Supporting Information for

S_EAr-Based Reductive Arylation of Indoles with Ketones: Skeletal Metamorphosis of Ketones into Aryl Architectures

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I. General Remarks

Unless otherwise noted, manipulations were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance (NMR) spectra were taken on a JEOL JNM-ECA 400 [^{1}H (400 MHz); ^{13}C{^{1}H} (100 MHz)], a JEOL JNM-ECZ 400S [^{1}H (400 MHz); ^{13}C{^{1}H}, ^{13}C{^{19}F} (100 MHz)], or a JEOL JNM-ECA 500 [^{1}H (500 MHz); ^{13}C{^{1}H} (125 MHz); ^{11}B{^{1}H} (160 MHz); ^{19}F (471 MHz)] spectrometer using $SiMe_4$ (^{1}H and ^{13}C{^{1}H}, δ = 0.00) or $CFCl_3$ (^{19}F, δ = 0.00) as an internal standard, and BF_3•Et_2O (^{11}B{^{1}H}, δ = 0.00) as an external standard. Analytical gas chromatography (GC) was performed on a Shimadzu model GC-2014 instrument equipped with a capillary column of InertCap 5 (5% diphenyl- and 95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm) and with a FID detector, using nitrogen as carrier gas. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with a Shimadzu model GCMS-QP2010 SE instrument equipped with a capillary column of InertCap 5 by electron ionization at 70 eV using helium as carrier gas. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9105 equipped with JAIGEL-1H and JAIGEL-2H columns using chloroform as eluent. Preparative recycling high-performance liquid chromatography (HPLC) was performed with JAI LC-5060 equipped with JAIGEL-SH-043-15 column using *n*-hexane/ethyl acetate (EtOAc) as eluent. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-T100GCV spectrometer. Melting points were measured with a Yanaco Micro Melting Point apparatus and are uncorrected. 1,4-Dioxane was distilled from sodium under argon just prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon just prior to use. Propionitrile (EtCN) was distilled from P_2O_5 under argon just prior to use. Toluene (PhMe), dichloromethane (CH_2Cl_2), 1,2-dichloroethane (DCE), and chlorobenzene (PhCl) were distilled from $CaCl_2$ under argon just prior to use. Dibutyl

ether (Bu_2O), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), butyl acetate (BuOAc), 4-methyltetrahydropyrane (4-Me–THP), cyclopentyl methyl ether (CPME), butyl alcohol (BuOH), and nitromethane ($MeNO_2$) were stored over molecular sieves 4 Å (MS 4 Å) under argon. Pyridine was stored over KOH pellets under argon. Dehydrated *N*,*N*-dimethylformamide (DMF) (>99.5%, water: 0.001% max) was purchased from Kanto Chemical Co. Inc. and used as received. Dehydrated *N*,*N*-dimethylacetamide (DMA) (>99.0%, water: 0.005% max) was purchased from Kanto Chemical Co. Inc. and used as received. The following indium salts, indole substrates, and ketone substrates were synthesized according to the respective literature methods: $In(ONf)_3$ (Nf = $SO_2C_4F_9$),[1] $In(NTf_2)_3$ (Tf = SO_2CF_3),[2] 2-butyl-6-methoxy-1*H*-indole,[3] *N*,*N*-dimethyl-1*H*-indole-1-carboxamide (**1b**),[4] 1-(1-pyrrolidinylcarbonyl)-1*H*-Indole (**1d**),[5] 2-[4-(trifluoromethyl)phenyl]-1*H*-indole (**1m**),[6] 2-(4-cyanophenyl)-1*H*-indole (**1n**),[6] 2-isopropyl-1*H*-indole (**1o**),[7] 1-methyl-1*H*-indole-2-carboxylic acid ethyl ester (**1y**),[8] 7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'a**),[9] 5-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'b**),[10] 5-chloro-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'c**),[9] 5-phenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'e**),[9] 5-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'f**),[9] 6-chloro-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2'g**),[11] and *n*-$C_6H_{13}C{\equiv}CB(dan)$.[12] Unless otherwise noted, other substrates and reagents were commercially available and used as received without further purification.

Herein, only ^1H NMR data are provided for known compounds in which not only ^1H and ^{13}C NMR data but also elemental analysis or HRMS data have already been reported in the literature. Regarding new compounds, ^1H and ^{13}C NMR data are provided along with HRMS data.

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[1] a) T. Tsuchimoto, H. Matsubayashi, M. Kaneko, Y. Nagase, T. Miyamura, E. Shirakawa, *J. Am. Chem. Soc*. **2008**, *130*, 15823–15835; b) S. Sekine, M. Kashiwa, M. Kawakami, T. Sonoda, A. Ono, T. Tsuchimoto, *ACS Omega* **2025**, *10*, 21510–21518.

[2] a) C. G. Frost, J. P. Hartley, D. Griffin, *Tetrahedron Lett*. **2002**, *43*, 4789–4791; b) M. Nakamura, K. Endo, E. Nakamura, *Adv. Synth. Catal*. **2005**, *347*, 1681–1686.

[3] J. L. Rutherford, M. P. Rainka, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 15168–15169.

[4] D. J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc.* **2010,** *132*, 6910–6911.

[5] B. Zhou, Y. Yang, S. Lin, Y. Li, *Adv. Synth. Catal*. **2013**, *355*, 360–364.

[6] W.-L. Chen, K. Li, W.-C. Liao, W.-F. Liang, P.-W. Qiu, C. Liang, G.-F. Su, D.-L. Mo, *Green Chem.* **2021**, *23*, 9610–9616.

[7] Z. Chen, C. Gu, O. Y. Yuen, C. M. So, *Chem. Sci.* **2022**, *13*, 4762–4769.

[8] W. Chen, K. Sana, Y. Jiang, E. V. S. Meyer, S. Lapp, M. R. Galinski, L. S. Liebeskind, *Organometallics* **2013**, *32*, 7594−7611.

[9] R. Tokunaga, T. Okusa, T. Tsuchimoto, *Adv. Synth. Catal.* **2023**, *365*, 1432–1441.

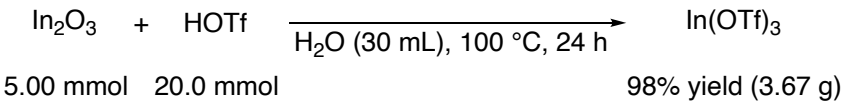
[10] J.-M. Durgnat, P. Vogel, *Helv. Chim. Acta* **1993**, *76*, 222–240.

[11] K. A. Black, P. Vogel, *J. Org. Chem.* **1986**, *51*, 5341–5348.

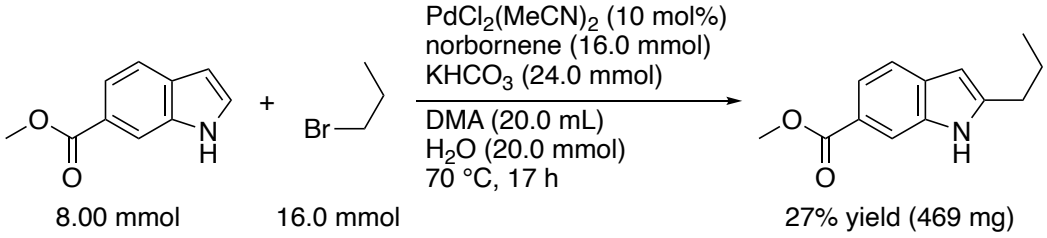
[12] T. Tsuchimoto, H. Utsugi, T. Sugiura, S. Horio, *Adv. Synth. Catal.* **2015**, *357*, 77–82. dan = 1,8-diaminonaphthyl.

Unless otherwise noted, signals of carbon atoms attached to boron atoms in $^{13}C\{^1H\}$ NMR spectra were not observed due to quadrupolar relaxation of boron.

II. Preparation of an Indium Salt, Indole Substrates, and Ketone Substrates



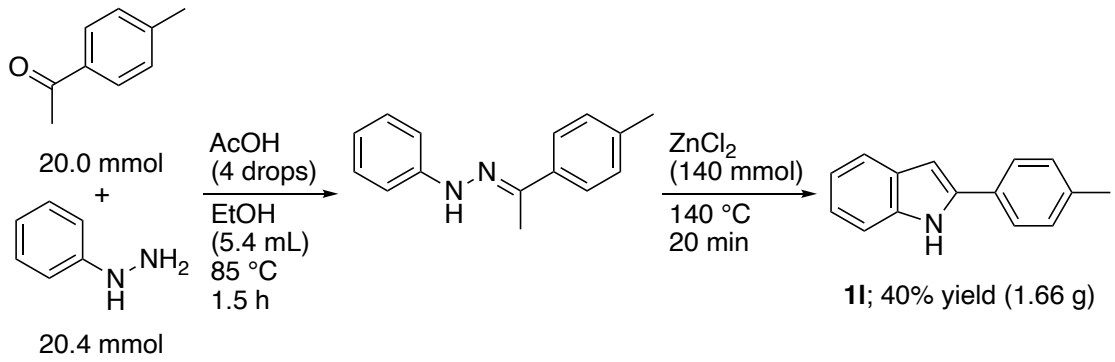
Preparation of Indium(III) Trifluoromethanesulfonate. The preparation of $In(OTf)_3$ was conducted with reference to the procedure reported in the literature.[1] In_2O_3 (1.39 g, 5.00 mmol) was placed in a 200 mL two-necked round-bottomed flask equipped with a reflux condenser. To this were added H_2O (30 mL) and HOTf (3.00 g, 20.0 mmol), and the resulting mixture was stirred at 100 °C for 24 h. Filtration through a pad of Celite to remove excess In_2O_3 and evaporation of H_2O gave hydrate of $In(OTf)_3$. The resulting hydrate was slowly warmed to 80 °C under vacuum (ca. 5 Pa), and the heating at 80 °C was continued for 7 h. After roughly breaking the solid in the flask into smaller pieces, the temperature was then slowly raised to 150 °C under vacuum (ca. 5 Pa), and the heating at 150 °C was continued for additional 8 h to provide $In(OTf)_3$ in 98% yield (3.67 g) as a white powder. $In(OTf)_3$ was characterized by $^{13}C\{^{19}F\}$ and ^{19}F NMR spectroscopy: $^{13}C\{^{19}F\}$ NMR (100 MHz, CD_3CN) δ 120.6, which was referenced to the *C*D_3 signal (1.32 ppm) of the solvent.[13]; ^{19}F NMR (471 MHz, CD_3CN) δ –77.7 (s, 9F).



Preparation of 2-Propyl-1*H*-indole-6-carboxylic Acid Methyl Ester. The indole substrate in the title was prepared according to following modified literature procedure.[14] Under an argon atmosphere, a 200 mL Schlenk tube was charged with 1*H*-indole-6-carboxylic acid methyl ester (1.40 g, 8.00 mmol), $KHCO_3$ (2.40 g, 24.0 mmol), $PdCl_2(MeCN)_2$ (208 mg, 0.800

[13] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.
[14] a) L. Jiao, T. Bach, *J. Am. Chem. Soc.* **2011**, *133*, 12990–12993; b) F. Xu, M. W. Smith, *Chem. Sci.* **2021**, *12*, 13756–13763.

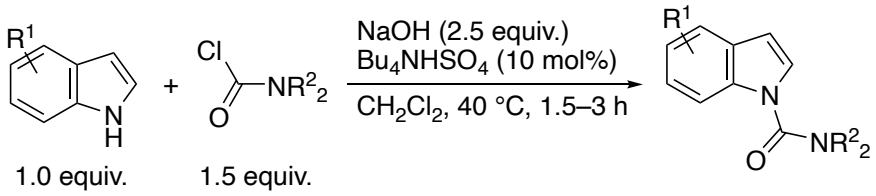
mmol), norbornene (1.51 g, 16.0 mmol), DMA (20.0 mL), and H_2O (360 mg, 20.0 mmol). The resulting mixture was degassed by three freeze-pump-thaw cycles. 1-Bromopropane (1.97 g, 16.0 mmol) was added, and the reaction mixture was stirred at 70 ºC for 17 h. After cooling to room temperature, the mixture was filtered through a Kiriyama funnel, and the residue was rinsed with Et_2O (30 mL). The organic layer was washed with H_2O (20 mL × 3) to remove DMA from the organic phase, washed with brine (20 mL), and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 4/1) provided 2-propyl-1*H*-indole-6-carboxylic acid methyl ester in 27% yield (469 mg) as a white solid (mp 85–87 ºC), which was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 8.05 (s, 1H), 7.77 (dd, J = 8.2, 1.4 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 6.30 (d, J = 1.4 Hz, 1H), 3.92 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 1.78 (sext, J = 7.4 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.4, 143.7, 135.1, 132.7, 122.5, 120.9, 119.2, 112.6, 100.2, 51.9, 30.4, 22.3, 13.9. HRMS (FD) Calcd for $C_{13}H_{15}NO_2$: $[M]^+$, 217.1097. Found: *m/z* 217.1104.



Preparation of 2-(4-Methylphenyl)-1*H*-indole (1l). A 100 mL round-bottomed flask was charged with phenylhydrazine (2.21 g, 20.4 mmol), 4-acetyltoluene (2.68 g, 20.0 mmol), acetic acid (4 drops using a 9-inch Pasteur pipette), and EtOH (5.4 mL). The mixture was stirred at 85 ºC for 1.5 h. After evaporation of volatiles under reduced pressure, $ZnCl_2$ (19.1 g, 140 mmol) was added to the crude reaction mixture including the corresponding hydrazone intermediate, and the resulting mixture was stirred by hand with a spatula at 140 ºC for 20 min. After monitoring the consumption of the hydrazone intermediate by GC analysis (note: additional stirring would be performed if any intermediate remains.), a concentrated HCl aqueous solution (ca. 12 N, 3.0 mL) diluted with water (50 mL) was added, and a solid stuck to the flask was stirred by hand with a

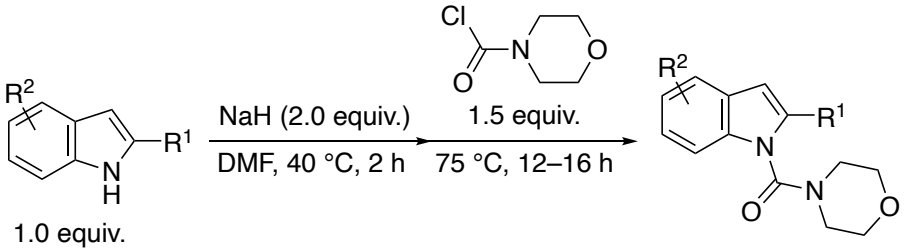
spatula. After filtration of the resulting mixture, a solid on the filter paper was washed with water (50 mL), a saturated $NaHCO_3$ aqueous solution (50 mL), and water (50 mL) again. The remaining solid was collected by being dissolved in EtOAc (100 mL), and the solution was dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent gave a crude product. The crude product was purified by recrystallization from hexane/CH_2Cl_2 after filtration through a pad of silica gel (hexane/EtOAc = 10/1), providing **1l** in 40% yield (1.66 g) as a cream-colored solid. Compound **1l** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[15] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58–7.55 (m, 2H), 7.40 (ddd, J = 8.1, 1.9, 1.0 Hz, 1H), 7.27–7.25 (m, 2H), 7.18 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.11 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H), 6.79 (dd, J = 1.8, 0.9 Hz, 1H), 2.40 (s, 3H).

II-I. Preparation of 1*H*-Indole-1-carboxamide Derivatives



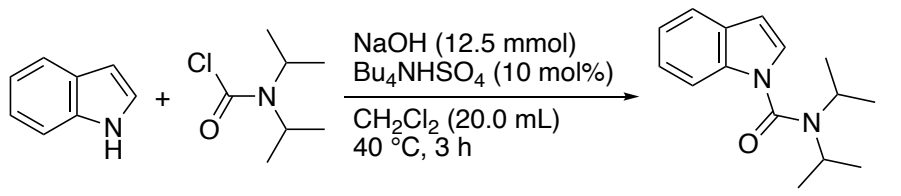
A General Procedure for Method A. An *N*-carbamoylation of indoles based on method A was performed according to the following modified literature procedure.[16] Under an argon atmosphere, a flame-dried Schlenk tube was charged with an indole (1.0 equiv.), Bu_4NHSO_4 (10 mol%), and NaOH (2.5 equiv.). To this were added CH_2Cl_2 and carbamoyl chloride (1.5 equiv.), and the resulting mixture was stirred at 40 °C for 1.5–3 h until the reaction was complete as confirmed by TLC. To this was added a saturated NH_4Cl aqueous solution, and the organic layer was separated and extracted with CH_2Cl_2 three times. The organic layers were combined and dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by purification yielded a 1*H*-indole-1-carboxamide. **NOTE**: Method A was ineffective for the *N*-carbamoylation of C2-substituted indoles, for which method B is available (see below).

[15] H.-P. Lin, N. Ibrahim, O. Provot, M. Alami, A. Hamze, *RSC Adv.* **2018**, *8*, 11536–11542.
[16] L. Ye, S.-H. Cai, D.-X. Wang, Y.-Q. Wang, L.-J. Lai, C. Feng, T.-P. Loh, *Org. Lett.* **2017**, *19*, 6164–6167.



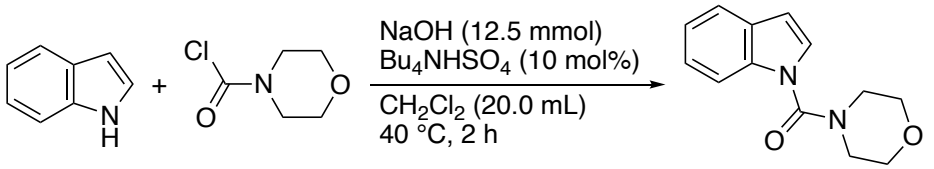
A General Procedure for Method B. An *N*-carbamoylation of indoles based on method B was performed according to the following modified literature procedure.[16] Under a flow of argon, a flame-dried Schlenk tube connected to a bubbler outlet for releasing H_2 gas was charged with a 55% dispersion of NaH (2.0 equiv.) in paraffin oil and DMF, and the resulting suspension was cooled to 0 ºC in an ice bath. To this was slowly added an indole (1.0 equiv.), and the resulting mixture was stirred at 40 ˚C for 2 h. After disconnecting the bubbler outlet, recooling the mixture to 0 °C, and adding 4-morpholinylcarbonyl chloride (1.5 equiv.), the mixture was stirred at 75 ˚C for 12–16 h until the reaction was complete as confirmed by TLC. To this was added a saturated NH_4Cl aqueous solution, and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with H_2O three times to remove DMF from the organic phase, washed with brine, and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by purification yielded a 1*H*-indole-1-yl-4-morpholinylmethanone.

Unless otherwise noted, new compounds prepared in this section were fully characterized by ^1H and $^{13}C\{1H\}$ NMR spectroscopy, and HRMS.



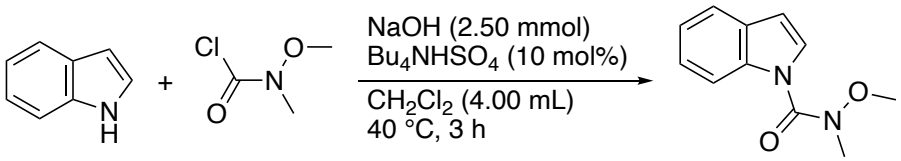
***N*,*N*-Bis(1-methylethyl)-1*H*-indole-1-carboxamide (1c).** The title compound was prepared based on method A using the following reagents: Indole (586 mg, 5.00 mmol), *N*,*N*-bis(1-methylethyl)carbamic chloride (1.23 g, 7.50 mmol), NaOH (500 mg, 12.5 mmol), Bu_4NHSO_4 (170 mg, 0.500 mmol), and CH_2Cl_2 (20.0 mL). Compound **1c** was isolated by column chromatography on silica gel (hexane/EtOAc = 10/1) in 91% yield (1.11 g) as a white solid. Compound **1c** has already appeared in the literature, and its spectral and analytical data are in good

agreement with those reported.[17] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.62–7.58 (m, 2H), 7.38 (d, J = 3.7 Hz, 1H), 7.23 (ddd, J = 8.4, 7.2, 1.0 Hz, 1H), 7.13 (td, J = 7.5, 1.1 Hz, 1H), 6.59 (d, J = 3.7 Hz, 1H), 3.82 (sept, J = 6.7 Hz, 2H), 1.40 (d, J = 6.9 Hz, 12H).



5.00 mmol 7.50 mmol **1e**; 98% yield (1.13 g)

1*H*-Indol-1-yl-4-morpholinylmethanone (1e). The title compound was prepared based on method A using the following reagents: Indole (586 mg, 5.00 mmol), 4-morpholinylcarbonyl chloride (1.12 g, 7.50 mmol), NaOH (500 mg, 12.5 mmol), Bu_4NHSO_4 (170 mg, 0.500 mmol), and CH_2Cl_2 (20.0 mL). Compound **1e** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 98% yield (1.13 g) as a white solid. Compound **1e** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[18] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.33–7.30 (m, 2H), 7.23–7.20 (m, 1H), 6.62 (d, J = 3.4 Hz, 1H), 3.79 (t, J = 4.4 Hz, 4H), 3.62 (t, J = 4.6 Hz, 4H).

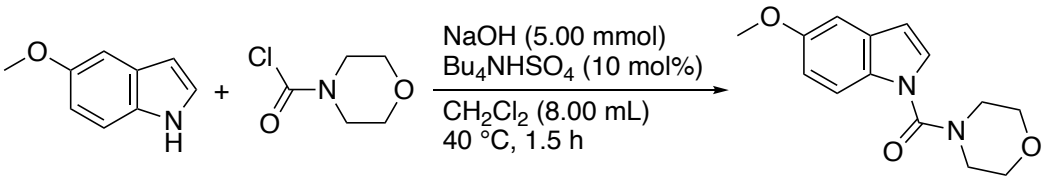


1.00 mmol 1.50 mmol **1f**; 99% yield (202 mg)

***N*-Methoxy-*N*-methyl-1*H*-indole-1-carboxamide (1f).** The title compound was prepared based on method A using the following reagents: Indole (117 mg, 1.00 mmol), *N*-methoxy-*N*-methylcarbamic chloride (185 mg, 1.50 mmol), NaOH (100 mg, 2.50 mmol), Bu_4NHSO_4 (34.0 mg, 0.100 mmol), and CH_2Cl_2 (4.00 mL). Compound **1f** was isolated by column chromatography on silica gel (hexane/EtOAc = 7/1) in 99% yield (202 mg) as a colorless oil. Compound **1f** has already appeared in the literature, and its spectral and analytical data are in good agreement with

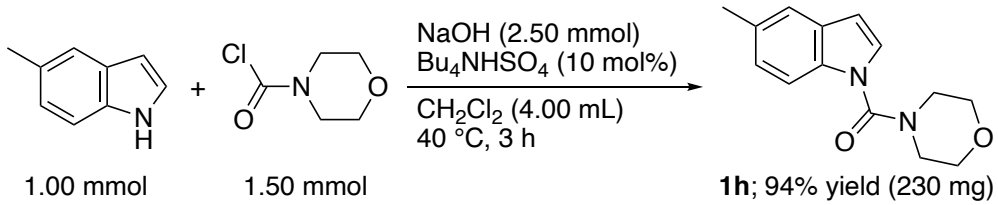
[17] C. G. Hartung, A. Fecher, B. Chapell, V. Snieckus, *Org. Lett.* **2003**, *5*, 1899–1902.
[18] S. T. Heller, E. E. Schultz, R. Sarpong, *Angew. Chem. Int. Ed*. **2012**, *51*, 8304–8308.

those reported.[19] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 8.2, 0.9, 0.9 Hz, 1H), 7.62 (d, *J* = 3.4 Hz, 1H), 7.58 (ddd, *J* = 7.8, 1.3, 1.2 Hz, 1H), 7.31 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.25–7.21 (m, 1H), 6.59 (dd, *J* = 3.7, 0.9 Hz, 1H), 3.63 (s, 3H), 3.37 (s, 3H).



2.00 mmol 3.00 mmol **1g**; 99% yield (515 mg)

(5-Methoxy-1*H*-indol-1-yl)-4-morpholinylmethanone (1g). The title compound was prepared based on method A using the following reagents: 5-Methoxy-1*H*-indole (294 mg, 2.00 mmol), 4-morpholinylcarbonyl chloride (449 mg, 3.00 mmol), NaOH (200 mg, 5.00 mmol), Bu_4NHSO_4 (67.9 mg, 0.200 mmol), and CH_2Cl_2 (8.00 mL). Compound **1g** was isolated by column chromatography on silica gel (hexane/EtOAc = 2/1) in 99% yield (515 mg) as a white solid (mp 104–106 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 3.85 (s, 3H), 3.78 (t, *J* = 4.8 Hz, 4H), 3.60 (t, *J* = 4.8 Hz, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.5, 154.4, 130.4, 130.1, 126.7, 114.0, 113.2, 106.2, 103.2, 66.7, 55.7, 47.1. HRMS (FD) Calcd for $C_{14}H_{16}N_2O_3$: $[M]^+$, 260.1155. Found: *m/z* 260.1141.

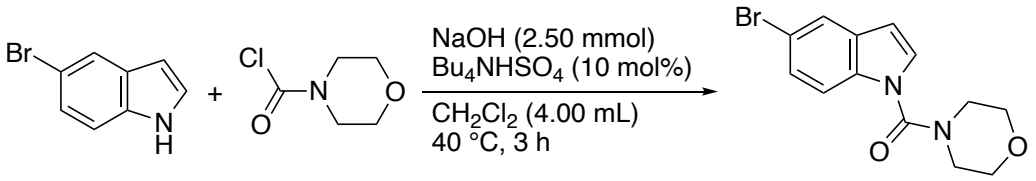


1.00 mmol 1.50 mmol **1h**; 94% yield (230 mg)

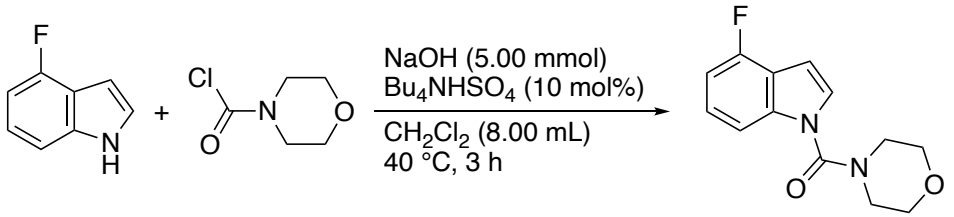
(5-Methyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1h). The title compound was prepared based on method A using the following reagents: 5-Methyl-1*H*-indole (131 mg, 1.00 mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), NaOH (100 mg, 2.50 mmol), Bu_4NHSO_4 (34.0 mg, 0.100 mmol), and CH_2Cl_2 (4.00 mL). Compound **1h** was isolated by column chromatography on silica gel (hexane/EtOAc = 2/1) in 94% yield (230 mg) as a white solid (mp 77–79 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.39 (s, 1H), 7.28 (d, *J* = 3.7

[19] J. Zhang, S. Zhang, T. Gogula, H. Zou*, ACS Catal.* **2020***, 10,* 7486−7494.

Hz, 1H), 7.13 (dd, J = 8.7, 1.4 Hz, 1H), 6.54 (d, J = 3.7 Hz, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.60 (t, J = 4.8 Hz, 4H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.4, 133.4, 131.6, 129.9, 126.2, 125.2, 120.9, 112.9, 106.0, 66.7, 47.1, 21.3. HRMS (FD) Calcd for $C_{14}H_{16}N_2O_2$: $[M]^+$, 244.1206. Found: *m/z* 244.1210.

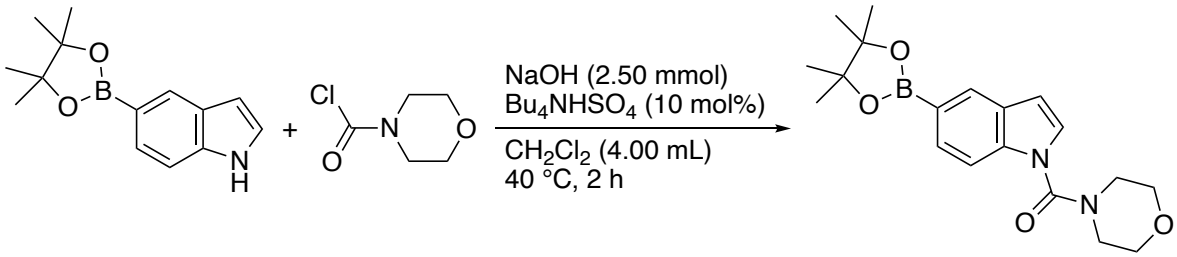


(5-Bromo-1*H*-indol-1-yl)-4-morpholinylmethanone (1i). The title compound was prepared based on method A using the following reagents: 5-Bromo-1*H*-indole (196 mg, 1.00 mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), NaOH (100 mg, 2.50 mmol), Bu_4NHSO_4 (34.0 mg, 0.100 mmol), and CH_2Cl_2 (4.00 mL). Compound **1i** was isolated by column chromatography on silica gel (hexane/EtOAc = 2/1) in 96% yield (297 mg) as a white solid (mp 64–66 ºC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 1.8 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.40 (dd, J = 8.7, 1.8 Hz, 1H), 7.30 (d, J = 3.7 Hz, 1H), 6.56 (dd, J = 3.7, 0.9 Hz, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.60 (t, J = 4.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.8, 134.0, 131.3, 127.2, 126.7, 123.7, 115.3, 114.7, 105.6, 66.7, 47.1. HRMS (FD) Calcd for $C_{13}H_{13}{}^{79}BrN_2O_2$: $[M]^+$, 308.0155. Found: *m/z* 308.0157.



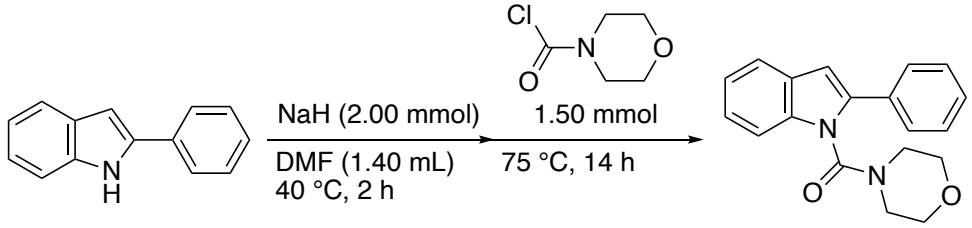
(4-Fluoro-1*H*-indol-1-yl)-4-morpholinylmethanone (1j). The title compound was prepared based on method A using the following reagents: 4-Fluoro-1*H*-indole (270 mg, 2.00 mmol), 4-morpholinylcarbonyl chloride (449 mg, 3.00 mmol), NaOH (200 mg, 5.00 mmol), Bu_4NHSO_4 (67.9 mg, 0.200 mmol), and CH_2Cl_2 (8.00 mL). Compound **1j** was isolated by column chromatography on silica gel (hexane/EtOAc = 1/1) in 98% yield (487 mg) as a white solid (mp 115–116 ºC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 3.4 Hz, 1H),

7.25–7.21 (m, 1H), 6.90 (dd, J = 10.0, 8.3 Hz, 1H), 6.72 (d, J = 3.4 Hz, 1H), 3.79 (t, J = 4.6 Hz, 4H), 3.61 (t, J = 4.6 Hz, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0 (d, J = 247.1 Hz), 153.9, 137.5 (d, J = 9.6 Hz), 126.0, 124.5 (d, J = 8.4 Hz), 118.5 (d, J = 22.8 Hz), 109.2 (d, J = 3.6 Hz), 107.1 (d, J = 19.2 Hz), 102.0, 66.7, 47.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ –122.1. HRMS (FD) Calcd for $C_{13}H_{13}FN_2O_2$: $[M]^+$, 248.0956. Found: *m/z* 248.0985.



1.00 mmol 1.50 mmol **1k**; 95% yield (338 mg)

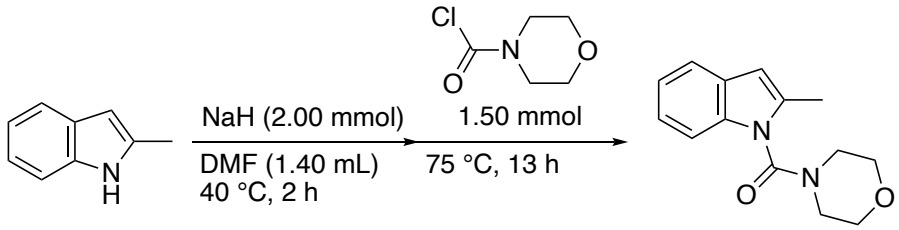
[5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl]-4-morpholinylmethanone (1k). The title compound was prepared based on method A using the following reagents: 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (243 mg, 1.00 mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), NaOH (100 mg, 2.50 mmol), Bu_4NHSO_4 (34.0 mg, 0.10 mmol), and CH_2Cl_2 (4.00 mL). Compound **1k** was isolated by column chromatography on silica gel (hexane/EtOAc = 1/1) in 95% yield (338 mg) as a white solid (mp 155–156 ºC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7,75 (dd, J = 8.2, 0.9 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 3.7 Hz, 1H), 6.62 (d, J = 3.7 Hz, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.59 (t, J = 4.8 Hz, 4H), 1.37 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.2, 137.1, 129.9, 129.3, 128.7, 126.3, 112.5, 106.6, 83.7, 66.7, 47.0, 24.9; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.9. HRMS (FD) Calcd for $C_{19}H_{25}BN_2O_4$: $[M]^+$, 356.1902. Found: *m/z* 356.1917.



1.00 mmol **1s**; 80% yield (245 mg)

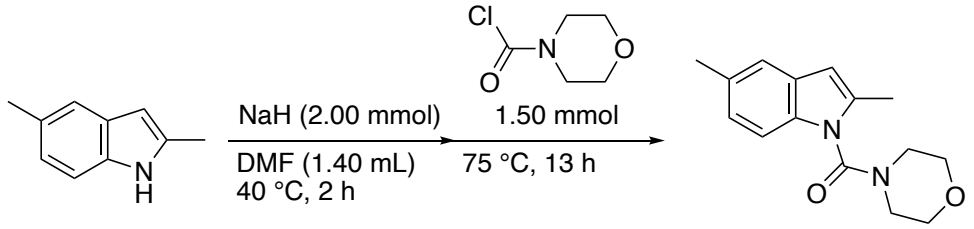
(2-Phenyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1s). The title compound was prepared based on method B using the following reagents: 2-Phenyl-1*H*-indole (193 mg, 1.00

mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), a 55% dispersion of NaH (87.3 mg, 2.00 mmol), and DMF (1.40 mL). Compound **1s** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 80% yield (245 mg) as a yellow solid (mp 117–118 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.58–7.55 (m, 3H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.41–7.37 (m, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 3.51–2.96 (br m, 8H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.0, 139.0, 137.0, 131.9, 128.8, 128.5, 128.4, 127.7, 123.6, 121.9, 120.8, 111.6, 104.7, 66.0, 46.4 (br), 44.6 (br). HRMS (FD) Calcd for $C_{19}H_{18}N_2O_2$: $[M]^+$, 306.1363. Found: *m/z* 306.1338.



1.00 mmol **1t**; 91% yield (222 mg)

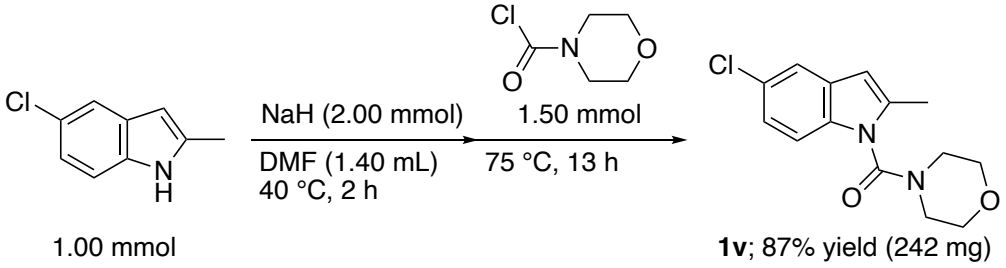
(2-Methyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1t). The title compound was prepared based on method B using the following reagents: 2-Methyl-1*H*-indole (131 mg, 1.00 mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), a 55% dispersion of NaH (87.3 mg, 2.00 mmol), and DMF (1.40 mL). Compound **1t** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 91% yield (222 mg) as a white solid (mp 69–72 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.30 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (td, *J* = 7.4, 1.0 Hz, 1H), 6.34–6.33 (m, 1H), 3.80–3.68 (m, 4H), 3.53 (br s, 4H), 2.48 (d, *J* = 0.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.2, 136.3, 135.4, 128.7, 122.3, 121.4, 120.2, 110.7, 104.6, 66.9, 46.4 (br), 13.4. HRMS (FD) Calcd for $C_{14}H_{16}N_2O_2$: $[M]^+$, 244.1206. Found: *m/z* 244.1210.



1.00 mmol **1u**; 90% yield (232 mg)

(2,5-Dimethyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1u). The title compound was prepared based on method B using the following reagents: 2,5-Dimethyl-1*H*-indole (145 mg, 1.00

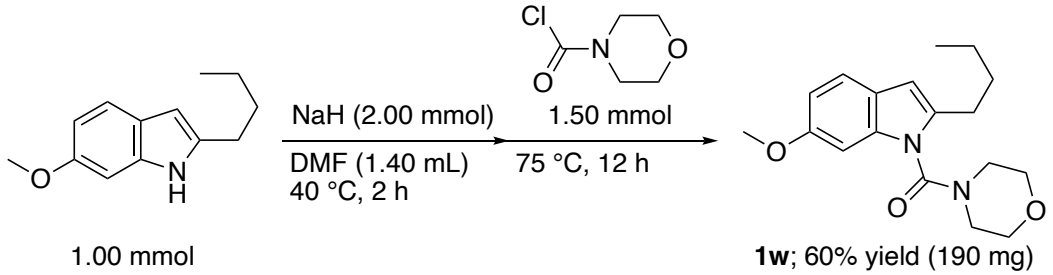
mmol), 4-Morpholinylcarbonyl chloride (224 mg, 1.50 mmol), a 55% dispersion of NaH (87.3 mg, 2.00 mmol), and DMF (1.40 mL). Compound **1u** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 90% yield (232 mg) as a cream-colored solid (mp 66–68 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.283–7.278 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.26–6.25 (m, 1H), 3.77 (dt, *J* = 11.9, 4.7 Hz, 2H), 3.70 (dt, *J* = 11.9, 4.8 Hz, 2H), 3.53–3.51 (br m, 4H), 2.46 (d, *J* = 0.9 Hz, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.4, 136.5, 133.7, 130.8, 128.9, 123.6, 120.0, 110.5, 104.3, 66.9, 46.44, 46.39, 21.3, 13.5. HRMS (FD) Calcd for $C_{15}H_{18}N_2O_2$: $[M]^+$, 258.1363. Found: *m/z* 258.1351.



1.00 mmol

1v; 87% yield (242 mg)

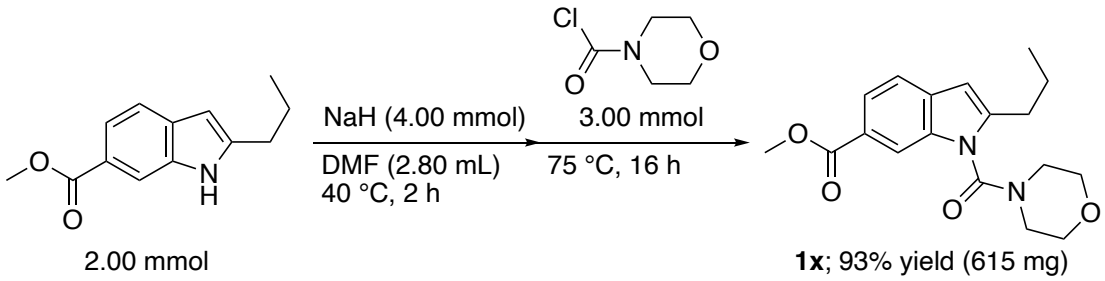
(5-Chloro-2-methyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1v). The title compound was prepared based on method B using the following reagents: 5-Chloro-2-methyl-1*H*-indole (166 mg, 1.00 mmol), 4-Morpholinylcarbonyl chloride (224 mg, 1.50 mmol), a 55% dispersion of NaH (87.3 mg, 2.00 mmol), and DMF (1.40 mL). Compound **1v** was isolated by column chromatography on silica gel (hexane/EtOAc = 3/1) in 87% yield (242 mg) as a white solid (mp 70–71 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.8 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.14 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.28(s, 1H), 3.77 (dt, *J* = 11.4, 4.7 Hz, 2H), 3.70 (dt, *J* = 12.4, 5.3 Hz, 2H), 3.51 (br s, 4H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.8, 137.8, 133.7, 129.8, 127.0, 122.5, 119.7, 111.6, 104.0, 66.8, 46.42, 46.38, 13.4. HRMS (FD) Calcd for $C_{14}H_{15}{}^{35}ClN_2O_2$: $[M]^+$, 278.0817. Found: *m/z* 278.0820.



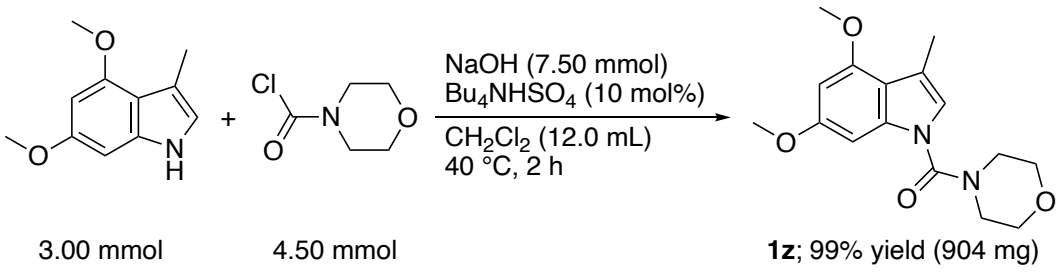
1.00 mmol

1w; 60% yield (190 mg)

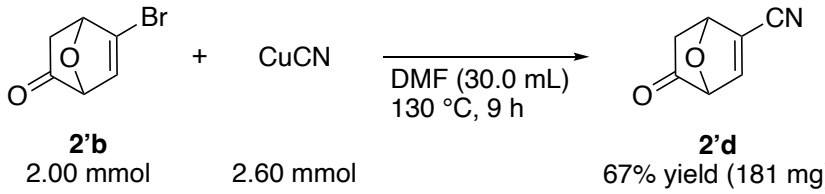
(2-Butyl-6-methoxy-1*H*-indol-1-yl)-4-morpholinylmethanone (1w). The title compound was prepared based on method B using the following reagents: 2-Butyl-6-methoxy-1*H*-indole (203 mg, 1.00 mmol), 4-morpholinylcarbonyl chloride (224 mg, 1.50 mmol), a 55% dispersion of NaH (87.3 mg, 2.00 mmol), and DMF (1.40 mL). Compound **1w** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 60% yield (190 mg) as a cream-colored solid (mp 77–78 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.79 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.27 (s, 1H), 3.84 (s, 3H), 3.80–3.69 (m, 4H), 3.53 (br s, 4H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.64 (quint, *J* = 7.6 Hz, 2H), 1.40 (sext, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.6, 153.4, 139.9, 136.2, 122.6, 120.7, 110.0, 103.3, 95.6, 66.8, 55.8, 46.2 (br), 31.0, 26.9, 22.3, 13.9. HRMS (FD) Calcd for $C_{18}H_{24}N_2O_3$: $[M]^+$, 316.1781. Found: *m/z* 316.1772.



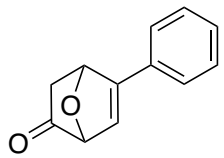
Methyl 2-Propyl-1-(morpholin-4-ylcarbonyl)-1*H*-indole-6-carboxylate (1x). The title compound was prepared based on method B using the following reagents: 2-Propyl-1*H*-indole-6-carboxylic acid methyl ester (435 mg, 2.00 mmol), 4-morpholinylcarbonyl chloride (449 mg, 3.00 mmol), a 55% dispersion of NaH (175 mg, 4.00 mmol), and DMF (2.80 mL). Compound **1x** was isolated by column chromatography on silica gel (hexane/EtOAc = 2/1) in 93% yield (615 mg) as a white solid (mp 95–98 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 6.42 (s, 1H), 3.94 (s, 3H), 3.85–3.57 (m, 8H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.74 (sext, *J* = 7.5 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.7, 152.6, 144.7, 134.8, 132.4, 124.1, 122.6, 119.9, 112.6, 103.9, 66.7, 52.1, 46.3 (br), 29.4, 21.9, 13.9. HRMS (FD) Calcd for $C_{18}H_{22}N_2O_4$: $[M]^+$, 330.1574. Found: *m/z* 330.1586.



(4,6-Dimethoxy-3-methyl-1*H*-indol-1-yl)-4-morpholinylmethanone (1z). The title compound was prepared based on method A using the following reagents: 4,6-Dimethoxy-3-methyl-1*H*-indole (574 mg, 3.00 mmol), 4-morpholinylcarbonyl chloride (673 mg, 4.50 mmol), NaOH (300 mg, 7.50 mmol), Bu_4NHSO_4 (102 mg, 0.300 mmol), and CH_2Cl_2 (12.0 mL). Compound **1z** was isolated by column chromatography on silica gel (hexane/EtOAc = 2/1) in 99% yield (904 mg) as a yellow solid (mp 113–114 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.8 Hz, 1H), 6.74 (q, *J* = 1.4 Hz, 1H), 6.26 (d, *J* = 1.8 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.77, (t, *J* = 4.8 Hz, 4H), 3.59, (t, *J* = 4.8 Hz, 4H), 2.36 (d, *J* = 0.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 155.2, 154.8, 137.8, 120.2, 116.1, 114.1, 93.6, 89.6, 66.8, 55.7, 55.3, 47.0, 12.2. HRMS (FD) Calcd for $C_{16}H_{20}N_2O_4$: $[M]^+$, 304.1418. Found: *m/z* 304.1422.



Preparation of 5-Cyano-7-oxabicyclo[2.2.1]hept-5-en-2-one (2'd). Under an argon atmosphere, a flame-dried 300 mL two-necked round-bottomed flask was charged with CuCN (233 mg, 2.60 mmol), **2'b** (376 mg, 2.00 mmol), and DMF (30.0 mL). The resulting mixture was stirred at 130 ºC for 9 h and then cooled to room temperature. Simple filtration through a pad of silica gel (hexane/EtOAc = 1/1) and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 4/1) gave **2'd** in 67% yield (181 mg) as a yellow solid (mp 101–102 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 2.3 Hz, 1H), 5.51 (d, *J* = 4.6 Hz, 1H), 4.83 (d, *J* = 1.4 Hz, 1H), 2.40 (dd, *J* = 16.5, 4.6 Hz, 1H), 2.07 (d, *J* = 16.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.7, 145.1, 126.0, 112.5, 83.6, 80.7, 32.7. HRMS (FI) Calcd for $C_7H_5NO_2$: $[M]^+$, 135.0315. Found: *m/z* 135.0300.



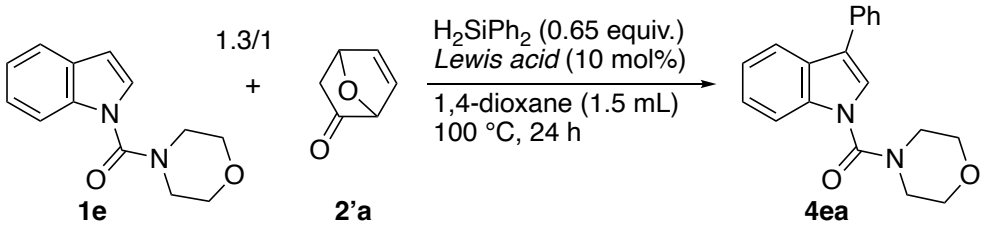
2'e

NOTE: Correction of the ^{1}H NMR Data of 5-Phenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (2'e). There is a typographical error in the ^{1}H NMR data of **2'e** in our previous publication.[9] Hence, its corrected ^{1}H NMR data are shown here, with the corrected value underlined and in bold. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), **6.56** (d, *J* = 2.3 Hz, 1H), 5.65 (d, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 1.7 Hz, 1H), 2.44 (dd, *J* = 16.0, 4.6 Hz, 1H), 1.95 (d, *J* = 15.5 Hz, 1H).

III. Examination of Suitable Reaction Conditions for Indium-Catalyzed 1:1 Phenylation of 1*H*-Indol-1-yl-4-morpholinylmethanone with 7-Oxabicyclo[2.2.1]hept-5-en-2-one

In this section, the promising results in each table are highlighted with a gray background. Unless otherwise notes, conversions and yields were determined by ^{1}H NMR.

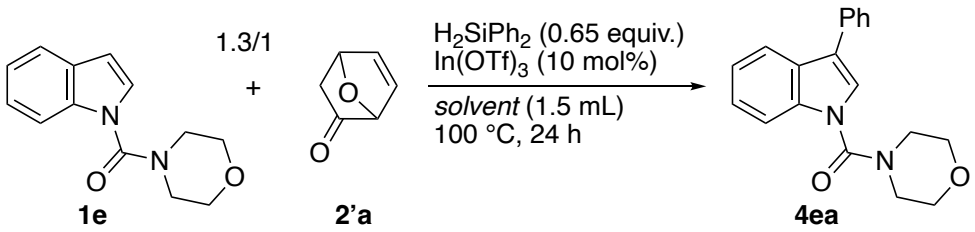
Table S1. Effect of Lewis acids[a]



Lewis acid	conv. (%) of **2'a**	yield (%) of **4ea**
$In(OTf)_3$	65	39
$In(ONf)_3$	71	38
$Cu(OTf)_2$	79	3
$Zn(OTf)_2$	19	<1

[a] All reactions were performed on a 0.30 mmol scale. Reagents: **1e** (0.39 mmol), **2'a** (0.30 mmol), H_2SiPh_2 (0.20 mmol), *Lewis acid* (30 μmol), 1,4-dioxane (1.5 mL).

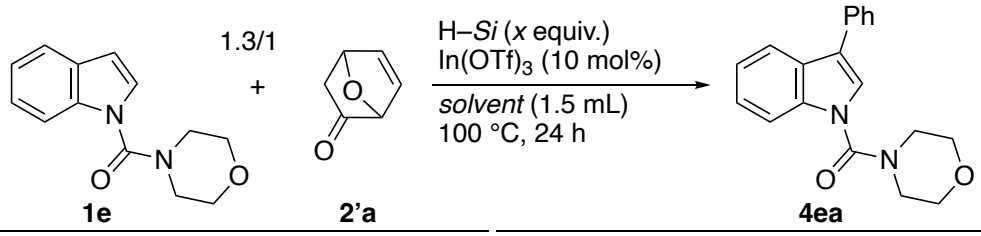
Table S2. Effect of solvents[a]



solvent	conv. (%) of **2'a**	yield (%) of **4ea**
1,4-dioxane	65	39
DME[b]	67	38
DEE	64	34
PhCl	64	21

[a] All reactions were performed on a 0.30 mmol scale. Reagents: **1e** (0.39 mmol), **2'a** (0.30 mmol), H_2SiPh_2 (0.20 mmol), $In(OTf)_3$ (30 μmol), *solvent* (1.5 mL). [b] Performed at 90 °C.

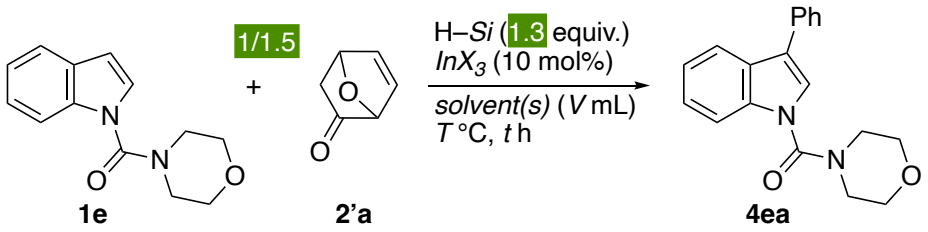
Table S3. Effect of hydrosilanes[a]



H–*Si* (*x*)	conv. (%) of **2'a**	yield (%) of **4ea**	H–*Si* (*x*)	conv. (%) of **2'a**	yield (%) of **4ea**
H_3SiPh (0.43)	67	31	H_2SiPh_2 (1.3)[b]	74	40
p-$(HSiMe_2)_2C_6H_4$ (0.65)	77	13	$HSiMePh_2$ (1.3)[b]	73	31
$(HSiMe_2)_2O$ (0.65)	66	13	$HSi(OEt)_3$ (1.3)[b]	80	16
$Ph_2HSi–SiHPh_2$ (0.65)	36	6	$HSi(i\text{-}Pr)_3$ (1.3)[b]	23	<1
H_2SiPh_2 (0.65)	65	39	$HSiBnMe_2$ (1.3)[b]	77	18
H_2SiPh_2 (1.3)	77	41	$HSi(t\text{-}Bu)Ph_2$ (1.3)[b]	19	<1
			$HSi(SiMe)_3$ (1.3)[b]	20	4

[a] All reactions were performed on a 0.30 mmol scale. Reagents: **1e** (0.39 mmol), **2'a** (0.30 mmol), H–*Si* (0.13–0.39 mmol), $In(OTf)_3$ (30 μmol), 1,4-dioxane (1.5 mL). [b] Performed for 3 h. Abbreviation: Bn = benzyl.

Table S4. Effect of various factors[a]



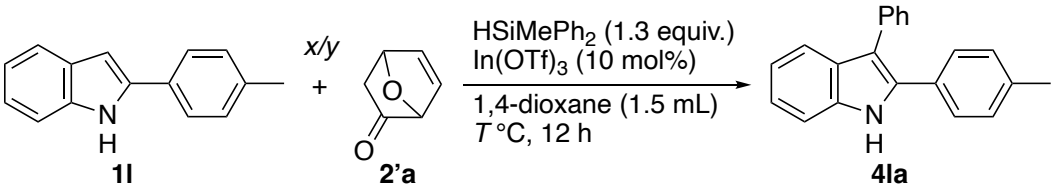
H–*Si*	InX_3	*solvent(s)* (*V*)	*T*	*t*	conv. (%) of **1e**	yield (%) of **4ea**
effect of *V*, *T*, *t*						
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane (1.5)	115	8	86	70 (66)
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane (1.5)	115	16	89	68
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane (1.5)	120	8	82	62
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane (2.0)	115	8	69	52
effect of InX_3 other than $In(OTf)_3$						
H_2SiPh_2	$In(NNf_2)_3$	1,4-dioxane (1.5)	115	8	12	<1
H_2SiPh_2	InI_3	1,4-dioxane (1.5)	115	8	9	<1
effect of *solvents* other than 1,4-dioxane						
H_2SiPh_2	$In(OTf)_3$	4-Me–THP (1.5)	115	8	66	56
H_2SiPh_2	$In(OTf)_3$	CPME (1.5)	115	8	73	56
H_2SiPh_2	$In(OTf)_3$	BuOH (1.5)	115	8	35	3
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane/DEE (1.3/0.2)	115	8	79	63
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane/Bu_2O (1.3/0.2)	115	8	80	61
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane/EtCN (1.3/0.2)	115	8	69	50
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane/PhCl (1.3/0.2)	115	8	85	65
H_2SiPh_2	$In(OTf)_3$	1,4-dioxane/$MeNO_2$ (1.3/0.2)	115	8	9	2
effect of H–*Si* other than H_2SiPh_2						
$HSiMe_2Cy$	$In(OTf)_3$	1,4-dioxane (1.5)	115	8	45	19
$H_2SiMePh$	$In(OTf)_3$	1,4-dioxane (1.5)	115	8	62	35
H_3Si–octyl	$In(OTf)_3$	1,4-dioxane (1.5)	115	8	16	5

[a] All reactions were performed on a 0.20 mmol scale. Reagents: **1e** (0.20 mmol), **2'a** (0.30 mmol), H–*Si* (0.26 mmol), InX_3 (20 μmol), *solvent(s)* (1.5 or 2.0 mL). A yield of isolated **4ea** is shown in parentheses. Abbreviation: Cy = cyclohexyl.

IV. Examination of Suitable Reaction Conditions for Indium-Catalyzed 1:1 Phenylation of 2-(*p*-Tolyl)indole with 7-Oxabicyclo[2.2.1]hept-5-en-2-one

In this section, the promising results in each table are highlighted with a gray background. Unless otherwise notes, conversions and yields were determined by ^{1}H NMR.

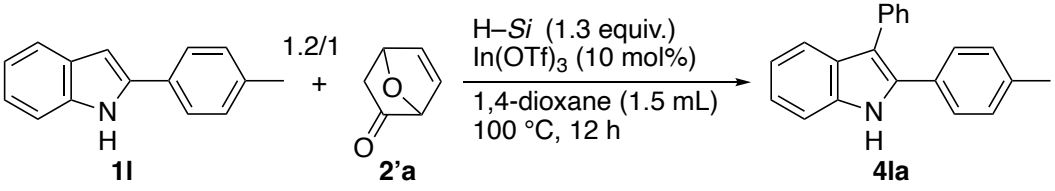
Table S5. Effect of amount of substrates and reaction temperature[a]



x/y	*T*	conv. (%) of **1l** or **2'a**	yield (%) of **4la**
1/1.5	90	>99 (**1l**)	41
1/1.2	90	>99 (**1l**)	42
1.2/1	90	99 (**2'a**)	47
1.5/1	90	>99 (**2'a**)	47
1.2/1	100	>99 (**2'a**)	50

[a] All reactions were performed on a 0.20 mmol scale. Reagents: **1l** (0.20, 0.24 or 0.30 mmol), **2'a** (0.20, 0.24 or 0.30 mmol), $HSiMePh_2$ (0.26 mmol), $In(OTf)_3$ (20 μmol), 1,4-dioxane (1.5 mL).

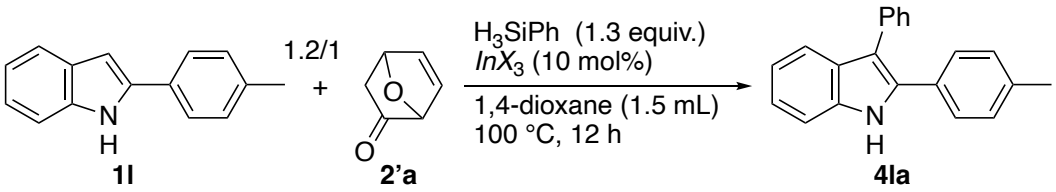
Table S6. Effect of hydrosilanes[a]



H–*Si*	conv. (%) of **2'a**	yield (%) of **4la**	H–*Si*	conv. (%) of **2'a**	yield (%) of **4la**
$HSiMePh_2$	>99	50	*p*-$(HSiMe_2)_2C_6H_4$	>99	43
$HSiMe_2Ph$	>99	45	H_2SiPh_2	>99	55
$HSiEt_3$	95	42			
$HSiBnMe_2$	>99	48	H_3SiPh	>99	59

[a] All reactions were performed on a 0.20 mmol scale. Reagents: **1l** (0.24 mmol), **2'a** (0.20 mmol), H–*Si* (0.26 mmol), $In(OTf)_3$ (20 μmol), 1,4-dioxane (1.5 mL).

Table S7. Effect of indium Lewis acids[a]

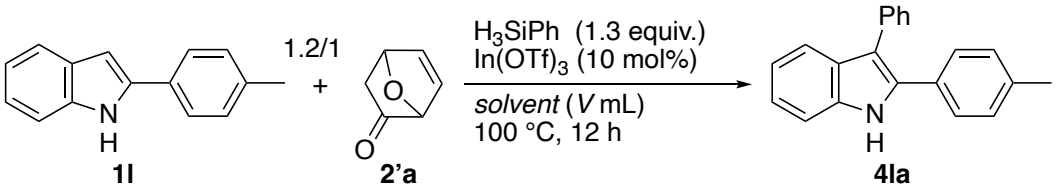


1l **2'a** **4la**

InX_3	conv. (%) of **1l** or **2'a**	yield (%) of **4la**
$In(OTf)_3$	>99	59
$In(ONf)_3$	>99	45
$In(NTf_2)_3$	58	<1
$InBr_3$	54	22

[a] All reactions were performed on a 0.20 mmol scale. Reagents: **1l** (0.24 mmol), **2'a** (0.20 mmol), H_3SiPh (0.26 mmol), InX_3 (20 μmol), 1,4-dioxane (1.5 mL).

Table S8. Effect of solvents[a]



1l **2'a** **4la**

solvent (*V*)	conv. (%) of **2'a**	yield (%) of **4la**	*solvent* (*V*)	conv. (%) of **2'a**	yield (%) of **4la**
1,4-dioxane (1.5)	>99	59 (50)	1,4-dioxane (2.0)	>99	56
4-Me–THP (1.5)	>99	57	4-Me–THP (2.0)	>99	57
THF[b] (1.5)	87	45	1,4-dioxane[c] (2.0)	>99	54
DEE (1.5)	>99	38	4-Me–THP[c] (2.0)	>99	49
CPME (1.5)	>99	38			

[a] All reactions were performed on a 0.20 mmol scale. Reagents: **1l** (0.24 mmol), **2'a** (0.20 mmol), H_3SiPh (0.26 mmol), $In(OTf)_3$ (20 μmol), *solvent* (1.5 or 2.0 mL). A yield of isolated **4la** is shown in parentheses. [b] Performed at 70 ºC. [c] Performed at 110 ºC.

V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones

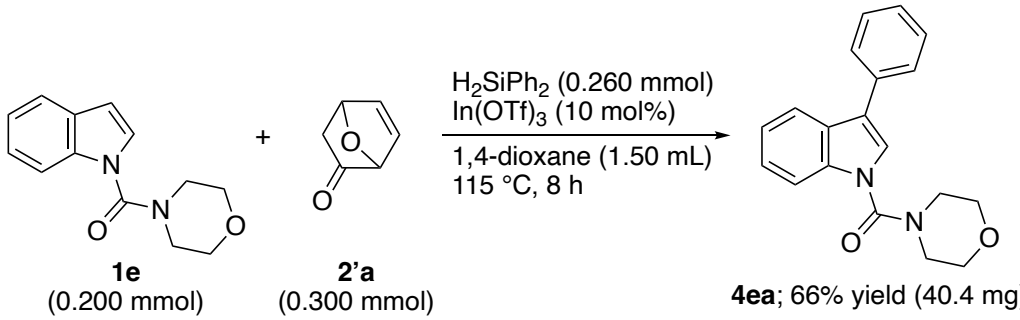
A General Procedure for Electronic Strategy and Electronic + Steric Strategy Using Conditions A in Table 2

$In(OTf)_3$ was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to room temperature (rt), the tube was filled with argon. To this was

added solvent 1,4-dioxane or BuOAc, and the solution was stirred at rt for 3 min. To this were added carbonyl compound **2'**, indole **1** (0.200 mmol), and H_2SiPh_2, and the resulting mixture was stirred at 90, 115, or 120 °C for the time specified in Table 2 and in the equation shown in this section. After cooling to rt, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by purification yielded product **4**. Unless otherwise noted, products **4** synthesized based on conditions A were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and also ^{19}F or $^{11}B\{^1H\}$ NMR spectroscopy for **4** with fluorine or boron atoms, respectively, as well as HRMS.

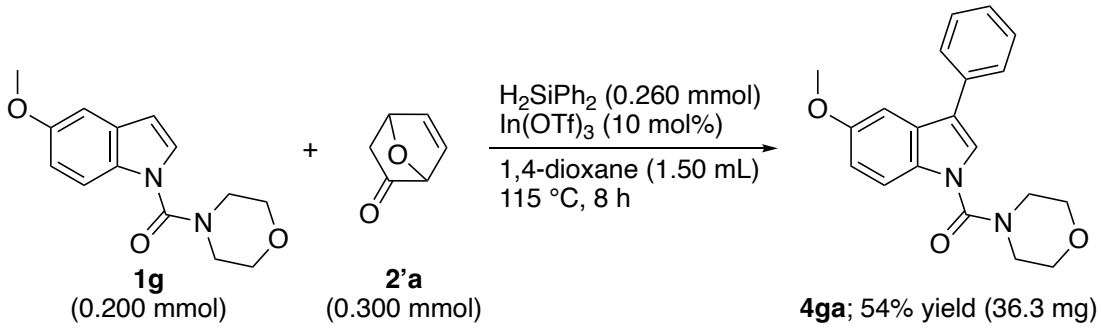
A General Procedure for Steric Strategy Using Conditions B in Table 2

$In(OTf)_3$ (11.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. To this was added solvent 1,4-dioxane (1.50 mL), and the solution was stirred at rt for 3 min. To this were added carbonyl compound **2'** (0.200 mmol), indole **1** (0.240 mmol), and H_3SiPh (28.1 mg, 0.260 mmol), and the resulting mixture was stirred at 100 °C for 12 h. After cooling to rt, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by purification yielded product **4**. Unless otherwise noted, products **4** synthesized based on conditions B were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS.

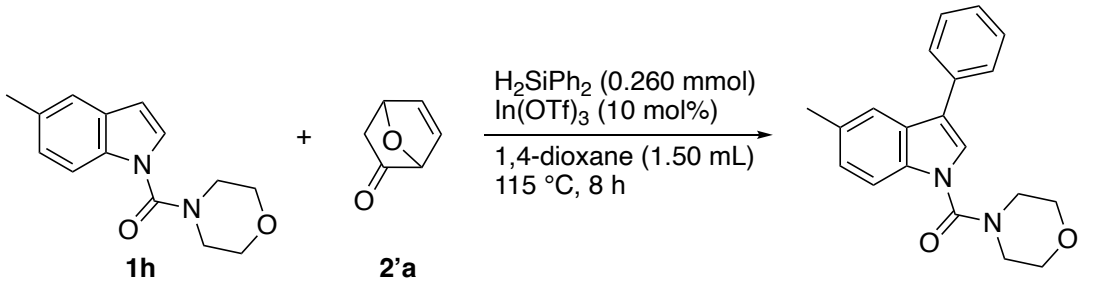


Compound 4ea. Compound **4ea** was synthesized based on conditions A using the following

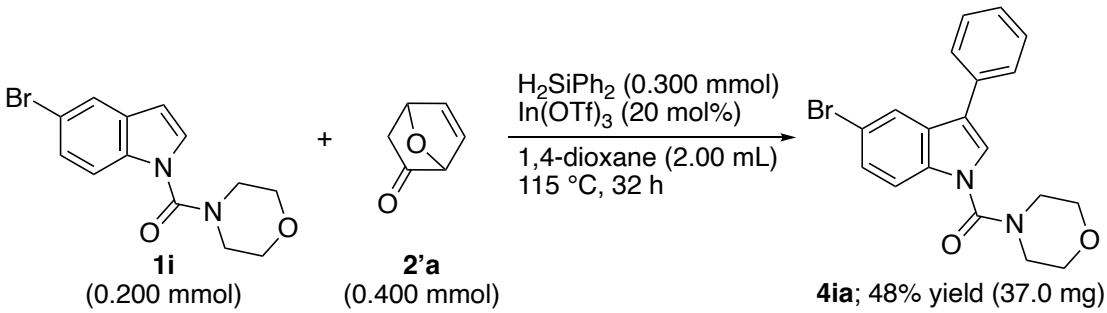
reagents: **1e** (46.1 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ea** was isolated by column chromatography on silica gel twice (benzene/EtOAc = 10/1) in 66% yield (40.4 mg) as a yellow solid (mp 98–100 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.9, 1.1 Hz, 1H), 7.75 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.66–7.63 (m, 2H), 7.50–7.45 (m, 2H), 7.44 (s, 1H), 7.39–7.34 (m, 2H), 7.30–7.26 (m, 1H), 3.81 (t, *J* = 4.8 Hz, 4H), 3.66 (t, *J* = 4.8 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.2, 135.9, 133.8, 128.9, 128.0, 127.8, 127.1, 124.2, 123.1, 122.4, 121.5, 120.2, 113.5, 66.7, 47.1. HRMS (FD) Calcd for $C_{19}H_{18}N_2O_2$: $[M]^+$, 306.1363. Found: *m/z* 306.1378.



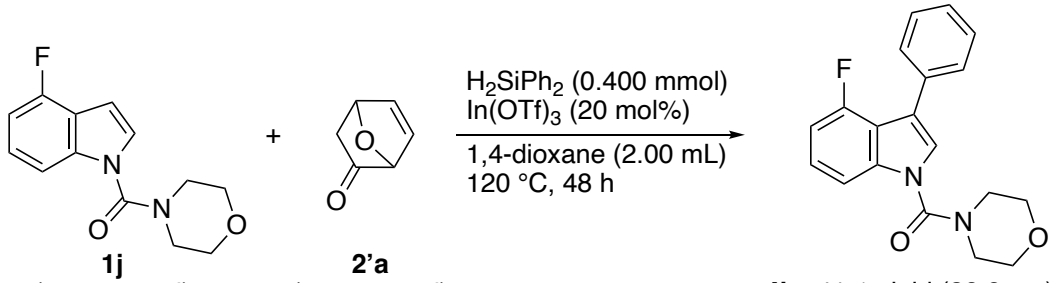
Compound 4ga. Compound **4ga** was synthesized based on conditions A using the following reagents: **1g** (52.1 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ga** was isolated by column chromatography on silica gel (benzene/EtOAc = 15/1) in 54% yield (36.3 mg) as a white solid (mp 112–114 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.2 Hz, 1H), 7.63–7.61 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 (s, 1H), 7.38–7.35 (m, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.00 (dd, *J* = 9.2, 2.3 Hz, 1H), 3.86 (s, 3H), 3.80 (t, *J* = 4.9 Hz, 4H), 3.65 (t, *J* = 4.6 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 154.3, 133.9, 130.8, 129.0, 128.7, 127.8, 127.1, 123.8, 121.4, 114.4, 113.5, 102.5, 66.7, 55.9, 47.2. HRMS (FD) Calcd for $C_{20}H_{20}N_2O_3$: $[M]^+$, 336.1468. Found: *m/z* 336.1438.



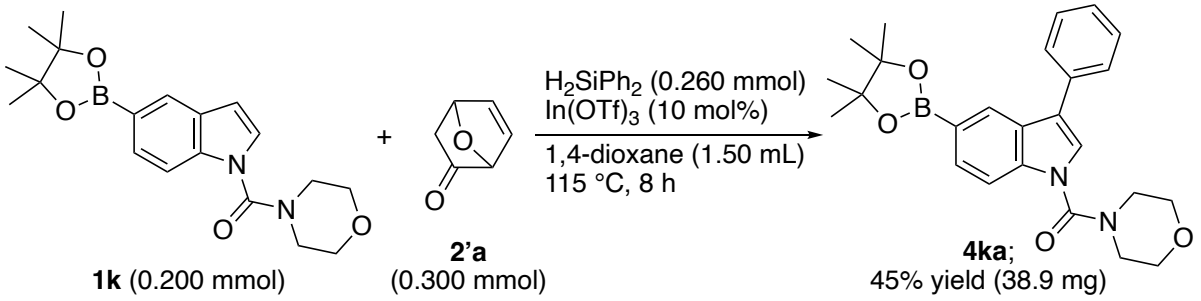
Compound 4ha. Compound **4ha** was synthesized based on conditions A using the following reagents: **1h** (48.9 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ha** was isolated by column chromatography on silica gel twice (benzene/EtOAc = 10/1) in 65% yield (41.7 mg) as a cream-colored solid (mp 65–67 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.61 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.38–7.33 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 3.80 (t, *J* = 4.8 Hz, 4H), 3.64 (t, *J* = 4.8 Hz, 4H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.3, 134.2, 134.0, 132.0, 128.9, 128.2, 127.9, 127.0, 125.6, 123.3, 121.2, 120.0, 113.2, 66.7, 47.2, 21.5. HRMS (FD) Calcd for $C_{20}H_{20}N_2O_2$: $[M]^+$, 320.1520. Found: *m/z* 320.1513.



Compound 4ia. Compound **4ia** was synthesized based on conditions A using the following reagents: **1i** (61.8 mg, 0.200 mmol), **2'a** (44.0 mg, 0.400 mmol), H_2SiPh_2 (55.3 mg, 0.300 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol), 1,4-dioxane (2.00 mL). Compound **4ia** was isolated by column chromatography on silica gel twice (benzene/EtOAc = 7/1) in 48% yield (37.0 mg) as a yellow solid (mp 137–138 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.60–7.57 (m, 2H), 7.50–7.44 (m, 3H), 7.41 (s, 1H), 7.38 (tt, *J* = 7.7, 1.5 Hz, 1H), 3.80 (t, *J* = 4.8 Hz, 4H), 3.65 (t, *J* = 4.8 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 134.7, 133.1, 129.6, 129.0, 127.8, 127.4, 127.1, 124.0, 122.8, 121.0, 115.9, 115.0, 66.7, 47.1. HRMS (FD) Calcd for $C_{19}H_{17}{}^{79}BrN_2O_2$: $[M]^+$, 384.0468. Found: *m/z* 384.0460.

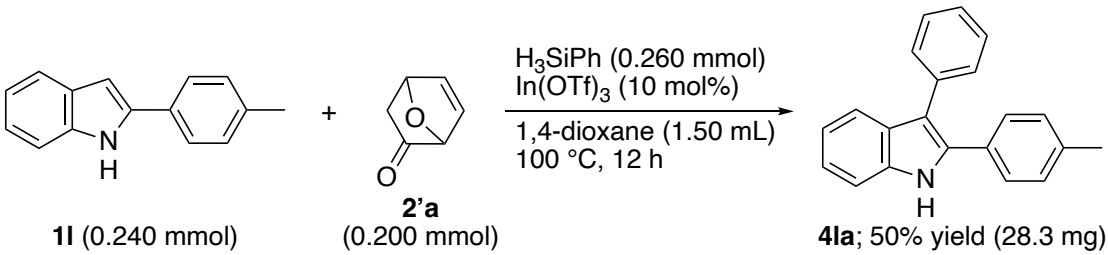


Compound 4ja. Compound **4ja** was synthesized based on conditions A using the following reagents: **1j** (49.7 mg, 0.200 mmol), **2'a** (50.6 mg, 0.460 mmol), H_2SiPh_2 (73.7 mg, 0.400 mmol), $In(OTf)_3$ (22.5 mg, 40.0 μmol), 1,4-dioxane (2.00 mL). Compound **4ja** was isolated by column chromatography on silica gel (benzene/EtOAc = 5/1) in 41% yield (26.6 mg) as a yellow solid (mp 162–164 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.45–7.42 (m, 2H), 7.36 (tt, *J* = 7.5, 1.6 Hz, 1H), 7.30 (s, 1H), 7.28 (dd, *J* = 8.3, 3.2 Hz, 1H), 6.94 (dd, *J* = 10.9, 8.0 Hz, 1H), 3.81 (t, *J* = 4.9 Hz, 4H), 3.66 (t, *J* = 4.9 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.7 (d, *J* = 249.5 Hz), 153.7, 138.3 (d, *J* = 9.6 Hz), 133.4, 128.9 (d, *J* = 3.9 Hz), 128.3, 127.2, 124.8 (d, *J* = 7.7 Hz), 123.9, 120.3 (d, *J* = 2.9 Hz), 116.4 (d, *J* = 19.3 Hz), 109.5 (d, *J* = 3.9 Hz), 108.1 (d, *J* = 20.2 Hz), 66.7, 47.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ –116.4. HRMS (FD) Calcd for $C_{19}H_{17}FN_2O_2$: $[M]^+$, 324.1269. Found: *m/z* 324.1246.



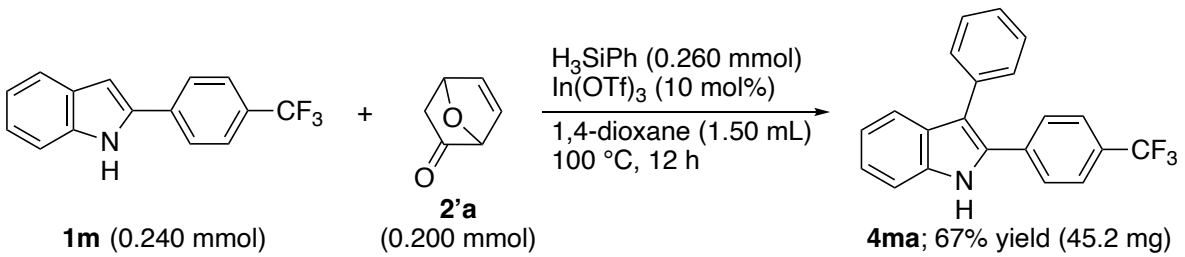
Compound 4ka. Compound **4ka** was synthesized based on conditions A using the following reagents: **1k** (71.2 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ka** was isolated by column chromatography on silica gel (benzene/EtOAc = 7/1) in 45% yield (38.9 mg) as a white solid (mp 104–106 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.82–7.80 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.67–7.65 (m, 2H), 7.51–7.47 (m, 2H), 7.43 (s, 1H), 7.37 (tt, *J* = 7.5, 1.3 Hz, 1H), 3.80 (t, *J* = 4.9 Hz, 4H), 3.64 (t, *J* = 4.9 Hz, 4H), 1.36 (s, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0, 137.8, 133.7, 130.4, 128.9, 128.1, 127.7, 127.6, 127.1, 123.3, 122.0, 112.7, 83.7, 66.7,

47.1, 24.9, $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.8. HRMS (FD) Calcd for $C_{25}H_{29}BN_2O_4$: $[M]^+$, 432.2215. Found: *m/z* 432.2185.



1l (0.240 mmol) **2'a** (0.200 mmol) **4la**; 50% yield (28.3 mg)

Compound 4la. Compound **4la** was synthesized based on conditions B using the following reagents: **1l** (49.8 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4la** was isolated by column chromatography on silica gel twice (hexane/benzene = 2/3) in 50% yield (28.3 mg) as a white solid. Compound **4la** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[20] Accordingly, only ^1H NMR data are provided here. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.46–7.41 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.33–7.21 (m, 4H), 7.16–7.12 (m, 3H), 2.35 (s, 3H).

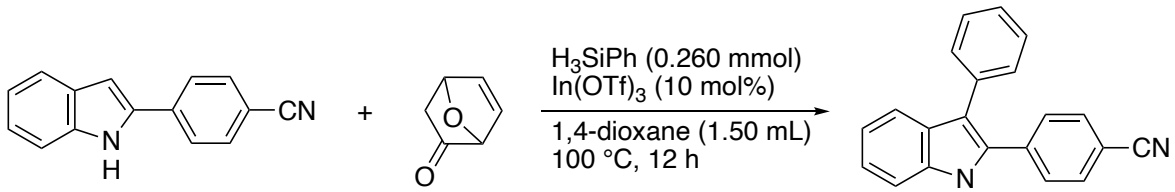


1m (0.240 mmol) **2'a** (0.200 mmol) **4ma**; 67% yield (45.2 mg)

Compound 4ma. Compound **4ma** was synthesized based on conditions B using the following reagents: **1m** (62.7 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ma** was isolated by recrystallization from hexane/$CHCl_3$ after column chromatography on silica gel twice (hexane/benzene = 3/2) in 67% yield (45.2 mg) as a white solid. Compound **4ma** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[21] Accordingly, only ^1H NMR data are provided here. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.58–7.51 (m, 4H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.43–7.31

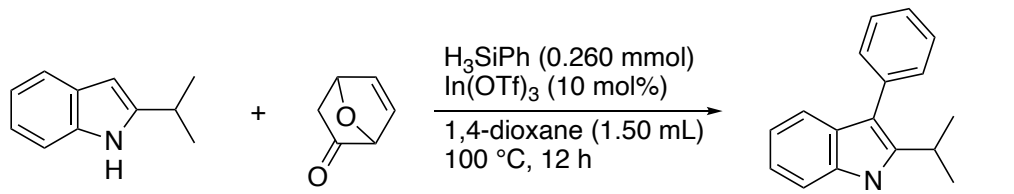
[20] R. K. Maurya, O. P. S. Patel, D. Anand, P. P. Yadav, *Org. Chem. Front.* **2018**, *5*, 1170–1175.
[21] J. Wang, G. Wang, X. Cheng, Y. Liu, J. Zhang, *Org. Biomol. Chem.* **2021**, *19*, 1329–1333.

(m, 5H), 7.28 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.17 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H).



1n (0.240 mmol) **2'a** (0.200 mmol) **4na**; 73% yield (43.0 mg)

Compound 4na. Compound **4na** was synthesized based on conditions B using the following reagents: **1n** (52.4 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4na** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 73% yield (43.0 mg) as a bright yellow solid. Compound **4na** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[22] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.60–7.58 (m, 2H), 7.52–7.50 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.44–7.33 (m, 5H), 7.30 (ddd, J = 7.9, 7.0, 1.2 Hz, 1H), 7.18 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H).

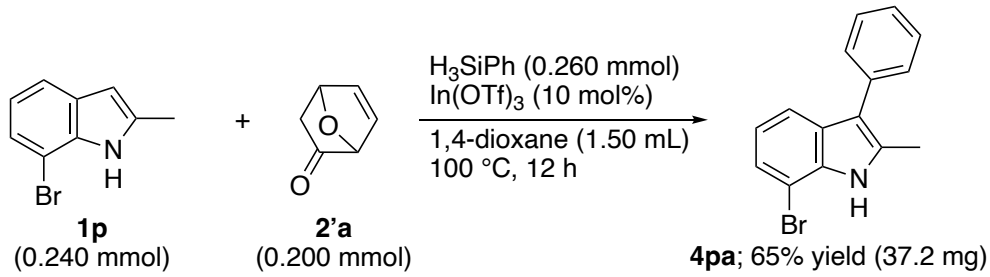


1o (0.240 mmol) **2'a** (0.200 mmol) **4oa**; 40% yield (18.8 mg)

Compound 4oa. Compound **4oa** was synthesized based on conditions B using the following reagents: **1o** (38.2 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4oa** was isolated by column chromatography on silica gel (hexane/EtOAc = 10/1) in 40% yield (18.8 mg) as a white solid. Compound **4oa** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[23] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.50–7.44 (m, 4H), 7.37

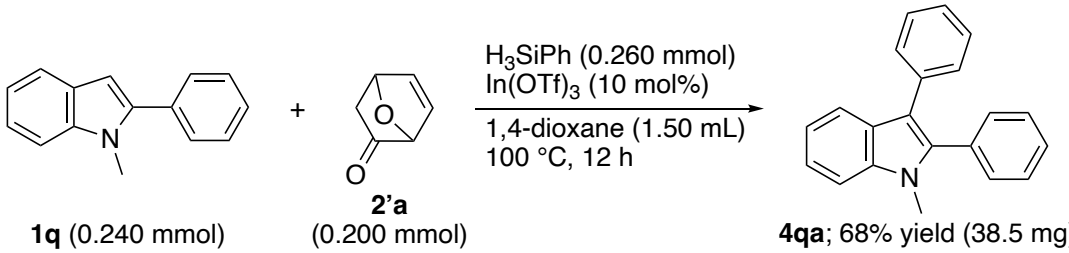
[22] J.-H. Chen, Z.-C. Chen, H. Zhao, T. Zhang, W.-J. Wang, Y. Zou, X.-J. Zhang, M. Yan, *Org. Biomol. Chem.* **2016**, *14,* 4071–4076.
[23] P. K. R. Panyam, T. Gandhi, *Adv. Synth. Catal.* **2017**, *359,* 1144–1151.

(d, J = 7.8 Hz, 1H), 7.34–7.29 (m, 1H), 7.18 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.10 (td, J = 7.5, 0.9 Hz, 1H), 3.41 (sept, J = 7.0 Hz, 1H), 1.34 (d, J = 6.9 Hz, 6H).



1p (0.240 mmol) **2'a** (0.200 mmol) **4pa**; 65% yield (37.2 mg)

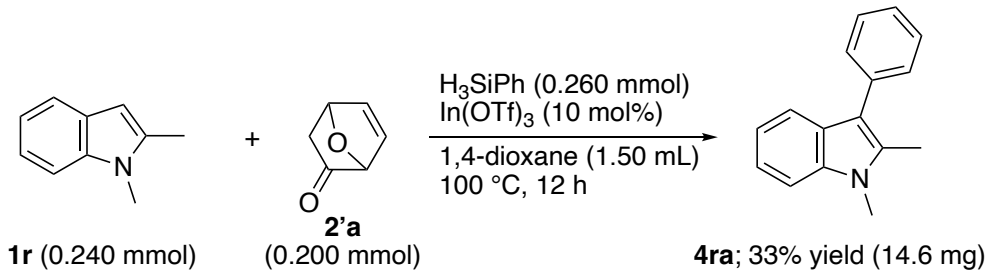
Compound 4pa. Compound **4pa** was synthesized based on conditions B using the following reagents: **1p** (50.4 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4pa** was isolated by column chromatography on silica gel (hexane/EtOAc = 20/1) in 65% yield (37.2 mg) as a white solid (mp 73–75 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.50–7.44 (m, 4H), 7.34–7.30 (m, 2H), 6.99 (t, J = 7.8 Hz, 1H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.9, 133.9, 132.2, 129.4, 129.1, 128.6, 126.2, 123.8, 121.1, 118.1, 115.8, 104.0, 12.5. HRMS (FD) Calcd for $C_{15}H_{12}{}^{79}BrN$: $[M]^+$, 285.0148. Found: *m/z* 285.0134.



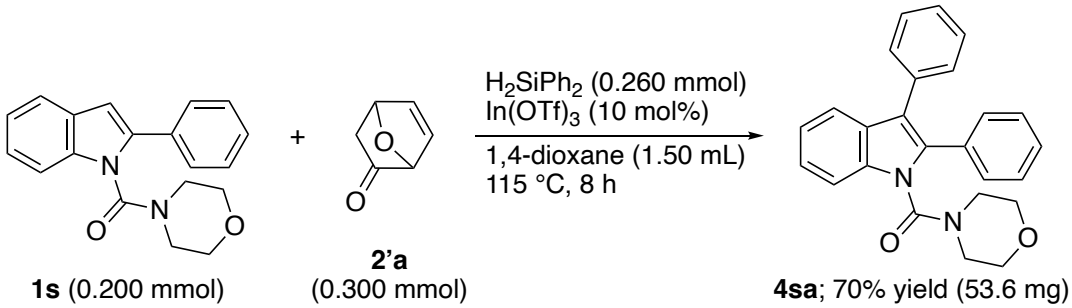
1q (0.240 mmol) **2'a** (0.200 mmol) **4qa**; 68% yield (38.5 mg)

Compound 4qa. Compound **4qa** was synthesized based on conditions B using the following reagents: **1q** (49.8 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4qa** was isolated by column chromatography on silica gel twice (hexane/benzene = 4/1) in 68% yield (38.5 mg) as a white solid. Compound **4qa** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[24] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.40–7.36 (m, 3H), 7.35–7.28 (m, 5H), 7.28–7.25 (m, 2H), 7.21–7.15 (m, 2H), 3.69 (s, 3H).

[24] X. Huang, W. Liang, Y. Shi, J. You, *Chem. Commun.* **2016**, *52,* 6253–6256.



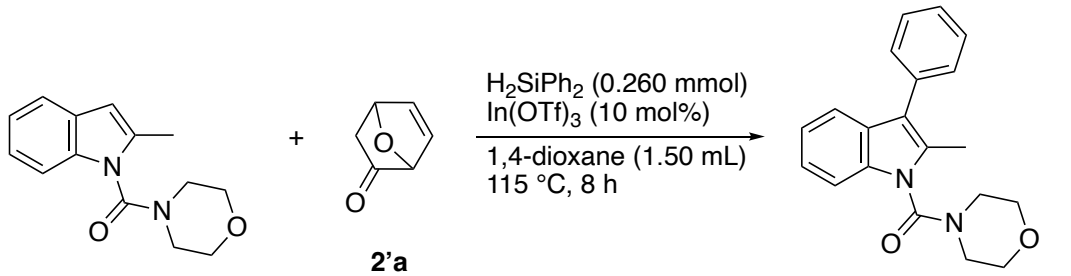
Compound 4ra. Compound **4ra** was synthesized based on conditions B using the following reagents: **1r** (34.8 mg, 0.240 mmol), **2'a** (22.0 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ra** was isolated by column chromatography on silica gel (hexane/EtOAc = 30/1) in 33% yield (14.6 mg) as a white solid. Compound **4ra** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[25] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 1H), 7.51–7.44 (m, 4H), 7.33–7.27 (m, 2H), 7.23–7.19 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 3.75 (s, 3H), 2.49 (s, 3H).



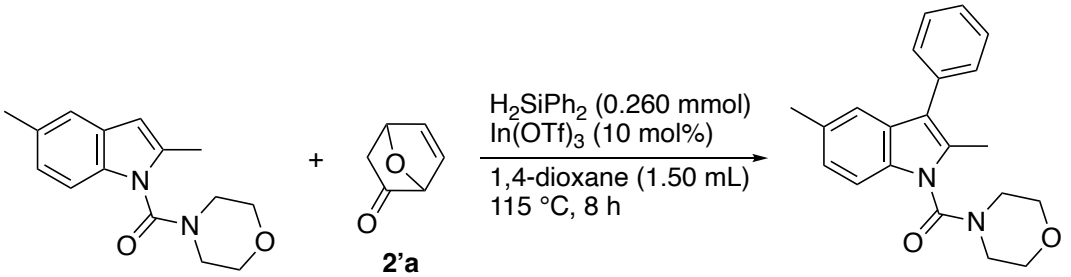
Compound 4sa. Compound **4sa** was synthesized based on conditions A using the following reagents: **1s** (61.3 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). A portion of compound **4sa** was purified by recrystallization from CH_2Cl_2/hexane after column chromatography on silica gel (benzene/EtOAc = 20/1). The remaining residue, which could not be purified by the above procedure, was further purified by recycling GPC. The combined fractions provided **4sa** in 70% yield (53.6 mg) as an orange solid (mp 169–170 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.36–7.27 (m, 11H), 7.23 (t, J = 7.7 Hz, 1H), 3.52–2.98 (br

[25] Y. Li, R. Wang, T. Wang, X.-F. Cheng, X. Zhou, F. Fei, X.-S. Wang, *Angew. Chem. Int. Ed.* **2017**, *56,* 15436–15440.

m, 8H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 152.8, 135.9, 134.4, 133.8, 131.0, 130.2, 129.9, 128.5, 128.3, 128.2, 126.7, 124.0, 121.9, 119.9, 118.0, 111.4, 66.1, 45.4 (br) (One carbon signal is missing due to overlapping.). HRMS (FD) Calcd for $C_{25}H_{22}N_2O_2$: $[M]^+$, 382.1676. Found: *m/z* 382.1686.

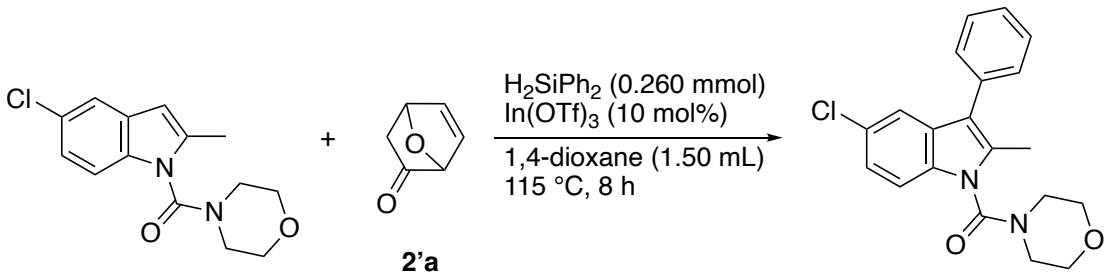


Compound 4ta. Compound **4ta** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ta** was isolated by column chromatography on silica gel (hexane/EtOAc = 3/1) in 88% yield (56.4 mg) as a white solid (mp 79–81 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.50–7.46 (m, 4H), 7.38–7.33 (m, 2H), 7.27–7.23 (m, 1H), 7.19–7.16 (m, 1H), 3.83–3.72 (br m, 4H), 3.60 (br s, 4H), 2.51 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.2, 134.7, 134.1, 132.3, 129.7, 128.6, 128.2, 126.6, 122.9, 121.6, 119.4, 118.2, 110.7, 66.9, 46.5 (br), 11.9. HRMS (FD) Calcd for $C_{20}H_{20}N_2O_2$: $[M]^+$, 320.1519. Found: *m/z* 320.1498.



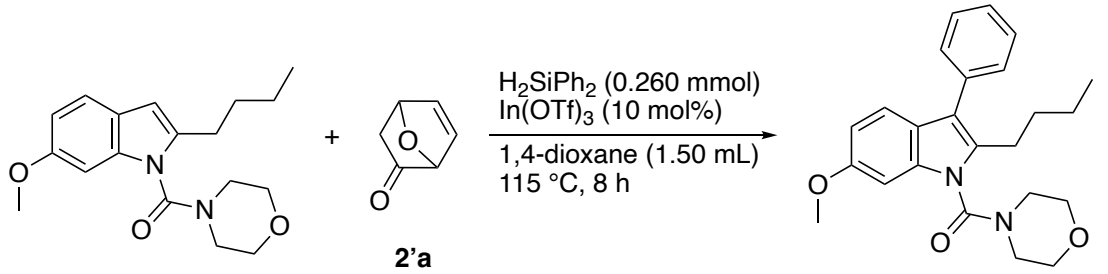
Compound 4ua. Compound **4ua** was synthesized based on conditions A using the following reagents: **1u** (51.7 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ua** was isolated by column chromatography on silica gel (hexane/EtOAc = 4/1) in 78% yield (52.2 mg) as a white solid (mp 118–119 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 4H), 7.37–7.33 (m, 2H), 7.23 (d, J = 8.2 Hz, 1H), 7.07 (dd, J = 8.5, 1.1 Hz, 1H), 3.83–3.70 (m, 4H), 3.60 (br s, 4H), 2.49

(s, 3H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.4, 134.3, 133.0, 132.5, 131.1, 129.8, 128.55, 128.46, 126.6, 124.3, 119.2, 118.0, 110.5, 66.9, 46.5 (br), 21.4, 12.0. HRMS (FD) Calcd for $C_{21}H_{22}N_2O_2$: $[M]^+$, 334.1676. Found: *m/z* 334.1648.



1v (0.200 mmol) **2'a** (0.300 mmol) **4va**; 81% yield (57.5 mg)

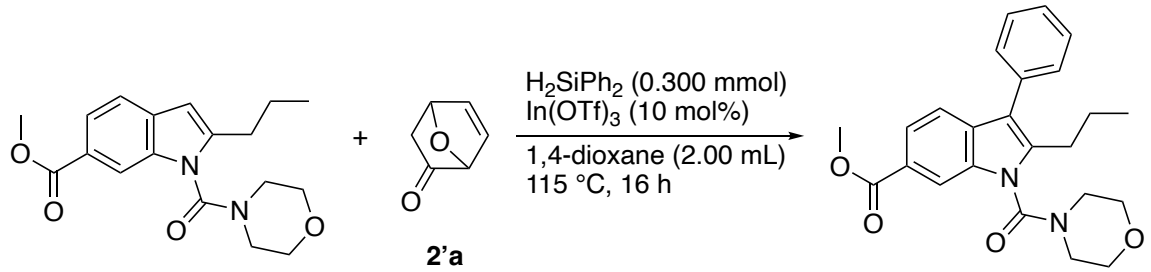
Compound 4va. Compound **4va** was synthesized based on conditions A using the following reagents: **1v** (55.7 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4va** was isolated by column chromatography on silica gel twice (benzene/EtOAc = 20/1) in 81% yield (57.5 mg) as a white solid (mp 73–75 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.7 Hz, 1H), 7.50–7.47 (m, 2H), 7.45–7.43 (m, 2H), 7.37 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.20 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.82–3.72 (br m, 4H), 3.58 (br s, 4H), 2.50 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 133.8, 133.4, 133.1, 129.6, 129.4, 128.7, 127.4, 126.9, 123.1, 119.0, 117.9, 111.6, 66.9, 46.4 (br), 12.0. HRMS (FD) Calcd for $C_{20}H_{19}{}^{35}ClN_2O_2$: $[M]^+$, 354.1130. Found: *m/z* 354.1103.



1w (0.200 mmol) **2'a** (0.300 mmol) **4wa**; 92% yield (72.2 mg)

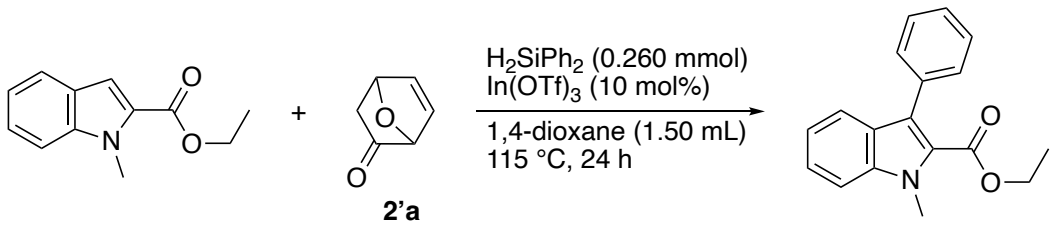
Compound 4wa. Compound **4wa** was synthesized based on conditions A using the following reagents: **1w** (63.3 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4wa** was isolated by column chromatography on silica gel (benzene/EtOAc = 25/1) in 92% yield (72.2 mg) as an orange gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 4H), 7.41 (d, *J* = 8.7 Hz, 1H),

7.36–7.32 (m, 1H), 6.85 (d, J = 2.3 Hz, 1H), 6.81 (dd, J = 8.7, 2.3 Hz, 1H), 3.86 (s, 3H), 3.85–3.62 (m, 8H), 2.96–2.91 (m, 2H), 1.52 (quint, J = 7.6 Hz, 2H), 1.26 (sext, J = 7.4 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.0, 153.4, 135.9, 135.6, 134.4, 129.8, 128.5, 126.6, 122.6, 120.1, 118.5, 110.0, 95.6, 66.8, 55.9, 46.3 (br), 32.3, 24.7, 22.3, 13.8. HRMS (FD) Calcd for $C_{24}H_{28}N_2O_3$: $[M]^+$, 392.2094. Found: *m/z* 392.2065.



1x (0.200 mmol) **2'a** (0.400 mmol) **4xa**; 41% yield (33.3 mg)

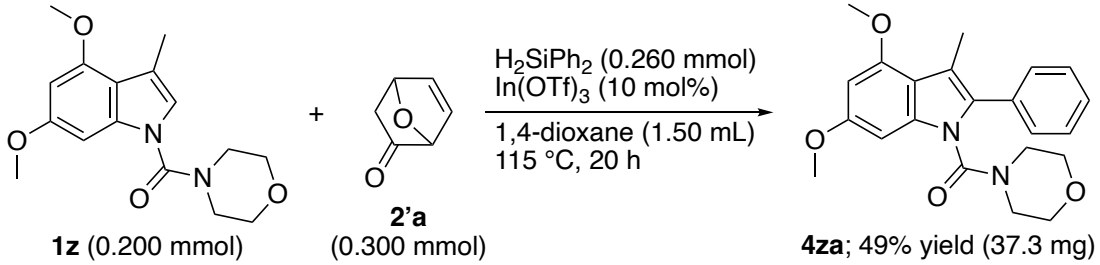
Compound 4xa. Compound **4xa** was synthesized based on conditions A using the following reagents: **1x** (66.1 mg, 0.200 mmol), **2'a** (44.0 mg, 0.400 mmol), H_2SiPh_2 (55.3 mg, 0.300 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (2.00 mL). Compound **4xa** was isolated by recycling GPC and recycling HPLC (hexane/EtOAc = 2/1) after column chromatography on silica gel (hexane/EtOAc = 3/1) in 41% yield (33.3 mg) as a white solid (mp 75–76 ºC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 0.9 Hz, 1H), 7.85 (dd, J = 8.2, 1.4 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.51–7.47 (m, 2H), 7.43 (dt, J = 6.9, 1.6 Hz, 2H), 7.38 (tt, J = 7.1, 1.6 Hz, 1H), 3.95 (s, 3H), 3.89–3.65 (m, 8H), 2.97 (br s, 2H), 1.61 (sext, J = 7.5 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 152.7, 140.8, 134.1, 133.5, 132.0, 129.9, 128.7, 127.1, 124.6, 122.7, 119.15, 119.10, 112.6, 66.6, 52.2, 46.0 (br), 27.1, 23.2, 13.9. HRMS (FD) Calcd for $C_{24}H_{26}N_2O_4$: $[M]^+$, 406.1887. Found: *m/z* 406.1862.



1y (0.200 mmol) **2'a** (0.300 mmol) **4ya**; 75% yield (41.9 mg)

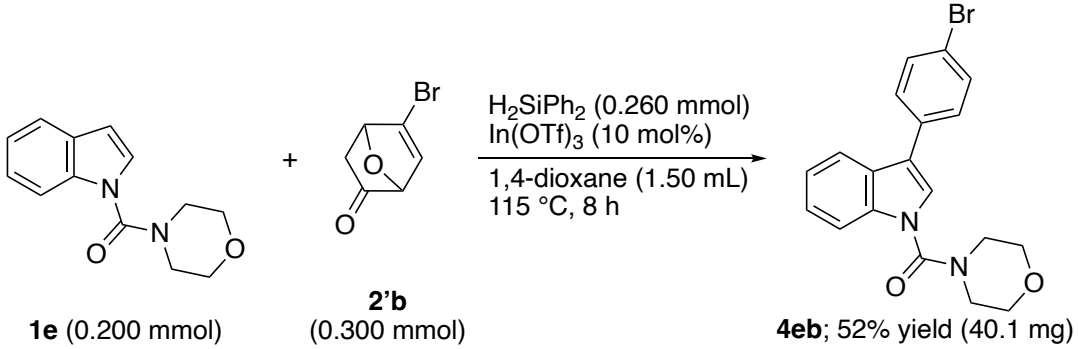
Compound 4ya. Compound **4ya** was synthesized based on conditions A using the following reagents: **1y** (40.6 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4ya** was isolated

by column chromatography on silica gel (hexane/EtOAc = 20/1) in 75% yield (41.9 mg) as a colorless oil. Compound **4ya** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[26] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 1H), 7.44–7.33 (m, 7H), 7.14 (ddd, J = 8.0, 6.6, 1.4 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 4.08 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).



1z (0.200 mmol) **2'a** (0.300 mmol) **4za**; 49% yield (37.3 mg)

Compound 4za. Compound **4za** was synthesized based on conditions A using the following reagents: **1z** (60.9 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4za** was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 2/1) in 49% yield (37.3 mg) as a yellow solid (mp 156–175 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 4H), 7.35 (tt, J = 6.9, 2.1 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 6.26 (d, J = 2.3 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.47–3.00 (br m, 8H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 155.5, 153.5, 137.7, 131.7, 131.6, 129.3, 128.4, 127.5, 113.5, 112.8, 93.3, 87.1, 66.1, 55.7, 55.3, 45.7 (br), 11.7. HRMS (FD) Calcd for $C_{22}H_{24}N_2O_4$: $[M]^+$, 380.1731. Found: *m/z* 380.1714.

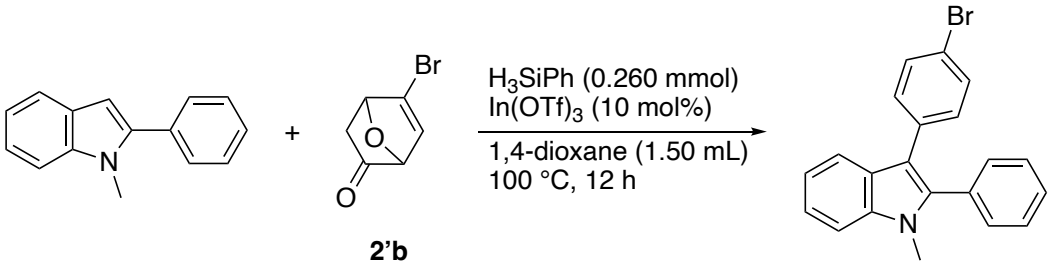


1e (0.200 mmol) **2'b** (0.300 mmol) **4eb**; 52% yield (40.1 mg)

Compound 4eb. Compound **4eb** was synthesized based on conditions A using the following reagents: **1e** (46.1 mg, 0.200 mmol), **2'b** (56.7 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg,

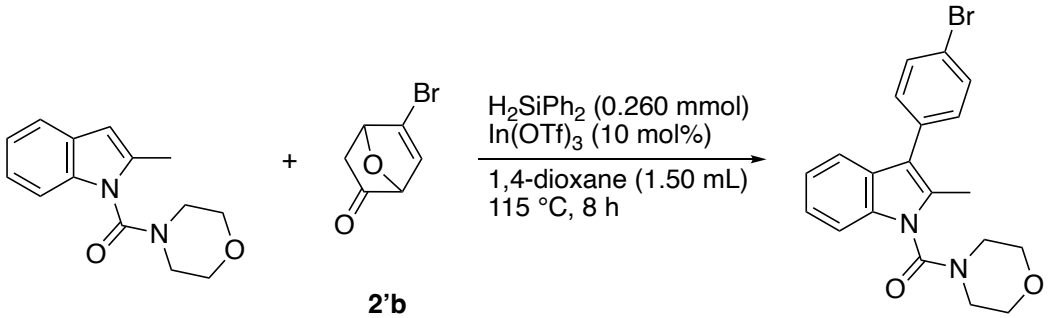
[26] X. Wang, B. Han, J. Wang, W. Yu, *Org. Biomol. Chem.* **2010**, *8,* 3865–3867.

0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4eb** was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 3/1) in 52% yield (40.1 mg) as a white solid (mp 53–56 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.61–7.57 (m, 2H), 7.52–7.49 (m, 2H), 7.45 (s, 1H), 7.37 (td, J = 7.7, 1.2 Hz, 1H), 7.31–7.27 (m, 1H), 3.80 (t, J = 4.8 Hz, 4H), 3.65 (t, J = 4.8 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0, 135.9, 132.8, 132.0, 129.3, 127.6, 124.4, 123.3, 122.6, 120.9, 120.3, 120.0, 113.5, 66.7, 47.1. HRMS (FD) Calcd for $C_{19}H_{17}{}^{79}BrN_2O_2$: $[M]^+$, 384.0468. Found: *m/z* 384.0468.



1q (0.240 mmol) **2'b** (0.200 mmol) **4qb**; 74% yield (53.6 mg)

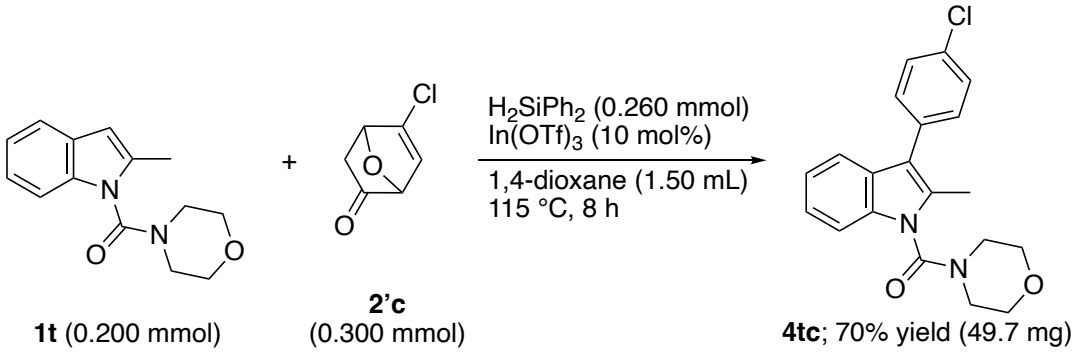
Compound 4qb. Compound **4qb** was synthesized based on conditions B using the following reagents: **1q** (49.8 mg, 0.240 mmol), **2'b** (37.8 mg, 0.200 mmol), H_3SiPh (28.1 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4qb** was isolated by column chromatography on silica gel twice (hexane/EtOAc = 30/1) in 74% yield (53.6 mg) as a yellow solid. Compound **4qb** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[27] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 1H), 7.42–7.36 (m, 6H), 7.33–7.29 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.17–7.14 (m, 2H), 3.67 (s, 3H).



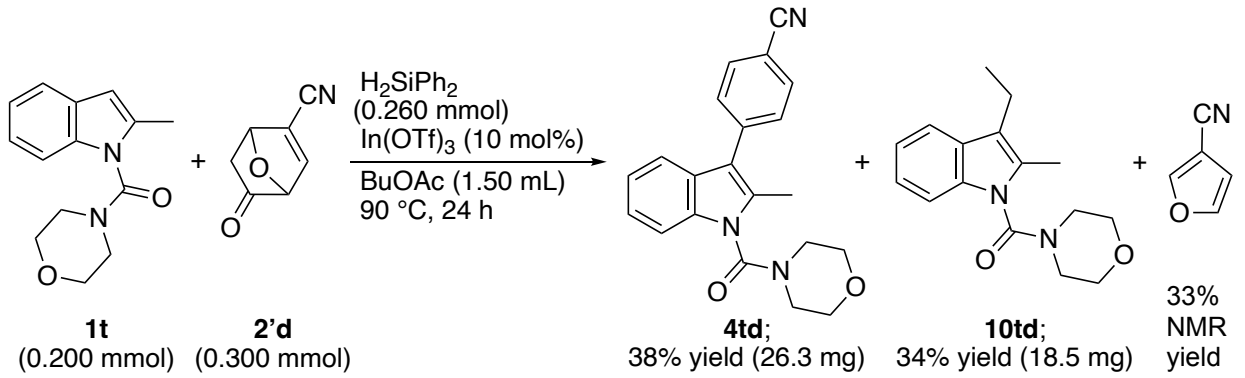
1t (0.200 mmol) **2'b** (0.300 mmol) **4tb**; 85% yield (67.9 mg)

[27] Y.-G. Luo, R. S. Basha, D. M. Reddy, Y.-J. Xue, T.-H. Chen, C.-F. Lee, *Org. Lett*. **2018**, *20*, 6872−6876.

Compound 4tb. Compound **4tb** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'b** (56.7 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4tb** was isolated by column chromatography on silica gel (benzene/EtOAc = 14/1) in 85% yield (67.9 mg) as a white solid (mp 140–142 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.37–7.33 (m, 3H), 7.28–7.24 (m, 1H), 7.20–7.16 (m, 1H), 3.84–3.70 (br m, 4H), 3.60 (br s, 4H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.9, 134.7, 133.1, 132.5, 131.7, 131.3, 127.8, 123.1, 121.8, 120.5, 119.1, 117.1, 110.8, 66.9, 46.4 (br), 11.9. HRMS (FD) Calcd for $C_{20}H_{19}{}^{79}BrN_2O_2$: $[M]^+$, 398.0624. Found: *m/z* 398.0601.



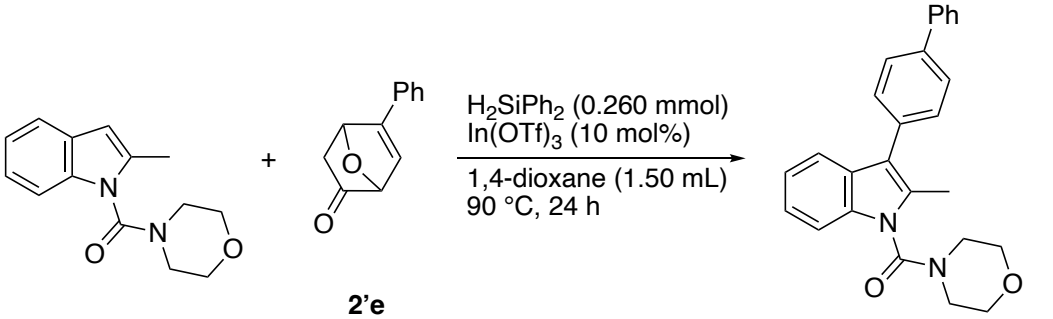
Compound 4tc. Compound **4tc** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'c** (43.4 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4tc** was isolated by column chromatography on silica gel twice (benzene/EtOAc = 20/1) in 70% yield (49.7 mg) as a white solid (mp 118–120 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.47–7.44 (m, 2H), 7.43–7.39 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28–7.24 (m, 1H), 7.20–7.16 (m, 1H), 3.84–3.71 (br m, 4H), 3.60 (br s, 4H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.0, 134.7, 132.6, 132.53, 132.47, 130.9, 128.8, 127.9, 123.1, 121.8, 119.2, 117.1, 110.8, 66.9, 46.4 (br), 11.9. HRMS (FD) Calcd for $C_{20}H_{19}{}^{35}ClN_2O_2$: $[M]^+$, 354.1130. Found: *m/z* 354.1118.



Compound 4td. Compound **4td** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'd** (40.5 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), BuOAc (1.50 mL). Compound **4td** was isolated by column chromatography on silica gel (benzene/EtOAc = 15/1) in 38% yield (26.3 mg) as a yellow solid (mp 196–197 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.62–7.59 (m, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.29 (td, J = 7.7, 1.1 Hz, 1H), 7.23–7.19 (m, 1H), 3.85–3.70 (br m, 4H), 3.60 (br s, 4H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.6, 139.4, 134.8, 133.4, 132.4, 130.1, 127.3, 123.5, 122.2, 119.1, 119.0, 116.6, 110.9, 110.0, 66.9, 46.4 (br), 12.0. HRMS (FD) Calcd for $C_{21}H_{19}N_3O_2$: $[M]^+$, 345.1472. Found: *m/z* 345.1443.

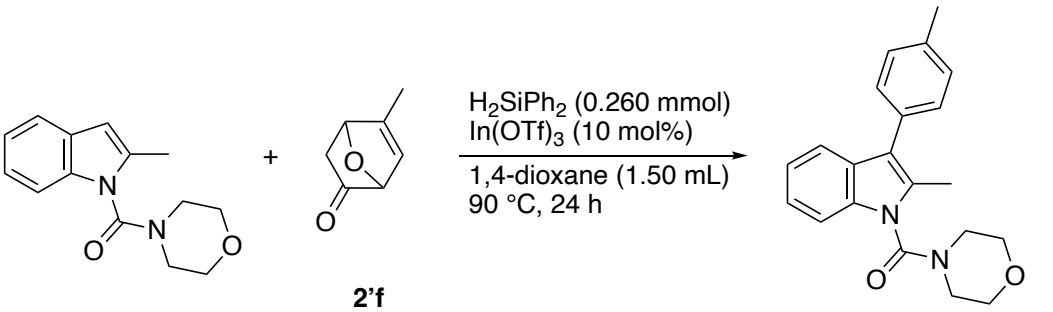
Compound 10td. Compound **10td** was generated as one of the two major by-products along with **4td**. Compound **10td** was isolated by recycling HPLC (hexane/EtOAc = 4/1) after column chromatography on silica gel (benzene/EtOAc = 15/1) in 34% yield (18.5 mg) as a white solid (mp 104–106 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.1, 1.6 Hz, 1H), 7.29 (dd, J = 7.3, 1.4 Hz, 1H), 7.21–7.13 (m, 2H), 3.78 (dt, J = 11.4, 4.8 Hz, 2H), 3.71 (dt, J = 11.9, 5.1 Hz, 2H), 3.54 (br s, 4H), 2.70 (q, J = 7.5 Hz, 2H), 2.40 (s, 3H), 1.22 (t, J = 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.6, 134.7, 131.3, 128.8, 122.3, 120.9, 118.5, 117.9, 110.7, 66.9, 46.4 (br), 17.3, 15.0, 10.9. HRMS (FD) Calcd for $C_{16}H_{20}N_2O_2$: $[M]^+$, 272.1519. Found: *m/z* 272.1531.

3-Cyanofuran. The title compound was also produced as one of the two major by-products along with **4td**. 3-Cyanofuran is commercially available. Not only ^{1}H NMR spectral data but also GC retention time of the by-product are in good agreement with those of commercially available 3-cyanofuran. Accordingly, the structure of the by-product was identified as 3-cyanofuran, and only ^{1}H NMR spectral data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 1.7 Hz, 1H), 7.49 (t, J = 1.7 Hz, 1H), 6.62 (d, J = 1.2 Hz, 1H). The yield of 3-cyanofuran was determined by ^{1}H NMR using nitromethane as an internal standard.



1t (0.200 mmol) **2'e** (0.300 mmol) **4te**; 25% yield (19.8 mg)

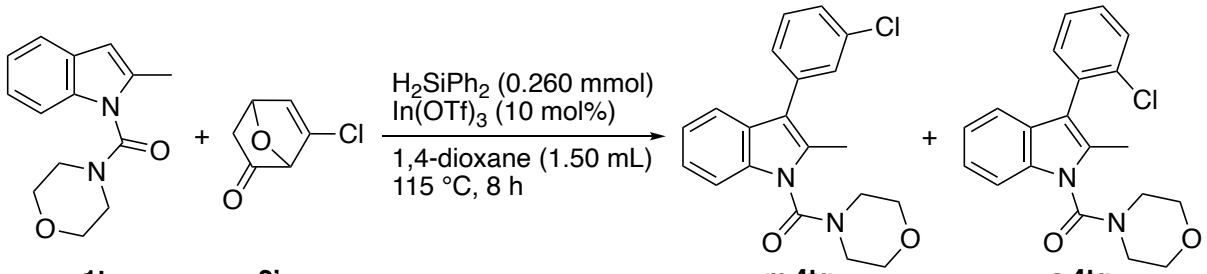
Compound 4te. Compound **4te** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'e** (55.9 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4te** was isolated by recycling GPC and recycling HPLC (hexane/EtOAc = 3/1) after column chromatography on silica gel (hexane/EtOAc = 3/1) in 25% yield (19.8 mg) as a white solid (mp 164–165 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.70 (m, 2H), 7.69–7.65 (m, 3H), 7.59–7.55 (m, 2H), 7.50–7.45 (m, 2H), 7.39–7.35 (m, 2H), 7.29–7.25 (m, 1H), 7.20 (td, *J* = 7.4, 1.1 Hz, 1H), 3.85–3.72 (br m, 4H), 3.62 (br s, 4H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.1, 140.9, 139.4, 134.7, 133.1, 132.5, 130.0, 128.8, 128.2, 127.3, 127.0, 123.0, 121.7, 119.5, 117.8, 110.7, 66.9, 46.5 (br), 12.1 (One carbon signal is missing due to overlapping.). HRMS (FD) Calcd for $C_{26}H_{24}N_2O_2$: $[M]^+$, 396.1832. Found: *m/z* 396.1809.



1t (0.200 mmol) **2'f** (0.300 mmol) **4tf**; 51% yield (34.1 mg)

Compound 4tf. Compound **4tf** was synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'f** (37.2 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4tf** was isolated by recycling HPLC (hexane/EtOAc = 3/1) after column chromatography on silica gel (hexane/EtOAc = 3/1) in 51% yield (34.1 mg) as a white solid (mp 115–118 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.39–7.36 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30–7.28 (m, 2H), 7.26–7.22 (m, 1H),

7.18–7.14 (m, 1H), 3.83–3.70 (br m, 4H), 3.60 (br s, 4H), 2.49 (s, 3H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.2, 136.3, 134.7, 132.1, 131.1, 129.6, 129.3, 128.4, 122.8, 121.6, 119.5, 118.2, 110.7, 66.9, 46.4 (br), 21.3, 11.9. HRMS (FD) Calcd for $C_{21}H_{22}N_2O_2$: $[M]^+$, 334.1676. Found: *m/z* 334.1685.



1t (0.200 mmol) + **2'g** (0.300 mmol) → ***m*-4tg**; 58% yield (41.2 mg) + ***o*-4tg**; 8% yield (5.6 mg)

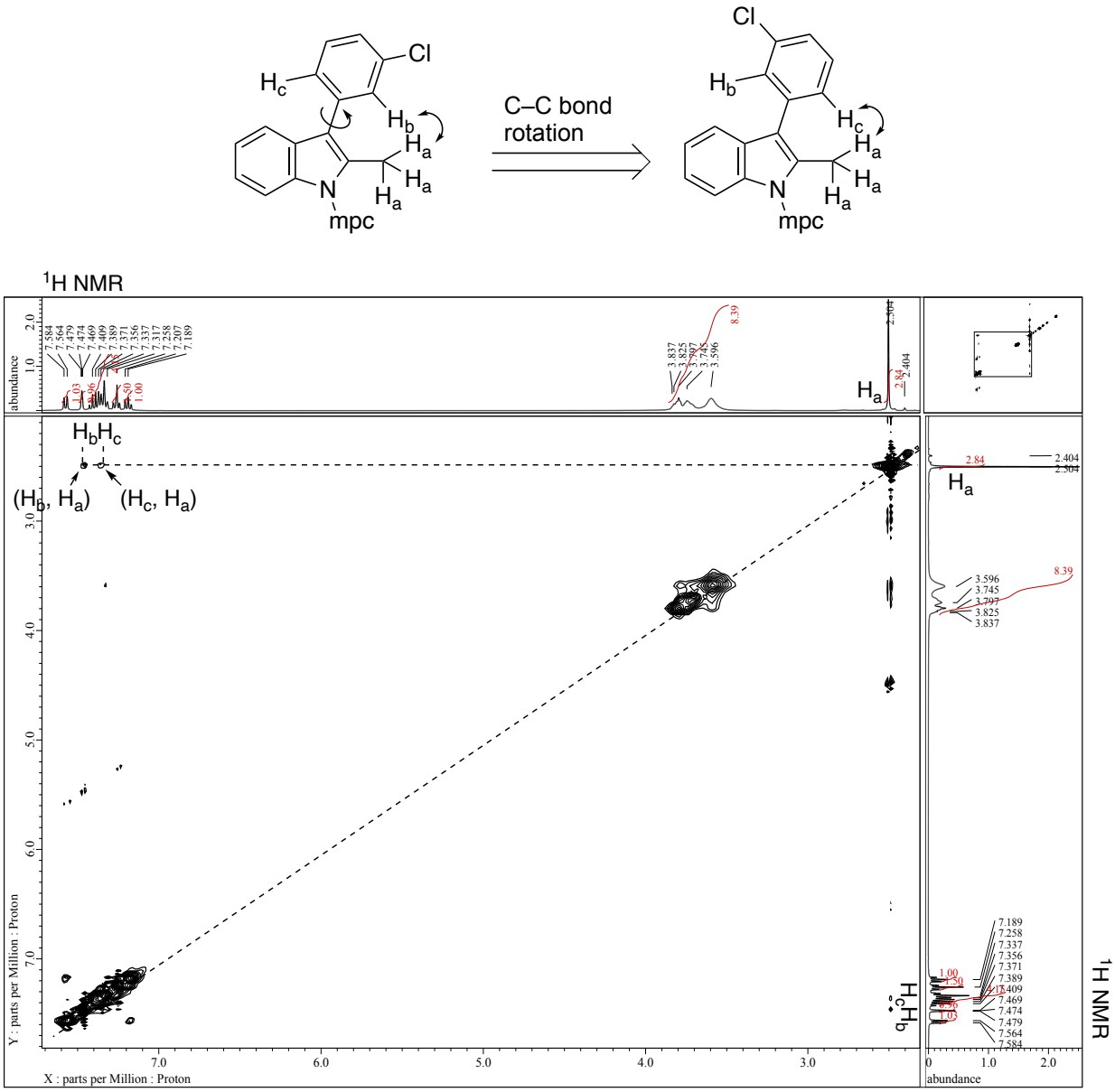
Compounds *m*-4tg and *o*-4tg. Compounds ***m*-4tg** and ***o*-4tg** were synthesized based on conditions A using the following reagents: **1t** (48.9 mg, 0.200 mmol), **2'g** (43.4 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compounds ***m*-4tg** and ***o*-4tg** were isolated by recycling HPLC (hexane/EtOAc = 2/1) after column chromatography on silica gel (benzene/EtOAc = 14/1) in 58% yield (41.2 mg) as a white solid (mp 68–71 ºC) and in 8% yield (5.6 mg) as a colorless gum, respectively.

The characterization data of ***m*-4tg**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 7.43–7.31 (m, 4H), 7.28–7.24 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 3.84–3.72 (br m, 4H), 3.60 (br s, 4H), 2.50 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.9, 136.0, 134.7, 134.4, 132.7, 129.8, 129.6, 127.9, 127.8, 126.7, 123.1, 121.8, 119.2, 116.9, 110.7, 66.9, 46.4 (br), 11.9. HRMS (FD) Calcd for $C_{20}H_{19}{}^{35}ClN_2O_2$: $[M]^+$, 354.1130. Found: *m/z* 354.1116.

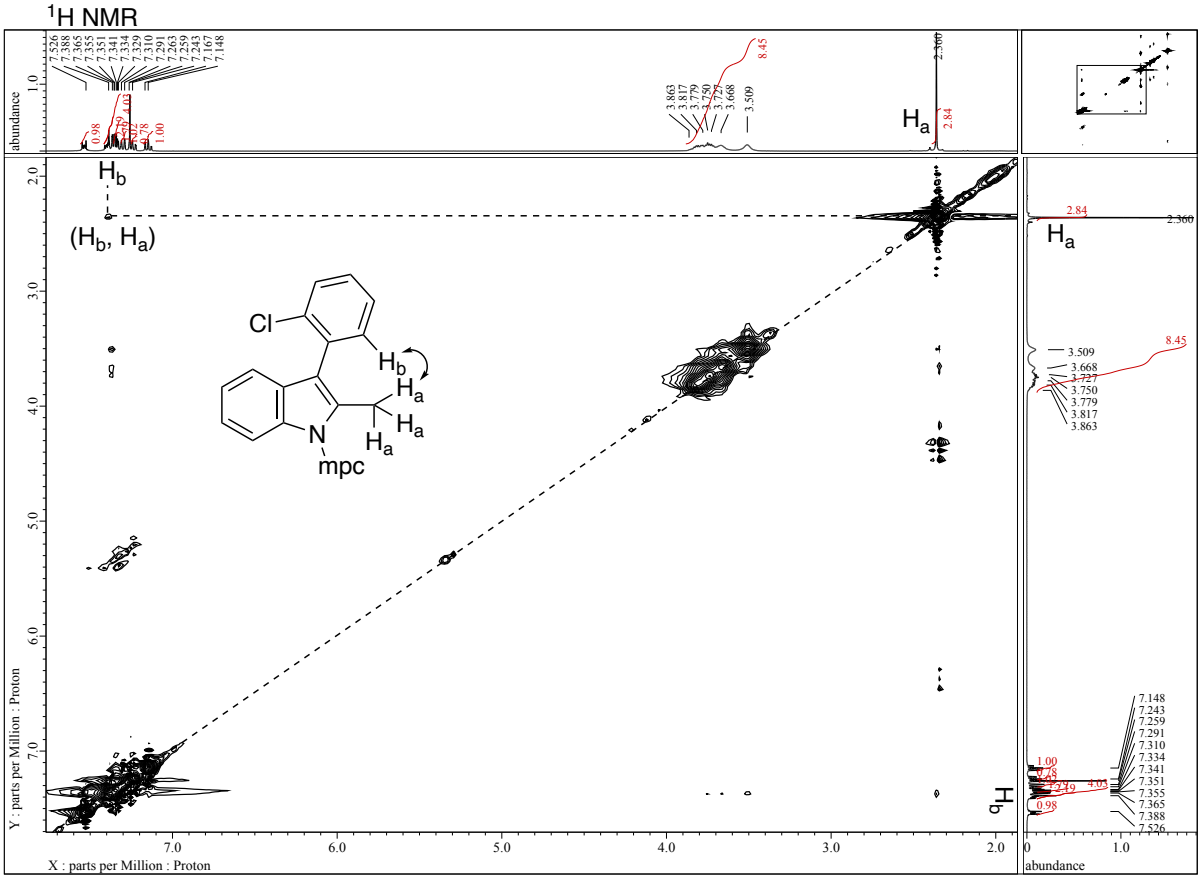
The characterization data of ***o*-4tg**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 1H), 7.41–7.33 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.26–7.22 (m, 1H), 7.17–7.13 (m, 1H), 3.86–3.51 (m, 8H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 134.7, 134.6, 133.5, 132.8, 129.9, 128.8, 128.4, 126.7, 122.8, 121.5, 119.6, 115.8, 110.7, 67.0, 66.8, 46.8 (br), 46.0 (br), 12.1 (One carbon signal in the aromatic region is missing due to overlapping.). HRMS (FD) Calcd for $C_{20}H_{19}{}^{35}ClN_2O_2$: $[M]^+$, 354.1130. Found: *m/z* 354.1130.

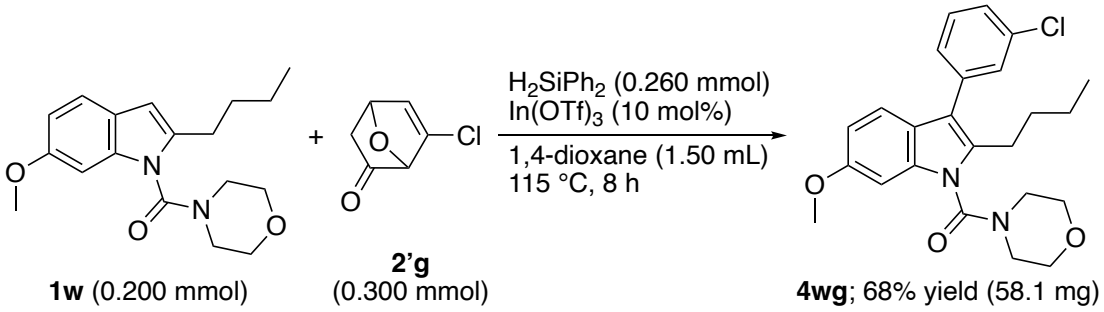
The regiochemistry of products, that is, the structures of ***m*-4tg** and ***o*-4tg** were supported by ^{1}H–^{1}H NOESY NMR experiments shown below.

A ^{1}H–^{1}H NOESY NMR spectrum of ***m*-4tg**:



A ^{1}H–^{1}H NOESY NMR spectrum of ***o*-4tg**:





1w (0.200 mmol) + **2'g** (0.300 mmol) → **4wg**; 68% yield (58.1 mg)

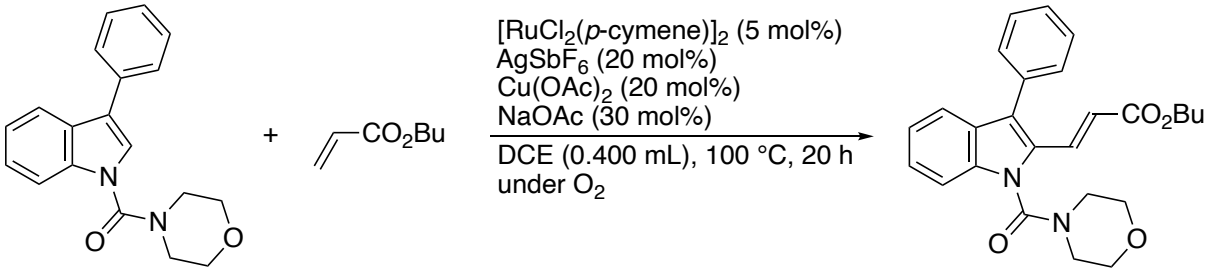
Compound 4wg. Compound **4wg** was synthesized based on conditions A using the following reagents: **1w** (63.3 mg, 0.200 mmol), **2'g** (43.4 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), 1,4-dioxane (1.50 mL). Compound **4wg** was isolated by column chromatography on silica gel (benzene/EtOAc = 15/1) in 68% yield (58.1 mg) as a yellow gum. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.43 (m, 1H), 7.41–7.37 (m, 2H), 7.33–7.31 (m, 2H), 6.84–6.81 (m, 2H), 3.86 (s, 3H), 3,85–3.61 (br m, 8H), 2.92 (br s, 2H), 1.52 (quint, J = 7.6 Hz, 2H), 1.27 (sext, J = 7.4 Hz, 2H), 0.84 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.2, 153.2, 136.3, 135.6, 134.3, 129.8, 129.7, 128.0, 126.8, 122.1, 119.8, 117.1, 110.3,

95.6, 66.8, 55.8, 46.4 (br), 32.2, 24.6, 22.3, 13.8 (One carbon signal is missing due to overlapping.). HRMS (FD) Calcd for $C_{24}H_{27}{}^{35}ClN_2O_3$: $[M]^+$, 426.1705. Found: *m/z* 426.1680.

VI. Synthetic Transformation of 1:1 Phenylation Products

Experimental procedures for the transformations shown in Schemes 8 and 9, as well as spectroscopic and analytical data for the products synthesized therein, are given in this section.

Ruthenium-Catalyzed Oxidative C2-Alkenylation of 4ea



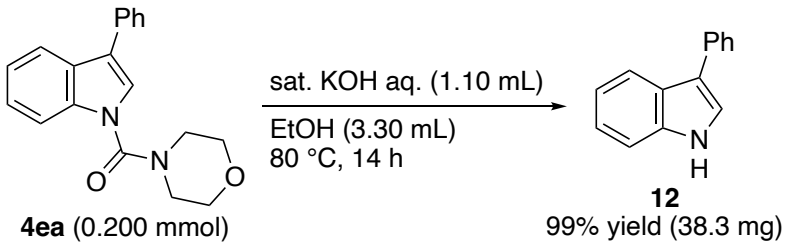
4ea (0.100 mmol) (0.150 mmol) **11**; 76% yield (32.9 mg)

This transformation was performed according to the following modified literature procedure.[28] Under an argon atmosphere, a flame-dried 20 mL Schlenk tube was charged with $Cu(OAc)_2$ (3.63 mg, 20.0 μmol), NaOAc (2.46 mg, 30.0 μmol), **4ea** (30.6 mg, 0.100 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.06 mg, 5.00 μmol), and $AgSbF_6$ (6.87 mg, 20.0 μmol). The tube was evacuated and backfilled with oxygen for three times. To this were added DCE (0.400 mL) and butyl acrylate (19.2 mg, 0.150 mmol), and the resulting mixture was stirred at 20 ℃ for 15 min and then at 100 ℃ for 20 h. After cooling to room temperature, H_2O (1 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 4). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 2/1) provided **11** in 76% yield (32.9 mg) as a yellow gum. Compound **11** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS, as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.64 (dd, *J* = 9.2, 0.9 Hz, 1H), 7.54–7.37 (m, 7H), 7.22 (ddd, *J* = 8.0, 6.4, 1.6 Hz, 1H), 6.14 (d, *J* = 16.5 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.74–3.50 (br m, 8H), 1.65 (quint, *J* = 7.1 Hz, 2H), 1.39 (sext, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,

[28] L.-Q. Zhang, S. Yang, X. Huang, J. You, F. Song, *Chem. Commun.* **2013**, *49*, 8830–8832.

$CDCl_3$) δ 166.7, 152.6, 137.2, 132.5, 131.9, 130.3, 129.5, 128.9, 127.9, 127.6, 126.6, 126.3, 122.4, 121.1, 118.5, 110.9, 66.6, 64.6, 45.9 (br), 30.7, 19.2, 13.8. HRMS (FD) Calcd for $C_{26}H_{28}N_2O_4$: $[M]^+$, 432.2044. Found: *m/z* 432.2029.

Removal of mpc Group under Reaction Conditions [a]



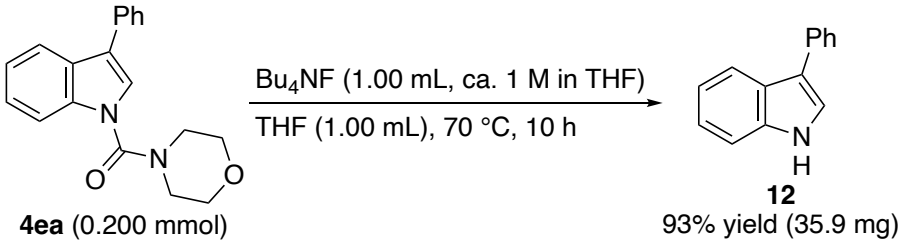
4ea (0.200 mmol)

12
99% yield (38.3 mg)

This transformation was carried out with the following modified literature procedure.[4] Under an argon atmosphere, a 50 mL Schlenk tube was charged with **4ea** (61.3 mg, 0.200 mmol), EtOH (3.30 mL), and a saturated aqueous KOH solution (1.10 mL), and the reaction mixture was stirred at 80 ºC for 14 h. After cooling to room temperature, a saturated aqueous NH_4Cl solution (20 mL) was added to neutralize the solution, and the aqueous phase was extracted with Et_2O (15 mL × 4). The combined organic layer was washed with H_2O (20 mL × 3) and with brine (20 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 4/1) afforded 3-phenyl-1*H*-indole (**12**) in 99% yield (38.3 mg) as a pale yellow solid. Compound **12** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[29] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69–7.66 (m, 2H), 7.47–7.41 (m, 3H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.31–7.23 (m, 2H), 7.22–7.18 (m, 1H).

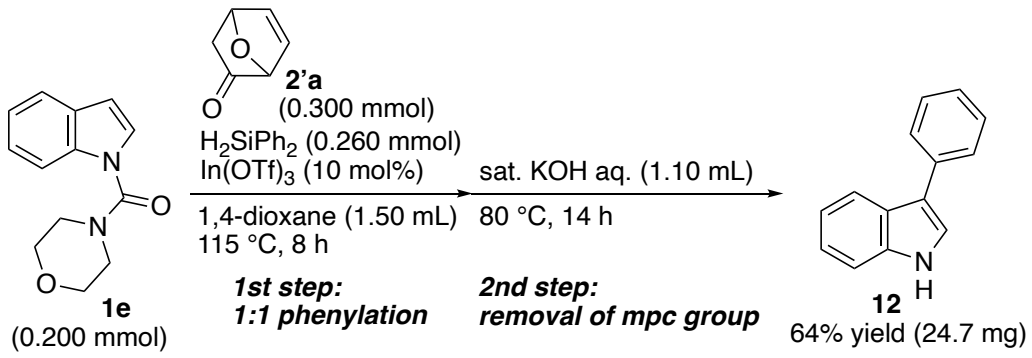
Removal of mpc Group under Reaction Conditions [b]

[29] S. Gore, S. Baskaran, B. König, *Org. Lett.* **2012**, *14*, 4568–4571.



This transformation was conducted with the following modified literature procedure.[30] Under an argon atmosphere, a flame-dried 20 mL Schlenk tube was charged with **4ea** (61.3 mg, 0.200 mmol), THF (1.00 mL), and Bu_4NF (1.00 mL, ca. 1 M in THF), and the reaction mixture was stirred at 70 ºC for 10 h. After cooling to room temperature, a saturated aqueous NH_4Cl solution (5 mL) was added, and the aqueous phase was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with a saturated aqueous NH_4Cl solution (5 mL × 3), and with brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 4/1) provided 3-phenyl-1*H*-indole (**12**) in 93% yield (35.9 mg) as a pale yellow solid. Compound **12** already appears in this section. Its ^1H NMR spectral data and literature information are thus collected there (*vide supra*).

Indium-Catalyzed 1:1 Phenylation and Removal of mpc Group Performed in One Pot

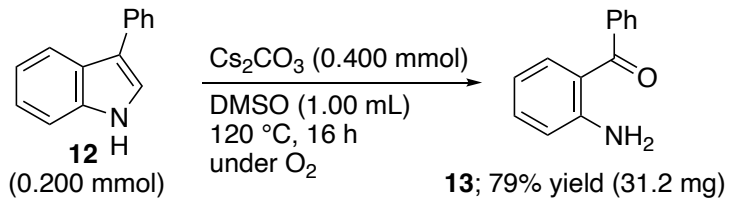


The first step was carried out according to the same procedure that is described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. Electronic Strategy and Electronic + Steric Strategy Using Conditions A in Table 2**", and the following reagents were used: **1e** (46.1 mg, 0.200 mmol), **2'a** (33.0 mg, 0.300 mmol), H_2SiPh_2

[30] H. Lv, J. Shi, B. Wu, Y. Guo, J. Huang, W. Yi, *Org. Biomol. Chem.* **2017***, 15,* 8054–8058.

(47.9 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). After the first step, the reaction mixture was cooled to room temperature. To the 20 mL Schlenk tube including a reaction mixture was added a saturated aqueous KOH solution (1.10 mL), and the resulting mixture was stirred at 80 ºC for 14 h for the second step. After cooling to room temperature, a saturated aqueous NH_4Cl solution (20 mL) was added to neutralize the solution, and the aqueous phase was extracted with Et_2O (15 mL × 4). The combined organic layer was washed with H_2O (20 mL × 3) and with brine (20 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 4/1) furnished 3-phenyl-1*H*-indole (**12**) in 64% yield (24.7 mg) as a pale yellow solid. Compound **12** already appears in this section. Its ^1H NMR spectral data and literature information are thus collected there (*vide supra*).

Dearomative Ring-Opening of 3-Phenyl-1*H*-Indole

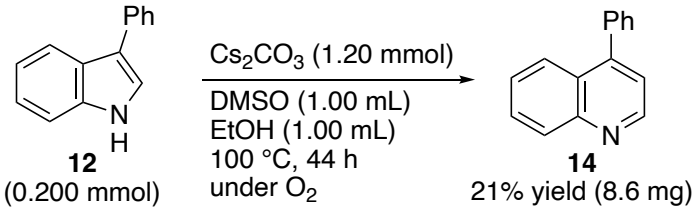


This transformation was carried out by using a modification of the procedure reported for the dearomative ring-opening of 2-aryl-1*H*-indoles.[31] Under an oxygen atmosphere, a 20 mL Schlenk tube was charged with **12** (38.6 mg, 0.200 mmol), Cs_2CO_3 (130 mg, 0.400 mmol), and DMSO (1.00 mL), and the reaction mixture was stirred at 120 ºC for 16 h. After cooling to room temperature, H_2O (5 mL) was poured into the mixture, and the aqueous phase was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with H_2O (5 mL × 3) and with brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) afforded 2-aminobenzophenone (**13**) in 79% yield (31.2 mg) as a pale yellow solid. 2-Aminobenzophenone is commercially available, and spectral and analytical data of **13** are in good agreement with those obtained from the commercial compound. Accordingly, only ^1H NMR data are provided here. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.63 (m, 2H), 7.53 (tt, J = 7.3, 1.8 Hz,

[31] S. Luo, Z. Hu, Q. Zhu, *Org. Chem. Front.* **2016**, *3*, 364–367.

1H), 7.48–7.43 (m, 3H), 7.29 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 6.75–6.73 (m, 1H), 6.60 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 6.09 (br s, 2H).

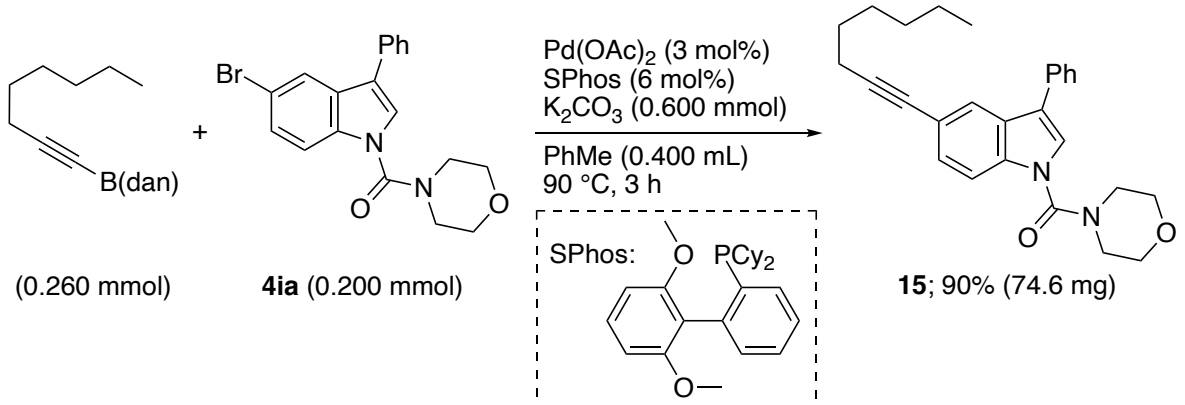
Homologative Ring-Expansion of 3-Phenyl-1*H*-Indole



Under an oxygen atmosphere, a 50 mL Schlenk tube was charged with **12** (38.6 mg, 0.200 mmol), Cs_2CO_3 (391 mg, 1.20 mmol), DMSO (1.00 mL), and EtOH (1.00 mL), and the reaction mixture was stirred at 100 ºC for 44 h. After cooling to room temperature, H_2O (5 mL) was poured into the mixture, and the aqueous phase was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with H_2O (5 mL × 3) and with brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 3/1) provided 4-phenylquinoline (**14**) in 21% yield (8.6 mg) as a pale yellow oil. Compound **14** has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[32] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.8 Hz, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.74 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 7.57–7.47 (m, 6H), 7.35 (d, *J* = 4.6 Hz, 1H).

Palladium-Catalyzed Direct Suzuki–Miyaura Coupling of HexylC≡CB(dan) with 4ia[33]

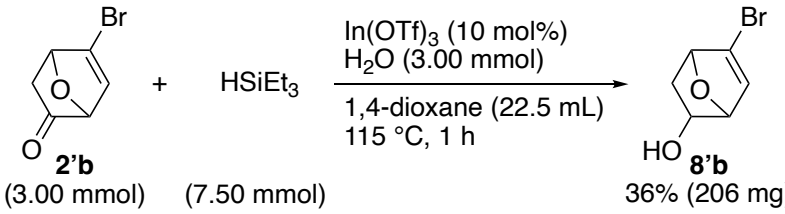
[32] T. Sasaki, K. Moriyama, H. Togo, *J. Org. Chem.* **2017**, *82*, 11727−11734.
[33] T. Tani, Y. Sawatsugawa, Y. Sano, Y. Hirataka, N. Takahashi, S. Hashimoto, T. Sugiura, T. Tsuchimoto, *Adv. Synth. Catal.* **2019***, 361,* 1815–1834.



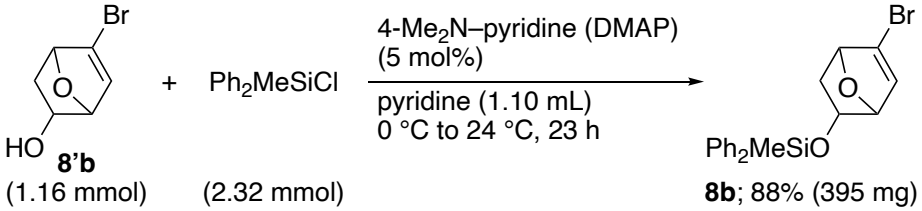
Under an argon atmosphere, a flame-dried 20 mL Schlenk tube was charged with $Pd(OAc)_2$ (1.35 mg, 6.00 μmol), SPhos (4.93 mg, 12.0 μmol), **4ia** (77.1 mg, 0.200 mmol), *n*-$C_6H_{13}C{\equiv}CB(dan)$ (71.8 mg, 0.260 mmol), K_2CO_3 (82.9 mg, 0.600 mmol), and toluene (0.400 mL), and the resulting mixture was stirred at 90 °C for 3 h. After cooling to room temperature, a saturated NH_4Cl aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with Et_2O (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by purification using recycling GPC after column chromatography on silica gel (hexane/EtOAc = 3/1) afforded **15** in 90% yield (74.6 mg) as a yellowish-green gum. Compound **15** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS, as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 0.9 Hz, 1H), 7.65–7.60 (m, 3H), 7.49–7.45 (m, 2H), 7.42 (s, 1H), 7.40 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.36 (tt, *J* = 7.3, 1,6 Hz, 1H), 3.80 (t, *J* = 4.8 Hz, 4H), 3.64 (t, *J* = 4.8 Hz, 4H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.65–1.57 (m, 2H), 1.50–1.42 (m, 2H), 1.36–1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.9, 135.0, 133.4, 128.9, 127.9, 127.8, 127.2, 123.7, 123.5, 121.4, 118.2, 113.4, 89.1, 80.9, 66.7, 47.1, 31.4, 28.8, 28.7, 22.6, 19.5, 14.1 (One carbon signal in the aromatic region is missing due to overlapping.). HRMS (FD) Calcd for $C_{27}H_{30}N_2O_2$: $[M]^+$, 414.2302. Found: m/z 414.2300.

VII. Mechanistic Studies

Experimental procedures for the reactions shown in Schemes 10 and 12, as well as spectroscopic and analytical data for the products synthesized therein, are given in this section. Firstly, the preparation of some starting substrates used for mechanistic studies is described.



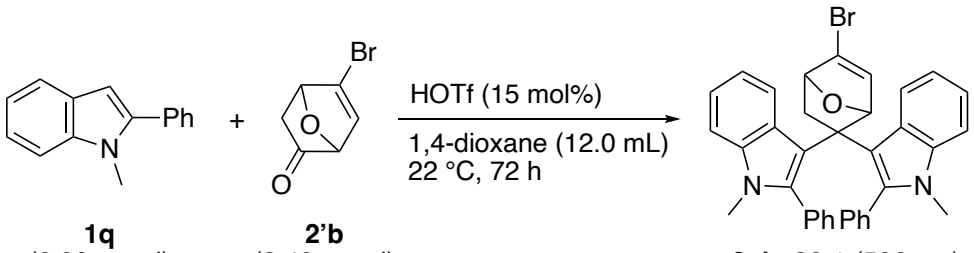
Preparation of 5-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-ol (8'b). $In(OTf)_3$ (169 mg, 0.300 mmol) was placed in a 200 mL two-necked round-bottomed flask equipped with a three-way stopcock, which was heated at 50 °C for 20 min, 70 °C for 20 min, 90 °C for 20 min, 120 °C for 20 min, and 150 °C for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the flask was filled with argon. To this was 1,4-dioxane (22.5 mL), and the solution was stirred at rt for 3 min. Subsequently, to this were added **2'b** (567 mg, 3.00 mmol), $HSiEt_3$ (872 mg, 7.50 mmol), and H_2O (54.1 mg, 3.00 mmol), and the resulting mixture was stirred at 115 ºC for 1 h. After cooling to rt, H_2O (5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (50 mL × 3). The combined organic layer was washed with brine (15 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by column chromatography on silica gel (hexane/Et_2O = 2/3) afforded **8'b** in 36% yield (206 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.44 (d, J = 1.4 Hz, 1H), 4.86 (dd, J = 4.1, 1.4 Hz, 1H), 4.75 (d, J = 4.6 Hz, 1H), 4.55 (tdd, J = 8.0, 4.5, 2.8 Hz, 1H), 2.32 (ddd, J = 12.4, 7.8, 4.6 Hz, 1H), 1.39 (d, J = 7.3 Hz, 1H), 1.17 (dd, J = 12.1, 2.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 131.0, 128.4, 84.5, 81.5, 70.5, 35.9. HRMS (EI) Calcd for $C_6H_7{}^{79}BrO_2$: $[M]^-$, 189.9635. Found: *m/z* 189.9624. **NOTE**: Adding H_2O to this reaction is effective because the coordination of H_2O to $HSiEt_3$ accelerates the reduction of the carbonyl moiety and results in preventing the formation of the corresponding silyl ether.



Preparation of Compound 8b. Compound **8b** was prepared with reference to a literature procedure.[34] A flame-dried 20 mL Schlenk tube was filled with argon and then charged with **8'b**

[34] V. Nair, B.-K. Chun, *Arkivoc*, **2003**, 9–21.

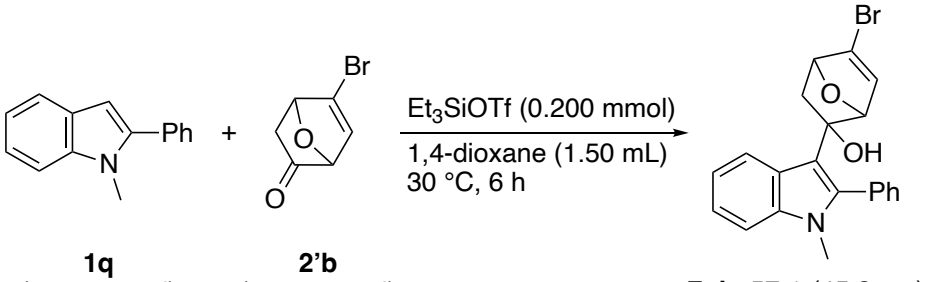
(222 mg, 1.16 mmol), pyridine (1.10 mL), and DMAP (7.09 mg, 58.0 μmol), and the resulting mixture was cooled to 0 ℃ in an ice bath. To this was slowly added $Ph_2MeSiCl$ (540 mg, 2.32 mmol), and the resulting mixture was stirred at 24 ℃ for 23 h. Ice water (5 mL) was added for quenching the reaction, and the aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with H_2O (5 mL × 3) and brine (5 mL × 2), and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by column chromatography on silica gel (hexane/Et_2O = 20/1) afforded **8b** in 88% yield (395 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 4H), 7.45–7.36 (m, 6H), 6.37 (d, *J* = 1.8 Hz, 1H), 4.68 (d, *J* = 4.6 Hz, 1H), 4.64 (dd, *J* = 4.4, 1.1 Hz, 1H), 4.54 (ddd, *J* = 7.3, 4.6, 2.7 Hz, 1H), 2.08 (ddd, *J* = 11.9, 7.6, 4.6 Hz, 1H), 1.24 (dd, *J* = 11.7, 2.5 Hz, 1H), 0.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.7, 135.6, 134.2, 131.9, 130.0, 128.0, 126.7, 84.4, 81.5, 71.1, 35.3, –2.6. HRMS (FD) Calcd for $C_{19}H_{19}{}^{79}BrO_2Si$: $[M]^+$, 386.0332. Found: *m/z* 386.0303.



1q (6.00 mmol) **2'b** (2.40 mmol) **6qb**; 36% (506 mg)

Preparation of Compound 6qb. Compound **6qb** was synthesized according to the following modified literature procedure.[9] Under an argon atmosphere, a 100 mL two-necked round-bottomed flask was charged with 1,4-dioxane (12.0 mL) and HOTf (54.0 mg, 0.360 mmol), and the resulting solution was stirred at rt for 3 min. To this were added **2'b** (454 mg, 2.40 mmol) and **1q** (1.24 g, 6.00 mmol), and the resulting mixture was stirred at 22 ℃ for 72 h. H_2O (3 mL) was added, and the aqueous phase was extracted with EtOAc (25 mL × 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution (5 mL), H_2O (5 mL × 2), and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 10/1) gave **6qb** in 36% yield (506 mg) as a white solid [145 ℃ (decomp.)]. Compound **6qb** was purified further by recycling HPLC (hexane/EtOAc = 10/1). Compound **6qb** was obtained as a mixture of two isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br s, 1H), 7.46–7.26 (m, 7H), 7.21–

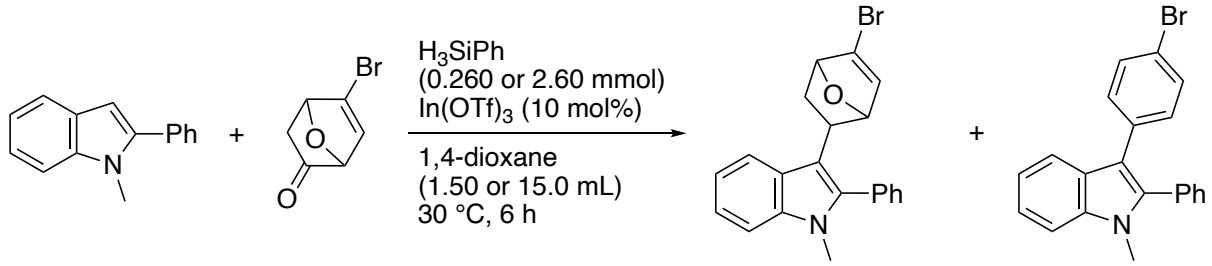
7.05 (m, 6H), 6.96–6.89 (m, 2H), 6.36–6.28 (br m, 2H), 5.99–5.96 (m, 2H), 4.64 (d, J = 4.0 Hz, 1H), 3.13 (s, 3H), 3.11 (s, 3H), 2.42 (br s, 1H), 2.22 (dd, J = 12.0, 4.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 137.2, 137.1, 136.38, 136.36, 134.5, 134.3, 133.3, 132.2, 131.26, 131.18, 130.9, 128.3, 128.1, 127.6, 127.54, 127.47, 127.42, 126.0, 121.8, 121.5, 121.1, 121.0, 120.7, 119.1, 118.8, 117.2, 109.1, 108.8, 85.5, 83.6, 48.1, 40.4, 30.10, 30.08. HRMS (FD) Calcd for $C_{36}H_{29}{}^{79}BrN_2O$: $[M]^+$, 584.1458. Found: *m/z* 584.1463.



1q (0.240 mmol) **2'b** (0.200 mmol) **7qb**; 57% (45.2 mg)

Preparation of Compound 7qb. A flame-dried 20 mL Schlenk tube was filled with argon and then charged with 1,4-dioxane (1.50 mL) and Et_3SiOTf (52.9 mg, 0.200 mmol). The resulting mixture was stirred at rt for 3 min. To this were added **2'b** (37.8 mg, 0.200 mmol) and **1q** (49.8 mg, 0.240 mmol), and the resulting solution was stirred at 30 °C for 6 h. H_2O (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution (1 mL), H_2O (1 mL × 2), and brine (1 mL), and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc/NEt_3 = 100/40/1) in 57% yield (45.2 mg) as an orange solid [138 °C (decomp.)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 9.2, 0.9 Hz, 1H), 7.52–7.42 (m, 5H), 7.34 (dd, J = 8.2, 0.9 Hz, 1H), 7.29 (ddd, J = 8.1, 6.9, 1.0 Hz, 1H), 7.20 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 5.88 (d, J = 1.8 Hz, 1H), 5.10 (s, 1H), 4.71 (d, J = 4.6 Hz, 1H), 3.46 (s, 3H), 2.64 (s, 1H), 2.10 (d, J = 12.4 Hz, 1H), 2.01 (dd, J = 12.4, 4.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.7, 136.8, 132.5, 132.1, 131.5, 131.4, 129.2, 128.6, 128.5, 128.4, 126.6, 122.1, 120.3, 120.2, 114.1, 109.7, 88.5, 82.7, 78.4, 42.0, 30.5. HRMS (FD) Calcd for $C_{21}H_{18}{}^{79}BrNO_2$: $[M]^+$, 395.0515. Found: *m/z* 395.0536.

Reaction of 1q, 2'b, and H_3SiPh Under Conditions C [Conditions C: $In(OTf)_3$ (10 mol%) in 1,4-Dioxane at 30 °C for 6 h] (Scheme 10a)

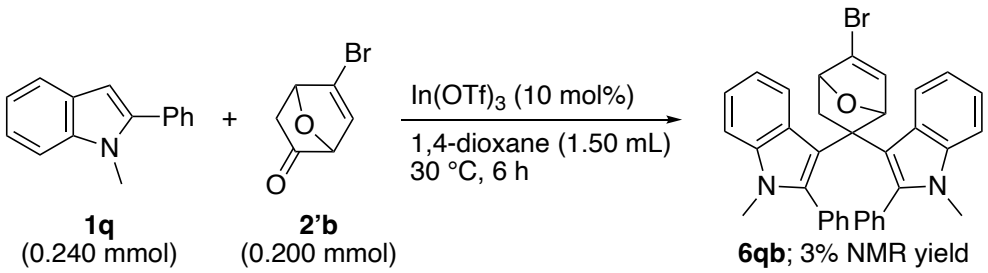


1q (0.240 or 2.40 mmol) | **2'b** (0.200 or 2.00 mmol) | **9qb** 59% NMR yield[a] 55% isolated yield (418 mg)[b] | **4qb** 10% NMR yield[a] 9% NMR yield[b]

[a] The yield on a 0.2 mmol scale. [b] The yield on a 2 mmol scale.

Based on the experimental procedure described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. A General Procedure for Steric Strategy Using Conditions B in Table 2**", a 0.2 or 2 mmol scale reaction of **2'b** was carried out at 30 °C for 6 h using the following reagents: **1q** (49.8 mg, 0.240 mmol or 498 mg, 2.40 mmol), **2'b** (37.8 mg, 0.200 mmol or 378 mg, 2.00 mmol), H_3SiPh (28.1 mg, 0.260 mmol or 281 mg, 2.60 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol or 112 mg, 0.200 mmol), and 1,4-dioxane (1.50 or 15.0 mL). NMR yields were determined using nitromethane as an internal standard. Compound **9qb** was isolated from the 2 mmol scale reaction by column chromatography on silica gel (hexane/EtOAc = 30/1) in 55% yield (418 mg) as a white solid (mp 158–160 ºC). Compound **9qb** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and HRMS, as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.37 (br d, J = 6.9 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.24–7.22 (m, 1H), 7.13 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 6.20 (d, J = 1.8 Hz, 1H), 4.89–4.86 (m, 2H), 3.58 (dt, J = 9.2, 4.7 Hz, 1H), 3.50 (s, 3H), 2.19 (ddd, J = 11.8, 9.3, 4.7 Hz, 1H), 1.97 (dd, J = 11.9, 5.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.0, 137.0, 133.7, 132.1, 130.9, 128.60, 128.57, 127.0, 126.3, 121.5, 120.4, 119.4, 109.6, 109.4, 84.9, 84.3, 37.3, 30.7, 29.7. HRMS (FD) Calcd for $C_{21}H_{18}{}^{79}BrNO$: $[M]^+$, 379.0566. Found: *m/z* 379.0590. Compound **4qb** already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

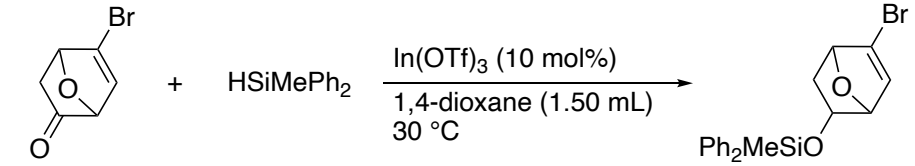
Reaction of 1q and 2'b in the Absence of H_3SiPh Under Conditions C (Scheme 10b)



1q (0.240 mmol) **2'b** (0.200 mmol) **6qb**; 3% NMR yield

Based on the experimental procedure described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. A General Procedure for Steric Strategy Using Conditions B in Table 2**", this reaction in the absence of H_3SiPh was carried out at 30 °C for 6 h using the following reagents: **1q** (49.8 mg, 0.240 mmol), **2'b** (37.8 mg, 0.200 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). The yield of **6qb** was determined by ^1H NMR using nitromethane as an internal standard. Compound **6qb** already appears in this section. See the above for the spectral and analytical data of **6qb**.

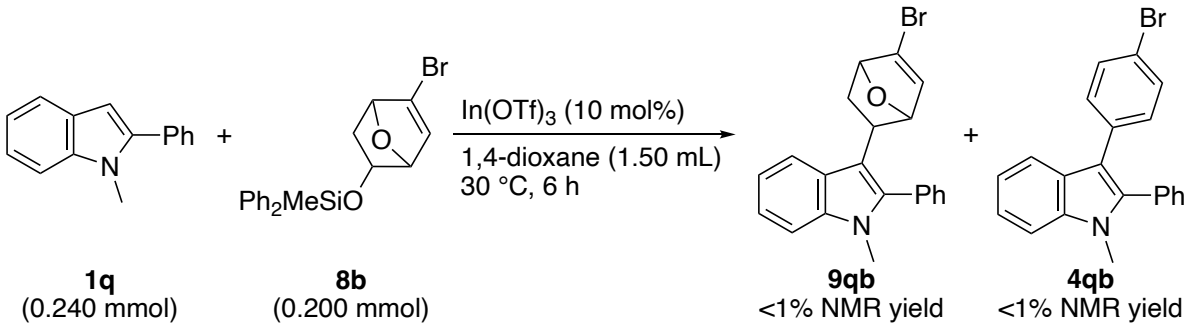
Reaction of 2'b and $HSiMePh_2$ in the Absence of 1q Under Conditions C (Scheme 10c)



2'b (0.200 mmol) (0.600 mmol) **8b**; <1% (6 h) 20% (24 h)

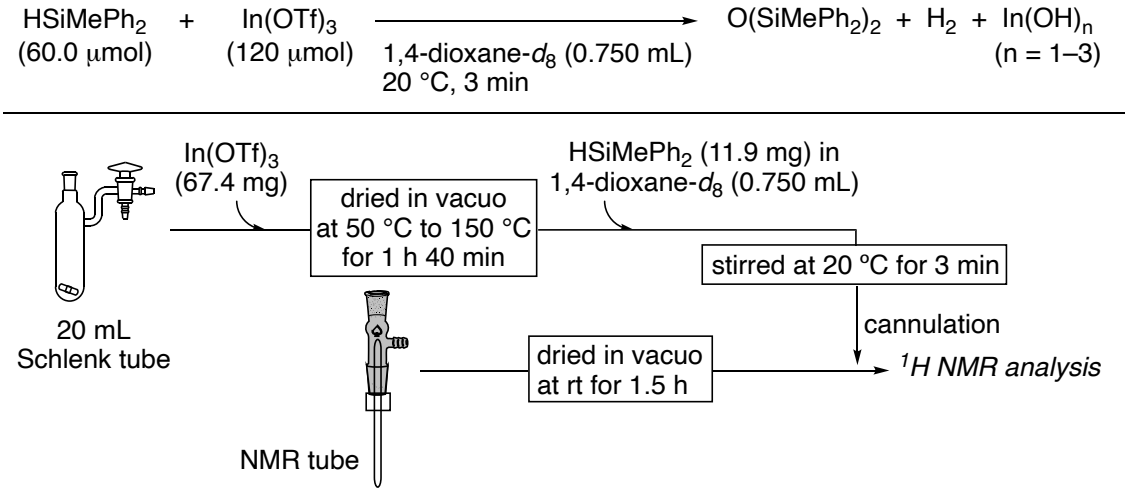
Based on the experimental procedure described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. A General Procedure for Steric Strategy Using Conditions B in Table 2**", this reaction in the absence of **1q** was carried out at 30 °C for 6 or 24 h using the following reagents: **2'b** (37.8 mg, 0.200 mmol), $HSiMePh_2$ (119 mg, 0.600 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). The yield of **8b** was determined by ^1H NMR using nitromethane as an internal standard. Compound **8b** already appears in this section. See the above for the spectral and analytical data of **8b**.

Reaction of 1q and 8b Under Conditions C (Scheme 10d)



$In(OTf)_3$ (11.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. To this was added solvent 1,4-dioxane (1.50 mL), and the solution was stirred at rt for 3 min. To this were added **8b** (77.5 mg, 0.200 mmol) and **1q** (49.8 mg, 0.240 mmol), and the resulting mixture was stirred at 30 ºC for 6 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^{1}H NMR. However, the ^{1}H NMR analysis indicated no formation of **9qb** and **4qb**.

Reaction of $HSiMePh_2$ with $In(OTf)_3$ in 1,4-Dioxane-d_8 (Scheme 10f)



$In(OTf)_3$ (67.4 mg, 120 μmol) was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under

a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. To this was added $HSiMePh_2$ (11.9 mg, 60.0 μmol) dissolved in 1,4-dioxane-d_8 (0.750 mL), and the resulting mixture was stirred at 20 °C for 3 min and transferred through a cannula into an NMR tube equipped with an adapter connected to dual vacuum/argon manifold. The ^1H NMR analysis of the solution indicated the formation of $O(SiMePh_2)_2$, H_2, and indium hydroxide [$In(OH)_n$], which were assigned by comparison with each of the ^1H NMR spectrum measured individually (**Figure S1**). $O(SiMePh_2)_2$ was separately prepared under similar reaction conditions to those described above and isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 50/1). $O(SiMePh_2)_2$ has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[35] Accordingly, only ^1H NMR data are provided here. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 6.9 Hz, 8H), 7.37 (tt, J = 7.2, 1.7 Hz, 4H), 7.31 (t, J = 7.2 Hz, 8H), 0.57 (s, 6H); ^1H NMR (400 MHz, 1,4-dioxane-d_0) δ 7.50 (d, J = 7.8 Hz, 8H), 7.34 (t, J = 7.1 Hz, 4H), 7.28 (t, J = 7.3 Hz, 8H), 0.56 (s, 6H). **NOTE**: 1,4-Dioxane-d_8 was stored over MS 4 Å under argon. The inside of the cannula and the NMR tube were dried at rt for 1.5 h under a reduced pressure of ca. 7 Pa until use. The ^1H NMR spectrum of $O(SiMePh_2)_2$ in 1,4-dioxane-d_0 was measured by a no-deuterium proton NMR method.

[35] N. Wu, C. Li, G. Dong, M. Jiang, Z. Xu, *New J. Chem.* **2022**, *46*, 4814–4818.

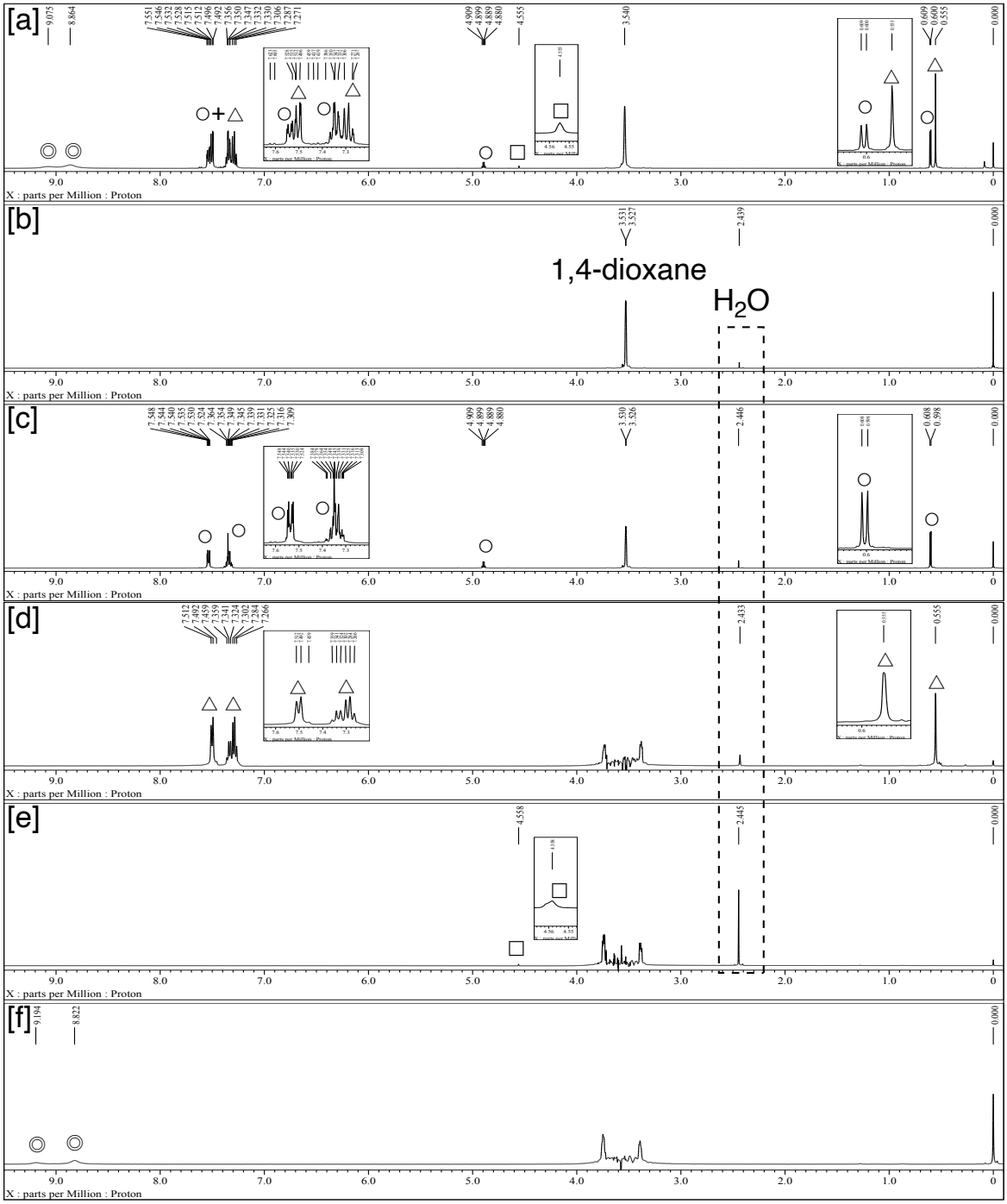
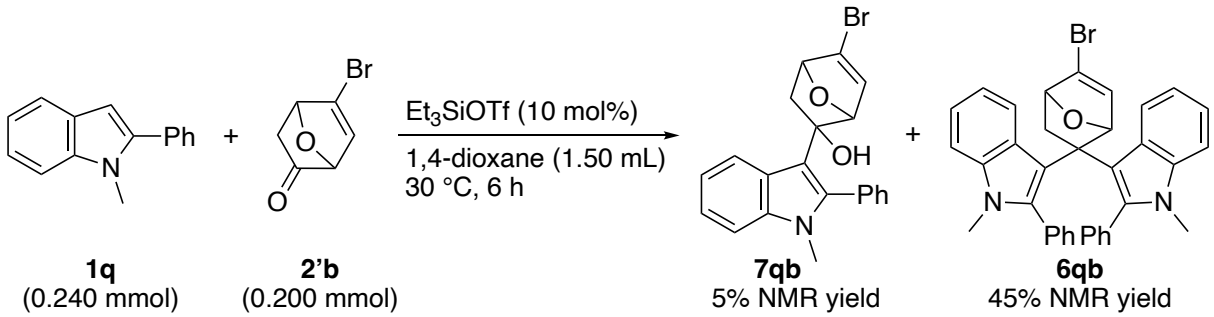


Figure S1. ^{1}H NMR spectra of [a] $HSiMePh_2$ + $In(OTf)_3$ at 20 °C for 3 min in 1,4-dioxane-d_8, [b] only 1,4-dioxane-d_8, [c] $HSiMePh_2$ (○) in 1,4-dioxane-d_8, [d] $O(SiMePh_2)_2$ (△) in 1,4-dioxane-d_0, [e] H_2 gas (□) in 1,4-dioxane-d_0, and [f] a 1/1 mixture of $In(OTf)_3$ + $In(OH)_3$ (◎) in 1,4-dioxane-d_0. Figures S1d–f show ^{1}H NMR spectra measured by a no-deuterium proton NMR method in 1,4-dioxane-d_0.

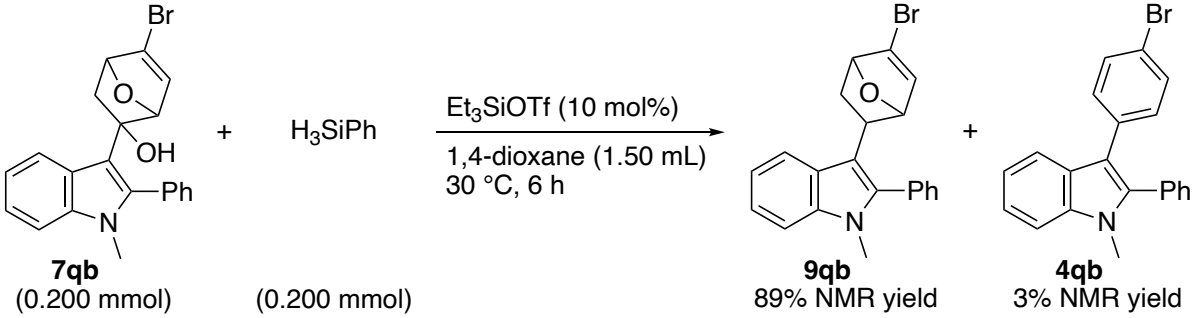
Reaction of 1q and 2'b in the Absence of H_3SiPh Under Conditions D [Conditions D: Et_3SiOTf (10 mol%) in 1,4-Dioxane at 30 °C for 6 h] (Scheme 10g)



1q (0.240 mmol) **2'b** (0.200 mmol) **7qb** 5% NMR yield **6qb** 45% NMR yield

A flame-dried 20 mL Schlenk tube was filled with argon and then charged with 1,4-dioxane (1.50 mL) and Et_3SiOTf (5.29 mg, 20.0 μmol). The resulting mixture was stirred at rt for 3 min. To this were added **2'b** (37.8 mg, 0.200 mmol) and **1q** (49.8 mg, 0.240 mmol), and the resulting solution was stirred at 30 °C for 6 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CHCl_3$ and nitromethane as an internal standard to estimate yields of **7qb** and **6qb** by a no-deuterium proton NMR method. Compounds **7qb** and **6qb** already appear in this section. See the above for the spectral and analytical data of **7qb** and **6qb**.

Reaction of 7qb with H_3SiPh Under Conditions D (Scheme 10h)

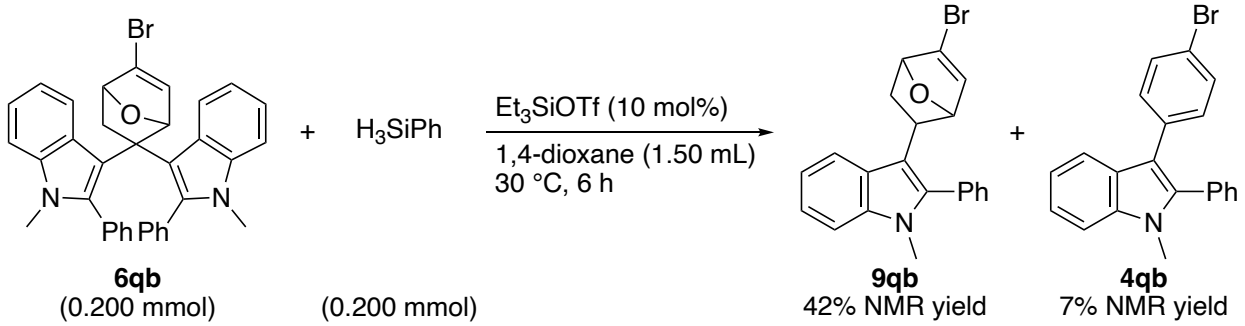


7qb (0.200 mmol) (0.200 mmol) **9qb** 89% NMR yield **4qb** 3% NMR yield

A flame-dried 20 mL Schlenk tube was filled with argon and then charged with **7qb** (79.3 mg, 0.200 mmol) dissolved in 1,4-dioxane (1.50 mL), Et_3SiOTf (5.29 mg, 20.0 μmol), and H_3SiPh (21.6 mg, 0.200 mmol). After stirring at 30 °C for 6 h, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture,

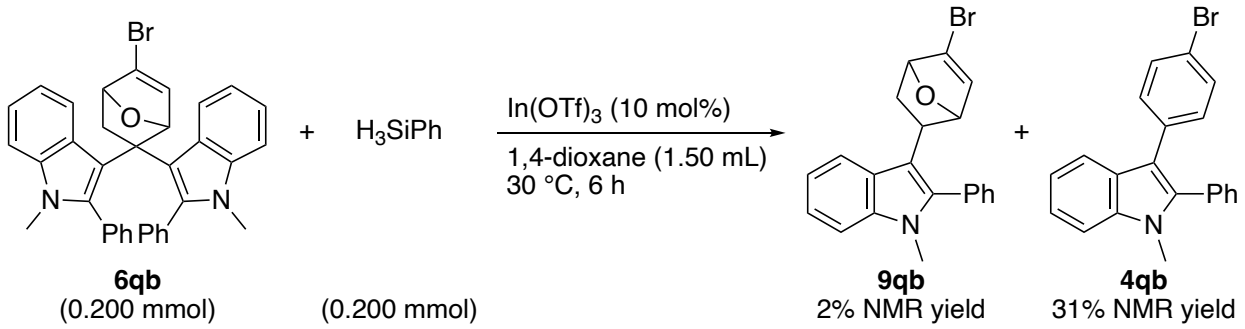
to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^1H NMR. Compound **9qb** already appears in this section. See the above for the spectral and analytical data of **9qb**. Compound **4qb** also already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

Reaction of 6qb with H_3SiPh Under Conditions D (Scheme 10i)



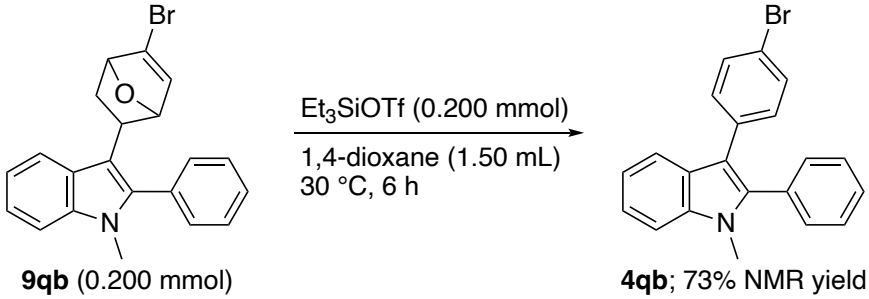
A flame-dried 20 mL Schlenk tube was filled with argon and then charged with 1,4-dioxane (1.50 mL) and Et_3SiOTf (5.29 mg, 20.0 μmol). The resulting mixture was stirred at rt for 3 min. To this were added **6qb** (117.1 mg, 0.200 mmol) and H_3SiPh (21.6 mg, 0.200 mmol), and the resulting solution was stirred at 30 °C for 6 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^1H NMR. Compound **9qb** already appears in this section. See the above for the spectral and analytical data of **9qb**. Compound **4qb** also already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

Reaction of 6qb with H_3SiPh Under Conditions C (Scheme 10i)



$In(OTf)_3$ (11.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. To this was added solvent 1,4-dioxane (1.50 mL), and the solution was stirred at rt for 3 min. To this were added **6qb** (117.1 mg, 0.200 mmol) and H_3SiPh (21.6 mg, 0.200 mmol), and the resulting mixture was stirred at 30 ºC for 6 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^1H NMR. Compound **9qb** already appears in this section. See the above for the spectral and analytical data of **9qb**. Compound **4qb** also already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

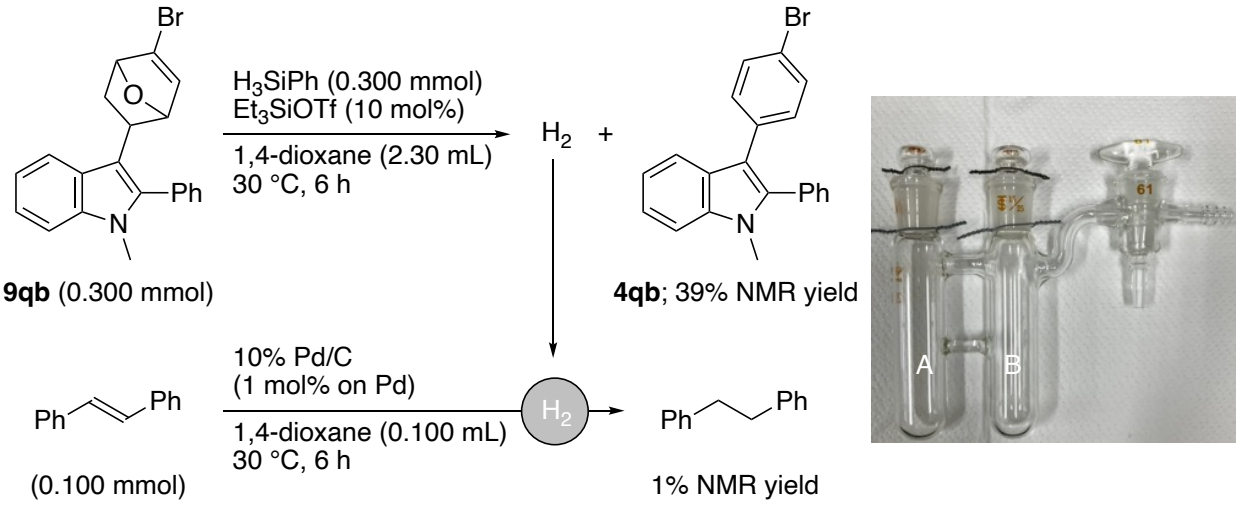
Reaction of 9qb with Et_3SiOTf (Scheme 10k)



A flame-dried 20 mL Schlenk tube was filled with argon and then charged with 1,4-dioxane (1.50 mL) and Et_3SiOTf (52.9 mg, 0.200 mmol). The resulting mixture was stirred at rt for 3 min. To this was added **9qb** (76.1 mg, 0.200 mmol), and the resulting mixture was stirred at 30 ºC for

6 h. H_2O (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution (1 mL), H_2O (1 mL × 2), and brine (1 mL), and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate a yield of **4qb** by ^1H NMR. Compound **4qb** already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

An H_2 Gas Trapping Experiment: Palladium-Catalyzed Hydrogenation of *trans*-Stilbene Conducted in Parallel with Reaction of 9qb with H_3SiPh Under Conditions D (Scheme 10l)

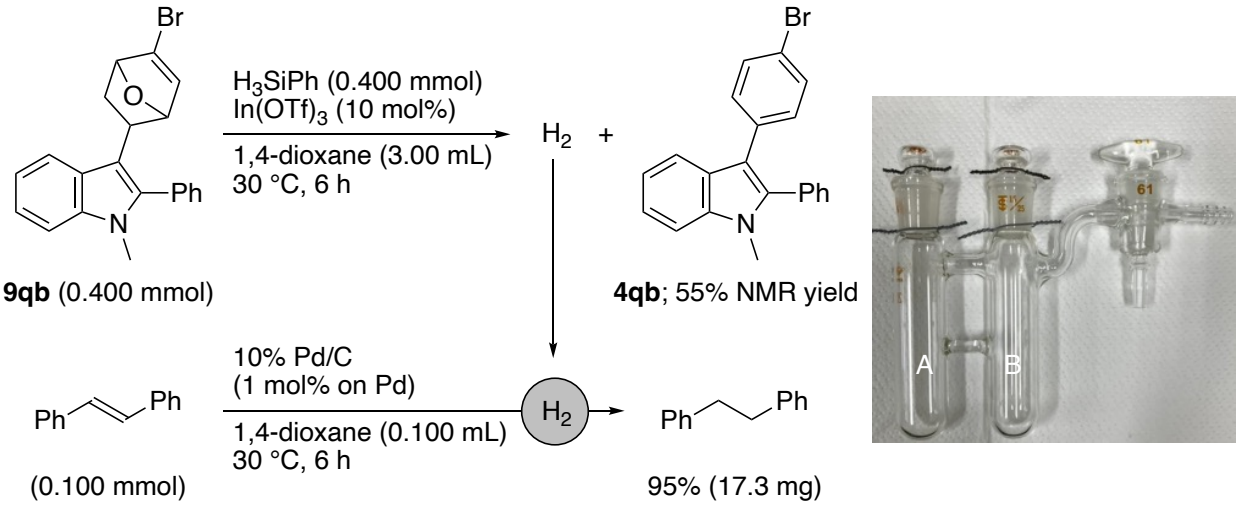


As shown in the above photo, a two-chamber Schlenk-type tube was used for this experiment. The two Schlenk tubes are connected at their upper portions by a perforated glass tube, enabling gas to freely pass between the two tubes. Under an argon atmosphere, the chamber of B of the flame-dried two-chamber Schlenk-type tube was charged with 10% Pd/C (1.06 mg, 1.00 μmol), *trans*-stilbene (18.0 mg, 0.100 mmol), and 1,4-dioxane (0.100 mL). The chamber of A was then charged with 1,4-dioxane (2.30 mL), Et_3SiOTf (7.93 mg, 30.0 μmol), **9qb** (114 mg, 0.300 mmol), and H_3SiPh (32.5 mg, 0.300 mmol). The mixtures in the two chambers were stirred at 30 ºC for 6 h, and the resulting each solution was treated separately for subsequent work up. Regarding the solution in the chamber of A, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration

through a cotton plug and evaporation of the solvent afforded a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate a yield of **4qb** by ^1H NMR. On the other hand, the solution in the chamber of B was filtered through a pad of Celite (CAUTION: the Celite pad may not be dried up after the filtration, due to possible ignition of the activated Pd/C.), and then evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate a yield of 1,2-diphenylethane by ^1H NMR.

Compound **4qb** already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**". For the spectral data of 1,2-diphenylethane, refer to the description in the next experimental procedure.

An H_2 Gas Trapping Experiment: Palladium-Catalyzed Hydrogenation of *trans*-Stilbene Conducted in Parallel with Reaction of 9qb with H_3SiPh Under Conditions C (Scheme 10l)

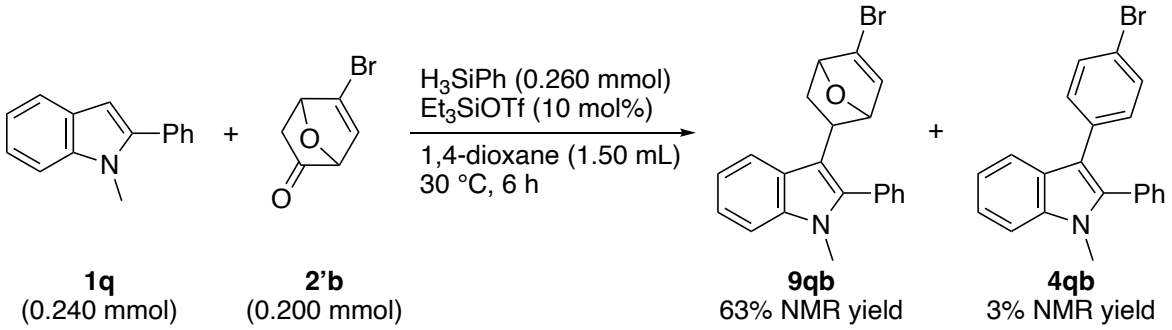


As shown in the above photo, a two-chamber Schlenk-type tube was used for this experiment. The two Schlenk tubes are connected at their upper portions by a perforated glass tube, enabling gas to freely pass between the two tubes. At first, $In(OTf)_3$ (22.5 mg, 40.0 μmol) was placed in the chamber of A, and the tube was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. Next, the chamber of B was charged with 10% Pd/C (1.06 mg, 1.00 μmol), *trans*-stilbene (18.0 mg, 0.100 mmol), and 1,4-dioxane (0.100 mL). To the chamber of A were then added 1,4-dioxane (3.00 mL), **9qb** (152 mg, 0.400 mmol), and H_3SiPh (43.3 mg,

0.400 mmol). The mixtures in the two chambers were stirred at 30 ºC for 6 h, and the resulting each solution was treated separately for subsequent work up. Regarding the solution in the chamber of A, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent afforded a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate a yield of **4qb** by ^{1}H NMR. On the other hand, the solution in the chamber of B was filtered through a pad of Celite (CAUTION: the Celite pad may not be dried up after the filtration, due to possible ignition of the activated Pd/C.), and then evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 40/1) furnished 1,2-diphenylethane in 95% yield (17.3 mg).

Compound **4qb** already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**". 1,2-Diphenylethane has already appeared in the literature, and its spectral and analytical data are in good agreement with those reported.[36] Accordingly, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 4H), 7.22–7.18 (m, 6H), 2.92 (s, 4H).

Reaction of 1q, 2'b, and H_3SiPh Under Conditions D (Scheme 10m)

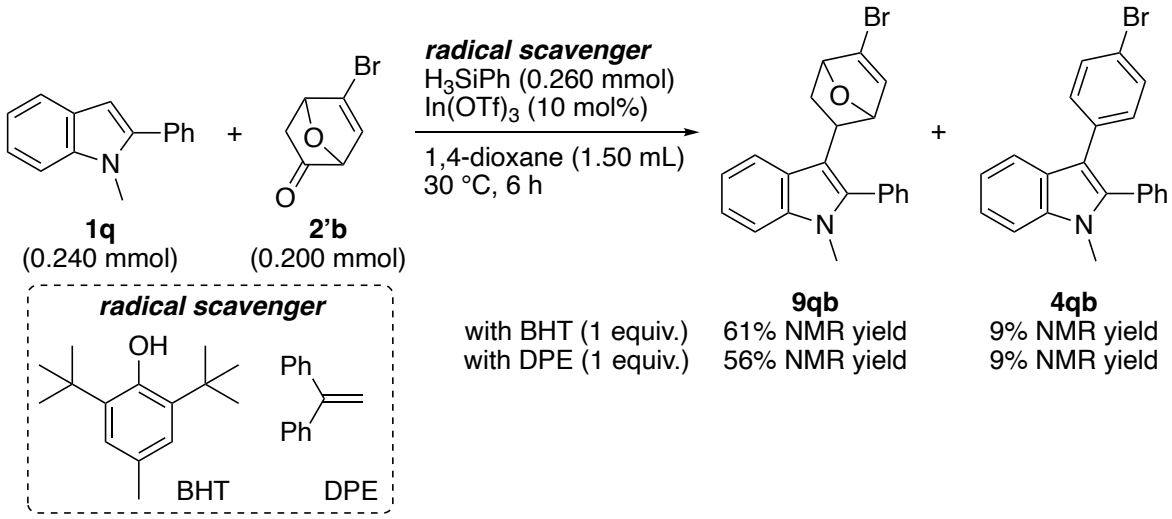


A flame-dried 20 mL Schlenk tube was filled with argon and then charged with 1,4-dioxane (1.50 mL) and Et_3SiOTf (5.29 mg, 20.0 μmol). The resulting mixture was stirred at rt for 3 min. To this were added **2'b** (37.8 mg, 0.200 mmol), **1q** (49.8 mg, 0.240 mmol), and H_3SiPh (28.1 mg, 0.260 mmol), and the resulting solution was stirred at 30 °C for 6 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium

[36] M. Blangetti, P. Fleming, D. F. O'Shea, *J. Org. Chem*. **2012**, *77*, 2870−2877.

sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^{1}H NMR. Compound **9qb** already appears in this section. See the above for the spectral and analytical data of **9qb**. Compound **4qb** also already appears in this Supporting Information. For the spectral data of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

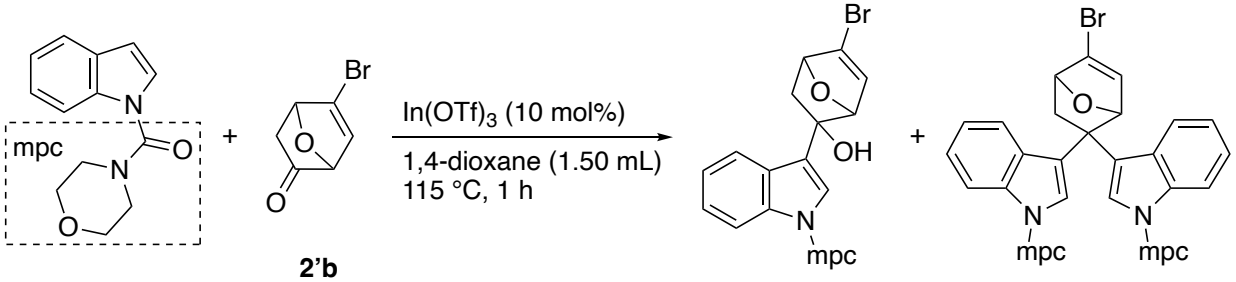
Reaction of 1q, 2'b, and H_3SiPh in the Presence of a Radical Scavenger Under Conditions C (Scheme 10m)



$In(OTf)_3$ (11.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 50 ºC for 20 min, 70 ºC for 20 min, 90 ºC for 20 min, 120 ºC for 20 min, and 150 ºC for 20 min under a reduced pressure of ca. 7 Pa. After cooling to rt, the tube was filled with argon. To this was added solvent 1,4-dioxane (1.50 mL), and the solution was stirred at rt for 3 min. To this were added **2'b** (37.8 mg, 0.200 mmol), **1q** (49.8 mg, 0.240 mmol), H_3SiPh (28.1 mg, 0.260 mmol), and a radical scavenger [BHT (44.1 mg, 0.200 mmol) or DPE (36.1 mg, 0.200 mmol)]. After stirring at 30 ºC for 6 h, a saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent provided a crude reaction mixture, to which were added $CDCl_3$ and nitromethane as an internal standard to estimate yields of **9qb** and **4qb** by ^{1}H NMR. Compound **9qb** already appears in this section. See the above for the spectral and analytical data of **9qb**. Compound **4qb** also already appears in this Supporting Information. For the spectral data

of **4qb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

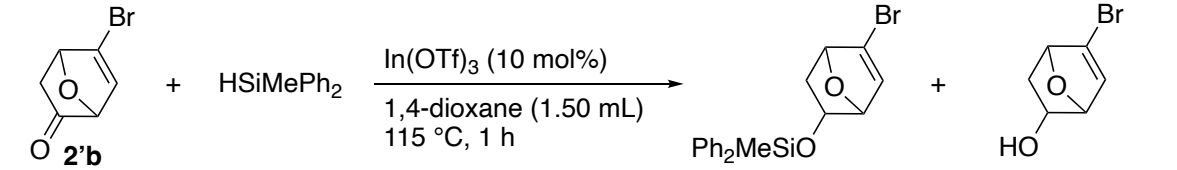
Reaction of 1e and 2'b in the Absence of H_2SiPh_2 Under Conditions E [Conditions E: $In(OTf)_3$ (10 mol%) in 1,4-Dioxane at 115 °C for 1 h] (Scheme 12a)



1e (0.200 mmol) **2'b** (0.300 mmol) **7eb**; <1% NMR yield **6eb**; <1% NMR yield

Based on the experimental procedure described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. A General Procedure for Electronic Strategy and Electronic + Steric Strategy Using Conditions A in Table 2**", this reaction in the absence of H_2SiPh_2 was carried out at 115 °C for 1 h using the following reagents: **1e** (46.1 mg, 0.200 mmol), **2'b** (56.7 mg, 0.300 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). ^{1}H NMR analysis of a crude reaction mixture showed no formation of **7eb** and **6eb**.

Reaction of 2'b and $HSiMePh_2$ in the Absence of 1e Under Conditions E (Scheme 12b)

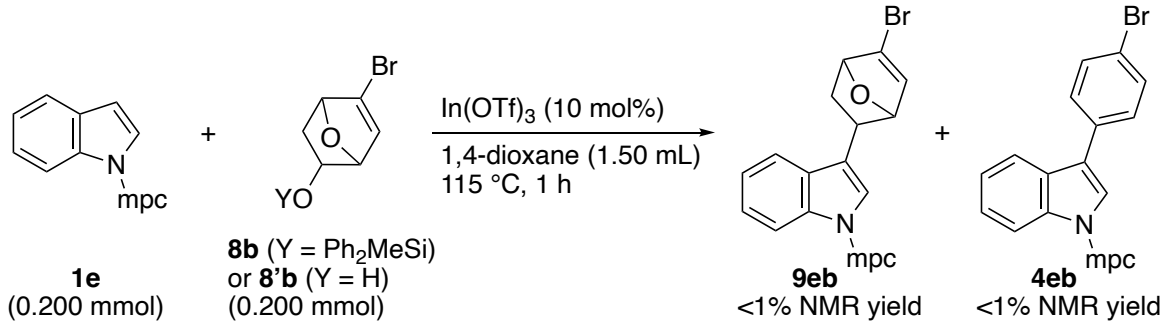


(0.200 mmol) (0.260 mmol) **8b**; 11% NMR yield **8'b**; 3% NMR yield

Based on the experimental procedure described in Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones. A General Procedure for Electronic Strategy and Electronic + Steric Strategy Using Conditions A in Table 2**", this reaction in the absence of **1e** was carried out at 115 °C for 1 h using the following reagents: **2'b** (37.8 mg, 0.200 mmol), $HSiMePh_2$ (51.6 mg, 0.260 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). ^{1}H NMR analysis of a crude reaction mixture showed the formation of **8b** and **8'b**, the yields of which were determined by ^{1}H NMR using nitromethane as an internal standard. Compounds **8b** and **8'b** already appear in this section. See the above for the spectral

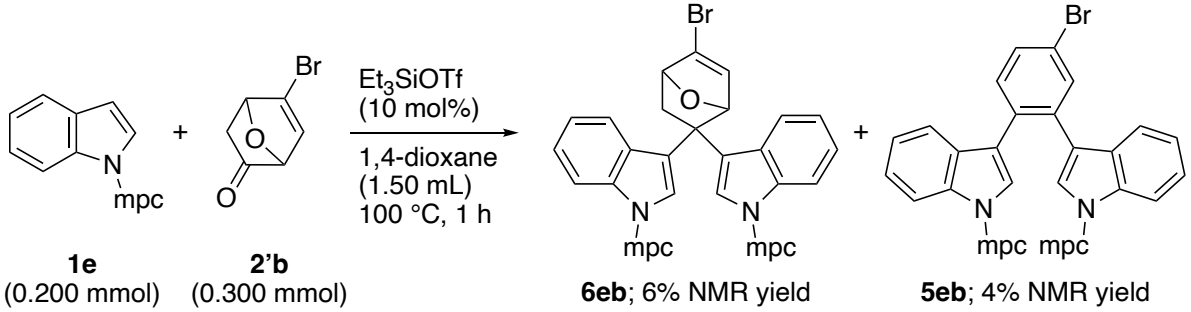
and analytical data of **8b** and **8'b**.

Reaction of 1e with 8b or 8'b Under Conditions E (Scheme 12c)



Based on the experimental procedure described in "**Reaction of 1q and 8b Under Conditions C (Scheme 10d)**", this reaction was carried out at 115 °C for 1 h using the following reagents: **1e** (46.1 mg, 0.200 mmol), **8b** (77.5 mg, 0.200 mmol) or **8'b** (38.2 mg, 0.200 mmol), $In(OTf)_3$ (11.2 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). Regardless of whether **8b** or **8'b** was used as a starting substrate, ^1H NMR analysis of the crude reaction mixtures showed no formation of **9eb** and **4eb**.

Reaction of 1e and 2'b in the Absence of H_2SiPh_2 Under Conditions F [Conditions F: Et_3SiOTf (10 mol%) in 1,4-Dioxane at 100 °C] (Scheme 12e)



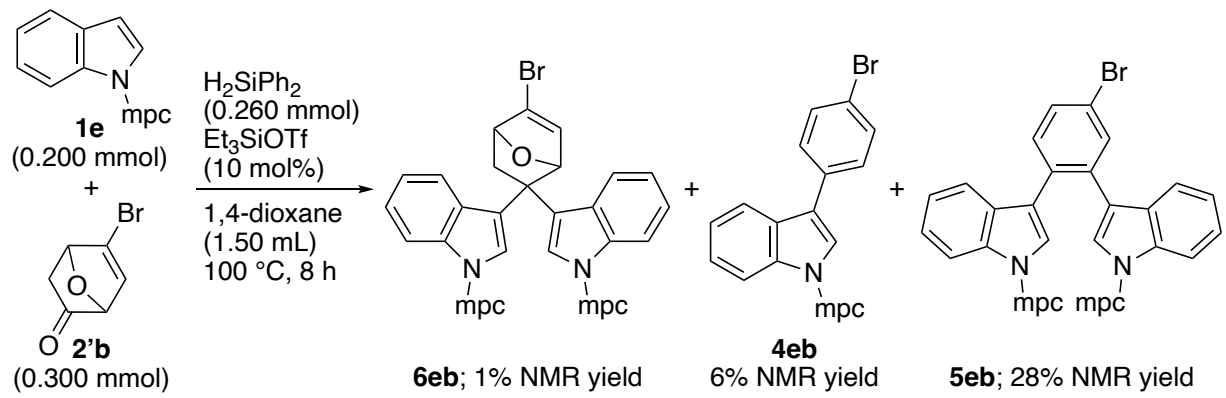
Based on the experimental procedure described in "**Reaction of 1q and 2'b in the Absence of H_3SiPh Under Conditions D (Scheme 10g)**", this reaction was carried out at 100 °C for 1 h using the following reagents: **1e** (46.1 mg, 0.200 mmol), **2'b** (56.7 mg, 0.300 mmol), Et_3SiOTf (5.29 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). ^1H NMR analysis of a crude reaction mixture showed the formation of **6eb** and **5eb**, the yields of which were determined by ^1H NMR using nitromethane as an internal standard. Compounds **6eb** and **5eb** were separately prepared under similar reaction conditions to those of the reaction performed here. The purification procedures

and characterization data of the two products are summarized below.

Compound 6eb. Compound **6eb** was purified as a colorless gum by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.23–7.18 (m, 2H), 7.16 (s, 1H), 7.01–6.96 (m, 2H), 5.98 (d, *J* = 1.7 Hz, 1H), 5.75 (t, *J* = 1.4 Hz, 1H), 5.07 (d, *J* = 2.9 Hz, 1H), 3.83–3.75 (m, 4H), 3.74–3.68 (m, 4H), 3.65–3.50 (m, 8H), 2.50–2.45 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.24, 154.19, 136.2, 136.0, 134.6, 128.4, 128.0, 126.2, 124.6, 124.3, 123.8, 123.2, 122.9, 122.6, 122.0, 121.7, 120.9, 120.5, 113.6, 113.3, 86.2, 84.3, 66.7, 66.6, 47.15, 47.09, 46.4, 39.2. HRMS (FD) Calcd for $C_{32}H_{31}{}^{79}BrN_4O_5$: $[M]^+$, 630.1472. Found: *m/z* 630.1479.

Compound 5eb. Compound **5eb** was purified as a colorless gum by recycling GPC, recycling HPLC (hexane/EtOAc = 1/3), and recrystallization from $CHCl_3$/hexane after column chromatography on silica gel (hexane/EtOAc = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.7 Hz, 1H), 7.70–7.68 (m, 2H), 7.61 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.28–7.24 (m, 2H), 7.12–7.07 (m, 2H), 6.96 (s, 1H), 6.90 (s, 1H), 3.59 (t, *J* = 4.9 Hz, 4H), 3.56 (t, *J* = 4.9 Hz, 4H), 3.27 (t, *J* = 4.9 Hz, 4H), 3.22 (t, *J* = 4.9 Hz, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.54, 153.50, 135.5, 135.4, 134.7, 133.8, 132.5, 131.7, 130.7, 128.2, 128.0, 124.5, 124.3, 124.19, 124.15, 122.5, 122.4, 121.5, 119.94, 119.87, 119.22, 119.17, 113.63, 113.59, 66.52, 66.50, 46.7, 46.6. HRMS (FD) Calcd for $C_{32}H_{29}{}^{79}BrN_4O_4$: $[M]^+$, 612.1367. Found: *m/z* 612.1394.

Reaction of 1e, 2'b, and H_2SiPh_2 Under Conditions F (Scheme 12f)



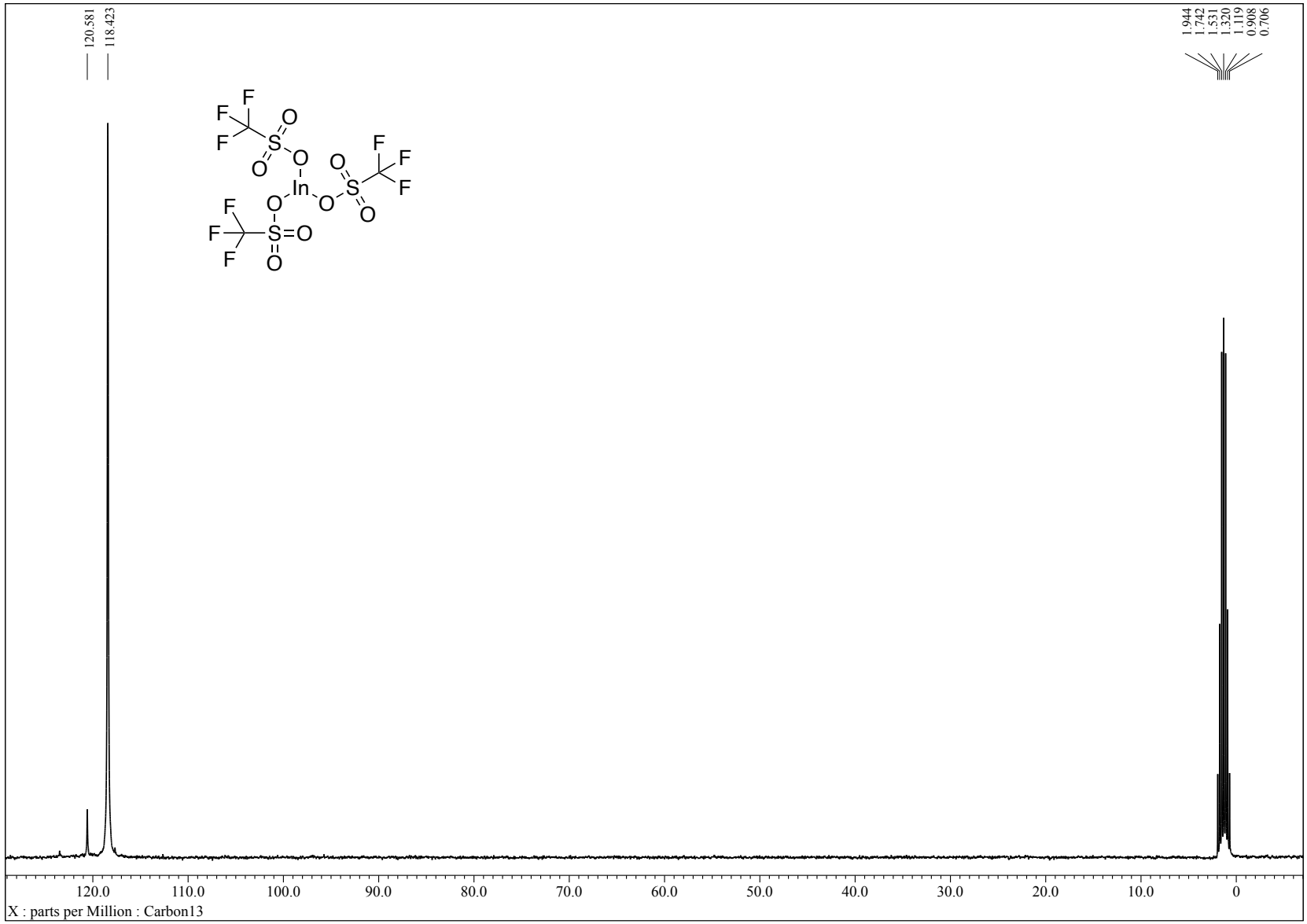
Based on the experimental procedure described in "**Reaction of 1q, 2'b, and H_3SiPh Under Conditions D (Scheme 10m)**", this reaction was carried out at 100 °C for 8 h using the following

reagents: **1e** (46.1 mg, 0.200 mmol), **2'b** (56.7 mg, 0.300 mmol), H_2SiPh_2 (47.9 mg, 0.260 mmol), Et_3SiOTf (5.29 mg, 20.0 μmol), and 1,4-dioxane (1.50 mL). ^1H NMR analysis of a crude reaction mixture showed the formation of **6eb**, **4eb** and **5eb**, the yields of which were determined by ^1H NMR using nitromethane as an internal standard. Compounds **6eb** and **5eb** already appear in this section. See the above for the spectral and analytical data of **6eb** and **5eb**. Compound **4eb** also already appears in this Supporting Information. For the spectral and analytical data of **4eb**, see Section "**V. Indium-Catalyzed 1:1 Arylation of Indoles with 7-Oxabicyclo[2.2.1]hept-5-en-2-ones**".

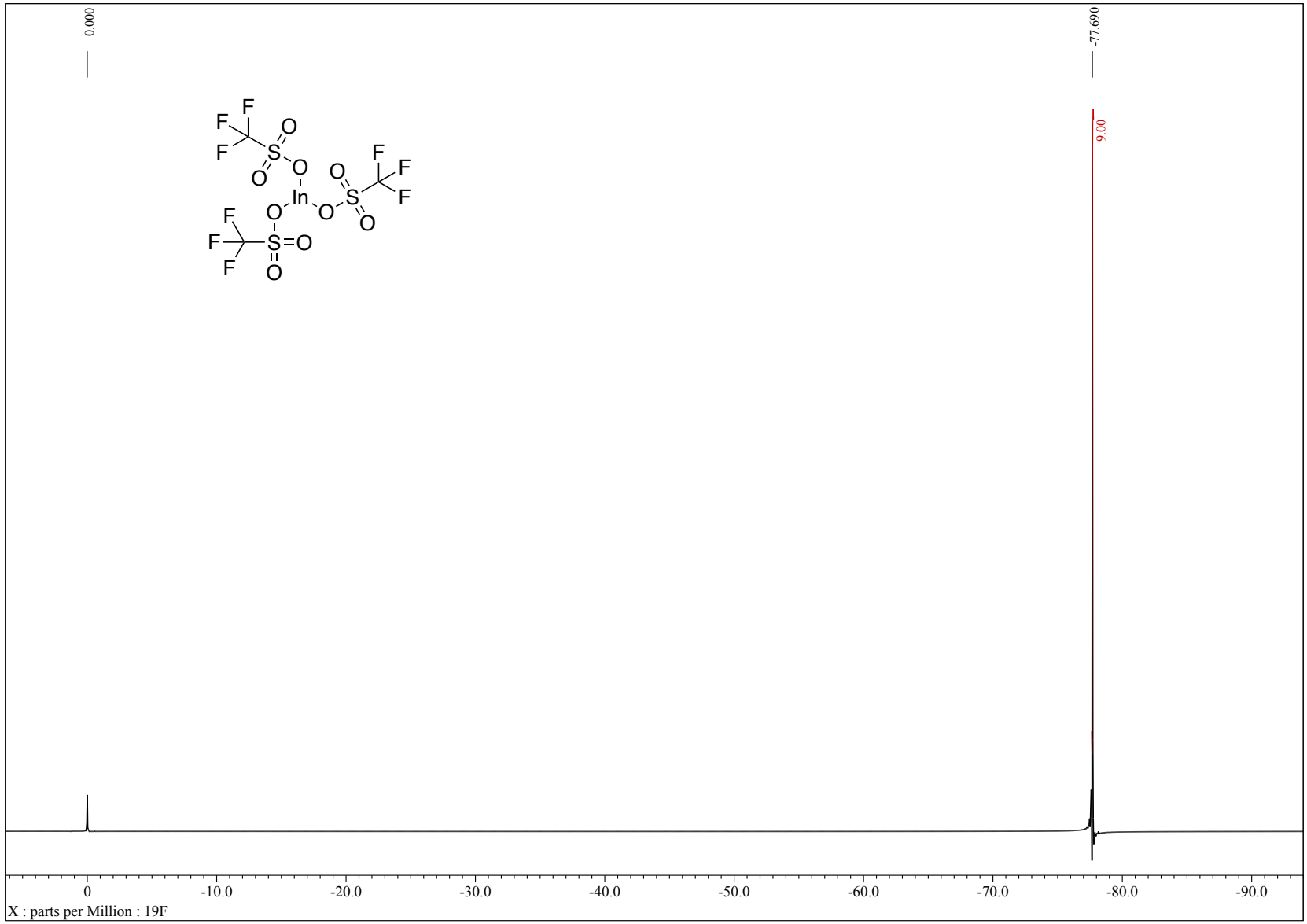
VIII. NMR Spectra

NMR spectra of $In(OTf)_3$, substrates and products are collected in the following pages. Only a ^1H NMR spectrum is provided in the case of a compound for which ^1H NMR, $^{13}C\{^1H\}$ NMR and HRMS or elemental analysis data have been already reported in the literature.

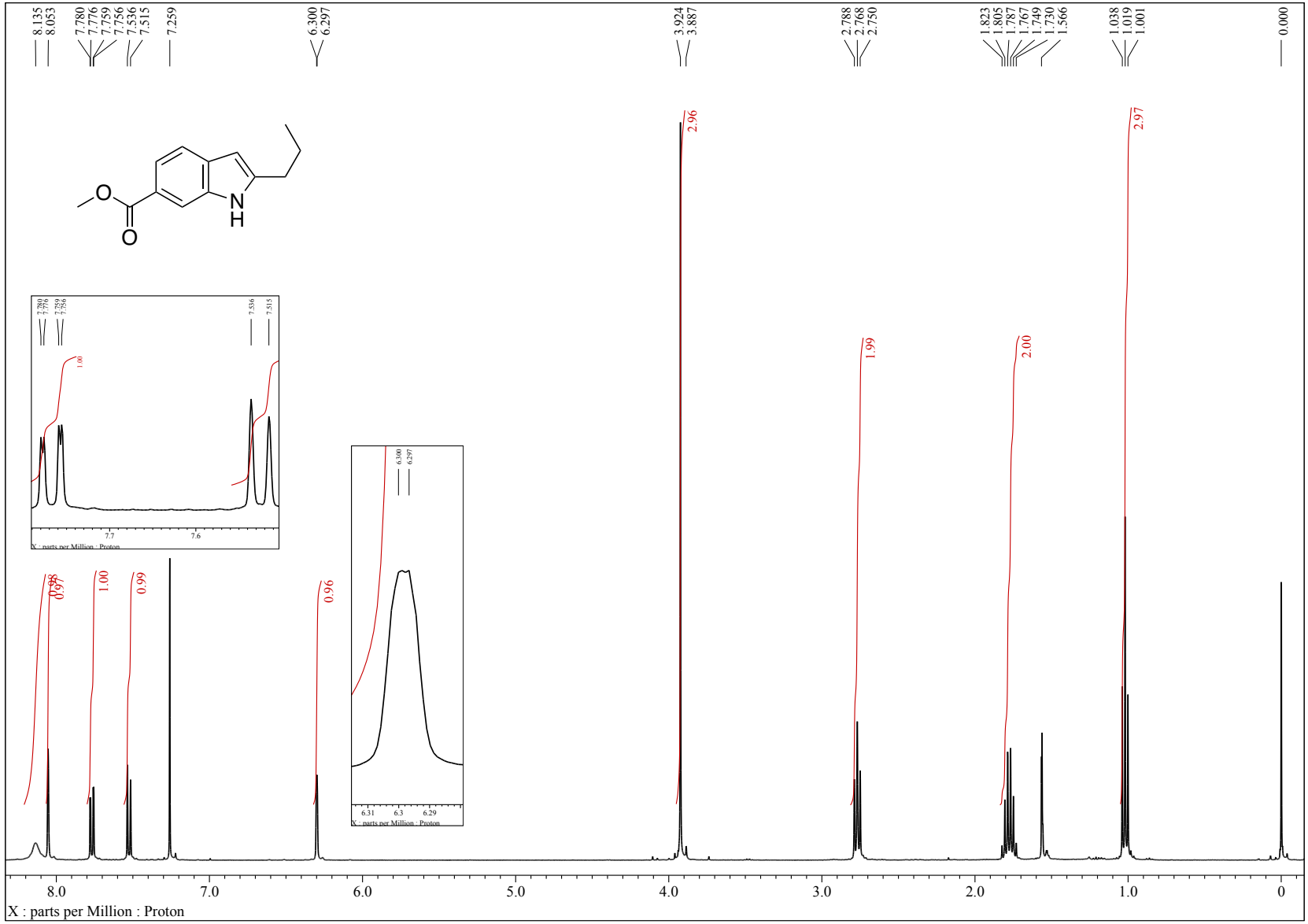
$^{13}C\{^{19}F\}$ NMR (100 MHz, CD_3CN)



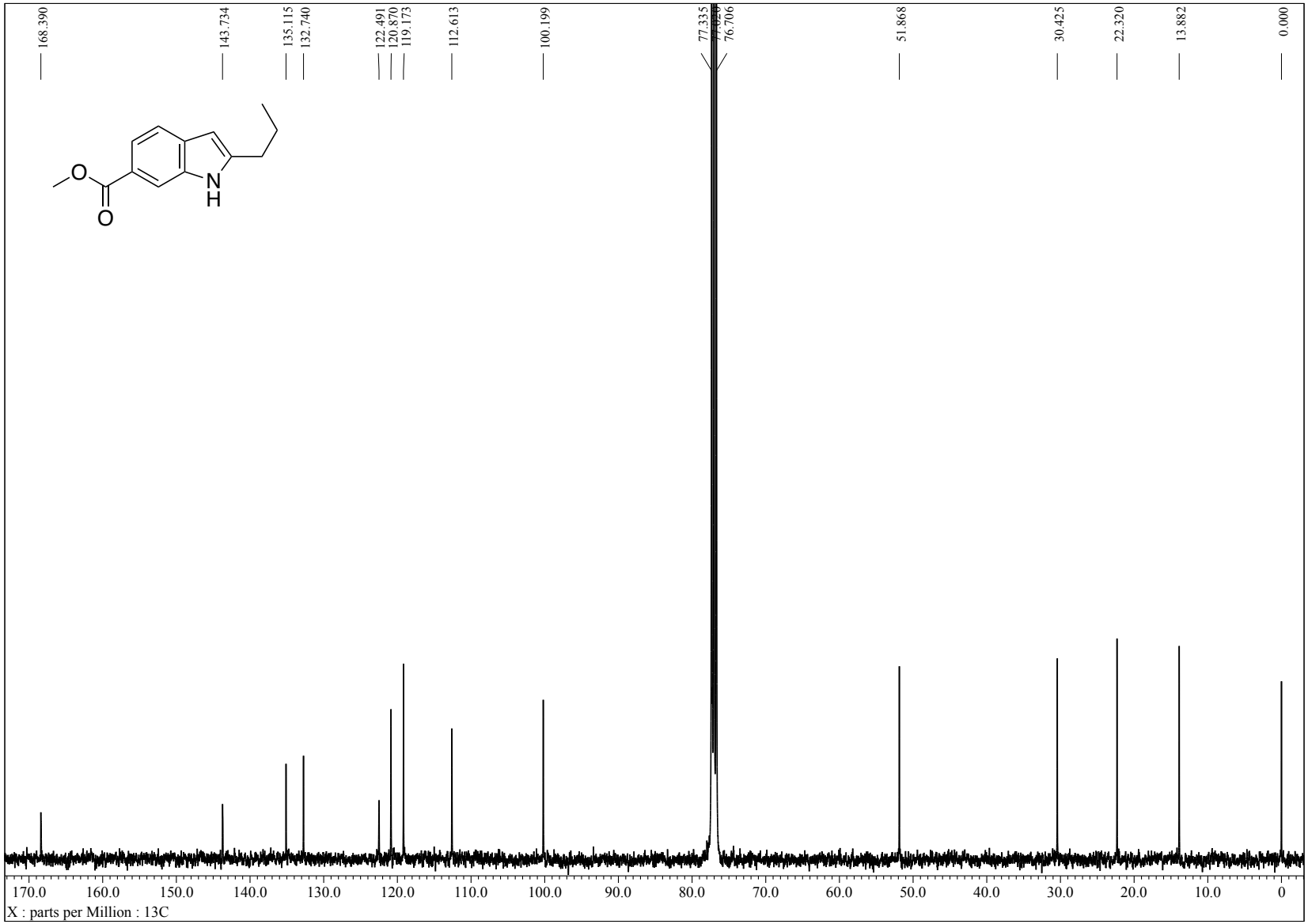
^{19}F NMR (471 MHz, CD_3CN)



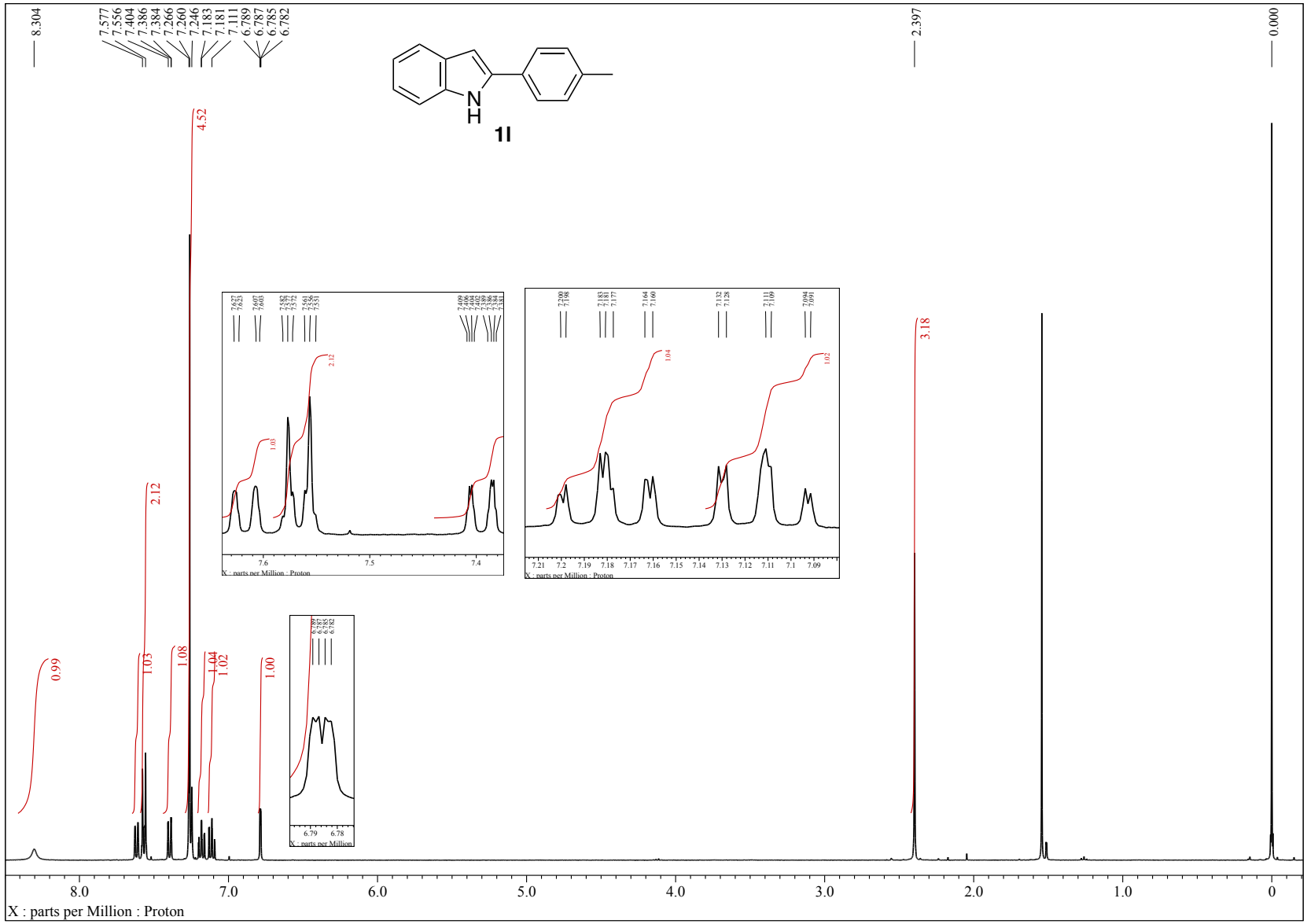
^{1}H NMR (400 MHz, $CDCl_3$)



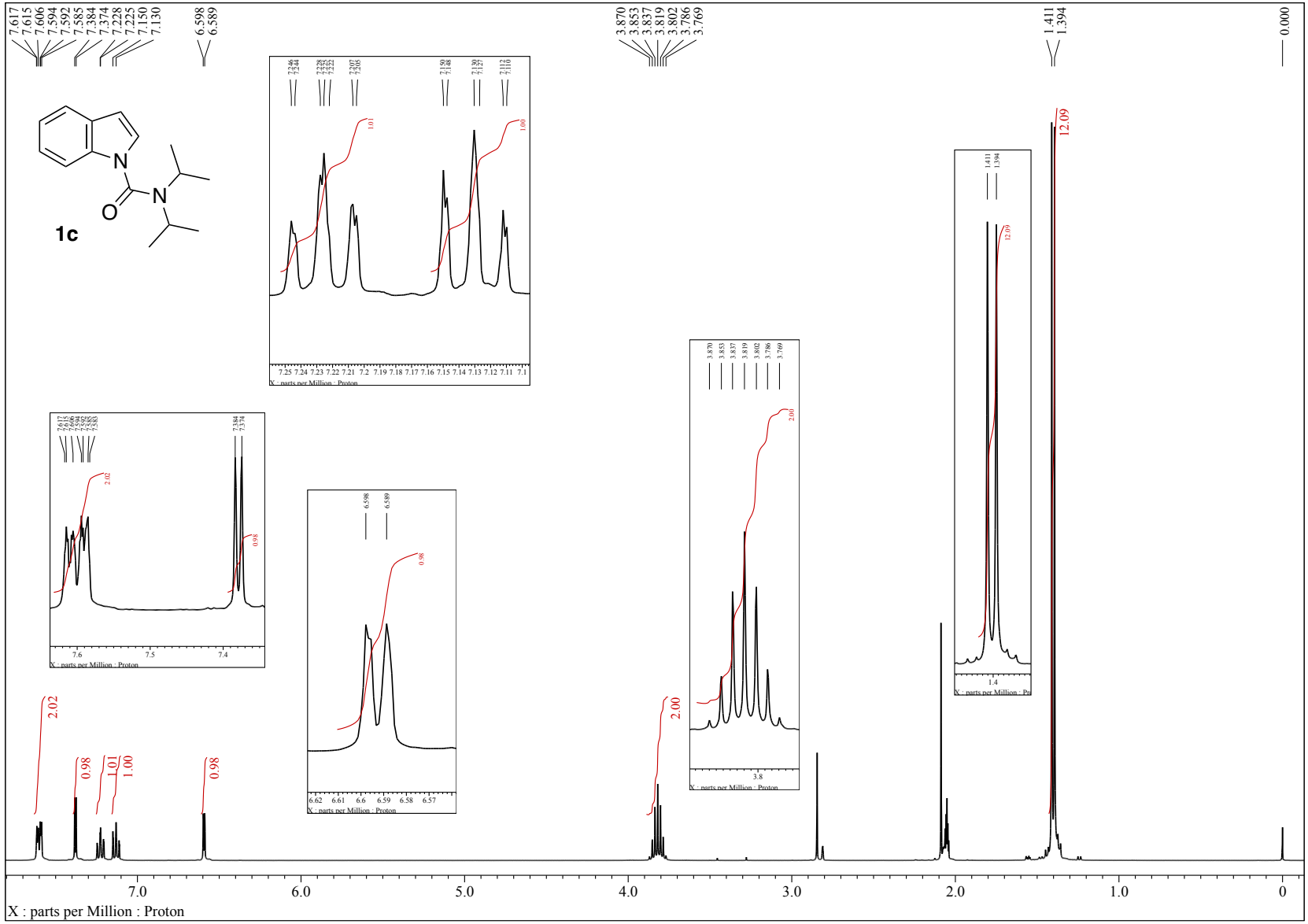
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



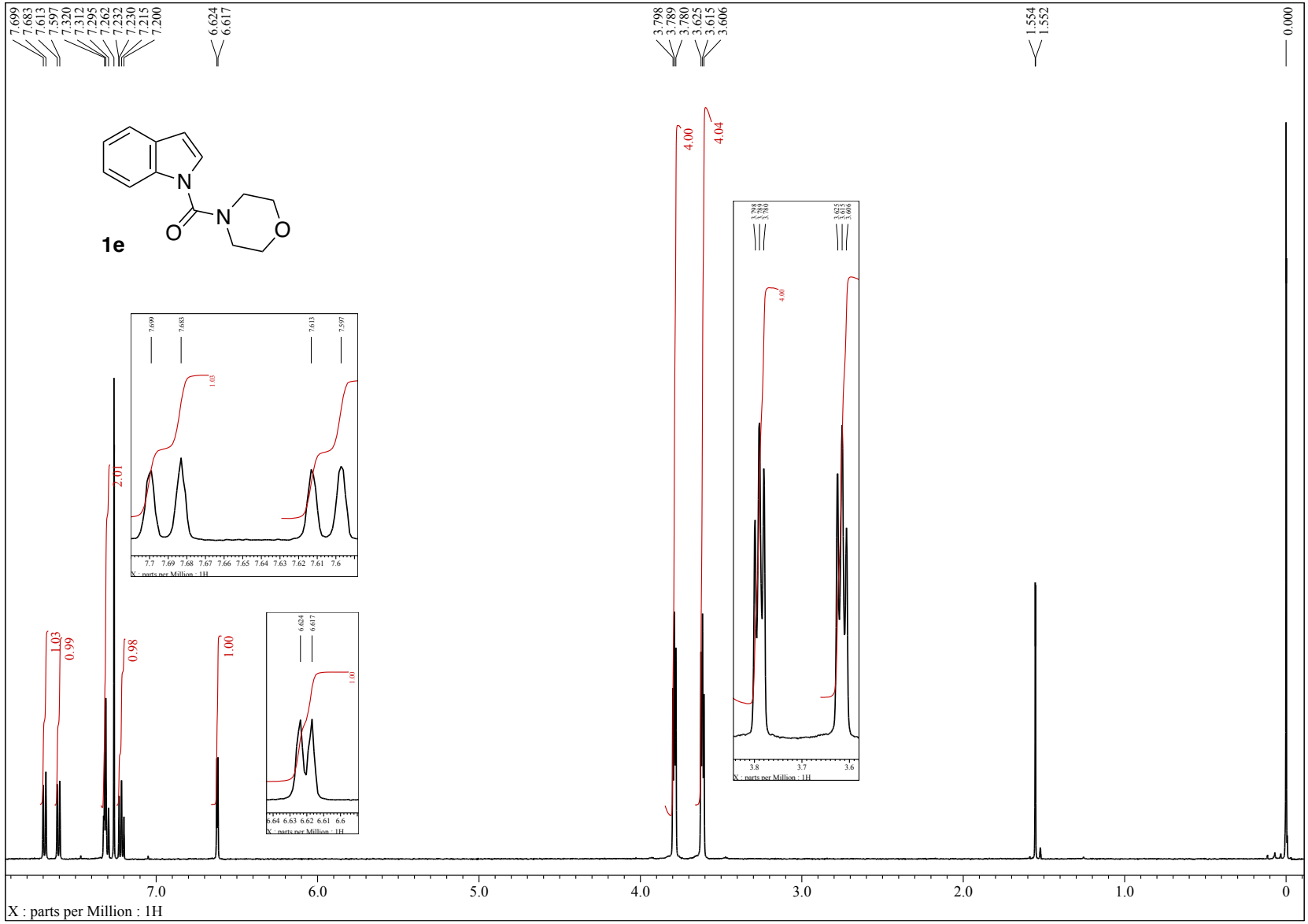
^{1}H NMR (400 MHz, $CDCl_3$)



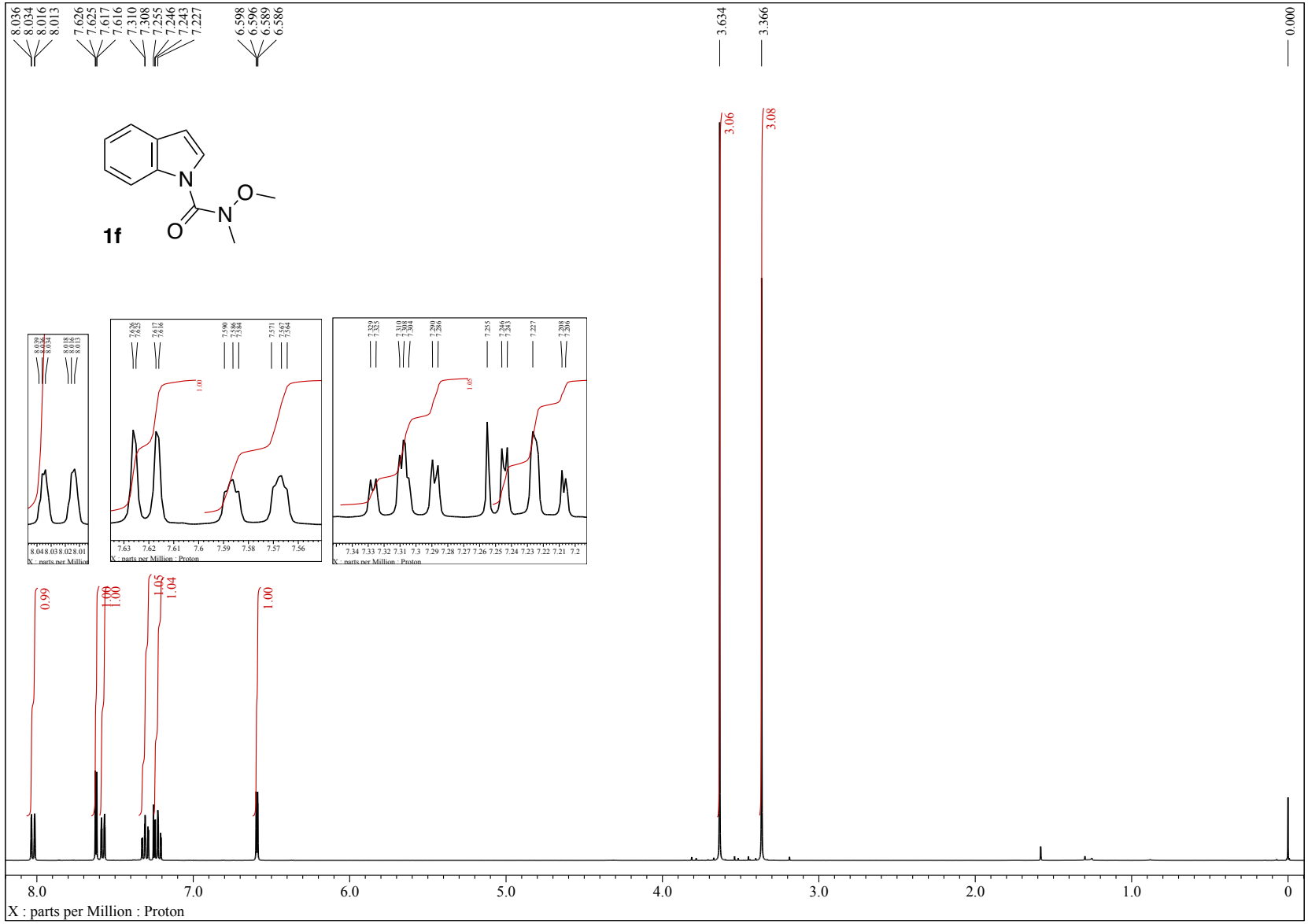
^{1}H NMR (400 MHz, acetone-d_6)



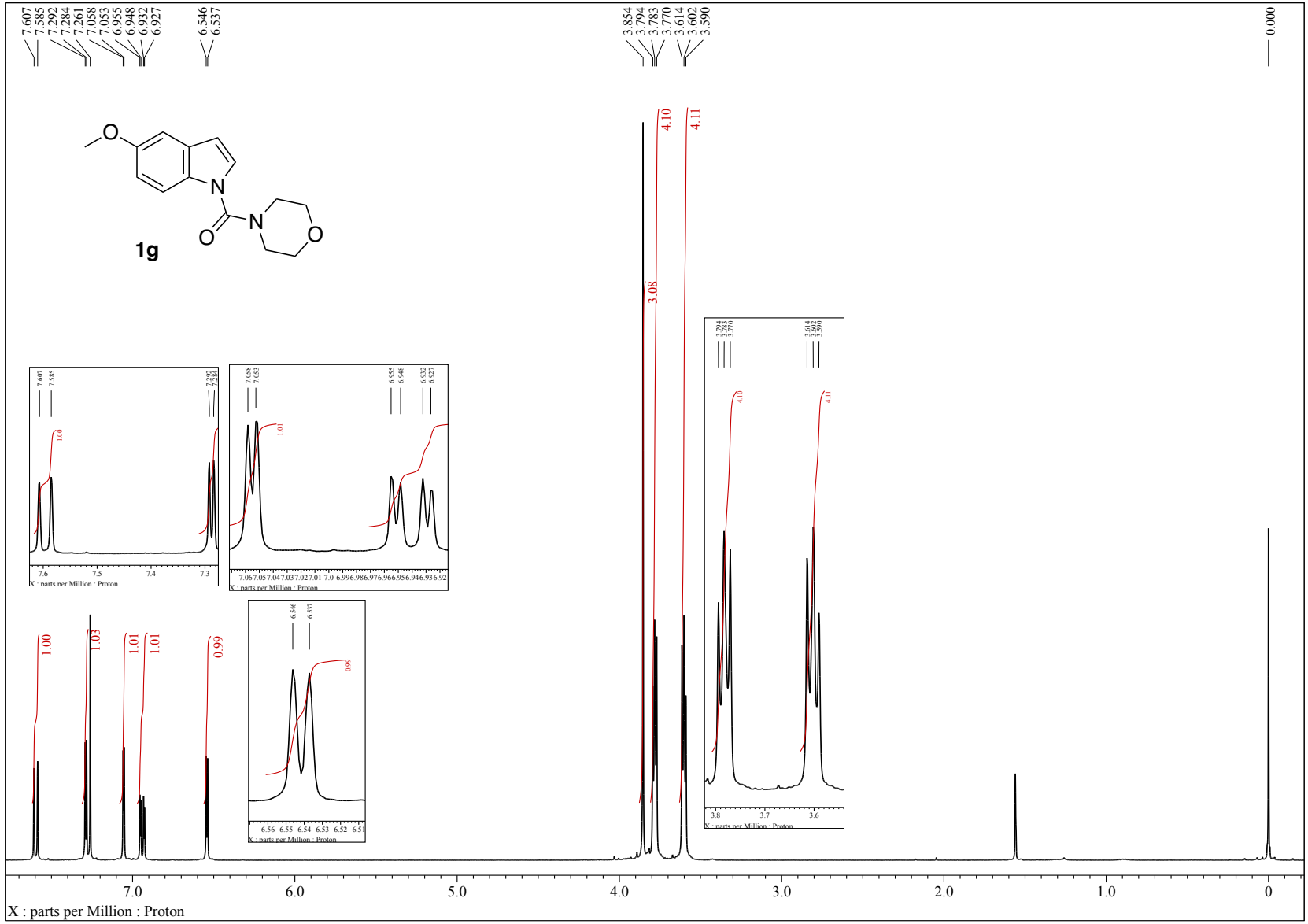
^{1}H NMR (500 MHz, $CDCl_3$)



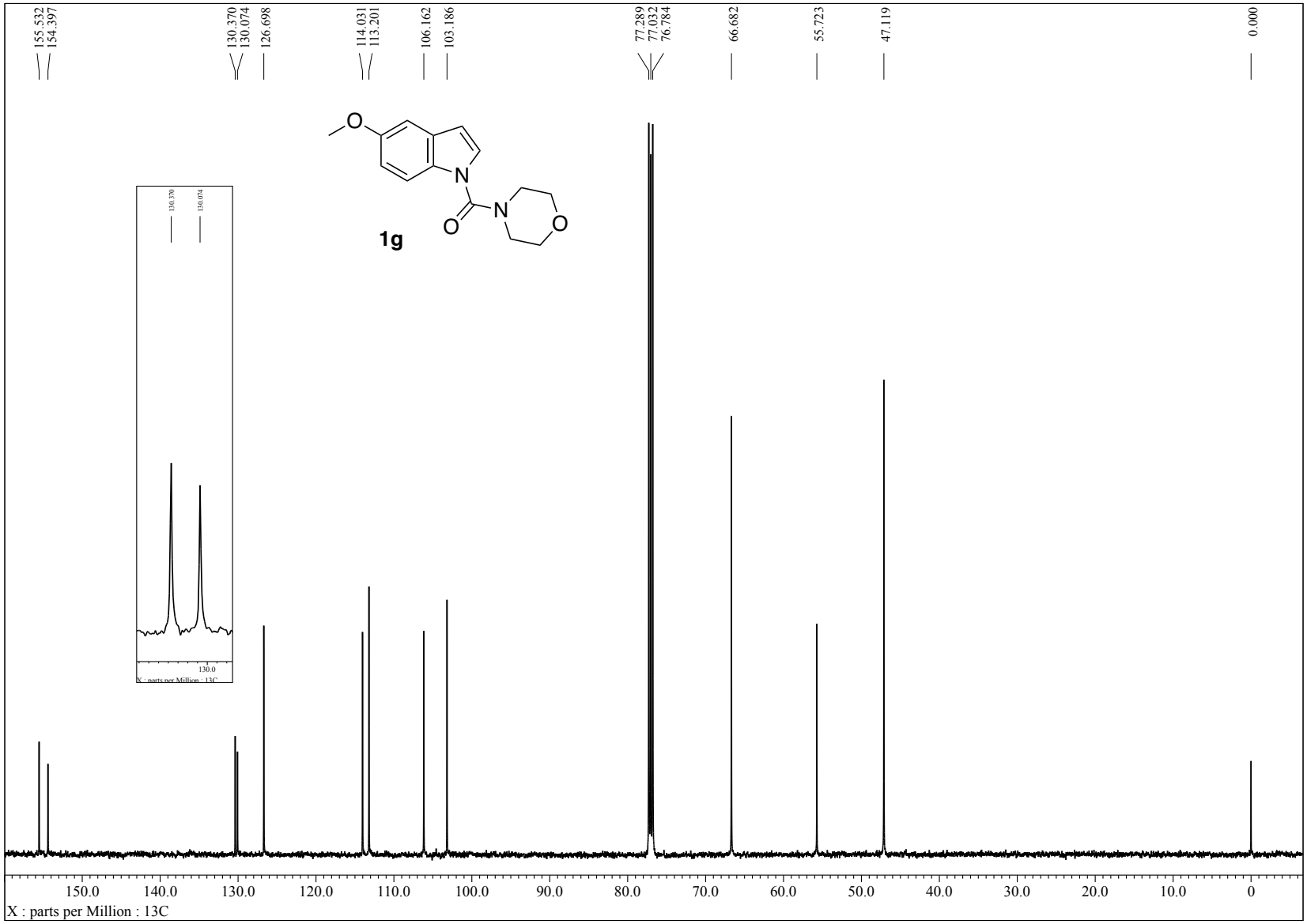
^{1}H NMR (400 MHz, $CDCl_3$)



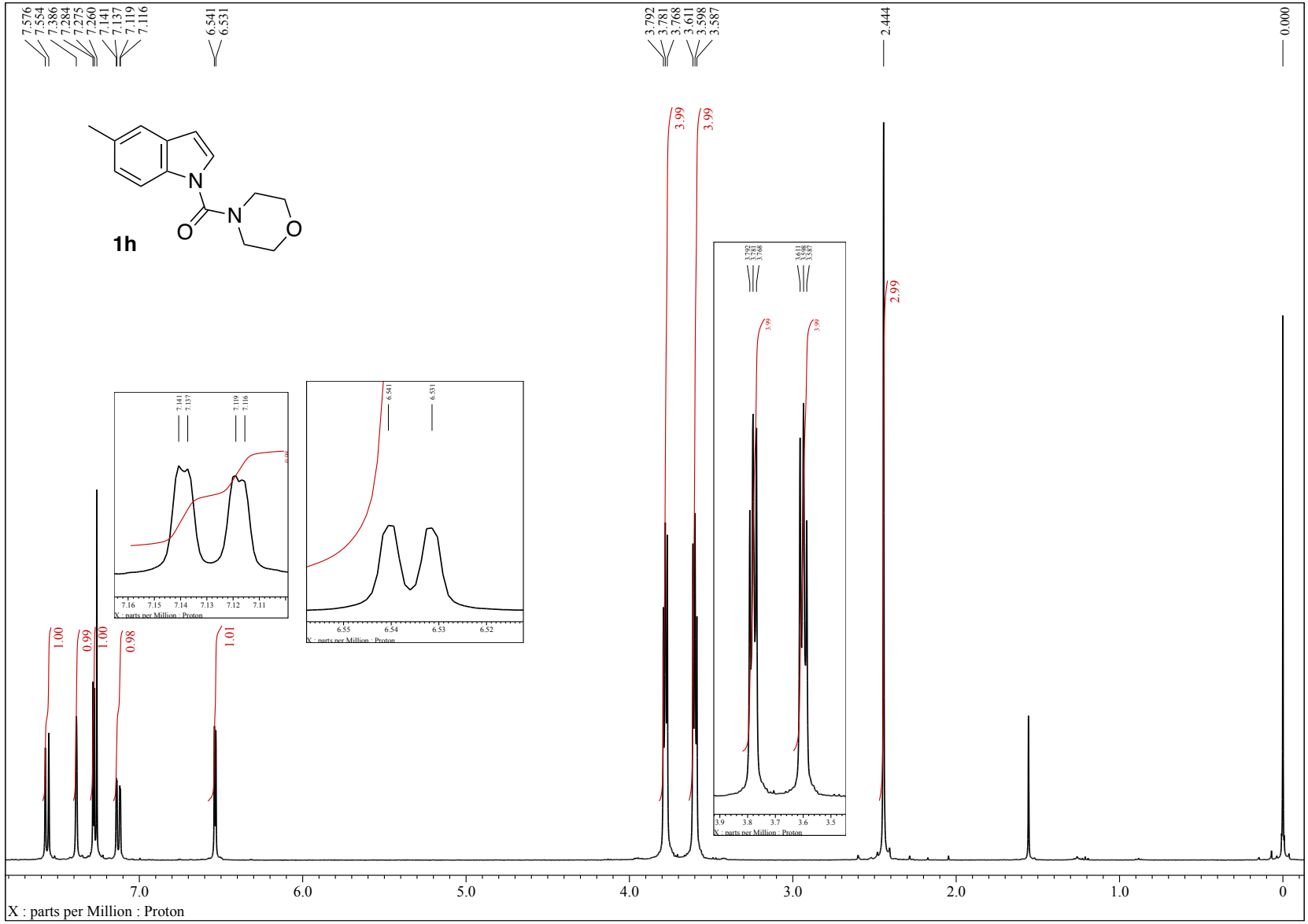
^{1}H NMR (400 MHz, $CDCl_3$)



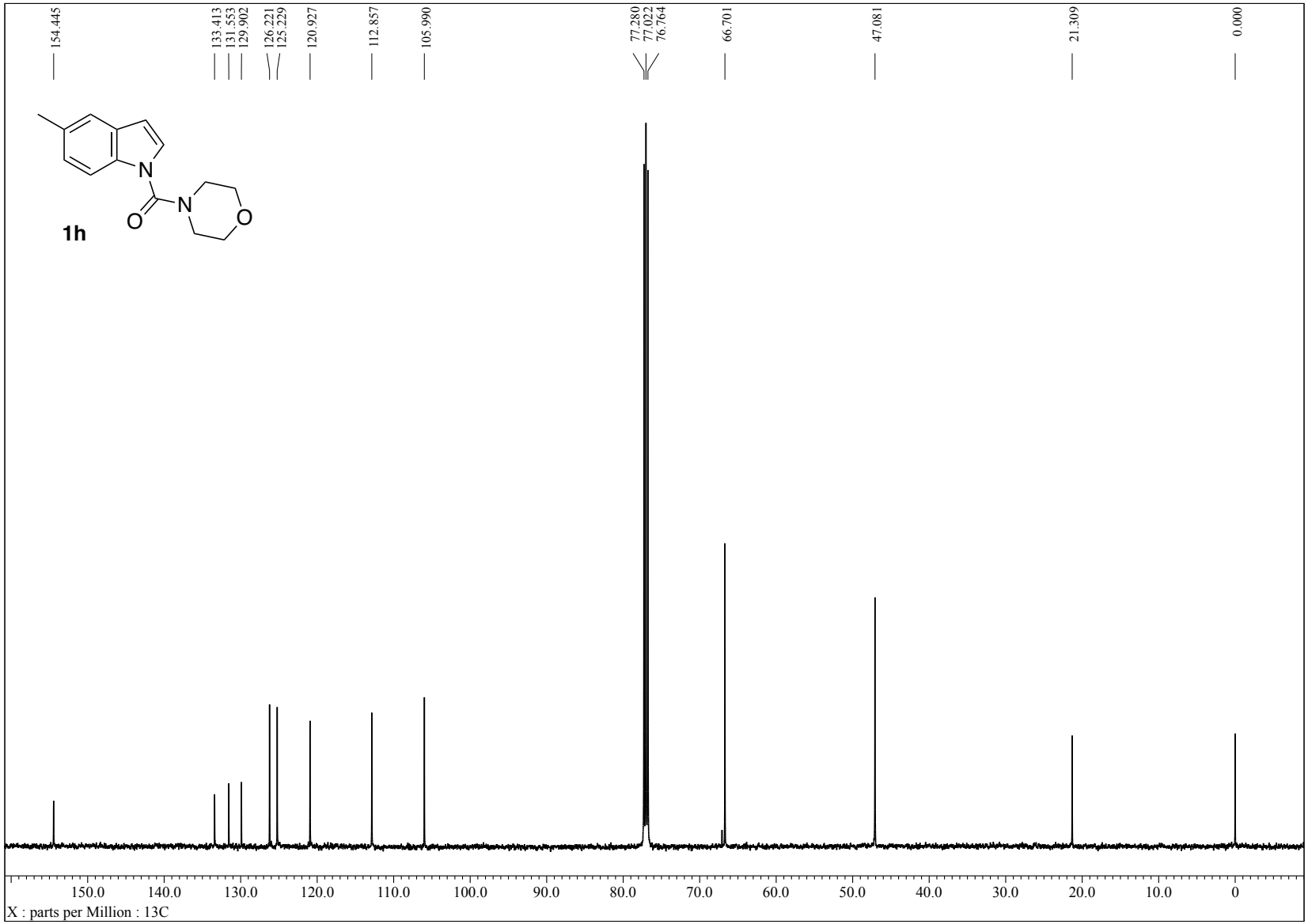
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



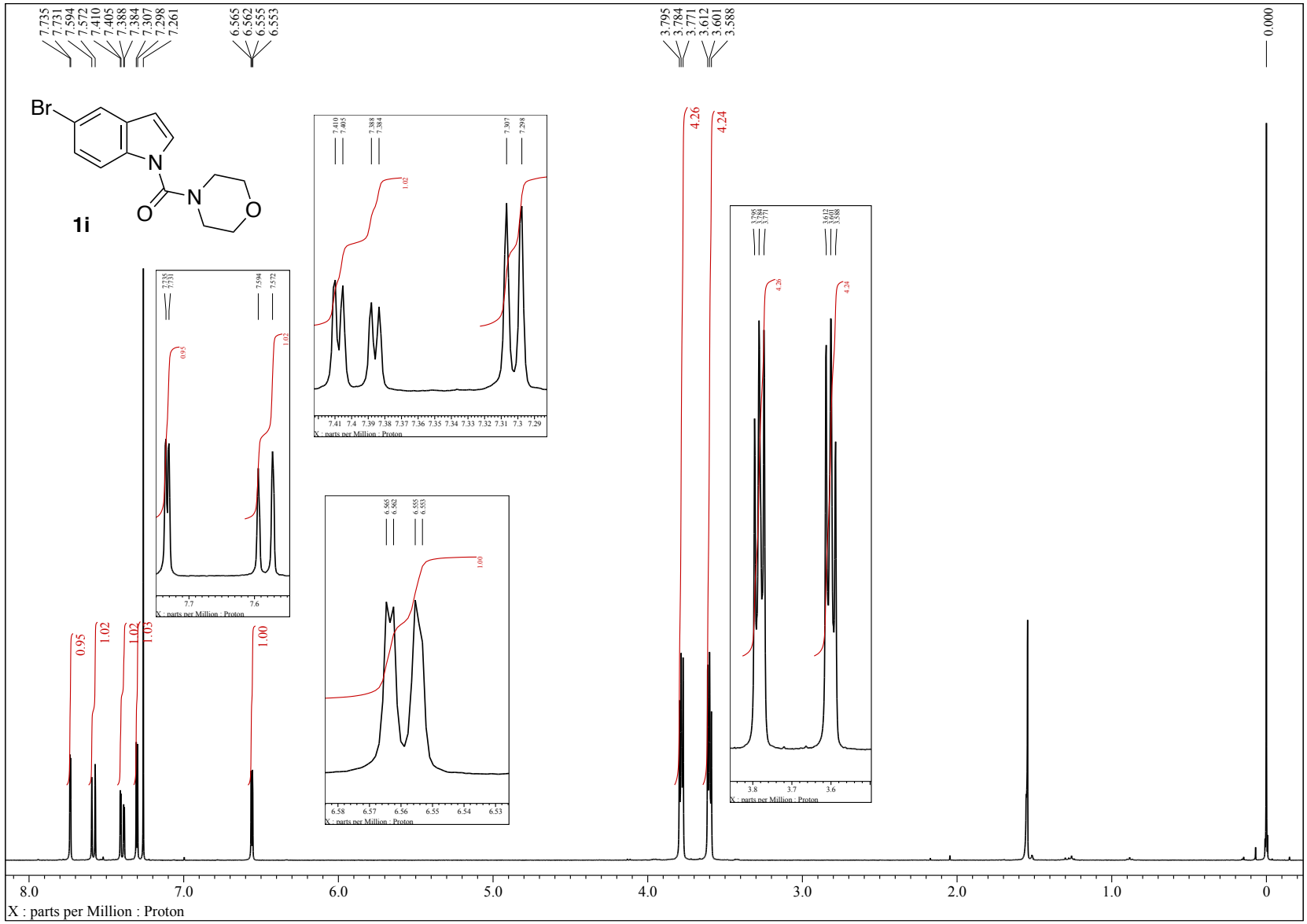
^{1}H NMR (400 MHz, $CDCl_3$)



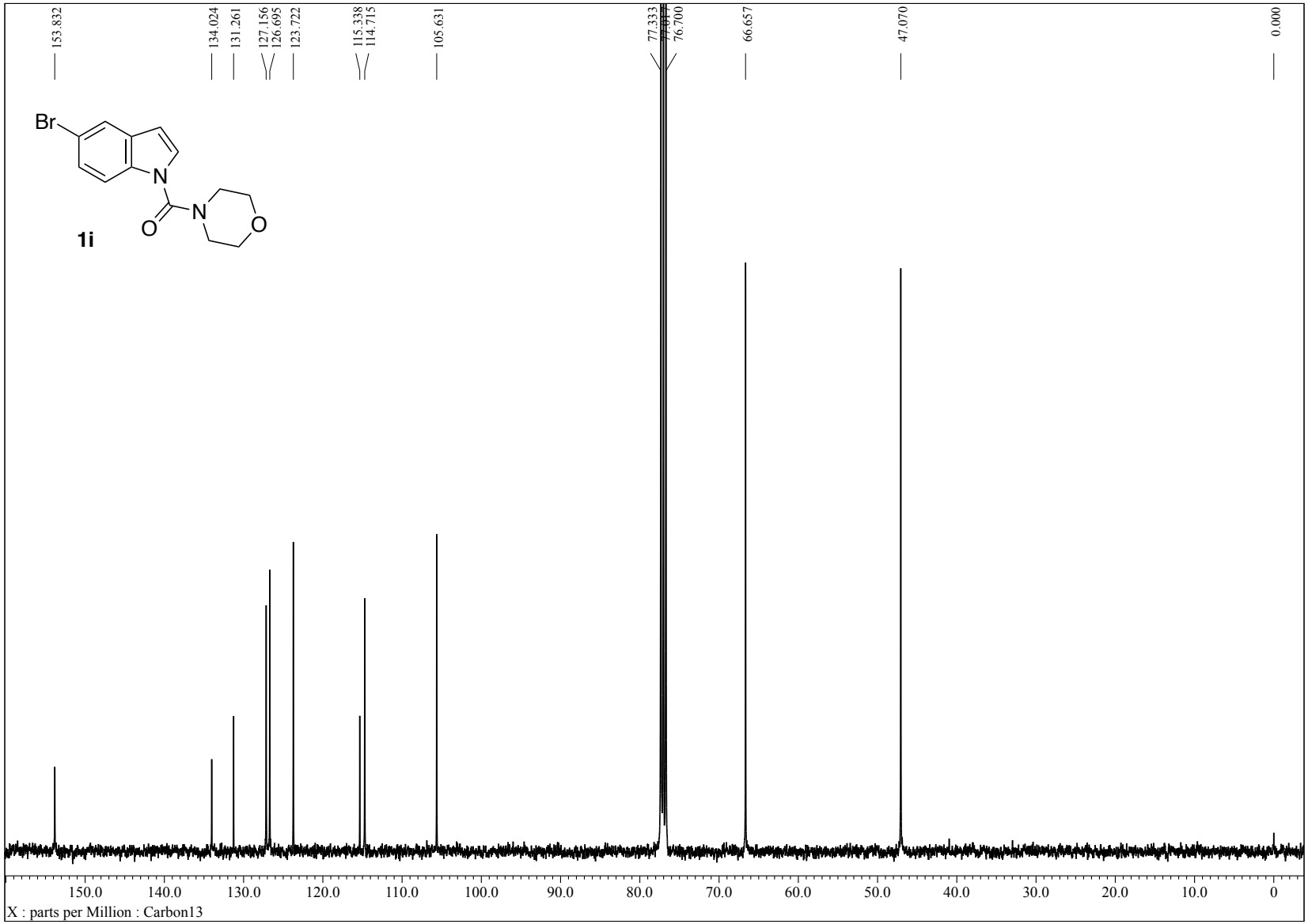
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



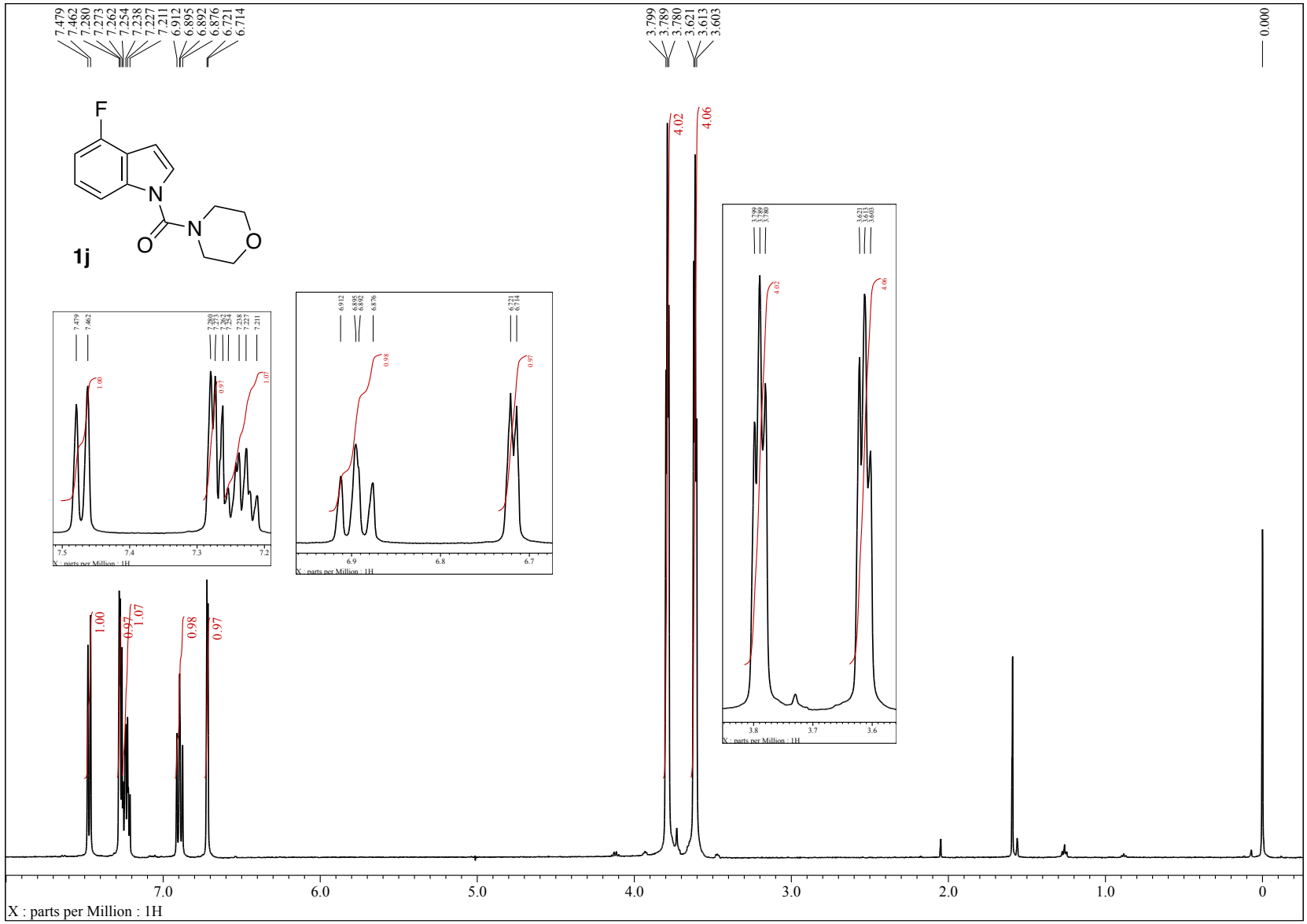
^{1}H NMR (400 MHz, $CDCl_3$)



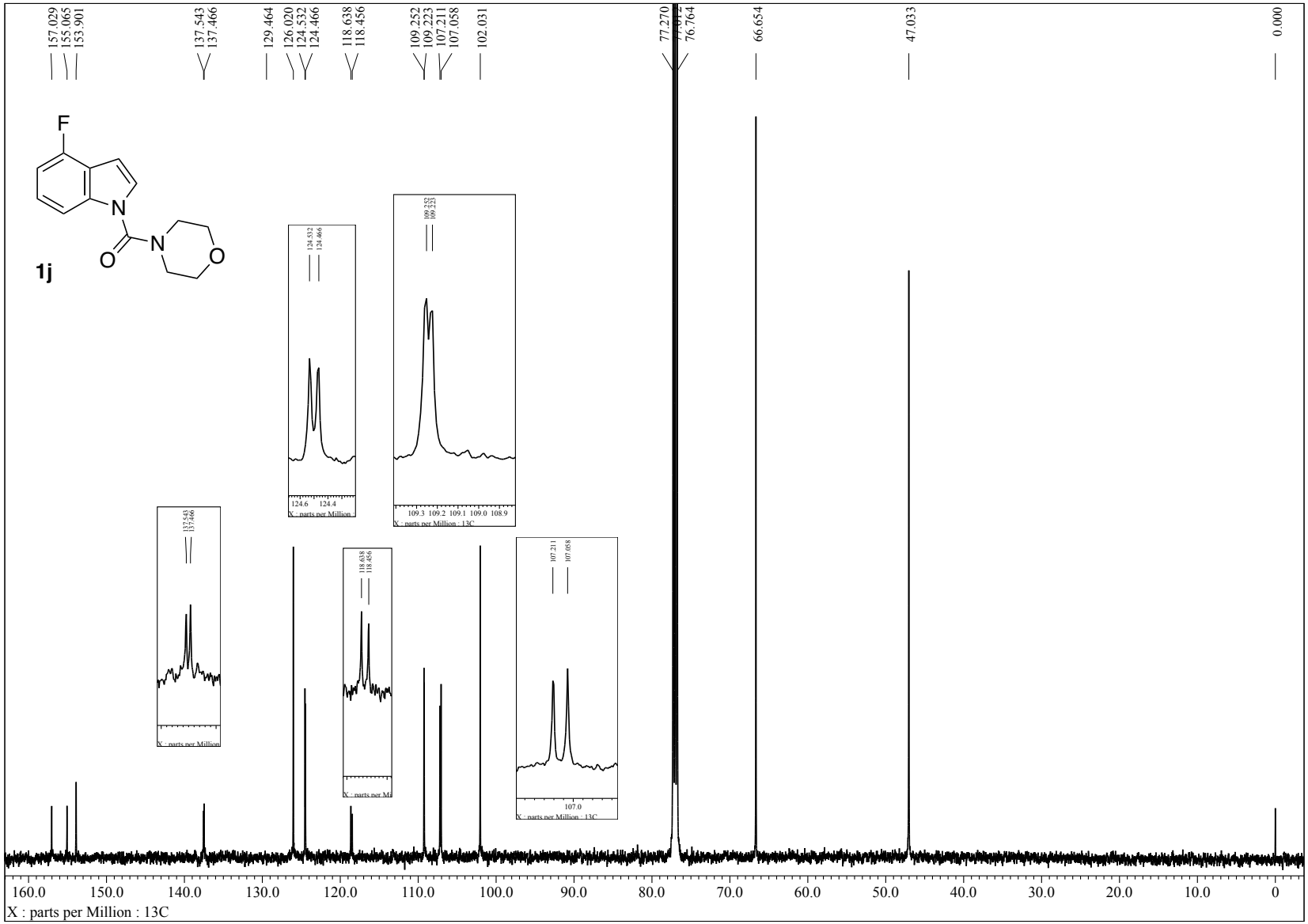
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



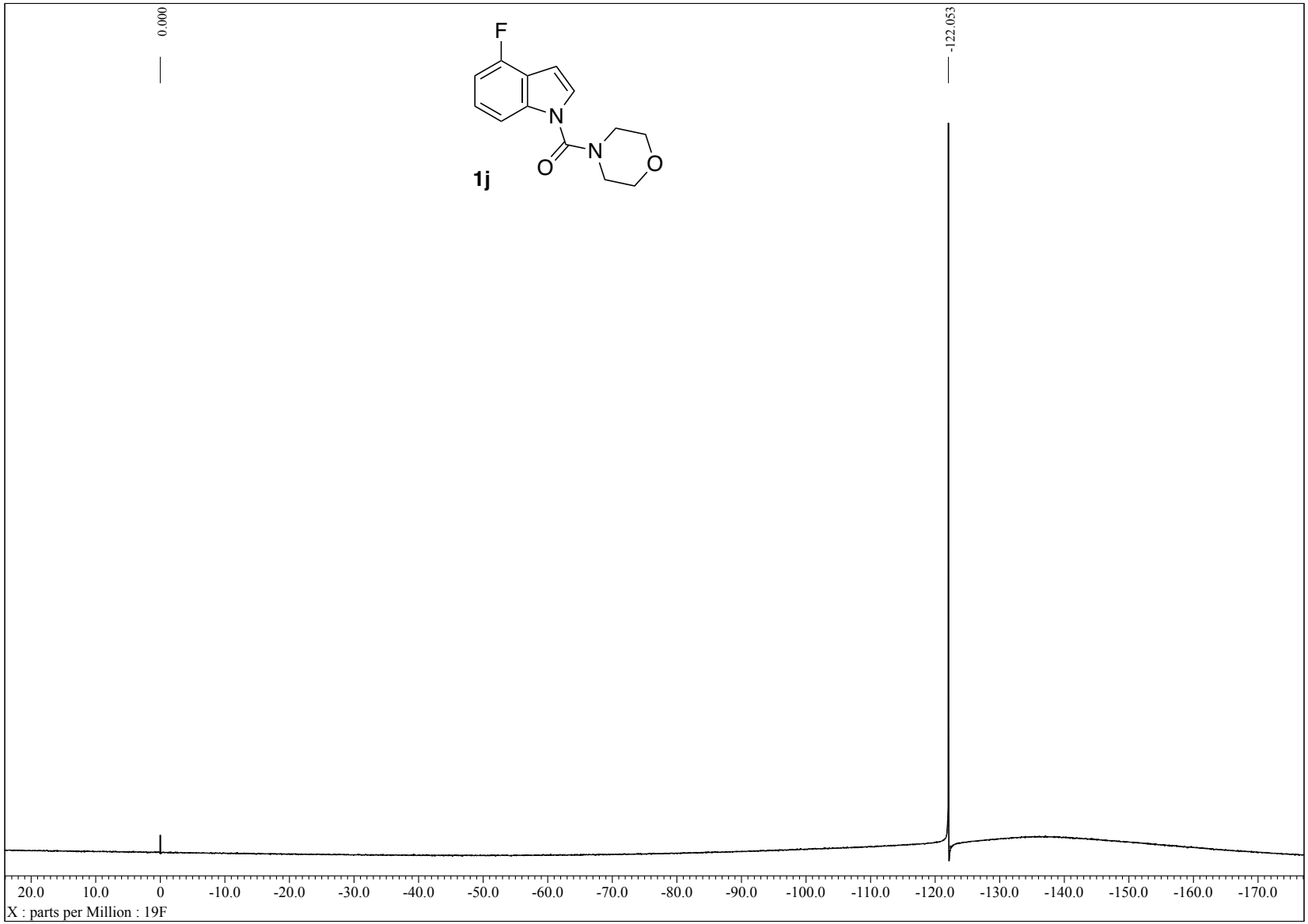
^{1}H NMR (400 MHz, $CDCl_3$)



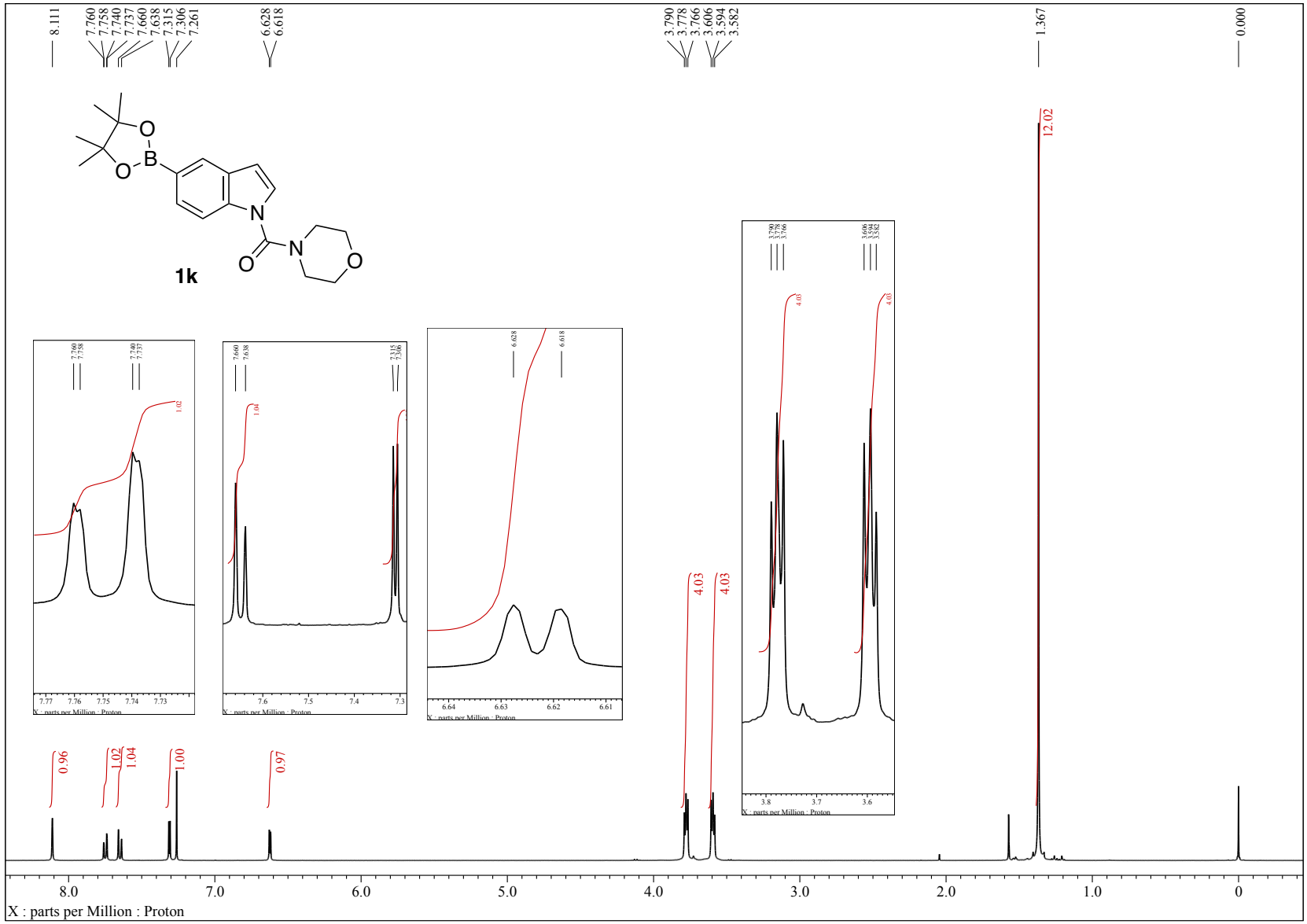
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

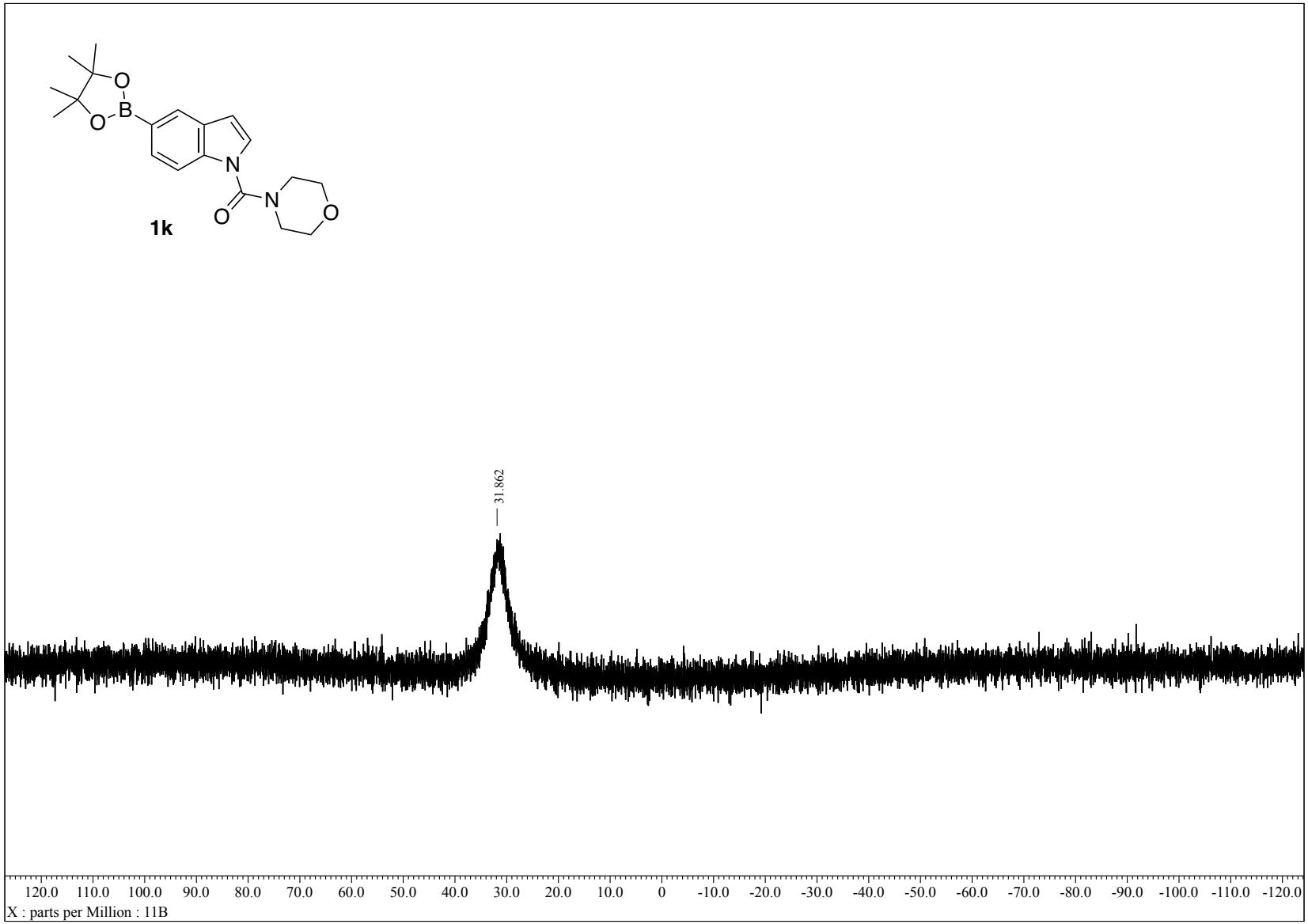


^{1}H NMR (400 MHz, $CDCl_3$)

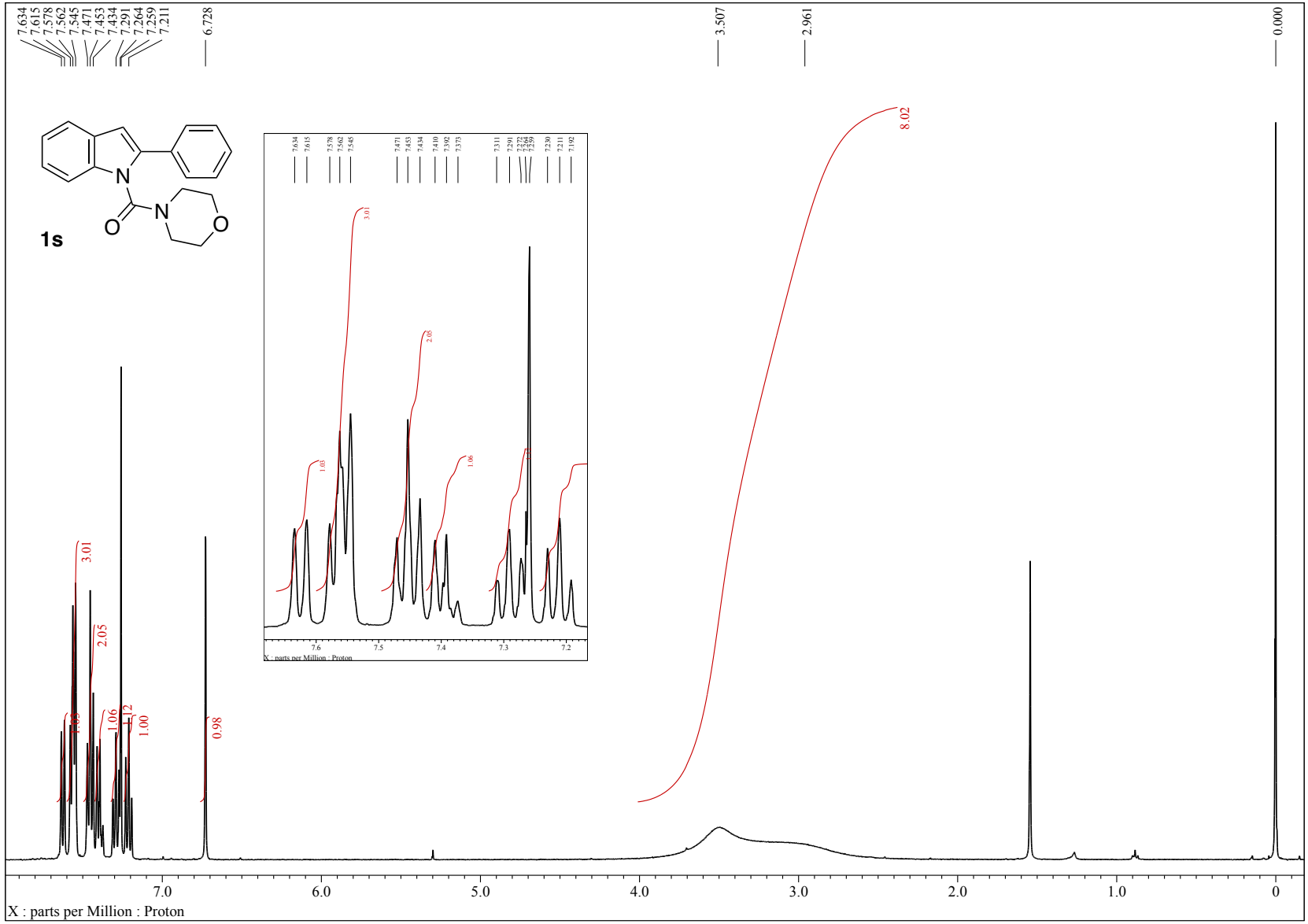


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

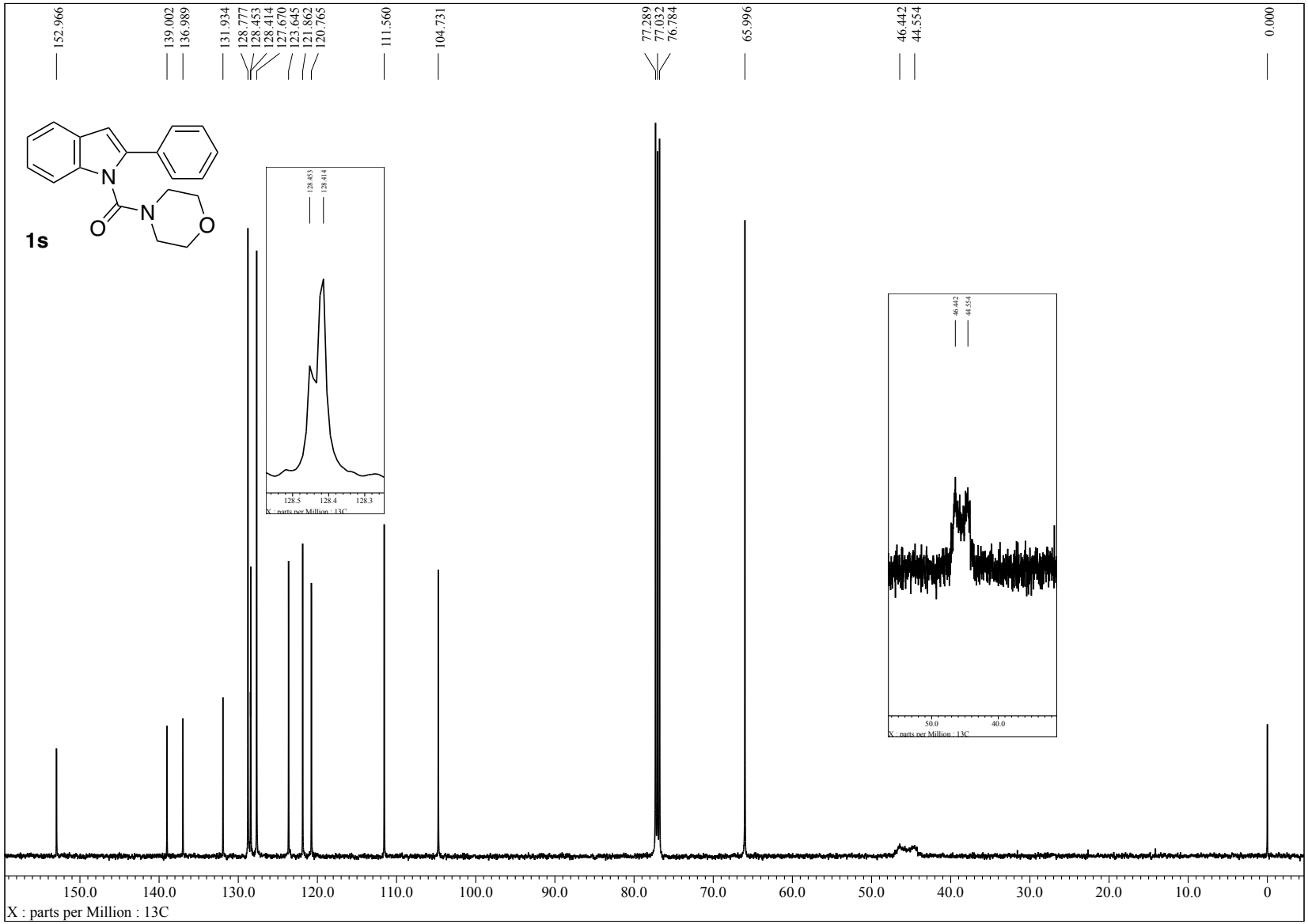
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



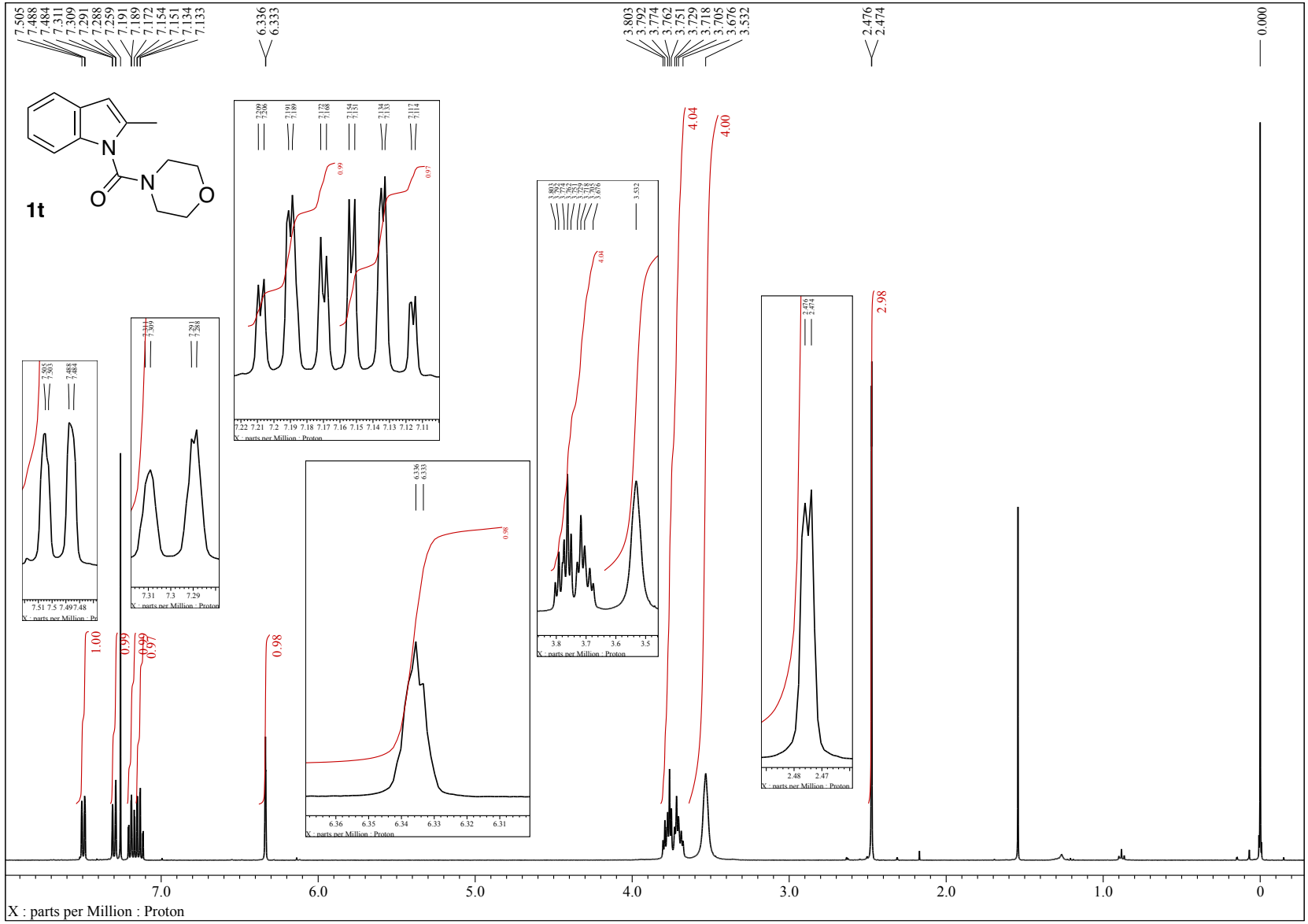
^{1}H NMR (400 MHz, $CDCl_3$)



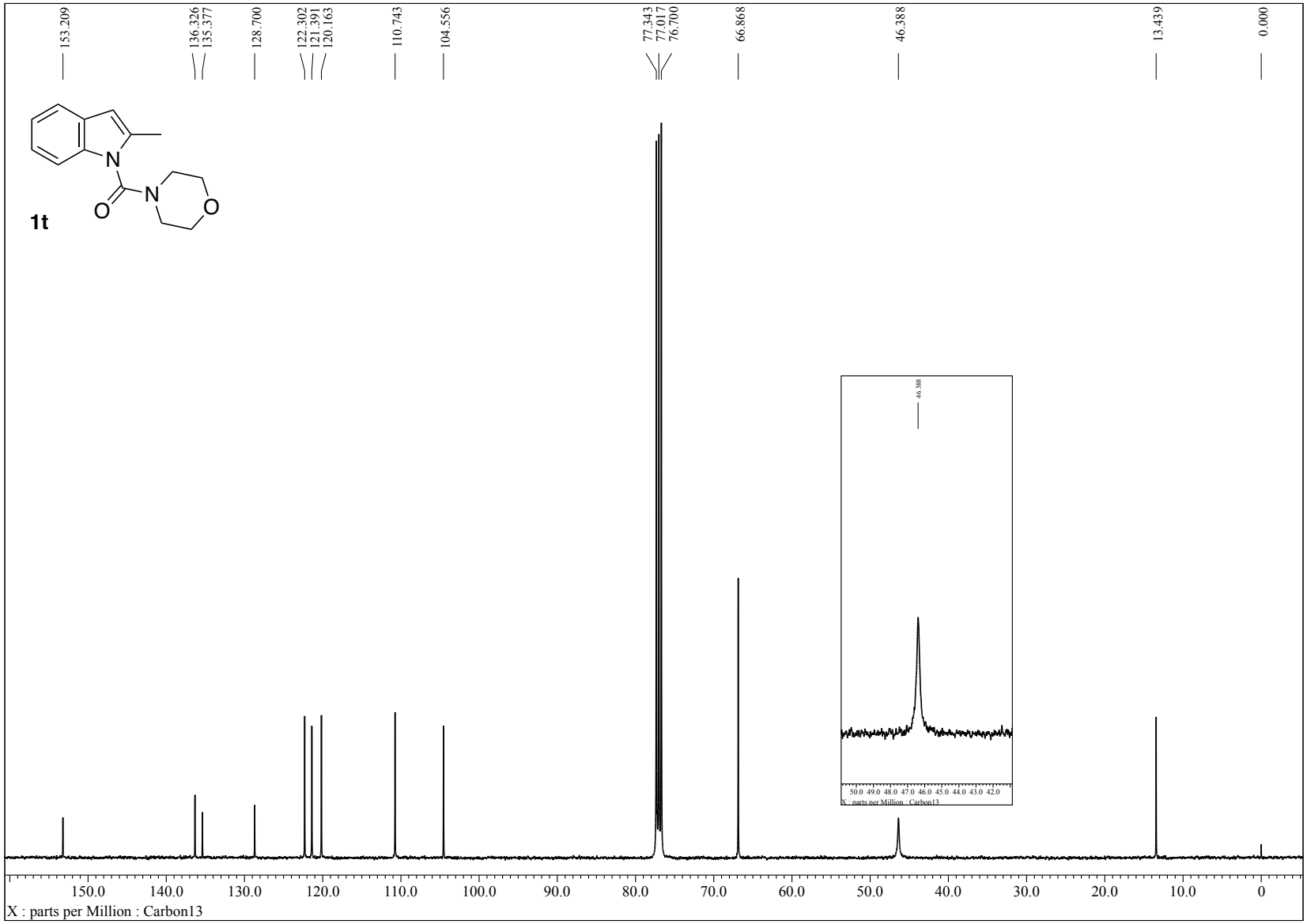
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



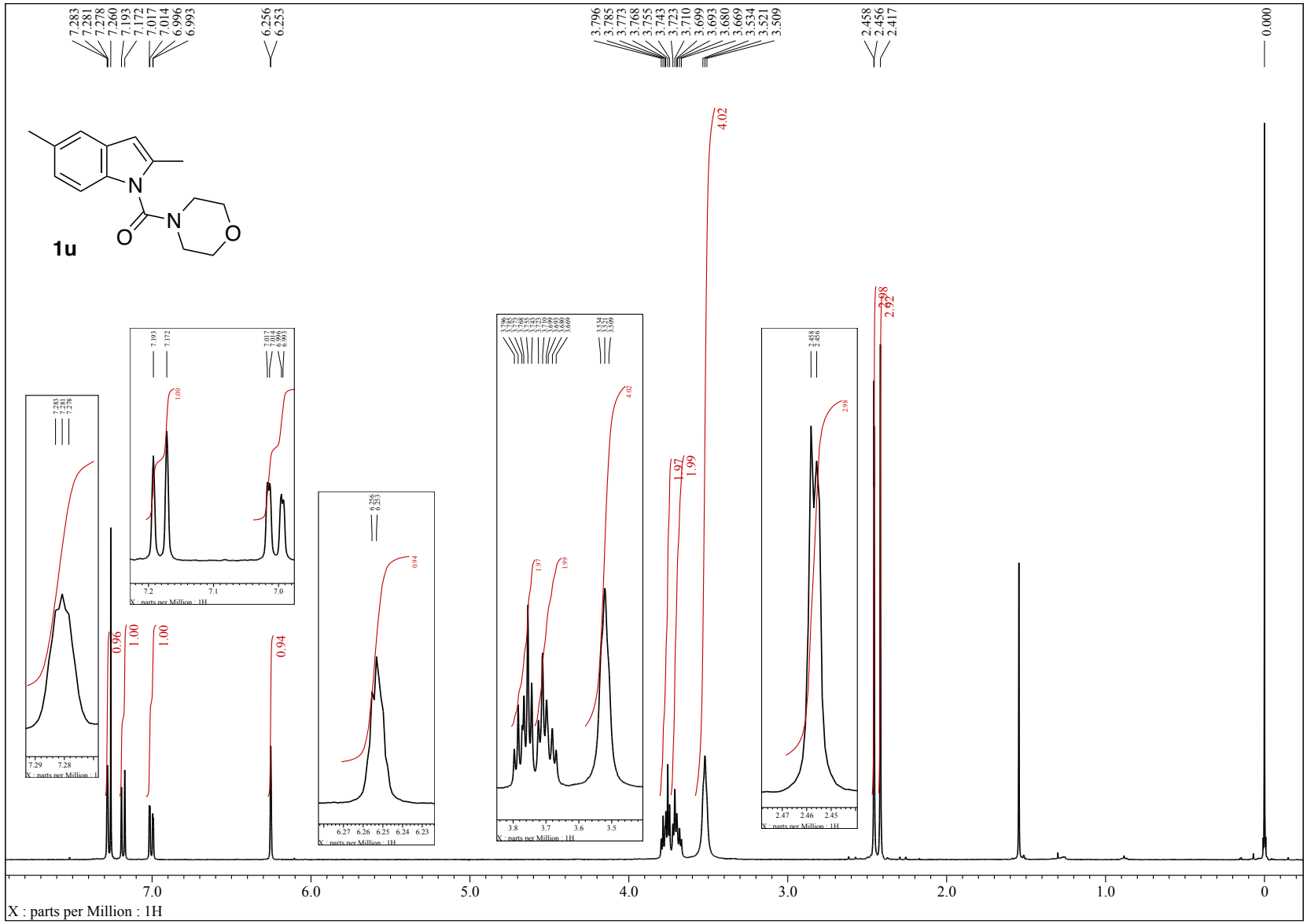
^{1}H NMR (400 MHz, $CDCl_3$)



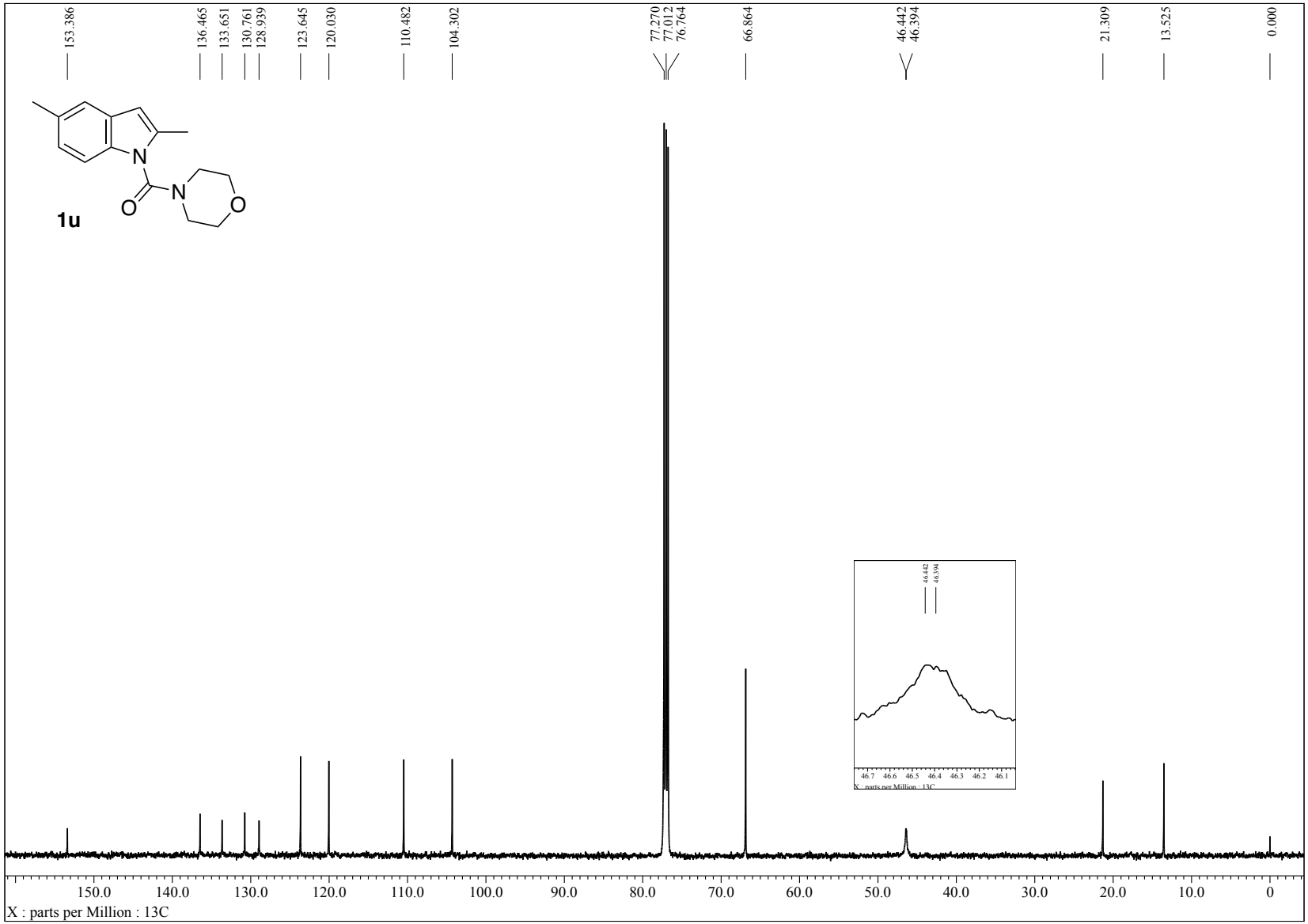
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



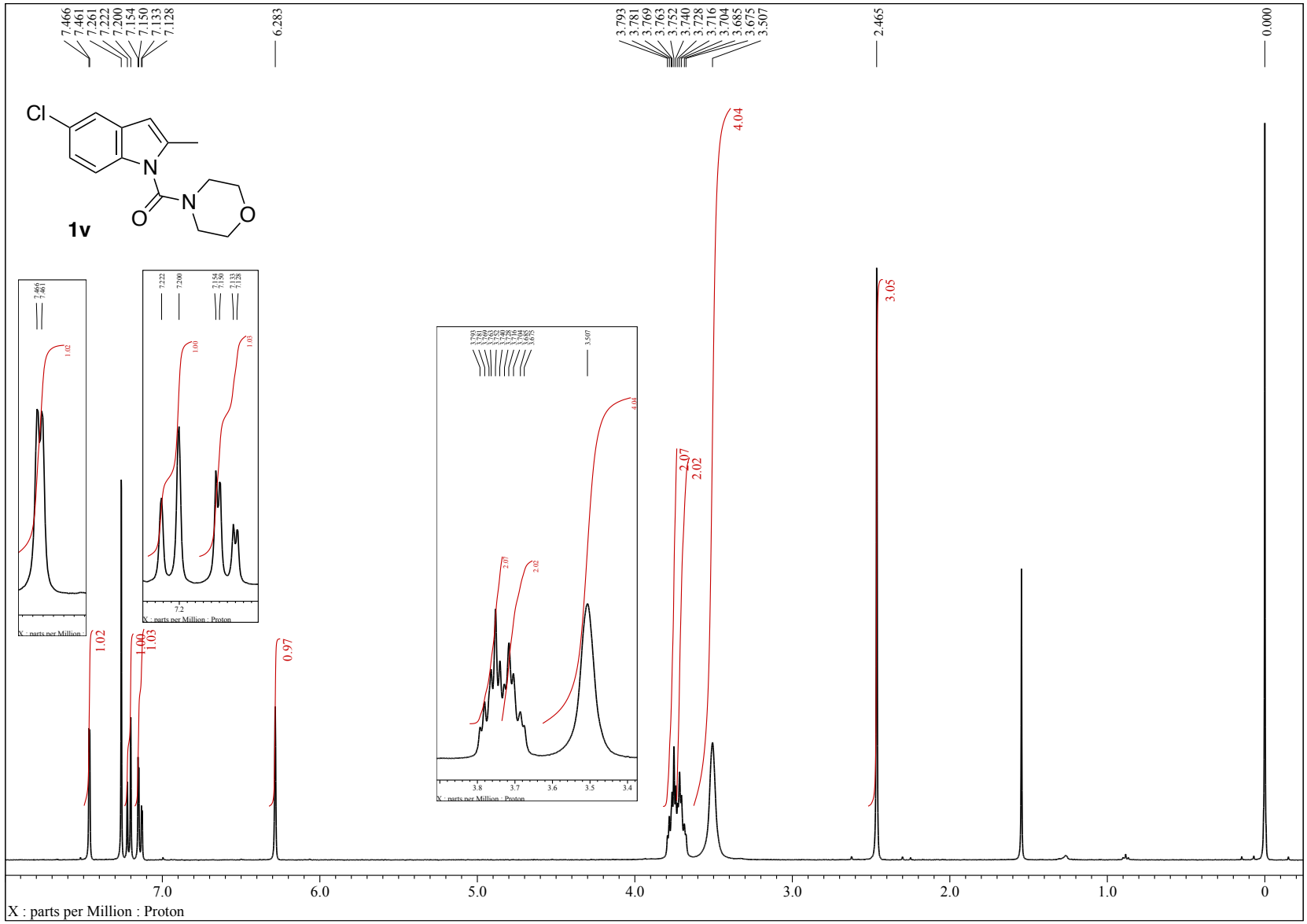
^{1}H NMR (400 MHz, $CDCl_3$)



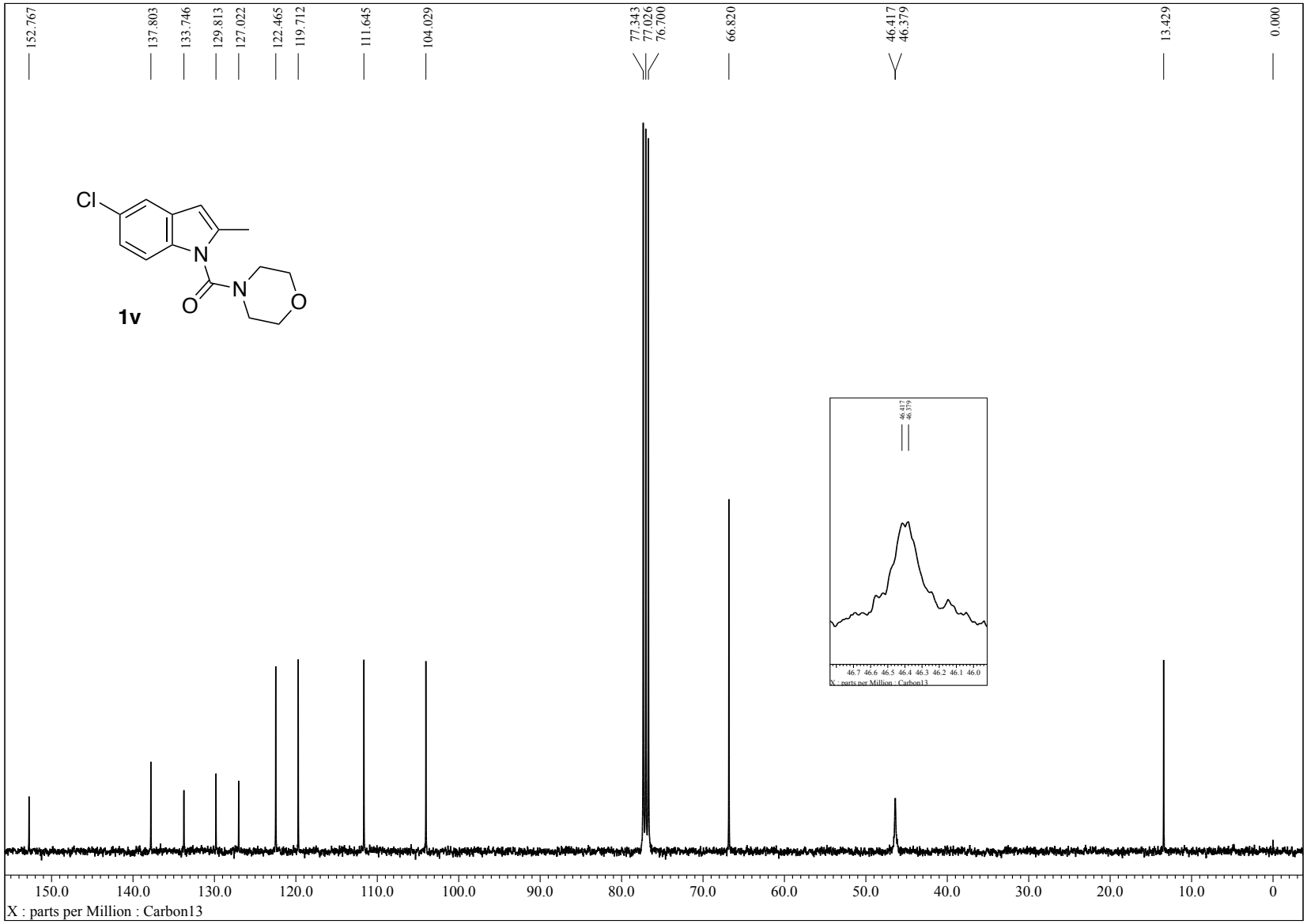
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



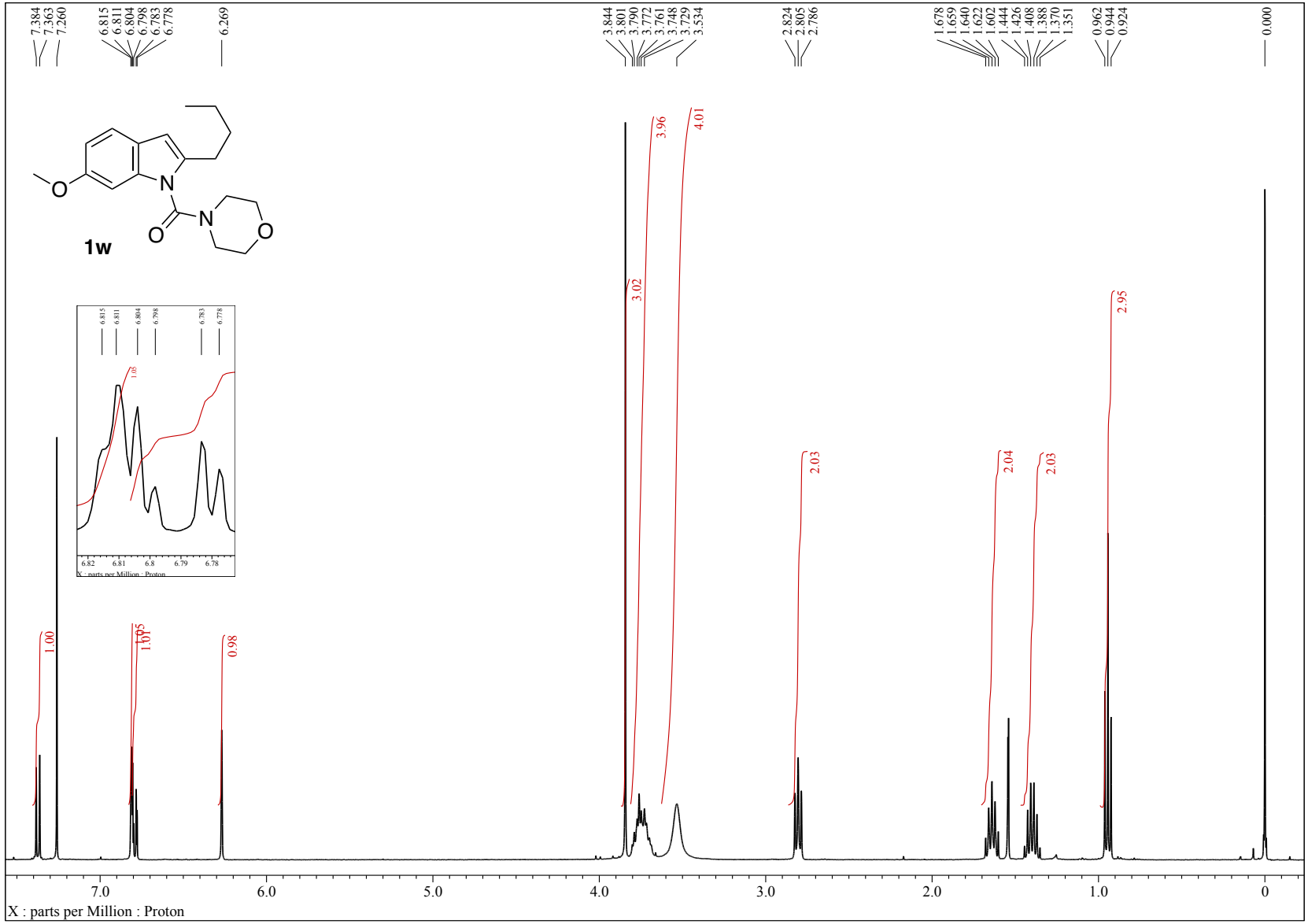
^{1}H NMR (400 MHz, $CDCl_3$)



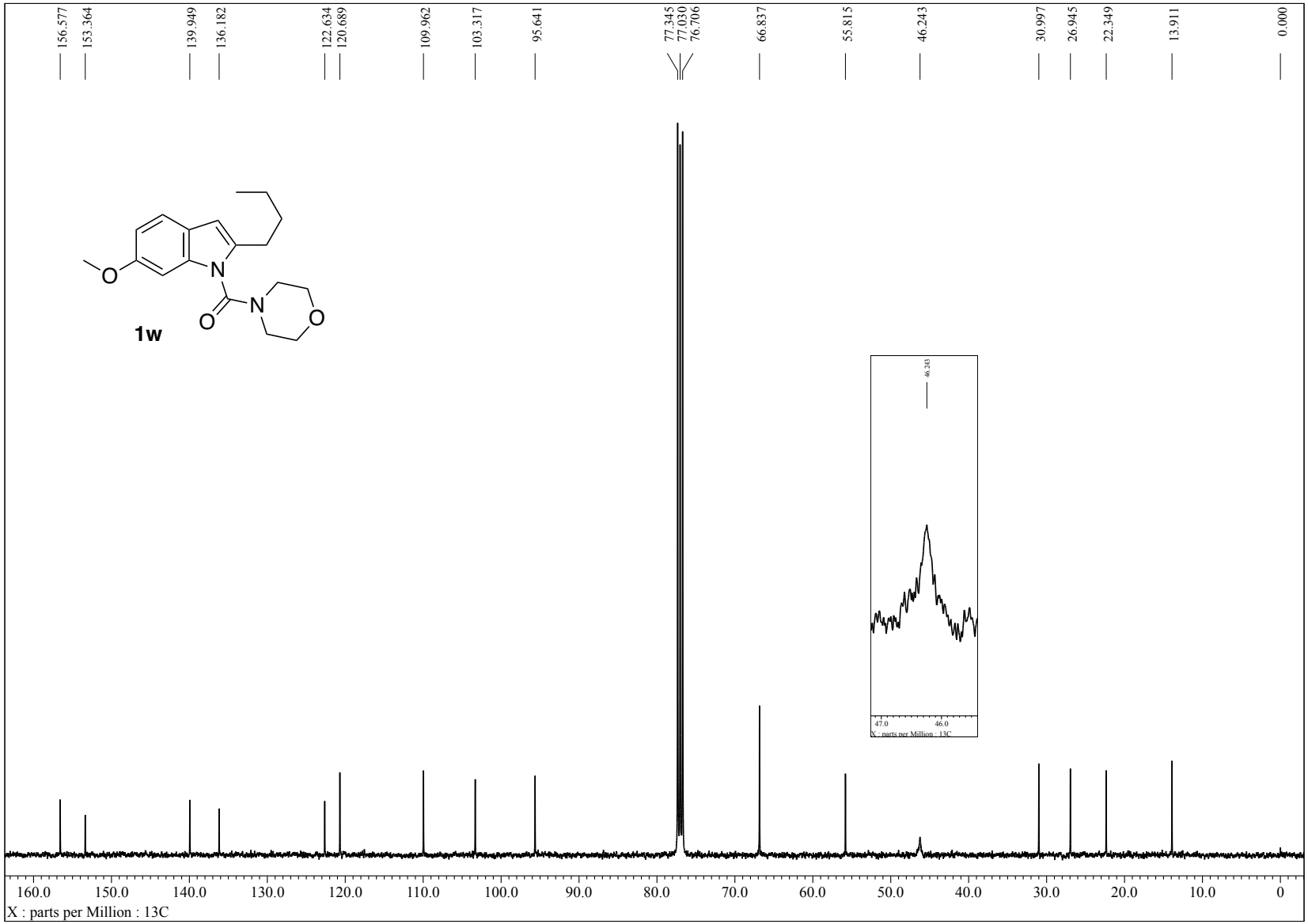
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



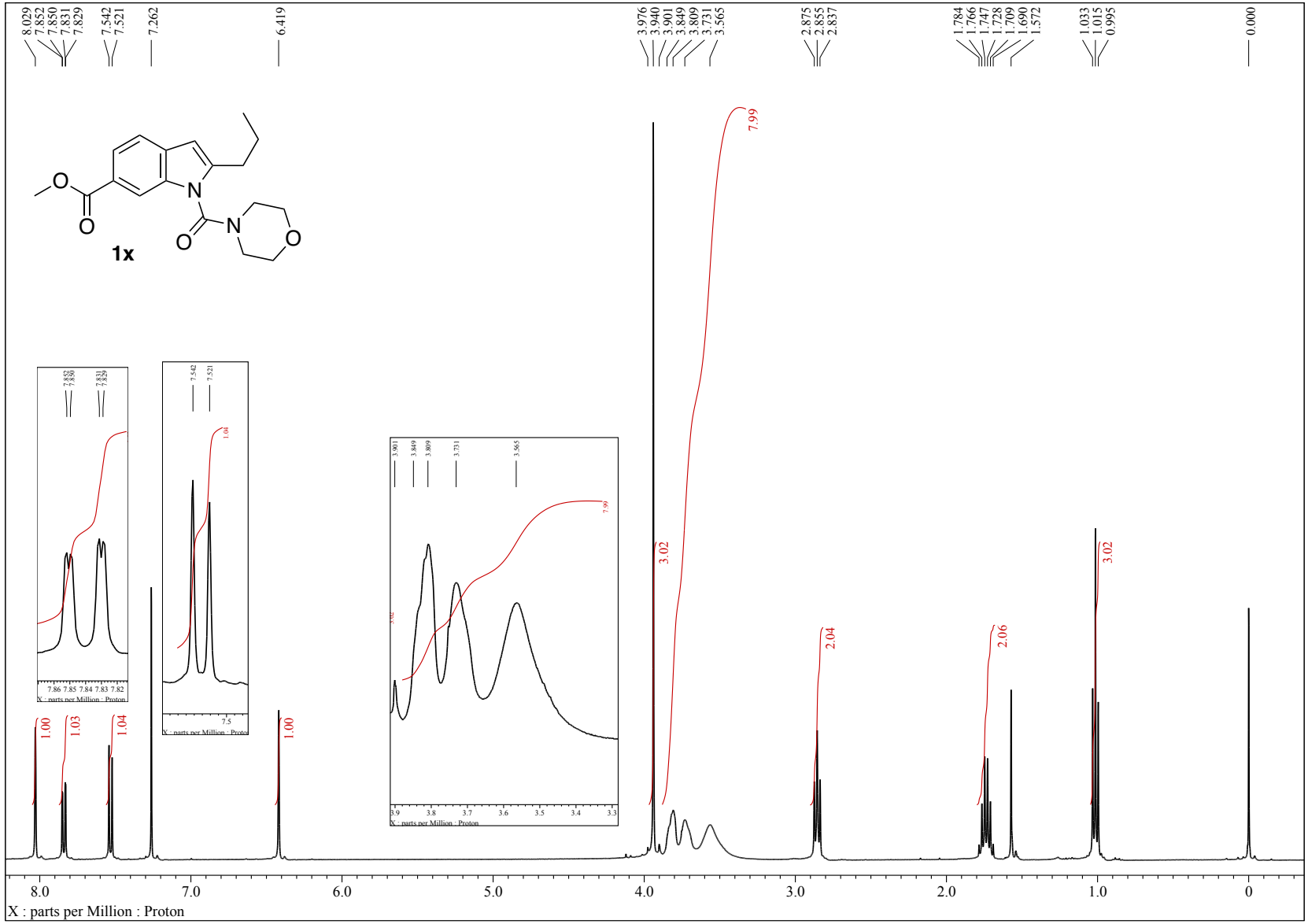
^{1}H NMR (400 MHz, $CDCl_3$)



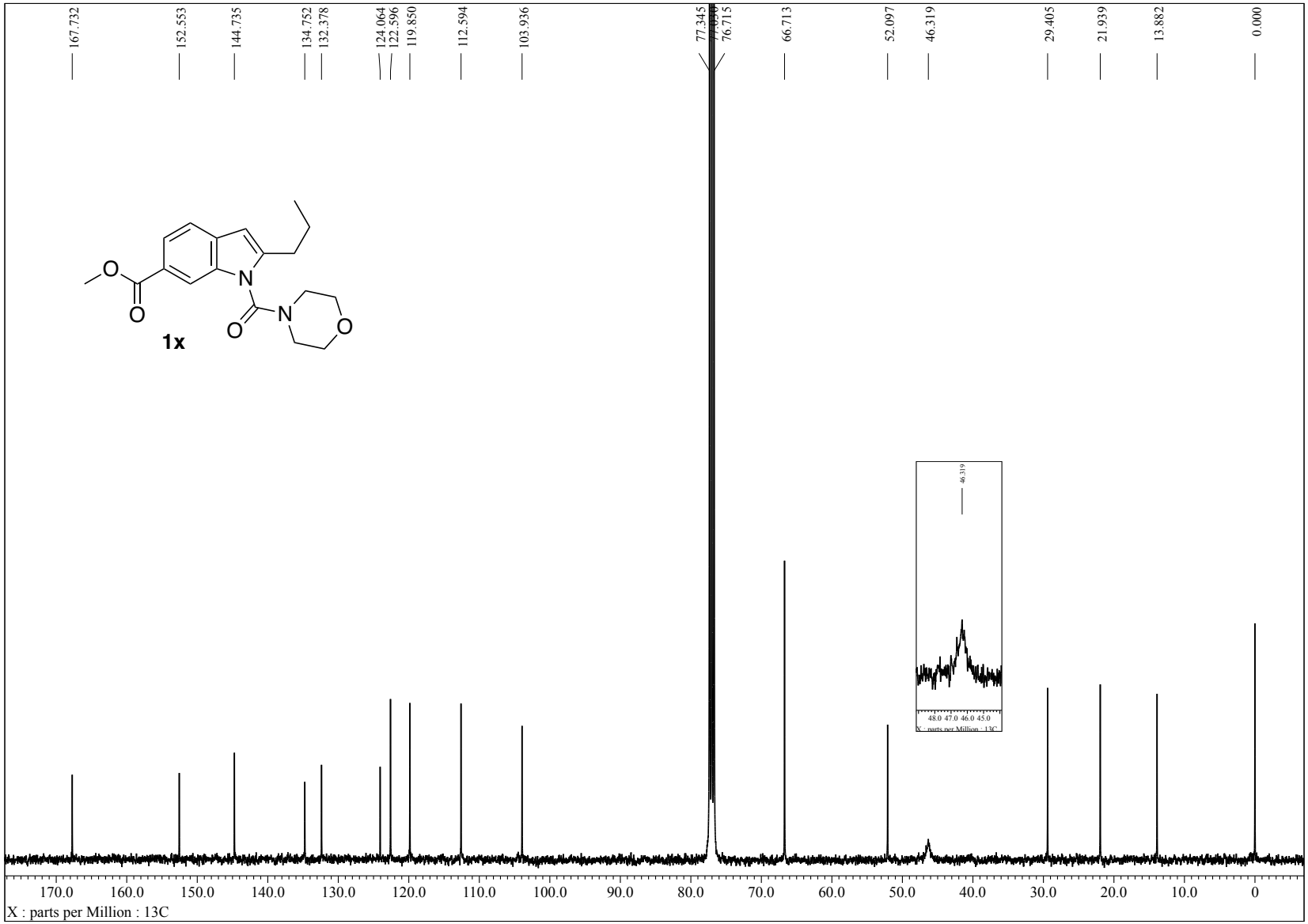
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



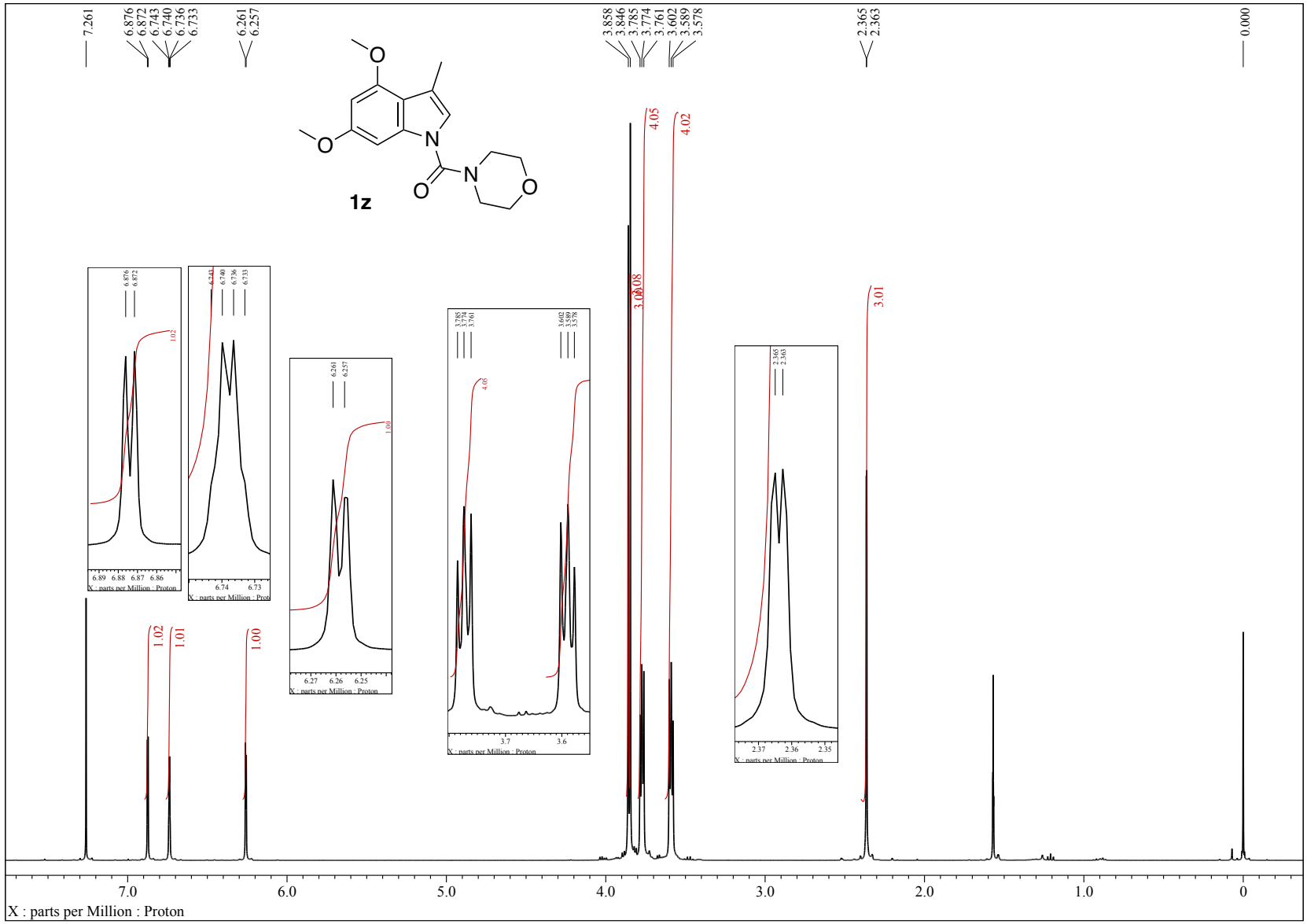
^{1}H NMR (400 MHz, $CDCl_3$)



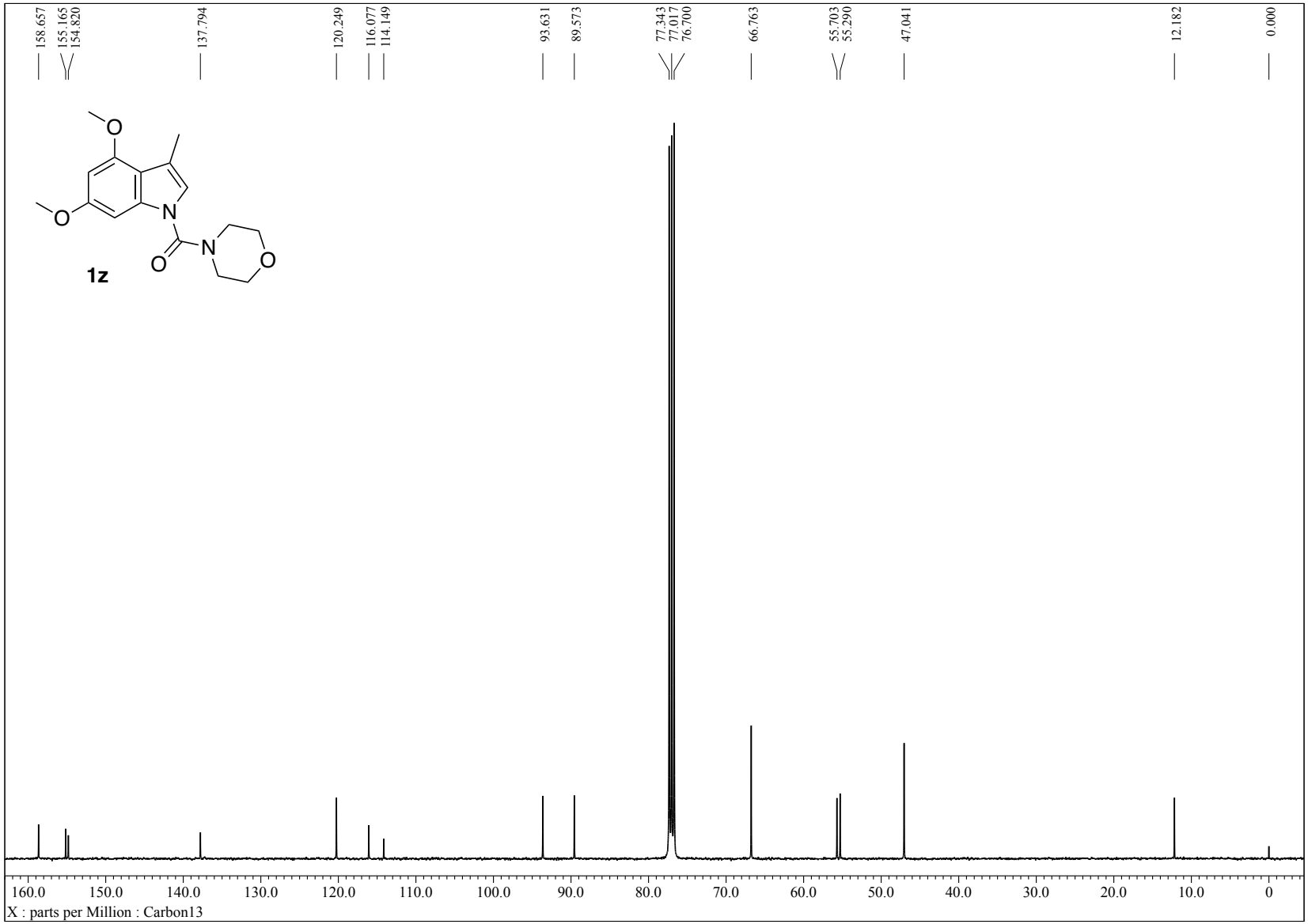
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



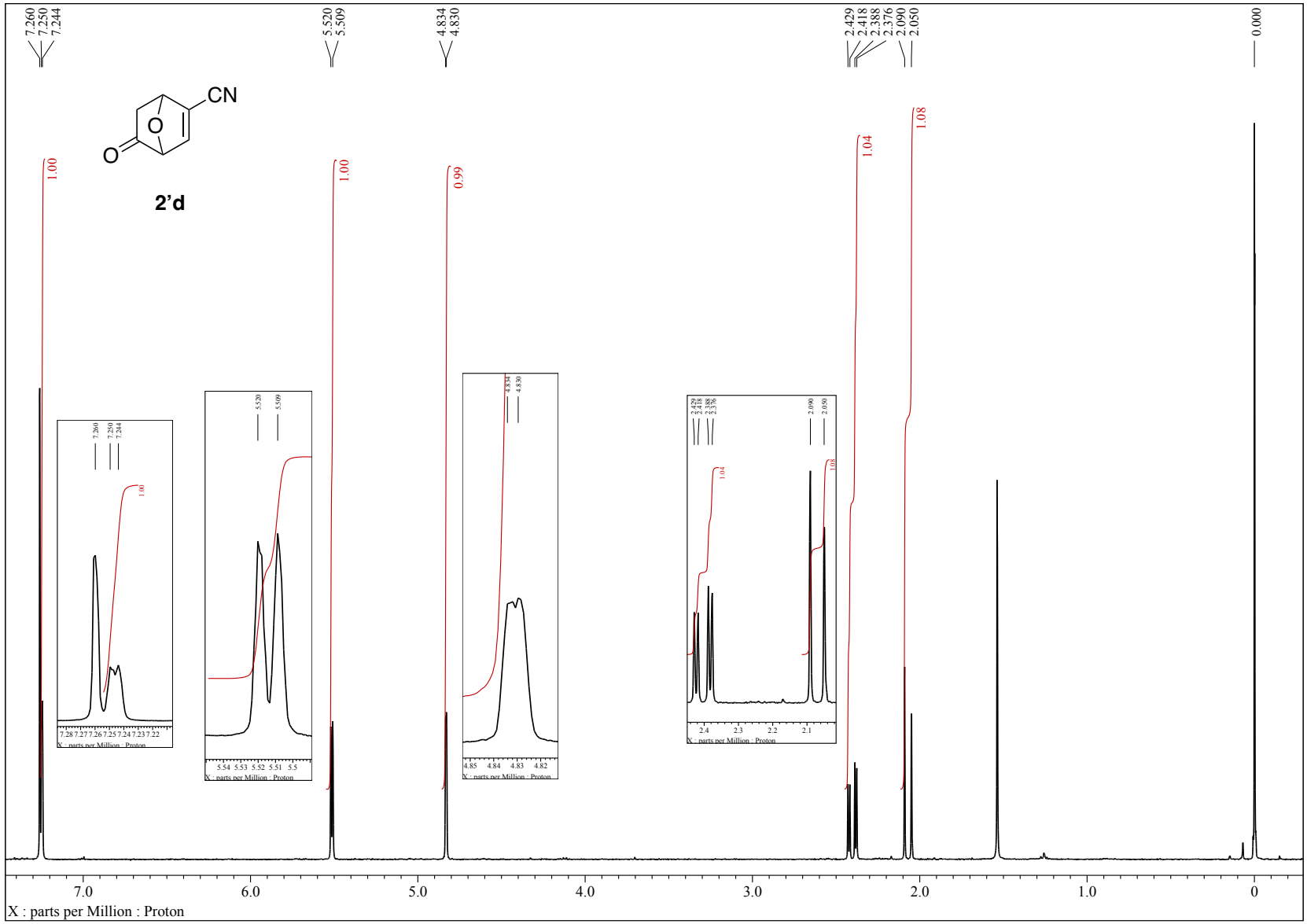
^{1}H NMR (400 MHz, $CDCl_3$)



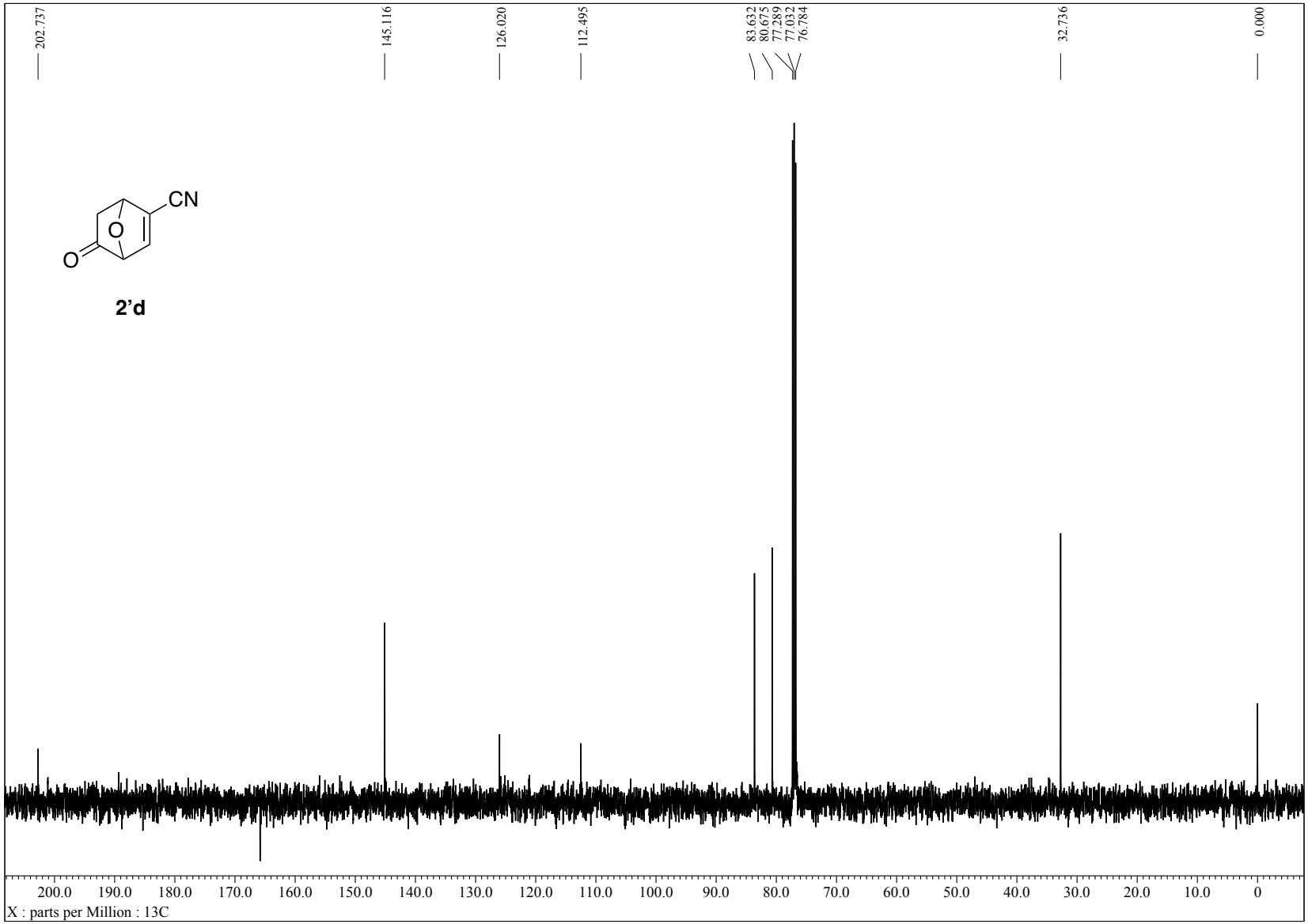
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



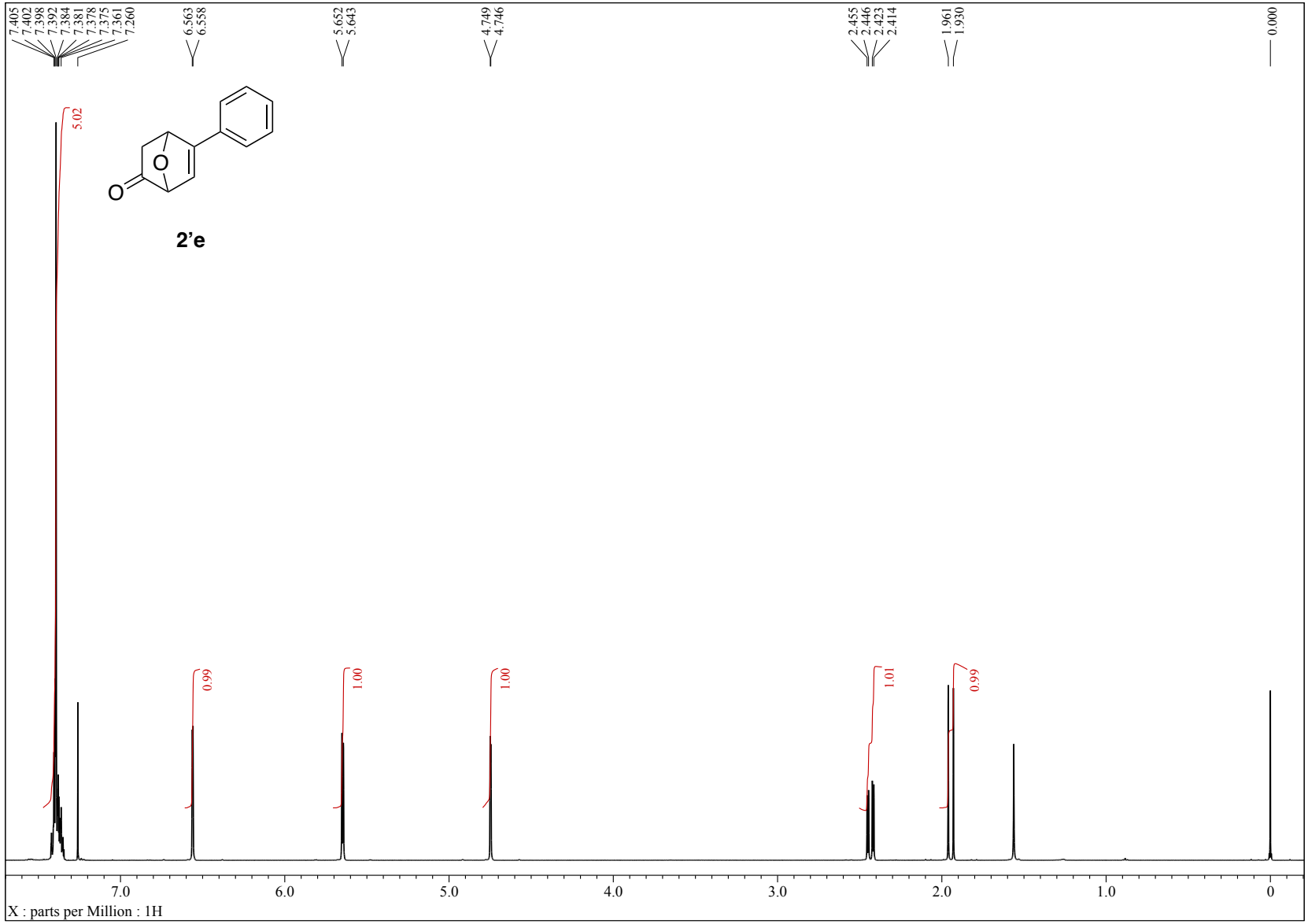
^{1}H NMR (400 MHz, $CDCl_3$)



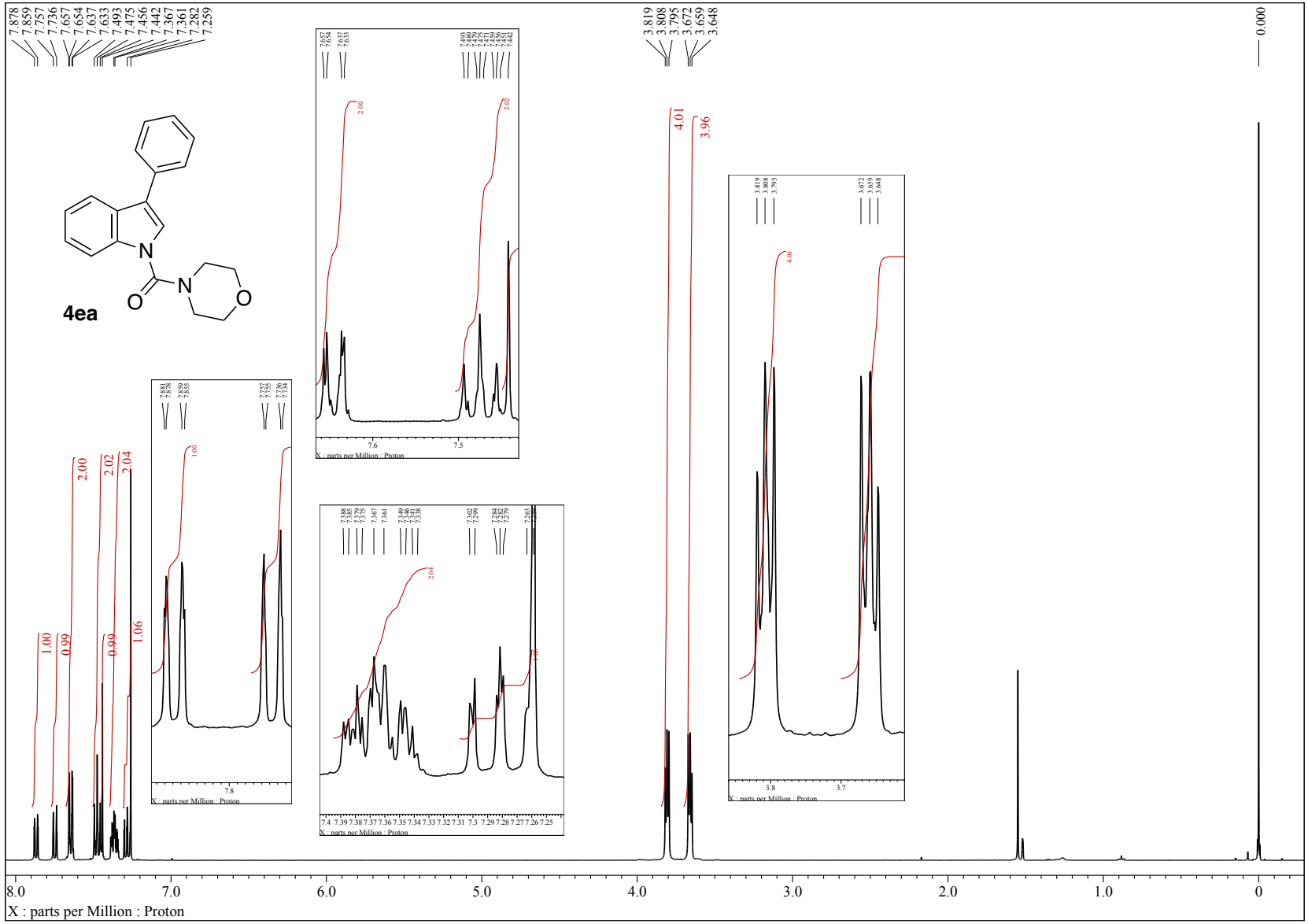
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



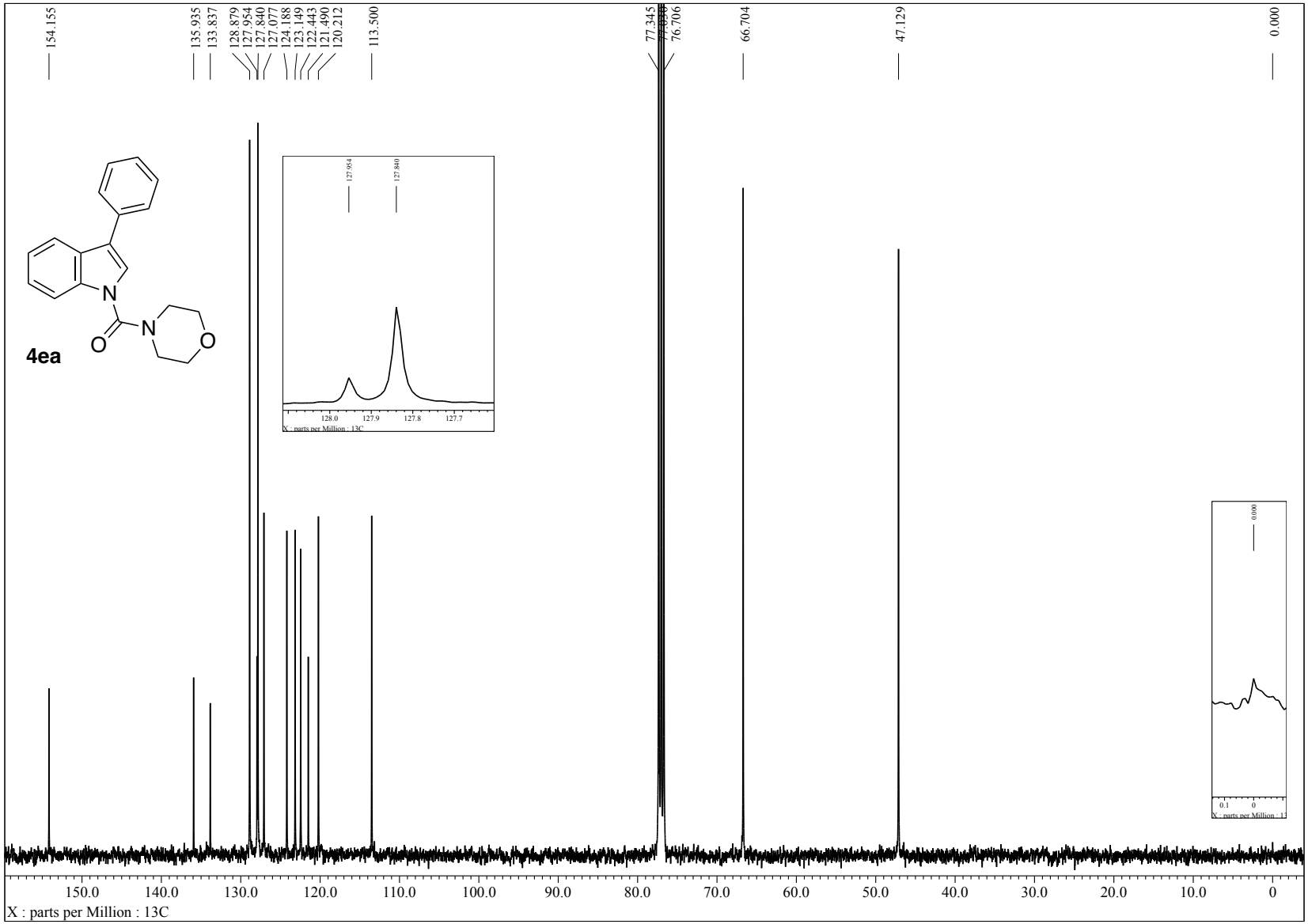
^{1}H NMR (500 MHz, $CDCl_3$)



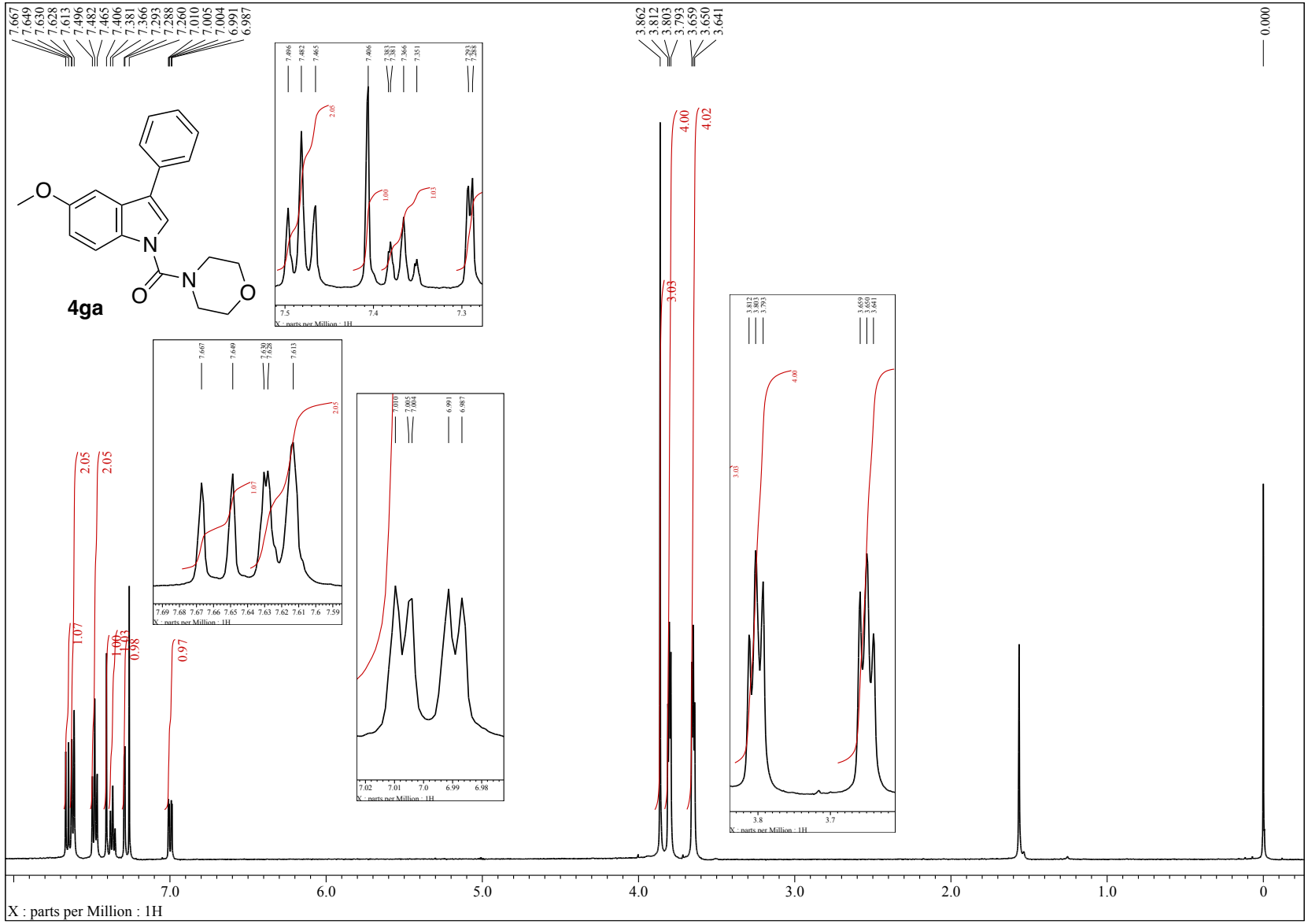
^{1}H NMR (400 MHz, $CDCl_3$)



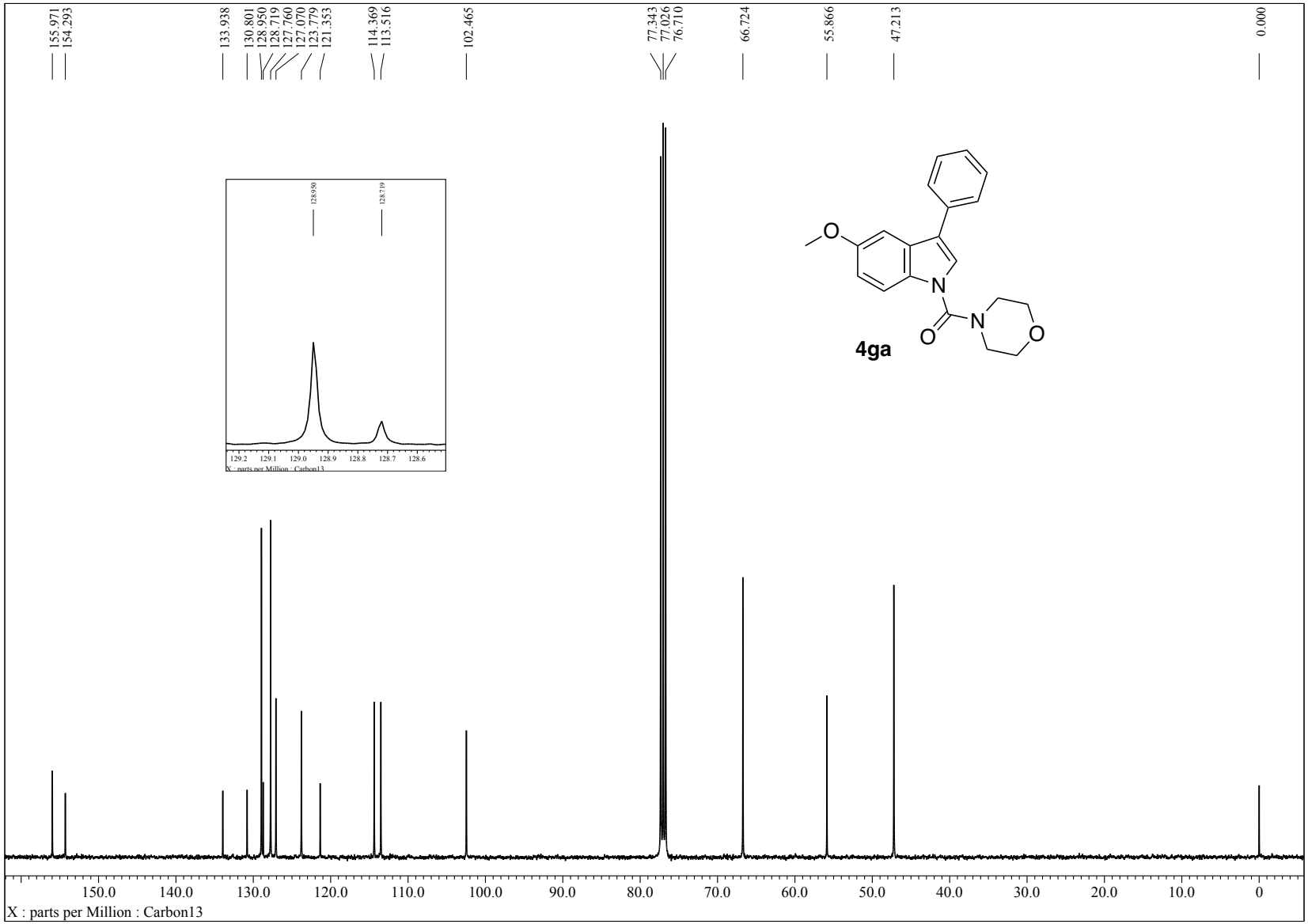
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



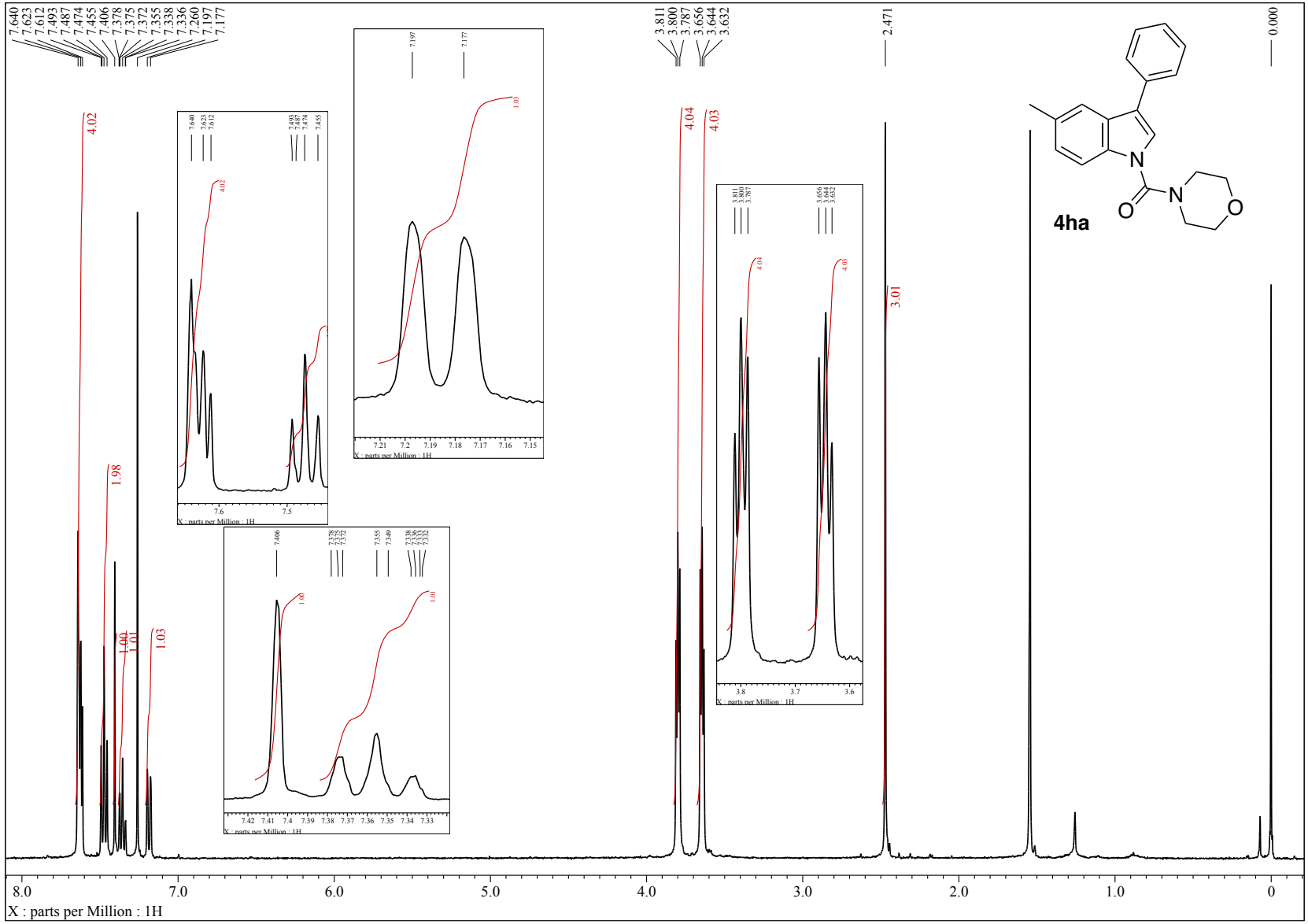
^{1}H NMR (500 MHz, $CDCl_3$)



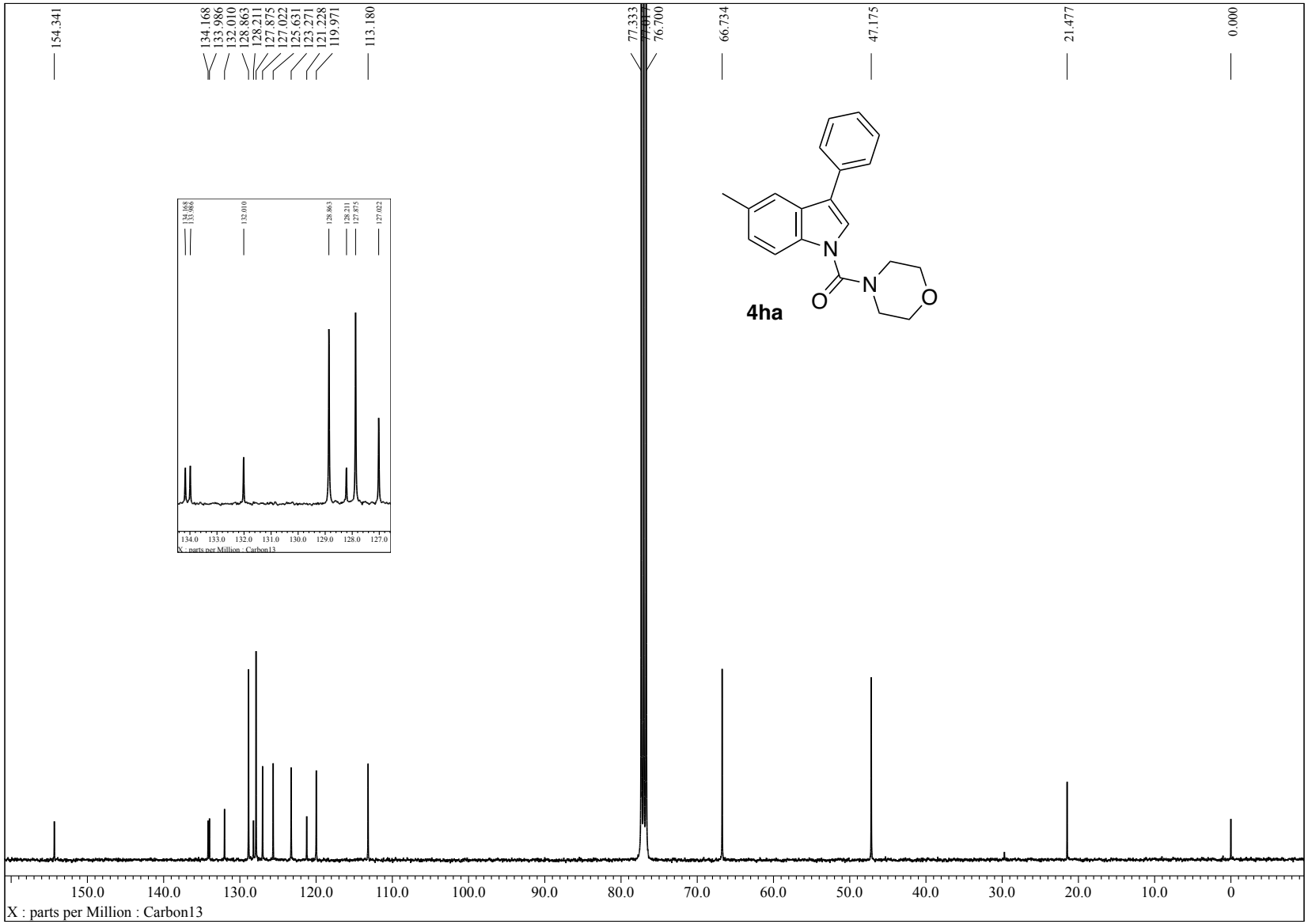
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



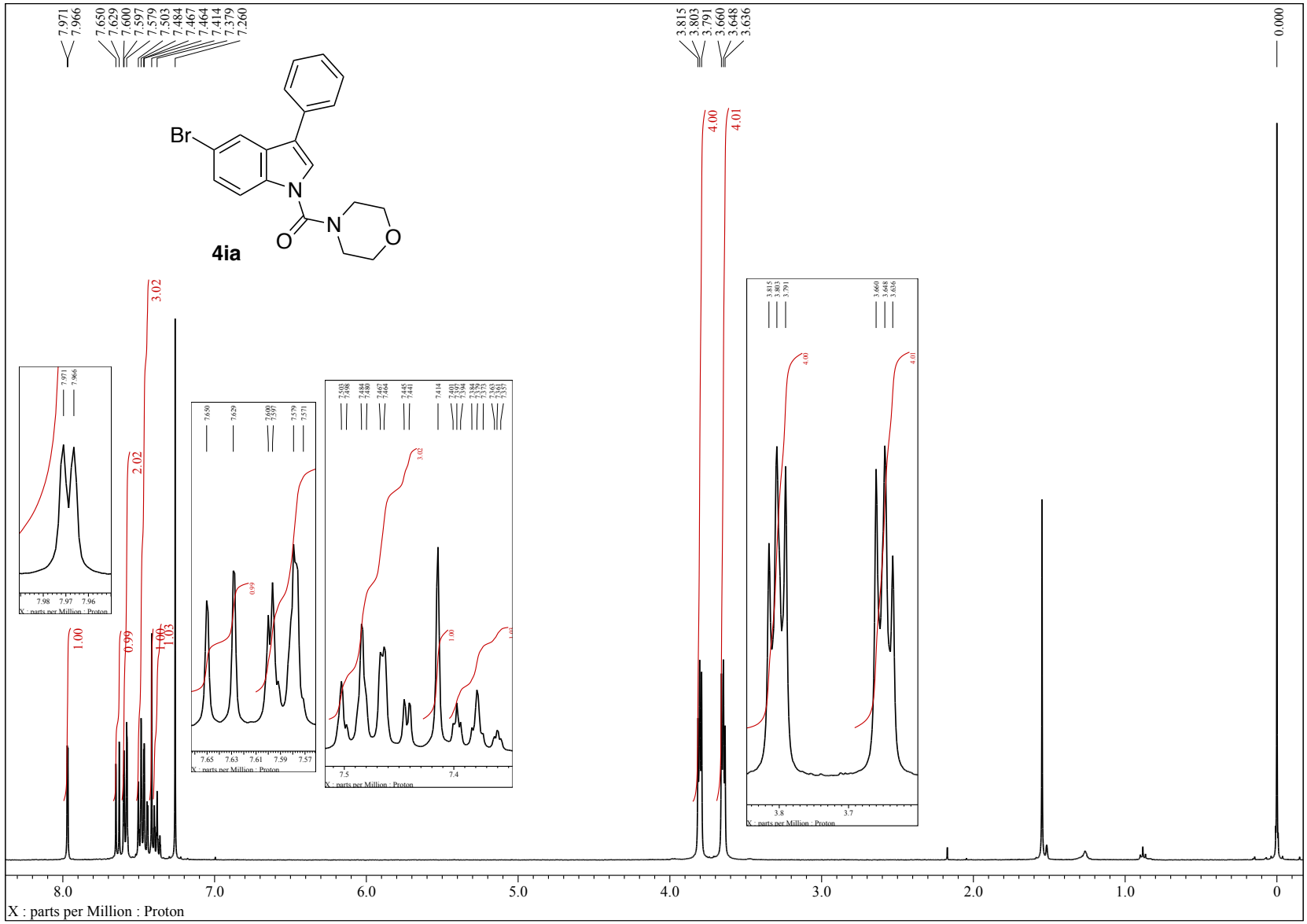
^{1}H NMR (500 MHz, $CDCl_3$)



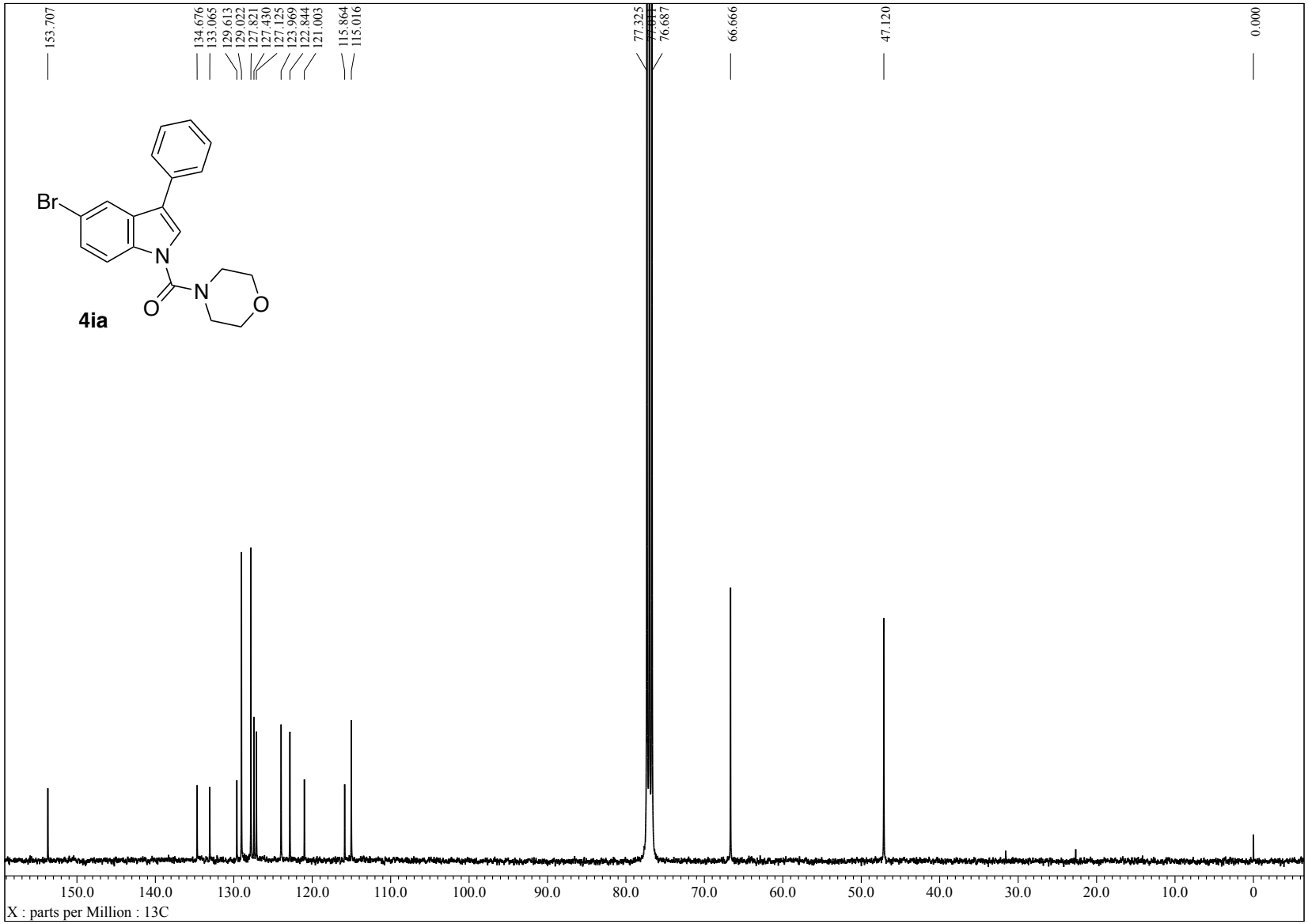
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



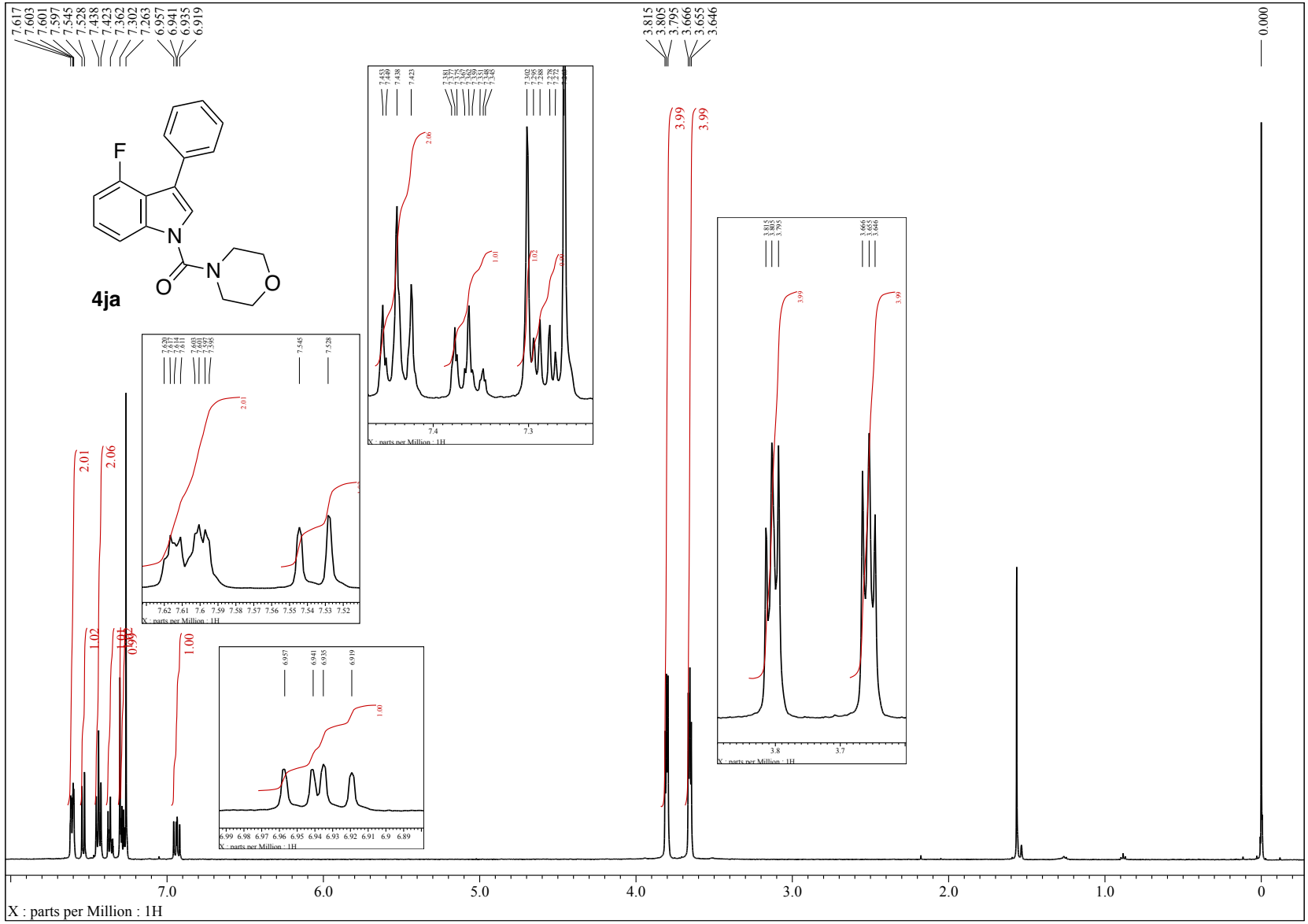
^{1}H NMR (400 MHz, $CDCl_3$)



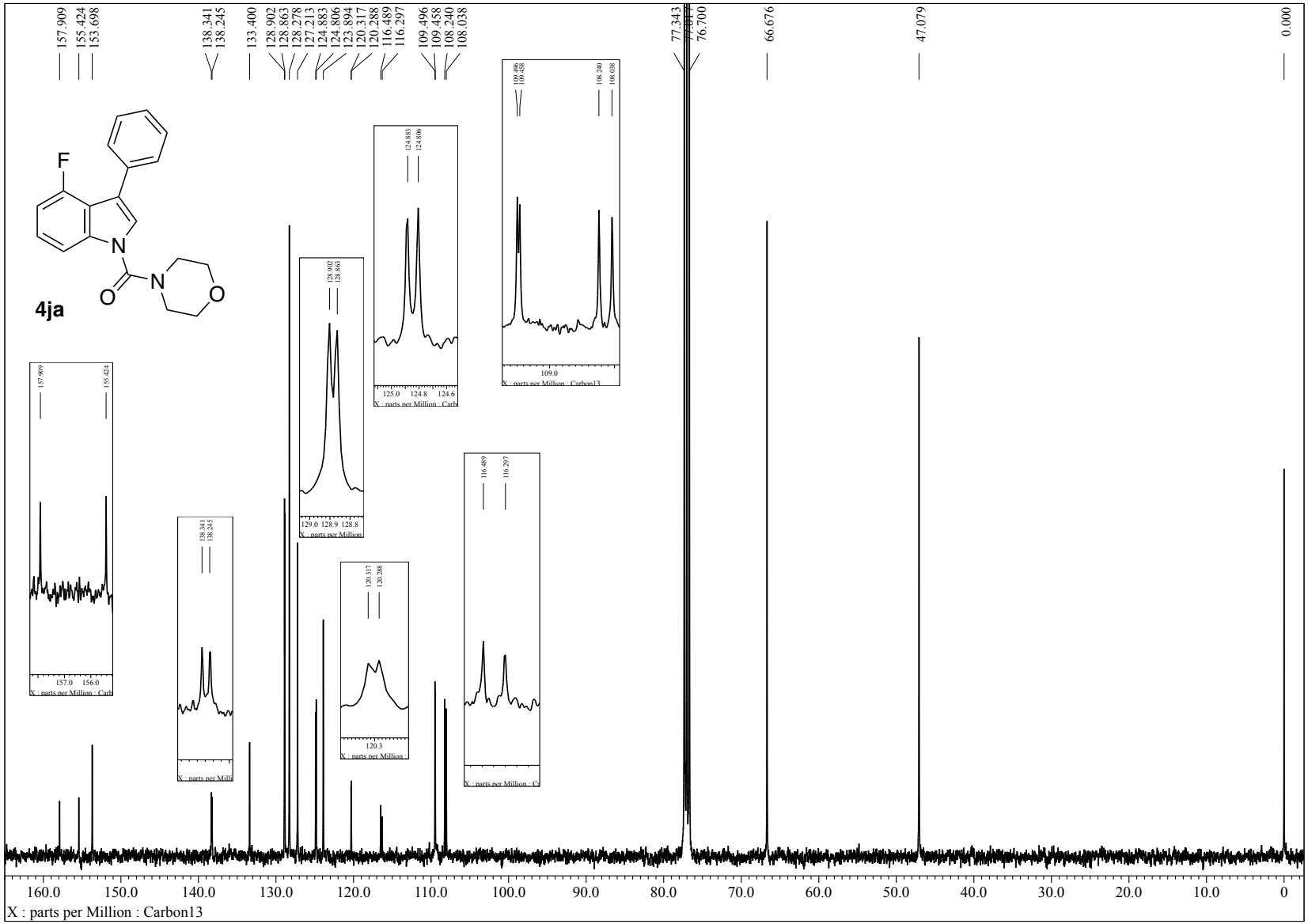
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



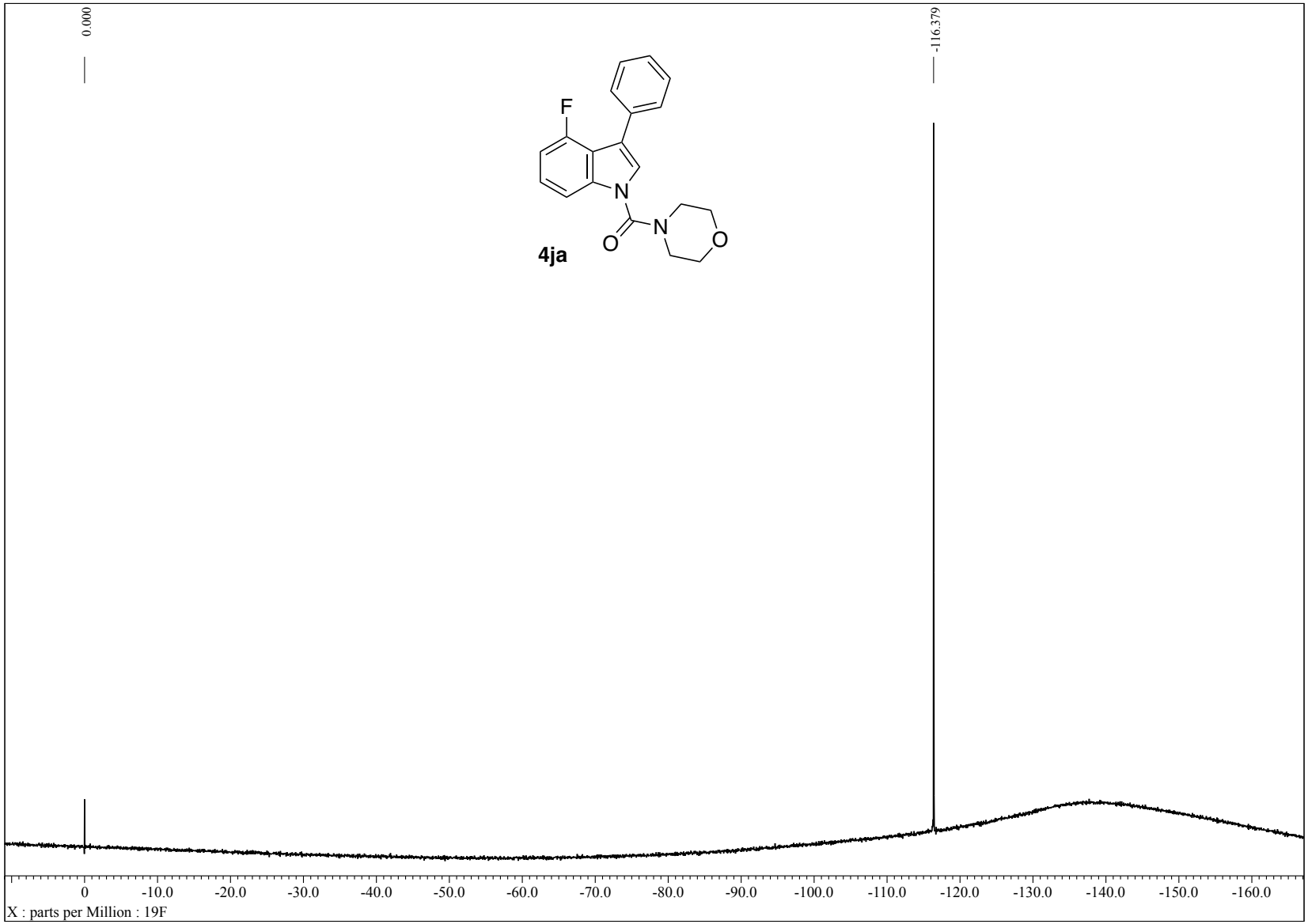
^{1}H NMR (500 MHz, $CDCl_3$)



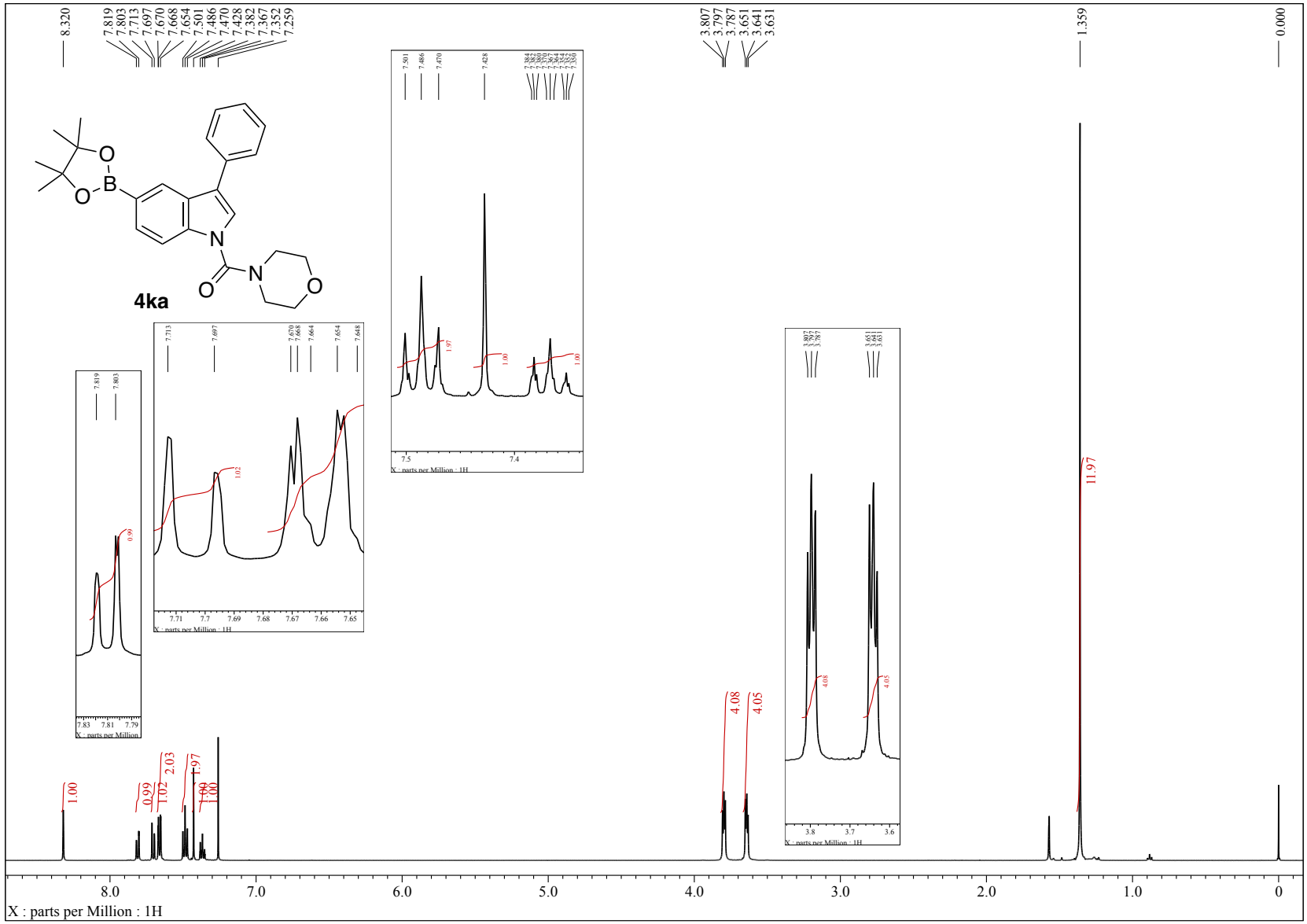
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



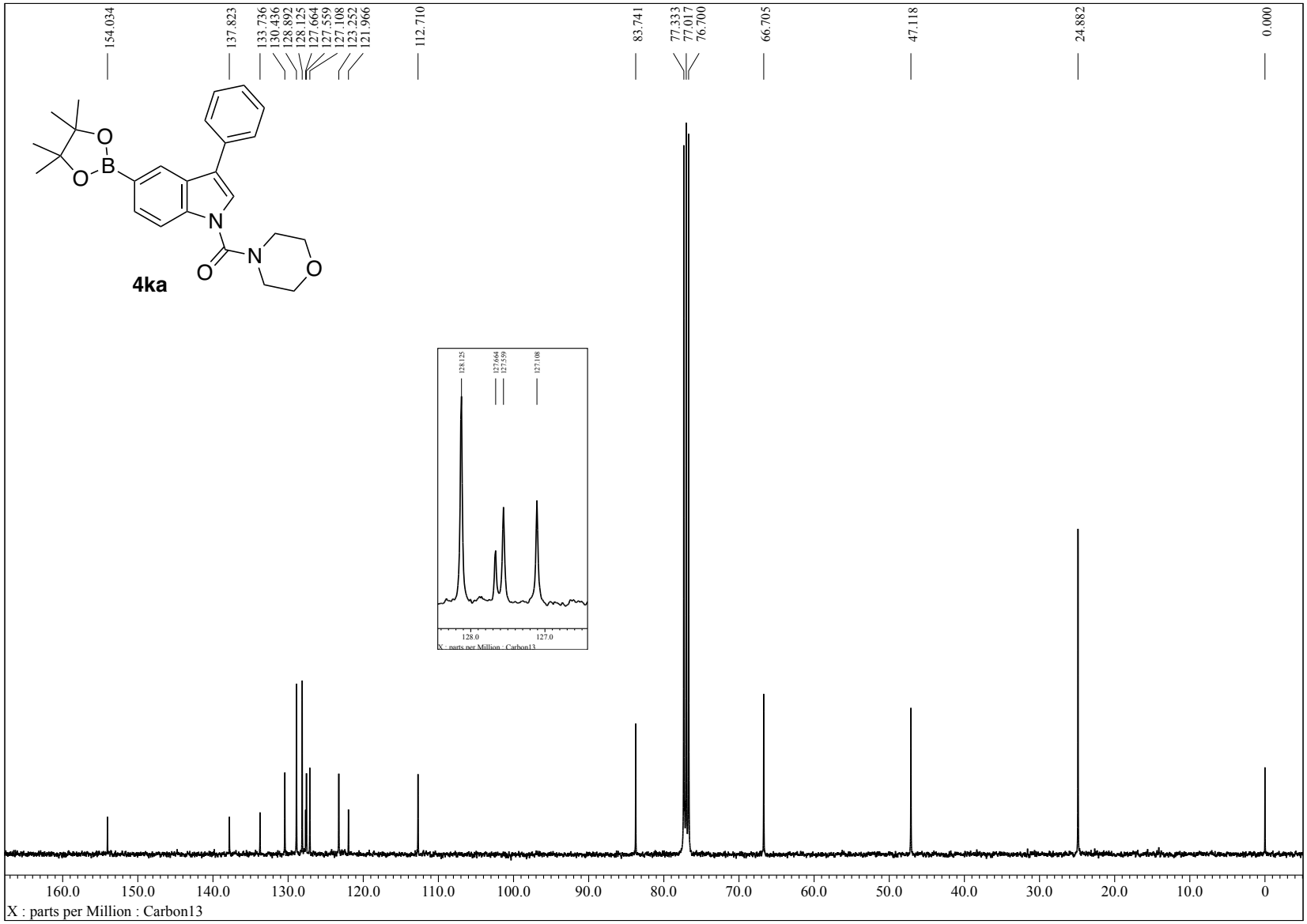
^{19}F NMR (471 MHz, $CDCl_3$)



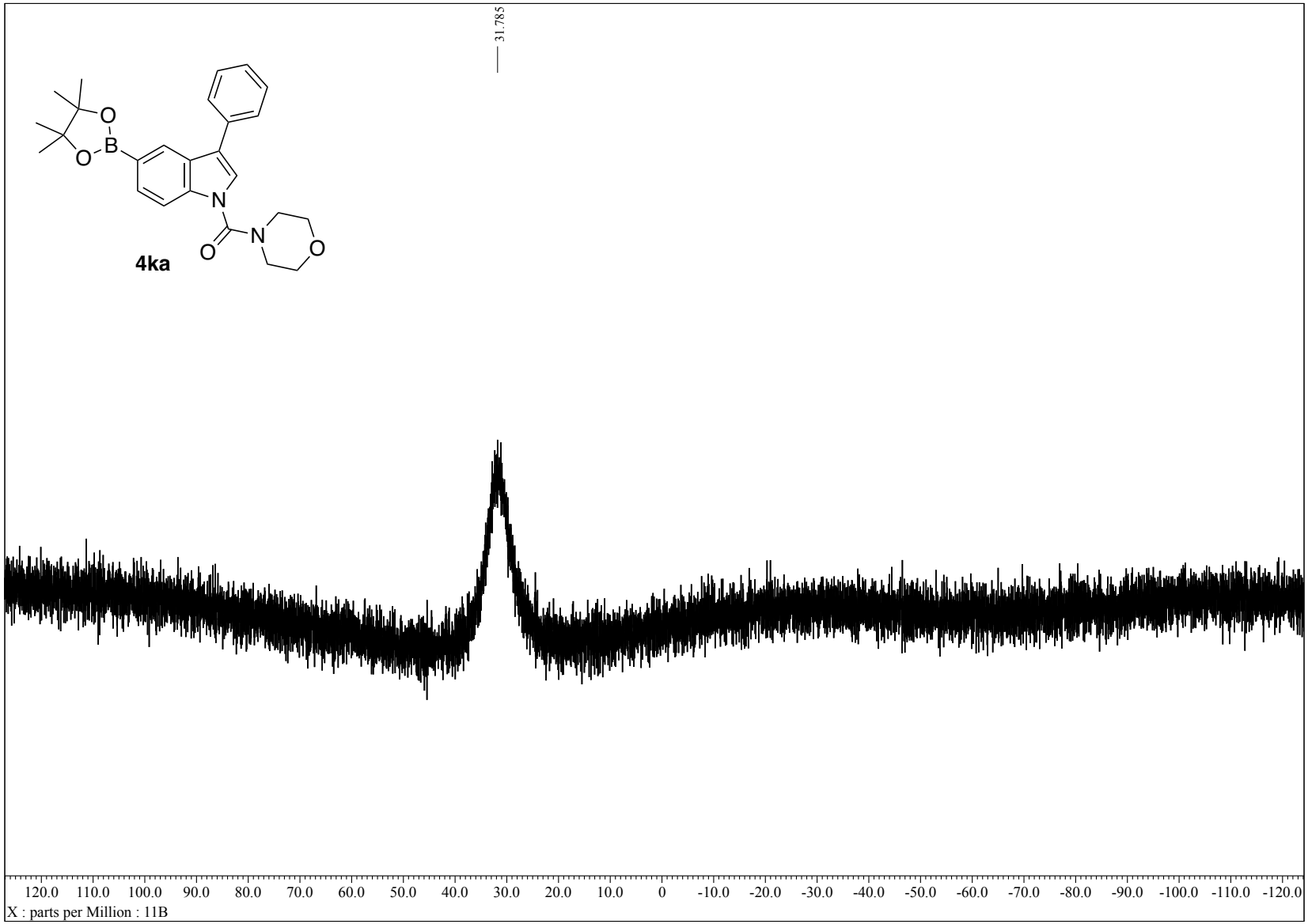
^{1}H NMR (500 MHz, $CDCl_3$)



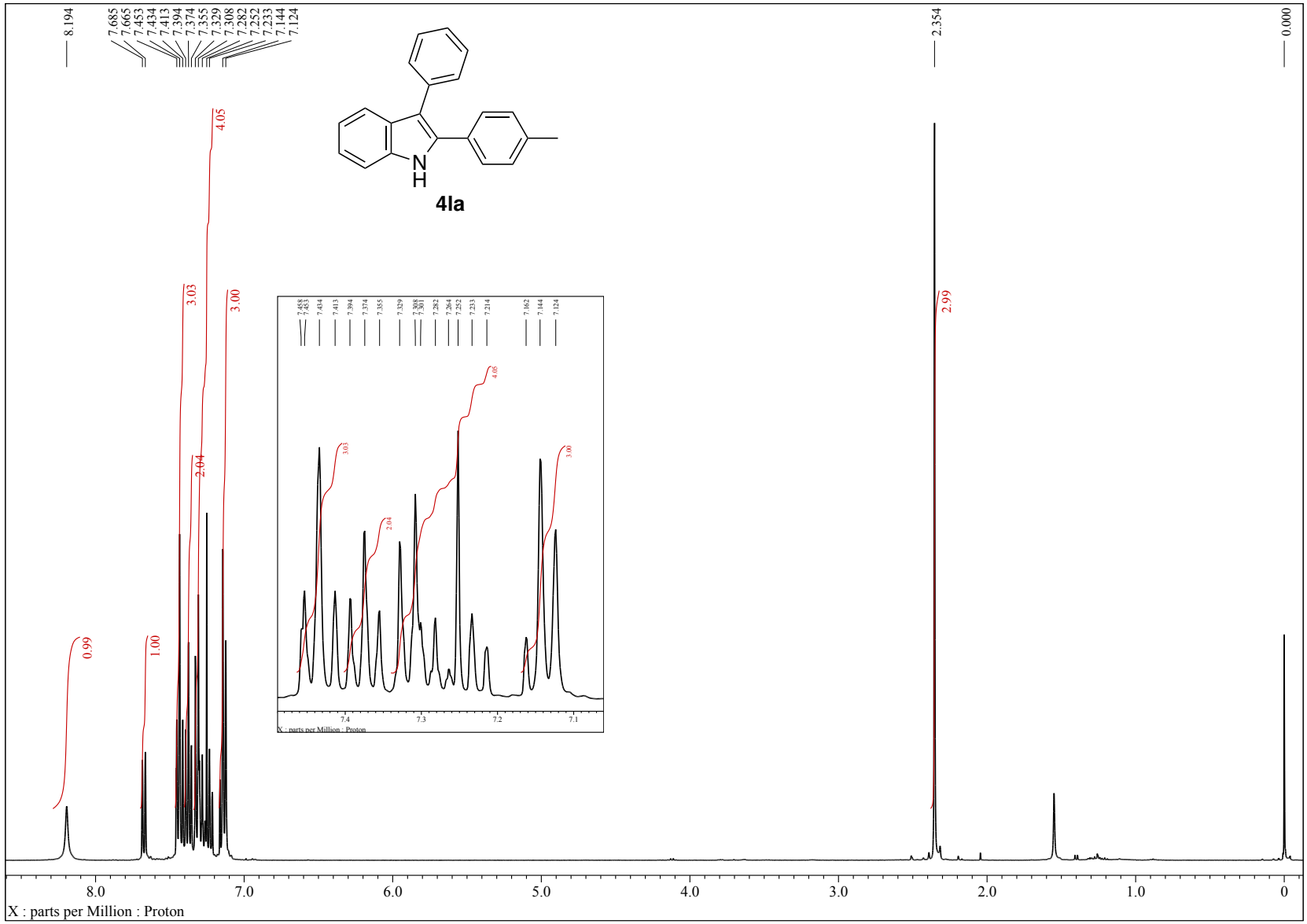
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



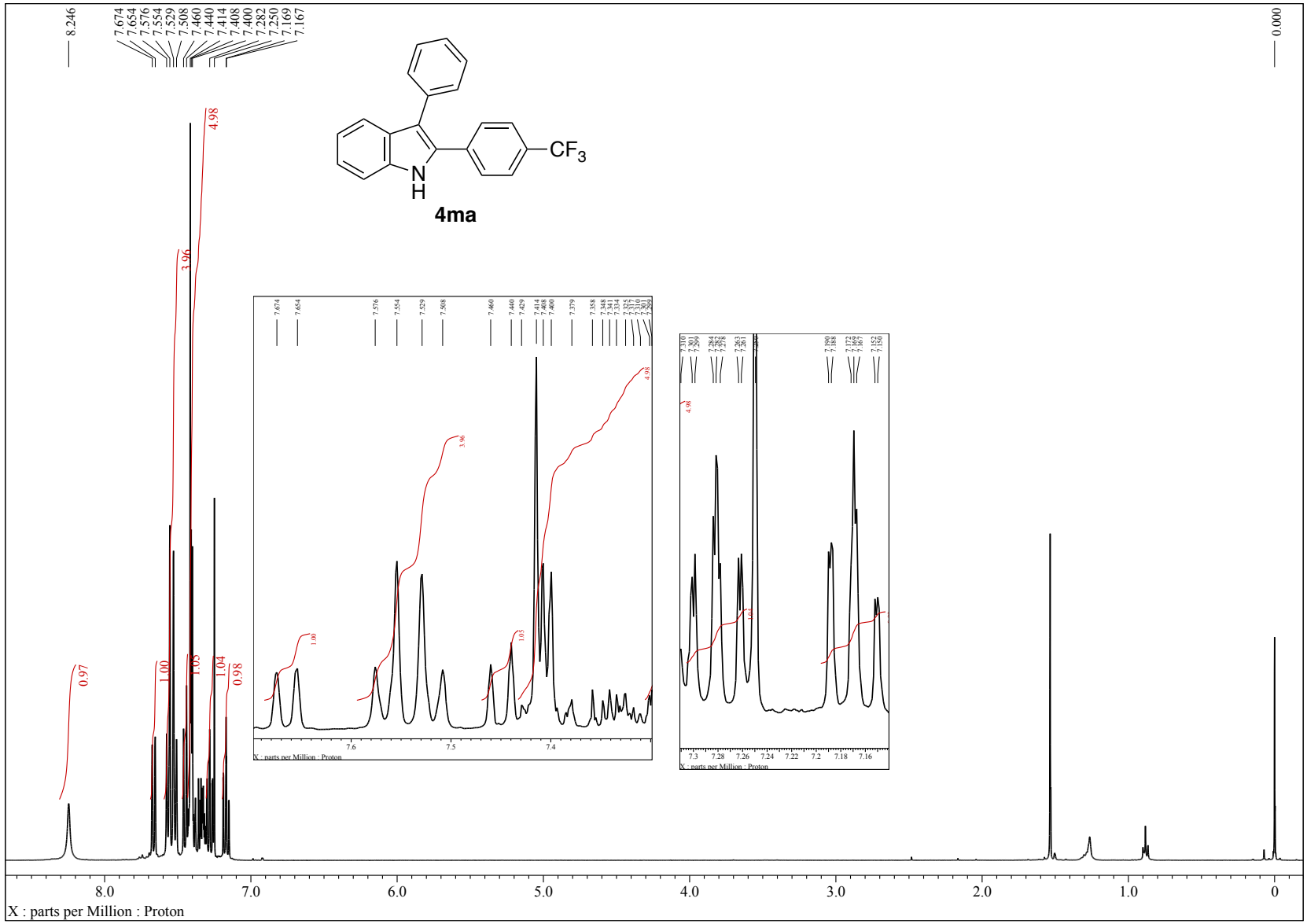
$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



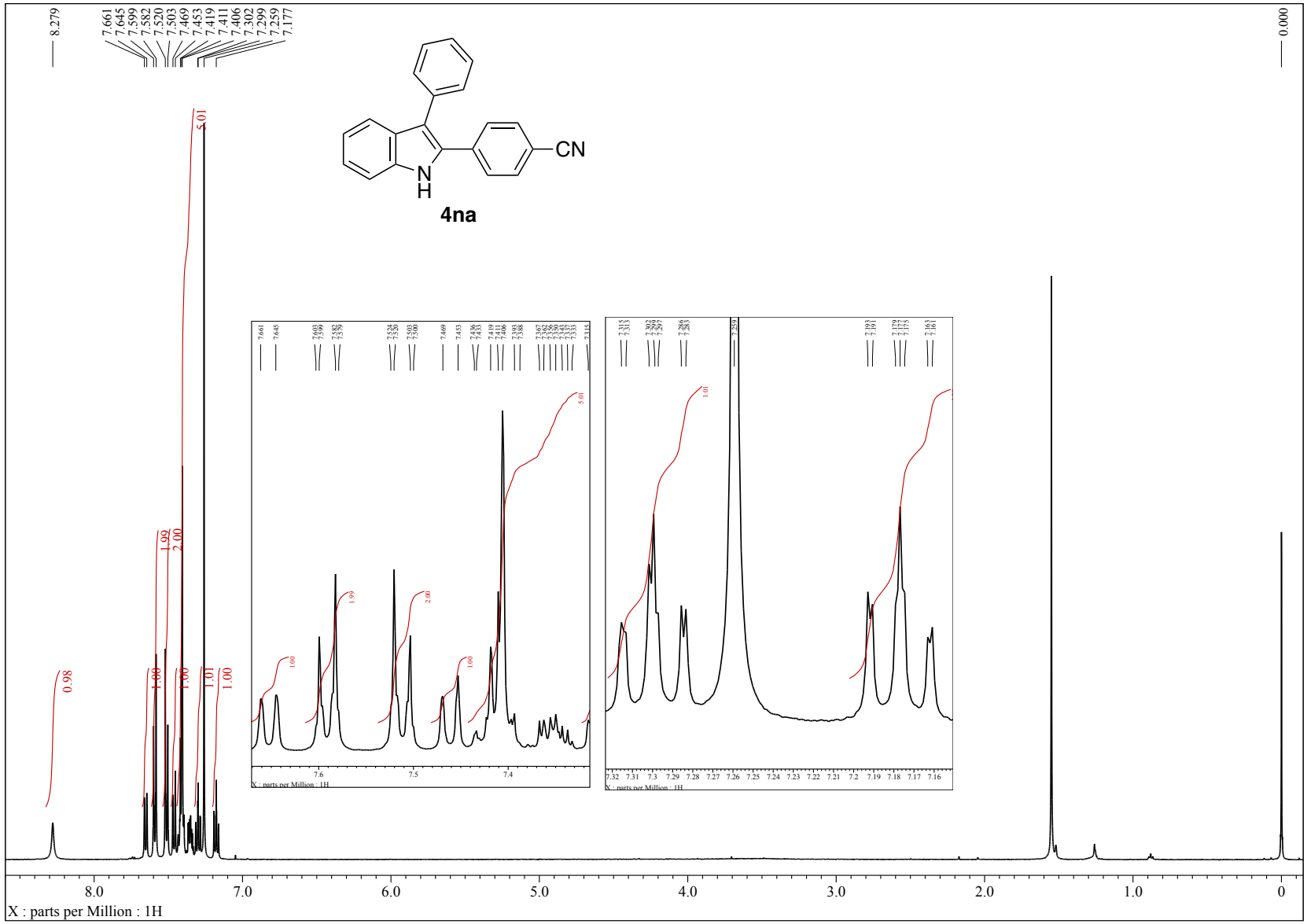
^{1}H NMR (400 MHz, $CDCl_3$)



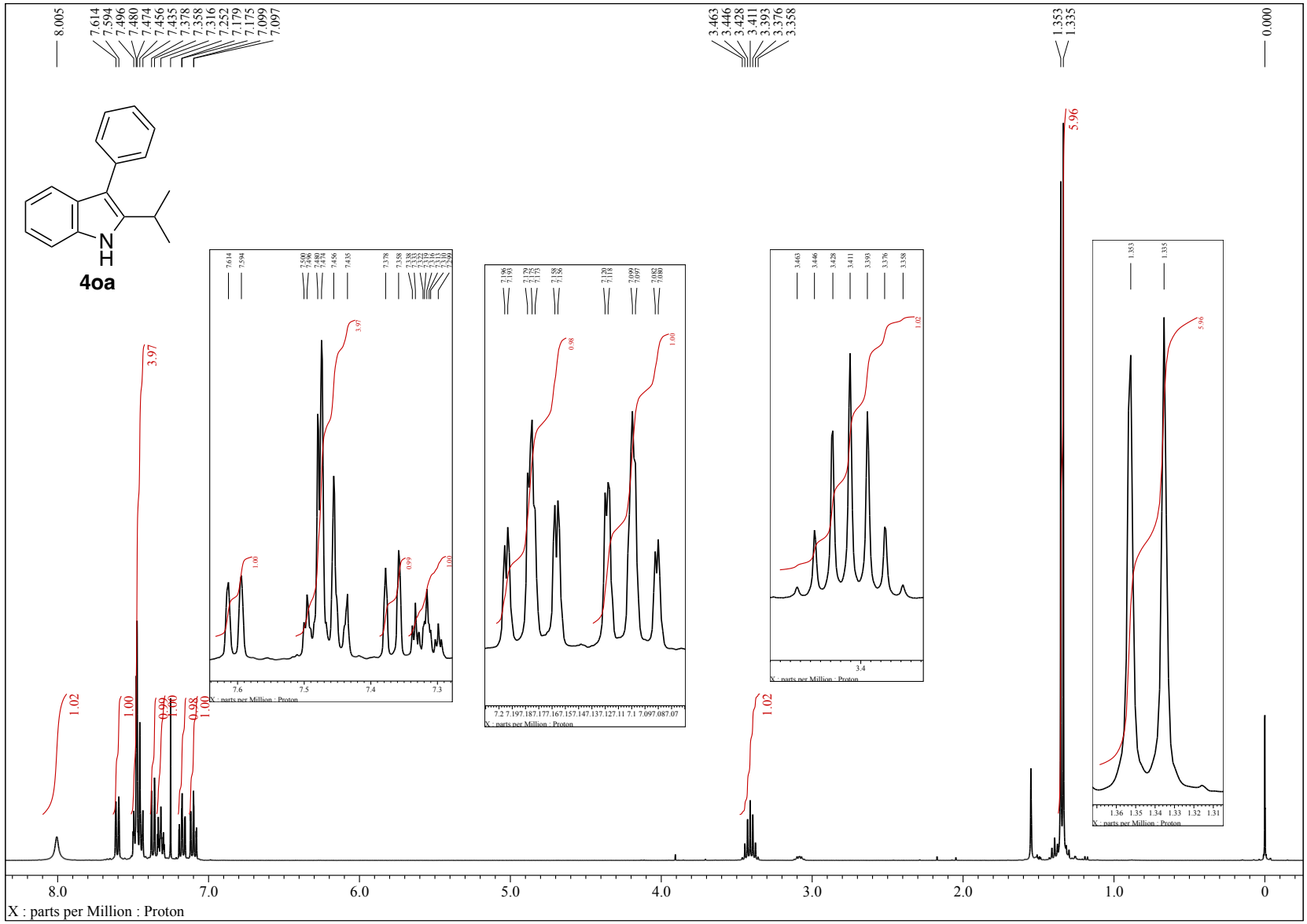
^{1}H NMR (400 MHz, $CDCl_3$)



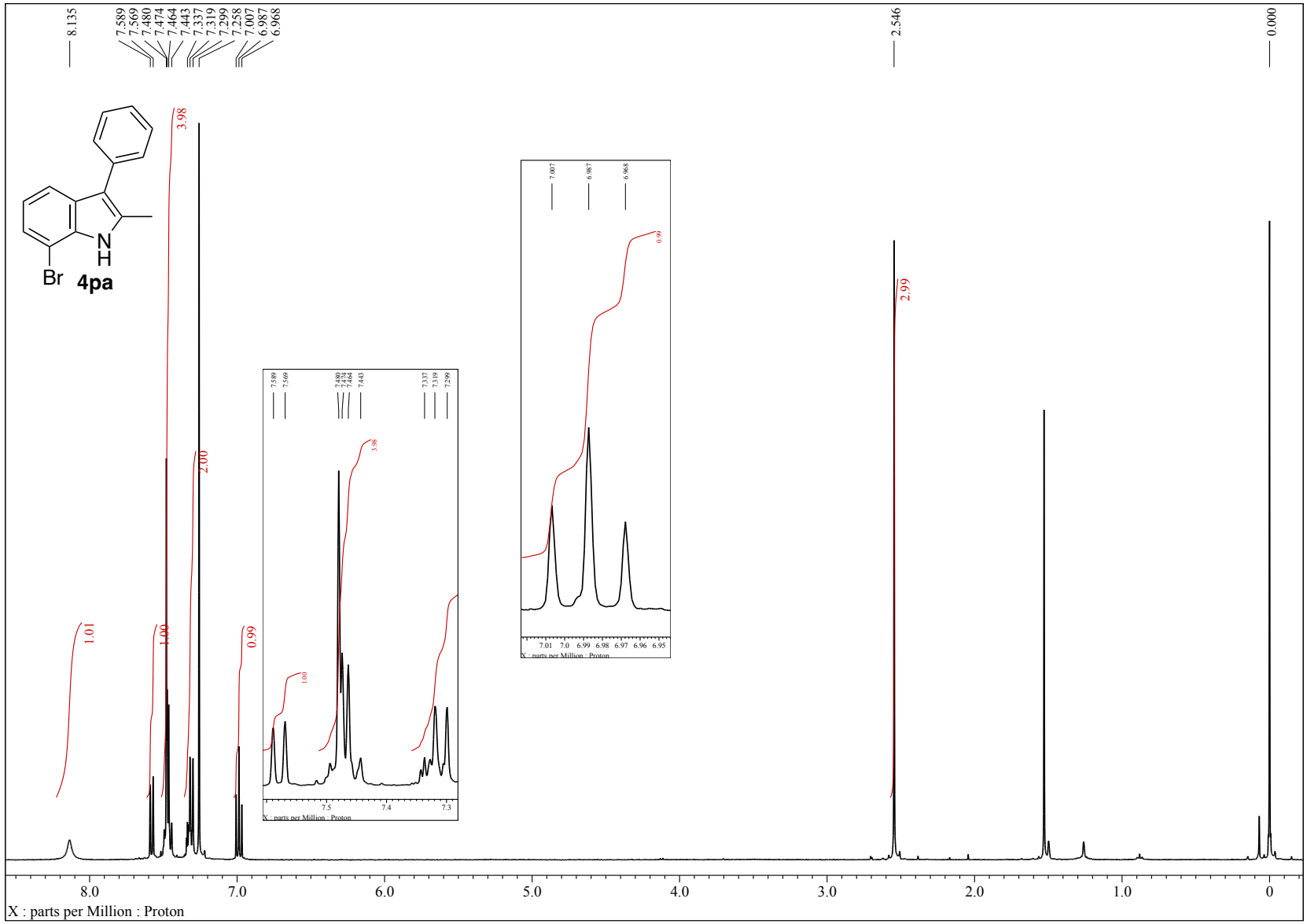
^{1}H NMR (400 MHz, $CDCl_3$)



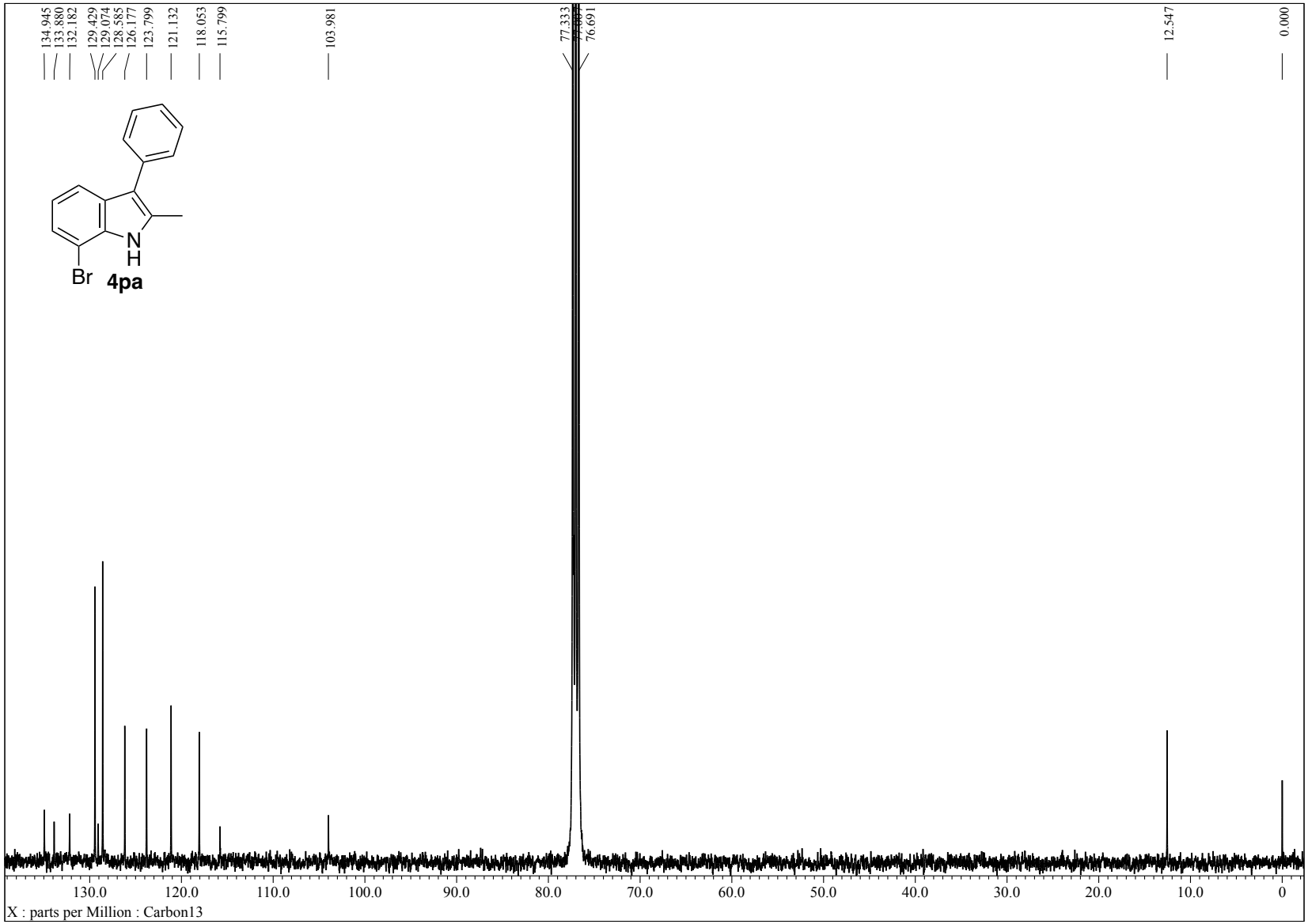
^{1}H NMR (400 MHz, $CDCl_3$)



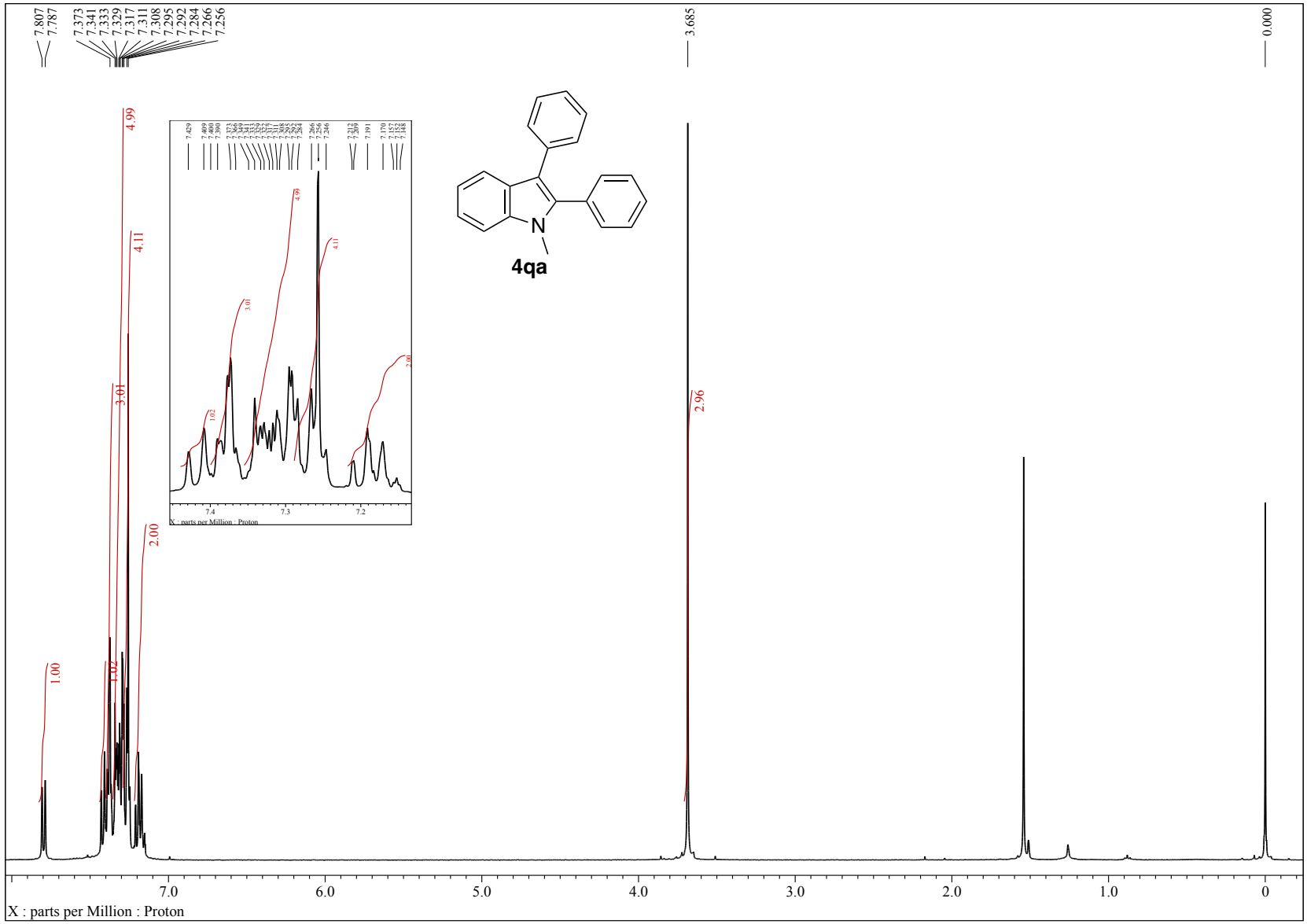
^{1}H NMR (500 MHz, $CDCl_3$)



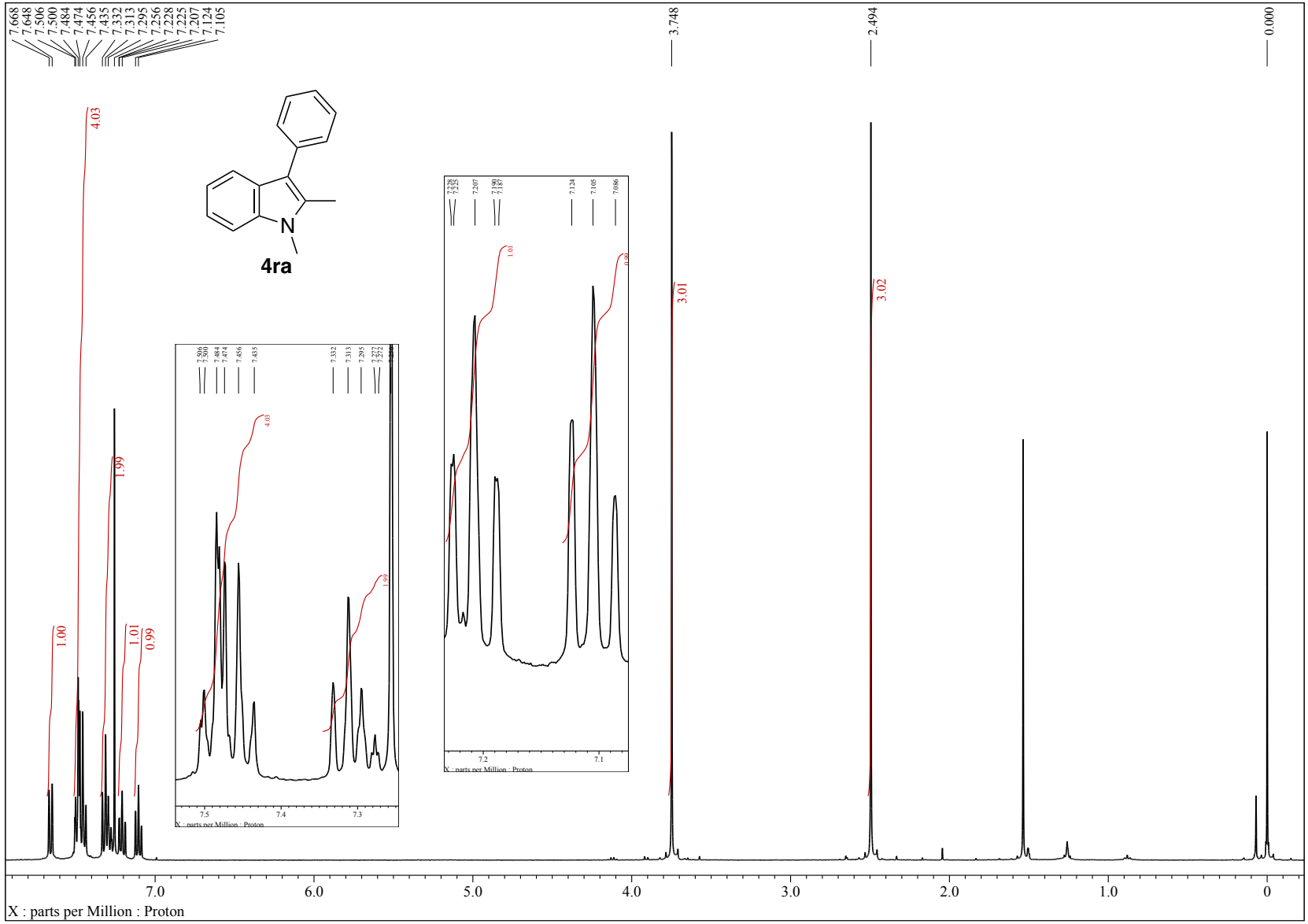
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



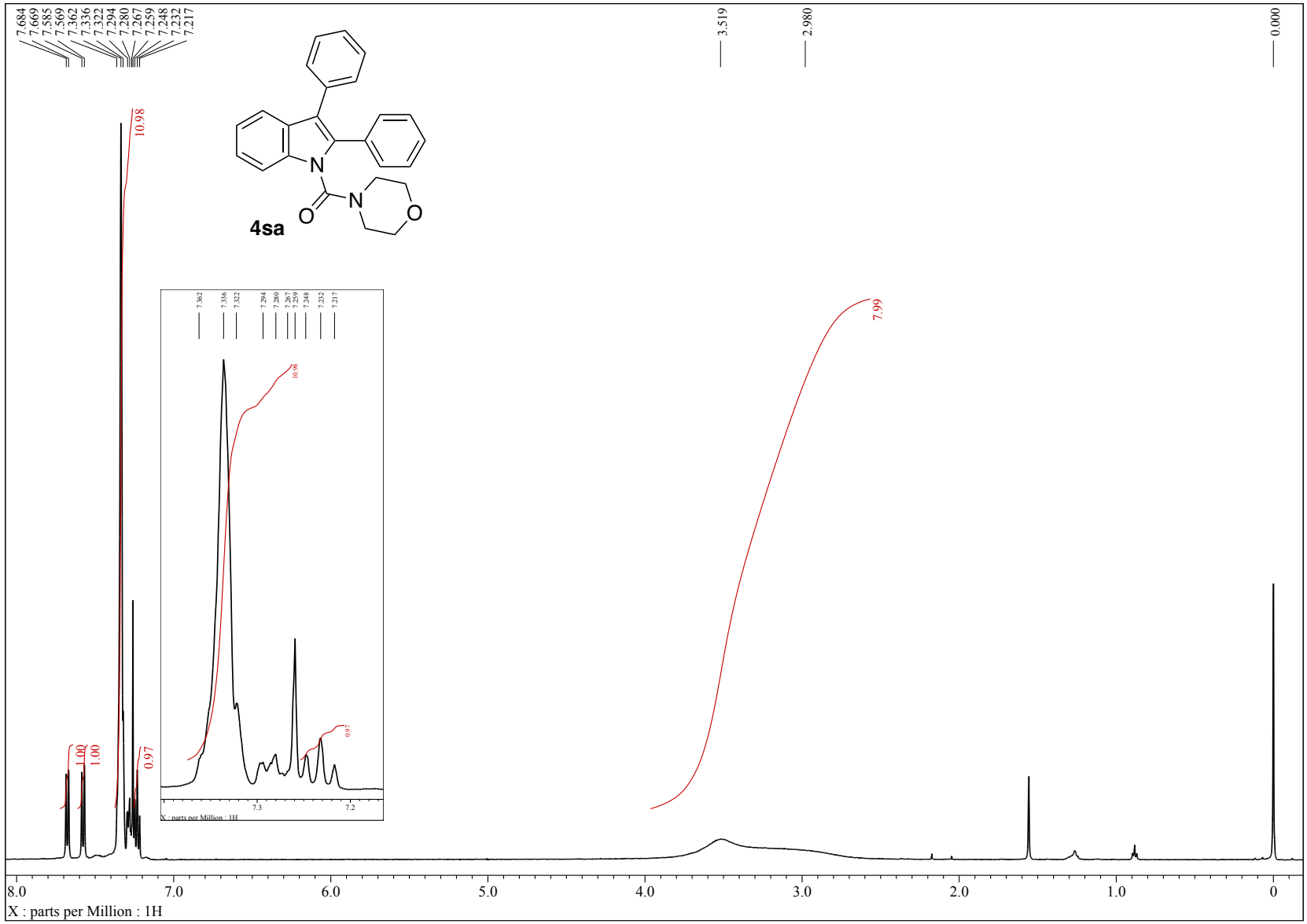
^{1}H NMR (400 MHz, $CDCl_3$)



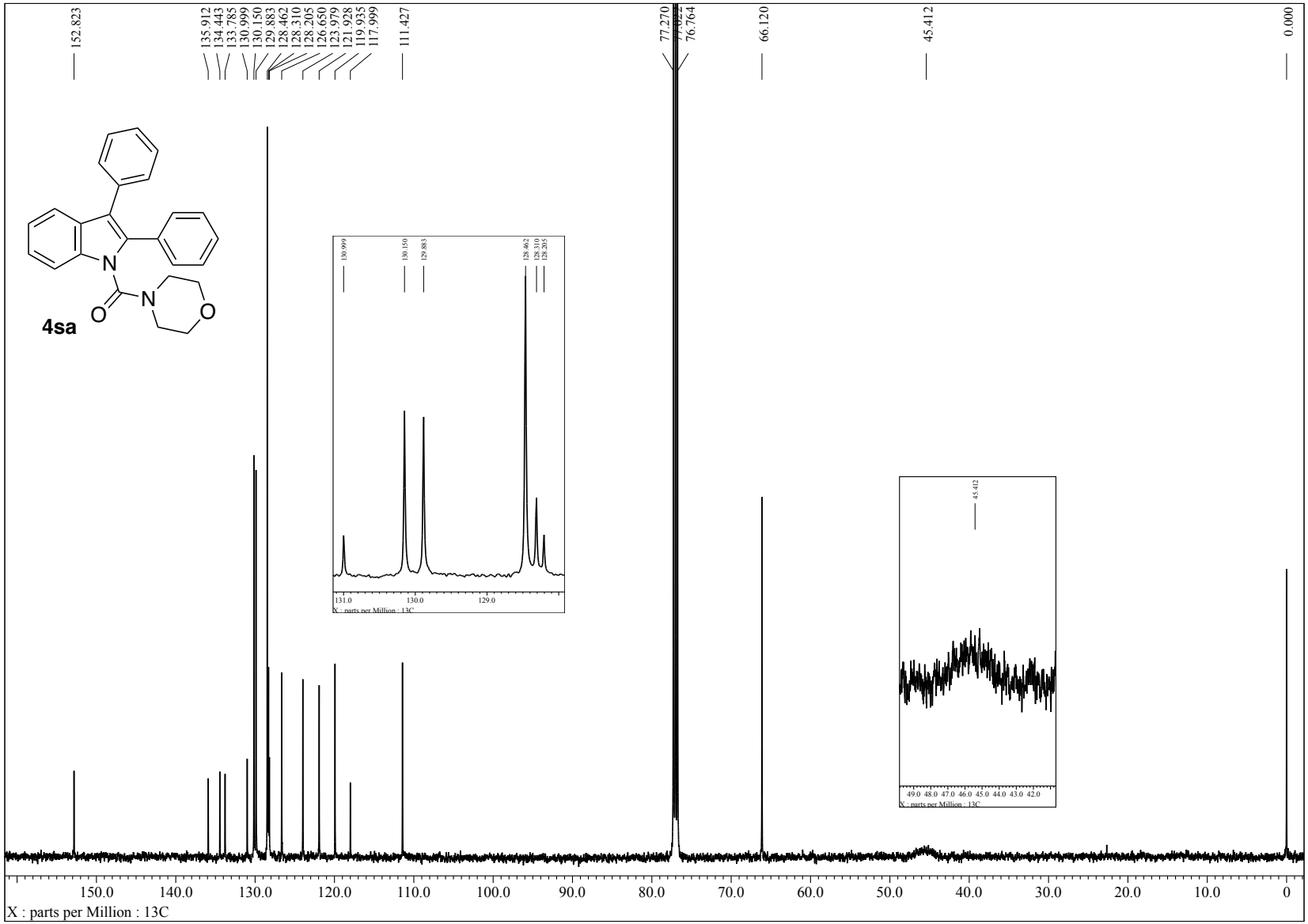
^{1}H NMR (400 MHz, $CDCl_3$)



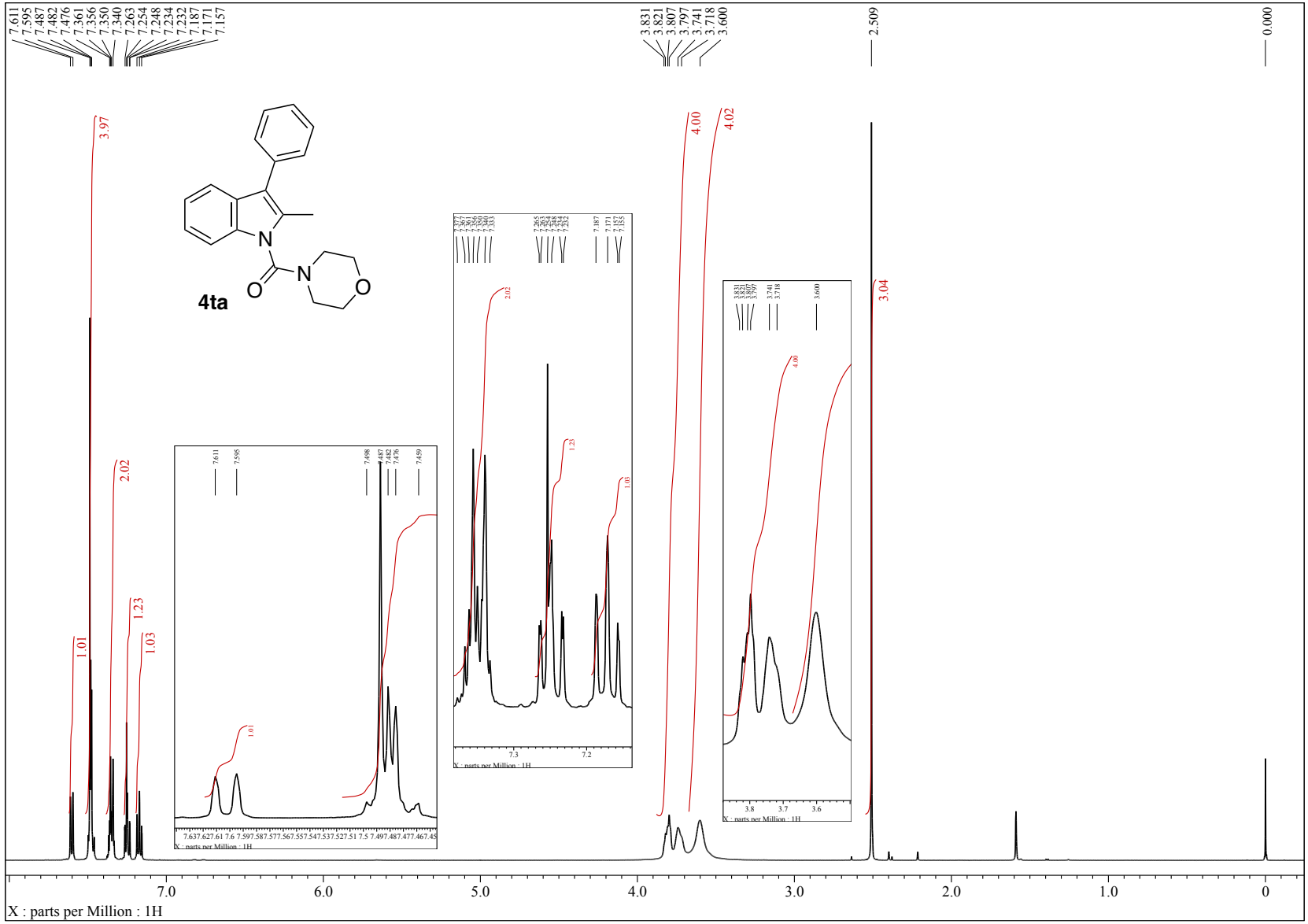
^{1}H NMR (500 MHz, $CDCl_3$)



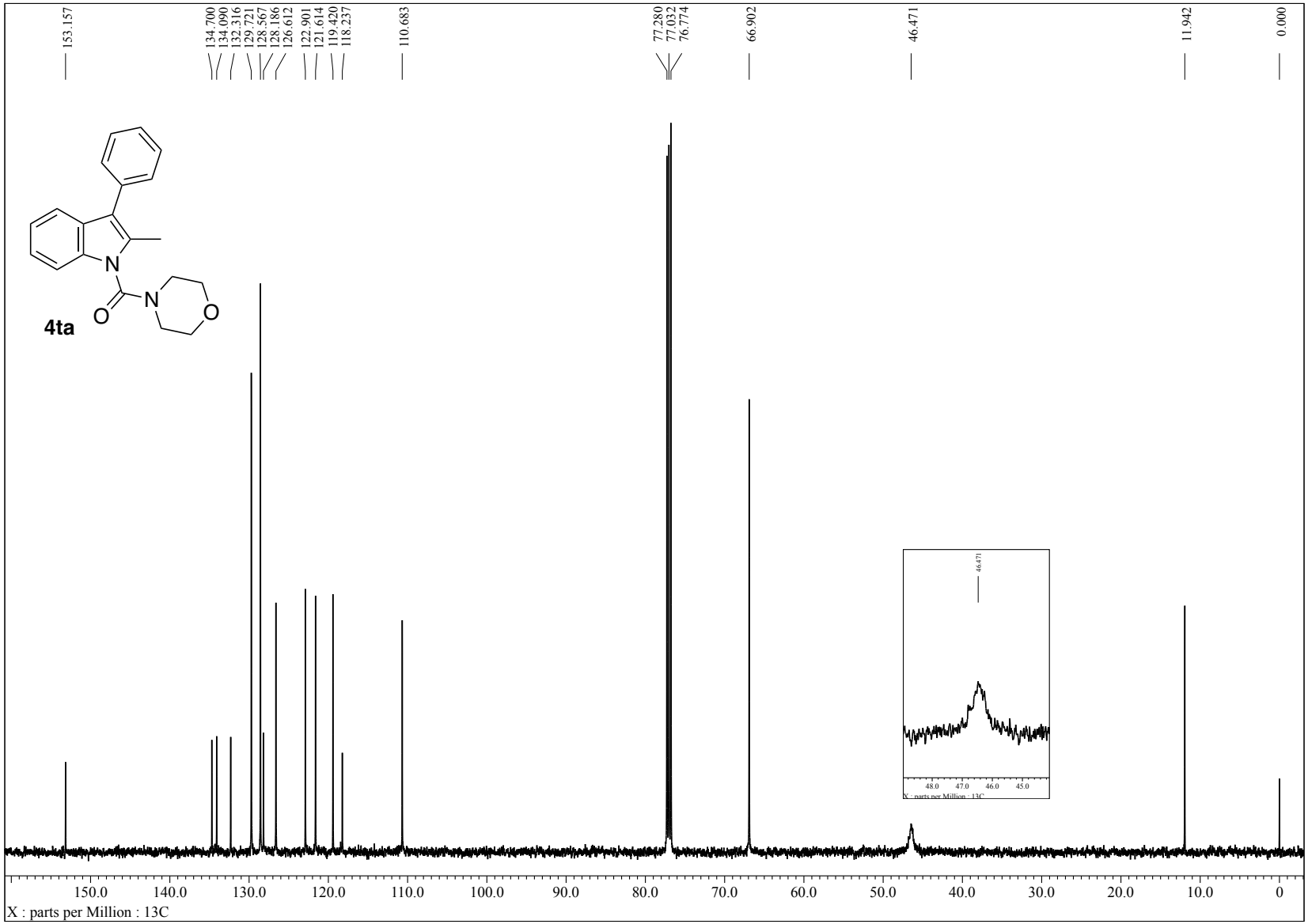
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



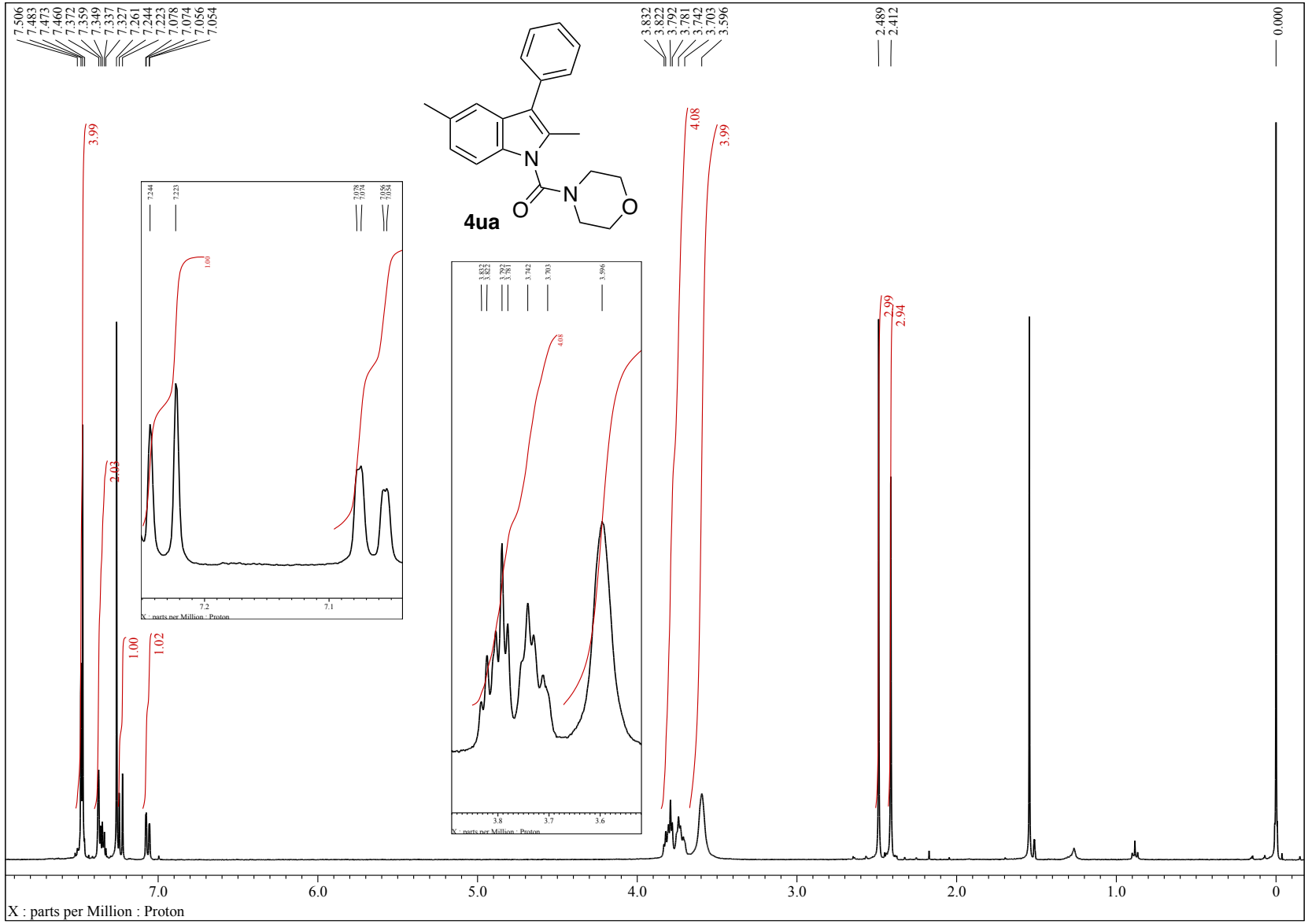
^{1}H NMR (500 MHz, $CDCl_3$)



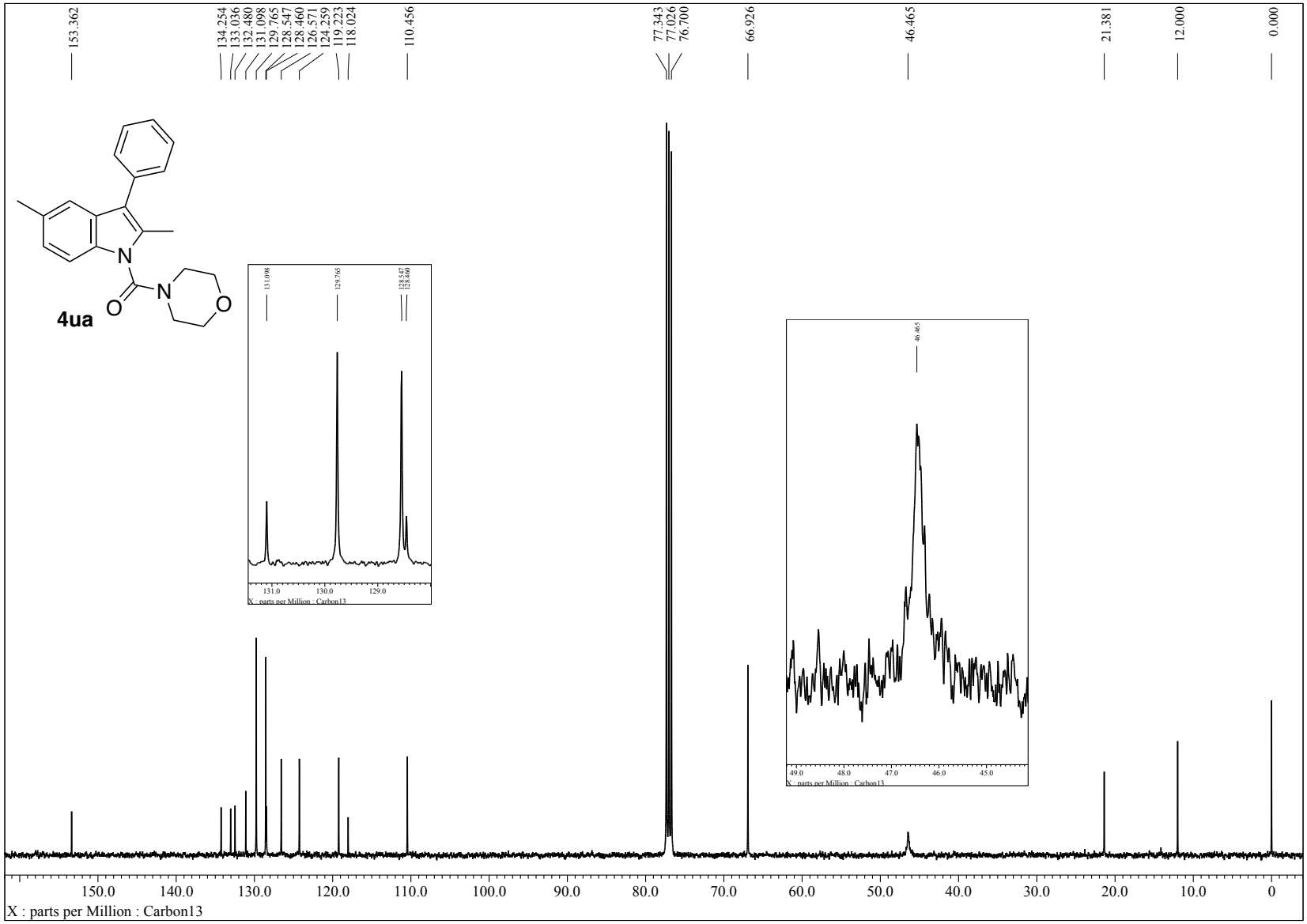
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



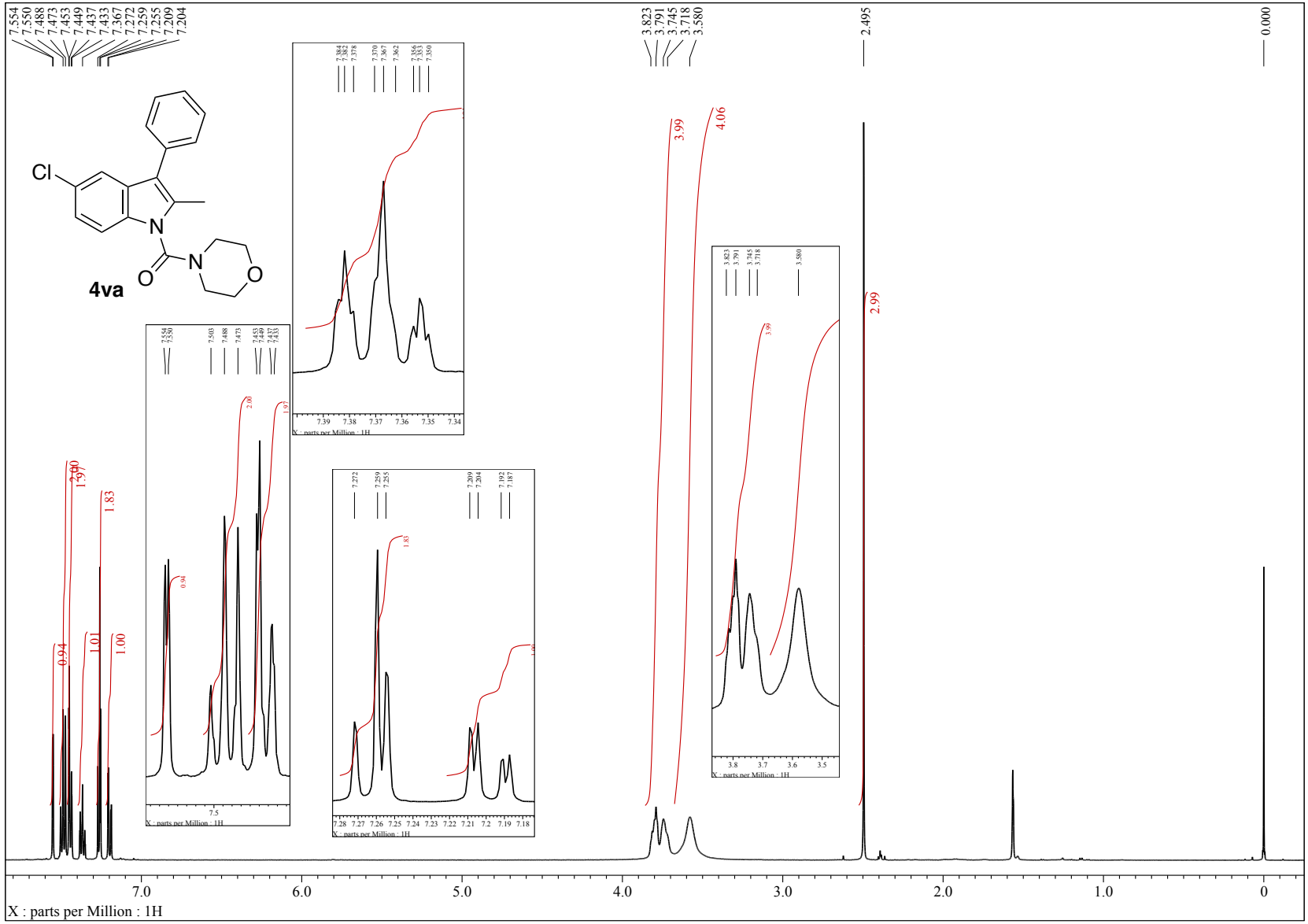
^{1}H NMR (400 MHz, $CDCl_3$)



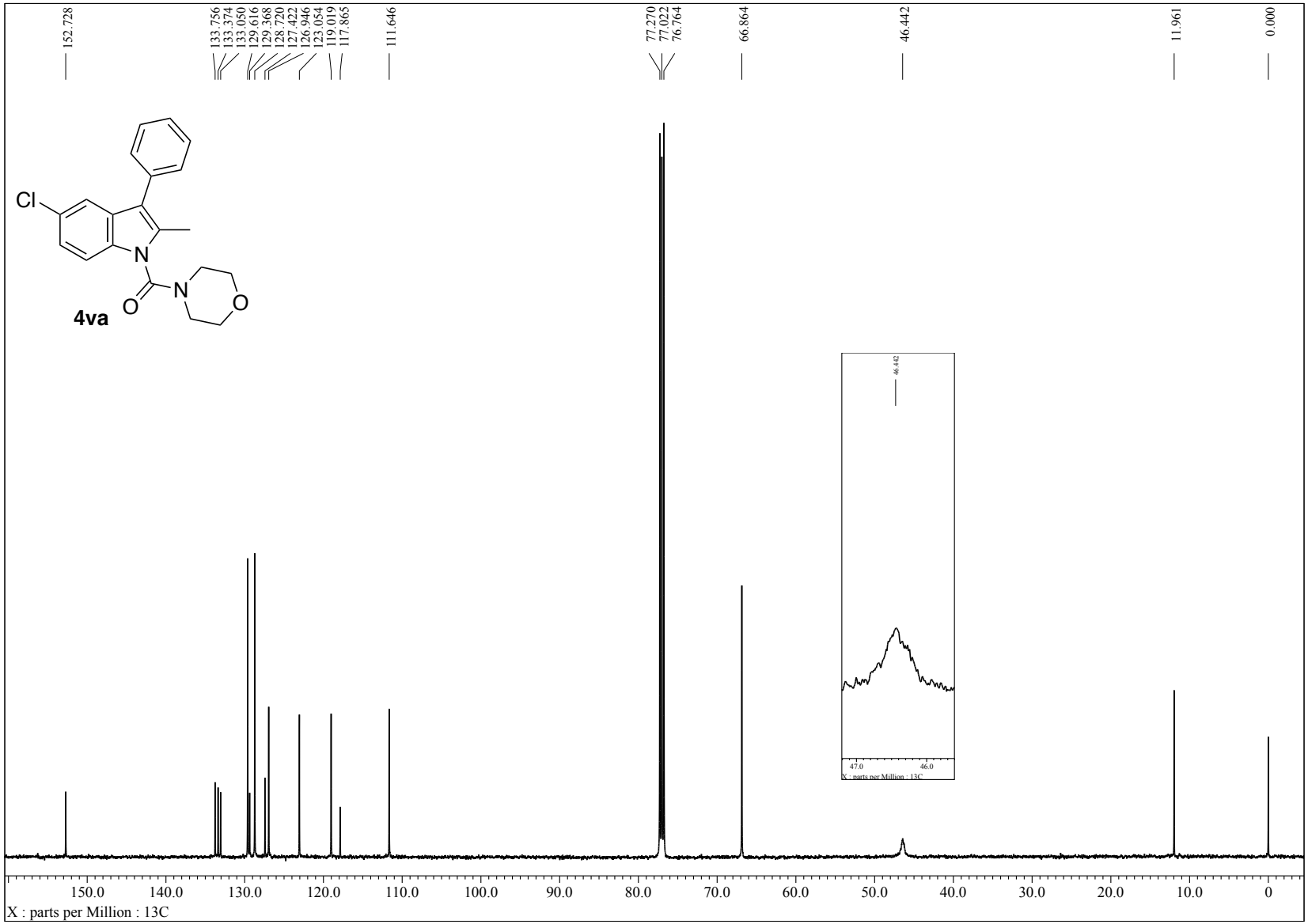
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



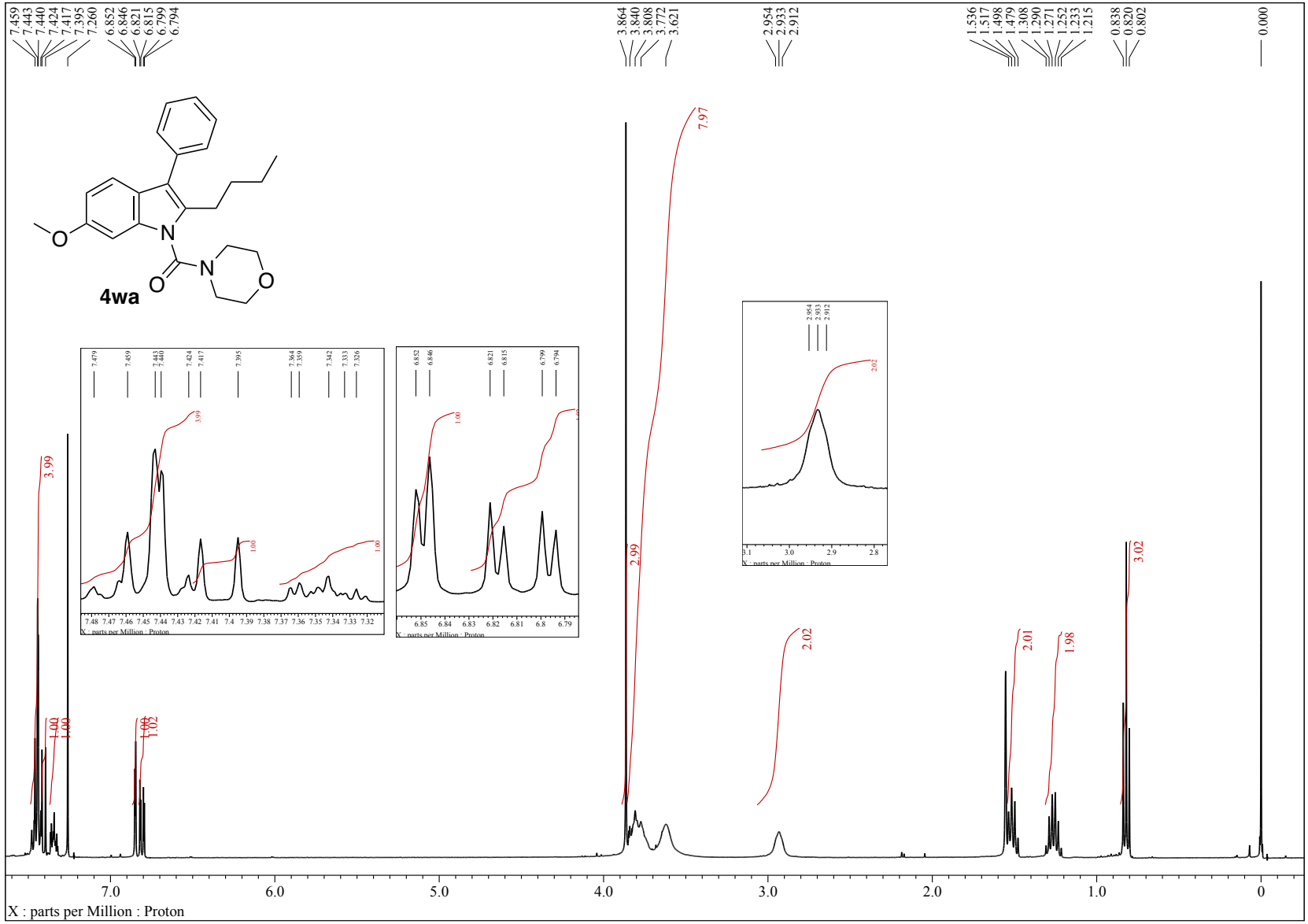
^{1}H NMR (400 MHz, $CDCl_3$)



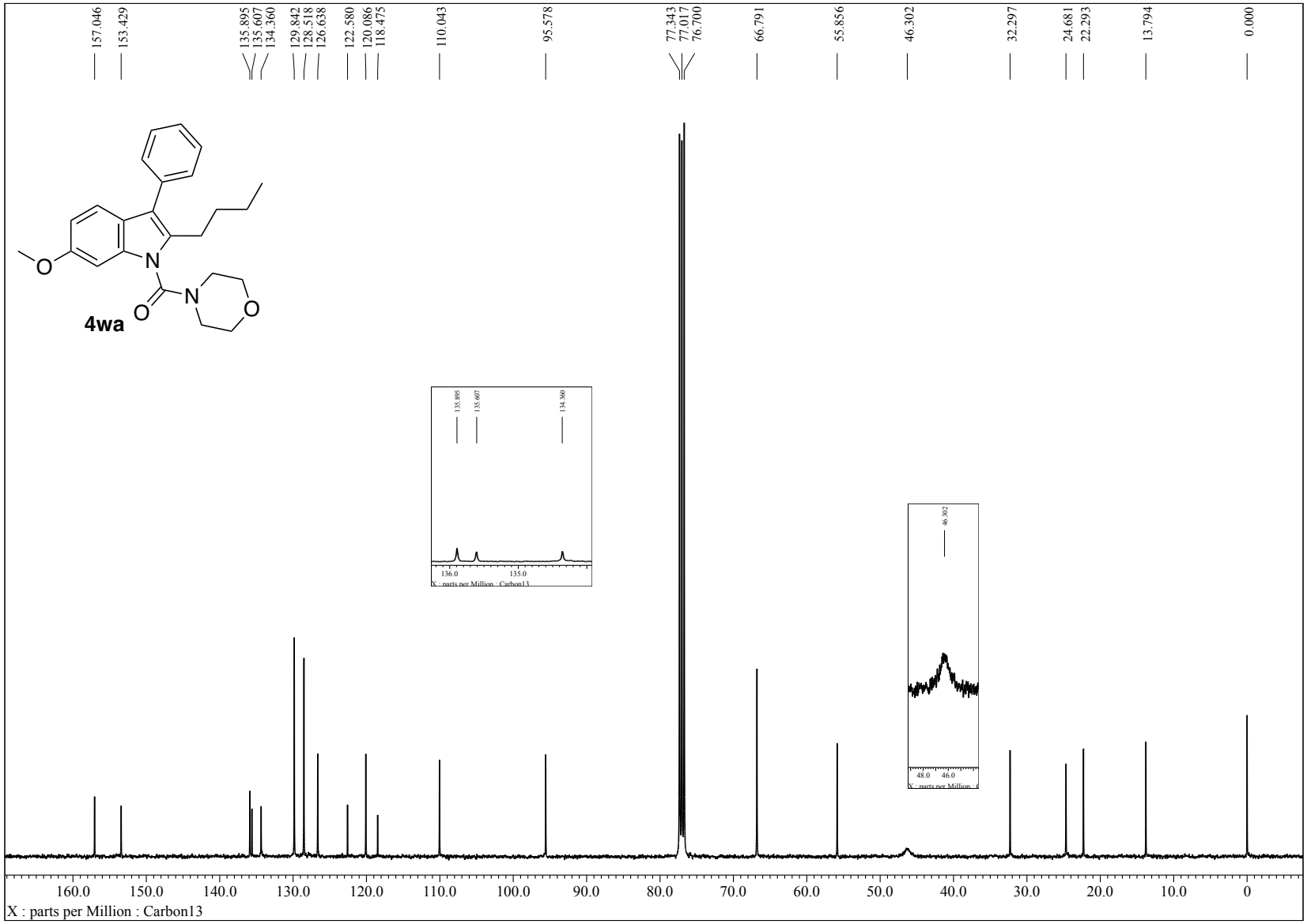
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



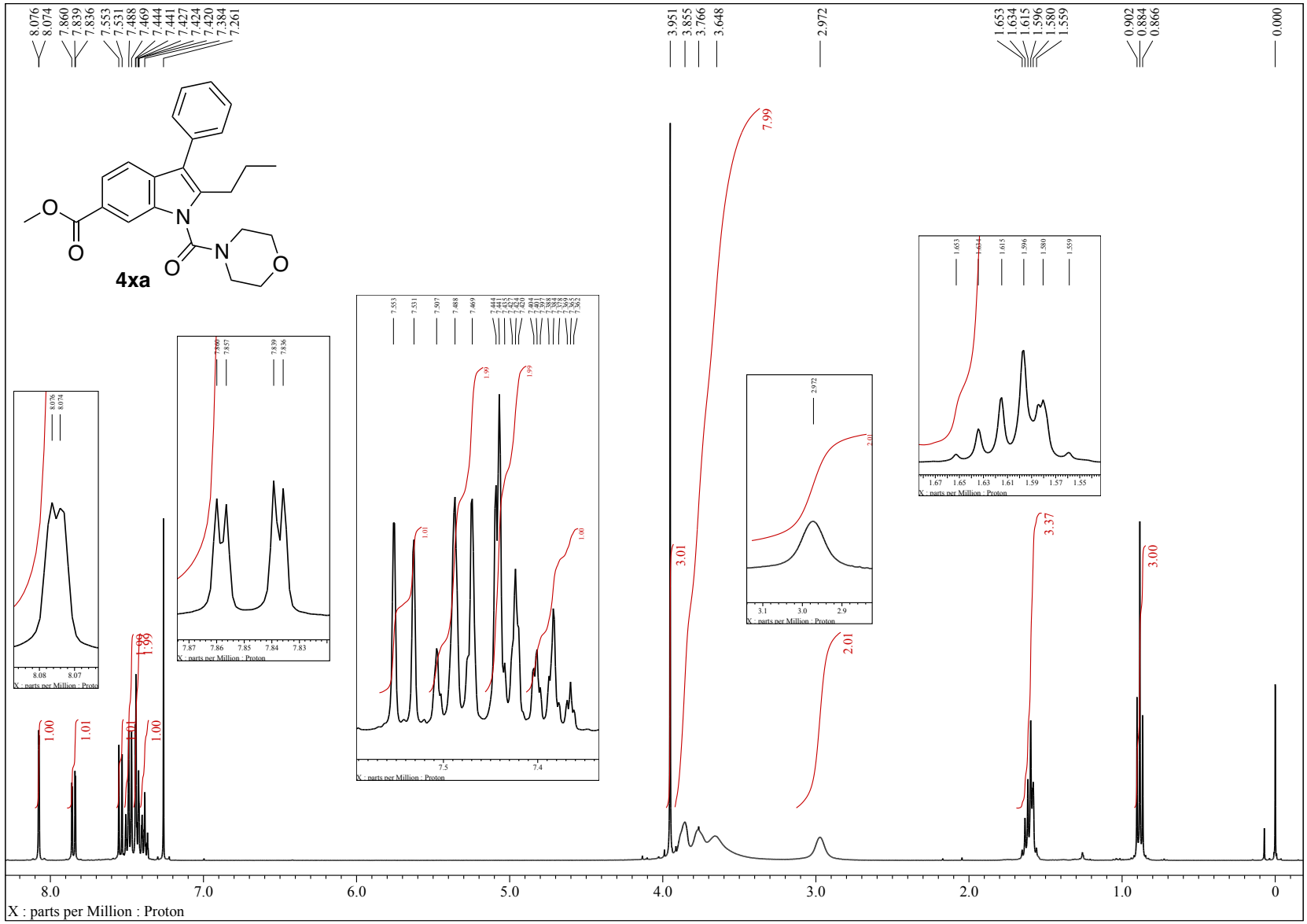
^{1}H NMR (400 MHz, $CDCl_3$)



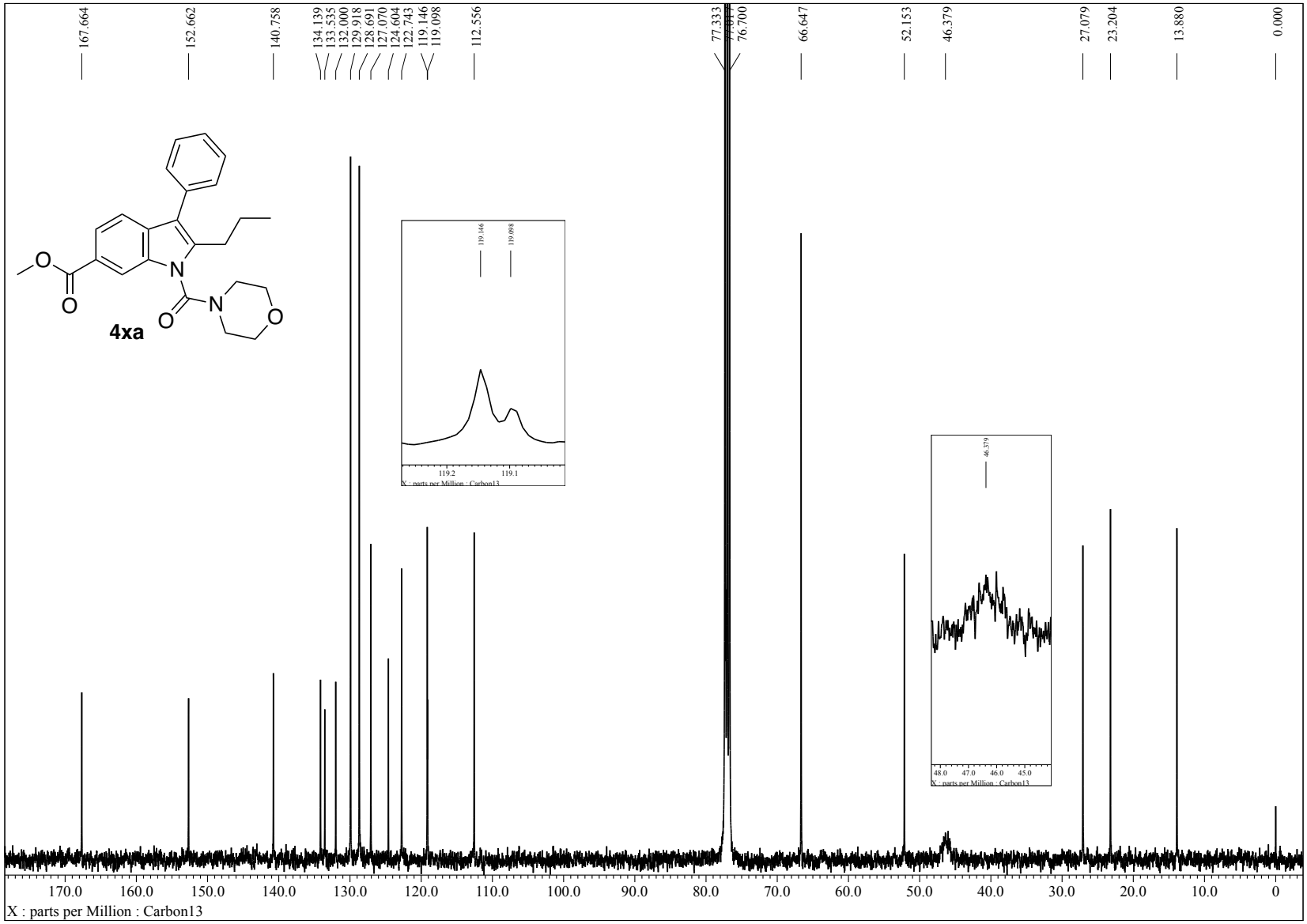
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



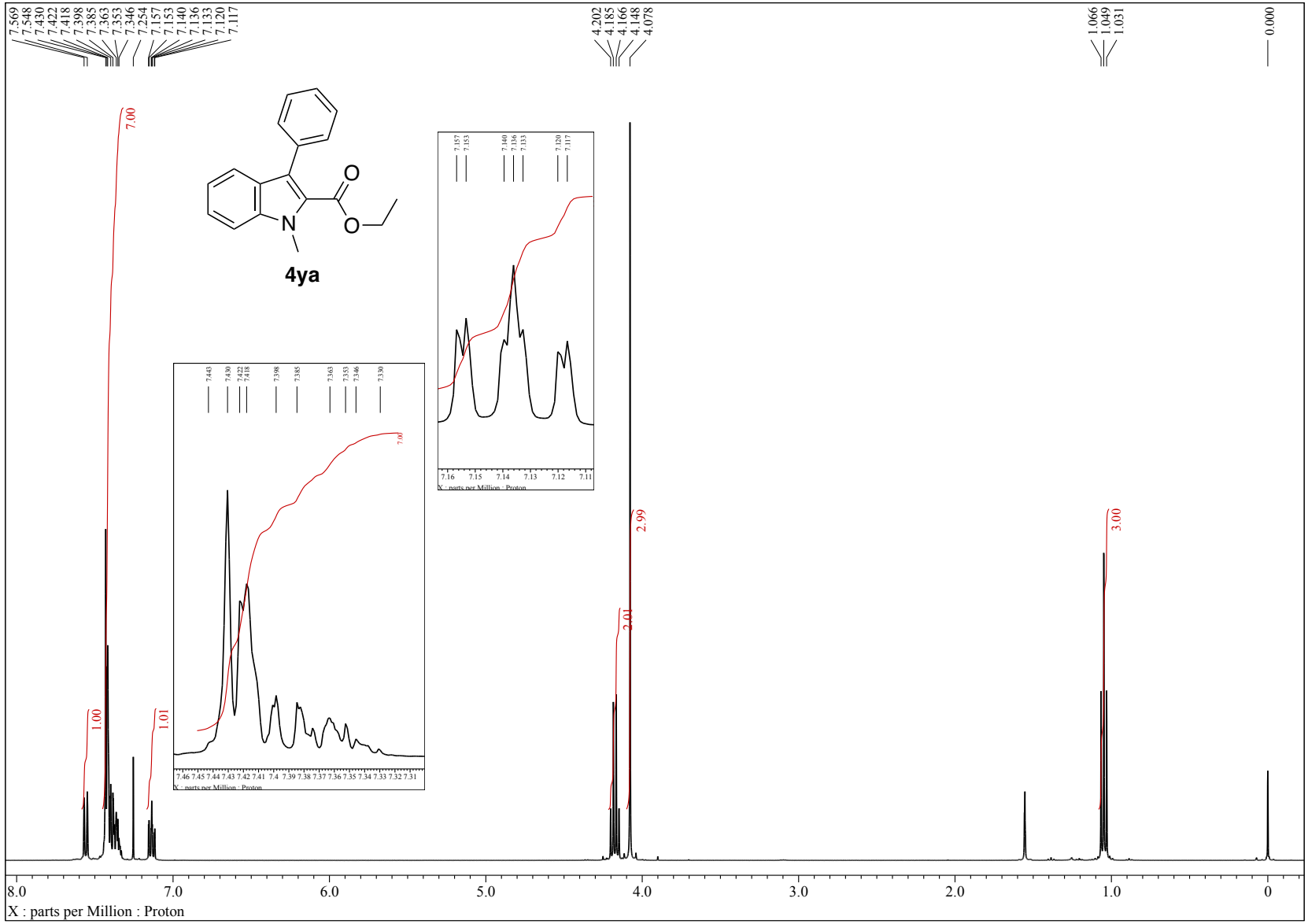
^{1}H NMR (400 MHz, $CDCl_3$)



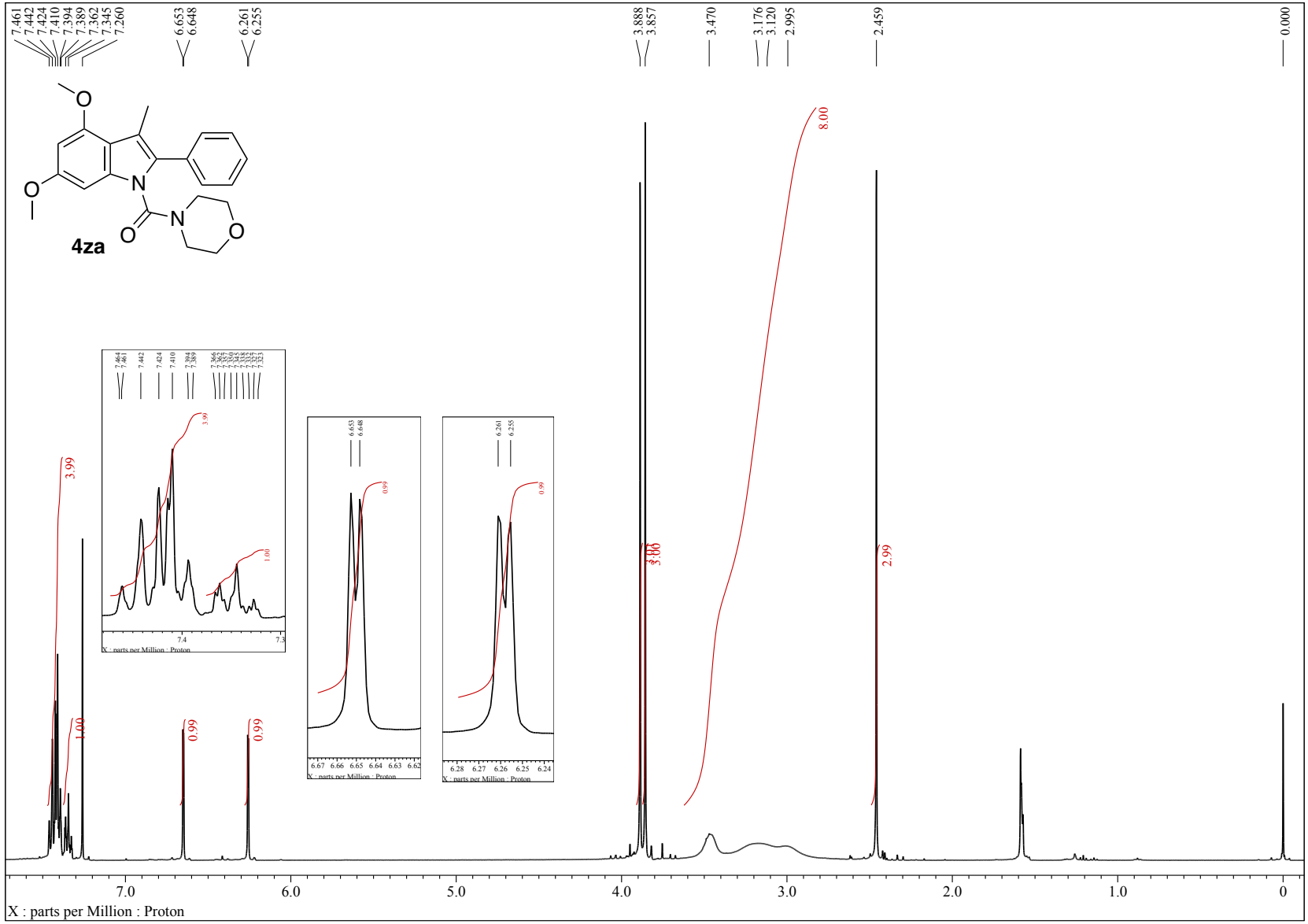
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



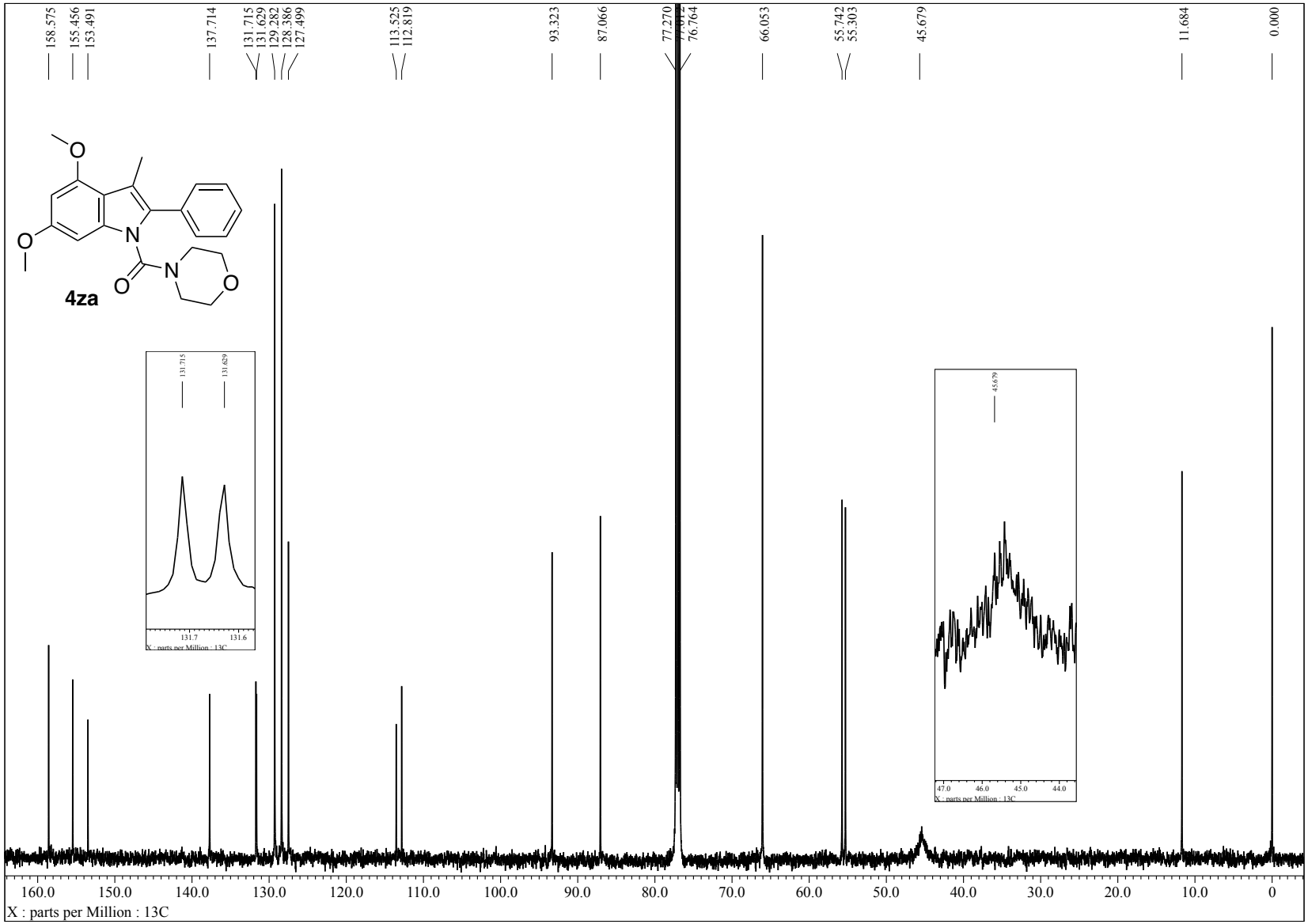
^{1}H NMR (400 MHz, $CDCl_3$)



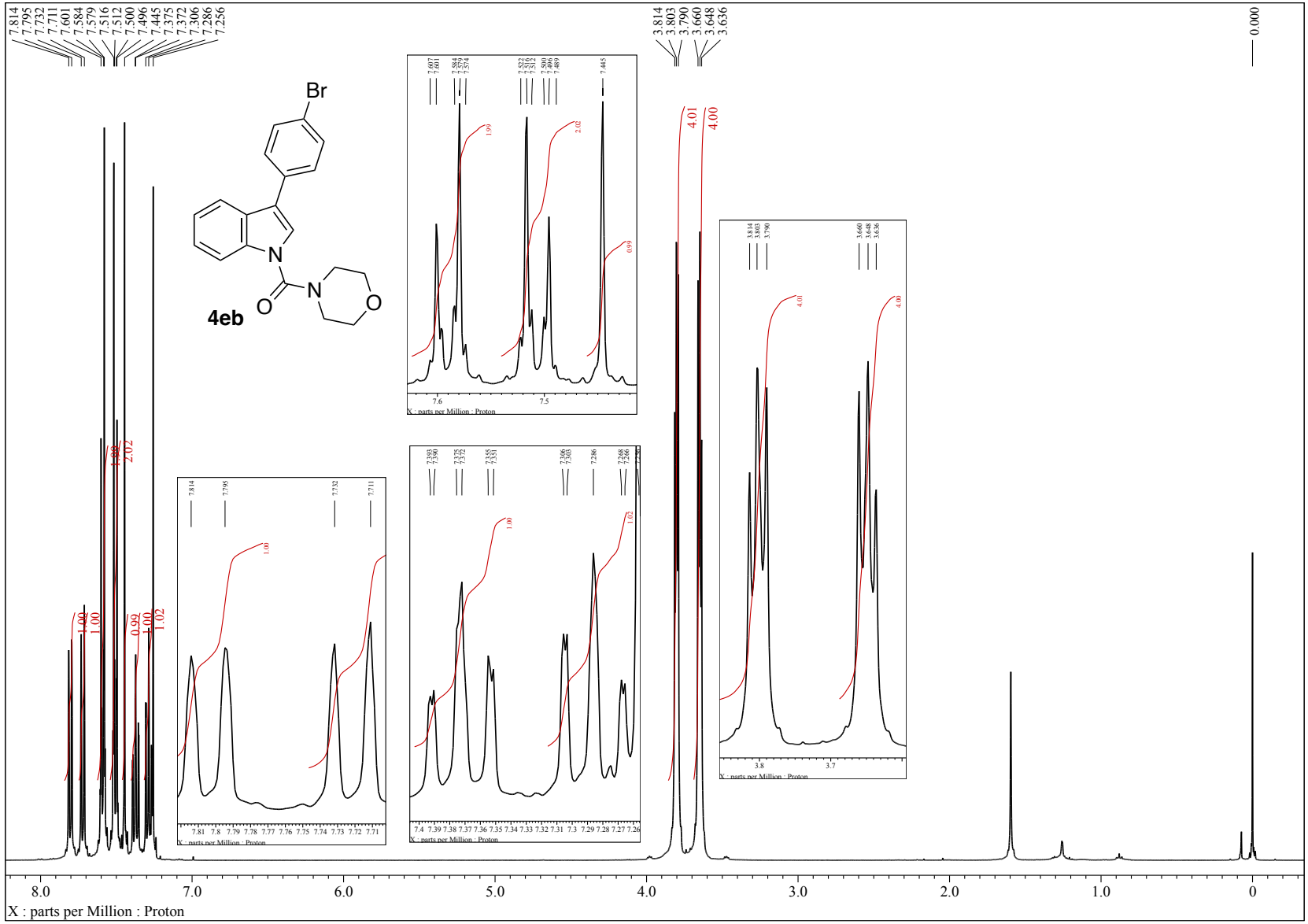
^{1}H NMR (400 MHz, $CDCl_3$)



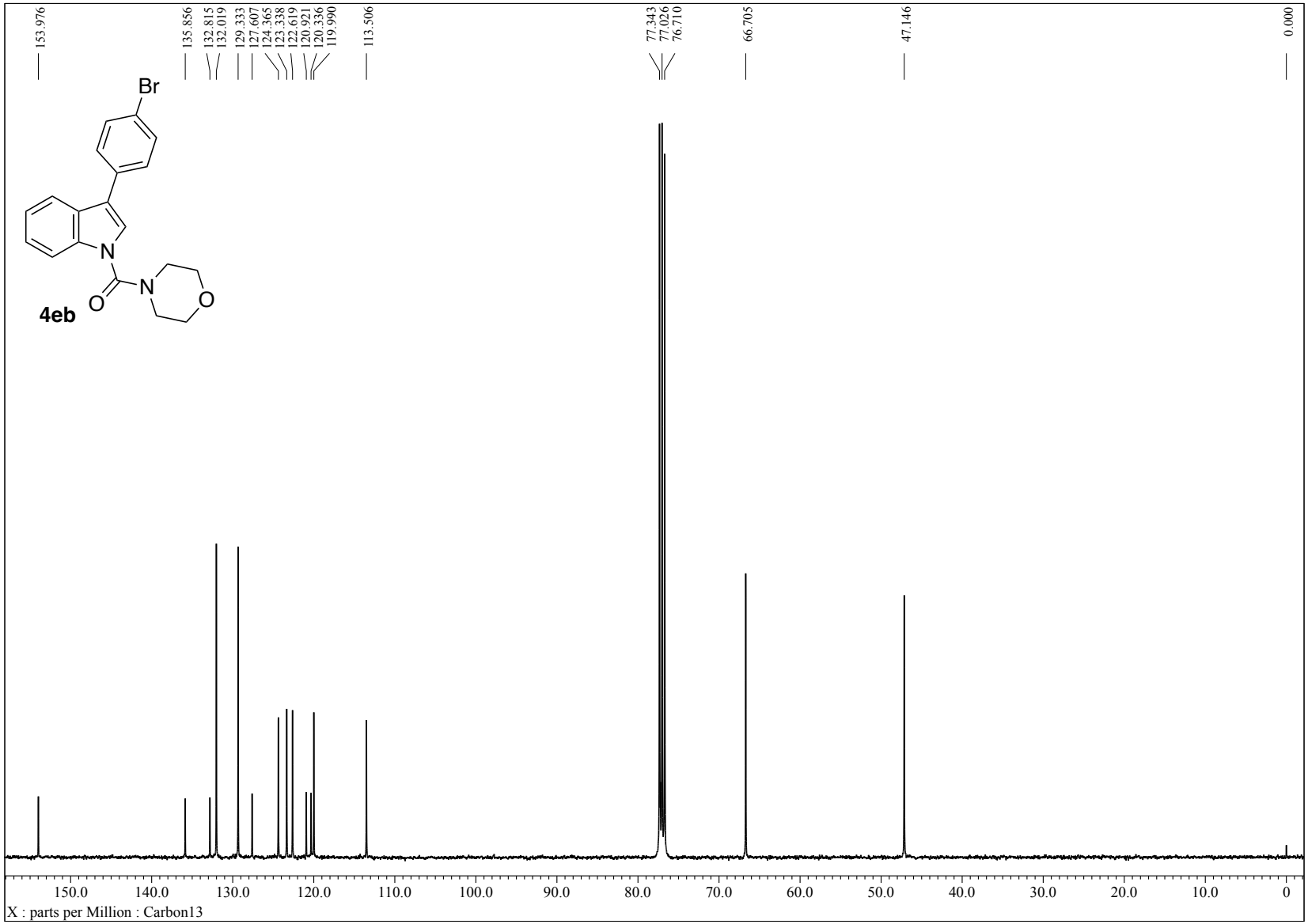
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



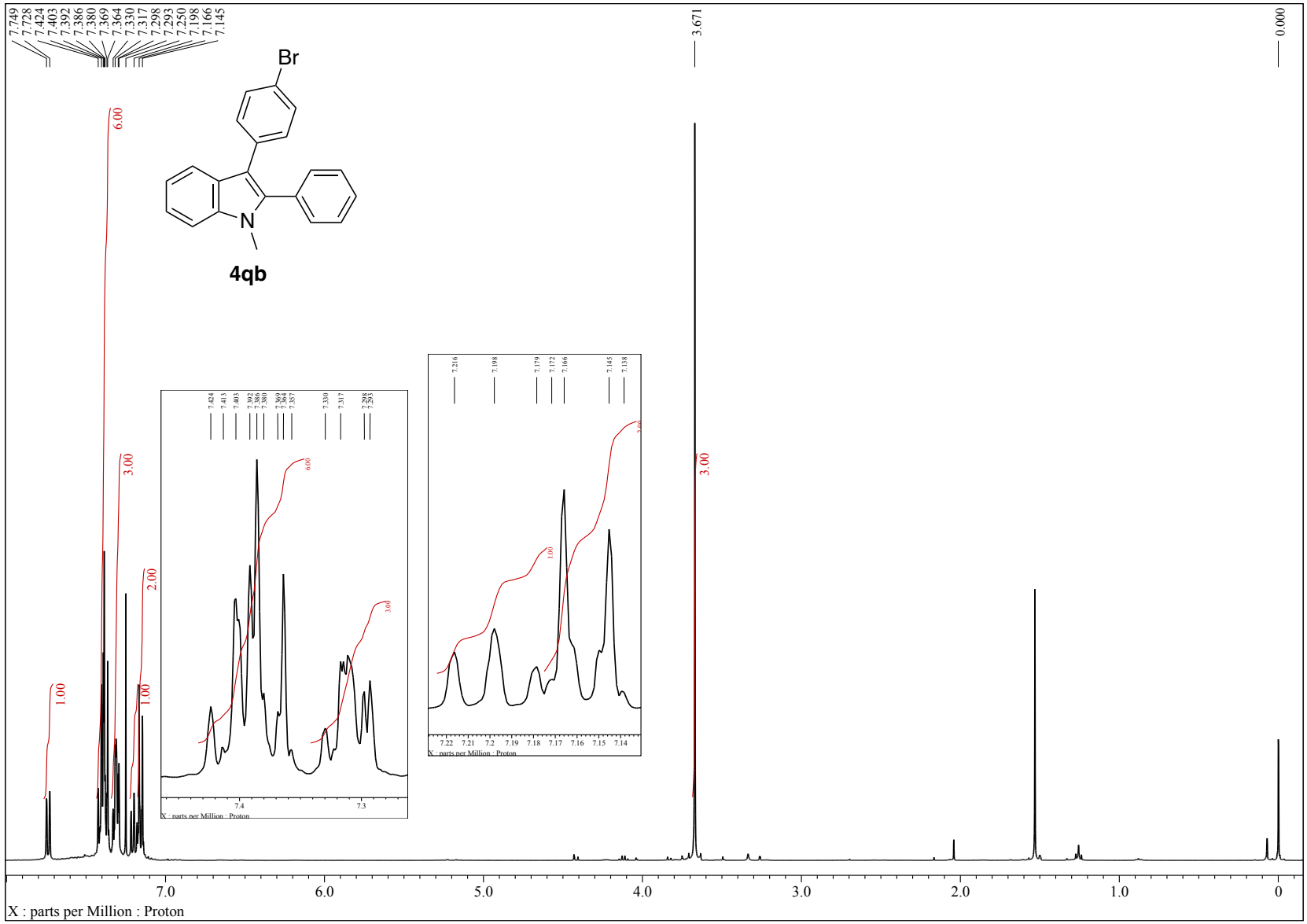
^{1}H NMR (400 MHz, $CDCl_3$)



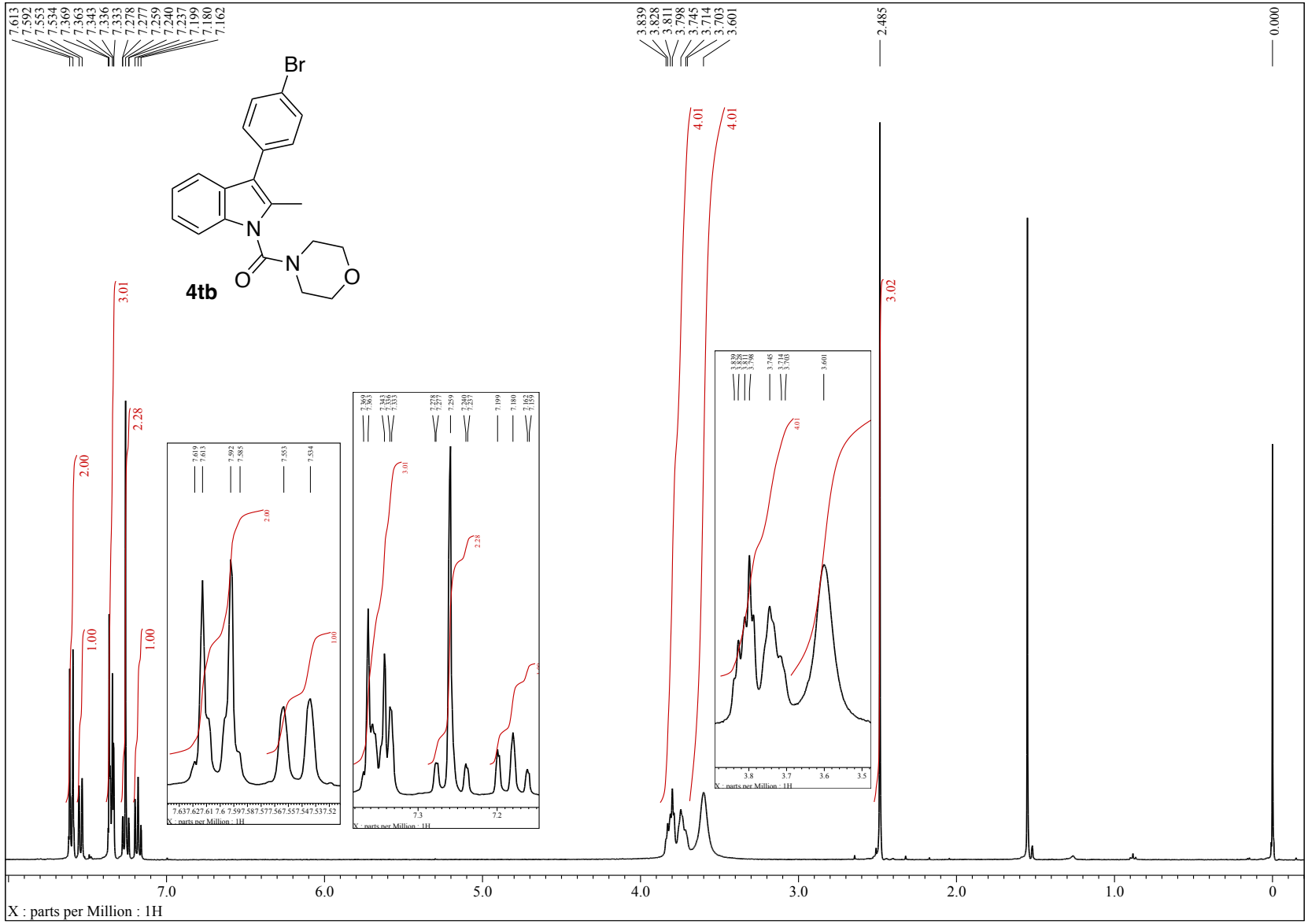
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



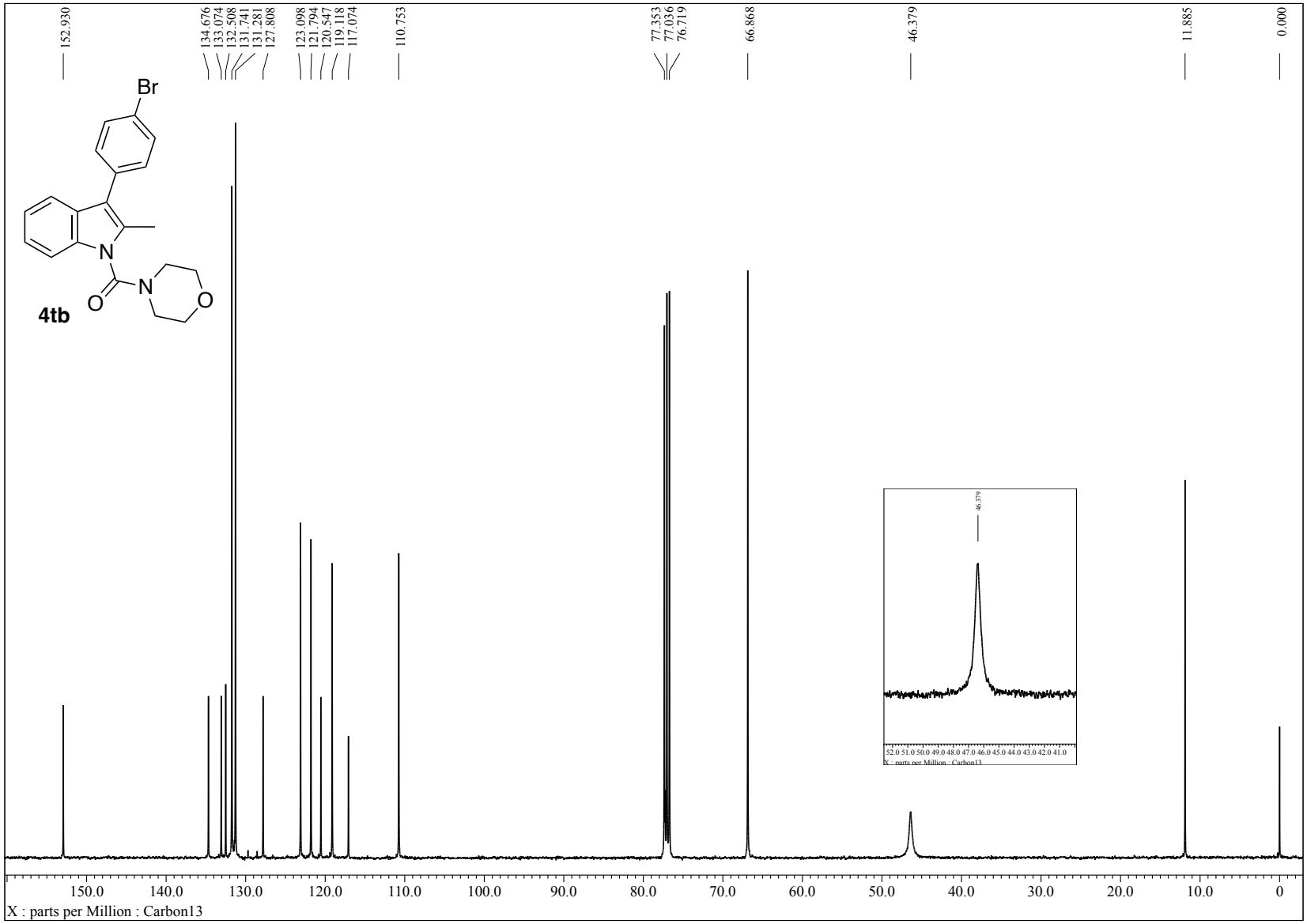
^{1}H NMR (400 MHz, $CDCl_3$)



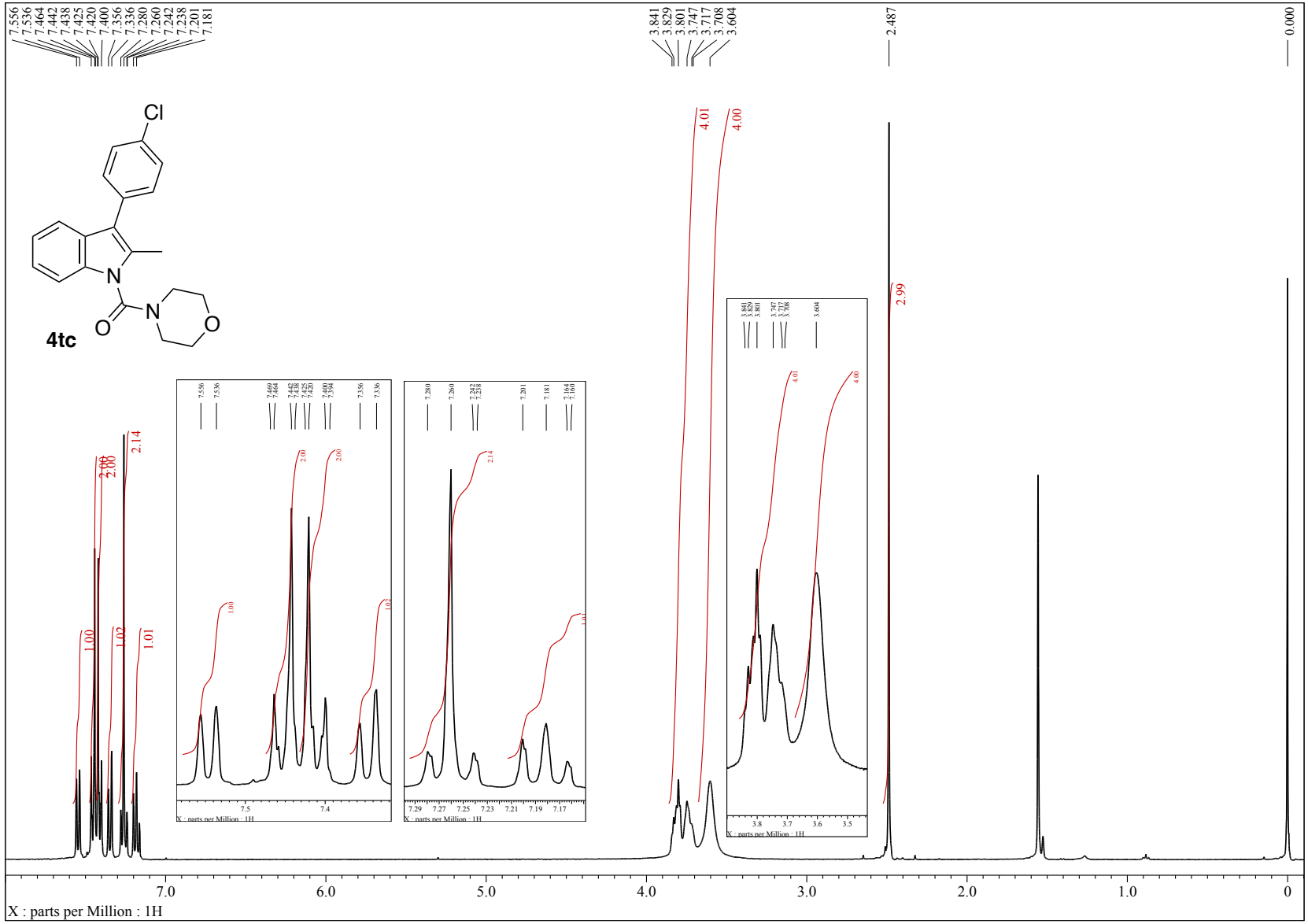
^{1}H NMR (400 MHz, $CDCl_3$)



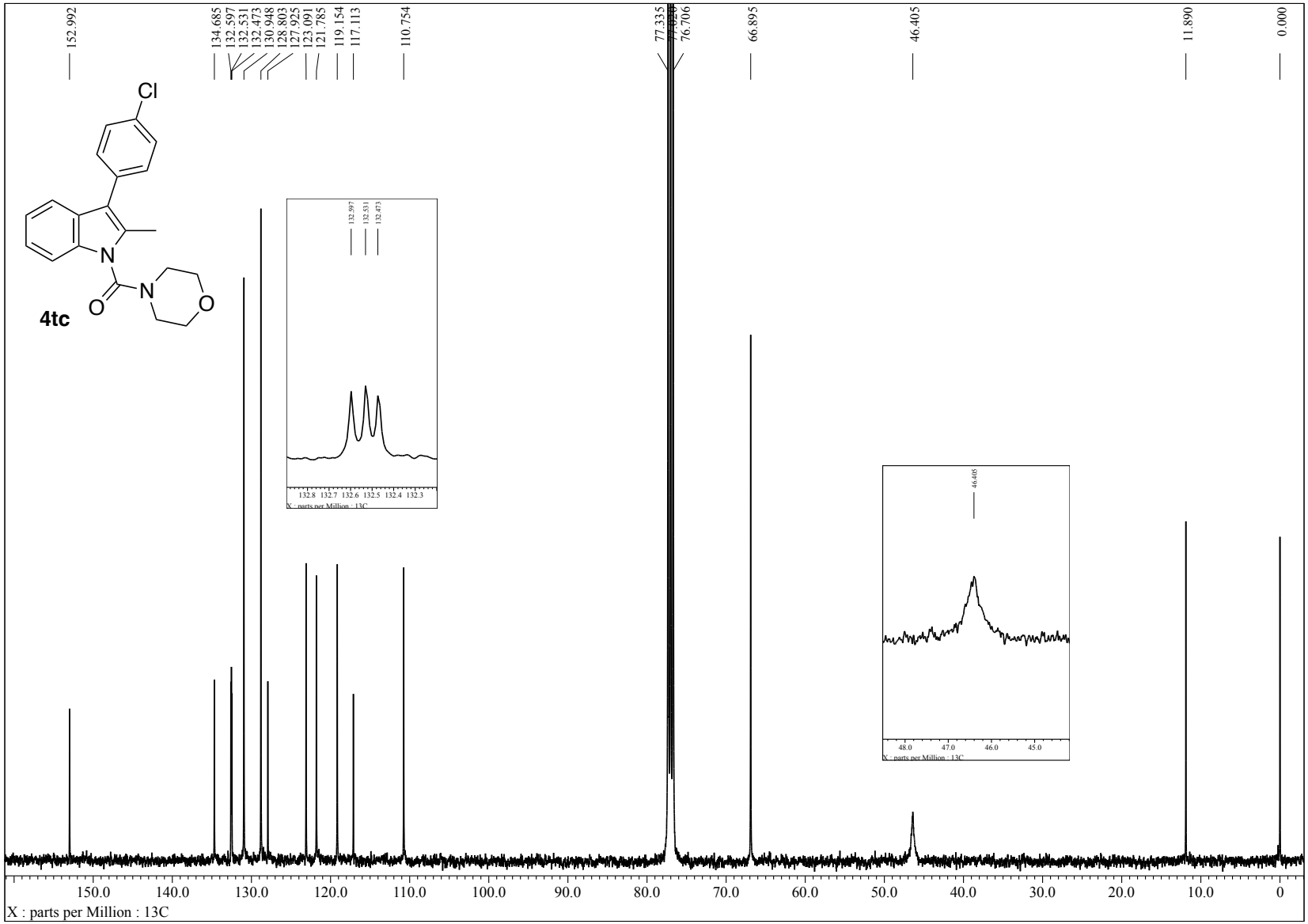
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



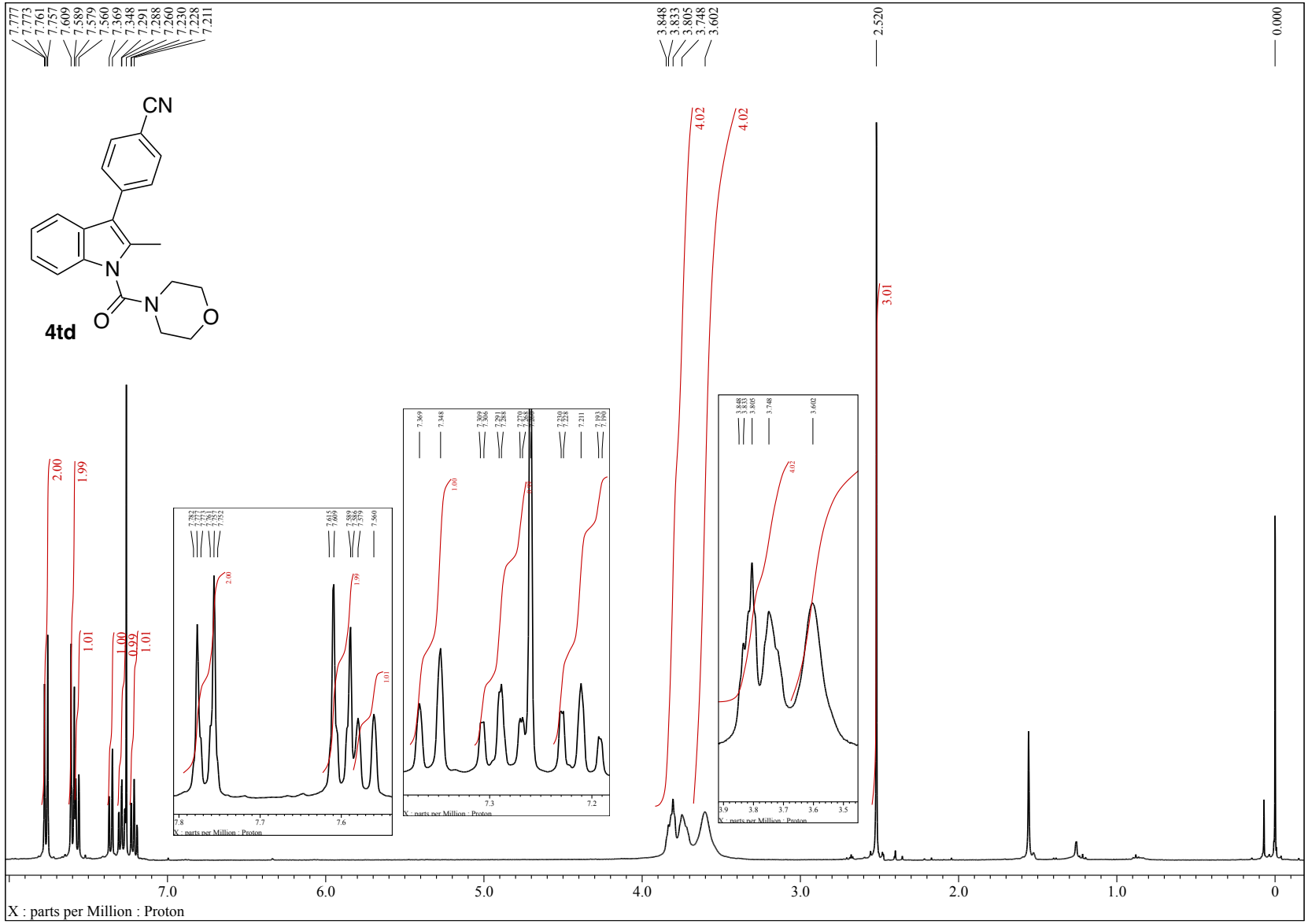
^{1}H NMR (400 MHz, $CDCl_3$)



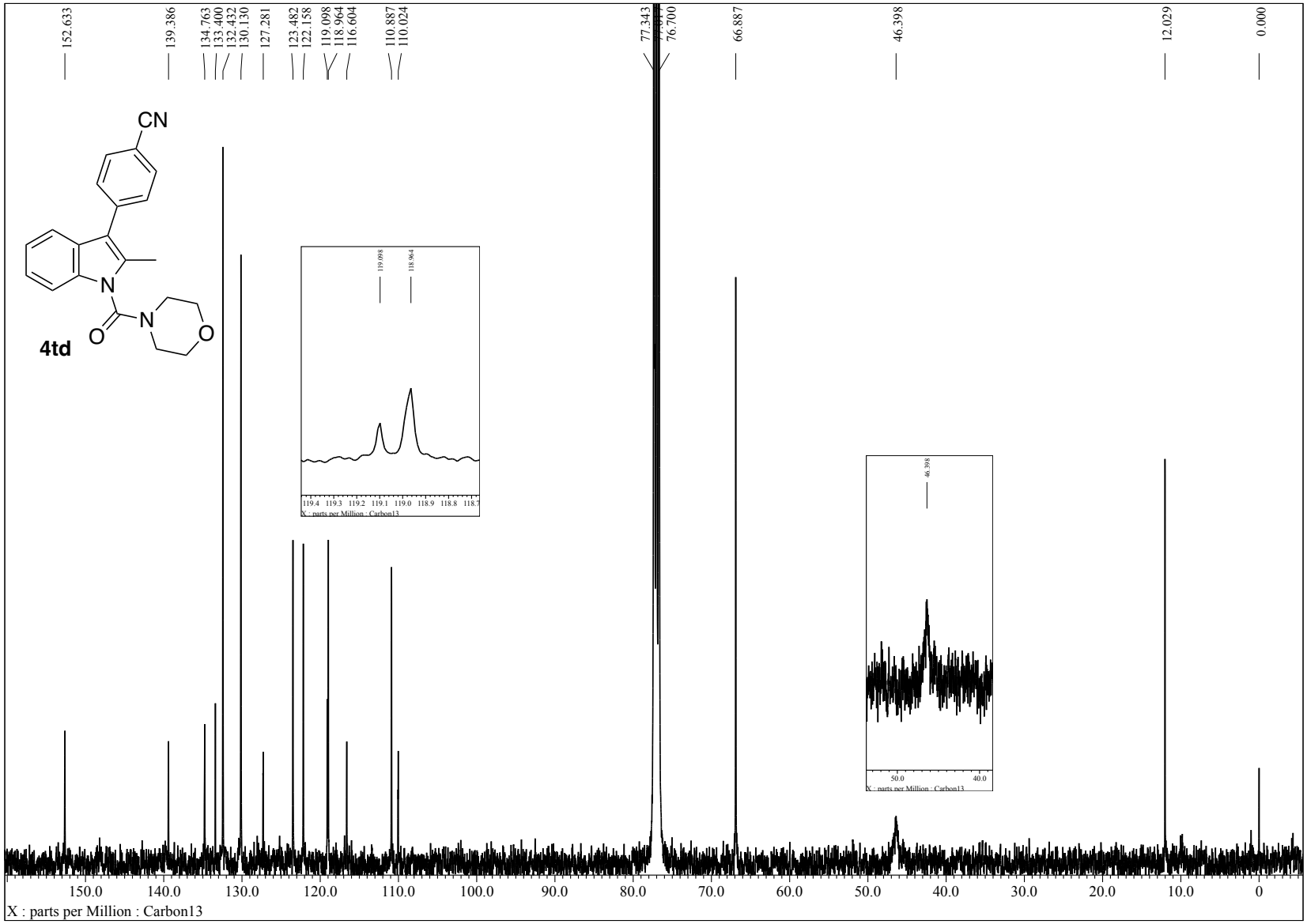
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



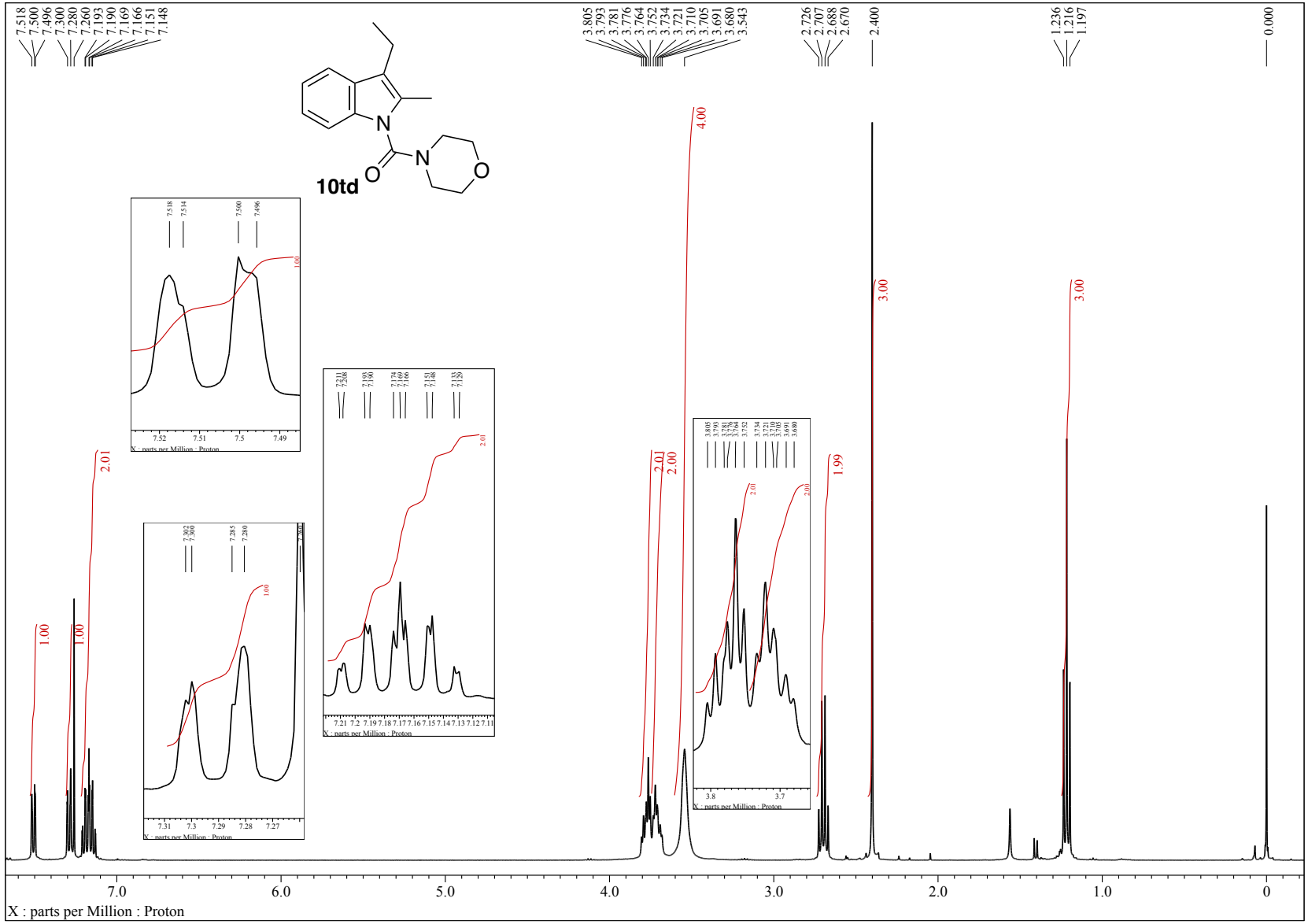
^{1}H NMR (400 MHz, $CDCl_3$)



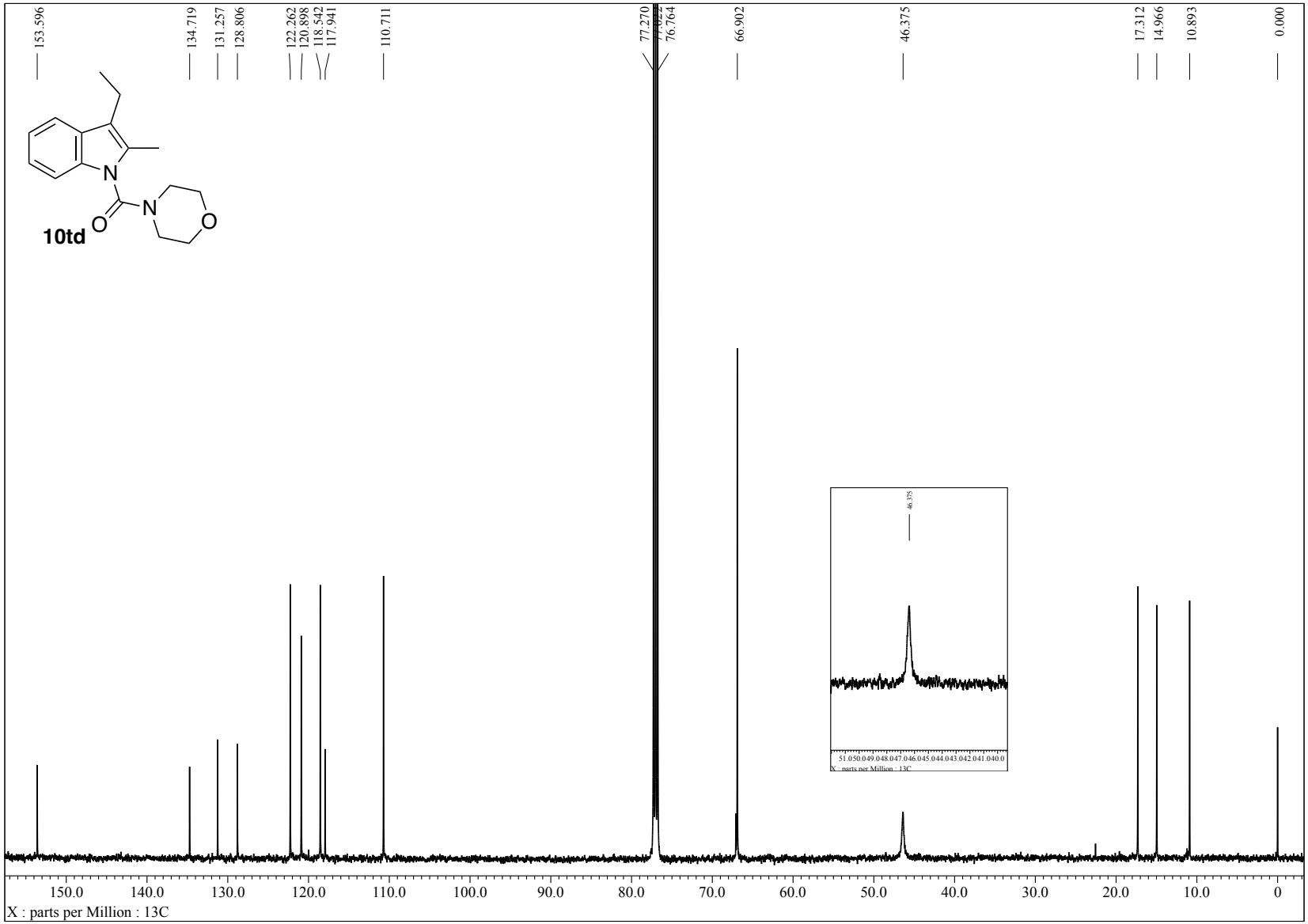
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



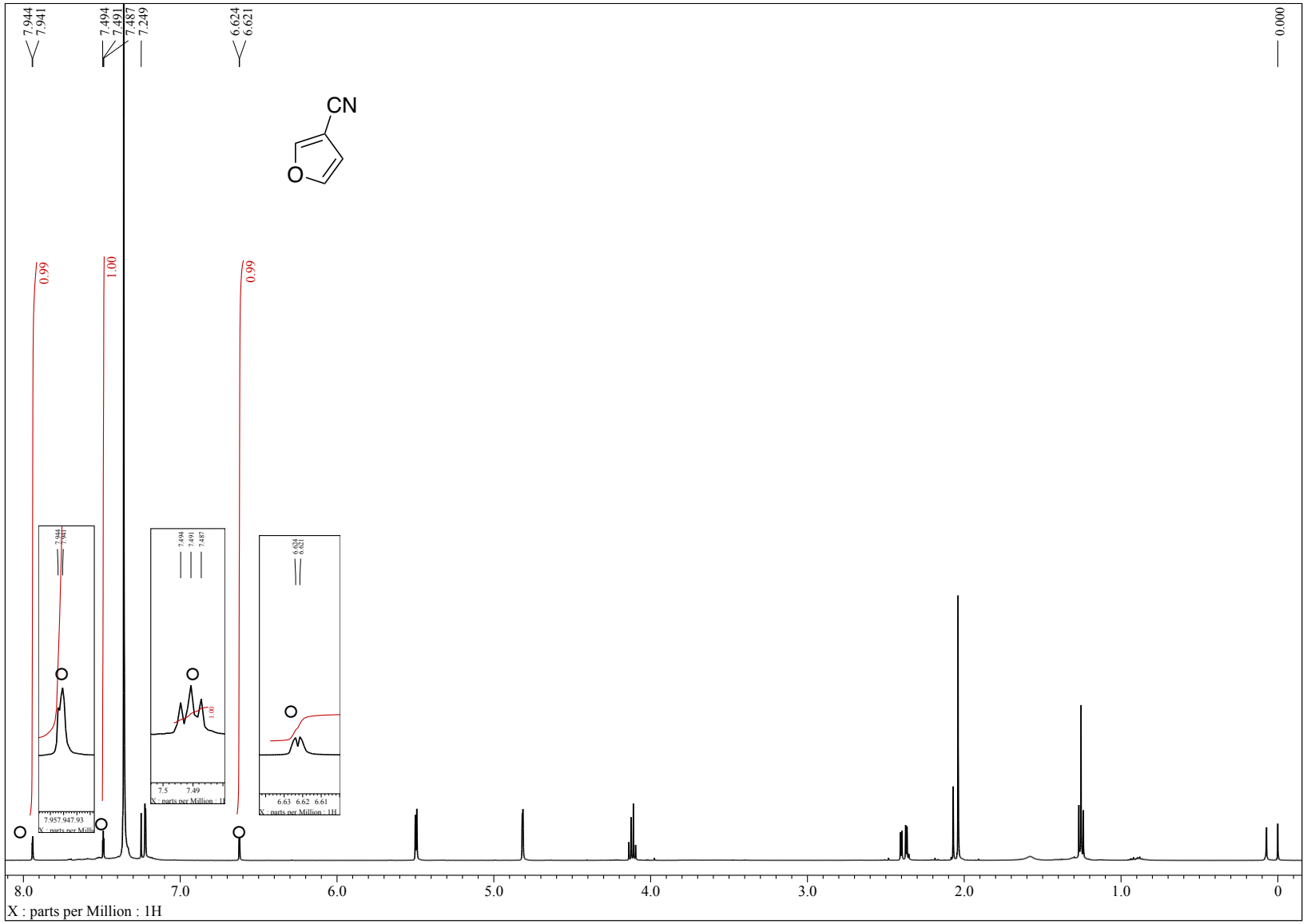
^{1}H NMR (400 MHz, $CDCl_3$)



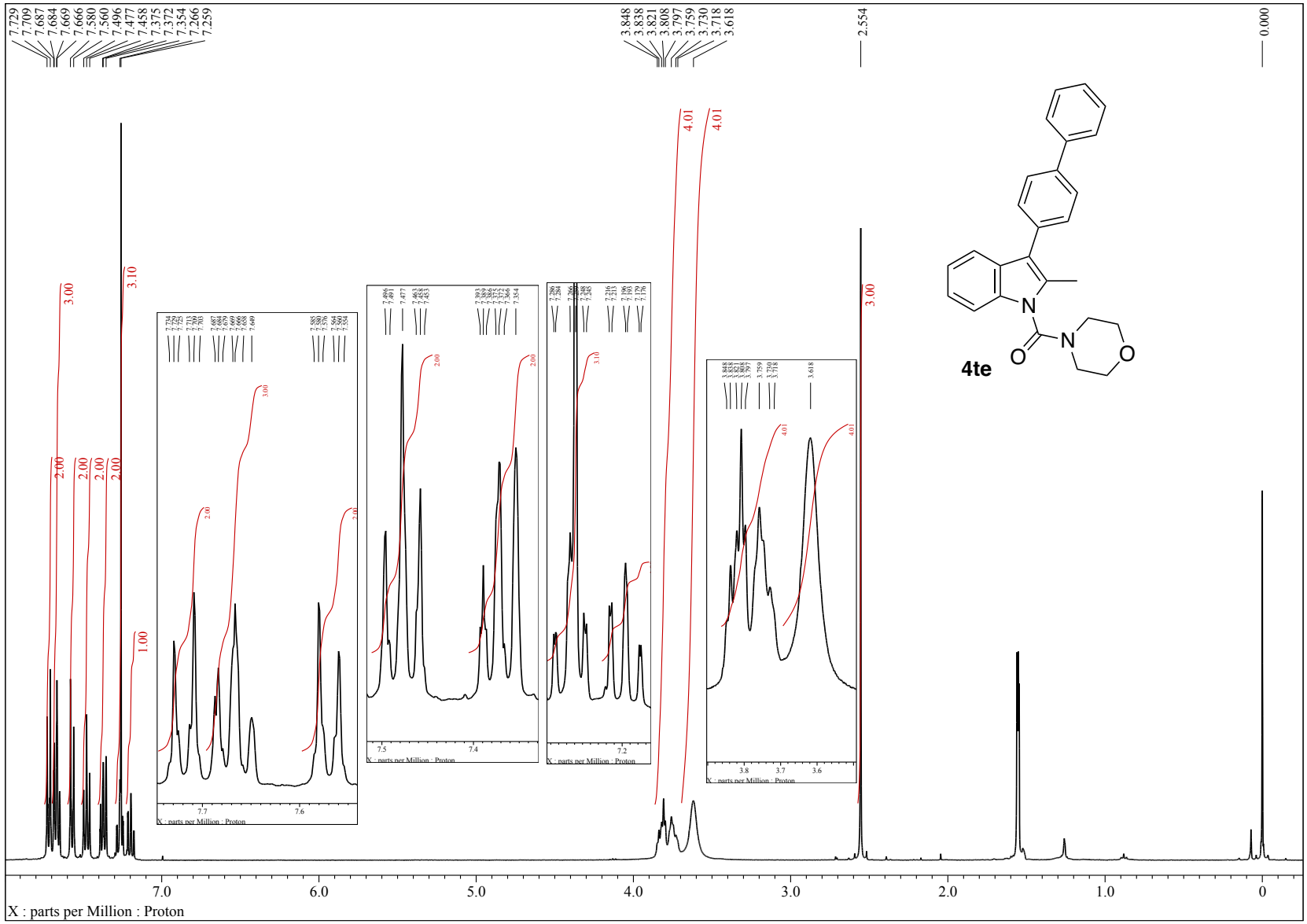
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



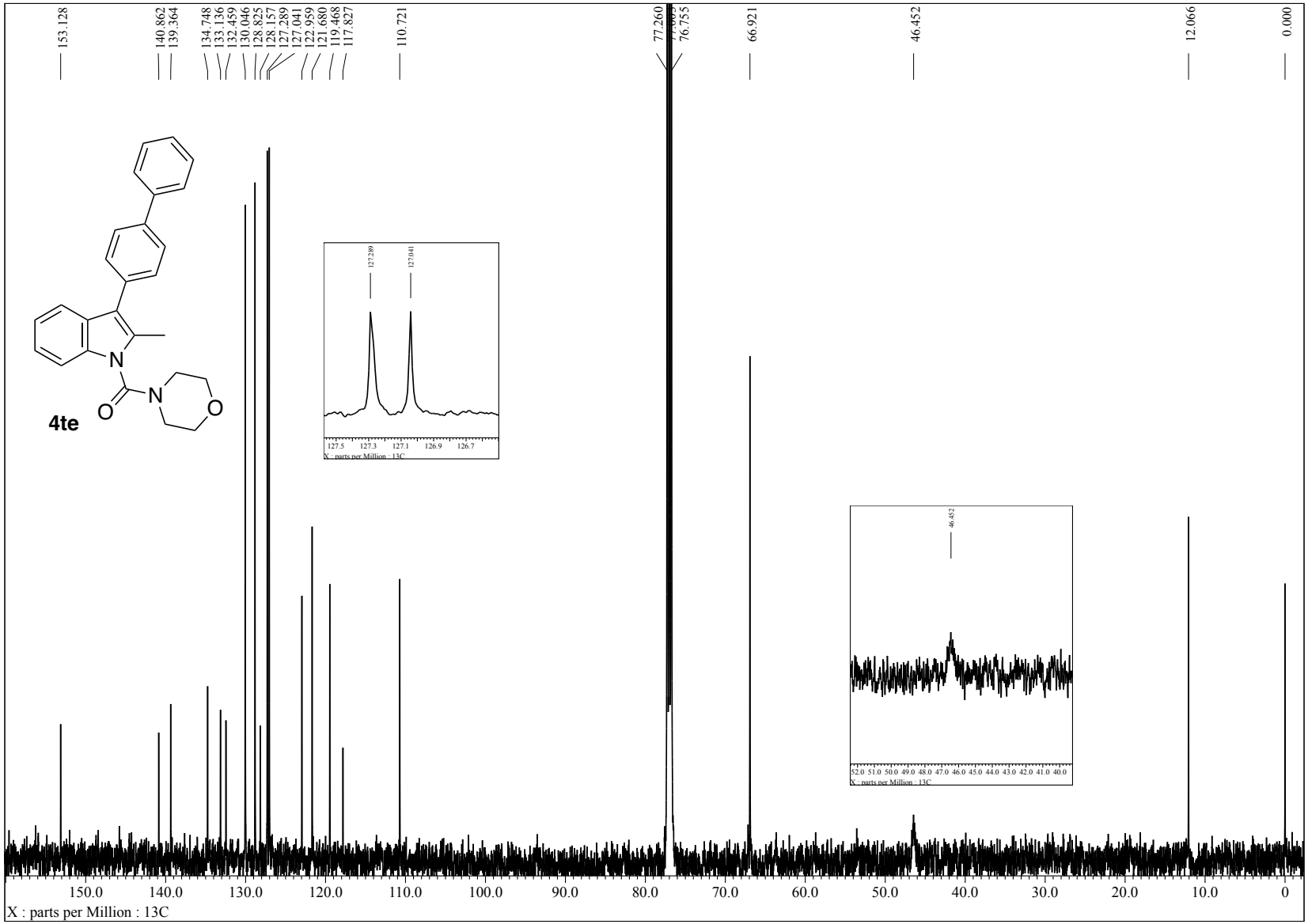
^{1}H NMR (500 MHz, $CDCl_3$)



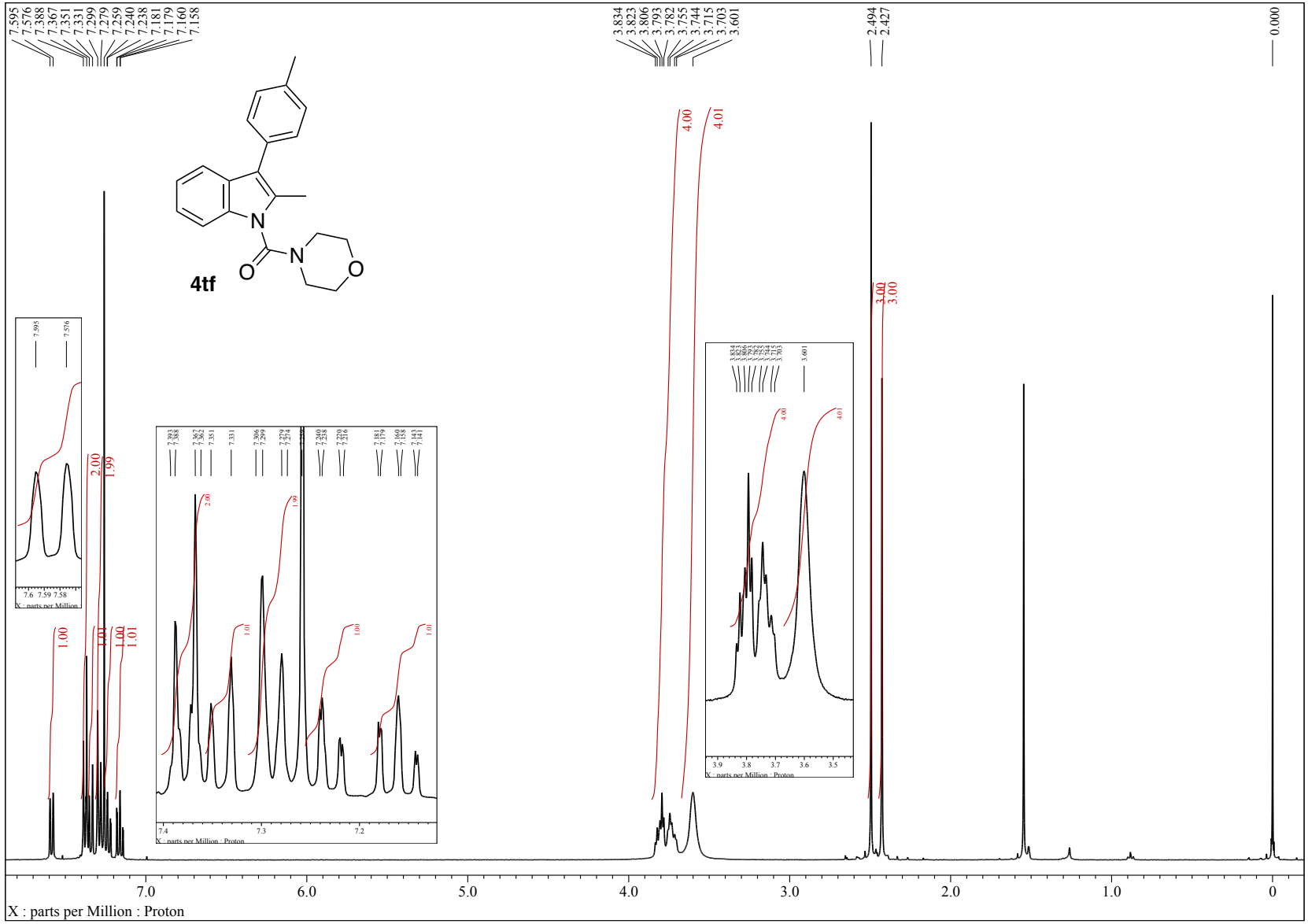
^{1}H NMR (400 MHz, $CDCl_3$)



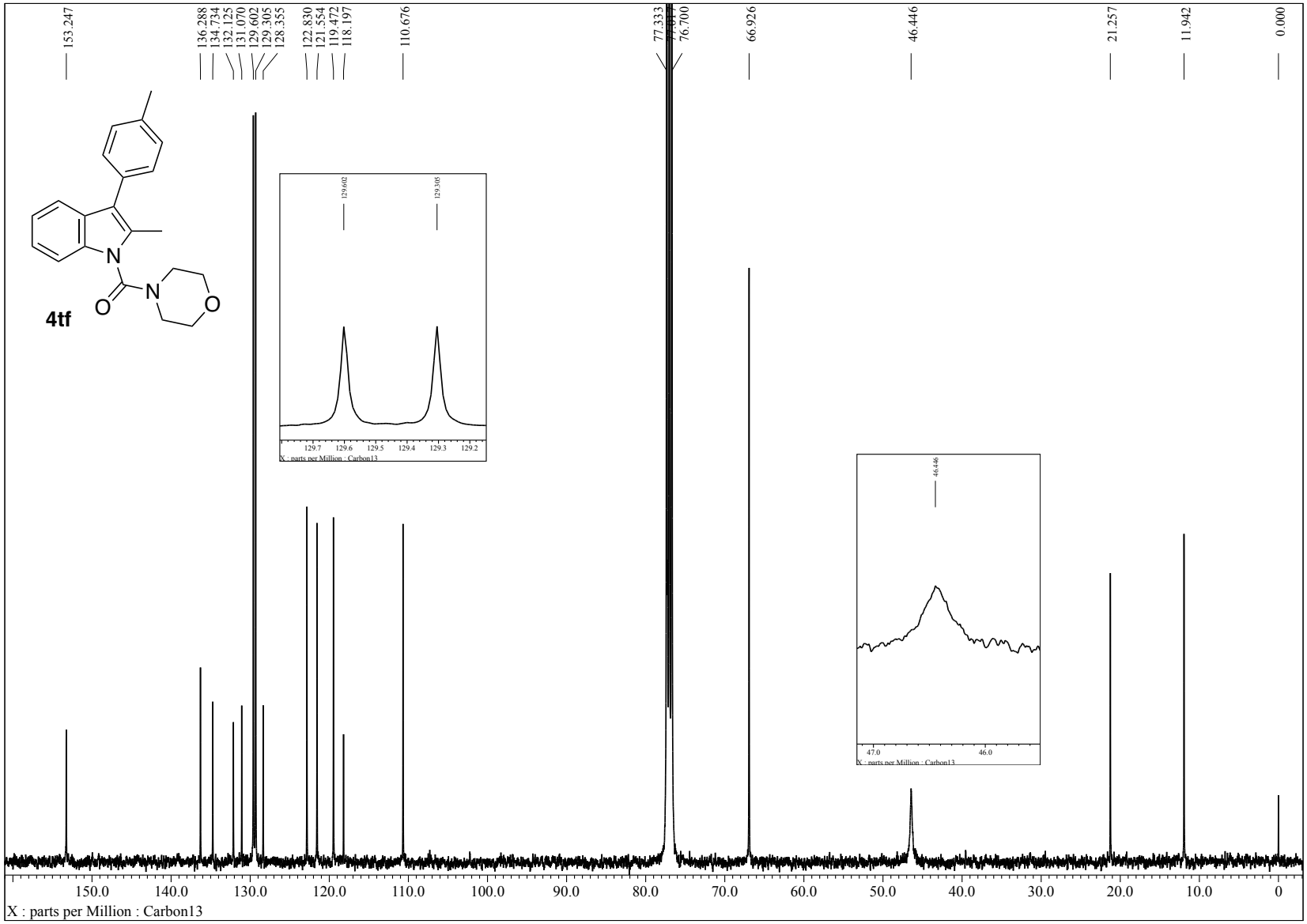
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



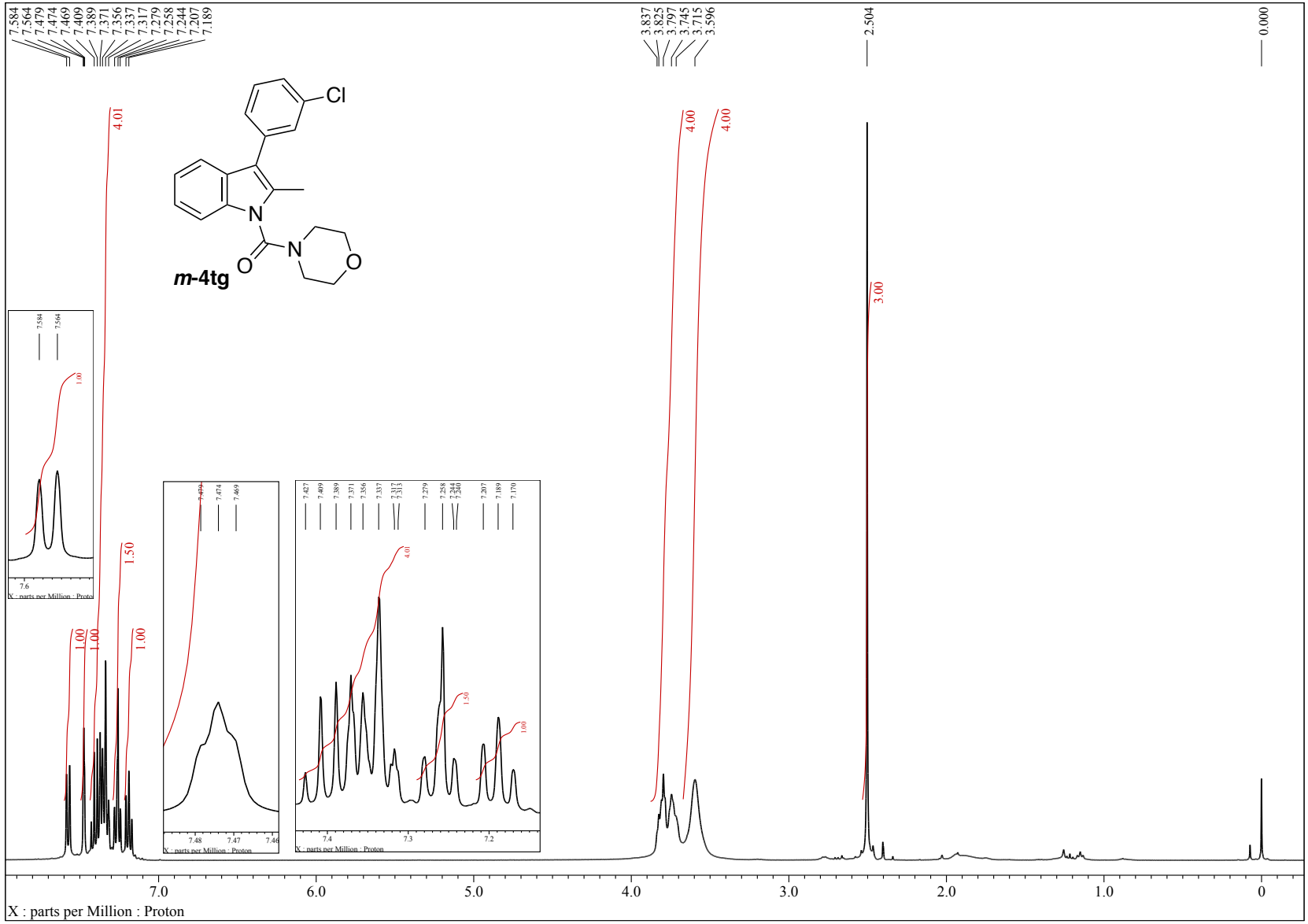
^{1}H NMR (400 MHz, $CDCl_3$)



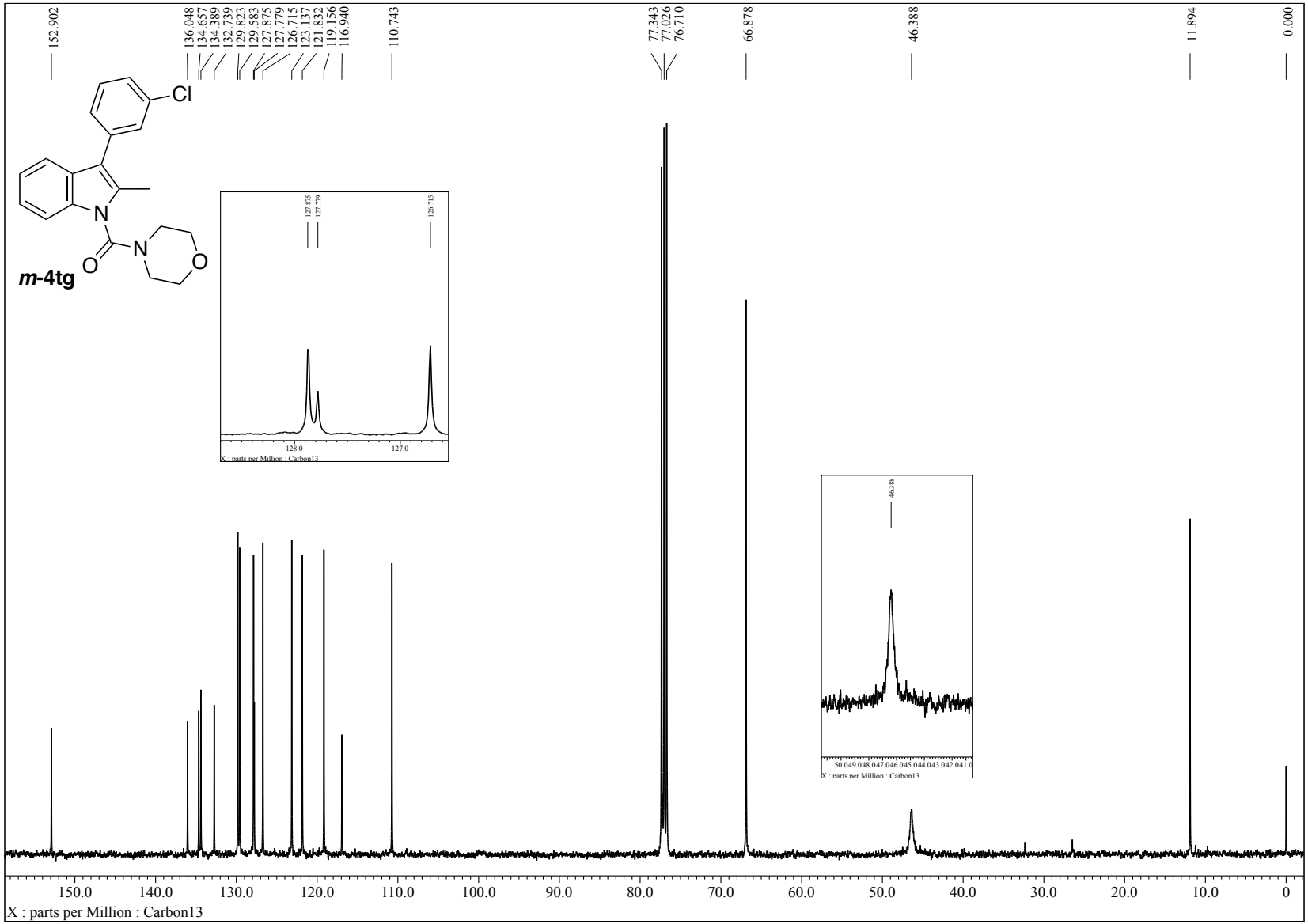
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



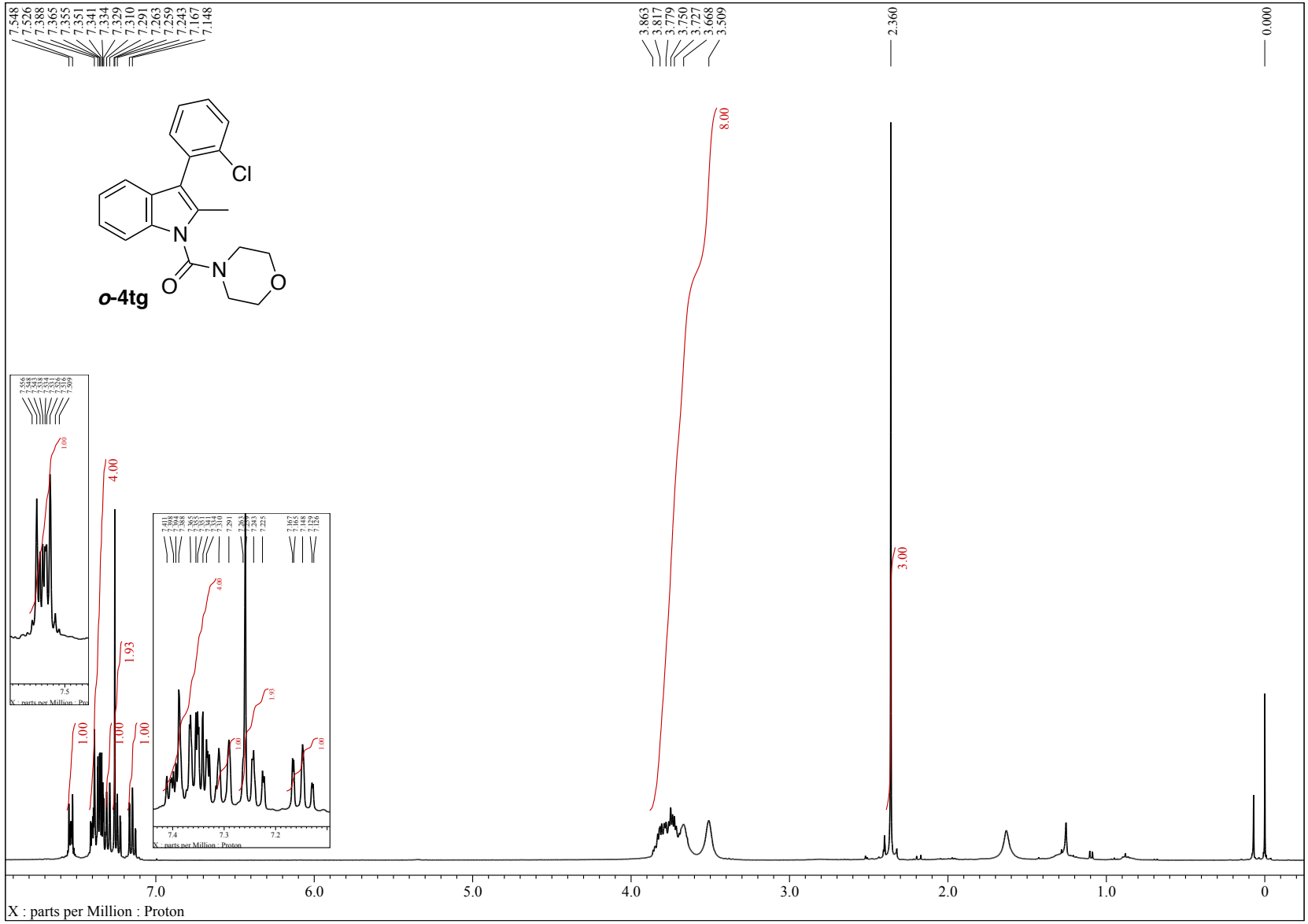
^{1}H NMR (400 MHz, $CDCl_3$)



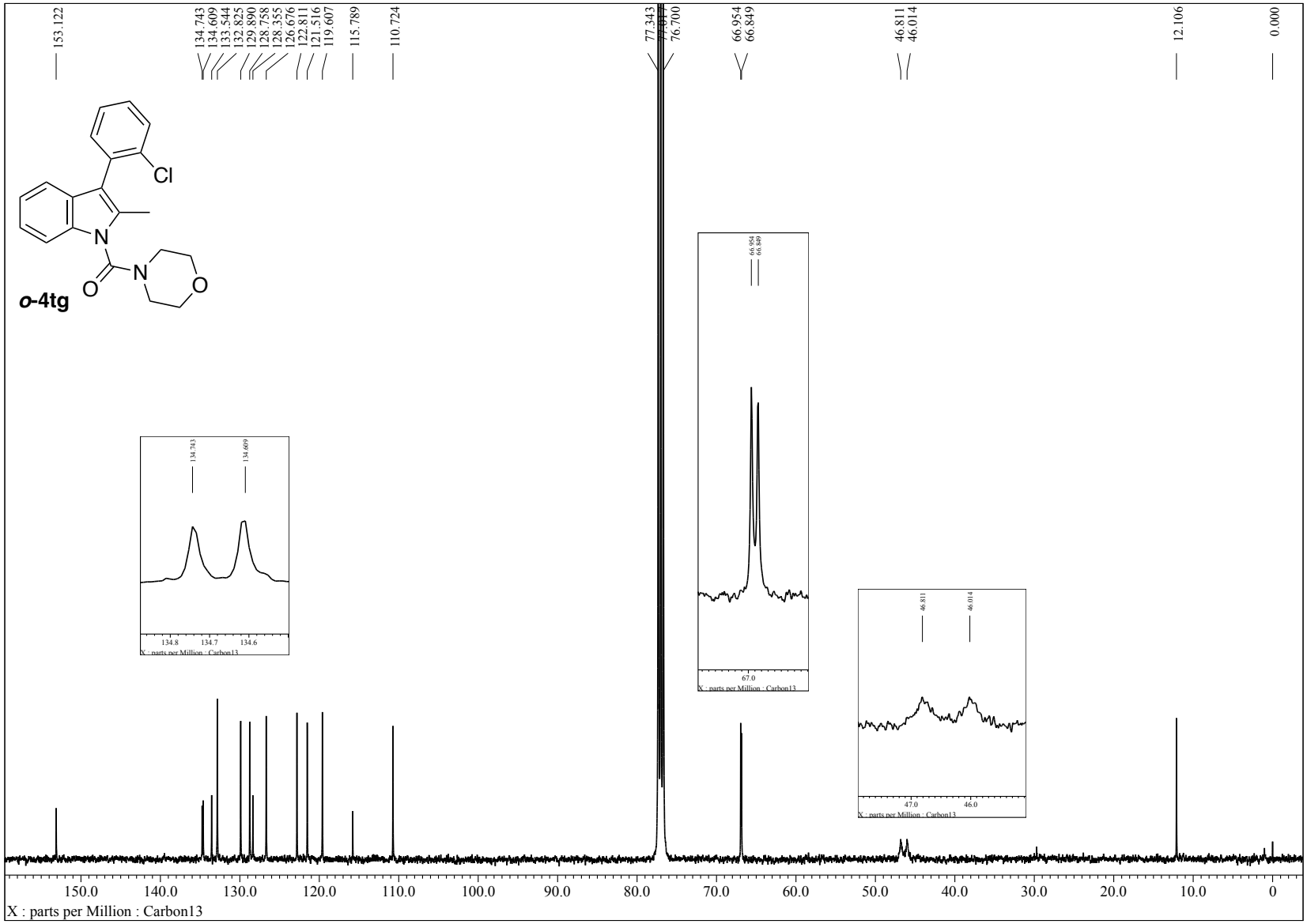
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



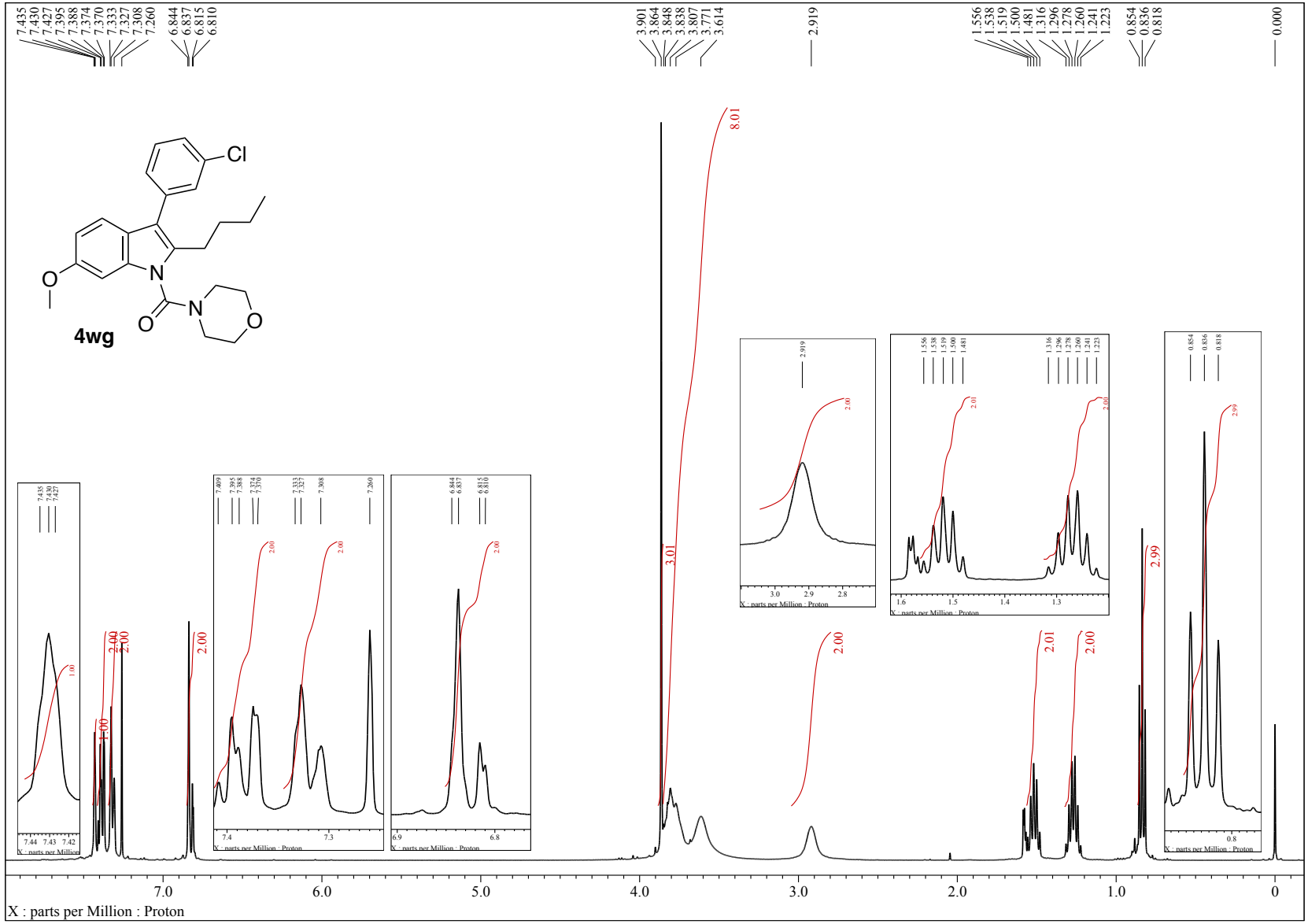
^{1}H NMR (400 MHz, $CDCl_3$)



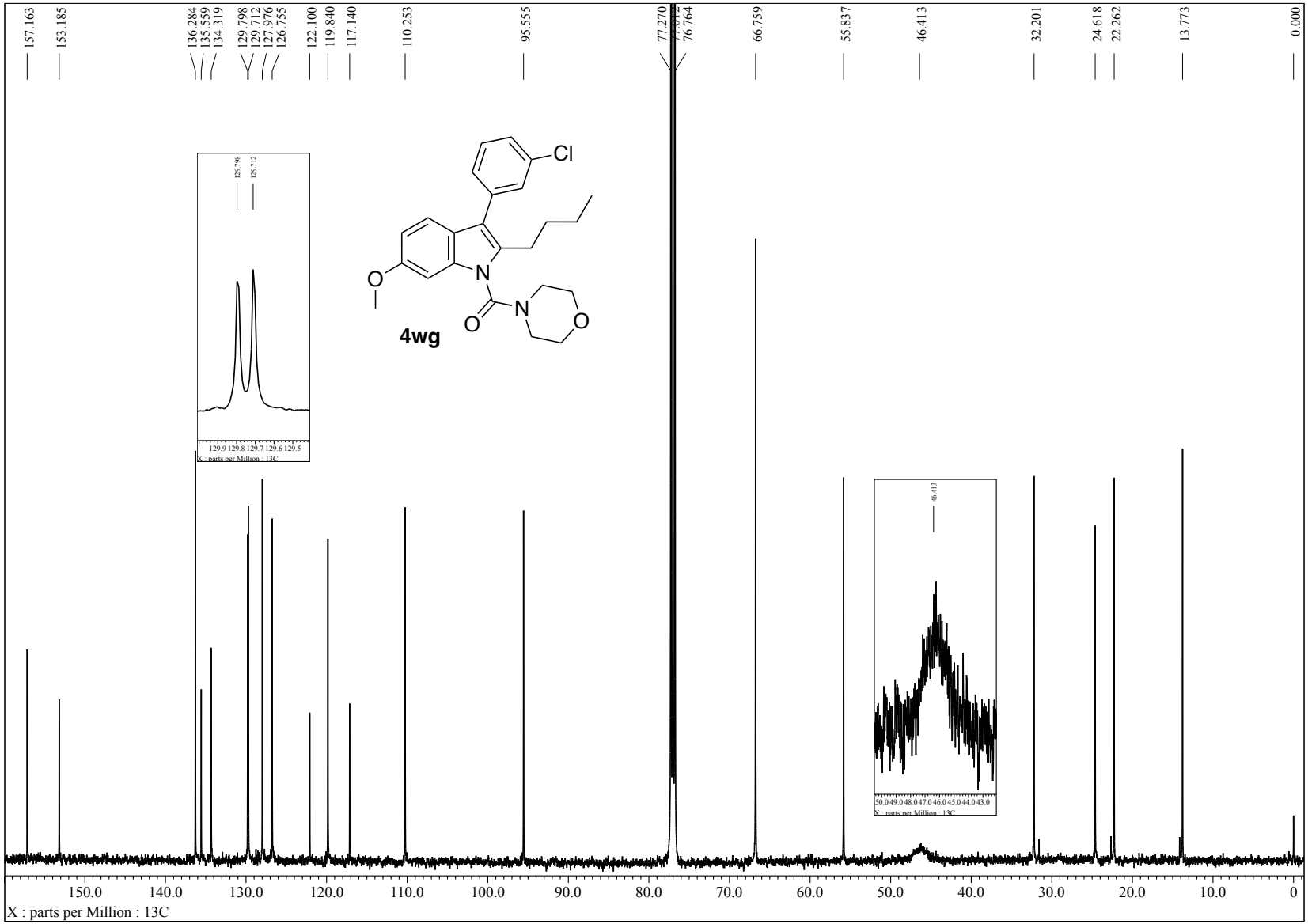
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



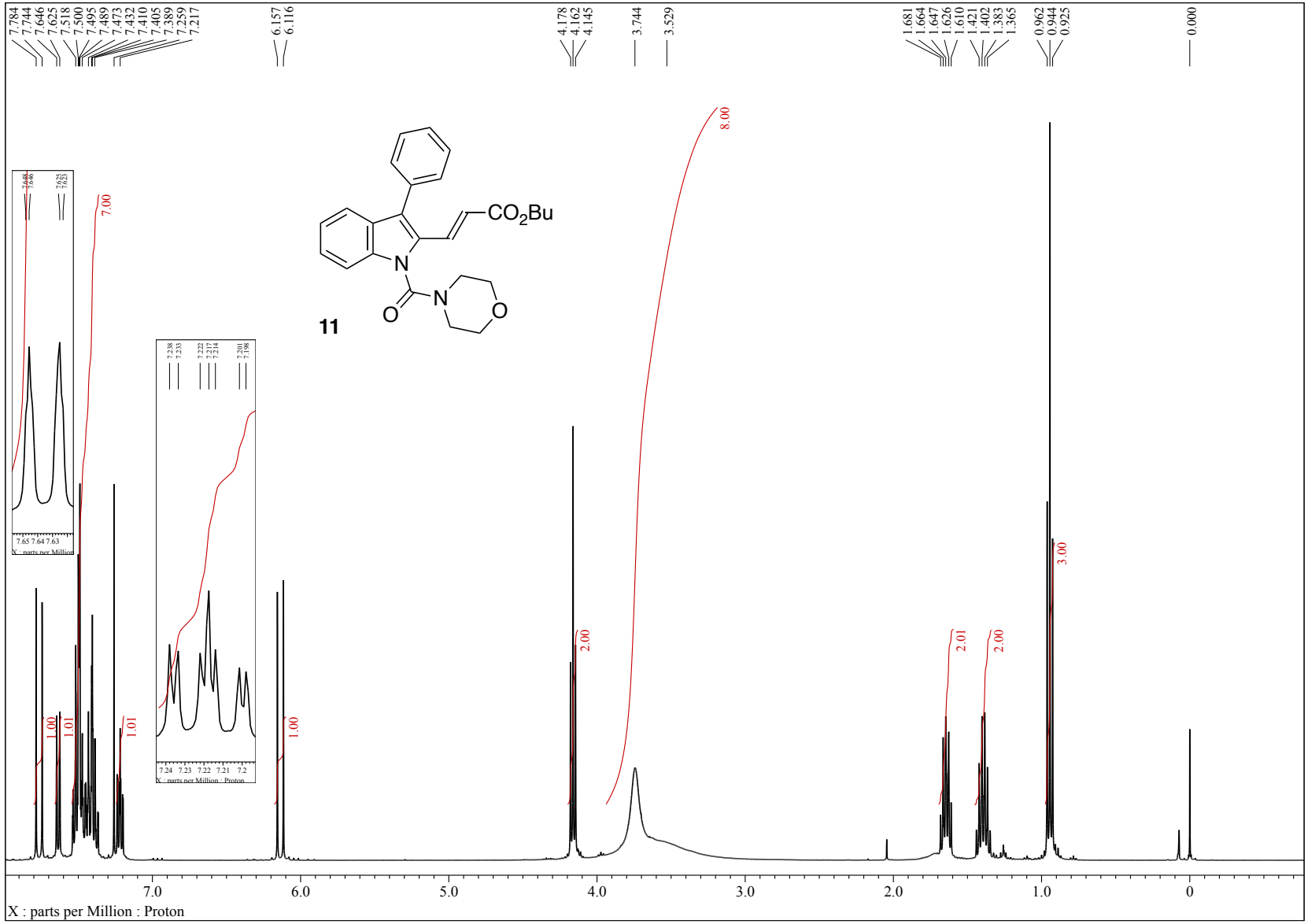
^{1}H NMR (400 MHz, $CDCl_3$)



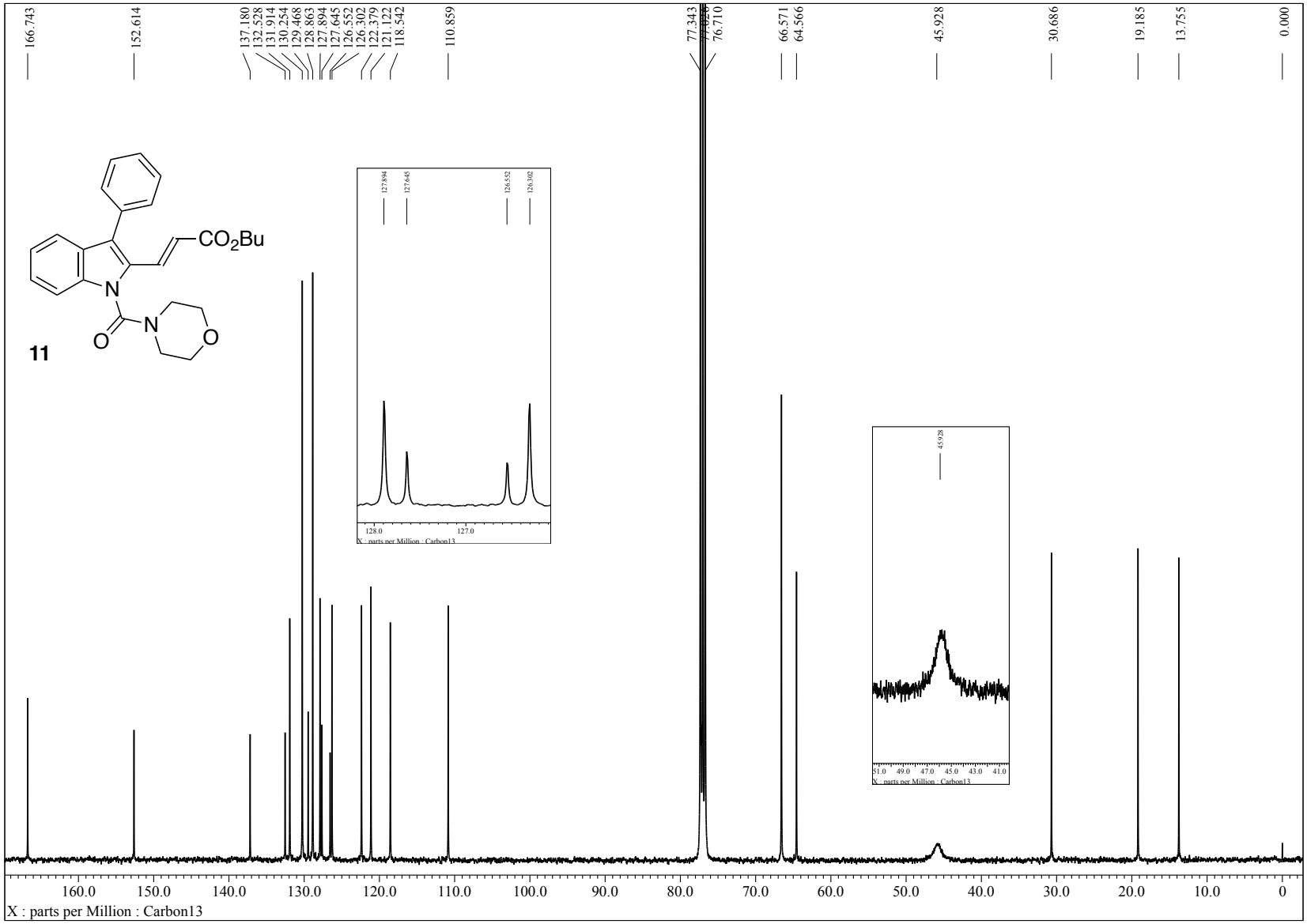
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



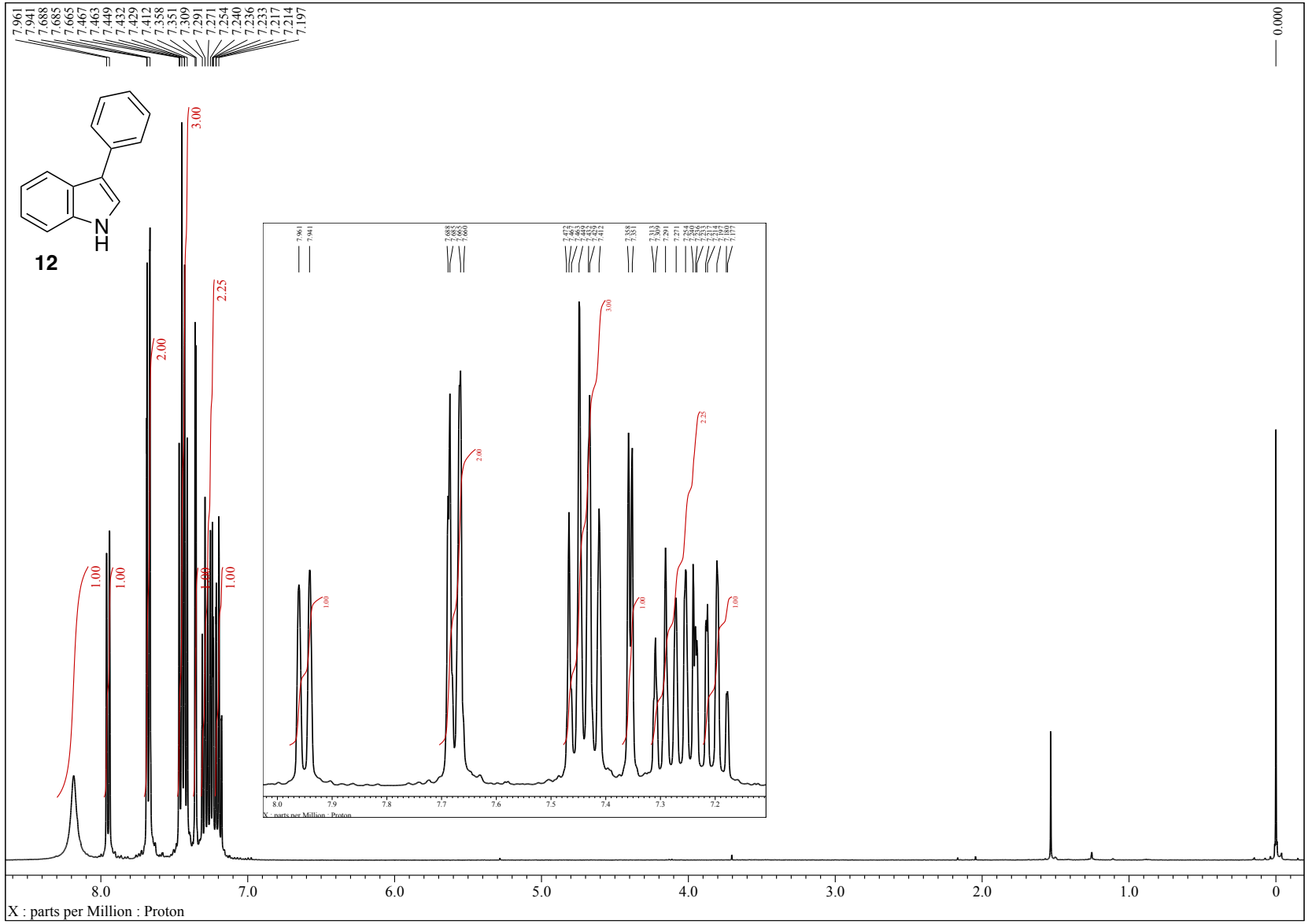
^{1}H NMR (400 MHz, $CDCl_3$)



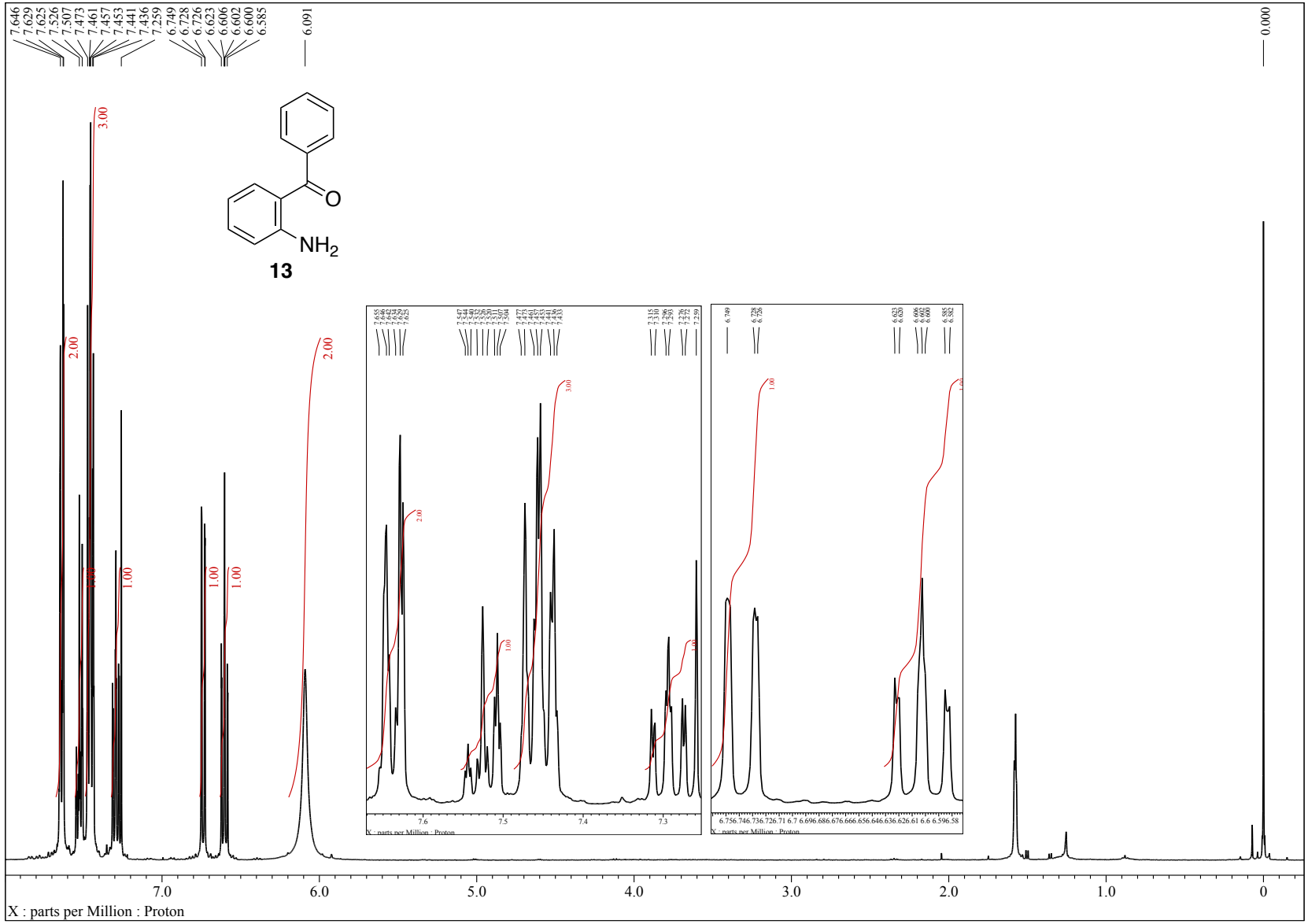
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



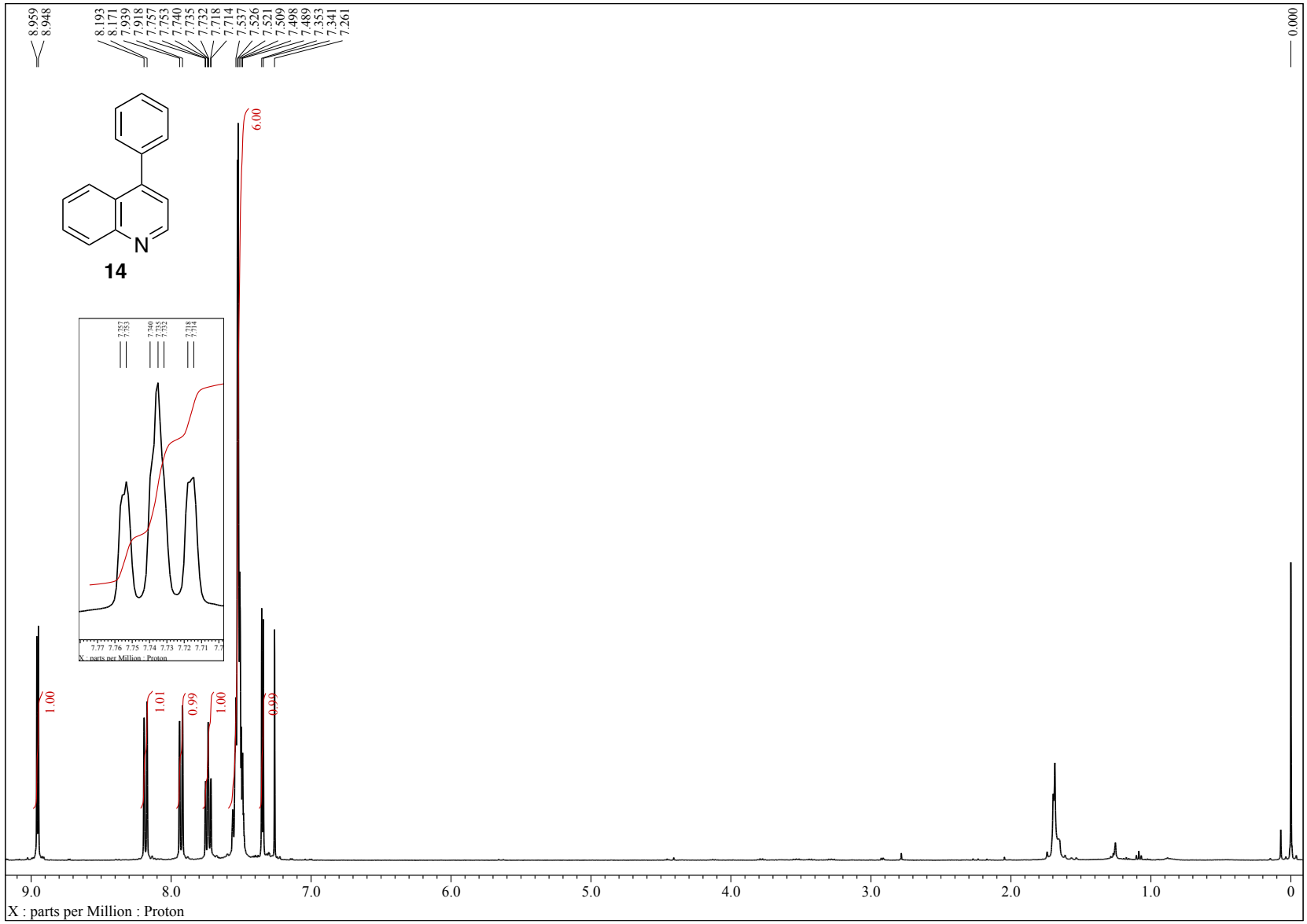
^{1}H NMR (400 MHz, $CDCl_3$)



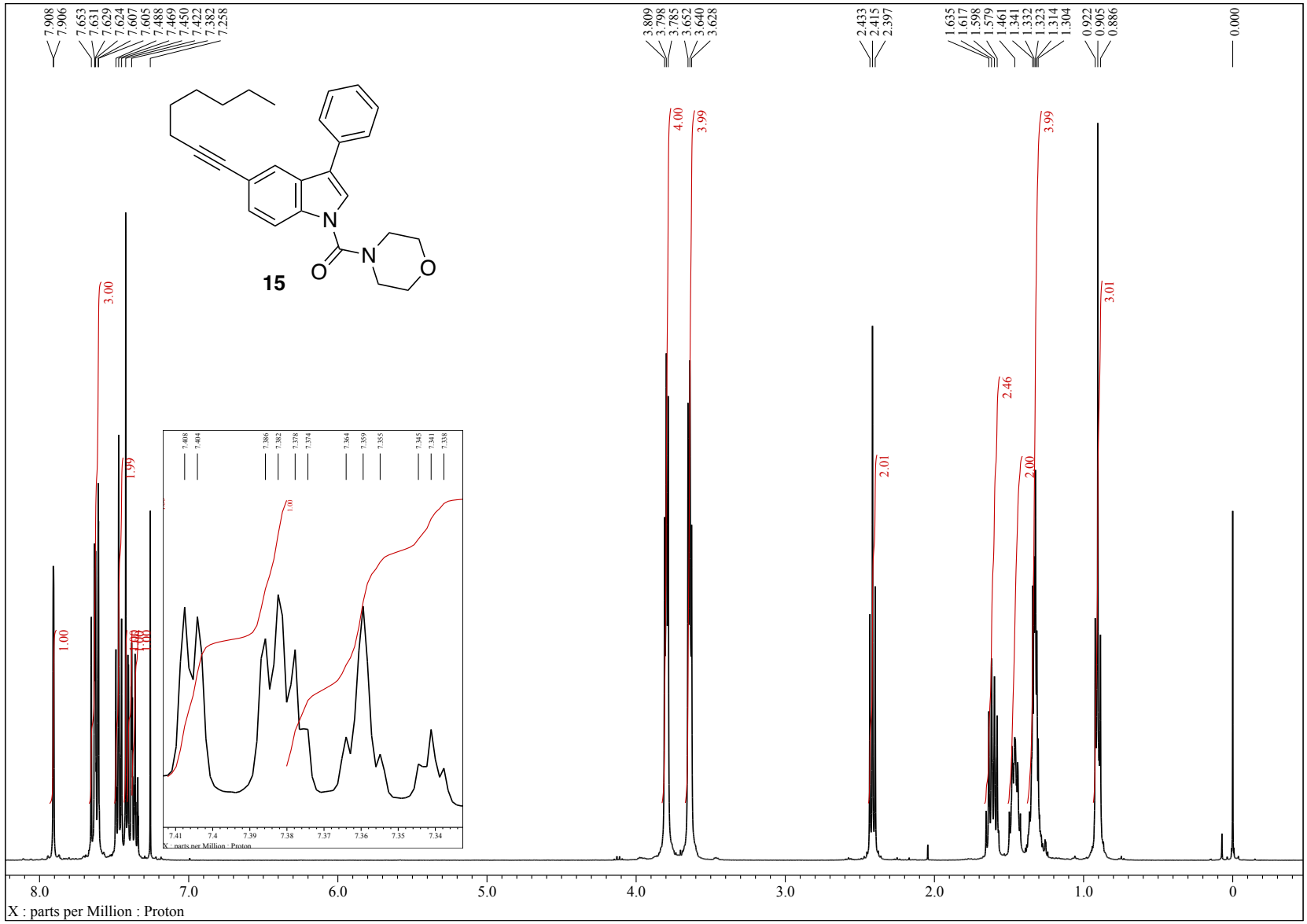
^{1}H NMR (400 MHz, $CDCl_3$)



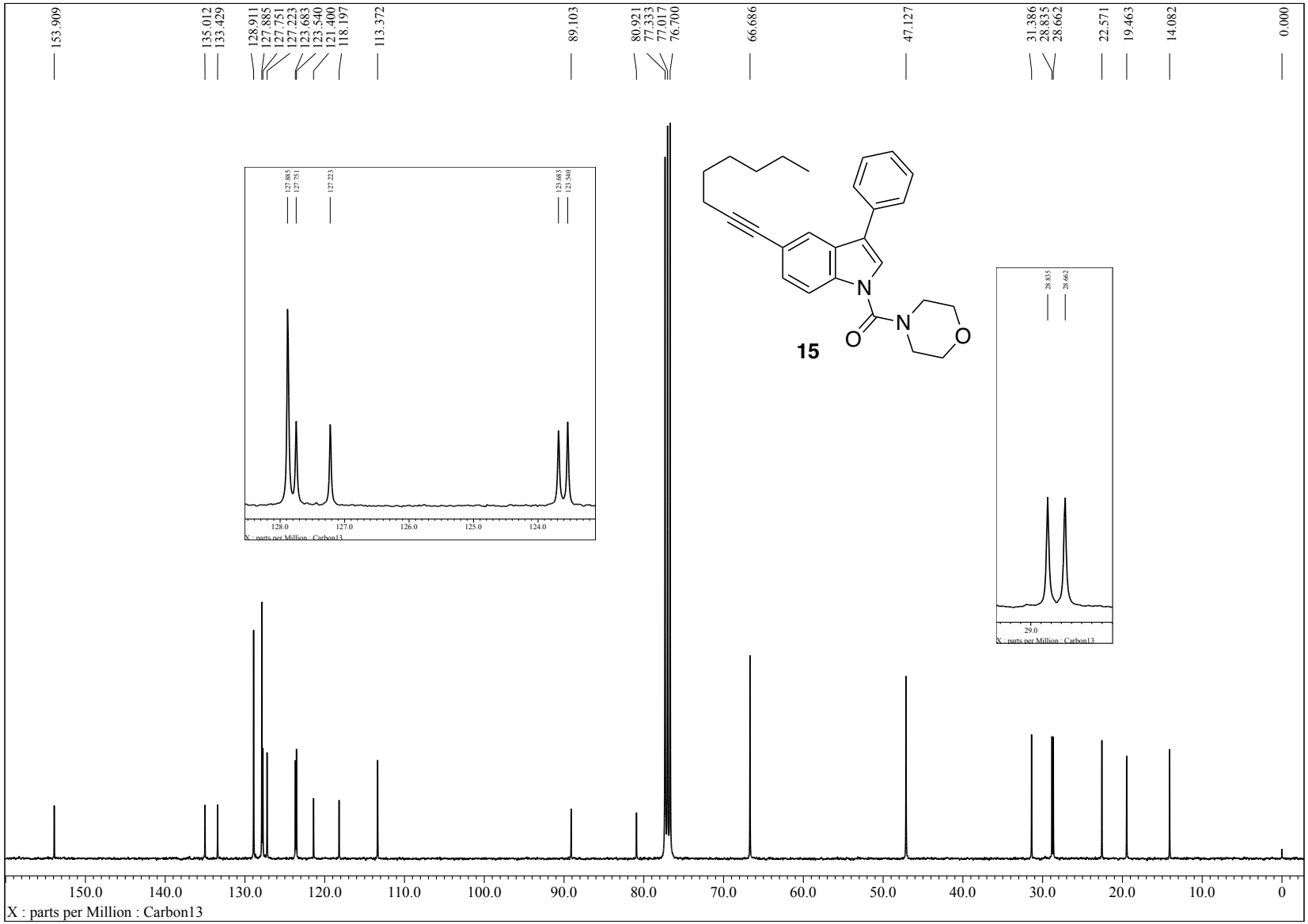
^{1}H NMR (400 MHz, $CDCl_3$)



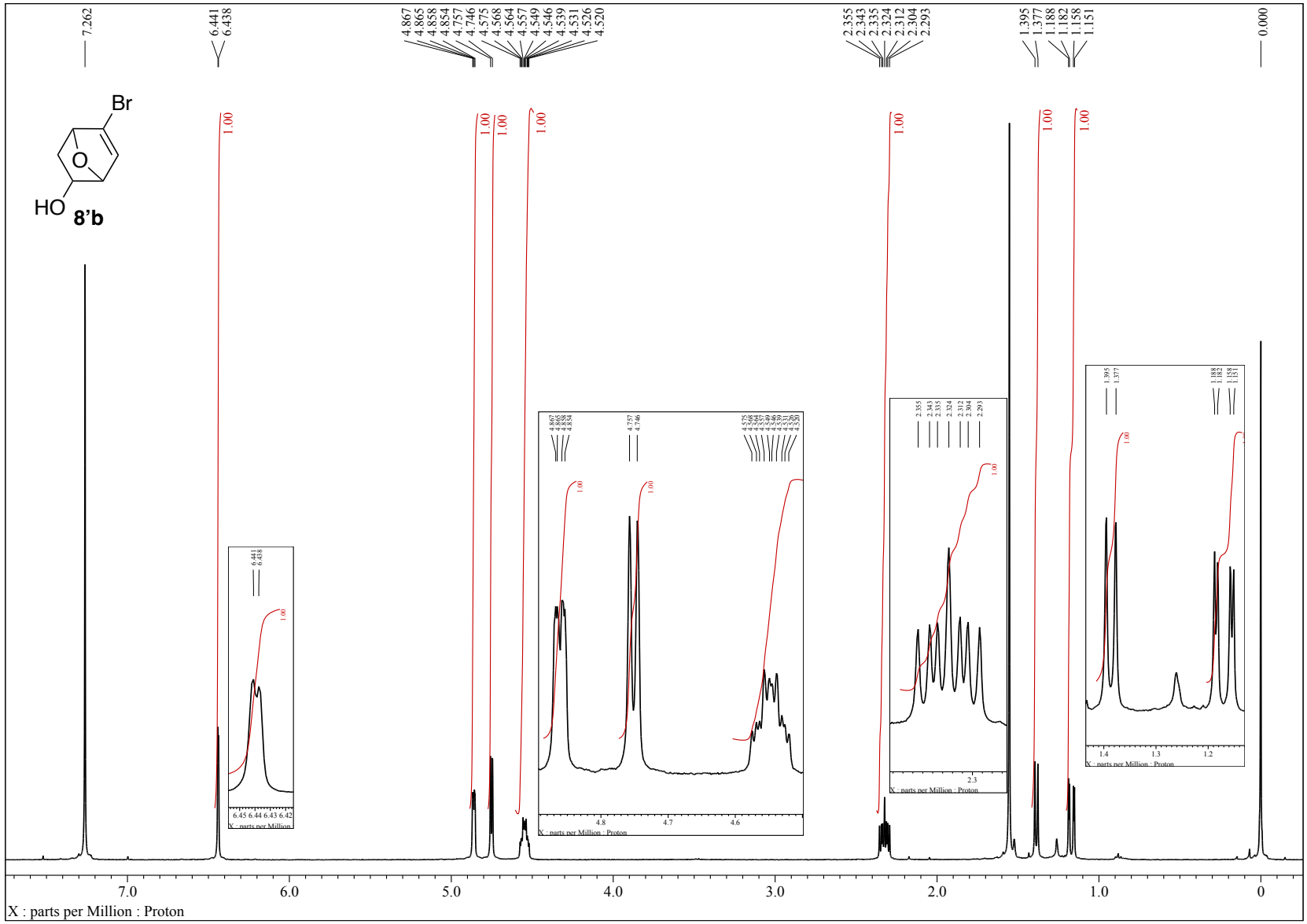
^{1}H NMR (400 MHz, $CDCl_3$)



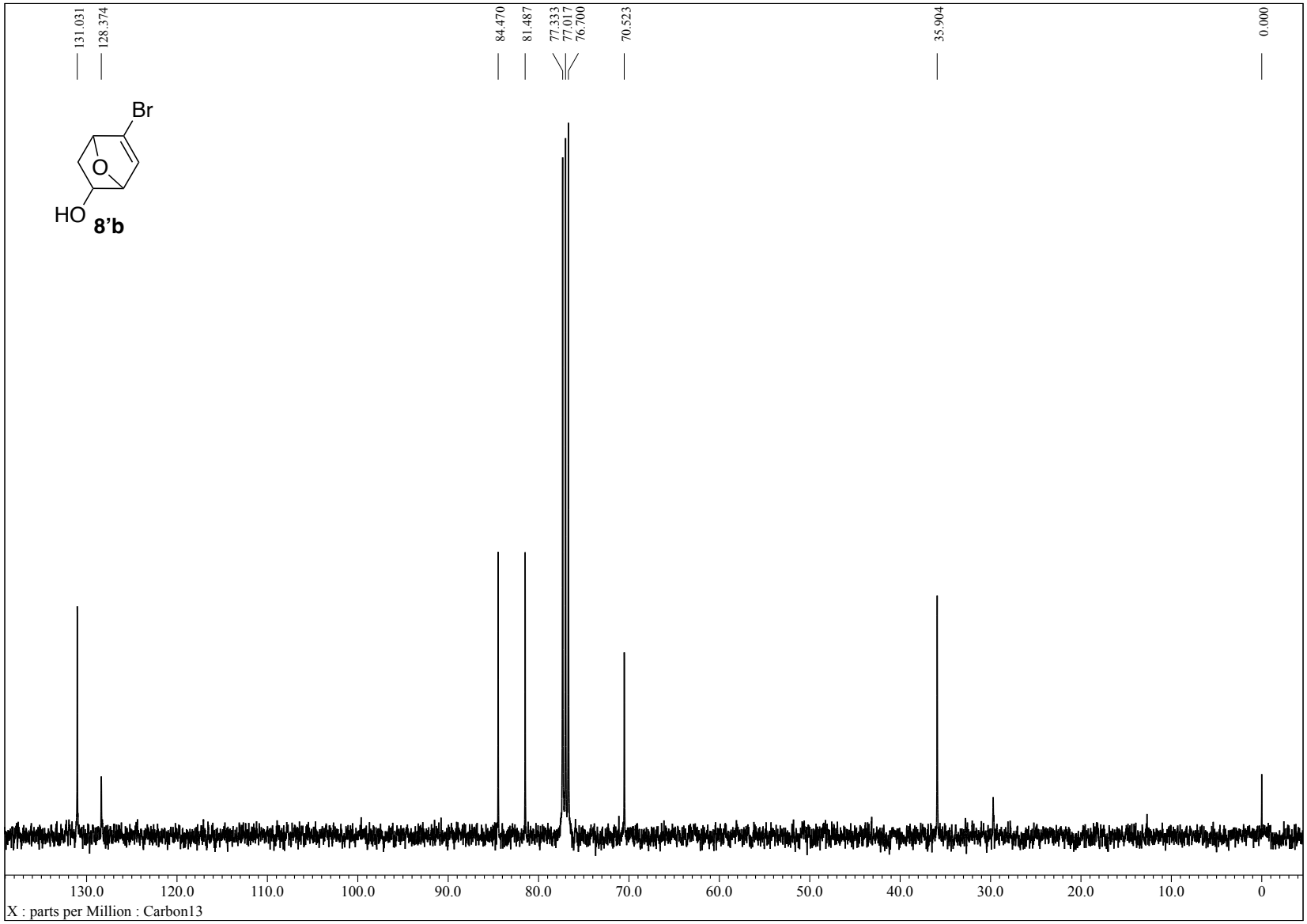
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



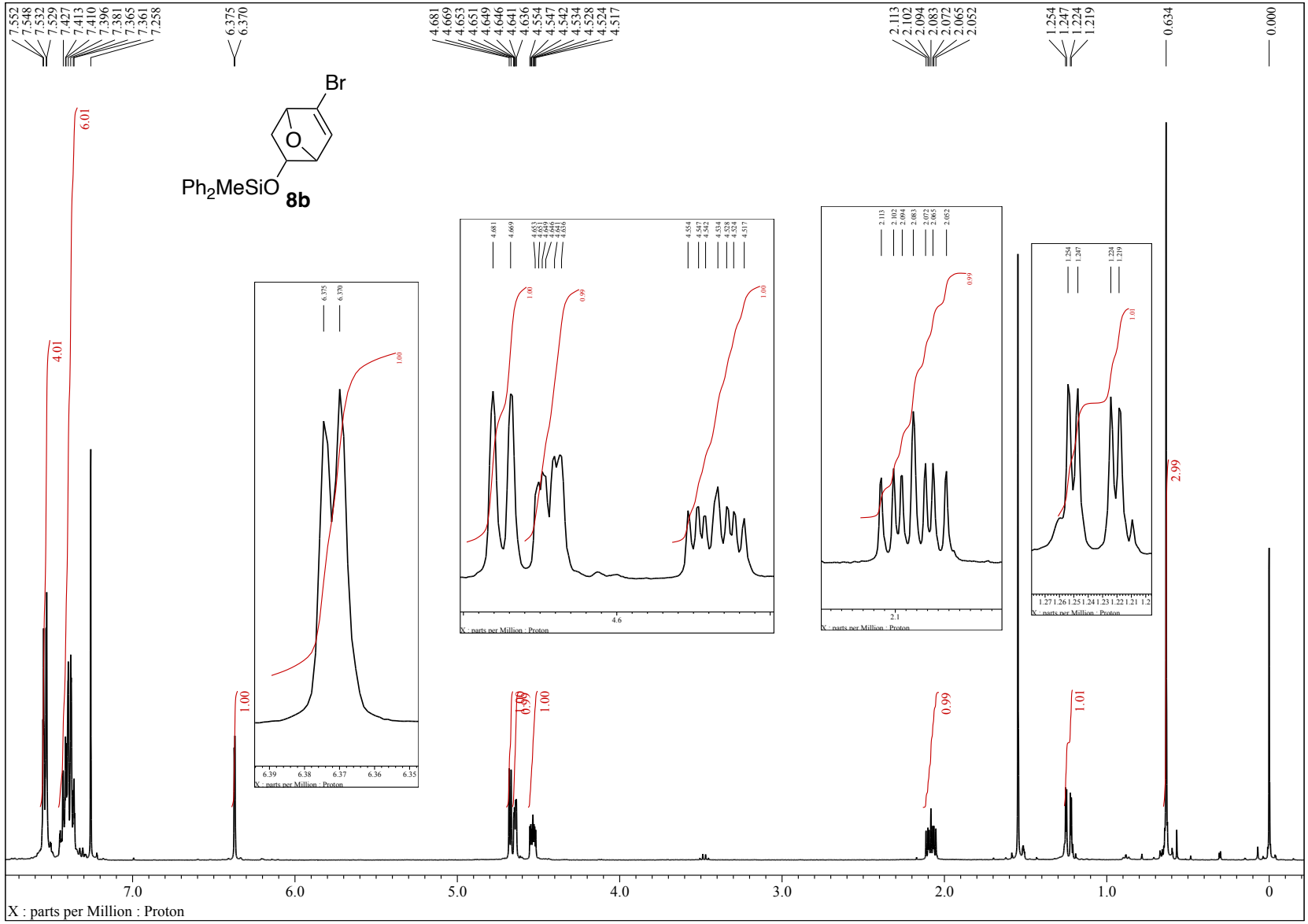
^{1}H NMR (400 MHz, $CDCl_3$)



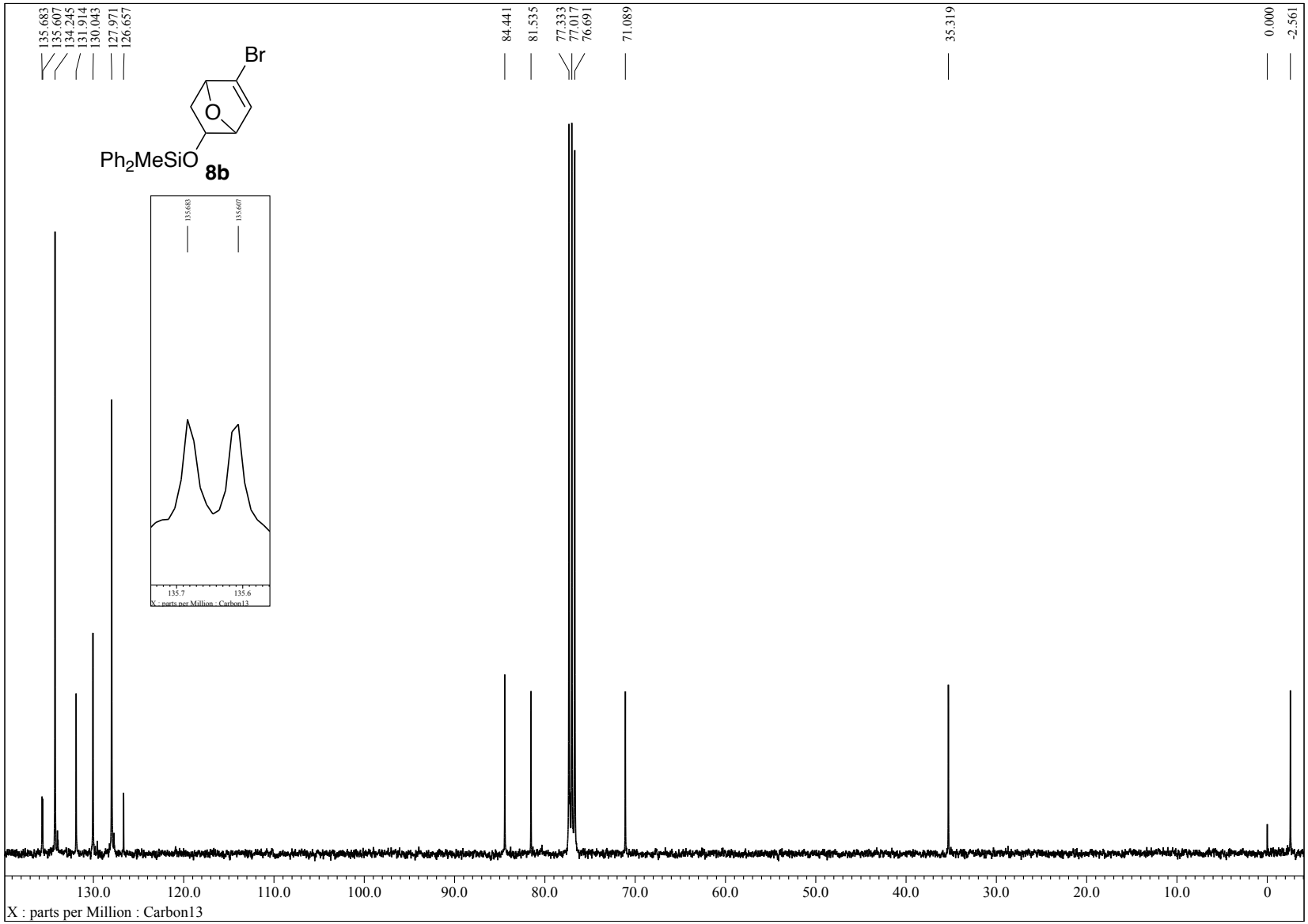
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



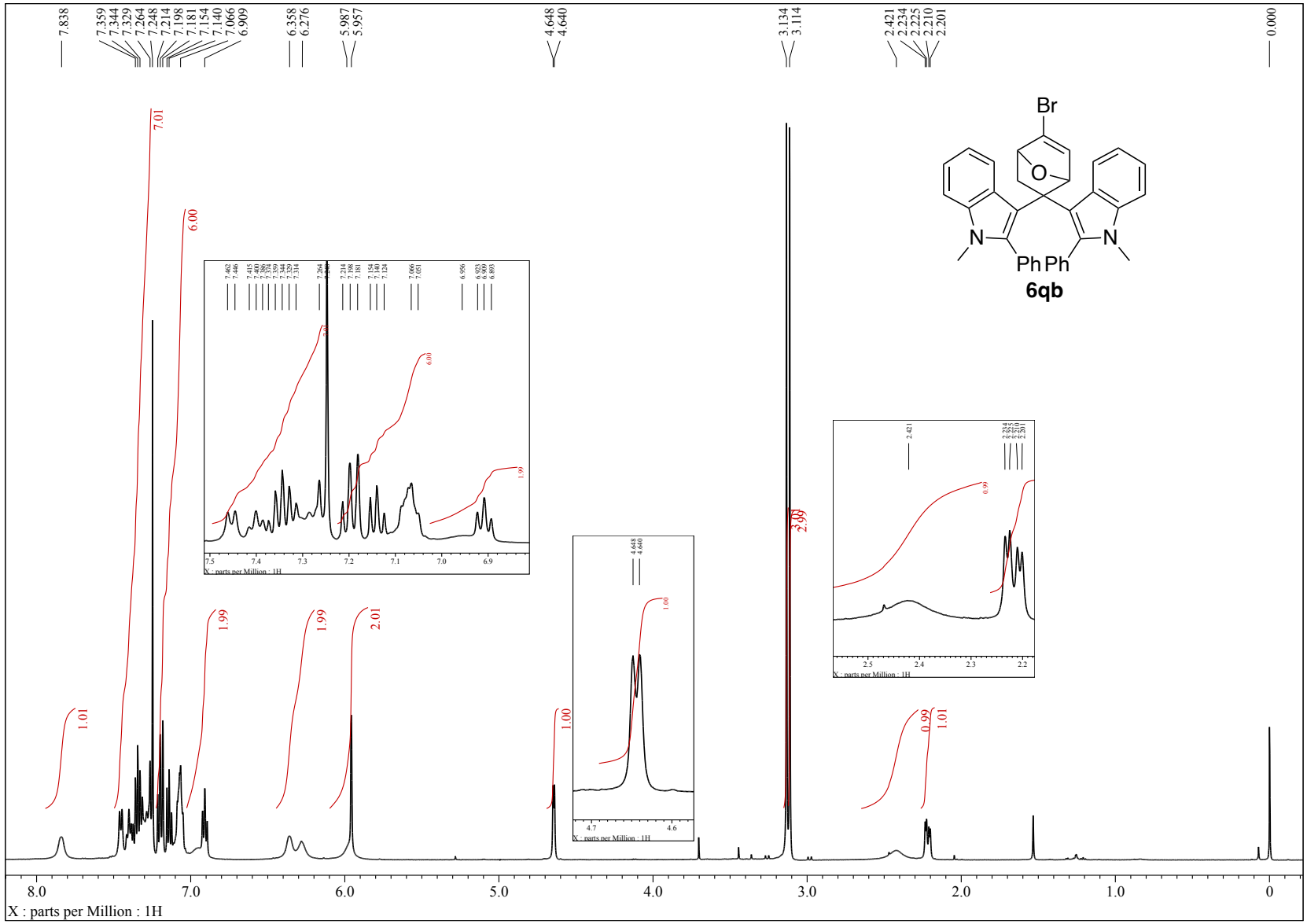
^{1}H NMR (400 MHz, $CDCl_3$)



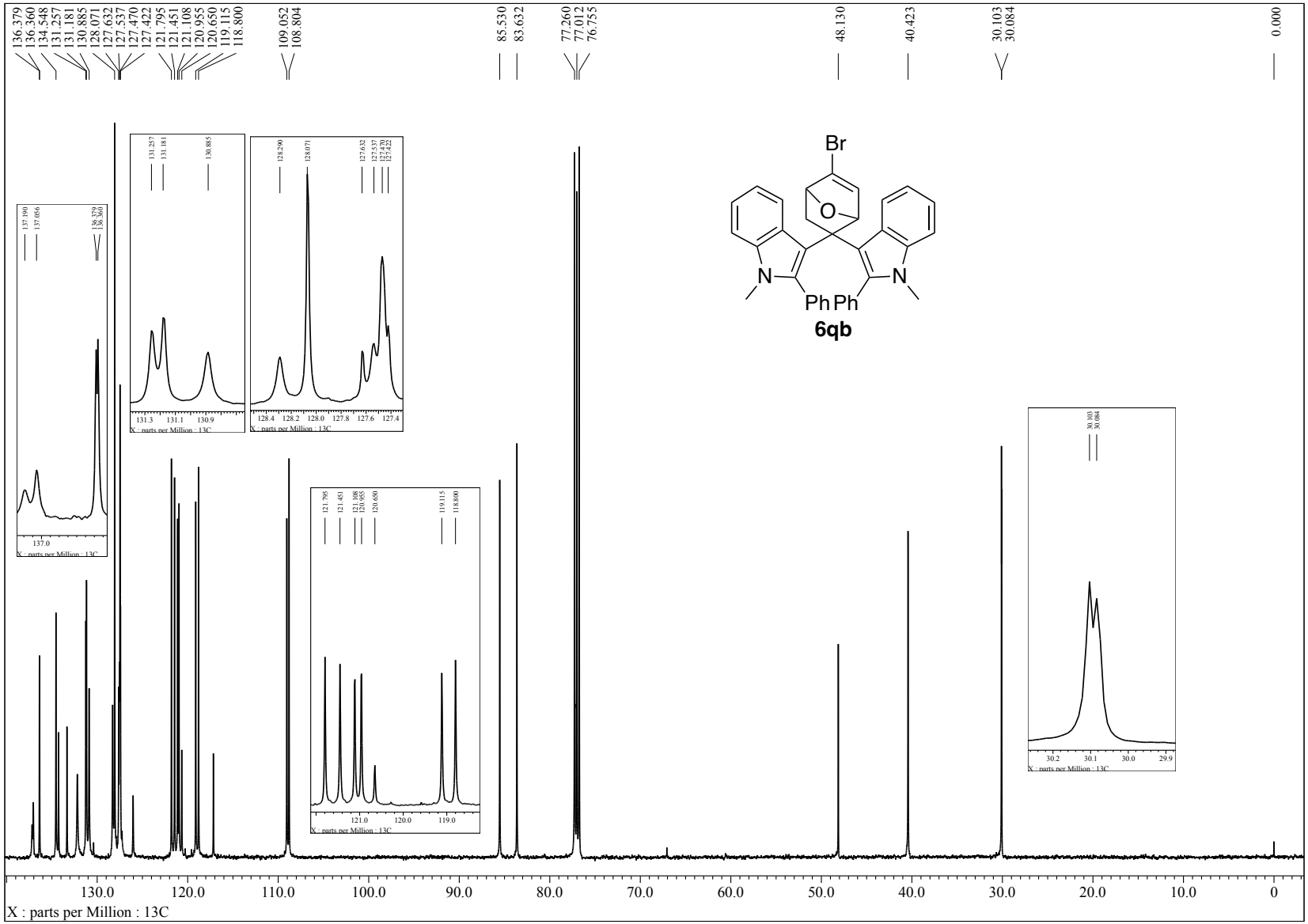
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



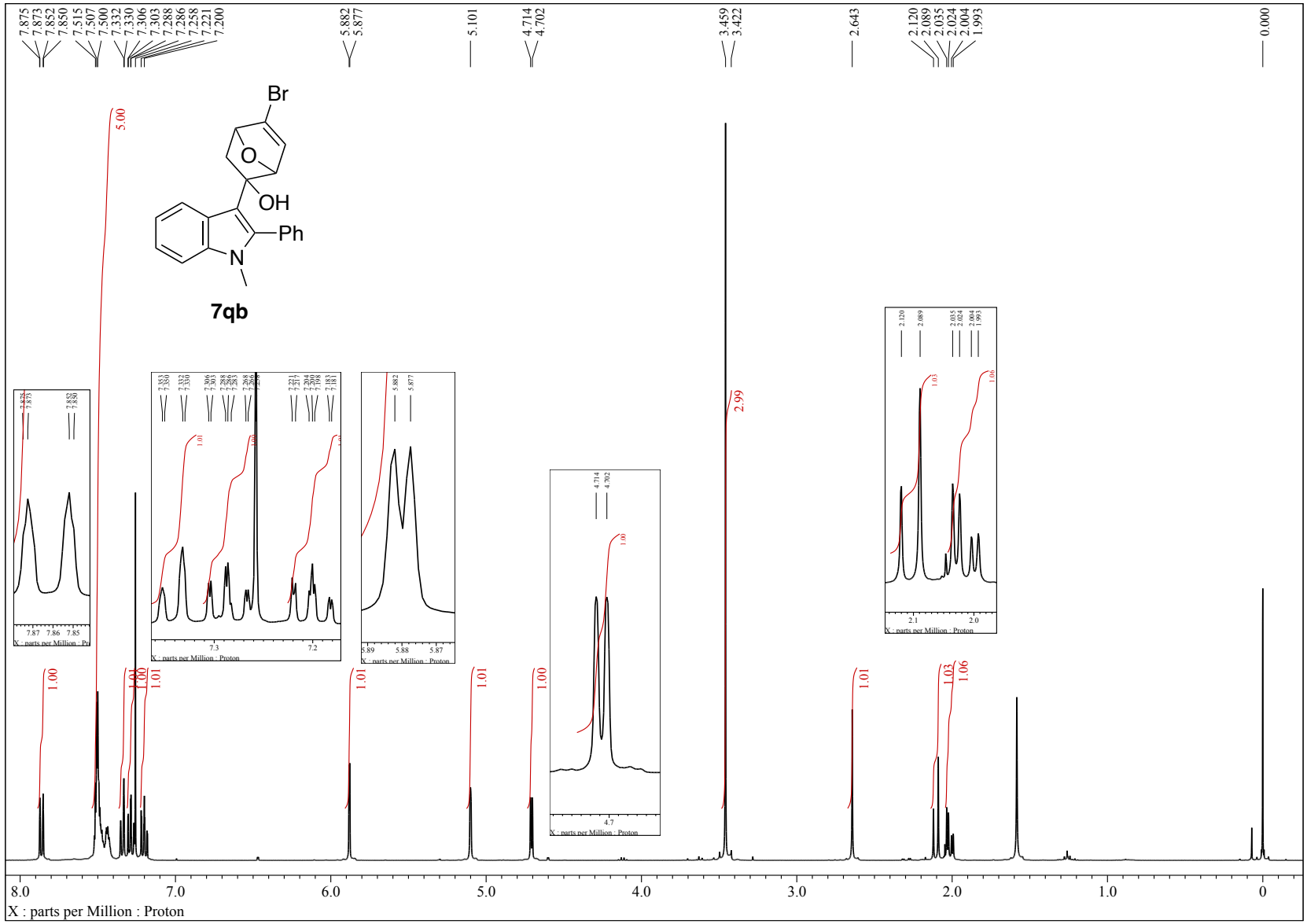
^{1}H NMR (500 MHz, $CDCl_3$)



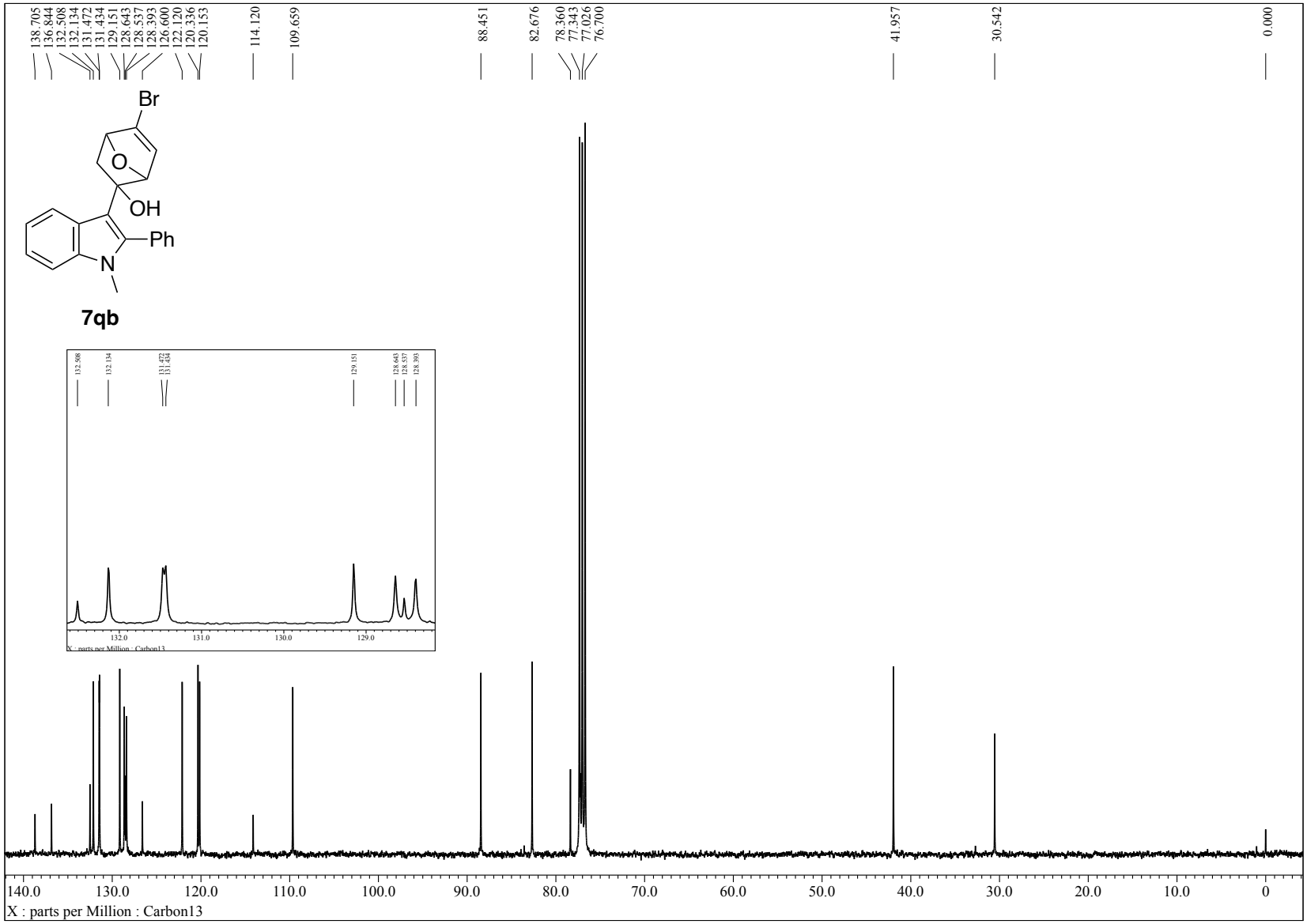
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



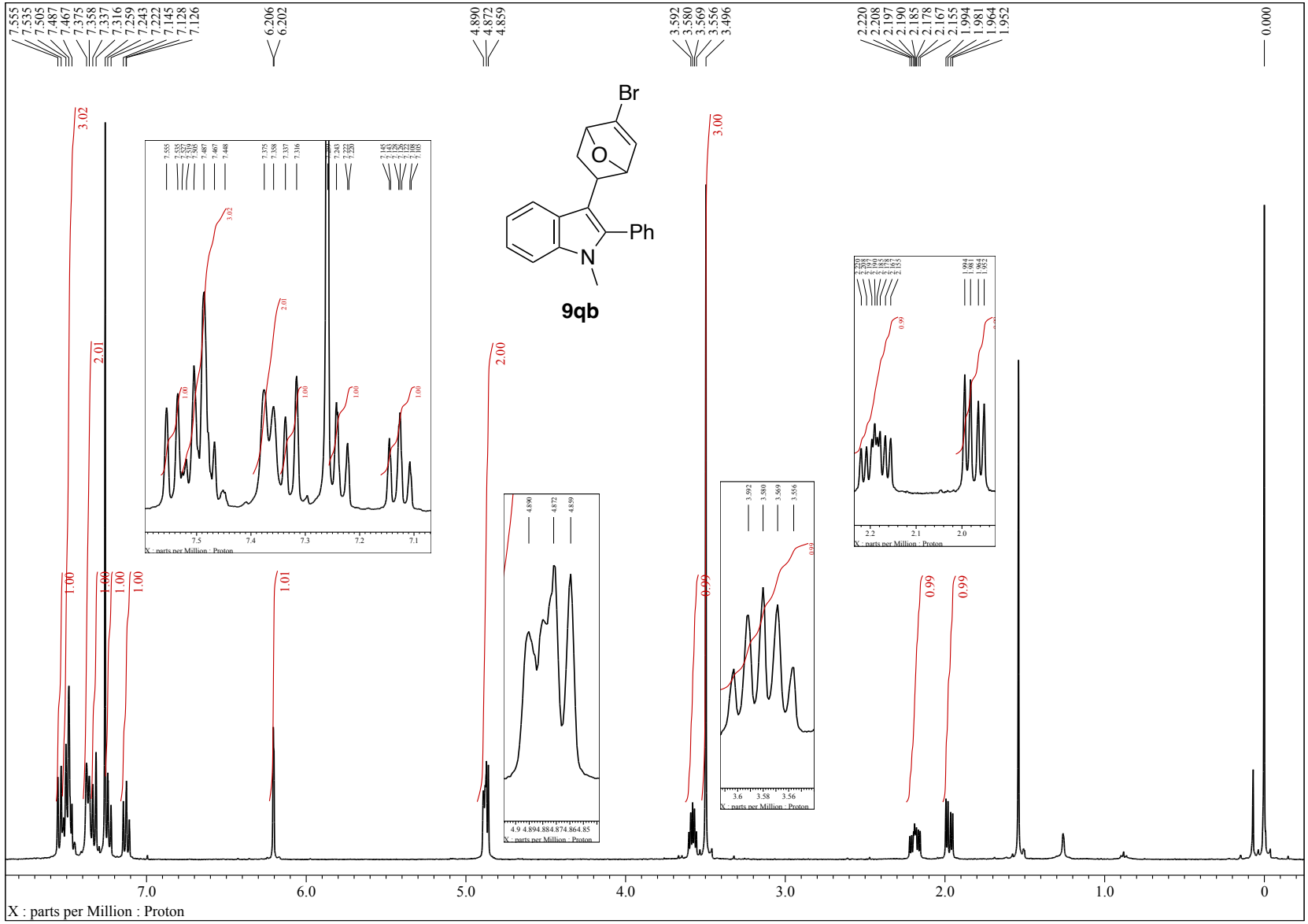
^{1}H NMR (400 MHz, $CDCl_3$)



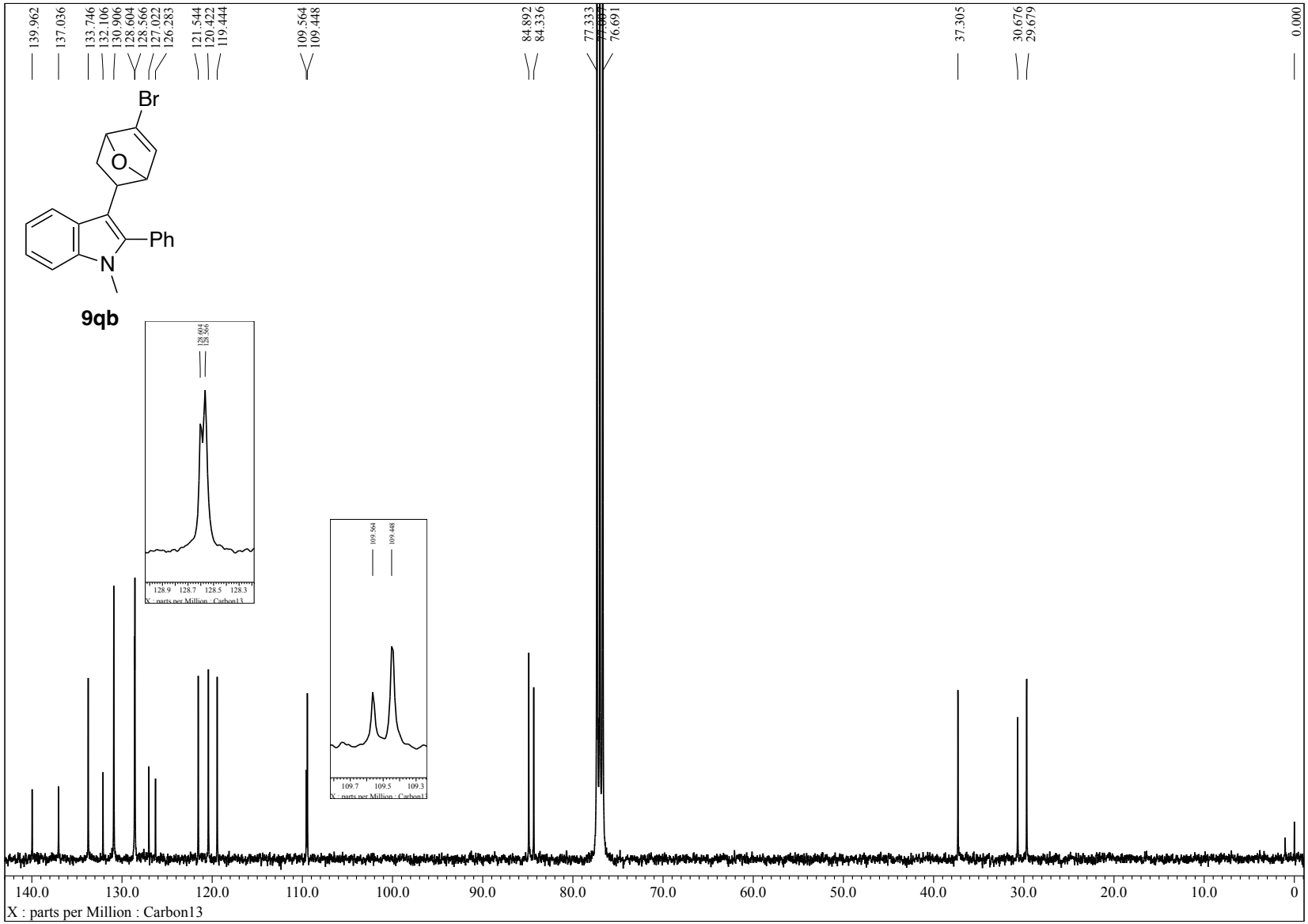
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



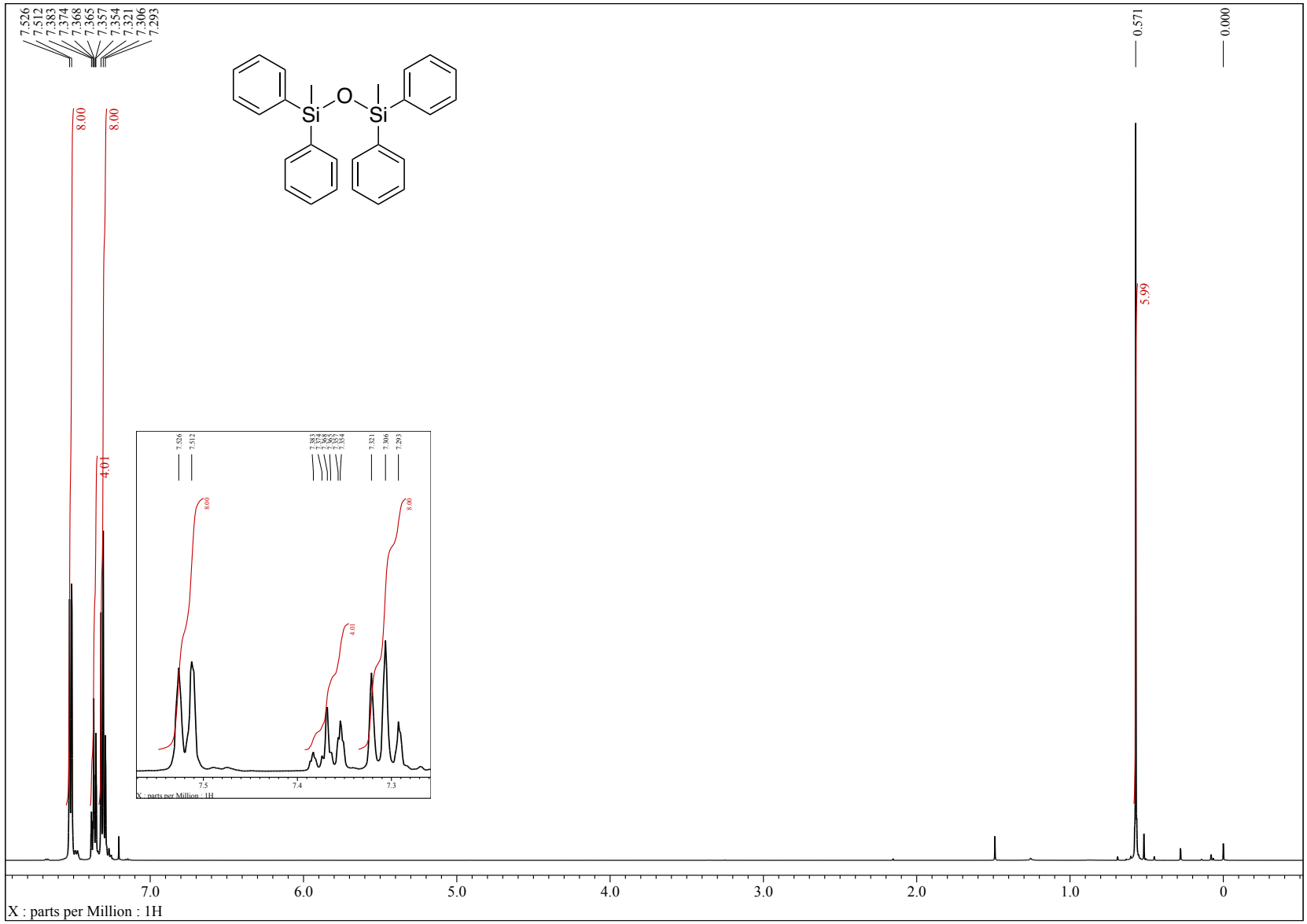
^{1}H NMR (400 MHz, $CDCl_3$)



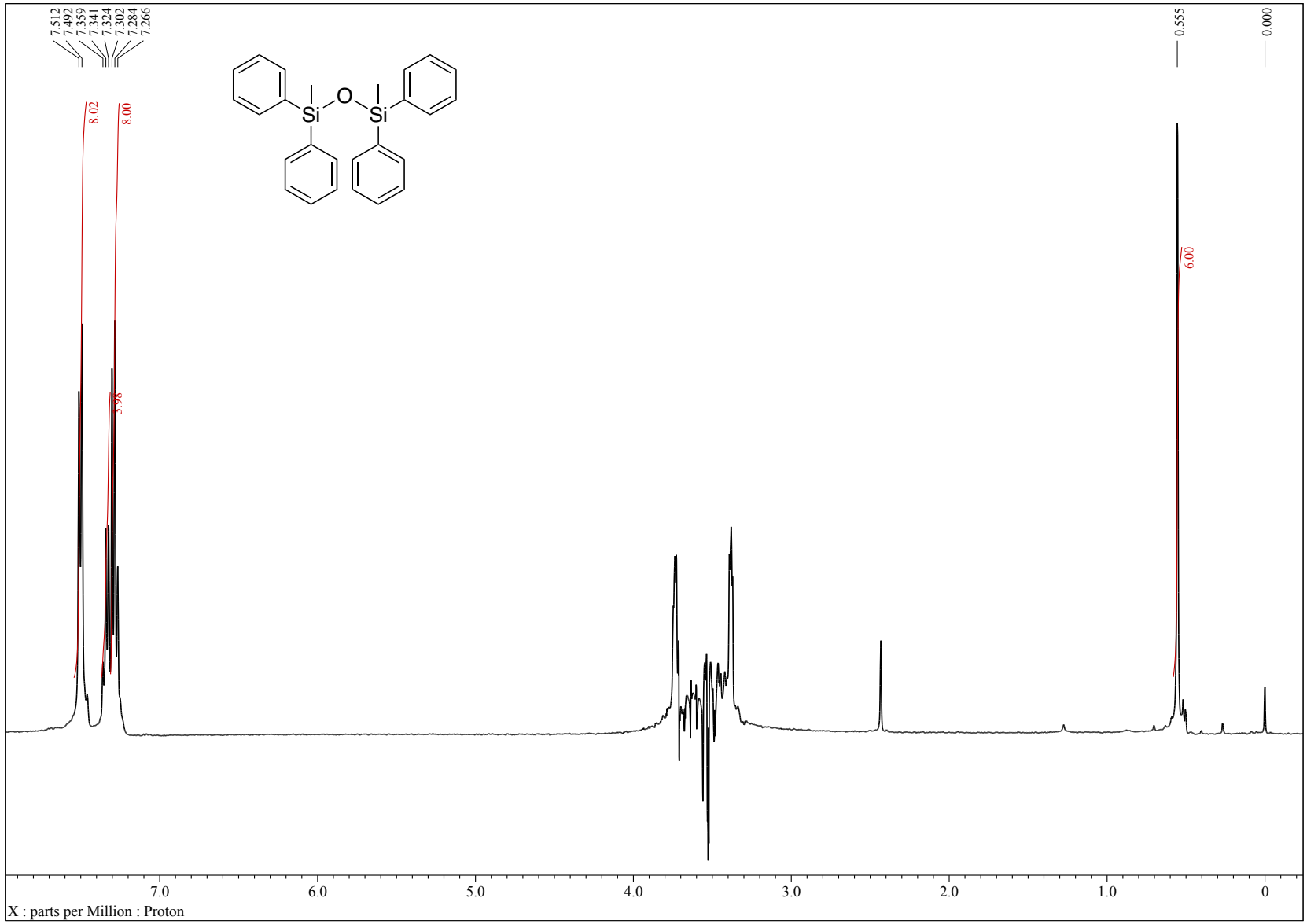
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



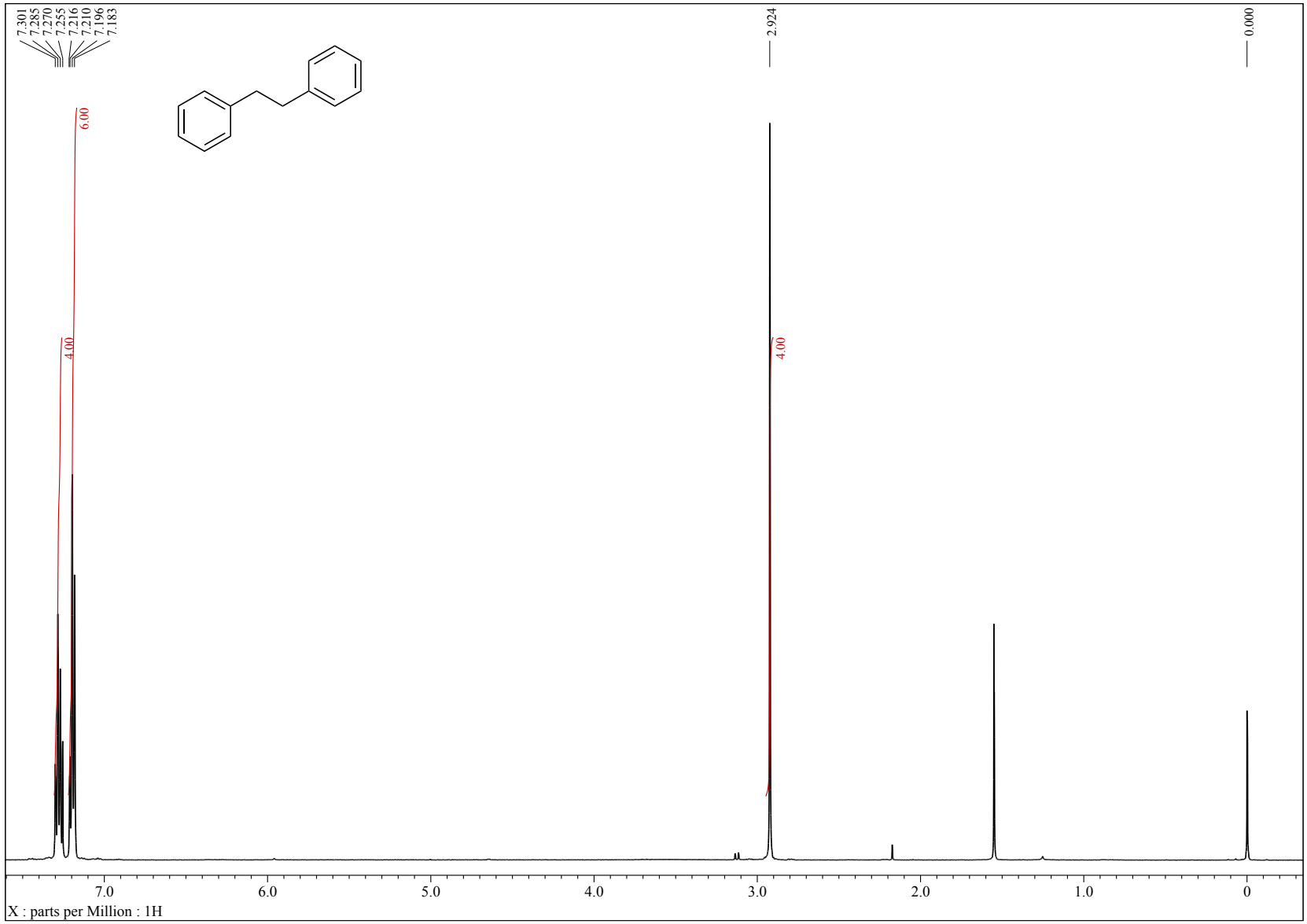
^{1}H NMR (500 MHz, $CDCl_3$)



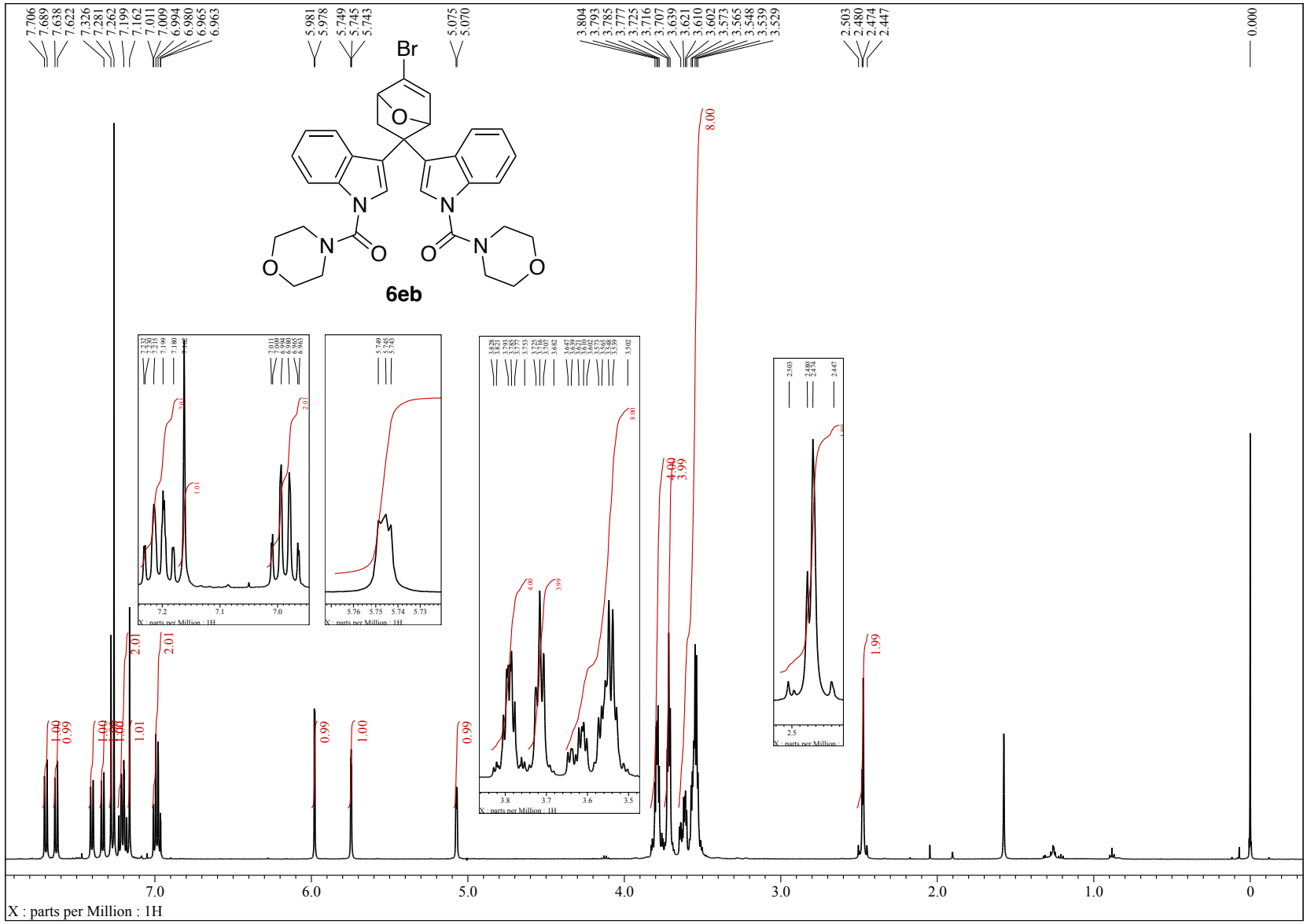
^{1}H NMR (400 MHz, 1,4-dioxane-d_0)



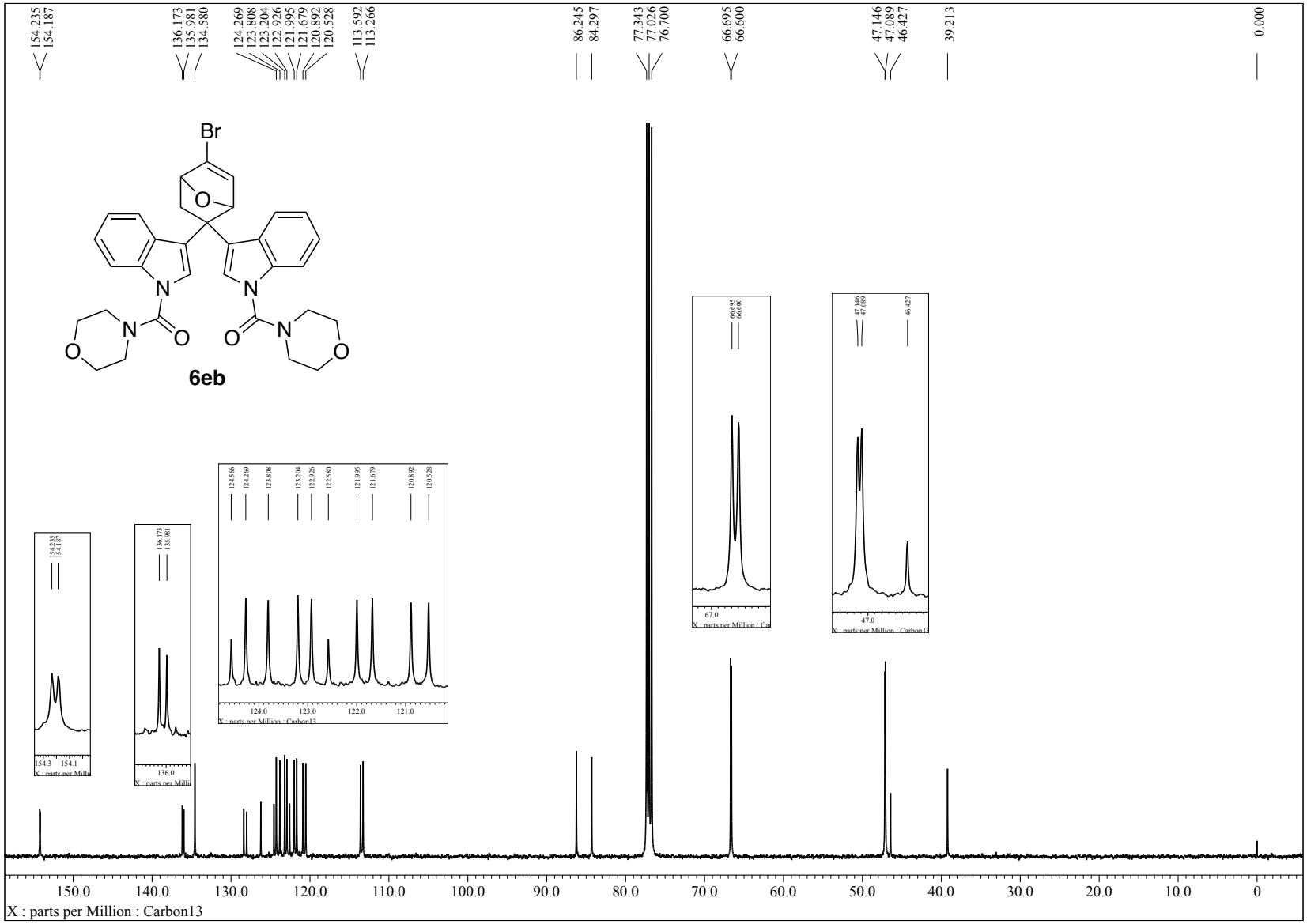
^{1}H NMR (500 MHz, $CDCl_3$)



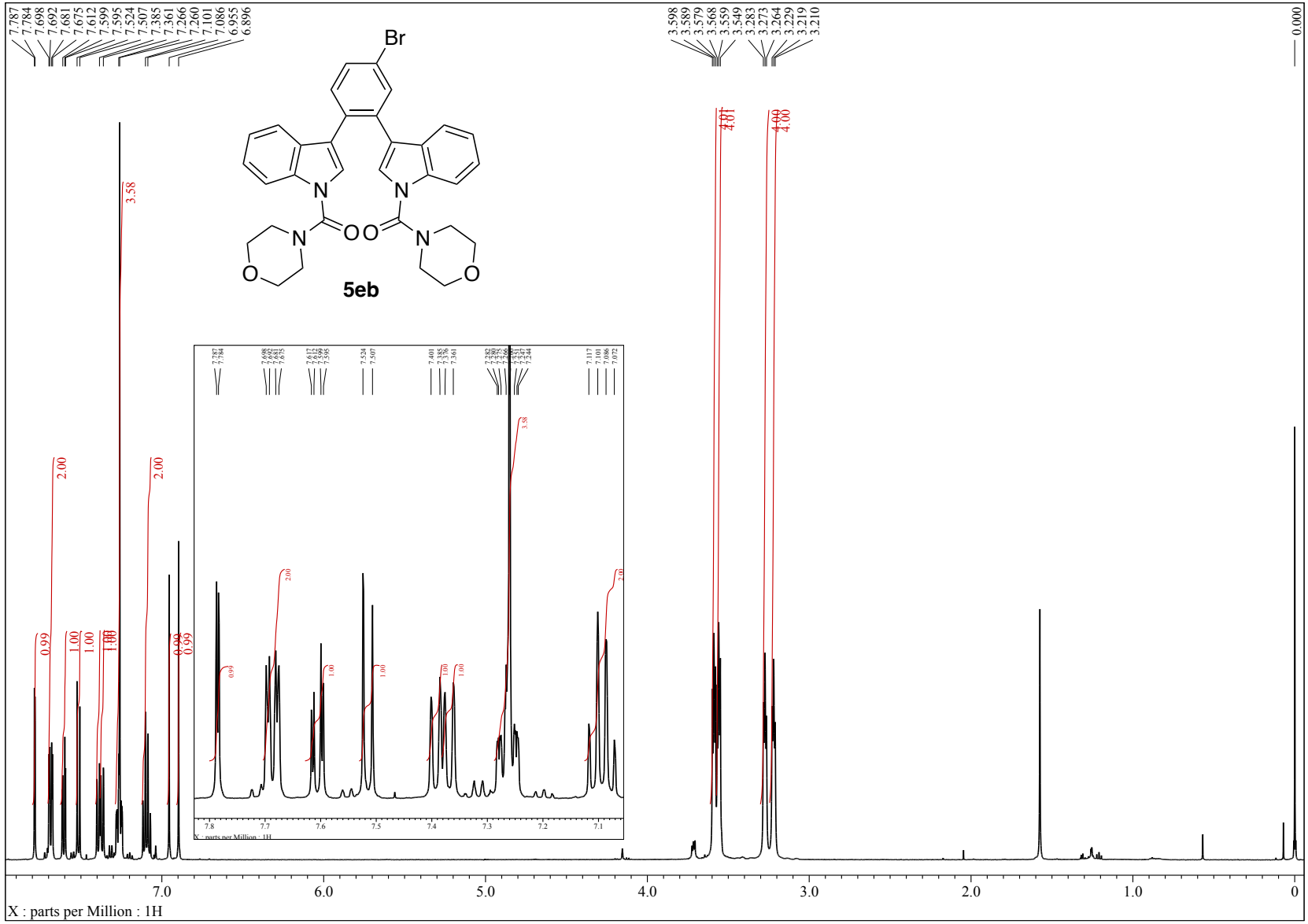
^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)