Supporting information

Catalytic Enantioselective Synthesis of Tetrahydroquinolines Containing All-carbon Quaternary Stereocenters via Formation of Aza-ortho-xylylene with 1,2-Dihydroquinoline as Precursor

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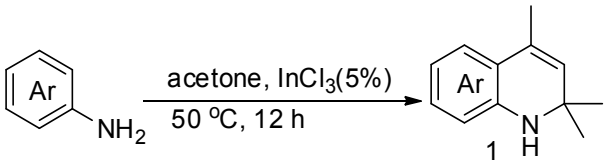
Content

General information

All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Alfa Aesar and Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents.

Melting points were measured on a Meltemp melting point apparatus and were not corrected. ^{1}H NMR spectra were recorded on commercial instruments (600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (151 Hz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 30℃with UV detector at 254 nm.

1. General procedural for synthesis of 2, 2, 4-trimethyl dihydroquinolines 1.

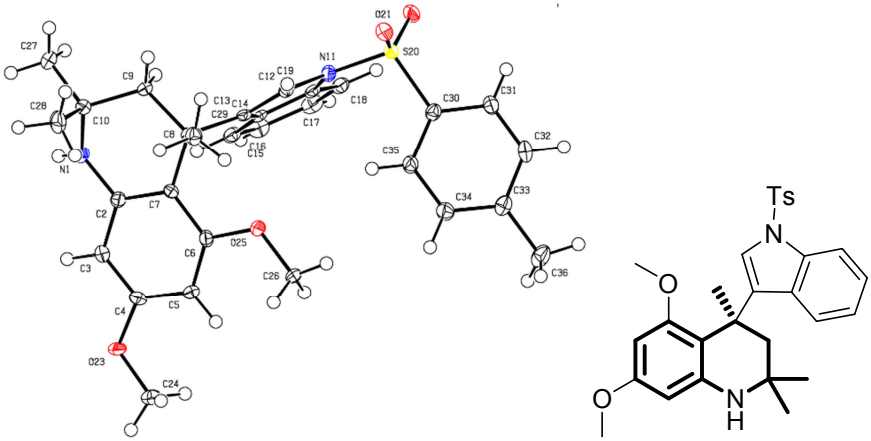


In a 25-mL round-bottomed flask, a mixture of aniline and catalytic $InCl_3$ (5%) was stirred in acetone at 50 ℃ for 12 h. Then the reaction solvent was evaporated, the residue was dissolved in CH_2Cl_2, washed with saturated Na_2CO_3 solution and brine, dried with anhydrous Na_2SO_4 and evaporated to get the crude product which was purified by flash column or recrystallization.

2. General procedural for preparation of chiral tetrahydroquinolines 3.

A reaction tube was charged with the dihydroquinoline **1** (0.2 mmol, 1 eq.), indole **2** (0.2 mmol, 1 eq.), anhydrous $CHCl_3$ (2 mL), **4c** (3 mol %), 4 Å molecular sieves (100 mg). The system was stirred under a nitrogen atmosphere at 0 ℃ for 48 h. Then the products were obtained by purification with flash silica gel chromatography.

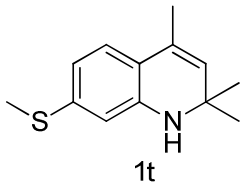
3. X-ray single crystal data for 3y (CCDC1423965):



Chemical formula	**$C_{29}H_{32}N_2O_4S$**
Formula weight	504.64
Space group	P21
Z	2
a/Å	12.9590(2)
b/Å	7.94026(11)
c/Å	14.0403(2)
α/°	90
β/°	116.595(2)
γ/°	90
Volume/$Å^3$	1291.86(4)
$\rho_{calc}g/cm^3$	1.297
Temperature/K	291

4. Characterization of selected products.

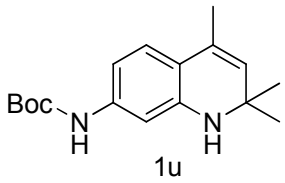
2,2,4-trimethyl-7-(methylthio)-1,2-dihydroquinoline (1t)



1t

Brown oil; δ_H (400 MHz, $CDCl_3$) 6.99 (1 H, d, *J* 8.0), 6.56 (1 H, dd, *J* 8.0, 1.9), 6.37 (1 H, d, *J* 1.8), 5.29 (1 H, d, *J* 1.3), 3.73 (1 H, s), 2.46 (3 H, s), 1.99 (3 H, d, *J* 1.4), 1.29 (6 H, s); δ_C (101 MHz, $CDCl_3$) 143.64, 138.11, 128.19, 127.71, 123.99, 119.11, 115.26, 110.55, 52.00, 31.14, 18.54, 15.78; HRMS (ESI):calcd. for $C_{14}H_{15}NNa$(M+Na):220.1097; found: 220.1093.

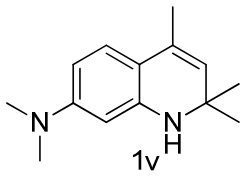
tert-butyl (2,2,4-trimethyl-1,2-dihydroquinolin-7-yl)carbamate (1u)



1u

White solid; M.P. 136-138 ℃; δ_H (400 MHz, $CDCl_3$) 6.95 (1 H, d, *J* 8.2), 6.82 (1 H, s), 6.49 (1 H, s), 6.40 (1 H, dd, *J* 8.2, 2.0), 5.23 (1 H, d, *J* 1.1), 3.74 (1 H, s), 1.97 (3 H, d, *J* 1.2), 1.53 (9 H, s), 1.26 (6 H, s); δ_C (101 MHz, $CDCl_3$) 152.69, 144.14, 138.55, 128.15, 126.83, 124.05, 116.99, 106.92, 102.60, 80.30, 51.90, 31.05, 28.39, 18.52. HRMS (ESI):calcd. for $C_{17}H_{25}N_2O_2$(M+H):289.1911; found:289.1898.

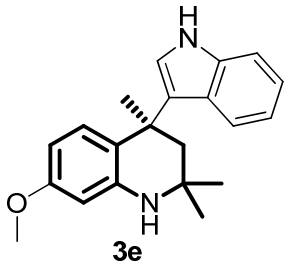
N,N,2,2,4-pentamethyl-1,2-dihydroquinolin-7-amine (1v)



1v

Brown oil; δ_H (400 MHz, $CDCl_3$) 6.98 (1 H, d, *J* 8.4), 6.11 (1 H, dd, *J* 8.4, 2.5), 5.87 (1 H, d, *J* 2.5), 5.15 (1 H, d, *J* 1.2), 3.67 (1 H, s), 2.93 (6 H, s), 1.98 (3 H, d, *J* 1.3), 1.29 (6 H, s); δ_C (101 MHz, $CDCl_3$) 151.19, 144.30, 128.52, 124.45, 124.39, 112.11, 102.20, 97.04, 51.86, 40.59, 31.09, 18.56. HRMS (ESI):calcd. for $C_{14}H_{21}N_2$(M+H):217.1699; found:217.1690.

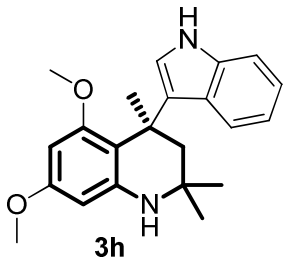
(R)-4-(1H-indol-3-yl)-7-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3e)



3e

Colorless oil (58 mg, 90%); $[\alpha]_D^{10}$ -8.8 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.82 (1 H, s), 7.52 (1 H, d, *J* 8.0), 7.31 (1 H, d, *J* 8.1), 7.15 (1 H, t, *J* 7.5), 7.03 (2 H, dd, *J* 7.9, 5.6), 6.72 (1 H, d, *J* 1.6), 6.25 (1 H, dd, *J* 8.5, 2.4), 6.14 (1 H, d, *J* 2.4), 3.78 (3 H, s), 3.70 (1 H, s), 2.66 (1 H, d, *J* 13.7), 1.91 (1 H, 0 d, *J* 13.7), 1.86 (3 H, s), 1.30 (3 H, s), 0.96 (3 H, s). δ_C (151 MHz, $CDCl_3$) 158.77, 144.50, 137.32, 129.76, 127.13, 125.61, 122.05, 121.54, 121.07, 118.98, 111.26, 103.39, 99.48, 55.06, 49.97, 48.94, 36.07, 31.46, 30.69, 30.39; HRMS (ESI):calcd. for $C_{21}H_{25}N_2O$(M+H):321.1691; found:321.1955.

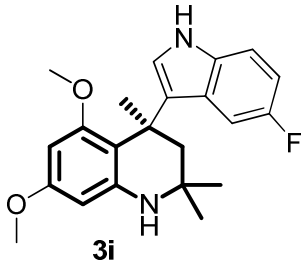
(R)-4-(1H-indol-3-yl)-5,7-dimethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3h)



3h

Colorless oil (63 mg, 90%); $[\alpha]_D^{10}$ -15.0 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.78 (1 H, s), 7.36 (1 H, d, *J* 7.9), 7.29 (1 H, d, *J* 8.1), 7.08 (1 H, t, *J* 7.5), 6.95 (1 H, t, *J* 7.5), 6.83 (1 H, s), 5.83 (2 H, s), 3.76 (3 H, s), 3.34 (3 H, s), 2.54 (1 H, d, *J* 13.7), 1.96 (3 H, s), 1.85 (1 H, d, *J* 13.7), 1.30 (3 H, s), 1.01 (3 H, s). δ_C (151 MHz, $CDCl_3$) 161.08, 159.39, 145.47, 136.97, 126.79, 125.66, 121.23, 120.97, 120.70, 118.67, 110.97, 109.75, 92.62, 90.30, 55.28, 55.00, 51.90, 49.45, 35.40, 30.42, 29.97, 28.60; HRMS (ESI):calcd. for $C_{22}H_{27}N_2O_2$(M+H): 351.2067; found: 351.2064.

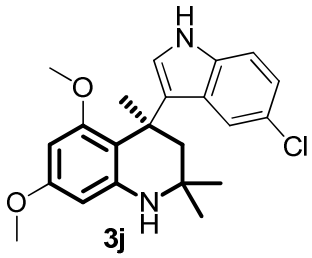
(R)-4-(5-fluoro-1H-indol-3-yl)-5,7-dimethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline(3i)



3i

Colorless oil (65 mg, 88%); $[\alpha]_D^{10}$ -25.0 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.86 (1 H, s), 7.16 (1 H, dd, *J* 8.7, 4.4), 6.99 (1 H, d, *J* 10.4), 6.89 (1 H, s), 6.82 (1 H, t, *J* 8.9), 5.82 (2 H, d, *J* 6.4), 3.76 (4 H, s), 3.34 (3 H, s), 2.44 (1 H, d, *J* 13.7), 1.94 (3 H, s), 1.83 (1 H, d, *J* 13.7), 1.29 (3 H, s), 1.02 (3 H, s). δ_C (151 MHz, $CDCl_3$) 160.95, 159.47, 157.77, 156.23, 145.50, 133.43, 127.12, 125.89, 125.83, 122.98, 111.37, 111.31, 109.35, 109.17, 109.13, 105.61, 105.45, 92.60, 90.23, 55.23, 54.98, 51.89, 49.37, 35.19, 30.50, 29.77, 28.42, 25.37; HRMS (ESI):calcd. for $C_{22}H_{26}FN_2O_2$(M+H):369.1973; found:369.1966.

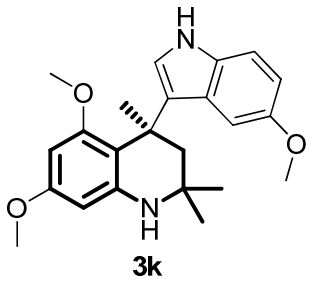
(R)-4-(5-chloro-1H-indol-3-yl)-5,7-dimethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3j)



3j

Colorless oil (66 mg, 86%); $[\alpha]_D^{10}$ -17.4 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.83 (1 H, s), 7.36 (1 H, s), 7.18 (1 H, d, *J* 8.6), 7.04 (1 H, dd, *J* 8.6, 1.8), 6.81 (1 H, d, *J* 2.1), 5.89 – 5.74 (2 H, m), 3.77 (4 H, s), 3.39 (3 H, s), 2.45 (1 H, d, *J* 13.7), 1.94 (3 H, s), 1.86 (1 H, d, *J* 13.7), 1.28 (3 H, s), 0.98 (3 H, s). δ_C (151 MHz, $CDCl_3$) 160.91, 159.54, 145.47, 135.28, 126.66, 126.49, 124.26, 122.86, 121.29, 120.16, 111.91, 109.00, 92.56, 90.12, 55.18, 55.04, 51.77, 49.36, 35.33, 30.15, 30.06, 28.75; HRMS (ESI):calcd. for $C_{22}H_{26}ClN_2O_2$(M+H):385.1677; found:385.1672.

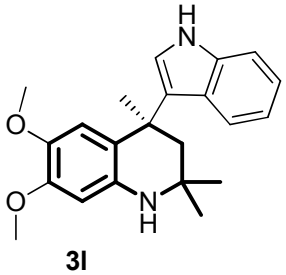
(R)-5,7-dimethoxy-4-(5-methoxy-1H-indol-3-yl)-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3k)



3k

Colorless oil (65 mg, 85%); $[\alpha]_D^{10}$ -20.7 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.67 (1 H, s), 7.15 (1 H, d, *J* 8.7), 6.85 (1 H, s), 6.79 (1 H, s), 6.74 (1 H, d, *J* 8.7), 5.80 (2 H, d, *J* 6.7), 3.74 (3 H, s), 3.70 (3 H, s), 3.32 (3 H, s), 2.49 (1 H, d, *J* 13.7), 1.95 (3 H, s), 1.82 (1 H, d, *J* 13.7), 1.29 (3 H, s), 1.03 (3 H, s). δ_C (151 MHz, $CDCl_3$) 161.14, 159.42, 152.99, 145.67, 132.09, 126.83, 126.01, 121.79, 111.33, 110.94, 109.64, 102.85, 92.48, 90.22, 55.64, 55.32, 54.99, 51.91, 49.37, 35.19, 30.62, 29.57, 28.33; HRMS (ESI):calcd. for $C_{23}H_{29}N_2O_3$(M+H):381.2173; found:381.2163.

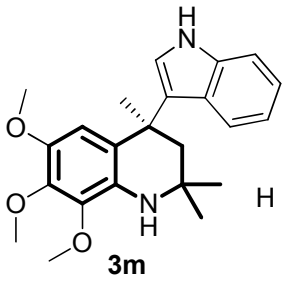
(R)-4-(1H-indol-3-yl)-6,7-dimethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3l)



3l

Colorless oil (59 mg, 85%); $[\alpha]_D^{10}$ -16.8 (C=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.55 (d, *J*=8.0, 1H), 7.32 (d, *J*=8.1, 1H), 7.16 (t, *J*=7.4, 1H), 7.05 (t, *J*=7.5, 1H), 6.75 (s, 2H), 6.24 (s, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.66 (d, *J*=13.7, 1H), 1.94 (d, *J*=13.7, 1H), 1.88 (s, 3H), 1.32 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.50, 141.50, 137.31, 126.79, 125.51, 122.13, 121.51, 121.02, 119.80, 118.96, 113.51, 111.32, 99.64, 56.89, 55.72, 50.12, 49.04, 36.35, 31.08, 30.86, 29.99; HRMS (ESI):calcd. for $C_{22}H_{27}N_2O_2$(M+H):351.2076; found:351.2079.

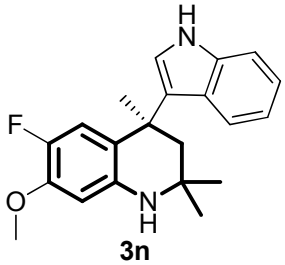
(R)-4-(1H-indol-3-yl)-6,7,8-trimethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3m)



3m

Colorless oil (68 mg, 89%); $[\alpha]_D^{10}$ -15.4 (C=0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.27 (d, *J*=8.2, 1H), 7.20 (d, *J*=8.0, 1H), 7.07 (t, *J*=7.5, 1H), 7.00 (s, 1H), 6.91 (t, *J*=7.5, 1H), 5.94 (s, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 3.62 (s, 1H), 2.96 (s, 3H), 2.49 (d, *J*=13.8, 1H), 1.99 (s, 3H), 1.76 (d, *J*=13.8, 1H), 1.34 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.18, 152.43, 140.13, 136.82, 134.63, 128.13, 125.69, 121.25, 120.70, 120.38, 118.94, 114.15, 110.87, 94.17, 60.45, 59.21, 55.58, 52.15, 49.57, 35.47, 31.70, 28.99, 28.50; HRMS (ESI):calcd. for $C_{23}H_{29}N_2O_3$ (M+H):381.2175; found:381.2180.

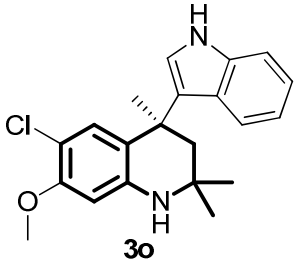
(R)-6-fluoro-4-(1H-indol-3-yl)-7-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3n)



3n

Colorless oil (59 mg, 87%); $[\alpha]_D^{10}$ -19.6 (C=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.49 (d, *J*=8.0, 1H), 7.35 (d, *J*=8.1, 1H), 7.17 (t, *J*=7.5, 1H), 7.04 (t, *J*=7.5, 1H), 6.84 (d, *J*=12.8, 1H), 6.81 (d, *J*=2.3, 1H), 6.19 (d, *J*=7.6, 1H), 3.87 (s, 3H), 3.63 (d, *J*=39.4, 1H), 2.65 (d, *J*=13.7, 1H), 1.89 (d, *J*=13.8, 1H), 1.84 (s, 3H), 1.31 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.24, 144.36, 139.65, 137.29, 126.70, 125.40, 121.75, 121.68, 120.89, 119.08, 115.95, 115.77, 111.26, 99.98, 56.13, 50.08, 48.61, 36.13, 30.91, 30.61, 30.41; HRMS (ESI):calcd. for $C_{21}H_{24}FN_2O$ (M+H):339.1877; found:339.1881.

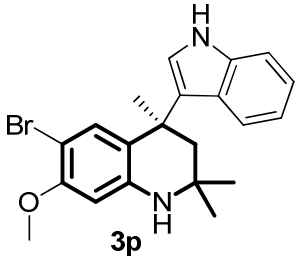
(R)-6-chloro-4-(1H-indol-3-yl)-7-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3o)



3o

Colorless oil (63 mg, 89%); $[\alpha]_D^{10}$ -17.2 (C=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (s, 1H), 7.53 (d, *J*=8.0, 1H), 7.35 (d, *J*=8.1, 1H), 7.17 (t, *J*=7.5, 1H), 7.10 (s, 1H), 7.05 (t, *J*=7.5, 1H), 6.74 (d, *J*=2.3, 1H), 6.17 (s, 1H), 3.88 (s, 3H), 2.68 (d, *J*=13.7, 1H), 1.89 (d, *J*=13.7, 1H), 1.85 (s, 3H), 1.30 (d, *J*=5.3, 3H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.70, 143.10, 137.33, 130.03, 126.47, 125.41, 121.96, 121.66, 121.44, 120.88, 119.08, 111.33, 110.10, 98.63, 77.37, 77.26, 77.06, 76.74, 55.96, 50.14, 48.45, 36.07, 31.27, 30.66, 30.23.

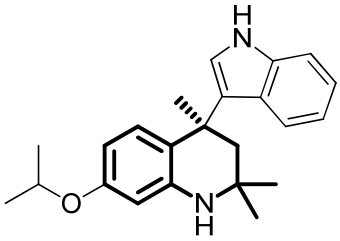
(R)-6-bromo-4-(1H-indol-3-yl)-7-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3p)



3p

Colorless oil (70 mg, 88%); $[\alpha]_D^{10}$ -14.1 (C=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.54 (d, *J*=8.0, 1H), 7.35 (d, *J*=8.1, 1H), 7.26 (s, 1H), 7.17 (t, *J*=7.2, 1H), 7.09 – 7.01 (m, 1H), 6.71 (d, *J*=2.4, 1H), 6.16 (s, 1H), 3.87 (s, 3H), 2.68 (d, *J*=13.7, 1H), 1.91 (d, *J*=5.9, 1H), 1.85 (s, 3H), 1.31 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.57, 143.83, 137.35, 132.94, 126.38, 125.41, 122.18, 122.05, 121.64, 120.86, 119.05, 111.38, 98.54, 98.20, 56.04, 50.14, 48.42, 36.08, 31.35, 30.69, 30.15.

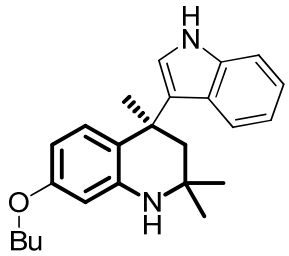
(R)-4-(1H-indol-3-yl)-7-isopropoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3q)



3q

Colorless oil (64 mg, 92%); $[\alpha]_D^{10}$ -13.6 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.84 (1 H, s), 7.54 (1 H, d, *J* 8.0), 7.31 (1 H, d, *J* 8.1), 7.15 (1 H, t, *J* 7.5), 7.03 (2 H, dd, *J* 11.9, 6.4), 6.70 (1 H, d, *J* 1.5), 6.24 (1 H, dd, *J* 8.5, 2.4), 6.13 (1 H, d, *J* 2.4), 4.51 (1 H, dt, *J* 12.1, 6.0), 3.64 (1 H, s), 2.66 (1 H, d, *J* 13.7), 1.92 (1 H, d, *J* 13.7), 1.86 (3 H, s), 1.35 (6 H, d, *J* 6.1), 1.29 (3 H, s), 0.95 (3 H, s). δ_C (151 MHz, $CDCl_3$) 157.07, 144.53, 137.32, 129.71, 127.11, 125.63, 122.14, 121.48, 121.11, 120.95, 118.92, 111.27, 105.22, 101.61, 69.64, 49.95, 48.94, 36.08, 31.54, 30.71, 30.29, 22.35. HRMS (ESI):calcd. for $C_{23}H_{29}N_2O$(M+H):349.2274; found: 349.2267.

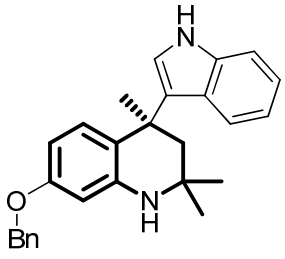
(R)- 7-butoxy-4-(1H-indol-3-yl)-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3r)



3r

Colorless oil (67 mg, 93%); $[\alpha]_D^{10}$ -12.0 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.82 (1 H, s), 7.54 (1 H, d, *J* 8.0), 7.31 (1 H, d, *J* 8.1), 7.16 (1 H, t, *J* 7.5), 7.04 (2 H, t, *J* 8.4), 6.71 (1 H, s), 6.26 (1 H, dd, *J* 8.5, 2.3), 6.15 (1 H, d, *J* 2.2), 3.95 (2 H, t, *J* 6.5), 3.68 (1 H, s), 2.67 (1 H, d, *J* 13.7), 1.92 (1 H, d, *J* 13.7), 1.87 (3 H, s), 1.83 – 1.74 (2 H, m), 1.52 (2 H, dd, *J* 15.0, 7.5), 1.31 (3 H, s), 1.01 (3 H, t, *J* 7.4), 0.97 (3 H, s). δ_C (151 MHz, $CDCl_3$) 158.36, 144.48, 137.33, 129.72, 127.13, 125.63, 122.11, 121.51, 121.10, 120.92, 118.96, 111.28, 104.07, 100.12, 67.48, 49.97, 48.98, 36.08, 31.56, 31.48, 30.72, 30.38, 19.37, 13.95. HRMS (ESI):calcd. for $C_{24}H_{31}N_2O$(M+H): 363.2431; found: 363.2422.

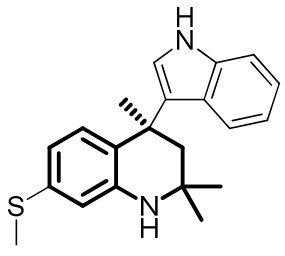
(R)-7-(benzyloxy)-4-(1H-indol-3-yl)-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (3s)



3s

Yellow oil (73 mg, 92%); $[\alpha]_D^{10}$ -5.9 (C=0.2, $CHCl_3$); δ_H (600 MHz, $CDCl_3$) 7.82 (1 H, s), 7.52 (1 H, d, *J* 8.0), 7.45 (2 H, d, *J* 7.4), 7.40 (2 H, t, *J* 7.5), 7.33 (2 H, dd, *J* 15.2, 7.7), 7.15 (1 H, t, *J* 7.5), 7.03 (2 H, dd, *J* 7.8, 5.6), 6.72 (1 H, d, *J* 2.1), 6.32 (1 H, dd, *J* 8.5, 2.4), 6.22 (1 H, d, *J* 2.3), 5.03 (2 H, s), 3.70 (1 H, s), 2.66 (1 H, d, *J* 13.7), 1.91 (1 H, d, *J* 13.7), 1.86 (3 H, s), 1.30 (3 H, s), 0.96 (3 H, s). δ_C (151 MHz, $CDCl_3$) 158.13, 144.49, 137.54, 137.32, 129.76, 128.54, 127.83, 127.58, 127.09, 125.60, 122.05, 121.54, 121.35, 121.08, 118.99, 111.25, 104.19, 100.46, 69.90, 49.99, 48.90, 36.09, 31.46, 30.68, 30.36; HRMS (ESI):calcd. for $C_{27}H_{28}N_2O$(M+H):396.2208; found:396.2215.

(R)-4-(1H-indol-3-yl)-2,2,4-trimethyl-7-(methylthio)-1,2,3,4-tetrahydroquinoline (3t)

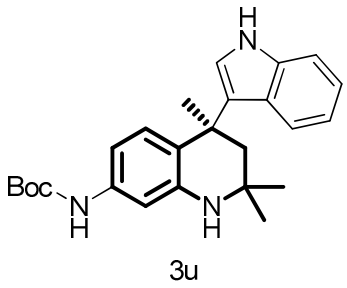


3t

Colorless oil (57 mg, 85%); $[\alpha]_D^{10}$ -29.0 (C=0.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.86 (1 H, s), 7.54 (1 H, d, *J* 8.0), 7.34 (1 H, d, *J* 8.1), 7.19 (1 H, dd, *J* 11.1, 4.0), 7.07 (2 H, dt, *J* 7.0, 3.4), 6.75 (1 H, d, *J* 2.4), 6.58 (1 H, dd, *J* 8.1, 1.9), 6.51 (1 H, d, *J* 1.8), 3.75 (1 H, s), 2.69 (1 H, d, *J* 13.7), 2.49 (3 H, s), 1.93 (1 H, d, *J* 13.7), 1.88 (3 H, s), 1.33 (3 H, s), 0.99 (3 H, s); δ_C (101 MHz, $CDCl_3$) 143.87, 137.28, 136.18, 129.36, 126.62, 125.61, 125.49, 122.07, 121.63, 121.02, 119.05, 115.79, 112.43, 111.32, 50.00, 48.72, 36.29, 31.40, 30.51, 30.46, 15.82. HRMS (ESI):calcd. for $C_{21}H_{25}N_2S$(M+H):337.1733; found:337.1717;

$C_{21}H_{24}N_2NaS$(M+Na):359.1552; found:359.1540.

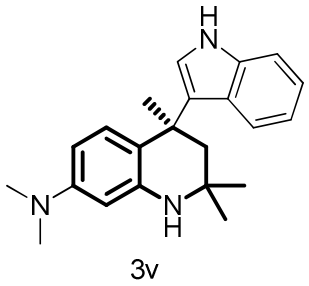
(R)-tert-butyl (4-(1H-indol-3-yl)-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolin-7-yl)carbamate (3u)



3u

White solid (58 mg, 72%); $[\alpha]_D^{10}$ -7.0 (C=0.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.93 (1 H, s), 7.52 (1 H, d, *J* 8.0), 7.33 (1 H, d, *J* 8.1), 7.16 (1 H, t, *J* 7.5), 7.07 – 7.02 (1 H, m), 7.00 (1 H, d, *J* 8.3), 6.93 (1 H, s), 6.73 (1 H, d, *J* 2.4), 6.41 (1 H, s), 6.37 (1 H, dd, *J* 8.3, 2.1), 3.75 (1 H, s), 2.65 (1 H, d, *J* 13.7), 1.90 (1 H, d, *J* 13.7), 1.85 (3 H, s), 1.55 (9 H, s), 1.29 (3 H, s), 0.95 (3 H, s); δ_C (101 MHz, $CDCl_3$) 152.94, 144.06, 137.26, 137.05, 129.22, 126.87, 125.53, 123.18, 122.05, 121.53, 121.05, 118.97, 111.25, 107.71, 104.26, 80.24, 49.89, 48.82, 36.14, 31.32, 30.52, 30.45, 28.41. HRMS (ESI):calcd. for $C_{25}H_{32}N_3O_2$(M+H):406.2489, found:406.2468; $C_{25}H_{31}N_3NaO_2$(M+Na):428.2308, found:428.2294.

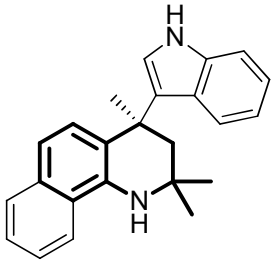
(R)-4-(1H-indol-3-yl)-N,N,2,2,4-pentamethyl-1,2,3,4-tetrahydroquinolin-7-amine (3v)



3v

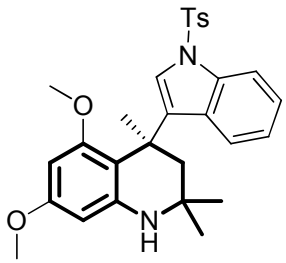
Colorless oil (47 mg, 70%); $[\alpha]_D^{10}$ -9.2 (C=0.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.86 (1 H, s), 7.59 (1 H, d, *J* 8.0), 7.33 (1 H, d, *J* 8.1), 7.23 – 7.12 (1 H, m), 7.07 (2 H, dd, *J* 11.1, 4.7), 6.74 (1 H, d, *J* 2.0), 6.20 (1 H, dd, *J* 8.5, 2.6), 5.99 (1 H, d, *J* 2.5), 2.94 (6 H, s), 2.68 (1 H, d, *J* 13.6), 1.94 (1 H, d, *J* 13.6), 1.87 (3 H, s), 1.31 (3 H, s), 0.97 (3 H, s); δ_C (101 MHz, $CDCl_3$) 150.00, 144.08, 137.32, 129.46, 127.41, 125.69, 122.22, 121.41, 121.16, 118.89, 117.75, 111.24, 103.56, 98.65, 49.91, 49.04, 40.80, 35.86, 31.59, 30.74, 30.22. HRMS (ESI):calcd. for $C_{22}H_{28}N_3$(M+H):334.2278, found:334.2261.

(R)-4-(1H-indol-3-yl)-2,2,4-trimethyl-1,2,3,4-tetrahydrobenzo[h]quinolone (3w)



3w

Green oil (63 mg, 93%); $[\alpha]_D^{10}$ -18.4 (C=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (dd, *J*=33.6, 7.9, 3H), 7.57 – 7.44 (m, 3H), 7.40 – 7.31 (m, 2H), 7.18 (dd, *J*=16.5, 8.3, 2H), 7.01 (t, *J*=7.5, 1H), 6.79 (d, *J*=2.1, 1H), 4.49 (s, 1H), 2.83 (d, *J*=13.6, 1H), 2.08 (d, *J*=13.7, 1H), 2.00 (s, 3H), 1.51 – 1.43 (m, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.59, 137.24, 133.18, 128.60, 127.55, 126.94, 125.58, 125.21, 124.65, 123.16, 122.21, 121.80, 121.61, 120.97, 119.96, 119.08, 116.81, 111.28, 49.97, 48.76, 36.83, 31.38, 30.68, 30.62; HRMS (ESI):calcd. for $C_{24}H_{25}N_2$(M+H):341.2015; found:341.2020.



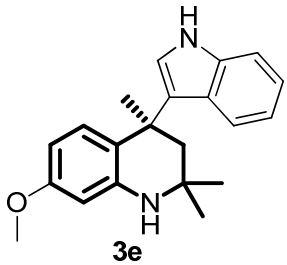
3y

(R)-5,7-dimethoxy-2,2,4-trimethyl-4-(1-tosyl-1H-indol-3-yl)-1,2,3,4-tetrahydroquinoline (3y)

White solid (68 mg, 88%);M.P 167-168℃; $[\alpha]_D^{10}$ -24.7 (C=0.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.97 (1 H, d, *J* 8.3), 7.76 (2 H, d, *J* 8.3), 7.32 (1 H, s), 7.21 (3 H, t, *J* 9.3), 7.11 (1 H, d, *J* 7.7), 7.04 (1 H, t, *J* 7.5), 5.81 (1 H, d, *J* 2.3), 5.73 (1 H, d, *J* 2.2), 3.82 (1 H, d, *J* 10.5), 3.76 (3 H, s), 3.12 (3 H, s), 2.35 (3 H, s), 2.32 (1 H, d, *J* 13.9), 1.93 (3 H, s), 1.73 (1 H, d, *J* 13.8), 1.34 (3 H, s), 1.10 (3 H, s); δ_C (101 MHz, $CDCl_3$) 160.52, 159.69, 145.34, 144.42, 135.86, 135.77,

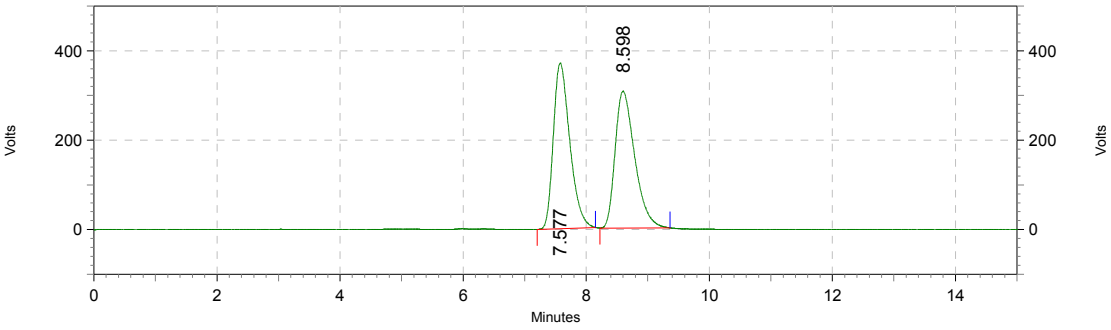
129.64, 129.52, 126.72, 123.73, 122.74, 122.20, 121.18, 113.57, 107.85, 92.58, 89.89, 54.98, 54.70, 51.08, 49.31, 35.13, 27.63, 21.52. HRMS (ESI):calcd. for $C_{29}H_{33}N_2O_4S$(M+H):505.2163; found:505.2166.

HPLC analysis results

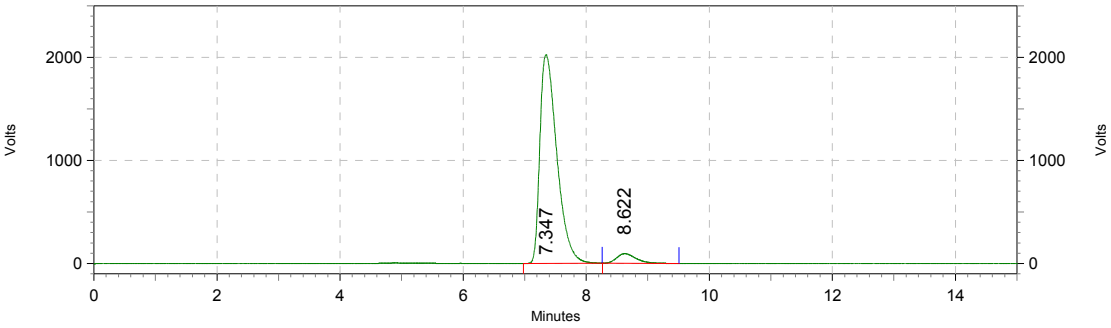


3e

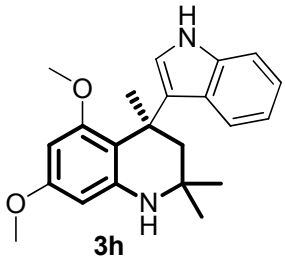
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	7.577	6875161	50.394
2	8.598	6767707	49.606

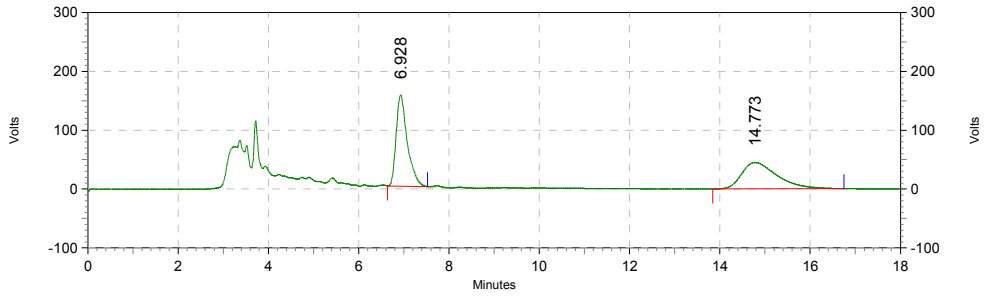


Peak#	RT(min)	Area	Area%
1	7.347	38764322	95.044
2	8.622	2021369	4.956

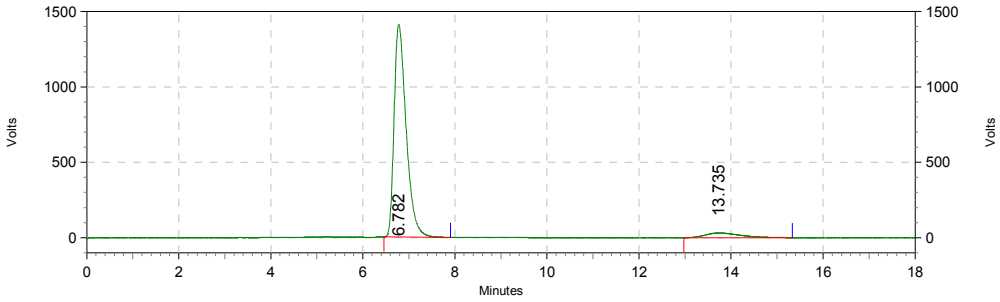


3h

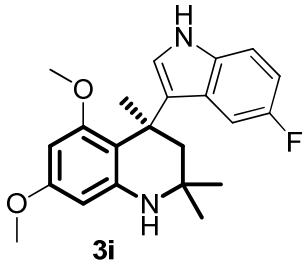
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	6.928	2659154	52.286
2	14.773	2426635	47.714

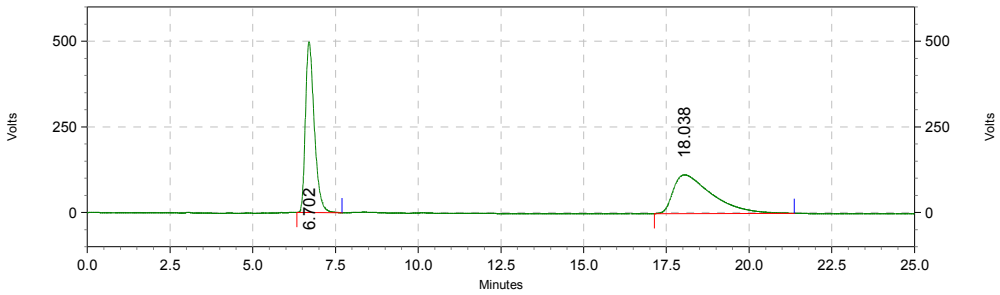


Peak#	RT(min)	Area	Area%
1	6.782	25589497	94.054
2	13.735	1617813	5.946

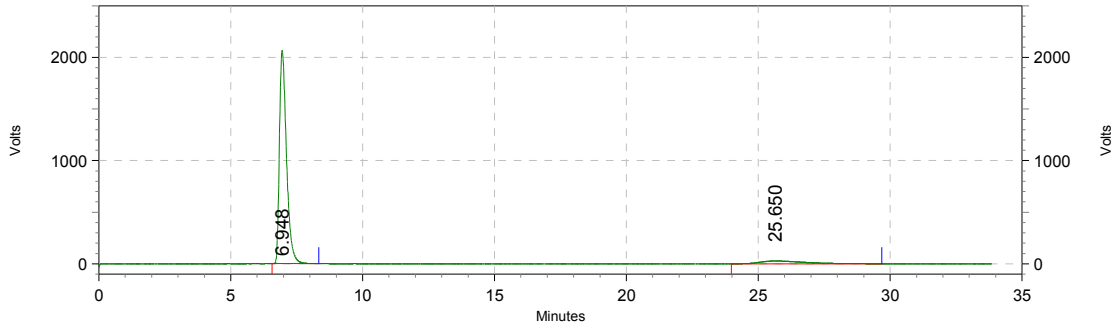


3i

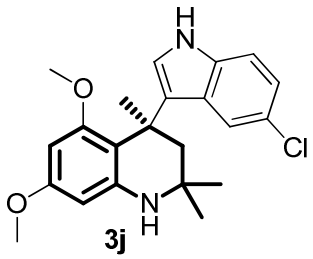
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	6.702	9266920	50.391
2	18.038	9122958	49.609

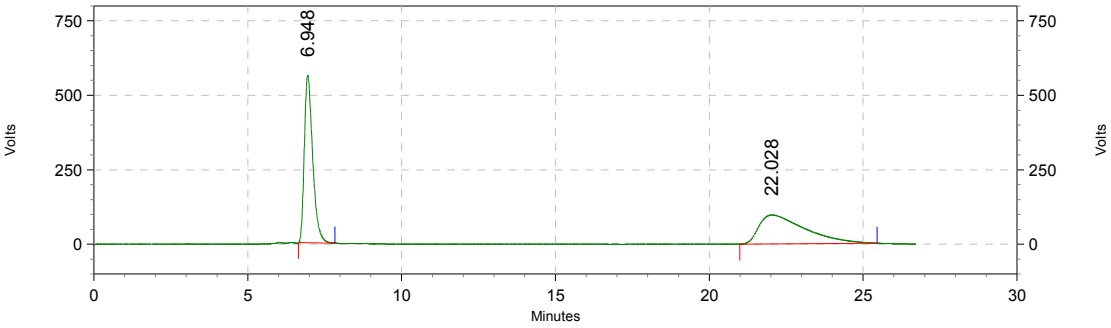


Peak#	RT(min)	Area	Area%
1	6.948	38437633	92.325
2	25.650	3195205	7.675

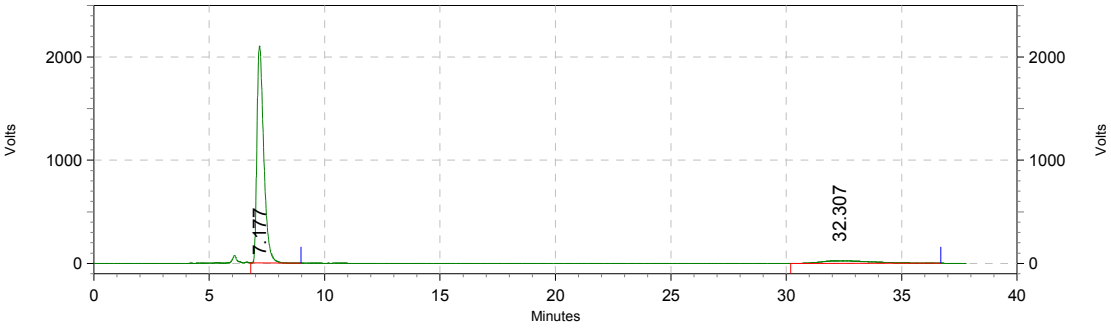


3j

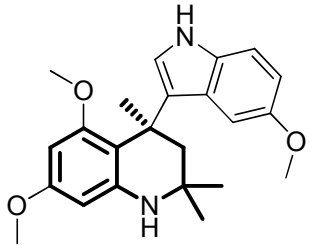
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	6.948	10614325	51.227
2	22.028	10105741	48.773

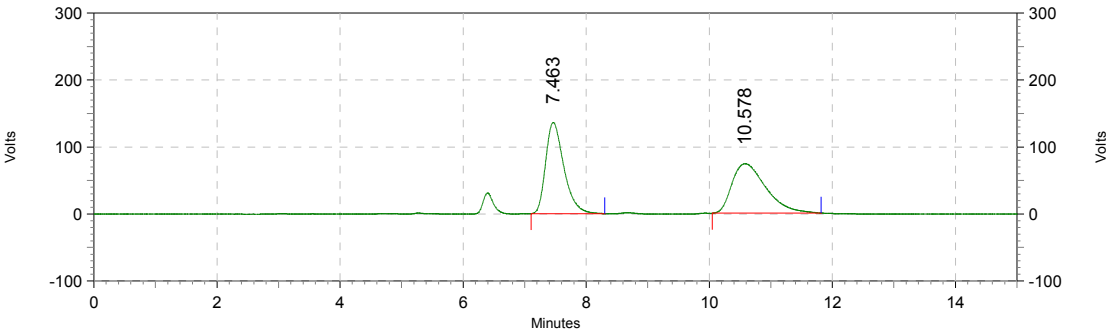


Peak#	RT(min)	Area	Area%
1	7.177	43140274	91.461
2	32.307	4027776	8.539

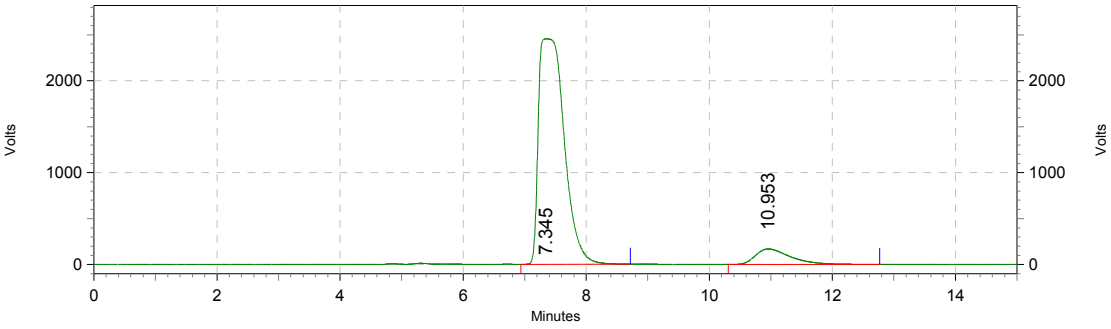


3k

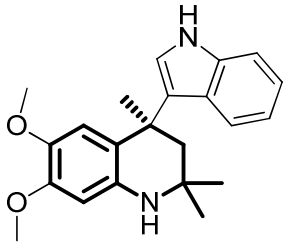
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	7.463	2800561	49.865
2	10.578	2815767	50.135

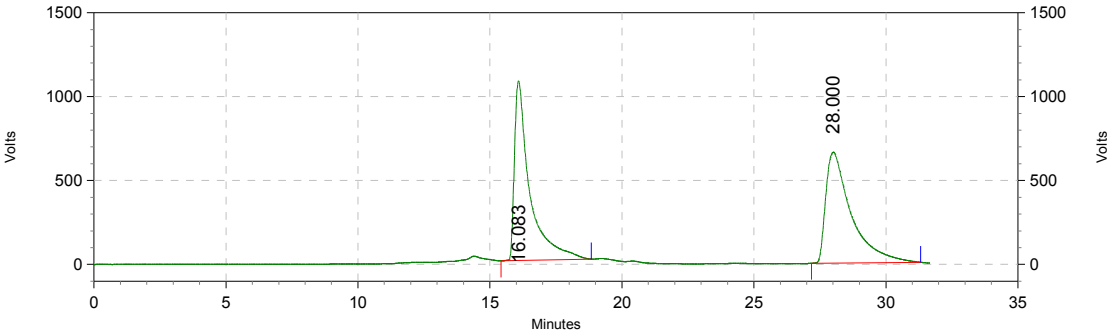


Peak#	RT(min)	Area	Area%
1	7.345	71095213	91.440
2	10.953	6655482	8.560

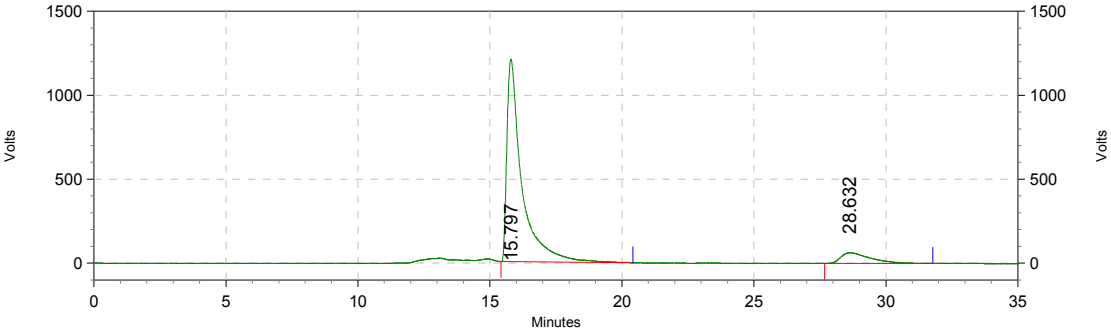


3l

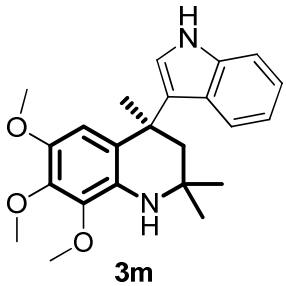
HPLC Conditions: Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (75/25); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	16.083	42889168	49.351
2	28.000	44016867	50.649

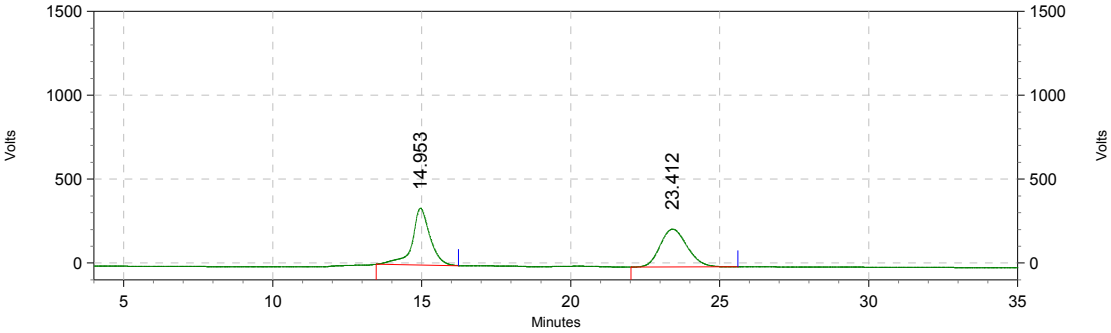


Peak#	RT(min)	Area	Area%
1	15.797	47208919	90.633
2	28.632	4878884	9.367

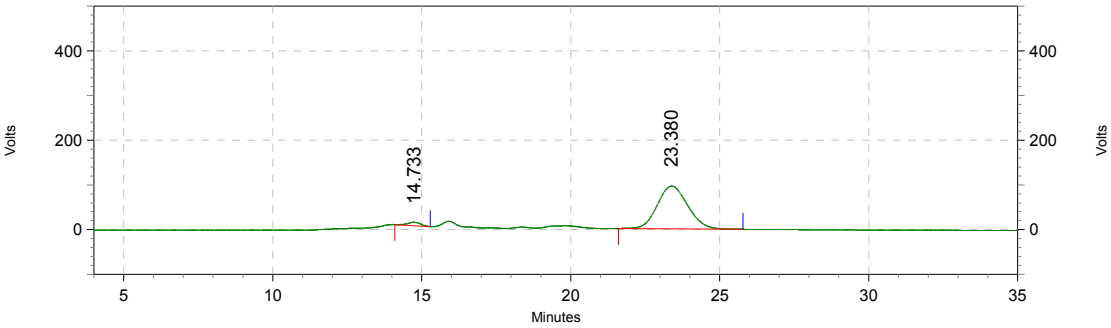


3m

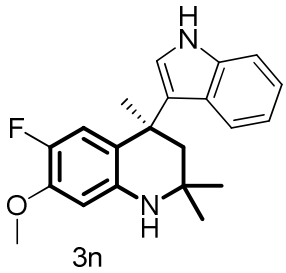
HPLC Conditions: Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (75/25); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	14.953	14010854	49.643
2	23.412	14212474	50.357

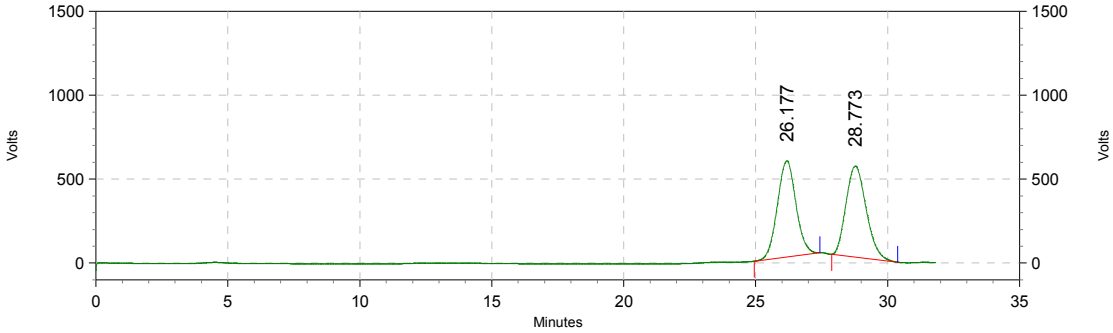


Peak#	RT(min)	Area	Area%
1	14.733	235538	3.358
2	23.380	6778933	96.642

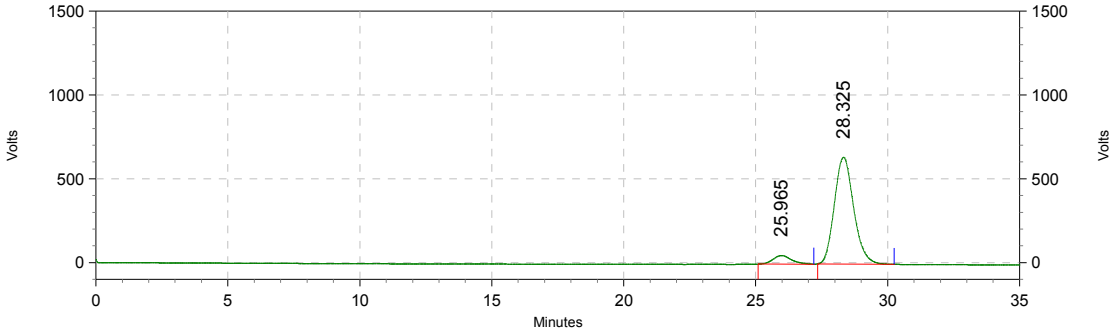


3n

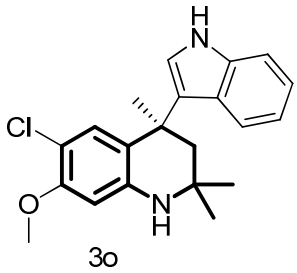
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	26.177	28052258	49.256
2	28.773	28900217	50.744

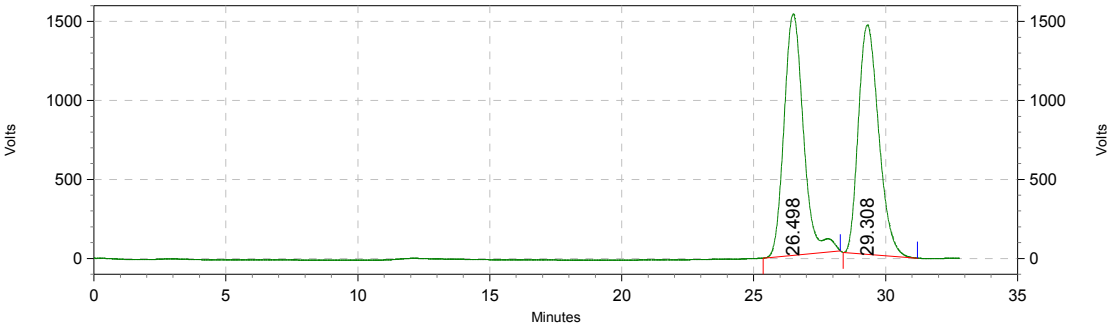


Peak#	RT(min)	Area	Area%
1	25.965	2485027	7.127
2	28.325	32383387	92.873

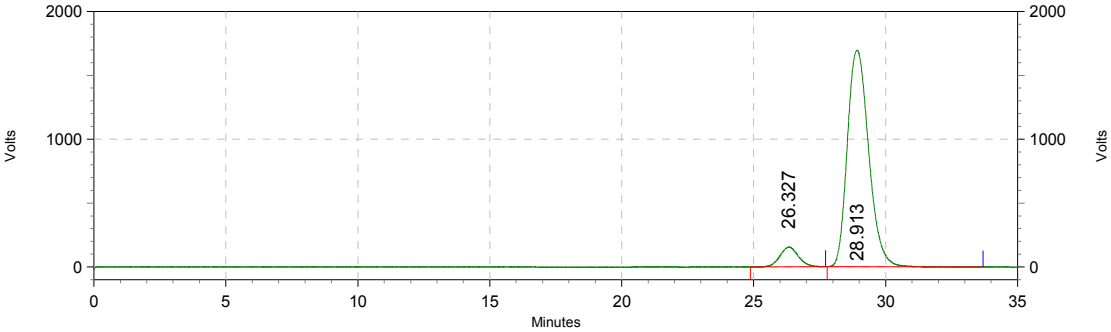


3o

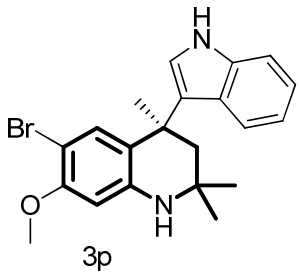
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	26.498	78449028	50.244
2	29.308	77686511	49.756

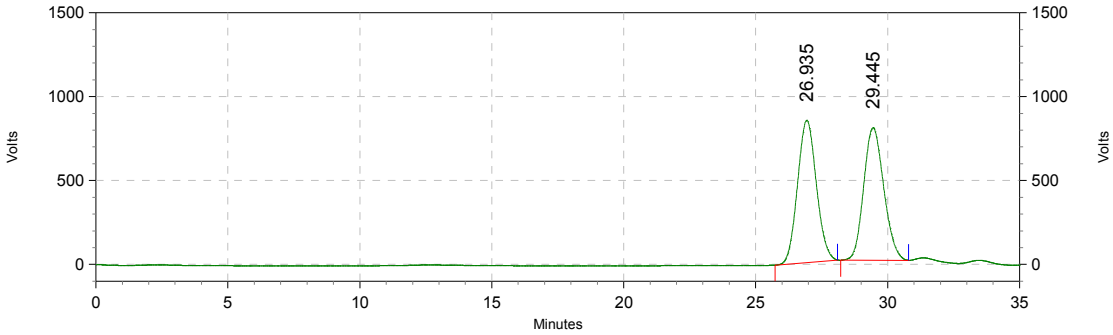


Peak#	RT(min)	Area	Area%
1	26.327	7525109	7.329
2	28.913	95145950	92.671

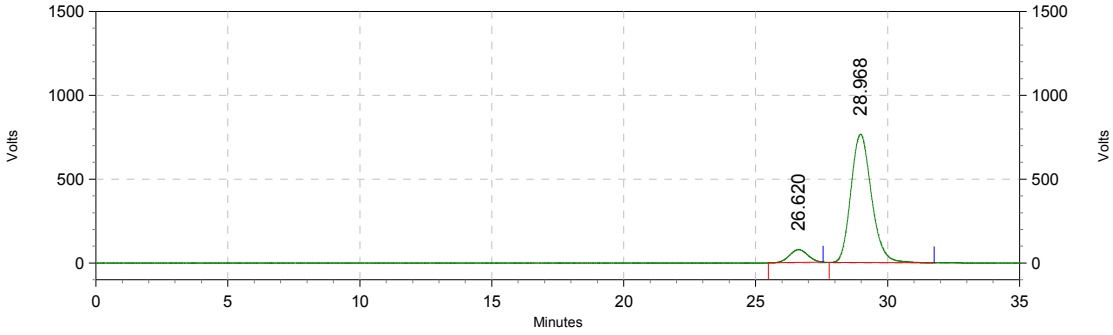


3p

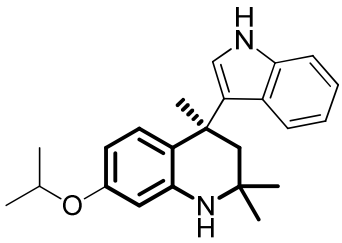
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	26.935	42098953	50.151
2	29.445	41845871	49.849

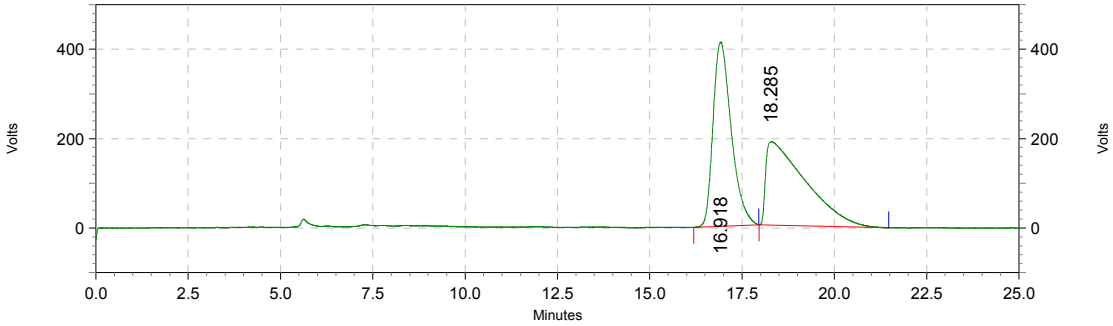


Peak#	RT(min)	Area	Area%
1	26.620	3721425	8.240
2	28.968	41442341	91.760

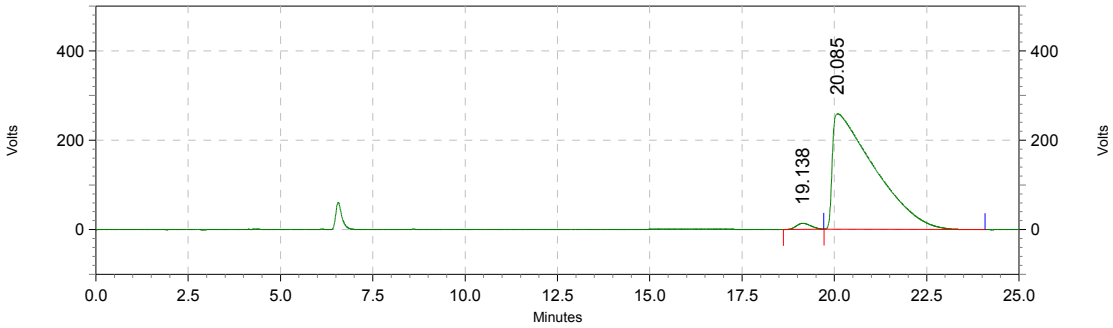


3q

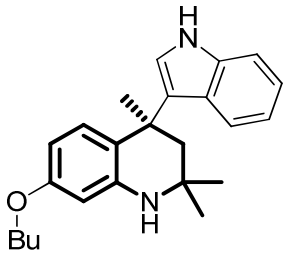
HPLC Conditions: Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	16.918	14123553	50.331
2	18.285	13937934	49.669

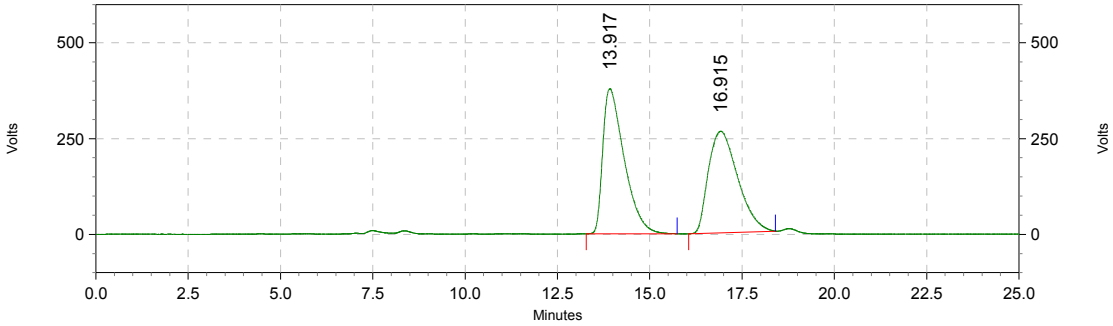


Peak#	RT(min)	Area	Area%
1	19.138	369009	1.777
2	20.085	20397123	98.223

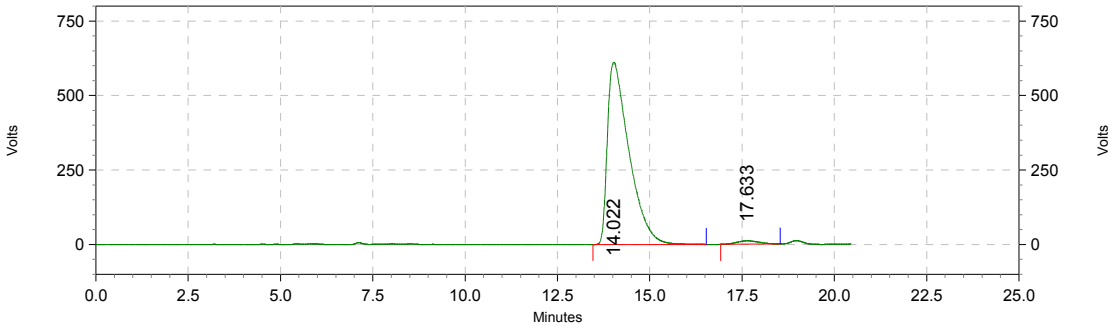


3r

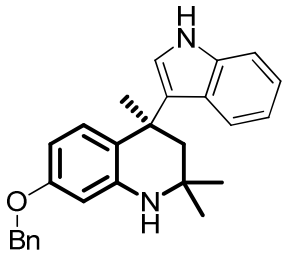
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	13.917	15240811	51.028
2	16.915	14626735	48.972

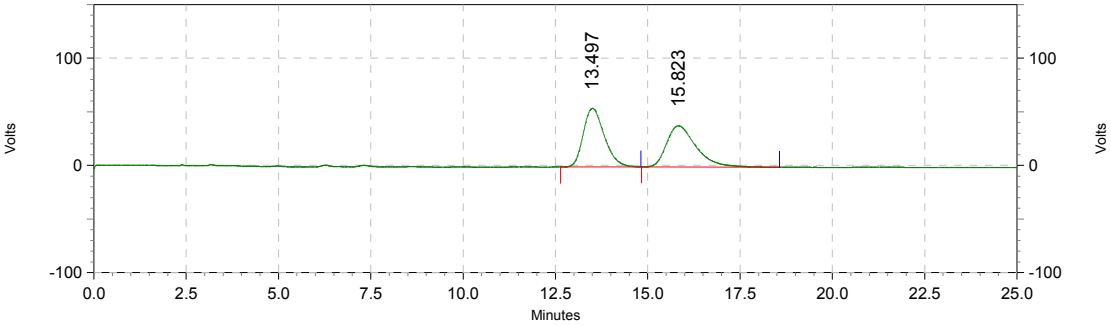


Peak#	RT(min)	Area	Area%
1	14.022	24777604	98.083
2	17.633	484143	1.917

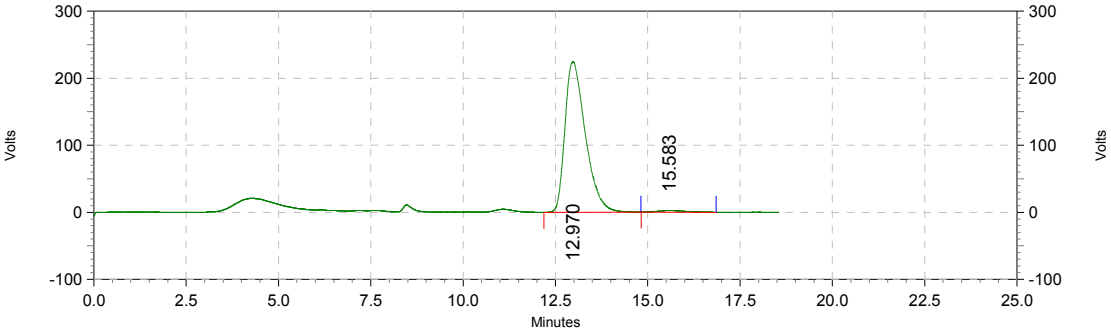


3s

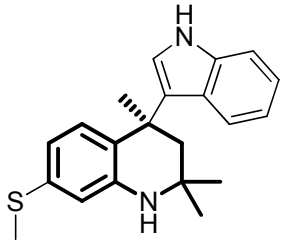
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (93/7); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	13.497	2169897	50.487
2	15.823	2128063	49.513

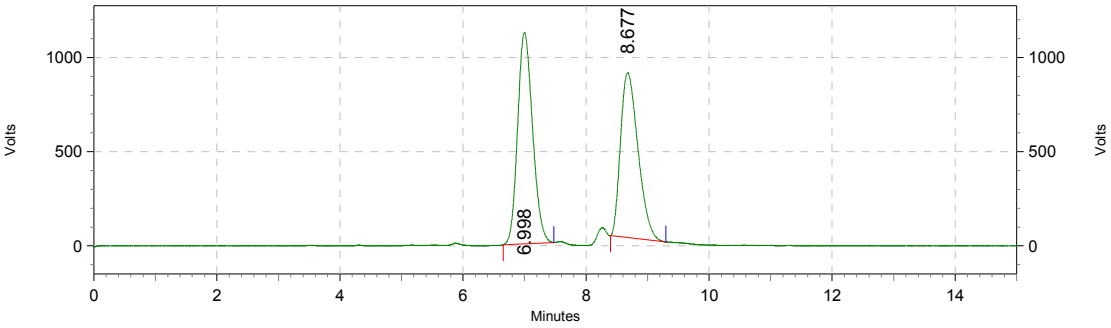


Peak#	RT(min)	Area	Area%
1	12.970	8599103	98.613
2	15.583	120928	1.387

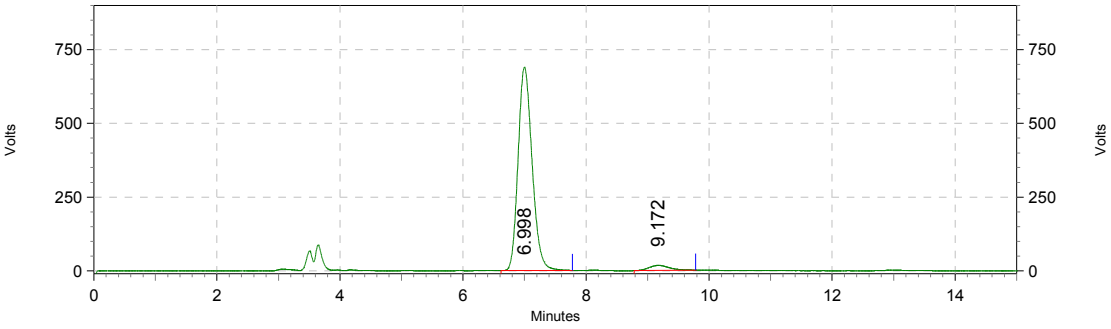


3t

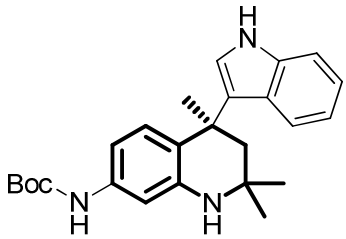
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	6.998	18936265	52.237
2	8.677	17314736	47.763

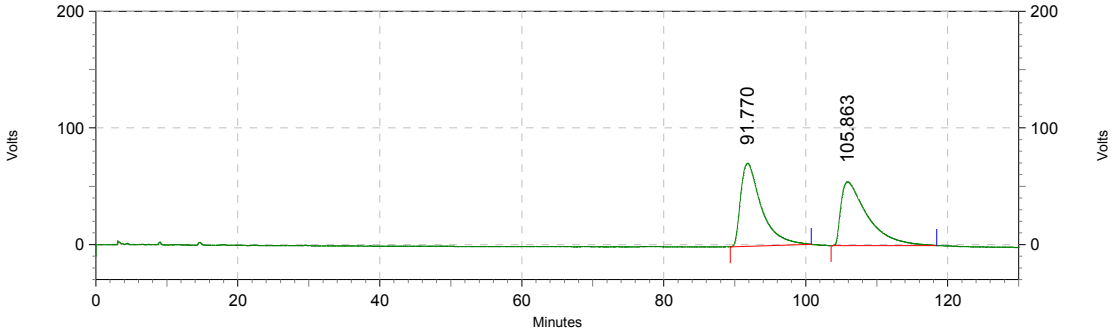


Peak#	RT(min)	Area	Area%
1	6.998	10925959	96.551
2	9.172	390275	3.449

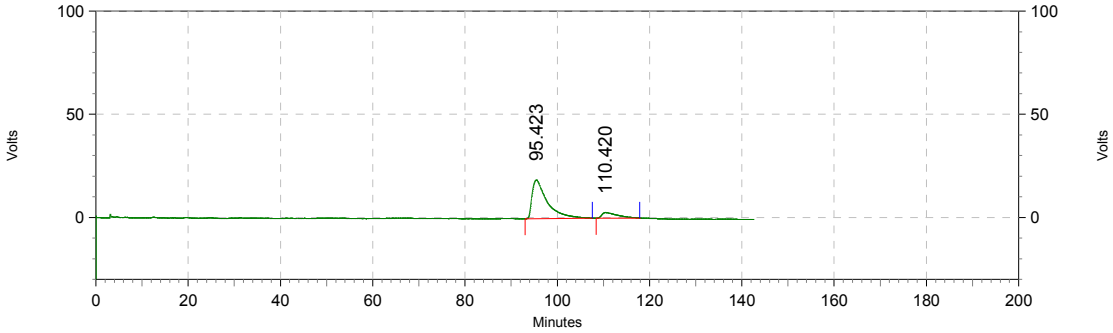


3u

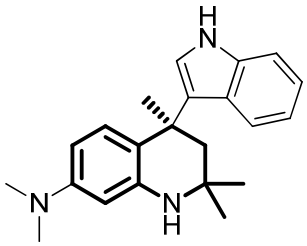
HPLC Conditions: Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (95/5); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	91.770	14407171	50.695
2	105.863	14012421	49.305

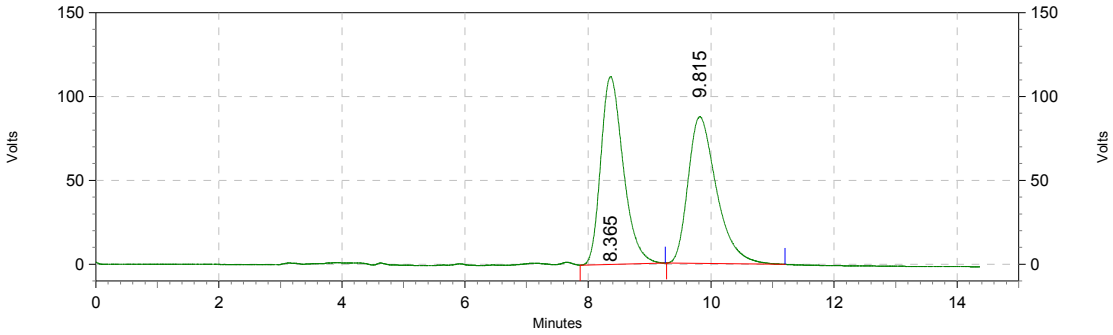


Peak#	RT(min)	Area	Area%
1	95.423	4214733	86.345
2	110.420	666528	13.655

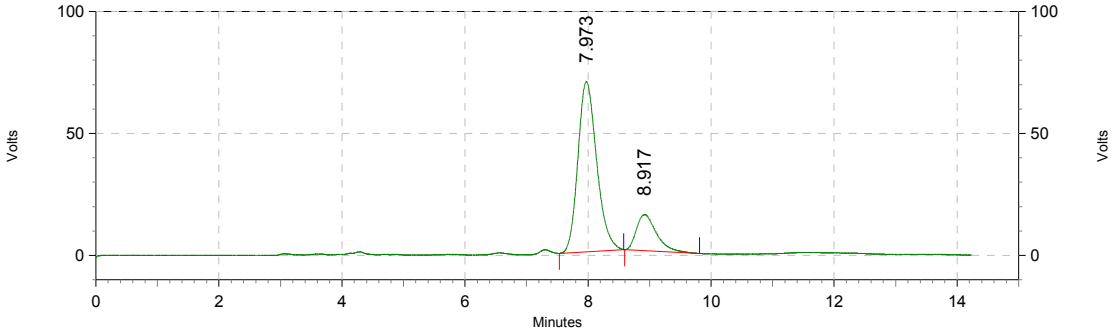


3v

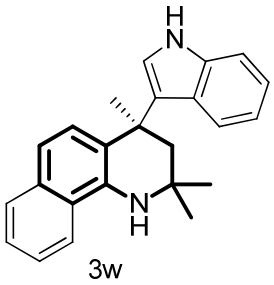
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (80/20); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm



Peak#	RT(min)	Area	Area%
1	8.365	2843272	50.309
2	9.815	2808351	49.691

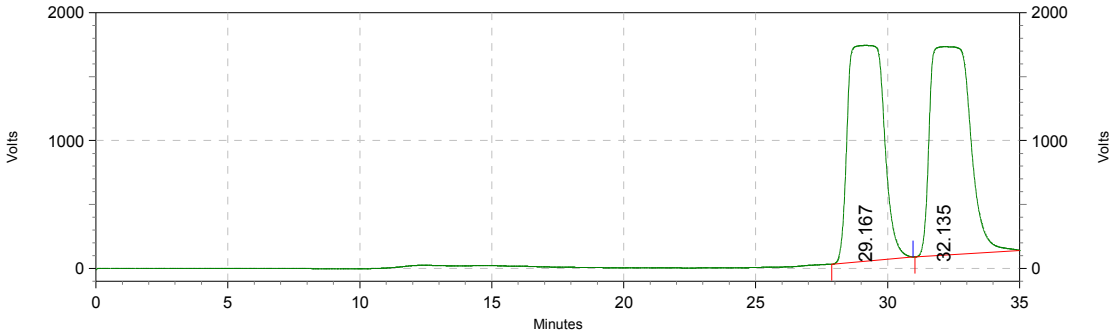


Peak#	RT(min)	Area	Area%
1	7.973	1478230	81.557
2	8.917	334275	18.443

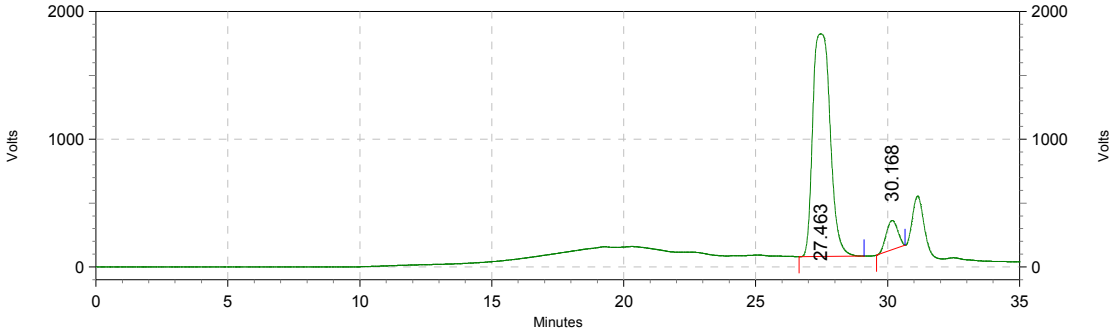


3w

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (85/15); **Flow rate: 1.0** mL/min; **Detection:** UV 254 nm

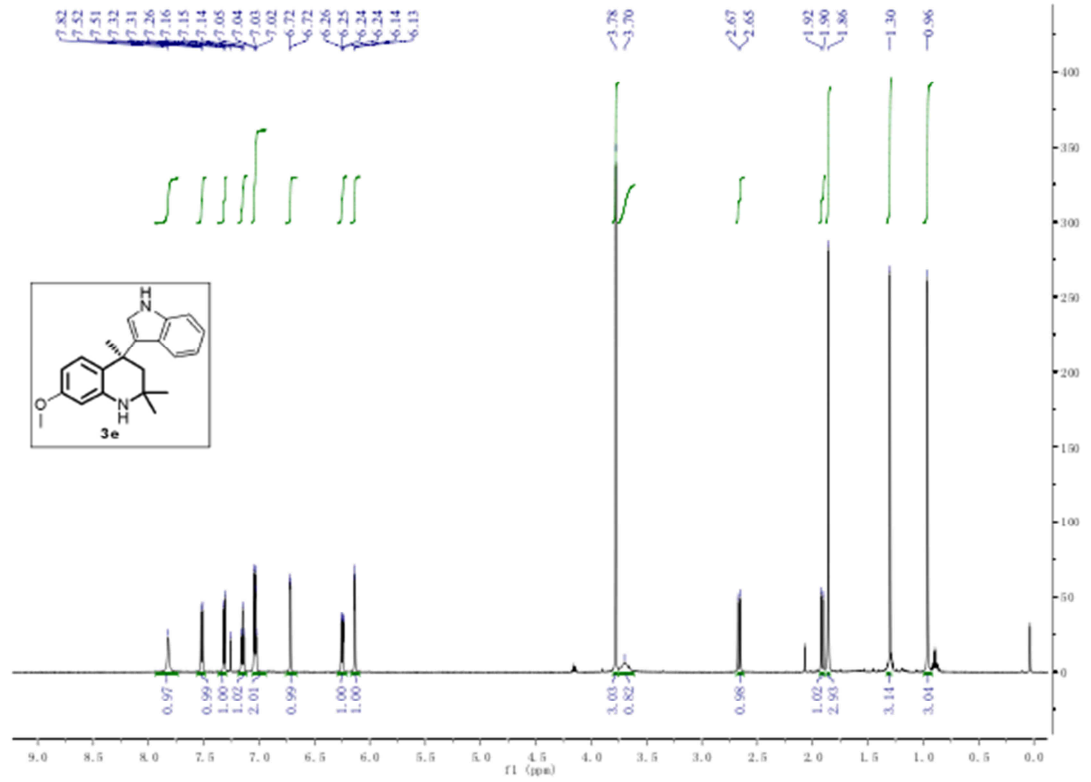


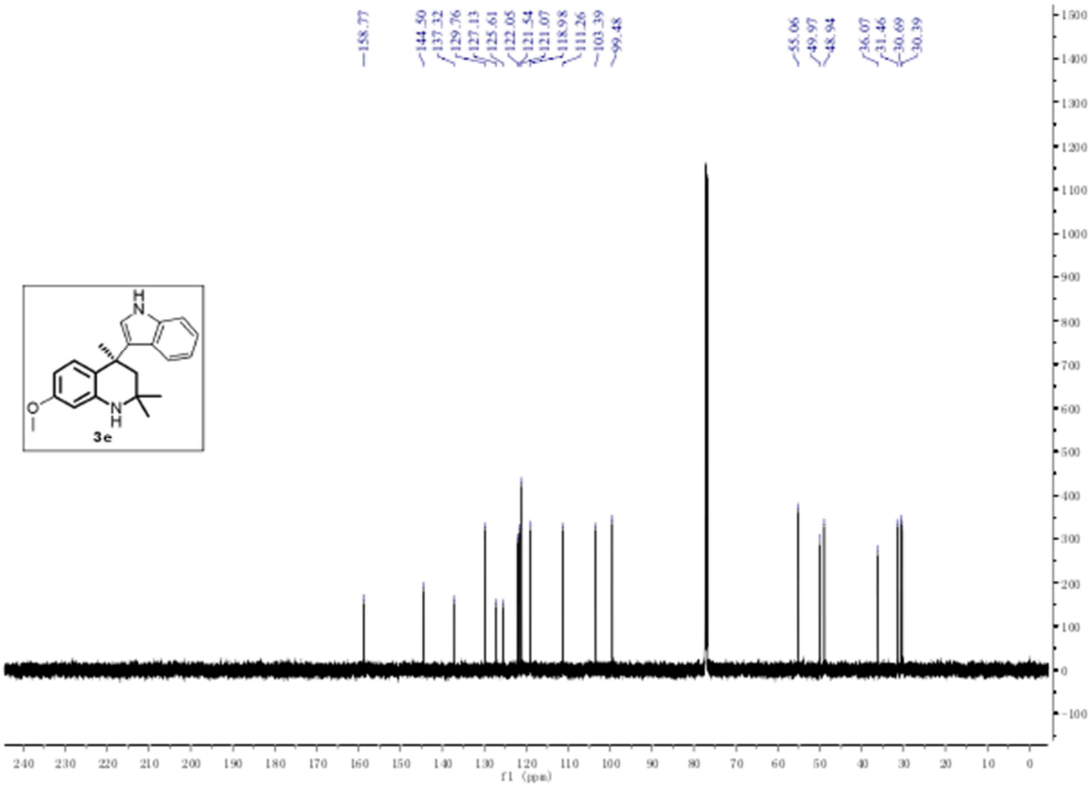
Peak#	RT(min)	Area	Area%
1	29.167	156771627	48.217
2	32.135	168364458	51.783



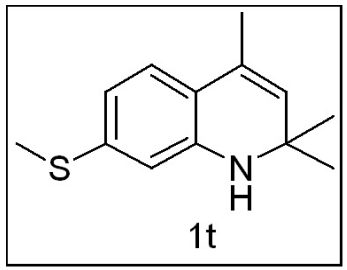
Peak#	RT(min)	Area	Area%
1	27.463	80374414	91.978
2	30.168	7009898	8.022

NMR-Spectrum of selected products





gx-11-1



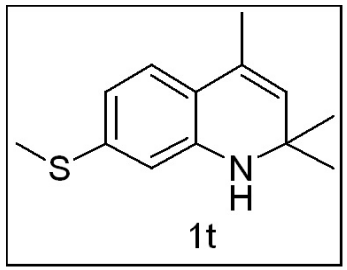
1t

7.29
7.00
6.98
6.57
6.56
6.55
6.54
6.37
6.37
5.29
5.29
3.73
2.46
1.99
1.99
1.29

1.02
1.00
1.01
1.00
0.79
2.92
2.98
5.90

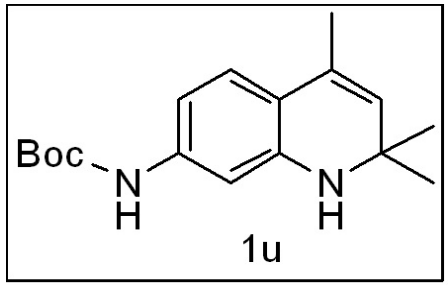
f1 (ppm)

gx-11-1


S
N
H
1t

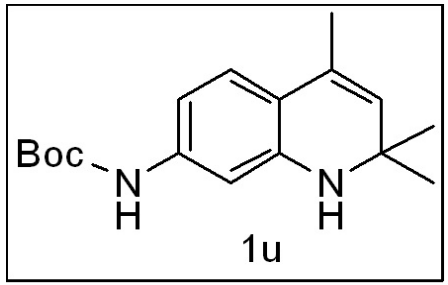
143.64
138.11
128.19
127.71
123.99
119.11
115.26
110.55
52.00
31.14
18.54
15.78
f1 (ppm)

gx-11-2


Boc
N
H
N
H
1u

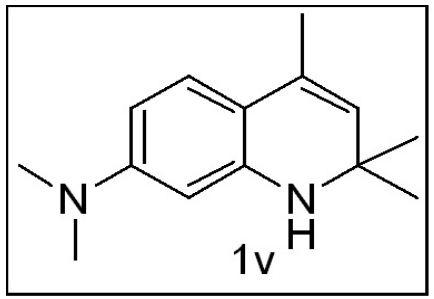
7.28
6.96
6.94
6.82
6.49
6.42
6.41
6.39
6.39
5.23
5.23
3.74
1.97
1.96
1.53
1.26
1.01
0.90
0.84
1.01
1.00
0.92
3.15
9.26
6.08
f1 (ppm)

gx-11-2


Boc
N
H
N
H
1u

152.69
144.14
138.55
128.15
126.83
124.05
116.99
106.92
102.60
80.30
51.90
31.05
28.39
18.52
f1 (ppm)

gx-11-3

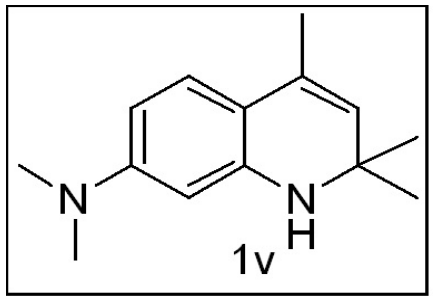


7.28 6.99 6.97 6.12 6.12 6.10 6.09 5.88 5.87 5.15 5.14 3.67 2.93 1.98 1.98 1.29

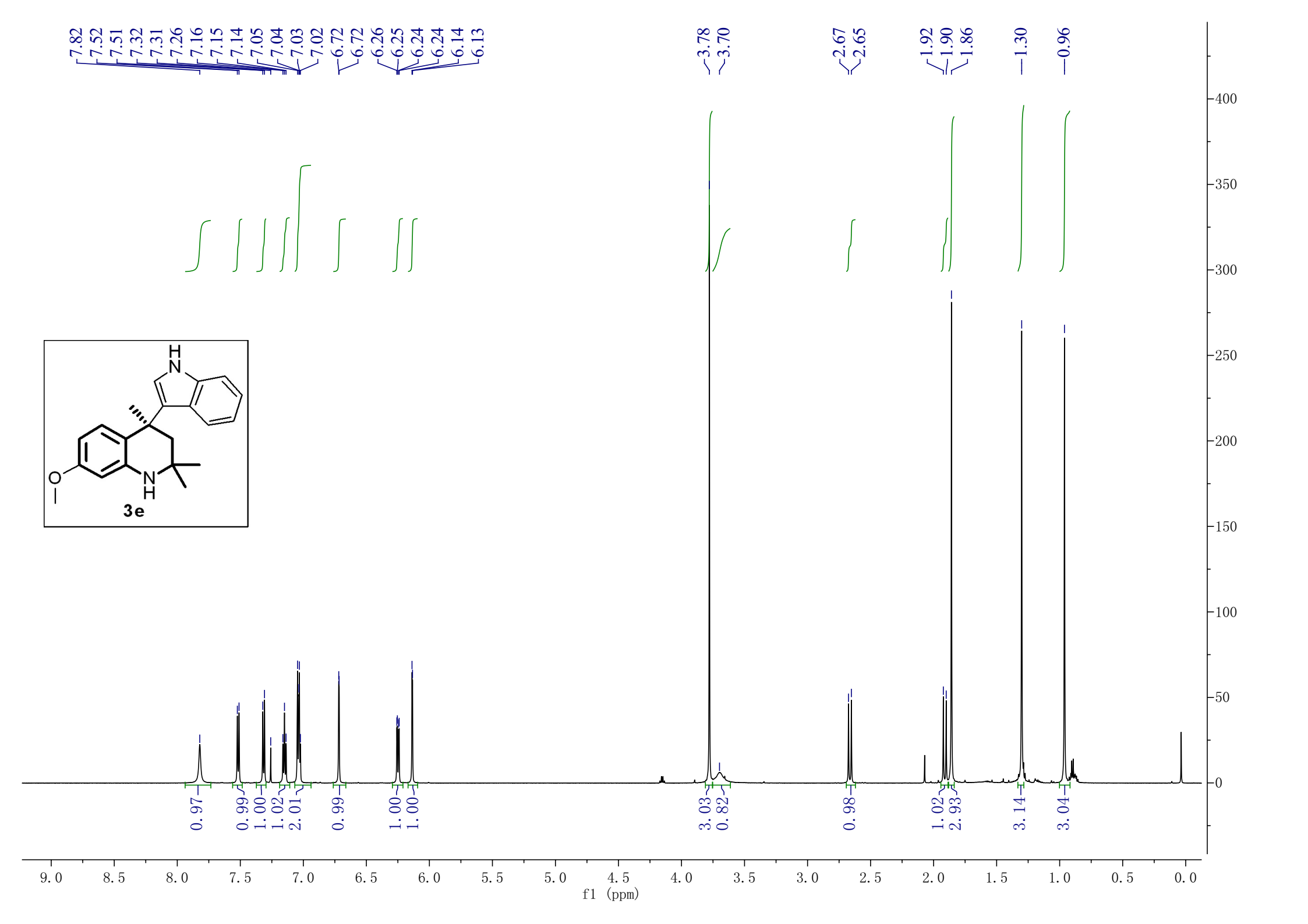
1.02 1.05 1.05 1.00 0.99 6.29 3.07 6.23

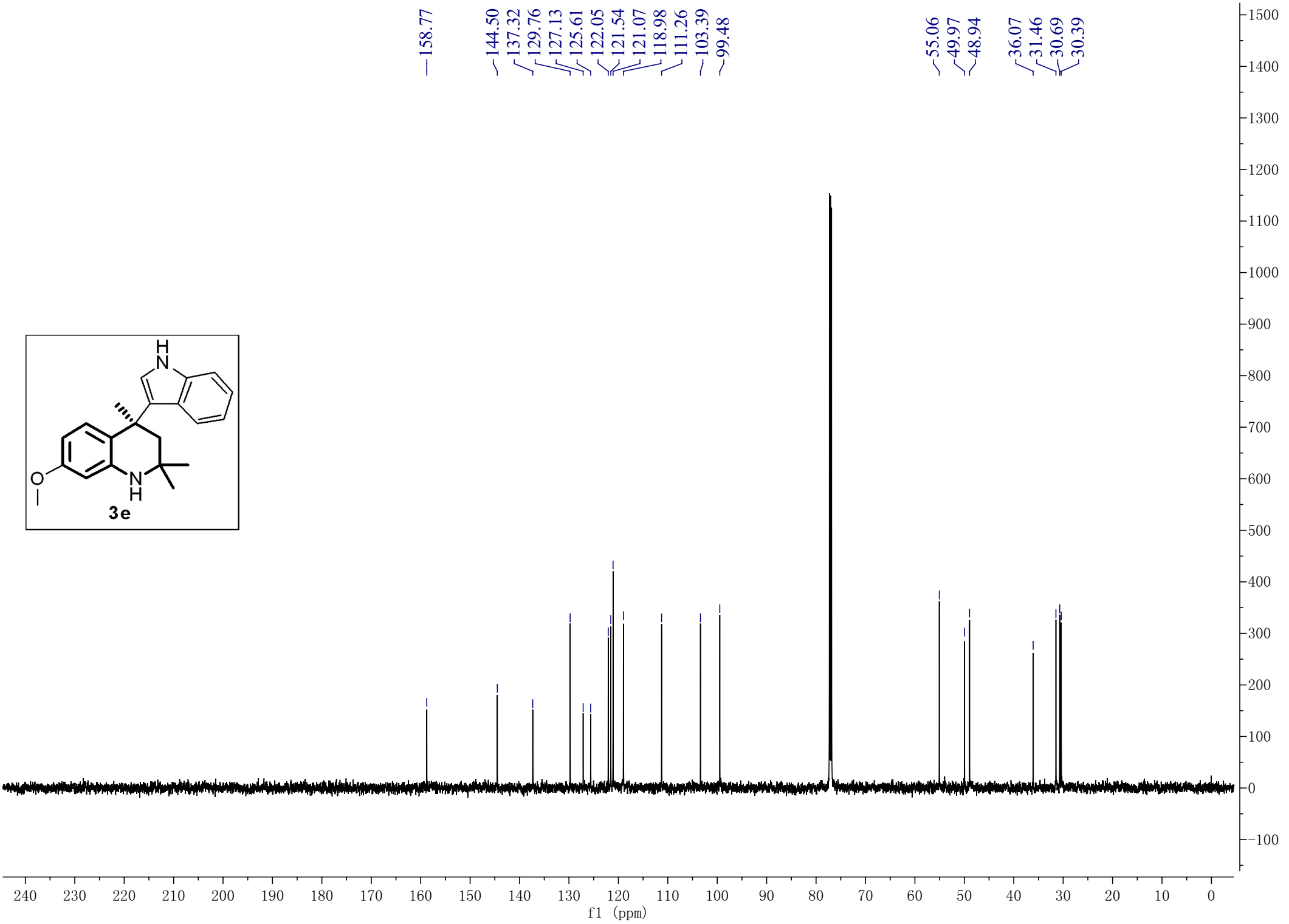
f1 (ppm)

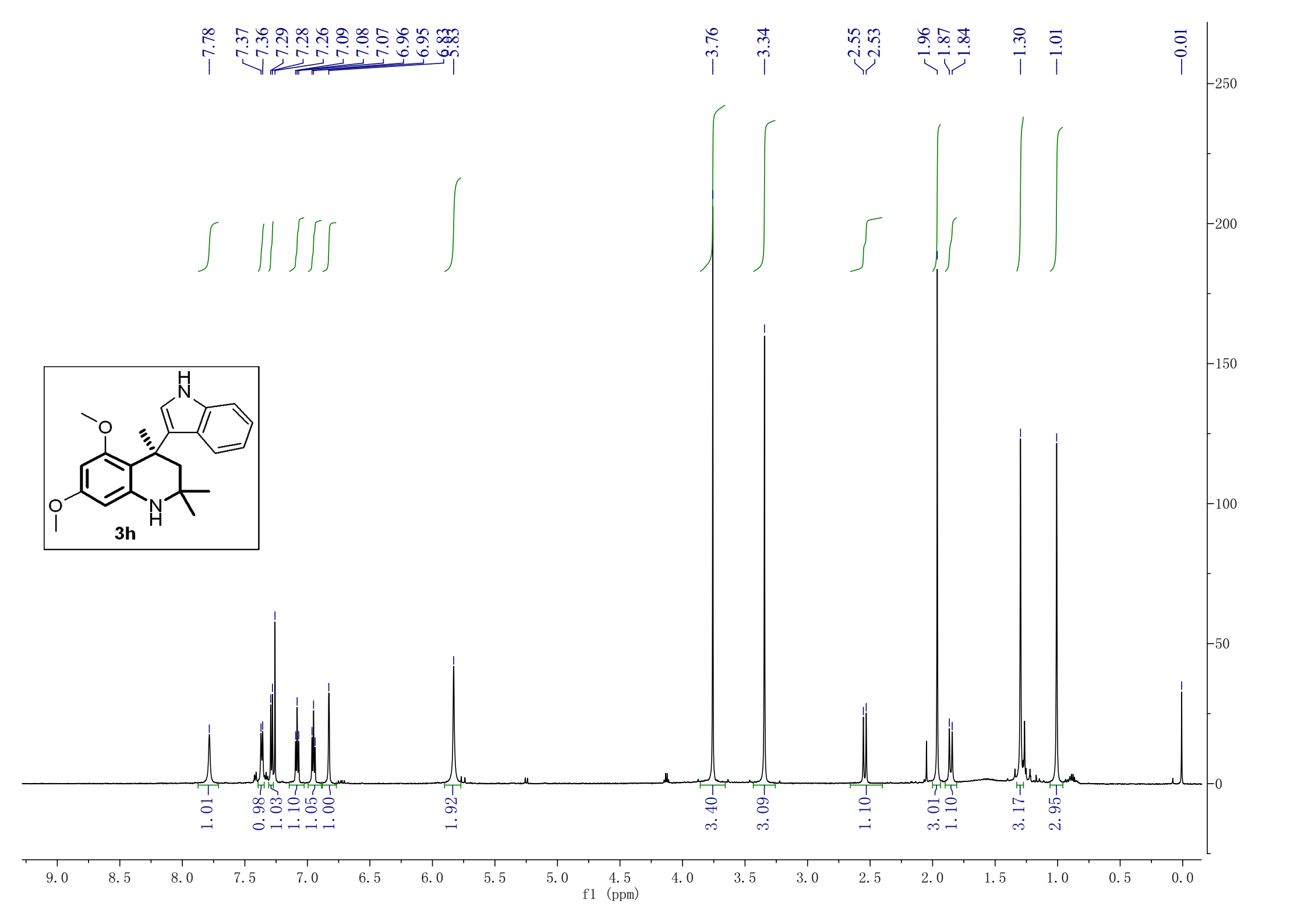
gx-11-3

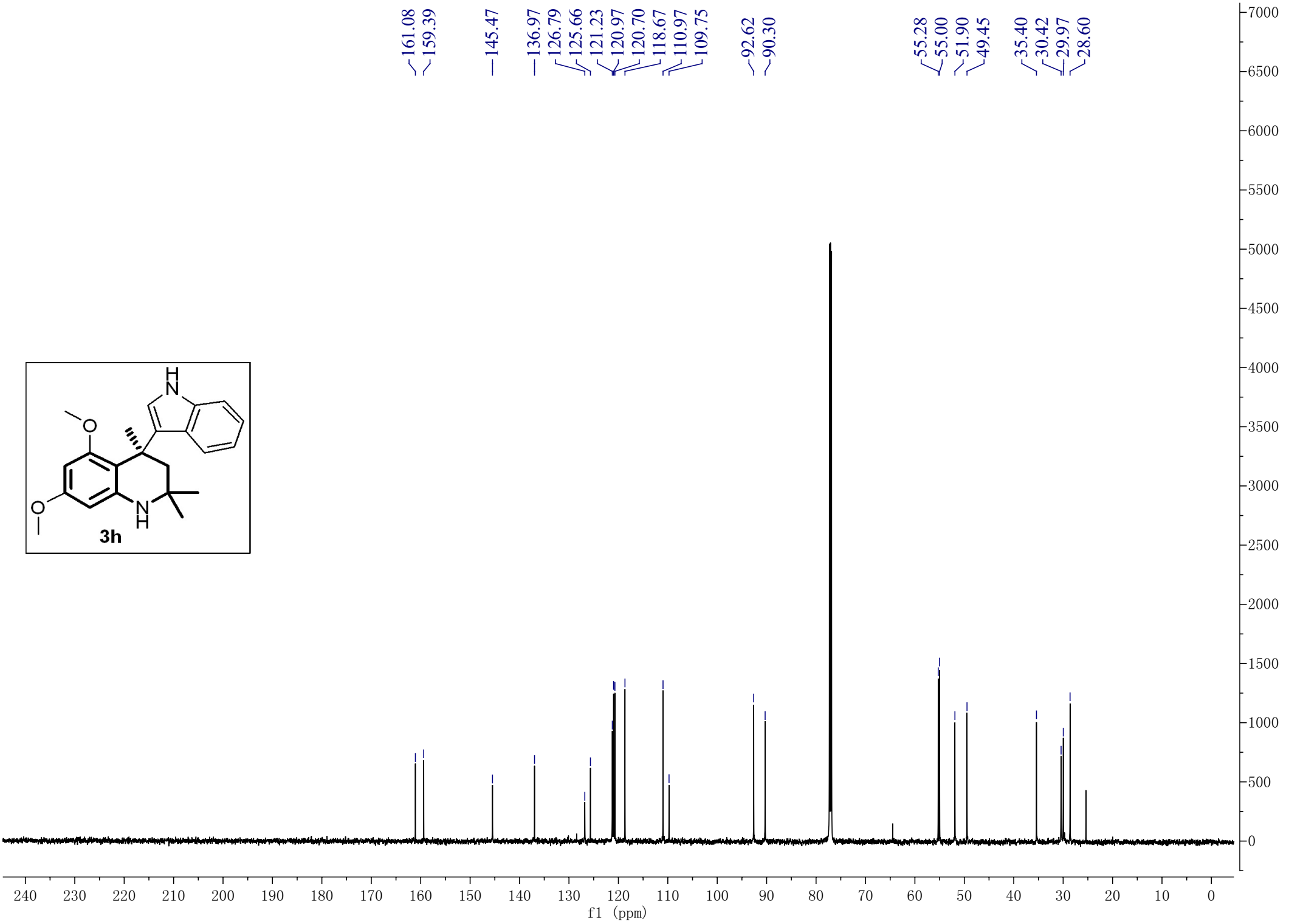

N
N
H
1v

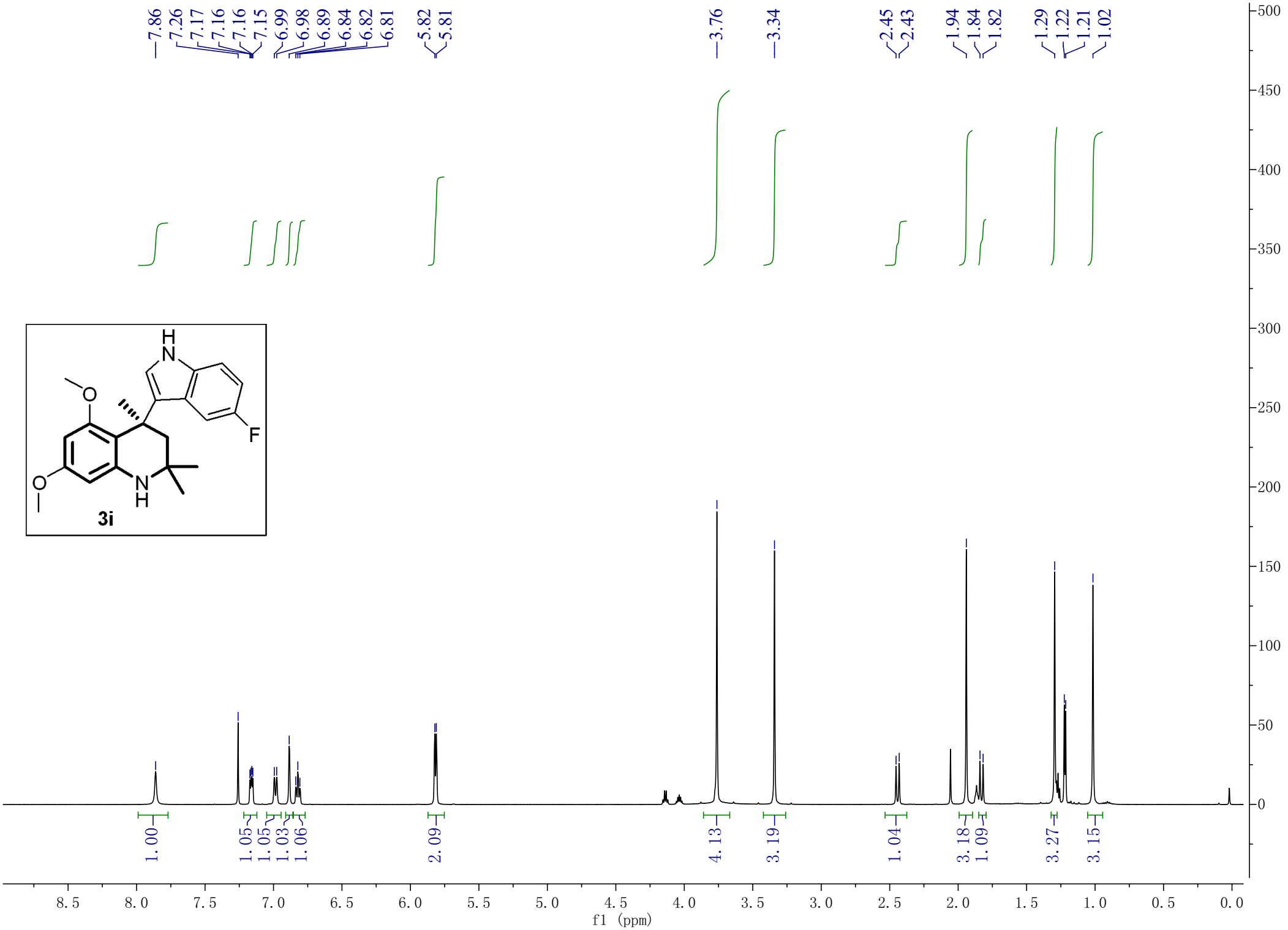
151.19
144.30
128.52
124.45
124.39
112.11
102.20
97.04
51.86
40.59
31.09
18.56
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

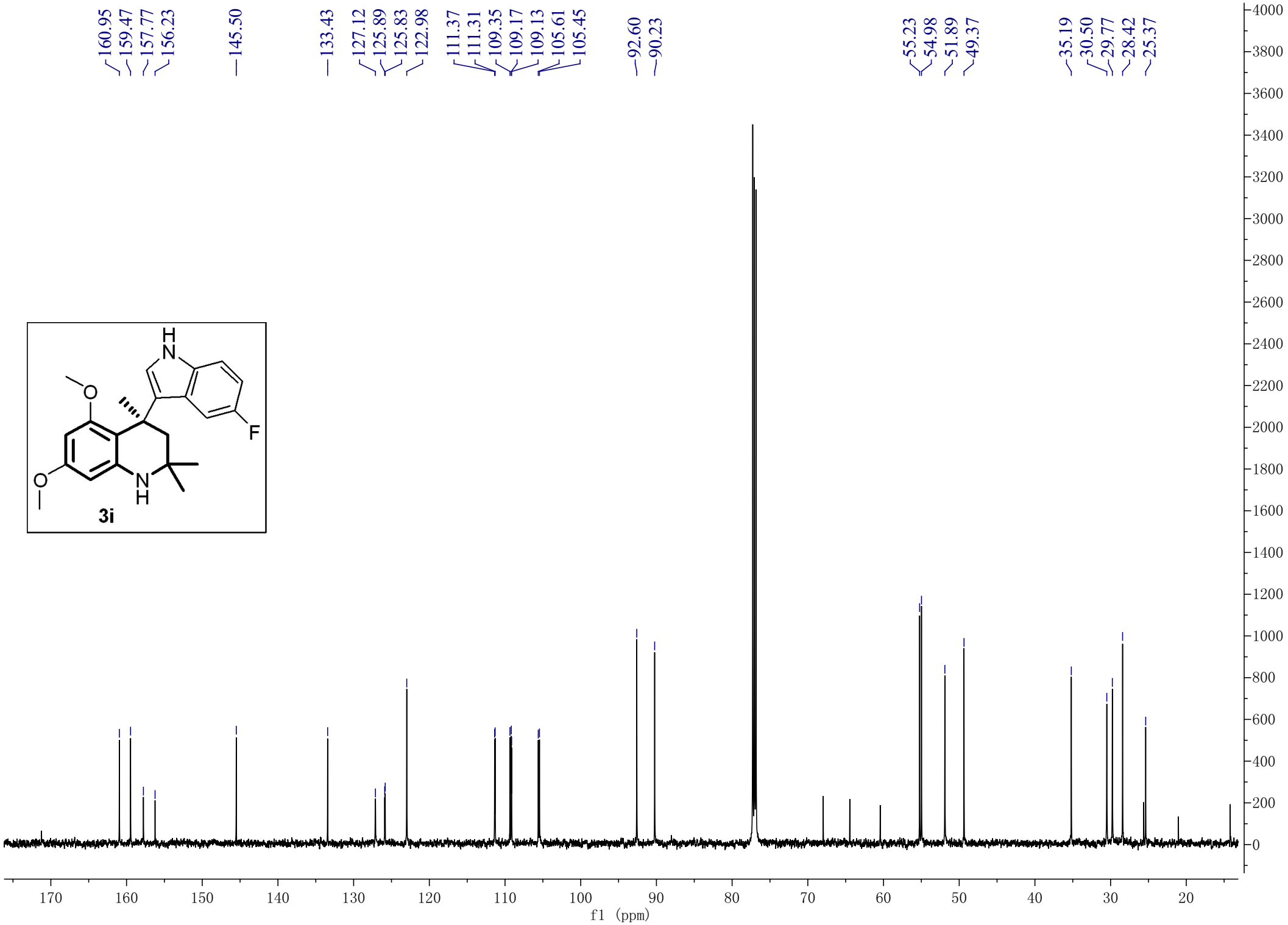

7.82
7.52
7.51
7.32
7.31
7.26
7.16
7.15
7.14
7.05
7.04
7.03
7.02
6.72
6.72
6.26
6.25
6.24
6.24
6.14
6.13
3.78
3.70
2.67
2.65
1.92
1.90
1.86
1.30
0.96
0.97
0.99
1.00
1.02
2.01
0.99
1.00
1.00
3.03
0.82
0.98
1.02
2.93
3.14
3.04
3e
f1 (ppm)

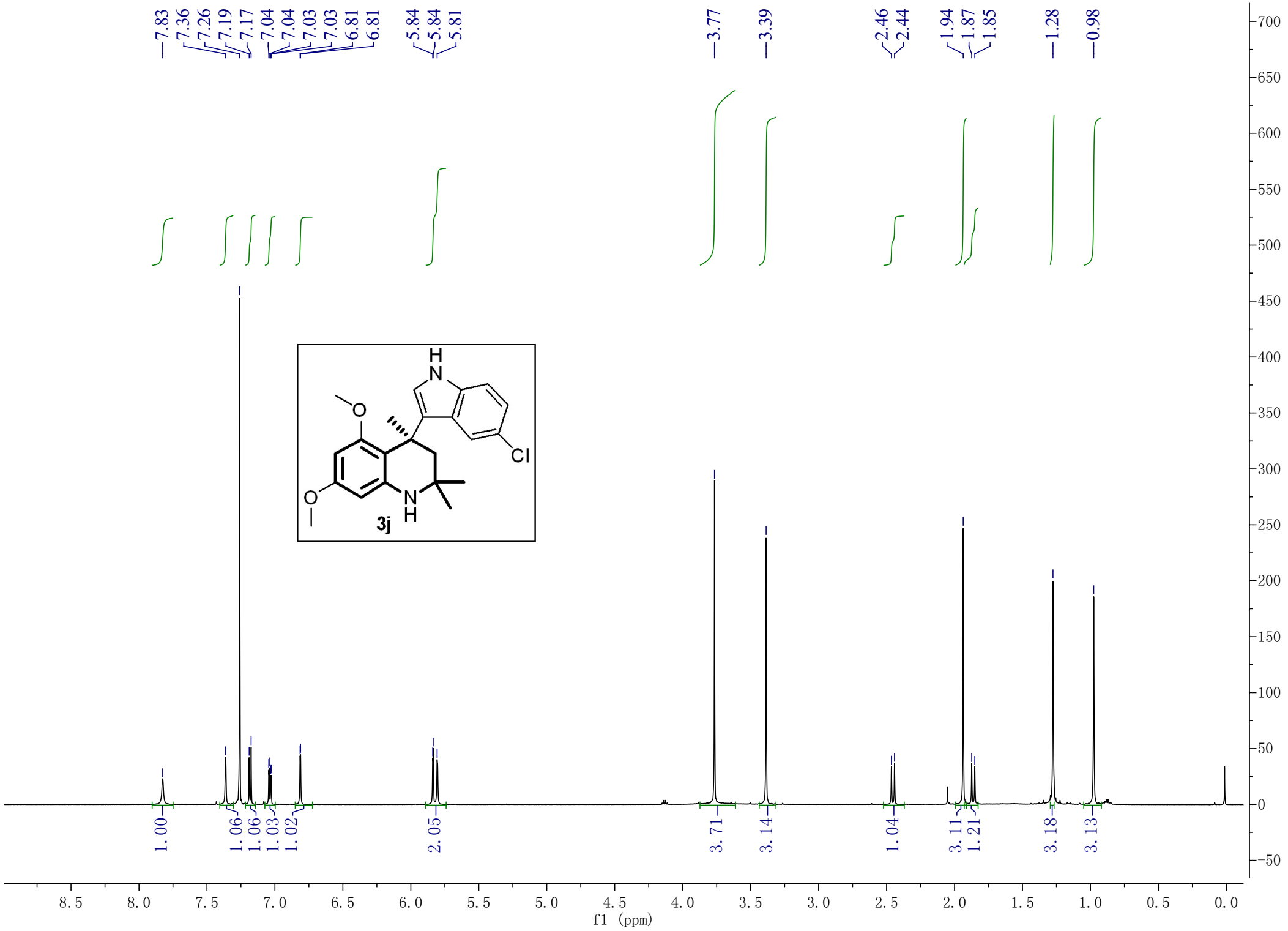

158.77
144.50
137.32
129.76
127.13
125.61
122.05
121.54
121.07
118.98
111.26
103.39
99.48
55.06
49.97
48.94
36.07
31.46
30.69
30.39
3e
f1 (ppm)

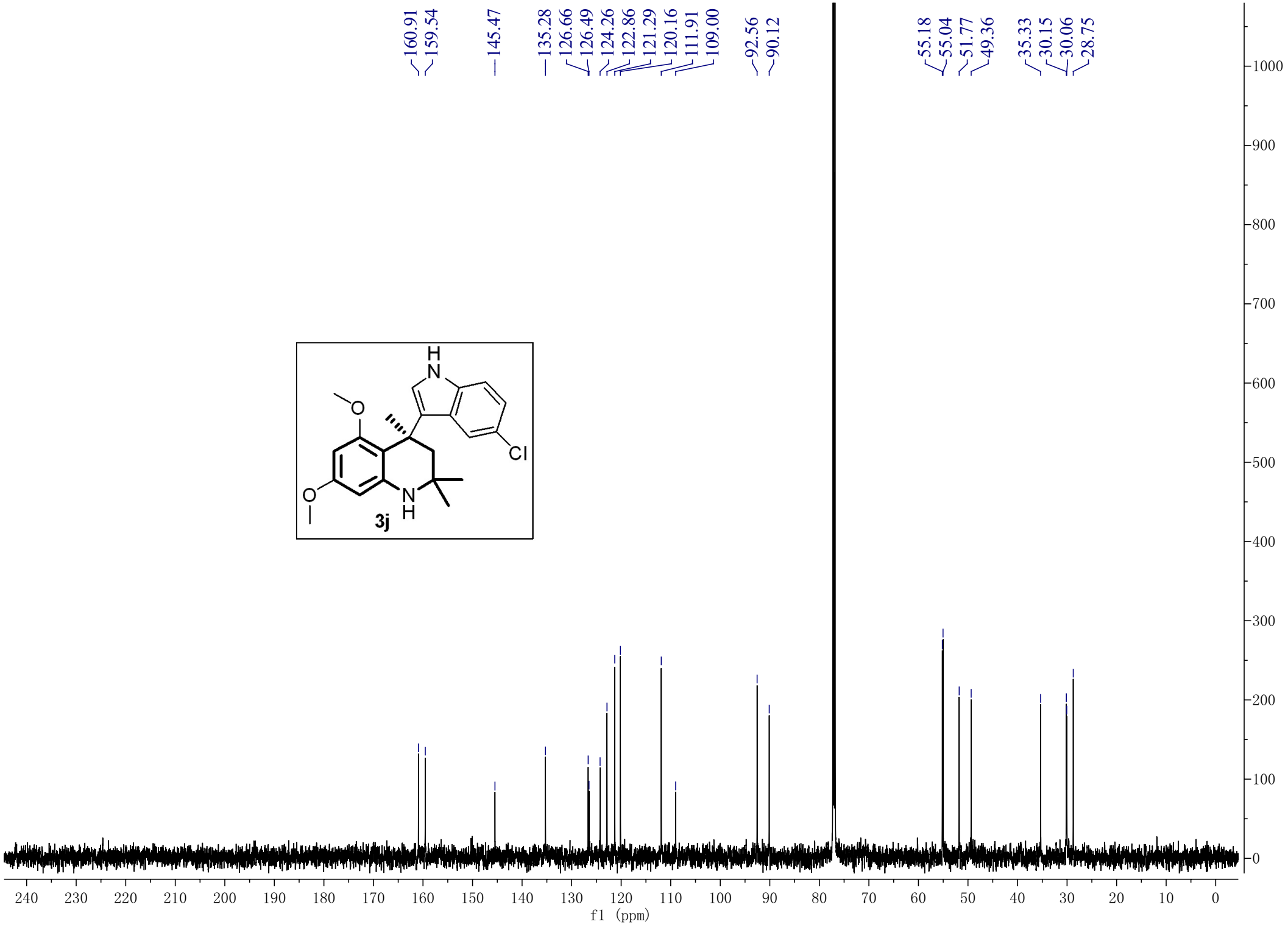

7.78
7.37
7.36
7.29
7.28
7.26
7.09
7.08
7.07
6.96
6.95
6.83
6.83
3.76
3.34
2.55
2.53
1.96
1.87
1.84
1.30
1.01
0.01
3h
1.01
0.98
1.03
1.10
1.05
1.00
1.92
3.40
3.09
1.10
3.01
1.10
3.17
2.95
f1 (ppm)


161.08
159.39
145.47
136.97
126.79
125.66
121.23
120.97
120.70
118.67
110.97
109.75
92.62
90.30
55.28
55.00
51.90
49.45
35.40
30.42
29.97
28.60
3h
f1 (ppm)

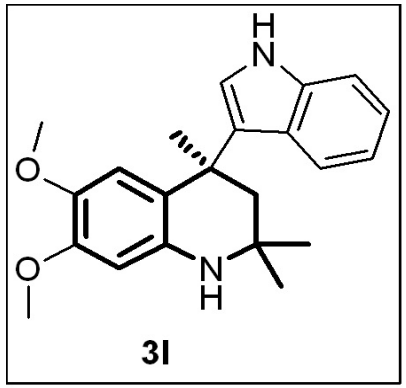

7.86
7.26
7.17
7.16
7.16
7.15
6.99
6.98
6.89
6.84
6.82
6.81
5.82
5.81
3.76
3.34
2.45
2.43
1.94
1.84
1.82
1.29
1.22
1.21
1.02
3i
1.00
1.05
1.05
1.03
1.06
2.09
4.13
3.19
1.04
3.18
1.09
3.27
3.15
f1 (ppm)


160.95
159.47
157.77
156.23
145.50
133.43
127.12
125.89
125.83
122.98
111.37
111.31
109.35
109.17
109.13
105.61
105.45
92.60
90.23
55.23
54.98
51.89
49.37
35.19
30.50
29.77
28.42
25.37
H
N
O
F
O
N
H
3i
f1 (ppm)


7.83
7.36
7.26
7.19
7.17
7.04
7.04
7.03
7.03
6.81
6.81
5.84
5.84
5.81
3.77
3.39
2.46
2.44
1.94
1.87
1.85
1.28
0.98
3j
1.00
1.06
1.06
1.03
1.02
2.05
3.71
3.14
1.04
3.11
1.21
3.18
3.13
f1 (ppm)


160.91
159.54
145.47
135.28
126.66
126.49
124.26
122.86
121.29
120.16
111.91
109.00
92.56
90.12
55.18
55.04
51.77
49.36
35.33
30.15
30.06
28.75
H
N
O
Cl
O
N
H
3j
1000
900
800
700
600
500
400
300
200
100
0
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

gx-714i



3l

8.065
7.557
7.537
7.333
7.312
7.285
7.180
7.162
7.142
7.068
7.050
6.749
6.240
3.873
3.704
2.677
2.643
2.399
2.383
2.366
1.323
0.999

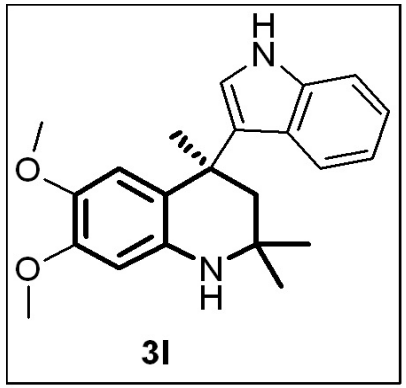
1.00
1.18
0.91
1.19
1.00
2.07
1.00
3.41
3.26
1.09
1.33
3.22
3.16
2.93

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 -0.

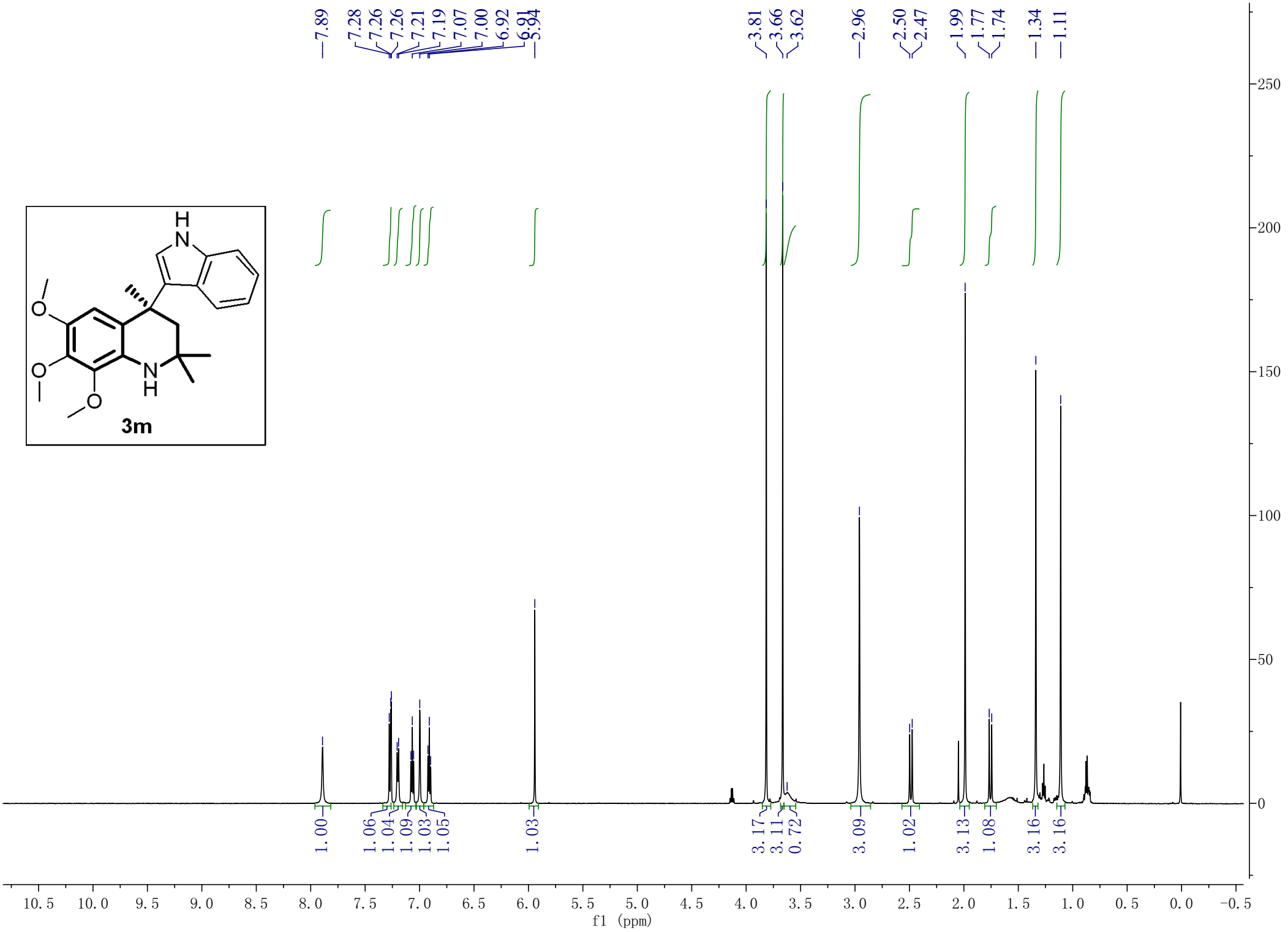
f1 (ppm)

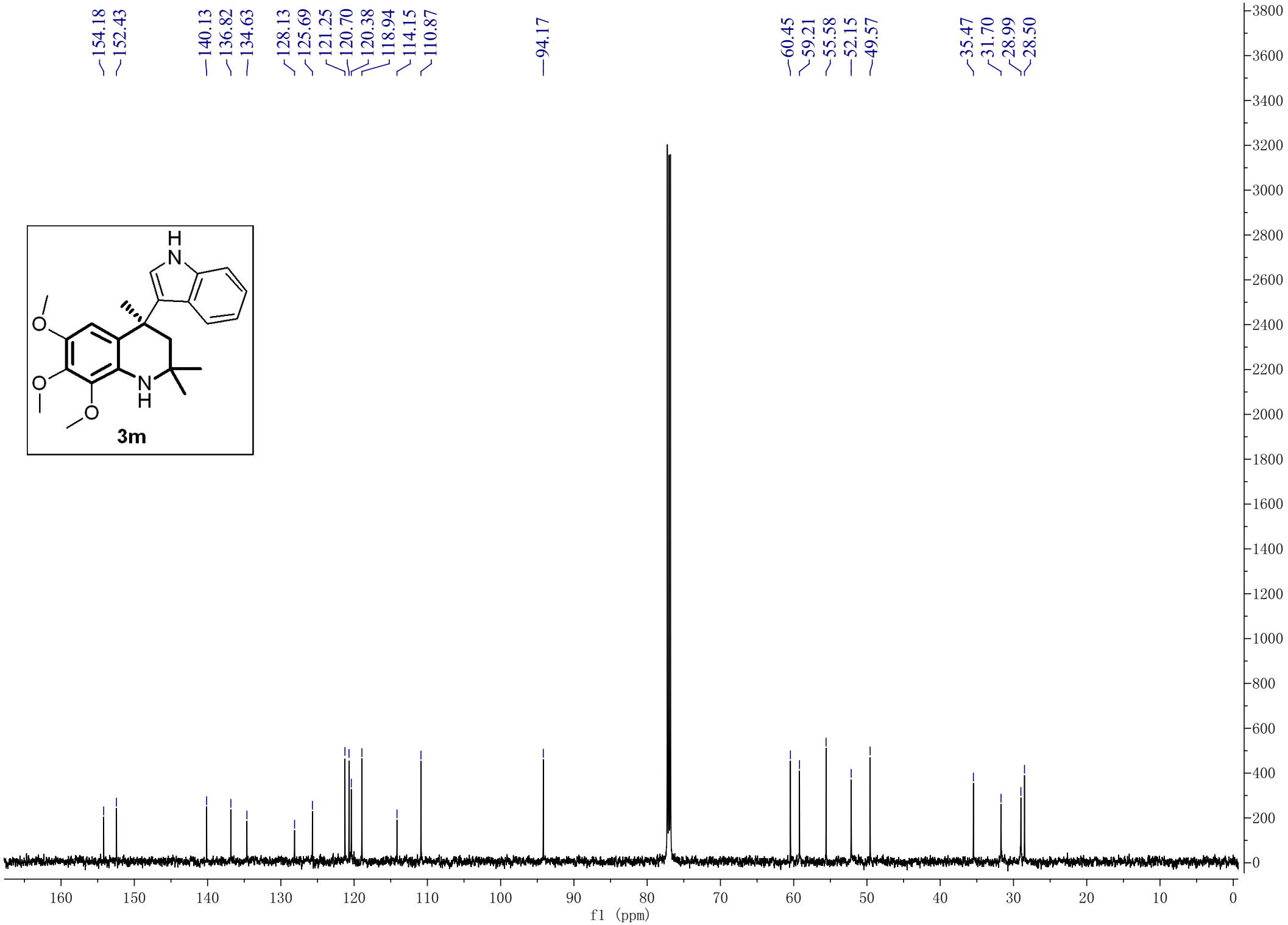
gx-714i

148.503
141.496
137.308
126.794
125.507
122.127
121.512
121.020
119.802
118.960
113.513
111.322
99.639
56.888
55.724
50.119
49.041
36.351
31.077
30.855
29.988

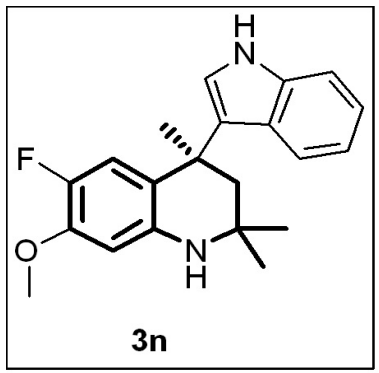


3l


7.89
7.28
7.26
7.26
7.21
7.19
7.07
7.00
6.92
6.91
3.94
3.81
3.66
3.62
2.96
2.50
2.47
1.99
1.77
1.74
1.34
1.11
1.00
1.06
1.04
1.09
1.03
1.05
1.03
3.17
3.11
0.72
3.09
1.02
3.13
1.08
3.16
3.16
250
200
150
100
50
0
10.5
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
-0.5
f1 (ppm)
H
N
O
O
O
N
H
3m


154.18
152.43
140.13
136.82
134.63
128.13
125.69
121.25
120.70
120.38
118.94
114.15
110.87
94.17
60.45
59.21
55.58
52.15
49.57
35.47
31.70
28.99
28.50
3m
f1 (ppm)

gx-714c



3n

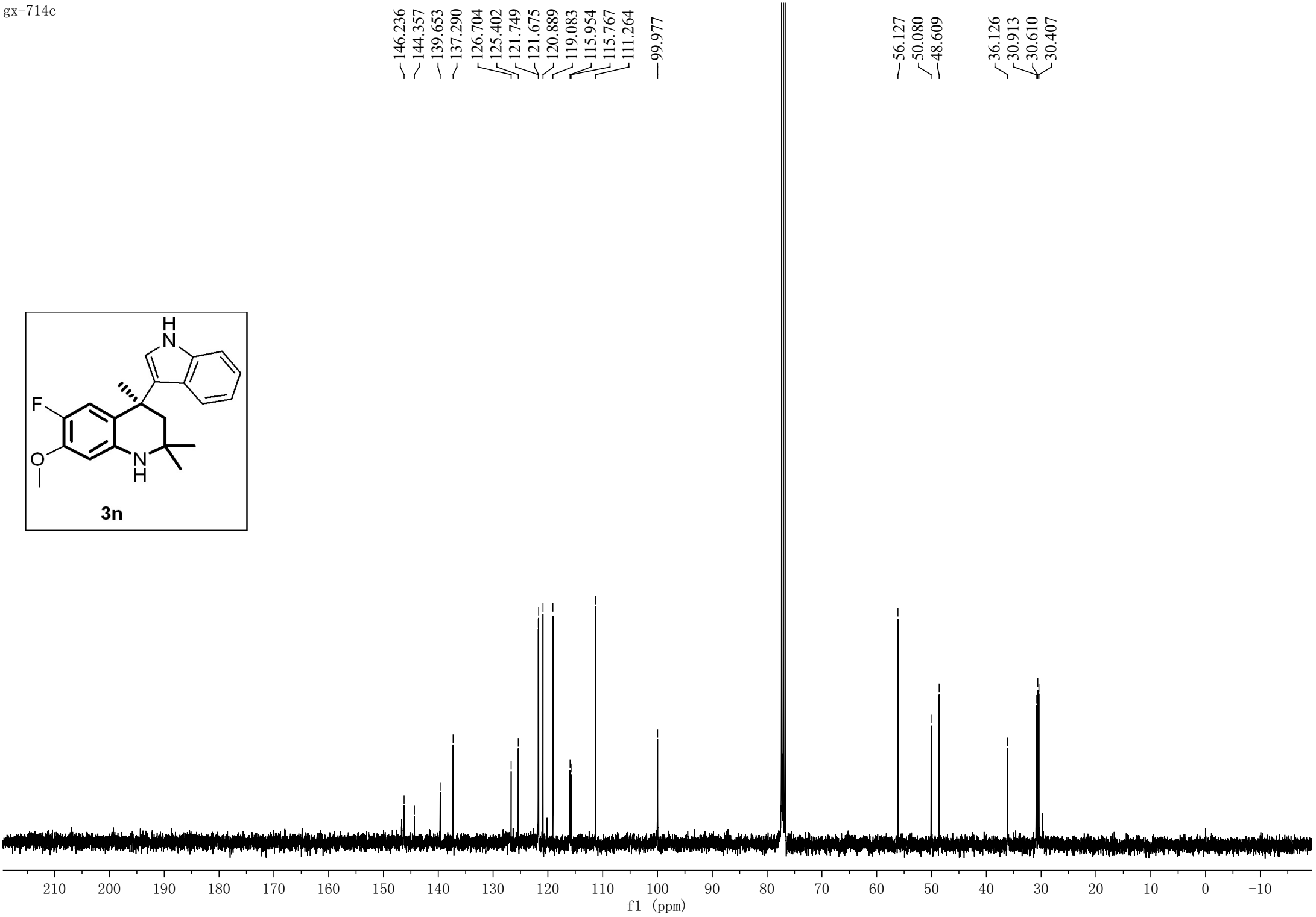
7.891
7.498
7.478
7.360
7.340
7.285
7.167
7.040
6.856
6.824
6.808
6.802
6.203
6.184
3.867
3.684
3.586
2.668
2.633
1.905
1.870
1.836
1.313
1.289
1.012

1.04
1.04
1.02
1.01
0.96
0.91
0.86
1.00
3.06
0.75
1.08
0.97
2.85
2.97
2.81

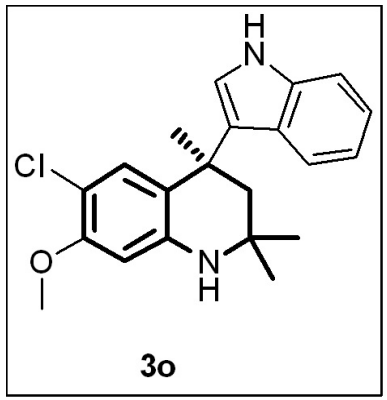
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

gx-714c


146.236
144.357
139.653
137.290
126.704
125.402
121.749
121.675
120.889
119.083
115.954
115.767
111.264
99.977
56.127
50.080
48.609
36.126
30.913
30.610
30.407
F
O
H
N
N
H
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

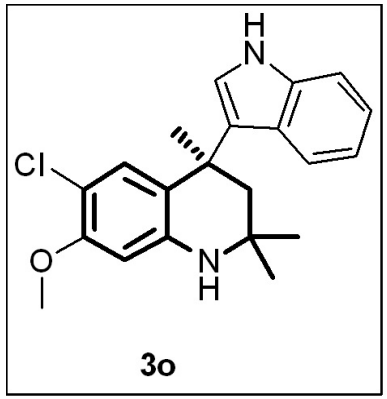
gx-714b



3o

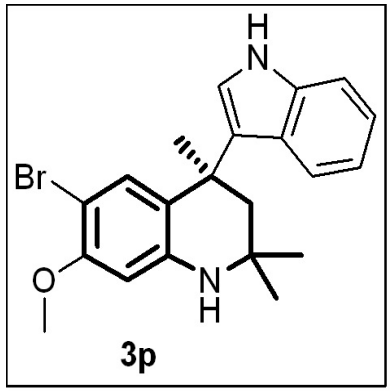
gx-714b

153.703
143.101
137.332
130.032
125.406
121.959
121.661
120.877
119.076
111.328
110.105
98.632
77.373
77.258
77.056
76.738
55.957
50.138
48.449
36.073
31.275
30.657
30.227



3o

gx-714j

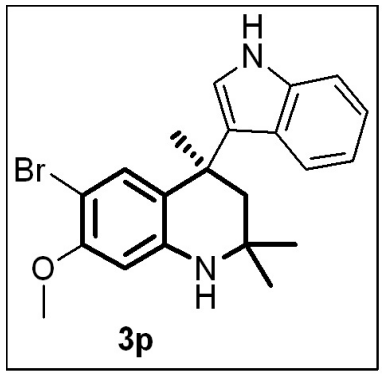


3p

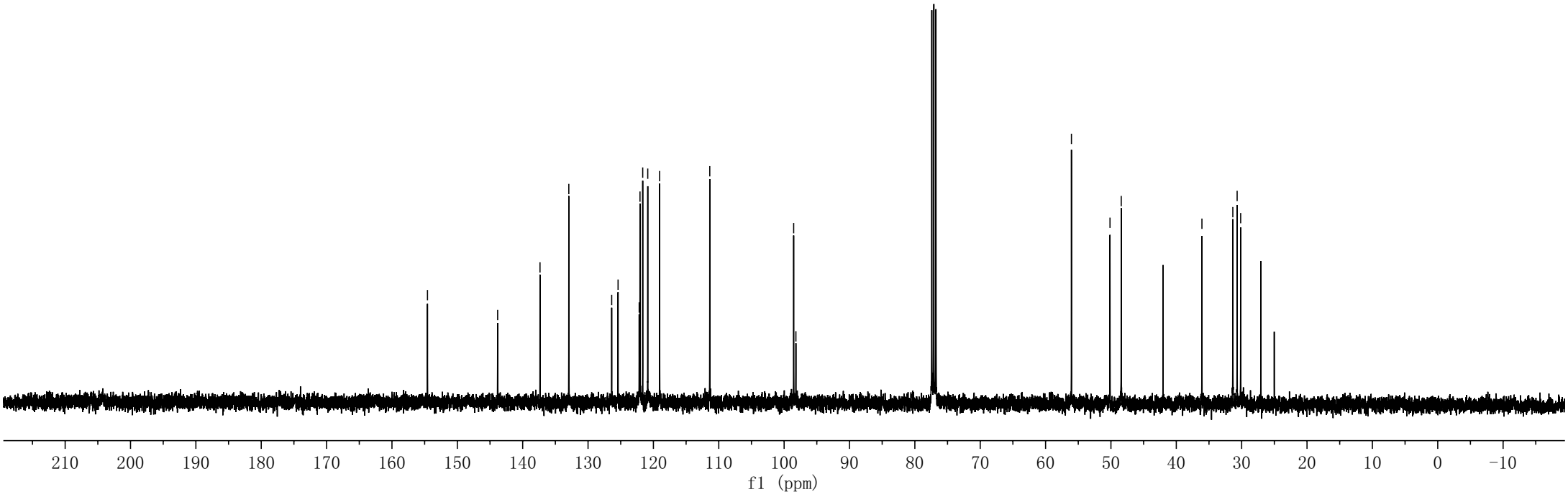
f1 (ppm)

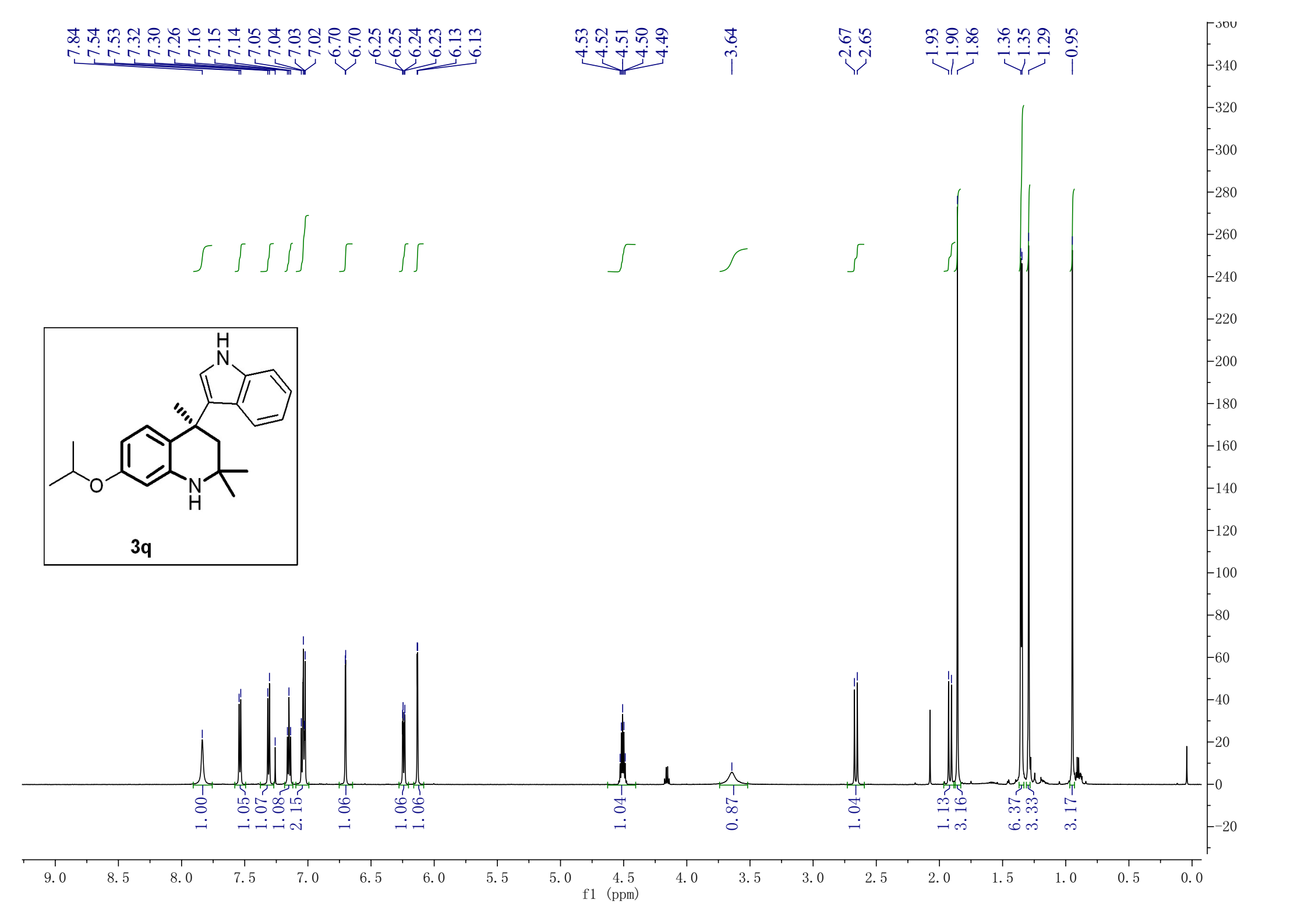
gx-714j

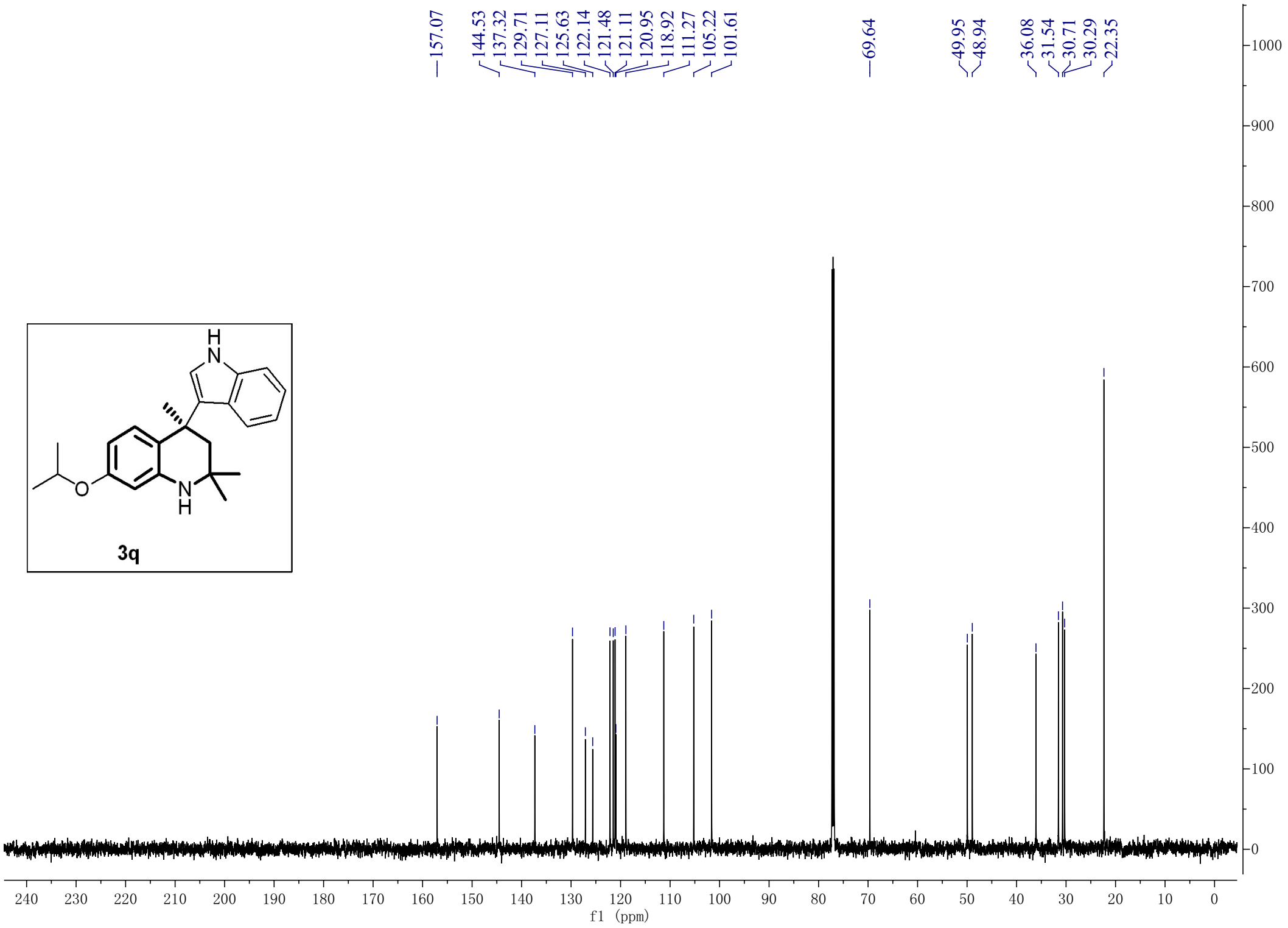
154.565
143.829
137.349
132.941
126.381
125.406
122.175
122.051
121.635
120.865
119.052
111.376
98.540
98.198
56.042
50.143
48.424
36.078
31.351
30.693
30.150

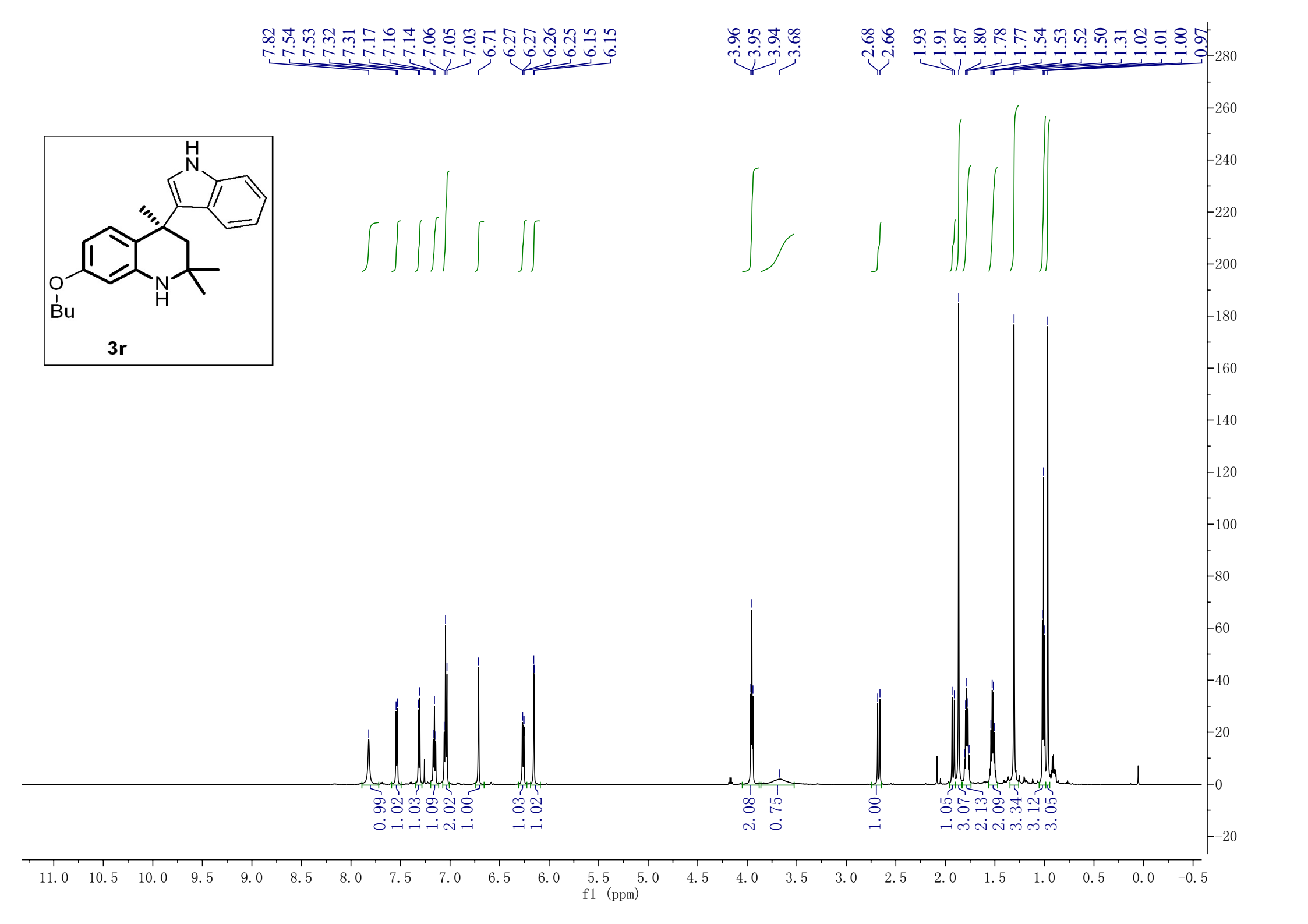


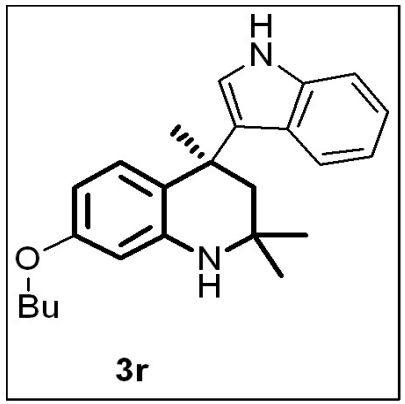
3p




7.84
7.54
7.53
7.32
7.30
7.26
7.16
7.15
7.14
7.05
7.04
7.03
7.02
6.70
6.70
6.25
6.25
6.24
6.23
6.13
6.13
4.53
4.52
4.51
4.50
4.49
3.64
2.67
2.65
1.93
1.90
1.86
1.36
1.35
1.29
0.95
3q
1.00
1.05
1.07
1.08
2.15
1.06
1.06
1.06
1.04
0.87
1.04
1.13
3.16
6.37
3.33
3.17
f1 (ppm)


157.07
144.53
137.32
129.71
127.11
125.63
122.14
121.48
121.11
120.95
118.92
111.27
105.22
101.61
69.64
49.95
48.94
36.08
31.54
30.71
30.29
22.35
1000
900
800
700
600
500
400
300
200
100
0
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H
N
O
N
H
3q

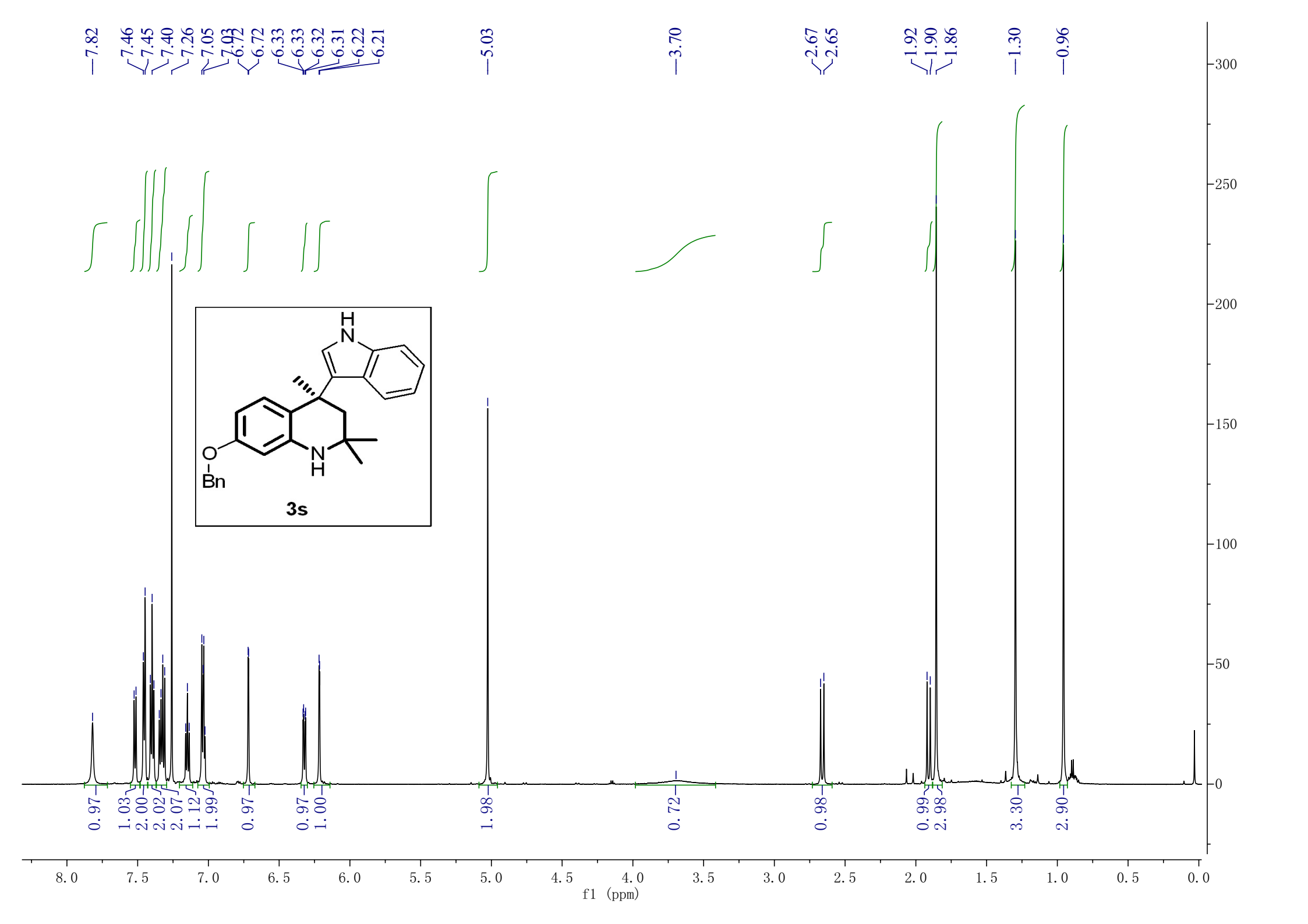

7.82
7.54
7.53
7.32
7.31
7.17
7.16
7.14
7.06
7.05
7.03
6.71
6.27
6.27
6.26
6.25
6.15
6.15
3.96
3.95
3.94
3.68
2.68
2.66
1.93
1.91
1.87
1.80
1.78
1.77
1.54
1.53
1.52
1.50
1.31
1.02
1.01
1.00
0.97
H
N
O
Bu
N
H
3r
0.99
1.02
1.03
1.09
2.02
1.00
1.03
1.02
2.08
0.75
1.00
1.05
3.07
2.13
2.09
3.34
3.12
3.05
f1 (ppm)

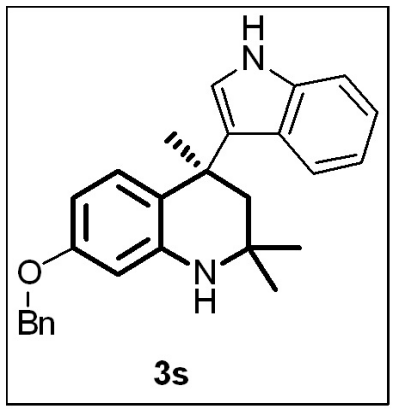


3r

158.36
144.48
137.33
129.72
127.13
125.63
122.11
121.51
121.10
120.92
118.96
111.28
104.07
100.12
67.48
49.97
48.98
36.08
31.56
31.48
30.72
30.38
19.37
13.95

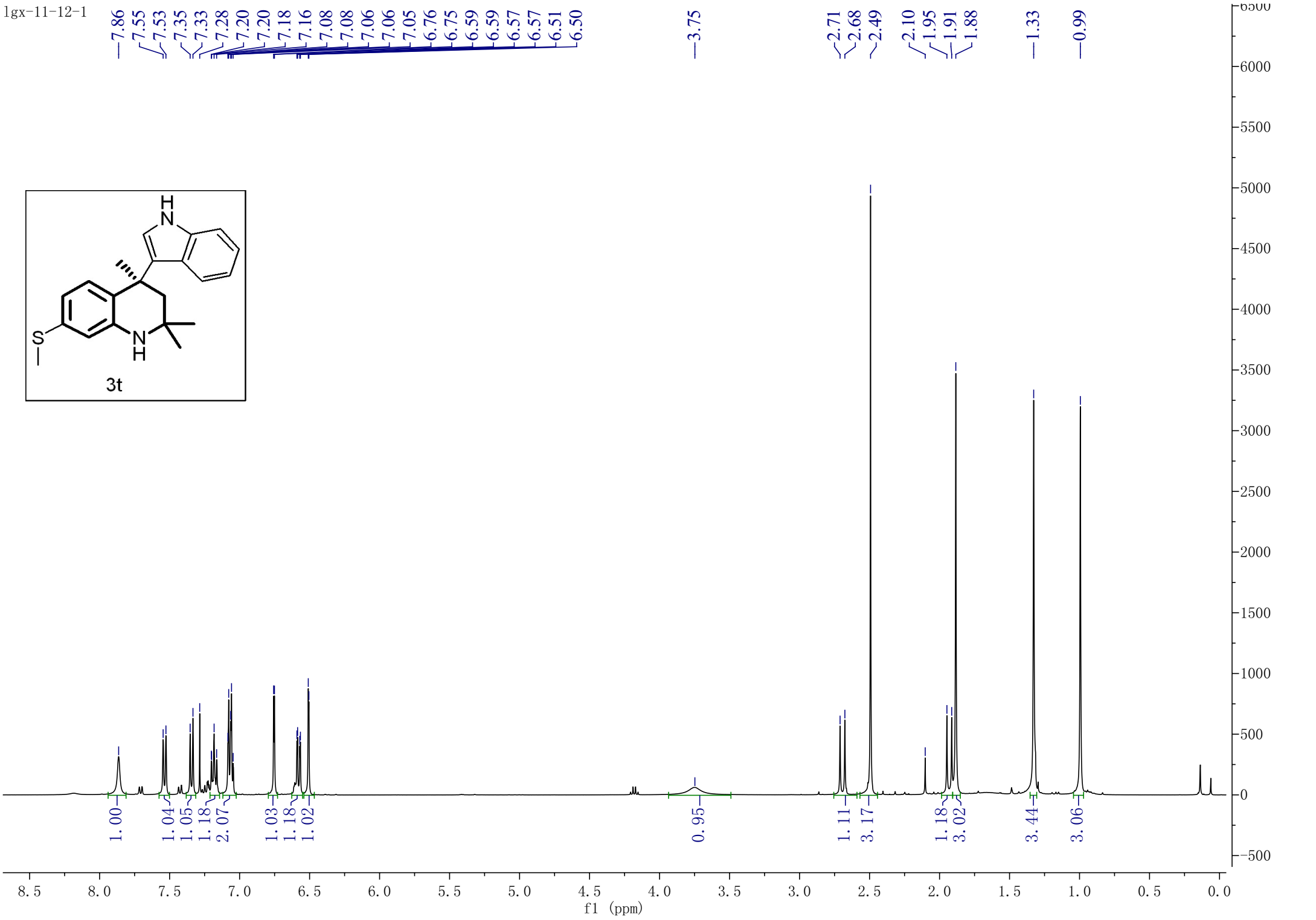
f1 (ppm)


7.82
7.46
7.45
7.40
7.26
7.05
7.03
6.72
6.72
6.33
6.33
6.32
6.31
6.22
6.21
5.03
3.70
2.67
2.65
1.92
1.90
1.86
1.30
0.96
H
N
O
Bn
N
H
3s
0.97
1.03
2.00
2.02
2.07
1.12
1.99
0.97
0.97
1.00
1.98
0.72
0.98
0.99
2.98
3.30
2.90
300
250
200
150
100
50
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
N
O
Bn
N
H

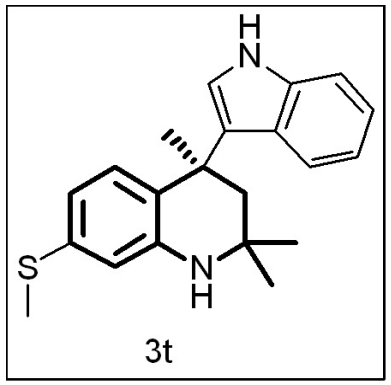
3s

158.13
144.49
137.54
137.32
129.76
128.54
127.83
127.58
127.09
125.60
122.05
121.54
121.35
121.08
118.99
111.25
104.19
100.46
69.90
49.99
48.90
36.09
31.46
30.68
30.36
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


lgx-11-12-1
7.86
7.55
7.53
7.35
7.33
7.28
7.20
7.20
7.18
7.16
7.08
7.08
7.06
7.06
7.05
6.76
6.75
6.59
6.59
6.57
6.57
6.51
6.50
3.75
2.71
2.68
2.49
2.10
1.95
1.91
1.88
1.33
0.99
3t
1.00
1.04
1.05
1.18
2.07
1.03
1.18
1.02
0.95
1.11
3.17
1.18
3.02
3.44
3.06
f1 (ppm)

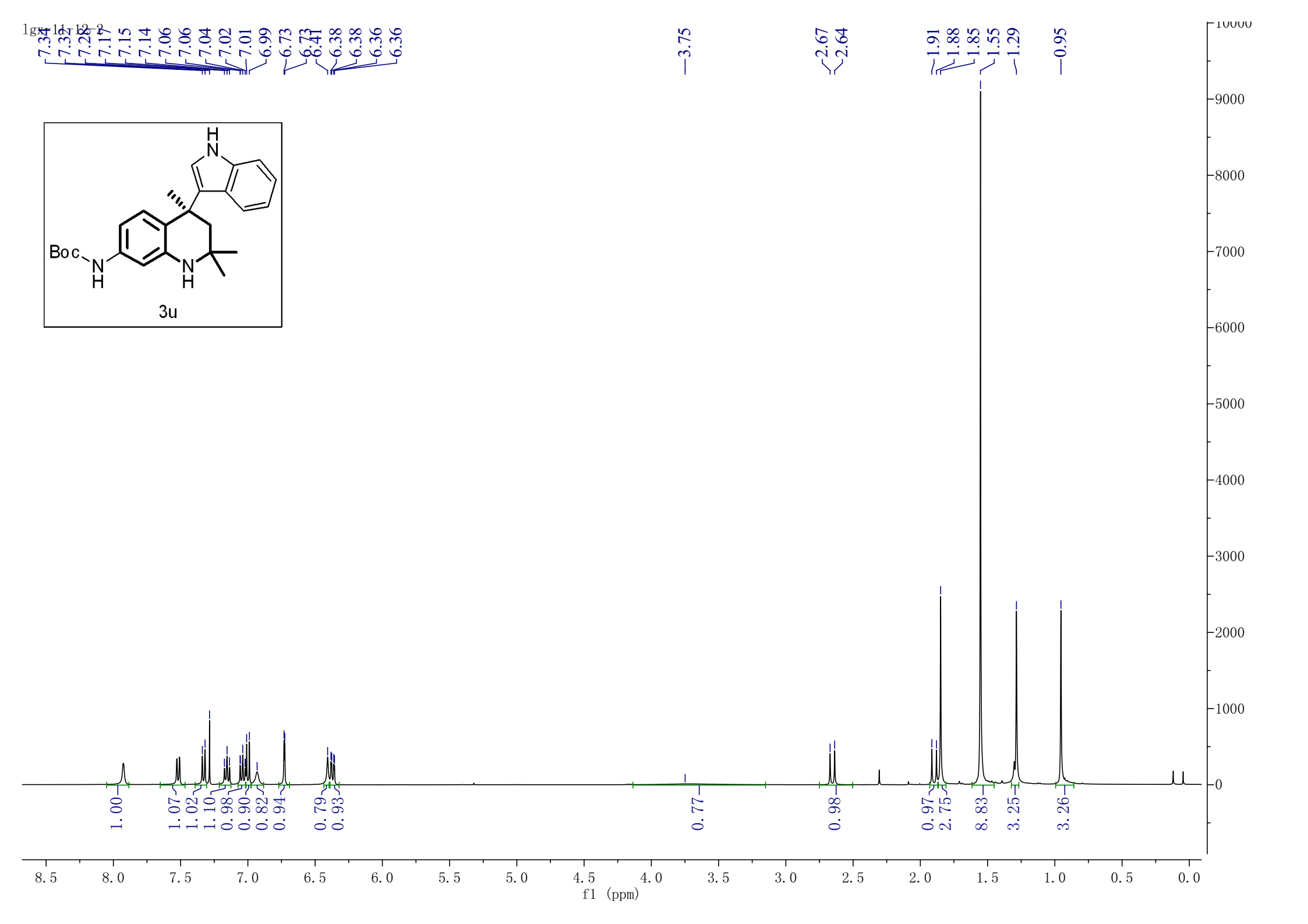
lgx-11-12-1

143.87
137.28
136.18
129.36
126.62
125.61
125.49
122.07
121.63
121.02
119.05
115.79
112.43
111.32
50.00
48.72
36.29
31.40
30.51
30.46
15.82

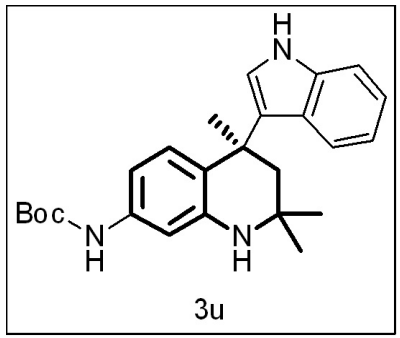


3t

f1 (ppm)

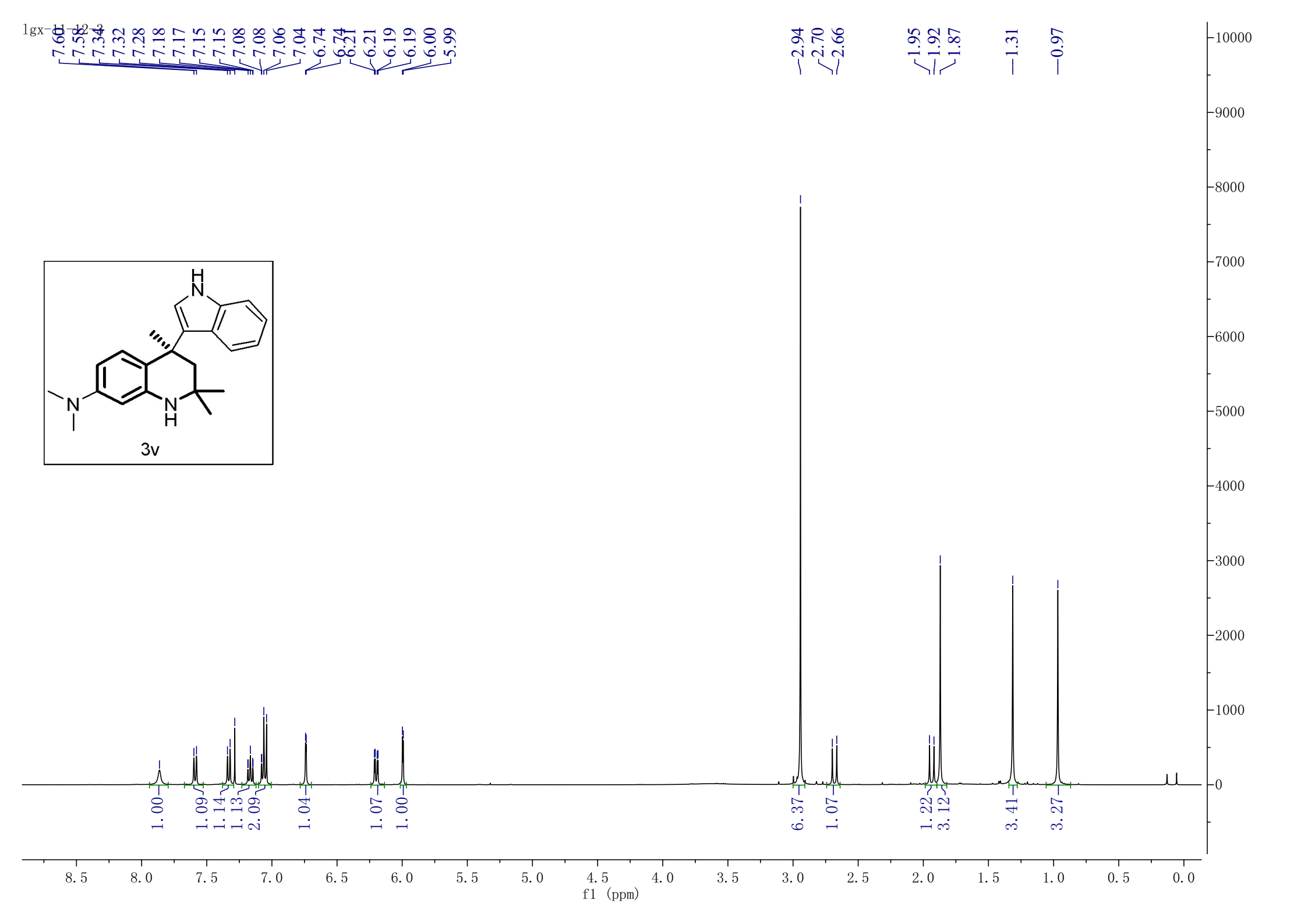

lgx-11-12-2
7.34
7.32
7.28
7.17
7.15
7.14
7.06
7.06
7.04
7.02
7.01
6.99
6.73
6.73
6.41
6.38
6.38
6.36
6.36
3.75
2.67
2.64
1.91
1.88
1.85
1.55
1.29
0.95
Boc
N
H
N
H
3u
1.00
1.07
1.02
1.10
0.98
0.90
0.82
0.94
0.79
0.93
0.77
0.98
0.97
2.75
8.83
3.25
3.26
f1 (ppm)

lgx-11-12-2

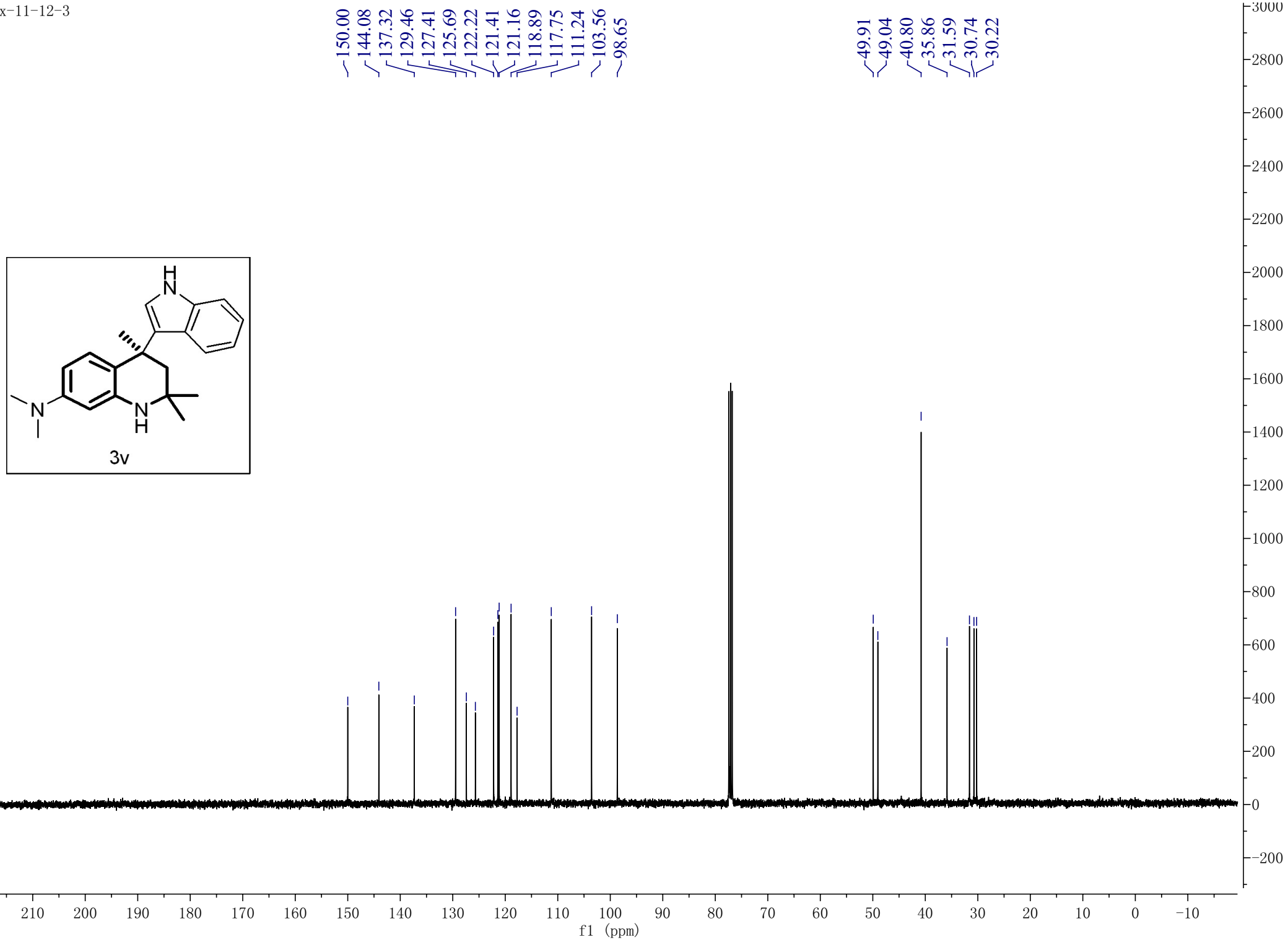

H
N
Boc
N
H
N
H

3u

152.94
144.06
137.26
137.05
129.22
126.87
125.53
122.05
121.53
121.05
118.97
111.25
107.71
104.26
80.24
49.89
48.82
36.14
31.32
30.52
30.45
28.41
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

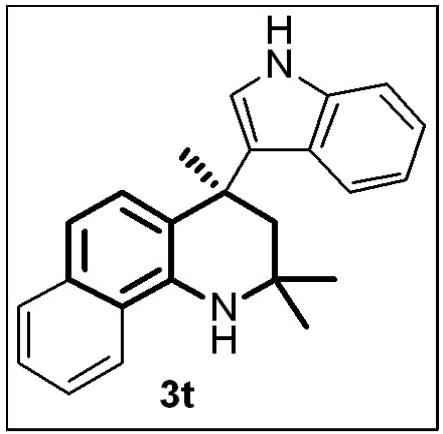

lgx-11-12-3
7.60
7.58
7.34
7.32
7.28
7.18
7.17
7.15
7.15
7.08
7.08
7.06
7.04
6.74
6.74
6.21
6.21
6.19
6.19
6.00
5.99
2.94
2.70
2.66
1.95
1.92
1.87
1.31
0.97
3v
1.00
1.09
1.14
1.13
2.09
1.04
1.07
1.00
6.37
1.07
1.22
3.12
3.41
3.27
f1 (ppm)

lgx-11-12-3


150.00
144.08
137.32
129.46
127.41
125.69
122.22
121.41
121.16
118.89
117.75
111.24
103.56
98.65
49.91
49.04
40.80
35.86
31.59
30.74
30.22
3v
f1 (ppm)

gx-7-1d

7.903
7.883
7.819
7.799
7.536
7.508
7.505
7.490
7.472
7.368
7.347
7.322
7.284
7.213
7.191
7.170
7.151
7.030
7.011
6.992
6.788
6.783



2.61
2.99
2.03
2.38
1.24
1.03
1.00
1.11
1.24
2.88
3.32
2.97

0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

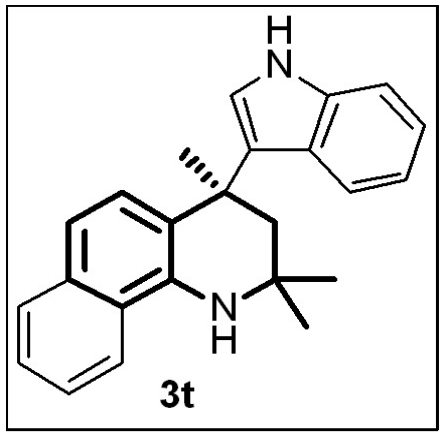
f1 (ppm)

gx-714d

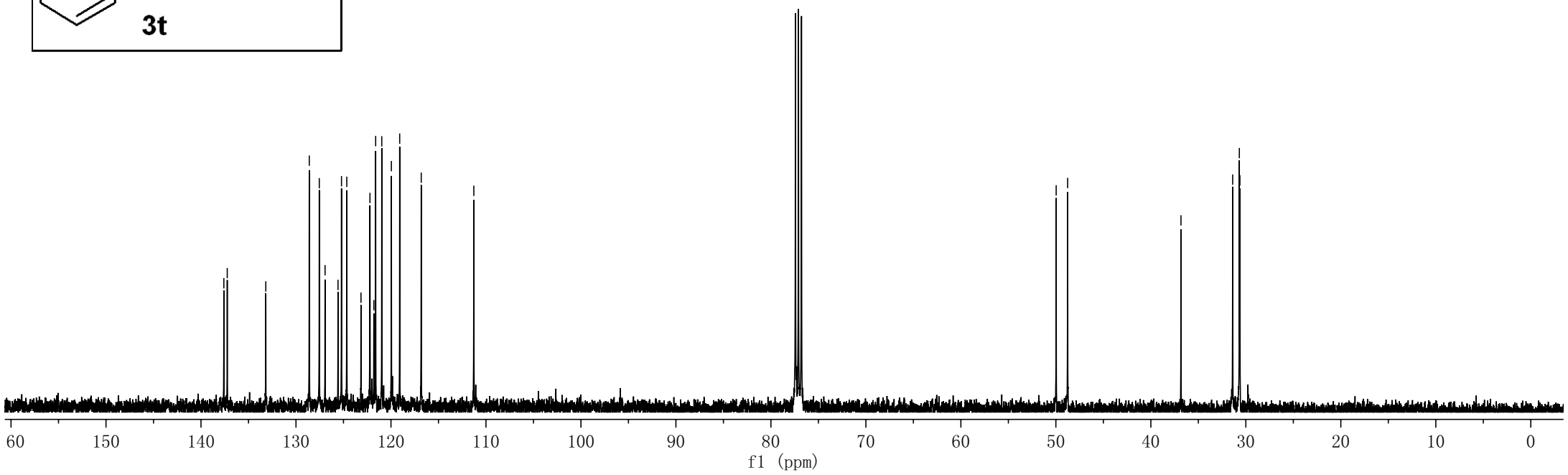
137.593
137.236
133.178
128.600
127.546
126.939
125.576
125.208
124.652
123.157
122.211
121.802
121.612
120.969
119.957
119.081
116.813
111.277

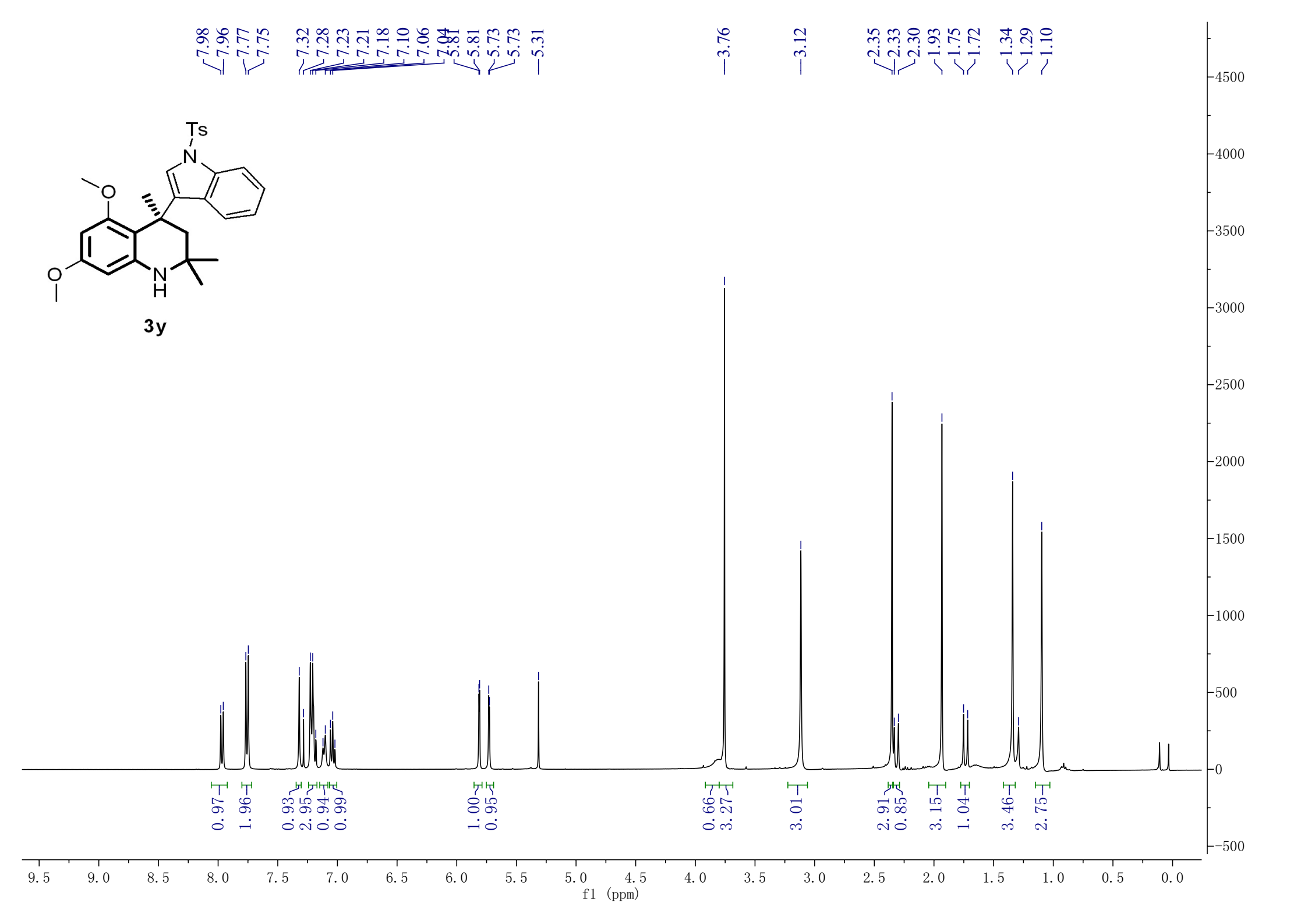
49.967
48.761

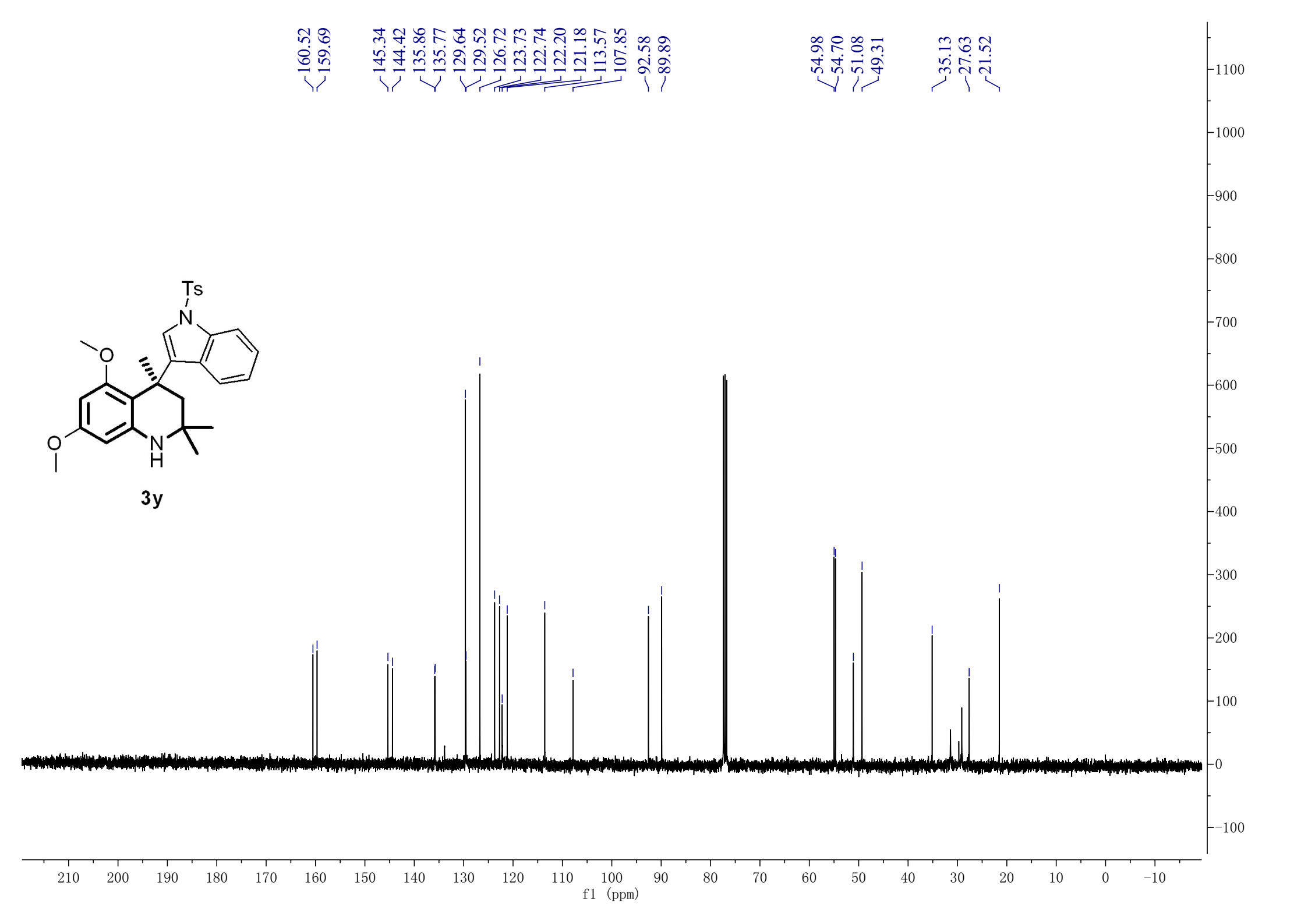
36.829
31.385
30.684
30.624



3t




7.98
7.96
7.77
7.75
7.32
7.28
7.23
7.21
7.18
7.10
7.06
7.04
5.81
5.81
5.73
5.73
5.31
3.76
3.12
2.35
2.33
2.30
1.93
1.75
1.72
1.34
1.29
1.10
Ts
N
O
O
N
H
3y
0.97
1.96
0.93
2.95
0.94
0.99
1.00
0.95
0.66
3.27
3.01
2.91
0.85
3.15
1.04
3.46
2.75
f1 (ppm)


160.52
159.69
145.34
144.42
135.86
135.77
129.64
129.52
126.72
123.73
122.74
122.20
121.18
113.57
107.85
92.58
89.89
54.98
54.70
51.08
49.31
35.13
27.63
21.52
Ts
N
O
O
N
H
3y
f1 (ppm)