Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

1,2-Alkylarylation of Activated Alkenes with Dual C-H Bonds of Arenes and Alkyl Halides Toward Polyhalo-Substituted Oxindoles

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(A) Typical Experimental Procedure

(a) Materials:

Substrates were prepared according to the known procedures.[1]

(b) Typical Experimental Procedure for the Cyclization of *N*-Arylacrylamides with Alkyl Halides:

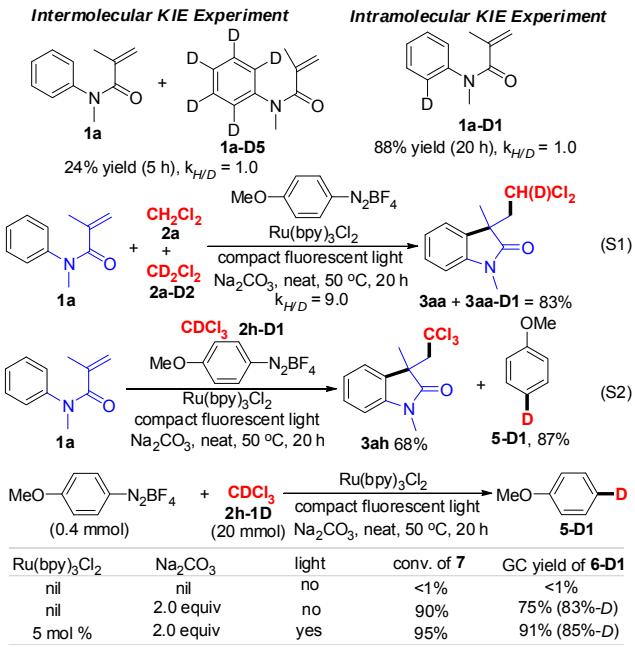
To a Schlenk tube were added *N*-arylacrylamides **1** (0.3 mmol), alkyl halides **2** (15 mmol), $Ru(bpy)_3Cl_2$ (5 mol%), Na_2CO_3 (2 equiv), 4-$MeOC_6H_4N_2BF_4$ (2 equiv). Then the tube was charged with Ar (1 atm), and was stirred at 50 ^oC under visible light for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction diluted in diethyl ether and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

(c) Scheme S1. Control Experiments

To understand the mechanism for the current tandem reaction, some control experiments were carried out (Scheme S1). The results demonstrated that no kinetic isotope effect (k_H/k_D = 1.0) was discovered from either intramolecular or intermolecular kinetic isotope effect experiments with DCM **2a**. These imply that the iron-catalyzed oxidative difunctionalization proceeds via either the SEAr mechanism or the free radical mechanism.[2] The deuterated experiment of substrate **1a** with DCM **2a** and DCM-D2 **2a-D2** (k_H/k_D = 9.0) supports that cleavage of the C-H bond of DCM is rate-limiting (eq S1). Using $CDCl_3$ (**2h-D1**) instead of $CHCl_3$

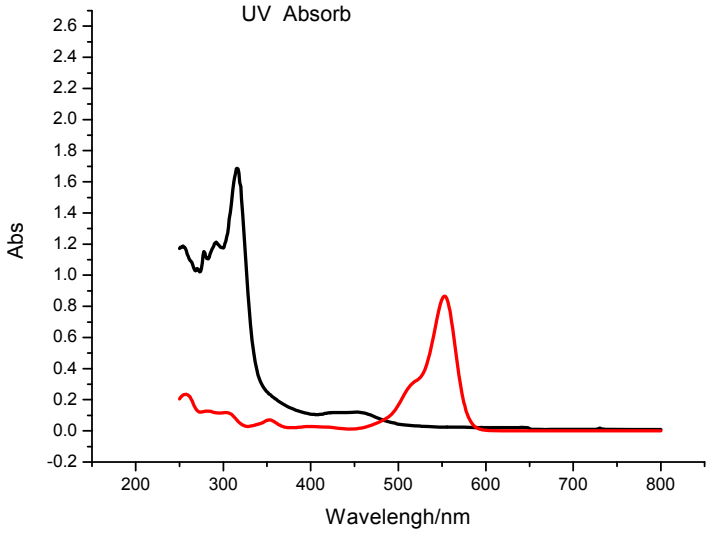
(**2h**), mono-deuterated anisole **5-D1** was observed (eq S2). The results suggest that 4-methoxybenzenediazonium tetrafluorobrorate is converted to aryl radical under the present conditions to trigger the current reaction. To verify this, the reaction between 4-methoxybenzenediazonium tetrafluorobrorate and $CDCl_3$ (**2h-D1**) was tested. Without Ru, base and light, 4-methoxybenzenediazonium tetrafluorobrorate is stable. However, 90% of this diazonium salt was decomposed by 2 equiv Na_2CO_3 into mono-deuterated anisole **5-D1** in 75% yield with 83% deuterium. The decomposition was selectively promoted in the presence of Ru and light: 95% of diazonium salt was consumed resulting in 91% yield of **5-D1**. These indicate that the yield of the current tandem reaction is based on the selectivity of aryl radical generation, and photocatalysts combined with visible light mainly effect the reaction by facilitating aryl radical generation. Notably, two radical inhibitors, TEMPO and 2,6-di-*tert*-butylphenol were added to the reaction: a stoichiometric amount of radical inhibitor (2 equiv) results in no conversion of substrate **1a**. All the results described above support that the current reaction includes a radical process.

Scheme S1. Control Experiments



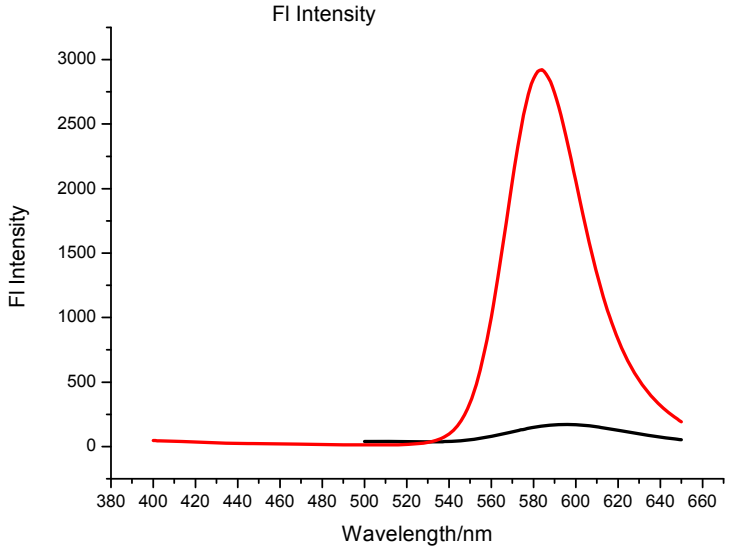
$Ru(bpy)_3Cl_2$	Na_2CO_3	light	conv. of **7**	GC yield of **6-D1**
nil	nil	no	<1%	<1%
nil	2.0 equiv	no	90%	75% (83%-*D*)
5 mol %	2.0 equiv	yes	95%	91% (85%-*D*)

(d) Figure S1. The Quantum Yield of the Reaction of Substrate 1a and CH_2Cl_2 (2a) under the Optimal Conditions



As UV-Vis absorbtion of Rhodamine B at 350nm: 0.0682 (red line)

Ax UV-Vis absorbtion of reaction system at 450nm: 0.1204 (black line)



Fs Integrated area of fluorescence of Rhodamine B: 145800 (red line)

Fx Integrated area of fluorescence of reaction system:13853(black line)

ns Rhodamine B is Dissolved in water, refractivity of water is 1.3

nx Solvent of reaction system is DCM, refractivity of DCM is 1.4

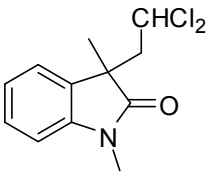
Φ_s quantum yield of Rhodamine B: 0.9

$\Phi x = \Phi s (nx/ns)^2 (As/Ax) (Fx/Fs)$

$= 0.9 \times (1.4/1.3)^2 \times (0.0682/0.1204) \times (13853/145800)$

$= 0.056$

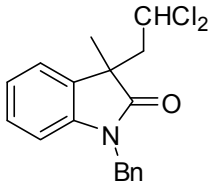
(B) Analytical data for 3-5



3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa):

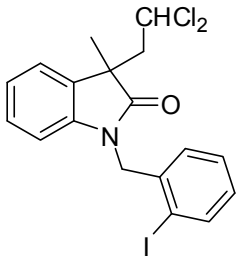
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 5.38 (dd, *J* = 4.0 Hz, 9.0 Hz, 1H), 3.20 (s, 3H), 3.02 (dd, *J* = 9.0 Hz, 14.5 Hz, 1H), 2.70 (dd, *J* = 4.0 Hz, 14.5 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.9, 143.4, 131.0, 128.6, 122.6 (2C), 108.6, 69.6, 50.1, 42.1, 26.4, 25.4; IR (KBr, cm^{-1}): 1715, 1502;

LRMS (EI 70 ev) *m*/z (%): 259 (M^++2, 15), 258 (3), 257 (M^+, 23), 161 (100), 160 (82); HRMS (ESI) for $C_{12}H_{14}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 258.0447, found 258.0436.



1-Benzyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3ba):

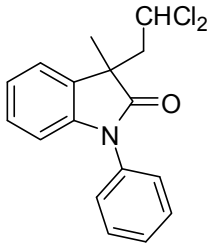
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32-7.27 (m, 4H), 7.26-7.25 (m, 1H), 7.23-7.19 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 5.45 (dd, *J* = 4.4 Hz, 9.2 Hz, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 15.2 Hz, 1H), 3.10 (dd, *J* = 8.8 Hz, 14.8 Hz, 1H), 2.76 (dd, *J* = 4.4 Hz, 14.8 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.0, 142.5, 135.6, 131.1, 128.7, 128.4 (2C), 127.6, 127.4, 122.7, 109.6, 69.6, 49.9, 47.1, 44.0, 26.1; IR (KBr, cm^{-1}): 1699, 1503; LRMS (EI 70 ev) *m*/z (%): 337 (3), 336 (M^++2, 4), 335 (20), 334 (M^+, 6), 333 (30), 239 (2), 238 (15), 237 (89), 236 (23), 91 (100); HRMS (ESI) for $C_{18}H_{18}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 334.0760, found 334.0763.



3-(2,2-Dichloroethyl)-1-(2-iodobenzyl)-3-methylindolin-2-one (3ca):

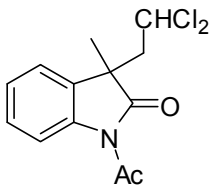
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (t, *J* = 7.6 Hz, 1H), 7.26-7.21 (m, 3H), 7.10 (t, *J* = 7.6Hz, 1H), 7.00-6.95 (m, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.52 (dd, *J* = 4.4 Hz, 8.8 Hz, 1H), 5.02 (d, *J* = 17.6 Hz, 1H), 4.82 (d, *J* = 16.8 Hz, 1H),

3.12 (dd, J = 8.8 Hz, 14.8 Hz, 1H), 2.80 (dd, J = 4.4 Hz, 14.8 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.1, 142.1, 139.6, 137.1, 131.0, 129.2, 128.6, 128.5, 127.0, 123.0, 122.7, 109.9, 97.7, 69.6, 49.8, 49.1, 47.4, 26.3; IR (KBr, cm^{-1}): 1722, 1485; LRMS (EI 70 ev) m/z (%): 461 (2), 460 (1), 459 (4), 458 (M^+, 1), 334 (60), 333 (19), 332 (100), 235 (91), 236 (21); HRMS (ESI) for $C_{18}H_{17}{}^{35}Cl_2INO$ [$(M+H)^+$]: calcd 459.9726, found 459.9710.



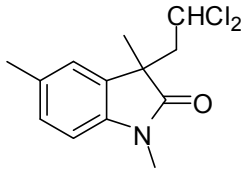
3-(2,2-Dichloroethyl)-3-methyl-1-phenylindolin-2-one (3da):

Yellow solid, mp 130.4-131.0 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52 (t, J = 7.0 Hz, 2H), 7.42-7.39 (m, 3H), 7.27-7.23 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.49 (dd, J = 4.0 Hz, 10.0 Hz, 1H), 3.15 (dd, J = 10.0 Hz, 15.0 Hz, 1H), 2.79 (dd, J = 4.0 Hz, 15.0 Hz, 1H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.3, 143.3, 134.4, 130.7, 129.6, 122.5, 128.1, 126.3, 123.1, 122.9, 109.9, 69.8, 50.2, 47.2, 26.1; IR (KBr, cm^{-1}): 1669, 1499; LRMS (EI 70 ev) m/z (%): 323 (3), 322 (3), 321 (M^++2, 16), 320 (5), 319 (M^+, 24), 224 (10), 223 (70), 222 (100); HRMS (ESI) for $C_{17}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 320.0603, found 320.0611.



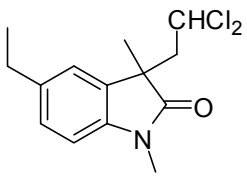
1-Acetyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3ea):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 9.6 Hz, 1H), 7.29-7.26 (m, 1H), 7.23 (t, *J* = 8.8 Hz, 1H), 5.31 (dd, *J* = 3.2 Hz, 10.0 Hz, 1H), 3.10 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 2.76 (dd, *J* = 3.2 Hz, 14.8 Hz, 1H), 2.68 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 180.0, 171.1, 139.6, 129.7, 129.1, 125.5, 122.2, 117.2, 69.4, 51.4, 50.8, 47.6, 26.7; IR (KBr, cm^{-1}): 1716, 1375; LRMS (EI 70 ev) *m*/z (%): 287 (M^++2, 4), 285 (M^+, 6), 245 (23), 243 (35), 147 (100), 146 (65); HRMS (ESI) for $C_{13}H_{14}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 286.0396, found 286.0395.



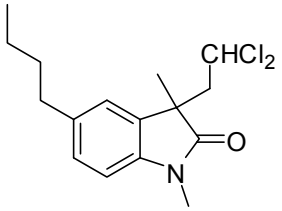
3-(2,2-Dichloroethyl)-1,3,5-trimethylindolin-2-one (3fa):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.10 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.39 (dd, *J* = 4.0 Hz, 9.5 Hz, 1H), 3.17 (s, 3H), 3.00 (dd, *J* = 9.5 Hz, 15.0 Hz, 1H), 2.67 (dd, *J* = 4.0 Hz, 14.5 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.9, 141.0, 132.2, 131.0, 128.8, 123.4, 108.3, 69.7, 50.1, 47.2, 26.4, 25.4, 21.1; IR (KBr, cm^{-1}): 1711, 1377; LRMS (EI 70 ev) *m*/z (%): 273 (M^++2, 22), 272 (6), 271 (M^+, 34), 176 (12), 175 (100), 174 (99); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 272.0603, found 272.0596.



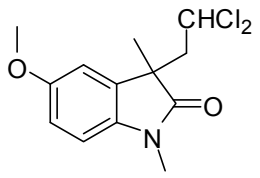
3-(2,2-Dichloroethyl)-5-ethyl-1,3-dimethylindolin-2-one (3ga):

Yellow solid, mp 50.8-51.3 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.37 (dd, *J* = 4.0 Hz, 9.2 Hz, 1H), 3.18 (s, 3H), 3.02 (dd, *J* = 9.6 Hz, 14.8 Hz, 1H), 2.68 (dd, *J* = 4.0 Hz, 12.8 Hz, 1H), 2.66-2.62 (m, 2H), 1.38 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.0, 141.1, 138.9, 130.9, 127.7, 122.2, 108.4, 69.7, 50.1, 47.2, 28.5, 26.4, 25.4, 16.0; IR (KBr, cm^{-1}): 1719, 1370; LRMS (EI 70 ev) *m*/*z* (%): 288 (4), 287 (M^{+}+2, 23), 286 (6), 285 (M^{+}, 35), 190 (13), 189 (100), 188 (84); HRMS (ESI) for $C_{14}H_{18}{}^{35}Cl_2NO$ [$(M+H)^{+}$]: calcd 286.0760, found 286.0757.



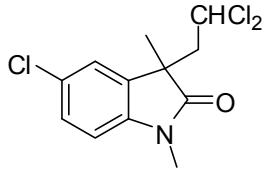
5-Butyl-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ha):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.11 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.37 (dd, *J* = 4.0 Hz, 9.2 Hz, 1H), 3.18 (s, 3H), 3.01 (dd, *J* = 9.2 Hz, 14.8 Hz, 1H), 2.68 (dd, *J* = 4.0 Hz, 14.8 Hz, 1H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.60-1.56 (m, 2H), 1.38-1.33 (m, 5H), 0.93 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.9, 141.1, 137.5, 130.9, 128.2, 122.7, 108.3, 69.7, 50.1, 47.2, 35.3, 34.0, 26.4, 25.4, 22.3, 13.9; IR (KBr, cm^{-1}): 1711, 1370; LRMS (EI 70 ev) *m*/*z* (%): 315 (M^{+}+2, 24), 314 (6), 313 (M^{+}, 35), 272 (63), 271 (16), 270 (100); HRMS (ESI) for $C_{16}H_{22}{}^{35}Cl_2NO$ [$(M+H)^{+}$]: calcd 314.1073, found 314.1070.



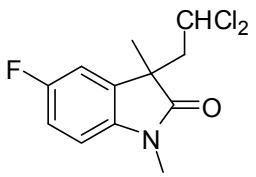
3-(2,2-Dichloroethyl)-5-methoxy-1,3-dimethylindolin-2-one (3ia):

Yellow solid, mp 75.8-76.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 6.83-6.75 (m, 3H), 5.40 (dd, *J* = 4.5 Hz, 9.5 Hz, 1H), 3.80 (s, 3H), 3.16 (s, 3H), 3.00 (dd, *J* = 9.5 Hz, 15.0 Hz, 1H), 2.66 (dd, *J* = 4.5 Hz, 15.0 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.5, 156.0, 136.8, 132.4, 112.3, 110.4, 108.8, 69.6, 55.8, 50.0, 47.5, 26.5, 25.4; IR (KBr, cm^{-1}): 1715, 1376; LRMS (EI 70 ev) *m*/z (%): 290 (5), 289 (M^{+}+2, 30), 288 (7), 287 (M^{+}, 48), 192 (9), 191 (77), 190 (100), 189 (8); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NO$ [$(M+H)^{+}$]: calcd 288.0553, found 288.0567.



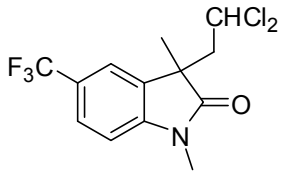
5-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ja):

Yellow solid, mp 86.0-86.8 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.28 (d, *J* = 8.5 Hz, 1H), 7.17 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 4.5 Hz, 9.5 Hz, 1H), 3.19 (s, 3H), 3.02 (dd, *J* = 9.0 Hz, 14.5 Hz, 1H), 2.70 (dd, *J* = 4.5 Hz, 15.0 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.4, 142.0, 132.9, 128.6, 128.0 (2C), 123.2, 109.5, 69.3, 49.9, 47.4, 26.5, 25.4; IR (KBr, cm^{-1}): 1738, 1408; LRMS (EI 70 ev) *m*/z (%): 294 (3), 293 (M^{+}+2, 20), 292 (3), 291 (M^{+}, 20), 197 (32), 196 (31), 195 (100), 194 (71); HRMS (ESI) for $C_{13}H_{13}{}^{35}Cl_3NO$ [$(M+H)^{+}$]: calcd 292.0057, found 292.0075.



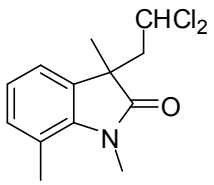
3-(2,2-Dichloroethyl)-5-fluoro-1,3-dimethylindolin-2-one (3ka):

Yellow solid, mp 126.9-127.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.01 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.78 (dd, *J* = 4.0 Hz, 8.4 Hz, 1H), 5.40 (dd, *J* = 4.4 Hz, 8.8 Hz, 1H), 3.18 (s, 3H), 3.01 (dd, *J* = 8.8 Hz, 14.8 Hz, 1H), 2.67 (dd, *J* = 4.4 Hz, 10.4 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 159.4 (d, *J* = 340 Hz, 1C), 139.2, 132.6 (d, *J* = 6.7 Hz, 1C), 114.8 (d, *J* = 22.3 Hz, 1C), 110.9 (d, *J* = 24.6 Hz, 1C), 109.9 (d, *J* = 8.0 Hz, 1C), 69.3, 49.8, 47.6, 26.5, 25.4; IR (KBr, cm^{-1}): 1709, 1384; LRMS (EI 70 ev) *m*/z (%): 278 (2), 277 (M^++2, 13), 276 (3), 275 (M^+, 22), 180 (11), 179 (100), 178 (74), 177 (6); HRMS (ESI) for $C_{13}H_{13}{}^{35}Cl_2FNO$ [$(M+H)^+$]: calcd 276.0353, found 276.0359.



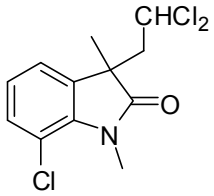
3-(2,2-Dichloroethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3la):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.37 (dd, *J* = 4.4 Hz, 8.8 Hz, 1H), 3.23 (s, 3H), 3.04 (dd, *J* = 8.8 Hz, 14.8 Hz, 1H), 2.74 (dd, *J* = 4.4 Hz, 14.8 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.8, 146.3, 126.4 (t, *J* = 4.0 Hz, 1C), 126.5, 125.0 (q, *J* = 153.4 Hz, 1C), 125.6, 119.7 (t, *J* = 3.6 Hz, 1C), 69.2, 49.7, 47.1, 26.6, 25.4; IR (KBr, cm^{-1}): 1715, 1376; LRMS (EI 70 ev) *m*/z (%): 327 (M^++2, 8), 326 (2), 325 (M^+, 13), 229 (100), 228 (59), 198 (10); HRMS (ESI) for $C_{13}H_{13}{}^{35}Cl_2F_3NO$ [$(M+H)^+$]: calcd 326.0321, found 326.0313.



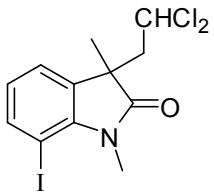
3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one (3ma):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.04-6.96 (m, 3H), 5.36 (dd, *J* = 4.0 Hz, 9.5 Hz, 1H), 3.48 (s, 3H), 3.01 (dd, *J* = 9.0 Hz, 14.5 Hz, 1H), 2.66 (dd, *J* = 4.0 Hz, 15.0 Hz, 1H), 2.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.7, 141.2, 132.3, 131.7, 122.6, 120.5, 120.3, 69.7, 50.4, 46.5, 29.8, 25.7, 19.0; IR (KBr, cm^{-1}): 1715, 1378; LRMS (EI 70 ev) *m*/z (%): 273 (M^++2, 18), 272 (4), 271 (M^+, 29), 176 (12), 175 (100), 174 (87); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 272.0603, found.



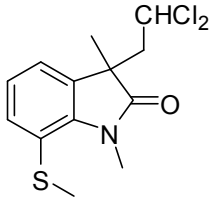
7-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3na):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 5.38 (dd, *J* = 4.4 Hz, 9.2 Hz, 1H), 3.57 (s, 3H), 3.03 (dd, *J* = 8.8 Hz, 14.8 Hz, 1H), 2.66 (dd, *J* = 4.4 Hz, 14.8 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 139.3, 133.9, 130.9, 123.4, 121.1, 116.1, 69.3, 50.2, 46.9, 29.8, 25.8; IR (KBr, cm^{-1}): 1702, 1395; LRMS (EI 70 ev) *m*/z (%): 293 (M^++2, 14), 292 (2), 291 (M^+, 15), 196 (28), 195 (100), 194 (60); HRMS (ESI) for $C_{12}H_{13}{}^{35}Cl_3NO$ [$(M+H)^+$]: calcd 292.0057, found. 292.0076.



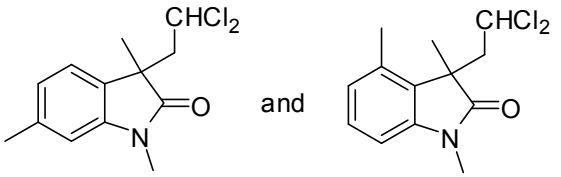
3-(2,2-Dichloroethyl)-7-iodo-1,3-dimethylindolin-2-one (3oa):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.71 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.38 (dd, *J* = 4.5 Hz, 9.0 Hz, 1H), 3.58 (s, 3H), 3.01 (dd, *J* = 9.5 Hz, 15.0 Hz, 1H), 2.67 (dd, *J* = 4.5 Hz, 15.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.6, 143.7, 141.2, 134.1, 124.3, 122.4, 72.1, 69.3, 50.2, 46.7, 30.4, 25.7; IR (KBr, cm^{-1}): 1720, 1365; LRMS (EI 70 ev) *m*/z (%): 385 (M^++2, 19), 384 (4), 383 (M^+, 29), 288 (12), 287 (100), 286 (50); HRMS (ESI) for $C_{12}H_{13}{}^{35}Cl_3INO$ [$(M+H)^+$]: calcd 383.9413, found 383.9401.



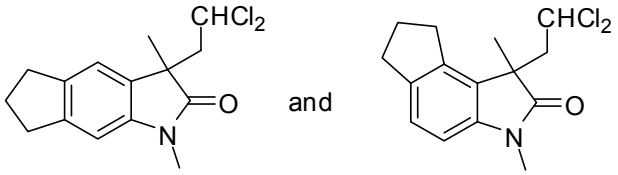
3-(2,2-Dichloroethyl)-1,3-dimethyl-7-(methylthio)indolin-2-one (3pa):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28 (d, *J* = 7.2 Hz, 1H), 7.08-7.02 (m, 2H), 5.37 (dd, *J* = 4.4 Hz, 9.2 Hz, 1H), 3.66 (s, 3H), 3.03 (dd, *J* = 9.6 Hz, 14.8 Hz, 1H), 2.67 (dd, *J* = 4.0 Hz, 14.8 Hz, 1H), 2.48 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.6, 142.0, 132.3, 131.4, 123.2, 120.8, 120.2, 69.5, 50.3, 46.5, 30.4, 25.7, 19.0; IR (KBr, cm^{-1}): 1700, 1392; LRMS (EI 70 ev) *m*/z (%): 307 (5), 306 (4), 305 (M^++2, 24), 304 (6), 303 (M^+, 35), 208 (16), 207 (100), 206 (71); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NOS$ [$(M+H)^+$]: calcd 304.0324, found 304.0320.



3-(2,2-Dichloroethyl)-1,3,6-trimethylindolin-2-one and 3-(2,2-dichloroethyl)-1,3,4-trimethylindolin-2-one (3qa):

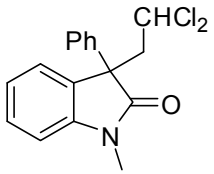
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.22 (t, *J* = 8.0 Hz, 0.65H), 7.06 (d, *J* = 7.5 Hz, 0.39H), 6.90 (d, *J* = 7.5 Hz, 0.40H), 6.85 (d, *J* = 7.5 Hz, 0.65H), 6.72 (s, 0.33H), 6.70 (d, *J* = 7.5 Hz, 0.65H), 5.36 (dd, *J* = 4.0 Hz, 9.5 Hz, 0.37H), 5.27 (dd, *J* = 3.5 Hz, 9.5 Hz, 0.62H), 3.19 (s, 2.00H), 3.18 (s, 1.00H), 3.09 (dd, *J* = 9.5 Hz, 15.0 Hz, 0.69H), 3.01 (dd, *J* = 9.5 Hz, 15.0 Hz, 0.38H), 2.89 (dd, *J* = 4.0 Hz, 15.0 Hz, 0.67H), 2.67 (dd, *J* = 4.0 Hz, 15.0 Hz, 0.39H), 2.39 (s, 1.00H), 2.36 (s, 2.00H), 1.44 (s, 1.96H), 1.36 (s, 1.15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.3, 179.0, 143.7, 143.4, 138.8, 133.9, 128.5, 128.0, 127.8, 125.1, 123.1, 122.3, 109.5, 106.3, 69.7, 50.2, 48.8, 47.9, 46.9, 26.5, 26.4, 25.4, 23.1, 21.8, 18.2.



3-(2,2-Dichloroethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[f]indol-2(*1H*)-one and 1-(2,2-dichloroethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[e]indol-2(*1H*)-one (3ra):

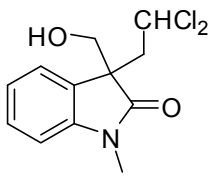
Yellow solid, mp 83.5-84.8 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.16 (t, *J* = 7.5 Hz, 0.72H), 7.04 (s, 0.27H), 6.75 (s, 0.28H), 6.65 (d, *J* = 7.5 Hz, 0.71H), 5.39 (dd, *J* = 3.5 Hz, 9.5 Hz, 0.28H), 5.28 (dd, *J* = 4.0 Hz, 9.5 Hz, 0.71H),

3.19 (s, 2.20H), 3.18 (s, 0.86H), 3.04 (dd, *J* = 9.5 Hz, 15.0 Hz, 0.69H), 3.01-2.88 (m, 3.48H), 2.83-2.77 (m, 1.56H), 2.66 (dd, *J* = 3.5 Hz, 14.5 Hz, 0.33H), 2.19-2.10 (m, 2.00H), 1.40 (s, 2.17H), 1.37 (s, 0.90H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.3, 178.8, 144.6, 141.9, 141.8, 139.6, 139.4, 138.2, 129.0, 125.8, 123.8, 118.7, 106.5, 105.2, 69.8 (2C), 50.3, 48.8, 47.4, 47.1, 33.2, 31.7, 30.3, 26.7, 26.5, 25.8, 25.6, 25.5, 23.2.



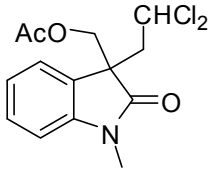
3-(2,2-Dichloroethyl)-1-methyl-3-phenylindolin-2-one (3sa):

Yellow solid, mp 107.1-108.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.41 (t, *J* = 7.5 Hz, 1H), 7.34-7.32 (m, 2H), 7.30-7.23 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.45 (dd, *J* = 4.0 Hz, 9.5 Hz, 1H), 3.59 (dd, *J* = 9.5 Hz, 15.0 Hz, 1H), 3.18 (s, 3H), 3.09 (dd, *J* = 4.0 Hz, 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.0, 144.4, 139.5, 129.2, 128.7, 128.5, 127.8, 126.4, 125.1, 122.7, 109.0, 69.7, 54.9, 50.1, 26.7; IR (KBr, cm^{-1}): 1722, 1403; LRMS (EI 70 ev) *m*/z (%): 323 (3), 322 (4), 321 (M^++2, 20), 320 (6), 319 (M^+, 30), 224 (17), 223 (100), 222 (63), 221 (4), 220 (10); HRMS (ESI) for $C_{17}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 320.0603, found 320.0596.



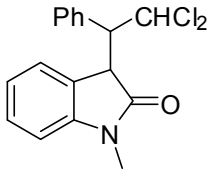
3-(2,2-Dichloroethyl)-3-(hydroxymethyl)-1-methylindolin-2-one (3ta):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (t, *J* = 7.6 Hz, 1H), 7.27-7.25 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.43 (dd, *J* = 4.4 Hz, 9.6 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.70 (d, *J* = 10.8 Hz, 1H), 3.22 (s, 3H), 3.16 (t, *J* = 11.2 Hz, 1H), 2.86 (dd, *J* = 4.4 Hz, 15.2 Hz, 1H), 2.82-2.79 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.7, 144.2, 129.2, 127.1, 123.3, 122.9, 108.8, 69.7, 67.6, 53.0, 45.5, 26.5; IR (KBr, cm^{-1}):1755, 1433; LRMS (EI 70 ev) *m*/z (%): 275 (M^++2, 14), 274 (15), 273 (M^+, 21), 160 (100); HRMS (ESI) for $C_{12}H_{14}{}^{35}Cl_2NO_2$ [$(M+H)^+$]: calcd 274.0396, found 274.0391.



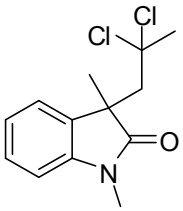
(3-(2,2-Dichloroethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ua):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.44 (dd, *J* = 4.4 Hz, 9.6 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.10 (d, *J* = 10.8 Hz, 1H), 3.23 (s, 3H), 3.05 (dd, *J* = 9.2 Hz, 14.4 Hz, 1H), 2.86 (dd, *J* = 4.4 Hz, 14.8 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.7, 170.0, 144.2, 129.3, 126.8, 123.8, 122.7, 108.6, 69.1, 67.2, 51.0, 45.6, 26.5, 20.5; IR (KBr, cm^{-1}): 1763, 1732, 1416; LRMS (EI 70 ev) *m*/z (%): 317 (M^++2, 11), 316 (3), 315 (M^+, 17), 245 (29), 244 (7), 243 (47), 161 (11), 160 (100), 159 (25); HRMS (ESI) for $C_{14}H_{16}{}^{35}Cl_2NO_3$ [$(M+H)^+$]: calcd 316.0502, found 316.0524.



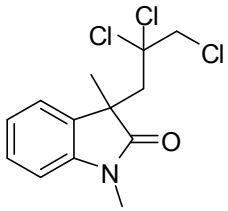
3-(2,2-Dichloro-1-phenylethyl)-1-methylindolin-2-one (3wa):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (t, *J* = 8.8 Hz, 1H), 7.31-7.22 (m, 3H), 7.15-7.10 (m, 3H), 7.10-7.04 (m,2H), 5.82 (d, *J* = 6.8 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 1H), 3.55 (dd, *J* = 3.2 Hz, 6.4 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.0, 140.3, 139.1, 129.6, 129.0, 128.6, 127.5, 127.4, 125.4, 124.0, 115.1, 71.4, 59.1, 44.1, 30.1; IR (KBr, cm^{-1}): 1685, 1601, 1471, 1369; LRMS (EI 70 ev) *m*/z (%): 323 (12), 322 (12), 321 (M^++2, 67), 320 (20), 319 (M^+, 96), 286 (8), 285 (6), 284 (26); HRMS (ESI) for $C_{17}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 320.0603, found 320.0611.



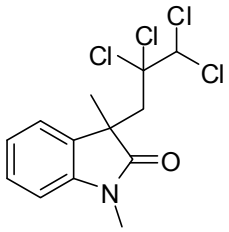
3-(2,2-Dichloropropyl)-1,3-dimethylindolin-2-one (3ab):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (t, *J* = 6.8 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.26-3.23 (m, 4H), 2.90 (d, *J* = 15.2 Hz, 1H), 1.81 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 143.1, 131.0, 128.3, 124.9, 122.1, 108.3, 87.5, 55.3, 47.6, 38.2, 27.2, 26.4; IR (KBr, cm^{-1}): 1722, 1486; LRMS (EI 70 ev) *m*/z (%): 274 (2), 273 (M^++2, 14), 272 (3), 271 (M^+, 24), 162 (3), 161 (29), 160 (100), 159 (3); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 272.0603, found 272.0591.



1,3-Dimethyl-3-(2,2,3-trichloropropyl)indolin-2-one (3ac):

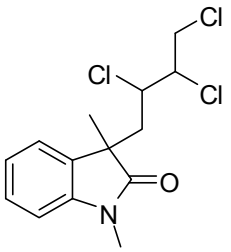
Yellow solid, mp 64.8-66.1 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 5.2 Hz, 13.2 Hz, 1H), 3.73 (d, *J* = 12.0 Hz, 1H), 3.40 (d, *J* = 12.0 Hz, 1H), 3.24-3.17 (m, 4H), 3.07 (d, *J* = 15.6 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 143.2, 130.2, 128.7, 124.2, 122.1, 108.4, 87.8, 54.5, 49.0, 47.2, 27.0, 26.5; IR (KBr, cm^{-1}): 1714, 1496; LRMS (EI 70 ev) *m*/z (%): 309 (5), 308 (2), 307 (M^{+}+2, 14), 306 (2), 305 (M^{+}, 4), 272 (8), 270 (12), 162 (5), 161 (49), 160 (100); HRMS (ESI) for $C_{13}H_{15}{}^{35}Cl_3NO$ [$(M+H)^{+}$]: calcd 306.0214, found 306.0212.



1,3-Dimethyl-3-(2,2,3,3-tetrachloropropyl)indolin-2-one (3ad):

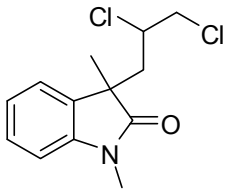
Yellow solid, mp 125.1-126.3 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.57 (s, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.22 (s, 3H), 3.11 (d, *J* = 15.6 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.1, 143.2, 130.2, 128.7, 124.7, 122.1, 108.6, 91.0, 78.6, 48.6, 47.1, 27.2, 26.6; IR (KBr, cm^{-1}): 1733, 1466; LRMS (EI 70 ev) *m*/z (%):343 (3), 342 (1), 341 (6), 340 (M^{+}+2, 1), 338 (M^{+}, 1),

305 (2), 306 (8), 304 (9), 161 (34) 160 (100); HRMS (ESI) for $C_{13}H_{14}{}^{35}Cl_4NO$ [$(M+H)^+$]: calcd 339.9824, found 339.9814.



1,3-Dimethyl-3-(2,3,4-trichlorobutyl)indolin-2-one (3af):

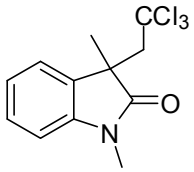
Yellow solid, mp 80.6-82.4 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.67 (d, *J* = 11.6 Hz, 1H), 3.46 (d, *J* = 11.6 Hz, 1H), 3.22-3.17 (m, 4H), 2.71-2.60 (m, 2H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.6, 143.1, 131.4, 128.7, 123.2, 122.3, 108.6, 70.0, 50.7, 47.4, 46.7, 42.0, 27.5, 26.5; IR (KBr, cm^{-1}): 1738, 1497; LRMS (EI 70 ev) *m*/z (%): 321 (M^++2, 7), 319 (M^+, 8), 284 (8), 248 (13), 160 (100); HRMS (ESI) for $C_{14}H_{17}{}^{35}Cl_3NO$ [$(M+H)^+$]: calcd 320.0370, found 320.0375.



3-(2,3-Dichloropropyl)-1,3-dimethylindolin-2-one (3ag)

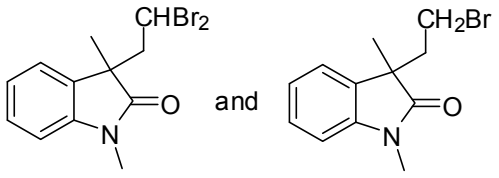
Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 3.66-3.59 (m, 1H), 3.58-3.47 (m, 2H), 3.22 (s, 3H), 2.62-2.56 (m, 1H), 2.46 (dd, *J* = 10.4, 15.2 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.9, 179.3, 143.5, 142.8, 132.7,

131.6, 130.7, 128.4, 128.2, 127.6, 123.2, 122.7, 122.5, 112.8, 108.4, 108.3, 57.3, 56.8, 49.2, 48.1, 46.6, 42.7, 42.3, 26.4, 26.3, 25.4; IR (KBr, cm^{-1}): 1702, 1497; LRMS (EI 70 ev) *m*/z (%): 273 (M^++2, 15), 271 (M^+, 23), 236 (23), 238 (8), 161 (100), 160 (87); HRMS (ESI) for $C_{13}H_{16}{}^{35}Cl_2NO$ [$(M+H)^+$]: calcd 272.0603, found 272.0591.



1,3-Dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (3ah):

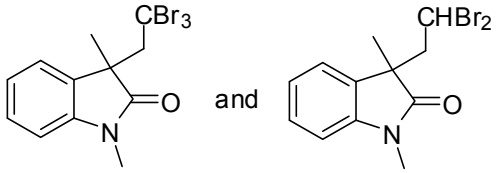
Yellow solid, mp 90.1-91.2 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (d, *J* = 6.8 Hz, 1H), 7.30-7.28 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.68 (d, *J* = 15.2 Hz, 1H), 3.33 (d, *J* = 15.2 Hz, 1H), 3.23 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.6, 143.2, 129.5, 128.4, 125.6, 122.0, 108.4, 96.1, 59.8, 47.9, 26.8, 26.5; IR (KBr, cm^{-1}): 1738, 1491; LRMS (EI 70 ev) *m*/z (%): 294 (4), 293 (M^++2, 2), 292 (14), 291 (M^+, 2), 290 (14), 161 (12), 160 (100), 159 (3); HRMS (ESI) for $C_{12}H_{13}{}^{35}Cl_3NO$ [$(M+H)^+$]: calcd 292.0057, found 292.0065.



3-(2,2-Dibromoethyl)-1,3-dimethylindolin-2-one (3ai) and 3-(2-Bromoethyl)-1,3-dimethylindolin-2-one (3ai'):

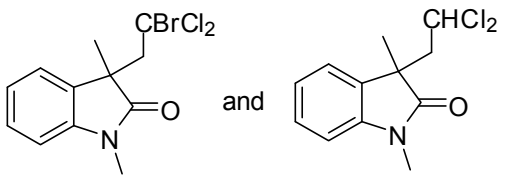
3ai/3ai' = 1 : 1; Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.33-7.27 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 8.5 Hz, 1H), 5.30

(dd, *J* = 4.0 Hz, 9.5 Hz, 0.48H), 3.26 (dd, *J* = 9.5 Hz, 15.0 Hz, 0.61H), 3.20 (s, 1.49H), 3.19 (s, 1.44H), 3.06-2.95 (m, 1.58H), 2.51-2.48 (m, 0.51), 2.33-2.29 (m, 0.51H), 1.38 (s, 1.53H), 1.37 (s, 1.47H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 179.2, 178.8, 143.5, 143.1, 132.3, 130.7, 128.6, 128.2, 122.7, 122.6 (2C), 122.5, 108.6, 108.2, 51.5, 48.5 (2C), 41.1, 39.6, 27.2, 26.5, 26.2, 25.6, 23.7.



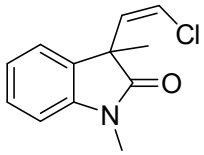
1,3-Dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (3aj) and 3-(2,2-Dibromoethyl)-1,3-dimethylindolin-2-one (3aj'):

3aj/3aj' = 2 : 1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.44 (d, *J* = 7.5 Hz, 0.60H), 7.33-7.29 (m, 0.96H), 7.17 (d, *J* = 7.0 Hz, 0.35H), 7.09 (t, *J* = 7.5 Hz, 0.33H), 7.05 (t, *J* = 7.5 Hz, 0.54H), 6.86 (d, *J* = 8.0 Hz, 0.95H), 5.29 (dd, *J* = 4.5 Hz, 9.5 Hz, 0.34H), 4.10 (d, *J* = 15.0 Hz, 0.67H), 3.72 (d, *J* = 15.5 Hz, 0.61H), 3.26 (dd, *J* = 9.5 Hz, 15.5 Hz, 0.37H), 3.23 (s, 1.87H), 3.19 (s, 1.05H), 2.98 (dd, *J* = 4.5 Hz, 15.0 Hz, 0.36H), 1.37 (s, 1.78H), 1.37 (s, 0.92H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.8, 178.3, 143.5 (2C), 130.7, 128.6 (3C), 126.5, 122.6, 121.8, 108.6, 108.3, 63.6, 51.5, 50.0, 48.5, 39.6, 32.8, 27.1, 26.6, 26.5, 25.6.



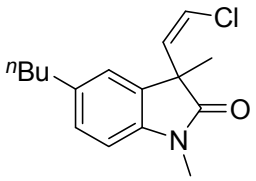
3-(2-Bromo-2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ak) and 3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa):

3ak/3ak' = 1 : 2; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.29 (m, 1.34H), 7.20 (d, *J* = 7.2 Hz, 0.70H), 7.12-7.04 (m, 1.00H), 6.87 (d, *J* = 7.6 Hz, 1.00H), 5.36 (dd, *J* = 4.0 Hz, 9.6 Hz, 0.65H), 3.84 (d, *J* = 15.2 Hz, 0.31H), 3.46 (d, *J* = 15.2 Hz, 0.31H), 3.23 (s, 1.00H), 3.21 (s, 2.00H), 3.04 (dd, *J* = 9.2 Hz, 14.8 Hz, 0.69H), 2.70 (dd, *J* = 4.0 Hz, 14.8 Hz, 0.69H), 1.39 (s, 2.00H), 1.38 (s, 1.00H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.0, 178.5, 143.3, 130.9, 129.2, 128.6, 128.5, 125.8, 122.7, 122.6, 121.9, 108.6, 108.4, 69.6, 61.2, 50.0, 48.6, 47.1, 26.8, 26.6, 26.4, 25.4.



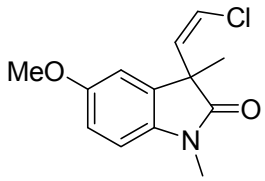
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethylindolin-2-one (4aa):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.10-6.03 (m, 2H), 3.21 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.3, 142.7, 133.3, 131.5, 128.5, 123.5, 122.7, 120.1, 108.4, 50.0, 26.3, 23.0; IR (KBr, cm^{-1}): 1716, 1612, 1494; LRMS (EI 70 ev) *m*/z (%): 223 (M^++2, 33), 222 (13), 221 (M^+, 100), 206 (79), 159 (11), 158 (84), 157 (11); HRMS (ESI) for $C_{12}H_{13}{}^{35}ClNO$ [$(M+H)^+$]: calcd 222.0680, found 222.0685.



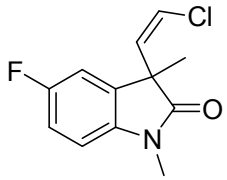
(*Z*)-5-butyl-3-(2-chlorovinyl)-1,3-dimethylindolin-2-one (4ha):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.10 (d, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.08-6.01 (m, 2H), 3.18 (m, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.61-1.55 (m, 2H), 1.48 (s, 3H), 1.38-1.32 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.3, 140.4, 137.6, 133.4, 131.3, 128.1, 123.7, 119.9, 108.2, 50.1, 35.3, 34.0, 26.3, 23.0, 22.3, 13.8; IR (KBr, cm^{-1}): 1744, 1636, 1477; LRMS (EI 70 ev) *m*/z (%) 279 (M^++2, 23), 278 (13), 277 (M^+, 70), 236 (50), 235 (23), 234 (100); HRMS (ESI) for $C_{16}H_{21}{}^{35}ClNO$ [$(M+H)^+$]: calcd 278.1306, found 278.1306.



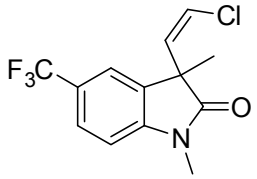
(*Z*)-3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ia):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 6.84-6.82 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.06 (s, 2H), 3.80 (s, 3H), 3.18 (m, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.0, 156.1, 136.2, 133.3, 132.8, 120.2, 112.5, 111.2, 108.8, 55.8, 50.5, 26.4, 23.0; IR (KBr, cm^{-1}): 1711, 1631, 1491; LRMS (EI 70 ev) *m*/z (%): 254 (5), 253 (M^++2, 35), 252 (15), 251 (M^+, 100), 238 (28), 237 (12), 236 (86); HRMS (ESI) for $C_{13}H_{15}{}^{35}ClNO_2$ [$(M+H)^+$]: calcd 252.0786, found 252.0788.



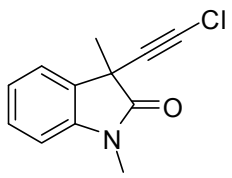
(*Z*)-3-(2-Chlorovinyl)-5-fluoro-1,3-dimethylindolin-2-one (4ka):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.02 (t, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 5.5 Hz, 1H), 6.09-6.03 (m, 2H), 3.21 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.1, 159.3 (d, *J* = 240.1 Hz, 1C), 138.7, 132.8 (2C), 120.8 (d, *J* = 23.4 Hz, 1C), 111.8 (d, *J* = 24.5 Hz, 1C), 109.0 (d, *J* = 8.1 Hz, 1C), 50.5, 26.5, 23.0; IR (KBr, cm^{-1}): 1720, 1608, 1481; LRMS (EI 70 ev) *m*/z (%): 242 (5), 241 (M^++2, 34), 240 (15), 239 (M^+, 99), 227 (3), 226 (23), 225 (9), 224 (71), 176 (100); HRMS (ESI) for $C_{12}H_{12}{}^{35}ClFNO$ [$(M+H)^+$]: calcd 240.0586, found 240.0577.



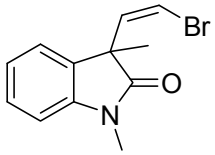
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (4la):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.09-6.03 (m, 2H), 3.25 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.3, 145.7, 132.2 (d, *J* = 24.9 Hz, 1C), 125.3 (q, *J* = 174.0 Hz, 1C), 126.4 (d, *J* = 3.9 Hz, 1C), 120.6 (t, *J* = 32.4 Hz, 1C), 108.3, 49.9, 26.6, 22.9; IR (KBr, cm^{-1}): 1733, 1655, 1471; LRMS (EI 70 ev) *m*/z (%): 292 (4), 291 (M^++2, 28), 290 (14), 289 (M^+, 88), 227 (13), 226 (100); HRMS (ESI) for $C_{13}H_{12}{}^{35}ClF_3NO$ [$(M+H)^+$]: calcd 290.0554, found 290.0550.



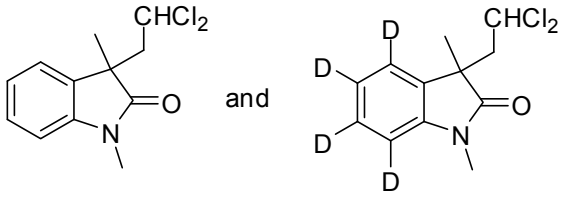
3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ah):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (t, *J* = 9.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.22 (m, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.2, 142.1, 131.3, 128.8 (2C), 123.2, 108.5, 67.5, 61.0, 42.8, 26.6, 25.1; IR (KBr, cm^{-1}): 1719, 1613, 1496; LRMS (EI 70 ev) *m*/z (%): 222 (5), 221 (M^++2, 34), 220 (15), 219 (M^+, 100), 184 (58); HRMS (ESI) for $C_{12}H_{11}{}^{35}ClNO$ [$(M+H)^+$]: calcd 220.0524, found 220.0516.



(*Z*)-3-(2-Bromovinyl)-1,3-dimethylindolin-2-one (4ai):

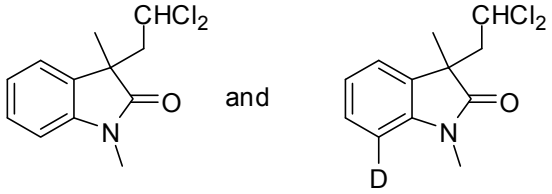
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.33 (d, *J* = 14.0 Hz, 1H), 6.16 (d, *J* = 13.6 Hz, 1H), 3.21 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.1, 142.8, 137.0, 131.1, 128.6, 123.7, 122.8, 108.5, 107.8, 26.4, 22.8; IR (KBr, cm^{-1}): 1715, 1610, 1494; LRMS (EI 70 ev) *m*/z (%): 267 (32), 266 (5), 265 (M^+, 36), 159 (13), 158 (100); HRMS (ESI) for $C_{12}H_{13}BrNO$ [$(M+H)^+$]: calcd 266.0175, found 266.0168.



3aa and 3aa-D4:

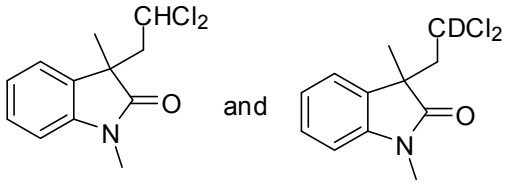
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (t, *J* = 8.0 Hz, 0.52H), 7.19 (d, *J* = 7.6 Hz, 0.52H), 7.10 (d, *J* = 7.6 Hz, 0.51H), 6.87 (d, *J* = 8.0 Hz, 0.51H), 5.39

(dd, *J* = 4.0 Hz, 8.8 Hz, 1.00H), 3.21 (s, 3H), 3.03 (dd, *J* = 9.2 Hz, 14.8 Hz, 1.00H), 2.70 (dd, *J* = 4.0 Hz, 14.8 Hz, 1.00H), 1.40 (s, 3.00H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.0, 143.4, 131.1, 128.6, 122.7 (2C), 108.6, 69.6, 50.2, 47.2, 26.4, 25.4.



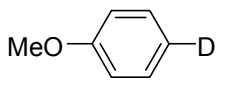
3aa and 3aa-D1:

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33(m, 1H), 7.19 (d, *J* = 6.4 Hz, 1.00H), 7.09 (t, *J* = 7.6 Hz, 1.00H), 6.86 (d, *J* = 8.0 Hz, 0.51H), 5.39 (dd, *J* = 3.6 Hz, 9.2 Hz, 1.00H), 3.20 (s, 3H), 3.02 (dd, *J* = 9.2 Hz, 10.8 Hz, 1.00H), 2.70 (dd, *J* = 4.0 Hz, 14.8 Hz, 1.00H), 1.39 (s, 3.00H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.9, 143.4, 143.3, 131.1, 128.6, 128.5, 122.6, 108.6, 69.6, 50.2, 47.1, 26.4, 25.4.



3aa and 3aa-D1':

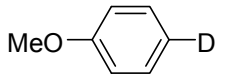
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (t, *J* = 8.0 Hz, 1.00H), 7.19 (d, *J* = 7.6 Hz, 1.00H), 7.10 (t, *J* = 7.6 Hz, 1.00H), 6.87 (d, *J* = 8.0 Hz, 1.00H), 5.36 (dd, *J* = 4.0 Hz, 9.2 Hz, 0.90H), 3.20 (s, 3H), 3.04 (dd, *J* = 8.8 Hz, 14.8 Hz, 1.00H), 2.70 (dd, *J* = 4.0 Hz, 14.8 Hz, 1.00H), 1.39 (s, 3.00H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.9, 143.4, 131.1, 128.6 (2C), 122.6, 108.6, 69.6, 50.2, 47.1, 26.4, 25.4.



(*-D* 83%) (**6-D1**)

Addition of Na_2CO_3, $MeOC_6H_4N_2BF_4$:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (d *J* = 8.8 Hz, 2.00H), 7.07 (s, 0.17H), 6.91 (d, *J* = 8.8 Hz, 2.00H), 3.81 (s, 3.00H).



(**6-D1**)

Addition of $Ru(bpy)_3Cl_2$, Na_2CO_3, $MeOC_6H_4N_2BF_4$ and visible light:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (d *J* = 8.8 Hz, 2.00H), 7.07 (s, 0.15H), 6.91 (d, *J* = 8.8 Hz, 2.00H), 3.81 (s, 3.00H).

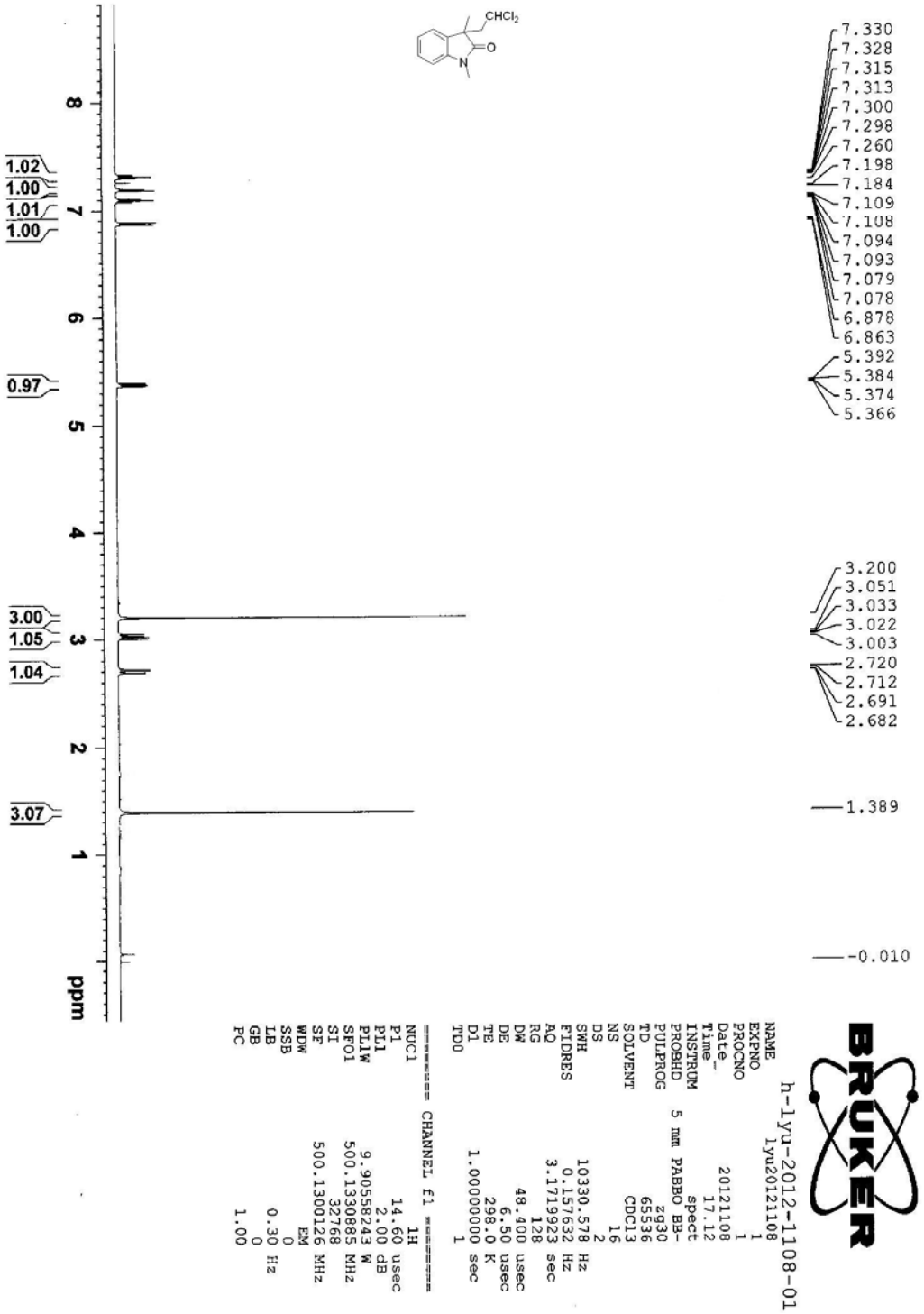
(C) References

(1) (a) Mu, X.; Wu, T.; Wang, H.-Y.; Guo, Y.-L.; Liu, G.-S. *J. Am. Chem. Soc.* **2012**, *134*, 878. (b) Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J. *Chem. Eur. J.* **2007**, *13*, 961. (c) Jones, K.; Thompson, M.; Wright, C. *J. Chem. Soc., Chem. Commun.* **1986**, 715.

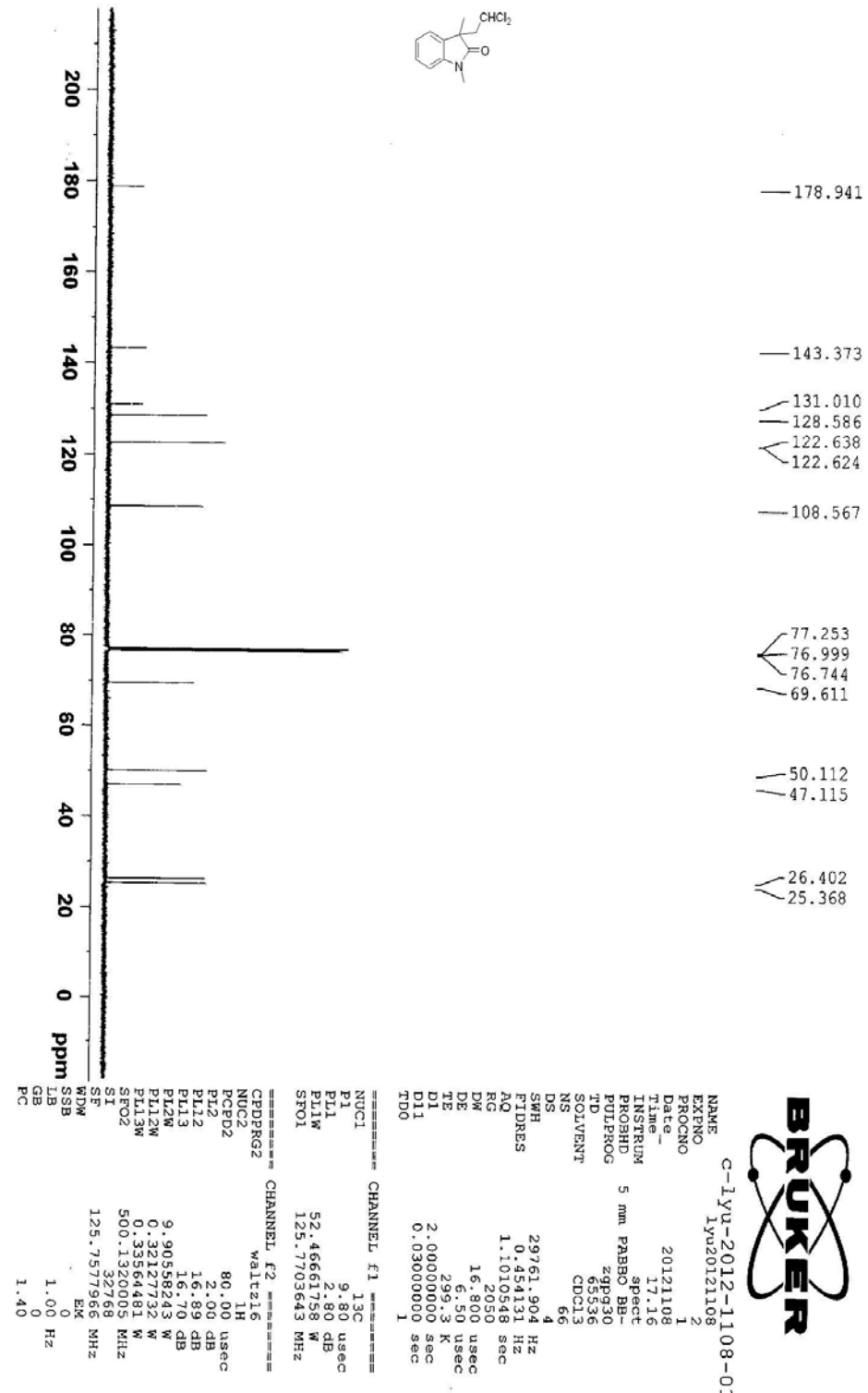
(2) (a) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (b) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(D) Spectra

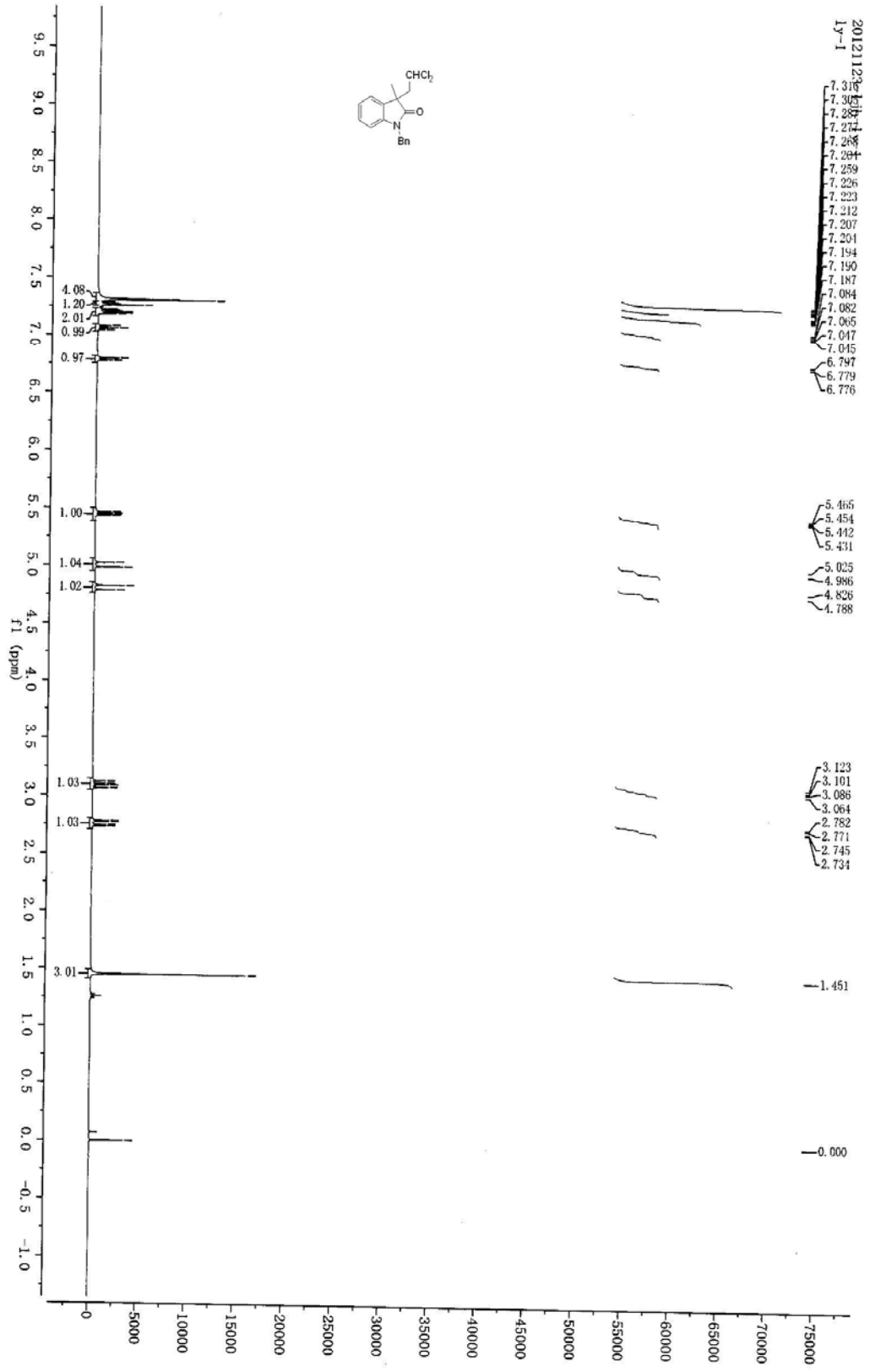
3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa)



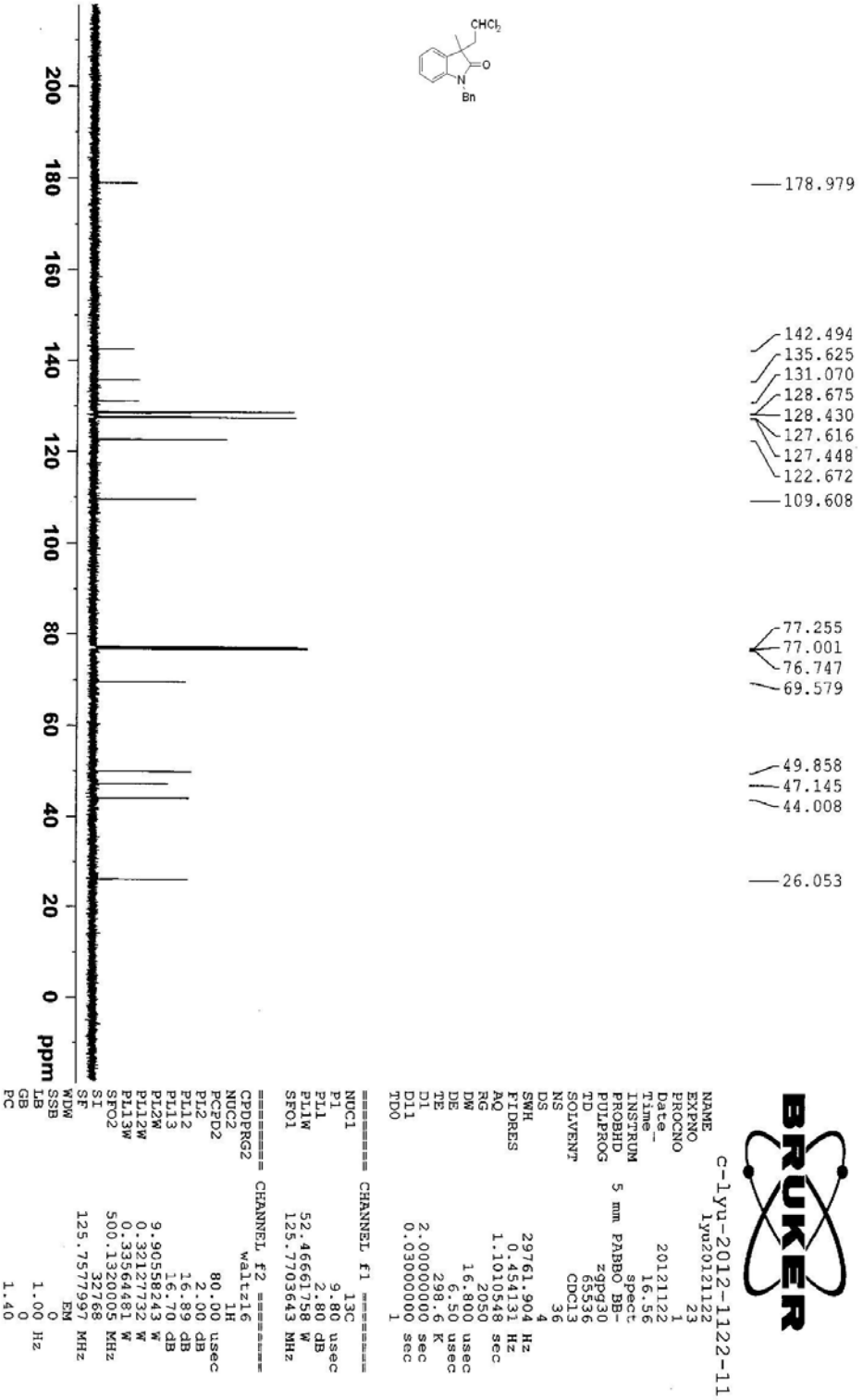
3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa)



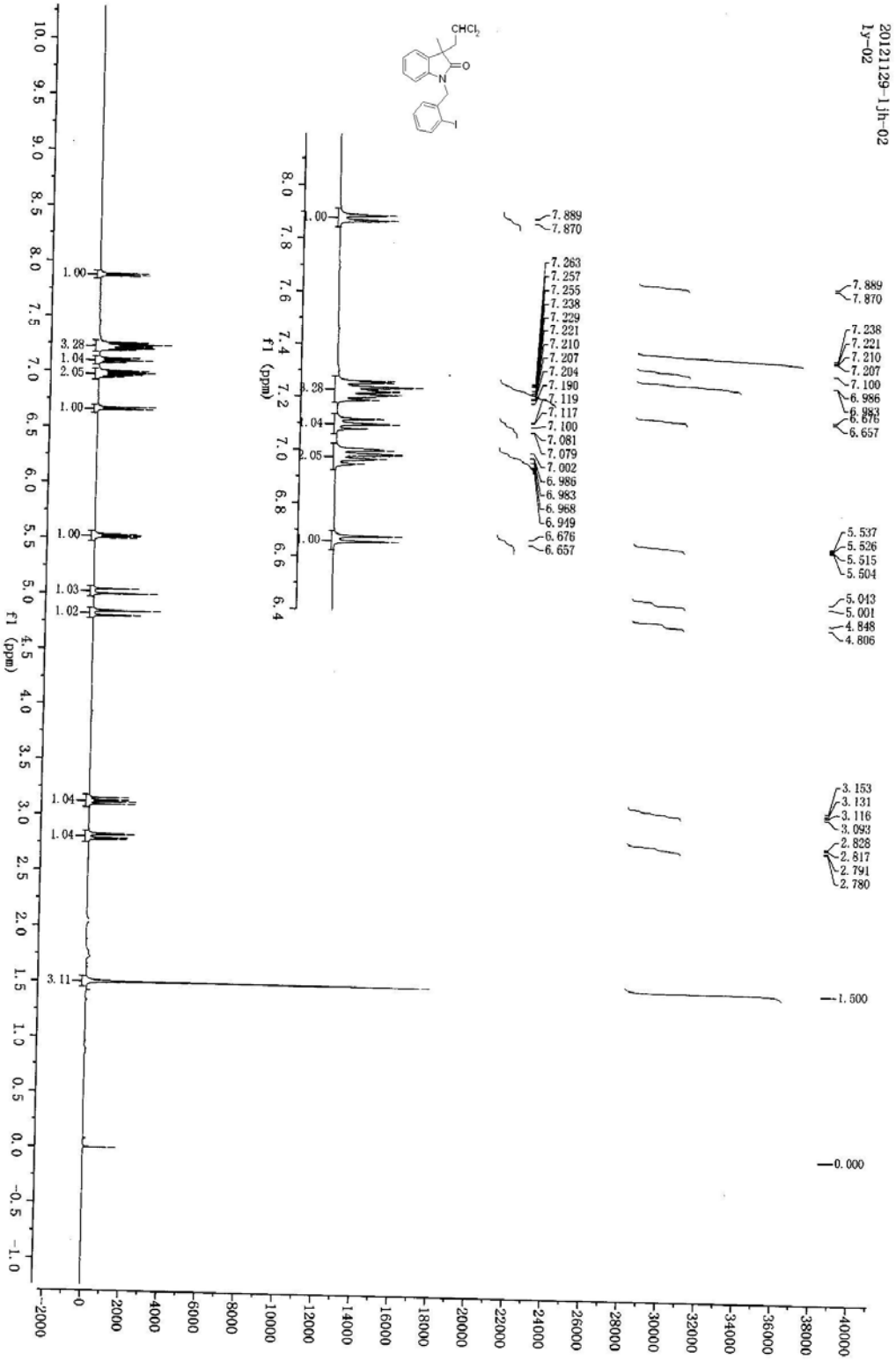
1-Benzyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3ba)



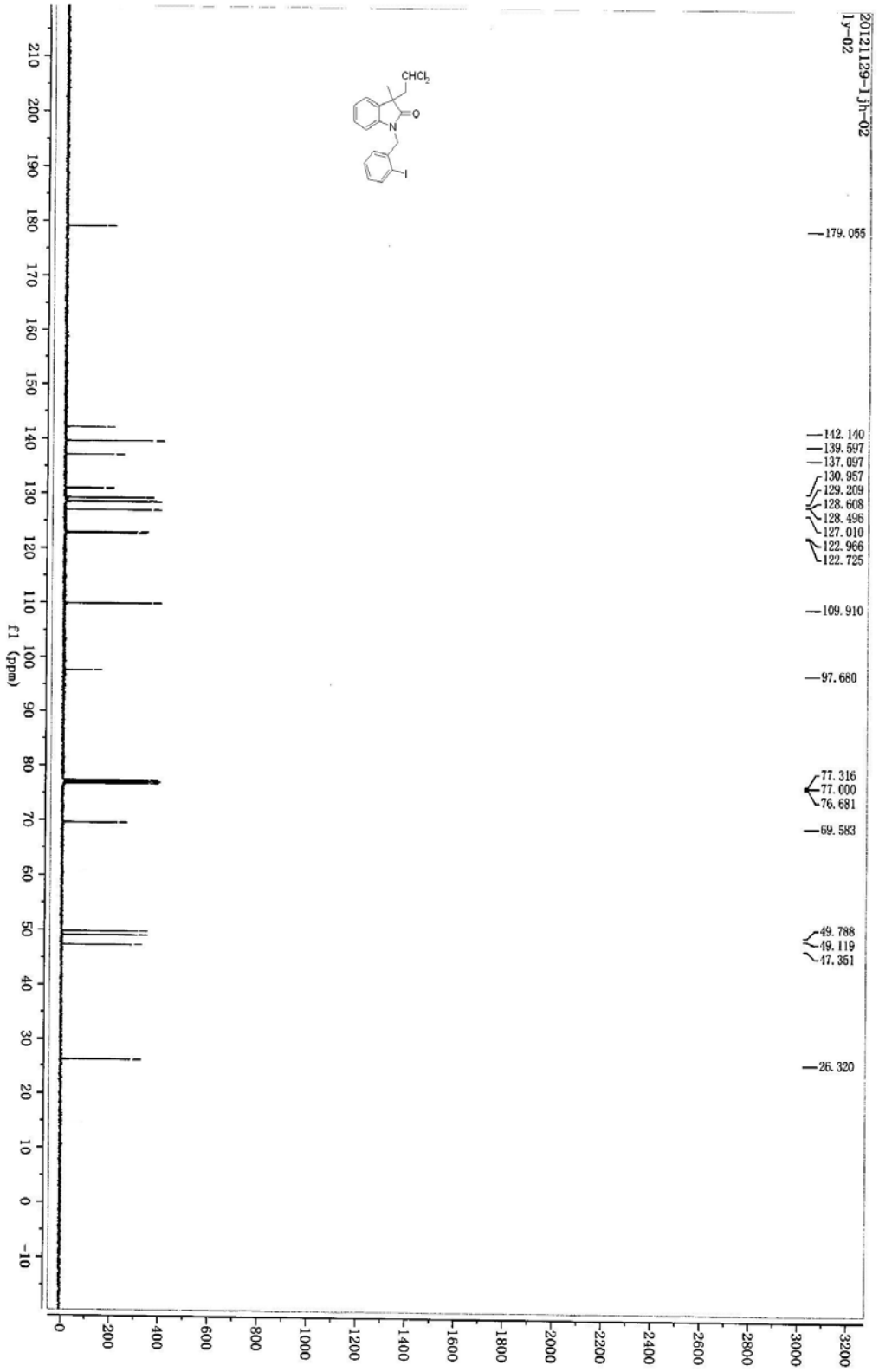
1-Benzyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3ba)



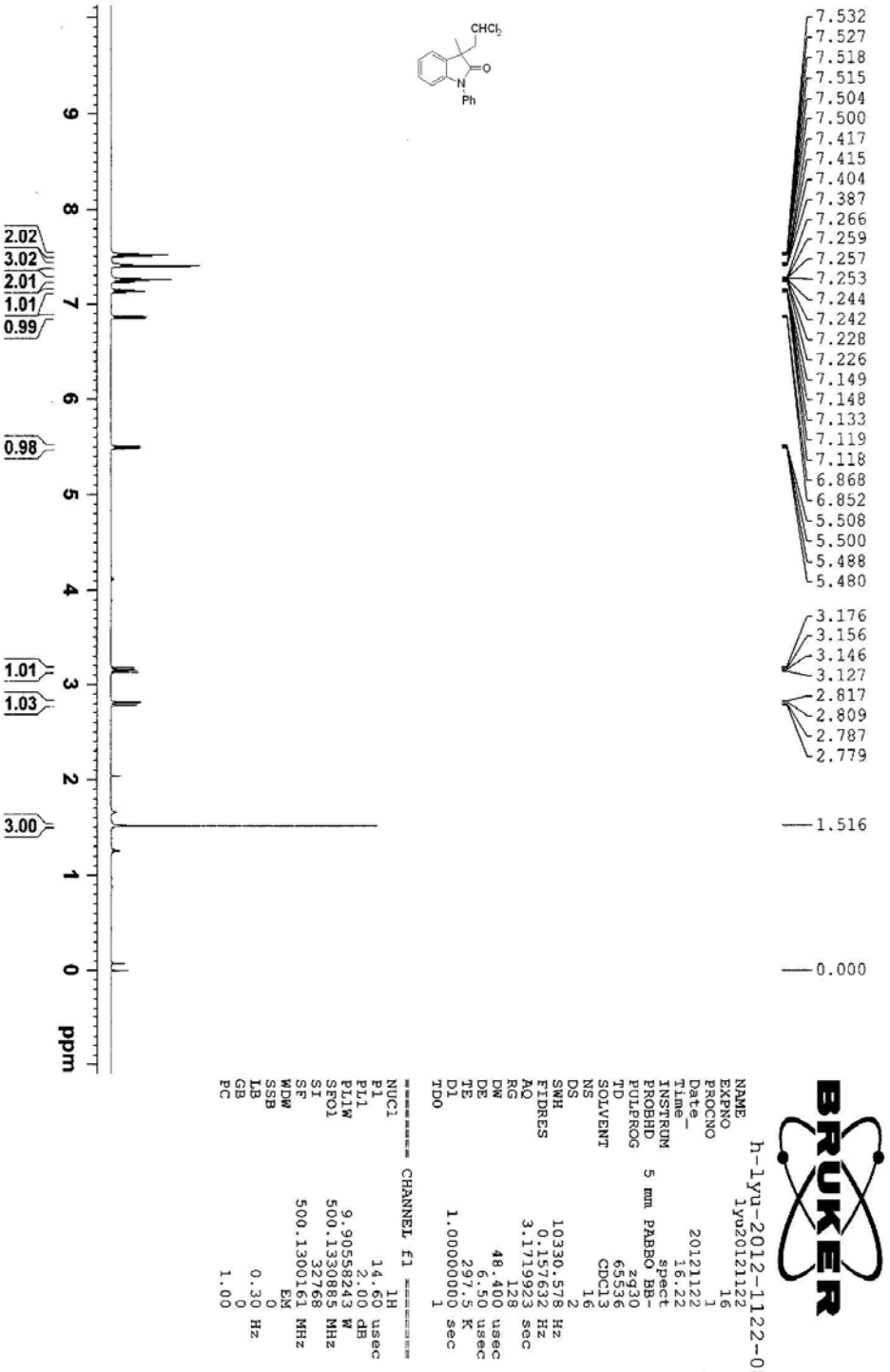
3-(2,2-Dichloroethyl)-1-(2-iodobenzyl)-3-methylindolin-2-one (3ca)



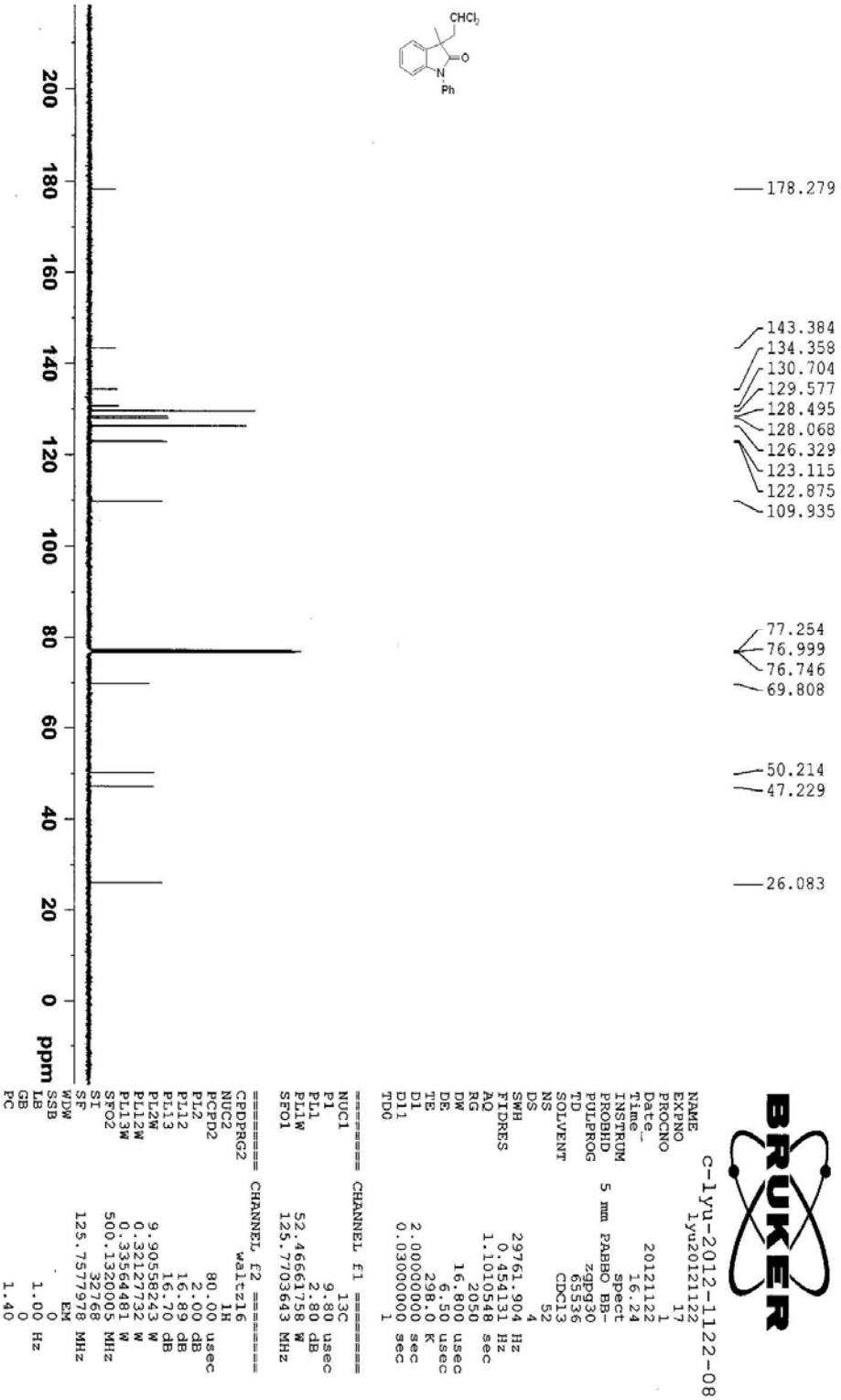
3-(2,2-Dichloroethyl)-1-(2-iodobenzyl)-3-methylindolin-2-one (3ca)



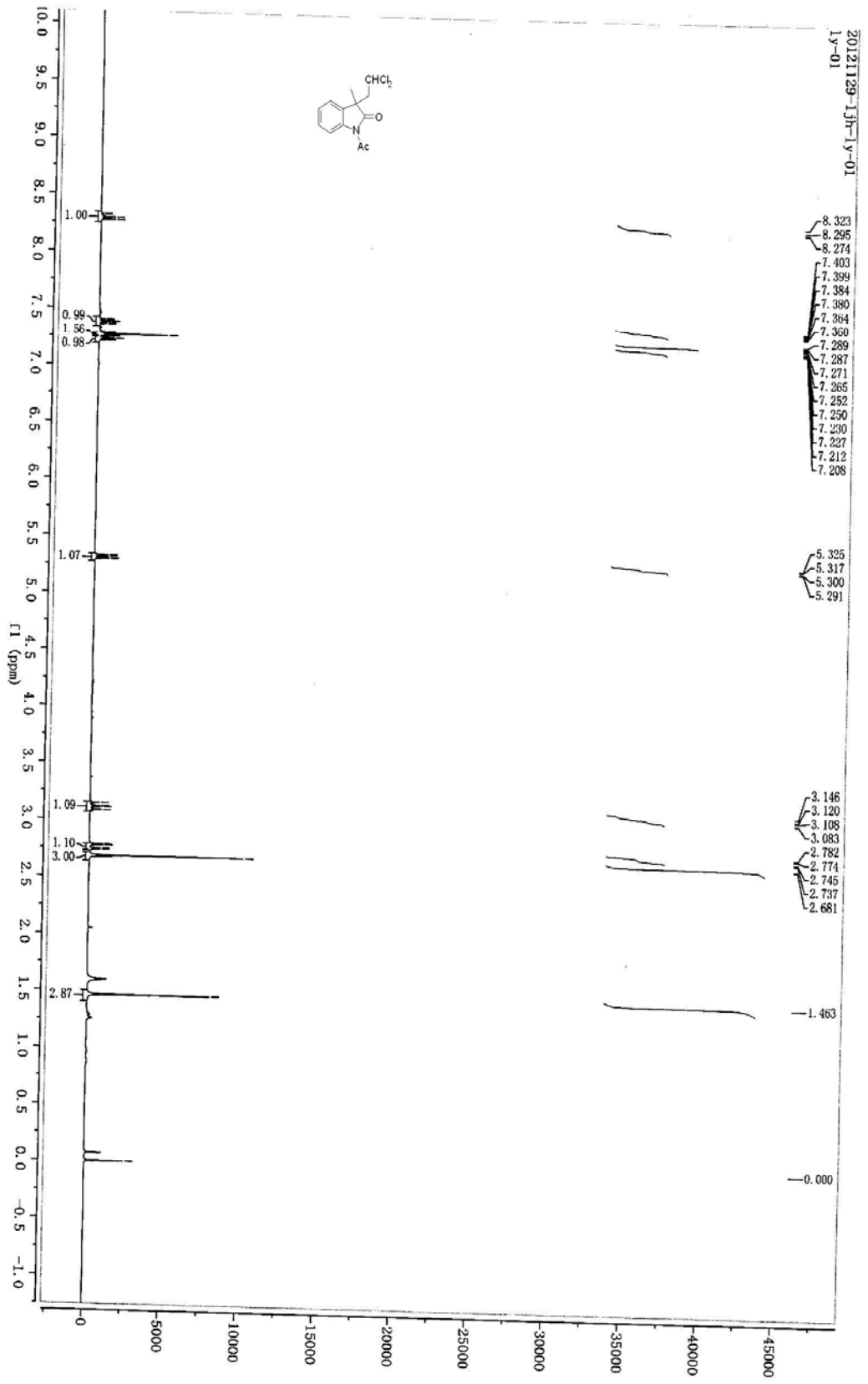
3-(2,2-Dichloroethyl)-3-methyl-1-phenylindolin-2-one (3da)



3-(2,2-Dichloroethyl)-3-methyl-1-phenylindolin-2-one (3da)



1-Acetyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3ea)



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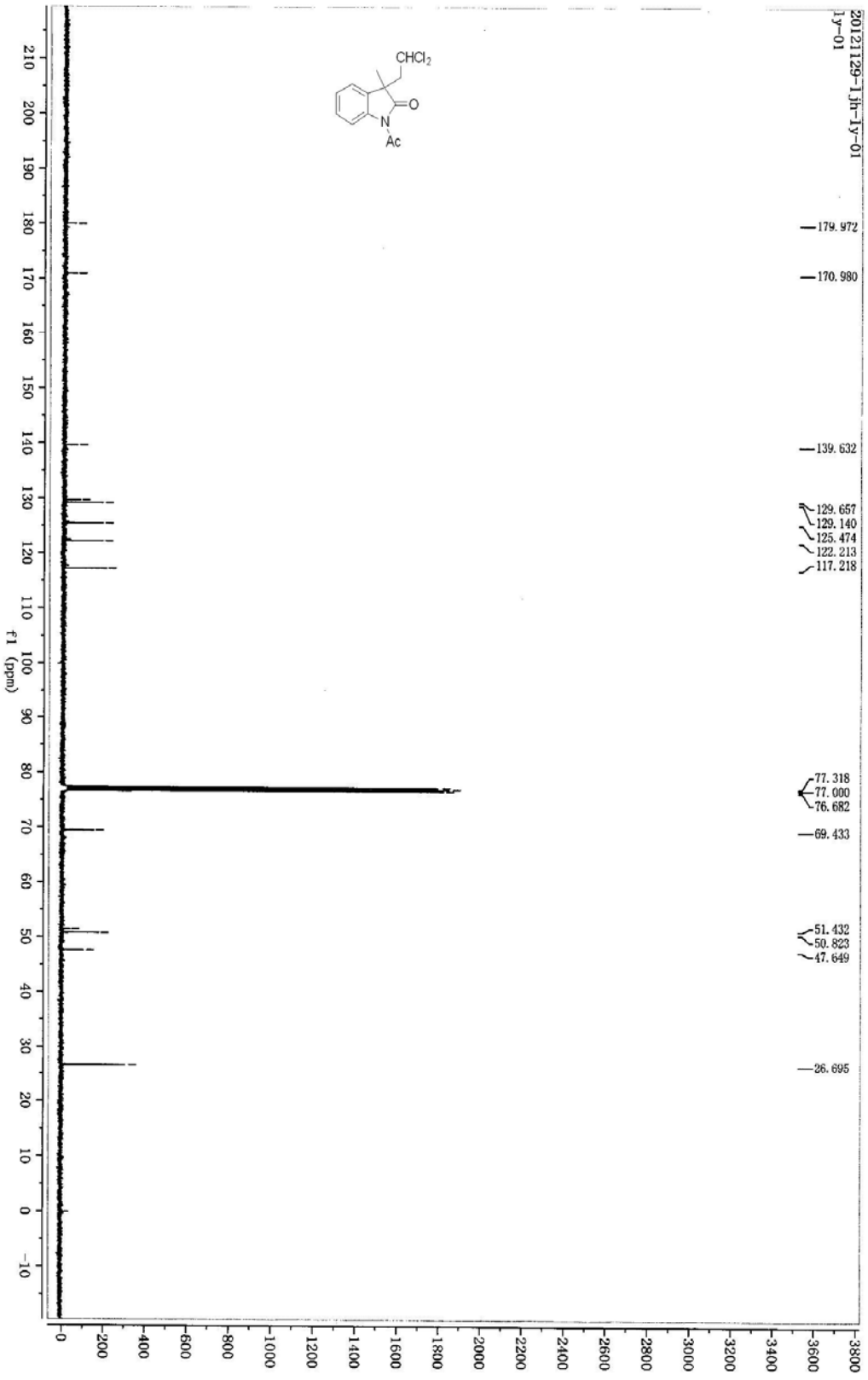
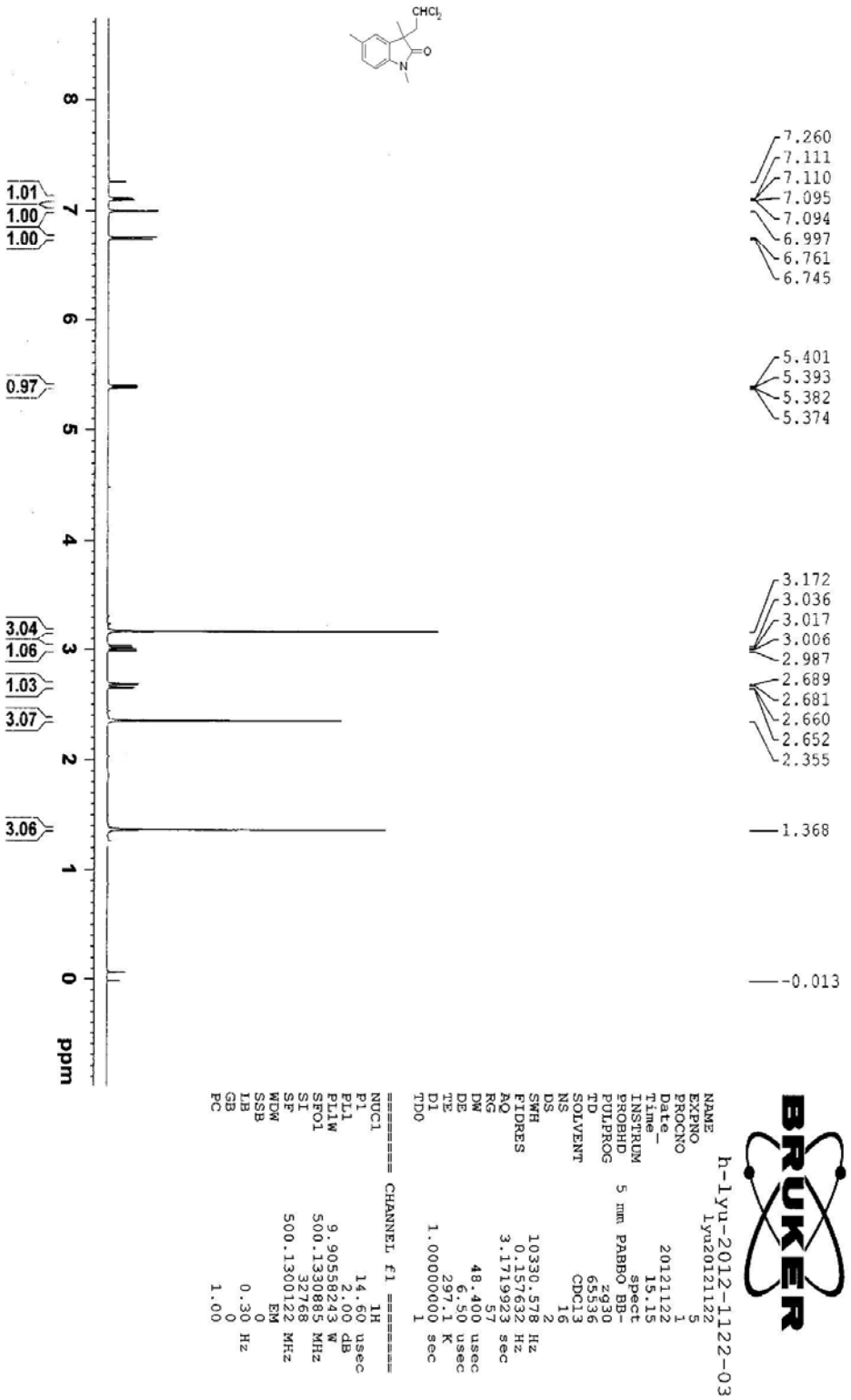
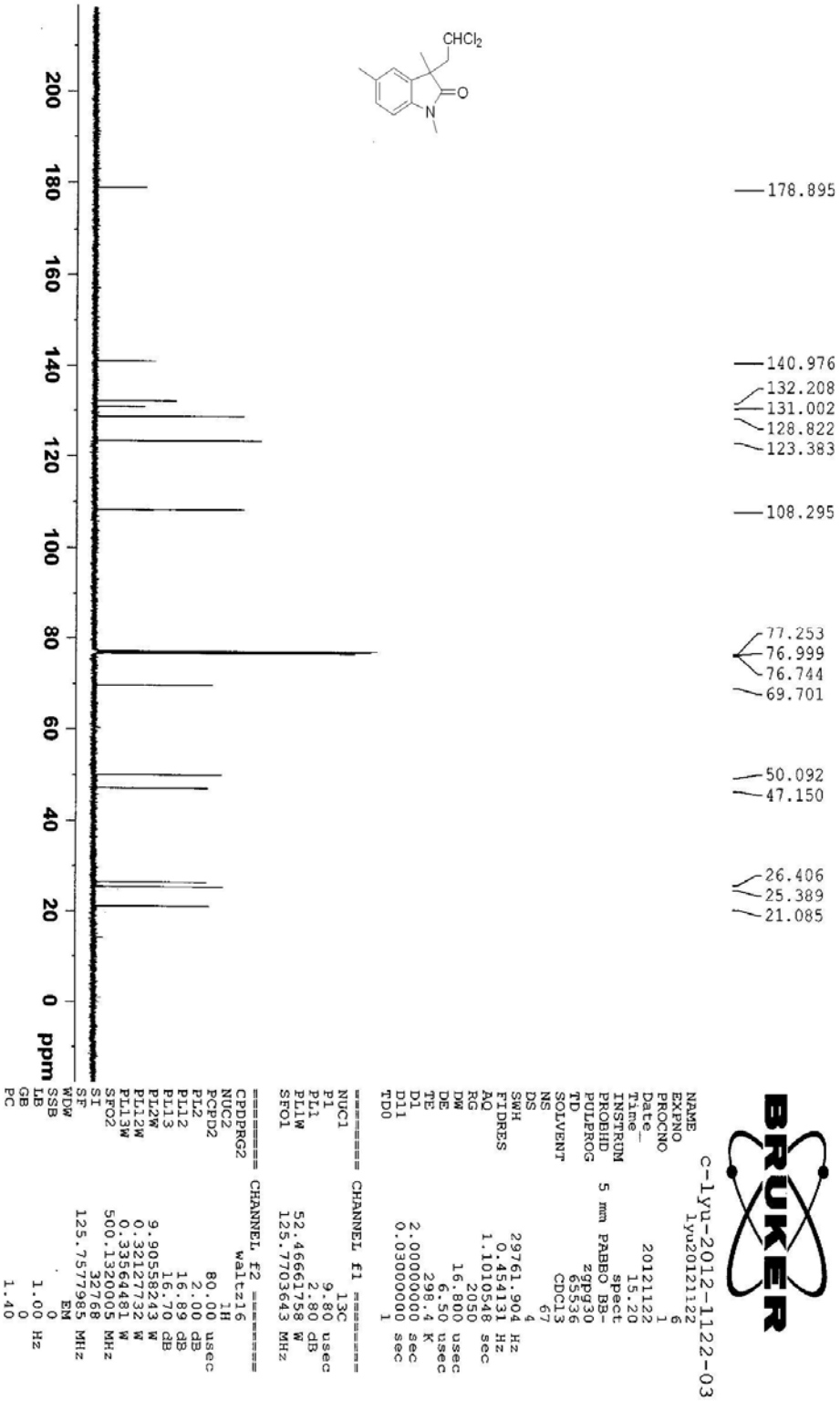


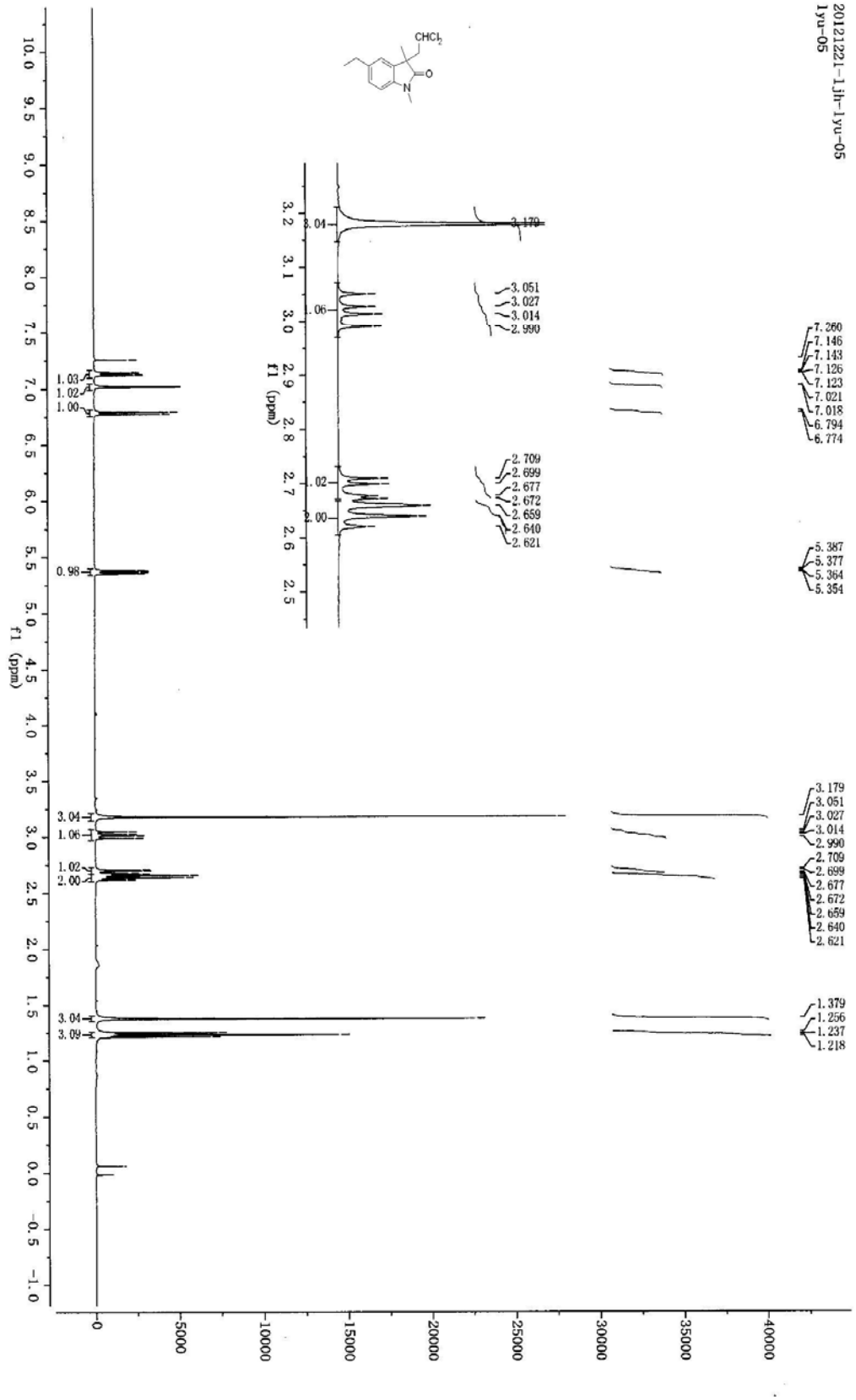
3-(2,2-Dichloroethyl)-1,3,5-trimethylindolin-2-one (3fa)



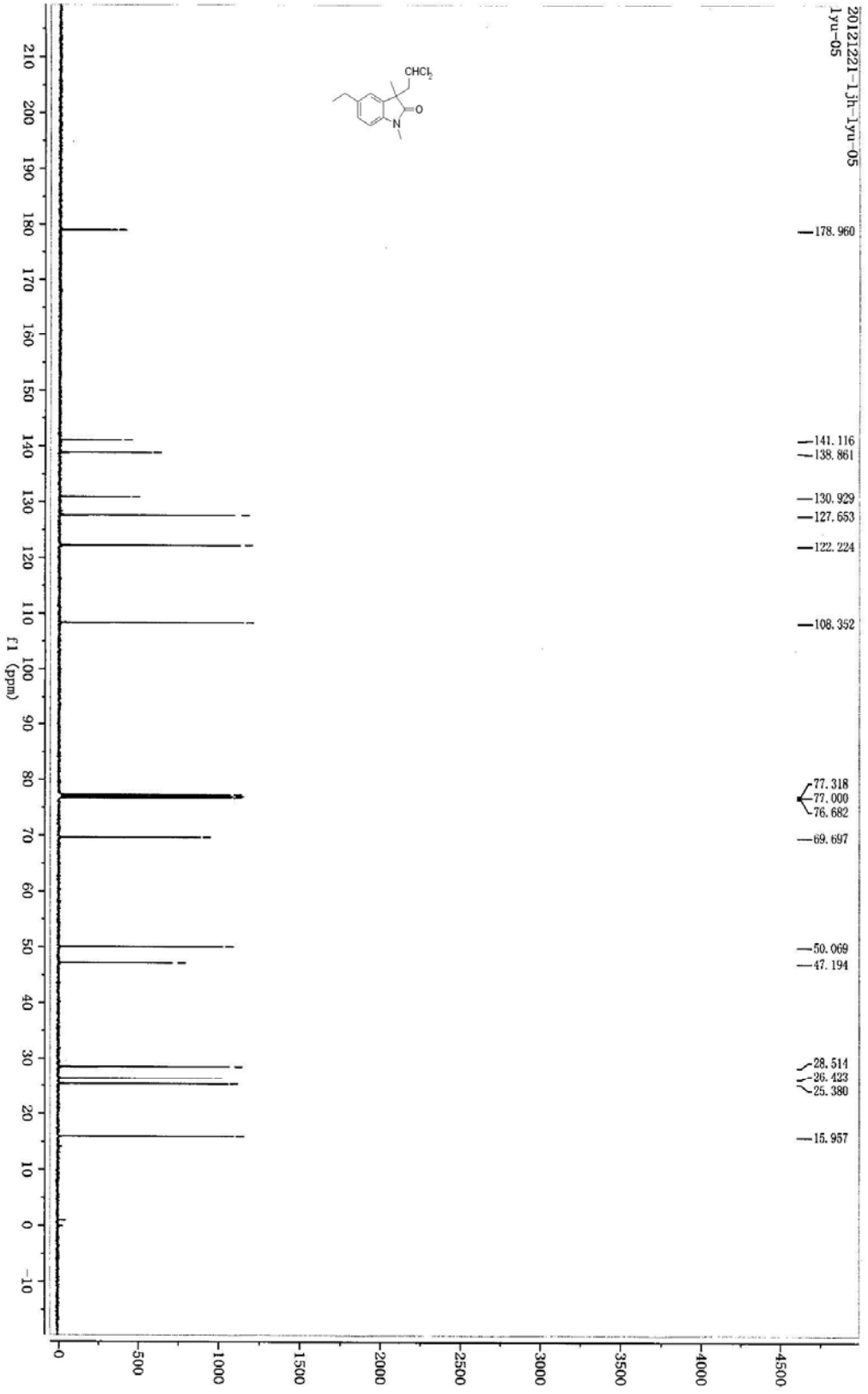
3-(2,2-Dichloroethyl)-1,3,5-trimethylindolin-2-one (3fa)



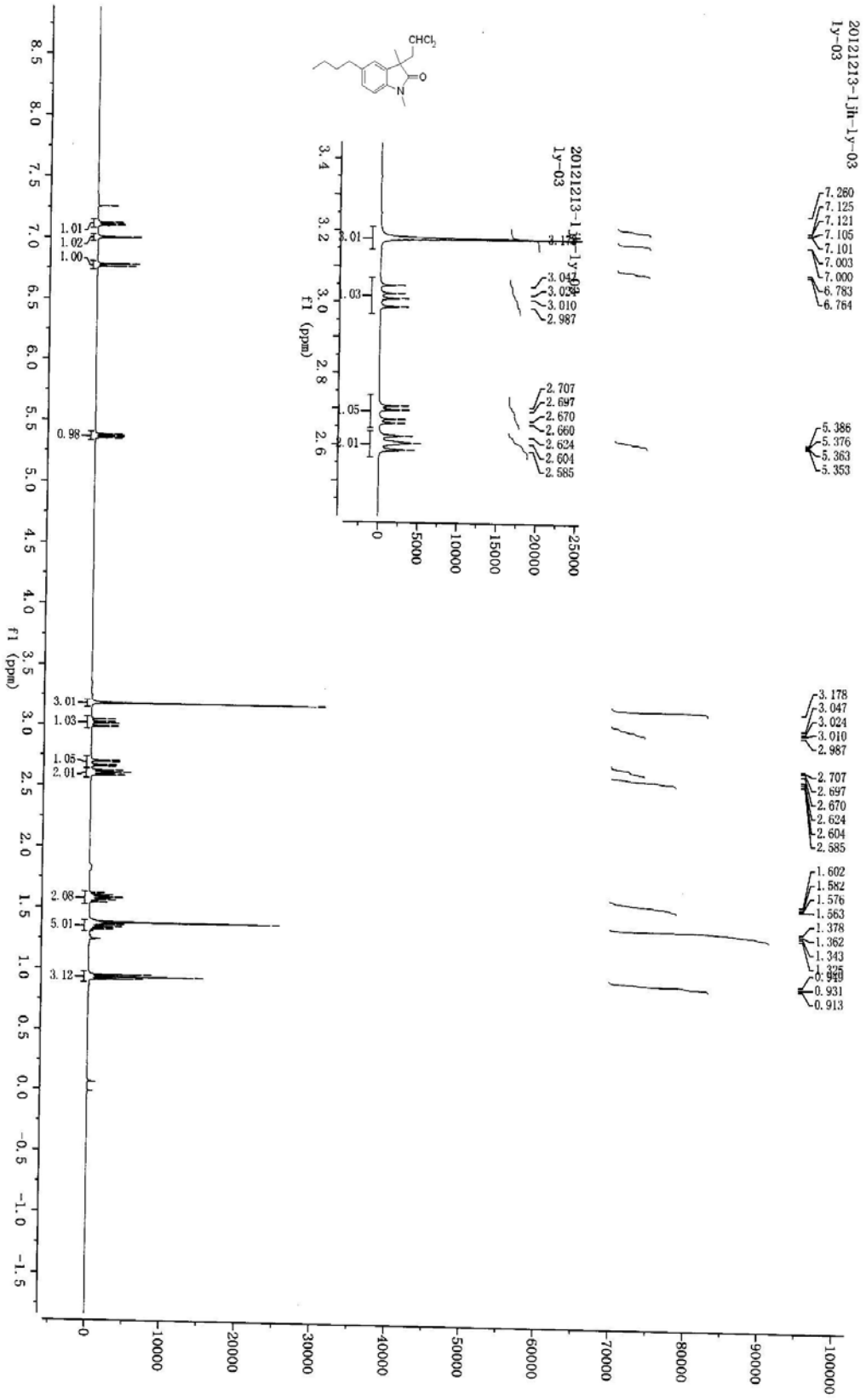
3-(2,2-Dichloroethyl)-5-ethyl-1,3-dimethylindolin-2-one (3ga)



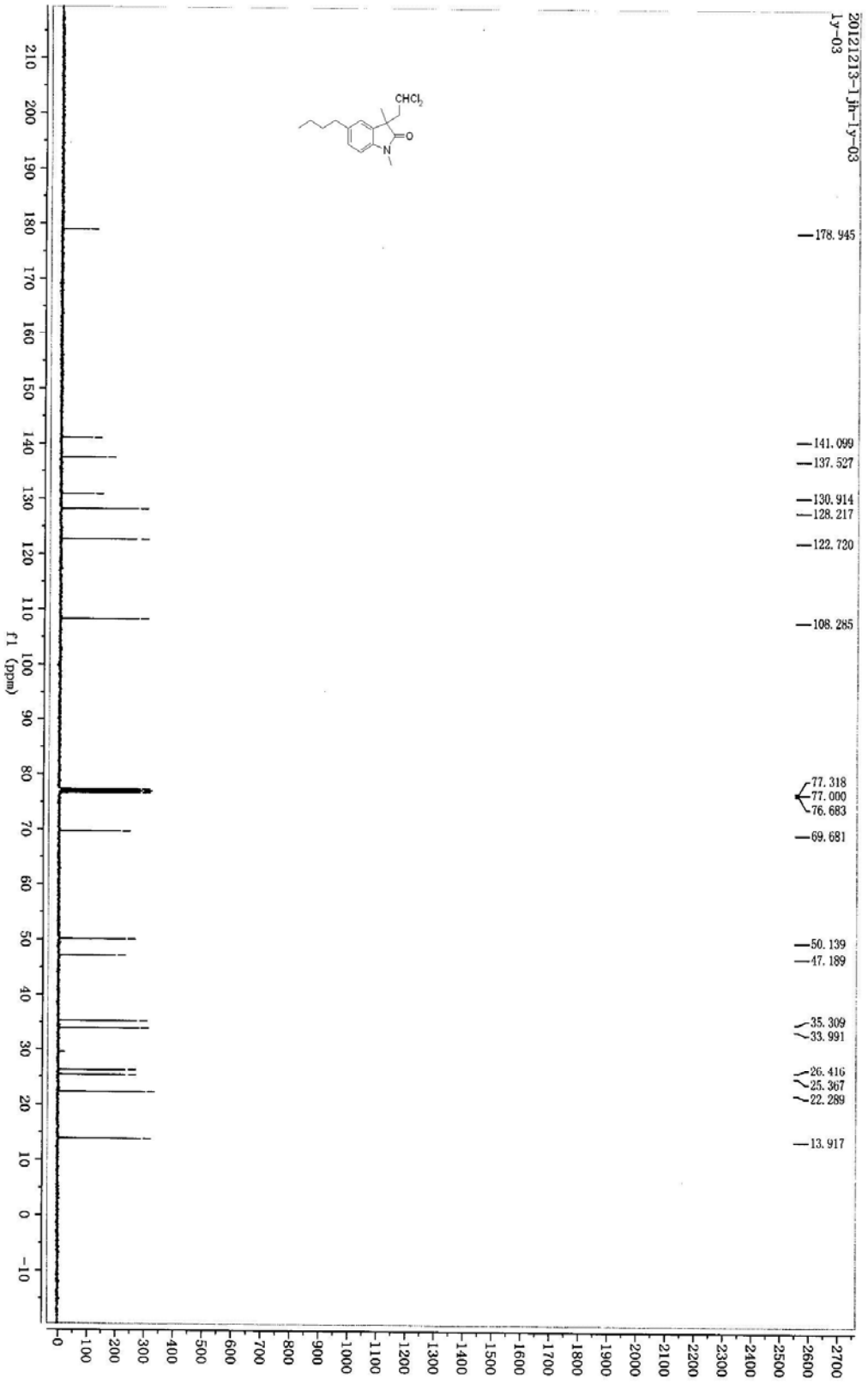
3-(2,2-Dichloroethyl)-5-ethyl-1,3-dimethylindolin-2-one (3ga)



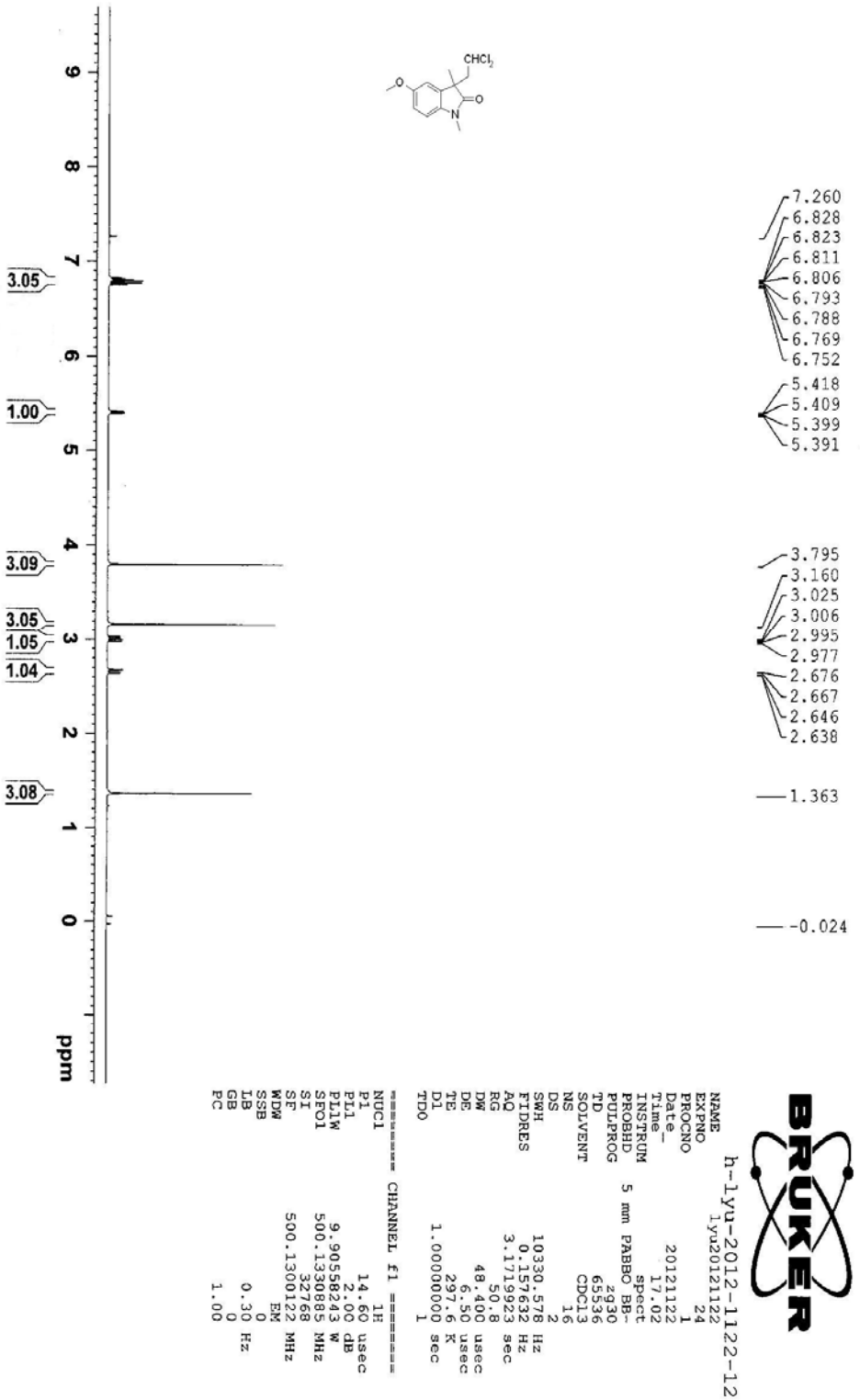
5-Butyl-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ha)



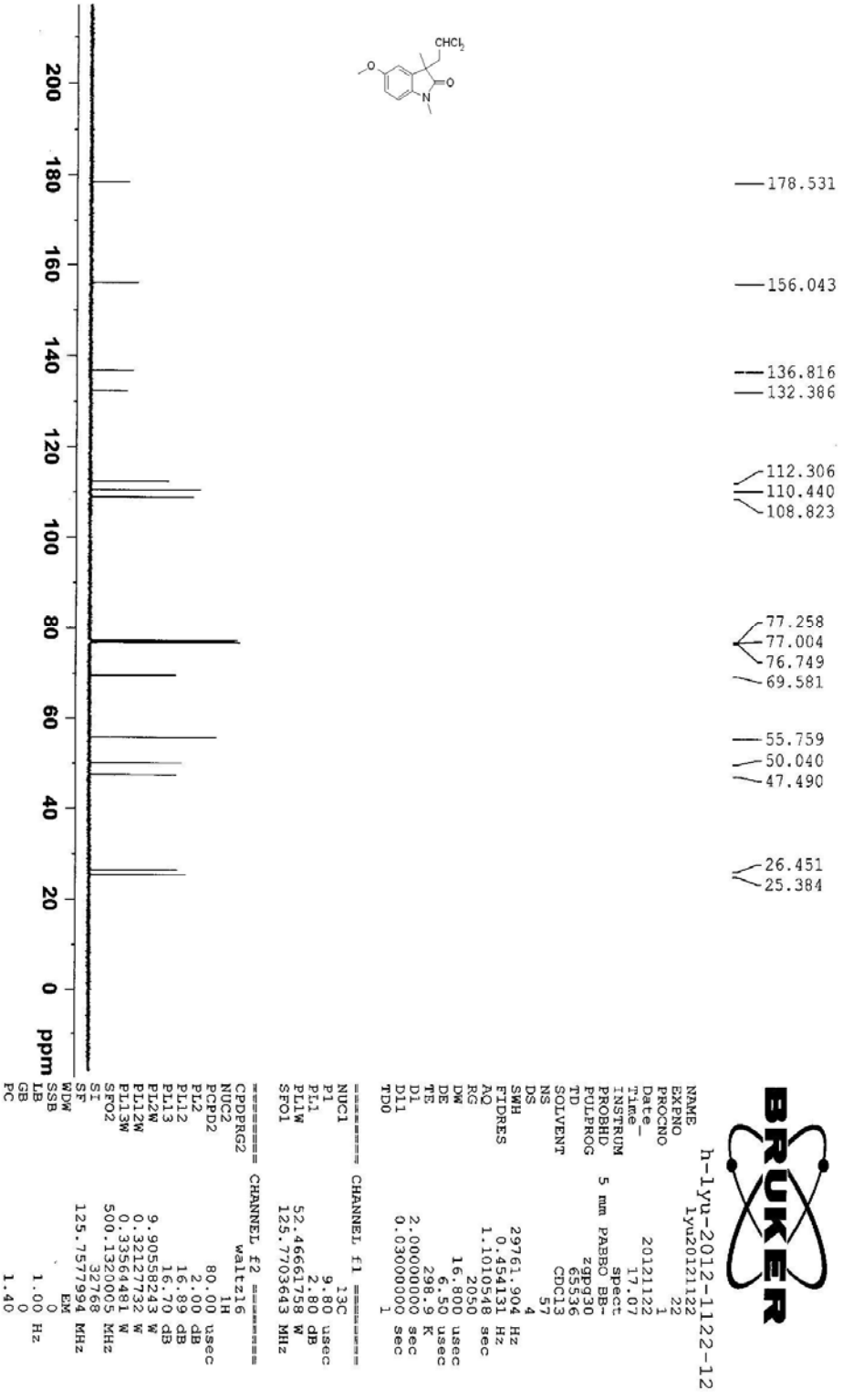
5-Butyl-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ha)



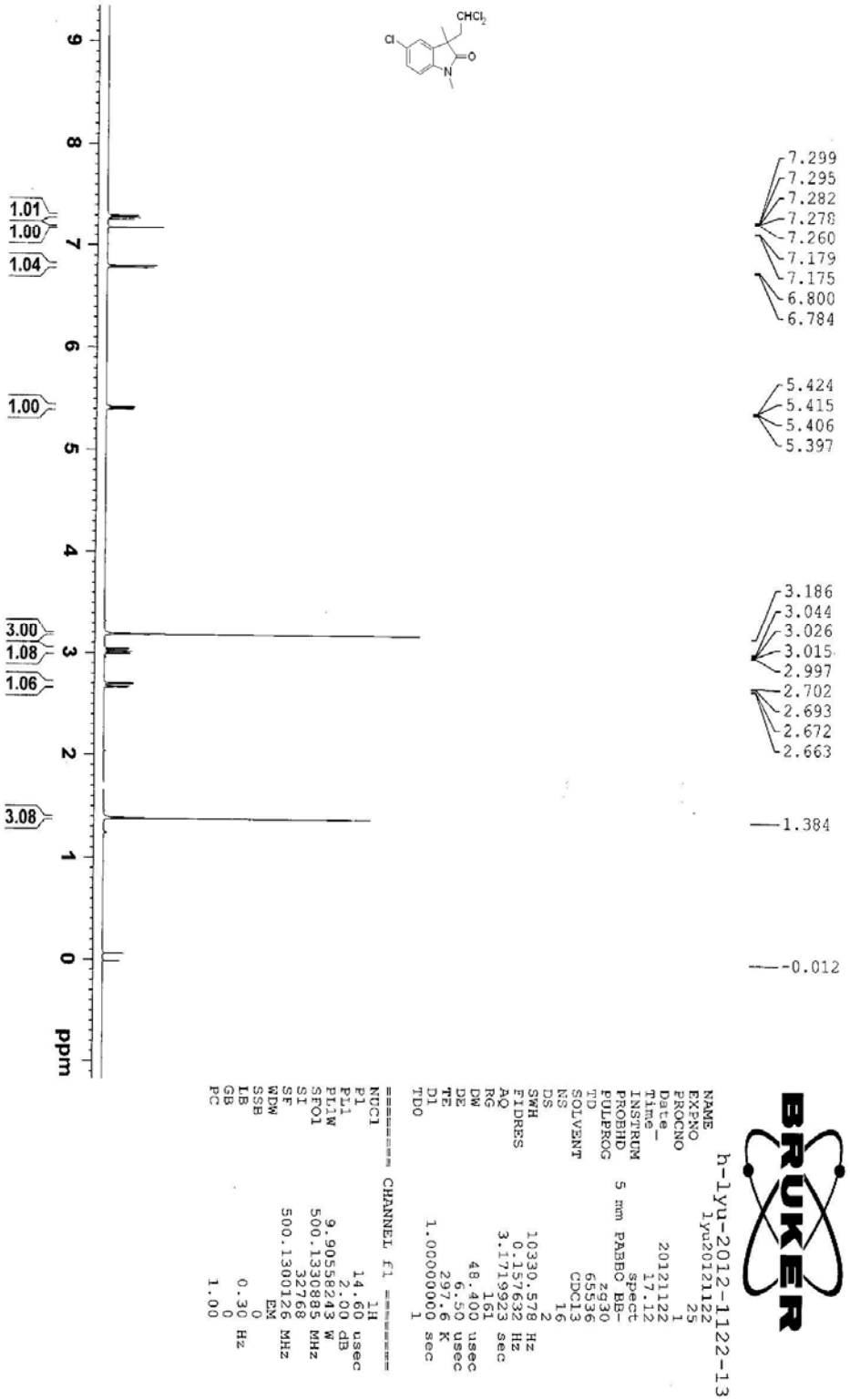
3-(2,2-Dichloroethyl)-5-methoxy-1,3-dimethylindolin-2-one (3ia)



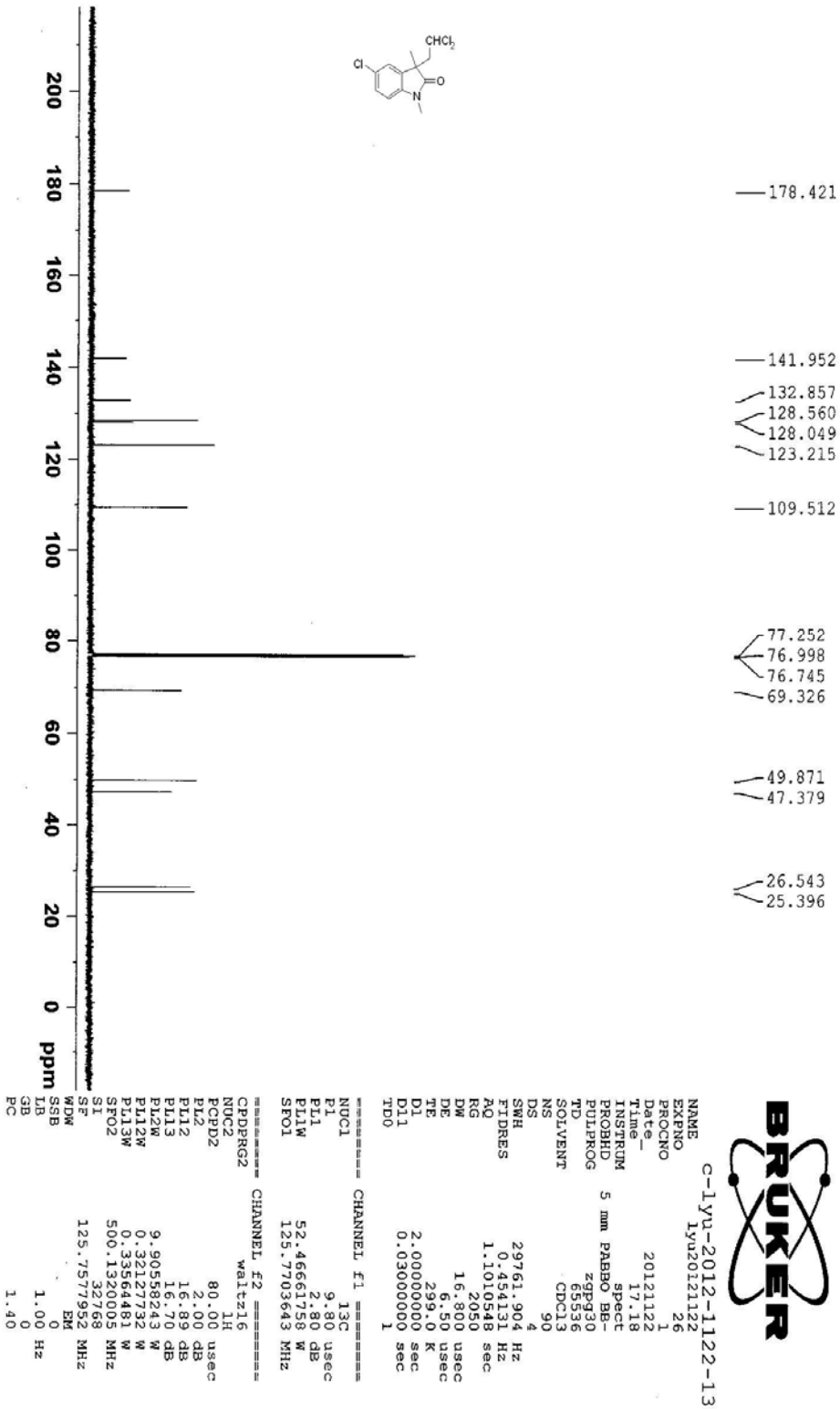
3-(2,2-Dichloroethyl)-5-methoxy-1,3-dimethylindolin-2-one (3ia)



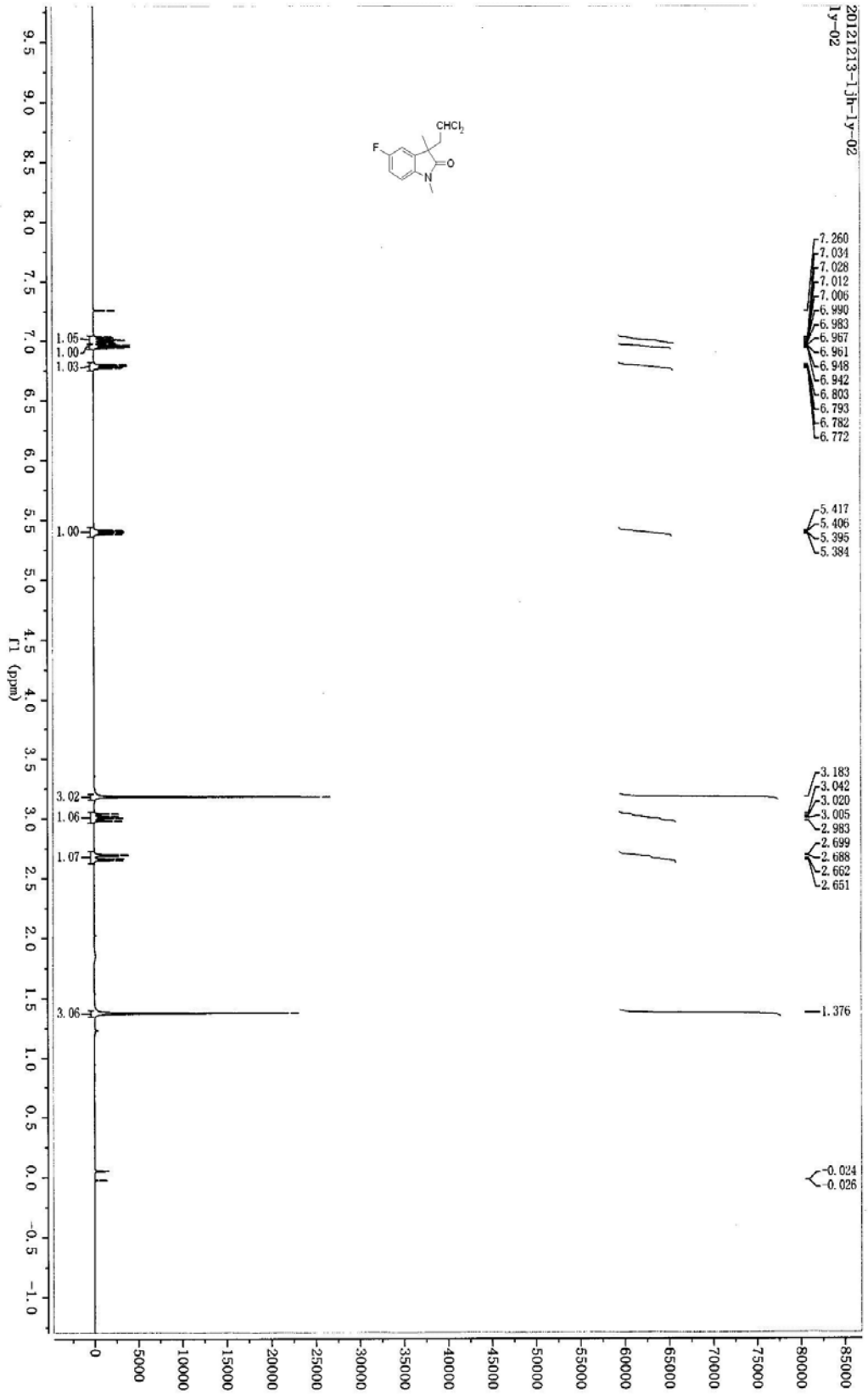
5-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ja)



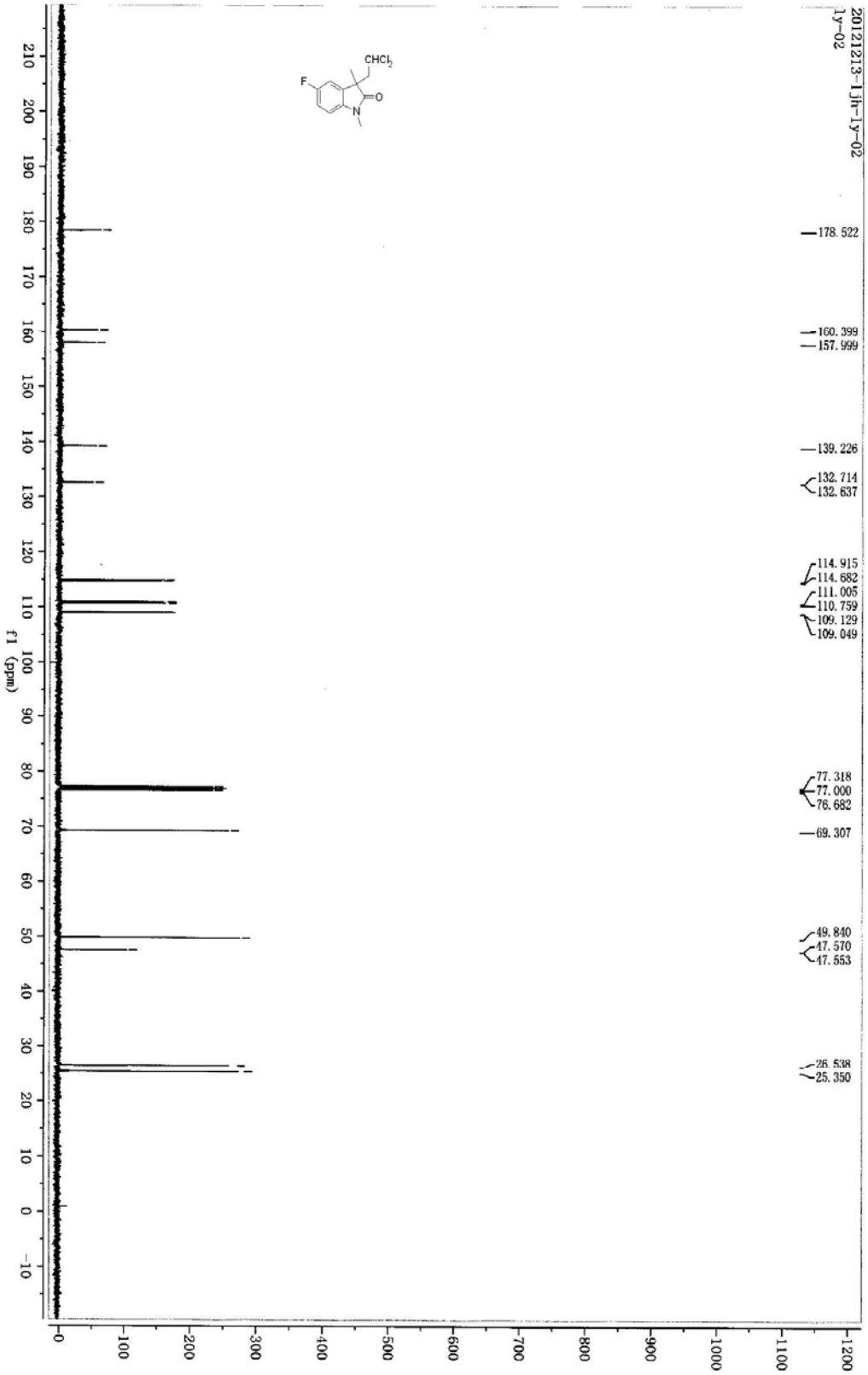
5-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ja)



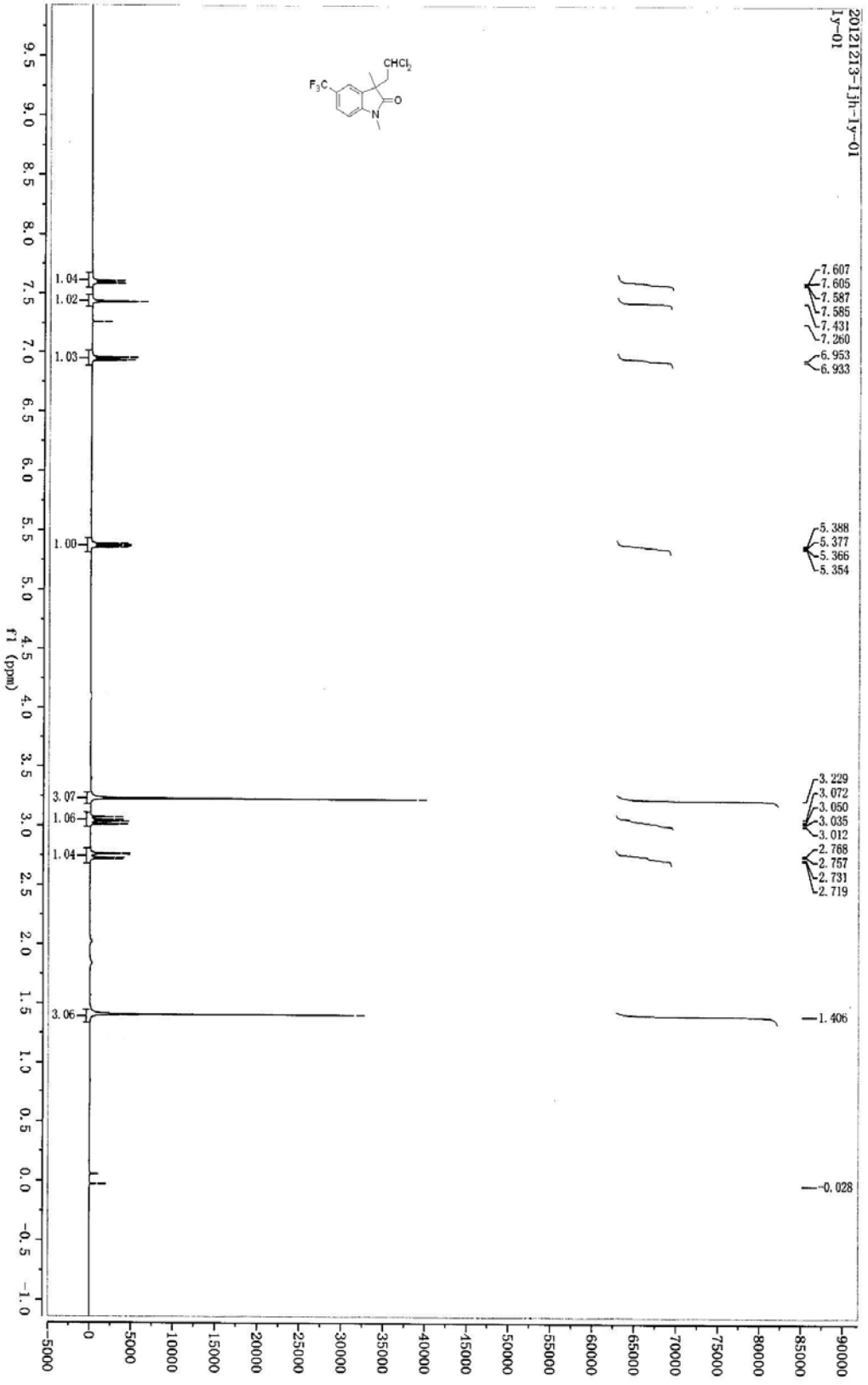
3-(2,2-Dichloroethyl)-5-fluoro-1,3-dimethylindolin-2-one (3ka)



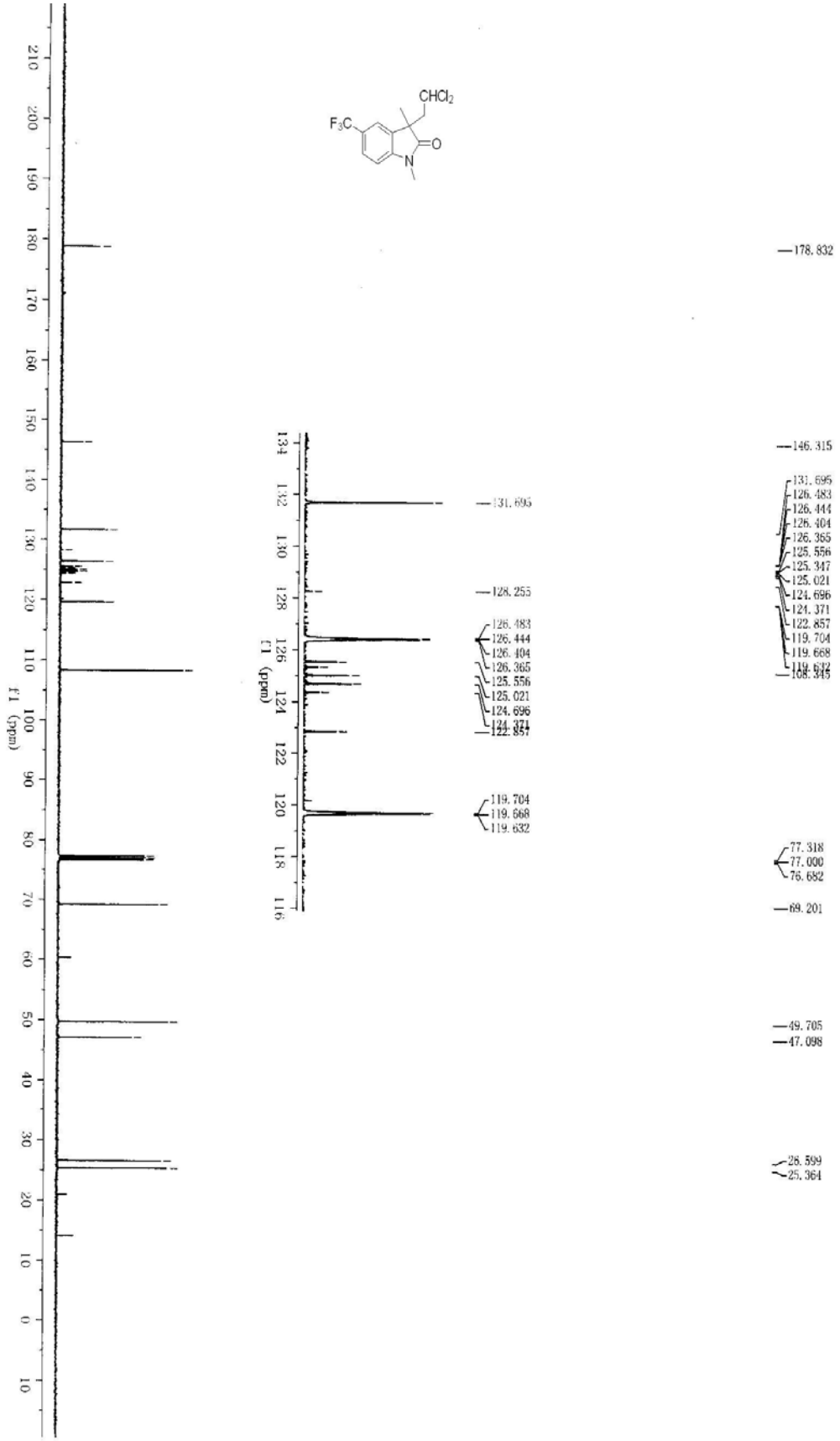
3-(2,2-Dichloroethyl)-5-fluoro-1,3-dimethylindolin-2-one (3ka)



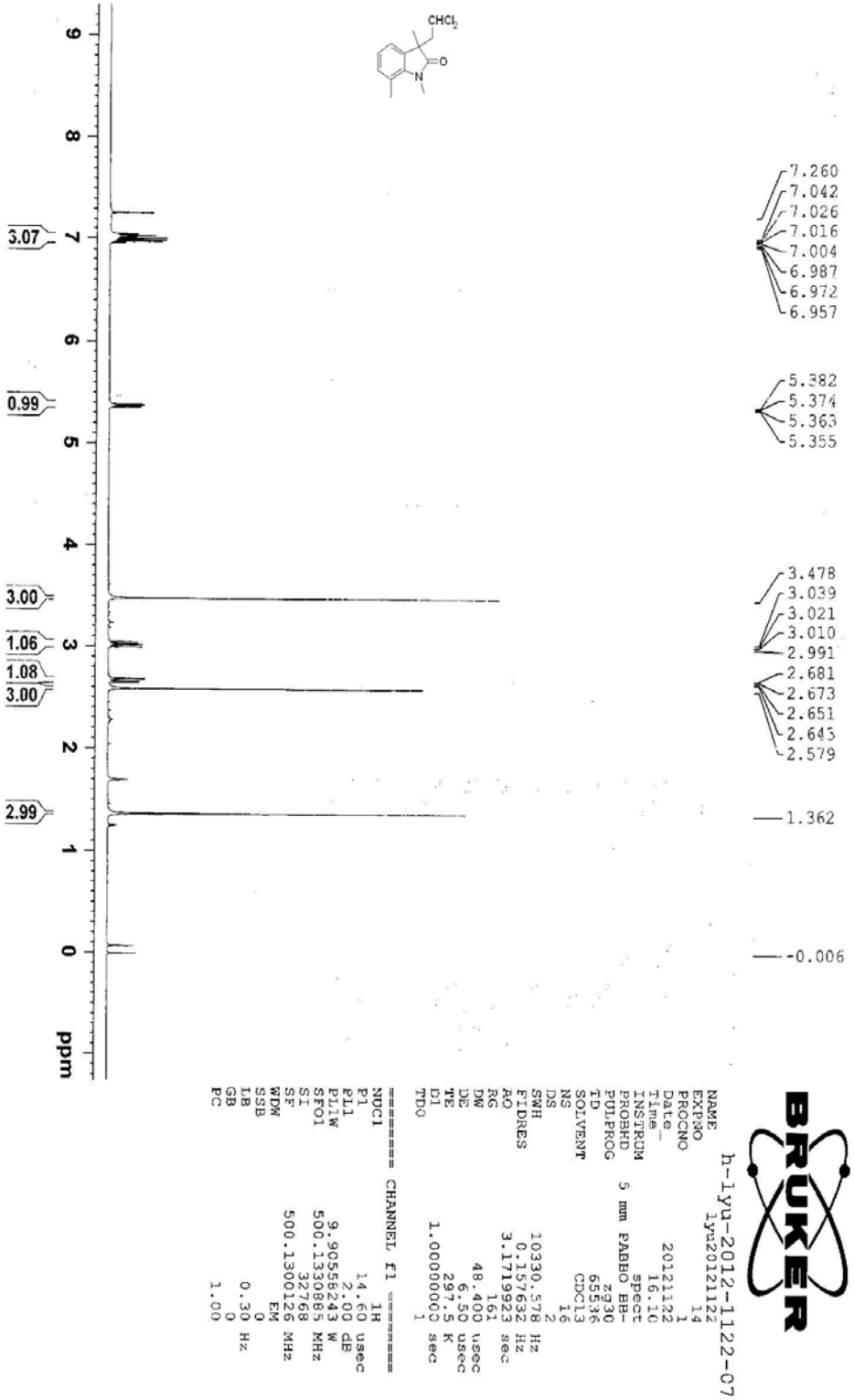
3-(2,2-Dichloroethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3la)



3-(2,2-Dichloroethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3la)



3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one (3ma)



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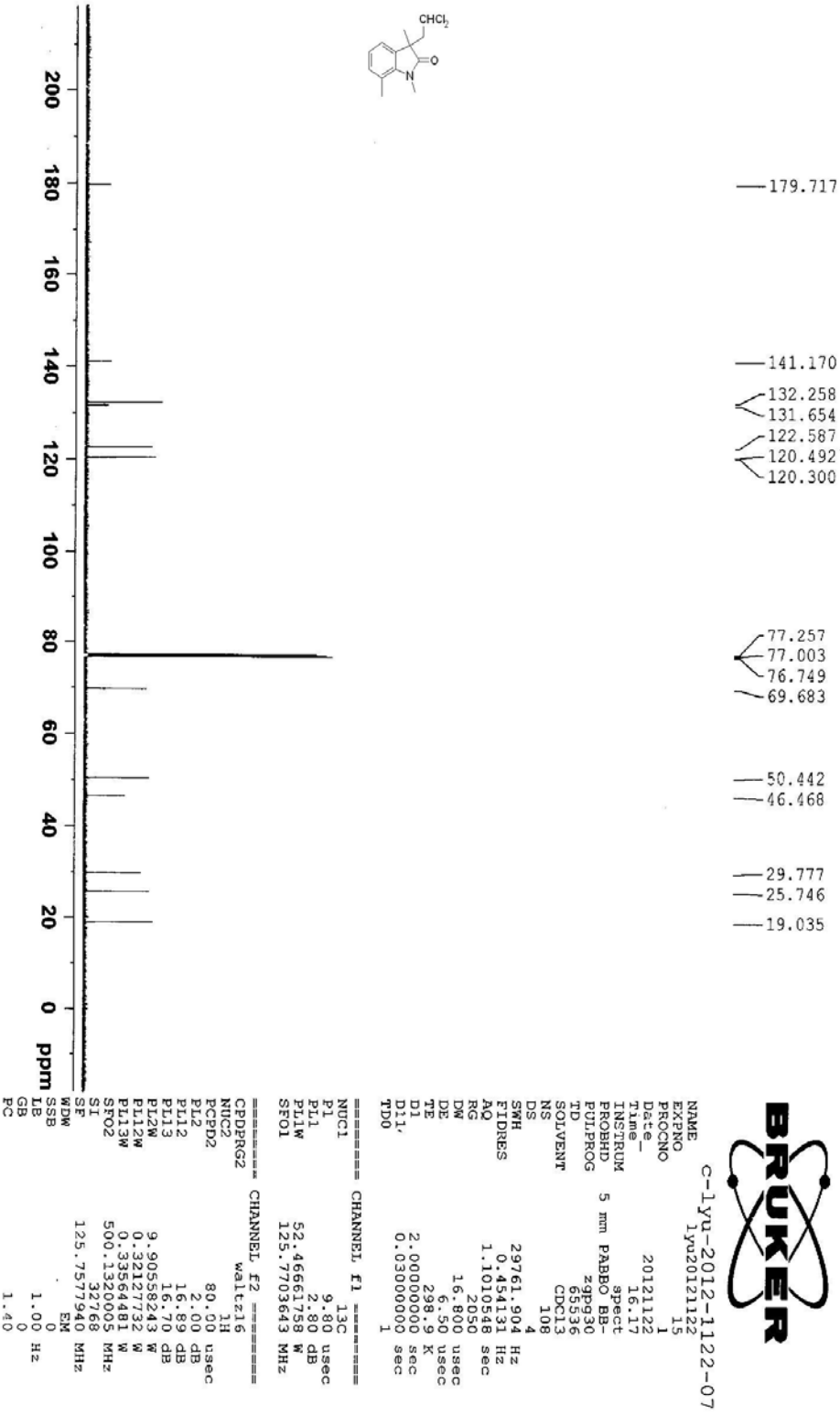
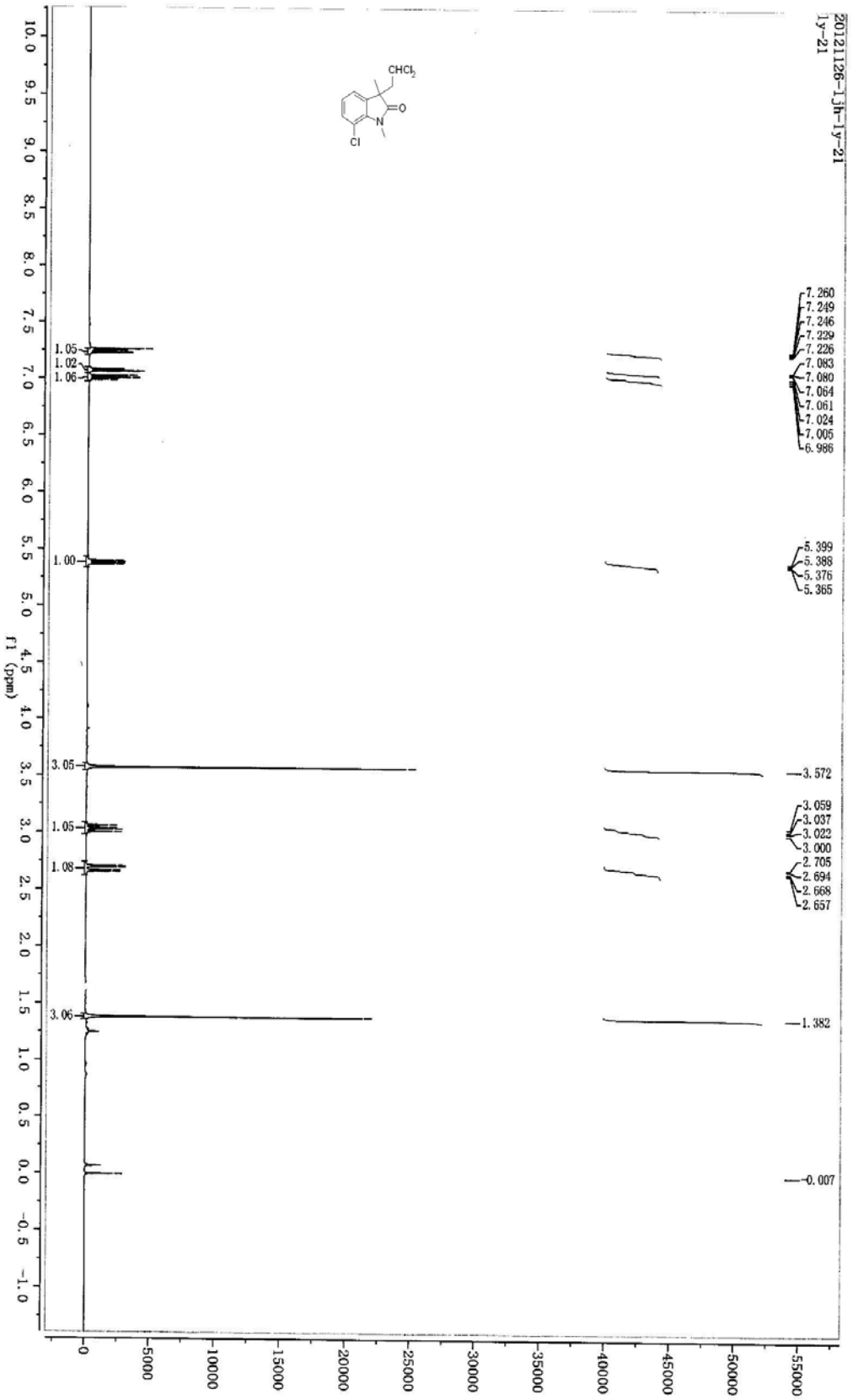
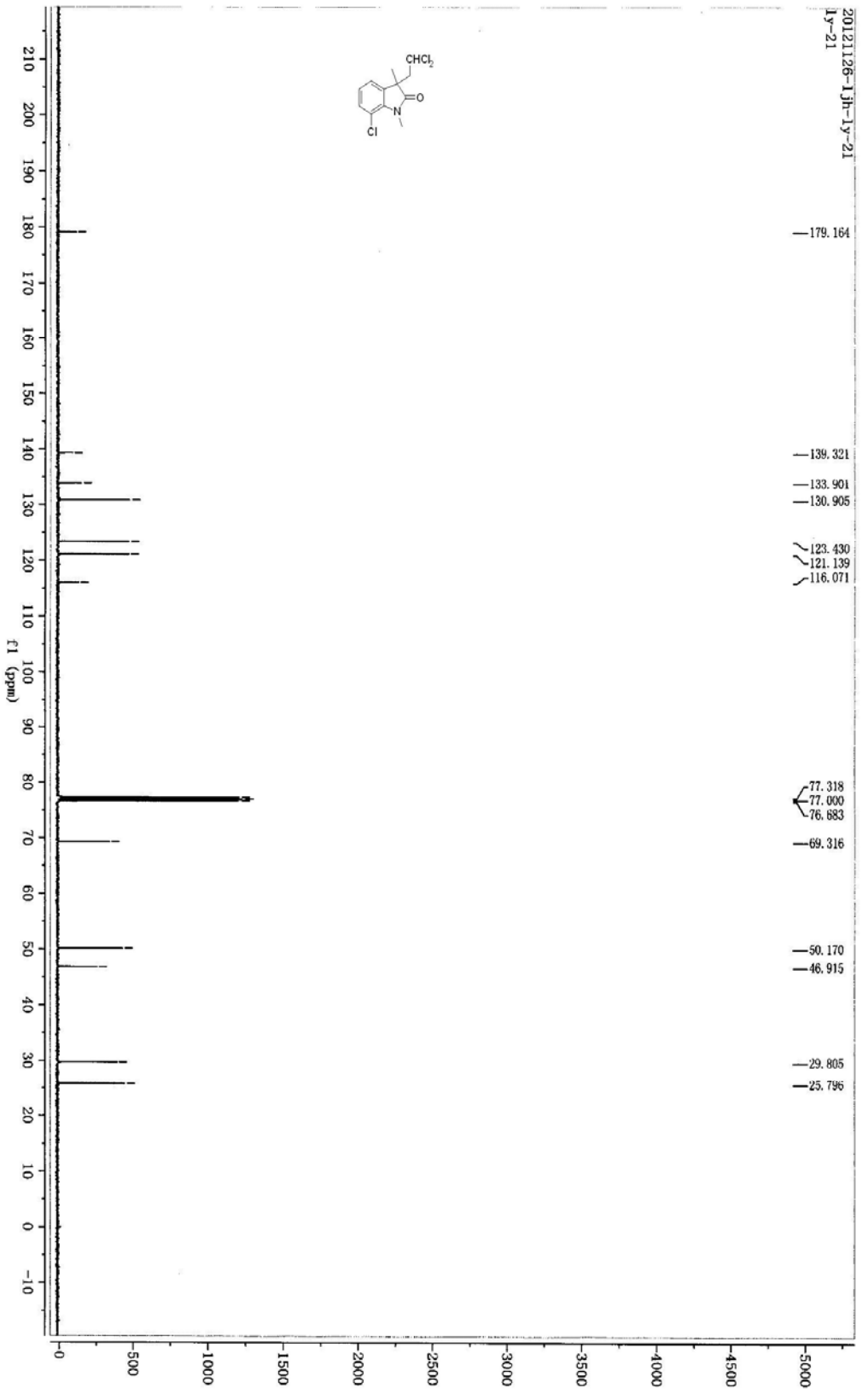


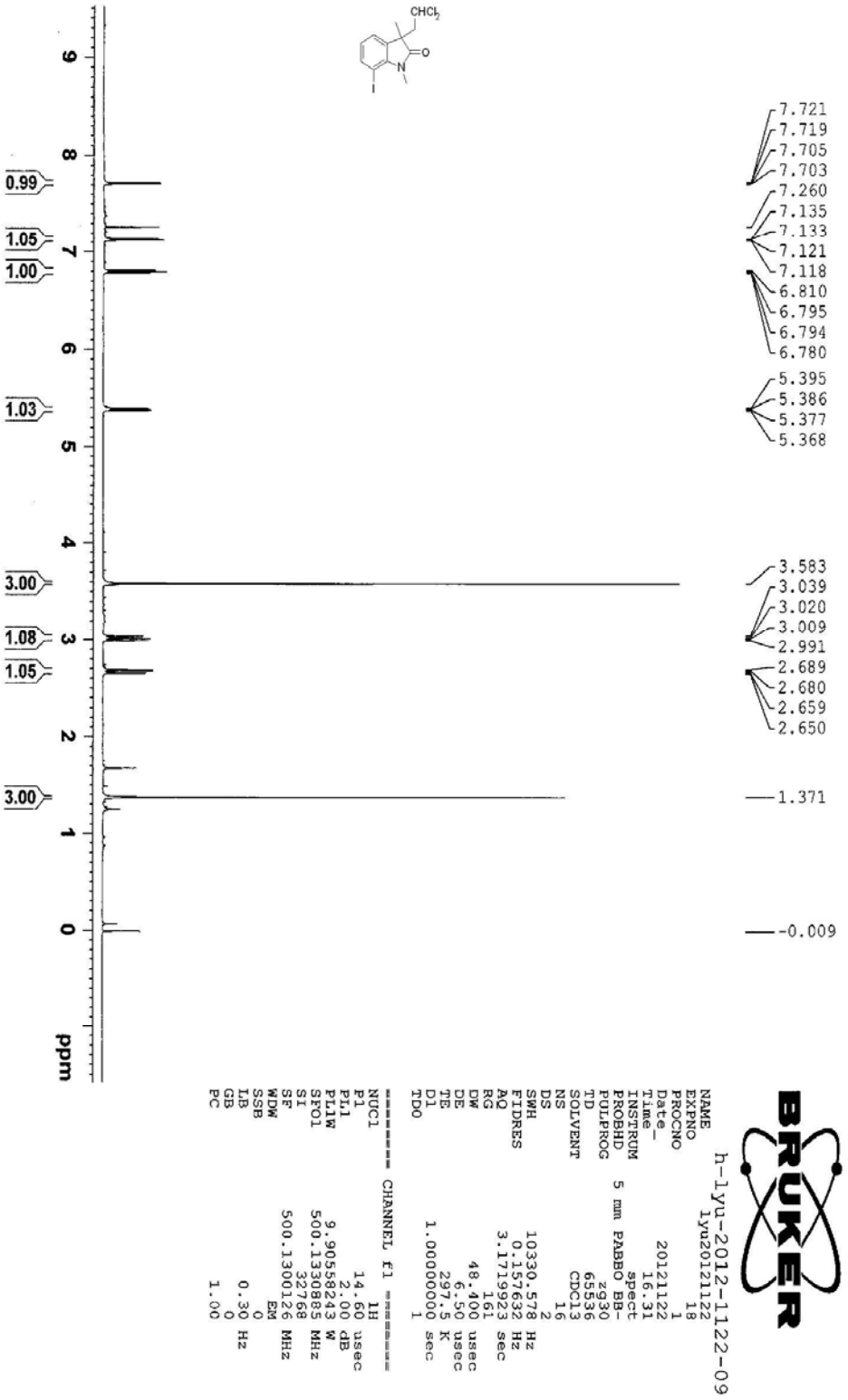
7-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3na)



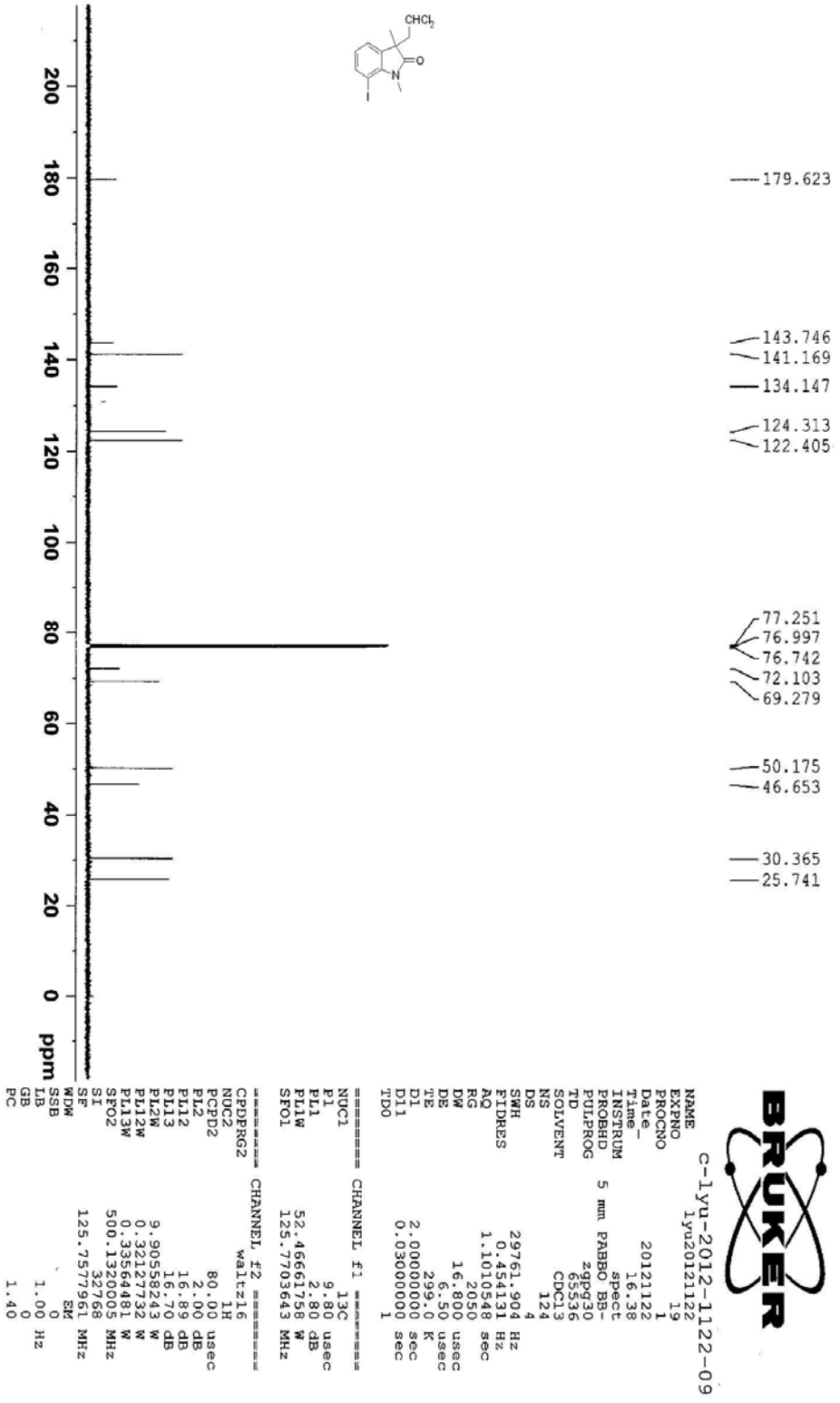
7-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3na)



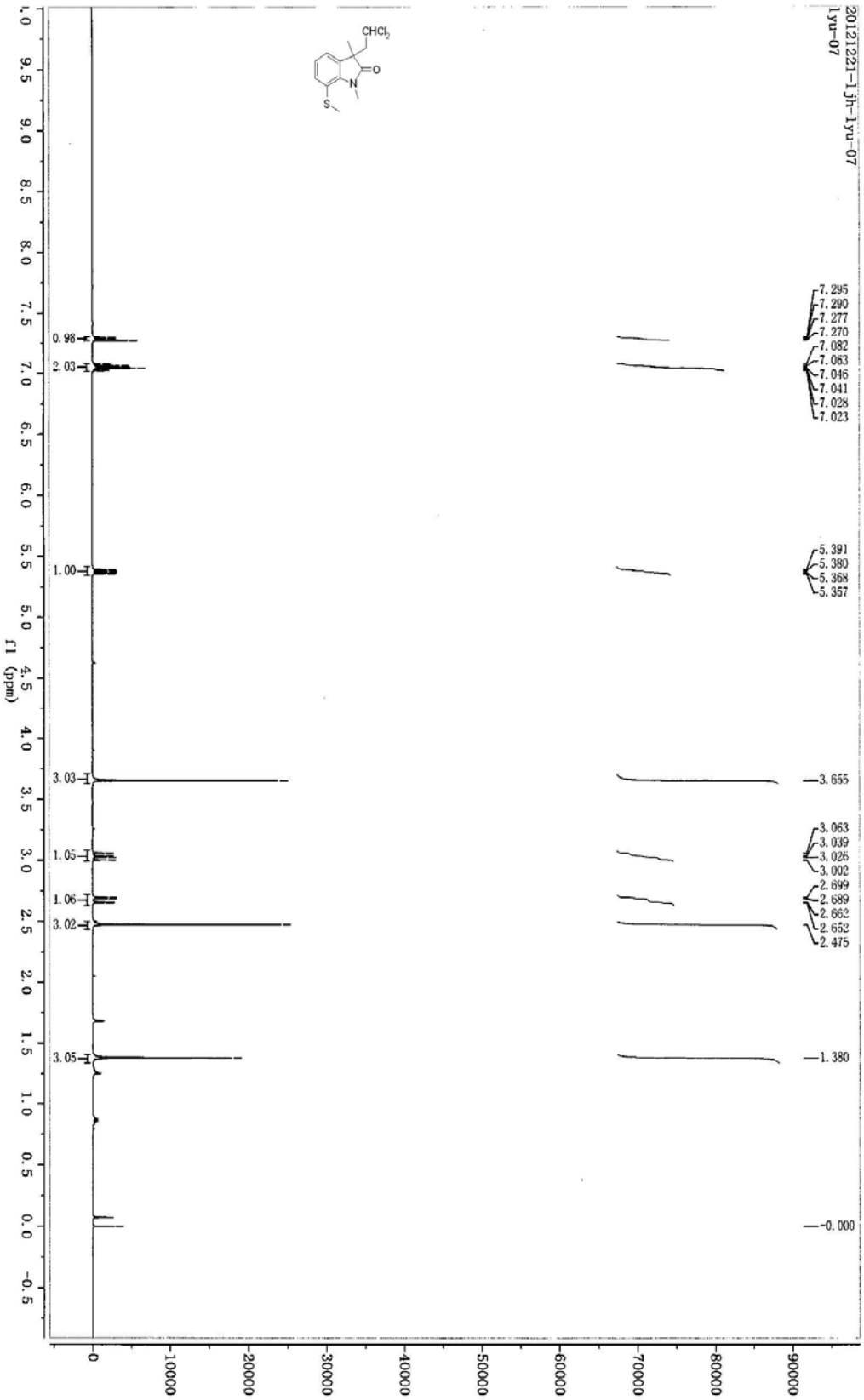
3-(2,2-Dichloroethyl)-7-iodo-1,3-dimethylindolin-2-one (3oa)



3-(2,2-Dichloroethyl)-7-iodo-1,3-dimethylindolin-2-one (3oa)



3-(2,2-Dichloroethyl)-1,3-dimethyl-7-(methylthio)indolin-2-one (3pa)



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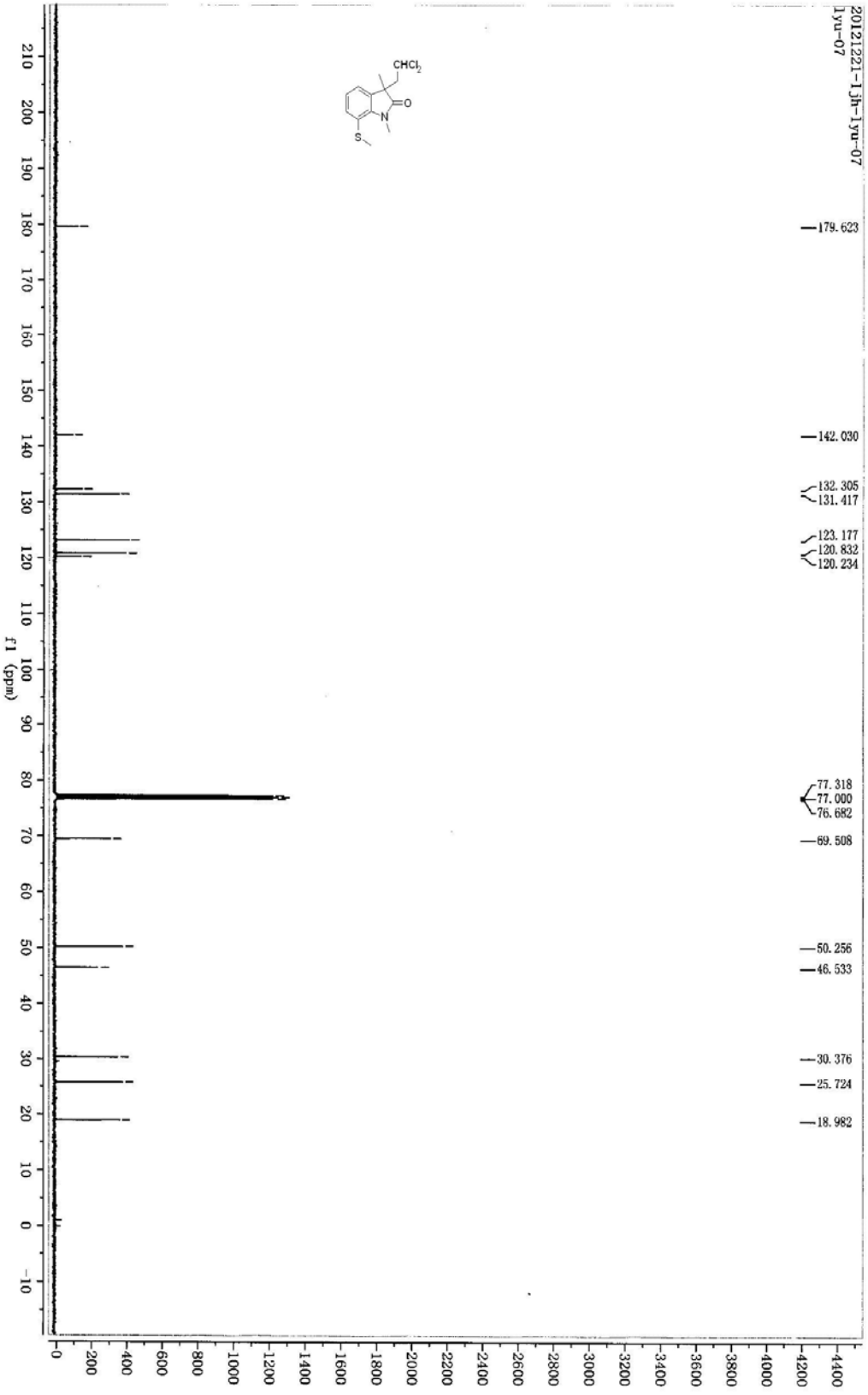
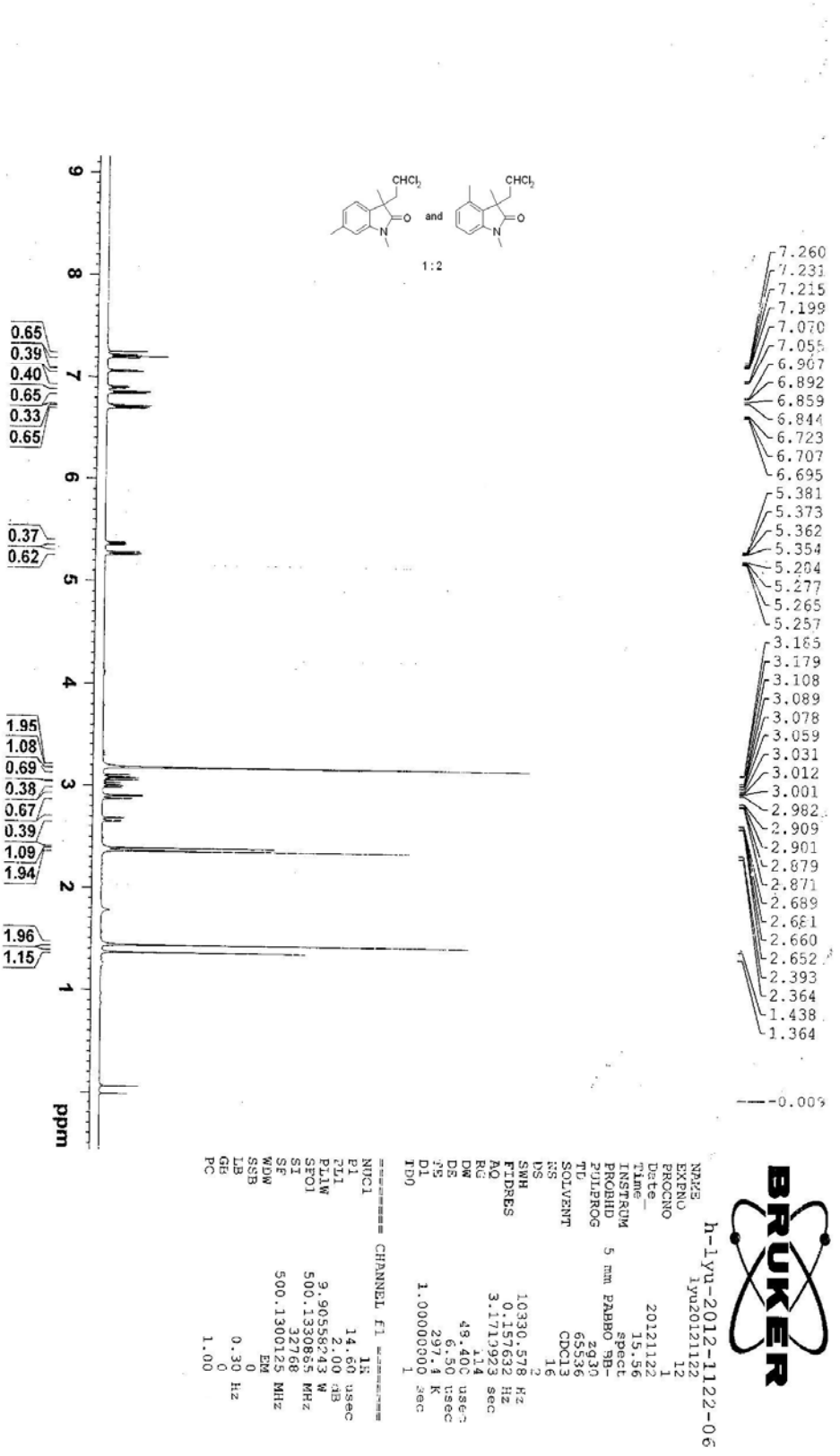
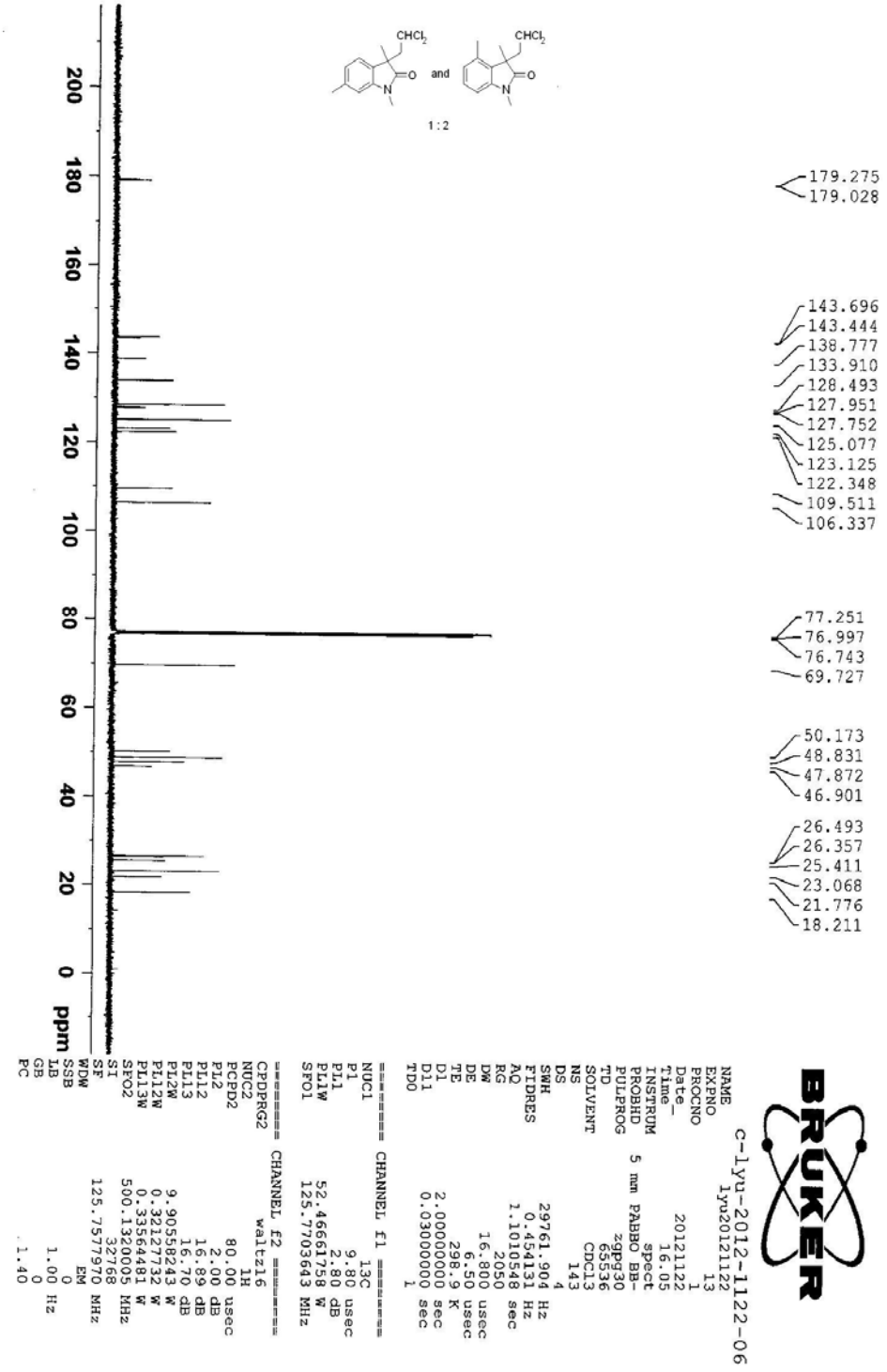


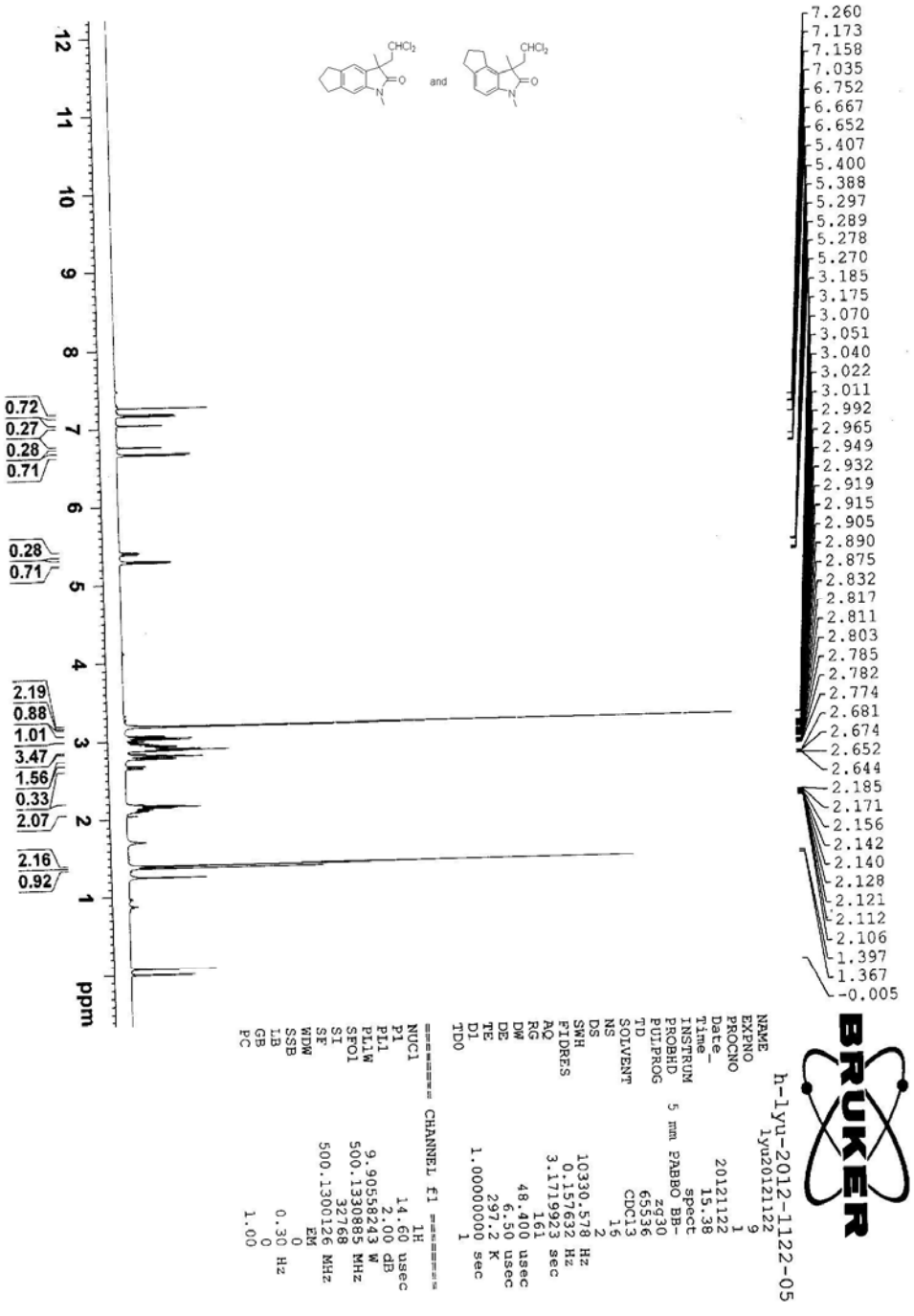
3-(2,2-Dichloroethyl)-1,3,6-trimethylindolin-2-one and 3-(2,2-dichloroethyl)-1,3,4-trimethylindolin-2-one (3qa)



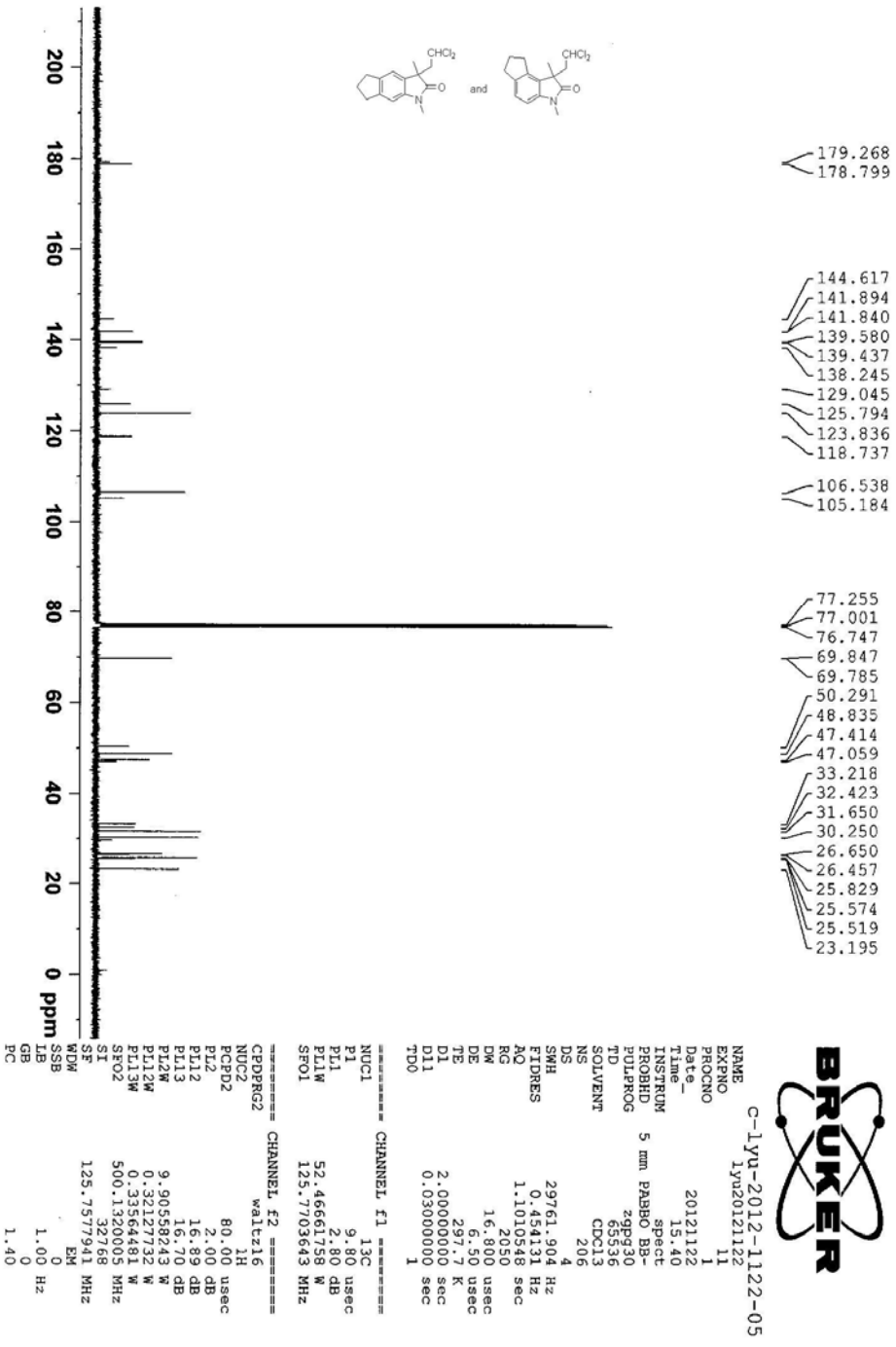
3-(2,2-Dichloroethyl)-1,3,6-trimethylindolin-2-one and 3-(2,2-dichloroethyl)-1,3,4-trimethylindolin-2-one (3qa)



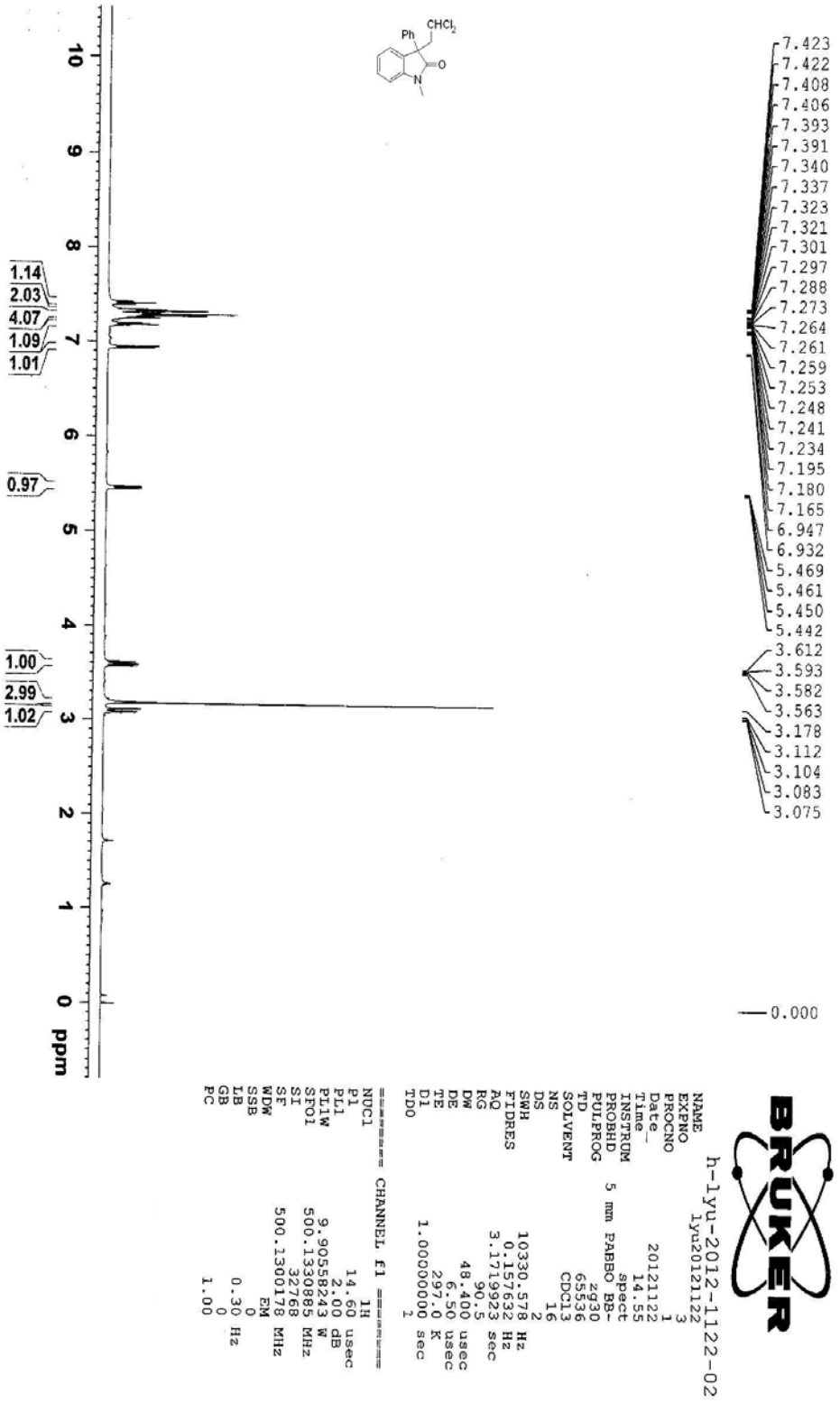
3-(2,2-Dichloroethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[f]indol-2(*1H*)-one and 1-(2,2-dichloroethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[e]indol-2(*1H*)-one (3ra):



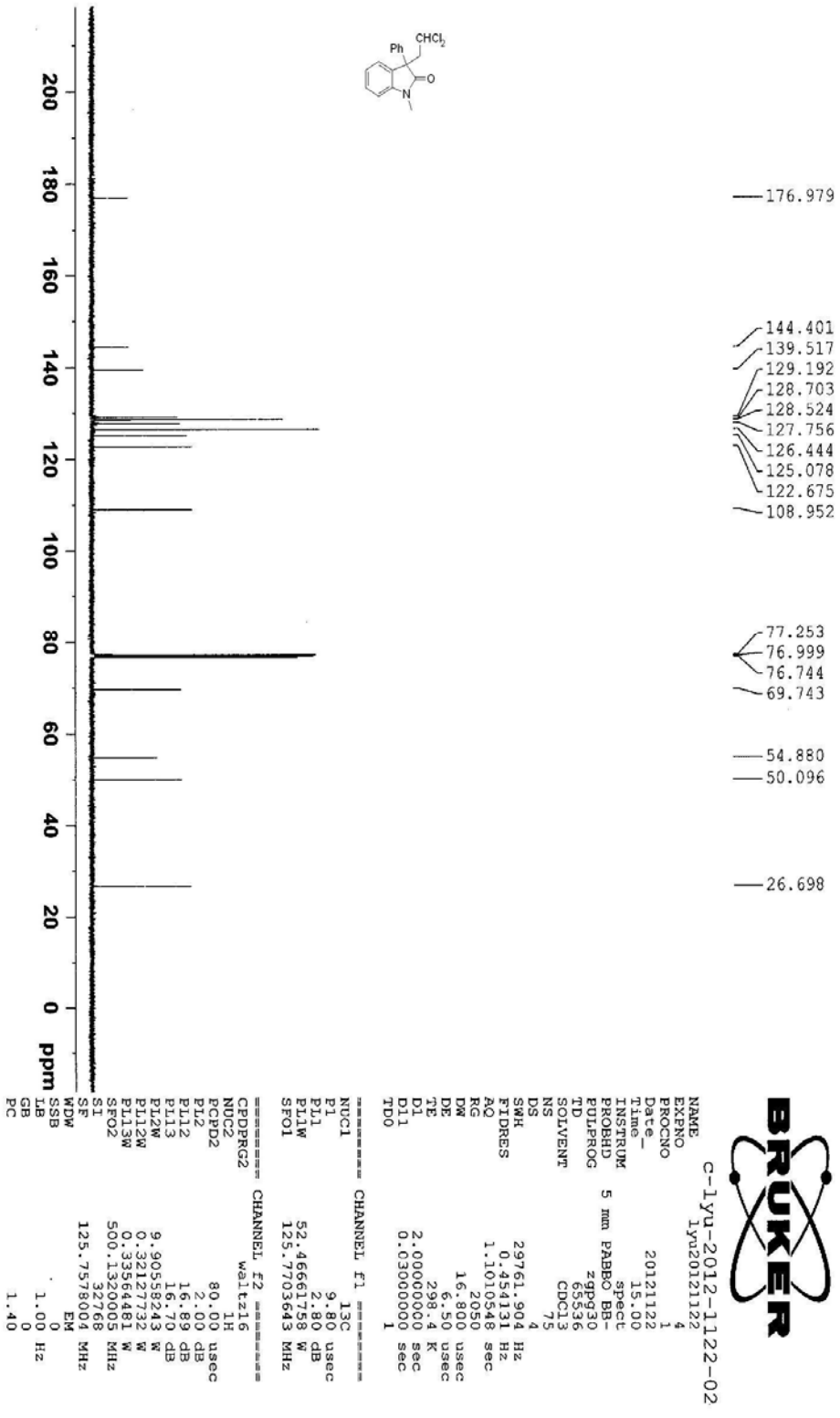
3-(2,2-Dichloroethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[f]indol-2(*1H*)-one and 1-(2,2-dichloroethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[e]indol-2(*1H*)-one (3ra):



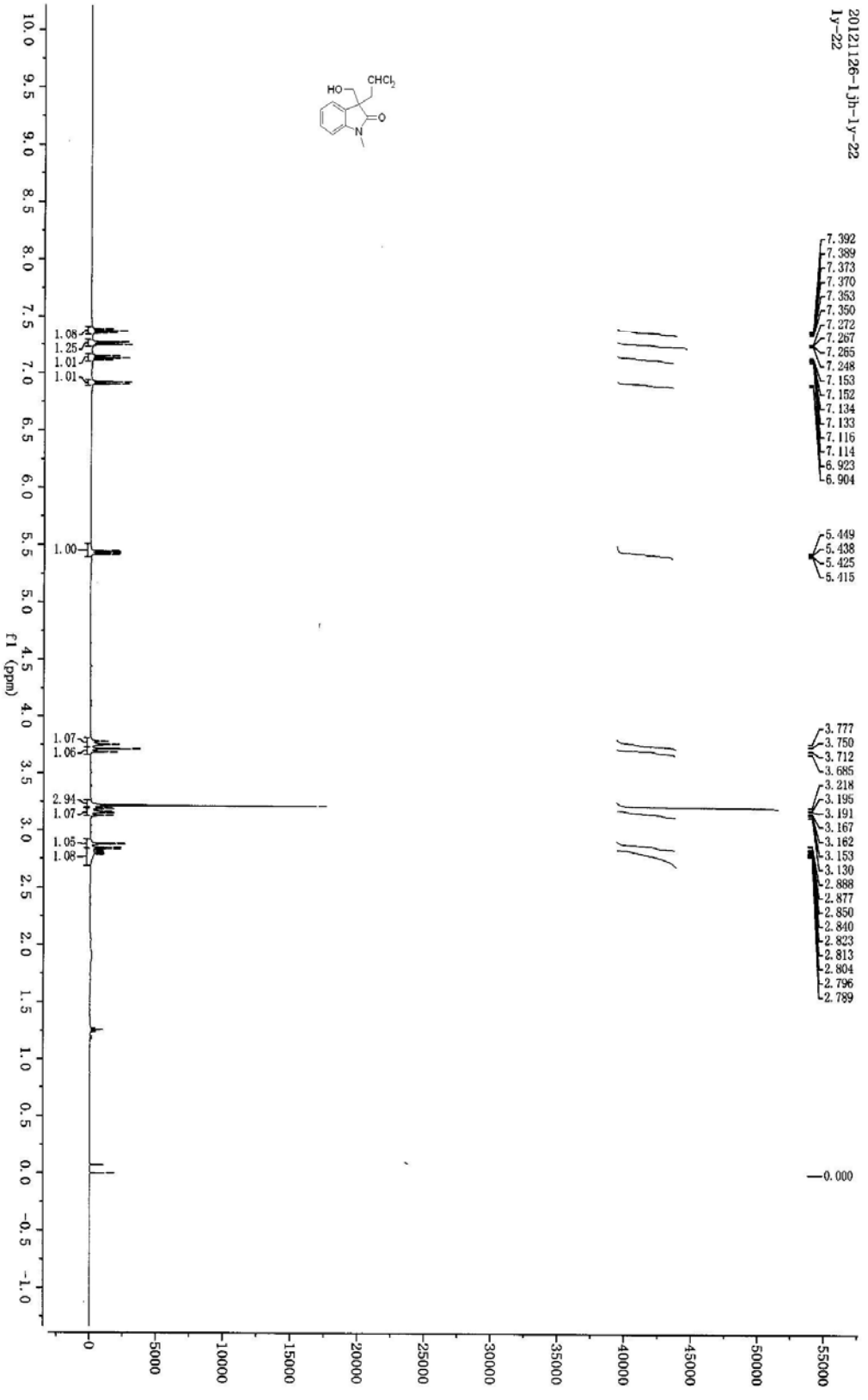
3-(2,2-Dichloroethyl)-1-methyl-3-phenylindolin-2-one (3sa)



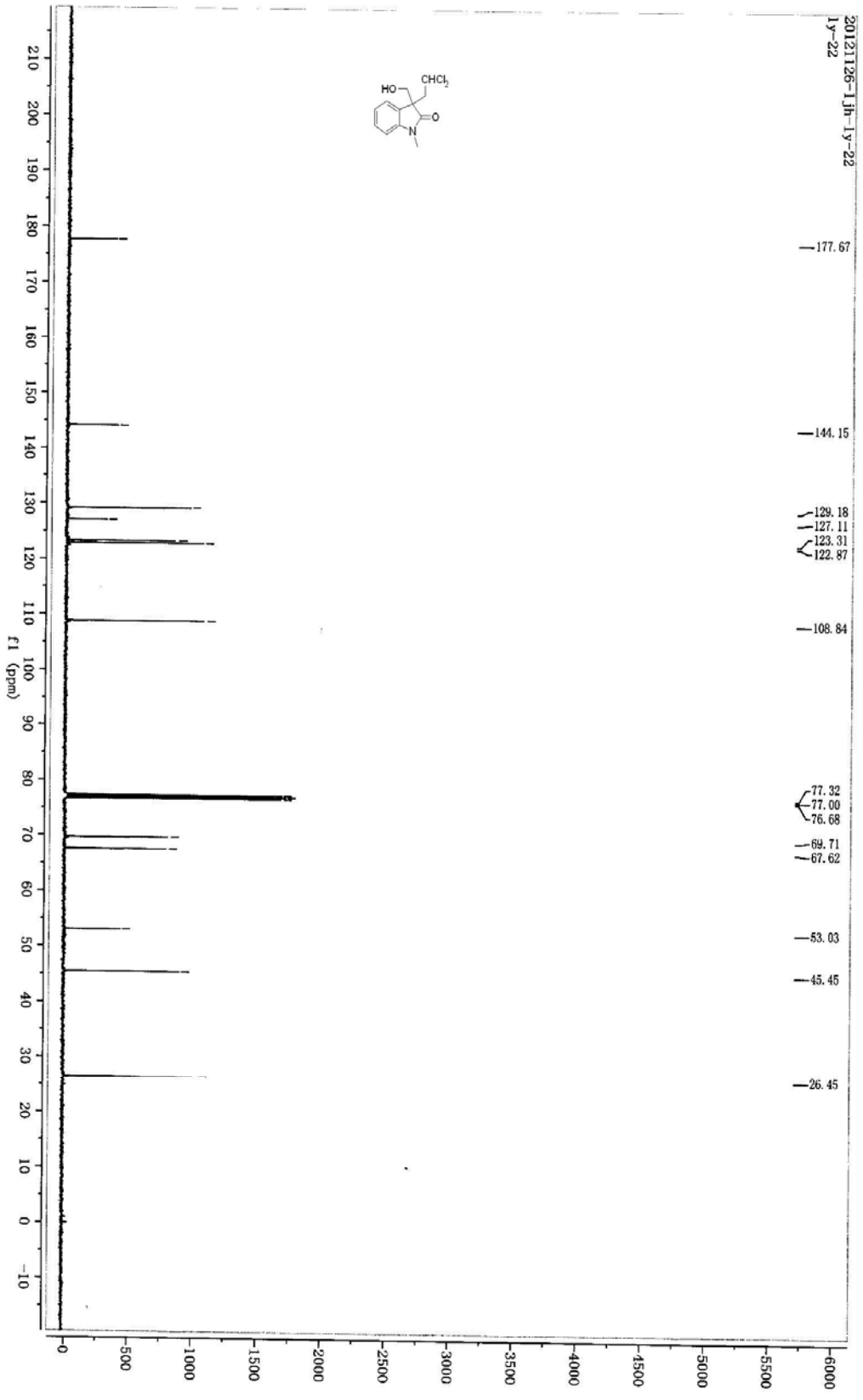
3-(2,2-Dichloroethyl)-1-methyl-3-phenylindolin-2-one (3sa)



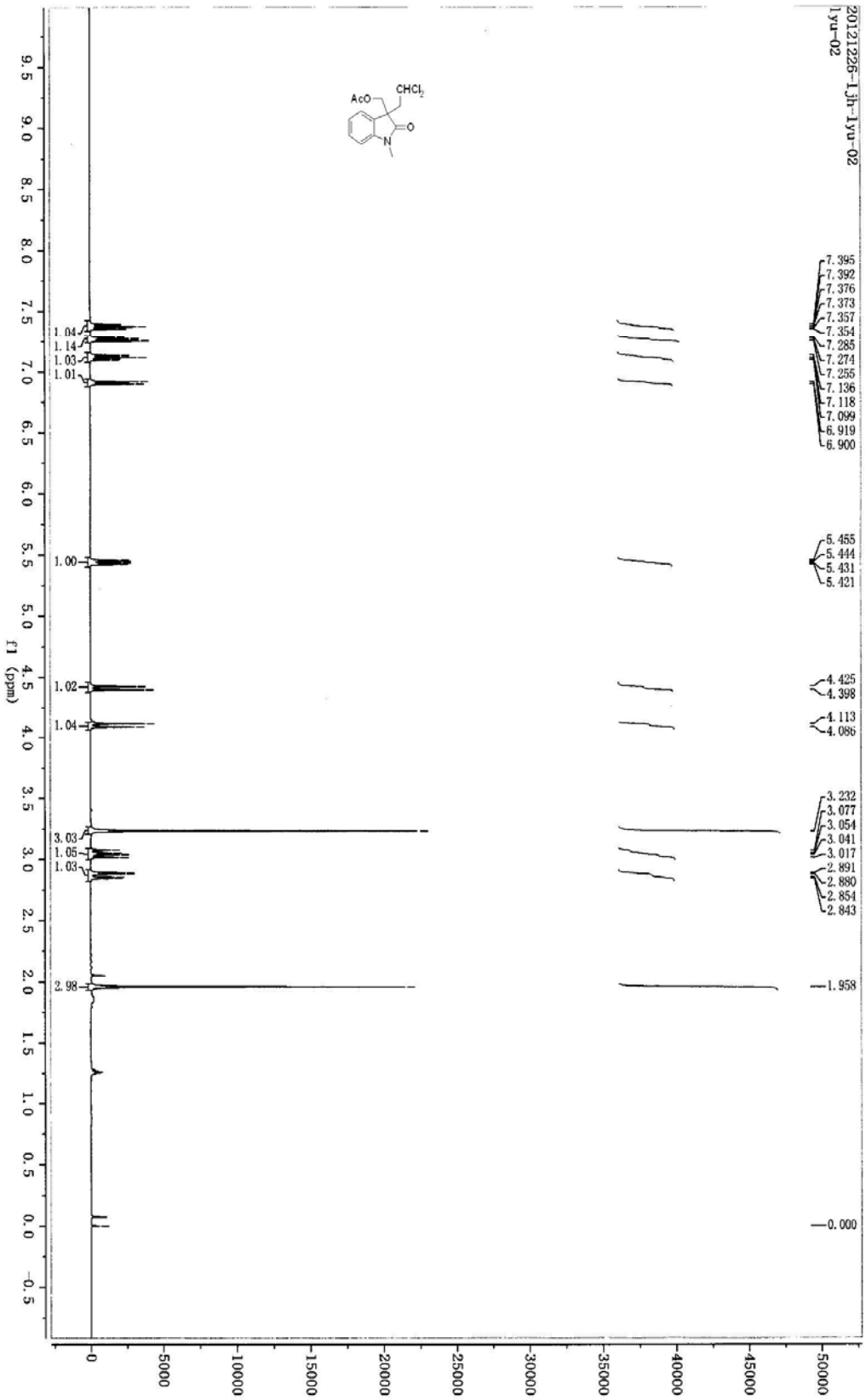
3-(2,2-Dichloroethyl)-3-(hydroxymethyl)-1-methylindolin-2-one (3ta)



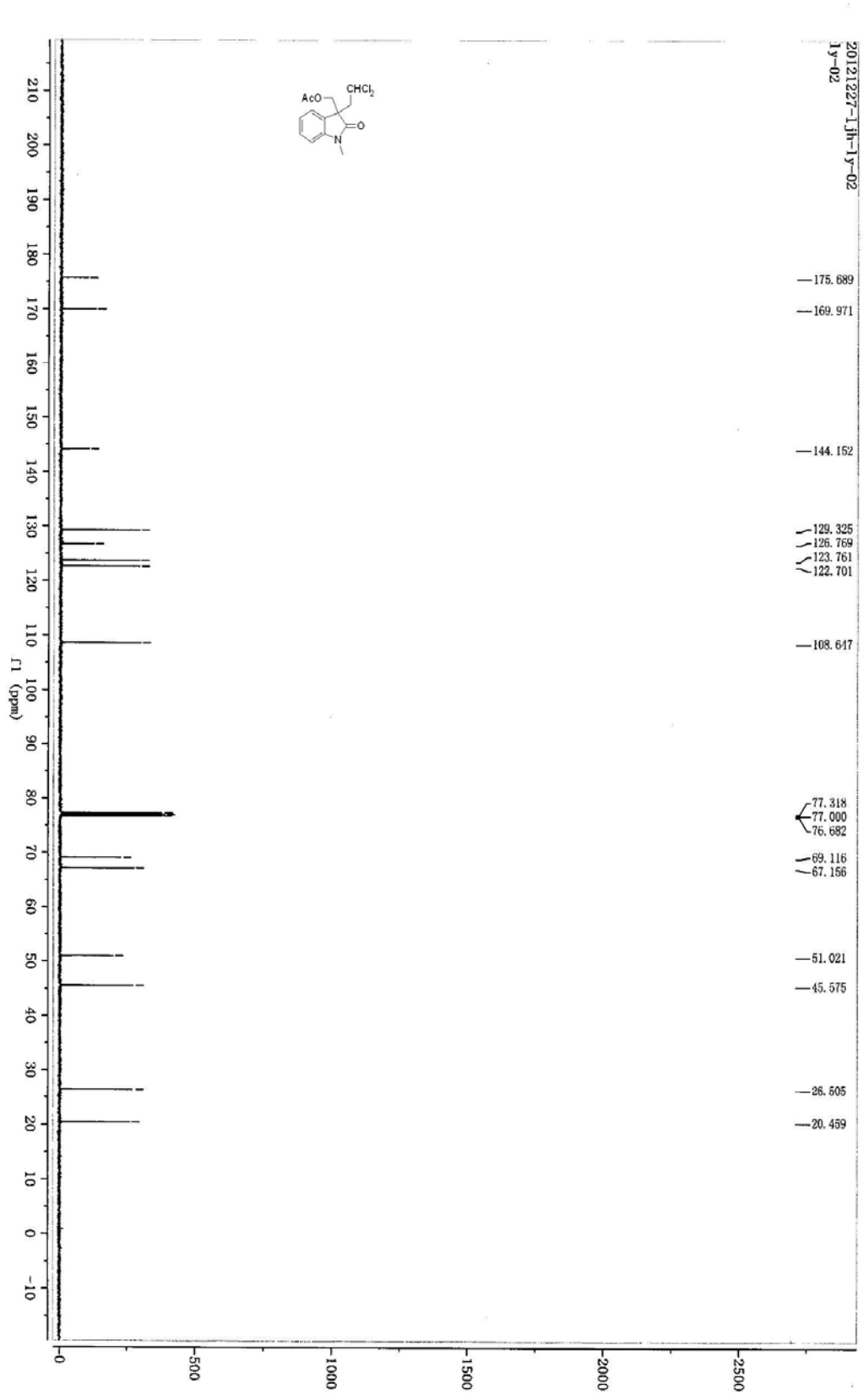
3-(2,2-Dichloroethyl)-3-(hydroxymethyl)-1-methylindolin-2-one (3ta)



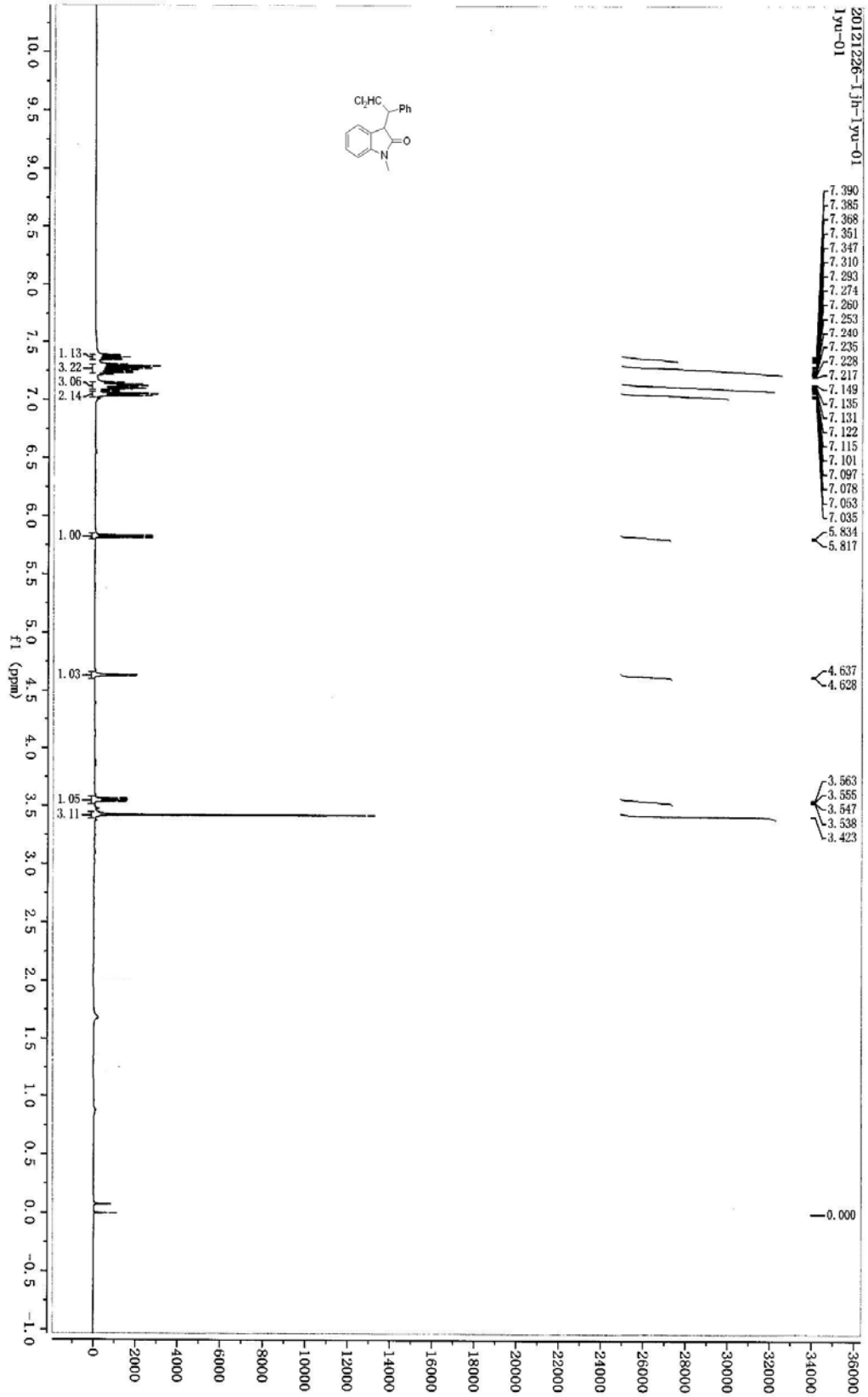
(3-(2,2-Dichloroethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ua)



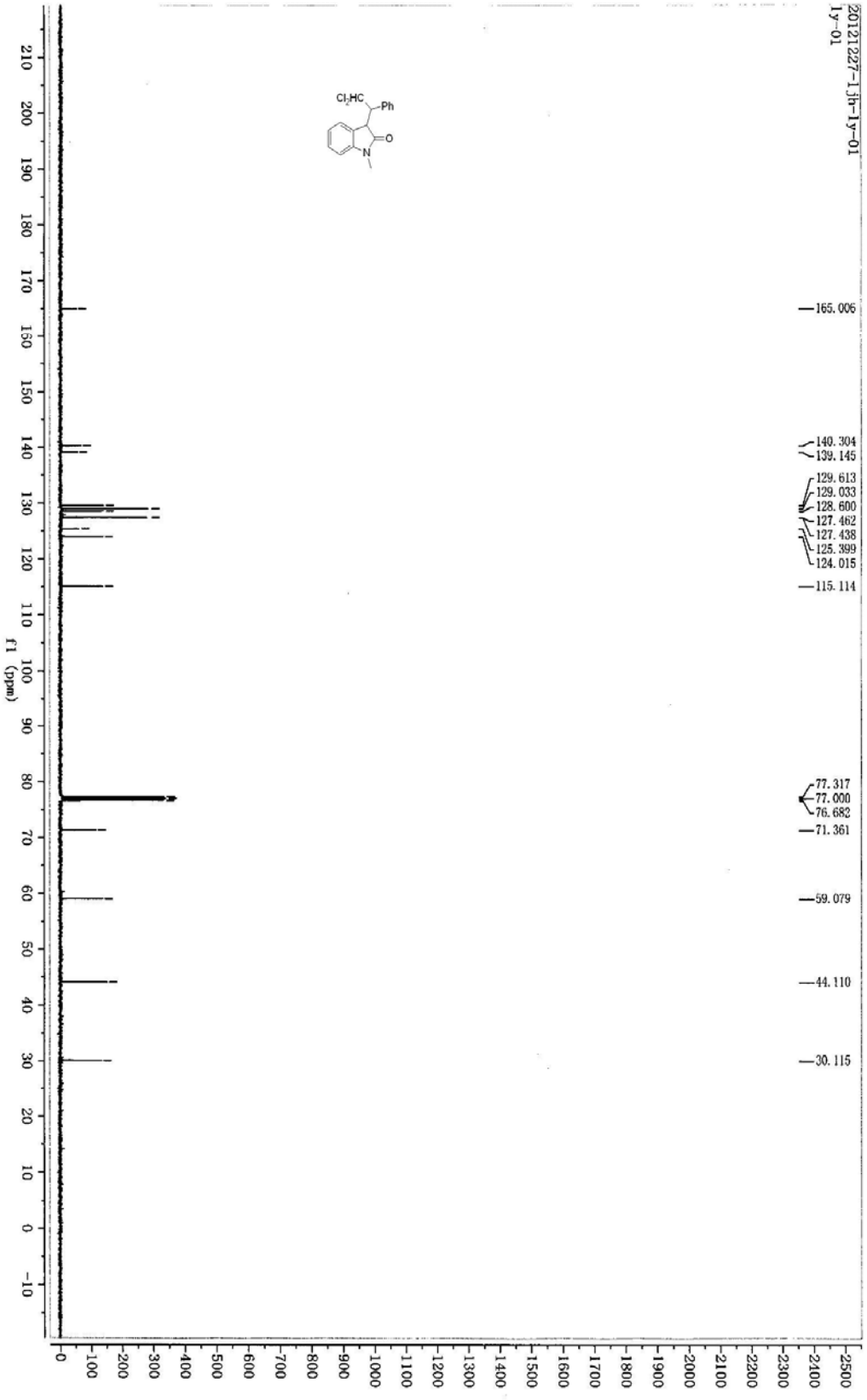
(3-(2,2-Dichloroethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3ua)



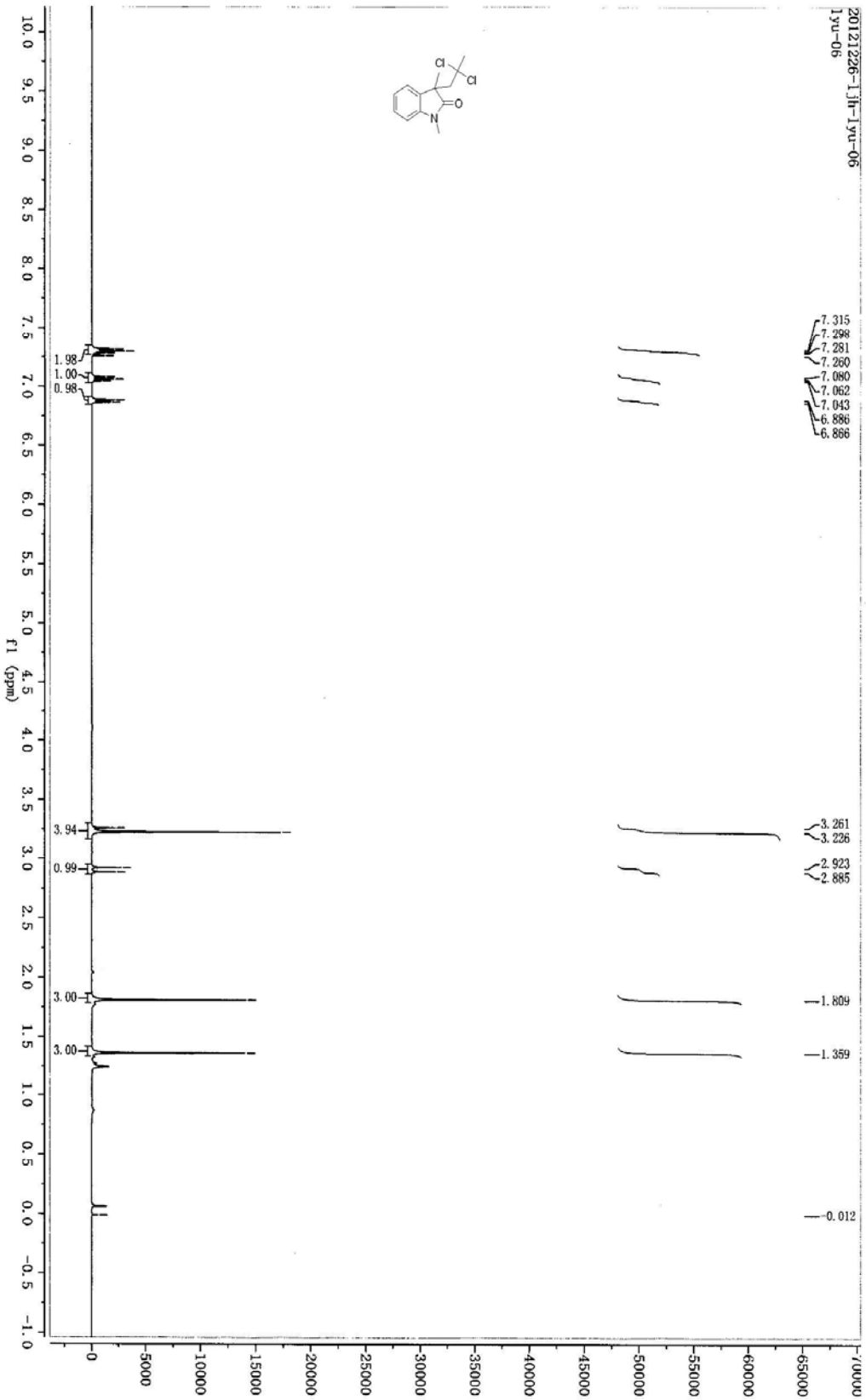
3-(2,2-Dichloro-1-phenylethyl)-1-methylindolin-2-one (3wa)



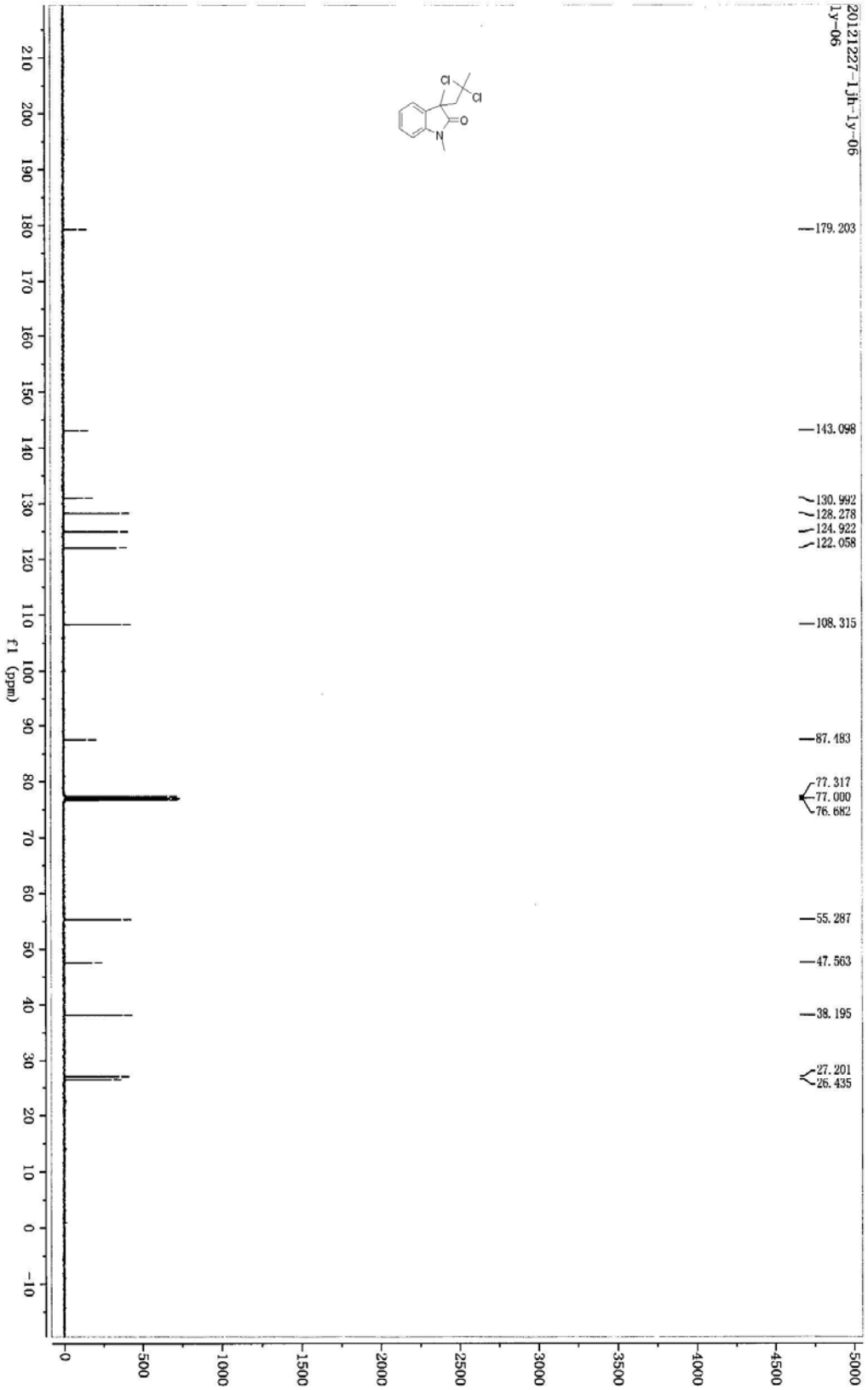
3-(2,2-Dichloro-1-phenylethyl)-1-methylindolin-2-one (3wa)



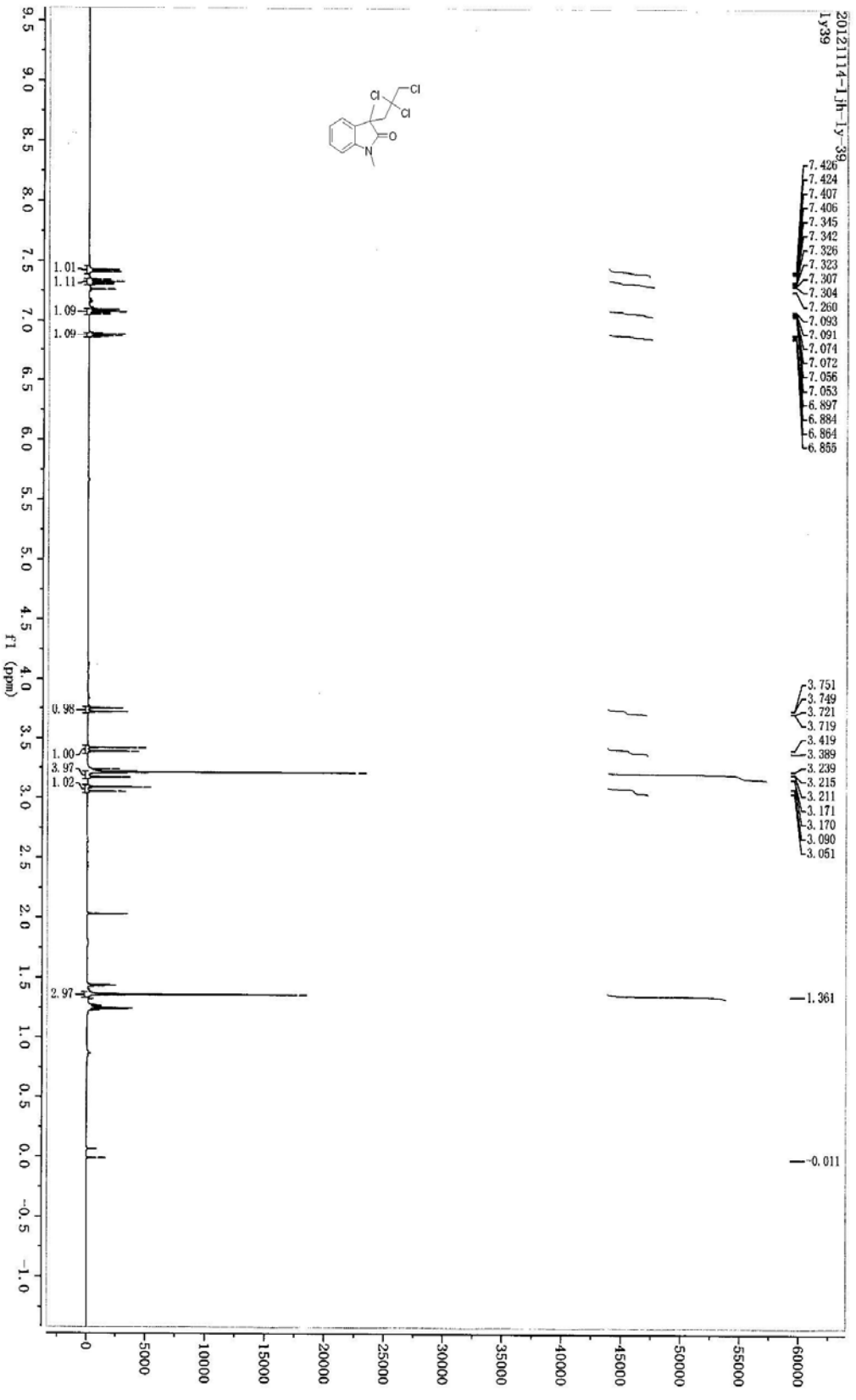
3-(2,2-Dichloropropyl)-1,3-dimethylindolin-2-one (3ab)



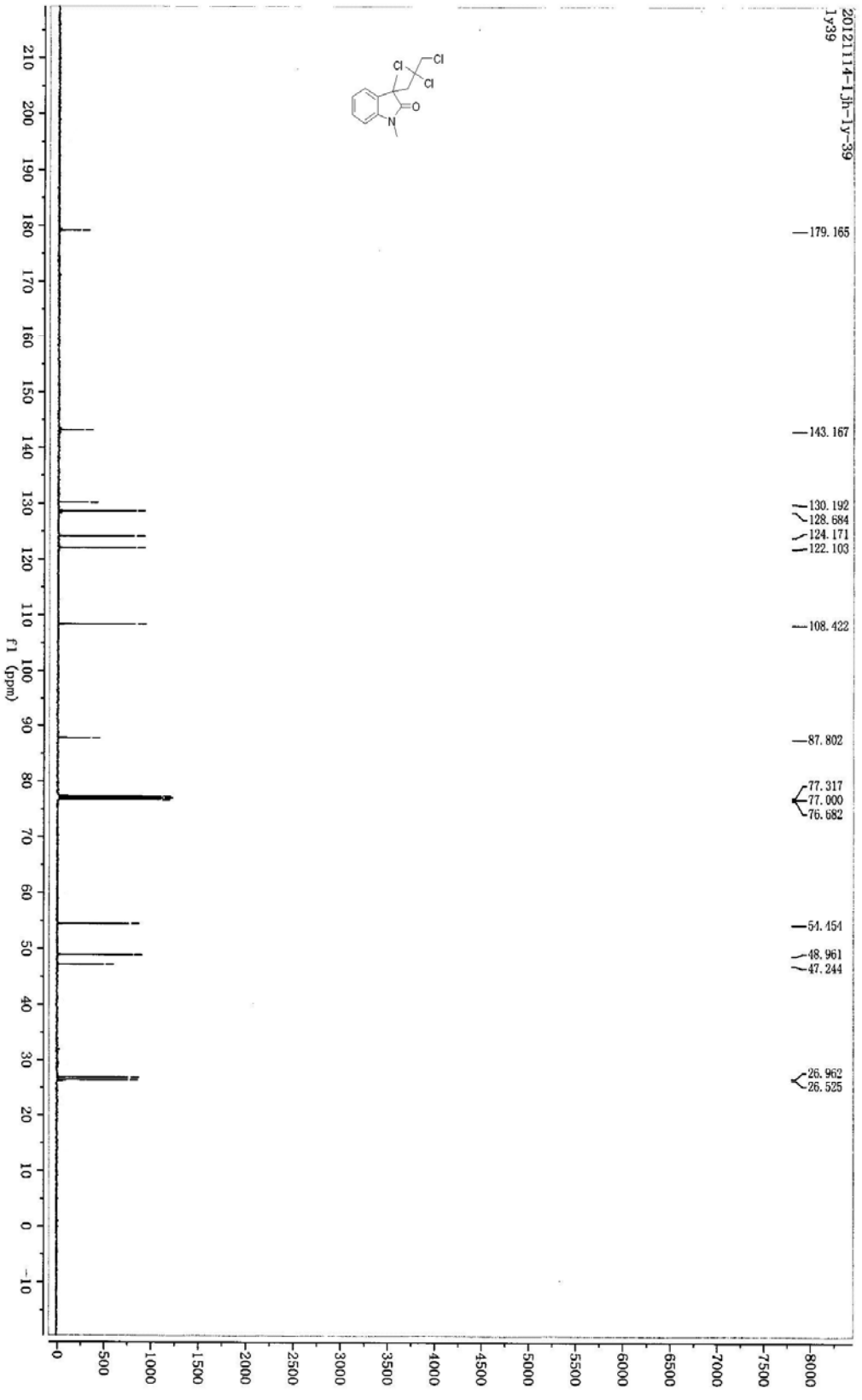
3-(2,2-Dichloropropyl)-1,3-dimethylindolin-2-one (3ab)



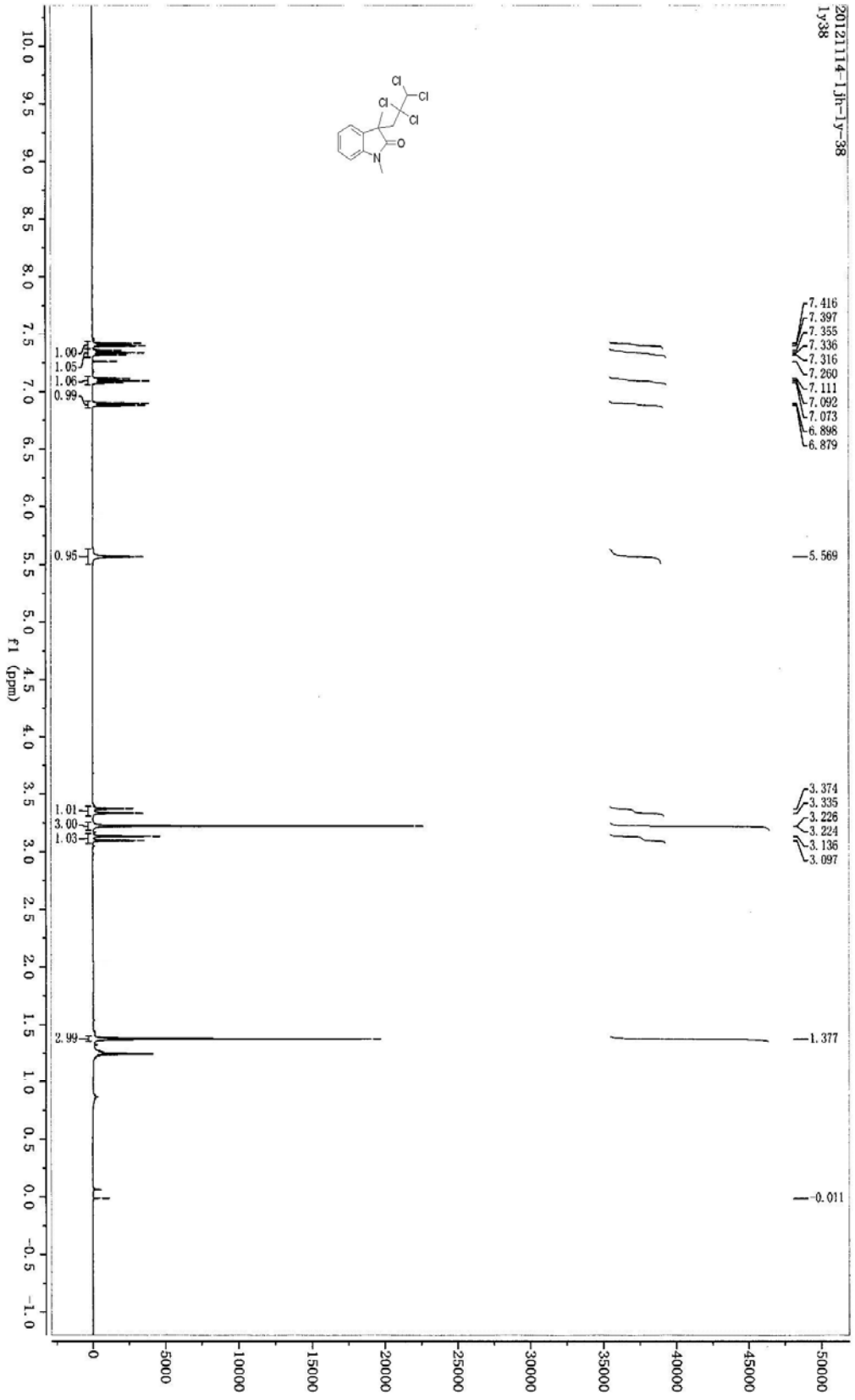
1,3-Dimethyl-3-(2,2,3-trichloropropyl)indolin-2-one (3ac)



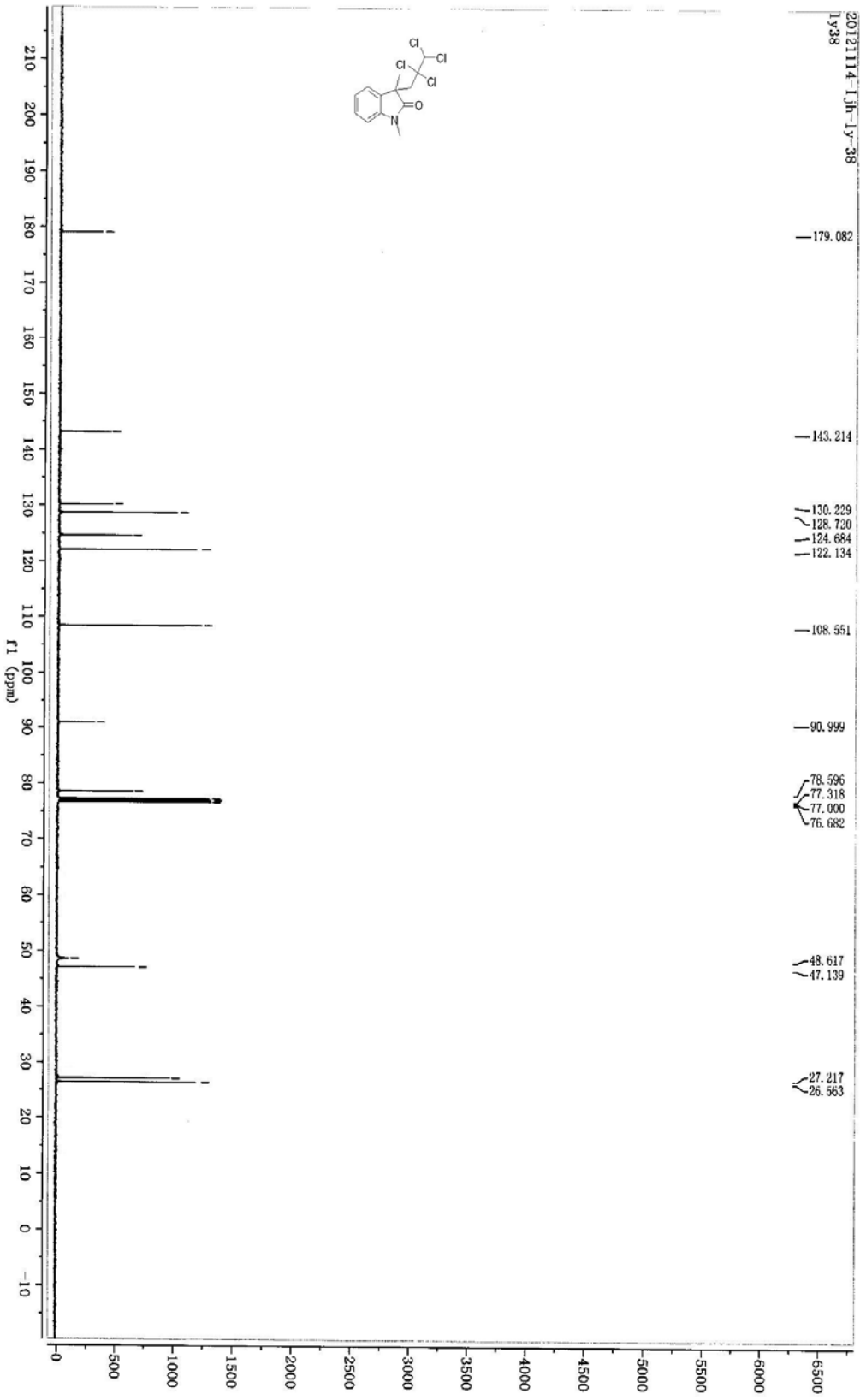
1,3-Dimethyl-3-(2,2,3-trichloropropyl)indolin-2-one (3ac)



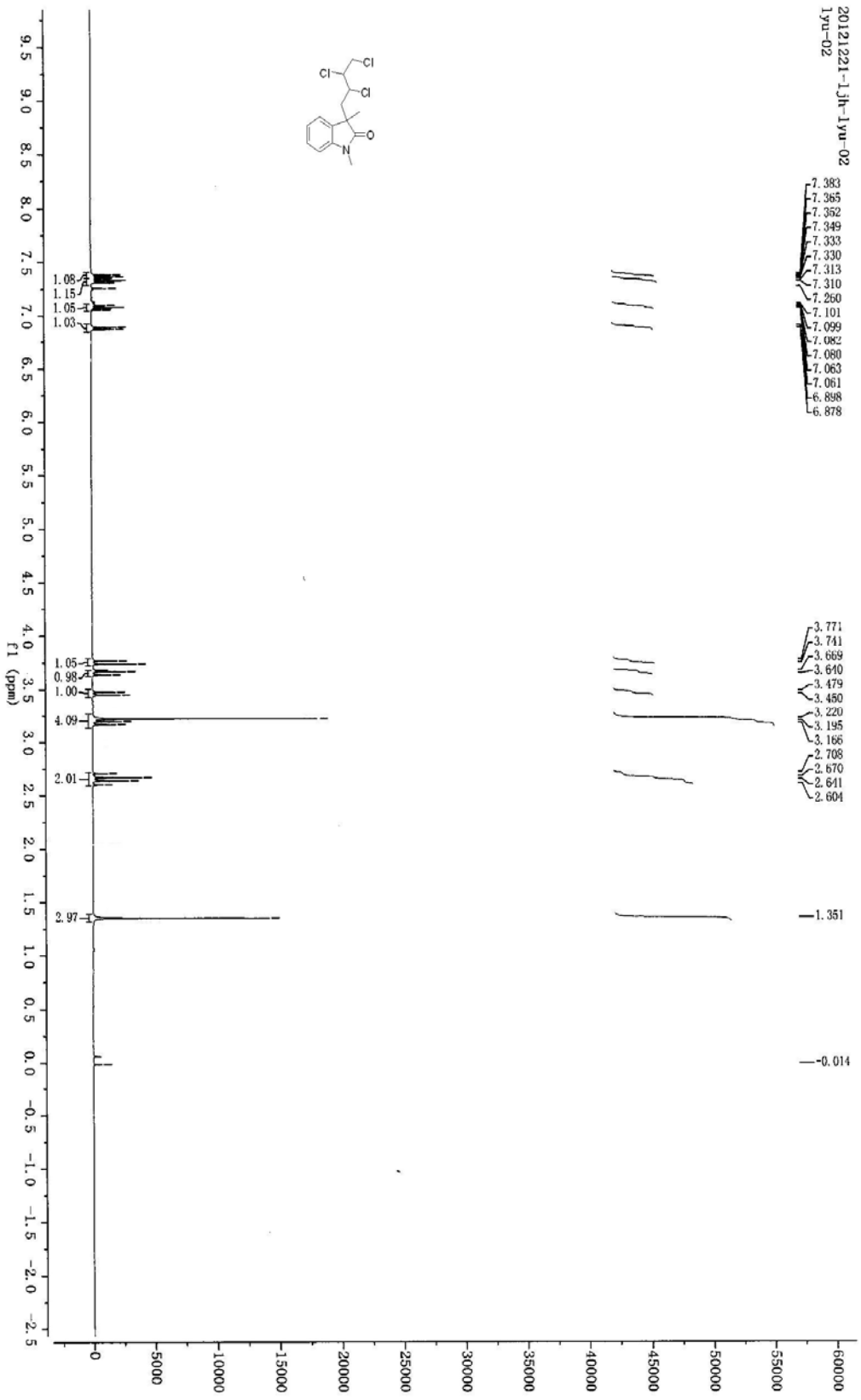
1,3-Dimethyl-3-(2,2,3,3-tetrachloropropyl)indolin-2-one (3ad)



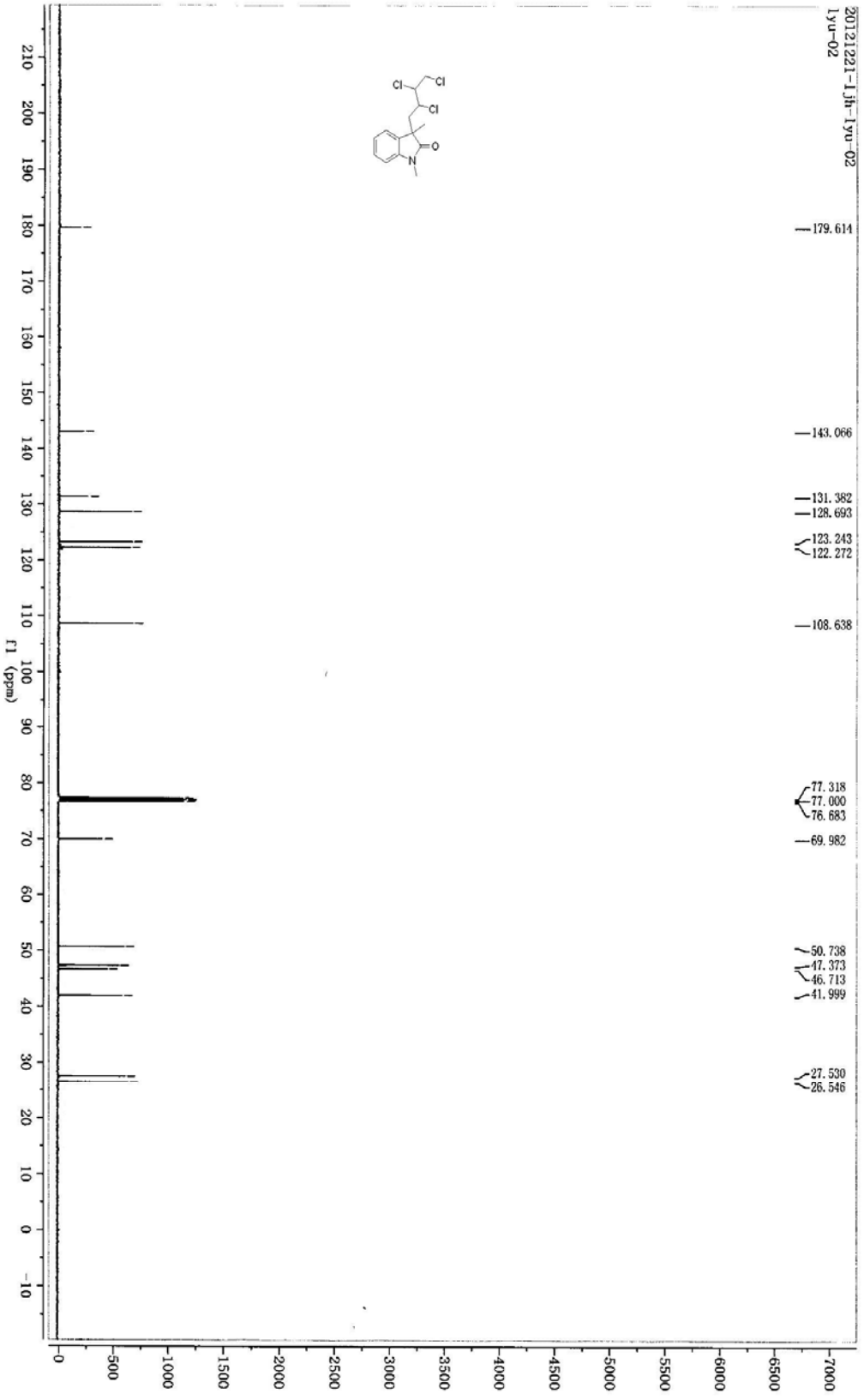
1,3-Dimethyl-3-(2,2,3,3-tetrachloropropyl)indolin-2-one (3ad)



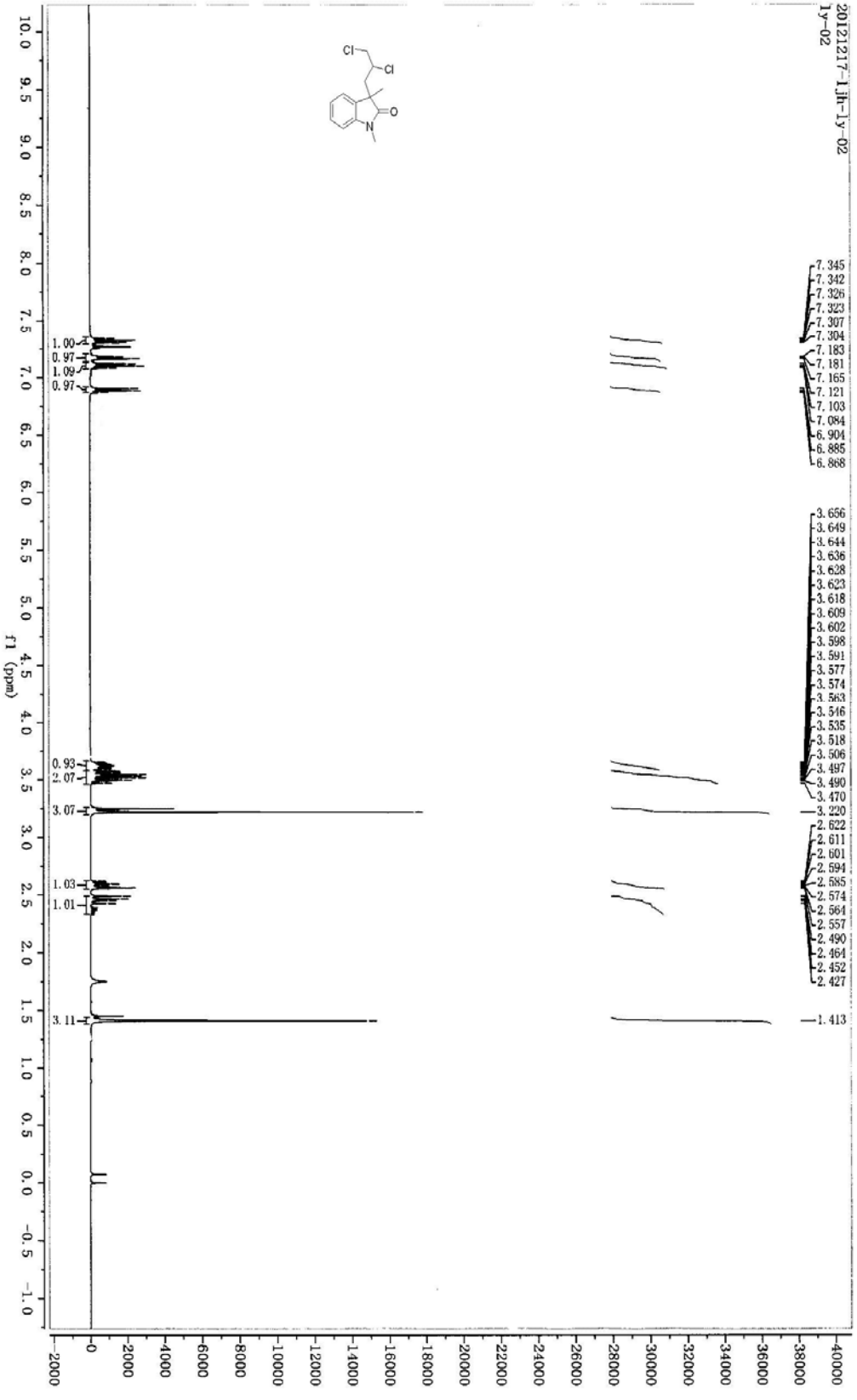
1,3-Dimethyl-3-(2,3,4-trichlorobutyl)indolin-2-one (3af)



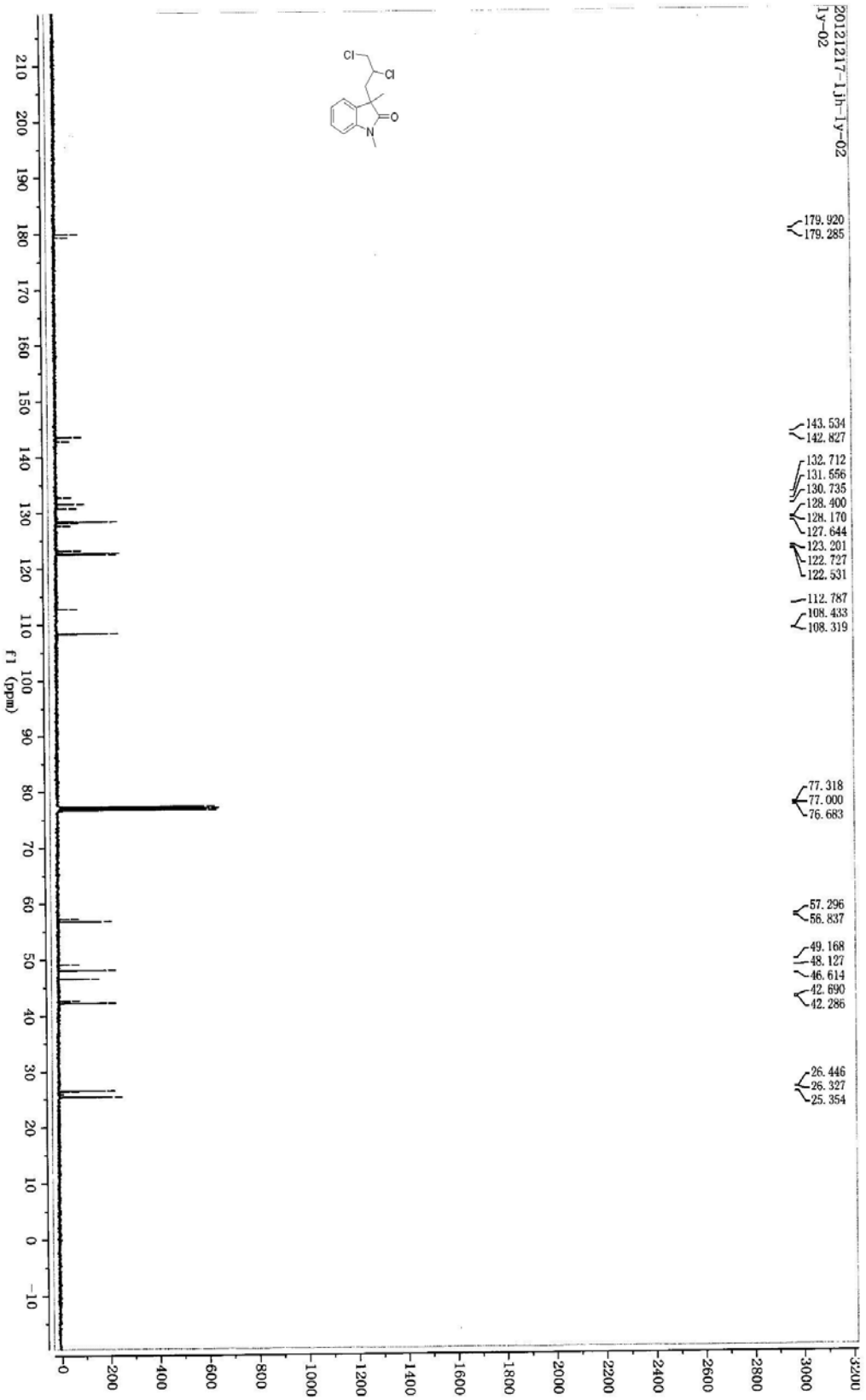
1,3-Dimethyl-3-(2,3,4-trichlorobutyl)indolin-2-one (3af)



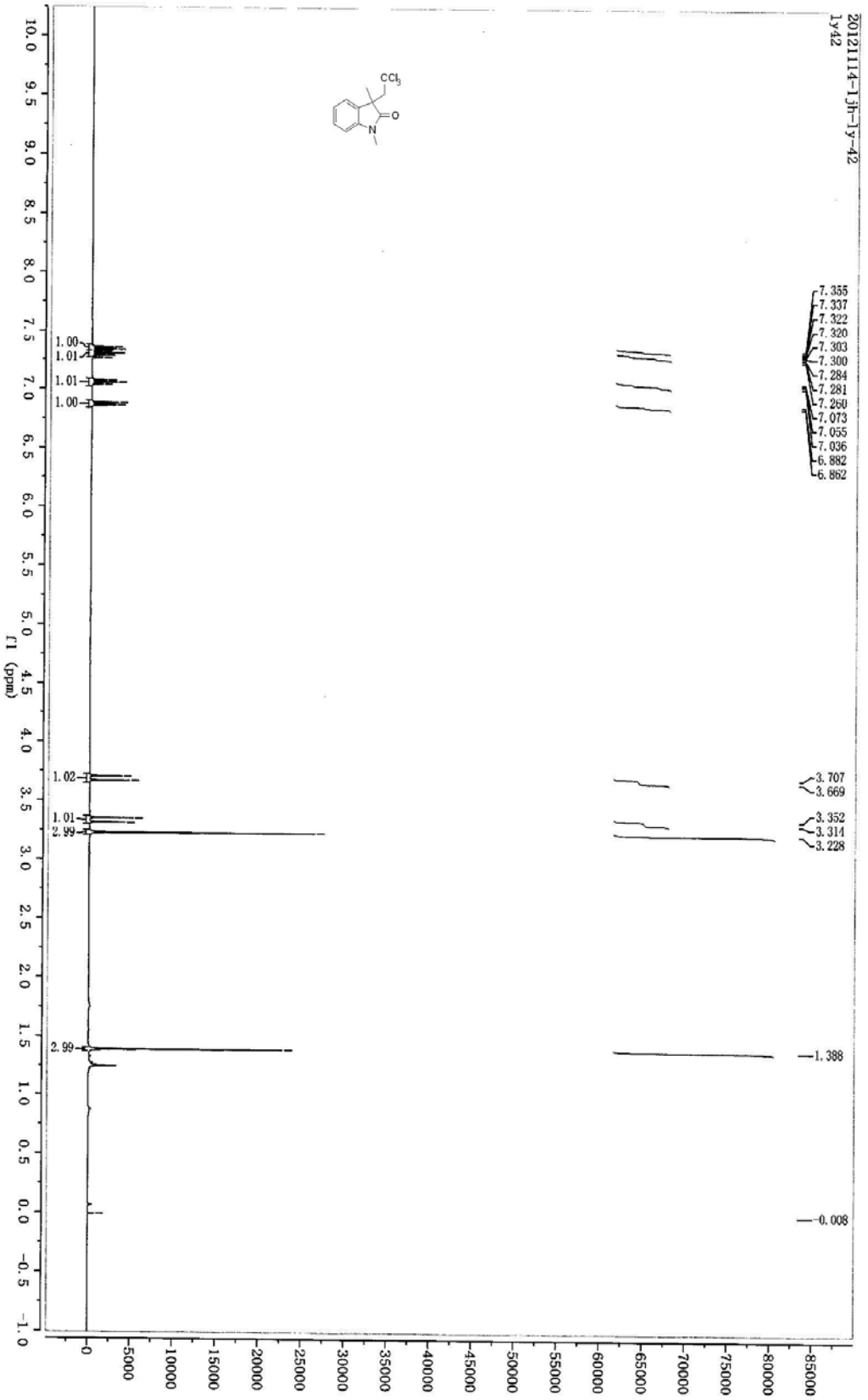
3-(2,3-Dichloropropyl)-1,3-dimethylindolin-2-one (3ag)



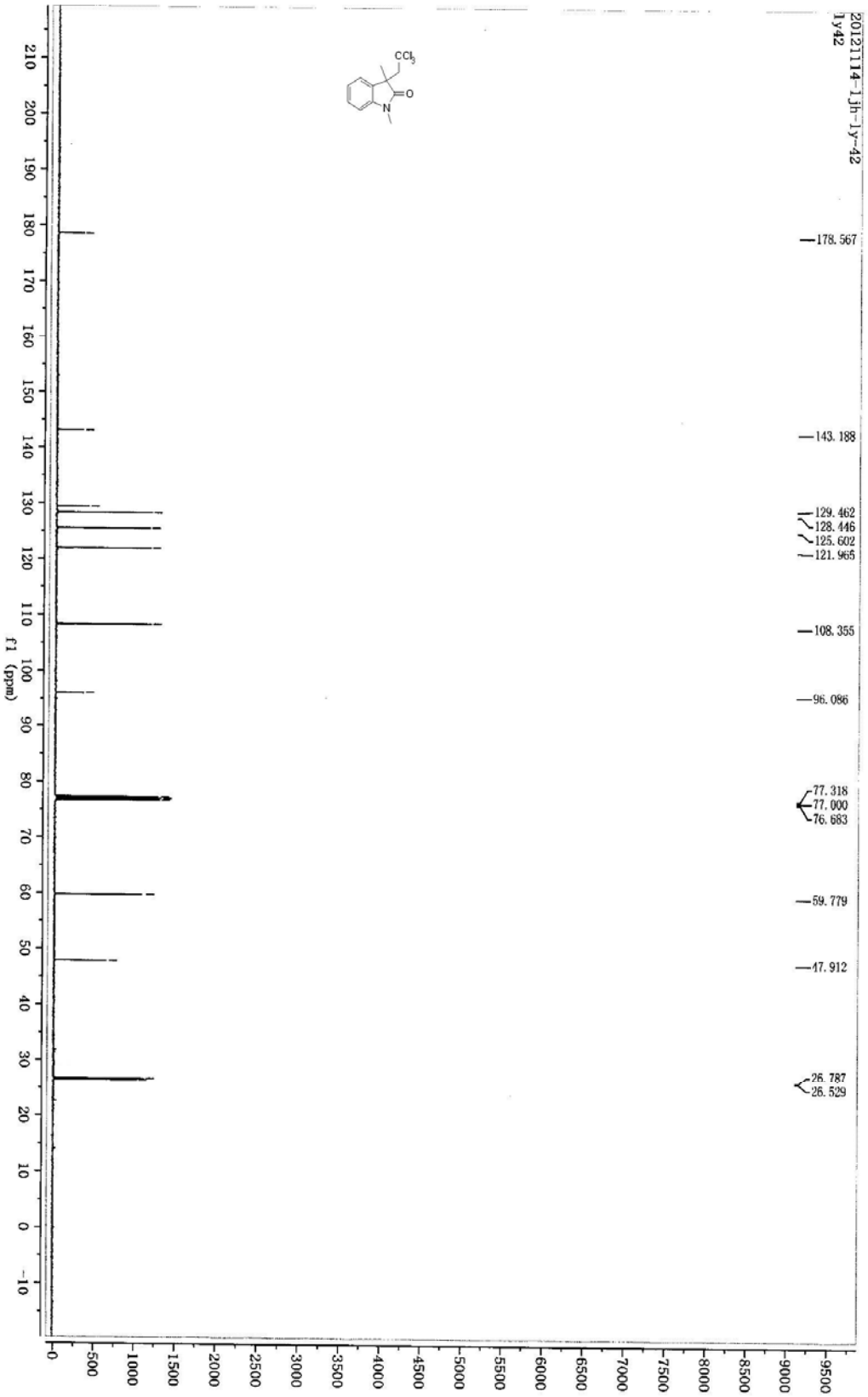
3-(2,3-Dichloropropyl)-1,3-dimethylindolin-2-one (3ag)



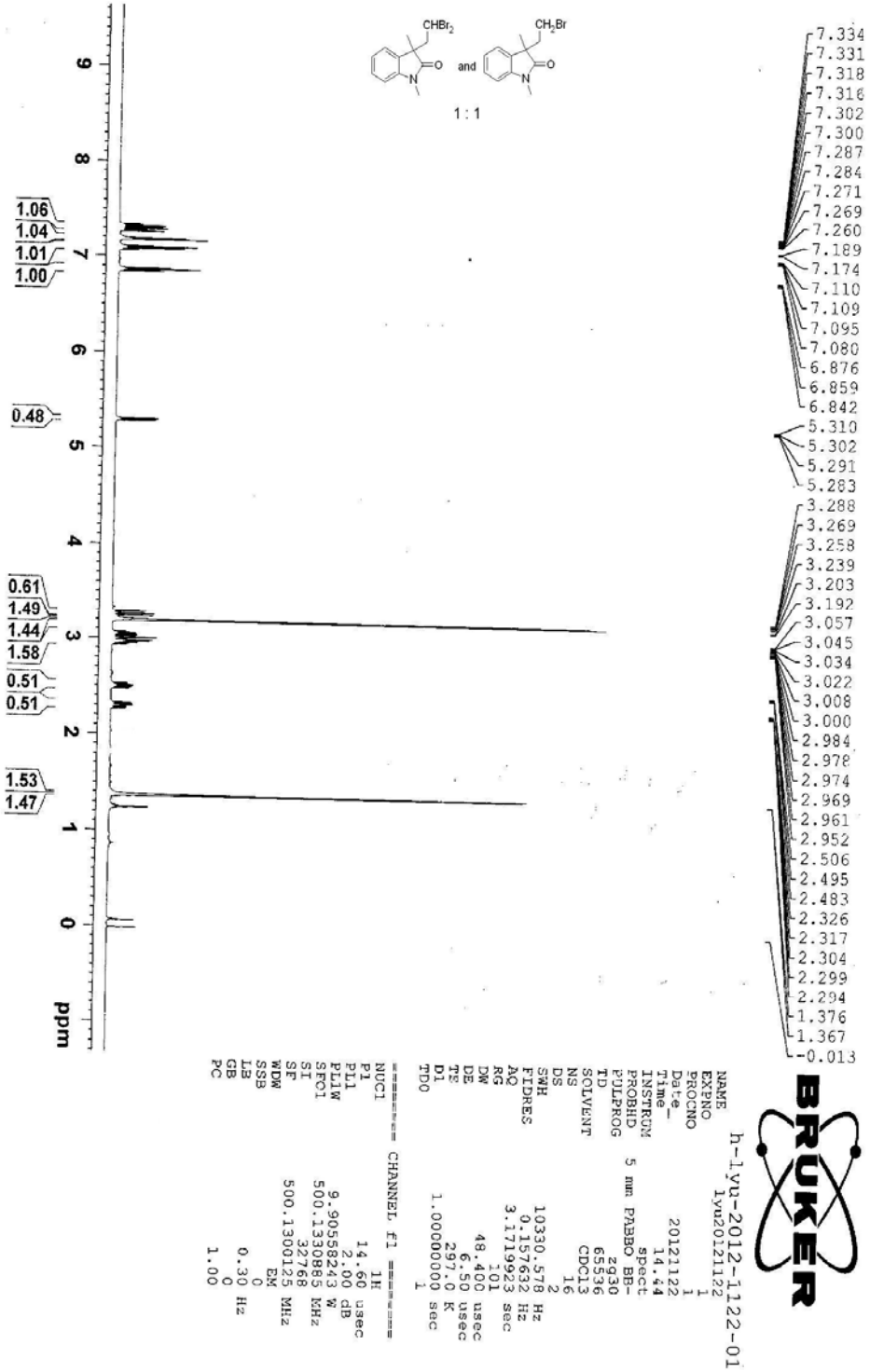
1,3-Dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (3ah)



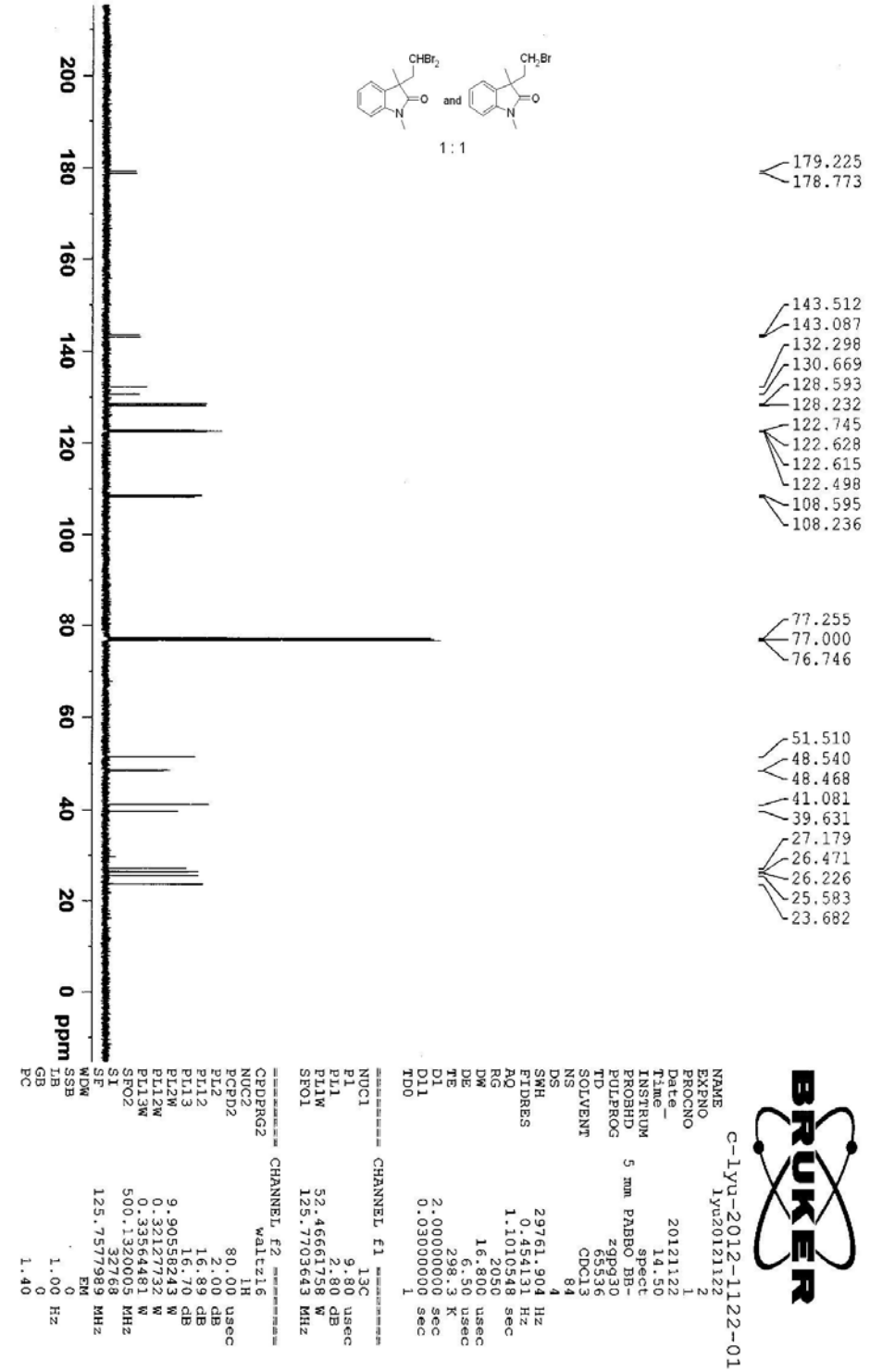
1,3-Dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (3ah)



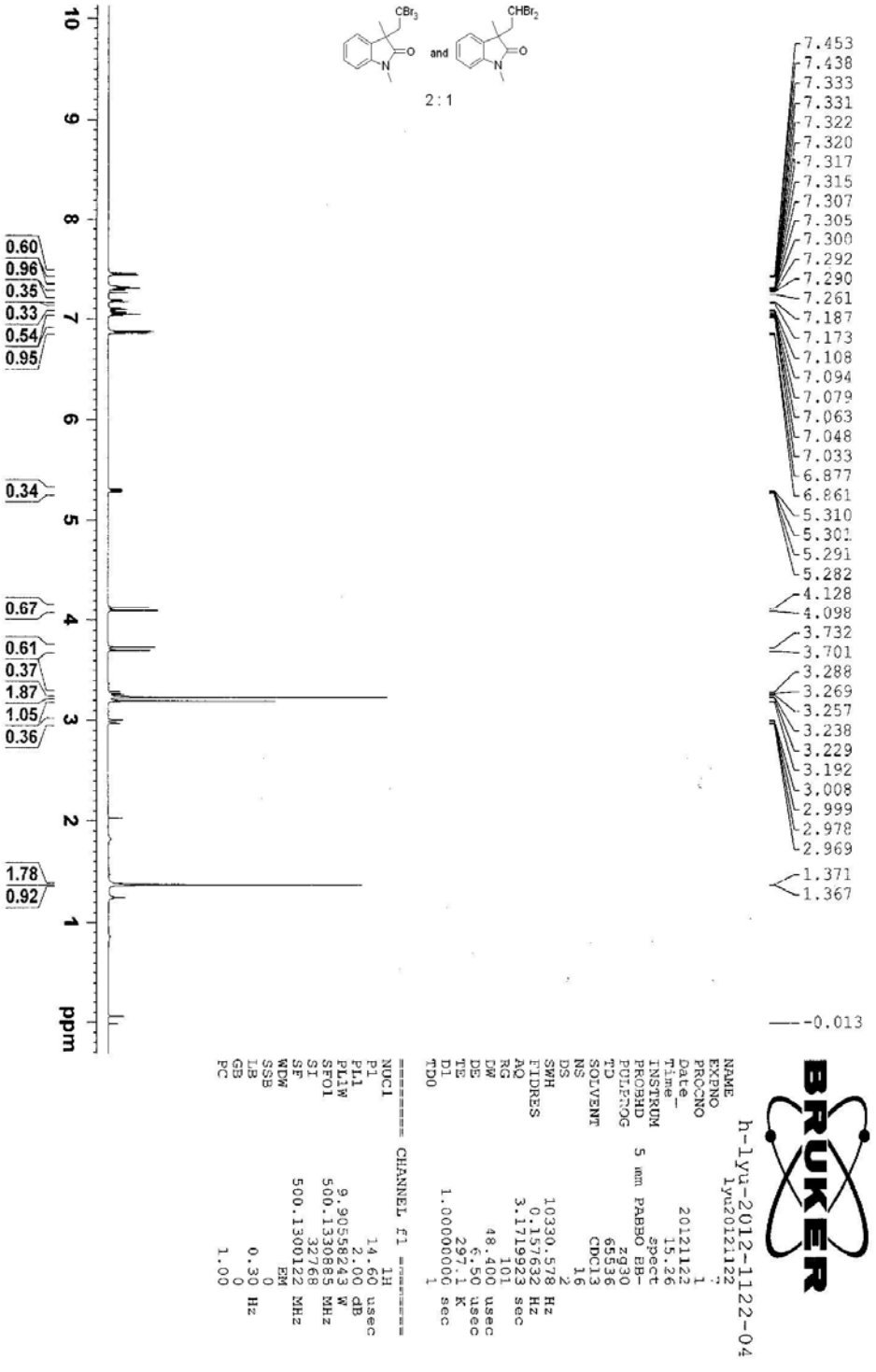
3-(2,2-Dibromoethyl)-1,3-dimethylindolin-2-one (3ai) and 3-(2-bromoethyl)-1,3-dimethylindolin-2-one (3ai')



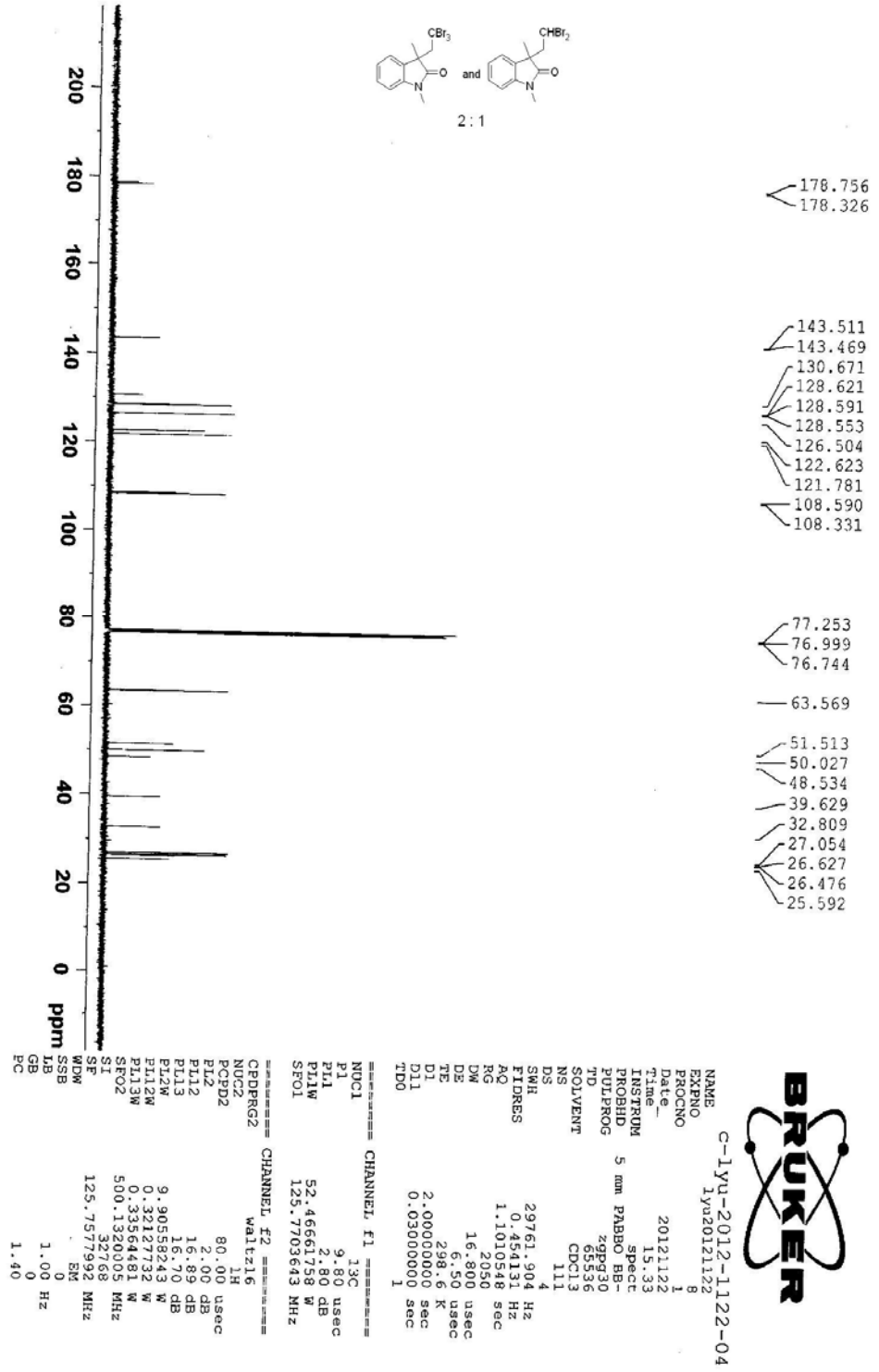
3-(2,2-Dibromoethyl)-1,3-dimethylindolin-2-one (3ai) and 3-(2-bromoethyl)-1,3-dimethylindolin-2-one (3ai')



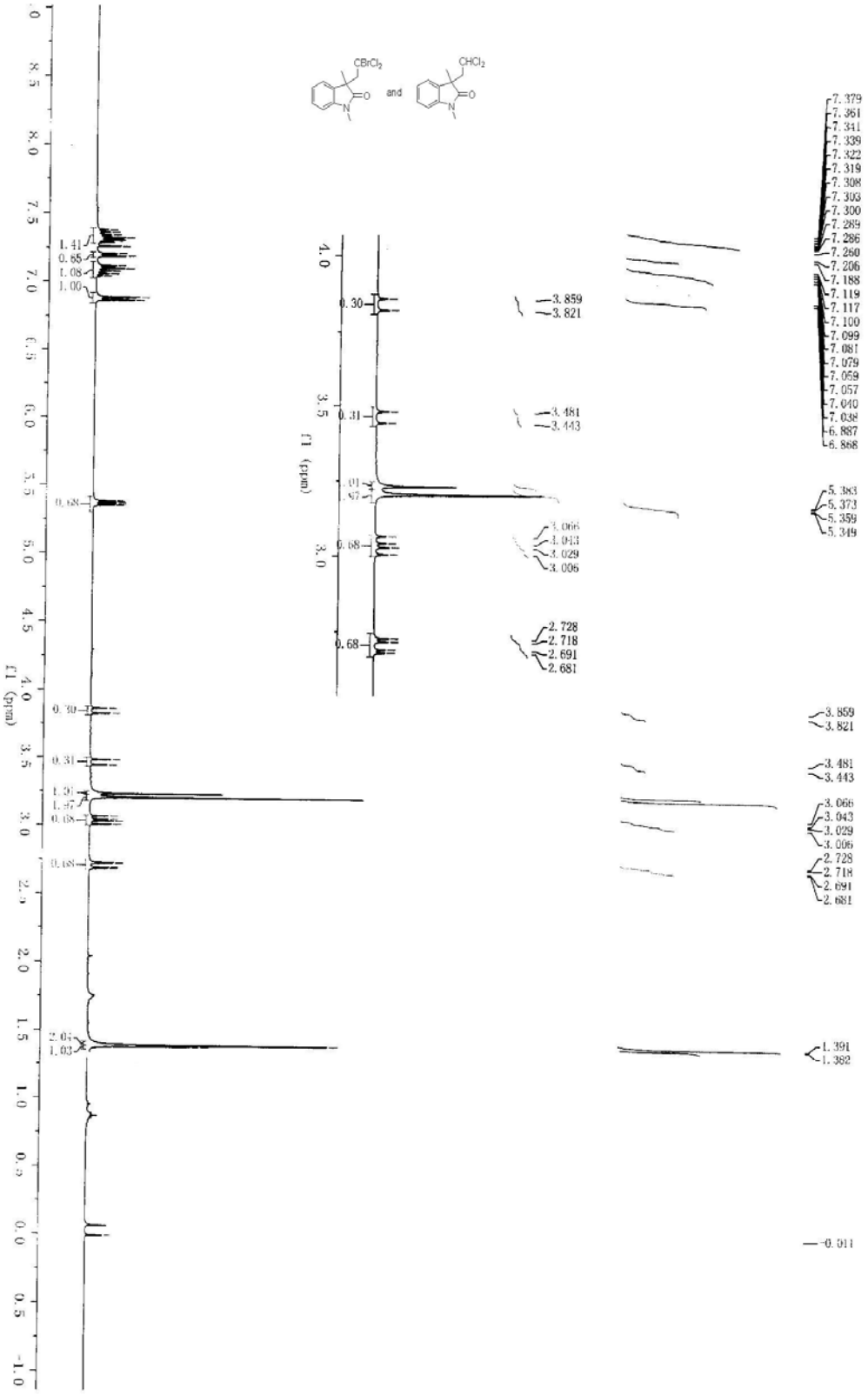
1,3-Dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (3aj) and 3-(2,2-dibromoethyl)-1,3-dimethylindolin-2-one (3aj')



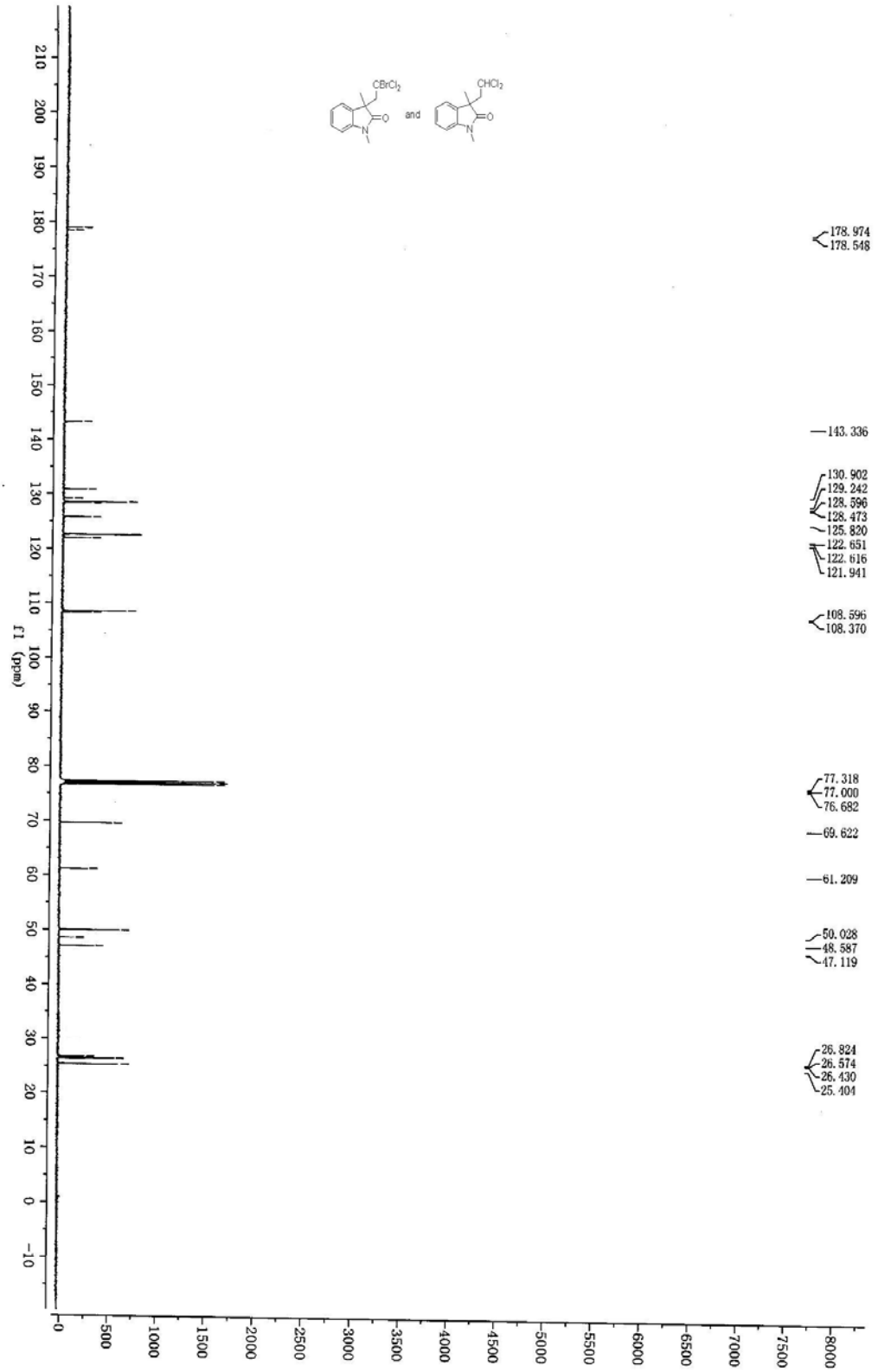
1,3-Dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (3aj) and 3-(2,2-dibromoethyl)-1,3-dimethylindolin-2-one (3aj')



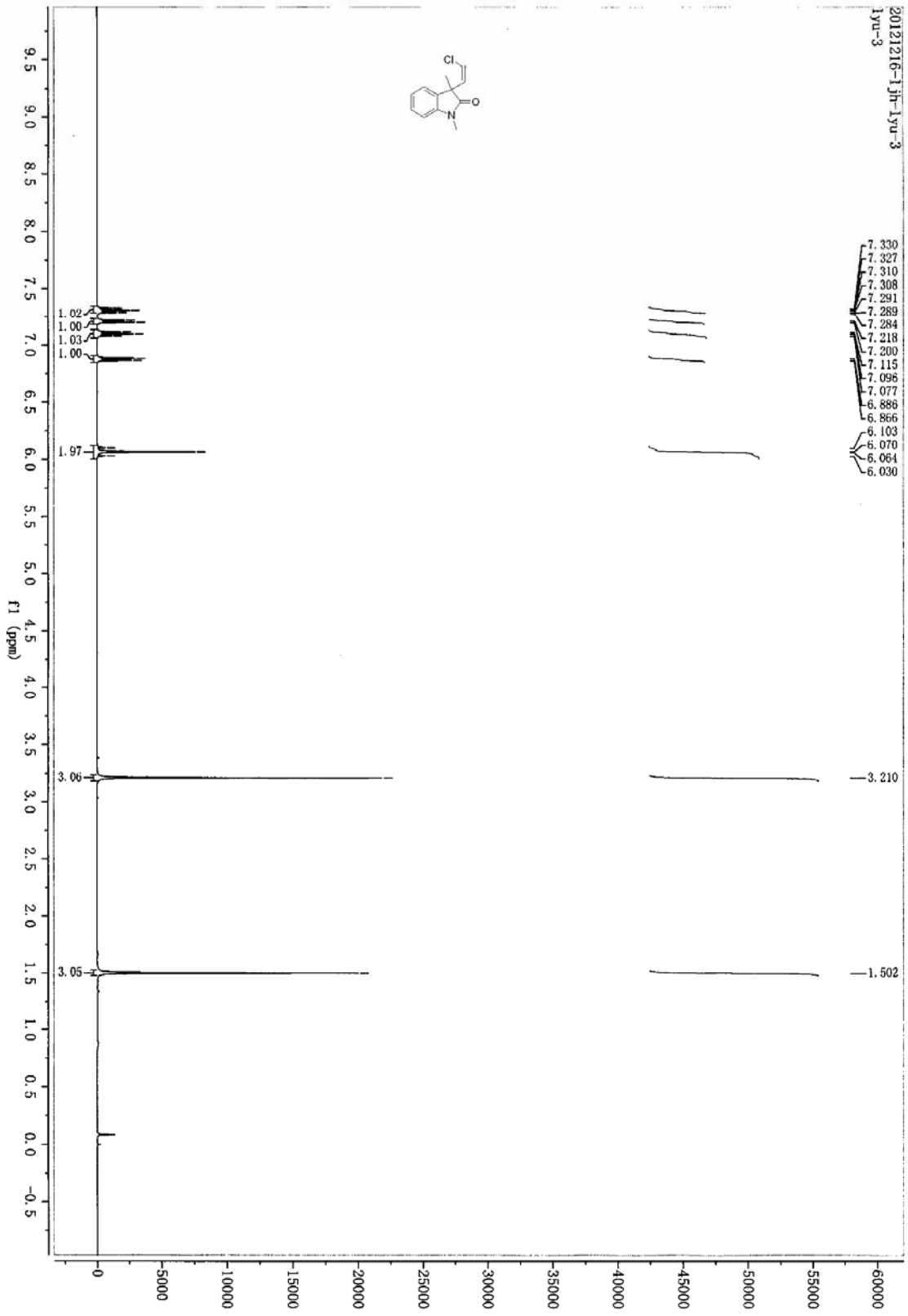
3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa) and 3-(2-bromo-2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ak)



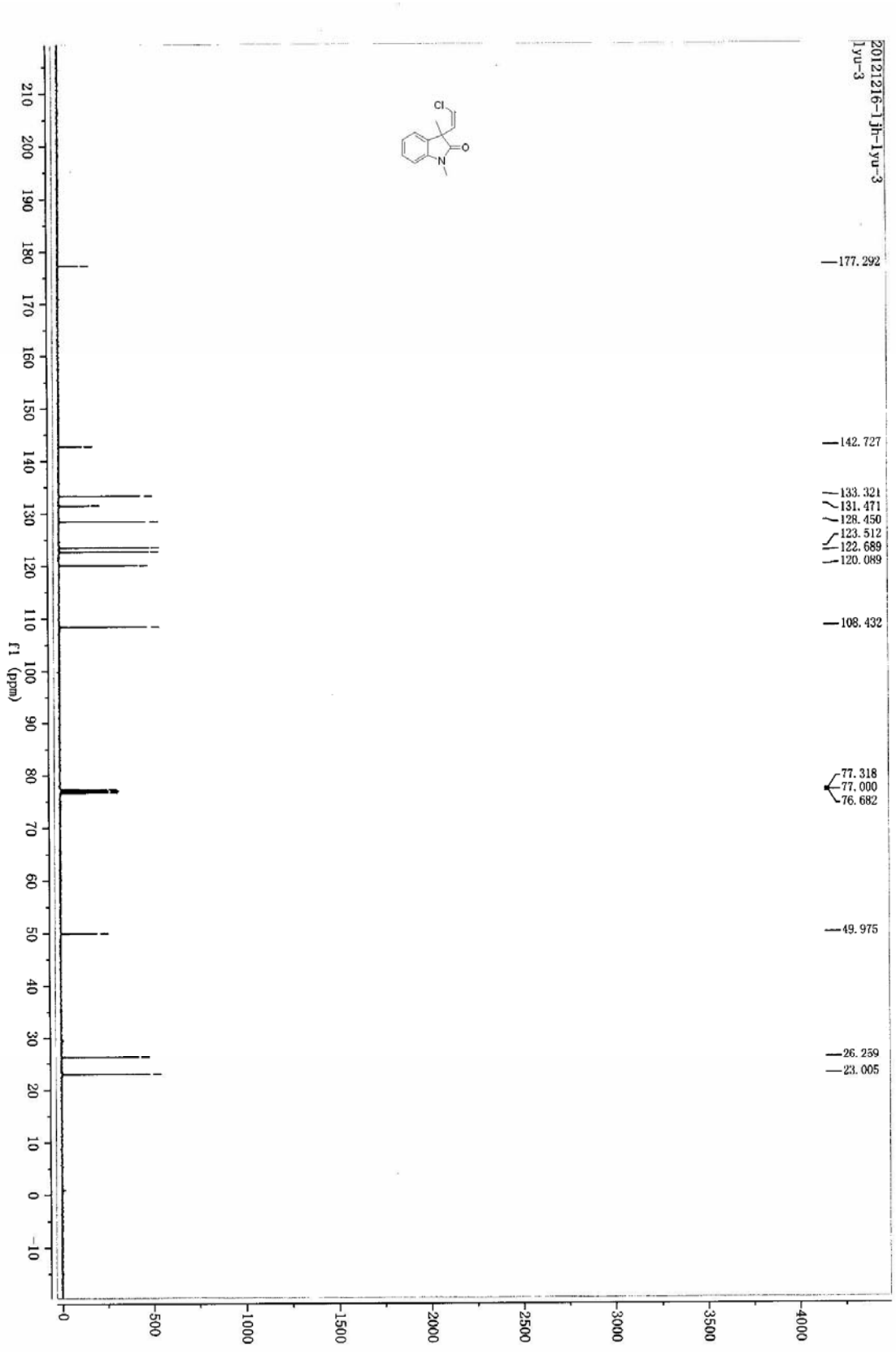
3-(2,2-Dichloroethyl)-1,3-dimethylindolin-2-one (3aa) and 3-(2-bromo-2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3ak)



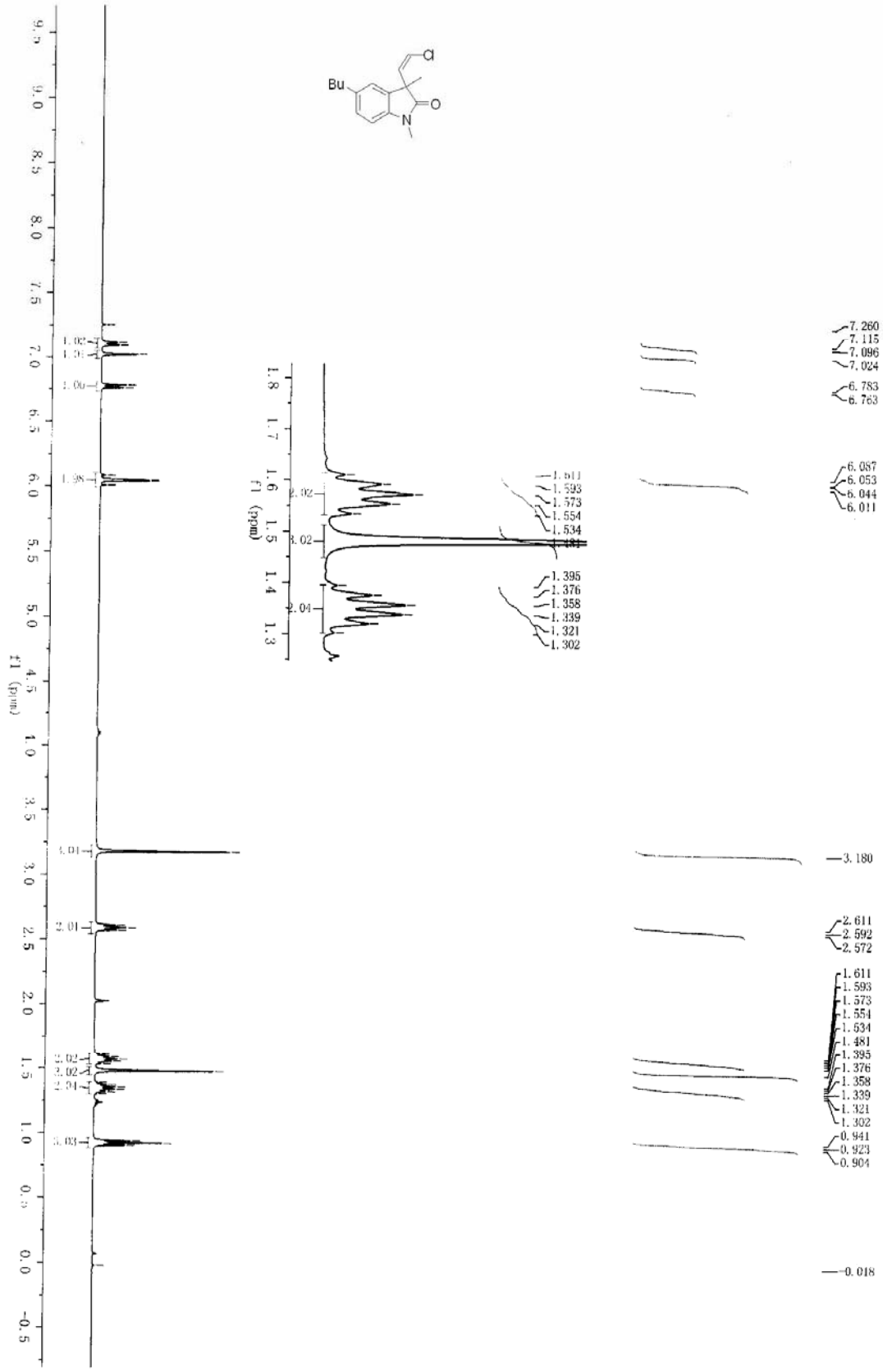
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethylindolin-2-one (4aa):



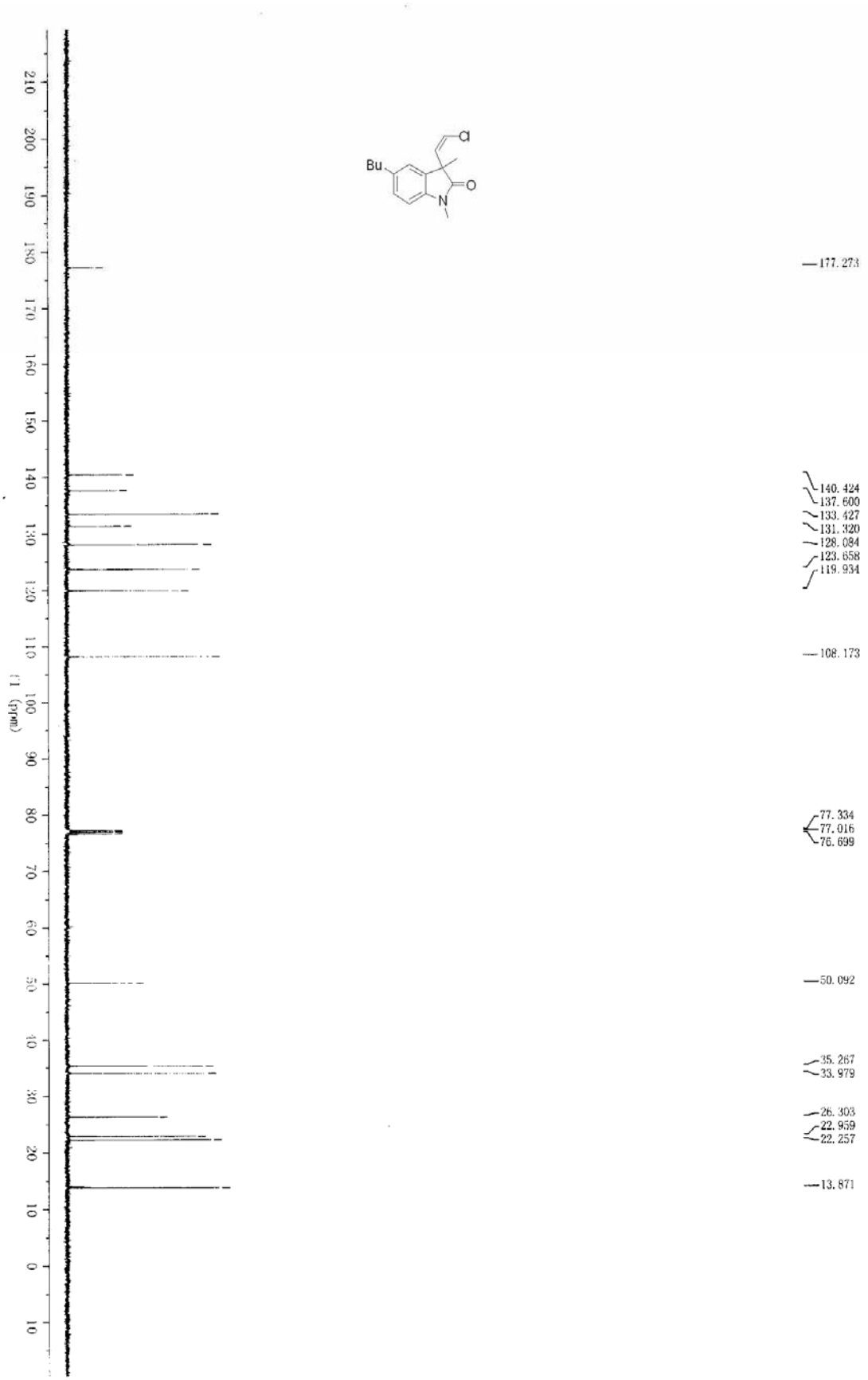
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethylindolin-2-one (4aa):



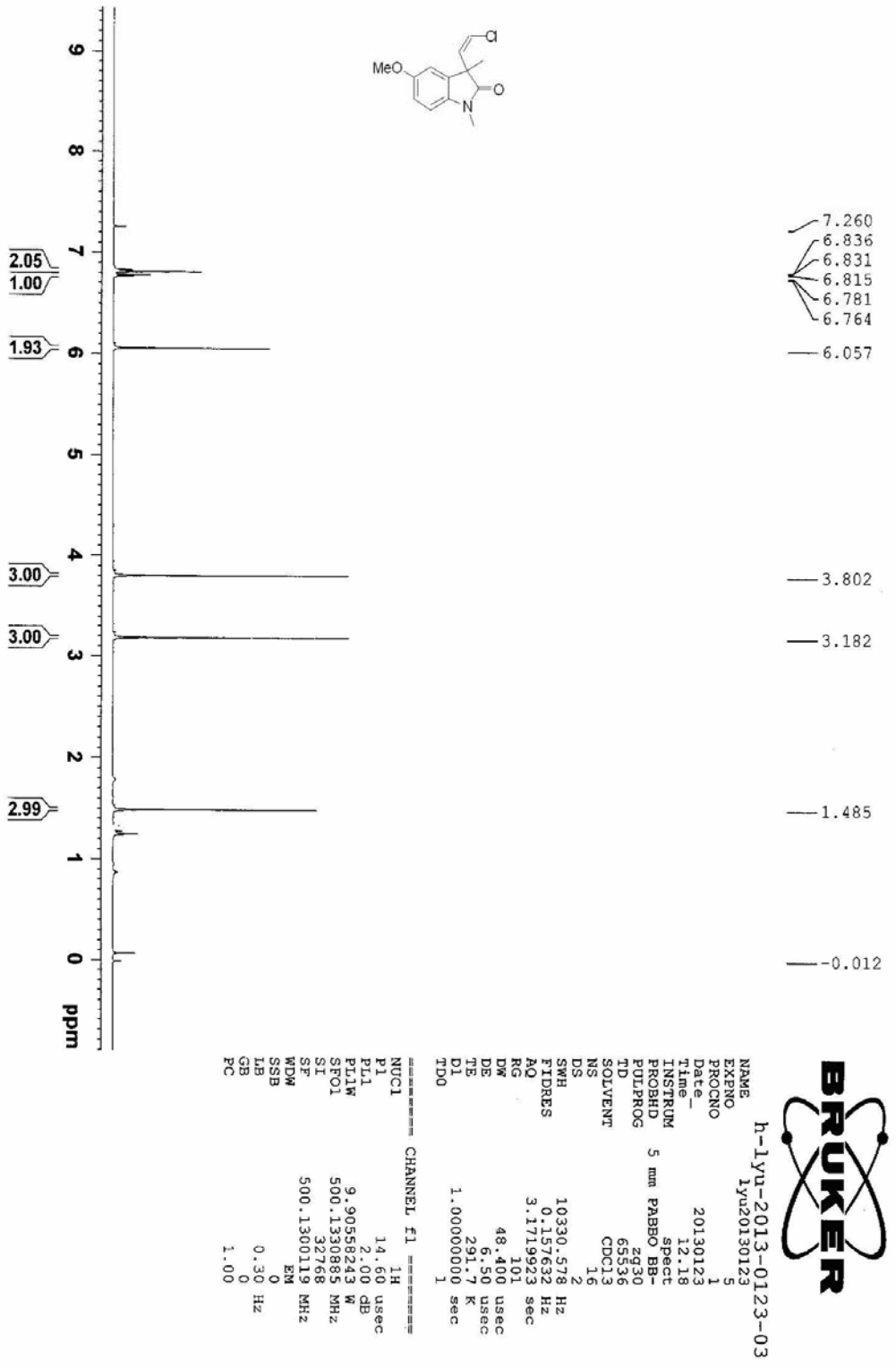
(*Z*)-5-butyl-3-(2-chlorovinyl)-1,3-dimethylindolin-2-one (4ha):



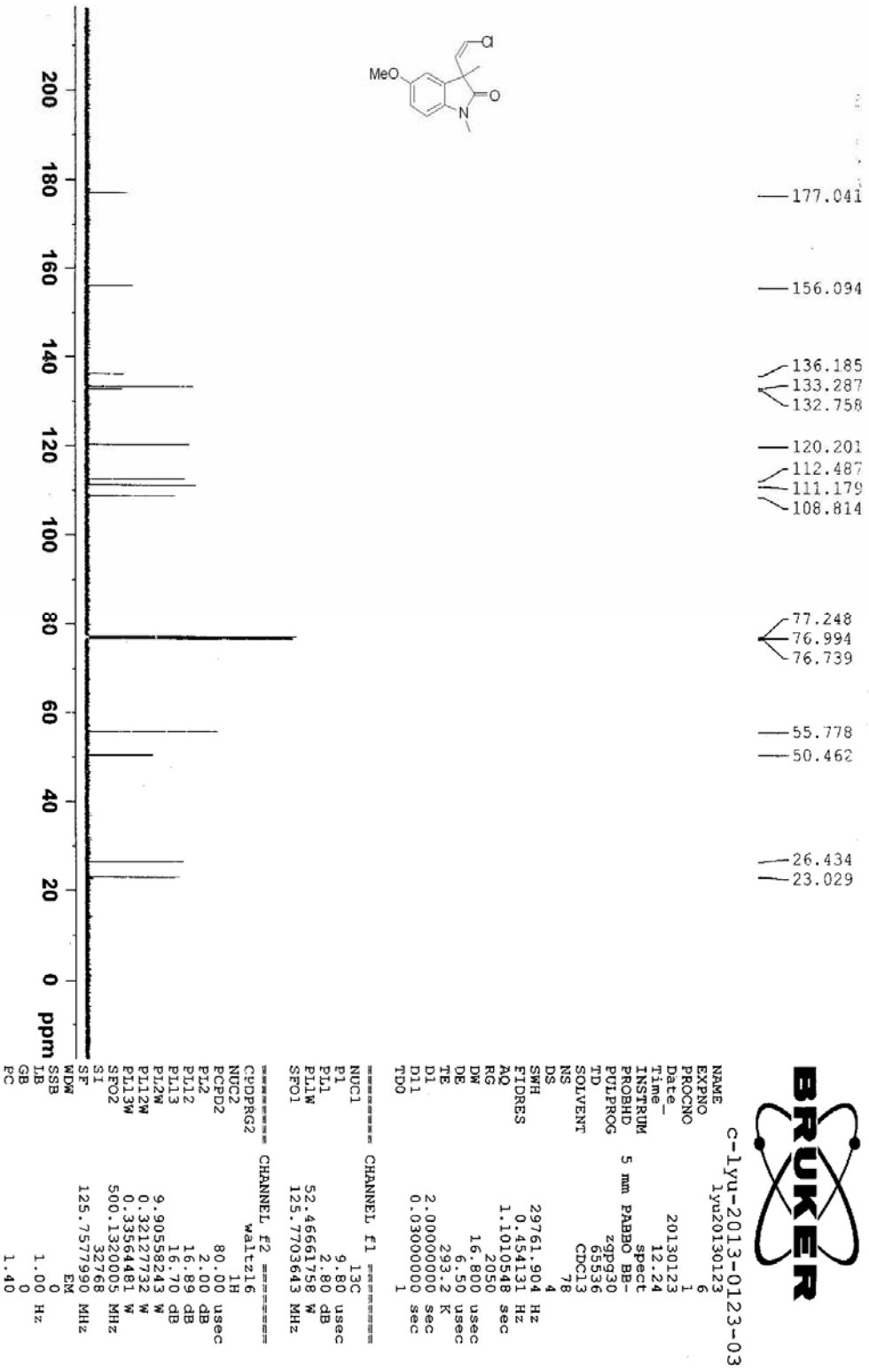
(*Z*)-5-butyl-3-(2-chlorovinyl)-1,3-dimethylindolin-2-one (4ha):



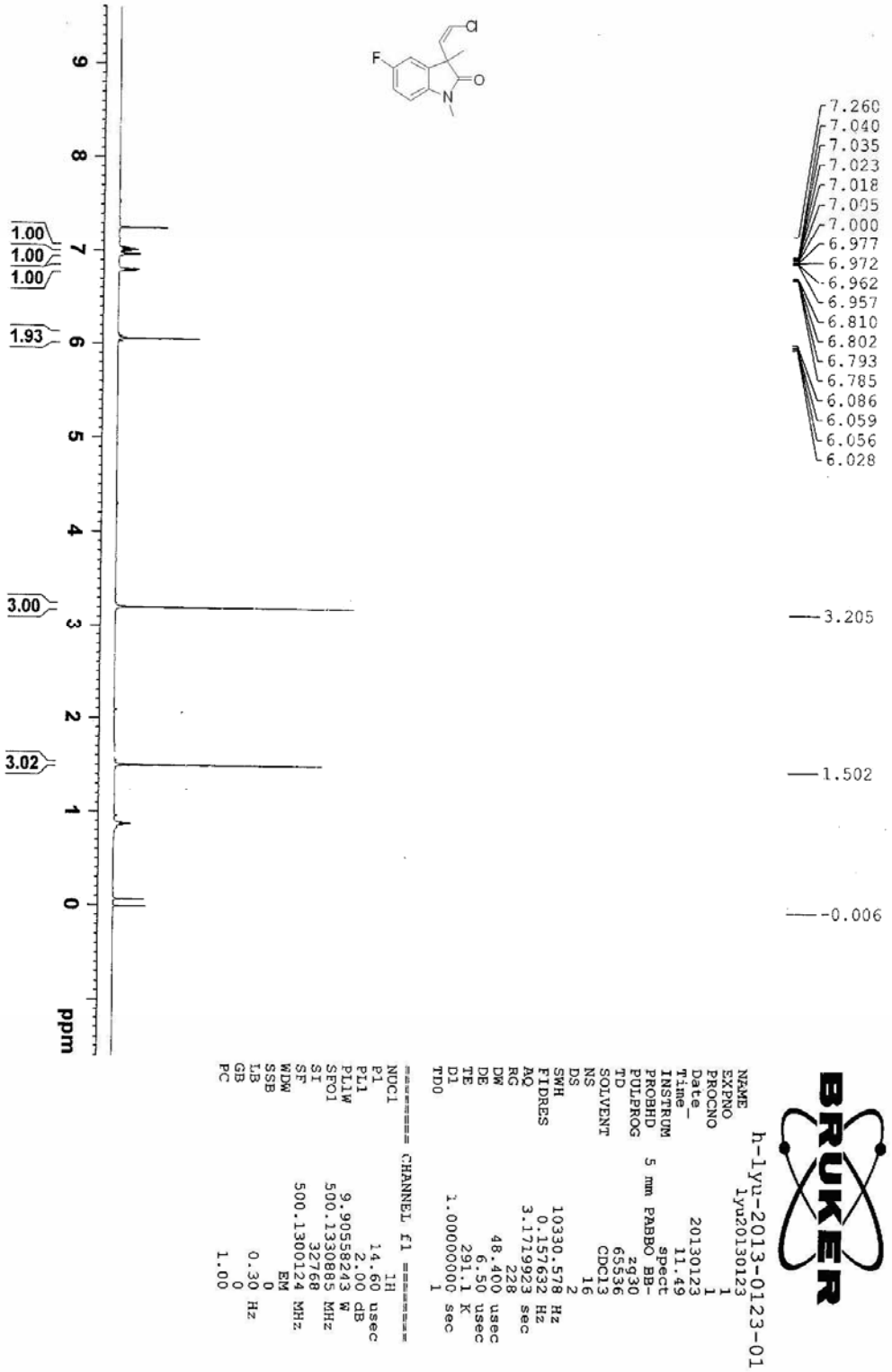
(*Z*)-3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ia):



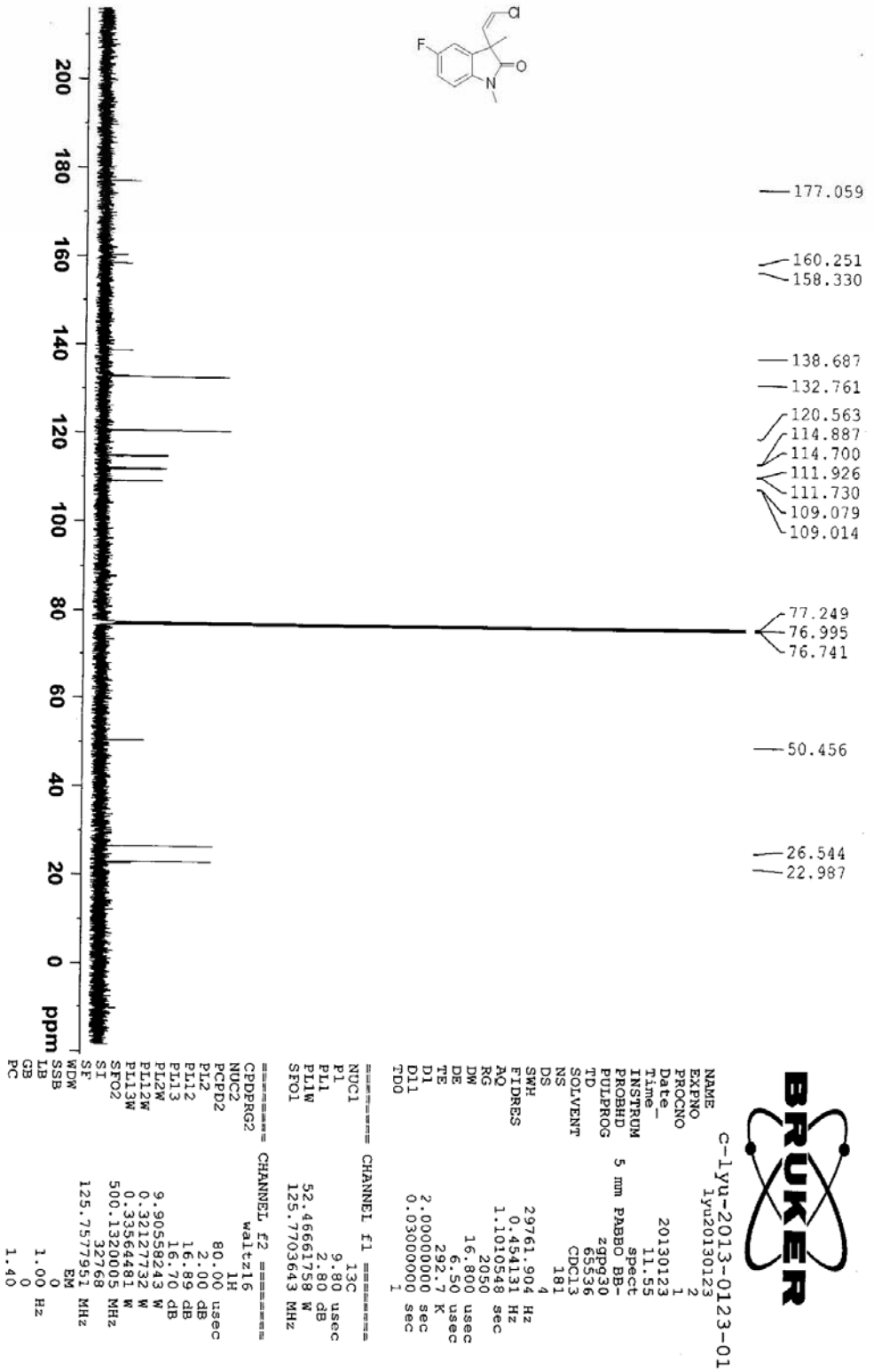
(*Z*)-3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ia):



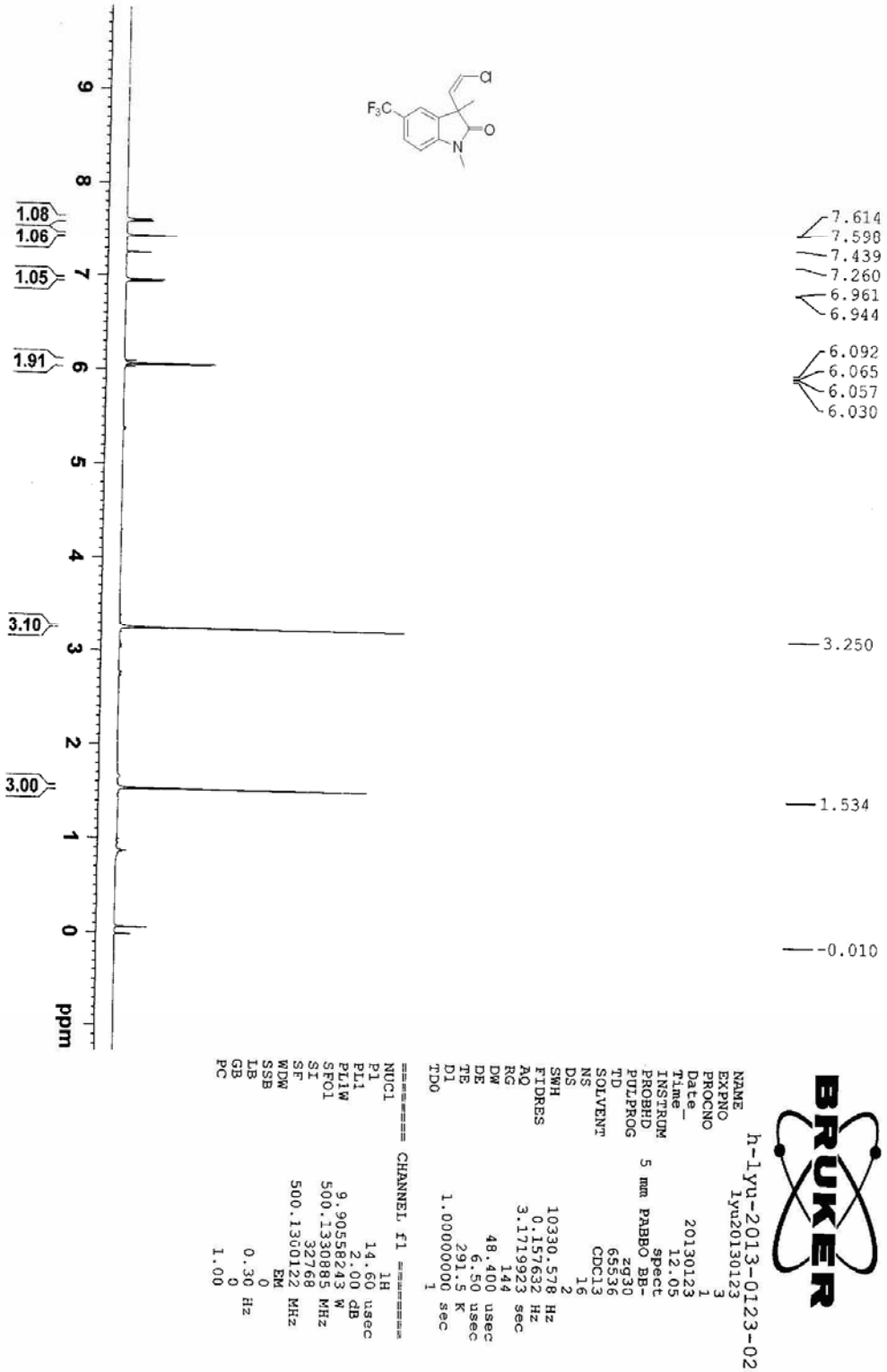
(*Z*)-3-(2-Chlorovinyl)-5-fluoro-1,3-dimethylindolin-2-one (4ka):



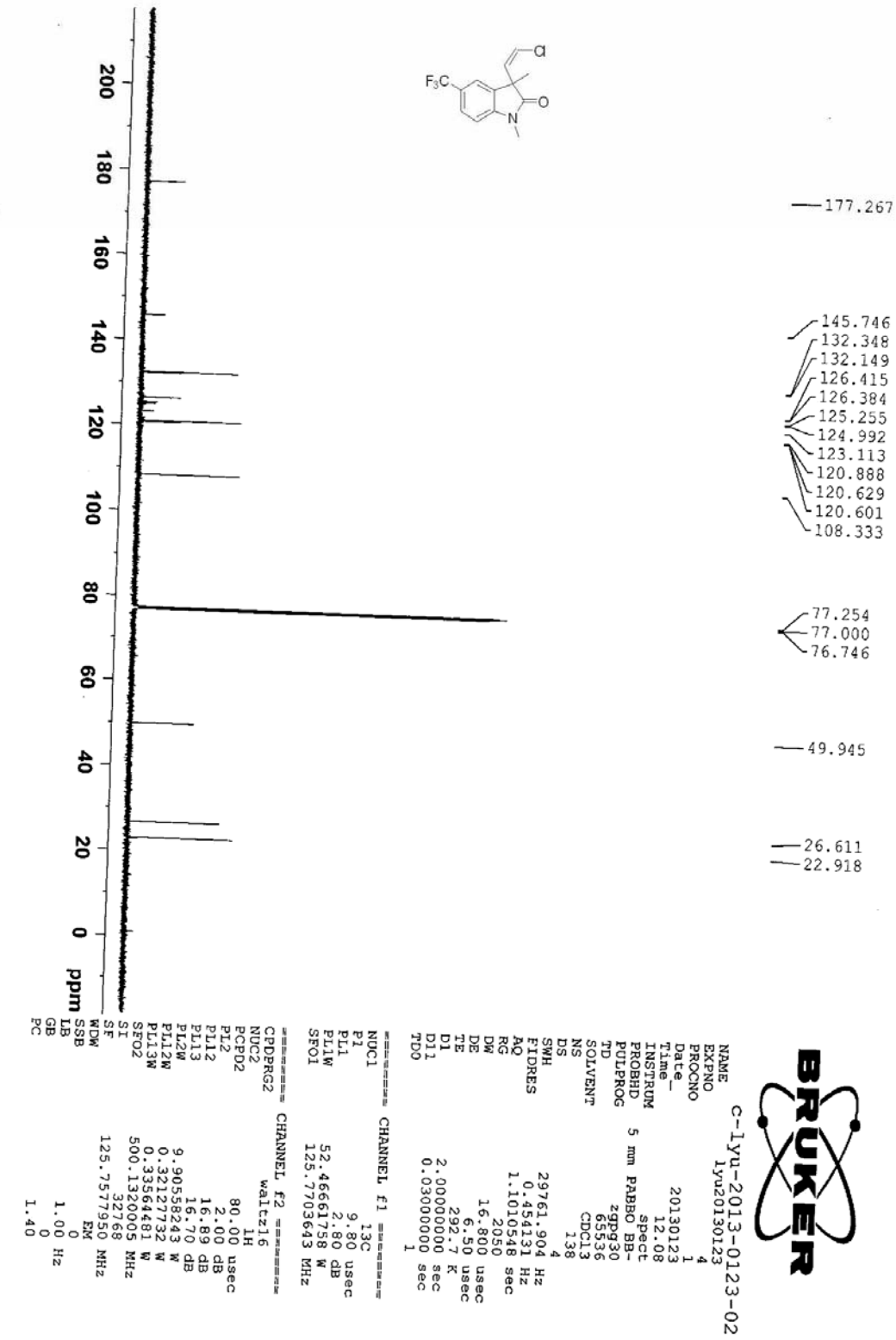
(*Z*)-3-(2-Chlorovinyl)-5-fluoro-1,3-dimethylindolin-2-one (4ka):



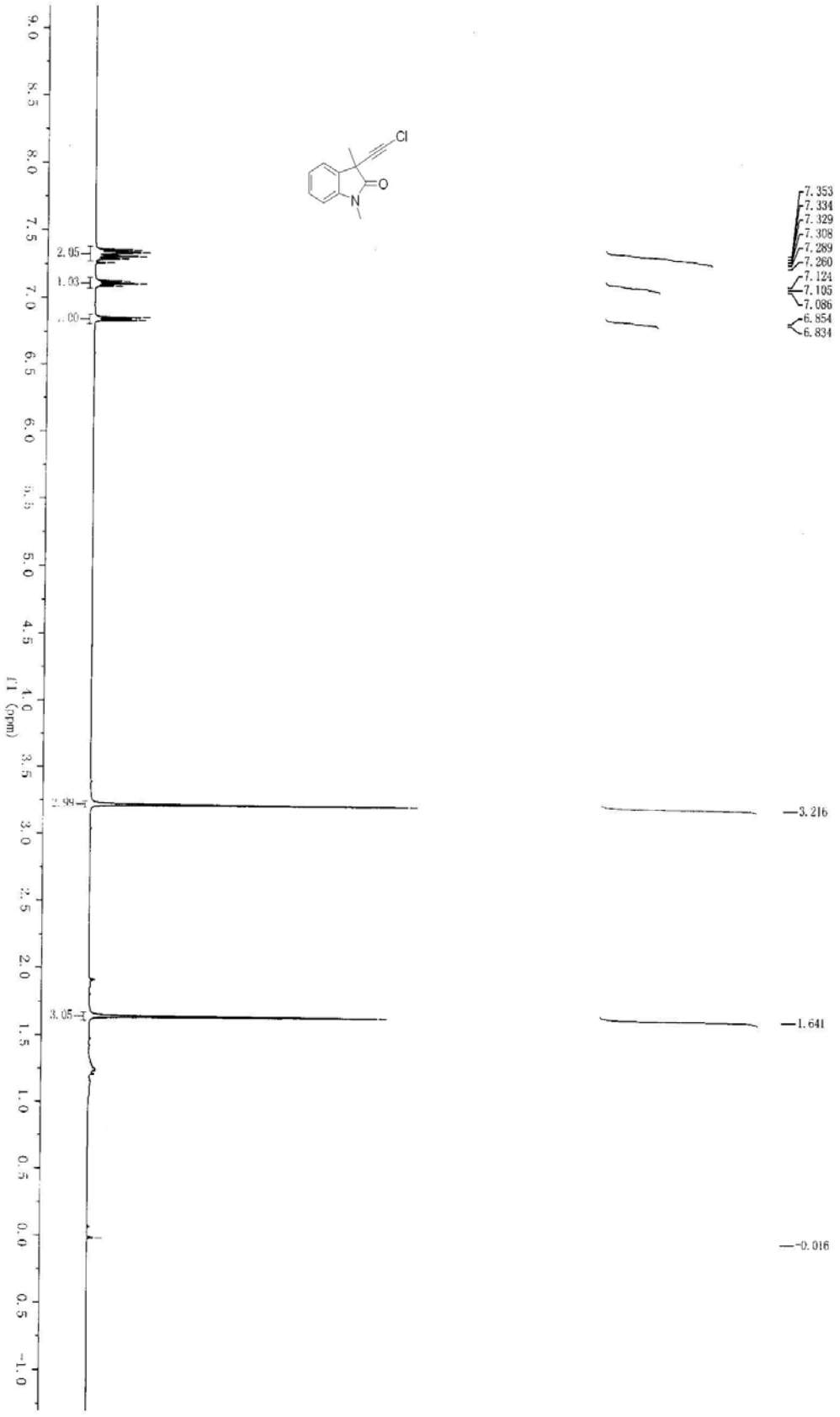
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (4la):



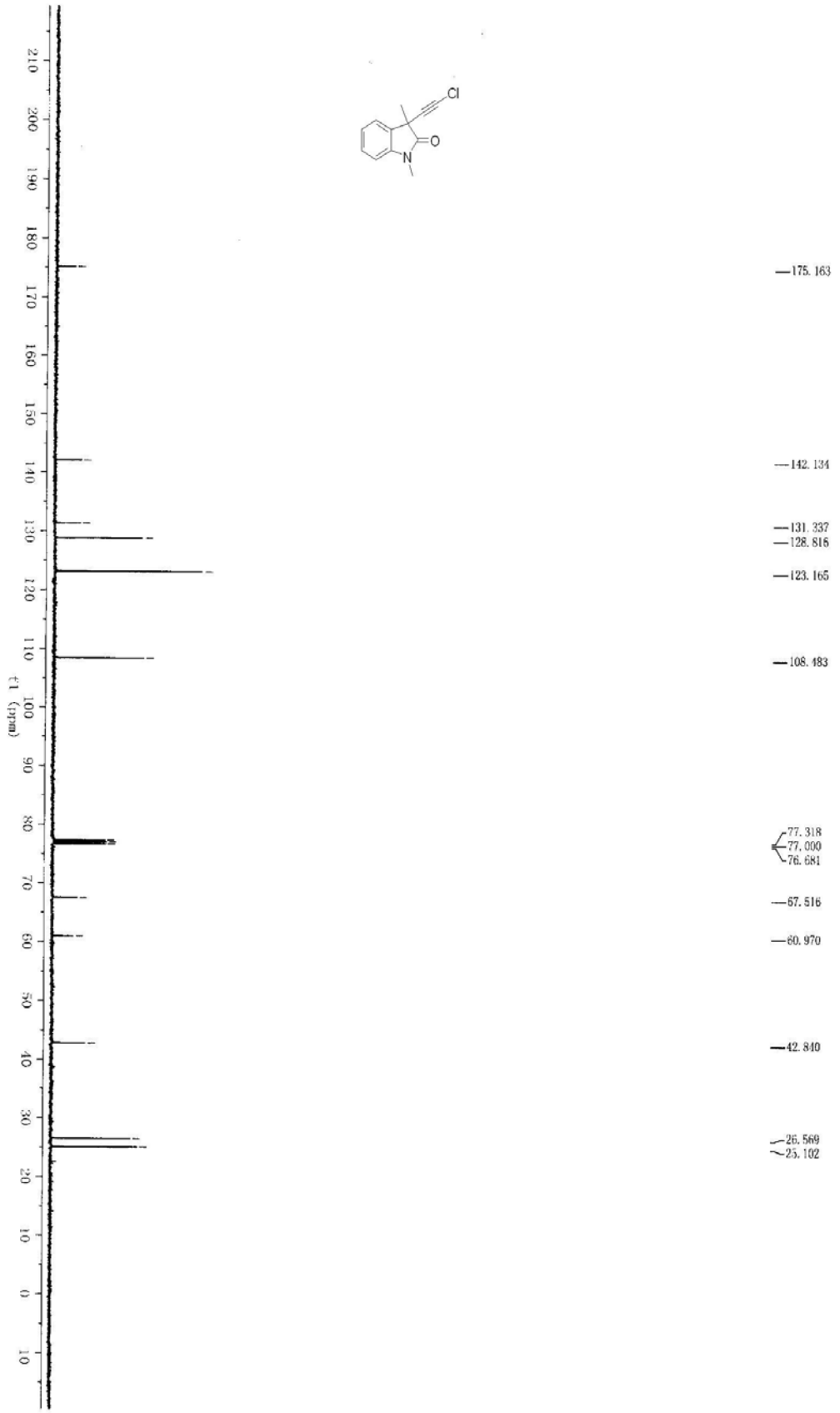
(*Z*)-3-(2-Chlorovinyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (4la):



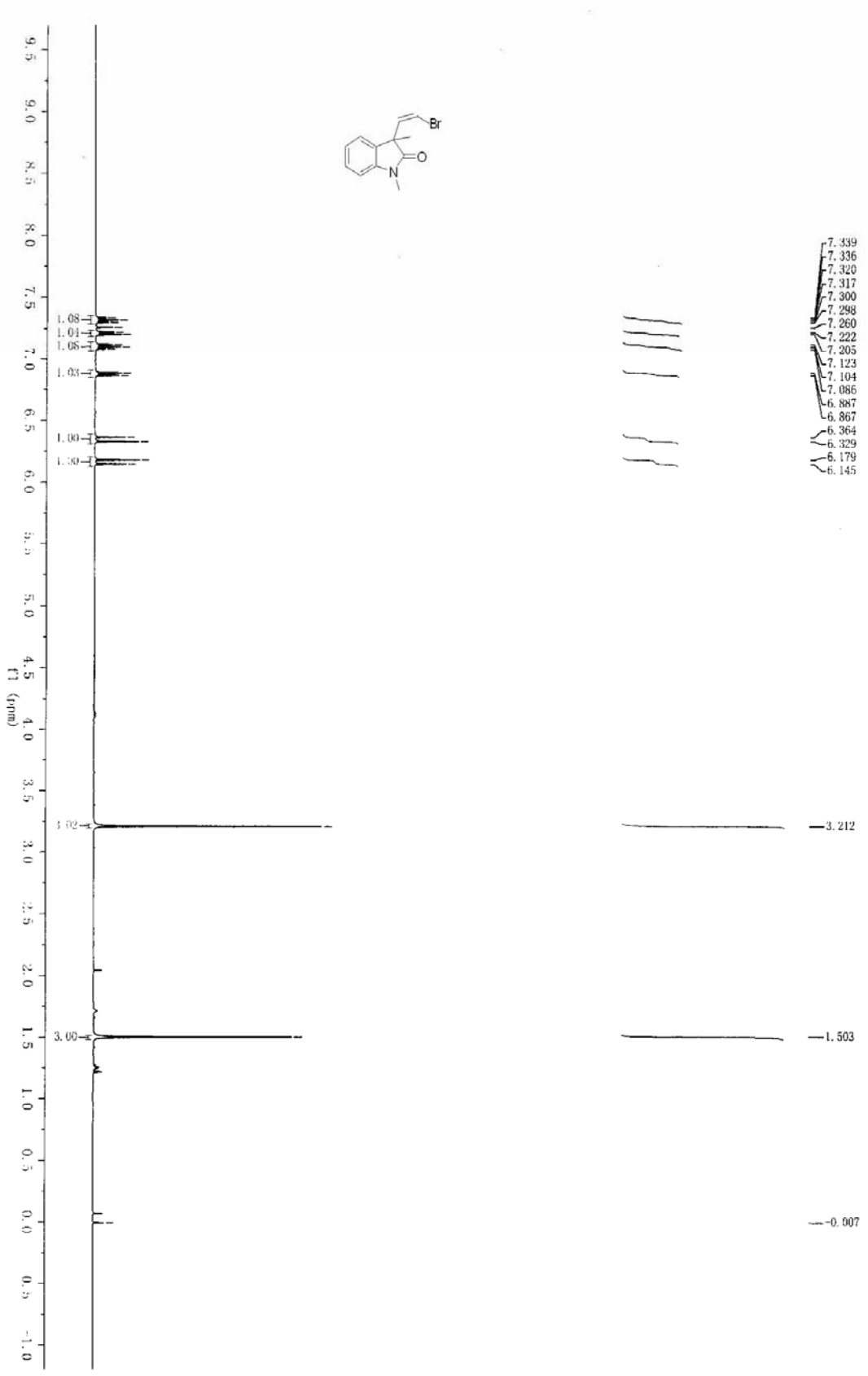
3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ah):



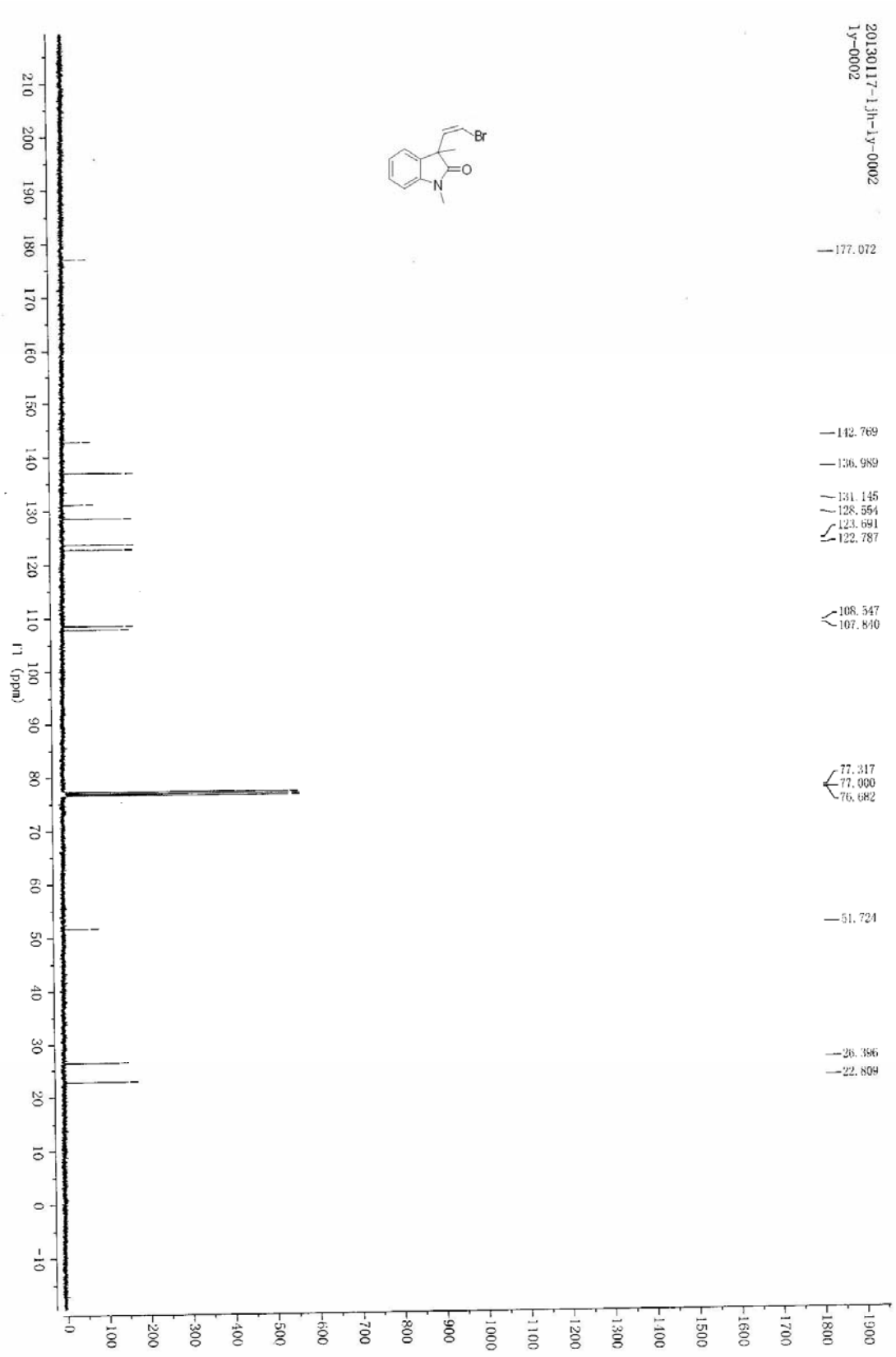
3-(2-Chlorovinyl)-5-methoxy-1,3-dimethylindolin-2-one (4ah):



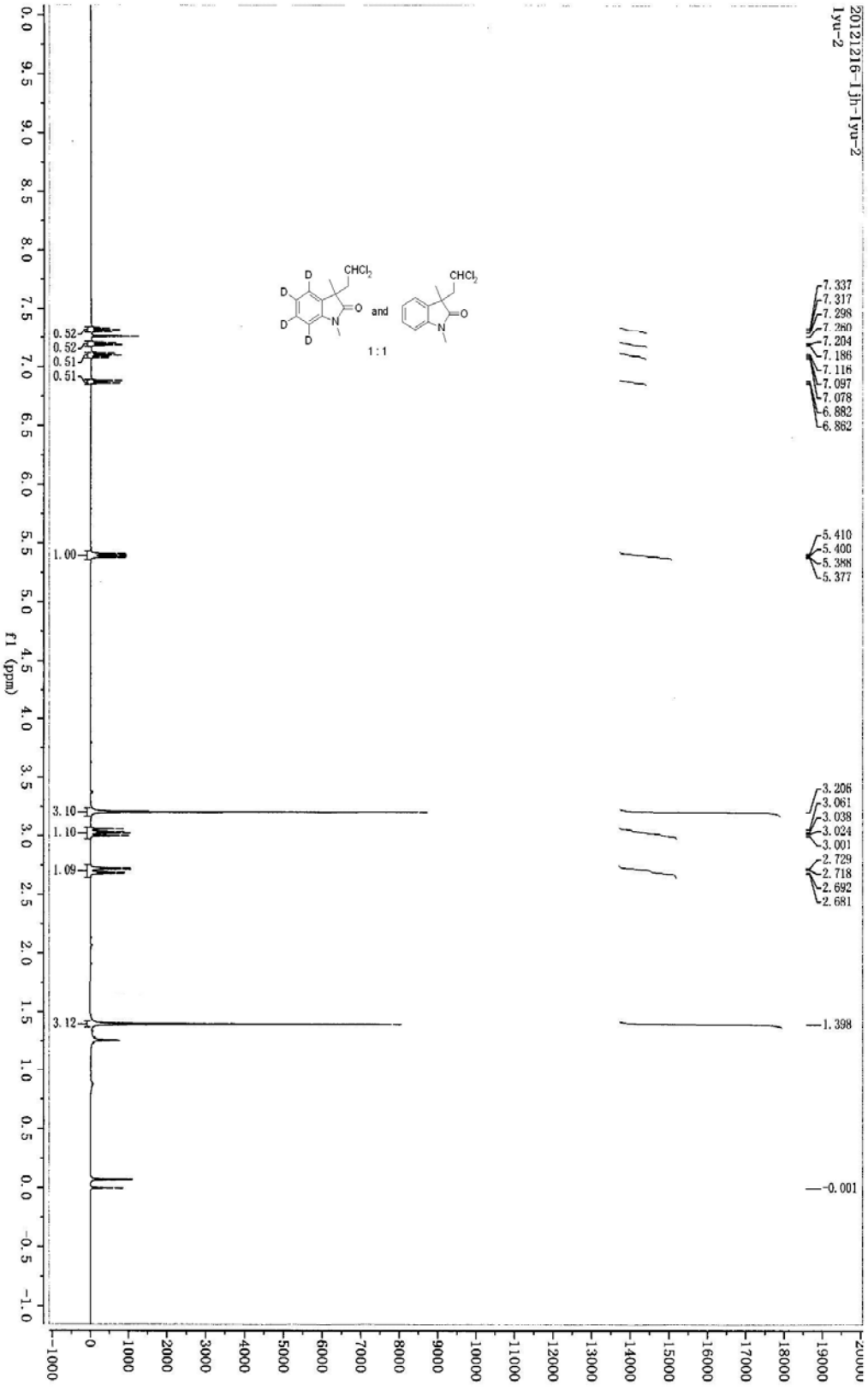
(*Z*)-3-(2-Bromovinyl)-1,3-dimethylindolin-2-one (4aj):



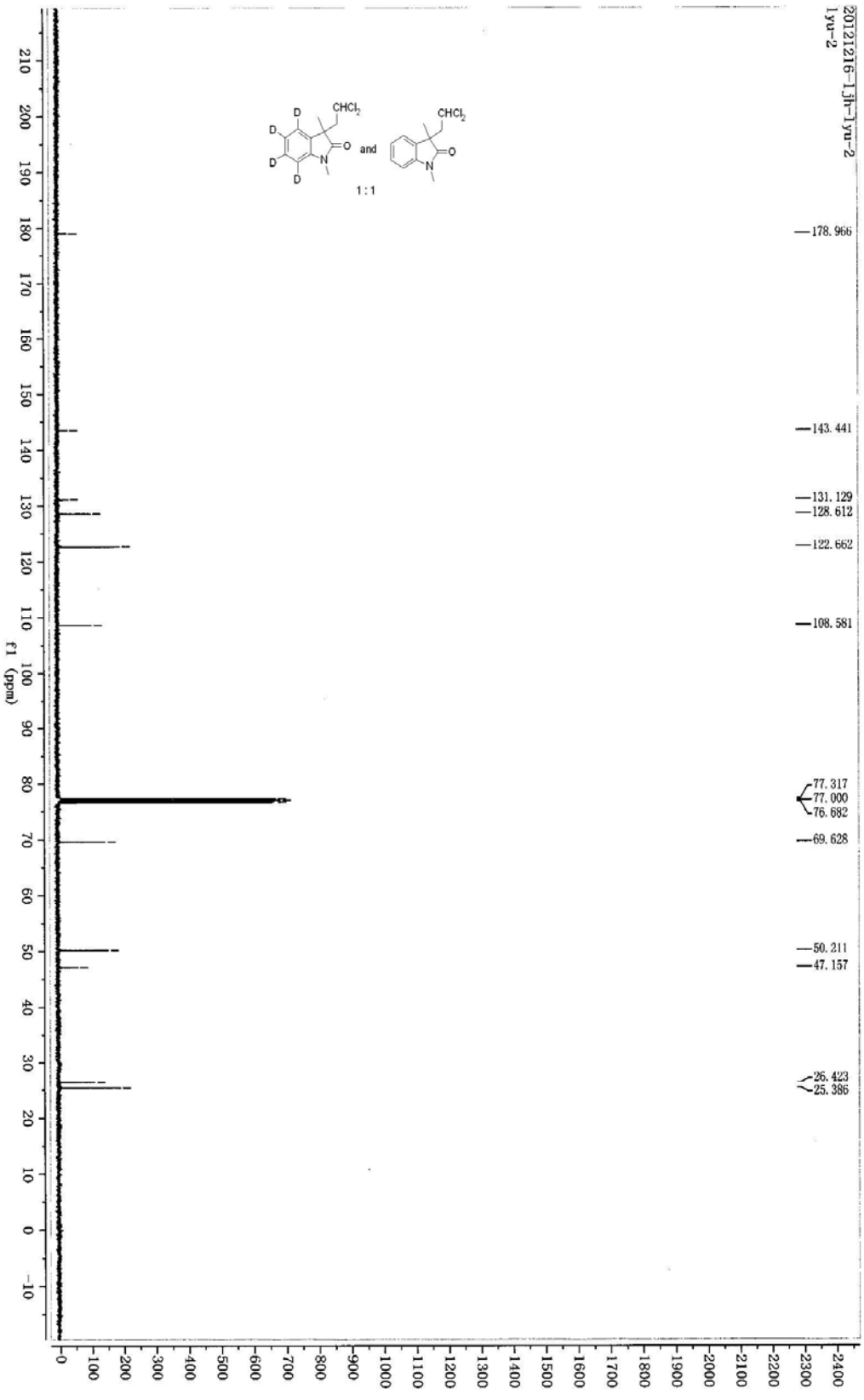
(*Z*)-3-(2-Bromovinyl)-1,3-dimethylindolin-2-one (4aj):



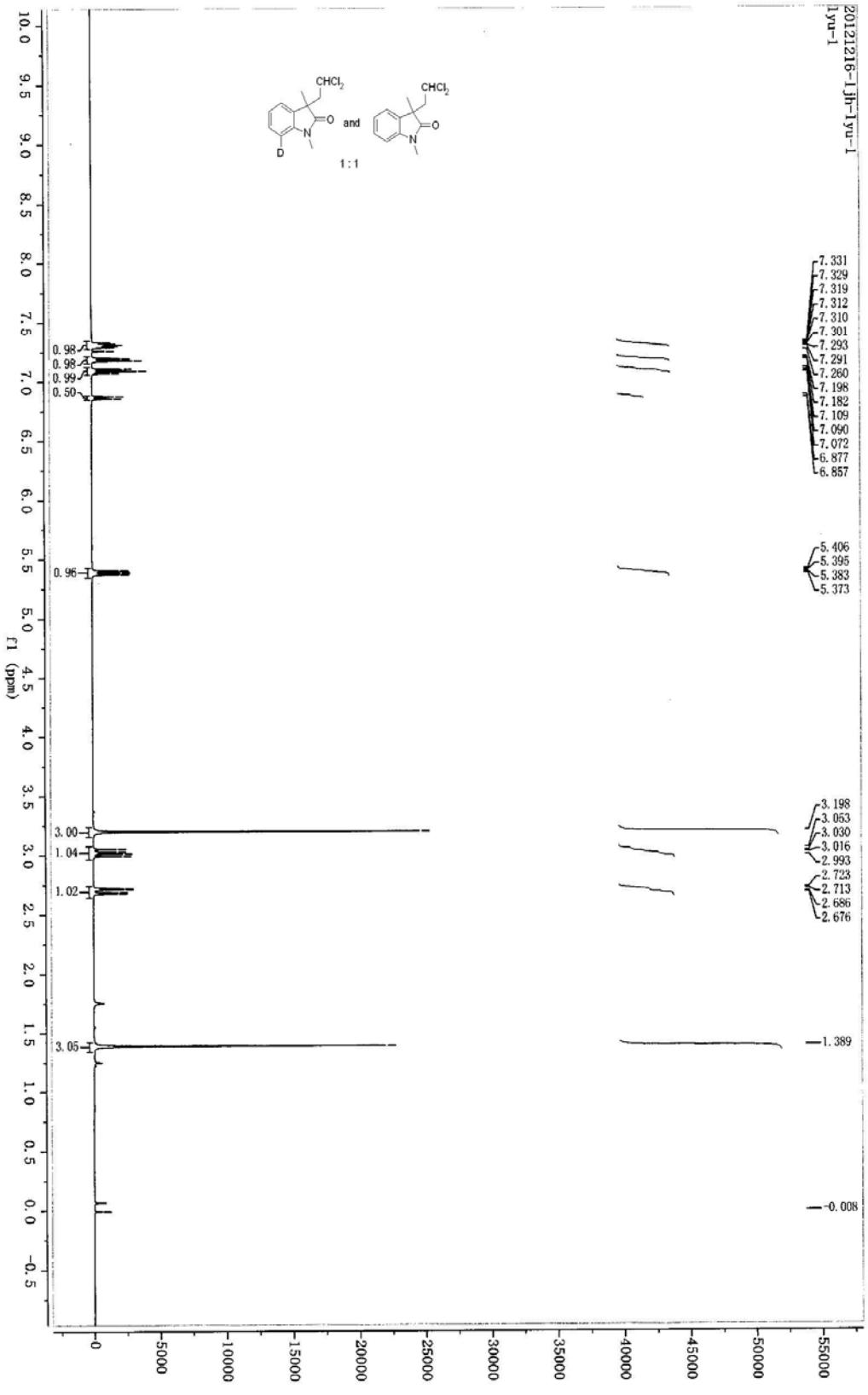
3aa and 3aa-D4:



3aa and 3aa-D4:



3aa and 3aa-D1:



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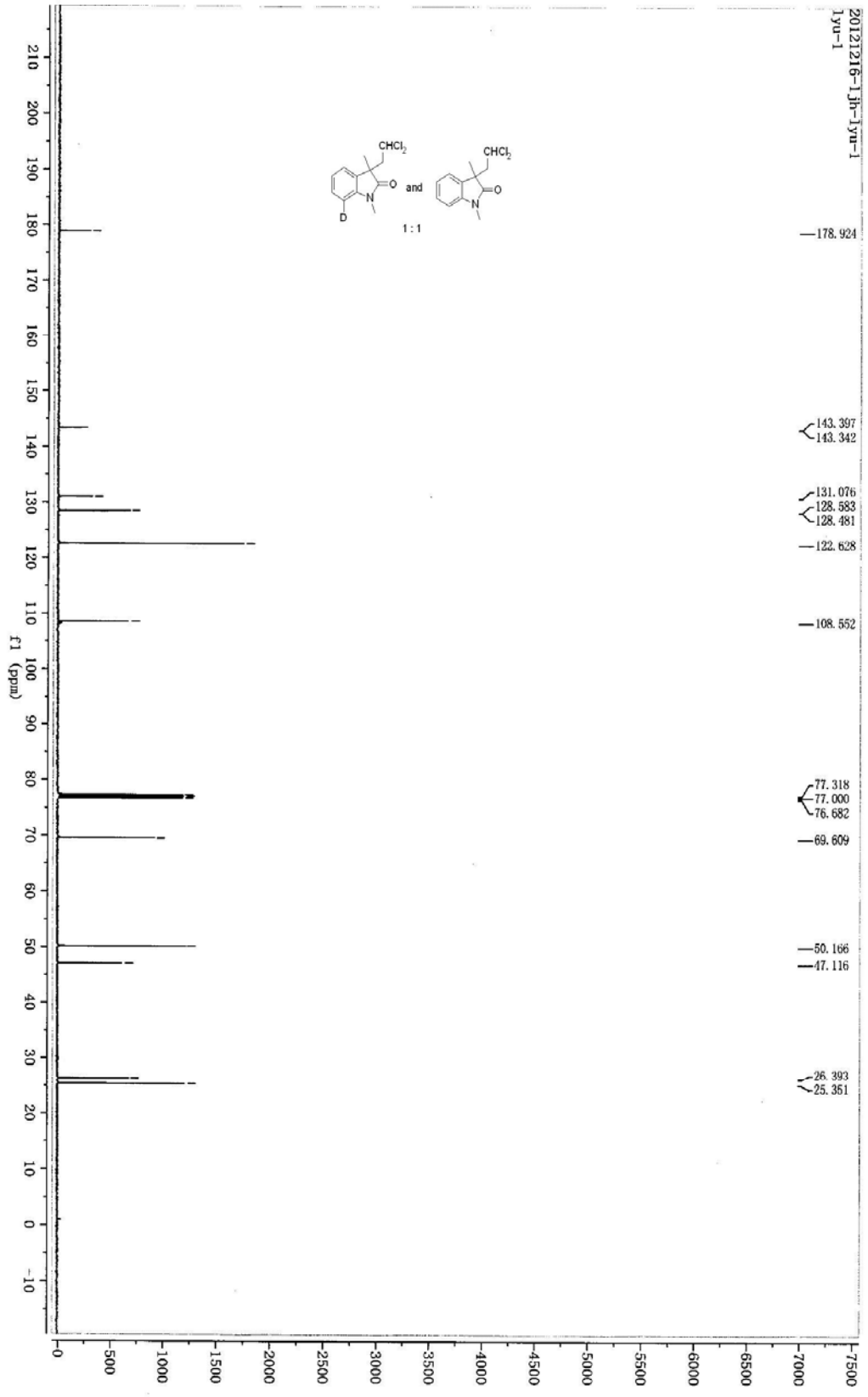
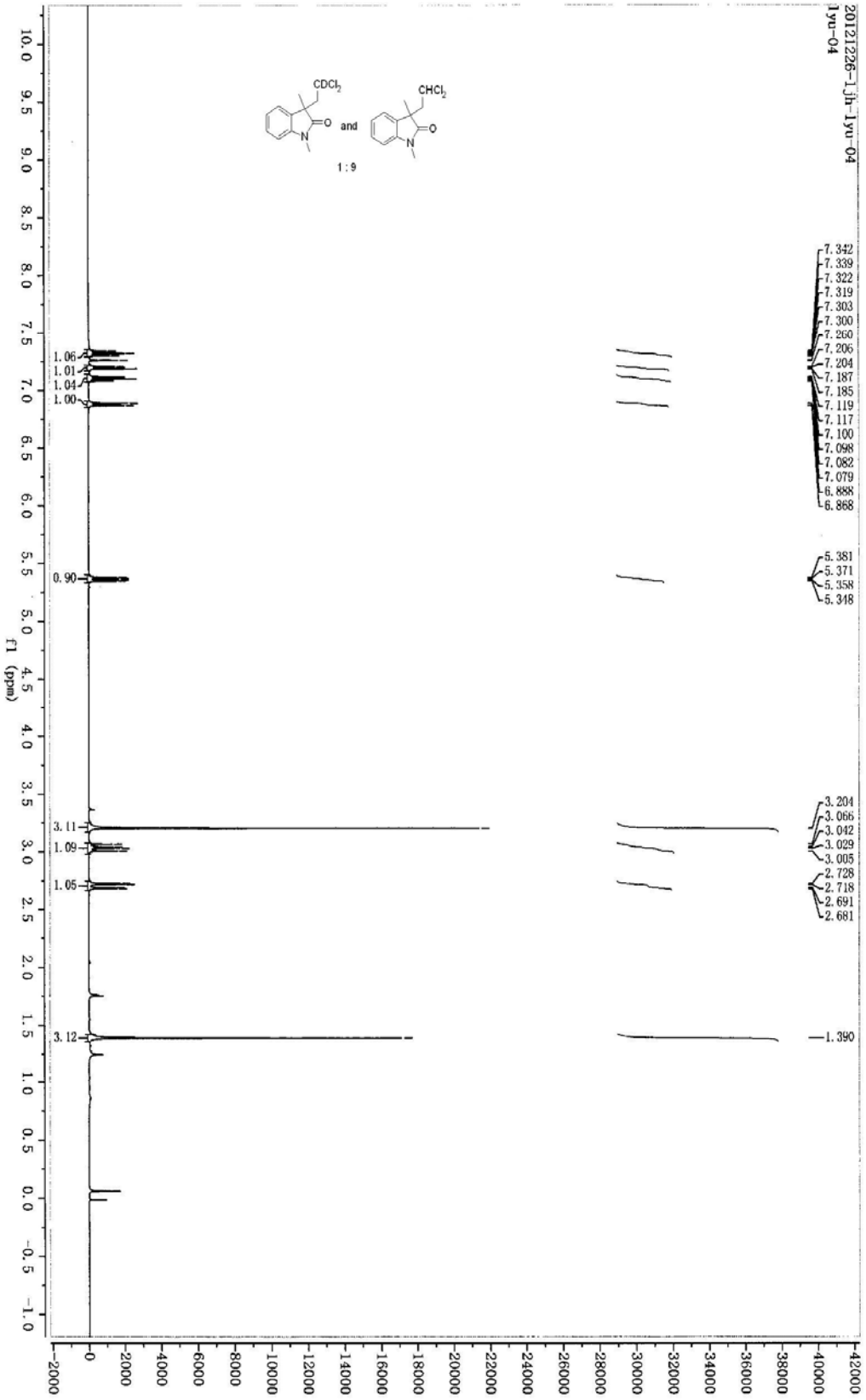
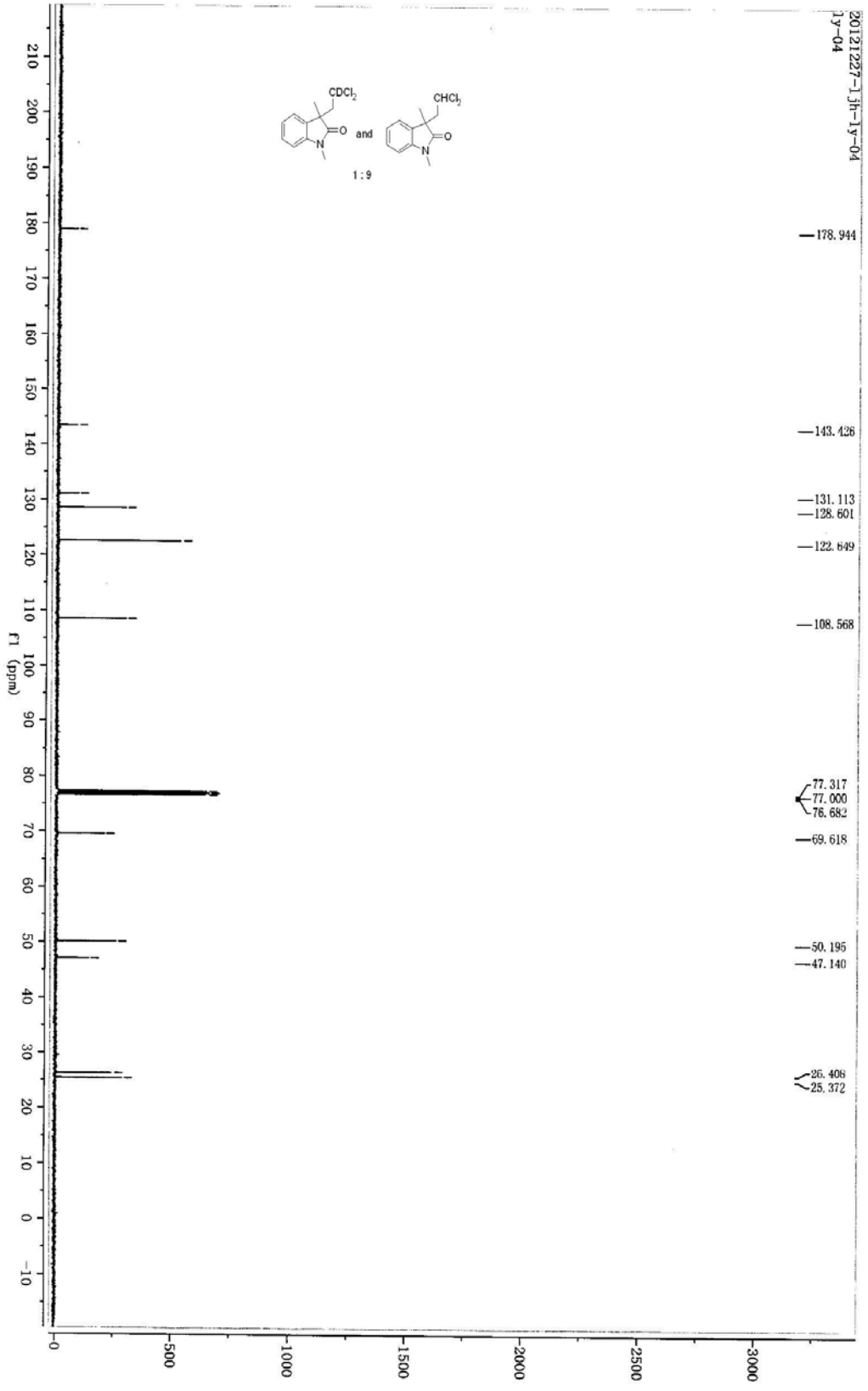


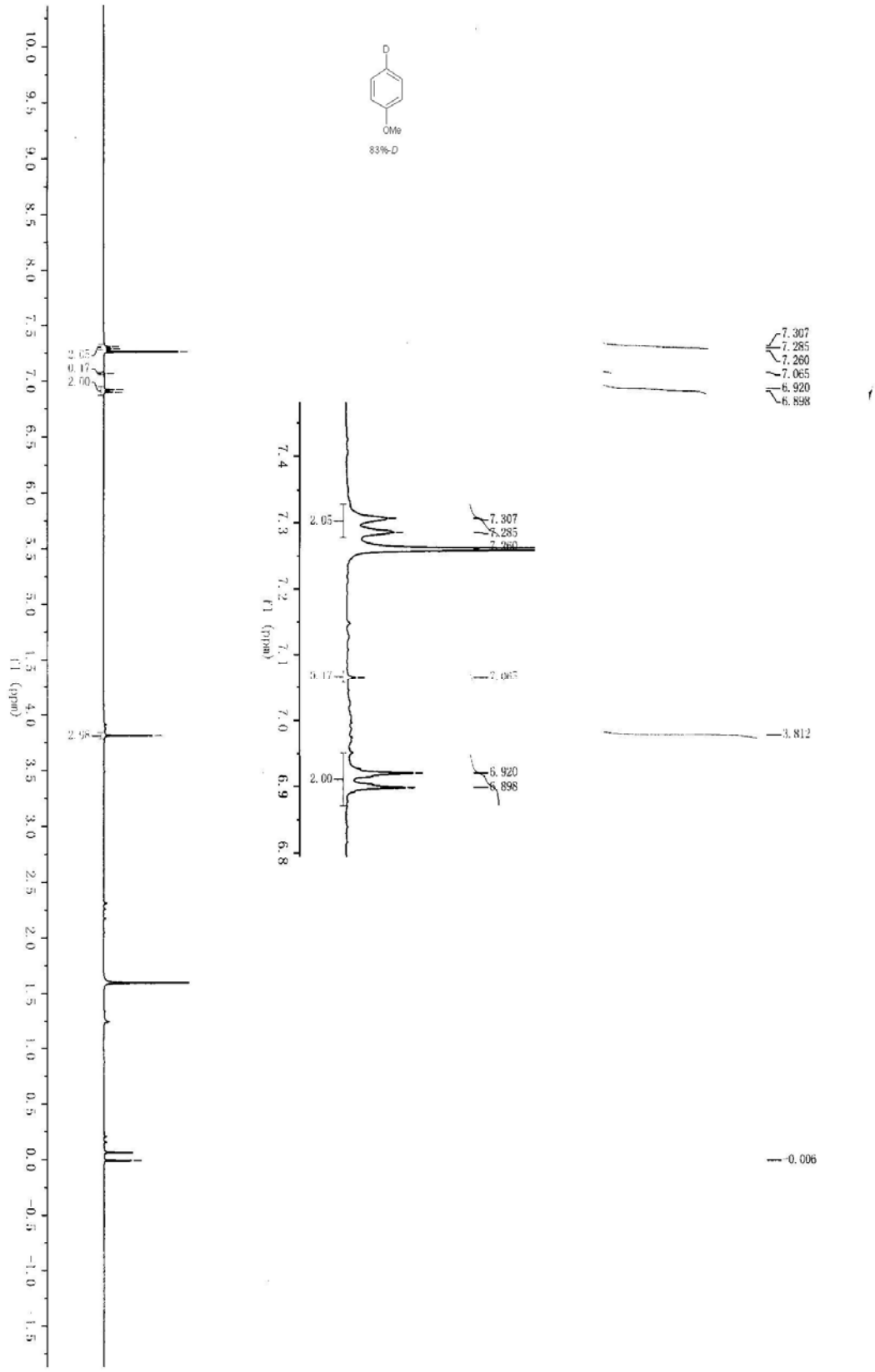
3aa and 3aa-D1':



3aa and 3aa-D1':



Addition of Na_2CO_3, $MeOC_6H_4N_2BF_4$



Addition of $Ru(bpy)_3Cl_2$, Na_2CO_3, $MeOC_6H_4N_2BF_4$ and visible light