Supporting Information

For

Rh(III)-Catalyzed Selective Coupling of *N*-methoxy-1*H*-indole-1-carboxamides and Aryl Boronic Acids

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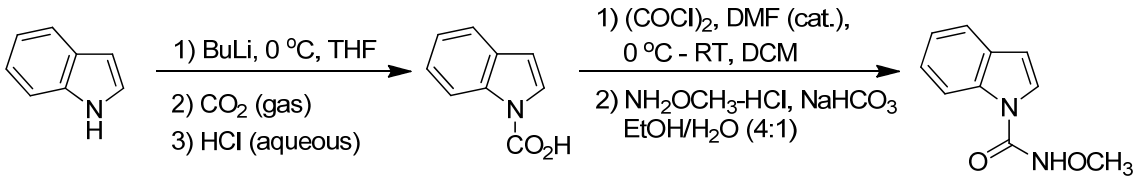
Contents

General Information:

Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on or BRUKER AVANCE III 400 spectrometer. CD_3OD and $CDCl_3$ were used as solvent. Chemical shifts were referenced relative to residual solvent signal (CD_3OD, ^{1}H NMR: δ 3.31 ppm, ^{13}C NMR: δ 49.0 ppm; $CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS were performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI). Melting points were measured with micro melting point apparatus.

The phenylboronic Acid, $[Cp^*RhCl_2]_2$, $Cu(OAc)_2$, Ag_2O, anhydrous MeOH were commercial available.

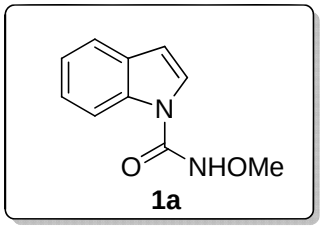
Typical procedure A for Synthesis Procedure and Characterization of 1:



A 250 mL three-necked flask with a stir-bar was charged with indole (4.68g, 40 mmol), which was then evacuated and backfilled with Argon for three times. THF (120 mL) was added and the solution was cooled to 0 °C. *n*-BuLi (19.2 mL, 2.5 M in hexane) was then added over 30 min to the solution and the reaction was kept at 0 °C for another 30 min. Next, CO_2 was bubbled to the reaction solution for 1 h at 0 °C and the solution was then quenched with H_2O (20 mL). The solution was transferred to a flask and evaporated to about 30 mL under vacuum. Aqueous HCl solution (6 M) was added to adjust the pH to 3 and the solution was extracted with ethyl acetate (60 mL * 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated to

afford the acid product 5.80 g (90% yield).

To a 250 mL flask charged with acid (1.61 g, 10 mmol) was added anhydrous DCM (20 mL) and DMF (0.1 mL), and cooled to 0 ^{o}C. $(COCl)_2$ (1.72 mL, 20 mmol) was added dropwise over 30 min, the solution was then warmed to RT and kept for 2 h. Then the solvent was concentrated to afford the crude acyl chloride to be used for next step. To a 100 mL flask charged with methoxylamine hydrochloride (1.67 g, 20 mmol) was added EtOH (40 mL) and H_2O (10 mL), $NaHCO_3$ (3.36 g, 40 mmol) was then added and the solution was kept at 0 ^{o}C. Afterwards, the acyl chloride was added dropwise to the solution at 0 ^{o}C over 30 min, then the solution was warmed to RT and kept for 5 h. Afterwards, the solution was filtered and the filtrate was concentrated. Then it was concentrated and the residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give product *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** as a pale yellow solid (1.3 g, 68.4% yield for two steps).

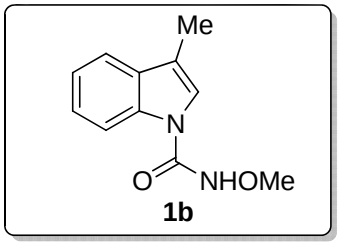


1a

***N*-methoxy-1*H*-indole-1-carboxamide(1a):** Prepared following the **Typical Procedure A** in 68.4 % yield (1.3 g, 6.84 mmol) for **1a**, from **indole** (1.17 g, 10 mmol). The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Pale yellow solid; m.p. 92-93 ^{o}C; R_f = 0.33 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 9.03 (s, 1H)， 8.14 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 7.6Hz, 1H), 7.44 (d, J = 3.6Hz, 1H), 7.32-7.28 (m, 1H), 7.25-7.21 (m, 1H), 6.59 (d, J = 3.6Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 153.5, 135.3, 130.1, 124.7, 123.6, 123.0, 121.2, 114.8, 108.3, 64.8; IR (KBr) *v*: 3208, 2968, 2926, 1681, 1491, 1447, 1332, 1212, 1077, 946, 872, 754 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{10}H_{10}N_2O_2$ (M^+):

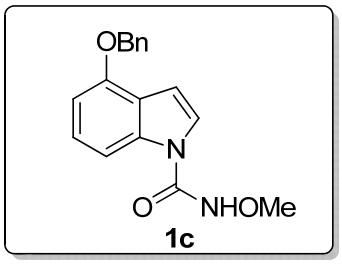
190.0742; Found: 190.0743.



1b

***N*-methoxy-3-methyl-1*H*-indole-1-carboxamide(1b):** Prepared following the **Typical Procedure A** in 40 % yield (400 mg, 1.96 mmol) for **1b**, from **3-Methylindole** (655 mg, 5 mmol) for two steps. The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

White solid; m.p. 128-129 ^{o}C; R_f = 0.68 (Petroleum ether/EtOAc 2:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.14-8.12 (d, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.36-7.32 (t, 1H), 7.28-7.24 (t, 1H), 7.14 (d, J = 0.8Hz, 1H), 3.89 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 153.4, 135.6, 131.1, 124.9, 122.8, 120.3, 119.3, 114.9, 65.0, 9.8; IR (KBr) v: 3213, 2958, 2926, 1686, 1488, 1436, 1348, 1056, 946, 832, 743 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_{12}N_2O_2$ (M^+): 204.0899; Found: 204.0901.

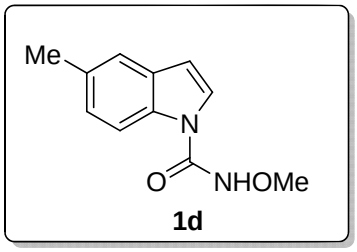


1c

4-(benzyloxy)-*N*-methoxy-1*H*-indole-1-carboxamide(1c): Prepared following the **Typical Procedure A** in 67.5 % yield (1.0 g, 3.37 mmol) for **1c**, from **4-Benzyloxyindole** (1.20 g, 5 mmol) for two steps. The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

Gray solid; m.p. 125-126 ^{o}C; R_f = 0.68 (Petroleum ether/EtOAc 2:1); ^{1}H NMR ($CDCl_3$,

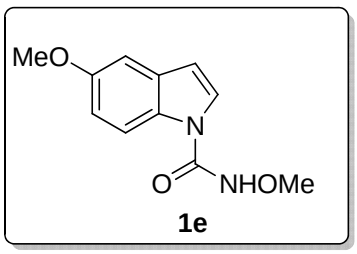
400MHz),δ: 8.51 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.42-7.38 (m, 2H), 7.36-7.34 (m, 1H), 7.31 (d, *J* = 3.6Hz, 1H), 7.25-7.20 (t, 1H), 6.80 (d, *J* = 3.6Hz, 1H), 6.73 (d, *J* = 8.0Hz, 1H), 5.19 (s, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 153.4, 152.4, 137.2, 136.5, 128.7, 128.1, 127.5, 125.7, 122.2, 120.9, 108.0, 105.6, 104.7, 70.2, 64.9; IR (KBr) *v*: 3161, 2979, 1676, 1587, 1504, 1442, 1275, 1160, 822, 743 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_3$ (M^+): 296.1161; Found: 296.1161.



1d

***N*-methoxy-5-methyl-1*H*-indole-1-carboxamide(1d):** Prepared following the **Typical Procedure A** in 63 % yield (630 mg, 3.08 mmol) for **1d**, from **5-Methylindole** (655 mg, 5 mmol) for two steps. The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

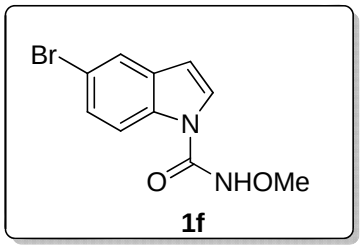
Pale yellow solid; m.p. 110-111 ^{o}C; R_f = 0.48 (Petroleum ether/EtOAc 2:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 9.05 (s, 1H)， 8.01 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 7.33 (s, 1H), 7.11 (d, *J* = 8.4Hz, 1H), 6.50 (d, *J* = 3.6Hz, 1H), 3.81 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 156.3, 133.5, 132.4, 130.3, 126.0, 123.7, 121.1, 114.4, 108.0, 64.7, 21.3; IR (KBr) *v*: 3213, 2973, 2937, 1676, 1441, 1343, 1212, 998, 848, 707 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_{12}N_2O_2$ (M^+): 204.0899; Found: 204.0903.



1e

***N*,5-dimethoxy-1*H*-indole-1-carboxamide(1e):** Prepared following the **Typical Procedure A** in 57 % yield (1.26 g, 5.72 mmol) for **1e**, from **5-Methoxyindole** (1.47 g, 10 mmol) for two steps. The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

Brown solid; m.p. 133-134 ^{o}C; R_f = 0.23 (Petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.82-8.62 (m, 1H)， 8.01 (d, J = 8.8 Hz, 1H), 7.39-7.38 (m, 1H), 7.01 (t, 1H), 6.94-6.90 (m, 1H), 6.52 (t, 1H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 156.0, 153.4, 131.0, 130.1, 124.1, 115.5, 113.6, 108.2, 103.7, 64.8, 55.8; IR (KBr) *v*: 3265, 2968, 2926, 1681, 1488, 1431, 1352, 1197, 1087, 946, 842, 732 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_{12}N_2O_3$ (M^+): 220.0848; Found: 220.0855.



1f

5-bromo-*N*-methoxy-1*H*-indole-1-carboxamide(1f): Prepared following the **Typical Procedure A** in 75 % yield (1.00 g, 3.74 mmol) for **1f**, from **5-bromoindole** (0.98 g, 5 mmol) for two steps. The final purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

White solid; m.p. 145-146 ^{o}C; R_f = 0.56 (Petroleum ether/EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.53 (s, 1H)， 8.01 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 1.6Hz, 1H), 7.41-7.37 (m, 2H), 6.55 (d, J = 3.6Hz, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 153.0, 134.1, 131.7, 127.7, 124.5, 123.9, 116.4, 116.3, 107.7, 65.0; IR (KBr) *v*: 3281, 3109, 2984, 2942, 1686, 1494, 1436, 1337, 1191, 998, 842, 801, 723 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{10}H_9BrN_2O_2$ (M^+): 267.9847; Found: 267.9850.

General Procedure B for Synthesis of 3:

A schlenk reaction tube containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then, MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 ^oC. After completion within 3 hours, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give *N*-methoxy-2-phenyl-1*H*-indole-1-carboxamide product **3a** as a white solid (50 mg, 94% yield).

General Procedure C for Synthesis of 4:

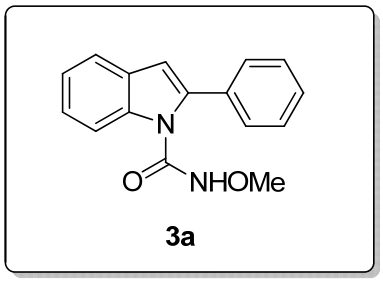
A schlenk reaction tube containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then, MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 ^oC. After completion within 12 hours, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to give **4a** as a white solid (39 mg, 76% yield).

General Procedure D for Synthesis of 5a:

A schlenk reaction tube containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-hydroxybenzenboronic acid (110 mg, 0.8 mmol) were evacuated and purged with nitrogen gas three times. Then, MeOH (2 mL) was added via syringe. The reaction mixture was kept at 90 ^oC. After completion within 2 hours, it was

diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **5a** as a yellow solid (18mg, 32% yield).

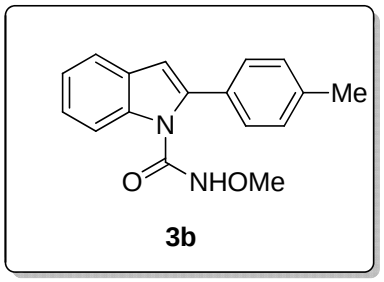
Characterization of 3, 4 and 5:



3a

***N*-methoxy-2-phenyl-1*H*-indole-1-carboxamide(3a):** Prepared following the **Typical Procedure B** in 94 % yield (50 mg, 0.187 mmol) for **3a**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and phenylboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

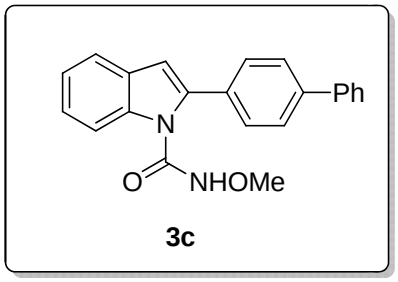
White solid; m.p. 119-120 ^oC; R_f = 0.48 (Petroleum ether/EtOAc 5:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.00 (d, *J* = 8.4Hz, 1H), 7.67 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.47-7.34 (m, 5H), 7.28-7.24 (m, 1H), 7.20-7.16 (m, 1H), 6.60 (s, 1H), 3.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.1, 137.9, 137.7, 131.7, 129.2, 129.1, 129.0, 128.6, 124.7, 123.0, 120.8, 114.0, 109.2, 64.6; IR (KBr) *v*: 3254, 3057, 2916, 1697, 1447, 1478, 1447, 1165, 1056, 863, 759, 691 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{14}N_2O_2$ (M^+): 266.1055; Found: 266.1059.



3b

***N*-methoxy-2-(p-tolyl)-1*H*-indole-1-carboxamide(3b):** Prepared following the **Typical Procedure B** in 61 % yield (34 mg, 0.121 mmol) for **3b**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Methylphenylboronic Acid **2b** (54mg, 0.4 mmol) in MeOH for 3h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

White solid; m.p. 177-178 ^oC; R_f = 0.54 (Petroleum ether/EtOAc 3:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.12 (d, *J* = 8.0Hz, 1H), 7.69 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.44-7.42 (d, 2H), 7.36-7.29 (m, 3H), 7.27-7.23 (m, 1H), 6.64 (s, 1H), 3.70 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.3, 139.4, 137.9, 137.7, 130.0, 129.0, 128.67, 128.61, 124.6, 123.0, 120.7, 114.2, 109.0, 107.1, 64.7, 21.5 cm^{-1}; IR (KBr) *v*: 3265, 2931, 1684, 1494, 1452, 1311, 1155, 1077, 795, 733; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_2$ (M^+): 280.1212; Found: 280.1212.

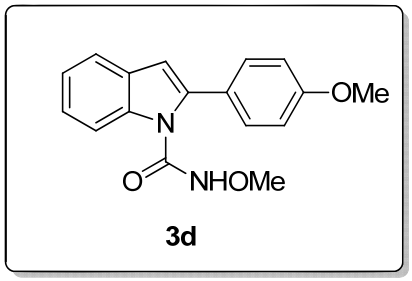


3c

2-([1,1'-biphenyl]-4-yl)-*N*-methoxy-1*H*-indole-1-carboxamide(3c): Prepared following the **Typical Procedure B** in 65 % yield (44 mg, 0.128 mmol) for **3c**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg,

0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Biphenylboronic Acid **2c** (80mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

White solid; m.p. 136-137 °C; R_f = 0.54 (Petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.10 (d, *J* = 8.0Hz, 1H), 7.81 (s, 1H), 7.72 (d, 2H), 7.66-7.60 (m, 5H), 7.51-7.47 (t, 2H), 7.42-7.34 (m, 2H), 7.29-7.28 (d, 1H), 6.74 (s, 1H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.2, 141.9, 140.1, 138.1, 137.4, 130.4, 129.1, 129.0, 128.97, 128.0, 127.85, 127.2, 124.8, 123.1, 120.8, 114.1, 109.4, 64.7; IR (KBr) *v*: 3242, 3030, 2933, 1695, 1486, 1406, 1299, 1152, 1108, 1079, 943, 910, 860, 805, 765, 694 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{22}H_{18}N_2O_2$ (M^+): 342.1368; Found: 342.1361.

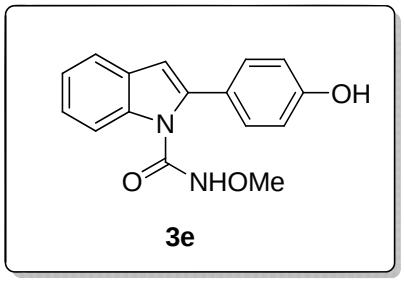


3d

***N*-methoxy-2-(4-methoxyphenyl)-1*H*-indole-1-carboxamide(3d):** Prepared following the **Typical Procedure B** in 65 % yield (40 mg, 0.135 mmol) for **3d**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Methoxyphenylboronic Acid **2d** (60mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

White solid; m.p. 148-149 °C; R_f = 0.18 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.10 (d, *J* = 8.4Hz, 1H), 7.76 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.47-7.45 (m, 1H), 7.33-7.30 (m, 1H), 7.27-7.23 (m, 1H), 7.02-7.00 (m, 2H), 6.60 (s, 1H), 3.87 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 160.4, 152.3, 137.8, 137.5, 130.1, 129.1, 124.4, 123.8, 123.0, 120.5, 114.8, 114.2, 108.6, 64.7, 55.6; IR

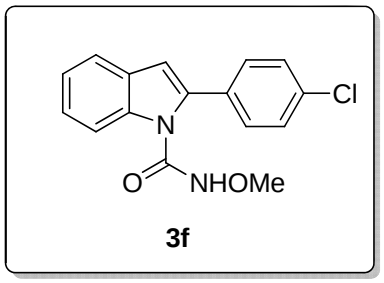
(KBr) *v*: 3228, 2947, 2827, 1692, 1608, 1494, 1447, 1327, 1249, 1186, 1014, 790, 743 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_3$ (M^+): 296.1161; Found: 296.1160.



3e

2-(4-hydroxyphenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3e): Prepared following the **Typical Procedure B** in 72 % yield (40 mg, 0.141 mmol) for **3e**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Hydroxyphenylboronic Acid **2e** (55mg, 0.4 mmol) in MeOH for 3h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:2) as eluent.

Brown solid; m.p. 148-149 ^oC; R_f = 0.40 (Petroleum ether/EtOAc 1:1); ^1H NMR (CD_3OD, 400MHz), δ: 7.67 (d, *J* = 8.0Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 1H), 6.89-6.86 (m, 2H), 6.61 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (CD_3OD, 100MHz), δ: 159.0, 153.8, 141.0, 138.8, 130.6, 130.4, 124.6, 124.2, 123.1, 121.5, 116.4, 112.7, 106.6, 64.3 cm^{-1}; IR (KBr) *v*: 3234, 2958, 2916, 1692, 1603, 1499, 1477, 1317, 1145, 806, 603; HRMS (EI) (*m/z*): calcd for $C_{16}H_{14}N_2O_3$ (M^+): 282.1004; Found: 282.1004.

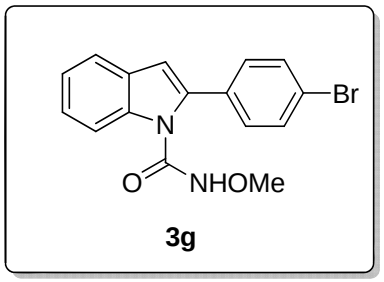


3f

2-(4-chlorophenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3f): Prepared following

the **Typical Procedure B** in 48 % yield (29 mg, 0.096 mmol) for **3f**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Chlorophenylboronic Acid **2f** (62mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Gray solid; m.p. 173-174 °C; R_f = 0.63 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.01 (d, *J* = 8.4Hz, 1H), 7.78 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 4H), 7.36-7.32 (t, 1H), 7.28-7.24 (t, 1H), 6.68 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$), δ: 151.9, 137.9, 136.7, 135.1, 130.2, 129.6, 129.4, 128.9, 124.9, 123.2, 120.9, 113.8, 119.5, 64.7; IR (KBr) *v*: 3244, 2942, 1681, 1535, 1483, 1442, 1155, 1077, 1103, 1014, 801, 743 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{13}ClN_2O_2$ (M^+): 300.0666; Found: 300.0662.

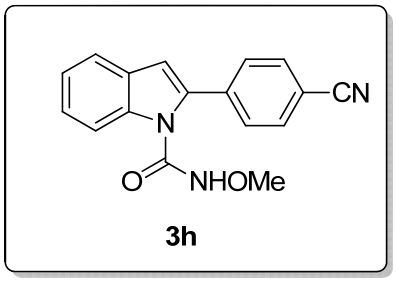


3g

2-(4-bromophenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3g): Prepared following the **Typical Procedure B** in 48 % yield (41 mg, 0.119 mmol) for **3g**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Bromophenylboronic Acid **2g** (80mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

White solid; m.p. 192-193 °C; R_f = 0.37 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 7.94 (d, *J* = 8.4Hz, 1H), 7.70 (s, 1H), 7.55-7.51 (m, 3H), 7.34-7.26 (m, 3H), 7.21-7.18 (t, 1H), 6.62 (s, 1H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$,

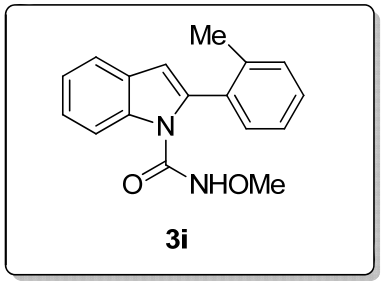
100MHz), δ: 151.9, 137.9, 136.7, 132.4, 130.6, 129.9, 128.9, 125.0, 123.3, 123.2, 121.0, 113.8, 109.6, 64.8; IR (KBr) *v*: 3249, 2947, 1686, 1530, 1488, 1442, 1150, 936, 832, 801, 738 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{13}BrN_2O_2$ (M^+): 344.0160; Found: 344.0160.



3h

2-(4-cyanophenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3h): Prepared following the **Typical Procedure B** in 43 % yield (25 mg, 0.086 mmol) for **3h**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 4-Cyanophenylboronic Acid **2h** (59mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

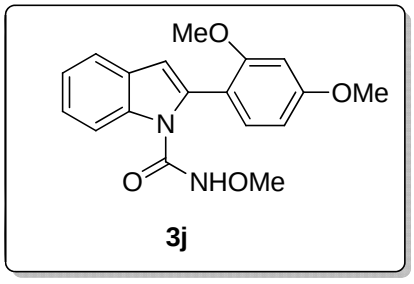
Brown solid; m.p. 156-157 °C; R_f = 0.4 (Petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.01 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.71-7.69 (m, 2H), 7.63-7.58 (m, 3H), 7.39-7.35 (m, 1H), 7.30-7.26 (m, 1H), 6.81 (s, 1H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 151.6, 138.0, 136.4, 136.3, 132.6, 128.7, 128.6, 125.2, 123.4, 121.5, 118.6, 113.3, 111.9, 110.9, 64.8; IR (KBr) *v*: 3235, 3051, 2937, 2224, 1699, 1605, 1562, 1447, 1266, 1075, 811, 675, 631 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{13}N_3O_2$ (M^+): 291.1008; Found: 291.1004.



3i

***N*-methoxy-2-(o-tolyl)-1*H*-indole-1-carboxamide(3i):** Prepared following the **Typical Procedure B** in 78 % yield (44 mg, 0.157 mmol) for **3i**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 2-Tolylboronic Acid **2i** (55mg, 0.4 mmol) in MeOH for 3h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Brown solid; m.p. 99-100 ^oC; R_f = 0.44 (Petroleum ether/EtOAc 5:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.28 (d, J = 8.4 Hz, 1H), 7.60-7.58 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 3H), 7.30-7.26 (t, 1H), 6.55 (s, 1H), 3.59 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.4, 138.3, 137.3, 136.3, 131.9, 131.0, 130.1, 130.0, 126.8, 124.7, 123.1, 120.6, 115.3, 109.9, 64.4, 20.1; IR (KBr) *v*: 3199, 2941, 1691, 1474, 1443, 1324, 1154, 952, 823, 756, 668 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_2$ (M^+): 280.1212; Found: 280.1212.

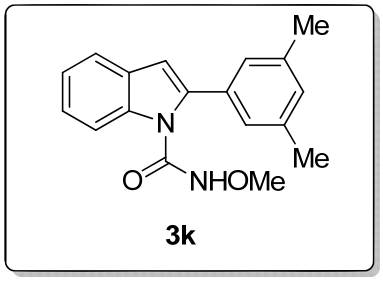


3j

2-(2,4-dimethoxyphenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3j): Prepared following the **Typical Procedure B** in 75 % yield (48 mg, 0.147 mmol) for **3j**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg,

0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 2-Tolylboronic Acid **2j** (55mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:3) as eluent.

Gray solid; m.p. 143-144 °C; R_f = 0.11 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.11 (d, *J* = 8.0Hz, 1H), 8.02 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.4Hz, 1H), 7.32-7.29 (m, 1H), 7.23-7.19 (m, 1H), 6.61 (dd, J_1 = 8.0Hz, J_2 = 2.0Hz, 1H), 6.55 (d, *J* = 2.4Hz, 1H), 6.51 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 162.5, 158.1, 152.9, 137.2, 134.6, 131.9, 128.9, 124.2, 122.5, 120.4, 114.2, 113.5, 108.7, 105.4, 99.0, 64.6, 55.8, 55.7 cm^{-1}; IR (KBr) *v*: 3129, 2968, 2926, 2827, 1697, 1603, 1494, 1442, 1317, 1165, 952, 811, 743; HRMS (EI) (*m/z*): calcd for $C_{18}H_{18}N_2O_4$ (M^+): 326.1267; Found: 326.1270.

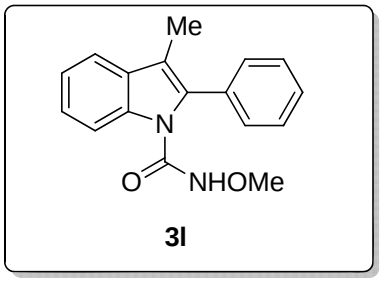


3k

2-(3,5-dimethylphenyl)-*N*-methoxy-1*H*-indole-1-carboxamide(3k): Prepared following the **Typical Procedure B** in 86 % yield (51 mg, 0.173 mmol) for **3k**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and 3,5-Dimethylbenzeneboronic Acid **2k** (60mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Yellow solid; m.p. 125-127 °C; R_f = 0.44 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.12 (d, *J* = 8.0Hz, 1H), 7.81 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.16 (s, 2H), 7.09 (s, 1H), 6.65 (s, 1H), 3.67 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.2, 139.0, 137.9, 131.5, 130.9,

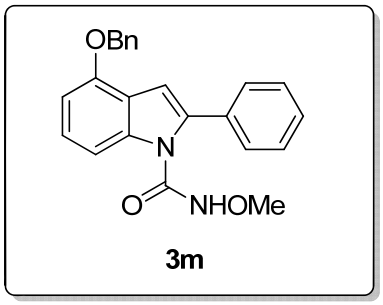
129.0, 126.5, 124.5, 123.0, 120.6, 114.2, 109.0, 64.5, 21.4; IR (KBr) *v*: 3208, 2958, 2921, 1692, 1603, 1483, 1452, 1035, 848, 790, 727 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{18}N_2O_2$ (M^+): 294.1368; Found: 294.1370.



3l

***N*-methoxy-3-methyl-2-phenyl-1*H*-indole-1-carboxamide(3l):** Prepared following the **Typical Procedure B** in 87 % yield (49 mg, 0.175 mmol) for **3k**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-methoxy-3-methyl-1*H*-indole-1-carboxamide **1b** (41 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

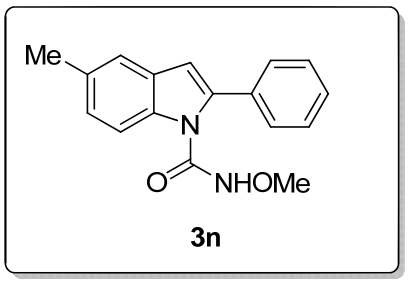
Brown solid; m.p. 114-116 °C; R_f = 0.32 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.13 (d, *J* = 8.0Hz, 1H), 7.57 (s, 1H), 7.53-7.47 (m, 3H), 7.46-7.41 (m, 3H), 7.36-7.31 (m, 1H), 7.28-7.23 (m, 1H), 3.54 (s, 3H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.4, 136.9, 132.8, 131.5, 130.1, 129.2, 129.1, 124.9, 122.7, 119.0, 116.6, 114.5, 64.4, 9.4; IR (KBr) *v*: 3176, 2935, 2861, 1722, 1678, 1606, 1493, 1453, 1195, 945, 801, 701, 665 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_2$ (M^+): 280.1212; Found: 280.1214.



3m

4-(benzyloxy)-*N*-methoxy-2-phenyl-1*H*-indole-1-carboxamide(3m): Prepared following the **Typical Procedure B** in 92 % yield (68 mg, 0.182 mmol) for **3m**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), 4-(benzyloxy)-*N*-methoxy-1*H*-indole-1-carboxamide **1c** (59 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

Gray solid; m.p. 125-126 °C; R_f = 0.43 (Petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 7.72-7.68 (m, 2H), 7.55-7.53 (m, 2H), 7.50-7.38 (m, 7H), 7.36-7.34 (m, 1H), 7.27-7.26 (m, 1H), 6.88 (s, 1H), 6.75 (d, *J* = 8.0Hz, 1H), 6.22 (s, 2H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.2, 152.1, 139.3, 137.2, 136.3, 131.7, 129.2, 129.0, 128.7, 128.6, 128.1, 127.5, 125.6, 119.9, 107.3, 106.6, 104.5, 70.2, 64.6; IR (KBr) *v*: 3254, 2926, 1702, 1577, 1468, 1332, 1259, 1160, 1024, 795, 749, 686 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{23}H_{20}N_2O_3$ (M^+): 372.1474; Found: 372.1471.

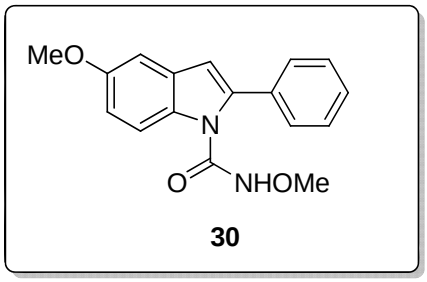


3n

***N*-methoxy-5-methyl-2-phenyl-1*H*-indole-1-carboxamide(3n):** Prepared following the **Typical Procedure B** in 57 % yield (32 mg, 0.114 mmol) for **3n**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-methoxy-5-methyl-1*H*-indole-1-carboxamide **1d** (41 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

Pale yellow solid; m.p. 150-151 °C; R_f = 0.42 (Petroleum ether/EtOAc 3:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 7.98 (d, *J* = 8.8Hz, 1H), 7.67 (s, 1H), 7.51-7.42 (m, 5H), 7.37

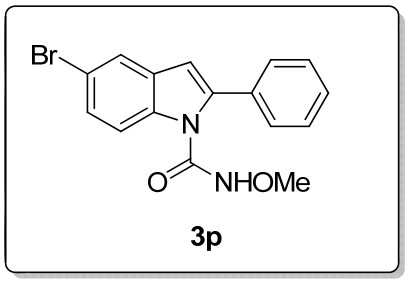
(s,1H), 7.16 (dd, J_1 = 8.4Hz, J_2 = 1.2Hz, 1H), 6.60 (s, 1H), 3.67 (s, 3H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 152.3, 137.7, 136.3, 132.6, 131.9, 129.24, 129.21, 129.1, 128.7, 126.2, 120.6, 113.9, 109.2, 64.6, 21.5; IR (KBr) *v*: 3239, 2963, 2926, 1686, 1592, 1478, 1348, 1254, 1017, 975, 733, 691 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_2$ (M^+): 280.1212; Found: 280.1217.



30

***N*,5-dimethoxy-2-phenyl-1*H*-indole-1-carboxamide(3o):** Prepared following the **Typical Procedure B** in 57 % yield (34 mg, 0.115 mmol) for **3o**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*,5-dimethoxy-1*H*-indole-1-carboxamide **1e** (44 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 ^{o}C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

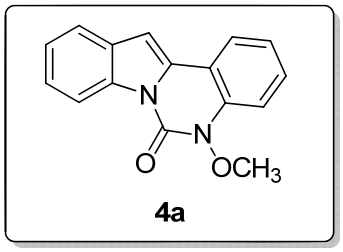
White solid; m.p. 163-164 ^{o}C; R_f = 0.23 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.02 (d, J = 9.2Hz, 1H), 7.63 (s, 3H), 7.52-7.43 (m, 5H), 7.03 (d, J = 2.8 Hz, 1H), 6.96 (dd, J_1 = 8.8Hz, J_2 = 2.4Hz, 1H), 6.60 (s, 1H), 3.86 (s, 3H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 156.2, 152.3, 138.2, 132.9, 131.8, 129.7, 129.3, 129.2, 128.7, 115.2, 113.9, 109.4, 102.9, 64.6, 55.9; IR (KBr) *v*: 3208, 3119, 2931, 1681, 1608, 1468, 1317, 1072, 801, 764, 701 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{16}N_2O_3$ (M^+): 296.1161; Found: 296.1171.



3p

5-bromo-*N*-methoxy-2-phenyl-1*H*-indole-1-carboxamide(3p): Prepared following the **Typical Procedure B** in 91 % yield (62 mg, 0.180 mmol) for **3p**, from $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), 5-bromo-*N*-methoxy-1*H*-indole-1-carboxamide **1f** (44 mg, 0.2 mmol), $Cu(OAc)_2$ (145 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 3h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

White solid; m.p. 174-176 ^oC; R_f = 0.29 (Petroleum ether/EtOAc 5:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 7.95 (d, J = 8.8Hz, 1H), 7.70 (s, 2H), 7.51-7.40 (m, 6H), 6.60 (m, 1H), 3.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 151.7, 138.8, 136.6, 131.2, 130.6, 129.6, 129.4, 128.8, 127.5, 123.3, 116.2, 115.7, 108.3, 64.6; IR (KBr) *v*: 3234, 2958, 2931, 1697, 1598, 1478, 1452, 1087, 1035, 874, 806, 769, 701 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{13}BrN_2O_2$ (M^+): 344.0160; Found: 344.0162.

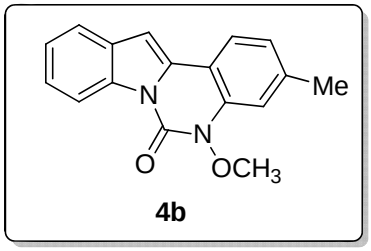


4a

5-methoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4a): Prepared following the **Typical Procedure C** in 76 % yield (40 mg, 0.151 mmol) for **4a**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and phenylboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using

mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

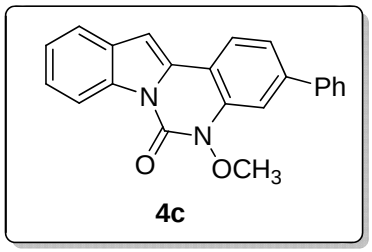
White solid; m.p. 164-165 ^{o}C; R_f = 0.47 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.68 (d, J = 7.6Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.70 (dd, J_1 = 6.8Hz, J_2 = 1.6Hz, 1H), 7.51-7.46 (m, 2H), 7.43-7.36 (m, 2H), 7.30-7.26 (m, 1H), 7.08 (s, 1H), 4.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.3, 134.5, 133.8, 132.6, 130.0, 129.6, 124.1, 124.0, 123.95, 123.86, 120.4, 116.2, 114.0, 112.2, 99.1, 63.4; IR (KBr) v: 2937, 1712, 1582, 1462, 1358, 1233, 1160, 946, 743, 707 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{12}N_2O_2$ (M^+): 264.0899; Found: 264.0895.



4b

5-methoxy-3-methylindolo[1,2-c]quinazolin-6(5*H*)-one(4b): Prepared following the **Typical Procedure C** in 50 % yield (40 mg, 0.151 mmol) for **4b**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-Methylbenzeneboronic Acid **2b** (54mg, 0.4 mmol) in MeOH for 12h at 60 ^{o}C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

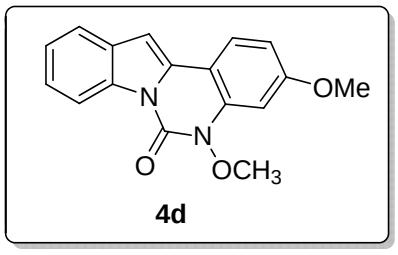
Pale yellow solid; m.p. 147-148 ^{o}C; R_f = 0.25 (Petroleum ether/EtOAc 10:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.67-8.65 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.41-7.34 (m, 2H), 7.25 (s, 1H), 7.08 (d, J = 8.0Hz, 1H), 7.00 (s, 1H), 4.14 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.4, 140.3, 134.4, 133.7, 132.8, 130.1, 125.0, 124.0, 123.8, 123.7, 120.3, 116.1, 112.3, 111.4, 98.2, 63.3, 22.1; IR (KBr) v: 2999, 2947, 1697, 1614, 1598, 1442, 1363, 1321, 1151, 972, 738, 649 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_2$ (M^+): 278.1055; Found: 278.1065.



4c

5-methoxy-3-phenylindolo[1,2-c]quinazolin-6(5*H*)-one(4c): Prepared following the **Typical Procedure C** in 84 % yield (57 mg, 0.167 mmol) for **4c**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and Biphenyl-4-boronic Acid **2c** (80mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Pale yellow solid; m.p. 178-180 ^oC; R_f = 0.25 (Petroleum ether/EtOAc 10:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.69 (d, *J* = 7.6Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.72-7.66 (m, 4H), 7.53-7.50 (m, 3H), 7.45-7.37 (m, 3H), 7.11 (s, 1H), 4.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.4, 142.8, 140.1, 134.6, 134.2, 132.4, 130.1, 129.2, 128.3, 127.3, 124.4, 124.1, 124.0, 123.0, 120.4, 116.1, 112.9, 110.5, 99.2, 66.5; IR (KBr) *v*: 3063, 2931, 1702, 1592, 1421, 1363, 1321, 1259, 795, 749, 681 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{22}H_{16}N_2O_2$ (M^+): 340.1212; Found: 340.1212.

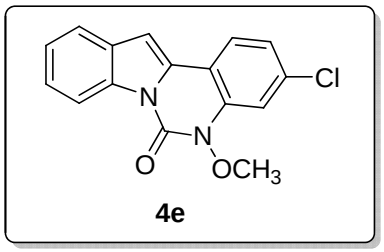


4d

3,5-dimethoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4d): Prepared following the **Typical Procedure C** in 76 % yield (45 mg, 0.153 mmol) for **4d**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-Methoxybenzeneboronic Acid **2d** (54mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column

chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

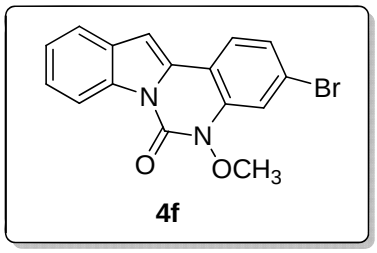
Pale yellow solid; m.p. 125-127 ^{o}C; R_f = 0.20 (Petroleum ether/EtOAc 10:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.63 (t, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.86 (m, 1H), 7.39-7.34 (m, 2H), 6.93 (m, 1H), 6.90 (s, 1H), 6.84-6.81 (m, 1H), 4.14 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 161.2, 145.4, 135.2, 134.2, 132.8, 130.3, 125.4, 124.0, 123.4, 120.1, 116.0, 110.8, 107.1, 97.2, 63.3, 56.8; IR (KBr) *v*: 2942, 2822, 1707, 1603, 1494, 1442, 1353, 1040, 795, 743 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_3$ (M^+): 294.1004; Found: 294.1000.



4e

3-chloro-5-methoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4e): Prepared following the **Typical Procedure C** in 36 % yield (21 mg, 0.070 mmol) for **4e**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-Chlorobenzeneboronic Acid **2f** (62mg, 0.4 mmol) in MeOH for 12h at 60 ^{o}C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

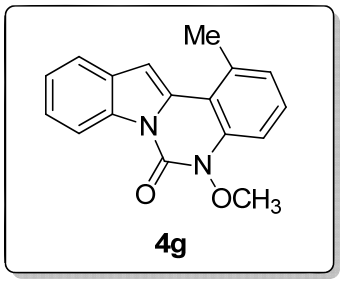
Pale yellow solid; m.p. 184-185 ^{o}C; R_f = 0.34 (Petroleum ether/EtOAc 20:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.64 (d, J = 8.0Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.69-7.67 (m, 1H), 7.43-7.36 (m, 4H), 7.23 (dd, J_1 = 8.4Hz, J_2 = 2.0Hz, 1H), 4.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 144.9, 135.3, 134.5, 134.4, 131.6, 129.7, 124.9, 124.20, 124.17, 124.1, 120.4, 116.0, 112.3, 112.2, 99.5, 63.3; IR (KBr) *v*: 3041, 2937, 1712, 1603, 1447, 1369, 1087, 801, 733 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{11}ClN_2O_2$ (M^+): 298.0509; Found: 298.0518.



4f

3-bromo-5-methoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4f): Prepared following the **Typical Procedure C** in 59 % yield (21 mg, 0.117 mmol) for **4f**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-Bromobenzeneboronic Acid **2g** (80mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Pale yellow solid; m.p. 164-165 ^oC; R_f = 0.31 (Petroleum ether/EtOAc 10:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.65 (d, *J* = 8.4Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71-7.69 (m, 1H), 7.61 (d, *J* = 2.0Hz, 1H), 7.43-7.37 (m, 3H), 7.08 (s, 1H), 4.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.0, 134.7, 134.5, 131.8, 130.0, 127.1, 125.1, 124.4, 124.3, 123.3, 120.6, 116.1, 115.2, 112.9, 99.7, 63.6; IR (KBr) *v*: 2942, 1707, 1587, 1436, 1379, 1082, 1020, 952, 806, 733 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{11}BrN_2O_2$ (M^+): 342.0004; Found: 342.0006.

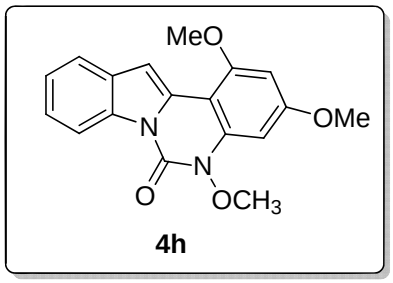


4g

5-methoxy-1-methylindolo[1,2-c]quinazolin-6(5*H*)-one(4g): Prepared following the **Typical Procedure C** in 35 % yield (19 mg, 0.068 mmol) for **4g**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 2-Tolylboronic Acid **2i** (55mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica

gel using mixture of ethyl acetate/petroleum ether (v/v, 1:15) as eluent.

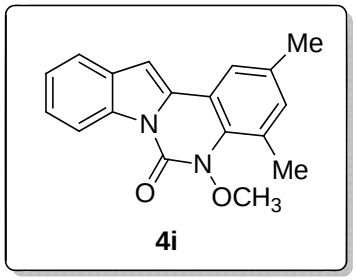
Yellow solid; m.p. 135-136 ^{o}C; R_f = 0.42 (Petroleum ether/EtOAc 10:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.74 (d, *J* = 8.0Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.42-7.37 (m, 4H), 7.19 (s, 1H), 7.17-7.14 (m, 1H), 4.14 (s, 3H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.2, 136.1, 134.5, 133.8, 132.2, 130.0, 128.7, 126.9, 124.3, 124.0, 120.5, 116.3, 113.3, 110.1, 104.9, 63.1, 24.1; IR (KBr) *v*: 2947, 1697, 1587, 1546, 1478, 1452, 1343, 1301, 972, 785, 733 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_2$ (M^+): 278.1055; Found: 278.1066.



4h

1,3,5-trimethoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4h): Prepared following the **Typical Procedure C** in 50 % yield (32 mg, 0.098 mmol) for **4h**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 2,4-Dimethoxybenzeneboronic Acid **2j** (55mg, 0.4 mmol) in MeOH for 12h at 60 ^{o}C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

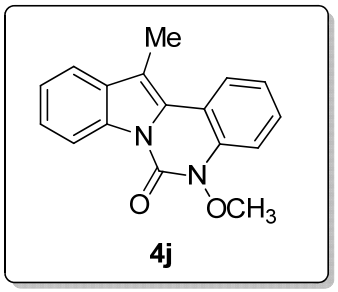
Gray solid; m.p. 162-163 ^{o}C; R_f = 0.11 (Petroleum ether/EtOAc 5:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.66 (m, 1H), 7.67-7.65 (m, 1H), 7.37-7.35 (m, 2H), 7.28-7.26 (m, 1H), 6.60 (s, 1H), 6.38 (s, 1H), 4.13 (s, 3H), 4.04 (d, 3H), 3.91 (d, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 161.5, 158.2, 145.4, 136.2, 133.5, 130.9, 130.1, 123.8, 123.2, 120.2, 115.9, 102.6, 97.6, 94.0, 88.9, 63.2, 56.1, 55.8; IR (KBr) *v*: 3062, 2963, 2937, 1697, 1614, 1473, 1358, 1020, 972, 790, 727 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{16}N_2O_4$ (M^+): 324.1110; Found: 324.1110.



4i

5-methoxy-2,4-dimethylindolo[1,2-c]quinazolin-6(5*H*)-one(4i): Prepared following the **Typical Procedure C** in 74 % yield (43 mg, 0.147 mmol) for **4i**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 3,5-Dimethylbenzeneboronic Acid **2k** (60mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:15) as eluent.

Yellow solid; m.p. 163-164 ^oC; R_f = 0.48 (Petroleum ether/EtOAc 10:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.66-8.64 (m, 1H), 7.69-7.67 (m, 1H), 7.59 (s, 1H), 7.37-7.35 (m, 2H), 7.06 (s, 1H), 7.02 (s, 1H), 3.79 (s, 3H), 2.66 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 146.3, 135.1, 134.4, 133.8, 132.9, 130.4, 130.1, 124.3, 124.0, 123.7, 122.3, 120.3, 116.2, 115.2, 63.2, 22.1, 20.7; IR (KBr) *v*: 2937, 1692, 1556, 1478, 1442, 1369, 1223, 1087, 975, 842, 738 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{16}N_2O_2$ (M^+): 292.1212; Found: 292.1216.

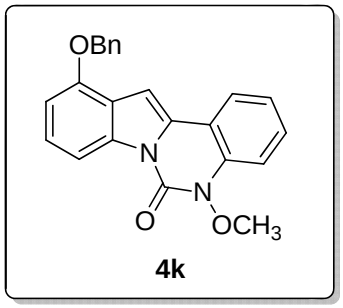


4j

5-methoxy-12-methylindolo[1,2-c]quinazolin-6(5*H*)-one(4j): Prepared following the **Typical Procedure C** in 40 % yield (22 mg, 0.079 mmol) for **4j**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-methoxy-3-methyl-1*H*-indole-1-carboxamide **1b** (41 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH

for 12h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Yellow solid; m.p. 129-130 °C; R_f = 0.35 (Petroleum ether/EtOAc 10:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.70-8.67 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.70-7.63 (m, 1H), 7.48-7.42 (m, 2H), 7.42-7.39 (m, 2H), 7.32-7.28 (m, 1H), 4.13 (s, 3H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.4, 133.9, 133.5, 131.4, 128.5, 127.2, 124.7, 124.3, 123.7, 123.6, 118.2, 116.1, 115.7, 112.0, 110.6, 63.2, 11.0; IR (KBr) *v*: 2962, 2860, 1698, 1606, 1467, 1452, 1364, 1307, 1093, 951, 801, 741, 698 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_2$ (M^+): 278.1055; Found: 278.1061.

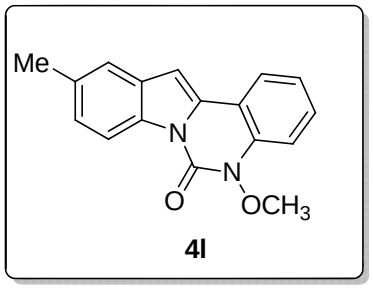


4k

11-(benzyloxy)-5-methoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4k): Prepared following the **Typical Procedure C** in 43 % yield (32 mg, 0.086 mmol) for **4k**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), 4-(benzyloxy)-*N*-methoxy-1*H*-indole-1-carboxamide **1c** (59 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 12h at 60 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Gray solid; m.p. 132-133 °C; R_f = 0.28 (Petroleum ether/EtOAc 10:1); ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.22 (d, *J* = 8.4Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.49-7.47 (m, 2H), 7.39-7.35 (m, 4H), 7.32-7.19 (m, 5H), 6.81 (d, *J* = 8.0Hz, 1H), 5.20 (s, 2H), 4.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 151.9, 145.4, 137.2, 135.7, 133.7, 131.4, 129.3, 128.8, 128.2, 127.7, 124.9, 124.0, 123.7, 121.2, 114.3, 112.2, 109.4, 105.3, 96.7, 70.3, 63.4; IR (KBr) *v*: 2968, 2921, 2853, 1702, 1572, 1462, 1301, 1092, 806,

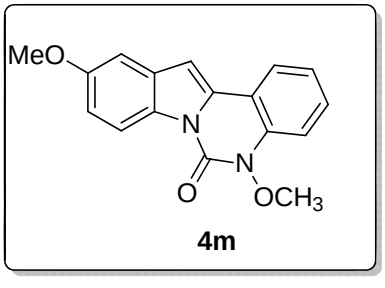
754 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{23}H_{18}N_2O_3$ (M^+): 370.1317; Found: 370.1315.



4l

5-methoxy-10-methylindolo[1,2-c]quinazolin-6(5*H*)-one(4l): Prepared following the **Typical Procedure C** in 60 % yield (33 mg, 0.118 mmol) for **4l**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-methoxy-5-methyl-1*H*-indole-1-carboxamide **1d** (41 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Yellow solid; m.p. 168-169 ^oC; R_f = 0.26 (Petroleum ether/EtOAc 10:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.52 (d, *J* = 8.4Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.48-7.43 (m, 3H), 7.29-7.22 (m, 2H), 7.00 (s, 1H), 4.15 (s, 3H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 145.3, 133.73, 133.67, 132.7, 132.6, 130.2, 129.5, 125.6, 123.86, 123.79, 120.2, 115.7, 114.1, 112.2, 98.7, 63.4, 21.8; IR (KBr) *v*: 3015, 2952, 2911, 2853, 1697, 1592, 1462, 1363, 1269, 1087, 946, 801, 738 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_2$ (M^+): 278.1055; Found: 278.1055.

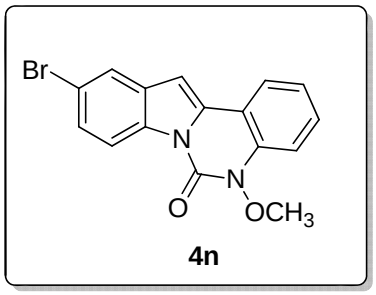


4m

5,10-dimethoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4m): Prepared following the **Typical Procedure C** in 70 % yield (41 mg, 0.139 mmol) for **4m**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2mol%), *N*-methoxy-5-methoxy-1*H*-indole-1-carboxamide **1e** (44 mg, 0.2 mmol),

Ag_2O (184 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

White solid; m.p. 180-181 ^oC; R_f = 0.23 (Petroleum ether/EtOAc 10:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.54 (d, *J* = 8.0Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.50-7.44 (m, 2H), 7.29-7.25 (m, 1H), 7.12 (d, *J* = 2.4Hz, 1H), 7.04-7.00 (m, 2H), 4.14 (s, 3H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 156.9, 145.1, 133.7, 133.2, 131.0, 129.5, 129.3, 123.9, 123.8, 116.9, 113.3, 112.2, 102.3, 98.8, 63.4, 55.8; IR (KBr) *v*: 2973, 1697, 1592, 1478, 1363, 1306, 1103, 801, 733 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_3$ (M^+): 294.1004; Found: 294.1014.

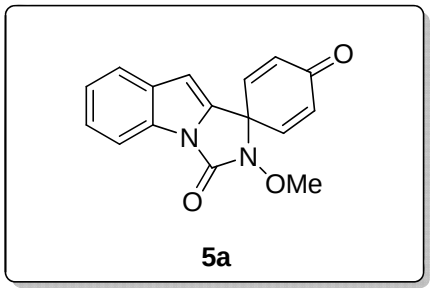


4n

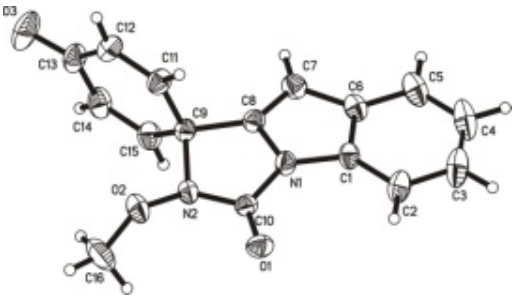
10-bromo-5-methoxyindolo[1,2-c]quinazolin-6(5*H*)-one(4n): Prepared following the **Typical Procedure C** in 56 % yield (38 mg, 0.111 mmol) for **4n**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), 5-bromo-*N*-methoxy-1*H*-indole-1-carboxamide **1f** (44 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and benzeneboronic Acid **2a** (49mg, 0.4 mmol) in MeOH for 12h at 60 ^oC. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:10) as eluent.

Pale yellow solid; m.p. 208-209 ^oC; R_f = 0.40 (Petroleum ether/EtOAc 5:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.53 (d, *J* = 8.8Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.54-7.46 (m, 3H), 7.32-7.28 (t, 1H), 7.00 (s, 1H), 4.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 146.0, 133.9, 133.7, 133.1, 131.7, 130.1, 126.8, 124.2, 124.1, 123.0, 117.6, 117.5, 113.5, 112.3, 98.1, 63.5; IR (KBr) *v*: 2963, 1702, 1592, 1468, 1259,

1092, 1030, 879, 806, 749 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{11}BrN_2O_2$ (M^+): 342.0004; Found: 342.0013.



5a



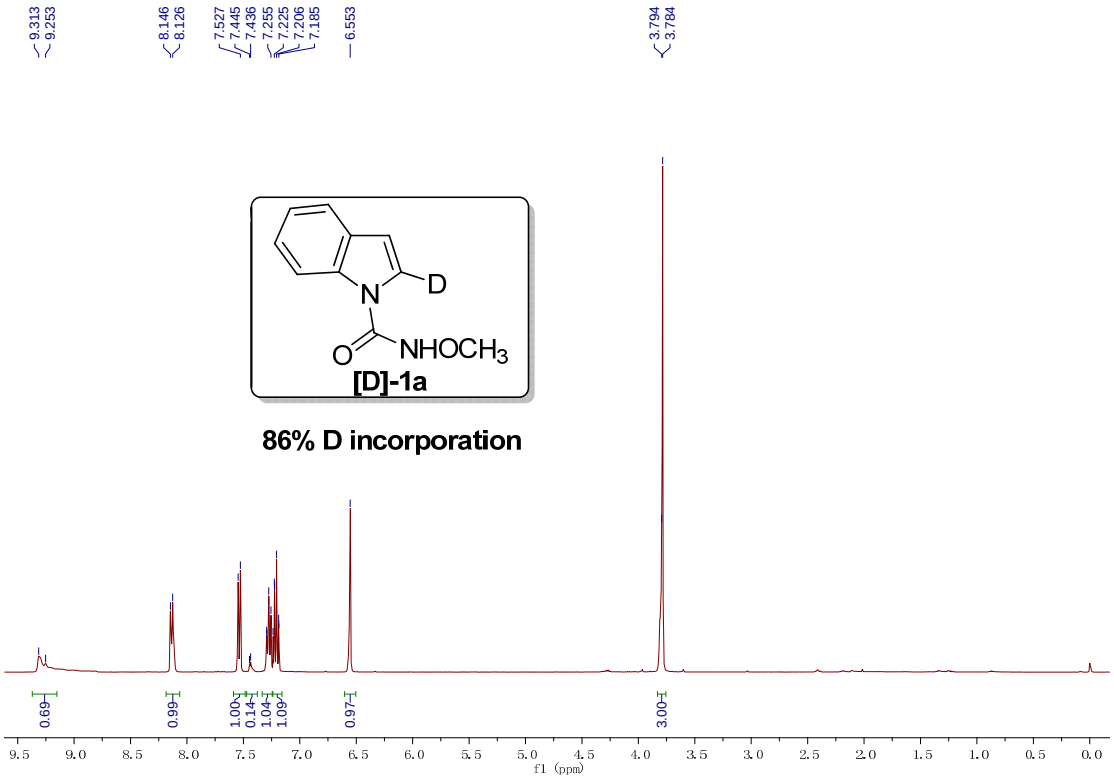
2'-methoxyspiro[cyclohexa[2,5]diene-1,1'-imidazo[1,5-a]indole]-3',4(2'*H*)-dione(5a): Prepared following the **Typical Procedure D** in 32 % yield (38 mg, 0.111 mmol) for **5a**, $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-methoxy-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and 4-Hydroxybenzeneboronic Acid **2e** (55mg, 0.4 mmol) in MeOH for 2h at 90 °C. The purification was performed by flash column chromatography on silica gel using mixture of ethyl acetate/petroleum ether (v/v, 1:5) as eluent.

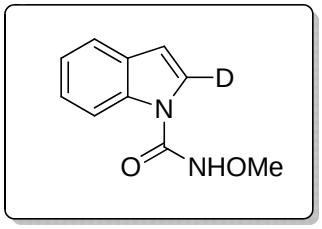
Yellow solid; m.p. 166-167°C; R_f = 0.48 (Petroleum ether/EtOAc 2:1); ^1H NMR ($CDCl_3$, 400MHz), δ: 8.02 (d, *J* = 8.0Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.41-7.37 (m, 1H), 7.33-7.29 (m, 1H), 6.85-6.81 (m, 2H), 6.52-6.48 (m, 2H), 6.39 (s, 1H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 184.5, 151.9, 144.0, 132.6, 131.63, 131.57, 131.4, 125.0, 124.1, 121.8, 113.4, 101.1, 66.8, 62.6; IR (KBr) *v*: 3113, 3009, 2979, 2938, 1760, 1673, 1634, 1609, 1589, 1440, 1303, 1029, 916, 819, 662 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{12}N_2O_3$ (M^+): 280.0848; Found: 280.0852.

Kinetic Isotope Effect (KIE) Study:

2-Deuterium indole was prepared according to literatue[1] and **[D]-1a** was synthesized with 86% D-incorporation following the general procedure.

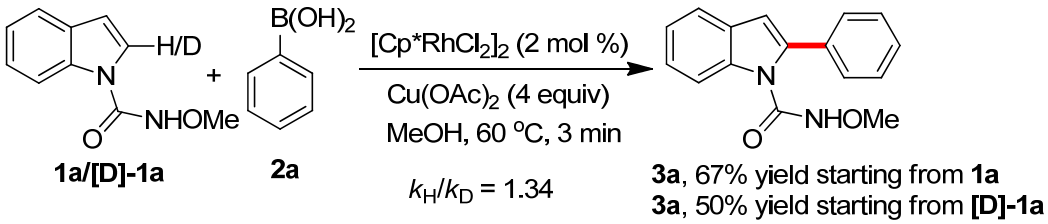
2-Deuterium Phenylboronic Acid was prepared according to literatue[2] and [D]-2a was synthesized with 100% D-incorporation following the general procedure.





Brown solid; m.p. 82-83 ^{o}C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 9.28 (s, 1H)， 8.13 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.6Hz, 1H), 7.44 (s, 0.14H), 7.29-7.26 (m, 1H), 7.24-7.19 (m, 1H), 6.55 (s, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 153.6, 135.3, 130.3, 124.6, 123.6, 122.9, 121.2, 114.8, 108.1, 64.7; IR (KBr) v: 3291, 2963, 2926, 2343, 1681, 1488, 1431, 1332, 1197, 816, 754, 645 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{10}H_9DN_2O_2$ (M^+): 191.0805; Found: 191.0808.

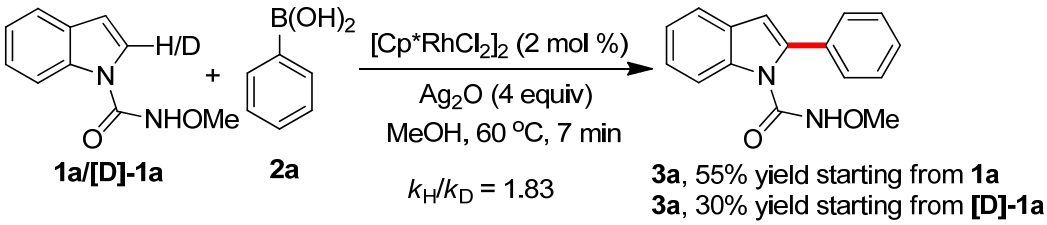
Intramolecular Kinetic Isotopic Effect of the Rh(Ⅲ)-Catalyzed C-C Coupling Reaction of 1a or [D]-1a with 2a when $Cu(OAc)_2$ was used as oxidant.



A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (181 mg, 0.8 mmol), phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then, MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 3 minutes, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **3a** as a white solid (26 mg, 50% yield).

A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **[D]-1a** (38 mg, 0.2 mmol), $Cu(OAc)_2$ (181 mg, 0.8 mmol), phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 3 minutes, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **3a** as a white solid (35 mg, 67% yield). An intramolecular kinetic isotopic effect of this reaction was thus determined to be $k_H/k_D = 1.34$.

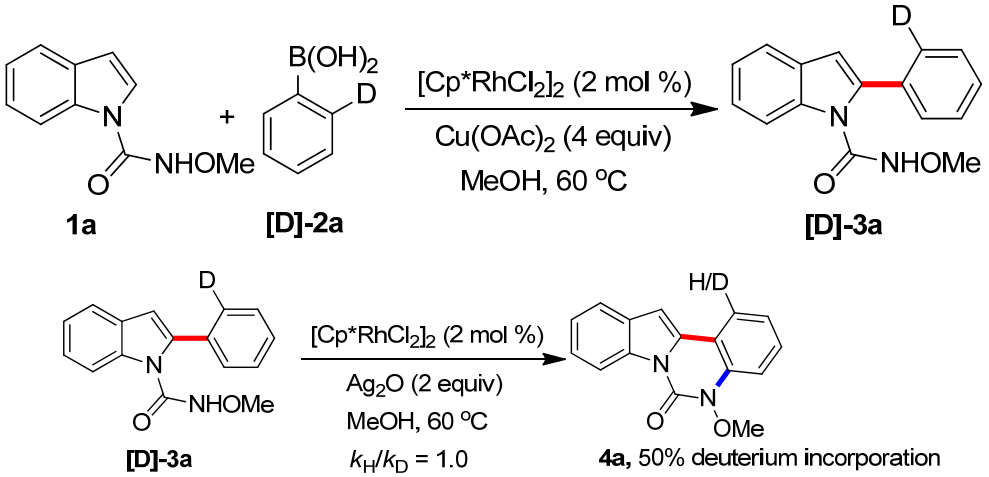
Intramolecular Kinetic Isotopic Effect of the Rh(Ⅲ)-Catalyzed C-C Coupling Reaction of 1a or [D]-1a with 2a when Ag_2O was used as oxidant.



A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 7 minutes, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **3a** as a white solid (29 mg, 55% yield).

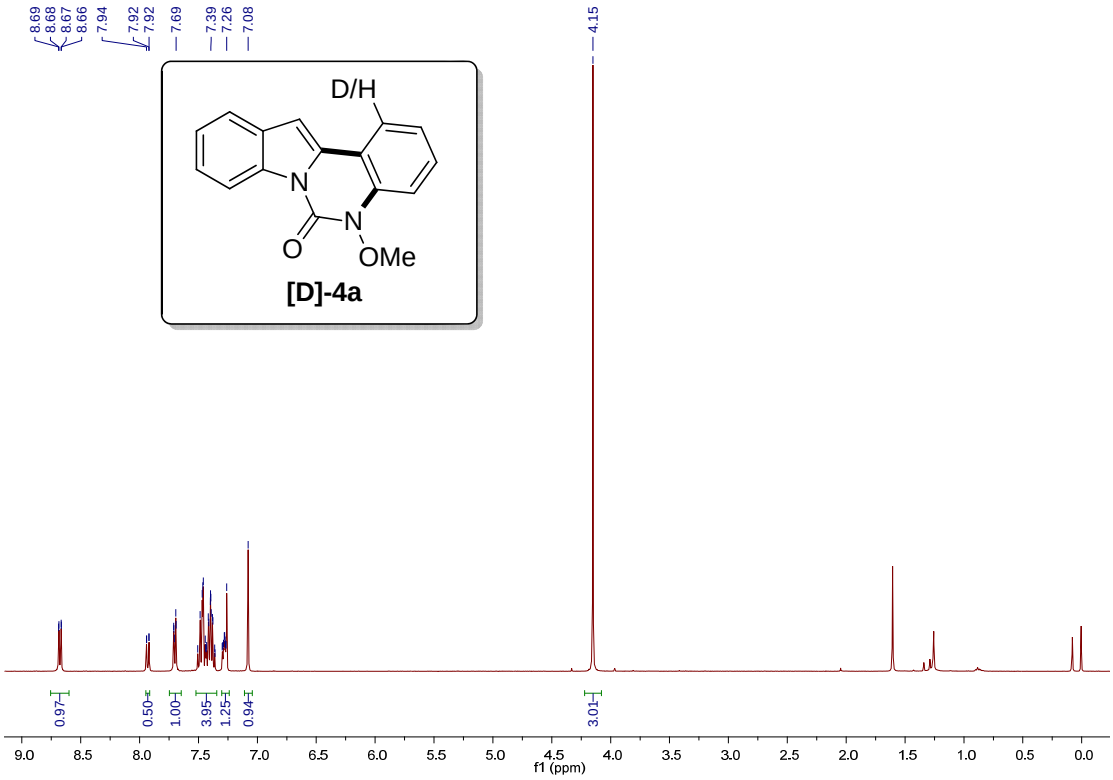
A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **[D]-1a** (38 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 7 minutes, it was with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and dilutedvolatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **3a** as a white solid (16 mg, 30% yield). An intramolecular kinetic isotopic effect of this reaction was thus determined to be $k_H/k_D = 1.83$.

Intramolecular Kinetic Isotopic Effect of the Rh(Ⅲ)-Catalyzed Oxidative Coupling Reaction of [D]-3a when Ag_2O was used as oxidant.



A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (2.4 mg, 2 mol%), *N*-(methoxy)-1*H*-indole-1-carboxamide **1a** (38.2 mg, 0.2 mmol), $Cu(OAc)_2$ (181 mg, 0.8 mmol), phenylboronic Acid **2a** (49mg, 0.4 mmol) were evacuated and purged with nitrogen gas three times. Then MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 3 minutes, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **[D]-3a** as a white solid (26 mg, 50% yield).

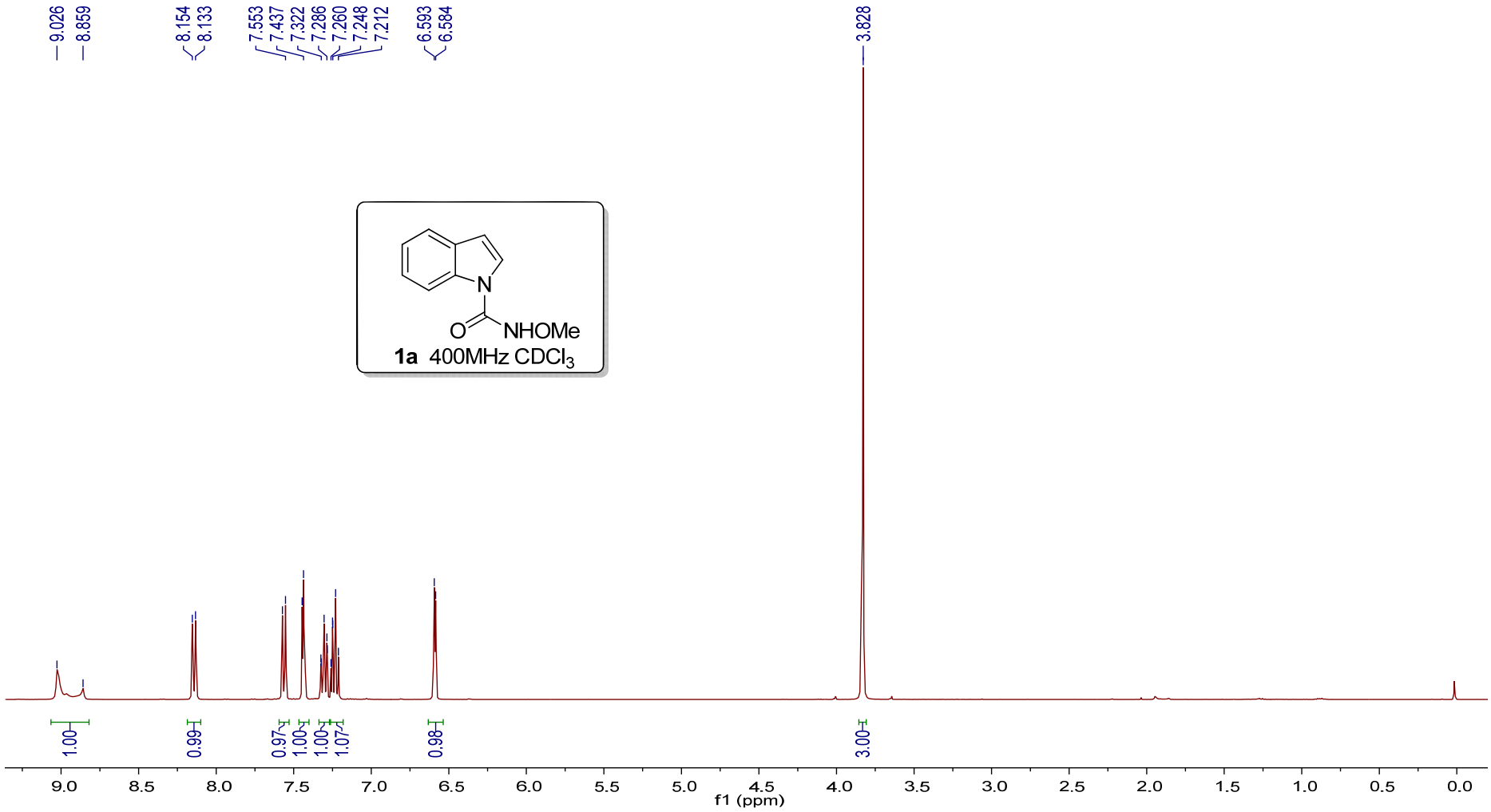
A sealed tube (20ml) containing $[Cp^*RhCl_2]_2$ (1.2 mg, 2 mol%), Ag_2O (46mg, 0.2 mmol), **[D]-3a** (26mg, 0.1 mmol) were evacuated and purged with nitrogen gas three times. Then MeOH (2 mL) was added via syringe. The reaction mixture was kept at 60 °C. After completion within 3 minutes, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to give **[D]-4a** as a pale yellow solid (18 mg, 70% yield). An intramolecular kinetic isotopic effect of this reaction was thus determined to be $k_H/k_D = 1.0$.



Reference:

1 C. S. Sevov, J. F. Hartwig, *J. Am. Chem. Soc*. **2013**, *135*, 2116.

2 J. Karthikeyan, C.-H. Cheng. *Angew. Chem. Int. Ed* **2012**, *51*, 12343.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7.553
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7.260
7.248
7.212
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6.584
3.828
N
O
NHOMe
1a 400MHz CDCl3
1.00
0.99
0.97
1.00
1.00
1.07
0.98
3.00
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
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1.0
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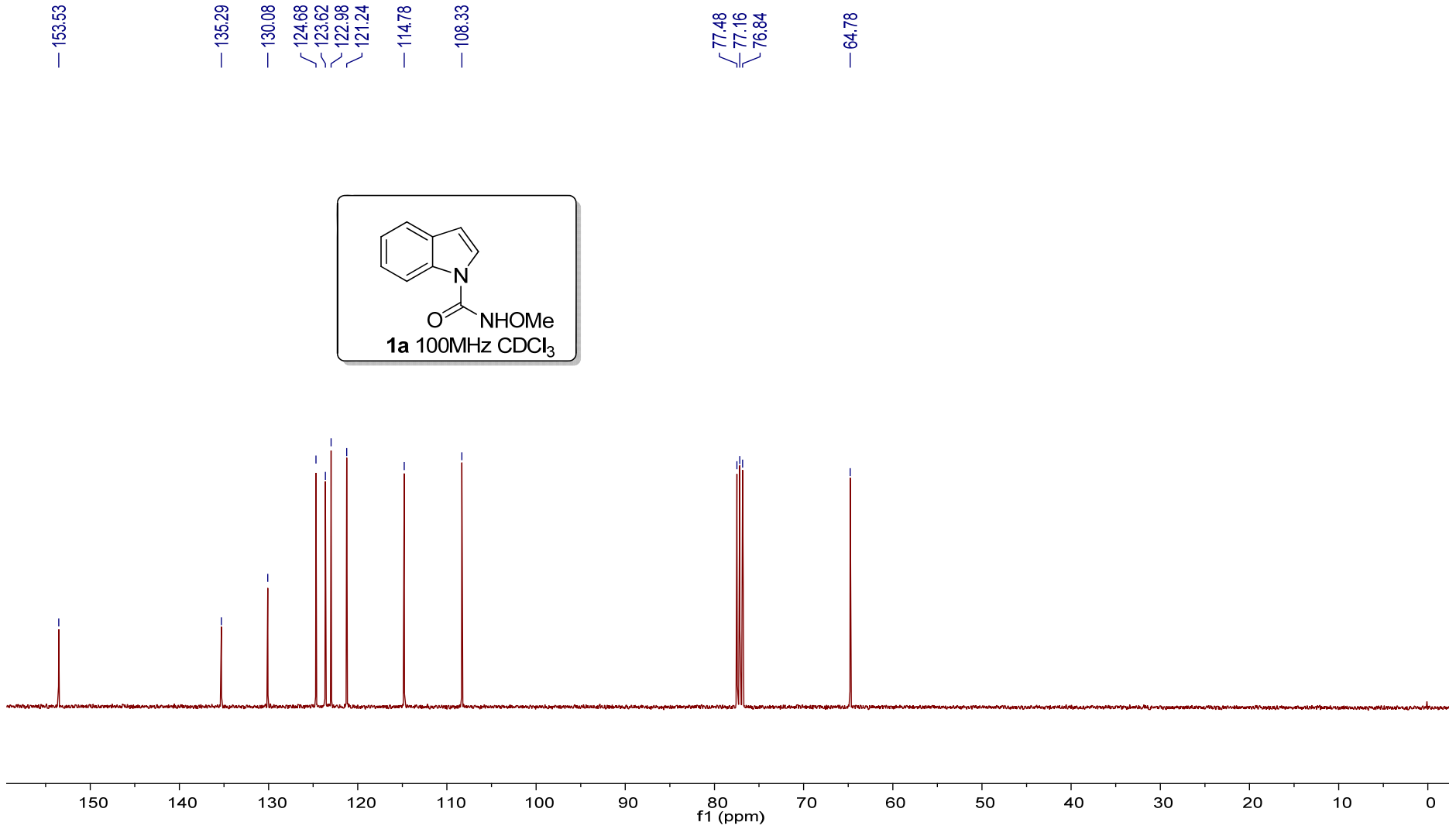
0.0
f1 (ppm)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124.68
123.62
122.98
121.24
114.78
108.33
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77.16
76.84
64.78
N
O
NHOMe
1a 100MHz CDCl3
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140
130
120
110
100
90
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50
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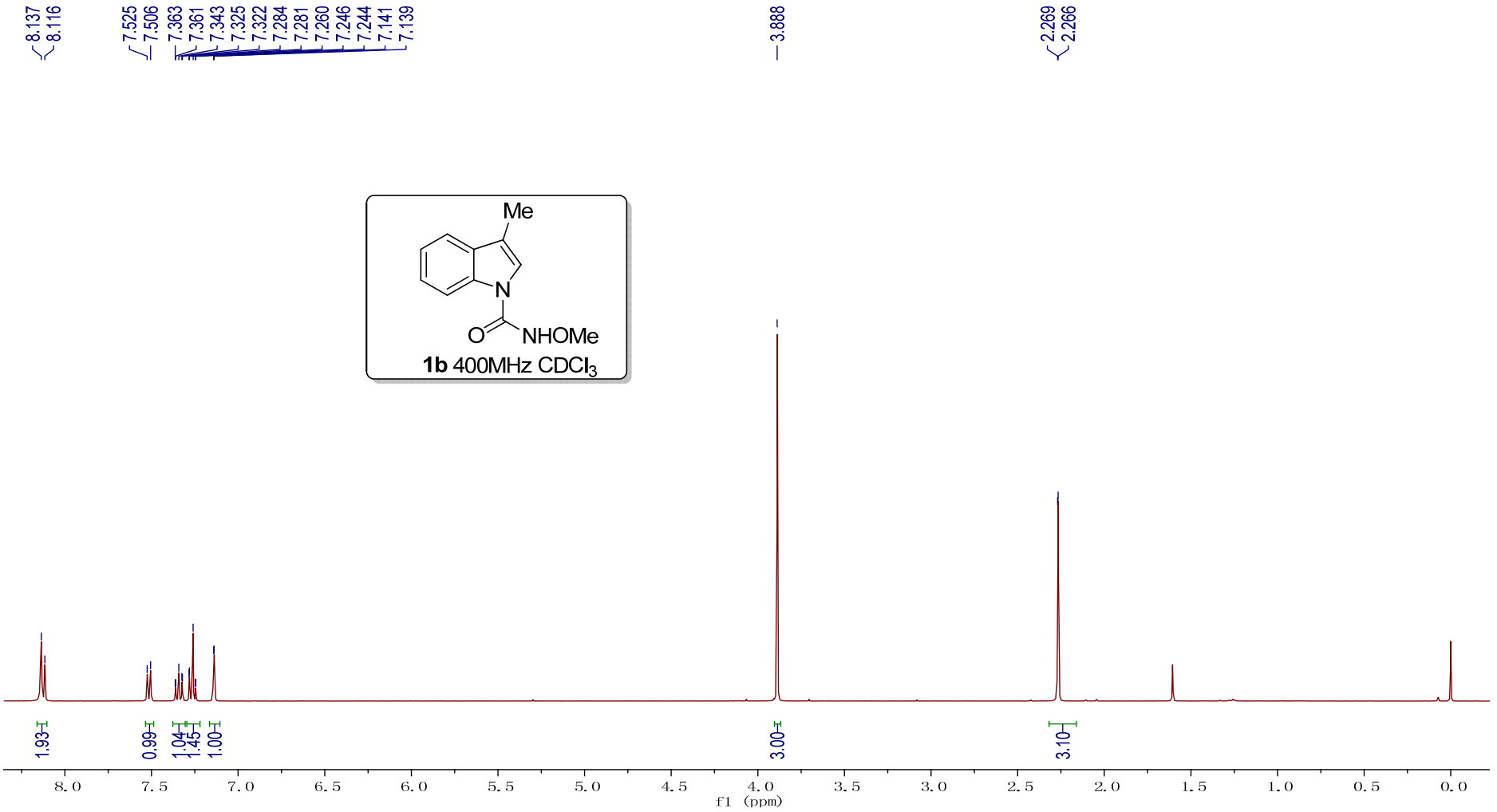
30
20
10
0
f1 (ppm)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7.325
7.322
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7.281
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7.244
7.141
7.139
3.888
2.269
2.266
Me
N
O
NHOMe
1b 400MHz CDCl3
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0.99
1.04
1.45
1.00
3.00
3.10
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7.5
7.0
6.5
6.0
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3.0
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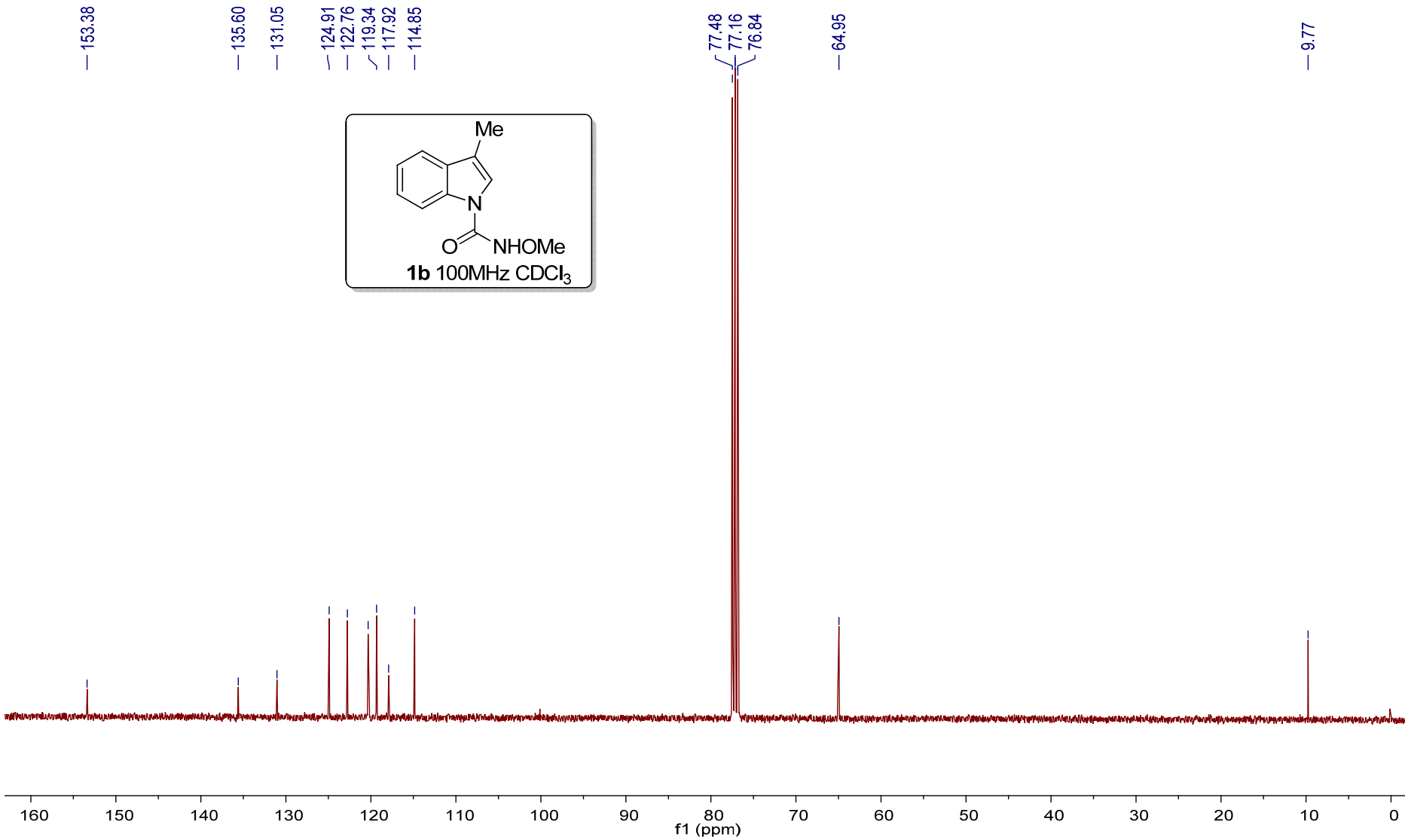
f1 (ppm)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117.92
114.85
77.48
77.16
76.84
64.95
9.77
Me
N
O
NHOMe
1b 100MHz CDCl3
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130
120
110
100
90
80
70
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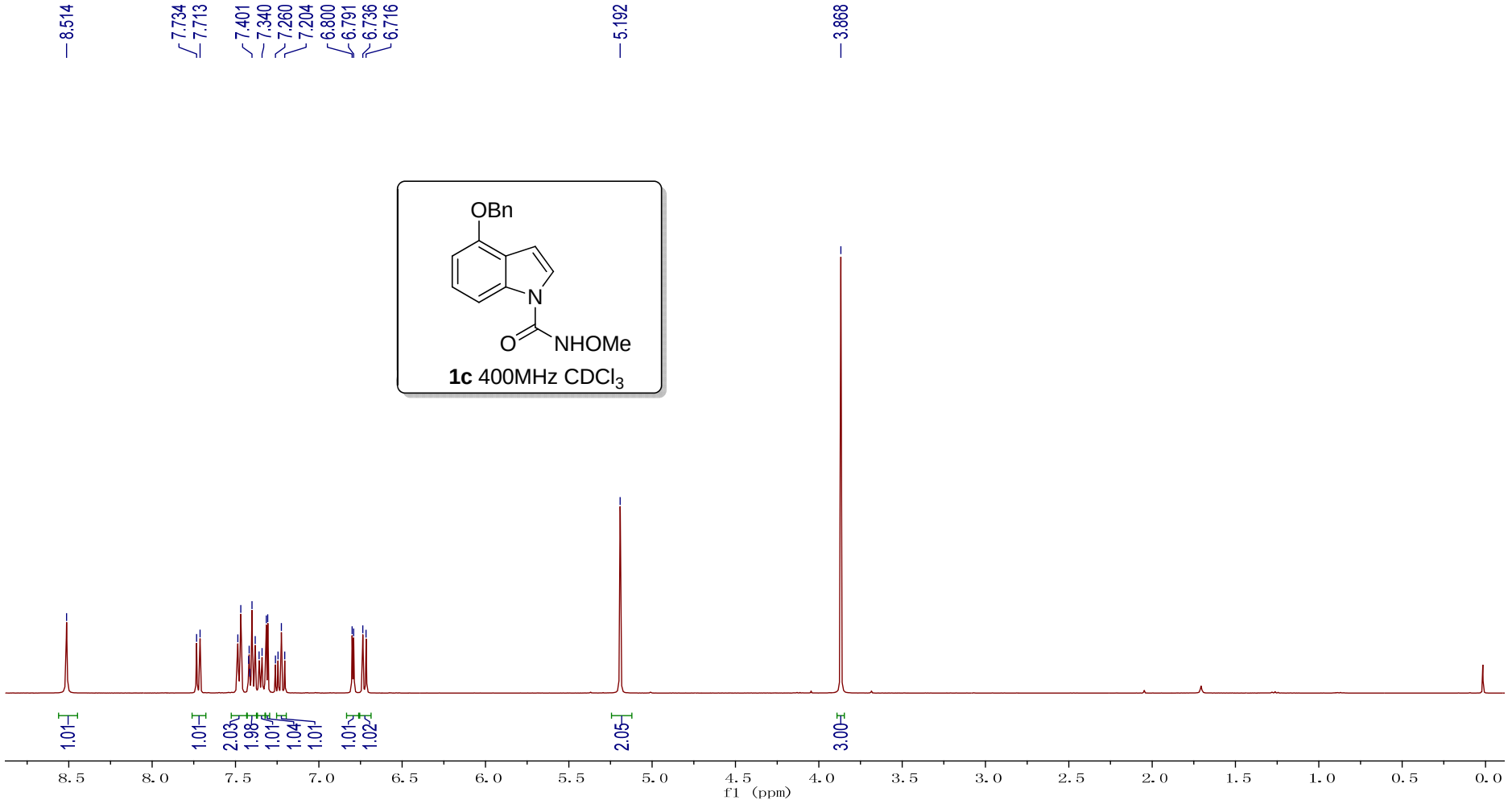
50
40
30
20
10
0
f1 (ppm)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7.260
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6.736
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5.192
3.868
OBn
N
O
NHOMe
1c 400MHz CDCl3
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1.01
2.03
1.98
1.01
1.04
1.01
1.01
1.02
2.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
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2.0
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1.0
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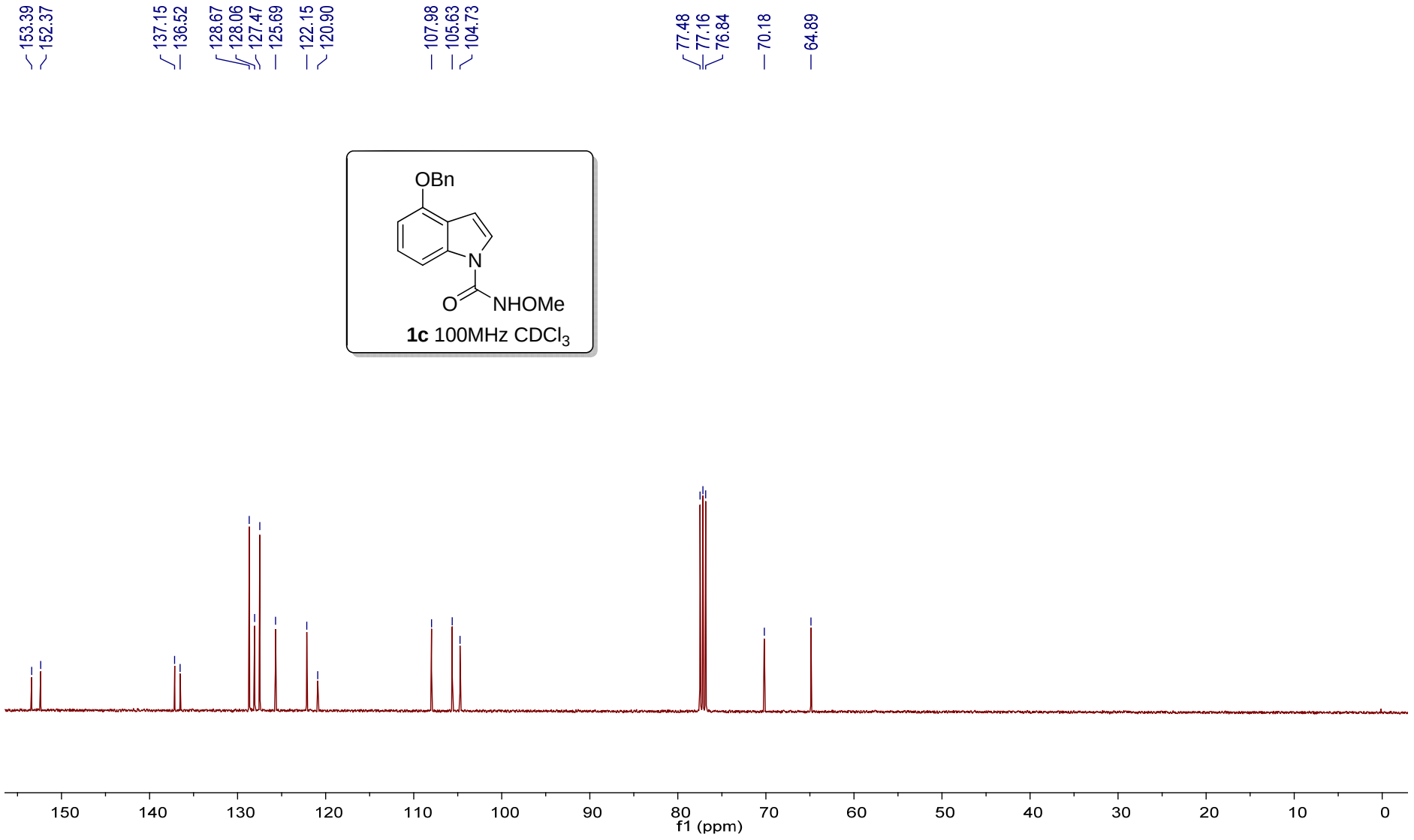
f1 (ppm)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105.63
104.73
77.48
77.16
76.84
70.18
64.89
OBn
N
O
NHOMe
1c 100MHz CDCl3
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90
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50
40
30
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10
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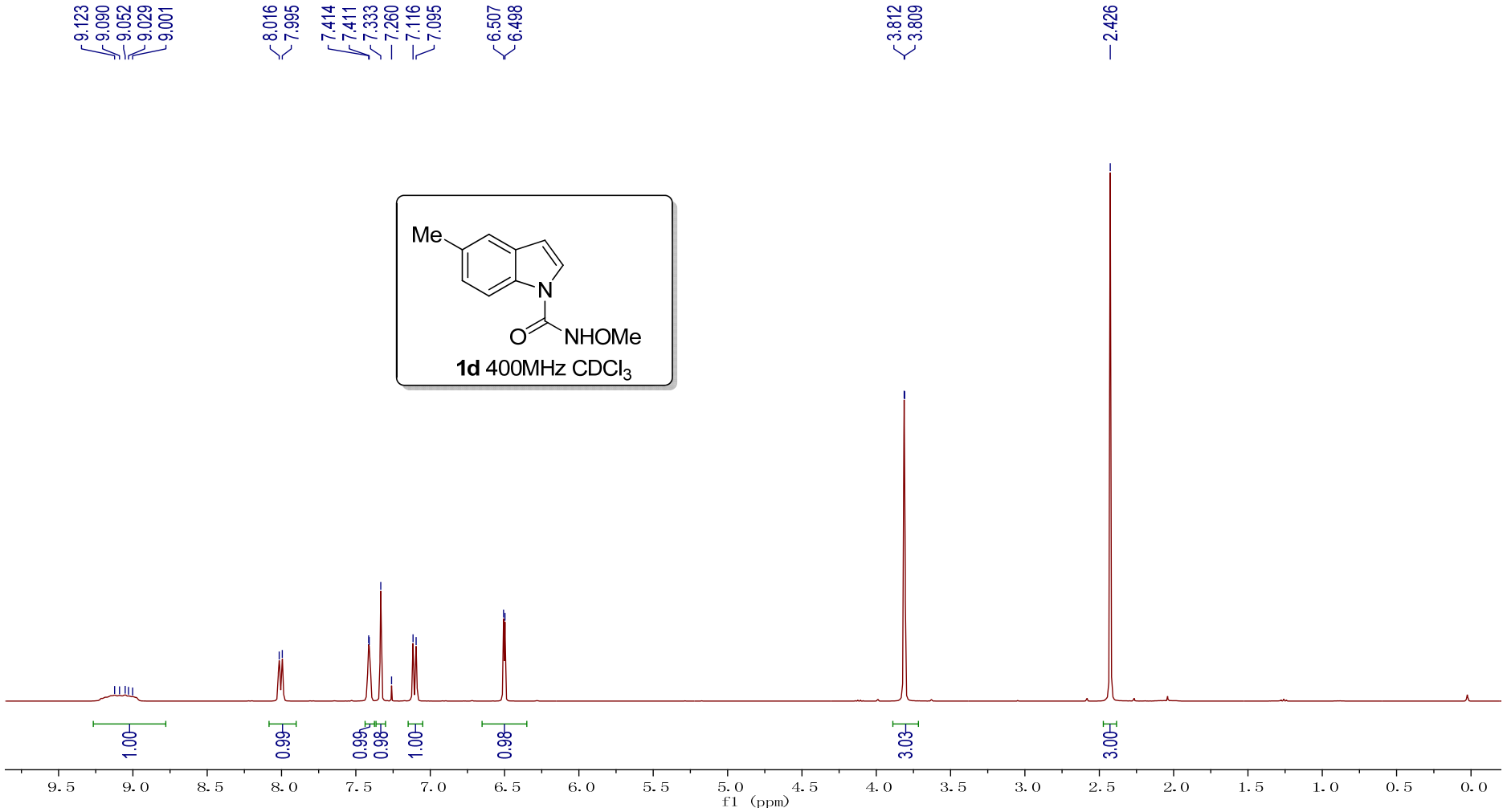
f1 (ppm)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7.414
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7.333
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6.507
6.498
3.812
3.809
2.426
Me
N
O
NHOMe
1d 400MHz CDCl3
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0.99
0.99
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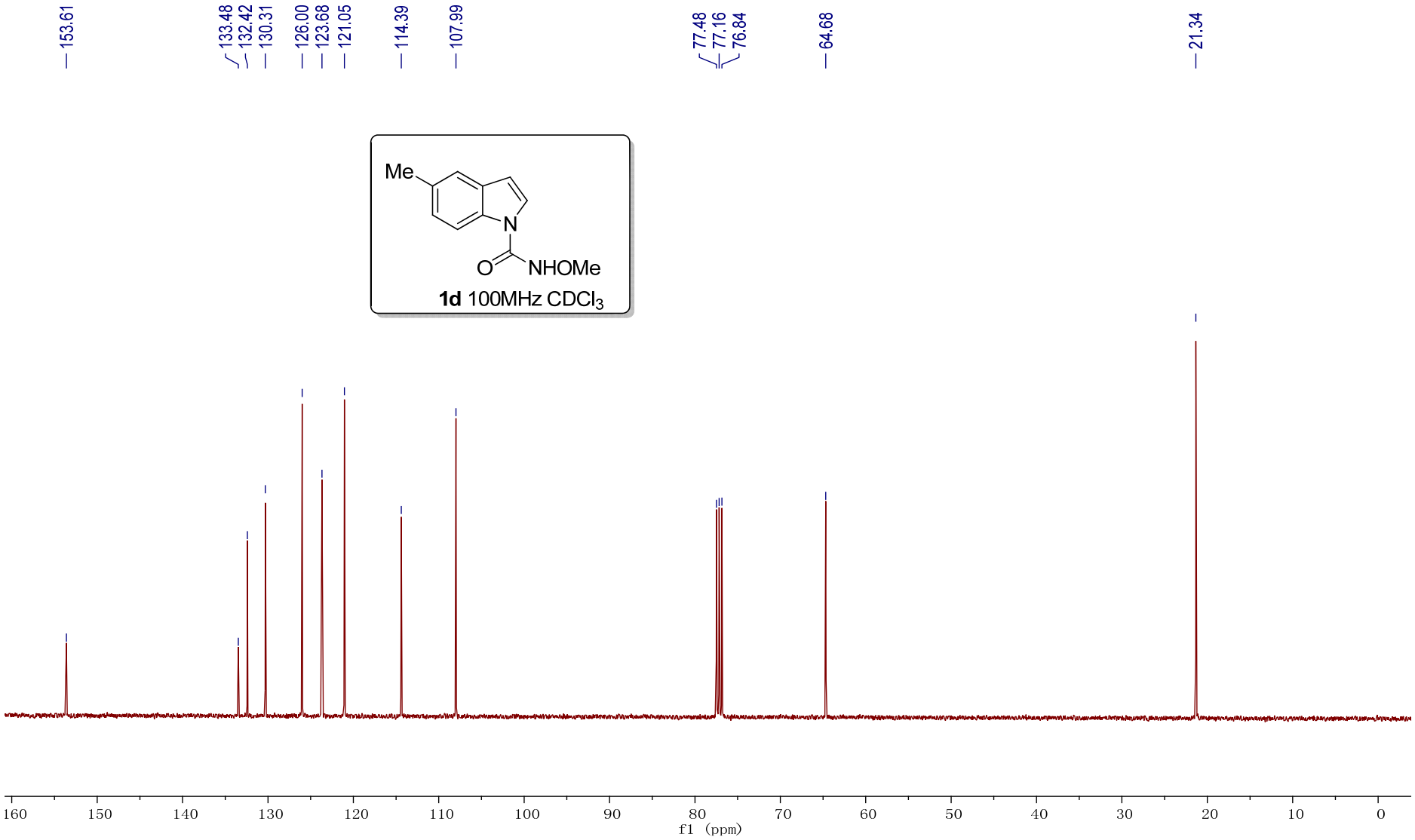
3.00
f1 (ppm)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121.05
114.39
107.99
77.48
77.16
76.84
64.68
21.34
Me
N
O
NHOMe
1d 100MHz CDCl3
160
150
140
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110
100
90
80
70
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50
40
30
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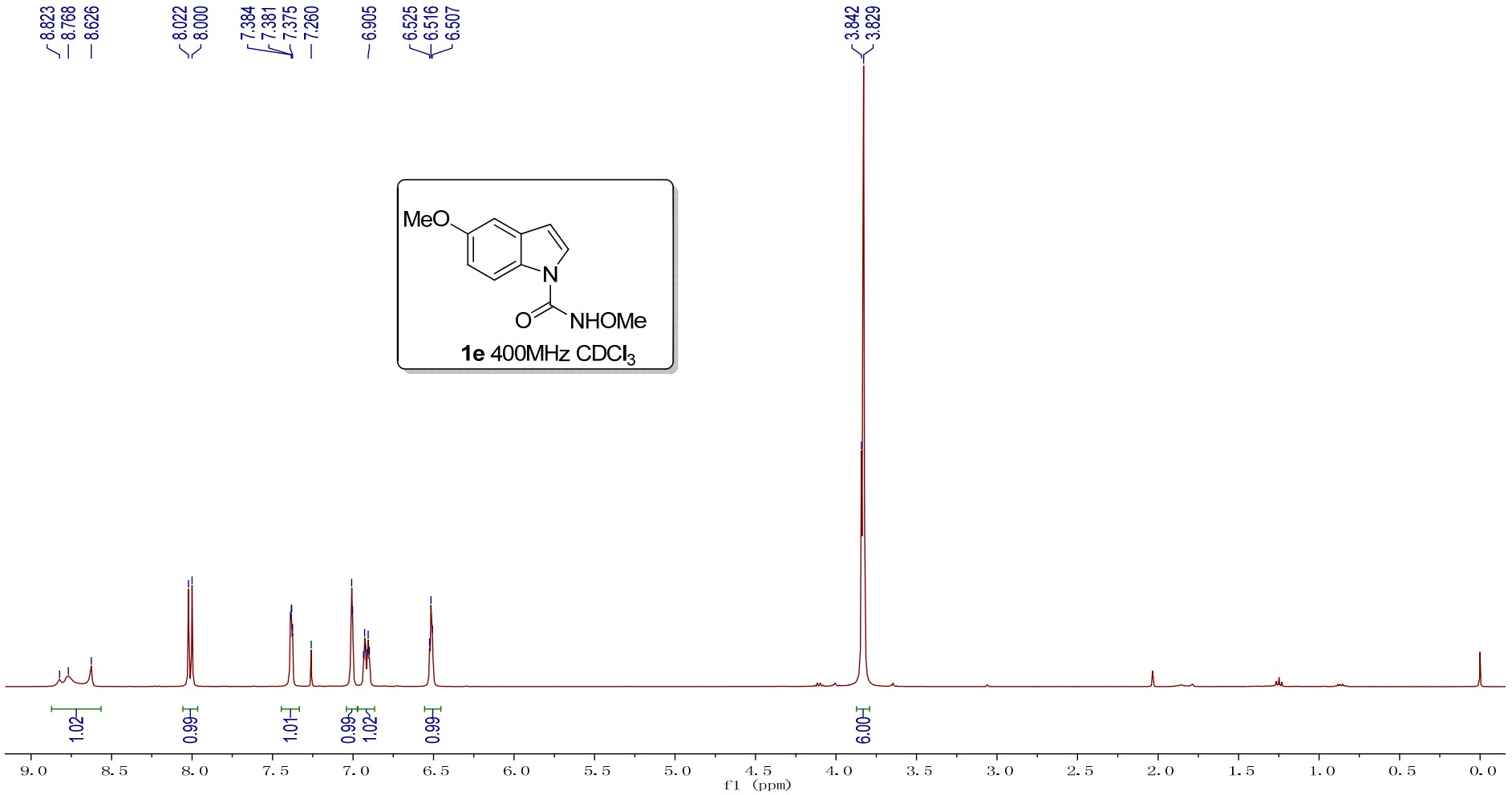
10
0
f1 (ppm)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6.507
3.842
3.829
MeO
N
O
NHOMe
1e 400MHz CDCl3
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0.99
1.01
0.99
1.02
0.99
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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1.5
1.0
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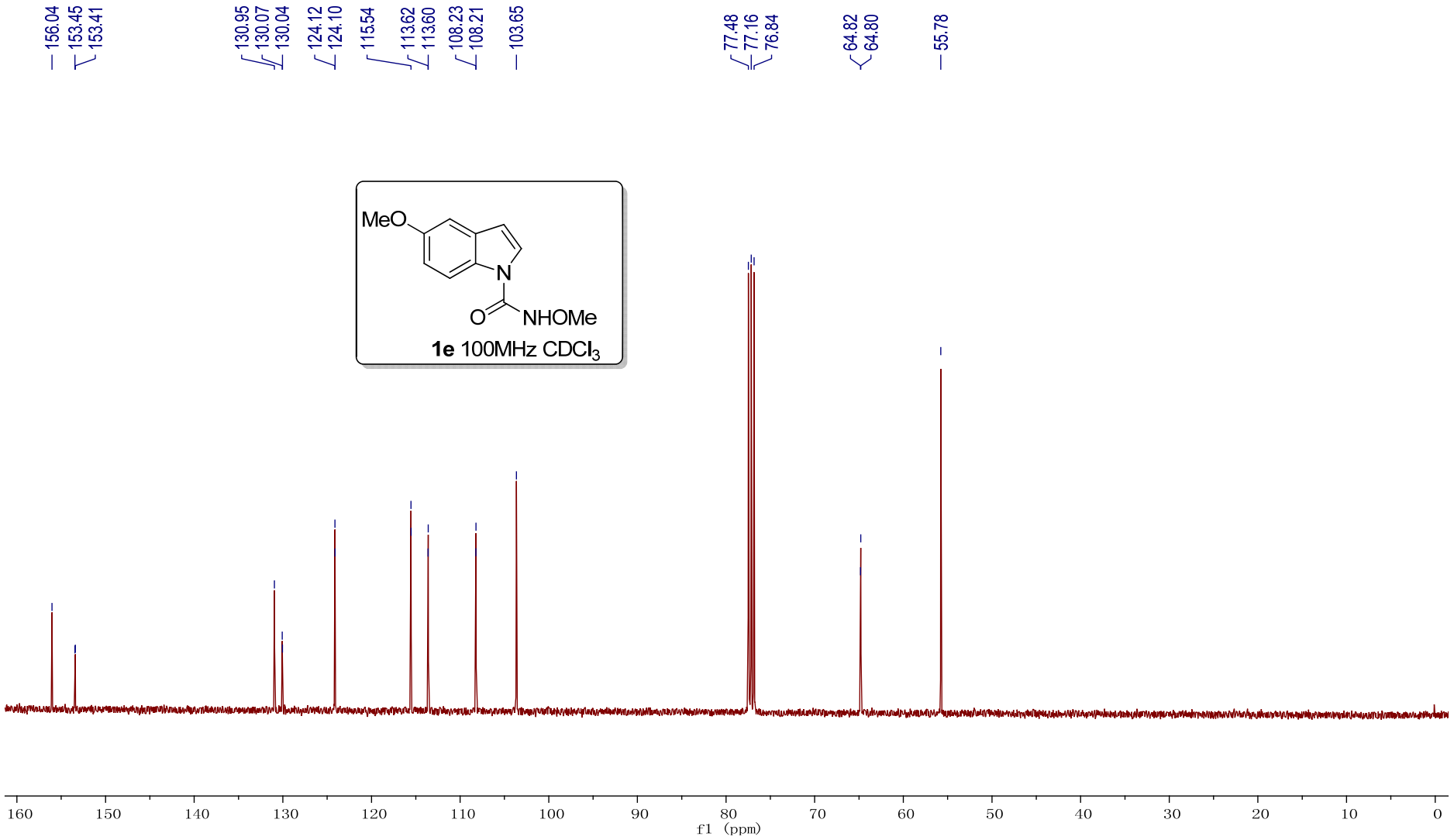
0.0
f1 (ppm)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77.16
76.84
64.82
64.80
55.78
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N
O
NHOMe
1e 100MHz CDCl3
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120
110
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90
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50
40
30
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10
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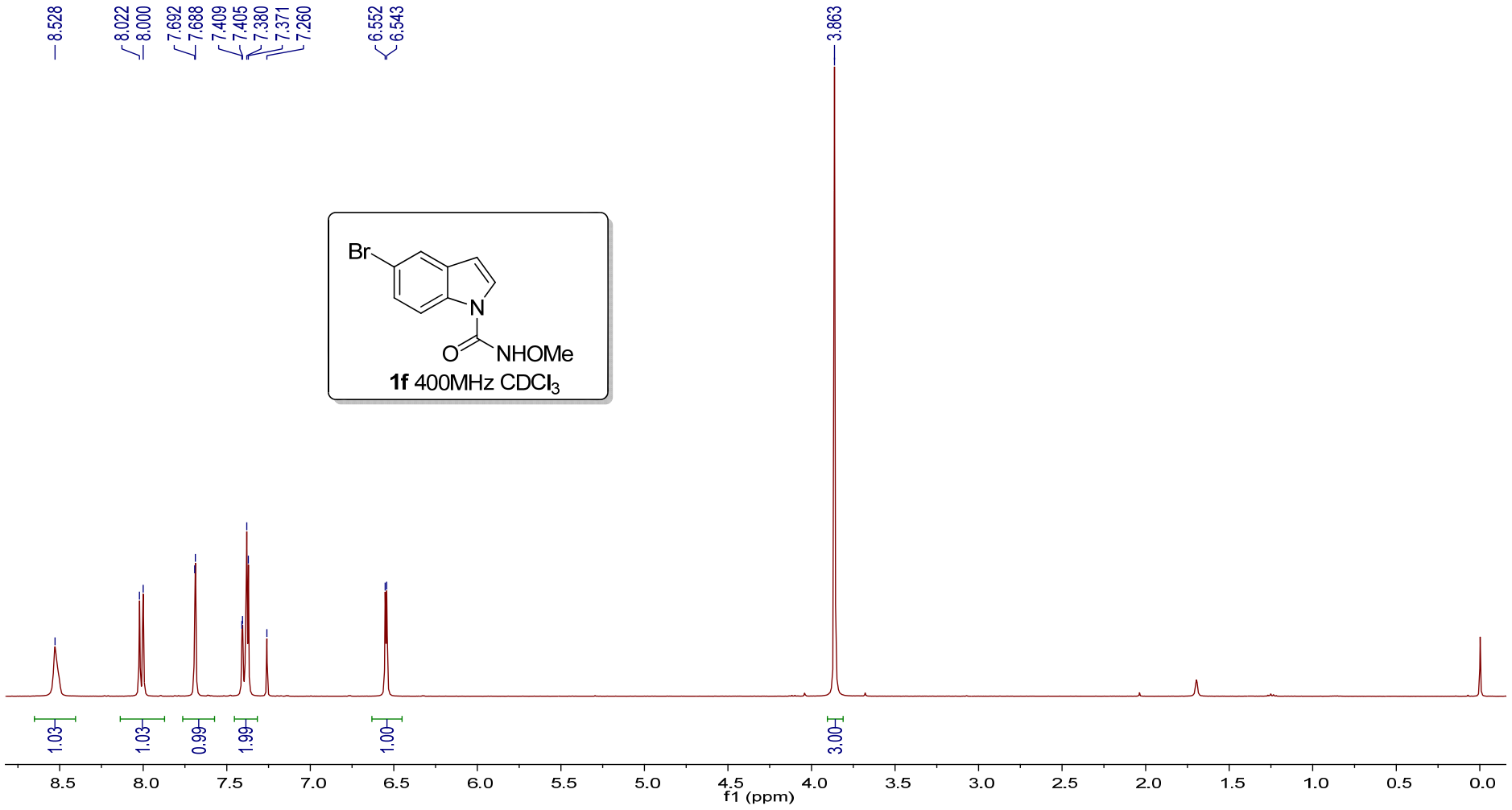
f1 (ppm)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7.405
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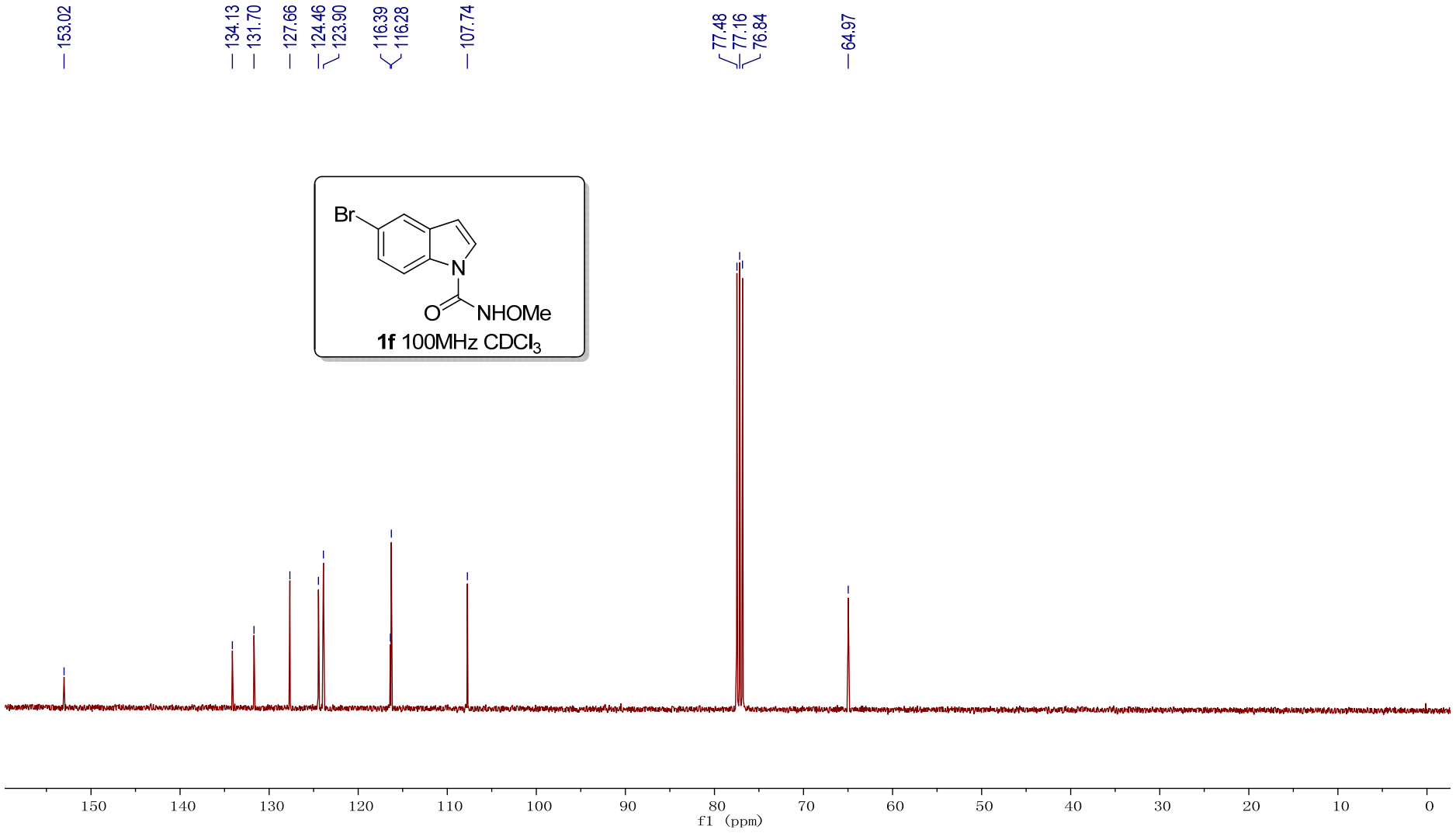
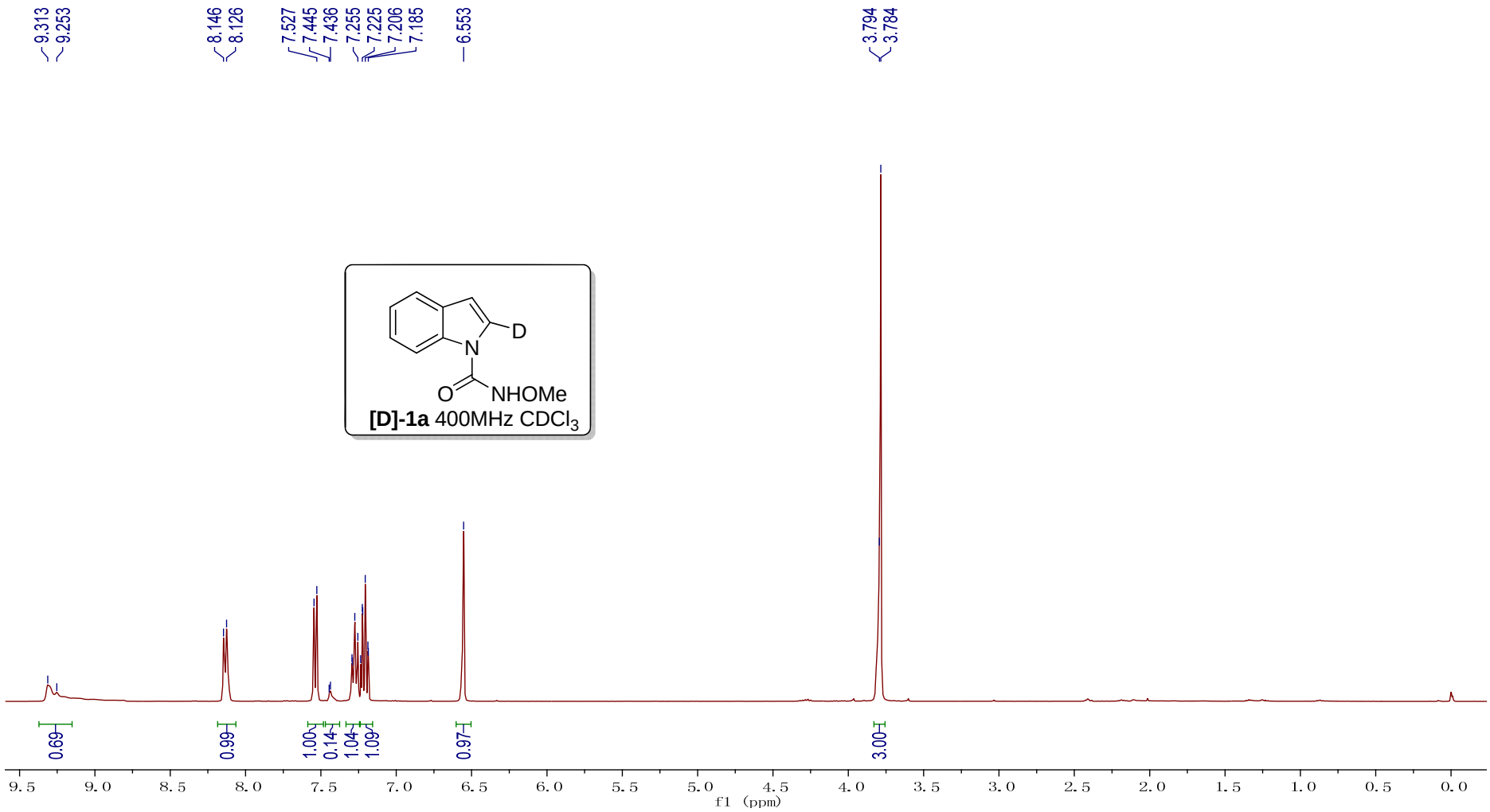
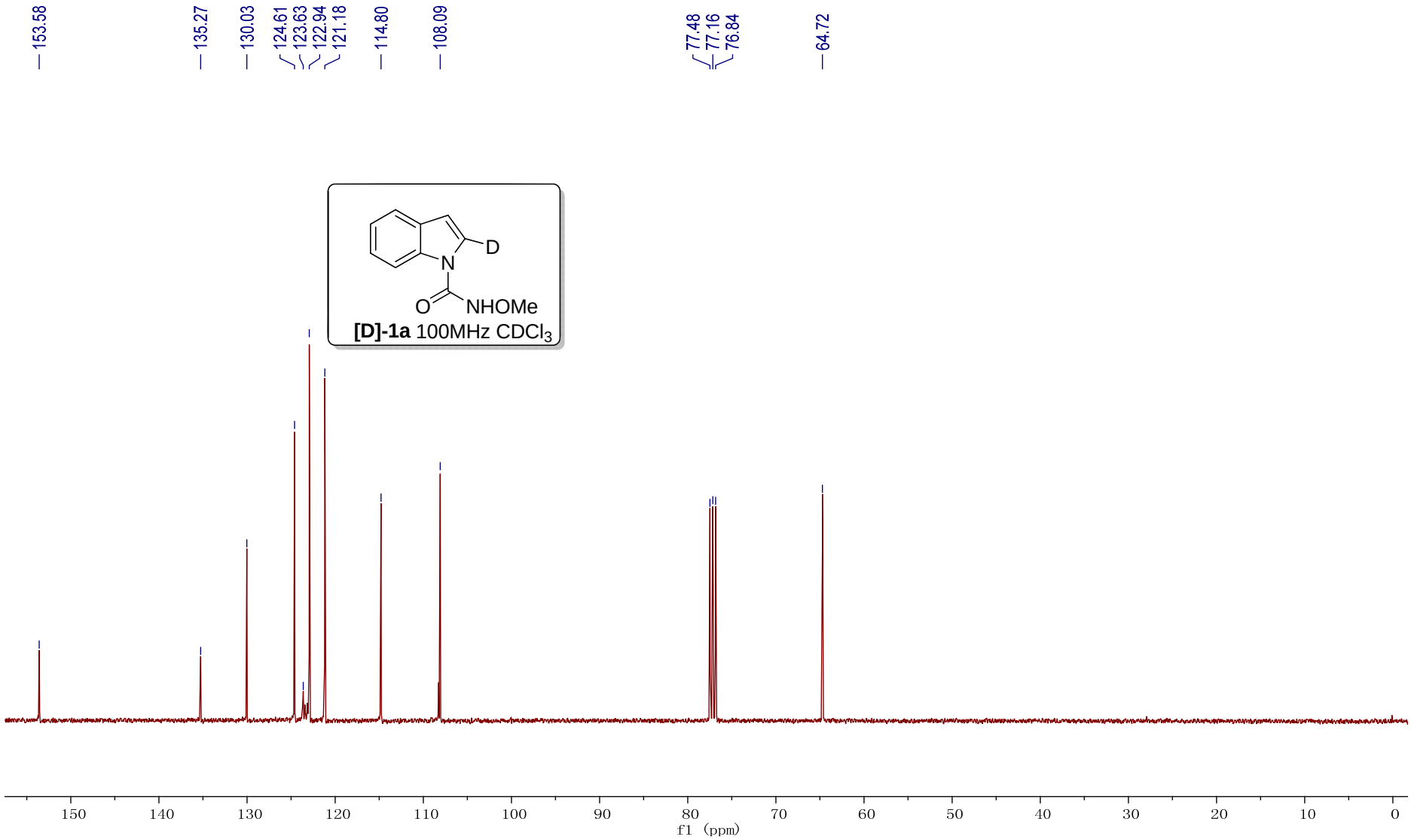
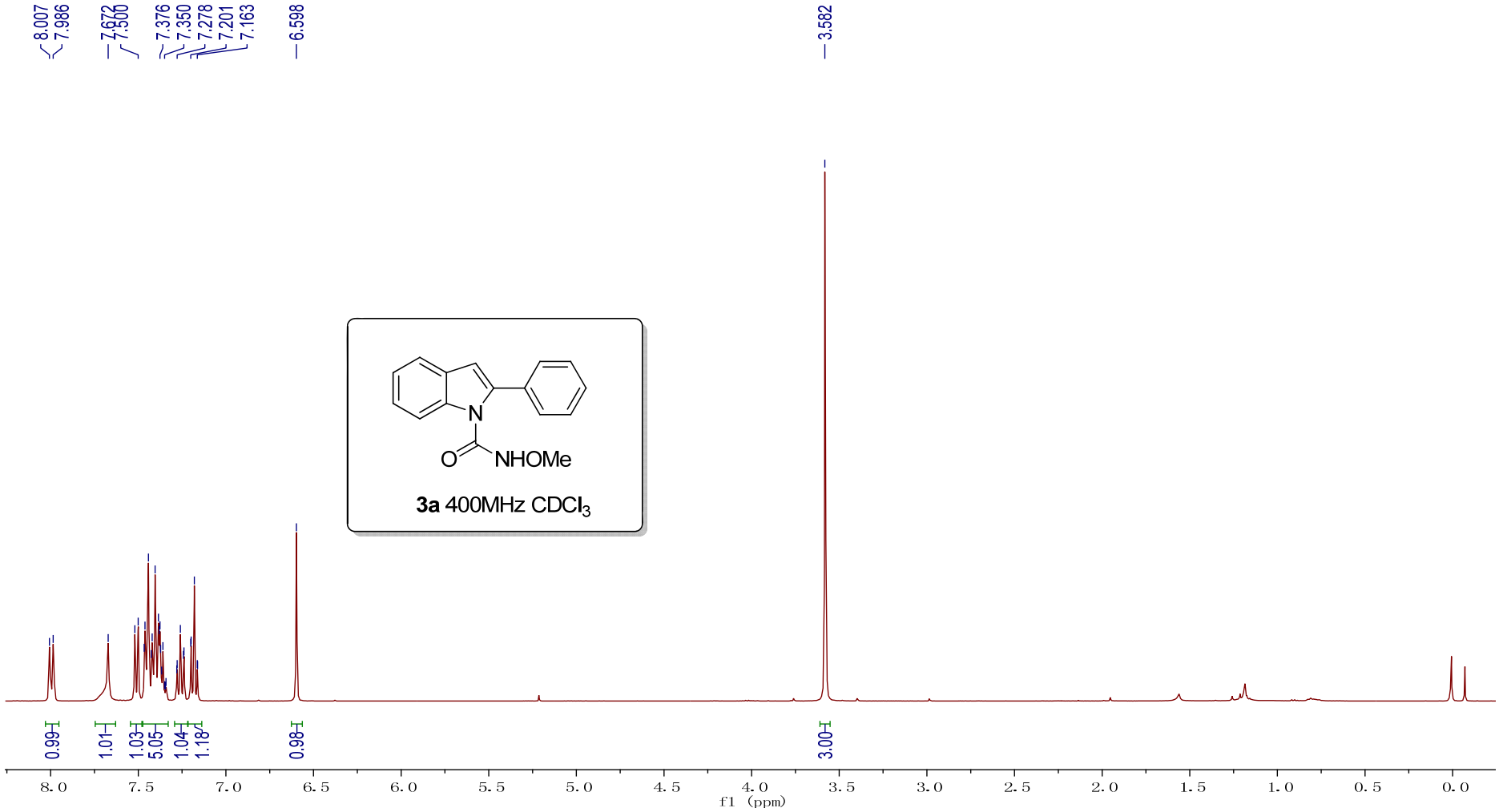
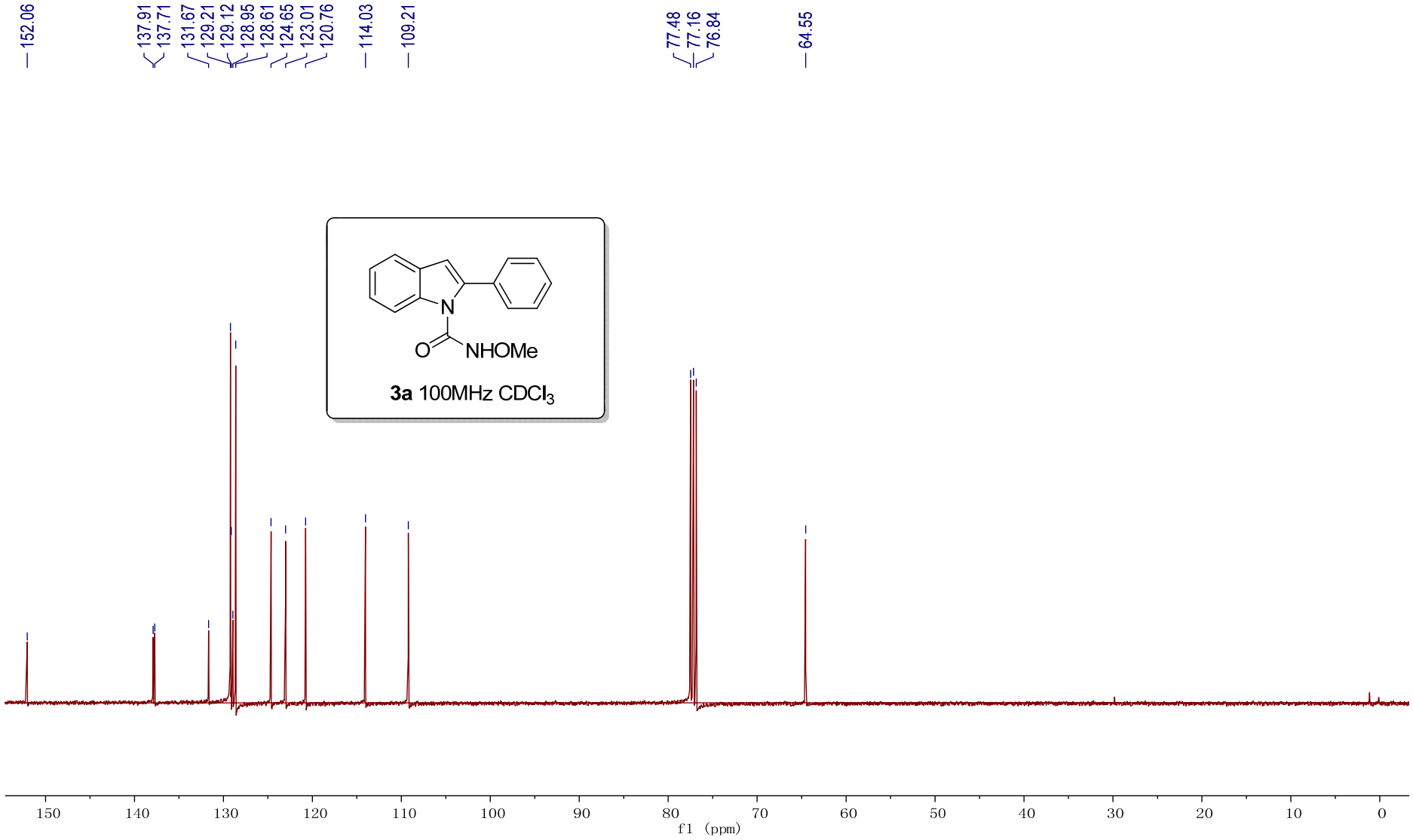
7.260
6.552
6.543
3.863
Br
N
O
NHOMe
1f 400MHz CDCl3
1.03
1.03
0.99
1.99
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.02
134.13
131.70
127.66
124.46
123.90
116.39
116.28
107.74
77.48
77.16
76.84
64.97
Br
N
O
NHOMe
1f 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.313
9.253
8.146
8.126
7.527
7.445
7.436
7.255
7.225
7.206
7.185
6.553
3.794
3.784
D
N
O
NHOMe
[D]-1a 400MHz CDCl3
0.69
0.99
1.00
0.14
1.04
1.09
0.97
3.00
f1 (ppm)


153.58
135.27
130.03
124.61
123.63
122.94
121.18
114.80
108.09
77.48
77.16
76.84
64.72
D
N
O
NHOMe
[D]-1a 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.007
7.986
7.672
7.500
7.376
7.350
7.278
7.201
7.163
6.598
3.582
N
O
NHOMe
3a 400MHz CDCl3
0.99
1.01
1.03
5.05
1.04
1.18
0.98
3.00
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)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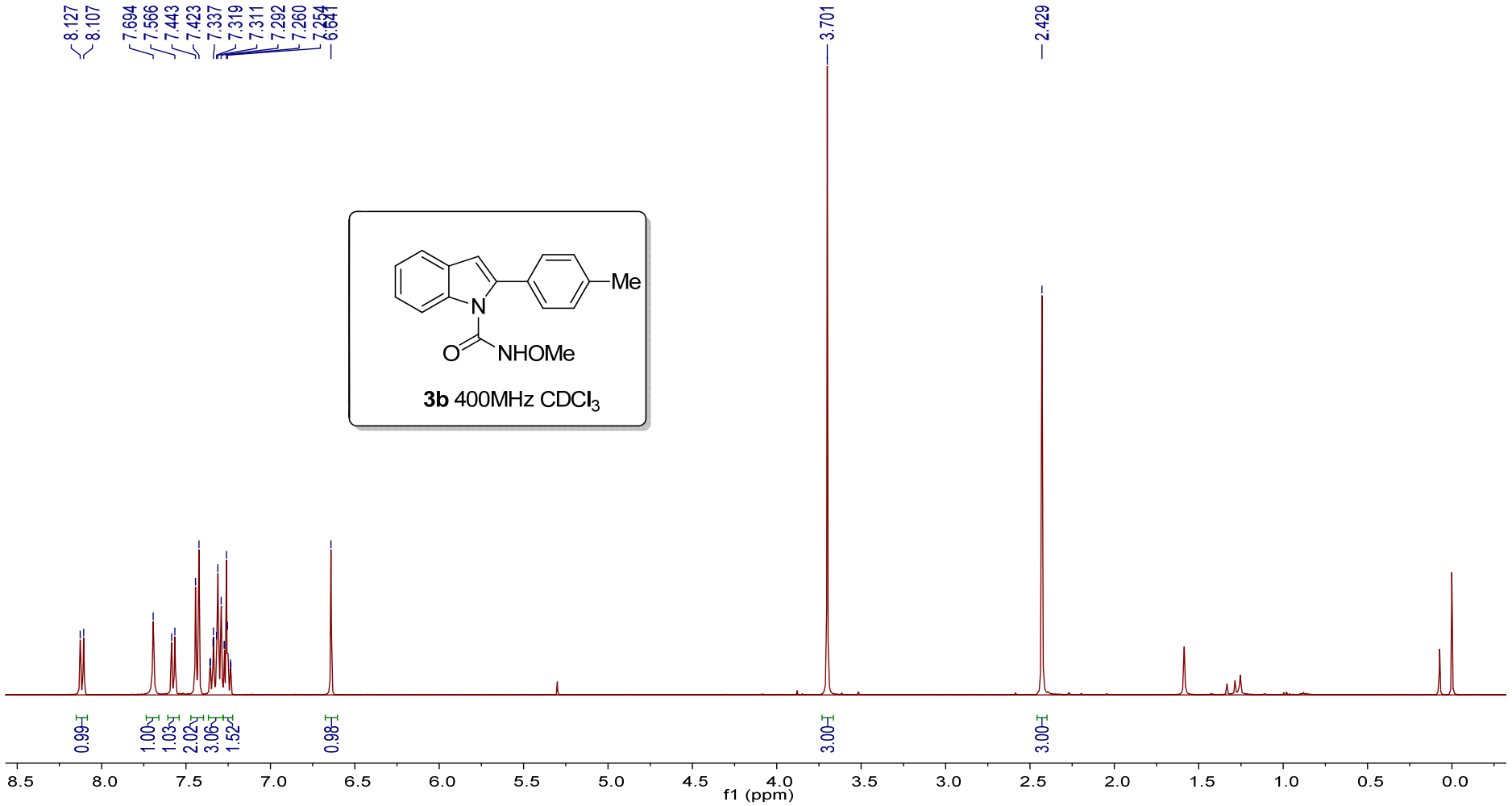
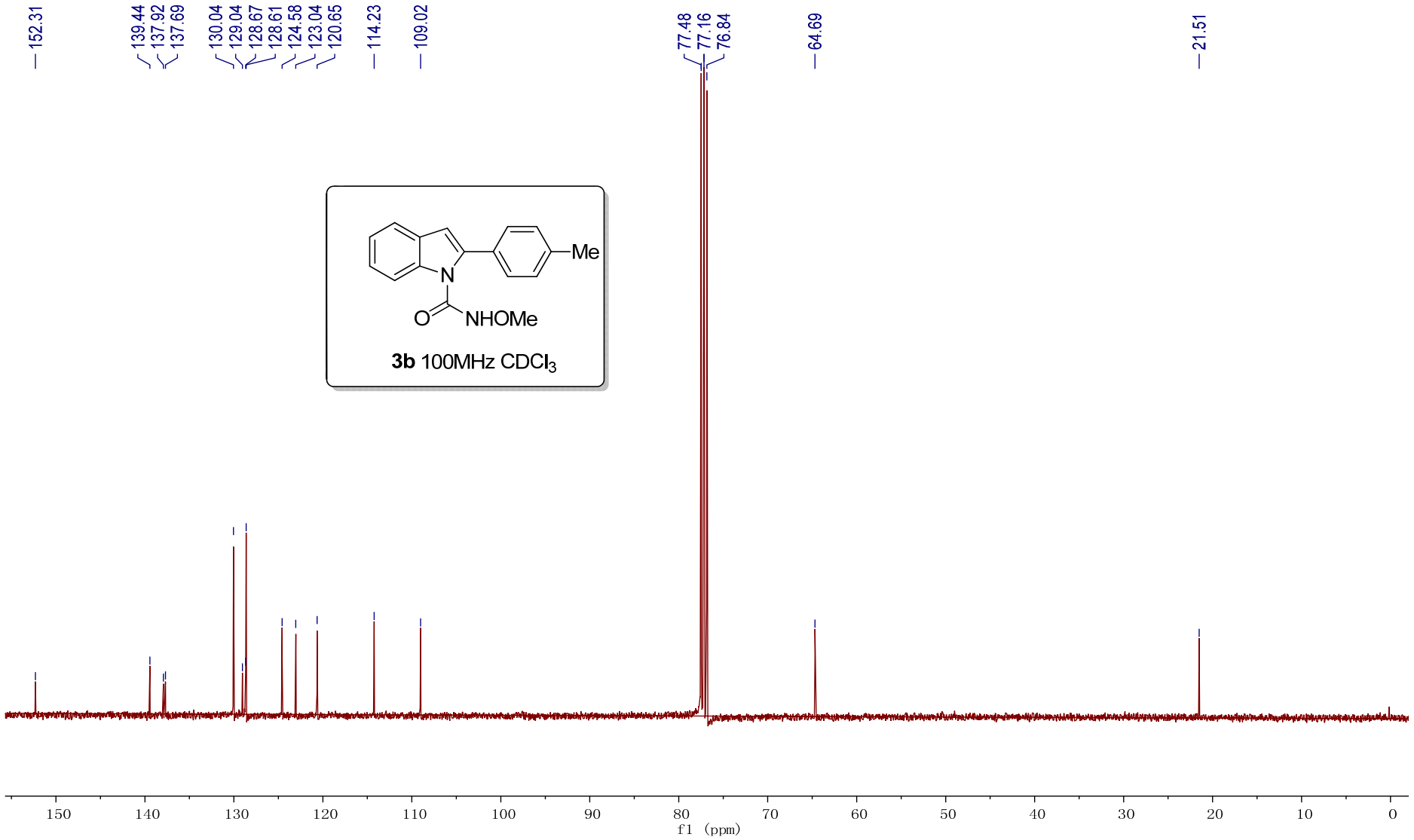
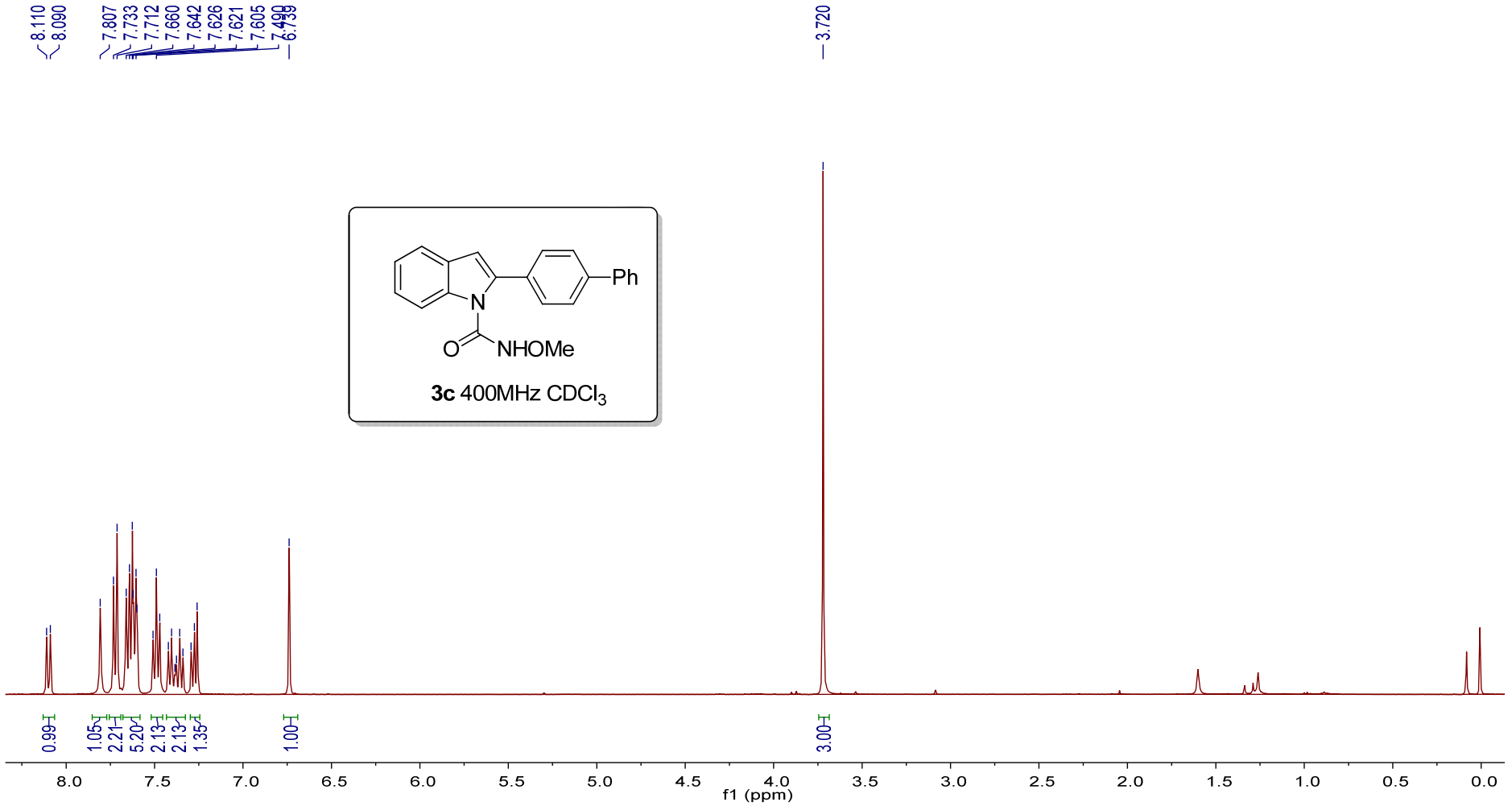
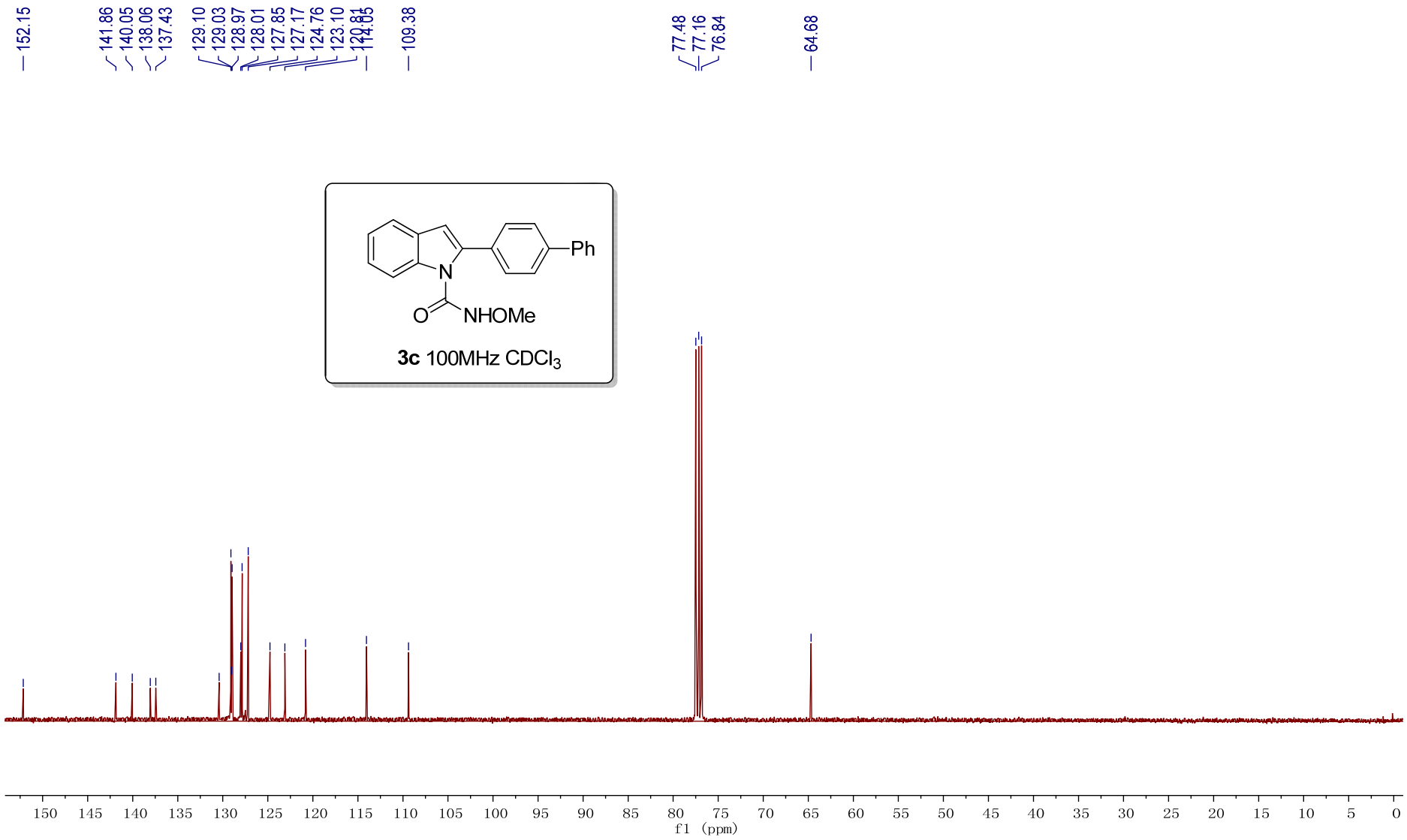
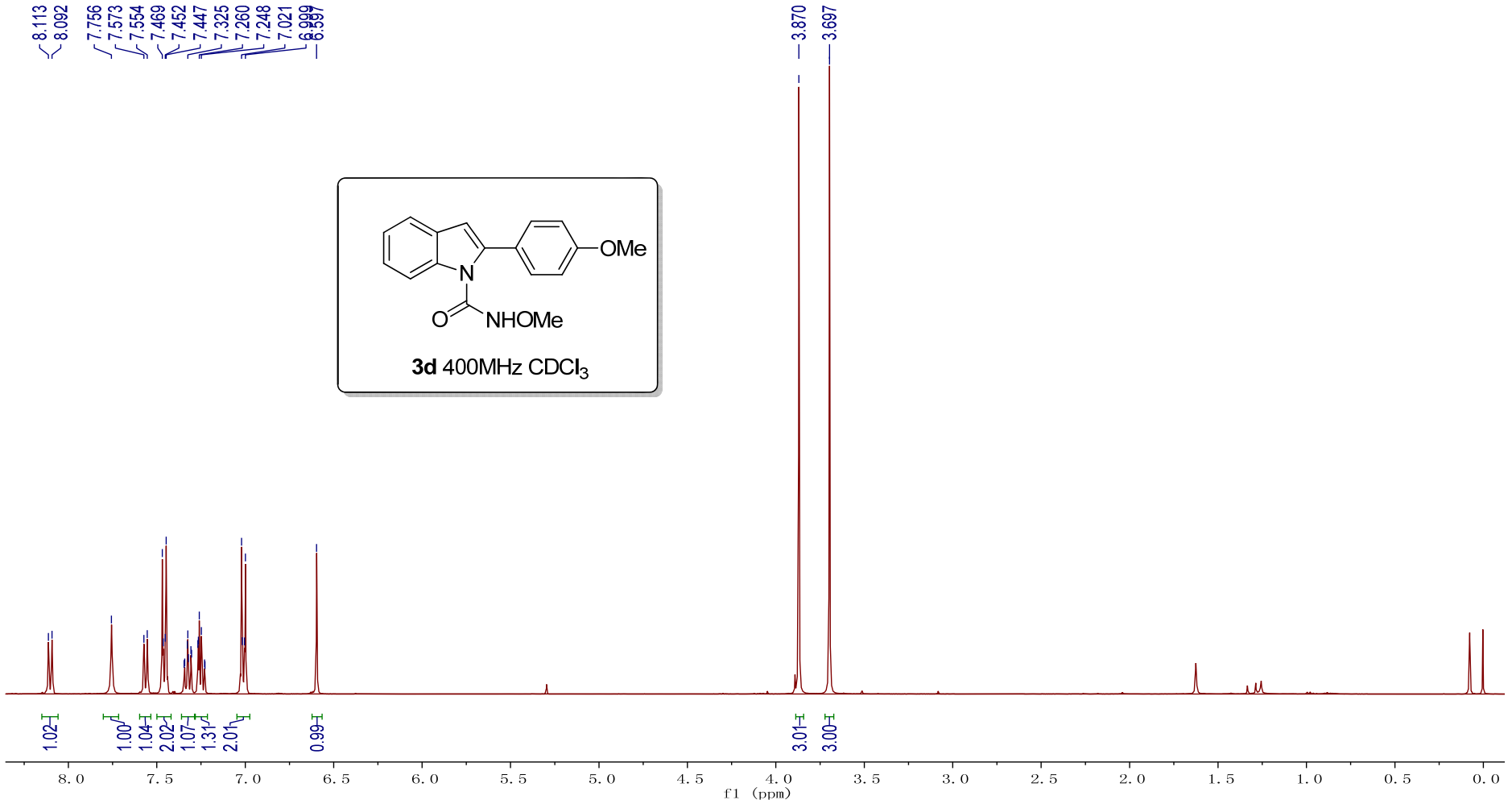
137.91
137.71
131.67
129.21
129.12
128.95
128.61
124.65
123.01
120.76
114.03
109.21
77.48
77.16
76.84
64.55
N
O
NHOMe
3a 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

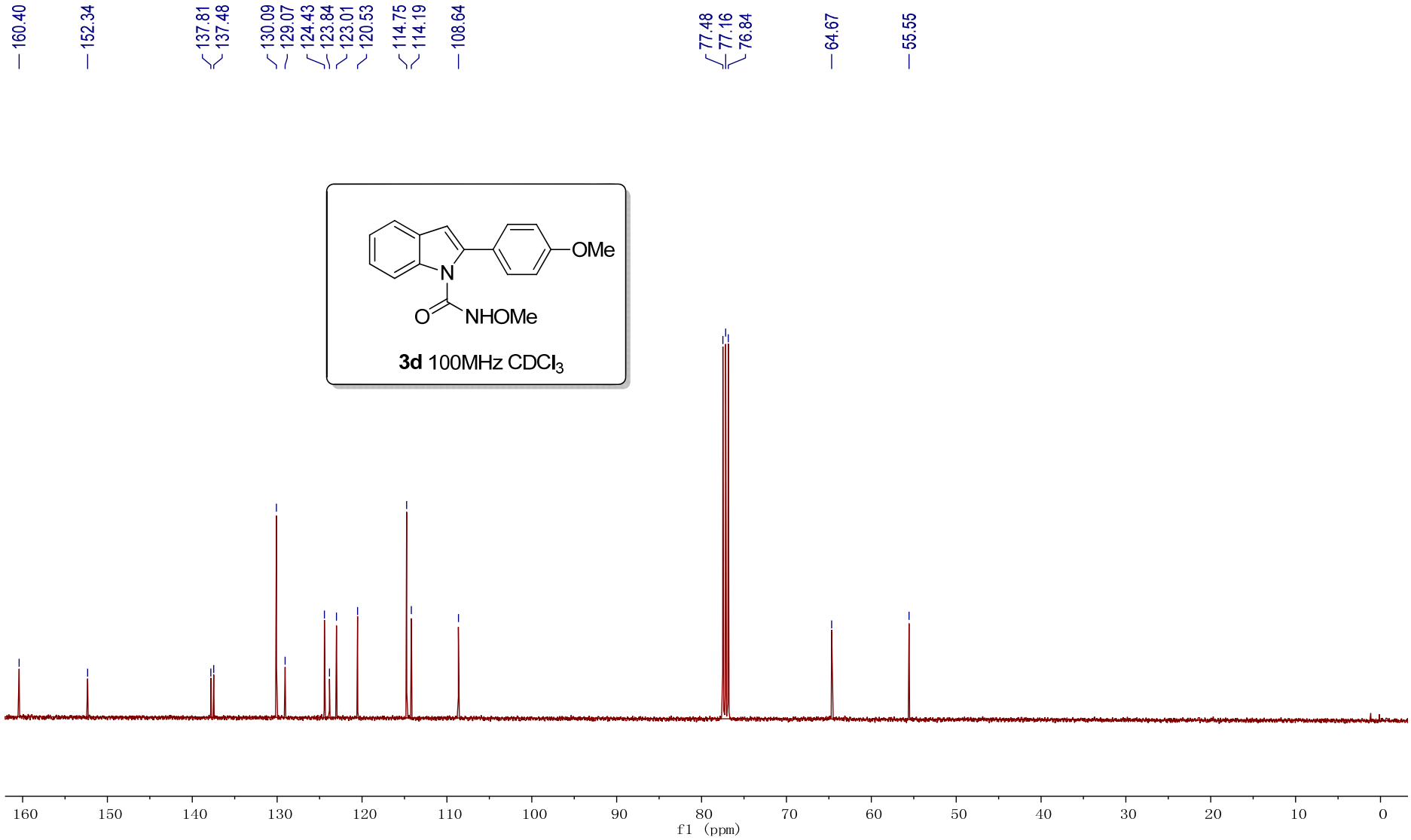

8.127
8.107
7.694
7.566
7.443
7.423
7.337
7.319
7.311
7.292
7.260
7.254
6.641
3.701
2.429
Me
N
O
NHOMe
3b 400MHz CDCl3
0.99
1.00
1.03
2.02
3.06
1.52
0.98
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

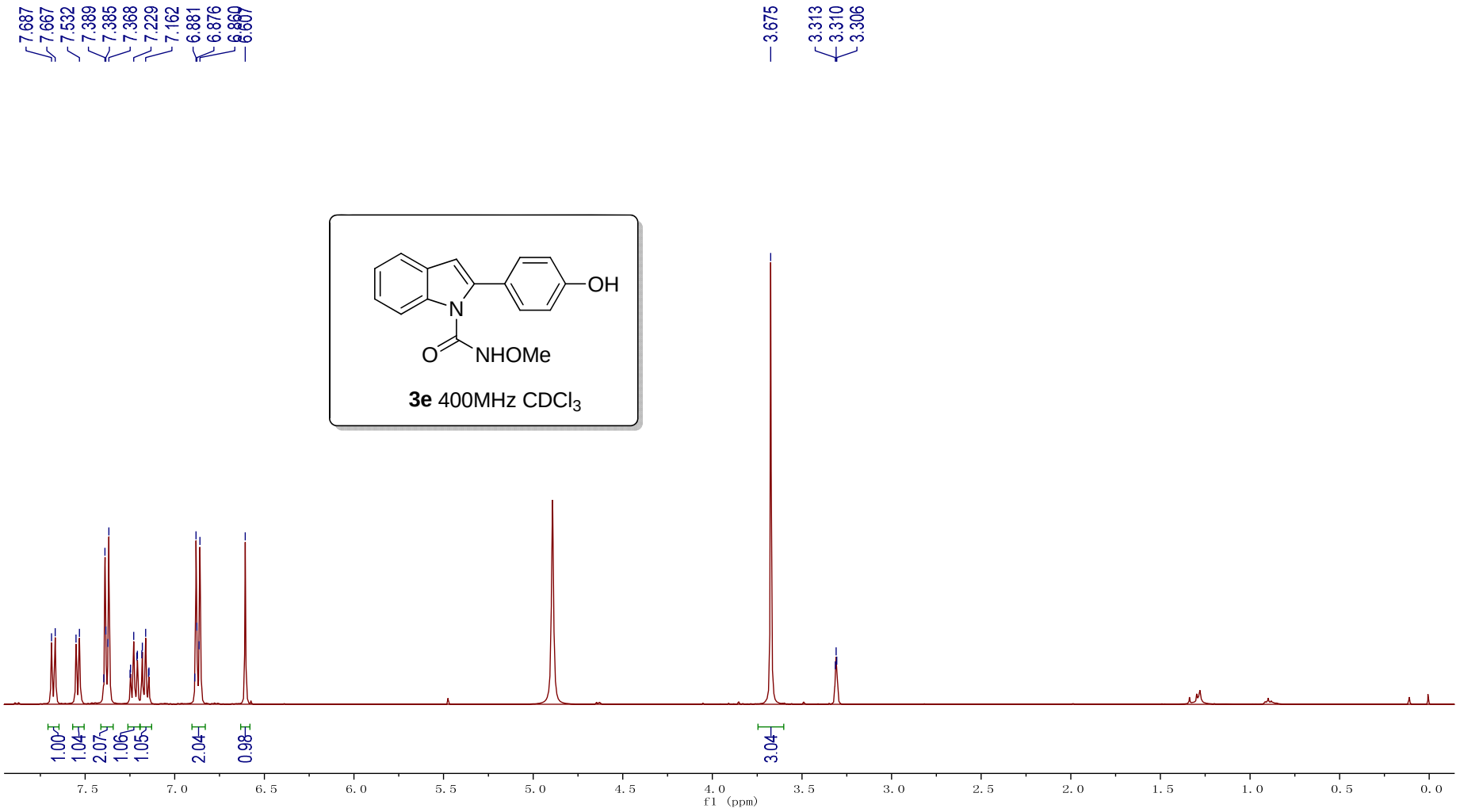

152.31
139.44
137.92
137.69
130.04
129.04
128.67
128.61
124.58
123.04
120.65
114.23
109.02
77.48
77.16
76.84
64.69
21.51
Me
N
O
NHOMe
3b 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

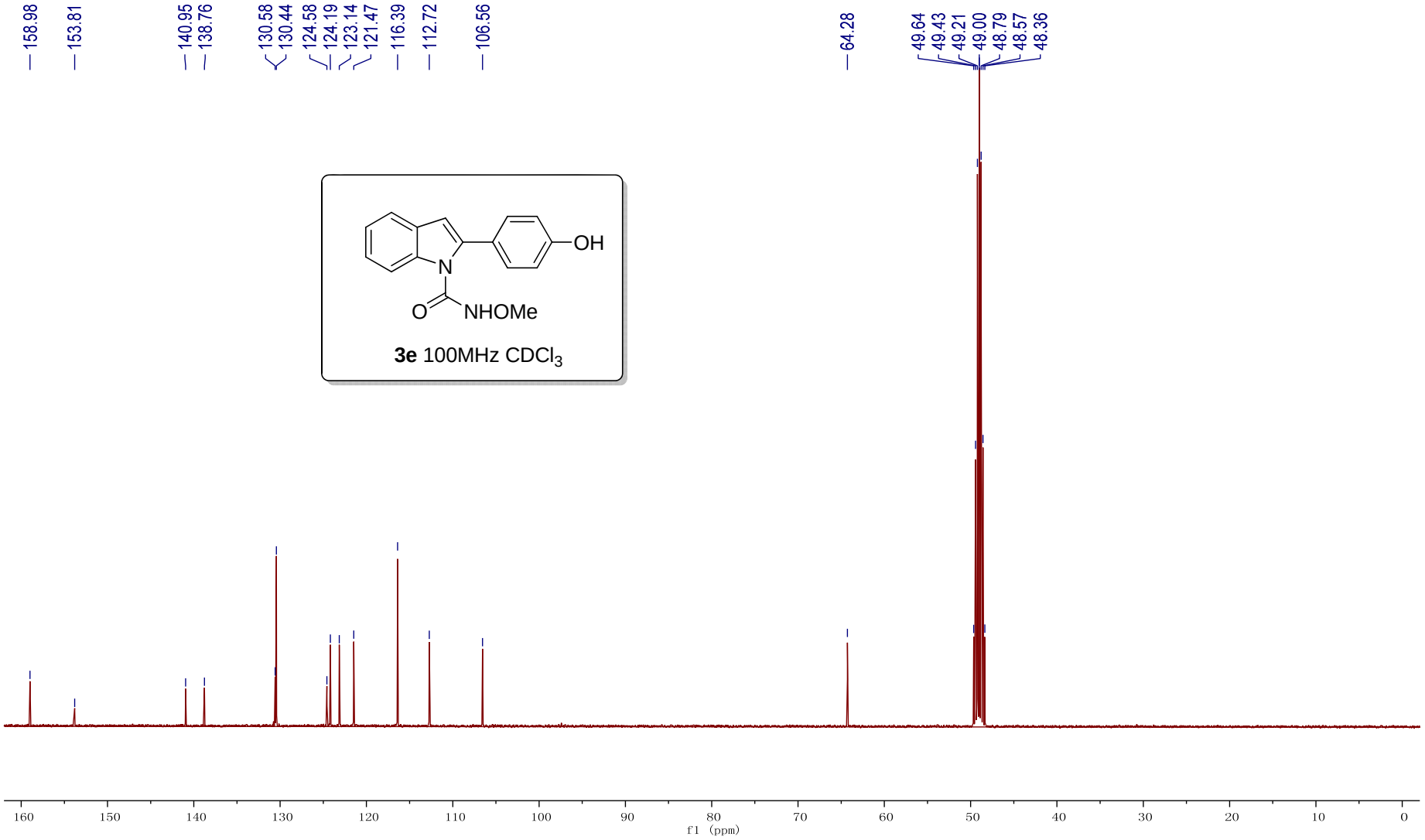

8.110
8.090
7.807
7.733
7.712
7.660
7.642
7.626
7.621
7.605
3.720
Ph
N
O
NHOMe
3c 400MHz CDCl3
0.99
1.05
2.21
5.20
2.13
2.13
1.35
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

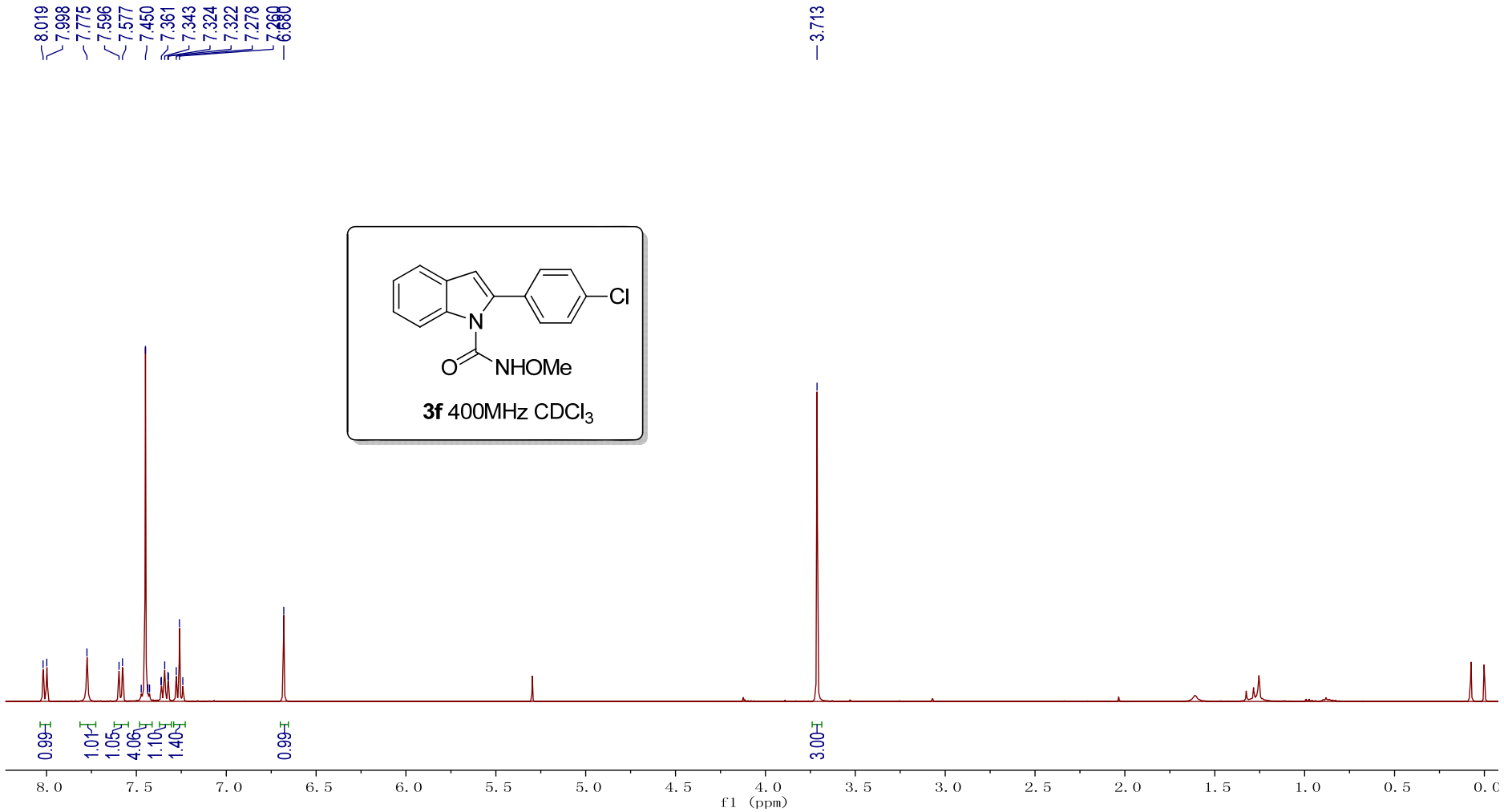

152.15
141.86
140.05
138.06
137.43
129.10
129.03
128.97
128.01
127.85
127.17
124.76
123.10
120.81
114.65
109.38
77.48
77.16
76.84
64.68
Ph
N
O
NHOMe
3c 100MHz CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

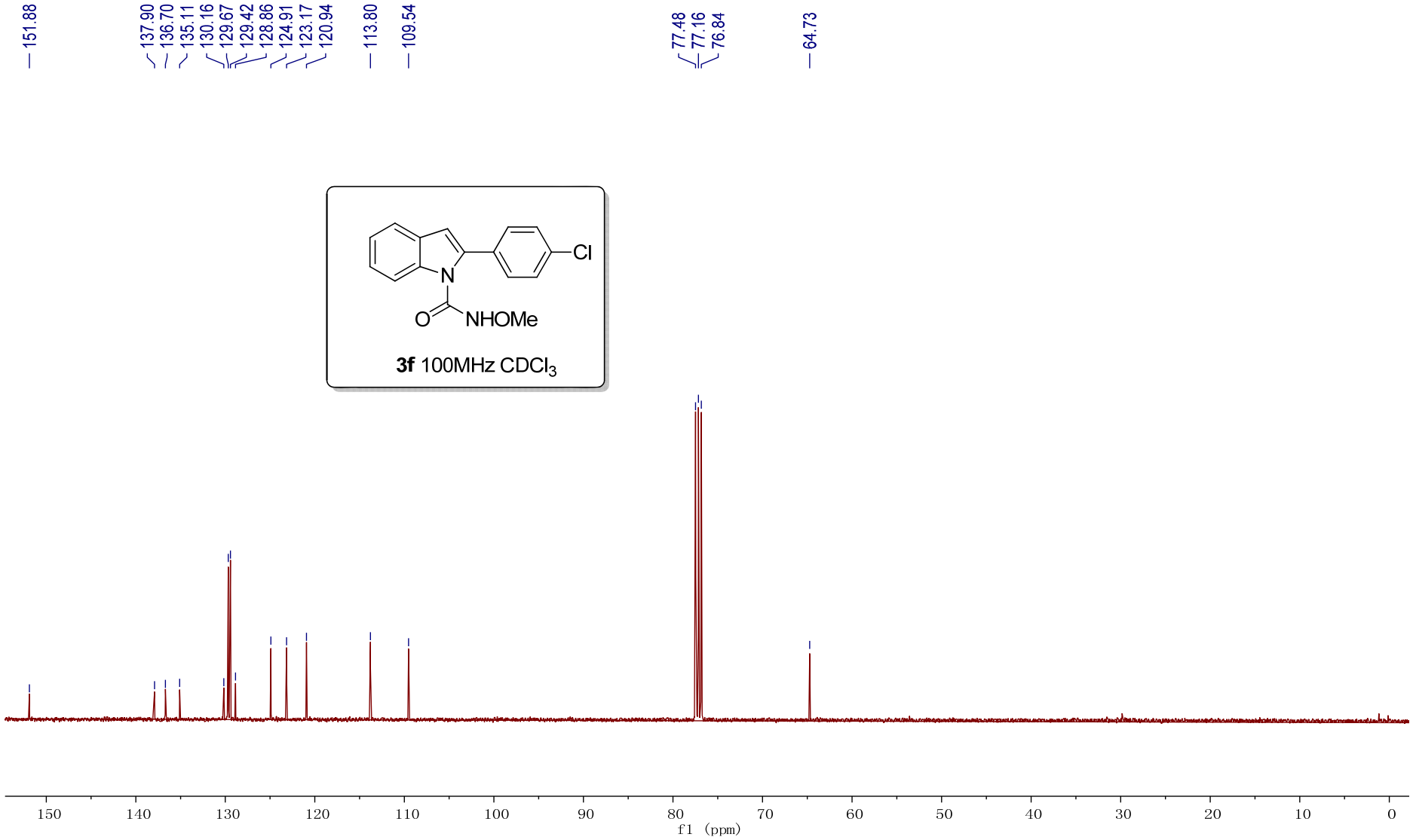

8.113
8.092
7.756
7.573
7.554
7.469
7.452
7.447
7.325
7.260
7.248
7.021
6.999
6.597
3.870
3.697
OMe
N
O
NHOMe
3d 400MHz CDCl3
1.02
1.00
1.04
2.02
1.07
1.31
2.01
0.99
3.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

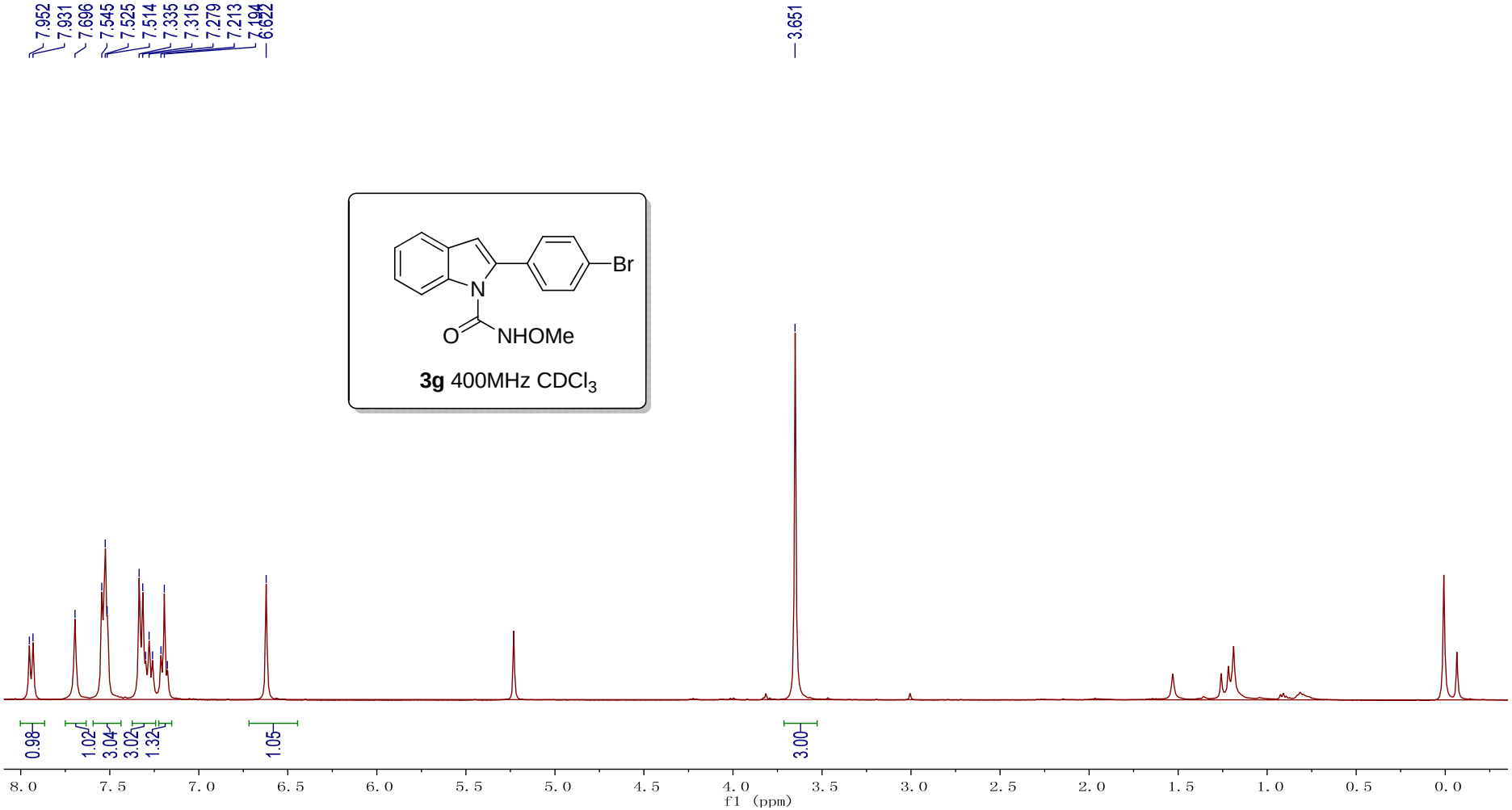

160.40
152.34
137.81
137.48
130.09
129.07
124.43
123.84
123.01
120.53
114.75
114.19
108.64
77.48
77.16
76.84
64.67
55.55
OMe
N
O
NHOMe
3d 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

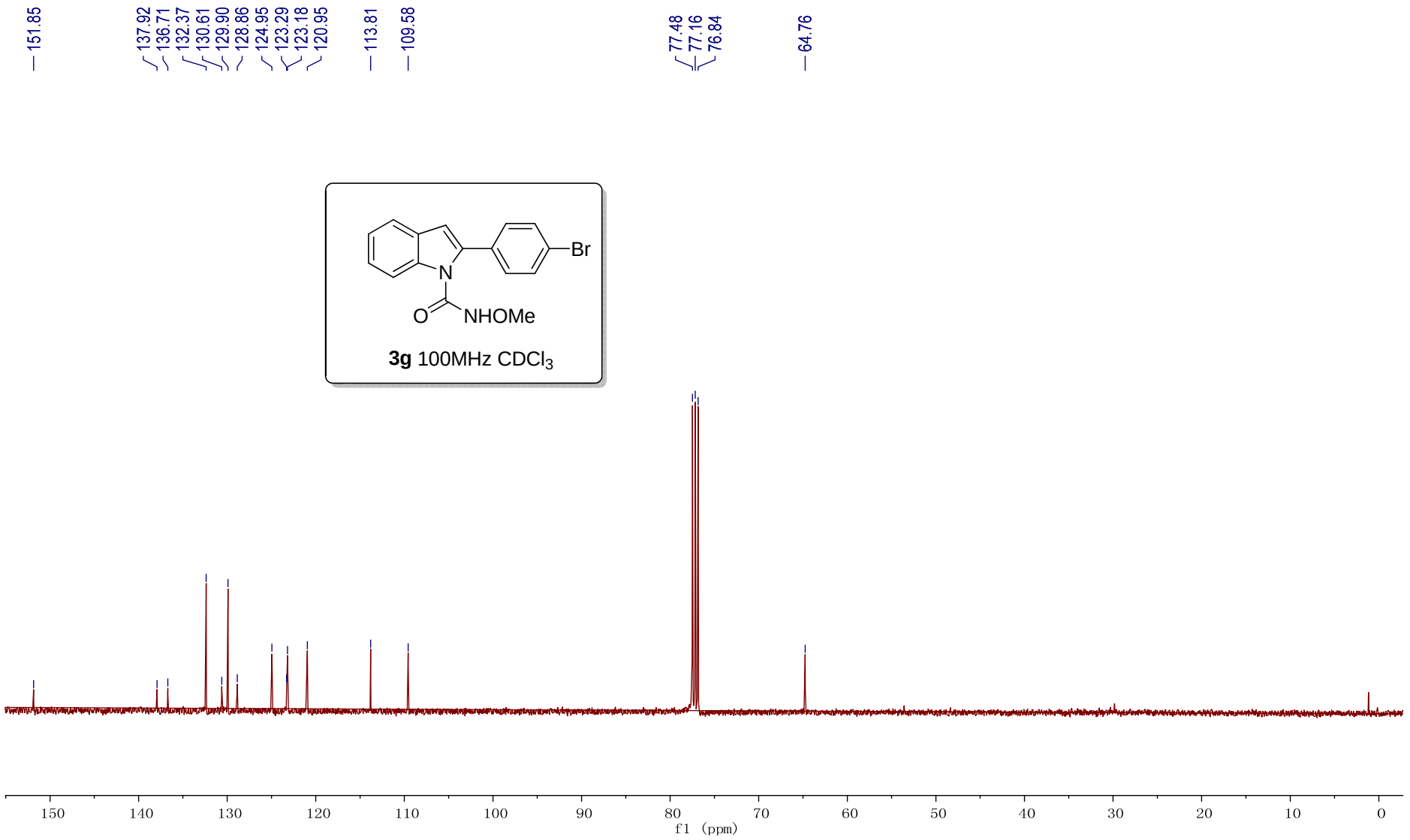

7.687
7.667
7.532
7.389
7.385
7.368
7.229
7.162
6.881
6.876
3.675
3.313
3.310
3.306
OH
N
O
NHOMe
3e 400MHz CDCl3
1.00
1.04
2.07
1.06
1.05
2.04
0.98
3.04
f1 (ppm)

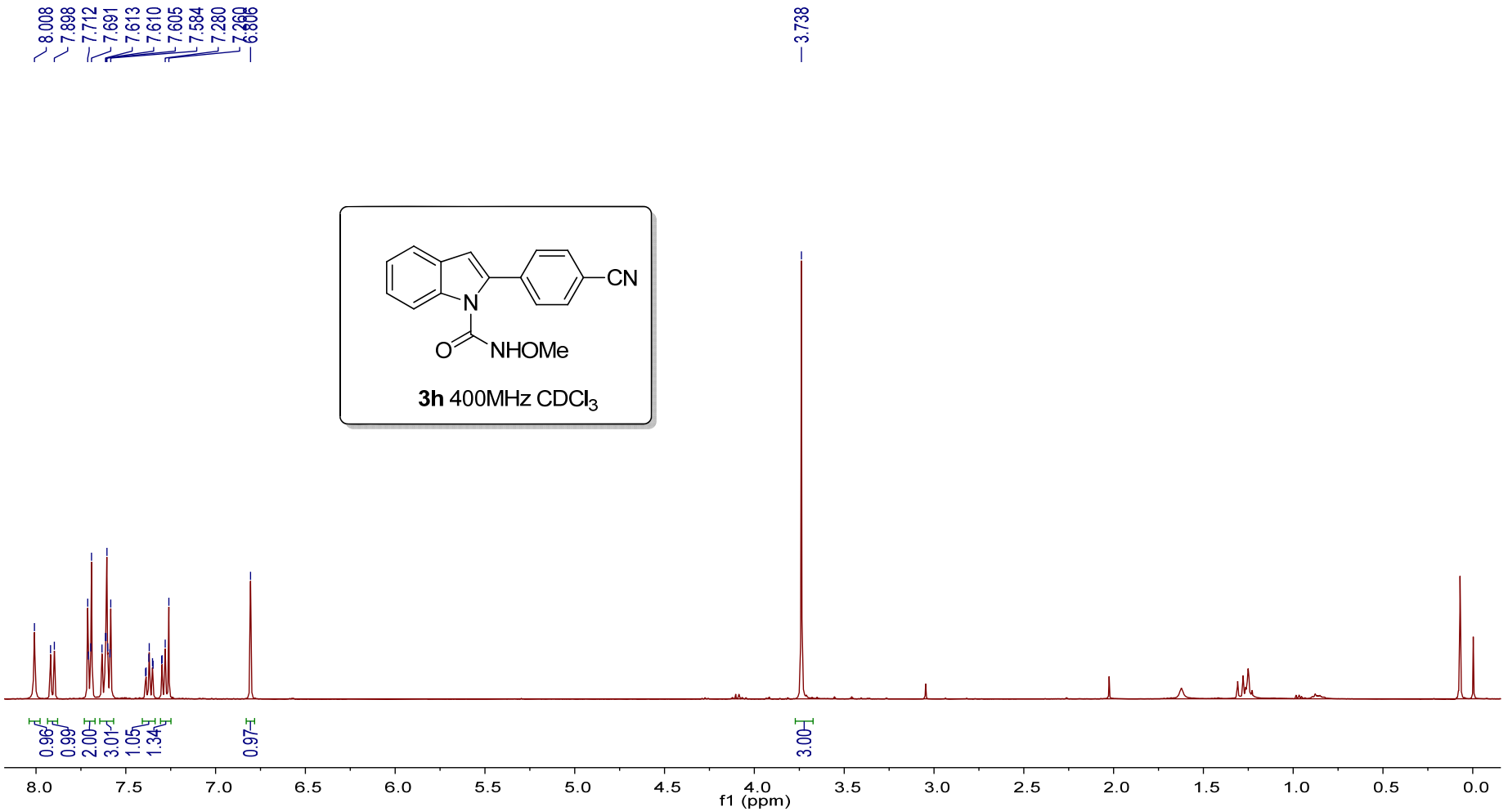

158.98
153.81
140.95
138.76
130.58
130.44
124.58
124.19
123.14
121.47
116.39
112.72
106.56
64.28
49.64
49.43
49.21
49.00
48.79
48.57
48.36
OH
N
O
NHOMe
3e 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

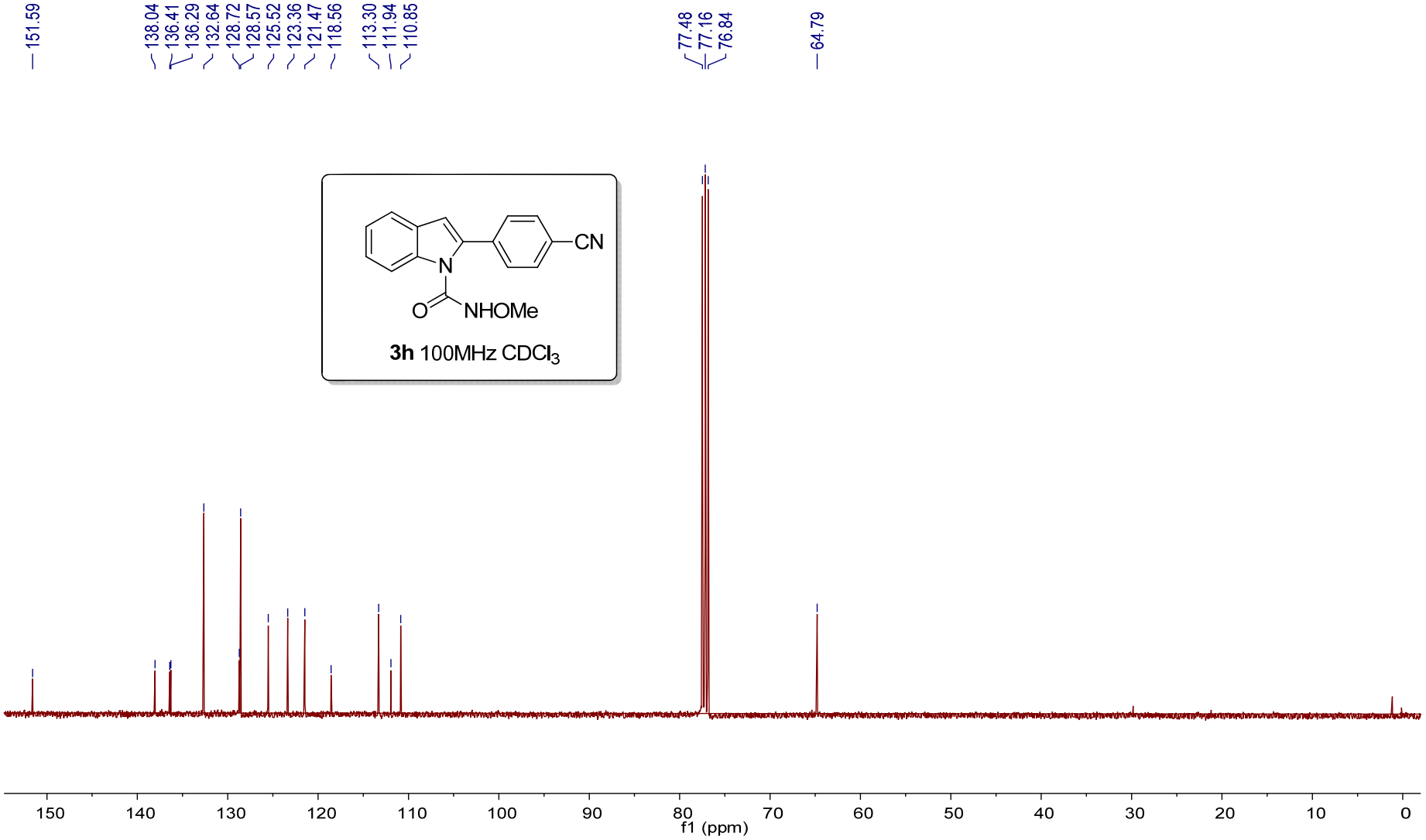

8.019
7.998
7.775
7.596
7.577
7.450
7.361
7.343
7.324
7.322
7.278
7.260
6.680
3.713
Cl
N
O
NHOMe
3f 400MHz CDCl3
0.99
1.01
1.05
4.06
1.10
1.40
0.99
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

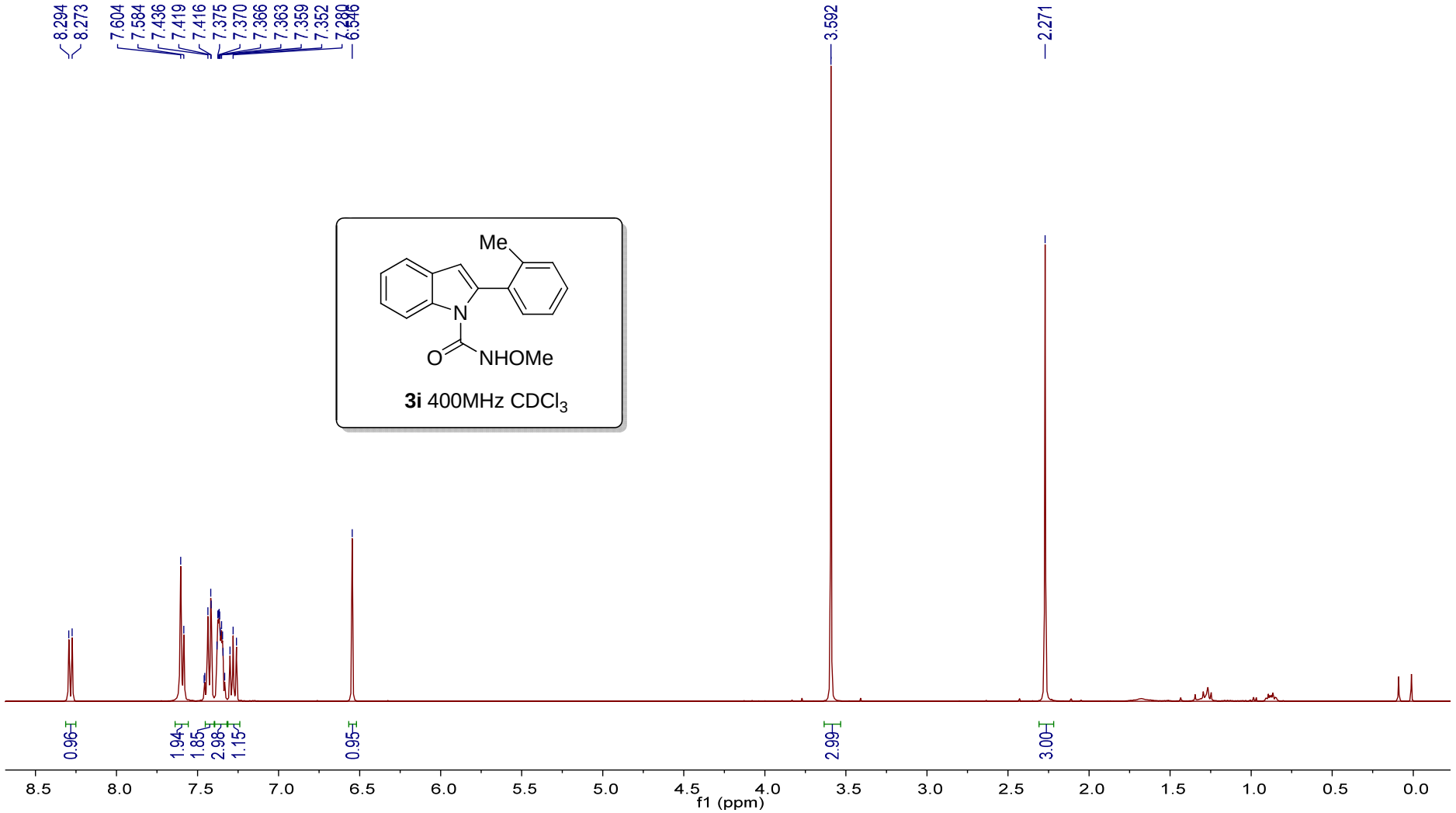

151.88
137.90
136.70
135.11
130.16
129.67
129.42
128.86
124.91
123.17
120.94
113.80
109.54
77.48
77.16
76.84
64.73
Cl
N
O
NHOMe
3f 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

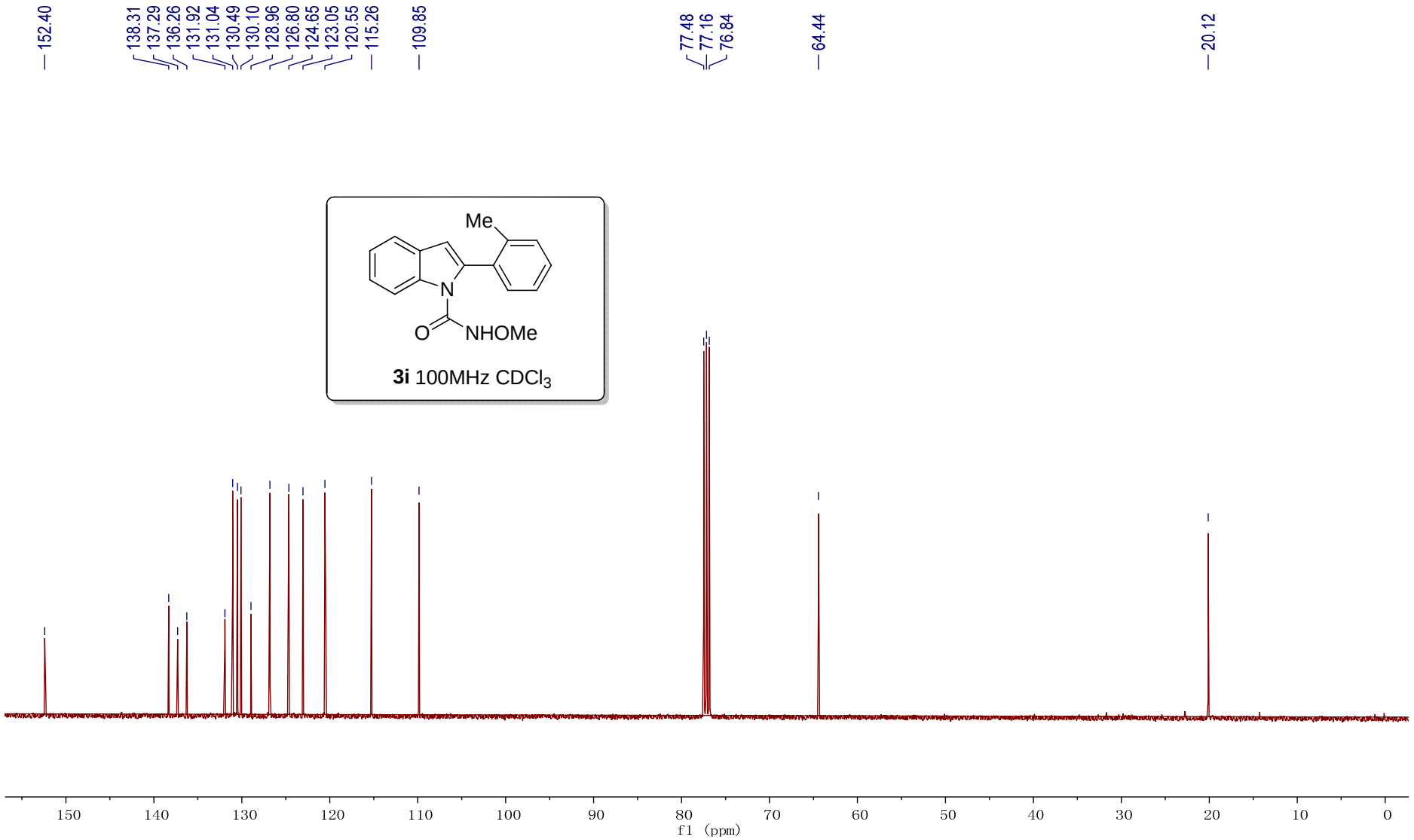

7.952
7.931
7.696
7.545
7.525
7.514
7.335
7.315
7.279
7.213
7.194
6.622
3.651
Br
N
O
NHOMe
3g 400MHz CDCl3
0.98
1.02
3.04
3.02
1.32
1.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

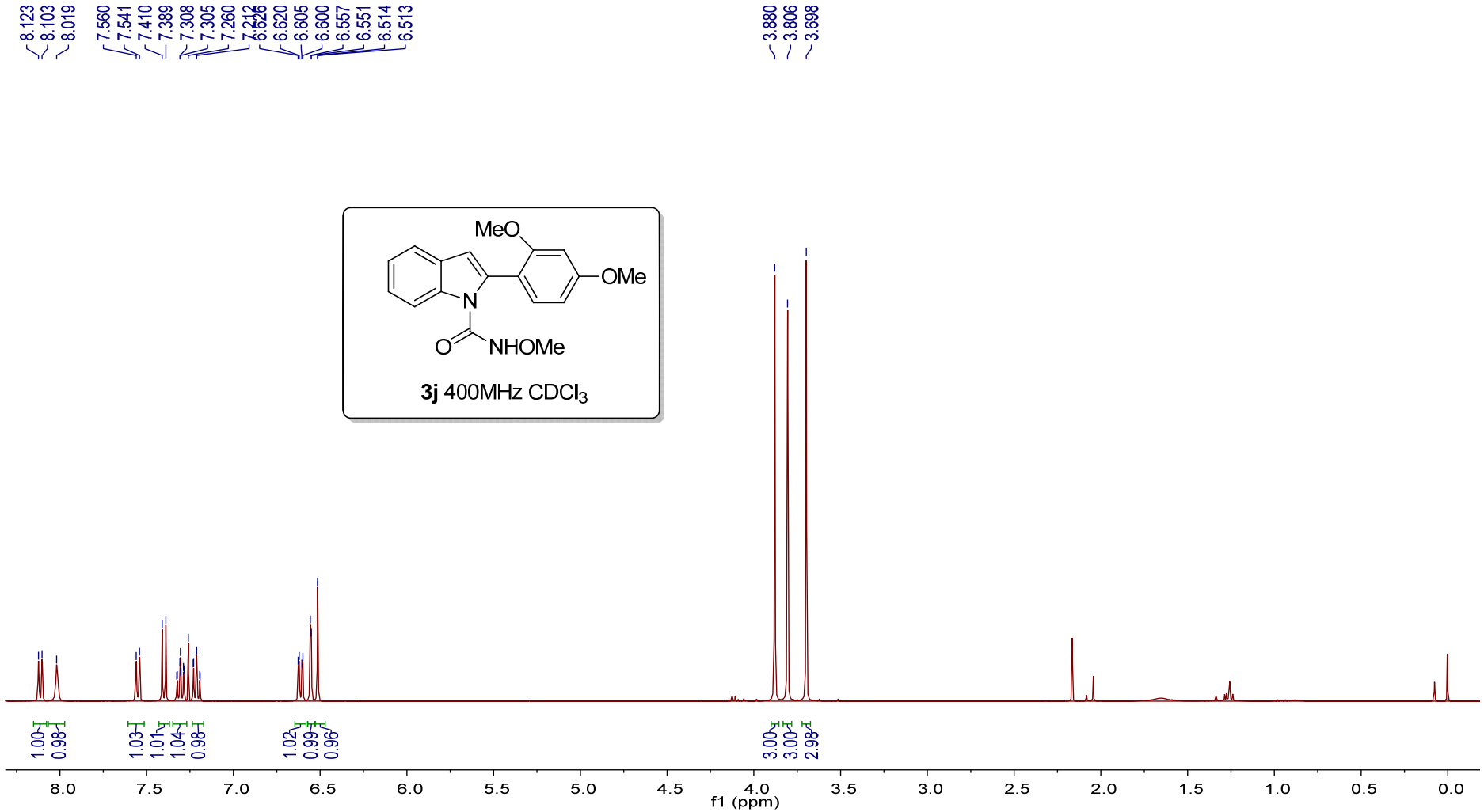

151.85
137.92
136.71
132.37
130.61
129.90
128.86
124.95
123.29
123.18
120.95
113.81
109.58
77.48
77.16
76.84
64.76
Br
N
O
NHOMe
3g 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

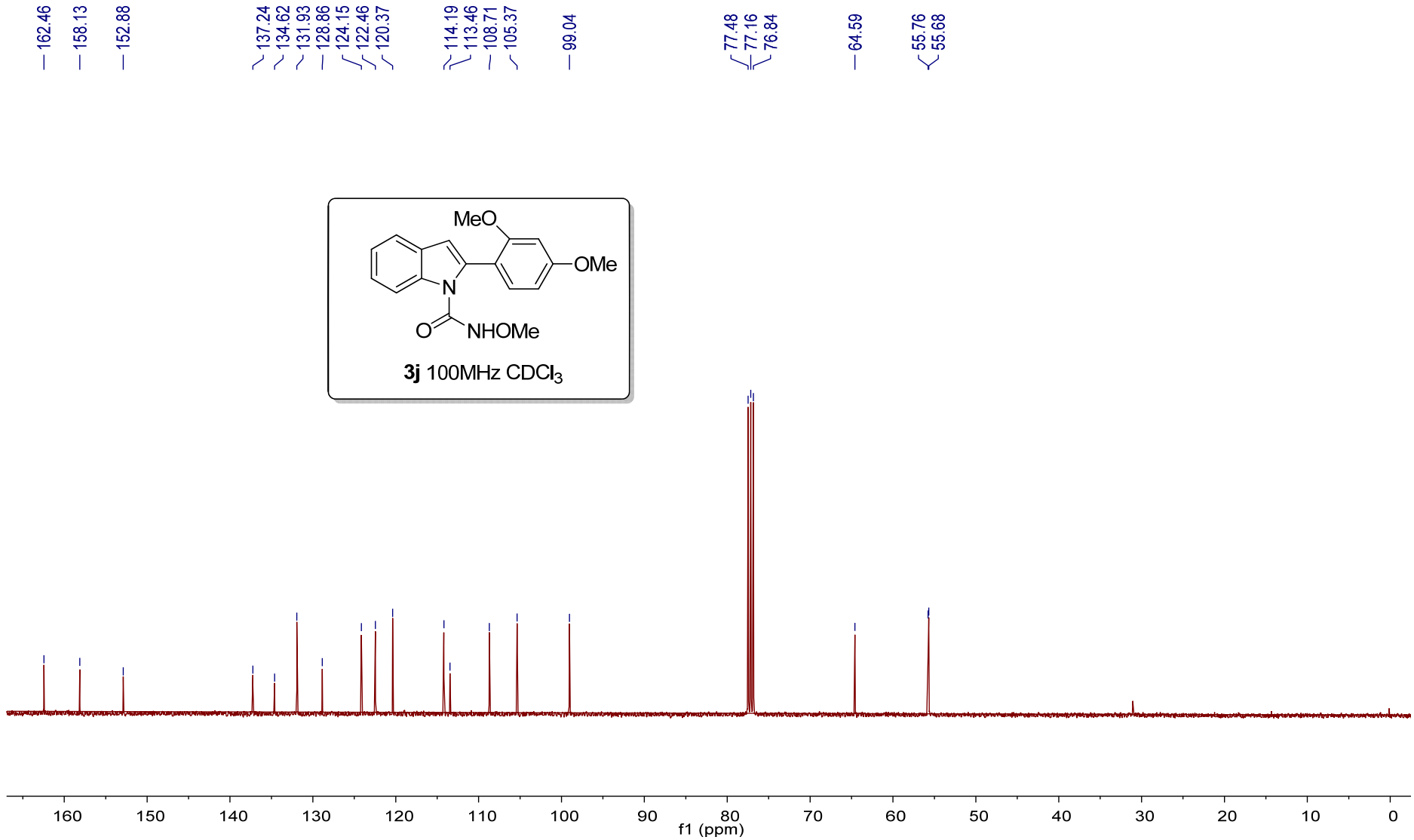

8.008
7.898
7.712
7.691
7.613
7.610
7.605
7.584
7.280
7.260
6.806
3.738
CN
N
O
NHOMe
3h 400MHz CDCl3
0.96
0.99
2.00
3.01
1.05
1.34
0.97
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

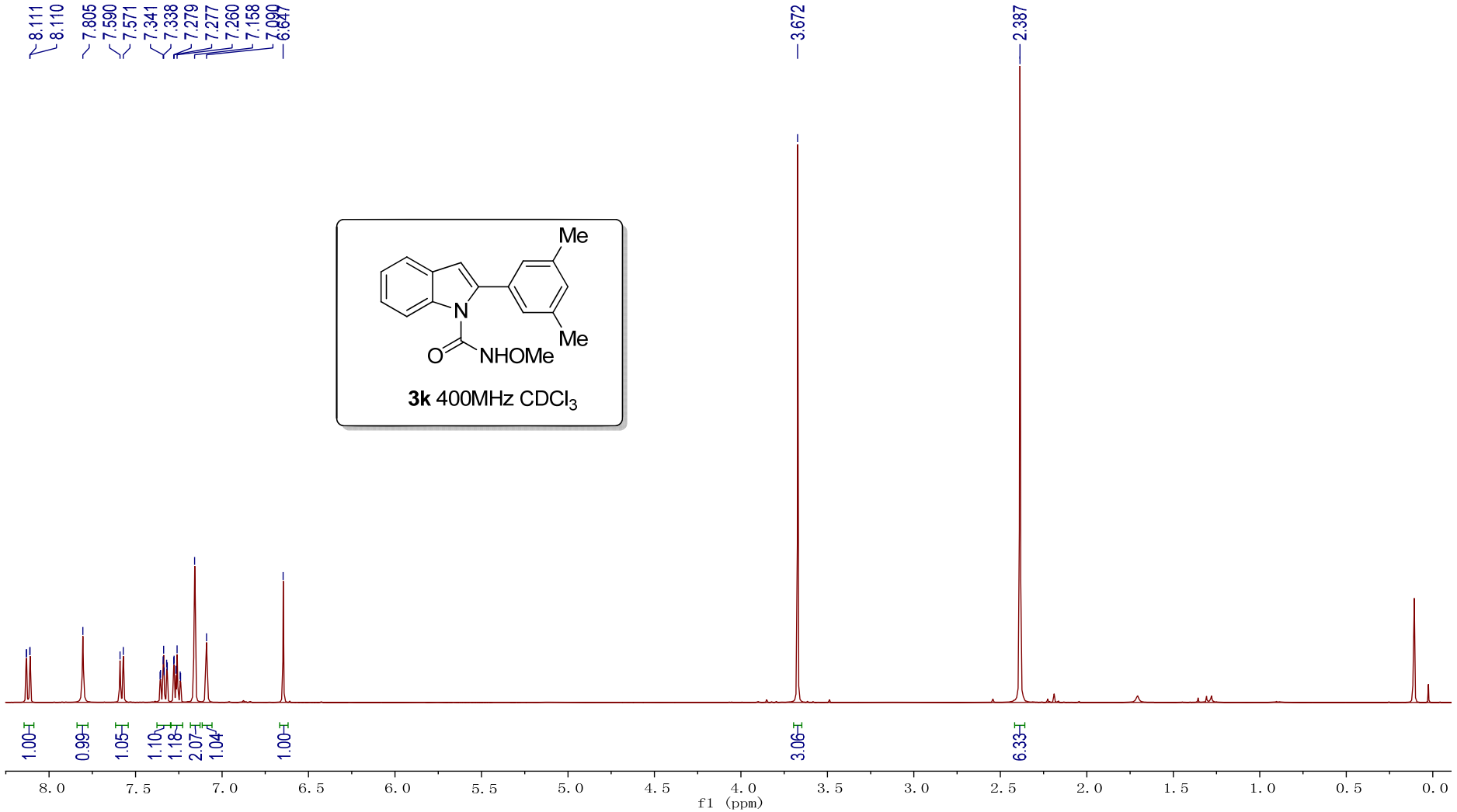

151.59
138.04
136.41
136.29
132.64
128.72
128.57
125.52
123.36
121.47
118.56
113.30
111.94
110.85
77.48
77.16
76.84
64.79
CN
N
O
NHOMe
3h 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

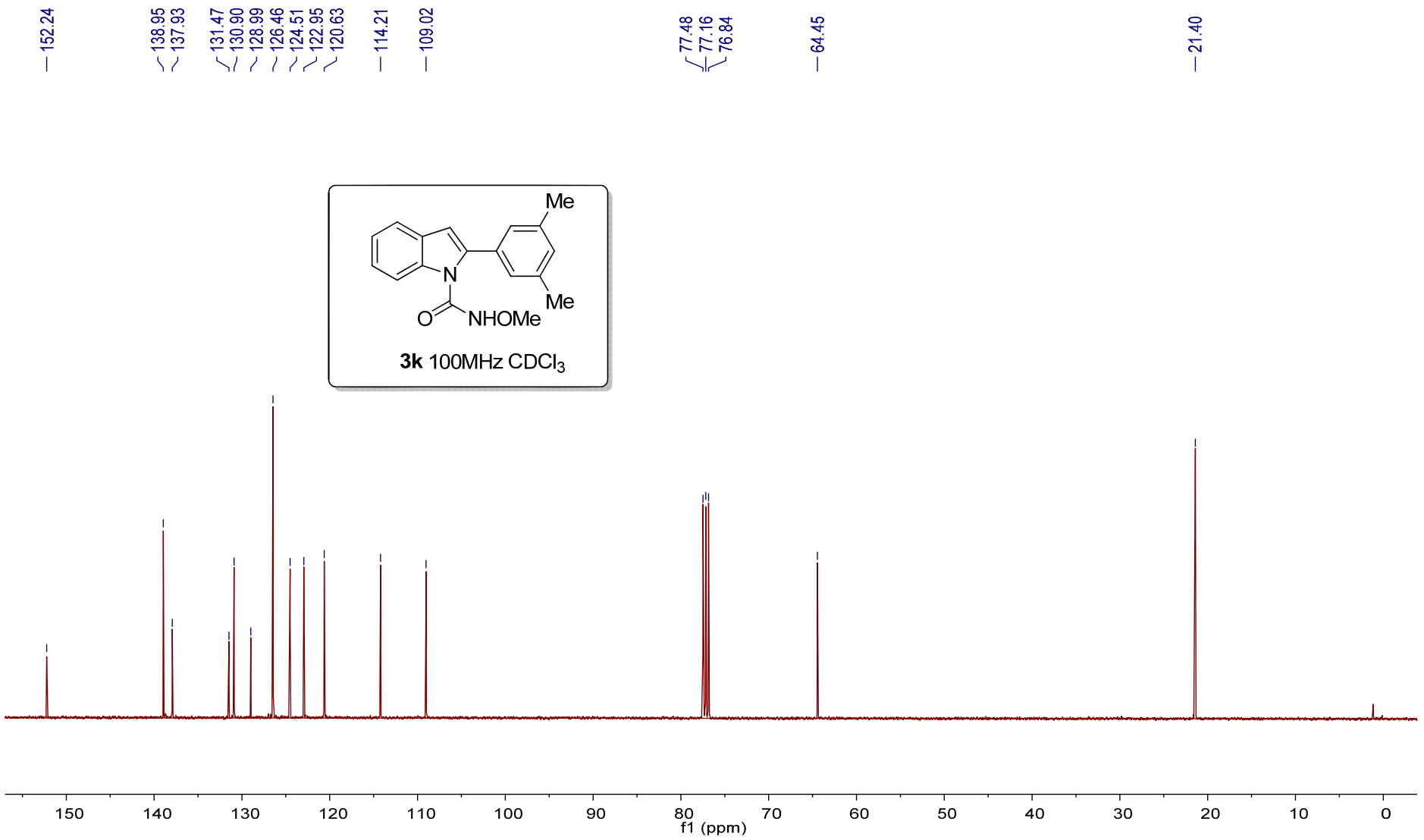

8.294
8.273
7.604
7.584
7.436
7.419
7.416
7.375
7.370
7.366
7.363
7.359
7.352
7.280
6.546
3.592
2.271
Me
N
O
NHOMe
3i 400MHz CDCl3
0.96
1.94
1.85
2.98
1.15
0.95
2.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

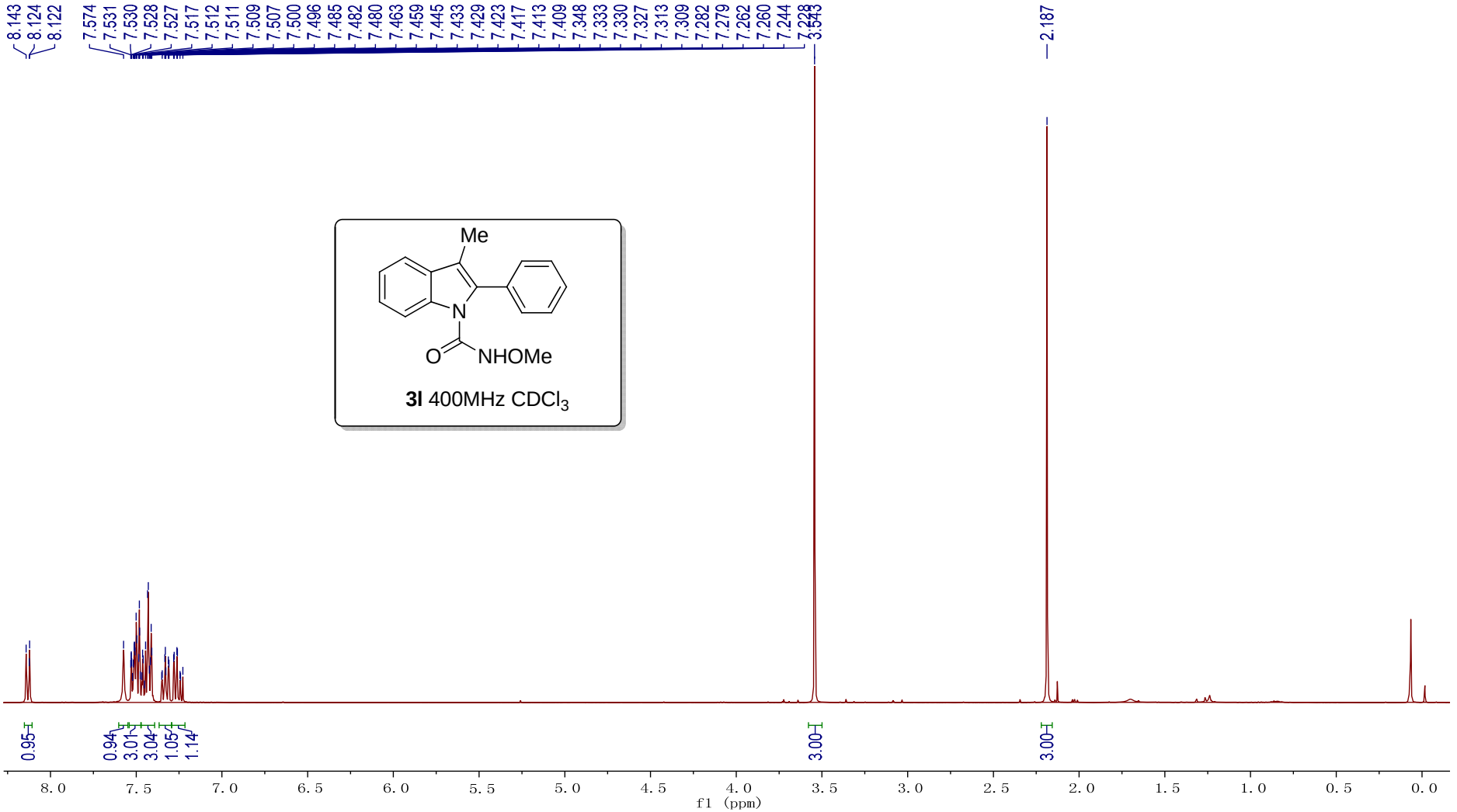

152.40
138.31
137.29
136.26
131.92
131.04
130.49
130.10
128.96
126.80
124.65
123.05
120.55
115.26
109.85
77.48
77.16
76.84
64.44
20.12
Me
N
O
NHOMe
3i 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

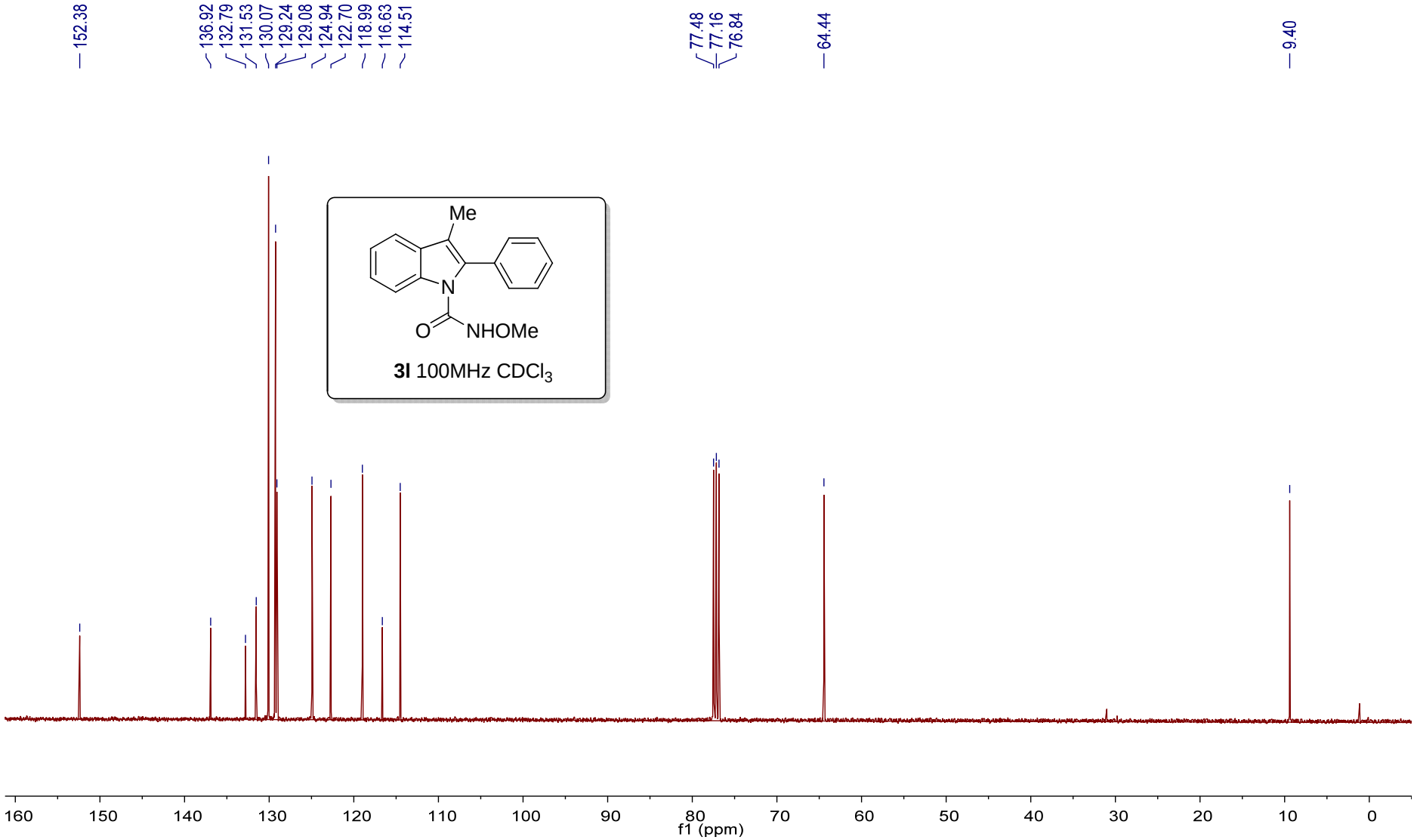

8.123
8.103
8.019
7.560
7.541
7.410
7.389
7.308
7.305
7.260
6.620
6.605
6.600
6.557
6.551
6.514
6.513
3.880
3.806
3.698
MeO
OMe
N
O
NHOMe
3j 400MHz CDCl3
1.00
0.98
1.03
1.01
1.04
0.98
1.02
0.99
0.96
3.00
3.00
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

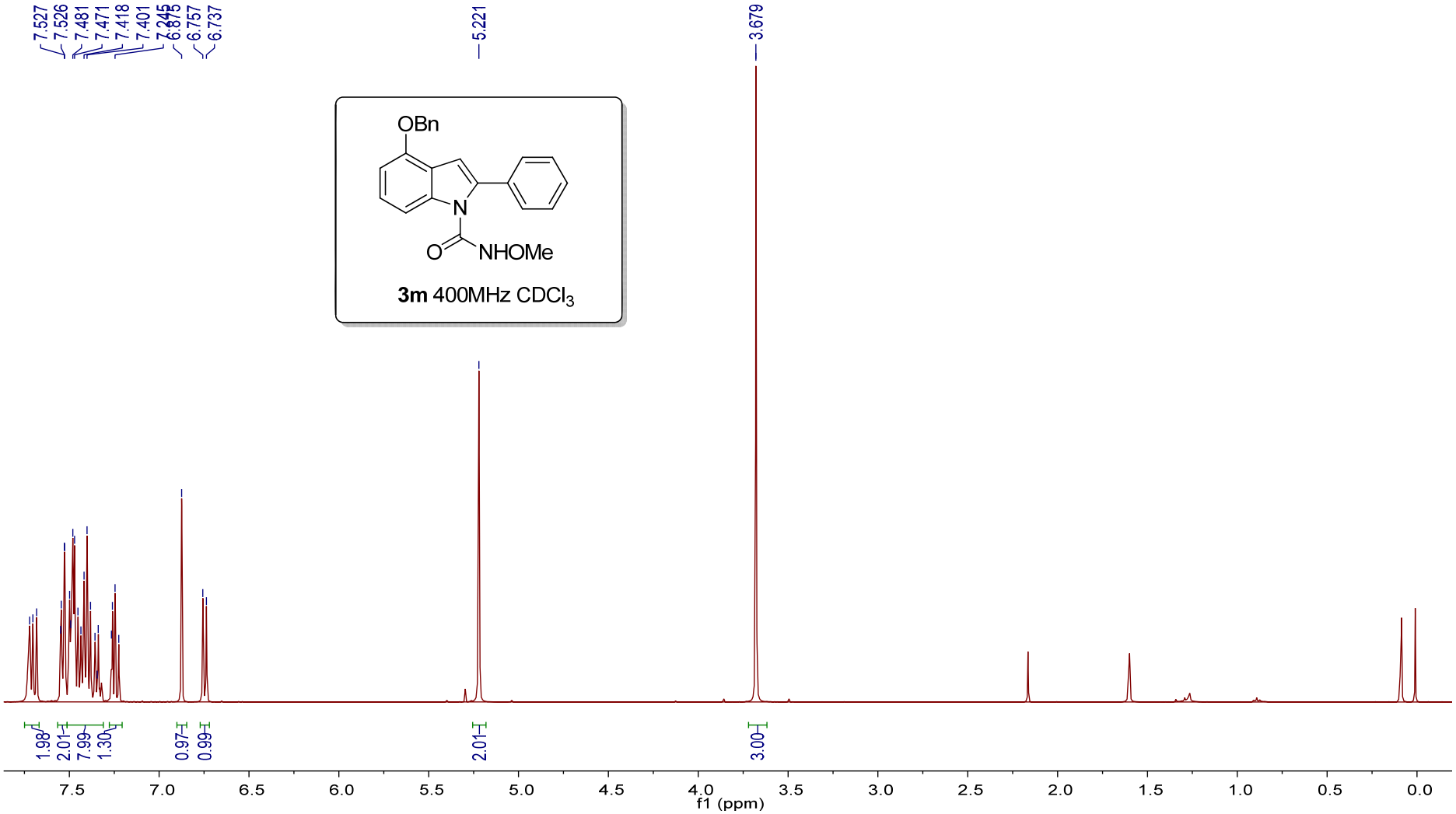

162.46
158.13
152.88
137.24
134.62
131.93
128.86
124.15
122.46
120.37
114.19
113.46
108.71
105.37
99.04
77.48
77.16
76.84
64.59
55.76
55.68
MeO
OMe
N
O
NHOMe
3j 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

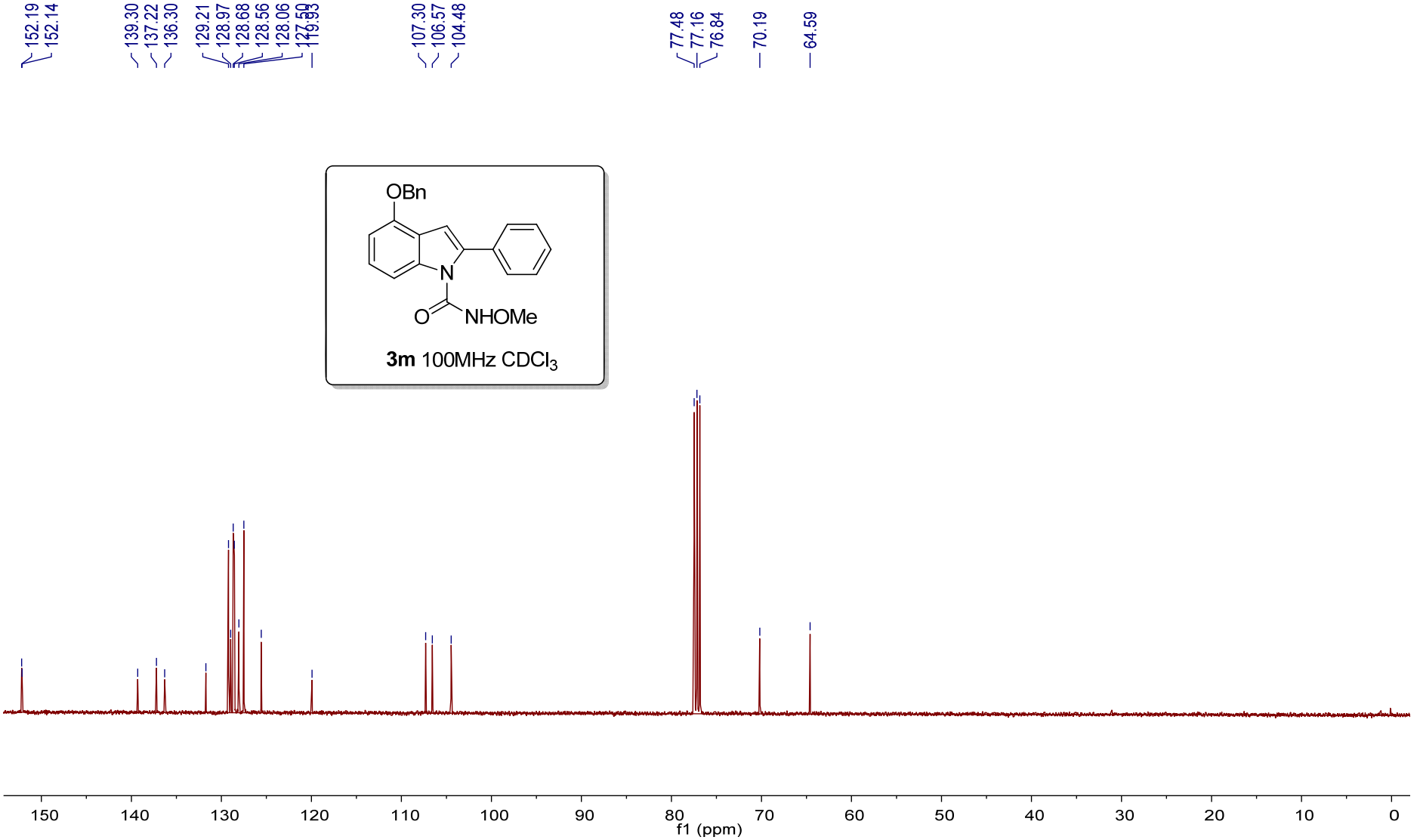

8.111
8.110
7.805
7.590
7.571
7.341
7.338
7.279
7.277
7.260
7.158
7.090
6.847
3.672
2.387
Me
Me
N
O
NHOMe
3k 400MHz CDCl3
1.00
0.99
1.05
1.10
1.18
2.07
1.04
1.00
3.06
6.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

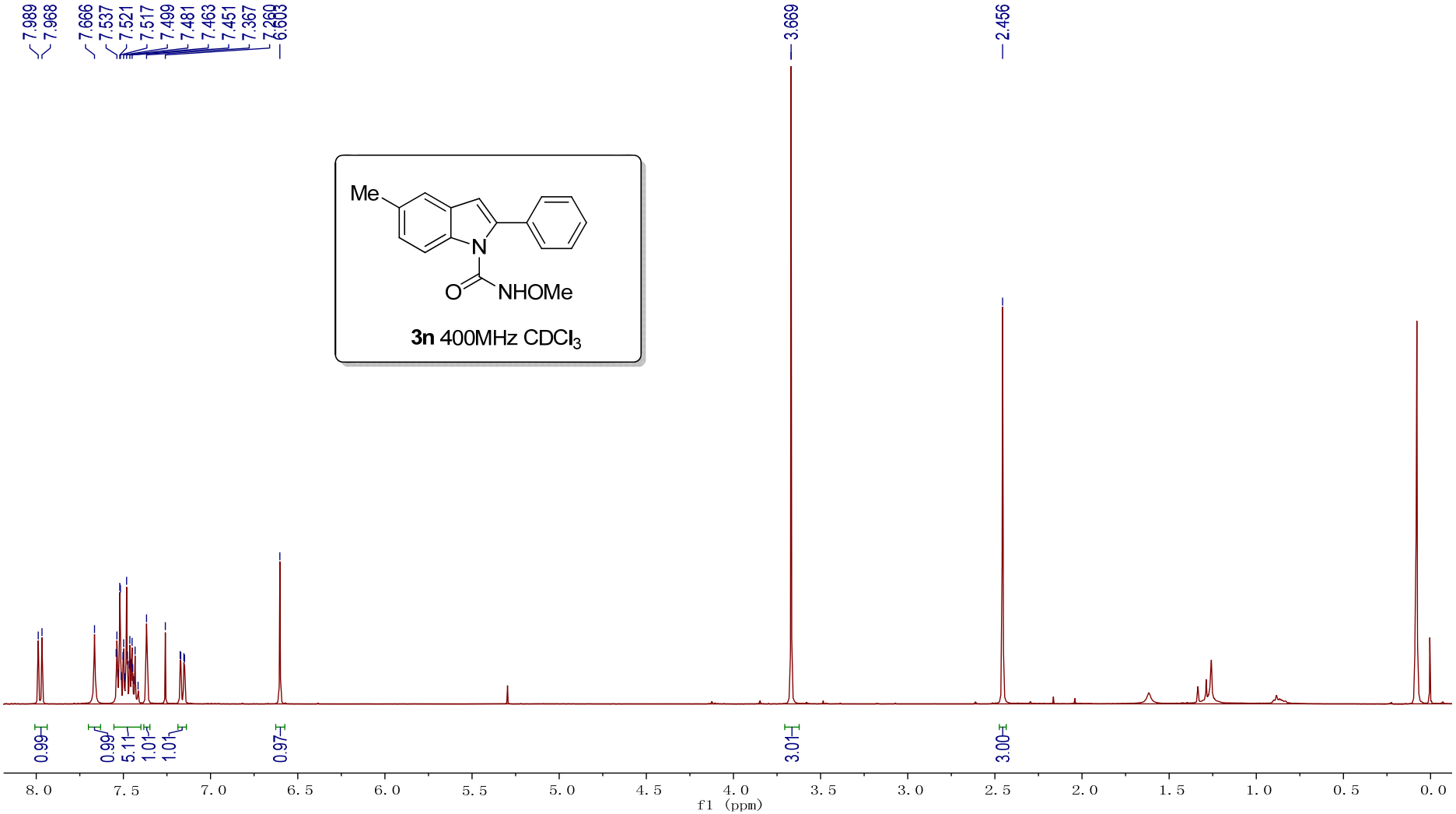

152.24
138.95
137.93
131.47
130.90
128.99
126.46
124.51
122.95
120.63
114.21
109.02
77.48
77.16
76.84
64.45
21.40
Me
Me
N
O
NHOMe
3k 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

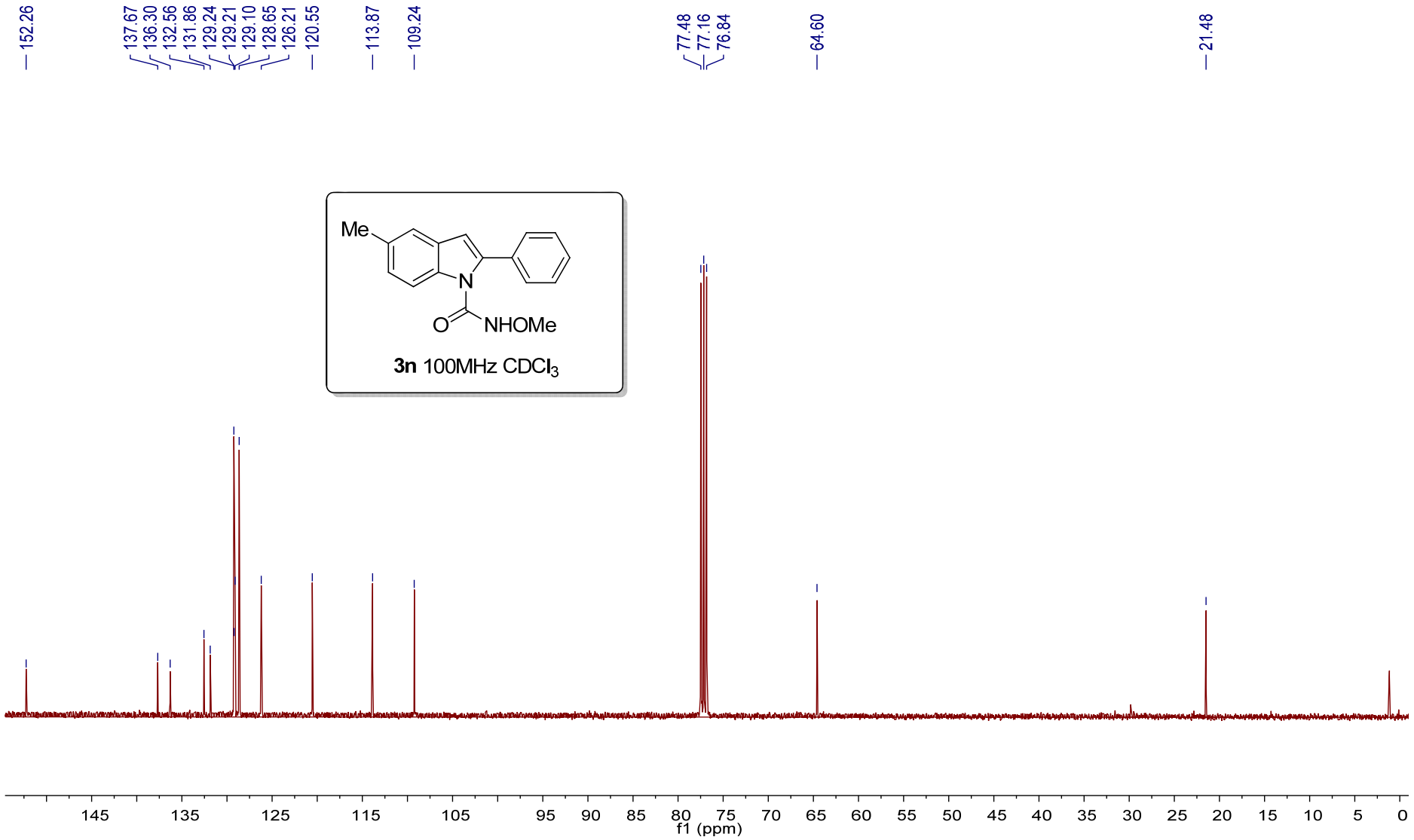

8.143
8.124
8.122
7.574
7.531
7.530
7.528
7.527
7.517
7.512
7.511
7.509
7.507
7.500
7.496
7.485
7.482
7.480
7.463
7.459
7.445
7.433
7.429
7.423
7.417
7.413
7.409
7.348
7.333
7.330
7.327
7.313
7.309
7.282
7.279
7.262
7.260
7.244
3.543
2.187
Me
N
O
NHOMe
3l 400MHz CDCl3
0.95
0.94
3.01
3.04
1.05
1.14
3.00
3.00
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)

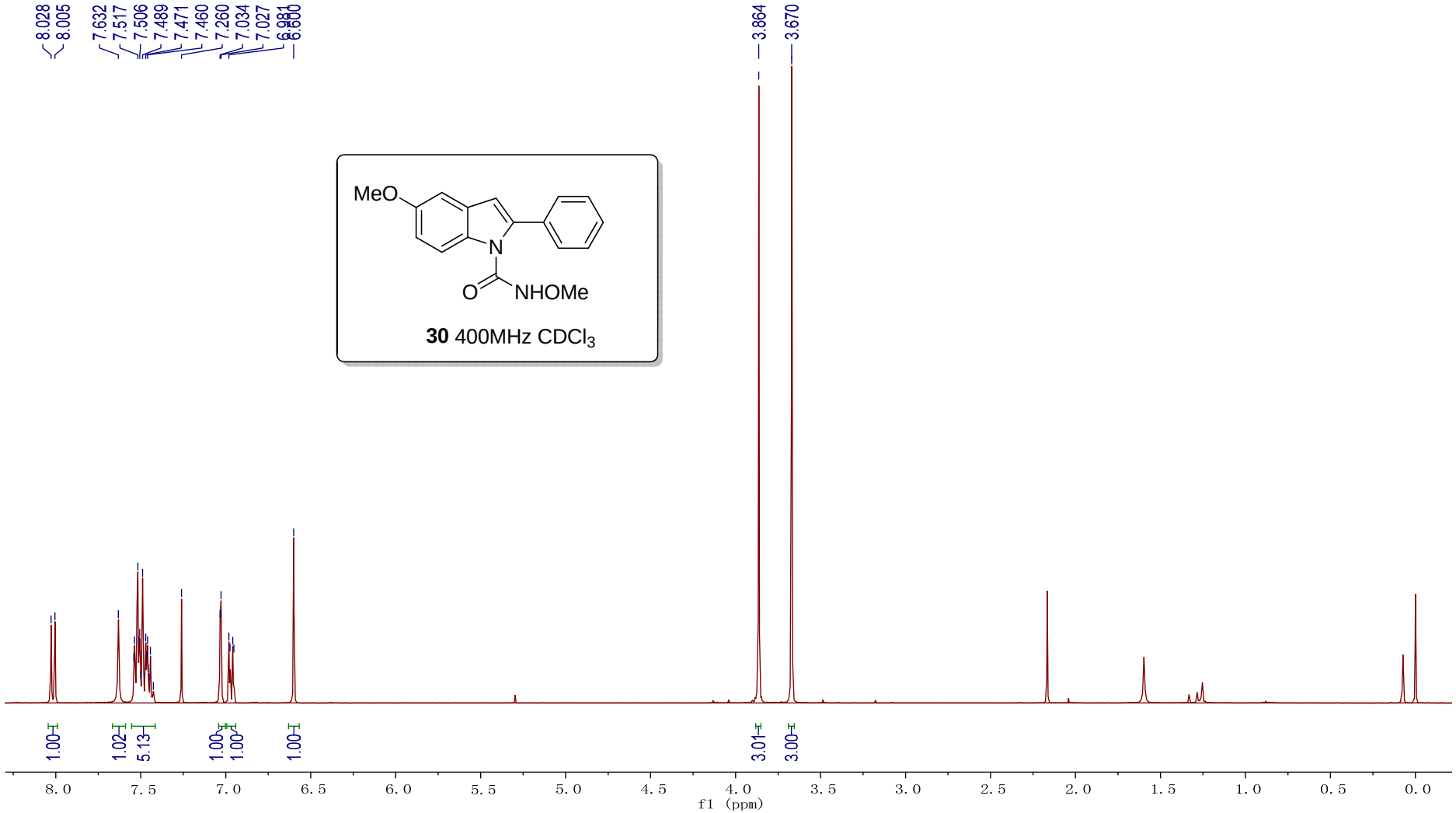

152.38
136.92
132.79
131.53
130.07
129.24
129.08
124.94
122.70
118.99
116.63
114.51
77.48
77.16
76.84
64.44
9.40
Me
N
O
NHOMe
3l 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

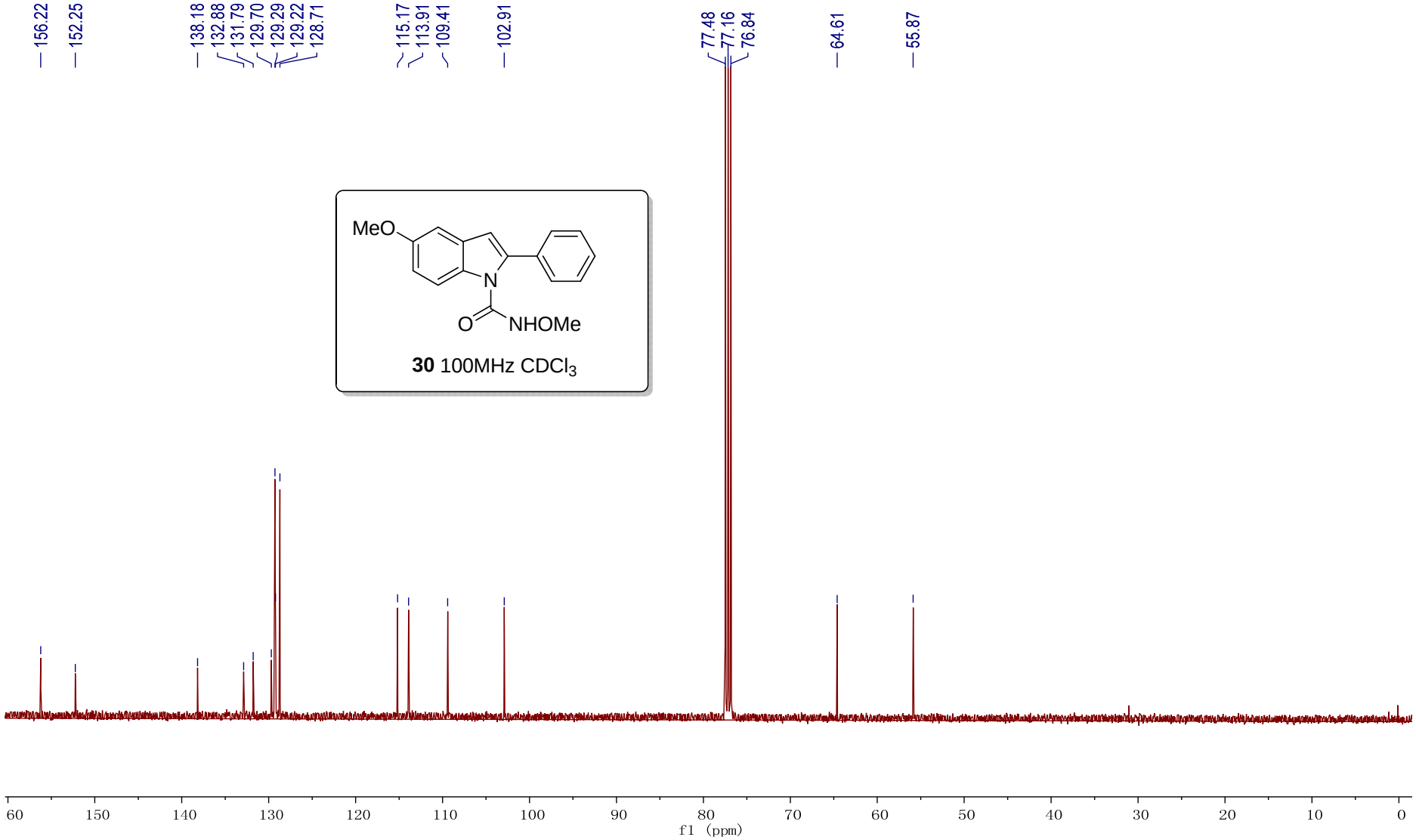

7.527
7.526
7.481
7.471
7.418
7.401
7.245
6.875
6.757
6.737
5.221
3.679
OBn
N
O
NHOMe
3m 400MHz CDCl3
1.98
2.01
7.99
1.30
0.97
0.99
2.01
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

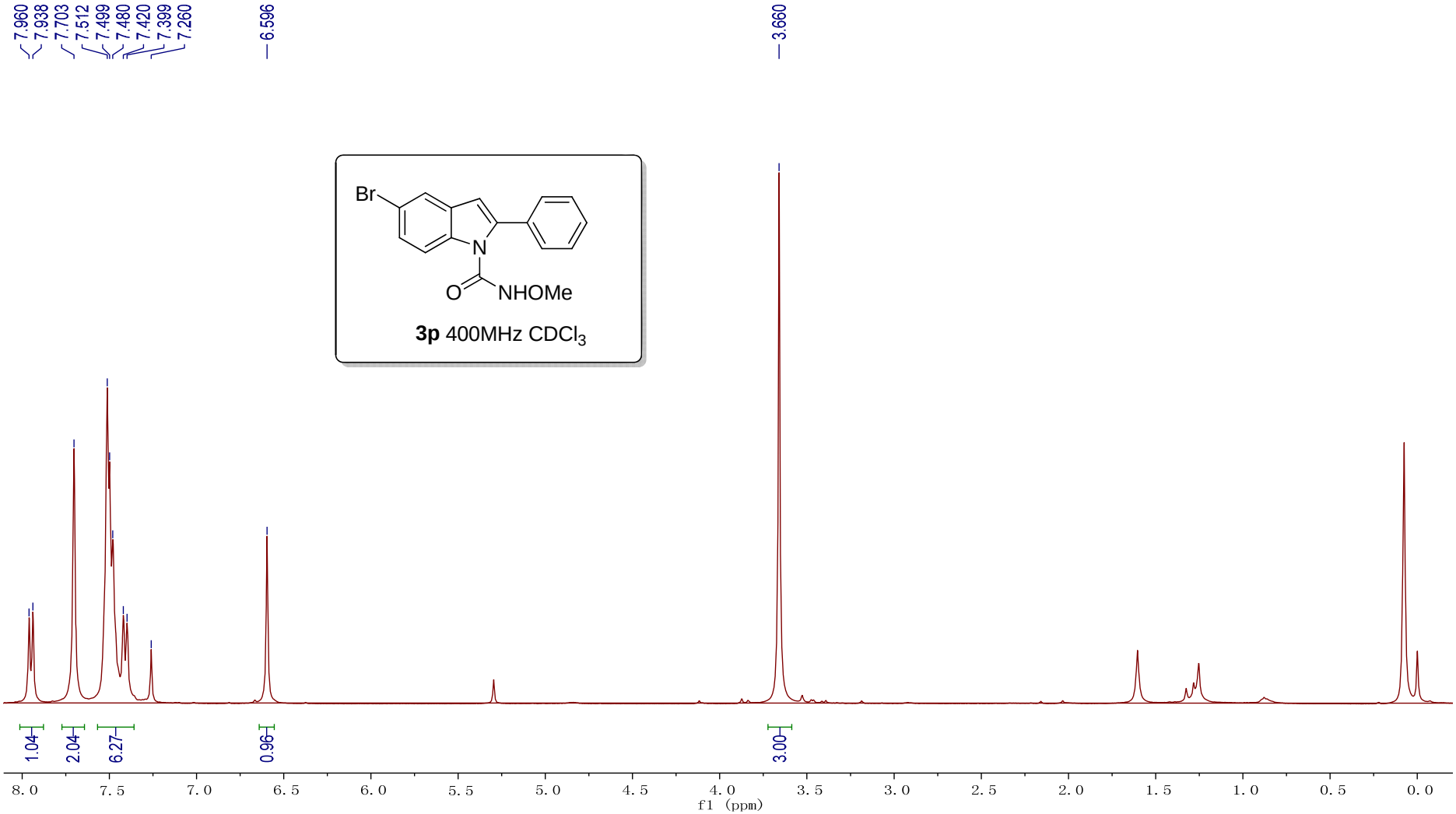

152.19
152.14
139.30
137.22
136.30
129.21
128.97
128.68
128.56
128.06
127.50
115.93
107.30
106.57
104.48
77.48
77.16
76.84
70.19
64.59
OBn
N
O
NHOMe
3m 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

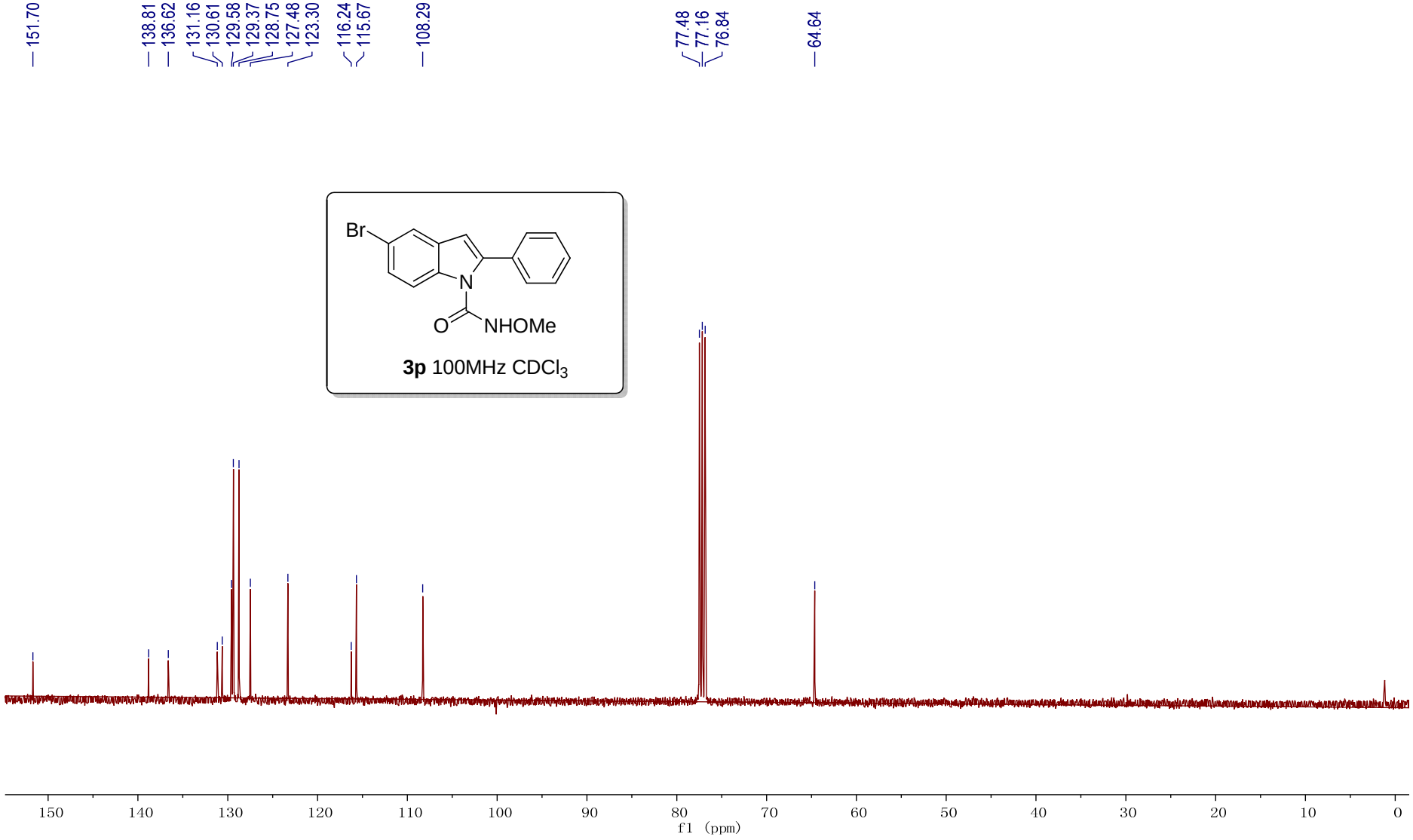

7.989
7.968
7.666
7.537
7.521
7.517
7.499
7.481
7.463
7.451
7.367
7.269
6.603
3.669
2.456
Me
N
O
NHOMe
3n 400MHz CDCl3
0.99
0.99
5.11
1.01
1.01
0.97
3.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

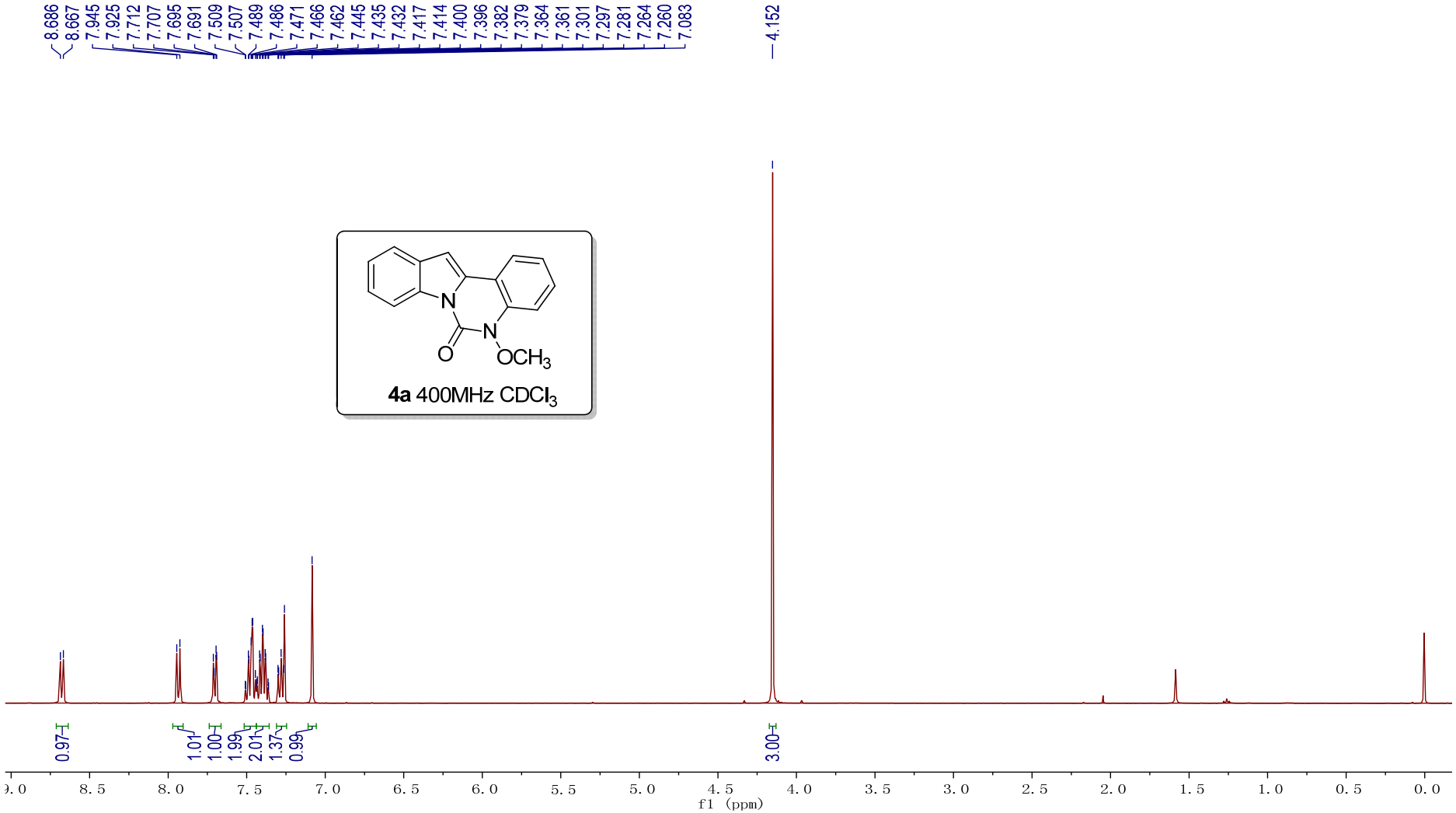

152.26
137.67
136.30
132.56
131.86
129.24
129.21
129.10
128.65
126.21
120.55
113.87
109.24
77.48
77.16
76.84
64.60
21.48
Me
N
O
NHOMe
3n 100MHz CDCl3
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

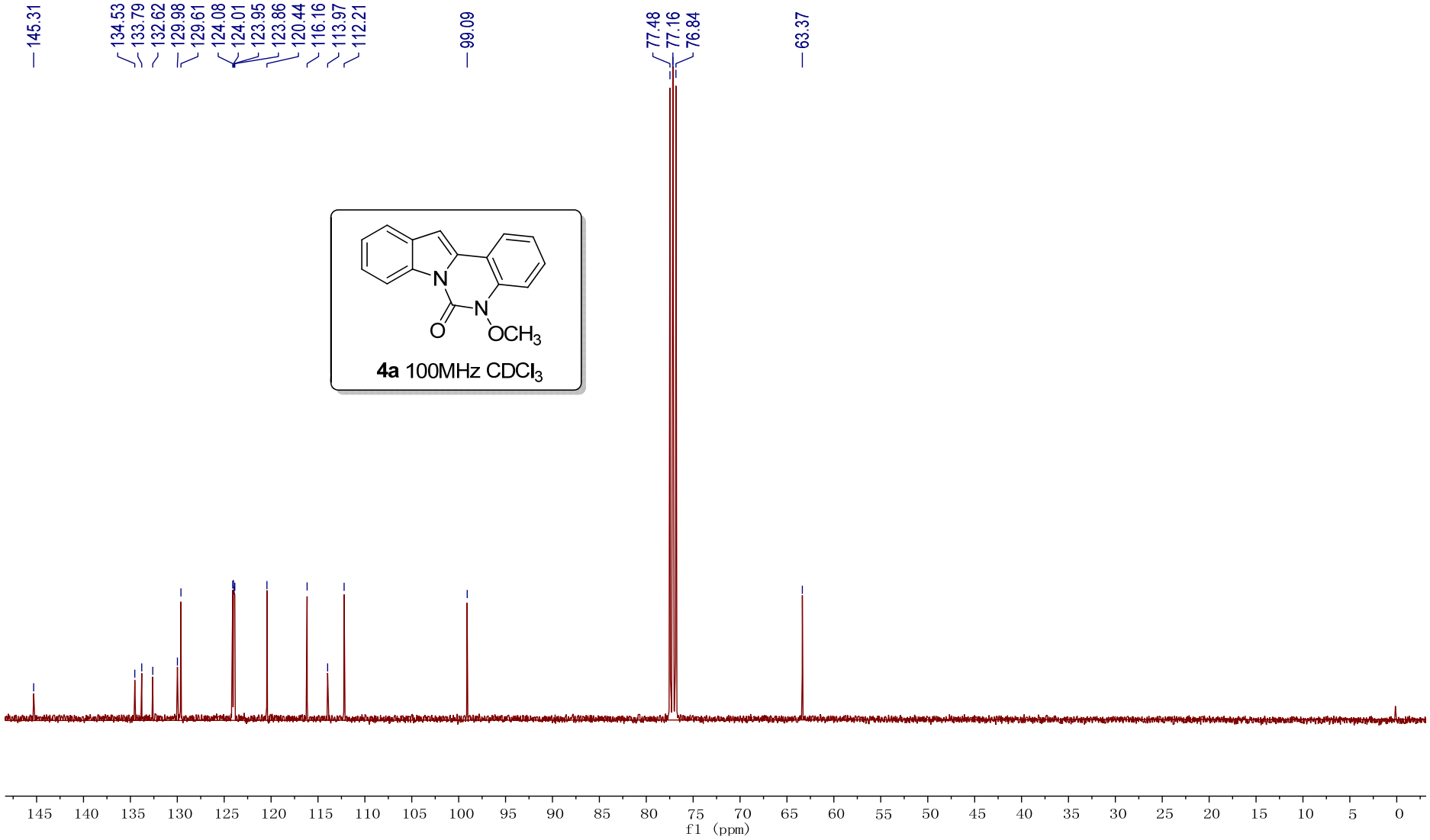

8.028
8.005
7.632
7.517
7.506
7.489
7.471
7.460
7.260
7.034
7.027
6.984
6.800
3.864
3.670
MeO
N
O
NHOMe
30 400MHz CDCl3
1.00
1.02
5.13
1.00
1.00
1.00
3.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

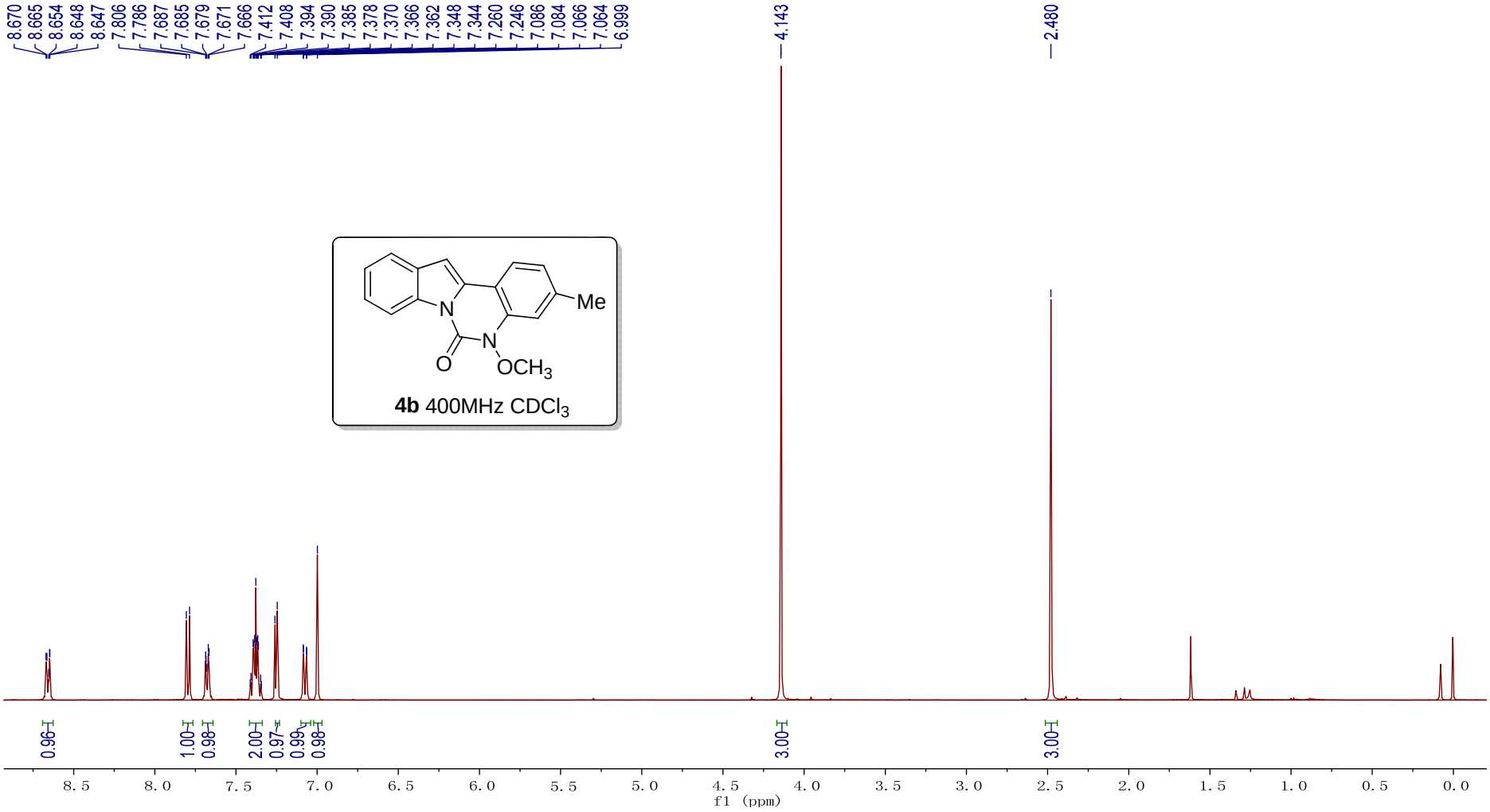

156.22
152.25
138.18
132.88
131.79
129.70
129.29
129.22
128.71
115.17
113.91
109.41
102.91
77.48
77.16
76.84
64.61
55.87
MeO
N
O
NHOMe
30 100MHz CDCl3
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

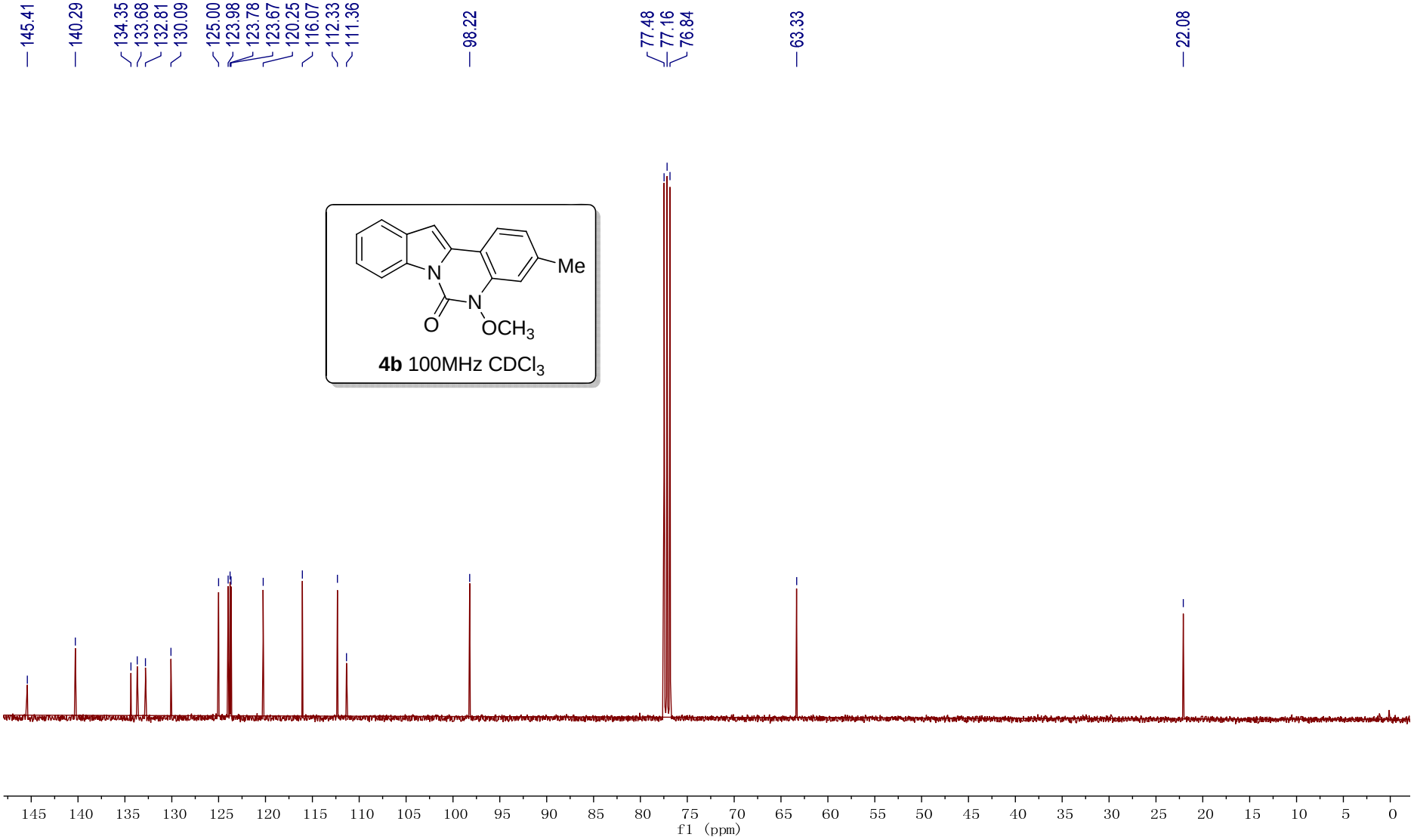

7.960
7.938
7.703
7.512
7.499
7.480
7.420
7.399
7.260
6.596
3.660
Br
N
O
NHOMe
3p 400MHz CDCl3
1.04
2.04
6.27
0.96
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

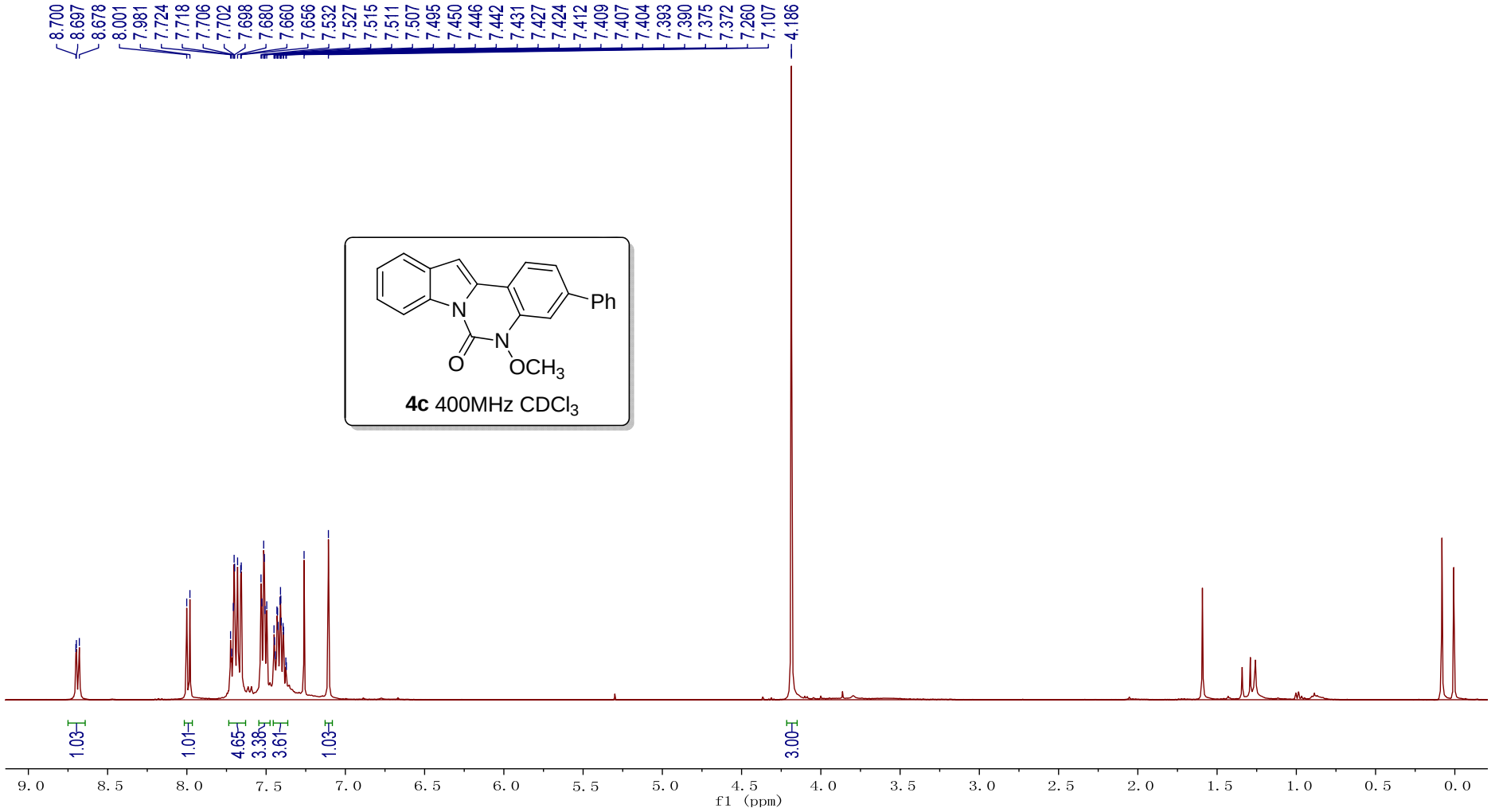

151.70
138.81
136.62
131.16
130.61
129.58
129.37
128.75
127.48
123.30
116.24
115.67
108.29
77.48
77.16
76.84
64.64
Br
N
O
NHOMe
3p 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

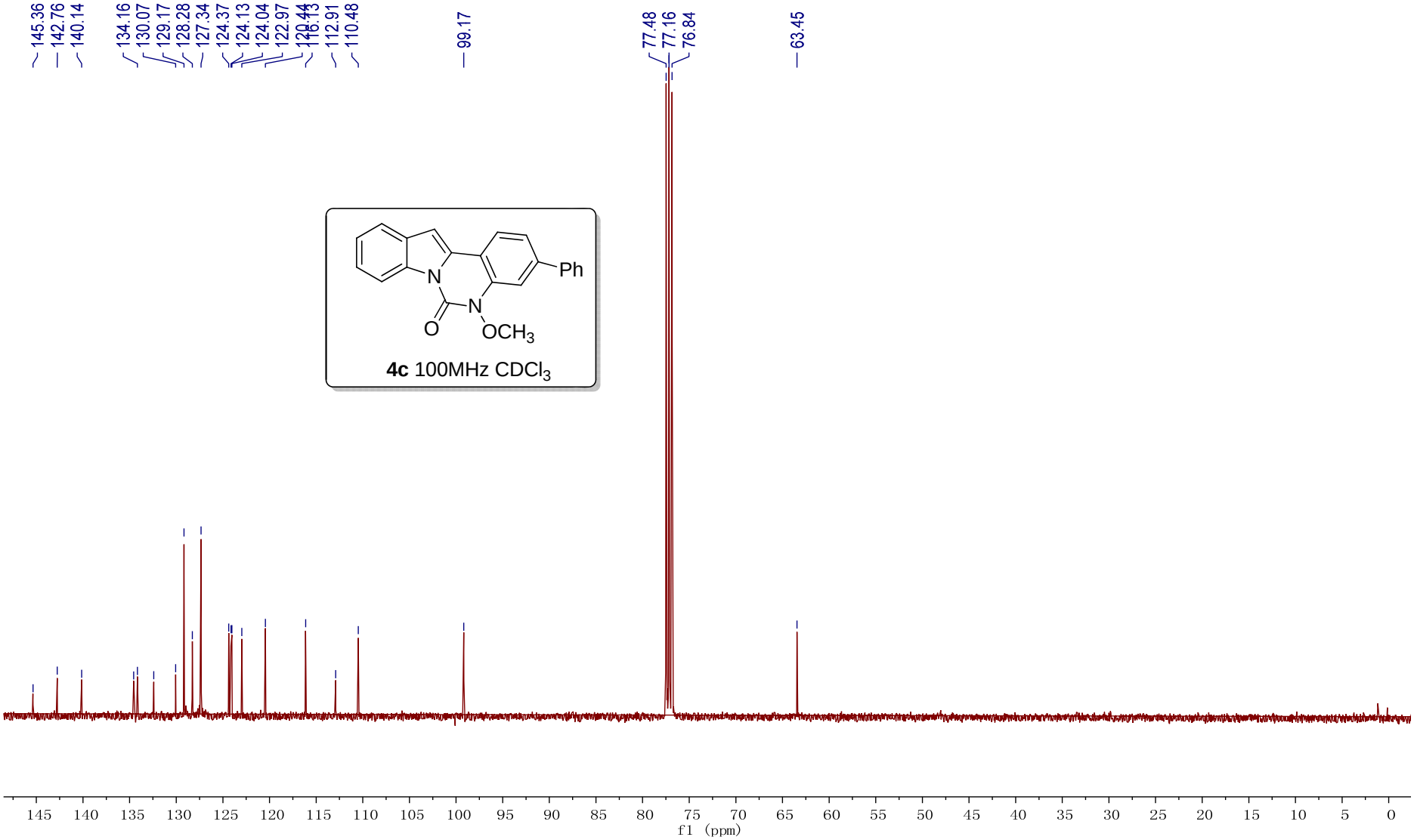

8.686
8.667
7.945
7.925
7.712
7.707
7.695
7.691
7.509
7.507
7.489
7.486
7.471
7.466
7.462
7.445
7.435
7.432
7.417
7.414
7.400
7.396
7.382
7.379
7.364
7.361
7.301
7.297
7.281
7.264
7.260
7.083
4.152
N
N
O
OCH3
4a 400MHz CDCl3
0.97
1.01
1.00
1.99
2.01
1.37
0.99
3.00
f1 (ppm)

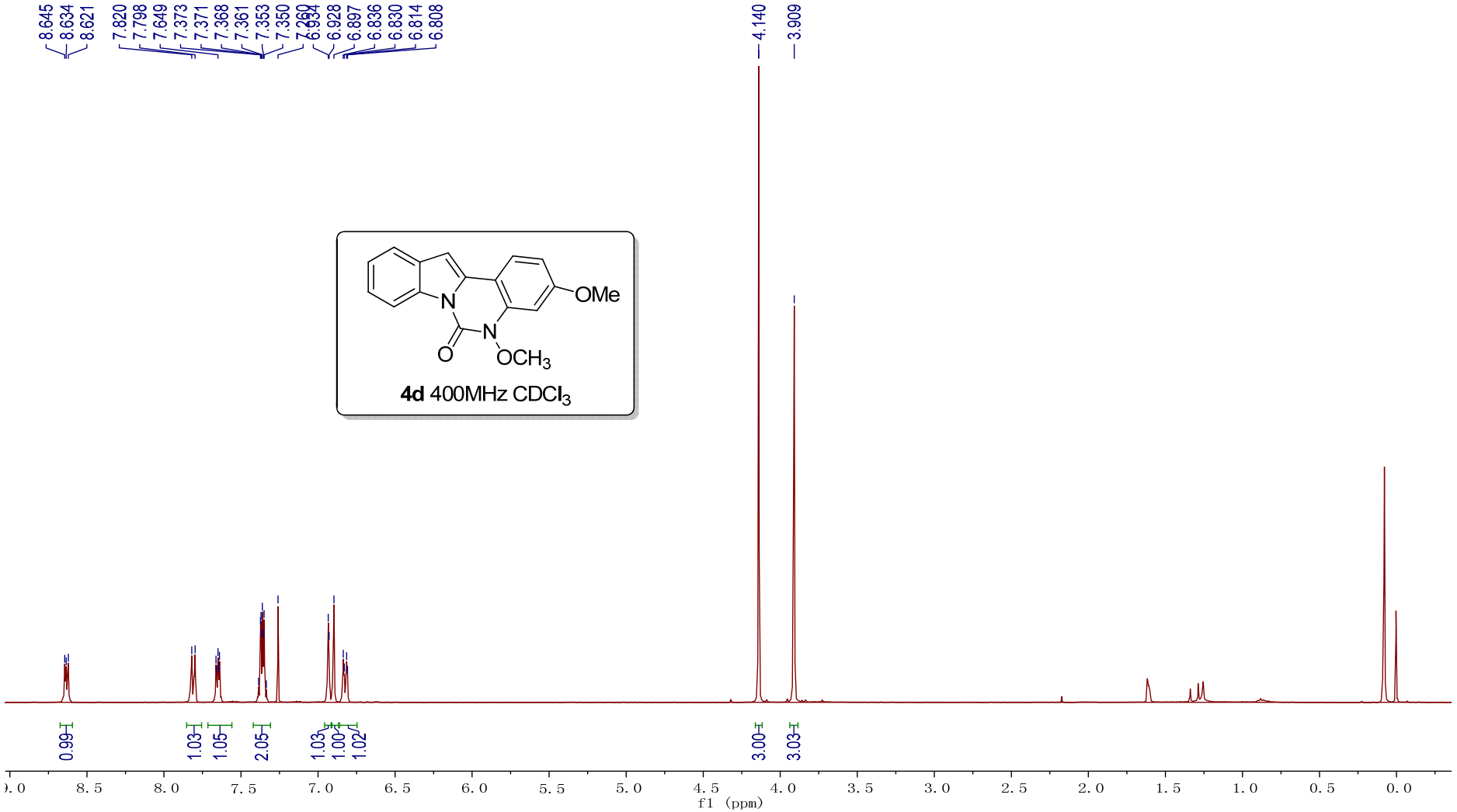

145.31
134.53
133.79
132.62
129.98
129.61
124.08
124.01
123.95
123.86
120.44
116.16
113.97
112.21
99.09
77.48
77.16
76.84
63.37
N
N
O
OCH3
4a 100MHz CDCl3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


8.670
8.665
8.654
8.648
8.647
7.806
7.786
7.687
7.685
7.679
7.671
7.666
7.412
7.408
7.394
7.390
7.385
7.378
7.370
7.366
7.362
7.348
7.344
7.260
7.246
7.086
7.084
7.066
7.064
6.999
4.143
2.480
Me
N
N
O
OCH3
4b 400MHz CDCl3
0.96
1.00
0.98
2.00
0.97
0.99
0.98
3.00
3.00
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)


145.41
140.29
134.35
133.68
132.81
130.09
125.00
123.98
123.78
123.67
120.25
116.07
112.33
111.36
98.22
77.48
77.16
76.84
63.33
22.08
Me
N
N
O
OCH3
4b 100MHz CDCl3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


8.700
8.697
8.678
8.001
7.981
7.724
7.718
7.706
7.702
7.698
7.680
7.660
7.656
7.532
7.527
7.515
7.511
7.507
7.495
7.450
7.446
7.442
7.431
7.427
7.424
7.412
7.409
7.407
7.404
7.393
7.390
7.375
7.372
7.260
7.107
4.186
Ph
N
N
O
OCH3
4c 400MHz CDCl3
1.03
1.01
4.65
3.38
3.61
1.03
3.00
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)


145.36
142.76
140.14
134.16
130.07
129.17
128.28
127.34
124.37
124.13
124.04
122.97
120.44
116.13
112.91
110.48
99.17
77.48
77.16
76.84
63.45
Ph
N
N
O
OCH3
4c 100MHz CDCl3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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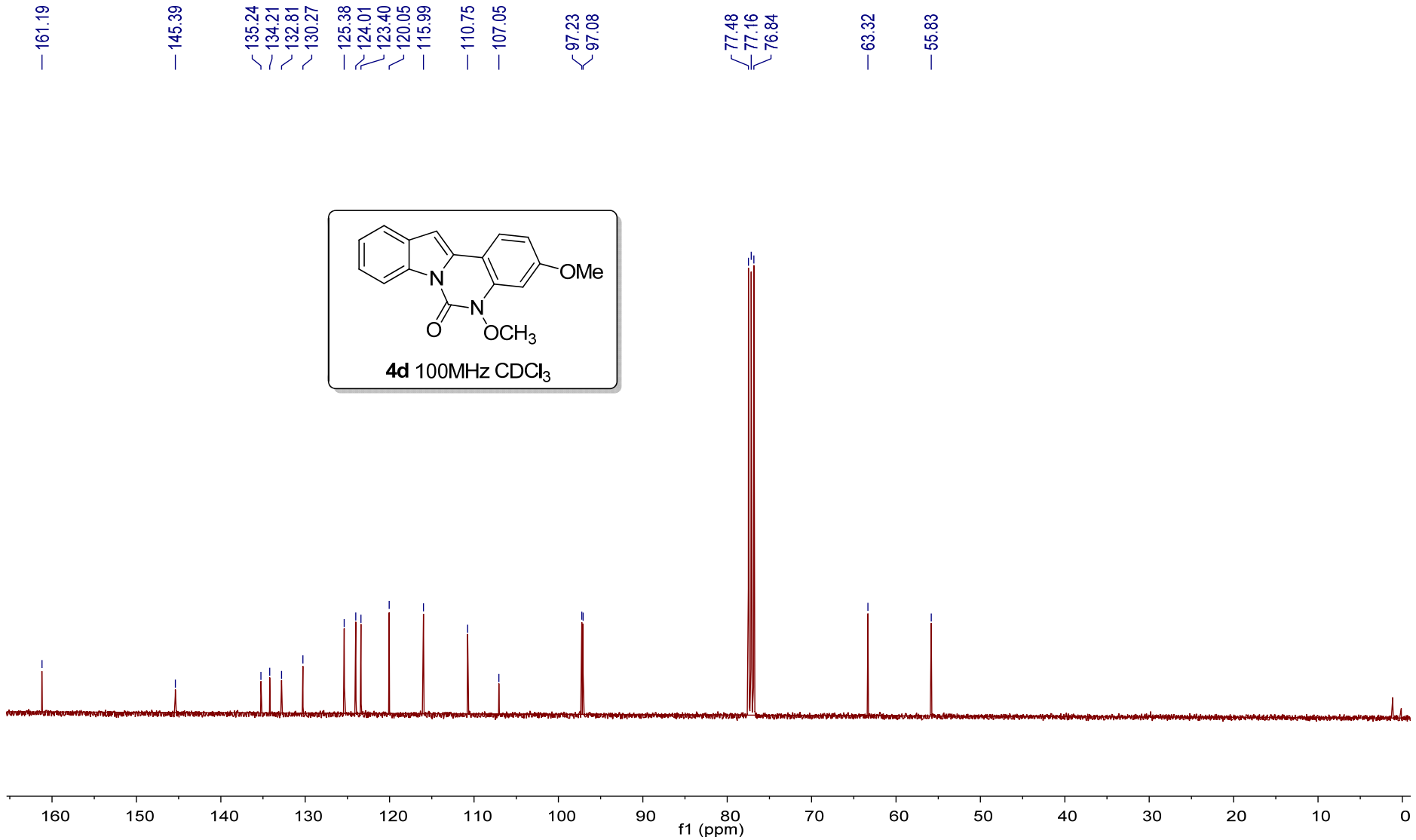
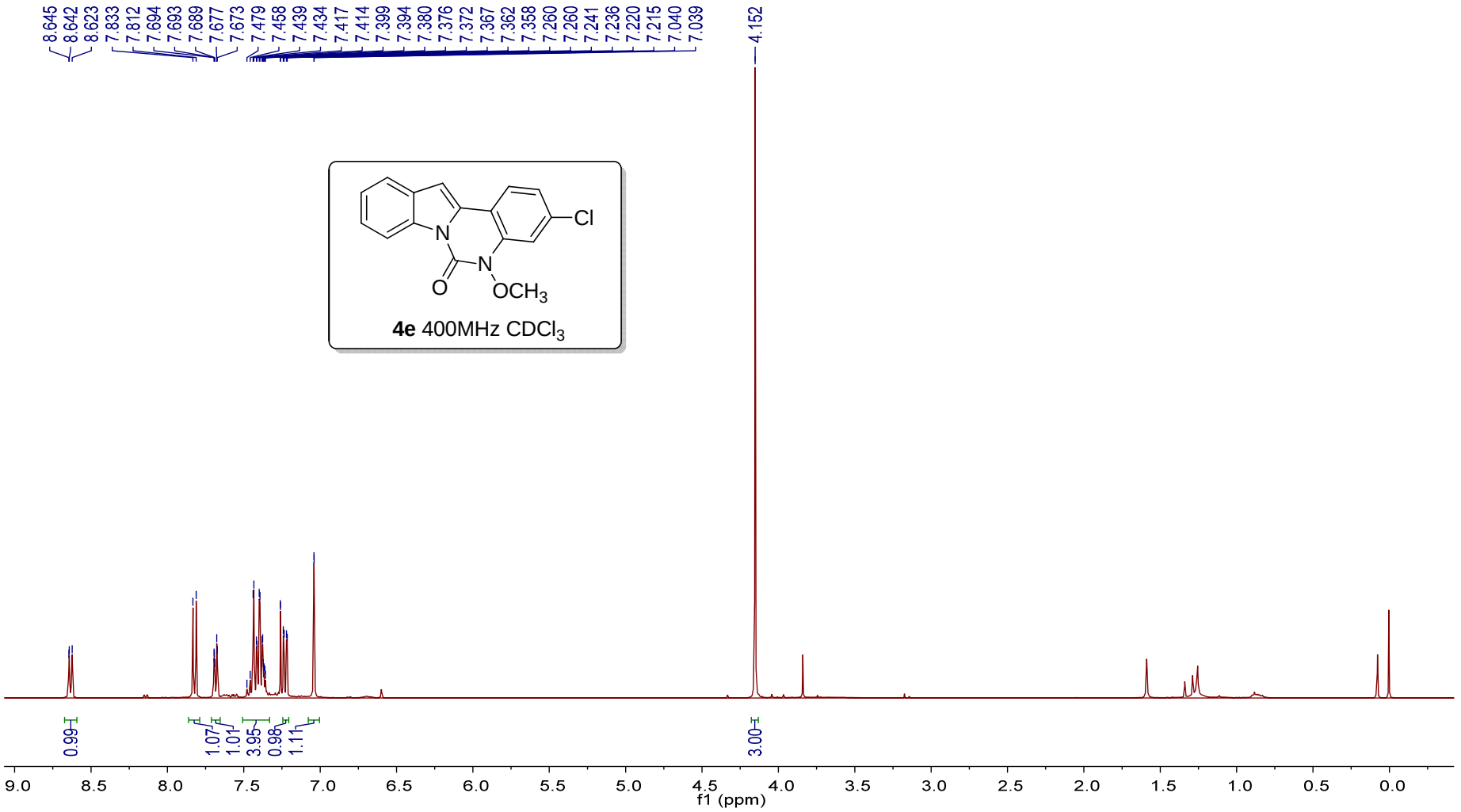
8.634
8.621
7.820
7.798
7.649
7.373
7.371
7.368
7.361
7.353
7.350
6.928
6.897
6.836
6.830
6.814
6.808
4.140
3.909
OMe
N
N
O
OCH3
4d 400MHz CDCl3
0.99
1.03
1.05
2.05
1.03
1.00
1.02
3.00
3.03
f1 (ppm)


161.19
145.39
135.24
134.21
132.81
130.27
125.38
124.01
123.40
120.05
115.99
110.75
107.05
97.23
97.08
77.48
77.16
76.84
63.32
55.83
OMe
N
N
O
OCH3
4d 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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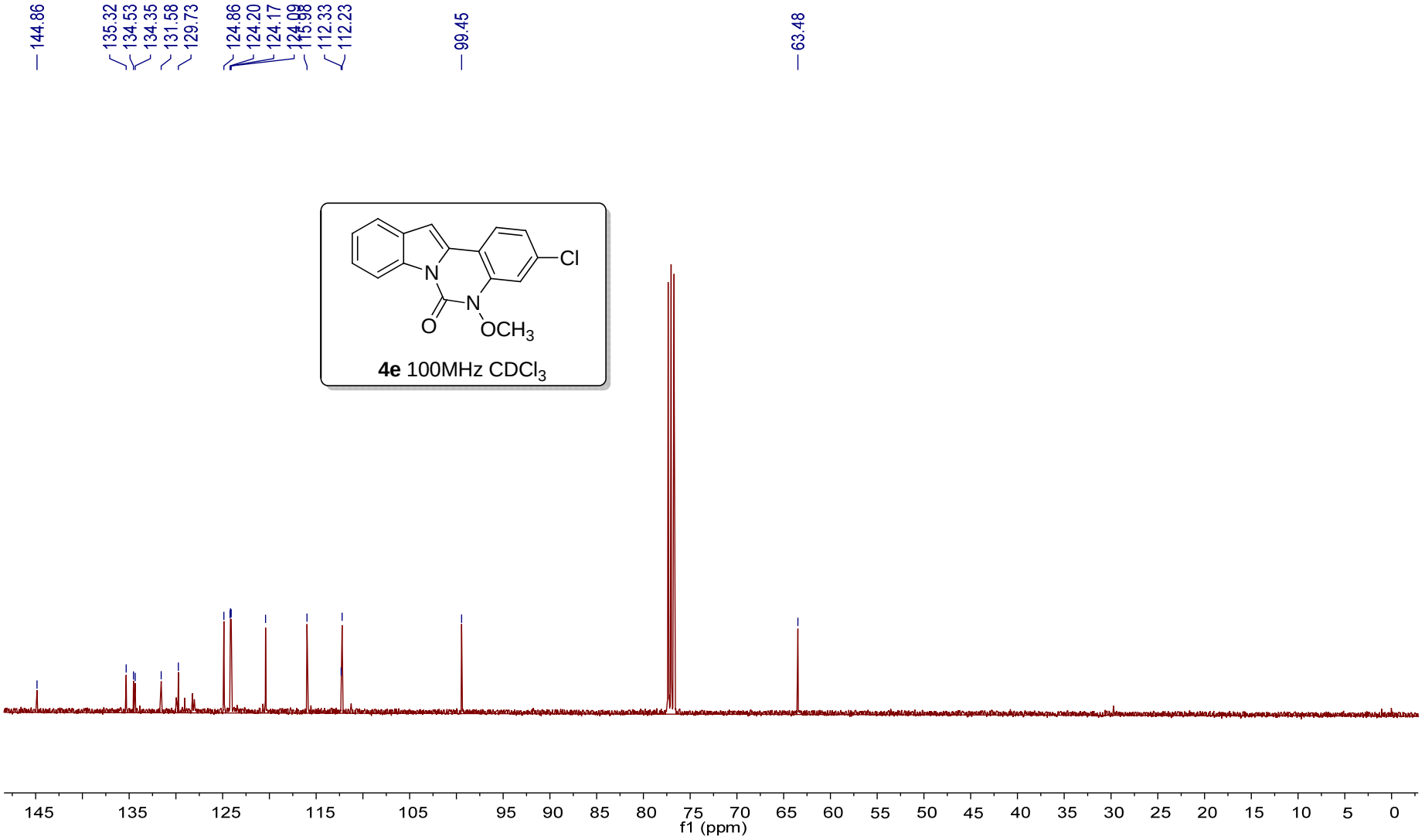
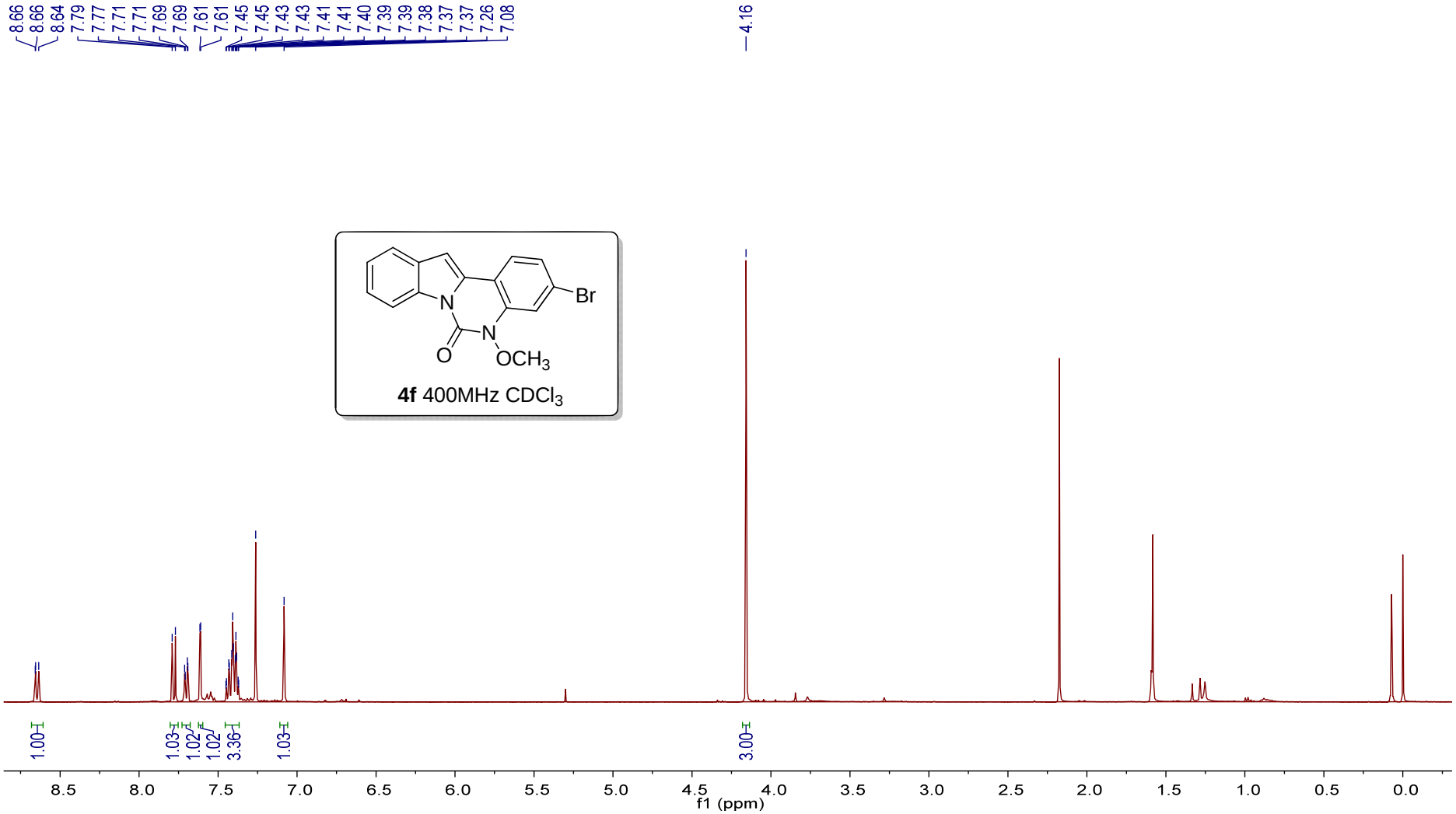
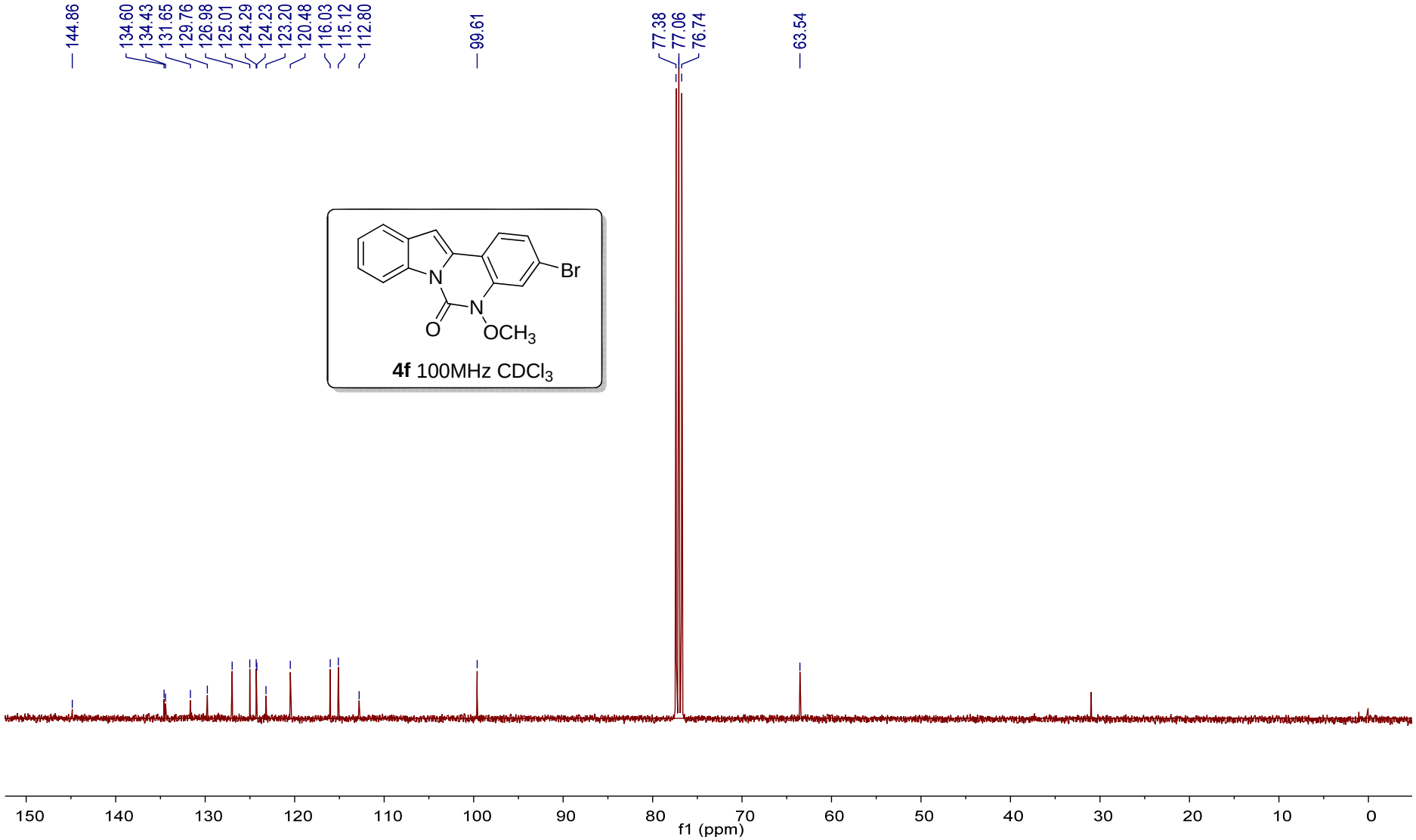
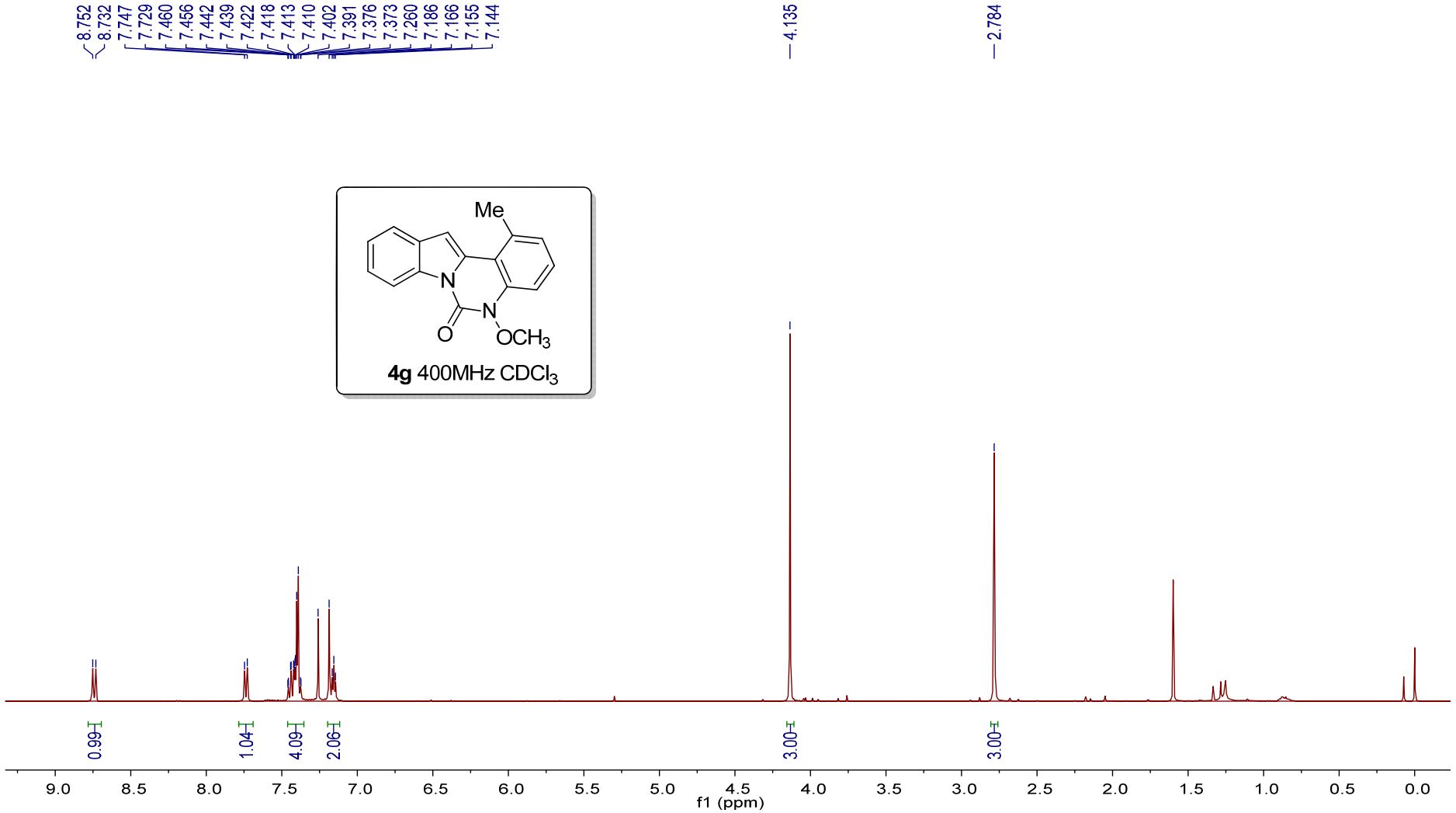
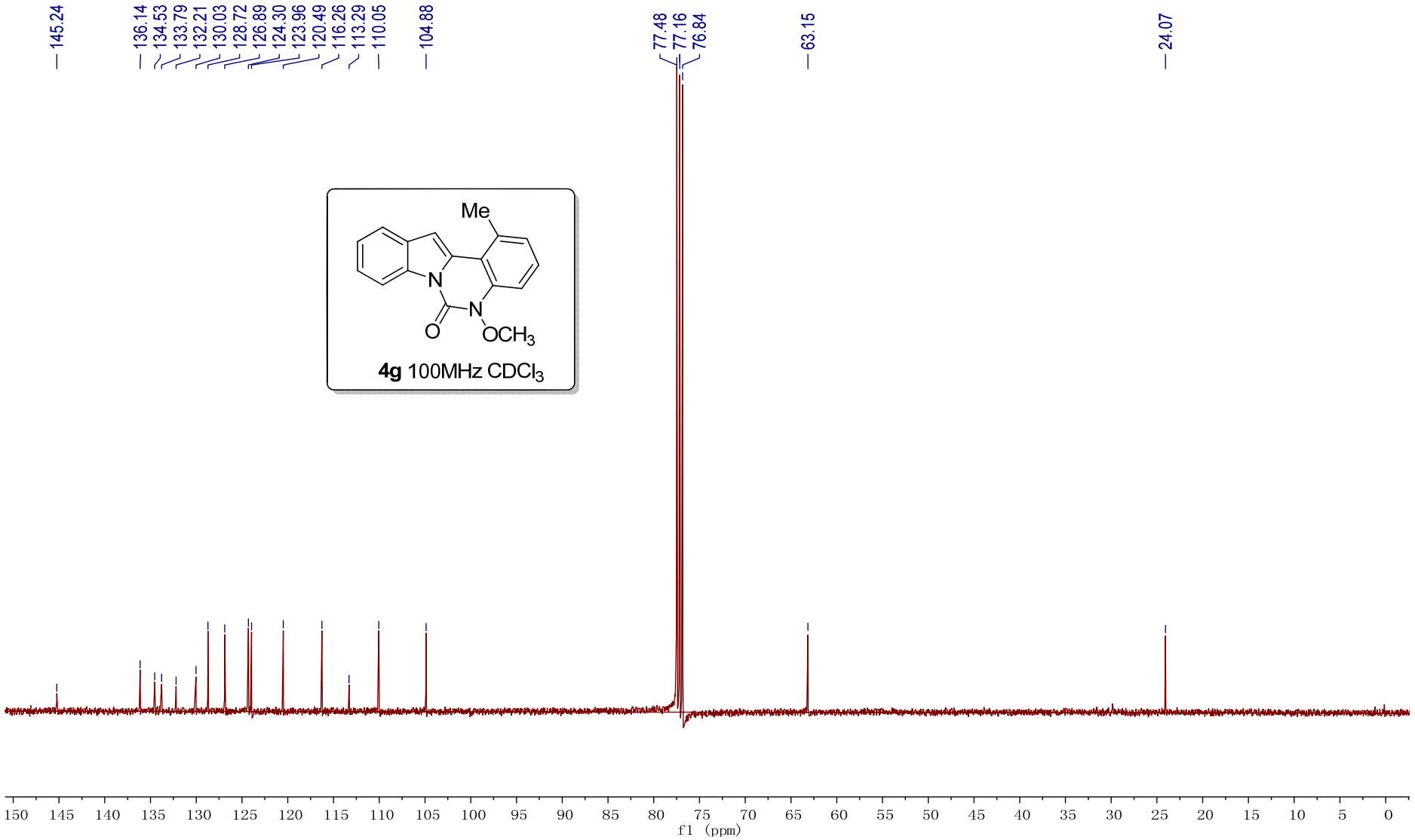
8.642
8.623
7.833
7.812
7.694
7.693
7.689
7.677
7.673
7.479
7.458
7.439
7.434
7.417
7.414
7.399
7.394
7.380
7.376
7.372
7.367
7.362
7.358
7.260
7.260
7.241
7.236
7.220
7.215
7.040
7.039
4.152
Cl
N
N
O
OCH3
4e 400MHz CDCl3
0.99
1.07
1.01
3.95
0.98
1.11
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.86
135.32
134.53
134.35
131.58
129.73
124.86
124.20
124.17
124.09
115.98
112.33
112.23
99.45
63.48
Cl
N
N
O
OCH3
4e 100MHz CDCl3
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


8.66
8.66
8.64
7.79
7.77
7.71
7.71
7.69
7.69
7.61
7.61
7.45
7.45
7.43
7.43
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.26
7.08
4.16
Br
N
N
O
OCH3
4f 400MHz CDCl3
1.00
1.03
1.02
1.02
3.36
1.03
3.00
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)


144.86
134.60
134.43
131.65
129.76
126.98
125.01
124.29
124.23
123.20
120.48
116.03
115.12
112.80
99.61
77.38
77.06
76.74
63.54
Br
N
N
O
OCH3
4f 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.752
8.732
7.747
7.729
7.460
7.456
7.442
7.439
7.422
7.418
7.413
7.410
7.402
7.391
7.376
7.373
7.260
7.186
7.166
7.155
7.144
4.135
2.784
Me
N
N
O
OCH3
4g 400MHz CDCl3
0.99
1.04
4.09
2.06
3.00
3.00
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)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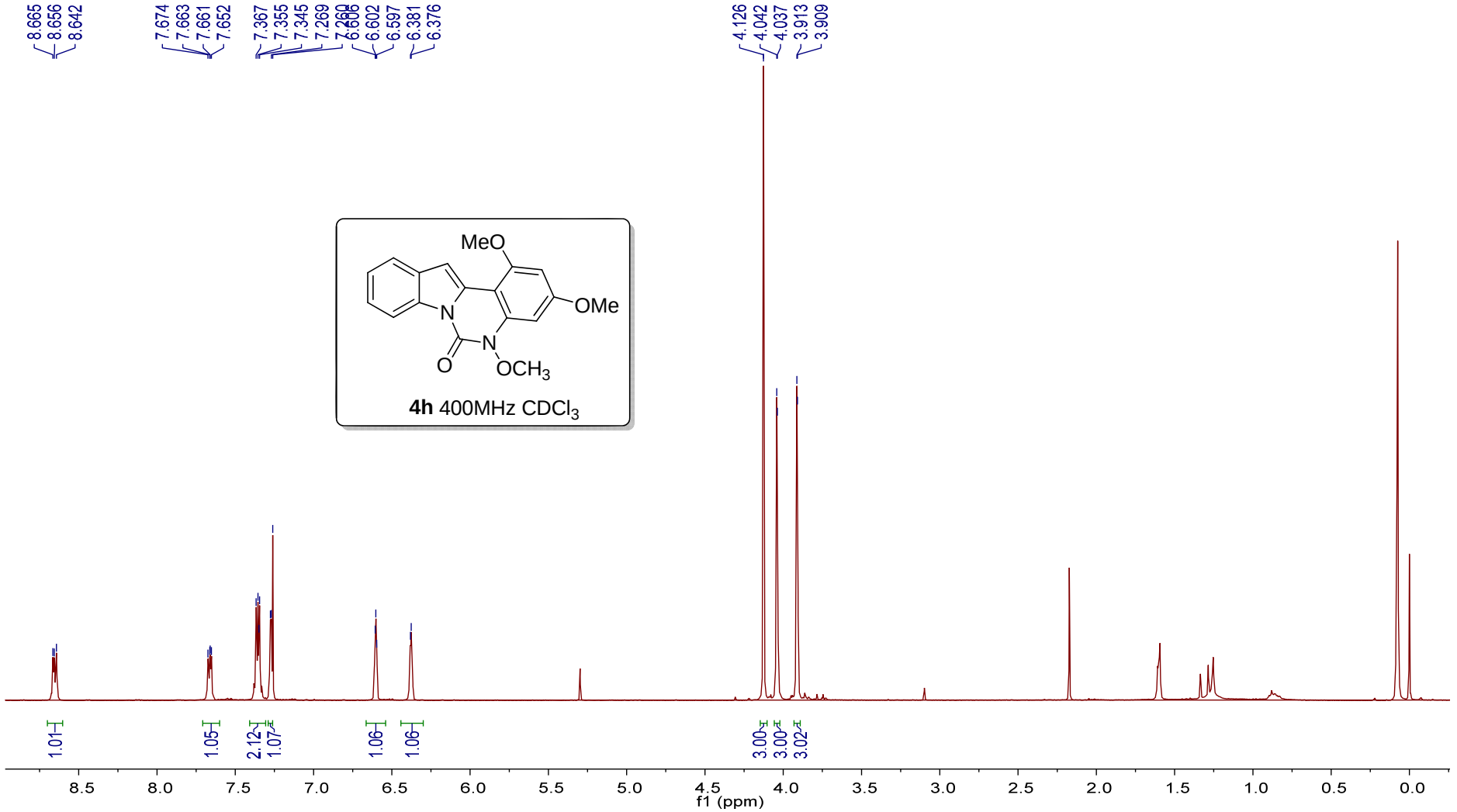
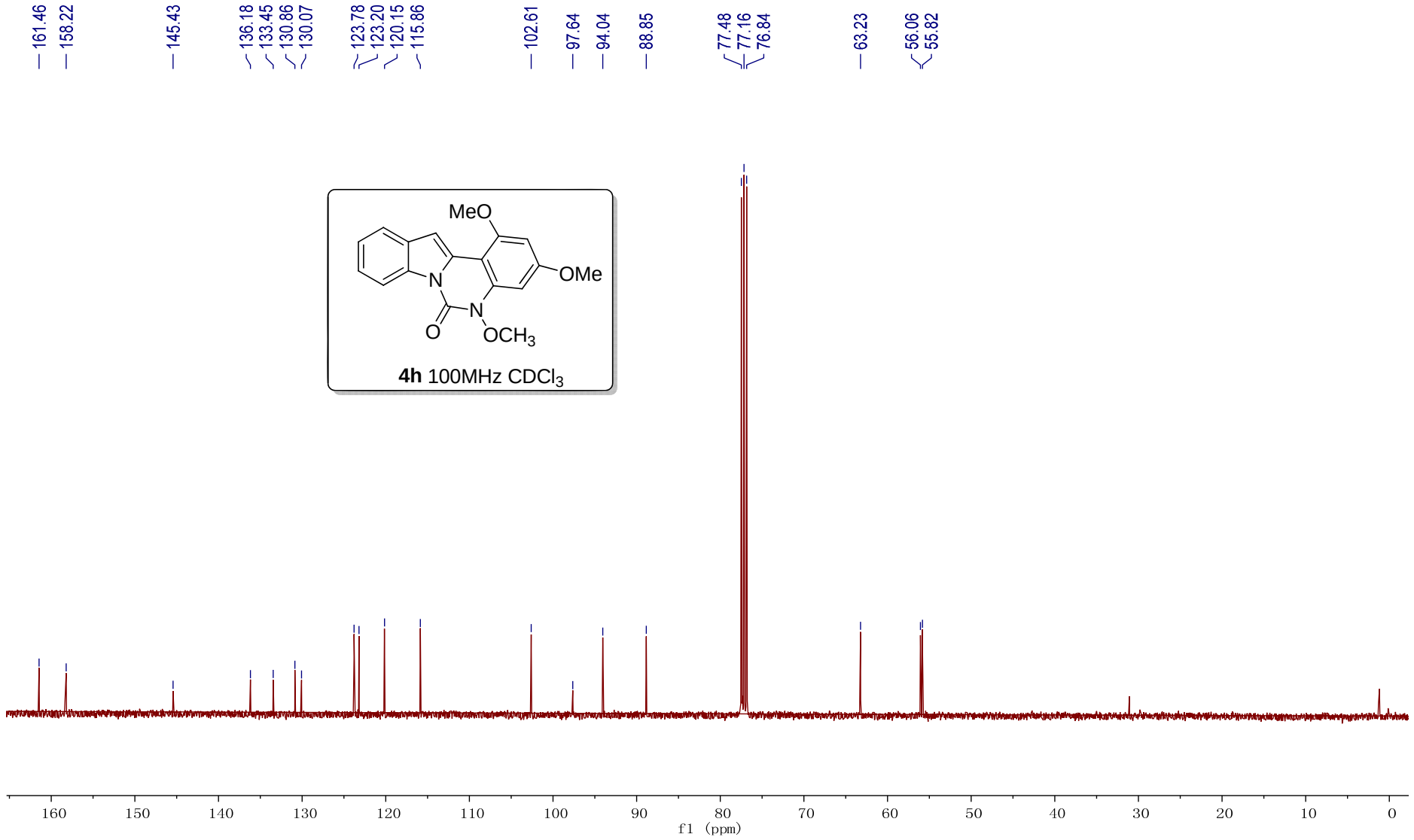
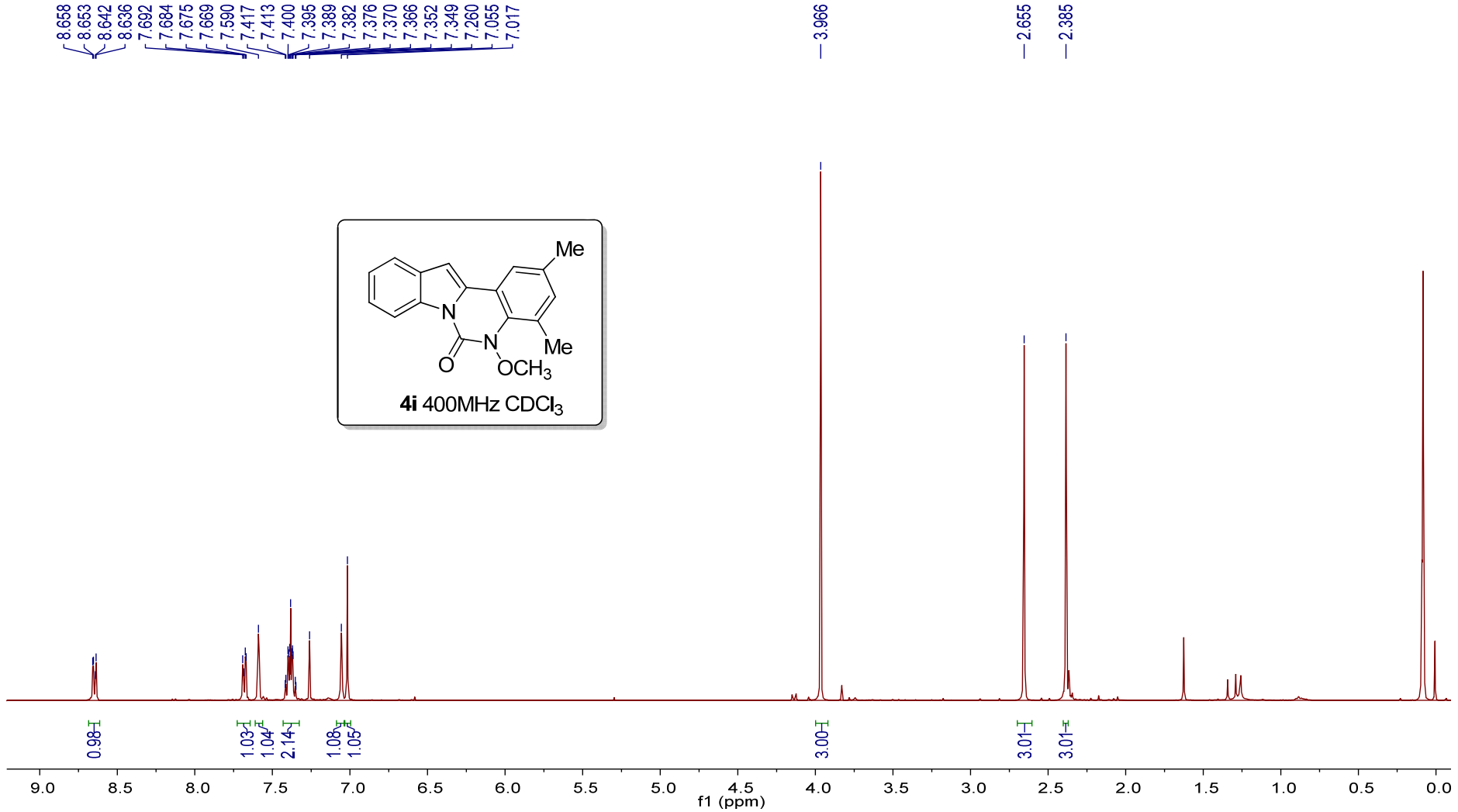
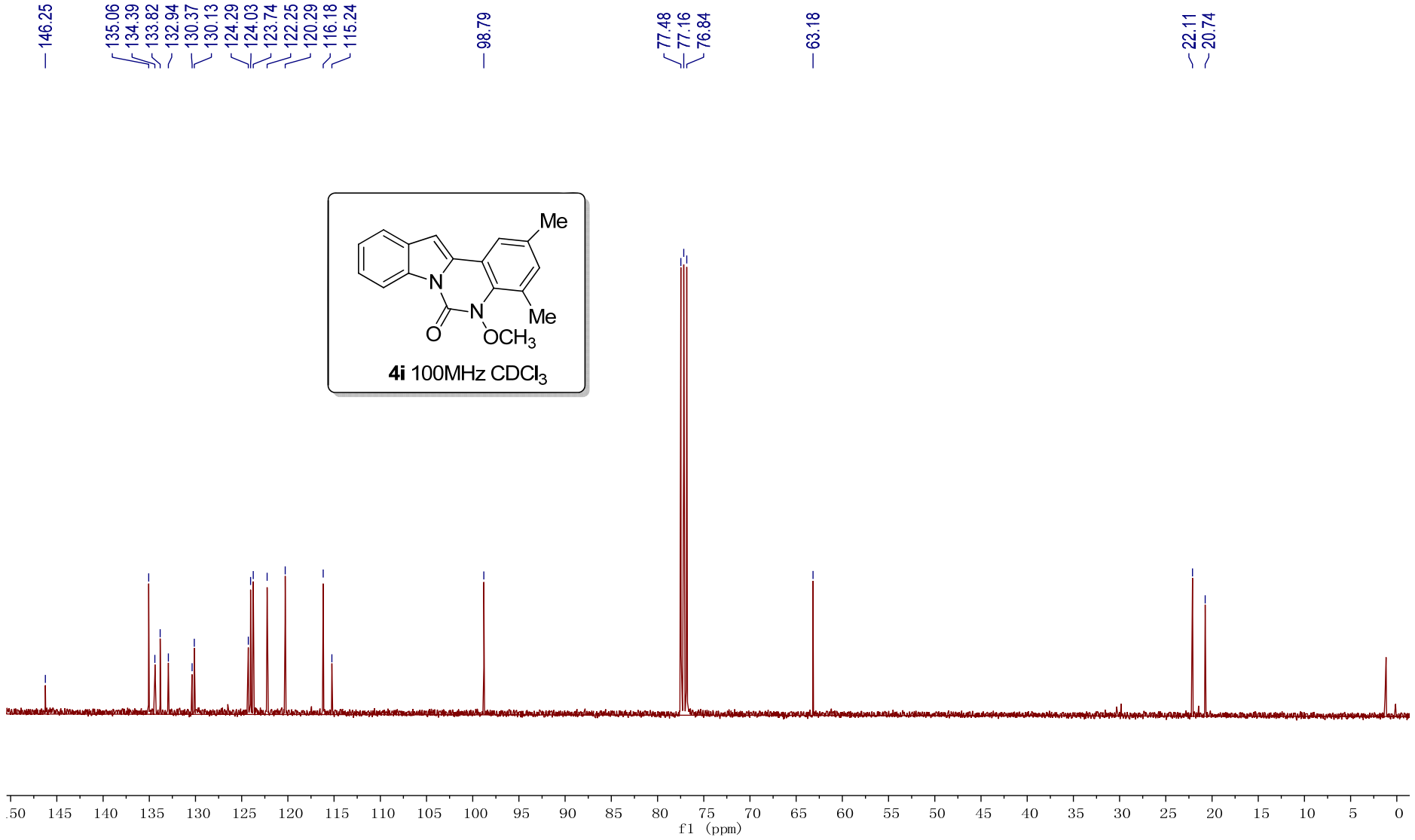
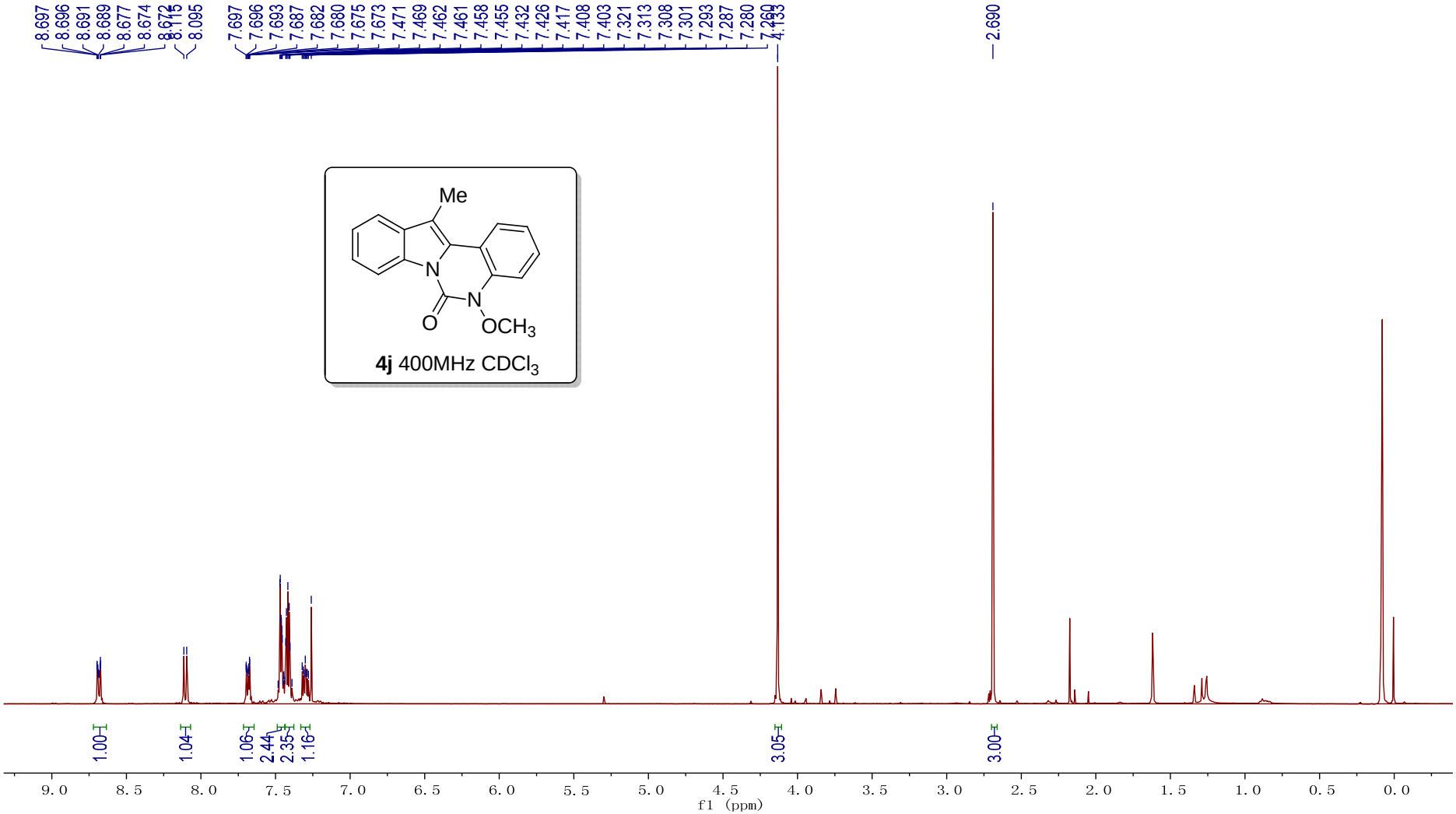
136.14
134.53
133.79
132.21
130.03
128.72
126.89
124.30
123.96
120.49
116.26
113.29
110.05
104.88
77.48
77.16
76.84
63.15
24.07
Me
N
N
O
OCH3
4g 100MHz CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

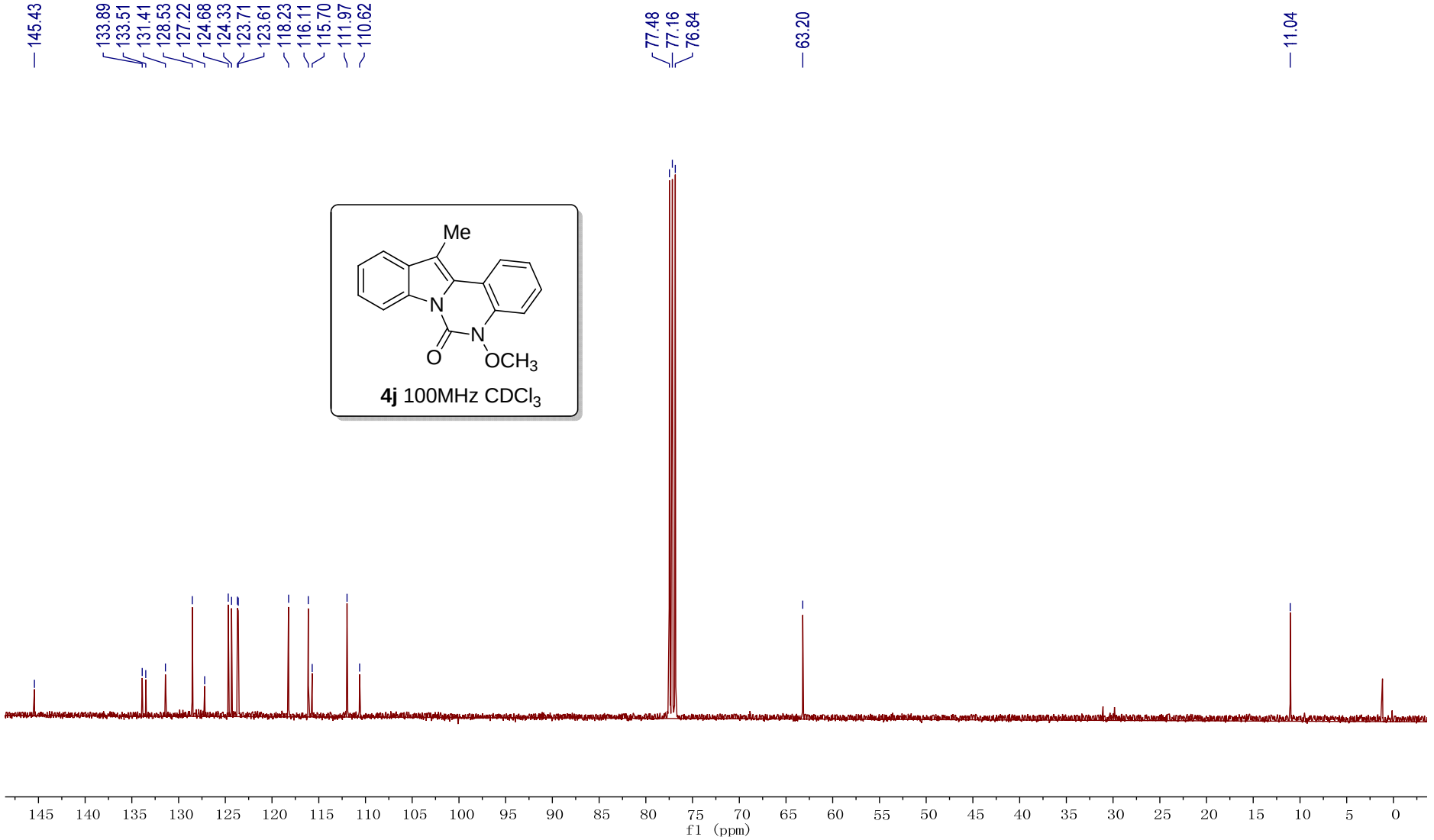

8.665
8.656
8.642
7.674
7.663
7.661
7.652
7.367
7.355
7.345
7.269
6.602
6.597
6.381
6.376
4.126
4.042
4.037
3.913
3.909
MeO
OMe
N
N
O
OCH3
4h 400MHz CDCl3
1.01
1.05
2.12
1.07
1.06
1.06
3.00
3.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

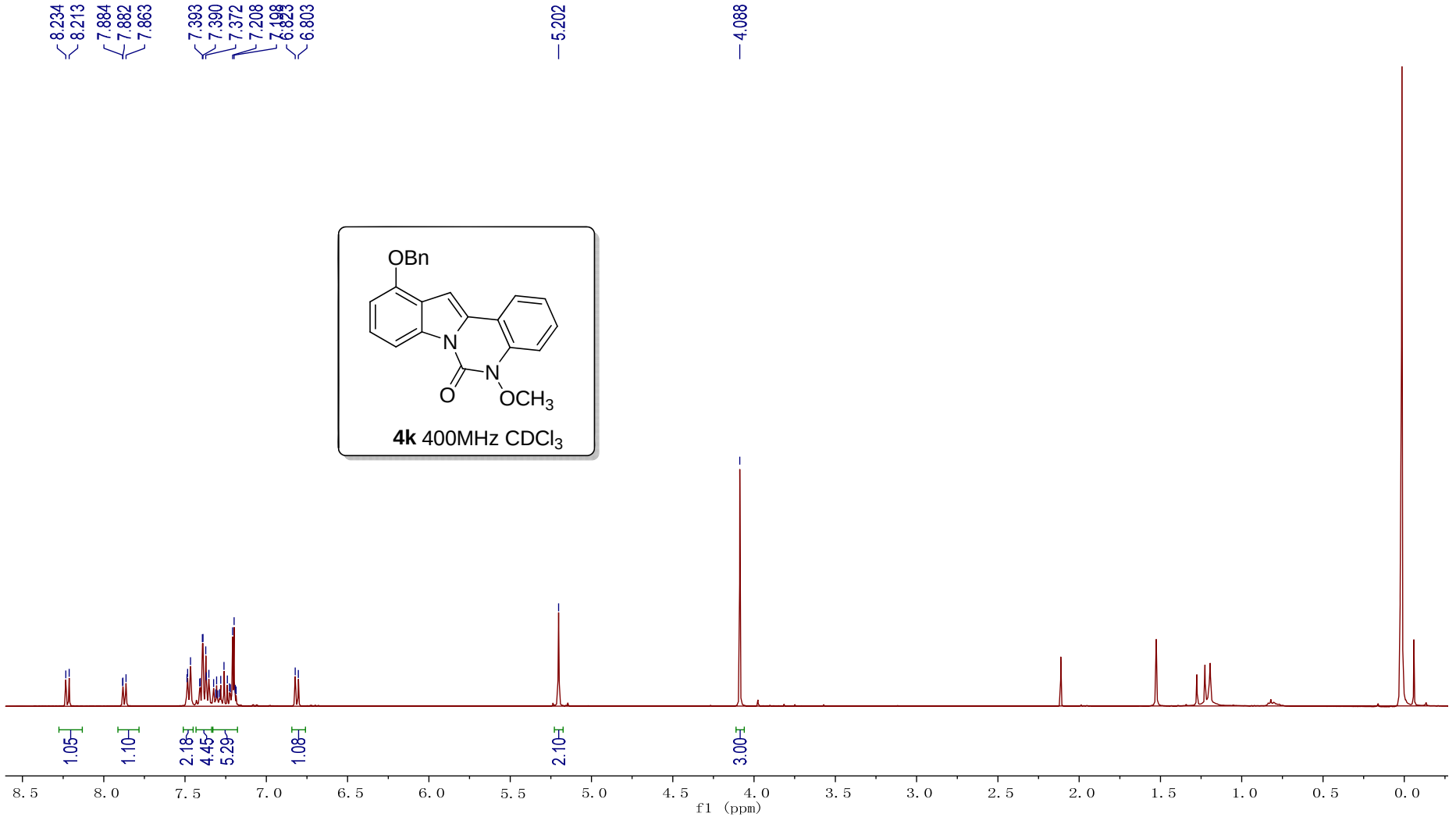

161.46
158.22
145.43
136.18
133.45
130.86
130.07
123.78
123.20
120.15
115.86
102.61
97.64
94.04
88.85
77.48
77.16
76.84
63.23
56.06
55.82
MeO
OMe
N
N
O
OCH3
4h 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

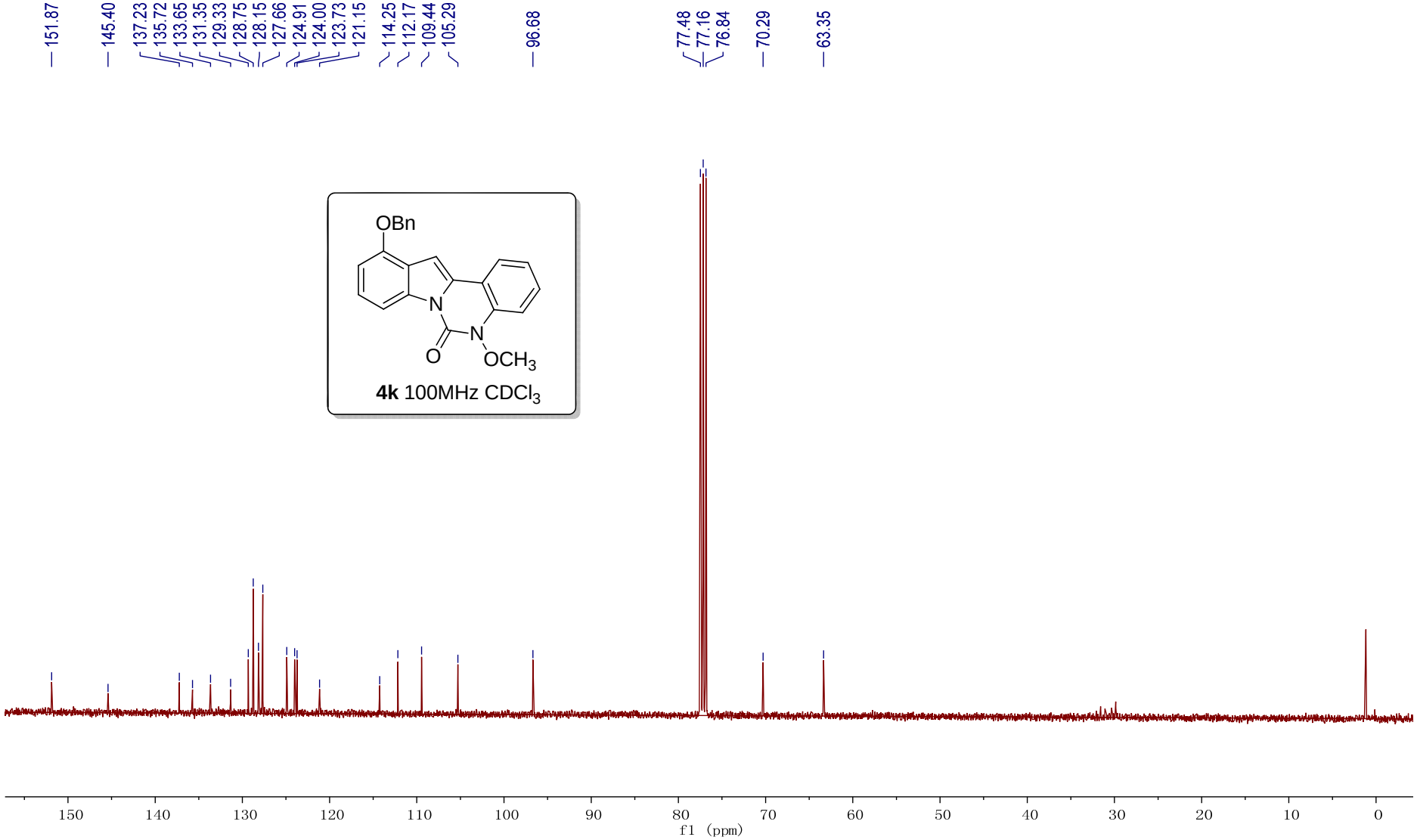

8.658
8.653
8.642
8.636
7.692
7.684
7.675
7.669
7.590
7.417
7.413
7.400
7.395
7.389
7.382
7.376
7.370
7.366
7.352
7.349
7.260
7.055
7.017
3.966
2.655
2.385
Me
N
N
Me
O
OCH3
4i 400MHz CDCl3
0.98
1.03
1.04
2.14
1.08
1.05
3.00
3.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

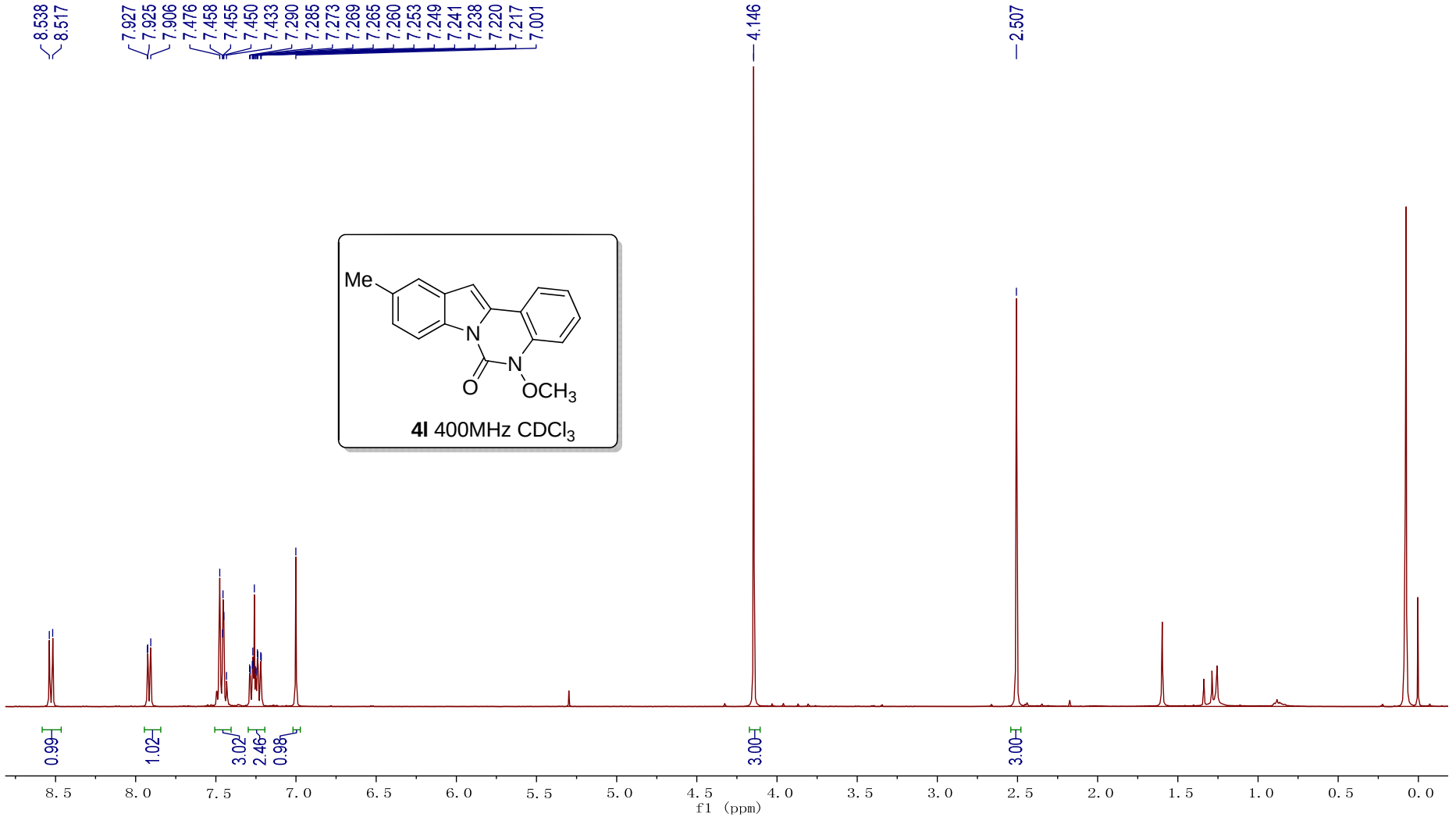

146.25
135.06
134.39
133.82
132.94
130.37
130.13
124.29
124.03
123.74
122.25
120.29
116.18
115.24
98.79
77.48
77.16
76.84
63.18
22.11
20.74
Me
N
N
Me
O
OCH3
4i 100MHz CDCl3
f1 (ppm)

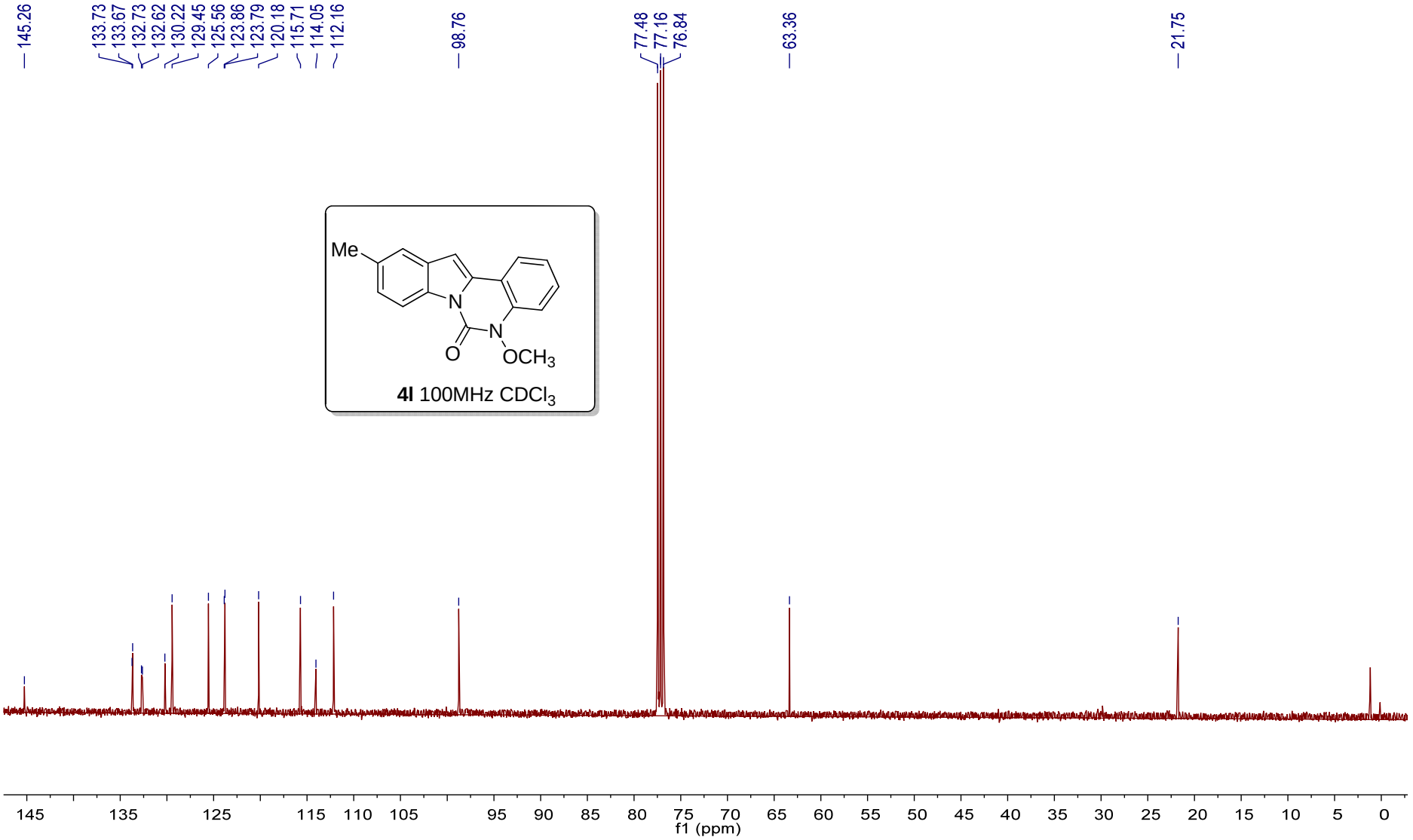

8.697
8.696
8.691
8.689
8.677
8.674
8.672
8.115
8.095
7.697
7.696
7.693
7.687
7.682
7.680
7.675
7.673
7.471
7.469
7.462
7.461
7.458
7.455
7.432
7.426
7.417
7.408
7.403
7.321
7.313
7.308
7.301
7.293
7.287
7.280
7.260
4.153
2.690
Me
N
N
O
OCH3
4j 400MHz CDCl3
1.00
1.04
1.06
2.44
2.35
1.16
3.05
3.00
9.0
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)

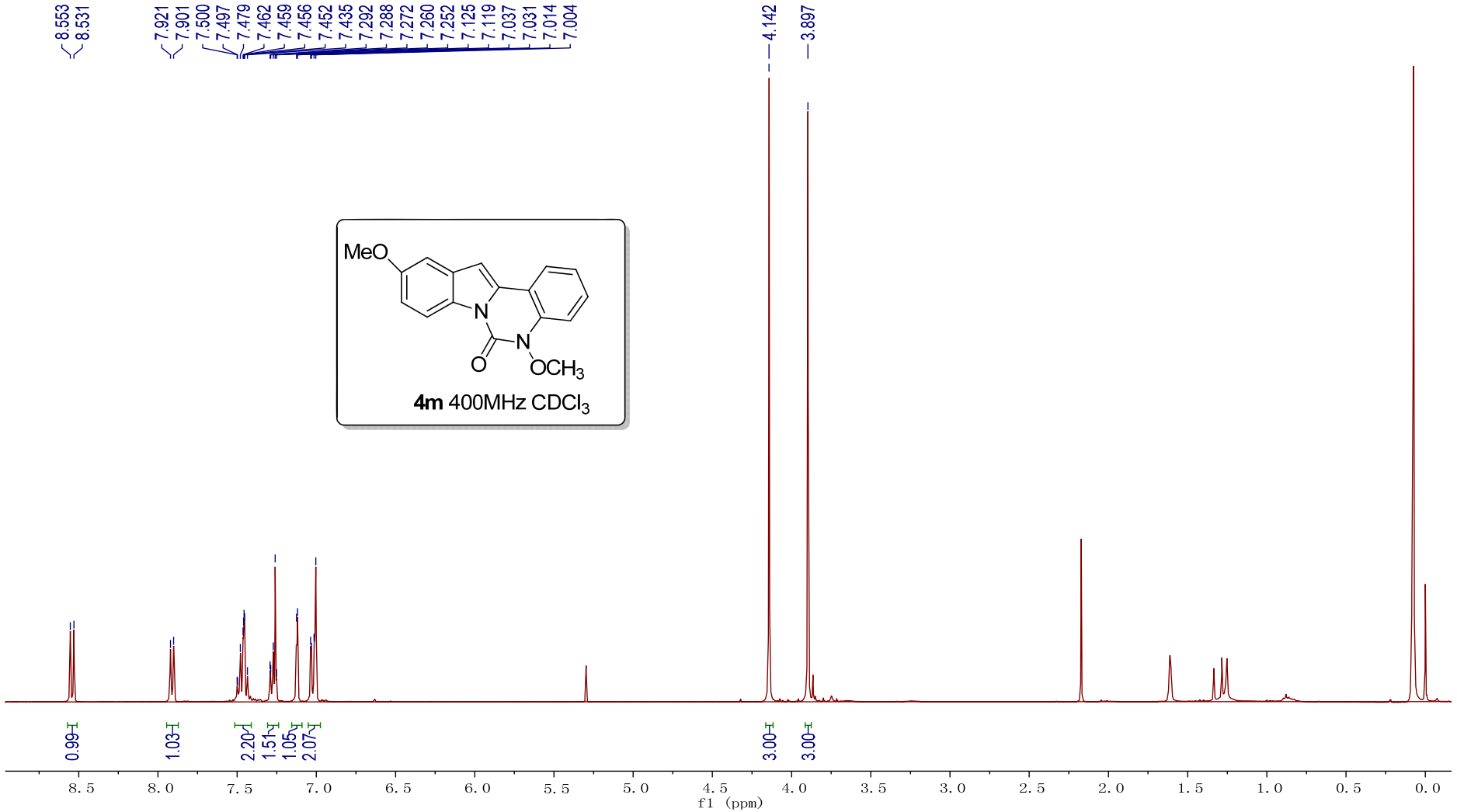

145.43
133.89
133.51
131.41
128.53
127.22
124.68
124.33
123.71
123.61
118.23
116.11
115.70
111.97
110.62
77.48
77.16
76.84
63.20
11.04
Me
N
N
O
OCH3
4j 100MHz CDCl3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

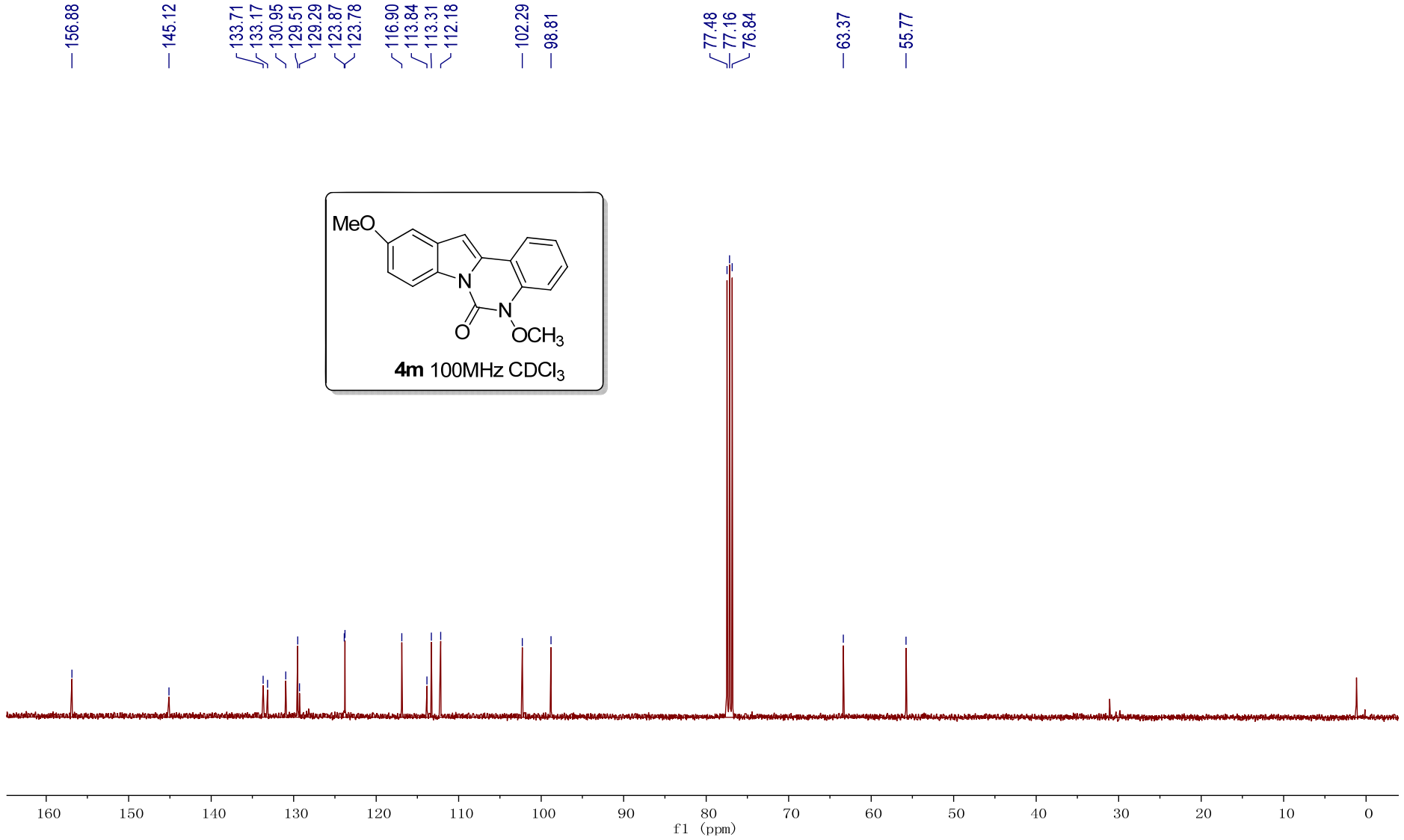

8.234
8.213
7.884
7.882
7.863
7.393
7.390
7.372
7.208
6.823
6.803
5.202
4.088
OBn
N
N
O
OCH3
4k 400MHz CDCl3
1.05
1.10
2.18
4.45
5.29
1.08
2.10
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

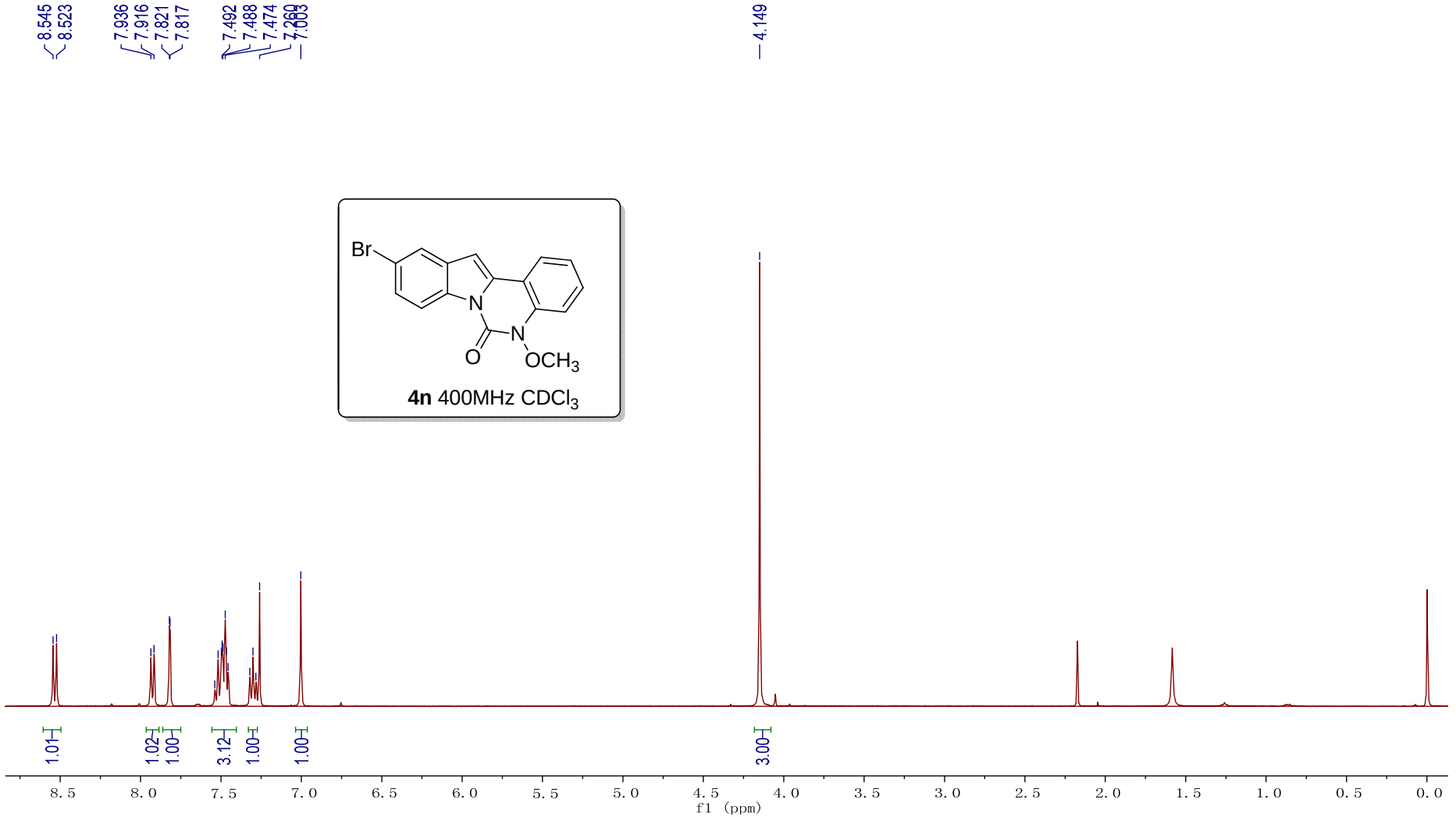

151.87
145.40
137.23
135.72
133.65
131.35
129.33
128.75
128.15
127.66
124.91
124.00
123.73
121.15
114.25
112.17
109.44
105.29
96.68
77.48
77.16
76.84
70.29
63.35
OBn
N
N
O
OCH3
4k 100MHz CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

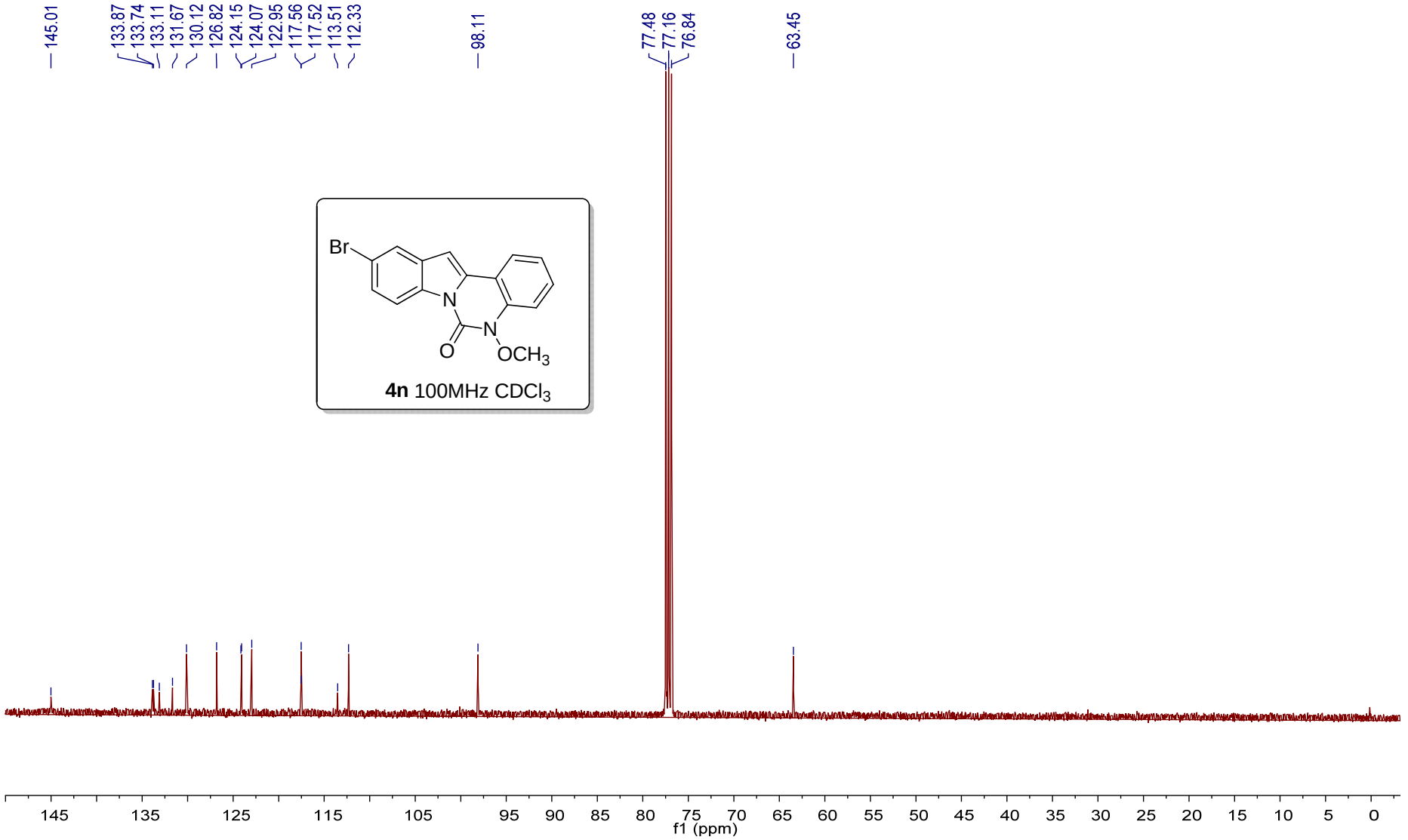

8.538
8.517
7.927
7.925
7.906
7.476
7.458
7.455
7.450
7.433
7.290
7.285
7.273
7.269
7.265
7.260
7.253
7.249
7.241
7.238
7.220
7.217
7.001
4.146
2.507
Me
N
N
O
OCH3
4l 400MHz CDCl3
0.99
1.02
3.02
2.46
0.98
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

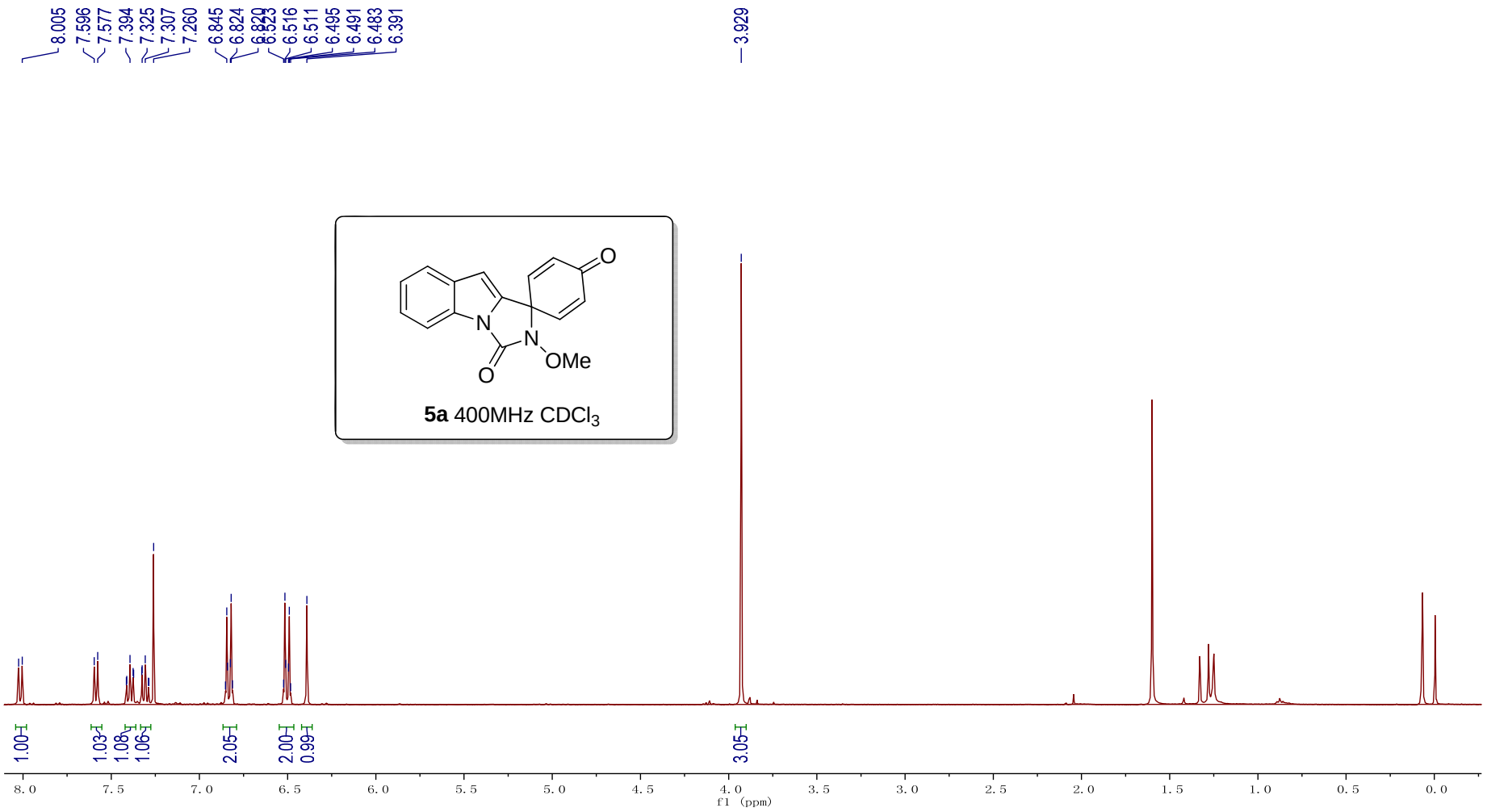

145.26
133.73
133.67
132.73
132.62
130.22
129.45
125.56
123.86
123.79
120.18
115.71
114.05
112.16
98.76
77.48
77.16
76.84
63.36
21.75
Me
N
N
O
OCH3
4l 100MHz CDCl3
145
135
125
115
110
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

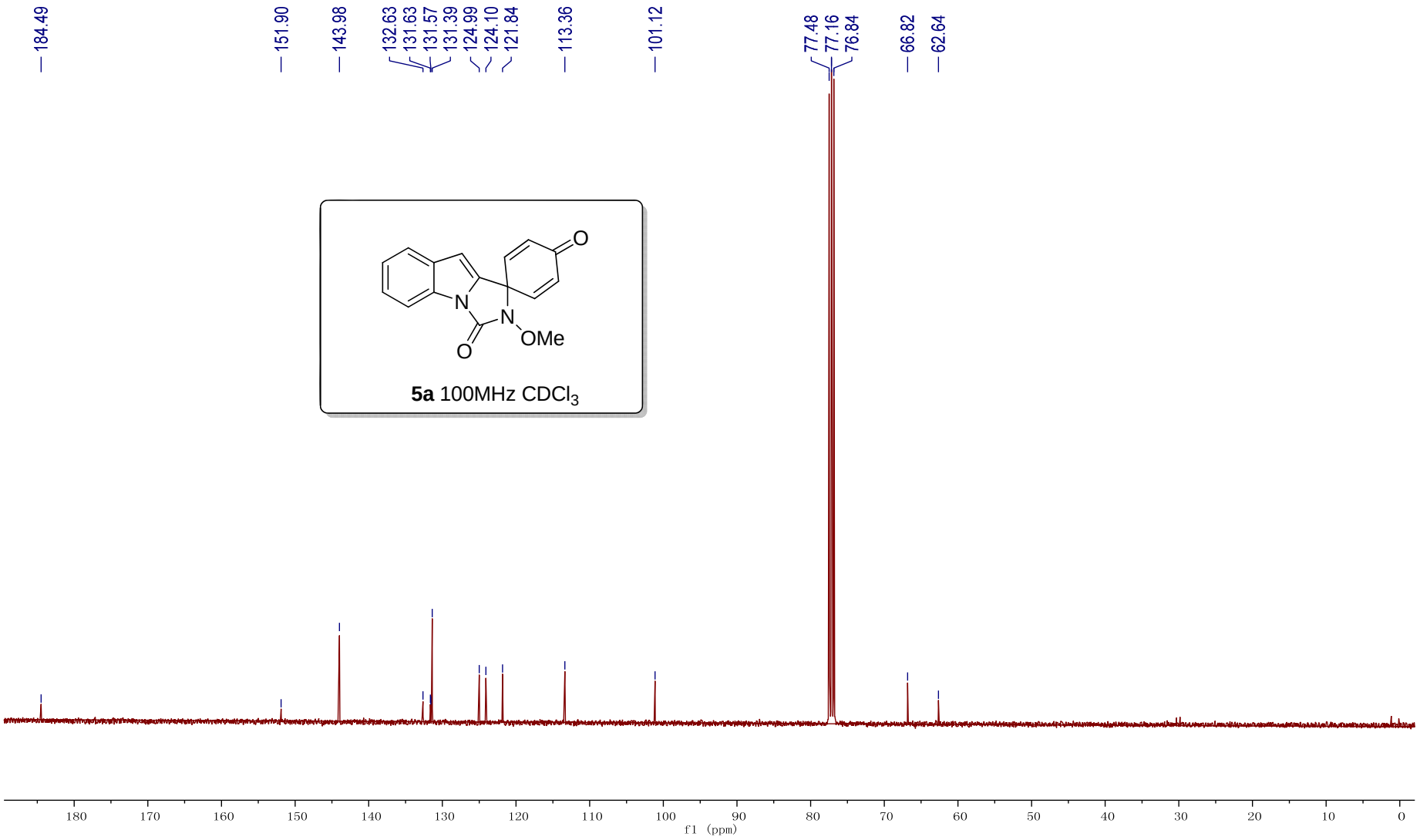

8.553
8.531
7.921
7.901
7.500
7.497
7.479
7.462
7.459
7.456
7.452
7.435
7.292
7.288
7.272
7.260
7.252
7.125
7.119
7.037
7.031
7.014
7.004
4.142
3.897
MeO
N
N
O
OCH3
4m 400MHz CDCl3
0.99
1.03
2.20
1.51
1.05
2.07
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.88
145.12
133.71
133.17
130.95
129.51
129.29
123.87
123.78
116.90
113.84
113.31
112.18
102.29
98.81
77.48
77.16
76.84
63.37
55.77
MeO
N
N
O
OCH3
4m 100MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.545
8.523
7.936
7.916
7.821
7.817
7.492
7.488
7.474
4.149
Br
N
N
O
OCH3
4n 400MHz CDCl3
1.01
1.02
1.00
3.12
1.00
1.00
3.00
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)


145.01
133.87
133.74
133.11
131.67
130.12
126.82
124.15
124.07
122.95
117.56
117.52
113.51
112.33
98.11
77.48
77.16
76.84
63.45
Br
N
N
O
OCH3
4n 100MHz CDCl3
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


8.005
7.596
7.577
7.394
7.325
7.307
7.260
6.845
6.824
6.516
6.511
6.495
6.491
6.483
6.391
3.929
O
N
N
OMe
O
5a 400MHz CDCl3
1.00
1.03
1.08
1.06
2.05
2.00
0.99
3.05
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)


184.49
151.90
143.98
132.63
131.63
131.57
131.39
124.99
124.10
121.84
113.36
101.12
77.48
77.16
76.84
66.82
62.64
O
N
N
OMe
O
5a 100MHz CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)