.265
7.272
7.292
7.329
7.341
7.343
7.348
7.360
7.572
7.594
7.796
7.800
7.815
7.820
7.834
7.839
8.746
8.757
1.00
0.84
1.03
0.96
1.00
1.00
0.0
5.0
10.0
ppm (t1)
Br
N
Br
O
5c

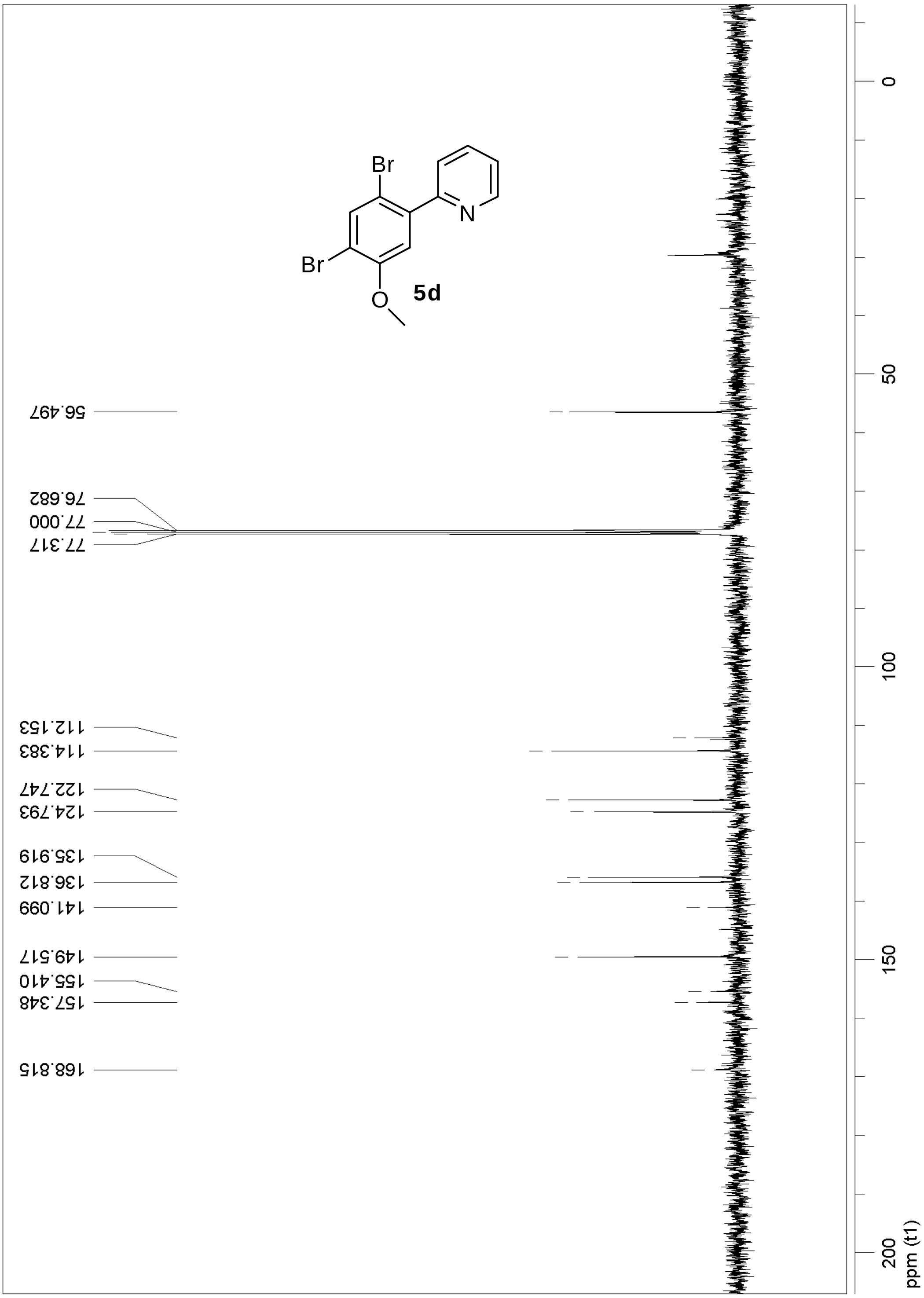

Br
N
Br
O
56.686
76.683
77.000
77.318
109.741
112.709
113.899
122.939
124.564
131.919
136.461
142.808
149.430
155.665
158.857
3000
2500
2000
1500
1000
500
0
-500
0
50
100
150
200
ppm (t1)

**5c**



**5d**

Br
Br
N
O
0.000000
1.255
1.588
3.924
7.118
7.262
7.306
7.309
7.319
7.321
7.325
7.327
7.337
7.340
7.638
7.658
7.759
7.764
7.778
7.783
7.798
7.802
7.839
8.713
8.724
3.00
0.90
0.95
0.83
0.99
0.79
0.93
200
150
100
50
0
0.0
5.0
10.0
ppm (t1)


**5d**
Br
Br
N
O
56.497
76.682
77.000
77.317
112.153
114.383
122.747
124.793
135.919
136.812
141.099
149.517
155.410
157.348
168.815
0
50
100
150
200
ppm (t1)