Supporting Information

Pd(II)-Catalyzed Annulation Reactions of Epoxides with Benzamides to Synthesize Isoquinolones

Huihong Wang,[a,†] Fei Cao,[a,†] Weiwei Gao,[a] Xiaodong Wang,[b] Yuhang Yang,[b] Tao Shi*,[b] and Zhen Wang*[a,b]

[a]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, No. 222 South Tianshui Road, Lanzhou 730000, China.

[b]School of Pharmacy, Lanzhou University, No. 199 West Donggang Road, Lanzhou 730000, China.

† H. W. and F. C. contributed equally to this work.

Corresponding authors: zhenw@lzu.edu.cn; shit18@lzu.edu.cn

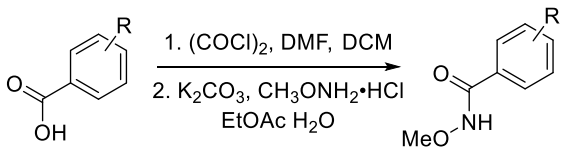
Table of Contents

1. General Information

All reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Methylene chloride (CH_2Cl_2) was distilled immediately before use from calcium hydride. Diethyl ether and tetrahydrofuran (THF) were distilled immediately before use from sodium-benzophenone ketyl. All other solvents were processed through the reference *Purification of Laboratory Chemicals (Seventh Edition)*. External bath temperatures were used to record all reaction temperatures. Silica gel (300~400 mesh) and petroleum ether, EtOAc, CH_2Cl_2 and MeOH were used for product purification by flash column chromatography. NMR spectra were recorded on Bruker 400 MHz (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR) spectrometers. Proton chemical shifts were reported relative to a residual solvent peak ($CDCl_3$ at 7.26 ppm) and carbon chemical shifts were reported relative to a residual solvent peak ($CDCl_3$ at 77.00 ppm) in order to compare with natural products conveniently. The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were measured on a BruckerDaltonics Apex II 47e Specification (for HRMS). Chiral HPLC analysis was performed using an Agilent 1100 Alliance instrument. Fourier transform infrared spectra (FT-IR) were recorded on an Agilent Technologies Cary 630 FT-IR instrument. Optical rotations were measured on an Autopol IV, and are reported as $[\alpha]_D^T$ (concentration in g/mL solvent).

2. Experimental Procedures and Characterization Data of Compounds

General Procedure for the Synthesis of N-alkoxybenzamide:



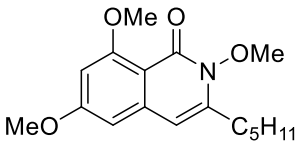
To a solution of the benzoic acid (3.0 mmol) in dry DCM (10 mL) was added oxalyl chloride (0.30 mL, 3.6 mmol), dropwise at 0 °C, followed by a catalytic amount of dry DMF (2 drops). The reaction was stirred at room temperature until the acid was completely consumed. The solvent was removed under vacuum to afford the corresponding crude acyl chloride. Methoxyamine hydrochloride (4.0 mmol) was added to a biphasic mixture of K_2CO_3 (828 mg, 6.0 mmol) in a mixture of EtOAc (12 mL) and H_2O (6 mL). The mixture was cooled to 0 °C, and then acyl chloride in a minimum amount of EtOAc was added dropwise. The reaction was stirred at room temperature for 4 h. The organic phase was separated, and the aqueous phase was extracted for three times with EtOAc and dried over with Na_2SO_4. The solvent was evaporated and the mixture was directly purified by flash column chromatography with EtOAc to give the product.

Procedure for alkylation of N-methoxybenzamide.

N-methoxybenzamide (0.1 mmol) and epoxide (0.2 mmol), CF_3COOK (15.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mmol%), TEA (3 μL, 20 mmol%) 4Å molecular sieve (10 mg) and hexafluoro isopropanol (0.3 mL) in a sealed tube was stirred at 100 °C in heating mantle. After 24 hours, the reaction mixture was concentrated and purified by column chromatography to give the product. (Petroleum ether : AcOEt = PE:EA)

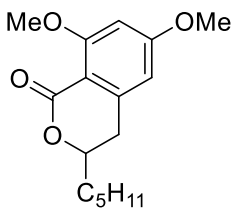
2,6,8-trimethoxy-3-pentylisoquinolin-1(2H)-one (3aa):

Purification by column chromatography on silica gel (PE: EA = 4:1 to 2:1), white solid (25.1 mg, 82% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.37 (s, 1H), 6.35 (s, 1H), 6.04 (s, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.85 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.41 – 1.32 (m, 4H), 0.93 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.0, 162.3, 157.3, 144.2, 140.5, 109.8, 102.5, 98.5, 97.4, 63.7, 56.1, 55.3, 31.4, 30.5, 27.6, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2957, 2937, 1660,

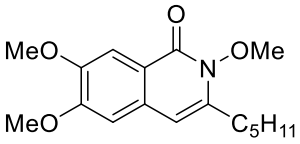


1621, 1468, 1244, 1269, 1036, 993, 751. **HRMS (ESI, m/z):** calcd for $C_{17}H_{24}NO_4^+$ [M + H] $^+$: 306.1700; found: 306.1703.

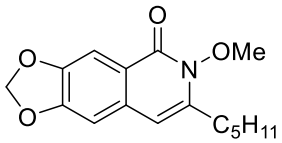
6,8-dimethoxy-3-pentylisochroman-1-one (4a): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), white solid **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.39 (d, *J* = 2.2 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 4.38 – 4.28 (m, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.92 – 2.72 (m, 2H), 1.88 – 1.75 (m, 1H), 1.70 – 1.59 (m, 1H), 1.57 – 1.47 (m, 1H), 1.46 – 1.37 (m, 1H), 1.34 – 1.26 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 164.2, 163.0, 162.7, 143.9, 107.0, 103.8, 97.7, 77.2, 56.1, 55.4, 34.8, 34.6, 31.5, 24.6, 22.5, 13.9. **IR (KBr, ν / cm^{-1})** 2937, 2862, 1720, 1595, 1459, 1412, 1340, 1258, 1108, 851, 758. **HRMS (ESI, m/z)**: calcd for $C_{16}H_{23}O_4^+$ [M + H] $^+$: 279.1591; found: 279.1594.



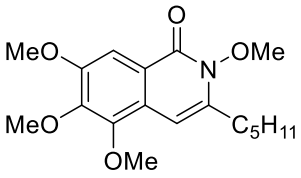
2,6,7-trimethoxy-3-pentylisoquinolin-1(2H)-one (3ab): Purification by column chromatography on silica gel (PE: EA = 4:1 to 2:1), White solid (23.4 mg, 77% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (s, 1H), 6.79 (s, 1H), 6.17 (s, 1H), 4.07 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H), 2.71 – 2.65 (m, 2H), 1.76 – 1.64 (m, 2H), 1.43 – 1.32 (m, 4H), 0.95 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 153.4, 148.6, 141.6, 131.5, 119.6, 107.3, 105.5, 102.8, 63.7, 56.1, 56.0, 31.4, 30.5, 27.9, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2937, 2868, 1668, 1602, 1565, 1444, 1414, 1373, 1209, 1153, 831. **HRMS (ESI, m/z):** calcd for $C_{17}H_{24}NO_4^+$ [M + H] $^+$: 306.1700; found: 306.1701



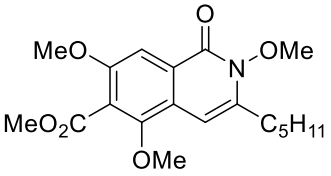
6-methoxy-7-pentyl-[1,3]dioxolo[4,5-g]isoquinolin-5(6H)-one (3ac): Purification by column chromatography on silica gel (PE: EA = 3:1 to 1.5:1), colorless oil (17.6 mg, 61% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.22 (s, 1H), 6.13 (s, 2H), 4.06 (s, 3H), 2.72 – 2.66 (m, 2H), 1.76 – 1.67 (m, 2H), 1.45 – 1.34 (m, 4H), 0.96 – 0.89 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 149.5, 143.9, 140.7, 122.9, 121.0, 120.4, 108.2, 102.1, 95.8, 63.8, 31.4, 30.8, 27.8, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2935, 2862, 1515, 1405, 1468, 1422, 1220,



1179, 978, 728. **HRMS (ESI, m/z):** calcd for $C_{16}H_{20}NO_4^+$ [M + H] $^+$: 290.1387; found: 290.1390.

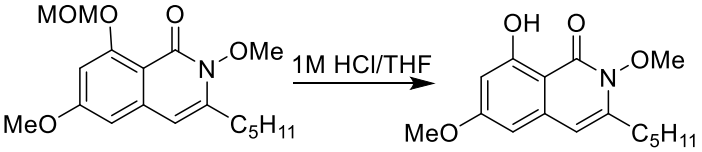
2,5,6,7-tetramethoxy-3-pentylisoquinolin-1(2H)-one (3ad): Purification by column chromatography on silica gel (PE: EA = 3:1 to 1:1), white solid (29.1 mg, 87% yield) 

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.06 (s, 1H), 4.03 (s, 3H), 3.96 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 2.68 – 2.59 (m, 2H), 1.67 (m, 2H), 1.42 – 1.29 (m, 4H), 0.93 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9, 156.6, 154.1, 142.8, 141.5, 134.8, 113.9, 102.4, 102.1, 63.6, 62.0, 61.4, 55.8, 31.3, 30.4, 27.6, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2959, 2862, 1664, 1604, 1455, 1369, 1215, 1131, 1107, 918, 833. **HRMS (ESI, m/z):** calcd for $C_{18}H_{26}NO_5^+$ [M + H] $^+$: 336.1805; found: 336.1811.

methyl 2,5,7-trimethoxy-1-oxo-3-pentyl-1,2-dihydroisoquinoline-6-carboxylate (3ae): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), white solid (29.1 mg, 80% yield) CCDC: 2042086. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.11 (s, 1H), 4.05 (s, 3H), 3.98 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H), 2.72 – 2.62 (m, 2H), 1.73 – 1.66 (m, 2H), 1.44 – 1.35 (m, 4H), 0.95 – 0.89 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 159.5, 159.2, 156.3, 145.2, 140.9, 118.2, 113.1, 102.5, 101.6, 63.8, 63.6, 56.0, 52.5, 31.4, 30.5, 27.6, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2933, 2860, 1660, 1612, 1500, 1463, 1246, 1161, 1030, 870. **HRMS (ESI, m/z):** calcd for $C_{19}H_{26}NO_6^+$ [M + H] $^+$: 364.1755; found: 364.1751.

8-hydroxy-2,6-dimethoxy-3-pentylisoquinolin-1(2H)-one (3af):

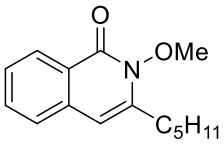


3af ' 3af

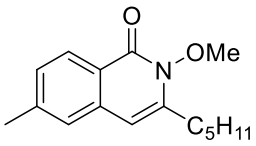
To the crude mixture of 3af' was added 1 mL THF and 1 mL 1M HCl solution, the resulting mixture was stirred at 50 ℃ for 2 h. The mixture was extracted three times with $CHCl_3$. The

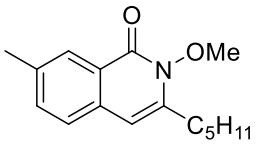
combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. purified by flash column chromatography (PE: EA = 1:1) to give the product **3af** as a white solid (29.1 mg, 78% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.43 (s, 1H), 6.42 (s, 1H), 6.34 (s, 1H), 6.18 (s, 1H), 4.07 (s, 3H), 3.85 (s, 3H), 2.71 – 2.62 (m, 2H), 1.73 – 1.66 (m, 2H), 1.43 – 1.34 (m, 4H), 0.97 – 0.88 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 162.6, 161.8, 142.8, 138.2, 106.2, 104.7, 99.6, 98.9, 64.2, 55.4, 31.3, 30.2, 27.7, 22.3, 13.9. **IR (KBr, ν / cm^{-1})** 2903, 2846, 1624, 1602, 1484, 1472, 1227, 1134, 1013, 937, 768. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_4^+$ [M + H] $^+$: 292.1543; found: 292.1545.

2-methoxy-3-pentylisoquinolin-1(2H)-one (3ag): Purification by column chromatography on silica gel (PE: EA = 4:1), colorless oil (8.8 mg, 36% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.33 (dd, *J* = 8.2, 2.7 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.42 – 7.30 (m, 2H), 6.19 (s, 1H), 4.05 (s, 3H), 2.64 (td, *J* = 7.8, 2.7 Hz, 2H), 1.72 – 1.61 (m, 2H), 1.39 – 1.29 (m, 4H), 0.91 – 0.83 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 143.0, 135.8, 132.0, 127.3, 125.6, 125.3, 103.2, 63.6, 31.2, 30.4, 27.7, 22.2, 13.8. **IR (KBr, ν / cm^{-1})** 2945, 2742, 1620, 1606, 1484, 1403, 1248, 1157, 1243, 995, 823. **HRMS (ESI, m/z):** calcd for $C_{15}H_{20}NO_2^+$ [M + H] $^+$: 246.1489; found: 246.1492.

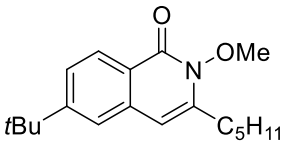


2-methoxy-6-methyl-3-pentylisoquinolin-1(2H)-one (3ah): Purification by column chromatography on silica gel (PE: EA = 4:1), colorless oil (13.8 mg, 53% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.19 (s, 1H), 4.08 (s, 3H), 2.73 – 2.67 (m, 2H), 2.46 (s, 3H), 1.76 – 1.68 (m, 2H), 1.43 – 1.36 (m, 4H), 0.96 – 0.90 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.0, 149.9, 143.2, 142.8, 136.2, 127.5, 125.2, 123.6, 103.2, 63.8, 31.4, 30.7, 27.9, 22.4, 21.8, 14.0. **IR (KBr, ν / cm^{-1})** 2965, 2939, 1664, 1602, 1563, 1453, 1340, 1131, 982, 772. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_2^+$ [M + H] $^+$: 260.1645; found: 260.1644.

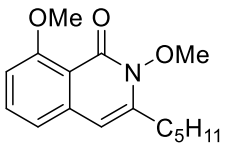


2-methoxy-7-methyl-3-pentylisoquinolin-1(2H)-one (3ai): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), colorless oil (12.2 mg, 47% yield) 

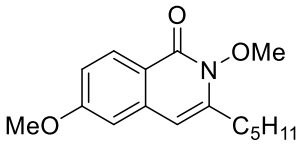
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 6.22 (s, 1H), 4.07 (s, 3H), 2.72 – 2.65 (m, 2H), 2.46 (s, 3H), 1.76 – 1.66 (m, 2H), 1.44 – 1.32 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 142.1, 135.8, 133.7, 133.7, 127.0, 125.7, 125.4, 103.3, 63.7, 31.4, 30.5, 27.9, 22.4, 21.3, 13.9. **IR (KBr, ν / cm^{-1})** 2978, 2947, 1668, 1602, 1463, 1366, 1150, 984, 840. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_2^+$ [M + H] $^+$: 260.1645; found: 260.1640.

6-(tert-butyl)-2-methoxy-3-pentylisoquinolin-1(2H)-one (3aj): Purification by column chromatography on silica gel (PE: EA = 5:1), colorless oil (18.3 mg, 61% yield) 

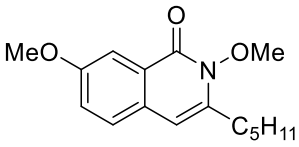
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 1H), 7.49 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 6.26 (s, 1H), 4.07 (s, 3H), 2.75 – 2.67 (m, 2H), 1.79 – 1.68 (m, 2H), 1.44 – 1.38 (m, 4H), 1.37 (s, 9H), 0.93 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 155.8, 143.0, 136.0, 127.3, 124.1, 123.5, 121.4, 103.8, 63.8, 35.1, 31.4, 31.1, 30.6, 27.9, 22.4, 14.0. **IR (KBr, ν / cm^{-1})** 2931, 2871, 1666, 1602, 1584, 1453, 1240, 1133, 1058, 838. **HRMS (ESI, m/z):** calcd for $C_{19}H_{28}NO_2^+$ [M + H] $^+$: 302.2115; found: 302.2121.

2,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3ak): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), colorless oil (14.9 mg, 54% yield) 

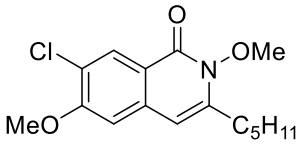
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.13 (s, 1H), 4.06 (s, 3H), 3.98 (s, 3H), 2.70 – 2.63 (m, 2H), 1.73 – 1.68 (m, 2H), 1.43 – 1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**δ 160.8, 157.6, 143.9, 139.0, 132.8, 117.8, 115.2, 107.1, 102.7, 63.6, 56.2, 31.4, 30.5, 27.6, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2931, 2860, 1669, 1602, 1564, 1453, 1404, 1151, 1091, 838. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_3^+$ [M + H] $^+$: 276.1594; found: 276.1590.

2,6-dimethoxy-3-pentylisoquinolin-1(2H)-one (3al): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), colorless oil (18.4 mg, 67% yield) 

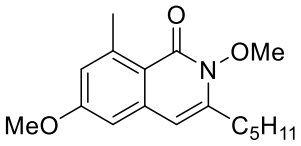
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.16 (s, 1H), 4.06 (s, 3H), 3.87 (s, 3H), 2.71 – 2.65 (m, 2H), 1.74 – 1.65 (m, 2H), 1.42 – 1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.7, 158.7, 143.7, 138.0, 129.5, 119.6, 115.5, 106.1, 103.0, 63.8, 55.4, 31.4, 30.6, 27.8, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2942, 2873, 1670, 1619, 1484, 1423, 1250, 1114, 1041, 982, 845. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_3^+$ [M + H] $^+$: 276.1594; found: 276.1596.

2,7-dimethoxy-3-pentylisoquinolin-1(2H)-one (3am): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), colorless oil (17.3 mg, 63% yield) 

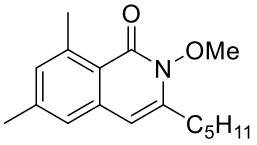
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.6 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.22 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.22 (s, 1H), 4.08 (s, 3H), 3.91 (s, 3H), 2.73 – 2.66 (m, 2H), 1.78 – 1.66 (m, 2H), 1.44 – 1.33 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$))** δ 158.6, 158.0, 140.6, 130.2, 127.1, 126.9, 123.1, 107.0, 103.2, 63.7, 55.6, 31.4, 30.5, 27.9, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2939, 2238, 1664, 1605, 1564, 1453, 1399, 1152, 1052, 915. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}NO_3^+$ [M + H] $^+$: 276.1594; found: 276.1596.

7-chloro-2,6-dimethoxy-3-pentylisoquinolin-1(2H)-one (3ao): Purification by column chromatography on silica gel (PE: EA = 3:1), colorless oil (6.8 mg, 22% yield) 

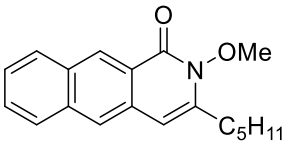
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 6.80 (s, 1H), 6.15 (s, 1H), 4.05 (s, 3H), 3.95 (s, 3H), 2.71 – 2.62 (m, 2H), 1.75 – 1.65 (m, 2H), 1.44 – 1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9, 157.7, 144.2, 136.5, 129.0, 122.1, 119.8, 105.9 102.5, 63.8, 56.2, 31.3, 30.5, 27.7, 22.4, 13.9. **IR (KBr, ν / cm^{-1})** 2961, 2875, 1663, 1607, 1485, 1443, 1235, 1158, 944, 833. **HRMS (ESI, m/z):** calcd for $C_{16}H_{21}ClNO_3^+$ [M + H] $^+$: 310.1204; found: 310.1205.

2,6-dimethoxy-8-methyl-3-pentylisoquinolin-1(2H)-one (3ap): Purification by column chromatography on silica gel (PE: EA = 3:1), colorless oil (21.3 mg, 74% yield) 

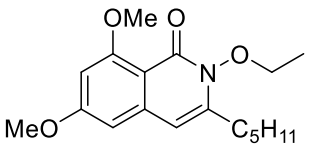
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 6.72 (s, 1H), 6.17 (s, 1H), 4.06 (s, 3H), 3.90 (s, 3H), 2.72 – 2.65 (m, 2H), 2.30 (s, 3H), 1.73 – 1.67 (m, 2H), 1.44 – 1.35 (m, 4H), 0.96 – 0.89 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.5, 158.7, 142.7, 136.3, 129.0, 126.9, 119.1, 103.8, 103.0, 63.8, 55.5, 31.4, 30.6, 27.9, 22.4, 16.3, 14.0. **IR (KBr, ν / cm^{-1})** 2923, 2852, 1668, 1612, 1463, 1346, 1155, 1021, 985. **HRMS (ESI, m/z):** calcd for $C_{17}H_{24}NO_3^+$ [M + H]$^+$: 290.1751; found: 290.1750.

2-methoxy-6,8-dimethyl-3-pentylisoquinolin-1(2H)-one (3aq): Purification by column chromatography on silica gel (PE: EA = 5:1 to 3:1), colorless oil (18.0 mg, 66% yield) 

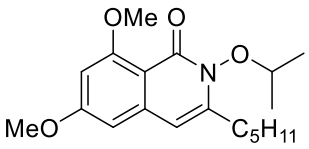
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.95 (s, 1H), 6.07 (s, 1H), 4.03 (s, 3H), 2.87 (s, 3H), 2.67 – 2.61 (m, 2H), 2.35 (s, 3H), 1.73 – 1.63 (m, 2H), 1.40 – 1.32 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 142.8, 141.7, 141.5, 137.8, 130.4, 123.6, 121.9, 103.3, 63.6, 31.4, 30.5, 27.8, 23.3, 22.4, 21.4, 14.0. **IR (KBr, ν / cm^{-1})** 2975, 2942, 1665, 1610, 1563, 1455, 1408, 1213, 1192, 1080, 947. **HRMS (ESI, m/z):** calcd for $C_{17}H_{24}NO_2^+$ [M + H]$^+$: 274.1802; found: 274.1801.

2-methoxy-3-pentylbenzo[g]isoquinolin-1(2H)-one (3ar): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), white solid (19.7 mg, 67% yield) 

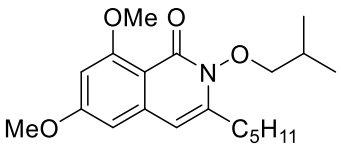
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.74 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 7.59 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 6.40 (s, 1H), 4.17 (s, 3H), 2.85 – 2.78 (m, 2H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.48 – 1.37 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 137.6, 133.7, 132.0, 131.7, 128.4, 128.2, 126.9, 126.1, 125.0, 124.3, 118.8, 103.9, 63.8, 31.5, 30.7, 27.8, 22.4, 14.0. **IR (KBr, ν / cm^{-1})** 2968, 2865, 1689, 1605, 1446, 1248, 1231, 1134, 1049, 862, 736. **HRMS (ESI, m/z):** calcd for $C_{19}H_{22}NO_2^+$ [M + H]$^+$: 296.1645; found: 296.1643.

2-ethoxy-6,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3ba): Purification by column chromatography on silica gel (PE: EA = 4:1 to 2:1), white solid (28.1 mg, 88% yield) 

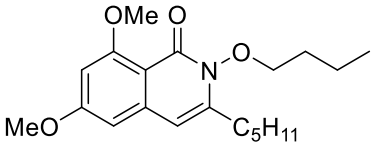
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 – 6.32 (m, 2H), 6.02 (s, 1H), 4.27 (q, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.42 – 1.32 (m, 7H), 0.94 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.0, 162.3, 157.4, 144.5, 140.5, 109.8, 102.3, 98.4, 97.4, 71.5, 56.1, 55.3, 31.4, 30.6, 27.6, 22.4, 13.9, 13.2. **IR (KBr, ν / cm^{-1})** 2944, 2861, 1622, 1615, 1485, 1461, 1342, 1156, 909, 855. **HRMS (ESI, m/z):** calcd for $C_{18}H_{26}NO_4^+$ [M + H] $^+$: 320.1856; found: 320.1854.

2-isopropoxy-6,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3bb): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), white solid (18.6 mg, 56% yield) 

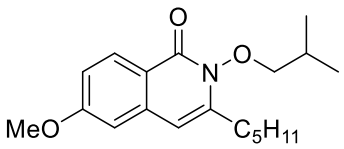
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 – 6.33 (m, 2H), 6.02 (s, 1H), 5.04 – 4.94 (m, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 2.66 – 2.59 (m, 2H), 1.64 (p, *J* = 6.7, 6.1 Hz, 2H), 1.38 – 1.31 (m, 4H), 1.25 (d, *J* = 6.3 Hz, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 162.2, 157.9, 145.7, 140.5, 109.8, 102.1, 98.3, 97.3, 76.7, 56.1, 55.3, 31.4, 31.1, 27.4, 22.3, 20.4, 13.9. **IR (KBr, ν / cm^{-1})** 2946, 2864, 1660, 1623, 1568, 1485, 1247, 1190, 987, 844. **HRMS (ESI, m/z):** calcd for $C_{19}H_{28}NO_4^+$ [M + H] $^+$: 334.2013; found: 334.2014.

2-isobutoxy-6,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3bc): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), white solid (32.0 mg, 92% yield) 

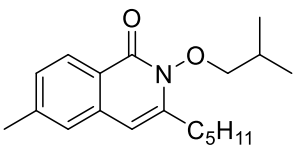
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 6.34 (s, 1H), 6.03 (s, 1H), 4.01 (d, *J* = 6.4 Hz, 2H), 3.93 (s, 3H), 3.85 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.10 (m, 1H), 1.70 (p, *J* = 7.1, 6.7 Hz, 2H), 1.37 (s, 4H), 1.05 (d, *J* = 6.7 Hz, 6H), 0.94 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 162.4, 157.4, 144.6, 140.5, 109.9, 102.4, 98.4, 97.3, 81.3, 56.1, 55.3, 31.4, 30.7, 27.8, 27.6, 22.4, 19.2, 14.0. **IR (KBr, ν / cm^{-1})** 2931, 2867, 1664, 1615, 1568, 1455, 1409, 1256, 1134, 1093, 839. **HRMS (ESI, m/z):** calcd for $C_{20}H_{30}NO_4^+$ [M + H] $^+$: 348.2169; found: 348.2170.

2-butoxy-6,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3bd): Purification by column chromatography on silica gel (PE: EA = 5:1 to 4:1), white solid (28.1 mg, 81% yield) 

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 – 6.34 (m, 1H), 6.34 – 6.32 (m, 1H), 6.02 (s, 1H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.91 (s, 3H), 3.83 (s, 3H), 2.64 – 2.58 (m, 2H), 1.75 (p, *J* = 6.8 Hz, 2H), 1.67 (q, *J* = 7.1 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 1.40 – 1.33 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 162.3, 157.3, 144.5, 140.5, 109.8, 102.3, 98.4, 97.3, 75.5, 56.1, 55.3, 31.4, 30.6, 30.1, 27.6, 22.3, 19.1, 13.9. **IR (KBr, ν / cm^{-1})** 2926, 2868, 1654, 1628, 1562, 1472, 1443, 1246, 1166, 982. **HRMS (ESI, m/z):** calcd for $C_{20}H_{30}NO_4^+$ [M + H] $^+$: 348.2169; found: 348.2166.

2-isobutoxy-6-methoxy-3-pentylisoquinolin-1(2H)-one (3bf): Purification by column chromatography on silica gel (PE: EA = 4:1 to 3:1), brown oil (23.7 mg, 75% yield) 

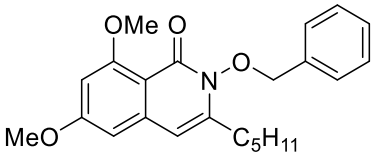
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.14 (s, 1H), 4.00 (d, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 2.69 – 2.61 (m, 2H), 2.19 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.76 – 1.65 (m, 2H), 1.42 – 1.30 (m, 4H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.94 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.6, 158.8, 144. 0, 138.0, 129.4, 119.6, 115. 4, 106.0, 102.9, 81.7, 55.3, 31.4, 30.9, 28.0, 27.6, 22.4, 19.1, 13.9. **IR (KBr, ν / cm^{-1})** 2955, 2861, 1664, 1614, 1500, 1463, 1343, 1153, 989, 836. **HRMS (ESI, m/z):** calcd for $C_{19}H_{28}NO_3^+$ [M + H] $^+$: 318.2064; found: 318.2065.

2-isobutoxy-6-methyl-3-pentylisoquinolin-1(2H)-one (3bg): Purification by column chromatography on silica gel (PE: EA = 5:1 to 4:1), yellow oil (18.6 mg, 62% yield) 

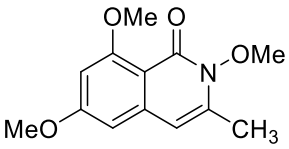
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.23 (m, 1H), 7.24 – 7.19 (m, 2H), 6.17 (s, 1H), 4.02 (d, *J* = 6.6 Hz, 2H), 2.71 – 2.64 (m, 2H), 2.44 (s, 3H), 2.20 (m, 1H), 1.77 – 1.67 (m, 2H), 1.41 – 1.33 (m, 4H), 1.08 (d, *J* = 6.7 Hz, 6H), 0.95 – 0.88 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1, 143.4, 142.5, 136.1, 127.4, 127.4, 125.1, 123.6, 103.1, 81.7, 31.4, 30.9, 28.0, 27.6, 22.4, 21.7, 19.2,

14.0. **IR (KBr, ν / cm^{-1})** 2933, 2860, 1672, 1616, 1521, 1265, 1246, 1127, 1030, 870. **HRMS (ESI, m/z):** calcd for $C_{19}H_{28}NO_2^+$ [M + H]$^+$: 302.2115; found: 302.2112.

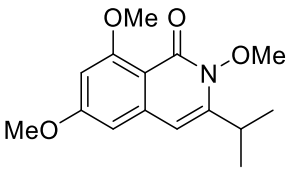
2-(benzyloxy)-6,8-dimethoxy-3-pentylisoquinolin-1(2H)-one (3bh): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), white solid (17.9 mg, 47% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 – 7.52 (m, 2H), 7.42 – 7.35 (m, 3H), 6.40 (dd, *J* = 16.8, 2.3 Hz, 2H), 6.04 (s, 1H), 5.25 (s, 2H), 3.98 (s, 3H), 3.87 (s, 3H), 2.63 – 2.55 (m, 2H), 1.65 (s, 2H), 1.34 – 1.29 (m, 4H), 0.89 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.1, 162.4, 157.6, 144.8, 140.7, 134.6, 129.7, 128.9, 128.5, 109.9, 102.4, 98.6, 97.4, 77.5, 56. 2, 55.4, 31.4, 30.7, 27.5, 22.3, 13.9. **IR (KBr, ν / cm^{-1})** 2923, 2854, 1666, 1627, 1564, 1462, 1408, 1155, 1032, 874, 732. **HRMS (ESI, m/z):** calcd for $C_{23}H_{28}NO_4^+$ [M + H]$^+$: 382.2013; found: 382.2010.



2,6,8-trimethoxy-3-methylisoquinolin-1(2H)-one (3ca): Purification by column chromatography on silica gel (PE: EA = 2:1), white solid (21.1 mg, 85% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.38 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 2.3 Hz, 1H), 6.05 (s, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.86 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.1, 162.4, 157.3, 140.6, 140.3, 109.9, 103.4, 98.4, 97.4, 63.6, 56.2, 55.4, 17.2. **IR (KBr, ν / cm^{-1})** 2931, 2843, 1665, 1643, 1524, 1457, 1406, 1371, 1248, 957. **HRMS (ESI, m/z):** calcd for $C_{13}H_{16}NO_4^+$ [M + H]$^+$: 250.1074; found: 250.1075.

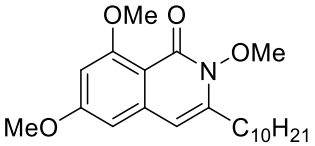


3-isopropyl-2,6,8-trimethoxyisoquinolin-1(2H)-one (3cb): Purification by column chromatography on silica gel (PE: EA = 1:1 to 1:2), white solid (22.7 mg, 82% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.39 (s, 2H), 6.07 (s, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.86 (s, 3H), 3.13 (hept, *J* = 6.9 Hz, 1H), 1.30 (s, 3H), 1.29 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.1, 162.3, 157.3, 149.9, 140.6, 109.8, 100.0, 98.8, 97.6, 63.9, 56.2, 55.4,

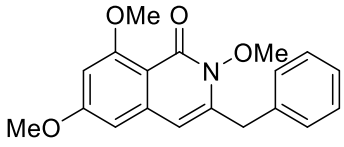


28.3, 22.0. **IR (KBr, ν / cm^{-1})** 2941, 2856, 1673, 1625, 1598, 1486, 1410, 1365, 1249, 1167, 909. **HRMS (ESI, m/z):** calcd for $C_{15}H_{20}NO_4^+$ [M + H] $^+$: 278.1387; found: 278.1391.

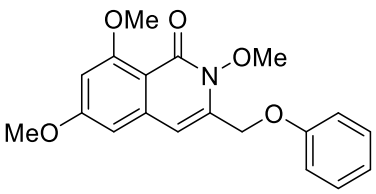
3-decyl-2,6,8-trimethoxyisoquinolin-1(2H)-one (3cc): Purification by column chromatography on silica gel (PE: EA = 2:1 to 1:1), white solid (30.0 mg, 80% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.36 (d, *J* = 2.1 Hz, 1H), 6.34 (d, *J* = 2.1 Hz, 1H), 6.02 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 2.65 – 2.58 (m, 2H), 1.65 (q, *J* = 7.4 Hz, 2H), 1.40 – 1.22 (m, 14H), 0.85 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.0, 162.2, 157.3, 144.2, 140.5, 109.7, 102.5, 98.5, 97.3, 63.6, 56.1, 55.3, 31.8, 30.4, 29.5, 29.4, 29.3, 29.2, 29.2, 27.9, 22.6, 14.0. **IR (KBr, ν / cm^{-1})** 2948, 2858, 1667, 1625, 1485, 1423, 1346, 1257, 1167, 987, 826. **HRMS (ESI, m/z):** calcd for $C_{22}H_{34}NO_4^+$ [M + H] $^+$: 376.2482; found: 376.2481.



3-benzyl-2,6,8-trimethoxyisoquinolin-1(2H)-one (3cd): Purification by column chromatography on silica gel (PE: EA = 1:1 to 1:2), white solid (24.3 mg, 75% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 6.40 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 2.3 Hz, 1H), 5.91 (s, 1H), 4.02 (s, 2H), 3.94 (s, 3H), 3.84 (s, 3H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.1, 162.3, 157.4, 143.1, 140.3, 136.7, 129.2, 128.7, 127.0, 109.9, 104.3, 98.8, 97.8, 63.8, 56.2, 55.4, 36.8. **IR (KBr, ν / cm^{-1})** 2985, 2875, 1665, 1612, 1548, 1446, 1408, 1367, 1265, 1087, 934, 778. **HRMS (ESI, m/z):** calcd for $C_{19}H_{20}NO_4^+$ [M + H] $^+$: 326.1387; found: 326.1383.

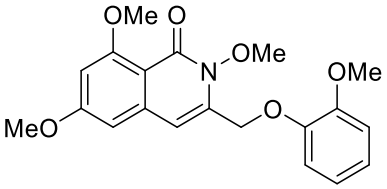


2,6,8-trimethoxy-3-(phenoxymethyl)isoquinolin-1(2H)-one (3ce): Purification by column chromatography on silica gel (PE: EA = 1:1 to 1:3), white solid (24.6 mg, 72% yield) **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.30 (m, 2H), 7.06 – 6.99 (m, 3H), 6.48 – 6.42 (m, 2H), 6.40 (s, 1H), 5.07 (s, 2H), 4.14 (s, 3H), 3.97 (s, 3H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.3, 162.4, 158.0, 152.9, 140.0, 138.7 129.7, 121.7, 114.8, 110.5, 103.9, 99.6, 98.4, 64.5, 64.4, 56.3, 55.5 **IR (KBr, ν / cm^{-1})** 2953, 2875, 1670,

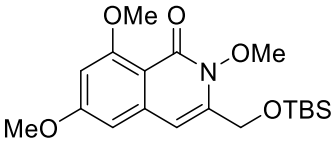


1617, 1584, 1483, 1440, 1264, 1141, 917. **HRMS (ESI, m/z):** calcd for $C_{19}H_{20}NO_5^+$ [M + H]$^+$: 342.1336; found: 342.1343.

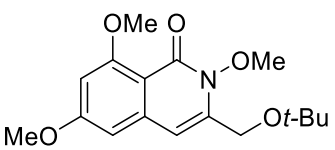
2,6,8-trimethoxy-3-((2-methoxyphenoxy)methyl)isoquinolin-1(2H)-one (3cf): Purification by column chromatography on silica gel (PE: EA = 1:1 to 1:2), white solid (22.6 mg, 61% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.01 – 6.91 (m, 4H), 6.47 – 6.41 (m, 2H), 6.41 (s, 1H), 5.12 (s, 2H), 4.15 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 162.4, 157.2, 149.9, 147.5, 140.1, 138.7, 122.5, 120.9, 114.7, 112.1, 110.5, 104.0, 99.6, 98.3, 65.9, 64.3, 56.3, 55.9, 55.4. **IR (KBr, ν / cm^{-1})** 2956, 2942, 1670, 1635, 1583, 1467, 1345, 1247, 1173, 1017, 947. **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_6^+$ [M + H]$^+$: 372.1442; found: 372.1441.



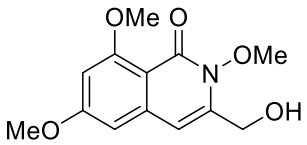
3-(((tert-butyldimethylsilyl)oxy)methyl)-2,6,8-trimethoxyisoquinolin-1(2H)-one (3cg): Purification by column chromatography on silica gel (PE: EA = 1:1), colorless oil (23.4 mg, 62% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.42 (s, 2H), 6.32 (s, 1H), 4.71 (s, 2H), 4.06 (s, 3H), 3.95 (s, 3H), 3.88 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 162.3 157.2, 142.7, 140.5, 110.0, 101.5, 99.3, 97.8, 64.0, 59.5, 56.2, 55.4, 25.9, 18.4, -5.4. **IR (KBr, ν / cm^{-1})** 2956, 2894, 1677, 1634, 1494, 1447, 1362, 1179, 1048, 993. **HRMS (ESI, m/z):** calcd for $C_{19}H_{29}NNaO_5Si^+$ [M + Na]$^+$: 402.1707; found: 402.1711.



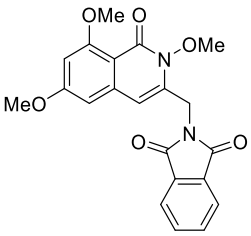
3-(tert-butoxymethyl)-2,6,8-trimethoxyisoquinolin-1(2H)-one (3ch): Purification by column chromatography on silica gel (PE: EA = 1:2), white solid (23.7 mg, 74% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.41 – 6.38 (m, 2H), 6.32 (s, 1H), 4.41 (s, 2H), 4.07 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 1.29 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)**δ 163.0, 162.2, 157.2, 141.4, 140.4, 110.1, 102.9, 99.2, 97.8, 74.3, 64.1, 58.6, 56.1, 55.3, 27.4. **IR (KBr, ν / cm^{-1})** 2936, 2892, 1664, 1621, 1567, 1466, 1407, 1348, 1132, 1047, 893. **HRMS (ESI, m/z):** calcd for $C_{17}H_{24}NO_5^+$ [M +H]$^+$: 322.1649; found: 322.1652.



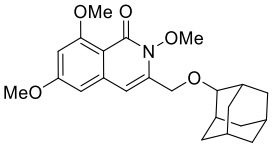
3-(hydroxymethyl)-2,6,8-trimethoxyisoquinolin-1(2H)-one (3ci): Purification by column chromatography on silica gel (PE: EA = 1:1 to EA) yellow oil (12.1 mg, 46% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.39 (d, *J* = 2.2 Hz, 1H), 6.30 (d, *J* = 2.2 Hz, 1H), 6.28 (s, 1H), 4.65 (s, 2H), 4.05 (s, 3H), 3.93 (s, 3H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 162.2, 157.3, 142.3, 140.3, 109.9, 102.7, 99.3, 98.0, 64.2, 59.7, 56.1, 55.4. **IR (KBr, ν / cm^{-1})** 3648, 2937, 2884, 1664, 1609, 1536, 1447, 1246, 1152, 1013, 924, 821. **HRMS (ESI, m/z):** calcd for $C_{13}H_{16}NO_5^+$ [M +H] $^+$: 266.1023; found: 266.1023.



2-((2,6,8-trimethoxy-1-oxo-1,2-dihydroisoquinolin-3-yl)methyl)isoindoline-1,3-dione (3cl): Purification by column chromatography on silica gel (EA only), white solid (25.2 mg, 64% yield), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.35 (d, *J* = 2.3 Hz, 1H), 6.10 (s, 1H), 4.91 (s, 2H), 4.16 (s, 3H), 3.94 (s, 3H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.5, 163.3, 162.4, 157.1, 139.8, 137.1, 134.4, 131.9, 123.7, 110.3, 103.5, 99.4, 98.4, 64.2, 56.3, 55.4, 36.9. **IR (KBr, ν / cm^{-1})** 2946, 2865, 1720, 1686, 1603, 1562, 1456, 1440, 1345, 1267, 1143, 920, 768. **HRMS (ESI, m/z):** calcd for $C_{21}H_{19}N_2O_6^+$ [M +H] $^+$: 395.1238; found: 395.1237.

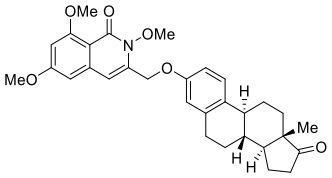


3-((((1R,3S,5r,7r)-adamantan-2-yl)oxy)methyl)-2,6,8-trimethoxyisoquinolin-1(2H)-one (3cm): Purification by column chromatography on silica gel (PE: EA = 1:1 to 1:3), colorless oil (26.7 mg, 67% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.44 (d, *J* = 2.2 Hz, 1H), 6.42 (d, *J* = 2.2 Hz, 1H), 6.37 (s, 1H), 4.53 (s, 2H), 4.09 (s, 3H), 3.95 (s, 3H), 3.88 (s, 3H), 3.63 (t, *J* = 2.3 Hz, 1H), 2.16 – 2.09 (m, 4H), 1.91 – 1.81 (m, 4H), 1.75 – 1.66 (m, 4H), 1.57 – 1.50 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 162.3, 157.3 141.1, 140.4, 110.2, 102.7, 99.2, 97.9, 82.4, 64.1, 63.8, 56.2, 55.4, 37.4, 36.4, 31.8, 31.6, 27.3, 27.3. **IR (KBr,**



ν / cm^{-1}) 2964, 2952, 2872, 1672, 1618, 1560, 1453, 1240, 1145, 1041, 799. **HRMS (ESI, m/z):** calcd for $C_{23}H_{30}NO_5^+$ [M +H] $^+$: 400.2118; found: 400.2123.

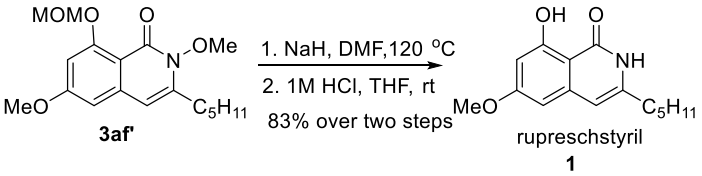
2,6,8-trimethoxy-3-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)isoquinolin-1(2H)-one (3cn):



Purification by column chromatography on silica gel (PE: EA = 1:1 to EA), white solid (30.0 mg, 58% yield) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 (s, 1H), 6.82 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 6.48 – 6.43 (m, 2H), 6.40 (s, 1H), 5.03 (s, 2H), 4.14 (s, 3H), 3.97 (s, 3H), 3.87 (s, 3H), 2.92 (dd, *J* = 9.6, 4.8 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.32 – 2.22 (m, 1H), 2.20 – 2.11 (m, 1H), 2.06 – 1.93 (m, 3H), 1.61 – 1.58 (m, 1H), 1.58 – 1.41 (m, 5H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.3, 162.4, 157.2, 156.1, 140.1, 138.8, 138.1, 133.2, 126.6, 114.8, 112.4, 110.5, 103.9, 99.6, 98.4, 77.2, 64.6, 64.4, 56.3, 55.5, 50.4, 48.0 44.0, 38.3, 35.9, 31.6, 29.7, 26.5, 25.9, 21.6, 13.8. **IR (KBr, ν / cm^{-1})** 2960, 2856, 1718, 1669, 1623, 1537, 1448, 1426, 1345, 1154, 1033, 923, 764. **HRMS (ESI, m/z):** calcd for $C_{31}H_{36}NO_6^+$ [M +H] $^+$: 518.2537; found: 518.2544.

Rupreschstyril (1)

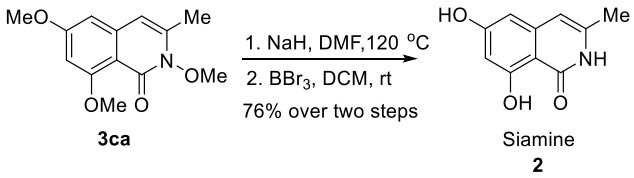
To a suspension of NaH (60% in mineral oil, 10.8 mg, 0.27 mmol) in dry DMF (1 mL) was added a solution of crude **3af'** (30.0 mg, 0.09 mmol) in dry DMF (1 mL) and stirred for 30 min at 120°C, after cooling to rt, the mixture was dilution with Et_2O, washed with saturated aq NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to leave the residue, which was used directly in the next step. To the residue was added 1 mL 1M HCl and1 mL of THF, the resulting mixture was stirred at RT for 1 h. Then the mixture was diluted with water and extracted three times with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (PE: EA = 3:1) gave 19.5 mg (83% over two steps) of Rupreschstyril (1) as brown crystals. Spectral data (NMR, MS) of the synthesized ruprechstyril are identical to those of the published data.



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (s, 1H), 10.28 (br, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 6.36 (d, *J* = 2.1 Hz, 1H), 6.22 (s, 1H), 3.84 (s, 3H), 2.52 (t, *J* = 9 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.40 – 1.31 (m, 4H), 0.89 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.0, 165.0, 162.9, 141.8, 141.2, 105.5, 105.2, 99.5, 99.0, 55.4, 33.3, 31.2, 28. 0, 22.4, 13.9. **HRMS (ESI, m/z):** calcd for $C_{15}H_{20}NO_3^+$ [M +H] $^+$: 262.1438; found: 262.1442.

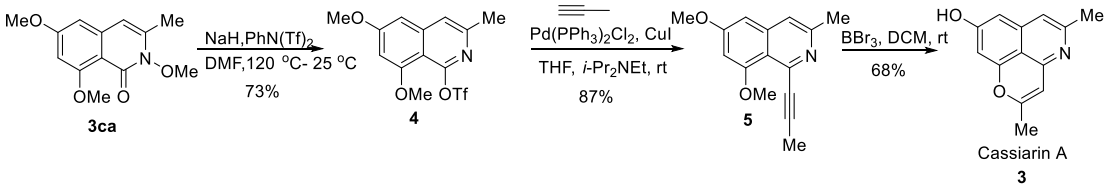
Siamine (2)

To a suspension of NaH (60% in mineral oil, 9.6 mg, 0.24 mmol) in dry DMF (1 mL) was added a solution of **3ca** (20.0 mg, 0.08 mmol) in dry DMF (1 mL) and stirred for 30 min at 120°C, after cooling to rt, the mixture was dilution with Et_2O, washed with saturated aq NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to leave the residue, which was used directly in the next step. To the residue was added 1 mL DCM and cooling to 0 °C, then the mixture was added dropwise 3eq BBr_3 (2mol/L solution in DCM). The resulting mixture was warm to rt and stirred for 24 h. the reaction was quenched with 1ml MeOH and concentrated under reduced pressure to leave the residue. Column chromatography with DCM–MeOH (20:1) as an eluent gave 11.5 mg (76% over two steps) of siamine (2)[1] as white crystals.



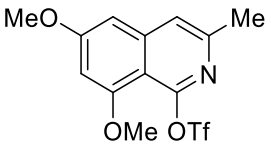
^{1}H NMR (400 MHz, methanol-d_4) δ 6.27 (d, *J* = 2.1 Hz, 1H), 6.20 (s, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR (101 MHz, methanol-d_4)** δ 166.4, 163.3, 162.8, 141.5, 137.5, 105.1, 103.7, 100.3, 99.6, 17.4. **HRMS (ESI, m/z):** calcd for $C_{10}H_9NO_3^+$ [M +H] $^+$: 191.0577; found: 191.0574.

Cassiarin A



6,8-dimethoxy-3-methylisoquinolin-1-yl trifluoromethanesulfonate (4):

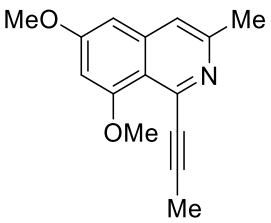
To a stirred solution of **3ca** (120 mg, 0.48 mmol) in dry DMF (5 mL) was added NaH (60% in mineral oil, 57.0 mg, 1.44 mmol)) at 0 °C. The reaction mixture was then warmed to 120 °C until the start material was completely consumed. The reaction mixture was then cooled to rt, and $PhN(Tf)_2$ (205.5 mg, 0.58 mmol) was added in one portion. The resulting mixture was stirred at rt for 14 h. After dilution with Et_2O, the mixture was washed with saturated aq NaCl, dried over Na_2SO_4, and concentrated. Purification of the crude product using column chromatography with PE–EtOAc (2:1) as an eluent provided 122 mg (73%) of the triflate **9** as white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 6.62 (d, *J* = 2.1 Hz, 1H), 6.53 (d, *J* = 2.1 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 2.54 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.7, 156.8, 150.5, 150.4, 144.2, 119.5, 117.1, 107.0, 100.2, 96.8, 55.7, 55.6, 23.2. **HRMS (ESI, m/z):** calcd for $C_{13}H_{13}F_3NO_5S^+$ $[M+H]^+$: 352.0461; found: 352.0457.

6,8-dimethoxy-3-methyl-1-(prop-1-yn-1-yl)isoquinoline (5):

1-Bromo-1-propene (102.5 mg, 0.85 mmol) was dissolved in 1.3 mL of THF. After cooling to –78 °C, to the solution was added *n*-BuLi (1.60 M in hexane, 0.64 mL, 1.02 mmol). The resulting mixture was stirred at –78 °C for 1 h. Water (15 μL, 0.85 mmol) was added, and the temperature was allowed to rise to 0 °C where the mixture was further stirred for 30 min. To the mixture was added a solution of triflate **9** (100.0 mg, 0.28 mmol) in THF (0.5 mL), $Pd(PPh_3)_2Cl_2$ (14.2 mg, 0.02 mmol), CuI (9.5 mg, 0.05 mmol), and *i*-Pr_2NH (0.5 mL). The resulting mixture was stirred at rt for 20 h. The reaction was quenched by addition of saturated aq NH_4Cl solution. After separation, the water layer was extracted three times with Et_2O. The combined organic layers were dried and concentrated.



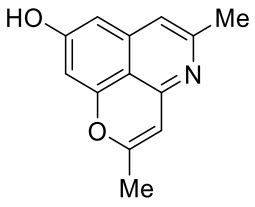
Purification of the crude product by column chromatography with PE–EtOAc (1:1) as an eluent provided 67 mg (87%) of the alkyne **10** as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.52 (d, *J* = 2.2 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 2.59 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3, 158.0, 152.3, 140.7, 140.0, 117.7, 116.1, 98.9, 96.6, 89.1, 81.6, 55.8, 55.4, 24.1, 5.0. **HRMS (ESI, m/z):** calcd for $C_{15}H_{16}NO_2^+$ [M +H] $^+$: 242.1176; found: 242.1172.

Cassiarin A (3):

To a solution of alkyne **5** (50.0 mg, 0.20mmol) in 1 mL of DCM was added 3eq BBr_3 (0.31ml, 2mol/L solution in DCM). The resulting mixture was stirred at rt for 30 h until the start material was completely consumed. The reaction was quenched with 1ml MeOH and added 2 mL of aq 10% ammonia solution, and then the resulting mixture was vigorously stirred for 1 h. After evaporation of the solvents, the residue was extracted with DCM–MeOH (4:1). The extract was purified by column chromatography with DCM– MeOH (10:1) to give 28.9 mg (68%) of cassiarin A (**1**) as a yellow solid. Spectral data (NMR, MS) of the synthesized Cassiarin A are identical to those of the published data[2].

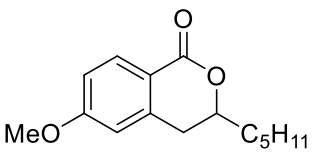
^{1}H NMR (400 MHz, $CDCl_3$: MeOD=1:1) δ 6.77 (s, 1H), 6.58 (s, 1H), 6.55 (s, 1H), 6.16 (s, 1H), 2.40 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$: MeOD=1:1)** δ 164.1, 161.7, 155.4, 149.2, 146.9, 137.8, 112.9, 110.2, 102.4, 101.8, 100.0, 21.1, 19.2. **HRMS (ESI, m/z):** calcd for $C13H_{12}NO_2^+$ [M +H] $^+$: 214.0863; found: 214.0862.



Cassiarin A
3

6-methoxy-3-pentylisochroman-1-one (3as):

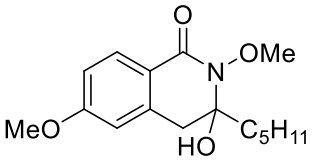
Purification by column chromatography on silica gel (PE: EA = 1.5 :1), colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.6 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 4.53 – 4.44 (m, 1H), 3.86 (s, 3H), 2.98 – 2.81 (m, 2H), 1.92 – 1.80 (m, 1H), 1.74 – 1.66 (m, 1H), 1.62 – 1.54 (m, 1H), 1.49 – 1.43 (m, 1H), 1.38 – 1.27 (m, 4H), 0.95 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ165.6, 163.7, 141.5, 132.5, 117.8, 113.3, 112.0, 78.4, 55.5, 34.9,



33.5, 31.5, 24.6, 22.5, 14.0. **HRMS (ESI, m/z):** calcd for $C_{15}H_{21}O_3^+$ [M + H]$^+$: 249.1485; found: 249.1474.

3-hydroxy-2,6-dimethoxy-3-pentyl-3,4-dihydroisoquinolin-1(2H)-one (3at):

Purification by column chromatography on silica gel (PE: EA = 2:1 to 1.5:1), white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.45 (s, 1H), 3.29 – 3.13 (m, 2H), 2.08 – 1.95 (m, 1H), 1.93 – 1.82 (m, 1H), 1.53 – 1.36 (m, 2H), 1.34 – 1.23 (m, 4H), 0.93 – 0.84 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.1, 163.0, 137.0, 130.3, 120.3, 112.9, 112.6, 91.1, 64.6, 55.4, 39.4, 37.9, 31.9, 23.7, 22.5, 13.9. **HRMS (ESI, m/z):** calcd for $C_{16}H_{23}NNaO_4^+$ [M + Na]$^+$: 316.1519; found: 316.1524.



3. Crystal Data and Structure Refinement for Compound 3ae

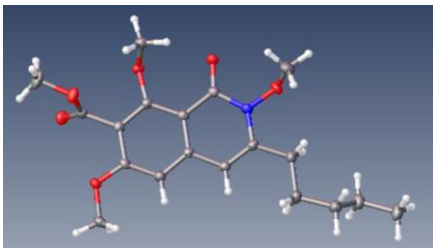
Experimental: Single crystals of $C_{19}H_{25}NO_6$ were obtained by recrystallization from mixed solvents of dichloromethane and ethanol. A suitable crystal was selected and carried out on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 296 K during data collection. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data:



Non-hydrogens atoms are shown as 30% ellipsoids.

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=10.210(4) b=13.109(4) c=14.900(5)

alpha=92.742(5) beta=92.289(6) gamma=110.147(5)

Temperature: 153 K

	Calculated	Reported
Volume	1866.7(11)	1866.6(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H25 N O6	?
Sum formula	C19 H25 N O6	C19 H25 N O6
Mr	363.40	363.40
Dx,g cm-3	1.293	1.293
Z	4	4
Mu (mm-1)	0.096	0.096
F000	776.0	776.0
F000'	776.43	
h,k,lmax	12,16,18	12,16,18
Nref	7839	7628
Tmin,Tmax	0.977,0.981	0.596,0.745
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.596 Tmax=0.745 AbsCorr = MULTI-SCAN

Data completeness= 0.973 Theta(max)= 26.617

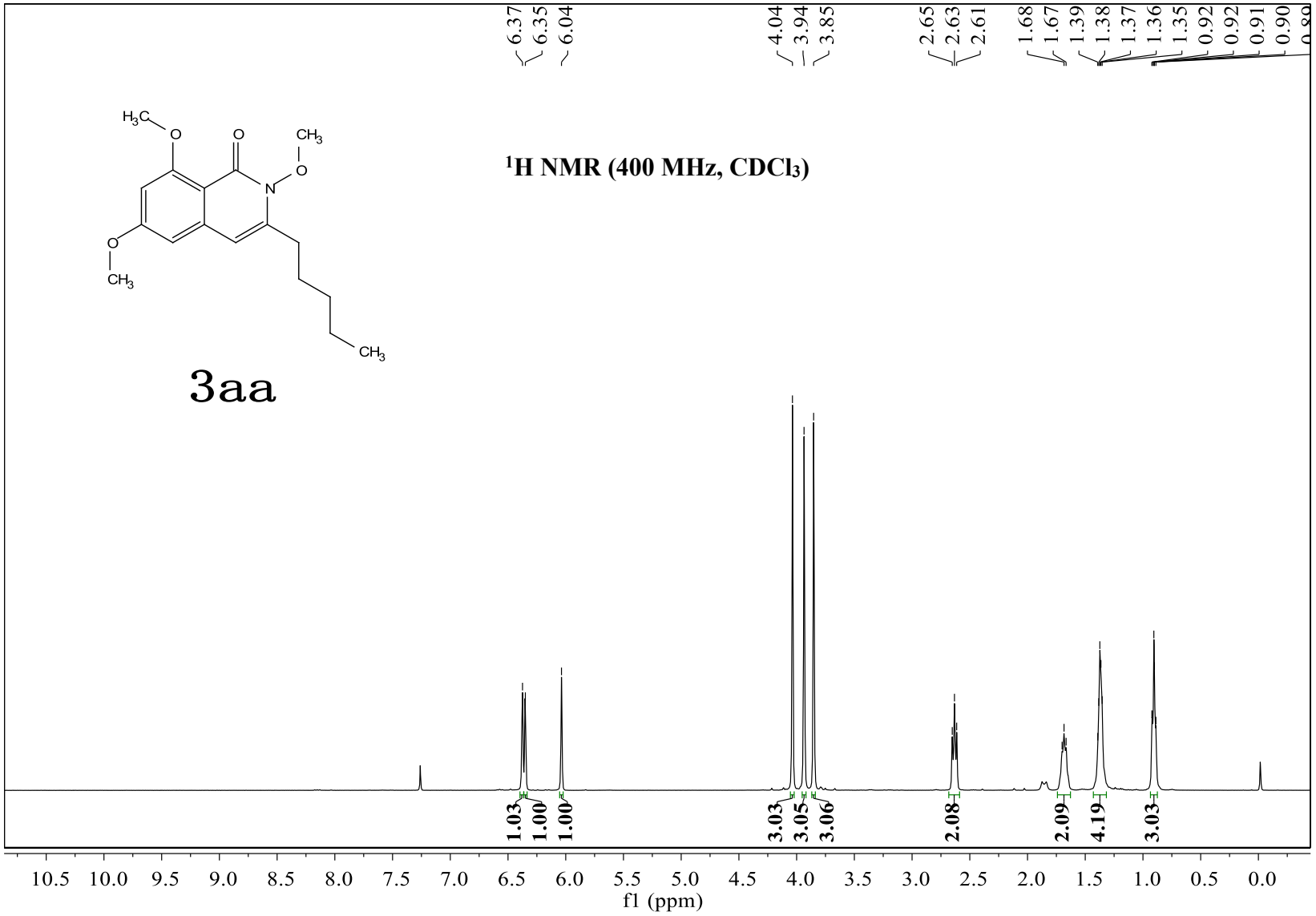
R(reflections)= 0.0719(4828) wR2(reflections)= 0.2345(7628)

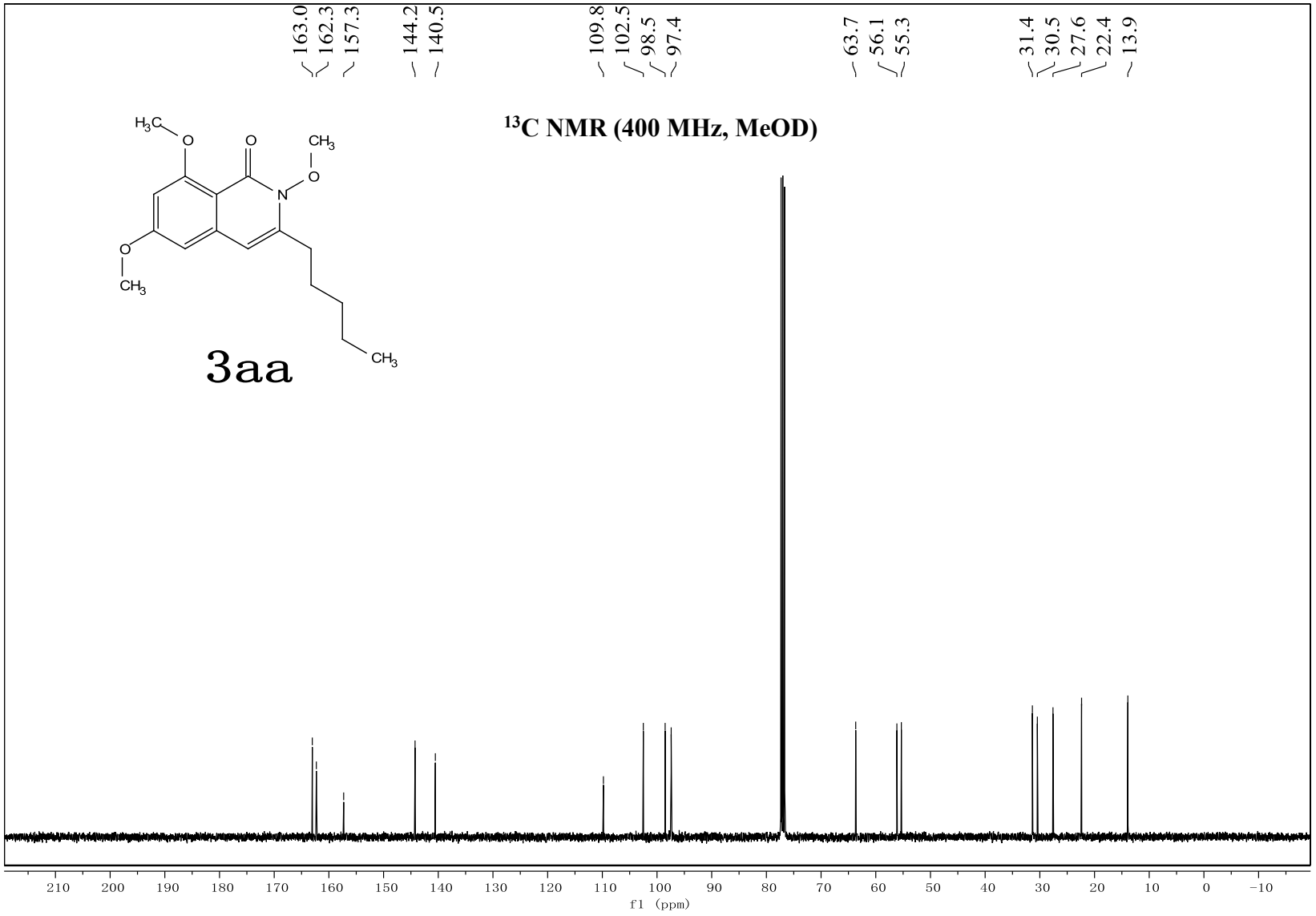
S = 1.000 Npar= 479

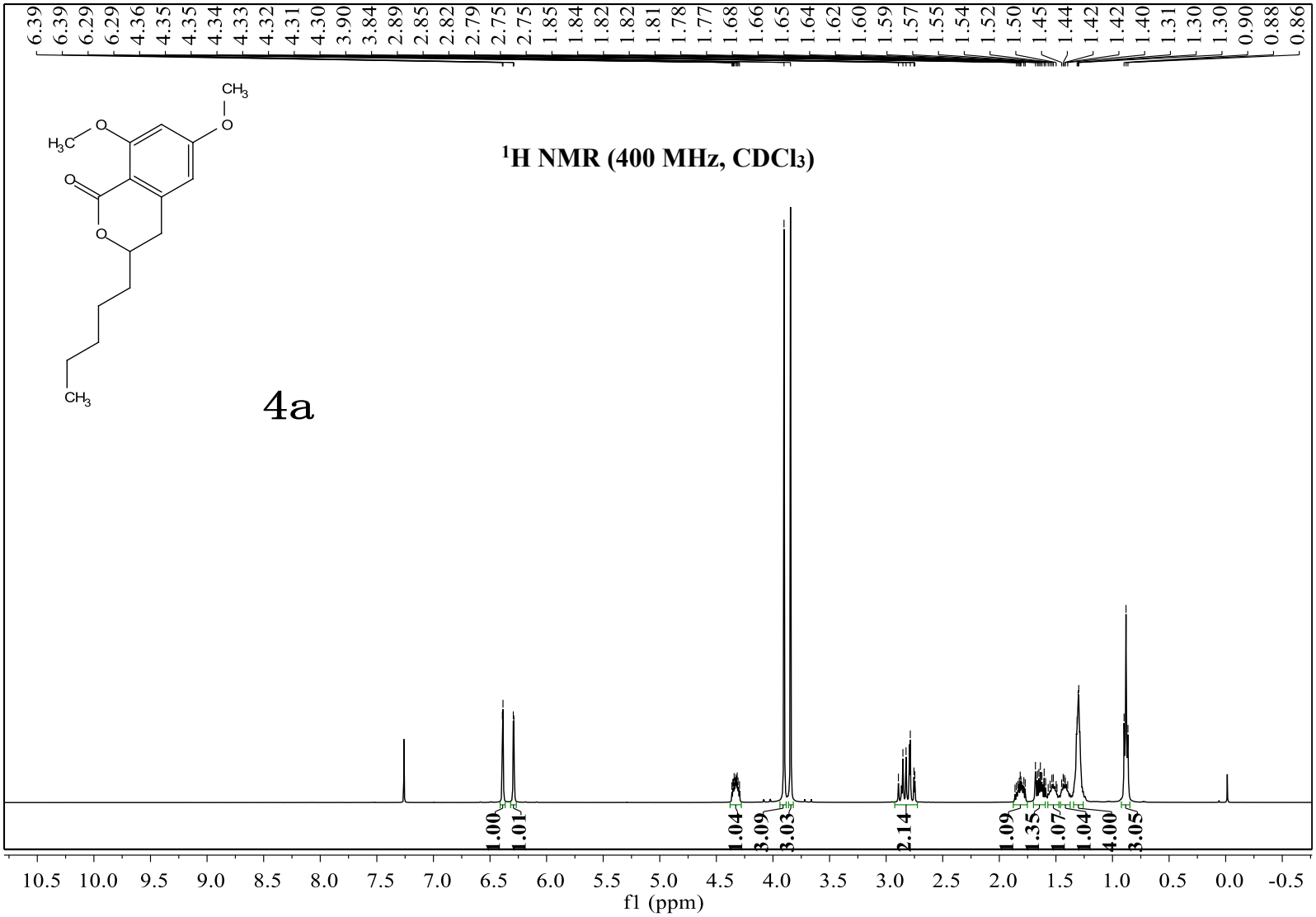
References:

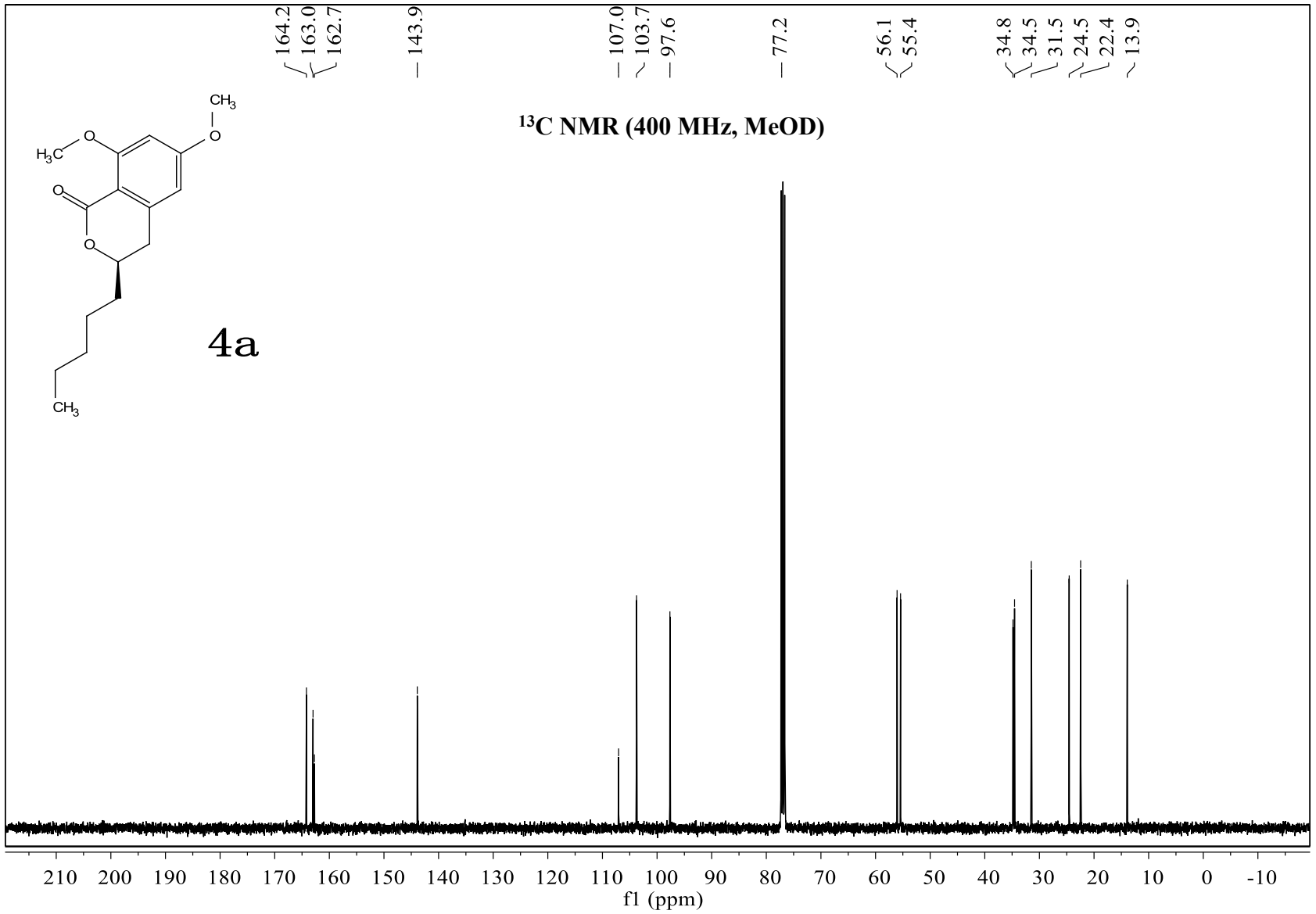
1. (a) B. Z. Ahn and F. Zymalowsky, *Tetrahedron Lett*., **1976**, 821. (b) B. D. Krane and M. Shamma, *J. Nat. Prod*., 1982, **45**, 377. (c) M. Kennedy, C. J. Moody, C. W. Rees, and J. J. Vaquero, *J. Chem. Soc*. Perkin I.,**1987**, 1395.

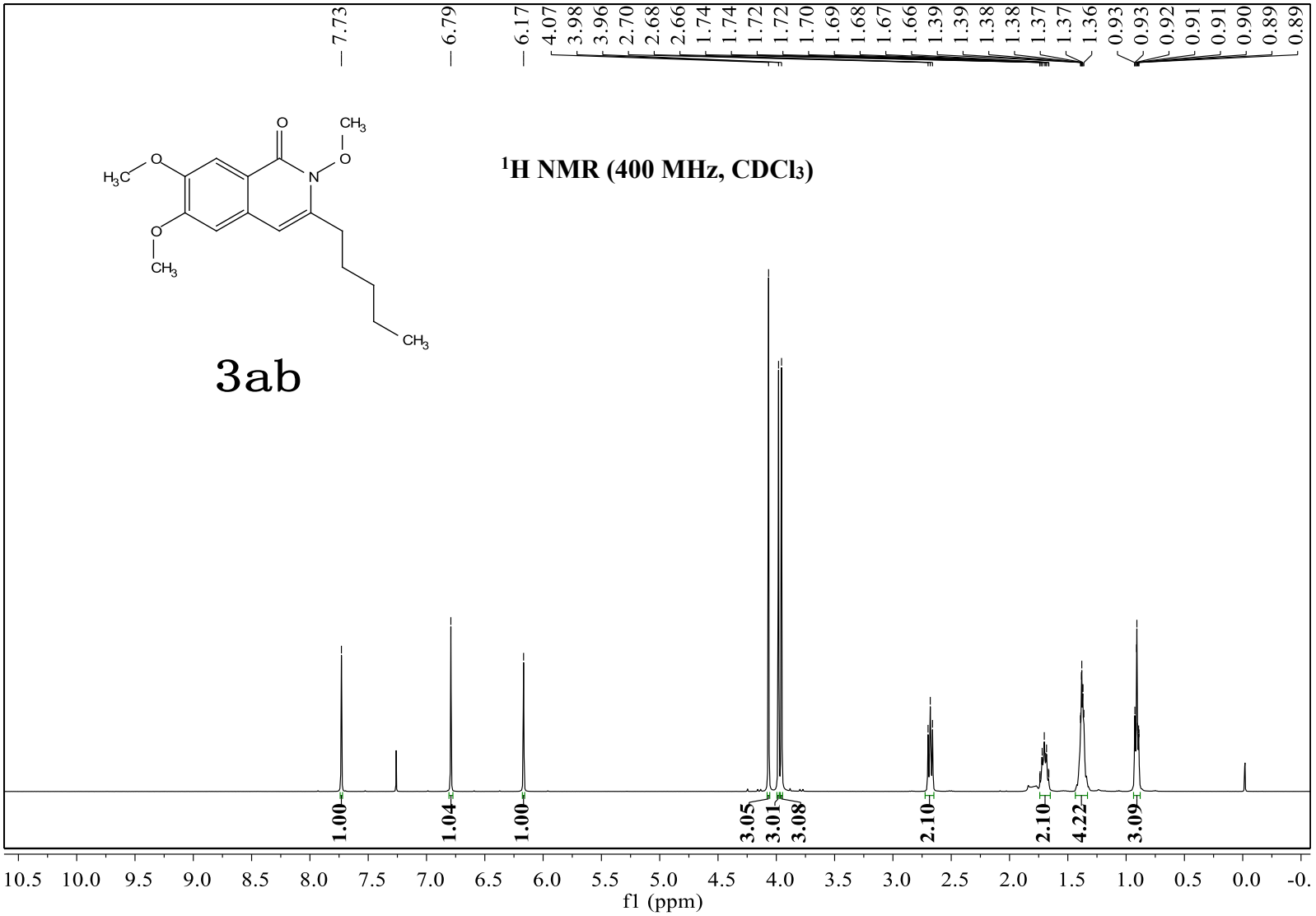
2. (a) H. Morita, S. Oshimi, Y. Hirasawa, K. Koyama, T. Honda, W. Ekasari, G. Indrayanto and N. C. Zaini, *Org. Lett.,* 2007, **9**, 3691. (b) M. Rudyanto, Y. Tomizawa, H. Morita and T. Honda, *Org. Lett.* 2008, **10**, 1921. (c) S. Gutierrez, A. Coppola, D. Sucunza, C. Burgos and J. J. Vaquero, *Org. Lett*. 2016, **18**, 3378.

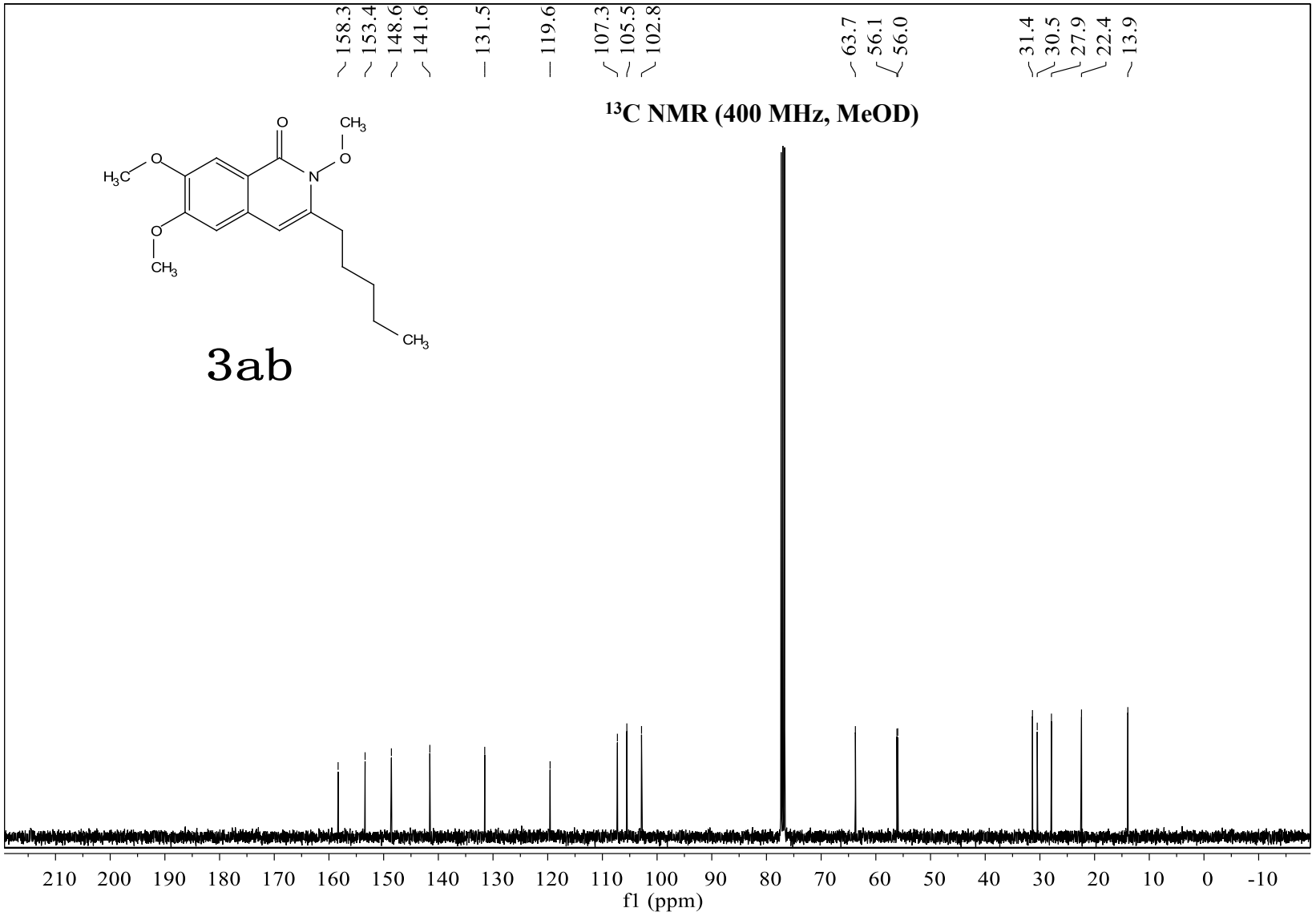

6.37
6.35
6.04
4.04
3.94
3.85
2.65
2.63
2.61
1.68
1.67
1.39
1.38
1.37
1.36
1.35
0.92
0.92
0.91
0.90
^{1}H NMR (400 MHz, CDCl$_3$)
3aa
1.03
1.00
1.00
3.03
3.05
3.06
2.08
2.09
4.19
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

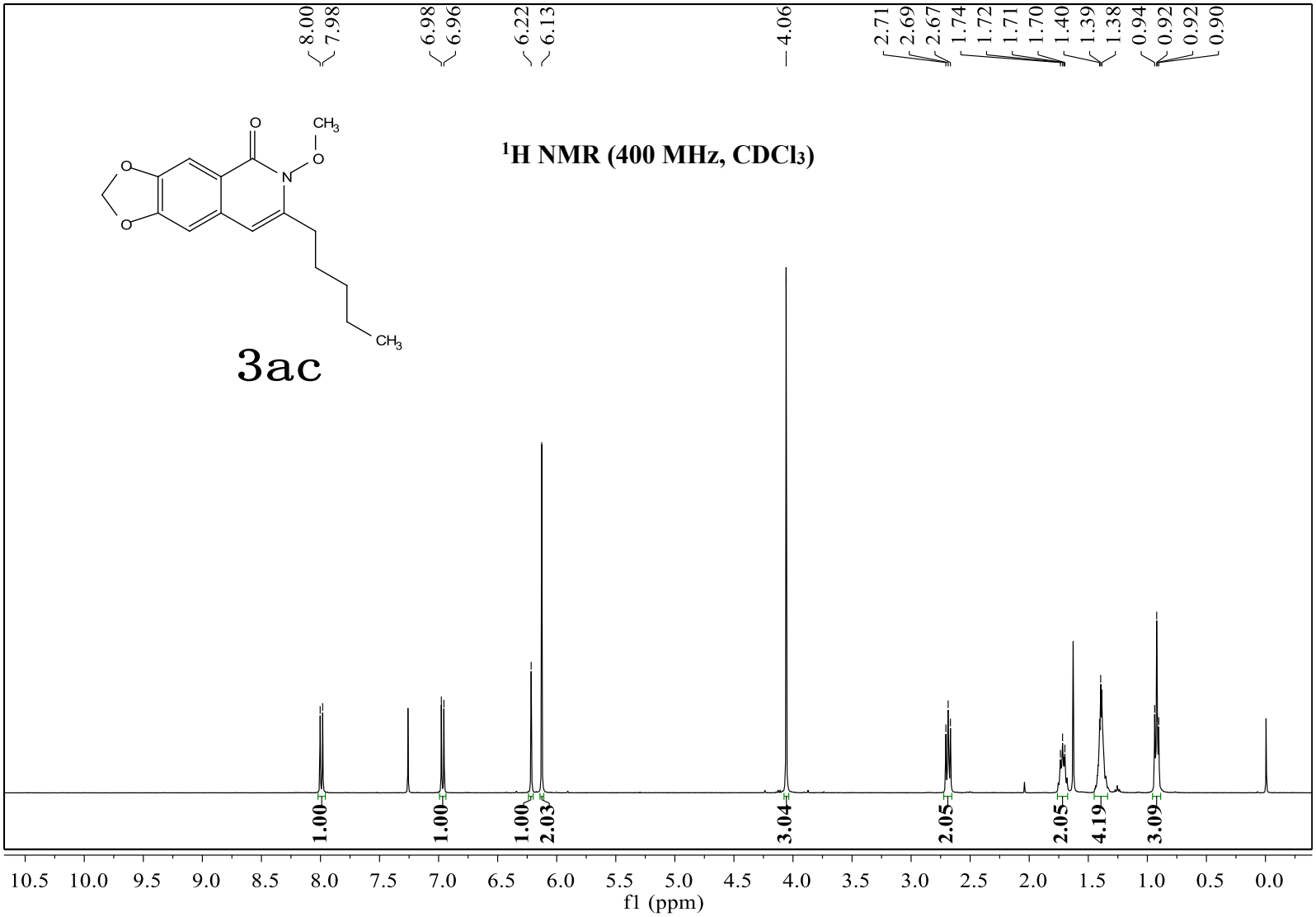

163.0
162.3
157.3
144.2
140.5
109.8
102.5
98.5
97.4
63.7
56.1
55.3
31.4
30.5
27.6
22.4
13.9
13C NMR (400 MHz, MeOD)
H3C
O
O
CH3
O
N
O
CH3
CH3
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

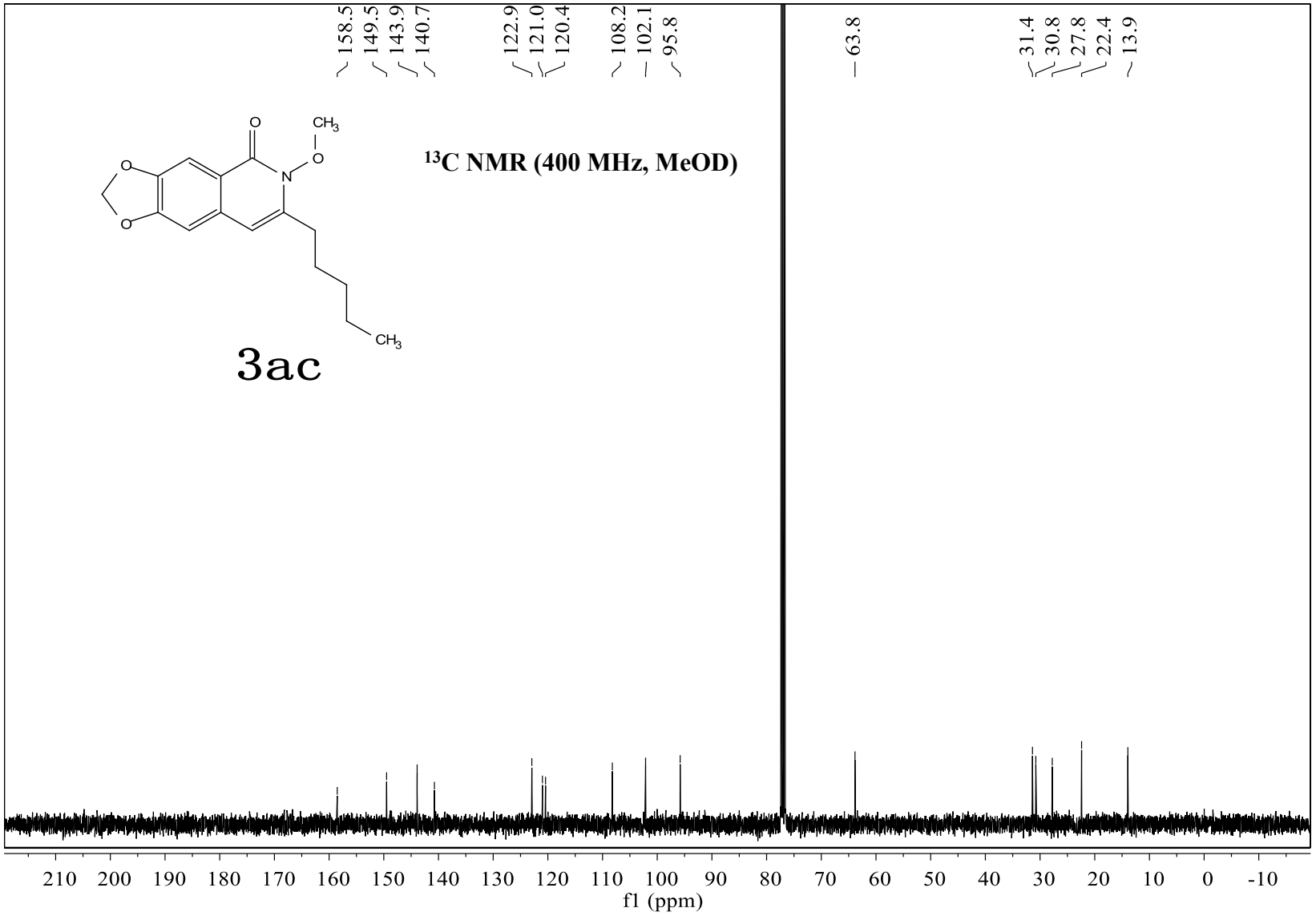

6.39 6.39 6.29 6.29 4.36 4.35 4.35 4.34 4.33 4.32 4.31 4.30 3.90 3.84 2.89 2.85 2.82 2.79 2.75 2.75 1.85 1.84 1.82 1.82 1.81 1.78 1.77 1.68 1.66 1.65 1.64 1.62 1.60 1.59 1.57 1.55 1.54 1.52 1.50 1.45 1.44 1.42 1.42 1.40 1.31 1.30 1.30 0.90 0.88 0.86
CH3
O
H3C
O
O
O
CH3
4a
1H NMR (400 MHz, CDCl3)
1.00 1.01 1.04 3.09 3.03 2.14 1.09 1.35 1.07 1.04 4.00 3.05
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)

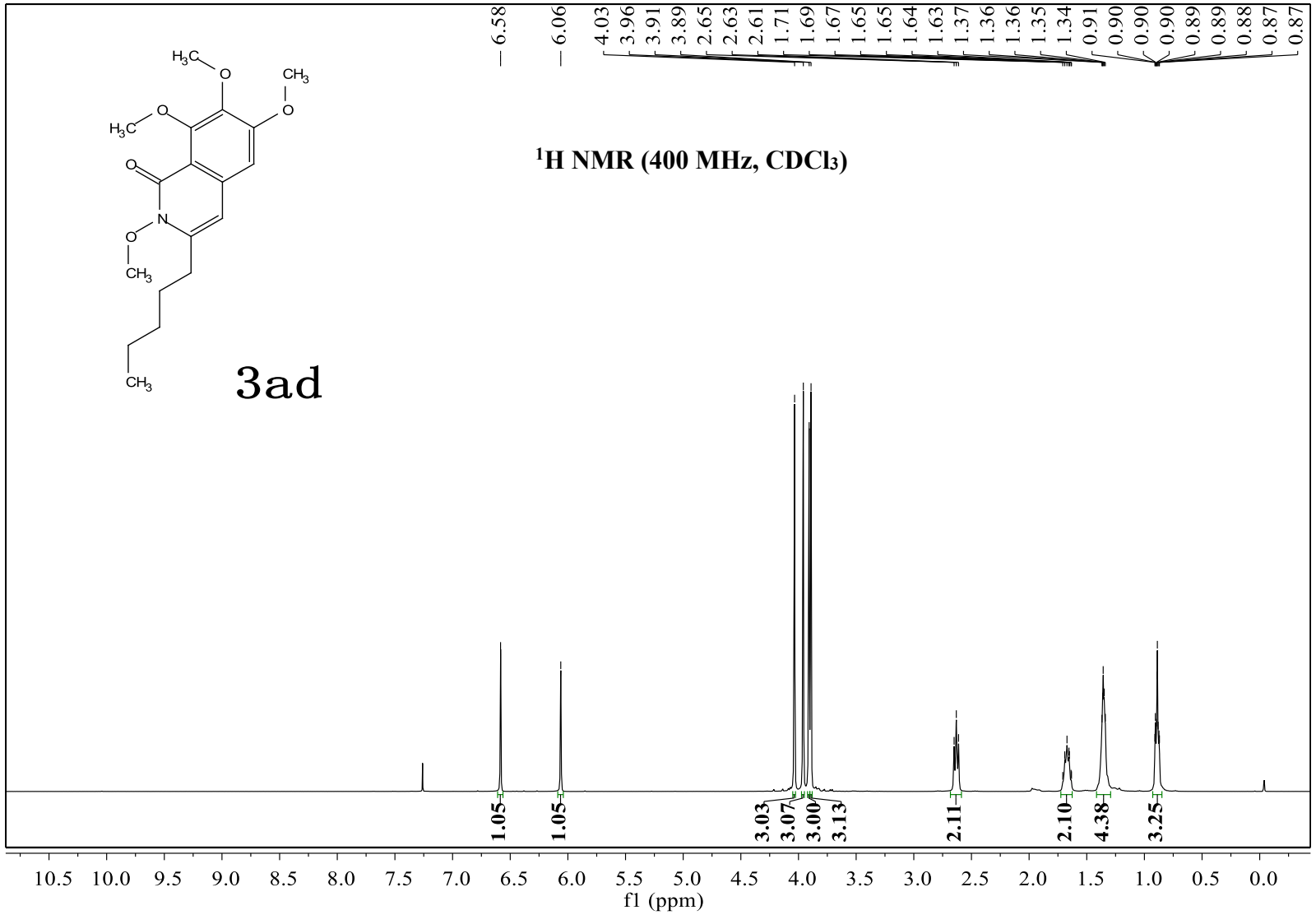

164.2
163.0
162.7
143.9
107.0
103.7
97.6
77.2
56.1
55.4
34.8
34.5
31.5
24.5
22.4
13.9
13C NMR (400 MHz, MeOD)
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

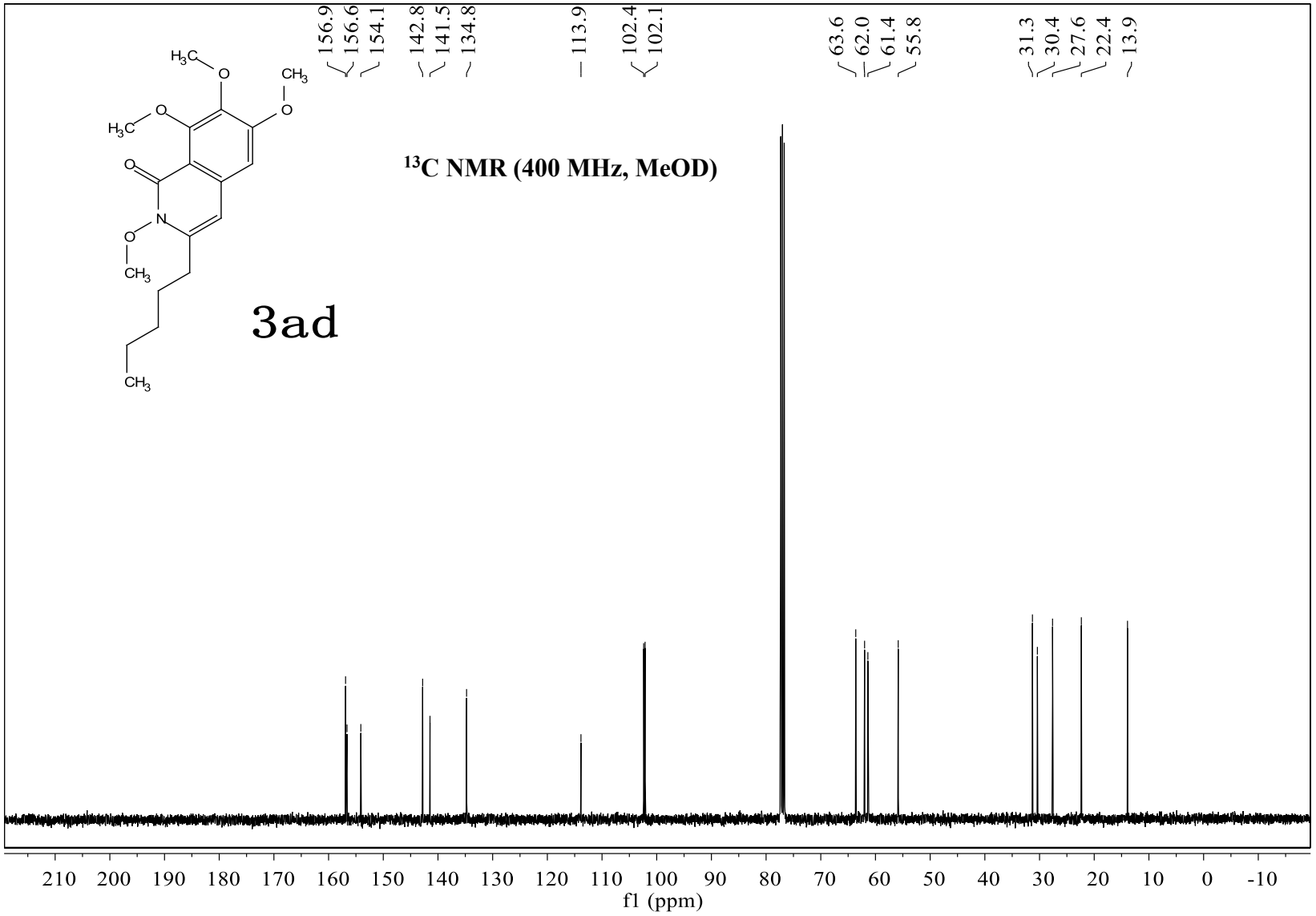

7.73
6.79
6.17
4.07
3.98
3.96
2.70
2.68
2.66
1.74
1.74
1.72
1.72
1.70
1.69
1.68
1.67
1.66
1.39
1.39
1.38
1.38
1.37
1.37
1.36
0.93
0.93
0.92
0.91
0.91
0.90
0.89
0.89
O
CH3
H3C
O
N
O
O
CH3
CH3
3ab
1H NMR (400 MHz, CDCl3)
1.00
1.04
1.00
3.05
3.01
3.08
2.10
2.10
4.22
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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.
f1 (ppm)

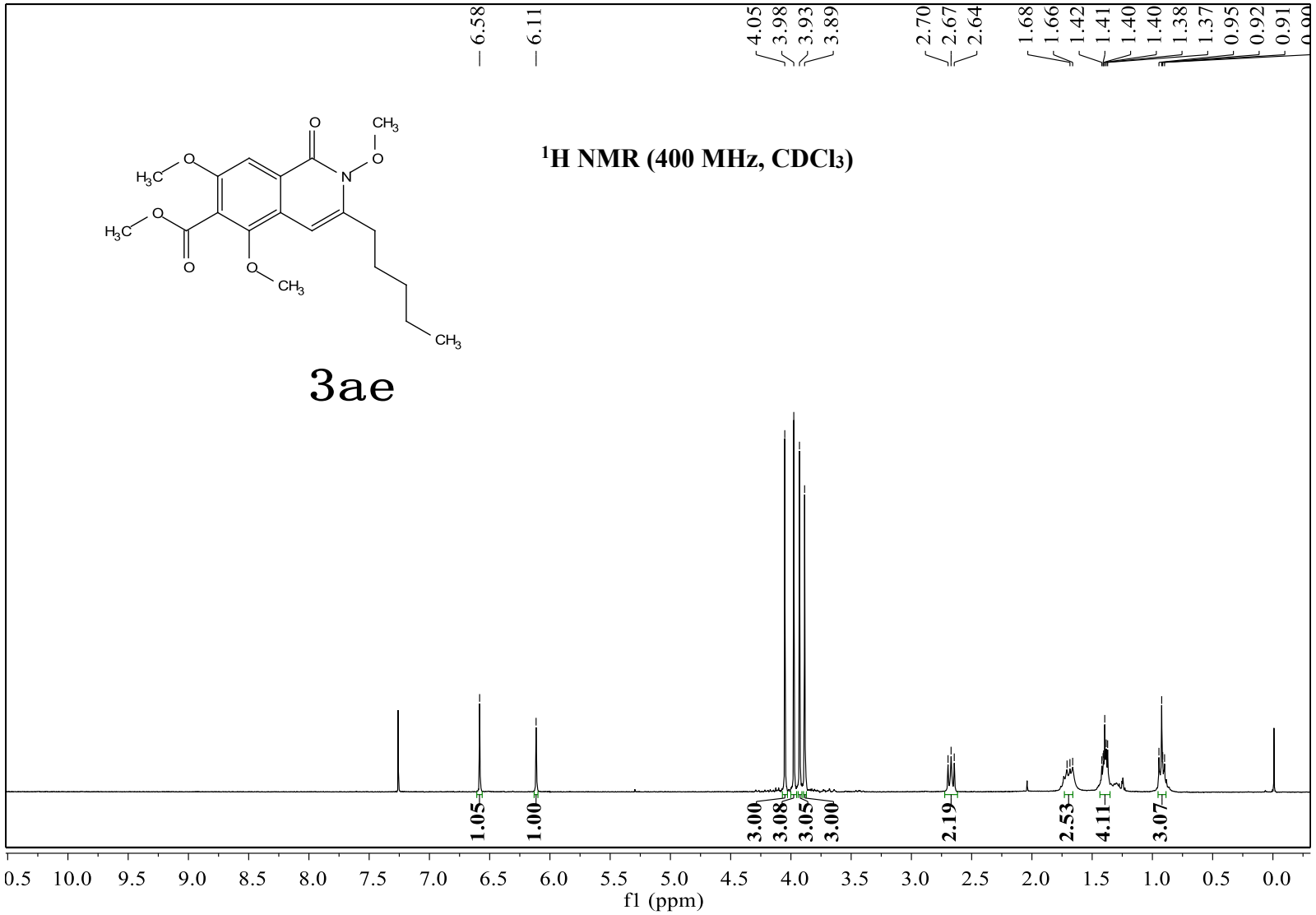

158.3
153.4
148.6
141.6
131.5
119.6
107.3
105.5
102.8
63.7
56.1
56.0
31.4
30.5
27.9
22.4
13.9
13C NMR (400 MHz, MeOD)
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

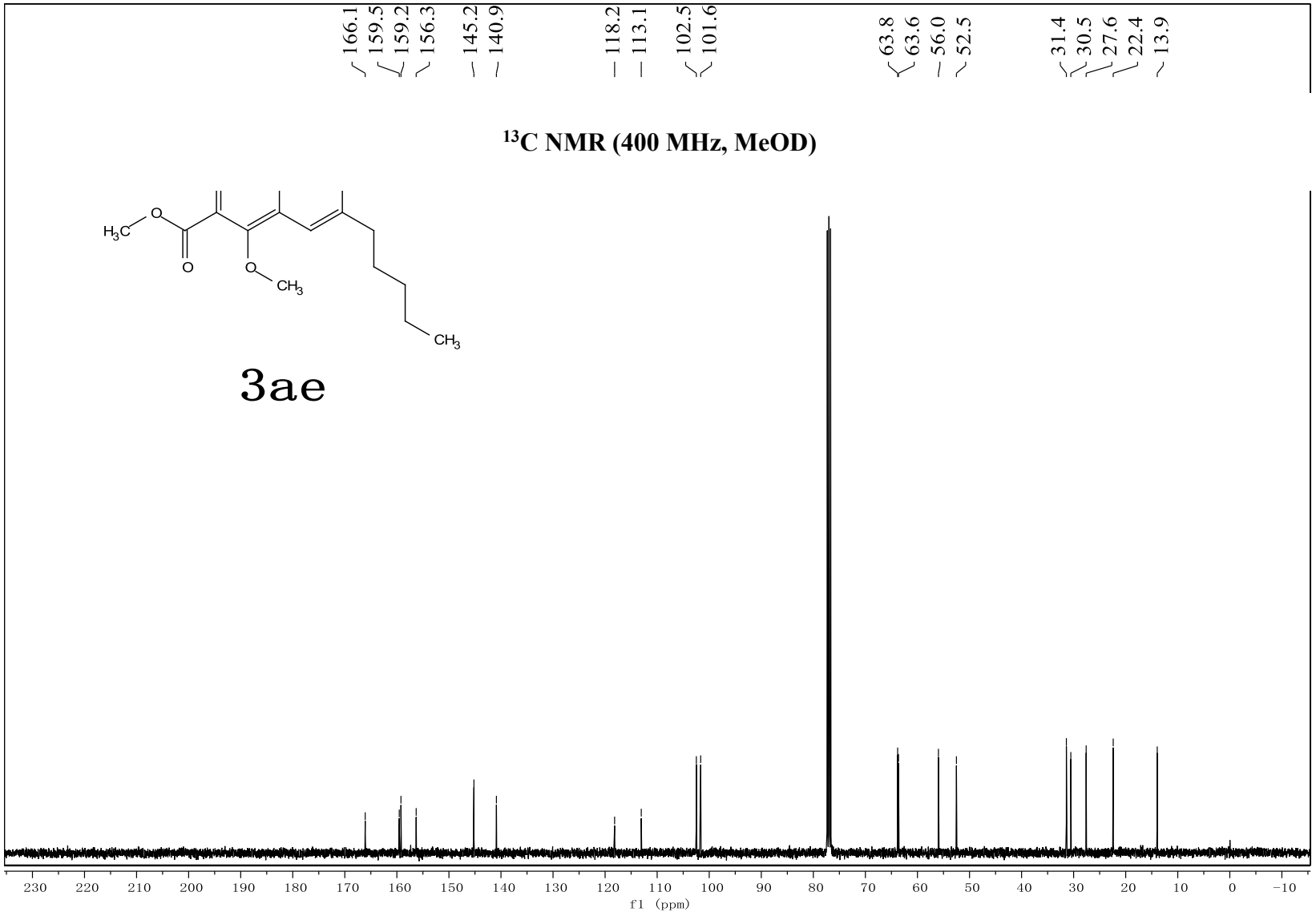

8.00
7.98
6.98
6.96
6.22
6.13
4.06
2.71
2.69
2.67
1.74
1.72
1.71
1.70
1.40
1.39
1.38
0.94
0.92
0.92
0.90
O
CH3
O
N
O
O
O
CH3
3ac
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
2.03
3.04
2.05
2.05
4.19
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

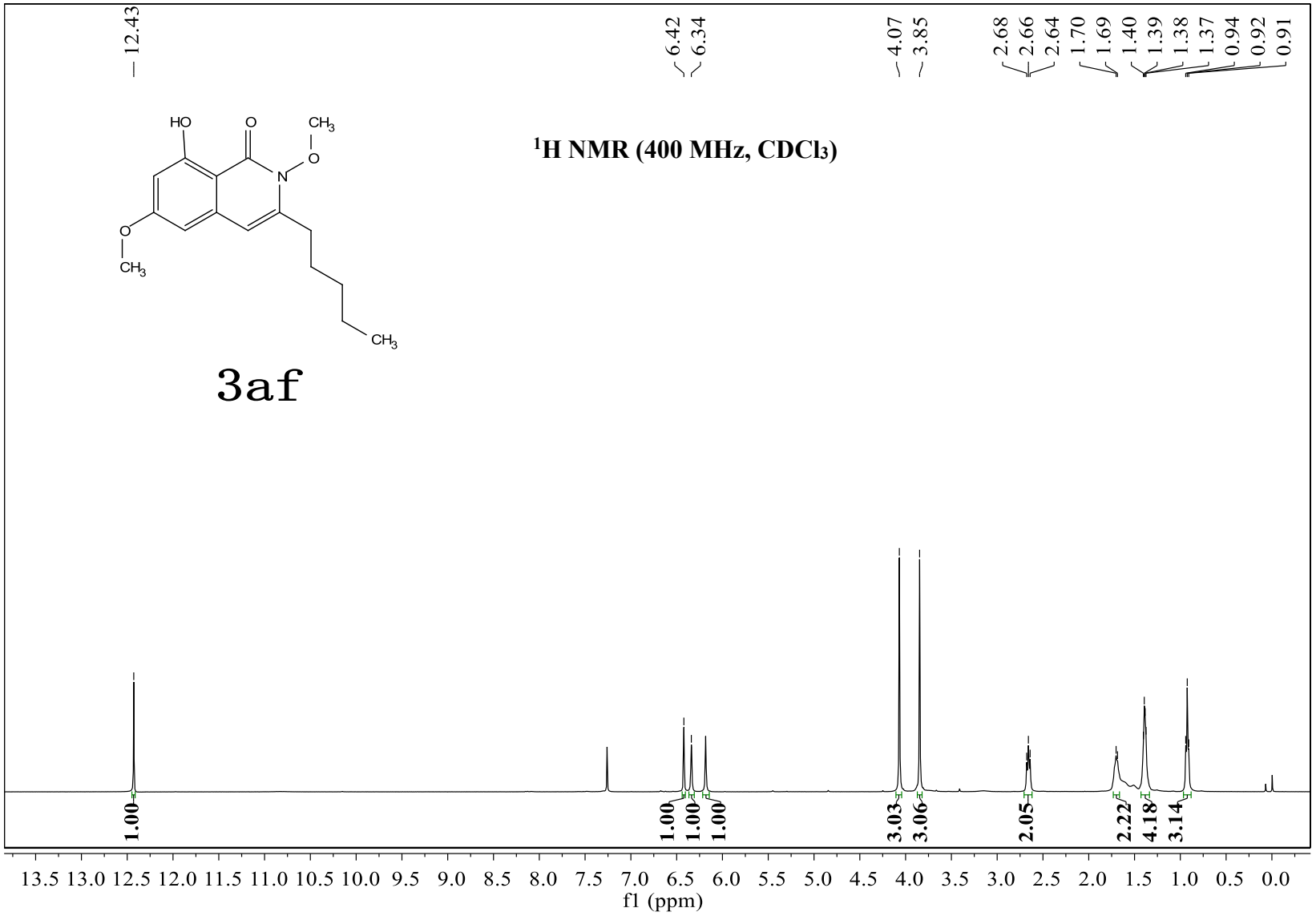

158.5
149.5
143.9
140.7
122.9
121.0
120.4
108.2
102.1
95.8
63.8
31.4
30.8
27.8
22.4
13.9
O
CH3
O
N
O
O
O
CH3
3ac
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

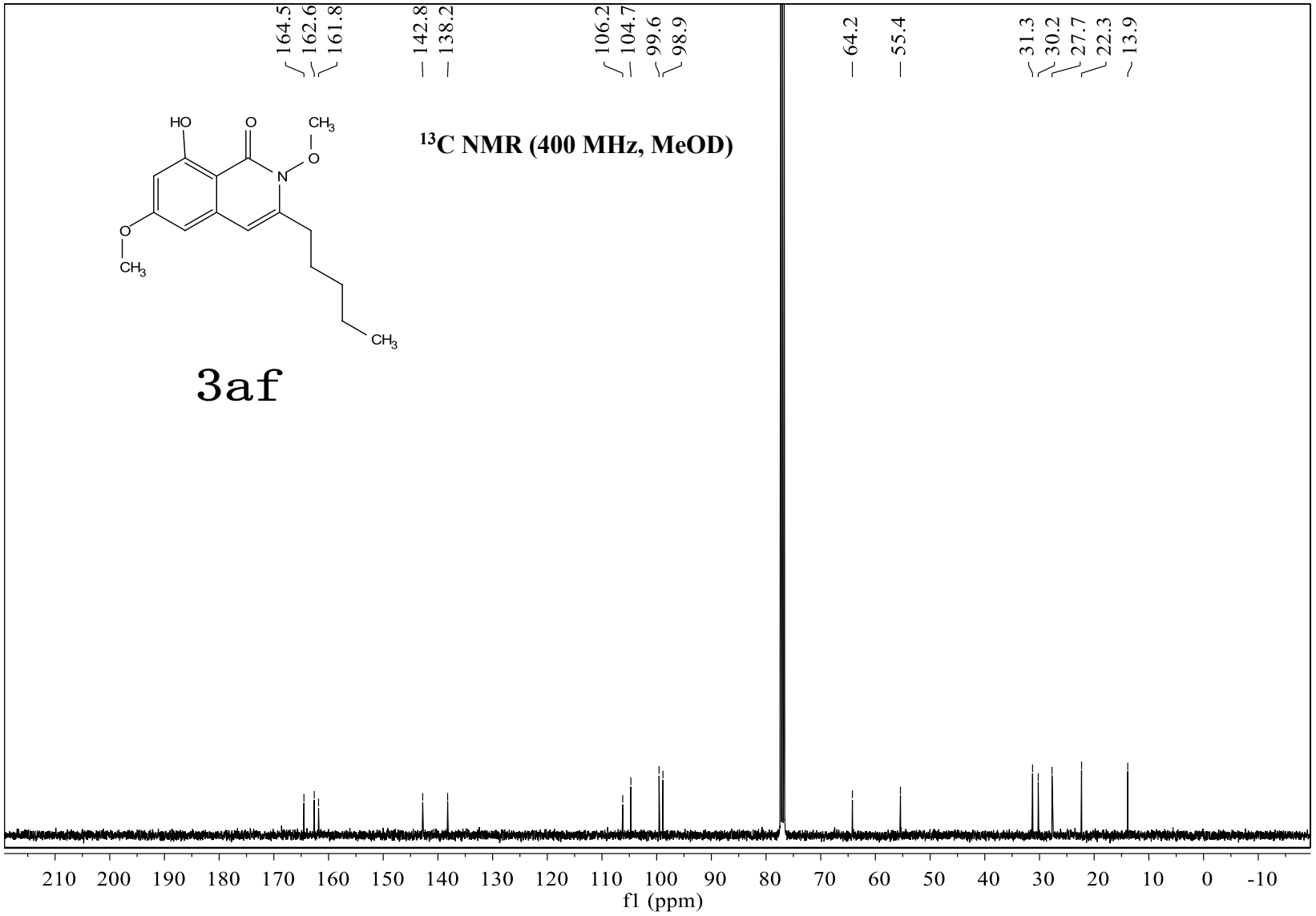

6.58
6.06
4.03
3.96
3.91
3.89
2.65
2.63
2.61
1.71
1.69
1.67
1.65
1.65
1.64
1.63
1.37
1.36
1.36
1.35
1.34
0.91
0.90
0.90
0.90
0.89
0.89
0.88
0.87
0.87
1H NMR (400 MHz, CDCl3)
3ad
1.05
1.05
3.03
3.07
3.00
3.13
2.11
2.10
4.38
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

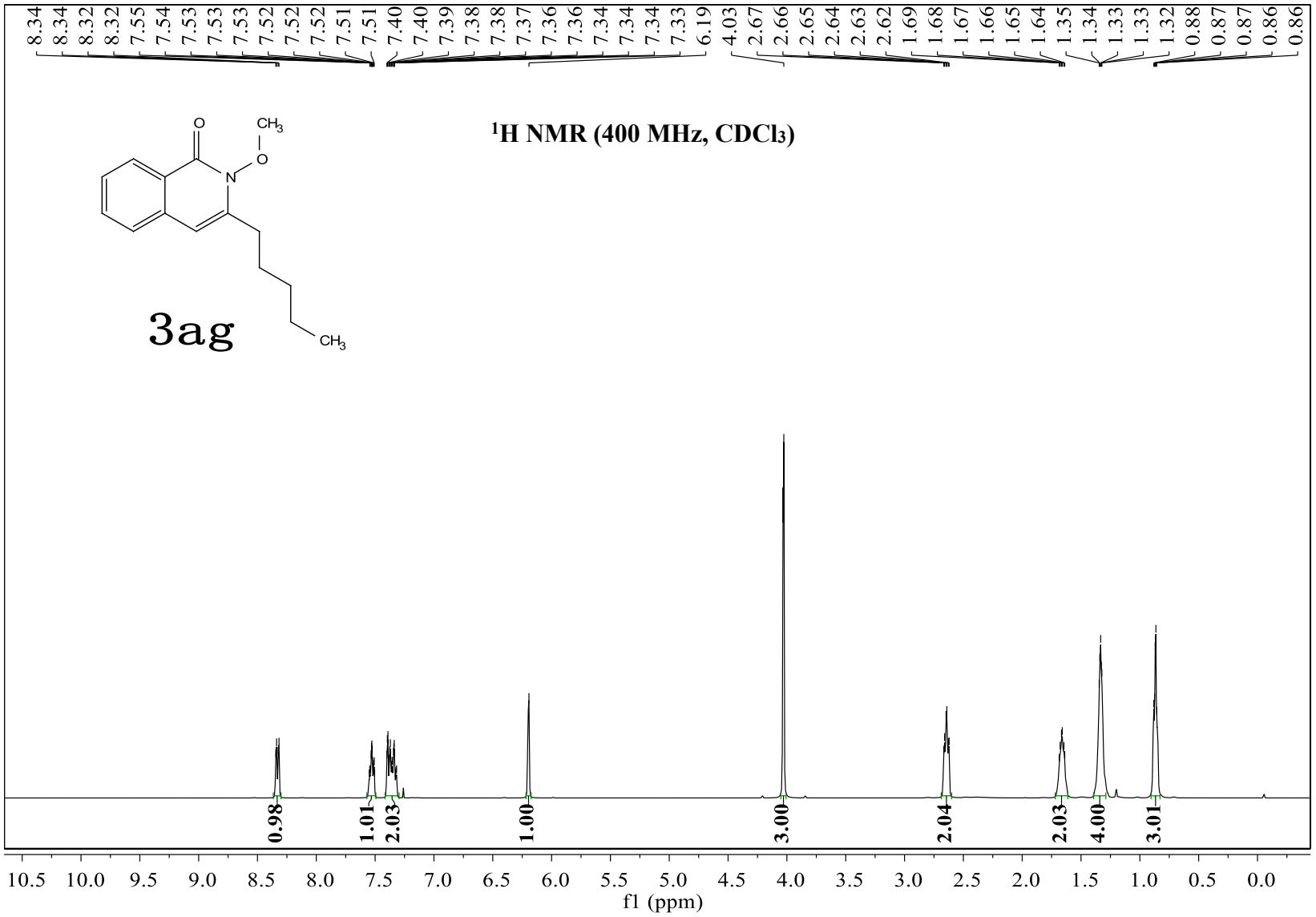

156.9
156.6
154.1
142.8
141.5
134.8
113.9
102.4
102.1
63.6
62.0
61.4
55.8
31.3
30.4
27.6
22.4
13.9
13C NMR (400 MHz, MeOD)
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

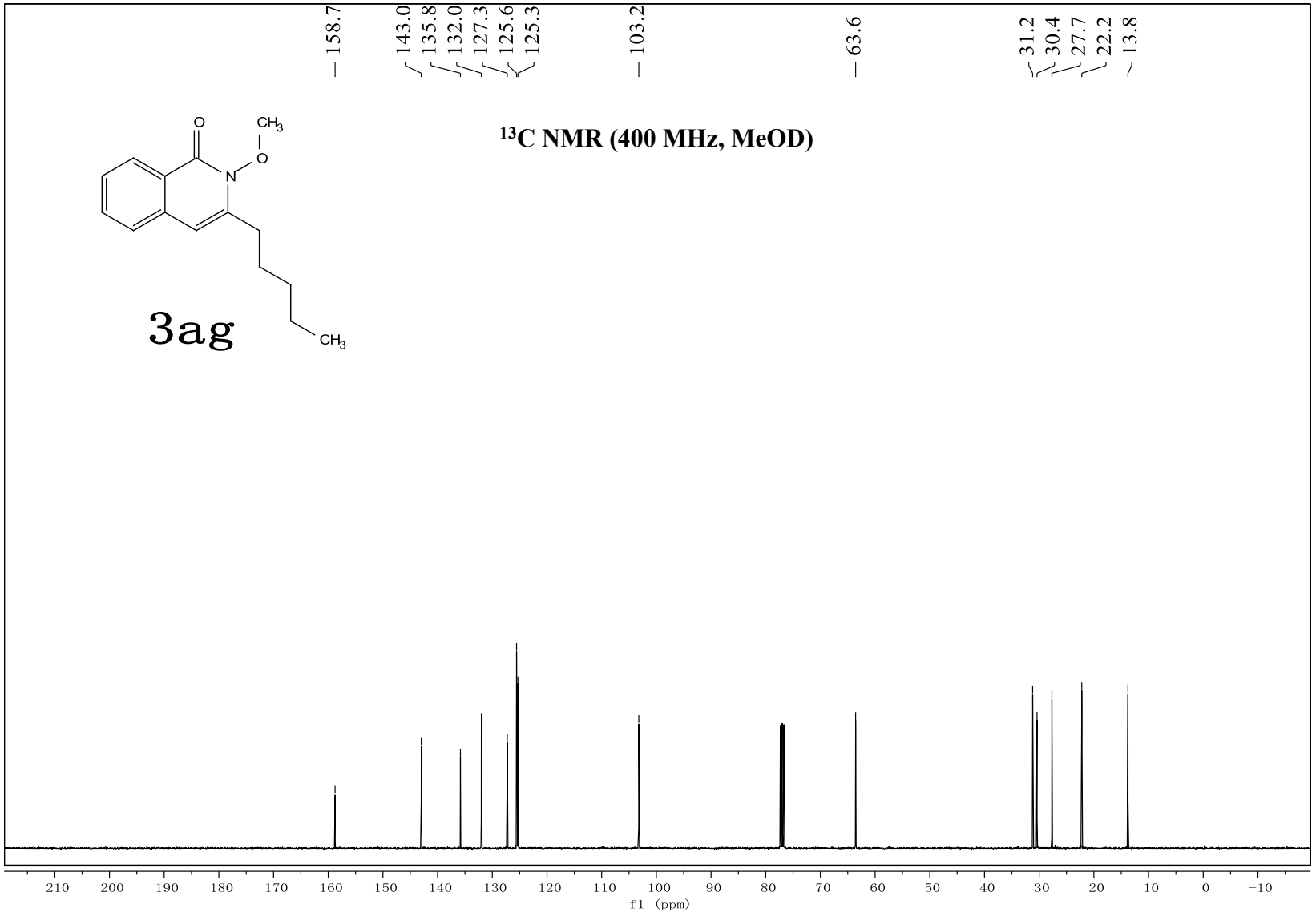

6.58
6.11
4.05
3.98
3.93
3.89
2.70
2.67
2.64
1.68
1.66
1.42
1.41
1.40
1.40
1.38
1.37
0.95
0.92
0.91
0.90
1H NMR (400 MHz, CDCl3)
3ae
1.05
1.00
3.00
3.08
3.05
3.00
2.19
2.53
4.11
3.07
f1 (ppm)


166.1
159.5
159.2
156.3
145.2
140.9
118.2
113.1
102.5
101.6
63.8
63.6
56.0
52.5
31.4
30.5
27.6
22.4
13.9
13C NMR (400 MHz, MeOD)
H3C
O
O
O
CH3
CH3
3ae
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

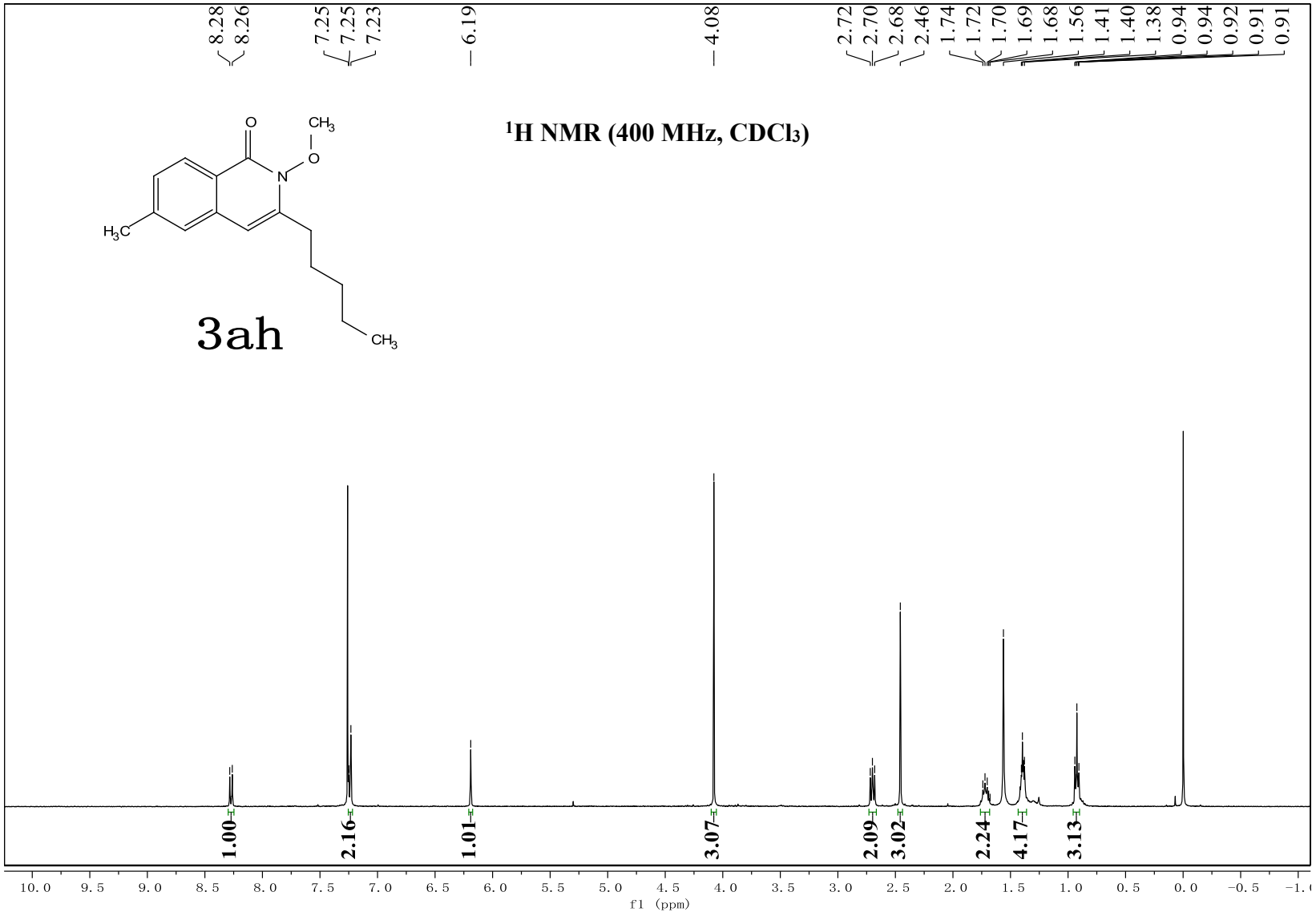

12.43
6.42
6.34
4.07
3.85
2.68
2.66
2.64
1.70
1.69
1.40
1.39
1.38
1.37
0.94
0.92
0.91
HO
O
CH3
N
O
O
CH3
CH3
1H NMR (400 MHz, CDCl3)
3af
1.00
1.00
1.00
1.00
3.03
3.06
2.05
2.22
4.18
3.14
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

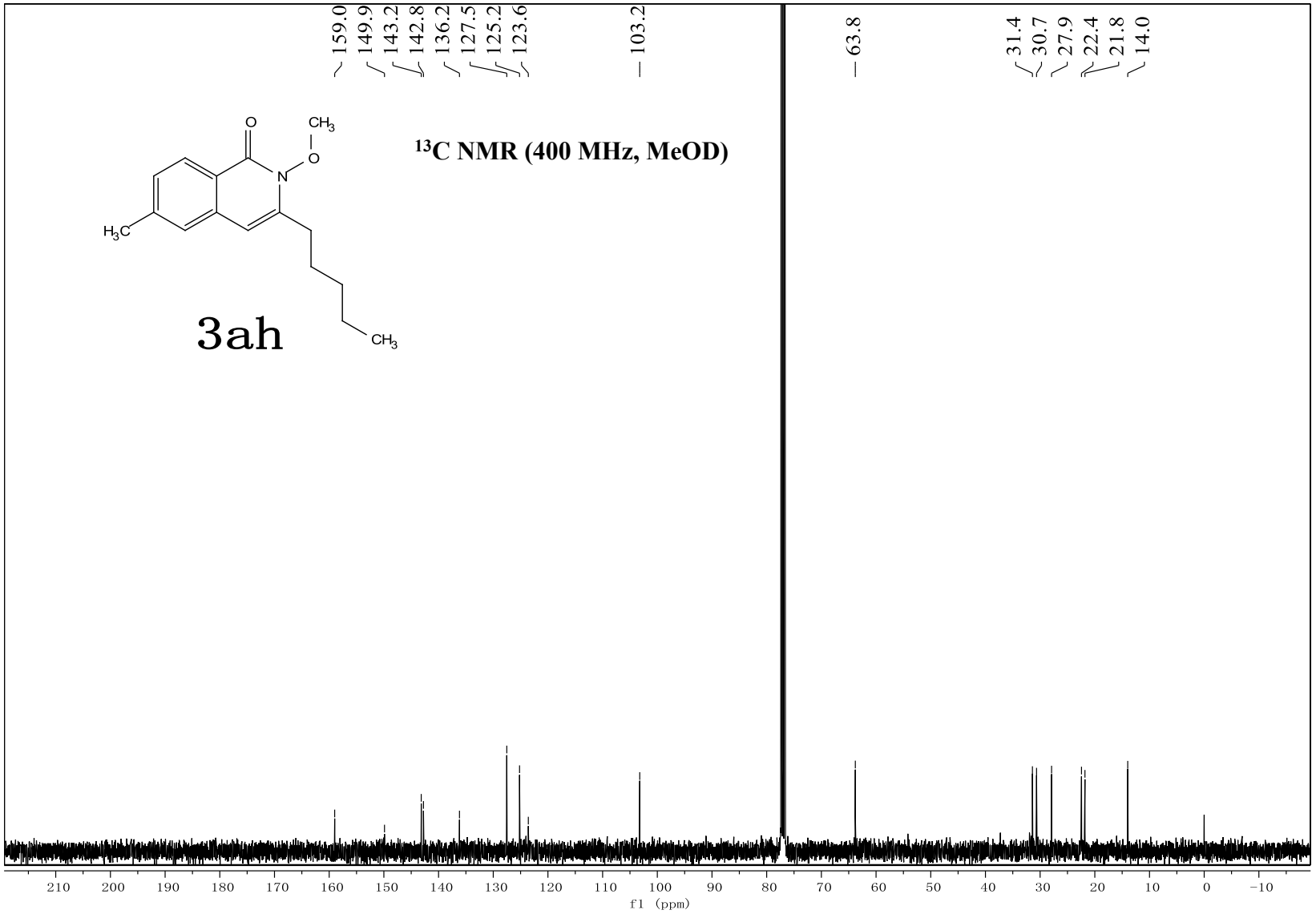

164.5
162.6
161.8
142.8
138.2
106.2
104.7
99.6
98.9
64.2
55.4
31.3
30.2
27.7
22.3
13.9
HO
O
CH3
N
O
O
CH3
CH3
13C NMR (400 MHz, MeOD)
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

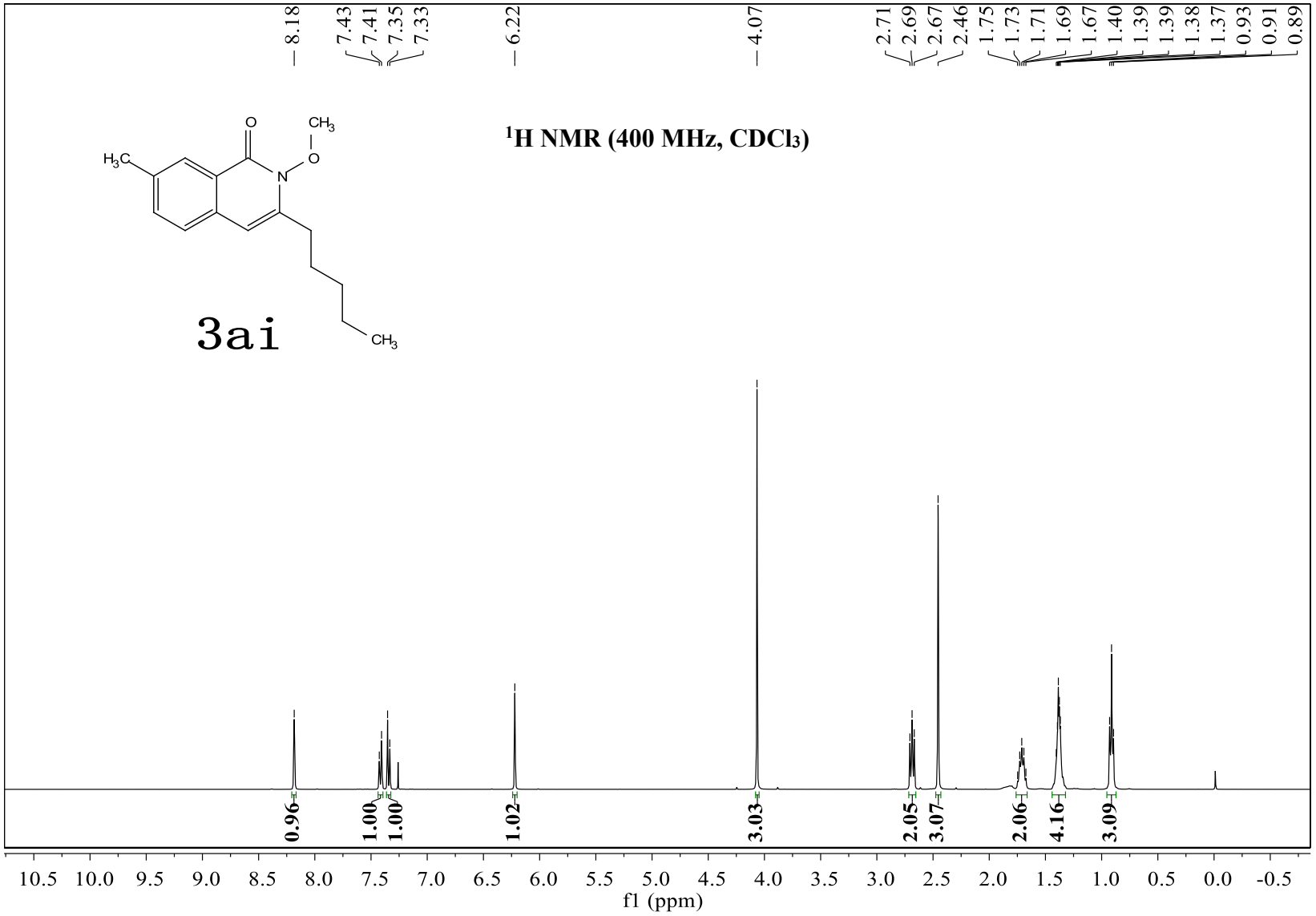

8.34 8.34 8.32 8.32 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.34 7.34 7.34 7.33 6.19 4.03 2.67 2.66 2.65 2.64 2.63 2.62 1.69 1.68 1.67 1.66 1.65 1.64 1.35 1.34 1.33 1.33 1.32 0.88 0.87 0.87 0.86 0.86
O
CH3
O
N
CH3
3ag
1H NMR (400 MHz, CDCl3)
0.98
1.01
2.03
1.00
3.00
2.04
2.03
4.00
3.01
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
f1 (ppm)

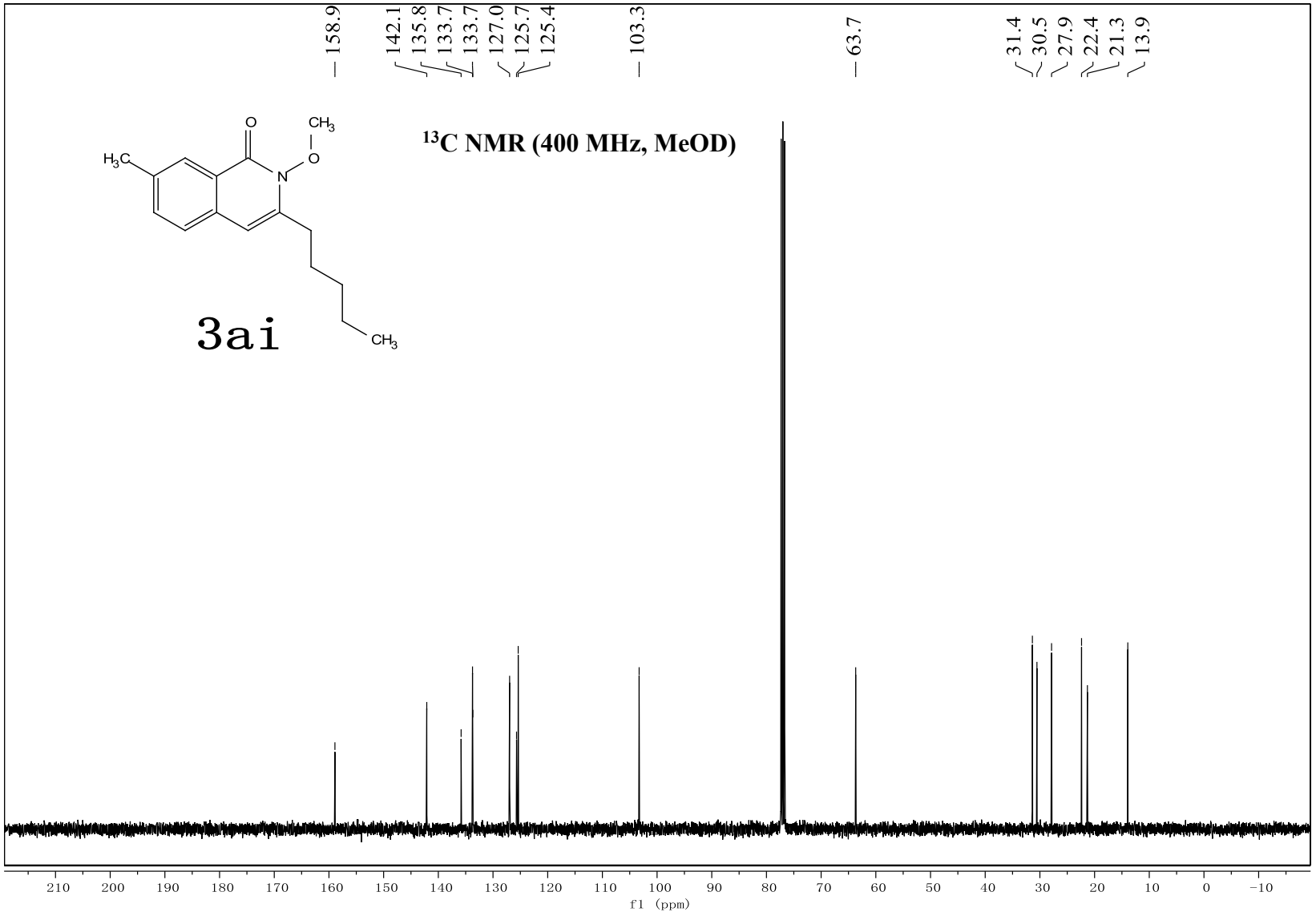


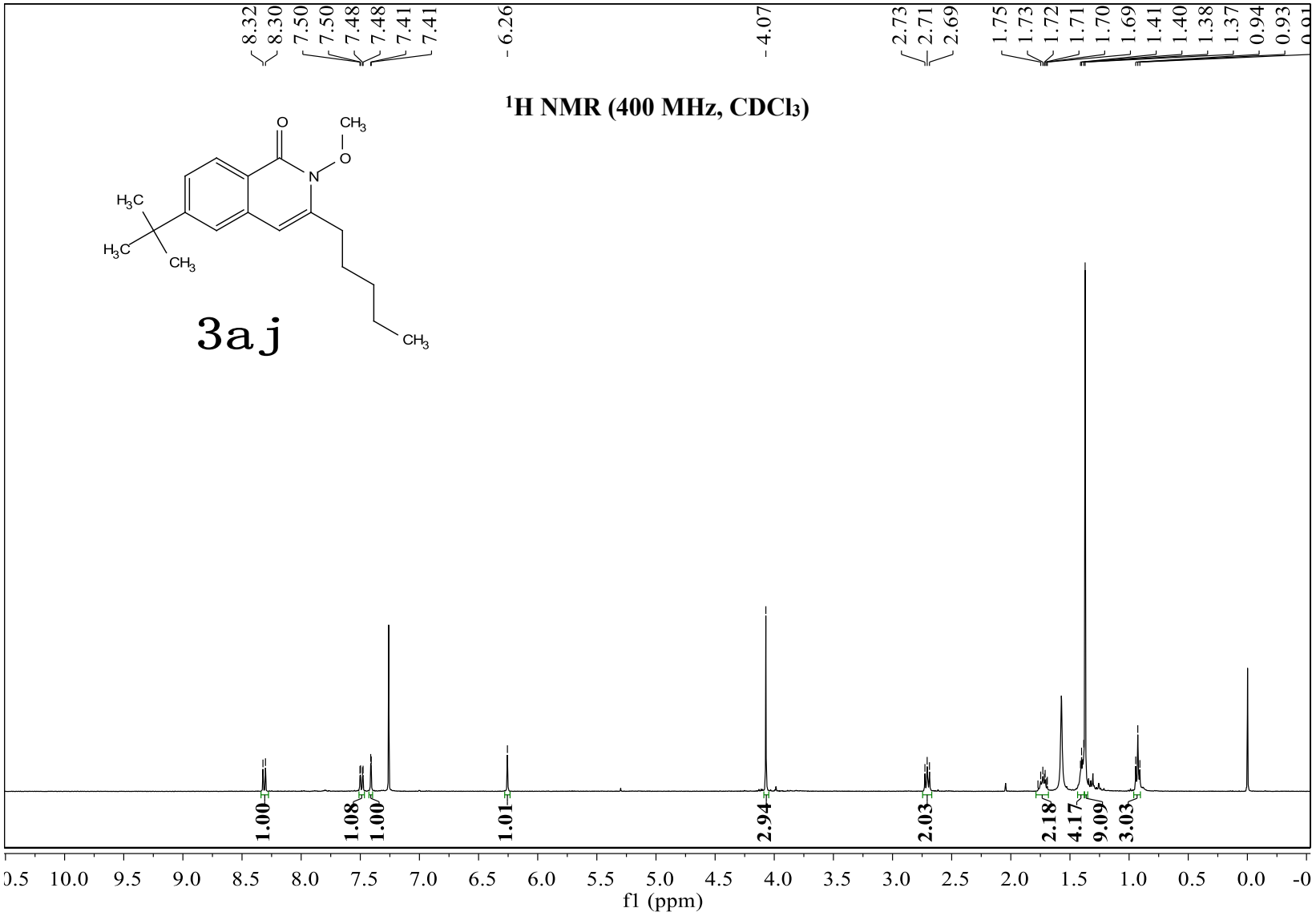
^{13}C NMR (400 MHz, MeOD)

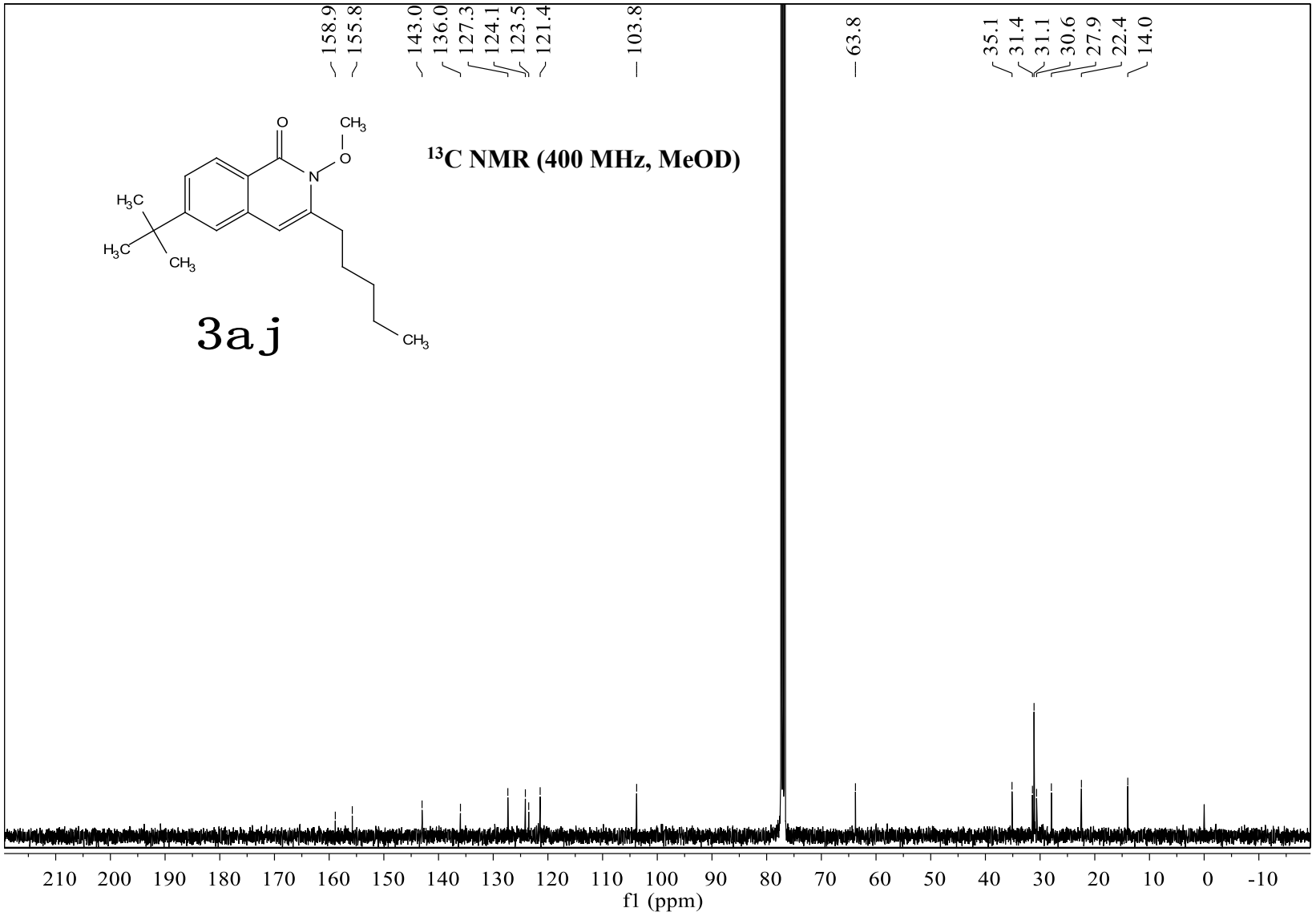

8.28
8.26
7.25
7.25
7.23
6.19
4.08
2.72
2.70
2.68
2.46
1.74
1.72
1.70
1.69
1.68
1.56
1.41
1.40
1.38
0.94
0.94
0.92
0.91
0.91
O
CH3
O
N
H3C
CH3
3ah
1H NMR (400 MHz, CDCl3)
1.00
2.16
1.01
3.07
2.09
3.02
2.24
4.17
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

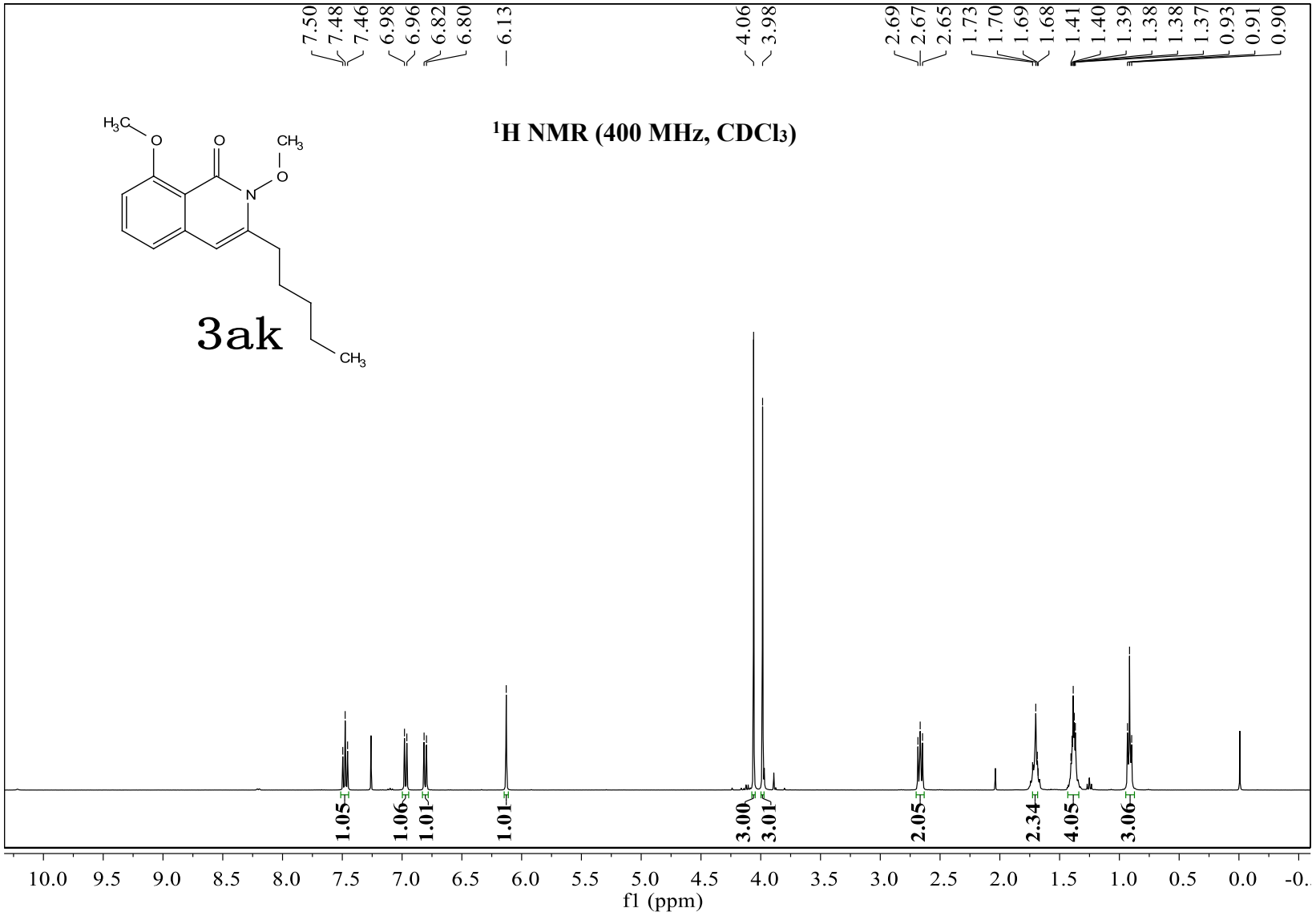

159.0
149.9
143.2
142.8
136.2
127.5
125.2
123.6
103.2
63.8
31.4
30.7
27.9
22.4
21.8
14.0
O
CH3
O
N
H3C
CH3
3ah
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

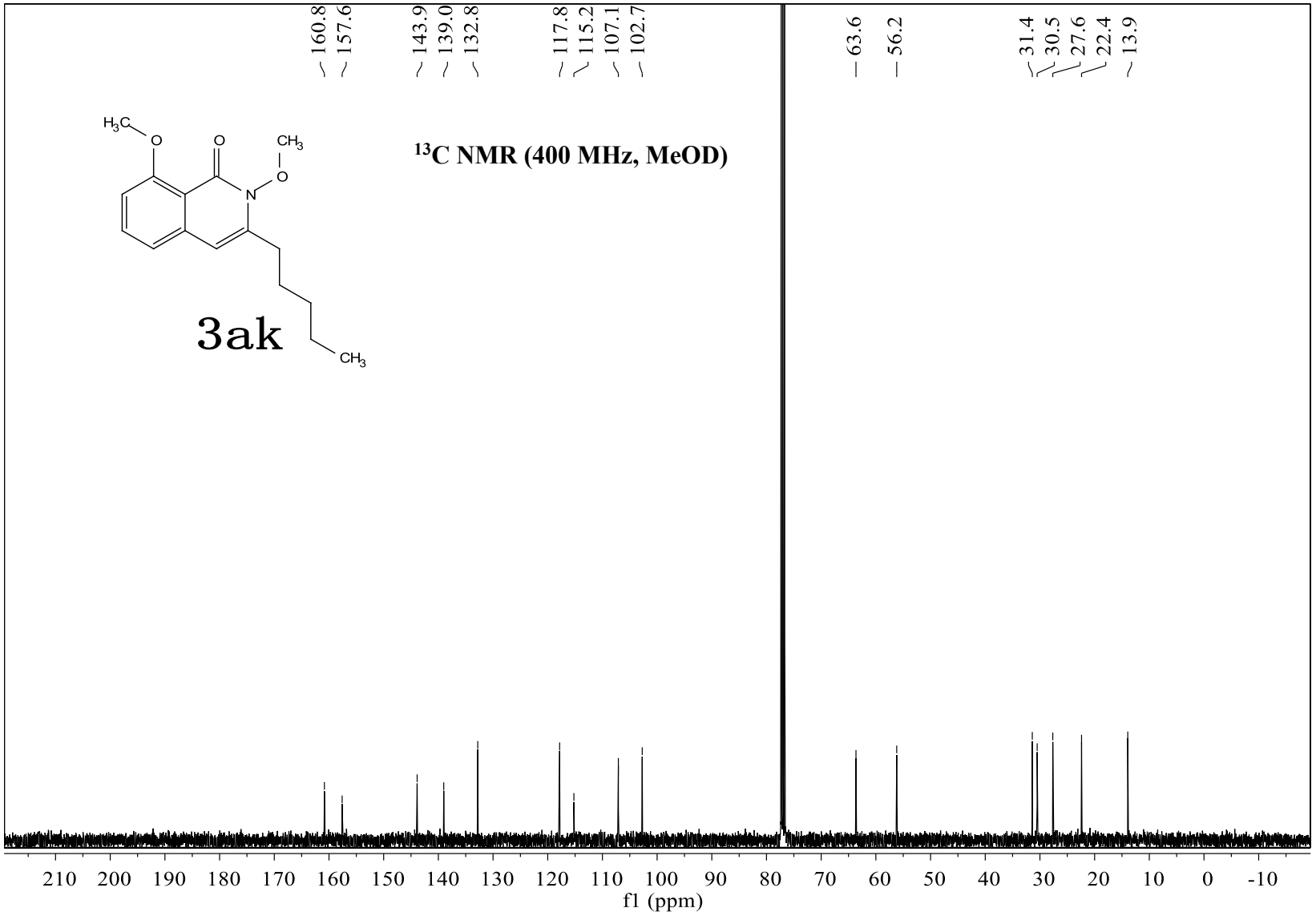

8.18
7.43
7.41
7.35
7.33
6.22
4.07
2.71
2.69
2.67
2.46
1.75
1.73
1.71
1.69
1.67
1.40
1.39
1.39
1.38
1.37
0.93
0.91
0.89
O
CH3
H3C
N
O
CH3
3ai
1H NMR (400 MHz, CDCl3)
0.96
1.00
1.00
1.02
3.03
2.05
3.07
2.06
4.16
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

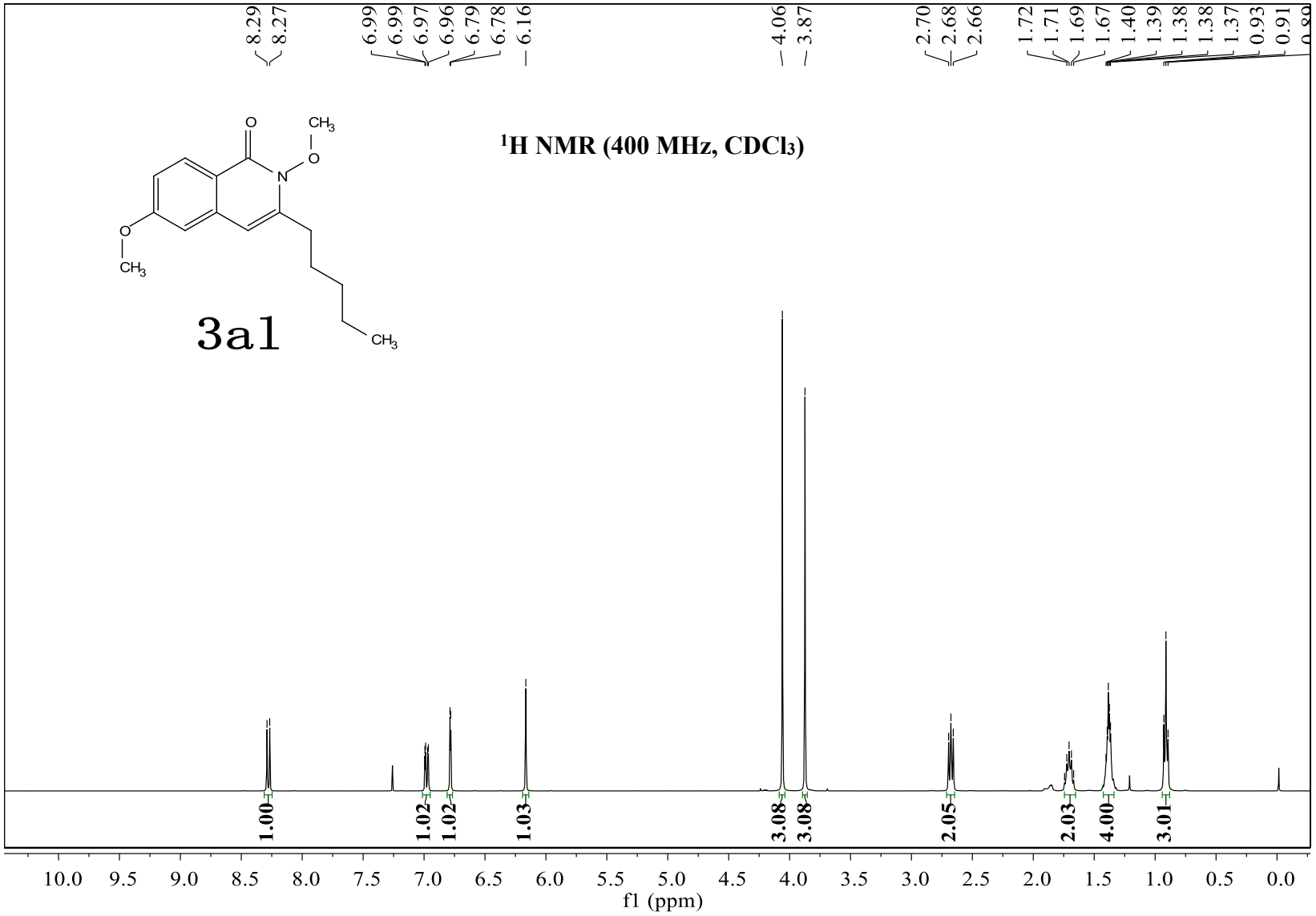

158.9
142.1
135.8
133.7
133.7
127.0
125.7
125.4
103.3
63.7
31.4
30.5
27.9
22.4
21.3
13.9
13C NMR (400 MHz, MeOD)
3ai
f1 (ppm)

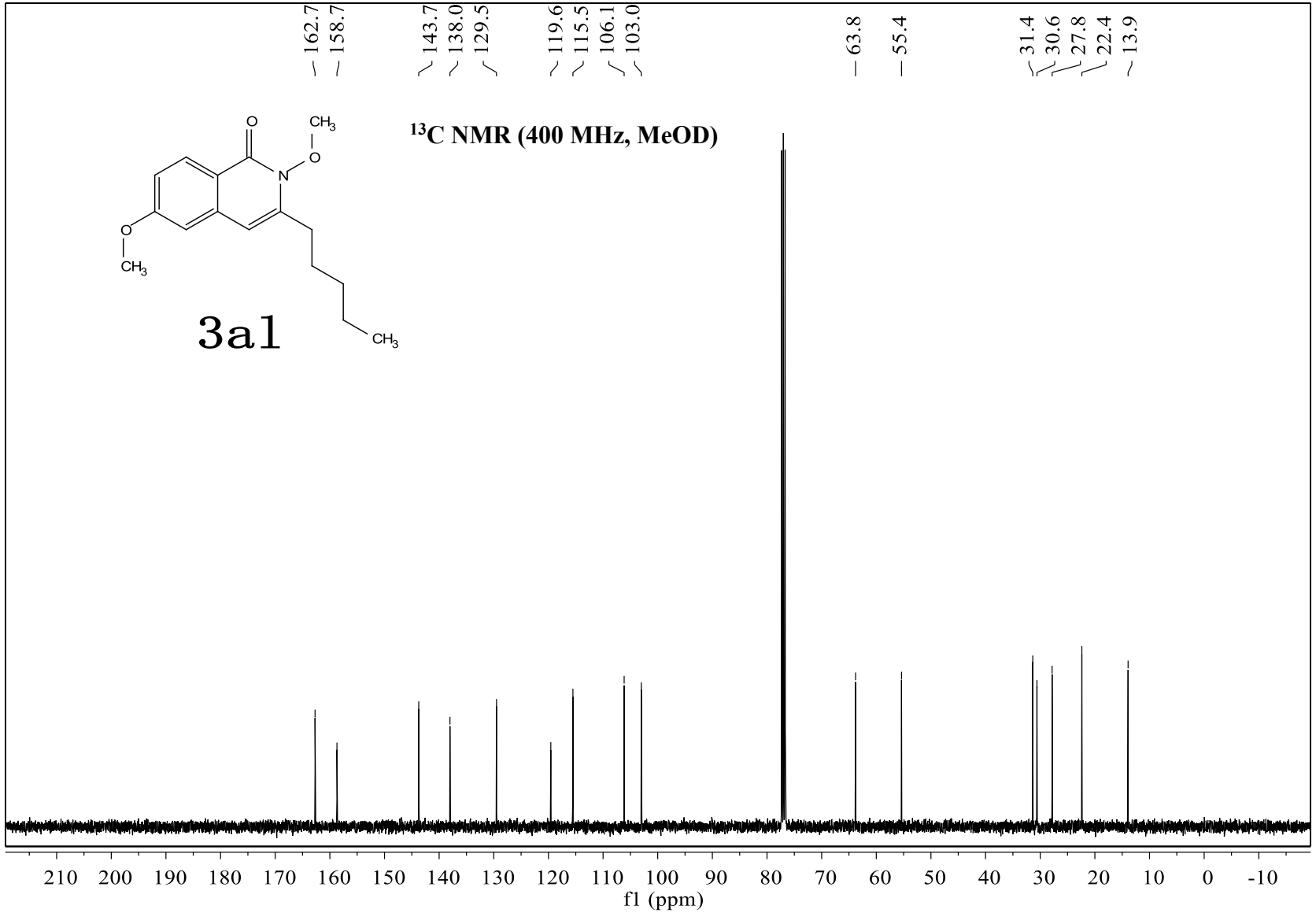

8.32
8.30
7.50
7.50
7.48
7.48
7.41
7.41
6.26
4.07
2.73
2.71
2.69
1.75
1.73
1.72
1.71
1.70
1.69
1.41
1.40
1.38
1.37
0.94
0.93
1H NMR (400 MHz, CDCl3)
O
CH3
O
N
H3C
H3C
CH3
CH3
3aj
1.00
1.08
1.00
1.01
2.94
2.03
2.18
4.17
9.09
3.03
f1 (ppm)

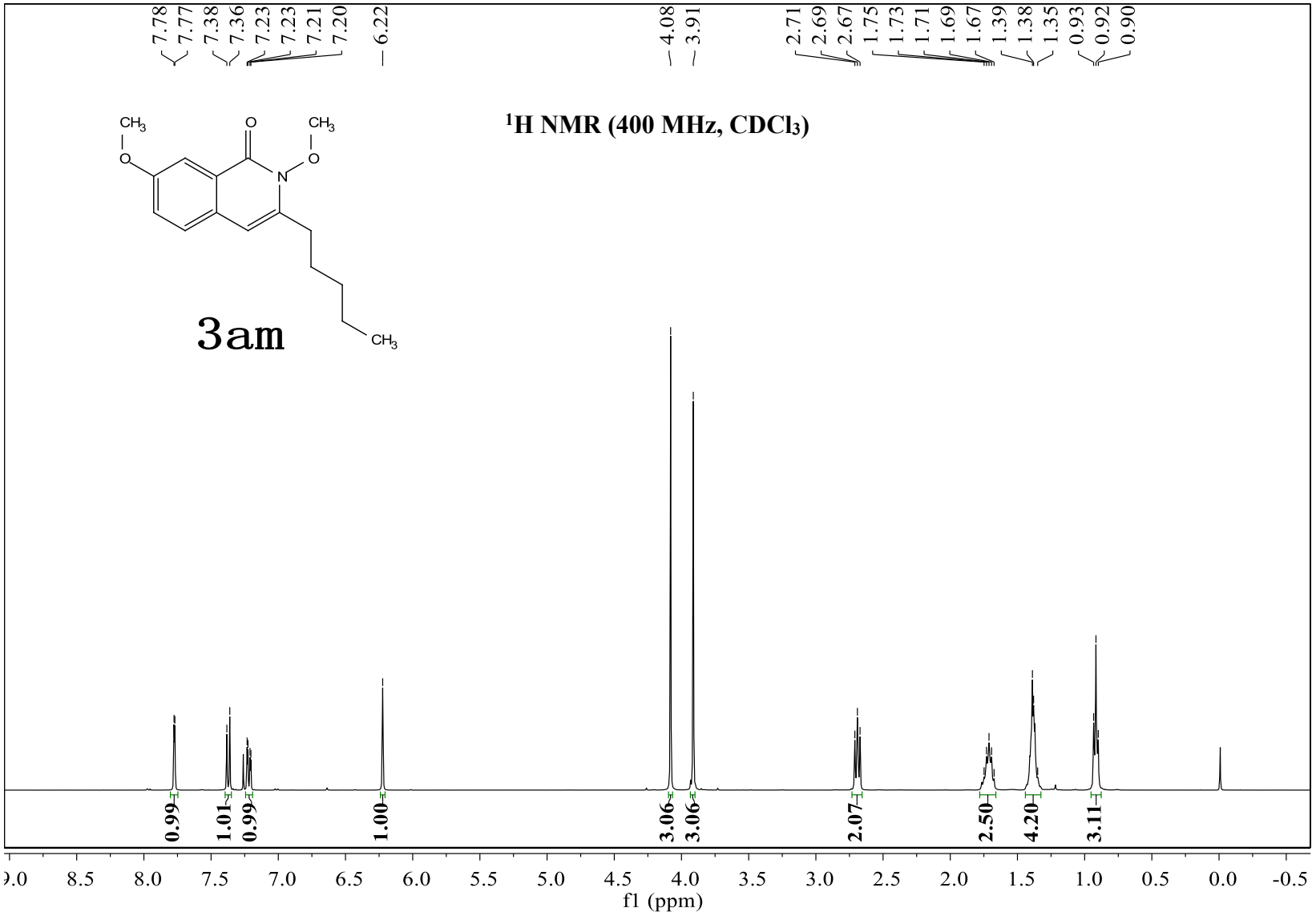

158.9
155.8
143.0
136.0
127.3
124.1
123.5
121.4
103.8
63.8
35.1
31.4
31.1
30.6
27.9
22.4
14.0
O
CH3
O
N
H3C
H3C
CH3
CH3
3aj
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.50
7.48
7.46
6.98
6.96
6.82
6.80
6.13
4.06
3.98
2.69
2.67
2.65
1.73
1.70
1.69
1.68
1.41
1.40
1.39
1.38
1.38
1.37
0.93
0.91
0.90
H3C
O
O
CH3
O
N
3ak
CH3
1H NMR (400 MHz, CDCl3)
1.05
1.06
1.01
1.01
3.00
3.01
2.05
2.34
4.05
3.06
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.
f1 (ppm)

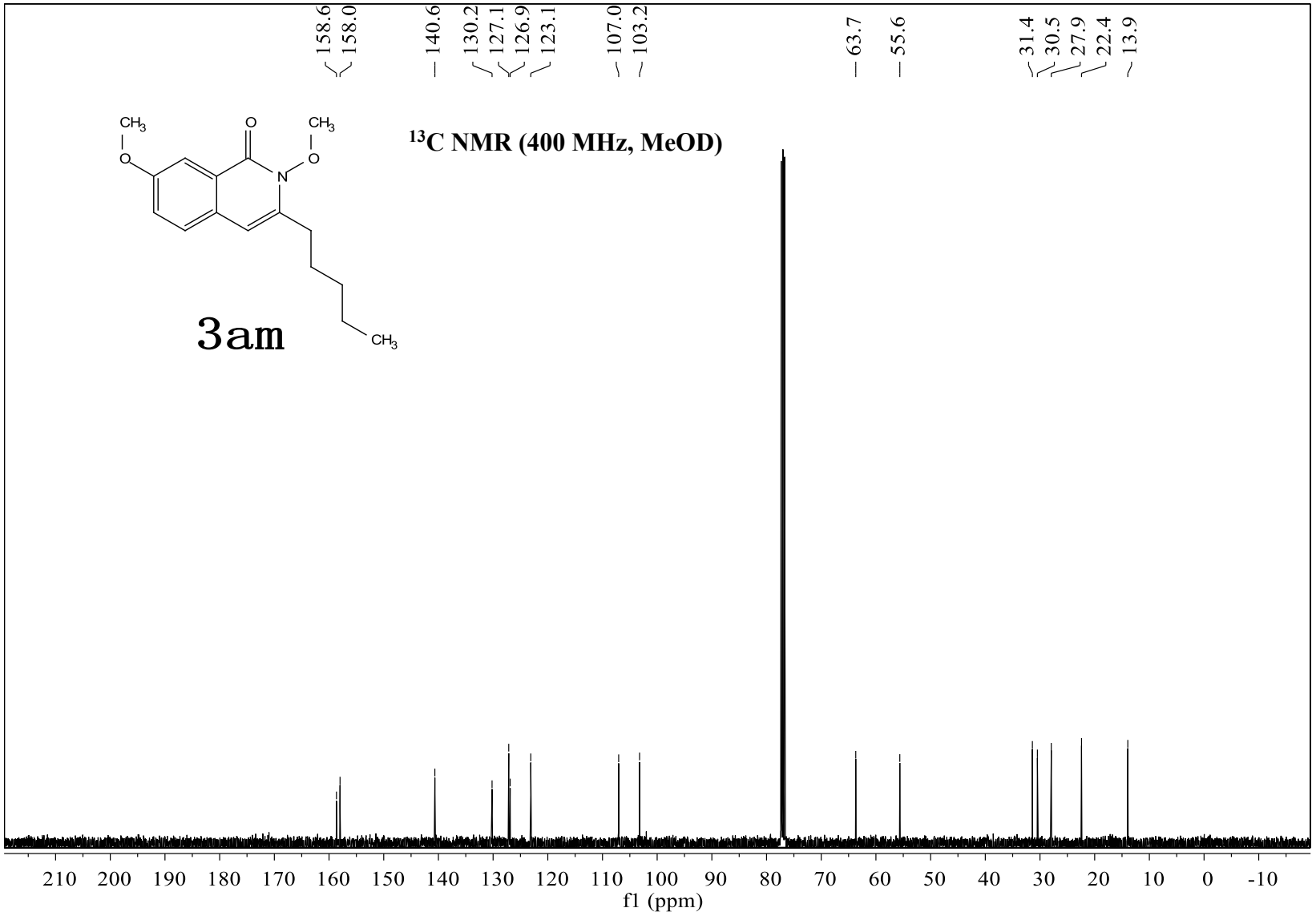

160.8
157.6
143.9
139.0
132.8
117.8
115.2
107.1
102.7
63.6
56.2
31.4
30.5
27.6
22.4
13.9
H3C
O
O
CH3
O
N
3ak
CH3
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

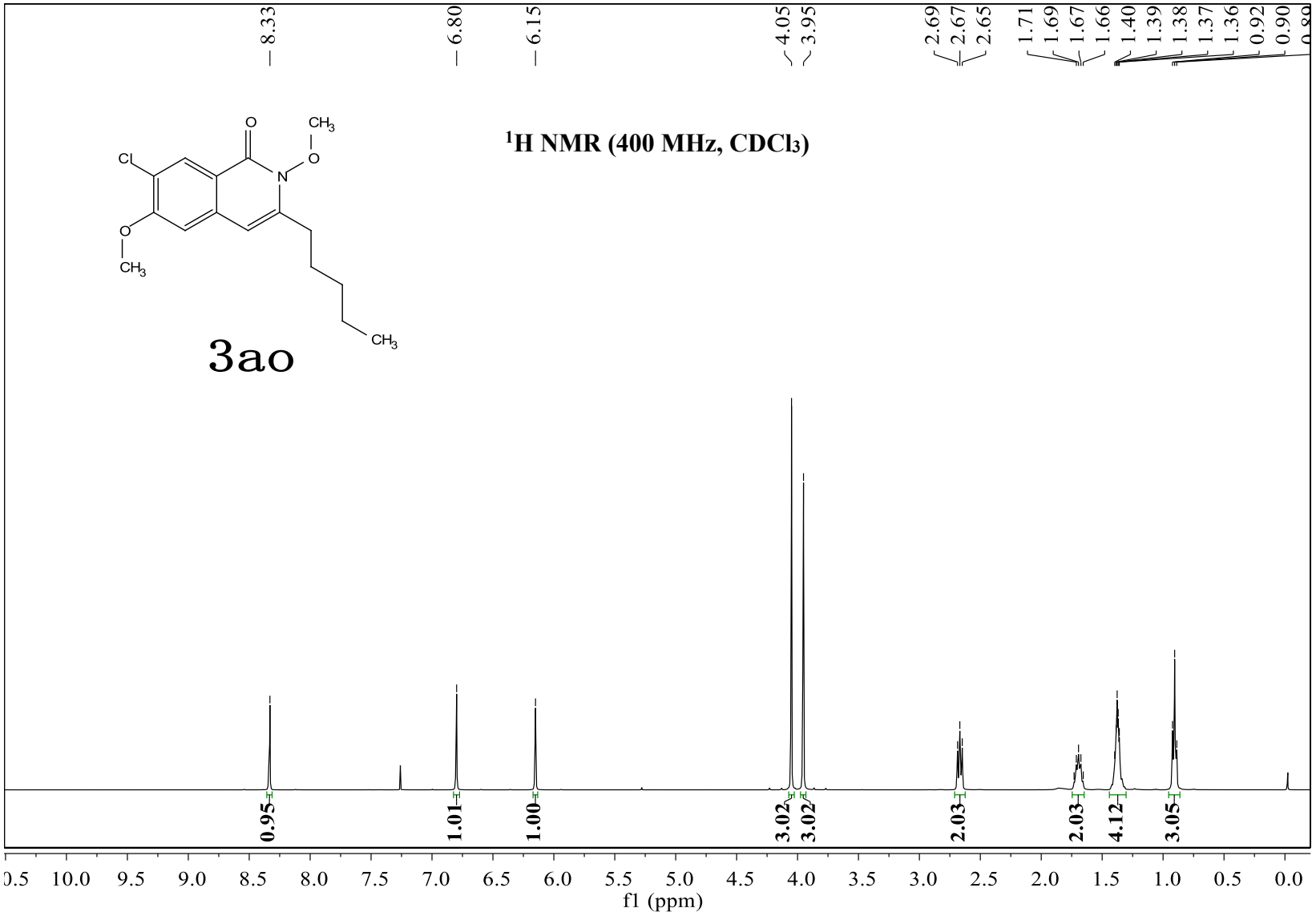

8.29
8.27
6.99
6.99
6.97
6.96
6.79
6.78
6.16
4.06
3.87
2.70
2.68
2.66
1.72
1.71
1.69
1.67
1.40
1.39
1.38
1.38
1.37
0.93
0.91
O
CH3
N
O
O
CH3
CH3
3a1
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.02
1.03
3.08
3.08
2.05
2.03
4.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

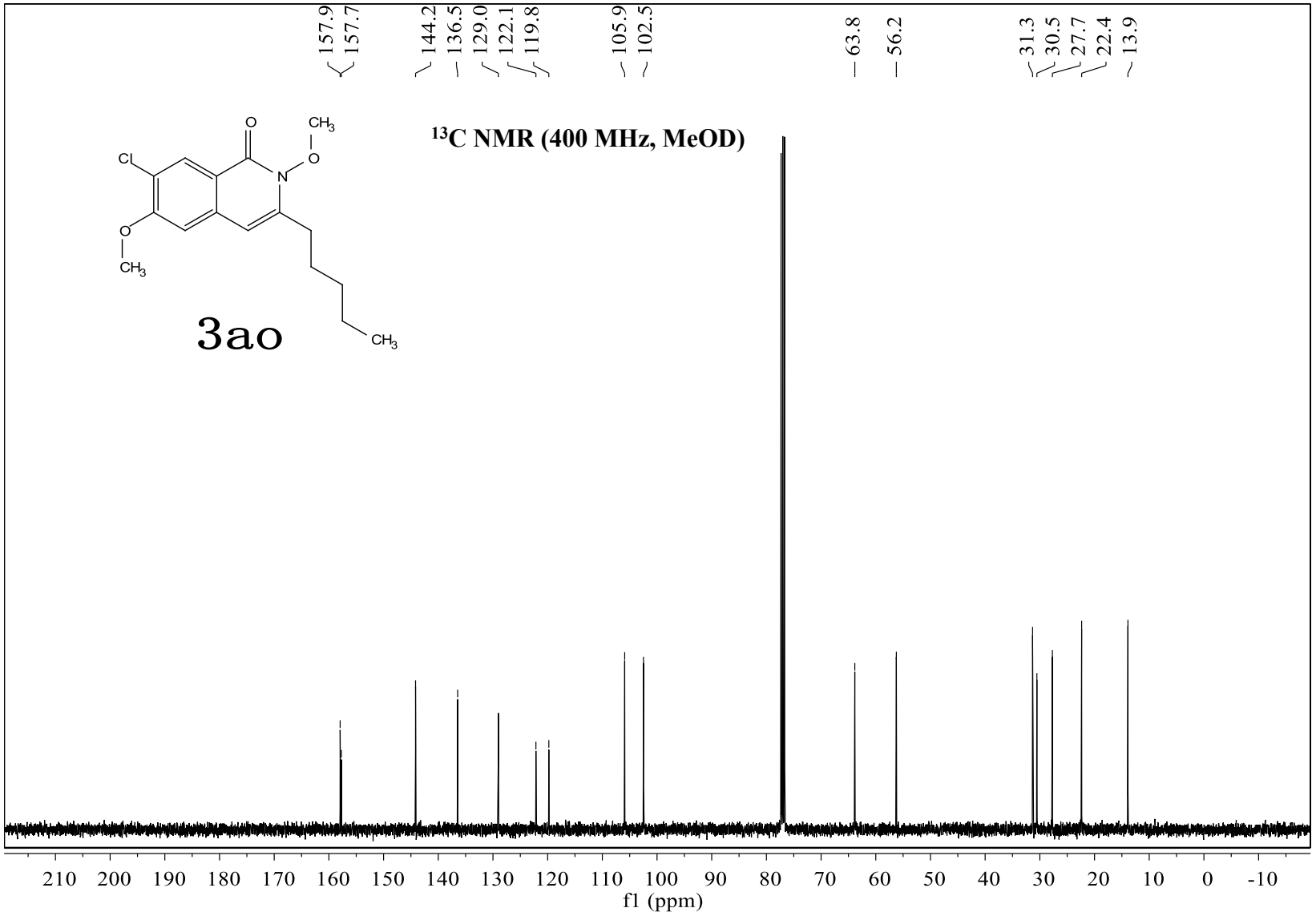

162.7
158.7
143.7
138.0
129.5
119.6
115.5
106.1
103.0
63.8
55.4
31.4
30.6
27.8
22.4
13.9
13C NMR (400 MHz, MeOD)
3a1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

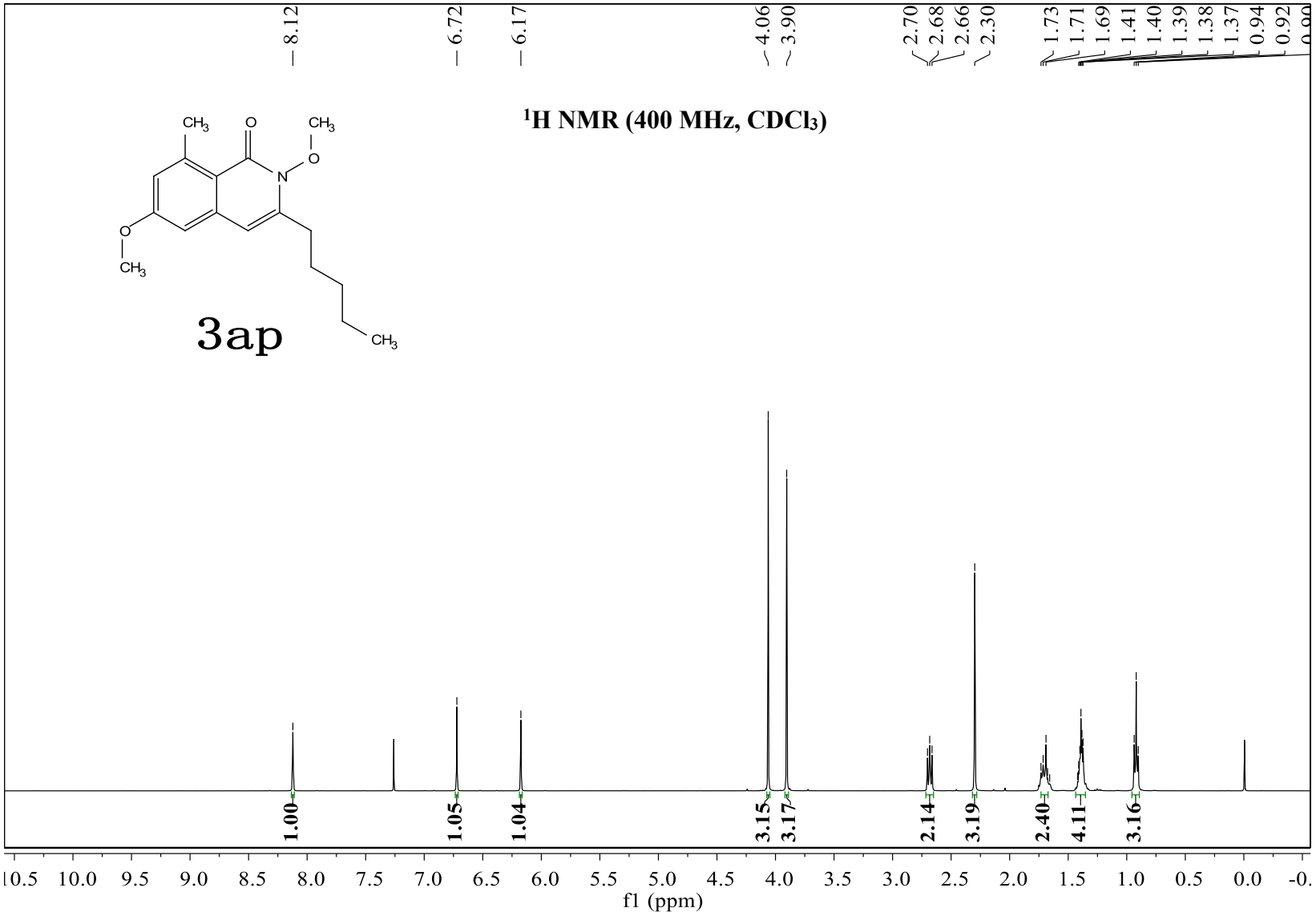


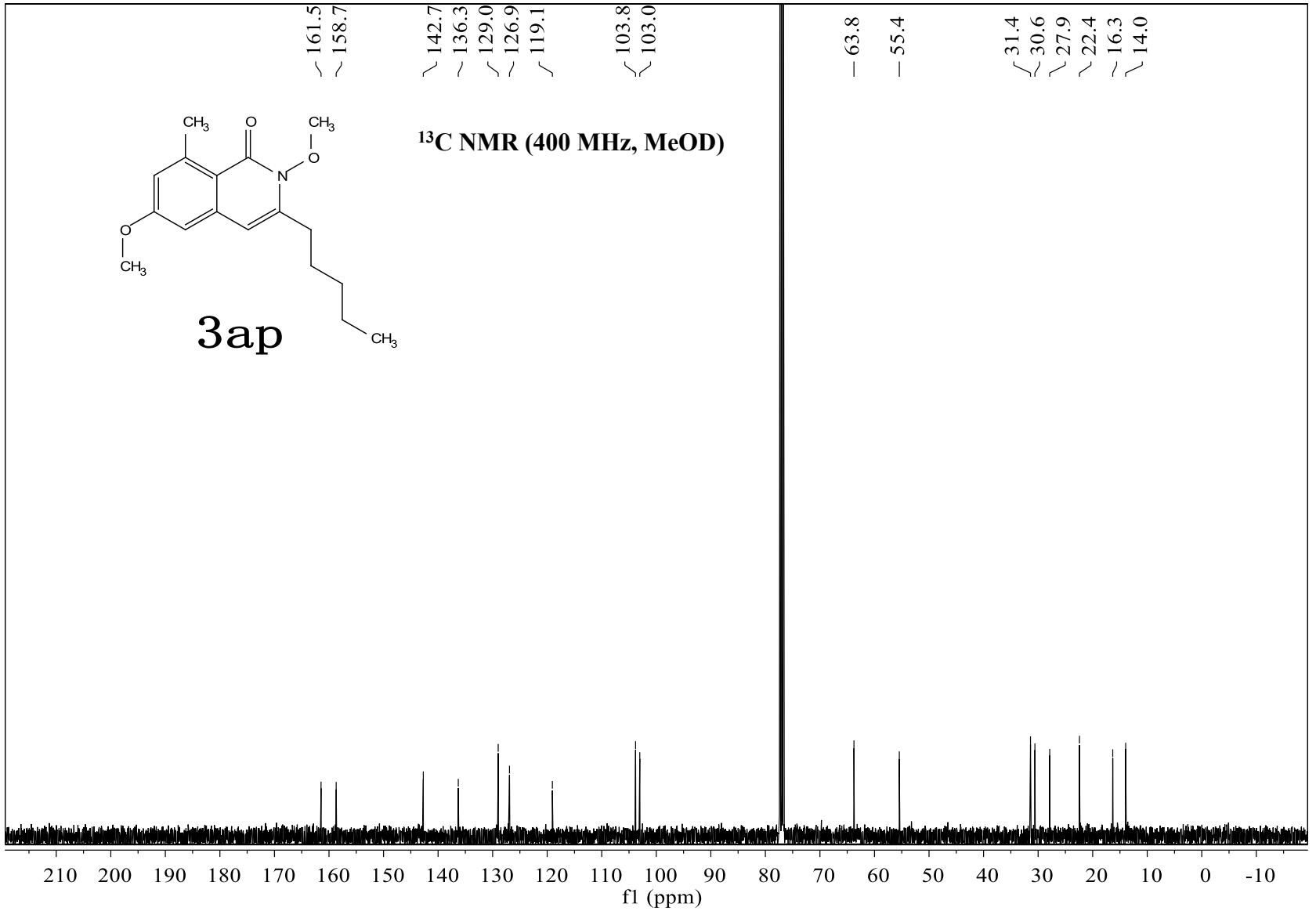
^{1}H NMR (400 MHz, $CDCl_3$)

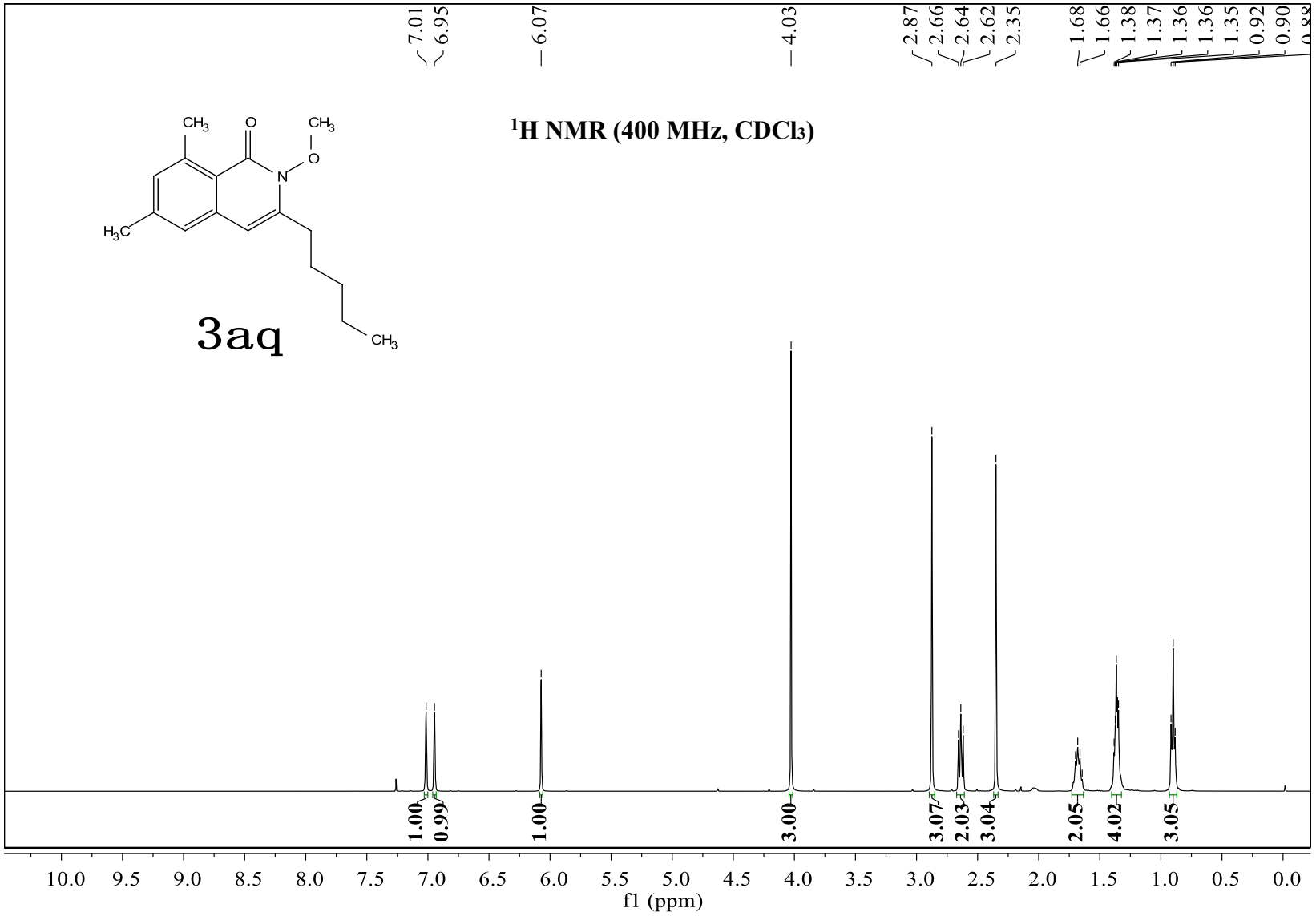

158.6
158.0
140.6
130.2
127.1
126.9
123.1
107.0
103.2
63.7
55.6
31.4
30.5
27.9
22.4
13.9
13C NMR (400 MHz, MeOD)
3am
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

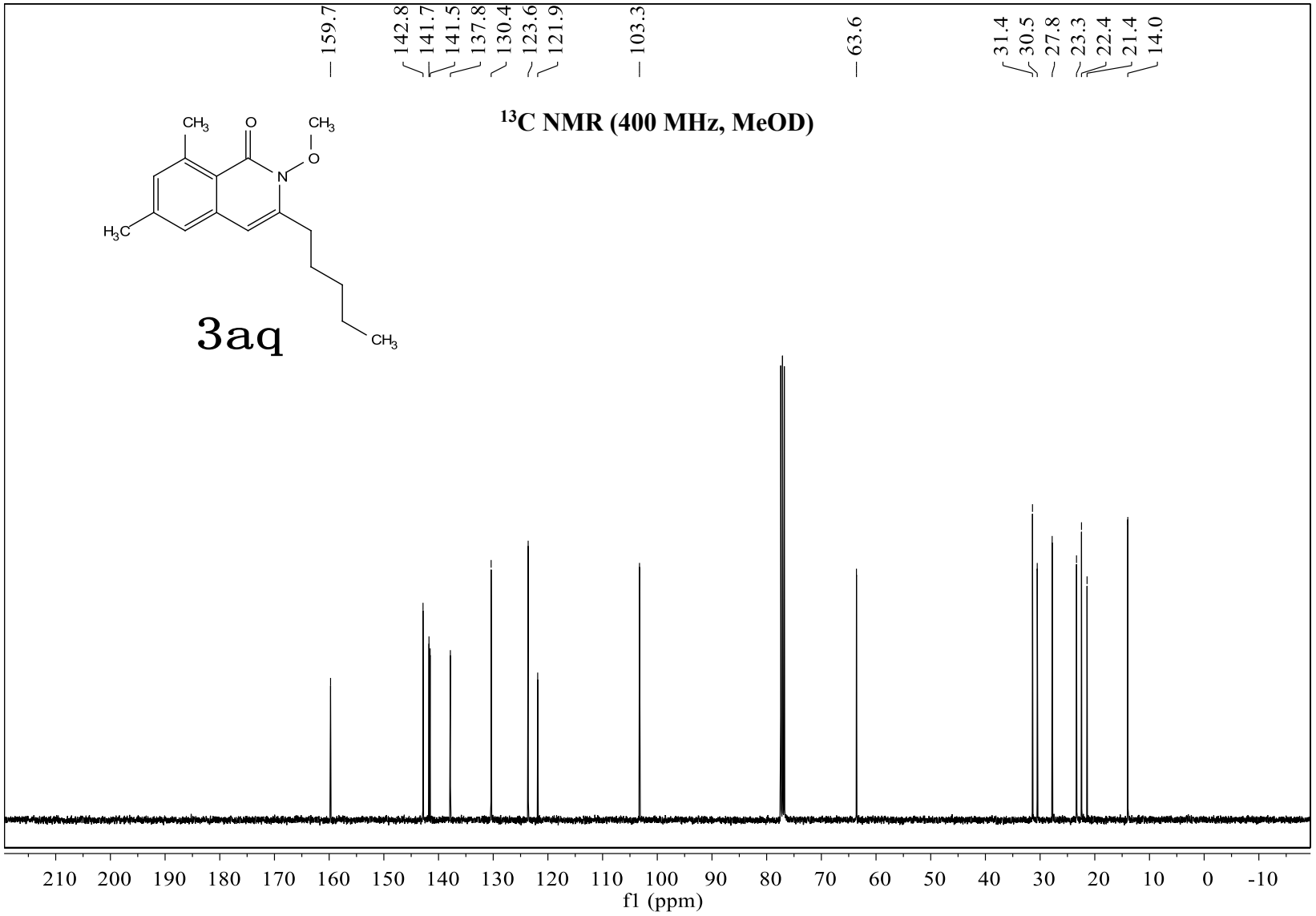

8.33
6.80
6.15
4.05
3.95
2.69
2.67
2.65
1.71
1.69
1.67
1.66
1.40
1.39
1.38
1.37
1.36
0.92
0.90
Cl
O
CH3
N
O
O
CH3
CH3
3ao
1H NMR (400 MHz, CDCl3)
0.95
1.01
1.00
3.02
3.02
2.03
2.03
4.12
3.05
f1 (ppm)

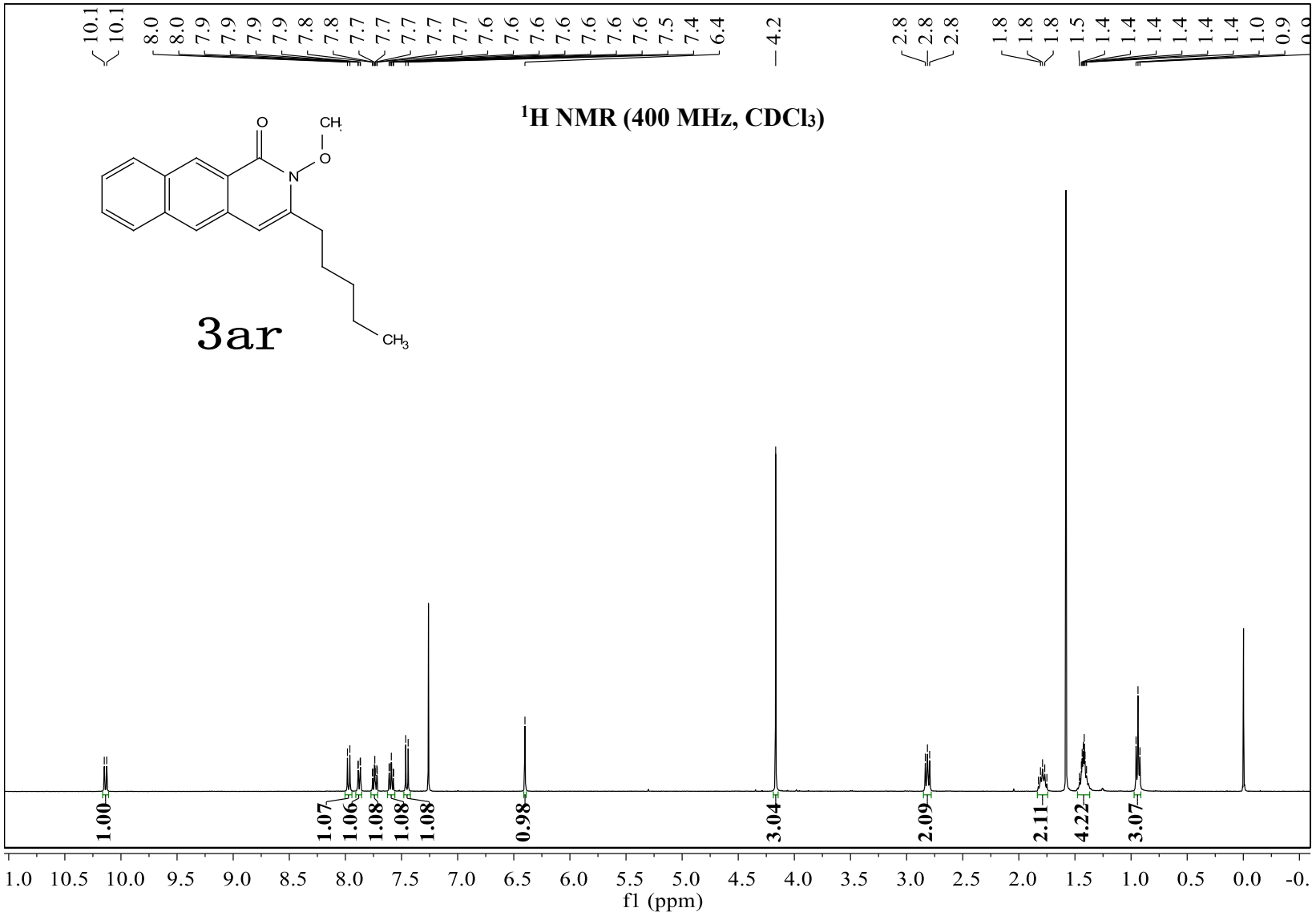

157.9
157.7
144.2
136.5
129.0
122.1
119.8
105.9
102.5
63.8
56.2
31.3
30.5
27.7
22.4
13.9
13C NMR (400 MHz, MeOD)
3ao
f1 (ppm)

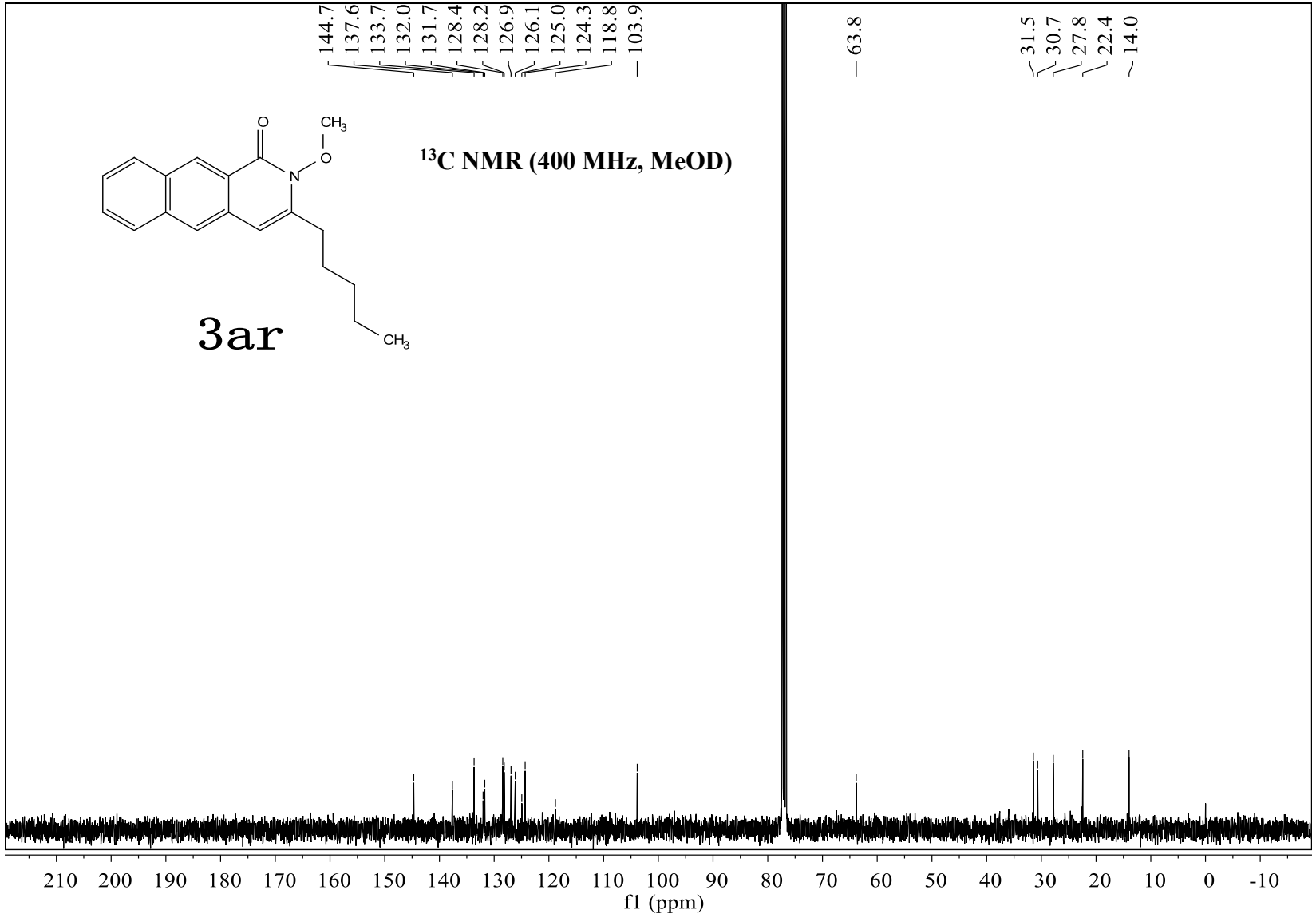

8.12
6.72
6.17
4.06
3.90
2.70
2.68
2.66
2.30
1.73
1.71
1.69
1.41
1.40
1.39
1.38
1.37
0.94
0.92
1H NMR (400 MHz, CDCl3)
CH3
O
CH3
O
N
O
CH3
CH3
3ap
1.00
1.05
1.04
3.15
3.17
2.14
3.19
2.40
4.11
3.16
f1 (ppm)

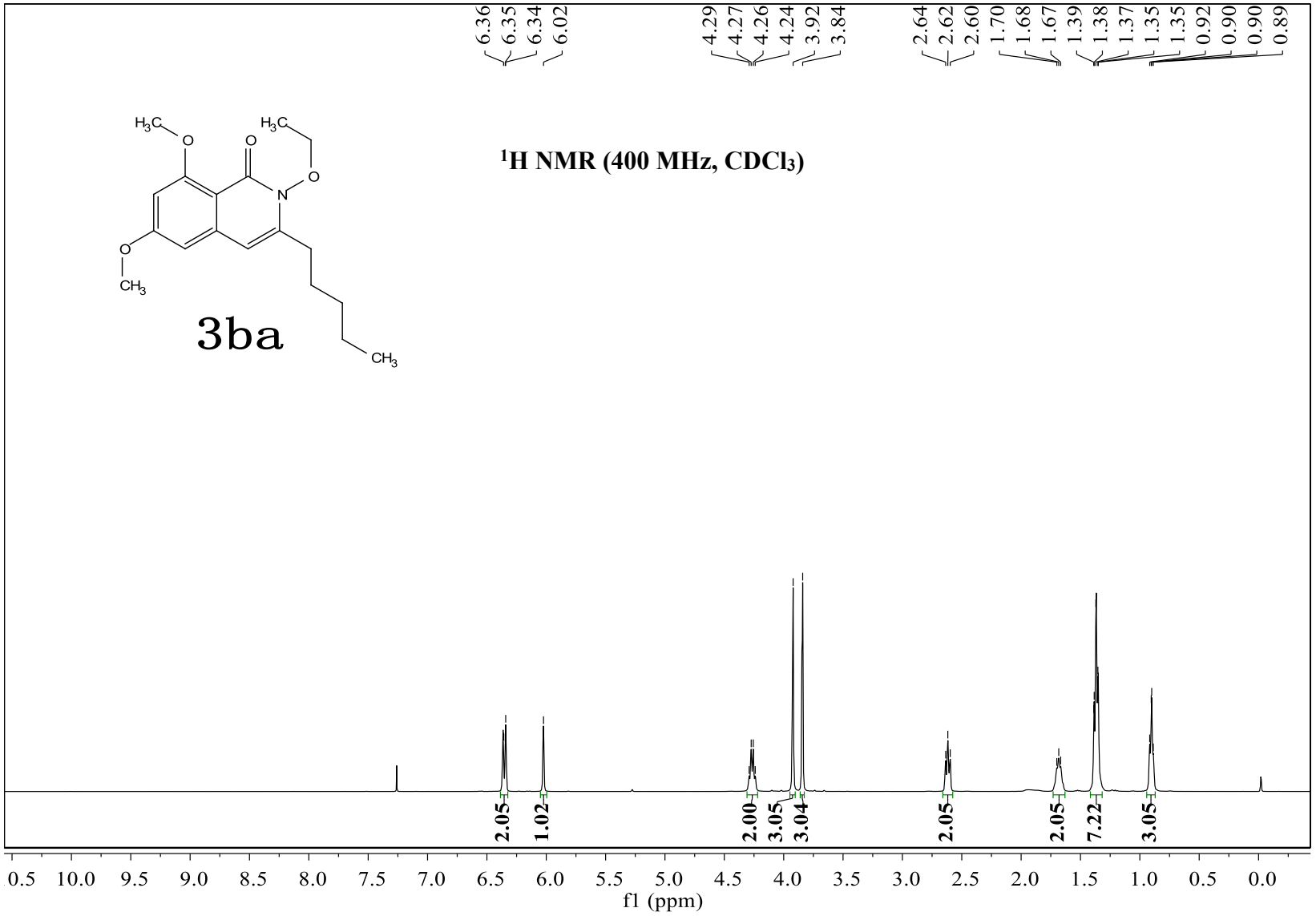

161.5
158.7
142.7
136.3
129.0
126.9
119.1
103.8
103.0
63.8
55.4
31.4
30.6
27.9
22.4
16.3
14.0
CH3
O
CH3
O
N
O
CH3
CH3
13C NMR (400 MHz, MeOD)
3ap
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

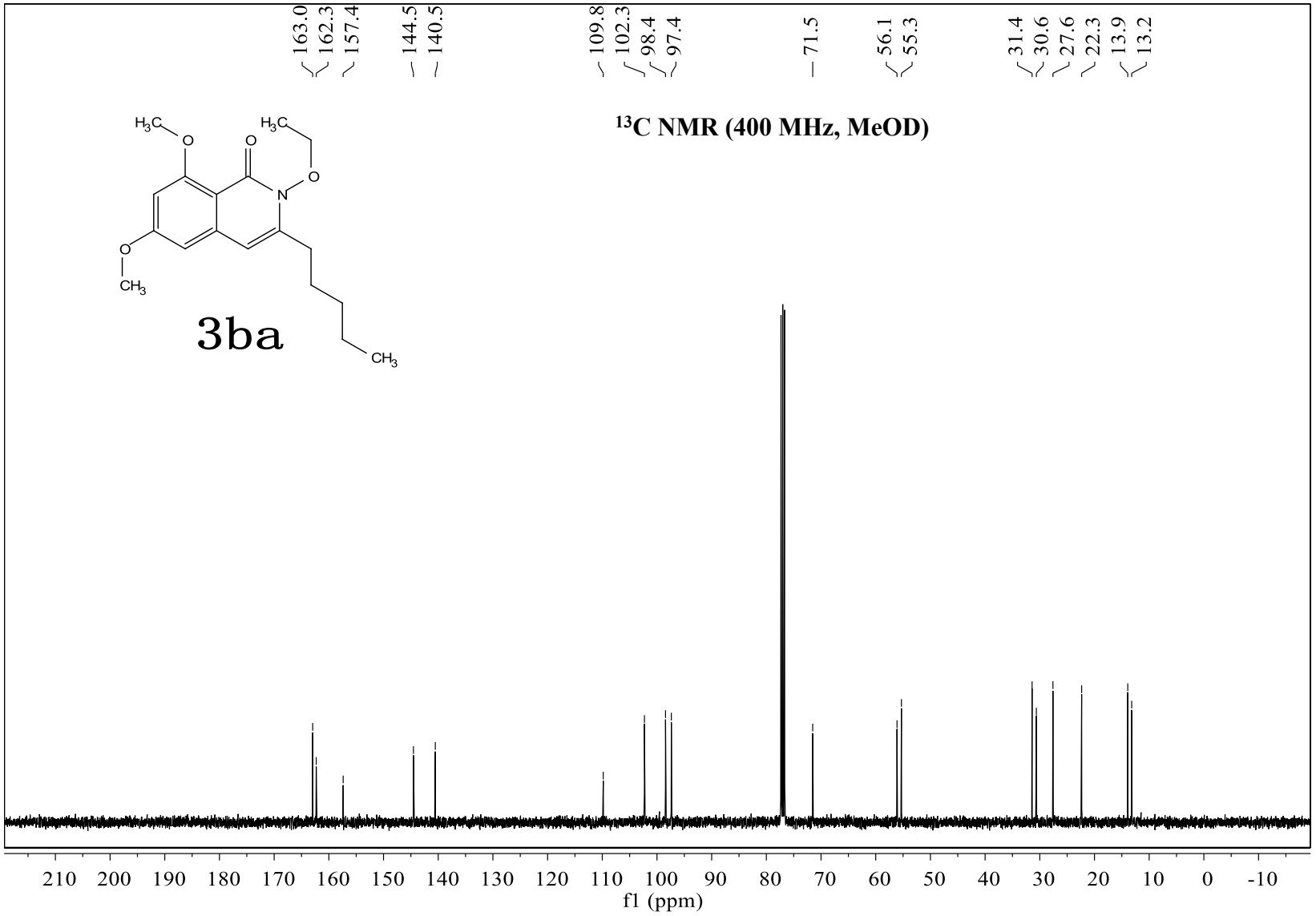

7.01
6.95
6.07
4.03
2.87
2.66
2.64
2.62
2.35
1.68
1.66
1.38
1.37
1.36
1.36
1.35
0.92
0.90
CH3
O
CH3
O
N
H3C
CH3
3aq
1H NMR (400 MHz, CDCl3)
1.00
0.99
1.00
3.00
3.07
2.03
3.04
2.05
4.02
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

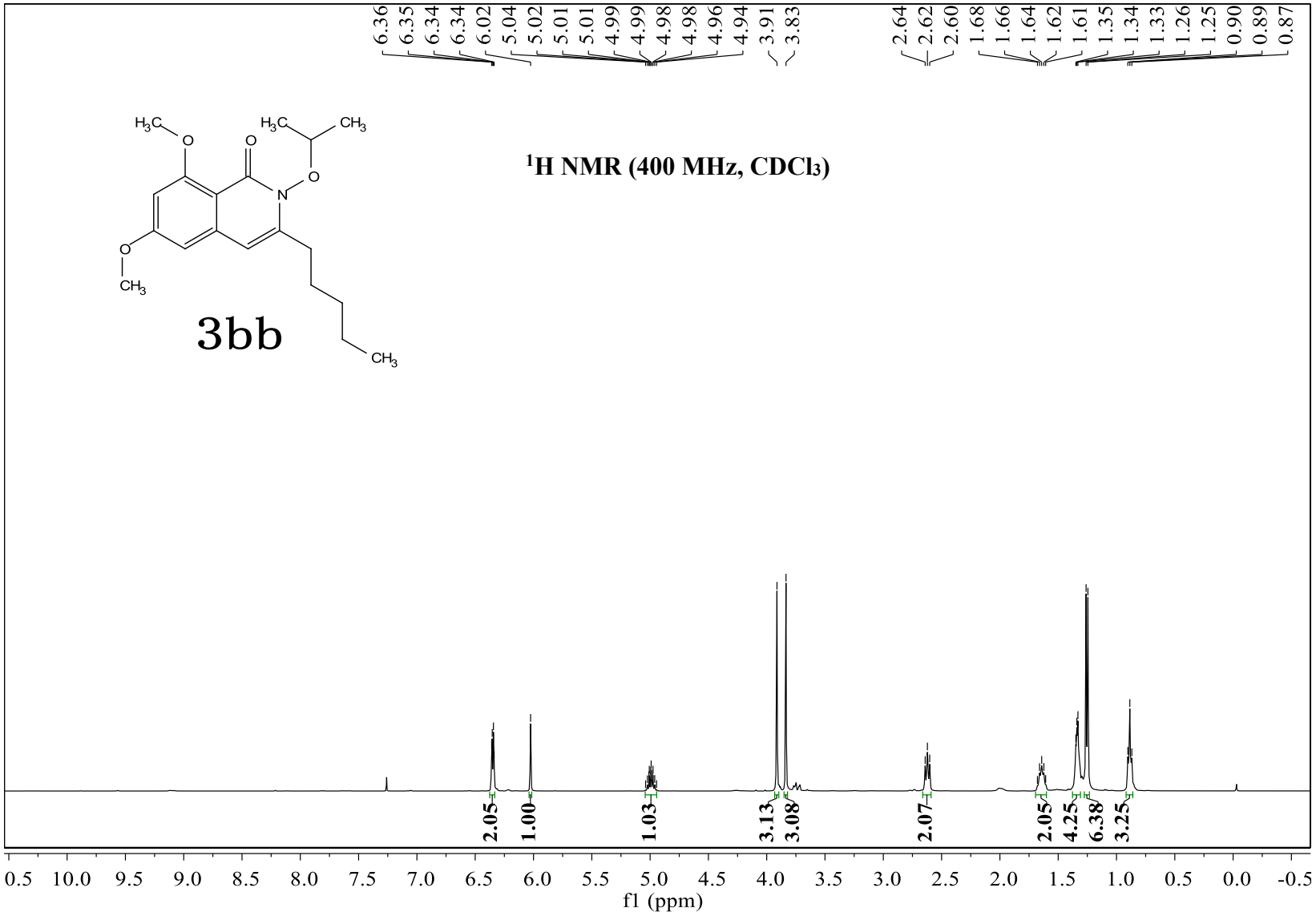

159.7
142.8
141.7
141.5
137.8
130.4
123.6
121.9
103.3
63.6
31.4
30.5
27.8
23.3
22.4
21.4
14.0
13C NMR (400 MHz, MeOD)
CH3
O
CH3
O
N
H3C
CH3
3aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

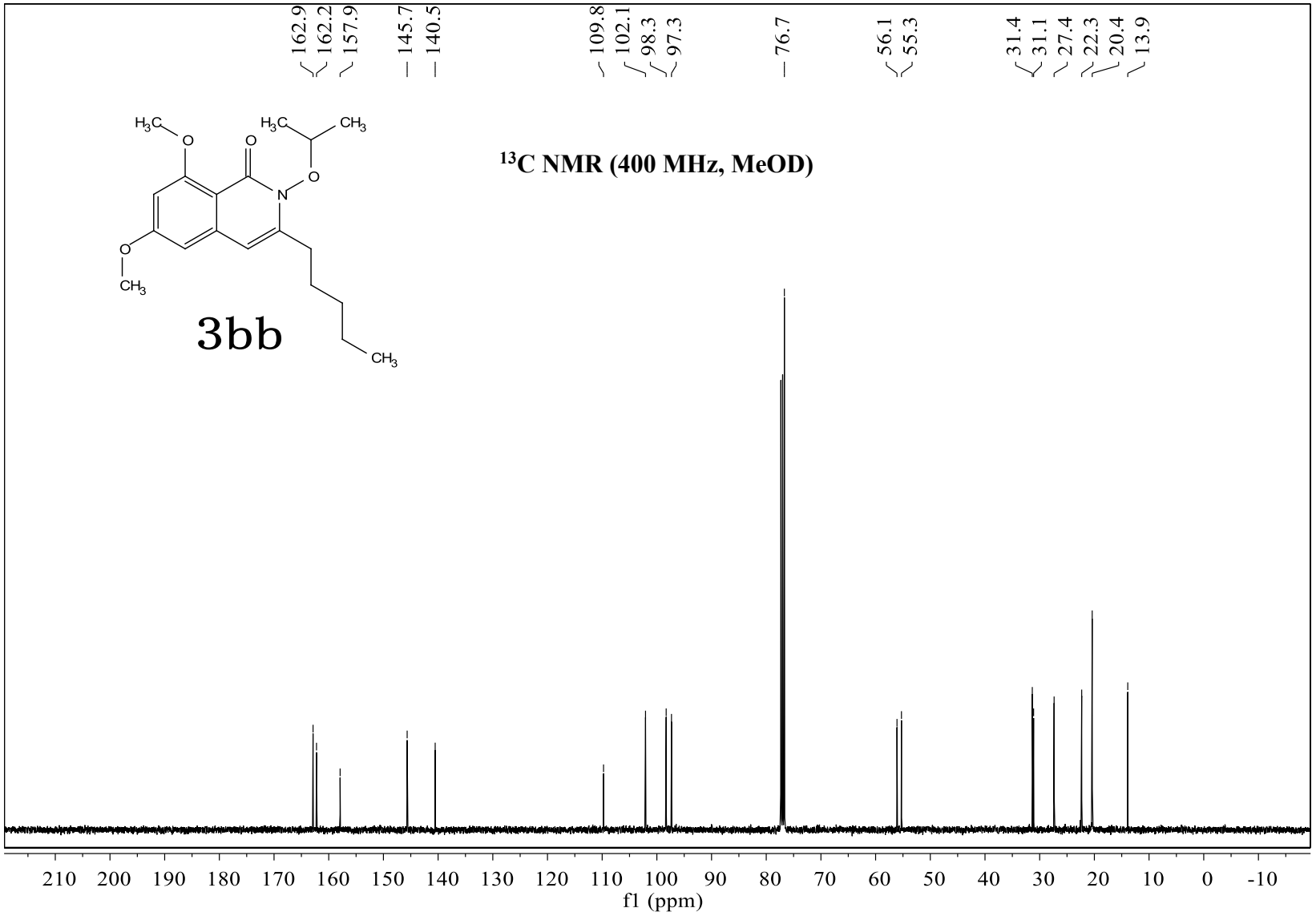

10.1
10.1
8.0
8.0
7.9
7.9
7.9
7.9
7.8
7.8
7.7
7.7
7.7
7.7
7.7
7.6
7.6
7.6
7.6
7.6
7.6
7.5
7.4
6.4
4.2
2.8
2.8
2.8
1.8
1.8
1.8
1.5
1.4
1.4
1.4
1.4
1.4
1.4
1.0
0.9
1H NMR (400 MHz, CDCl3)
O
CH3
O
N
3ar
CH3
1.00
1.07
1.06
1.08
1.08
1.08
0.98
3.04
2.09
2.11
4.22
3.07
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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.
f1 (ppm)

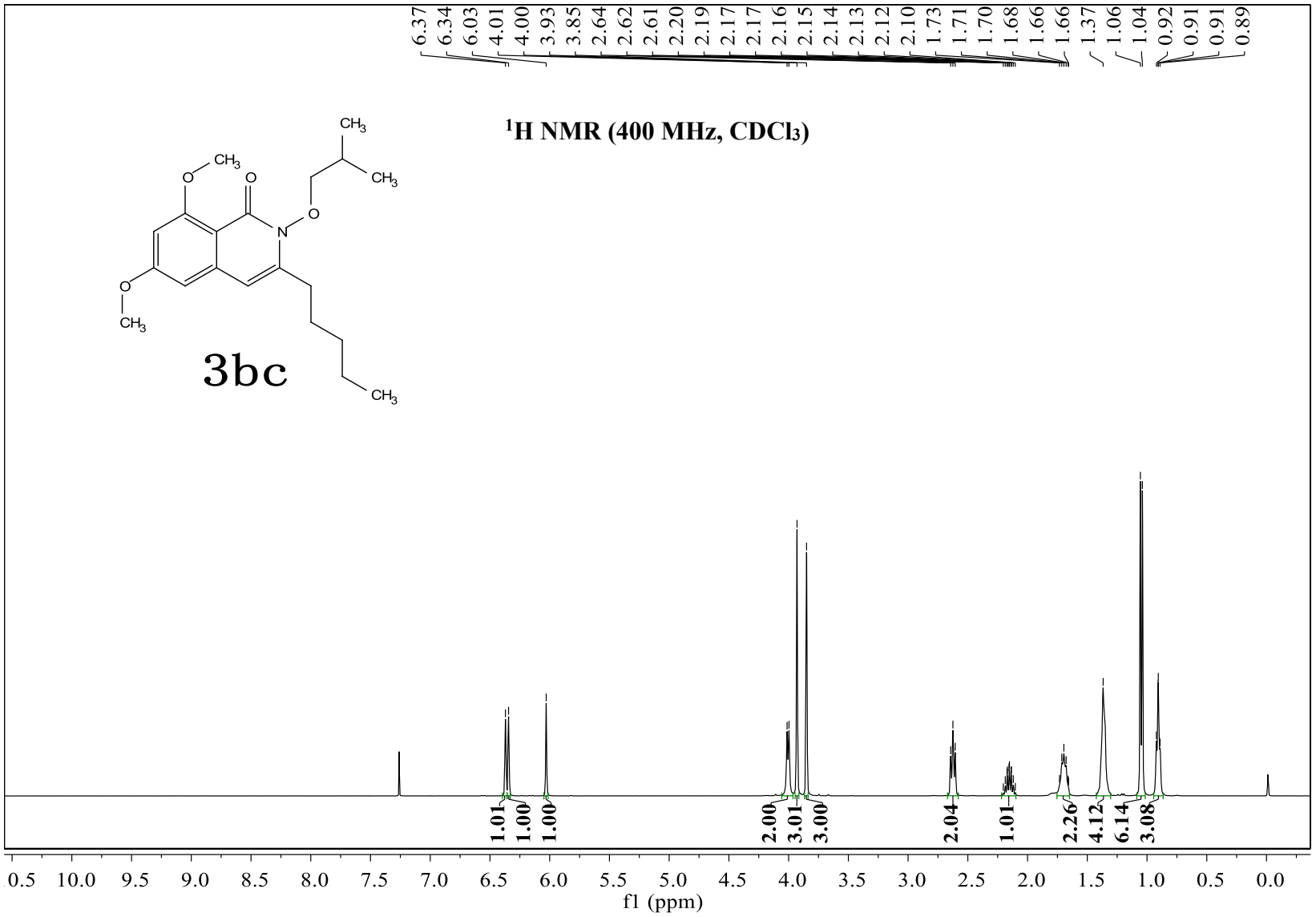

144.7
137.6
133.7
132.0
131.7
128.4
128.2
126.9
126.1
125.0
124.3
118.8
103.9
63.8
31.5
30.7
27.8
22.4
14.0
O
CH3
O
N
CH3
3ar
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

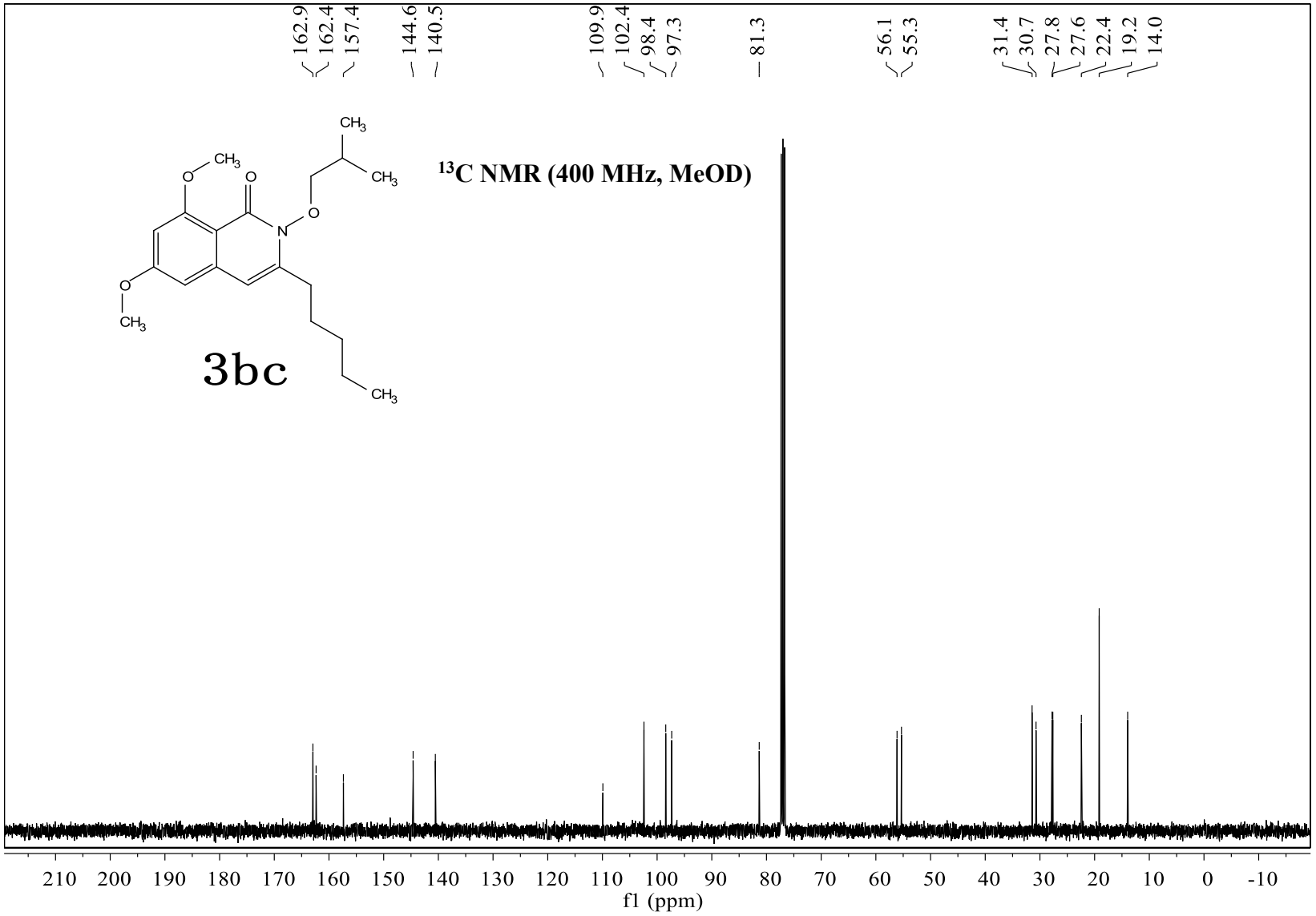

6.36
6.35
6.34
6.02
4.29
4.27
4.26
4.24
3.92
3.84
2.64
2.62
2.60
1.70
1.68
1.67
1.39
1.38
1.37
1.35
1.35
0.92
0.90
0.90
0.89
H3C
O
O
H3C
O
N
O
O
CH3
CH3
3ba
1H NMR (400 MHz, CDCl3)
2.05
1.02
2.00
3.05
3.04
2.05
2.05
7.22
3.05
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

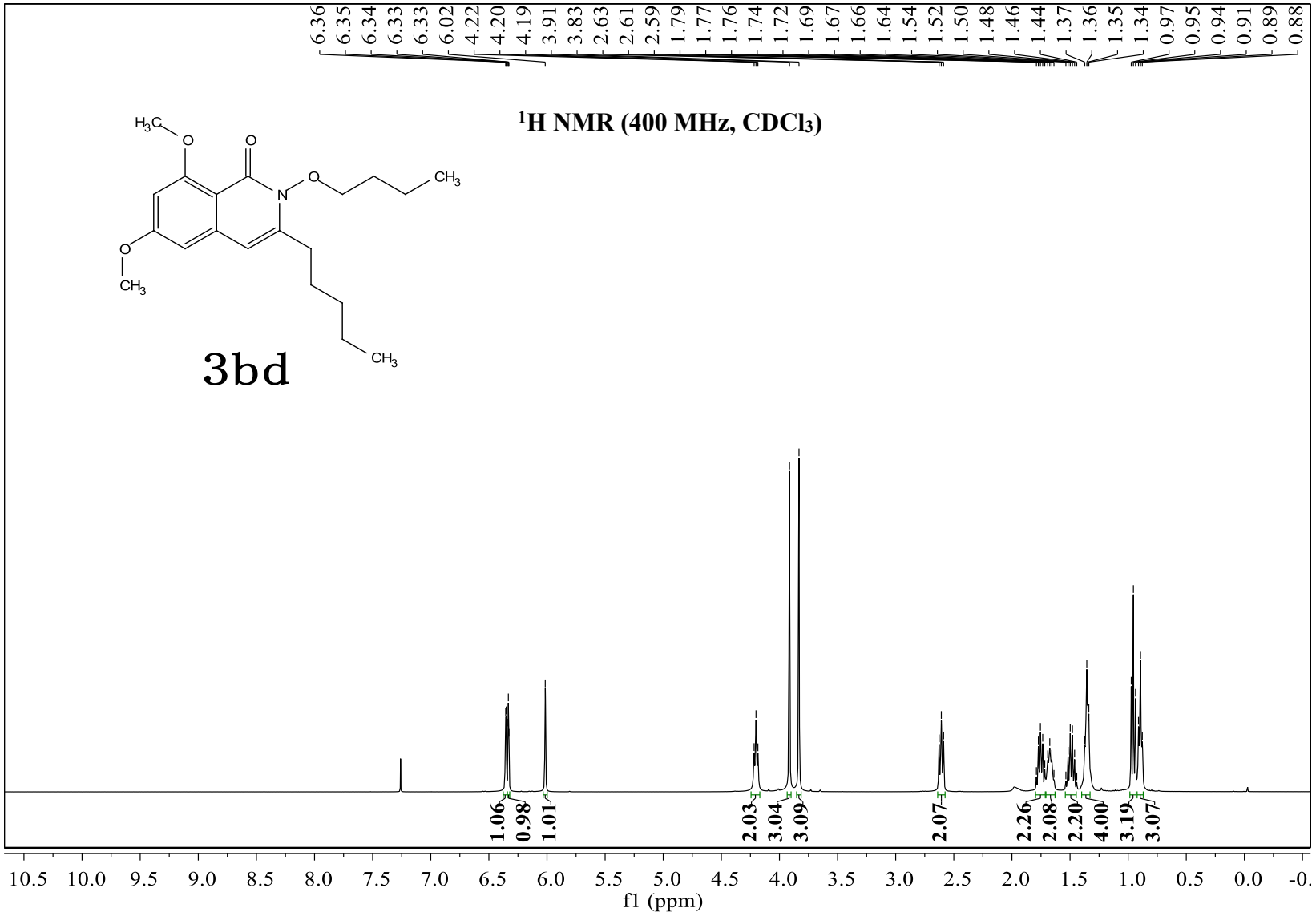

163.0
162.3
157.4
144.5
140.5
109.8
102.3
98.4
97.4
71.5
56.1
55.3
31.4
30.6
27.6
22.3
13.9
13.2
^{13}C NMR (400 MHz, MeOD)
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

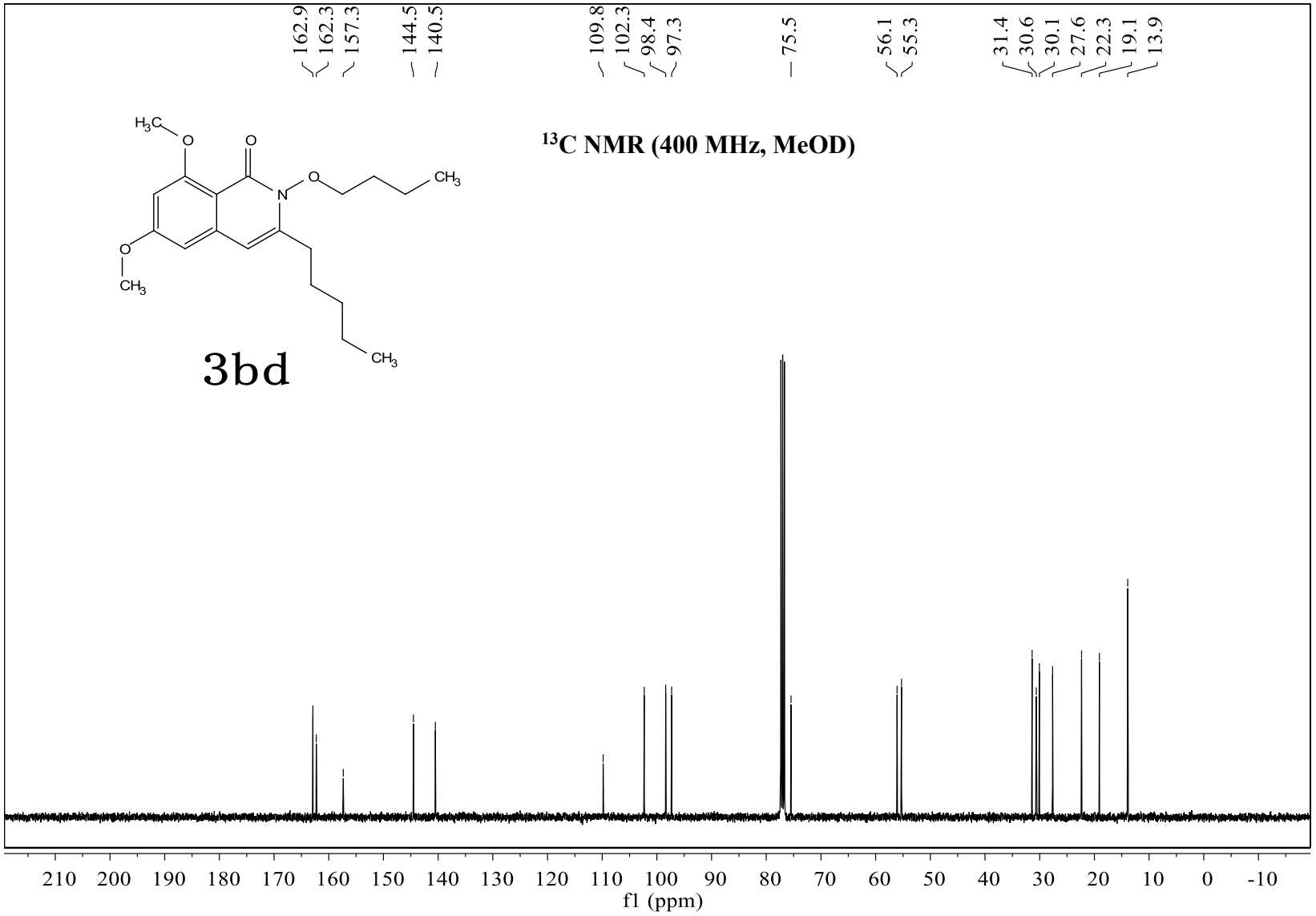

6.36
6.35
6.34
6.34
6.02
5.04
5.02
5.01
5.01
4.99
4.99
4.98
4.98
4.96
4.94
3.91
3.83
2.64
2.62
2.60
1.68
1.66
1.64
1.62
1.61
1.35
1.34
1.33
1.26
1.25
0.90
0.89
0.87
H3C
O
O
H3C
CH3
N
O
O
CH3
CH3
3bb
1H NMR (400 MHz, CDCl3)
2.05
1.00
1.03
3.13
3.08
2.07
2.05
4.25
6.38
3.25
0.5 10.0 9.5 9.0 8.5 8.0 7.5 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)

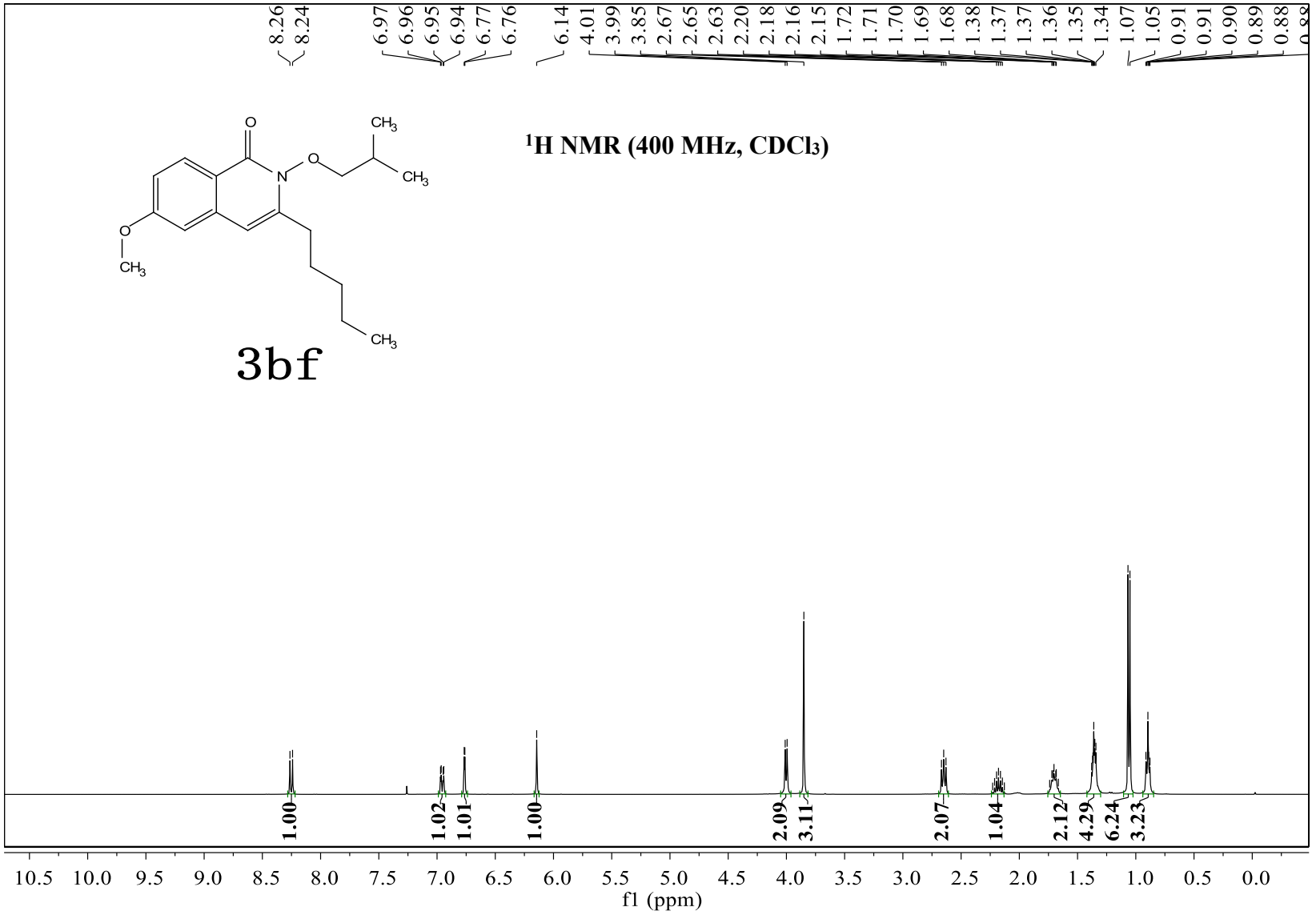

162.9
162.2
157.9
145.7
140.5
109.8
102.1
98.3
97.3
76.7
56.1
55.3
31.4
31.1
27.4
22.3
20.4
13.9
H3C
O
O
H3C
CH3
O
N
O
O
CH3
CH3
3bb
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

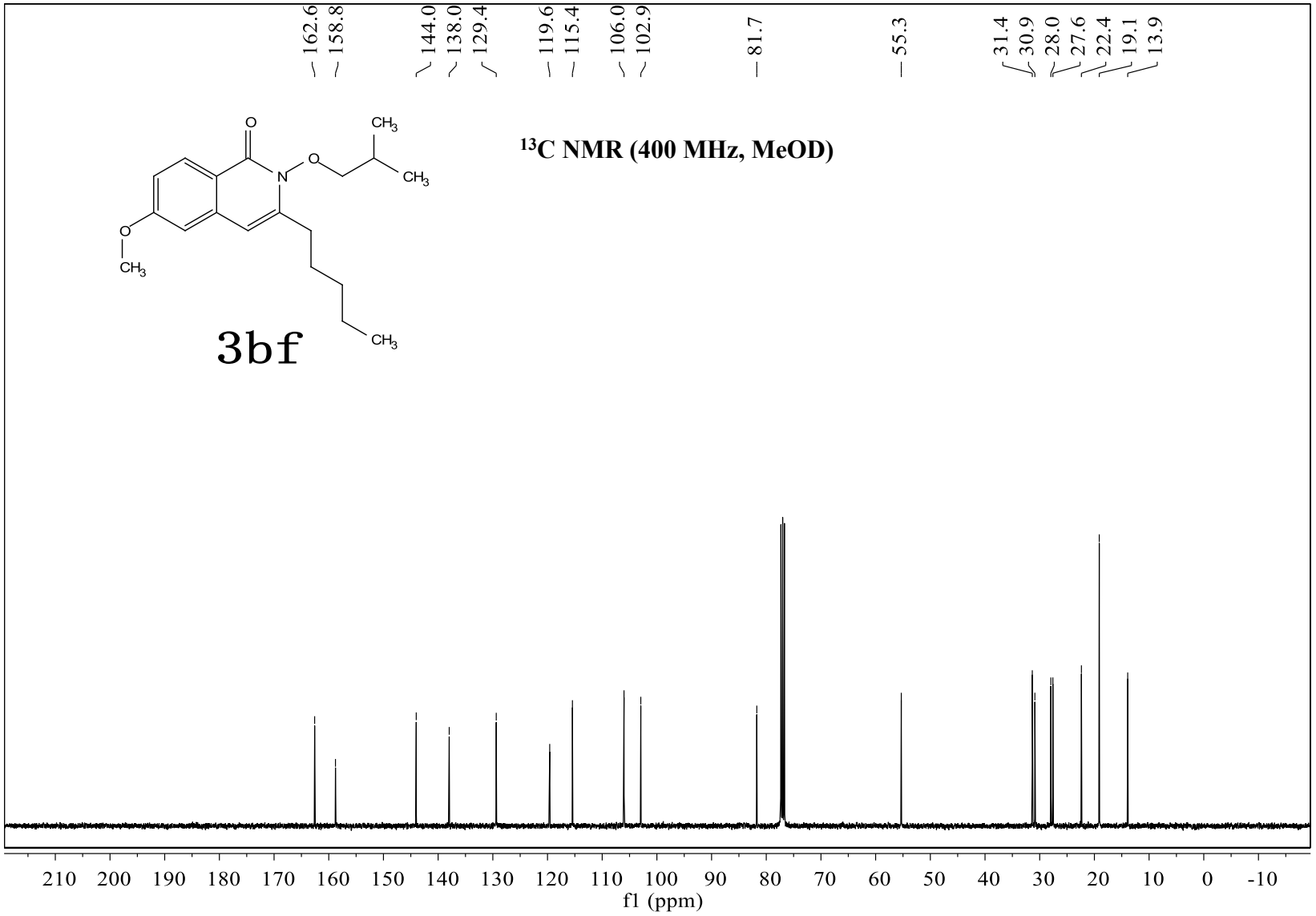

6.37
6.34
6.03
4.01
4.00
3.93
3.85
2.64
2.62
2.61
2.20
2.19
2.17
2.17
2.16
2.15
2.14
2.13
2.12
2.10
1.73
1.71
1.70
1.68
1.66
1.66
1.37
1.06
1.04
0.92
0.91
0.91
0.89
1H NMR (400 MHz, CDCl3)
3bc
1.01
1.00
1.00
2.00
3.01
3.00
2.04
1.01
2.26
4.12
6.14
3.08
f1 (ppm)

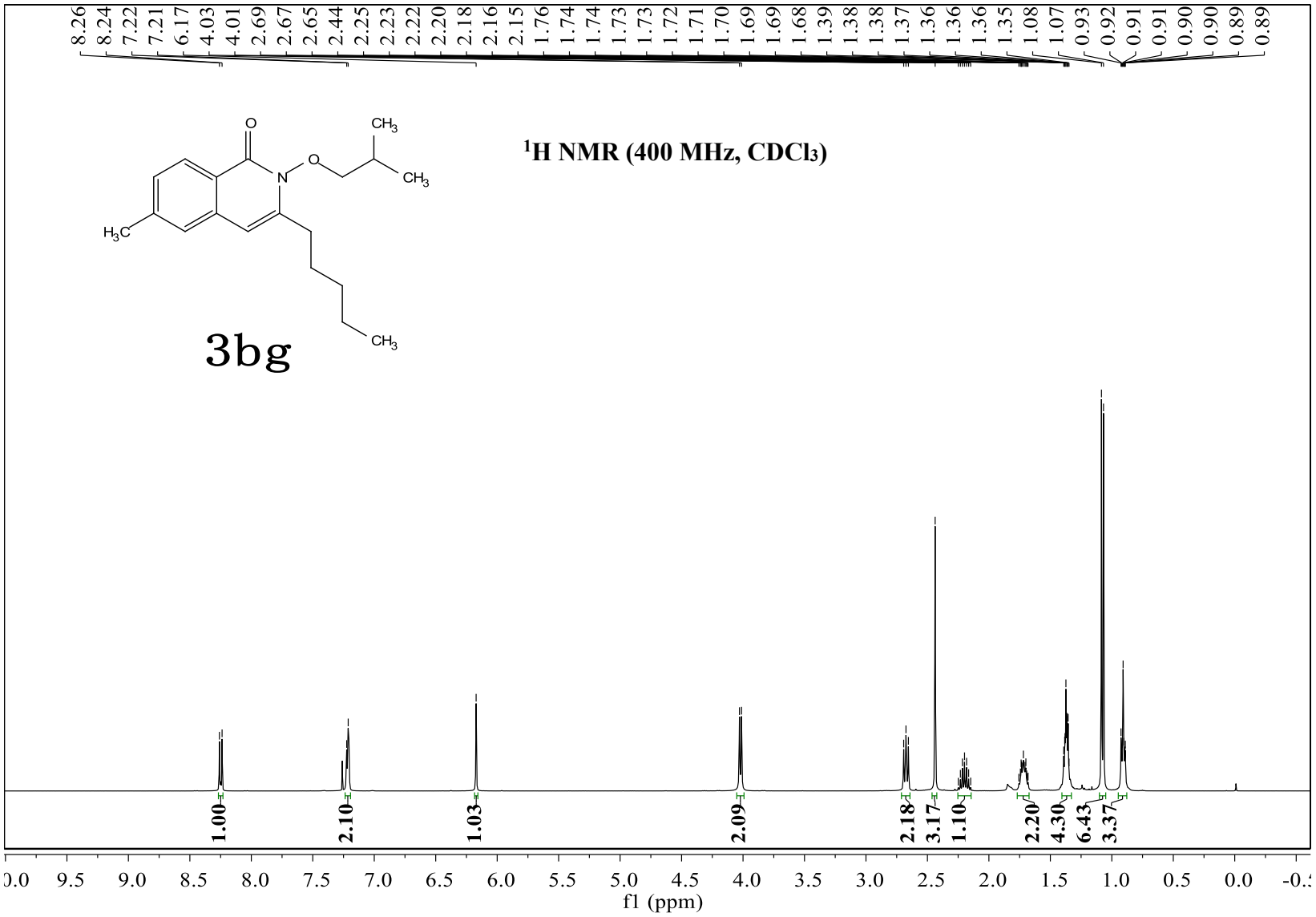

162.9
162.4
157.4
144.6
140.5
109.9
102.4
98.4
97.3
81.3
56.1
55.3
31.4
30.7
27.8
27.6
22.4
19.2
14.0
^{13}C NMR (400 MHz, MeOD)
3bc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

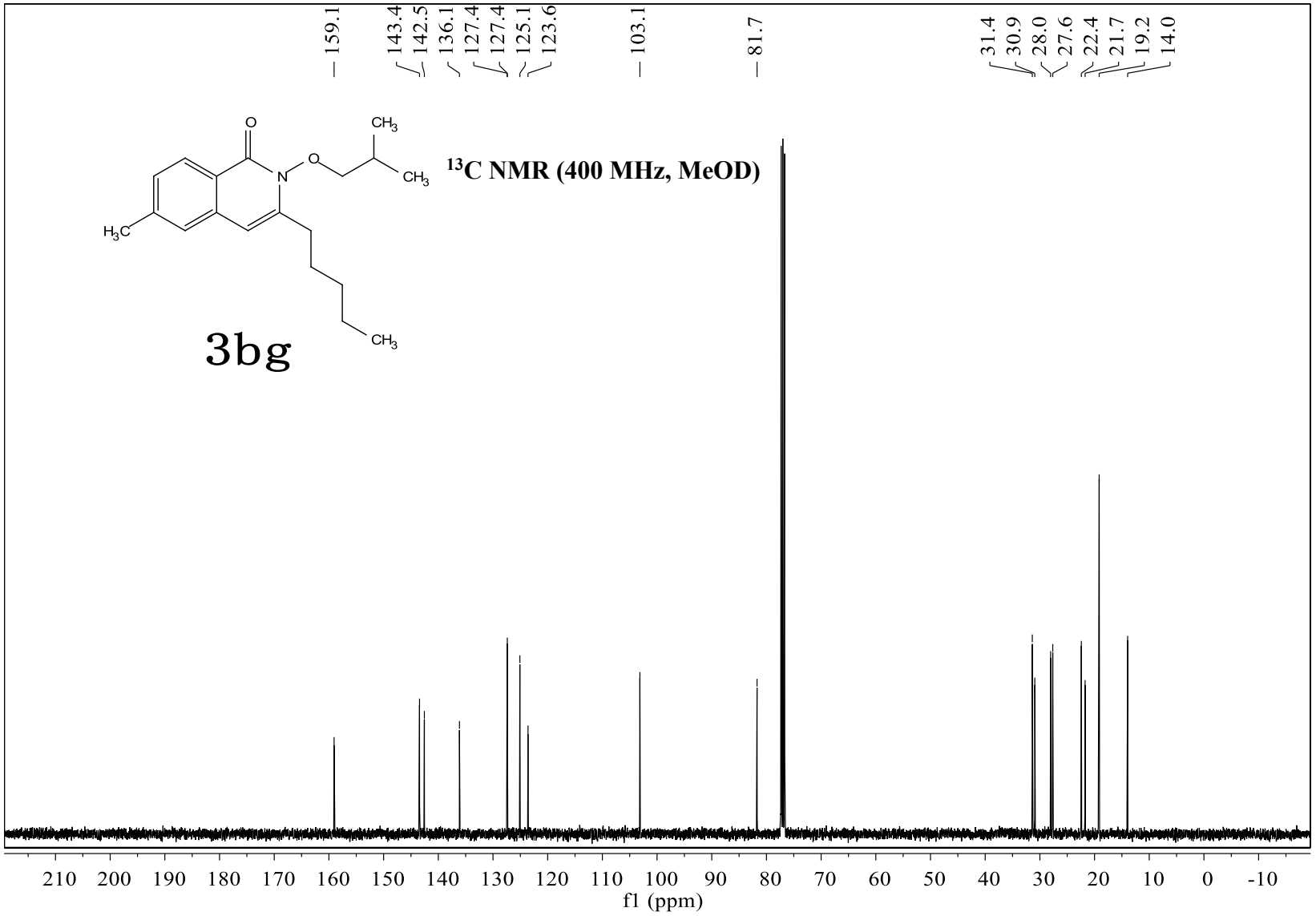

6.36 6.35 6.34 6.33 6.33 6.02 4.22 4.20 4.19 3.91 3.83 2.63 2.61 2.59 1.79 1.77 1.76 1.74 1.72 1.69 1.67 1.66 1.64 1.54 1.52 1.50 1.48 1.46 1.44 1.37 1.36 1.35 1.34 0.97 0.95 0.94 0.91 0.89 0.88
1H NMR (400 MHz, CDCl3)
H3C
O
O
O
N
O
CH3
O
CH3
CH3
3bd
1.06 0.98 1.01 2.03 3.04 3.09 2.07 2.26 2.08 2.20 4.00 3.19 3.07
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.
f1 (ppm)

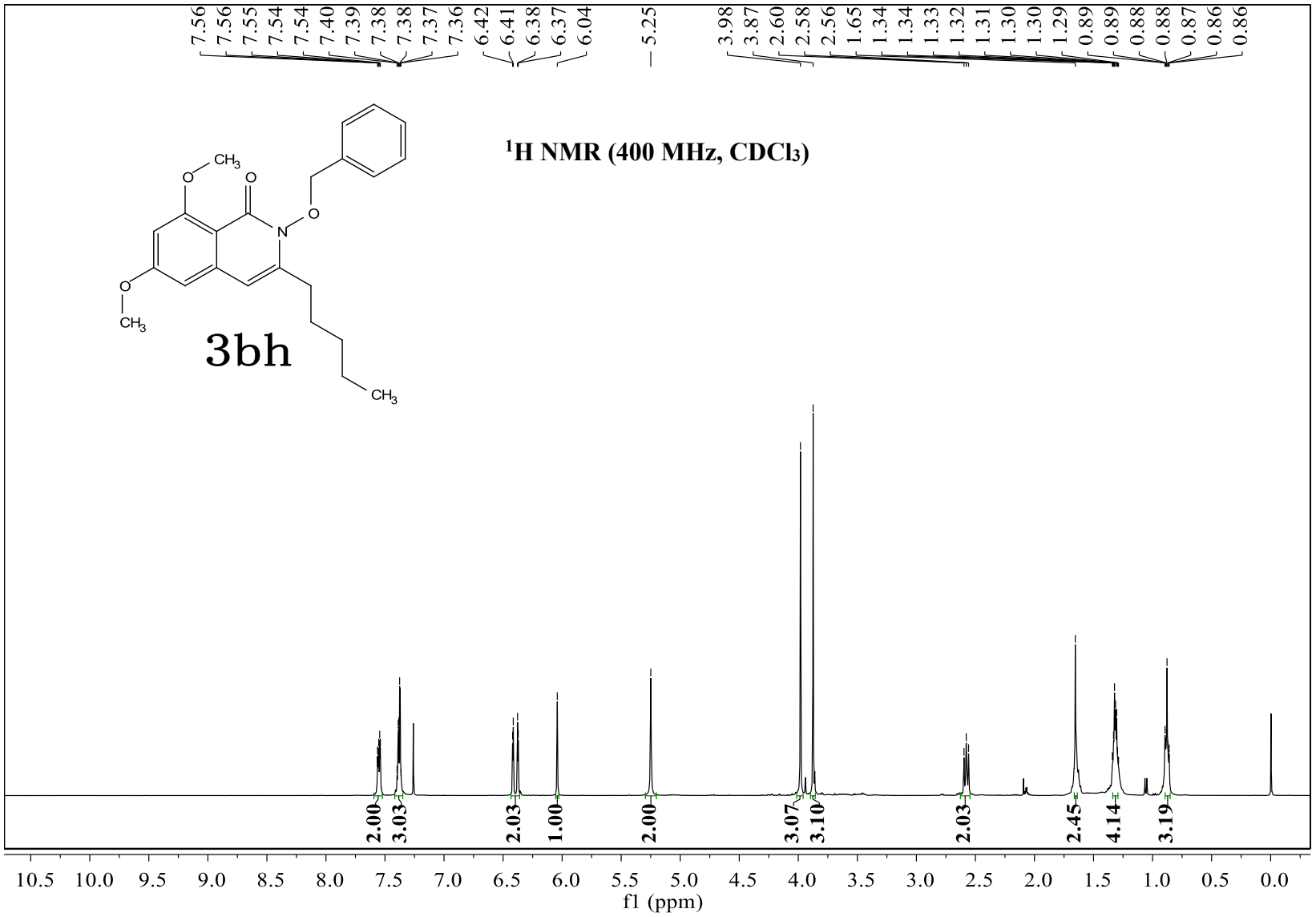

162.9
162.3
157.3
144.5
140.5
109.8
102.3
98.4
97.3
75.5
56.1
55.3
31.4
30.6
30.1
27.6
22.3
19.1
13.9
^{13}C NMR (400 MHz, MeOD)
3bd
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

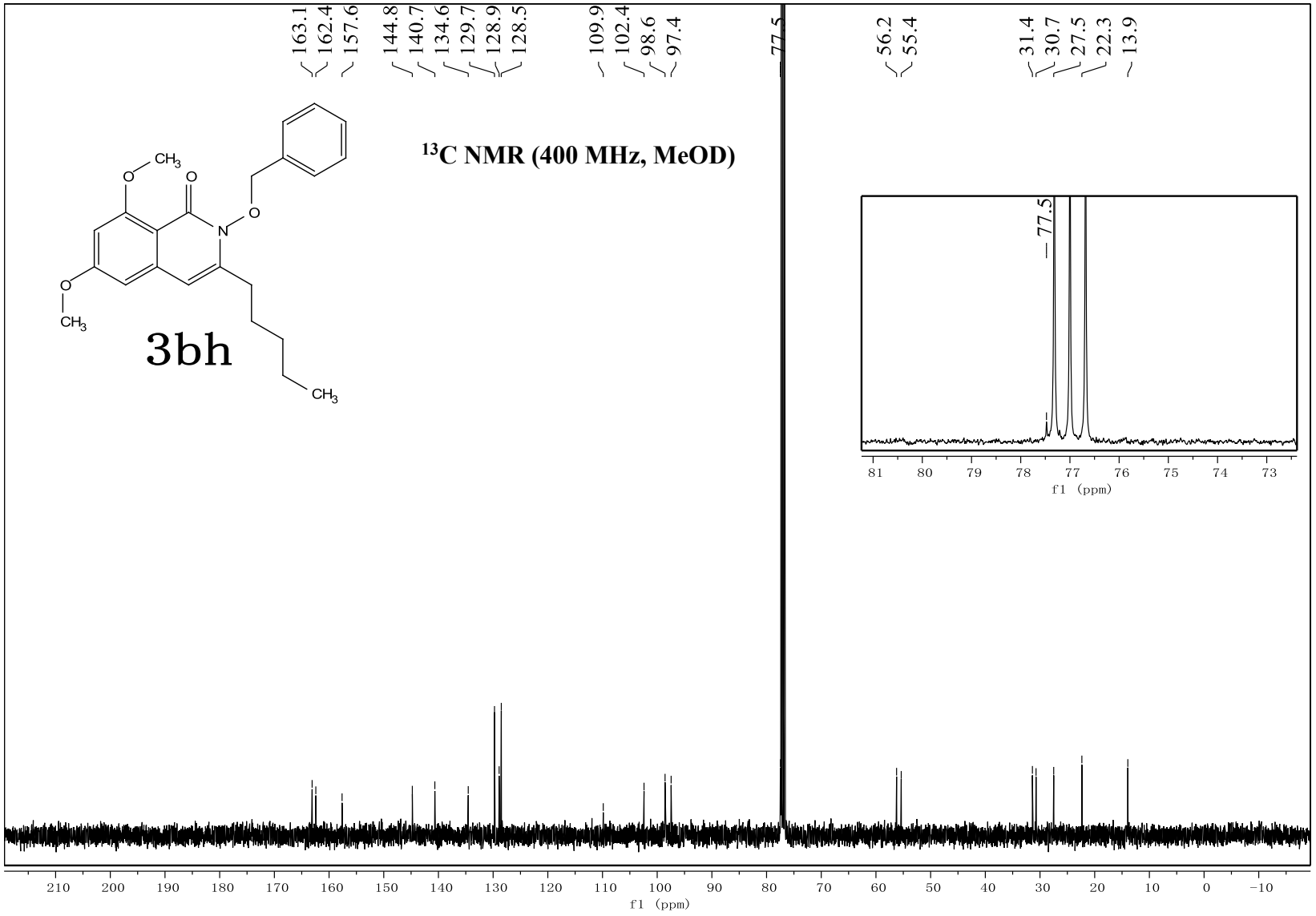

8.26
8.24
6.97
6.96
6.95
6.94
6.77
6.76
6.14
4.01
3.99
3.85
2.67
2.65
2.63
2.20
2.18
2.16
2.15
1.72
1.71
1.70
1.69
1.68
1.38
1.37
1.37
1.36
1.35
1.34
1.07
1.05
0.91
0.91
0.90
0.89
0.88
O
CH3
N
O
CH3
O
CH3
CH3
3bf
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.01
1.00
2.09
3.11
2.07
1.04
2.12
4.29
6.24
3.23
10.5 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
f1 (ppm)

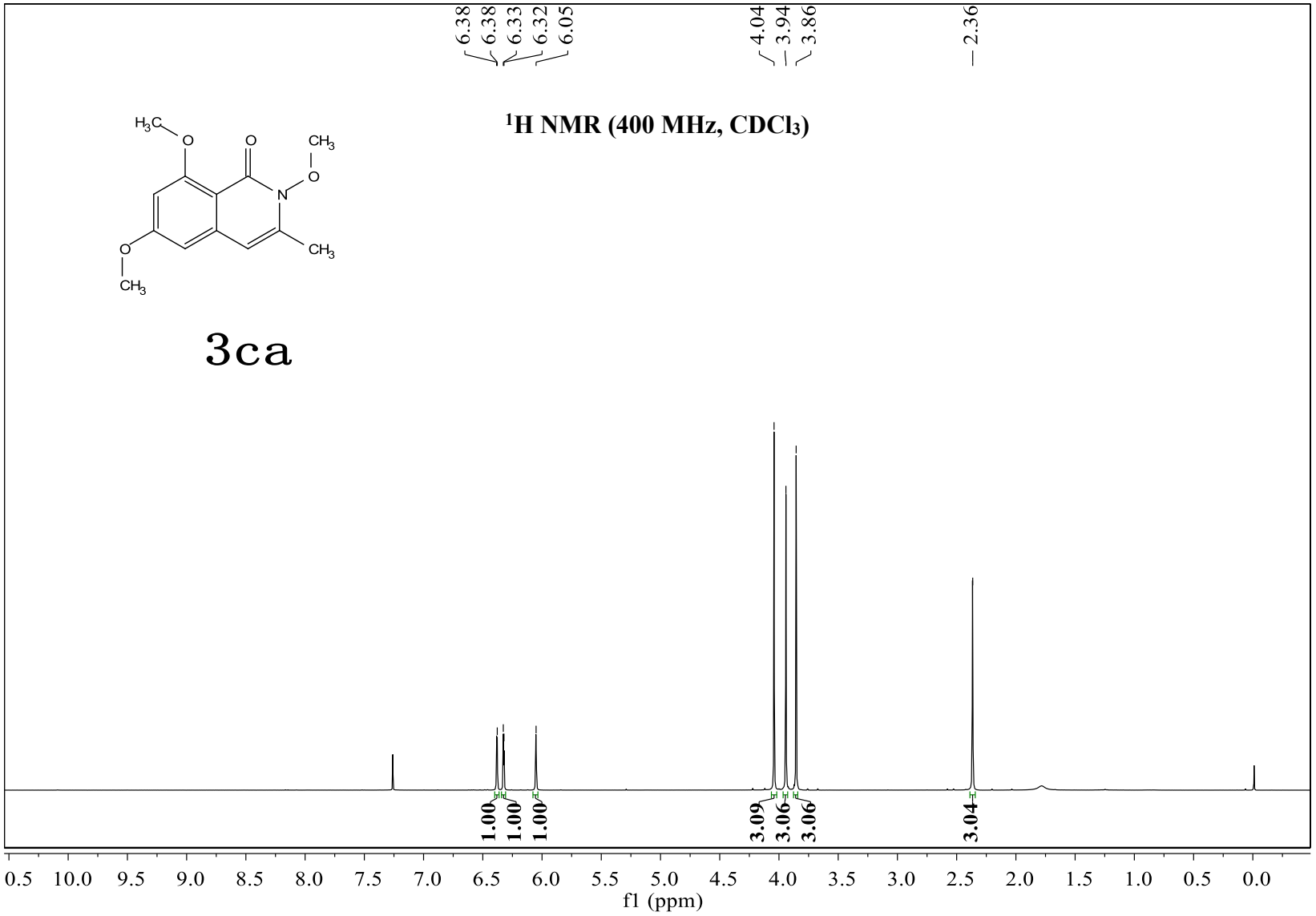

162.6
158.8
144.0
138.0
129.4
119.6
115.4
106.0
102.9
81.7
55.3
31.4
30.9
28.0
27.6
22.4
19.1
13.9
O
N
O
CH3
CH3
O
CH3
CH3
3bf
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

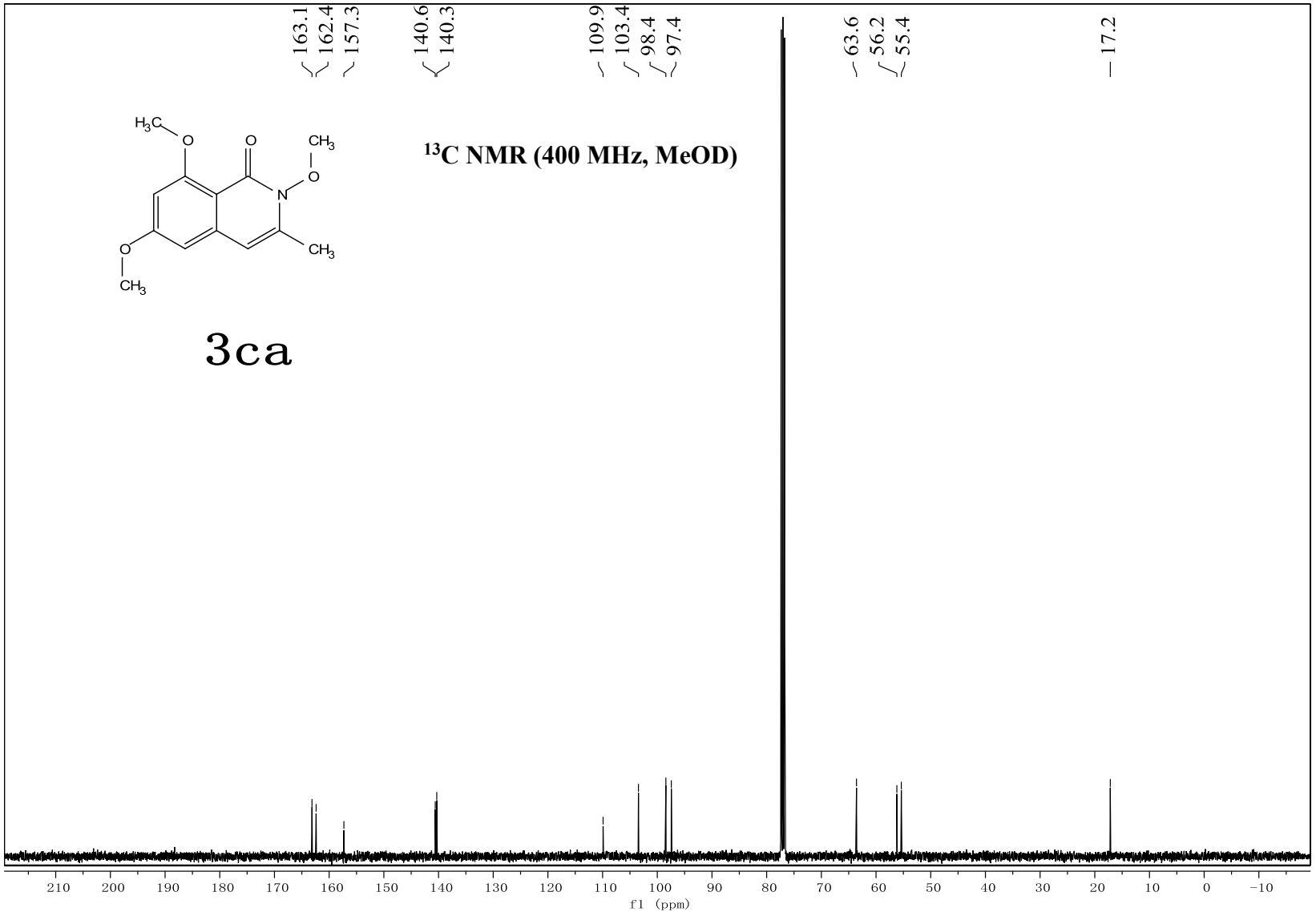

8.26 8.24 7.22 7.21 6.17 4.03 4.01 2.69 2.67 2.65 2.44 2.25 2.23 2.22 2.20 2.18 2.16 2.15 1.76 1.74 1.74 1.73 1.73 1.72 1.71 1.70 1.69 1.69 1.68 1.39 1.38 1.38 1.37 1.36 1.36 1.36 1.35 1.08 1.07 0.93 0.92 0.91 0.91 0.90 0.90 0.89 0.89
O
CH3
N
O
CH3
H3C
CH3
3bg
1H NMR (400 MHz, CDCl3)
1.00 2.10 1.03 2.09 2.18 3.17 1.10 2.20 4.30 6.43 3.37
f1 (ppm)

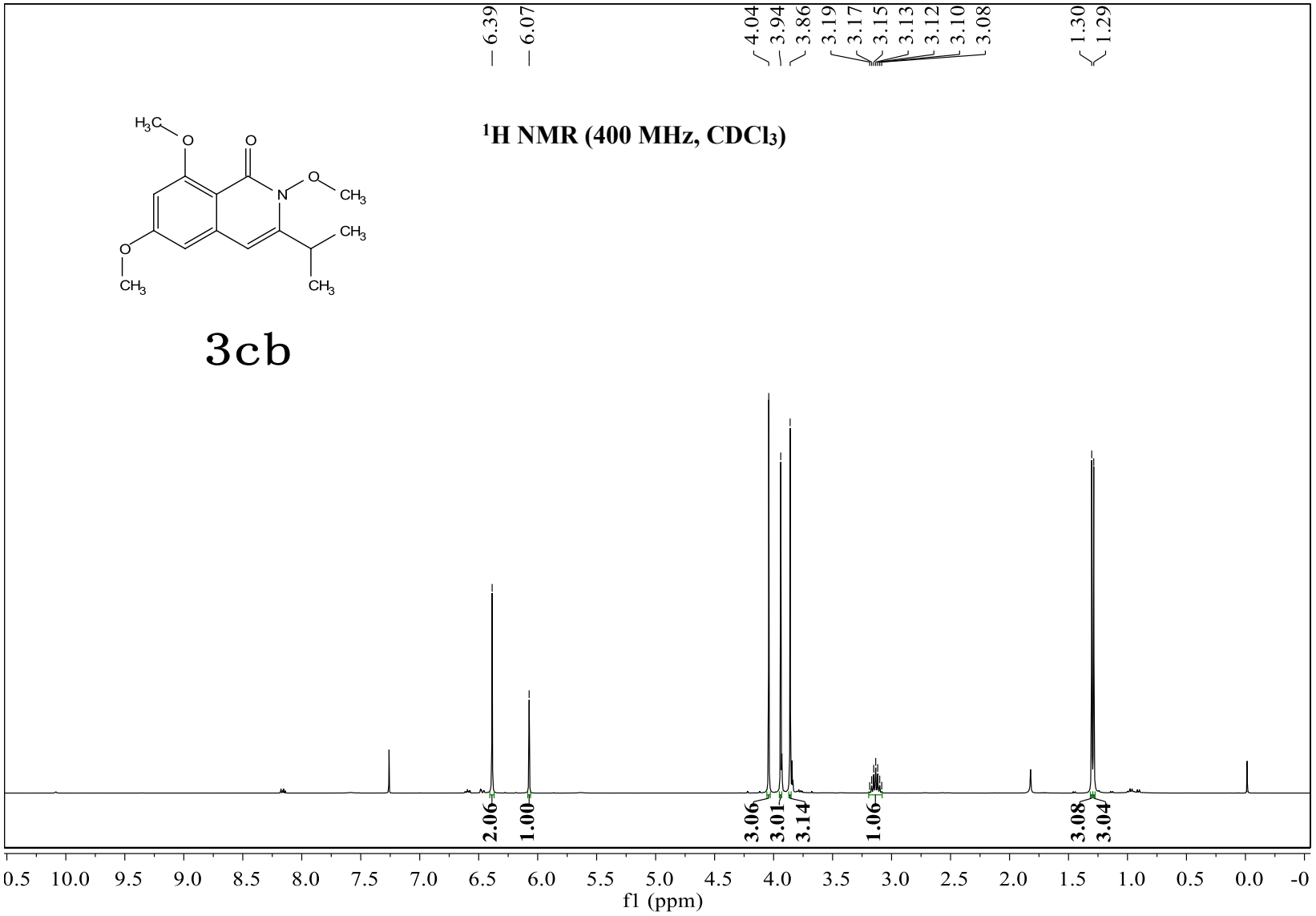

159.1
143.4
142.5
136.1
127.4
127.4
125.1
123.6
103.1
81.7
31.4
30.9
28.0
27.6
22.4
21.7
19.2
14.0
O
N
O
CH3
CH3
H3C
CH3
3bg
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

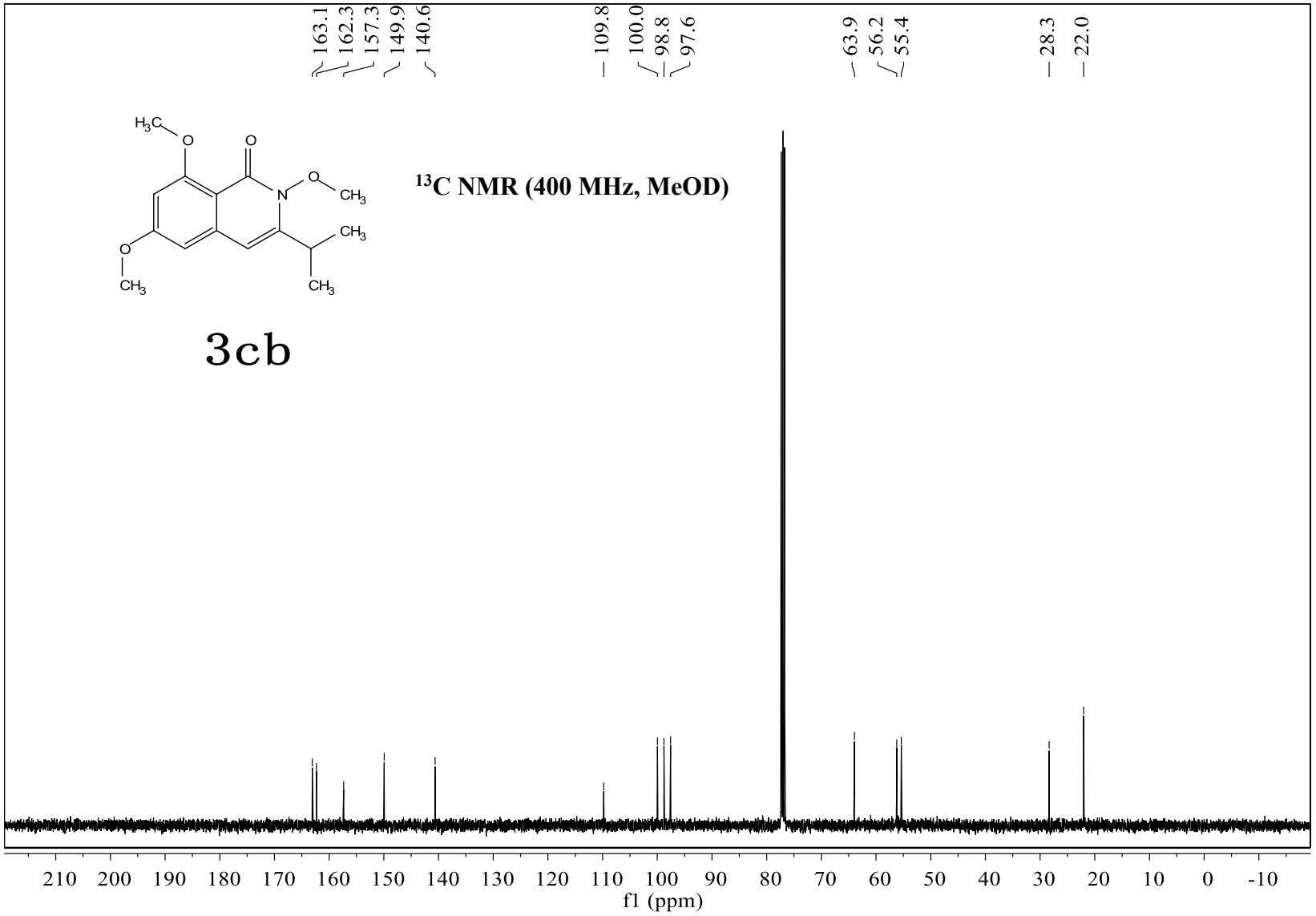

7.56 7.56 7.55 7.54 7.54 7.40 7.39 7.38 7.38 7.37 7.36 6.42 6.41 6.38 6.37 6.04 5.25 3.98 3.87 2.60 2.58 2.56 1.65 1.34 1.34 1.33 1.32 1.31 1.30 1.30 1.29 0.89 0.89 0.88 0.88 0.87 0.86 0.86
^{1}H NMR (400 MHz, CDCl$_3$)
3bh
2.00 3.03 2.03 1.00 2.00 3.07 3.10 2.03 2.45 4.14 3.19
10.5 10.0 9.5 9.0 8.5 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
f1 (ppm)

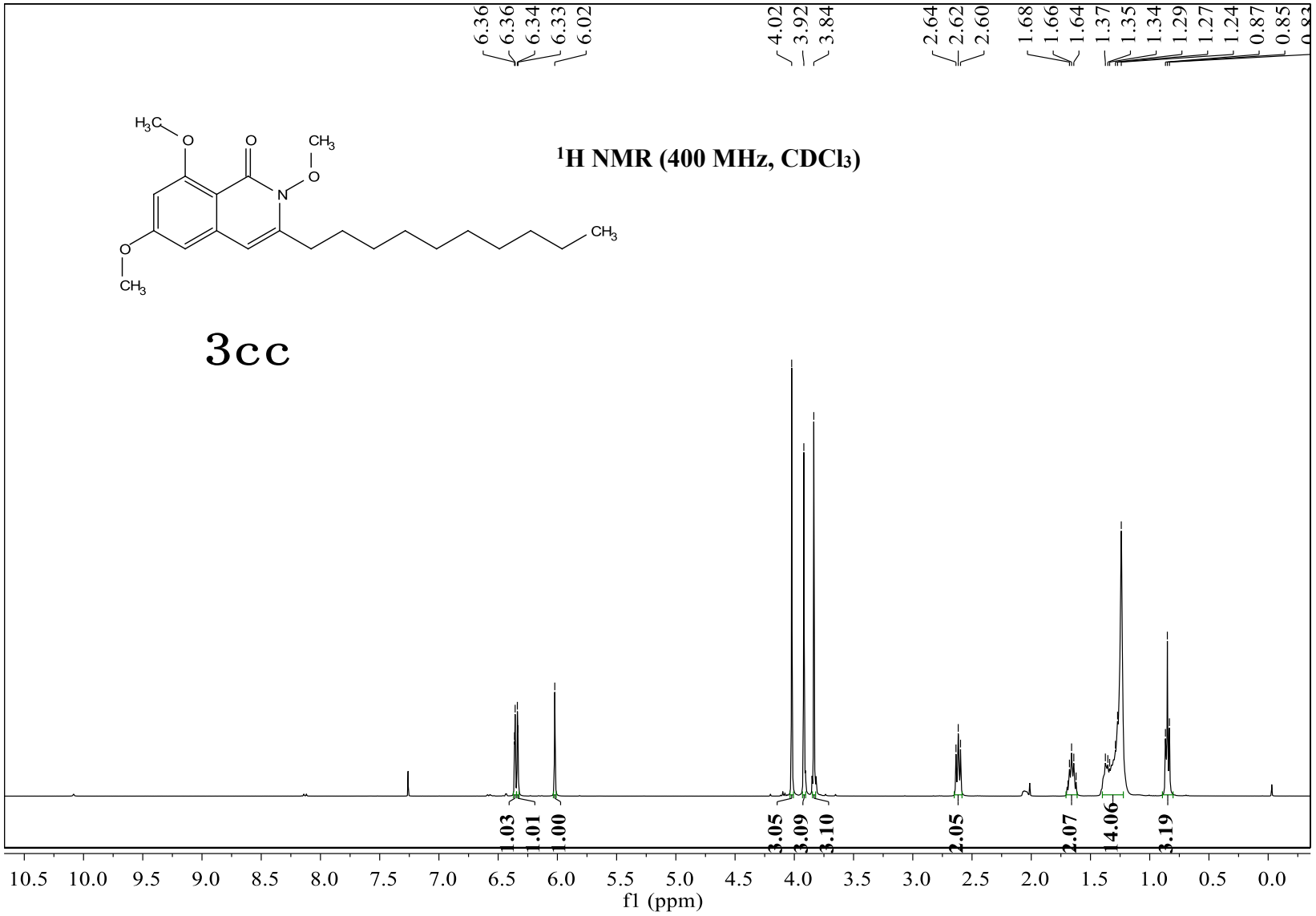

163.1
162.4
157.6
144.8
140.7
134.6
129.7
128.9
128.5
109.9
102.4
98.6
97.4
77.5
56.2
55.4
31.4
30.7
27.5
22.3
13.9
13C NMR (400 MHz, MeOD)
3bh
77.5
81 80 79 78 77 76 75 74 73
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

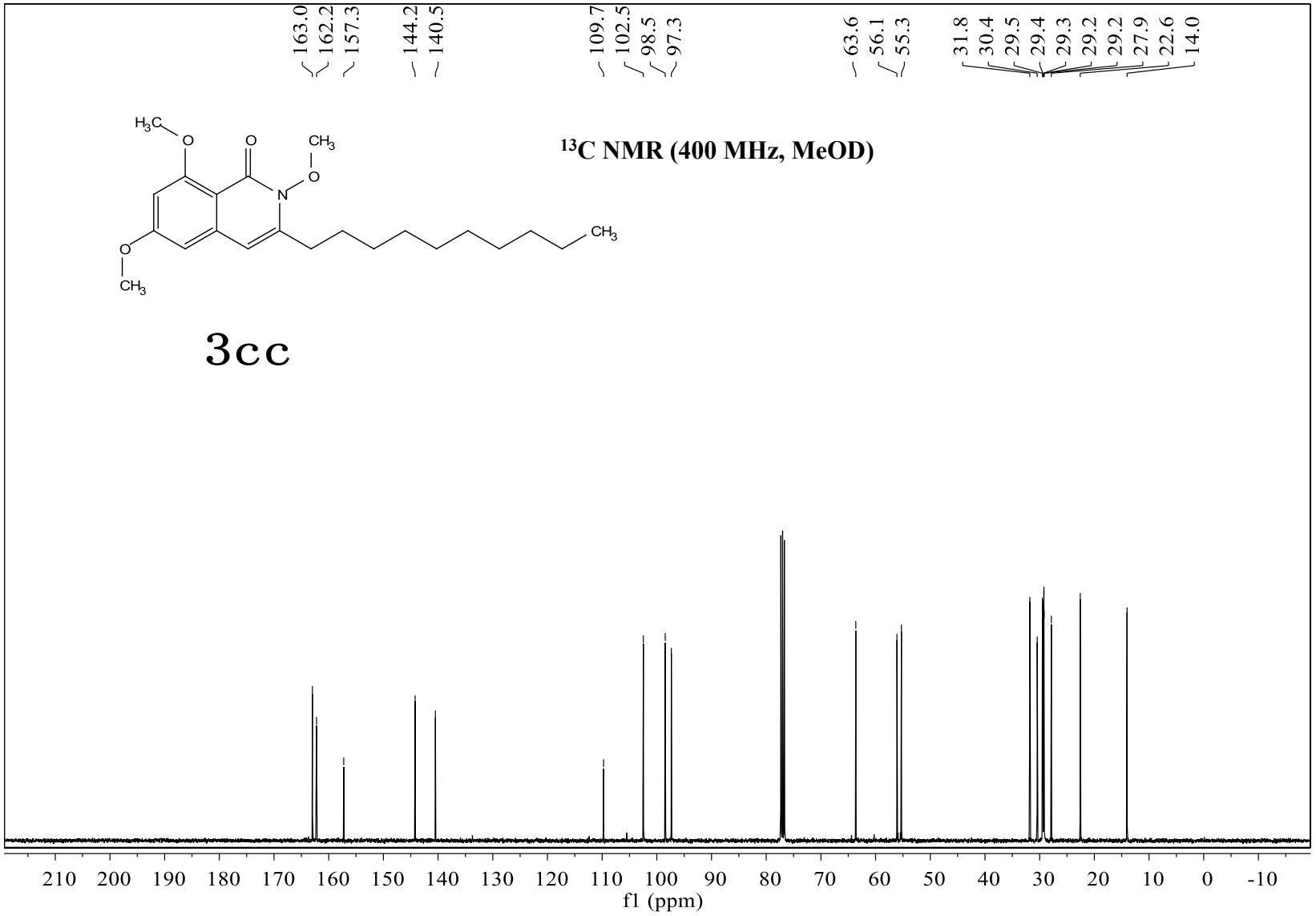

6.38
6.38
6.33
6.32
6.05
4.04
3.94
3.86
2.36
^{1}H NMR (400 MHz, CDCl$_3$)
3ca
1.00
1.00
1.00
3.09
3.06
3.06
3.04
f1 (ppm)

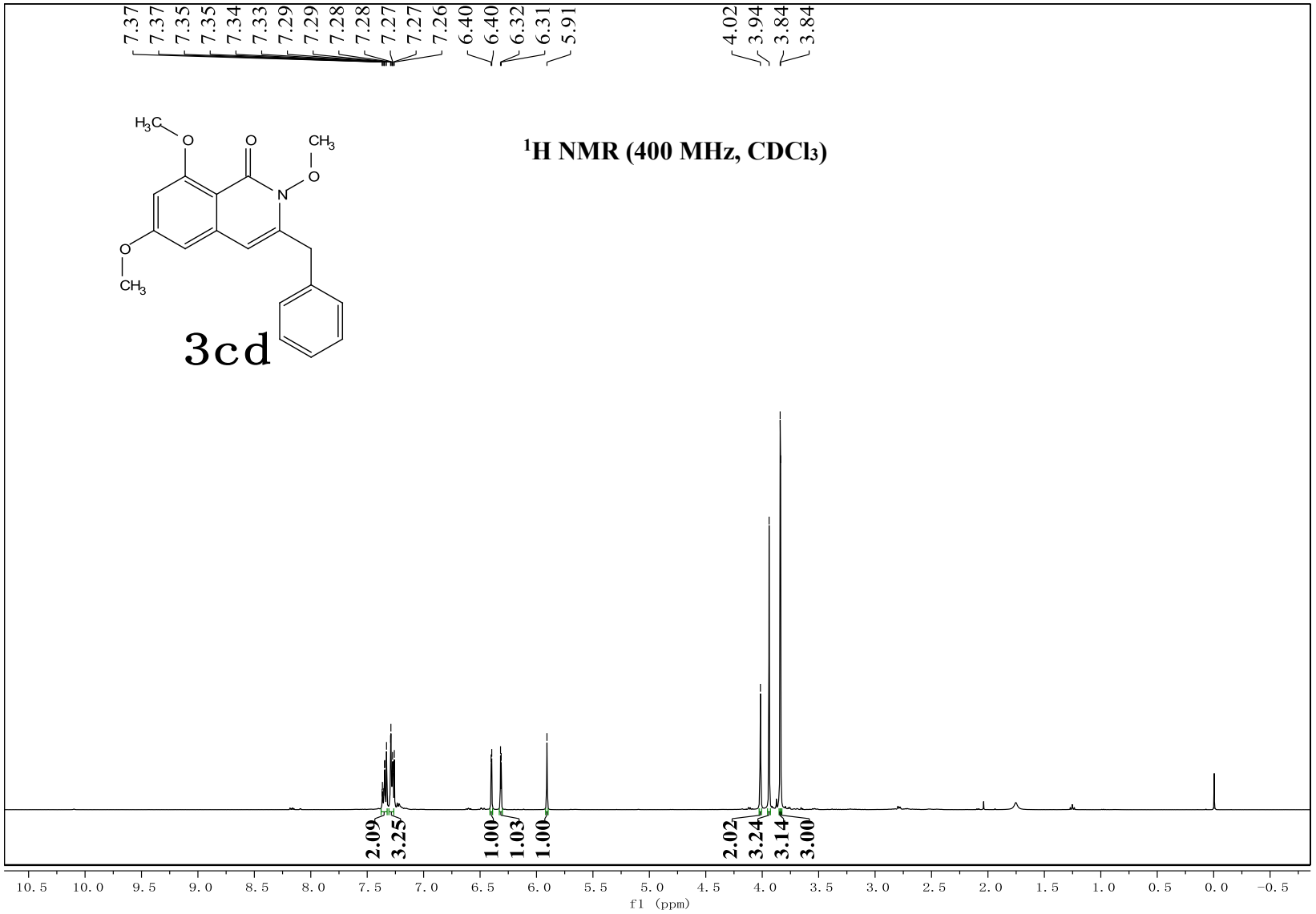

163.1
162.4
157.3
140.6
140.3
109.9
103.4
98.4
97.4
63.6
56.2
55.4
17.2
^{13}C NMR (400 MHz, MeOD)
3ca
f1 (ppm)

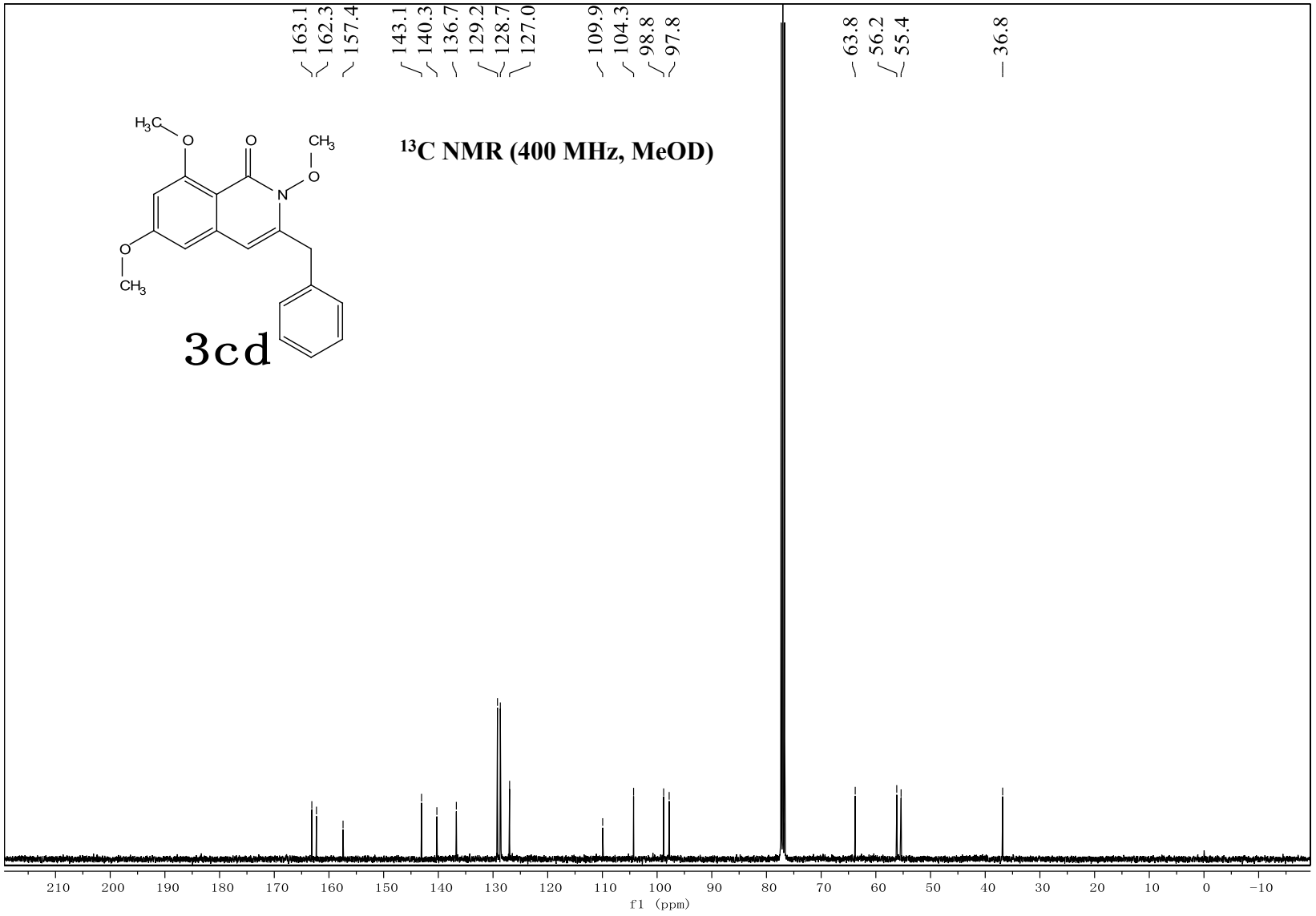

6.39
6.07
4.04
3.94
3.86
3.19
3.17
3.15
3.13
3.12
3.10
3.08
1.30
1.29
^{1}H NMR (400 MHz, CDCl$_3$)
3cb
2.06
1.00
3.06
3.01
3.14
1.06
3.08
3.04
f1 (ppm)

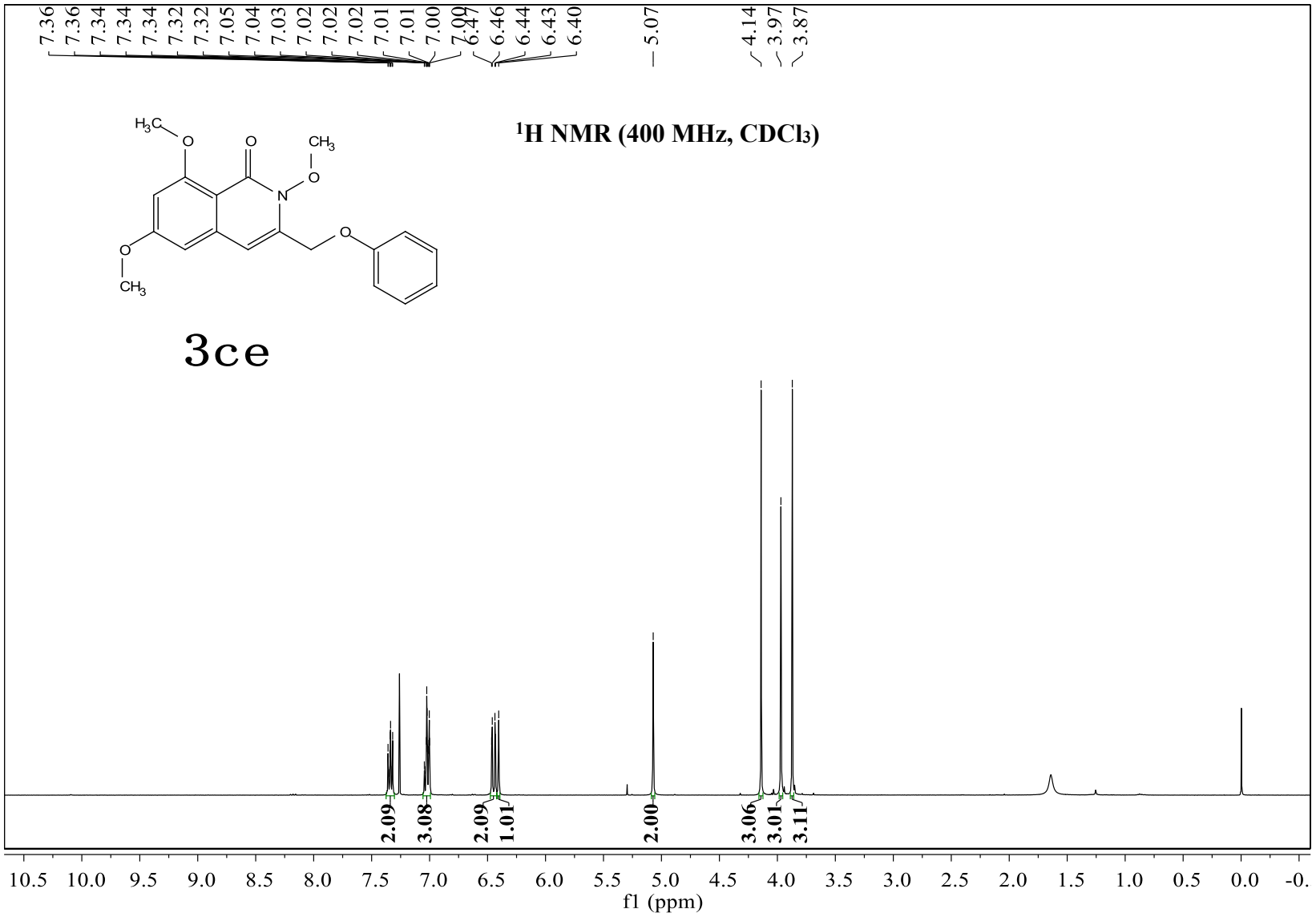

163.1
162.3
157.3
149.9
140.6
109.8
100.0
98.8
97.6
63.9
56.2
55.4
28.3
22.0
^{13}C NMR (400 MHz, MeOD)
3cb
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

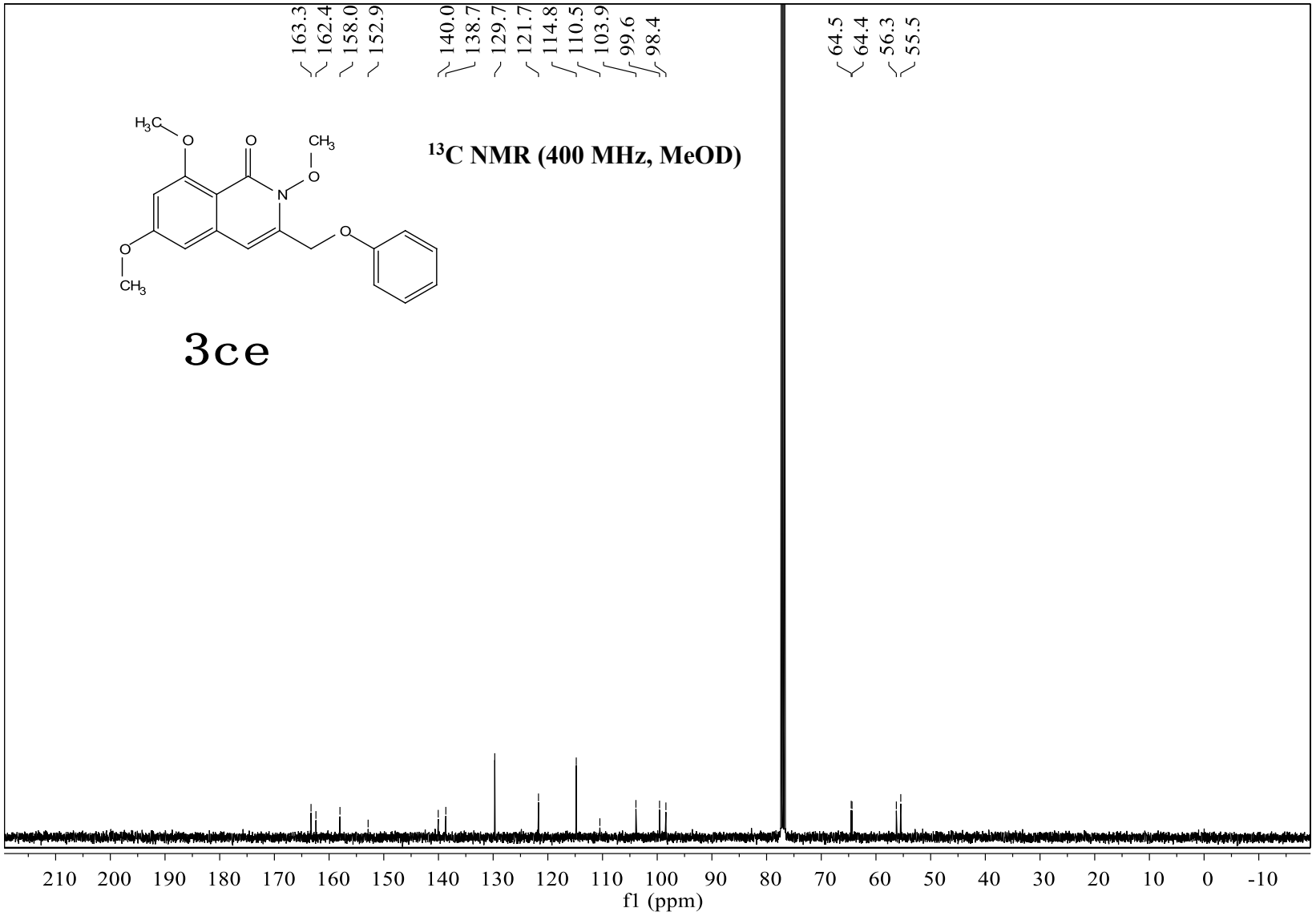

6.36
6.36
6.34
6.33
6.02
4.02
3.92
3.84
2.64
2.62
2.60
1.68
1.66
1.64
1.37
1.35
1.34
1.29
1.27
1.24
0.87
0.85
H3C
O
O
CH3
O
N
O
CH3
CH3
1H NMR (400 MHz, CDCl3)
3cc
1.03
1.01
1.00
3.05
3.09
3.10
2.05
2.07
14.06
3.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

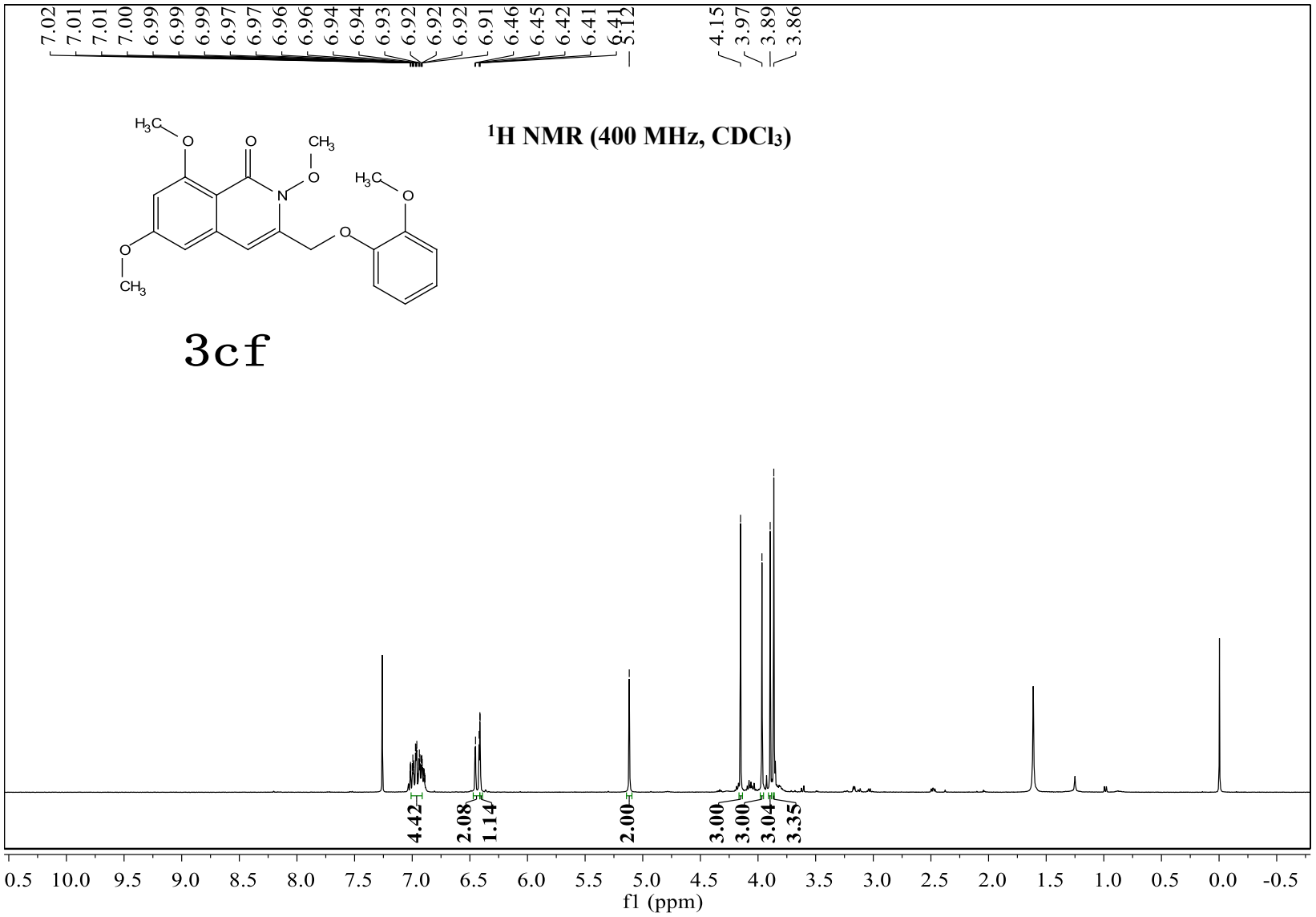

163.0
162.2
157.3
144.2
140.5
109.7
102.5
98.5
97.3
63.6
56.1
55.3
31.8
30.4
29.5
29.4
29.3
29.2
29.2
27.9
22.6
14.0
H3C
O
O
CH3
O
N
O
CH3
O
CH3
13C NMR (400 MHz, MeOD)
3cc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37
7.37
7.35
7.35
7.34
7.33
7.29
7.29
7.28
7.28
7.27
7.27
7.26
6.40
6.40
6.32
6.31
5.91
4.02
3.94
3.84
3.84
H3C
O
O
CH3
O
N
O
O
CH3
3cd
1H NMR (400 MHz, CDCl3)
2.09
3.25
1.00
1.03
1.00
2.02
3.24
3.14
3.00
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)

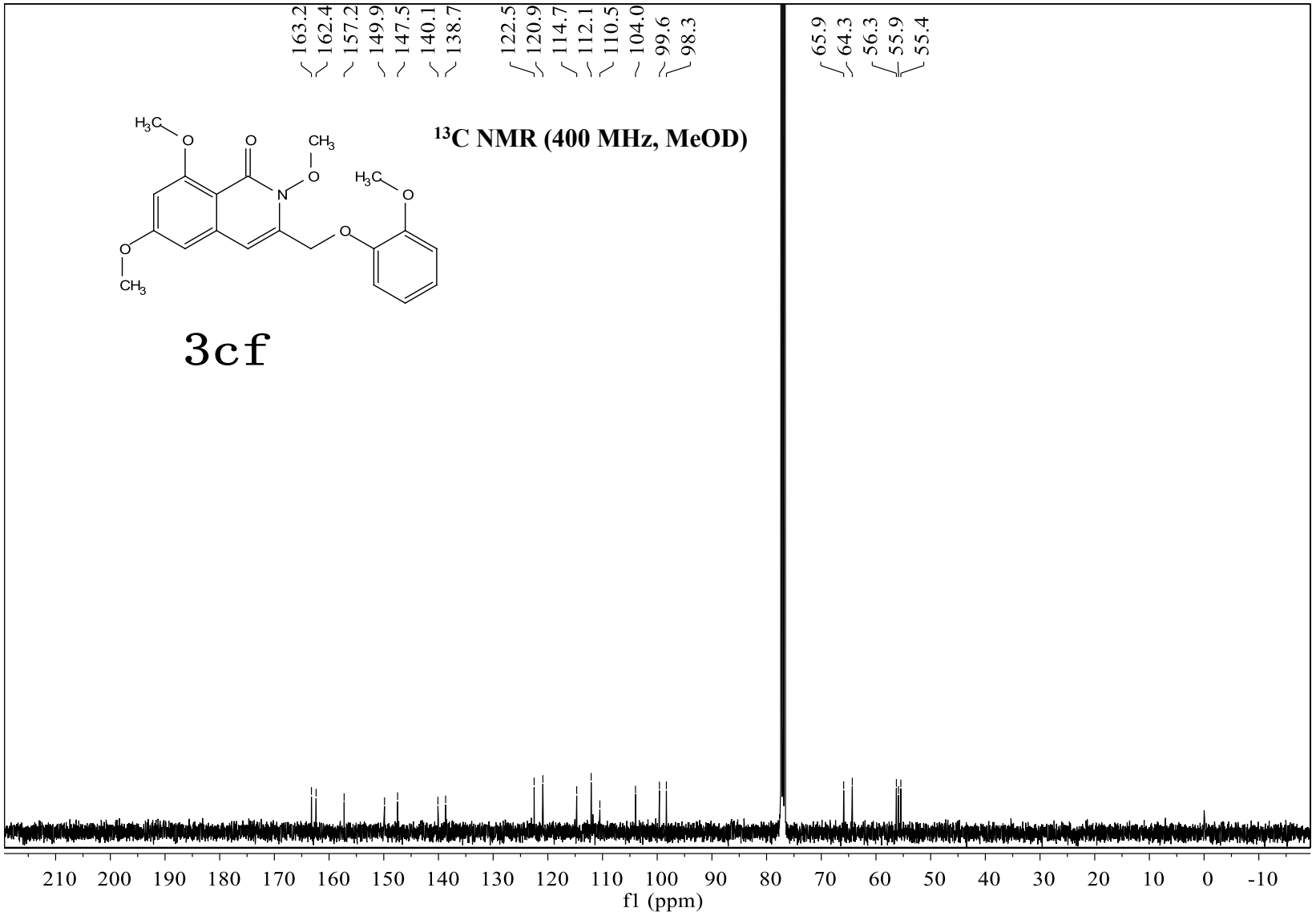

163.1
162.3
157.4
143.1
140.3
136.7
129.2
128.7
127.0
109.9
104.3
98.8
97.8
63.8
56.2
55.4
36.8
H3C
O
O
CH3
O
N
O
CH3
3cd
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

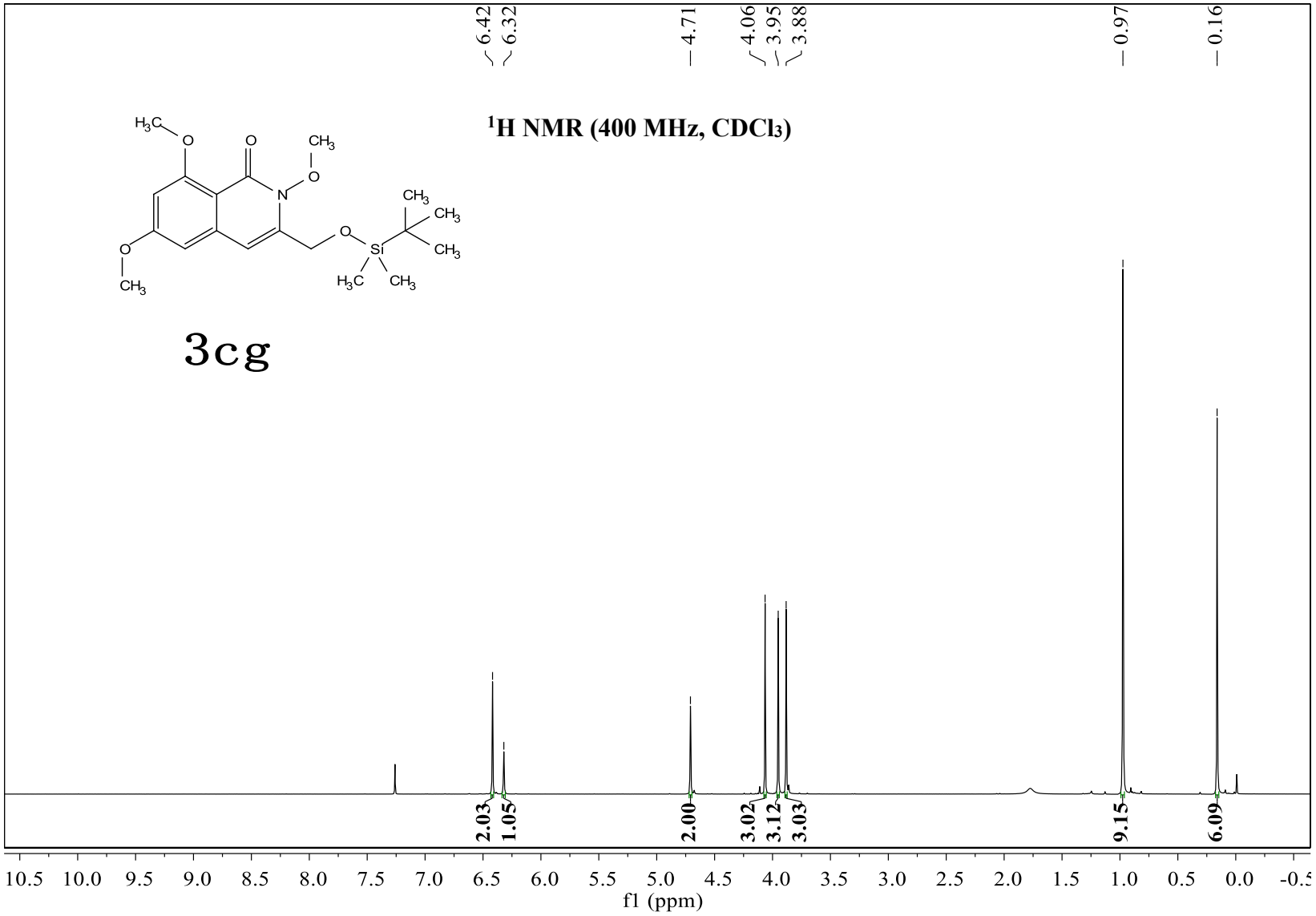

7.36
7.36
7.34
7.34
7.34
7.32
7.32
7.05
7.04
7.03
7.02
7.02
7.02
7.01
7.01
7.00
7.00
6.47
6.46
6.44
6.43
6.40
5.07
4.14
3.97
3.87
H3C
O
O
CH3
O
N
O
O
CH3
3ce
1H NMR (400 MHz, CDCl3)
2.09
3.08
2.09
1.01
2.00
3.06
3.01
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

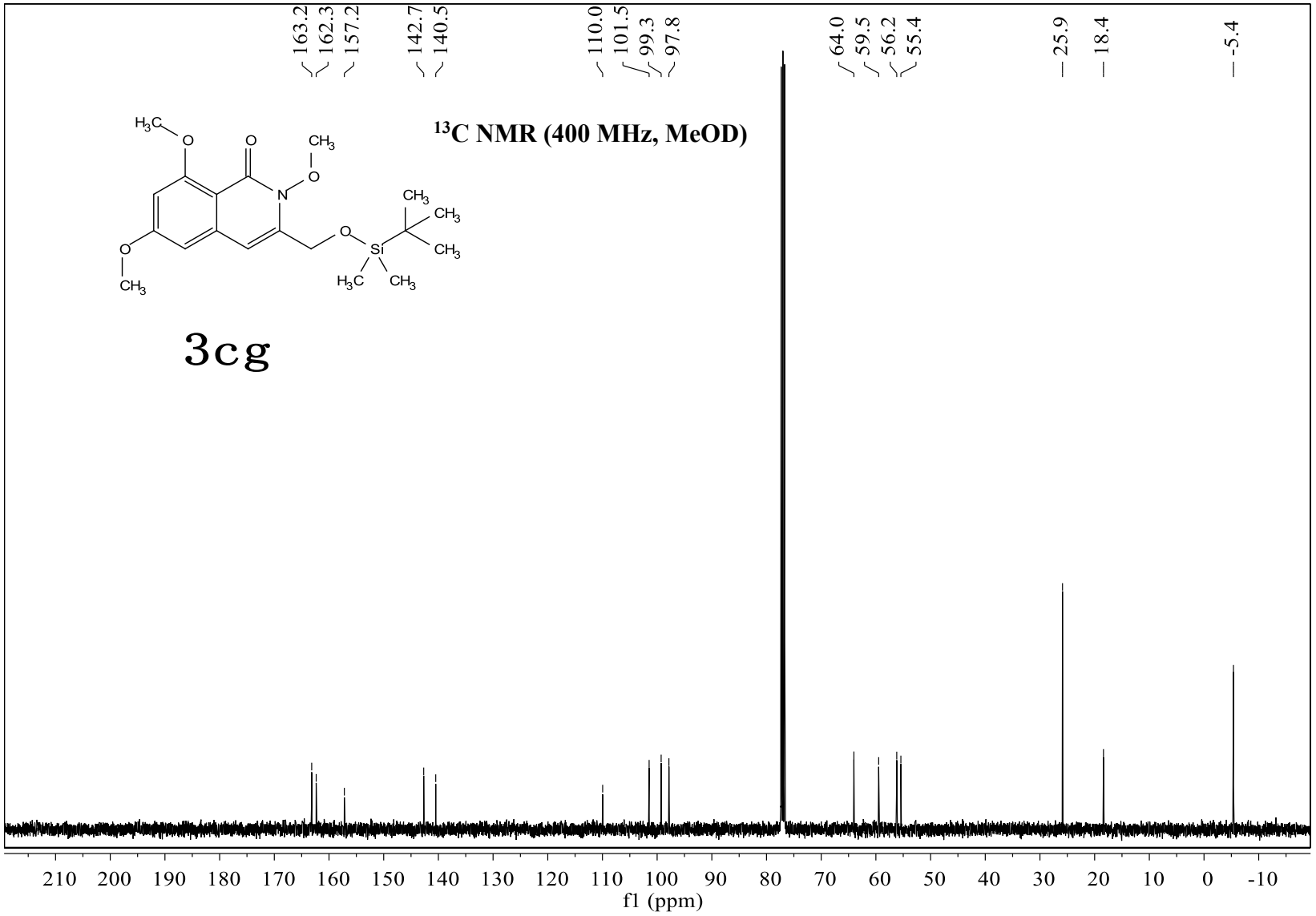

163.3
162.4
158.0
152.9
140.0
138.7
129.7
121.7
114.8
110.5
103.9
99.6
98.4
64.5
64.4
56.3
55.5
H3C
O
O
CH3
O
N
O
O
CH3
13C NMR (400 MHz, MeOD)
3ce
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

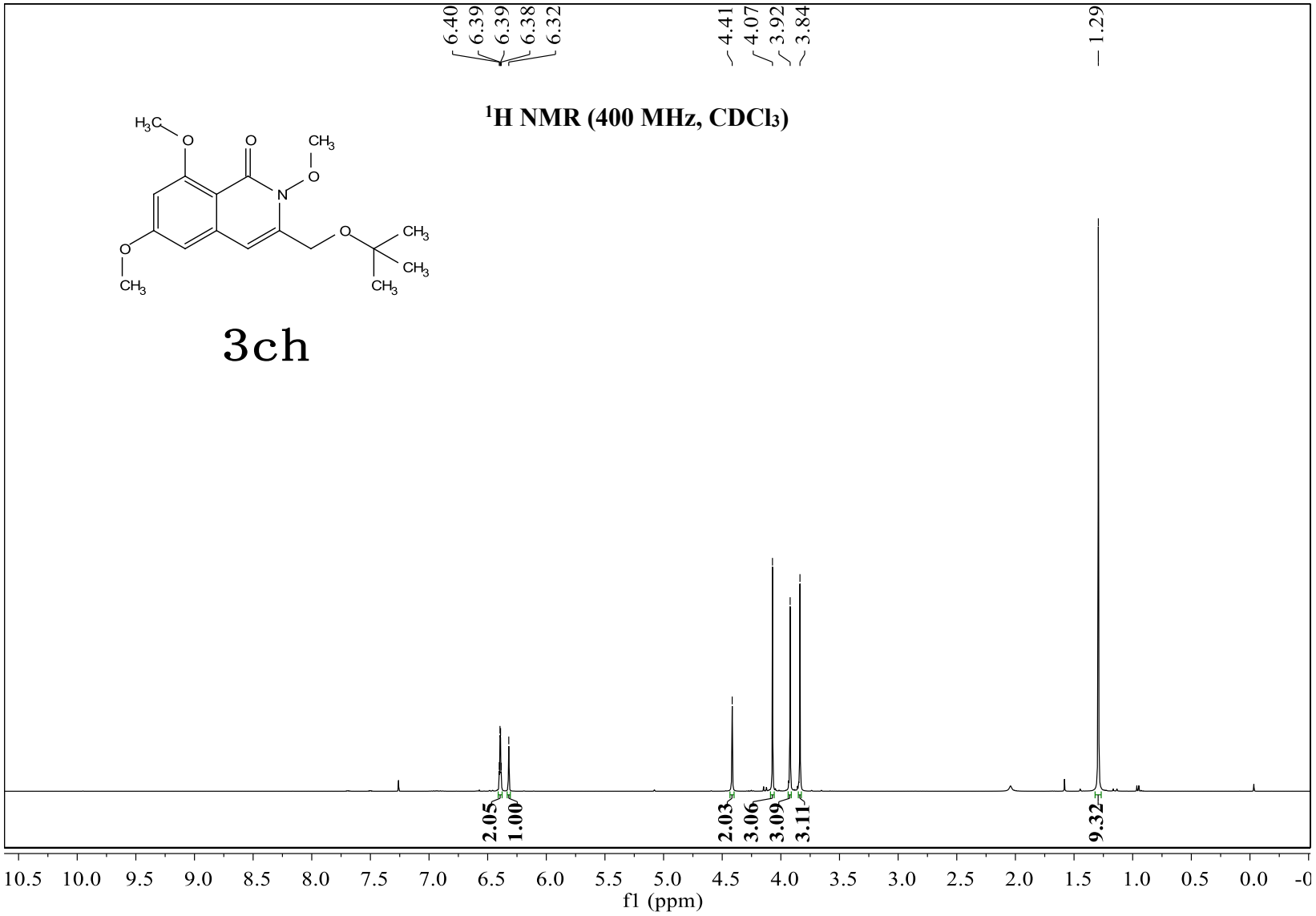


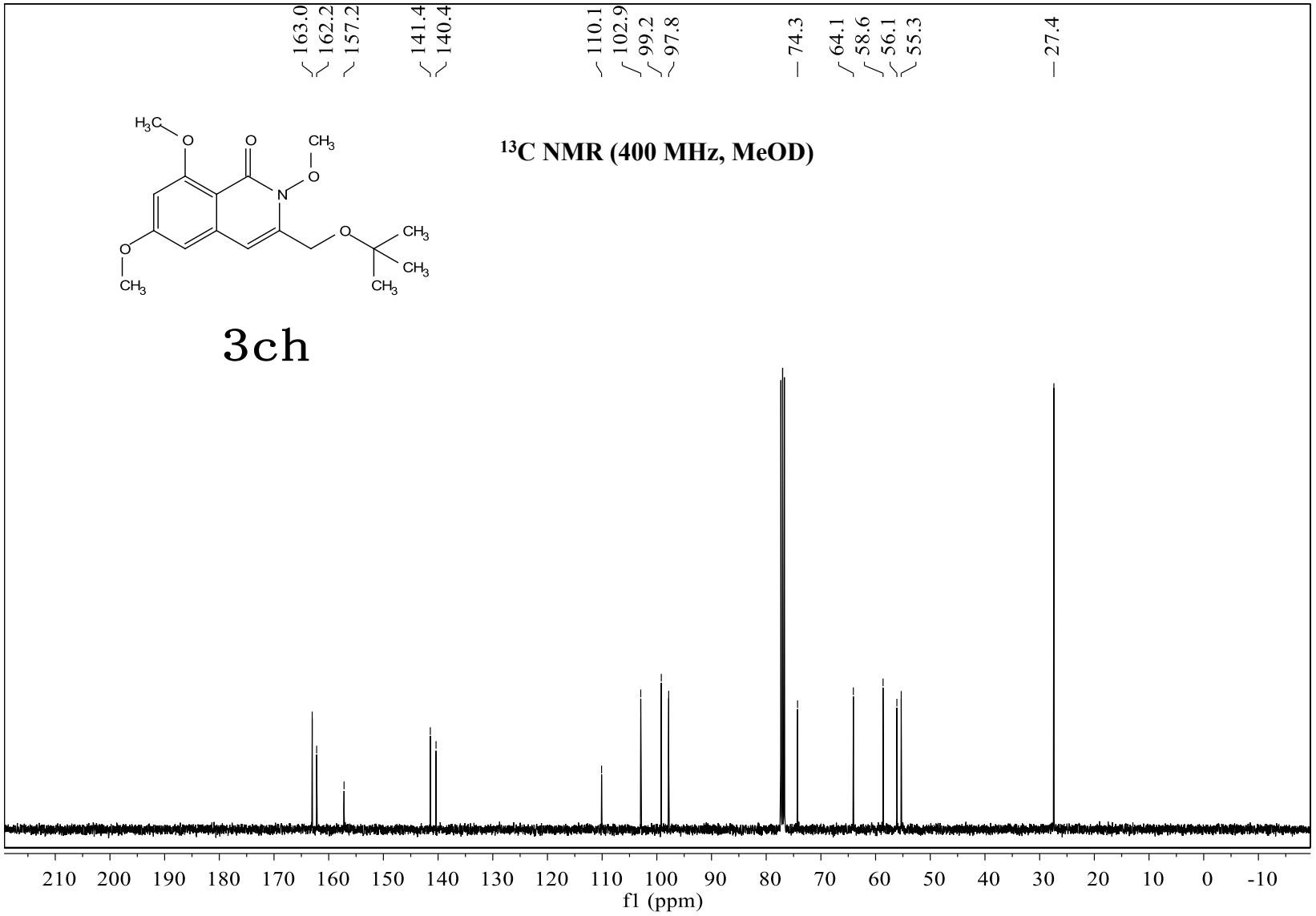
^{1}H NMR (400 MHz, $CDCl_3$)

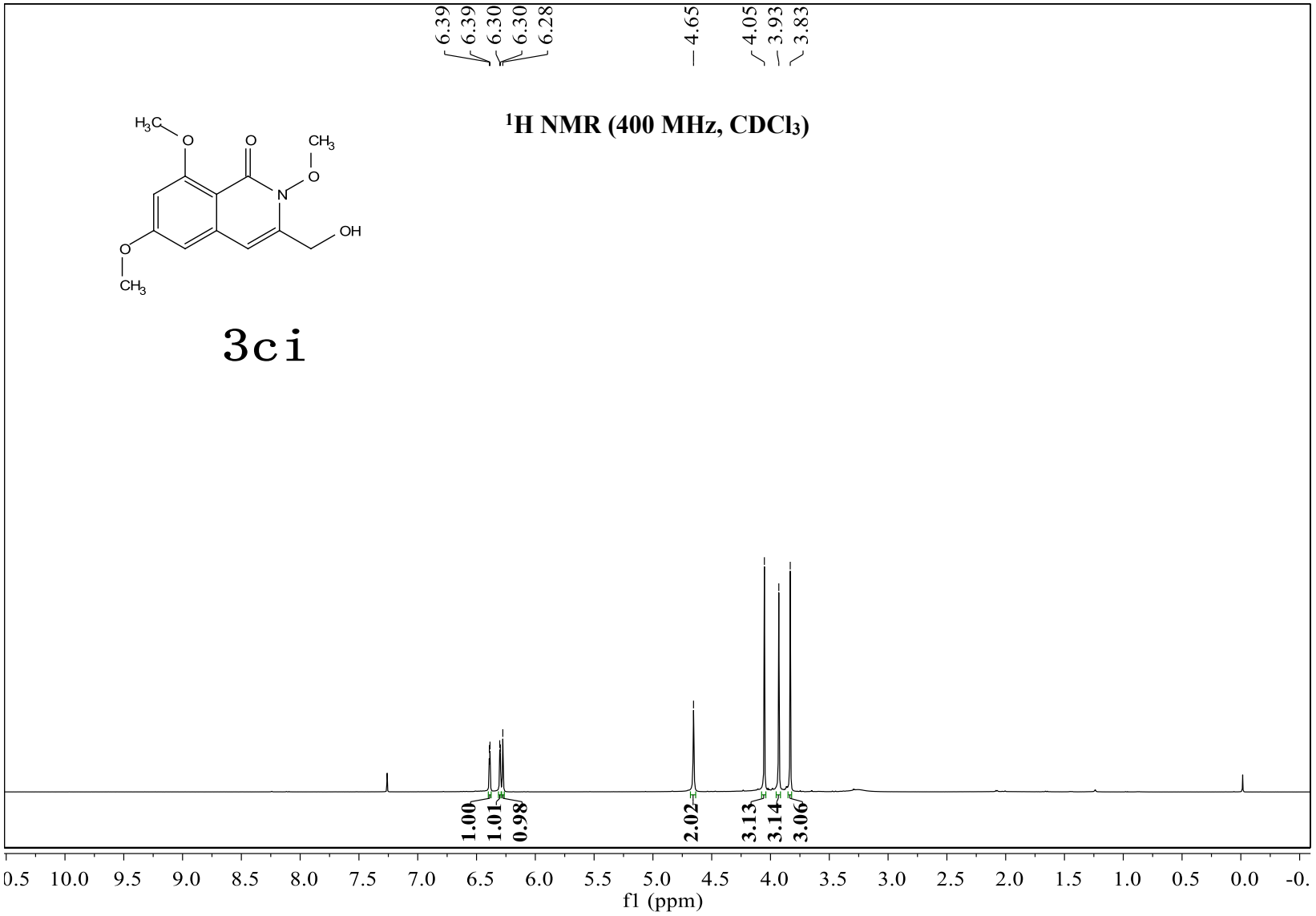

163.2
162.4
157.2
149.9
147.5
140.1
138.7
122.5
120.9
114.7
112.1
110.5
104.0
99.6
98.3
65.9
64.3
56.3
55.9
55.4
13C NMR (400 MHz, MeOD)
3cf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

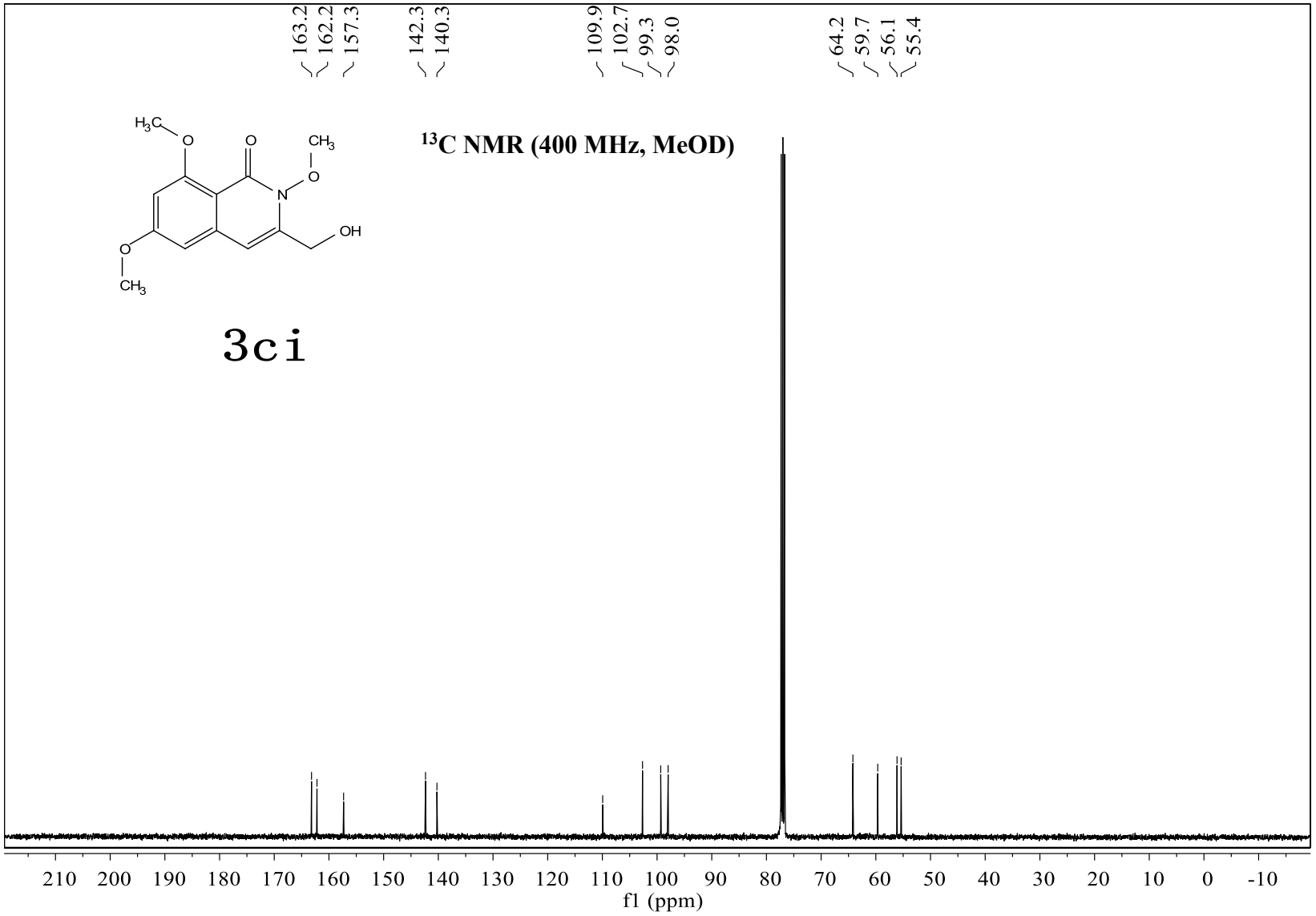

6.42
6.32
4.71
4.06
3.95
3.88
0.97
0.16
1H NMR (400 MHz, CDCl3)
3cg
2.03
1.05
2.00
3.02
3.12
3.03
9.15
6.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

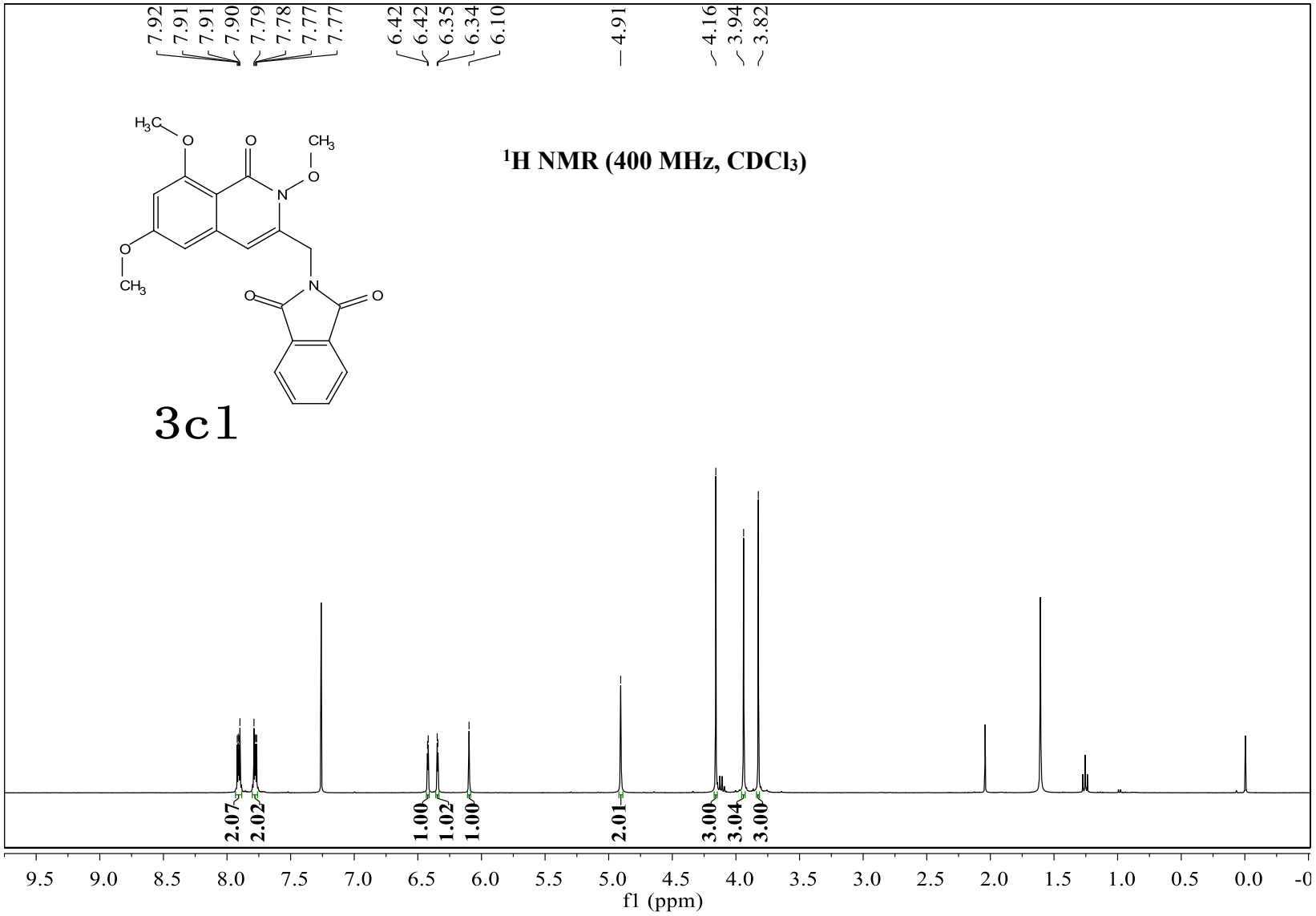

163.2
162.3
157.2
142.7
140.5
110.0
101.5
99.3
97.8
64.0
59.5
56.2
55.4
25.9
18.4
-5.4
13C NMR (400 MHz, MeOD)
3cg
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

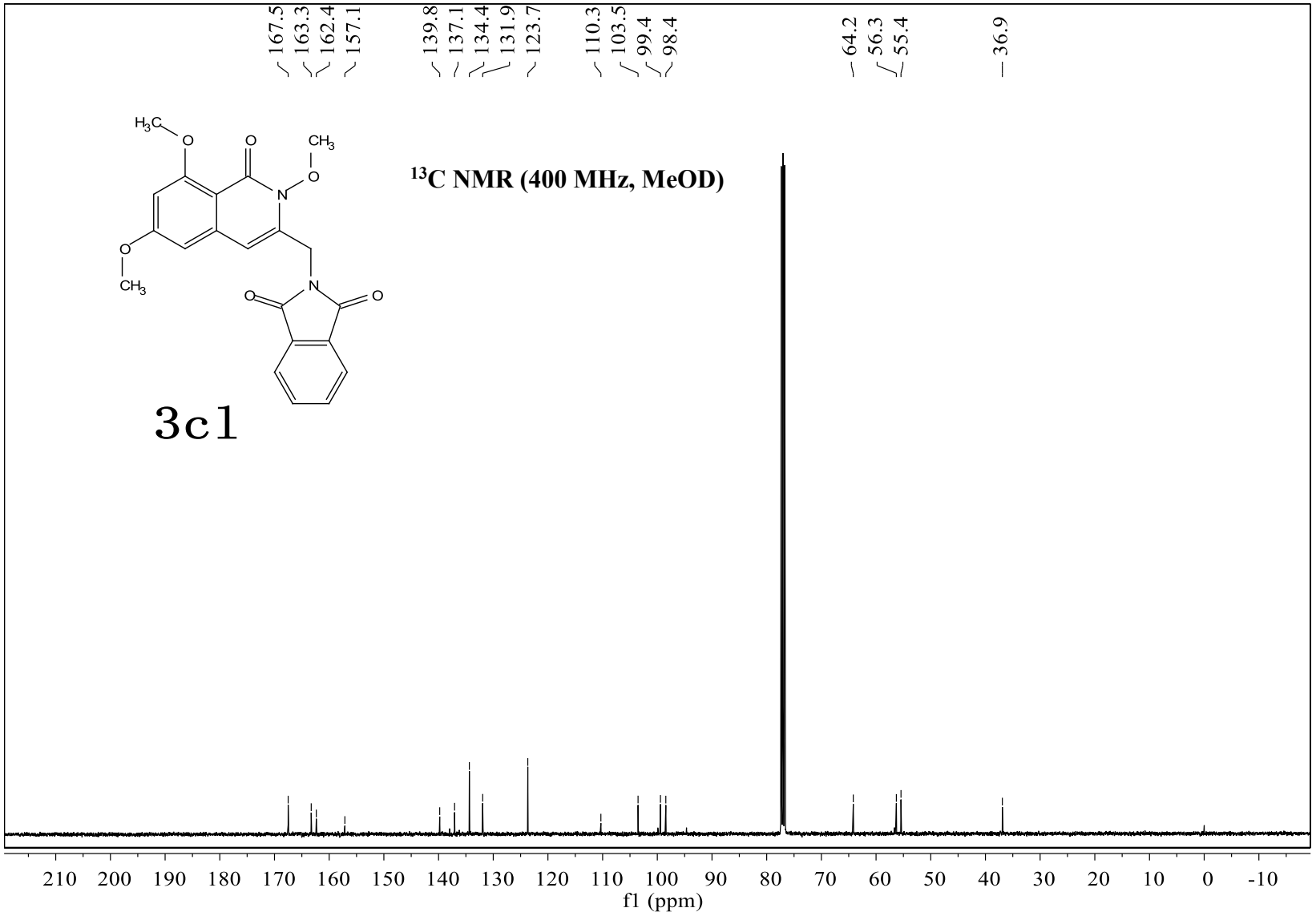

6.40
6.39
6.39
6.38
6.32
4.41
4.07
3.92
3.84
1.29
¹H NMR (400 MHz, CDCl3)
3ch
2.05
1.00
2.03
3.06
3.09
3.11
9.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

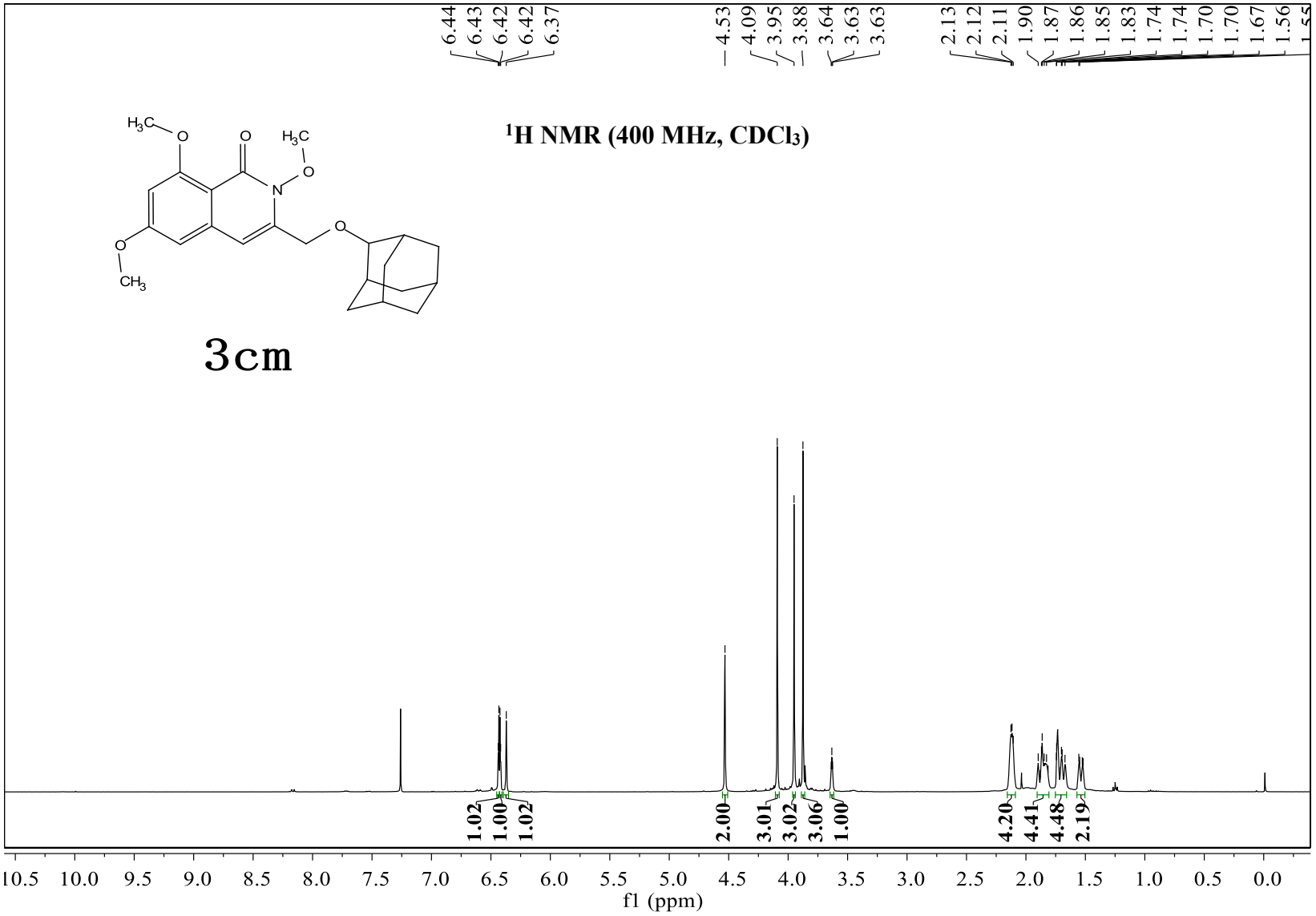

163.0
162.2
157.2
141.4
140.4
110.1
102.9
99.2
97.8
74.3
64.1
58.6
56.1
55.3
27.4
H3C
O
O
CH3
O
N
O
O
CH3
CH3
CH3
CH3
13C NMR (400 MHz, MeOD)
3ch
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

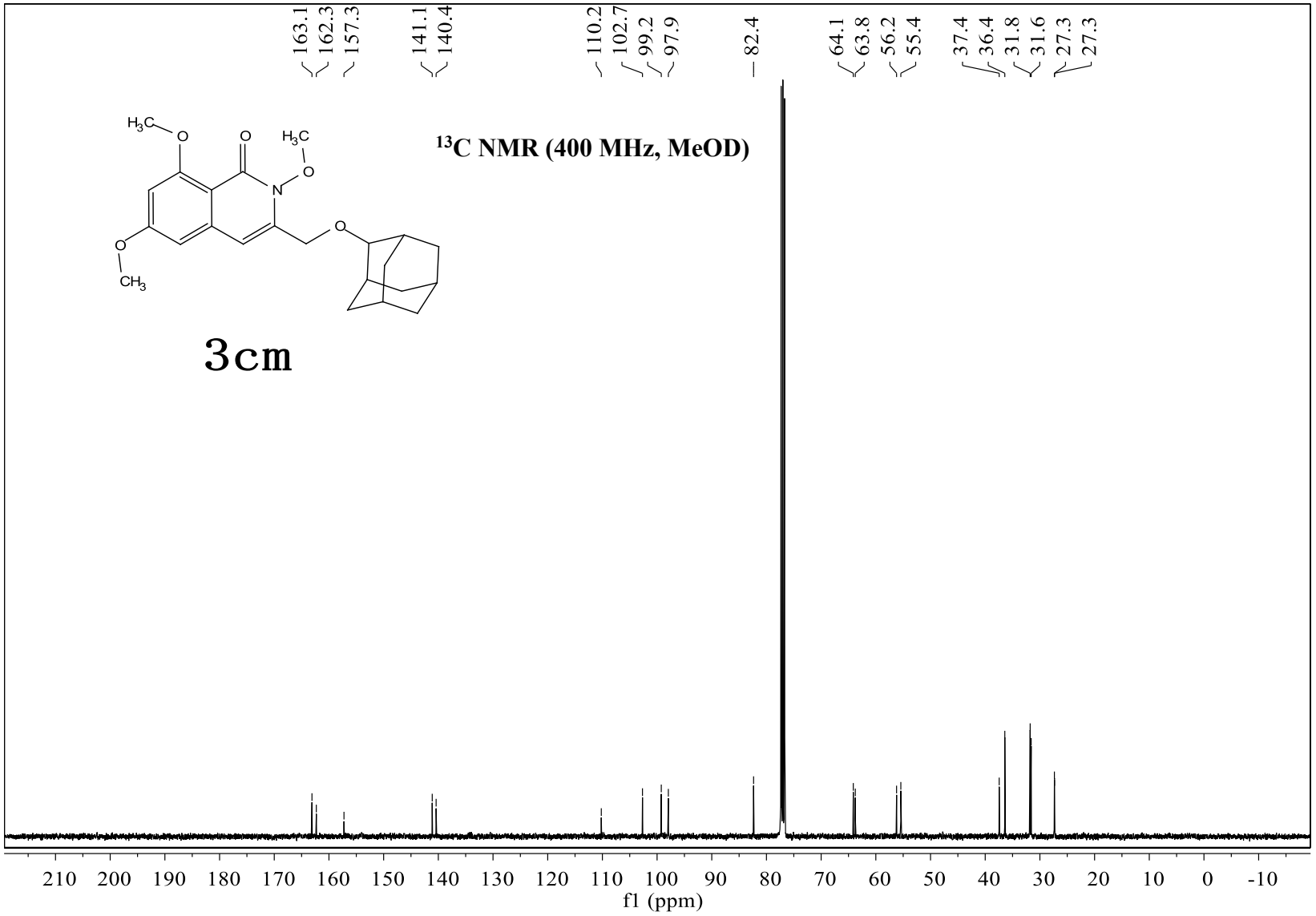

6.39
6.39
6.30
6.30
6.28
4.65
4.05
3.93
3.83
^{1}H NMR (400 MHz, CDCl$_3$)
H$_3$C
O
O
CH$_3$
O
N
OH
O
CH$_3$
3ci
1.00
1.01
0.98
2.02
3.13
3.14
3.06
f1 (ppm)

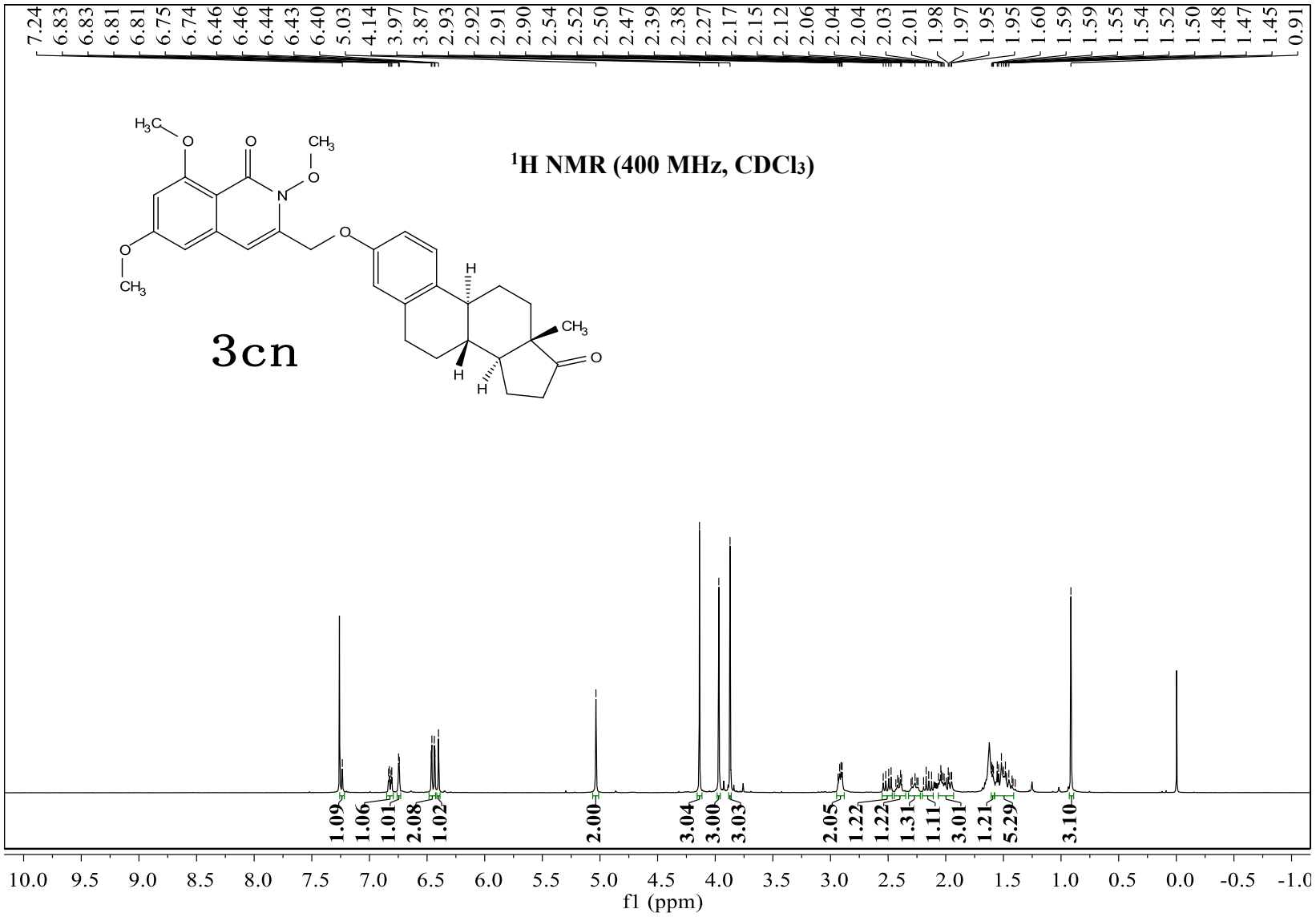

163.2
162.2
157.3
142.3
140.3
109.9
102.7
99.3
98.0
64.2
59.7
56.1
55.4
H3C
O
O
CH3
O
N
OH
O
CH3
13C NMR (400 MHz, MeOD)
3ci
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

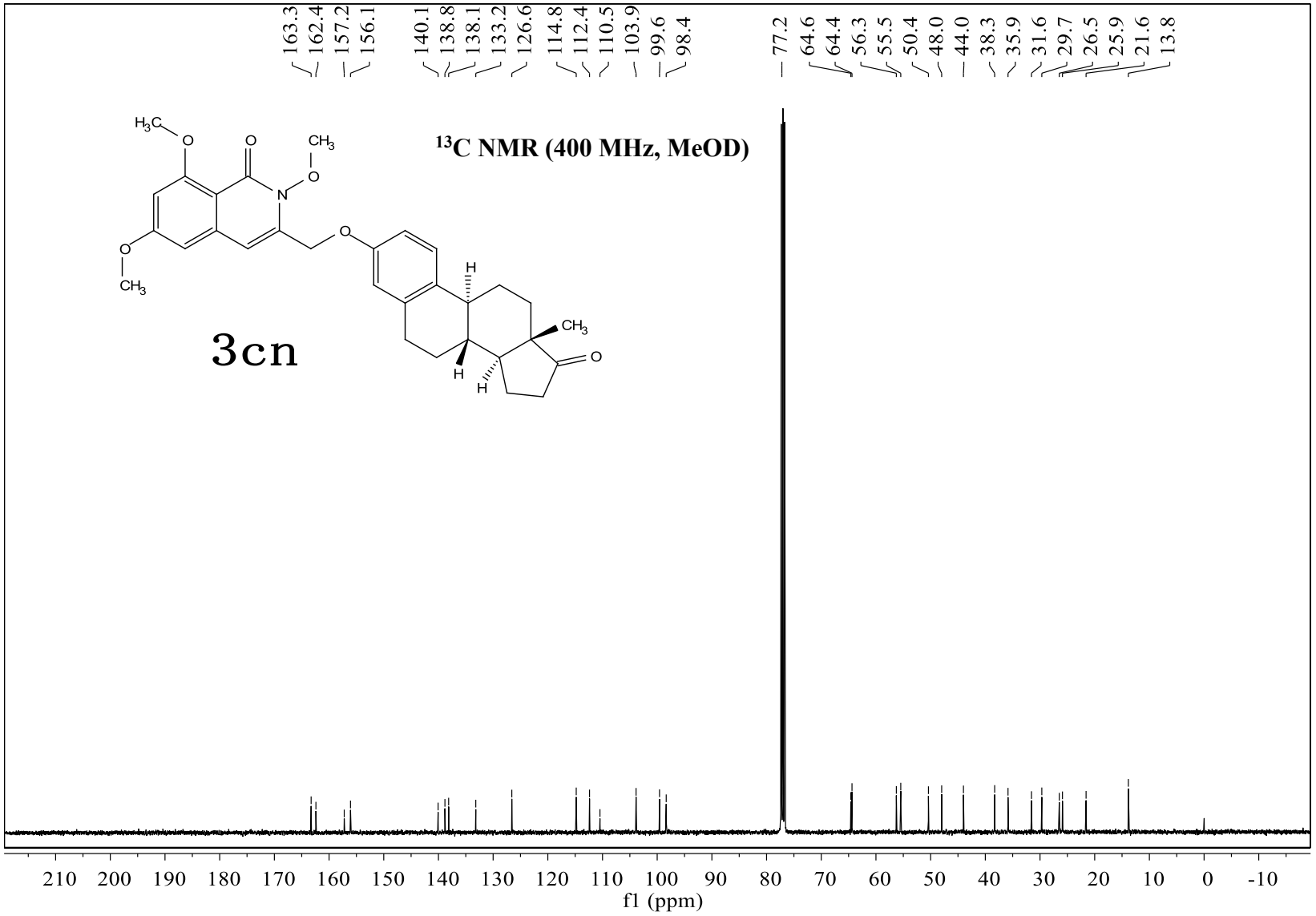

7.92
7.91
7.91
7.90
7.79
7.78
7.77
7.77
6.42
6.42
6.35
6.34
6.10
4.91
4.16
3.94
3.82
H3C
O
O
CH3
O
N
O
O
CH3
N
O
O
3c1
1H NMR (400 MHz, CDCl3)
2.07
2.02
1.00
1.02
1.00
2.01
3.00
3.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

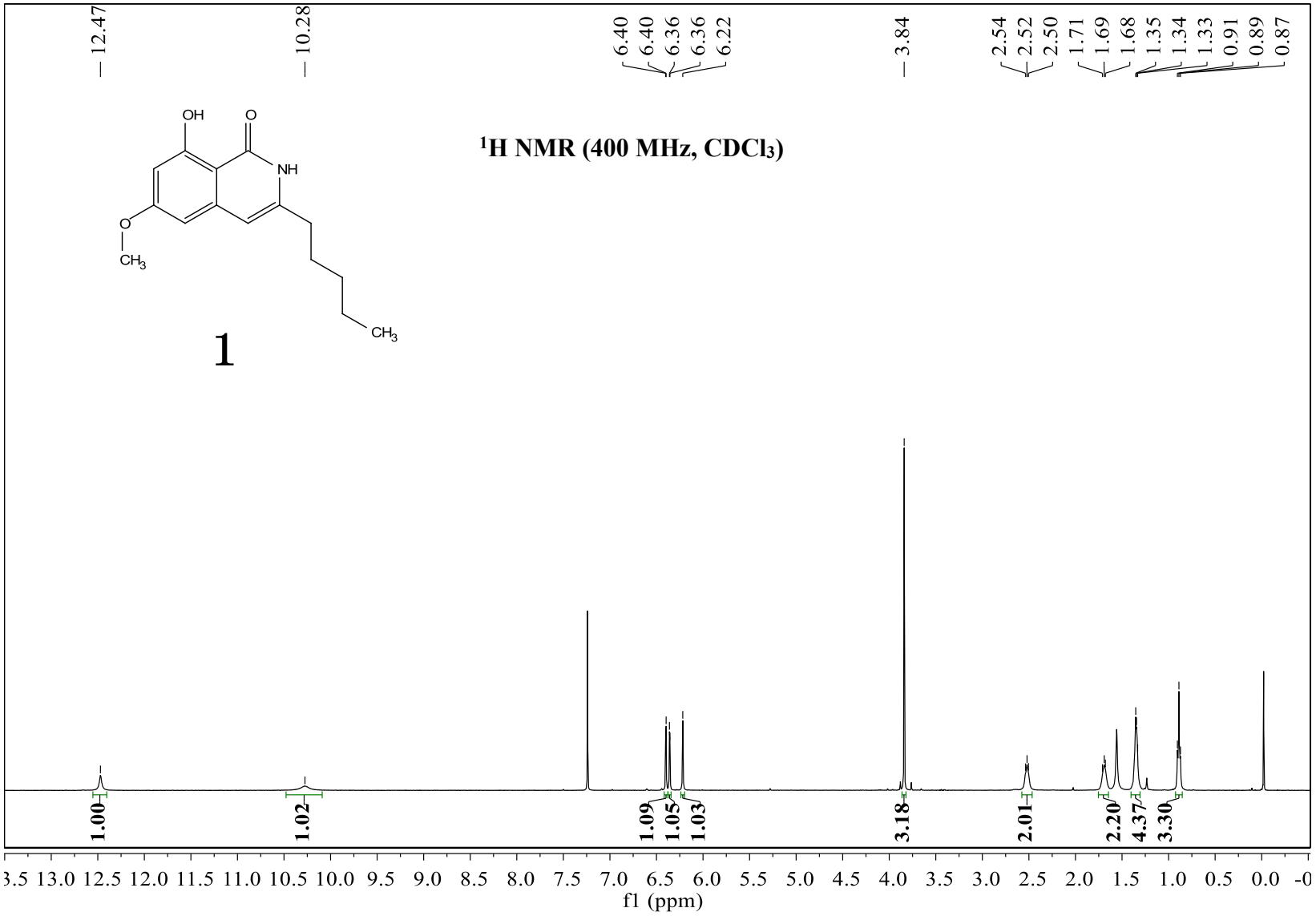

167.5
163.3
162.4
157.1
139.8
137.1
134.4
131.9
123.7
110.3
103.5
99.4
98.4
64.2
56.3
55.4
36.9
H3C
O
O
CH3
O
N
O
CH3
N
O
O
13C NMR (400 MHz, MeOD)
3c1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

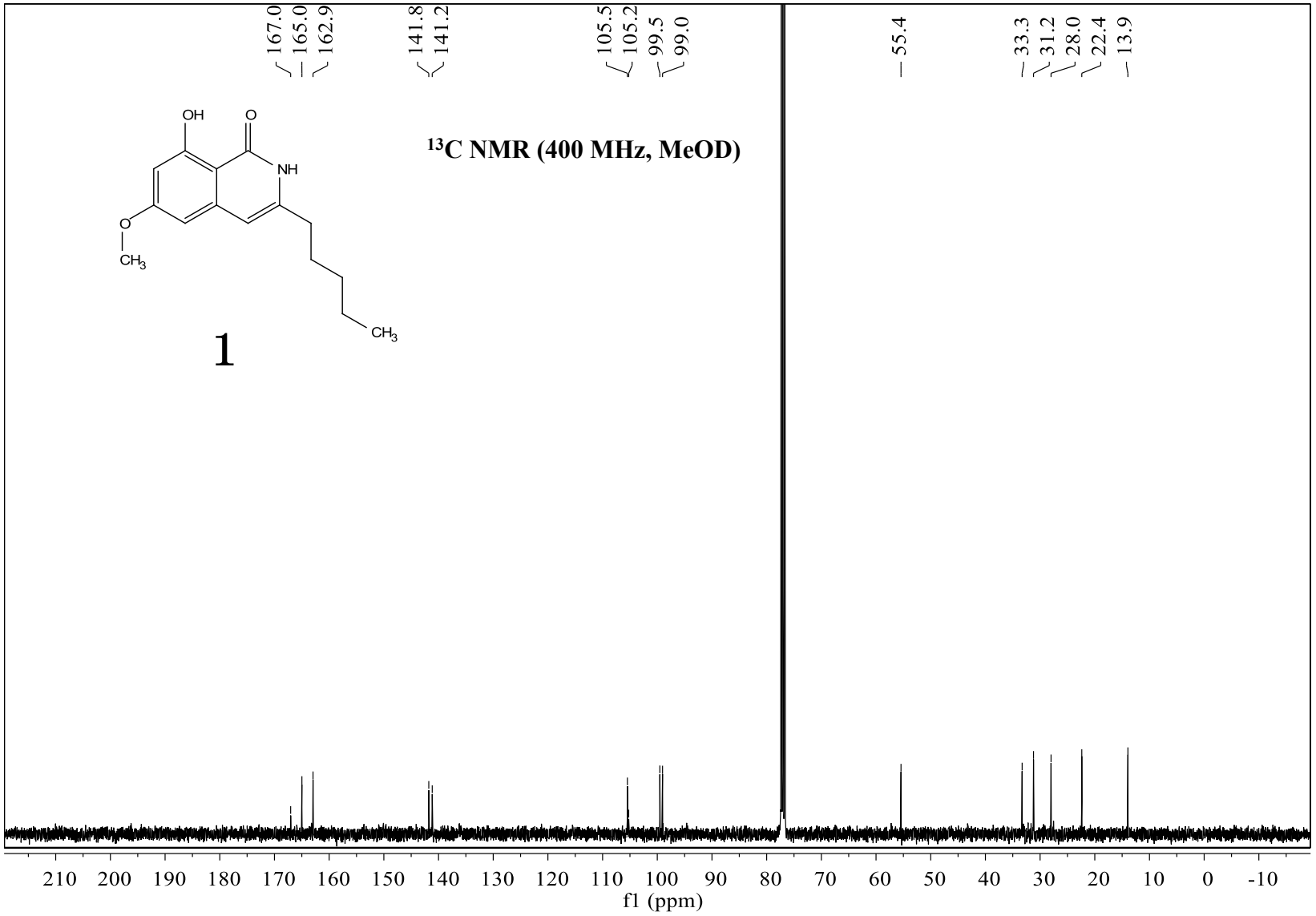

6.44
6.43
6.42
6.42
6.37
4.53
4.09
3.95
3.88
3.64
3.63
3.63
2.13
2.12
2.11
1.90
1.87
1.86
1.85
1.83
1.74
1.74
1.70
1.70
1.67
1.56
^{1}H NMR (400 MHz, CDCl$_3$)
3cm
1.02
1.00
1.02
2.00
3.01
3.02
3.06
1.00
4.20
4.41
4.48
2.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

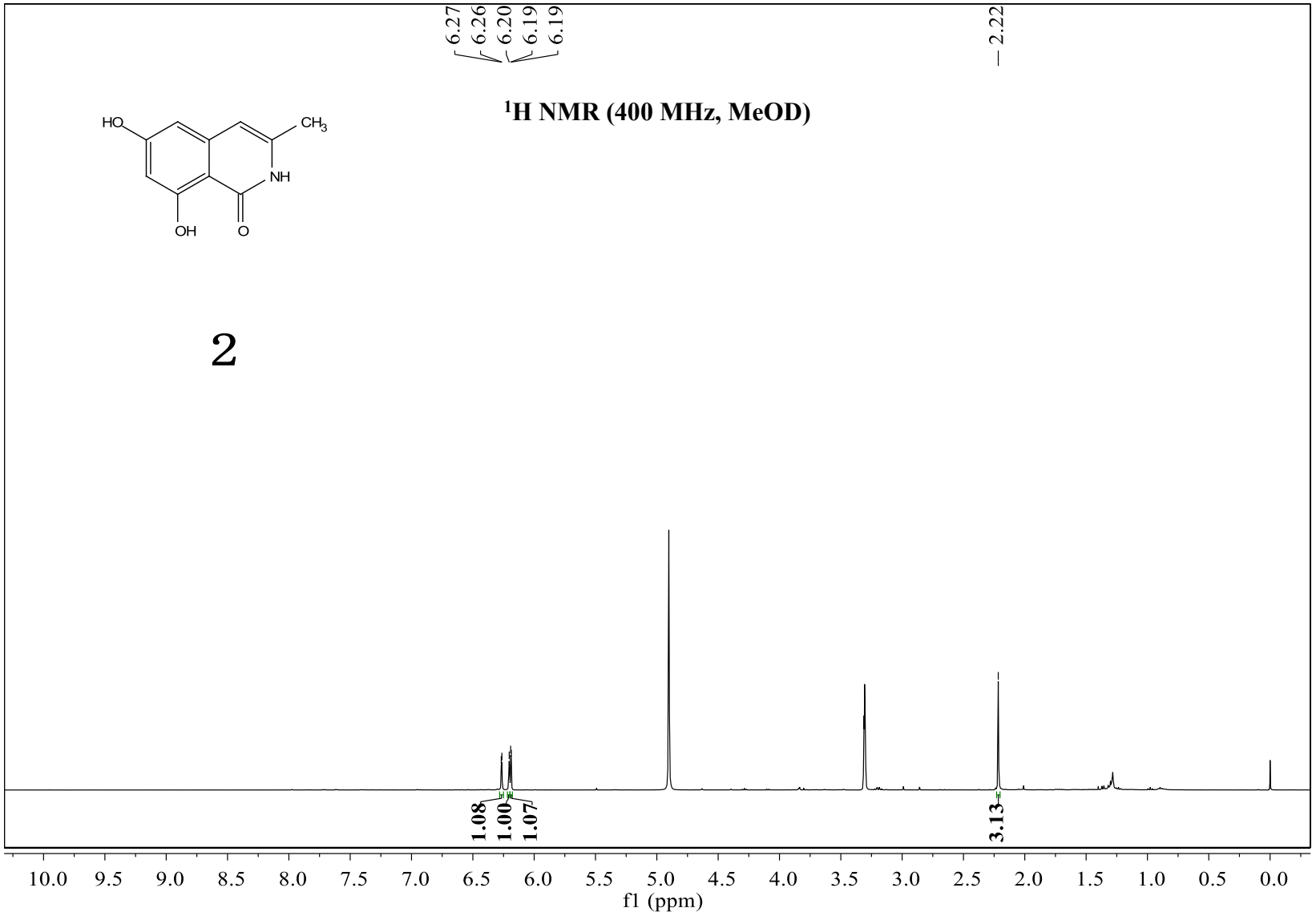

163.1
162.3
157.3
141.1
140.4
110.2
102.7
99.2
97.9
82.4
64.1
63.8
56.2
55.4
37.4
36.4
31.8
31.6
27.3
27.3
^{13}C NMR (400 MHz, MeOD)
3cm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.24 6.83 6.83 6.81 6.81 6.75 6.74 6.46 6.46 6.44 6.43 6.40 5.03 4.14 3.97 3.87 2.93 2.92 2.91 2.90 2.54 2.52 2.50 2.47 2.39 2.38 2.27 2.17 2.15 2.12 2.06 2.04 2.04 2.03 2.01 1.98 1.97 1.95 1.95 1.60 1.59 1.59 1.55 1.54 1.52 1.50 1.48 1.47 1.45 0.91
1H NMR (400 MHz, CDCl3)
3cn
1.09 1.06 1.01 2.08 1.02 2.00 3.04 3.00 3.03 2.05 1.22 1.22 1.31 1.11 3.01 1.21 5.29 3.10
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 -1.0
f1 (ppm)

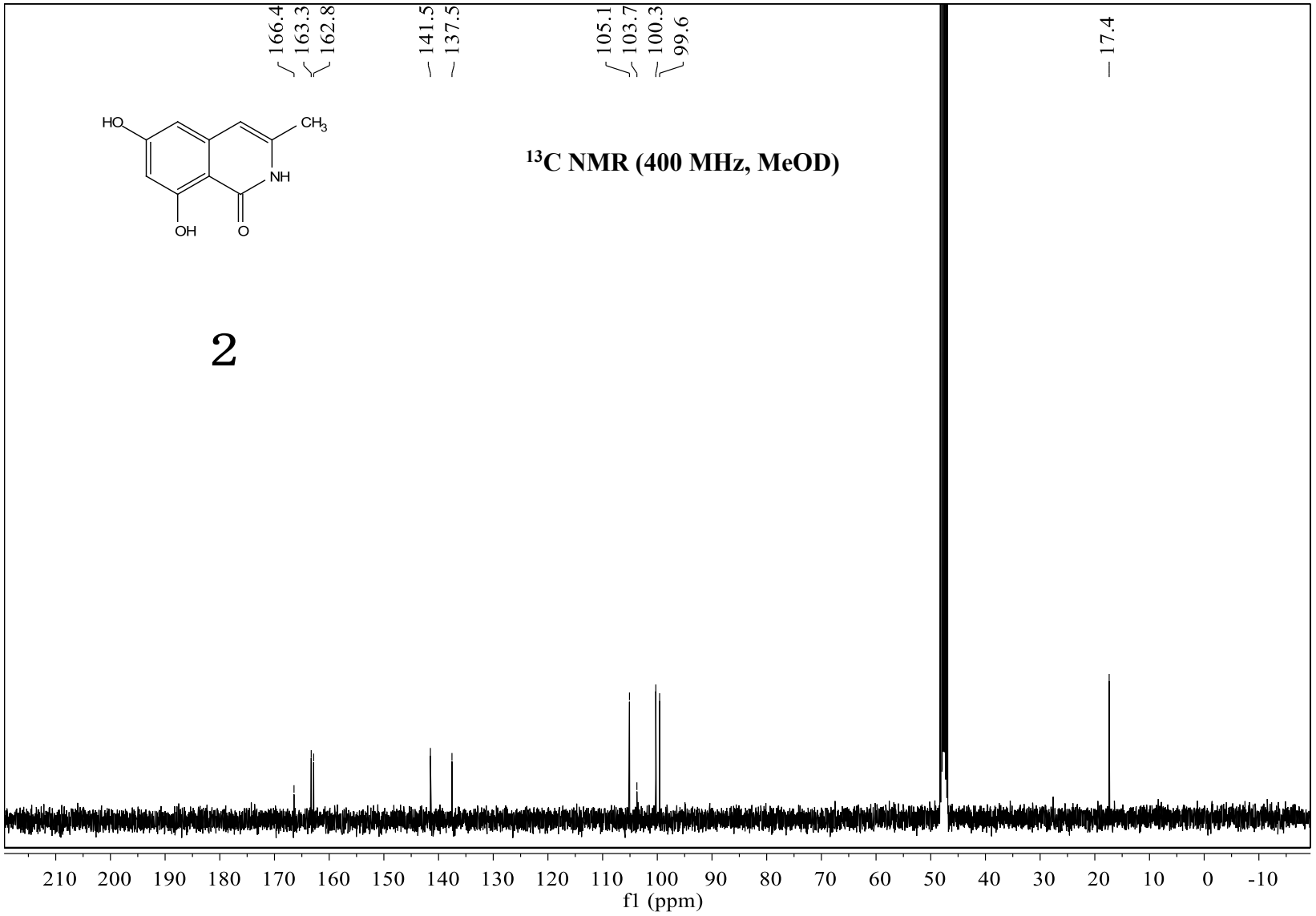

163.3
162.4
157.2
156.1
140.1
138.8
138.1
133.2
126.6
114.8
112.4
110.5
103.9
99.6
98.4
77.2
64.6
64.4
56.3
55.5
50.4
48.0
44.0
38.3
35.9
31.6
29.7
26.5
25.9
21.6
13.8
13C NMR (400 MHz, MeOD)
3cn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

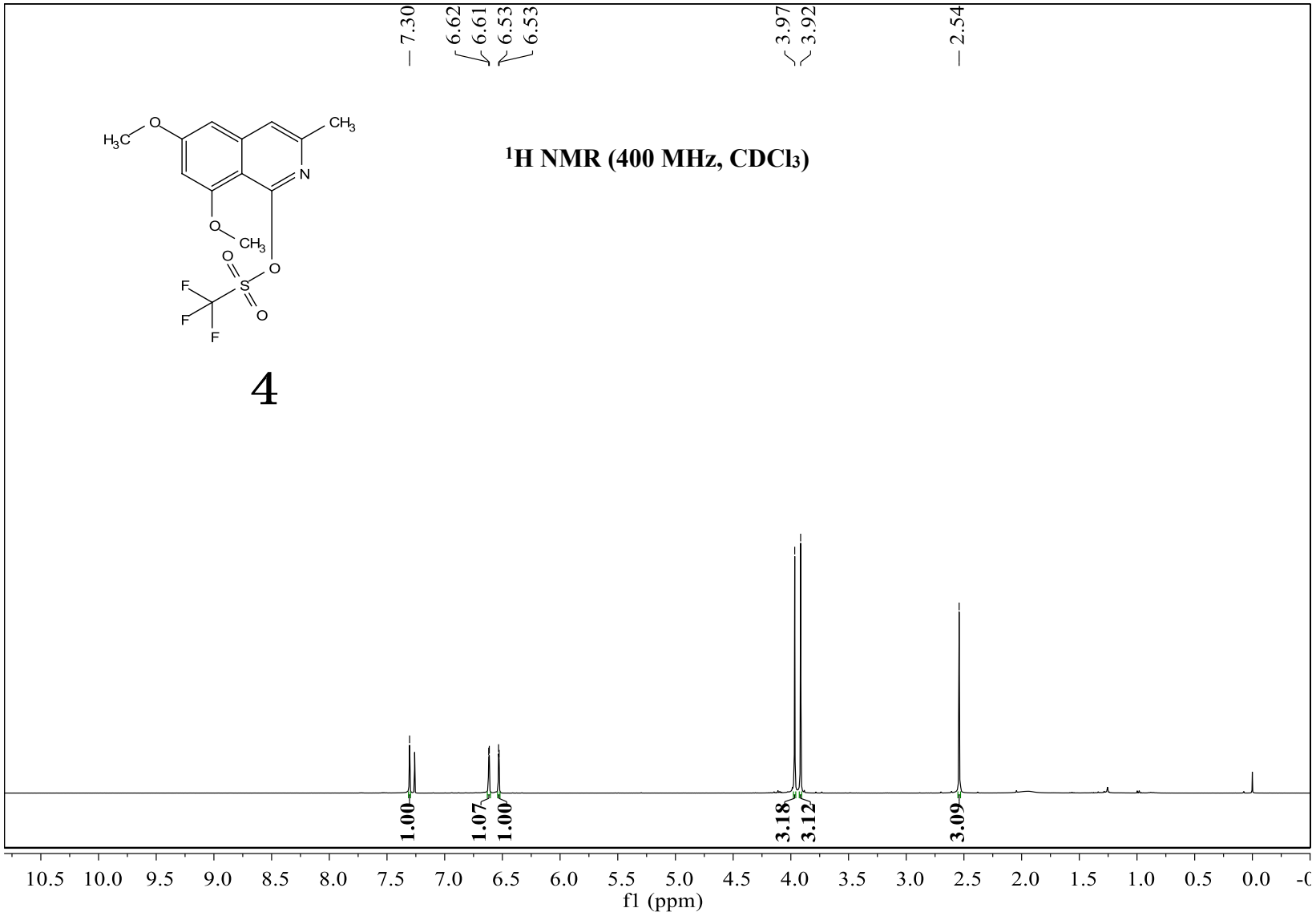

12.47
10.28
6.40
6.40
6.36
6.36
6.22
3.84
2.54
2.52
2.50
1.71
1.69
1.68
1.35
1.34
1.33
0.91
0.89
0.87
OH
O
NH
O
CH3
CH3
1
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.09
1.05
1.03
3.18
2.01
2.20
4.37
3.30
f1 (ppm)

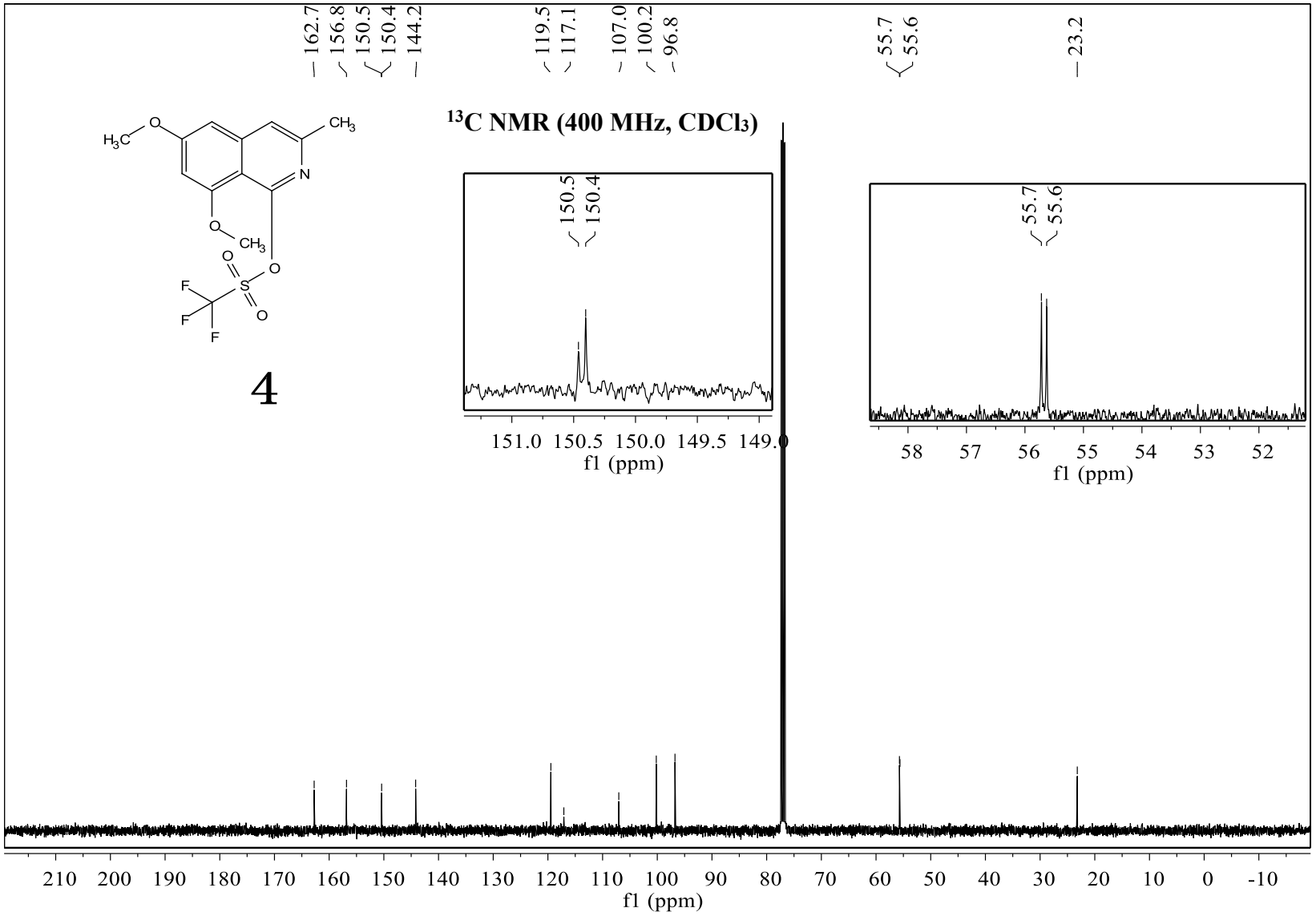

167.0
165.0
162.9
141.8
141.2
105.5
105.2
99.5
99.0
55.4
33.3
31.2
28.0
22.4
13.9
OH
O
NH
O
CH3
CH3
1
13C NMR (400 MHz, MeOD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

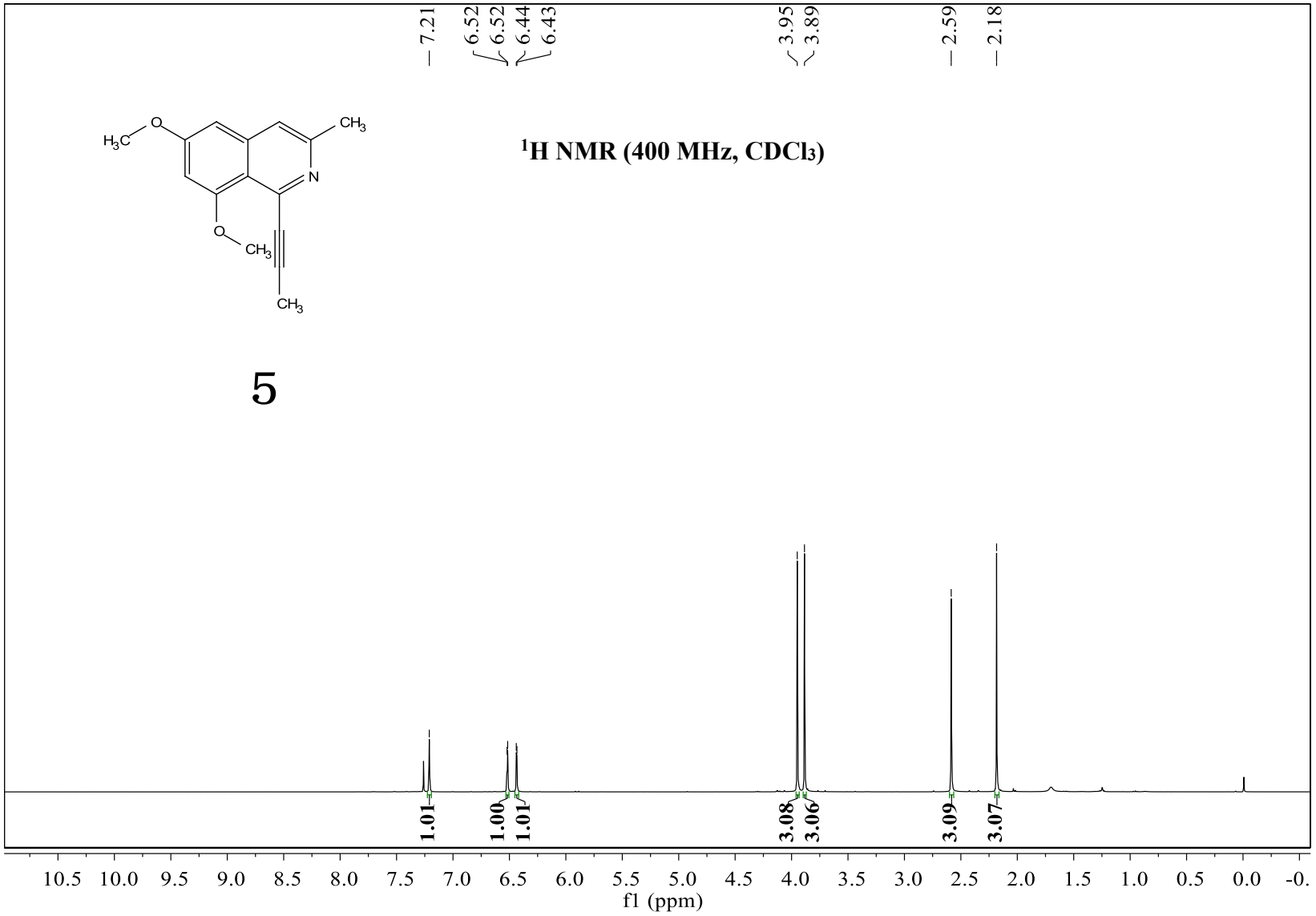


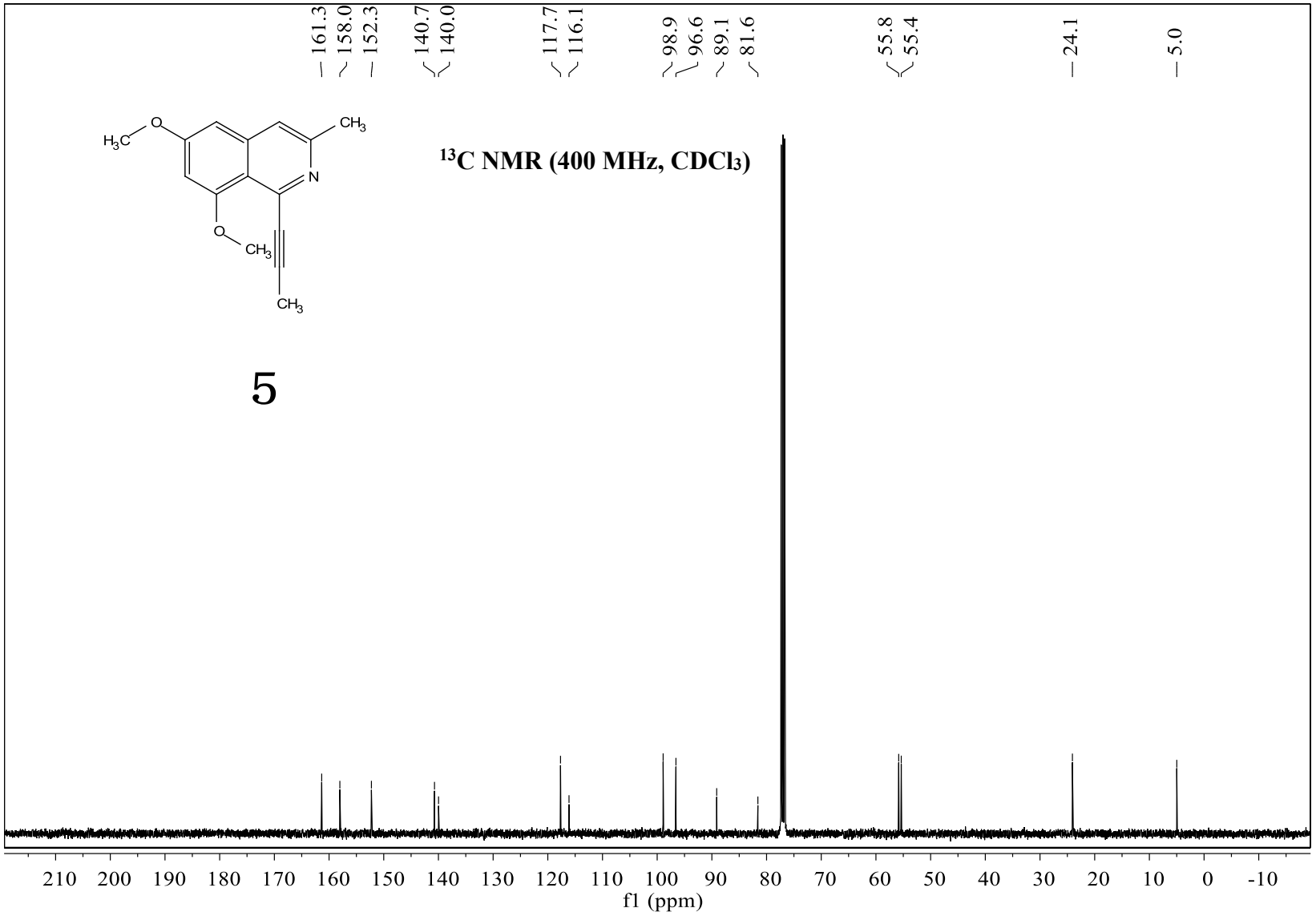
^{1}H NMR (400 MHz, MeOD)

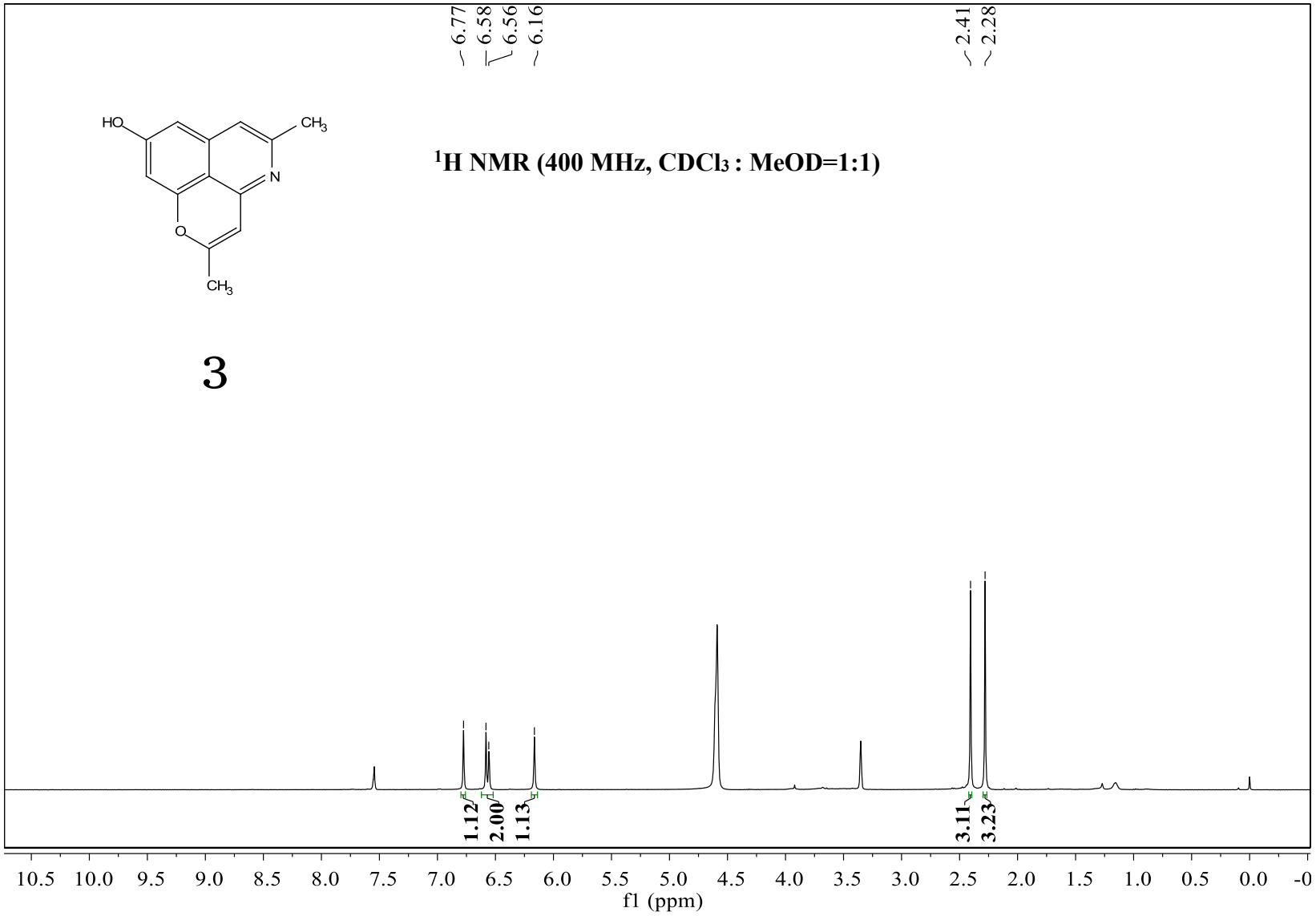

166.4
163.3
162.8
141.5
137.5
105.1
103.7
100.3
99.6
17.4
HO
CH3
NH
OH
O
13C NMR (400 MHz, MeOD)
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

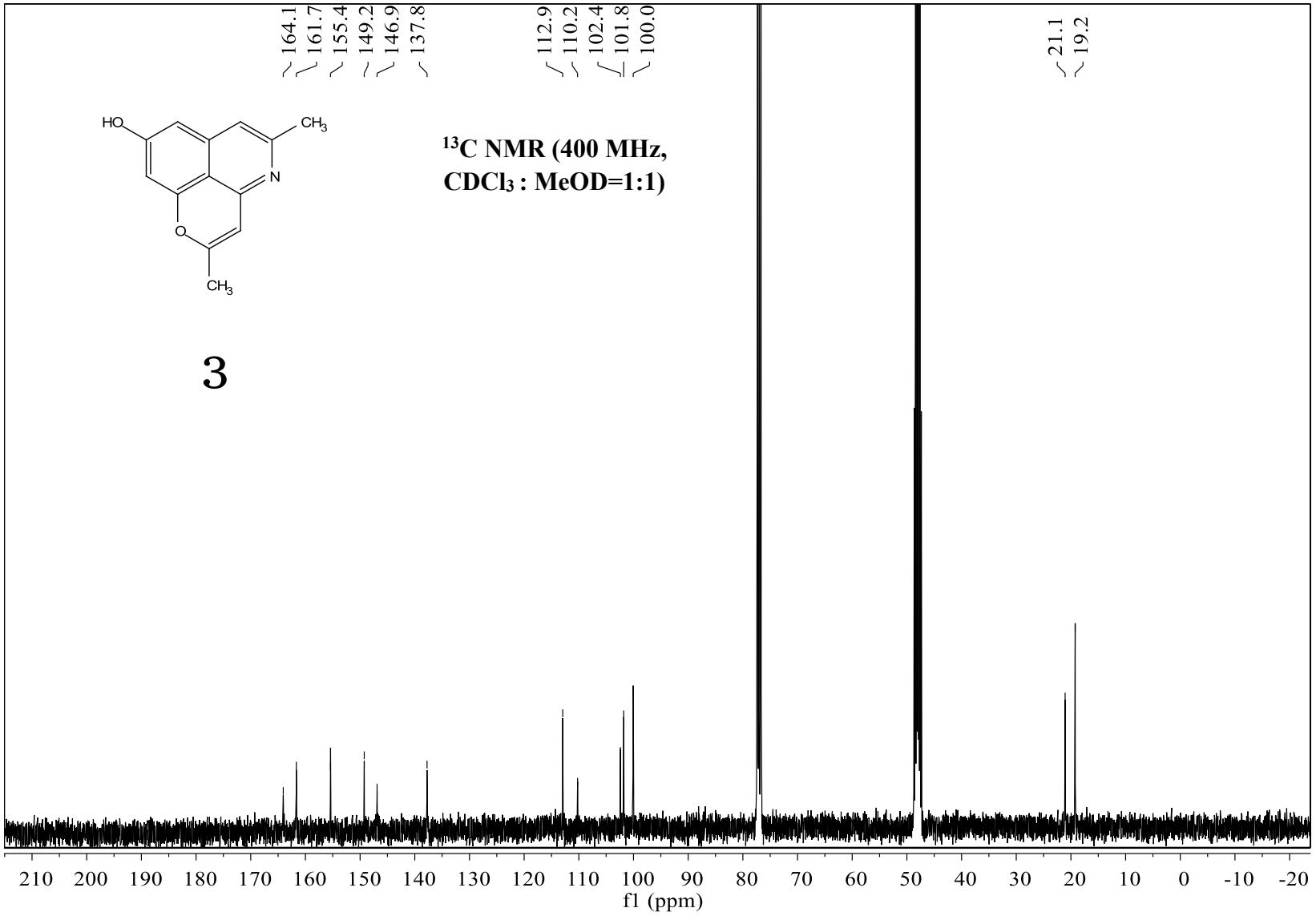

7.30
6.62
6.61
6.53
6.53
3.97
3.92
2.54
1H NMR (400 MHz, CDCl3)
4
1.00
1.07
1.00
3.18
3.12
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

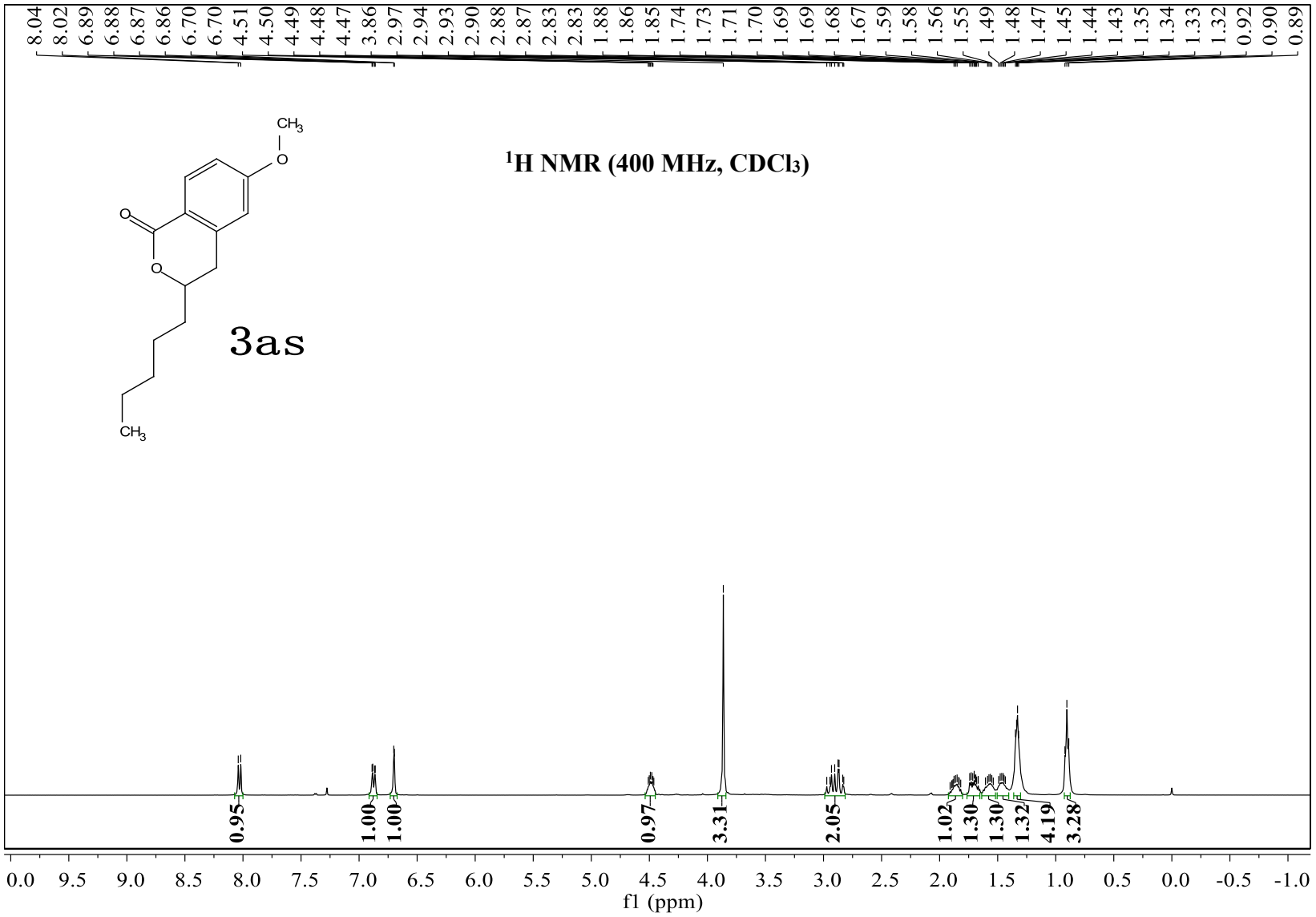

162.7
156.8
150.5
150.4
144.2
119.5
117.1
107.0
100.2
96.8
55.7
55.6
23.2
13C NMR (400 MHz, CDCl3)
4
151.0 150.5 150.0 149.5 149.0
f1 (ppm)
58 57 56 55 54 53 52
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

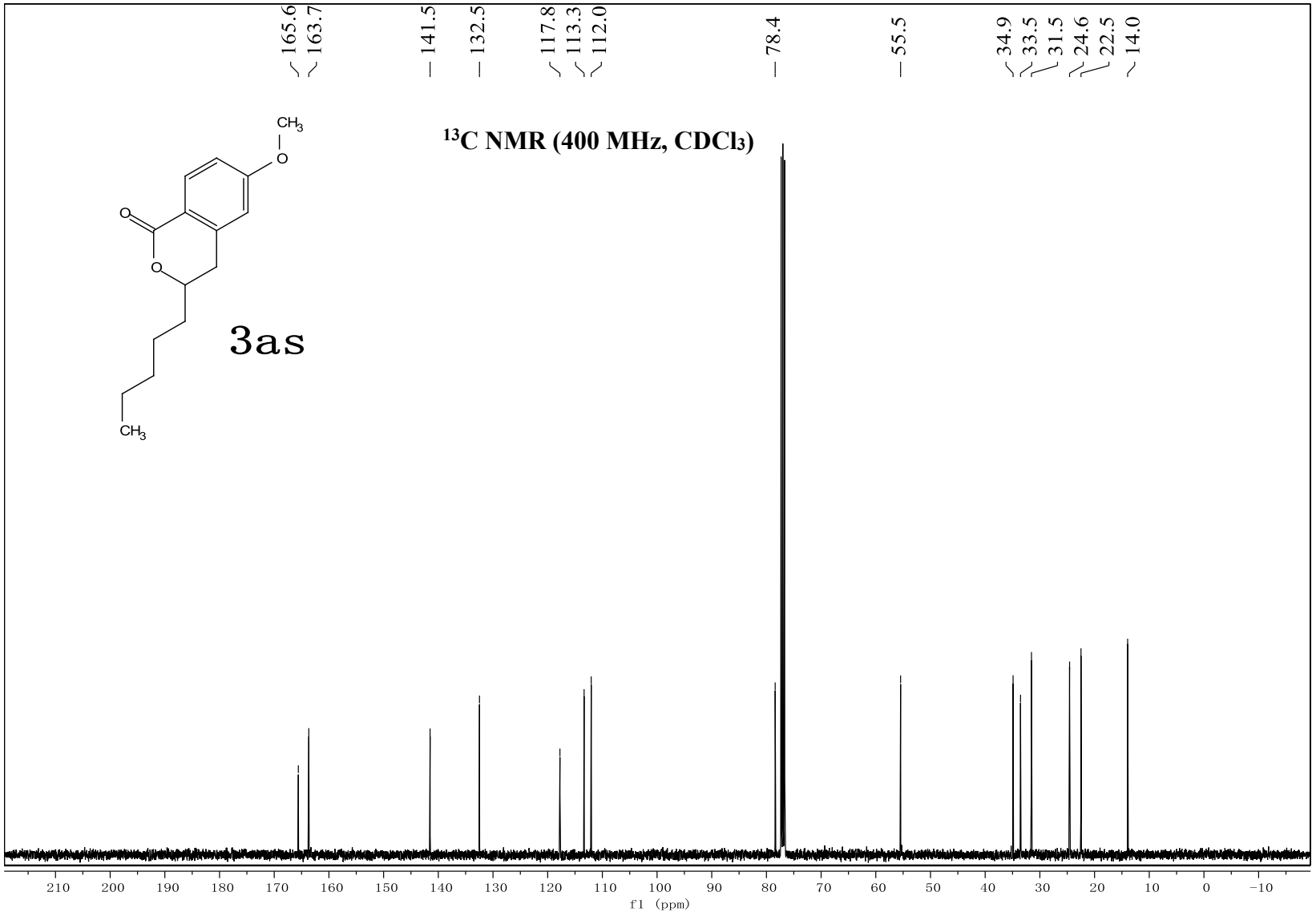

7.21
6.52
6.52
6.44
6.43
3.95
3.89
2.59
2.18
O
H3C
CH3
N
O
CH3
CH3
1H NMR (400 MHz, CDCl3)
5
1.01
1.00
1.01
3.08
3.06
3.09
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

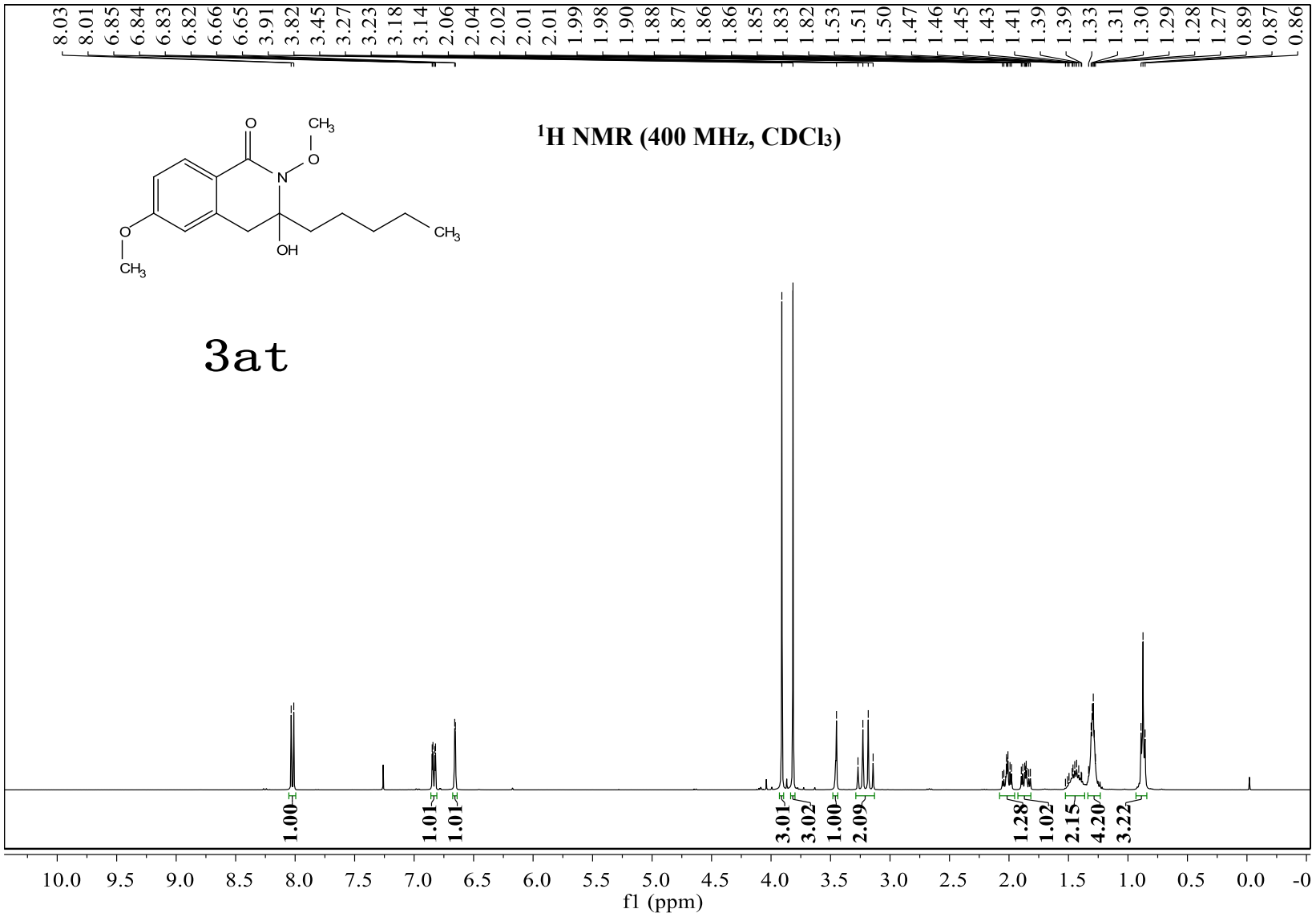

161.3
158.0
152.3
140.7
140.0
117.7
116.1
98.9
96.6
89.1
81.6
55.8
55.4
24.1
5.0
^{13}C NMR (400 MHz, CDCl$_3$)
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

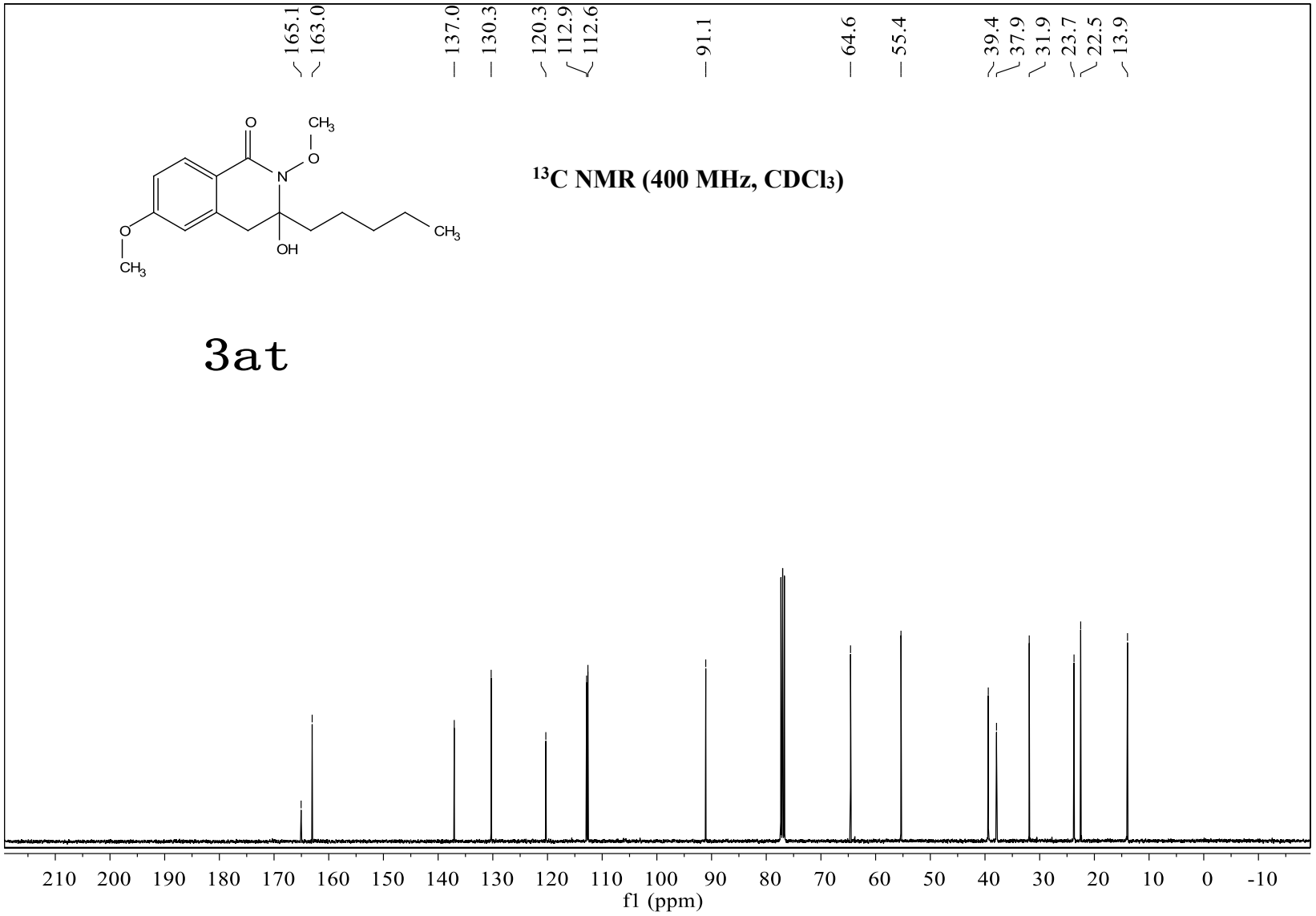

6.77
6.58
6.56
6.16
2.41
2.28
HO
CH3
N
O
CH3
3
1H NMR (400 MHz, CDCl3 : MeOD=1:1)
1.12
2.00
1.13
3.11
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


164.1
161.7
155.4
149.2
146.9
137.8
112.9
110.2
102.4
101.8
100.0
21.1
19.2
HO
CH3
N
O
CH3
13C NMR (400 MHz,
CDCl3 : MeOD=1:1)
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.04 8.02 6.89 6.88 6.87 6.86 6.70 6.70 4.51 4.50 4.49 4.48 4.47 3.86 2.97 2.94 2.93 2.90 2.88 2.87 2.83 2.83 1.88 1.86 1.85 1.74 1.73 1.71 1.70 1.69 1.69 1.68 1.67 1.59 1.58 1.56 1.55 1.49 1.48 1.47 1.45 1.44 1.43 1.35 1.34 1.33 1.32 0.92 0.90 0.89
CH3
O
O
O
CH3
3as
1H NMR (400 MHz, CDCl3)
0.95 1.00 1.00 0.97 3.31 2.05 1.02 1.30 1.30 1.32 4.19 3.28
0.0 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 -1.0
f1 (ppm)


165.6
163.7
141.5
132.5
117.8
113.3
112.0
78.4
55.5
34.9
33.5
31.5
24.6
22.5
14.0
^{13}C NMR (400 MHz, CDCl$_3$)
3as
CH$_3$
O
O
O
CH$_3$
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)


8.03 8.01 6.85 6.84 6.83 6.82 6.66 6.65 3.91 3.82 3.45 3.27 3.23 3.18 3.14 2.06 2.04 2.02 2.01 2.01 1.99 1.98 1.90 1.88 1.87 1.86 1.86 1.85 1.83 1.82 1.53 1.51 1.50 1.47 1.46 1.45 1.43 1.41 1.39 1.39 1.33 1.31 1.30 1.29 1.28 1.27 0.89 0.87 0.86
O
CH3
O
N
O
CH3
OH
CH3
1H NMR (400 MHz, CDCl3)
3at
1.00 1.01 1.01 3.01 3.02 1.00 2.09 1.28 1.02 2.15 4.20 3.22
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
f1 (ppm)


165.1
163.0
137.0
130.3
120.3
112.9
112.6
91.1
64.6
55.4
39.4
37.9
31.9
23.7
22.5
13.9
O
CH3
O
N
O
CH3
OH
CH3
13C NMR (400 MHz, CDCl3)
3at
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)