Electronic Supplementary Information

An Oxidative Cross-Dehydrogenative–Coupling Reaction in Water using Molecular Oxygen as the Oxidant: Vanadium Catalyzed Indolation of Tetrahydroisoquinolines

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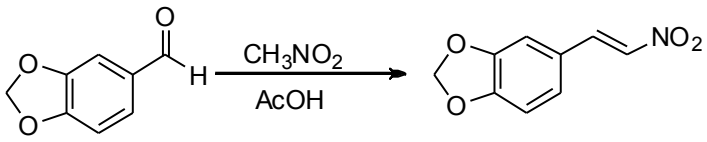
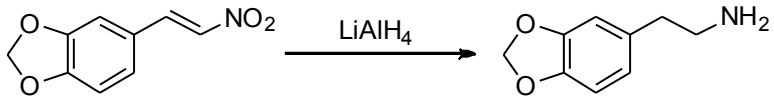
Typical experimental procedure for the Preparation of Nitroolefin



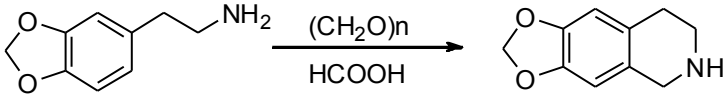
Heliotropin (5 g, 33.3 mmol) and ammonium acetate (2.56 g, 33.3 mmol) were taken into the RB flask. Nitromethane (8.9 mL, 166.5 mmol) and glacial acetic (10 mL) acid were added at room temperature. The reaction mixture was refluxed for 1.5h, and then reaction mixture was cooled in an ice bath, filtered through sintered crucible and washed successively with water, hexane and 1% ethanol in hexane. The crude mixture was concentrated under vacuo.

Typical experimental procedure for the reduction of nitroolefin



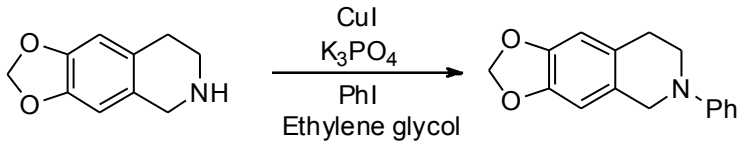
The crude nitroolefin (2 g, 10.3 mmol) in dry THF (10 mL) was added drop wise to a stirred solution of $LiAlH_4$ (0.98 g, 25.9 mmol) in THF (20 mL). The reaction mixture was refluxed for 4h and then cooled in ice bath, quenched with saturated solution of Na_2SO_4 until effervescence ceases completely. Then filtered through sintered crucible and washed successively with ethyl acetate and concentrated under vacuo.

Typical experimental procedure for the preparation of [1, 3]dioxolo[7, 8-g]- 1, 2, 3, 4-tetrahydroisoquinoline



The amine (1.35 g, 8.18 mmol) obtained in previous step was added to formic acid (3.5 mL) at 0 ^{o}C and stirred for 10 min at same temperature until complete dissolution of amine. Then paraformaldehyde (0.25 g, 8.18 mmol) was added and stirred at 50 ^{o}C for 24h, added saturated NaOH solution and extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then purified by column chromatography on silica gel using MeOH/ $CHCl_3$.

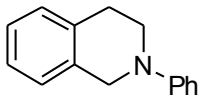
Typical experimental procedure for the preparation of *N*-phenyl THIQ.



Copper (I) iodide (0.21g, 1.13 mmol) and potassium phosphate (4.8 g, 22.6 mmol) were taken into the RB flask filled with nitrogen. 2-Propanol (10 mL), ethylene glycol (1.24 mL, 22.6 mmol), 1,2,3,4-tetrahydro-isoquinoline (2 g, 11.3 mmol) and iodobenzene (1.26 mL, 11.3 mmol) were added successively at room temperature. The reaction mixture was heated at 90 °C for 24 h and then allowed to cool to room temperature. The solvent was removed under vacuo, added water (20 mL) and extracted with dichloromethane (3x 30 mL). The organic layer was dried over sodium sulfate. The solvent was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/ethyl acetate=95:5), to give the desired product **4a** with 30% isolated yields.

Characterization data for *N*-phenyl THIQ

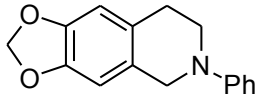
1, 2, 3, 4-Tetrahydro-2-phenylisoquinoline (1a).[1]



1a

Pale yellow solid; Yield - 60%; ***mp***: 44 - 46 °C (lit.[1] 45 °C); R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2824, 1599, 1505, 1388, 1238, 1156, 1034, 934, 873, 749; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (2H, t, *J* = 7.9 Hz), 7.15 (4H, d, *J* = 3.8 Hz), 6.97 (2H, d, *J* = 8.1 Hz), 6.81 (1H, t, *J* = 7.2 Hz), 4.39 (2H, s), 3.54 (2H, t, *J* = 5.8 Hz), 2.96 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.5, 134.8, 134.4, 129.1, 128.4, 126.4, 126.2, 125.9, 118.6, 115.0, 50.6, 46.4, 29.0; **HRESI-MS** *(m/z)*: Calculated for $C_{15}H_{15}N$ (M + H): 210.1283, found (M + H): 210.1286.

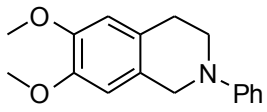
[1,3]dioxolo[7, 8-g]-2-phenyl-1, 2, 3, 4-tetrahydroisoquinoline (1b)



1b

Pale yellow solid; Yield - 30%; ***mp***: 65 - 66 °C; R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2807, 1583, 1508, 1460, 1385, 1273, 1241, 1207, 1190, 1036, 823, 755; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (2H, t, *J* = 7.8 Hz), 6.95 (2H, d, *J* = 8.1 Hz), 6.82 (1H, t, *J* = 7.2 Hz), 6.61 (2H, s), 5.90 (2H, s), 4.29 (2H, s), 3.51 (2H, t, *J* = 5.8 Hz), 2.86 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.3, 146.1, 145.9, 129.1, 127.8, 127.2, 118.7, 115.2, 108.3, 106.4, 100.6, 50.7, 46.6, 28.9; **HRESI-MS** *(m/z)*: Calculated for $C_{16}H_{15}NO_2$ (M + H): 254.1181, found (M + H): 254.1185.

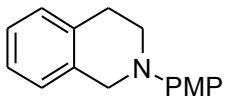
6, 7-dimethoxy-2-phenyl-1, 2, 3, 4-tetrahydroisoquinoline (1c).[2]



1c

Pale yellow solid; Yield - 30%; ***mp***: 91- 93 °C; R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3446, 1601, 1519, 1466, 1384, 1271, 1238, 1116, 1025, 861, 761; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 (2H, t, *J* = 7.8 Hz), 6.98 (2H, d, *J* = 8.2 Hz), 6.82 (1H, t, *J* = 7.2 Hz), 6.64 (2H, d, *J* = 4.2 Hz), 4.33(2H, s), 3.87 (3H, s), 3.86 (3H,s), 3.54 (2H, t, *J* = 5.8 Hz), 2.89 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.5, 147.5, 147.4, 129.1, 126.6, 126.1, 118.7, 115.3, 111.2, 109.3, 55.94, 55.90, 50.4, 46.7, 28.5; **HRESI-MS** *(m/z)*: Calculated for $C_{17}H_{19}NO_2$ (M + Na): 292.1313, found (M + Na): 292.1314.

1, 2, 3, 4-Tetrahydro-2- (4-methoxyphenyl)isoquinoline (1d).[1]



1d

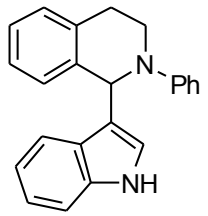
Pale yellow solid; Yield - 50%; ***mp***: 93 - 95 °C (lit.[1] 95 °C); R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3456, 1584, 1510, 1459, 1384, 1273, 1242, 1151, 1036, 823, 755; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 – 7.18 (4H, m), 6.98 (2H, d, *J* = 8.8 Hz), 6.86 (2H, d, *J* = 8.8 Hz), 4.29 (2H, s), 3.77 (3H, s), 3.43 (2H, t, *J* = 5.8 Hz), 2.98 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.4, 145.2, 134.5, 134.4, 128.6, 126.4, 126.2, 125.8, 118.0, 114.5, 55.5, 52.6, 48.4, 29.0; **HRESI-MS** *(m/z)*: Calculated for $C_{16}H_{17}NO$ (M + H): 240.1388, found (M + H): 240.1387.

Typical experimental procedure for the synthesis of Indolyl tetrahydroisoquinoline

A well-stirred mixture of V_2O_5 (10 mol% , 18.2 mg, 0.1 mmol), *N*-phenyl tetrahydroisoquinoline **1a** (209 mg, 1 mmol) and indole **2a** (140 mg, 1.2 mmol) in water (2mL) was heated at reflux under oxygen atmosphere (oxygen balloon) for 24h. The reaction mixture was cooled to room temperature, added aq. KOH (20%) solution and extracted with dichloromethane (3 x 15 mL). The combined organic layer was washed with water, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc / hexane 5 : 95) to afford **3a** (71%, 231 mg).

Characterization data for indolation of *N*-phenyl THIQ

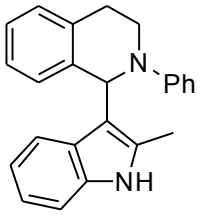
Compound (3a).[3]



3a

Pale yellow solid; Yield - 71%; ***mp***: 166 - 169 °C (lit.[3] 179 - 180 °C); R_f (20% EtOAc/Hexane) 0.25; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3409, 2922, 1615, 1596, 1494, 1339, 1214, 1094, 1032, 937, 746; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (1H, broad s), 7.54 (1H, d, J = 7.9 Hz), 7.29 – 7.21 (4H, m), 7.17 – 7.12 (4H, m), 7.03 – 7.00 (3H, m), 6.77 (1H, t, J = 7.2 Hz), 6.59 (1H, s), 6.16 (1H, s), 3.60 (2H, dd, J_1 = 4.6Hz, J_2 = 7.2 Hz), 3.09 – 3.01 (1H, m), 2.79 (1H, dt, J_1 = 4.2 Hz, J_2 = 16.1 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.7, 137.3, 136.5, 135.5, 129.1, 128.7, 128.0, 126.6, 126.4, 125.6, 124.1, 122.0, 120.0, 119.5, 119.2, 118.0, 115.7, 111.0, 56.5, 42.2, 26.5; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{20}N_2$ (M + H): 325.1705, found (M+ H): 325.1706.

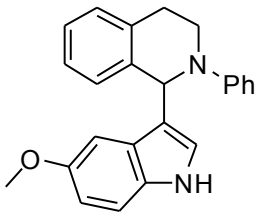
Compound (3b).[3]



3b

Pale yellow solid; Yield - 50%; ***mp***: 148 - 150 °C (lit.[3] 80 - 85 °C); R_f (20% EtOAc/Hexane) 0.25; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3405, 2924, 1640, 1597, 1494, 1460, 1368, 1302, 1213, 1127, 936, 741; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (1H, broad s), 7.18 – 7.13 (5H, m), 7.06 – 6.98 (6H, m), 6.90 – 6.86 (1H, m), 6.83 – 6.79 (1H, m), 5.95 (1H, s), 3.70 – 3.56 (2H, m), 3.11 – 2.95 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.9, 138.0, 135.3, 134.8, 133.2, 128.7, 128.66, 128.60, 128.2, 126.2, 126.0, 120.7, 120.1, 119.45, 119.42, 119.1, 113.4, 109.9, 57.1, 45.8, 27.9, 12.2; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{22}N_2$ (M+s): 338.1783, found (M+): 338.1780.

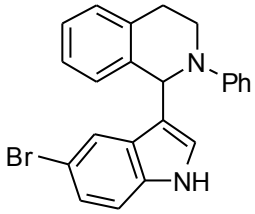
Compound (3c).[3]



3c

Pale yellow solid; Yield - 50%; ***mp***: 173 - 175 °C (lit.[3] 172 - 174 °C); R_f (20% EtOAc/Hexane) 0.25; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3422, 2925, 1598, 1118, 1019, 1036, 553; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (1H, broad s), 7.27 – 7.16 (8H, m), 7.02 (2H, d, J = 8.0 Hz), 6.87 (1H, s), 6.80 – 6.75 (2H, m), 6.56 (1H, s), 6.13 (1H, s), 3.65 (3H, s), 3.60 – 3.58 (2H, m), 3.10 – 3.03 (1H, m), 2.81 (1H, dt, J_1 = 4 Hz, J_2 = 16 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.8, 149.9, 137.4, 135.5, 131.5, 129.1, 128.7, 127.9, 126.8, 126.6, 125.6, 124.9, 118.6, 118.2, 116.1, 112.2, 111.6, 101.8, 56.8, 55.6, 42.0, 26.9; **MS** *(m/z)*: 354 (M^+); **Elemental analysis**: Calcd for $C_{24}H_{22}N_2O$; C, 81.33; H, 6.26; N, 7.90; found - C, 81.01; H, 6.38; N, 8.36.

Compound (3d).

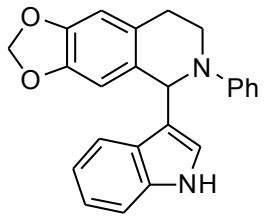


3d

Pale yellow solid; Yield - 44%; ***mp***: 185 - 187 °C; R_f (20% EtOAc/Hexane) 0.25; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3408, 2927, 1597, 1499, 1212, 1101, 1032, 937, 884, 751; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (1H, broad s), 7.59 (1H, s), 7.25 – 7.11

(8H, m), 6.99 (2H, d, J = 8.1 Hz), 6.80 (1H, t, J = 7.2 Hz), 6.57 (1H, d, J = 1.4 Hz), 6.06 (1H, s), 3.60 – 3.51 (2H, m), 3.08 – 2.96 (1H, m), 2.78 (1H, dt, J_1 = 4.4 Hz, J_2 = 16.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.8, 136.9, 135.3, 135.1, 129.1, 128.8, 128.0, 127.9, 126.7, 125.7, 125.3, 124.9, 122.6, 118.9, 118.7, 116.4, 112.9, 112.4, 56.6, 42.5, 26.5; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{19}BrN_2$ (M): 425.0629, found (M): 425.0628.

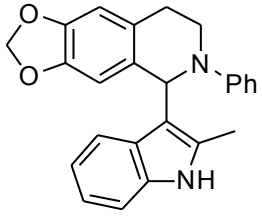
Compound (3e).



3e

Pale yellow solid; Yield - 65%; ***mp***: 178- 180 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3448, 2927, 1637, 1474, 1233, 1035, 746; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (1H, broad s), 7.53 (1H, d, J = 7.9 Hz), 7.32 (1H, d, J = 8.1 Hz), 7.25 – 7.21 (3H, m), 7.18 – 7.14 (1H, m), 7.04 – 7.00 (3H, m), 6.78 (1H, t, J = 7.2 Hz), 6.73 (1H, s), 6.68 (1H, d, J = 1.8 Hz), 6.60 (1H, s), 6.05 (1H, s), 5.89 (2H, dd, J_1 = 1.3 Hz, J_2 = 4.6 Hz), 3.62 – 3.51 (2H,m), 3.00 – 2.92 (1H, m), 2.66 (1H, dt, J_1 = 4.0 Hz, J_2 = 16.1 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.8, 146.3, 145.5, 136.6, 130.2, 129.1, 128.6, 126.5, 124.1, 122.1, 120.1, 119.6, 119.2, 118.3, 116.2, 111.0, 108.6, 108.0, 100.6, 56.5, 42.2, 26.5; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{20}N_2O_2$ (M + Na): 391.1422, found (M + Na): 391.1411.

Compound (3f).

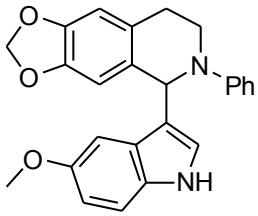


3f

Pale yellow solid; Yield - 77%; ***mp***: 125 - 127 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3402, 2901, 1711, 1599, 1482, 1462, 1382, 1231, 1037, 744; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (1H, broad s), 7.17 – 7.09 (4H, m), 7.03 – 6.96 (3H, m), 6.90 (1H, t, J = 7.6 Hz), 6.81 (1H, t, J = 7.2 Hz), 6.61 (1H, s), 6.49 (1H, s), 5.81 – 5.82 (3H, m), 3.64 – 3.50 (2H,m), 2.98 – 2.91 (1H, m), 2.83 (1H, dt, J_1 = 4.4 Hz, J_2 = 16.1 Hz), 1.98 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.8, 146.0, 145.9, 134.9, 133.3, 130.8, 128.8,

128.5, 128.3, 120.7, 120.2, 119.5, 119.4, 119.1, 113.2, 110.0, 108.2, 108.0, 100.6, 57.0, 45.6, 27.7, 12.1; **MS** *(m/z)*: 382 (M^+); **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{22}N_2O_2$ (M +): 382.1681, found (M +): 382.1682.

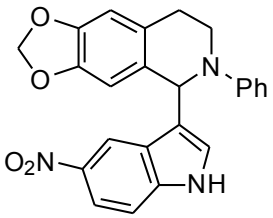
Compound (3g).



3g

Pale yellow solid; Yield - 77%; ***mp***: 77 - 79 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3407, 2924, 1596, 1482, 1380, 1233, 1172, 1038, 923, 748; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (1H, broad s), 7.24 – 7.16 (3H, m), 7.01 (1H, d, J = 8 Hz), 6.89 (1H, d, J = 2.3 Hz), 6.81 – 6.76 (2H, m), 6.71 (1H, s), 6.61 (2H, s), 6.01 (1H, s), 5.89 (2H, dd, J_1 = 1.3 Hz, J_2 = 3.0 Hz), 3.67 (3H, s), 3.58 – 3.48 (2H,m), 3.00 – 2.92 (1H, m), 2.66 (1H, dt, J_1 = 4.0 Hz, J_2 = 16.1 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.9, 150.0, 146.2, 145.5, 131.6, 130.4, 129.1, 128.6, 126.9, 125.0, 118.7, 118.5, 116.5, 112.2, 111.6, 108.5, 108.0, 101.9, 100.6, 56.7, 55.6, 42.0, 26.7; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}N_2O_3$ (M + Na): 421.1528, found (M + Na): 421.1534.

Compound (3h).

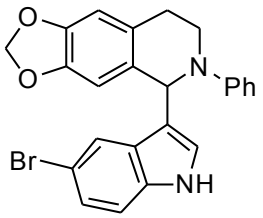


3h

Pale yellow solid; Yield - 51%; ***mp***: 213 - 215 °C; R_f (20% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3394, 2919, 1614, 1594, 1486, 1383, 1333, 1233, 1034, 941, 758; **^{1}H NMR** (400 MHz, $CDCl_3$ + DMSO): δ 11.3 (1H, broad s), 8.34 (1H, d, J = 1.6 Hz), 7.95 (1H, dd, J_1 = 1.8 Hz, J_2 = 9.0 Hz), 7.41 (1H, d, J = 9.0 Hz), 7.23 – 7.19 (2H, m), 7.02 (2H, d, J = 8.0 Hz), 6.87 (1H, s), 6.77 (1H, t, J = 7.2 Hz), 6.71 (1H,s), 6.63 (1H, s),

6.07 (1H, s), 5.91 (2H, s), 3.57 – 3.43 (2H, m), 2.99 – 2.91 (1H,m), 2.71 – 2.67 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$ + DMSO): 148.5, 145.2, 144.4, 139.6, 138.8, 128.4, 128.0, 127.0, 124.3, 119.1, 117.7, 115.8, 115.5, 115.4, 110.5, 107.4, 106.6, 99.5, 55.1, 40.9, 25.2; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{19}N_3O_4$ (M + Na): 436.1273, found (M + Na): 436.1275.

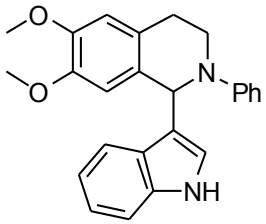
Compound (3i).



3i

Pale yellow solid; Yield - 48%; ***mp***: 191 - 193°C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3417, 2892, 1611, 1484, 1250, 1234, 1038, 778; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (1H, broad s), 7.60 (1H, s), 7.25 – 7.16 (5H, m), 7.01 (2H, d, J = 8.0 Hz), 6.83 (1H, t, J = 7.2 Hz), 6.68 – 6.60 (3H, m), 5.95 (1H, s), 5.91 (2H, d, J = 5.2 Hz), 3.58 – 3.46 (2H, m), 2.99 – 2.90 (1H,m), 2.65 – 2.61 (1H, d); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.9, 146.4, 145.6, 135.2, 129.8, 129.1, 128.5, 128.2, 125.4, 125.0, 122.7, 119.1, 119.0, 117.0, 113.0, 112.4, 108.7, 107.9, 100.7, 56.6, 42.5, 26.4; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{19}BrN_2O_2$(M + H): 447.0708, found (M + H): 447.0708.

Compound (3j)

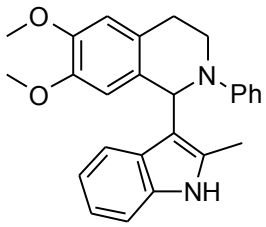


3j

Pale yellow solid; Yield - 70%; ***mp***: 160 - 163 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3372, 1605, 1496, 1337, 1246, 1223, 1105, 1009, 740; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (1H, broad s), 7.53 (1H, d, J = 8 Hz), 7.32 (1H, d, J = 8 Hz), 7.26 – 7.22 (2H, m), 7.17 – 7.14 (1H, m), 7.06 – 7.00 (3H, m), 6.80 – 6.75 (2H, m), 6.62 (2H, s), 6.10 (1H, s), 3.86 (3H, s), 3.79 (3H, s), 3.64 – 3.52 (2H, m), 3.03 – 2.95 (1H, m), 2.63 – 2.59 ((1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.9, 147.7, 147.0, 136.5, 129.1, 129.0, 127.4, 126.6, 124.3, 122.1, 120.0, 119.6, 119.4, 118.3, 116.4, 111.5, 110.9, 56.0, 55.9,

55.8, 41.9, 25.6; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{24}N_2O_2$ (M + Na): 407.1735, found (M + Na): 407.1736.

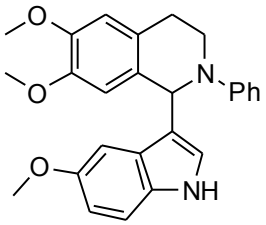
Compound (3k)



3k

Pale yellow solid; Yield - 87%; ***mp***: 200 - 203 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3389, 1593, 1501, 1359, 1251, 1239, 1111, 853, 739; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (1H, broad s), 7.20 – 7.17 (3H, m), 7.05 – 7.00 (4H, m), 6.91 – 6.87 (1H, m), 6.81 (1H, t, J = 7.2 Hz), 6.63 (1H, s), 6.58 (1H, s), 5.94 (1H, s), 3.86 (3H, s), 3.67 (3H, s), 3.60 (2H, dd, J_1 = 3.9 Hz, J_2 = 7.7 Hz), 3.03 – 2.95 (2H,m), 2.75 (1H, dt, J_1 = 3.8 Hz, J_2 = 16.2 Hz), 1.98 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.6, 147.6, 147.5, 134.8, 133.3, 129.4, 128.8, 128.0, 127.3, 120.7, 119.7, 119.4, 119.0, 118.8, 113.2, 111.2, 110.8, 109.9, 56.2, 55.85, 55.80, 44.7, 26.4, 12.2; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}N_2O_2$ (M + Na): 421.1892, found (M + Na): 421.1896.

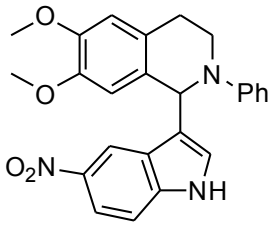
Compound (3l)



3l

Pale yellow solid; Yield - 69%; ***mp***: 152 - 154 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3380, 2931, 1595, 1486, 1360, 1268, 1246, 1223, 1209, 1172, 1103, 1057, 928, 745; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (1H, broad s), 7.25 – 7.17 (3H, m), 7.05 (2H, d, J = 8.0 Hz), 6.89 (1H, d, J = 1.8 Hz), 6.81 – 6.74 (3H, m), 6.63 (1H, s), 6.56 (1H, s), 6.07 (1H, s), 3.86 (3H, s), 3.79 (3H, s), 3.66 (3H, s), 3.56 – 3.49 (2H, m), 3.04 – 2.95 (1H, m), 2.65 – 2.61 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.9, 150.1, 147.7, 147.0, 131.5, 129.2, 129.1, 127.4, 127.0, 125.1, 118.9, 118.5, 116.7, 112.3, 111.6, 111.4, 110.9, 101.8, 56.3, 55.9, 55.86, 55.68, 41.7, 26.0; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{26}N_2O_3$ (M + Na): 437.1841, found (M + Na): 437.1844.

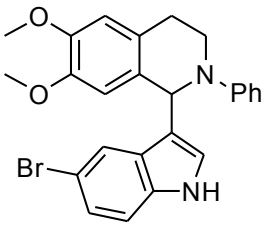
Compound (3m)



3m

Pale yellow solid; Yield - 65%; ***mp***: 208 - 210 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3339, 2923, 1597, 1515, 1469, 1332, 1246, 1094, 738; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (1H, broad s), 8.42 (1H, d, J = 2.0 Hz), 8.03 (1H, dd, J_1 = 2.1 Hz, J_2 = 9 Hz), 7.31 (1H, d, J = 8.9 Hz), 7.27 – 7.23 (3H, m), 7.01 (1H, d, J = 8.3 Hz), 6.85 – 6.81 (2H, m), 6.76 (1H, s), 6.05 (1H, s), 3.87 (3H, s), 3.83 (3H, s), 3.59 – 3.46 (2H, m), 3.03 – 2.95 (1H, m), 2.72 (1H, dt, J_1 = 4.2 Hz, J_2 = 16.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.9, 148.0, 147.3, 141.7, 139.5, 129.2, 128.3, 127.4, 127.0, 125.8, 121.6, 119.5, 117.7, 117.6, 117.2, 111.5, 111.0, 110.7, 56.5, 56.0, 55.9, 42.7, 26.3; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{23}N_3O_4$ (M + Na): 452.1586, found (M + Na): 452.1584.

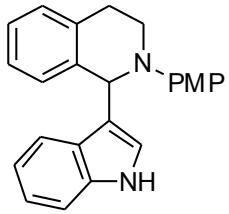
Compound (3n)



3n

Pale yellow solid; Yield - 61%; ***mp***: 184 - 187 °C; R_f (30% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3340, 2925, 1596, 1513, 1462, 1256, 1106, 884, 695; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (1H, broad s), 7.61 (1H, s), 7.27 – 7.23 (3H, m), 7.16 (1H, d, J = 8.6 Hz), 7.03 (2H, d, J = 8.1 Hz), 6.82 (1H, t, J = 7.2 Hz), 6.72 (1H, s), 6.61 (2H, d, J = 10.2 Hz), 5.99 (1H, s), 3.85 (3H, s), 3.80 (3H, s), 3.61 – 3.47 (2H, m), 3.01 – 2.92 (1H, m), 2.64 – 2.60 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.9, 147.8, 147.0, 135.1, 129.1, 128.6, 128.1, 127.3, 125.5, 124.9, 122.6, 119.1, 118.9, 116.9, 112.9, 112.4, 111.4, 110.8, 56.2, 55.9, 55.8, 42.2, 25.7; **MS** *(m/z)*: 462(M^+) **Elemental analysis**: Calcd for $C_{25}H_{23}BrN_2O_2$; C, 64.80; H, 5.00; N, 6.05; found - C, 64.86; H, 5.05; N, 5.96.

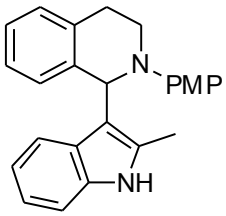
Compound (3o).[3]



3o

Pale yellow solid; Yield - 64%; ***mp***: 158 - 160 °C (lit.[3] 162 - 163 °C); R_f (20% EtOAc/Hexane) 0.25; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3415, 2924, 1605, 1510, 1455, 1243, 1098, 1035, 937, 826, 743; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (1H, broad s), 7.41 (1H, d, J = 7.9 Hz), 7.28 – 7.23 (1H, m), 7.19 – 7.10 (5H, m), 7.00 – 6.89 (3H, m), 6.81 – 6.76 (2H, m), 6.53 (1H, d, J = 2.1 Hz), 5.95 (1H, s), 3.73 (3H, s), 3.57 – 3.43 (2H, m), 3.06 – 2.96 (1H, m), 2.78 (1H, dt, J_1 = 4 Hz, J_2 = 16 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.2, 144.7, 137.5, 136.4, 135.3, 128.9, 128.8, 128.1, 126.8, 126.4, 125.6, 124.2, 121.9, 120.2, 119.6, 119.5, 119.1, 118.4, 114.3, 110.9, 57.9, 55.5, 43.7, 26.8; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{22}N_2O$ (M + Na): 377.1630, found (M+ Na): 377.1630.

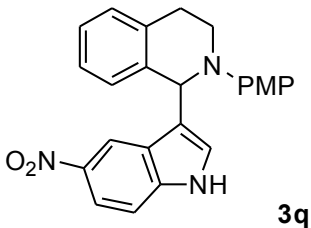
Compound (3p).



3p

Pale yellow solid; Yield - 50%; ***mp***: 174 - 175 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3349, 2921, 1605, 1508, 1459, 1365, 1234, 1013, 934, 833, 749; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (1H, broad s), 7.23 – 6.85 (10H, m), 6.66 (2H, d, J = 8.4 Hz), 5.60 (1H, s), 3.69 (3H, s), 3.58 – 3.38 (2H, m), 3.18 – 2.99 (2H, m), 1.93(3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.8, 145.5, 138.5, 134.99, 134.96, 133.58, 128.45, 128.44, 128.0, 125.9, 125.8, 123.4, 120.5, 119.4, 119.1, 113.7, 113.1, 109.9, 59.2, 55.3, 48.5, 29.1, 11.8; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{24}N_2O$ (M+H): 369.1967, found (M+H): 369.1963.

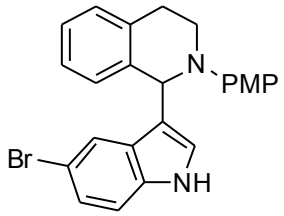
Compound (3q).[3]



3q

Pale yellow solid; Yield - 58%; ***mp***: 156 - 159 °C (lit.[3] 155 - 156 °C); R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3400, 2923, 1620, 1512, 1471, 1330, 1306, 1259, 1248, 1090, 1035, 813; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.21 (1H, d, J = 2 Hz), 7.96 (1H, dd, J_1 = 2 Hz, J_2 = 9 Hz), 7.26 – 7.24 (1H, m), 7.21 – 7.18 (2H, m), 7.14 – 7.11 (2H, m), 6.92 (2H, d, J = 8.8 Hz), 6.77 (2H, d, J = 8.8 Hz), 6.68 (1H, s), 5.92 (1H, s), 3.73 (3H, s), 3.42 – 3.39 (2H, m), 3.09 – 3.01 (1H, m), 2.87 (1H, dt, J_1 = 4 Hz, J_2 = 16 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.2, 144.5, 141.5, 139.3, 136.8, 135.1, 129.0, 127.9, 127.3, 126.8, 126.1, 125.8, 121.07, 121.04, 117.7, 117.5, 114.4, 110.9, 58.4, 55.5, 44.2, 27.4; **MS** *(m/z)*: 399 (M^+); **Elemental analysis**: Calcd for $C_{24}H_{21}N_3O_3$; C, 72.16; H, 5.30; N, 10.52; found - C, 72.17; H, 5.67; N, 10.27.

Compound (3r).

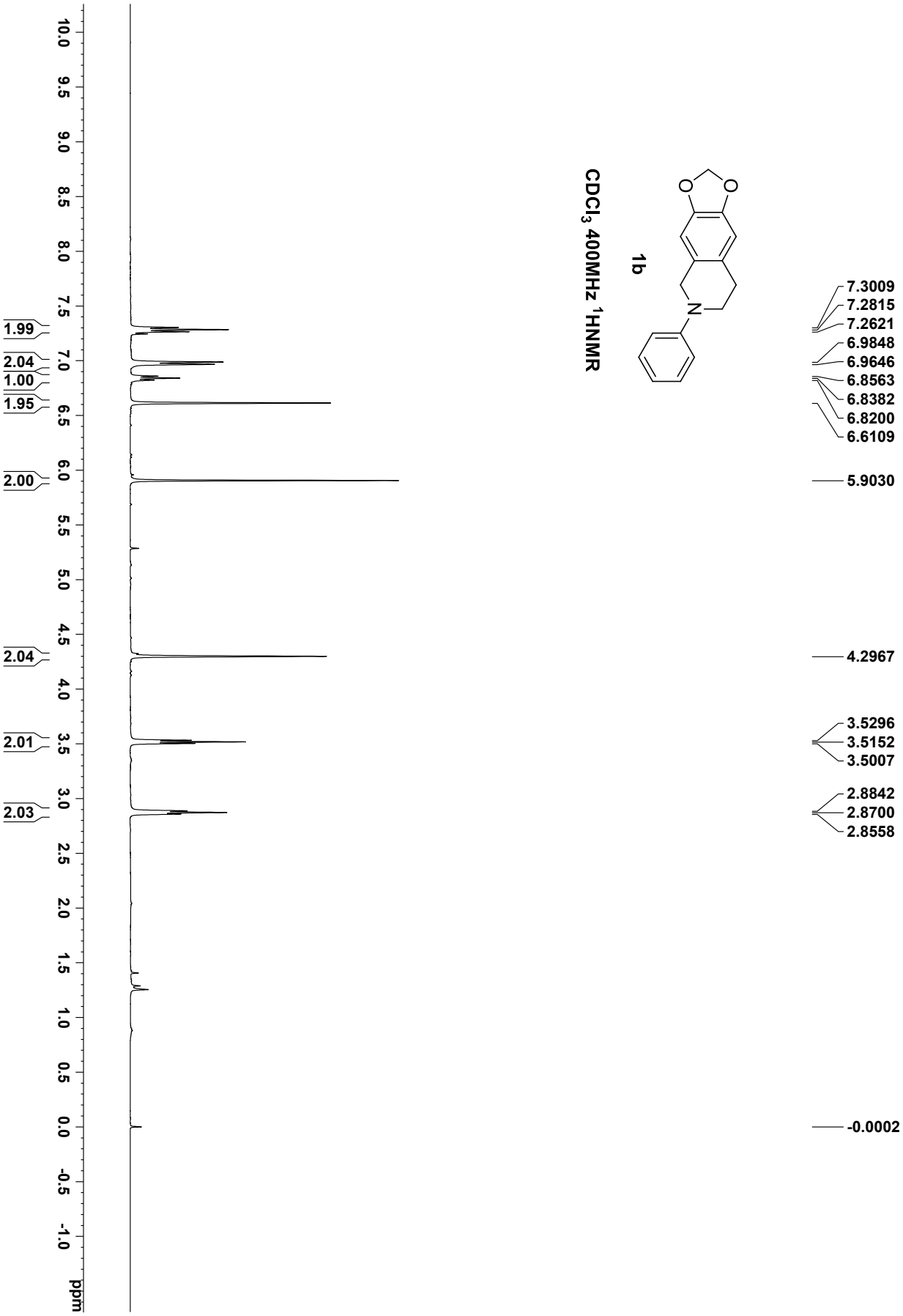


3r

Pale yellow solid; Yield - 83%; ***mp***: 121 - 122 °C; R_f (20% EtOAc/Hexane) 0.2; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 3419, 2920, 1631, 1509, 1463, 1243, 1117, 1090, 1036, 917, 883; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (1H, broad s), 7.38 (1H, s), 7.22 – 7.06 (6H, m), 6.91 (2H, d, J= 8.9 Hz), 6.77 (2H, d, J= 8.9 Hz), 6.45 (1H, d, J= 1.9 Hz), 5.84 (1H, s), 3.74 (3H, s), 3.47 – 3.36 (2H, m), 3.05 – 2.97 (1H, m), 2.78 (1H, dt, J_1 = 3.6 Hz, J_2 = 16.4 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$): 153.8, 144.6, 137.1, 135.1, 134.9, 128.9, 128.4, 128.0, 126.5, 125.68, 125.66, 124.7, 122.7, 120.5, 118.5, 114.3, 112.8, 112.3, 58.2, 55.5, 43.8, 26.9; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{21}BrN_2O$ (M+H): 433.0915, found (M+H): 433.0916.

References

1) Jerome, M; Philippe, H.; Christophe, T.; Sylviane, G. –R.; Henri, -P. H. *Synth. Commun.,* **2001**, *31*, 987-992.
2) Sud, A.; Sureshkumar, D.; Klussmann, M. *Chem. Commun.,* **2009**, 3169-3171.
3) Li, Z. ; Li, C. –J. *J. Am. Chem. Soc.* **2005**, *127*, 6968-6969.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6.8563
6.8382
6.8200
6.6109
5.9030
4.2967
3.5296
3.5152
3.5007
2.8842
2.8700
2.8558
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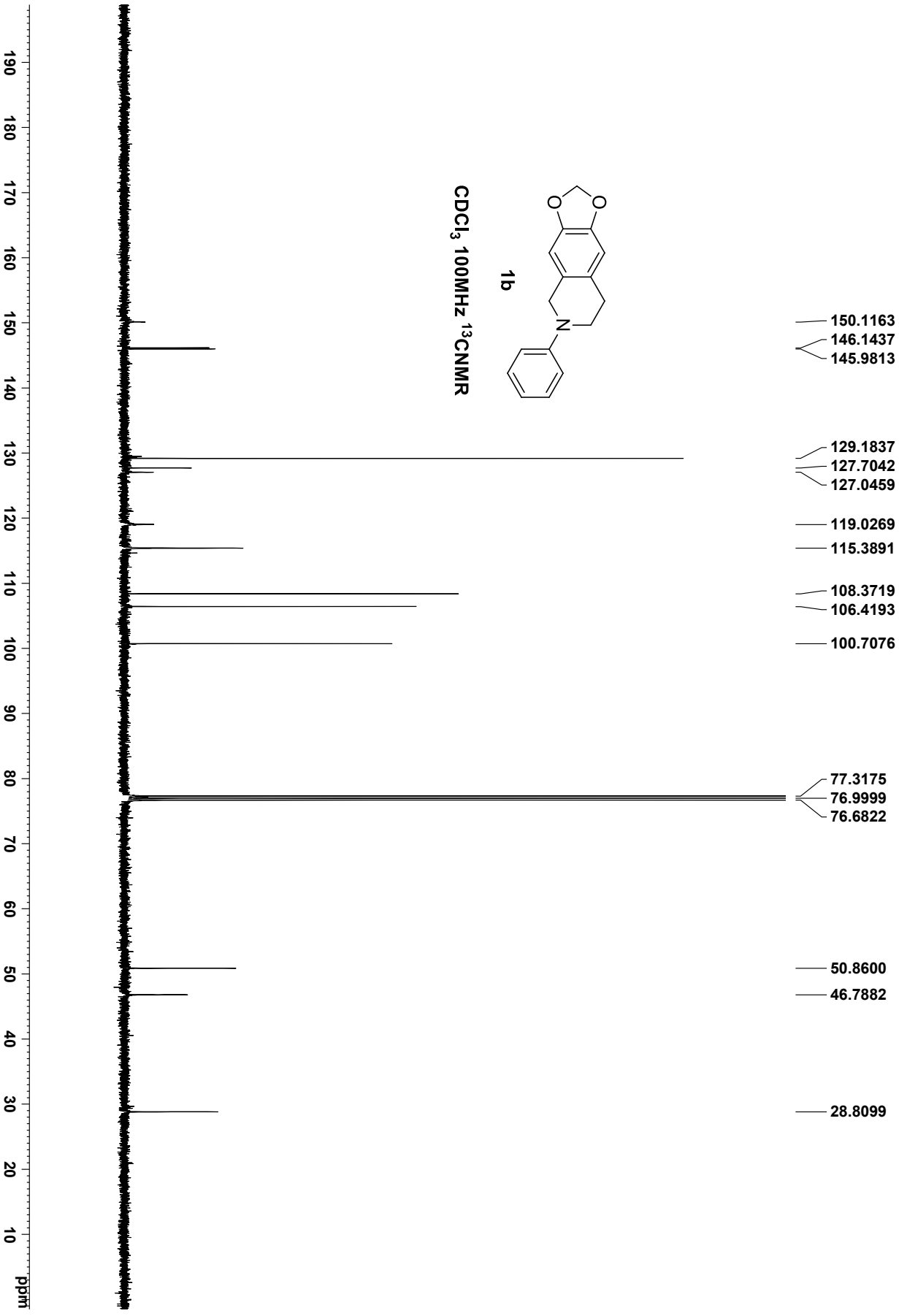
2.04
1.00
1.95
2.00
2.04
2.01
2.03
ppm


CDCl3 100MHz 13CNMR
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127.7042
127.0459
119.0269
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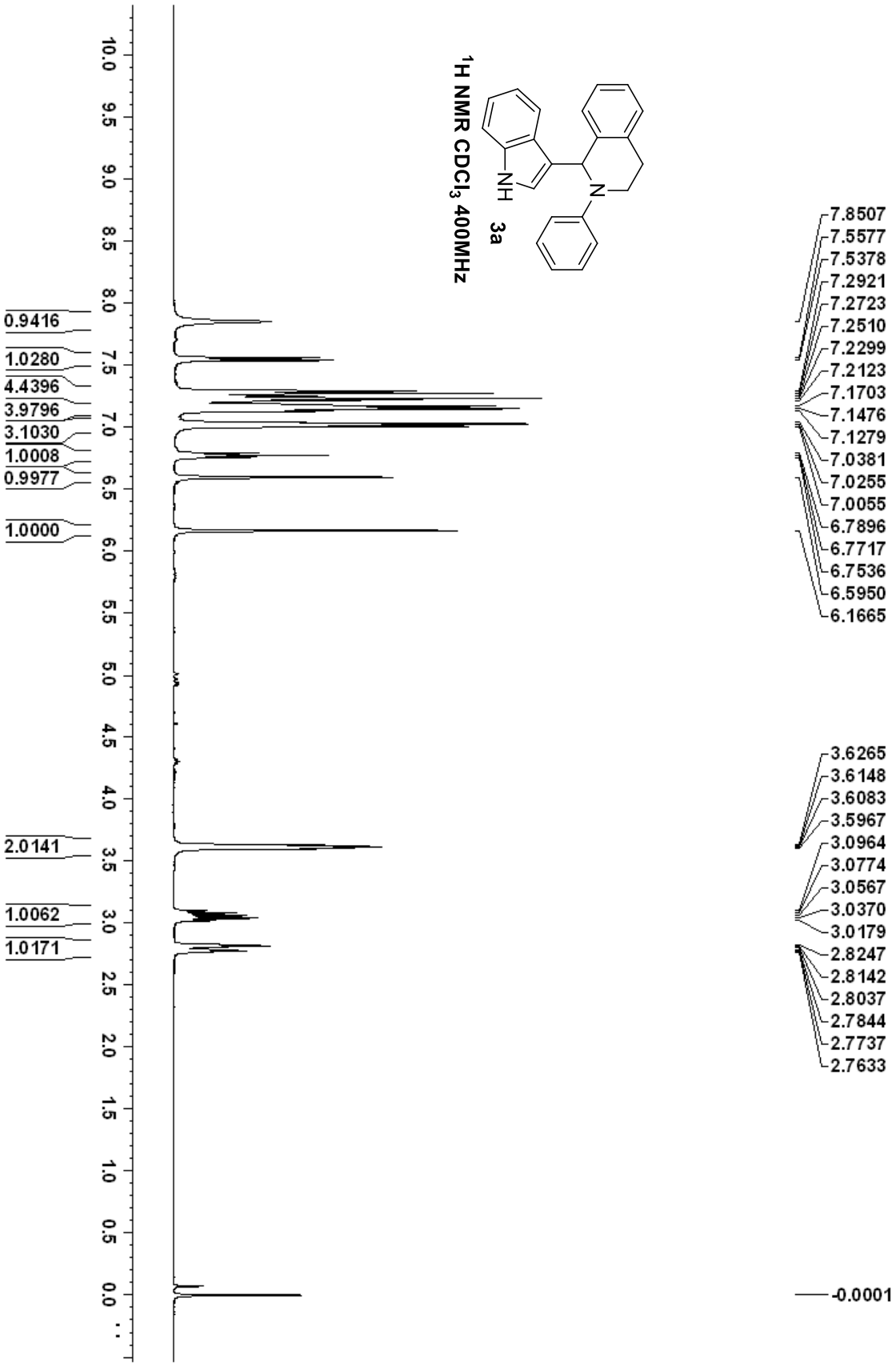
28.8099
ppm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N
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0.9977
1.0000
2.0141
1.0062
1.0171
7.8507
7.5577
7.5378
7.2921
7.2723
7.2510
7.2299
7.2123
7.1703
7.1476
7.1279
7.0381
7.0255
7.0055
6.7896
6.7717
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6.5950
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3.0774
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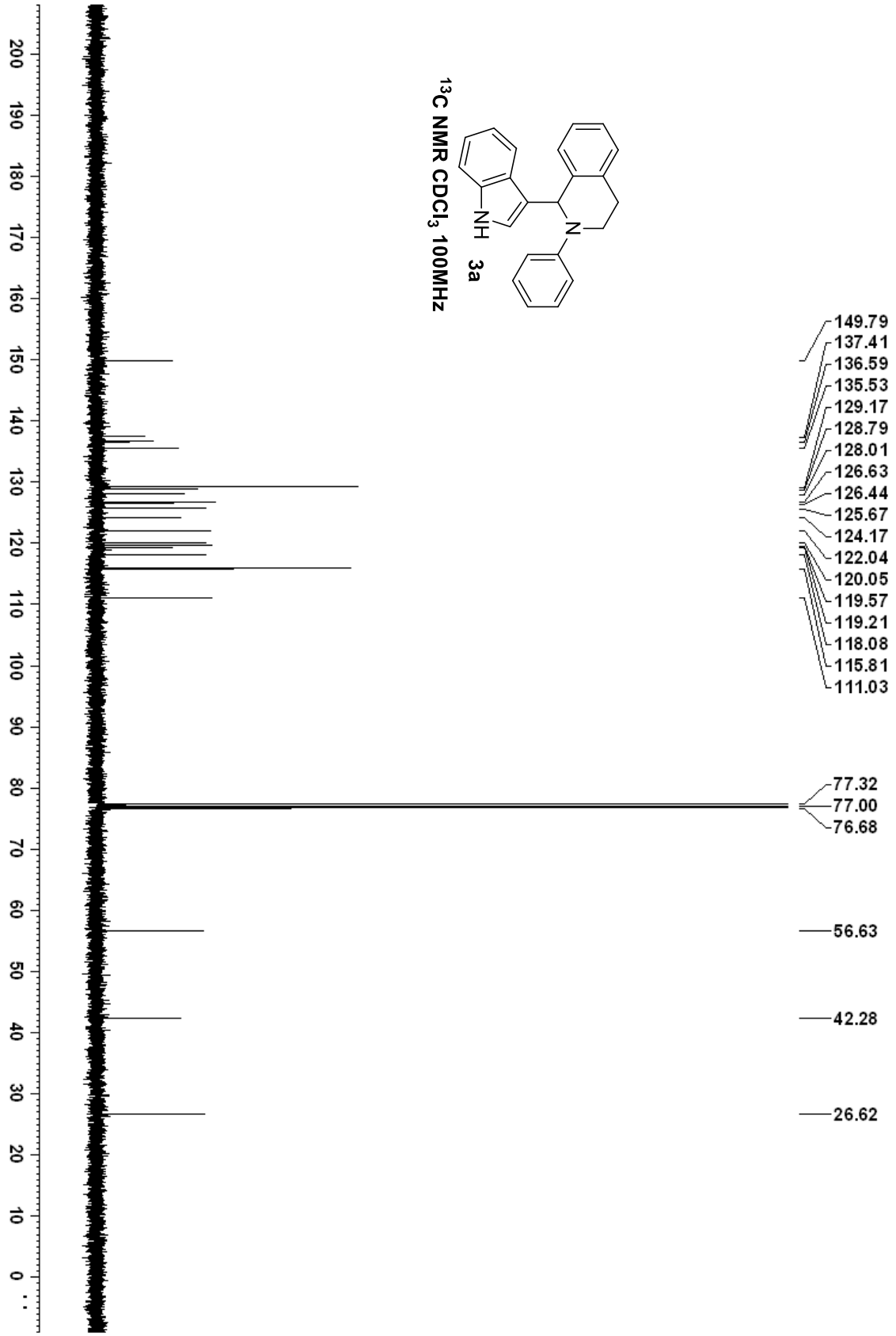
2.7633
-0.0001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NH
N
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129.17
128.79
128.01
126.63
126.44
125.67
124.17
122.04
120.05
119.57
119.21
118.08
115.81
111.03
77.32
77.00
76.68
56.63
42.28
26.62
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180
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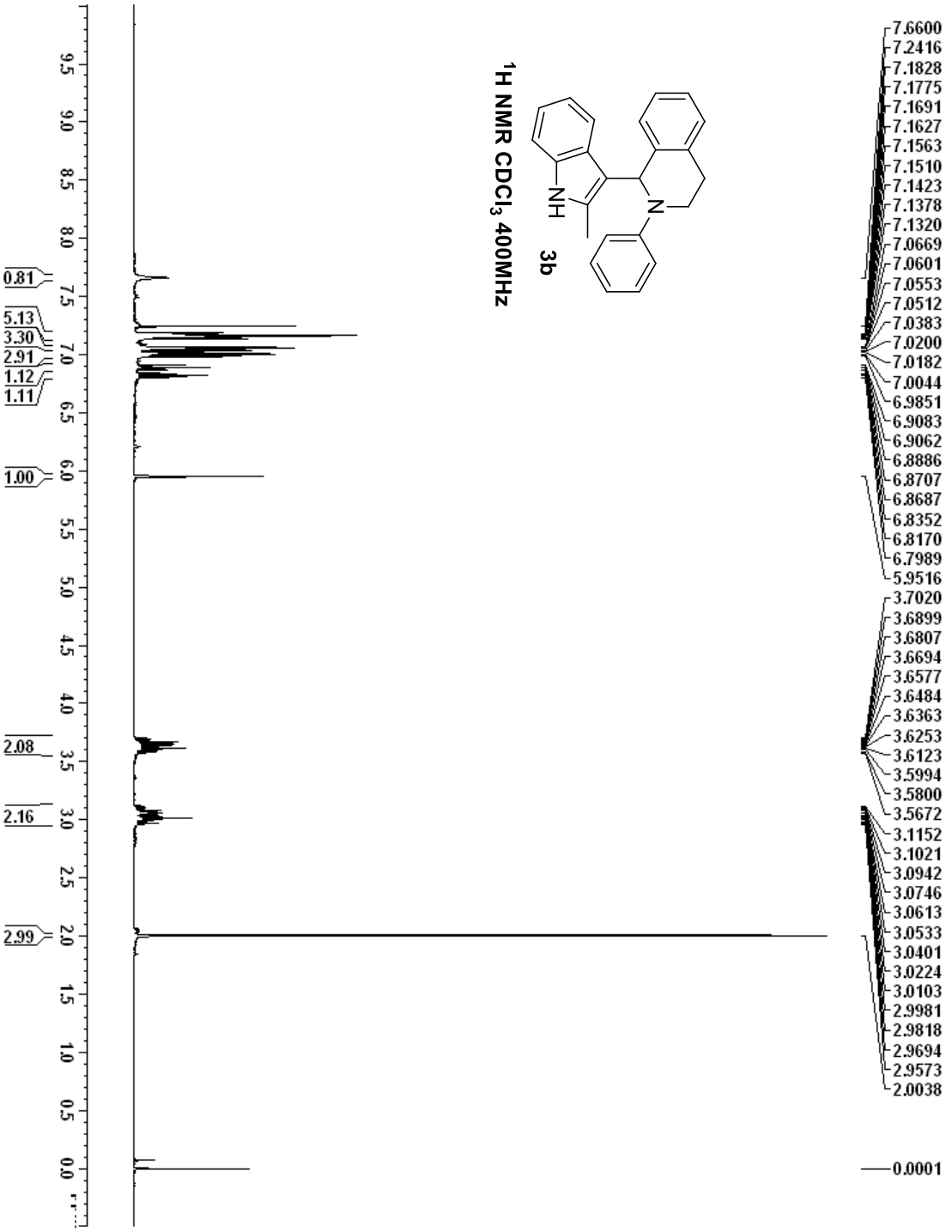
10
0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N
3b
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1.11
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3.5994
3.5800
3.5672
3.1152
3.1021
3.0942
3.0746
3.0613
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3.0103
2.9981
2.9818
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2.9573
2.0038
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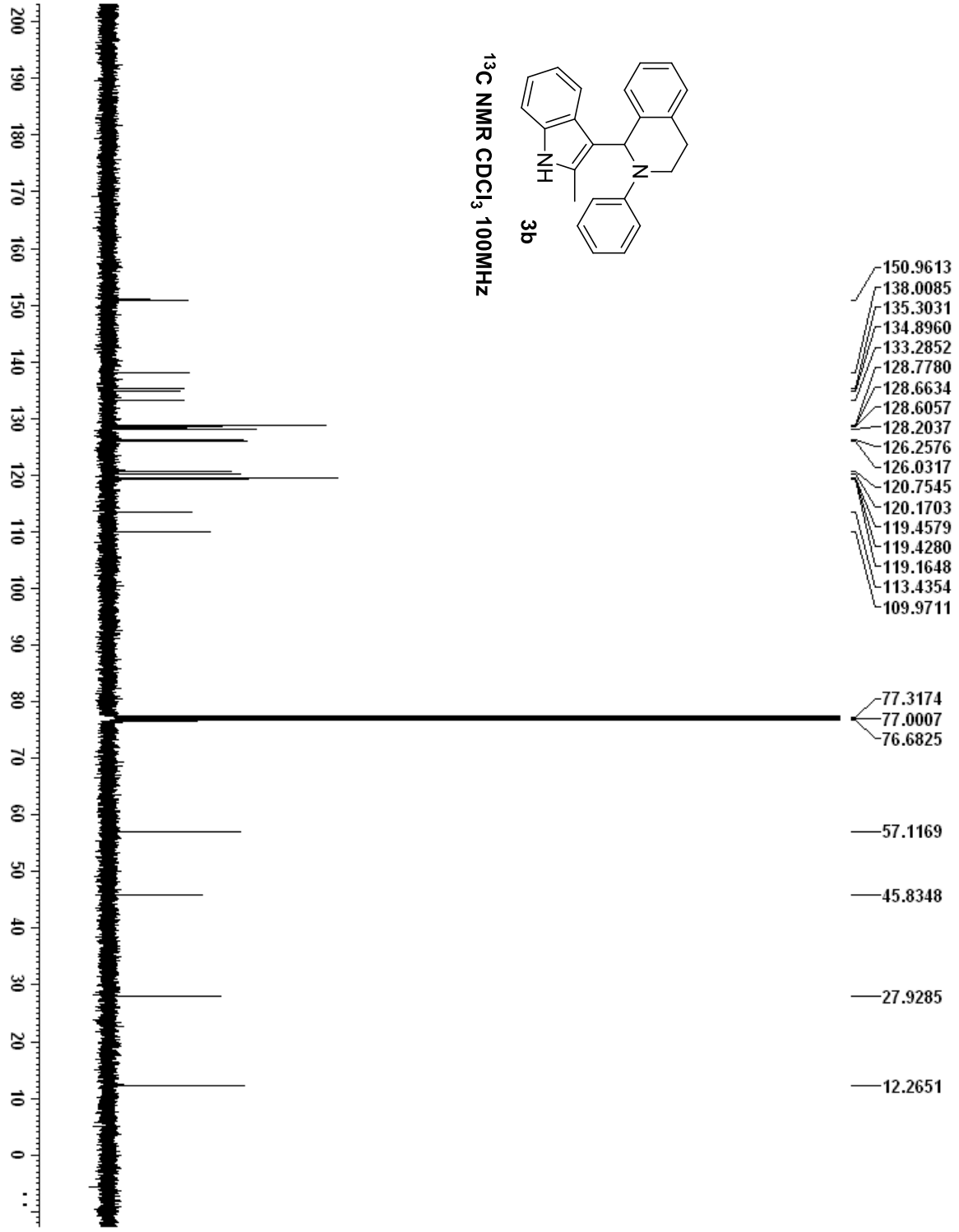
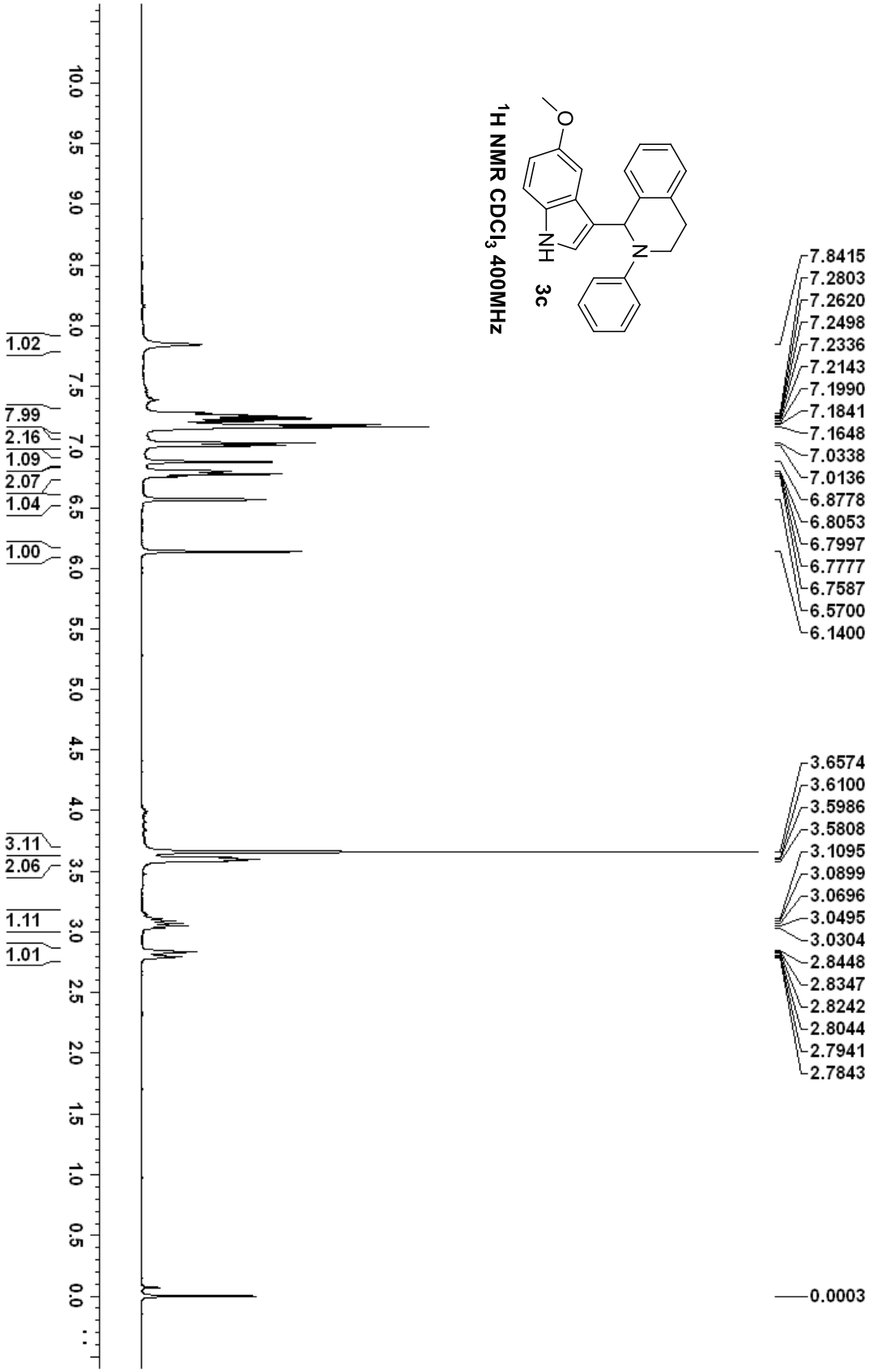

^{13}C NMR CDCl$_3$ 100MHz
3b
NH
N
150.9613
138.0085
135.3031
134.8960
133.2852
128.7780
128.6634
128.6057
128.2037
126.2576
126.0317
120.7545
120.1703
119.4579
119.4280
119.1648
113.4354
109.9711
77.3174
77.0007
76.6825
57.1169
45.8348
27.9285
12.2651


^{1}H NMR CDCl$_3$ 400MHz
3c
NH
O
N
1.02
7.99
2.16
1.09
2.07
1.04
1.00
3.11
2.06
1.11
1.01
7.8415
7.2803
7.2620
7.2498
7.2336
7.2143
7.1990
7.1841
7.1648
7.0338
7.0136
6.8778
6.8053
6.7997
6.7777
6.7587
6.5700
6.1400
3.6574
3.6100
3.5986
3.5808
3.1095
3.0899
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3.0304
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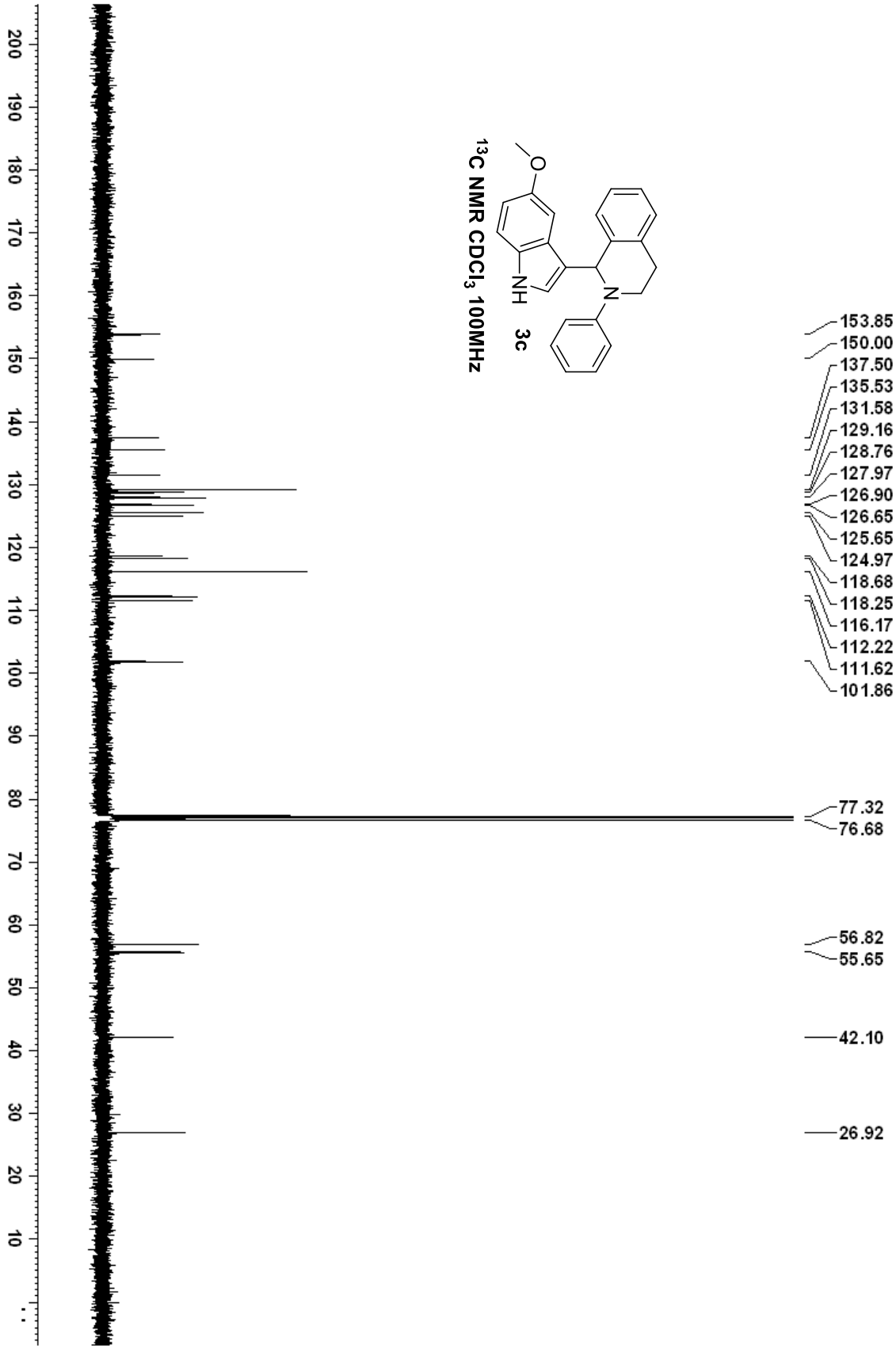
2.8044
2.7941
2.7843
0.0003


^{13}C NMR CDCl$_3$ 100MHz
3c
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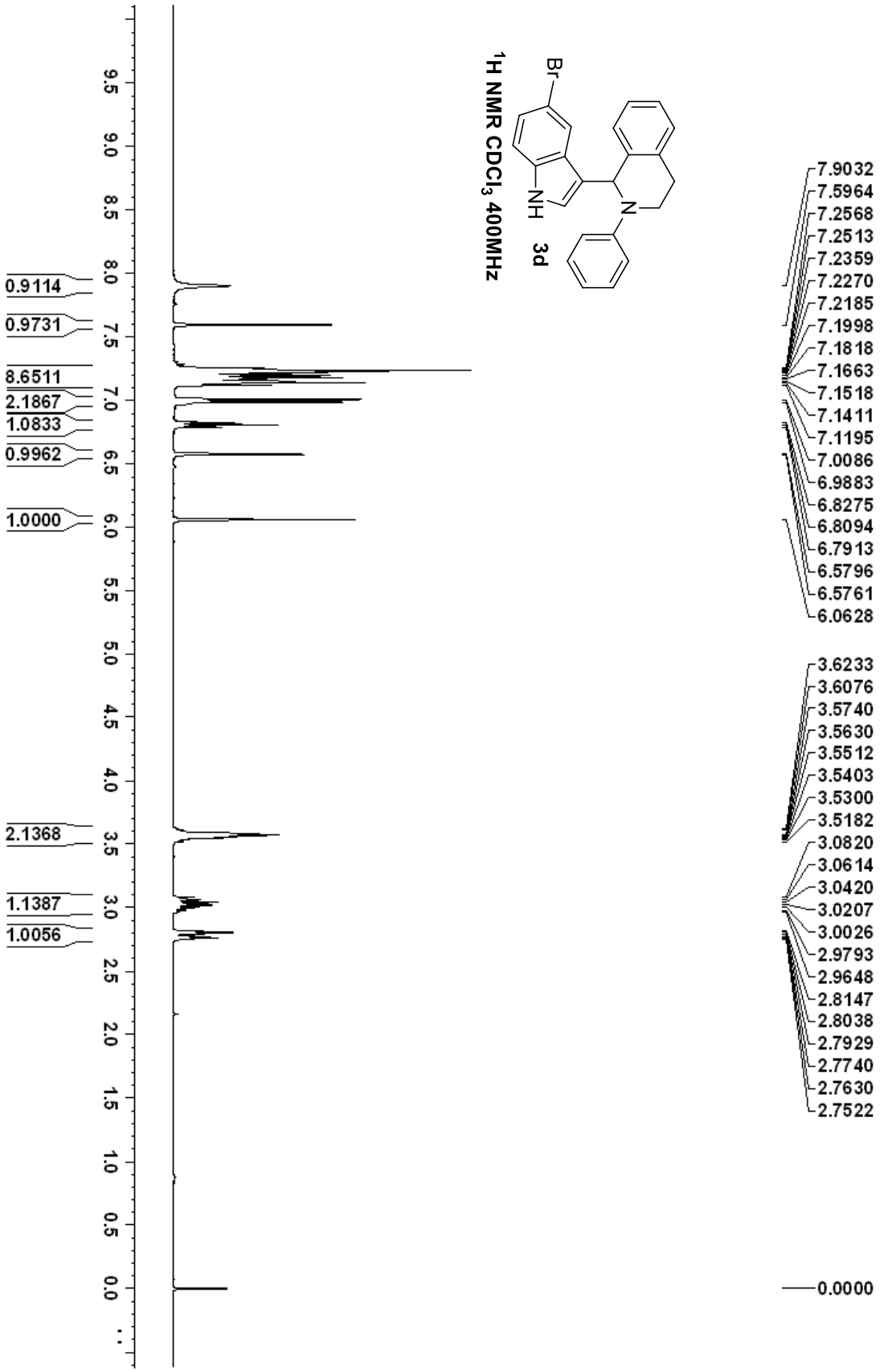
150.00
137.50
135.53
131.58
129.16
128.76
127.97
126.90
126.65
125.65
124.97
118.68
118.25
116.17
112.22
111.62
101.86
77.32
76.68
56.82
55.65
42.10
26.92


^{1}H NMR CDCl$_3$ 400MHz
Br
NH
N
3d
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0.9731
8.6511
2.1867
1.0833
0.9962
1.0000
2.1368
1.1387
1.0056
7.9032
7.5964
7.2568
7.2513
7.2359
7.2270
7.2185
7.1998
7.1818
7.1663
7.1518
7.1411
7.1195
7.0086
6.9883
6.8275
6.8094
6.7913
6.5796
6.5761
6.0628
3.6233
3.6076
3.5740
3.5630
3.5512
3.5403
3.5300
3.5182
3.0820
3.0614
3.0420
3.0207
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2.9648
2.8147
2.8038
2.7929
2.7740
2.7630
2.7522
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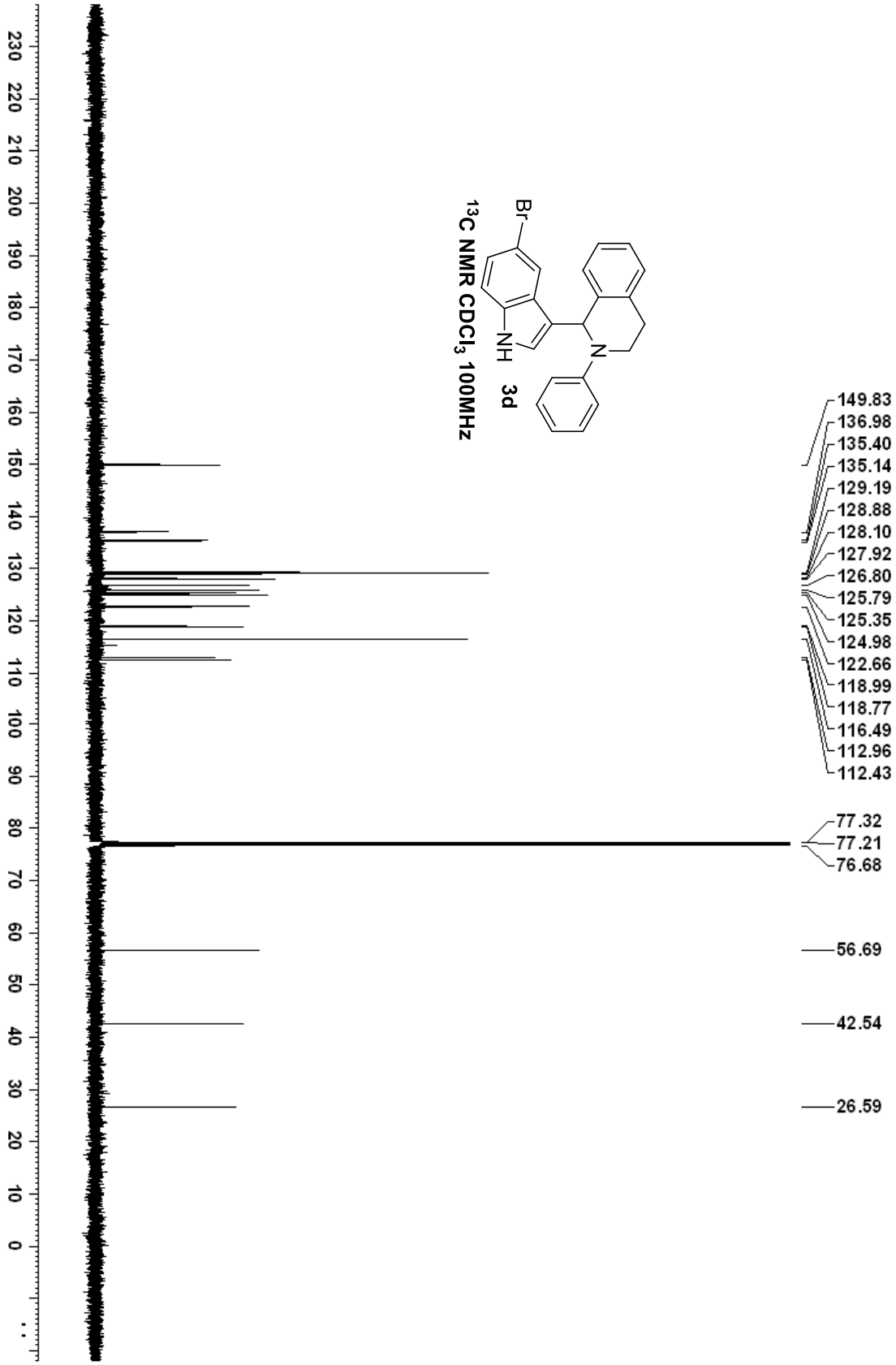
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Br
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N
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136.98
135.40
135.14
129.19
128.88
128.10
127.92
126.80
125.79
125.35
124.98
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112.43
77.32
77.21
76.68
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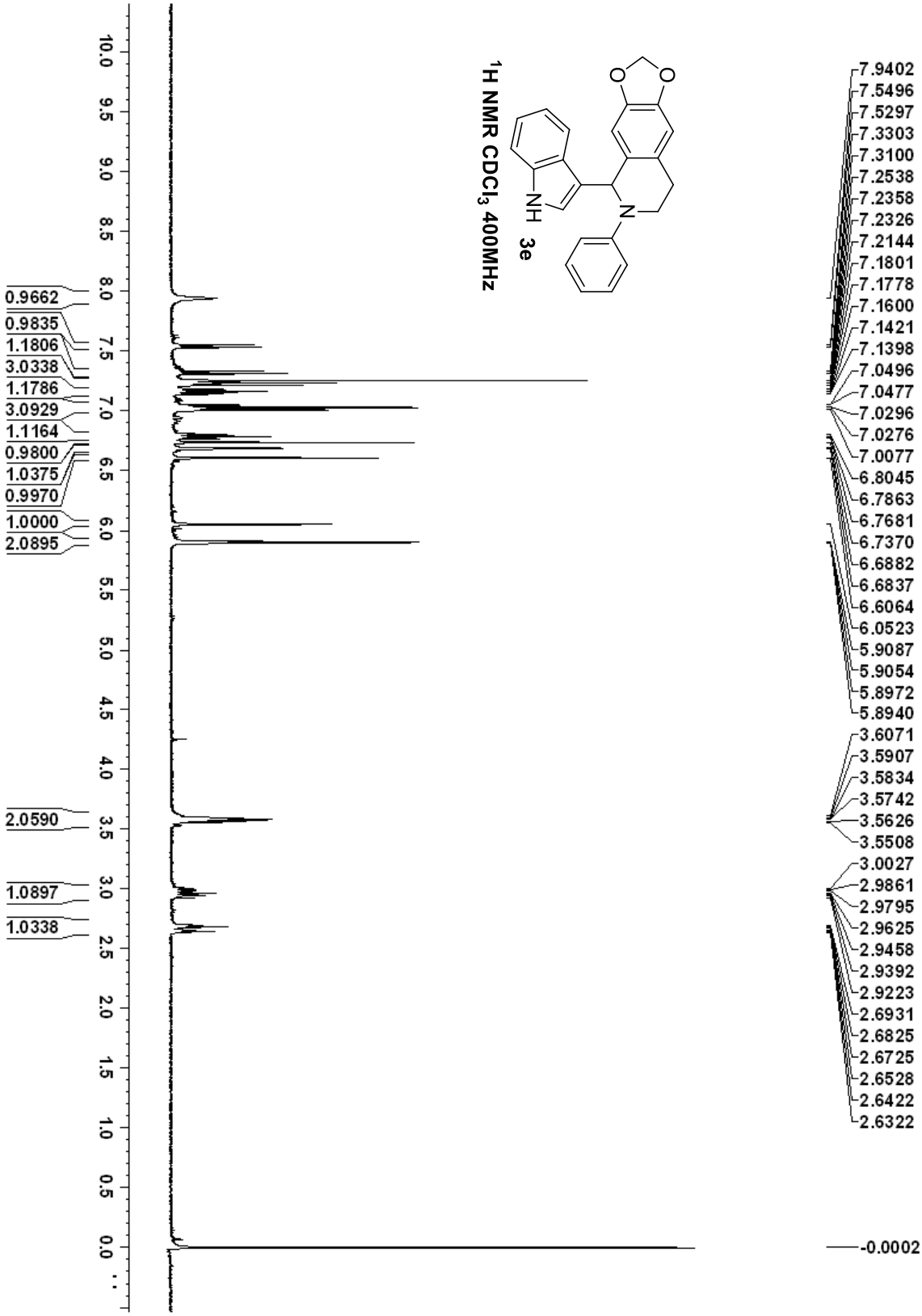
42.54
26.59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3e
NH
N
O
O
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0.9835
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3.0338
1.1786
3.0929
1.1164
0.9800
1.0375
0.9970
1.0000
2.0895
2.0590
1.0897
1.0338
7.9402
7.5496
7.5297
7.3303
7.3100
7.2538
7.2358
7.2326
7.2144
7.1801
7.1778
7.1600
7.1421
7.1398
7.0496
7.0477
7.0296
7.0276
7.0077
6.8045
6.7863
6.7681
6.7370
6.6882
6.6837
6.6064
6.0523
5.9087
5.9054
5.8972
5.8940
3.6071
3.5907
3.5834
3.5742
3.5626
3.5508
3.0027
2.9861
2.9795
2.9625
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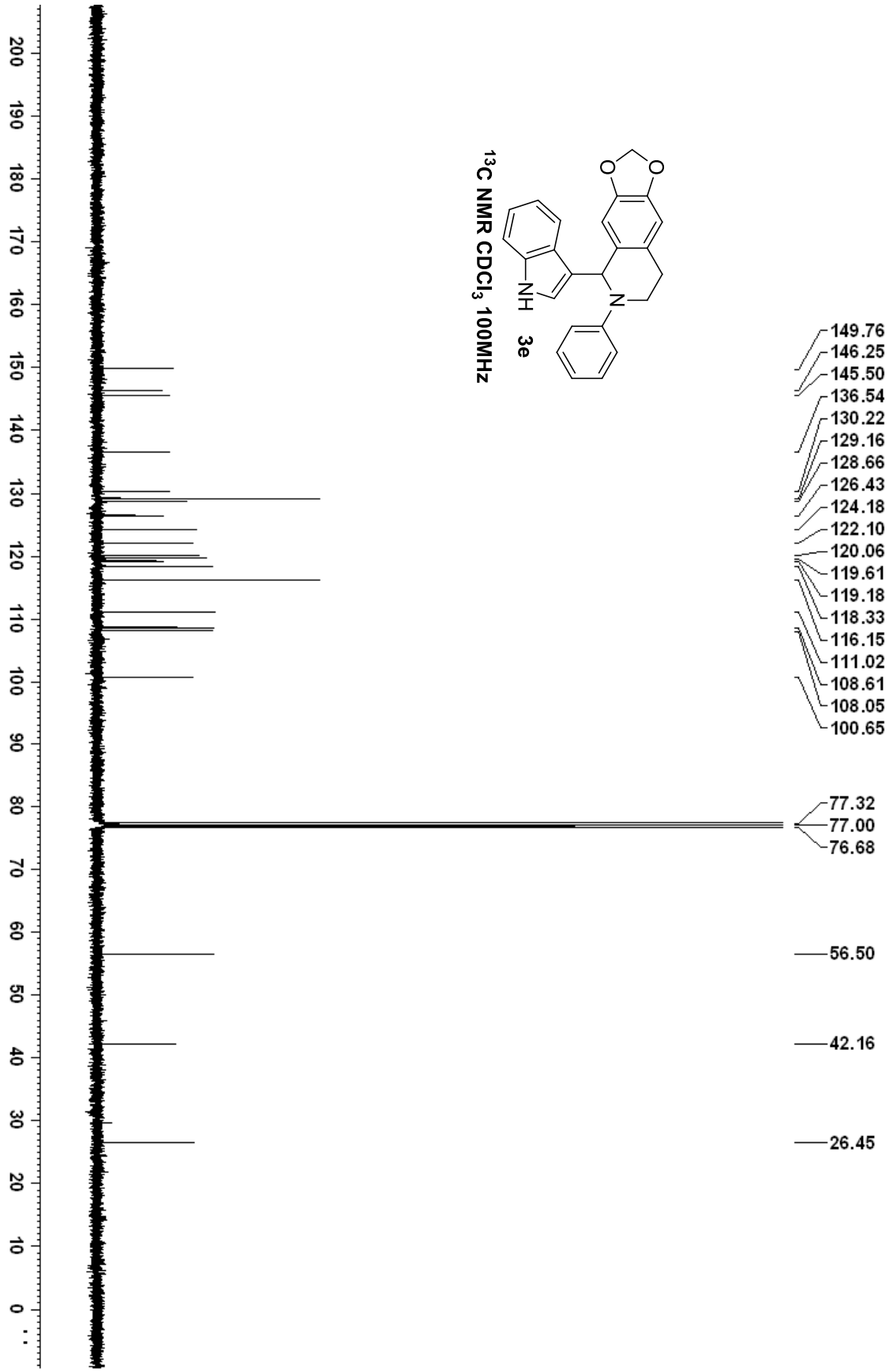
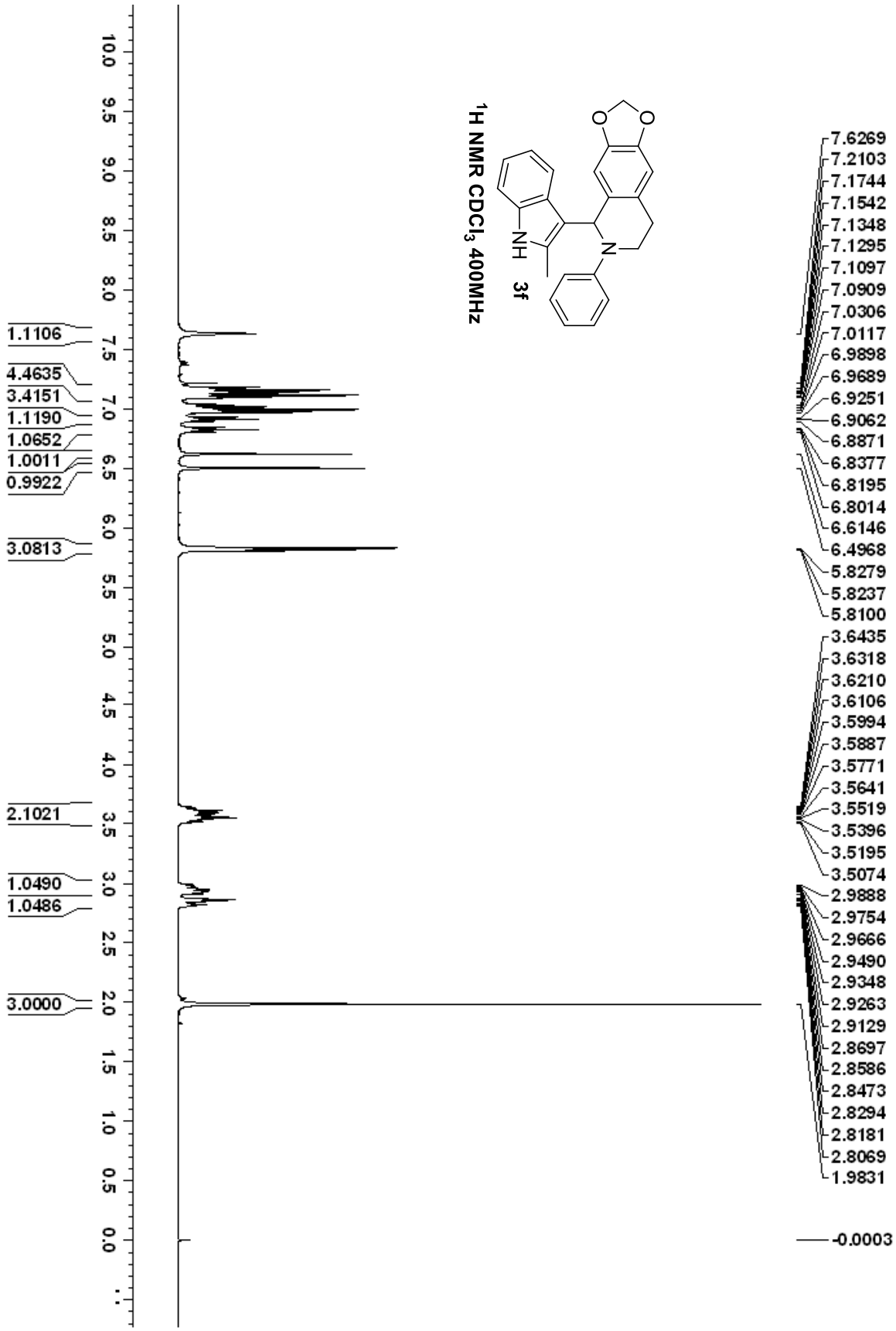
2.9223
2.6931
2.6825
2.6725
2.6528
2.6422
2.6322
-0.0002


^{13}C NMR CDCl$_3$ 100MHz
3e
NH
N
O
O
149.76
146.25
145.50
136.54
130.22
129.16
128.66
126.43
124.18
122.10
120.06
119.61
119.18
118.33
116.15
111.02
108.61
108.05
100.65
77.32
77.00
76.68
56.50
42.16
26.45


^{1}H NMR CDCl$_3$ 400MHz
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N
O
O
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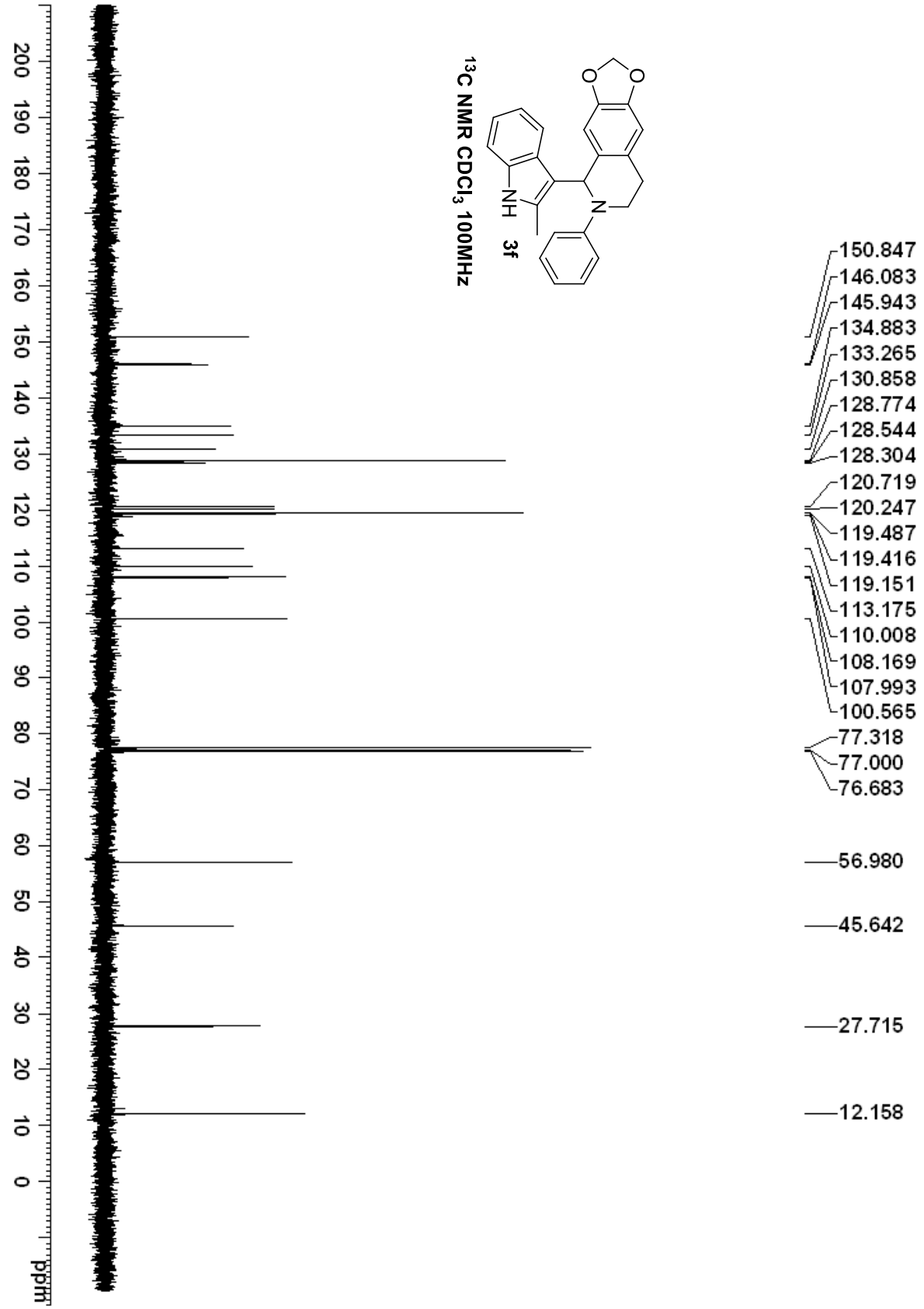
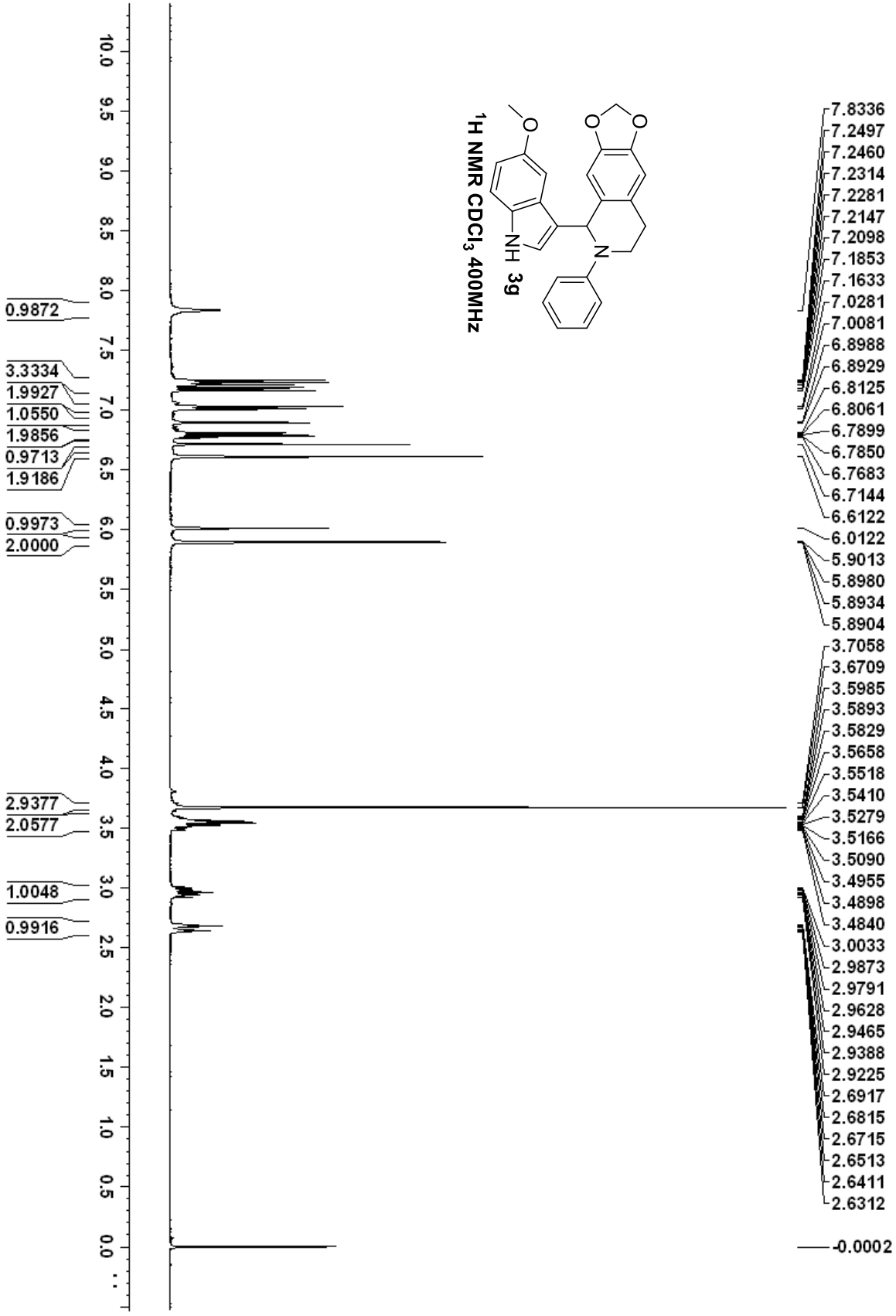
4.4635
3.4151
1.1190
1.0652
1.0011
0.9922
3.0813
2.1021
1.0490
1.0486
3.0000
7.6269
7.2103
7.1744
7.1542
7.1348
7.1295
7.1097
7.0909
7.0306
7.0117
6.9898
6.9689
6.9251
6.9062
6.8871
6.8377
6.8195
6.8014
6.6146
6.4968
5.8279
5.8237
5.8100
3.6435
3.6318
3.6210
3.6106
3.5994
3.5887
3.5771
3.5641
3.5519
3.5396
3.5195
3.5074
2.9888
2.9754
2.9666
2.9490
2.9348
2.9263
2.9129
2.8697
2.8586
2.8473
2.8294
2.8181
2.8069
1.9831
-0.0003
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


^{13}C NMR CDCl$_3$ 100MHz
3f
NH
N
O
O
150.847
146.083
145.943
134.883
133.265
130.858
128.774
128.544
128.304
120.719
120.247
119.487
119.416
119.151
113.175
110.008
108.169
107.993
100.565
77.318
77.000
76.683
56.980
45.642
27.715
12.158
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


^{1}H NMR CDCl$_3$ 400MHz
NH 3g
0.9872
3.3334
1.9927
1.0550
1.9856
0.9713
1.9186
0.9973
2.0000
2.9377
2.0577
1.0048
0.9916
7.8336
7.2497
7.2460
7.2314
7.2281
7.2147
7.2098
7.1853
7.1633
7.0281
7.0081
6.8988
6.8929
6.8125
6.8061
6.7899
6.7850
6.7683
6.7144
6.6122
6.0122
5.9013
5.8980
5.8934
5.8904
3.7058
3.6709
3.5985
3.5893
3.5829
3.5658
3.5518
3.5410
3.5279
3.5166
3.5090
3.4955
3.4898
3.4840
3.0033
2.9873
2.9791
2.9628
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2.6917
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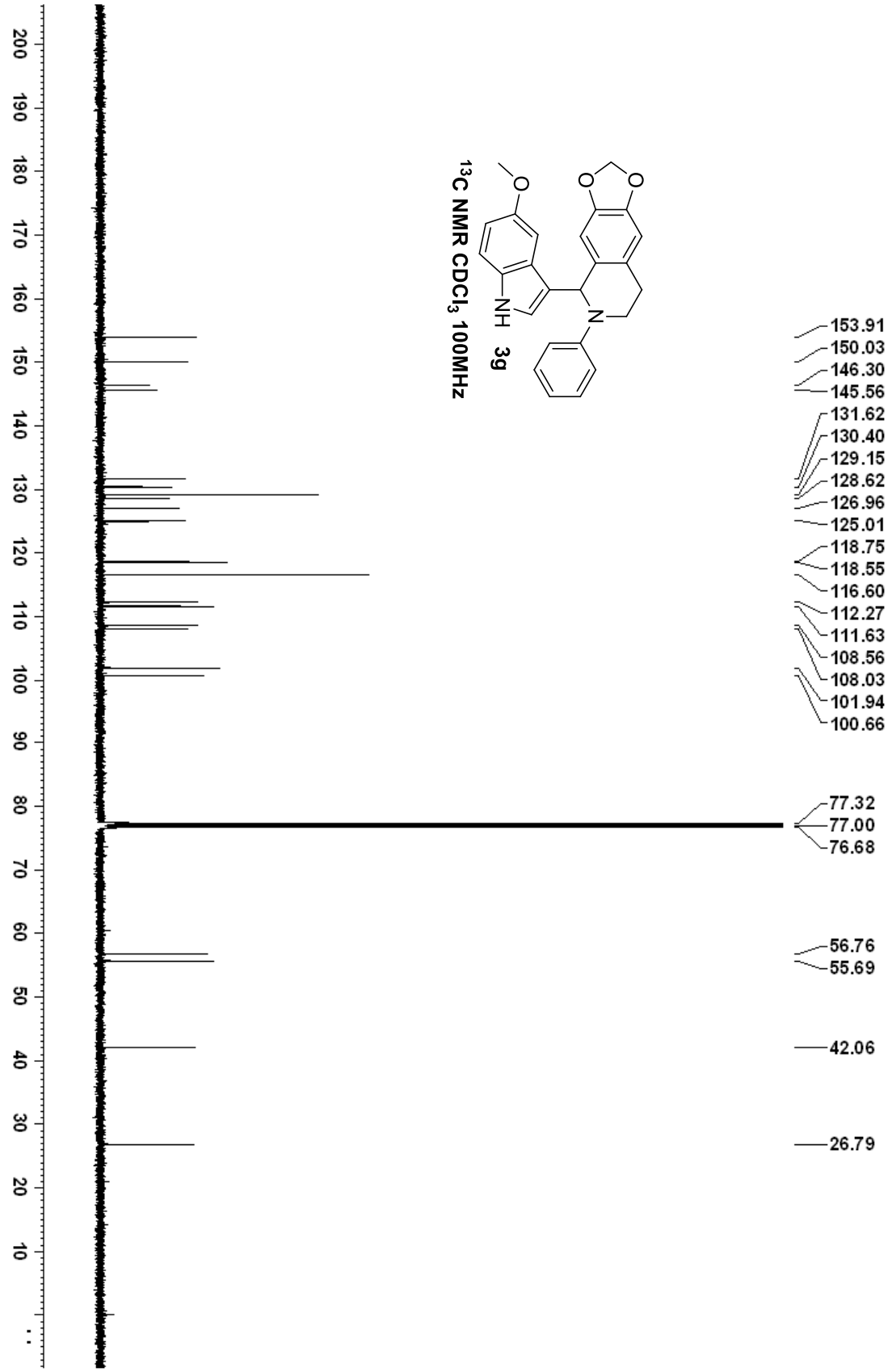
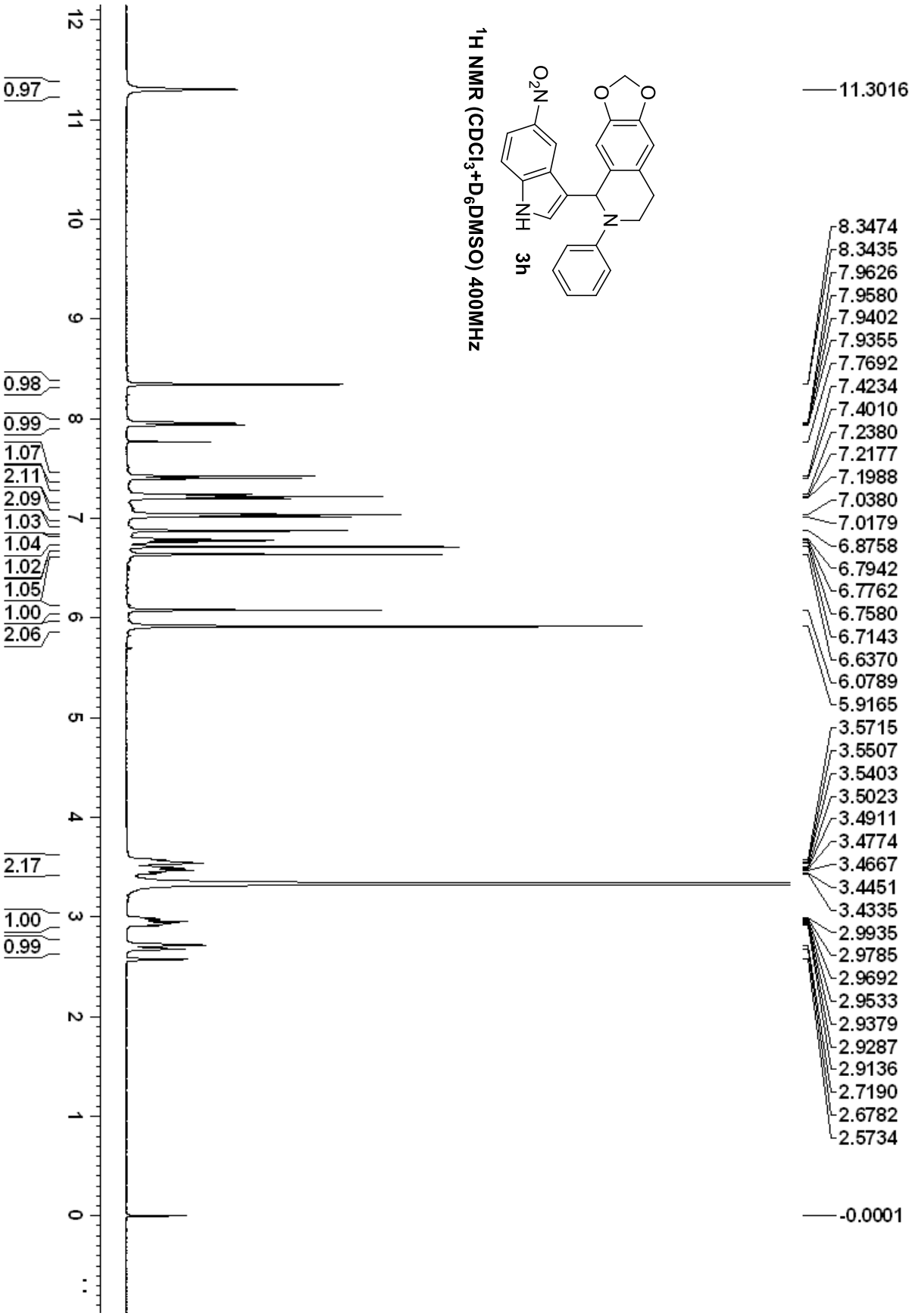
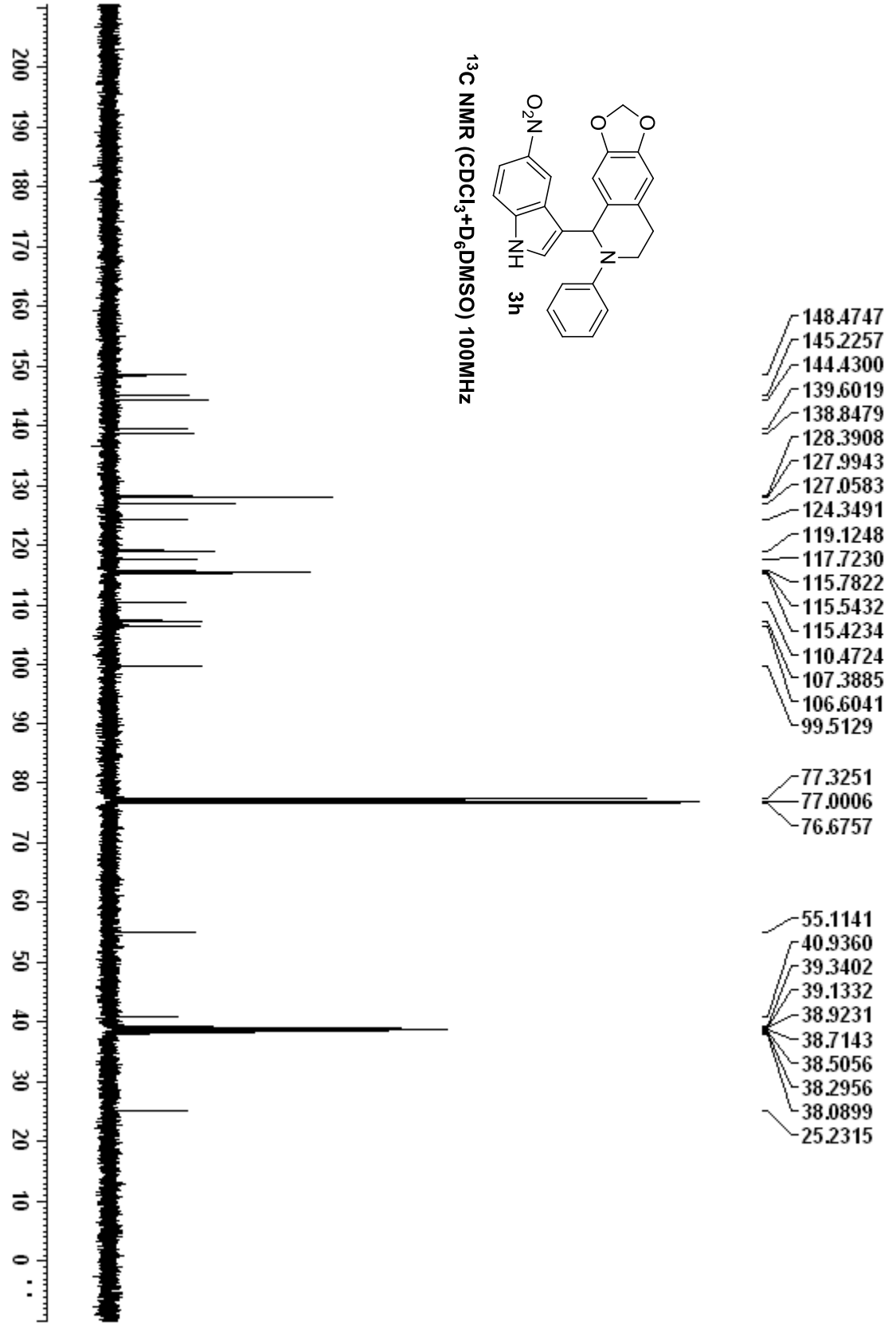
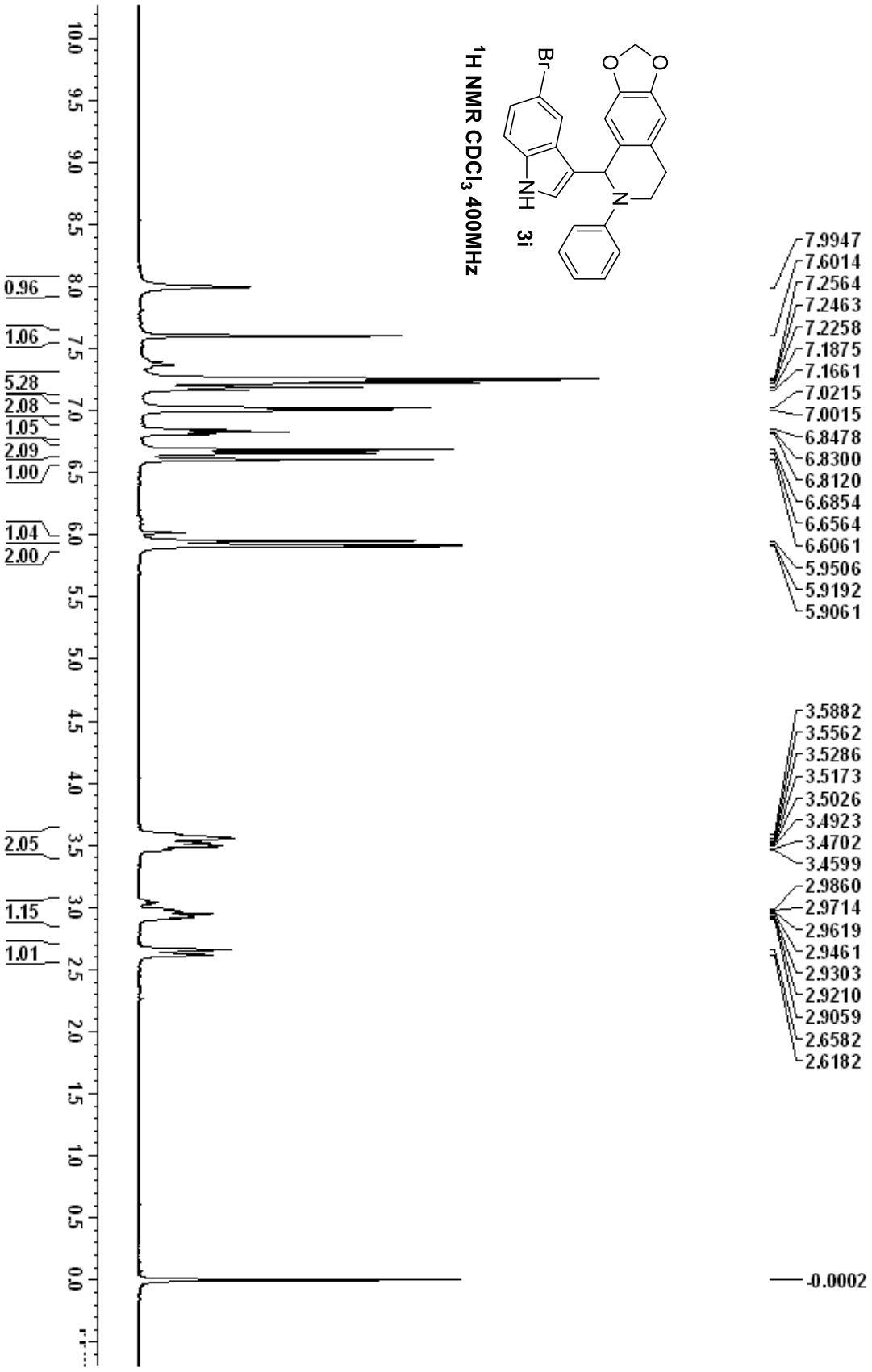
2.6715
2.6513
2.6411
2.6312
-0.0002


^{13}C NMR CDCl$_3$ 100MHz
3g
153.91
150.03
146.30
145.56
131.62
130.40
129.15
128.62
126.96
125.01
118.75
118.55
116.60
112.27
111.63
108.56
108.03
101.94
100.66
77.32
77.00
76.68
56.76
55.69
42.06
26.79


^{1}H NMR (CDCl$_3$+D$_6$DMSO) 400MHz
O$_2$N
NH
3h
11.3016
8.3474
8.3435
7.9626
7.9580
7.9402
7.9355
7.7692
7.4234
7.4010
7.2380
7.2177
7.1988
7.0380
7.0179
6.8758
6.7942
6.7762
6.7580
6.7143
6.6370
6.0789
5.9165
3.5715
3.5507
3.5403
3.5023
3.4911
3.4774
3.4667
3.4451
3.4335
2.9935
2.9785
2.9692
2.9533
2.9379
2.9287
2.9136
2.7190
2.6782
2.5734
-0.0001
0.97
0.98
0.99
1.07
2.11
2.09
1.03
1.04
1.02
1.05
1.00
2.06
2.17
1.00
0.99


^{13}C NMR (CDCl$_3$+D$_6$DMSO) 100MHz
O$_2$N
NH
3h
148.4747
145.2257
144.4300
139.6019
138.8479
128.3908
127.9943
127.0583
124.3491
119.1248
117.7230
115.7822
115.5432
115.4234
110.4724
107.3885
106.6041
99.5129
77.3251
77.0006
76.6757
55.1141
40.9360
39.3402
39.1332
38.9231
38.7143
38.5056
38.2956
38.0899
25.2315


^{1}H NMR CDCl$_3$ 400MHz
Br
NH
N
O
O
3i
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7.6014
7.2564
7.2463
7.2258
7.1875
7.1661
7.0215
7.0015
6.8478
6.8300
6.8120
6.6854
6.6564
6.6061
5.9506
5.9192
5.9061
3.5882
3.5562
3.5286
3.5173
3.5026
3.4923
3.4702
3.4599
2.9860
2.9714
2.9619
2.9461
2.9303
2.9210
2.9059
2.6582
2.6182
-0.0002
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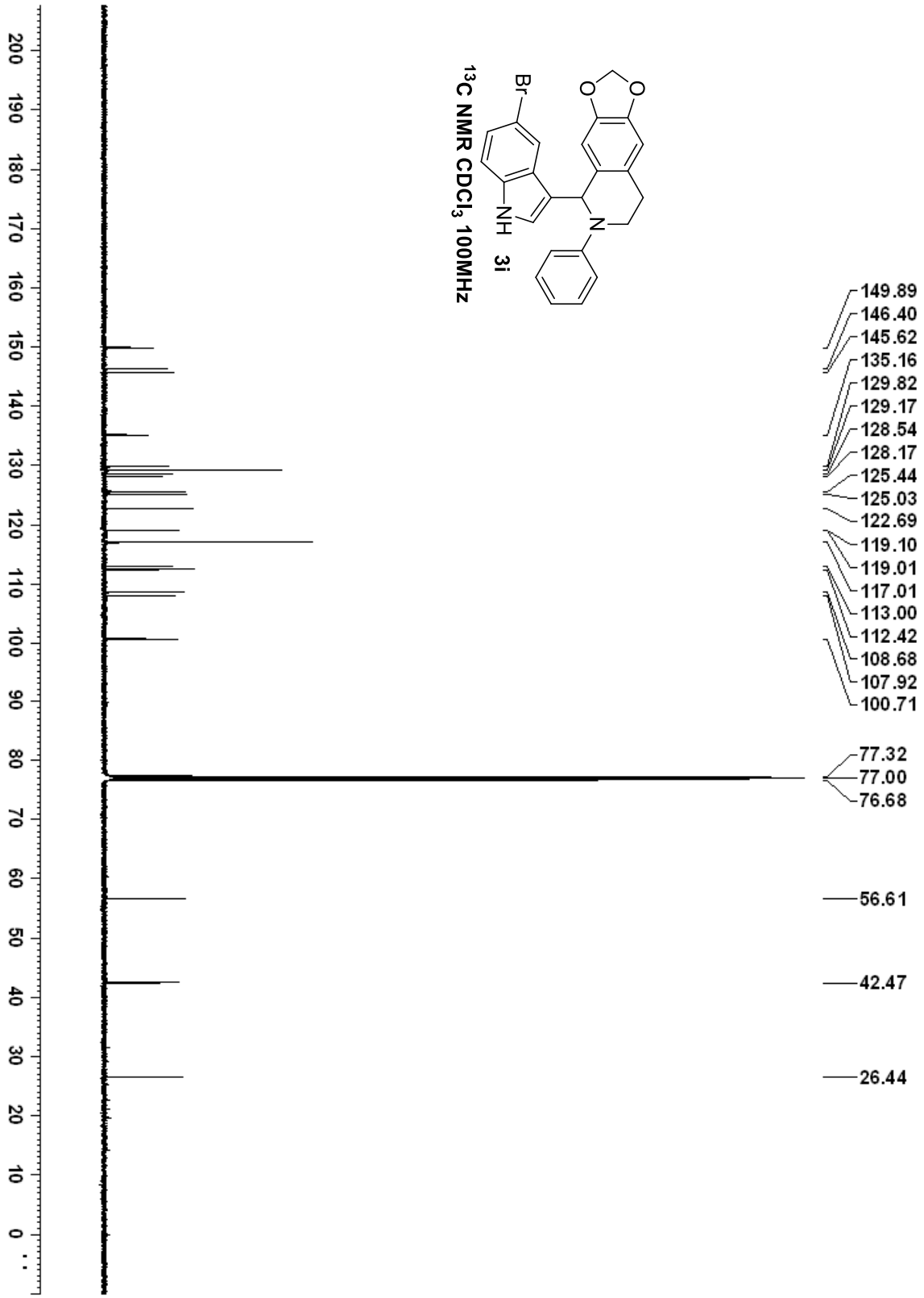
2.08
1.05
2.09
1.00
1.04
2.00
2.05
1.15
1.01


^{13}C NMR CDCl$_3$ 100MHz
Br
NH
N
O
O
3i
149.89
146.40
145.62
135.16
129.82
129.17
128.54
128.17
125.44
125.03
122.69
119.10
119.01
117.01
113.00
112.42
108.68
107.92
100.71
77.32
77.00
76.68
56.61
42.47
26.44
200
190
180
170
160
150
140
130
120
110
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90
80
70
60
50
40
30
20
10
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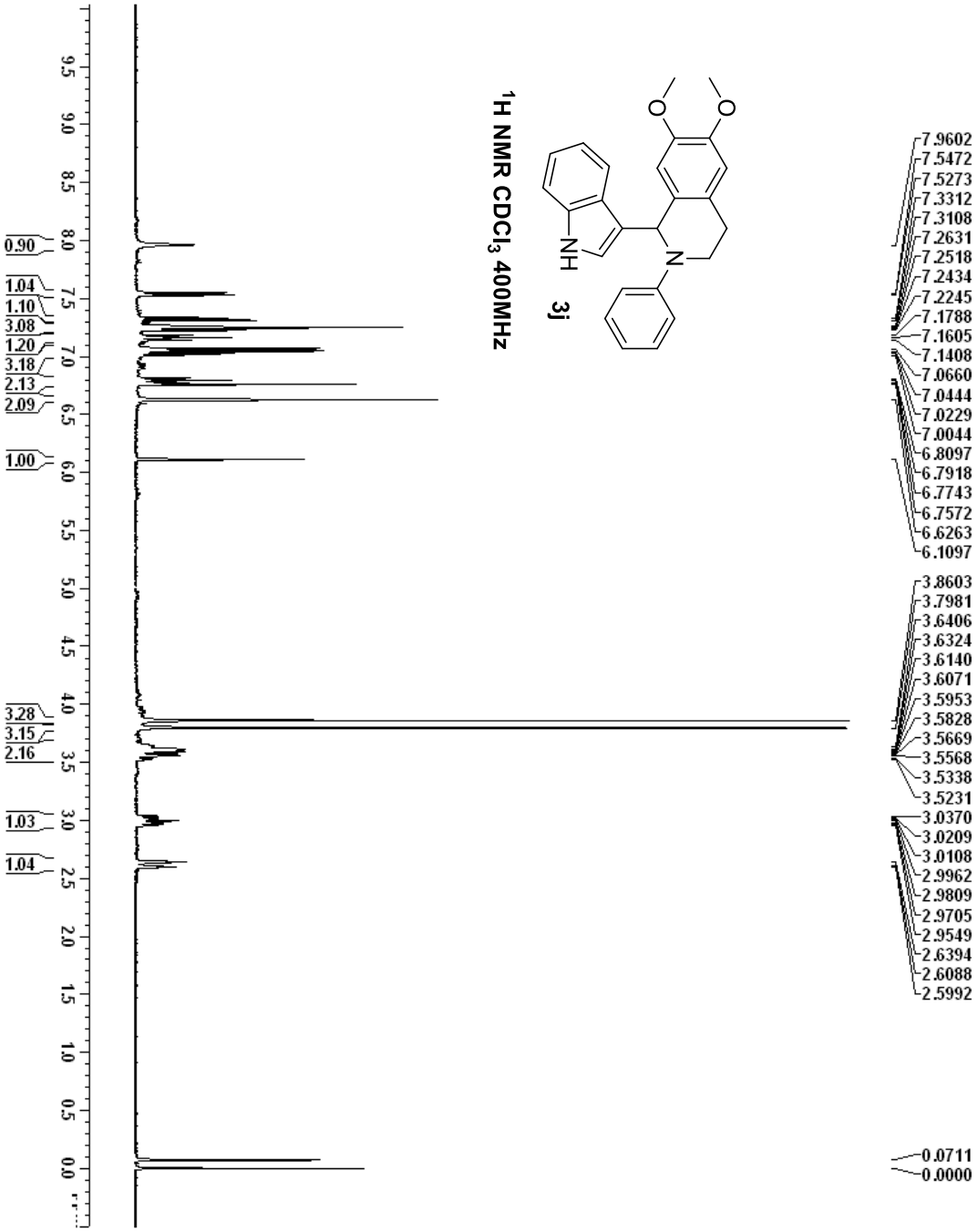
^{1}H NMR CDCl$_3$ 400MHz
3j
NH
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O
O
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3.08
1.20
3.18
2.13
2.09
1.00
3.28
3.15
2.16
1.03
1.04
7.9602
7.5472
7.5273
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7.3108
7.2631
7.2518
7.2434
7.2245
7.1788
7.1605
7.1408
7.0660
7.0444
7.0229
7.0044
6.8097
6.7918
6.7743
6.7572
6.6263
6.1097
3.8603
3.7981
3.6406
3.6324
3.6140
3.6071
3.5953
3.5828
3.5669
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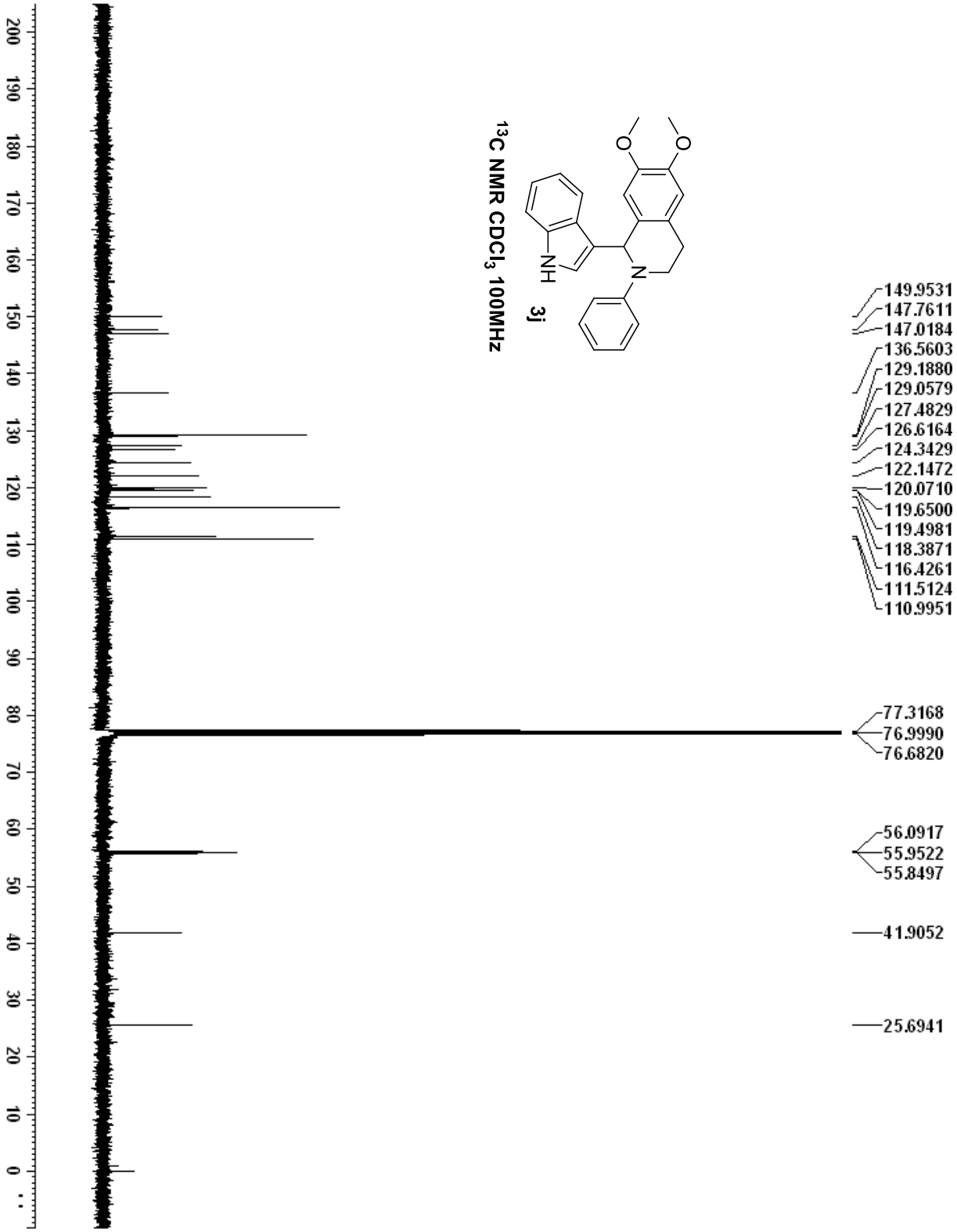
^{13}C NMR CDCl$_3$ 100MHz
3j
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129.0579
127.4829
126.6164
124.3429
122.1472
120.0710
119.6500
119.4981
118.3871
116.4261
111.5124
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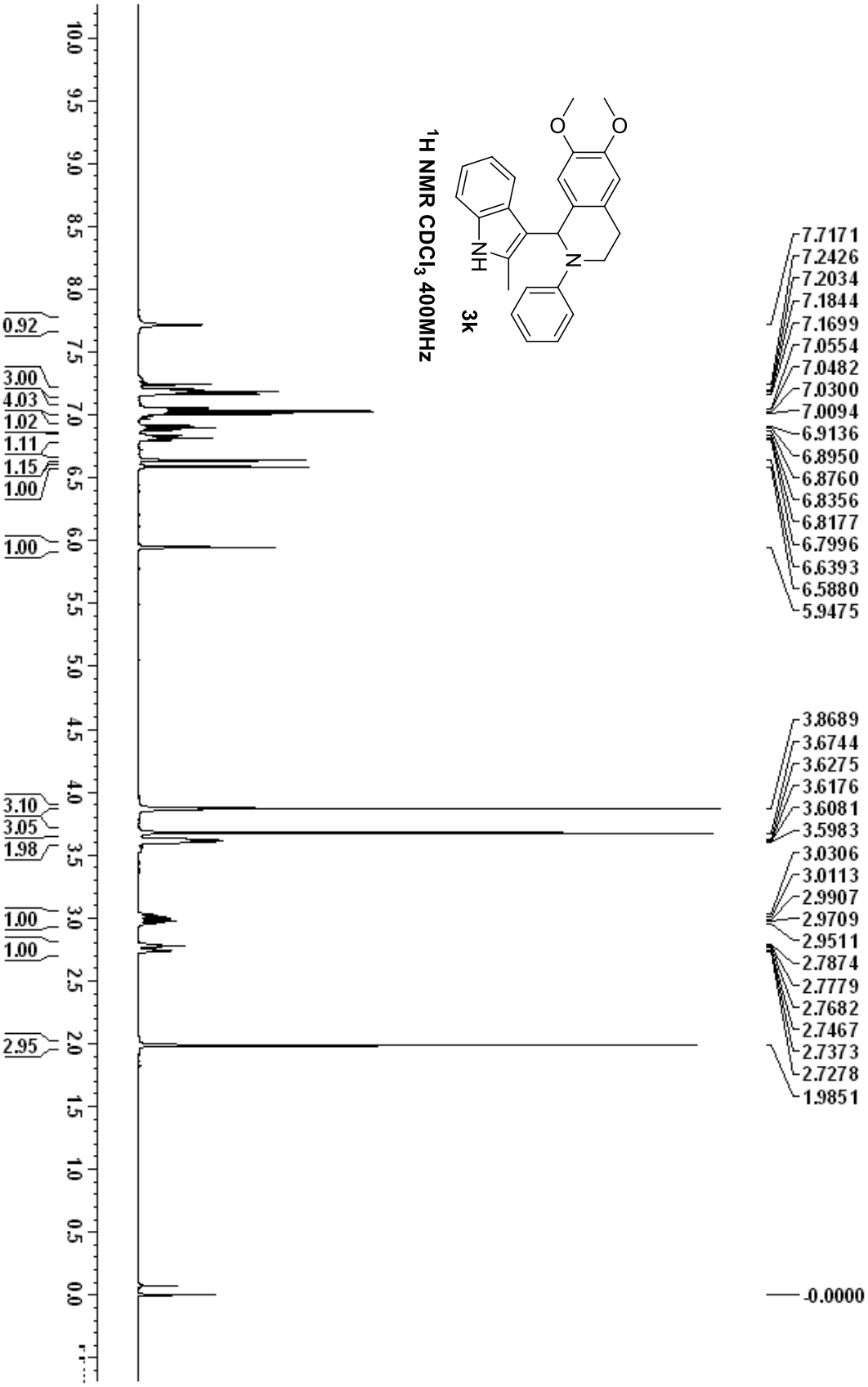
77.3168
76.9990
76.6820
56.0917
55.9522
55.8497
41.9052
25.6941


^{1}H NMR CDCl$_3$ 400MHz
3k
NH
N
O
O
0.92
3.00
4.03
1.02
1.11
1.15
1.00
1.00
3.10
3.05
1.98
1.00
1.00
2.95
7.7171
7.2426
7.2034
7.1844
7.1699
7.0554
7.0482
7.0300
7.0094
6.9136
6.8950
6.8760
6.8356
6.8177
6.7996
6.6393
6.5880
5.9475
3.8689
3.6744
3.6275
3.6176
3.6081
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3.0113
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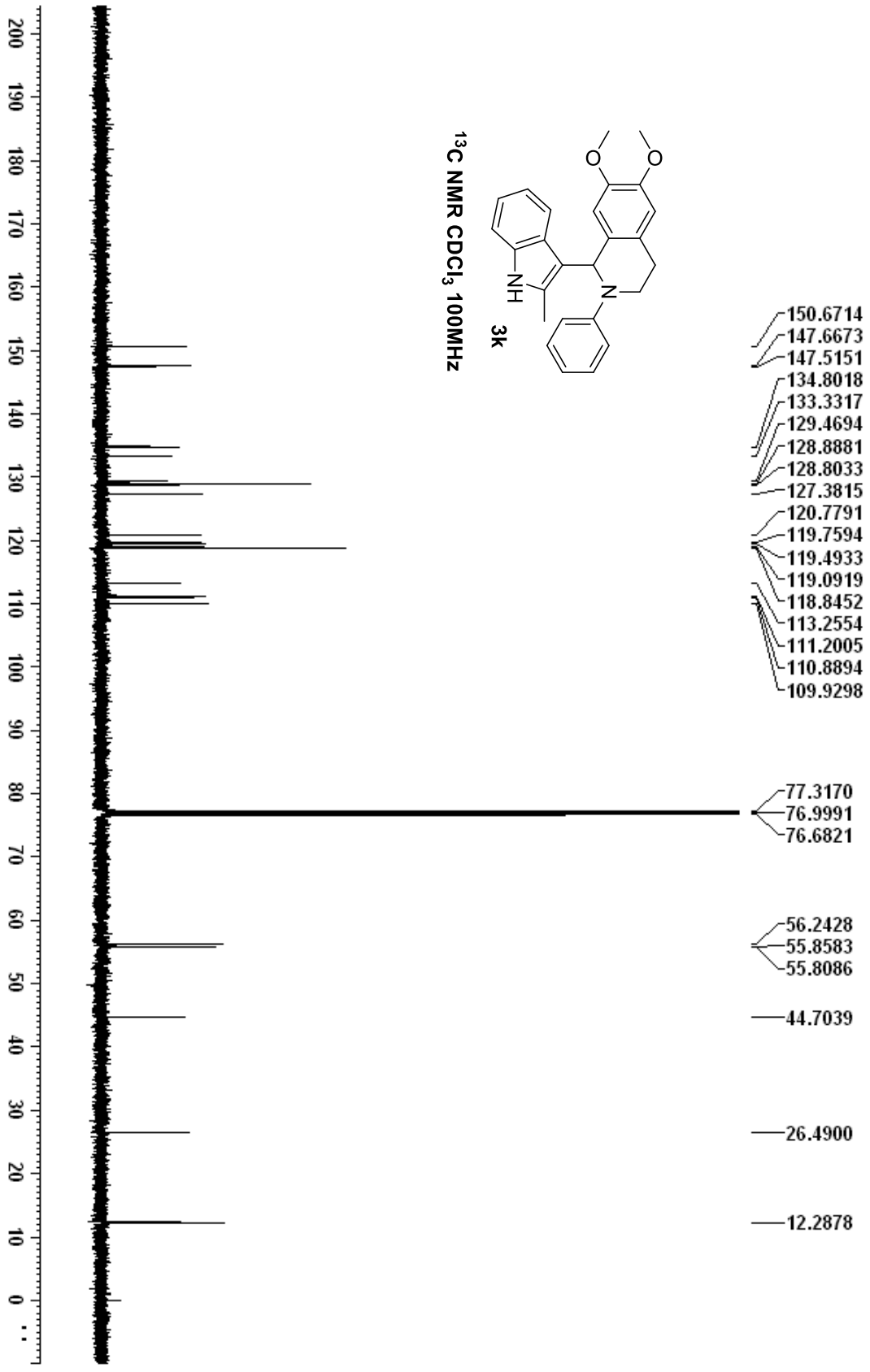
^{13}C NMR CDCl$_3$ 100MHz
3k
NH
N
O
O
150.6714
147.6673
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134.8018
133.3317
129.4694
128.8881
128.8033
127.3815
120.7791
119.7594
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118.8452
113.2554
111.2005
110.8894
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76.6821
56.2428
55.8583
55.8086
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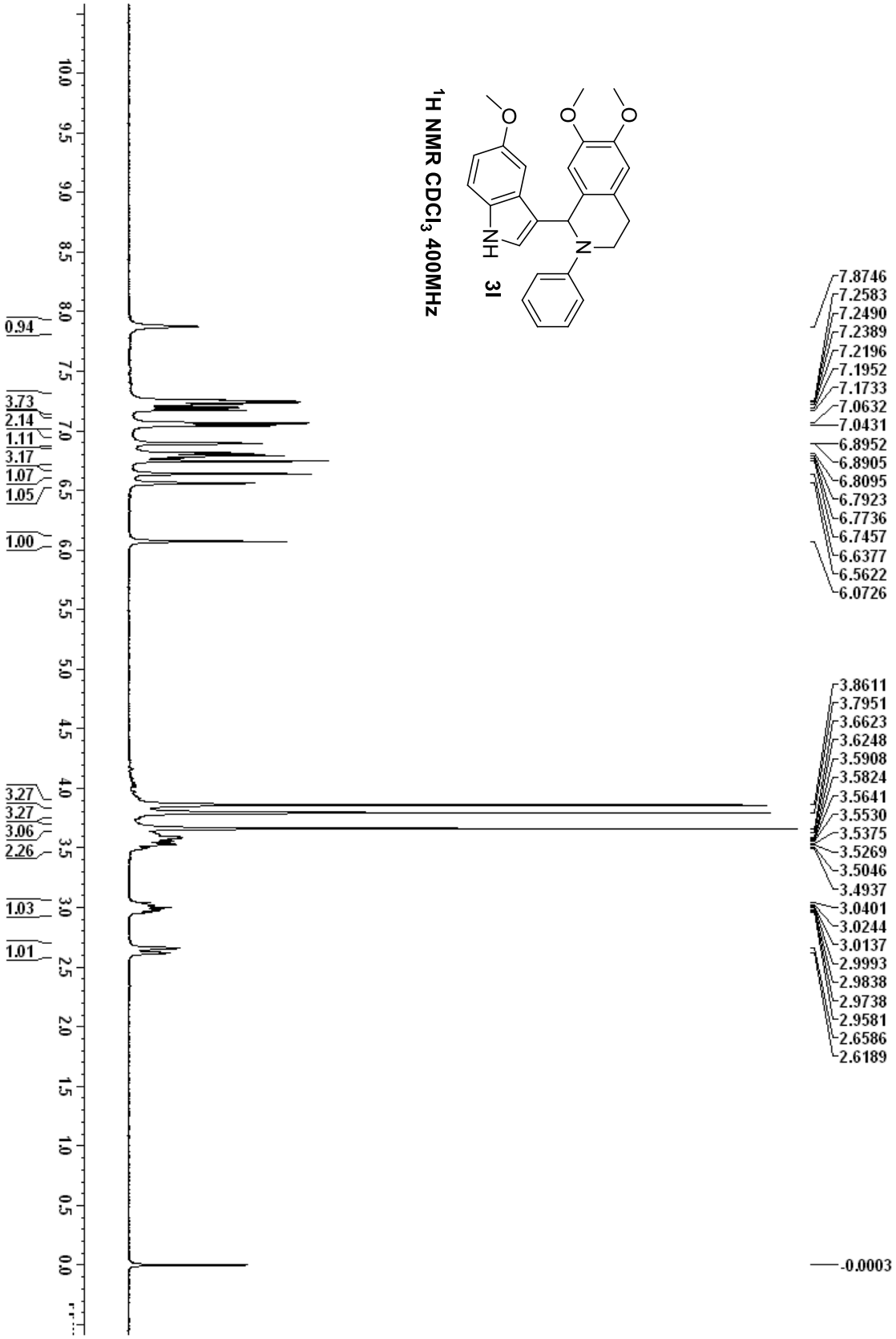
26.4900
12.2878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3l
NH
O
O
O
N
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2.14
1.11
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1.07
1.05
1.00
3.27
3.27
3.06
2.26
1.03
1.01
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7.2583
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7.2196
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7.1733
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6.7923
6.7736
6.7457
6.6377
6.5622
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3.5269
3.5046
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3.0401
3.0244
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2.6586
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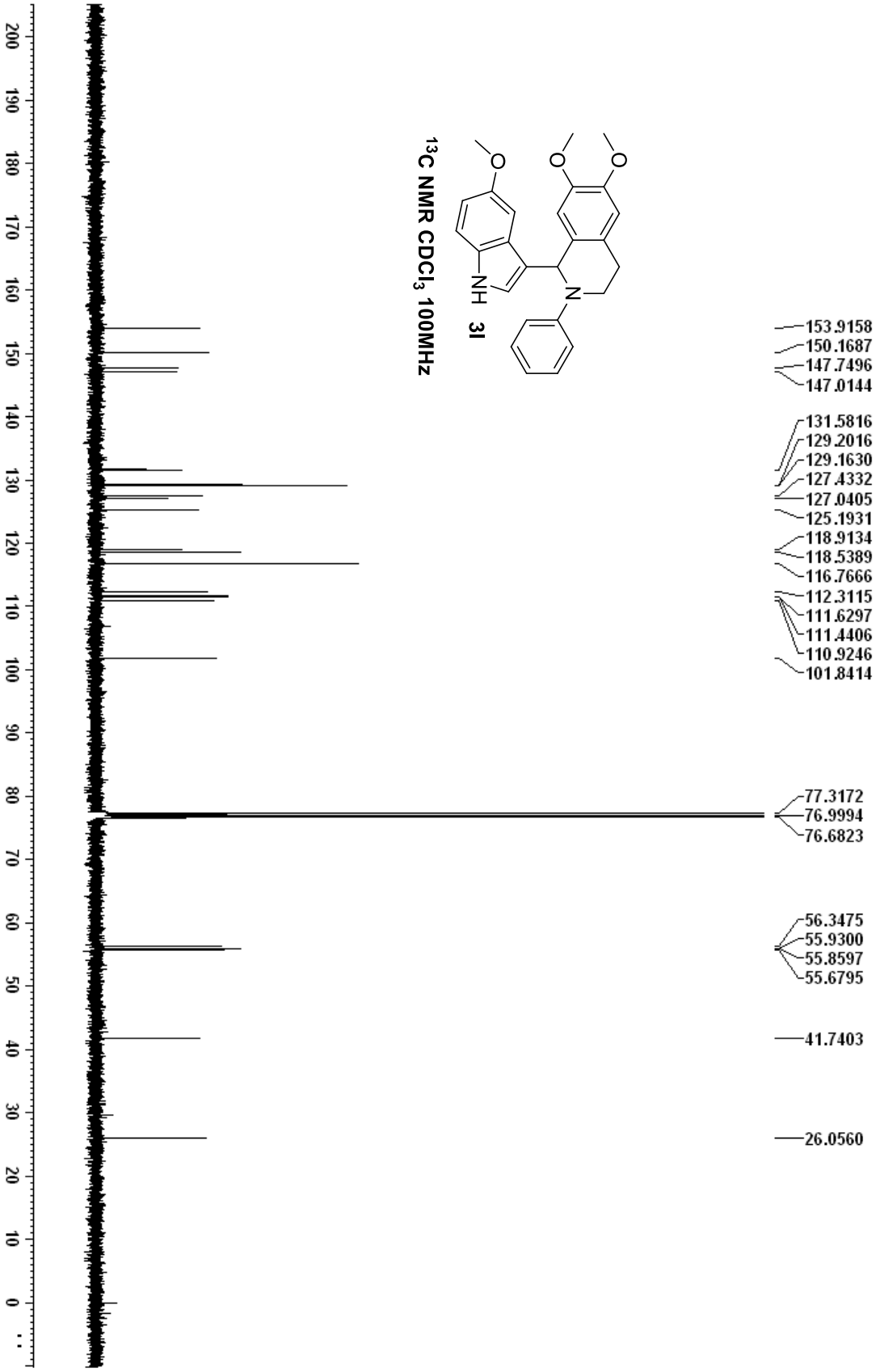
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147.7496
147.0144
131.5816
129.2016
129.1630
127.4332
127.0405
125.1931
118.9134
118.5389
116.7666
112.3115
111.6297
111.4406
110.9246
101.8414
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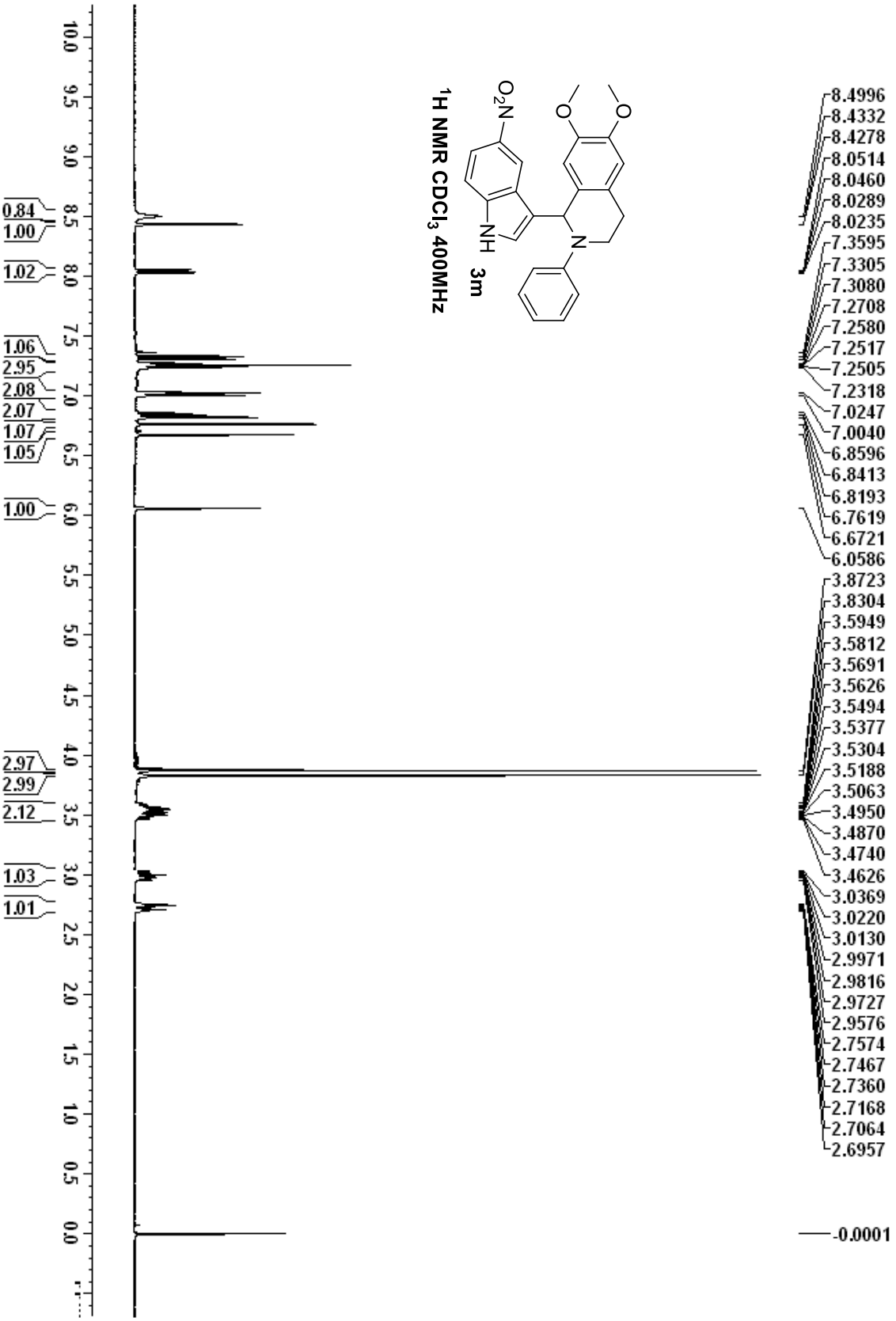
76.9994
76.6823
56.3475
55.9300
55.8597
55.6795
41.7403
26.0560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3m
O$_2$N
NH
N
O
O
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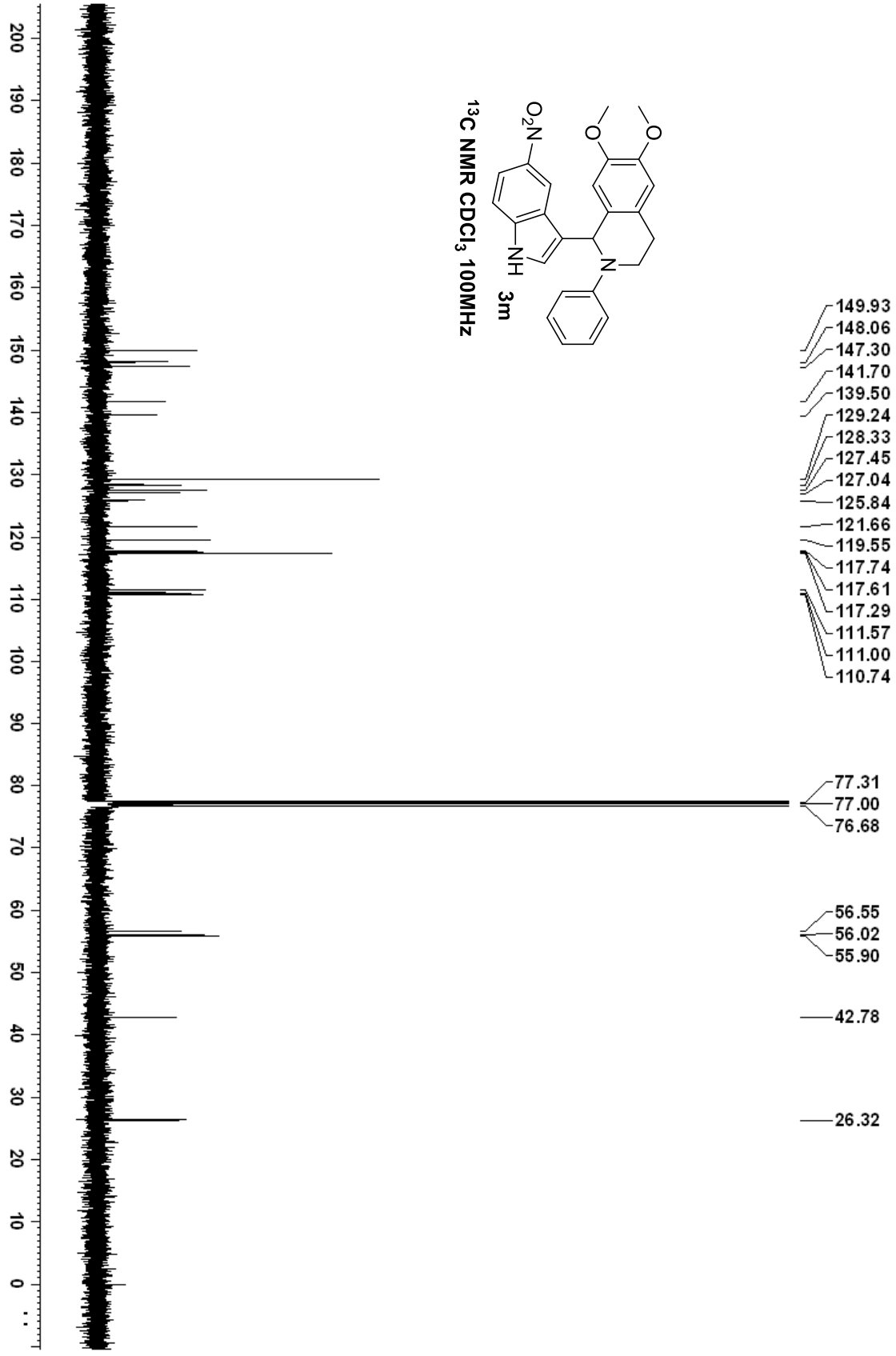
1.02
1.06
2.95
2.08
2.07
1.07
1.05
1.00
2.97
2.99
2.12
1.03
1.01
8.4996
8.4332
8.4278
8.0514
8.0460
8.0289
8.0235
7.3595
7.3305
7.3080
7.2708
7.2580
7.2517
7.2505
7.2318
7.0247
7.0040
6.8596
6.8413
6.8193
6.7619
6.6721
6.0586
3.8723
3.8304
3.5949
3.5812
3.5691
3.5626
3.5494
3.5377
3.5304
3.5188
3.5063
3.4950
3.4870
3.4740
3.4626
3.0369
3.0220
3.0130
2.9971
2.9816
2.9727
2.9576
2.7574
2.7467
2.7360
2.7168
2.7064
2.6957
-0.0001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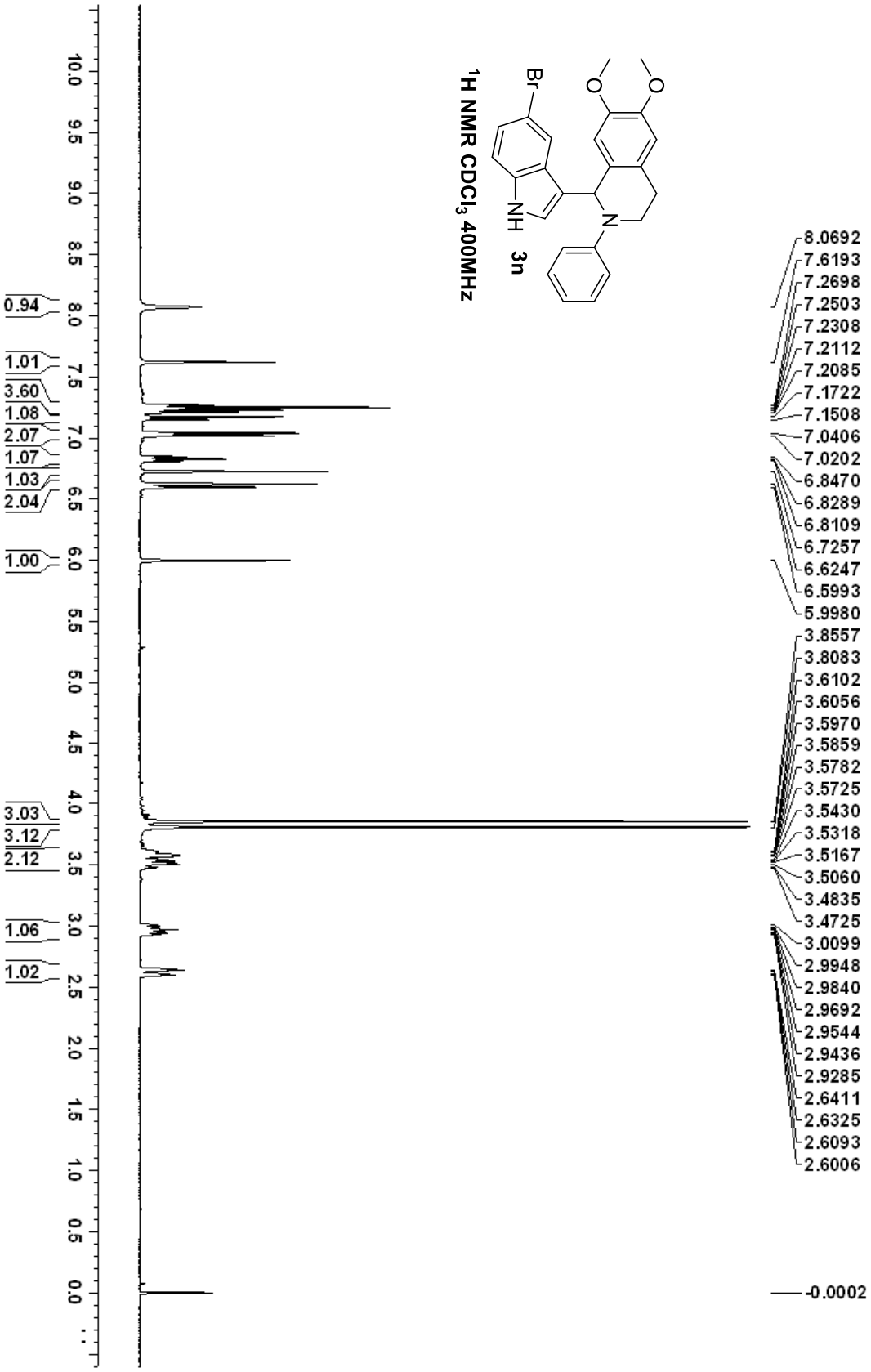
3m
O$_2$N
NH
N
O
O
149.93
148.06
147.30
141.70
139.50
129.24
128.33
127.45
127.04
125.84
121.66
119.55
117.74
117.61
117.29
111.57
111.00
110.74
77.31
77.00
76.68
56.55
56.02
55.90
42.78
26.32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Br
O
O
NH
N
3n
0.94
1.01
3.60
1.08
2.07
1.07
1.03
2.04
1.00
3.03
3.12
2.12
1.06
1.02
8.0692
7.6193
7.2698
7.2503
7.2308
7.2112
7.2085
7.1722
7.1508
7.0406
7.0202
6.8470
6.8289
6.8109
6.7257
6.6247
6.5993
5.9980
3.8557
3.8083
3.6102
3.6056
3.5970
3.5859
3.5782
3.5725
3.5430
3.5318
3.5167
3.5060
3.4835
3.4725
3.0099
2.9948
2.9840
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2.9544
2.9436
2.9285
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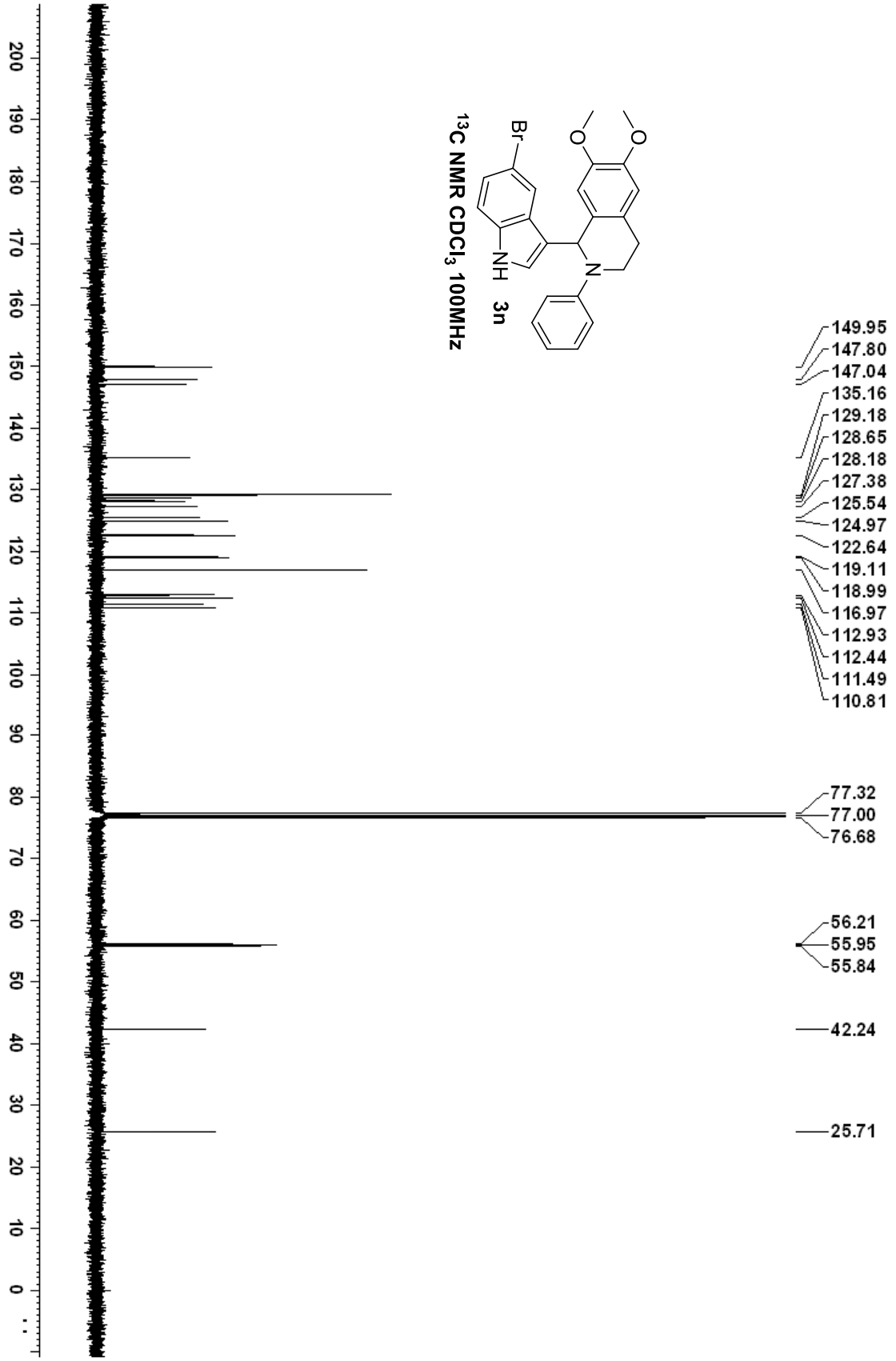
2.6325
2.6093
2.6006
-0.0002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Br
NH
N
O
O
3n
149.95
147.80
147.04
135.16
129.18
128.65
128.18
127.38
125.54
124.97
122.64
119.11
118.99
116.97
112.93
112.44
111.49
110.81
77.32
77.00
76.68
56.21
55.95
55.84
42.24
25.71
200
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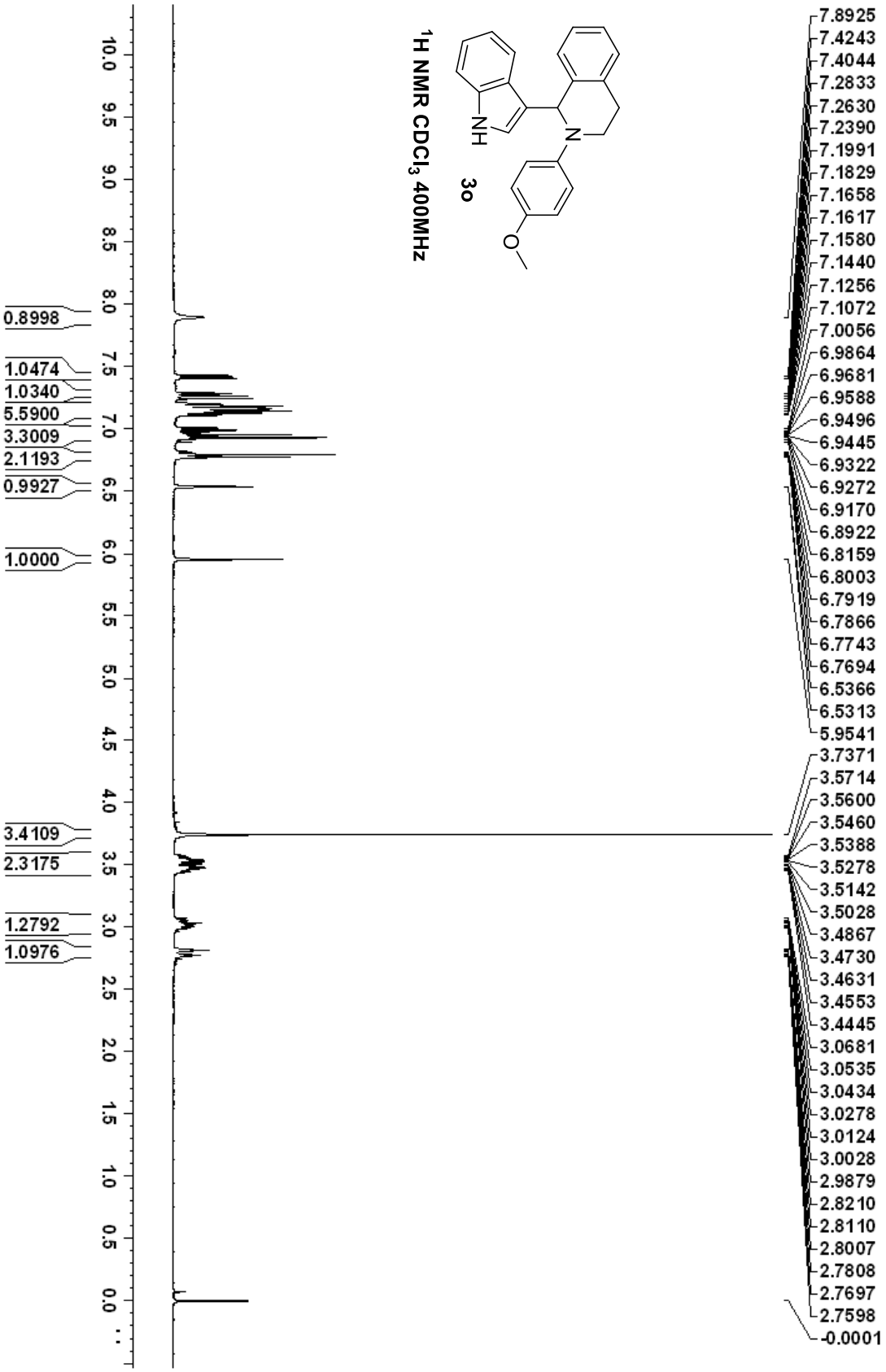
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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NH
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O
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1.0340
5.5900
3.3009
2.1193
0.9927
1.0000
3.4109
2.3175
1.2792
1.0976
7.8925
7.4243
7.4044
7.2833
7.2630
7.2390
7.1991
7.1829
7.1658
7.1617
7.1580
7.1440
7.1256
7.1072
7.0056
6.9864
6.9681
6.9588
6.9496
6.9445
6.9322
6.9272
6.9170
6.8922
6.8159
6.8003
6.7919
6.7866
6.7743
6.7694
6.5366
6.5313
5.9541
3.7371
3.5714
3.5600
3.5460
3.5388
3.5278
3.5142
3.5028
3.4867
3.4730
3.4631
3.4553
3.4445
3.0681
3.0535
3.0434
3.0278
3.0124
3.0028
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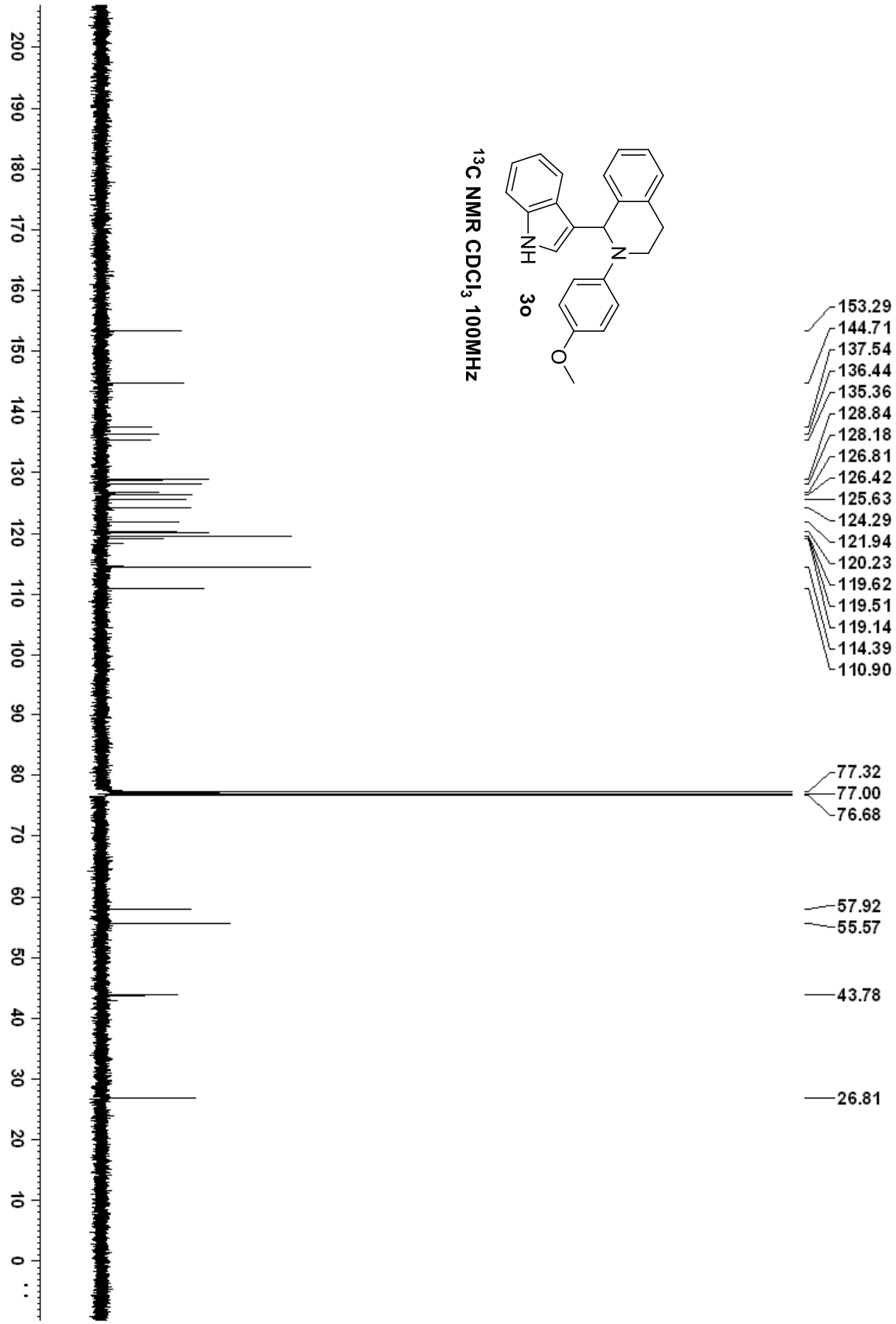
2.8210
2.8110
2.8007
2.7808
2.7697
2.7598
-0.0001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3o
NH
N
O
153.29
144.71
137.54
136.44
135.36
128.84
128.18
126.81
126.42
125.63
124.29
121.94
120.23
119.62
119.51
119.14
114.39
110.90
77.32
77.00
76.68
57.92
55.57
43.78
26.81
200
190
180
170
160
150
140
130
120
110
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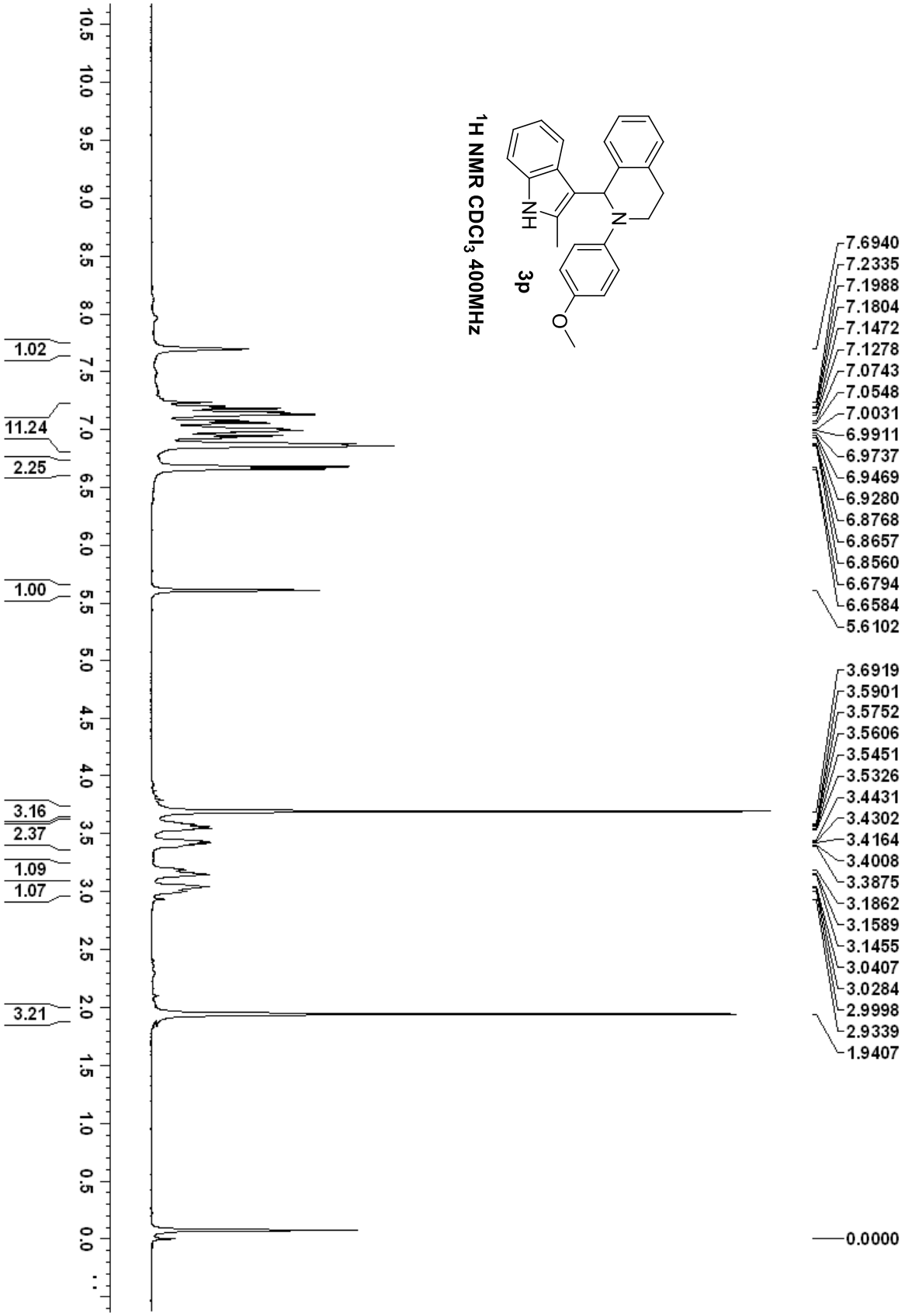
90
80
70
60
50
40
30
20
10
0


^{1}H NMR CDCl$_3$ 400MHz
3p
NH
N
O
1.02
11.24
2.25
1.00
3.16
2.37
1.09
1.07
3.21
7.6940
7.2335
7.1988
7.1804
7.1472
7.1278
7.0743
7.0548
7.0031
6.9911
6.9737
6.9469
6.9280
6.8768
6.8657
6.8560
6.6794
6.6584
5.6102
3.6919
3.5901
3.5752
3.5606
3.5451
3.5326
3.4431
3.4302
3.4164
3.4008
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3.1589
3.1455
3.0407
3.0284
2.9998
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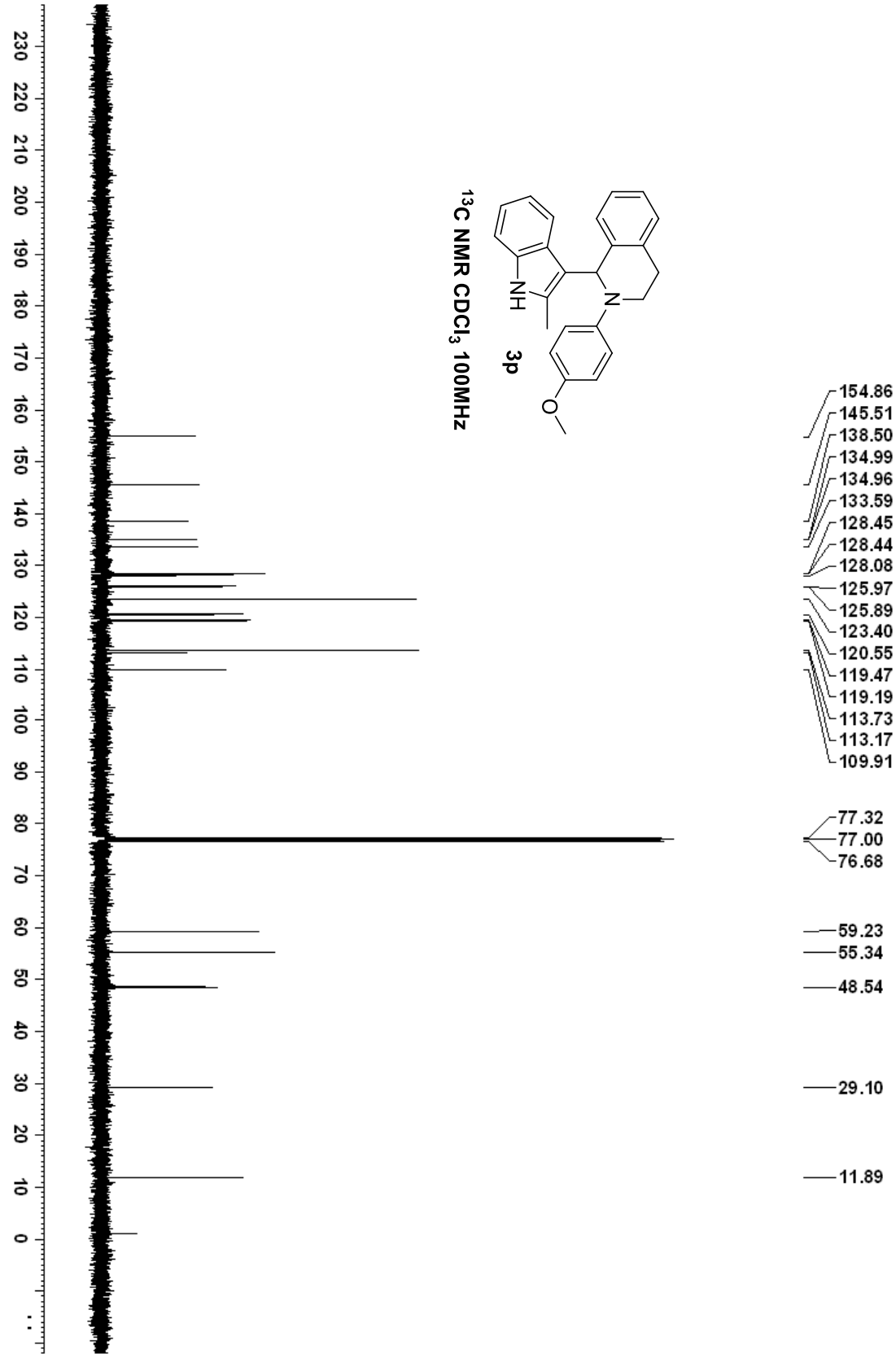
1.9407
0.0000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N
O
3p
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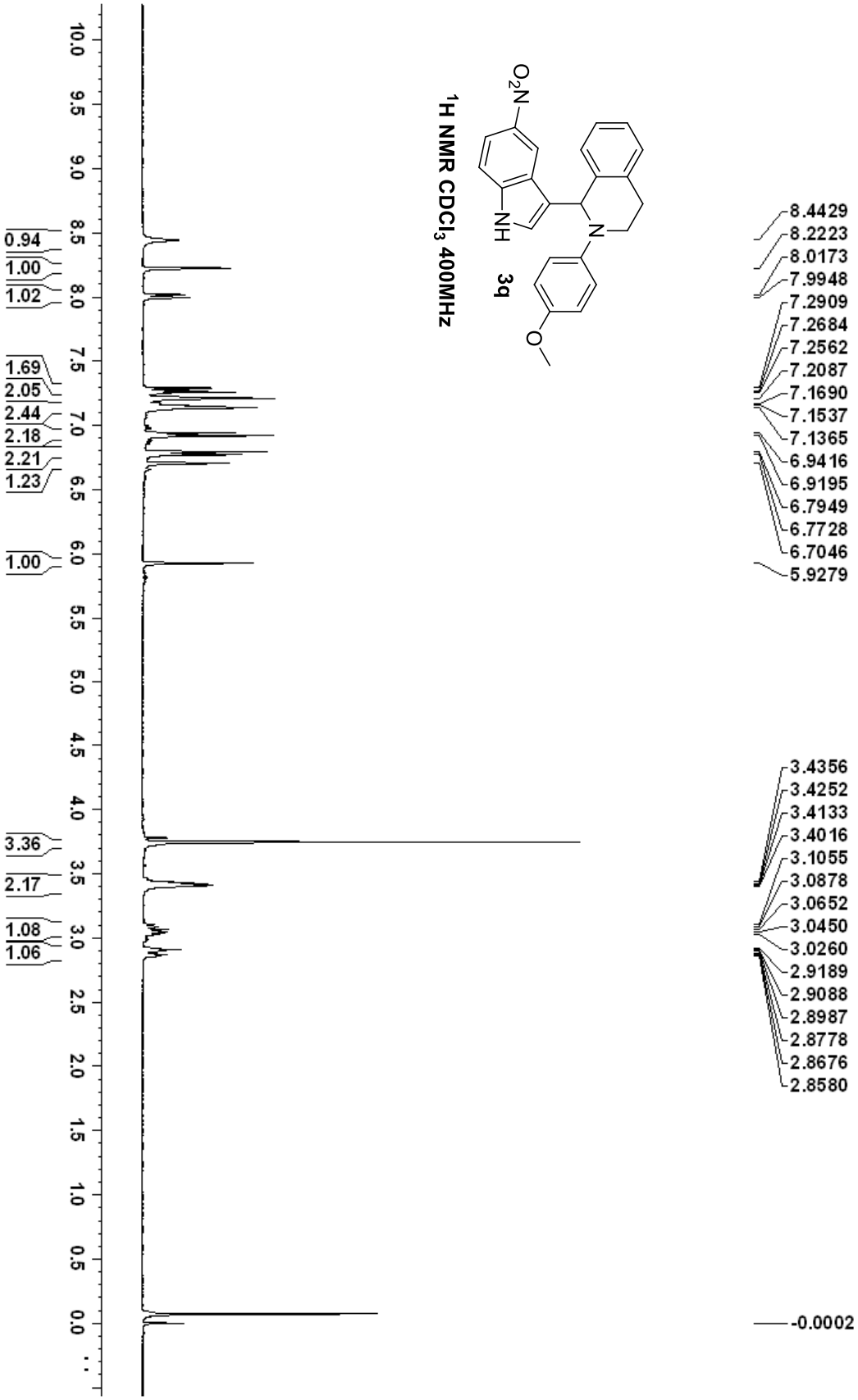
138.50
134.99
134.96
133.59
128.45
128.44
128.08
125.97
125.89
123.40
120.55
119.47
119.19
113.73
113.17
109.91
77.32
77.00
76.68
59.23
55.34
48.54
29.10
11.89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3q
O$_2$N
NH
N
O
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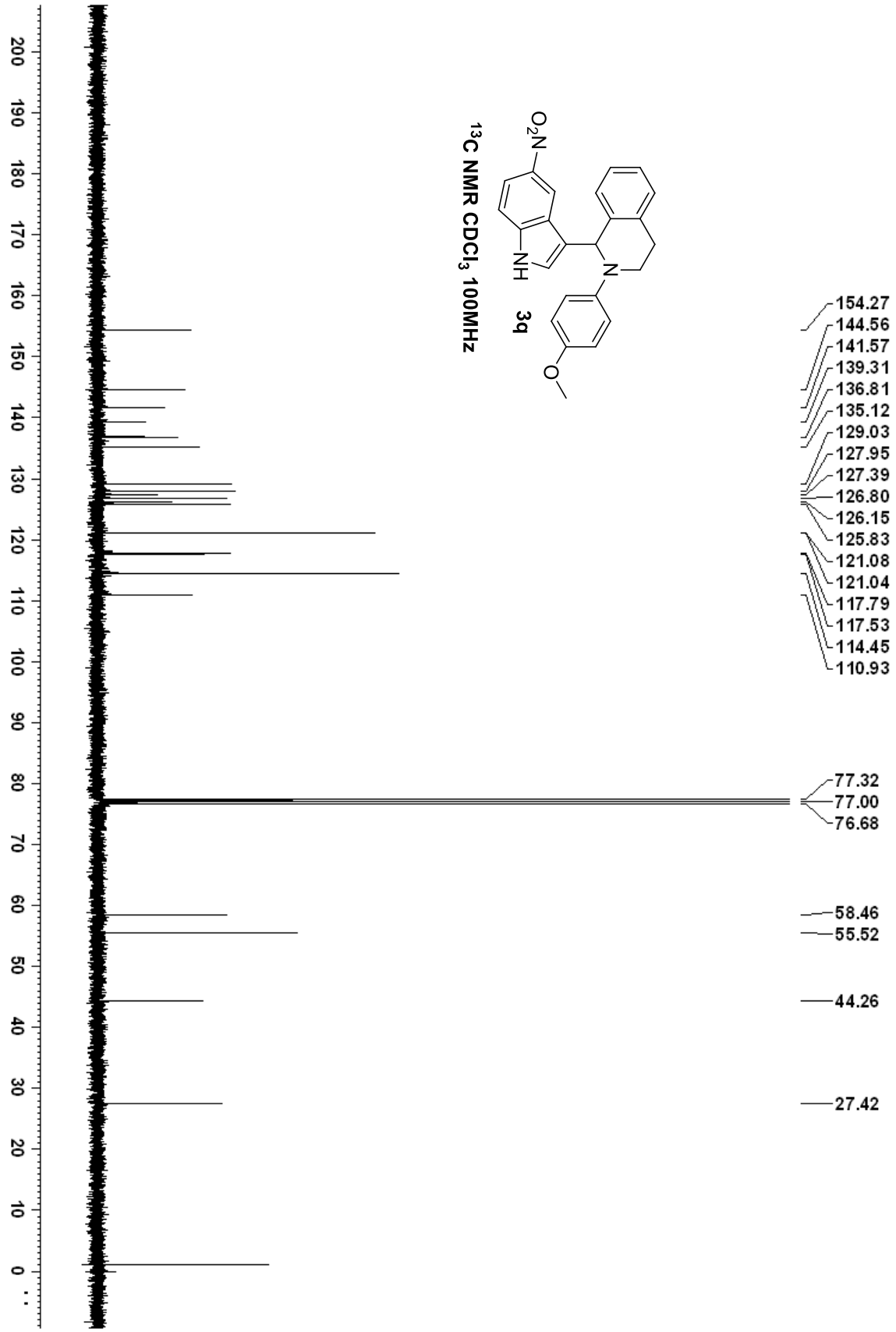
8.2223
8.0173
7.9948
7.2909
7.2684
7.2562
7.2087
7.1690
7.1537
7.1365
6.9416
6.9195
6.7949
6.7728
6.7046
5.9279
3.4356
3.4252
3.4133
3.4016
3.1055
3.0878
3.0652
3.0450
3.0260
2.9189
2.9088
2.8987
2.8778
2.8676
2.8580
-0.0002
0.94
1.00
1.02
1.69
2.05
2.44
2.18
2.21
1.23
1.00
3.36
2.17
1.08
1.06


^{13}C NMR CDCl$_3$ 100MHz
O_2N
NH
N
O
3q
154.27
144.56
141.57
139.31
136.81
135.12
129.03
127.95
127.39
126.80
126.15
125.83
121.08
121.04
117.79
117.53
114.45
110.93
77.32
77.00
76.68
58.46
55.52
44.26
27.42
200
190
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150
140
130
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70
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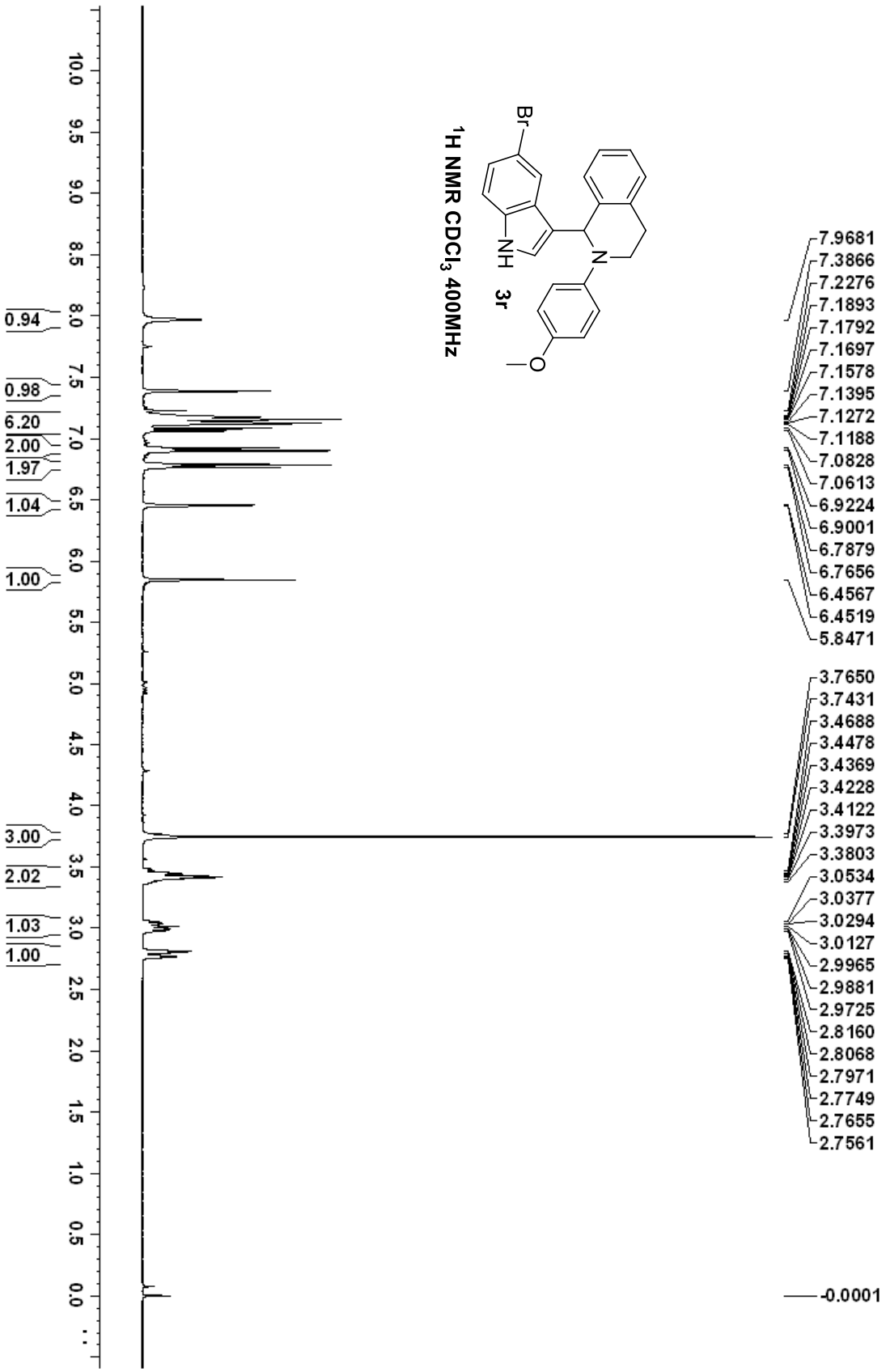
10
0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Br
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N
O
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1.97
1.04
1.00
3.00
2.02
1.03
1.00
7.9681
7.3866
7.2276
7.1893
7.1792
7.1697
7.1578
7.1395
7.1272
7.1188
7.0828
7.0613
6.9224
6.9001
6.7879
6.7656
6.4567
6.4519
5.8471
3.7650
3.7431
3.4688
3.4478
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3.4122
3.3973
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3.0534
3.0377
3.0294
3.0127
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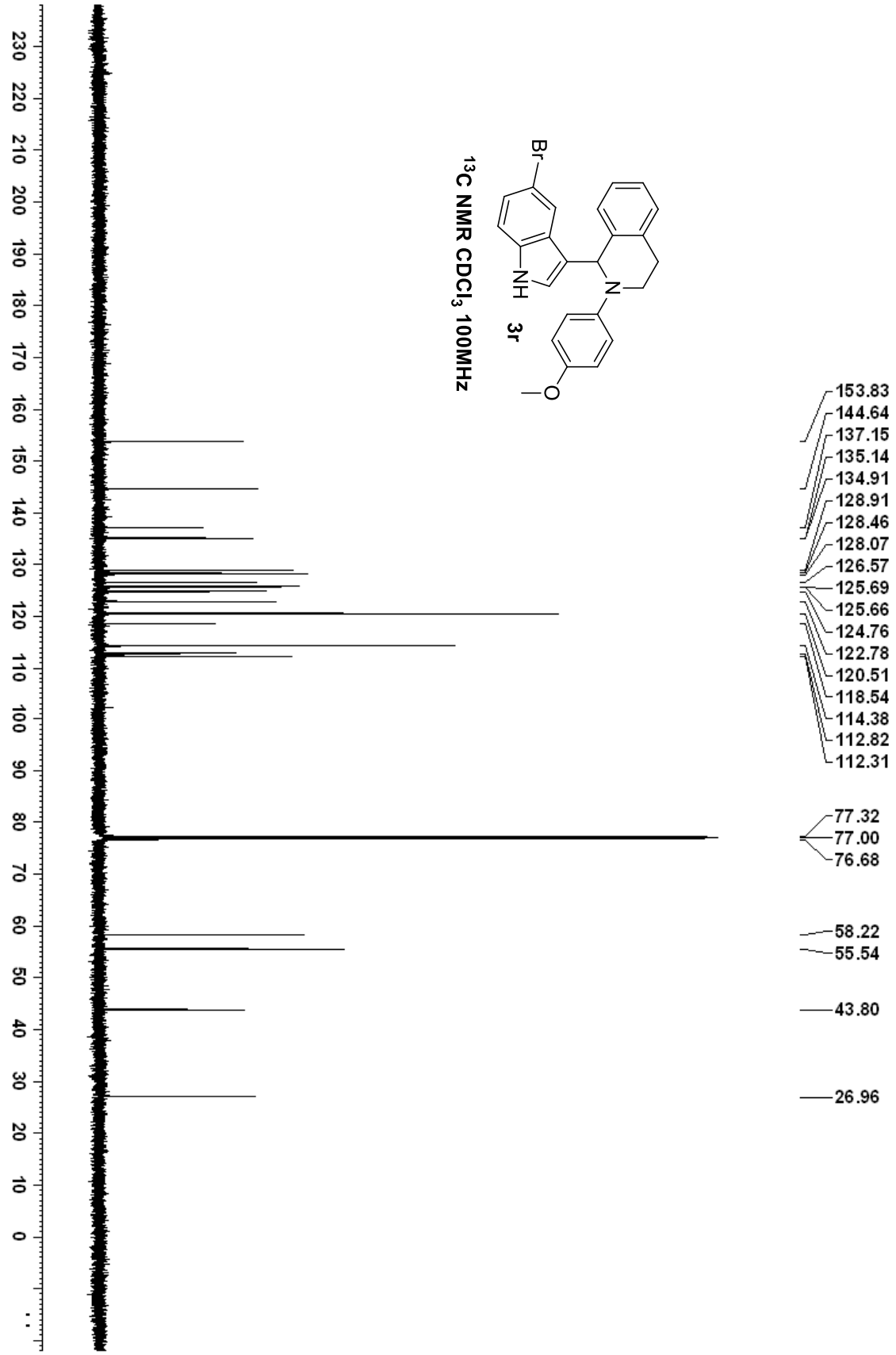
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3r
Br
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128.46
128.07
126.57
125.69
125.66
124.76
122.78
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77.00
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